Method Development and Mechanistic Insights into Palladium-Catalyzed C–CN Bond Activation and Iridium-Catalyzed Sequential C–O/C–H Bond Activation Reactions

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DEDICATION

To my family,

Thank you for always encouraging me to strive for my goals. This has been a long process and I could not have accomplished this without your love and support.

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ABBREVIATIONS

AAKT	Abboud-Abraham-Kamlet-Taft
AQ	Acquisition time
Bn	Benzyl
Bpin	Pinacol borane
$CDCl_3$	Deuterated chloroform
COD	1,5-cyclooctadiene
COE	Cyclooctene
D1	Relaxation delay
DCM	Dichloromethane
DMB	1,2-dimethoxybenzene
DMPE	1,2-bis(dimethylphosphino)ethane
DMPU	N,N′-dimethylpropylene urea
DMSO	Dimethyl sulfoxide
DPPE	1,2-bis(diphenylphosphino)ethane
dtbpy	4,4′-di-tert-butyl-2,2′-bipyridine
E.E.	Enantiomeric Excess
E.R.	Enantiomeric Ratio
EAS	Electrophilic aromatic substitution
EDG	Electron-donating group
Et_2O	Diethyl ether
EtOAc	Ethyl acetate
EWG	Electron-withdrawing group
FT	Fourier Transform
KIE	Kinetic Isotope Effect
LSER	Linear Solvation Energy Relationship

NMR	Nuclear Magnetic Resonance
PFMCH	Perfluoromethylcyclohexane
PhMe	Toluene
PPh_3	Triphenylphosphine
Py	Pyridine
SBM	Sigma-bond metathesis
T1	Transverse relaxation (5*T1 = D1 + AQ)
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TM	Transition metal
TMS	Tetramethylsilane
TrixiePhos	*rac*-2-di-tert-butylphosphino-1,1′-binaphthyl
UV	Ultraviolet

CHAPTER 1: C–C BOND ACTIVATION METHODOLOGIES

1.1 Introduction to C–C σ-bond Activation

The formation of new C–C bonds is at the heart of organic chemistry. Many of these methods involve the formation of new C–C σ-bonds from π-bonds, polarized C–X bonds (e.g. C–Br, C–I, etc.), or non-bonding lone pairs of electrons. Less common, however, is the formation of new C–C σ-bonds from existing C–C σ-bonds. Due to the abundance of C–C σ-bonds in organic molecules, methods for the selective activation and functionalization of these bonds present a difficult but exciting opportunity for growth in organic chemistry. Transition-metal catalysts are often used to overcome some of the difficulties presented by the activation of C–C σ-bonds.

Two major difficulties are present in the selective activation of C–C σ-bonds. First, the thermal free energy of the products is often higher than the starting materials. This is the case for the hydration of the ethane C–C σ-bond with water where the ΔG for the reaction is +3.7 kcal/mol. Second, the kinetic barrier for the activation of the C–C σ-bond is usually high due to the linear directionality of the C–C σ-bonding orbitals and the relative energy of the C–C σ-bonding orbitals relative to metal catalyst orbitals (Figure 1.1).[1]

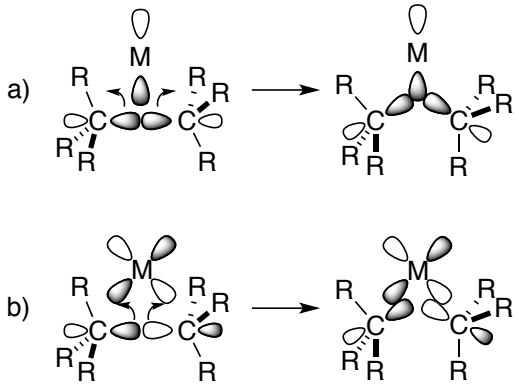


Figure 1.1. a) Interaction of metal bonding orbital with C–C σ-bonding orbital. b) interaction of metal anti-bonding orbital with C–C σ-anti-bonding orbital.

Transition metal catalysts operate by opening an alternative mechanistic pathway, when compared to traditional polar or radical methods for breaking and making new bonds, thereby lowering the kinetic barrier for chemical reactions to occur. The most common methods for activating C–C bonds include ring-strain promoted C–C bond activation, functional group directed C–C bond activation, β-carbon elimination, and C–CN bond activation.

1.2 Ring-strain Driven C–C Bond Activation

C. F. H. Tipper presented the seminal example of C–C bond activation using ring-strain for the stoichiometric activation of cyclopropane by $PtCl_2$ (Scheme 1.1).[2]

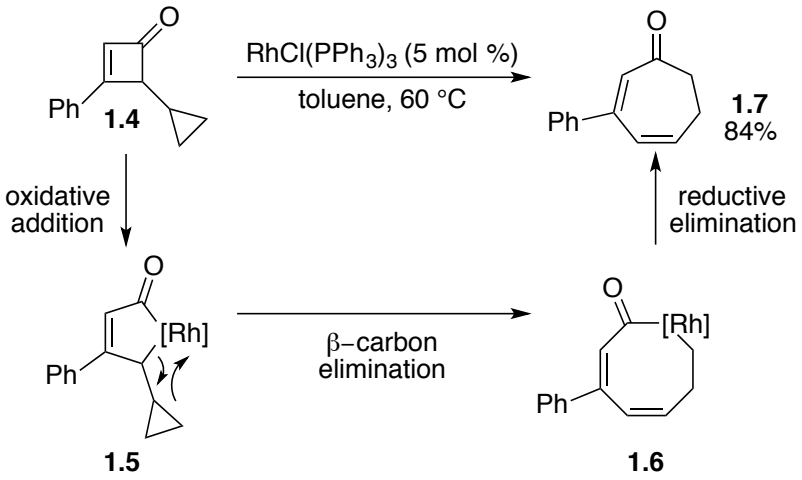
1.1 **1.2** **1.3**

Scheme 1.1. Activation of cyclopropane by $PtCl_2$.

Scheme 1.1 shows how the platinum metal inserts itself into the cyclopropane bond forming **1.2** which is then trapped with pyridine to form the final platinum (IV) complex **1.3**. The reaction is not catalytic in platinum but it

does show how the relief of ring strain can be used to drive oxidative addition into the C–C bond.

Liebeskind *et al*. disclosed an example of using ring strain to drive C–C bond activation for the synthesis of medium-sized-ring ketones (Scheme 1.2).[3]



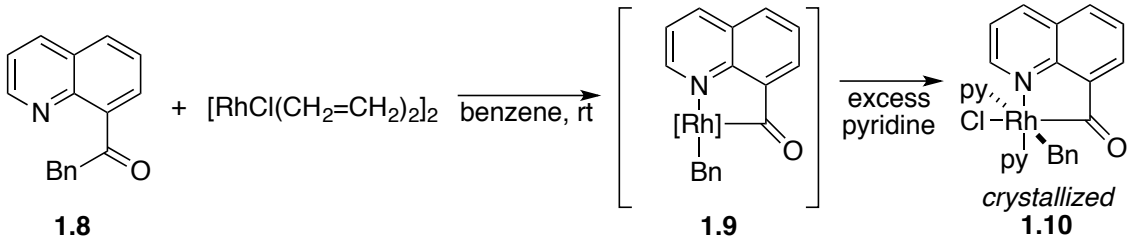
Scheme 1.2. Synthesis of medium-sized-rings by strain-assisted oxidative addition.

Wilkinson's catalyst ($RhCl(PPh_3)_3$) is used to form the 7-membered ring **1.7** from **1.4**. The rhodium catalyst inserts into the C–C(O) bond of **1.4** forming the 5-membered rhodium intermediate **1.5**. The rhodium activates α to the carbonyl due to the electron-withdrawing nature of the carbonyl which weakens the C–C bond. The other C–C bond α to the carbonyl is less reactive with rhodium due to the partial double-bond character conferred by resonance. Subsequent β-carbon elimination forms the 8-membered rhodacycle **1.6**, which undergoes reductive elimination to form the product **1.7**. Rhodium is used in other examples of ring-strain-driven oxidative addition in catalytic reactions,[4] as well as nickel[5] and ruthenium.[6]

1.3 Functional Group Directed C–C Bond Activation

Jun and Suggs published the C–C bond activation of 8-quinolyl ketone **1.8** using a $[RhCl(CH_2{=}CH_2)_2]_2$ catalyst (Scheme 1.3).[7] The nitrogen on the quinoline

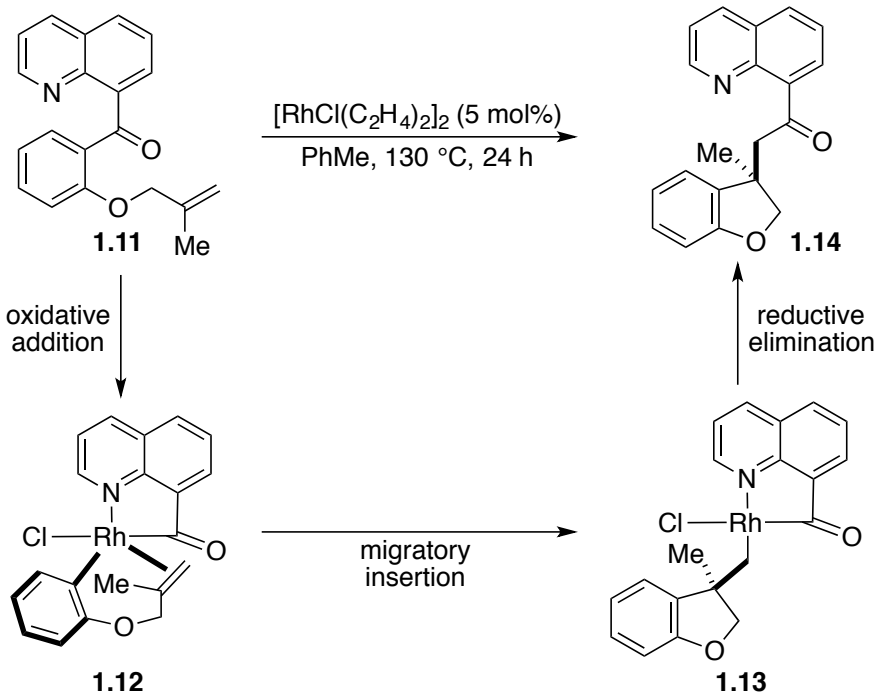
ring directs the rhodium catalyst into proximity with the C–C(O) bond, thereby promoting insertion of the metal into the C–C(O) bond forming rhodacycle **1.9**. Adding excess pyridine to the solution forms the octahedral bis-pyridine adduct **1.10** which is crystallized. Suggs and coworkers explored this and similar stoichiometric quinoline-directed C–C activation with rhodium in subsequent work.[8,9] They also developed a catalytic variant for the ethylene-olysis of 8-acylquinolines using an ethylene pressurized system.[10]



1.8 **1.9** **1.10**

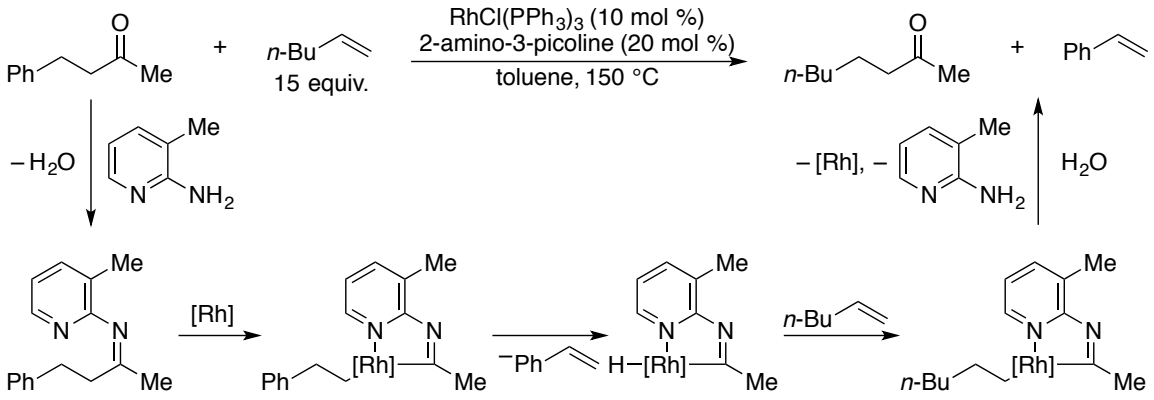
Scheme 1.3. Quinoline-directed C–C bond activation with $[RhCl(CH_2{=}CH_2)_2]_2$.

Douglas and Dreis used the quinoline directing group in a catalytic carboacylation reaction converting alkene **1.11** to dihydrobenzofuran product **1.14** by an intramolecular cyclization.[11,12] Rhodium coordination to the quinoline nitrogen and subsequent C_{acyl}–C_{aryl} bond activation forms the rhodium intermediate **1.12** (Scheme 1.4). Oxidative addition is followed by migratory insertion of the alkene into the aryl–rhodium bond, which forms intermediate **1.13**. Reductive elimination forms **1.14** and regenerates the catalyst. Douglas was also able to perform a quinoline-directed carboacylation intermolecularly between 8-acylquinoline derivatives and various bicyclic norbornenes.[13] The mechanism of this reaction was studied by Johnson *et al*. and it was determined using natural abundance $^{12}C/^{13}C$ kinetic isotope experiments on methyl-substituted alkenes that the turnover-limiting step was C_{acyl}–C_{aryl} bond activation.[14,15]



Scheme 1.4. Rhodium catalyzed carboacylation of 8-acylquinolines.

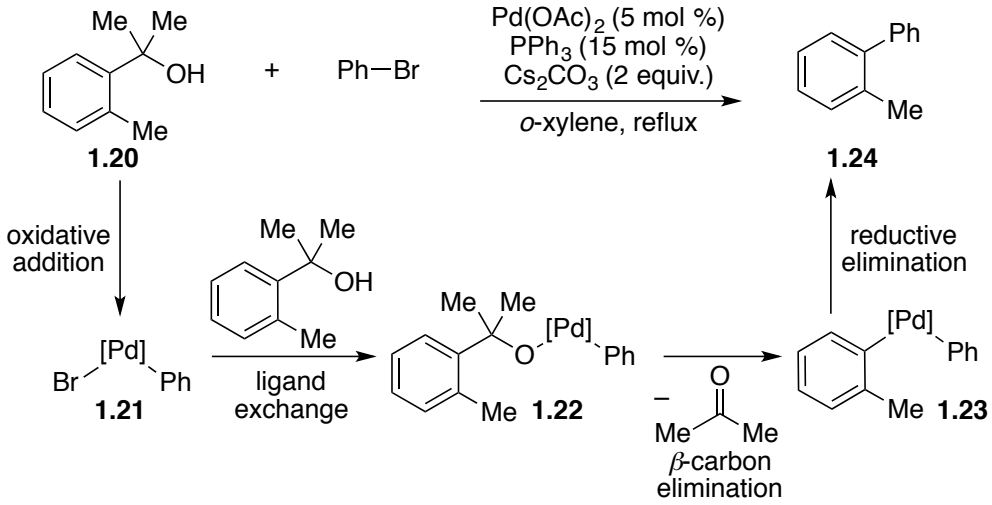
The quinoline directing group has the drawback that no method currently exists for its cleavage after the desired reaction has taken place. Jun and coworkers developed a cooperative catalysis method using 2-amino-3-picoline and a rhodium precatalyst.[16,17] The amino-group on 2-amino-3-picoline reacts with a carbonyl to form an imine in solution, thus placing the pyridine nitrogen in proximity to the C–C bond and forming the directing group *in situ* (Scheme 1.5). The use of 2-amino-3-picoline in cooperative catalysis is also utilized for the synthesis of [3.3.1] bicyclic rings[18] and in intramolecular hydroacylation for the synthesis of medium-sized rings.[19]



Scheme 1.5. Cooperative catalysis approach to C–C bond activation with [Rh] and 2-amino-3-picoline.

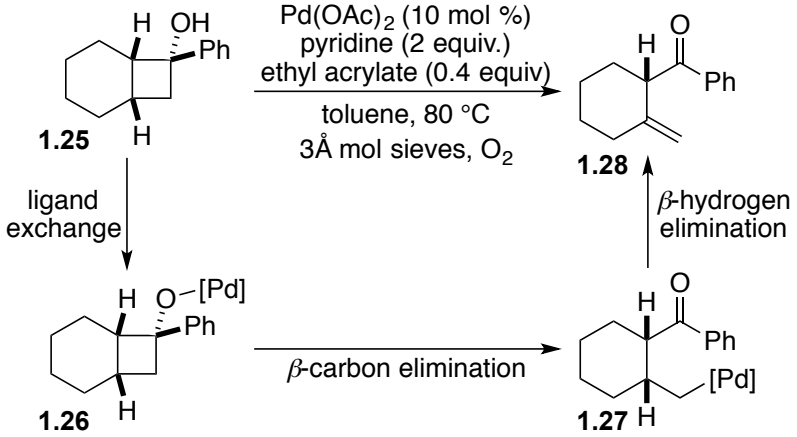
1.4 β-carbon Elimination for C–C Activation

β-carbon elimination is different than the previously presented examples of C–C bond activation reactions in that the σ-bond broken may lead to the extrusion of a by-product, as highlighted by Miura *et al*. (Scheme 1.6).[20] In Miura's methodology, initial oxidative addition of palladium into the Ph–Br bond gives palladium(II) intermediate **1.21**. Ligand exchange of the bromide with the tertiary alcohol **1.20** gives **1.22**. β-carbon elimination then occurs to relieve steric congestion at the carbon α to the oxygen coordinated to palladium yielding di-aryl palladium **1.23**. Reductive elimination gives the biaryl product **1.24**.



Scheme 1.6. Palladium catalyzed arylation by β-carbon elimination.

Uemura *et al*. disclosed a method using ring-strain to drive β-carbon elimination with cyclobutanol **1.25** (Scheme 1.7).[21] This method is more atom economical than Miura's methodology (Scheme 1.6) in that acetone is not a by-product of the reaction and all carbons are present in the reaction product **1.28**. Also, this reaction is unique in that it is a palladium(II)/palladium(0) cycle unlike other mechanisms presented thus far. The mechanism begins with coordination of the palladium(II) to **1.25.** β-carbon elimination from intermediate **1.26** yields the ketone **1.27** and subsequent β-hydride elimination yields the product **1.28**. The resulting palladium catalyst is turned over with O_2.

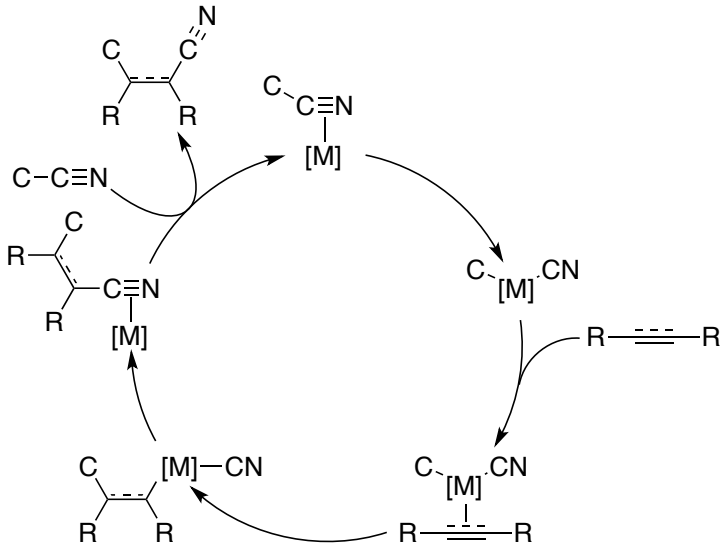


Scheme 1.7. Palladium-catalyzed oxidative ring cleavage by β-carbon elimination.

1.5 C–CN Bond Activation Methods

Nitriles are common functional groups found in organic molecules including pharmaceuticals, organic materials, and polymers. The ability to use transition metal catalysts to selectively activate and functionalize the C–CN bond is an opportunity for fine chemical synthesis and late stage modifications in complex molecule synthesis. The C–CN bond dissociation energy is >100 kcal/mol, which makes it unreactive in many organic transformations. However, low-valent transition metals, especially palladium and nickel complexes, are shown to cleave the C–CN bond.[22,23] Using transition metal catalysts to selectively activate

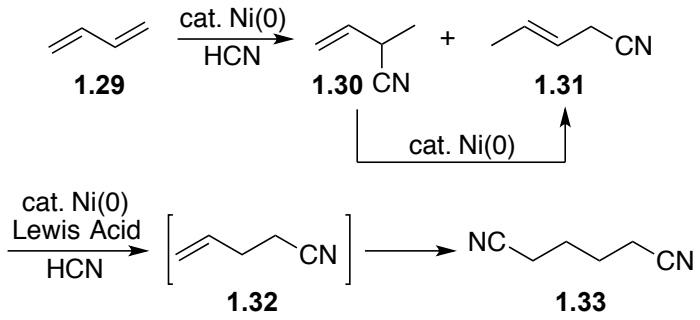
the C–CN bond with subsequent addition across a π-bond provides access to two new C–C bonds with perfect atom economy. A hypothetical mechanism by which this reaction occurs is illustrated in Scheme 1.8. This method has been successfully applied to a variety of C–CN activation reactions.



Scheme 1.8. Hypothetical mechanism for C–CN addition across a π-bond.

1.5.1 Mechanism of C–CN Bond Activation for Adiponitrile and Model Systems

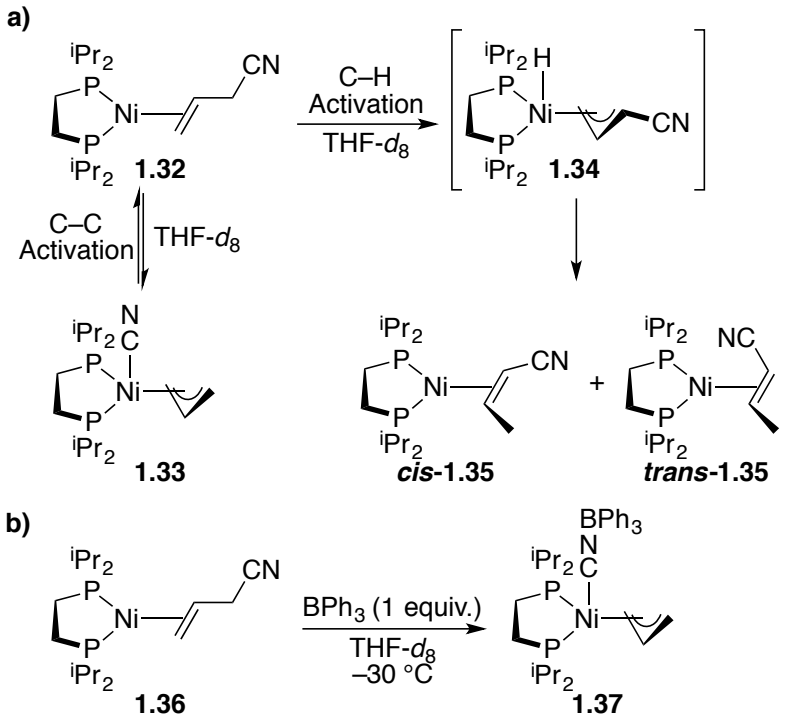
The DuPont and Jones groups each studied the oxidative addition of nickel(0) into the C–CN bond extensively, the results of which are of particular interest for DuPont in their adiponitrile process (Scheme 1.9).[24-27] In this process 1,3-butadiene (**1.29**) undergoes hydrocyanation in the presence of a nickel(0) catalyst and Lewis acid to make adiponitrile **1.33**. The conversion of the secondary nitrile **1.30** to the primary nitrile **1.31** proceeds by C–CN activation to form a π-allyl nickel cyanide that reductively eliminates to form **1.31**.



Scheme 1.9. DuPont's adiponitrile synthesis.

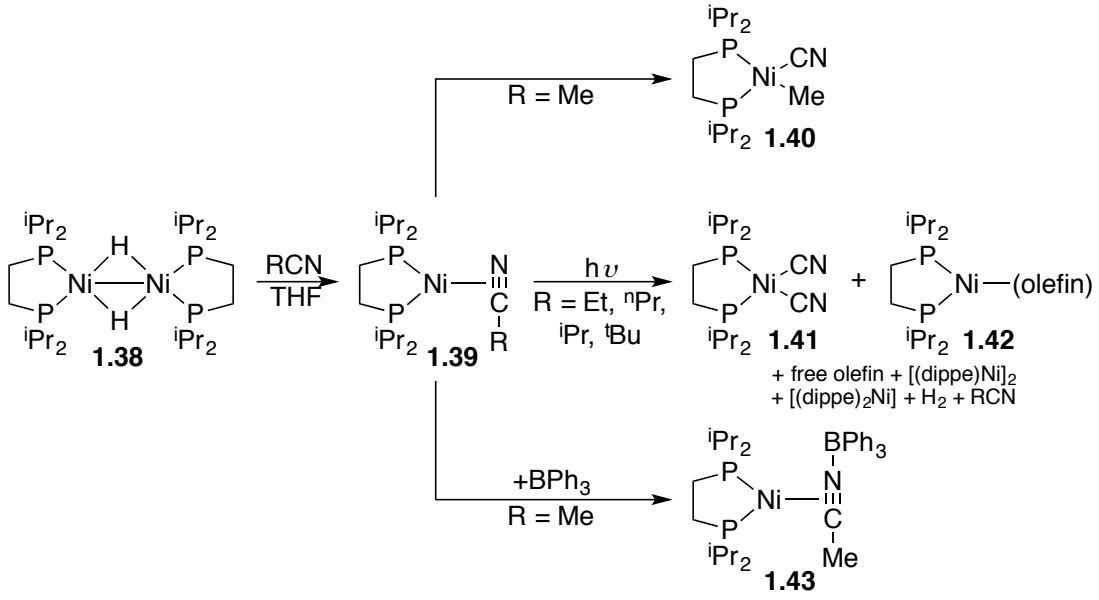
Jones and coworkers found that C–CN bond activation is reversible and in competition with C–H bond activation using (dippe)Ni(allyl cyanide) **1.32** (Scheme 1.10a), which is a model system applicable to the adiponitrile synthesis. Jones observed the C–CN activation complex **1.33** and products ***cis*-1.35** and ***trans*-1.35** resulting from C–H activation by ^{1}H and ^{31}P NMR spectroscopy at 20 °C. Specifically, the C–CN activation product **1.33** is present in the ^{31}P NMR spectrum as a singlet at 80.8 ppm. This signal rapidly grows in, reaches a maximum, and then slowly disappears leaving only signals corresponding to ***cis*-1.35** and ***trans*-1.35** remaining. The C–H activation pathway is hypothesized to form π-allyl nickel hydride **1.34** which reductively eliminates irreversibly to form the thermodynamic alkene product as ***cis*-1.35** and ***trans*-1.35** isomers.

Lewis acids are commonly used in C–CN bond activation reactions that proceed by oxidative addition of a transition metal into a C–CN bond. DuPont researchers found that $ZnCl_2$, $AlCl_3$, and BPh_3 Lewis acids greatly accelerated the rate of C–CN activation.[26] Jones found that the addition of BPh_3 to **1.36** at –30 °C exclusively formed the C–CN activation product **1.37** without the competitive C–H activation products (Scheme 1.10b).



Scheme 1.10. Nickel(0) catalyzed C–CN vs C–H activation of allyl cyanide.

Jones and coworkers reported the stoichiometric reaction of various alkyl cyanides with $[(dippe)NiH]_2$ (Scheme 1.11, **1.38**).[28] Alkyl cyanides larger than acetonitrile were found to undergo C–CN activation slowly under thermal conditions. However, photolytic conditions ($\lambda > 300$ nm) formed $(dippe)Ni(CN)_2$ **1.41** as a yellow precipitate and other nickel olefin products **1.42**. This result suggests that after C–CN activation, β-hydride elimination occurs rapidly to form a nickel–hydride which undergoes disproportionation to form the observed products. In the C–CN activation reaction of η_2-acetonitrile complex **1.39** (R = Me), Jones found that C–CN activation occurs thermally forming **1.40**. Jones *et al*. hypothesized that the addition of BPh_3 will increase the rate of C–CN activation. Interestingly, they found that the addition of BPh_3 slowed oxidative addition yielding the η_2-Lewis adduct **1.43**. This is consistent with a result for a palladium system reported by Moloy *et al*. where adding Lewis acid increased the rate of reductive elimination, the microscopic reverse of oxidative addition.[29]



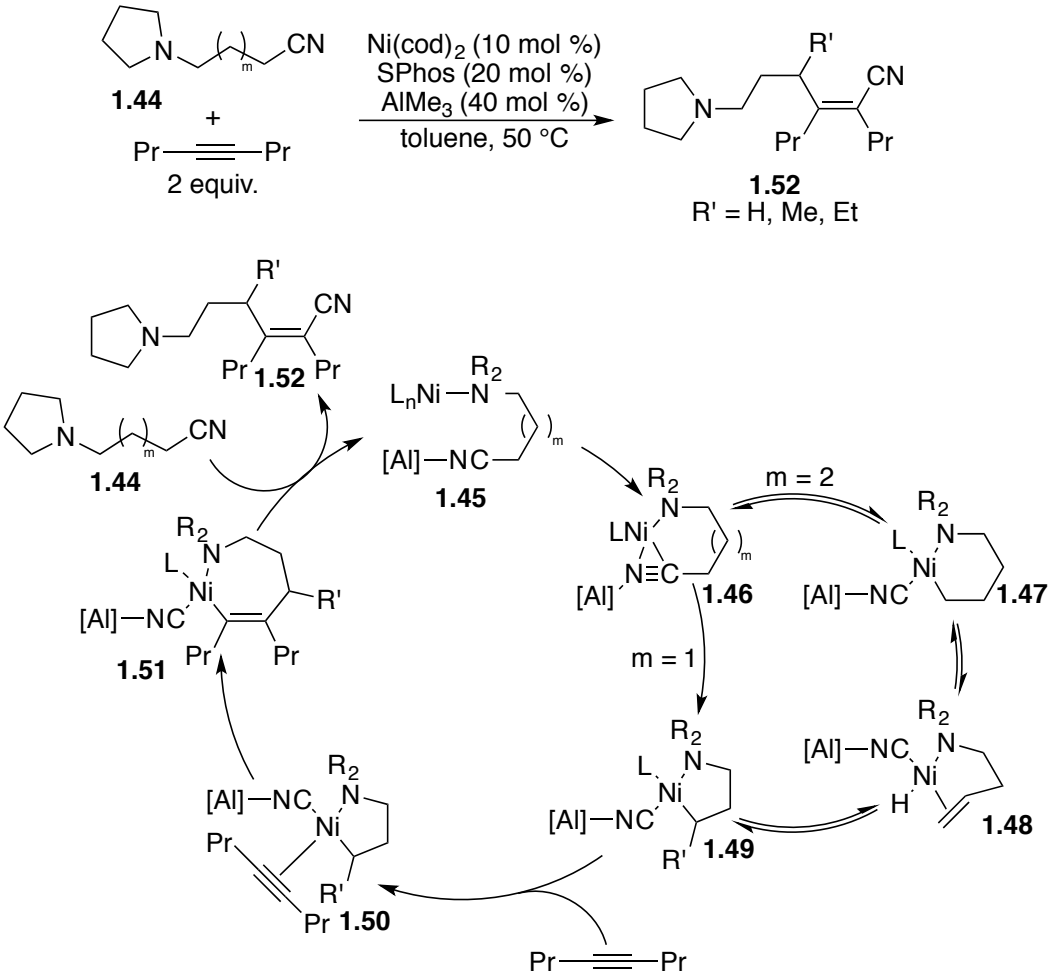
Scheme 1.11. Stoichiometric reaction of $[(dippe)NiH]_2$ with alkyl cyanides.

With the mechanistic results for stoichiometric C–CN activation reactions reported by Jones, it is prudent to explore various catalytic C–CN activation reactions including alkylcyanation,[30-32] alkenylcyanation,[31,33] alkynylcyanation,[34] allylcyanation,[35] arylcyanation,[31,33,36-40] acylcyanation,[41-43] cyanoesterification,[44-48] and cyanoamidation.[47,49-53]

1.5.2 Alkylcyanation

Nakao and Hiyama explored the intermolecular nickel-catalyzed alkylcyanation of alkynes using a $AlMe_3$ Lewis acid co-catalyst.[30] Due to the competitive β-hydride elimination reaction observed in prior work,[31,32] Nakao utilized chelation from a secondary amino group at the γ-position on the alkylnitrile **1.44** (Scheme 1.12). Other chelating groups are also explored including ethers, thioethers, and pyridine. The reaction exclusively occurs at the γ-position to the directing group. This is explained on the right side of the mechanism for M = 2 giving R′ = Me (Scheme 1.12). Chelating groups that did

not work included phthalimide, phosphine, and ester. The stereochemistry of the resulting alkene is exclusively cis.

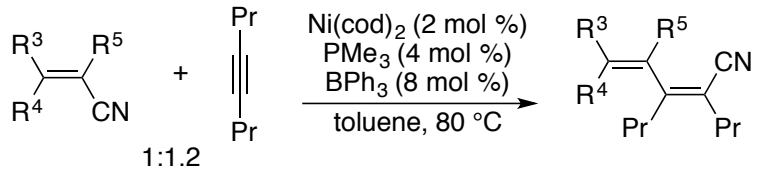


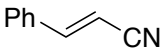
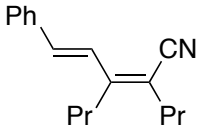
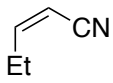
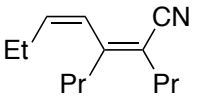
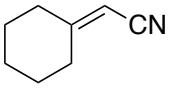
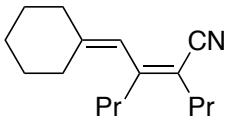
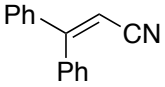
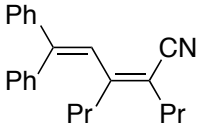
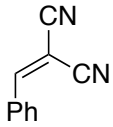
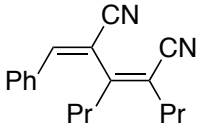
Scheme 1.12. Directing-group assisted alkylcyanation of alkynes.

1.5.3 Alkenylcyanation

Nakao and Hiyama presented the first example of alkenylcyanation of 3-hexyne (Table 1.1) and subsequently expanded the substrate scope in 2010.[31,33] The nickel(0) pre-catalyst, with BPh_3 Lewis acid and PMe_3 ligand, performs the alkenylcyanation of alkynes in good to excellent yields (Table 1.1, entries 1–5). The stereochemistry of *Z*-ethyl alkene (Table 1.1, entry 2) is eroded but mostly maintained as the less stable *Z*-olefin (4*Z*/4*E* = 84:16).

Table 1.1. Alkenylcyanation of 3-hexyne with Nickel Catalyst and Boron Lewis Acid



entry	alkenyl–CN	time (h)	product	yield (%)[a]
1		20		94
2		15		78[b]
3		21		91
4		46		94
5[c]		13		81[d]

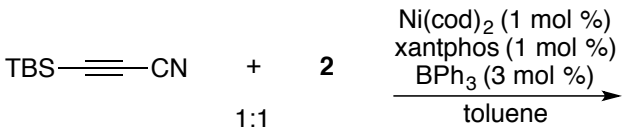
[a] Isolated yields of isomerically pure products, unless otherwise noted. [b] 4*Z*/4*E* = 84:16. [c] The reaction was carried out using $Ni(cod)_2$ (4 mol %), dppb (4 mol %), and BPh_3 (16 mol %). [d] An isomer was also obtained in ~2% yield.

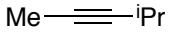
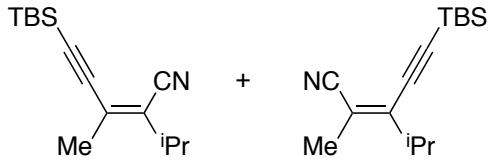
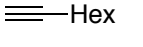
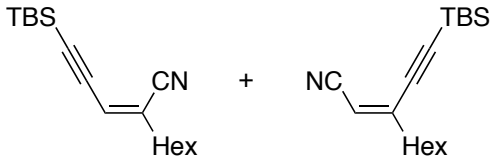
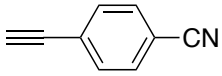
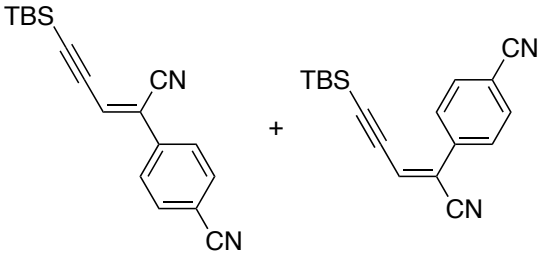
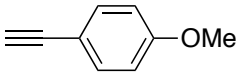
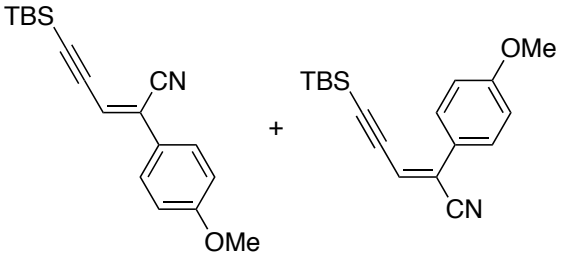
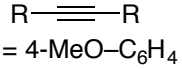
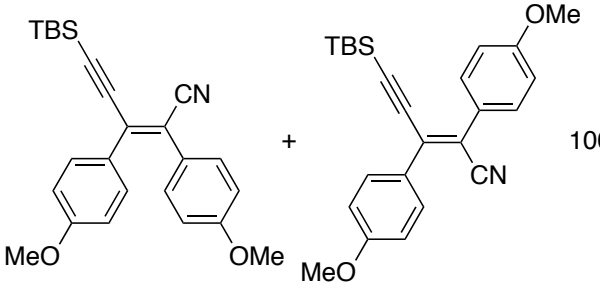
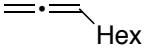
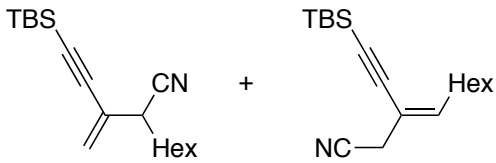
1.5.4 Alkynylcyanation

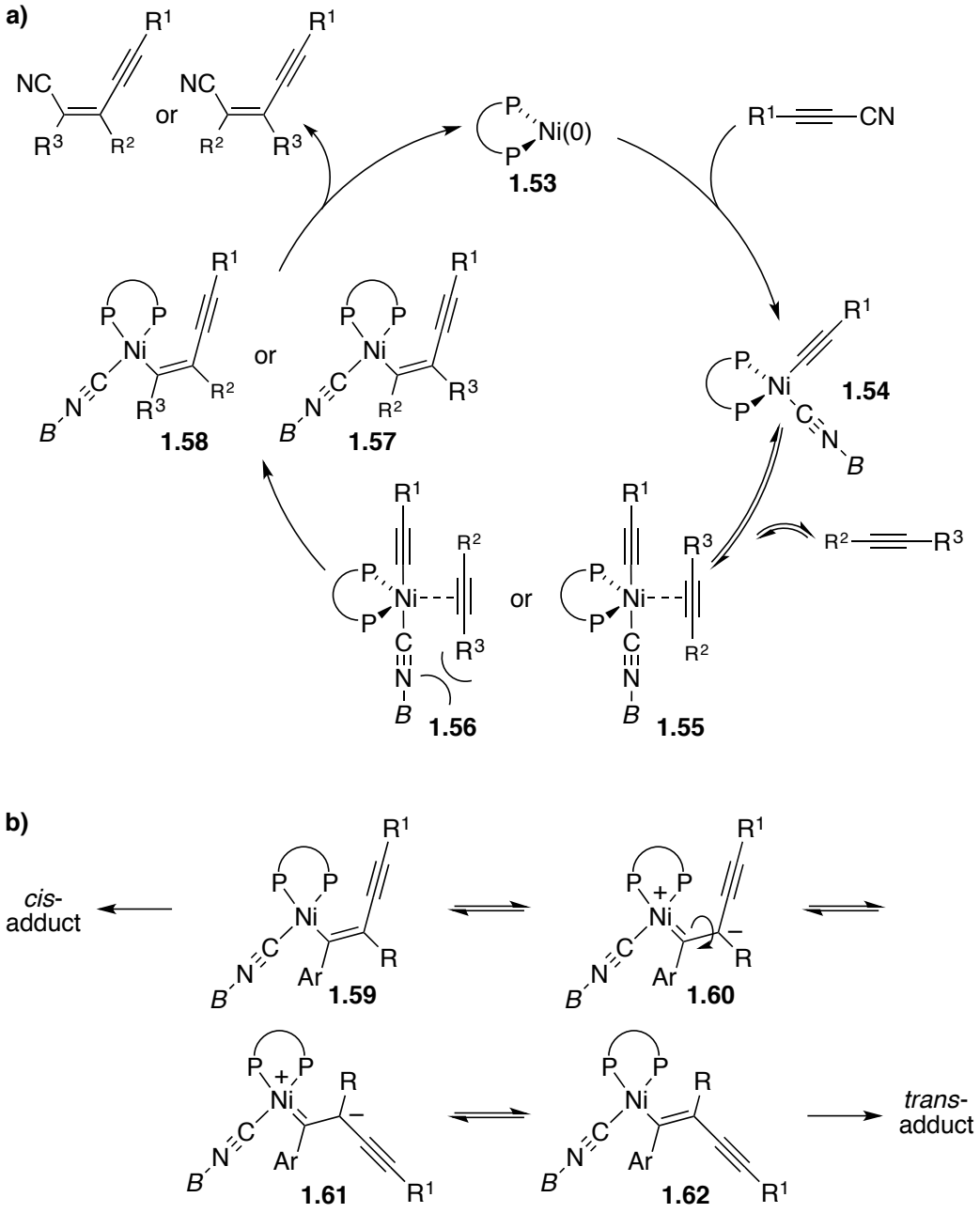
Nakao and Hiyama explored the alkynylcyanation of alkynes and allenes by C–CN activation of alkynylcyanides (Table 1.2).[34] The regiochemistry of the product favors cyanation at the alkyne carbon with the smallest substituent except in the case of terminal alkynes (Table 1.2, entries 1 versus 2). Nakao *et al*. hypothesize that the bulkiness of the BPh_3 coordinated to the cyanide provides the steric bias for the cyanide preferentially forming a bond to the

carbon with the least bulky substituent (Scheme 1.13a, **1.55** versus **1.56**). The authors give no explanation for the change in regiochemistry for terminal alkynes. Mixtures of *cis*- and *trans*-addition of the alkynylcyanides across aryl-substituted alkynes are observed (Table 1.2, entries 3–5). This is the only example of *trans*-addition of R–CN across an alkyne. The *trans*-addition is rationalized in Scheme 1.13b where the nickel donates a pair of electrons into the alkene after migratory insertion (**1.59**) to form a zwitterion with a formal positive charge on nitrogen (**1.60**). Rotation about the C–C bond, as indicated in **1.60** (Scheme 1.13b), gives **1.61** which forms **1.62** after the electrons reform the C–C double bond again. Nakao *et al*. hypothesize that electron-rich arenes stabilize the formal positive charge on nickel, thus favoring the *trans*-product formation (Table 1.2, entry 3 versus 4). Allenes undergo alkynylcyanation to give the addition of the alkyne at the 2nd carbon of the allene preferentially. Addition of the cyanide to the 3-position is favored over addition to the 1-position (Table 1.2, entry 6).

Table 1.2. Nickel-Catalyzed Alkynylcyanation of Alkynes and Allenes



entry	2	time (h)	temp (°C)	products	yield (%)
1		49	80		82 (22:78)
2		15	40		96 (83:13)
3		17	40		96 (98:2)
4		48	40		93 (75:25)
5	 R = 4-MeO–C_6H_4	48	40		100 (11:89)
6		19	50		73 (93:7)



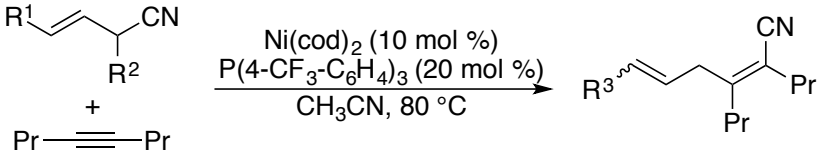
Scheme 1.13. Nickel-catalyzed alkynylcyanation of alkyne with boron Lewis acid.

1.5.5 Allylcyanation

Jones *et al*. demonstrated the stoichiometric C–CN activation of allyl cyanide in a model system for DuPont's adiponitrile synthesis.[24,26] An additional example of C–CN activation of allyl cyanides was presented by Nakao and

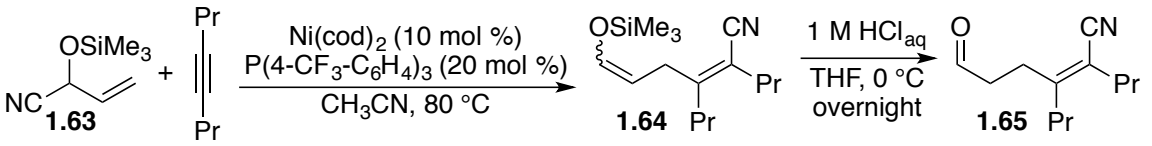
Hiyama in the intermolecular allylcyanation of alkynes with a nickel(0) catalyst.[35] A Lewis acid is not utilized as in the alkyl-, alkenyl-, and alkynylcyanation reactions. Nakao *et al*. found that substituents at the γ-position to the CN group give stereoisomers at the resulting olefin in the products when R^1 or R^2 is methyl (Table 1.3).

Table 1.3. Nickel-Catalyzed Allylcyanation of 3-hexyne with Alkyl-Substituted Allyl Cyanides

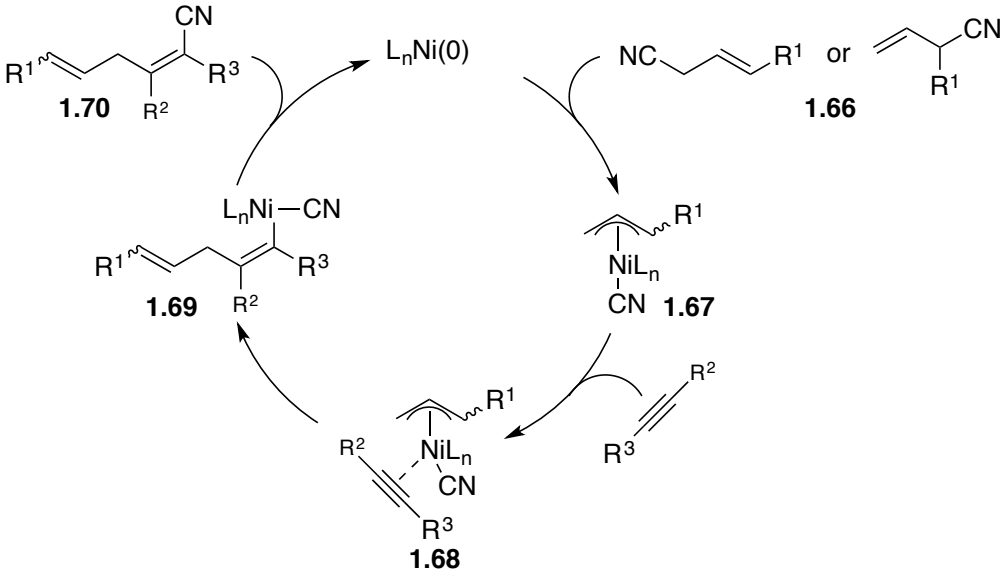


Entry	R^1	R^2	time (h)	R^3	5*E*:5*Z*	yield (%)
1	H	H	8	H	–	78
2	Me	H	17	Me	83:17	55
3	H	Me	17	Me	85:15	69
4	*t*-Bu	H	18	*t*-Bu	>99:1	49
5	Ph	H	18	Ph	>99:1	86

α-siloxyallyl cyanides **1.63** form the corresponding silyl enol ether **1.64** in good to excellent yields (Scheme 1.14). Subjecting the silyl enol ether products to acidic conditions overnight afforded the aldehyde products **1.65**. Nakao *et al*. explored the scope of the α-siloxyallyl cyanides and demonstrated that substituents at the α- or β-positions are tolerated. Various alkyne reacting partners are also explored.[35] The reaction mechanism begins with coordination of allyl cyanide **1.66** to the nickel(0) forming π-allyl nickel(II) intermediate **1.67** after C–CN activation (Scheme 1.15). Coordination of alkyne forms the η_2-nickel complex **1.68**. Migratory insertion then preferentially yields the linear product where the unsubstituted carbon of the allyl fragment forms a bond to the alkyne carbon with the smallest substituent **1.69**. Reductive elimination turns over the nickel catalyst and produces product **1.70**.



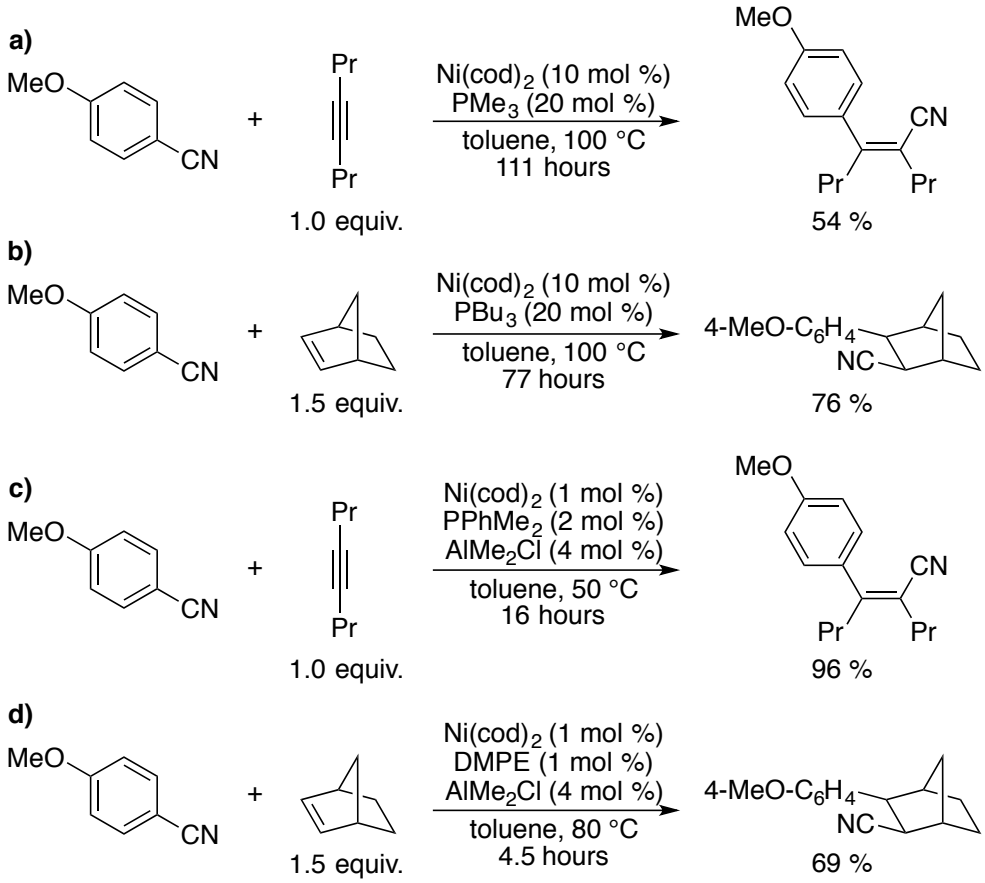
Scheme 1.14. Allylcyanation of alkynes with α-siloxyallyl cyanides for the synthesis of aldehydes.



Scheme 1.15. Mechanism of allylcyanation of alkynes.

1.5.6 Arylcyanation

Nakao and Hiyama presented the first example of intermolecular nickel-catalyzed arylcyanation of alkynes in 2004[36] (Scheme 1.16a) with subsequent substrate scope expansions in alkynes[40] and norbornene derivatives[37] in 2006 (Scheme 1.16b). These methods utilize a nickel(0) catalyst and phosphine ligand but no Lewis acid catalyst. The authors hypothesize that oxidative addition of the nickel into the C–CN bond is the rate-limiting step for the system. Nakao and Hiyama improved the efficiency of the arylcyanation of alkynes in 2007 with the use of an aluminum Lewis acid co-catalyst (Scheme 1.16c).[31] Nakao *et al.* expanded the substrate scope for the nickel/Lewis acid co-catalyzed intermolecular arylcyanation in 2010 to include additional alkynes and norbornene derivatives (Scheme 1.16d).[33]

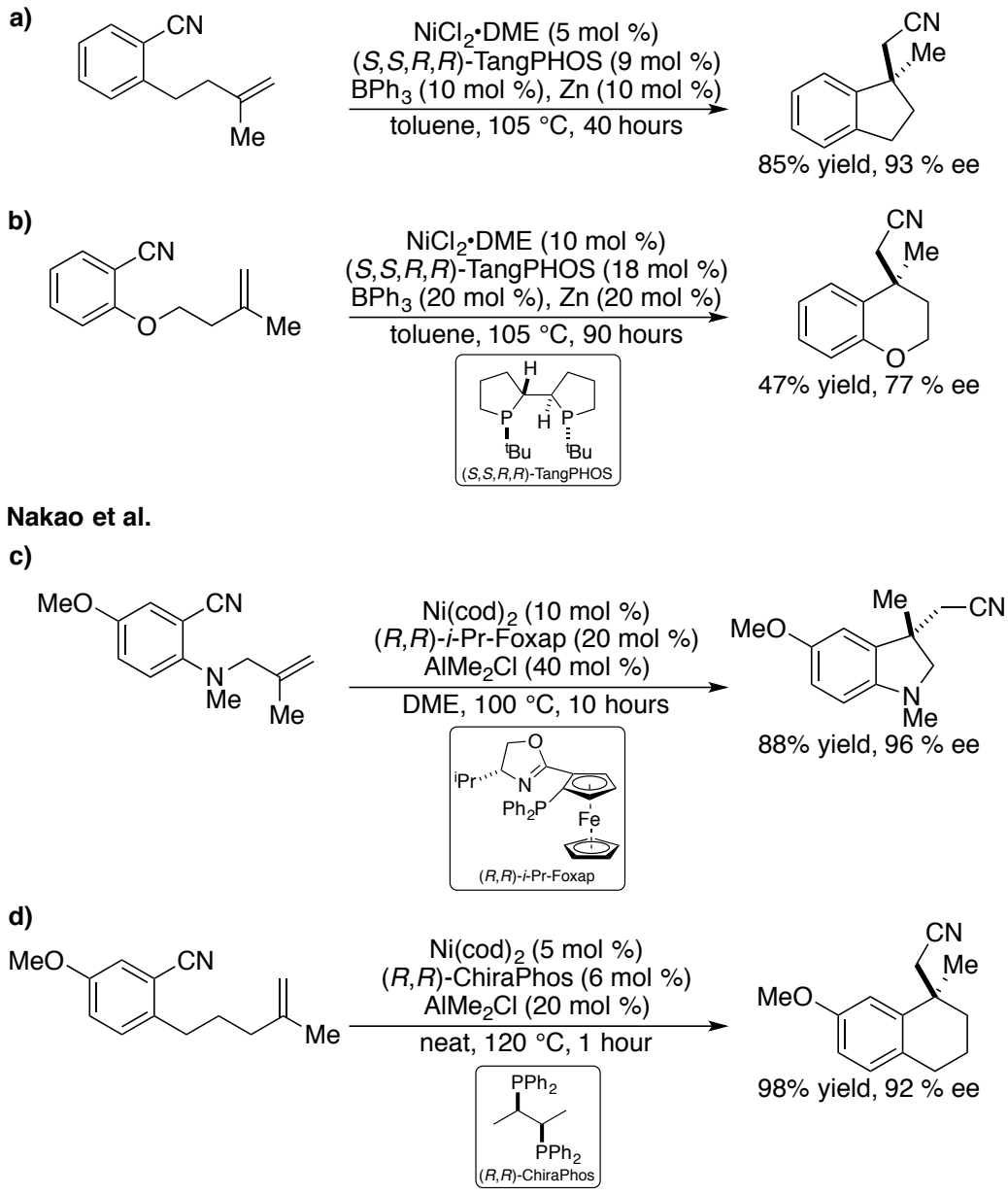


Scheme 1.16. a) Arylcyanation of alkynes without Lewis acid co-catalyst (2004). **b)** Arylcyanation of norbornene without Lewis acid co-catalyst (2006). **c)** Arylcyanation of alkynes with aluminum Lewis acid co-catalyst (2007). **d)** Arylcyanation of norbornene with aluminum Lewis acid co-catalyst (2010).

Jacobsen *et al.*[39] and Nakao *et al.*[38] separately published the first intramolecular examples of arylcyanation of alkenes (Scheme 1.17). Not only are these the first intramolecular examples of arylcyanation, but they both demonstrate enantioselectivity using chiral phosphine ligands alongside Lewis acid co-catalysts. Jacobsen found that reducing the nickel(II) pre-catalyst with zinc to nickel(0) yields a more active catalyst; in addition, all reactions are performed with the same chiral ligand, (*S*,*S*,*R*,*R*,)-TangPHOS. This system is very good for the synthesis of 5-membered rings; however, the enantioselectivity for 6-membered rings is significantly poorer (Scheme 1.17).[39]

Nakao uses a $Ni(cod)_2$ pre-catalyst and performs most of the reactions with achiral phosphine ligands (PMe_3, $PCyPh_2$, PMe_2Ph, and DMPE). The two

enantioselective examples are illustrated in Scheme 1.17a and b. The products of these reactions are precursors to natural products. The (*R*,*R*)-*i*-Pr-Foxap ligand performs best for producing 5-membered ring product with high enantioselectivity (Scheme 1.17c). (*R*,*R*)-ChiraPhos is a better ligand for making the 6-membered ring product with high enantioselectivity (Scheme 1.17d). Both the Jacobsen and Nakao systems utilize Lewis acids: BPh_3 and $AlMe_2Cl$, respectively.



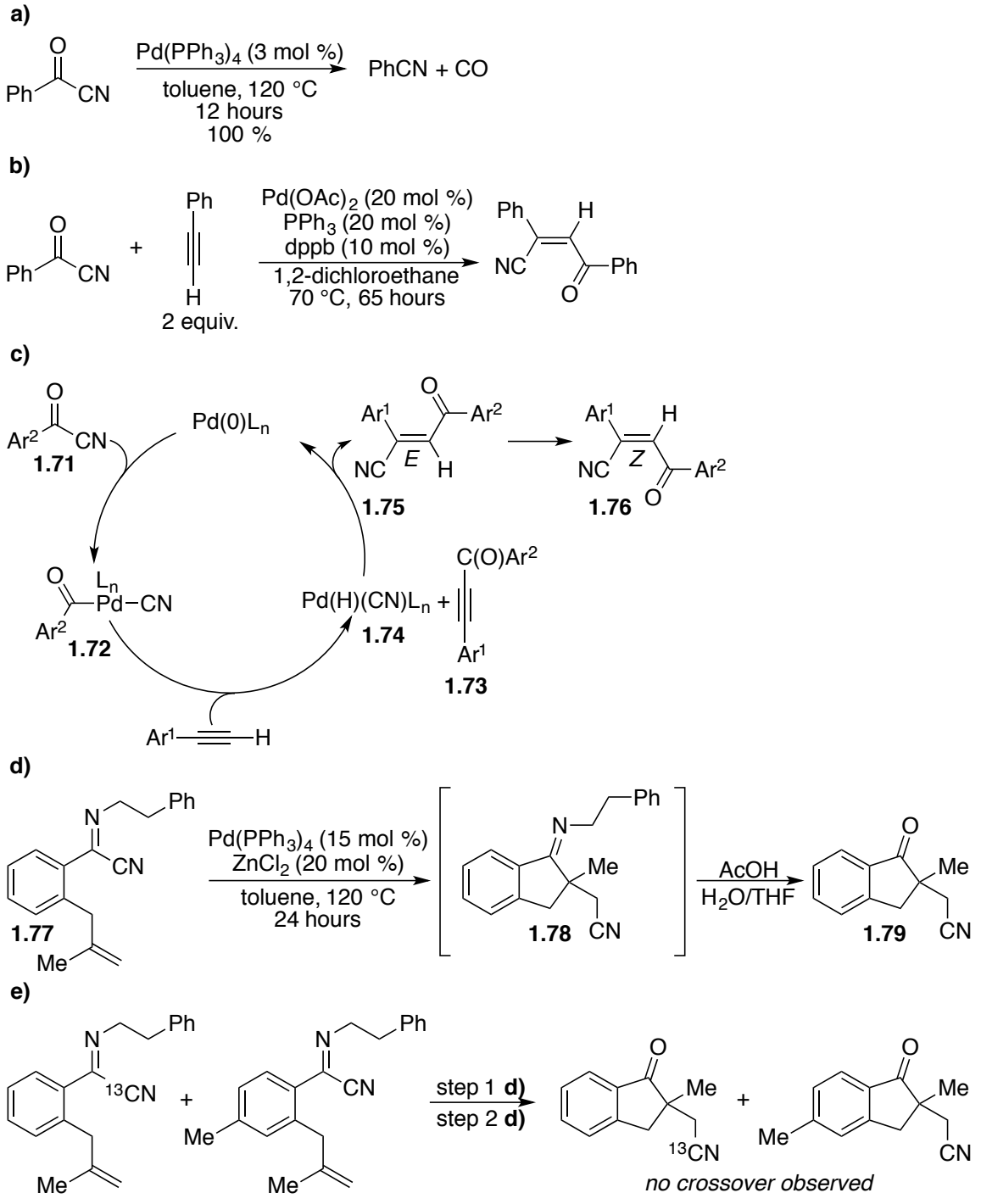
Scheme 1.17. Asymmetric intramolecular arylcyanation of alkenes with chiral phosphine ligands.

1.5.7 Acylcyanation

Acylcyanation is among the most difficult of the carbocyanation reactions developed due to the various competing pathways after C–CN activation. The first major decomposition pathway after C–CN activation is decarbonylation

(Scheme 1.18a) resulting in the extrusion of CO.[47,54] Nozaki and Takaya developed the acylcyanation of alkynes using a palladium catalyst system (Scheme 1.18b).[41,42] The mechanism proceeds by initial C–CN activation of **1.71** to form acylpalladium cyanide **1.72** (Scheme 1.18c). Coordination of terminal alkyne to **1.72** yields alkyne acylation product **1.73** and cyanopalladium hydride **1.74**. Hydrocyanation of acylalkyne **1.73** yields the *E*-alkene **1.75** which subsequently isomerizes to the *Z*-alkene **1.76**. The necessity for the reaction to proceed through the cyanopalladium hydride intermediate **1.74** and acyl–alkyne **1.73** limits the scope of the reaction to terminal alkynes. Nozaki's results indicate that migratory insertion of alkynes into an acylpalladium–cyanide bond is difficult. Heating the reaction above 100 °C also leads to decomposition of the acylnitriles substrates, thus heating to force migratory insertion is unlikely to work.

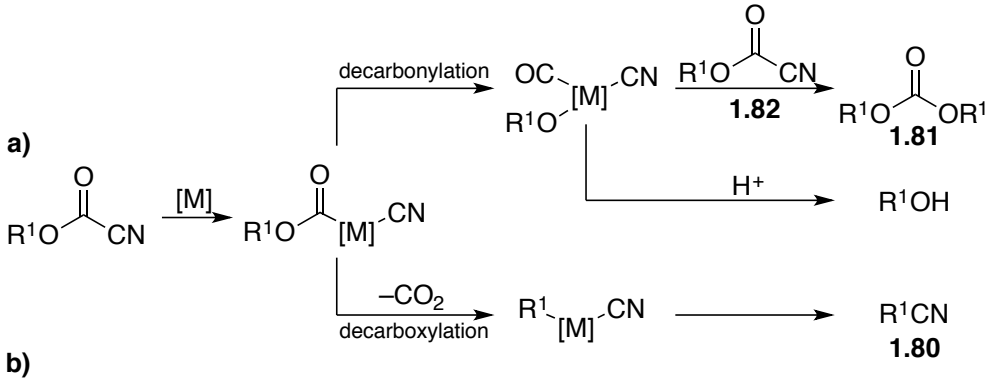
Douglas *et al*. developed an intramolecular acylcyanation of alkenes using α-iminonitriles to overcome the difficulties associated with direct acylcyanation of alkynes (Scheme 1.18d).[43] α-iminonitriles (**1.77**) are unable to undergo decarbonylation which makes them an ideal surrogate for the acyl group. Also, the intramolecular nature of the reaction encourages migratory insertion, although high reaction temperatures are still required for full conversion to cyclized imine product **1.78**. Subsequent hydrolysis of the imines using acetic acid affords the corresponding ketone **1.79**. Douglas *et al*. performed ^{13}CN crossover experiments to determine if cyanide dissociates from the metal over the course of the reaction (Scheme 1.18e). No crossover products are observed, thus supporting a mechanism where the cyanide stays associated to the palladium.



Scheme 1.18. a) Palladium-catalyzed decarbonylation of acyl cyanides. **b)** Formal acylcyanation of terminal alkynes by alkynylacylation and subsequent hydrocyanation. **c)** Mechanism of the formal acylcyanation of terminal alkynes. **d)** Palladium-catalyzed intramolecular acylcyanation of alkenes using α-iminonitriles. **e)** ^{13}CN crossover experiment in the intramolecular acylcyanation of alkenes using α-iminonitriles.

1.5.8 Cyanoesterification

Cyanoesterification presents a similar challenge to acylcyanation in that decarbonylation after C–CN activation is a competitive decomposition pathway (Scheme 1.19a). However, additional difficulties are also present due to the reactivity of the cyanoformate esters to nucleophilic addition from nucleophilic functional groups as well as the possibility for decarboxylation (loss of CO_2) giving alkylnitriles **1.80** after reductive elimination. Also, a commonly observed byproduct of cyanoesterification is **1.81**, which results from decarbonylation followed by disproportionation with an additional cyanoformate ester **1.82**.



Entry	R^1	time (h)	yield %
1	Et	6	94
2	Me	6	43
3	^{n}Pr	6	72
4	^{i}Pr	12	80
5	^{n}Bu	12	67
6	^{t}Bu	24	0
7	Bn	3	31

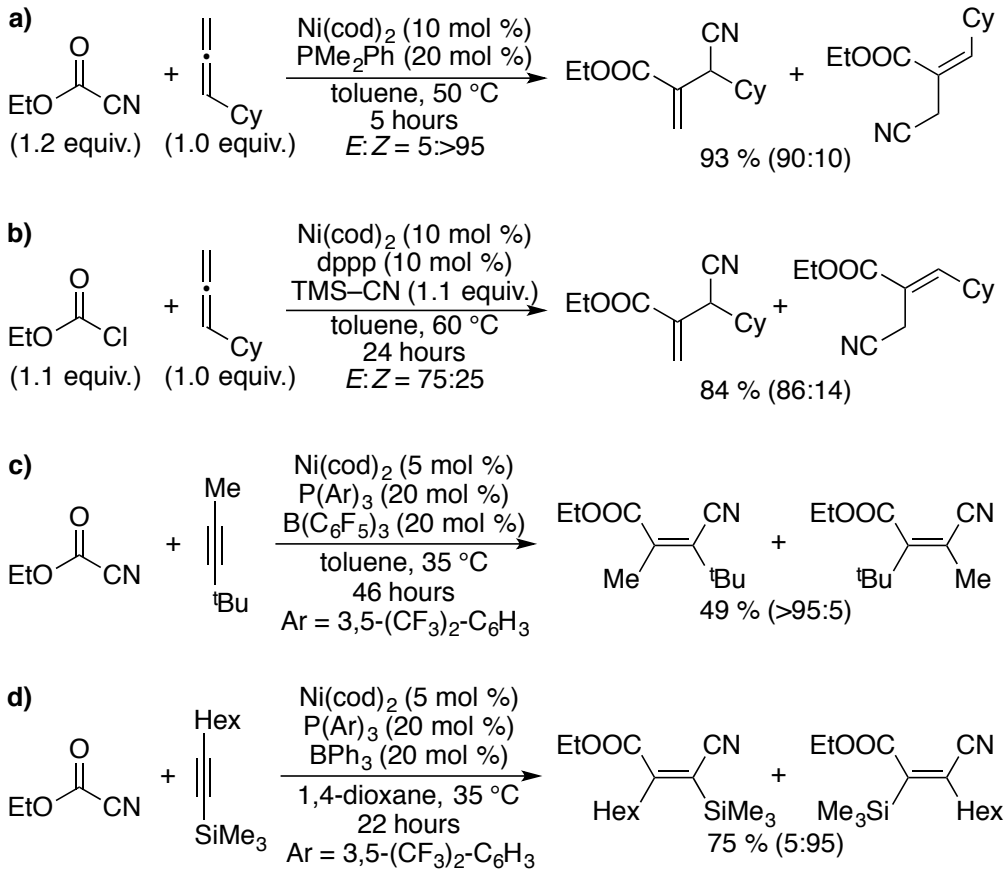
Scheme 1.19. a) Decomposition pathways for cyanoesterification by C–CN activation. **b)** Palladium-catalyzed cyanoesterification of norbornene with cyanoformate esters.

Nishihara and coworkers presented the first palladium-catalyzed cyanoesterification of norbornene using methyl and ethyl cyanoformate esters (Scheme 1.19b).[44] Nishihara further explored the scope of this reaction with respect to the R^1-substituent on the cyanoformate ester **1.82**.[45] Using larger alkyl

cyanoformate esters (R^1 = ^{t}Bu, Bn, ^{n}Bu) leads to decreased product formation. Using R^1 = Ph exclusively forms the disproportionation product **1.81**.

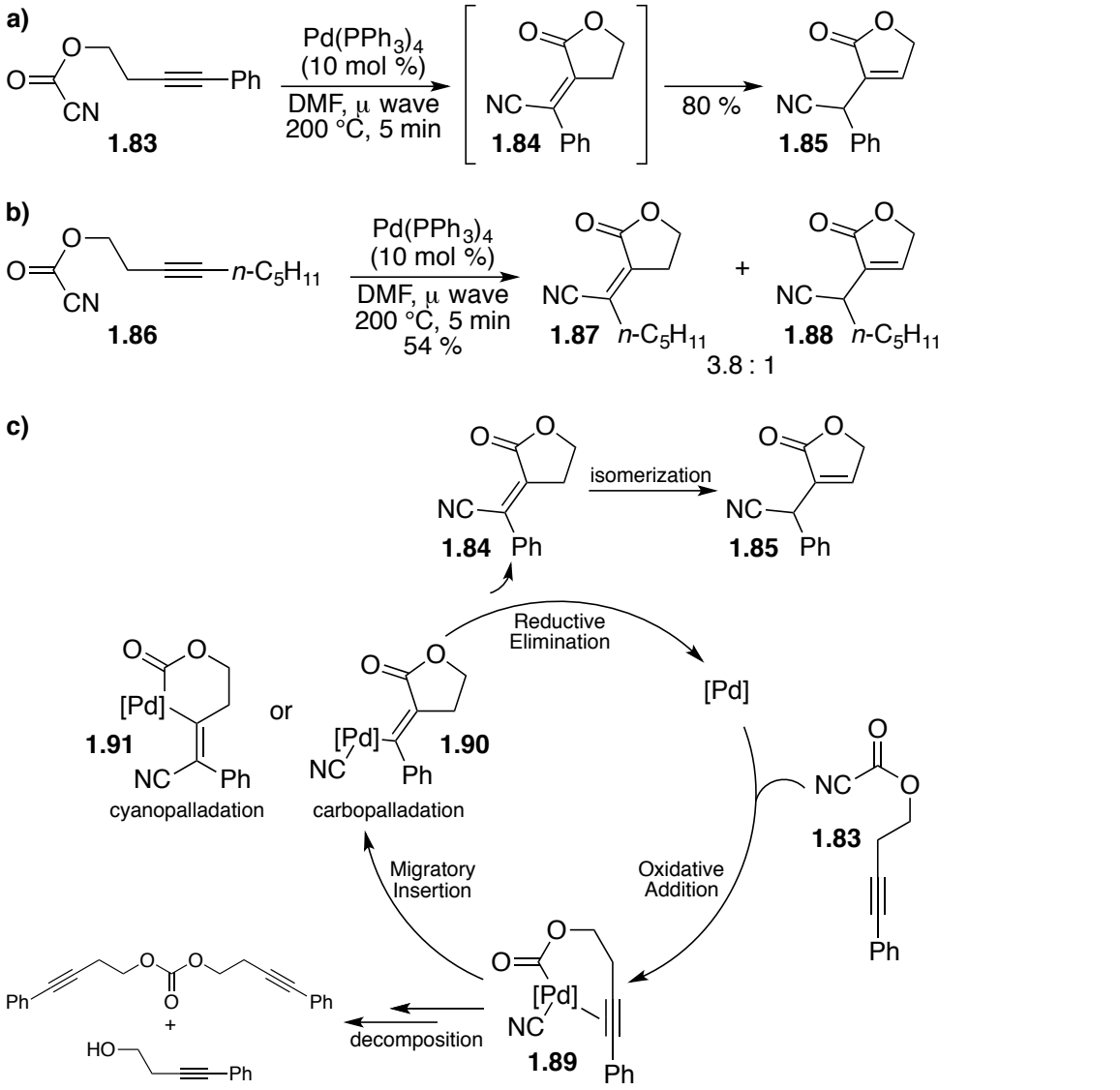
Nakao *et al*. expanded the scope of the reacting partner to allenes using a nickel(0) catalyst system (Scheme 1.20a).[46] The formate ester is selective for acylating the 2-position of the allene and cyanation is generally selective for the 3-position of the allene. Cyanation at the 1-position is a minor product for most 2-component cyanoesterifications. Nakao then sought a 3-component system for broadening the substrate scope and realized this using TMS–CN, ethyl chloroformate, and the bidentate phosphine ligand dppp (Scheme 1.20b). This system is less selective than the 2-component system and is thought to proceed by nickel oxidative addition into the C–Cl bond and a subsequent transmetallation step with the TMS–CN to produce the nickel cyanide *in situ* with TMS–Cl as a byproduct.

Nakao also explored the intermolecular nickel-catalyzed cyanoesterification of alkynes with a boron Lewis acid (Scheme 1.20c & d).[47] The reaction is highly selective for esterification at the alkyne carbon bearing the smaller substituent. However, when the substituent is a silane, the selectivity is reversed (Scheme 1.20d). This is hypothesized to be due to the ester oxygen coordinating to the silicon and directing the migratory insertion to occur at the carbon with the silicon. Thiocyanoformate esters were also attempted but lead to decarbonylation products.[47]



Scheme 1.20. a) 2-component nickel-catalyzed cyanoesterification of allenes. **b)** 3-component nickel-catalyzed cyanoesterification of allenes. **c)** Nickel-catalyzed cyanoesterification of alkynes with boron Lewis acid co-catalyst. **d)** Cyanoesterification of TMS-alkyne resulting in alkene with ester and TMS group on same alkene carbon.

Douglas *et al*. developed the only reported example of intramolecular cyanoesterification of cyanoformate alkynes **1.83** using a palladium catalyst in a microwave oven (Scheme 1.21).[48] Douglas found that aryl-substituted alkynes at the γ-position to the ester oxygen form butenolides **1.85** in good to excellent yields (Scheme 1.21a). It is hypothesized that the reaction proceeds through the exocyclic olefin **1.84** and isomerizes to the conjugated butenolide under the reaction conditions. Incomplete isomerization to the endocyclic butenolide **1.88** is observed when alkyl-substituted alkyne **1.86** is subjected to the reaction conditions (Scheme 1.21 b). Attempting to make the δ-lactone using a longer tether is unsuccessful.



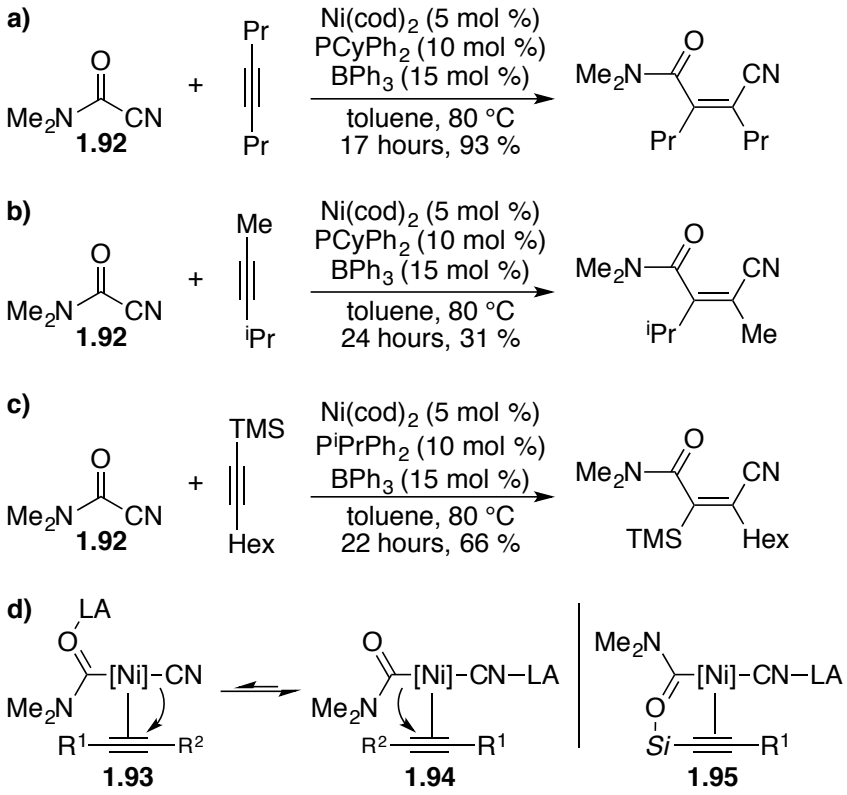
Scheme 1.21. a) Palladium-catalyzed intramolecular cyanoesterification of aryl-substituted alkynes. **b)** Palladium-catalyzed intramolecular cyanoesterification of alkyl-substituted alkynes. **c)** Mechanism of palladium-catalyzed intramolecular cyanoesterification of alkynes.

The mechanism of the reaction is thought to proceed by initial C–CN bond activation by oxidative addition of the palladium into the C–CN bond of **1.83** giving palladium cyanide intermediate **1.89** (Scheme 1.21c). Migratory insertion of the tethered alkyne can proceed by either carbopalladation (**1.90**) or cyanopalladation (**1.91**). Mechanistic studies by Takemoto for intramolecular cyanoamidation suggest that migratory insertion proceeds through carbopalladation.[50] Thus, carbopalladation is hypothesized to be the likely

pathway of migratory insertion for cyanoesterification; however, cyanopalladation cannot be ruled out. Subsequent reductive elimination forms exocyclic olefin **1.84** which isomerizes to **1.85** under the reaction conditions.

1.5.9 Cyanoamidation

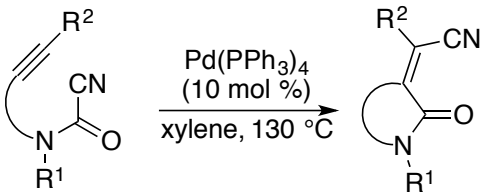
Nakao *et al*. demonstrated the only example of intermolecular nickel-catalyzed cyanoamidation of alkynes with BPh_3 as the Lewis acid.[47] This method is limited to secondary cyanoformamides like **1.92** (Scheme 1.22). Alkynes with linear, non-bulky alkyl substituents perform well in this reaction (Scheme 1.22a). The regioselectivity for this reaction is opposite cyanoesterification in that the acyl group favors the alkyne carbon with the larger substituent (Scheme 1.22b).[47] Nakao hypothesizes that this result is consistent with reversible coordination of the Lewis acid to the nitrile (**1.93**) and carbonyl (**1.94**) (Scheme 1.22d). When the Lewis acid is coordinated to the carbonyl, migratory insertion of the alkyne into the nickel–CN bond is more favored than into the nickel–carbonyl bond. The reluctance of the amide to undergo migratory insertion when not coordinated to Lewis acid is thought to be due to the less nucleophilic nature of the amide carbonyl carbon when compared to ester carbonyl carbon in cyanoesterification. Silane-substituted alkynes favor acylation at the carbon with the silicon similar to the nickel-catalyzed cyanoesterification of alkynes with cyanoformate esters (Scheme 1.22c).[47] This selectivity is likely due to coordination of the amide carbonyl oxygen to the silicon (**1.95**) (Scheme 1.22d).

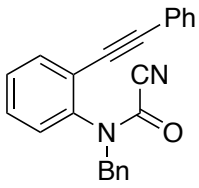
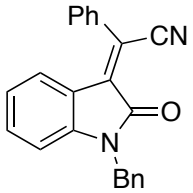
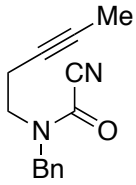
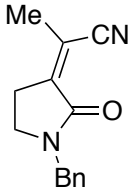
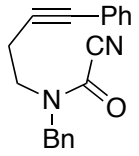
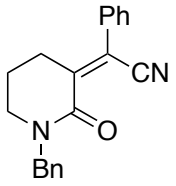
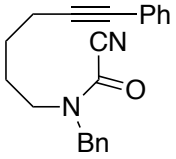
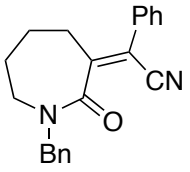
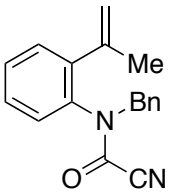
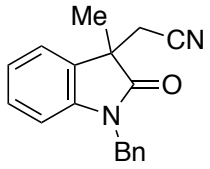


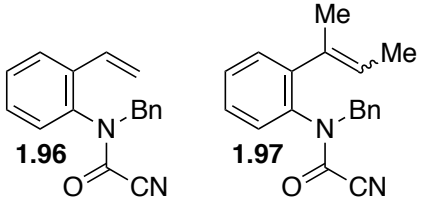
Scheme 1.22. Nickel-catalyzed cyanoamidation of alkynes with BPh_3 Lewis acid co-catalyst.

Takemoto *et al*. published the first examples of palladium-catalyzed intramolecular cyanoamidation of alkynes and alkenes (Table 1.4).[49-52] Both benzene-fused (Table 1.4, entry 1) and varying length aliphatic tethers are successful substrates in the alkyne cyanoamidation (Table 1.4, entries 2–4). A trace amount of the *E*-isomer is observed in the cyanoamidation of alkynes (Table 1.4, entries 1–4). Mono- and tri-substituted alkenes, **1.96** and **1.97** respectively, only give β-hydride elimination products.[50]

Table 1.4. Palladium-Catalyzed Intramolecular Cyanoamidation of Alkynes and Alkenes



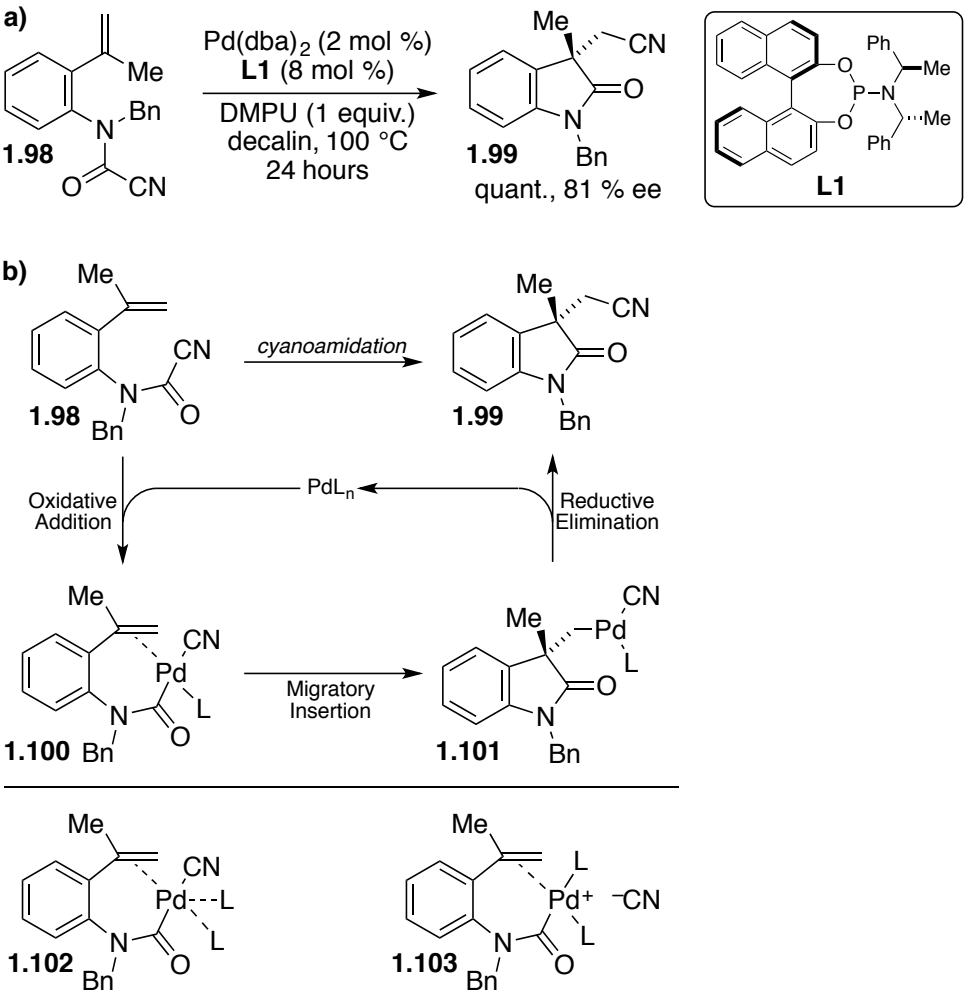
entry	substrate	time (h)	product	yield (%)
1		8		45
2		1		84
3		1		89
4		1		79
5		3		quant.



1.96 **1.97**

Failed Substrates

Takemoto subsequently disclosed the first enantioselective, palladium-catalyzed, intramolecular cyanoamidation of alkenes for the synthesis of 3,3-disubstituted oxindoles **1.99** (Scheme 1.23a).[51,52] This reaction has some unique characteristics in that it utilizes the Lewis-basic *N,N'*-dimethylpropylene urea (DMPU) additive (instead of commonly deployed Lewis acid), a phosphoramidite chiral ligand **L1**, and nonpolar decalin as the solvent. Takemoto hypothesizes that the mechanism (Scheme 1.23b) proceeds by oxidative addition of the palladium into the C–CN bond of **1.98** to give acylpalldium cyanide **1.100**. After oxidative addition, Takemoto postulates that it may be possible for more than one ligand to be coordinated to palladium, as in **1.102**. Also, Takemoto notes that cyanide may dissociate from the palladium, giving palladium-cation intermediate **1.103**. However, he states that both possibilities are unlikely because the reaction is catalyzed by large, monodentate ligands and not bidentate ligands.[51] Precedence for cyanide dissociation is present in the enantioselective Heck literature using similar phosphoramidite ligands.[55] Migratory insertion likely occurs via carbopalladation to give palladium–CN intermediate **1.101**. Reductive elimination turns over the catalyst and forms the oxindole product **1.99**. The mechanism of this reaction is of interest to us and is the topic of Chapter 2.[56]

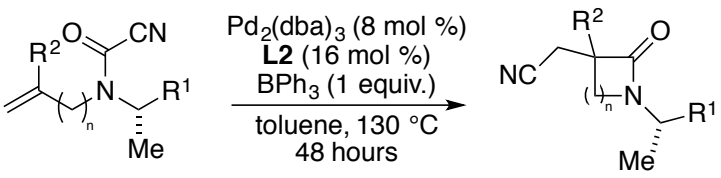


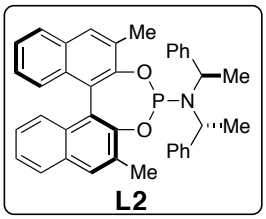
Scheme 1.23. Enantioselective, intramolecular cyanoamidation for the synthesis of 3,3-disubstituted oxindoles.

Douglas *et al*. recently published a diastereoselective variant for the intramolecular cyanoamidation of alkenes.[53] This reaction utilizes a chiral phenylethyl- or naphthylethyl-group on the amide nitrogen to obtain diastereoselectivity (Table 1.5). Douglas uses a chiral phosphoramidite ligand to improve diastereoselectivity for δ-lactams (Table 1.5, entries 1–4) but the chiral ligands are less successful with other substrates. The reaction conditions produce γ-lactams (Table 1.5, entries 5–6) in good yields but with greatly diminished diastereomeric ratios. β-lactam (Table 1.5, entry 7) forms in good yield but with no diastereoselectivity. The cyclization using n = 4 for making ε-

lactam (Table 1.5, entry 7) is completely unsuccessful. This methodology has the downfall that the directing group is currently unable to be removed and the diastereomers are largely inseparable on silica gel chromatography.[53]

Table 1.5. Diastereoselective Cyanoamidation of Alkenes





entry	n	R^1	R^2	yield (%)	d.r.
1	3	Ph	Me	53	8.7:1
2	3	Np	Me	46	8.3:1
3	3	Ph	Et	61	~6:1
4	3	Ph	^{i}Pr	38	~5:1
5[a]	2	Ph	Me	39	2:1
6[a]	2	Np	Me	53	1.9:1
7[a]	1	Ph	Me	43	1:1
8[a]	4	Ph	Me	0	–

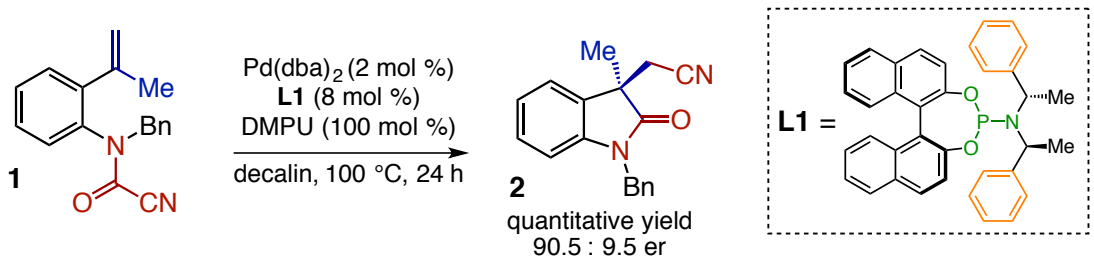
[a] Conditions: $Pd(PPh_3)_4$ (8 mol %), BPh_3 (1 equiv.), toluene (130 °C), 48 h

CHAPTER 2: MECHANISTIC MODEL FOR ENANTIOSELECTIVE INTRAMOLECULAR CYANOAMIDATION VIA PALLADIUM-CATALYZED C–CN BOND ACTIVATION

2.1 Introduction

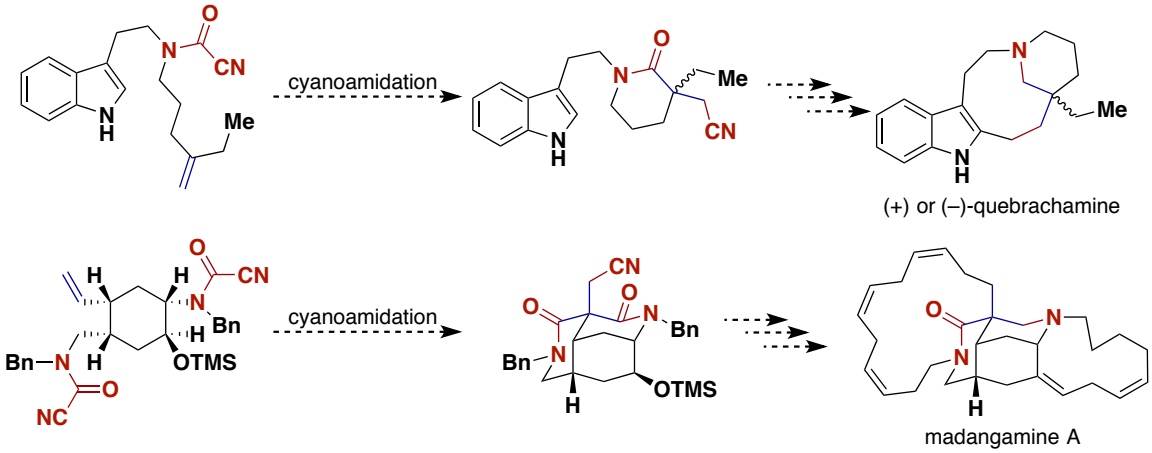
Metal-catalyzed C–CN bond activation has been widely developed, as was discussed in Chapter 1.5. However, mechanistic understanding is lacking in comparison to the breadth of the methodology. Jones *et al*. published a mechanistic study on the isomerization of allyl cyanides, insights of which are relevant to DuPont's adiponitrile process.[26,27] Jones performed stoichiometric reactions to identify nickel intermediates likely involved in the catalytic mechanism (Scheme 1.10). Catalytic reaction results also showed a relationship between solvent polarity and the chemoselectivity of the isomerization. Also, Jones measured activation parameters for the rate-limiting C–CN bond activation step. Aside from Jones' mechanistic results for C–CN activation, the only insights have been limited to X-ray structures of isolated intermediates,[38,44,47] which are thought to be catalytically relevant, and insights from divergent reactivity obtained with atypical substrates from various methodology studies.[36,37,50]

Jones showed varying results with Lewis acids in catalyzing[24,57] or inhibiting[28,57] C–CN activation but gave little basis for predicting the impact of Lewis acids on C–CN activation. The lack of mechanistic details with regards to the impact of Lewis acid and the general lack of mechanistic understanding of C–CN activation reactions motivated us to study these topics.



Scheme 2.1. Takemoto's enantioselective cyanoamidation reaction.

Takemoto *et al*. published the first enantioselective, intramolecular cyanoamidation of alkenes using a cyanoformamide **1**, a palladium catalyst, and phosphoramidite chiral ligand **L1** to synthesize oxindole products **2** (Scheme 2.1).[51] This reaction was selected for our mechanistic study because of the utility of this reaction in synthesizing oxindole products in high yields, with good selectivity, and without the formation of visible byproducts. Also, our group envisions being able to use the cyanoamidation reaction as the key step in the enantioselective synthesis of (+) or (–)-quebrachamine and madangamine A (Scheme 2.2).



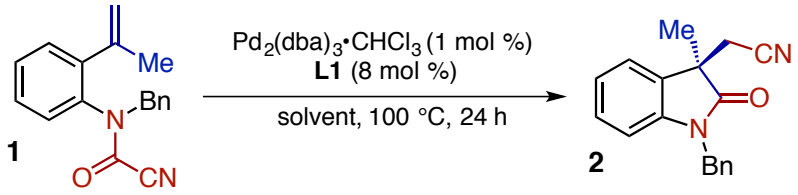
Scheme 2.2. Proposed synthesis of (+) or (–)-quebrachamine and madangamine A.

The reaction is unique in that it uses a polar/Lewis basic DMPU additive, which is uncommonly utilized in C–CN activation methodologies, and the highest enantioselectivity is achieved using very non-polar decalin as the solvent. We utilized the Abboud-Abraham-Kamlet-Taft (AAKT) linear solvation energy relationship (LSER) model, ^{13}CN crossover studies, initial rates kinetics, natural abundance kinetic isotope effect measurements, and other mechanistic experiments to study this reaction.[56] The information presented in this chapter is reprinted with permission from *The Journal of Organic Chemistry*, **2017**, *82*, 3721–3726. Copyright 2017 American Chemical Society.

2.2 Results and Discussion

2.2.1 Abboud-Abraham-Kamlet-Taft Linear Solvation Energy Relationship Model for Enantioselectivity

Table 2.1. Solvent Screen for AAKT Model LSER for Enantioselectivity



entry	solvent	e.r.[a]	entry	solvent	e.r.[a]
1	decalin[b]	89:11	11	MEK	83:17
2	decalin	89:11	12	dioxane	82:18
3	toluene	85:15	13	$PhCF_3$	82:18
4	toluene[b]	85:15	14	DCE	79:21
5	DMPU[c]	–	15	NMP	79:21
6	decalin[d]	80:20	16	DMF	76:24
7	toluene[d]	77:23	17	MeCN	71:29
8	cyclohexane	89:11	18	heptane	84:16
9	*m*-xylene	85:15	19	PFMCH	75:25
10	2-propanol	84:16			

[a] Complete conversion to 2 observed by ^{1}H NMR spectroscopy. [b] With 100 mol % of DMPU. [c] No reaction. [d] With 100 mol % of BPh_3.

We began our study by trying to reproduce Takemoto's results. We chose to use e.r. instead of e.e. (which Takemoto used) because e.r. directly compares the activation barriers for the enantiodetermining step of the reaction. Although we achieved full conversion to oxindole product **2** consistently, the best e.r. we reproducibly obtained was 89:11 (Table 2.1, entry 1). It was imperative that the reaction vials were heated under a nitrogen atmosphere in the glovebox as

incomplete conversion was observed when heating outside the box. Excluding DMPU from the reaction produced the same result as with DMPU in decalin (entry 2). We then decided to change the solvent to toluene because it is significantly easier to remove *en vacuo* and d_8-toluene is readily available for NMR experiments, including initial rates kinetics. Toluene as the solvent gave an e.r. of 85:15 both with and without DMPU (entry 3 & 4). Also, decalin did not dissolve all the reaction components until heating to 100 °C whereas toluene completely dissolved all components at room temperature. This would be significantly useful when performing future kinetic experiments where making stock solutions is essential for reducing measurement errors. DMPU as the solvent gave no conversion to product, suggesting that it completely inhibits the cyanoamidation reaction (entry 5). Using BPh_3 as an additive instead of DMPU significantly reduced the e.r. in both decalin and toluene (entries 6 & 7).

The significant change in e.r. by changing the solvent from decalin to toluene led us to investigate the possibility for other solvents to affect the enantioselectivity. We performed an additional 10 cyanoamidation reactions with solvents varying dielectric constant (ε) to attempt to obtain a relationship between the dielectric constant of the solvent and the e.r. achieved. Varying the solvents gave significant differences in e.r. for oxindole **2** (entries 8–17). Notable examples were cyclohexane which gave an identical e.r. of 89:11 to that of decalin (entry 8) and acetonitrile (the highest dielectric solvent we tested) which gave an e.r. of 71:29. The noticeable trend in solvent polarity when compared to e.r. led us to quantify the trend using single linear regression analysis of e.r. and dielectric constant (Figure 2.1).[58-60] However, after linear regression gave an R^2 value of 0.665, we sought the literature to find a different model for relating solvent parameters to enantioselectivity.

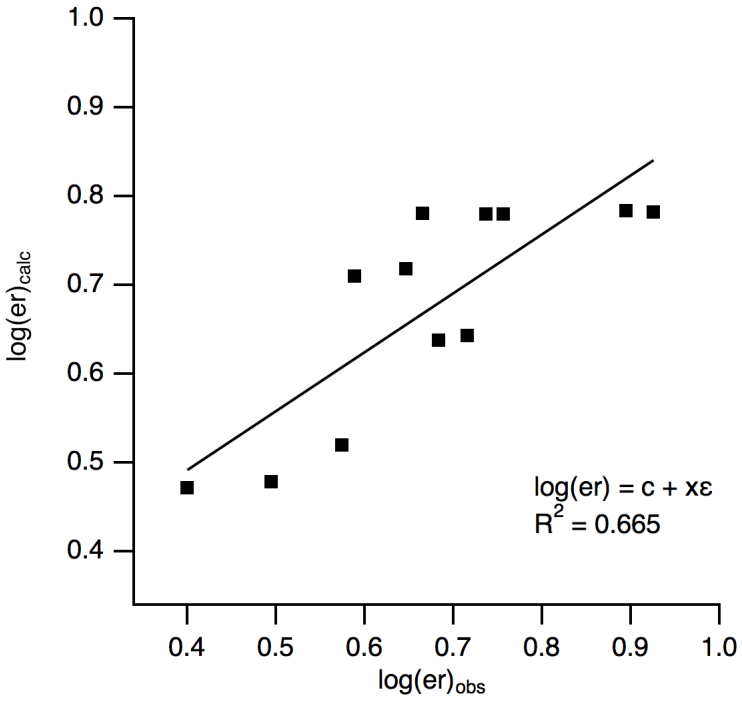


Figure 2.1. Plot of observed log(er) vs. calculated log(er) with dielectric constant (ε) by single parameter regression analysis.

The Abboud-Abraham-Kamlet-Taft (AAKT) multiparameter solvatochromic equation[61-63] (Equation 2.1) is a significantly more expansive model for solvent polarity and has been applied to various systems including nonaqueous biocatalysis for enzyme enantioselectivity.[64] The AAKT parameters are π^* (polarizability/dipolarity), α (hydrogen bond acidity), and β (hydrogen bond basicity). A full list of the AAKT fit parameters are included in the appendix. Using the solvents in Table 2.1 (entries 2–3, 8–17) with the fit parameters for each solvent gave the fit in Figure 2.2 with a R^2 value of 0.798. Acetonitrile appeared to be an outlier and a Grubb's test of the residuals permitted us to reject the acetonitrile data point. Acetonitrile could be an outlier due to competitive coordination to palladium with our ligand. Without acetonitrile, we achieved a significantly improved R^2 value of 0.922 (Figure 2.3).

$$\log(er) = c + x\pi^* + y\alpha + z\beta$$

Equation 1. AAKT multiparameter solvatochromic equation for linear solvation energy relationship model.

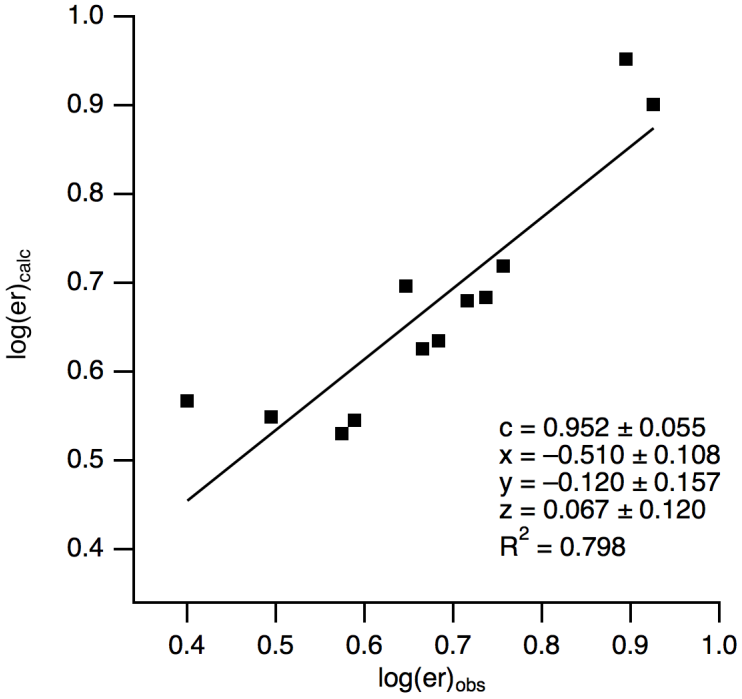


Figure 2.2. Plot of observed log(er) vs. calculated log(er) with AAKT equation output.

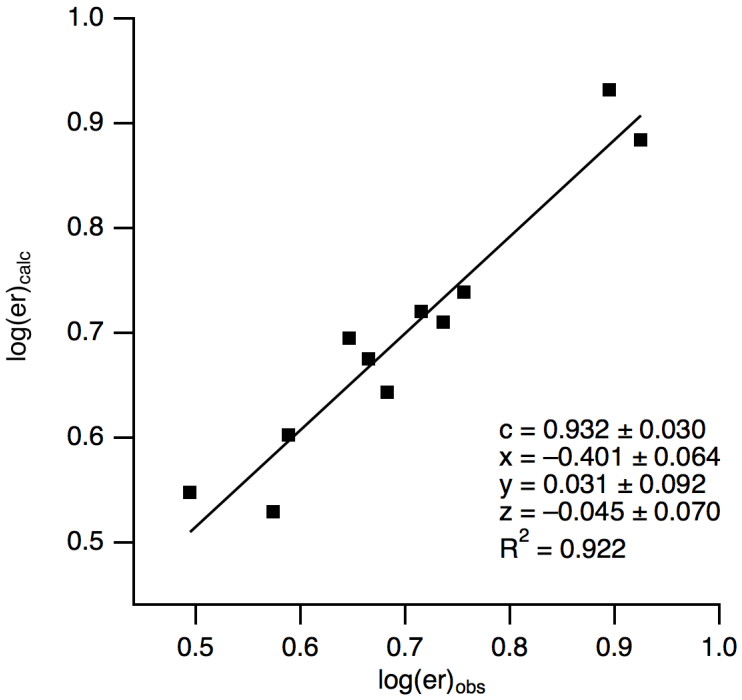
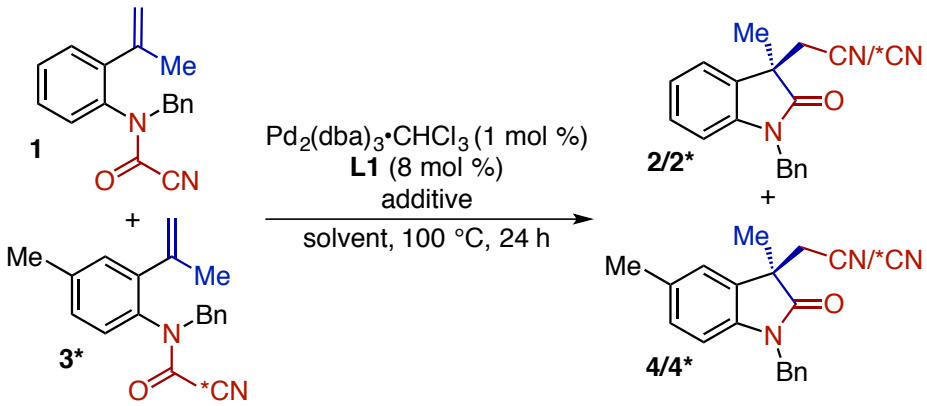


Figure 2.3. Plot of observed log(er) vs. calculated log(er) with AAKT equation output without acetonitrile data point.

Comparing the parameter coefficients (x, y, z) to their errors clearly showed that π^* is the major contributor to the fit. This suggests that the solvent polarizability/dipolarity plays a major role in the enantioselectivity of the reaction. Performing a single regression analysis with only π^* gave a fit of $R^2 = 0.917$ (experimental section) confirming this analysis. The result of an inverse correlation between π^* and e.r. led us to search for solvents with lower π^* values than decalin ($\pi^* = 0.11$) and cyclohexane ($\pi^* = 0$), which had already been tested. Heptane ($\pi^* = -0.08$) and perfluoromethylcyclohexane (PFMCH) ($\pi^* = -0.40$) as solvents yielded full conversion of **1** to oxindole **2**, however with lower than predicted e.r. values (entries 18 and 19). Upon inspection of the reactions over the course of heating, it was noted that the reactions remained heterogeneous. As all other reactions were homogeneous at 100 °C, this is likely to account for the decrease in e.r. with heptane and PFMCH.

2.2.2 ^{13}CN Crossover Experiments

Table 2.2. ^{13}CN Crossover Experiment Results



entry	solvent	additive	4*:2*	e.r. 2
1	decalin	DMPU 100 mol %	47:53	–
2	toluene	DMPU 100 mol %	51:49	–
3	decalin	–	49:51	–
4	toluene	–	51:49	–

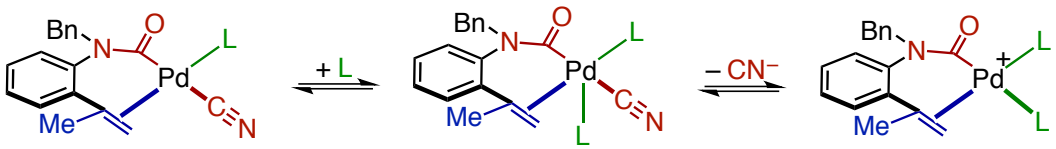
5	toluene	BPh_3 50 mol %	36:64	80:20
6	toluene	BPh_3 100 mol %	35:65	77:23
7	toluene	BPh_3 200 mol %	30:70	73:27

Takemoto *et al*. noted that cationic palladium intermediates are commonly hypothesized as intermediates in the asymmetric Heck reaction. However, Takemoto states that the cationic pathway is unlikely to be operable in this reaction due to the phosphoramidite ligand **L1** being a large, monodentate ligand and bidentate ligands gave poor enantioselectivity in the optimization of this reaction.[52] Enantioselective Heck reactions for which a cationic palladium intermediate is proposed use bidentate ligands.[55,65,66]

To test Takemoto's conjecture, we synthesized ^{13}CN-labeled substrate **3*** (Table 2.2). Subjecting a 1:1 mixture of **1** and **3*** to the cyanoamidation reaction conditions with 100 mol % of DMPU in both toluene and decalin unexpectedly gave complete crossover of the label (a ~1:1:1:1 distribution of **2**, **2***, **4**, and **4***) (Table 2.2, entries 1 and 2).[43,51,67] Excluding DMPU from the reaction mixture gave full crossover as well (entries 3 and 4). Using 100 mol % of BPh_3 in place of DMPU gave a mixture of **2***/**4*** which favored **4*** (entry 6). A similar partial retention of the label was also observed when decreasing the BPh_3 loading to 50 mol % (entry 5). Increasing the BPh_3 loading to 200 mol % led to a greater retention of the ^{13}CN label (entry 7). To check for background reactivity, the control of heating **1** with **3*** without catalyst was performed and no crossover was observed. Interestingly, the e.r. also decreased with increased BPh_3 loading (entries 5–7). Crossover studies with oxindoles **4*** and **2** were also performed and no crossover was observed. This result suggests that reductive elimination is irreversible. Resubjecting enantioenriched **2** to the standard reaction conditions did not give erosion of e.r. suggesting that the enantiodetermining step is also irreversible.

2.2.3 Ligand Concentration Dependence

With the result that ^{13}CN crossover occurs under the reaction conditions, we hypothesized that cyanide anion could be dissociating from the palladium by an associative ligand exchange mechanism with a second **L1** ligand (Scheme 2.3). Our current conditions use 8 mol % **L1** and 1 mol % $Pd_2(dba)_3$•$CHCl_3$, thus we have a 4:1 ratio of ligand to metal. We hypothesized that by decreasing the equivalents of **L1** to 4 mol %, we would see more retention of the ^{13}CN label in a crossover experiment. However, this was not the case and it was also noted that the e.r. did not change. Decreasing the ligand loading to 2 mol % (1:1 **L1**:Pd) and performing the cyanoamidation reaction with **1** at 100 °C for 24 hours gave complete conversion to oxindole **2** with negligible change in e.r. (see publication supplementary information). This suggests that the palladium catalyst does not have two **L1** ligands attached to it during the enantiodetermining step.



Scheme 2.3. Hypothesized ligand exchange by associative mechanism.

2.2.4 Initial Rates Kinetics

DMPU and BPh_3 give very different results for the experiments performed thus far. DMPU appears to have no effect as an additive with respect to changing the e.r. of **2**, the conversion to **2**, or the crossover of the ^{13}CN label under the reaction conditions. In fact, using DMPU as a solvent completely shut down reactivity (Table 2.1, entry 5). In contrast, using BPh_3 as an additive decreased the e.r. of **2** in both toluene and decalin as solvents and it appeared to promote retention of the ^{13}CN label in crossover studies to a greater extent with increased BPh_3 loading. With these contrasting results in hand we performed kinetics experiments using the method of initial rates.

Initial rates kinetics were performed in triplicate using variable temperature NMR spectroscopy. d_8-toluene was used as the solvent and the reaction temperatures were maintained at 90 °C rather than 100 °C due to the reaction being too fast at 100 °C. By varying the concentration of DMPU, we found that DMPU has a general inhibitory effect on the rate of the reaction which is indicated by the trend line in Figure 2.4. This result matches our observation that DMPU is a poor solvent for this reaction. Initial rates kinetics varying the BPh_3 concentration resulted in an observed increase in the rate of the reaction with increasing BPh_3 concentration. The results appear to follow classical saturation kinetics behavior (Figure 2.5). Although a general increase in the rate is observed with BPh_3, the impact is small (only 28% increase compared to no BPh_3).

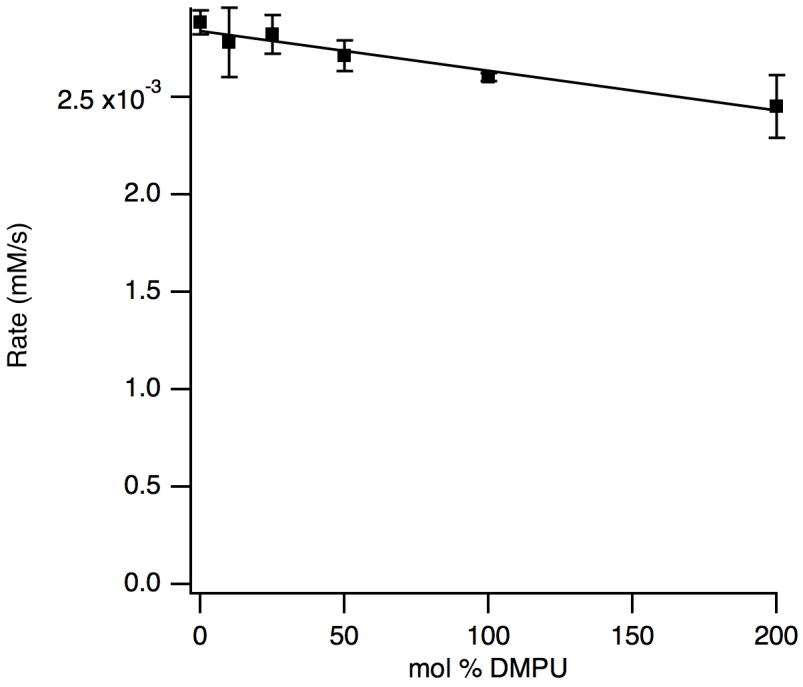


Figure 2.4. Initial rates kinetics with varying DMPU concentration.

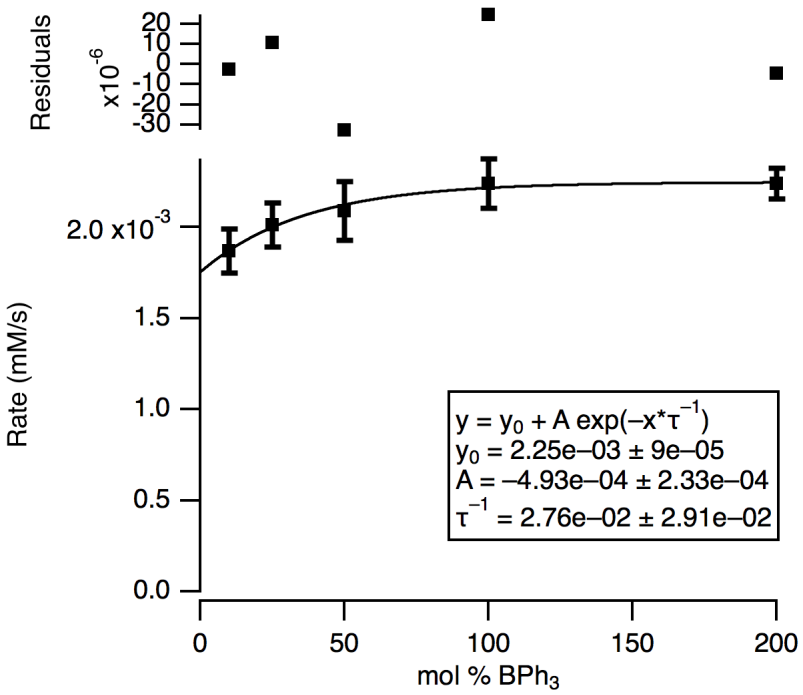


Figure 2.5. Initial rates kinetics with varying BPh_3 concentration.

2.2.5 ^{11}B and ^{13}CN NMR Spectra for Boron Lewis Acid Coordination to Nitrile

BPh_3 influencing the observed e.r., amount of ^{13}CN crossover, and rate of the reaction led us to attempt to observe whether the BPh_3 coordinates to the nitrile prior to the catalytic reaction occurring. Boron has two naturally occurring, stable isotopes, ^{10}B and ^{11}B. Both isotopes are quadrupolar and NMR spin active. ^{10}B has a +3 spin and ^{11}B has a –3/2 spin. ^{11}B NMR spectroscopy has been used to determine if boron Lewis acids are coordinating to nitriles.[57] When the BPh_3 Lewis acid is coordinated to the nitrile, you would expect to see a change in the chemical shift for the ^{11}B signal in the ^{11}B spectrum when compared to the pure BPh_3 spectrum. Also, due to the quadrupolar nature of boron, you would expect to observe a broadening of the carbon signal for the nitrile in the ^{13}C NMR spectrum as well as a shift in the signal. Using ^{13}CN-labeled **3*** to improve the signal-to-noise ratio of the nitrile signal in the ^{13}C NMR spectrum, we obtained the ^{13}C spectrum for pure cyanoformamide **3*** and a 1:1

mixture of **3***:BPh_3 (Figure 2.6). No change in the chemical shift was observed for the nitrile and negligible broadening was observed. Likewise, ^{11}B NMR spectra were taken of the pure BPh_3 and a 1:1 mixture of **3***:BPh_3 (Figure 2.7). No change in the $^{11}BPh_3$ signal was observed. These results suggest that the equilibrium between free BPh_3/cyanoformamide and the cyanoformamide–BPh_3 adduct does not favor the adduct at room temperature.

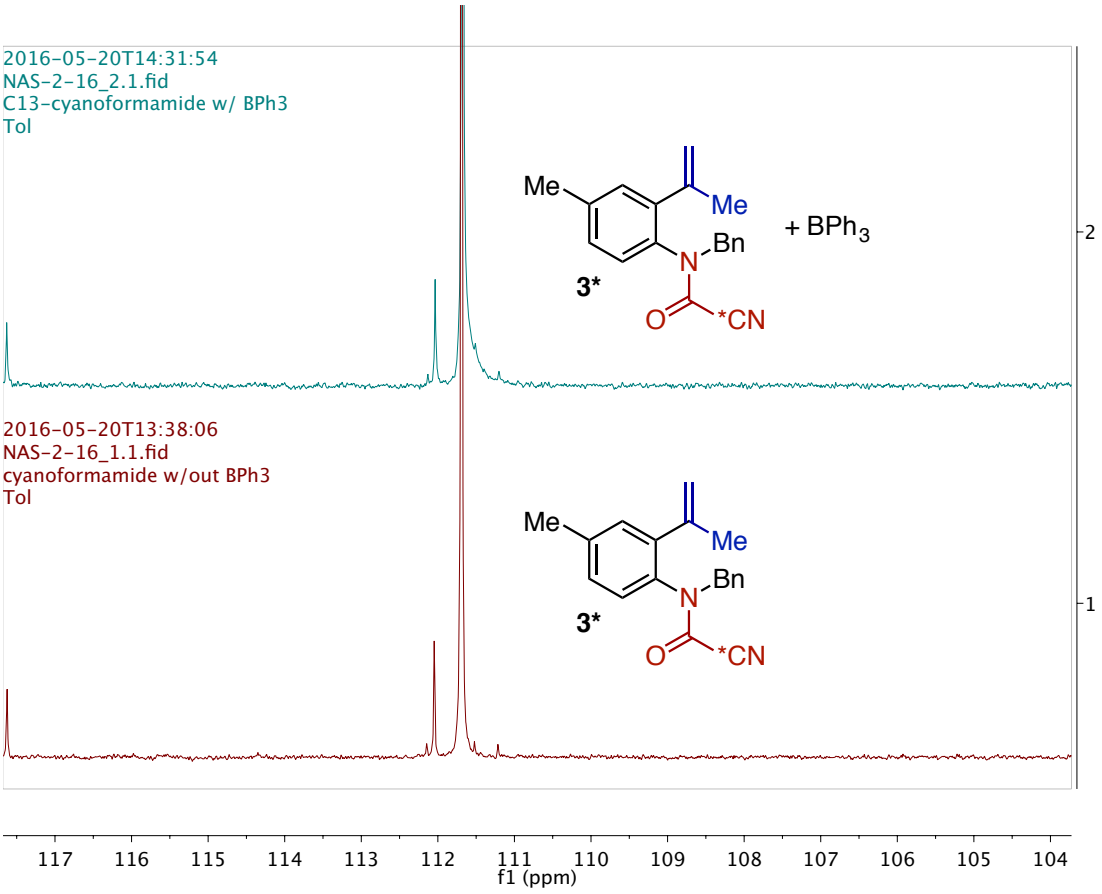


Figure 2.6. ^{13}C NMR spectra of 1) pure cyanoformamide **3*** and 2) 1:1 mixture of **3*** to BPh_3.

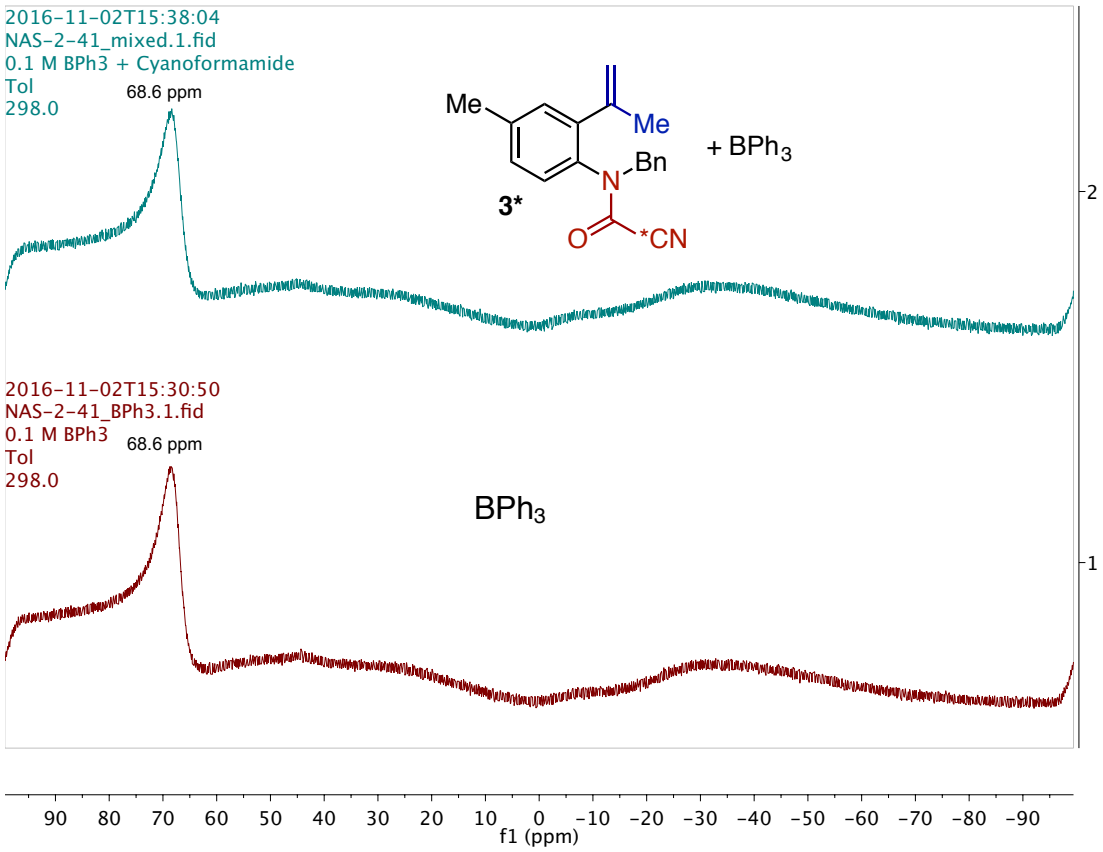


Figure 2.7. ^{11}B NMR spectra of 1) pure BPh_3 and 2) 1:1 mixture of **3*** to BPh_3.

2.2.6 Natural Abundance Kinetic Isotope Effect (Singleton Studies)

Kinetic isotope effects of naturally abundant $^{12}C/^{13}C$ are very small but Singleton *et al*. and others have demonstrated the utility of this method in determining the turnover-limiting step in various methodologies including the intramolecular quinoline-directed carboacylation of alkenes.[14,15,68] The cyanoamidation reaction of cyanoformamide **1** was performed on gram scale to >85% conversion to oxindole **2** with either 100 mol % DMPU or BPh_3 as the additive. The exact % conversion to product was determined using quantitative ^{1}H NMR spectroscopy and then the starting material was isolated and analyzed using quantitative ^{13}C NMR spectroscopy. This method uses an inverse-gated decoupling of the ^{1}H's to remove ^{1}H coupling during the acquisition but not during

the delay, thus minimizing nuclear overhauser effect enhancements. Long delays (120 s) are necessary for full relaxation of the carbon nuclei. Statistically significant isotope enrichment was observed at the carbonyl carbon (C1) as well as the nitrile carbon (C2) for both the reactions using either DMPU or BPh_3 as the additive. However, the level of isotopic enrichment was statistically different at the nitrile carbon when comparing the reaction with DMPU to the reaction with BPh_3. This result suggests that BPh_3 affects the turnover-limiting step of the reaction. No enrichment was observed at the olefinic carbons (C3 and C4). These results suggest that C–CN activation is the turnover-limiting step of the reaction.

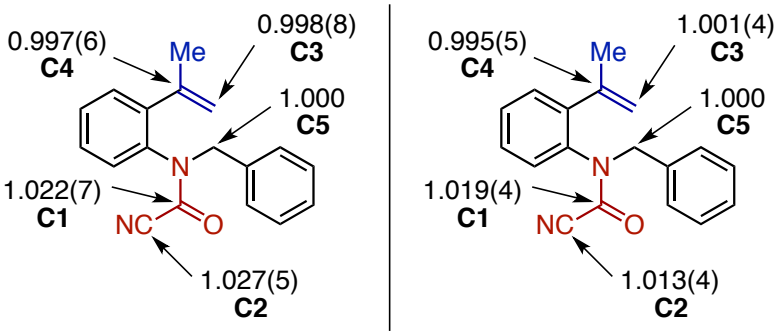
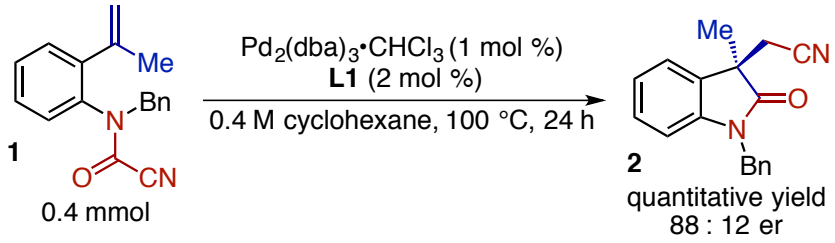


Figure 2.8. Map of ^{13}C enrichment after natural abundance measurement of the $^{12}C/^{13}C$ KIE: 100 mol % of DMPU (left); 100 mol % of BPh_3 (right).

2.2.7 Proposed Mechanistic Model and Optimized Alkene Cyanoamidation

With the results from the various mechanistic experiments in hand, we reoptimized the reaction conditions (Scheme 2.4). Cyclohexane was used as the solvent because it gives a similar e.r. to to decalin on small scale, has a lower boiling point making it easier to remove by rotatory evaporation, and is less exotic than decalin and thus more likely to be available to someone performing this reaction in a laboratory. The ligand loading was also decreased from 8 mol % to 2 mol % (1:1 **L1** to Pd) as it had no effect on the conversion or e.r. in toluene. The reaction was scaled up to 0.4 mmol and performed at 0.4 M

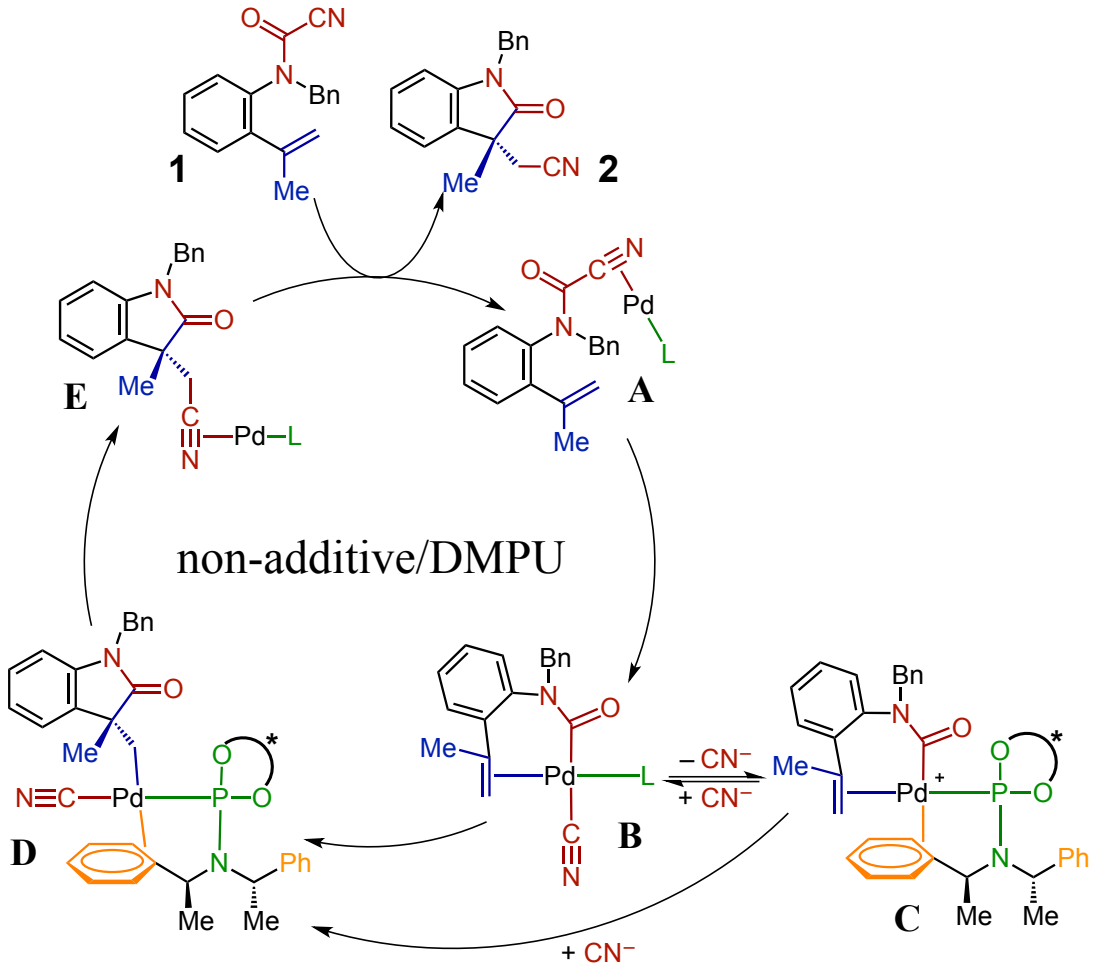
substrate in cyclohexane. These updated conditions gave quantitative yield and an e.r. of 88:12.



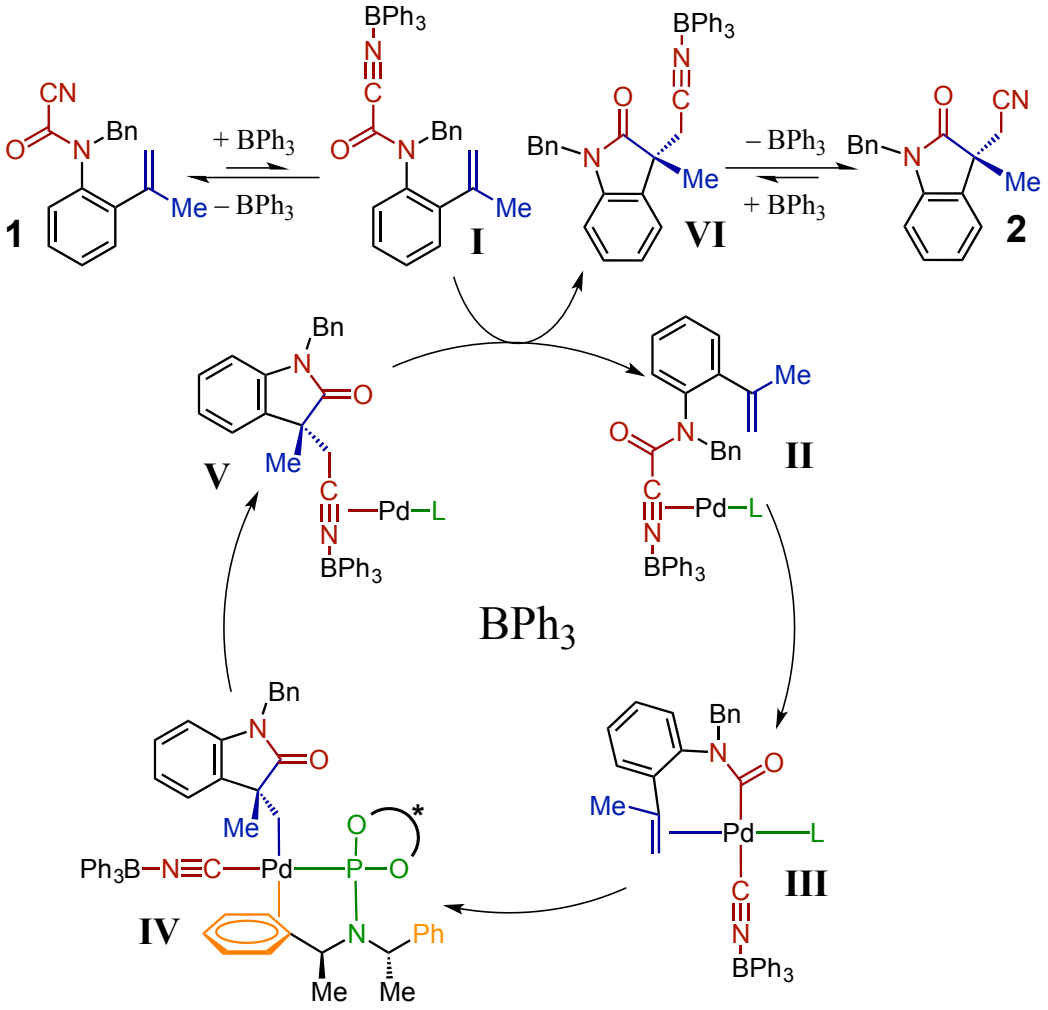
Scheme 2.4. Optimized reaction conditions for the intramolecular cyanoamidation of alkenes.

Given the mechanistic results we postulate two different mechanisms. The first mechanism is operable when no Lewis acid is present in solution. Initial η^2-coordination of the nitrile of **1** to palladium forms **A** (Scheme 2.5). This structure is consistent with other structures observed by Jones *et al.*[57] Turnover-limiting palladium oxidative addition into the C–CN bond of **A** gives palladium–cyanide **B**. At this point crossover may occur forming the rigid cation **C** by dissociation of CN^- from **B**. Trost *et al.* proposed a similar secondary coordination of the phosphoramidite phenyl-group in phosphoramidite/palladium-catalyzed enantioselective trimethylenemethane reactions.[69,70] As was previously emphasized, palladium cation intermediates also find precedence in the asymmetric Heck literature. Also, this intermediate was rejected by Takemoto *et al.* but they neglected to consider possible secondary coordination from the phenyl-group.[51,52] This cationic pathway is more likely to be favored with polar solvents, however non-polar solvents (solvents with lower π^* values) likely aid in improving the enantioselectivity through this cationic pathway by limiting solvent-cation intermolecular interactions which would disrupt the secondary coordination of the phenylethyl arm of **L1**. Following the pathway of **B** to **C**, migratory insertion by carbopalladation of the alkene into the amide–palladium bond would give **D**. The less enantioselective pathway from **B** to **D** may be operable, lending to the 88:12 e.r. observed. Irreversible reductive elimination forms **E** and **2** with coordination of **1**, thereby turning-over the catalyst.

The mechanism is slightly modified in the presence of BPh_3 (Scheme 2.6). This new pathway operates concurrently with the first pathway, consistent with partial retention of our ^{13}CN label but not full retention. Reversible coordination of BPh_3 to the nitrile of cyanoformamide **1** forms **I**. This equilibrium favors **1** and free BPh_3 as was noted in the ^{11}B and ^{13}C spectra from *2.2.5*. It is our hypothesis that coordination of palladium to **I** to form the η^2-nitrile–palladium adduct **II** is turnover-limiting in this cycle. This conjecture is grounded in the observation that the magnitude of the $^{12}C/^{13}C$ KIE is lower for the BPh_3 additive system when compared to the DMPU system. Also, no enrichment at C3 or C4 is observed, indicating that the turnover-limiting step is not changing to migratory insertion. Oxidative addition of the palladium into the C–CN bond gives palladium–cyanide intermediate **III**. At this point, formation of the palladium cation postulated in Scheme 2.5 is inhibited due to a stronger palladium–CN bond formed from the Lewis adduct with BPh_3.[57] This cycle reflects the observation that the ^{13}CN label in **3*** is retained to a greater extent in the product **4***. Also, the decreased e.r. observed with added BPh_3 is reflected in that the rigid cation **C** in Scheme 2.5 is not formed and migratory insertion through less rigid **III** is thought to impart less enantioselectivity. Both cycles only have one phosphoramidite **L1** bound to palladium, reflecting the decrease in the **L1**/palladium ratio to 1:1 having no effect on the e.r. of the reaction. The inherent e.r. of the BPh_3 pathway was estimated to be 62:38 using the assumption that the ^{13}CN label would be fully retained if all the material proceeded through the BPh_3-catalyzed pathway (appendix).

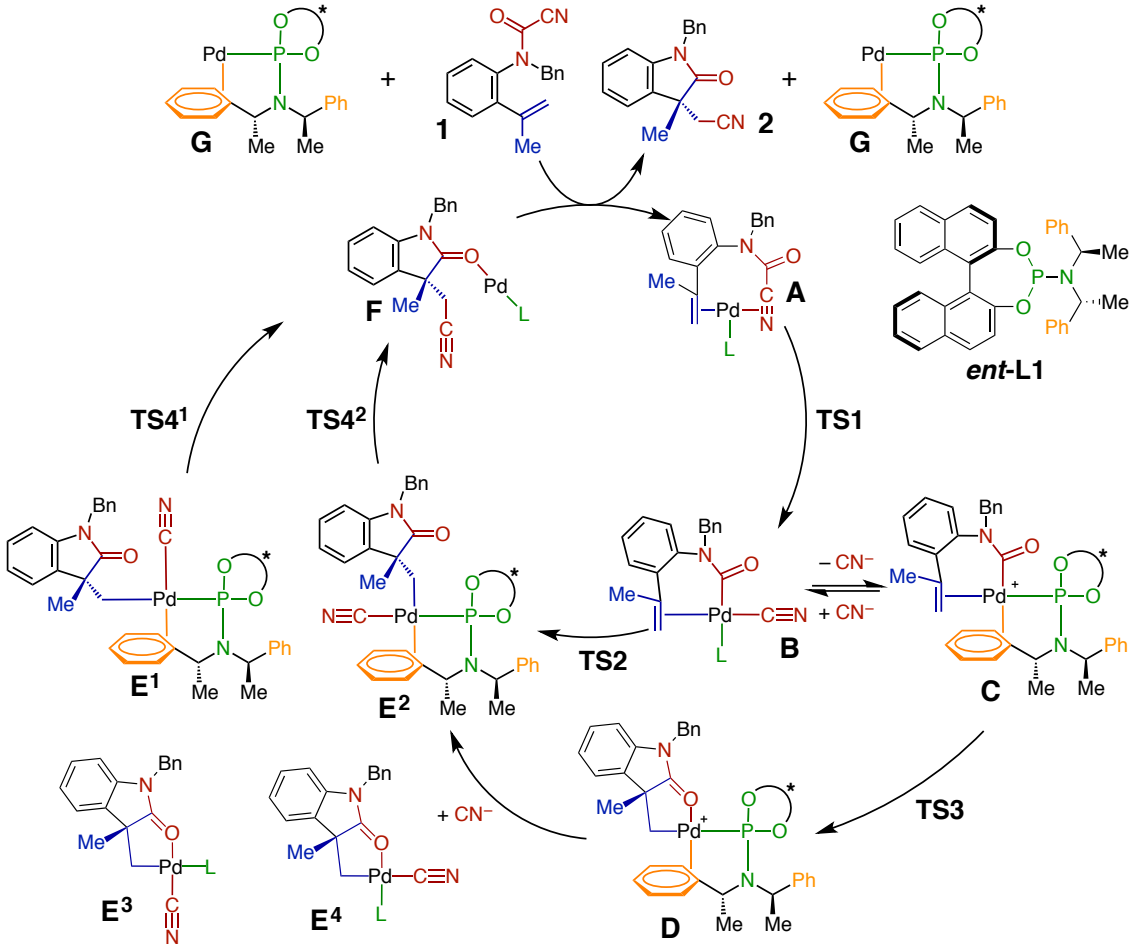


Scheme 2.5. Lewis acid free alkene cyanoamidation mechanism.



Scheme 2.6. Alkene cyanoamidation mechanism with BPh_3 Lewis acid.

2.3 Computational Results



Scheme 2.7. Updated catalytic cycle for computations.

With our results from the mechanistic studies in 2.2 published, I pursued further understanding of this system using the Gaussian 09 computational chemistry suite. The structures of the intermediates along the catalytic cycle have been modified from Scheme 2.5 to account for my observations of the lowest energy ground state structures computed (Scheme 2.7). Also, the structures were built with the enantiomer of **L1**. This was done because I intended to draw a direct comparison to Takemoto's results, who used the enantiomer of **L1**. I used 3 different density functional models (B3LYP, BP86, and M06) to analyze this system. I used M06 to obtain the geometry optimized ground state and transition state structures for all the complexes with the 6-31g(d,p) basis set for all non-

metal atoms and lanl2dz for palladium along with the corresponding core potential. Then I used the coordinates for each structure from the M06 computations to reoptimize each geometry with either B3LYP or BP86 with the same basis sets as used in the M06 calculations. With all the ground state and transition state structures energies minimized, I used the SMD solvation model with the solvent set to toluene and the higher level 6-311+g(2df,2pd) basis set for non-metal atoms and lanl2tz(f) basis set for palladium to obtain more accurate electronic energies. Thermal corrections from the frequency calculations on the lower basis set structures were applied to the higher basis set electronic energies to obtain the Gibbs thermal energies (Tables 2.3–5). All ground state structures frequency calculations were inspected to ensure that no imaginary frequencies existed and all transition state structures frequency calculations were inspected to ensure that only 1 imaginary mode existed. The imaginary frequency for transition state structures was visualized using the Avogadro software package to ensure that it corresponded to the transition state expected.

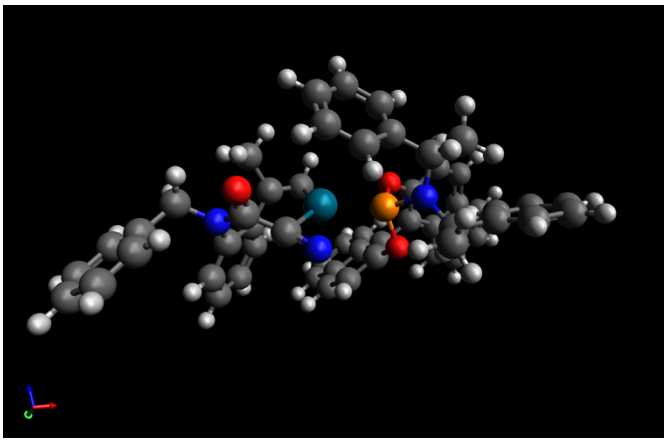


Figure 2.9. Palladium complex **A**, pre-oxidative addition.

Structure **A** was found to be at its lowest ground state energy structure when the olefin was coordinated η^2 to the palladium along with the η^2-nitrile in a bidentate fashion (Figure 2.9). π-coordination from the phenethyl-group of the ligand into the dz^2 is also visible and very common in all structures where the phenethyl-group is not occupying an equatorial coordination position. Computing

the η^1-coordination geometry for the nitrile to the palladium led to a much higher energy structure and was disregarded. The structure with η^1-coordination of the carbonyl oxygen was also significantly higher in energy than **A**.

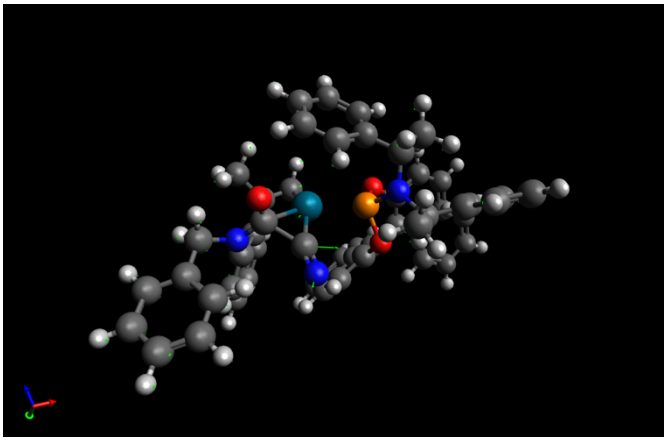


Figure 2.10 Transition state structure **TS1**, oxidative addition.

TS1 shows significant C–CN bond-breaking and subsequent C_{acyl}–palladium/palladium–CN bond formation. π-coordination from the phenethyl-arm is also apparent in this transition state.

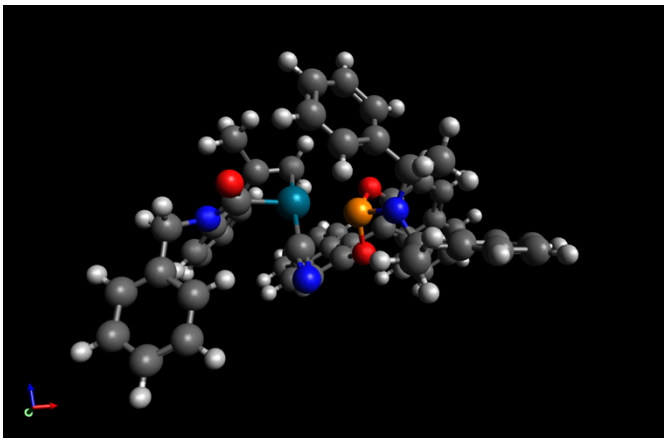


Figure 2.11. Palladium complex **B**, pre-migratory insertion.

Structure **B** was found to be at its lowest energy when the CN was *cis* to the acyl-group and the olefin was coordinated η^2 to the palladium. Moving the CN *trans* to the acyl-group was higher in energy as well as was coordinating the phenethyl-group in the equatorial plane by dissociating the η^2-olefin-group.

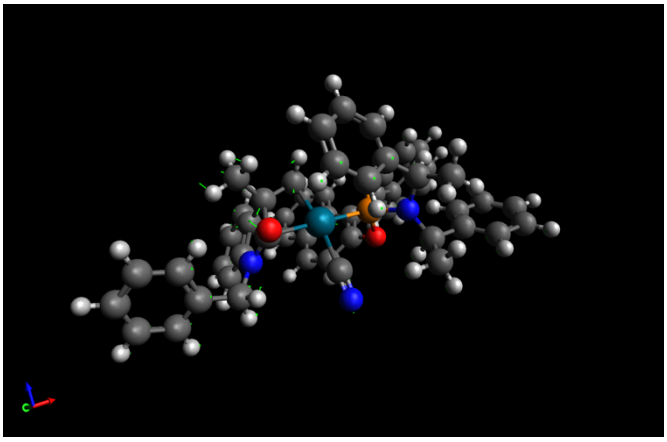


Figure 2.12. Transition state structure **TS2**, migratory insertion.

TS2 shows the acyl-carbon migrating towards the internal olefin carbon while the terminal olefin carbon is forming a bond to palladium.

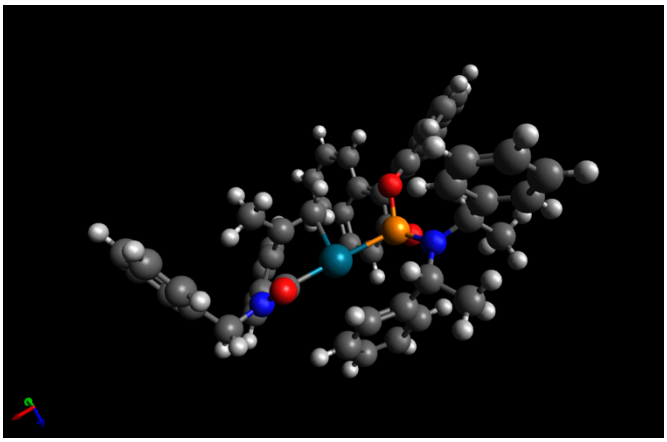


Figure 2.13. Palladium cation complex **(*S*)-C**, pre-migratory insertion.

(*S*)-C shows the phenethyl-arm rotated such that the phenyl-group can coordinate η^2 to the palladium cation. The acyl-group being *trans* to the phosphorous is lower in energy than *trans* to the phenyl-group.

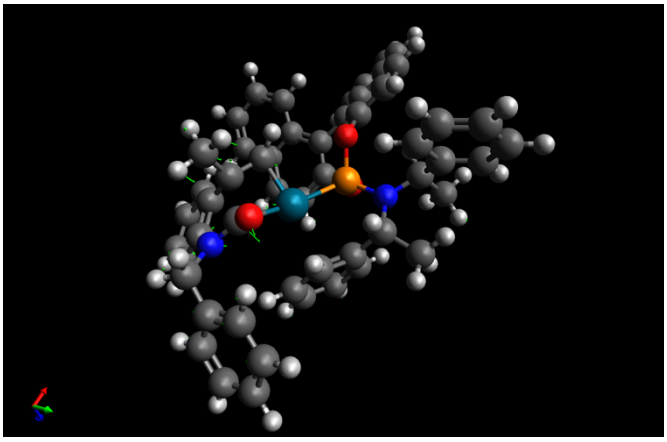


Figure 2.14. Transition state structure for palladium cation **(*S*)-TS3**, migratory insertion.

(*S*)-TS3 shows a very early transition state where there is not significant bond formation between the acyl carbon and the internal carbon of the olefin. The terminal carbon of the olefin is significantly closer to the palladium (2.084 Å in **(*S*)-TS3** compared to 2.222 Å in **(*S*)-C**) indicating hybridization change for the terminal methylene carbon.

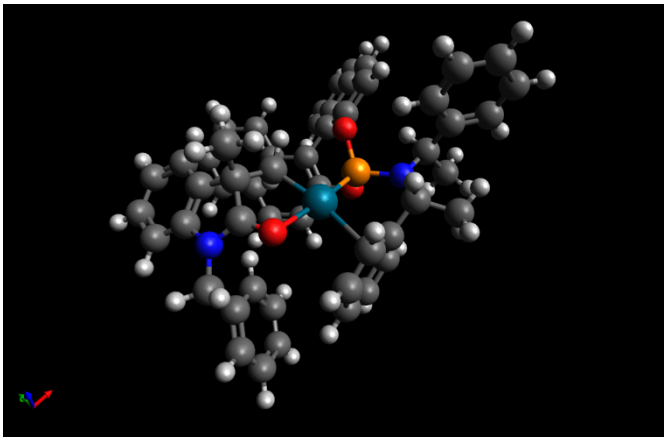


Figure 2.15. Palladium cation complex **(*S*)-D**, post-migratory insertion.

Structure **(*S*)-D** results from following the migratory insertion trajectory and minimizing to a ground state. This structure shows the oxygen of the carbonyl taking the open coordination site left by the acyl-carbon migrating to form a bond with the internal olefinic carbon. The isomer with the carbonyl oxygen *trans* to the phenyl group is higher in energy and would require an isomerization to occur after migratory insertion.

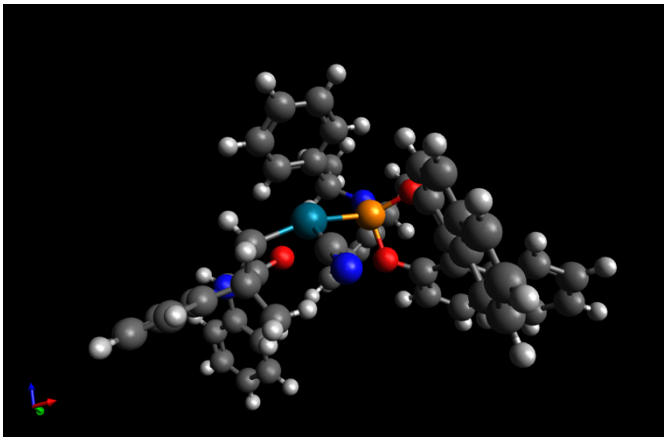


Figure 2.16. Palladium complex **(*S*)-E^{1}**, pre-reductive elimination.

While trying to find the transition state structure for reductive elimination, it was found that reductive elimination from intermediate **(*S*)-E^{3}** would not converge and always minimized to the starting ground state configuration. Also, **(*S*)-E^{4}** is incapable of undergoing reductive elimination as the CN needs to be *cis* to the methylene for bond formation to occur. Thus, I pursued structures where the oxygen of the carbonyl was displaced by the phenethyl-arm of the ligand. **(*S*)-E^{1}** is one possible isomer by which reductive elimination may occur through. In this isomer the CN-group is *trans* to the phenyl-group of the ligand. It also appears that the carbonyl stabilizes this configuration by donating into the Dz^{2}-orbital of the palladium (O–Pd bond distance = 2.762 Å).

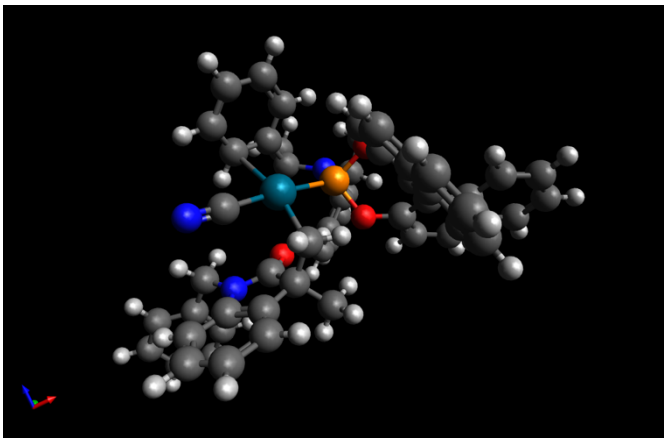


Figure 2.17. Palladium complex **(*S*)-E^{2}**, pre-reductive elimination.

(*S*)-E^2 is the second isomer by which I found reductive elimination could occur through. This isomer is similar to **(*S*)-E^1** except the CN-group is *cis* to the phenyl-group of the ligand. As in **(*S*)-E^1**, donation of the carbonyl oxygen into the dz^2-orbital of palladium is observed but the bond distance is slightly longer (O–Pd bond distance = 3.023 Å).

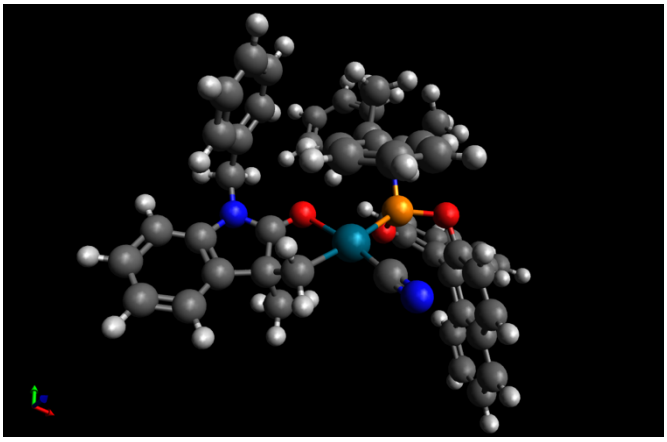


Figure 2.18. Palladium complex **(*S*)-E^3**, incapable of reductive elimination.

(*S*)-E^3 is unlikely to be catalytically viable as I was incapable of finding a transition state structure for reductive elimination for this structure. Further searching for a possible structure may be necessary. However, this structure is very stable, thus it may be an off-cycle intermediate

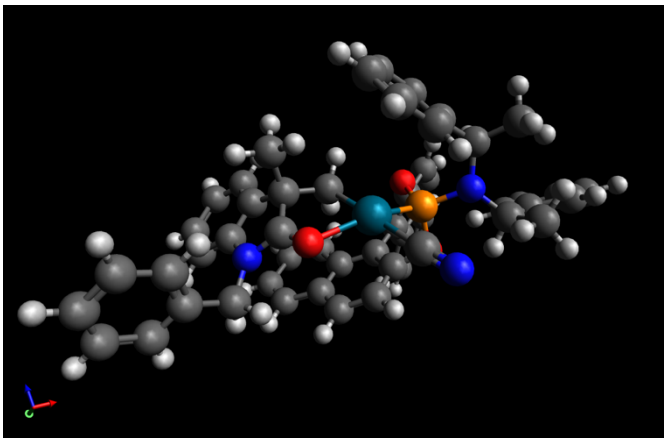


Figure 2.19. Palladium complex **(*S*)-E^4**, incapable of reductive elimination.

(*S*)-E^4 is an important structure because following the trajectory from **(*S*)-TS2** and minimizing to the best ground state structure gives **(*S*)-E^4**. As the

methylene-group is *trans* to the CN, reductive elimination cannot occur. Thus, isomerization must occur forming either **(*S*)-E^1** or **(*S*)-E^2**.

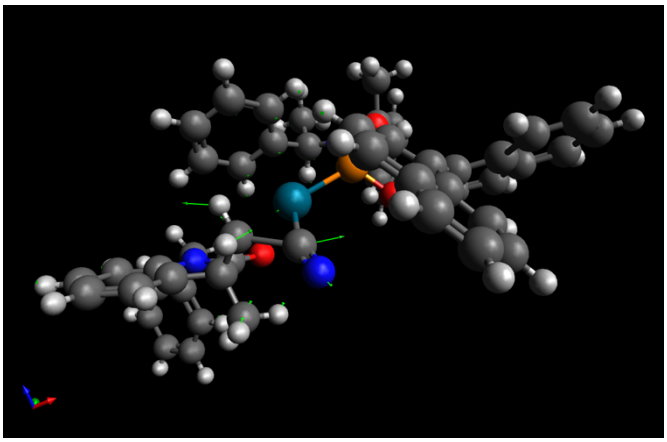


Figure 2.20. Transition state structure **(*S*)-TS4^1**, reductive elimination.

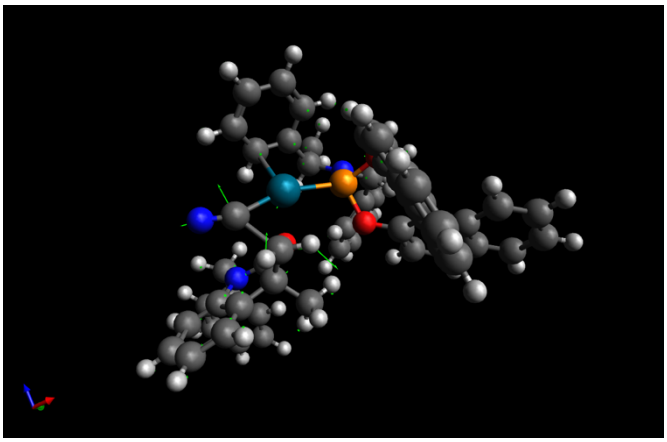


Figure 2.21. Transition state structure **(*S*)-TS4^2**, reductive elimination.

Both **(*S*)-TS4^1** and **(*S*)-TS4^2** share similar characteristics in that there is significant bond formation between the methylene-carbon and the CN-carbon. Also, both structures have donation from the carbonyl oxygen into the Dz^2-orbital of the palladium. The results of these calculations are tabulated (Tables 2.3–5)

Table 2.3. Gibbs Relative Energies Using B3LYP DFT Functional with Toluene Solvation

Structure	Relative Energy (kcal)	Structure	Relative Energy (kcal)
1 + G	0	**(*R*)-D + CN^-**	+28.3
A	+4.5	**(*S*)-E^1**	
TS1	+19.1	**(*S*)-E^2**	–7.1
(*S*)-B	+2.6	**(*S*)-E^3**	–8.7
(*S*)-TS2	+16.0	**(*S*)-E^4**	–16.1
(*S*)-C + CN^-	+54.6	**(*S*)-$TS4^1$**	10.2
(*R*)-C + CN^-	+51.0	**(*S*)-$TS4^2$**	14.3
(*S*)-TS3 + CN^-	+61.7	**(*S*)-F**	–20.9
(*R*)-TS3 + CN^-	+59.7	**(*S*)-2 + G**	–27.3
(*S*)-D + CN^-	+27.5		

SMD (toluene) B3LYP/6-311+G(2df,2pd)(LANL2TZ(f))//B3LYP/6-31G(d,p)(LANL2DZ)

Table 2.4. Gibbs Relative Energies Using BP86 DFT Functional with Toluene Solvation

Structure	Relative Energy (kcal)	Structure	Relative Energy (kcal)
1 + G	0	**(*R*)-D + CN^-**	+27.6
A	–1.4	**(*S*)-E^1**	–15.5
TS1	+10.6	**(*S*)-E^2**	–9.8
(*S*)-B	–4.4	**(*S*)-E^3**	–11.4
(*S*)-TS2	+4.4	**(*S*)-E^4**	–18.2
(*S*)-C + CN^-	+51.0	**(*S*)-$TS4^1$**	+5.2
(*R*)-C + CN^-	+50.2	**(*S*)-$TS4^2$**	+8.4
(*S*)-TS3 + CN^-	+57.1	**(*S*)-F**	–19.7
(*R*)-TS3 + CN^-	+54.8	**(*S*)-2 + G**	–28.1
(*S*)-D + CN^-	+27.2		

SMD (toluene) BP86/6-311+G(2df,2pd)(LANL2TZ(f))//BP86/6-31G(d,p)(LANL2DZ)

Table 2.5. Gibbs Relative Energies Using M06 DFT Functional with Toluene Solvation

Structure	Relative Energy (kcal)	Structure	Relative Energy (kcal)
1 + G	0	**(*S*)-D + CN^-**	+20.9
(*S*)-A	–8.9	**(*R*)-D + CN^-**	+19.5
(*R*)-A	–12.5	**(*S*)-E^1**	–17.5
(*S*)-TS1	+1.4	**(*S*)-E^2**	–24.7
(*R*)-TS1	+0.7	**(*R*)-E^2**	–27.1
(*S*)-B	–14.6	**(*S*)-E^3**	–24.2
(*R*)-B	–11.6	**(*S*)-E^4**	–18.9
(*S*)-TS2	–3.6	**(*R*)-E^4**	–15.1
(*R*)-TS2	–2.5	**(*S*)-$TS4^1$**	–9.2
(*S*)-C + CN^-	+41.6	**(*S*)-$TS4^2$**	–6.2
(*R*)-C + CN^-	+41.7	**(*S*)-F**	–36.2
(*S*)-TS3 + CN^-	+45.9	**(*S*)-2 + G**	–32.2
(*R*)-TS3 + CN^-	+44.9		

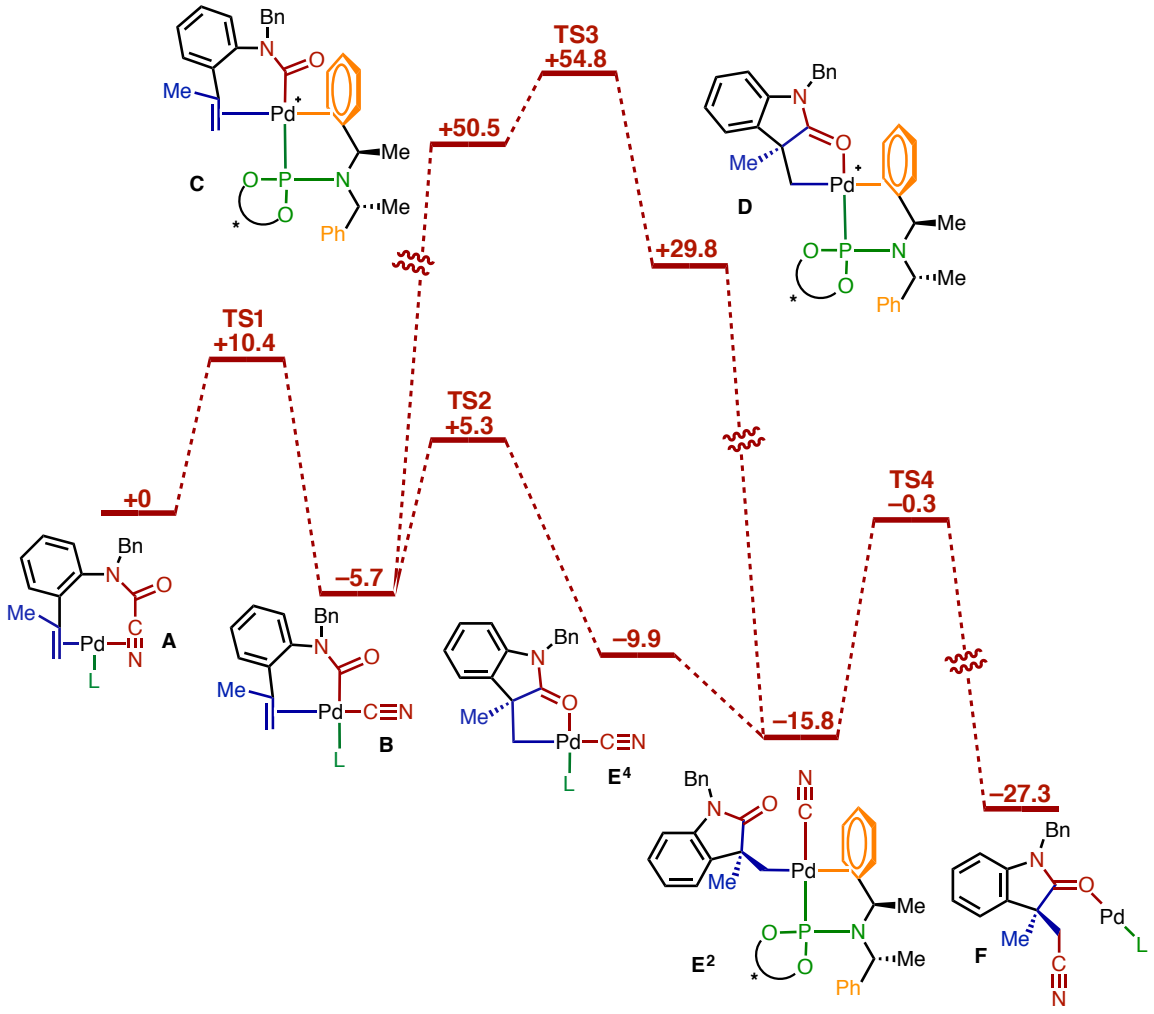
SMD (toluene) M06/6-311+G(2df,2pd)(LANL2TZ(f))//M06/6-31G(d,p)(LANL2DZ)

Table 2.6. Average Gibbs Energies

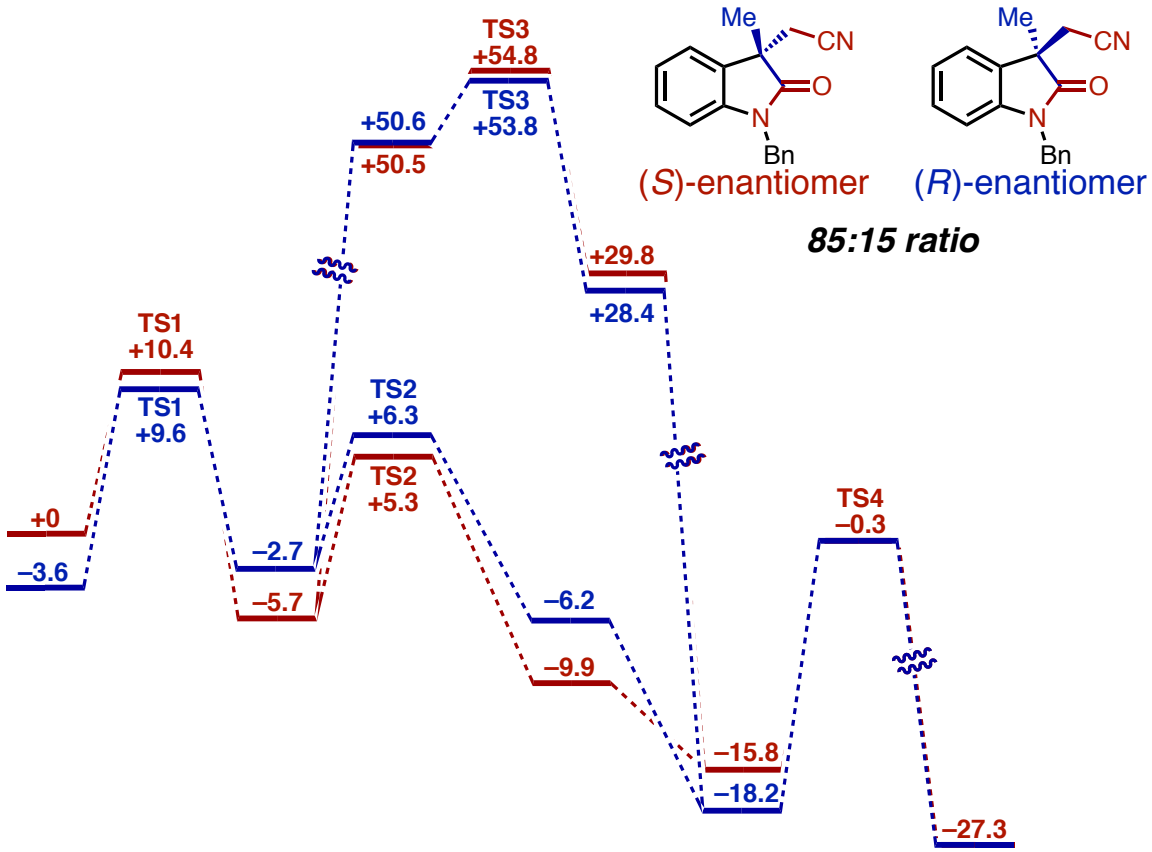
Structure	Relative Energy (kcal)	Structure	Relative Energy (kcal)
1 + G	0	**(*R*)-D + CN^-**	+19.5
A	–8.9	**(*S*)-E^1**	–14.9
TS1	+1.4	**(*S*)-E^2**	–13.9
(*S*)-B	–14.6	**(*S*)-E^3**	–14.8
(*S*)-TS2	–3.6	**(*S*)-E^4**	–17.7
(*S*)-C + CN^-	+41.6	**(*S*)-$TS4^1$**	+2.1
(*R*)-C + CN^-	+41.7	**(*S*)-$TS4^2$**	+5.5
(*S*)-TS3 + CN^-	+45.7	**(*S*)-F**	–25.6
(*R*)-TS3 + CN^-	+44.9	**(*S*)-2 + G**	–29.2
(*S*)-D + CN^-	+20.9		

The results of these calculations were set relative to **1** and **G** dissociated from each other in solution. The results between the 3 functionals (Tables 2.3–5) were inconsistent, thus the relative energies were averaged to observe trends (Table 2.6).

The first trend worth noting is that migratory insertion through a palladium cation is HIGHLY unlikely as the $\Delta G^{\ddagger} \approx +60$ kcal. Also, the preferred isomer based on these calculations is the (*R*)-enantiomer for the cationic pathway, which is not the predominant enantiomer formed in the actual catalytic reaction. Both results suggest that the reaction does not proceed through palladium cation **C**. The neutral pathway was computed for the (*R*)-enantiomer using the M06 functional and it was found that the (*S*)-enantiomer would be favored in migratory insertion for the neutral pathway, further supporting migratory insertion occuring through a neutral palladium complex. This is further highlighted in Schemes 2.8 and 2.9.



Scheme 2.8. Energy profile from M06 calculations of (*S*)-enantiomer.



Scheme 2.9. Energy profile comparison for the (*R*) and (*S*)-enantiomers using the M06 functional.

In addition to these results, it is evident that the first turnover of the catalyst should have reductive elimination as the rate-limiting step based on the $\Delta G^{\ddagger} \approx 10$ kcal for oxidative addition and $\Delta G^{\ddagger} \approx 20$ kcal for reductive elimination. It is likely that the CN^- dissociates during isomerization to **E²** for *cis*-reductive elimination to occur as reductive elimination cannot occur from comple **E⁴** which directly results from migratory insertion.

2.4 Conclusion

Our results from the AAKT analysis of the LSER for enantioselectivity, ^{13}CN crossover experiments, natural abundance $^{12}C/^{13}C$ KIE experiments, and initial rates kinetics experiments led us to propose a rigid bidentate palladium cation intermediate as the origin of high enantioselectivity. DMPU is an inhibitor in this

reaction but does not change the enantioselectivity. BPh_3 was found to increase the rate of the reaction but significantly decreased the e.r.

The computational results obtained in 2.3 suggest that the proposed cationic palladium pathway is unlikely to be operating in the enantioselective alkene cyanoamidation reaction. However, this result is inconsistent with the observed ^{13}CN crossover from 2.2. Upon inspecting the computed structures, it seems unlikely that crossover occurs by a bimetallic pathway due to the steric bulkiness of the **L1** ligand. My results suggest that crossover may be occurring through isomerization post-migratory insertion. More investigation into possible catalytically relevant structures is necessary to obtain a better grasp of how isomerization is occurring and to obtain a model for enantioselectivity that may lead us in designing new ligands to improve the enantioselectivity of the enantioselective alkene cyanoamidation reaction. Our AAKT results and the BPh_3 additive results suggest that optimizing future asymmetric cyanoamidation reactions should include very non-polar solvents and not use a Lewis acid additive.

2.5 Experimental Section

General Information

All reactions were carried out using oven-dried glassware. Cyanoformamide **1** and **3*** were prepared by literature procedures.[51] Solvents were dried and degassed prior to use or used fresh from new bottles. $Pd_2(dba)_3 \cdot CHCl_3$ was purified by literature procedure from Pd_2dba_3, which was purchased from commercial sources.[71] Phosphoramidite **L1** was prepared according to a literature procedure.[72] All other chemicals were purchased from commercial vendors and used as received. All cyanoamidation reactions were carried out in a nitrogen-filled glove box in 1 dram vials sealed with PTFE lined caps or 5 mm NMR tubes. Heating was applied by aluminum blocks. Analytical

thin layer chromatography (TLC) was carried out using 0.25 mm silica plates. Flash chromatography was performed using 230–400 mesh (particle size 0.04–0.063 mm) silica gel. ^{1}H NMR (300 and 500 MHz), ^{13}C NMR (75, 100 and 125 MHz), and ^{11}B NMR (128 MHz) spectra were obtained on FT NMR instruments. ^{1}H NMR spectra were reported as δ values in ppm relative to tetramethylsilane (TMS), ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.16 ppm, and ^{11}B NMR spectra were absolute referenced to TMS from a ^{1}H NMR spectrum obtained on the same instrument.

All computational structures were optimized in the gas phase and verified as minima or first-order saddle points by calculations of the full Hessian using Gaussian 09.[73] All geometries reported are RB3LYP, RM06, or RBP86 (closed-shell species) with the LANL2DZ basis set for Pd and 6-31G(d,p) basis set for H, C, N, O, and P atoms. Electronic energies were further evaluated with the LANL2TZ(f) basis set for palladium and 6-311+G(2df,2pd) basis set for H, C, N, O, and P atoms with SMD (solvent = toluene) solvation. All ZPE, enthalpic, and entropic free energy corrections (unscaled) utilize values computed at the lower basis set level at 373.15 K and 1 atm.

General Procedure for 0.1 mmol Scale Cyanoamidation

Under N_2 atmosphere in a glovebox, 0.0276 g (0.1 mmol) of cyanoformamide **1**, 0.0043 g (0.008 mmol) of **L1,** and 0.0010 g (0.001 mmol) of $Pd_2(dba)_3$•$CHCl_3$ were weighed in a 1 dram screw top reaction vial. If DMPU was used in the reaction, 0.0128 g (12 µL) (0.1 mmol) were added via microsyringe. If BPh_3 was used, 0.0242 g (0.1 mmol) or other desired quantity were weighed in the reaction vial. 1 ml of the solvent was added via syringe as well as a 5 mm stir bar and the reaction vial was sealed. The reactions were heated at 100 °C for 24 hours in an aluminum heating block on a preheated hot plate in the glovebox. Once completed, the reactions were allowed to cool to room temperature and removed from the glovebox. Depending on the solvent boiling point, the reaction

mixtures were concentrated either *in vacuo* by rotatory evaporation or with a Kugelrohr. The crude oxindole **2** was then dissolved in ~1 ml $CDCl_3$ and filtered through a 0.2 µm syringe filter. ^{1}H NMR was taken to determine conversion to oxindole. HPLC [Chiralcel OD-H, hexanes/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 14.3 min, (minor) 17.5 min **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 1.57 (s, 3H), 2.64 (d, 1H, *J* = 16.5 Hz), 2.90 (d, 1H, *J* = 16.5 Hz), 4.93 (s, 2H), 6.78 (d, 1H, *J* = 7.6 Hz), 7.09 (t, 1H, *J* = 7.6 Hz), 7.27 (m, 6H), 7.47 (m, 1H).

Table 2.7. Enantiomeric Ratio Measurement HPLC Data

solvent	additive	L1	HPLC integration major enantiomer	HPLC integration minor enantiomer	er	log(major/minor)
decalin	-	8 mol %	89.3807	10.6193	89:11	0.925147862
cyclohexane	-	8 mol %	88.7035	11.2965	89:11	0.89499685
***m*-xylene**	-	8 mol %	85.0863	14.9137	85:15	0.756274236
toluene	-	8 mol %	84.5018	15.4982	85:15	0.736584699
2-propanol	-	8 mol %	83.8563	16.1437	84:16	0.715532618
MEK	-	8 mol %	82.8212	17.1788	83:17	0.683148695
TFT	-	8 mol %	82.2295	17.7705	82:18	0.665328002
dioxane	-	8 mol %	81.5938	18.4062	82:18	0.646693023
DCE	-	8 mol %	79.4975	20.5025	79:21	0.588546651
NMP	-	8 mol %	78.9470	21.0530	79:21	0.574021641
DMF	-	8 mol %	75.7366	24.2634	76:24	0.494354147

MeCN	-	8 mol %	71.4966	28.5034	71:29	0.399388722
heptane	-	8 mol %	83.5633	16.4367	84:16	0.706200954
PFMCH	-	8 mol %	75.3666	24.6334	75:25	0.485654564
toluene	100 mol % DMPU	8 mol %	84.5439	15.4561	85:15	-
decalin	100 mol % DMPU	8 mol %	89.2363	10.7637	89:11	-
toluene	100 mol % BPh_3	8 mol %	77.3274	22.6726	77:23	-
decalin	100 mol % BPh_3	8 mol %	79.7316	20.2684	80:20	-

Abboud-Abraham-Kamlet-Taft (AAKT) Model Linear Solvation Energy Relationships

Table 2.8. Abboud-Abraham-Kamlet-Taft Solvent Parameters and Dielectric Constants

solvent	α	β	π^*	dielectric constant (ε)
decalin	0	0.08	0.11	2.1
cyclohexane	0	0	0	1.9
m-xylene	0	0.1	0.47	2.4
toluene	0	0.11	0.54	2.4
2-propanol	0.76	0.95	0.48	17.9
MEK	0.06	0.48	0.67	18.5
TFT	0	0	0.64	2.3
dioxane	0	0.37	0.55	9.4
DCE	0	0.1	0.81	10.3
NMP	0.03	0.76	0.97	32
DMF	0	0.69	0.88	36.7

MeCN	0.19	0.31	0.75	37.5
heptane	0	0	-0.06	1.9
PFMCH	0	-0.08	-0.40	1.9

log(er) = c + xε

Table 2.9. Linear Regression Output Dielectric Constant Fit

x	-0.008787774	c	0.80031809
se(x)	± 0.001973928	se(c)	± 0.03889472
R^2	0.664650317	se	± 0.09160066
F	19.81961965	degrees of freedom	10
regression ss	0.166300099	residual ss	0.08390681

Table 2.10. Calculated Values Dielectric Constant Fit

solvent	**$log(er)_{calc}$**
decalin	0.781863765
cyclohexane	0.78362132
m-xylene	0.779227433
toluene	0.779227433
2-propanol	0.643016943
MEK	0.637744279
TFT	0.780106211
dioxane	0.717713018
DCE	0.709804022
NMP	0.519109336
DMF	0.4778068
MeCN	0.470776582

log(er) = c + xπ* + yα + zβ

Table 2.11. Linear Regression Output AAKT

z	0.06668889	y	-0.119620789	x	-0.510246496	c	0.951684655
se(z)	± 0.119896476	se(y)	± 0.157455952	se(x)	± 0.107965066	se(c)	± 0.055044003
R^2	0.797802263	se	± 0.079523008	-	-	-	-
F	10.52174336	degrees of freedom	8	-	-	-	-
regression ss	0.199615635	residual ss	0.05059127	-	-	-	-

Table 2.12. Calculated Values, Residuals, and Grubb's Test AAKT

solvent	$log(er)_{calc}$	residual	Grubb's Test MeCN
decalin	0.900892652	0.02425521	3.077755187
cyclohexane	0.951684655	0.056687806	Grubb's Test cyclohexane
m-xylene	0.718537691	0.037736545	1.304270576
toluene	0.683487325	0.053097374	-
2-propanol	0.679208983	0.036323634	-
MEK	0.634652923	0.048495772	-
TFT	0.625126898	0.040201104	-
dioxane	0.695723972	0.049030949	-
DCE	0.545053883	0.043492768	-
NMP	0.5300197	0.04400194	-
DMF	0.548683073	0.054328926	-
MeCN	0.566945389	0.167556667	-

log(er) = c + xπ* + yα + zβ (No MeCN)

Table 2.13. Linear Regression Output AAKT (w/out MeCN)

z	-0.044575475	y	0.03062126	x	-0.401216829	c	0.932062453
se(z)	± 0.06979587	se(y)	± 0.091992547	se(x)	± 0.06358011	se(c)	± 0.030261258
R^2	0.922188342	se	0.043257806	-	-	-	-
F	27.65360423	degrees of freedom	7	-	-	-	-
regression ss	0.155239405	residual ss	0.013098664	-	-	-	-

Table 2.14. Calculated Values AAKT (w/out MeCN)

solvent	log(er)calc
decalin	0.884362564
cyclohexane	0.932062453
m-xylene	0.739032996
toluene	0.710502063
2-propanol	0.720403832
MEK	0.643688226
TFT	0.675283683
dioxane	0.694900272
DCE	0.602619274
NMP	0.529538493
DMF	0.548234566

Table 2.15. Coefficient Values and T-Tests AAKT (w/out MeCN)

	c	x	y	z

value	0.9321	– 0.401	0.031	– 0.045
error	± 0.0303	± 0.063	± 0.092	± 0.070
t-test value	–	– 6.310	0.333	– 0.639

log(er) = c + xπ*

Table 2.16. Linear Regression Output Using π* Only

x	–0.427844871	c	0.934331526
se(x)	± 0.042884798	se(c)	± 0.026476726
R^2	0.917075707	se	0.039383182
F	99.5327311	degrees of freedom	9
regression ss	0.154378754	residual ss	0.013959315

Table 2.17. Calculated Values Using π* Only

solvent	Log(er)calc
decalin	0.88726859
cyclohexane	0.934331526
m-xylene	0.733244437
toluene	0.703295296
2-propanol	0.728965988
MEK	0.647675463
TFT	0.660510809
dioxane	0.699016847
DCE	0.587777181
NMP	0.540714245
DMF	0.55782804

General Procedure for ^{13}CN Crossover Experiments

Under N_2 atmosphere in a glovebox, 0.024 g (0.087 mmol) of cyanoformamide **1** and 0.025 g (0.086 mmol) of ^{13}CN labeled cyanoformamide **3***, 0.0075 g (0.014 mmol) of **L1,** and 0.0017 g (0.0017 mmol) of $Pd_2(dba)_3$•$CHCl_3$ were weighed in a screw top 1 dram reaction vial. If DMPU was used in the reaction, 21 µL (0.022 g) (0.17 mmol) was added via microsyringe. If BPh_3 was used 0.042 g (0.17 mmol) or other desired quantity was weighed in the reaction vial. 1.74 ml of solvent (toluene or decalin) was added via syringe as well as a 5 mm stir bar and the reaction vial was sealed. The reactions were heated at 100 °C for 24 hours in an aluminum heating block on a preheated hot plate in the glovebox. Once completed, the reactions were allowed to cool to room temperature and removed from the glovebox. The reaction mixtures were concentrated *in vacuo* by rotatory evaporation. The crude mixture of oxindoles **2**, **2***, **4**, **4*** was then dissolved in ~1 ml $CDCl_3$ and filtered through a 0.2 µm syringe filter. ^{1}H NMR spectra were then taken to determine conversion to oxindole. The extent of crossover was determined of integration of ^{13}C NMR spectra (see appendix). HPLC [Chiralcel OD-H, hexanes/2-propanol = 90/10, 1.0 mL/min, λ = 254 nm, retention times: (major) 14.3 min, (minor) 17.5 min.

Table 2.18. ^{13}CN Crossover and Ligand Loading Data

solvent	**L1** loading	additive	**4*:2*** (^{13}C NMR integration)	**er**
decalin	8 mol %	DMPU 100 mol %	46.99:53.01	-
toluene	8 mol %	DMPU 100 mol %	51.43:48.57	-
decalin	8 mol %	-	49.07:50.93	-
toluene	8 mol %	-	51.50:48.50	-
toluene	8 mol %	BPh_3 50 mol %	36.22:63.78	79.85:20.15
toluene	8 mol %	BPh_3 100 mol %	35.28:64.72	77.33:22.67
toluene	8 mol %	BPh_3 200 mol %	30.07:69.93	72.93:27.07

toluene	4 mol %	-	52.24:47.76	84.08:15.92
toluene	2 mol %	-	-	84.15:15.85
toluene	4 mol %	BPh_3 100 mol %	-	77.53:22.47

Initial Rate Kinetics Method

In a nitrogen filled glovebox, two stock solutions were made in d_8-toluene: stock A (0.2 M cyanoformamide, 0.002 M $Pd_2(dba)_3$, and 0.016 M **L1**) and stock B (0.4 M additive (BPh_3 or DMPU). 1.2 mL of stock A was added to separate vials and then stock B was added to make solutions of 0, 0.1, 0.25, 0.5, 1, and 2 equivalents of additive respectively. d_8-Toluene was then added to bring the total volume to 2.4 mL in all vials. 0.7 mL from each vial was added to separate NMR tubes so that each reaction was run in triplicate and the tubes were sealed with plastic caps and the caps secured with electrical tape. The tubes were then placed in the NMR spectrometer autosampler and sequentially monitored via variable temperature NMR spectroscopy at 90 °C (calibrated using pure glycol standard) for 1 hour (roughly 10% conversion). Spectra were processed using the integrals graph function in MestReNova after performing phase and baseline corrections. The data was exported to Microsoft EXCEL and the data fit with a linear line to obtain rates. All data was normalized to obtain mM/second rates based on the integral of the peak at 3.93 ppm being from the starting material, which is 90% of the total starting material (as it is one of 2 peaks corresponding to rotational isomers that are resolved in the spectra with the lesser isomer being 10% of the total). The rates obtained were averaged and standard deviations obtained. The average rates were plotted with error bars equivalent to the standard deviation against the concentration of additive in the experiment.

General Procedure for Collection of Sample for $^{12}C/^{13}C$ Kinetic Isotope Effect Determination

A 250 mL round bottom was charged with a stir bar, $Pd_2(dba)_3$ (0.140 mmol), and phosphoramidite **L1** (1.16 mmol) in a glove box under nitrogen atmosphere. Decalin was then added to the catalyst (40 mL). Cyanoformamide **1** was added (7.25 mmol) and the reaction mixture was diluted with additional decalin until the reaction mixture was 0.1 M (72 mL total). DMPU (7.25 mmol) was added and the reaction flask was sealed with a rubber septum and electrical tape. The flask was then removed from the glove box, a nitrogen inlet was inserted with positive nitrogen pressure, and the reaction was heated to 100 °C in an oil bath.

After 1 hour, a 0.1 mL sample was removed and filtered through a plug of silica gel. The silica gel was rinsed first with hexanes to remove decalin and then with ethyl acetate to flush off the product and starting material. The sample was concentrated, and an NMR spectrum of the crude material was taken to determine the approximate percent conversion. This process was repeated until the reaction was determined to be ~90% complete.

The reaction mixture was removed from the oil bath, diluted with cold hexanes, and immersed in an ice bath to quickly cool to room temperature. The reaction mixture was then flushed down a large column of silica to remove the catalyst. Decalin was removed by first flushing the column of silica with hexanes (~250 mL). Then, the column was rinsed several times with ethyl acetate (~500 mL combined) to ensure all the starting material was obtained. The solution was then concentrated, and silica gel column chromatography was used to separate the enriched starting material from the product (90:10 Hex EtOAc as eluent). Concentration of fractions yielded enriched **1** for the natural abundance KIE ^{13}C NMR experiment.

Pure samples of the recovered enriched **1** and unreacted substrate **1** were quantitatively analyzed by ^{13}C NMR spectroscopy. Spectra were obtained on a Bruker Avance III 500 MHz spectrometer (125 MHz, $CDCl_3$) at 300 K with an

inverse-gated decoupling pulse sequence and calibrated 30° pulses, collecting 256K points total. T1 values were measured prior to obtaining data, and D1 values were set to 120 s with acquisition times of 11.5 s. Five acquisitions were obtained for each sample. Each spectrum was processed using a –1.00 Hz exponential and a 3.00 Hz Gaussian apodization, as well as a 3rd Order Bernstein polynomial baseline correction.

NMR Measurements

Pure samples of the recovered enriched **1** and unreacted substrate **1** were quantitatively analyzed by ^{13}C NMR spectroscopy using Singleton's method. Spectra were obtained on a Bruker Avance III 500 MHz spectrometer (125 MHz, $CDCl_3$) at 300 K with an inverse-gated decoupling pulse sequence and calibrated 30° pulses, collecting 256K points total. T1 values were measured prior to obtaining data, and D1 values were set to 120 s with acquisition times of 11.5 s. Five acquisitions were obtained for each sample. Each spectrum was processed using a –1.00 Hz exponential and a 3.00 Hz Gaussian apodization, as well as a 3rd Order Bernstein polynomial baseline correction.

The integrations of the recovered, ^{13}C enriched starting material and the unreacted starting material are found for both DMPU and BPh_3 additive trials in Tables 2.19 and 2.20 respectively. Table 2.21 contains the relative integrations of the ^{13}C enriched sample relative to the unreacted cyanoformamide **1**, using equation R/R_o, where R = enriched integral and R_o = unreacted integration. $^{12}C/^{13}C$ kinetic isotope effects were calculated using equation 1 and are reported in Table 2.22. Standard deviations were calculated using Singleton's method.[68]

$$KIE = \frac{\ln(1-F)}{\ln\left[\frac{(1-F)R}{R_o}\right]} \quad (1)$$

F: percent conversion of the substrate **1** during cyanoamidation reaction – determined by ^{1}H NMR spectroscopy.

R/R_o: proportion of ^{13}C observed in the recovered starting material relative to the ^{13}C in the unreacted cyanoformamide **1**.

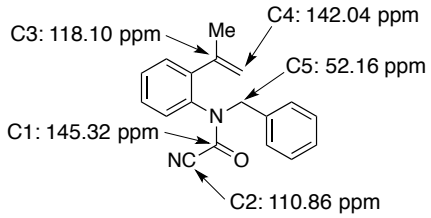


Figure 2.22. ^{13}C NMR chemical shifts.

Table 2.19. Integrations for DMPU Additive Reaction for the Cyanoamidation of **1**

	C1	**C4**	**C3**	**C2**	**C5**
^{13}C NMR δ (125 MHz, $CDCl_3$)	145.32	142.04	118.10	110.86	52.16
Control [a]					100
Spec. #1	103.0576	100.1260	95.0800	104.3735	(std)
Spec. #2	101.5615	99.9286	95.0271	103.8490	–
Spec. #3	101.6822	100.0435	95.1332	102.7529	–
Spec. #4	103.8015	102.0095	96.8470	104.0119	–
Spec. #5	102.6530	99.3785	94.6964	103.8607	–
Control Avg.	102.5512	100.2972	95.3567	103.7696	100 (std)
Std. Dev. [b]	0.9440	1.0007	0.8503	0.6066	–
Enriched [a]					100
Spec. #1	106.3292	98.5039	93.0379	109.3709	(std)
Spec. #2	110.2083	100.9196	94.3450	112.2794	–
Spec. #3 [c]	114.7171	101.6621	100.2022	112.9533	–
Spec. #4	108.7246	99.9855	97.0957	111.3783	–
Spec. #5	108.1326	99.1786	94.8453	110.6279	–
Enriched Avg.	108.3487	99.6469	94.8310	110.9141	100 (std)
Std. Dev. [b]	1.6046	1.0425	1.6912	1.2306	–

a) Each spectrum was integrated after baseline and phase correction. *b*) The standard deviation is from the integrated spectra. *c*) Spectrum was not used in the calculation and was rejected at the 95% confidence level using the Grubbs Test based on the value for **C1**. The starting material was recovered after the reaction was run to 92.0 ± 0.5% conversion.

Table 2.20. Integrations for BPh_3 Additive Reaction for the Cyanoamidation of **1**

	C1	**C4**	**C3**	**C2**	**C5**
^{13}C NMR δ (125 MHz, $CDCl_3$)	145.32	142.04	118.10	110.86	52.16
Control [a]					
Spec. #1	104.5100	101.6178	96.0340	105.4467	100 (std)
Spec. #2	104.1677	101.0919	95.3248	104.0597	–
Spec. #3	103.8226	101.5538	95.7521	104.4261	–
Spec. #4	103.8222	102.9792	95.2570	105.0759	–
Spec. #5	103.6878	101.7225	94.6790	104.9960	–
Control Avg.	104.0021	101.7930	95.4094	104.8009	100 (std)
Std. Dev. [b]	0.3349	0.7056	0.5176	0.5524	–
Enriched [a]					
Spec. #1	108.5256	101.5708	95.7420	107.0602	100 (std)
Spec. #2	108.4047	100.8741	94.6298	108.4075	–
Spec. #3	108.2941	100.9855	95.9781	107.0078	–
Spec. #4	106.8136	99.9043	96.1219	107.8037	–
Spec. #5 [c]	103.8852	96.6252	94.4896	107.1096	–
Enriched Avg.	108.0095	100.8337	95.6180	107.5698	100 (std)
Std. Dev. [b]	0.8029	0.6908	0.6771	0.6663	–

a) Each spectrum was integrated after baseline and phase correction. *b*) The standard deviation is from the integrated spectra. *c*) Spectrum was not used in the calculation and was rejected at the 95% confidence level using the Grubbs Test based on the value for **C1**. The starting material was recovered after the reaction was run to 87.5 ± 0.5% conversion.

Table 2.21. Ratios of Integrations for the Cyanoamidation Natural Abundance KIE Experiments

	C1	**C4**	**C3**	**C2**	**C5**
^{13}C NMR δ (125 MHz, $CDCl_3$)	145.32	142.04	118.10	110.86	52.16
Enriched/Control (R/Ro) - DMPU	1.0565	0.9935	0.9945	1.0688	1.0000
Std. Dev.	0.0184	0.0144	0.0198	0.0134	–
Enriched/Control (R/Ro) - BPh_3	1.0385	0.9906	1.0022	1.0264	1.0000
Std. Dev.	0.0084	0.0097	0.0089	0.0083	–

Table 2.22. Calculated ^{12}C/^{13}C KIE for the Cyanoamidation of **1**

	C1	**C4**	**C3**	**C2**	**C5**
^{13}C NMR δ (125 MHz, $CDCl_3$)	145.32	142.04	118.10	110.86	52.16
KIE (92.0 ± 0.5% conv) DMPU	1.022	0.997	0.998	1.027	1.000
Std. Dev.	±0.007	±0.006	±0.008	±0.005	–
KIE (87.5 ± 0.5% conv) BPh_3	1.019	0.995	1.001	1.013	1.000
Std. Dev.	±0.004	±0.005	±0.004	±0.004	–

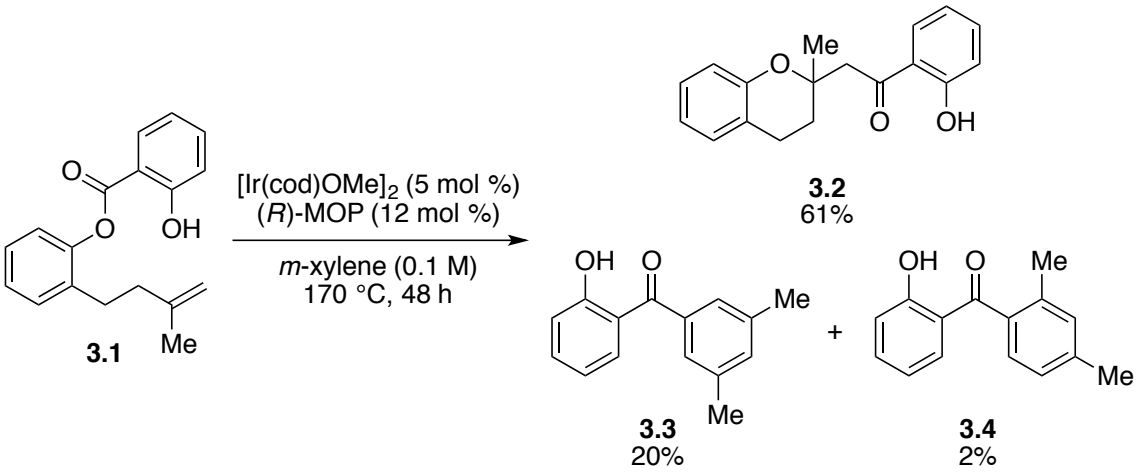
Calculation for BPh_3 Pathway Enantiomeric Ratio

Assuming full retention of ^{13}CN label if all material goes through the BPh_3 pathway (during crossover experiments), at 100% BPh_3 loading, the % of material going through the BPh_3 pathway is 30% (65 – 35 from Table 2.2, entry 6). The change in er from the no BPh_3 additive pathway was –7 with respect to the major enantiomer (comparing Table 2.1, entry 3 to Table 2.2, entry 6). Multiplying –7 by 3.33 (100/30 from the 30% material going through the BPh_3 pathway) gives –23 er with respect to the major enantiomer. The calculated er for the exclusively BPh_3 catalyzed pathway would then be 62:38 (85 – 23 for major enantiomer).

CHAPTER 3: LATE TRANSITION METAL-CATALYZED C–O BOND ACTIVATION AND THE OXYACYLATION REACTION

3.1 Introduction to C–O Bond Activation

The activation of the C_{acyl}–Y bond (Y = H, C, O) has led to the development of metal-catalyzed reactions with high atom economy such as the carboacylation,[12] hydroacylation,[74-77] and oxyacylation[78-80] of olefins. These reactions exhibit common characteristics including a "cut-and-stitch" approach to adding the C_{acyl}–Y moieties across olefins. The mechanism of these reactions proceeds via oxidative addition of the metal catalyst into the C_{acyl}–Y bond. However, after insertion of the metal into the C_{acyl}–Y bond, unproductive decarbonylation has been reported.[81] To prevent decarbonylation from the proposed C_{acyl}–M–Y intermediate, directing groups that chelate with the metal catalyst are used. The quinoline and phenol directing groups have seen particular utility in the Douglas group.[12,78,80,82]



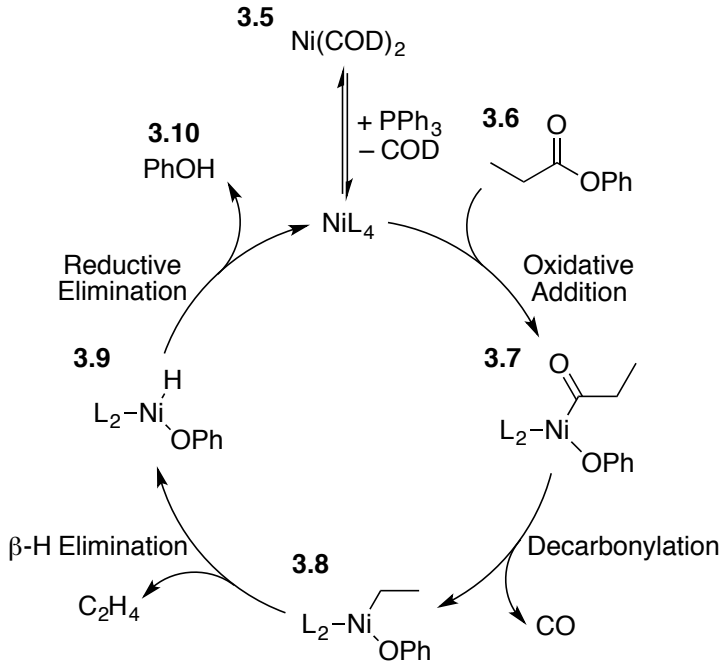
Scheme 3.1. Initial tandem C_{acyl}–O/C–H bond activation findings.

In the development of an oxyacylation reaction using salicylate esters as the substrate, an unexpected transformation was observed in which the substrate **3.1** (Scheme 3.1) was converted to the desired oxyacylation product **3.2** as well as the "undesired" byproducts **3.3** and **3.4**. Studies showed that the aryl-fragment

present in **3.3** and **3.4** was from the C–H activation of the *m*-xylene solvent and subsequent reductive elimination of the biaryl ketones **3.3** and **3.4**. This type of transformation has never been observed and warranted further investigation. To better understand the C_{acyl}–O activation step in Scheme 3.1, the development of C_{acyl}–Y bond activation will be presented. Attention will be primarily focused on the development of C_{acyl}–O bond activation reactions and will include both decarbonylative as well as non-decarbonylative activation pathways.

3.2 Background for Acyl C–O Activation

3.2.1 Decarbonylative C–O Activation



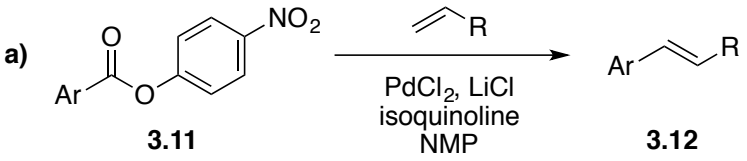
Scheme 3.2. Nickel-catalyzed decarbonylation mechanism.

The activation of C_{acyl}–O bonds was first studied by Akio Yamamoto using a $Ni(cod)_2$ catalyst.[81,83] After insertion of the nickel catalyst into the C_{acyl}–O bond forming the organometallic species **3.7**, decarbonylation of the nickel–acyl intermediate was rapid. β-hydride elimination of the resulting nickel–alkyl species

3.8 liberated ethane and reductive elimination of phenol completed the catalytic cycle (Scheme 3.2). The authors observed a nickel species that was hypothesized to be $Ni(CO)(PPh_3)_3$, which supported their decarbonylation hypothesis.[81,83] Yamamoto later published similar cases of decarbonylation with ruthenium(II),[84] rhodium(I)[84], and cobalt(I)[85].

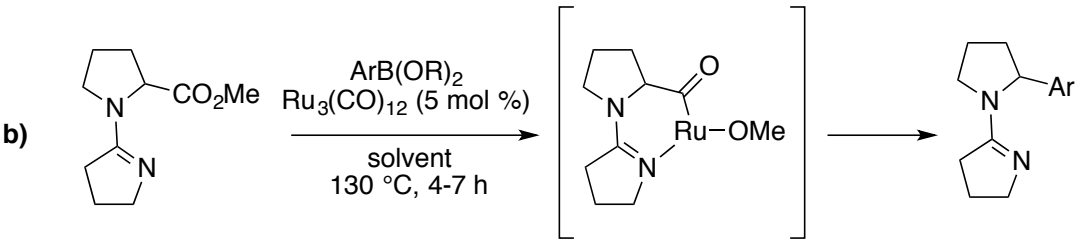
The formation of new C–C bonds via decarbonylative C–O bond activation was developed by Gooßen in 2002 (Scheme 3.3).[86] The decarbonylative Heck coupling illustrated in Scheme 3.3a likely proceeds through oxidative addition into the C_{acyl}–O bond of **3.11**. Migratory insertion of olefin into the aryl–palladium bond followed by β-H elimination gives the coupled products **3.12**. Sames showed that C–H activation α to the nitrogen of the pyrrolidine in **3.13** is significantly slower than C–O activation of the ester (Scheme 3.3b). After decarbonylation from the 6-member ring chelate intermediate **3.14**, transmetalation followed by reductive elimination gave the α-arylated product **3.15**.[87]

Gooßen



3.11 **3.12**

Sames



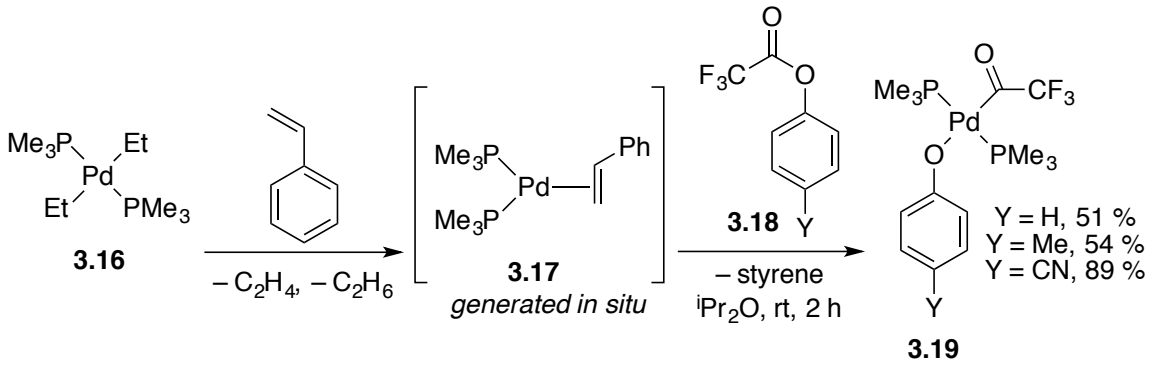
3.13 **3.14** **3.15**

Scheme 3.3. Catalytic decarbonylative reactions proceeding via C–O activation.

3.2.2 Non-Decarbonylative C–O Activation

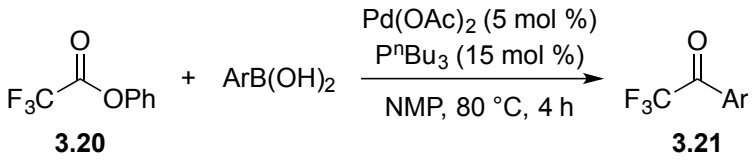
3.2.2.1 Undirected Methods

In 1999, Yamamoto found that preferential insertion into the C_{acyl}–O bond of aryl trifluoroacetate derivatives **3.18** was possible with a low valent palladium(0) complex **3.17** (Scheme 3.4). Decarbonylative decomposition of the acyl palladium(II) intermediate **3.19** was not observed, likely due to the electron-withdrawing nature of the CF_3-group on the acyl carbon. This was the first stoichiometric non-decarbonylative C_{acyl}–O activation without chelation.[88]



Scheme 3.4. C–O activation of trifluoromethyl esters.

Yamamoto reported conditions to form new C–C bonds from the activation of the trifluoromethyl C_{acyl}–O bonds of **3.20** (Scheme 3.5). This Suzuki-like coupling was the first example of the activation of C_{acyl}–O bonds coupled with aryl boronic acids to construct new C_{acyl}–C bonds, affording **3.21**.[89]



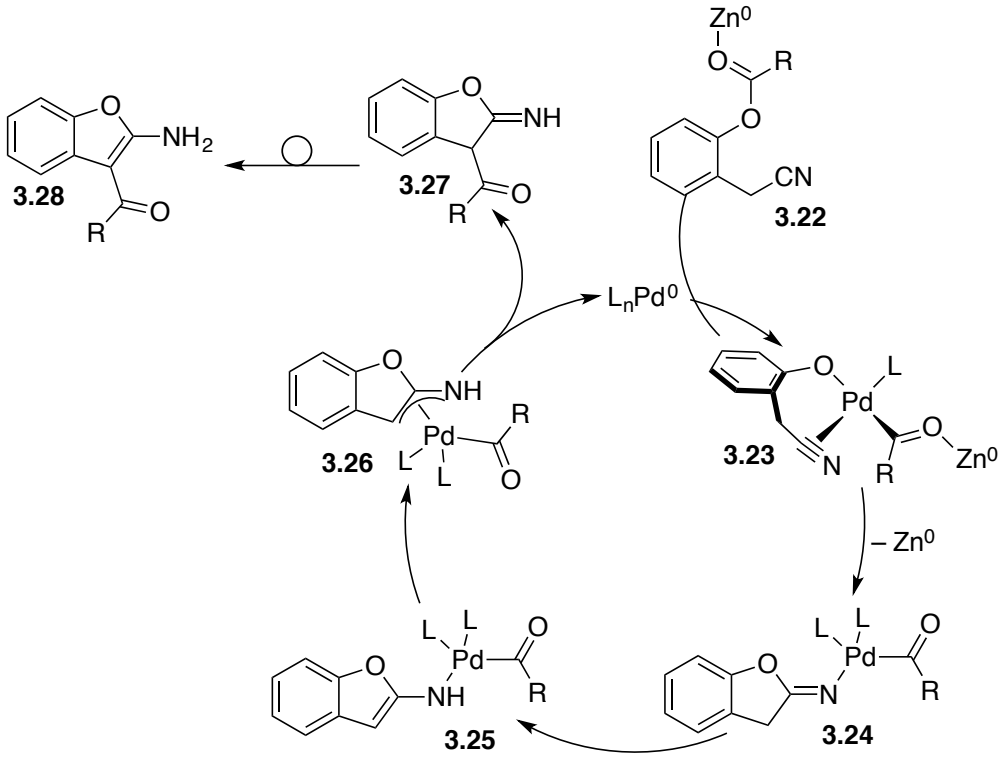
Scheme 3.5. Acyl "Suzuki-like" coupling with aryl trifluoromethyl esters.

3.2.2.2 Acyl C–O Activation Using Directing Groups

3.2.2.2.1 Cyano π-bonds

Ohe developed a method for the catalytic cycloisomerisation of 2-(cyanomethyl)phenyl esters (**3.22**) via a C–O activation mechanism wherein a

CN π-bond forms a chelate with the inserted acyl palladium(II) intermediate **3.23** (Scheme 3.6). Chelation of 4-coordinate palladium center prevents decarbonylation of the palladium–C_{acyl} intermediate. The authors hypothesized that reductive elimination from **3.24** would yield the *N*-acyl-2-aminobenzofuran after tautomerization. However, they instead observed acyl migration to the 3-position on the benzofuran ring **3.28**. The catalytic cycle in Scheme 3.6 was proposed to explain this result in which **3.24** tautomerizes to the benzofuran **3.25**. The palladium then forms the π-complex **3.26** which reductively eliminates forming the exocyclic imine **3.27**. Tautomerization then forms the more conjugated 3-acyl-2-aminobenzofuran **3.28**.[90]

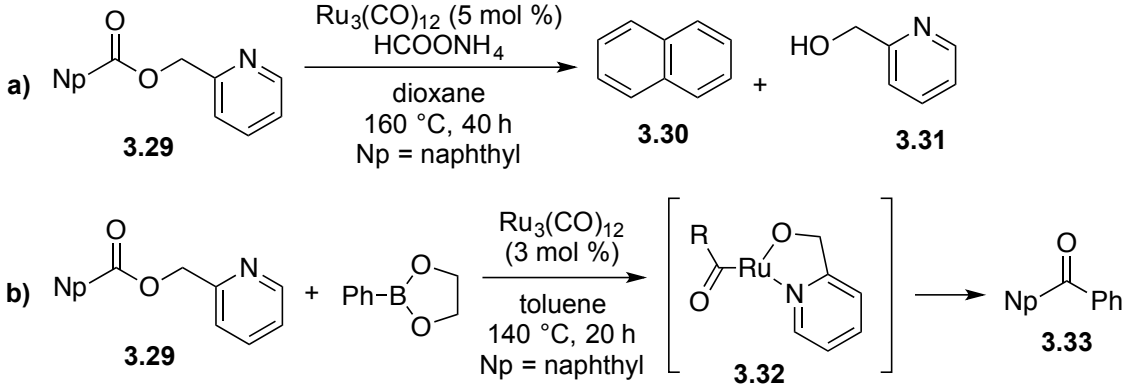


Scheme 3.6. Mechanism for the formation of 3-acyl-2-aminobenzofurans.

3.2.2.2.2 Pyridyl Directing Group

Chatani and Murai reported a chelation-controlled C–O activation of **3.29** with $Ru_3(CO)_{12}$ with subsequent transfer hydrogenation from the ammonium formate that afforded the reduced naphthalene product **3.30** and 2-

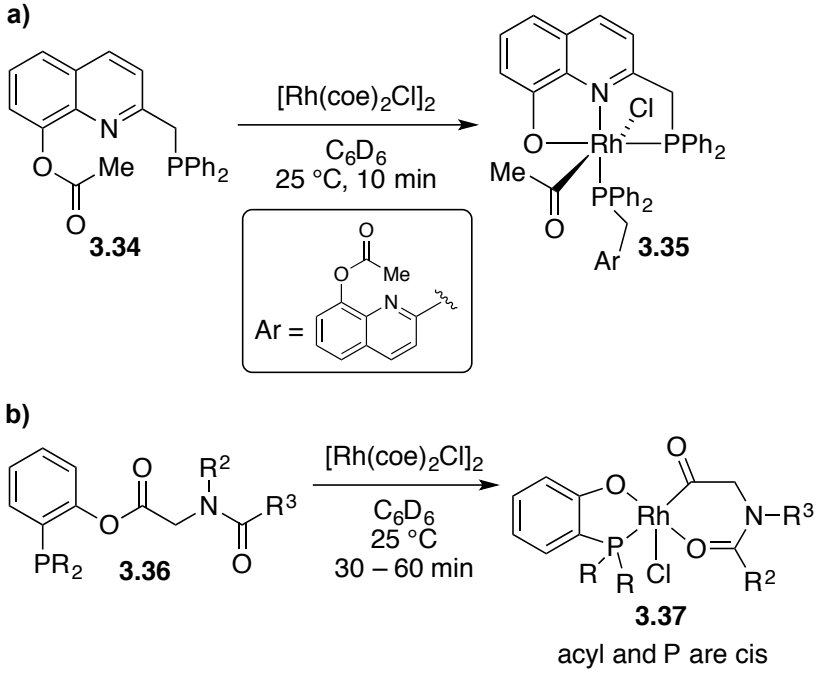
hydroxymethyl-pyridine **3.31** (Scheme 3.7a).[91] This reaction was further developed into a coupling reaction between acyl carbonyl **3.29** and aryl boronates (Scheme 3.7b). The 5-membered chelate intermediate **3.32** was stabilized via 2-pyridyloxy-group chelation to prevent decarbonylation. The authors hypothesized that transmetalation was more rapid than decarbonylation, which allowed for reductive elimination to yield the coupled product **3.33**.[91,92] Similar results were achieved with shorter reaction times and lower temperatures using a $Pd(OAc)_2$ pre-catalyst with triphenylphosphine as the ligand.[93]



Scheme 3.7. Directed acyl "Suzuki-like" coupling using 2-pyridylmethyl directing group.

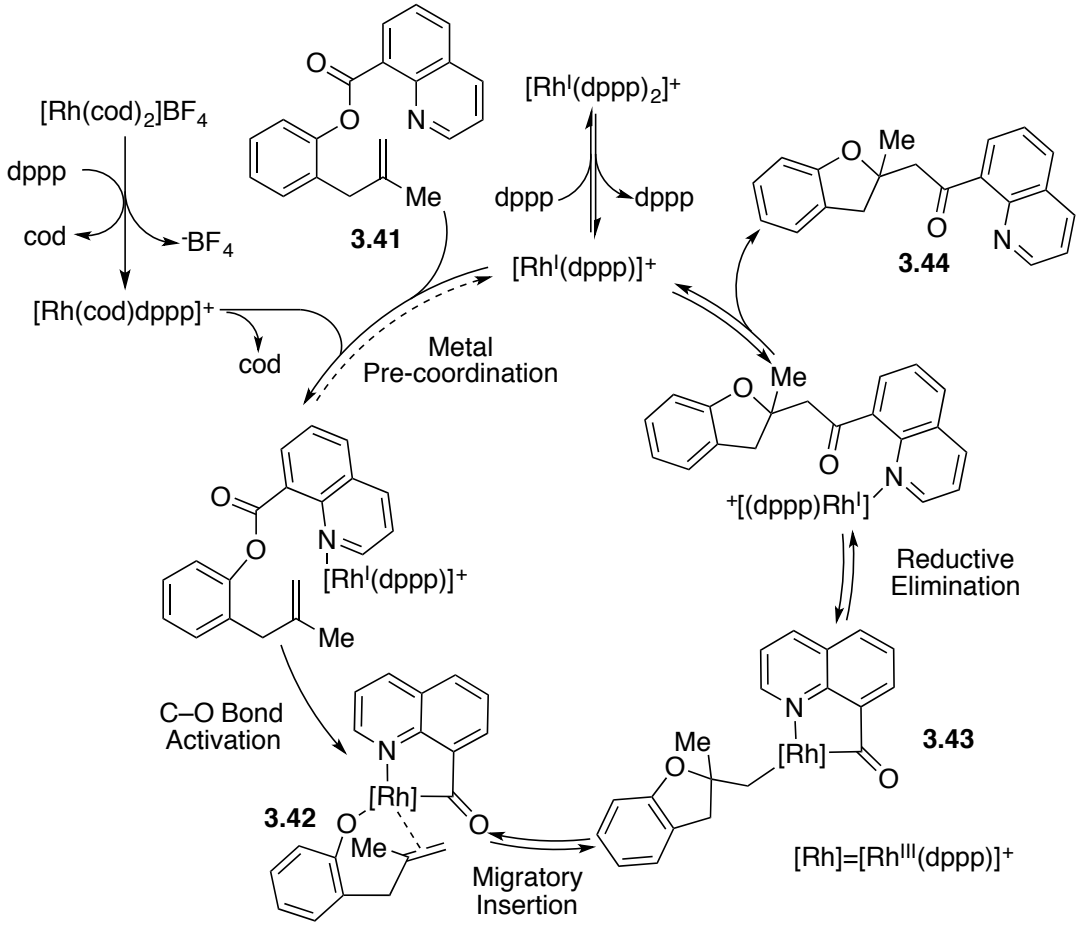
3.2.2.2.3 Quinoline Directing Groups

In 1995 Grotjahn found that insertion of rhodium(I) into the C_{acyl}–O bond of **3.34** and subsequent chelation of the resulting rhodium intermediate **3.35** by the phosphine substituent allowed for the isolation of a complex that did not undergo decarbonylation (Scheme 3.8a).[94] In 1999, Grotjahn demonstrated that protected amino acid **3.36**, where five-membered chelation is also possible, could stabilize the rhodium oxidative addition product **3.37** (Scheme 3.8b).[95]



Scheme 3.8. Directed C–O activation without decarbonylation using chelation.

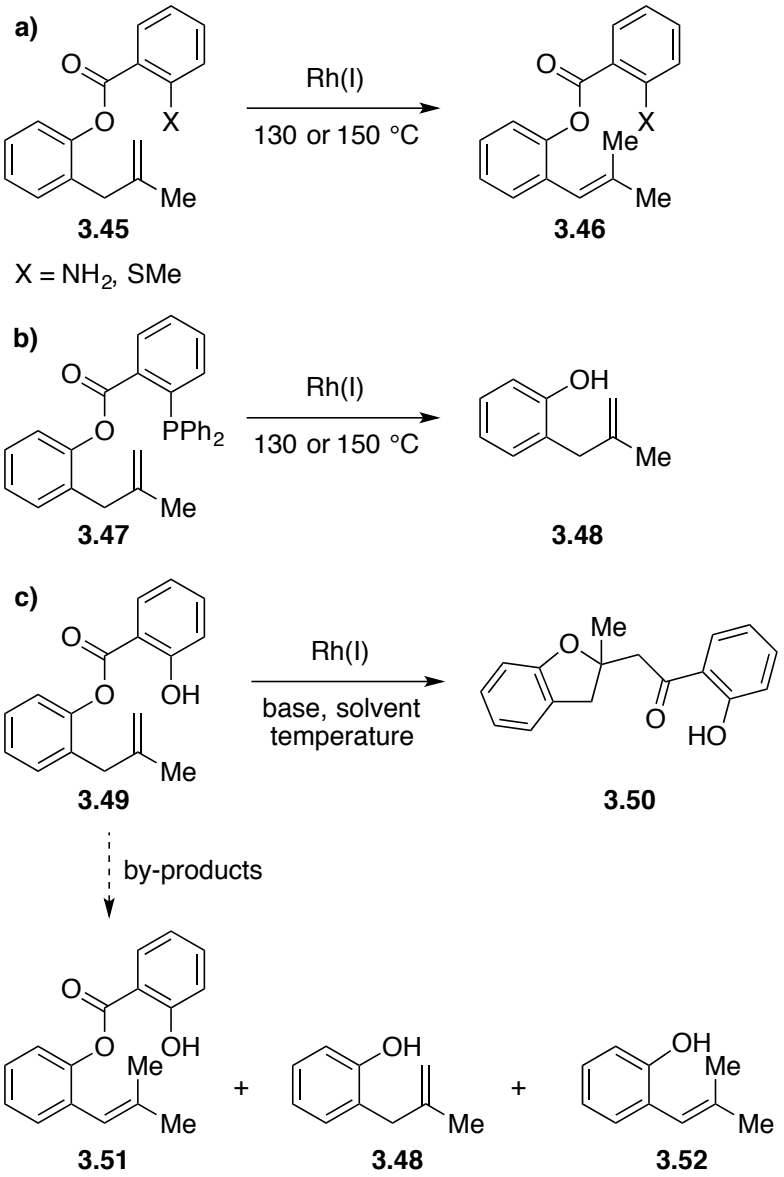
In 2011 Douglas published the first intramolecular oxyacylation of olefins using a quinoline-directed C–O activation to afford cyclized product **3.44** (Scheme 3.9).[78] The mechanism of this reaction and an expanded substrate scope were reported in a subsequent publication.[80] This chemistry is limited by the inability to remove the quinoline directing group after completion of the reaction. The current limitation of not being able to remove the quinoline directing group led us to investigate other directing groups.



Scheme 3.9. Mechanistic hypothesis for intramolecular alkene oxyacylation.

3.2.2.2.4 Hydroxy Directing Group

With the precedence of other chelation directed C–O activation reactions in mind (*e.g.* quinoline, pyridyl, π-bonds), a few potential directing groups were identified as possible candidates for the development of an oxyacylation reaction using salicylate derivatives (Scheme 3.10a–c). The phenol directing group has been used in many hydroacylation reactions during the last decade, with the first example coming from Miura in 1999.[74,76,77,96-100] When co-workers in the Douglas group attempted oxyacylation with aniline or thioether directing groups **3.45**, double-bond isomerization afforded the more substituted olefin **3.46** as the major product (Scheme 3.10a). The phosphine directing group **3.47** primarily yielded the corresponding phenol **3.48** (Scheme 3.10b).[79]



Scheme 3.10. Directing group screening for rhodium(I)-catalyzed alkene oxyacylation.

The desired oxyacylation reaction was reported in 2014 by Douglas *et al*. using the phenol directing group in **3.49**.[82] However, byproducts **3.48**, **3.51**, and **3.52** deteriorated the yield of the desired **3.50** (Scheme 3.10c). Reaction optimization using higher temperatures with the use of a monodentate phosphine, (*R*)-MOP, an iridium pre-catalyst, and mesitylene as the solvent minimized these products. During the optimization with **3.1**, reactions employing *m*-xylene as the solvent generated product **3.2** along with unprecedented non-

oxyacylation byproducts **3.3** and **3.4** which were subsequently isolated and identified as a mixture of acylated *m*-xylenes (Scheme 3.1). These products likely resulted from the C–H activation of the arene solvent after insertion of the iridium into the C_{acyl}–O bond and subsequent reductive elimination of the biaryl ketones **3.3** and **3.4**. Figure 1.1 shows the crude ^{1}H NMR spectrum of the identified coupled products.[79]

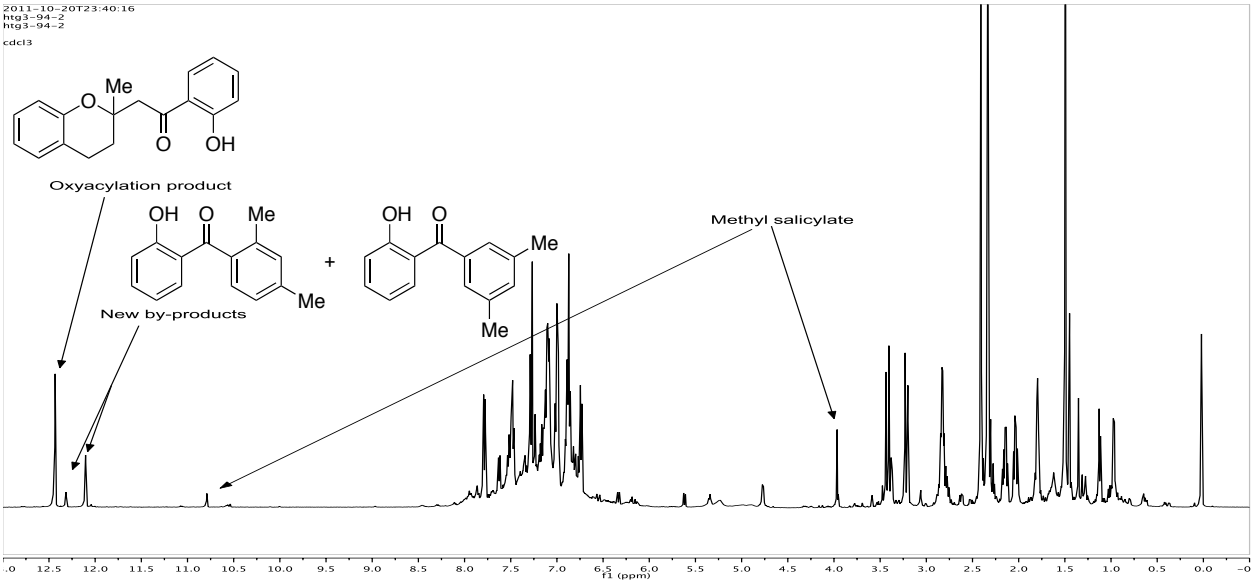
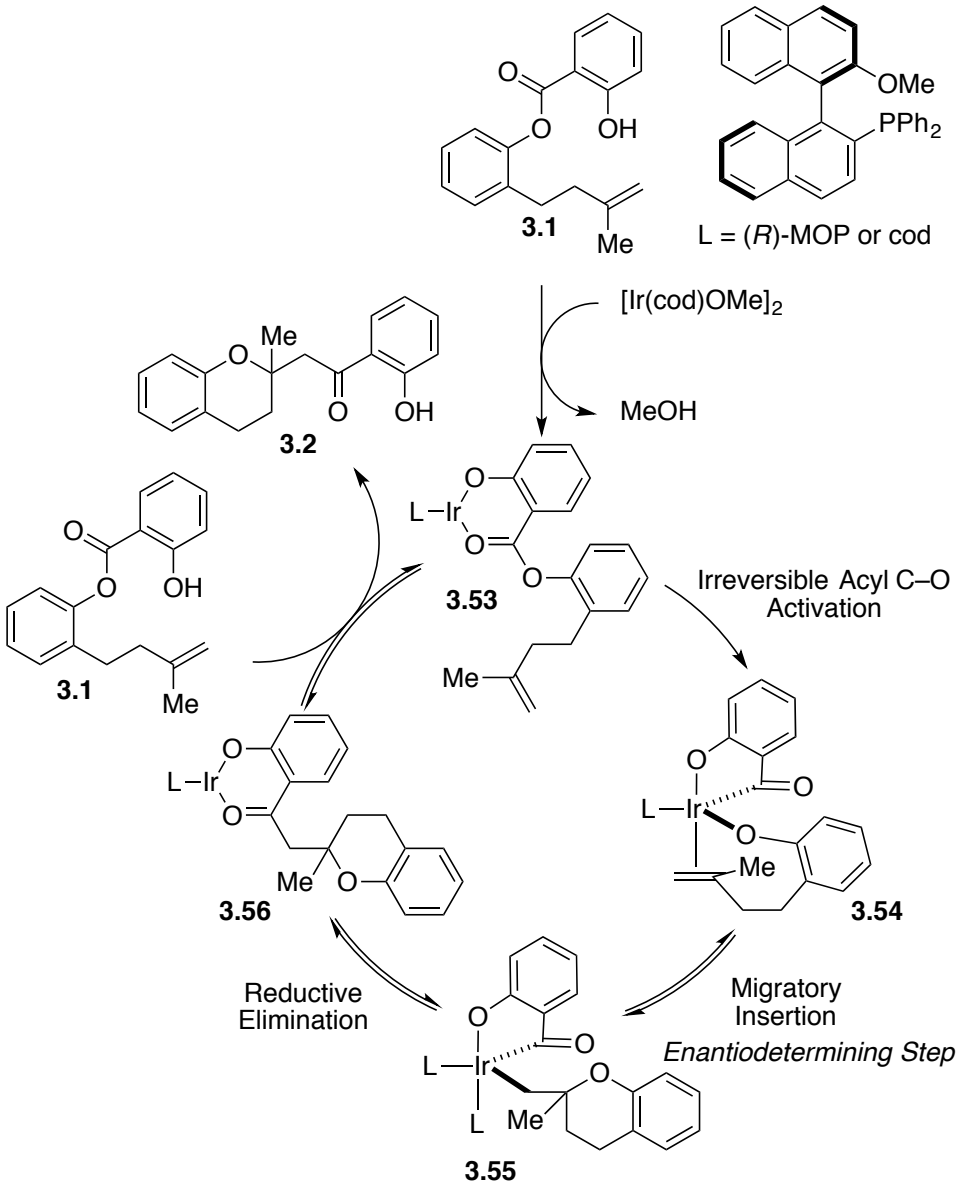


Figure 3.1 ^{1}H NMR spectrum of the alkene oxyacylation reaction mixture derived from phenol **3.1**.

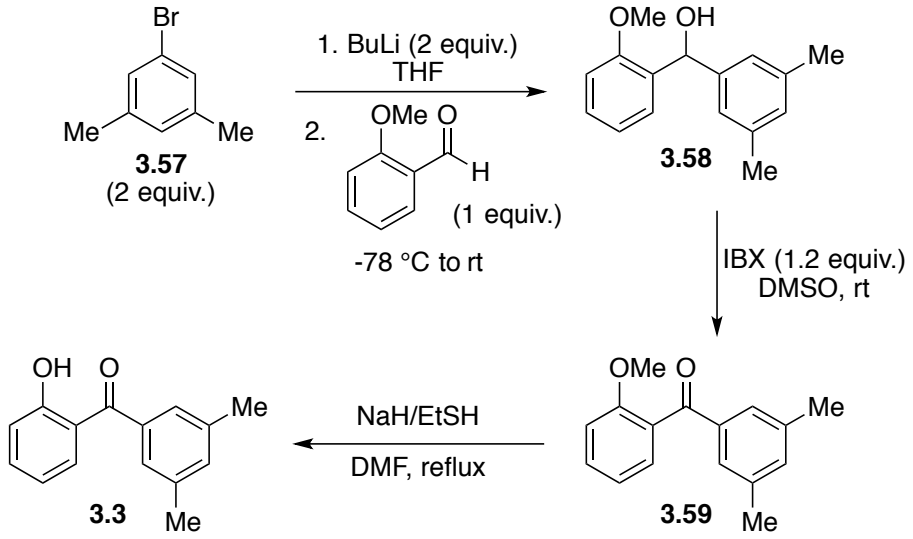
To minimize byproduct formation the reaction was further optimized using mesitylene as the solvent. Attempts at asymmetric induction were unsuccessful using chiral phosphine ligands. Crossover studies showed that the key enantiodetermining step of **3.54** to **3.55** is reversible. Scheme 3.11 shows a hypothesized mechanism for this transformation.[79,82]



Scheme 3.11. Proposed mechanism for phenol-directed alkene oxyacylation of **3.1**.

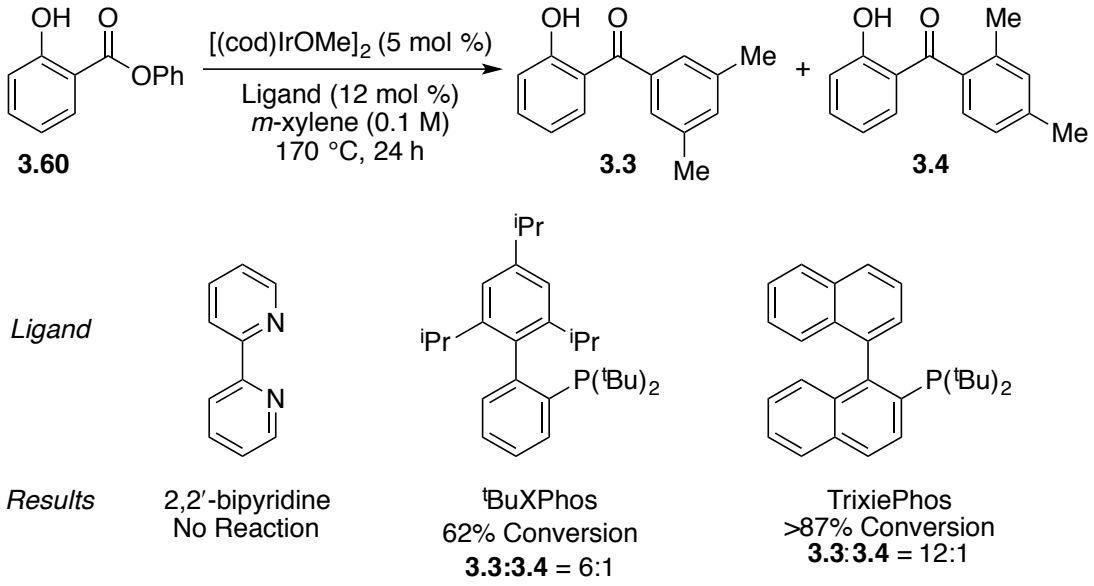
3.3A Serendipitous Discovery: Sequential C–H and C–O Activation

The proposed byproducts of the oxyacylation reaction were confirmed by independent synthesis of the major byproduct **3.3**. The synthetic route to **3.3** is outlined in Scheme 3.12.



Scheme 3.12. Independent synthesis of **3.3**.

The reaction was attempted using phenyl salicylate as the substrate, *m*-xylene as the solvent, and the ligand was varied to determine the best conditions for studying this unusual transformation (Scheme 3.13). The bulky *rac*-2-di-*t*-butylphosphino-1,1′-binaphthyl (TrixiePhos) catalyzed the reaction nearly to completion with high selectivity for the 1,3,5-trisubstituted ketone **3.3**. This reaction is novel because the iridium catalyst not only activates the C_{acyl}–O bond, it also activates the C_{aryl}–H bond with high steric control. This steric control is indicative of a C–H activation mechanism similar to aryl C–H borylation and silylation chemistry that is the subject of Chapter 4.[79]



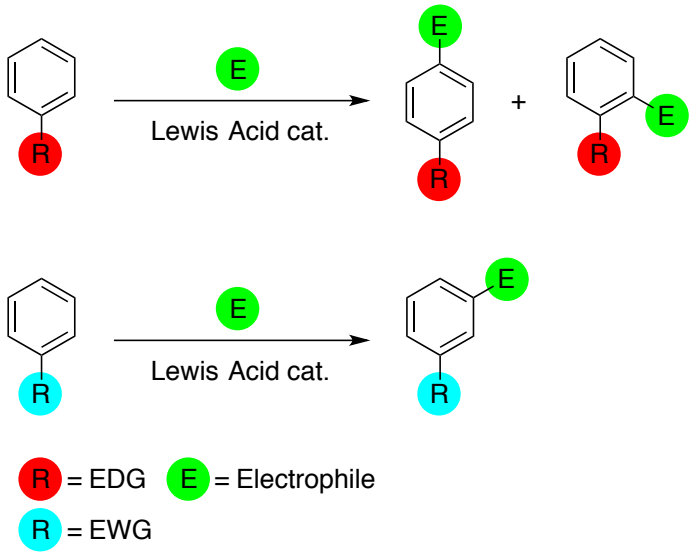
Scheme 3.13. Ligand screening for sequential C–H and C–O activation reaction.

CHAPTER 4: METAL-CATALYZED, STERICS-CONTROLLED C–H BOND ACTIVATION METHODOLOGIES

4.1 Electrophilic Aromatic Substitution

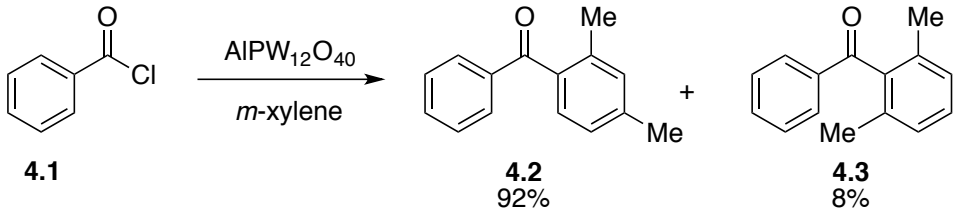
One reason the reaction of phenyl salicylate with *m*-xylene is of interest is because of the preferential formation of the new C_{acyl}–C_{aryl} bond at the most sterically accessible site on the aryl ring; not the most electron rich site. C_{aryl}–H activation reactions that show preferential steric control are mechanistically distinct from reactions that are under electronic control (such as electrophilic aromatic substitution, EAS) and thus should be presented as such. To elaborate on this concept, the following chapter will focus on various mechanistically distinct forms of C_{aryl}–H functionalization (EAS) and activation. A distinction will also be drawn between formal oxidative addition C_{aryl}–H activation mechanisms and 1,2-addition mechanisms.

The direct functionalization of aryl C–H bonds to form new C–C bonds has been a topic of extensive research for much of the past century and continues to be an area for fruitful discovery.[101-105] Traditional methods for forming new C–C bonds from unfunctionalized arenes includes Friedel-Crafts alkylation and acylation. The substituents on the arene starting material in an EAS reaction are known to have a large effect on the substitution of the products formed. Electron-donating groups (EDGs) promote ortho- and para-substitution on the arene product relative to the position of the EDG and electron-withdrawing groups (EWGs) promote meta-substitution in the product (Scheme 4.1).[106]



Scheme 4.1 Electrophilic aromatic substitution.

The mechanism of the EAS reaction helps to explain the observed selectivity with respect to the electron-donating/withdrawing effects of the substituent on the aryl starting material. The stabilization of the tetrahedral arenium cation intermediate by the substituents on the aromatic ring is the major-contributing factor to the observed selectivity. In these mechanisms, the Lewis acid is traditionally a metal that does not undergo redox chemistry during the transformation and is used to increase the electrophilicity of the electrophile. Precedence for the acylation of *m*-xylene using benzoyl chloride (**4.1**) showed that high selectivity was observed for formation of the 1,2,4-product **4.2** with minor amounts of 1,2,6-substituted product **4.3** (Scheme 4.2).[107] This represents a large contrast between the results observed for a reaction proceeding under a Friedel-Crafts mechanism and the C–H activation observed by Douglas.



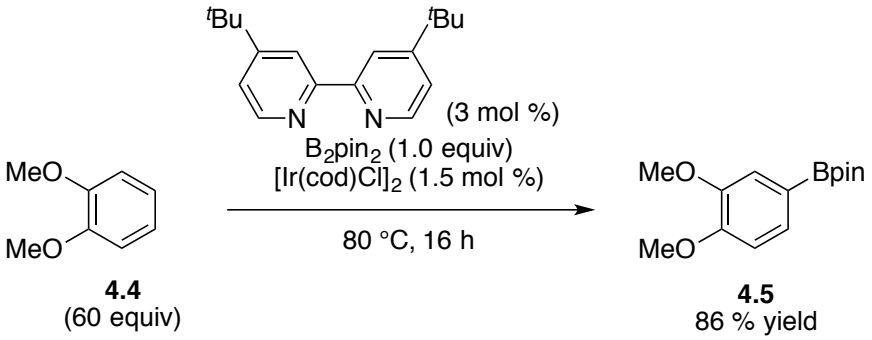
Scheme 4.2. Friedel-Crafts Acylation of *m*-xylene.

4.2 Aryl C–H Activation by Oxidative Addition Mechanism

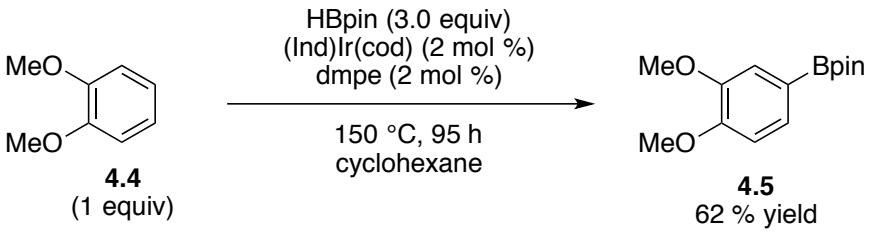
4.2.1 Seminal Reports of Aryl C–H Borylation

In 2002 Hartwig published a method for the direct borylation of an C_{aryl}–H bond using $[(cod)IrCl]_2$, 4,4'-di-*tert*–butyl-2,2'-bipyridine (dtbpy), and B_2pin_2.[108] Concurrently, Smith and Maleczka published a similar result using (ind)Ir(cod), one of the bidentate phosphine ligands (1,2-bis(diphenylphosphino)ethane (dppe) or 1,2-bis(dimethylphosphino)ethane (dmpe)), and HBpin to perform a similar borylation of a C_{aryl}–H bond (Scheme 4.3).[109]

Hartwig



Maleczka and Smith



Scheme 4.3. Sterics controlled C–H borylation.

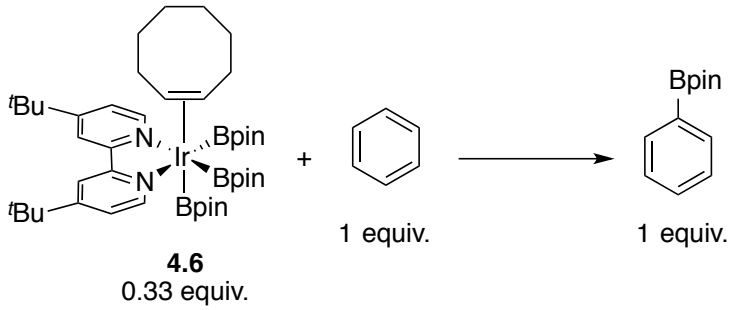
These systems are unique in that they provide direct access to borylated precursors, which see utility in C–C bond forming reactions like Suzuki cross-coupling reactions, with high selectivity for borylation at the most sterically accessible site. This is substantially different from a traditional EAS

transformation in that the selectivity is governed by steric and not electronic factors.

4.2.2 Aryl C–H Borylation Optimization and Mechanism

Hartwig subsequently reported an "improved" borylation system that was also studied mechanistically. Many of the methods performed in studying the mechanism of the borylation reaction could also be useful in studying the tandem C–O/C–H activation reaction presented in Chapter 1. Thus a thorough synopsis of Hartwig's findings will be presented in this section.

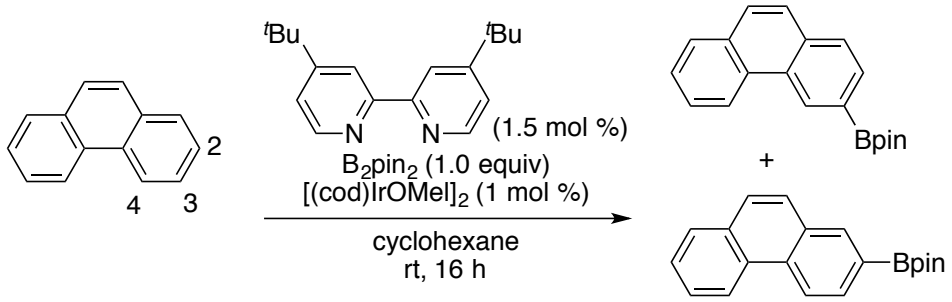
Hartwig and coworkers were later successful in lowering the concentration of the reaction from neat to 0.33 M arene in hexanes and at room temperature using an $[Ir(cod)OMe]_2$ catalyst and dtbpy as the ligand.[110] By preparing the (dtbpy)Ir(coe)$(Bpin)_3$ complex **4.6** in Scheme 4.4, the authors were able to react **4.6** with stoichiometric benzene and found that the complex formed one equivalent of PhBpin. This result led the authors to conclude that the trisboryl complex **4.6** was a competent species in the catalytic cycle and could be used to obtain kinetic isotope (KIE) data for the competition reaction between C_6H_6 and C_6D_6. The observed stoichiometric KIE of 4.6 ± 0.4 (consistent with the KIE observed for the competition reaction under catalytic conditions, 5.0 ± 0.4) led the authors to conclude that C–H bond cleavage was rate-limiting (Scheme 4.4).[111]



Scheme 4.4. Stoichiometric reaction of **4.6** with benzene.

Other observations included inverse dependence on cyclooctene (COE), iridium(I) complexes being inactive towards C–H activation, and an unusual electronic effect with respect to the arene where electron-rich phenyl-based arenes reacted slower than electron-poor phenyl-based arenes in a same-pot competition reaction. However, electron-rich heterocycles (furan and thiophene) reacted faster than electron-neutral phenyl-based arenes. The authors explained this unusual behavior: the arene that can form the more stable η^2-arene intermediate prior to oxidative addition is the faster reacting species.

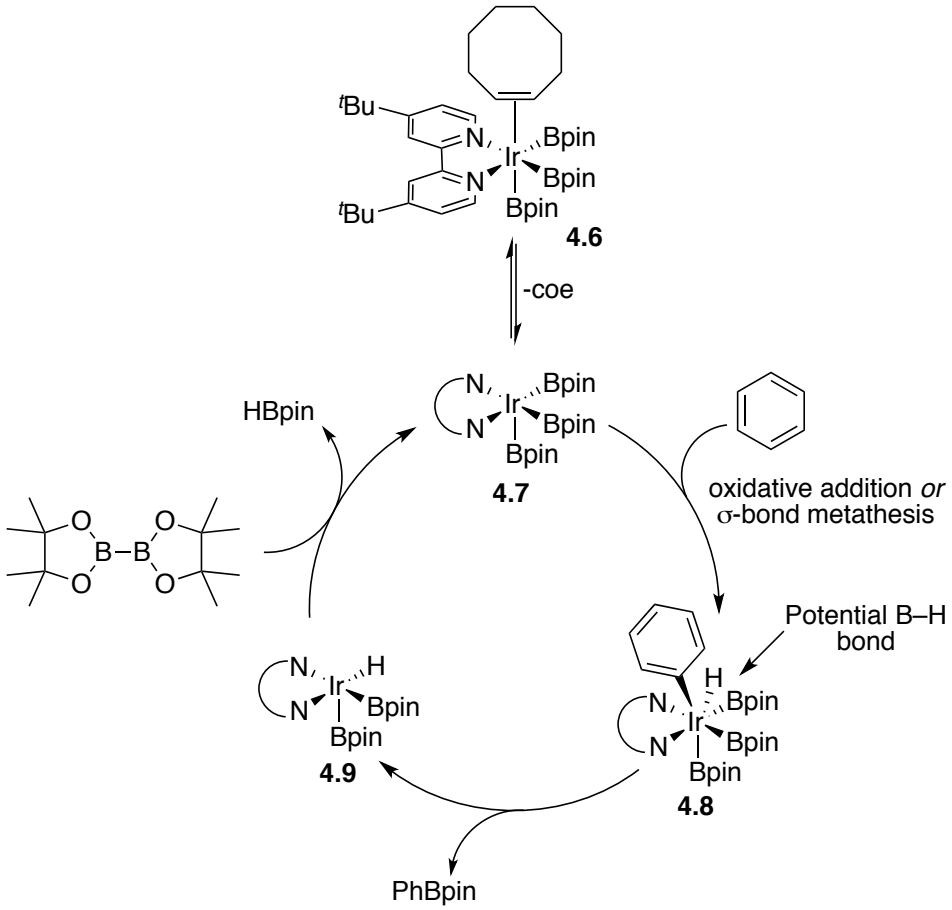
When trying to probe if the stability of the η^2-complex can override the inherent selectivity for activating the least-sterically hindered site, the authors found that sterics still governed the regioselectivity in the case of phenanthrene, where the 2- and 3-position were the sites that were activated and not the 4-position (Scheme 4.5).



Scheme 4.5. Borylation of phenanthrene.

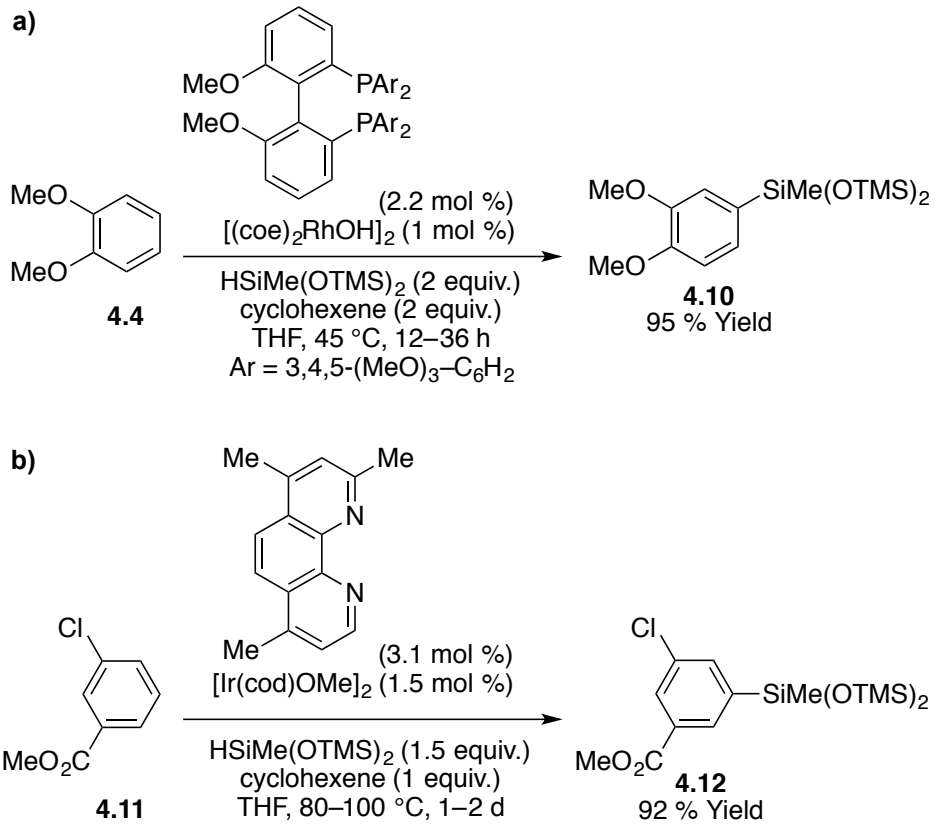
Based on these observations, Hartwig and co-workers proposed the mechanism in Scheme 4.6. The authors note that they do not have a means for studying whether a σ-bond metathesis mechanism is at play for C–H activation, or if the iridium is formally undergoing oxidative addition into the aryl C–H bond and forming an iridium(V) intermediate **4.8**. Computational models support the formation of a formal iridium(V) intermediate over a σ-bond metathesis mechanism.[111] These mechanistic details are important to the chemistry that we observe in that they have been used to inform our way of thinking about the C–H

activation step in our cycle. Also, the C–H borylation chemistry developed by Hartwig has high functional group tolerance that we hope to be able to achieve.



Scheme 4.6. Mechanism for iridium-catalyzed C–H borylation.

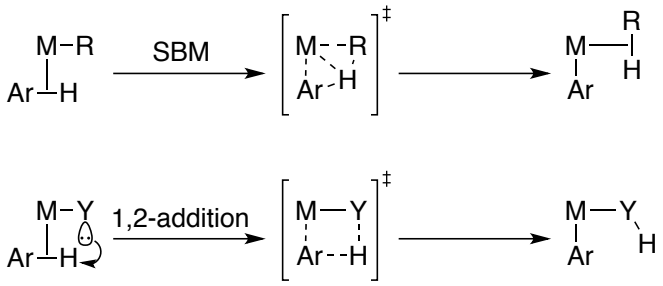
More recently Hartwig published a method for the direct silylation of arenes with high steric regiocontrol using a rhodium catalyst (Scheme 4.7a)[112] and an iridium catalyst (Scheme 4.7b).[113] The mechanism for the rhodium-catalyzed silylation reaction was also reported in a follow-up publication.[114]



Scheme 4.7. Aryl C–H silylation with high steric regiocontrol.

4.3 Aryl C–H Activation by 1,2-Addition Mechanisms

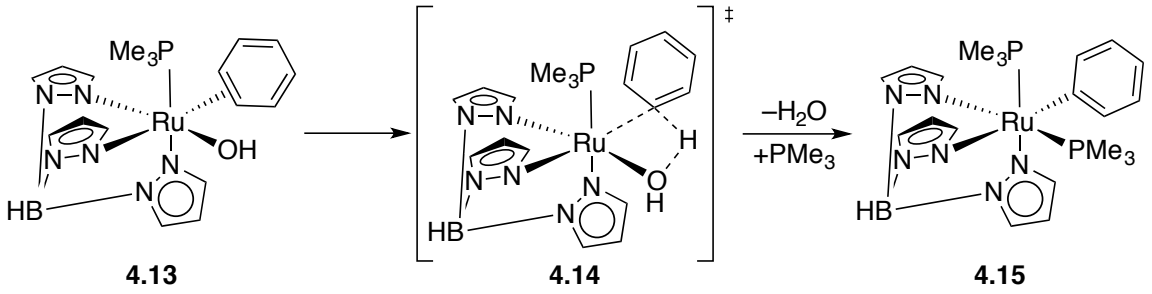
A review published by Gunnoe made a strong case for drawing a distinction between a σ-bond metathesis (SBM) mechanism and a mechanism referred to as a 1,2-addition of a C–H bond across a M–Y bond where Y is an anionic (X-type) ligand (*e.g.*, imido, amido, alcoxide, hydroxide, *etc.*).[115] The 1,2-addition mechanism is also referred to as concerted metallation deprotonation (CMD). In a SBM mechanism, the overall transformation contains a 4-centered, 4-electron transition state. In 1,2-addition across an M–Y bond, there are still 4 atoms in the transition state, however the lone-pair on the Y-atom can facilitate what is essentially an overall deprotonation of the C–H σ-adduct (Scheme 4.8).



Scheme 4.8. σ-bond metathesis vs. 1,2-addition mechanisms.

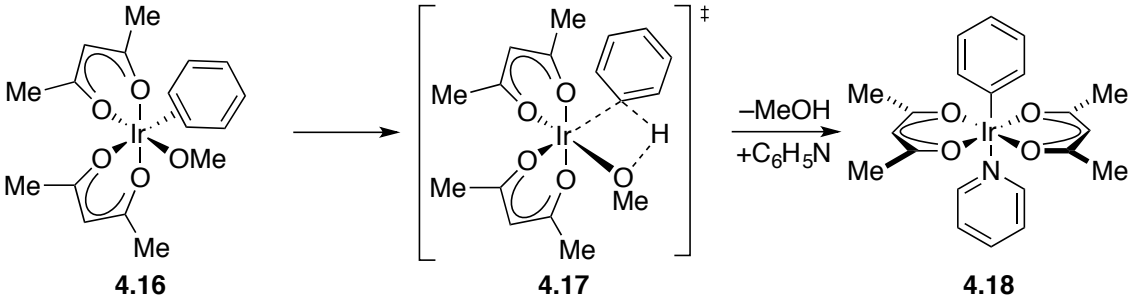
This type of mechanism is highlighted by Gunnoe in the case of the ruthenium(II)–hydroxide complex **4.13** and Periana with the iridium(III)–methoxide complex **4.16** (Scheme 4.9). Computational studies found that complexes **4.13** and **4.16** proceed through transition state structures **4.14** and **4.17**, respectively, which utilize the lone pair electrons on the oxygen atom to deprotonate the C_{aryl}–H bond. Loss of H_2O and methanol followed by subsequent coordination of trimethylphospine and pyridine form **4.15** and **4.18**, respectively.[116,117]

Gunnoe



4.13 **4.14** **4.15**

Periana



4.16 **4.17** **4.18**

Scheme 4.9. Observations of 1,2-addition mechanisms.

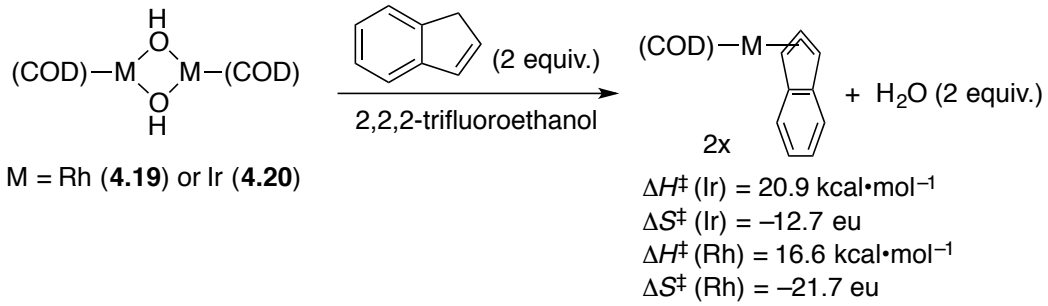
According to Gunnoe, 1,2-addition C–H activations have certain advantages over a SBM mechanism for mid to late transition metals. For SBM to occur, the orientation of the M–R σ-bond has to completely change directionality to engage in the transfer of the hydrogen from the aryl group to the R-group (Scheme 4.8). Also, the Ar–H bond must also change its directionality towards the metal in order to form the new M–Ar bond. In the case of 1,2-addition, the lone pair on the Y-group is already positioned such that the directionality of the M–Y bond does not need to change. This leads (in many cases) to lower kinetic barriers for 1,2-addition when compared to SBM mechanisms for late transition metals.[115]

Gunnoe describe common trends that are observed for complexes that undergo 1,2-addition. Typically, transition metals with low oxidation states (i.e. electron-rich metals) are observed to undergo more facile 1,2-addition than high

oxidation-state metals. This is likely due to the amount of back-bonding occurring between the metal and the Y-group with the basic lone-pair of electrons that are deprotonating the σ-adduct. Many complexes are also coordinately saturated when they form the σ-adduct with the molecule undergoing C–H bond cleavage; this makes oxidative addition pathways unlikely. Gunnoe states that an *a priori* prediction for the thermodynamic and kinetic barriers for 1,2-addition is not possible due to the changes in the bonding energies during the course of the reaction. In many cases an M–Y, X-type bond is sacrificed for the formation of an L-type bond. Also, the π-back-bonding ability of the Y-group is often greatly diminished (or lost with amino L-type ligands), which is energetically unfavorable. The strength of the newly formed M–Ar bond is also important in that stronger M–Ar bonds will lower the energy of the complex, and often times, lower the transition state of the bond-forming event.[115,118]

To illustrate the difficulty of predicting the barriers to activation for 1,2-addition reactions, Bercaw and co-workers have reported on the activation of the indenyl C–H bond by complexes of the type $[(cod)M(\mu\text{-}OH)]_2$ where M = rhodium (**4.19**) or iridium (**4.20**) (Scheme 4.10). Based on the general trend that 3rd row transition metals (TMs) usually form stronger M–C bonds than 2nd row TMs, one would predict the iridium–indenyl bond to be stronger than the rhodium–indenyl bond (Scheme 4.10). This reasoning would lead to the conclusion that $\Delta H^{\ddagger}$ would be lower for iridium than for rhodium (based on the assumption that there is significant M–indenyl bond character in the transition state of the rate-limiting step). However, the iridium–OH BDE is also expected to be higher than that of the rhodium–OH bond, this would lead to the conclusion that the iridium $\Delta H^{\ddagger}$ would be higher than the analogous rhodium complex (this time under the assumption there is significant M–OH bond character in the transition state of the rate-limiting step). In this particular system, the $\Delta H^{\ddagger}$ for iridium is actually higher than the analogous rhodium complex.[119,120]

Bercaw

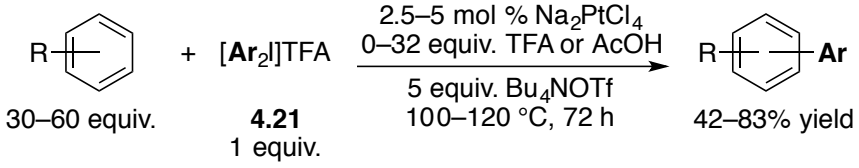


Scheme 4.10. C–H activation of indene by [(cod)M(μ-OH)]$_2$ complexes.

4.4 Direct C–C Bond Formation via Sterics Controlled C–H Activation

A search for reactions that undergo direct C_{aryl}–C bond formation via sterics controlled C_{aryl}–H activation was performed to highlight the novelty of the tandem C_{acyl}–O/C_{aryl}–H activation reaction being investigated. Four papers of note were found from that search.

Oxidative biaryl formation via C–H activation was the most common form of direct C–C bond formation found.[101,104] A common characteristic of these reactions is the use of d^{10}-metals; palladium is particularly prevalent in this literature.[75,121] Another characteristic is the use of strong, stoichiometric oxidants to achieve catalytic reactivity.[75,121]

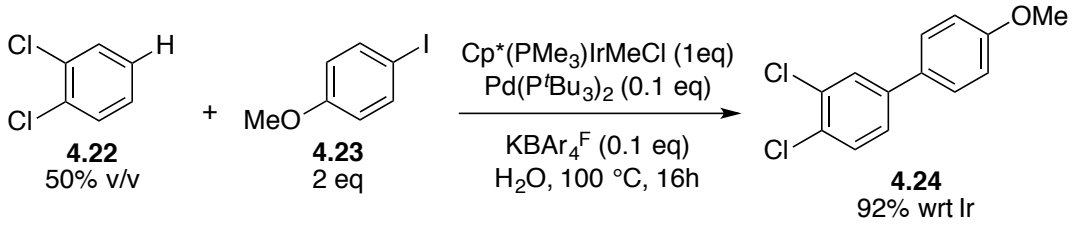


Scheme 4.11. Platinum-catalyzed C–H arylation of simple arenes.

Sanford reported an example that did not formally use a stoichiometric oxidant; rather the substrate was already oxidized as a hypervalent iodine compound **4.21** (Scheme 4.11). The reaction was a sterics controlled C–H arylation using a platinum(II) catalyst that is coupled with an arene that undergoes C–H activation. The pre-functionalized hypervalent iodine source

allows the chemistry to occur without the need for an added stoichiometric oxidant.[122]

Though there is a large amount of literature for the formation of new C–C bonds via C–H activation using rhodium complexes, none of the reported reactions occur via steric control.[103] The only use of a group 9 TM for the direct formation of a C–C bond via C–H activation of an arene was from the Lewis group using stoichiometric Cp*(PMe_3)IrMeCl and catalytic palladium for the coupling of **4.22** with **4.23** to form biaryl **4.24** (Scheme 4.12). Though this reaction is stoichiometric in iridium, it highlights steric regiocontrol for C–C bond formation.[123]



Scheme 4.12. Direct C–C bond formation via C–H activation using stoichiometric iridium.

CHAPTER 5: OVERCOMING ELECTRONIC CONTROL IN ARENE ACYLATION USING IRIDIUM-CATALYZED BOND FUNCTIONALIZATION

5.1 Introduction

Chapter 3 introduced the investigation of oxyacylation and the discovery of the sequential C–O, C–H activation reaction for the synthesis of 2-hydroxybenzophenones with steric-control. The reaction was then compared to Friedel-Crafts acylation in Chapter 4 which proceeds with high electronic control.

Typically, acylating arenes contrary to electronic-controlled selectivity challenges chemists.

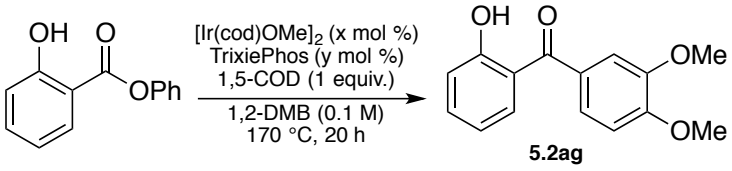
Acylation of arenes under steric-control is synthetically possible but typically requires multiple steps and precious metal catalysts. The functionalization of arenes using steric-controlled C–H borylation can make a highly useful C–B bond.[108,110] Boryl group manipulation and Suzuki-Miyaura cross coupling would affect a steric-controlled acylation.[124,125] However, to the best of our knowledge there has not been a steric-selective C–H acylation of arenes with a single metal catalyst.

5.2 Results and Discussion

5.2.1 Reaction Optimization

We began our study of this reaction by optimizing the reaction conditions based on the results from oxyacylation.

5.2.1.1 Control Experiments



5.2ag

Table 5.1. Control Experiments

Entry	[Ir] (mol %)	TrixiePhos (mol %)	Yield 5.2ag (%) (^{1}H NMR)
1	0	3	0
2	1	0	24
3	0	0	0

The reaction was attempted without the iridium catalyst, the phosphine ligand, and without both the iridium catalyst and the phosphine ligand (Table 5.1).

In both cases where iridium was eliminated, no conversion to product **5.2ag** was observed (Table 5.1 entries 1 & 3). With only phosphine eliminated from the reaction, the reaction proceeded to 24% conversion to **5.2ag**. These results suggest that iridium is required for the reaction to proceed but phosphine is not. However, phosphine is required for high catalyst turnover.

5.2.1.2 Catalyst and Ligand Optimization

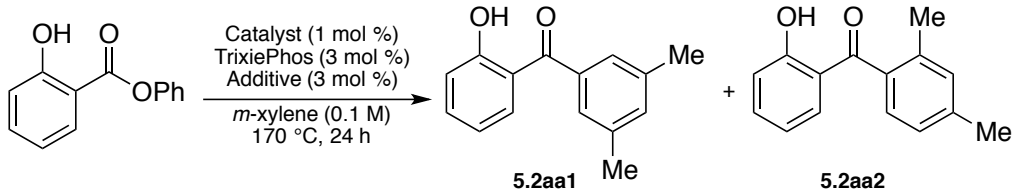


Table 5.2. Effect of Catalyst Choice on the Product Yield

Entry	Catalyst	Additive	Yield 5.2aa1 (%) (^{1}H NMR)
1	$[Ir(cod)OPh]_2$	–	81
2	$[Ir(cod)Cl]_2$	KOPh	44
3	$[Ir(cod)Cl]_2$	K_2CO_3	3
4	$[Ir(coe)_2Cl]_2$	KOPh	49
5	$[Ir(coe)_2Cl]_2$	K_2CO_3	1

$[Ir(cod)OPh]_2$ precatalyst was compared to other precatalyst plus additive combinations to (Table 5.2, entries 2–5). Complexes with 1,5-cyclooctadiene (cod) as the ancillary ligand performed best. However, the $[Ir(cod)OPh]_2$ complex clearly performed best (Table 5.2, entry 1) relative to the other pre-catalyst combinations.

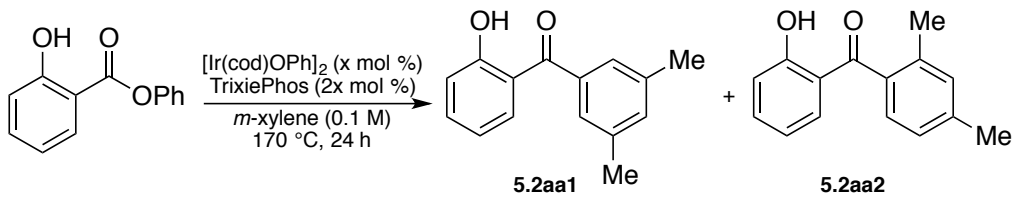


Table 5.3 Catalyst Loading Optimization

Entry	$[Ir]_2$ (mol %)	Yield 5.2aa1 (%) (^{1}H NMR)	Ratio 5.2aa1:5.2aa2

			(^{1}H NMR)
1	0.5	49	>20:1
2	1	70	18:1
3	2.5	69	15:1
4	5	60	11:1
5	10	43	7:1

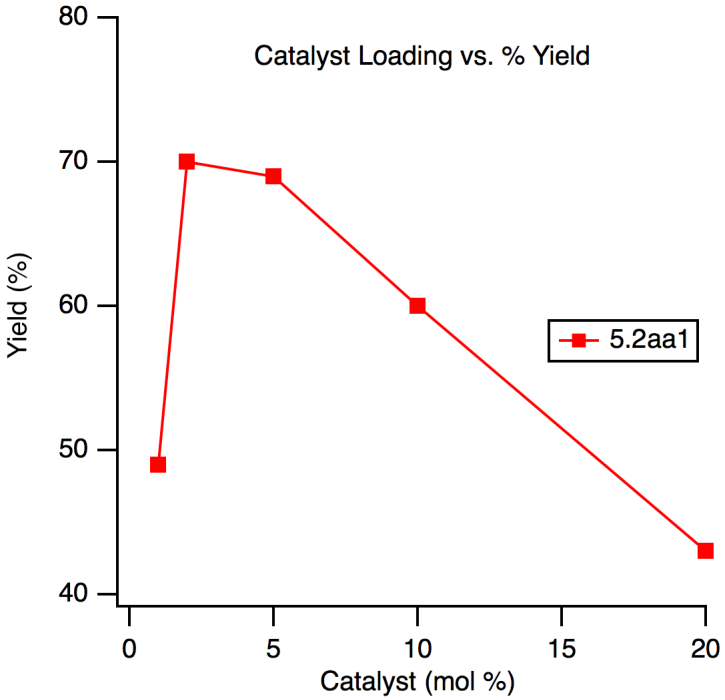


Figure 5.1. Percent yield of **5.2aa1** as a function of catalyst loading.

The best catalyst loading was 1 mol % $[Ir]_2$ based on the catalyst loading optimization (Table 5.3). Interestingly, the conversion to product went down as the catalyst loading went up. The reaction was run for 24 hours so the results indicate that higher catalyst loading inhibits conversion to **5.2aa1** at higher than 1% catalyst loading or higher catalyst loading increases the rate of catalyst decomposition. It was determined that 1% $[Ir]_2$ loading was the optimal loading for this reaction.

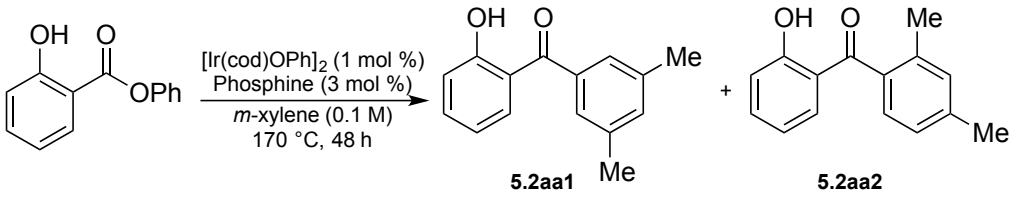


Table 5.4. Phosphine Ligand Optimization

Entry	Phosphine	Yield 5.2aa1 (%) (^{1}H NMR)
1	^{t}Bu-Xphos	44
2	Xphos	6
3	^{t}Bu-BrettPhos	58
4	BrettPhos	4
5	Cy-JohnPhos	8
6	JohnPhos	61
7	^{t}Bu-MePhos	55
8	MePhos	7
9	^{t}Bu-DavePhos	47
10	DavePhos	6
11	RuPhos	11
12	S-Phos	10
13	TrixiePhos	60
14	P(*o*-tol)$_3$	2

Various Buchwald-type ligands were tested along with P(*o*-tol)$_3$. It was found that all phosphines with the general (bi-aryl)P(^{t}Bu)$_2$ formula were active in this reaction. JohnPhos and TrixiePhos were the best phosphine ligands for this reaction. However, because the reactions were only run on a 1 mL scale, the 1% yield difference between the reactions run with JohnPhos and TrixiePhos (Table 5.4, entries 6 & 13) was deemed negligible and we pursued reaction optimization with TrixiePhos as it has a higher molecular weight which aids in the quantitative measurement of the ligand on small scales.

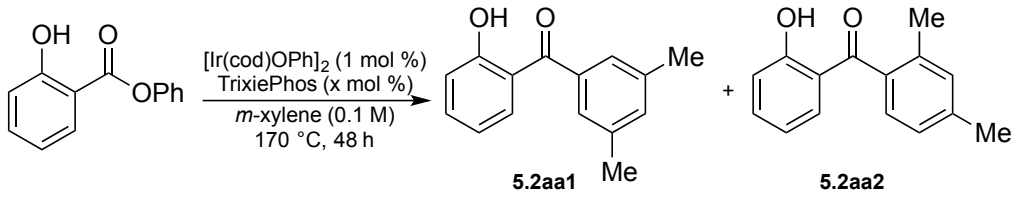


Table 5.5. Phosphine Loading Optimization

Entry	TrixiePhos (mol %)	Yield 5.2aa1 (%) (^{1}H NMR)
1	0.5	29
2	1	50
3	2	75
4	4	78
5	8	53
6	16	23
7	32	15

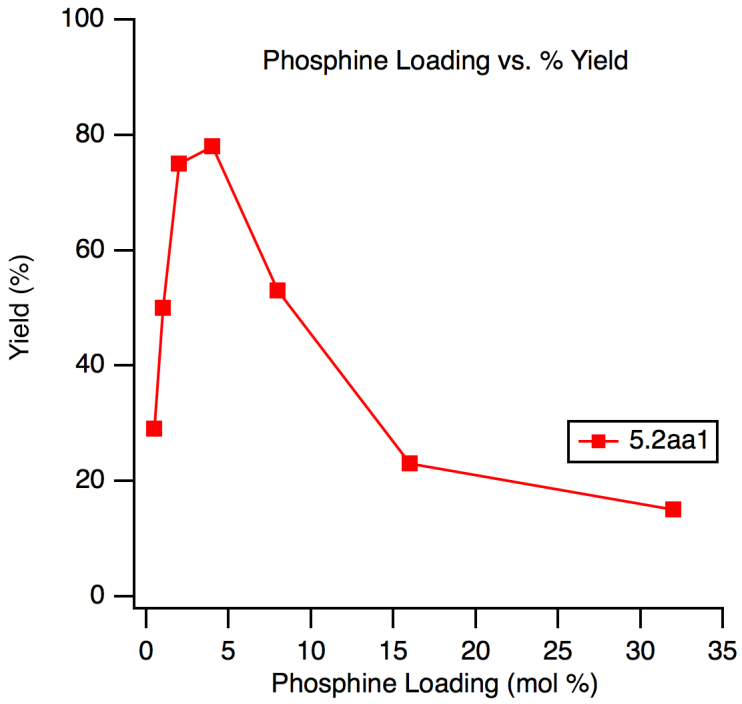


Figure 5.2. Percent yield of **5.2aa1** as a function of phosphine loading.

The optimal phosphine loading was determined to be 3% when the iridium loading was 2% (1% dimer) based on the results of the volcano plot (Figure 5.2).

The results also suggest that increased phosphine loading inhibits the conversion of substrate to **5.2aa1**.

5.2.1.3 Effect of Arene Dilution and Substrate Concentration Optimization

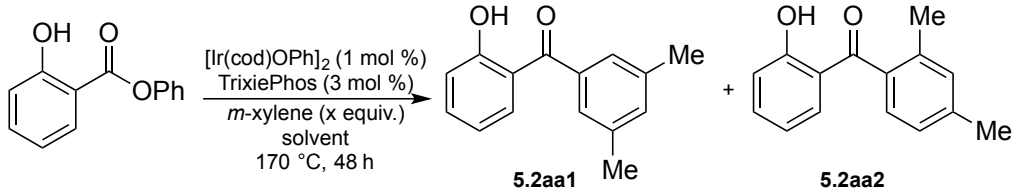


Table 5.6. Effect of Arene Dilution on Product Yield

Entry	*m*-xylene (equiv.)	Additional Solvent	Yield 5.2aa1 (%) (^{1}H NMR)
1	40.5	Decalin	51
2	20.3	Decalin	33
3	8.1	Decalin	13
4	4.0	Decalin	6
5	2.0	Decalin	3
6	40.5	Mesitylene	59
7	20.3	Mesitylene	39
8	8.1	Mesitylene	18
9	4.0	Mesitylene	9
10	2.0	Mesitylene	5

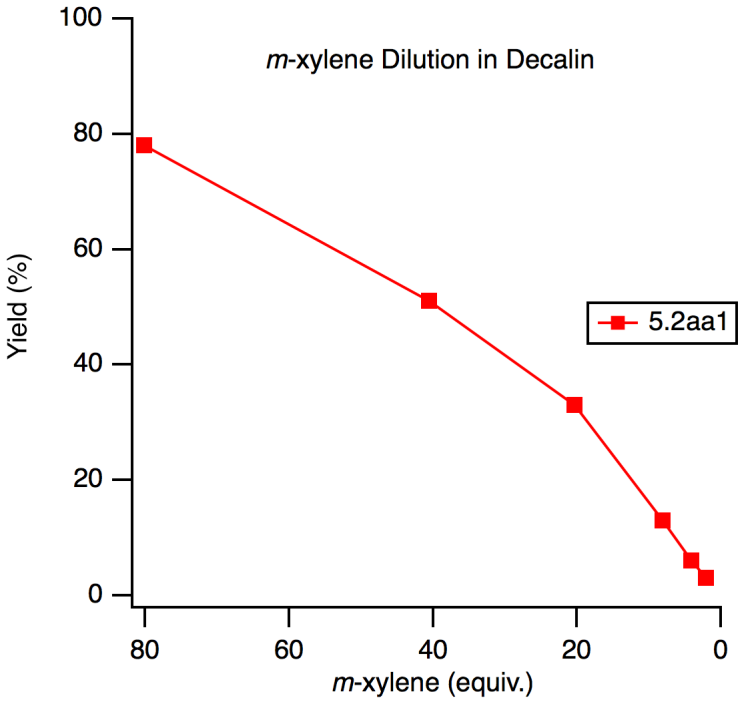


Figure 5.3. Percent yield of **5.2aa1** as a function of *m*-xylene dilution in decalin.

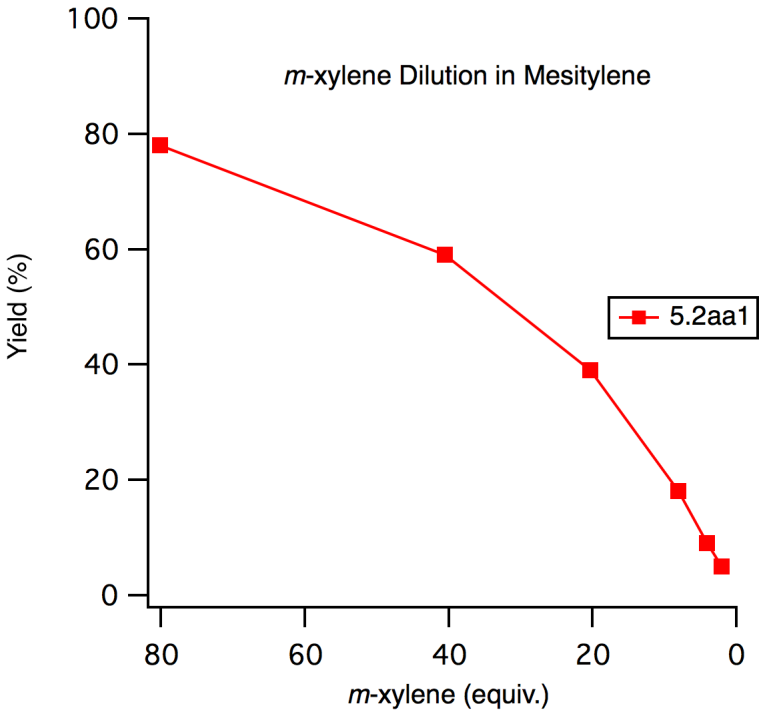


Figure 5.4. Percent yield of **5.2aa1** as a function of *m*-xylene dilution in mesitylene.

Both the reactions of *m*-xylene in decalin (Figure 5.3) and *m*-xylene in mesitylene (Figure 5.4) show that the yield of product **5.2aa1** sharply decreases as the equivalents of *m*-xylene decrease. Although kinetic studies were not performed, these results suggest that the reaction rate is dependent on the concentration of *m*-xylene because the conversion to product decreases while the reaction time remains constant.

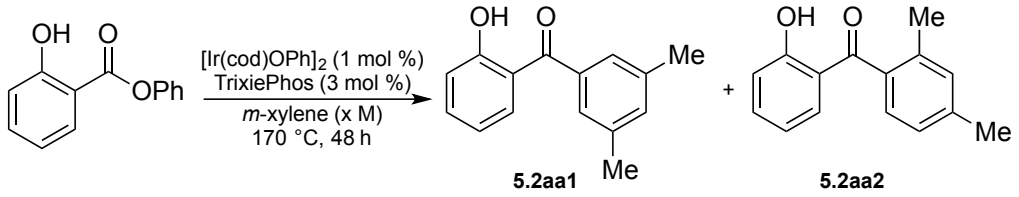


Table 5.7. Effect of Substrate Concentration on Product Yield

Entry	Phenyl salicylate (mmol)	Phenyl Salicylate (M)	Yield 5.2aa1 (%) (^{1}H NMR)
1	0.05	0.05	76
2	0.05	0.07	77
3	0.1	0.10	80
4	0.1	0.14	80
5	0.2	0.20	69
6	0.2	0.29	61
7	0.2	0.40	51

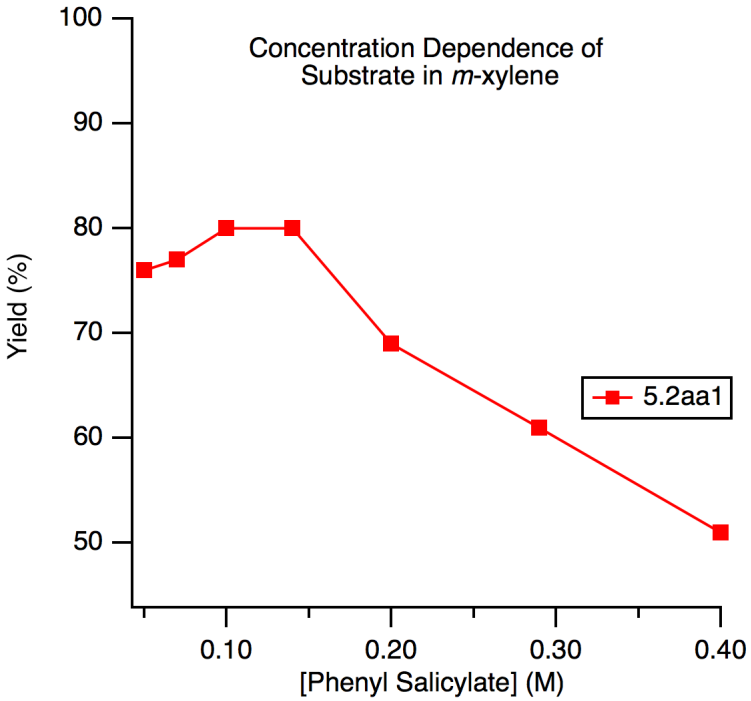


Figure 5.5. Percent yield of **5.2aa1** as a function of phenyl salicylate concentration in *m*-xylene.

Figure 5.5 shows that the yield of **5.2aa1** increases as the concentration of phenyl salicylate increases up to roughly 0.15 M. After the concentration of starting material reaches 0.15 M, the conversion to product **5.2aa1** sharply decreases. This could be due to the effective concentration of *m*-xylene decreasing as the concentration of phenyl salicylate increases. As was shown in the *m*-xylene dilution studies (Figures 5.3 & 5.4), decreasing the concentration of *m*-xylene decreases the conversion of starting material to product.

5.2.1.4 Alkene Additive Screen and 1,5-COD Concentration Optimization

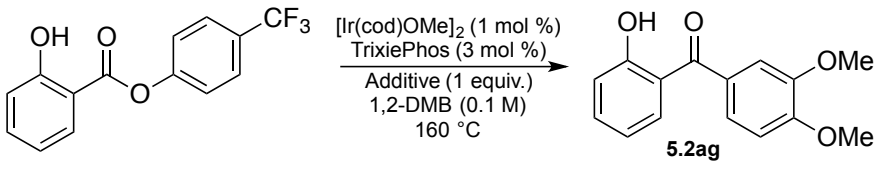


Table 5.8. Alkene Additive Initial Rates Kinetics

Time (min)	Yield 5.2ag (mM) w/ COD	Yield 5.2ag (mM) w/ COE
0	0	0

15	2.8	1.7
30	5.6	3
45	7.9	4.5
60	10.3	6.1
75	12.2	7.6

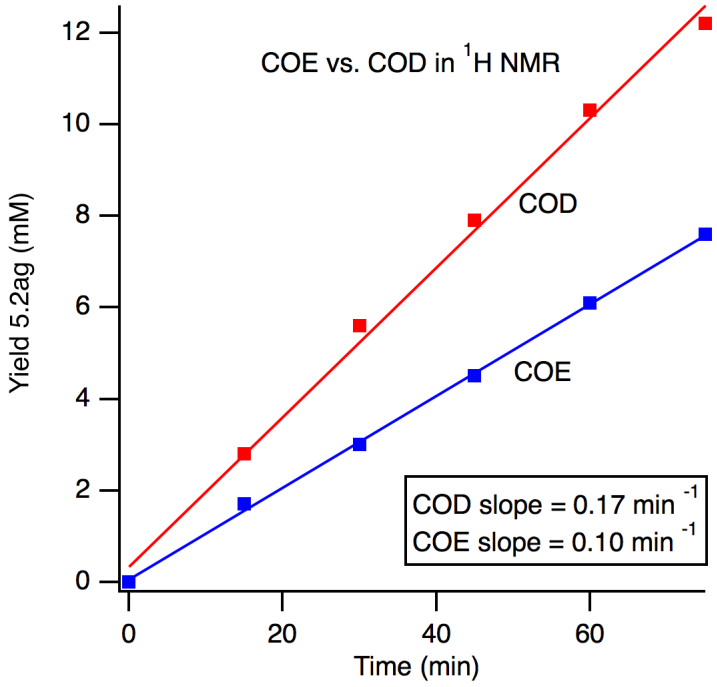
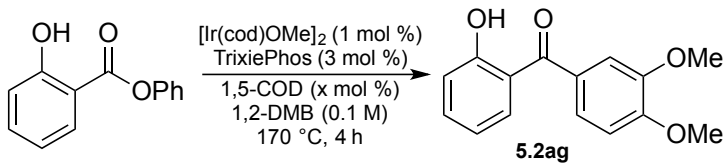


Figure 5.6. Alkene additive effect on the rate of formation of **5.2ag**.

The results of added cod vs coe show that cod is a better ancillary ligand for this reaction in increasing the rate of the reaction. Using norbornadiene as an ancillary ligand yielded almost no conversion to product after 45 minutes (see appendix).



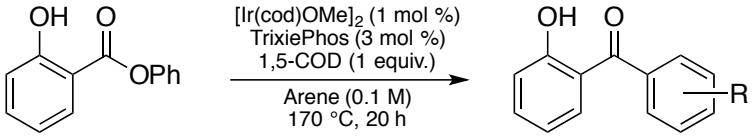
5.2ag

Table 5.9. Effect of 1,5-COD Additive on Product Yield

Entry	COD (μL)	COD (mol %)	Yield 2ag (%) (^{1}H NMR)
1	0	0	39
2	20	2	47
3	40	4	50
4	60	6	53
5	80	8	49
6	120	12	53
7	160	16	59
8	200	20	59
9[1]	12	20	20
10[1]	61	100	27
11[1]	310	500	52

[1] Reactions were run on a 5 mL scale for 2 hours.

Adding cod to the reaction increased the conversion of phenyl salicylate to product **5.2ag** (Table 5.9). Based on the results in Table 5.9, there is no inhibitory effect of added cod. Also, adding cod to the reaction visibly improved the stability of the catalyst and prevented an iridium mirror from forming on the reaction vials.



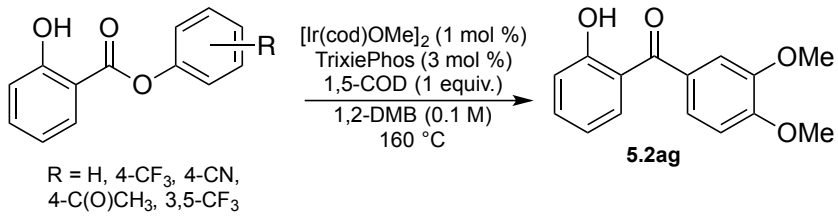
Scheme 5.1. Optimized reaction conditions for acylation of arenes.

With the optimization results in hand, we chose the optimum reaction conditions as illustrated in Scheme 5.1. $[Ir(cod)OMe]_2$ was selected over other pre-catalysts, including $[Ir(cod)OPh]_2$, because it is widely commercially available and has improved solubility. The solubility was an important reason for choosing the methoxide dimer over the phenoxide dimer as the methoxide dimer is much more soluble in aromatic solvents than the phenoxide dimer, enabling the use of stock solutions to reduce measurement error when performing kinetic

experiments. Although, it is important to note that the methoxide from the pre-catalyst does trans-esterify with the phenyl salicylate substrate forming 2 mol % of methyl salicylate, which is inert under our reaction conditions. TrixiePhos was chosen as the optimum ligand with a loading of 3 mol %. 1 equivalent of 1,5-cyclooctadiene (cod) was chosen as the best alkene additive.

5.2.2 Initial Rates Kinetics and Kinetic Isotope Effects

5.2.2.1 Effect of p-substituted Phenolic Leaving Group



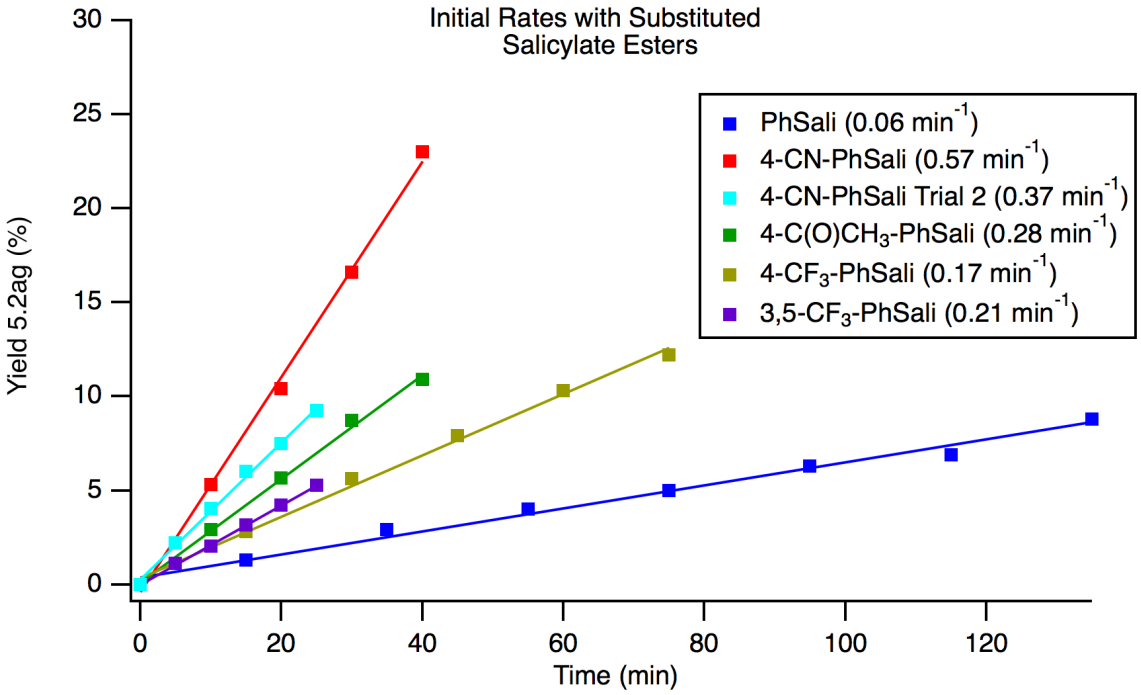
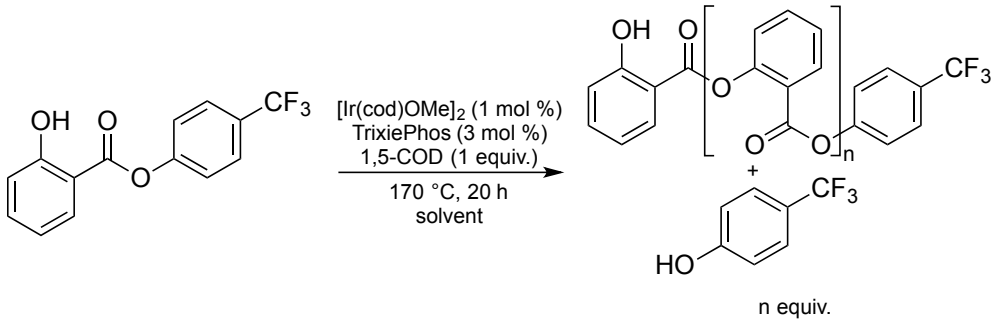


Figure 5.7. Initial rates kinetics of various substituted salicylate esters.

We used substituted salicylate esters with varying substituents to augment the electron density of the phenolic leaving group (Figure 5.7). It was found that

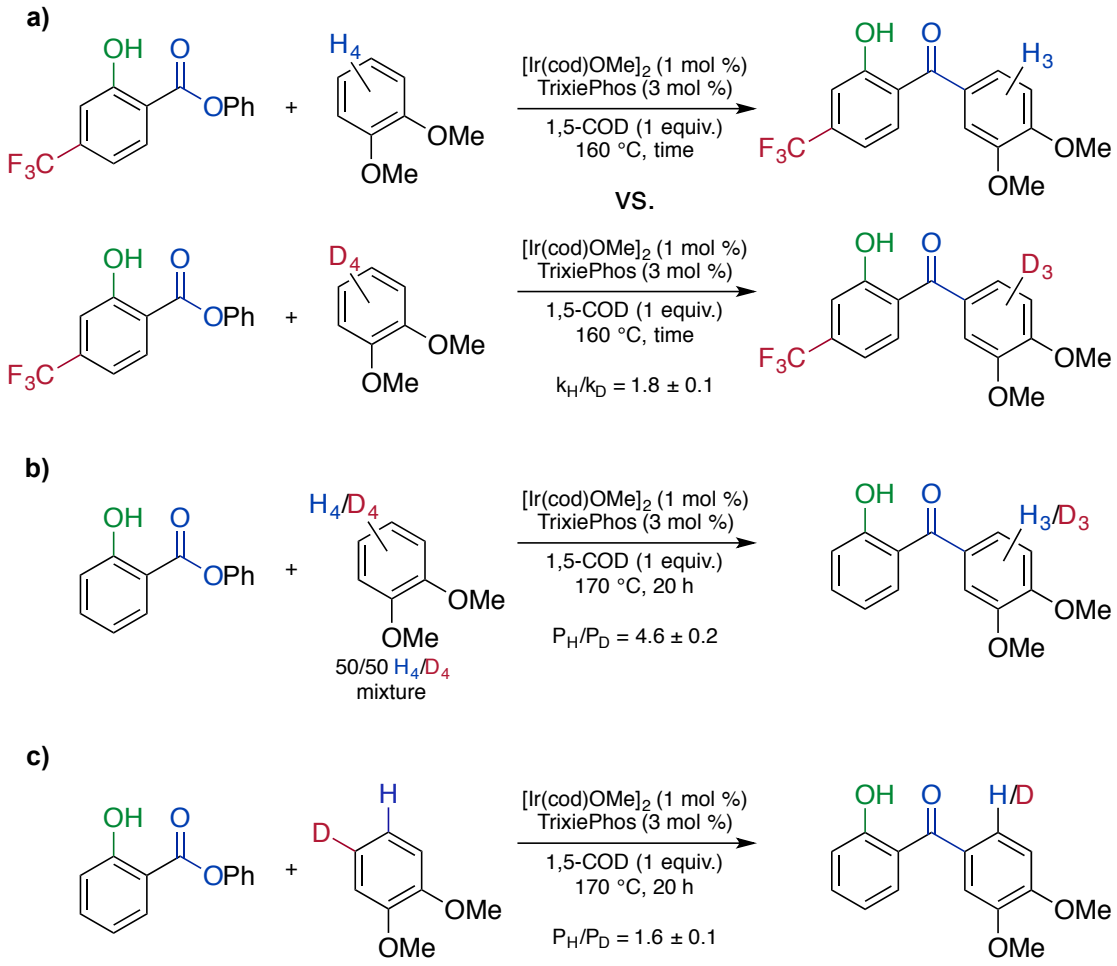
phenol leaving groups with strong electron withdrawing groups formed **5.2ag** more rapidly than base phenyl salicylate. These results suggest that weakening the C–O ester bond by withdrawing electron density from the oxygen increases the rate of the reaction. However, when attempting to perform multiple trials to obtain error bars for a Hammett study, it was found that irreproducibility was a significant issue. This result is illustrated in the two trials using 4-CN–phenyl salicylate (Figure 5.7), the second trial showed a decrease in the rate of the reaction from 0.57% yield per minute to 0.37% yield per minute. An attempt at making a Hammett plot demonstrated that the data was erratic and unable to be used in a Hammett analysis.



Scheme 5.2. Proposed oligomerization of substrate.

While performing the initial rates kinetics experiment with the 4-CF_3–phenyl salicylate, ^{19}F NMR spectra were taken to follow the kinetics with the formation of free 4-CF_3–phenol. Interestingly, it was observed that a large amount of free 4-CF_3–phenol (~25%) forms within the first 15 minutes without concurrent formation of **5.2ag**, which was being monitored in the ^{1}H NMR spectrum. This result suggests that a reaction occurs which forms free phenol but does not form product. We hypothesize that this background reaction is oligomerization of the starting material by trans-esterification as illustrated in Scheme 5.2.

5.2.2.2 Kinetic Isotope Effects



Scheme 5.3. a) Independent rates kinetic isotope effect **b)** Intermolecular competition kinetic isotope effect **c)** Intramolecular competition kinetic isotope effect.

The independent rates KIE experiment resulted in a k_H/k_D of 1.8 (Scheme 5.3a), suggesting that C–H bond cleavage is rate-limiting in this reaction. However, because the magnitude of the KIE is not large, there may not be significant bond breakage in the transition state. The intermolecular competition KIE experiment showed a P_H/P_D of 4.6 (Scheme 5.3b), suggesting that the 1,2-dimethoxybenzene solvent can reversibly associate to the iridium such that the weaker C–H bond is selected over the stronger C–D bond. The intramolecular competition KIE experiment resulted in a P_H/P_D of 1.6 (Scheme 5.3c), suggesting

that upon solvent coordination to the iridium to form a σ-complex, the metal can slip between the bonds and select the weaker C–H bond over the C–D bond.

5.2.3 Role of Phosphine and Iridium Decomposition Pathway

We found that having phosphine present was necessary for the reaction to proceed to high conversions. This result was initially rationalized by proposing that the phosphine underwent a modification (either functionalization or oxidation) under the reaction conditions. Isolation of the ligand after the reaction showed that the ligand was unchanged during the reaction. Running the reaction with 3 mol % of oxidized TrixiePhos gave similar results as to the reaction without any ligand, thus we believe that the ligand is neither oxidized or functionalized under the reaction conditions.

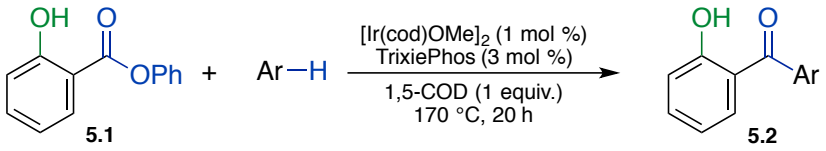
A time-course experiment was performed collecting ^{31}P NMR spectra at various points in the catalytic reaction, in an attempt to observe an iridium-phosphine complex (see appendix for spectra). However, the intensity of the ^{31}P signal for TrixiePhos decreased over the course of the reaction. We hypothesize that the signal erosion is due to the formation of an intermediate on the catalytic cycle that is under a dynamic equilibrium, broadening the new signal.

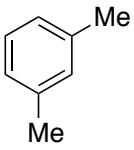
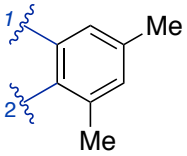
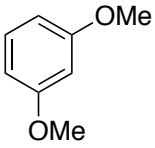
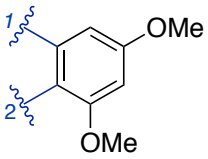
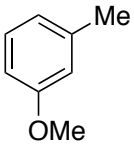
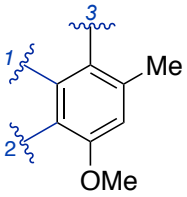
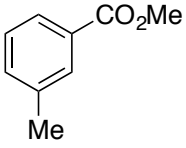
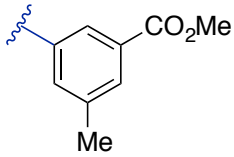
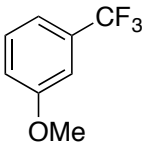
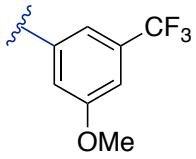
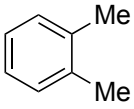
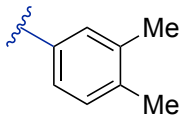
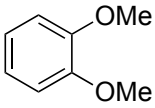
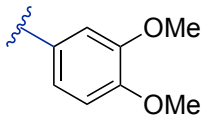
The requirement of additional phosphine for high catalyst turnover led us to search for a possible iridium decomposition product. Decarbonylation is a common decomposition pathway for metal-catalyzed C–O activation reactions.[81] We hypothesized that decarbonylation could be a decomposition pathway for our reaction. We ran a reaction in mesitylene with 10 mol % $[Ir(cod)OMe]_2$ to increase the concentration of possible decomposition products. After the reaction was complete and the mesitylene removed, an IR was taken of the crude material (see appendix for spectrum). The IR clearly shows a peak at ~2028 cm^{-1}, consistent with the formation of an iridium–CO complex. This result suggests

that decomposition by decarbonylation is likely the main iridium decomposition pathway for this reaction.

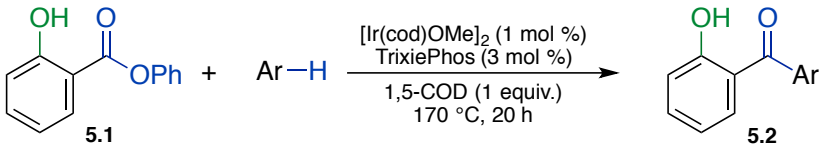
5.2.4 Arene Substrate Scope

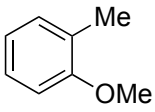
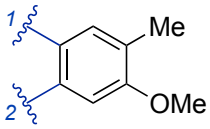
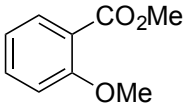
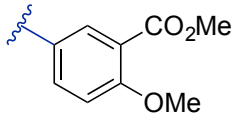
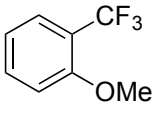
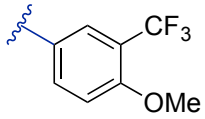
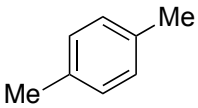
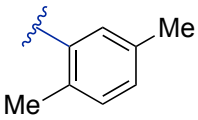
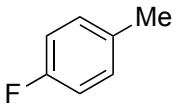
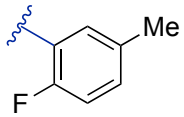
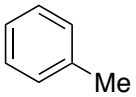
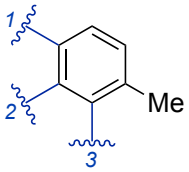
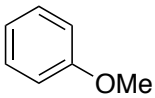
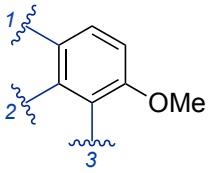
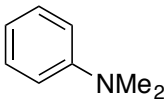
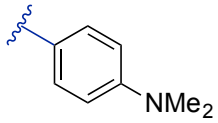
Table 5.10. Arene Substrate Scope



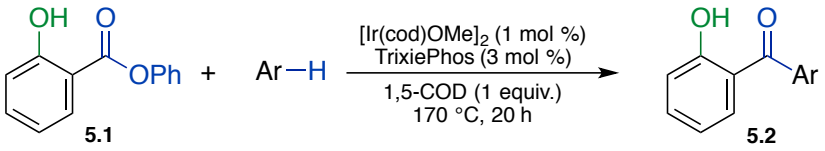
Entry	Arene	Product(s)	Yield (%)	Ratio (1:2:3)
5.2aa			61	11:1
5.2ab			80	1.5:1[a]
5.2ac			71	9:2.4:1[b]
5.2ad			40	–
5.2ae			trace	–
5.2af			79	–
5.2ag			93	–

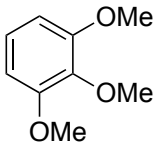
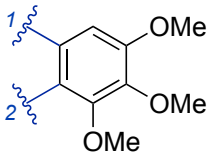
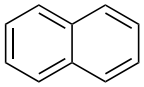
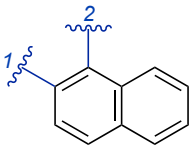
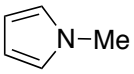
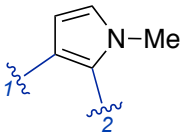
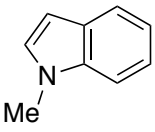
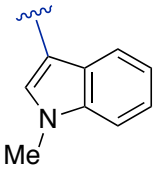
[a] Isolated as an inseparable mixture; product distribution determined by ^{1}H NMR. [b] Minor product **2a_3** inseparable from **2a_1**; product distribution determined by ^{1}H NMR.

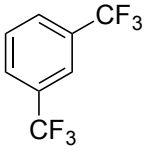
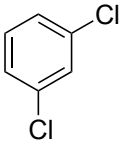
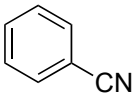
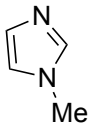


Entry	Arene	Product(s)	Yield (%)	Ratio (1:2:3)
5.2ah			71	2.6:1
5.2ai			62	–
5.2aj			35	–
5.2ak			14[c,d]	–
5.2al			9[c]	–
5.2am			50	17:17:1[a]
5.2an			74	10:2.3:1[a,b]
5.2ao			87[c]	–

[a] Isolated as an inseparable mixture; product distribution determined by ^{1}H NMR. [b] Minor product **2a_3** inseparable from **2a_1**; product distribution determined by ^{1}H NMR. [c] After 20 hours, a second charge of catalyst (1 mol % $[Ir(cod)OMe]_2$, 3 mol % TrixiePhos) was added and allowed to react at 170 °C for 20 hours. [d] Unable to be fully purified, yield is an upper limit.



Entry	Arene	Product(s)	Yield (%)	Ratio (1:2)
5.2ap			76	5:1[a]
5.2aq			78	>20:1[a]
5.2ar			67	10:1
5.2as			73	–

				
5.2at	**5.2au**	**5.2av**	**5.2aw**	**5.2ax**

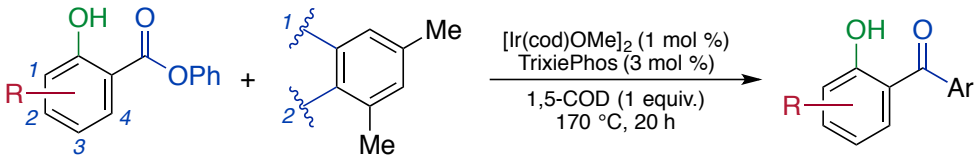
[a] Isolated as an inseparable mixture; product distribution determined by ^{1}H NMR.

With optimized reaction conditions in hand, the scope of the reaction was investigated. Mono-, di-, and tri-substituted benzene rings were successful substrates in this reaction. Electron-rich arenes (Table 5.10, **5.2aa**–**5.2ac**, **5.2af**–**5.2ah**, **5.2an**, **5.2ao**) perform well under these reaction conditions, especially compared to electron-poor arenes (**5.2ad**, **5.2ae**, **5.2ai**, **5.2aj**). Very electron-poor arenes, halogen functionalized arenes, and some heterocycles were unsuccessful (**5.2at**–**5.2ax**). Regioselectivity for the reaction generally favored

substitution at the most sterically accessible site. Unsymmetrical 1,2-disubstituted arenes with multiple C–H bonds in a similar steric environment, favor acylation at the most electron-rich site (**5.2ah**–**5.2aj**). Arenes with only a weak electronic and steric bias, like toluene (**5.2am**), are primarily acylated at a mixture of the most sterically accessible sites. The reaction tolerates arenes with basic functional groups such as methyl, methoxy, methyl ester, fluoro, trifluoromethyl, and dimethylamino. *N*-methylated heteroarenes (**5.2ar** and **5.2as**) were good substrates for this reaction. Acylation primarily occurred at the most sterically accessible 3-position of *N*-methylpyrrole (**5.2ar**, 10:1 ratio of regioisomers) and *N*-methylindole (**5.2as**). This selectivity is contrary to Friedel-Crafts acylation for *N*-methylpyrrole, confirming steric control of regioselectivity, but consistent with electronic control for *N*-methylindole.[126] Acylation of naphthalene occurs almost exclusively at the β-position, contrary to Friedel-Crafts acylation selectivity which shows acylation predominantly at the α-position.[127] Our chemistry shows good selectivity for the steric-controlled product, although with a noticeable decrease in selectivity as the electron density of the ring increases.

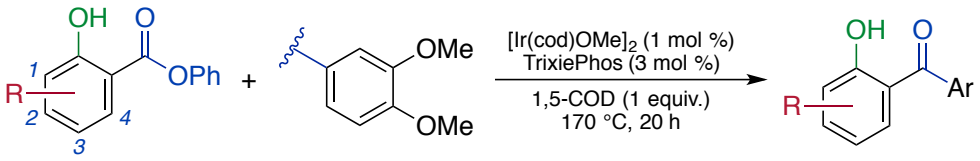
5.2.5 Salicylate Substrate Scope

Table 5.11. Salicylate Substrate Scope



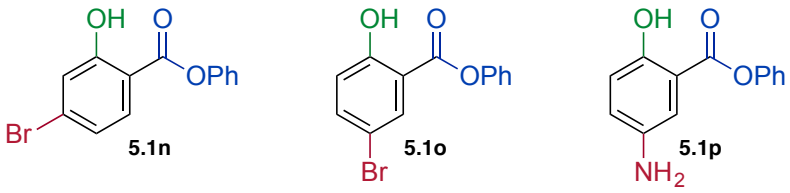
5.1 5.2

Entry	R	Yield (%)	Ratio (1:2)	Entry	R	Yield (%)	Ratio (1:2)
5.2ba	2-Me	45	10:1 [a,b]	**5.2bg**	3-Me	30	18:1 [a,b]
5.2bb	2-OMe	38	10:1 [a,b]	**5.2bh**	3-OMe	41	>20:1 [a,b]
5.2bc	2-F	52	>20:1 [a,b]	**5.2bi**	3-Cl	44	19:1 [a,b]
5.2bd	2-CF_3	45	13:1 [a,b]	**5.2bj**	1-Me	43	10:1 [a,b]
5.2be	2-OH	16	–	**5.2bm**	4-OH	trace	–
5.2bf	2-Cl	43	20:1 [a,b]				



5.1 5.2

Entry	R	Yield (%)	Entry	R	Yield (%)
5.2ca	2-Me	77	**5.2ch**	3-OMe	83
5.2cb	2-OMe	80	**5.2ci**	3-Cl	80
5.2cc	2-F	82	**5.2cj**	1-Me	88
5.2cd	2-CF_3	88	**5.2ck**	2-NO_2	49
5.2ce	2-OH	67	**5.2cl**	3-NO_2	47
5.2cf	2-Cl	46	**5.2cm**	4-OH	23 [c]
5.2cg	3-Me	97			

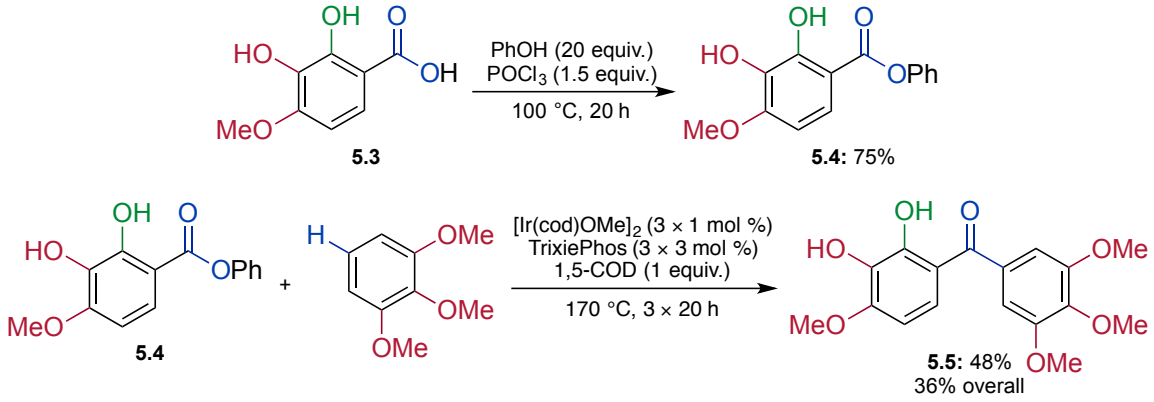


5.1n **5.1o** **5.1p**

[a] Isolated as an inseparable mixture; product distribution determined by ^{1}H NMR. [b] **5.2aa1** also produced in the mixture; product distribution determined by ^{1}H NMR. [c] Yield determined by ^{1}H NMR ; product decomposed during attempted purification.

The phenyl salicylate substrate scope was investigated using various functional groups and substitution patterns on the salicylate ester in the acylation of both *m*-xylene and 1,2-dimethoxybenzene (Table 5.11). The acylation of *m*-xylene was performed with two charges of catalyst and generally proceeded in decent yields and good regioselectivity for acylation at the most sterically accessible site (**5.2ba**–**5.2bm**). The unexpected byproduct **5.2aa1** was also observed in many of the reactions with *m*-xylene, suggesting that defunctionalization of the salicylate ester is a competing catalytic pathway. Acylation with the more electron-rich arene, 1,2-dimethoxybenzene, yielded product in excellent yield with most substrates (**5.2ca**–**5.2cd**, **5.2cg**–**5.2cj**). Salicylates with methyl, methoxy, fluoro, chloro, and trifluoromethyl groups in the 2- and 3-positions were well tolerated in both the reaction with *m*-xylene and 1,2-dimethoxybenzene. The hydroxy functional group was tolerated better when in the 2-position than in the 4-position of phenyl salicylate with both *m*-xylene and 1,2-dimethoxybenzene (**5.2be** versus **5.2bm** and **5.2ce** versus **5.2cm**). The nitro functional group was tolerated using 1,2-dimethoxybenzene but not with *m*-xylene (**5.2ck** and **5.2cl**). Steric bulk around the hydroxy directing group was well tolerated using the 1-methyl–salicylate substrate with both *m*-xylene and 1,2-dimethoxybenzene (**5.2bj** in 43% and **5.2cj** in 88%). Unsuccessful substrates included both bromo-substituted salicylates (**1n** and **1o**) and the amino-substituted salicylate **1p**. The bromo-substituted salicylates were unsuccessful likely due to competitive oxidative addition of the iridium into the Br–C bond. **1p** was likely undreactive due to insolubility in the reaction conditions.

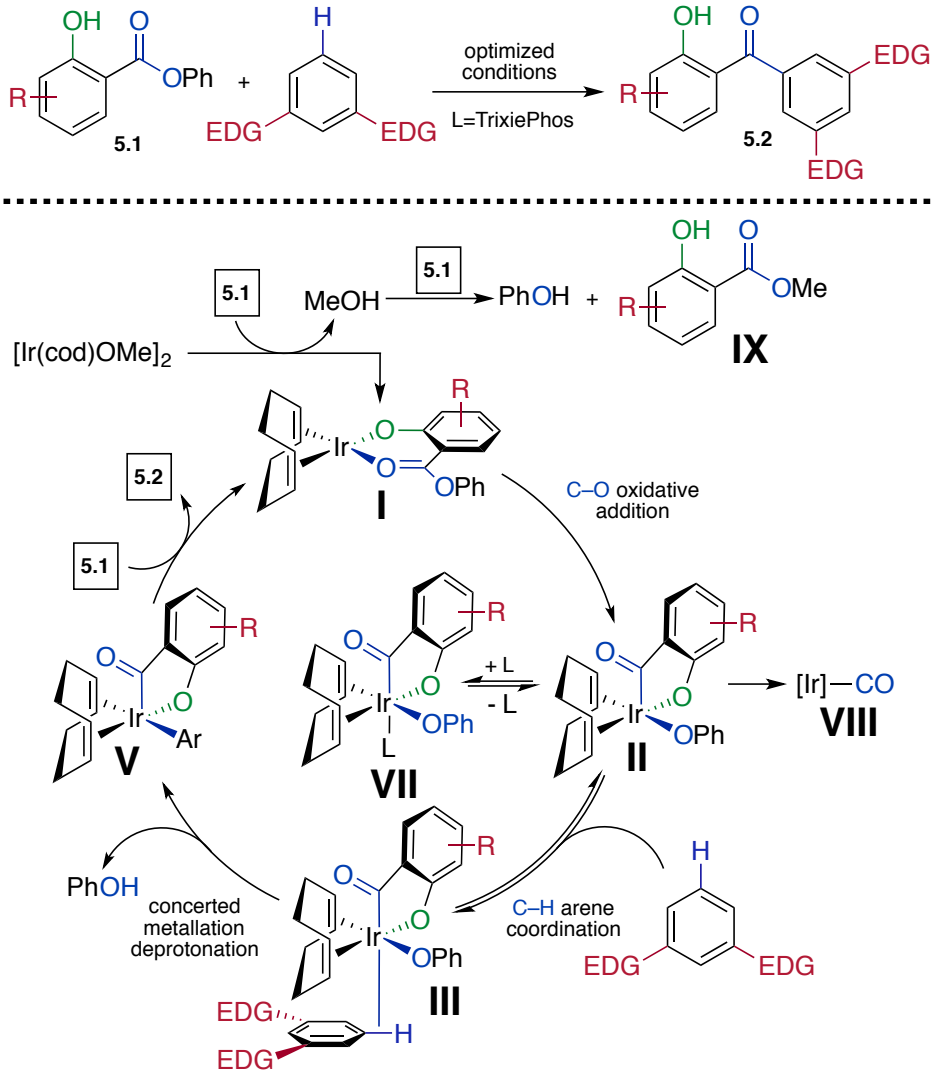
5.2.6 Synthesis of 2-hydroxyphenstatin



Scheme 5.4. Synthesis of 2-hydroxyphenstatin.

2-Hydroxyphenstatin **5.5** is a potent anti-cancer and anti-mitotic target that we envisioned could be synthesized efficiently using our methodology (Scheme 5.4).[128] The most efficient previous synthetic route for **5.5** utilizes a low-yielding *ortho*-selective Friedel-Crafts acylation (25% yield) of 1,2,3-trihydroxybenzene.[129] Our approach began by synthesizing the di-hydroxy acid **5.3** with a BCl_3 deprotection of the trimethoxybenzoic acid using literature procedure.[130] Esterification of **5.3** with phenol using $POCl_3$ formed the phenyl ester **5.4** in 75% yield. Acylation of 1,2,3-trimethoxybenzene with **5.4**, using 3 charges of catalyst, yielded 2-hydroxyphenstatin **5.5** in 48% yield (36% overall yield).

5.2.7 Proposed Mechanism

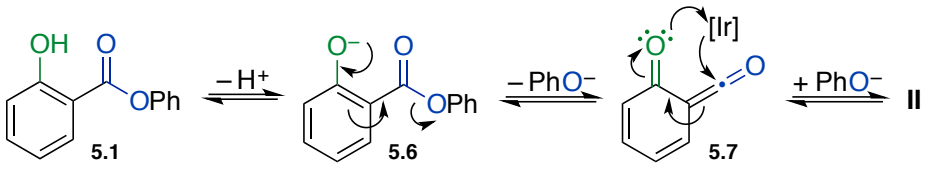


Scheme 5.5. Proposed mechanism for sterics-selective acylation of arenes.

Our mechanistic proposal begins with **1** breaking up the $[Ir(cod)OMe]_2$ and forming iridium complex **I** (Scheme 5.5). C–O activation of the ester bond forms **II**. Subsequent coordination of the arene π-bond followed by slipping to the aryl C–H bond forms the iridium σ-complex **III**. C–H activation proceeds by concerted metallation deprotonation, the phenoxide ligand's lone pair of electrons deprotonates the arene with simultaneous Ar–iridium bond formation forming **V**

and free phenol.[131] Reductive elimination forms the C_{acyl}–C_{aryl} bond and **2** after another substrate molecule exchanges reforming the active catalyst.

Included in this mechanism is the results of our intermolecular and intramolecular competition KIE experiments where arene binding is reversible. Also, we propose that the active catalyst has 1,5-COD as the ancillary ligand instead of TrixiePhos. This is consistent with added 1,5-COD improving the overall conversion of the starting material to product and with TrixiePhos not being required for catalytic turnover. TrixiePhos is proposed to be in a dynamic equilibrium with **II** forming **VII**. **VII** is thought to be off cycle, consistent with TrixiePhos being an inhibitor at high concentrations, but necessary for sequestering **II** as a stable complex which is incapable of undergoing decomposition by decarbonylation. Decarbonylation is hypothesized to be the primary decomposition pathway of **II**. If decarbonylation to form **VIII** proceeds via a bimetallic mechanism, we expect that lower concentrations of **II** (induced by phosphine) would improve the conversion of starting material to product. This hypothesis is consistent with our data (Scheme 5.5).



Scheme 5.6. Ketene C–O activation pathway.

A second possibility for C–O activation to occur is through ketene intermediate **5.7** (Scheme 5.6). Ketene **5.7** has been proposed as a high-energy intermediate produced from **5.1** in pyrolysis studies at ~280 °C.[132] The formation of the phenoxide anion would be more favored with electron withdrawing substituents over electron donating substituents on the phenoxide in this pathway due to the electron withdrawing substituents ability to stabilize the anionic charge. This is consistent with our initial rates kinetics data for leaving group effect where electron withdrawing substituents increased the rate of the reaction.

Direct oxidative addition of iridium into the C_{acyl}–O of phenyl salicylate and ketene trapping of iridium yield **II**; however, distinguishing which mechanism is operating in our reaction has remained elusive for us.

5.2.8 Computational Results

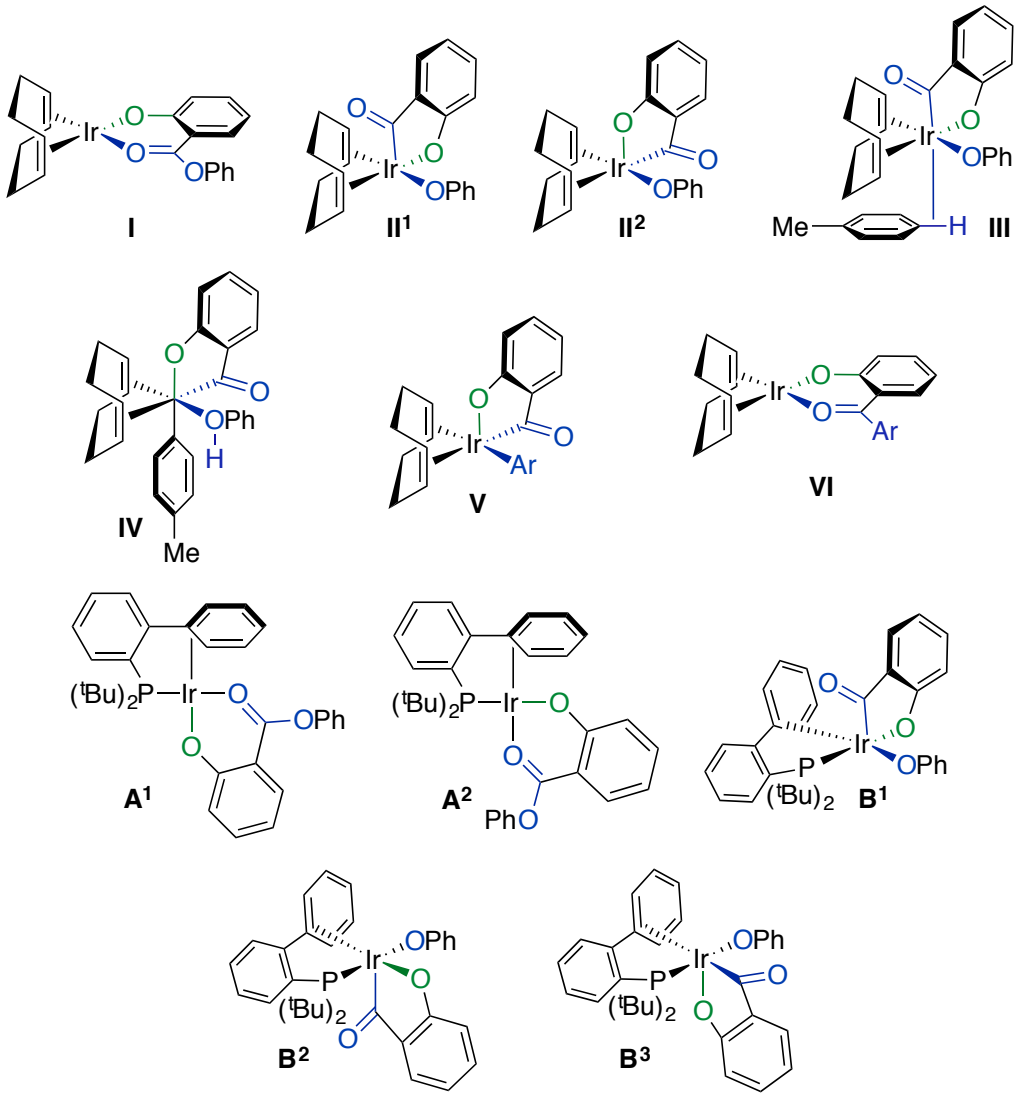


Table 5.12. Relative Energies of Catalytic Intermediates and Transition States Using M06L Functional

Structure	Relative Gibbs Energy (kcal)	Structure	Relative Gibbs Energy (kcal)
I	0	**TS3**	+29.6
TS1_COD	+22.8	**VI**	+3.0
II[1]	+7.4	**A[1]**	+11.3
II[2]	+26.3	**A[2]**	+15.2
III	+18.8	**TS1_JohnPhos**	+44.7
TS2	+58.6	**B[1]**	+16.4
IV	+48.4	**B[2]**	+16.6
V	+13.7	**B[3]**	+22.0

SMD (toluene) M06L/6-311+G(2df,2pd)(SDD)//M06L/6-31G(d,p)(SDD)

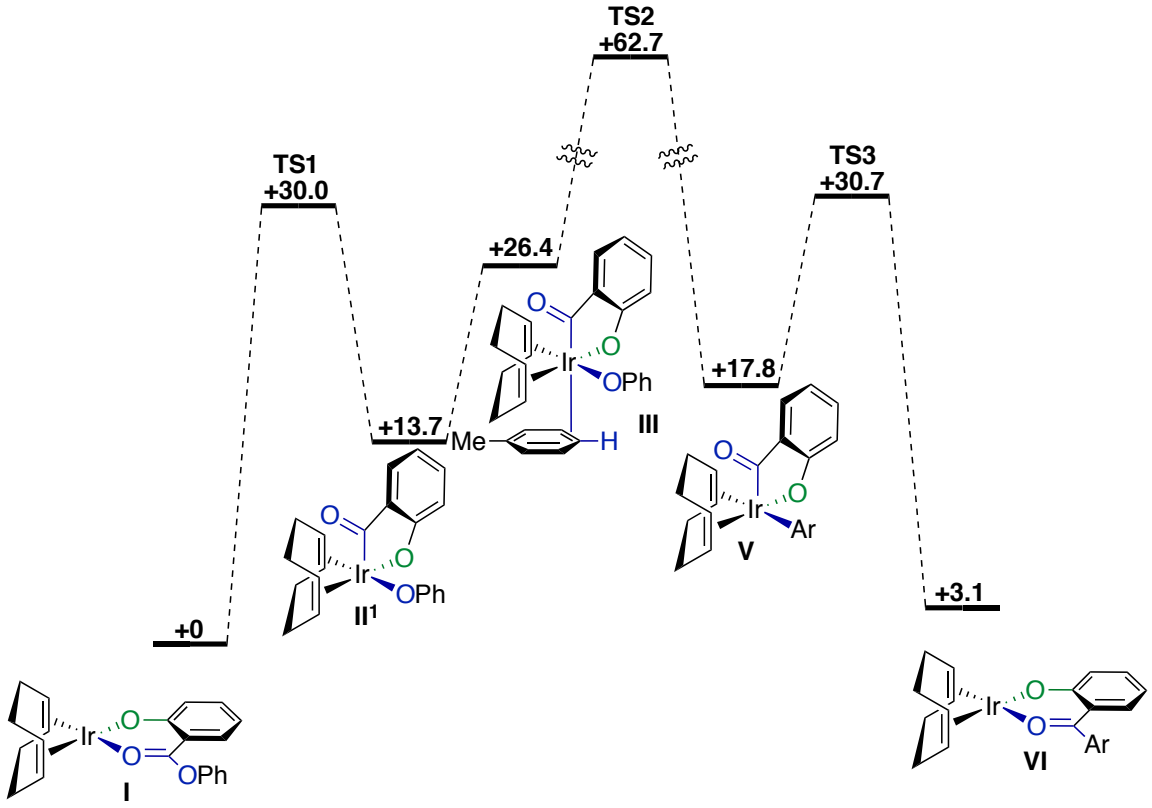
Table 5.13. Relative Energies of Catalytic Intermediates and Transition States Using M06 Functional

Structure	Relative Gibbs Energy (kcal)	Structure	Relative Gibbs Energy (kcal)
I	0	**TS3**	+30.7
TS1_COD	+30.0	**VI**	+3.1
II[1]	+13.7	**A[1]**	+14.3
II[2]	+32.6	**A[2]**	+15.0
III	+26.4	**TS1_JohnPhos**	+50.3
TS2	+62.7	**B[1]**	+25.0
IV	+50.9	**B[2]**	+23.5
V	+17.8	**B[3]**	+31.6

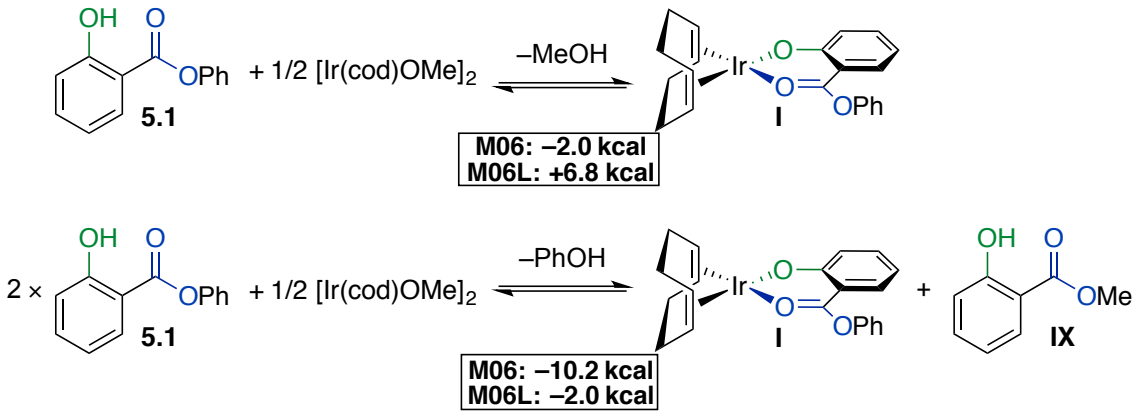
SMD (toluene) M06/6-311+G(2df,2pd)(SDD)//M06/6-31G(d,p)(SDD)

With the synthetic study complete, I began preliminary investigations into the mechanism of the reaction using the Gaussian 09 computational chemistry

suite.[73] Initial findings are summarized in Tables 5.12 and 5.13 using JohnPhos as a model ligand for TrixiePhos. The M06 and M06L density functionals were used to perform these calculations with 6-31G(d,p) basis sets on H, C, O, and P atoms and the SDD basis set on iridium for geometry optimization and 6-311+G(2df,2pd) basis sets on H, C, O, and P atoms and the SDD basis set on iridium for single point energy calculations with SMD solvation using toluene as the solvent. Comparing **I** to **A** clearly shows that the coordination of phosphine to iridium is uphill relative to COD as an ancillary ligand. Comparing **II**^{1} to **II**^{2} demonstrates how the acyl group prefers the axial position over the oxygen of the 5-membered chelating group. This result is also true for the phosphine ligated intermediates **B**$^{1-3}$. Inspection of the JohnPhos complexes **B**$^{1-3}$ also shows a large amount of steric congestion around the iridium. This result suggests that COD must fully dissociate if there is an equilibrium between **II** and JohnPhos ligated iridium(III) complex. The oxidative addition transition state complex **TS1_COD** has a relative energy of +30 kcal (M06 functional) which seems reasonable given the temperature for the reaction is 170 °C. The transition state for concerted metallation deprotonation is much higher than expected (+63 kcal using M06). Further work on finding a transition state that is more practical is necessary. Finally, the reductive elimination product **VI** is uphill by ~3 kcal, suggesting that the reaction is under thermodynamic equilibrium. This system is better represented in the energy profile in Scheme 5.7 for the M06 results. The result that the reaction appears to be uphill led me to calculate the theoretical equilibrium for a few reactions (Schemes 5.8 & 9).



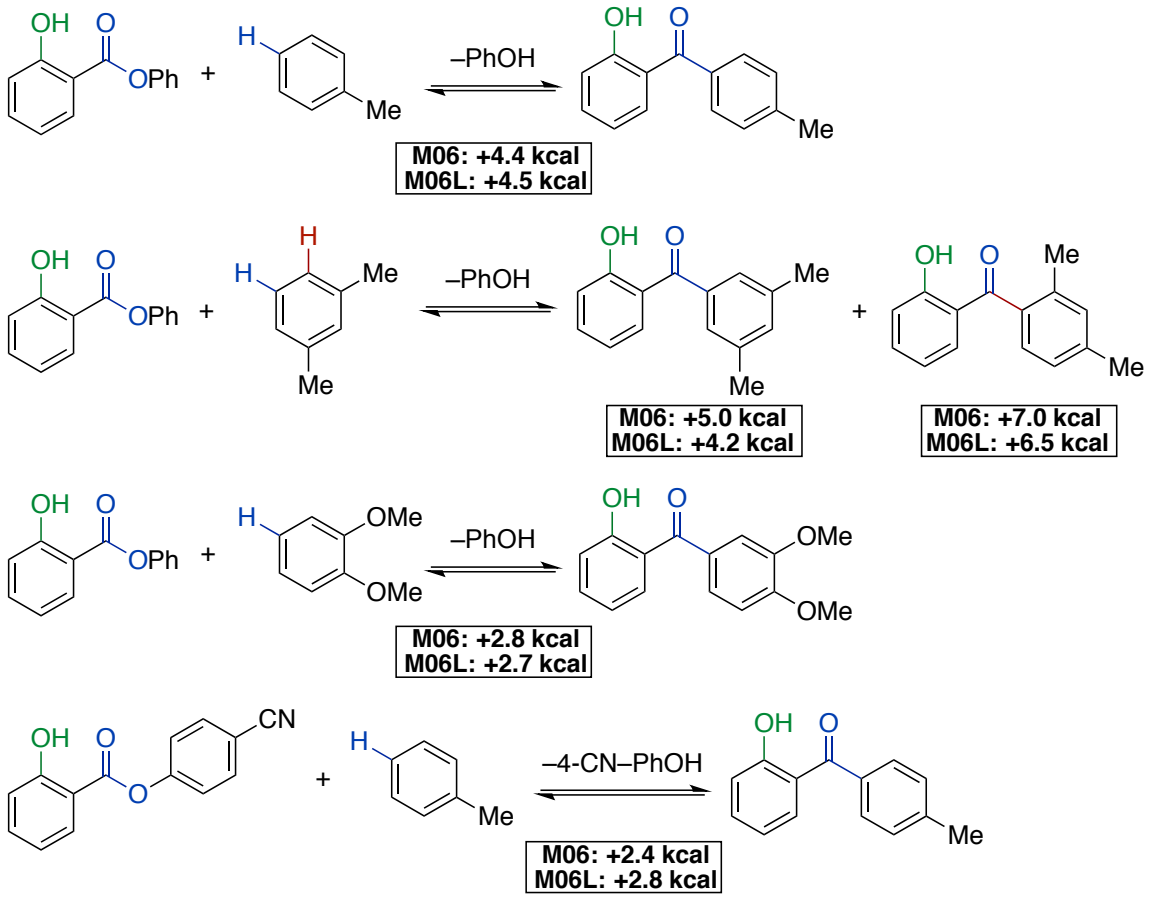
Scheme 5.7. Energy profile for acylation of toluene using M06 functional.



Scheme 5.8. Equilibrium for breaking up $[Ir(cod)OMe]_2$ with phenyl salicylate.

Scheme 5.8 is the equilibrium for the reaction of phenyl salicylate (**5.1**) with a half of an equivalent of $[Ir(cod)OMe]_2$ forming methanol and **I** with coupled formation of methyl salicylate **IX**. This equilibrium was calculated using the same functionals and basis sets as the calculations in Table 5.12 and 5.13. The ΔG for the reaction is theoretically uphill by 6.8 kcal for M06L; however, using two

equivalents of phenyl salicylate with subsequent formation of methyl salicylate and phenol as products is downhill by 2.0 kcal (Scheme 5.8). These results suggest that the formation of methyl salicylate drives the formation of **I** using the $[Ir(cod)OMe]_2$ pre-catalyst. The equilibrium is downhill using the M06 functional to a greater extent than when using the M06 functional.



Scheme 5.9. Equilibria for the reactions of various phenyl salicylates with arenes.

The last theoretical equilibria calculated were the reactions between phenyl salicylates and arenes. Each structures geometry in these equilibria were optimized using the M06 and M06L functionals following the same methods as in tables 5.12 and 5.13. Solvation was performed using the implicit SMD model with the correct respective solvent (anisole was used to model DMB). The computed ΔG values for all the reactions are uphill. If the reaction is in fact uphill, the use of solvent quantities of arene may be what drives the formation of product. The use

of the electron rich arene DMB is less uphill than toluene which may be why electron rich arenes perform better in the reaction. The use of th nitrile electron withdrawing group on the leaving group is less uphill as well, suggesting that using electron withdrawing groups on the leaving group could promote high conversion to product.

5.3 Conclusions

We demonstrated the first steric-selective acylation of arenes by sequential C_{acyl}–O, C_{aryl}–H bond activation. The unique mechanism of this reaction was investigated using initial rates kinetics and kinetic isotope effect studies. This mechanism is distinct from Friedel-Crafts acylation and may provide future investigators with hypotheses for linking novel mechanistic steps in catalytic transformations. The scope of the reaction with respect to the arene and the salicylate ester was investigated. The reaction proceeds in good yield with simple arenes and a wide range of functionalized salicylate esters. The utility of the reaction was then demonstrated with the synthesis of the potent anti-cancer agent 2-hydroxyphenstatin.

Current computational results suggest that the catalyst favors the COD complexes over the JohnPhos complexes. Also, the thermodynamics of the reaction is uphill and solvent quantities of arene are required to drive the reaction to completion. More investigations into ways to decrease the concentration of arene by overcoming the thermodynamics is necessary.

5.4 Experimental Section

General Experimental Procedures: All acylation reactions were prepared under inert atmosphere in an oxygen-regulated glovebox. Reaction progress was monitored using thin-layer chromatography (TLC) on 0.25 mm silica plates from

SiliCycle. Eluted plates were visualized with UV light. Silica Gel Flash Column Chromatography was performed on 230–400 mesh (particle size 0.04–0.063 mm) silica gel purchased from SiliCycle.

Materials. Unless otherwise indicated, chemicals were obtained from commercial sources and used without further purification. All arenes were degassed by bubbling a stream of argon through the liquid in a schlenk bomb flask, and stored over 3 Å molecular sieves in a nitrogen-filled glovebox.

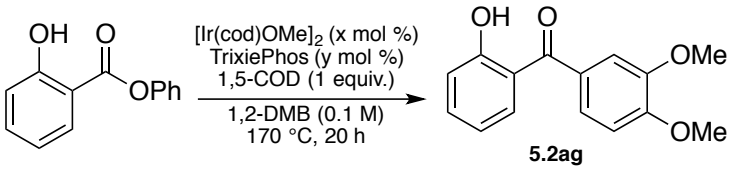
Instrumentation: NMR characterization data were collected at 300 K on Bruker FT NMR instruments. ^{1}H NMR spectra were internally referenced to TMS (δ = 0 ppm). ^{13}C NMR spectra were internally referenced to the residual solvent signal (δ = 77.2 ppm). Data from ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Melting point ranges for solid products were determined on a MEL-TEMP instrument, and are reported uncorrected. IR Spectra were obtained as films either neat or from CH_2Cl_2 on sodium chloride plates on a Thermo Scientific FT-IR or with an ATR source using a Nicolet iS5 FT-IR spectrometer. Data are presented as absorption frequency (cm^{-1}). High-resolution mass spectrometry (HRMS) using GC-MS was performed on an Agilent 7200-QTOF GC/MS, GC column RTX-5MS 30 m length, 0.255 mm ID, 0.25 μm df. Method: inlet temperature 250 ˚C, source temperature 280 ˚C. The initial column temperature of 120 ˚C was held for 4 minutes after injection. Column temperature was ramped to 325 ˚C over 10 minutes and then held for 31 minutes. High-resolution mass spectrometry (HRMS) using ESI experiments were performed on a Bruker BioTOF II instrument using sodium trifluoroacetate internal standard and ammonium bicarbonate additive.

Computations: All computational structures were optimized in the gas phase and verified as minima or first-order saddle points by calculations of the full Hessian using Gaussian 09.[73] All geometries reported are RM06L (closed-shell

species) with the SDD basis set for iridium and 6-31G(d,p) basis set for H, C, O, and P atoms. Electronic energies were further evaluated with the 6-311+G(d,p) basis set and SMD (solvent = toluene) solvation for structures in Scheme 5.9. All ZPE, enthalpic, and entropic free energy corrections (unscaled) utilize values computed at the lower basis set level at 443.15 K and 1 atm.

REACTION OPTMIZATION

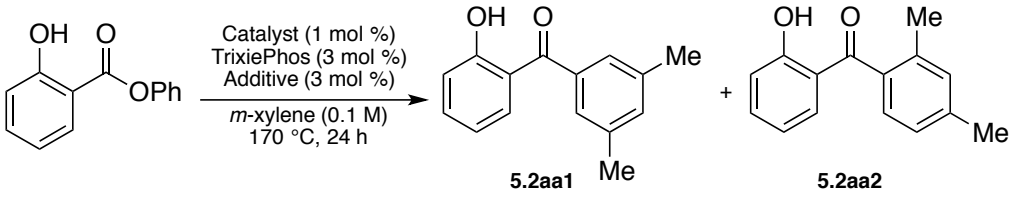
Control Experiments



5.2ag

Reactions were prepared using phenyl salicylate (0.2 mmol, 1.0 equiv.) *Rac*-2-(di-*t*-butyldiphosphino)-1,1'-binapthyl (TrixiePhos, y mol %), $[Ir(cod)OMe]_2$ (x mol %), 1,5-cyclooctadiene (1,5-COD, 1.0 equiv.), and 1,2-dimethoxybenzene (1,2-DMB, 0.1 M) in PTFE-lined crimp-top vials. The vials sealed, removed from the glovebox, and heated to 170 °C in an oil bath for twenty hours. Product yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene internal standard (0.8 mL, 0.1 M in $CDCl_3$).

Catalyst Optimization

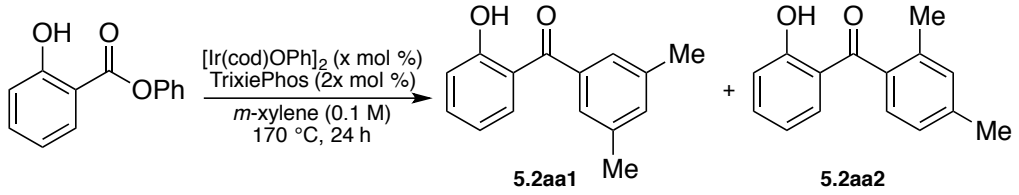


5.2aa1 **5.2aa2**

Reactions were prepared using phenyl salicylate (0.1 mmol, 1.0 equiv.), TrixiePhos (0.003 mmol, 3 mol %), catalyst (0.001 mmol, 1 mol %), base (0.018 mmol, 3 mol %), and *m*-xylene (1.0 mL, 0.1 M) in PTFE-lined crimp-top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil

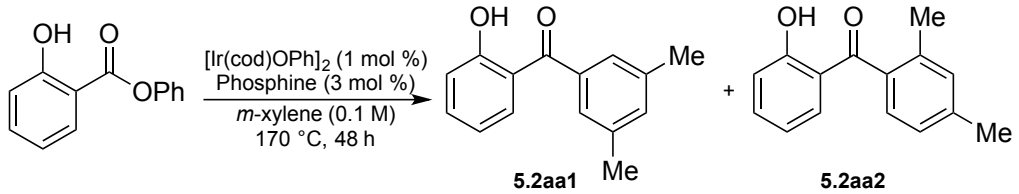
bath for 24 h. Product yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene internal standard (0.7 mL, 0.143 M in $CDCl_3$).

Catalyst Loading Optimization



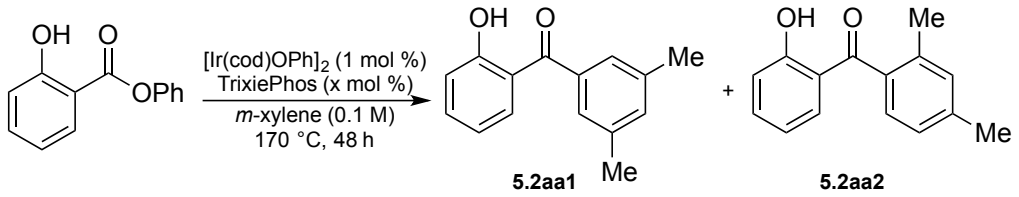
Reactions were prepared using phenyl salicylate (0.1 mmol, 1.0 equiv.), $[Ir(cod)OPh]_2$ (x mol %), TrixiePhos (2x mol %) and *m*-xylene (1.0 mL, 0.1 M) in PTFE-lined crimp-top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 24 h. Product yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene internal standard (0.7 mL, 0.143 M in $CDCl_3$).

Phosphine Screen



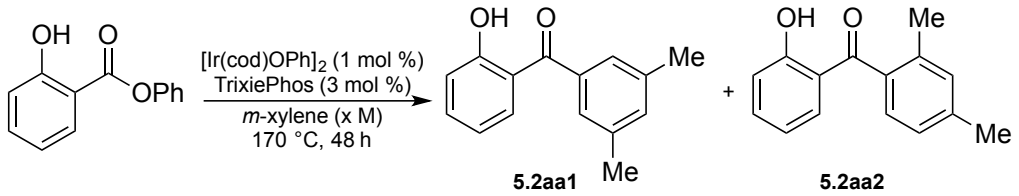
Reactions were prepared using phenyl salicylate (0.1 mmol, 1.0 equiv.), $[Ir(cod)OPh]_2$ (0.001 mmol, 1 mol %), Phosphine (0.003 mmol, 3 mol %) and *m*-xylene (1.0 mL, 0.1 M) in PTFE-lined crimp-top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 48 h. Product yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene internal standard (0.7 mL, 0.143 M in $CDCl_3$).

Phosphine Loading Optimization



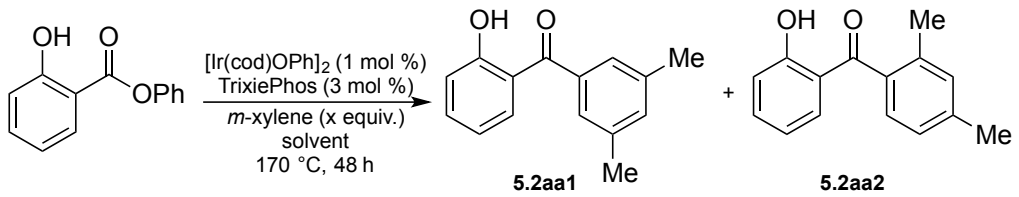
Reactions were prepared using phenyl salicylate (0.1 mmol, 1.0 equiv.), $[Ir(cod)OPh]_2$ (0.001 mmol, 1 mol %), TrixiePhos (x mol %) and *m*-xylene (1.0 mL, 0.1 M) in PTFE-lined crimp-top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 48 h. Product yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene internal standard (0.7 mL, 0.143 M in $CDCl_3$).

Substrate Concentration Optimization



Reactions were prepared using phenyl salicylate (1.0 equiv.), $[Ir(cod)OPh]_2$ (1 mol %), TrixiePhos (3 mol %) and *m*-xylene (volume required to obtain listed concentration of phenyl salicylate) in PTFE-lined crimp-top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 48 h. Product yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene internal standard (0.7 mL, 0.143 M in $CDCl_3$).

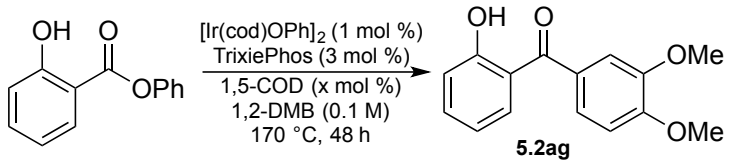
Effect of Arene Dilution



Reactions were prepared in PTFE-lined crimp-top vials using phenyl salicylate (0.1 mmol, 1.0 equiv.), $[Ir(cod)OPh]_2$ (0.001 mmol, 1 mol %), TrixiePhos (0.003

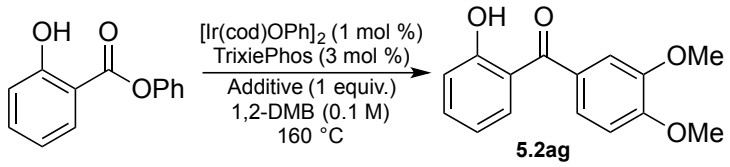
mmol, 3 mol %), *m*-xylene (x equiv.), and additional solvent to dilute to a final volume of 1.0 mL. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 48 h. Product yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene internal standard (0.7 mL, 0.143 M in $CDCl_3$).

COD Equivalents Optimization



Reactions were prepared using phenyl salicylate (1.0 equiv.), $[Ir(cod)OPh]_2$ (1 mol %), TrixiePhos (3 mol %), 1,5-COD (volume required to obtain listed concentrations) and 1,2-dimethoxybenzene (0.1 M final concentration relative to phenyl salicylate, 1 mL final volume) in PTFE-lined crimp top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 4 hr. Product yield was determined by ^{1}H NMR using dibromomethane internal standard.

Alkene Additive Screen



Reactions were prepared using phenyl salicylate (1 equiv.), $[Ir(cod)OMe]_2$ (1 mol %), TrixiePhos (3 mol %), alkene additive (1 equiv.) and 1,2-dimethoxybenzene (0.8 mL) in a 5 mm J-young NMR tube. The tube was sealed, removed from the glovebox, and heated to 160 °C. Single-scan ^{1}H NMR spectra were taken at regular intervals. The reaction progress was monitored until approximately 10% completion was observed, relative to trimethyl(phenyl)silane internal standard.

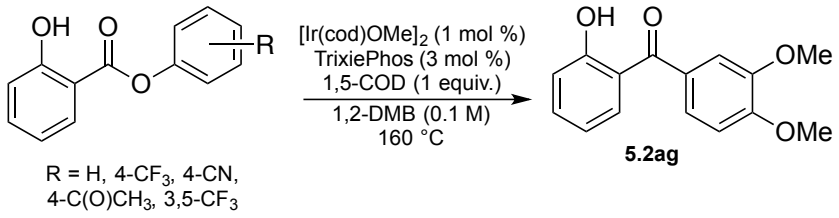
IRIDIUM CARBONYL FROM CATALYST DECOMPOSITION

TrixiePhos (10 mg, 0.24 mmol, 30 mol %), $[Ir(cod)OMe]_2$ (50 mg, 0.08 mmol, 10 mol %, phenyl salicylate (0.171 g, 0.8 mmol, 1 equiv.), 1,5-COD (98 µL, 0.8 mmol, 1 equiv.), and mesitylene (8 mL, 0.1 M) were added to a 10 mL PTFE-lined crimp-top vial. The vial was sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 20 h. The solvent was removed *in vacuo.* An IR spectrum was obtained of the crude product mixture. Distinguishing peaks at 1981 and 2027 cm^{-1} indicated the probable presence of an Ir–CO complex.

PHOSPHORUS DEGRADATION

TrixiePhos (5.0 mg, 0.013 mmol, 3 mol %), $[Ir(cod)OMe]_2$ (3.0 mg, 0.005 mmol, 1 mol %), phenyl salicylate (90.1 mg, 0.421 mmol, 1 equiv.), 1.5-COD (51 µL, 0.416 mmol, 1 equiv.) and 1,3-dimethoxybenzene (4.3 mL, 0.1 M) were mixed in a 20 mL scintillation vial. 0.6 mL of the solution was transferred to a J-Young NMR tube, the tube was sealed and removed from the glovebox. A ^{31}P NMR spectrum was taken (t=0), and the reaction mixture was heated to 170 °C in an oil bath. ^{31}P NMR spectra were taken at regular increments.

KINETIC STUDIES

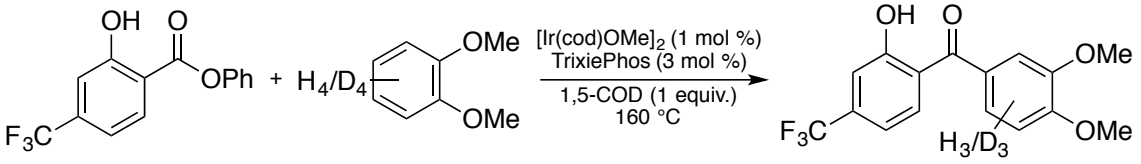


Initial Rates General. Reactions were prepared using *p*-substituted phenyl salicylate (1 equiv.), $[Ir(cod)OMe]_2$ (1 mol %), TrixiePhos (3 mol %), 1,5-COD (1 equiv.) and 1,2-dimethoxybenzene (0.8 mL) in a 5 mm J-young NMR tube. The tube was sealed, removed from the glovebox, and heated to 160 °C. Single-scan ^{1}H NMR spectra were taken at regular intervals. The reaction progress was monitored until approximately 10% completion was observed, relative to trimethyl(phenyl)silane internal standard.

Kinetic Isotopes General. The kinetic isotope effects were determined by the following equation:

$$KIE = \frac{Prod_H}{Prod_D} = \frac{k_H}{k_D}$$

Initial Rates



Proteo - Reactions were performed in triplicate using 0.7 mL aliquots from a stock solution containing phenyl 4-(trifluoromethyl)salicylate (0.4 mmol, 1 equiv.), $[Ir(cod)OMe]_2$ (0.004 mmol, 1 mol %), TrixiePhos (0.012 mmol, 3 mol %), 1,5-COD (0.4 mmol, 1 equiv.), 1-methoxy-3-(trifluoromethyl)benzene (0.463 mmol, 1.16 equiv.) and H_4-1,2-dimethoxybenzene (4 mL) in a J-Young NMR tube. Once sealed, the tubes were removed from the glovebox, and single-scan ^1H and ^{19}F NMR spectra were taken for time (t) = 0 min. The reaction mixtures were heated to 160 °C in an oil bath and monitored for 70 minutes. Product formation was monitored by ^{19}F using 1-methoxy-3-(trifluoromethyl)benzene internal standard. Linear fits were obtained, removing the t=0 data point due to an observed induction period.

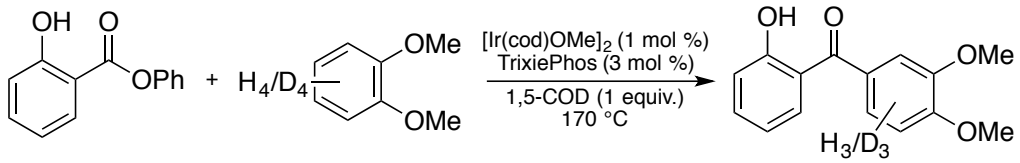
Deutero - Reactions were performed in triplicate using 0.7 mL aliquots from a stock solution containing phenyl 4-(trifluoromethyl)salicylate (0.4 mmol, 1 equiv.), $[Ir(cod)OMe]_2$ (0.004 mmol, 1 mol %), TrixiePhos (0.012 mmol, 3 mol %), 1,5-COD (0.4 mmol, 1 equiv.), 1-methoxy-3-(trifluoromethyl)benzene (0.407 mmol, 1.02 equiv.) and D_4-1,2-dimethoxybenzene (4 mL) in a J-Young NMR tube. Once sealed, the tubes were removed from the glovebox, and single-scan ^1H and ^{19}F NMR spectra were taken for time (t) = 0 min. The reaction mixtures were heated to 160 °C in an oil bath and monitored for 90 minutes. Product formation was monitored by ^{19}F using 1-methoxy-3-(trifluoromethyl)benzene internal standard.

Linear fits were obtained, removing the t=0 data point due to an observed induction period.

Table 5.14. Initial Rates Kinetics Results

Entry	k_H (%/min)	k_D (%/min)	KIE
1	0.360	0.198	–
2	0.380	0.220	–
3	0.348	0.201	–
Average	0.363 ± 0.012	0.206 ± 0.016	1.77 ± 0.13

Intermolecular Competition

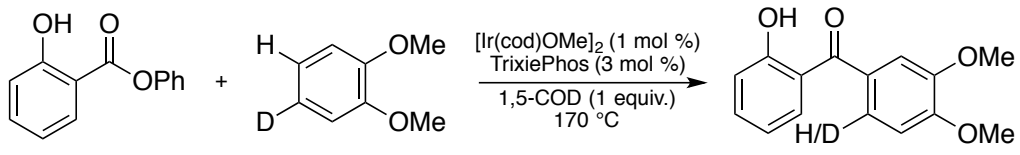


Reactions were prepared in triplicate using phenyl salicylate (1 equiv.), $[Ir(cod)OMe]_2$ (1 mol %), TrixiePhos (3 mol %), 1,5-COD (1 equiv.), H_4-1,2-dimethoxybenzene (0.5 mL) and D_4-1,2-dimethoxybenzene (92.8% d_4 by ^{1}H NMR, 0.5 mL) in PTFE-lined crimp top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 20 hours. Crude mixtures were analyzed by ESI-MS.

$$Prod_H = I_{257}$$

$$Prod_D = I_{260}$$

Intramolecular Competition



Reactions were prepared in triplicate using phenyl salicylate (1 equiv.), $[Ir(cod)OMe]_2$ (1 mol %), TrixiePhos (3 mol %), 1,5-COD (1 equiv.), 4-D_1-1,2-

dimethoxybenzene (90.4% d_4 by ^{1}H NMR, 1 mL) in PTFE-lined crimp top vials. The vials were sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 20 hours. Crude mixtures were analyzed by ESI-MS. Correction factors are used to account for ^{13}C of products.

$$k_H = I_{259} + (I_{258} - (I_{257} \times 0.16))$$

$$k_D = I_{257} \times 1.16$$

Table 5.15. Product Ratios and KIE Values from Inter- and Intramolecular Competition Experiments

Entry	$Prod_H/k_H$	$Prod_D/k_D$	KIE
Inter1	3332	704	4.73
Inter2	4546	983	4.62
Inter3	5577	1259	4.43
Average			4.59 ± 0.15
Intra1	1057	687	1.54
Intra2	770	457	1.68
Intra3	1437	843	1.70
Average			1.64 ± 0.09

ARENE SUBSTRATE SCOPE

Although we used $[Ir(cod)OPh]_2$ during our optimization study, we found that commercially available $[Ir(cod)OMe]_2$ was more convenient in our substrate scope study.

Procedure A. TrixiePhos (10 mg, 0.024 mmol, 3 mol %), $[Ir(cod)OMe]_2$ (5 mg, 0.008 mmol, 1 mol %), phenyl salicylate (0.171 g, 0.8 mmol, 1 equiv.), 1,5-COD (98 µL, 0.8 mmol, 1 equiv.), and arene (8 mL, 0.1 M) were added to a 10 mL PTFE-lined crimp-top vial. The vial was sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 20 hours. The solvent was removed *in vacuo*. Oligomer and residual starting material were hydrolyzed (see general procedure below), and the aqueous layer was extracted with ethyl acetate (3 × 12 mL). The

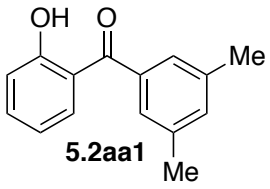
organic extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Procedure B. TrixiePhos (14 mg, 0.036 mmol, 3 mol %), $[Ir(cod)OMe]_2$ (8 mg, 0.012 mmol, 1 mol %), phenyl salicylate (0.257 g, 1.2 mmol, 1 equiv.), 1,5-cyclooctadiene (1,5-COD, 147 µL, 1.2 mmol, 1 equiv.), and arene (12 mL, 0.1 M) were added to a dry 15 mL pressure tube. The pressure tube was sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 20 hours. The solvent was removed *in vacuo*. Oligomer and residual starting material were hydrolyzed (see general procedure below), and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The organic extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

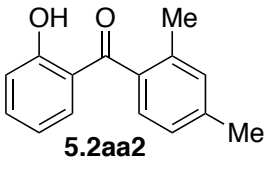
Procedure C. Followed procedure B, then after 20 hours, the reaction mixture was cooled to rt, brought into the glovebox, where TrixiePhos (14 mg, 0.036 mmol, 3 mol %) and $[Ir(cod)OMe]_2$ (8 mg, 0.012 mmol, 1 mol %) was added. The pressure tube was sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 20 hours. The solvent was removed *in vacuo*. Oligomer and residual starting material were hydrolyzed (see general procedure below), and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The organic extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

Procedure D. Followed procedure A, then after 20 hours, the reaction mixture was cooled to rt, brought into the glovebox, and TrixiePhos (10 mg, 0.024 mmol, 3 mol %) and $[Ir(cod)OMe]_2$ (5 mg, 0.008 mmol, 1 mol %) was added. The vial was sealed, removed from the glovebox, and heated to 170 °C for 20 hours. The solvent was removed *in vacuo*. Oligomer and residual starting material were hydrolyzed (see general procedure below), and the aqueous layer was extracted with ethyl acetate (3 × 12 mL). The organic extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography.

General procedure for hydrolysis. Crude material was dissolved in toluene (10 mL), NaOH (30%, 5 mL for procedure A/C, 6.5 mL for procedure B/D) was added, and the mixture was allowed to stir overnight. The mixture was cooled to 0 °C, and HCl (6 M, 7 mL for Procedure A/C, 8 mL for Procedure B or D) was added dropwise.

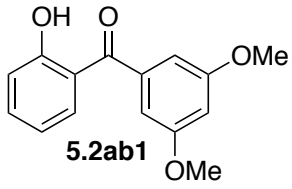


5.2aa1



5.2aa2

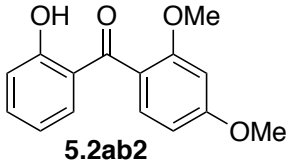
(3,5-Dimethylphenyl)(2-hydroxyphenyl)methanone (**5.2aa1**), (2,4-Dimethylphenyl)(2-hydroxyphenyl)methanone (**5.2aa2**). Prepared using procedure A. Brown oil (0.110 g, 0.487 mmol, 61%) as an inseparable mixture of regioisomers (11:1 2aa1:2aa2). R_f = 0.31 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) 2aa1: δ 12.07 (s, 1H), 7.60 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.27 (br s, 2H), 7.22 (br s, 1H), 7.06 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.87 (dd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 2.39 (s, 6H); 2aa2: δ 12.28 (s, 1H), 7.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13– 7.08 (m, 2H), 6.80 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, only 2aa1 observed) δ 202.3, 163.3, 138.2, 138.1, 136.3, 133.8, 133.7, 127.0, 119.4, 118.7, 118.5, 21.4. IR (neat) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}O_2$ $[M–H]^-$ *m/z* 225.0921; found 225.0927.



5.2ab1

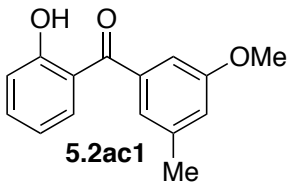
(3,5-Dimethoxyphenyl)(2-hydroxyphenyl)methanone (**5.2ab1**). Prepared using procedure C with no hydrolysis in the same reaction as 2ab2; isolated by column chromatography. Brown oil (0.099 g, 0.384 mmol, 48%). R_f = 0.33 (5% ethyl

acetate in hexanes with 1% acetic acid additive). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 1H), 7.64 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49 (ddd, *J* = 8.8, 7.2, 2.0 Hz, 1H), 7.05 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.86 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 2H), 6.65 (t, *J* = 2.4 Hz, 1H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 163.3, 160.7, 139.8, 136.6, 133.7, 119.2, 118.8, 118.5, 107.1, 104.1, 55.7. IR (neat) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}O_4$ $[M–H]^-$ *m/z* 257.0819; found 257.0826.

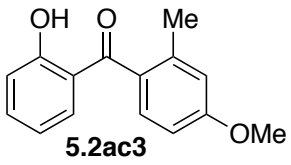


5.2ab2

(2,4-Dimethoxyphenyl)(2-hydroxyphenyl)methanone (**5.2ab2**). Prepared using procedure C with no hydrolysis in the same reaction as 2ab1; isolated by column chromatography. Brown oil (0.066 g, 0.256 mmol, 32%). R_f = 0.22 (5% ethyl acetate in hexanes with 1% acetic acid additive). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (s, 1H), 7.45 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.40 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28 (d, *J* = 8.4 H, 1H), 7.01 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.80 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.56 (dd, *J* = 8, 2 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 163.3, 163.0, 158.7, 136.2, 133.9, 131.1, 120.9, 120.6, 118.6, 118.1, 104.7, 99.0, 55.8, 55.7. IR (thin film, CH_2Cl_2) 1606 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}O_4$ $[M–H]^-$ *m/z* 257.0819; found 227.0832.



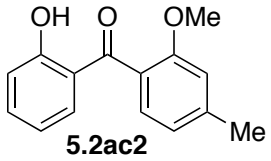
5.2ac1



5.2ac3

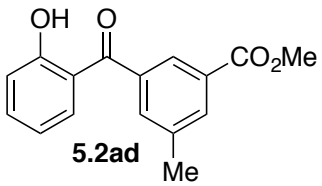
(3-Methoxy-5-methylphenyl)(2-hydroxyphenyl)methanone (**5.2ac1**), (4-methoxy-2-methylphenyl)(2-hydroxyphenyl)methanone (**5.2ac3**). Prepared using procedure A in the same reaction as 2ac2; isolated by column chromatography

as an inseparable mixture of isomers (9:1 2ac1: 2ac3). Yellow oil (0.109 mg, 0.450 mmol, 57%) R_f = 0.42 (10% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) 2ac1: δ 12.01 (s, 1H), 7.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.08–7.04 (m, 2H), 7.00–6.98 (m, 1H), 6.95–6.93 (m, 1H), 6.87 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 3.84 (s, 3H), 2.40 (s, 3H); 2ac3: δ 12.27 (s, 1H), 7.37 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.84–6.76 (m, 3H), 3.86 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, only 2ac1 observed) δ 201.8, 163.3, 159.6, 139.9, 139.2, 136.5, 133.8, 122.5, 119.3, 118.81, 118.76, 118.5, 111.3, 55.6, 21.7. IR (thin film, CH_2Cl_2) 1627 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{14}O_3$ $[M–H]^-$ *m/z* 241.0870; found 241.0870.



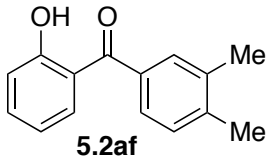
5.2ac2

(2-Methoxy-4-methylphenyl)(2-hydroxyphenyl)methanone (**5.2ac2**). Prepared using procedure A in the same reaction as 2ac1 and 2ac3; isolated by column chromatography. Yellow solid (0.027 g, 0.11 mmol, 14%). mp = 97–99 °C. R_f = 0.31 (10% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.21 (s, 1H), 7.45 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.02 (dd, *J* = 8.4, 9.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.79 (t, *J* = 8.0 Hz, 1H), 3.76 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.3, 163.0, 156.9, 142.8, 136.4, 134.0, 129.2, 125.2, 121.3, 120.5, 118.7, 118.1, 112.4, 55.7, 22.0. IR (thin film, CH_2Cl_2) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{14}O_3$ $[M–H]^-$ *m/z* 241.0870; found 241.0875.



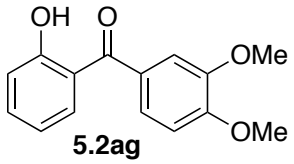
5.2ad

Methyl 5-(2-Hydroxybenzoyl)-3-methylbenzoate (**5.2ad**).[133] Prepared using procedure A with no hydrolysis. Brown oil (0.086 g, 0.321 mmol, 40%). R_f = 0.24 (10% diethyl ether in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.94 (s, 1H), 8.12 (br s, 1H), 8.08 (br s, 1H), 7.68 (br s, 1H), 7.53 (ddd, *J* = 8, 6.4, 1.6 Hz, 2H), 7.09 (dd, *J* = 8.8, 1.2 Hz), 6.95–6.85 (m, 2H), 3.94 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 166.5, 163.4, 139.1, 138.4, 136.8, 133.8, 133.5, 133.5, 130.4, 127.6, 119.1, 119.0, 118.7, 52.5, 21.4. IR (thin film, CH_2Cl_2) 1725, 1628 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{13}O_4$ $[M–H]^-$ *m/z* 269.0819; found 269.0830.



5.2af

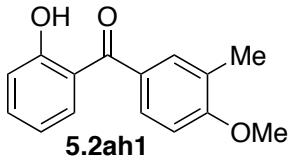
(3,4-Dimethylphenyl)(2-hydroxyphenyl)methanone (**5.2af**). Prepared using procedure C. Yellow oil (0.143 g, 0.630 mmol, 79%). mp = 74–77 °C. R_f = 0.27 (4% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.06 (s, 1H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52–7.47 (m, 2H), 7.42 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.06 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.87 (ddd, *J* = 8.4, 7.6, 2.0, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 163.1, 141.4, 136.9, 136.0, 135.6, 133.6, 130.4, 129.5, 127.1, 119.4, 118.5, 118.3, 20.0, 19.8. IR (thin film, CH_2Cl_2) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}O_2$ $[M–H]^-$ *m/z* 225.0921; found 225.0921.



5.2ag

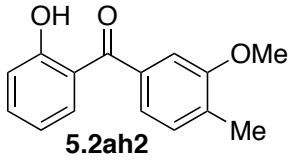
(3,4-Dimethoxyphenyl)(2-hydroxyphenyl)methanone (**5.2ag**). Prepared using procedure A with no hydrolysis. Brown solid (0.192 g, 0.74 mmol, 93%). mp = 67–68 °C. R_f = 0.29 (20% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88 (s, 1H), 7.67 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.33 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.07 (dd, *J* = 8.4, 0.9

Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.89 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 163.0, 152.8, 149.1, 136.0, 133.4, 130.5, 124.4, 119.5, 118.6, 118.5, 112.2, 110.1, 56.3, 56.2. IR (thin film, CH_2Cl_2) 1624 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}O_4$ $[M–H]^-$ *m/z* 257.0819; found 257.0829.



5.2ah1

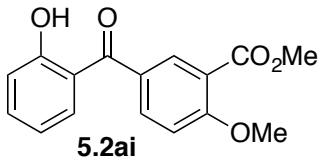
2-Hydroxyphenyl)(4-methoxy-3-methylphenyl)methanone (**5.2ah1**). Prepared using procedure A in the same reaction as 2ah2; isolated by column chromatography. Yellow oil (0.098 g, 0.404 mmol, 50%). R_f = 0.21 (4% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.00 (s, 1H), 7.66 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.50 (ddd, *J* = 8.8, 7.6, 1.6 Hz, 1H), 7.24 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.19 – 7.16 (m, 2H), 7.07 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.88 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 3.89 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 163.2, 157.9, 136.7, 136.2, 133.7, 131.9, 130.2, 122.2, 119.4, 118.7, 118.5, 110.3, 55.6, 16.6. IR (neat) 1629 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{15}O_5$ $[M–H]^-$ *m/z* 241.0870; found 241.0865.



5.2ah2

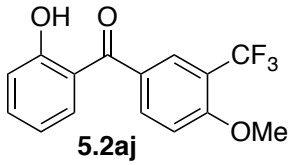
(2-Hydroxyphenyl)(3-methoxy-4-methylphenyl)methanone (**5.2ah2**). Prepared using procedure A in the same reaction as 2ah1; isolated by column chromatography. Yellow solid (0.039 g, 0.16 mmol, 20%). mp = 75-76 °C. R_f = 0.16 (4% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 7.65 (dd, *J* = 8, 1.6 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.49 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.06 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.88 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 3.92 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3,

162.9, 161.2, 135.7, 133.4, 132.1, 129.9, 129.7, 127.0, 119.5, 118.4, 118.3, 109.1, 55.6, 16.3. IR (thin film, CH_2Cl_2) 1625 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{15}O_5$ $[M–H]^-$ *m/z* 241.0870; found 241.0877.



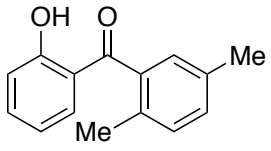
5.2ai

Methyl 5-(2-Hydroxybenzoyl)-2-methoxybenzoate (**5.2ai**). Prepared using procedure A with no hydrolysis. Yellow solid (0.113 g, 0.394 mmol, 49%). mp = 117–119 °C. R_f = 0.07 (25% ethyl acetate in hexanes with 2% acetic acid additive). ^1H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.21 (d, *J* = 2.4 Hz), 7.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.59 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.12–7.06 (m, 2H), 6.91 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 4.01 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 165.8, 163.1, 162.1, 136.3, 135.2, 133.7, 133.2, 129.9, 120.1, 119.2, 118.9, 118.6, 111.9, 56.5, 52.5. IR (thin film, CH_2Cl_2) 1731, 1626 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{13}O_5$ $[M–H]^-$ *m/z* 285.0768; found 285.0762.



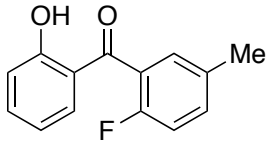
5.2aj

(2-Hydroxyphenyl)(4-methoxy-3-(trifluoromethyl)phenyl)methanone (**5.2aj**). Prepared using procedure A light yellow solid (0.083 g, 0.280 mmol, 35%). mp = 68–70 °C. R_f = 0.34 (20% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1H), 7.99 (d, *J* = 1.9 Hz, 1H), 7.91 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.59–7.49 (m, 2H), 7.12 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.91 (t, *J* = 7.6 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 163.2, 160.6, 136.5, 135.3, 133.0, 129.9, 129.2 (q, *J* = 5.3 Hz), 124.5, 121.8, 119.2 – 118.8 (m), 118.7, 111.7, 56.5. IR (thin film, CH_2Cl_2) 1632 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_4$ $[M–H]^-$ *m/z* 295.0588, found 295.0598.



5.2ak

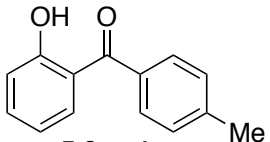
(2,5-Dimethylphenyl)(2-hydroxyphenyl)methanone (**5.2ak**). Prepared using procedure C. Due to low yield, the product was unable to be fully purified, and is obtained with minor impurities. Brown oil (0.026 g, 0.114 mmol, 14%). R_f = 0.43 (10% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 7.49 (ddd, *J* = 8.8, 7.6, 1.6 Hz, 2H), 7.31 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.21 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.07 (br s, 1H), 7.05 (dd, *J* = 8.0, 0.8 Hz, 1H), 2.35 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 163.4, 137.9, 136.8, 135.1, 133.9, 132.4, 131.0, 130.9, 128.0, 120.1, 119.0, 118.4, 21.0, 19.2. IR (neat) 1629 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}O_2$ $[M–H]^-$ *m/z* 225.0921; found 225.0932.



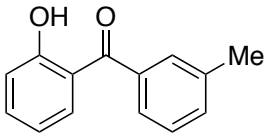
5.2al

(2-Fluoro-5-methylphenyl)(2-hydroxyphenyl)methanone (**5.2al**). Prepared using procedure C. Brown oil (0.024 g, 0.104 mmol, 9%). R_f = 0.47 (10% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.98 (s, 1H), 7.51 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.43 (ddd, *J* = 8.0, 2.8, 1.6 Hz, 1H), 7.32 (ddddd, *J* = 8.0, 7.2, 4.8, 2.4, 0.4 Hz, 1H), 7.25 (dd, *J* = 6.4, 2.0 Hz, 1H), 7.07 (t, *J* = 9.2 Hz, 1H), 7.05 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.86 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 163.1, 157.2 (d, $J_{C–F}$ = 247.3), 137.1, 134.2 (d, $J_{C–F}$ = 3.7 Hz), 133.6 (d, $J_{C–F}$ = 6.2 Hz), 133.5 (d, $J_{C–F}$ = 12.0 Hz), 130.1 (d, $J_{C–F}$ = 2.7 Hz), 126.1 (d, $J_{C–F}$ = 15.9 Hz), 119.9, 119.2, 118.4, 116.1 (d, *J* = 21.5 Hz), 20.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ –117.56. IR (neat) 1629 cm^{-1}. HRMS (QTOF)

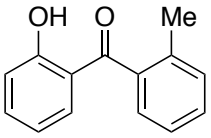
calcd for $C_{14}H_{11}FO_2$ $[M–H]^-$ *m/z* 230.0738; found 230.0742. "Through-space" $^5J_{C–F}$ coupling has been reported in the literature.[134,135]



5.2am1

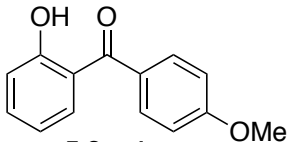


5.2am2

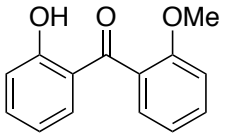


5.2am3

(2-Hydroxyphenyl)(*o*-tolyl)methanone (**5.2am1**), (2-Hydroxyphenyl)(*m*-tolyl)methanone (**5.2aa2**), (2-Hydroxyphenyl)(*p*-tolyl)methanone (**5.2am3**). Prepared using procedure B. Yellow oil (0.128 g, 0.601 mmol, 50%) as an inseparable mixture of regioisomers (1:17:17 2am1:2am2:2am3). R_f = 0.44 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) 2am1: δ 12.03 (s, 1H), 2.45 (s, 3H); 2am2: δ 12.05 (s, 1H), 7.31 (dd, *J* = 8.0, 0.5 Hz, 2H), 2.44 (s, 3H); 2am3: δ 12.25 (s, 1H), 6.81 (ddd, *J* = 8.5, 8, 1 Hz, 1H), 2.30 (s, 3H); Overlapping signals from 2am1 and 2am2: δ 7.63–7.58 (m), 7.53–7.44 (m), 7.41–7.36 (m), 7.07 (m), 6.87 (m). ^{13}C NMR (126 MHz, $CDCl_3$, only 2am1 and 2am2 observed) δ 202.0, 201.5, 163.3, 163.2, 142.9, 138.4, 138.1, 136.4, 136.2, 135.3, 133.8, 133.7, 132.8, 129.7, 129.6, 129.2, 128.3, 126.5, 119.42, 119.36, 118.74, 118.68, 118.49, 118.48, 21.8, 21.5. IR (neat) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{11}O_2$ $[M–H]^-$ *m/z* 211.0765; found 211.0769.



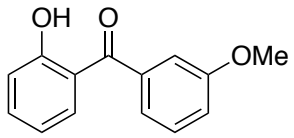
5.2an1



5.2an3

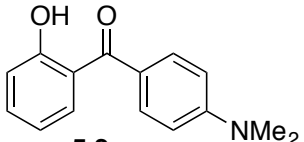
(2-Hydroxyphenyl)(4-methoxyphenyl)methanone (**5.2an1**), (2-Hydroxyphenyl)(2-methoxyphenyl)methanone (**5.2an3**). Prepared using procedure C in the same reaction as 2an2; isolated by column chromatography as an inseparable mixture (10;1 2an1:2an3). Brown oil (0.164 g, 0.719 mmol, 60%) . R_f = 0.24 (8% diethyl ether in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) 2an1: δ 11.96 (s, 1H), 7.74–7.70 (m, 2H), 7.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.49 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.06

(d, *J* = 8.4 Hz, 1H), 7.02–6.97 (m, 2H), 6.88 (ddd, *J* = 8.4, 7.2, 1.2 Hz), 3.90 (s, 3H); 2an3: δ 12.17 (s, 1H), 7.33 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.80 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, only 2an1 observed) δ 200.2, 163.1, 136.0, 133.4, 132.0, 130.5, 119.5, 118.6, 118.5, 113.8, 55.7. IR (neat) 1625 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{11}O_3$ $[M–H]^-$ *m/z* 227.0717; found 227.0711.



5.2an2

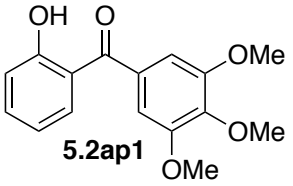
(2-Hydroxyphenyl)(3-methoxyphenyl)methanone (**5.2an2**). Prepared using procedure C in the same reaction as 2an1; isolated by column chromatography. Brown oil (0.038 g, 0.166 mmol, 14%). R_f = 0.32 (8% diethyl ether in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 7.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 (app t, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.20 (m, 1H) 7.12 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.87 (t, *J* = 8.0 Hz, 1H) 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 163.4, 159.7, 139.3, 136.5, 133.7, 129.5, 121.8, 119.3, 118.8, 118.5, 118.1, 114.1, 55.6. IR (neat) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{11}O_3$ $[M–H]^-$ *m/z* 227.0717; found 227.0714.



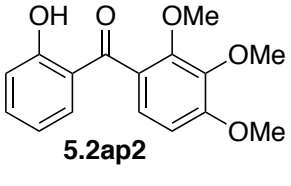
5.2ao

(4-(Dimethylamino)phenyl)(2-hydroxyphenyl)methanone (**5.2ao**). Prepared using procedure C with no hydrolysis. Yellow solid (0.167 g, 0.692 mmol, 87%). mp = 58–60 °C. R_f = 0.33 (20% ethyl acetate in hexanes), 0.45 (3% ethyl acetate in benzene). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.00 (s, 1H), 7.75–7.70 (m, 2H), 7.68 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.05 (dd, *J* = 8.4,

0.8 Hz, 1H), 6.87 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.74–6.69 (m, 2H), 3.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 162.7, 153.3, 135.1, 133.2, 132.5, 125.0, 120.1, 118.4, 118.2, 110.8, 40.2. IR (thin film, CH_2Cl_2) 1621 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{14}NO_2$ $[M–H]^-$ *m/z* 240.1030; found 240.1033.

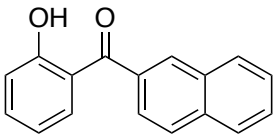


5.2ap1

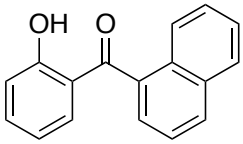


5.2ap2

(3,4,5-Trimethoxyphenyl)(2-hydroxyphenyl)methanone (**5.2ap1**), (2,3,4-Trimethoxy)(2-hydroxyphenyl)methanone (**5.2ap2**). Prepared using procedure A. Yellow oil (0.176 g, 0.610 mmol, 76%) as an inseparable mixture of isomers (5:1 2ap1:2ap2). R_f = 0.22 (15% ethyl acetate in hexanes). 2ap1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.87 (s, 1H), 7.67 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.52 (ddd, *J* = 7.0, 5.7, 1.4 Hz, 1H), 7.09 (d, *J* = 6.7 Hz, 1H), 6.94 (s, 2H), 6.90 (t, *J* = 6.0 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 6H); 2ap2: δ 12.18 (s, 1H), 7.48 (ddd, *J* = 6.9, 5.7, 1.4 Hz, 1H), 7.41 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 2H), 6.83 (t, *J* = 5.9 Hz, 1H), 6.74 (d, *J* = 6.8 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) 2ap1: δ 200.7, 163.3, 153.1, 141.7, 136.4, 133.4, 133.1, 119.3, 118.6, 107.1, 61.2, 56.5; 2ap2: δ 201.0, 163.1, 156.1, 151.9, 142.3, 136.6, 133.9, 125.7, 124.1, 120.4, 118.8, 118.2, 106.9, 62.1, 56.3. IR (neat) 1625 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{15}O_5$ $[M–H]^-$ *m/z* 287.0925; found 287.0931.



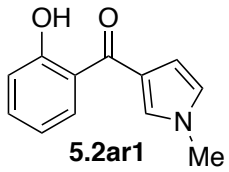
5.2aq1



5.2aq2

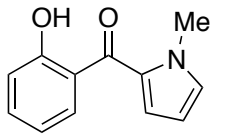
(2-Hydroxyphenyl)(napthanlen-2-yl)methanone (**5.2aq1**), (2-Hydroxyphenyl)(naphthalen-1-yl)methanone (**5.2aq2**). Prepared using procedure A. Yellow solid (0.150 g, 0.61 mmol, 78%) as an inseparable mixture of isomers (>20:1 ratio). mp = 80–82 °C. R_f = 0.19 (4% ethyl acetate in hexanes). ^{1}H NMR

(400 MHz, $CDCl_3$) 2aq1: δ 12.04 (s, 1H), 8.19 (br s, 1H), 7.99–7.91 (m, 3H), 7.78 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66–7.56 (m, 2H), 7.54 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.11 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.90 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H); 2aq2: δ 12.34 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$, only 2aq1 observed) δ 201.6, 163.4, 136.5, 135.3, 135.0, 133.8, 132.3, 130.6, 129.3, 128.5, 128.4, 128.0, 127.2, 125.5, 119.5, 118.9, 118.6. IR (thin film, CH_2Cl_2) 1625 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{14}O_3$ $[M–H]^-$ *m/z* 247.0765; found 247.0767.



5.2ar1

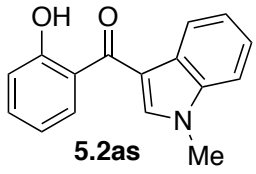
(2-Hydroxyphenyl)(1-methyl-1*H*-pyrrol-3-yl)methanone (**5.2ar1**). Prepared using procedure B in the same reaction as 2ar2; isolated by column chromatography. Brown oil (0.143 g, 0.71 mmol, 59%). R_f = 0.24 (20% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 12.22 (s, 1H), 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.28 (t, *J* = 2.0 Hz, 1H), 7.02 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.90 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.70–6.65 (m, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 162.5, 135.0, 131.9, 128.5, 123.8, 123.4, 120.7, 118.6, 118.2, 111.6, 36.9. IR (neat) 1621 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{11}NO_2$ $[M–H]^-$ *m/z* 200.0717; found 200.0720.



5.2ar2

(2-Hydroxyphenyl)(1-methyl-1*H*-pyrrol-2-yl)methanone (**5.2ar2**). Prepared using procedure B in the same reaction as 2ar1; isolated by column chromatography. Brown oil (0.018 g, 0.09 mmol, 7%). R_f = 0.48 (20% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (ddd, *J* = 8.8, 7.6, 1.6 Hz, 1H), 7.01 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.94 (t, *J* = 2.0 Hz, 1H),

6.89 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.83 (dd, *J* = 4.0, 1.6 Hz, 1H), 6.20 (dd, *J* = 4.0, 2.4 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 162.2, 134.9, 132.3, 131.7, 129.7, 122.7, 120.7, 118.5, 118.0, 108.5, 37.1. IR (thin film, CH_2Cl_2) 1621 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{11}NO_2$ $[M–H]^-$ *m/z* 200.0717; found 200.0719.



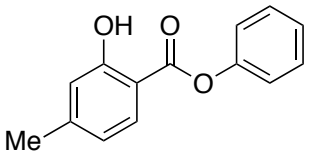
5.2as

(2-Hydroxyphenyl)(1-methyl-1*H*-indol-3-yl)methanone (**5.2as**). Prepared using procedure A. Brown solid (0.146 g, 0.581 mmol, 73%). mp = 111–116 °C. R_f = 0.47 (50% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.03 (s, 1H), 8.33 – 8.26 (m, 1H), 7.85 (dd, *J* = 8.0, 9.6 Hz, 1H), 7.63 (s, 1H), 7.46 (ddd, *J* = 8.8, 7.6, 2.0 Hz), 7.40 – 7.31 (m, 3H), 7.05 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.91 (ddd, *J* = 8.4, 7.6, 1.2 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 162.0, 137.5, 137.0, 134.7, 131.5, 127.4, 123.9, 122.9, 122.5, 121.5, 118.7, 118.2, 114.8, 109.9, 33.8. IR (thin film, CH_2Cl_2) 1679 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{13}NO_2$ $[M–H]^-$ *m/z* 250.0874; found 250.0873.

SALICYLATE ESTERS

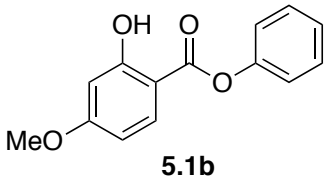
General procedure for salicylate ester synthesis. Salicyclic acid (10 mmol, 1 equiv.) and phenol (4.70 g, 50 mmol, 5 equiv.) were weighed in a 5 dram reaction vial, and then 10 mL of dry toluene was added. Phosphorus oxychloride (0.61g, 0.37 mL, 4 mmol, 0.4 equiv.) was dripped in to the solution via syringe. A stir bar was then added and the reaction vial was sealed. The reaction mixture was then heated at 110 °C in an aluminum heating block on a hot plate fitted with a thermocouple for 16-18 h. The mixture was allowed to cool to room temperature, transferred to a separatory funnel, and quenched with saturated aqueous sodium carbonate solution (3 × 10 mL). The aqueous washes were then extracted with diethyl ether (3 × 10 mL). The organic layers were combined, dried with sodium

sulfate, and concentrated *in vacuo*. The crude product was purified by column chromatography.



5.1a

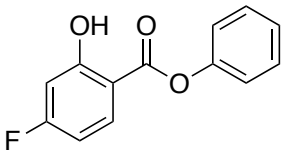
Phenyl 2-Hydroxy-4-methylbenzoate (**5.1a**). White solid (1.20 g, 5.30 mmol, 53%). mp = 43–44 °C. R_f = 0.33 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.49–7.39 (m, 2H), 7.34–7.25 (m, 1H), 7.21 (d, *J* = 1.3 Hz, 1H), 7.19 (dd, *J* = 2.1, 0.9 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 162.3, 150.3, 148.2, 130.3, 129.7, 126.4, 121.8, 120.9, 118.1, 109.4, 22.1. IR (neat) 1683 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{12}O_3$ $[M–H]^-$ *m/z* 227.0714, found 227.0724.



5.1b

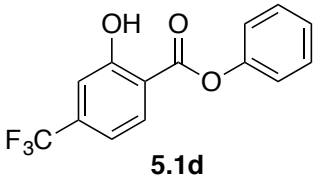
Phenyl 2-Hydroxy-4-methoxybenzoate (**5.1b**). Phenol (264 mg, 2.8 mmol, 1.4 equiv.), 4-methoxysalicylic acid (336.3 mg, 2.0 mmol, 1 equiv.), and DMAP (49 mg, 0.4 mmol, 0.2 equiv.) were dissolved in methylene chloride (8 mL). DCC (743 mg, 3.6 mmol, 1.8 equiv.) was added; the reaction mixture was heated to reflux and allowed to reflux overnight. Removal of the solvent and purification by column chromatography (2% ethyl acetate in hexanes to 3% ethyl acetate in hexanes) ultimately gave a white solid (0.358 g, 1.46 mmol, 73%). mp = 59–61 °C. R_f = 0.28 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.49–7.39 (m, 2H), 7.34–7.25 (m, 1H), 7.24–7.15 (m, 2H), 6.53 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 166.4, 164.7, 150.4, 131.9, 129.7, 126.3,

121.9, 108.2, 105.0, 101.0, 55.7. IR (neat) 1671 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{12}O_4$ $[M–H]^-$ *m/z* 243.0663, found 243.0661.



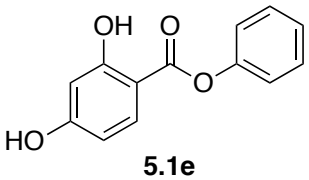
5.1c

Phenyl 4-Fluoro-2-hydroxybenzoate (**5.1c**). White solid (1.20 g, 5.20 mmol 52%). mp = 58–60 °C. R_f = 0.32 (5% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 10.73 (d, *J* = 1.6 Hz, 1H), 8.09 (dd, *J* = 8.9, 6.5 Hz, 1H), 7.51–7.40 (m, 2H), 7.37–7.27 (m, 1H), 7.24–7.16 (m, 2H), 6.77–6.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 167.9 (d, $J_{C–F}$ = 255.4 Hz), 164.5 (d, $J_{C–F}$ = 14.3 Hz), 150.1, 132.8 (d, $J_{C–F}$ = 11.5 Hz), 129.6, 126.6, 121.7, 108.8 (d, $J_{C–F}$ = 2.4 Hz), 108.0 (d, $J_{C–F}$ = 22.7 Hz), 104.8 (d, $J_{C–F}$ = 24.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ –99.65. IR (neat) 1682 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_9FO_3$ $[M–H]^-$ *m/z* 231.0463, found 231.0473.



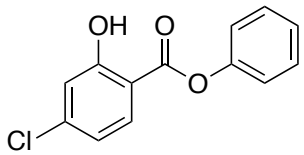
5.1d

Phenyl 2-Hydroxy-4-(trifluoromethyl)benzoate (**5.1d**). White solid (1.24 g, 4.40 mmol, 44%). mp = 68–69 °C. R_f = 0.39 (5% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.52–7.41 (m, 2H), 7.37–7.28 (m, 2H), 7.24–7.18 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 162.2, 150.0, 137.7 (q, $J_{C–F}$ = 32.9 Hz), 131.4, 129.9, 127.3, 123.2 (q, $J_{C–F}$ = 273.8 Hz), 121.5, 115.8 (q, $J_{C–F}$ = 3.6 Hz), 115.3 (q, $J_{C–F}$ = 4.0 Hz), 114.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.85. IR (neat) 1686 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_9F_3O_3$ $[M–H]^-$ *m/z* 281.0431, found 281.0436.



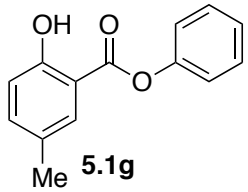
5.1e

Phenyl 2,4-Dihydroxybenzoate (**5.1e**). White solid (0.65g, 2.80 mmol, 28%). mp = 144–145 °C. R_f = 0.28 (20% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 6.47–6.38 (m, 2H), 5.78 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 164.3, 162.8, 150.2, 132.6, 129.8, 126.5, 121.8, 108.5, 105.4, 103.5, 77.5, 77.2, 76.8. IR (neat) 1658 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{10}O_4$ $[M–H]^-$ *m/z* 229.0506, found 229.0510 (avg of 6).



5.1f

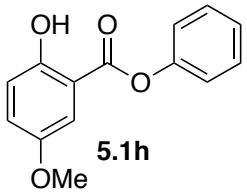
Phenyl 4-Chloro-2-hydroxybenzoate (**5.1f**). White solid (1.47g, 5.9 mmol, 59%). mp = 52–53 °C. R_f = 0.40 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.50–7.40 (m, 2H), 7.36–7.27 (m, 1H), 7.24–7.16 (m, 2H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.95 (dd, *J* = 8.6, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 162.8, 150.1, 142.5, 131.5, 129.8, 126.7, 121.7, 120.4, 118.2, 110.6. IR (neat) 1673 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_9ClO_3$ $[M–H]^-$ *m/z* 247.0167, found 247.0161.



5.1g

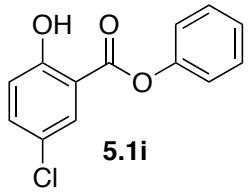
Phenyl 2-Hydroxy-5-methylbenzoate (**5.1g**). White solid (1.61 g, 7.70 mmol, 77%). mp = 87–89 °C. R_f = 0.36 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.50–7.39 (m, 2H), 7.34

(dd, *J* = 8.5, 2.3 Hz, 1H), 7.35–7.26 (m, 1H), 7.24–7.16 (m, 3H), 6.94 (d, *J* = 8.5 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 160.3, 150.3, 137.6, 130.1, 129.8, 128.8, 126.5, 121.8, 117.7, 111.5, 20.6. IR (neat) 1682 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{12}O_3$ $[M–H]^-$ *m/z* 227.0714, found 227.0707.



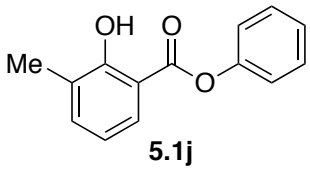
5.1h

Phenyl 2-Hydroxy-5-methoxybenzoate (**5.1h**). White solid (0.75 g, 3.10 mmol, 31%). mp = 40–41 °C. R_f = 0.26 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.51 (d, *J* = 3.1 Hz, 1H), 7.51–7.40 (m, 2H), 7.36–7.27 (m, 1H), 7.27–7.15 (m, 2H), 7.16 (dd, *J* = 9.1, 3.2 Hz, 1H), 6.98 (d, *J* = 9.1 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 156.9, 152.3, 150.2, 129.8, 126.6, 125.2, 121.8, 119.0, 112.1, 111.4, 77.5, 77.2, 76.8, 56.1. IR (neat) 1687 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{12}O_4$ $[M–H]^-$ *m/z* 243.0663, found 243.0653 (avg of 8).



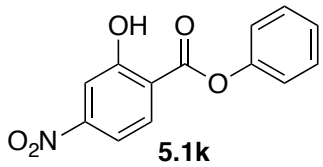
5.1i

Phenyl 5-Chloro-2-hydroxybenzoate (**5.1i**). White solid (1.30 g, 5.20 mmol, 52%). mp = 94–96 °C. R_f = 0.39 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.04 (d, *J* = 2.7 Hz, 1H), 7.52–7.41 (m, 3H), 7.37–7.27 (m, 1H), 7.22–7.18 (m, 2H), 6.99 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 160.9, 150.0, 136.5, 129.8, 129.7, 126.7, 124.4, 121.6, 119.6, 112.9, 77.5, 77.2, 76.8. IR (neat) 1685 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_9ClO_3$ $[M–H]^-$ *m/z* 247.0167, found 247.0179 (avg of 6).



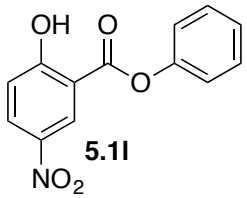
5.1j

Phenyl 2-Hydroxy-3-methylbenzoate (**5.1j**). White solid (0.76 g, 3.30 mmol, 33%). mp = 145–145 °C. R_f = 0.45 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 7.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.49–7.40 (m, 2H), 7.39 (ddt, *J* = 7.4, 1.7, 0.8 Hz, 1H), 7.35–7.25 (m, 1H), 7.24–7.17 (m, 2H), 6.87 (t, *J* = 7.7 Hz, 1H), 2.30 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 160.8, 150.3, 137.4, 129.8, 128.0, 127.1, 126.5, 121.8, 118.9, 111.2, 15.8. IR (neat) 1685 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{12}O_3$ $[M–H]^-$ *m/z* 227.0714, found 227.0725 (avg of 6).



5.1k

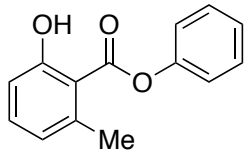
Phenyl 2-Hydroxy-4-nitrobenzoate (**5.1k**). White solid (3 mmol scale, 0.237 g, 0.90 mmol, 30%). mp = 148–150 °C. R_f = 0.36 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.73 (s, 1H), 8.27 (d, *J* = 8.7 Hz, 1H), 7.87 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 162.7, 152.7, 149.8, 131.9, 130.0, 127.1, 121.5, 116.8, 113.9, 113.4. IR (neat) 1686 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_9NO_5$ $[M–H]^-$ *m/z* 258.0408, found 258.0420.



5.1l

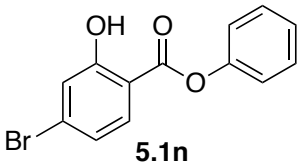
Phenyl 2-Hydroxy-5-nitrobenzoate (**5.1l**). White solid (1.558 g, 6.01 mmol 60%). mp = 148–150 °C. R_f = 0.18 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 11.17 (s, 1H), 9.04 (d, *J* = 2.8 Hz, 1H), 8.42 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.54–7.44 (m, 2H), 7.41–7.31 (m, 1H), 7.28–7.20 (m, 2H), 7.16 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 166.8, 149.8, 140.4, 131.3, 130.0, 127.2, 127.1, 121.5, 119.1, 111.9. IR (neat) 1693 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_9NO_5$ $[M–H]^-$ *m/z* 258.0408, found 258.0418.



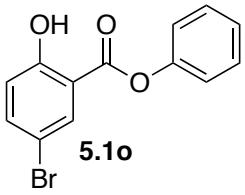
5.1m

Phenyl 2,6-Dihydroxybenzoate (**5.1m**). White solid (0.88 g, 3.80 mmol, 38%). mp = 91–94 °C. R_f = 0.36 (5% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 2H), 7.54–7.44 (m, 2H), 7.44–7.33 (m, 2H), 7.27–7.18 (m, 2H), 6.56 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 161.3, 148.6, 137.6, 130.1, 127.5, 122.1, 108.7, 99.8. IR (neat) 1683 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{10}O_4$ $[M–H]^-$ *m/z* 229.0506, found 229.0508 (avg of 11).



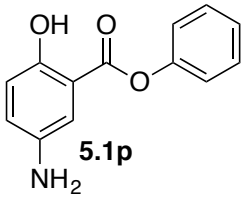
5.1n

Phenyl 4-Bromo-2-hydroxybenzoate (**5.1n**). Off-white solid (5 mmol scale, 1.16g, 3.95 mmol, 79%). mp = 69–72 °C. R_f = 0.38 (5% ethyl acetate in hexanes).^1H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.50–7.40 (m, 2H), 7.36–7.27 (m, 1H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.24–7.16 (m, 2H), 7.11 (dd, *J* = 8.5, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 162.7, 150.0, 131.4, 131.0, 129.8, 126.7, 123.2, 121. 7, 121.3, 111.0. IR (neat) 1673 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_9BrO_3$ $[M–H]^-$ *m/z* 290.9662, found 290.9667.



5.1o

Phenyl 5-Bromo-2-hydroxybenzoate (**5.1o**). White solid (1.11 g, 3.80 mmol, 38%). mp = 94–96 °C. R_f = 0.36 (5% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 8.19 (d, *J* = 2.5 Hz, 1H), 7.61 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.51–7.41 (m, 2H), 7.37–7.27 (m, 1H), 7.23–7.18 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 161.3, 150.0, 139.3, 132.7, 129.9, 126.8, 121.6, 120.0, 113.5, 111.3, 77.5, 77.2, 76.8. IR (neat) 1694 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_9BrO_3$ $[M–H]^-$ *m/z* 290.9662, found 290.9653.

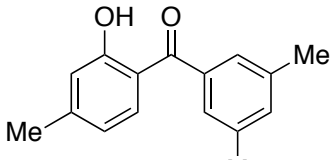


5.1p

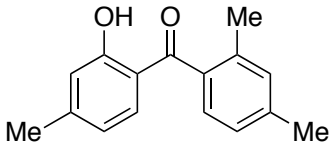
Phenyl 5-Amino-2-hydroxybenzoate (**5.1p**). Brown solid (0.383 g, 1.70 mmol, 17%). mp = 72–73 °C. R_f = 0.28 (40% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.49–7.39 (m, 2H), 7.37 (d, *J* = 2.9 Hz, 1H), 7.34–7.25 (m, 1H), 7.24–7.15 (m, 2H), 6.94 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 3.52 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 155.6, 150.3, 138.7, 129.7, 126.4, 125.3, 121.8, 118.6, 114.9, 111.7, 77.5, 77.2, 76.8. IR (neat) 1678 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{11}NO_3$ $[M–H]^-$ *m/z* 228.0666, found 228.0679 (avg of 8).

SALICYLATE SUBSTRATE SCOPE

For all acylations of *m*-xylene, yield determined for the desired products based on relative integration in the ^{1}H NMR.

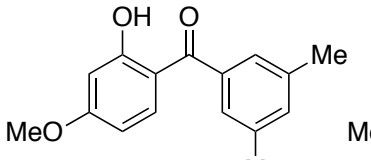


5.2ba1

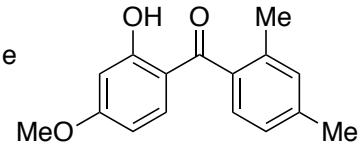


5.2ba2

(3,5-Dimethylphenyl)(2-hydroxy-4-methylphenyl)methanone (**5.2ba1**), (2,4-Dimethylphenyl)(2-hydroxy-4-methylphenyl)methanone (**5.2ba2**): Prepared using procedure C; isolated by column chromatography. Yellow solid (0.086g, 0.358 mmol, 45%), as an inseparable mixture (2.3:1 2ba1/2ba2:2aa1, 10:1 2ba1:2ba2). R_f = 0.36 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) 2ba1: δ 12.15 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.26–7.22 (m, 2H), 7.20 (m, 1H), 6.88–6.85 (m, 1H), 6.68 (dd, *J* = 8.2, 1.6 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 6H); 2ba2: δ 11.95 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, only 2ba1 observed) δ 201.7, 163.5, 148.0, 138.3, 138.1, 133.7, 133.4, 126.9, 120.0, 118.5, 117.2, 22.1, 21.4. IR (neat) 1624 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_2$ $[M–H]^-$ *m/z* 239.1078, found 239.1086.



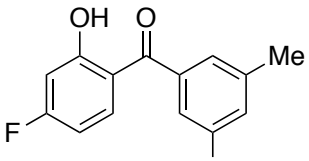
5.2bb1



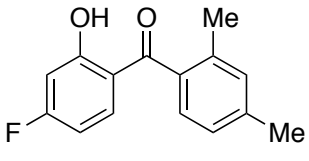
5.2bb2

(3,5-Dimethylphenyl)(2-hydroxy-4-methoxyphenyl)methanone (**5.2bb1**) , (2,4-Dimethylphenyl)(2-hydroxy-4-methoxyphenyl)methanone (**5.2bb2**). Prepared using procedure C; isolated by column chromatography. Brown oil (0.0769g, 0.300 mmol, 38%), as an inseparable mixture (4:1 2bb1/2bb2:2aa1, 10:1 2bb1:2bb2). R_f = 0.28 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) 2bb1: δ 12.72 (s, 1H), 7.52 (d, *J* = 9.0 Hz), 7.22 (br s, 2H), 6.51 (d, *J* = 2.5 Hz, 1H), 6.41 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.86 (s, 3H), 2.38 (s, 6H); 2bb2: δ 12.83 (s, 1H), 3.85 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$, only 2bb1 observed) δ 200.7, 166.4, 166.3, 138.5, 135.5, 133.9, 133.2, 126.7, 113.4, 107.4, 101.2,

55.8, 21.4. IR (neat) 1621 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_3$ $[M–H]^-$ *m/z* 256.1099, found 255.1036.

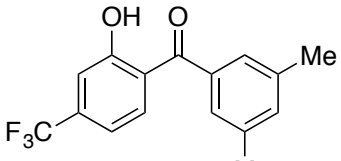


5.2bc1

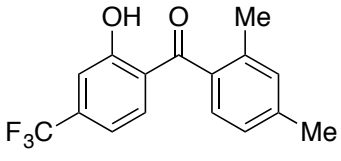


5.2bc2

(3,5-Dimethylphenyl)(4-fluoro-2-hydroxyphenyl)methanone (**5.2bc1**), (2,4-Dimethylphenyl)(4-fluoro-2-hydroxyphenyl)methanone (**5.2bc2**). Prepared using procedure C; isolated by column chromatography. Yellow oil (0.102g, 0.416 mmol, 52%), as an inseparable mixture (4:1 2bc1/2bc2:2aa1, >20:1 2bc1:2bc2). R_f = 0.32 (5% Ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) 2bc1: δ 12.46 (d, $^5J_{H–F}$ = 1.5 Hz, 1H), 7.62 (dd, *J* = 9.0, 6.6 Hz, 1H), 7.24–7.23 (m, 2H), 7.23–7.21 (m, 1H), 6.74 (dd, *J* = 10.4, 2.5 Hz, 1H), 6.58 (ddd, *J* = 9.0, 8.0, 2.5 Hz, 1H) 2.39 (s, 6H); 2bc2: δ 12.63 (d, $^5J_{H–F}$ = 1.4 Hz, 1H), 2.39 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) -98.79 (q, J = 8.6 Hz). ^{13}C NMR (126 MHz, $CDCl_3$, only 2bc1 observed) δ 201.2, 167.5 (d, $^1J_{C–F}$ = 257.1 Hz), 165.9 (d, $^3J_{C–F}$ = 14.2 Hz), 138.3, 138.0, 136.2 (d, $^3J_{C–F}$ = 11.7 Hz), 126.8, 116.5 (d, $^4J_{C–F}$ = 2.2 Hz), 107.0 (d, $^2J_{C–F}$ = 22.5 Hz), 105.1 (d, $^2J_{C-F}$ = 23.8 Hz), 21.4. ^{19}F NMR (471 MHz, $CDCl_3$) –99.43 (q, *J* = 8.3 Hz). IR (neat) 1623 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}FO_2$ $[M–H]^-$ *m/z* 243.0827, found 243.0833.



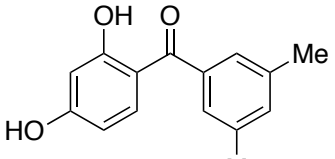
5.2bd1



5.2bd2

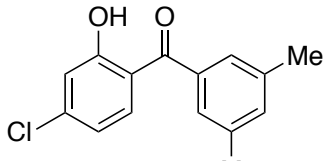
(3,5-Dimethylphenyl)(2-hydroxy-4-(trifluoromethyl)phenyl)methanone (**5.2bd1**), (2,4-Dimethylphenyl)(2-hydroxy-4-(trifluoromethyl)phenyl)methanone (**5.2bd2**). Prepared using procedure C; isolated by column chromatography. Brown oil (0.105g, 0.357 mmol, 45%), as an inseparable mixture (7:1 2bd1/2bd2:2aa1, 13:1 2bd1:2bd2). R_f = 0.39 (5% ethyl acetate in hexanes). ^{1}H (500 MHz, CD_2Cl_2)

2bd1: δ 11.99 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 1.3 Hz, 1H), 7.29 (s, 3H), 7.14 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.40 (s, 3H); 2bd2: δ 12.26 (s, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 7.07 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.40 (s, 6H). ^{13}C (126 MHz, CD_2Cl_2, only 2bd1 observed) δ 201.1, 163.4, 139.0, 137.8, 137.2 (q, $^{2}J_{C–F}$ = 32.8 Hz), 135.0, 134.8, 127.5, 127.4, 123.8 (q, $^{1}J_{C–F}$ = 273.4 Hz), 116.0 (q, $^{3}J_{C–F}$ = 3.9 Hz), 115.5 (q, $^{3}J_{C–F}$ = 3.6 Hz), 21.5. ^{19}F (471 MHz, CD_2Cl_2) 2bd1: δ –64.13; 2bd2: δ –64.18. IR (neat) 1639 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{13}F_3O_2$ $[M–H]^-$ *m/z* 293.0795, found 293.0789.

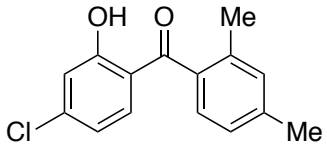


5.2be

(3,5-Dimethylphenyl)(2,4-dihydroxyphenyl)methanone (**5.2be**). Prepared using procedure C; isolated by column chromatography. Yellow solid (0.0306g, 0.126 mmol, 16%). R_f = 0.16 (10% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, Acetone-d_6) δ 12.70 (s, 1H), 9.64 (br s, 1H), 7.52–7.48 (m, 1H), 7.25 (s, 1H), 7.24 (s, 2H), 6.45–6.41 (m, 2H), 2.38 (s, 6H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 201.2, 167.3, 165.8, 139.5, 138.9, 136.9, 133.7, 127.2, 113.5, 108.7, 103.8, 21.3. IR (neat) 1623 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{14}O_3$ $[M–H]^-$ *m/z* 241.0870, found 241.0874.



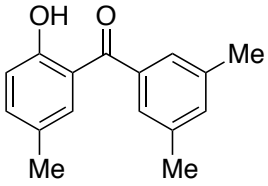
5.2bf1



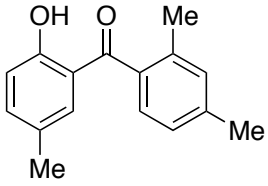
5.2bf2

(3,5-Dimethylphenyl)(4-chloro-2-hydroxyphenyl)methanone (**5.2bf1**), (2,4-Dimethylphenyl)(4-chloro-2-hydroxyphenyl)methanone (**5.2bf2**). Prepared using procedure C; isolated by column chromatography. Brown solid (0.0897g, 0.344 mmol, 43%), as an inseparable mixture (18:1 2bf1/2bf2:2aa1, 20:1 2bf1:2bf2). R_f = 0.40 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) 2bf1: δ 12.22

(s, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.24 (br s, 2H), 7.23 (br s, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.1 Hz, 1H), 2.39 (s, 6H); 2bf2: δ 12.42 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, only 2bf1 observed) δ 201.5, 164.0, 142.2, 138.4, 137.8, 134.7, 134.0, 126.9, 119.4, 118.6, 118.0, 21.4. IR (neat) 1618 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}ClO_2$ $[M–H]^-$ *m/z* 259.0531, found 259.0533.

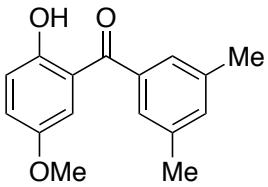


5.2bg1

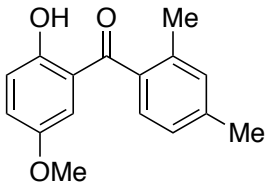


5.2bg2

(3,5-Dimethylphenyl)(2-hydroxy-5-methylphenyl)methanone (**5.2bg1**), (2,4-Dimethylphenyl)(2-hydroxy-5-methylphenyl)methanone (**5.2bg2**). Prepared using procedure C; isolated by column chromatography. Yellow solid (0.0574g, 0.239 mmol, 30%), as an inseparable mixture (1.8:1 2bg1/2bg2:2aa1, 18:1 2bg1:2bg2). R_f = 0.37 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) 2bg1: δ 11.87 (s, 1H), 7.36 (d, *J* = 1.9 Hz, 1H), 7.31 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.26 (m, 1H), 7.22 (br s, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 2.39 (s, 6H), 2.25 (s, 3H); 2bg1: δ 12.12 (s 1H). ^{13}C NMR (126 MHz, $CDCl_3$, only 2bg1 observed) δ 202.3, 161.2, 138.3, 137.4, 133.5, 133.4, 127.8, 126.9, 119.1, 118.4, 118.2, 21.4, 20.6. IR (neat) 1630 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_2$ $[M–H]^-$ *m/z* 239.1078, found 239.1089.



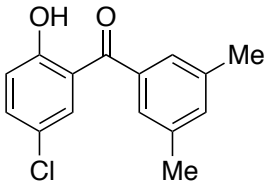
5.2bh1



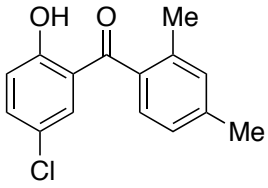
5.2bh2

(3,5-Dimethylphenyl)(2-hydroxy-5-methoxyphenyl)methanone (**5.2bh1**), (2,4-Dimethylphenyl)(2-hydroxy-5-methoxyphenyl)methanone (**5.2bh2**). Prepared using procedure C; isolated by column chromatography. Orange oil (0.085g, 0.331 mmol, 41%), as an inseparable mixture (2.6:1 2bh1/2bh2:2aa1, >20:1

2bh1:2bh2). R_f = 0.26(5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 11.61 (s, 1H), 7.29 (br s, 2H), 7.22 (br s, 1H), 7.14 (dd, *J* = 9.1, 3.1 Hz, 1H), 7.08 (d, *J* = 3.1 Hz, 1H), 7.01 (d, *J* = 9.1 Hz, 1H), 3.70 (s, 3H), 2.39 (s, 6H) 2bh2: δ 11.89 (s, 1H), 3.64 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, only 2bh1 observed) δ 201.8, 157.6, 151.5, 138.2, 138.1, 133.7, 126.9, 124.1, 119.3, 119. 0, 116.6, 56.1, 21.4. IR (neat) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_3$ $[M–H]^-$ *m/z* 255.1027, found 255.1034.

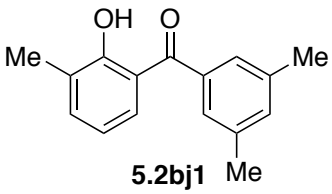


5.2bi1

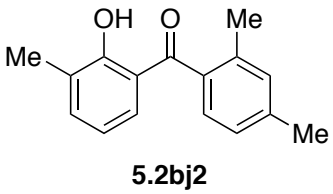


5.2bi2

(3,5-Dimethylphenyl)(5-chloro-2-hydroxyphenyl)methanone (**5.2bi1**), (2,4-Dimethylphenyl)(5-chloro-2-hydroxyphenyl)methanone (**5.2bi2**). Prepared using procedure C; isolated by column chromatography. Yellow solid (0.092g, 0.351 mmol, 44%), as an inseparable mixture (5.5:1 2bi1/2bi2:2aa1, 19:1 2bi1:2bi2). R_f = 0.39 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) 2bi1: δ 11.94 (s, 1H), 7.56 (d, *J* = 2.6 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.25 (m, 3H), 7.02 (d, *J* = 8.9 Hz, 1H), 2.40 (s, 6H); 2bi2:z δ 12.18 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, only 2bi1 observed) δ 201.3, 161.8, 138.5, 137.5, 136.2, 134.1, 132.6, 126.8, 123.4, 120.10, 120.08, 21.4. IR (neat) 1621 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}ClO_2$ $[M–H]^-$ *m/z* 259.0531, found 259.0535.



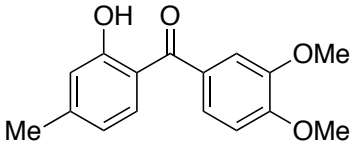
5.2bj1



5.2bj2

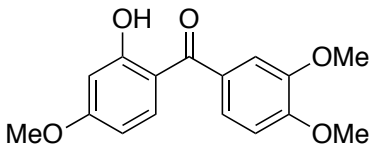
(3,5-Dimethylphenyl)(2-hydroxy-3-methylphenyl)methanone (**5.2bj1**), (2,4-Dimethylphenyl)(2-hydroxy-3-methylphenyl)methanone (**5.2bj2**). Prepared using procedure C; isolated by column chromatography. Brown oil (0.082g, 0.343

mmol, 43%), as an inseparable mixture (3:1 2bj1/2bj2:2aa1, 10:1 2bj1:2bj2). R_f = 0.45 (5% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.15 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.25 (br s, 2H), 7.20 (br s, 1H) 6.87 (m, 1H), 6.68 (dd, *J* = 8.0, 0.9 Hz, 1H), 2.38 (s, 6H), 2.37 (s, 3H); 2bj2: δ 11.95 (s, 1H), 7.55 (s, 1H), 6.95 (s, 2H), 2.40 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$, only 2bj1 observed) δ 201.8, 163.5, 148.0, 138.3, 138.1, 133.7, 133.4, 126.9, 126.8, 120.0, 118.4, 117.2, 22.1. IR (neat) 1618 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_2$ $[M–H]^-$ *m/z* 239.1078, found 239.1073.



5.2ca

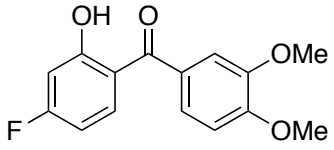
(3,4-Dimethoxyphenyl)(2-hydroxy-4-methylphenyl)methanone (**5.2ca**). Prepared using procedure A; isolated by column chromatography. Light yellow solid (0.169g, 0.616 mmol, 77%). mp = 135–138 °C. R_f = 0.39 (30% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.00 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.36–7.23 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.88 (s, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 4H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 163.2, 152.5, 149.0, 147.6, 133.3, 130.7, 124.1, 119.9, 118.5, 117.2, 112.1, 110.1, 56.2, 56.1, 22.0. IR (thin film, CH_2Cl_2) 1625 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_4$ $[M–H]^-$ *m/z* 271.0976, found 271.0977.



5.2cb

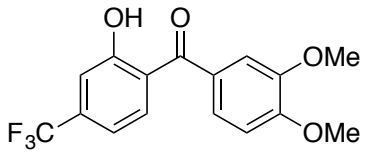
(3,4-Dimethoxyphenyl)(2-hydroxy-4-methoxyphenyl)methanone (**5.2cb**). Prepared using procedure A; isolated by column chromatography. Light yellow solid (0.183 g, 0.640 mmol, 80%). mp = 135–137 °C. R_f = 0.29 (30% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 7.59 (d, *J* = 9.0

Hz, 1H), 7.31–7.23 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.43 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 166.2, 166.0, 152.3, 149.1, 135.1, 130.9, 123.7, 113.4, 112.0, 110.1, 107.3, 101.3, 56.2, 56.2, 55.7. IR (thin film, CH_2Cl_2) 1623 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_5$ $[M–H]^-$ *m/z* 287.0925, found 287.0922.



5.2cc

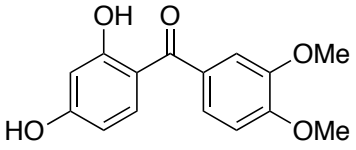
(3,4-Dimethoxyphenyl)(4-fluoro-2-hydroxyphenyl)methanone (**5.2cc**). Prepared using procedure A; isolated by column chromatography. Light yellow solid (0.656 mmol, 0.182 g, 82%). mp = 103–105 °C. R_f = 0.37 (30% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.31 (s, 1H), 7.69 (dd, *J* = 8.9, 6.6 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 10.4, 2.5 Hz, 1H), 6.60 (td, *J* = 8.6, 2.6 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 168.5, 165.9, 165.5 (d, *J* = 14.3 Hz), 152.8, 149.2, 135.6 (d, *J* = 11.6 Hz), 130.3, 124.1, 116.4 (d, *J* = 2.3 Hz), 111.0 (d, *J* = 189.5 Hz), 106.7 (d, *J* = 22.5 Hz), 105.1 (d, *J* = 23.8 Hz), 56.2, 56.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –100.00. IR (thin film, CH_2Cl_2) 1628 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}FO_4$ $[M–H]^-$ *m/z* 275.0725, found 275.0724.



5.2cd

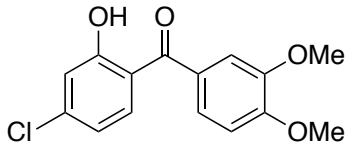
(3,4-Dimethoxyphenyl)(2-hydroxy-4-(trifluoromethyl)phenyl)methanone (**5.2cd**). Prepared using procedure A; isolated by column chromatography. Yellow solid (0.230 g, 0.705 mmol, 88%). mp = 74–76 °C. R_f = 0.37 (30% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 7.79 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.36–7.31 (m, 3H), 7.13 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H),

3.99 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 162.7, 153.4, 149.4, 136.7 (q, *J* = 33.0 Hz), 133.8, 129.8, 124.8, 123.3 (q, *J* = 273.5 Hz), 121.7, 115.8 (q, *J* = 3.9 Hz), 114.9 (q, *J* = 3.6 Hz), 112.1, 110.2, 56.3, 56.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.78. IR (thin film, CH_2Cl_2) 1638 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{13}F_3O_4$ $[M–H]^-$ *m/z* 325.0693, found 325.0689.



5.2ce

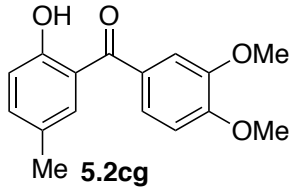
(3,4-Dimethoxyphenyl)(2,4-dihydroxyphenyl)methanone (**5.2ce**). Prepared using procedure A; isolated by column chromatography. Light yellow solid (0.146 g, 0.536 mmol, 67%). mp = 174–172 °C. R_f = 0.36 (40% hexanes in ethyl acetate). ^{1}H NMR (400 MHz, Acetone-d_6) δ 12.51 (s, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.18–7.11 (m, 2H), 6.95 (d, *J* = 8.9 Hz, 1H), 6.34–6.27 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 199.4, 167.0, 165.5, 153.5, 150.1, 136.6, 131.6, 124.2, 113.5, 113.2, 111.5, 108.5, 103.9, 56.3, 56.2. IR (thin film, CH_2Cl_2) 1626 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{14}O_5$ $[M–H]^-$ *m/z* 273.0768, found 273.0766.



5.2cf

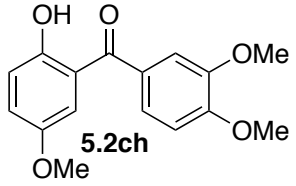
(3,4-Dimethoxyphenyl)(4-chloro-2-hydroxyphenyl)methanone (**5.2cf**). Prepared using procedure A; isolated by column chromatography. Light yellow solid (0.108 g, 0.368 mmol, 46%). mp = 114–116 °C. R_f = 0.37 (30% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.06 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.32–7.28 (m, 2H), 7.09 (d, *J* = 2.1 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 163.7, 153.0, 149.3, 141.8, 134.3, 130.2, 124.3, 119.3, 118.6, 118.1,

112.1, 110.2, 56.3, 56.2. IR (thin film, CH_2Cl_2) 1622 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}ClO_4$ $[M–H]^-$ *m/z* 291.0430, found 291.0432.



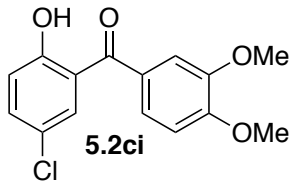
5.2cg

(3,4-Dimethoxyphenyl)(2-hydroxy-5-methylphenyl)methanone (**5.2cg**). Prepared using procedure A; isolated by column chromatography. Light yellow solid (0.211 g, 0.776 mmol, 97%). mp = 113–116 °C. R_f = 0.34 (30% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.35–7.29 (m, 3H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 160.9, 152.7, 149.1, 137.0, 133.1, 130.7, 127.7, 124.3, 119.2, 118.2, 112.2, 110.1, 56.2, 56.2, 20.7. IR (thin film, CH_2Cl_2) 1630 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_4$ $[M–H]^-$ *m/z* 271.0976, found 271.0982.



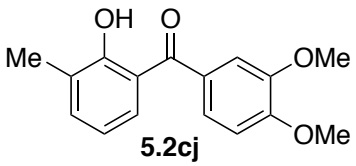
5.2ch

(3,4-Dimethoxyphenyl)(2-hydroxy-5-methoxyphenyl)methanone (**5.2ch**). Prepared using procedure A; isolated by column chromatography. Yellow-orange solid (0.192 g, 0.664 mmol, 83%). mp = 86–87 °C. R_f = 0.28 (30% ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 11.41 (s, 1H), 7.37 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 1H), 7.17–7.09 (m, 2H), 7.06–6.98 (m, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 157.1, 152.7, 151.4, 149.0, 130.4, 124.2, 123.5, 119.2, 119.0, 116.2, 112.1, 110.0, 56.1, 56.1, 56.0. IR (thin film, CH_2Cl_2) 1632 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_5$ $[M–H]^-$ *m/z* 287.0925, found 287.0931.



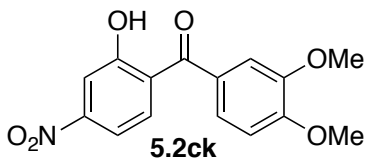
5.2ci

(3,4-Dimethoxyphenyl)(5-chloro-2-hydroxyphenyl)methanone (**5.2ci**). Prepared using procedure A; isolated by column chromatography. Light yellow solid (0.187 g, 0.640 mmol, 80%). mp = 127–130 °C. R_f = 0.29 (20% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 7.64 (d, *J* = 2.7 Hz, 1H), 7.44 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.36–7.27 (m, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 161.4, 153.2, 149.3, 135.7, 132.3, 129.8, 124.5, 123.4, 120.2, 120.1, 112.1, 110.2, 56.3, 56.2. IR (thin film, CH_2Cl_2) 1623 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}ClO_4$ $[M–H]^-$ *m/z* 291.0430, found 291.0424.



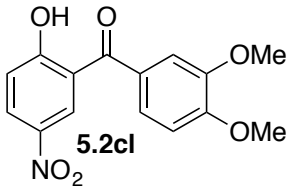
5.2cj

(3,4-Dimethoxyphenyl)(2-hydroxy-3-methylphenyl)methanone (**5.2cj**). Prepared using procedure A; isolated by column chromatography. Yellow solid (0.192 g, 0.704 mmol, 88%). mp = 81–84 °C. R_f = 0.26 (20% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.34–7.28 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 7.7 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 2.32 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 161.4, 152.7, 149.0, 136.8, 131.1, 130.8, 127.5, 124.4, 118.8, 117.9, 112.2, 110.0, 56.2, 56.2, 15.8. IR (neat) 1597 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{16}O_4$ $[M–H]^-$ *m/z* 279.0976, found 279.0976.



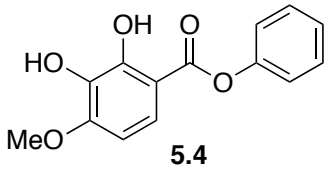
5.2ck

(4-Nitro-2-hydroxyphenyl)(3,4-dimethoxyphenyl)methanone (**5.2ck**). Prepared using procedure A; isolated by column chromatography. Orange solid (0.118 g, 0.392mmol, 49%). mp = 128–130 °C. R_f = 0.25 (5% acetic acid 15% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.76 (s, 1H), 7.89 (d, *J* = 2.1 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 2.2 Hz, 1H), 7.38–7.30 (m, 2H), 6.97 (d, *J* = 8.9 Hz, 1H), 4.00 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 163.0, 153.8, 151.7, 149.5, 134.1, 129.5, 125.0, 123.6, 113.8, 113.0, 112.1, 110.2, 56.4, 56.3. IR (thin film, CH_2Cl_2) 1623 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}NO_6$ [M–H]$^-$ *m/z* 302.0670, found 302.0666.



5.2cl

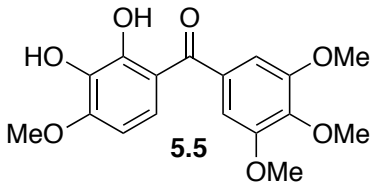
(5-Nitro-2-hydroxyphenyl)(3,4-dimethoxyphenyl)methanone (**5.2cl**). Prepared using procedure A; isolated by column chromatography. Light brown solid (0.114 g, 0.376mmol, 47%). mp = 179–182 °C. R_f = 0.25 (5% acetic acid 15% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.59 (s, 1H), 8.69 (d, *J* = 2.7 Hz, 1H), 8.38 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.37 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.17 (d, *J* = 9.2 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 4.01 (s, 3H), 3.97 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 167.9, 153.9, 149.6, 139.5, 130.5, 129.5, 128.9, 124.8, 119.5, 118.4, 112.0, 110.5, 56.4, 56.3. IR (thin film, CH_2Cl_2) 1622 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{13}NO_6$ [M–H]$^-$ *m/z* 302.0670, found 302.0670.



5.4

Phenyl 2,3-Dihydroxy-4-methoxybenzoate (**5.4**). In a nitrogen-filled glovebox, 2,3-dihydroxy-4-methoxybenzoic acid[130] (500 mg, 2.72 mmol, 1 equiv.), phenol

(5.11 g, 54.3 mmol, 20 equiv.), and phosphorus oxychloride (631.5 mg, 4.07 mmol, 1.5 equiv.) were added to a 25 mL screw top pressure vessel with a stir bar. The vessel was sealed, removed from the glovebox, and heated to 100 °C for 20 hours. The vessel was cooled to room temperature and the solvent and remaining phenol removed *in vacuo*. The product was purified by flash chromatography (20%→30% ethyl acetate in hexanes). Off-white/yellow powder (0.532 g, 2.04 mmol, 75% yield). mpt = 145–147 °C. R_f = 0.16 (20% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.45 (t, *J* = 7.5 Hz. 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 1H), 4.97 (br s, 1H), 3.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9, 152.3, 150.3, 149.9, 133.6, 129.7, 126.4, 122.1, 121.8, 106.2, 103.4, 56.4. IR (thin film, CH_2Cl_2) 1667 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{12}O_5$ $[M–H]^-$ *m/z* 259.0612, found 259.0599.



5.5

(2,3-Dihydroxy-4-methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (Hydroxyphenstatin, **5.5**). TrixiePhos (18 mg, 0.045 mmol, 3 mol %), $[Ir(cod)OMe]_2$ (10 mg, 0.015 mmol, 1 mol %), phenyl salicylate (0.390 g, 1.5 mmol, 1 equiv.), 1,5-COD (0.18 mL, 1.5 mmol, 1 equiv.), and 1,2,3-trimethoxybenzene (19.8 g, 78.5 equiv.) were added to a 75 mL PTFE-sealed screw top pressure vessel. The vessel was sealed, removed from the glovebox, and heated to 170 °C in an oil bath for 20 hours. The vessel was then cooled to room temperature and brought into the glovebox and TrixiePhos (18 mg, 0.045 mmol, 3 mol %) and $[Ir(cod)OMe]_2$ (10 mg, 0.015 mmol, 1 mol %) was added. The vessel was sealed, brought out of box, and heated to 170 °C for an additional 20 hours. After 20 hours, the vessel was then cooled and a third charge of iridium and phosphine was added as before. The vessel was heated to

170 °C for an additional 20 hours. The vessel was then cooled to room temperature and contents were transferred to a 50 mL pear-shaped flask. The solvent was removed *in vacuo*. Product was purified by column chromatography (20:80:2 EtOAc:Hex:AcOH for ~10 column volumes, 40:60:2 for ~4 column volumes, 50:50:2 for ~4 column volumes). Yellow/brown solid obtained (0.240 g, 0.718 mmol, 48% yield). R_f = 0.22 (50% ethyl acetate in hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.22 (s, 1H), 7.26 (d, *J* = 9.0 Hz, 1H), 6.92 (s, 2H), 6.51 (d, *J* = 9.0 Hz, 1H), 5.56 (bs, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.90 (s, 6H). IR (neat) 1635 cm^{-1}. All data are consistent with prior synthesis.[128]

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APPENDIX

Cyanoamidation Calculations

Reference 72. Gaussian 09 Full Reference

Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

XYZ coordinates and absolute energies (au)

1: M06/6-311+G(2df,2pd) SCF= -879.89647098 hartree
Gibbs correction= 0.228832 hartree
Total Gibbs Energy= -879.667639 hartree

C	0.62405	-1.43510	2.52964
C	0.25346	-0.33860	1.76409
C	0.78211	-0.16089	0.48790
C	1.67335	-1.09340	-0.06413
C	2.01434	-2.20104	0.71857
C	1.50274	-2.37199	1.99856
H	0.21754	-1.56213	3.52913
H	-0.46812	0.38691	2.13545
H	2.72145	-2.92068	0.31167
H	1.79798	-3.23828	2.58518
C	2.26487	-0.94430	-1.41794
C	2.92936	0.35587	-1.77537
C	2.23076	-1.97348	-2.27103
H	1.73270	-2.90723	-2.01830
H	2.69383	-1.90871	-3.25325
N	0.31728	0.93972	-0.29846
C	-0.63333	0.65429	-1.38545
H	-0.75489	1.58819	-1.94303
H	-0.17199	-0.09096	-2.04644
C	0.56225	2.23802	0.02637
C	1.56204	2.41791	1.09794
O	0.06919	3.21248	-0.50920
N	2.35394	2.65848	1.91161
C	-1.94461	0.15725	-0.84886
C	-2.85042	1.05721	-0.28443
C	-2.24215	-1.20364	-0.85111
C	-4.04223	0.59902	0.26254
H	-2.60926	2.12007	-0.28140
C	-3.43653	-1.66328	-0.30595
H	-1.52408	-1.90474	-1.27821
C	-4.33722	-0.76207	0.25058
H	-4.74656	1.30507	0.69599
H	-3.66270	-2.72684	-0.31349
H	-5.27170	-1.11966	0.67643
H	3.58741	0.22564	-2.63995
H	3.52739	0.73850	-0.93917
H	2.20207	1.13689	-2.03056

2: M06/6-311+G(2df,2pd) SCF= -879.9528452 hartree
Gibbs correction= 0.233895 hartree
Total Gibbs Energy= -879.7189502 hartree

C	-1.89454	3.01821	0.79825
C	-2.53534	1.78121	0.69225
C	-1.89273	0.75062	0.03424
C	-0.62358	0.95246	-0.51596
C	0.02989	2.16963	-0.42076

C	-0.63015	3.20171	0.24828
H	-2.38325	3.83877	1.31652
H	-3.52508	1.63234	1.12355
H	1.02605	2.31038	-0.83259
H	-0.13947	4.16721	0.34376
N	-0.18522	-0.22497	-1.14007
C	-1.10725	-1.23693	-0.99234
O	-0.98690	-2.38267	-1.37335
C	-2.32231	-0.66216	-0.24721
C	-3.54867	-0.74945	-1.15154
H	-3.72549	-1.78944	-1.44886
H	-4.43719	-0.36889	-0.63347
H	-3.40211	-0.15052	-2.05653
C	-2.56233	-1.50452	1.01782
H	-2.76753	-2.54031	0.71499
H	-3.44537	-1.12946	1.55240
C	1.11449	-0.41868	-1.75052
H	1.24409	0.30657	-2.56685
H	1.07515	-1.41944	-2.20011
C	2.25062	-0.30785	-0.76638
C	3.40337	0.40152	-1.09619
C	2.16098	-0.92197	0.48211
C	4.45786	0.49201	-0.19285
H	3.47360	0.88995	-2.06853
C	3.20702	-0.82184	1.38961
H	1.26176	-1.47195	0.75444
C	4.35948	-0.11690	1.05330
H	5.35313	1.04879	-0.45994
H	3.11214	-1.29301	2.36504
H	5.17808	-0.03751	1.76471
C	-1.41761	-1.50302	1.91990
N	-0.48598	-1.50022	2.61237

Cyanide: M06/6-311+G(2df,2pd) SCF= -92.88407522 hartree
Gibbs correction= -0.019906 hartree
Total Gibbs Energy= -92.90398122 hartree

C	0.00000	0.00000	-0.63760
N	0.00000	0.00000	0.54652

(*S*)-A: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.581028 hartree
Gibbs correction= 0.733463 hartree
Total Gibbs Energy= -2941.847565 hartree

Pd	-1.14085	-0.55870	0.31839
P	1.18161	-0.79681	-0.06136
O	1.75760	0.14679	-1.30298
O	2.02237	-0.11727	1.22589
N	2.01361	-2.23083	-0.44293
C	2.24522	2.24125	-0.29749
C	1.43906	1.47847	-1.11964
C	0.29025	1.98141	-1.75904
H	-0.29351	1.30744	-2.38224

C	-0.06166	3.28927	-1.56219
H	-0.94807	3.69950	-2.04350
C	0.68970	4.11579	-0.69150
C	0.28813	5.44819	-0.42881
H	-0.58998	5.83295	-0.94701
C	0.97788	6.23335	0.45880
H	0.65638	7.25335	0.65528
C	2.10247	5.70830	1.12901
H	2.63672	6.32418	1.84871
C	2.52537	4.42486	0.88751
H	3.38736	4.02907	1.41847
C	1.84704	3.59190	-0.03794
C	3.42849	1.60660	0.33461
C	3.26111	0.45285	1.08492
C	4.32887	-0.14682	1.78391
H	4.11556	-1.02670	2.38736
C	5.58921	0.37491	1.68569
H	6.42099	-0.08085	2.22090
C	5.84112	1.49421	0.85643
C	7.15447	1.99415	0.68427
H	7.96589	1.50981	1.22653
C	7.40331	3.05276	-0.15054
H	8.41677	3.42502	-0.27919
C	6.33830	3.65106	-0.85598
H	6.53873	4.47677	-1.53480
C	5.05258	3.19595	-0.70267
H	4.24395	3.65777	-1.26355
C	4.75638	2.11421	0.16537
C	2.59528	-2.47692	-1.78438
H	2.54298	-1.50509	-2.28697
C	1.73104	-3.41304	-2.61990
H	0.69534	-3.05310	-2.59893
H	1.73777	-4.44877	-2.26583
H	2.06932	-3.41375	-3.66322
C	4.07848	-2.80142	-1.74395
C	4.62703	-3.93826	-2.33821
H	3.97877	-4.66204	-2.82919
C	6.00120	-4.16537	-2.30611
H	6.40893	-5.05999	-2.77206
C	6.84837	-3.25538	-1.68453
H	7.92098	-3.43426	-1.66003
C	6.31266	-2.10899	-1.10259
H	6.96147	-1.37589	-0.62536
C	4.94295	-1.88570	-1.13933
H	4.52931	-0.97862	-0.70168
C	2.13152	-3.18053	0.69006
H	2.97361	-2.84916	1.32645
C	2.41654	-4.62696	0.30189
H	3.33448	-4.73622	-0.28068
H	1.58099	-5.07052	-0.24977
C	-1.14770	0.96177	1.87612

H	-0.66852	0.57186	2.77349
H	-0.61904	1.77656	1.38129
C	-2.49412	0.68585	1.63447
C	-3.25888	-0.10432	2.67356
H	-3.83368	-0.94662	2.27444
H	-2.56060	-0.51633	3.41011
H	-3.96555	0.54892	3.20706
C	-3.24594	1.48996	0.62433
C	-4.30213	0.96324	-0.15154
C	-2.89002	2.82142	0.37195
C	-4.92292	1.71699	-1.14375
C	-3.52317	3.58205	-0.60381
H	-2.09841	3.27344	0.96597
C	-4.53820	3.03241	-1.37675
H	-5.71588	1.25416	-1.72755
H	-3.21814	4.61642	-0.75455
H	-5.03259	3.61789	-2.14739
C	-4.13826	-1.49604	-0.21442
O	-4.51652	-2.62467	0.06195
N	-4.80690	-0.35607	0.09391
C	-6.08601	-0.47741	0.81005
H	-6.09507	0.29106	1.59385
H	-6.08544	-1.46263	1.29012
C	-7.27965	-0.32719	-0.09216
C	-7.53952	-1.29436	-1.06668
C	-8.11748	0.78139	0.00885
C	-8.61891	-1.14697	-1.92846
H	-6.88654	-2.16378	-1.13811
C	-9.20303	0.92700	-0.85045
H	-7.90817	1.54178	0.76114
C	-9.45307	-0.03574	-1.82186
H	-8.81460	-1.90390	-2.68455
H	-9.85055	1.79655	-0.76341
H	-10.29862	0.07719	-2.49649
C	0.87656	-3.16682	1.54794
C	-0.36574	-3.47807	0.98262
C	0.94363	-2.88007	2.90832
C	-1.51805	-3.48897	1.76012
H	-0.43010	-3.67980	-0.08735
C	-0.20483	-2.90666	3.69710
H	1.90519	-2.61950	3.35070
C	-1.43495	-3.20972	3.12463
H	-2.48153	-3.70149	1.29776
H	-0.13625	-2.68425	4.75988
H	-2.33483	-3.22360	3.73659
H	2.53381	-5.19891	1.22929
C	-2.83670	-1.34078	-0.89817
N	-1.96982	-1.55976	-1.67874

(*R*)-A: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.586007 hartree
Gibbs correction= 0.732763 hartree

Total Gibbs Energy= -2941.853244 hartree

Pd	-0.99282	0.04658	0.79560
P	1.24717	0.77187	0.60169
O	2.53758	0.17463	1.49379
O	1.76771	0.30755	-0.91331
N	1.60316	2.40973	0.74921
C	3.04459	-1.89967	0.43087
C	2.56220	-1.20162	1.52170
C	2.06516	-1.83827	2.67581
H	1.72512	-1.21113	3.49741
C	2.01295	-3.20397	2.72536
H	1.63838	-3.71426	3.61150
C	2.39512	-3.97727	1.60166
C	2.25757	-5.38657	1.60707
H	1.88146	-5.86447	2.51085
C	2.57432	-6.13177	0.50071
H	2.45890	-7.21297	0.51521
C	3.03716	-5.48829	-0.66599
H	3.26447	-6.07665	-1.55196
C	3.19766	-4.12546	-0.69712
H	3.54626	-3.64075	-1.60531
C	2.90034	-3.32610	0.43557
C	3.67522	-1.15734	-0.68534
C	3.02031	-0.09837	-1.29280
C	3.56680	0.58249	-2.40413
H	2.97904	1.38268	-2.84861
C	4.79854	0.23617	-2.88184
H	5.22244	0.75228	-3.74171
C	5.55803	-0.77616	-2.24819
C	6.86416	-1.09068	-2.69273
H	7.25538	-0.55750	-3.55836
C	7.62510	-2.02910	-2.04461
H	8.62949	-2.25949	-2.39164
C	7.10324	-2.68148	-0.90925
H	7.71461	-3.40486	-0.37448
C	5.83367	-2.40769	-0.46356
H	5.45617	-2.91214	0.42161
C	5.00737	-1.46437	-1.12662
C	2.88992	2.92289	0.24050
H	3.40017	2.04098	-0.17390
C	3.81372	3.40983	1.35262
H	3.80285	2.67476	2.16376
H	3.52739	4.38547	1.75721
H	4.84491	3.48566	0.98852
C	2.71540	3.87205	-0.93271
C	3.56784	4.95995	-1.12784
H	4.35270	5.17316	-0.40547
C	3.42570	5.78877	-2.23769
H	4.09957	6.63302	-2.36734
C	2.42733	5.54265	-3.17219
H	2.31286	6.19196	-4.03716

C	1.57205	4.45938	-2.98859
H	0.78314	4.25702	-3.70965
C	1.71400	3.63154	-1.88099
H	1.03625	2.78848	-1.74618
C	0.47331	3.29798	1.12568
H	-0.20523	3.40458	0.26214
C	0.90473	4.70214	1.53772
H	1.46243	5.22310	0.75372
H	1.49897	4.68132	2.45819
C	-1.22025	-1.81115	1.90175
H	-0.53267	-2.46665	1.36849
H	-0.99991	-1.66340	2.95889
C	-2.49427	-1.49778	1.42173
C	-3.89771	1.02476	-0.15937
O	-4.38359	2.03707	0.32127
N	-4.52411	-0.16979	-0.28529
C	-5.91712	-0.27973	0.17306
H	-6.10702	0.59207	0.80941
H	-5.99057	-1.18342	0.79226
C	-6.89797	-0.33815	-0.96460
C	-7.59162	-1.51222	-1.24912
C	-7.09262	0.78427	-1.77325
C	-8.46955	-1.56982	-2.32772
H	-7.42988	-2.39176	-0.62622
C	-7.96407	0.72670	-2.85340
H	-6.55312	1.70349	-1.54594
C	-8.65423	-0.45137	-3.13270
H	-9.00499	-2.49185	-2.54226
H	-8.10993	1.60450	-3.47876
H	-9.33686	-0.49496	-3.97823
C	-0.32322	2.71139	2.27592
C	0.31801	2.24023	3.42570
C	-1.71890	2.72097	2.23720
C	-0.42192	1.76271	4.50060
H	1.40780	2.22784	3.45877
C	-2.46090	2.25257	3.31899
H	-2.23914	3.09244	1.35364
C	-1.81496	1.76569	4.45026
H	0.09018	1.39331	5.38699
H	-3.54775	2.26170	3.26034
H	-2.39341	1.39423	5.29390
H	-0.00264	5.27976	1.74668
C	-2.94177	-2.03123	0.09958
C	-2.40874	-3.22828	-0.39818
C	-3.86571	-1.36314	-0.73331
C	-2.74544	-3.72271	-1.65127
H	-1.71571	-3.78869	0.22468
C	-4.19589	-1.84988	-1.99579
C	-3.63761	-3.03256	-2.46332
H	-2.30524	-4.65697	-1.99234
H	-4.89792	-1.28340	-2.60435

H	-3.89995	-3.40851	-3.44855
C	-3.52932	-1.03208	2.42271
H	-4.24488	-1.84114	2.63410
H	-3.04049	-0.75985	3.36459
H	-4.11056	-0.16088	2.10620
C	-2.50280	1.08994	-0.64897
N	-1.51677	1.48322	-1.16173

(*S*)-TS1: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.560949 hartree
Gibbs correction= 0.729887 hartree
Total Gibbs Energy= -2941.831062 hartree

Pd	-1.33909	-0.60709	0.75070
P	0.95423	-0.79391	0.15685
O	1.32987	0.09503	-1.18670
O	1.96858	-0.08339	1.28491
N	1.68248	-2.25527	-0.29481
C	1.96547	2.21971	-0.33717
C	1.04960	1.44003	-1.01631
C	-0.16080	1.93711	-1.53573
H	-0.81941	1.25488	-2.06959
C	-0.46743	3.25721	-1.34512
H	-1.39778	3.66656	-1.73528
C	0.39302	4.10100	-0.60108
C	0.04430	5.44901	-0.34347
H	-0.88723	5.82775	-0.76352
C	0.85010	6.25575	0.41811
H	0.56899	7.28828	0.61140
C	2.04413	5.73791	0.96237
H	2.67246	6.37194	1.58367
C	2.41805	4.43946	0.72035
H	3.33617	4.04983	1.15305
C	1.61755	3.58409	-0.07845
C	3.22819	1.59920	0.13519
C	3.17683	0.47075	0.93699
C	4.33610	-0.12268	1.47609
H	4.21572	-0.98565	2.12762
C	5.56831	0.38422	1.16685
H	6.47147	-0.06572	1.57653
C	5.69241	1.47965	0.27887
C	6.96530	1.96398	-0.10809
H	7.84901	1.48726	0.31466
C	7.08580	2.99830	-0.99965
H	8.06855	3.35883	-1.29363
C	5.92682	3.58644	-1.54796
H	6.02300	4.39234	-2.27181
C	4.67852	3.14630	-1.18526
H	3.79475	3.60040	-1.62605
C	4.51622	2.09063	-0.25222
C	2.05089	-2.55151	-1.70340
H	1.95261	-1.59145	-2.22118
C	1.04388	-3.47781	-2.37173

H	0.03593	-3.06944	-2.22870
H	1.05924	-4.49958	-1.97957
H	1.23350	-3.52793	-3.45059
C	3.51379	-2.92450	-1.86245
C	3.93806	-4.09934	-2.48358
H	3.20485	-4.81516	-2.85132
C	5.29559	-4.37211	-2.63810
H	5.60644	-5.29529	-3.12260
C	6.24901	-3.47099	-2.17882
H	7.30840	-3.68555	-2.30013
C	5.83595	-2.28728	-1.57190
H	6.56761	-1.56083	-1.22119
C	4.48221	-2.01847	-1.42289
H	4.16216	-1.08274	-0.96684
C	1.98300	-3.17355	0.82991
H	2.96337	-2.88447	1.25358
C	2.07887	-4.64755	0.45259
H	2.85128	-4.84230	-0.29527
H	1.11959	-5.03573	0.09420
C	-1.11496	0.86200	2.50653
H	-0.67581	0.33974	3.35587
H	-0.48745	1.60093	2.00860
C	-2.46176	0.75712	2.23684
C	-3.37054	0.00144	3.17286
H	-4.14133	-0.57602	2.65223
H	-2.79154	-0.68956	3.79573
H	-3.88657	0.71096	3.83433
C	-3.08705	1.65463	1.22125
C	-3.95688	1.16818	0.22182
C	-2.81224	3.02570	1.23974
C	-4.51240	2.03728	-0.71607
C	-3.39171	3.89371	0.32285
H	-2.14201	3.41295	2.00512
C	-4.24331	3.39958	-0.65933
H	-5.15544	1.62962	-1.49250
H	-3.17259	4.95824	0.37778
H	-4.69440	4.06909	-1.38772
C	-3.38928	-1.23481	0.16885
O	-3.63938	-2.38538	0.46916
N	-4.30857	-0.20865	0.18361
C	-5.72267	-0.56973	0.33097
H	-6.17672	0.12023	1.05564
H	-5.73800	-1.57331	0.77571
C	-6.50131	-0.56086	-0.95919
C	-5.91927	-0.97607	-2.15909
C	-7.83790	-0.16413	-0.95246
C	-6.67084	-0.99485	-3.32890
H	-4.86777	-1.26224	-2.18707
C	-8.59111	-0.19126	-2.12179
H	-8.29180	0.17203	-0.02021
C	-8.00793	-0.60716	-3.31385

H	-6.20533	-1.31327	-4.25873
H	-9.63233	0.12306	-2.10254
H	-8.59145	-0.62250	-4.23151
C	0.95077	-3.04391	1.93811
C	-0.40036	-3.31599	1.68737
C	1.33743	-2.69589	3.22965
C	-1.34122	-3.22904	2.70800
H	-0.72363	-3.57315	0.67718
C	0.40196	-2.62371	4.25915
H	2.38475	-2.46891	3.42767
C	-0.93782	-2.89044	3.99940
H	-2.38950	-3.41131	2.48033
H	0.72230	-2.35564	5.26353
H	-1.67155	-2.83461	4.80161
H	2.33995	-5.20472	1.35945
C	-2.20110	-1.03383	-1.06733
N	-2.18385	-1.07333	-2.24420

(*R*)-TS1: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.56095 hartree
Gibbs correction= 0.7287 hartree
Total Gibbs Energy= -2941.83225 hartree

Pd	-1.23020	0.25734	1.10036
P	1.04121	0.97393	0.74302
O	2.47520	0.43122	1.43546
O	1.30819	0.47519	-0.81601
N	1.35880	2.61866	0.76579
C	2.70091	-1.72622	0.43332
C	2.51531	-0.93992	1.55598
C	2.33665	-1.48547	2.84290
H	2.24371	-0.79636	3.67991
C	2.25282	-2.84236	2.99845
H	2.11334	-3.28112	3.98511
C	2.26587	-3.69392	1.86577
C	2.03021	-5.08484	1.99336
H	1.87366	-5.49305	2.99104
C	1.98304	-5.89684	0.88877
H	1.79314	-6.96187	0.99853
C	2.17487	-5.34418	-0.39538
H	2.12038	-5.98605	-1.27190
C	2.42351	-4.00298	-0.55051
H	2.55661	-3.58464	-1.54496
C	2.48523	-3.13667	0.56972
C	3.13349	-1.10015	-0.83756
C	2.44646	-0.02951	-1.38231
C	2.82008	0.55989	-2.61079
H	2.20904	1.37777	-2.98745
C	3.91598	0.09810	-3.28241
H	4.20615	0.53985	-4.23423
C	4.70931	-0.94151	-2.74059
C	5.88198	-1.37866	-3.40093
H	6.13696	-0.91835	-4.35470

C	6.68542	-2.34418	-2.85148
H	7.58654	-2.66960	-3.36556
C	6.34537	-2.89953	-1.60162
H	6.99568	-3.64375	-1.14746
C	5.20622	-2.50551	-0.94400
H	4.97355	-2.93763	0.02509
C	4.33525	-1.53196	-1.49663
C	2.50390	3.14447	-0.00824
H	2.95250	2.25874	-0.48228
C	3.60399	3.70399	0.88647
H	3.78684	2.99654	1.70194
H	3.35658	4.67894	1.31736
H	4.53739	3.81238	0.32191
C	2.06188	4.03747	-1.15427
C	2.76265	5.19331	-1.50149
H	3.63067	5.50030	-0.92157
C	2.36003	5.97143	-2.58417
H	2.91815	6.87074	-2.83621
C	1.24943	5.60571	-3.33556
H	0.93201	6.21720	-4.17723
C	0.54486	4.45263	-2.99898
H	-0.33137	4.15034	-3.56857
C	0.94886	3.67426	-1.92114
H	0.38163	2.77701	-1.67430
C	0.27805	3.48961	1.30080
H	-0.52631	3.56857	0.54933
C	0.73677	4.90627	1.62543
H	1.13440	5.43117	0.75189
H	1.48388	4.91170	2.42711
C	-0.98625	-1.49478	2.62599
H	-0.08128	-1.91816	2.20234
H	-0.92396	-1.11642	3.64629
C	-2.20302	-1.65767	2.01134
C	-3.31312	0.50403	0.30848
O	-3.97407	1.38210	0.82205
N	-3.82873	-0.67687	-0.17907
C	-5.28550	-0.78057	-0.31829
H	-5.70963	0.02407	0.29621
H	-5.60529	-1.73644	0.12019
C	-5.77289	-0.66792	-1.73865
C	-6.81079	-1.48564	-2.18231
C	-5.21645	0.26639	-2.61569
C	-7.29995	-1.36839	-3.47973
H	-7.23723	-2.22457	-1.50398
C	-5.70030	0.37685	-3.91409
H	-4.38441	0.89200	-2.29102
C	-6.74459	-0.43601	-4.34877
H	-8.10896	-2.01426	-3.81389
H	-5.25557	1.10228	-4.59133
H	-7.11896	-0.34658	-5.36602
C	-0.31228	2.88251	2.55896

C	0.50943	2.51848	3.63017
C	-1.69250	2.71181	2.67558
C	-0.03893	1.97921	4.78784
H	1.58981	2.63531	3.53638
C	-2.24277	2.17058	3.83664
H	-2.34665	2.97816	1.84571
C	-1.41796	1.80131	4.89391
H	0.61151	1.69846	5.61395
H	-3.32042	2.03011	3.89758
H	-1.84578	1.37694	5.80006
H	-0.13546	5.46386	1.98439
C	-2.26015	-2.34640	0.68800
C	-1.47899	-3.48310	0.44808
C	-3.04415	-1.84576	-0.37277
C	-1.49288	-4.11992	-0.78557
H	-0.85747	-3.87714	1.25172
C	-3.05225	-2.48439	-1.61121
C	-2.28663	-3.62550	-1.81542
H	-0.87563	-5.00279	-0.93798
H	-3.64458	-2.05927	-2.41784
H	-2.29707	-4.11471	-2.78616
C	-3.47268	-1.43596	2.79156
H	-3.83611	-2.40304	3.16526
H	-3.28262	-0.78785	3.65452
H	-4.28026	-0.99044	2.20578
C	-1.95375	1.07156	-0.64469
N	-1.87252	1.60057	-1.69284

(*S*)-B: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.588464 hartree
Gibbs correction= 0.731754 hartree
Total Gibbs Energy= -2941.85671 hartree

Pd	-1.44177	-0.84680	0.61712
P	0.91218	-0.86542	0.09933
O	1.22242	0.06281	-1.22089
O	1.84651	-0.09934	1.25015
N	1.71259	-2.27947	-0.34097
C	1.61868	2.23179	-0.33392
C	0.79974	1.37275	-1.03993
C	-0.45093	1.74417	-1.56745
H	-1.03030	0.99932	-2.10893
C	-0.89486	3.02416	-1.37004
H	-1.86166	3.33732	-1.76075
C	-0.12971	3.94787	-0.61675
C	-0.60869	5.25751	-0.36949
H	-1.55960	5.54828	-0.81451
C	0.09456	6.13176	0.41848
H	-0.28670	7.13317	0.60384
C	1.31475	5.72496	0.99876
H	1.86061	6.41074	1.64251
C	1.81911	4.47136	0.75879
H	2.75942	4.16889	1.21290

C	1.12733	3.55063	-0.06891
C	2.93026	1.74184	0.15755
C	2.99104	0.59813	0.93628
C	4.19576	0.12698	1.49420
H	4.15855	-0.75682	2.12724
C	5.36855	0.77683	1.22682
H	6.30684	0.42276	1.65083
C	5.38876	1.89657	0.36117
C	6.60857	2.52556	0.01293
H	7.52954	2.14388	0.45211
C	6.63380	3.57963	-0.86320
H	7.57677	4.05146	-1.12826
C	5.42981	4.04239	-1.43376
H	5.45243	4.86350	-2.14635
C	4.23005	3.46105	-1.10757
H	3.31261	3.82021	-1.56637
C	4.16461	2.38049	-0.19156
C	2.15695	-2.54790	-1.74097
H	1.86738	-1.64772	-2.29422
C	1.37948	-3.68454	-2.38920
H	0.30585	-3.49330	-2.28755
H	1.60531	-4.66996	-1.97256
H	1.60891	-3.71545	-3.46099
C	3.67002	-2.63094	-1.86655
C	4.32567	-3.75134	-2.37961
H	3.75082	-4.62216	-2.68908
C	5.71232	-3.77116	-2.50840
H	6.20211	-4.65604	-2.90921
C	6.46687	-2.66639	-2.13180
H	7.54970	-2.68184	-2.23345
C	5.82333	-1.53604	-1.63517
H	6.39696	-0.65461	-1.35210
C	4.44004	-1.52040	-1.51080
H	3.94222	-0.62329	-1.14515
C	2.13263	-3.11364	0.81232
H	3.05699	-2.67601	1.23335
C	2.44147	-4.56745	0.47669
H	3.24458	-4.66751	-0.25772
H	1.55114	-5.09618	0.12089
C	-0.95788	0.45038	2.40009
H	-0.44516	-0.16155	3.14326
H	-0.36522	1.21759	1.90253
C	-2.33610	0.47645	2.34289
C	-3.14454	-0.25675	3.38399
H	-4.15204	-0.51296	3.04613
H	-2.63712	-1.17383	3.70229
H	-3.24938	0.40170	4.25661
C	-3.02986	1.50558	1.52547
C	-4.03698	1.13940	0.60812
C	-2.71250	2.85542	1.67757
C	-4.71305	2.13058	-0.10594

C	-3.40443	3.84042	0.98298
H	-1.92374	3.13338	2.37590
C	-4.40774	3.47215	0.09424
H	-5.47598	1.84649	-0.82661
H	-3.15563	4.88737	1.13897
H	-4.95760	4.23086	-0.45826
C	-3.47816	-1.24051	0.69483
O	-3.81869	-2.38416	0.89341
N	-4.37622	-0.21624	0.45032
C	-5.75987	-0.58600	0.12964
H	-6.43458	0.08518	0.67787
H	-5.89437	-1.59741	0.53271
C	-6.07679	-0.56196	-1.34370
C	-5.15030	-1.01531	-2.28327
C	-7.32261	-0.10915	-1.77859
C	-5.47022	-1.01648	-3.63593
H	-4.16825	-1.36466	-1.96773
C	-7.64437	-0.11509	-3.13248
H	-8.04566	0.25522	-1.04786
C	-6.71695	-0.56873	-4.06488
H	-4.73290	-1.37133	-4.35275
H	-8.61857	0.24276	-3.45886
H	-6.96369	-0.56896	-5.12428
C	1.07687	-3.10478	1.90401
C	-0.23252	-3.51676	1.62913
C	1.41433	-2.75375	3.21003
C	-1.18523	-3.56629	2.64171
H	-0.51343	-3.77899	0.60826
C	0.46905	-2.81818	4.23001
H	2.42974	-2.42185	3.42635
C	-0.83137	-3.22600	3.94632
H	-2.20747	-3.84673	2.39793
H	0.74904	-2.54883	5.24609
H	-1.57272	-3.27726	4.74172
H	2.76768	-5.05560	1.40208
C	-1.64738	-1.64385	-1.23635
N	-1.67706	-2.02772	-2.34227

(*R*)-B: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.584525 hartree
Gibbs correction= 0.732703 hartree
Total Gibbs Energy= -2941.851822 hartree

Pd	-1.27726	-0.83126	0.02238
P	1.11417	-0.85183	-0.56778
O	1.97508	0.00093	-1.73129
O	1.73686	-0.15022	0.78705
N	1.83949	-2.33871	-0.77707
C	2.11168	2.20930	-0.80768
C	1.69962	1.34797	-1.80846
C	0.99207	1.79210	-2.94461
H	0.76105	1.05834	-3.71486
C	0.58093	3.09421	-3.02348

H	0.02824	3.45170	-3.89073
C	0.81021	3.98111	-1.94217
C	0.26409	5.28751	-1.94072
H	-0.31227	5.60794	-2.80780
C	0.44216	6.12528	-0.86884
H	0.01250	7.12424	-0.87597
C	1.18132	5.68422	0.24927
H	1.30642	6.34202	1.10617
C	1.73929	4.42984	0.26921
H	2.29699	4.09545	1.14027
C	1.57913	3.54114	-0.82301
C	3.09040	1.75117	0.20544
C	2.88018	0.59216	0.92910
C	3.77279	0.14676	1.92794
H	3.51650	-0.75889	2.47322
C	4.91589	0.85162	2.17624
H	5.60921	0.52349	2.94870
C	5.23296	2.00374	1.41708
C	6.44692	2.69883	1.62976
H	7.11214	2.34340	2.41558
C	6.78666	3.78151	0.86026
H	7.72405	4.30560	1.02974
C	5.91945	4.20039	-0.16868
H	6.19875	5.04031	-0.80068
C	4.72795	3.55431	-0.38987
H	4.08221	3.88683	-1.19776
C	4.33051	2.44979	0.40585
C	3.30049	-2.46608	-0.56118
H	3.62632	-1.46225	-0.24963
C	4.05906	-2.73844	-1.85507
H	3.69125	-2.06305	-2.63403
H	3.95432	-3.77001	-2.20469
H	5.12780	-2.53714	-1.71851
C	3.63511	-3.38166	0.60279
C	4.74963	-4.22232	0.58460
H	5.38863	-4.26703	-0.29497
C	5.05421	-5.02045	1.68469
H	5.92549	-5.67131	1.65007
C	4.24750	-4.99365	2.81662
H	4.48183	-5.62514	3.67073
C	3.13447	-4.15765	2.84339
H	2.47716	-4.12750	3.70978
C	2.83565	-3.35489	1.74947
H	1.95126	-2.72100	1.79224
C	0.92739	-3.50983	-0.91370
H	0.50227	-3.74237	0.07585
C	1.61754	-4.76821	-1.42671
H	2.44018	-5.09043	-0.78148
H	1.98383	-4.63829	-2.45130
C	-1.73791	0.56597	-1.72654
H	-0.89116	1.23262	-1.60489

H	-1.79227	-0.01923	-2.64607
C	-2.84062	0.71718	-0.92099
C	-3.09673	-1.10793	0.98375
O	-3.66790	-2.16948	0.89812
N	-3.56410	-0.04935	1.73621
C	-4.77924	-0.28696	2.54218
H	-4.72723	0.34845	3.43234
H	-4.73636	-1.32898	2.87050
C	-6.03364	-0.01800	1.75845
C	-6.70456	-1.06301	1.12004
C	-6.49802	1.28939	1.59360
C	-7.81499	-0.80376	0.32329
H	-6.32720	-2.07763	1.23324
C	-7.60326	1.54970	0.79124
H	-5.98040	2.10871	2.09219
C	-8.26266	0.50291	0.15285
H	-8.33029	-1.62513	-0.16967
H	-7.95427	2.57182	0.66745
H	-9.12884	0.70567	-0.47314
C	-0.21470	-3.18231	-1.85688
C	0.03680	-2.66451	-3.13202
C	-1.53322	-3.44641	-1.48127
C	-1.00979	-2.41349	-4.01194
H	1.06412	-2.44327	-3.42342
C	-2.58268	-3.19844	-2.36441
H	-1.74612	-3.82707	-0.48285
C	-2.32430	-2.68176	-3.63003
H	-0.80018	-2.01468	-5.00268
H	-3.60382	-3.39746	-2.04600
H	-3.14391	-2.48704	-4.31911
H	0.87047	-5.56942	-1.44445
C	-2.76981	1.68029	0.21119
C	-2.26480	2.96809	0.01536
C	-3.12496	1.27549	1.51171
C	-2.14802	3.86178	1.07160
H	-1.96251	3.27071	-0.98737
C	-2.99900	2.17489	2.57003
C	-2.52570	3.46264	2.34988
H	-1.74775	4.85760	0.89245
H	-3.23940	1.85119	3.58004
H	-2.42834	4.14698	3.18919
C	-4.17673	0.18746	-1.36537
H	-4.67374	0.97952	-1.94214
H	-4.05100	-0.68590	-2.01524
H	-4.84982	-0.07512	-0.54624
C	-0.69346	-1.89368	1.64568
N	-0.30350	-2.55101	2.53207

(*S*)-TS2: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.571544 hartree
Gibbs correction= 0.732367 hartree
Total Gibbs Energy= -2941.839177 hartree

Pd	-1.17999	-0.90272	0.11195
P	1.09234	-0.86628	-0.04851
O	1.56713	0.11883	-1.27189
O	1.79836	-0.12505	1.25957
N	1.99774	-2.23797	-0.38399
C	1.78867	2.25308	-0.25416
C	1.09256	1.41297	-1.09969
C	-0.08953	1.78125	-1.76823
H	-0.57746	1.04722	-2.40638
C	-0.58794	3.04165	-1.57372
H	-1.50775	3.35262	-2.06687
C	0.05381	3.94735	-0.69430
C	-0.48270	5.23740	-0.46306
H	-1.37822	5.52597	-1.01222
C	0.09857	6.09536	0.43440
H	-0.32472	7.08253	0.60442
C	1.24638	5.68981	1.14786
H	1.69333	6.36188	1.87677
C	1.80348	4.45414	0.93229
H	2.68574	4.15227	1.49115
C	1.24112	3.55226	-0.00662
C	3.02186	1.75242	0.40117
C	2.97680	0.58282	1.14118
C	4.09256	0.09221	1.84709
H	3.97163	-0.81100	2.44093
C	5.28960	0.74922	1.76684
H	6.16043	0.38028	2.30630
C	5.42598	1.89873	0.95254
C	6.67878	2.54133	0.80232
H	7.53185	2.14377	1.35083
C	6.81922	3.62894	-0.02019
H	7.78705	4.11144	-0.13241
C	5.70377	4.11381	-0.73479
H	5.82082	4.96282	-1.40407
C	4.47383	3.51959	-0.60210
H	3.62609	3.89611	-1.16869
C	4.28853	2.40394	0.25339
C	2.55790	-2.49306	-1.74315
H	2.31935	-1.58477	-2.30875
C	1.84379	-3.61965	-2.47541
H	0.76425	-3.43310	-2.46639
H	2.04015	-4.61108	-2.05691
H	2.16228	-3.63125	-3.52443
C	4.07620	-2.57091	-1.72512
C	4.78301	-3.63799	-2.28123
H	4.24489	-4.47265	-2.72619
C	6.17592	-3.65199	-2.27260
H	6.70702	-4.49511	-2.70923
C	6.88484	-2.59629	-1.71166
H	7.97245	-2.60872	-1.70510
C	6.19030	-1.51933	-1.16685

H	6.72814	-0.67597	-0.73623
C	4.80185	-1.50843	-1.18010
H	4.26577	-0.65412	-0.77056
C	2.26917	-3.10016	0.79705
H	3.08981	-2.63442	1.37239
C	2.71017	-4.52084	0.47002
H	3.60638	-4.55131	-0.15493
H	1.90965	-5.09256	-0.00988
C	-1.33004	0.17373	1.88701
H	-1.04683	-0.41331	2.76474
H	-0.73510	1.07697	1.73155
C	-2.74289	0.23650	1.54342
C	-3.68966	-0.25464	2.63597
H	-4.73294	-0.27226	2.30094
H	-3.40086	-1.26254	2.95427
H	-3.61001	0.42926	3.48994
C	-3.19269	1.45012	0.80457
C	-3.93702	1.18320	-0.35224
C	-2.93512	2.76500	1.16402
C	-4.45021	2.21266	-1.13299
C	-3.46215	3.80679	0.40274
H	-2.33754	2.97501	2.05053
C	-4.21337	3.52690	-0.73533
H	-5.04073	1.99934	-2.01986
H	-3.28478	4.83677	0.70247
H	-4.62742	4.34199	-1.32494
C	-3.41162	-1.01873	0.24588
O	-3.69026	-2.17344	0.47939
N	-4.09036	-0.18026	-0.60207
C	-5.00190	-0.72656	-1.60427
H	-4.71455	-1.77729	-1.72535
H	-4.79857	-0.22797	-2.56091
C	-6.44874	-0.59480	-1.21215
C	-7.35533	0.08307	-2.02363
C	-6.89743	-1.16905	-0.01963
C	-8.69246	0.19363	-1.65177
H	-7.01179	0.52406	-2.95976
C	-8.23008	-1.05509	0.35461
H	-6.18977	-1.72150	0.59894
C	-9.13058	-0.37186	-0.46009
H	-9.39103	0.72553	-2.29369
H	-8.57177	-1.50775	1.28280
H	-10.17398	-0.28431	-0.16601
C	1.05225	-3.17674	1.70197
C	-0.16976	-3.64061	1.20243
C	1.14238	-2.82294	3.04650
C	-1.28263	-3.73120	2.03070
H	-0.25752	-3.89680	0.14606
C	0.03412	-2.92527	3.88336
H	2.08914	-2.45051	3.43759
C	-1.18022	-3.37565	3.37468

H	-2.23540	-4.05077	1.61732
H	0.11956	-2.64700	4.93154
H	-2.05024	-3.45072	4.02434
H	2.94198	-5.01607	1.41972
C	-1.31282	-1.70061	-1.80648
N	-1.34871	-2.05597	-2.92233

(*R*)-TS2: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.570082 hartree
Gibbs correction= 0.732619 hartree
Total Gibbs Energy= -2941.837463 hartree

Pd	1.05483	-0.79715	0.43077
P	-1.24274	-0.86319	0.54063
O	-2.22521	-0.01585	1.59069
O	-1.69688	-0.17685	-0.88322
N	-1.96047	-2.36110	0.64330
C	-2.15318	2.20093	0.69003
C	-1.90375	1.31926	1.72492
C	-1.31913	1.72186	2.94150
H	-1.20951	0.97603	3.72633
C	-0.87529	3.00808	3.08601
H	-0.41858	3.33680	4.01816
C	-0.93846	3.91237	1.99687
C	-0.35333	5.19953	2.08026
H	0.12144	5.49196	3.01619
C	-0.37086	6.05286	1.00639
H	0.08663	7.03672	1.08011
C	-0.97961	5.64804	-0.20049
H	-0.97511	6.31766	-1.05729
C	-1.57147	4.41418	-0.30639
H	-2.02765	4.10747	-1.24418
C	-1.57737	3.51044	0.78549
C	-3.02140	1.78714	-0.43659
C	-2.78026	0.62408	-1.14372
C	-3.57384	0.22323	-2.24038
H	-3.29602	-0.69014	-2.76246
C	-4.65059	0.97886	-2.60912
H	-5.26492	0.68509	-3.45843
C	-5.00348	2.13850	-1.87761
C	-6.15688	2.88602	-2.21477
H	-6.74383	2.56606	-3.07470
C	-6.53662	3.97438	-1.47240
H	-7.42727	4.53860	-1.73789
C	-5.77423	4.34615	-0.34699
H	-6.08887	5.19019	0.26247
C	-4.64213	3.64914	-0.00402
H	-4.07947	3.94642	0.87620
C	-4.20230	2.53727	-0.76654
C	-3.36108	-2.50093	0.17794
H	-3.64676	-1.49348	-0.15982
C	-4.32327	-2.81294	1.31817
H	-4.10183	-2.15044	2.16128

H	-4.26333	-3.85076	1.65949
H	-5.35639	-2.62046	1.00700
C	-3.47483	-3.39085	-1.04719
C	-4.56884	-4.23624	-1.24154
H	-5.35233	-4.30017	-0.48923
C	-4.66871	-5.01471	-2.39192
H	-5.52724	-5.67010	-2.52330
C	-3.67460	-4.96309	-3.36245
H	-3.74893	-5.57985	-4.25534
C	-2.58079	-4.12182	-3.17751
H	-1.78089	-4.07334	-3.91319
C	-2.48509	-3.33815	-2.03410
H	-1.61130	-2.70019	-1.90952
C	-1.06640	-3.52438	0.91621
H	-0.46910	-3.72612	0.01258
C	-1.81510	-4.80231	1.27422
H	-2.50548	-5.12394	0.48931
H	-2.35593	-4.70196	2.22197
C	1.54551	0.45362	2.03409
H	0.86978	1.30443	1.99236
H	1.56385	-0.07773	2.99033
C	2.79670	0.59411	1.31625
C	3.27635	-0.78911	0.06404
O	3.72437	-1.87107	0.36796
N	3.66103	-0.02162	-1.00504
C	4.42308	-0.61794	-2.09969
H	3.97580	-0.29257	-3.04758
H	4.25946	-1.69881	-2.02321
C	5.88667	-0.27555	-2.03301
C	6.63483	-0.66182	-0.91709
C	6.51335	0.42065	-3.06350
C	7.98452	-0.34504	-0.83435
H	6.14488	-1.22798	-0.12438
C	7.86769	0.73409	-2.98404
H	5.93592	0.71607	-3.93977
C	8.60383	0.35529	-1.86763
H	8.56007	-0.65219	0.03611
H	8.34620	1.27823	-3.79517
H	9.66116	0.60167	-1.80221
C	-0.11552	-3.20247	2.05280
C	-0.59824	-2.70713	3.26825
C	1.25232	-3.44237	1.91428
C	0.27230	-2.44648	4.32001
H	-1.66462	-2.50616	3.37545
C	2.12564	-3.18166	2.96838
H	1.64285	-3.80581	0.96452
C	1.63877	-2.68195	4.17185
H	-0.11592	-2.06170	5.26115
H	3.19060	-3.35339	2.82984
H	2.32069	-2.47623	4.99463
H	-1.06745	-5.59217	1.40684

C	2.85620	1.71081	0.33222
C	2.40775	3.00916	0.53491
C	3.35326	1.33843	-0.92277
C	2.50807	3.94308	-0.49381
H	1.98134	3.29523	1.49703
C	3.46800	2.26265	-1.95417
C	3.04553	3.56918	-1.72256
H	2.15859	4.96041	-0.33127
H	3.86798	1.97365	-2.92229
H	3.12804	4.30159	-2.52210
C	4.05529	0.36877	2.15243
H	4.10966	1.16926	2.90036
H	3.99888	-0.59768	2.66485
H	4.96673	0.39891	1.54473
C	0.93174	-1.90764	-1.32866
N	0.86000	-2.56118	-2.29821

(*S*)-C: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2849.59289hartree
Gibbs correction= 0.729863 hartree
Total Gibbs Energy= -2848.863027 hartree

Pd	1.18674	-0.85570	0.20563
P	-1.25313	-0.80237	0.39533
O	-1.96753	0.19789	1.49629
O	-1.89129	-0.22320	-0.99826
N	-1.98298	-2.25463	0.74989
C	-2.05574	2.30249	0.36740
C	-1.53276	1.51092	1.37028
C	-0.52650	1.94001	2.25668
H	-0.18413	1.24854	3.02473
C	-0.01044	3.20022	2.11907
H	0.76229	3.55961	2.79643
C	-0.44093	4.04098	1.06277
C	0.15962	5.30716	0.85611
H	0.91632	5.64201	1.56487
C	-0.19573	6.09009	-0.21222
H	0.27366	7.05863	-0.36377
C	-1.17033	5.63104	-1.12292
H	-1.43561	6.24379	-1.98069
C	-1.78626	4.41789	-0.93887
H	-2.53228	4.07653	-1.65136
C	-1.45710	3.59099	0.16451
C	-3.15372	1.77882	-0.48053
C	-3.03564	0.55858	-1.12031
C	-4.01754	0.05120	-1.99357
H	-3.83319	-0.90355	-2.48184
C	-5.16566	0.76456	-2.20009
H	-5.93087	0.39221	-2.87838
C	-5.39168	1.98189	-1.51524
C	-6.60794	2.68748	-1.67602
H	-7.34994	2.28812	-2.36535
C	-6.85342	3.83712	-0.97123

H	-7.79230	4.36965	-1.09764
C	-5.88771	4.31827	-0.06367
H	-6.09426	5.21415	0.51656
C	-4.69221	3.66391	0.10322
H	-3.96814	4.04436	0.81854
C	-4.39375	2.48784	-0.62933
C	-3.42861	-2.45847	0.48850
H	-3.75033	-1.53104	-0.00750
C	-4.25245	-2.52704	1.76745
H	-3.96143	-1.70229	2.42619
H	-4.13571	-3.47042	2.30914
H	-5.31614	-2.40414	1.53632
C	-3.66272	-3.56841	-0.51902
C	-4.70348	-4.48637	-0.37573
H	-5.35296	-4.44606	0.49579
C	-4.92351	-5.46631	-1.34039
H	-5.73770	-6.17492	-1.20960
C	-4.10770	-5.54115	-2.46263
H	-4.27864	-6.30811	-3.21367
C	-3.06902	-4.62704	-2.61814
H	-2.42544	-4.67652	-3.49333
C	-2.85014	-3.64972	-1.65496
H	-2.03481	-2.93629	-1.78184
C	-1.05286	-3.33291	1.17583
H	-0.53792	-3.73366	0.28557
C	-1.72133	-4.50799	1.87526
H	-2.47396	-4.98612	1.24232
H	-2.17937	-4.21357	2.82464
C	0.95547	0.97616	-1.03015
H	0.34458	0.69635	-1.88782
H	0.49771	1.63807	-0.29624
C	2.33642	0.87401	-1.09262
C	3.00262	0.43301	-2.36555
H	4.00292	0.01427	-2.22229
H	2.38560	-0.28769	-2.91163
H	3.12246	1.32617	-2.99348
C	3.14889	1.53244	-0.04246
C	4.08667	0.77958	0.67878
C	2.96939	2.88041	0.27278
C	4.83343	1.37507	1.69290
C	3.73807	3.48116	1.26169
H	2.23188	3.46411	-0.27783
C	4.66820	2.72665	1.97076
H	5.53873	0.78406	2.27227
H	3.61086	4.53890	1.47847
H	5.26365	3.18836	2.75389
C	3.19257	-1.31905	-0.12273
O	3.26752	-2.39488	-0.67069
N	4.22897	-0.59489	0.37077
C	5.59067	-1.18684	0.22223
H	5.47598	-2.26699	0.35537

H	6.20440	-0.80672	1.04429
C	6.18763	-0.85819	-1.11339
C	6.80095	0.37995	-1.32481
C	6.07336	-1.75708	-2.17649
C	7.27827	0.72030	-2.58476
H	6.90392	1.07996	-0.49598
C	6.55658	-1.41725	-3.43583
H	5.59256	-2.71970	-2.01209
C	7.15356	-0.17727	-3.64216
H	7.75694	1.68382	-2.74101
H	6.46887	-2.12373	-4.25741
H	7.53195	0.08714	-4.62647
C	-0.01162	-2.72477	2.09397
C	-0.38993	-2.09185	3.28084
C	1.35421	-2.78610	1.75812
C	0.56773	-1.53334	4.11806
H	-1.44638	-2.01737	3.53339
C	2.31596	-2.22569	2.62098
H	1.67052	-3.39289	0.90868
C	1.92264	-1.58621	3.78780
H	0.25571	-1.05150	5.04195
H	3.37140	-2.32340	2.37645
H	2.66561	-1.15153	4.45080
H	-0.94849	-5.25171	2.09751

(*R*)-C: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2849.591819 hartree
Gibbs correction= 0.728849 hartree
Total Gibbs Energy= -2848.86297 hartree

Pd	-0.93646	-0.95993	-0.13647
P	1.43408	-0.63976	-0.36219
O	1.75059	0.40176	-1.59875
O	2.18722	0.12188	0.88220
N	2.31094	-1.98948	-0.75660
C	1.32544	2.48178	-0.49130
C	0.94676	1.52958	-1.41550
C	-0.27810	1.55838	-2.10856
H	-0.49370	0.76665	-2.82286
C	-1.16933	2.56287	-1.84204
H	-2.13175	2.59582	-2.35140
C	-0.88073	3.53692	-0.85544
C	-1.84520	4.51047	-0.49834
H	-2.79115	4.52289	-1.03850
C	-1.60742	5.39619	0.52103
H	-2.35695	6.13504	0.79267
C	-0.38804	5.34066	1.22817
H	-0.20937	6.03281	2.04722
C	0.57473	4.41943	0.89578
H	1.50798	4.38462	1.45210
C	0.36762	3.49723	-0.16060
C	2.65955	2.37756	0.14699
C	3.04703	1.20965	0.77720

C	4.29406	1.05688	1.41224
H	4.51442	0.11212	1.90482
C	5.18569	2.09418	1.39481
H	6.15123	1.99795	1.88763
C	4.88142	3.29811	0.71710
C	5.82543	4.35089	0.65061
H	6.77858	4.22336	1.16105
C	5.55357	5.49723	-0.04952
H	6.28639	6.29828	-0.09844
C	4.32216	5.62775	-0.72363
H	4.11745	6.52659	-1.29997
C	3.38131	4.62946	-0.66866
H	2.44403	4.74478	-1.20645
C	3.61889	3.44135	0.06710
C	3.79222	-1.90948	-0.83818
H	4.01946	-0.85792	-0.59754
C	4.29207	-2.11531	-2.26062
H	3.70428	-1.49025	-2.94102
H	4.22353	-3.15620	-2.59201
H	5.33842	-1.80320	-2.34651
C	4.47280	-2.73920	0.23539
C	5.61341	-3.49678	-0.03274
H	6.02173	-3.53395	-1.04005
C	6.24097	-4.21939	0.97897
H	7.12684	-4.80611	0.74850
C	5.73911	-4.19398	2.27424
H	6.22842	-4.76022	3.06256
C	4.60468	-3.43717	2.55457
H	4.20518	-3.40811	3.56569
C	3.97879	-2.71689	1.54445
H	3.09409	-2.12200	1.77258
C	1.52989	-3.25023	-0.67870
H	1.31466	-3.47677	0.38114
C	2.25310	-4.46102	-1.25733
H	3.20336	-4.65449	-0.75260
H	2.42791	-4.34767	-2.33223
C	-0.77460	-0.12721	1.94550
H	-0.39119	-0.99700	2.47950
H	-0.10638	0.72900	1.85971
C	-2.12990	0.02096	1.71473
C	-2.87928	-0.95026	-0.69951
O	-2.77325	-0.54606	-1.83865
N	-3.99929	-1.29241	-0.04713
C	-5.28726	-0.99153	-0.74148
H	-6.05061	-1.64714	-0.31406
H	-5.14842	-1.26265	-1.79283
C	-5.64360	0.45539	-0.57542
C	-5.27513	1.39132	-1.54494
C	-6.27009	0.89056	0.59551
C	-5.51746	2.74581	-1.33779
H	-4.79396	1.05082	-2.46025

C	-6.50880	2.24405	0.80273
H	-6.56838	0.16124	1.34880
C	-6.12693	3.17369	-0.16164
H	-5.24301	3.46768	-2.10431
H	-7.00061	2.57496	1.71400
H	-6.32008	4.23173	-0.00236
C	0.20193	-3.11933	-1.40983
C	0.16678	-2.75049	-2.76618
C	-0.97900	-3.59936	-0.81176
C	-0.99289	-2.90890	-3.50755
H	1.07251	-2.36085	-3.23096
C	-2.13932	-3.78105	-1.57657
H	-0.95411	-3.92772	0.22851
C	-2.14336	-3.44341	-2.91991
H	-1.00159	-2.63246	-4.55881
H	-3.03149	-4.18716	-1.10374
H	-3.04118	-3.58473	-3.51614
H	1.61184	-5.33814	-1.11855
C	-3.06159	-1.03631	2.18835
C	-3.03570	-1.43182	3.52812
C	-3.98144	-1.64936	1.32714
C	-3.91204	-2.39729	4.00803
H	-2.33055	-0.95059	4.20332
C	-4.84347	-2.63574	1.80009
C	-4.81688	-2.99958	3.14070
H	-3.88717	-2.67880	5.05704
H	-5.52461	-3.13534	1.11491
H	-5.49771	-3.76500	3.50286
C	-2.69687	1.36716	1.35866
H	-3.22978	1.75901	2.23595
H	-1.90176	2.07065	1.08920
H	-3.42921	1.33761	0.54311

(*S*)-TS3: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2849.587451 hartree
Gibbs correction= 0.731148 hartree
Total Gibbs Energy= -2848.856303 hartree

Pd	-1.15947	0.09805	-0.44906
P	0.90151	0.88532	0.29228
O	1.62280	0.14394	1.56959
O	2.01958	0.65774	-0.87701
N	0.90710	2.48685	0.73120
C	2.69205	-1.73844	0.55456
C	1.70407	-1.23220	1.37462
C	0.71417	-2.02447	1.98523
H	-0.02064	-1.53533	2.62190
C	0.70101	-3.37213	1.74676
H	-0.05076	-4.00938	2.20953
C	1.63717	-3.95350	0.85597
C	1.56960	-5.33163	0.53498
H	0.81595	-5.94173	1.03183
C	2.42664	-5.88498	-0.38115

H	2.36472	-6.94301	-0.62215
C	3.38817	-5.07377	-1.01933
H	4.05329	-5.51016	-1.76014
C	3.49184	-3.73854	-0.71711
H	4.23499	-3.12620	-1.22071
C	2.63469	-3.13702	0.23850
C	3.72063	-0.82579	0.00102
C	3.35593	0.31972	-0.68091
C	4.28861	1.18280	-1.28774
H	3.91650	2.04439	-1.83847
C	5.62471	0.91417	-1.17145
H	6.35979	1.56438	-1.64172
C	6.07517	-0.19465	-0.41684
C	7.45845	-0.43581	-0.23810
H	8.16687	0.23359	-0.72313
C	7.89696	-1.47707	0.53779
H	8.96104	-1.65139	0.67331
C	6.95963	-2.31396	1.17725
H	7.30786	-3.12266	1.81495
C	5.61144	-2.11460	1.01146
H	4.90589	-2.76280	1.52412
C	5.12304	-1.06377	0.19544
C	2.17557	3.25671	0.74498
H	2.93514	2.53967	0.39965
C	2.60996	3.64039	2.15290
H	2.53018	2.76391	2.80487
H	2.01924	4.45377	2.58381
H	3.65937	3.95444	2.14954
C	2.15884	4.37291	-0.28236
C	2.68738	5.63544	-0.01145
H	3.09501	5.85934	0.97187
C	2.69841	6.62507	-0.99124
H	3.11164	7.60390	-0.76039
C	2.18382	6.36602	-2.25566
H	2.19115	7.14005	-3.01876
C	1.65844	5.10800	-2.53828
H	1.25461	4.89435	-3.52510
C	1.64717	4.12145	-1.56017
H	1.23399	3.13828	-1.78895
C	-0.44267	3.10421	0.86190
H	-0.84283	3.30425	-0.14702
C	-0.45678	4.42066	1.62462
H	0.17370	5.17670	1.14817
H	-0.14762	4.29387	2.66696
C	-0.26778	-1.41719	-1.56840
H	0.39548	-0.99327	-2.32414
H	0.22328	-2.03574	-0.81430
C	-1.61052	-1.74984	-1.94570
C	-1.90506	-1.73233	-3.43872
H	-2.97039	-1.84558	-3.66132
H	-1.54245	-0.80707	-3.89710

H	-1.37439	-2.58006	-3.88896
C	-2.33690	-2.74917	-1.12317
C	-3.64080	-2.38281	-0.77170
C	-1.82122	-3.96189	-0.67897
C	-4.44153	-3.21544	-0.00079
C	-2.62353	-4.81304	0.07596
H	-0.80330	-4.25096	-0.94035
C	-3.92405	-4.44144	0.40801
H	-5.44529	-2.91327	0.28699
H	-2.23552	-5.77541	0.40008
H	-4.54324	-5.10934	1.00095
C	-3.00721	-0.28887	-1.63681
O	-3.10591	0.72450	-2.28955
N	-4.01409	-1.10766	-1.23447
C	-5.40392	-0.74498	-1.59797
H	-5.96594	-1.68297	-1.65920
H	-5.35275	-0.30951	-2.60429
C	-6.04093	0.21691	-0.63547
C	-5.84551	1.59231	-0.78698
C	-6.80413	-0.24899	0.43657
C	-6.38280	2.48253	0.13667
H	-5.26512	1.95674	-1.63337
C	-7.34159	0.64120	1.36060
H	-6.99535	-1.31703	0.54162
C	-7.12442	2.00811	1.21511
H	-6.23046	3.55151	0.00896
H	-7.93893	0.26846	2.18889
H	-7.54648	2.70514	1.93460
C	-1.35049	2.10402	1.55079
C	-1.01877	1.62541	2.82486
C	-2.52900	1.64326	0.93514
C	-1.82949	0.70045	3.46490
H	-0.09919	1.96615	3.29792
C	-3.34022	0.69917	1.59147
H	-2.87242	2.10601	0.00661
C	-2.98378	0.21992	2.84290
H	-1.55908	0.34456	4.45658
H	-4.26031	0.36374	1.11746
H	-3.61410	-0.50939	3.34479
H	-1.48580	4.79606	1.62797

(*R*)-TS3: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2849.587078 hartree
Gibbs correction= 0.729175 hartree
Total Gibbs Energy= -2848.857903 hartree

Pd	-0.94380	-0.60311	-0.21676
P	1.33625	-0.67169	-0.35464
O	1.87225	0.30338	-1.56059
O	2.17672	-0.09956	0.92528
N	1.90204	-2.15786	-0.81312
C	2.06114	2.40637	-0.43411
C	1.41190	1.60711	-1.35179

C	0.24345	1.99330	-2.03365
H	-0.20314	1.30424	-2.74730
C	-0.30692	3.21784	-1.76520
H	-1.21153	3.53829	-2.27968
C	0.26719	4.06796	-0.78790
C	-0.34213	5.30178	-0.45310
H	-1.23954	5.59879	-0.99391
C	0.17992	6.10060	0.53098
H	-0.29565	7.04555	0.78046
C	1.33332	5.68838	1.23055
H	1.73310	6.31447	2.02424
C	1.95489	4.50369	0.92292
H	2.83875	4.19645	1.47546
C	1.45575	3.66392	-0.10418
C	3.30507	1.91357	0.20226
C	3.32486	0.69028	0.84443
C	4.46180	0.18789	1.50463
H	4.39367	-0.77402	2.00723
C	5.61859	0.91878	1.49335
H	6.50549	0.55068	2.00542
C	5.69229	2.14719	0.79585
C	6.90536	2.87397	0.73066
H	7.77244	2.48149	1.25921
C	6.99151	4.03580	0.00875
H	7.92836	4.58451	-0.03927
C	5.86163	4.51036	-0.68901
H	5.93847	5.41769	-1.28293
C	4.66751	3.83548	-0.63417
H	3.81189	4.21073	-1.18915
C	4.53622	2.64499	0.12367
C	3.37423	-2.32692	-0.98985
H	3.79997	-1.35399	-0.69584
C	3.75073	-2.50392	-2.45383
H	3.22070	-1.75599	-3.05219
H	3.51051	-3.49672	-2.84457
H	4.82489	-2.33877	-2.59036
C	3.95396	-3.33814	-0.01908
C	4.92961	-4.25544	-0.41008
H	5.26680	-4.28836	-1.44359
C	5.48466	-5.13926	0.51219
H	6.24330	-5.84692	0.18706
C	5.07256	-5.11945	1.83882
H	5.50493	-5.81117	2.55715
C	4.10156	-4.20648	2.24143
H	3.77271	-4.18138	3.27773
C	3.54967	-3.32408	1.32072
H	2.79462	-2.60719	1.64540
C	0.97756	-3.30704	-0.67505
H	0.97911	-3.65127	0.37352
C	1.39000	-4.48890	-1.54988
H	2.38322	-4.86439	-1.28972

H	1.36697	-4.21323	-2.61050
C	-0.97312	0.76128	1.35443
H	-0.51050	0.19873	2.16788
H	-0.45778	1.68665	1.08578
C	-2.40251	0.71137	1.20771
C	-3.06702	-0.04154	-0.53897
O	-3.00301	0.53936	-1.59821
N	-4.09652	-0.78100	-0.05374
C	-5.34213	-0.85116	-0.85036
H	-5.85641	-1.77969	-0.57735
H	-5.03578	-0.93152	-1.89780
C	-6.19417	0.36506	-0.62539
C	-6.08768	1.45768	-1.48953
C	-7.04380	0.44710	0.48056
C	-6.81627	2.61709	-1.24691
H	-5.42207	1.39516	-2.34847
C	-7.76846	1.60802	0.72411
H	-7.14005	-0.40394	1.15378
C	-7.65355	2.69482	-0.13837
H	-6.73341	3.46048	-1.92793
H	-8.43066	1.66232	1.58451
H	-8.22484	3.60039	0.04994
C	-0.46300	-2.98641	-1.05363
C	-0.79522	-2.24736	-2.20936
C	-1.48386	-3.70568	-0.40626
C	-2.09608	-2.29500	-2.72961
H	-0.00731	-1.73714	-2.76586
C	-2.76384	-3.76003	-0.93952
H	-1.23991	-4.27331	0.49102
C	-3.06757	-3.07201	-2.11478
H	-2.32922	-1.73306	-3.63039
H	-3.52794	-4.35313	-0.44182
H	-4.06302	-3.14259	-2.54680
H	0.67491	-5.30396	-1.39771
C	-3.15029	-0.26981	2.03617
C	-2.98367	-0.47390	3.40129
C	-4.07565	-1.04370	1.32982
C	-3.76263	-1.42422	4.05538
H	-2.26567	0.12801	3.95573
C	-4.84641	-2.00661	1.96957
C	-4.68765	-2.18177	3.34122
H	-3.65309	-1.56994	5.12637
H	-5.55712	-2.61666	1.41692
H	-5.29115	-2.92439	3.85633
C	-3.09100	2.04292	0.93712
H	-3.02811	2.63710	1.85709
H	-2.57990	2.58332	0.13239
H	-4.15014	1.92822	0.67939

(*S*)-D: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2849.631763 hartree
Gibbs correction= 0.735683 hartree

Total Gibbs Energy= -2848.89608 hartree

Pd	-0.61732	-1.51125	0.73799
P	1.32868	-0.75821	-0.09413
O	1.26186	0.07215	-1.50413
O	2.05161	0.31722	0.88767
N	2.37173	-1.99464	-0.44639
C	0.88530	2.32868	-0.80038
C	0.43340	1.19154	-1.43655
C	-0.85862	1.06176	-1.97754
H	-1.11974	0.12399	-2.46688
C	-1.74364	2.09790	-1.84002
H	-2.75098	2.02830	-2.25065
C	-1.37962	3.26474	-1.12216
C	-2.31721	4.30182	-0.90334
H	-3.31501	4.19588	-1.32653
C	-1.98526	5.40429	-0.15845
H	-2.71278	6.19620	0.00229
C	-0.69995	5.50403	0.41348
H	-0.44713	6.36831	1.02263
C	0.23725	4.52135	0.20764
H	1.22334	4.61073	0.65554
C	-0.06204	3.38331	-0.58201
C	2.28872	2.39784	-0.32926
C	2.81584	1.41193	0.48158
C	4.11960	1.46357	1.01040
H	4.44693	0.66165	1.66875
C	4.93239	2.51400	0.68265
H	5.94020	2.57643	1.08832
C	4.48950	3.51970	-0.20848
C	5.35219	4.57081	-0.60193
H	6.35341	4.60490	-0.17587
C	4.94355	5.51464	-1.50782
H	5.61455	6.31513	-1.80774
C	3.65120	5.43343	-2.06561
H	3.33759	6.16648	-2.80464
C	2.78634	4.43443	-1.69310
H	1.79949	4.38251	-2.14477
C	3.16668	3.45706	-0.74002
C	3.81220	-1.69990	-0.66851
H	3.90232	-0.61543	-0.50423
C	4.22712	-1.91694	-2.11696
H	3.49235	-1.44293	-2.77643
H	4.31245	-2.97242	-2.38997
H	5.19636	-1.44233	-2.30460
C	4.68198	-2.35493	0.38771
C	5.88963	-2.97640	0.06933
H	6.21833	-3.03668	-0.96582
C	6.68814	-3.52876	1.06792
H	7.62460	-4.01184	0.80009
C	6.29205	-3.46524	2.39813
H	6.91531	-3.89854	3.17609

C	5.09093	-2.84287	2.72776
H	4.77271	-2.78632	3.76605
C	4.29448	-2.29315	1.73090
H	3.35537	-1.80602	1.99690
C	1.83255	-3.36753	-0.25640
H	1.84865	-3.61205	0.81954
C	2.62507	-4.44700	-0.98024
H	3.66405	-4.49013	-0.64164
H	2.59929	-4.31006	-2.06623
C	-1.00480	0.38876	1.49502
H	-0.14161	0.73940	2.07038
H	-1.15789	1.01266	0.61029
C	-2.28256	0.28314	2.32990
C	-1.97229	0.04665	3.81076
H	-2.89029	-0.08263	4.39465
H	-1.34630	-0.84537	3.93013
H	-1.43090	0.91104	4.21148
C	-3.25710	1.41600	2.11831
C	-4.46869	0.88949	1.65853
C	-3.12214	2.77944	2.29743
C	-5.56013	1.68362	1.36617
C	-4.21882	3.60214	2.02221
H	-2.17498	3.20586	2.62798
C	-5.41562	3.06018	1.56531
H	-6.49244	1.26705	0.99228
H	-4.13131	4.67700	2.15783
H	-6.25647	3.71549	1.35346
C	-3.07758	-0.88864	1.80188
O	-2.59834	-2.02101	1.60426
N	-4.34108	-0.51912	1.51838
C	-5.27202	-1.40359	0.84614
H	-6.29015	-1.07325	1.08865
H	-5.15054	-2.39885	1.29110
C	-5.06836	-1.48420	-0.64915
C	-5.83609	-2.40180	-1.36969
C	-4.14741	-0.69024	-1.32906
C	-5.69176	-2.52034	-2.74675
H	-6.55734	-3.02732	-0.84380
C	-4.00396	-0.80839	-2.71004
H	-3.53335	0.03255	-0.78950
C	-4.77325	-1.71988	-3.42355
H	-6.30108	-3.23498	-3.29453
H	-3.28753	-0.17619	-3.23402
H	-4.66446	-1.80452	-4.50197
C	0.39381	-3.40960	-0.73479
C	0.07585	-3.05090	-2.06182
C	-0.62194	-3.92960	0.08672
C	-1.21431	-3.19612	-2.53570
H	0.85871	-2.64852	-2.70397
C	-1.92621	-4.08849	-0.41377
H	-0.37453	-4.28749	1.08701

C	-2.22225	-3.71381	-1.71116
H	-1.45187	-2.90901	-3.55800
H	-2.70133	-4.48374	0.23693
H	-3.23723	-3.80944	-2.09219
H	2.15955	-5.41284	-0.75605

(*R*)-D: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2849.630495 hartree
Gibbs correction= 0.732125 hartree
Total Gibbs Energy= -2848.89837 hartree

Pd	-0.87187	-1.15838	-0.19184
P	1.35388	-0.94570	-0.39951
O	2.00373	-0.16132	-1.68081
O	1.95925	-0.10333	0.85252
N	2.09095	-2.42906	-0.48405
C	2.01750	2.12389	-0.95850
C	1.54664	1.14873	-1.81409
C	0.57791	1.38502	-2.80540
H	0.29485	0.56402	-3.46063
C	0.01792	2.62975	-2.90346
H	-0.72959	2.84246	-3.66608
C	0.35316	3.64409	-1.97234
C	-0.33035	4.88452	-1.97446
H	-1.08428	5.05932	-2.74064
C	-0.06065	5.83822	-1.02589
H	-0.59464	6.78489	-1.03332
C	0.90966	5.58546	-0.03318
H	1.11008	6.33629	0.72698
C	1.60268	4.39983	-0.01526
H	2.34201	4.21598	0.75969
C	1.35591	3.39672	-0.98587
C	3.13066	1.82053	-0.02891
C	3.07118	0.73596	0.82312
C	4.07480	0.43802	1.76446
H	3.93669	-0.41930	2.41975
C	5.18741	1.23109	1.82747
H	5.97005	1.02344	2.55446
C	5.35319	2.31629	0.93477
C	6.53192	3.09947	0.95796
H	7.29297	2.86633	1.70065
C	6.71822	4.11768	0.05952
H	7.62857	4.71076	0.08200
C	5.72922	4.38286	-0.90964
H	5.88944	5.17271	-1.63924
C	4.56897	3.64974	-0.94879
H	3.82556	3.86284	-1.71201
C	4.33221	2.60688	-0.01888
C	3.55146	-2.52793	-0.22060
H	3.86216	-1.49836	0.01439
C	4.33545	-2.90303	-1.47062
H	3.99225	-2.28660	-2.30819
H	4.23300	-3.95626	-1.74671

H	5.40097	-2.69706	-1.32210
C	3.83837	-3.34539	1.02502
C	4.89342	-4.25636	1.08277
H	5.51703	-4.42824	0.20831
C	5.16225	-4.95791	2.25558
H	5.98730	-5.66555	2.27998
C	4.38198	-4.75757	3.38757
H	4.59185	-5.30723	4.30149
C	3.32885	-3.84800	3.34268
H	2.71270	-3.68274	4.22337
C	3.06086	-3.14901	2.17222
H	2.23509	-2.43679	2.14628
C	1.18854	-3.60919	-0.52143
H	0.82059	-3.81445	0.49847
C	1.85876	-4.87923	-1.02686
H	2.69853	-5.17846	-0.39328
H	2.20163	-4.77379	-2.06137
C	-0.98111	0.74212	0.62639
H	-0.74473	0.57895	1.68505
H	-0.27996	1.46254	0.19378
C	-2.43621	1.12096	0.38499
C	-3.27371	-0.05347	0.81517
O	-3.02247	-1.22622	0.47882
N	-4.26920	0.35398	1.62315
C	-5.31226	-0.54325	2.11638
H	-5.74766	-0.07768	3.00790
H	-4.82584	-1.47247	2.43531
C	-6.35026	-0.82187	1.06352
C	-6.46542	-2.09420	0.50780
C	-7.18977	0.20056	0.61657
C	-7.41679	-2.34783	-0.47611
H	-5.80524	-2.88905	0.85349
C	-8.13548	-0.04996	-0.36957
H	-7.10134	1.19894	1.04597
C	-8.25173	-1.32638	-0.91524
H	-7.50783	-3.34592	-0.89783
H	-8.78992	0.74922	-0.70872
H	-8.99726	-1.52387	-1.68143
C	-0.00441	-3.29609	-1.40354
C	0.18912	-2.92882	-2.75133
C	-1.31633	-3.48048	-0.93378
C	-0.89392	-2.74636	-3.58991
H	1.20436	-2.78122	-3.11878
C	-2.41066	-3.29416	-1.79735
H	-1.48064	-3.84692	0.08048
C	-2.20034	-2.92406	-3.11314
H	-0.73087	-2.46921	-4.62868
H	-3.41859	-3.42953	-1.41446
H	-3.04603	-2.78105	-3.78052
H	1.11733	-5.68511	-1.00210
C	-2.99187	2.22706	1.24169

C	-2.61828	3.55089	1.37367
C	-4.11575	1.73570	1.91552
C	-3.37886	4.37579	2.20679
H	-1.74914	3.93873	0.83886
C	-4.88777	2.54020	2.73358
C	-4.49453	3.87457	2.87081
H	-3.10093	5.41827	2.33541
H	-5.76496	2.16379	3.25484
H	-5.07807	4.53212	3.50982
C	-2.74023	1.40845	-1.09305
H	-2.18129	2.29781	-1.40749
H	-2.44335	0.56624	-1.73323
H	-3.81046	1.60173	-1.23339

(*S*)-E[1]: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.593039 hartree
Gibbs correction= 0.731853 hartree
Total Gibbs Energy= -2941.861186 hartree

Pd	-0.32521	-1.77114	0.78024
P	1.20035	0.04453	1.14153
O	2.79920	0.02590	1.57379
O	1.31515	0.72674	-0.35888
N	0.62453	1.24459	2.17081
C	3.89590	-0.54794	-0.47131
C	3.51076	-0.89226	0.80812
C	3.75991	-2.15350	1.37769
H	3.42341	-2.33593	2.39600
C	4.39201	-3.10816	0.63018
H	4.59472	-4.09359	1.04555
C	4.73910	-2.85300	-0.71757
C	5.30833	-3.86827	-1.52181
H	5.50253	-4.83835	-1.06665
C	5.58288	-3.64829	-2.84621
H	6.00818	-4.44028	-3.45795
C	5.28852	-2.39552	-3.42187
H	5.47755	-2.23120	-4.48020
C	4.75330	-1.38474	-2.66378
H	4.51607	-0.43008	-3.12554
C	4.47796	-1.57147	-1.28693
C	3.65504	0.82914	-0.96082
C	2.39450	1.39557	-0.89206
C	2.10856	2.67174	-1.42399
H	1.08342	3.03220	-1.36265
C	3.10664	3.41440	-1.98941
H	2.89514	4.39638	-2.40932
C	4.43666	2.93195	-2.01099
C	5.48935	3.72294	-2.53008
H	5.24380	4.70043	-2.94343
C	6.78607	3.27917	-2.50221
H	7.58787	3.89674	-2.89986
C	7.07859	2.02035	-1.93828
H	8.10951	1.67695	-1.89181

C	6.07691	1.22458	-1.44045
H	6.32130	0.26104	-1.00196
C	4.72151	1.64049	-1.47588
C	1.04429	2.64913	1.98429
H	1.71263	2.63278	1.11156
C	1.91276	3.15702	3.12976
H	2.66623	2.39680	3.36178
H	1.34690	3.37535	4.04050
H	2.43936	4.07142	2.83272
C	-0.12537	3.53530	1.59190
C	-0.28484	4.82564	2.09863
H	0.43174	5.22258	2.81498
C	-1.36108	5.61716	1.70377
H	-1.46830	6.61988	2.11201
C	-2.29747	5.12808	0.80063
H	-3.14300	5.74284	0.50064
C	-2.14524	3.84337	0.28481
H	-2.87433	3.44291	-0.41979
C	-1.06504	3.05892	0.67010
H	-0.96187	2.05293	0.26587
C	-0.56238	0.88937	2.98881
H	-1.47248	0.99064	2.37665
C	-0.73622	1.76626	4.22321
H	-0.90856	2.81437	3.96016
H	0.12639	1.69920	4.89564
C	-1.88808	-2.93115	0.02899
H	-1.55726	-3.83084	-0.49817
H	-2.48049	-3.22612	0.90721
C	-2.69252	-2.03014	-0.90642
C	-1.91473	-1.63417	-2.17513
H	-2.56698	-1.08090	-2.86360
H	-1.04308	-1.01987	-1.92477
H	-1.55529	-2.53680	-2.68207
C	-4.03549	-2.59173	-1.31125
C	-5.02588	-1.64222	-1.04303
C	-4.37626	-3.78549	-1.91728
C	-6.35498	-1.84322	-1.37146
C	-5.71560	-4.01778	-2.24605
H	-3.61068	-4.52914	-2.13494
C	-6.68600	-3.05686	-1.97989
H	-7.11128	-1.08617	-1.17606
H	-6.00038	-4.95389	-2.71982
H	-7.72151	-3.24865	-2.25101
C	-3.09788	-0.72814	-0.22320
O	-2.35720	0.05349	0.36731
N	-4.44182	-0.53517	-0.39969
C	-5.13022	0.67806	-0.01319
H	-4.45209	1.19790	0.67755
H	-6.04084	0.41822	0.54428
C	-5.46022	1.55700	-1.19213
C	-6.74288	2.07057	-1.36507

C	-4.46538	1.88173	-2.11768
C	-7.03174	2.90226	-2.44350
H	-7.52337	1.81503	-0.64794
C	-4.75206	2.71091	-3.19512
H	-3.45871	1.48169	-1.98571
C	-6.03712	3.22294	-3.36021
H	-8.03815	3.29462	-2.57014
H	-3.97055	2.95765	-3.90991
H	-6.26167	3.86920	-4.20542
C	-0.45246	-0.55480	3.43071
C	0.64377	-0.97916	4.19488
C	-1.46245	-1.47609	3.12424
C	0.72811	-2.28996	4.63598
H	1.44392	-0.27165	4.41238
C	-1.36798	-2.80087	3.57272
H	-2.34644	-1.13388	2.58555
C	-0.27676	-3.20837	4.32374
H	1.58570	-2.60589	5.22608
H	-2.15694	-3.50808	3.32629
H	-0.20171	-4.23758	4.66481
H	-1.61599	1.41092	4.77170
C	0.71287	-2.65931	-0.63216
N	1.32629	-3.18163	-1.48159

(*S*)-E^2: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.605407 hartree
Gibbs correction= 0.732739 hartree
Total Gibbs Energy= -2941.872668 hartree

Pd	-0.70658	-0.85323	1.52579
P	0.96572	0.68360	0.92226
O	2.49484	0.48381	1.53782
O	1.32591	0.66367	-0.68601
N	0.64273	2.26784	1.32944
C	3.47065	-1.09638	0.03712
C	2.94039	-0.80492	1.27810
C	2.75037	-1.77134	2.28375
H	2.31732	-1.45241	3.22975
C	3.09114	-3.07189	2.03187
H	2.95279	-3.83765	2.79281
C	3.58631	-3.45397	0.76110
C	3.87257	-4.81040	0.47421
H	3.73911	-5.54434	1.26758
C	4.28759	-5.19592	-0.77411
H	4.49735	-6.24179	-0.98440
C	4.42240	-4.23173	-1.79415
H	4.72443	-4.54152	-2.79189
C	4.16875	-2.90596	-1.54357
H	4.26711	-2.17644	-2.34304
C	3.76530	-2.46870	-0.25681
C	3.63294	-0.00749	-0.95430
C	2.56350	0.81098	-1.27240
C	2.63840	1.80349	-2.27287

H	1.74051	2.38039	-2.48837
C	3.81785	2.01541	-2.93045
H	3.88725	2.77305	-3.70905
C	4.97500	1.27465	-2.59074
C	6.21678	1.53609	-3.21755
H	6.25262	2.30174	-3.99135
C	7.34908	0.85482	-2.85266
H	8.29886	1.06687	-3.33748
C	7.28042	-0.11388	-1.83030
H	8.18273	-0.63684	-1.52201
C	6.08777	-0.39919	-1.21324
H	6.05469	-1.14110	-0.41974
C	4.89265	0.26837	-1.58268
C	1.39753	3.37512	0.70896
H	2.10794	2.87929	0.03060
C	2.27356	4.11737	1.71122
H	2.82092	3.38530	2.31439
H	1.70520	4.77031	2.38104
H	3.01269	4.73434	1.18770
C	0.52136	4.24357	-0.17702
C	0.67894	5.62933	-0.23699
H	1.41883	6.12300	0.38961
C	-0.10924	6.39914	-1.08880
H	0.02682	7.47812	-1.11765
C	-1.06757	5.79415	-1.89313
H	-1.68749	6.39584	-2.55387
C	-1.23009	4.41252	-1.84102
H	-1.98203	3.92395	-2.45709
C	-0.44257	3.64142	-0.99421
H	-0.59862	2.56332	-0.96106
C	-0.60866	2.44131	2.11494
H	-1.47107	2.26875	1.44884
C	-0.76914	3.82206	2.73625
H	-0.76286	4.61845	1.98613
H	0.00300	4.02195	3.48696
C	-0.38147	-1.94091	-0.22113
H	0.63140	-1.68893	-0.54903
H	-0.43182	-2.99229	0.07117
C	-1.42571	-1.59663	-1.30201
C	-0.72782	-1.24014	-2.61825
H	-1.46063	-1.04591	-3.41109
H	-0.10782	-0.34654	-2.47963
H	-0.08664	-2.06941	-2.94096
C	-2.43913	-2.69890	-1.46424
C	-3.70467	-2.21841	-1.13211
C	-2.28036	-4.01961	-1.83696
C	-4.83220	-3.01903	-1.16391
C	-3.40369	-4.85018	-1.87659
H	-1.29250	-4.40719	-2.08623
C	-4.65874	-4.35173	-1.54143
H	-5.81288	-2.62860	-0.90346

H	-3.29624	-5.89259	-2.16616
H	-5.52372	-5.01020	-1.57154
C	-2.31916	-0.41047	-0.88834
O	-1.97343	0.74946	-0.70223
N	-3.60858	-0.86234	-0.78463
C	-4.66976	-0.09630	-0.16867
H	-4.18215	0.79042	0.25937
H	-5.07957	-0.68940	0.66266
C	-5.75337	0.31449	-1.13023
C	-7.09566	0.09254	-0.83095
C	-5.41931	0.94810	-2.32830
C	-8.09355	0.49909	-1.71260
H	-7.35899	-0.40708	0.10160
C	-6.41288	1.35145	-3.21104
H	-4.36863	1.12306	-2.55936
C	-7.75355	1.12822	-2.90467
H	-9.13803	0.31744	-1.46921
H	-6.14261	1.84344	-4.14290
H	-8.53104	1.44294	-3.59707
C	-0.64091	1.39944	3.21827
C	0.42145	1.30160	4.13093
C	-1.75303	0.56072	3.38326
C	0.36752	0.39611	5.17761
H	1.29928	1.93138	3.99127
C	-1.79575	-0.36151	4.44106
H	-2.61654	0.67081	2.72531
C	-0.73994	-0.44295	5.33331
H	1.19726	0.33430	5.87868
H	-2.65150	-1.02568	4.52606
H	-0.77040	-1.16170	6.14811
H	-1.73817	3.84834	3.24692
C	-2.22972	-2.14348	1.88503
N	-3.18892	-2.76083	2.14934

(*R*)-E[2]: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.613824 hartree
Gibbs correction= 0.737192 hartree
Total Gibbs Energy= -2941.876632 hartree

Pd	-2.22979	-0.56463	-1.57259
P	-1.53144	-0.28758	0.65755
O	-1.48889	-1.61261	1.65887
O	0.04532	0.18429	0.78890
N	-2.43013	0.79649	1.55479
C	0.61490	-2.59950	1.08505
C	-0.76572	-2.63337	1.05049
C	-1.49151	-3.61117	0.34443
H	-2.57803	-3.56541	0.36924
C	-0.81370	-4.55882	-0.37297
H	-1.35483	-5.32112	-0.93036
C	0.60046	-4.52883	-0.45386
C	1.30104	-5.44380	-1.27570
H	0.72869	-6.19985	-1.81116

C	2.66396	-5.36966	-1.41047
H	3.19083	-6.07497	-2.04868
C	3.37961	-4.35936	-0.73644
H	4.45502	-4.27352	-0.87564
C	2.73131	-3.46284	0.07623
H	3.29379	-2.66556	0.55647
C	1.32925	-3.53497	0.26677
C	1.29700	-1.56055	1.88854
C	0.97572	-0.22738	1.71642
C	1.62252	0.80486	2.42999
H	1.31449	1.83174	2.23928
C	2.59447	0.49582	3.34077
H	3.10398	1.28390	3.89277
C	2.92816	-0.85305	3.60848
C	3.88869	-1.18340	4.59410
H	4.39201	-0.37102	5.11668
C	4.16949	-2.49096	4.89522
H	4.90592	-2.73402	5.65723
C	3.48408	-3.52339	4.22257
H	3.68750	-4.56063	4.47824
C	2.55625	-3.23428	3.25298
H	2.03064	-4.04243	2.75171
C	2.25976	-1.89403	2.89811
C	-1.88983	1.36061	2.80697
H	-0.92397	0.85137	2.94563
C	-2.71162	0.96370	4.02799
H	-2.93748	-0.10640	3.96581
H	-3.65087	1.51819	4.11599
H	-2.13622	1.12825	4.94597
C	-1.56075	2.83817	2.67700
C	-1.70454	3.72275	3.74706
H	-2.11012	3.37355	4.69441
C	-1.33601	5.06032	3.61915
H	-1.45891	5.73325	4.46500
C	-0.81766	5.53552	2.42019
H	-0.53312	6.58043	2.32155
C	-0.67373	4.66197	1.34555
H	-0.27831	5.01366	0.39284
C	-1.04168	3.32750	1.47249
H	-0.92744	2.66795	0.61286
C	-3.57927	1.38292	0.81522
H	-3.19966	2.09069	0.05811
C	-4.55719	2.14330	1.70060
H	-4.07823	2.97430	2.22764
H	-5.04333	1.48270	2.42658
C	-0.31333	-1.13005	-2.14000
H	0.12302	-1.59509	-1.25152
H	-0.42454	-1.88834	-2.92160
C	0.57376	0.00678	-2.63544
C	0.56170	1.25779	-1.74314
O	-0.38183	2.00354	-1.53115

N	1.83901	1.46270	-1.27160
C	2.22496	2.61173	-0.47960
H	2.89051	2.27550	0.32820
H	1.30402	2.98364	-0.01172
C	2.87591	3.69587	-1.29807
C	2.18181	4.25915	-2.37221
C	4.15558	4.15567	-0.99831
C	2.76604	5.26294	-3.13388
H	1.17574	3.90528	-2.59939
C	4.74088	5.16443	-1.75889
H	4.69878	3.71969	-0.15941
C	4.04745	5.71765	-2.82890
H	2.21911	5.69581	-3.96843
H	5.74216	5.51396	-1.51726
H	4.50366	6.50313	-3.42699
C	-4.32647	0.27867	0.09278
C	-4.82887	-0.82135	0.80678
C	-4.60205	0.38063	-1.27859
C	-5.59581	-1.78044	0.16686
H	-4.59574	-0.91712	1.86694
C	-5.37796	-0.59859	-1.91922
H	-4.26776	1.25792	-1.83405
C	-5.87230	-1.67258	-1.19945
H	-5.98222	-2.62565	0.73261
H	-5.55252	-0.51860	-2.98855
H	-6.46498	-2.43486	-1.69825
H	-5.33958	2.55971	1.05667
C	2.01310	-0.43994	-2.52137
C	2.66300	-1.53537	-3.05729
C	2.70926	0.45389	-1.70255
C	4.02192	-1.71597	-2.78270
H	2.12216	-2.24862	-3.67909
C	4.05347	0.28887	-1.41016
C	4.70257	-0.81541	-1.96950
H	4.54828	-2.56867	-3.20542
H	4.59163	0.99847	-0.78577
H	5.76045	-0.96653	-1.76585
C	0.23508	0.47029	-4.05403
H	0.27980	-0.37685	-4.74808
H	-0.77600	0.88621	-4.09121
H	0.95182	1.23315	-4.38579
C	-2.71055	-0.86394	-3.50717
N	-3.03332	-1.04134	-4.61814

(*S*)-E[3]: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.607505 hartree
Gibbs correction= 0.735578 hartree
Total Gibbs Energy= -2941.871927 hartree

Pd	-0.76065	-1.50688	0.44615
P	0.87687	0.22652	0.78203
O	2.28607	0.18712	1.64621
O	1.50345	0.41497	-0.74851

N	0.28715	1.72554	1.26111
C	3.85261	-0.92534	0.22487
C	3.05902	-0.93052	1.35492
C	2.95826	-2.02897	2.22474
H	2.28003	-1.96593	3.07155
C	3.66627	-3.16485	1.94792
H	3.57707	-4.03498	2.59498
C	4.46225	-3.25137	0.78146
C	5.14600	-4.44898	0.46000
H	5.07186	-5.28454	1.15442
C	5.86507	-4.56358	-0.70108
H	6.38078	-5.49090	-0.93906
C	5.91664	-3.47786	-1.59987
H	6.46326	-3.57724	-2.53499
C	5.27529	-2.29901	-1.31172
H	5.31407	-1.47705	-2.02156
C	4.54652	-2.13581	-0.10616
C	3.91543	0.28993	-0.61907
C	2.75415	0.88500	-1.08306
C	2.77501	1.97035	-1.98715
H	1.82236	2.36110	-2.33917
C	3.96719	2.50775	-2.38367
H	3.99195	3.34070	-3.08442
C	5.18688	2.01322	-1.86377
C	6.42206	2.61315	-2.20682
H	6.41322	3.44577	-2.90922
C	7.59822	2.16999	-1.65947
H	8.54129	2.64132	-1.92570
C	7.57764	1.10780	-0.73230
H	8.50617	0.77267	-0.27586
C	6.39673	0.49572	-0.39266
H	6.39773	-0.31495	0.33088
C	5.16441	0.91089	-0.95884
C	1.03713	2.94540	0.90292
H	1.91706	2.58982	0.34868
C	1.62116	3.66386	2.11555
H	2.06131	2.91642	2.78394
H	0.88346	4.24347	2.67789
H	2.42157	4.34570	1.80537
C	0.27054	3.81611	-0.07944
C	0.33025	5.20982	-0.02949
H	0.90424	5.70039	0.75366
C	-0.34229	5.99084	-0.96626
H	-0.28369	7.07519	-0.90271
C	-1.08387	5.39040	-1.97622
H	-1.60739	5.99885	-2.70997
C	-1.14394	4.00032	-2.04109
H	-1.71048	3.51741	-2.83681
C	-0.47911	3.21952	-1.10153
H	-0.54705	2.13269	-1.16075
C	-1.12352	1.79130	1.72812

H	-1.79733	1.75133	0.85484
C	-1.45166	3.07047	2.49124
H	-1.32377	3.97403	1.88474
H	-0.85521	3.15215	3.40703
C	-2.27680	-2.80485	-0.13520
H	-2.01492	-3.86675	-0.10820
H	-3.10487	-2.60886	0.55993
C	-2.60044	-2.33333	-1.55938
C	-1.51506	-2.77840	-2.54981
H	-1.72584	-2.41655	-3.56337
H	-0.53171	-2.41424	-2.22962
H	-1.48153	-3.87368	-2.57331
C	-3.97496	-2.65320	-2.09088
C	-4.63035	-1.45831	-2.41019
C	-4.60684	-3.86150	-2.31502
C	-5.90921	-1.43283	-2.93753
C	-5.89821	-3.86089	-2.85004
H	-4.10546	-4.79600	-2.06643
C	-6.53623	-2.66274	-3.15536
H	-6.41632	-0.49791	-3.16737
H	-6.41077	-4.80329	-3.02495
H	-7.54215	-2.67811	-3.56760
C	-2.64592	-0.82419	-1.52017
O	-1.78365	-0.10412	-0.99475
N	-3.78872	-0.36635	-2.08511
C	-4.15439	1.03918	-2.03861
H	-4.90819	1.21110	-2.81799
H	-3.26574	1.62030	-2.31555
C	-4.64788	1.48368	-0.68355
C	-4.24844	2.71885	-0.17321
C	-5.51444	0.68398	0.06592
C	-4.72696	3.15932	1.05777
H	-3.54360	3.33442	-0.73518
C	-5.97792	1.11809	1.30308
H	-5.82290	-0.28934	-0.31492
C	-5.58945	2.35937	1.80014
H	-4.40952	4.12628	1.44255
H	-6.64389	0.48263	1.88242
H	-5.95295	2.69808	2.76727
C	-1.46848	0.62816	2.63327
C	-0.64956	0.27289	3.70857
C	-2.68313	-0.03519	2.45813
C	-1.02671	-0.75152	4.56829
H	0.30070	0.78919	3.85120
C	-3.07183	-1.04380	3.33442
H	-3.32474	0.24113	1.62023
C	-2.23930	-1.41232	4.38445
H	-0.37013	-1.04044	5.38564
H	-4.02060	-1.55516	3.17963
H	-2.52569	-2.21960	5.05365
H	-2.50542	3.01014	2.78725

C	-0.14377	-2.94376	1.62185
N	0.19720	-3.78567	2.36051

(*S*)-E[4]: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.599709 hartree
Gibbs correction= 0.736292 hartree
Total Gibbs Energy= -2941.863417 hartree

Pd	-0.50430	-1.68123	-0.37457
P	1.60338	-0.95770	-0.24413
O	1.84690	0.07806	-1.49903
O	1.82496	0.04043	1.05857
N	2.97105	-1.91809	-0.33168
C	0.84239	2.06786	-0.67188
C	0.80804	1.00448	-1.54847
C	-0.26532	0.74864	-2.42292
H	-0.19819	-0.10419	-3.09406
C	-1.36898	1.55680	-2.36301
H	-2.21603	1.37976	-3.02486
C	-1.44927	2.60450	-1.41190
C	-2.63399	3.36391	-1.26027
H	-3.47123	3.15459	-1.92681
C	-2.73811	4.32681	-0.28941
H	-3.66194	4.88811	-0.17089
C	-1.65072	4.57230	0.57327
H	-1.74482	5.31895	1.35841
C	-0.47822	3.87083	0.43795
H	0.35092	4.06048	1.11528
C	-0.33549	2.87429	-0.55905
C	2.04345	2.26464	0.17721
C	2.49166	1.24154	0.99447
C	3.60360	1.38849	1.84754
H	3.87939	0.54959	2.48254
C	4.30630	2.56135	1.85159
H	5.16780	2.68739	2.50538
C	3.94730	3.61898	0.98180
C	4.70832	4.81152	0.92964
H	5.56651	4.90584	1.59377
C	4.38143	5.81955	0.05971
H	4.97581	6.72924	0.02450
C	3.27511	5.66778	-0.80180
H	3.02758	6.45964	-1.50485
C	2.51188	4.52741	-0.76864
H	1.66881	4.41969	-1.44639
C	2.81282	3.47158	0.12856
C	3.84262	-1.94024	-1.54491
H	3.33994	-1.26876	-2.25025
C	3.86273	-3.29673	-2.23314
H	2.83358	-3.62371	-2.41909
H	4.39012	-4.07160	-1.67033
H	4.35959	-3.19731	-3.20566
C	5.20251	-1.31380	-1.27587
C	6.40140	-1.99655	-1.48597

H	6.38420	-3.02497	-1.84162
C	7.62698	-1.37771	-1.25073
H	8.54886	-1.93009	-1.41978
C	7.67386	-0.06187	-0.80602
H	8.63109	0.42104	-0.62266
C	6.48503	0.63560	-0.60847
H	6.50191	1.67239	-0.27603
C	5.26559	0.01519	-0.84701
H	4.34314	0.57954	-0.71555
C	3.36333	-2.51402	0.97348
H	3.83301	-1.72215	1.58499
C	4.36436	-3.65714	0.88096
H	5.30033	-3.35795	0.40198
H	3.94402	-4.52137	0.35712
C	-1.07447	-0.42427	1.22258
H	-0.56051	-0.71881	2.14692
H	-0.79468	0.60661	0.97455
C	-2.59352	-0.55440	1.35677
C	-2.97011	-1.71328	2.29011
H	-4.05678	-1.86482	2.32678
H	-2.48661	-2.63794	1.95132
H	-2.61588	-1.49017	3.30401
C	-3.36143	0.69249	1.71174
C	-4.33648	0.91817	0.73467
C	-3.25641	1.55370	2.78576
C	-5.23733	1.96466	0.81076
C	-4.14192	2.63280	2.87509
H	-2.48793	1.39412	3.54138
C	-5.12242	2.82485	1.90680
H	-6.00687	2.10875	0.05526
H	-4.06941	3.32331	3.71188
H	-5.81329	3.65990	1.99926
C	-3.16188	-0.87702	-0.00598
O	-2.72768	-1.76759	-0.75101
N	-4.19844	-0.04706	-0.28834
C	-4.95416	-0.07386	-1.52457
H	-4.41235	-0.75879	-2.19016
H	-4.92413	0.92803	-1.97981
C	-6.37782	-0.52336	-1.32515
C	-7.43980	0.22250	-1.83063
C	-6.64240	-1.71175	-0.64233
C	-8.75168	-0.21113	-1.66061
H	-7.23637	1.15151	-2.36407
C	-7.95063	-2.14425	-0.46872
H	-5.81192	-2.30085	-0.25207
C	-9.00855	-1.39433	-0.97786
H	-9.57340	0.37957	-2.05883
H	-8.14731	-3.07238	0.06281
H	-10.03246	-1.73404	-0.84110
C	2.13423	-3.01072	1.71303
C	1.29844	-3.96173	1.11837

C	1.83873	-2.55509	2.99619
C	0.18400	-4.43936	1.79638
H	1.50021	-4.29511	0.10033
C	0.72740	-3.03886	3.68154
H	2.47772	-1.79980	3.45360
C	-0.10089	-3.98170	3.08188
H	-0.46830	-5.16402	1.31402
H	0.50623	-2.67378	4.68223
H	-0.97383	-4.35645	3.61288
H	4.59443	-3.97190	1.90514
C	0.08890	-2.82219	-2.00763
N	0.52600	-3.40478	-2.92528

(*R*)-E[4]: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.593174 hartree
Gibbs correction= 0.735779 hartree
Total Gibbs Energy= -2941.857395 hartree

Pd	0.99910	-1.68011	0.45605
P	-1.07102	-0.83411	0.46624
O	-1.75415	0.19495	1.57093
O	-1.12099	0.10222	-0.87716
N	-2.27039	-1.99145	0.46843
C	-1.43764	2.44010	0.77470
C	-1.27544	1.47491	1.75019
C	-0.71986	1.76002	3.01488
H	-0.70323	0.96110	3.75326
C	-0.24390	3.01279	3.28208
H	0.16661	3.25435	4.26147
C	-0.24245	4.00690	2.27331
C	0.33802	5.27705	2.50402
H	0.75376	5.48357	3.48976
C	0.39172	6.21936	1.50822
H	0.84357	7.19076	1.69449
C	-0.12580	5.91573	0.23203
H	-0.05485	6.64991	-0.56697
C	-0.71704	4.70083	-0.01348
H	-1.10592	4.47823	-1.00358
C	-0.81430	3.71517	0.99966
C	-2.26780	2.17324	-0.42326
C	-2.07282	1.04597	-1.19876
C	-2.77101	0.81299	-2.40212
H	-2.51959	-0.07610	-2.97468
C	-3.74203	1.68756	-2.79799
H	-4.28899	1.52236	-3.72437
C	-4.07876	2.80169	-1.99198
C	-5.14311	3.66025	-2.35601
H	-5.66916	3.46022	-3.28841
C	-5.51606	4.70509	-1.55064
H	-6.33948	5.35475	-1.83693
C	-4.83718	4.91988	-0.33443
H	-5.15055	5.72762	0.32291
C	-3.78871	4.11442	0.03671

H	-3.29064	4.29043	0.98573
C	-3.35645	3.04258	-0.78518
C	-3.63167	-1.59588	0.02794
H	-3.54530	-0.53359	-0.24349
C	-4.65123	-1.61522	1.16257
H	-4.20485	-1.16268	2.05368
H	-4.99977	-2.62129	1.41280
H	-5.52735	-1.01522	0.89168
C	-4.05101	-2.30951	-1.24539
C	-5.38920	-2.60970	-1.50799
H	-6.15837	-2.37235	-0.77595
C	-5.75801	-3.22244	-2.70303
H	-6.80580	-3.45092	-2.88691
C	-4.79535	-3.54926	-3.65150
H	-5.08465	-4.03748	-4.57944
C	-3.45893	-3.25358	-3.39809
H	-2.68201	-3.51159	-4.11467
C	-3.09196	-2.63427	-2.20966
H	-2.03669	-2.42909	-2.03479
C	-1.87764	-3.41694	0.68511
H	-1.38040	-3.78236	-0.22593
C	-3.05587	-4.34155	0.97084
H	-3.80321	-4.33892	0.17227
H	-3.53566	-4.10423	1.92672
C	1.67288	-0.65226	2.16148
H	1.07060	0.18646	2.51239
H	1.70506	-1.44871	2.91753
C	3.07152	-0.20707	1.72930
C	3.41301	-1.06689	0.50994
O	3.24216	-2.29501	0.45458
N	3.82136	-0.27606	-0.52041
C	3.97457	-0.76775	-1.87755
H	3.14990	-0.37401	-2.49101
H	3.83272	-1.85545	-1.82068
C	5.30450	-0.41382	-2.48854
C	6.47312	-0.41777	-1.72667
C	5.38095	-0.09849	-3.84479
C	7.69693	-0.11822	-2.31347
H	6.41768	-0.65200	-0.66426
C	6.60587	0.19598	-4.43474
H	4.46950	-0.08640	-4.44210
C	7.76736	0.18761	-3.66961
H	8.60098	-0.12266	-1.70862
H	6.65092	0.43945	-5.49384
H	8.72525	0.42316	-4.12749
C	-0.90313	-3.54327	1.84045
C	-1.18249	-2.96320	3.08167
C	0.25577	-4.31087	1.69697
C	-0.31069	-3.13067	4.15080
H	-2.08418	-2.36139	3.19763
C	1.12972	-4.47856	2.76868

H	0.48226	-4.75938	0.73023
C	0.85032	-3.88680	3.99617
H	-0.53807	-2.67222	5.11113
H	2.03720	-5.06235	2.63448
H	1.53369	-4.01497	4.83274
H	-2.65555	-5.35834	1.05035
C	3.14829	1.17215	1.12960
C	2.85423	2.41184	1.66381
C	3.62424	1.08067	-0.18220
C	3.02754	3.54993	0.87032
H	2.47043	2.49727	2.68083
C	3.80931	2.19180	-0.98599
C	3.49708	3.43656	-0.43398
H	2.77675	4.52900	1.27244
H	4.18245	2.09854	-2.00334
H	3.62158	4.33145	-1.03927
C	4.11711	-0.42033	2.82569
H	3.85903	0.18008	3.70637
H	4.13790	-1.47725	3.11750
H	5.11909	-0.12401	2.48782
C	0.56077	-2.63026	-1.35098
N	0.27533	-3.13611	-2.36847

(*S*)-TS4[1]: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.578493 hartree
Gibbs correction= 0.730421 hartree
Total Gibbs Energy= -2941.848072 hartree

Pd	-0.59992	-0.68218	0.47206
P	1.39792	0.49562	0.52450
O	2.62067	-0.11076	1.47198
O	2.21020	0.63021	-0.91116
N	1.28905	2.03754	1.18909
C	3.75632	-1.61633	0.00965
C	2.94366	-1.40953	1.10506
C	2.38462	-2.45750	1.85906
H	1.75774	-2.20372	2.71123
C	2.62799	-3.75043	1.48696
H	2.20551	-4.57924	2.05206
C	3.39009	-4.03500	0.32898
C	3.58205	-5.36928	-0.10121
H	3.14863	-6.17055	0.49549
C	4.27489	-5.64792	-1.25039
H	4.40766	-6.67682	-1.57606
C	4.79691	-4.59167	-2.02481
H	5.32109	-4.81118	-2.95208
C	4.63964	-3.28749	-1.62725
H	5.03389	-2.48309	-2.24258
C	3.95046	-2.96579	-0.43170
C	4.36190	-0.44835	-0.67075
C	3.57554	0.60786	-1.09840
C	4.10721	1.69918	-1.81912
H	3.42197	2.47378	-2.15576

C	5.44887	1.76327	-2.07089
H	5.86589	2.59769	-2.63227
C	6.32119	0.76322	-1.58041
C	7.72020	0.85843	-1.77314
H	8.10573	1.70542	-2.33939
C	8.57065	-0.08085	-1.25011
H	9.64427	0.00413	-1.40022
C	8.04598	-1.15243	-0.49861
H	8.72036	-1.88442	-0.06006
C	6.69258	-1.27914	-0.30750
H	6.30702	-2.10609	0.28238
C	5.78128	-0.34101	-0.85655
C	2.45864	2.93840	1.15737
H	3.24581	2.35223	0.65877
C	3.01253	3.22797	2.54793
H	3.07047	2.28698	3.10464
H	2.40224	3.93633	3.11704
H	4.02746	3.63614	2.47990
C	2.23579	4.15197	0.27113
C	2.75217	5.40763	0.59461
H	3.29914	5.54873	1.52427
C	2.57236	6.49443	-0.25763
H	2.98137	7.46450	0.01641
C	1.87302	6.34378	-1.44871
H	1.73004	7.19318	-2.11252
C	1.35528	5.09538	-1.78356
H	0.80477	4.96275	-2.71227
C	1.53535	4.01196	-0.93234
H	1.13104	3.03713	-1.20405
C	-0.08760	2.50023	1.47840
H	-0.61322	2.71578	0.53002
C	-0.14195	3.76763	2.32714
H	0.38163	4.60914	1.86451
H	0.26736	3.58742	3.32784
C	-2.20687	-2.18214	0.42792
H	-2.15083	-3.26293	0.56851
H	-2.38843	-1.75935	1.43614
C	-3.34756	-1.83976	-0.53028
C	-3.14781	-2.38968	-1.94513
H	-4.04171	-2.19242	-2.55116
H	-2.27883	-1.92386	-2.41875
H	-2.97910	-3.47178	-1.91137
C	-4.66068	-2.30451	0.05426
C	-5.51921	-1.21001	0.18631
C	-5.09104	-3.56475	0.42339
C	-6.80639	-1.33639	0.68176
C	-6.38490	-3.71635	0.93134
H	-4.43311	-4.42657	0.31624
C	-7.22626	-2.61537	1.05614
H	-7.47187	-0.47937	0.75726
H	-6.73786	-4.70155	1.22542

H	-8.23250	-2.74917	1.44629
C	-3.57190	-0.32721	-0.65116
O	-2.78286	0.50532	-1.06319
N	-4.85843	-0.04773	-0.23782
C	-5.45822	1.26530	-0.32740
H	-4.63249	1.94863	-0.56752
H	-5.85869	1.55516	0.65632
C	-6.53655	1.34657	-1.37732
C	-7.77614	1.91020	-1.08477
C	-6.29114	0.86990	-2.66604
C	-8.76004	2.00169	-2.06519
H	-7.97242	2.27924	-0.07757
C	-7.27273	0.95717	-3.64475
H	-5.31955	0.43320	-2.89885
C	-8.50995	1.52361	-3.34634
H	-9.72527	2.44141	-1.82459
H	-7.07223	0.58324	-4.64609
H	-9.27825	1.58960	-4.11310
C	-0.89738	1.44439	2.21588
C	-0.36547	0.74869	3.31431
C	-2.26301	1.31219	1.93874
C	-1.17691	-0.05949	4.09871
H	0.69646	0.85027	3.53957
C	-3.07943	0.51018	2.73628
H	-2.67854	1.84298	1.08250
C	-2.53865	-0.17812	3.81595
H	-0.74801	-0.59610	4.94193
H	-4.13896	0.41185	2.50140
H	-3.17294	-0.80603	4.43702
H	-1.19390	4.04918	2.44751
C	-0.50243	-2.39539	-0.49214
N	-0.07306	-3.25843	-1.16407

(*S*)-TS4[2]: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.57423 hartree
Gibbs correction= 0.73096 hartree
Total Gibbs Energy= -2941.84327 hartree

Pd	-0.34442	-1.45769	1.55756
P	1.13701	0.36799	1.14846
O	2.77489	0.37772	1.47535
O	1.22169	0.59235	-0.50557
N	0.70043	1.84077	1.82047
C	3.72171	-0.79152	-0.37446
C	3.36864	-0.75991	0.96051
C	3.52977	-1.86068	1.82431
H	3.21604	-1.75018	2.86041
C	4.05857	-3.02390	1.33587
H	4.19844	-3.88542	1.98644
C	4.39482	-3.14269	-0.03487
C	4.88132	-4.36477	-0.55866
H	5.02594	-5.19830	0.12731
C	5.14764	-4.50434	-1.89614

H	5.51542	-5.44981	-2.28739
C	4.92427	-3.41976	-2.76943
H	5.11001	-3.53836	-3.83443
C	4.46816	-2.21695	-2.29035
H	4.29227	-1.39301	-2.97682
C	4.20899	-2.02905	-0.90906
C	3.52832	0.42370	-1.19880
C	2.29406	1.05163	-1.23180
C	2.03436	2.15535	-2.07363
H	1.02976	2.57436	-2.06921
C	3.03387	2.67090	-2.85033
H	2.84201	3.51849	-3.50620
C	4.34190	2.13361	-2.79143
C	5.39975	2.70730	-3.53640
H	5.17459	3.55490	-4.18247
C	6.67782	2.22104	-3.43810
H	7.48408	2.67288	-4.01082
C	6.94669	1.13972	-2.57395
H	7.96455	0.76976	-2.47420
C	5.93877	0.55331	-1.84948
H	6.16590	-0.27151	-1.17921
C	4.60105	1.01421	-1.94579
C	1.26766	3.09945	1.29756
H	1.93793	2.78612	0.48302
C	2.18054	3.79179	2.30336
H	2.84783	3.04406	2.74457
H	1.63421	4.29362	3.10780
H	2.80440	4.54089	1.80215
C	0.21466	3.97894	0.64537
C	0.23704	5.36975	0.76054
H	1.00553	5.85582	1.35800
C	-0.72344	6.15282	0.12446
H	-0.68955	7.23512	0.23009
C	-1.72391	5.55659	-0.63368
H	-2.47971	6.16769	-1.12183
C	-1.75295	4.16998	-0.75669
H	-2.53768	3.68690	-1.33575
C	-0.79068	3.38821	-0.12898
H	-0.83434	2.30435	-0.22902
C	-0.48913	1.78997	2.71816
H	-1.39469	1.66488	2.10157
C	-0.67590	3.03959	3.56852
H	-0.79850	3.94254	2.96312
H	0.15397	3.18316	4.26901
C	-0.83561	-2.45275	-0.39591
H	0.16646	-2.06059	-0.62384
H	-0.80764	-3.52441	-0.60018
C	-1.90671	-1.74562	-1.23370
C	-1.24988	-1.10472	-2.46602
H	-2.00664	-0.63970	-3.11103
H	-0.53175	-0.33926	-2.14597

H	-0.72618	-1.86761	-3.05431
C	-3.04979	-2.64245	-1.63040
C	-4.25186	-2.06055	-1.22724
C	-3.06204	-3.84314	-2.31227
C	-5.48021	-2.63913	-1.49255
C	-4.28988	-4.45413	-2.58336
H	-2.12962	-4.30789	-2.63255
C	-5.47848	-3.85545	-2.17906
H	-6.40962	-2.16483	-1.18594
H	-4.31629	-5.40195	-3.11488
H	-6.42654	-4.33973	-2.40095
C	-2.63463	-0.61137	-0.49249
O	-2.13277	0.38376	0.00823
N	-3.98088	-0.86245	-0.54894
C	-4.97845	0.02238	0.00716
H	-4.42719	0.72726	0.64361
H	-5.65009	-0.55670	0.65650
C	-5.76511	0.76129	-1.04532
C	-7.14595	0.90367	-0.92891
C	-5.11259	1.33529	-2.13734
C	-7.86660	1.61617	-1.88311
H	-7.66104	0.44859	-0.08265
C	-5.83014	2.04390	-3.09294
H	-4.03281	1.21988	-2.23376
C	-7.20980	2.18751	-2.96715
H	-8.94484	1.71759	-1.78251
H	-5.31187	2.48523	-3.94139
H	-7.77149	2.74020	-3.71661
C	-0.37239	0.58492	3.63351
C	0.73533	0.44029	4.47573
C	-1.36702	-0.40376	3.64500
C	0.85351	-0.66873	5.30268
H	1.52574	1.19032	4.44628
C	-1.23496	-1.53037	4.46761
H	-2.26429	-0.27410	3.03703
C	-0.12582	-1.66231	5.29389
H	1.72110	-0.76739	5.95176
H	-1.99974	-2.30263	4.43362
H	-0.02185	-2.53879	5.92860
H	-1.58720	2.90690	4.16234
C	-1.71168	-2.85888	1.25594
N	-2.63653	-3.53464	1.52557

(*S*)-F: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2942.624038 hartree
Gibbs correction= 0.73302 hartree
Total Gibbs Energy= -2941.891018 hartree

Pd	0.61907	-0.86056	0.80075
P	-1.03256	0.38876	0.04157
O	-2.01725	-0.28867	-1.13462
O	-2.24310	0.79457	1.12048
N	-0.63343	1.83318	-0.73888

C	-3.62388	-1.53134	0.10152
C	-2.50917	-1.50879	-0.71135
C	-1.80348	-2.66879	-1.08062
H	-0.92400	-2.56784	-1.71351
C	-2.21726	-3.88470	-0.61108
H	-1.65990	-4.78358	-0.86872
C	-3.32470	-3.97560	0.26684
C	-3.72159	-5.22412	0.80385
H	-3.17411	-6.11324	0.49420
C	-4.75390	-5.31255	1.70167
H	-5.04547	-6.27703	2.11081
C	-5.42562	-4.14181	2.11009
H	-6.22621	-4.20739	2.84352
C	-5.07325	-2.91755	1.59867
H	-5.59171	-2.02290	1.93327
C	-4.02973	-2.79320	0.64700
C	-4.30980	-0.25483	0.40272
C	-3.59970	0.83173	0.89091
C	-4.24547	2.03037	1.26946
H	-3.63770	2.83006	1.68510
C	-5.59525	2.16838	1.10773
H	-6.09507	3.08847	1.40639
C	-6.35898	1.13270	0.52114
C	-7.74397	1.29384	0.27796
H	-8.21620	2.22557	0.58726
C	-8.47075	0.31187	-0.34401
H	-9.53335	0.44770	-0.53095
C	-7.82686	-0.87211	-0.75885
H	-8.39453	-1.64106	-1.27801
C	-6.48818	-1.06275	-0.52213
H	-6.00679	-1.97681	-0.85887
C	-5.71089	-0.08017	0.14369
C	-1.68165	2.75477	-1.22179
H	-2.63058	2.26348	-0.95675
C	-1.71237	2.89137	-2.73807
H	-1.81331	1.90394	-3.19527
H	-0.80966	3.36407	-3.14299
H	-2.57829	3.48432	-3.05144
C	-1.68375	4.07640	-0.46048
C	-1.90696	5.30210	-1.08621
H	-2.05202	5.34962	-2.16297
C	-1.92991	6.48790	-0.35359
H	-2.09808	7.43182	-0.86782
C	-1.73418	6.46816	1.02059
H	-1.74962	7.39343	1.59193
C	-1.51399	5.24941	1.65906
H	-1.35501	5.21703	2.73495
C	-1.48856	4.07053	0.92576
H	-1.29408	3.12316	1.42671
C	0.80721	2.05411	-0.97289
H	1.30090	1.60076	-0.09267

C	1.21204	3.52632	-0.98222
H	0.91832	4.02664	-0.05614
H	0.77611	4.07907	-1.82133
C	2.81886	-2.58562	-1.73466
H	3.27993	-2.91741	-2.67627
H	2.31621	-1.63084	-1.95025
C	3.93487	-2.38220	-0.68589
C	4.49212	-3.71131	-0.18149
H	5.31731	-3.54024	0.51832
H	3.71143	-4.28513	0.32905
H	4.87416	-4.30440	-1.02129
C	5.00166	-1.46527	-1.22056
C	5.02861	-0.30223	-0.44820
C	5.88131	-1.61729	-2.27460
C	5.92564	0.72391	-0.69452
C	6.78885	-0.58977	-2.55010
H	5.86892	-2.52199	-2.88216
C	6.80620	0.56125	-1.76708
H	5.95669	1.61332	-0.06961
H	7.48983	-0.69288	-3.37424
H	7.52430	1.34797	-1.98546
C	3.37711	-1.57114	0.48365
O	2.50513	-1.95468	1.26603
N	4.04266	-0.37865	0.54792
C	3.70999	0.69057	1.47413
H	2.67263	0.49944	1.79819
H	3.70172	1.63530	0.90974
C	4.65186	0.77481	2.64352
C	5.36442	1.94297	2.90432
C	4.80927	-0.32569	3.48928
C	6.22811	2.01519	3.99366
H	5.23663	2.80697	2.25133
C	5.67351	-0.25575	4.57402
H	4.23882	-1.23352	3.29388
C	6.38578	0.91465	4.82783
H	6.77959	2.93215	4.18808
H	5.78840	-1.11581	5.22960
H	7.06111	0.96766	5.67852
C	1.38362	1.30153	-2.17150
C	0.62294	0.46386	-2.98974
C	2.75970	1.37861	-2.42031
C	1.20735	-0.22883	-4.04896
H	-0.43623	0.33319	-2.78757
C	3.34906	0.68497	-3.47097
H	3.39908	1.97900	-1.77166
C	2.56994	-0.11568	-4.30196
H	0.58612	-0.86635	-4.67504
H	4.42404	0.76205	-3.62779
H	3.02504	-0.65665	-5.12914
H	2.29951	3.60585	-1.07576
C	1.81726	-3.57223	-1.35263

N	1.03178	-4.38572	-1.08851

G: M06/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2062.637734 hartree
Gibbs correction= 0.472004 hartree
Total Gibbs Energy= -2062.16573 hartree

Pd	2.57045	-2.39231	-0.29397
P	0.98175	-0.77556	-0.46148
O	-0.27298	-0.42571	-1.51350
O	0.15058	-0.70786	0.99319
N	1.77051	0.75138	-0.56752
C	-2.28288	-1.02596	-0.39516
C	-1.36355	-1.25978	-1.40013
C	-1.50081	-2.30742	-2.33041
H	-0.73844	-2.41859	-3.09732
C	-2.58269	-3.14197	-2.24851
H	-2.71213	-3.95192	-2.96443
C	-3.53696	-2.98726	-1.21460
C	-4.62937	-3.87991	-1.09181
H	-4.73533	-4.66992	-1.83424
C	-5.52299	-3.76537	-0.05873
H	-6.35487	-4.46025	0.02754
C	-5.34908	-2.75103	0.90593
H	-6.04262	-2.67664	1.74034
C	-4.30867	-1.86191	0.80728
H	-4.18148	-1.09339	1.56488
C	-3.38118	-1.93437	-0.26300
C	-2.06130	0.10178	0.54082
C	-0.85849	0.19297	1.22243
C	-0.63995	1.16377	2.22196
H	0.30478	1.13949	2.76061
C	-1.60090	2.09842	2.49228
H	-1.44112	2.85166	3.26226
C	-2.80528	2.12551	1.74883
C	-3.77054	3.14023	1.95811
H	-3.57585	3.88647	2.72771
C	-4.91502	3.19197	1.20475
H	-5.64661	3.97930	1.36959
C	-5.13522	2.22450	0.20203
H	-6.03204	2.27846	-0.41077
C	-4.22493	1.22047	-0.01496
H	-4.40171	0.48851	-0.79889
C	-3.03842	1.12695	0.75623
C	1.59773	1.62607	-1.74807
H	0.73304	1.20689	-2.27425
C	2.75997	1.51546	-2.73004
H	2.96335	0.45454	-2.91838
H	3.68440	1.97848	-2.36995
H	2.50186	1.98473	-3.68718
C	1.16926	3.04215	-1.39956
C	1.79732	4.17476	-1.91964
H	2.66369	4.06784	-2.56991

C	1.33499	5.45169	-1.60898
H	1.84202	6.32163	-2.02122
C	0.23263	5.61574	-0.77849
H	-0.12795	6.61313	-0.53696
C	-0.40968	4.49188	-0.26499
H	-1.28401	4.60017	0.37517
C	0.05442	3.22089	-0.57688
H	-0.45599	2.34318	-0.18563
C	2.65483	1.11021	0.57226
H	2.01881	1.52419	1.37640
C	3.71429	2.16856	0.27533
H	3.29137	3.10062	-0.10645
H	4.47340	1.80369	-0.42504
C	3.37029	-0.09951	1.15122
C	4.17160	-0.91390	0.30905
C	3.26773	-0.42155	2.49284
C	4.78851	-2.06957	0.82400
H	4.40446	-0.56802	-0.70011
C	3.90300	-1.55762	3.01516
H	2.65469	0.20281	3.14282
C	4.63479	-2.38931	2.18625
H	5.46843	-2.64420	0.19873
H	3.80231	-1.79306	4.07183
H	5.11665	-3.27805	2.58701
H	4.22492	2.39156	1.21908

1: B3LYP/6-311+G(2df,2pd) SCF= -880.5514829 hartree
Gibbs correction= 0.227543 hartree
Total Gibbs Energy= -880.3239399 hartree

C	1.07164	-1.47911	2.51405
C	0.46759	-0.46511	1.77428
C	0.89732	-0.18084	0.47408
C	1.93201	-0.93006	-0.12506
C	2.50938	-1.95945	0.63529
C	2.09238	-2.23234	1.93719
H	0.73787	-1.68278	3.52641
H	-0.35339	0.10880	2.19125
H	3.31766	-2.53299	0.19326
H	2.56990	-3.02888	2.49969
C	2.44574	-0.67774	-1.50745
C	2.99228	0.69371	-1.83705
C	2.47670	-1.67933	-2.39787
H	2.08773	-2.66538	-2.16296
H	2.88966	-1.53755	-3.39242
N	0.20951	0.84254	-0.26662
C	-0.75417	0.44065	-1.32075
H	-0.89608	1.31678	-1.95584
H	-0.27299	-0.34332	-1.90948
C	0.26166	2.16122	0.08024
C	1.27077	2.50528	1.10604
O	-0.41664	3.05370	-0.41075

N	2.03605	2.90705	1.88177
C	-2.08046	-0.04018	-0.76748
C	-3.03231	0.88160	-0.30680
C	-2.37167	-1.40734	-0.70298
C	-4.24899	0.43866	0.20997
H	-2.81060	1.94349	-0.35751
C	-3.59127	-1.85092	-0.18825
H	-1.64144	-2.12869	-1.06078
C	-4.53158	-0.92828	0.27018
H	-4.98031	1.16116	0.56052
H	-3.80555	-2.91491	-0.14709
H	-5.48176	-1.27114	0.66920
H	3.49234	0.68506	-2.80885
H	3.71348	1.01802	-1.07878
H	2.20551	1.45301	-1.87233

2: B3LYP/6-311+G(2df,2pd) SCF= -880.6016728 hartree
Gibbs correction= 0.234239 hartree
Total Gibbs Energy= -880.3674338 hartree

C	-1.98287	3.05397	0.70231
C	-2.62423	1.81355	0.57756
C	-1.94271	0.75699	-0.00752
C	-0.62805	0.93936	-0.46701
C	0.02472	2.16175	-0.35334
C	-0.67654	3.21856	0.24062
H	-2.50426	3.88755	1.16170
H	-3.64269	1.68759	0.93558
H	1.04563	2.29040	-0.69360
H	-0.18730	4.18225	0.34559
N	-0.14718	-0.25984	-1.02854
C	-1.10607	-1.25316	-0.97753
O	-0.98559	-2.39258	-1.39368
C	-2.37081	-0.66488	-0.30350
C	-3.55322	-0.75565	-1.28725
H	-3.70757	-1.79420	-1.59366
H	-4.47097	-0.37962	-0.82434
H	-3.35625	-0.15829	-2.18111
C	-2.70232	-1.51137	0.95768
H	-2.87956	-2.54567	0.64212
H	-3.62286	-1.13918	1.42059
C	1.15986	-0.45922	-1.63884
H	1.27253	0.23558	-2.48035
H	1.12623	-1.47320	-2.05114
C	2.33492	-0.30650	-0.68729
C	3.51822	0.28380	-1.14630
C	2.27903	-0.78368	0.62782
C	4.63186	0.38912	-0.31169
H	3.57021	0.66180	-2.16500
C	3.38934	-0.67112	1.46439
H	1.36679	-1.23224	1.00859
C	4.56906	-0.08794	0.99779

H	5.54300	0.84945	-0.68292
H	3.32789	-1.03953	2.48400
H	5.43165	-0.00178	1.65205
C	-1.63836	-1.51662	1.96486
N	-0.78407	-1.53046	2.75065

Cyanide: B3LYP/6-311+G(2df,2pd)SCF= -92.9528561 hartree
Gibbs correction= -0.019901 hartree
Total Gibbs Energy= -92.9727571 hartree

C	0.00000	0.00000	-0.63760
N	0.00000	0.00000	0.54652

A: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.435617 hartree
Gibbs correction= 0.729445 hartree
Total Gibbs Energy= -2943.706172 hartree

Pd	-1.12437	-0.50562	0.59297
P	1.20051	-0.43473	0.11976
O	1.74823	0.32354	-1.26717
O	1.94359	0.59306	1.24710
N	2.04560	-1.88310	-0.04183
C	2.08957	2.63982	-0.75549
C	1.37363	1.65370	-1.41573
C	0.27951	1.93088	-2.26505
H	-0.22664	1.10057	-2.74448
C	-0.11847	3.23178	-2.44507
H	-0.95118	3.46349	-3.10342
C	0.52149	4.29026	-1.74628
C	0.06739	5.63074	-1.87391
H	-0.75816	5.83359	-2.55143
C	0.64192	6.64804	-1.14785
H	0.28169	7.66749	-1.25073
C	1.69506	6.35789	-0.24949
H	2.13036	7.15589	0.34527
C	2.17123	5.07210	-0.11544
H	2.97163	4.86865	0.58532
C	1.62184	3.99841	-0.87123
C	3.26050	2.25995	0.08279
C	3.12529	1.28370	1.06492
C	4.15667	1.01375	1.99748
H	3.95347	0.29768	2.78680
C	5.36263	1.66111	1.90117
H	6.15090	1.46518	2.62313
C	5.60986	2.57173	0.83998
C	6.88275	3.18018	0.67349
H	7.66295	2.95343	1.39574
C	7.13303	4.02289	-0.38466
H	8.11238	4.47625	-0.50596
C	6.11177	4.28332	-1.32790
H	6.31685	4.92679	-2.17865
C	4.86120	3.72355	-1.18436
H	4.09489	3.92606	-1.92291

C	4.55755	2.86491	-0.09048
C	3.34061	-1.97394	-0.80511
H	3.74031	-0.95715	-0.77953
C	3.11697	-2.31083	-2.28889
H	2.44047	-1.57778	-2.73041
H	2.68643	-3.30180	-2.43540
H	4.07332	-2.26592	-2.82082
C	4.40191	-2.85446	-0.14131
C	4.66993	-4.16234	-0.56731
H	4.09847	-4.59700	-1.37906
C	5.66382	-4.92751	0.04795
H	5.85159	-5.94037	-0.29782
C	6.41704	-4.39508	1.09461
H	7.19163	-4.98972	1.57063
C	6.17537	-3.08518	1.51386
H	6.76694	-2.65123	2.31548
C	5.18218	-2.32546	0.89690
H	5.01245	-1.30295	1.21872
C	1.35321	-3.06715	0.55792
H	0.37340	-2.66225	0.85084
C	1.99659	-3.55141	1.86585
H	2.11648	-2.70283	2.54515
H	2.97620	-4.00854	1.72621
C	-1.20441	0.20301	2.66061
H	-0.70134	-0.48702	3.33162
H	-0.73073	1.17336	2.55631
C	-2.54443	-0.01964	2.32808
C	-3.25206	-1.21140	2.96119
H	-3.84700	-1.80359	2.26548
H	-2.52007	-1.88070	3.42029
H	-3.92942	-0.86325	3.75308
C	-3.37114	1.10067	1.75843
C	-4.42998	0.90715	0.83454
C	-3.08066	2.43039	2.11268
C	-5.10124	1.99570	0.27112
C	-3.76325	3.51482	1.56450
H	-2.30201	2.61367	2.84483
C	-4.77378	3.30276	0.62990
H	-5.88722	1.80337	-0.45043
H	-3.50057	4.52313	1.87104
H	-5.30680	4.13804	0.18652
C	-4.19924	-1.29731	-0.28090
O	-4.58899	-2.42287	-0.57027
N	-4.89753	-0.40944	0.47954
C	-6.20115	-0.86048	1.02568
H	-6.28759	-0.43255	2.02761
H	-6.13749	-1.94752	1.11563
C	-7.41006	-0.48237	0.19064
C	-7.62562	-1.07840	-1.06164
C	-8.33974	0.44938	0.66715
C	-8.74427	-0.73705	-1.82067

H	-6.91480	-1.81229	-1.42935
C	-9.46338	0.78723	-0.09088
H	-8.18357	0.91406	1.63770
C	-9.66614	0.19624	-1.33808
H	-8.90116	-1.20570	-2.78811
H	-10.17681	1.51080	0.29336
H	-10.53875	0.45722	-1.93007
C	1.02851	-4.17155	-0.45147
C	0.12933	-3.89116	-1.49338
C	1.53299	-5.47243	-0.34097
C	-0.23819	-4.87666	-2.40716
H	-0.28589	-2.89163	-1.58888
C	1.16763	-6.46283	-1.25840
H	2.21841	-5.72372	0.46099
C	0.28403	-6.16848	-2.29550
H	-0.93896	-4.63701	-3.20178
H	1.57344	-7.46563	-1.15540
H	-0.00311	-6.93863	-3.00587
H	1.33967	-4.28397	2.34696
C	-2.84597	-0.88486	-0.74243
N	-1.98713	-0.81269	-1.56353

TS1: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.411981 hartree
Gibbs correction= 0.729136 hartree
Total Gibbs Energy= -2943.682845 hartree

Pd	-1.32171	-0.66561	0.43671
P	0.96076	-0.60936	-0.24602
O	1.37915	0.45249	-1.46479
O	1.87522	0.07913	0.99709
N	1.71947	-1.97737	-0.86352
C	2.00397	2.53888	-0.45697
C	1.12744	1.80268	-1.23965
C	-0.00784	2.36318	-1.86560
H	-0.64120	1.72230	-2.46878
C	-0.28719	3.69378	-1.67859
H	-1.15152	4.14213	-2.16042
C	0.51856	4.49393	-0.82532
C	0.18960	5.85276	-0.57061
H	-0.67421	6.27749	-1.07561
C	0.93091	6.61159	0.30502
H	0.66548	7.64751	0.49488
C	2.03326	6.03050	0.97398
H	2.60206	6.62039	1.68710
C	2.39020	4.72132	0.73595
H	3.23142	4.29218	1.26635
C	1.66479	3.91351	-0.18461
C	3.21640	1.88639	0.11194
C	3.09495	0.70986	0.84338
C	4.18499	0.14881	1.55126
H	3.99654	-0.72686	2.16325
C	5.42914	0.72225	1.46666

H	6.26578	0.30503	2.02080
C	5.64944	1.84815	0.62941
C	6.94950	2.39505	0.45852
H	7.77506	1.94810	1.00666
C	7.16716	3.45355	-0.39268
H	8.16670	3.85825	-0.52109
C	6.08357	4.00379	-1.11641
H	6.25960	4.82188	-1.80890
C	4.80770	3.50894	-0.95841
H	3.99158	3.93666	-1.52818
C	4.53948	2.42926	-0.07058
C	2.89074	-1.89722	-1.80904
H	3.35562	-0.93167	-1.60082
C	2.45161	-1.86621	-3.28220
H	1.74922	-1.04665	-3.43957
H	1.96948	-2.79393	-3.59919
H	3.32438	-1.70840	-3.92455
C	3.95178	-2.96095	-1.52078
C	3.99790	-4.18684	-2.20180
H	3.26204	-4.41288	-2.96682
C	4.98810	-5.13075	-1.91952
H	5.00036	-6.07333	-2.45948
C	5.95981	-4.86343	-0.95545
H	6.73249	-5.59544	-0.73875
C	5.93550	-3.64221	-0.27925
H	6.69589	-3.41499	0.46296
C	4.94283	-2.70358	-0.56208
H	4.94224	-1.75087	-0.04208
C	1.07118	-3.31001	-0.63680
H	1.85030	-4.02914	-0.90440
C	-0.12429	-3.57666	-1.56310
H	0.15907	-3.41410	-2.60427
H	-0.97662	-2.92951	-1.34590
C	-1.02180	0.09472	2.62387
H	-0.47822	-0.64751	3.20008
H	-0.48004	0.99625	2.35925
C	-2.38449	-0.01147	2.45892
C	-3.14906	-1.11867	3.16261
H	-3.92778	-1.56356	2.54125
H	-2.47041	-1.91252	3.48243
H	-3.63885	-0.70325	4.05298
C	-3.17339	1.12622	1.88083
C	-4.14536	0.93770	0.86669
C	-2.96783	2.42904	2.36267
C	-4.87680	2.02752	0.38121
C	-3.70350	3.50962	1.88089
H	-2.23207	2.58243	3.14595
C	-4.66541	3.30686	0.89142
H	-5.59846	1.86553	-0.41066
H	-3.52804	4.50352	2.28178
H	-5.24302	4.14144	0.50549

C	-3.40570	-1.21174	-0.09918
O	-3.52705	-2.42257	-0.20277
N	-4.40447	-0.36697	0.34951
C	-5.76989	-0.92056	0.44874
H	-6.19657	-0.60001	1.40422
H	-5.64986	-2.00761	0.48561
C	-6.70958	-0.54900	-0.68717
C	-6.25706	-0.41403	-2.00692
C	-8.07563	-0.39544	-0.41926
C	-7.15990	-0.13257	-3.03374
H	-5.19954	-0.50819	-2.23496
C	-8.97851	-0.12254	-1.44798
H	-8.43618	-0.49001	0.60272
C	-8.52186	0.01008	-2.76013
H	-6.79415	-0.02503	-4.05088
H	-10.03479	-0.00533	-1.22221
H	-9.22083	0.22852	-3.56246
C	0.78721	-3.56406	0.84799
C	-0.48818	-3.88628	1.32993
C	1.85778	-3.54001	1.75727
C	-0.68543	-4.17573	2.68494
H	-1.33957	-3.91193	0.65949
C	1.66063	-3.81996	3.10750
H	2.85406	-3.30422	1.39407
C	0.38369	-4.14057	3.57876
H	-1.68112	-4.43531	3.03400
H	2.50462	-3.80056	3.79176
H	0.22898	-4.36925	4.62955
H	-0.45348	-4.61611	-1.46184
C	-2.37577	-0.46065	-1.30758
N	-2.53214	-0.09681	-2.41584

(*S*)-B: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.443333 hartree
Gibbs correction= 0.734105 hartree
Total Gibbs Energy= -2943.709228 hartree

Pd	-1.42213	-0.91013	0.32914
P	0.93730	-0.63480	-0.25069
O	1.24686	0.45374	-1.46284
O	1.76232	0.13722	0.99962
N	1.80850	-1.93192	-0.85605
C	1.64818	2.59451	-0.45352
C	0.85718	1.77509	-1.24398
C	-0.31893	2.21640	-1.88868
H	-0.86974	1.51275	-2.50284
C	-0.73352	3.51170	-1.70328
H	-1.63129	3.87215	-2.19747
C	-0.02498	4.38733	-0.83765
C	-0.49494	5.70430	-0.58434
H	-1.39278	6.03893	-1.09747
C	0.15536	6.53326	0.30003
H	-0.21753	7.53573	0.48858

C	1.30545	6.06798	0.97914
H	1.80352	6.71225	1.69806
C	1.79799	4.80315	0.74326
H	2.67424	4.46195	1.28096
C	1.16798	3.92707	-0.18482
C	2.91903	2.06903	0.12022
C	2.91797	0.88455	0.84745
C	4.05870	0.42611	1.54749
H	3.95965	-0.46822	2.15324
C	5.23984	1.12052	1.46342
H	6.11571	0.78357	2.01139
C	5.34431	2.26960	0.63539
C	6.58311	2.94494	0.46802
H	7.44994	2.57864	1.01216
C	6.69253	4.02628	-0.37507
H	7.64636	4.52991	-0.50086
C	5.55862	4.47082	-1.09435
H	5.65133	5.30741	-1.78080
C	4.33874	3.84990	-0.93976
H	3.48357	4.19819	-1.50615
C	4.18101	2.74263	-0.05957
C	2.92598	-1.74154	-1.85609
H	3.29062	-0.72801	-1.68033
C	2.42240	-1.78370	-3.30732
H	1.60749	-1.07059	-3.43758
H	2.05682	-2.76969	-3.60163
H	3.23825	-1.51425	-3.98634
C	4.10711	-2.67576	-1.59179
C	4.27420	-3.89380	-2.26740
H	3.54678	-4.20968	-3.00808
C	5.37438	-4.71471	-2.00877
H	5.48060	-5.65386	-2.54430
C	6.33471	-4.32955	-1.07353
H	7.19250	-4.96579	-0.87559
C	6.18806	-3.11448	-0.40159
H	6.93705	-2.79586	0.31824
C	5.08678	-2.29845	-0.66127
H	4.99052	-1.34812	-0.14534
C	1.35331	-3.32850	-0.54654
H	2.23576	-3.93954	-0.75532
C	0.22944	-3.83051	-1.46253
H	0.51706	-3.73066	-2.50992
H	-0.70103	-3.27685	-1.32865
C	-0.89573	-0.23697	2.49253
H	-0.30233	-1.00443	2.98012
H	-0.37479	0.66393	2.18978
C	-2.26990	-0.27878	2.54711
C	-2.96203	-1.34879	3.37144
H	-3.94805	-1.61429	2.99010
H	-2.35246	-2.25166	3.43889
H	-3.09961	-0.94802	4.38399

C	-3.08889	0.88590	2.09438
C	-4.14704	0.71396	1.16966
C	-2.83307	2.16670	2.60235
C	-4.93780	1.81375	0.81255
C	-3.62356	3.25683	2.24407
H	-2.01873	2.29444	3.30946
C	-4.68259	3.07203	1.35500
H	-5.73792	1.68450	0.09348
H	-3.41674	4.23782	2.66030
H	-5.30832	3.91180	1.06723
C	-3.39945	-1.50310	0.45287
O	-3.61358	-2.69328	0.32481
N	-4.40650	-0.56823	0.63068
C	-5.80104	-1.00843	0.41998
H	-6.40663	-0.63296	1.25133
H	-5.77072	-2.09991	0.49080
C	-6.42611	-0.59594	-0.90259
C	-5.69254	-0.59713	-2.09649
C	-7.78611	-0.26123	-0.94053
C	-6.31489	-0.26913	-3.30181
H	-4.63476	-0.84096	-2.09474
C	-8.40870	0.06018	-2.14804
H	-8.36312	-0.25254	-0.01806
C	-7.67251	0.05746	-3.33367
H	-5.73048	-0.27123	-4.21732
H	-9.46417	0.31810	-2.15951
H	-8.15212	0.31186	-4.27472
C	1.08006	-3.52726	0.94766
C	-0.16095	-3.95342	1.43892
C	2.13463	-3.35086	1.85905
C	-0.33794	-4.20269	2.80462
H	-1.00059	-4.09481	0.76782
C	1.95588	-3.58673	3.22047
H	3.10593	-3.03603	1.48715
C	0.71481	-4.01771	3.70006
H	-1.30330	-4.55195	3.16042
H	2.78752	-3.45076	3.90651
H	0.57620	-4.21663	4.75905
H	0.03657	-4.89031	-1.26599
C	-1.84396	-0.95512	-1.63749
N	-2.05006	-0.90066	-2.78764

(*S*)-TS2: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.417445 hartree
Gibbs correction= 0.729674 hartree
Total Gibbs Energy= -2943.687771 hartree

Pd	-1.26075	-0.62165	-0.02339
P	1.02359	-0.71513	-0.03703
O	1.73838	0.16386	-1.23648
O	1.69041	-0.01900	1.32026
N	1.81956	-2.19002	-0.26984
C	2.26730	2.28673	-0.27596

C	1.52121	1.54276	-1.17600
C	0.57467	2.10125	-2.05992
H	0.04308	1.44145	-2.73694
C	0.34933	3.45531	-2.01495
H	-0.36883	3.91077	-2.69095
C	1.01728	4.27625	-1.06687
C	0.73463	5.66589	-0.97299
H	0.01605	6.09433	-1.66684
C	1.33964	6.45136	-0.01955
H	1.11033	7.51100	0.04432
C	2.25256	5.87068	0.89182
H	2.71076	6.48651	1.66040
C	2.56235	4.53055	0.81836
H	3.25721	4.10053	1.52989
C	1.97471	3.69213	-0.16999
C	3.30913	1.60914	0.54988
C	2.98537	0.50062	1.32289
C	3.90870	-0.10723	2.20237
H	3.56943	-0.92726	2.82547
C	5.19850	0.35567	2.26815
H	5.91116	-0.10147	2.94894
C	5.62894	1.41467	1.42692
C	6.98217	1.84882	1.42699
H	7.67909	1.36959	2.10975
C	7.40805	2.84037	0.57432
H	8.44603	3.15953	0.57855
C	6.49028	3.43350	-0.32399
H	6.83264	4.19735	-1.01604
C	5.16817	3.04761	-0.33723
H	4.48345	3.50527	-1.04057
C	4.68460	2.04136	0.54603
C	2.17270	-2.61542	-1.66990
H	1.99357	-1.72062	-2.26854
C	1.23705	-3.67867	-2.25983
H	0.21206	-3.30333	-2.25708
H	1.27300	-4.63617	-1.73407
H	1.50399	-3.85713	-3.30579
C	3.67274	-2.89841	-1.82704
C	4.16139	-4.06595	-2.42566
H	3.47476	-4.83631	-2.75976
C	5.53457	-4.26446	-2.59574
H	5.88987	-5.18070	-3.05937
C	6.44327	-3.29543	-2.17354
H	7.51048	-3.44960	-2.30566
C	5.96716	-2.12104	-1.58435
H	6.66217	-1.35217	-1.25820
C	4.59763	-1.92569	-1.41685
H	4.23660	-1.00856	-0.96376
C	1.89566	-3.06793	0.94135
H	2.39697	-2.46656	1.70660
C	2.78071	-4.31360	0.76327

H	3.79873	-4.04938	0.47775
H	2.37677	-5.01190	0.02848
C	-1.49398	-0.07049	1.99121
H	-1.24178	-0.87312	2.68150
H	-0.88847	0.82605	2.10182
C	-2.90011	0.10831	1.66721
C	-3.88785	-0.67034	2.55008
H	-4.91640	-0.58643	2.19196
H	-3.60907	-1.72543	2.59030
H	-3.83913	-0.25043	3.56118
C	-3.33777	1.47469	1.24152
C	-4.06891	1.51973	0.03925
C	-3.05809	2.66101	1.91783
C	-4.54867	2.73110	-0.46283
C	-3.53846	3.87758	1.42616
H	-2.48147	2.63079	2.83793
C	-4.28229	3.90484	0.24477
H	-5.12192	2.76615	-1.38133
H	-3.33809	4.79747	1.96637
H	-4.65947	4.84945	-0.13598
C	-3.53055	-0.77243	-0.00343
O	-3.79861	-1.95277	-0.10778
N	-4.23314	0.26686	-0.56818
C	-5.16329	0.00380	-1.67912
H	-4.85674	-0.95863	-2.09413
H	-4.99350	0.76032	-2.45062
C	-6.62228	-0.02802	-1.26503
C	-7.53696	0.89291	-1.78587
C	-7.07851	-1.00501	-0.36701
C	-8.88287	0.84968	-1.41383
H	-7.19837	1.64529	-2.49446
C	-8.42031	-1.04586	0.00877
H	-6.37530	-1.73672	0.02082
C	-9.32627	-0.11763	-0.51238
H	-9.58122	1.57161	-1.82765
H	-8.76258	-1.80840	0.70286
H	-10.37191	-0.15254	-0.22016
C	0.54724	-3.47207	1.55006
C	-0.57190	-3.82937	0.78879
C	0.45289	-3.54153	2.94807
C	-1.75126	-4.25082	1.40839
H	-0.53670	-3.76445	-0.29125
C	-0.71902	-3.97106	3.57126
H	1.30969	-3.25793	3.55620
C	-1.82740	-4.32919	2.79982
H	-2.61338	-4.49726	0.79775
H	-0.76765	-4.02044	4.65567
H	-2.74358	-4.66194	3.27959
H	2.81195	-4.83379	1.72484
C	-1.33457	-0.91082	-2.07073
N	-1.34077	-1.00935	-3.23711

(*S*)-C: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.381115 hartree
Gibbs correction= 0.727629 hartree
Total Gibbs Energy= -2850.653486 hartree

Pd	1.31584	-0.50929	0.40596
P	-1.13360	-0.72672	0.58151
O	-2.13355	0.18228	1.55195
O	-1.69149	-0.28961	-0.91429
N	-1.64817	-2.27509	0.95743
C	-2.64539	2.16121	0.28002
C	-2.04518	1.56715	1.37886
C	-1.33652	2.29315	2.36119
H	-0.93535	1.75707	3.21469
C	-1.18807	3.65122	2.21839
H	-0.66487	4.22870	2.97535
C	-1.69039	4.31684	1.06748
C	-1.47021	5.70738	0.87289
H	-0.94141	6.26164	1.64373
C	-1.90554	6.33962	-0.26847
H	-1.72940	7.40167	-0.40822
C	-2.57481	5.59795	-1.26994
H	-2.89606	6.09395	-2.18083
C	-2.82334	4.25313	-1.10348
H	-3.33500	3.70236	-1.88318
C	-2.41044	3.56951	0.07416
C	-3.47644	1.34365	-0.64891
C	-2.97578	0.18411	-1.22207
C	-3.67585	-0.55229	-2.20424
H	-3.19901	-1.42267	-2.64127
C	-4.93596	-0.15635	-2.57574
H	-5.47982	-0.70960	-3.33589
C	-5.55989	0.95567	-1.95152
C	-6.89576	1.31873	-2.27108
H	-7.42046	0.74657	-3.03127
C	-7.52004	2.35880	-1.62290
H	-8.54329	2.62416	-1.86962
C	-6.82878	3.07231	-0.61666
H	-7.33208	3.87435	-0.08517
C	-5.52619	2.75737	-0.29638
H	-5.02154	3.31004	0.48648
C	-4.83891	1.70489	-0.96244
C	-3.00835	-2.74293	0.54416
H	-3.40833	-1.92204	-0.05626
C	-3.98005	-2.87240	1.72737
H	-3.91862	-1.97033	2.34025
H	-3.78446	-3.74050	2.35856
H	-5.00595	-2.95138	1.35543
C	-2.93720	-3.94519	-0.40202
C	-3.83005	-5.02045	-0.30424
H	-4.57328	-5.04487	0.48527
C	-3.78104	-6.07635	-1.21862

H	-4.48195	-6.90020	-1.12218
C	-2.84010	-6.07495	-2.24727
H	-2.80160	-6.89683	-2.95560
C	-1.94786	-5.00619	-2.35893
H	-1.21144	-4.99188	-3.15722
C	-1.99855	-3.95284	-1.44659
H	-1.30167	-3.12543	-1.54679
C	-0.61163	-3.20242	1.52005
H	-0.01980	-3.61165	0.69163
C	-1.18712	-4.40135	2.29094
H	-1.83072	-5.01627	1.66187
H	-1.73911	-4.09035	3.18009
C	0.99740	1.53779	-0.45105
H	0.22316	1.41570	-1.20166
H	0.72493	2.07312	0.45404
C	2.33186	1.40006	-0.80513
C	2.71932	1.09571	-2.23638
H	3.65097	0.53476	-2.32303
H	1.92527	0.56136	-2.76265
H	2.88044	2.05684	-2.74161
C	3.38642	1.89613	0.12307
C	4.41134	1.03961	0.56824
C	3.36585	3.22429	0.57150
C	5.39402	1.52076	1.44007
C	4.35921	3.70764	1.42026
H	2.57617	3.88454	0.22598
C	5.37321	2.85192	1.85263
H	6.16822	0.86000	1.81288
H	4.34266	4.74436	1.74014
H	6.14635	3.21466	2.52244
C	3.24689	-0.97432	-0.12366
O	3.15054	-2.06195	-0.66900
N	4.40153	-0.32083	0.15046
C	5.68488	-1.01697	-0.20500
H	5.46311	-2.08345	-0.16123
H	6.41098	-0.79048	0.57629
C	6.21413	-0.62940	-1.56624
C	7.14217	0.41206	-1.70446
C	5.78041	-1.31432	-2.71226
C	7.62404	0.76807	-2.96450
H	7.49550	0.94143	-0.82369
C	6.26244	-0.95683	-3.97194
H	5.07187	-2.13141	-2.61065
C	7.18377	0.08513	-4.10004
H	8.34817	1.57165	-3.05850
H	5.92764	-1.49888	-4.85126
H	7.56428	0.35753	-5.07983
C	0.32605	-2.42579	2.43986
C	-0.15211	-1.79904	3.60218
C	1.70903	-2.37754	2.16396
C	0.72416	-1.15184	4.47017

H	-1.21444	-1.81709	3.82260
C	2.58810	-1.71667	3.04789
H	2.10832	-2.96484	1.34179
C	2.09665	-1.10151	4.19451
H	0.33816	-0.68837	5.37345
H	3.65311	-1.71588	2.83940
H	2.77290	-0.60030	4.87960
H	-0.34758	-5.02158	2.61837

(*R*)-C: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.384714 hartree
Gibbs correction= 0.725405 hartree
Total Gibbs Energy= -2850.659309 hartree

Pd	-1.20719	-0.70308	-0.16683
P	1.21737	-0.68614	-0.40463
O	1.82317	0.32821	-1.56558
O	1.91011	-0.03340	0.95584
N	1.95538	-2.12968	-0.80201
C	2.04835	2.46229	-0.47375
C	1.42475	1.66596	-1.41988
C	0.39256	2.12639	-2.26510
H	-0.02024	1.44978	-3.00530
C	-0.04948	3.42063	-2.13802
H	-0.82754	3.79980	-2.79442
C	0.48116	4.27295	-1.13299
C	-0.02369	5.58867	-0.94824
H	-0.80083	5.94449	-1.61940
C	0.44905	6.39284	0.06248
H	0.05398	7.39518	0.19607
C	1.44584	5.90509	0.93975
H	1.80029	6.53272	1.75185
C	1.97150	4.64223	0.77622
H	2.73192	4.28552	1.46015
C	1.52598	3.79113	-0.27334
C	3.19912	1.92410	0.30419
C	3.08971	0.72712	0.99699
C	4.10889	0.23322	1.84147
H	3.93711	-0.68846	2.38491
C	5.29084	0.92207	1.94925
H	6.07777	0.55559	2.60210
C	5.51724	2.09828	1.18774
C	6.76874	2.76950	1.23241
H	7.54142	2.38192	1.89074
C	7.00653	3.87451	0.44897
H	7.96834	4.37648	0.48552
C	5.99697	4.34599	-0.42197
H	6.19559	5.20111	-1.06103
C	4.76645	3.72874	-0.47549
H	4.01278	4.10026	-1.15880
C	4.47453	2.59879	0.33835
C	3.45098	-2.22016	-0.76875
H	3.77300	-1.23548	-0.41526

C	4.06370	-2.35310	-2.17149
H	3.60087	-1.61876	-2.83433
H	3.94121	-3.34744	-2.60385
H	5.13435	-2.13198	-2.13293
C	3.95824	-3.21837	0.27743
C	5.09650	-4.00439	0.05281
H	5.61711	-3.95490	-0.89706
C	5.57988	-4.86526	1.04182
H	6.46266	-5.46551	0.84265
C	4.93497	-4.95694	2.27434
H	5.30955	-5.62844	3.04076
C	3.80183	-4.17641	2.51287
H	3.29044	-4.23723	3.46939
C	3.32205	-3.31626	1.52541
H	2.44367	-2.71027	1.72592
C	1.05648	-3.32464	-0.93371
H	0.72958	-3.62771	0.06968
C	1.73850	-4.55159	-1.56670
H	2.62411	-4.86573	-1.01521
H	2.00312	-4.36837	-2.61000
C	-1.01221	-0.71266	2.05119
H	-0.90374	-1.76265	2.30955
H	-0.15456	-0.07283	2.23153
C	-2.28253	-0.16672	1.89707
C	-3.10823	-0.41864	-0.70328
O	-2.81660	0.06151	-1.79194
N	-4.31608	-0.62122	-0.16807
C	-5.50685	-0.13627	-0.94813
H	-6.25881	-0.92563	-0.95156
H	-5.15017	-0.01247	-1.97107
C	-6.06407	1.15571	-0.40018
C	-5.44277	2.37456	-0.71529
C	-7.19693	1.16030	0.42301
C	-5.94212	3.57293	-0.20598
H	-4.57809	2.38228	-1.37420
C	-7.69885	2.36040	0.92916
H	-7.69407	0.22481	0.66443
C	-7.07066	3.56717	0.61808
H	-5.46022	4.51157	-0.46237
H	-8.58168	2.35249	1.56103
H	-7.46380	4.50106	1.00806
C	-0.19068	-3.02217	-1.76651
C	-0.08925	-2.46557	-3.05506
C	-1.44411	-3.49798	-1.33776
C	-1.20204	-2.40334	-3.89057
H	0.87096	-2.09676	-3.40268
C	-2.55608	-3.45179	-2.18838
H	-1.53194	-3.96446	-0.35940
C	-2.43631	-2.90582	-3.46446
H	-1.10420	-1.97835	-4.88497
H	-3.50678	-3.85335	-1.84990

H	-3.29452	-2.87398	-4.12856
H	1.01985	-5.37564	-1.54928
C	-3.47649	-1.04130	2.10230
C	-3.62752	-1.68725	3.33823
C	-4.47258	-1.21584	1.12273
C	-4.74529	-2.47169	3.61415
H	-2.86455	-1.54656	4.09783
C	-5.58470	-2.01959	1.39366
C	-5.72497	-2.63493	2.63644
H	-4.84817	-2.94899	4.58304
H	-6.33865	-2.18819	0.63463
H	-6.59727	-3.25067	2.83048
C	-2.50808	1.33090	1.94790
H	-2.79351	1.59576	2.97411
H	-1.60505	1.88611	1.68529
H	-3.32860	1.65042	1.30102

(*S*)-TS3: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.372713 hartree
Gibbs correction= 0.730461 hartree
Total Gibbs Energy= -2850.642252 hartree

Pd	-1.21527	-0.01152	-0.31152
P	0.87334	0.79591	0.35036
O	1.72006	0.10367	1.59333
O	1.91080	0.54535	-0.90724
N	0.86959	2.41132	0.77461
C	2.95744	-1.69607	0.58100
C	1.96096	-1.26887	1.44339
C	1.15062	-2.14915	2.19221
H	0.41827	-1.73057	2.87400
C	1.31789	-3.50439	2.04427
H	0.71681	-4.19758	2.62583
C	2.25574	-4.02058	1.10940
C	2.37790	-5.42023	0.89328
H	1.76580	-6.09219	1.48894
C	3.24317	-5.91709	-0.05355
H	3.32666	-6.98783	-0.21198
C	4.01868	-5.02650	-0.83239
H	4.68324	-5.41989	-1.59563
C	3.94002	-3.66543	-0.63426
H	4.53971	-2.99981	-1.24284
C	3.07495	-3.11518	0.35242
C	3.83787	-0.69873	-0.09036
C	3.29874	0.35354	-0.81463
C	4.08562	1.25222	-1.56922
H	3.58762	2.02091	-2.14993
C	5.45260	1.13407	-1.54825
H	6.06773	1.81296	-2.13169
C	6.08312	0.14988	-0.74250
C	7.49908	0.07647	-0.65202
H	8.09267	0.77028	-1.24094
C	8.10808	-0.83914	0.17403

H	9.19061	-0.88296	0.24104
C	7.31673	-1.71450	0.95321
H	7.79796	-2.41750	1.62644
C	5.94154	-1.68123	0.87467
H	5.35608	-2.35314	1.49017
C	5.27635	-0.76539	0.01307
C	2.13400	3.21033	0.71090
H	2.87377	2.51848	0.29989
C	2.67160	3.57903	2.10198
H	2.66636	2.68888	2.73527
H	2.09755	4.36472	2.59532
H	3.70764	3.92058	2.01909
C	2.03891	4.35764	-0.29917
C	2.57602	5.62444	-0.03508
H	3.03720	5.83472	0.92374
C	2.52872	6.63624	-0.99807
H	2.94977	7.61105	-0.77055
C	1.94567	6.39874	-2.24192
H	1.90796	7.18605	-2.98851
C	1.41152	5.13842	-2.51949
H	0.95695	4.93972	-3.48574
C	1.45997	4.12942	-1.55814
H	1.04477	3.15236	-1.78849
C	-0.48260	3.03402	0.97365
H	-0.91167	3.25989	-0.01058
C	-0.46114	4.35037	1.76593
H	0.15325	5.10780	1.27915
H	-0.11511	4.20637	2.79133
C	-0.39373	-1.60564	-1.36564
H	0.36617	-1.23433	-2.04889
H	-0.02168	-2.25802	-0.57739
C	-1.70570	-1.87845	-1.89533
C	-1.86316	-1.75144	-3.41338
H	-2.90392	-1.82845	-3.73280
H	-1.44815	-0.80783	-3.77417
H	-1.30889	-2.57767	-3.87307
C	-2.54439	-2.90536	-1.21468
C	-3.85966	-2.51111	-0.91858
C	-2.11602	-4.18835	-0.86694
C	-4.75451	-3.39236	-0.31109
C	-3.00991	-5.08075	-0.27251
H	-1.09849	-4.49752	-1.08680
C	-4.32197	-4.68324	-0.00343
H	-5.76503	-3.08465	-0.06949
H	-2.68639	-6.08715	-0.02779
H	-5.01457	-5.37876	0.45974
C	-3.09082	-0.36618	-1.54886
O	-3.13026	0.70187	-2.12888
N	-4.15091	-1.17065	-1.25990
C	-5.51304	-0.71523	-1.66865
H	-6.10835	-1.61830	-1.81247

H	-5.38795	-0.22994	-2.64102
C	-6.19009	0.23490	-0.70356
C	-6.04687	1.62074	-0.86523
C	-6.99064	-0.24682	0.34172
C	-6.67814	2.50447	0.01159
H	-5.44229	2.00176	-1.68276
C	-7.62063	0.63630	1.21979
H	-7.14010	-1.31649	0.46406
C	-7.46257	2.01437	1.05759
H	-6.56623	3.57537	-0.12921
H	-8.24379	0.24943	2.02041
H	-7.95858	2.70219	1.73558
C	-1.39843	2.03948	1.68201
C	-1.08151	1.56990	2.97013
C	-2.61064	1.62829	1.08936
C	-1.94963	0.72132	3.64881
H	-0.14752	1.87064	3.43344
C	-3.48367	0.76630	1.78487
H	-2.92958	2.07114	0.14858
C	-3.15119	0.31087	3.05617
H	-1.69505	0.38109	4.64843
H	-4.42678	0.48476	1.33096
H	-3.82808	-0.34541	3.59410
H	-1.48682	4.72815	1.81030

(*R*)-TS3: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.374963 hartree
Gibbs correction= 0.729576 hartree
Total Gibbs Energy= -2850.645387 hartree

Pd	-1.05616	-0.41769	-0.33130
P	1.22893	-0.66572	-0.45984
O	1.97931	0.25422	-1.60959
O	1.97644	-0.12621	0.91143
N	1.74530	-2.19029	-0.88528
C	2.47185	2.33621	-0.50287
C	1.76794	1.63560	-1.46772
C	0.82689	2.23343	-2.33236
H	0.34551	1.62251	-3.08807
C	0.55584	3.57379	-2.20340
H	-0.15079	4.05580	-2.87283
C	1.17084	4.34213	-1.17849
C	0.83780	5.71113	-0.99118
H	0.12782	6.17011	-1.67386
C	1.38984	6.43904	0.03700
H	1.12565	7.48319	0.17279
C	2.29578	5.81920	0.92935
H	2.71159	6.38957	1.75443
C	2.65584	4.49968	0.76450
H	3.34862	4.04179	1.45995
C	2.12488	3.72167	-0.30188
C	3.52556	1.64687	0.29277
C	3.24671	0.47212	0.97557

C	4.17689	-0.15672	1.83234
H	3.87557	-1.04744	2.37018
C	5.43792	0.36841	1.96329
H	6.15786	-0.10219	2.62652
C	5.83121	1.50764	1.21378
C	7.15977	2.00644	1.28326
H	7.86315	1.51633	1.95080
C	7.55481	3.07431	0.51197
H	8.57387	3.44412	0.56742
C	6.63124	3.68031	-0.37109
H	6.95201	4.50507	-1.00029
C	5.33076	3.23216	-0.44875
H	4.64470	3.70446	-1.14101
C	4.87842	2.14645	0.35172
C	3.23320	-2.43380	-0.94883
H	3.67834	-1.52176	-0.53902
C	3.74402	-2.51365	-2.39449
H	3.35164	-1.66576	-2.95901
H	3.45890	-3.43521	-2.90420
H	4.83574	-2.44327	-2.40490
C	3.68015	-3.56132	-0.01456
C	4.62852	-4.51434	-0.40844
H	5.03588	-4.49795	-1.41328
C	5.06907	-5.49726	0.48225
H	5.80549	-6.22456	0.15383
C	4.56840	-5.54642	1.78219
H	4.90971	-6.31174	2.47240
C	3.62427	-4.60095	2.18904
H	3.22778	-4.62684	3.19998
C	3.18909	-3.61855	1.30029
H	2.45939	-2.88504	1.63172
C	0.78878	-3.33731	-0.86604
H	0.80095	-3.78497	0.13467
C	1.19006	-4.44300	-1.86520
H	2.16788	-4.86327	-1.63113
H	1.18977	-4.06504	-2.89076
C	-0.95536	0.94271	1.24422
H	-0.50346	0.35465	2.04037
H	-0.37799	1.81434	0.94365
C	-2.39215	1.03639	1.19954
C	-3.21577	0.19603	-0.51193
O	-3.18463	0.69519	-1.62034
N	-4.26546	-0.42838	0.08795
C	-5.52431	-0.63287	-0.68050
H	-5.91081	-1.62279	-0.42725
H	-5.22442	-0.64680	-1.72866
C	-6.56105	0.44116	-0.42964
C	-6.41211	1.70942	-1.01331
C	-7.68180	0.18686	0.36944
C	-7.36173	2.70517	-0.78617
H	-5.55795	1.90581	-1.65543

C	-8.63490	1.18243	0.59216
H	-7.81970	-0.79592	0.81244
C	-8.47405	2.44390	0.01817
H	-7.24120	3.68085	-1.24744
H	-9.50256	0.97068	1.20955
H	-9.21619	3.21785	0.18870
C	-0.66433	-2.98162	-1.19278
C	-1.02516	-2.17345	-2.29685
C	-1.67474	-3.72975	-0.55807
C	-2.34641	-2.17266	-2.77708
H	-0.25606	-1.65190	-2.85944
C	-2.97778	-3.73699	-1.05123
H	-1.41660	-4.35427	0.29284
C	-3.31434	-2.97100	-2.17214
H	-2.59730	-1.56197	-3.63791
H	-3.72871	-4.35506	-0.56815
H	-4.32292	-3.00099	-2.57194
H	0.45704	-5.25133	-1.80071
C	-3.18062	0.15421	2.10677
C	-2.96504	0.02031	3.47981
C	-4.19508	-0.59467	1.48908
C	-3.78401	-0.82324	4.23245
H	-2.17990	0.59460	3.96276
C	-5.01000	-1.44975	2.23173
C	-4.80127	-1.54934	3.60819
H	-3.63457	-0.90724	5.30386
H	-5.78996	-2.03367	1.75781
H	-5.43688	-2.20470	4.19519
C	-2.97949	2.41395	0.88397
H	-2.81947	3.04778	1.76392
H	-2.47205	2.86751	0.02976
H	-4.05249	2.37667	0.68740

(*S*)-D: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.427442 hartree
Gibbs correction= 0.73071 hartree
Total Gibbs Energy= -2850.696732 hartree

Pd	0.83038	-1.14018	0.46350
P	-1.41480	-0.88147	0.41590
O	-2.12690	-0.02009	1.62686
O	-1.89218	-0.03192	-0.90662
N	-2.21409	-2.34131	0.50870
C	-2.21427	2.25352	0.83458
C	-1.72354	1.32105	1.73271
C	-0.82830	1.63886	2.77549
H	-0.52515	0.85480	3.46073
C	-0.37794	2.93028	2.90000
H	0.29625	3.20026	3.70778
C	-0.76216	3.92519	1.96101
C	-0.23902	5.24416	2.03958
H	0.43556	5.48667	2.85616
C	-0.56555	6.19178	1.09779

H	-0.15725	7.19534	1.16557
C	-1.42626	5.85127	0.02823
H	-1.66317	6.59399	-0.72760
C	-1.96683	4.58764	-0.06661
H	-2.62097	4.34571	-0.89528
C	-1.67300	3.58862	0.90269
C	-3.24462	1.85533	-0.16554
C	-3.04675	0.76711	-1.00129
C	-3.93328	0.42372	-2.04580
H	-3.68601	-0.41452	-2.68728
C	-5.08328	1.15178	-2.22031
H	-5.76846	0.90406	-3.02577
C	-5.41151	2.21179	-1.33508
C	-6.64081	2.91325	-1.45915
H	-7.31145	2.64417	-2.27053
C	-6.98543	3.89887	-0.56405
H	-7.92995	4.42452	-0.66339
C	-6.11106	4.21396	0.50171
H	-6.39719	4.97188	1.22466
C	-4.90307	3.56568	0.63886
H	-4.25518	3.81612	1.46972
C	-4.50048	2.55878	-0.28188
C	-3.66897	-2.41105	0.15219
H	-3.91731	-1.40121	-0.18623
C	-4.56199	-2.64677	1.37946
H	-4.26655	-1.95863	2.17464
H	-4.51275	-3.66743	1.76161
H	-5.60402	-2.43147	1.12536
C	-3.92521	-3.32317	-1.05096
C	-5.02922	-4.18420	-1.10454
H	-5.70890	-4.25631	-0.26257
C	-5.27512	-4.96258	-2.23896
H	-6.13619	-5.62396	-2.25702
C	-4.42284	-4.89323	-3.33997
H	-4.61380	-5.49993	-4.21976
C	-3.32143	-4.03532	-3.30120
H	-2.65130	-3.97017	-4.15355
C	-3.07785	-3.25827	-2.16909
H	-2.22073	-2.59104	-2.15423
C	-1.36175	-3.56078	0.68560
H	-0.93525	-3.83547	-0.28736
C	-2.13028	-4.78846	1.20219
H	-2.93657	-5.07750	0.52816
H	-2.53364	-4.62311	2.20334
C	1.13389	0.71071	-0.42411
H	0.30824	0.98910	-1.07671
H	1.20487	1.39842	0.42276
C	2.46496	0.56046	-1.18306
C	2.27823	-0.25456	-2.48852
H	3.23244	-0.40377	-3.00085
H	1.82974	-1.22940	-2.27500

H	1.61108	0.29155	-3.16123
C	3.26604	1.82393	-1.45303
C	4.53959	1.66811	-0.88155
C	2.97143	2.97169	-2.17445
C	5.53548	2.62524	-1.00957
C	3.95826	3.95971	-2.30402
H	1.99354	3.11019	-2.62639
C	5.21977	3.78396	-1.73287
H	6.52248	2.48212	-0.58524
H	3.74008	4.86708	-2.85783
H	5.97581	4.55355	-1.85213
C	3.39774	-0.18348	-0.24638
O	3.03660	-1.19413	0.40583
N	4.59337	0.43094	-0.17008
C	5.69737	-0.00873	0.68888
H	5.30473	-0.85485	1.26036
H	5.91983	0.79655	1.39723
C	6.95036	-0.39684	-0.07439
C	8.19256	0.11281	0.31882
C	6.89087	-1.29665	-1.14620
C	9.35928	-0.26952	-0.34699
H	8.25106	0.80806	1.15317
C	8.05398	-1.67413	-1.81568
H	5.93255	-1.70304	-1.45979
C	9.29140	-1.16179	-1.41691
H	10.31702	0.13298	-0.03142
H	7.99640	-2.37078	-2.64669
H	10.19654	-1.45753	-1.93837
C	-0.20907	-3.27753	1.64844
C	-0.46273	-2.86831	2.97916
C	1.11314	-3.61001	1.28940
C	0.56554	-2.81484	3.90997
H	-1.47547	-2.60919	3.27137
C	2.14816	-3.55922	2.24162
H	1.31799	-3.99384	0.29308
C	1.87527	-3.16647	3.54508
H	0.35151	-2.51309	4.93093
H	3.15604	-3.82977	1.94650
H	2.67052	-3.13585	4.28331
H	-1.42594	-5.62326	1.25960

(*R*)-D: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.425969 hartree
Gibbs correction= 0.730527 hartree
Total Gibbs Energy= -2850.695442 hartree

Pd	-0.98370	-1.02406	-0.29212
P	1.27249	-0.94439	-0.40027
O	2.01925	-0.18370	-1.65873
O	1.86111	-0.10642	0.88129
N	1.94218	-2.46988	-0.47384
C	2.31962	2.09690	-0.94068
C	1.73947	1.18295	-1.80502

C	0.87357	1.54719	-2.85718
H	0.50045	0.77135	-3.51671
C	0.54057	2.86885	-3.02389
H	-0.10733	3.17232	-3.84123
C	1.00762	3.85332	-2.11162
C	0.59362	5.20862	-2.22308
H	-0.05876	5.48567	-3.04675
C	0.99704	6.14928	-1.30403
H	0.67174	7.18080	-1.39688
C	1.82968	5.76652	-0.22633
H	2.12790	6.50598	0.51075
C	2.26730	4.46601	-0.10108
H	2.90225	4.19177	0.73252
C	1.88992	3.47020	-1.04461
C	3.33529	1.64817	0.05337
C	3.07380	0.60296	0.92553
C	3.95561	0.22184	1.96103
H	3.65831	-0.57523	2.63313
C	5.16175	0.86319	2.08952
H	5.84420	0.58644	2.88780
C	5.54985	1.86896	1.16601
C	6.83209	2.47589	1.24356
H	7.49821	2.17856	2.04878
C	7.23143	3.40578	0.31230
H	8.21572	3.85893	0.37627
C	6.35991	3.75704	-0.74429
H	6.68712	4.46905	-1.49593
C	5.10260	3.20105	-0.83689
H	4.45828	3.47703	-1.66237
C	4.64421	2.25541	0.12191
C	3.38918	-2.65847	-0.12887
H	3.72731	-1.66825	0.18871
C	4.24675	-2.99255	-1.35845
H	4.00611	-2.29414	-2.16312
H	4.10405	-4.01075	-1.72315
H	5.30594	-2.86647	-1.11546
C	3.57596	-3.56679	1.08975
C	4.59004	-4.53173	1.14617
H	5.24502	-4.68812	0.29604
C	4.77709	-5.30645	2.29433
H	5.56870	-6.04950	2.31479
C	3.95491	-5.12910	3.40605
H	4.10014	-5.73269	4.29667
C	2.94335	-4.16689	3.36438
H	2.29820	-4.01682	4.22523
C	2.75837	-3.39384	2.21859
H	1.97170	-2.64472	2.20140
C	0.98728	-3.61660	-0.61598
H	0.56464	-3.84545	0.37036
C	1.63826	-4.90798	-1.13754
H	2.42995	-5.25971	-0.47602

H	2.03564	-4.78438	-2.14704
C	-1.04770	0.79003	0.71007
H	-0.85633	0.50967	1.74929
H	-0.28771	1.49137	0.36866
C	-2.47789	1.30950	0.47916
C	-3.39688	0.11558	0.64570
O	-3.15286	-1.00556	0.13795
N	-4.43056	0.41329	1.45606
C	-5.48680	-0.54305	1.81198
H	-5.82286	-0.28509	2.82102
H	-5.01858	-1.52911	1.86516
C	-6.64620	-0.57291	0.83236
C	-7.08989	-1.79905	0.32554
C	-7.30727	0.60218	0.44894
C	-8.17995	-1.85502	-0.54540
H	-6.58398	-2.71622	0.61701
C	-8.39069	0.54766	-0.42731
H	-6.97595	1.56373	0.83166
C	-8.83139	-0.68133	-0.92462
H	-8.51618	-2.81399	-0.92814
H	-8.89508	1.46446	-0.71769
H	-9.67811	-0.72215	-1.60302
C	-0.16089	-3.23958	-1.55105
C	0.09062	-2.88649	-2.89737
C	-1.49929	-3.39835	-1.13680
C	-0.95783	-2.71531	-3.79037
H	1.11555	-2.75969	-3.23122
C	-2.55690	-3.22190	-2.05047
H	-1.71280	-3.74918	-0.13000
C	-2.28736	-2.88402	-3.36972
H	-0.74694	-2.45924	-4.82443
H	-3.57896	-3.35057	-1.71153
H	-3.10099	-2.75615	-4.07679
H	0.86498	-5.68068	-1.17460
C	-3.05006	2.26781	1.51031
C	-2.64155	3.52455	1.93211
C	-4.23741	1.71184	2.01701
C	-3.42405	4.20991	2.87299
H	-1.72920	3.97084	1.54689
C	-5.03294	2.37972	2.93751
C	-4.60201	3.64453	3.36307
H	-3.11241	5.18962	3.22019
H	-5.95463	1.95317	3.31873
H	-5.20116	4.18991	4.08526
C	-2.64609	1.88520	-0.95062
H	-1.99061	2.75180	-1.06984
H	-2.36933	1.13965	-1.70144
H	-3.67729	2.20287	-1.12687

(*S*)-E[1]: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.462662 hartree
Gibbs correction= 0.730596 hartree

Total Gibbs Energy= -2943.732066 hartree

Pd	-0.72212	-1.85307	0.35348
P	1.03015	-0.26693	0.99042
O	2.62734	-0.59362	1.34285
O	1.24152	0.59295	-0.43210
N	0.68363	0.82723	2.22810
C	3.79029	-0.74684	-0.75699
C	3.32293	-1.35408	0.39802
C	3.52933	-2.71829	0.69005
H	3.12129	-3.12616	1.60608
C	4.19567	-3.50537	-0.21380
H	4.35066	-4.55952	-0.00480
C	4.63031	-2.97513	-1.45698
C	5.24792	-3.80591	-2.43064
H	5.41399	-4.85156	-2.18508
C	5.60833	-3.31033	-3.66203
H	6.07268	-3.95792	-4.40004
C	5.35168	-1.95472	-3.97304
H	5.60891	-1.56983	-4.95581
C	4.77019	-1.11819	-3.04573
H	4.57054	-0.08646	-3.30830
C	4.40890	-1.58806	-1.75167
C	3.61477	0.71805	-0.95432
C	2.36408	1.31008	-0.82697
C	2.13307	2.66470	-1.17098
H	1.12109	3.04598	-1.10130
C	3.17602	3.46222	-1.56574
H	3.00003	4.50014	-1.83495
C	4.50249	2.95673	-1.59022
C	5.60418	3.79628	-1.90599
H	5.40649	4.83407	-2.16239
C	6.89324	3.31715	-1.87226
H	7.72839	3.96992	-2.10879
C	7.12889	1.97079	-1.50919
H	8.14791	1.59860	-1.45492
C	6.08040	1.12638	-1.21639
H	6.28207	0.10118	-0.93128
C	4.73163	1.57894	-1.26374
C	1.40169	2.12917	2.27798
H	2.08543	2.09824	1.42558
C	2.32924	2.26669	3.49867
H	2.89134	1.33819	3.61934
H	1.79725	2.48100	4.42696
H	3.05335	3.07025	3.33119
C	0.48015	3.32707	2.01093
C	0.71308	4.57946	2.59596
H	1.52928	4.70944	3.29830
C	-0.09638	5.67745	2.29244
H	0.10485	6.63627	2.76229
C	-1.15564	5.54578	1.39564
H	-1.78621	6.39860	1.16131

C	-1.39790	4.30429	0.80334
H	-2.21850	4.18596	0.10043
C	-0.58918	3.20858	1.10708
H	-0.79260	2.25073	0.63928
C	-0.52354	0.53013	3.07214
H	-1.41792	0.66856	2.45192
C	-0.67772	1.45493	4.29456
H	-0.70006	2.51258	4.03051
H	0.11038	1.27738	5.02954
C	-2.30756	-2.99552	-0.36710
H	-1.99797	-3.92302	-0.84895
H	-2.93139	-3.22863	0.50117
C	-3.02384	-2.04897	-1.35683
C	-2.21572	-1.92475	-2.67664
H	-2.68070	-1.21455	-3.36742
H	-1.19071	-1.60909	-2.46448
H	-2.17802	-2.90363	-3.16286
C	-4.49313	-2.28985	-1.66108
C	-5.21666	-1.12730	-1.34590
C	-5.15672	-3.37952	-2.20513
C	-6.58286	-1.01603	-1.56429
C	-6.54033	-3.29579	-2.42174
H	-4.61495	-4.28815	-2.45171
C	-7.23906	-2.12876	-2.10931
H	-7.12461	-0.10424	-1.33799
H	-7.07133	-4.14579	-2.83906
H	-8.30819	-2.07546	-2.29139
C	-3.08678	-0.68573	-0.68749
O	-2.12337	-0.15414	-0.09485
N	-4.33758	-0.16750	-0.77112
C	-4.73646	1.10182	-0.16598
H	-3.91813	1.37946	0.50508
H	-5.62756	0.92636	0.44590
C	-4.99742	2.20779	-1.17261
C	-6.21836	2.88934	-1.17966
C	-4.00317	2.58262	-2.08737
C	-6.44828	3.92763	-2.08575
H	-6.99388	2.61106	-0.46961
C	-4.23245	3.61642	-2.99453
H	-3.04856	2.06284	-2.08746
C	-5.45644	4.29146	-2.99612
H	-7.40209	4.44715	-2.08066
H	-3.45526	3.89683	-3.69952
H	-5.63371	5.09624	-3.70346
C	-0.53183	-0.90766	3.58826
C	0.61370	-1.50087	4.13546
C	-1.74066	-1.61419	3.63061
C	0.55288	-2.77857	4.69169
H	1.55915	-0.96816	4.10650
C	-1.80526	-2.88747	4.19766
H	-2.63723	-1.16250	3.21238

C	-0.65590	-3.47602	4.72533
H	1.45271	-3.23200	5.09727
H	-2.74946	-3.42445	4.21353
H	-0.69876	-4.47408	5.15067
H	-1.62925	1.20560	4.77290
C	0.20952	-3.53067	0.68849
N	0.74945	-4.54232	0.91732

(*S*)-E^2: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.455041 hartree
Gibbs correction= 0.730413 hartree
Total Gibbs Energy= -2943.724628 hartree

Pd	-0.67546	-1.17673	1.48334
P	0.97952	0.44811	0.94860
O	2.55278	0.21453	1.47270
O	1.27062	0.55892	-0.68594
N	0.67192	1.98143	1.54926
C	3.62120	-1.06591	-0.25285
C	3.11569	-0.98396	1.03503
C	3.13200	-2.06658	1.94117
H	2.73076	-1.91418	2.93715
C	3.64671	-3.27336	1.53841
H	3.67378	-4.11453	2.22528
C	4.11052	-3.45561	0.20790
C	4.57253	-4.72335	-0.23775
H	4.59639	-5.54418	0.47422
C	4.96204	-4.91801	-1.54249
H	5.30596	-5.89373	-1.87253
C	4.89417	-3.84508	-2.46149
H	5.17520	-4.00637	-3.49820
C	4.46825	-2.59862	-2.05806
H	4.41358	-1.79175	-2.77874
C	4.08248	-2.35235	-0.71070
C	3.63121	0.15081	-1.11226
C	2.47190	0.89180	-1.30325
C	2.40752	1.98507	-2.20002
H	1.45513	2.48743	-2.32944
C	3.53427	2.38623	-2.87078
H	3.48913	3.21956	-3.56643
C	4.77969	1.74419	-2.64126
C	5.96913	2.20521	-3.26658
H	5.89947	3.04278	-3.95589
C	7.18460	1.62050	-2.99660
H	8.08823	1.98542	-3.47570
C	7.25590	0.55022	-2.07508
H	8.21886	0.10624	-1.83981
C	6.11816	0.06828	-1.46565
H	6.19624	-0.74507	-0.75473
C	4.83940	0.63020	-1.73910
C	1.41726	3.16436	1.04368
H	2.08048	2.75826	0.27466
C	2.36828	3.76663	2.09263

H	2.92670	2.95838	2.57031
H	1.85143	4.34380	2.86163
H	3.09422	4.42655	1.60770
C	0.51605	4.16816	0.31437
C	0.76649	5.54697	0.35716
H	1.58087	5.93693	0.95829
C	-0.02527	6.44258	-0.36627
H	0.18689	7.50697	-0.31476
C	-1.08285	5.97535	-1.14564
H	-1.70172	6.67167	-1.70432
C	-1.34061	4.60388	-1.19555
H	-2.16574	4.22352	-1.79105
C	-0.54962	3.70711	-0.47639
H	-0.77985	2.64758	-0.52258
C	-0.51679	2.05512	2.46639
H	-1.41888	1.90356	1.86233
C	-0.67571	3.39689	3.19853
H	-0.72950	4.23999	2.50923
H	0.12732	3.56729	3.91884
C	-0.61683	-2.01465	-0.41667
H	0.34432	-1.70345	-0.82176
H	-0.63021	-3.09249	-0.26732
C	-1.78036	-1.56570	-1.33916
C	-1.20331	-1.11632	-2.70688
H	-2.00310	-0.83568	-3.39987
H	-0.54121	-0.25932	-2.56095
H	-0.63283	-1.93279	-3.15981
C	-2.85270	-2.62410	-1.51399
C	-4.09575	-2.09546	-1.14336
C	-2.77110	-3.92885	-1.97578
C	-5.26885	-2.83486	-1.22643
C	-3.94094	-4.69759	-2.06178
H	-1.81331	-4.35536	-2.26236
C	-5.17078	-4.15279	-1.69118
H	-6.22800	-2.41202	-0.94962
H	-3.88828	-5.72223	-2.41686
H	-6.07074	-4.75661	-1.76205
C	-2.60722	-0.37814	-0.77998
O	-2.19793	0.74403	-0.48915
N	-3.92575	-0.76451	-0.71068
C	-4.97007	0.08176	-0.15089
H	-4.44316	0.89891	0.35131
H	-5.51109	-0.49136	0.61016
C	-5.93819	0.63957	-1.17985
C	-7.31886	0.49072	-1.01472
C	-5.46053	1.34326	-2.29390
C	-8.21049	1.03122	-1.94477
H	-7.70042	-0.05086	-0.15203
C	-6.34795	1.87955	-3.22544
H	-4.38912	1.47075	-2.42320
C	-7.72656	1.72490	-3.05366

H	-9.28023	0.90478	-1.80393
H	-5.96513	2.42152	-4.08580
H	-8.41718	2.14272	-3.78055
C	-0.44255	0.93276	3.50295
C	0.68187	0.79412	4.33891
C	-1.53429	0.06712	3.69634
C	0.70483	-0.16993	5.34109
H	1.53906	1.44319	4.19102
C	-1.50054	-0.91533	4.70225
H	-2.43758	0.19834	3.10722
C	-0.38577	-1.03108	5.52421
H	1.57752	-0.25672	5.98266
H	-2.34134	-1.59194	4.80711
H	-0.35751	-1.79004	6.30016
H	-1.61514	3.35740	3.75789
C	-2.07871	-2.54496	1.91952
N	-2.91035	-3.28640	2.27480

(*S*)-E^3: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.459543 hartree
Gibbs correction= 0.732366 hartree
Total Gibbs Energy= -2943.727177 hartree

Pd	-0.87594	-1.51722	0.47524
P	0.86635	0.17990	0.73718
O	2.28938	0.05085	1.59847
O	1.50093	0.28015	-0.81121
N	0.38718	1.72326	1.22137
C	3.88251	-1.04833	0.17066
C	3.09213	-1.05631	1.30921
C	3.06719	-2.13002	2.22319
H	2.41267	-2.07134	3.08341
C	3.83069	-3.24165	1.97478
H	3.81058	-4.07908	2.66562
C	4.60051	-3.34317	0.78631
C	5.32830	-4.52607	0.48510
H	5.31136	-5.33904	1.20626
C	6.02009	-4.65322	-0.69686
H	6.56604	-5.56571	-0.91812
C	6.00032	-3.59610	-1.63621
H	6.52173	-3.70715	-2.58275
C	5.31878	-2.42933	-1.36790
H	5.30547	-1.63693	-2.10628
C	4.61456	-2.25039	-0.14399
C	3.92865	0.15904	-0.69852
C	2.75995	0.73694	-1.17983
C	2.77541	1.77519	-2.14338
H	1.82711	2.13792	-2.52155
C	3.96702	2.30407	-2.56750
H	3.98059	3.09648	-3.31088
C	5.19447	1.85286	-2.01501
C	6.42935	2.45653	-2.37407
H	6.41908	3.25609	-3.11059

C	7.61014	2.05478	-1.79380
H	8.54750	2.52822	-2.07086
C	7.59629	1.03118	-0.81803
H	8.52404	0.73207	-0.33877
C	6.41759	0.41270	-0.46276
H	6.42645	-0.36275	0.29329
C	5.17918	0.78449	-1.05811
C	1.25647	2.88924	0.91077
H	2.10990	2.46194	0.37702
C	1.87874	3.53496	2.16180
H	2.25556	2.74430	2.81386
H	1.17800	4.15349	2.72497
H	2.73064	4.16105	1.87817
C	0.61235	3.86538	-0.08316
C	0.88517	5.23987	-0.04665
H	1.52199	5.64780	0.73070
C	0.34540	6.10803	-0.99958
H	0.57176	7.16930	-0.94549
C	-0.47743	5.61861	-2.01271
H	-0.89645	6.29244	-2.75443
C	-0.75481	4.25037	-2.06264
H	-1.38689	3.85270	-2.85277
C	-0.21824	3.38418	-1.10911
H	-0.44750	2.32471	-1.16019
C	-1.01520	1.86673	1.74714
H	-1.71098	1.71987	0.91278
C	-1.32236	3.25171	2.34770
H	-1.12236	4.07189	1.65756
H	-0.77309	3.41425	3.27773
C	-2.39666	-2.86335	0.01270
H	-2.09480	-3.90880	0.07803
H	-3.19593	-2.66979	0.73421
C	-2.80840	-2.47624	-1.42580
C	-1.75506	-2.97739	-2.44948
H	-2.00271	-2.66435	-3.46854
H	-0.76314	-2.60170	-2.18473
H	-1.72494	-4.07034	-2.42225
C	-4.21032	-2.82471	-1.89589
C	-4.86677	-1.64289	-2.28224
C	-4.85799	-4.04312	-2.03638
C	-6.15385	-1.64581	-2.80480
C	-6.16053	-4.06904	-2.55676
H	-4.36542	-4.96500	-1.74061
C	-6.79484	-2.88599	-2.93763
H	-6.65693	-0.72958	-3.09678
H	-6.67902	-5.01685	-2.66289
H	-7.80242	-2.91929	-3.34093
C	-2.85668	-0.95802	-1.46970
O	-1.96984	-0.21507	-1.00262
N	-4.01565	-0.53040	-2.03342
C	-4.35398	0.88339	-2.19220

H	-5.06853	0.95256	-3.01939
H	-3.44253	1.39626	-2.50885
C	-4.90318	1.55415	-0.94256
C	-4.42817	2.81923	-0.57745
C	-5.90286	0.95411	-0.16415
C	-4.94784	3.47994	0.53800
H	-3.63980	3.28905	-1.15999
C	-6.41430	1.60951	0.95661
H	-6.28144	-0.02876	-0.42858
C	-5.94160	2.87586	1.30895
H	-4.56803	4.46131	0.80669
H	-7.18555	1.13091	1.55317
H	-6.34271	3.38492	2.18034
C	-1.34555	0.82916	2.81899
C	-0.44944	0.52343	3.85200
C	-2.62496	0.25813	2.84515
C	-0.81775	-0.35166	4.87385
H	0.54628	0.95596	3.84420
C	-2.99770	-0.60737	3.87453
H	-3.33265	0.49513	2.05457
C	-2.09262	-0.91999	4.88911
H	-0.10621	-0.59280	5.65830
H	-3.99123	-1.04706	3.87584
H	-2.37434	-1.60742	5.68104
H	-2.38859	3.26752	2.58983
C	-0.22638	-2.85228	1.73647
N	0.13374	-3.64658	2.51546

(*S*)-E[4]: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.469851 hartree
Gibbs correction= 0.730925 hartree
Total Gibbs Energy= -2943.738926 hartree

Pd	-1.12390	-0.30620	-0.73059
P	1.08319	-0.35440	-0.35131
O	2.06487	0.32274	-1.48171
O	1.41211	0.65032	0.94449
N	1.80129	-1.85695	-0.20840
C	2.41673	2.61948	-0.87309
C	1.89346	1.68437	-1.75129
C	1.22166	2.02163	-2.94536
H	0.85320	1.22213	-3.57838
C	1.03760	3.34762	-3.24879
H	0.53043	3.63009	-4.16706
C	1.46654	4.36699	-2.35719
C	1.20773	5.73690	-2.63305
H	0.70442	5.98966	-3.56266
C	1.56614	6.72131	-1.74176
H	1.35652	7.76392	-1.96202
C	2.19364	6.36897	-0.52420
H	2.45069	7.14352	0.19268
C	2.47586	5.05226	-0.23383
H	2.94667	4.80177	0.70899

C	2.14469	4.00909	-1.14342
C	3.18921	2.16913	0.31829
C	2.64897	1.23034	1.18860
C	3.27216	0.88134	2.40921
H	2.75846	0.18979	3.06824
C	4.48769	1.42735	2.73835
H	4.96517	1.17617	3.68157
C	5.15458	2.29956	1.83793
C	6.45308	2.79946	2.12569
H	6.91649	2.52330	3.06939
C	7.11972	3.59896	1.22670
H	8.11510	3.96886	1.45397
C	6.51013	3.92363	-0.00768
H	7.04788	4.53143	-0.72951
C	5.24437	3.47121	-0.30862
H	4.79799	3.72197	-1.26312
C	4.51363	2.66179	0.60600
C	3.23286	-2.07870	-0.64940
H	3.68776	-1.08780	-0.59899
C	3.31181	-2.51906	-2.11881
H	2.77017	-1.80957	-2.74653
H	2.88410	-3.50774	-2.28523
H	4.36017	-2.53678	-2.43523
C	4.05360	-2.95402	0.29869
C	4.29397	-4.31243	0.05389
H	3.86232	-4.79280	-0.81591
C	5.08337	-5.06807	0.92412
H	5.25418	-6.12041	0.71476
C	5.65576	-4.47708	2.05075
H	6.27232	-5.06515	2.72473
C	5.44109	-3.11906	2.29533
H	5.89579	-2.64124	3.15886
C	4.65340	-2.36822	1.42346
H	4.50396	-1.31019	1.61555
C	0.92929	-2.93194	0.36957
H	-0.07690	-2.49407	0.32229
C	1.20608	-3.17276	1.86134
H	1.17654	-2.21821	2.39431
H	2.17763	-3.63139	2.04801
C	-1.57419	0.23864	1.26391
H	-0.92857	-0.17789	2.03979
H	-1.47205	1.32895	1.28578
C	-3.04093	-0.19434	1.47722
C	-3.13300	-1.72406	1.71891
H	-4.17103	-2.05378	1.82442
H	-2.66955	-2.26829	0.89110
H	-2.59942	-1.97432	2.64066
C	-3.88914	0.54906	2.49588
C	-5.02502	1.06279	1.84623
C	-3.74139	0.73617	3.86198
C	-6.02100	1.75417	2.52242

C	-4.72907	1.44294	4.56459
H	-2.86806	0.34979	4.38003
C	-5.85253	1.93923	3.90204
H	-6.90258	2.12580	2.01230
H	-4.61923	1.60283	5.63284
H	-6.61326	2.47708	4.45984
C	-3.77476	0.13914	0.19092
O	-3.32139	-0.10193	-0.94630
N	-4.94084	0.78162	0.45459
C	-5.83640	1.30070	-0.57837
H	-5.30872	1.15122	-1.52526
H	-5.95260	2.37948	-0.42604
C	-7.19578	0.62575	-0.60629
C	-8.36604	1.39039	-0.56004
C	-7.29798	-0.76731	-0.71652
C	-9.61981	0.77725	-0.61988
H	-8.29770	2.47321	-0.48220
C	-8.54812	-1.38132	-0.77167
H	-6.39544	-1.37089	-0.76399
C	-9.71293	-0.61041	-0.72315
H	-10.51993	1.38407	-0.58286
H	-8.61415	-2.46201	-0.85821
H	-10.68621	-1.09027	-0.76770
C	0.83726	-4.20015	-0.48394
C	0.32328	-4.11129	-1.78814
C	1.15933	-5.46607	0.02082
C	0.15656	-5.25443	-2.56835
H	0.05710	-3.14390	-2.20341
C	0.99051	-6.61321	-0.76048
H	1.55118	-5.56952	1.02656
C	0.49135	-6.51169	-2.05816
H	-0.24062	-5.15790	-3.57464
H	1.24956	-7.58500	-0.34891
H	0.35851	-7.40289	-2.66524
H	0.43039	-3.82081	2.28244
C	-0.80152	-0.76656	-2.71889
N	-0.58287	-1.02224	-3.83986

(*S*)-TS4[1]: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.423321 hartree
Gibbs correction= 0.726335 hartree
Total Gibbs Energy= -2943.696986 hartree

Pd	-0.62600	-0.68685	0.55493
P	1.38528	0.49140	0.63518
O	2.69988	-0.07294	1.50814
O	2.06943	0.51253	-0.88587
N	1.35130	2.07885	1.21670
C	3.84790	-1.59280	0.04677
C	3.09406	-1.37117	1.18725
C	2.70156	-2.40549	2.06396
H	2.13141	-2.14516	2.94905
C	3.04693	-3.70142	1.77523

H	2.76118	-4.50835	2.44438
C	3.74266	-4.01521	0.57773
C	4.03559	-5.36210	0.23399
H	3.74215	-6.14758	0.92570
C	4.65395	-5.67230	-0.95455
H	4.86355	-6.70673	-1.21060
C	4.99525	-4.63835	-1.85687
H	5.45308	-4.88580	-2.81026
C	4.74257	-3.32078	-1.54537
H	4.99697	-2.54406	-2.25603
C	4.13067	-2.95928	-0.31320
C	4.31143	-0.43487	-0.76697
C	3.41853	0.53350	-1.21132
C	3.80754	1.56678	-2.09890
H	3.04628	2.25418	-2.44918
C	5.11602	1.68347	-2.48999
H	5.41402	2.47056	-3.17726
C	6.10391	0.80294	-1.97639
C	7.47663	0.96871	-2.30237
H	7.75236	1.76786	-2.98586
C	8.43921	0.15179	-1.75621
H	9.48641	0.29174	-2.00785
C	8.05929	-0.86328	-0.84796
H	8.82035	-1.49139	-0.39378
C	6.73430	-1.06136	-0.52651
H	6.46625	-1.83827	0.17867
C	5.70690	-0.25342	-1.09086
C	2.50737	2.98456	0.97988
H	3.21178	2.38186	0.39943
C	3.27209	3.33270	2.26863
H	3.43394	2.41495	2.83810
H	2.74987	4.05380	2.90037
H	4.25503	3.74767	2.02392
C	2.15735	4.17521	0.07846
C	2.73186	5.44019	0.26383
H	3.41000	5.61498	1.09210
C	2.44278	6.49533	-0.60579
H	2.89962	7.46687	-0.43860
C	1.57334	6.30607	-1.67903
H	1.34620	7.12699	-2.35297
C	0.99667	5.04962	-1.87748
H	0.31715	4.88592	-2.70922
C	1.28724	3.99733	-1.00957
H	0.83579	3.02475	-1.17776
C	0.02432	2.55825	1.71959
H	-0.64556	2.71266	0.86380
C	0.08423	3.89367	2.48353
H	0.51554	4.69766	1.88681
H	0.64005	3.79722	3.41904
C	-2.26096	-2.21918	0.22879
H	-2.19486	-3.30158	0.29087

H	-2.47588	-1.87596	1.25375
C	-3.37979	-1.79729	-0.74915
C	-2.99124	-1.92563	-2.24055
H	-3.85519	-1.69962	-2.87370
H	-2.17894	-1.23710	-2.47918
H	-2.64951	-2.93972	-2.45721
C	-4.66321	-2.55980	-0.45298
C	-5.68578	-1.64677	-0.15316
C	-4.93716	-3.91962	-0.46842
C	-6.98308	-2.05848	0.13133
C	-6.23744	-4.35759	-0.17574
H	-4.15716	-4.63829	-0.70528
C	-7.24304	-3.43560	0.11807
H	-7.77215	-1.34469	0.33987
H	-6.46273	-5.41954	-0.18328
H	-8.24775	-3.78570	0.33621
C	-3.81938	-0.34149	-0.48581
O	-3.11281	0.65982	-0.53125
N	-5.16843	-0.33597	-0.18730
C	-5.91269	0.88079	0.11044
H	-5.15453	1.66215	0.22189
H	-6.41934	0.76179	1.07545
C	-6.91878	1.27152	-0.95862
C	-8.24910	1.53744	-0.61881
C	-6.51936	1.40649	-2.29501
C	-9.16915	1.92941	-1.59429
H	-8.56861	1.44052	0.41657
C	-7.43677	1.79313	-3.27067
H	-5.48580	1.21127	-2.56781
C	-8.76490	2.05559	-2.92307
H	-10.19949	2.13075	-1.31523
H	-7.11495	1.89332	-4.30330
H	-9.47846	2.35666	-3.68455
C	-0.63158	1.53010	2.64337
C	0.05458	1.01253	3.75666
C	-1.98350	1.19722	2.47174
C	-0.59425	0.18438	4.66880
H	1.10326	1.25660	3.89636
C	-2.63505	0.36926	3.39516
H	-2.52578	1.58669	1.61537
C	-1.94449	-0.13914	4.49348
H	-0.04895	-0.20697	5.52315
H	-3.68365	0.12431	3.24940
H	-2.44956	-0.78153	5.20893
H	-0.94182	4.17514	2.73805
C	-0.52488	-2.27462	-0.58895
N	-0.04626	-3.03824	-1.34421

(*S*)-TS4[2]: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.418287 hartree
Gibbs correction= 0.727714 hartree
Total Gibbs Energy= -2943.690573 hartree

Pd	-0.43210	-1.37298	1.43705
P	1.21448	0.31799	1.07928
O	2.84699	0.24893	1.48880
O	1.40044	0.46816	-0.58896
N	0.83664	1.83342	1.71072
C	3.90868	-0.93461	-0.30731
C	3.48555	-0.89060	1.01236
C	3.66485	-1.96515	1.91216
H	3.32591	-1.84360	2.93536
C	4.25888	-3.12216	1.47430
H	4.41282	-3.95295	2.15734
C	4.64399	-3.26851	0.11459
C	5.18825	-4.49065	-0.36444
H	5.33677	-5.30260	0.34282
C	5.50345	-4.65488	-1.69326
H	5.91214	-5.59644	-2.04799
C	5.27492	-3.59639	-2.60318
H	5.49821	-3.73546	-3.65707
C	4.76576	-2.39238	-2.16852
H	4.58889	-1.59619	-2.88145
C	4.45228	-2.17606	-0.79725
C	3.75449	0.27443	-1.16328
C	2.52137	0.90659	-1.27719
C	2.30780	1.98620	-2.16925
H	1.30958	2.40407	-2.23739
C	3.34931	2.48254	-2.90995
H	3.18654	3.30588	-3.60011
C	4.65912	1.95512	-2.76078
C	5.76105	2.51616	-3.46013
H	5.57385	3.34103	-4.14298
C	7.03837	2.04261	-3.26871
H	7.87397	2.48358	-3.80416
C	7.26213	0.98766	-2.35396
H	8.27357	0.63162	-2.18032
C	6.21222	0.41069	-1.67347
H	6.40702	-0.38828	-0.96861
C	4.87359	0.85554	-1.86463
C	1.49240	3.05577	1.17749
H	2.16761	2.68670	0.39997
C	2.42187	3.73139	2.20180
H	3.02916	2.96273	2.68483
H	1.88380	4.29149	2.96875
H	3.10383	4.42194	1.69572
C	0.51355	3.99172	0.45717
C	0.69160	5.38256	0.45832
H	1.50713	5.82796	1.01789
C	-0.17271	6.21857	-0.25323
H	-0.01397	7.29335	-0.23439
C	-1.23454	5.67957	-0.97862
H	-1.91063	6.32957	-1.52672
C	-1.42193	4.29593	-0.98736

H	-2.24989	3.85920	-1.53873
C	-0.55674	3.45952	-0.28123
H	-0.72996	2.38853	-0.29753
C	-0.37794	1.87320	2.59866
H	-1.26929	1.75913	1.97124
C	-0.53738	3.18600	3.38291
H	-0.58721	4.05722	2.72880
H	0.26432	3.32571	4.11164
C	-1.10244	-2.37679	-0.52546
H	-0.12864	-1.95152	-0.77918
H	-1.04933	-3.44856	-0.69818
C	-2.21608	-1.70955	-1.36297
C	-1.58000	-1.13057	-2.65281
H	-2.34185	-0.68414	-3.29957
H	-0.84484	-0.36582	-2.38762
H	-1.08004	-1.92378	-3.21689
C	-3.38095	-2.62815	-1.67459
C	-4.57003	-2.03450	-1.22982
C	-3.42205	-3.85785	-2.31323
C	-5.80868	-2.63791	-1.40977
C	-4.66027	-4.49014	-2.49829
H	-2.50881	-4.33229	-2.66326
C	-5.83439	-3.88328	-2.05121
H	-6.72488	-2.16338	-1.07689
H	-4.70439	-5.45592	-2.99207
H	-6.78831	-4.37998	-2.20252
C	-2.92443	-0.54200	-0.62906
O	-2.40074	0.46575	-0.16658
N	-4.27710	-0.79850	-0.61959
C	-5.23987	0.06434	0.05022
H	-4.63891	0.77427	0.62705
H	-5.81909	-0.53951	0.75787
C	-6.17187	0.80780	-0.89116
C	-7.55296	0.80605	-0.67002
C	-5.65980	1.53882	-1.97135
C	-8.41056	1.51989	-1.51065
H	-7.96134	0.24367	0.16670
C	-6.51384	2.24802	-2.81448
H	-4.58754	1.54993	-2.14739
C	-7.89274	2.24094	-2.58636
H	-9.48113	1.50677	-1.32680
H	-6.10411	2.80923	-3.64965
H	-8.55740	2.79349	-3.24415
C	-0.35395	0.71176	3.59305
C	0.70919	0.55324	4.49702
C	-1.43362	-0.18657	3.65826
C	0.69324	-0.47256	5.43957
H	1.55784	1.22895	4.44688
C	-1.44254	-1.22509	4.60235
H	-2.28842	-0.04641	3.00232
C	-0.38109	-1.36806	5.49285

H	1.52208	-0.57749	6.13441
H	-2.27561	-1.92041	4.61870
H	-0.38645	-2.17189	6.22305
H	-1.47910	3.12727	3.93689
C	-1.86824	-2.70279	1.20105
N	-2.76754	-3.37418	1.55611

(*S*)-F: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.475541 hartree
Gibbs correction= 0.728968 hartree
Total Gibbs Energy= -2943.746573 hartree

Pd	0.82439	-0.80576	0.13804
P	-1.03685	0.34854	0.10847
O	-2.06978	-0.00166	-1.18545
O	-2.14385	0.06332	1.35043
N	-0.94462	2.03459	-0.04886
C	-3.40473	-1.84660	-0.45606
C	-2.39801	-1.34865	-1.26814
C	-1.67525	-2.15598	-2.17625
H	-0.90468	-1.70347	-2.79028
C	-1.95345	-3.49779	-2.25304
H	-1.40998	-4.12700	-2.95247
C	-2.91546	-4.09165	-1.39279
C	-3.15144	-5.49281	-1.41260
H	-2.60338	-6.09821	-2.13023
C	-4.03564	-6.07733	-0.53559
H	-4.20147	-7.15060	-0.55677
C	-4.71607	-5.27573	0.41044
H	-5.39279	-5.74022	1.12212
C	-4.52419	-3.91188	0.44397
H	-5.04593	-3.31508	1.18239
C	-3.63818	-3.26846	-0.46508
C	-4.17417	-0.90716	0.40398
C	-3.52339	-0.02464	1.26138
C	-4.24114	0.78221	2.18026
H	-3.67710	1.40561	2.86298
C	-5.61148	0.77033	2.19567
H	-6.15623	1.38534	2.90695
C	-6.33672	-0.01511	1.26254
C	-7.75544	0.03002	1.20711
H	-8.28062	0.65798	1.92257
C	-8.45172	-0.68721	0.26205
H	-9.53618	-0.64000	0.22462
C	-7.74464	-1.47376	-0.67667
H	-8.29018	-2.01779	-1.44253
C	-6.36968	-1.55199	-0.63697
H	-5.84757	-2.15059	-1.37312
C	-5.61531	-0.84579	0.34272
C	-2.18642	2.84775	-0.17117
H	-2.99473	2.14674	0.05764
C	-2.46644	3.33294	-1.60155
H	-2.38747	2.48922	-2.28854

H	-1.77383	4.10998	-1.93103
H	-3.48525	3.72888	-1.66468
C	-2.28590	3.93933	0.90376
C	-2.66810	5.25301	0.60728
H	-2.86271	5.54563	-0.41858
C	-2.80374	6.20920	1.61952
H	-3.09818	7.22305	1.36209
C	-2.56434	5.86661	2.94855
H	-2.67036	6.60864	3.73487
C	-2.18533	4.55732	3.25906
H	-1.99308	4.27614	4.29110
C	-2.04864	3.60882	2.24807
H	-1.73294	2.59933	2.49205
C	0.41341	2.59518	-0.29888
H	1.06862	1.73246	-0.09895
C	0.83696	3.67735	0.70231
H	0.70562	3.30936	1.72167
H	0.27014	4.60567	0.60940
C	3.81115	-0.51485	-2.77771
H	4.48461	-0.35216	-3.62702
H	3.47790	0.47319	-2.44211
C	4.61737	-1.23261	-1.64891
C	4.97677	-2.67696	-2.04546
H	5.58214	-3.14956	-1.26752
H	4.06806	-3.26678	-2.18867
H	5.55270	-2.68367	-2.97606
C	5.81856	-0.39420	-1.25567
C	5.66891	0.02070	0.07614
C	6.94500	-0.02102	-1.97406
C	6.62638	0.79856	0.71638
C	7.91941	0.77084	-1.34934
H	7.07758	-0.33694	-3.00551
C	7.75714	1.17101	-0.02213
H	6.51667	1.09623	1.75278
H	8.80570	1.06955	-1.89992
H	8.52129	1.77838	0.45344
C	3.80008	-1.23114	-0.34093
O	2.74308	-1.84930	-0.16102
N	4.45159	-0.47508	0.59271
C	3.92211	-0.20247	1.93213
H	2.83183	-0.31353	1.85567
H	4.12970	0.84718	2.16171
C	4.48746	-1.10471	3.01188
C	5.22077	-0.56878	4.07567
C	4.26016	-2.48815	2.96965
C	5.72778	-1.39694	5.07981
H	5.38970	0.50466	4.12647
C	4.76980	-3.31561	3.96903
H	3.67543	-2.91021	2.15707
C	5.50605	-2.77275	5.02587
H	6.29445	-0.96639	5.90041

H	4.58521	-4.38521	3.92784
H	5.89943	-3.41945	5.80478
C	0.68229	2.96410	-1.76494
C	0.59986	1.96226	-2.74649
C	1.07254	4.24809	-2.16696
C	0.88938	2.23551	-4.08274
H	0.29634	0.95967	-2.46046
C	1.35750	4.52774	-3.50732
H	1.15491	5.04610	-1.43660
C	1.26749	3.52413	-4.47060
H	0.81609	1.43990	-4.81916
H	1.65141	5.53397	-3.79405
H	1.48883	3.74137	-5.51184
H	1.89712	3.90995	0.55368
C	2.64112	-1.24598	-3.27293
N	1.72102	-1.80020	-3.71276

G: B3LYP/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2063.860792 hartree
Gibbs correction= 0.471438 hartree
Total Gibbs Energy= -2063.389354 hartree

Pd	1.59752	-2.55005	0.44365
P	0.62563	-0.63990	-0.20932
O	-0.56177	-0.47003	-1.41417
O	-0.14410	0.26493	0.99282
N	1.80456	0.41111	-0.82641
C	-2.64535	-0.59053	-0.24091
C	-1.73102	-1.15265	-1.11918
C	-1.93263	-2.41331	-1.72633
H	-1.18613	-2.77295	-2.42619
C	-3.05627	-3.14102	-1.42510
H	-3.22917	-4.10567	-1.89464
C	-3.98990	-2.66607	-0.46527
C	-5.11365	-3.44871	-0.08608
H	-5.26323	-4.40871	-0.57380
C	-5.98419	-3.01638	0.88732
H	-6.83524	-3.62749	1.17338
C	-5.75572	-1.77763	1.53067
H	-6.42682	-1.44911	2.31912
C	-4.68657	-0.98595	1.17318
H	-4.52120	-0.04500	1.68384
C	-3.77943	-1.38757	0.15287
C	-2.41357	0.78956	0.26776
C	-1.20450	1.14219	0.85955
C	-1.01206	2.41350	1.45874
H	-0.06680	2.60652	1.95296
C	-1.99810	3.36367	1.40706
H	-1.84990	4.33331	1.87472
C	-3.21012	3.10829	0.71389
C	-4.20438	4.11347	0.57727
H	-4.03178	5.07807	1.04807
C	-5.35144	3.88330	-0.14641

H	-6.10220	4.66125	-0.24956
C	-5.53945	2.63034	-0.77410
H	-6.43034	2.45566	-1.37064
C	-4.60141	1.62935	-0.64510
H	-4.76081	0.68201	-1.14501
C	-3.41464	1.81969	0.11818
C	1.50181	1.83564	-1.13300
H	0.54006	2.03278	-0.65415
C	1.28646	2.11704	-2.62763
H	0.55702	1.40902	-3.02557
H	2.20817	2.03779	-3.21130
H	0.89130	3.12864	-2.76629
C	2.50876	2.76896	-0.44997
C	3.19829	3.77692	-1.13394
H	3.05630	3.90812	-2.20121
C	4.07353	4.63474	-0.45905
H	4.59921	5.40769	-1.01284
C	4.27062	4.50103	0.91349
H	4.94835	5.16835	1.43812
C	3.58728	3.49924	1.60970
H	3.73099	3.38503	2.68073
C	2.71980	2.64330	0.93374
H	2.20462	1.85465	1.47384
C	3.11189	-0.13584	-1.32239
H	3.75129	0.74867	-1.41593
C	2.99323	-0.78441	-2.71262
H	2.61710	-0.06997	-3.44519
H	2.30158	-1.63128	-2.69812
C	3.79107	-1.05270	-0.29607
C	3.73808	-2.46974	-0.41462
C	4.44960	-0.50525	0.80487
C	4.26532	-3.28809	0.60423
H	3.42974	-2.92812	-1.34984
C	4.99493	-1.32303	1.80581
H	4.51251	0.57439	0.90186
C	4.87973	-2.70725	1.72567
H	4.25948	-4.36710	0.47978
H	5.50214	-0.86791	2.65178
H	5.29102	-3.33980	2.50693
H	3.97152	-1.13950	-3.05449

1: BP86/6-311+G(2df,2pd) SCF= -880.5324667 hartree
Gibbs correction= 0.21781 hartree
Total Gibbs Energy= -880.3146567 hartree

C	1.15414	-1.22422	2.64974
C	0.54150	-0.25941	1.83987
C	0.91518	-0.11597	0.49072
C	1.90051	-0.96132	-0.08643
C	2.48327	-1.94067	0.74869
C	2.12301	-2.07341	2.09672
H	0.86434	-1.31740	3.70066

H	-0.24754	0.38458	2.23927
H	3.25933	-2.58410	0.32247
H	2.60693	-2.83598	2.71523
C	2.36052	-0.85667	-1.50819
C	2.85919	0.48157	-2.01768
C	2.38774	-1.96325	-2.28459
H	2.02623	-2.93051	-1.92151
H	2.76779	-1.92685	-3.31089
N	0.21877	0.85578	-0.31354
C	-0.74775	0.38738	-1.34399
H	-0.90863	1.24393	-2.01767
H	-0.25398	-0.42260	-1.90559
C	0.27170	2.20630	-0.05232
C	1.28971	2.61654	0.94134
O	-0.41789	3.07104	-0.60572
N	2.06014	3.10826	1.68121
C	-2.06403	-0.08651	-0.75169
C	-3.02378	0.85036	-0.31396
C	-2.34021	-1.46083	-0.62482
C	-4.23559	0.41507	0.24082
H	-2.81030	1.91988	-0.41500
C	-3.55488	-1.89651	-0.07189
H	-1.60013	-2.19367	-0.96624
C	-4.50400	-0.95890	0.36287
H	-4.97605	1.15021	0.57322
H	-3.75934	-2.96856	0.01775
H	-5.45281	-1.29694	0.79249
H	3.32377	0.36977	-3.01014
H	3.60643	0.91117	-1.32756
H	2.04739	1.22310	-2.10584

2: BP86/6-311+G(2df,2pd) SCF= -880.5835179 hartree
Gibbs correction= 0.224132 hartree
Total Gibbs Energy= -880.3593859 hartree

C	-1.96493	3.08669	0.66171
C	-2.62248	1.84411	0.55497
C	-1.94726	0.76547	-0.01678
C	-0.62188	0.93086	-0.48067
C	0.04728	2.15590	-0.38522
C	-0.64875	3.23318	0.19570
H	-2.48282	3.93899	1.11173
H	-3.65085	1.73229	0.91670
H	1.07808	2.26912	-0.73038
H	-0.14679	4.20174	0.28731
N	-0.15102	-0.28385	-1.02734
C	-1.12621	-1.27623	-0.96674
O	-1.01260	-2.43022	-1.37757
C	-2.38844	-0.66076	-0.29412
C	-3.58110	-0.75942	-1.27190
H	-3.73796	-1.80972	-1.56904
H	-4.50309	-0.37556	-0.80337

H	-3.38736	-0.16671	-2.17989
C	-2.71845	-1.49198	0.98617
H	-2.89851	-2.53899	0.67931
H	-3.64672	-1.11044	1.44862
C	1.15861	-0.50973	-1.63360
H	1.27605	0.15962	-2.50699
H	1.11099	-1.54736	-2.01302
C	2.33708	-0.33163	-0.68466
C	3.53216	0.23561	-1.16779
C	2.27631	-0.76258	0.65471
C	4.65336	0.36105	-0.33302
H	3.58585	0.57878	-2.20835
C	3.39441	-0.62870	1.49116
H	1.35152	-1.19124	1.05509
C	4.58611	-0.07065	1.00064
H	5.57577	0.80363	-0.72374
H	3.32931	-0.96161	2.53203
H	5.45685	0.03225	1.65655
C	-1.64827	-1.48341	1.98957
N	-0.77969	-1.48754	2.77980

Cyanide: BP86/6-311+G(2df,2pd) SCF= -92.94987852 hartree
Gibbs correction= -0.020133 hartree
Total Gibbs Energy= -92.97001152 hartree

C	0.00000	0.00000	-0.64455
N	0.00000	0.00000	0.55247

A: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.492006 hartree
Gibbs correction= 0.7009 hartree
Total Gibbs Energy= -2943.791106 hartree

Pd	-1.10050	-0.80252	0.03427
P	1.19405	-0.58608	-0.39934
O	1.69063	0.53215	-1.56939
O	1.91817	0.16596	0.96087
N	2.14513	-1.88383	-0.93886
C	1.98560	2.66252	-0.47898
C	1.26216	1.84561	-1.35225
C	0.12603	2.29362	-2.07320
H	-0.38970	1.58467	-2.72633
C	-0.30534	3.59733	-1.91148
H	-1.17501	3.96371	-2.46814
C	0.34414	4.47272	-0.99143
C	-0.13818	5.79747	-0.77161
H	-0.99834	6.14095	-1.35794
C	0.44841	6.62643	0.17128
H	0.06393	7.63892	0.33303
C	1.54042	6.14924	0.94392
H	1.98555	6.79204	1.71085
C	2.04586	4.87243	0.74316
H	2.87927	4.51740	1.35408
C	1.48783	4.00084	-0.24180

C	3.18513	2.11294	0.21443
C	3.09055	0.90774	0.92863
C	4.15092	0.44111	1.75448
H	3.97607	-0.46022	2.34921
C	5.34766	1.13202	1.81002
H	6.15987	0.78349	2.45802
C	5.55407	2.28950	1.00327
C	6.81242	2.96077	0.97840
H	7.61901	2.57964	1.61554
C	7.02126	4.05748	0.15720
H	7.99429	4.55928	0.14192
C	5.97087	4.51843	-0.68060
H	6.14342	5.36766	-1.35019
C	4.72912	3.89911	-0.66638
H	3.93365	4.25903	-1.32386
C	4.46909	2.78014	0.18335
C	3.42278	-1.69414	-1.72219
H	3.77267	-0.68522	-1.44802
C	3.17350	-1.68927	-3.24354
H	2.43899	-0.90987	-3.49387
H	2.79081	-2.65536	-3.61136
H	4.11451	-1.47547	-3.77894
C	4.51704	-2.67833	-1.29197
C	4.74957	-3.89561	-1.96785
H	4.14666	-4.16068	-2.84260
C	5.76246	-4.77418	-1.54851
H	5.92178	-5.71371	-2.08849
C	6.57145	-4.44700	-0.45012
H	7.36446	-5.12924	-0.12616
C	6.36268	-3.23182	0.22245
H	6.99906	-2.95719	1.07078
C	5.34643	-2.35990	-0.19595
H	5.20036	-1.40614	0.32310
C	1.54467	-3.25635	-0.88508
H	2.38090	-3.91872	-1.17822
C	0.41344	-3.46255	-1.91062
H	0.73553	-3.12460	-2.90664
H	-0.48790	-2.88670	-1.63762
C	-1.07143	-0.70129	2.19826
H	-0.56850	-1.57658	2.62343
H	-0.57468	0.25887	2.37140
C	-2.44171	-0.78953	1.86000
C	-3.17320	-2.09411	2.16628
H	-3.86086	-2.42361	1.37380
H	-2.44335	-2.90078	2.33696
H	-3.77322	-1.97444	3.08956
C	-3.24930	0.46877	1.66617
C	-4.35231	0.57065	0.76545
C	-2.90820	1.64014	2.38207
C	-5.01968	1.79291	0.57282
C	-3.58540	2.85429	2.20341

H	-2.08987	1.58595	3.10602
C	-4.64329	2.93912	1.28851
H	-5.84169	1.83156	-0.14712
H	-3.28091	3.73259	2.78219
H	-5.17441	3.88285	1.12995
C	-4.19032	-1.25291	-0.93076
O	-4.62587	-2.25486	-1.51564
N	-4.86668	-0.57979	0.05681
C	-6.18602	-1.12952	0.47043
H	-6.25224	-1.01157	1.56480
H	-6.15389	-2.20550	0.22895
C	-7.38821	-0.48596	-0.20352
C	-7.61423	-0.66820	-1.58504
C	-8.30421	0.27954	0.54358
C	-8.73074	-0.08612	-2.20221
H	-6.91053	-1.27528	-2.16450
C	-9.42583	0.85757	-0.07380
H	-8.13667	0.42333	1.61760
C	-9.63942	0.67797	-1.44913
H	-8.89687	-0.23524	-3.27452
H	-10.13056	1.44905	0.52050
H	-10.51256	1.12826	-1.93325
C	1.18236	-3.67424	0.54923
C	-0.01127	-4.35961	0.85226
C	2.10723	-3.45263	1.59301
C	-0.27373	-4.80773	2.15920
H	-0.75022	-4.54880	0.06903
C	1.84545	-3.89325	2.89761
H	3.04298	-2.93064	1.36896
C	0.65035	-4.57376	3.18860
H	-1.20571	-5.34463	2.36782
H	2.57958	-3.71042	3.69000
H	0.44531	-4.92218	4.20646
H	0.14096	-4.52931	-1.98539
C	-2.81527	-0.77495	-1.25824
N	-1.97777	-0.51331	-2.09523

TS1: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.473082 hartree
Gibbs correction= 0.701132 hartree
Total Gibbs Energy= -2943.77195 hartree

Pd	-1.32570	-0.66402	0.49805
P	0.91728	-0.59149	-0.21768
O	1.33515	0.47897	-1.45095
O	1.86049	0.09301	1.03428
N	1.65699	-1.96556	-0.86952
C	2.02602	2.55867	-0.43380
C	1.10337	1.83721	-1.19736
C	-0.04351	2.42409	-1.78996
H	-0.71533	1.79078	-2.37679
C	-0.28811	3.77094	-1.59386
H	-1.16439	4.24253	-2.05203

C	0.56599	4.55700	-0.76533
C	0.27728	5.92955	-0.50305
H	-0.59949	6.37698	-0.98535
C	1.06949	6.67739	0.35332
H	0.83252	7.72827	0.54968
C	2.18178	6.06848	0.99311
H	2.79085	6.64956	1.69373
C	2.50150	4.74076	0.74630
H	3.35395	4.28513	1.25585
C	1.72613	3.94701	-0.15380
C	3.23633	1.87526	0.10497
C	3.10071	0.68983	0.84292
C	4.19722	0.09895	1.52866
H	3.99920	-0.77958	2.14955
C	5.46206	0.64777	1.41822
H	6.30730	0.20626	1.95824
C	5.69192	1.77560	0.57639
C	7.00497	2.29710	0.37950
H	7.83868	1.82444	0.91172
C	7.22929	3.36347	-0.47673
H	8.24313	3.74942	-0.62488
C	6.13867	3.94410	-1.17754
H	6.31897	4.76859	-1.87535
C	4.84645	3.47284	-0.99391
H	4.01867	3.92356	-1.54718
C	4.57303	2.39009	-0.10268
C	2.82241	-1.88675	-1.83097
H	3.30433	-0.92028	-1.60904
C	2.36146	-1.83372	-3.30109
H	1.66263	-0.99613	-3.43920
H	1.85603	-2.75902	-3.62079
H	3.23275	-1.68159	-3.96117
C	3.86786	-2.97540	-1.56148
C	3.88896	-4.19666	-2.26903
H	3.14408	-4.39143	-3.04733
C	4.86500	-5.17089	-2.00115
H	4.85929	-6.11127	-2.56264
C	5.84574	-4.93908	-1.02512
H	6.60956	-5.69642	-0.81958
C	5.84496	-3.72345	-0.32160
H	6.61494	-3.52430	0.43175
C	4.86572	-2.75480	-0.58878
H	4.88023	-1.80269	-0.04707
C	0.99186	-3.29583	-0.65220
H	1.77061	-4.02445	-0.94341
C	-0.22406	-3.53214	-1.56564
H	0.04300	-3.34514	-2.61624
H	-1.07185	-2.87499	-1.31293
C	-0.98439	-0.00871	2.64330
H	-0.44863	-0.77660	3.21059
H	-0.44536	0.92364	2.44959

C	-2.36683	-0.11034	2.45973
C	-3.13797	-1.23685	3.13539
H	-3.96542	-1.62165	2.52048
H	-2.46616	-2.07472	3.37807
H	-3.57615	-0.85660	4.07764
C	-3.15622	1.06086	1.94516
C	-4.15777	0.91407	0.93859
C	-2.94720	2.34820	2.48752
C	-4.92153	2.02443	0.53029
C	-3.71110	3.44956	2.07944
H	-2.18664	2.46763	3.26588
C	-4.70810	3.28435	1.10532
H	-5.66906	1.89394	-0.25644
H	-3.53270	4.43185	2.52887
H	-5.31131	4.13739	0.77834
C	-3.39547	-1.21273	-0.09363
O	-3.53153	-2.43021	-0.24388
N	-4.40877	-0.36713	0.35907
C	-5.78703	-0.90902	0.36430
H	-6.26026	-0.63011	1.32198
H	-5.66939	-2.00782	0.35348
C	-6.66845	-0.47420	-0.80106
C	-6.13672	-0.21805	-2.08139
C	-8.06146	-0.38349	-0.60763
C	-6.98992	0.11829	-3.14470
H	-5.05429	-0.26027	-2.24735
C	-8.91296	-0.05543	-1.67380
H	-8.48278	-0.57178	0.38758
C	-8.37820	0.19670	-2.94744
H	-6.56259	0.32035	-4.13258
H	-9.99331	0.01251	-1.50607
H	-9.03955	0.45942	-3.77992
C	0.72692	-3.56401	0.83698
C	-0.55054	-3.89641	1.33154
C	1.81578	-3.55553	1.73708
C	-0.72908	-4.22000	2.68965
H	-1.41643	-3.90614	0.66352
C	1.63603	-3.86603	3.09140
H	2.81446	-3.30936	1.35893
C	0.35879	-4.20272	3.57475
H	-1.72697	-4.49422	3.04915
H	2.49570	-3.85903	3.77055
H	0.21740	-4.45772	4.63057
H	-0.56590	-4.57818	-1.48125
C	-2.33667	-0.42198	-1.25221
N	-2.49912	-0.02558	-2.36567

(*S*)-B: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.497906 hartree
Gibbs correction= 0.702051 hartree
Total Gibbs Energy= -2943.795855 hartree

Pd	-1.43215	-0.86706	0.33400

P	0.88252	-0.59435	-0.23755
O	1.23013	0.50467	-1.45217
O	1.73873	0.14950	1.03747
N	1.71345	-1.91336	-0.88109
C	1.73491	2.62687	-0.41164
C	0.88664	1.84228	-1.19813
C	-0.28615	2.34008	-1.81961
H	-0.88535	1.65701	-2.42865
C	-0.63929	3.66239	-1.62069
H	-1.53715	4.06863	-2.09914
C	0.12986	4.50594	-0.76558
C	-0.27231	5.84923	-0.50133
H	-1.17118	6.22970	-0.99996
C	0.43947	6.65050	0.37707
H	0.11552	7.67764	0.57464
C	1.58284	6.12709	1.03736
H	2.12894	6.74953	1.75414
C	2.01218	4.83080	0.78981
H	2.88747	4.44022	1.31460
C	1.32089	3.98533	-0.13121
C	2.98746	2.03714	0.14174
C	2.93687	0.83722	0.86544
C	4.06788	0.31664	1.55023
H	3.93224	-0.58491	2.15441
C	5.28847	0.96128	1.45905
H	6.16069	0.57551	1.99876
C	5.43851	2.11745	0.63799
C	6.70976	2.74081	0.46344
H	7.57189	2.32528	0.99796
C	6.86010	3.83403	-0.37477
H	7.84275	4.29868	-0.50593
C	5.73552	4.33991	-1.07985
H	5.85938	5.18584	-1.76408
C	4.48135	3.76877	-0.91762
H	3.62747	4.16309	-1.47411
C	4.28278	2.65553	-0.04440
C	2.82009	-1.74334	-1.90421
H	3.21108	-0.72819	-1.72798
C	2.27995	-1.77650	-3.34654
H	1.47320	-1.03770	-3.45859
H	1.87819	-2.76285	-3.62759
H	3.09030	-1.52955	-4.05386
C	3.98273	-2.71093	-1.65820
C	4.11127	-3.93361	-2.35134
H	3.36386	-4.22057	-3.09786
C	5.19746	-4.79094	-2.10878
H	5.27508	-5.73481	-2.65887
C	6.18092	-4.43821	-1.17249
H	7.03031	-5.10411	-0.98717
C	6.07174	-3.21960	-0.48260
H	6.84142	-2.92629	0.23960

C	4.98382	-2.36757	-0.72489
H	4.91305	-1.41208	-0.19329
C	1.21301	-3.30293	-0.59279
H	2.06860	-3.94281	-0.87718
C	0.01438	-3.72734	-1.45846
H	0.22489	-3.55179	-2.52322
H	-0.90167	-3.16858	-1.21040
C	-0.89840	-0.34183	2.47621
H	-0.29917	-1.13465	2.93622
H	-0.39008	0.60481	2.27125
C	-2.29188	-0.41634	2.50239
C	-2.96696	-1.54900	3.26482
H	-3.97180	-1.78696	2.88829
H	-2.35128	-2.46088	3.24643
H	-3.07623	-1.22415	4.31664
C	-3.13003	0.77219	2.14795
C	-4.20943	0.64765	1.22544
C	-2.89519	2.02312	2.75326
C	-5.04107	1.75507	0.96834
C	-3.72510	3.12276	2.49411
H	-2.06447	2.11460	3.46101
C	-4.80480	2.97966	1.60888
H	-5.85766	1.65946	0.24804
H	-3.53350	4.08080	2.98735
H	-5.46263	3.82938	1.39906
C	-3.41512	-1.51469	0.37706
O	-3.60666	-2.70751	0.16100
N	-4.44174	-0.59975	0.59122
C	-5.82941	-1.04097	0.31078
H	-6.46053	-0.76409	1.17406
H	-5.76987	-2.14351	0.26981
C	-6.44030	-0.50245	-0.97663
C	-5.68235	-0.37208	-2.15783
C	-7.81270	-0.18122	-1.00322
C	-6.29464	0.06969	-3.34099
H	-4.61080	-0.60056	-2.16051
C	-8.42422	0.25366	-2.18976
H	-8.40759	-0.27392	-0.08590
C	-7.66451	0.38064	-3.36350
H	-5.69096	0.16946	-4.24911
H	-9.49163	0.50006	-2.19331
H	-8.13681	0.72513	-4.28979
C	1.01946	-3.54140	0.91173
C	-0.19602	-4.00652	1.45325
C	2.12220	-3.37449	1.77906
C	-0.29935	-4.30578	2.82455
H	-1.07196	-4.13802	0.81176
C	2.01594	-3.65956	3.14702
H	3.07537	-3.02876	1.36297
C	0.80108	-4.13026	3.67688
H	-1.24636	-4.68828	3.22110

H	2.88586	-3.52967	3.80019
H	0.71844	-4.36686	4.74307
H	-0.18436	-4.80436	-1.32121
C	-1.85650	-0.77427	-1.62520
N	-2.08061	-0.63691	-2.77929

(*S*)-TS2: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.482465 hartree
Gibbs correction= 0.700632 hartree
Total Gibbs Energy= -2943.781833 hartree

Pd	-1.29140	-0.57169	-0.21646
P	0.96247	-0.57667	-0.41441
O	1.62162	0.45833	-1.54708
O	1.63317	0.09527	0.99358
N	1.75257	-1.98730	-0.89262
C	2.16617	2.52882	-0.42771
C	1.38412	1.82870	-1.35047
C	0.38955	2.43517	-2.15755
H	-0.17790	1.80713	-2.85113
C	0.15426	3.79102	-2.01888
H	-0.60356	4.28251	-2.63887
C	0.85863	4.56264	-1.04775
C	0.56741	5.94623	-0.85539
H	-0.18719	6.41233	-1.49940
C	1.20403	6.68209	0.13121
H	0.96586	7.74170	0.27094
C	2.15473	6.05052	0.97649
H	2.63629	6.62334	1.77611
C	2.47505	4.71113	0.80530
H	3.20038	4.23799	1.47171
C	1.86170	3.92864	-0.22056
C	3.22788	1.81300	0.33616
C	2.91623	0.63792	1.03514
C	3.84308	0.00009	1.90226
H	3.50205	-0.87440	2.46364
C	5.12585	0.50216	2.03035
H	5.84144	0.02737	2.71108
C	5.54689	1.62326	1.25597
C	6.89152	2.09686	1.31070
H	7.59382	1.59492	1.98632
C	7.30967	3.15323	0.51728
H	8.34648	3.50203	0.56324
C	6.39114	3.77190	-0.37234
H	6.72851	4.58777	-1.02015
C	5.07130	3.34842	-0.43580
H	4.37829	3.82783	-1.13168
C	4.59747	2.27841	0.38387
C	2.98917	-1.94753	-1.77133
H	3.44181	-0.96289	-1.57413
C	2.63078	-1.99382	-3.26837
H	1.92296	-1.18656	-3.50710
H	2.16873	-2.94916	-3.56429

H	3.54218	-1.85841	-3.87575
C	4.02394	-2.99713	-1.35181
C	4.14458	-4.24502	-1.99962
H	3.48405	-4.49357	-2.83645
C	5.11617	-5.17692	-1.59781
H	5.18990	-6.13911	-2.11576
C	5.99187	-4.87493	-0.54431
H	6.75276	-5.59902	-0.23452
C	5.89083	-3.63215	0.10272
H	6.57885	-3.37890	0.91663
C	4.91696	-2.70557	-0.29862
H	4.85176	-1.73423	0.20418
C	1.07753	-3.31702	-0.67981
H	1.87998	-4.04172	-0.90950
C	-0.08084	-3.58914	-1.65467
H	0.24359	-3.43258	-2.69363
H	-0.94006	-2.92097	-1.48046
C	-1.36430	-0.34936	1.87824
H	-1.01773	-1.22439	2.44147
H	-0.78509	0.56605	2.05260
C	-2.81128	-0.20632	1.68439
C	-3.68107	-1.13540	2.55958
H	-4.74952	-1.06510	2.30119
H	-3.35172	-2.17970	2.44635
H	-3.55321	-0.83023	3.61287
C	-3.35432	1.17812	1.48274
C	-4.21197	1.30995	0.36210
C	-3.07169	2.30306	2.26891
C	-4.81685	2.53794	0.05117
C	-3.67581	3.53669	1.96931
H	-2.39524	2.20889	3.12513
C	-4.54510	3.64551	0.87079
H	-5.48663	2.63453	-0.80667
H	-3.47272	4.40983	2.59693
H	-5.01690	4.60659	0.64196
C	-3.51101	-0.91755	0.00796
O	-3.68018	-2.11234	-0.22836
N	-4.35067	0.11707	-0.36969
C	-5.34142	-0.09061	-1.44485
H	-4.99102	-0.97875	-1.99491
H	-5.28035	0.76851	-2.13437
C	-6.76033	-0.28783	-0.93513
C	-7.78338	0.61709	-1.27269
C	-7.07145	-1.40412	-0.12974
C	-9.09505	0.41970	-0.81006
H	-7.55455	1.47899	-1.91119
C	-8.37925	-1.59915	0.33652
H	-6.28004	-2.12206	0.11376
C	-9.39432	-0.68693	-0.00107
H	-9.88137	1.13204	-1.08162
H	-8.61039	-2.47069	0.95842

H	-10.41581	-0.84196	0.36206
C	0.73166	-3.55794	0.79758
C	-0.57023	-3.88465	1.22578
C	1.76741	-3.53074	1.75739
C	-0.82751	-4.17549	2.57800
H	-1.39781	-3.90250	0.51114
C	1.51131	-3.81501	3.10572
H	2.78652	-3.29291	1.43196
C	0.20856	-4.13988	3.52311
H	-1.84532	-4.43681	2.88813
H	2.33141	-3.79560	3.83201
H	0.00653	-4.36986	4.57474
H	-0.42074	-4.63425	-1.55294
C	-1.60474	-0.41626	-2.23824
N	-1.78789	-0.22794	-3.39266

(*S*)-C: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.436668 hartree
Gibbs correction= 0.6991 hartree
Total Gibbs Energy= -2850.737568 hartree

Pd	1.30320	-0.39960	0.50973
P	-1.09420	-0.69863	0.65349
O	-2.20053	0.16287	1.58160
O	-1.62756	-0.32730	-0.88859
N	-1.53465	-2.28070	1.04636
C	-2.79505	2.08641	0.23096
C	-2.18082	1.55495	1.36817
C	-1.54455	2.35184	2.35336
H	-1.12583	1.85913	3.23542
C	-1.48420	3.72367	2.18047
H	-1.01624	4.35730	2.94178
C	-2.00527	4.33082	0.99885
C	-1.87820	5.73463	0.77651
H	-1.40294	6.34558	1.55220
C	-2.33261	6.31446	-0.39712
H	-2.22658	7.39191	-0.55751
C	-2.92524	5.50323	-1.40133
H	-3.25954	5.95894	-2.33882
C	-3.08378	4.13805	-1.20883
H	-3.53843	3.52794	-1.99296
C	-2.65199	3.50893	-0.00144
C	-3.54256	1.19256	-0.70049
C	-2.94430	0.04625	-1.23343
C	-3.56617	-0.76130	-2.22119
H	-3.01381	-1.61347	-2.62746
C	-4.84763	-0.45717	-2.64189
H	-5.33375	-1.06788	-3.41014
C	-5.56500	0.62994	-2.06286
C	-6.91626	0.89910	-2.43254
H	-7.38345	0.26928	-3.19770
C	-7.63021	1.92083	-1.82755
H	-8.66841	2.11440	-2.11449

C	-7.01519	2.70628	-0.81700
H	-7.58910	3.49380	-0.31818
C	-5.69629	2.48245	-0.44702
H	-5.24612	3.08990	0.34172
C	-4.92068	1.45586	-1.06631
C	-2.82302	-2.86389	0.54295
H	-3.23339	-2.08618	-0.12545
C	-3.87435	-3.03180	1.65661
H	-3.93945	-2.09806	2.23586
H	-3.65294	-3.86064	2.34530
H	-4.86436	-3.21769	1.20761
C	-2.57908	-4.08982	-0.34761
C	-3.36947	-5.25261	-0.25029
H	-4.15874	-5.31952	0.50446
C	-3.16069	-6.33728	-1.11933
H	-3.78550	-7.23144	-1.02584
C	-2.15930	-6.27719	-2.09952
H	-1.99635	-7.12359	-2.77415
C	-1.36779	-5.12159	-2.20939
H	-0.58452	-5.06207	-2.97230
C	-1.57781	-4.03913	-1.34269
H	-0.95801	-3.13995	-1.43857
C	-0.46556	-3.12948	1.67620
H	0.16888	-3.55842	0.87580
C	-1.01305	-4.30864	2.50353
H	-1.60480	-4.99496	1.88058
H	-1.62274	-3.96947	3.35514
C	0.91478	1.62915	-0.26481
H	0.10202	1.55109	-0.99384
H	0.69590	2.17666	0.65946
C	2.24439	1.45248	-0.68677
C	2.54704	1.17276	-2.14943
H	3.48692	0.62128	-2.30290
H	1.72265	0.62834	-2.63518
H	2.66393	2.14927	-2.65598
C	3.35513	1.95120	0.17884
C	4.43362	1.09948	0.52794
C	3.35520	3.27904	0.65278
C	5.48805	1.58482	1.32325
C	4.41517	3.76683	1.42924
H	2.52598	3.93868	0.37727
C	5.48209	2.91693	1.76055
H	6.30868	0.92562	1.61868
H	4.41086	4.80674	1.76875
H	6.31163	3.28534	2.37160
C	3.21240	-0.90435	-0.11843
O	3.08235	-1.99912	-0.67266
N	4.39520	-0.25874	0.09629
C	5.65755	-0.96614	-0.32676
H	5.40972	-2.03796	-0.30967
H	6.42075	-0.77900	0.44373

C	6.14333	-0.53913	-1.69604
C	7.12228	0.46596	-1.83445
C	5.61443	-1.14919	-2.85496
C	7.56381	0.85798	-3.10731
H	7.54705	0.93785	-0.94142
C	6.05574	-0.75490	-4.12713
H	4.86536	-1.94186	-2.75116
C	7.03010	0.24935	-4.25504
H	8.33030	1.63362	-3.20268
H	5.64781	-1.24086	-5.01928
H	7.37995	0.55049	-5.24764
C	0.40626	-2.24231	2.56400
C	-0.12411	-1.60628	3.70841
C	1.78938	-2.08184	2.26977
C	0.70103	-0.84410	4.54553
H	-1.18911	-1.70797	3.93798
C	2.61420	-1.29843	3.12252
H	2.24115	-2.70996	1.49229
C	2.06948	-0.67755	4.25137
H	0.27742	-0.37732	5.44092
H	3.68208	-1.20923	2.90276
H	2.70526	-0.08094	4.91231
H	-0.15368	-4.87177	2.90345

(*R*)-C: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.437877 hartree
Gibbs correction= 0.699152 hartree
Total Gibbs Energy= -2850.738725 hartree

Pd	-1.16080	-0.57699	-0.23584
P	1.19778	-0.64437	-0.41343
O	1.87713	0.32960	-1.58875
O	2.02189	-0.12103	0.94583
N	1.72425	-2.16656	-0.88543
C	2.38224	2.39671	-0.42611
C	1.61400	1.70197	-1.36243
C	0.57273	2.29665	-2.11706
H	0.03619	1.68905	-2.85091
C	0.27343	3.63298	-1.91399
H	-0.51357	4.11691	-2.50242
C	0.96340	4.39227	-0.92244
C	0.61284	5.75065	-0.66051
H	-0.17525	6.21270	-1.26558
C	1.24253	6.46844	0.34360
H	0.96255	7.50869	0.53690
C	2.24490	5.84577	1.13440
H	2.72281	6.40663	1.94394
C	2.62419	4.53259	0.89418
H	3.39408	4.06684	1.51409
C	2.01701	3.77029	-0.14963
C	3.50790	1.70355	0.26302
C	3.29660	0.48928	0.92422
C	4.30247	-0.16093	1.68415

H	4.05320	-1.08752	2.20795
C	5.57145	0.38588	1.74130
H	6.35359	-0.10241	2.33241
C	5.89000	1.56809	1.01196
C	7.21609	2.09405	1.00482
H	7.98251	1.58610	1.60066
C	7.53507	3.21087	0.24949
H	8.55710	3.60220	0.24674
C	6.53353	3.83757	-0.53862
H	6.79324	4.70236	-1.15755
C	5.22981	3.36179	-0.54058
H	4.47647	3.85062	-1.16301
C	4.85772	2.22904	0.24533
C	3.18931	-2.50498	-0.86401
H	3.67413	-1.58734	-0.48027
C	3.75692	-2.70595	-2.28122
H	3.43721	-1.86894	-2.92055
H	3.43407	-3.64986	-2.74578
H	4.85914	-2.69980	-2.24966
C	3.51489	-3.60926	0.15202
C	4.43764	-4.63509	-0.13675
H	4.91409	-4.68539	-1.12010
C	4.76170	-5.60398	0.82834
H	5.48098	-6.39142	0.58104
C	4.16870	-5.56567	2.09872
H	4.42024	-6.32230	2.84852
C	3.24994	-4.54685	2.40075
H	2.78244	-4.50440	3.39017
C	2.92899	-3.57899	1.43734
H	2.21812	-2.78293	1.68666
C	0.64781	-3.20483	-0.91590
H	0.42163	-3.53517	0.11801
C	1.04541	-4.46139	-1.72071
H	1.93536	-4.94775	-1.29550
H	1.22683	-4.21839	-2.77943
C	-0.87067	0.50355	1.66195
H	-0.46751	-0.29922	2.28952
H	-0.20231	1.35021	1.47369
C	-2.26139	0.66978	1.53569
C	-3.16182	-0.25414	-0.70158
O	-3.15186	0.25783	-1.82053
N	-4.27839	-0.60901	0.00412
C	-5.60882	-0.46181	-0.68327
H	-6.22716	-1.32927	-0.40552
H	-5.38825	-0.52859	-1.75900
C	-6.31058	0.83858	-0.35040
C	-6.01354	2.00875	-1.08335
C	-7.26224	0.90184	0.68803
C	-6.65533	3.21849	-0.77774
H	-5.28482	1.95996	-1.89990
C	-7.90388	2.11209	0.99201

H	-7.50812	-0.00239	1.25598
C	-7.60050	3.27205	0.26047
H	-6.42659	4.11785	-1.35863
H	-8.64675	2.14772	1.79521
H	-8.10693	4.21430	0.49293
C	-0.65063	-2.66688	-1.54594
C	-0.63538	-2.09837	-2.85763
C	-1.89506	-3.15523	-1.04346
C	-1.79196	-2.08110	-3.64096
H	0.31154	-1.72554	-3.26165
C	-3.04562	-3.16376	-1.85726
H	-1.91693	-3.63164	-0.05649
C	-2.99010	-2.64413	-3.15588
H	-1.75812	-1.65467	-4.64807
H	-3.97524	-3.59184	-1.47009
H	-3.87830	-2.66663	-3.79494
H	0.21140	-5.18042	-1.67460
C	-3.17890	-0.32713	2.16217
C	-3.05053	-0.68014	3.52089
C	-4.20447	-0.92896	1.38854
C	-3.94145	-1.58438	4.11534
H	-2.26338	-0.20985	4.11932
C	-5.08732	-1.84943	1.98317
C	-4.96104	-2.16432	3.34370
H	-3.84428	-1.82954	5.17697
H	-5.86437	-2.33619	1.38765
H	-5.65796	-2.87564	3.79714
C	-2.82658	2.02358	1.14298
H	-2.96562	2.60384	2.07474
H	-2.13245	2.57708	0.49207
H	-3.81174	1.96046	0.65734

(*S*)-TS3: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.429181 hartree
Gibbs correction= 0.701458 hartree
Total Gibbs Energy= -2850.727723 hartree

Pd	-1.18901	-0.08417	-0.24938
P	0.85259	0.76601	0.38453
O	1.76510	0.10527	1.62094
O	1.89249	0.58901	-0.90837
N	0.77202	2.38543	0.84109
C	3.10027	-1.61059	0.54980
C	2.07146	-1.25867	1.42653
C	1.30872	-2.20417	2.15647
H	0.54260	-1.84052	2.84679
C	1.56208	-3.55375	1.98358
H	0.99767	-4.29940	2.55393
C	2.54048	-3.99580	1.04352
C	2.75663	-5.38657	0.80686
H	2.18105	-6.11171	1.39316
C	3.66436	-5.81458	-0.14855
H	3.81962	-6.88395	-0.32251

C	4.38543	-4.85993	-0.91449
H	5.08244	-5.19975	-1.68714
C	4.21505	-3.50012	-0.69603
H	4.77447	-2.77896	-1.29664
C	3.30902	-3.02141	0.29885
C	3.91329	-0.54677	-0.10639
C	3.29840	0.49116	-0.81330
C	4.02474	1.45422	-1.56066
H	3.47026	2.20413	-2.13231
C	5.40710	1.42190	-1.55022
H	5.97859	2.15347	-2.13132
C	6.10701	0.46152	-0.76312
C	7.53123	0.47389	-0.68252
H	8.08070	1.22102	-1.26585
C	8.20654	-0.42481	0.12741
H	9.29908	-0.40205	0.18656
C	7.47391	-1.36616	0.89789
H	8.00649	-2.05620	1.56015
C	6.08863	-1.41699	0.82829
H	5.54296	-2.14062	1.43860
C	5.35972	-0.52414	-0.01452
C	1.96791	3.28143	0.69682
H	2.73747	2.63943	0.23197
C	2.55874	3.69745	2.05716
H	2.67553	2.80406	2.68978
H	1.94077	4.43220	2.59438
H	3.55945	4.13680	1.90972
C	1.71090	4.41627	-0.30411
C	2.12217	5.74072	-0.05283
H	2.60439	5.99653	0.89535
C	1.92478	6.74809	-1.01281
H	2.25116	7.77055	-0.79673
C	1.31409	6.44810	-2.23928
H	1.15948	7.23396	-2.98531
C	0.90398	5.13052	-2.50344
H	0.42900	4.88352	-3.45867
C	1.10228	4.12565	-1.54532
H	0.78361	3.09954	-1.76270
C	-0.61603	2.91894	1.06604
H	-1.06841	3.16980	0.08649
C	-0.65636	4.19392	1.92993
H	-0.09642	5.01593	1.46051
H	-0.26734	4.01722	2.94462
C	-0.33687	-1.64974	-1.32430
H	0.43555	-1.26822	-2.00292
H	0.03068	-2.32159	-0.53560
C	-1.65477	-1.91383	-1.87584
C	-1.78411	-1.77375	-3.40106
H	-2.82585	-1.86109	-3.74438
H	-1.37057	-0.81320	-3.74523
H	-1.20498	-2.59434	-3.86076

C	-2.50193	-2.95728	-1.22333
C	-3.83412	-2.56651	-0.95233
C	-2.07890	-4.25103	-0.87797
C	-4.75046	-3.46039	-0.37726
C	-2.99353	-5.15627	-0.31558
H	-1.04783	-4.55858	-1.08020
C	-4.32109	-4.76217	-0.07468
H	-5.77539	-3.15219	-0.15566
H	-2.67326	-6.17419	-0.07480
H	-5.03010	-5.47095	0.36364
C	-3.03298	-0.41069	-1.54636
O	-3.06060	0.67059	-2.13004
N	-4.11284	-1.21810	-1.28511
C	-5.46997	-0.74668	-1.70846
H	-6.06493	-1.65234	-1.90382
H	-5.31582	-0.21790	-2.66509
C	-6.16918	0.16784	-0.71853
C	-5.98751	1.56513	-0.79854
C	-7.02702	-0.35380	0.27182
C	-6.63828	2.41942	0.10521
H	-5.33950	1.97659	-1.57972
C	-7.67700	0.50040	1.17636
H	-7.20739	-1.43376	0.32610
C	-7.48030	1.88882	1.09638
H	-6.49751	3.50232	0.02705
H	-8.34675	0.08254	1.93470
H	-7.99275	2.55604	1.79662
C	-1.45966	1.82833	1.72928
C	-1.10625	1.32923	3.00832
C	-2.66113	1.36794	1.12301
C	-1.92675	0.40776	3.66485
H	-0.17951	1.67050	3.47952
C	-3.48381	0.42826	1.79971
H	-3.02691	1.85180	0.20881
C	-3.11459	-0.05296	3.05931
H	-1.64701	0.04743	4.66035
H	-4.42360	0.11274	1.33781
H	-3.75518	-0.76950	3.58241
H	-1.70869	4.51009	2.02055

(*R*)-TS3: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.432721 hartree
Gibbs correction= 0.701203 hartree
Total Gibbs Energy= -2850.731518 hartree

Pd	-1.04450	-0.39831	-0.33867
P	1.21020	-0.63205	-0.46226
O	2.00515	0.27306	-1.61528
O	1.99193	-0.14398	0.93096
N	1.64059	-2.18383	-0.92499
C	2.61842	2.31507	-0.45760
C	1.84837	1.66700	-1.42491
C	0.90870	2.33014	-2.25179

H	0.36836	1.75455	-3.00819
C	0.71073	3.69021	-2.08883
H	0.00311	4.22502	-2.73138
C	1.40038	4.40951	-1.06789
C	1.14768	5.79663	-0.84718
H	0.43668	6.30914	-1.50478
C	1.77436	6.48020	0.18232
H	1.56962	7.54317	0.34364
C	2.67460	5.79381	1.04050
H	3.14864	6.32968	1.86903
C	2.95824	4.44985	0.84260
H	3.64952	3.93521	1.51432
C	2.35204	3.71914	-0.22416
C	3.64792	1.55012	0.30142
C	3.31068	0.36715	0.96719
C	4.22271	-0.34227	1.78954
H	3.87762	-1.23630	2.31442
C	5.52492	0.10802	1.90675
H	6.23506	-0.42659	2.54658
C	5.97077	1.24852	1.17793
C	7.33193	1.67200	1.23400
H	8.02478	1.11880	1.87767
C	7.77480	2.74654	0.47990
H	8.82258	3.05914	0.52597
C	6.86695	3.43185	-0.37047
H	7.22431	4.26210	-0.98799
C	5.53237	3.05662	-0.43493
H	4.85273	3.58928	-1.10437
C	5.03362	1.97100	0.34738
C	3.10763	-2.54504	-0.96129
H	3.61839	-1.65807	-0.54066
C	3.63072	-2.67624	-2.40289
H	3.31905	-1.79375	-2.98154
H	3.26703	-3.57991	-2.91458
H	4.73314	-2.70299	-2.40005
C	3.44065	-3.70539	-0.01424
C	4.30931	-4.74802	-0.39493
H	4.73454	-4.76906	-1.40257
C	4.64690	-5.76937	0.50961
H	5.32479	-6.56817	0.19198
C	4.11994	-5.76831	1.80924
H	4.38190	-6.56568	2.51176
C	3.25394	-4.73431	2.20236
H	2.83769	-4.72130	3.21518
C	2.92116	-3.71343	1.29983
H	2.25068	-2.90688	1.61903
C	0.58271	-3.23995	-0.89665
H	0.53244	-3.67494	0.12089
C	0.89582	-4.39365	-1.87784
H	1.83939	-4.89565	-1.61879
H	0.94283	-4.02842	-2.91626

C	-0.93627	0.91079	1.28441
H	-0.48699	0.28706	2.06838
H	-0.35217	1.80205	1.02232
C	-2.38410	1.00884	1.23683
C	-3.19413	0.28751	-0.50845
O	-3.14124	0.86153	-1.59387
N	-4.27837	-0.34715	0.04550
C	-5.54091	-0.46334	-0.74403
H	-5.95596	-1.46909	-0.56636
H	-5.22680	-0.40374	-1.79685
C	-6.55213	0.61841	-0.41369
C	-6.36216	1.93010	-0.90160
C	-7.68993	0.33408	0.36577
C	-7.28998	2.93813	-0.60090
H	-5.49204	2.14927	-1.53053
C	-8.62084	1.34237	0.66160
H	-7.85779	-0.68443	0.73414
C	-8.41985	2.64623	0.18224
H	-7.13885	3.95030	-0.98981
H	-9.50473	1.10760	1.26307
H	-9.14697	3.43207	0.41014
C	-0.82461	-2.73640	-1.26172
C	-1.07110	-1.91658	-2.40536
C	-1.92730	-3.42833	-0.68707
C	-2.36061	-1.86382	-2.98462
H	-0.22940	-1.44455	-2.92383
C	-3.19289	-3.38465	-1.28245
H	-1.75665	-4.05995	0.19193
C	-3.40794	-2.62060	-2.44650
H	-2.52113	-1.25026	-3.87563
H	-4.01234	-3.96615	-0.84788
H	-4.38970	-2.61921	-2.92990
H	0.08844	-5.14058	-1.81182
C	-3.18228	0.08724	2.10177
C	-2.96691	-0.14096	3.47007
C	-4.22291	-0.60159	1.43682
C	-3.81445	-1.01317	4.17282
H	-2.16079	0.38659	3.99054
C	-5.06810	-1.48270	2.12877
C	-4.85962	-1.67336	3.50395
H	-3.66649	-1.16890	5.24545
H	-5.87097	-2.01723	1.61504
H	-5.51889	-2.34996	4.05610
C	-2.96260	2.41284	1.00435
H	-2.78941	2.99772	1.92546
H	-2.45152	2.91248	0.16703
H	-4.04615	2.39491	0.81085

(*S*)-D: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.477573 hartree
Gibbs correction= 0.702113 hartree
Total Gibbs Energy= -2850.77546 hartree

Pd	0.81834	-1.13392	0.51218
P	-1.40268	-0.88342	0.44074
O	-2.15031	-0.01719	1.65101
O	-1.88356	-0.04091	-0.91095
N	-2.19648	-2.35956	0.55109
C	-2.26515	2.25890	0.82106
C	-1.74805	1.33570	1.73168
C	-0.84383	1.67835	2.76672
H	-0.51650	0.89831	3.45953
C	-0.41186	2.98843	2.87705
H	0.27203	3.27875	3.68190
C	-0.82710	3.97374	1.93233
C	-0.32933	5.30943	1.99747
H	0.35470	5.57276	2.81189
C	-0.68858	6.25112	1.04673
H	-0.29762	7.27165	1.10585
C	-1.55570	5.88469	-0.01694
H	-1.81767	6.62297	-0.78163
C	-2.07359	4.59984	-0.09972
H	-2.73586	4.33328	-0.92689
C	-1.74808	3.61036	0.87713
C	-3.29089	1.82938	-0.17209
C	-3.07081	0.72469	-1.00025
C	-3.95769	0.34675	-2.04086
H	-3.69340	-0.50249	-2.67696
C	-5.13173	1.05428	-2.22283
H	-5.81983	0.77879	-3.02910
C	-5.47926	2.12561	-1.34943
C	-6.72620	2.80613	-1.48055
H	-7.40038	2.50907	-2.29147
C	-7.08753	3.80741	-0.59374
H	-8.04942	4.31847	-0.69982
C	-6.21218	4.15645	0.46855
H	-6.51152	4.92648	1.18673
C	-4.98365	3.52708	0.61314
H	-4.33002	3.80217	1.44425
C	-4.56529	2.50937	-0.29693
C	-3.64081	-2.46534	0.14540
H	-3.90070	-1.45373	-0.21684
C	-4.56513	-2.71416	1.35165
H	-4.31810	-1.99811	2.15036
H	-4.48682	-3.73472	1.75511
H	-5.61445	-2.54155	1.05984
C	-3.83116	-3.40172	-1.05569
C	-4.89375	-4.32564	-1.11799
H	-5.58885	-4.42193	-0.27876
C	-5.07956	-5.13127	-2.25450
H	-5.91134	-5.84258	-2.28105
C	-4.20673	-5.02736	-3.34740
H	-4.35144	-5.65689	-4.23098
C	-3.14580	-4.10767	-3.29929

H	-2.45971	-4.01556	-4.14780
C	-2.96211	-3.30294	-2.16518
H	-2.13545	-2.58342	-2.14010
C	-1.31250	-3.56052	0.71026
H	-0.90707	-3.84562	-0.28075
C	-2.04898	-4.79115	1.27608
H	-2.86950	-5.10954	0.61667
H	-2.44099	-4.60242	2.28763
C	1.11374	0.74117	-0.35049
H	0.27097	1.04534	-0.98573
H	1.21097	1.41325	0.51859
C	2.43042	0.58621	-1.14277
C	2.21129	-0.25057	-2.43511
H	3.15845	-0.40781	-2.97563
H	1.76462	-1.22873	-2.18617
H	1.51716	0.28762	-3.10085
C	3.22575	1.85062	-1.45055
C	4.51688	1.70641	-0.89209
C	2.91798	2.99220	-2.19223
C	5.51658	2.66729	-1.05192
C	3.90791	3.98344	-2.35385
H	1.92500	3.12344	-2.63452
C	5.18582	3.81859	-1.79470
H	6.51828	2.52941	-0.63691
H	3.67865	4.88838	-2.92433
H	5.94492	4.59312	-1.94030
C	3.38031	-0.14496	-0.20809
O	3.03155	-1.15402	0.47720
N	4.58453	0.47871	-0.15812
C	5.70414	0.05670	0.69798
H	5.31617	-0.79295	1.28628
H	5.92734	0.87868	1.40179
C	6.95635	-0.32885	-0.07608
C	8.20267	0.21090	0.29401
C	6.89645	-1.25496	-1.13605
C	9.37326	-0.16906	-0.38249
H	8.25952	0.92814	1.12186
C	8.06376	-1.62930	-1.81680
H	5.93229	-1.68459	-1.43169
C	9.30497	-1.08781	-1.44083
H	10.33638	0.25712	-0.08427
H	8.00619	-2.34808	-2.64055
H	10.21544	-1.38220	-1.97220
C	-0.13588	-3.23056	1.63550
C	-0.36521	-2.82472	2.98306
C	1.19064	-3.56318	1.24692
C	0.68501	-2.78279	3.90122
H	-1.38173	-2.56454	3.29505
C	2.24554	-3.52956	2.19054
H	1.37375	-3.95191	0.23818
C	1.99309	-3.14555	3.50937

H	0.48916	-2.48442	4.93612
H	3.25484	-3.80758	1.87583
H	2.80626	-3.12977	4.24167
H	-1.32647	-5.62111	1.34136

(*R*)-D: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2851.478342 hartree
Gibbs correction= 0.703581 hartree
Total Gibbs Energy= -2850.774761 hartree

Pd	-1.02883	-0.68178	-1.03751
P	1.13475	-0.84456	-0.59325
O	2.24618	-0.09800	-1.58447
O	1.51591	-0.19105	0.88765
N	1.62722	-2.43954	-0.75857
C	2.71157	2.03936	-0.52980
C	2.19012	1.31334	-1.60269
C	1.63285	1.91624	-2.75671
H	1.29583	1.27503	-3.57579
C	1.55296	3.29595	-2.82606
H	1.14794	3.78169	-3.72031
C	1.96824	4.10438	-1.72626
C	1.81273	5.52283	-1.75561
H	1.39708	5.98451	-2.65822
C	2.16595	6.30092	-0.66477
H	2.03894	7.38748	-0.69809
C	2.68160	5.68310	0.50589
H	2.93586	6.29710	1.37576
C	2.86525	4.30856	0.56075
H	3.25884	3.84827	1.47024
C	2.53648	3.47705	-0.55266
C	3.41137	1.33315	0.58050
C	2.80389	0.26748	1.25163
C	3.37701	-0.35760	2.38823
H	2.82073	-1.15106	2.89267
C	4.62271	0.04721	2.83081
H	5.07076	-0.42142	3.71341
C	5.35369	1.05121	2.13190
C	6.67310	1.41441	2.53484
H	7.10249	0.92631	3.41673
C	7.40424	2.34869	1.81935
H	8.41805	2.61522	2.13365
C	6.84004	2.94692	0.66164
H	7.42951	3.66220	0.07918
C	5.55200	2.62976	0.25342
H	5.14203	3.09254	-0.64727
C	4.75819	1.69153	0.98060
C	3.04293	-2.79098	-0.35855
H	3.43370	-1.86991	0.11337
C	3.94159	-3.03940	-1.58325
H	3.81794	-2.21015	-2.29567
H	3.71779	-3.98461	-2.09990
H	4.99936	-3.05984	-1.27209

C	3.07978	-3.86620	0.73507
C	3.99664	-4.93574	0.69328
H	4.67977	-5.04133	-0.15452
C	4.05340	-5.87555	1.73676
H	4.77487	-6.69720	1.68338
C	3.19249	-5.76476	2.83823
H	3.23603	-6.49890	3.64884
C	2.27397	-4.70312	2.89295
H	1.59746	-4.60517	3.74848
C	2.22155	-3.76359	1.85288
H	1.50457	-2.93589	1.90768
C	0.59501	-3.51023	-0.93360
H	0.28775	-3.87516	0.06572
C	1.14591	-4.72099	-1.72064
H	1.98208	-5.20042	-1.19111
H	1.46866	-4.42419	-2.73146
C	-1.22467	1.03655	0.13951
H	-1.39642	0.63055	1.15041
H	-0.32406	1.66679	0.13543
C	-2.46122	1.75781	-0.43983
C	-3.49316	0.67173	-0.69116
O	-3.20985	-0.43657	-1.24079
N	-4.70333	1.03180	-0.19395
C	-5.92089	0.21148	-0.29596
H	-5.67035	-0.59050	-1.01146
H	-6.71500	0.83084	-0.74924
C	-6.39185	-0.36547	1.03122
C	-7.73419	-0.21506	1.42680
C	-5.50903	-1.08974	1.85675
C	-8.19058	-0.77976	2.62894
H	-8.42971	0.34205	0.78742
C	-5.96216	-1.64684	3.06109
H	-4.46343	-1.21833	1.55403
C	-7.30417	-1.49372	3.44955
H	-9.23714	-0.65630	2.92501
H	-5.26794	-2.20492	3.69782
H	-7.65667	-1.93027	4.38936
C	-0.66939	-3.03858	-1.66630
C	-0.61150	-2.31222	-2.89505
C	-1.90946	-3.63587	-1.30201
C	-1.75294	-2.21744	-3.72728
H	0.35253	-1.93697	-3.25522
C	-3.02685	-3.54099	-2.13597
H	-1.96731	-4.20886	-0.36973
C	-2.94981	-2.83761	-3.35583
H	-1.68110	-1.67470	-4.67486
H	-3.96452	-4.02146	-1.84011
H	-3.82475	-2.77765	-4.00999
H	0.34108	-5.46704	-1.82181
C	-3.23486	2.70608	0.46922
C	-2.86809	3.88556	1.11920

C	-4.57427	2.25688	0.53714
C	-3.84901	4.59517	1.84220
H	-1.83775	4.25337	1.07451
C	-5.56304	2.94822	1.23903
C	-5.17407	4.13257	1.89652
H	-3.57456	5.51542	2.36643
H	-6.59146	2.58295	1.29567
H	-5.92253	4.69707	2.46081
C	-2.12043	2.45414	-1.78825
H	-1.35778	3.22953	-1.61227
H	-1.70738	1.72130	-2.50214
H	-3.01167	2.93038	-2.22779

(*S*)-E[1]: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.513598 hartree
Gibbs correction= 0.700168 hartree
Total Gibbs Energy= -2943.81343 hartree

Pd	-0.88287	-1.59131	0.82464
P	1.03281	-0.19242	1.10605
O	2.61183	-0.73663	1.32963
O	1.19960	0.51086	-0.43444
N	1.04003	1.04056	2.27749
C	3.52080	-1.19471	-0.86842
C	3.08368	-1.65680	0.37602
C	3.13652	-3.02018	0.75723
H	2.75745	-3.31193	1.73866
C	3.60871	-3.95629	-0.14319
H	3.64793	-5.01390	0.13833
C	3.99172	-3.57411	-1.46199
C	4.40366	-4.54722	-2.42092
H	4.45415	-5.59616	-2.10698
C	4.71159	-4.18455	-3.72240
H	5.01950	-4.94318	-4.44960
C	4.60507	-2.82431	-4.11678
H	4.81799	-2.54047	-5.15297
C	4.22438	-1.85011	-3.20461
H	4.13536	-0.81027	-3.52834
C	3.92745	-2.18208	-1.84708
C	3.52458	0.26400	-1.16789
C	2.37131	1.03933	-0.97963
C	2.28897	2.38660	-1.43027
H	1.34041	2.91519	-1.31073
C	3.39251	3.00193	-1.98862
H	3.32783	4.03804	-2.33918
C	4.63760	2.31422	-2.08086
C	5.80980	2.96545	-2.56723
H	5.72725	4.00737	-2.89802
C	7.02902	2.30757	-2.60523
H	7.92314	2.82084	-2.97413
C	7.11806	0.96694	-2.14488
H	8.08615	0.45497	-2.14713
C	5.99221	0.29917	-1.68389

H	6.07976	-0.72885	-1.32398
C	4.71370	0.93655	-1.65157
C	2.04548	2.14239	2.15415
H	2.60245	1.90703	1.22862
C	3.11180	2.10514	3.26882
H	3.46218	1.06871	3.38639
H	2.73895	2.46794	4.23857
H	3.98169	2.72119	2.98334
C	1.39631	3.51246	1.90333
C	1.95532	4.70148	2.41589
H	2.84691	4.65789	3.04839
C	1.38179	5.95199	2.13030
H	1.83508	6.86006	2.54247
C	0.23519	6.03914	1.32714
H	-0.21447	7.01334	1.10831
C	-0.33101	4.86292	0.80834
H	-1.22600	4.91609	0.17870
C	0.24437	3.61497	1.09152
H	-0.20266	2.70480	0.67745
C	-0.15455	1.15768	3.18600
H	-0.99934	1.59095	2.61436
C	0.09375	2.08298	4.39844
H	0.38382	3.10300	4.10621
H	0.85558	1.65894	5.07160
C	-2.58267	-2.72412	0.36610
H	-2.37070	-3.78067	0.14875
H	-3.23069	-2.65042	1.25598
C	-3.17776	-1.99082	-0.86121
C	-2.31434	-2.26416	-2.12878
H	-2.69050	-1.70970	-3.00482
H	-1.26516	-1.98599	-1.93271
H	-2.34737	-3.34214	-2.35671
C	-4.65712	-2.17483	-1.17973
C	-5.27946	-0.90462	-1.19169
C	-5.41142	-3.30950	-1.48122
C	-6.63100	-0.73061	-1.49913
C	-6.78144	-3.16042	-1.78269
H	-4.94892	-4.30220	-1.47320
C	-7.37797	-1.88898	-1.79432
H	-7.09101	0.26115	-1.52565
H	-7.38475	-4.04464	-2.01126
H	-8.44041	-1.78968	-2.03882
C	-3.12722	-0.50255	-0.53497
O	-2.13793	0.07826	-0.01275
N	-4.32757	0.09084	-0.82166
C	-4.62620	1.49965	-0.55327
H	-3.74505	1.88270	-0.00845
H	-5.49454	1.55205	0.12893
C	-4.89270	2.32382	-1.80560
C	-6.02882	3.15115	-1.87942
C	-3.99057	2.30141	-2.88780

C	-6.26239	3.94561	-3.01392
H	-6.73464	3.17662	-1.04009
C	-4.22549	3.08962	-4.02344
H	-3.10156	1.66265	-2.83942
C	-5.36175	3.91434	-4.08940
H	-7.15140	4.58346	-3.05804
H	-3.51819	3.06212	-4.85896
H	-5.54364	4.52900	-4.97707
C	-0.60540	-0.19401	3.74259
C	0.30670	-1.07262	4.36219
C	-1.98021	-0.50159	3.78438
C	-0.14554	-2.24162	4.98909
H	1.37822	-0.84771	4.32928
C	-2.43587	-1.66183	4.43116
H	-2.69608	0.18056	3.31026
C	-1.51821	-2.53747	5.03036
H	0.57593	-2.92924	5.44125
H	-3.50773	-1.88681	4.45454
H	-1.86779	-3.45355	5.51708
H	-0.84972	2.14561	4.96522
C	-0.11699	-3.23628	1.50016
N	0.33054	-4.24008	1.94028

(*S*)-E^{2}: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.505258 hartree
Gibbs correction= 0.700798 hartree
Total Gibbs Energy= -2943.80446 hartree

Pd	-0.67947	-0.90936	1.57370
P	1.02683	0.55177	0.92342
O	2.60895	0.30987	1.47334
O	1.32658	0.53143	-0.73622
N	0.77832	2.15224	1.40075
C	3.62709	-1.14955	-0.15924
C	3.10308	-0.95643	1.12183
C	3.04474	-1.98195	2.09899
H	2.62380	-1.74464	3.07985
C	3.51120	-3.24498	1.78354
H	3.47978	-4.04773	2.52826
C	3.99798	-3.53557	0.47446
C	4.41241	-4.85429	0.12073
H	4.38197	-5.63342	0.89094
C	4.82330	-5.15324	-1.16843
H	5.13143	-6.17134	-1.42770
C	4.82330	-4.13711	-2.16079
H	5.11975	-4.37994	-3.18663
C	4.44306	-2.83993	-1.84680
H	4.43822	-2.07187	-2.62410
C	4.04074	-2.48792	-0.52224
C	3.69398	0.00566	-1.09902
C	2.55636	0.78363	-1.35248
C	2.54403	1.82072	-2.32519
H	1.60534	2.35473	-2.49994

C	3.69979	2.13369	-3.01474
H	3.69339	2.92654	-3.77081
C	4.92116	1.45574	-2.73038
C	6.13826	1.82470	-3.37636
H	6.10843	2.62437	-4.12544
C	7.33444	1.20285	-3.05561
H	8.26294	1.49952	-3.55418
C	7.35444	0.18937	-2.06099
H	8.30341	-0.28273	-1.78577
C	6.18486	-0.20494	-1.42641
H	6.22047	-0.97861	-0.65558
C	4.92874	0.39436	-1.74921
C	1.50903	3.27924	0.75494
H	2.14680	2.79062	-0.00413
C	2.49891	3.97487	1.71257
H	3.07918	3.20661	2.24658
H	2.00234	4.62427	2.44966
H	3.21127	4.59276	1.13993
C	0.57627	4.21489	-0.03028
C	0.81334	5.60348	-0.10346
H	1.64741	6.04836	0.44765
C	-0.01261	6.43542	-0.87796
H	0.18960	7.51134	-0.91757
C	-1.09173	5.89340	-1.59187
H	-1.73908	6.54232	-2.19125
C	-1.33688	4.51207	-1.52482
H	-2.18090	4.07420	-2.06801
C	-0.51151	3.67808	-0.75488
H	-0.73334	2.60623	-0.70661
C	-0.41928	2.32672	2.29594
H	-1.33550	2.19539	1.68833
C	-0.49663	3.70739	2.97512
H	-0.50908	4.52671	2.24089
H	0.33176	3.86178	3.68442
C	-0.62060	-1.95622	-0.23484
H	0.36662	-1.72654	-0.65943
H	-0.68269	-3.01787	0.03748
C	-1.76048	-1.55928	-1.21845
C	-1.14556	-1.14388	-2.58451
H	-1.93219	-0.89759	-3.31803
H	-0.49677	-0.26527	-2.44164
H	-0.54219	-1.97133	-2.99375
C	-2.80143	-2.65616	-1.38430
C	-4.07537	-2.15075	-1.05335
C	-2.67050	-3.98273	-1.79576
C	-5.23100	-2.93432	-1.12602
C	-3.82152	-4.79409	-1.87341
H	-1.68607	-4.39228	-2.04919
C	-5.08190	-4.27191	-1.54135
H	-6.21456	-2.52742	-0.87670
H	-3.73040	-5.83762	-2.19118

H	-5.96816	-4.91193	-1.60362
C	-2.63593	-0.36653	-0.72379
O	-2.26894	0.78936	-0.46420
N	-3.95507	-0.79449	-0.67437
C	-5.03239	0.03325	-0.13993
H	-4.52676	0.93219	0.25719
H	-5.49931	-0.50061	0.70817
C	-6.08817	0.42768	-1.16409
C	-7.45646	0.30123	-0.85915
C	-5.71529	0.96300	-2.41310
C	-8.43653	0.70296	-1.78169
H	-7.75601	-0.11535	0.11032
C	-6.69184	1.35948	-3.33792
H	-4.65204	1.06593	-2.65671
C	-8.05609	1.23142	-3.02473
H	-9.49717	0.59551	-1.53038
H	-6.38824	1.77141	-4.30645
H	-8.81804	1.54038	-3.74811
C	-0.39769	1.23923	3.37639
C	0.71892	1.10274	4.24017
C	-1.53828	0.42906	3.60790
C	0.68523	0.20446	5.31032
H	1.61265	1.70764	4.05683
C	-1.55851	-0.48814	4.68816
H	-2.44338	0.58268	3.00945
C	-0.45408	-0.59633	5.53649
H	1.55242	0.12082	5.97448
H	-2.43681	-1.12422	4.82528
H	-0.46982	-1.30659	6.36931
H	-1.43822	3.74858	3.54739
C	-2.14737	-2.17514	2.07694
N	-3.03836	-2.85691	2.45276

(*S*)-E[3]: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.509149 hartree
Gibbs correction= 0.702216 hartree
Total Gibbs Energy= -2943.806933 hartree

Pd	-0.88392	-1.41905	0.62509
P	0.86544	0.19739	0.79489
O	2.32020	0.04718	1.63277
O	1.47008	0.26625	-0.79254
N	0.45335	1.77125	1.28882
C	3.87023	-1.08657	0.15730
C	3.08890	-1.08781	1.31596
C	3.06027	-2.16991	2.22924
H	2.40793	-2.10970	3.10242
C	3.81196	-3.29872	1.96408
H	3.79001	-4.14529	2.65821
C	4.57035	-3.40565	0.76191
C	5.28454	-4.59985	0.44573
H	5.26602	-5.42255	1.16970
C	5.96625	-4.73041	-0.75356

H	6.50392	-5.65564	-0.98598
C	5.94655	-3.66517	-1.69268
H	6.45866	-3.77856	-2.65417
C	5.27604	-2.48354	-1.40952
H	5.26021	-1.67940	-2.14917
C	4.58678	-2.30154	-0.17137
C	3.91589	0.12111	-0.71283
C	2.73458	0.71717	-1.17711
C	2.74720	1.75356	-2.15219
H	1.78906	2.13061	-2.51789
C	3.94655	2.26866	-2.60436
H	3.95647	3.06326	-3.35878
C	5.18332	1.80262	-2.07054
C	6.42509	2.38809	-2.45768
H	6.41174	3.19246	-3.20242
C	7.61983	1.96642	-1.89596
H	8.56588	2.42860	-2.19658
C	7.61017	0.94186	-0.91242
H	8.54999	0.62711	-0.44661
C	6.42074	0.33880	-0.52825
H	6.42955	-0.44150	0.23664
C	5.17199	0.73024	-1.10204
C	1.36106	2.90472	0.94095
H	2.18847	2.43405	0.37873
C	2.04171	3.53418	2.17474
H	2.41547	2.72604	2.82143
H	1.36915	4.17781	2.76158
H	2.90999	4.13955	1.86269
C	0.71904	3.89878	-0.04054
C	1.01099	5.27767	0.00428
H	1.66882	5.67156	0.78464
C	0.46690	6.16456	-0.94044
H	0.70878	7.23126	-0.88092
C	-0.38014	5.68994	-1.95231
H	-0.80430	6.38040	-2.68883
C	-0.67717	4.31775	-2.01010
H	-1.33002	3.93207	-2.80150
C	-0.13569	3.43243	-1.06500
H	-0.37681	2.36546	-1.12036
C	-0.95435	1.99003	1.77878
H	-1.64573	1.93888	0.91488
C	-1.16234	3.36566	2.45005
H	-0.89797	4.20830	1.79379
H	-0.59717	3.43866	3.39275
C	-2.42039	-2.78663	0.23467
H	-2.13812	-3.83586	0.40229
H	-3.24289	-2.50883	0.91504
C	-2.76248	-2.51165	-1.25089
C	-1.64245	-3.07201	-2.17796
H	-1.83751	-2.84168	-3.23878
H	-0.66734	-2.65209	-1.87870

H	-1.59627	-4.16696	-2.05941
C	-4.13316	-2.91621	-1.77896
C	-4.77600	-1.76800	-2.30100
C	-4.76391	-4.15752	-1.87077
C	-6.02909	-1.82938	-2.91824
C	-6.03371	-4.24017	-2.47938
H	-4.28128	-5.05477	-1.46900
C	-6.65189	-3.09163	-2.99913
H	-6.51869	-0.93871	-3.32440
H	-6.54091	-5.20760	-2.54727
H	-7.63500	-3.17020	-3.47412
C	-2.82016	-0.99686	-1.40510
O	-1.96826	-0.19921	-0.93071
N	-3.95146	-0.62560	-2.08019
C	-4.30107	0.77482	-2.35786
H	-4.95310	0.77436	-3.24913
H	-3.36501	1.28681	-2.63420
C	-4.95911	1.50635	-1.19351
C	-4.39153	2.70124	-0.71083
C	-6.14625	1.02637	-0.60198
C	-5.00316	3.41224	0.33503
H	-3.46139	3.07826	-1.15167
C	-6.75119	1.73072	0.44966
H	-6.59627	0.09352	-0.95853
C	-6.18407	2.92783	0.91829
H	-4.55039	4.34140	0.69615
H	-7.67055	1.34461	0.90226
H	-6.65947	3.47761	1.73718
C	-1.38678	0.92729	2.79213
C	-0.55789	0.55889	3.87160
C	-2.69889	0.41466	2.73505
C	-1.02377	-0.32296	4.85704
H	0.46465	0.94784	3.92309
C	-3.17105	-0.45300	3.73275
H	-3.35248	0.70597	1.90456
C	-2.33210	-0.82985	4.79244
H	-0.36175	-0.62007	5.67686
H	-4.19175	-0.84588	3.67236
H	-2.69087	-1.52350	5.55964
H	-2.23281	3.44897	2.69967
C	-0.25373	-2.68605	1.94622
N	0.09574	-3.45224	2.77821

(*S*)-E[4]: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.519656 hartree
Gibbs correction= 0.701913 hartree
Total Gibbs Energy= -2943.817743 hartree

Pd	1.11590	0.25202	-0.72750
P	-1.06973	0.35121	-0.35591
O	-2.10356	-0.29937	-1.48453
O	-1.41816	-0.66314	0.95817
N	-1.74871	1.88444	-0.21609

C	-2.50531	-2.60340	-0.87030
C	-1.94971	-1.67244	-1.75121
C	-1.27844	-2.02539	-2.94793
H	-0.87646	-1.22708	-3.57865
C	-1.13044	-3.36497	-3.25830
H	-0.62153	-3.66064	-4.18230
C	-1.59706	-4.37955	-2.37099
C	-1.37925	-5.76121	-2.65357
H	-0.87465	-6.02651	-3.58972
C	-1.77506	-6.74565	-1.76234
H	-1.59528	-7.80158	-1.98965
C	-2.39816	-6.37861	-0.53997
H	-2.68366	-7.15400	0.17879
C	-2.64181	-5.04539	-0.24169
H	-3.11122	-4.77965	0.70860
C	-2.27427	-4.00509	-1.14901
C	-3.25810	-2.13392	0.32686
C	-2.68006	-1.20399	1.20220
C	-3.28561	-0.84623	2.43689
H	-2.74073	-0.17028	3.10204
C	-4.52130	-1.36584	2.77737
H	-4.98642	-1.10654	3.73500
C	-5.22246	-2.21856	1.87524
C	-6.53578	-2.68937	2.17280
H	-6.98852	-2.40150	3.12868
C	-7.23385	-3.47584	1.27037
H	-8.24434	-3.82438	1.50730
C	-6.63995	-3.81330	0.02499
H	-7.20226	-4.41034	-0.70057
C	-5.35672	-3.38751	-0.28723
H	-4.91751	-3.64687	-1.25364
C	-4.59702	-2.59556	0.62747
C	-3.20698	2.12449	-0.56041
H	-3.67690	1.13253	-0.45142
C	-3.37965	2.53899	-2.03384
H	-2.90635	1.79062	-2.68615
H	-2.92376	3.51531	-2.25213
H	-4.45510	2.59041	-2.27662
C	-3.93591	3.04415	0.42654
C	-4.16538	4.40884	0.15863
H	-3.78951	4.85498	-0.76565
C	-4.86984	5.21227	1.07069
H	-5.03502	6.27081	0.84251
C	-5.36616	4.66368	2.26338
H	-5.91835	5.29047	2.97184
C	-5.16223	3.30017	2.53253
H	-5.56112	2.85489	3.45056
C	-4.45882	2.50144	1.61924
H	-4.31719	1.43537	1.82836
C	-0.81181	2.96323	0.25296
H	0.18606	2.48170	0.15301

C	-0.98202	3.28316	1.74959
H	-0.93363	2.34823	2.33130
H	-1.93906	3.77439	1.97887
C	1.56229	-0.24944	1.28712
H	0.91500	0.19038	2.06173
H	1.45491	-1.34783	1.32618
C	3.03550	0.18824	1.48013
C	3.12976	1.73314	1.64599
H	4.17540	2.07042	1.74018
H	2.66404	2.23295	0.77968
H	2.58500	2.03152	2.55696
C	3.88860	-0.50764	2.53488
C	5.02636	-1.06141	1.90114
C	3.74840	-0.62896	3.91771
C	6.03039	-1.72839	2.60701
C	4.74344	-1.30962	4.65055
H	2.87226	-0.21179	4.42572
C	5.86774	-1.84604	4.00228
H	6.91460	-2.13014	2.10477
H	4.63863	-1.41904	5.73461
H	6.63563	-2.36374	4.58601
C	3.76168	-0.20939	0.20349
O	3.30213	-0.02371	-0.95594
N	4.93482	-0.84833	0.49369
C	5.82482	-1.42272	-0.52236
H	5.28434	-1.30930	-1.47869
H	5.93385	-2.50368	-0.31995
C	7.19219	-0.75704	-0.58547
C	8.36403	-1.52959	-0.48404
C	7.30399	0.63400	-0.78165
C	9.62897	-0.92566	-0.57475
H	8.28553	-2.61425	-0.33994
C	8.56582	1.23903	-0.86722
H	6.39771	1.24314	-0.87332
C	9.73176	0.46079	-0.76358
H	10.53233	-1.53939	-0.49444
H	8.63996	2.32061	-1.02139
H	10.71639	0.93480	-0.83237
C	-0.75237	4.18716	-0.67071
C	-0.30660	4.02384	-2.00132
C	-1.03844	5.48813	-0.21202
C	-0.17066	5.13043	-2.85154
H	-0.06354	3.02363	-2.37844
C	-0.90140	6.59808	-1.06424
H	-1.37557	5.64512	0.81668
C	-0.47020	6.42315	-2.38739
H	0.17754	4.97754	-3.87841
H	-1.13134	7.60085	-0.68745
H	-0.36071	7.28782	-3.05095
H	-0.16223	3.94090	2.08640
C	0.83122	0.65161	-2.71096

N	0.65179	0.87476	-3.85984

(*S*)-TS4[1]: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.48047 hartree
Gibbs correction= 0.699974 hartree
Total Gibbs Energy= -2943.780496 hartree

Pd	-0.63108	-0.62822	0.79466
P	1.42406	0.36310	0.67107
O	2.78195	-0.22545	1.49419
O	2.07132	0.43869	-0.89093
N	1.41333	1.91739	1.36564
C	3.94903	-1.64068	-0.08014
C	3.18762	-1.50441	1.08244
C	2.82072	-2.60288	1.89898
H	2.23686	-2.41055	2.80311
C	3.20088	-3.87959	1.53108
H	2.92868	-4.73927	2.15302
C	3.90940	-4.10501	0.31479
C	4.24046	-5.42619	-0.10886
H	3.96169	-6.26534	0.53875
C	4.87508	-5.65079	-1.31974
H	5.11423	-6.67102	-1.63736
C	5.19254	-4.55226	-2.16191
H	5.66380	-4.73154	-3.13407
C	4.90039	-3.25308	-1.77215
H	5.13686	-2.42012	-2.43858
C	4.27323	-2.98100	-0.51840
C	4.36704	-0.42414	-0.83164
C	3.42570	0.54097	-1.21806
C	3.77046	1.63620	-2.05804
H	2.97665	2.31854	-2.37146
C	5.08008	1.82221	-2.45594
H	5.34438	2.66131	-3.10910
C	6.10861	0.94891	-1.99706
C	7.47696	1.17908	-2.32774
H	7.72012	2.03120	-2.97314
C	8.47930	0.35938	-1.83388
H	9.52661	0.55029	-2.09018
C	8.14274	-0.72158	-0.97644
H	8.93551	-1.35336	-0.56200
C	6.81931	-0.98310	-0.65071
H	6.57910	-1.81309	0.01804
C	5.75622	-0.17587	-1.16101
C	2.60855	2.80759	1.22271
H	3.30345	2.23577	0.57960
C	3.36365	2.99880	2.55341
H	3.51064	2.01240	3.01826
H	2.83108	3.64951	3.26406
H	4.35982	3.43551	2.36700
C	2.29403	4.09478	0.44602
C	2.83549	5.34272	0.81614
H	3.46967	5.42191	1.70424

C	2.57435	6.49683	0.05774
H	3.00701	7.45468	0.36634
C	1.76379	6.42565	-1.08464
H	1.55743	7.32575	-1.67314
C	1.21863	5.18827	-1.46608
H	0.58379	5.11699	-2.35584
C	1.48318	4.03689	-0.70988
H	1.05846	3.07523	-1.01891
C	0.07640	2.47009	1.73788
H	-0.40292	2.91820	0.84413
C	0.17409	3.58190	2.80735
H	0.76949	4.43797	2.45603
H	0.60516	3.19335	3.74440
C	-2.36968	-2.10187	0.70197
H	-2.33709	-3.15337	1.01316
H	-2.60624	-1.52231	1.62382
C	-3.46471	-1.88333	-0.37019
C	-3.15691	-2.55269	-1.73633
H	-4.02791	-2.45709	-2.40691
H	-2.28051	-2.07917	-2.20190
H	-2.93220	-3.62132	-1.59538
C	-4.82234	-2.34130	0.15733
C	-5.73506	-1.26400	0.09079
C	-5.25339	-3.58337	0.62502
C	-7.07341	-1.39782	0.47783
C	-6.59631	-3.73768	1.02954
H	-4.55956	-4.42980	0.67655
C	-7.48996	-2.65716	0.95345
H	-7.77673	-0.56420	0.39888
H	-6.94390	-4.70748	1.39931
H	-8.53178	-2.79149	1.26272
C	-3.71895	-0.37584	-0.63099
O	-2.90231	0.47202	-1.00332
N	-5.07179	-0.11711	-0.39660
C	-5.66460	1.20508	-0.58034
H	-4.80379	1.87189	-0.77144
H	-6.14483	1.52543	0.36370
C	-6.66708	1.28520	-1.72427
C	-7.94717	1.83063	-1.51438
C	-6.31379	0.84858	-3.01683
C	-8.86228	1.93913	-2.57456
H	-8.22877	2.17704	-0.51215
C	-7.22747	0.95159	-4.07528
H	-5.31651	0.42955	-3.19075
C	-8.50452	1.49713	-3.85726
H	-9.85565	2.36410	-2.39541
H	-6.94108	0.60819	-5.07498
H	-9.21689	1.57668	-4.68508
C	-0.89097	1.40895	2.29126
C	-0.53089	0.56192	3.38035
C	-2.26884	1.52354	1.96987

C	-1.50945	-0.12161	4.11641
H	0.52461	0.47805	3.66028
C	-3.24663	0.84648	2.71975
H	-2.56460	2.16229	1.13173
C	-2.87275	0.02467	3.79521
H	-1.20704	-0.76581	4.94845
H	-4.30375	0.95862	2.45885
H	-3.63580	-0.49578	4.38281
H	-0.84456	3.94321	3.02488
C	-0.65920	-2.36316	-0.12422
N	-0.24315	-3.28725	-0.74990

(*S*)-TS4[2]: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.474816 hartree
Gibbs correction= 0.699399 hartree
Total Gibbs Energy= -2943.775417 hartree

Pd	-0.47456	-0.95706	1.69991
P	1.25780	0.49501	1.05865
O	2.91485	0.36243	1.42990
O	1.39591	0.45474	-0.64304
N	1.01155	2.10800	1.53157
C	3.82162	-1.09565	-0.26792
C	3.43190	-0.88385	1.05812
C	3.53624	-1.88204	2.06120
H	3.22144	-1.63175	3.07820
C	4.02737	-3.13164	1.73034
H	4.12318	-3.90958	2.49586
C	4.37757	-3.44188	0.38266
C	4.81465	-4.75048	0.01866
H	4.91028	-5.50538	0.80763
C	5.09291	-5.07088	-1.30052
H	5.42064	-6.08123	-1.56630
C	4.93162	-4.08735	-2.31255
H	5.12347	-4.34812	-3.35875
C	4.52565	-2.79988	-1.99100
H	4.39661	-2.05681	-2.78184
C	4.25705	-2.42474	-0.63896
C	3.73325	0.03081	-1.23984
C	2.53663	0.74741	-1.38909
C	2.37722	1.75226	-2.38408
H	1.40287	2.24174	-2.47082
C	3.43737	2.09350	-3.20148
H	3.31451	2.86202	-3.97281
C	4.71251	1.47887	-3.03223
C	5.83549	1.87872	-3.81553
H	5.68888	2.65201	-4.57857
C	7.08668	1.31955	-3.60930
H	7.94201	1.63961	-4.21329
C	7.25915	0.34065	-2.59502
H	8.25280	-0.08130	-2.41076
C	6.18325	-0.08218	-1.82698
H	6.33704	-0.82769	-1.04296

C	4.87304	0.45128	-2.02849
C	1.67808	3.22633	0.80616
H	2.28396	2.72651	0.02807
C	2.70437	3.97760	1.68017
H	3.32758	3.23909	2.20724
H	2.23608	4.64242	2.42202
H	3.37086	4.58790	1.04698
C	0.67879	4.11266	0.04568
C	0.87206	5.50369	-0.08474
H	1.72567	5.98610	0.40101
C	-0.02094	6.28957	-0.83264
H	0.14982	7.36834	-0.91750
C	-1.12642	5.69883	-1.46245
H	-1.82622	6.31194	-2.04018
C	-1.32959	4.31444	-1.33942
H	-2.19276	3.83894	-1.81689
C	-0.43624	3.52768	-0.59642
H	-0.61867	2.45127	-0.50649
C	-0.17370	2.31864	2.43975
H	-1.10205	2.23821	1.84170
C	-0.18434	3.69718	3.12805
H	-0.19386	4.52172	2.39939
H	0.67182	3.82182	3.80981
C	-1.12857	-2.33472	-0.01973
H	-0.11318	-2.02761	-0.32721
H	-1.13216	-3.42984	0.04039
C	-2.18130	-1.79813	-1.02502
C	-1.45908	-1.38322	-2.33713
H	-2.18006	-1.02540	-3.09153
H	-0.73567	-0.58051	-2.11932
H	-0.91956	-2.24591	-2.76269
C	-3.31663	-2.77496	-1.28562
C	-4.54759	-2.14583	-1.00341
C	-3.30260	-4.09070	-1.74863
C	-5.77325	-2.79723	-1.17467
C	-4.52624	-4.77041	-1.92209
H	-2.35464	-4.59432	-1.97025
C	-5.74153	-4.12724	-1.63747
H	-6.72141	-2.29456	-0.96599
H	-4.52740	-5.80482	-2.27977
H	-6.68525	-4.66459	-1.77763
C	-2.94968	-0.55010	-0.49548
O	-2.46743	0.52357	-0.11548
N	-4.30926	-0.82708	-0.55653
C	-5.32113	0.09103	-0.04150
H	-4.74524	0.91546	0.41719
H	-5.88620	-0.41645	0.76211
C	-6.27699	0.62900	-1.09797
C	-7.66168	0.66554	-0.84706
C	-5.79289	1.13705	-2.31976
C	-8.54820	1.20191	-1.79526

H	-8.04813	0.27157	0.10089
C	-6.67659	1.66773	-3.27046
H	-4.71669	1.11178	-2.52365
C	-8.05740	1.70285	-3.01074
H	-9.62301	1.22118	-1.58555
H	-6.28693	2.05671	-4.21737
H	-8.74675	2.11675	-3.75415
C	-0.20538	1.22168	3.51012
C	0.85178	1.08383	4.43856
C	-1.33194	0.36454	3.62481
C	0.78463	0.12950	5.46134
H	1.73673	1.72150	4.34134
C	-1.38492	-0.60848	4.65377
H	-2.20821	0.53387	2.98698
C	-0.33139	-0.72376	5.56825
H	1.60962	0.04318	6.17697
H	-2.25043	-1.27515	4.70726
H	-0.37391	-1.47732	6.36134
H	-1.10524	3.76629	3.73075
C	-1.97412	-2.25024	1.68499
N	-2.94510	-2.79926	2.10644

(*S*)-F: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2944.519433 hartree
Gibbs correction= 0.699159 hartree
Total Gibbs Energy= -2943.820274 hartree

Pd	0.81908	-0.86090	0.13686
P	-0.98115	0.35187	0.04870
O	-2.03701	-0.02411	-1.24249
O	-2.11826	0.19450	1.31483
N	-0.80133	2.02927	-0.19613
C	-3.44477	-1.78126	-0.39119
C	-2.39476	-1.37633	-1.21971
C	-1.66615	-2.27964	-2.03775
H	-0.85573	-1.89926	-2.66577
C	-1.98940	-3.62440	-2.01713
H	-1.43960	-4.32990	-2.64969
C	-3.00350	-4.11905	-1.14464
C	-3.29116	-5.51436	-1.06455
H	-2.73774	-6.19730	-1.71963
C	-4.23025	-6.00208	-0.16956
H	-4.43553	-7.07638	-0.11450
C	-4.91276	-5.10340	0.69305
H	-5.63328	-5.49069	1.42139
C	-4.67012	-3.73847	0.62879
H	-5.19484	-3.06045	1.30651
C	-3.73060	-3.19651	-0.30081
C	-4.18920	-0.75065	0.38374
C	-3.50629	0.17358	1.19088
C	-4.20472	1.08582	2.03217
H	-3.61910	1.74618	2.67607
C	-5.58493	1.13344	2.02291

H	-6.11710	1.83257	2.67780
C	-6.33356	0.30240	1.14037
C	-7.75426	0.39857	1.05798
H	-8.26666	1.10923	1.71707
C	-8.47196	-0.37147	0.15654
H	-9.56195	-0.28389	0.09847
C	-7.78273	-1.26262	-0.70821
H	-8.34413	-1.85024	-1.44244
C	-6.40257	-1.39146	-0.64048
H	-5.88798	-2.07301	-1.32212
C	-5.63076	-0.63502	0.29501
C	-1.99876	2.90830	-0.34192
H	-2.85330	2.24591	-0.10878
C	-2.23051	3.39145	-1.78548
H	-2.19007	2.52951	-2.46739
H	-1.47883	4.12624	-2.11385
H	-3.22992	3.85108	-1.87206
C	-2.04108	4.02050	0.72200
C	-2.38352	5.35012	0.40815
H	-2.58585	5.63331	-0.62893
C	-2.46850	6.33126	1.41260
H	-2.73263	7.35950	1.14188
C	-2.21681	5.99848	2.75091
H	-2.28326	6.76232	3.53301
C	-1.87726	4.67401	3.07844
H	-1.67587	4.40009	4.12006
C	-1.79053	3.69963	2.07470
H	-1.50687	2.67262	2.32911
C	0.58706	2.50014	-0.48207
H	1.19669	1.60292	-0.21194
C	1.05854	3.63864	0.43658
H	0.90747	3.35818	1.48974
H	0.52383	4.58628	0.26579
C	3.86051	-0.91333	-2.75163
H	4.57320	-0.85267	-3.59480
H	3.53072	0.11845	-2.53300
C	4.61604	-1.51853	-1.51581
C	4.99094	-2.99699	-1.75859
H	5.55474	-3.40031	-0.90256
H	4.07933	-3.60004	-1.89765
H	5.62015	-3.08974	-2.65979
C	5.79787	-0.63518	-1.14725
C	5.56962	-0.07385	0.12858
C	6.97114	-0.33285	-1.83943
C	6.49301	0.78114	0.73887
C	7.91136	0.53470	-1.24571
H	7.16503	-0.76221	-2.82882
C	7.67034	1.07998	0.02590
H	6.32074	1.19097	1.73748
H	8.83569	0.77972	-1.77748
H	8.41146	1.74614	0.47898

C	3.72252	-1.38567	-0.26063
O	2.64804	-2.00312	-0.07485
N	4.32226	-0.52119	0.62856
C	3.70128	-0.08189	1.88655
H	2.59962	-0.17751	1.72723
H	3.92519	0.99206	2.00799
C	4.15480	-0.86492	3.10649
C	4.82390	-0.21759	4.16229
C	3.88704	-2.24636	3.20850
C	5.22796	-0.93482	5.30011
H	5.02173	0.85962	4.09840
C	4.29506	-2.96335	4.34220
H	3.34843	-2.75128	2.39922
C	4.96766	-2.31069	5.38990
H	5.74648	-0.41767	6.11436
H	4.07924	-4.03470	4.41248
H	5.28229	-2.87285	6.27536
C	0.87280	2.74009	-1.97482
C	0.70462	1.67259	-2.88490
C	1.36387	3.96449	-2.47137
C	1.00935	1.82525	-4.24542
H	0.32110	0.71365	-2.51750
C	1.66402	4.12331	-3.83599
H	1.51407	4.80994	-1.79279
C	1.48838	3.05573	-4.72857
H	0.86928	0.97993	-4.92786
H	2.03763	5.08740	-4.19869
H	1.72222	3.17945	-5.79150
H	2.13554	3.81820	0.27293
C	2.69252	-1.68067	-3.20062
N	1.76496	-2.27483	-3.60777

G: BP86/6-311+G(2df,2pd)(LANL2TZ(f)) SCF= -2063.927013 hartree
Gibbs correction= 0.452862 hartree
Total Gibbs Energy= -2063.474151 hartree

Pd	1.62899	-2.51909	0.42990
P	0.64318	-0.63262	-0.23710
O	-0.55627	-0.45408	-1.45346
O	-0.12557	0.28711	0.98624
N	1.82954	0.42512	-0.85781
C	-2.63992	-0.58257	-0.24718
C	-1.71750	-1.15608	-1.12835
C	-1.90776	-2.43711	-1.71004
H	-1.15282	-2.80729	-2.40938
C	-3.03218	-3.17472	-1.38832
H	-3.19759	-4.15941	-1.83982
C	-3.97345	-2.68606	-0.43434
C	-5.09594	-3.47228	-0.03722
H	-5.23839	-4.45165	-0.50872
C	-5.97647	-3.02328	0.93408
H	-6.82963	-3.64051	1.23432

C	-5.75666	-1.76494	1.55525
H	-6.43523	-1.42254	2.34371
C	-4.68542	-0.96702	1.17937
H	-4.52302	-0.00598	1.67358
C	-3.77245	-1.38414	0.16290
C	-2.41036	0.80542	0.24398
C	-1.18807	1.17039	0.83023
C	-0.99307	2.45656	1.41159
H	-0.03514	2.66053	1.89796
C	-1.98915	3.41096	1.35266
H	-1.83822	4.39609	1.80825
C	-3.21133	3.14172	0.67082
C	-4.21521	4.14481	0.52902
H	-4.03955	5.12496	0.98761
C	-5.37734	3.89782	-0.18451
H	-6.13796	4.67818	-0.29130
C	-5.56788	2.63005	-0.79511
H	-6.47124	2.44139	-1.38489
C	-4.61730	1.62762	-0.66115
H	-4.77640	0.66297	-1.14892
C	-3.41927	1.83486	0.09015
C	1.53116	1.86385	-1.12170
H	0.55527	2.04763	-0.63966
C	1.33482	2.19473	-2.61315
H	0.60802	1.49250	-3.04856
H	2.27393	2.13756	-3.18883
H	0.93468	3.21704	-2.72560
C	2.54148	2.76709	-0.39532
C	3.22530	3.81785	-1.03664
H	3.07077	4.00255	-2.10399
C	4.10777	4.64748	-0.32131
H	4.63110	5.45642	-0.84255
C	4.31755	4.44181	1.04926
H	5.00328	5.08874	1.60657
C	3.63997	3.39671	1.70226
H	3.79468	3.22624	2.77333
C	2.76517	2.56784	0.98591
H	2.25134	1.74205	1.49003
C	3.15561	-0.10375	-1.34911
H	3.80153	0.79359	-1.38264
C	3.06132	-0.69449	-2.77103
H	2.71423	0.05979	-3.49141
H	2.34610	-1.53294	-2.80530
C	3.78825	-1.07484	-0.34210
C	3.60413	-2.49402	-0.49101
C	4.45880	-0.59802	0.78995
C	3.97304	-3.37255	0.57234
H	3.35875	-2.91291	-1.47411
C	4.87270	-1.47716	1.81927
H	4.61336	0.48082	0.90266
C	4.59363	-2.84396	1.73650

H	3.90986	-4.45608	0.42601
H	5.39401	-1.07656	2.69493
H	4.88824	-3.51972	2.54642
H	4.04897	-1.05938	-3.10365

Acylation Calculations

5.1: M06L/6-311+G(2df,2pd) SCF= -727.2545534 hartree (solvent=toluene)
SCF= -727.2540142 hartree (solvent=*m*-xylene)
SCF= -727.2542687 hartree (solvent=anisole)
Gibbs correction= 0.131871 hartree
Total Gibbs Energy= -727.1226824 hartree (solvent=toluene)
Total Gibbs Energy= -727.1221432 hartree (solvent=*m*-xylene)
Total Gibbs Energy= -727.1223977 hartree (solvent=anisole)

C	3.27969	-1.84868	0.37616
C	1.96693	-1.42654	0.28687
C	1.65388	-0.08442	0.00788
C	2.70773	0.84565	-0.18372
C	4.03521	0.40538	-0.09178
C	4.31171	-0.92144	0.18420
H	3.50759	-2.88703	0.59281
H	1.15055	-2.12589	0.43211
H	4.82502	1.13373	-0.24251
H	5.34720	-1.24433	0.25221
O	2.50241	2.14024	-0.45182
H	1.52971	2.27875	-0.47961
C	0.27668	0.38891	-0.08791
O	-0.04753	1.55026	-0.31573
O	-0.63175	-0.60551	0.09440
C	-1.99645	-0.32000	0.06002
C	-2.78087	-1.18681	-0.69116
C	-2.55999	0.71096	0.80455
C	-4.16136	-1.01388	-0.70341
H	-2.30210	-1.98308	-1.25194
C	-3.94179	0.87276	0.77901
H	-1.92917	1.37528	1.38226
C	-4.74470	0.01681	0.02875
H	-4.77999	-1.68816	-1.28831
H	-4.39182	1.67649	1.35445
H	-5.82195	0.15201	0.01683

5.2am1: M06L/6-311+G(2df,2pd) SCF= -691.3283533 hartree
Gibbs correction= 0.15372 hartree
Total Gibbs Energy= -691.1746333 hartree

C	-3.71778	0.34692	0.07952
C	-2.72500	1.10469	0.70583
C	-1.38851	0.72560	0.65078

C	-1.00944	-0.44171	-0.02266
C	-2.00771	-1.22548	-0.61789
C	-3.33387	-0.82792	-0.58135
H	-3.00635	2.00304	1.25088
H	-0.63945	1.31854	1.16819
H	-1.71475	-2.15096	-1.10487
H	-4.09419	-1.43972	-1.06248
C	-5.15243	0.77475	0.10735
H	-5.32929	1.55202	0.85470
H	-5.46489	1.17797	-0.86268
H	-5.81942	-0.06443	0.32644
C	0.38376	-0.95824	-0.04202
O	0.54571	-2.19375	-0.00089
C	1.53757	-0.05443	-0.09684
C	1.43001	1.30018	-0.47009
C	2.83344	-0.56974	0.19077
C	2.53281	2.13316	-0.50563
H	0.45795	1.68405	-0.76373
C	3.94075	0.28989	0.18572
C	3.78838	1.62127	-0.15628
H	2.42610	3.16986	-0.80759
H	4.91091	-0.12881	0.43235
H	4.66032	2.26993	-0.17138
O	3.04891	-1.85493	0.48035
H	2.18423	-2.31564	0.34132

Phenol: M06L/6-311+G(2df,2pd) SCF= -307.5365093 hartree (solvent=toluene)
SCF= -307.5361959 hartree (solvent=*m*-xylene)
SCF= -307.5369823 hartree (solvent=anisole)
Gibbs correction= 0.057576 hartree
Total Gibbs Energy= -307.4789333 hartree (solvent=toluene)
Total Gibbs Energy= -307.4786199 hartree (solvent=*m*-xylene)
Total Gibbs Energy= -307.4794063 hartree (solvent=anisole)

C	-1.85230	0.02702	0.00005
C	-1.12897	1.21578	0.00005
C	0.26288	1.19710	-0.00012
C	0.94005	-0.02405	-0.00025
C	0.22129	-1.22148	-0.00007
C	-1.16712	-1.18767	0.00006
H	-2.93749	0.04555	0.00010
H	-1.64721	2.17079	0.00009
H	0.82589	2.12889	-0.00007
H	0.76784	-2.15911	-0.00012

H	-1.72027	-2.12291	0.00012
O	2.29933	-0.11059	0.00013
H	2.66165	0.78127	0.00054

***m*-xylene**: M06L/6-311+G(2df,2pd) SCF= -310.9401098 hartree
Gibbs correction= 0.099063 hartree
Total Gibbs Energy= -310.8410468 hartree

C	0.00067	-0.94803	-0.01771
C	-1.22135	-0.27248	-0.00876
C	-1.20700	1.12566	0.00068
C	-0.00123	1.81836	0.00449
C	1.20628	1.12674	-0.00163
C	1.22272	-0.27028	-0.01011
C	-2.51670	-1.02720	0.00856
H	-2.14872	1.67076	-0.00185
H	2.14757	1.67248	-0.00552
C	2.51749	-1.02591	0.00966
H	0.00072	-2.03797	-0.03536
H	-2.39127	-2.05457	-0.34341
H	-3.27457	-0.54666	-0.61720
H	-2.93342	-1.08242	1.02111
H	3.32468	-0.45824	-0.46142
H	2.43421	-1.98646	-0.50655
H	2.83755	-1.24335	1.03549
H	-0.00200	2.90524	0.00364

5.2aa1: M06L/6-311+G(2df,2pd) SCF= -730.6517722 hartree
Gibbs correction= 0.173938 hartree
Total Gibbs Energy= -730.4778342 hartree

C	3.49761	0.53975	-0.01472
C	2.49410	1.38983	-0.47625
C	1.17807	0.91651	-0.49641
C	0.87975	-0.38427	-0.08357
C	1.91609	-1.22574	0.34154
C	3.22908	-0.77174	0.39931
C	2.80913	2.77792	-0.94754
H	0.38599	1.55815	-0.87626
H	1.67097	-2.24635	0.62430
C	4.33584	-1.65586	0.88949
C	-0.48728	-0.96500	-0.17845
O	-0.58739	-2.16227	-0.50996
C	-1.68328	-0.16209	0.09653

C	-1.63453	1.07593	0.76826
C	-2.95852	-0.66881	-0.28413
C	-2.77693	1.81610	1.00951
H	-0.67467	1.43653	1.12474
C	-4.10770	0.10370	-0.06535
C	-4.01389	1.32807	0.57089
H	-2.71512	2.76139	1.53864
H	-5.06158	-0.30076	-0.38771
H	-4.91700	1.90662	0.74704
O	-3.11573	-1.86298	-0.85945
H	-2.22423	-2.29279	-0.84581
H	4.52474	0.90339	0.01288
H	3.87595	2.99907	-0.86411
H	2.26732	3.53314	-0.36852
H	2.52161	2.92119	-1.99439
H	4.00025	-2.68792	1.01461
H	4.72105	-1.31585	1.85721
H	5.18434	-1.65962	0.19810

5.2aa2: M06L/6-311+G(2df,2pd) SCF= -730.6509883 hartree
Gibbs correction= 0.176724 hartree
Total Gibbs Energy= -730.4742643 hartree

C	-3.54230	-0.73471	-0.17476
C	-2.49958	-1.44816	-0.76960
C	-1.20453	-0.95121	-0.73791
C	-0.91058	0.27906	-0.13482
C	-1.95541	1.02803	0.44966
C	-3.24073	0.48715	0.43276
H	-2.70407	-2.39943	-1.25550
H	-0.40179	-1.51176	-1.21000
C	-1.73020	2.35960	1.10055
H	-4.04358	1.04793	0.91064
C	-4.94882	-1.24792	-0.20770
H	-5.48005	-0.88734	-1.09625
H	-4.98100	-2.34029	-0.23949
H	-5.52202	-0.91486	0.66168
C	0.46852	0.83063	-0.21188
O	0.61419	2.03434	-0.50368
C	1.63646	-0.02587	0.02517
C	1.53732	-1.29935	0.62130
C	2.93260	0.45711	-0.31332
C	2.65106	-2.08994	0.83380

H	0.55960	-1.65046	0.93695
C	4.05323	-0.36292	-0.12060
C	3.91023	-1.61749	0.44342
H	2.55001	-3.06327	1.30260
H	5.02433	0.02698	-0.40760
H	4.79140	-2.23468	0.59830
O	3.13699	1.67411	-0.82248
H	2.25703	2.12721	-0.80824
H	-2.58257	2.62869	1.72980
H	-1.59276	3.14513	0.35289
H	-0.82757	2.37444	1.71709

1,2-Dimethoxybenzene: M06L/6-311+G(2df,2pd) SCF= -461.3853036 hartree
Gibbs correction= 0.108249 hartree
Total Gibbs Energy= -461.2770546 hartree

C	0.70703	-0.13818	-0.00001
C	1.39256	1.07124	0.00030
C	0.69260	2.28190	0.00023
C	-0.69193	2.28209	-0.00013
C	-1.39226	1.07166	-0.00039
C	-0.70713	-0.13797	-0.00028
H	2.47715	1.07743	0.00071
H	1.24493	3.21666	0.00049
H	-2.47686	1.07820	-0.00072
O	1.28962	-1.36806	0.00003
O	-1.28999	-1.36770	-0.00068
C	2.69915	-1.39636	-0.00005
H	2.98228	-2.44902	-0.00055
H	3.11734	-0.90906	-0.89141
H	3.11735	-0.90981	0.89173
C	-2.69954	-1.39588	0.00069
H	-3.11852	-0.90932	-0.89071
H	-2.98274	-2.44852	0.00128
H	-3.11685	-0.90858	0.89242
H	-1.24398	3.21703	-0.00021

5.2ag: M06L/6-311+G(2df,2pd) SCF= -881.100121 hartree
Gibbs correction= 0.18436 hartree
Total Gibbs Energy= -880.915761 hartree

C	-2.85974	-0.73244	-0.16487
C	-1.80234	-1.57024	-0.50603
C	-0.49046	-1.09863	-0.48483

C	-0.22095	0.22514	-0.13681
C	-1.29468	1.08195	0.17011
C	-2.59806	0.61906	0.17747
H	-1.99692	-2.59587	-0.79898
H	0.31480	-1.75960	-0.78809
H	-1.06500	2.11752	0.39410
C	1.13049	0.82799	-0.19099
O	1.22202	2.03848	-0.48363
C	2.34045	0.03845	0.07582
C	2.31844	-1.18911	0.76652
C	3.60367	0.55476	-0.32978
C	3.47285	-1.91618	0.99430
H	1.37095	-1.55099	1.15312
C	4.76381	-0.20573	-0.12839
C	4.69532	-1.42430	0.52274
H	3.43043	-2.85318	1.54003
H	5.70725	0.20512	-0.47286
H	5.60744	-1.99208	0.68726
O	3.73936	1.74808	-0.91439
H	2.84809	2.17577	-0.86731
O	-4.16246	-1.09515	-0.13833
O	-3.69141	1.36063	0.48498
C	-4.46006	-2.43507	-0.47763
H	-5.54137	-2.53507	-0.39019
H	-4.15572	-2.66879	-1.50583
H	-3.97255	-3.14244	0.20536
C	-3.45883	2.71737	0.80744
H	-4.43621	3.14843	1.02219
H	-2.81398	2.81839	1.69003
H	-2.99685	3.25834	-0.02823

Toluene: M06L/6-311+G(2df,2pd) SCF= -271.6160472 hartree
Gibbs correction= 0.078037 hartree
Total Gibbs Energy= -271.5380102 hartree

C	-0.91280	0.00012	-0.01064
C	-0.19480	-1.19968	-0.00843
C	1.19676	-1.20268	0.00212
C	1.89862	-0.00008	0.00822
C	1.19696	1.20258	0.00212
C	-0.19466	1.19975	-0.00843
H	-0.73813	-2.14278	-0.01781
H	1.73466	-2.14703	0.00082
H	2.98498	-0.00018	0.01276
H	1.73495	2.14687	0.00082

H	-0.73785	2.14292	-0.01781
C	-2.41215	0.00006	0.00825
H	-2.82353	-0.88128	-0.49208
H	-2.79931	-0.00702	1.03414
H	-2.82341	0.88810	-0.48012

1,5-COD: M06L/6-31G(2df,2pd) SCF= -312.0836913 hartree
Gibbs correction= 0.126543 hartree
Total Gibbs Energy= -311.9571483 hartree

C	-0.87337	-1.63240	-0.20553
C	0.38687	-1.81077	0.20178
C	-0.38687	1.81077	-0.20178
C	1.23043	-0.79727	0.92077
C	0.87337	1.63240	0.20553
C	1.68805	0.38396	0.02243
H	-1.35117	-2.44733	-0.74834
H	0.67943	-0.38735	1.77846
H	-0.86565	2.76120	0.03168
H	1.35117	2.44733	0.74834
H	0.86565	-2.76120	-0.03168
H	2.11036	-1.29705	1.33850
H	2.73926	0.61005	0.22829
H	1.64811	0.05763	-1.02599
C	-1.68805	-0.38396	-0.02243
H	-1.64811	-0.05763	1.02599
H	-2.73926	-0.61005	-0.22829
C	-1.23043	0.79727	-0.92077
H	-0.67943	0.38735	-1.77846
H	-2.11036	1.29705	-1.33850

JohnPhos: M06L/6-31G(2df,2pd) SCF= -1119.901881 hartree
Gibbs correction= 0.329089 hartree
Total Gibbs Energy= -1119.572792 hartree

C	0.99116	3.63977	0.06180
C	1.80302	2.51888	-0.03907
C	1.26918	1.22648	-0.16627
C	-0.13776	1.05742	-0.15335
C	-0.93374	2.20825	-0.04157
C	-0.39127	3.48421	0.05225
H	1.43548	4.62800	0.14264
H	2.88479	2.63170	-0.04782
H	-2.01348	2.09960	-0.00664
H	-1.04557	4.34811	0.13165
C	2.24112	0.11050	-0.28694
C	3.26977	-0.01243	0.65572
C	2.20742	-0.79568	-1.35443
C	4.22070	-1.02317	0.55209
H	3.30458	0.68517	1.49038
C	3.16273	-1.79886	-1.46601
H	1.42573	-0.70353	-2.10334
C	4.16898	-1.92127	-0.50973

H	5.00134	-1.10879	1.30309
H	3.12153	-2.48863	-2.30448
H	4.91023	-2.71104	-0.59478
P	-0.85304	-0.65072	-0.17339
C	-2.46771	-0.52260	-1.18732
C	-1.27601	-0.86471	1.67219
C	-2.07821	-2.15783	1.82922
H	-2.16309	-2.41531	2.89259
H	-3.09693	-2.06618	1.43826
H	-1.59472	-2.99945	1.32082
C	0.08437	-1.04849	2.35686
H	0.66122	-1.86591	1.91106
H	0.69187	-0.13872	2.29424
H	-0.06350	-1.27377	3.42080
C	-2.00522	0.28657	2.36047
H	-2.99335	0.48178	1.93619
H	-2.15033	0.04289	3.42151
H	-1.42796	1.21480	2.31766
C	-2.77793	-1.96856	-1.60541
H	-3.01021	-2.60796	-0.74802
H	-3.64966	-1.98377	-2.27246
H	-1.93518	-2.42116	-2.13650
C	-3.72887	0.05538	-0.54469
H	-4.54880	0.02948	-1.27520
H	-4.05653	-0.52838	0.32071
H	-3.62238	1.09531	-0.22510
C	-2.13699	0.26516	-2.45890
H	-2.95517	0.15687	-3.18210
H	-1.99879	1.33266	-2.26742
H	-1.22394	-0.10706	-2.93844

IX: M06L/6-31G(2df,2pd) SCF= -535.4814154 hartree
Gibbs correction= 0.089398 hartree
Total Gibbs Energy= -535.3920174 hartree

C	-2.89659	-0.66942	-0.00009
C	-1.98426	-1.73172	0.00007
C	-0.62925	-1.45805	0.00013
C	-0.15735	-0.13445	0.00007
C	-1.09009	0.93299	-0.00003
C	-2.46160	0.64388	-0.00014
H	-3.96395	-0.87440	-0.00015
H	-2.33631	-2.75803	0.00014
H	0.09820	-2.26311	0.00025
H	-3.15826	1.47561	-0.00025
C	1.26971	0.17792	0.00014
O	1.73458	1.31858	0.00025
O	2.06257	-0.90924	-0.00002
O	-0.72599	2.22086	-0.00005
H	0.25760	2.24039	0.00001
C	3.46426	-0.62343	-0.00024
H	3.74139	-0.04868	0.88637

H	3.96200	-1.59155	-0.00055
H	3.74101	-0.04822	-0.88668

Methanol: M06L/6-31G(2df,2pd) SCF= -115.7493009 hartree
Gibbs correction= 0.015199 hartree
Total Gibbs Energy= -115.7341019 hartree

O	-0.74563	0.12120	0.00000
C	0.65521	-0.01898	0.00000
H	1.03884	-0.54042	-0.89053
H	1.03884	-0.54041	0.89053
H	1.07700	0.98854	-0.00000
H	-1.12086	-0.76342	0.00000

[Ir(cod)OMe]$_2$: M06L/6-31G(2df,2pd)(SDD) SCF= -1063.519213 hartree
Gibbs correction= 0.354631 hartree
Total Gibbs Energy= -1063.164582 hartree

C	-2.24731	-1.57942	0.72429
C	-3.06785	-1.31240	-0.41711
C	-2.44603	1.10833	1.25575
C	-4.44853	-0.68258	-0.30305
C	-3.06159	1.41220	0.00085
C	-4.38693	0.84317	-0.45426
H	-1.54339	-2.41311	0.64019
H	-5.10645	-1.10266	-1.07040
H	-1.76313	1.85825	1.66334
H	-2.81508	2.37747	-0.45055
H	-2.92803	-1.96238	-1.28437
H	-4.90233	-0.96138	0.65576
H	-4.51052	1.10459	-1.51135
H	-5.22271	1.32458	0.07621
C	-2.62032	-1.24192	2.14961
H	-1.72283	-1.38512	2.76337
H	-3.37053	-1.94742	2.53814
C	-3.09996	0.20713	2.29200
H	-4.19086	0.26835	2.19841
H	-2.87099	0.57588	3.29698
C	2.24688	-1.57896	0.72533
C	3.06733	-1.31303	-0.41639
C	2.44656	1.10906	1.25503
C	4.44824	-0.68359	-0.30293
C	3.06203	1.41185	-0.00017
C	4.38711	0.84207	-0.45513
H	1.54262	-2.41244	0.64193

H	4.90207	-0.96192	0.65600
H	1.76404	1.85954	1.66223
H	2.81576	2.37687	-0.45223
H	2.92715	-1.96359	-1.28316
H	5.10592	-1.10438	-1.07010
H	5.22313	1.32357	0.07490
H	4.51060	1.10276	-1.51241
C	2.62027	-1.24067	2.15037
H	3.37033	-1.94616	2.53918
H	1.72284	-1.38321	2.76439
C	3.10036	0.20833	2.29177
H	2.87165	0.57778	3.29655
H	4.19127	0.26915	2.19800
Ir	1.48280	0.07146	-0.30352
Ir	-1.48283	0.07145	-0.30360
O	-0.00001	-0.98786	-1.38986
O	0.00001	1.51893	-0.80647
C	0.00007	-2.36502	-1.65515
H	-0.88866	-2.63196	-2.24154
H	0.88717	-2.63122	-2.24434
H	0.00177	-2.98376	-0.74393
C	-0.00003	2.83618	-0.32171
H	0.88653	3.37142	-0.68648
H	-0.88534	3.37207	-0.68855
H	-0.00129	2.89102	0.77814

4-CN-Phenol: M06L/6-31G(2df,2pd)(SDD) SCF= -399.8041429 hartree
Gibbs correction= 0.05112 hartree
Total Gibbs Energy= -399.7530229 hartree

O	-3.06402	0.08689	-0.00002
C	-1.71204	0.01431	-0.00012
C	-1.01930	-1.20078	-0.00005
C	-1.00809	1.22340	-0.00001
C	0.36639	-1.20757	0.00002
H	-1.56819	-2.13977	0.00000
C	0.37461	1.21391	0.00002
H	-1.56526	2.15397	0.00010
C	1.08103	-0.00106	0.00001
H	0.90621	-2.14907	0.00008
H	0.92488	2.14935	0.00009
C	2.50488	-0.00864	0.00003
N	3.67392	-0.01512	-0.00002

H	-3.42778	-0.80520	0.00060

4-CN-Phenyl Salicylate: M06L/6-31G(2df,2pd)(SDD) SCF= -819.5191559 hartree
Gibbs correction= 0.124986 hartree
Total Gibbs Energy= -819.3941699 hartree

C	3.95720	-1.82504	0.37562
C	2.64176	-1.41610	0.27877
C	2.31803	-0.07428	0.00456
C	3.36463	0.86765	-0.17403
C	4.69531	0.43920	-0.07449
C	4.98175	-0.88619	0.19629
H	4.19402	-2.86203	0.58840
H	1.83231	-2.12519	0.41436
H	5.47922	1.17564	-0.21521
H	6.01953	-1.19974	0.27036
O	3.15133	2.16153	-0.43622
H	2.18020	2.29850	-0.47134
C	0.94157	0.38733	-0.09798
O	0.59900	1.54313	-0.31850
O	0.03595	-0.62455	0.06537
C	-1.32297	-0.36005	0.04339
C	-2.10422	-1.27581	-0.65624
C	-1.89922	0.69630	0.74662
C	-3.48286	-1.13455	-0.66385
H	-1.61951	-2.08902	-1.18550
C	-3.27869	0.83622	0.73429
H	-1.27896	1.39886	1.28739
C	-4.08189	-0.07325	0.03022
H	-4.10328	-1.84057	-1.20570
H	-3.74520	1.65289	1.27526
C	-5.49974	0.07742	0.02488
N	-6.66179	0.19952	0.02122

I: M06L/6-31G(2df,2pd)(SDD) SCF= -1143.251047 hartree
Gibbs correction= 0.278996 hartree
Total Gibbs Energy= -1142.972051 hartree

C	3.10525	0.29360	0.76826
C	3.16291	0.14303	-0.64877
C	1.50204	-1.96113	0.73012
C	3.67293	-1.12050	-1.32436
C	1.37238	-1.96310	-0.68945
C	2.52851	-2.08804	-1.65585

H	3.16570	1.31396	1.15307
H	4.20725	-0.85356	-2.24175
H	0.62564	-2.27816	1.29921
H	0.40900	-2.29101	-1.08985
H	3.25909	1.06150	-1.23072
H	4.41758	-1.60477	-0.68148
H	2.14644	-1.86095	-2.65789
H	2.89381	-3.12536	-1.70027
C	3.48503	-0.78078	1.76099
H	3.14717	-0.44889	2.74935
H	4.57930	-0.87503	1.83220
C	2.83831	-2.13414	1.43519
H	3.50539	-2.74430	0.81457
H	2.69473	-2.70471	2.35839
Ir	1.17430	0.00351	0.02007
O	0.90126	2.06043	-0.03755
C	-0.22528	2.71007	-0.05510
C	-1.55006	2.14527	-0.04743
C	-0.13177	4.12918	-0.09155
C	-2.67254	3.01382	-0.08631
C	-1.24318	4.93580	-0.12595
H	0.87057	4.54534	-0.09455
C	-2.53604	4.37968	-0.12510
H	-3.66123	2.56955	-0.08373
H	-1.11877	6.01581	-0.15518
H	-3.41277	5.01821	-0.15415
C	-1.78197	0.72700	-0.00052
O	-0.94389	-0.19976	0.04394
O	-3.09393	0.38728	0.01046
C	-3.46366	-0.95786	-0.00486
C	-4.33159	-1.37502	0.99537
C	-3.06385	-1.81298	-1.02629
C	-4.80548	-2.68400	0.97665
H	-4.62491	-0.67397	1.77000
C	-3.54231	-3.11903	-1.02980
H	-2.38888	-1.45928	-1.79802
C	-4.41051	-3.55833	-0.03190
H	-5.48454	-3.01813	1.75557
H	-3.23427	-3.79603	-1.82136
H	-4.77965	-4.57938	-0.04324

TS1_COD: M06L/6-31G(2df,2pd)(SDD) SCF= -1143.214579 hartree
Gibbs correction= 0.278913 hartree
Total Gibbs Energy= -1142.935666 hartree

C	-2.34105	0.01696	1.66484
C	-2.24453	-1.21768	0.96227
C	-2.54052	1.20054	-0.84990
C	-3.30376	-1.69686	-0.01479
C	-2.21074	0.00893	-1.54457
C	-2.98136	-1.28684	-1.45915
H	-1.79931	0.07861	2.61103
H	-3.38709	-2.78619	0.04560
H	-2.15840	2.13235	-1.27171
H	-1.59387	0.11155	-2.43835
H	-1.63050	-1.99472	1.42148
H	-4.28111	-1.30654	0.29231
H	-2.36146	-2.06031	-1.92507
H	-3.90064	-1.22900	-2.06013
C	-3.46794	1.01071	1.50317
H	-3.16889	1.93274	2.01446
H	-4.37249	0.66075	2.02241
C	-3.77290	1.32690	0.03141
H	-4.56197	0.66891	-0.35095
H	-4.17406	2.34192	-0.04855
Ir	-0.92566	0.20601	0.12757
O	0.58782	-0.30964	1.48367
C	1.57975	-1.04198	1.05935
C	1.63747	-1.56746	-0.26328
C	2.63970	-1.38435	1.93107
C	2.65014	-2.46860	-0.65187
C	3.63915	-2.24550	1.52372
H	2.62483	-0.96718	2.93287
C	3.64966	-2.80899	0.23596
H	2.64039	-2.85602	-1.66724
H	4.43313	-2.49951	2.22211
H	4.44000	-3.48979	-0.06203
C	0.72061	-1.13103	-1.28105
O	0.32298	-1.55130	-2.31626
O	0.65003	0.68666	-1.27128
C	1.75614	1.34270	-0.80560
C	3.01074	1.06418	-1.35537
C	1.63047	2.31424	0.19064
C	4.12946	1.75186	-0.89972

H	3.09408	0.30524	-2.12859
C	2.75467	3.00045	0.63524
H	0.64502	2.50927	0.61236
C	4.00856	2.71931	0.09634
H	5.10340	1.52771	-1.32596
H	2.64972	3.75434	1.41051
H	4.88634	3.25206	0.44971

II[1]: M06L/6-31G(2df,2pd)(SDD) SCF= -1143.24065 hartree
Gibbs correction= 0.280348 hartree
Total Gibbs Energy= -1142.960302 hartree

C	-1.27882	2.18050	0.35051
C	-0.59065	2.55107	-0.82663
C	1.25400	1.26469	1.22129
C	0.60885	3.48210	-0.82190
C	1.88091	1.42496	-0.02715
C	1.93761	2.71497	-0.81234
H	-2.32477	1.89244	0.23805
H	0.56716	4.12401	-1.70684
H	1.55146	0.39194	1.79779
H	2.63300	0.68006	-0.29605
H	-1.15114	2.48253	-1.76051
H	0.54330	4.15657	0.03850
H	2.22154	2.46985	-1.84202
H	2.74912	3.34750	-0.42451
C	-0.86603	2.61314	1.73450
H	-1.45544	2.04417	2.45853
H	-1.13449	3.66812	1.88906
C	0.62799	2.39349	2.02070
H	1.19592	3.31290	1.83634
H	0.75620	2.17030	3.08350
Ir	-0.04879	0.52010	-0.38735
O	-1.67370	-0.13982	-1.50964
C	-2.46340	-0.92108	-0.82434
C	-2.24970	-1.10559	0.56708
C	-3.56318	-1.58006	-1.41928
C	-3.09403	-1.93109	1.33743
C	-4.37943	-2.38204	-0.64718
H	-3.73590	-1.44690	-2.48213
C	-4.15668	-2.56683	0.73183
H	-2.88721	-2.04929	2.39706
H	-5.21761	-2.88875	-1.11979

H	-4.81663	-3.20569	1.30954
C	-1.12465	-0.42031	1.16671
O	-0.77326	-0.39409	2.31894
O	0.82817	-1.21373	-0.95279
C	1.96976	-1.70425	-0.44243
C	3.05297	-1.95270	-1.30209
C	2.10249	-2.01949	0.92028
C	4.23167	-2.49858	-0.80657
H	2.94067	-1.71443	-2.35620
C	3.28858	-2.56252	1.40342
H	1.25602	-1.84852	1.58155
C	4.36172	-2.80320	0.54767
H	5.05955	-2.68410	-1.48677
H	3.37079	-2.80503	2.46023
H	5.28541	-3.22749	0.92969

II^{2}: M06L/6-31G(2df,2pd)(SDD) SCF= -1143.209816 hartree
Gibbs correction= 0.279677 hartree
Total Gibbs Energy= -1142.930139 hartree

C	0.53346	-1.15452	-1.78063
C	-0.47260	-1.82938	-1.03998
C	2.17431	-1.41562	0.66617
C	-0.26649	-3.10781	-0.24310
C	1.12374	-1.76629	1.45677
C	0.18311	-2.91537	1.21598
H	0.19486	-0.56786	-2.63603
H	-1.21340	-3.65604	-0.23244
H	2.82663	-0.61349	1.00550
H	0.99988	-1.23762	2.40197
H	-1.49573	-1.67971	-1.38644
H	0.43501	-3.75295	-0.78467
H	-0.70336	-2.74412	1.83041
H	0.63812	-3.84675	1.58218
C	1.97746	-1.58716	-1.87375
H	2.56692	-0.72527	-2.20555
H	2.06841	-2.33507	-2.67592
C	2.59474	-2.14370	-0.58049
H	2.36155	-3.20774	-0.47647
H	3.68500	-2.08559	-0.66899
Ir	0.06475	-0.02649	-0.01338
O	-1.58863	-0.58230	1.12765
C	-2.69895	-0.02172	0.67842

C	-2.65658	0.83204	-0.44402
C	-3.93805	-0.26488	1.30180
C	-3.82311	1.43417	-0.93595
C	-5.07794	0.34429	0.80328
H	-3.97562	-0.91685	2.16879
C	-5.03569	1.19274	-0.31456
H	-3.74350	2.08545	-1.80217
H	-6.03030	0.15557	1.29353
H	-5.94677	1.65329	-0.68347
C	-1.32950	1.03591	-1.02848
O	-1.08442	1.72292	-2.00757
O	0.39156	1.56520	1.37737
C	1.58908	1.77382	0.90254
C	2.73165	1.87777	1.74079
C	1.77308	1.71206	-0.52139
C	3.98989	1.83603	1.18331
H	2.57969	1.95201	2.81315
C	3.08335	1.62970	-1.04570
H	0.95725	2.00573	-1.17777
C	4.17766	1.66928	-0.20873
H	4.86218	1.90509	1.82919
H	3.21917	1.59166	-2.12401
H	5.18405	1.62510	-0.61362

III: M06L/6-31G(2df,2pd)(SDD) SCF= -1414.867185 hartree
Gibbs correction= 0.387137 hartree
Total Gibbs Energy= -1414.480048 hartree

C	0.54805	-1.94927	1.65800
C	-0.75830	-1.96605	1.12491
C	0.03607	0.78594	2.17542
C	-1.98197	-1.54899	1.91970
C	-1.16597	0.82287	1.44831
C	-2.35330	-0.07583	1.70087
H	1.27034	-2.63215	1.20832
H	-2.82873	-2.17460	1.61694
H	0.67328	1.66415	2.10846
H	-1.38125	1.73807	0.89080
H	-0.93201	-2.64185	0.28675
H	-1.81227	-1.75971	2.98198
H	-3.01933	-0.00207	0.83497
H	-2.92590	0.30998	2.55721
C	0.88328	-1.46833	3.04713

H	1.97083	-1.39892	3.13247
H	0.56891	-2.22341	3.78203
C	0.26399	-0.10373	3.38360
H	-0.68926	-0.23312	3.90959
H	0.92279	0.42368	4.07915
Ir	0.27133	-0.27729	0.26318
O	0.94133	-1.47689	-1.30668
C	2.24442	-1.47346	-1.40930
C	3.03239	-0.82722	-0.42225
C	2.91227	-2.12544	-2.46987
C	4.43956	-0.82132	-0.49525
C	4.29213	-2.10981	-2.52247
H	2.31968	-2.62189	-3.23138
C	5.06836	-1.46184	-1.54219
H	5.00148	-0.30739	0.27920
H	4.79249	-2.61085	-3.34789
H	6.15111	-1.46620	-1.61345
C	2.33702	-0.15986	0.66021
O	2.79942	0.41572	1.61277
O	0.48227	1.26545	-1.05779
C	0.36852	2.56513	-0.74153
C	-0.63040	3.33849	-1.35913
C	1.25193	3.20040	0.14869
C	-0.74227	4.69746	-1.08705
H	-1.29910	2.85173	-2.06439
C	1.12681	4.55954	0.41651
H	2.04349	2.61338	0.60775
C	0.12887	5.31767	-0.19311
H	-1.52032	5.27711	-1.57839
H	1.82405	5.03204	1.10440
H	0.03650	6.37872	0.01877
C	-2.34538	0.03784	-2.01125
C	-3.51468	0.75670	-1.76279
C	-4.63526	0.11424	-1.24407
C	-4.61205	-1.25622	-0.95421
C	-3.43749	-1.96724	-1.21774
C	-2.31360	-1.33105	-1.74334
H	-1.45950	0.52815	-2.40436
H	-3.55328	1.82286	-1.97314
H	-5.54469	0.68084	-1.05210
H	-1.40773	-1.89472	-1.95342

H	-3.40682	-3.03641	-1.00959
C	-5.79784	-1.93003	-0.33307
H	-5.81271	-3.00270	-0.54443
H	-5.78847	-1.81901	0.75882
H	-6.74102	-1.50231	-0.68447

TS2: M06L/6-31G(2df,2pd)(SDD) SCF= -1414.804557 hartree
Gibbs correction= 0.387874 hartree
Total Gibbs Energy= -1414.416683 hartree

C	1.25471	-1.38825	1.93966
C	-0.13311	-1.71110	1.87662
C	0.38787	1.26131	2.00875
C	-1.12160	-1.27315	2.94621
C	-0.96503	0.97017	1.75526
C	-1.79731	0.07245	2.64113
H	1.93424	-2.08096	1.44115
H	-1.88860	-2.04588	3.05213
H	0.79652	2.15637	1.54620
H	-1.51628	1.69604	1.15505
H	-0.39387	-2.61298	1.32251
H	-0.60074	-1.23466	3.91111
H	-2.75146	-0.11101	2.13967
H	-2.03642	0.60201	3.57501
C	1.86695	-0.55033	3.03342
H	2.90529	-0.34079	2.76420
H	1.90360	-1.13391	3.96489
C	1.12277	0.77218	3.24550
H	0.40195	0.68172	4.06758
H	1.83518	1.54340	3.54990
Ir	0.26560	-0.23183	0.42023
O	0.88785	-1.69233	-0.94661
C	2.12476	-1.54199	-1.35918
C	2.93740	-0.52142	-0.81566
C	2.68094	-2.39445	-2.33748
C	4.26609	-0.34651	-1.24388
C	3.98971	-2.20813	-2.74118
H	2.06304	-3.18093	-2.75922
C	4.79425	-1.18684	-2.20331
H	4.85073	0.45544	-0.80131
H	4.40618	-2.86972	-3.49741
H	5.81776	-1.06332	-2.54271
C	2.34077	0.32520	0.20578

O	2.88719	1.25522	0.76188
O	-0.05101	1.04934	-1.40935
C	-0.40032	2.36570	-1.30287
C	-1.65444	2.80494	-1.74107
C	0.52174	3.28491	-0.79087
C	-1.98427	4.15398	-1.64699
H	-2.35293	2.08650	-2.16116
C	0.17841	4.62997	-0.70618
H	1.49863	2.93122	-0.47213
C	-1.07544	5.07183	-1.12590
H	-2.96004	4.48799	-1.98997
H	0.90067	5.33876	-0.30974
H	-1.33824	6.12301	-1.05494
C	-1.86561	-0.65044	-0.63191
C	-3.07943	0.00988	-0.34412
C	-4.31906	-0.58361	-0.54934
C	-4.41366	-1.89245	-1.03579
C	-3.22355	-2.57064	-1.31799
C	-1.98594	-1.96460	-1.12800
H	-0.96515	0.30167	-1.25169
H	-3.06242	1.03424	0.02835
H	-5.23114	-0.03084	-0.32702
H	-1.08346	-2.51956	-1.36939
H	-3.27398	-3.59136	-1.69566
C	-5.74590	-2.53298	-1.27276
H	-5.69132	-3.62235	-1.19618
H	-6.49984	-2.17773	-0.56448
H	-6.12174	-2.30300	-2.27688

V: M06L/6-31G(2df,2pd)(SDD) SCF= -1414.824617 hartree
Gibbs correction= 0.391675 hartree
Total Gibbs Energy= -1414.432942 hartree

C	1.51268	-1.38465	1.79963
C	0.14635	-1.81678	1.90205
C	0.45104	1.15922	2.06290
C	-0.72909	-1.49228	3.10529
C	-0.90451	0.77180	1.97654
C	-1.55533	-0.21235	2.92007
H	2.17209	-2.02211	1.20902
H	-1.40285	-2.33516	3.28547
H	0.73071	2.09633	1.58606
H	-1.58543	1.47456	1.49397

H	-0.09762	-2.74188	1.37919
H	-0.09398	-1.42202	3.99721
H	-2.53221	-0.47350	2.50108
H	-1.75086	0.26815	3.89014
C	2.19138	-0.53273	2.84179
H	3.16802	-0.22989	2.45616
H	2.38818	-1.13870	3.73893
C	1.37362	0.71426	3.18741
H	0.77099	0.54607	4.08839
H	2.05027	1.53927	3.42529
Ir	0.22735	-0.29572	0.46878
O	0.77065	-1.66343	-1.03555
C	1.96383	-1.45955	-1.55116
C	2.78779	-0.41371	-1.07387
C	2.45300	-2.27816	-2.59271
C	4.06036	-0.18850	-1.62695
C	3.70966	-2.04012	-3.11872
H	1.82541	-3.08280	-2.96342
C	4.52571	-0.99662	-2.64581
H	4.65444	0.63014	-1.22826
H	4.07397	-2.67875	-3.92056
H	5.50688	-0.83190	-3.08024
C	2.25560	0.39727	0.01307
O	2.81791	1.36971	0.49096
O	-0.23840	1.18859	-1.30144
C	-0.56852	2.53076	-1.16325
C	-1.82441	3.00027	-1.53888
C	0.40987	3.38791	-0.66812
C	-2.10582	4.35734	-1.40352
H	-2.56832	2.31195	-1.93341
C	0.10719	4.73939	-0.53549
H	1.38514	2.99202	-0.40064
C	-1.14614	5.22948	-0.89790
H	-3.08350	4.72828	-1.69704
H	0.86560	5.41454	-0.15001
H	-1.37123	6.28619	-0.79261
C	-1.77943	-0.94551	-0.13348
C	-2.88261	-0.08856	-0.26843
C	-4.10489	-0.51982	-0.79181
C	-4.28963	-1.84431	-1.18461
C	-3.20118	-2.71447	-1.04628

C	-1.98108	-2.27429	-0.54431
H	-1.00616	0.69679	-1.64473
H	-2.81207	0.95286	0.04847
H	-4.93170	0.18474	-0.88357
H	-1.15399	-2.97972	-0.49670
H	-3.31310	-3.75547	-1.34916
C	-5.59936	-2.32515	-1.73169
H	-6.03303	-3.11417	-1.10730
H	-6.33165	-1.51571	-1.79473
H	-5.48757	-2.74988	-2.73532

VI: M06L/6-31G(2df,2pd)(SDD) SCF= -1107.308363 hartree
Gibbs correction= 0.299009 hartree
Total Gibbs Energy= -1107.009354 hartree

C	2.65374	0.74998	-0.25170
C	2.62262	-0.16242	-1.29676
C	1.55558	-1.42460	1.30143
C	3.28615	-1.52254	-1.25232
C	1.30382	-2.25761	0.19396
C	2.31659	-2.64702	-0.85897
H	2.41274	1.78662	-0.48610
H	3.70704	-1.74454	-2.23800
H	0.84621	-1.48463	2.12204
H	0.44608	-2.92653	0.26826
H	2.34995	0.22348	-2.27956
H	4.13903	-1.49159	-0.56729
H	1.76625	-2.97446	-1.74959
H	2.87561	-3.53204	-0.52060
C	3.25265	0.49931	1.10450
H	2.87928	1.27175	1.78371
H	4.34309	0.63650	1.06509
C	2.91935	-0.88080	1.69406
H	3.68798	-1.61299	1.42227
H	2.95288	-0.80595	2.78493
Ir	0.57942	-0.28783	-0.29261
O	-0.09660	1.26727	-1.50539
C	-0.54689	2.28186	-0.81032
C	-0.44309	2.26622	0.60302
C	-1.12021	3.41663	-1.42358
C	-0.90202	3.34314	1.38206
C	-1.56451	4.46645	-0.64116
H	-1.20541	3.43848	-2.50548

C	-1.46100	4.44335	0.76139
H	-0.80861	3.28443	2.46266
H	-2.00849	5.33291	-1.12596
H	-1.81859	5.28303	1.34865
C	0.13659	1.07628	1.21493
O	0.34522	0.88139	2.38763
C	-1.35168	-0.95328	-0.02814
C	-1.80733	-1.67736	1.08710
C	-3.10310	-2.17440	1.15426
C	-4.00871	-1.97772	0.10416
C	-3.56844	-1.25286	-1.00381
C	-2.27483	-0.73569	-1.06543
H	-1.14309	-1.84640	1.93420
H	-3.42396	-2.72413	2.03851
H	-1.97783	-0.15219	-1.93379
H	-4.25606	-1.07748	-1.83037
C	-5.40192	-2.52457	0.17730
H	-5.40493	-3.61937	0.22839
H	-5.92961	-2.17042	1.06956
H	-5.99435	-2.23497	-0.69463

TS3: M06L/6-31G(2df,2pd)(SDD) SCF= -1107.286886 hartree
Gibbs correction= 0.302929 hartree
Total Gibbs Energy= -1106.983957 hartree

C	2.42510	1.15767	-0.11116
C	2.61101	0.27842	-1.21292
C	1.71911	-1.14326	1.30874
C	3.52884	-0.93019	-1.18218
C	1.63786	-1.97760	0.17026
C	2.77842	-2.21537	-0.79409
H	2.08135	2.16607	-0.34779
H	3.98071	-1.06373	-2.16995
H	0.98264	-1.29715	2.09322
H	0.87414	-2.75816	0.18144
H	2.40253	0.69969	-2.19732
H	4.36652	-0.74735	-0.50039
H	2.36012	-2.67090	-1.69911
H	3.47373	-2.96124	-0.38061
C	3.05839	0.99943	1.24511
H	2.52563	1.66029	1.93799
H	4.09975	1.35349	1.22436
C	2.98309	-0.44029	1.76589

H	3.86117	-1.01679	1.45513
H	3.00467	-0.42984	2.85984
Ir	0.70845	-0.10895	-0.30139
O	-0.12920	1.42066	-1.44801
C	-0.92616	2.22157	-0.76711
C	-1.21465	1.95992	0.59315
C	-1.48875	3.37017	-1.35835
C	-1.99390	2.84555	1.34913
C	-2.27294	4.22488	-0.60029
H	-1.27813	3.57234	-2.40419
C	-2.52750	3.97822	0.75643
H	-2.17137	2.61435	2.39598
H	-2.69235	5.11166	-1.07015
H	-3.13439	4.66777	1.33463
C	-0.68985	0.72595	1.19691
O	-0.54570	0.53034	2.38996
C	-1.27130	-0.81327	0.26973
C	-1.51248	-1.83895	1.20482
C	-2.48266	-2.79931	0.98652
C	-3.28493	-2.76996	-0.16590
C	-3.08120	-1.73362	-1.07809
C	-2.10633	-0.76231	-0.86443
H	-0.95033	-1.84143	2.13533
H	-2.64221	-3.58265	1.72559
H	-1.97431	0.02704	-1.59815
H	-3.70028	-1.68148	-1.97167
C	-4.34456	-3.80338	-0.38400
H	-3.94231	-4.81733	-0.28913
H	-5.14505	-3.71612	0.35919
H	-4.80168	-3.71282	-1.37219

VII: M06L/6-31G(2df,2pd)(SDD) SCF= -1107.327864 hartree
Gibbs correction= 0.301592 hartree
Total Gibbs Energy= -1107.026272 hartree

C	3.19731	0.31205	1.05847
C	3.41792	0.47380	-0.33942
C	1.95040	-2.06577	0.36827
C	4.17149	-0.54517	-1.17966
C	1.96637	-1.77701	-1.02733
C	3.21956	-1.54986	-1.84238
H	3.06802	1.22610	1.64210
H	4.75322	-0.02595	-1.94819

H	1.07776	-2.60274	0.74538
H	1.10736	-2.12523	-1.60704
H	3.43492	1.49899	-0.71366
H	4.90823	-1.06254	-0.55362
H	2.91060	-1.15995	-2.81914
H	3.73481	-2.50099	-2.04637
C	3.62734	-0.89578	1.85906
H	3.14853	-0.82517	2.84244
H	4.71125	-0.87205	2.04926
C	3.21869	-2.21780	1.19382
H	4.02699	-2.59869	0.55807
H	3.06580	-2.98305	1.96169
Ir	1.40697	-0.05032	0.02939
O	0.83380	1.91038	0.39388
C	-0.33012	2.42200	0.13111
C	-1.54372	1.69130	-0.15925
C	-0.41278	3.84204	0.16497
C	-2.71000	2.43763	-0.49094
C	-1.57061	4.51519	-0.13857
H	0.50033	4.37105	0.41873
C	-2.73587	3.81070	-0.49463
H	-3.59852	1.89223	-0.79136
H	-1.57855	5.60257	-0.12112
H	-3.63873	4.34152	-0.77822
C	-1.62209	0.25283	-0.16272
O	-0.62654	-0.53489	-0.23558
C	-2.92594	-0.45129	-0.08193
C	-3.08166	-1.66317	-0.77042
C	-4.25743	-2.38850	-0.66770
C	-5.30772	-1.95209	0.15091
C	-5.13500	-0.76263	0.86365
C	-3.96860	-0.01637	0.74625
H	-2.26284	-2.01978	-1.38816
H	-4.36701	-3.31764	-1.22322
H	-3.84952	0.89618	1.32376
H	-5.92637	-0.41997	1.52667
C	-6.57795	-2.73813	0.24992
H	-7.19199	-2.61479	-0.64954
H	-6.38249	-3.80996	0.35046
H	-7.18431	-2.42307	1.10263

A[1]: M06L/6-31G(2df,2pd)(SDD) SCF= -1951.051324 hartree
Gibbs correction= 0.48171 hartree
Total Gibbs Energy= -1950.569614 hartree

C	-3.09968	4.68544	-0.96798
C	-3.38654	3.35293	-0.77842
C	-2.39468	2.42618	-0.37971
C	-1.05286	2.87628	-0.14950
C	-0.80214	4.26258	-0.33983
C	-1.78800	5.13549	-0.74022
H	-3.87461	5.37571	-1.28484
H	-4.39419	2.98547	-0.93918
H	0.21096	4.60804	-0.15470
H	-1.54434	6.18618	-0.88092
O	-0.04642	2.14766	0.24582
C	-2.75888	1.05126	-0.15240
O	-2.01641	0.09417	0.10875
O	-4.09910	0.82187	-0.23958
C	-4.58453	-0.44085	0.09071
C	-4.56012	-0.87949	1.41010
C	-5.17761	-1.19415	-0.91314
C	-5.15435	-2.09637	1.72613
H	-4.07751	-0.27256	2.16971
C	-5.76818	-2.41247	-0.58502
H	-5.17324	-0.81985	-1.93197
C	-5.76079	-2.86434	0.73255
H	-5.14057	-2.44690	2.75432
H	-6.23628	-3.00764	-1.36390
H	-6.22484	-3.81309	0.98525
Ir	0.15527	0.06893	0.20090
P	2.37961	0.23644	0.25662
C	3.07690	1.47289	-1.01938
C	3.11411	0.58475	1.97033
C	4.52176	1.18449	-1.43289
H	4.61765	0.23074	-1.95808
H	4.84739	1.97218	-2.12362
H	5.22223	1.18459	-0.59293
C	2.19068	1.33410	-2.26284
H	1.16332	1.64996	-2.05988
H	2.59837	1.96101	-3.06615
H	2.15788	0.30060	-2.62765
C	2.97655	2.91012	-0.50438
H	1.97183	3.13267	-0.13878

H	3.69862	3.11987	0.29078
H	3.20168	3.59674	-1.33037
C	2.32228	1.73416	2.60362
H	2.47694	2.68817	2.09437
H	1.24798	1.52424	2.59254
H	2.64346	1.85689	3.64547
C	4.60515	0.91968	1.98989
H	4.92031	1.06900	3.03029
H	5.22557	0.11535	1.58309
H	4.83878	1.84089	1.44959
C	2.87377	-0.67063	2.81306
H	3.25132	-0.50135	3.82863
H	1.80410	-0.89001	2.88862
H	3.38236	-1.55219	2.40852
C	3.01164	-1.37694	-0.31508
C	4.34737	-1.79389	-0.38042
C	1.99822	-2.22024	-0.79843
C	4.68218	-3.01251	-0.96012
H	5.13898	-1.15185	-0.00437
C	2.34993	-3.43387	-1.40254
C	3.68030	-3.82444	-1.48991
H	5.72255	-3.32107	-1.01106
H	1.55924	-4.08048	-1.77752
H	3.93748	-4.77139	-1.95710
C	0.55754	-1.89730	-0.57707
C	0.07783	-1.99976	0.80023
C	-0.37526	-2.24834	-1.63124
C	-1.23870	-2.53753	1.03405
H	0.81482	-2.18208	1.58248
C	-1.64086	-2.66979	-1.35114
H	-0.02456	-2.18790	-2.66045
C	-2.07109	-2.84331	-0.00090
H	-1.55679	-2.70495	2.06117
H	-2.32663	-2.90911	-2.16060
H	-3.06682	-3.23405	0.19232

A^{2}: M06L/6-31G(2df,2pd)(SDD) SCF= -1951.046237 hartree
Gibbs correction= 0.48274 hartree
Total Gibbs Energy= -1950.563497 hartree

C	4.71780	3.58505	-0.53853
C	4.38665	2.25490	-0.48175
C	3.06057	1.82526	-0.20651

C	2.03054	2.80488	0.02529
C	2.42470	4.17688	-0.03347
C	3.71506	4.55131	-0.30868
H	5.73649	3.88916	-0.75607
H	5.14556	1.49945	-0.65250
H	1.64329	4.91008	0.14413
H	3.96711	5.60877	-0.35139
O	0.79631	2.56257	0.29122
C	2.77384	0.42817	-0.13304
O	1.67624	-0.14545	0.06630
O	3.87202	-0.35713	-0.31873
C	3.77828	-1.73365	-0.16478
C	4.12498	-2.52218	-1.25511
C	3.43820	-2.29814	1.06004
C	4.11903	-3.90762	-1.11800
H	4.38971	-2.04349	-2.19249
C	3.43187	-3.68411	1.18209
H	3.16960	-1.65817	1.89435
C	3.76808	-4.49141	0.09674
H	4.38551	-4.53076	-1.96687
H	3.15799	-4.13277	2.13327
H	3.75997	-5.57241	0.19945
Ir	-0.26958	0.74440	0.25920
P	-1.35210	-1.22302	0.09963
C	-0.79383	-2.27220	-1.39604
C	-1.37676	-2.30025	1.66461
C	-1.85189	-3.25120	-1.90933
H	-2.73042	-2.73763	-2.30794
H	-1.41460	-3.83459	-2.72929
H	-2.18771	-3.96504	-1.15181
C	-0.49790	-1.26832	-2.51675
H	0.34185	-0.61424	-2.26281
H	-0.24774	-1.81581	-3.43457
H	-1.36209	-0.62872	-2.73155
C	0.48757	-3.04192	-1.07588
H	1.25553	-2.40182	-0.63592
H	0.31320	-3.88559	-0.40069
H	0.89624	-3.45798	-2.00565
C	0.05425	-2.36633	2.20694
H	0.72660	-2.92937	1.55517
H	0.47091	-1.36005	2.32954

H	0.04797	-2.86032	3.18713
C	-1.91865	-3.71828	1.49019
H	-1.90162	-4.22693	2.46257
H	-2.95594	-3.73522	1.14275
H	-1.31625	-4.31926	0.80393
C	-2.23458	-1.56221	2.69544
H	-2.25293	-2.13727	3.62916
H	-1.81200	-0.57834	2.92173
H	-3.26979	-1.42878	2.36377
C	-3.08041	-0.79932	-0.30977
C	-4.16344	-1.67637	-0.44992
C	-3.25980	0.56739	-0.57626
C	-5.39763	-1.21589	-0.89538
H	-4.03810	-2.73504	-0.24146
C	-4.49987	1.01621	-1.04732
C	-5.55825	0.13167	-1.21374
H	-6.22688	-1.90875	-1.00735
H	-4.62970	2.07682	-1.25224
H	-6.51620	0.49523	-1.57596
C	-2.19669	1.56163	-0.24388
C	-1.93122	1.76052	1.17811
C	-2.07037	2.72064	-1.10707
C	-1.67180	3.09181	1.65943
H	-2.41705	1.08528	1.88146
C	-1.74275	3.94515	-0.60771
H	-2.27003	2.58846	-2.16911
C	-1.56626	4.13998	0.79537
H	-1.57294	3.24625	2.73079
H	-1.63764	4.79352	-1.27923
H	-1.36129	5.13935	1.17065

TS1_JohnPhos: M06L/6-31G(2df,2pd)(SDD) SCF= -1951.001626 hartree
Gibbs correction= 0.485174 hartree
Total Gibbs Energy= -1950.516452 hartree

C	5.03665	-1.51248	1.48354
C	3.88781	-0.79653	1.79394
C	2.95187	-0.51802	0.79461
C	3.10968	-1.00135	-0.52734
C	4.30022	-1.69431	-0.82928
C	5.23463	-1.94326	0.16593
H	5.77566	-1.72437	2.24967
H	3.70382	-0.43028	2.80084

H	4.44191	-2.05803	-1.84298
H	6.13350	-2.50347	-0.08286
O	2.15536	-0.85470	-1.41134
C	1.76567	0.27337	1.10943
O	1.33459	0.62877	2.17857
O	1.61762	1.36350	-0.18105
C	1.60358	2.71466	-0.02911
C	2.12973	3.34493	1.10238
C	1.13268	3.47767	-1.10140
C	2.13495	4.73518	1.16290
H	2.50696	2.75053	1.92684
C	1.14778	4.86556	-1.02630
H	0.78619	2.95903	-1.99184
C	1.63731	5.50312	0.11234
H	2.53474	5.22204	2.04853
H	0.78057	5.44993	-1.86613
H	1.64368	6.58711	0.17441
Ir	0.28264	-0.28944	-0.61016
P	-1.85832	0.42373	-0.05865
C	-2.17467	1.46806	1.50929
C	-2.71783	1.22069	-1.56142
C	-3.59940	2.01060	1.62319
H	-4.35988	1.22562	1.61211
H	-3.69061	2.52460	2.58783
H	-3.84038	2.74430	0.84897
C	-1.90018	0.54900	2.70731
H	-0.92804	0.05350	2.62399
H	-1.87421	1.16071	3.61657
H	-2.67756	-0.20994	2.83568
C	-1.18865	2.63264	1.57324
H	-0.17131	2.26695	1.69955
H	-1.21874	3.29048	0.70041
H	-1.42495	3.24449	2.45242
C	-2.36024	2.70512	-1.63923
H	-2.84649	3.29487	-0.85743
H	-1.28314	2.87792	-1.56567
H	-2.69617	3.10441	-2.60388
C	-4.23864	1.06471	-1.59138
H	-4.62292	1.57185	-2.48509
H	-4.53925	0.01586	-1.66075
H	-4.73778	1.51310	-0.72852

C	-2.15899	0.51855	-2.80392
H	-2.58713	0.97755	-3.70347
H	-1.06630	0.59388	-2.86711
H	-2.42570	-0.54389	-2.82145
C	-2.77180	-1.10594	0.35856
C	-4.13206	-1.22064	0.67896
C	-1.92497	-2.19999	0.58618
C	-4.63295	-2.38382	1.25357
H	-4.81016	-0.39335	0.50399
C	-2.43331	-3.35909	1.18450
C	-3.77636	-3.44765	1.52711
H	-5.68813	-2.45095	1.50249
H	-1.76364	-4.19893	1.35489
H	-4.15867	-4.35180	1.99265
C	-0.52170	-2.20930	0.08756
C	-0.35577	-2.22487	-1.35696
C	0.47039	-2.91160	0.87091
C	0.66226	-3.05922	-1.93730
H	-1.24238	-2.04259	-1.96576
C	1.47095	-3.62168	0.27325
H	0.38635	-2.87091	1.95538
C	1.53985	-3.73940	-1.14613
H	0.71228	-3.14284	-3.01897
H	2.21843	-4.12113	0.88439
H	2.30919	-4.36424	-1.59037

B[1]: M06L/6-31G(2df,2pd)(SDD) SCF= -1951.04452 hartree
Gibbs correction= 0.482915 hartree
Total Gibbs Energy= -1950.561605 hartree

C	-4.44817	1.79296	1.98608
C	-3.11069	1.53074	2.20486
C	-2.28863	1.16959	1.12195
C	-2.80285	1.08090	-0.19601
C	-4.17355	1.36209	-0.39835
C	-4.96665	1.70299	0.67931
H	-5.09788	2.06631	2.81176
H	-2.67306	1.58698	3.19792
H	-4.57967	1.27617	-1.40151
H	-6.02308	1.90343	0.51418
O	-2.00384	0.75931	-1.17506
C	-0.87619	0.87498	1.29929
O	-0.21268	1.08405	2.28991

O	-0.96684	-1.77330	-0.26191
C	-2.30208	-1.96297	-0.23149
C	-2.97156	-2.07828	0.99550
C	-3.03191	-2.11288	-1.41990
C	-4.33701	-2.34047	1.03052
H	-2.40210	-1.94481	1.91317
C	-4.39505	-2.37792	-1.37645
H	-2.50746	-1.99829	-2.36511
C	-5.05629	-2.49095	-0.15333
H	-4.84305	-2.41865	1.98973
H	-4.94921	-2.48957	-2.30552
H	-6.12375	-2.69083	-0.12427
Ir	-0.13500	0.08479	-0.45415
P	1.88962	-0.92344	0.10010
C	1.91791	-2.11088	1.60065
C	2.62669	-1.85832	-1.40500
C	3.30293	-2.29445	2.22643
H	3.67062	-1.36746	2.67422
H	3.20971	-3.02817	3.03608
H	4.06146	-2.67311	1.53759
C	1.00975	-1.52257	2.67784
H	-0.02600	-1.46739	2.33632
H	1.04652	-2.18190	3.55348
H	1.31518	-0.52211	2.98787
C	1.33189	-3.47228	1.20991
H	0.34821	-3.36126	0.74650
H	1.97803	-4.05187	0.54647
H	1.21003	-4.05987	2.12777
C	1.53514	-2.73141	-2.03463
H	1.16830	-3.51755	-1.37401
H	0.66529	-2.13529	-2.32951
H	1.94180	-3.20842	-2.93488
C	3.84944	-2.71270	-1.06269
H	4.21243	-3.18342	-1.98444
H	4.67581	-2.11417	-0.66607
H	3.63431	-3.51637	-0.35702
C	3.06533	-0.84646	-2.46878
H	3.59798	-1.38367	-3.26194
H	2.20786	-0.36493	-2.94417
H	3.73811	-0.07425	-2.08252
C	3.02721	0.46938	0.40957

C	4.37564	0.32979	0.76921
C	2.49099	1.76186	0.23333
C	5.17614	1.43937	1.01170
H	4.80616	-0.65993	0.87707
C	3.31106	2.86888	0.49723
C	4.63374	2.71529	0.89078
H	6.21482	1.30597	1.29961
H	2.89680	3.86504	0.36197
H	5.24503	3.59204	1.08528
C	1.12216	2.04734	-0.29596
C	0.78456	1.72702	-1.66473
C	0.41170	3.14935	0.29808
C	-0.17148	2.52074	-2.36841
H	1.52687	1.20250	-2.25898
C	-0.56206	3.83031	-0.38223
H	0.65813	3.41970	1.32101
C	-0.84971	3.52576	-1.73606
H	-0.36043	2.29853	-3.41444
H	-1.09811	4.63531	0.11250
H	-1.59845	4.10274	-2.27065

B^{2}: M06L/6-31G(2df,2pd)(SDD) SCF= -1951.044223 hartree
Gibbs correction= 0.482944 hartree
Total Gibbs Energy= -1950.561279 hartree

C	-2.41607	4.38286	-1.90133
C	-1.68432	3.27847	-2.30010
C	-1.25690	2.34964	-1.33967
C	-1.55341	2.52559	0.02897
C	-2.29095	3.65786	0.42271
C	-2.71116	4.56060	-0.53950
H	-2.76132	5.10676	-2.63268
H	-1.43304	3.10669	-3.34291
H	-2.52387	3.79624	1.47368
H	-3.28662	5.42971	-0.22921
O	-1.08720	1.65969	0.90698
C	-0.44992	1.17826	-1.68556
O	0.04782	0.94293	-2.76039
O	-2.41338	-0.35199	-0.49782
C	-3.12400	-0.97804	0.42681
C	-2.68068	-1.17799	1.75377
C	-4.37944	-1.52141	0.07567
C	-3.43162	-1.91816	2.66309

H	-1.74428	-0.71681	2.07414
C	-5.12347	-2.24677	0.99389
H	-4.73077	-1.37038	-0.94164
C	-4.65722	-2.46469	2.29357
H	-3.05540	-2.05635	3.67480
H	-6.08234	-2.66089	0.68874
H	-5.24471	-3.03816	3.00415
Ir	-0.38393	-0.03075	-0.04405
P	1.78095	0.33247	0.70280
C	2.62724	2.00637	0.35995
C	1.85161	-0.03921	2.57603
C	4.15070	1.99661	0.52589
H	4.63920	1.40945	-0.25565
H	4.50393	3.02927	0.42006
H	4.49762	1.63734	1.49660
C	2.34440	2.38508	-1.09712
H	1.32113	2.73576	-1.23666
H	3.00976	3.21006	-1.37694
H	2.52313	1.56102	-1.79521
C	2.01780	3.07566	1.27045
H	0.92411	3.03757	1.27499
H	2.37342	2.99352	2.30208
H	2.32049	4.06350	0.90373
C	0.74626	0.74038	3.29830
H	0.90610	1.81958	3.29311
H	-0.24108	0.56008	2.86596
H	0.72190	0.41472	4.34533
C	3.18938	0.27186	3.24685
H	3.12878	-0.03275	4.29876
H	4.02848	-0.27450	2.80622
H	3.42306	1.33941	3.23850
C	1.54766	-1.52993	2.75693
H	1.64571	-1.78693	3.81785
H	0.51612	-1.76331	2.46999
H	2.22698	-2.17816	2.19279
C	2.81870	-0.91170	-0.14360
C	4.18645	-1.10842	0.09857
C	2.18797	-1.66213	-1.15563
C	4.94002	-1.97705	-0.68127
H	4.67898	-0.55759	0.89250
C	2.96916	-2.51138	-1.95312

C	4.33116	-2.66105	-1.72973
H	5.99910	-2.10695	-0.47886
H	2.47872	-3.08578	-2.73523
H	4.91184	-3.32951	-2.35908
C	0.71005	-1.72841	-1.35256
C	-0.08757	-2.32280	-0.31926
C	0.19948	-1.80912	-2.68633
C	-1.28815	-3.00943	-0.63662
H	0.39105	-2.54339	0.63216
C	-1.00671	-2.40462	-2.95337
H	0.79029	-1.38115	-3.48900
C	-1.75527	-3.01972	-1.92657
H	-1.84430	-3.49250	0.16125
H	-1.37597	-2.42839	-3.97461
H	-2.69270	-3.51534	-2.16099

B^3: M06L/6-31G(2df,2pd)(SDD) SCF= -1951.030452 hartree
Gibbs correction= 0.477892 hartree
Total Gibbs Energy= -1950.55256 hartree

C	-4.22314	-2.83656	-0.98025
C	-3.41046	-2.49141	0.08640
C	-2.29338	-1.67433	-0.12692
C	-1.98991	-1.18846	-1.41862
C	-2.81310	-1.55341	-2.49797
C	-3.91107	-2.36661	-2.26477
H	-5.09998	-3.45743	-0.82609
H	-3.62401	-2.82338	1.09866
H	-2.58101	-1.18162	-3.49118
H	-4.55003	-2.63761	-3.10212
O	-0.93175	-0.40793	-1.59956
C	-1.39160	-1.23097	0.94344
O	-1.45149	-1.55906	2.11620
O	-1.61339	1.56296	0.76859
C	-2.94225	1.40929	0.72158
C	-3.63339	1.49681	-0.50055
C	-3.67518	1.17334	1.89689
C	-5.01323	1.33854	-0.54097
H	-3.05730	1.65739	-1.40928
C	-5.05720	1.03421	1.84575
H	-3.13331	1.09491	2.83540
C	-5.73570	1.11091	0.63000
H	-5.52922	1.38781	-1.49741

H	-5.60977	0.85193	2.76466
H	-6.81460	0.98957	0.59449
Ir	-0.19693	0.18920	0.22890
P	1.83323	-0.90256	0.14472
C	2.35609	-1.11517	1.96660
C	2.00180	-2.52154	-0.82658
C	3.86223	-1.22545	2.19572
H	4.39842	-0.31826	1.90543
H	4.04273	-1.38797	3.26523
H	4.30958	-2.07036	1.66250
C	1.84269	0.16203	2.64657
H	0.74371	0.24283	2.59210
H	2.09313	0.14558	3.71452
H	2.28774	1.06669	2.21510
C	1.65846	-2.32352	2.59250
H	0.57389	-2.28568	2.47292
H	2.02987	-3.27125	2.19228
H	1.86695	-2.32862	3.66925
C	0.70735	-3.31227	-0.60717
H	0.51058	-3.52963	0.44704
H	-0.15532	-2.78113	-1.00904
H	0.78396	-4.27048	-1.13420
C	3.17385	-3.43709	-0.45974
H	3.09488	-4.34900	-1.06389
H	4.15801	-3.01358	-0.66873
H	3.15382	-3.74755	0.58812
C	2.07750	-2.12932	-2.30561
H	2.02312	-3.03438	-2.92204
H	1.23423	-1.48673	-2.58329
H	3.00871	-1.61075	-2.55357
C	3.15377	0.24360	-0.45731
C	4.45730	-0.22250	-0.68820
C	2.92749	1.63625	-0.51361
C	5.52084	0.63868	-0.92350
H	4.65808	-1.28597	-0.64409
C	4.02053	2.49649	-0.70510
C	5.30554	2.01271	-0.90401
H	6.51422	0.23548	-1.09729
H	3.83057	3.56661	-0.73749
H	6.12855	2.70381	-1.06187
C	1.59276	2.28728	-0.50767

C	0.71444	2.05111	-1.58475
C	1.30275	3.34624	0.37277
C	-0.40135	2.86584	-1.78170
H	0.95358	1.27334	-2.30593
C	0.17197	4.12847	0.18887
H	1.98412	3.54866	1.19681
C	-0.67622	3.89724	-0.89543
H	-1.06013	2.66724	-2.62205
H	-0.05019	4.92656	0.89101
H	-1.56036	4.51255	-1.03426

5.1: M06/6-311+G(2df,2pd) SCF= -726.8597914 hartree (solvent=toluene)
SCF= -727.2540142 hartree (solvent=*m*-xylene)
SCF= -727.2542687 hartree (solvent=anisole)
Gibbs correction= 0.131313 hartree
Total Gibbs Energy= -726.7284784 hartree (solvent=toluene)
Total Gibbs Energy= -726.7279334 hartree (solvent=*m*-xylene)
Total Gibbs Energy= -726.7285541 hartree (solvent=anisole)

C	3.28711	-1.83403	0.38223
C	1.97347	-1.41953	0.30055
C	1.65280	-0.08282	0.01398
C	2.69490	0.85046	-0.19325
C	4.02400	0.41861	-0.10841
C	4.31059	-0.90252	0.17495
H	3.52307	-2.87052	0.60478
H	1.16113	-2.12303	0.45744
H	4.80640	1.15430	-0.27218
H	5.34941	-1.21914	0.23667
O	2.48248	2.13802	-0.46957
H	1.51214	2.28362	-0.49589
C	0.26817	0.37932	-0.07583
O	-0.06444	1.52984	-0.31478
O	-0.62923	-0.60866	0.12993
C	-1.99135	-0.33021	0.07779
C	-2.75286	-1.11561	-0.77433
C	-2.57105	0.62439	0.90220
C	-4.13119	-0.93752	-0.80641
H	-2.25630	-1.85569	-1.39595
C	-3.94945	0.79482	0.85655
H	-1.95024	1.22487	1.55951
C	-4.73109	0.01828	0.00632
H	-4.73629	-1.54948	-1.47049

H	-4.41531	1.54178	1.49430
H	-5.80865	0.15780	-0.02088

Phenol: M06/6-311+G(2df,2pd) SCF= -307.3610449 hartree (solvent=toluene)
SCF= -307.3607256 hartree (solvent=*m*-xylene)
SCF= -307.3616898 hartree (solvent=anisole)
Gibbs correction= 0.057062 hartree
Total Gibbs Energy= -307.3039829 hartree (solvent=toluene)
Total Gibbs Energy= -307.3036636 hartree (solvent=*m*-xylene)
Total Gibbs Energy= -307.3046278 hartree (solvent=anisole)

C	-1.84960	0.02861	-0.00001
C	-1.12577	1.21503	0.00001
C	0.26488	1.19483	0.00000
C	0.93821	-0.02520	-0.00003
C	0.22021	-1.22027	-0.00002
C	-1.16681	-1.18560	-0.00001
H	-2.93606	0.04809	-0.00001
H	-1.64429	2.17113	0.00003
H	0.83059	2.12677	0.00002
H	0.76984	-2.15782	-0.00002
H	-1.72179	-2.12103	-0.00001
O	2.29364	-0.11112	0.00002
H	2.66581	0.77738	0.00018

5.2am1: M06/6-311+G(2df,2pd) SCF= -690.9262895 hartree
Gibbs correction= 0.152768 hartree
Total Gibbs Energy= -690.7735215 hartree

C	3.70908	-0.34404	0.08096
C	2.72351	-1.08341	0.73485
C	1.38895	-0.70210	0.68296
C	1.00988	0.44631	-0.01686
C	2.00018	1.21239	-0.64062
C	3.32490	0.81283	-0.60467
H	3.00882	-1.96968	1.29961
H	0.64253	-1.28053	1.22249
H	1.70581	2.12691	-1.14935
H	4.08503	1.41018	-1.10651
C	5.14300	-0.77678	0.10076
H	5.34369	-1.47257	0.92162
H	5.41400	-1.28490	-0.83344
H	5.81808	0.07955	0.20628
C	-0.38399	0.96451	-0.03827

O	-0.54729	2.19193	-0.00155
C	-1.53693	0.05519	-0.09559
C	-1.42159	-1.29544	-0.47349
C	-2.82985	0.56482	0.19248
C	-2.51898	-2.13207	-0.51467
H	-0.44541	-1.67563	-0.76288
C	-3.93249	-0.29819	0.17973
C	-3.77569	-1.62549	-0.16764
H	-2.40722	-3.16876	-0.81886
H	-4.90399	0.12038	0.42769
H	-4.64624	-2.27748	-0.18718
O	-3.05417	1.84297	0.49011
H	-2.20326	2.32217	0.35240

Toluene: M06/6-311+G(2df,2pd) SCF= -271.4333762 hartree
Gibbs correction= 0.077331 hartree
Total Gibbs Energy= -271.3560452 hartree

C	-0.91036	0.00015	-0.01085
C	-0.19490	-1.19813	-0.00887
C	1.19497	-1.20124	0.00201
C	1.89595	-0.00012	0.00823
C	1.19523	1.20110	0.00200
C	-0.19470	1.19825	-0.00886
H	-0.73984	-2.14175	-0.01784
H	1.73313	-2.14657	0.00120
H	2.98334	-0.00024	0.01337
H	1.73355	2.14634	0.00120
H	-0.73943	2.14197	-0.01781
C	-2.40930	0.00007	0.00928
H	-2.81874	-0.88289	-0.49347
H	-2.79464	-0.00701	1.03724
H	-2.81870	0.88971	-0.48151

5.2aa1: M06/6-311+G(2df,2pd) SCF= -730.2228341 hartree
Gibbs correction= 0.173112 hartree
Total Gibbs Energy= -730.0497221 hartree

C	3.49408	0.52428	-0.01762
C	2.49875	1.37205	-0.50213
C	1.18564	0.90592	-0.53239
C	0.87833	-0.38634	-0.09995
C	1.90031	-1.22297	0.35104
C	3.21508	-0.77261	0.41632

C	2.83433	2.75828	-0.96595
H	0.40196	1.54499	-0.93676
H	1.65081	-2.24087	0.64513
C	4.30621	-1.65427	0.94562
C	-0.49069	-0.96414	-0.20361
O	-0.59515	-2.14948	-0.54671
C	-1.68370	-0.15832	0.08907
C	-1.62148	1.06833	0.77596
C	-2.95905	-0.65448	-0.28790
C	-2.75637	1.80903	1.03890
H	-0.65505	1.42291	1.12433
C	-4.10164	0.11767	-0.04453
C	-3.99803	1.33029	0.60793
H	-2.68531	2.74879	1.57889
H	-5.05929	-0.28287	-0.36545
H	-4.89823	1.90948	0.80172
O	-3.13029	-1.83404	-0.88072
H	-2.25134	-2.28188	-0.88566
H	4.52523	0.88123	0.00952
H	3.80172	2.78630	-1.47900
H	2.89778	3.45601	-0.12131
H	2.07545	3.14695	-1.65274
H	4.06133	-2.71374	0.81929
H	4.46942	-1.48344	2.01725
H	5.25846	-1.46201	0.43961

5.2aa2: M06/6-311+G(2df,2pd) SCF= -730.2217552 hartree
Gibbs correction= 0.175089 hartree
Total Gibbs Energy= -730.0466662 hartree

C	-3.53890	-0.71199	-0.19262
C	-2.51294	-1.40520	-0.83139
C	-1.21523	-0.91612	-0.80010
C	-0.91102	0.28578	-0.15493
C	-1.93965	1.01828	0.46984
C	-3.22642	0.48735	0.44915
H	-2.73244	-2.33397	-1.35534
H	-0.42277	-1.46033	-1.31000
C	-1.69617	2.32939	1.15649
H	-4.02467	1.03880	0.94826
C	-4.93893	-1.24484	-0.17220
H	-5.67684	-0.43673	-0.21915
H	-5.12292	-1.92455	-1.01055

H	-5.13410	-1.80531	0.75098
C	0.47044	0.83540	-0.23566
O	0.62027	2.02828	-0.53489
C	1.63340	-0.02677	0.01734
C	1.51709	-1.29232	0.62182
C	2.93053	0.44505	-0.31335
C	2.62112	-2.08771	0.85374
H	0.53155	-1.63558	0.92566
C	4.04222	-0.37900	-0.09889
C	3.88602	-1.62532	0.47501
H	2.50847	-3.05814	1.32841
H	5.01824	0.00606	-0.38114
H	4.76258	-2.24655	0.64566
O	3.15057	1.65038	-0.83395
H	2.28421	2.12237	-0.83740
H	-2.55686	2.60407	1.77442
H	-1.52168	3.12693	0.42757
H	-0.80880	2.30172	1.79785

***m*-xylene**: M06/6-311+G(2df,2pd) SCF= -310.7307118 hartree
Gibbs correction= 0.097228 hartree
Total Gibbs Energy= -310.6334838 hartree

C	0.00091	-0.94755	-0.01892
C	-1.21848	-0.27182	-0.00957
C	-1.20543	1.12393	-0.00036
C	-0.00140	1.81684	0.00467
C	1.20461	1.12553	-0.00072
C	1.21999	-0.26923	-0.00986
C	-2.51483	-1.02606	0.01003
H	-2.14967	1.66736	-0.00372
H	2.14769	1.67084	-0.00418
C	2.51531	-1.02521	0.01022
H	0.00211	-2.03905	-0.03732
H	-2.40573	-2.02608	-0.42312
H	-3.29554	-0.49807	-0.54863
H	-2.88486	-1.15535	1.03532
H	3.32310	-0.45165	-0.45698
H	2.43087	-1.98235	-0.51600
H	2.83003	-1.24899	1.03772
H	-0.00214	2.90478	0.00395

5.2ag: M06/6-311+G(2df,2pd) SCF= -880.6307319 hartree

Gibbs correction= 0.182822 hartree

Total Gibbs Energy= -880.4479099 hartree

C	-2.85483	-0.72818	-0.17001
C	-1.80265	-1.56068	-0.52923
C	-0.49067	-1.08952	-0.51720
C	-0.22113	0.22639	-0.15715
C	-1.28858	1.08005	0.17027
C	-2.59037	0.61866	0.18456
H	-1.99735	-2.58547	-0.82972
H	0.31272	-1.74916	-0.83307
H	-1.05495	2.11415	0.40406
C	1.13222	0.83000	-0.21483
O	1.22610	2.02846	-0.52011
C	2.34000	0.03929	0.07115
C	2.30584	-1.17526	0.78002
C	3.60273	0.54426	-0.33436
C	3.45365	-1.90187	1.02926
H	1.35201	-1.52983	1.16126
C	4.75717	-0.21506	-0.10860
C	4.68023	-1.42017	0.56187
H	3.40332	-2.83187	1.58824
H	5.70373	0.19086	-0.45484
H	5.59006	-1.98816	0.74340
O	3.75120	1.72091	-0.94090
H	2.87241	2.16754	-0.91283
O	-4.15108	-1.09319	-0.13578
O	-3.67452	1.35660	0.50911
C	-4.46801	-2.41894	-0.48575
H	-5.55096	-2.51234	-0.38879
H	-4.17924	-2.64425	-1.52197
H	-3.98284	-3.14182	0.18513
C	-3.45908	2.70606	0.84496
H	-4.44040	3.12840	1.06829
H	-2.81428	2.80571	1.72965
H	-3.00700	3.26381	0.01286

1,2-Dimethoxybenzene: M06/6-311+G(2df,2pd) SCF= -461.1355502 hartree

Gibbs correction= 0.107085 hartree

Total Gibbs Energy= -461.0284652 hartree

C	0.70676	-0.13563	-0.00001
C	1.39023	1.07219	0.00009
C	0.69086	2.28236	0.00006

C	-0.69085	2.28236	-0.00008
C	-1.39023	1.07220	-0.00017
C	-0.70676	-0.13563	-0.00012
H	2.47620	1.08160	0.00021
H	1.24345	3.21834	0.00014
H	-2.47620	1.08161	-0.00032
O	1.29036	-1.35862	0.00002
O	-1.29036	-1.35862	-0.00022
C	2.69315	-1.40533	-0.00011
H	2.96834	-2.46200	-0.00027
H	3.11809	-0.92515	-0.89390
H	3.11826	-0.92538	0.89372
C	-2.69315	-1.40533	0.00041
H	-3.11858	-0.92553	-0.89336
H	-2.96834	-2.46199	0.00084
H	-3.11777	-0.92498	0.89427
H	-1.24344	3.21835	-0.00013

4-CN-Phenyl Salicylate: M06/6-311+G(2df,2pd) SCF= -819.0748187 hartree
Gibbs correction= 0.124872 hartree
Total Gibbs Energy= -818.9499467 hartree

C	3.96063	-1.81244	0.38271
C	2.64500	-1.40946	0.29217
C	2.31565	-0.07311	0.00791
C	3.35193	0.87025	-0.18745
C	4.68366	0.44844	-0.09408
C	4.97814	-0.87106	0.18664
H	4.20394	-2.84742	0.60360
H	1.83855	-2.12140	0.44056
H	5.46131	1.19093	-0.24884
H	6.01882	-1.17954	0.25551
O	3.13344	2.15696	-0.45981
H	2.16457	2.30225	-0.49282
C	0.93238	0.37923	-0.08868
O	0.58403	1.52550	-0.31892
O	0.03671	-0.62434	0.09811
C	-1.32041	-0.36684	0.06347
C	-2.08652	-1.22585	-0.71447
C	-1.90386	0.63549	0.83115
C	-3.46404	-1.08117	-0.73401
H	-1.58898	-1.99910	-1.29239
C	-3.28138	0.78049	0.80627

H	-1.28659	1.29401	1.43194
C	-4.06804	-0.07405	0.02572
H	-4.08006	-1.74359	-1.33547
H	-3.75987	1.55742	1.39585
C	-5.49008	0.07887	0.00886
N	-6.64621	0.20124	-0.00431

4-CN-Phenol: M06/6-311+G(2df,2pd) SCF= -399.5793369 hartree
Gibbs correction= 0.050721 hartree
Total Gibbs Energy= -399.5286159 hartree

O	-3.05674	0.08613	0.00004
C	-1.70886	0.01507	0.00000
C	-1.01947	-1.19898	0.00000
C	-1.00679	1.22261	0.00001
C	0.36540	-1.20573	-0.00001
H	-1.57121	-2.13806	0.00001
C	0.37480	1.21250	-0.00001
H	-1.56846	2.15218	0.00004
C	1.07621	-0.00134	-0.00002
H	0.90823	-2.14718	-0.00001
H	0.92861	2.14755	-0.00001
C	2.50438	-0.00924	-0.00003
N	3.66753	-0.01575	-0.00005
H	-3.42999	-0.80264	0.00031

1,5-COD: M06/6-311+G(2df,2pd) SCF= -311.8774299 hartree
Gibbs correction= 0.125668 hartree
Total Gibbs Energy= -311.7517619 hartree

C	-0.87180	-1.62825	-0.20369
C	0.38594	-1.80649	0.20308
C	-0.38594	1.80649	-0.20308
C	1.23538	-0.79657	0.92254
C	0.87180	1.62825	0.20369
C	1.69213	0.38177	0.02399
H	-1.34914	-2.44607	-0.74545
H	0.69032	-0.38832	1.78669
H	-0.86279	2.75965	0.03001
H	1.34914	2.44607	0.74545
H	0.86279	-2.75965	-0.03001
H	2.11733	-1.30381	1.33162
H	2.74192	0.61547	0.23803
H	1.66047	0.05398	-1.02578

C	-1.69213	-0.38177	-0.02399
H	-1.66047	-0.05398	1.02578
H	-2.74192	-0.61547	-0.23803
C	-1.23538	0.79657	-0.92254
H	-0.69032	0.38832	-1.78669
H	-2.11733	1.30381	-1.33162

JohnPhos: M06/6-311+G(2df,2pd) SCF= -1119.378626 hartree
Gibbs correction= 0.326213 hartree
Total Gibbs Energy= -1119.052413 hartree

C	1.04207	3.63443	-0.02039
C	1.83708	2.50045	-0.07873
C	1.28150	1.21620	-0.15694
C	-0.12301	1.06666	-0.14250
C	-0.90305	2.22991	-0.07990
C	-0.34079	3.49856	-0.02971
H	1.50015	4.61965	0.02565
H	2.92156	2.59596	-0.09035
H	-1.98623	2.14322	-0.05645
H	-0.98252	4.37564	0.01266
C	2.24021	0.08304	-0.24089
C	3.20034	-0.08555	0.76028
C	2.26024	-0.78365	-1.33730
C	4.14320	-1.10473	0.68061
H	3.19222	0.58639	1.61787
C	3.20690	-1.79532	-1.42395
H	1.52815	-0.65079	-2.13140
C	4.14904	-1.96243	-0.41297
H	4.87554	-1.22671	1.47545
H	3.21077	-2.45680	-2.28716
H	4.88712	-2.75826	-0.48017
P	-0.84477	-0.64883	-0.11571
C	-2.37566	-0.57625	-1.26326
C	-1.39925	-0.77225	1.70719
C	-2.17481	-2.07863	1.87261
H	-2.32722	-2.28403	2.94207
H	-3.16713	-2.03641	1.40672
H	-1.62992	-2.92970	1.44338
C	-0.08691	-0.89016	2.48844
H	0.52976	-1.72260	2.12692
H	0.50970	0.02855	2.41664
H	-0.30583	-1.06176	3.55238

C	-2.20340	0.38238	2.29396
H	-3.17355	0.51757	1.80466
H	-2.40008	0.18068	3.35775
H	-1.65500	1.32963	2.23820
C	-2.66528	-2.04135	-1.61459
H	-2.97991	-2.62489	-0.74137
H	-3.47658	-2.09193	-2.35548
H	-1.78223	-2.53093	-2.04203
C	-3.67387	0.05483	-0.76679
H	-4.43196	-0.01292	-1.56182
H	-4.08068	-0.46782	0.10683
H	-3.57479	1.11567	-0.51301
C	-1.92691	0.12476	-2.54684
H	-2.69264	-0.00928	-3.32455
H	-1.77304	1.20011	-2.40626
H	-0.99005	-0.30123	-2.93148

[Ir(cod)OMe]$_2$: M06/6-311+G(2df,2pd) SCF= -1062.861165 hartree
Gibbs correction= 0.354007 hartree
Total Gibbs Energy= -1062.507158 hartree

C	-2.38710	-1.53960	0.78926
C	-3.11775	-1.33066	-0.41590
C	-2.60995	1.18157	1.15818
C	-4.49449	-0.68514	-0.45268
C	-3.11722	1.41569	-0.15200
C	-4.39592	0.82453	-0.70216
H	-1.68023	-2.37694	0.80006
H	-5.09388	-1.15007	-1.24426
H	-1.95295	1.95053	1.57498
H	-2.82162	2.35123	-0.63855
H	-2.91210	-2.01904	-1.24096
H	-5.02967	-0.89326	0.48320
H	-4.39677	1.00803	-1.78482
H	-5.27764	1.34924	-0.29973
C	-2.84089	-1.11497	2.16751
H	-1.97215	-1.20737	2.83376
H	-3.60765	-1.80219	2.56065
C	-3.33548	0.33535	2.19314
H	-4.41895	0.38272	2.02226
H	-3.17537	0.76129	3.19076
C	2.38707	-1.53957	0.78933
C	3.11773	-1.33070	-0.41585

C	2.60998	1.18162	1.15813
C	4.49447	-0.68520	-0.45266
C	3.11724	1.41566	-0.15207
C	4.39592	0.82446	-0.70221
H	1.68019	-2.37690	0.80017
H	5.02965	-0.89329	0.48323
H	1.95300	1.95061	1.57490
H	2.82165	2.35118	-0.63866
H	2.91205	-2.01911	-1.24087
H	5.09385	-1.15019	-1.24422
H	5.27765	1.34917	-0.29981
H	4.39677	1.00791	-1.78487
C	2.84089	-1.11489	2.16756
H	3.60764	-1.80211	2.56071
H	1.97215	-1.20724	2.83382
C	3.33551	0.33542	2.19312
H	3.17542	0.76140	3.19071
H	4.41898	0.38276	2.02221
Ir	1.52042	0.05341	-0.26608
Ir	-1.52042	0.05341	-0.26609
O	-0.00000	-1.06833	-1.19045
O	0.00000	1.45237	-0.73462
C	0.00000	-2.45030	-1.40191
H	-0.88771	-2.74248	-1.98116
H	0.88761	-2.74244	-1.98134
H	0.00011	-3.03174	-0.46408
C	0.00000	2.78099	-0.29522
H	0.88536	3.30911	-0.67821
H	-0.88525	3.30917	-0.67837
H	-0.00009	2.86717	0.80461

Methanol: M06/6-311+G(2df,2pd) SCF= -115.6994043 hartree
Gibbs correction= 0.014923 hartree
Total Gibbs Energy= -115.6844813 hartree

O	0.74282	0.12181	0.00000
C	-0.65401	-0.01982	0.00000
H	-1.03449	-0.54284	0.89145
H	-1.03449	-0.54283	-0.89145
H	-1.08163	0.98716	0.00000
H	1.13208	-0.75705	-0.00000

IX: M06/6-311+G(2df,2pd) SCF= -535.2118099 hartree

Gibbs correction= 0.089783 hartree
Total Gibbs Energy= -535.1220269 hartree

C	2.89134	-0.67350	-0.00045
C	1.97782	-1.73326	-0.00007
C	0.62554	-1.45557	0.00030
C	0.15908	-0.13209	0.00034
C	1.09008	0.93113	-0.00003
C	2.45918	0.63871	-0.00043
H	3.95914	-0.88102	-0.00075
H	2.32752	-2.76153	-0.00008
H	-0.10487	-2.25956	0.00058
H	3.15515	1.47297	-0.00070
C	-1.27107	0.18151	0.00069
O	-1.73054	1.31823	-0.00016
O	-2.06167	-0.89671	0.00026
O	0.73312	2.21685	0.00006
H	-0.24825	2.25371	0.00053
C	-3.46089	-0.62718	-0.00030
H	-3.74434	-0.05501	-0.88847
H	-3.95304	-1.59998	-0.00052
H	-3.74505	-0.05505	0.88768

I: M06/6-311+G(2df,2pd) SCF= -1142.578371 hartree
Gibbs correction= 0.27753 hartree
Total Gibbs Energy= -1142.300841 hartree

C	3.11763	0.29799	0.71591
C	3.14090	0.12068	-0.69289
C	1.49273	-1.95503	0.75688
C	3.61340	-1.15782	-1.36743
C	1.32534	-1.97885	-0.65310
C	2.44495	-2.10827	-1.66150
H	3.18787	1.32742	1.07915
H	4.12638	-0.90683	-2.30341
H	0.62428	-2.24811	1.35335
H	0.34412	-2.29861	-1.02105
H	3.21882	1.03031	-1.29432
H	4.36751	-1.65044	-0.73964
H	2.02425	-1.86088	-2.64542
H	2.79660	-3.15046	-1.73124
C	3.49253	-0.75610	1.73240
H	3.14853	-0.39662	2.71126
H	4.58765	-0.85358	1.80898

C	2.84092	-2.11502	1.44251
H	3.49986	-2.74060	0.82594
H	2.70911	-2.66461	2.38213
Ir	1.15574	0.00979	0.02363
O	0.90056	2.05355	-0.05922
C	-0.21904	2.70732	-0.06016
C	-1.54205	2.15012	-0.03503
C	-0.12192	4.12609	-0.10102
C	-2.66380	3.02002	-0.06286
C	-1.22986	4.93330	-0.12254
H	0.88418	4.53724	-0.11817
C	-2.52576	4.38268	-0.10461
H	-3.65484	2.57703	-0.04696
H	-1.10252	6.01391	-0.15516
H	-3.40107	5.02559	-0.12290
C	-1.78034	0.73185	0.01709
O	-0.94607	-0.19024	0.08086
O	-3.08266	0.38893	0.00387
C	-3.43615	-0.95734	-0.00648
C	-4.17477	-1.43076	1.06619
C	-3.13165	-1.76185	-1.09677
C	-4.61616	-2.75046	1.04920
H	-4.39684	-0.76261	1.89398
C	-3.57440	-3.07894	-1.09919
H	-2.55339	-1.35622	-1.92299
C	-4.31547	-3.57544	-0.02943
H	-5.19759	-3.13238	1.88468
H	-3.34090	-3.72030	-1.94550
H	-4.66071	-4.60615	-0.03926

TS1_COD: M06/6-311+G(2df,2pd) SCF= -1142.531564 hartree
Gibbs correction= 0.278465 hartree
Total Gibbs Energy= -1142.253099 hartree

C	2.34610	-0.04299	-1.66410
C	2.28091	-1.23914	-0.91078
C	2.51620	1.26177	0.82283
C	3.34286	-1.65278	0.09216
C	2.22067	0.09658	1.55864
C	3.00725	-1.19189	1.51770
H	1.79341	-0.03196	-2.60756
H	3.44567	-2.74379	0.07880
H	2.09861	2.19801	1.20297

H	1.59834	0.21966	2.44697
H	1.67281	-2.04585	-1.32864
H	4.31596	-1.25715	-0.22698
H	2.39098	-1.95557	2.00771
H	3.92471	-1.10070	2.12006
C	3.42203	1.01135	-1.53834
H	3.06396	1.90273	-2.07011
H	4.33927	0.69571	-2.06053
C	3.73142	1.38975	-0.08200
H	4.54737	0.77164	0.31447
H	4.09947	2.42155	-0.04711
Ir	0.91038	0.20092	-0.13340
O	-0.53573	-0.35436	-1.52017
C	-1.53077	-1.07148	-1.08229
C	-1.57138	-1.56309	0.24521
C	-2.61116	-1.41031	-1.92599
C	-2.60073	-2.41346	0.68959
C	-3.62481	-2.22759	-1.47034
H	-2.60531	-1.01821	-2.93967
C	-3.62804	-2.74924	-0.16541
H	-2.57755	-2.76925	1.71786
H	-4.44186	-2.47850	-2.14446
H	-4.43404	-3.39676	0.16751
C	-0.60730	-1.11141	1.22345
O	-0.21913	-1.51474	2.26462
O	-0.62777	0.74054	1.23656
C	-1.76422	1.34397	0.78902
C	-2.98261	1.04082	1.40135
C	-1.72047	2.27953	-0.24599
C	-4.14826	1.65339	0.96073
H	-2.99766	0.31754	2.21461
C	-2.89136	2.89217	-0.67521
H	-0.76202	2.50550	-0.71322
C	-4.10979	2.57798	-0.07999
H	-5.09496	1.40648	1.43601
H	-2.84995	3.61852	-1.48383
H	-5.02482	3.05458	-0.42278

II[1]: M06/6-311+G(2df,2pd) SCF= -1142.556675 hartree
Gibbs correction= 0.277701 hartree
Total Gibbs Energy= -1142.278974 hartree

C	-1.23772	2.20153	0.39671

C	-0.57662	2.56958	-0.78934
C	1.30601	1.24522	1.22182
C	0.64457	3.47187	-0.81673
C	1.90722	1.39711	-0.03156
C	1.95525	2.67439	-0.83926
H	-2.29134	1.92598	0.30585
H	0.59697	4.10991	-1.70627
H	1.59387	0.35861	1.78584
H	2.63700	0.63618	-0.32227
H	-1.15933	2.50856	-1.71208
H	0.61800	4.15301	0.04246
H	2.19277	2.40171	-1.87606
H	2.79491	3.29762	-0.49409
C	-0.79119	2.60994	1.77891
H	-1.36823	2.02828	2.50564
H	-1.05199	3.66478	1.95597
C	0.70650	2.37930	2.03319
H	1.27897	3.29532	1.83775
H	0.85305	2.15246	3.09483
Ir	-0.05217	0.51710	-0.38039
O	-1.67831	-0.08942	-1.49429
C	-2.47586	-0.87276	-0.82516
C	-2.26128	-1.08114	0.55724
C	-3.58318	-1.50947	-1.42645
C	-3.10947	-1.90581	1.32129
C	-4.40507	-2.31048	-0.66271
H	-3.75534	-1.35692	-2.48840
C	-4.18144	-2.51847	0.71285
H	-2.89669	-2.04116	2.37915
H	-5.25218	-2.80032	-1.13967
H	-4.84843	-3.15869	1.28324
C	-1.11730	-0.42334	1.15836
O	-0.74771	-0.43036	2.29843
O	0.77146	-1.23925	-0.91401
C	1.92371	-1.73139	-0.43438
C	3.01745	-1.88344	-1.29969
C	2.05803	-2.13976	0.90128
C	4.21046	-2.42609	-0.83777
H	2.89757	-1.57468	-2.33657
C	3.25821	-2.67782	1.35228
H	1.20340	-2.04203	1.56915

C	4.34221	-2.82304	0.49072
H	5.04742	-2.53854	-1.52455
H	3.34301	-2.99386	2.39043
H	5.27746	-3.24611	0.84891

II^2: M06/6-311+G(2df,2pd) SCF= -1142.528706 hartree
Gibbs correction= 0.279867 hartree
Total Gibbs Energy= -1142.248839 hartree

C	0.66027	1.10730	1.77851
C	-0.37700	1.80489	1.11633
C	2.16133	1.38864	-0.74575
C	-0.19195	3.10567	0.34991
C	1.07448	1.78386	-1.45950
C	0.19251	2.96023	-1.13361
H	0.36738	0.48899	2.63087
H	-1.13333	3.66449	0.39899
H	2.77951	0.58918	-1.15227
H	0.87779	1.28530	-2.41105
H	-1.38400	1.65706	1.51291
H	0.54264	3.72444	0.88279
H	-0.72399	2.85052	-1.71973
H	0.67770	3.88705	-1.47654
C	2.10734	1.54049	1.80642
H	2.71007	0.67943	2.11973
H	2.23019	2.29713	2.59819
C	2.67362	2.08711	0.48553
H	2.47193	3.16160	0.40151
H	3.76604	1.98966	0.51483
Ir	0.08248	0.02680	0.00170
O	-1.57455	0.65670	-1.06950
C	-2.68326	0.07956	-0.64847
C	-2.64515	-0.79753	0.45029
C	-3.92000	0.33093	-1.27050
C	-3.80862	-1.41191	0.93009
C	-5.05828	-0.28941	-0.78759
H	-3.95369	1.00322	-2.12406
C	-5.01893	-1.16102	0.31248
H	-3.72551	-2.08180	1.78338
H	-6.01097	-0.09313	-1.27678
H	-5.93119	-1.63248	0.66810
C	-1.32001	-1.01422	1.03566
O	-1.08863	-1.69765	2.01463

O	0.29607	-1.56097	-1.40746
C	1.47664	-1.79417	-0.92303
C	2.63185	-1.90460	-1.74840
C	1.63519	-1.72690	0.50660
C	3.87659	-1.88792	-1.17295
H	2.48793	-1.97622	-2.82359
C	2.95156	-1.68069	1.04464
H	0.83951	-2.09799	1.15177
C	4.05068	-1.73547	0.22739
H	4.75799	-1.97184	-1.80641
H	3.07252	-1.66241	2.12676
H	5.05425	-1.72003	0.64427

III: M06/6-311+G(2df,2pd) SCF= -1414.000195 hartree
Gibbs correction= 0.385396 hartree
Total Gibbs Energy= -1413.614799 hartree

C	0.46949	-1.84083	1.78798
C	-0.84023	-1.83115	1.28017
C	0.09706	0.94979	2.15686
C	-2.03424	-1.30716	2.05704
C	-1.10938	1.00003	1.45301
C	-2.33321	0.17213	1.77037
H	1.15400	-2.58113	1.36599
H	-2.91533	-1.90165	1.78511
H	0.77554	1.79040	2.01926
H	-1.29015	1.88771	0.83877
H	-1.05925	-2.54050	0.47939
H	-1.87134	-1.47475	3.12957
H	-3.01428	0.23911	0.91287
H	-2.86567	0.62743	2.62031
C	0.86054	-1.29124	3.13756
H	1.95388	-1.26372	3.19043
H	0.53319	-1.98756	3.92505
C	0.31135	0.11780	3.40778
H	-0.63443	0.06335	3.96283
H	1.01382	0.65167	4.05706
Ir	0.25266	-0.24291	0.28862
O	0.82324	-1.56249	-1.20096
C	2.11910	-1.63393	-1.33371
C	2.95727	-0.96914	-0.41068
C	2.72889	-2.38393	-2.36185
C	4.35968	-1.03423	-0.50765

C	4.10474	-2.43991	-2.44021
H	2.09293	-2.89782	-3.07772
C	4.93415	-1.77020	-1.52015
H	4.96064	-0.49723	0.22254
H	4.56253	-3.01807	-3.24096
H	6.01469	-1.83290	-1.61308
C	2.31454	-0.19520	0.63652
O	2.82198	0.42776	1.52671
O	0.55497	1.20679	-1.09987
C	0.48130	2.52433	-0.86615
C	-0.52934	3.27615	-1.48639
C	1.41450	3.19571	-0.05983
C	-0.60979	4.65014	-1.29448
H	-1.23218	2.75548	-2.13549
C	1.32063	4.56982	0.12983
H	2.22026	2.62412	0.39786
C	0.30845	5.30688	-0.47930
H	-1.39925	5.21370	-1.78861
H	2.05652	5.07175	0.75556
H	0.24209	6.38158	-0.32881
C	-2.25441	-0.11746	-1.98920
C	-3.36116	0.68945	-1.72829
C	-4.52812	0.13402	-1.21441
C	-4.61325	-1.23547	-0.94310
C	-3.50410	-2.03683	-1.22179
C	-2.33471	-1.48757	-1.74178
H	-1.33272	0.30955	-2.37994
H	-3.31298	1.75954	-1.92430
H	-5.39138	0.76889	-1.01521
H	-1.47172	-2.11583	-1.95443
H	-3.56220	-3.10914	-1.02976
C	-5.85281	-1.82237	-0.33587
H	-5.99405	-2.86613	-0.63687
H	-5.80280	-1.80657	0.76166
H	-6.74842	-1.26130	-0.62403

TS2: M06/6-311+G(2df,2pd) SCF= -1413.942132 hartree
Gibbs correction= 0.385189 hartree
Total Gibbs Energy= -1413.556943 hartree

C	1.08728	-1.59757	1.87520
C	-0.30502	-1.83139	1.73548
C	0.37772	1.09691	2.12031

C	-1.32170	-1.41917	2.78827
C	-0.97191	0.90638	1.80241
C	-1.88942	-0.00537	2.58435
H	1.74777	-2.29120	1.34988
H	-2.14650	-2.14038	2.77442
H	0.85611	1.99660	1.73718
H	-1.45759	1.70377	1.23589
H	-0.58998	-2.67049	1.09821
H	-0.85837	-1.51086	3.78039
H	-2.83869	-0.07628	2.04334
H	-2.11931	0.45865	3.55635
C	1.70470	-0.87976	3.04936
H	2.76557	-0.71873	2.83297
H	1.66704	-1.53249	3.93548
C	1.03747	0.46943	3.33634
H	0.28470	0.36686	4.12970
H	1.78961	1.16863	3.71611
Ir	0.23503	-0.26853	0.39711
O	0.81279	-1.65180	-1.04046
C	2.06352	-1.53692	-1.41624
C	2.90945	-0.61616	-0.76905
C	2.60036	-2.32897	-2.45131
C	4.25563	-0.47420	-1.14373
C	3.92708	-2.17881	-2.80383
H	1.95166	-3.04095	-2.95509
C	4.76810	-1.25437	-2.15886
H	4.86530	0.25658	-0.61669
H	4.33105	-2.79372	-3.60637
H	5.80688	-1.15703	-2.46245
C	2.32039	0.17968	0.30248
O	2.89841	1.03295	0.93465
O	0.06002	1.12618	-1.30474
C	-0.17876	2.45935	-1.16123
C	-1.37608	3.01111	-1.62575
C	0.79367	3.28702	-0.59294
C	-1.60358	4.37725	-1.49833
H	-2.11180	2.36227	-2.09708
C	0.55258	4.65082	-0.47371
H	1.73315	2.85022	-0.25998
C	-0.64615	5.20344	-0.91787
H	-2.53788	4.79823	-1.86394

H	1.31570	5.28879	-0.03284
H	-0.82794	6.27088	-0.82119
C	-1.89292	-0.49062	-0.73714
C	-3.07633	0.21388	-0.43679
C	-4.33824	-0.32130	-0.65743
C	-4.48341	-1.61260	-1.17248
C	-3.32571	-2.32810	-1.48453
C	-2.06550	-1.77827	-1.27938
H	-0.92774	0.41916	-1.24246
H	-3.01693	1.23187	-0.04718
H	-5.22883	0.26648	-0.43258
H	-1.18301	-2.35436	-1.55051
H	-3.41921	-3.32985	-1.90531
C	-5.84109	-2.21387	-1.37051
H	-5.84076	-2.94913	-2.18237
H	-6.17908	-2.73344	-0.46430
H	-6.59066	-1.44890	-1.60101

IV: M06/6-311+G(2df,2pd) SCF= -1413.965022 hartree
Gibbs correction= 0.389287 hartree
Total Gibbs Energy= -1413.575735 hartree

C	1.45023	-1.53017	1.74137
C	0.07665	-1.92599	1.80643
C	0.47287	1.03043	2.15094
C	-0.80541	-1.65448	3.01747
C	-0.88613	0.68690	2.03918
C	-1.57021	-0.32706	2.92640
H	2.09714	-2.15440	1.12097
H	-1.52322	-2.47677	3.11443
H	0.78258	1.98585	1.72853
H	-1.54547	1.43440	1.59384
H	-0.18612	-2.81209	1.22645
H	-0.18581	-1.68812	3.92446
H	-2.56492	-0.51475	2.50716
H	-1.72843	0.10019	3.92931
C	2.14953	-0.76435	2.83622
H	3.14185	-0.47705	2.47463
H	2.31443	-1.43006	3.69851
C	1.37722	0.49121	3.24865
H	0.76846	0.29721	4.14211
H	2.08637	1.27790	3.52642
Ir	0.21874	-0.32221	0.45511

O	0.72340	-1.59664	-1.11644
C	1.92078	-1.39927	-1.62147
C	2.77382	-0.41996	-1.07586
C	2.38313	-2.15897	-2.71557
C	4.05335	-0.19718	-1.60703
C	3.64823	-1.92791	-3.22079
H	1.72678	-2.91475	-3.14004
C	4.49682	-0.94850	-2.67665
H	4.67011	0.57531	-1.15146
H	3.99461	-2.52202	-4.06510
H	5.48570	-0.78710	-3.09772
C	2.25168	0.33948	0.05874
O	2.83588	1.27243	0.57787
O	-0.16096	1.23050	-1.21800
C	-0.45987	2.57487	-1.05548
C	-1.70046	3.07677	-1.43263
C	0.53022	3.39791	-0.53126
C	-1.95516	4.43505	-1.26877
H	-2.45637	2.41218	-1.84907
C	0.25355	4.75069	-0.36875
H	1.49668	2.97440	-0.26605
C	-0.98448	5.27409	-0.73262
H	-2.92247	4.83417	-1.56390
H	1.02191	5.40235	0.04000
H	-1.18923	6.33375	-0.60472
C	-1.80751	-0.88728	-0.16105
C	-2.89000	0.00111	-0.24021
C	-4.12225	-0.36372	-0.78792
C	-4.33979	-1.65198	-1.26575
C	-3.27435	-2.55345	-1.18994
C	-2.04462	-2.17826	-0.66257
H	-0.90352	0.76452	-1.64228
H	-2.79961	1.02175	0.13682
H	-4.93067	0.36800	-0.83122
H	-1.23604	-2.90756	-0.67474
H	-3.41122	-3.56875	-1.56586
C	-5.66229	-2.07073	-1.83501
H	-6.15383	-2.81798	-1.19898
H	-6.34594	-1.22072	-1.93372
H	-5.54672	-2.52561	-2.82638

V: M06/6-311+G(2df,2pd) SCF= -1106.625359 hartree
Gibbs correction= 0.300769 hartree
Total Gibbs Energy= -1106.32459 hartree

C	2.67691	0.71755	-0.25112
C	2.62802	-0.18395	-1.29773
C	1.55394	-1.44855	1.31599
C	3.25170	-1.56324	-1.26744
C	1.27620	-2.26925	0.21442
C	2.25199	-2.66080	-0.87332
H	2.44654	1.76019	-0.47924
H	3.65270	-1.79242	-2.26167
H	0.84768	-1.49552	2.14226
H	0.40193	-2.91883	0.29013
H	2.34306	0.21040	-2.27595
H	4.11455	-1.56465	-0.59156
H	1.66385	-2.94250	-1.75845
H	2.78898	-3.57468	-0.57320
C	3.27420	0.45536	1.10515
H	2.90684	1.23178	1.78613
H	4.36744	0.58065	1.06331
C	2.92813	-0.92170	1.69394
H	3.68594	-1.66460	1.41435
H	2.97184	-0.84686	2.78638
Ir	0.57390	-0.28336	-0.28096
O	-0.07775	1.25284	-1.50169
C	-0.52397	2.27702	-0.82197
C	-0.43401	2.26910	0.58772
C	-1.07716	3.41350	-1.44648
C	-0.88607	3.35186	1.35913
C	-1.51512	4.47077	-0.67332
H	-1.14998	3.42825	-2.53093
C	-1.42559	4.45482	0.72985
H	-0.80179	3.29407	2.44191
H	-1.94389	5.34129	-1.16687
H	-1.77978	5.30292	1.30936
C	0.12863	1.07163	1.20948
O	0.32191	0.87813	2.37979
C	-1.35847	-0.92190	-0.00345
C	-1.86270	-1.53363	1.15470
C	-3.15740	-2.03371	1.20328
C	-4.00659	-1.95160	0.09549

C	-3.51835	-1.33449	-1.05378
C	-2.22654	-0.81217	-1.10028
H	-1.24265	-1.60805	2.04898
H	-3.52383	-2.49621	2.12086
H	-1.89055	-0.30510	-2.00393
H	-4.16572	-1.24539	-1.92679
C	-5.39863	-2.50581	0.15872
H	-5.39207	-3.59198	0.31619
H	-5.96715	-2.06869	0.98897
H	-5.95239	-2.30827	-0.76515

TS3: M06/6-311+G(2df,2pd) SCF= -1106.604445 hartree
Gibbs correction= 0.300494 hartree
Total Gibbs Energy= -1106.303951 hartree

C	2.47390	1.05495	-0.11073
C	2.62303	0.17921	-1.21054
C	1.67979	-1.23385	1.31518
C	3.48110	-1.07268	-1.19229
C	1.56024	-2.05231	0.17658
C	2.66905	-2.32259	-0.81690
H	2.16055	2.07673	-0.34070
H	3.92215	-1.21919	-2.18504
H	0.94174	-1.36753	2.10363
H	0.76166	-2.79919	0.18189
H	2.41296	0.60761	-2.19351
H	4.32992	-0.93842	-0.51046
H	2.20334	-2.72834	-1.72510
H	3.33183	-3.11670	-0.43703
C	3.08430	0.87022	1.25330
H	2.55505	1.54268	1.94102
H	4.13659	1.19639	1.24870
C	2.96483	-0.56776	1.77065
H	3.82748	-1.17062	1.46101
H	2.98477	-0.55652	2.86639
Ir	0.69173	-0.14379	-0.29446
O	-0.07012	1.40253	-1.44605
C	-0.80793	2.25788	-0.77164
C	-1.11155	2.02072	0.58585
C	-1.29910	3.43509	-1.36622
C	-1.84087	2.94796	1.33943
C	-2.03328	4.33391	-0.61213
H	-1.07387	3.61845	-2.41411

C	-2.30726	4.10612	0.74377
H	-2.03226	2.72822	2.38762
H	-2.40031	5.24322	-1.08520
H	-2.87710	4.83151	1.31812
C	-0.64720	0.76412	1.19511
O	-0.51158	0.56524	2.38131
C	-1.31112	-0.77456	0.26181
C	-1.62830	-1.75280	1.22077
C	-2.64601	-2.66329	1.00781
C	-3.41436	-2.62648	-0.16435
C	-3.13228	-1.63792	-1.10395
C	-2.11148	-0.71440	-0.89363
H	-1.08926	-1.76016	2.16641
H	-2.87070	-3.41266	1.76693
H	-1.91825	0.04532	-1.64730
H	-3.72533	-1.58231	-2.01626
C	-4.52965	-3.60413	-0.36936
H	-5.36533	-3.39680	0.31115
H	-4.91821	-3.56594	-1.39190
H	-4.20252	-4.63075	-0.16641

VI: M06/6-311+G(2df,2pd) SCF= -1106.647711 hartree
Gibbs correction= 0.299717 hartree
Total Gibbs Energy= -1106.347994 hartree

C	3.20653	0.31757	1.04797
C	3.42300	0.46964	-0.34581
C	1.95429	-2.07459	0.37465
C	4.16386	-0.55230	-1.19331
C	1.96209	-1.79311	-1.01697
C	3.19975	-1.54817	-1.85107
H	3.07186	1.23719	1.62493
H	4.74018	-0.03313	-1.96835
H	1.07823	-2.60389	0.75919
H	1.09561	-2.14071	-1.58902
H	3.42796	1.49413	-0.72703
H	4.90451	-1.07744	-0.57583
H	2.86477	-1.13663	-2.81264
H	3.71389	-2.49473	-2.08466
C	3.61611	-0.88580	1.86620
H	3.10764	-0.80402	2.83603
H	4.69641	-0.86292	2.08355
C	3.22023	-2.21382	1.20613

H	4.03638	-2.59533	0.57825
H	3.06549	-2.97423	1.98089
Ir	1.40168	-0.05215	0.03058
O	0.84355	1.90069	0.37308
C	-0.31752	2.41184	0.11900
C	-1.53204	1.68496	-0.15345
C	-0.39797	3.83251	0.14294
C	-2.70325	2.42849	-0.47486
C	-1.55670	4.50259	-0.15038
H	0.52124	4.36007	0.38451
C	-2.72928	3.79848	-0.48613
H	-3.59879	1.88113	-0.75540
H	-1.56348	5.59107	-0.13882
H	-3.63657	4.33038	-0.75786
C	-1.61059	0.24693	-0.15018
O	-0.62220	-0.53875	-0.21609
C	-2.92045	-0.45086	-0.07149
C	-3.10549	-1.61961	-0.81839
C	-4.28679	-2.33650	-0.72129
C	-5.30599	-1.93180	0.14641
C	-5.10234	-0.78553	0.91603
C	-3.93145	-0.04695	0.80604
H	-2.30859	-1.95331	-1.47846
H	-4.42462	-3.23552	-1.32091
H	-3.78655	0.83588	1.42503
H	-5.87360	-0.46989	1.61727
C	-6.58647	-2.70455	0.23420
H	-7.27436	-2.42025	-0.57247
H	-6.41164	-3.78210	0.14183
H	-7.10313	-2.52258	1.18221

A[1]: M06/6-311+G(2df,2pd) SCF= -1950.06313 hartree
Gibbs correction= 0.48441 hartree
Total Gibbs Energy= -1949.57872 hartree

C	-3.08360	4.68037	-0.96969
C	-3.37455	3.35275	-0.77078
C	-2.38871	2.42831	-0.35484
C	-1.05007	2.87071	-0.11925
C	-0.79457	4.25593	-0.31391
C	-1.77260	5.12654	-0.72999
H	-3.85335	5.37175	-1.30055
H	-4.38326	2.98612	-0.93673

H	0.21721	4.60160	-0.11457
H	-1.52459	6.17692	-0.87341
O	-0.05635	2.13949	0.28819
C	-2.76283	1.05669	-0.10954
O	-2.02572	0.10276	0.15037
O	-4.09808	0.84178	-0.17351
C	-4.59464	-0.42476	0.10148
C	-4.63250	-0.88781	1.40971
C	-5.12774	-1.15942	-0.94645
C	-5.22118	-2.11961	1.66903
H	-4.19914	-0.28456	2.20354
C	-5.71632	-2.39118	-0.67546
H	-5.07942	-0.75700	-1.95497
C	-5.76490	-2.87225	0.62987
H	-5.25759	-2.49257	2.68984
H	-6.14189	-2.97404	-1.48881
H	-6.22945	-3.83269	0.83909
Ir	0.14631	0.07317	0.21460
P	2.38759	0.25155	0.23444
C	3.05929	1.44639	-1.09354
C	3.14015	0.63683	1.93405
C	4.50758	1.17578	-1.50326
H	4.62722	0.19450	-1.97462
H	4.80100	1.93349	-2.24363
H	5.21459	1.24927	-0.66975
C	2.17453	1.24033	-2.32739
H	1.13664	1.53663	-2.13671
H	2.56782	1.85298	-3.15169
H	2.17186	0.19348	-2.65968
C	2.93231	2.89963	-0.63597
H	1.92224	3.11633	-0.27499
H	3.65510	3.15350	0.14892
H	3.14268	3.55619	-1.49253
C	2.36806	1.80701	2.55017
H	2.53553	2.74946	2.01920
H	1.28896	1.61532	2.55403
H	2.70468	1.94343	3.58786
C	4.63251	0.96411	1.93485
H	4.94818	1.15199	2.97110
H	5.24902	0.13914	1.55939
H	4.86796	1.86607	1.35944

C	2.90347	-0.59618	2.80889
H	3.29372	-0.39792	3.81688
H	1.83263	-0.81208	2.90347
H	3.40889	-1.48987	2.42241
C	3.02084	-1.38143	-0.30167
C	4.35474	-1.79946	-0.36654
C	2.00572	-2.23873	-0.74365
C	4.68330	-3.03882	-0.90060
H	5.15303	-1.14753	-0.01961
C	2.34898	-3.47655	-1.29862
C	3.67649	-3.87175	-1.38289
H	5.72416	-3.34997	-0.94986
H	1.55323	-4.13797	-1.63868
H	3.92819	-4.83927	-1.81177
C	0.56214	-1.91142	-0.53487
C	0.06615	-2.00544	0.82676
C	-0.35272	-2.26523	-1.60374
C	-1.25218	-2.54498	1.04743
H	0.78926	-2.16399	1.62912
C	-1.61448	-2.70030	-1.34160
H	0.01524	-2.20174	-2.62834
C	-2.06284	-2.86867	0.00479
H	-1.58881	-2.69872	2.07189
H	-2.28714	-2.95044	-2.16018
H	-3.06173	-3.26170	0.18716

A^{2}: M06/6-311+G(2df,2pd) SCF= -1950.057391 hartree
Gibbs correction= 0.479765 hartree
Total Gibbs Energy= -1949.577626 hartree

C	4.72966	3.57368	-0.51735
C	4.39670	2.24674	-0.46729
C	3.07007	1.81863	-0.19171
C	2.04459	2.79268	0.05092
C	2.43967	4.16558	-0.00070
C	3.72653	4.53885	-0.27772
H	5.74858	3.87972	-0.73709
H	5.15471	1.48978	-0.64531
H	1.65491	4.89568	0.18553
H	3.97993	5.59727	-0.31474
O	0.81803	2.54853	0.32571
C	2.77888	0.42086	-0.12157
O	1.67886	-0.14156	0.05344

O	3.87163	-0.36427	-0.27337
C	3.77767	-1.74026	-0.15150
C	4.06862	-2.50655	-1.27109
C	3.49993	-2.32506	1.07717
C	4.06910	-3.89333	-1.15949
H	4.29177	-2.00708	-2.21023
C	3.49868	-3.71189	1.17508
H	3.28254	-1.69488	1.93609
C	3.78054	-4.49795	0.06029
H	4.29633	-4.50206	-2.03131
H	3.27620	-4.17931	2.13185
H	3.78119	-5.58179	0.14474
Ir	-0.25874	0.75050	0.25137
P	-1.35355	-1.23239	0.09218
C	-0.83870	-2.26434	-1.42903
C	-1.34555	-2.30683	1.66022
C	-1.88240	-3.27823	-1.89952
H	-2.80436	-2.79409	-2.23840
H	-1.46583	-3.82569	-2.75708
H	-2.14033	-4.02208	-1.13784
C	-0.62818	-1.25289	-2.56064
H	0.18947	-0.55692	-2.34097
H	-0.38486	-1.79775	-3.48449
H	-1.53119	-0.65737	-2.75052
C	0.47811	-2.99278	-1.16646
H	1.25112	-2.32692	-0.76895
H	0.35844	-3.83801	-0.47740
H	0.85125	-3.40514	-2.11551
C	0.09307	-2.36803	2.17870
H	0.76319	-2.91126	1.50341
H	0.50193	-1.35913	2.31821
H	0.10162	-2.88467	3.14969
C	-1.88076	-3.72856	1.50124
H	-1.83280	-4.23263	2.47736
H	-2.92910	-3.75438	1.18212
H	-1.28796	-4.32721	0.80124
C	-2.19053	-1.57571	2.70540
H	-2.17081	-2.14742	3.64384
H	-1.78301	-0.57992	2.91631
H	-3.23847	-1.46843	2.39946
C	-3.09843	-0.80693	-0.27174

C	-4.18536	-1.68080	-0.38427
C	-3.28211	0.55786	-0.52190
C	-5.43225	-1.21408	-0.78066
H	-4.05912	-2.74246	-0.18525
C	-4.53649	1.01562	-0.94005
C	-5.60175	0.13644	-1.07537
H	-6.26752	-1.90476	-0.86982
H	-4.67136	2.07946	-1.13032
H	-6.57286	0.50694	-1.39633
C	-2.20593	1.55570	-0.23517
C	-1.92169	1.81272	1.16348
C	-2.08018	2.67089	-1.15376
C	-1.65691	3.16226	1.58597
H	-2.37669	1.15840	1.90861
C	-1.75579	3.91639	-0.71354
H	-2.28994	2.48725	-2.20776
C	-1.56770	4.17216	0.67889
H	-1.54056	3.36150	2.64918
H	-1.66077	4.73553	-1.42328
H	-1.36458	5.18866	1.00970

TS1_JohnPhos: M06/6-311+G(2df,2pd) SCF= -1950.00439 hartree
Gibbs correction= 0.483102 hartree
Total Gibbs Energy= -1949.521288 hartree

C	5.08559	-1.44225	1.37152
C	3.91017	-0.78338	1.70451
C	2.94559	-0.56049	0.72376
C	3.10544	-1.02202	-0.59868
C	4.31529	-1.65993	-0.92690
C	5.27656	-1.86546	0.05146
H	5.85068	-1.61880	2.12281
H	3.72449	-0.42597	2.71575
H	4.45538	-2.01077	-1.94711
H	6.19800	-2.38119	-0.21482
O	2.12589	-0.89649	-1.45946
C	1.70555	0.16143	1.03801
O	1.26717	0.48212	2.11396
O	1.60706	1.34418	-0.21806
C	1.60851	2.68250	-0.02167
C	2.07884	3.25653	1.16240
C	1.22716	3.50007	-1.08837
C	2.10169	4.64124	1.28490

H	2.39684	2.61631	1.98049
C	1.25606	4.88235	-0.95115
H	0.93925	3.02412	-2.02464
C	1.67998	5.46168	0.24205
H	2.45695	5.08377	2.21327
H	0.95640	5.51010	-1.78799
H	1.69912	6.54309	0.35166
Ir	0.30583	-0.31625	-0.60820
P	-1.85803	0.46775	-0.05915
C	-2.19980	1.49023	1.51754
C	-2.63227	1.29281	-1.59275
C	-3.61728	2.05672	1.59028
H	-4.39235	1.28481	1.54308
H	-3.72967	2.55935	2.56100
H	-3.81473	2.80835	0.81752
C	-1.97900	0.55135	2.70945
H	-0.98949	0.08027	2.67464
H	-2.02015	1.15184	3.62863
H	-2.74946	-0.22528	2.78267
C	-1.19871	2.63781	1.63539
H	-0.19058	2.25482	1.80200
H	-1.18200	3.30667	0.76734
H	-1.46853	3.24413	2.51146
C	-2.21176	2.75956	-1.65924
H	-2.71277	3.37173	-0.90091
H	-1.13150	2.89220	-1.54013
H	-2.49139	3.16496	-2.64172
C	-4.15546	1.20895	-1.68866
H	-4.47054	1.73978	-2.59819
H	-4.50518	0.17516	-1.78102
H	-4.66920	1.68287	-0.84571
C	-2.05540	0.55799	-2.80665
H	-2.44960	1.01554	-3.72512
H	-0.95796	0.61260	-2.84472
H	-2.34862	-0.50021	-2.81638
C	-2.82614	-1.05169	0.28574
C	-4.20490	-1.13839	0.51955
C	-2.02463	-2.17012	0.53030
C	-4.76945	-2.30244	1.02394
H	-4.85076	-0.28740	0.32833
C	-2.59736	-3.33354	1.05566

C	-3.95935	-3.39758	1.31026
H	-5.84045	-2.34896	1.20574
H	-1.96029	-4.19662	1.24173
H	-4.39282	-4.30750	1.71866
C	-0.58371	-2.21753	0.14827
C	-0.28684	-2.32348	-1.25799
C	0.32486	-2.85618	1.07132
C	0.79377	-3.17056	-1.68590
H	-1.10242	-2.16298	-1.96762
C	1.37982	-3.59210	0.62196
H	0.12761	-2.74939	2.13750
C	1.59163	-3.79131	-0.77390
H	0.95656	-3.30972	-2.75127
H	2.06286	-4.05100	1.33390
H	2.41024	-4.42680	-1.10228

B[1]: M06/6-311+G(2df,2pd) SCF= -1950.043999 hartree
Gibbs correction= 0.482333 hartree
Total Gibbs Energy= -1949.561666 hartree

C	-4.52461	1.77429	1.90002
C	-3.18952	1.53802	2.15114
C	-2.34070	1.18208	1.08988
C	-2.81859	1.07065	-0.23376
C	-4.18717	1.32268	-0.47228
C	-5.00934	1.65955	0.58269
H	-5.19985	2.04391	2.70779
H	-2.77336	1.61018	3.15377
H	-4.56567	1.21358	-1.48558
H	-6.06624	1.83824	0.39103
O	-1.98948	0.74741	-1.18367
C	-0.92951	0.88931	1.30041
O	-0.29460	1.06324	2.30840
O	-0.96451	-1.73348	-0.20074
C	-2.29329	-1.94902	-0.21734
C	-3.00170	-2.06812	0.98442
C	-2.97559	-2.12045	-1.42826
C	-4.36282	-2.34932	0.97292
H	-2.46172	-1.92549	1.92046
C	-4.33443	-2.40536	-1.43203
H	-2.41515	-2.00412	-2.35469
C	-5.03659	-2.51895	-0.23340
H	-4.90142	-2.43281	1.91498

H	-4.85300	-2.53553	-2.38028
H	-6.10192	-2.73777	-0.24061
Ir	-0.14611	0.11000	-0.42081
P	1.88955	-0.94740	0.12083
C	1.97877	-2.07307	1.66239
C	2.51493	-1.92623	-1.40866
C	3.39473	-2.30879	2.19313
H	3.83842	-1.38914	2.58960
H	3.32016	-3.01693	3.02991
H	4.08147	-2.74765	1.46312
C	1.19034	-1.38861	2.77468
H	0.12467	-1.33659	2.53845
H	1.30989	-1.98043	3.69283
H	1.53926	-0.37050	2.97535
C	1.30535	-3.41624	1.36933
H	0.30702	-3.27804	0.93872
H	1.90111	-4.05673	0.70942
H	1.19652	-3.95266	2.32220
C	1.41495	-2.85737	-1.93045
H	1.17370	-3.66847	-1.23895
H	0.47964	-2.32374	-2.13264
H	1.76694	-3.30982	-2.86835
C	3.77813	-2.74604	-1.14332
H	4.07142	-3.24039	-2.07993
H	4.62584	-2.12461	-0.83138
H	3.62483	-3.53503	-0.40113
C	2.83206	-0.93095	-2.52807
H	3.29025	-1.47989	-3.36174
H	1.92097	-0.46802	-2.92261
H	3.53285	-0.14375	-2.22411
C	3.07849	0.42952	0.33556
C	4.44113	0.26694	0.61867
C	2.56278	1.72611	0.16309
C	5.28126	1.36074	0.77338
H	4.85576	-0.72968	0.73548
C	3.42381	2.81933	0.33148
C	4.76472	2.64459	0.63952
H	6.33338	1.20919	1.00161
H	3.02595	3.82299	0.19309
H	5.40924	3.51191	0.76144
C	1.16389	2.04603	-0.26774

C	0.74064	1.79026	-1.61582
C	0.52607	3.14200	0.41466
C	-0.24012	2.63126	-2.22856
H	1.42264	1.26042	-2.27906
C	-0.44554	3.89140	-0.18492
H	0.84389	3.36276	1.43128
C	-0.82842	3.64364	-1.52848
H	-0.50934	2.44502	-3.26498
H	-0.91334	4.70420	0.36554
H	-1.58332	4.26932	-1.99779

B^{2}: M06/6-311+G(2df,2pd) SCF= -1950.04431 hartree
Gibbs correction= 0.480337 hartree
Total Gibbs Energy= -1949.563973 hartree

C	-2.29920	4.38495	-1.98440
C	-1.62185	3.24121	-2.36269
C	-1.22803	2.32138	-1.38261
C	-1.49780	2.53840	-0.01960
C	-2.18201	3.70854	0.35473
C	-2.57149	4.60481	-0.62425
H	-2.62093	5.10783	-2.72917
H	-1.38810	3.03098	-3.40400
H	-2.39737	3.87839	1.40649
H	-3.10574	5.50626	-0.32901
O	-1.05578	1.67256	0.86516
C	-0.47887	1.10379	-1.70310
O	-0.02331	0.80180	-2.77314
O	-2.40018	-0.37292	-0.48356
C	-3.16645	-0.92616	0.43974
C	-2.80870	-1.03160	1.79946
C	-4.40111	-1.48515	0.04854
C	-3.62286	-1.70510	2.70606
H	-1.89264	-0.54915	2.14455
C	-5.20681	-2.14423	0.96280
H	-4.68515	-1.39627	-0.99859
C	-4.82460	-2.27382	2.29977
H	-3.31406	-1.77241	3.74848
H	-6.14947	-2.57375	0.62631
H	-5.45956	-2.79685	3.01047
Ir	-0.39330	-0.04565	-0.03200
P	1.80249	0.35803	0.67926
C	2.64181	2.01193	0.23273

C	1.90255	0.06026	2.56705
C	4.16307	2.03109	0.40848
H	4.66442	1.39461	-0.32816
H	4.50346	3.06040	0.22984
H	4.50465	1.74896	1.40790
C	2.37003	2.28555	-1.24890
H	1.34233	2.61096	-1.42729
H	3.02777	3.10277	-1.57464
H	2.57618	1.41707	-1.88674
C	2.02164	3.13558	1.06673
H	0.92668	3.08472	1.08846
H	2.39169	3.13404	2.09908
H	2.30872	4.09832	0.62205
C	0.83294	0.89465	3.27964
H	1.04210	1.96751	3.24501
H	-0.16772	0.74969	2.86147
H	0.81154	0.59532	4.33686
C	3.25671	0.36749	3.20520
H	3.19847	0.11288	4.27266
H	4.07547	-0.22497	2.78126
H	3.51649	1.42949	3.14694
C	1.58302	-1.41687	2.81323
H	1.68096	-1.62313	3.88751
H	0.54936	-1.66048	2.53933
H	2.26215	-2.09467	2.28098
C	2.82813	-0.93854	-0.11738
C	4.19829	-1.11807	0.11653
C	2.18035	-1.76605	-1.05048
C	4.93416	-2.05999	-0.58863
H	4.71016	-0.49983	0.84780
C	2.94127	-2.69868	-1.76885
C	4.30330	-2.84132	-1.55048
H	5.99733	-2.17564	-0.39309
H	2.43653	-3.34051	-2.48853
H	4.86832	-3.57620	-2.11892
C	0.70138	-1.82315	-1.26388
C	-0.13186	-2.35568	-0.23629
C	0.22388	-1.93476	-2.60623
C	-1.34362	-3.02053	-0.55858
H	0.30622	-2.54132	0.74468
C	-0.98014	-2.52280	-2.88652

H	0.84567	-1.54382	-3.40701
C	-1.76925	-3.08228	-1.85828
H	-1.93926	-3.45008	0.24384
H	-1.32062	-2.58030	-3.91743
H	-2.71210	-3.56698	-2.09904

B^{3}: M06/6-311+G(2df,2pd) SCF= -1950.02900023 hartree
Gibbs correction= 0.4778 hartree
Total Gibbs Energy= -1949.5512 hartree

C	-4.17654	-2.85637	-0.94097
C	-3.38219	-2.47295	0.12465
C	-2.27635	-1.64792	-0.10236
C	-1.96368	-1.18864	-1.39596
C	-2.76569	-1.59329	-2.47453
C	-3.85381	-2.41506	-2.23229
H	-5.04698	-3.48716	-0.78227
H	-3.60024	-2.78158	1.14476
H	-2.52431	-1.24286	-3.47490
H	-4.47874	-2.71890	-3.07034
O	-0.91503	-0.39963	-1.57623
C	-1.38671	-1.16092	0.95968
O	-1.43555	-1.45052	2.13698
O	-1.63587	1.58048	0.73260
C	-2.95994	1.39594	0.68093
C	-3.65163	1.51056	-0.53534
C	-3.68502	1.10218	1.84496
C	-5.02571	1.31420	-0.58399
H	-3.08073	1.72909	-1.43669
C	-5.06121	0.92082	1.78689
H	-3.13714	1.00708	2.78032
C	-5.74062	1.02011	0.57496
H	-5.54405	1.38978	-1.53855
H	-5.60896	0.69113	2.69927
H	-6.81678	0.86866	0.53360
Ir	-0.19433	0.23921	0.22056
P	1.82963	-0.92544	0.15548
C	2.33778	-1.22769	1.97042
C	1.97201	-2.50032	-0.89760
C	3.83849	-1.38824	2.20615
H	4.40768	-0.49741	1.92087
H	4.00090	-1.55339	3.28041
H	4.26142	-2.25220	1.68052

C	1.86538	0.02758	2.71375
H	0.77259	0.16446	2.65138
H	2.10226	-0.07183	3.78271
H	2.36613	0.93366	2.34850
C	1.61687	-2.44799	2.54508
H	0.53001	-2.38280	2.44068
H	1.97044	-3.38538	2.09964
H	1.83612	-2.50219	3.62071
C	0.70732	-3.33603	-0.67615
H	0.57178	-3.64083	0.36735
H	-0.19339	-2.81045	-0.99851
H	0.78717	-4.25090	-1.27899
C	3.17234	-3.40924	-0.62210
H	3.07155	-4.30242	-1.25406
H	4.13711	-2.96183	-0.87573
H	3.20990	-3.75551	0.41681
C	1.99024	-2.03571	-2.35632
H	1.94651	-2.91751	-3.01058
H	1.11707	-1.40928	-2.57953
H	2.90064	-1.47797	-2.60564
C	3.16285	0.23301	-0.41227
C	4.47691	-0.21269	-0.61861
C	2.91148	1.61427	-0.51121
C	5.51964	0.66007	-0.89282
H	4.70671	-1.26829	-0.52961
C	3.98018	2.48892	-0.75705
C	5.27236	2.02648	-0.94641
H	6.52341	0.27166	-1.04670
H	3.76673	3.55398	-0.82846
H	6.07872	2.72811	-1.14584
C	1.57319	2.26436	-0.46427
C	0.69262	2.10846	-1.55095
C	1.31790	3.29055	0.46607
C	-0.39449	2.97001	-1.70849
H	0.91514	1.36582	-2.31538
C	0.21676	4.11657	0.32002
H	2.01331	3.43811	1.29172
C	-0.63706	3.96280	-0.77375
H	-1.05618	2.83870	-2.56140
H	0.02197	4.89205	1.05637
H	-1.49946	4.61534	-0.88541

Acylation Spectra and Data

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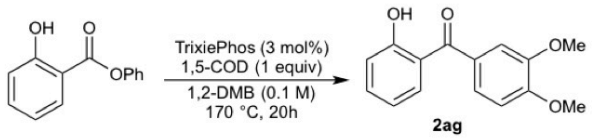
No Ir control
399.87
298.0
CDCl3



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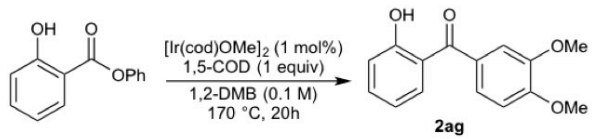
No Phos control
399.87
298.0
CDCl3



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No Ir or Phos control
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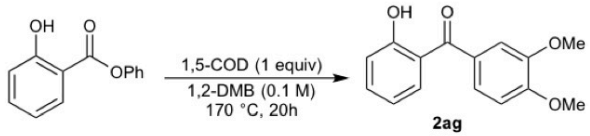
298.0
CDCl3



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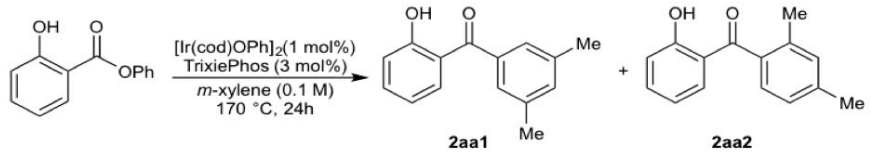
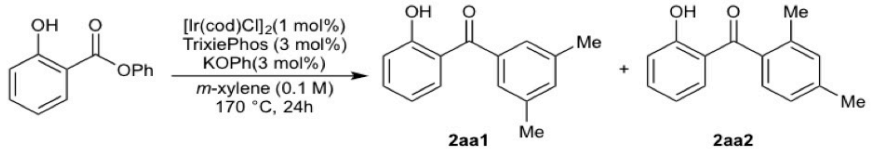
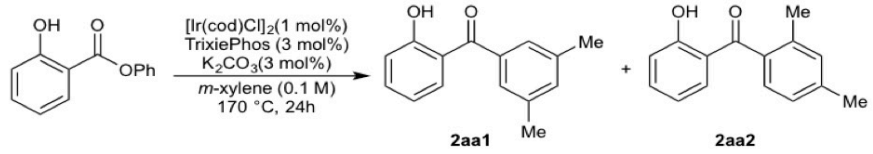
NAS1-89/10
[Ir(cod)OPh] Dimer, no additive
500.13
294.0
C6D6



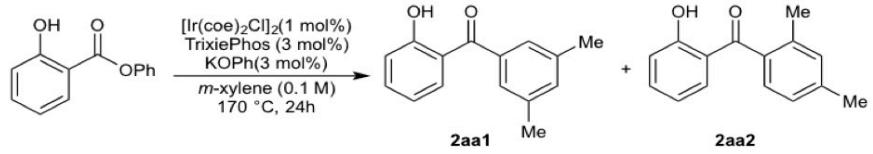
NAS1-89/20
[Ir(cod)Cl] Dimer, with KOPh
500.13
294.0
C6D6



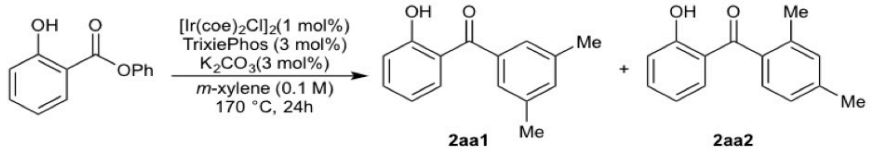
NAS1-89/30
[Ir(cod)Cl] Dimer, with K2CO3
500.13
294.0
C6D6

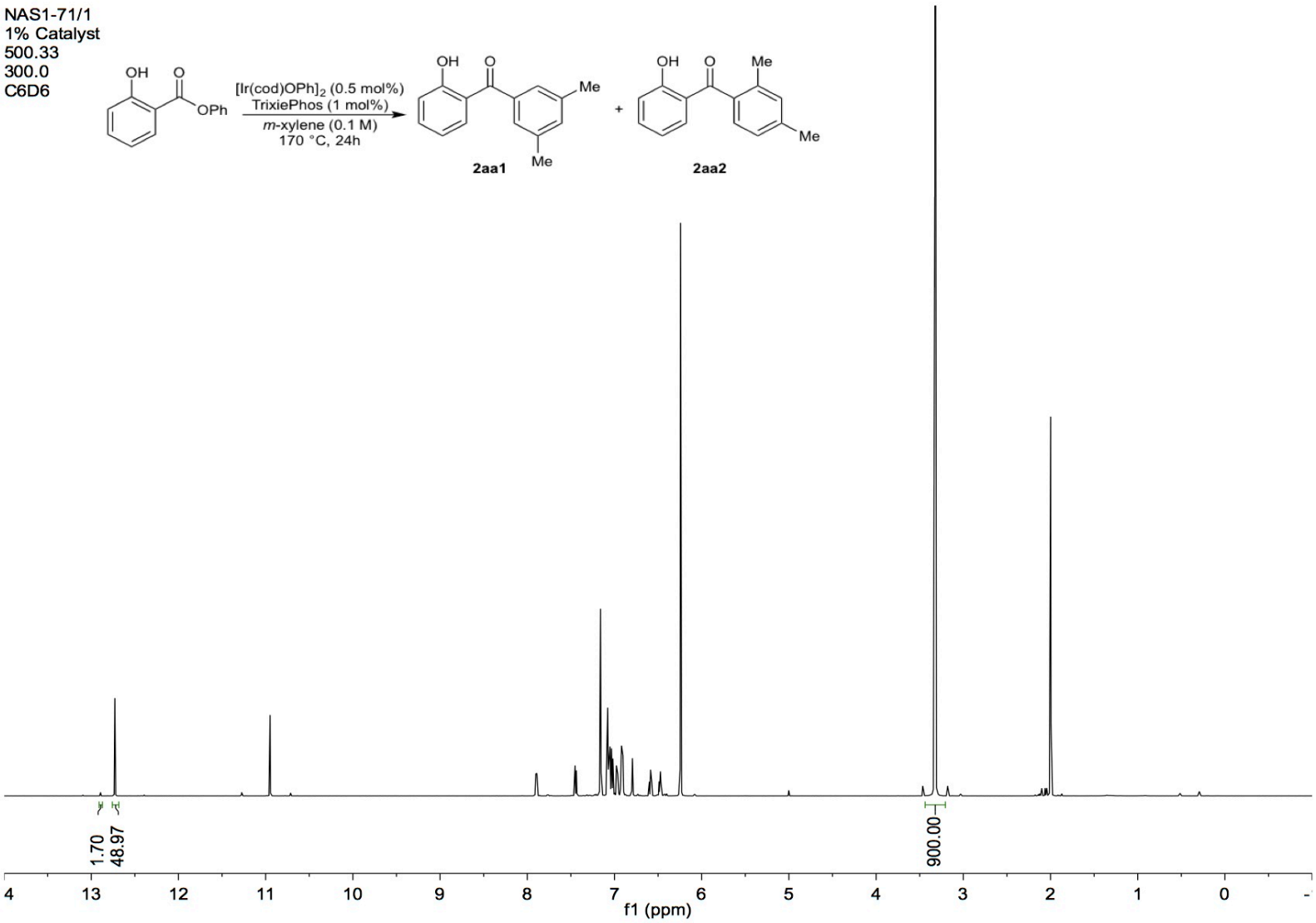


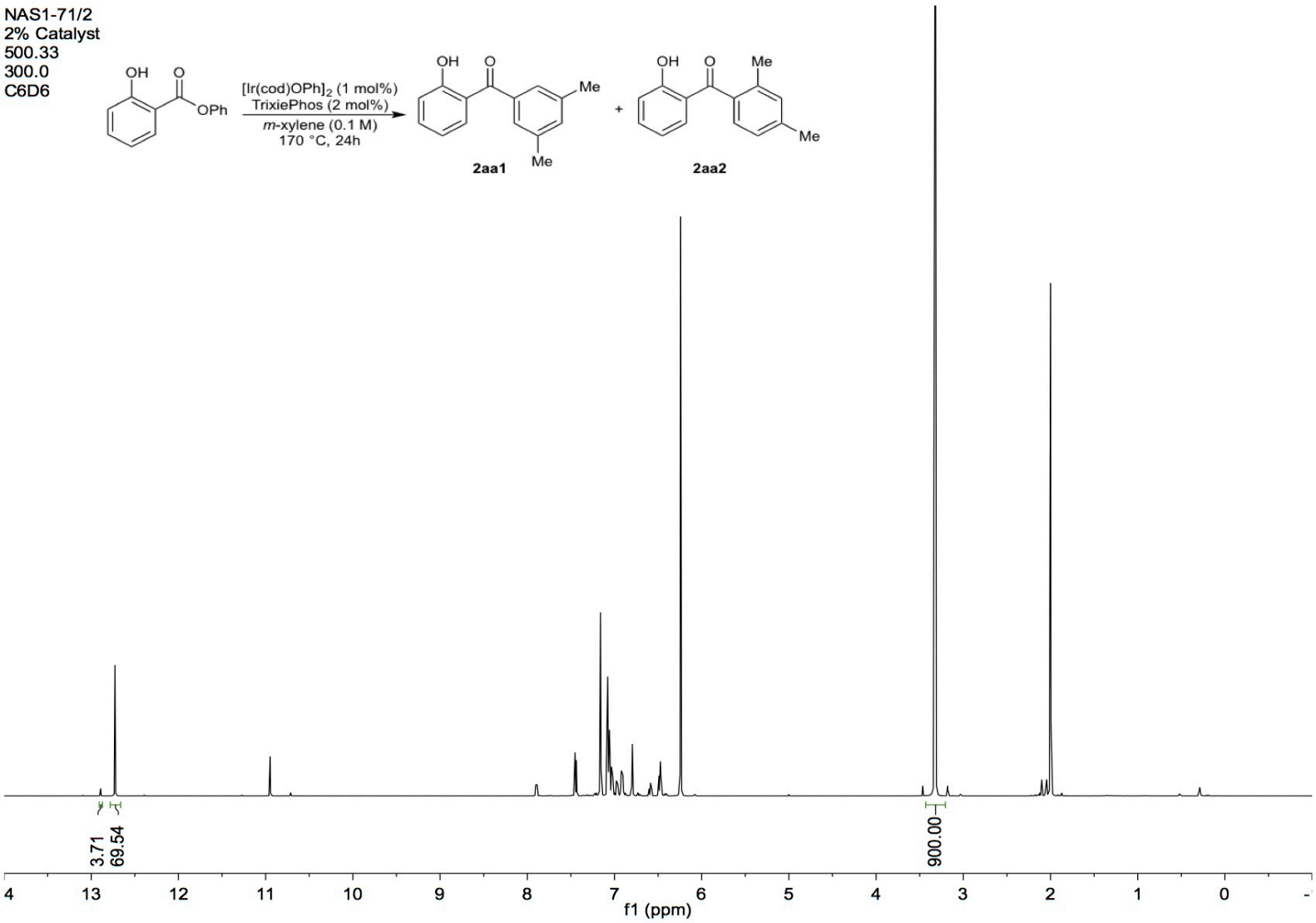
NAS1-89/40
[Ir(coe)2Cl] Dimer, with KOPh
500.13
294.0
C6D6

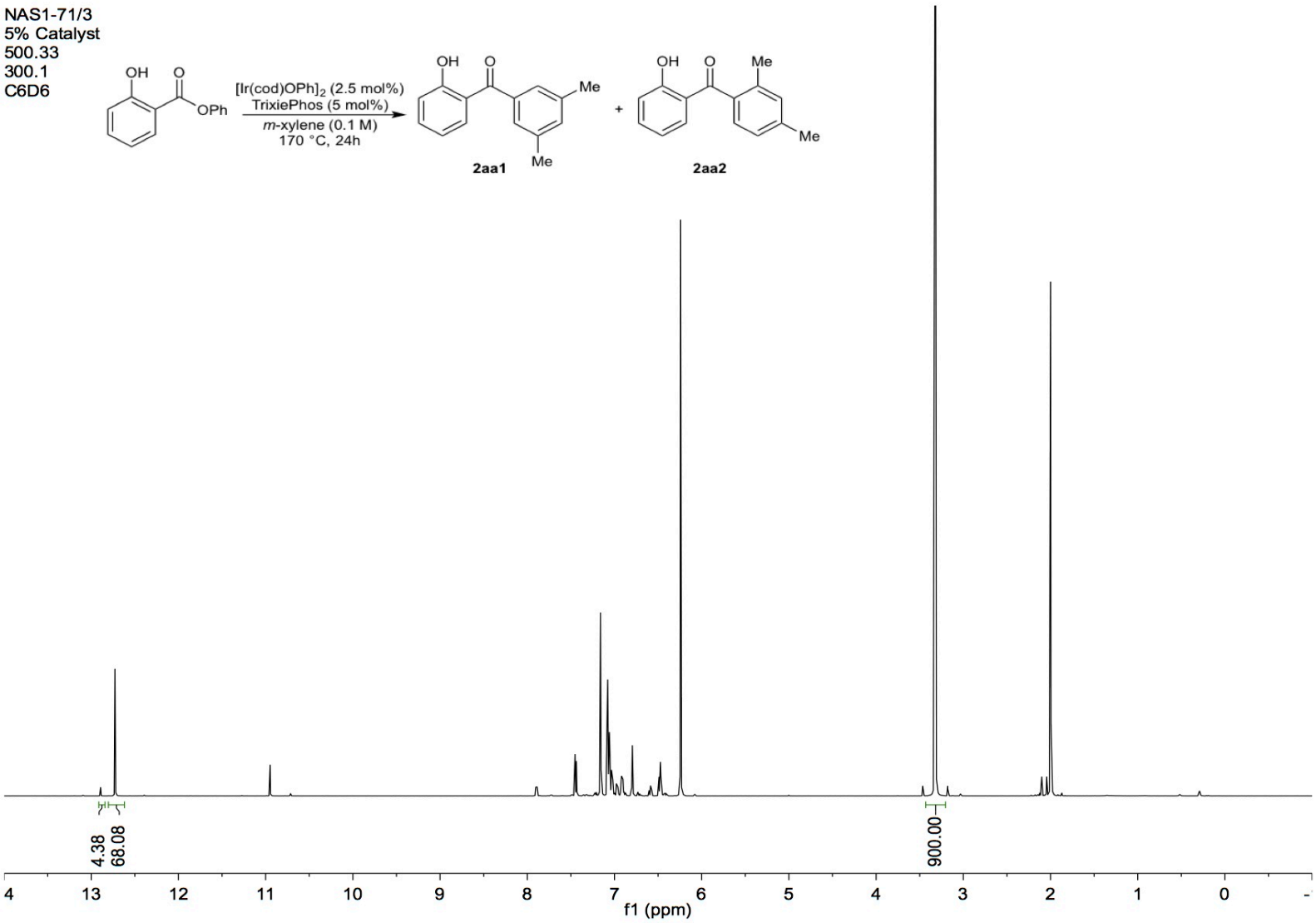


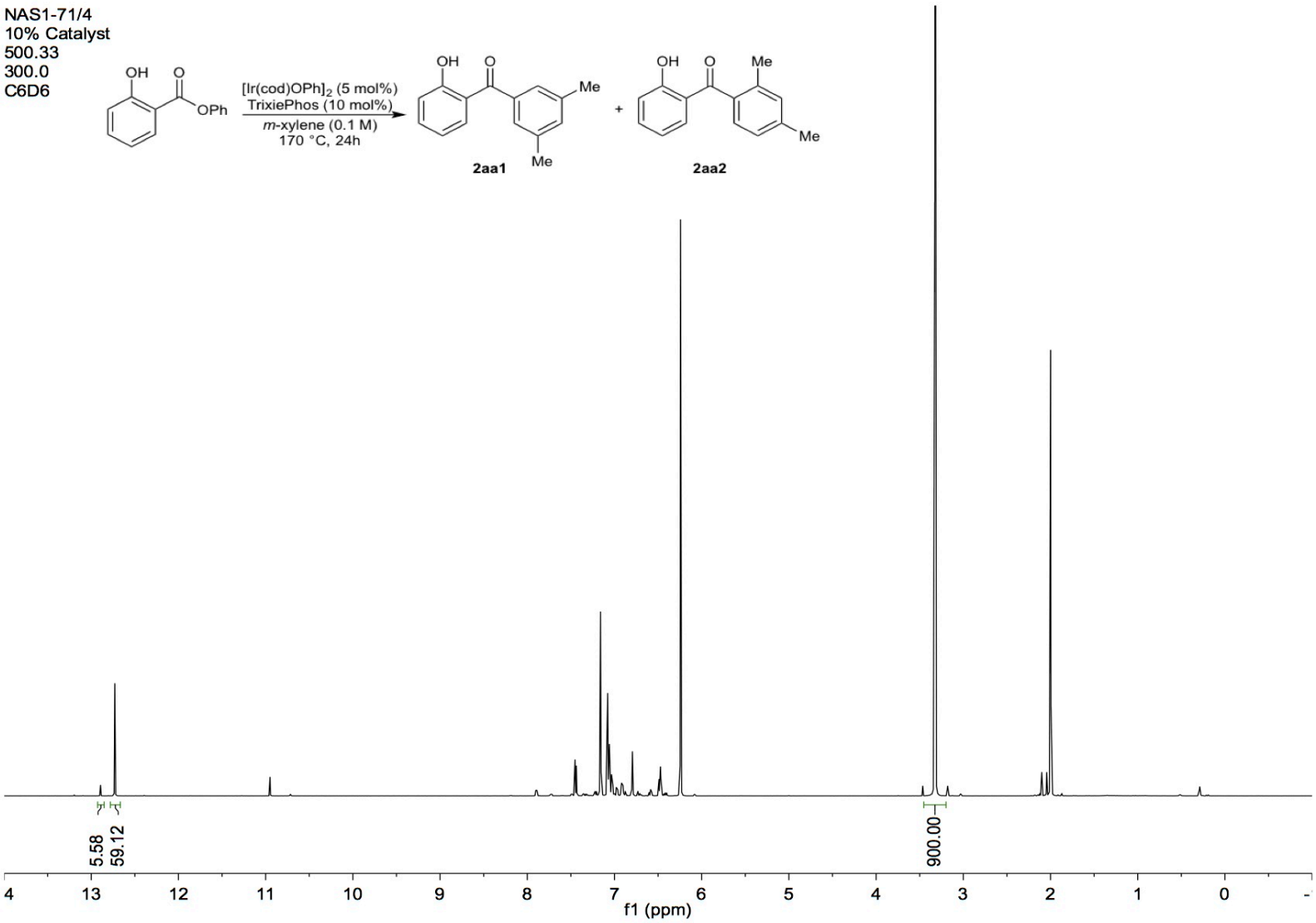
NAS1-89/50
[Ir(coe)2Cl] Dimer, with K2CO3
500.13
294.0
C6D6

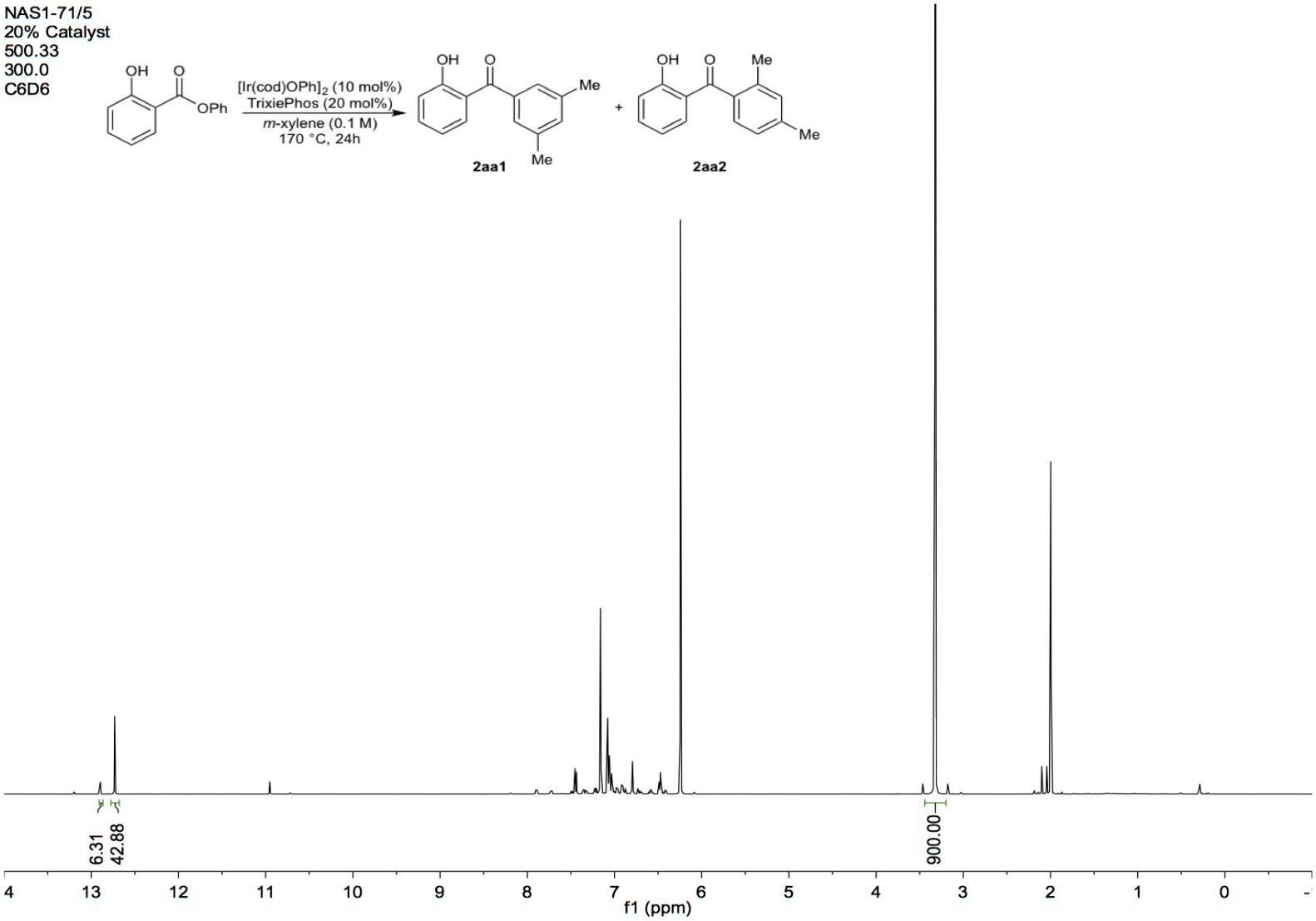



NAS1-71/1
1% Catalyst
500.33
300.0
C6D6
OH
O
OPh
[Ir(cod)OPh]2 (0.5 mol%)
TrixiePhos (1 mol%)
m-xylene (0.1 M)
170 °C, 24h
OH
O
Me
Me
2aa1
+
OH
O
Me
Me
2aa2
1.70
48.97
300.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

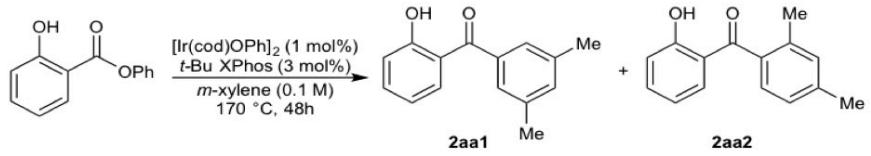

NAS1-71/2
2% Catalyst
500.33
300.0
C6D6
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (2 mol%)
m-xylene (0.1 M)
170 °C, 24h
OH
O
Me
Me
2aa1
+
OH
O
Me
Me
2aa2
3.71
69.54
900.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


NAS1-71/3
5% Catalyst
500.33
300.1
C6D6
OH
O
OPh
[Ir(cod)OPh]2 (2.5 mol%)
TrixiePhos (5 mol%)
m-xylene (0.1 M)
170 °C, 24h
OH
O
Me
Me
2aa1
+
OH
O
Me
Me
2aa2
4.38
68.08
900.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

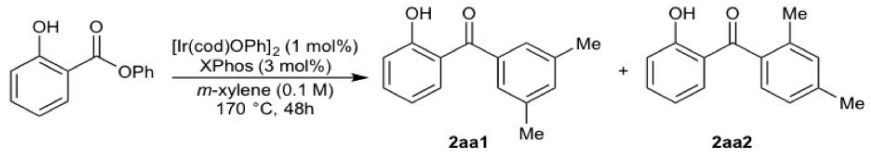

NAS1-71/4
10% Catalyst
500.33
300.0
C6D6
OH
O
OPh
[Ir(cod)OPh]2 (5 mol%)
TrixiePhos (10 mol%)
m-xylene (0.1 M)
170 °C, 24h
OH
O
Me
Me
2aa1
+
OH
O
Me
Me
2aa2
5.58
59.12
900.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


NAS1-71/5
20% Catalyst
500.33
300.0
C6D6
OH
O
OPh
[Ir(cod)OPh]2 (10 mol%)
TrixiePhos (20 mol%)
m-xylene (0.1 M)
170 °C, 24h
OH
O
Me
Me
2aa1
+
OH
O
Me
Me
2aa2
6.31
42.88
900.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

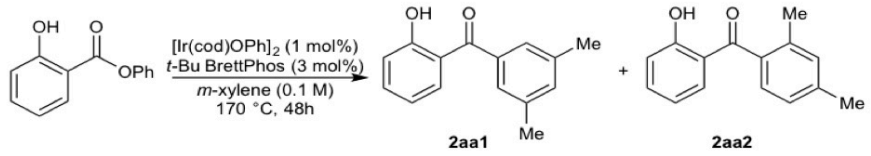
NAS1-103/10
t-Bu XPhos
500.13
297.0
C6D6



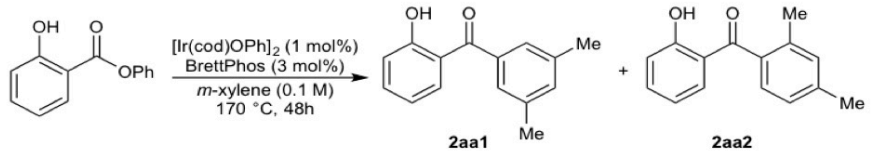
NAS1-103/20
XPhos
500.13
297.0
C6D6



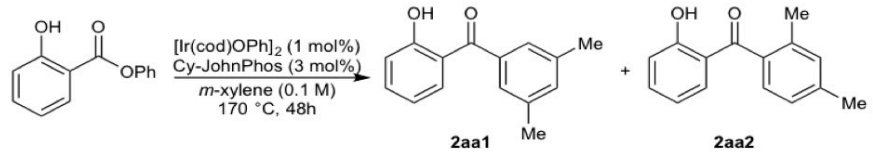
NAS1-103/30
t-Bu BrettPhos
500.13
297.0
C6D6



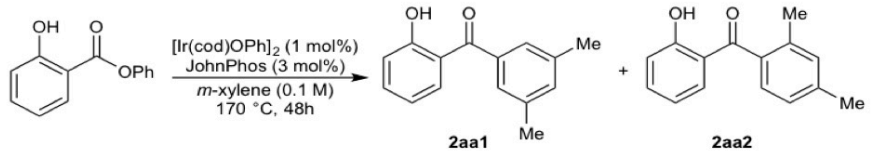
NAS1-103/40
BrettPhos
500.13
297.0
C6D6



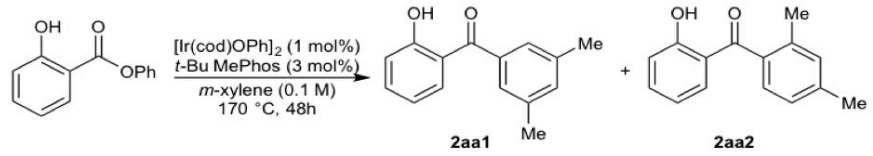
NAS1-103/50
Cy-JohnPhos
500.13
297.0
C6D6



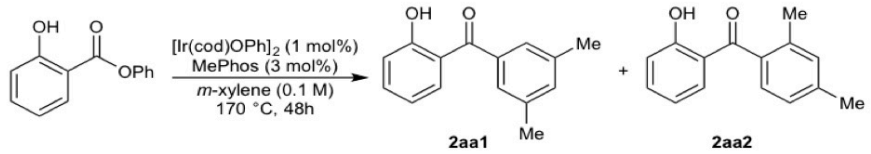
NAS1-103/100
JohnPhos
500.13
297.0
C6D6



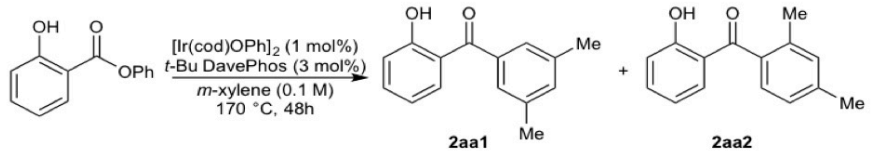
NAS1-103/110
t-Bu MePhos
500.13
297.0
C6D6



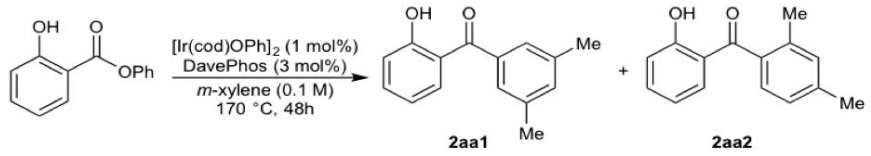
NAS1-103/60
MePhos
500.13
297.0
C6D6



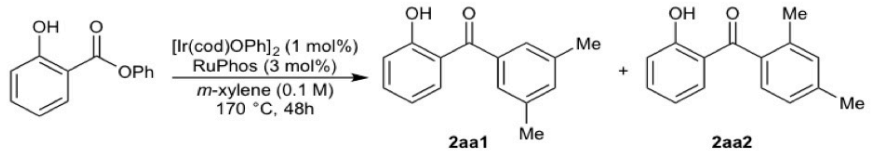
NAS1-103/120
t-Bu DavePhos
500.13
297.0
C6D6



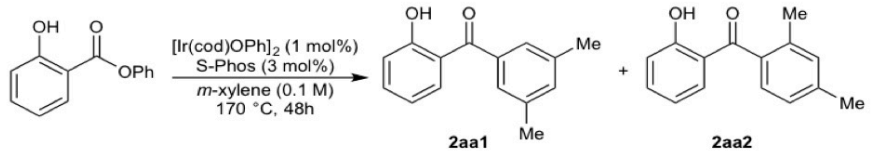
NAS1-103/70
DavePhos
500.13
297.0
C6D6



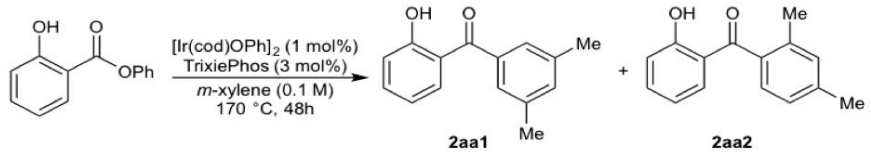
NAS1-103/80
RuPhos
500.13
297.0
C6D6



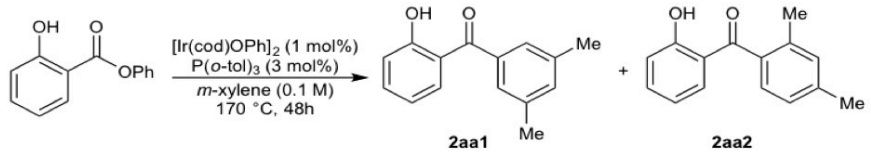
NAS1-103/90
S-Phos
500.13
297.0
C6D6



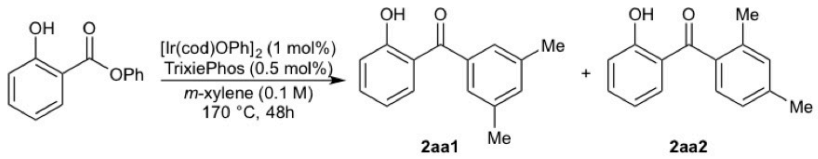
NAS1-103/130
TrixiePhos
500.13
297.0
C6D6



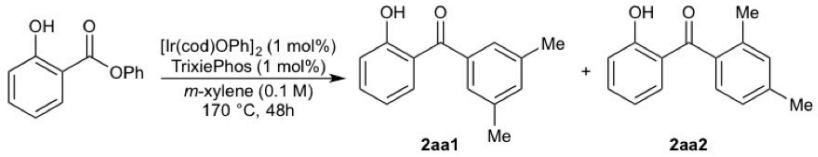
NAS1-103/140
P(o-tol)3
500.13
297.0
C6D6



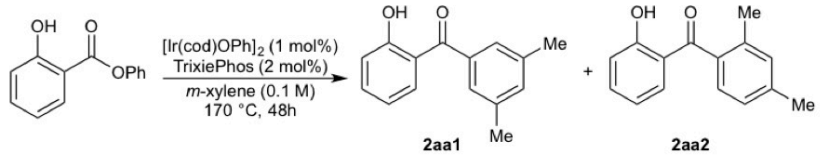
NAS1-73.1.fid
0.5 mol% TrixiePhos
500.33
300.0
C6D6



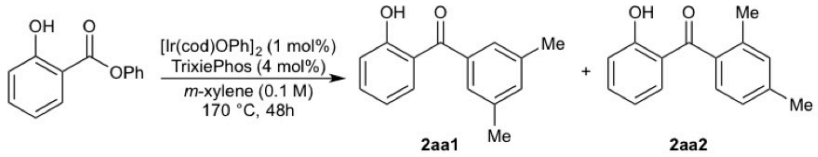
NAS1-73.2.fid
1 mol% TrixiePhos
500.33
300.1
C6D6



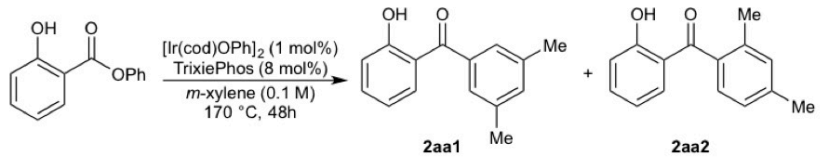
NAS1-73.3.fid
2 mol% TrixiePhos
500.33
300.0
C6D6



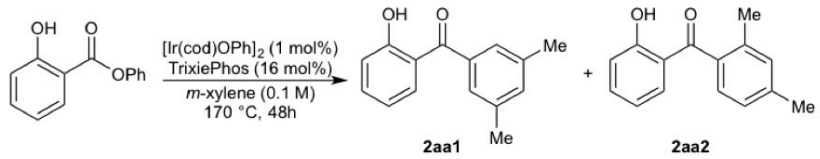
NAS1-73.4.fid
4 mol% TrixiePhos
500.33
299.9
C6D6



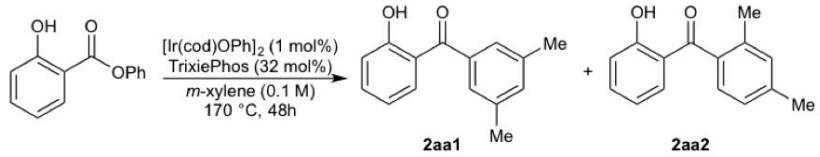
NAS1-73.5.fid
8 mol% TrixiePhos
500.33
300.0
C6D6



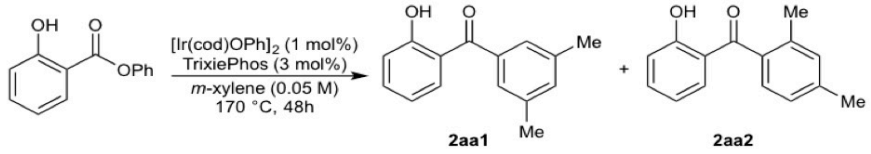
NAS1-73.6.fid
16 mol% TrixiePhos
500.33
300.0
C6D6



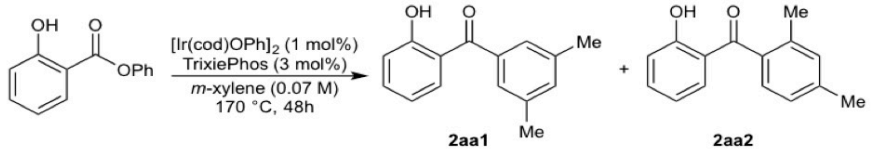
NAS1-73.7.fid
32 mol% TrixiePhos
500.33
300.0
C6D6



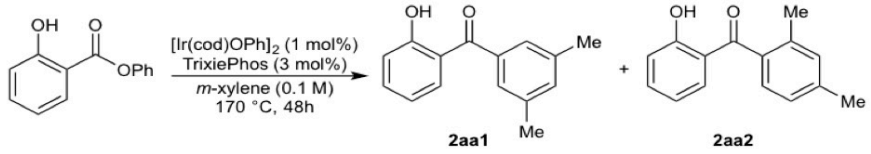
NAS1-85/10
0.05M Phenyl Salicylate
500.13
294.0
C6D6



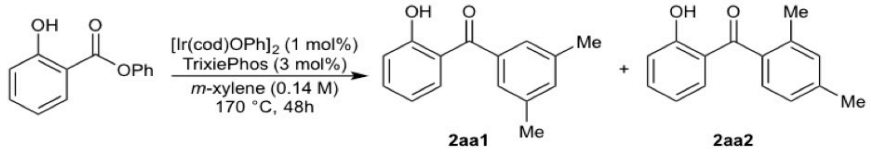
NAS1-85/20
0.07M Phenyl Salicylate
500.13
294.0
C6D6



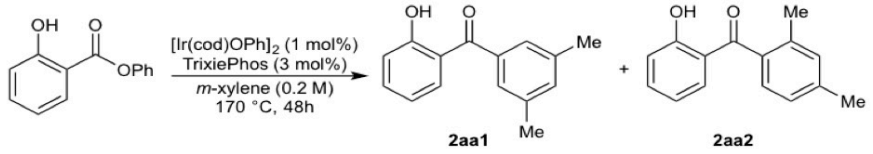
NAS1-85/30
0.1M Phenyl Salicylate
500.13
294.0
C6D6



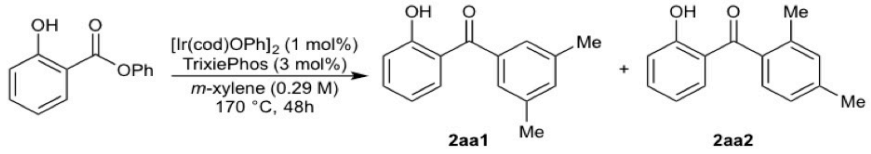
NAS1-85/40
0.14M Phenyl Salicylate
500.13
294.0
C6D6



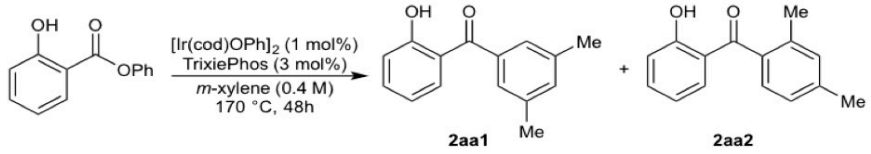
NAS1-85/50
0.2M Phenyl Salicylate
500.13
294.0
C6D6



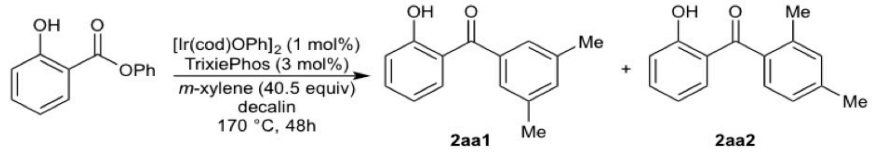
NAS1-85/60
0.29M Phenyl Salicylate
500.13
294.0
C6D6



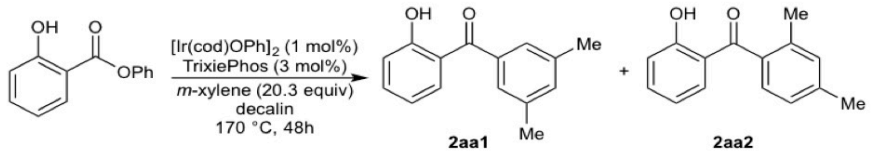
NAS1-85/70
0.4M Phenyl Salicylate
500.13
294.0
C6D6



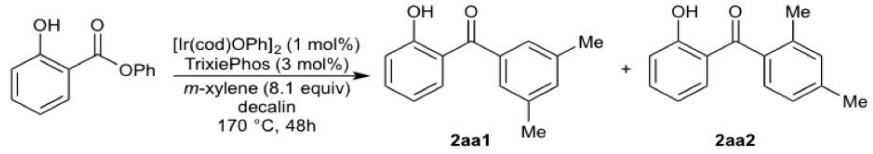
NAS1-75/1
40.5 equiv m-xylene in decalin
500.33
300.0
C6D6



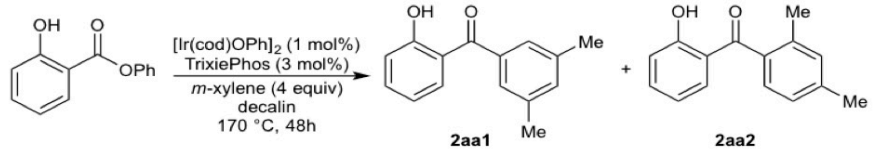
NAS1-75/2
20.3 equiv m-xylene in decalin
500.33
300.0
C6D6



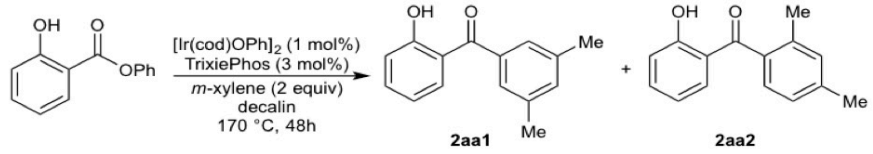
NAS1-75/3
8.1 equiv m-xylene in decalin
500.33
300.0
C6D6



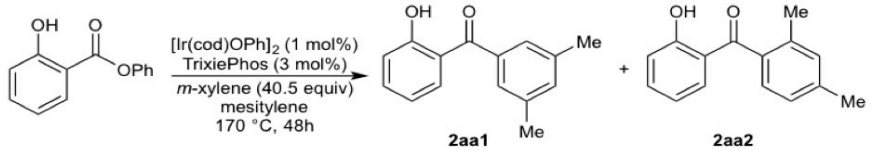
NAS1-75/4
4 equiv m-xylene in decalin
500.33
300.1
C6D6



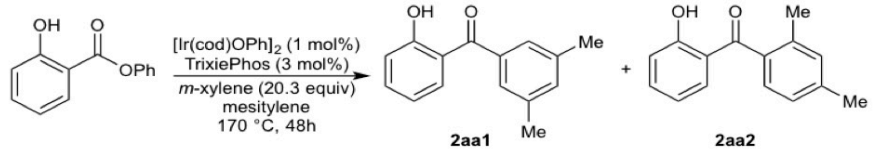
NAS1-75/5
2 equiv m-xylene in decalin
500.33
300.0
C6D6



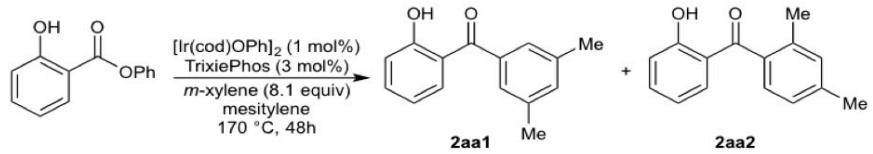
NAS1-75/6
40.5 equiv m-xylene in mesitylene
500.33
300.0
C6D6



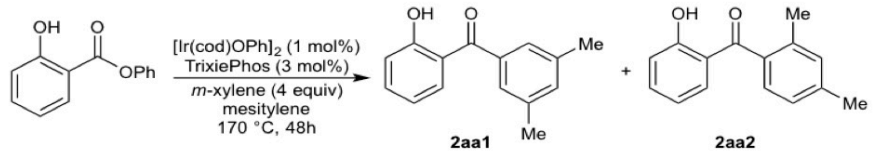
NAS1-75/7
20.3 equiv m-xylene in mesitylene
500.33
300.1
C6D6



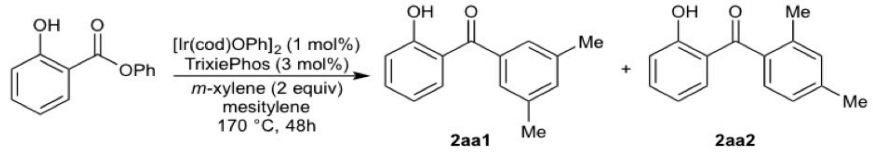
NAS1-75/8
8.1 equiv m-xylene in mesitylene
500.33
300.1
C6D6



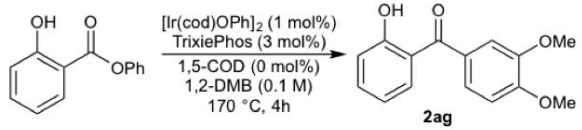
NAS1-75/9
4 equiv m-xylene in mesitylene
500.33
300.1
C6D6



NAS1-75/10
2 equiv m-xylene in mesitylene
500.33
300.1
C6D6

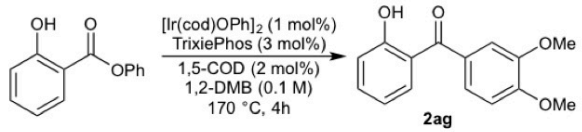


NAS1-178.10.fid
0% COD
500.13
296.0
CDCl3



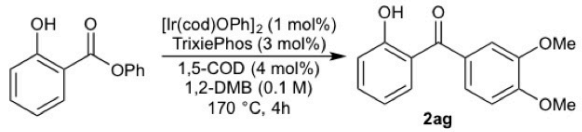
2ag

NAS1-178.20.fid
2% COD
500.13
296.0
CDCl3



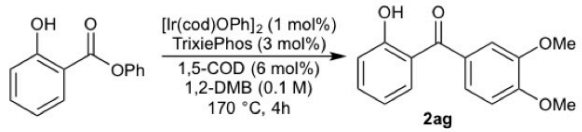
2ag

NAS1-178.30.fid
4% COD
500.13
296.0
CDCl3



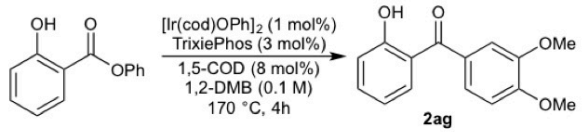
2ag

NAS1-178.40.fid
6% COD
500.13
296.0
CDCl3



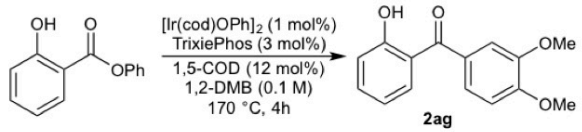
2ag

NAS1-178.50.fid
8% COD
500.13
296.0
CDCl3



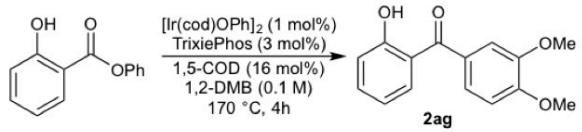
2ag

NAS1-178.60.fid
12% COD
500.13
296.0
CDCl3



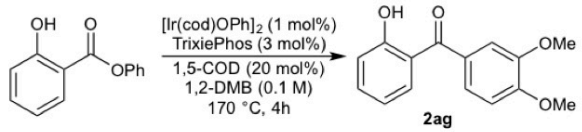
2ag

NAS1-178.70.fid
16% COD
500.13
296.0
CDCl3



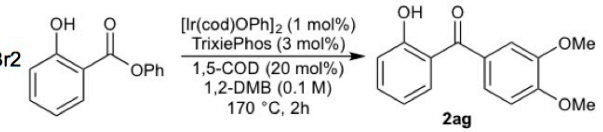
2ag

NAS1-178.80.fid
20% COD
500.13
296.0
CDCl3



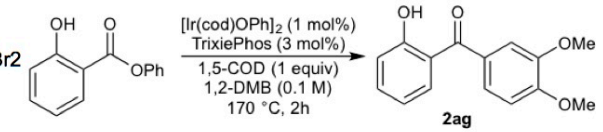
2ag

cdocba-160726-2.10.fid
20% COD for 2 hours
400.13
298.0
CDCl3
Yield in mmol rel. to CH2Br2



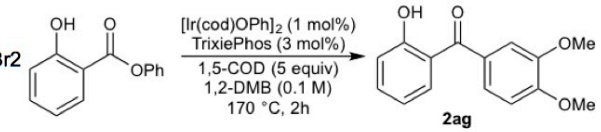
2ag

cdocba-160726-13.10.fid
1 equiv COD for 2 hours
400.13
298.0
CDCl3
Yield in mmol rel. to CH2Br2

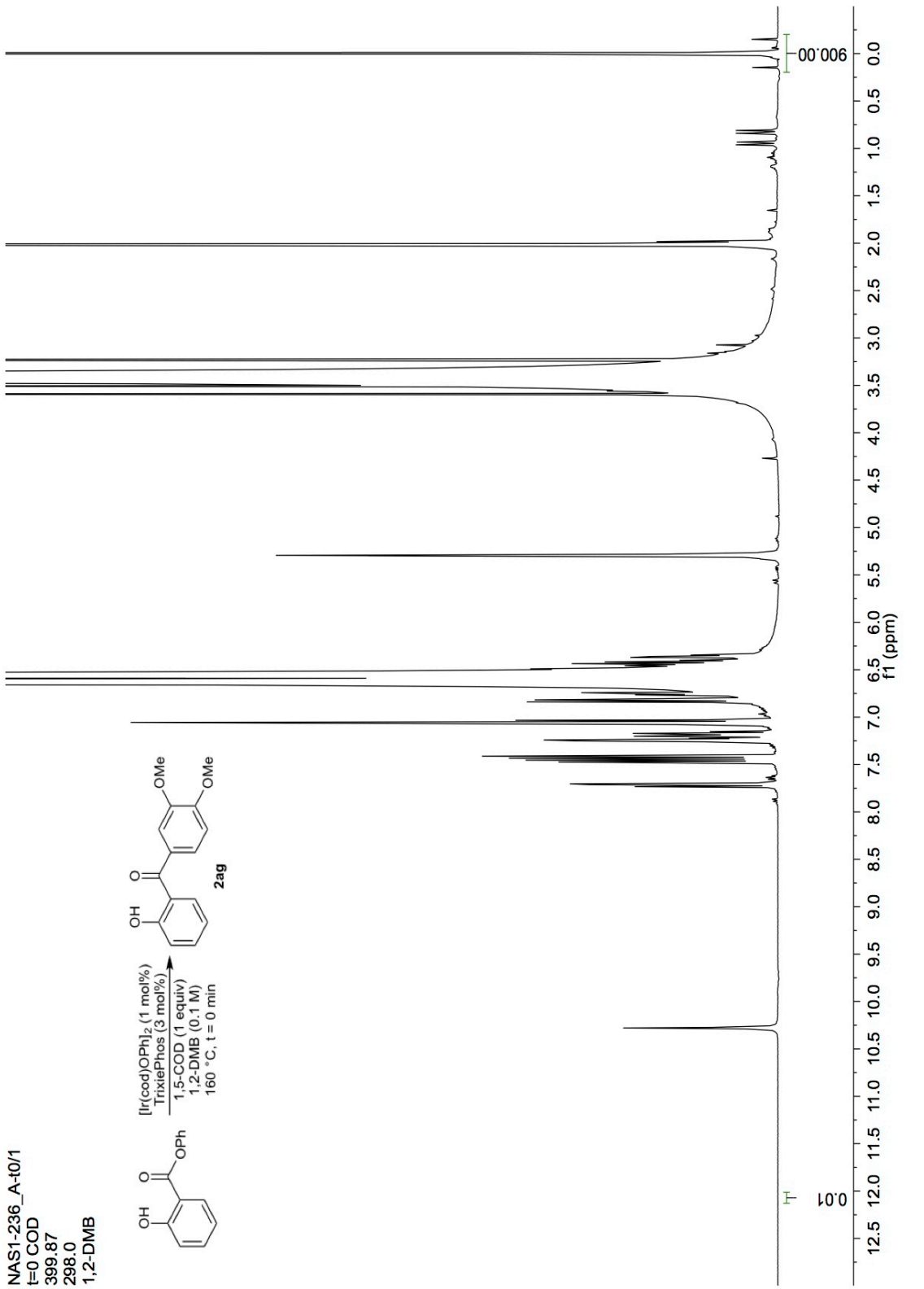


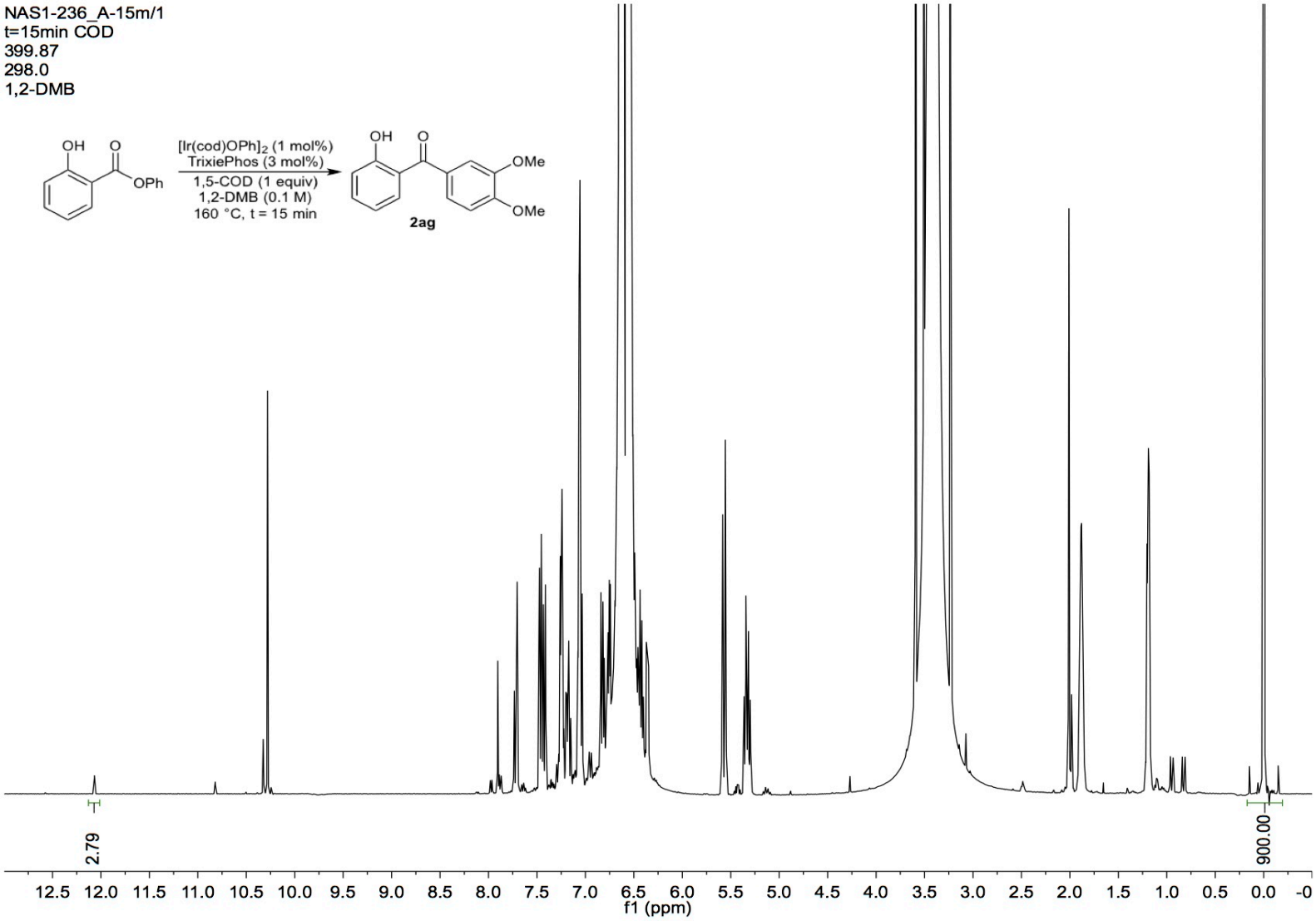
2ag

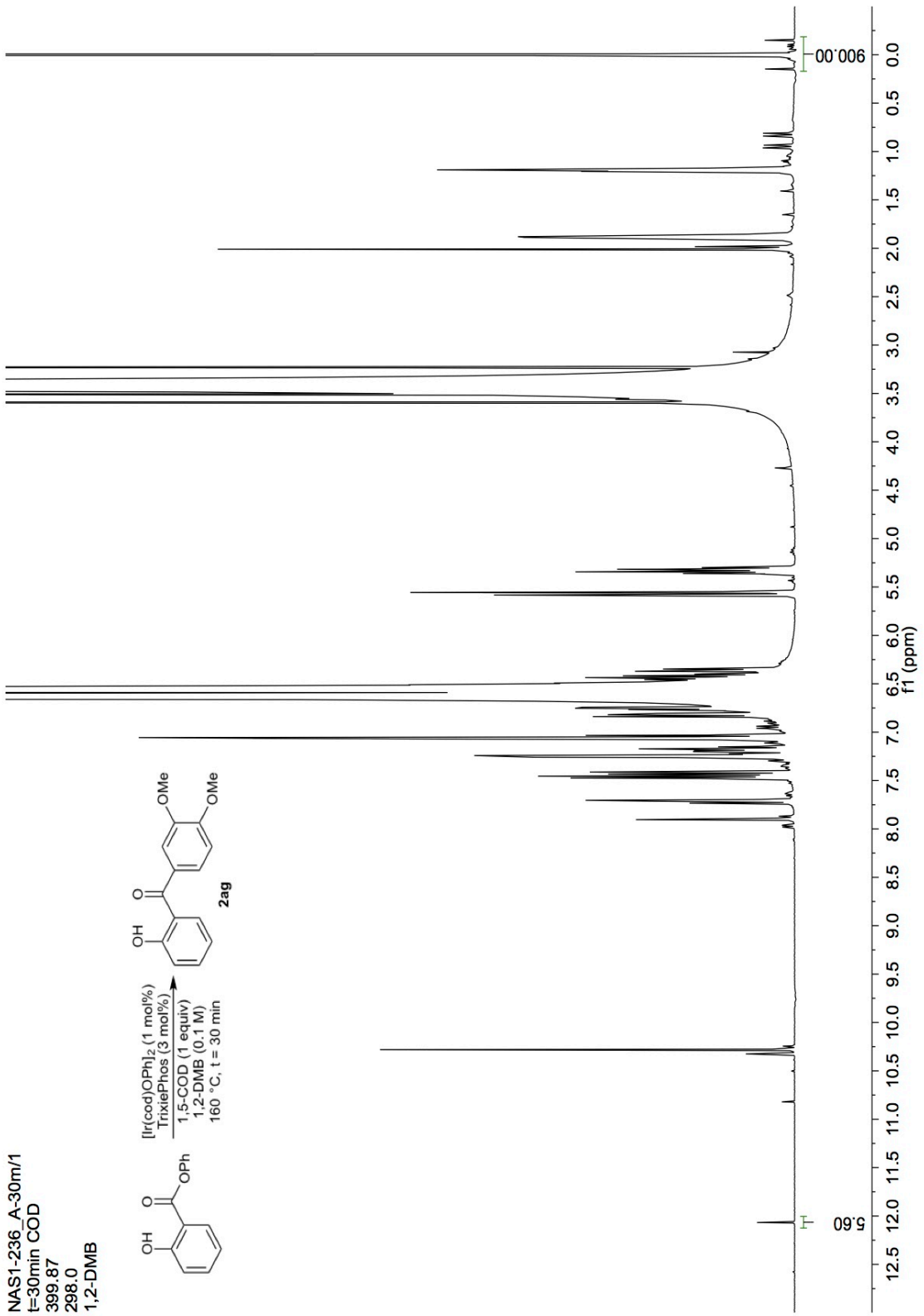
cdocba-160726-14.10.fid
5 equiv COD for 2 hours
400.13
298.0
CDCl3
Yield in mmol rel. to CH2Br2

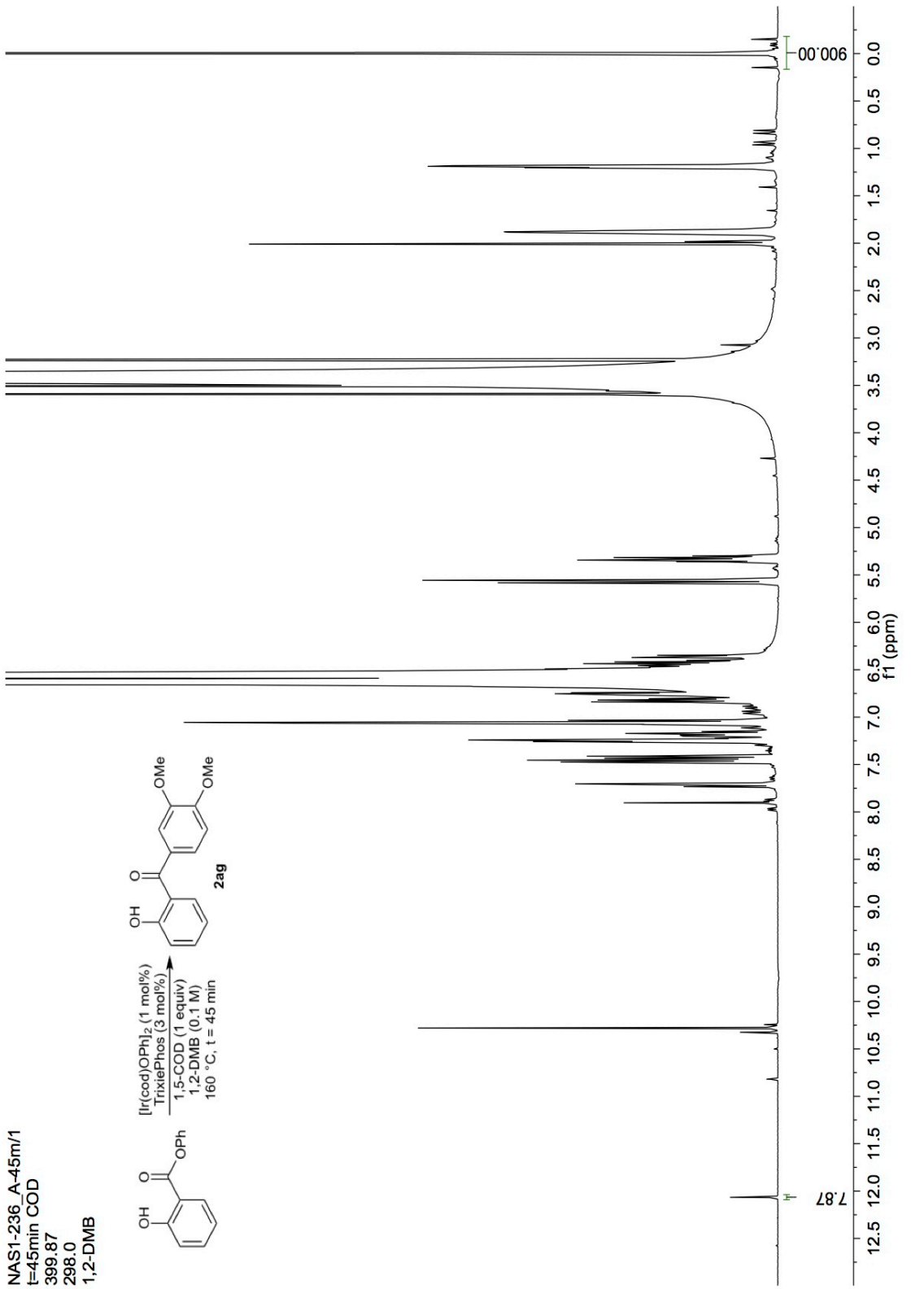


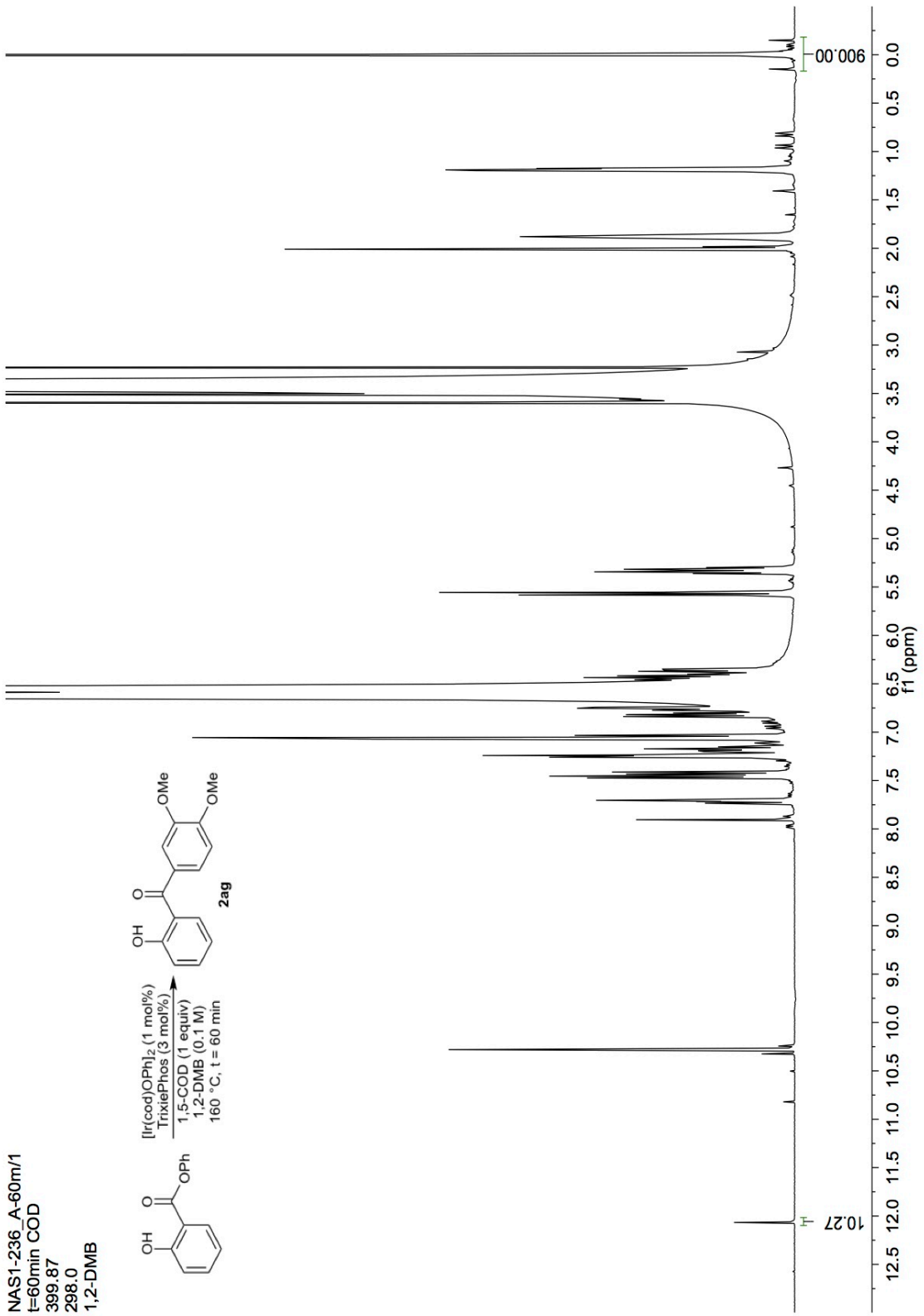
2ag

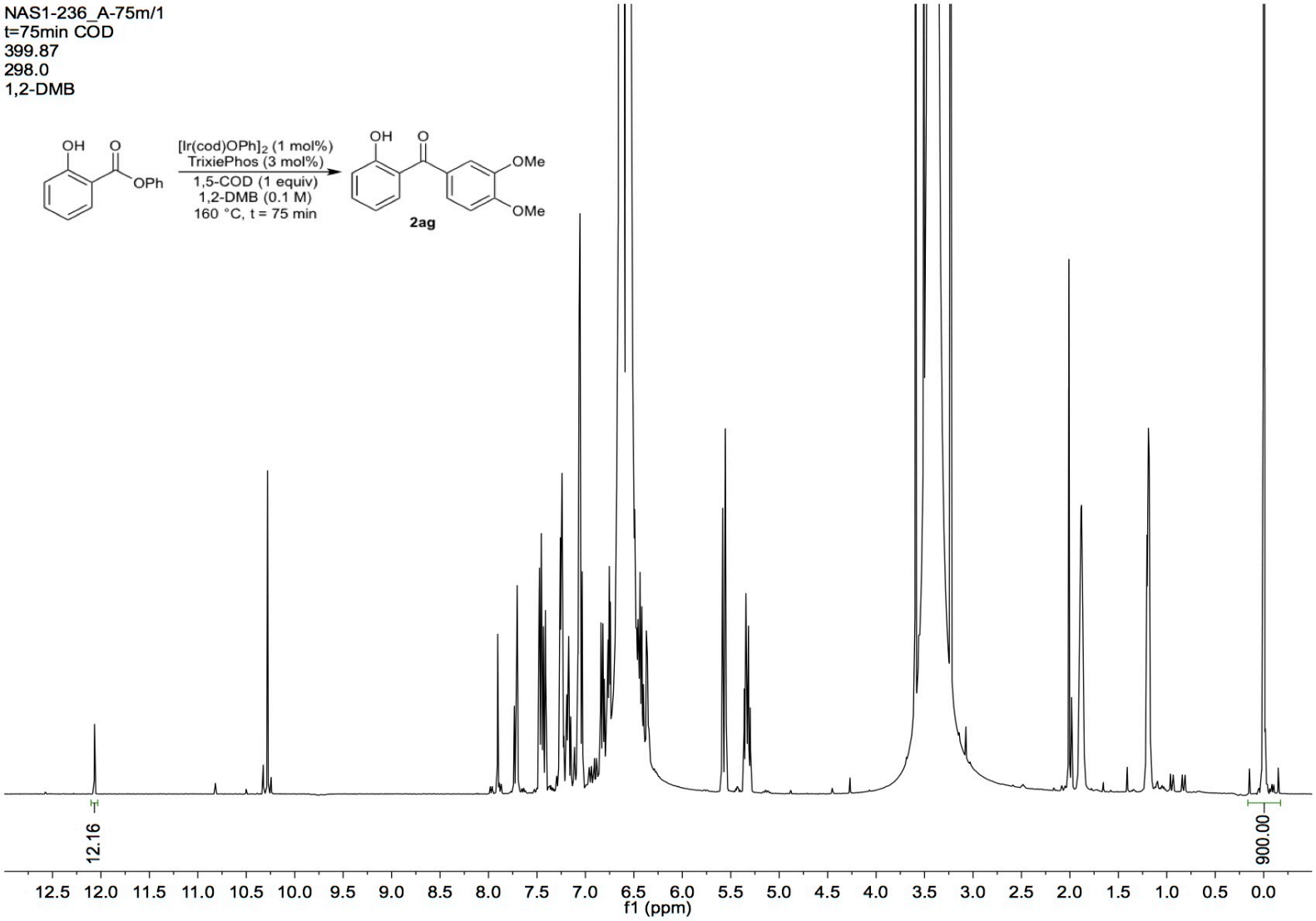

NAS1-236_A-t0/1
t=0 COD
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 0 min
OH
O
OMe
OMe
2ag
0.01
900.00
f1 (ppm)

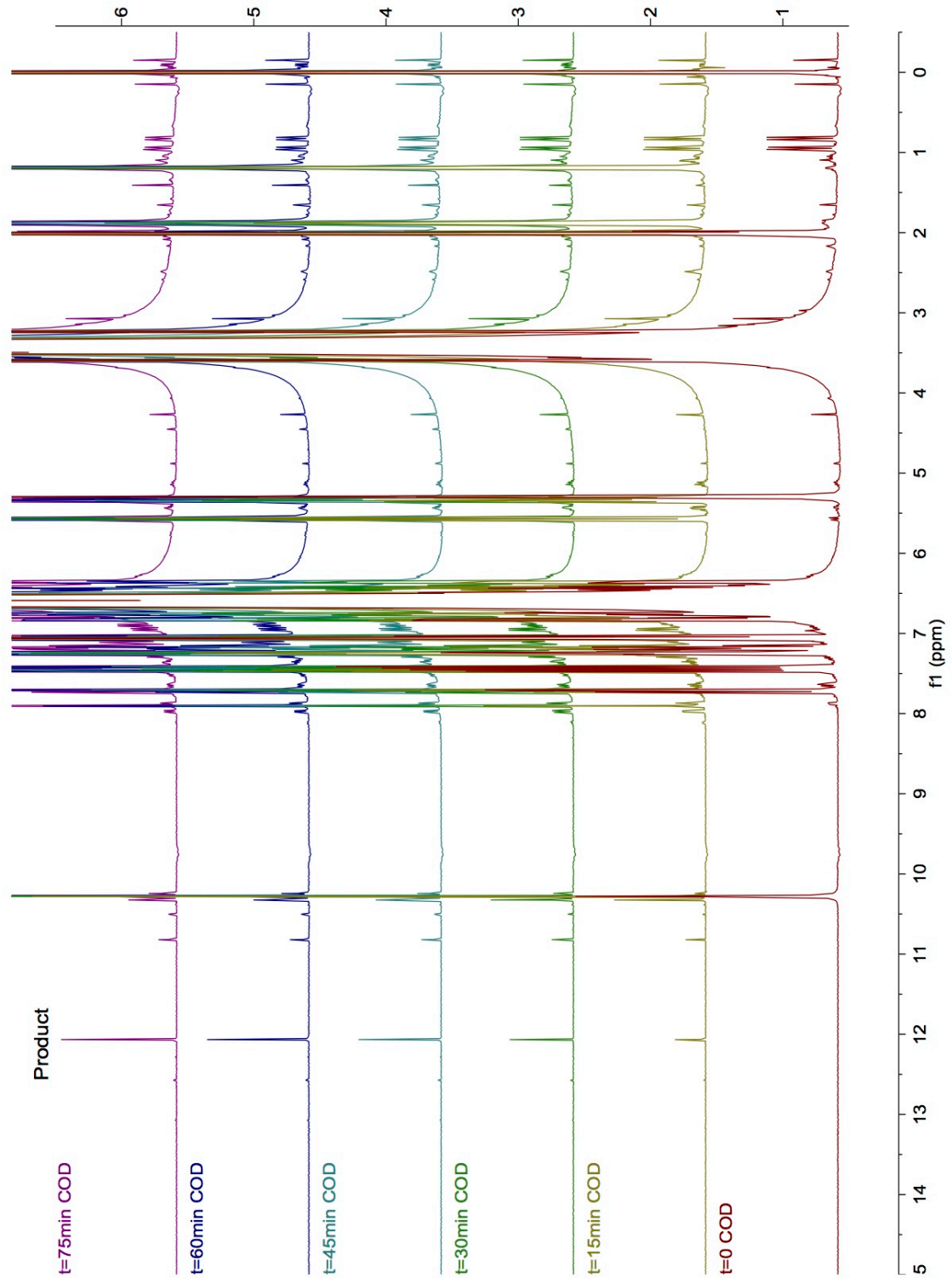

NAS1-236_A-15m/1
t=15min COD
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 15 min
OH
O
OMe
OMe
2ag
2.79
900.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

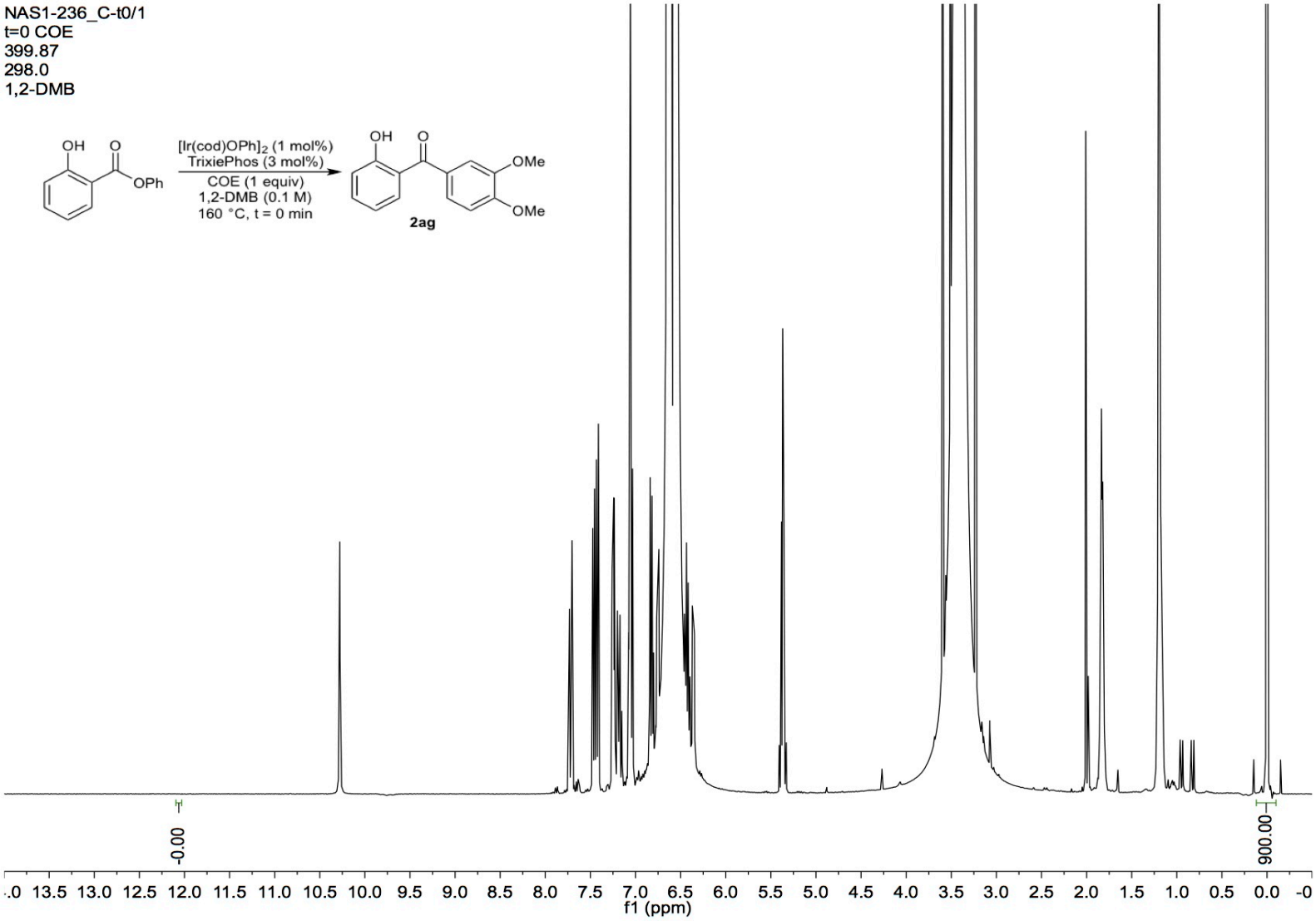

NAS1-236_A-30m/1
t=30min COD
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 30 min
OH
O
OMe
OMe
2ag
900.00
5.60
f1 (ppm)

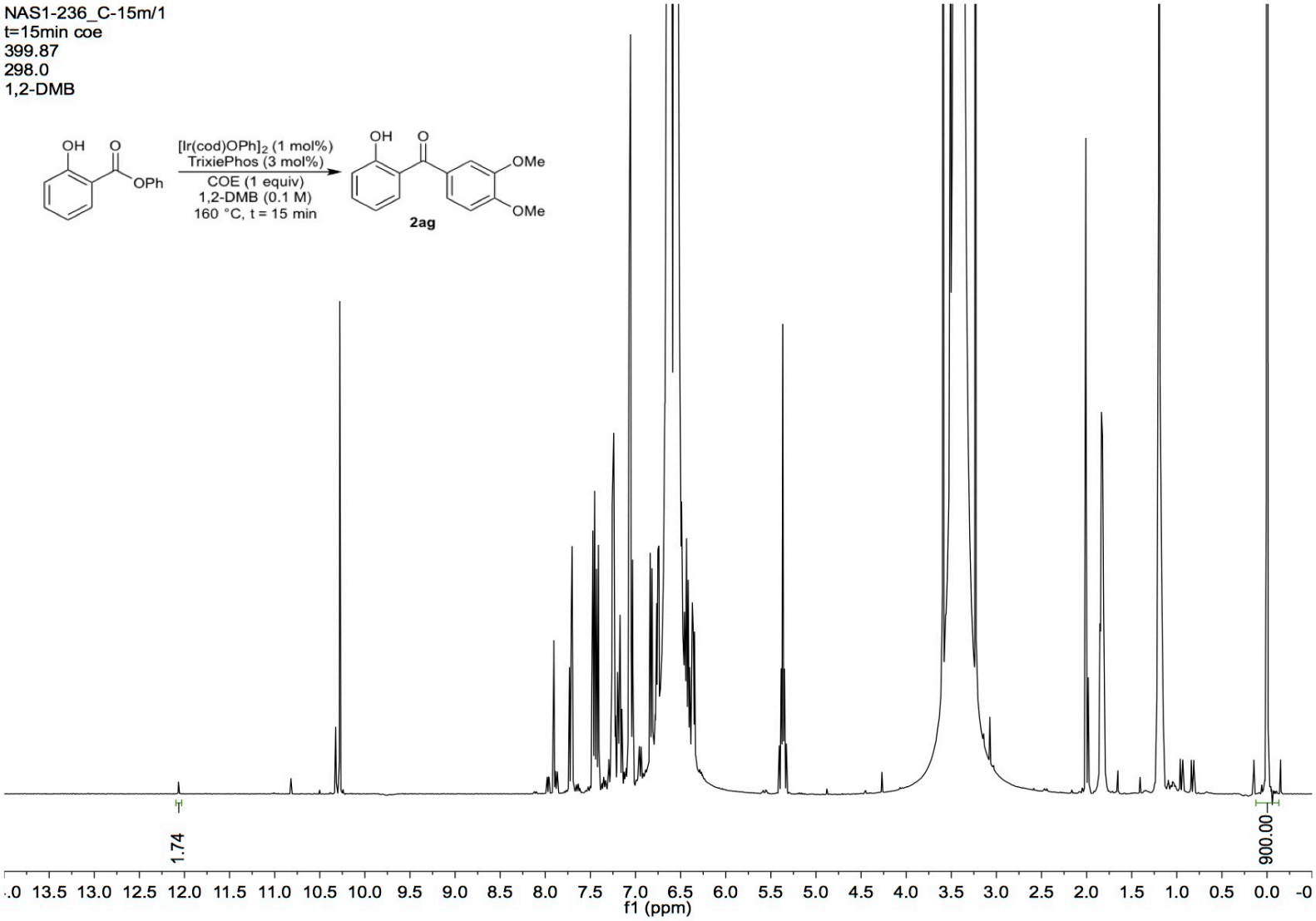

NAS1-236_A-45m/1
t=45min COD
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 45 min
OH
O
OMe
OMe
2ag
7.87
900.00
f1 (ppm)

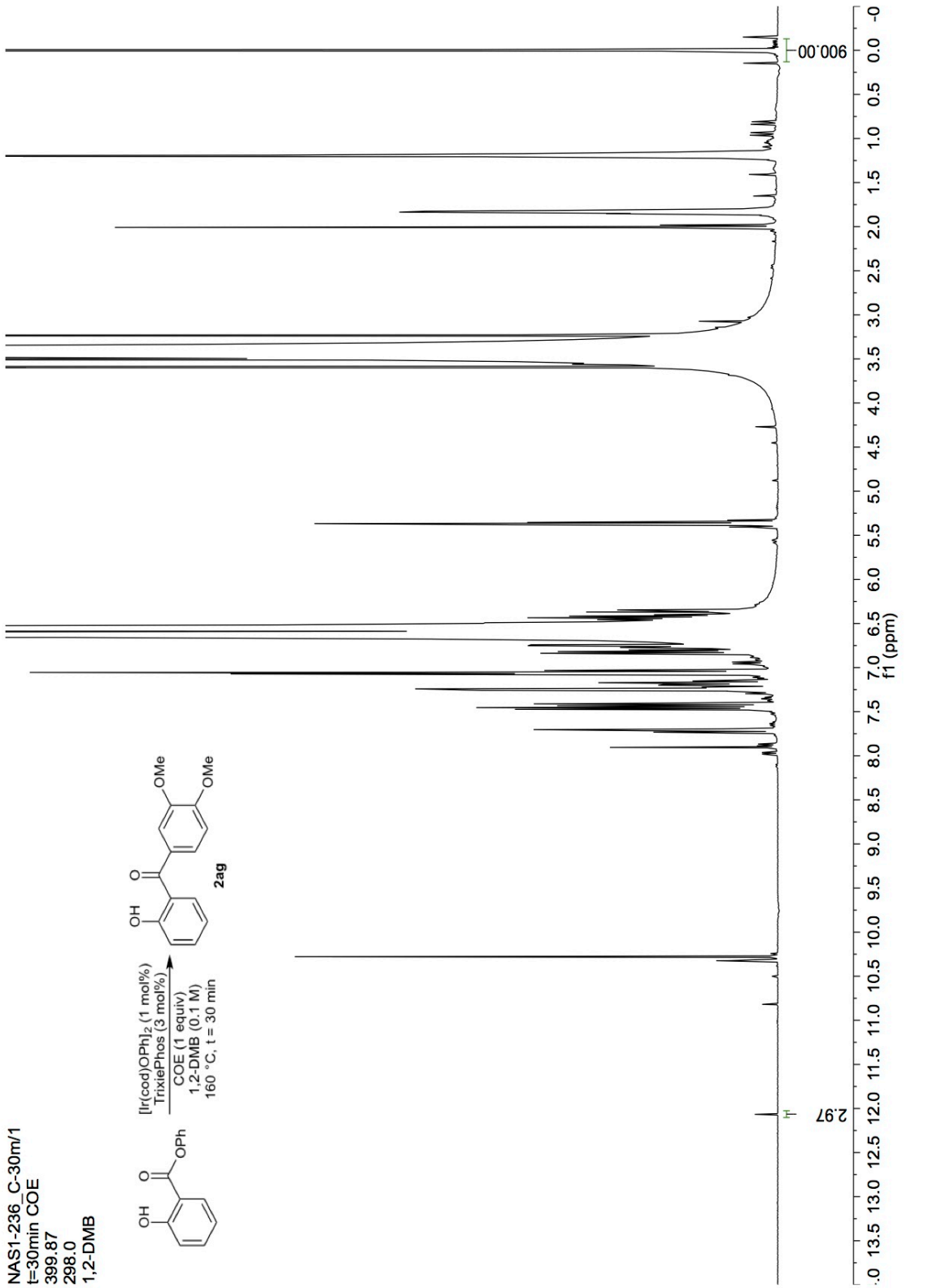

NAS1-236_A-60m/1
t=60min COD
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 60 min
OH
O
OMe
OMe
2ag
10.27
900.00
f1 (ppm)

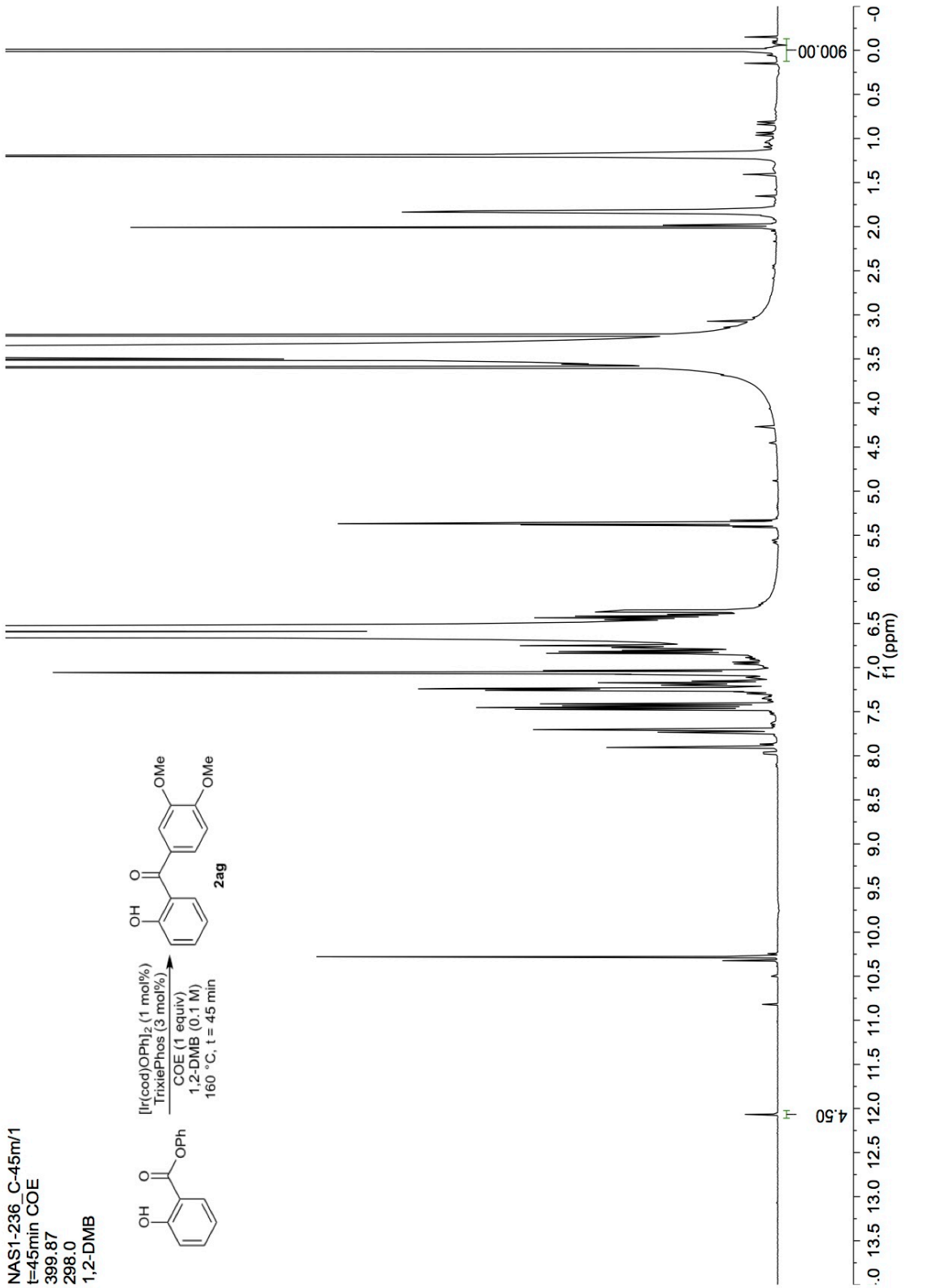

NAS1-236_A-75m/1
t=75min COD
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 75 min
OH
O
OMe
OMe
2ag
12.16
900.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

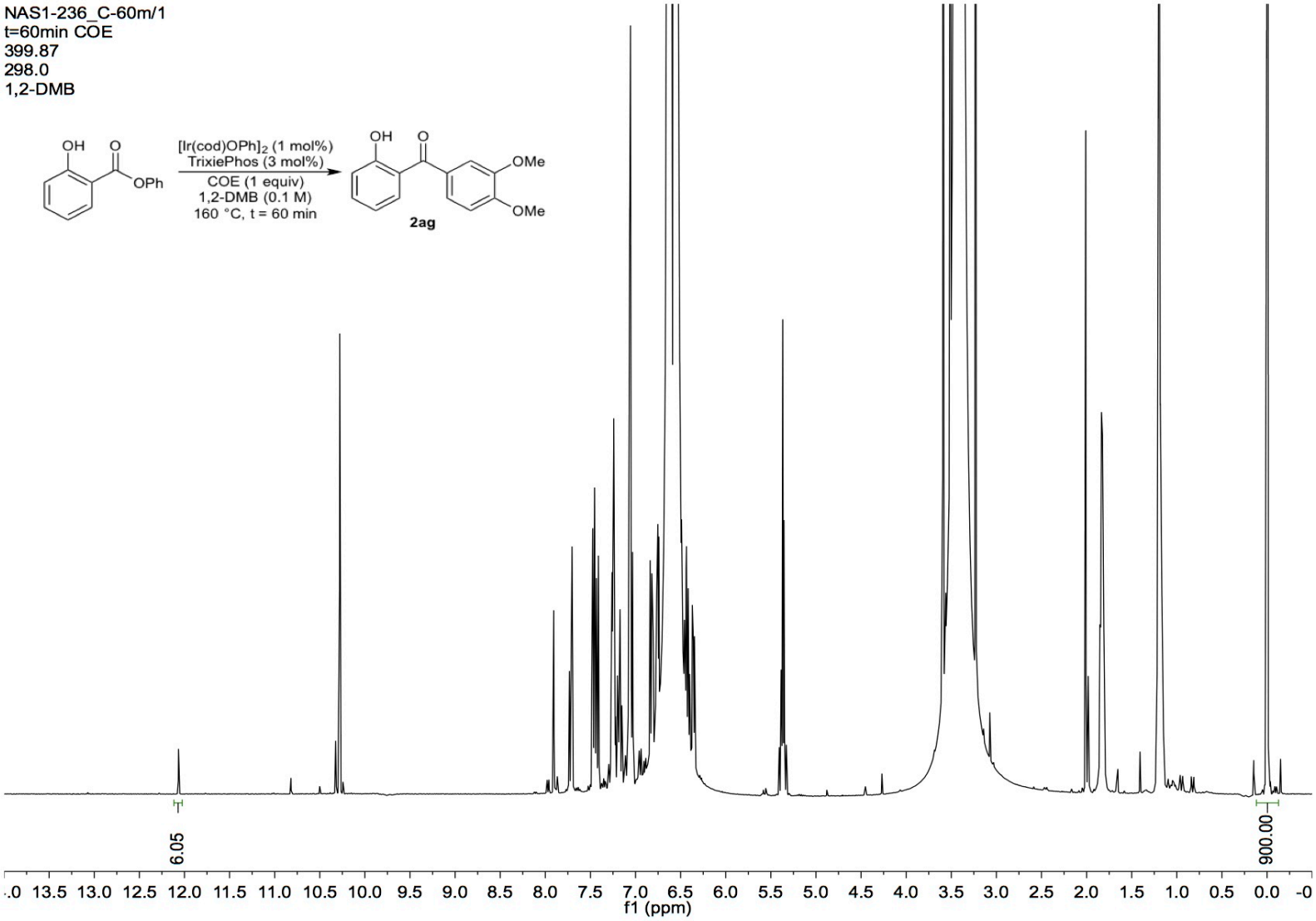

Product
t=75min COD
t=60min COD
t=45min COD
t=30min COD
t=15min COD
t=0 COD
f1 (ppm)

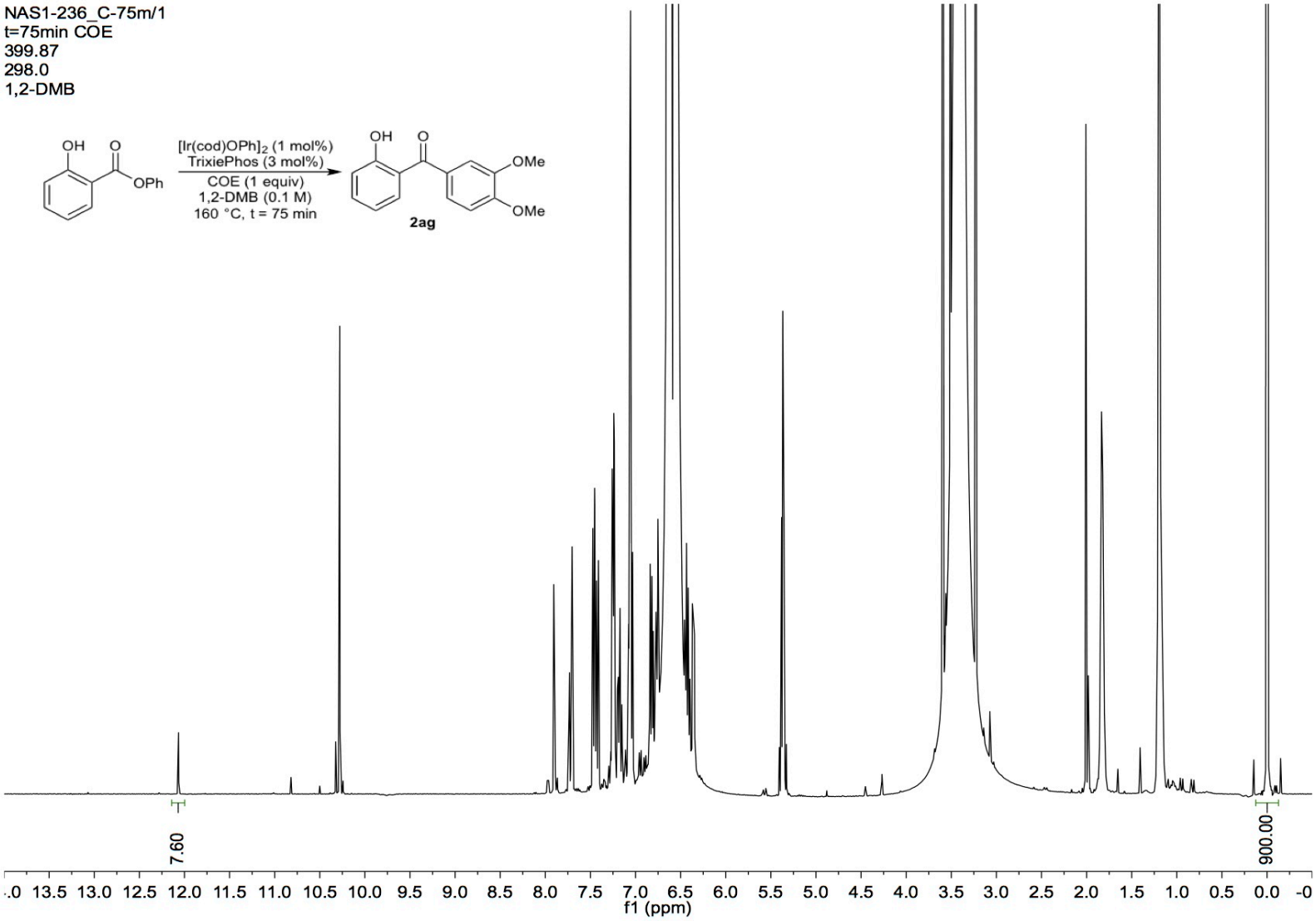

NAS1-236_C-t0/1
t=0 COE
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
COE (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 0 min
OH
O
OMe
OMe
2ag
-0.00
9.00
f1 (ppm)

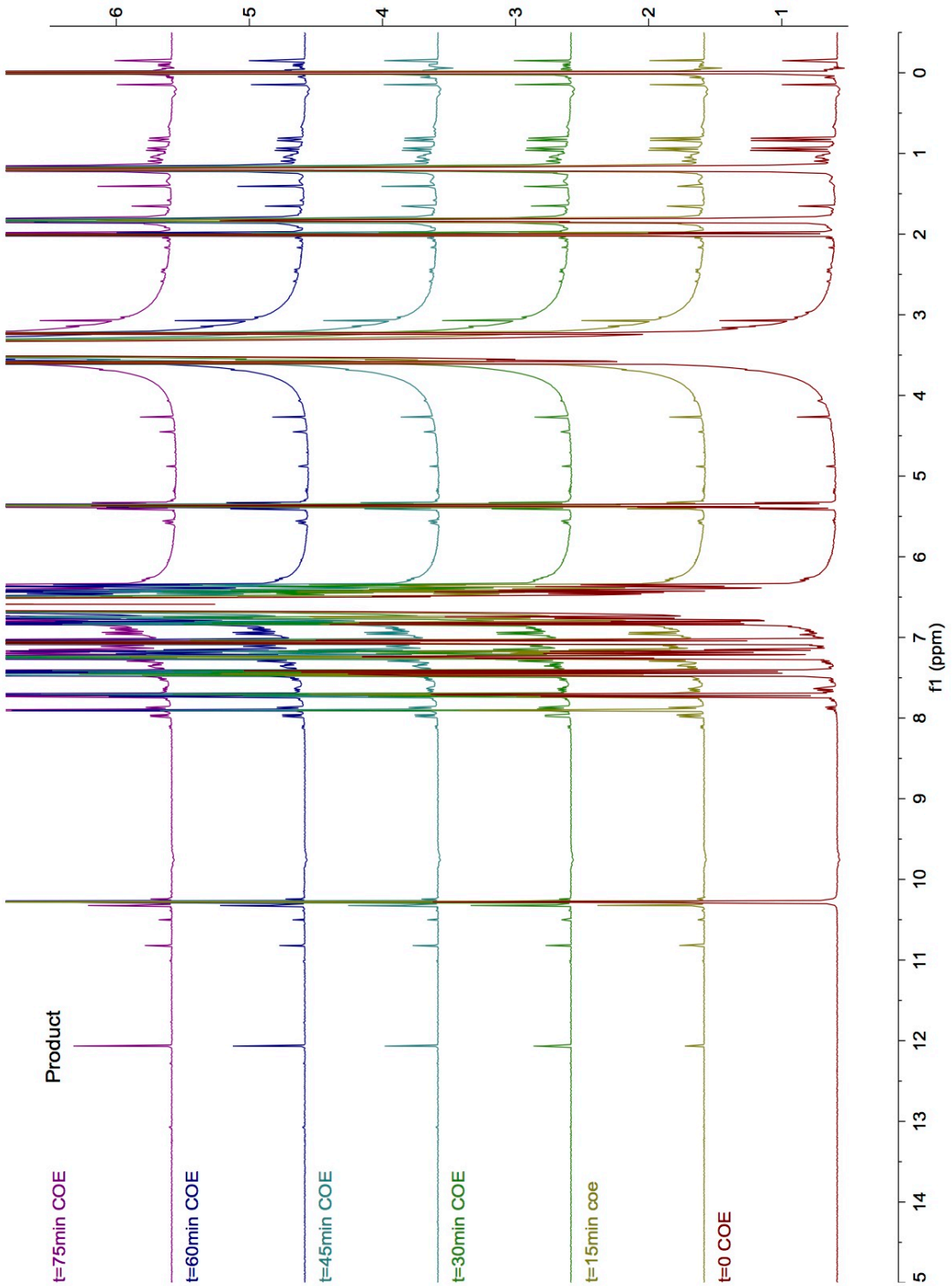

NAS1-236_C-15m/1
t=15min coe
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
COE (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 15 min
OH
O
OMe
OMe
2ag
1.74
900.00
f1 (ppm)


NAS1-236_C-30m/1
t=30min COE
399.87
298.0
1,2-DMB
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
COE (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 30 min
2ag
900.00
2.97
f1 (ppm)

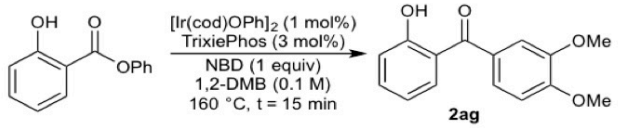

NAS1-236_C-45m/1
t=45min COE
399.87
298.0
1,2-DMB
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
COE (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 45 min
2ag
4.50
900.00
f1 (ppm)


NAS1-236_C-60m/1
t=60min COE
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
COE (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 60 min
OH
O
OMe
OMe
2ag
6.05
900.00
f1 (ppm)


NAS1-236_C-75m/1
t=75min COE
399.87
298.0
1,2-DMB
OH
O
OPh
[Ir(cod)OPh]2 (1 mol%)
TrixiePhos (3 mol%)
COE (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 75 min
OH
O
OMe
OMe
2ag
7.60
900.00
f1 (ppm)

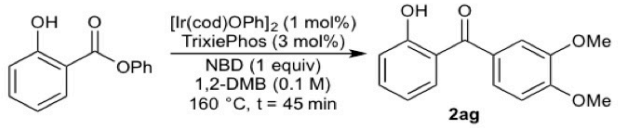

Product
t=75min COE
t=60min COE
t=45min COE
t=30min COE
t=15min coe
t=0 COE
f1 (ppm)

NAS1-237_D-15m/1
15 min NBD
399.87
298.0
1,2-DMB

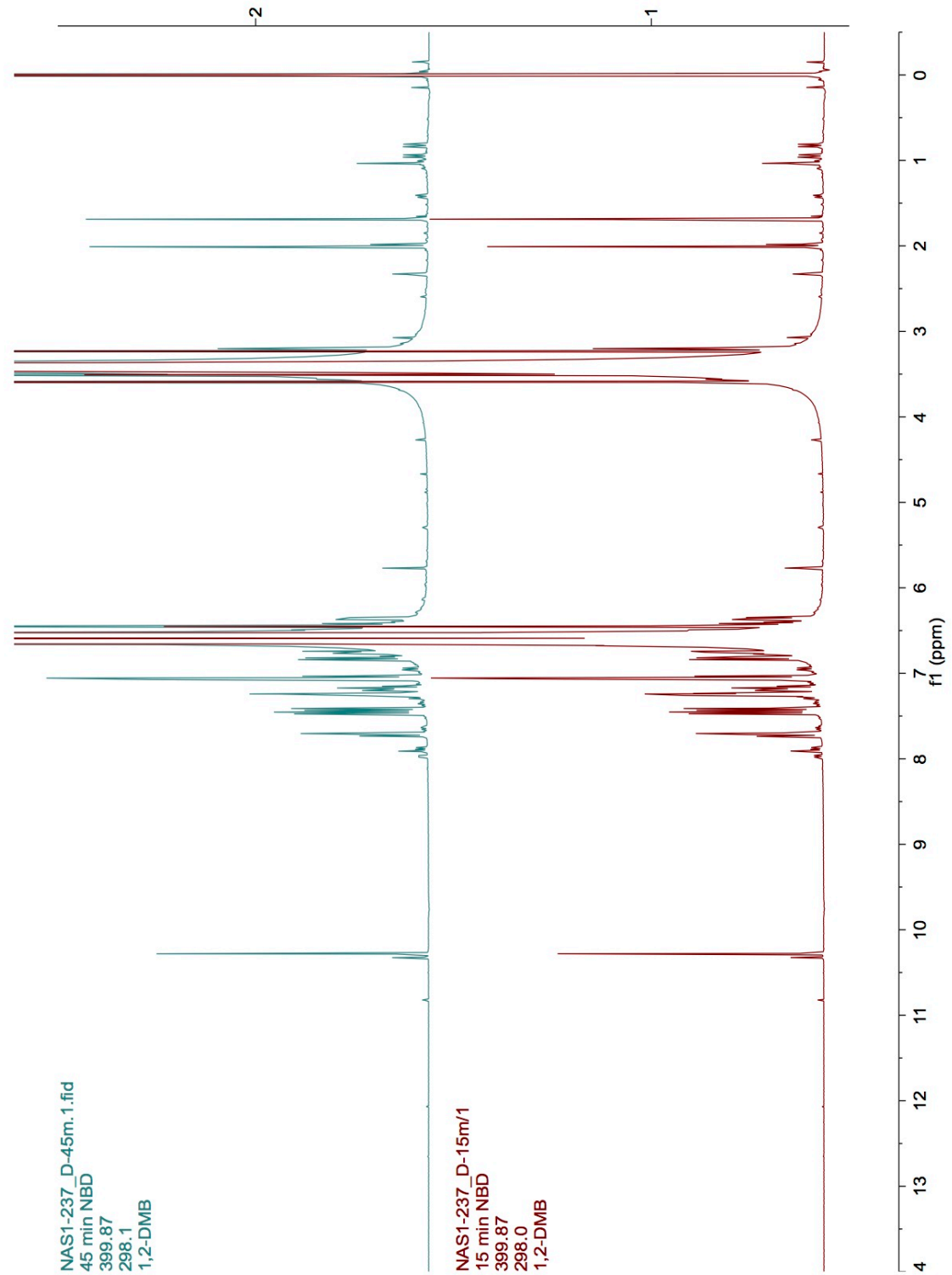


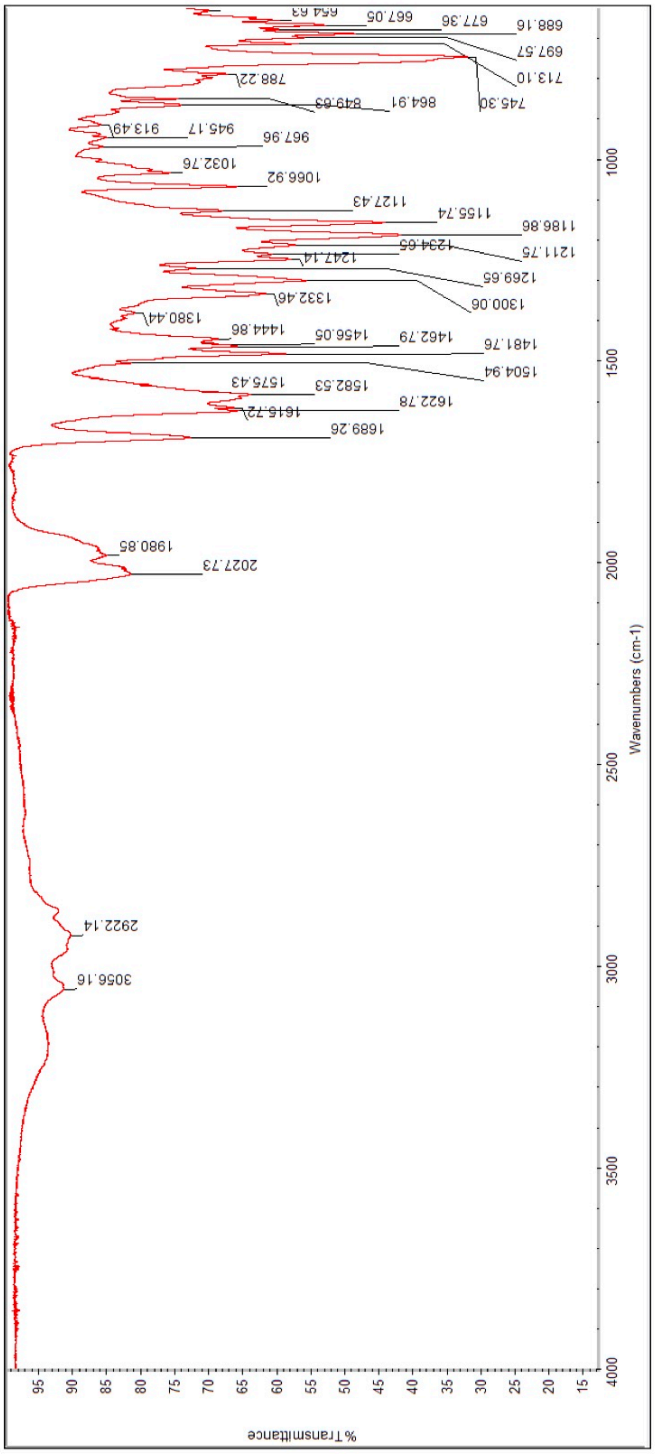
2ag

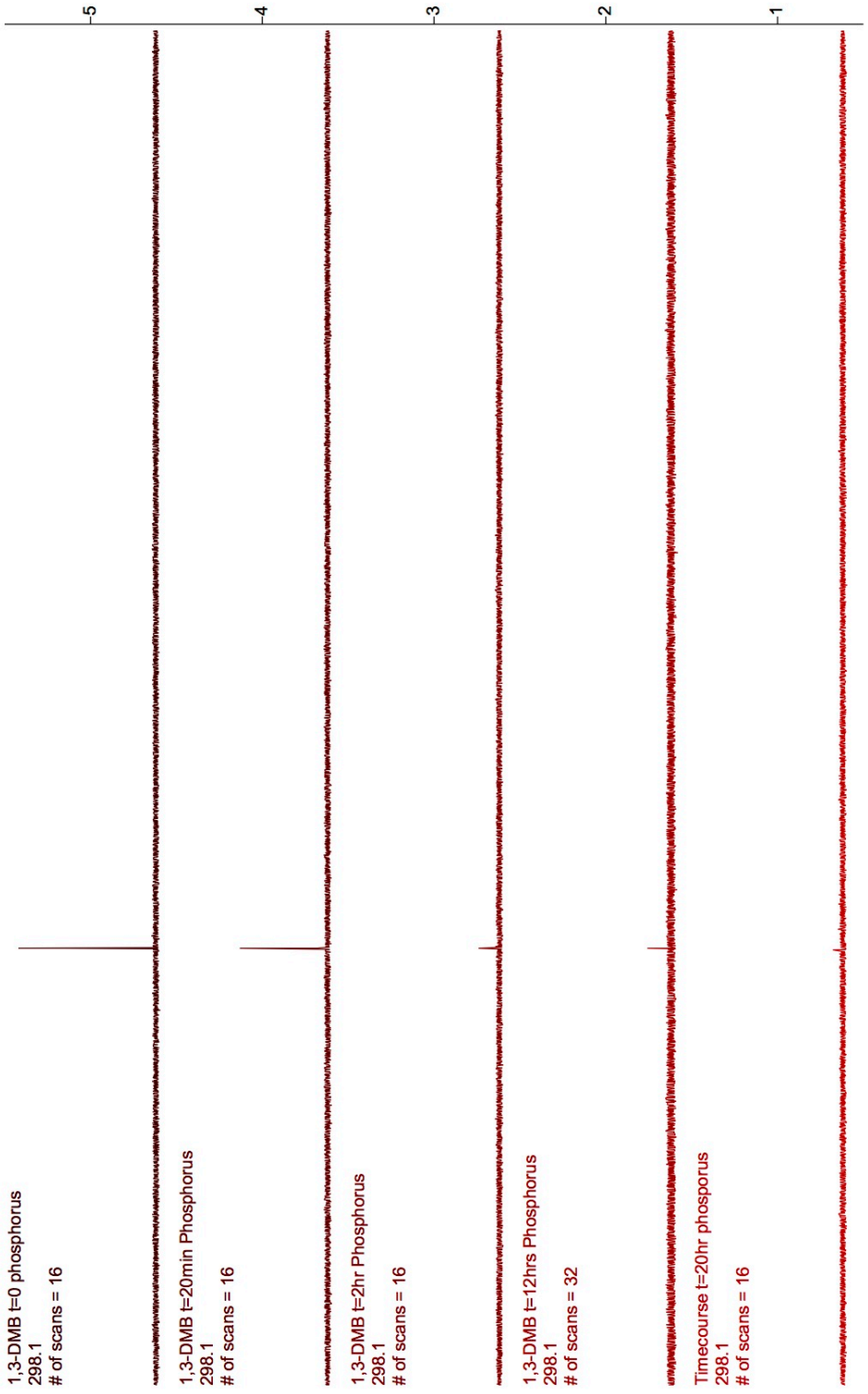
NAS1-237_D-45m.1.fid
45 min NBD
399.87
298.1
1,2-DMB

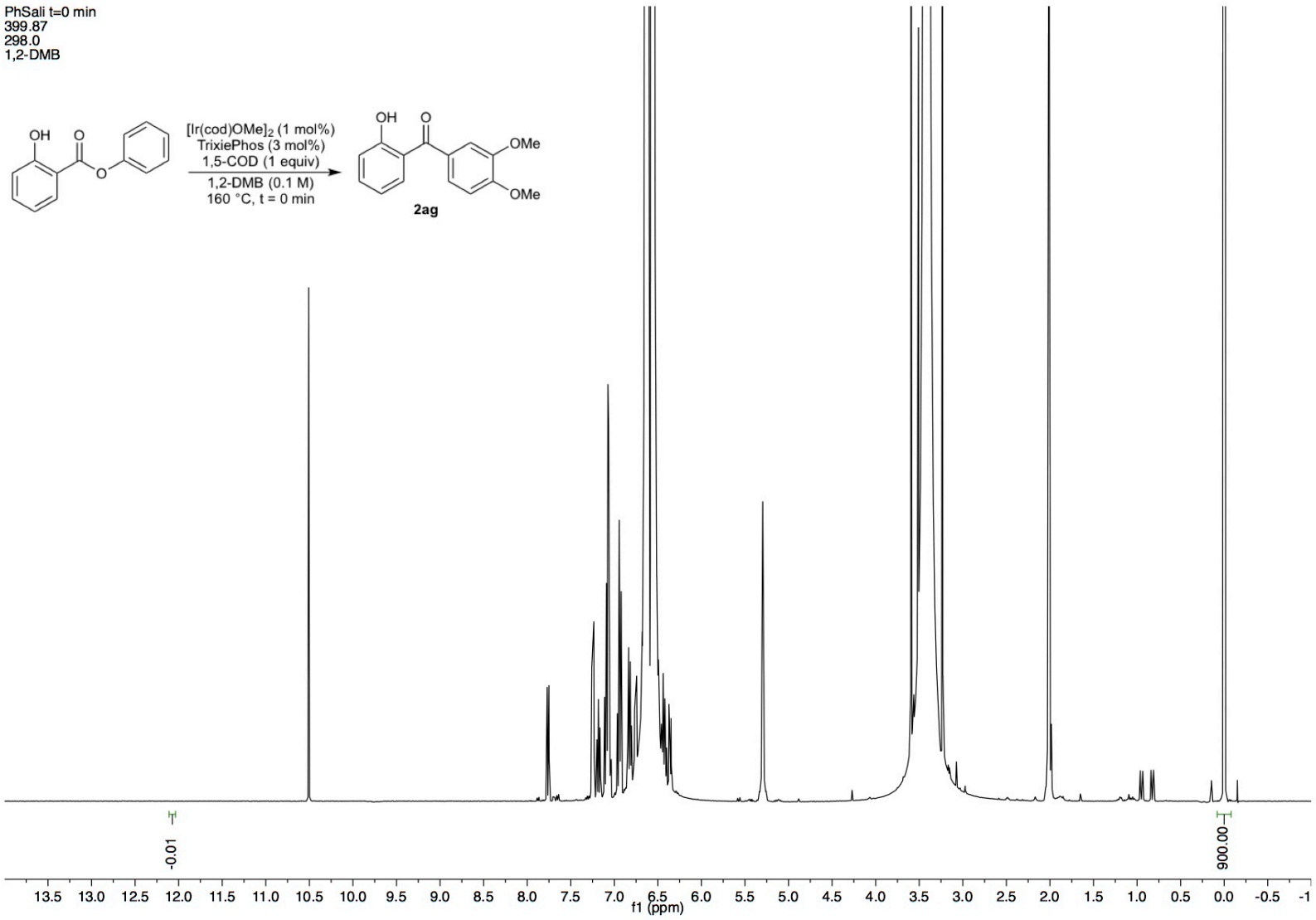


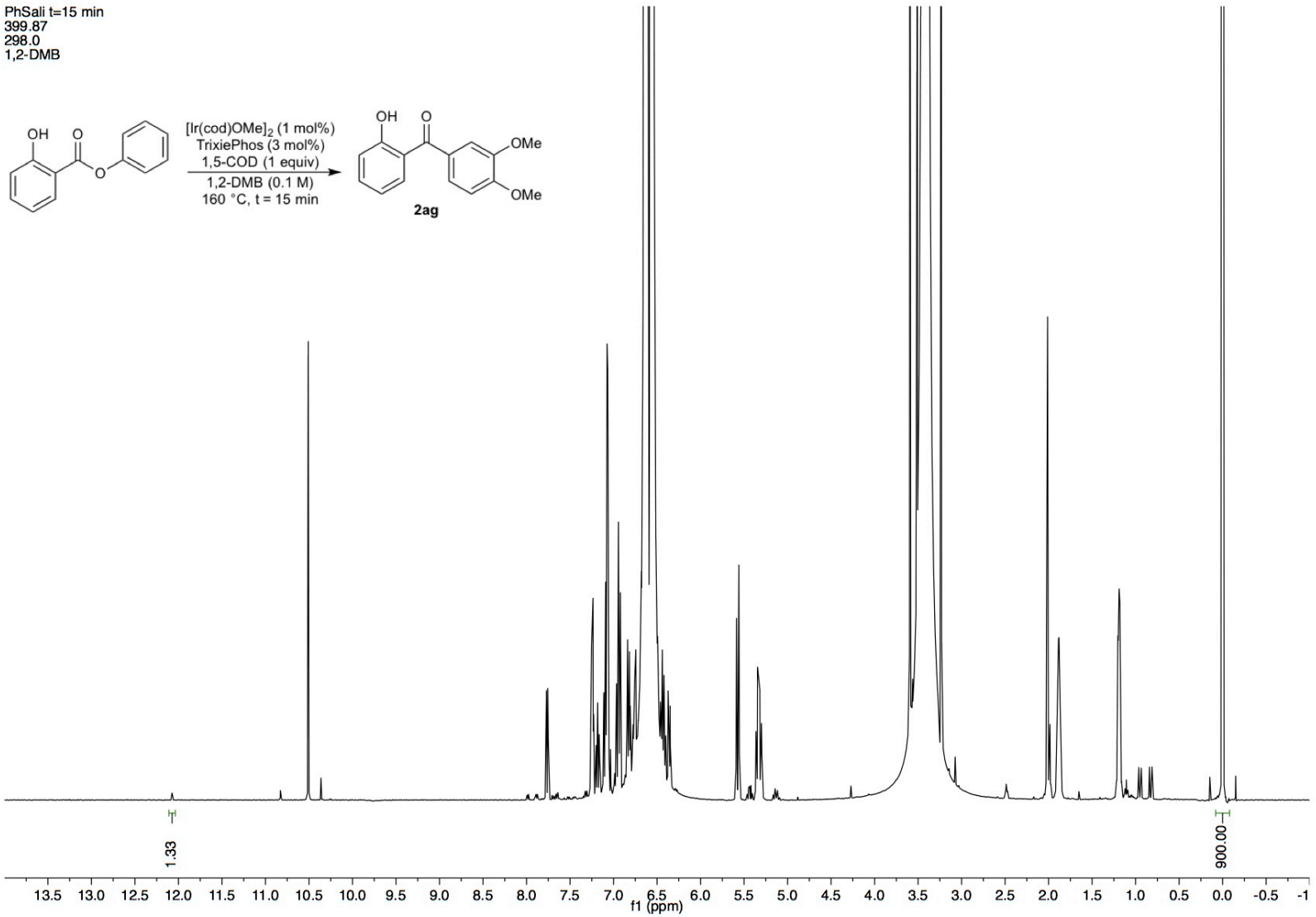
2ag

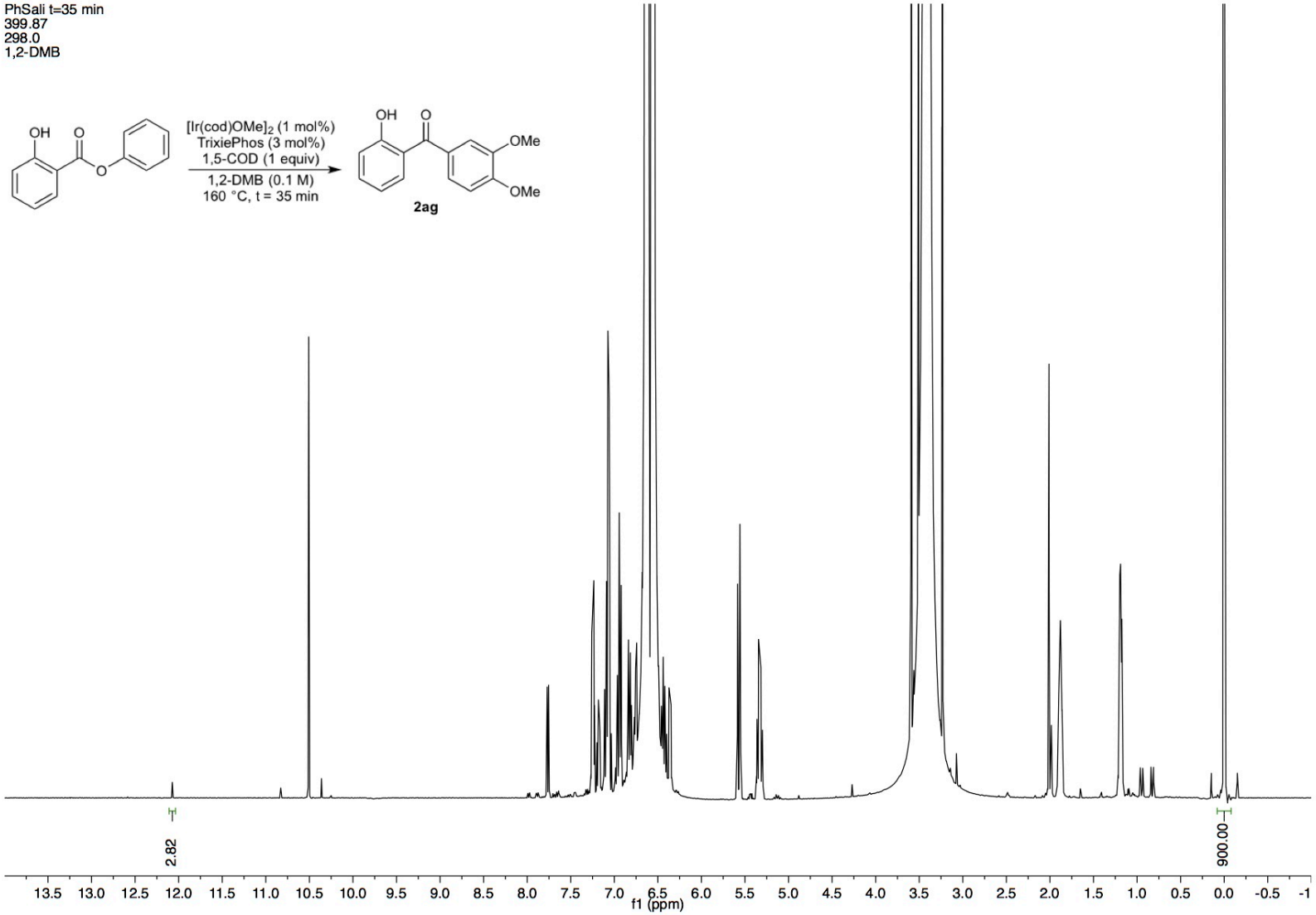

NAS1-237_D-45m.1.fid
45 min NBD
399.87
298.1
1,2-DMB
NAS1-237_D-15m/1
15 min NBD
399.87
298.0
1,2-DMB
f1 (ppm)

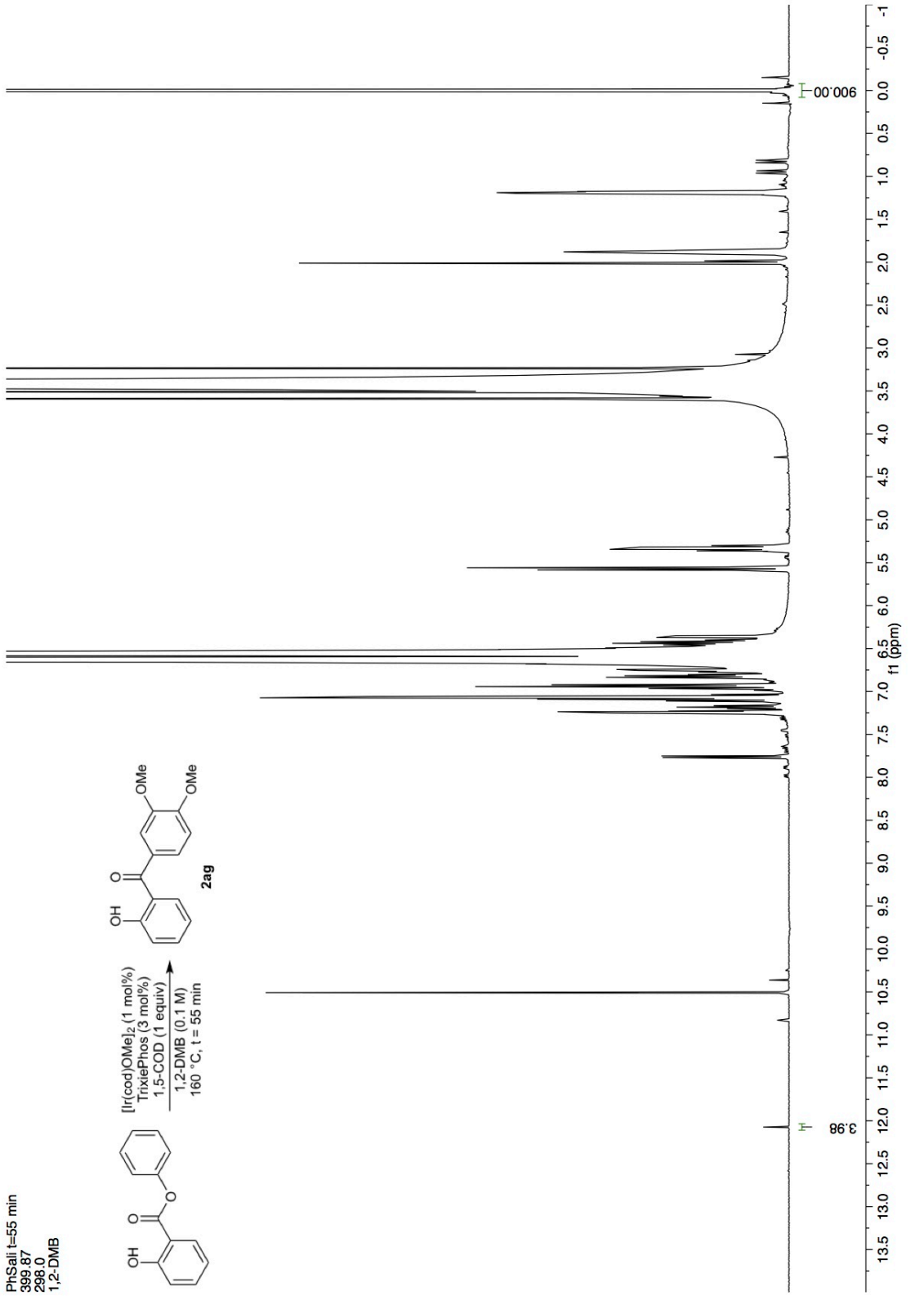

%Transmittance
Wavenumbers (cm-1)
4000
3500
3000
2500
2000
1500
1000
3056.16
2922.14
2027.73
1980.85
1689.26
1622.78
1615.72
1582.53
1575.43
1504.94
1481.76
1462.79
1456.05
1444.86
1380.44
1332.46
1300.06
1269.65
1247.14
1234.65
1211.75
1186.86
1155.74
1127.43
1066.92
1032.76
967.96
945.17
913.49
864.91
849.83
788.22
745.30
713.10
697.57
688.16
677.36
667.05
654.63

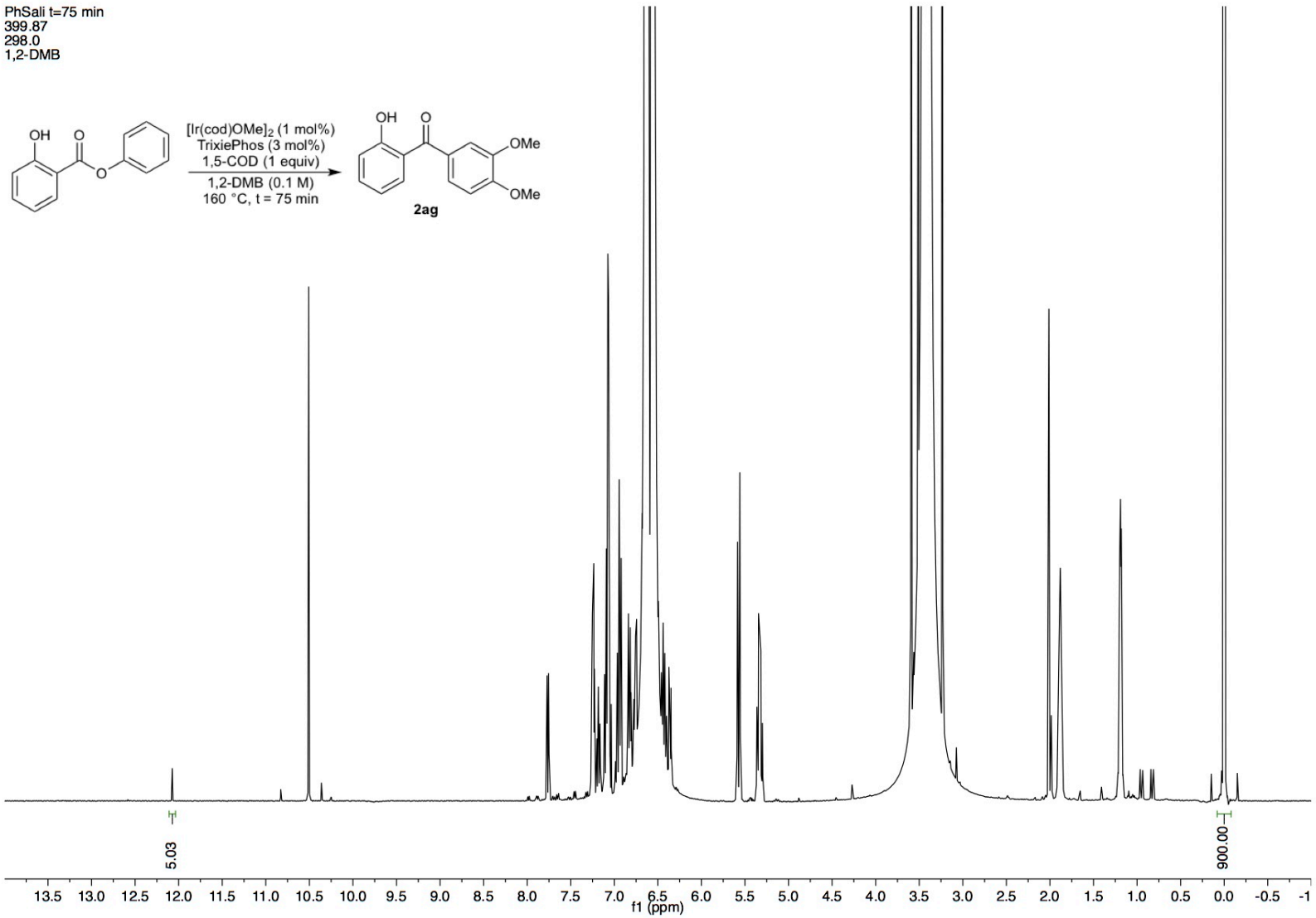

1,3-DMB t=0 phosphorus
298.1
# of scans = 16
1,3-DMB t=20min Phosphorus
298.1
# of scans = 16
1,3-DMB t=2hr Phosphorus
298.1
# of scans = 16
1,3-DMB t=12hrs Phosphorus
298.1
# of scans = 32
Timecourse t=20hr phosporus
298.1
# of scans = 16
5
4
3
2
1
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

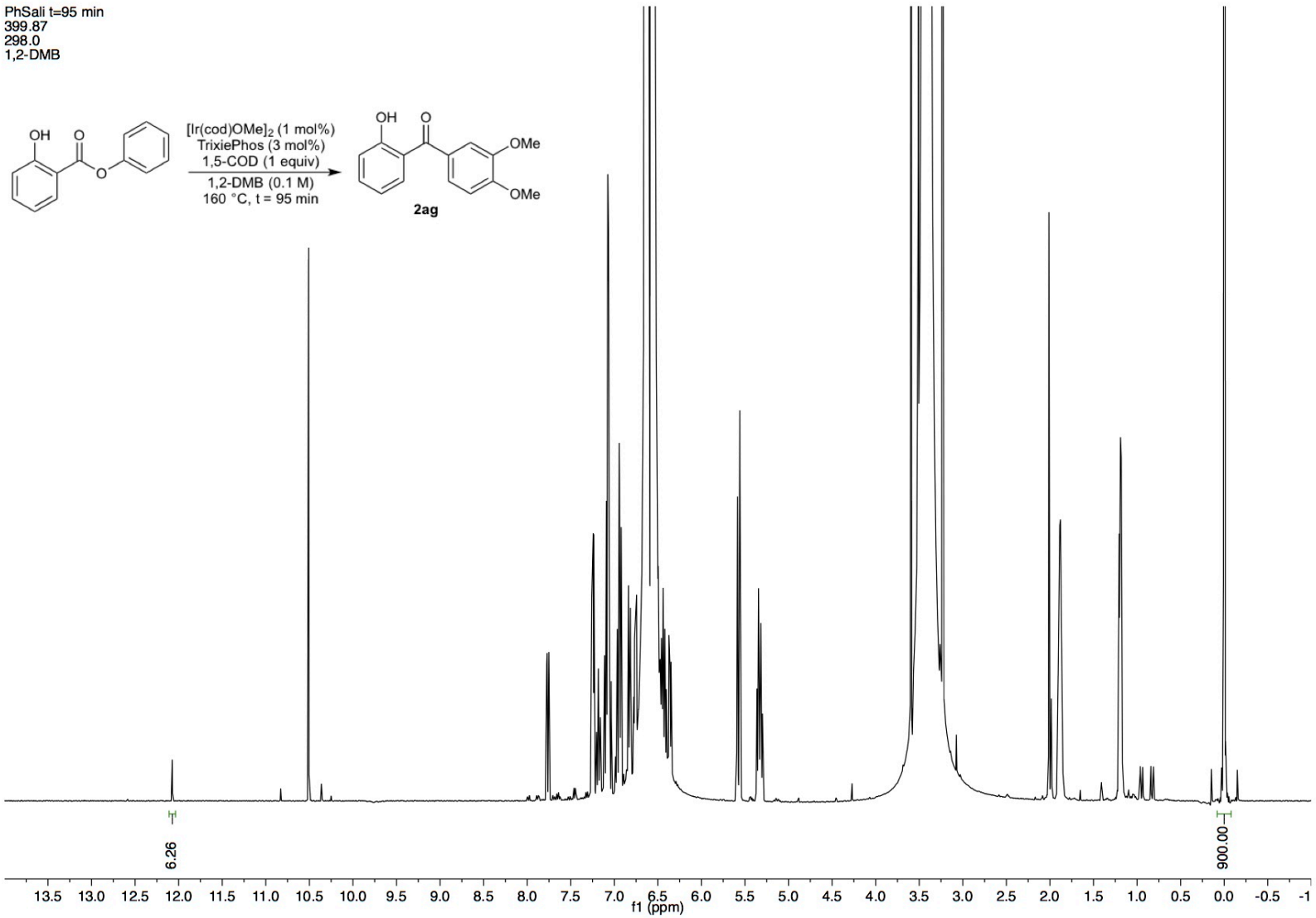

PhSali t=0 min
399.87
298.0
1,2-DMB
OH
O
O
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 0 min
OH
O
OMe
OMe
2ag
-0.01
00.006
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

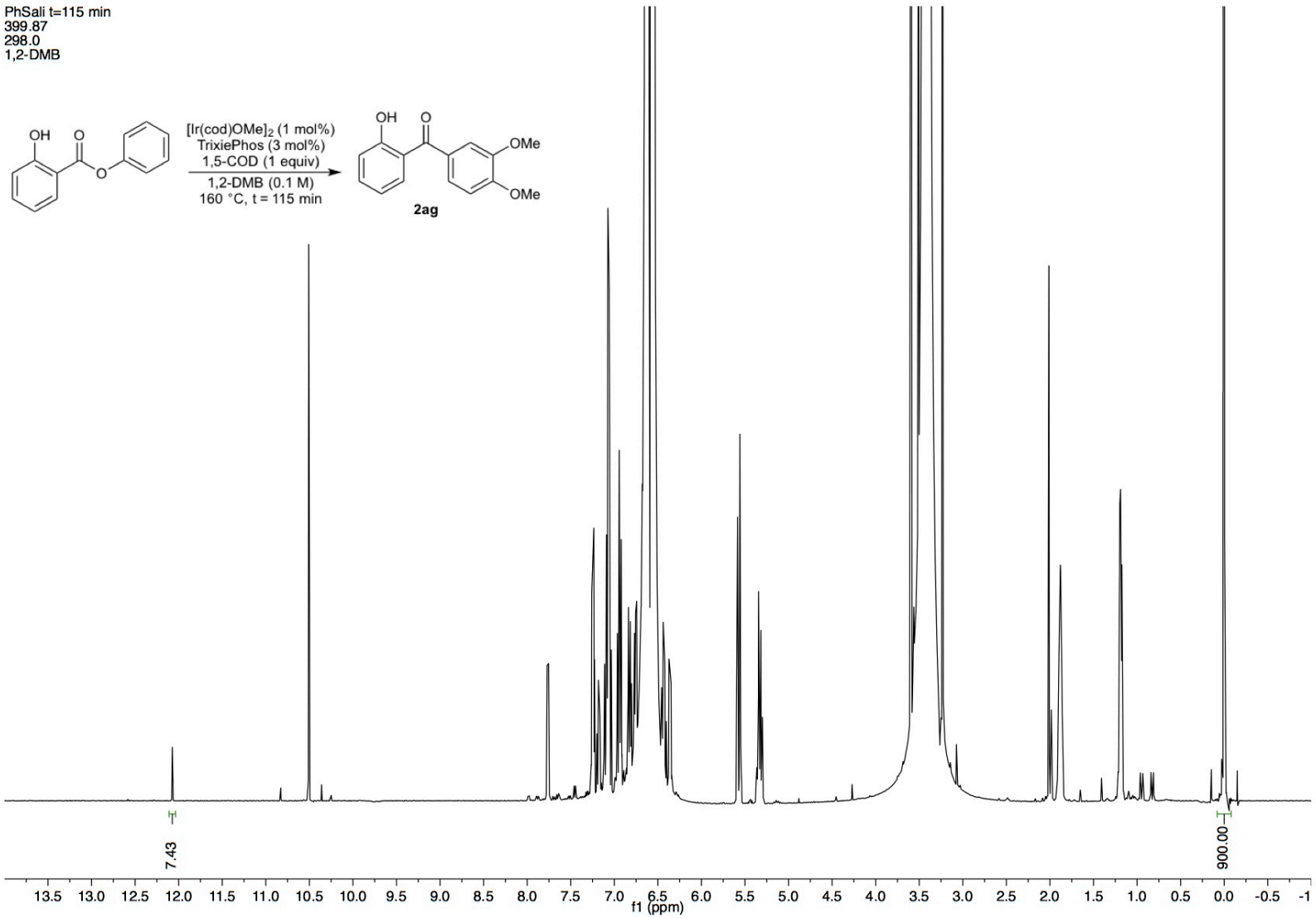

PhSali t=15 min
399.87
298.0
1,2-DMB
OH
O
O
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 15 min
OH
O
OMe
OMe
2ag
1.33
00.006
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

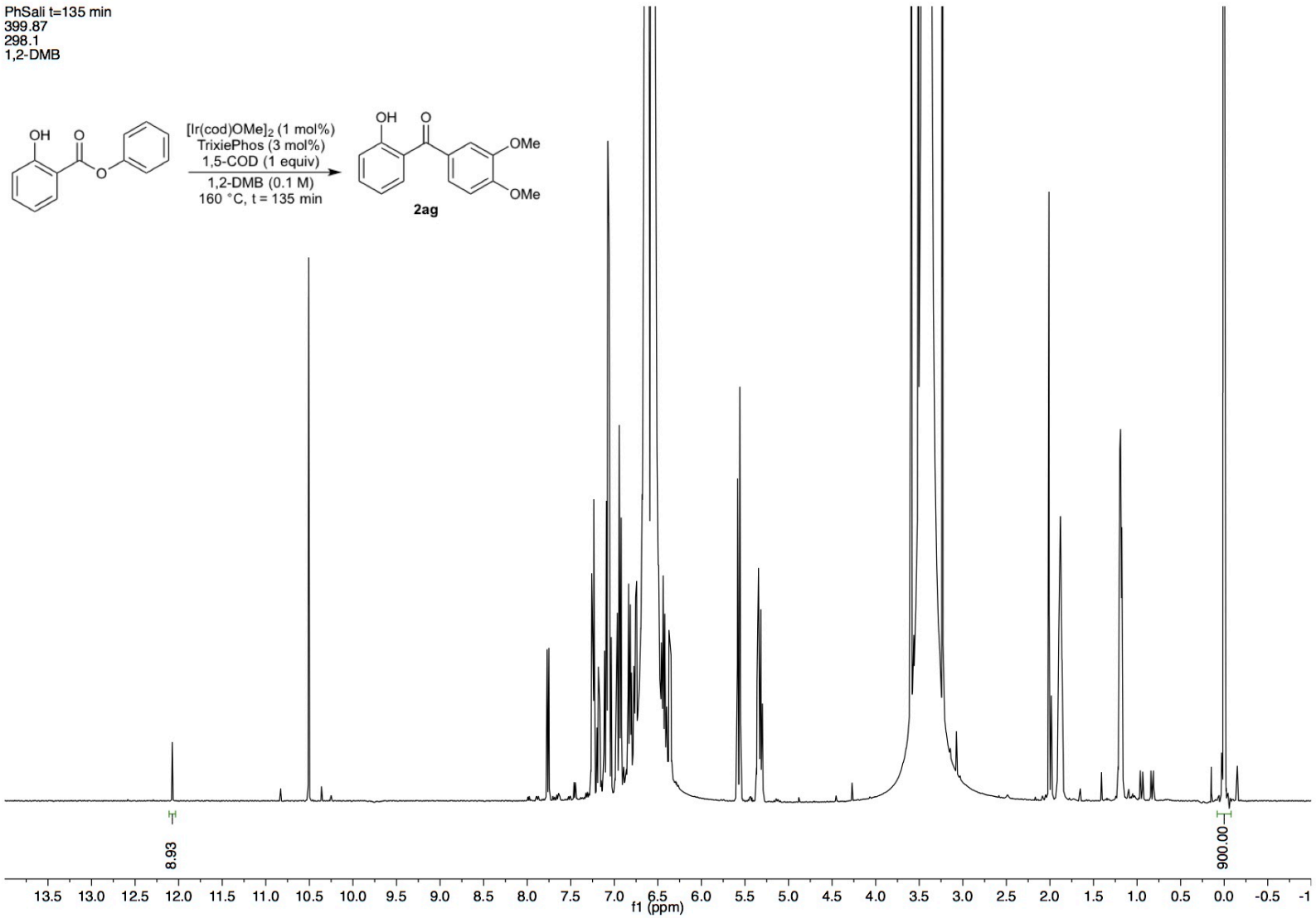

PhSali t=35 min
399.87
298.0
1,2-DMB
OH
O
O
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 35 min
OH
O
OMe
OMe
2ag
2.82
00.006
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

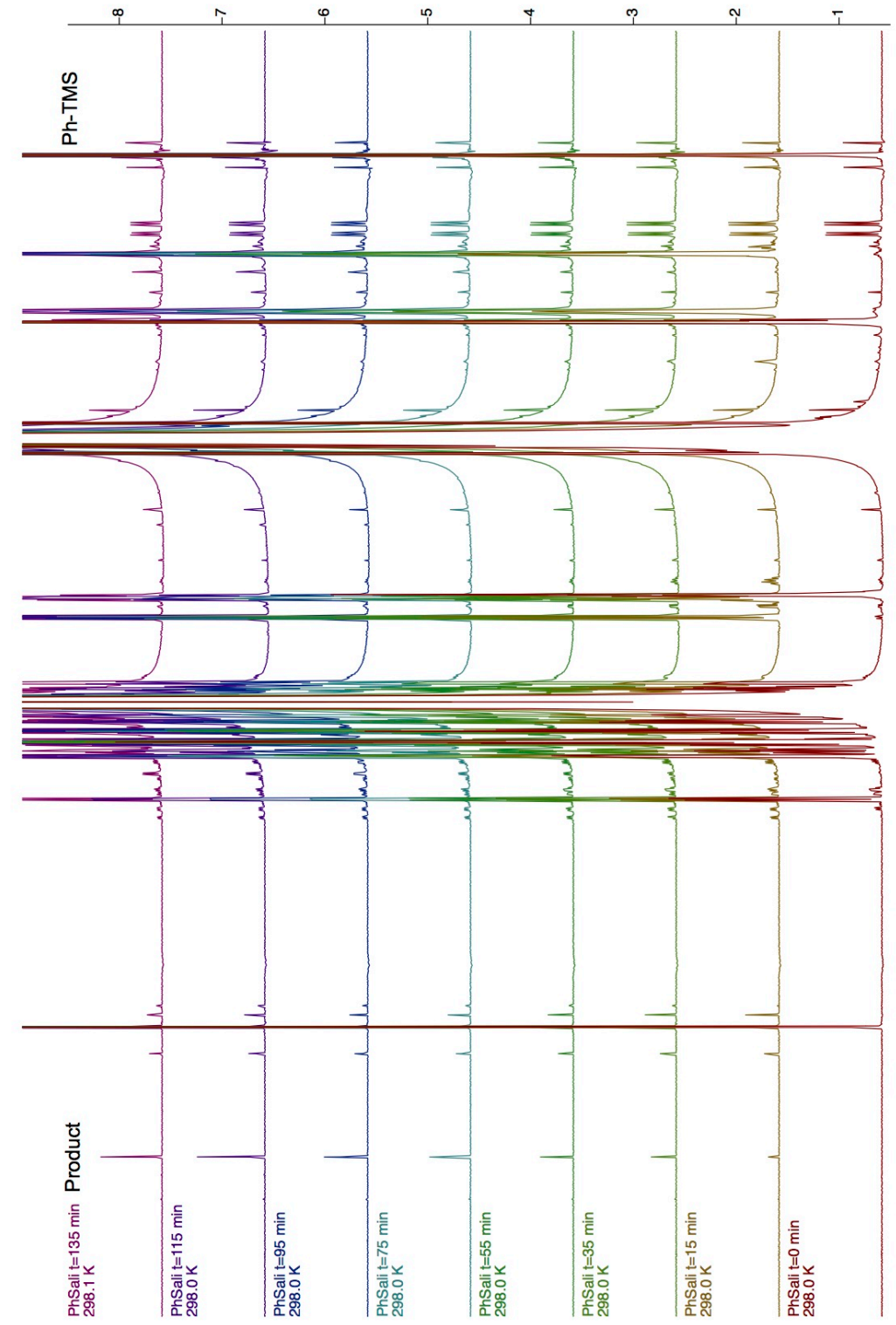

PhSali t=55 min
399.87
298.0
1,2-DMB
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0,1 M)
160 °C, t = 55 min
OMe
OMe
O
OH
2ag
3.98
900.00
f1 (ppm)

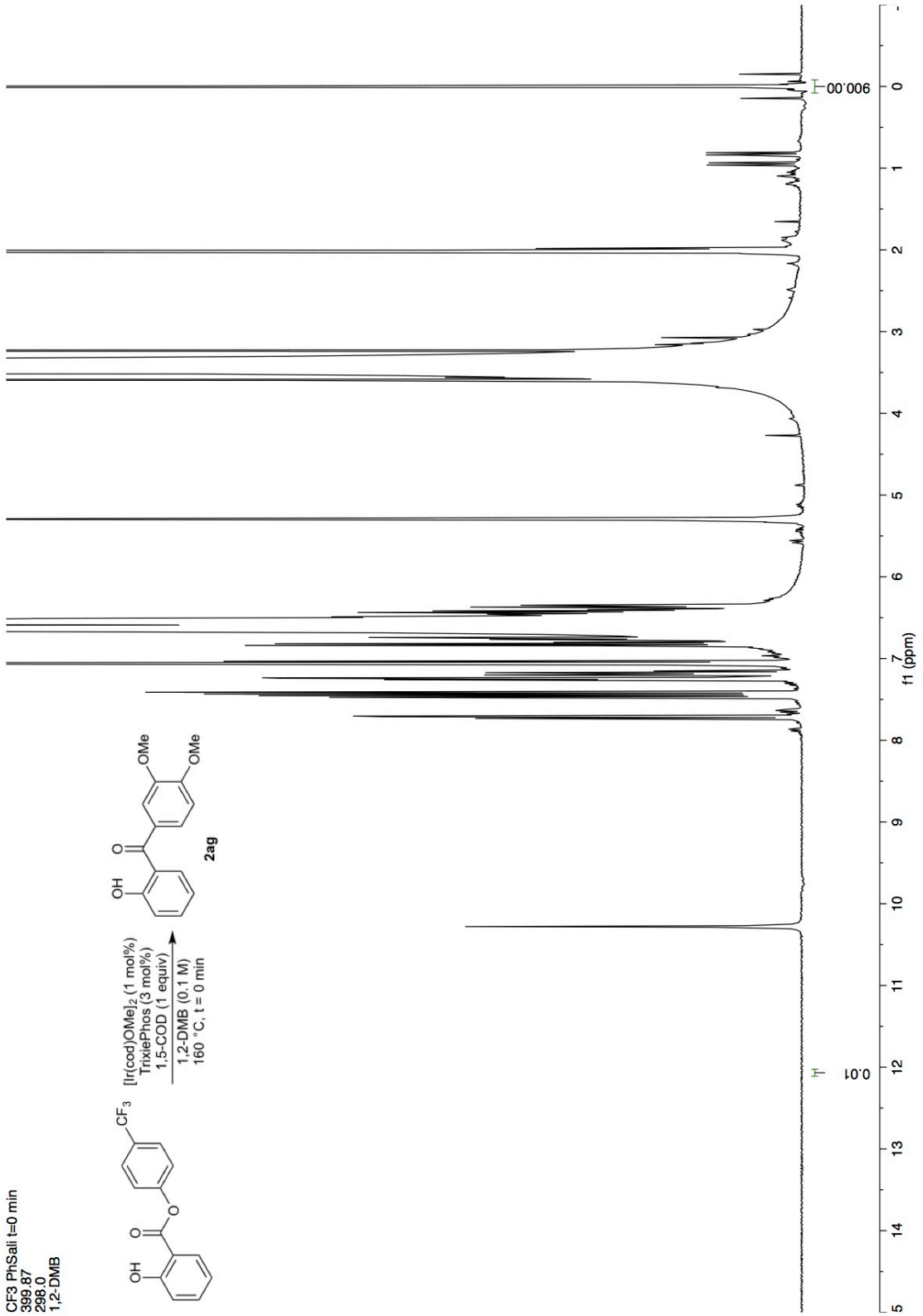

PhSali t=75 min
399.87
298.0
1,2-DMB
OH
O
O
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 75 min
OH
O
OMe
OMe
2ag
5.03
900.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

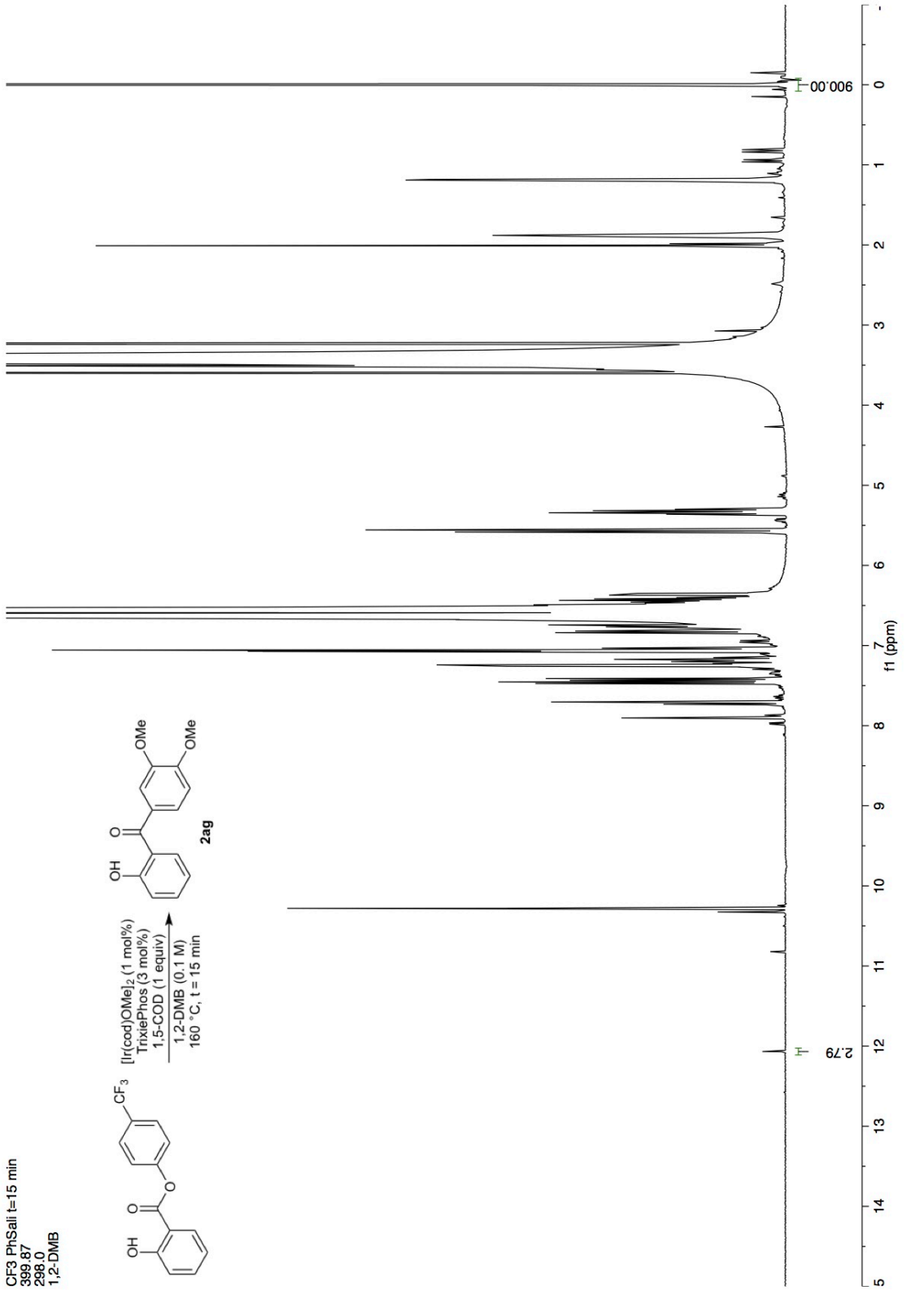

PhSali t=95 min
399.87
298.0
1,2-DMB
OH
O
O
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 95 min
OH
O
OMe
OMe
2ag
6.26
00.006
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

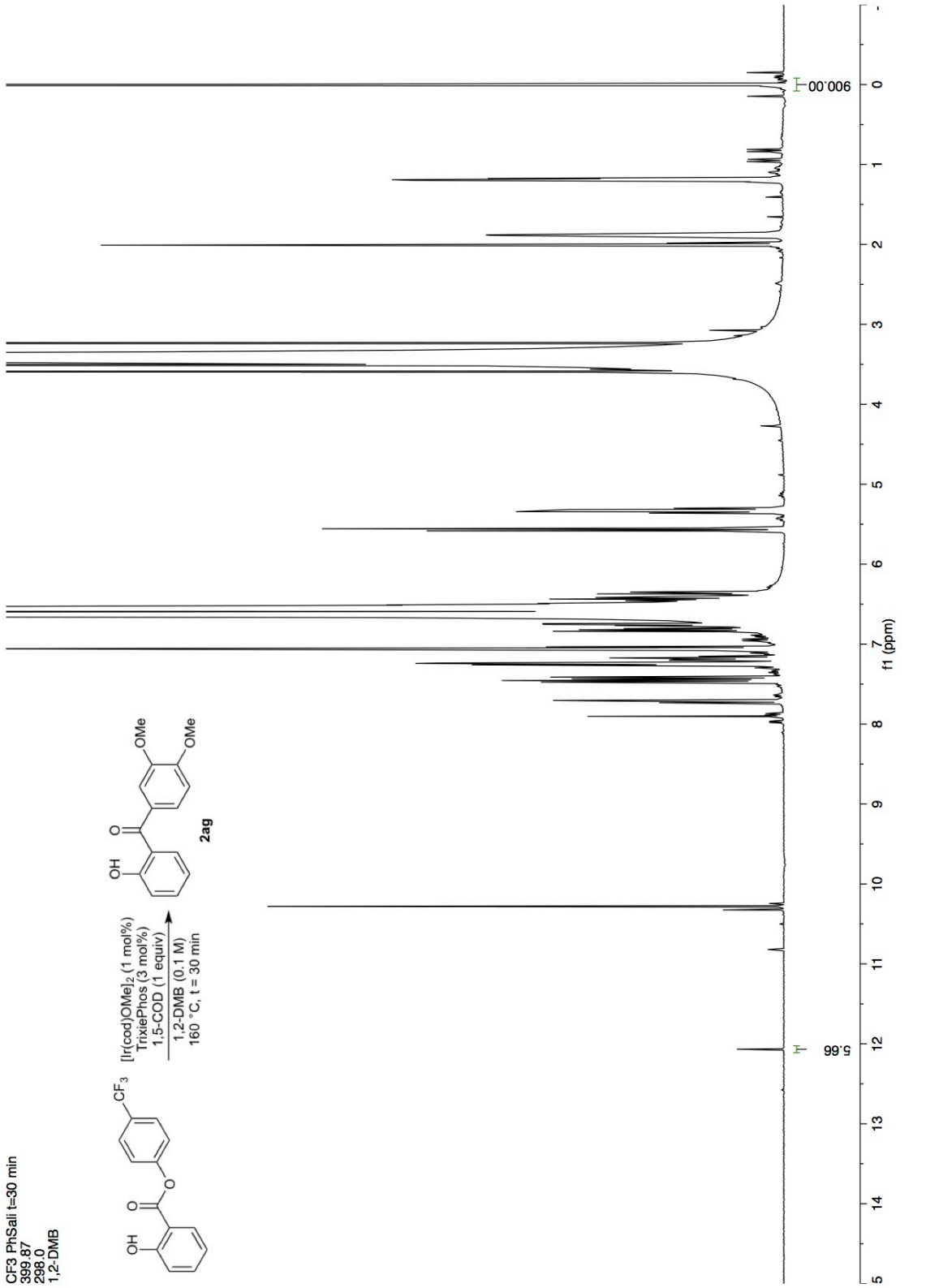

PhSali t=115 min
399.87
298.0
1,2-DMB
OH
O
O
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 115 min
OH
O
OMe
OMe
2ag
7.43
00.006
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

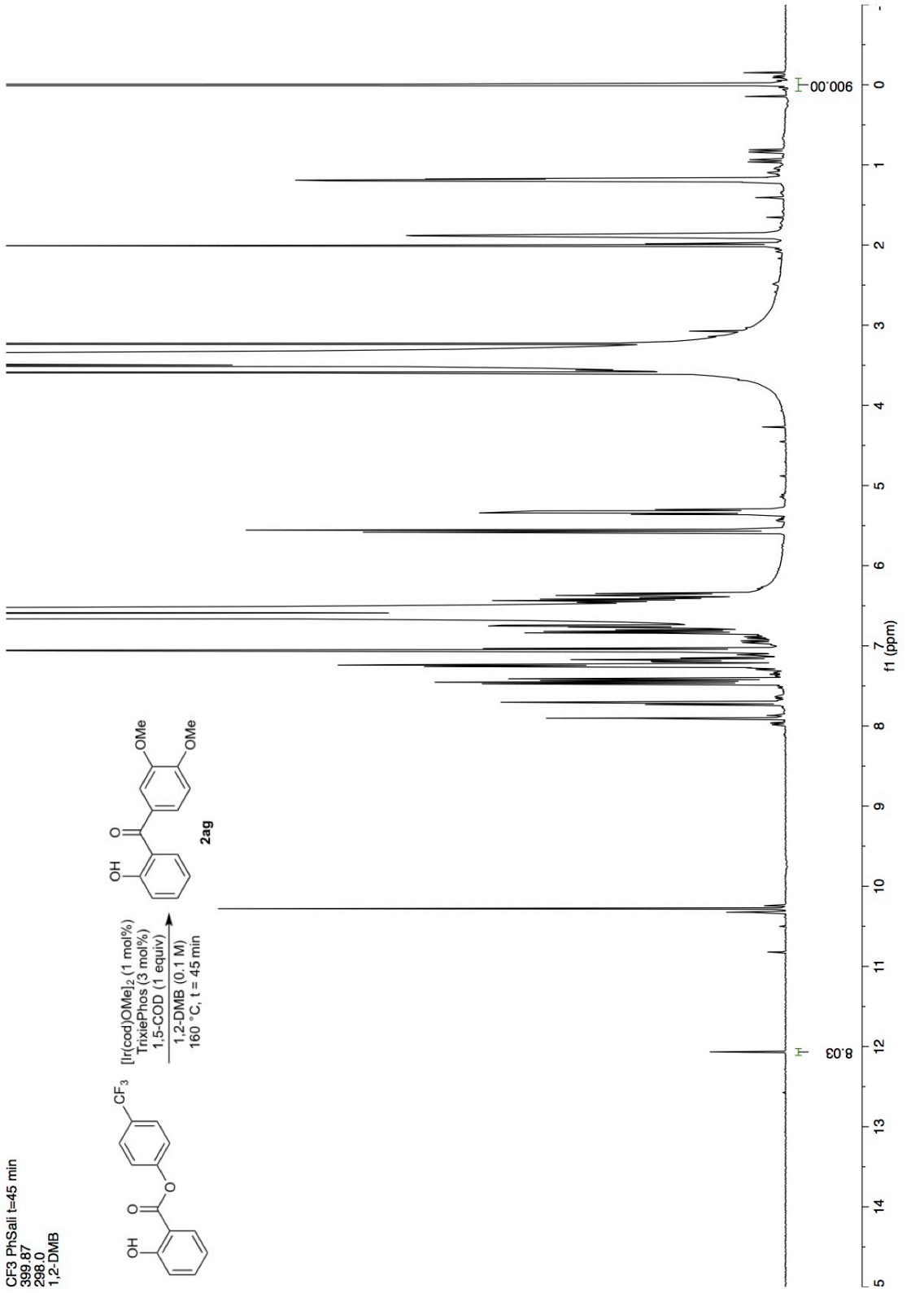

PhSali t=135 min
399.87
298.1
1,2-DMB
OH
O
O
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 135 min
OH
O
OMe
OMe
2ag
8.93
00.006
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

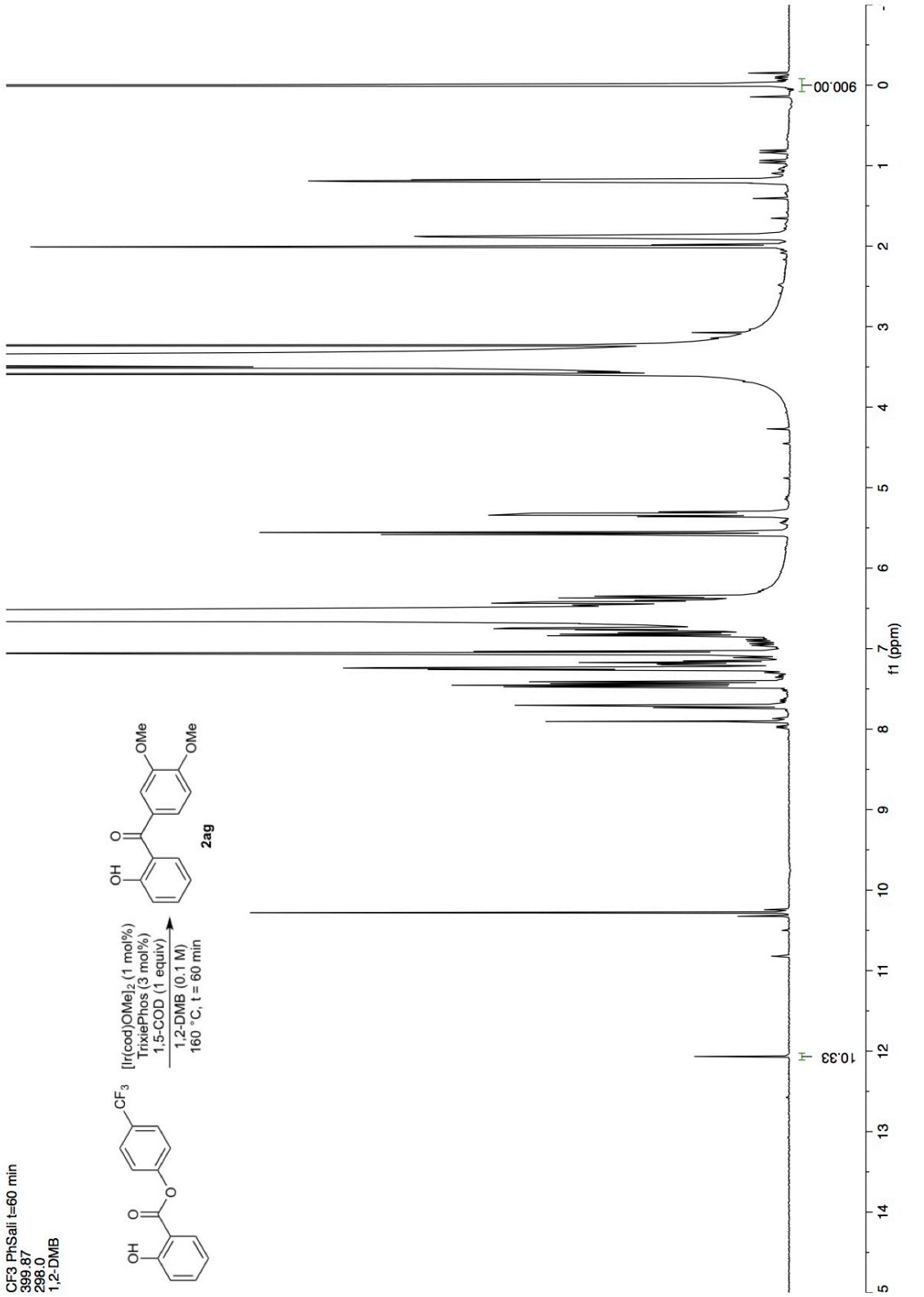

Product
Ph-TMS
PhSali t=135 min
298.1 K
PhSali t=115 min
298.0 K
PhSali t=95 min
298.0 K
PhSali t=75 min
298.0 K
PhSali t=55 min
298.0 K
PhSali t=35 min
298.0 K
PhSali t=15 min
298.0 K
PhSali t=0 min
298.0 K
f1 (ppm)

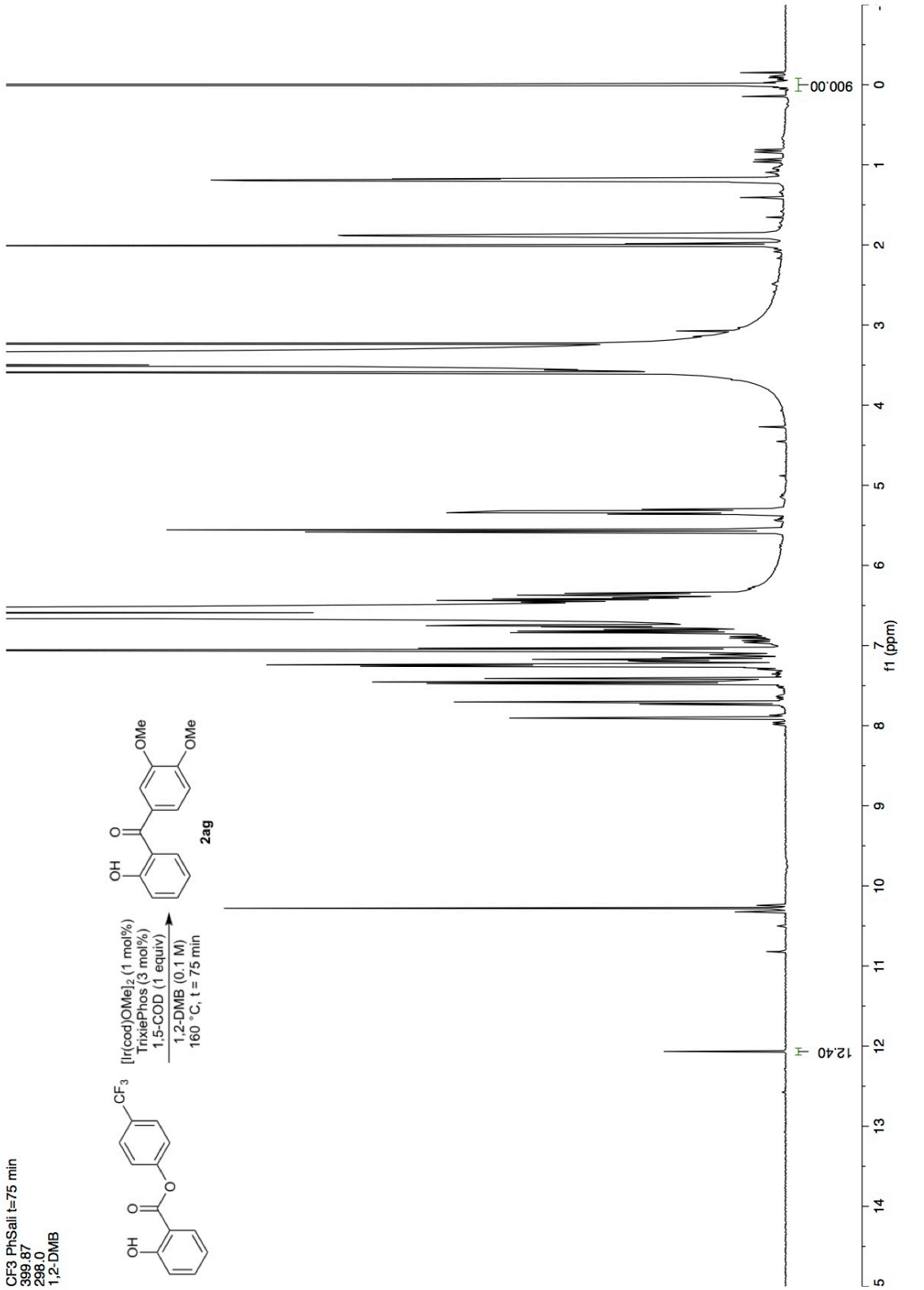

CF3 PhSali t=0 min
399.87
298.0
1,2-DMB
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 0 min
2ag
900.00
0.01
f1 (ppm)

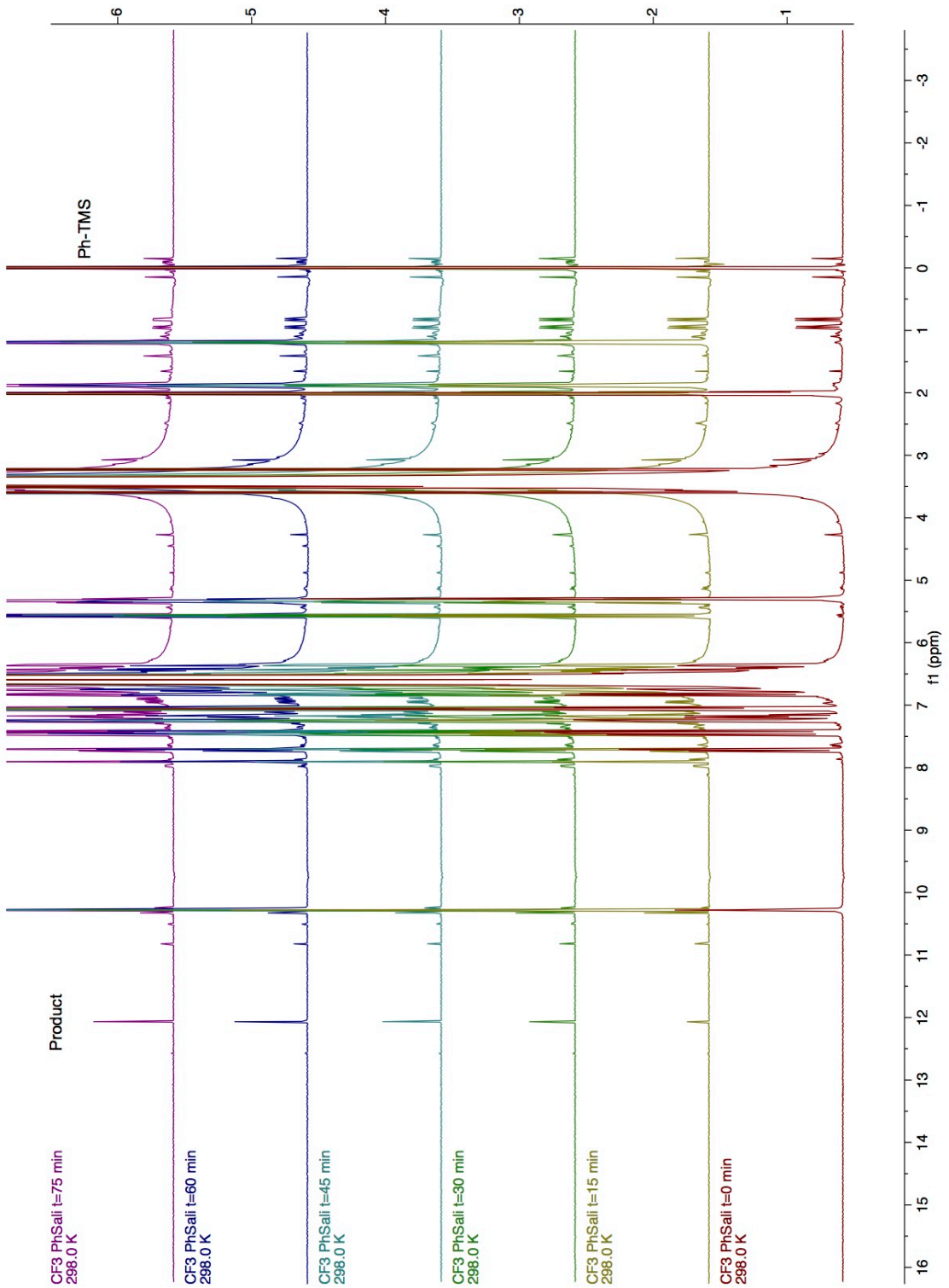

CF3 PhSali t=15 min
399.87
298.0
1,2-DMB
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 15 min
2ag
900.00
2.79
f1 (ppm)

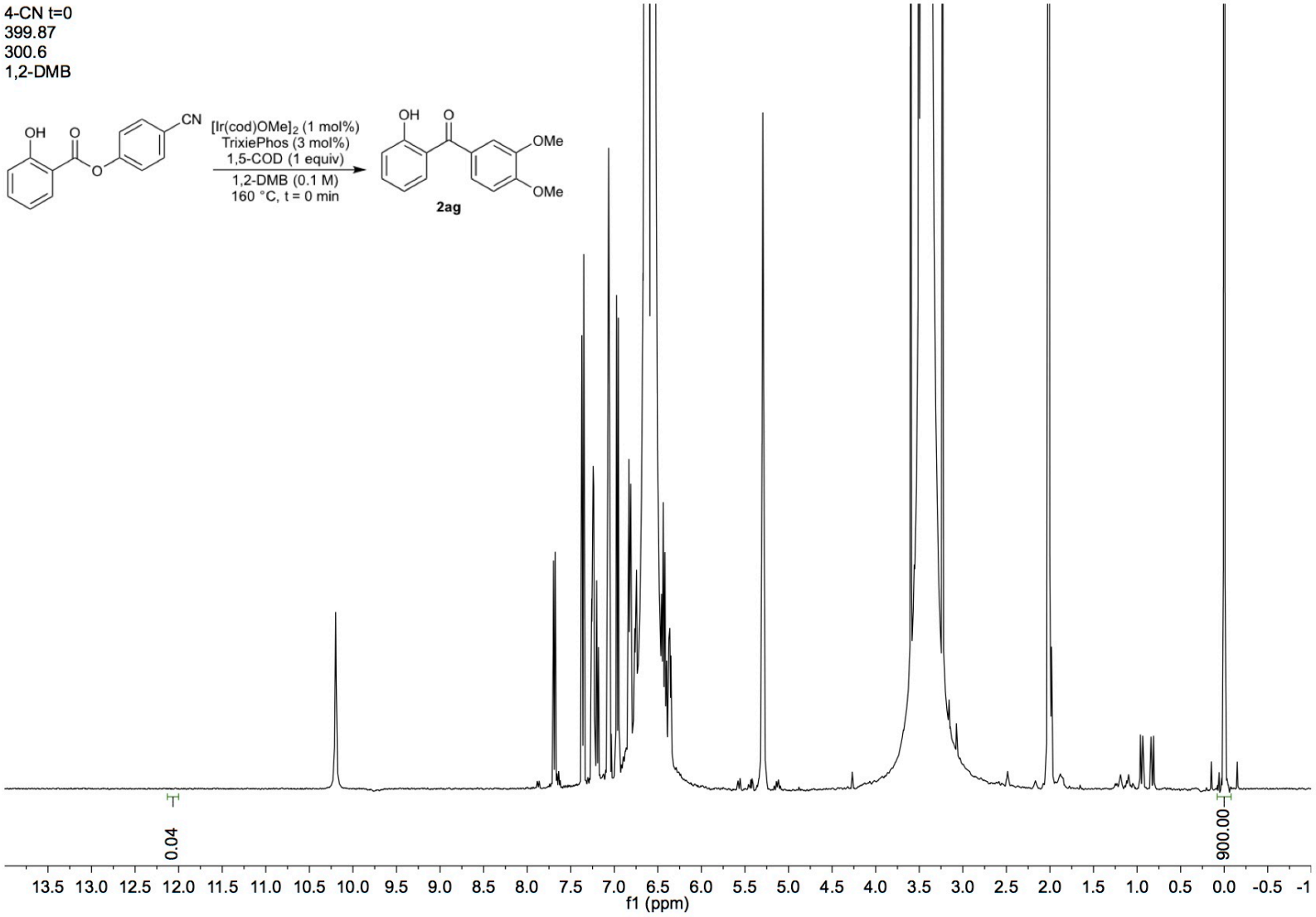

CF3 PhSali t=30 min
399.87
298.0
1,2-DMB
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 30 min
2ag
900.00
5.66
f1 (ppm)

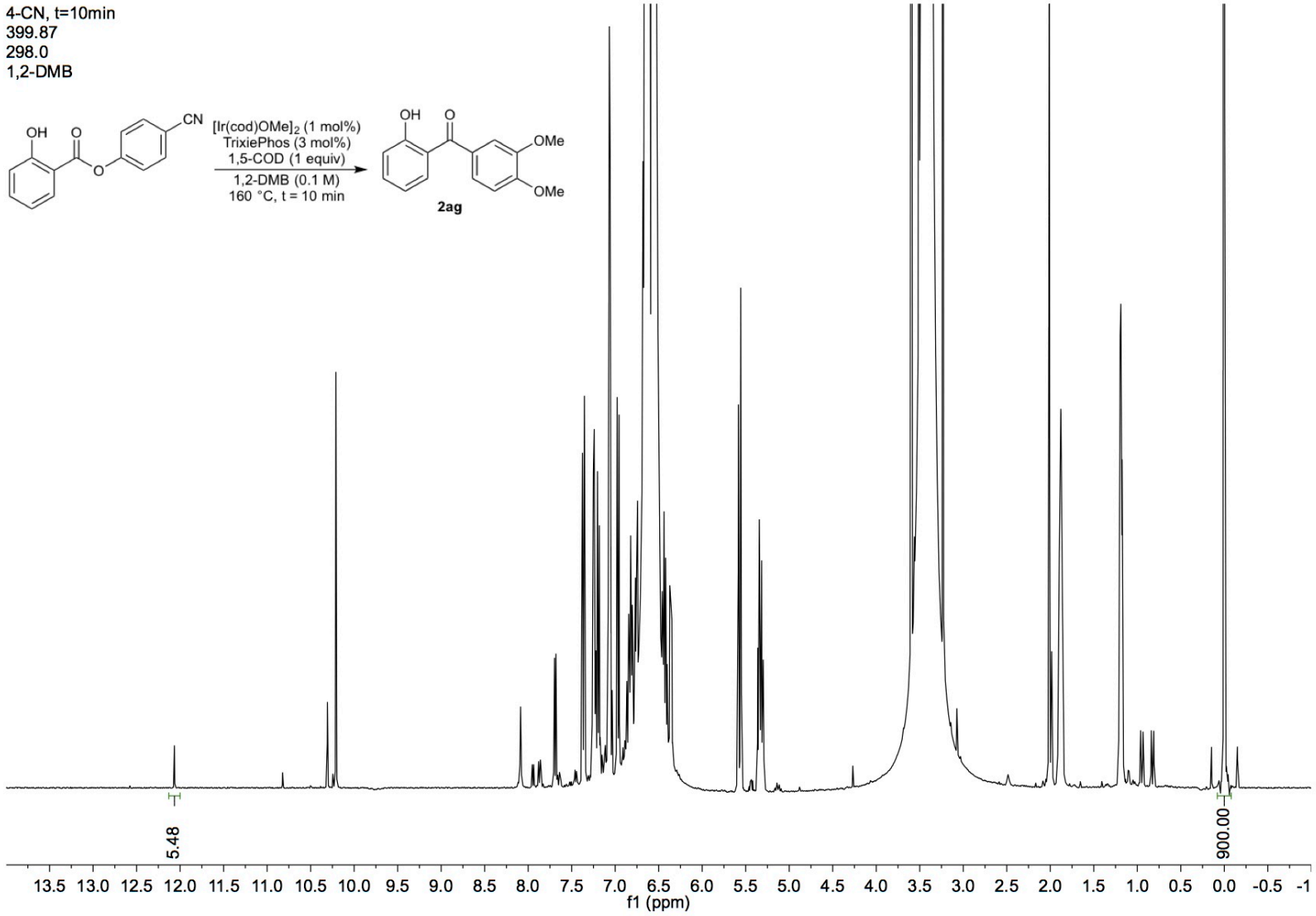

CF3 PhSali t=45 min
399.87
298.0
1,2-DMB
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 45 min
2ag
900.00
8.03
f1 (ppm)

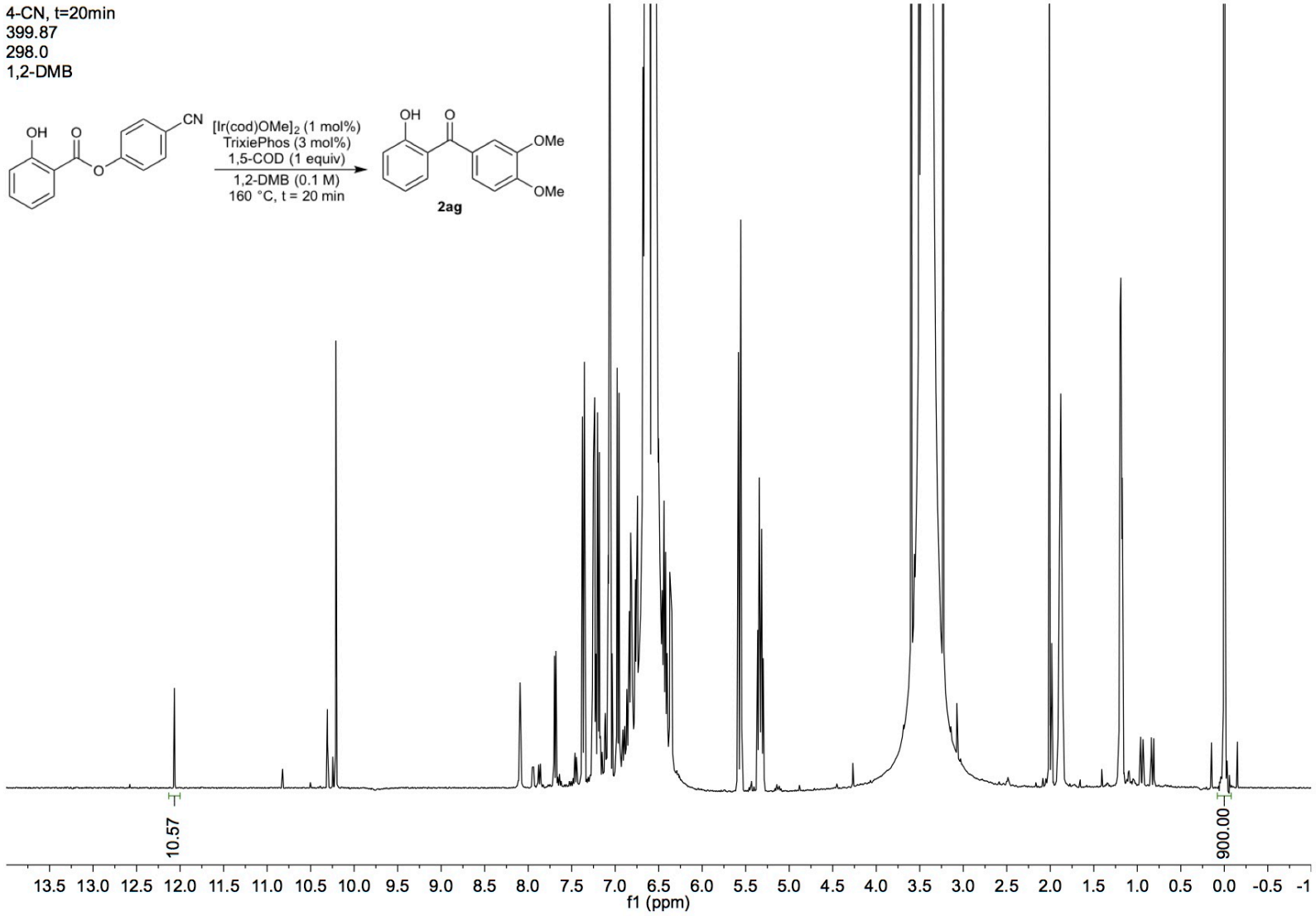

CF3 PhSali t=60 min
399.87
298.0
1,2-DMB
CF3
O
OH
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 60 min
OMe
OMe
2ag
10.33
900.00
f1 (ppm)

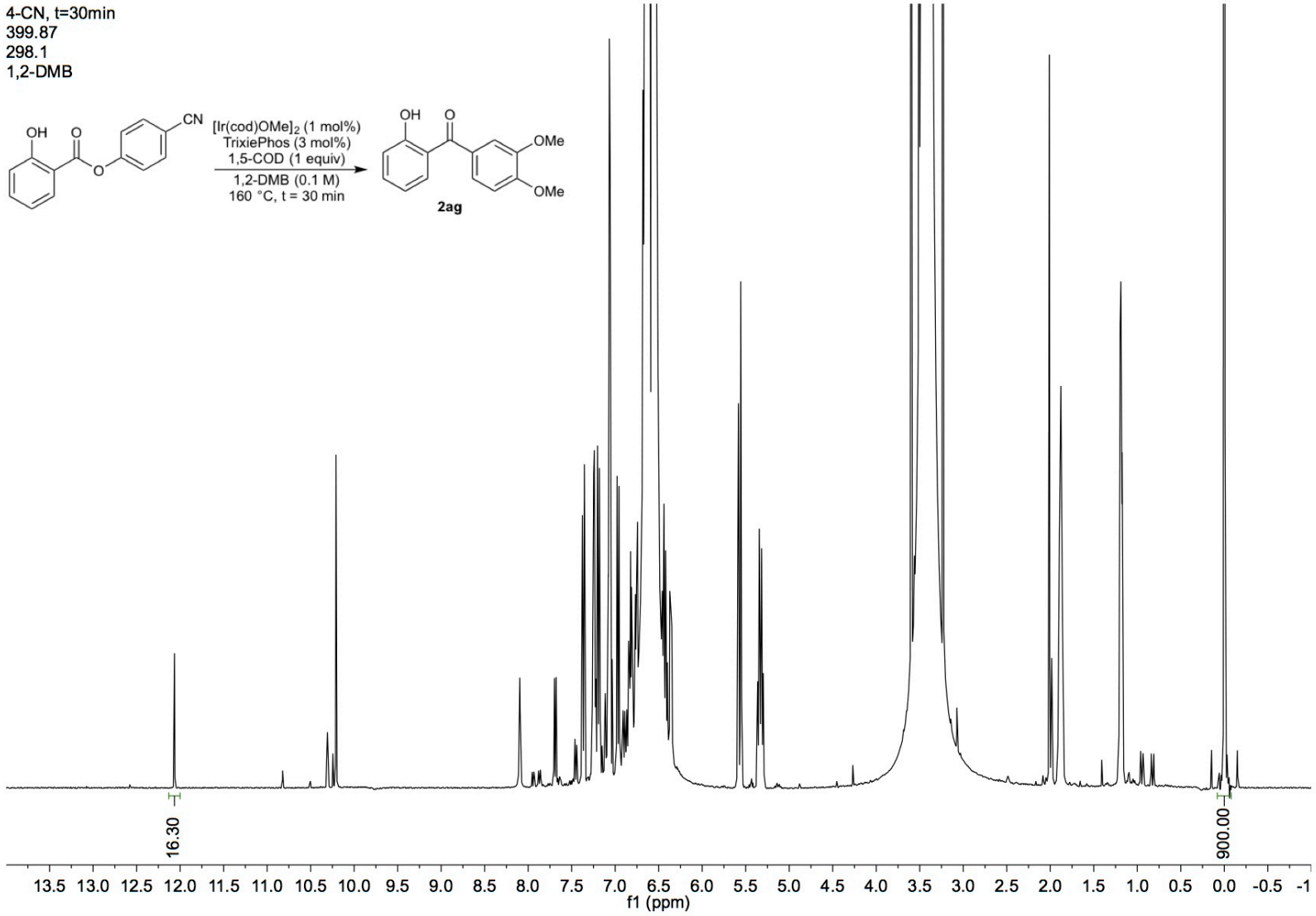

CF3 PhSali t=75 min
399.87
298.0
1,2-DMB
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 75 min
2ag
12.40
900.00
f1 (ppm)

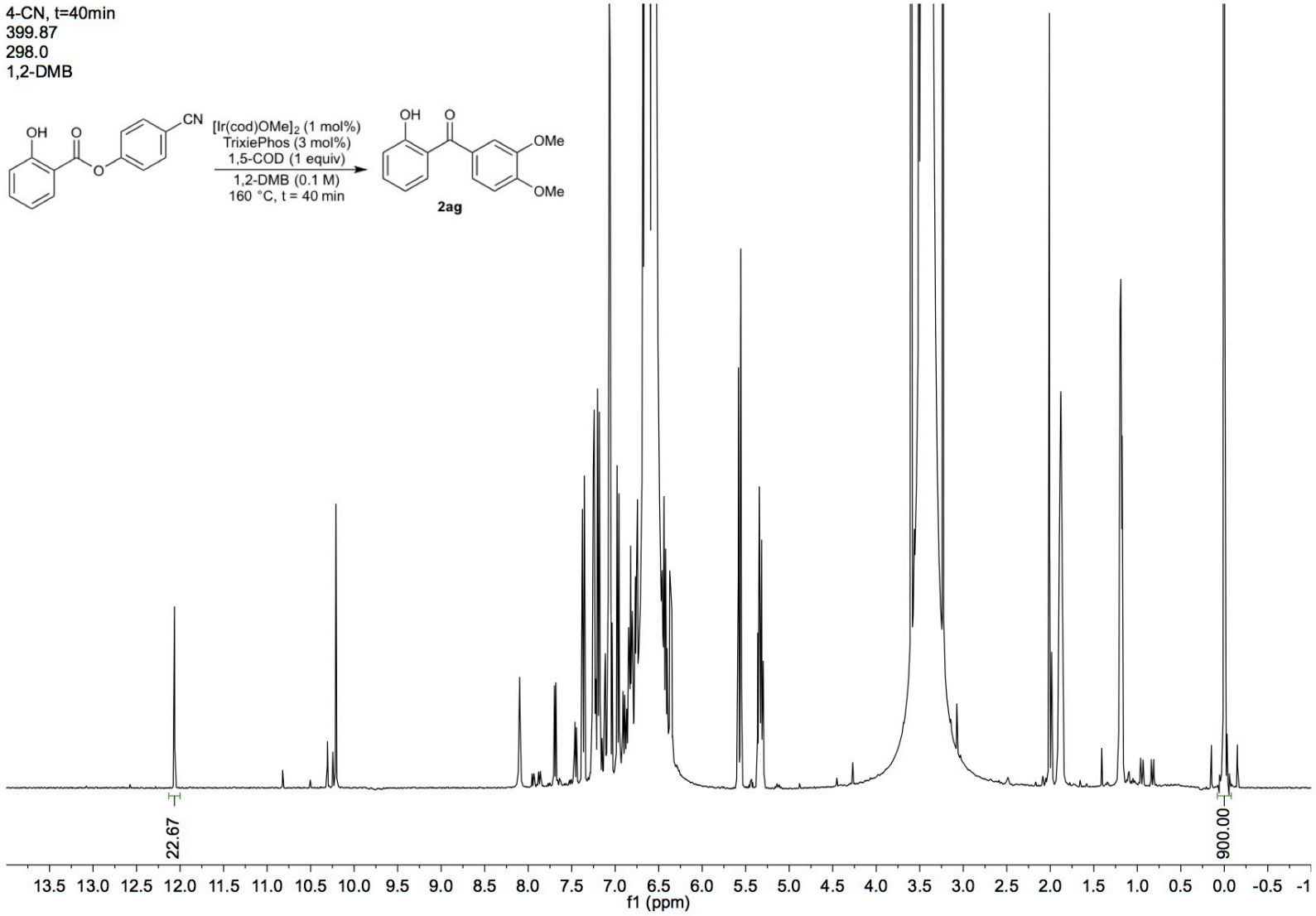

Product
Ph-TMS
CF3 PhSali t=75 min
298.0 K
CF3 PhSali t=60 min
298.0 K
CF3 PhSali t=45 min
298.0 K
CF3 PhSali t=30 min
298.0 K
CF3 PhSali t=15 min
298.0 K
CF3 PhSali t=0 min
298.0 K
f1 (ppm)

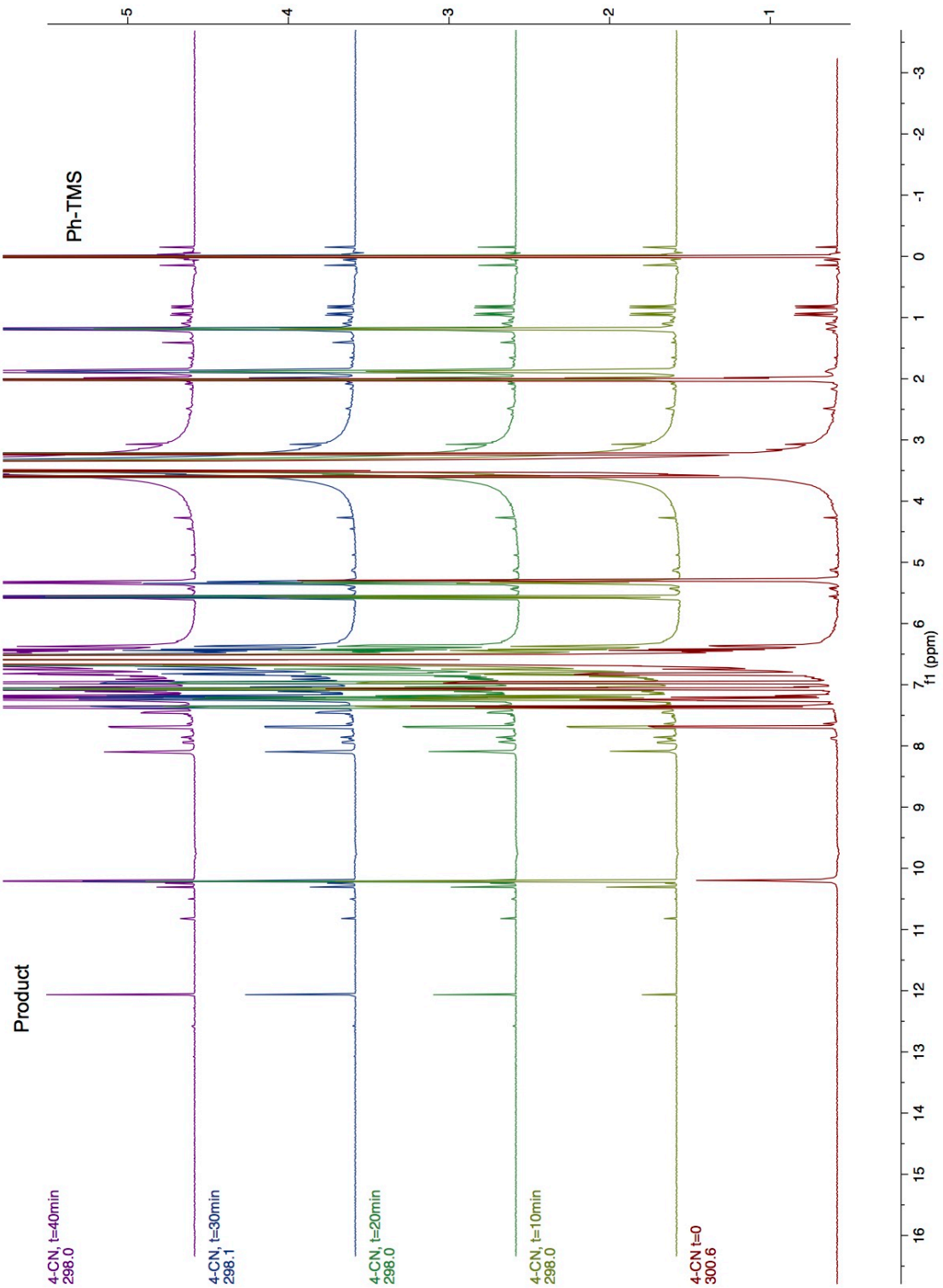

4-CN t=0
399.87
300.6
1,2-DMB
OH
O
O
CN
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 0 min
OH
O
OMe
OMe
2ag
0.04
00.006
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


4-CN, t=10min
399.87
298.0
1,2-DMB
OH
O
O
CN
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 10 min
OH
O
OMe
OMe
2ag
5.48
900.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

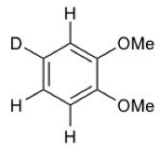

4-CN, t=20min
399.87
298.0
1,2-DMB
OH
O
O
CN
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 20 min
OH
O
OMe
OMe
2ag
10.57
900.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


4-CN, t=30min
399.87
298.1
1,2-DMB
OH
O
O
CN
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 30 min
OH
O
OMe
OMe
2ag
16.30
900.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

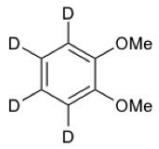

4-CN, t=40min
399.87
298.0
1,2-DMB
OH
O
O
CN
[Ir(cod)OMe]2 (1 mol%)
TrixiePhos (3 mol%)
1,5-COD (1 equiv)
1,2-DMB (0.1 M)
160 °C, t = 40 min
OH
O
OMe
OMe
2ag
22.67
900.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

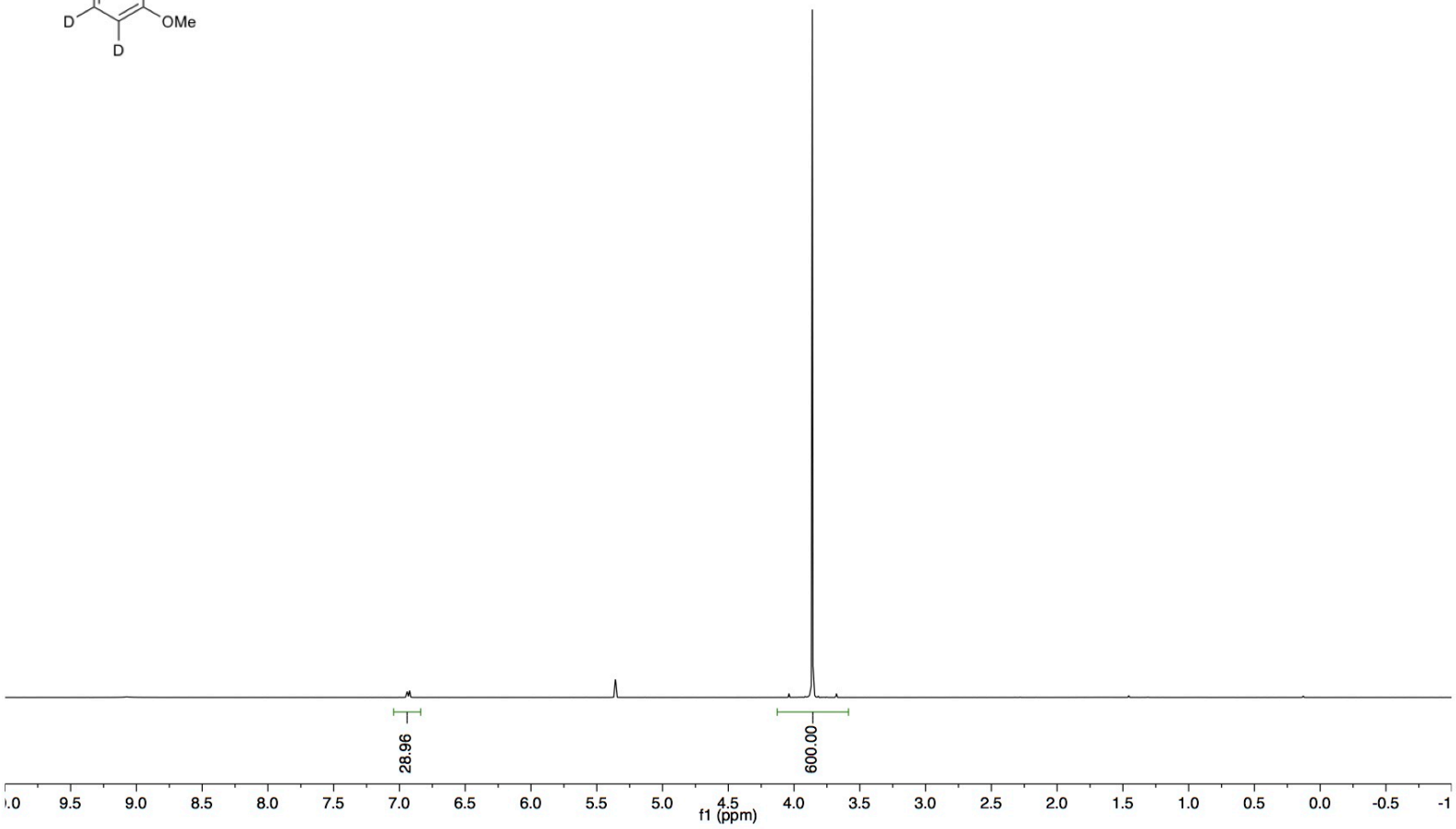

Product
Ph-TMS
4-CN, t=40min
298.0
4-CN, t=30min
298.1
4-CN, t=20min
298.0
4-CN, t=10min
298.0
4-CN t=0
300.6
f1 (ppm)

Purified d1-veratrole
298.0

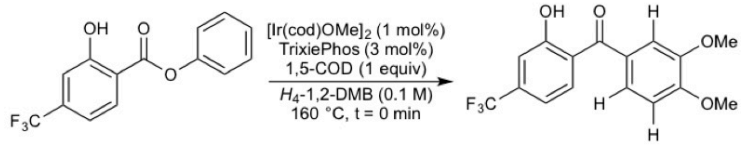


d4-veratrole
298.0 K

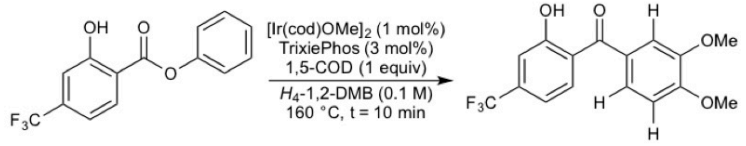




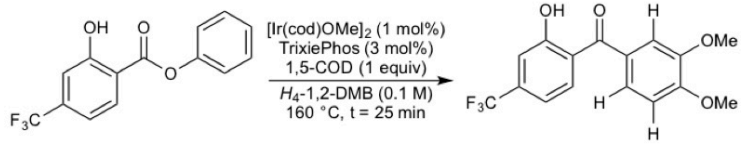
Proteo Experiment 1, t = 0 min
19F
298.1



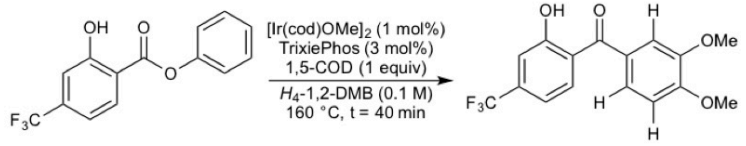
Proteo Experiment 1, t = 10 min
19F
298.0



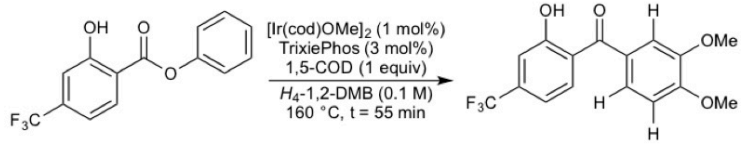
Proteo Experiment 1, t = 25 min
19F
298.0



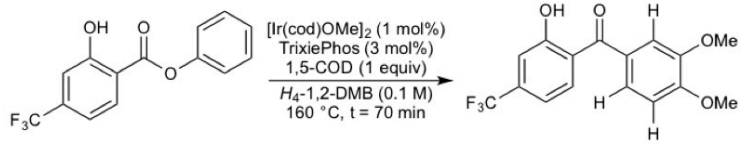
Proteo Experiment 1, t = 40 min
19F
298.0

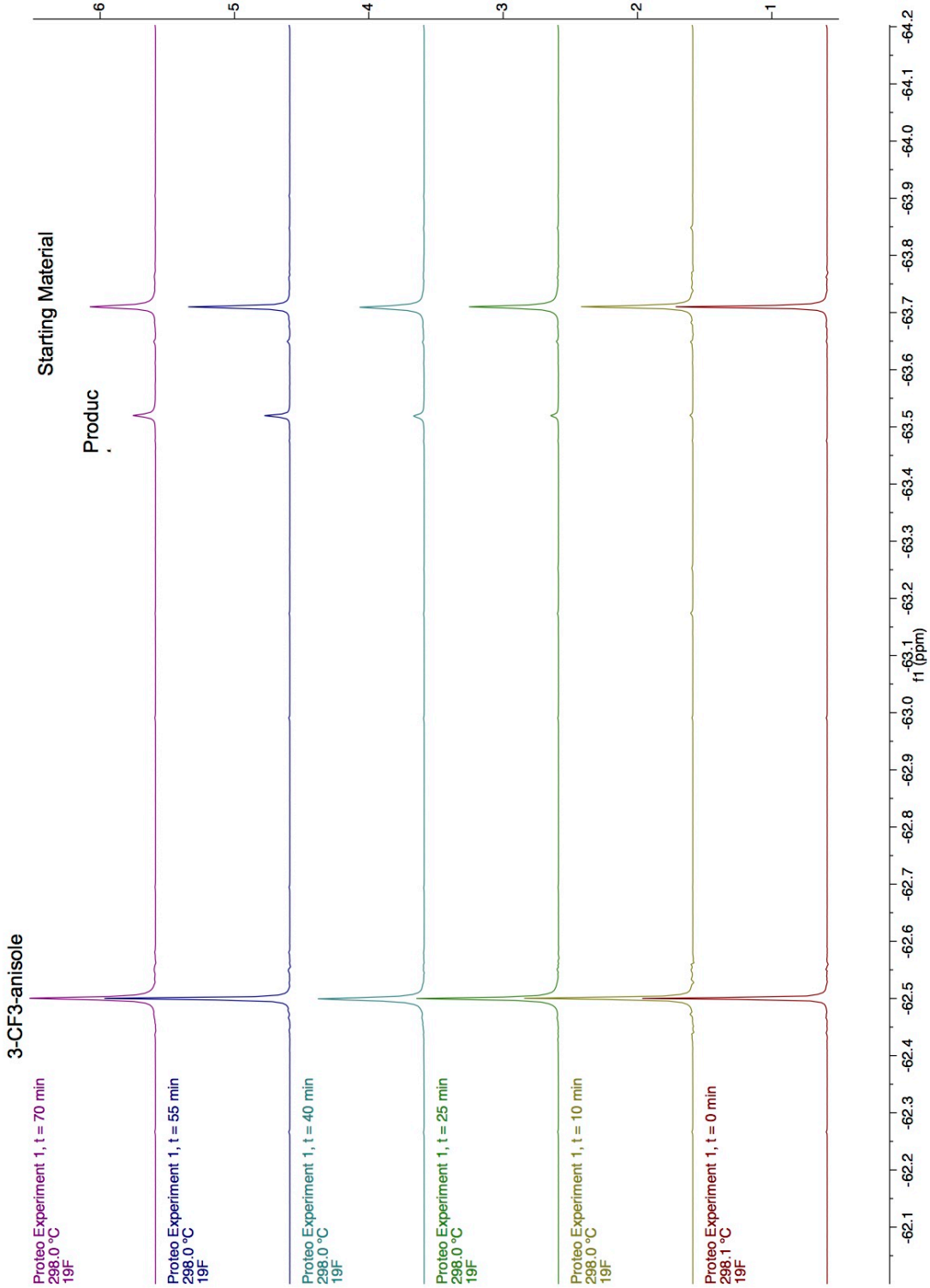


Proteo Experiment 1, t = 55 min
19F
298.0

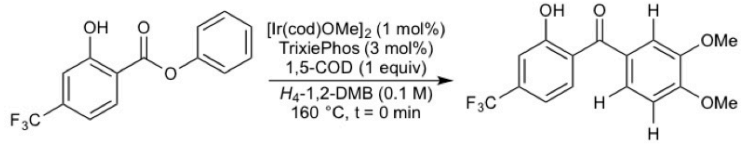


Proteo Experiment 1, t = 70 min
19F
298.0

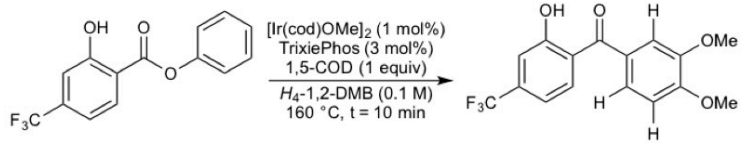



3-CF3-anisole
Starting Material
Produc
Proteo Experiment 1, t = 70 min
298.0 °C
19F
Proteo Experiment 1, t = 55 min
298.0 °C
19F
Proteo Experiment 1, t = 40 min
298.0 °C
19F
Proteo Experiment 1, t = 25 min
298.0 °C
19F
Proteo Experiment 1, t = 10 min
298.0 °C
19F
Proteo Experiment 1, t = 0 min
298.1 °C
19F
6
5
4
3
2
1
-62.1
-62.2
-62.3
-62.4
-62.5
-62.6
-62.7
-62.8
-62.9
-63.0
-63.1
-63.2
-63.3
-63.4
-63.5
-63.6
-63.7
-63.8
-63.9
-64.0
-64.1
-64.2
f1 (ppm)

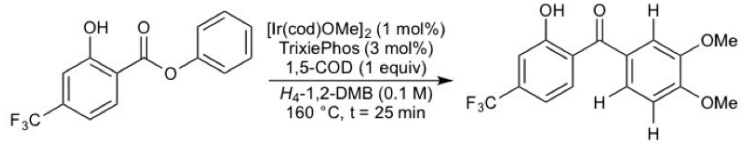
Proteo Experiment 2, t = 0 min
19F
298.0



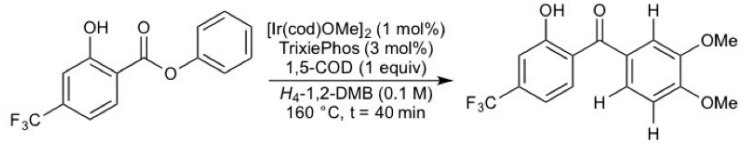
Proteo Experiment 2, t = 10 min
19F
298.0



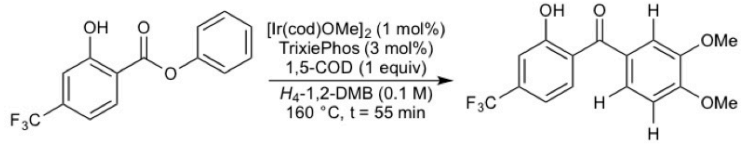
Proteo Experiment 2, t = 25 min
19F
298.0



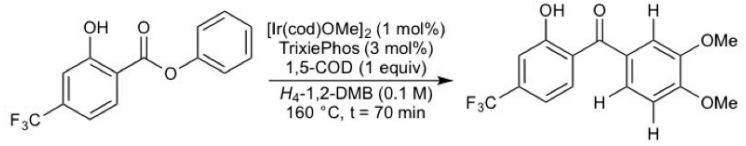
Proteo Experiment 2, t = 40 min
19F
298.0

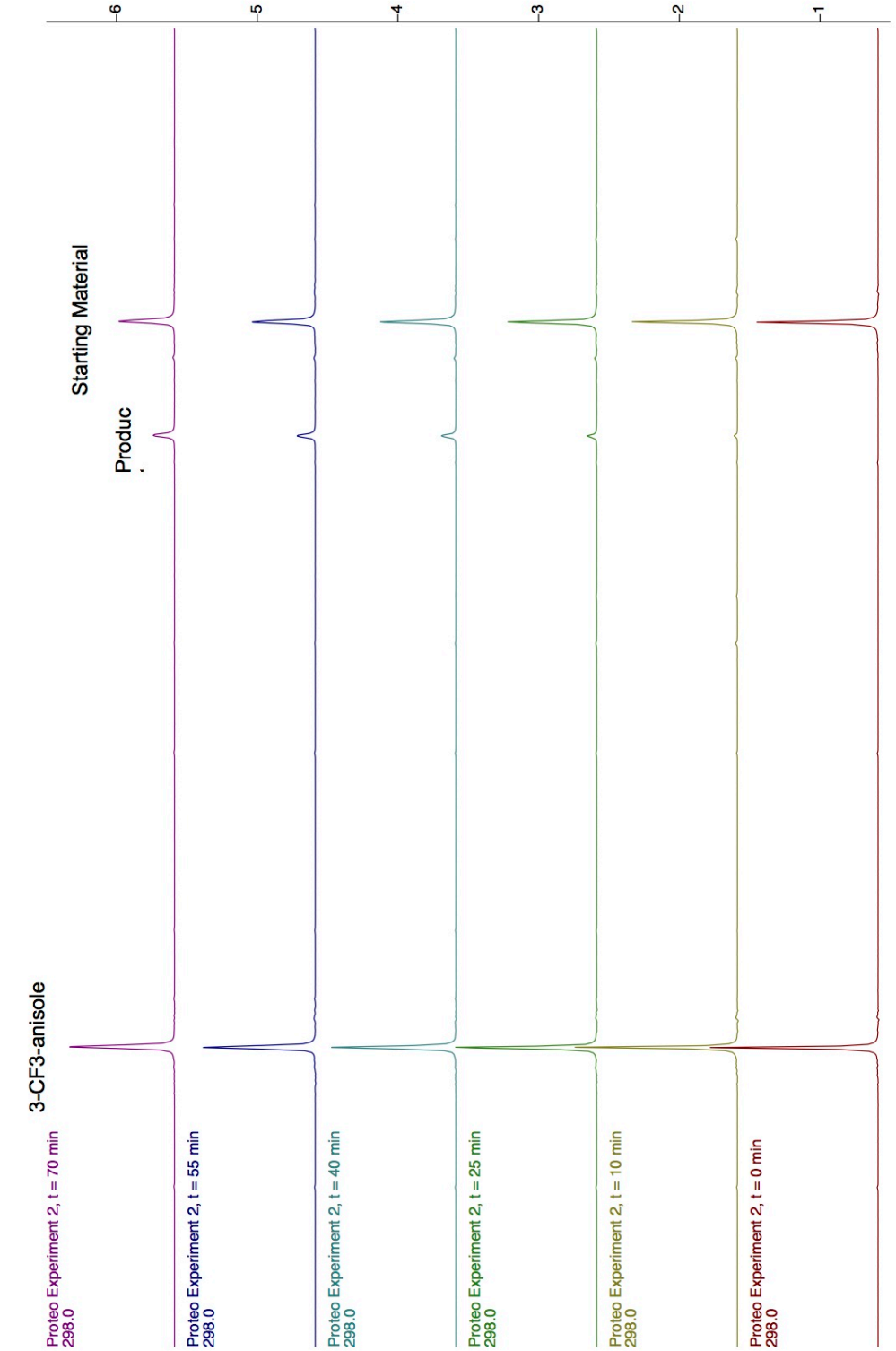


Proteo Experiment 2, t = 55 min
19F
298.0

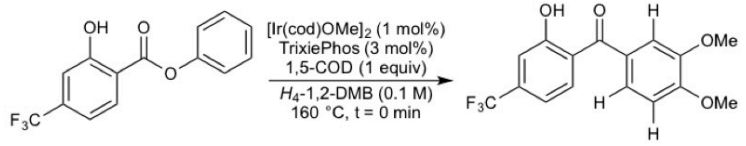


Proteo Experiment 2, t = 70 min
19F
298.0

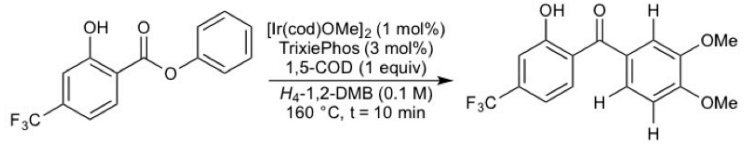



3-CF3-anisole
Starting Material
Produc
Proteo Experiment 2, t = 70 min
298.0
Proteo Experiment 2, t = 55 min
298.0
Proteo Experiment 2, t = 40 min
298.0
Proteo Experiment 2, t = 25 min
298.0
Proteo Experiment 2, t = 10 min
298.0
Proteo Experiment 2, t = 0 min
298.0
6
5
4
3
2
1
-62.1
-62.2
-62.3
-62.4
-62.5
-62.6
-62.7
-62.8
-62.9
-63.0
-63.1
-63.2
-63.3
-63.4
-63.5
-63.6
-63.7
-63.8
-63.9
-64.0
-64.1
-64.2
f1 (ppm)

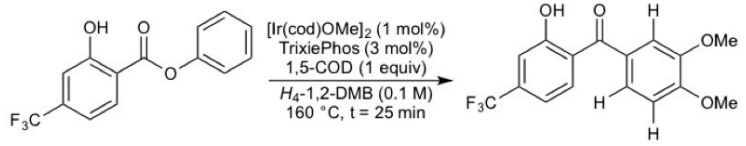
Proteo Experiment 3, t = 0 min
19F
298.1



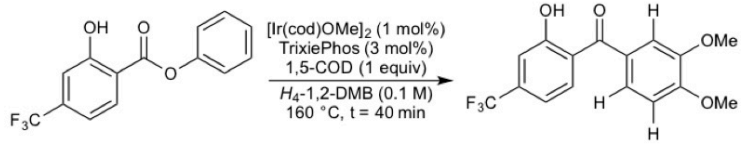
Proteo Experiment 3, t = 10 min
19F
298.0



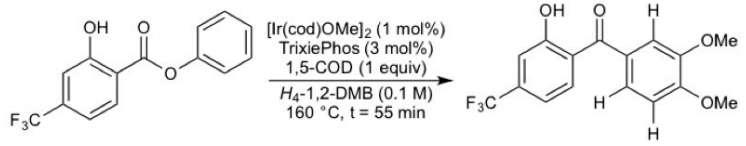
Proteo Experiment 3, t = 25 min
19F
298.0



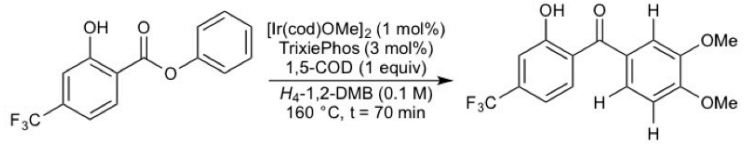
Proteo Experiment 3, t = 40 min
19F
298.0

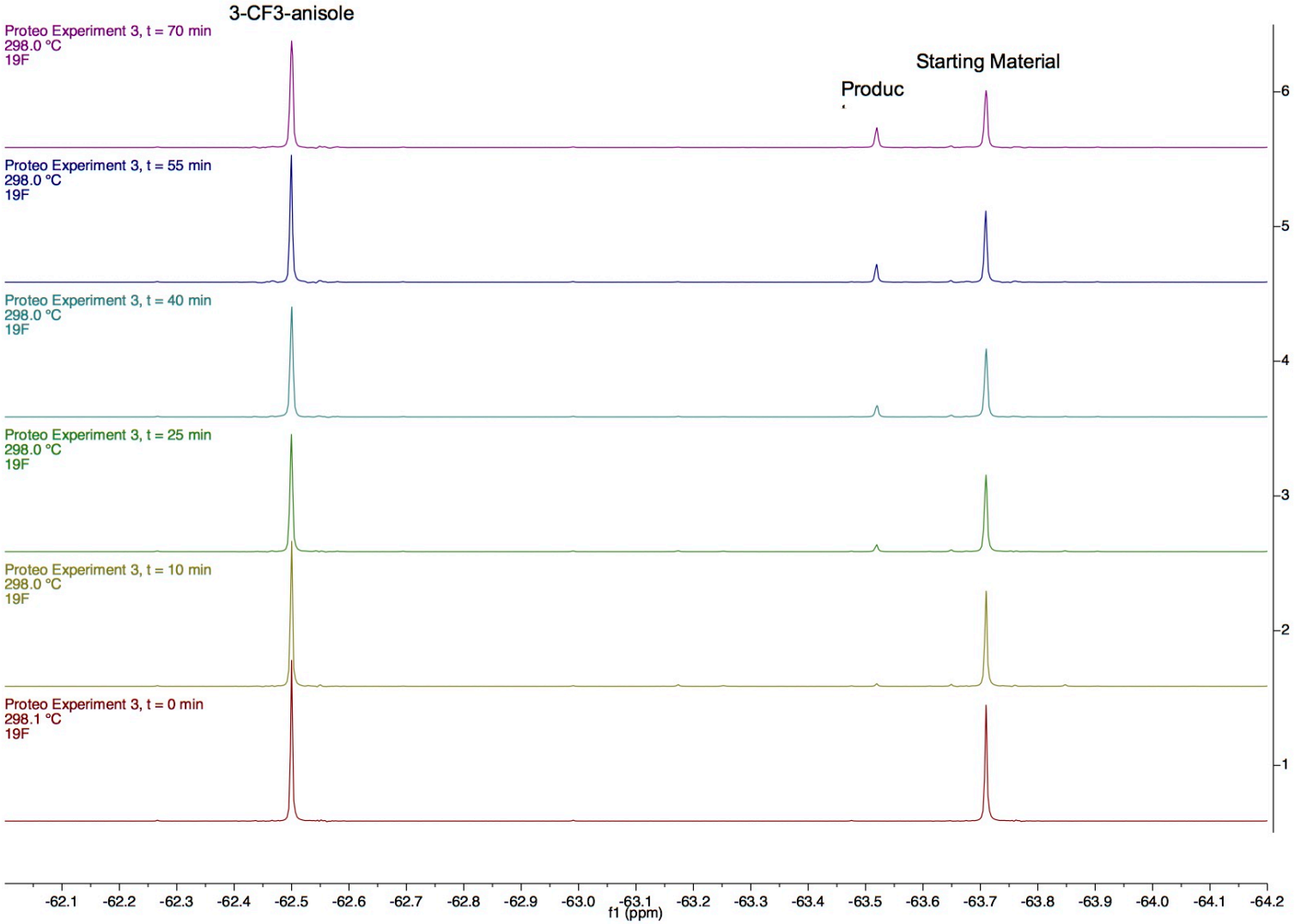


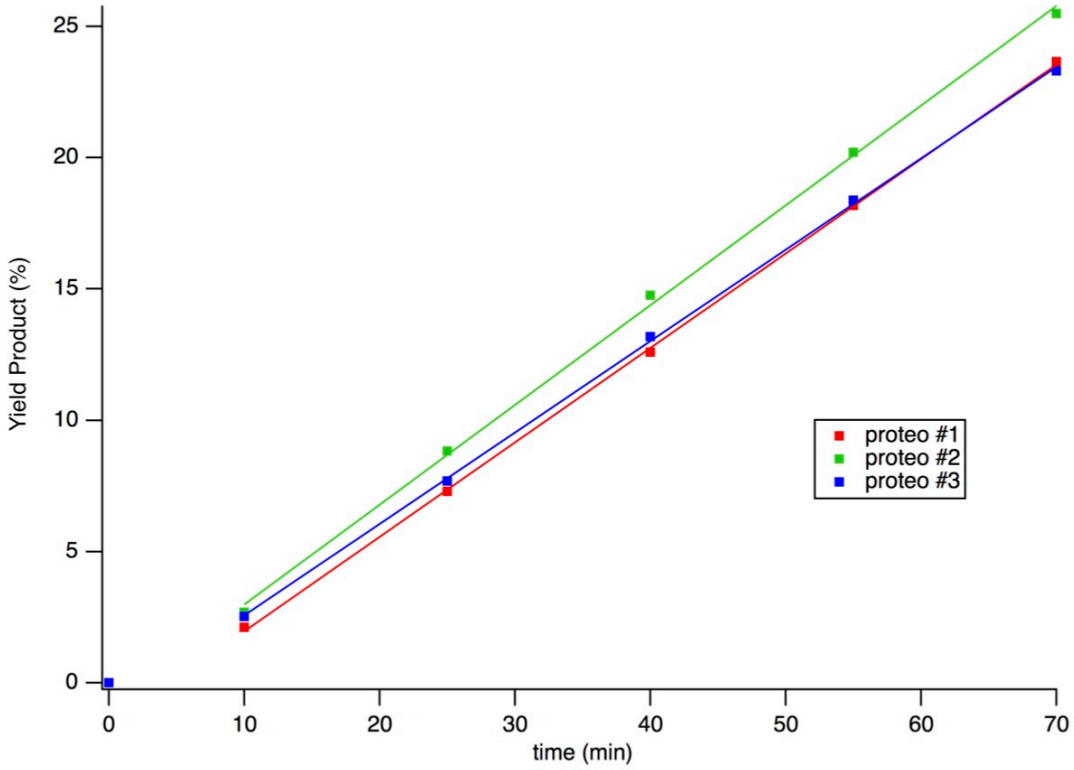
Proteo Experiment 3, t = 55 min
19F
298.0



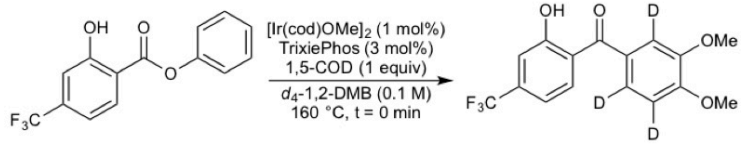
Proteo Experiment 3, t = 70 min
19F
298.0



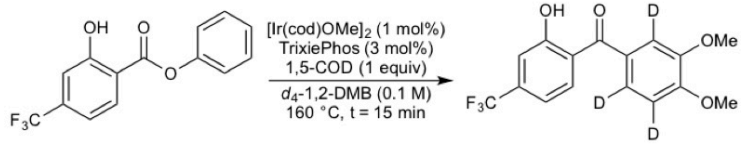

3-CF3-anisole
Proteo Experiment 3, t = 70 min
298.0 °C
19F
Starting Material
Produc
Proteo Experiment 3, t = 55 min
298.0 °C
19F
Proteo Experiment 3, t = 40 min
298.0 °C
19F
Proteo Experiment 3, t = 25 min
298.0 °C
19F
Proteo Experiment 3, t = 10 min
298.0 °C
19F
Proteo Experiment 3, t = 0 min
298.1 °C
19F
6
5
4
3
2
1
-62.1 -62.2 -62.3 -62.4 -62.5 -62.6 -62.7 -62.8 -62.9 -63.0 -63.1 -63.2 -63.3 -63.4 -63.5 -63.6 -63.7 -63.8 -63.9 -64.0 -64.1 -64.2
f1 (ppm)


Yield Product (%)
25
20
15
10
5
0
0
10
20
30
40
50
60
70
time (min)
proteo #1
proteo #2
proteo #3

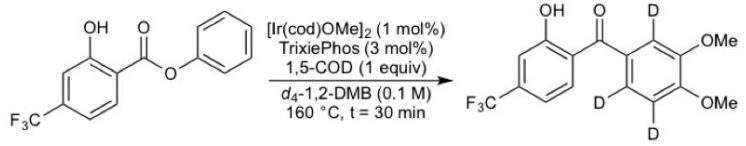
Deutero Experiment 1, t = 0 min
19F
298.0



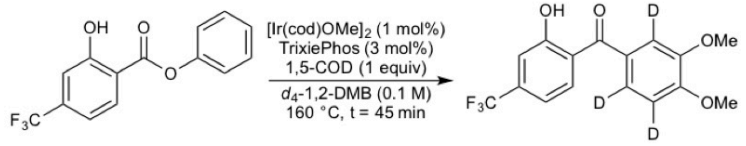
Deutero Experiment 1, t = 15 min
19F
298.0



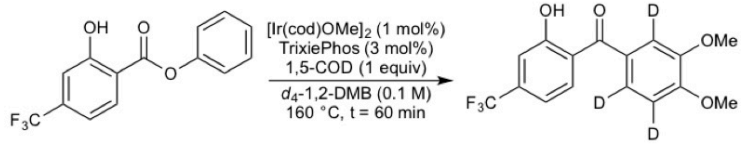
Deutero Experiment 1, t = 30 min
19F
298.0



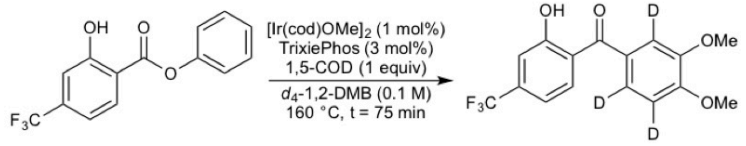
Deutero Experiment 1, t = 45 min
19F
298.0



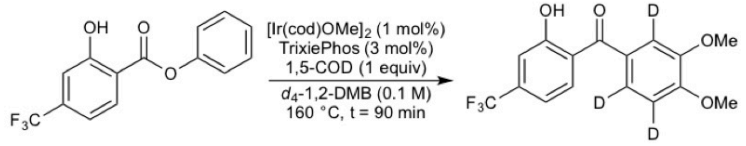
Deutero Experiment 1, t = 60 min
19F
298.0

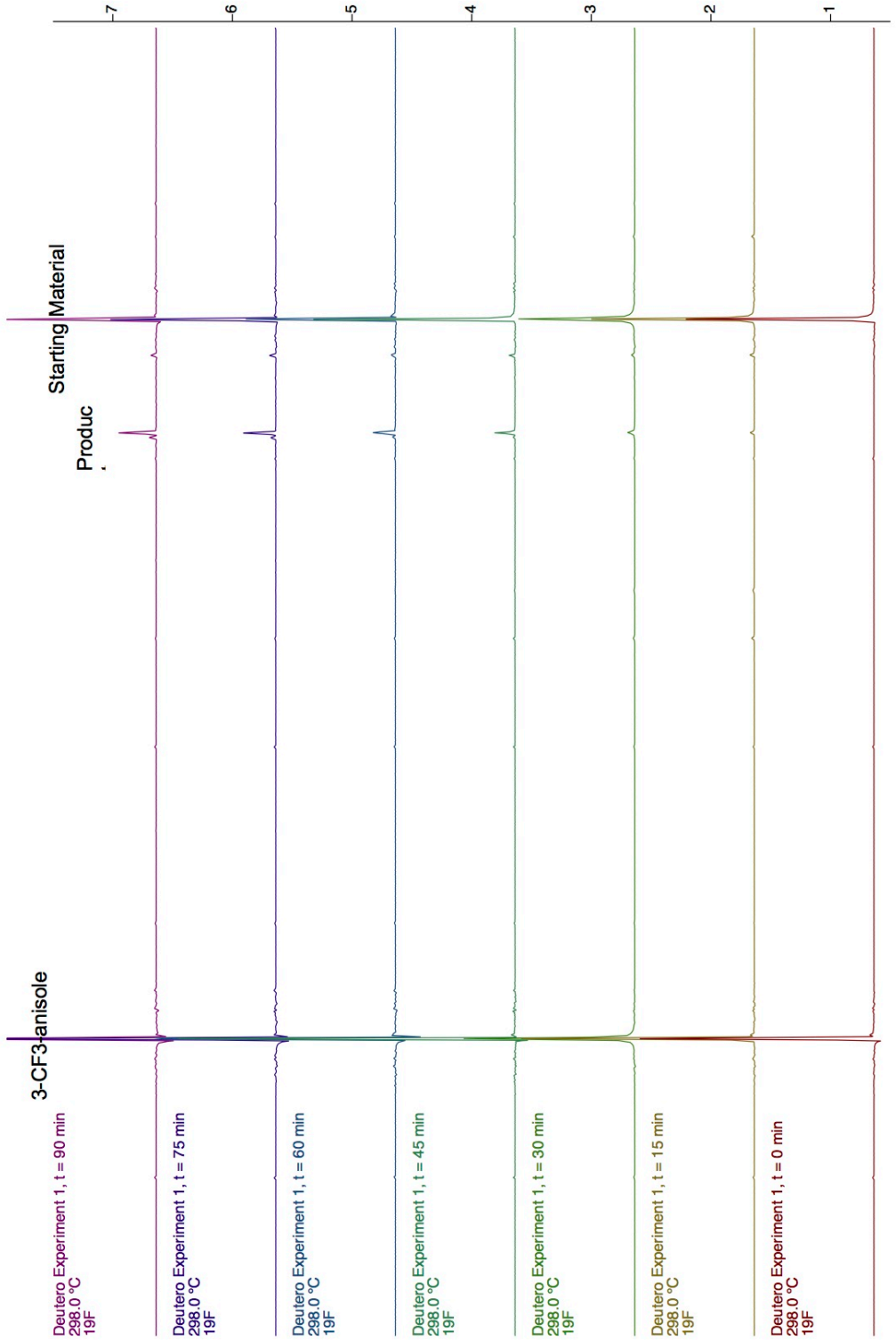


Deutero Experiment 1, t = 75 min
19F
298.0

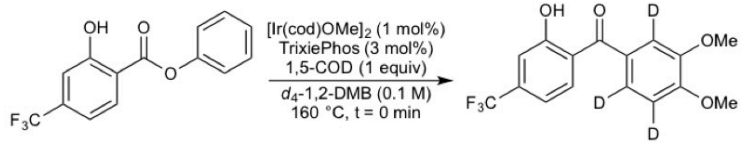


Deutero Experiment 1, t = 90 min
19F
298.0

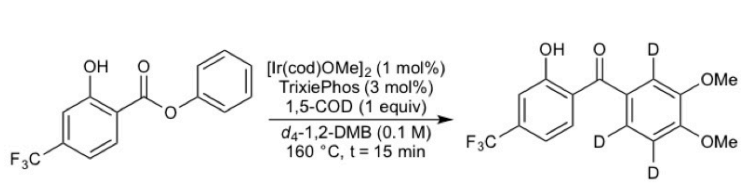



3-CF3-anisole
Starting Material
Produc
Deutero Experiment 1, t = 90 min
298.0 °C
19F
Deutero Experiment 1, t = 75 min
298.0 °C
19F
Deutero Experiment 1, t = 60 min
298.0 °C
19F
Deutero Experiment 1, t = 45 min
298.0 °C
19F
Deutero Experiment 1, t = 30 min
298.0 °C
19F
Deutero Experiment 1, t = 15 min
298.0 °C
19F
Deutero Experiment 1, t = 0 min
298.0 °C
19F
-62.1 -62.2 -62.3 -62.4 -62.5 -62.6 -62.7 -62.8 -62.9 -63.0 -63.1 -63.2 -63.3 -63.4 -63.5 -63.6 -63.7 -63.8 -63.9 -64.0 -64.1 -64.2
f1 (ppm)
7 6 5 4 3 2 1

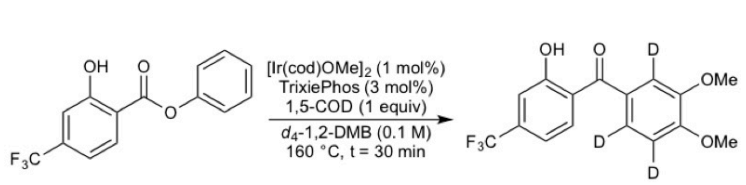
Deutero Experiment 2, t = 0 min
19F
298.0



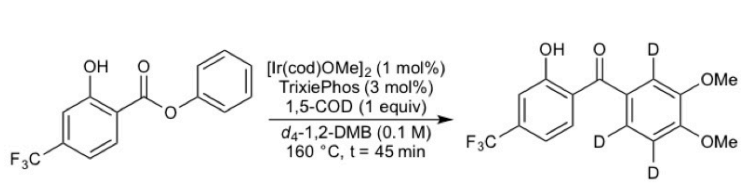
Deutero Experiment 2, t = 15 min
19F
298.0



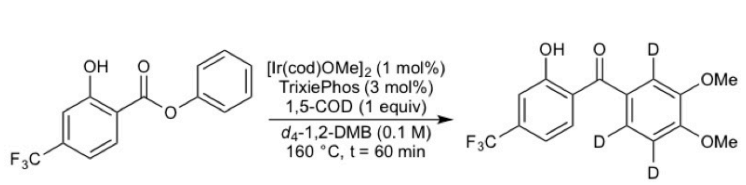
Deutero Experiment 2, t = 30 min
19F
298.0



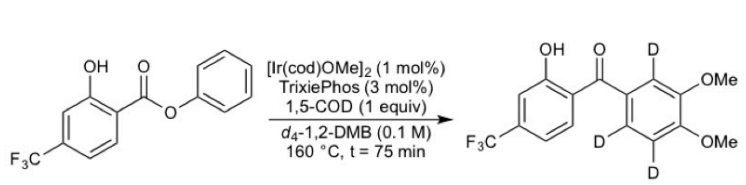
Deutero Experiment 2, t = 45 min
19F
298.0



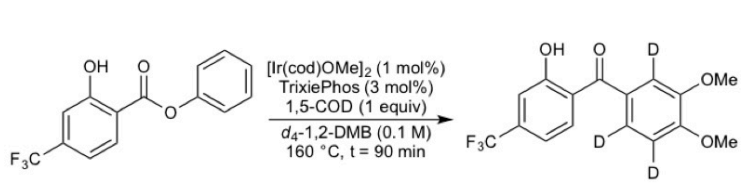
Deutero Experiment 2, t = 60 min
19F
298.0

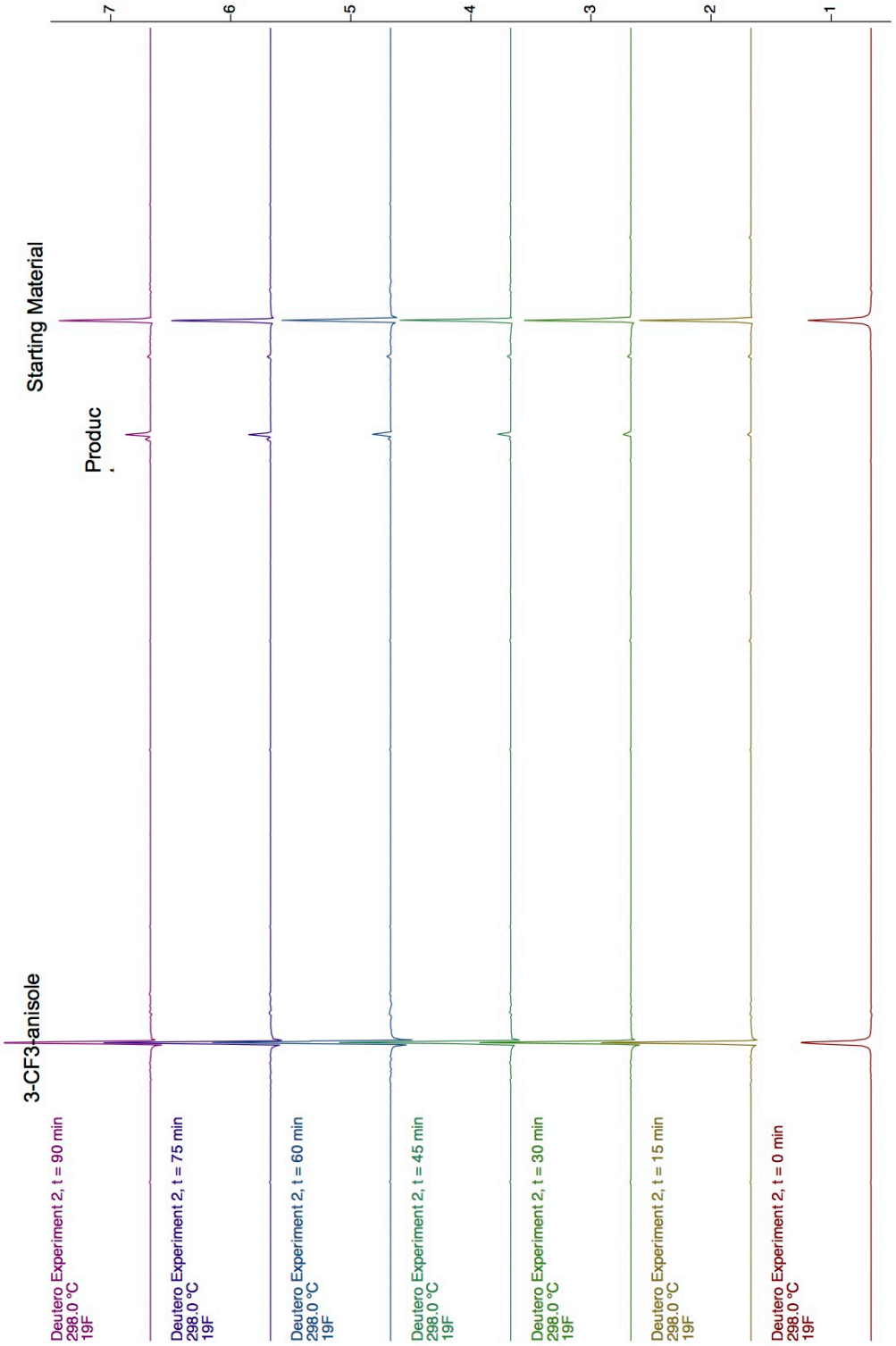


Deutero Experiment 2, t = 75 min
19F
298.0

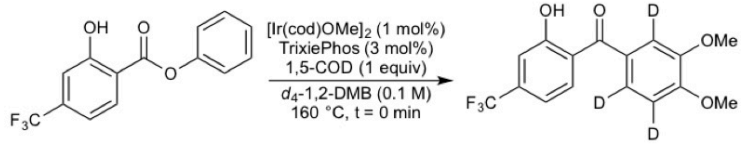


Deutero Experiment 2, t = 90 min
19F
298.0

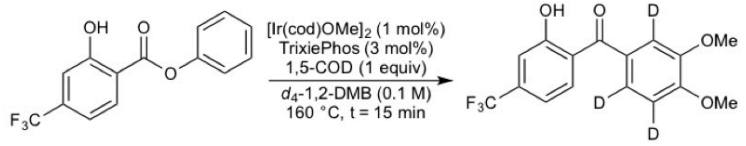



3-CF3-anisole
Starting Material
Produc
Deutero Experiment 2, t = 90 min
298.0 °C
19F
Deutero Experiment 2, t = 75 min
298.0 °C
19F
Deutero Experiment 2, t = 60 min
298.0 °C
19F
Deutero Experiment 2, t = 45 min
298.0 °C
19F
Deutero Experiment 2, t = 30 min
298.0 °C
19F
Deutero Experiment 2, t = 15 min
298.0 °C
19F
Deutero Experiment 2, t = 0 min
298.0 °C
19F
-62.1 -62.2 -62.3 -62.4 -62.5 -62.6 -62.7 -62.8 -62.9 -63.0 -63.1 -63.2 -63.3 -63.4 -63.5 -63.6 -63.7 -63.8 -63.9 -64.0 -64.1 -64.2
f1 (ppm)

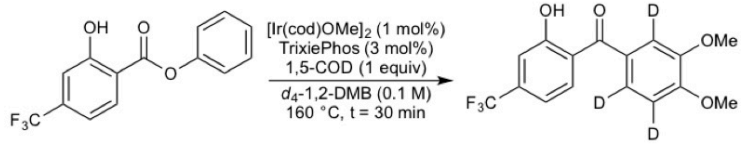
Deutero Experiment 3, t = 0 min
19F
298.0



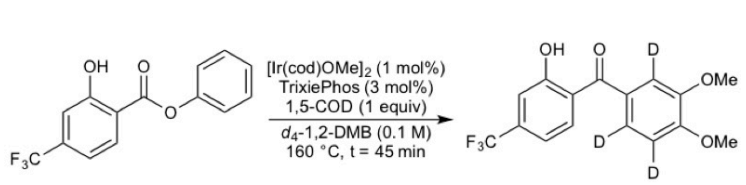
Deutero Experiment 3, t = 15 min
19F
298.0



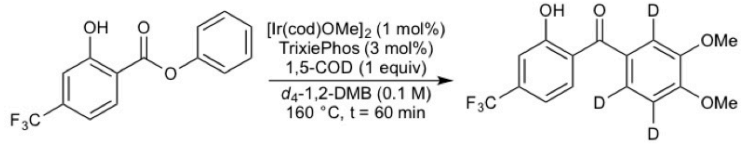
Deutero Experiment 3, t = 30 min
19F
298.0



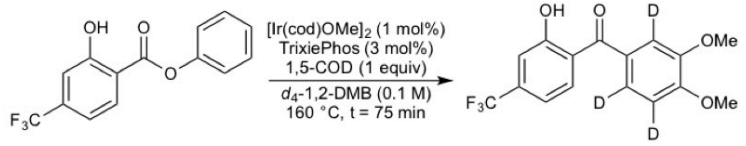
Deutero Experiment 3, t = 45 min
19F
298.0



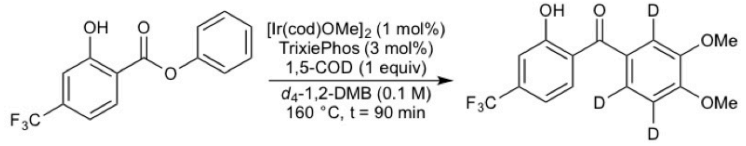
Deutero Experiment 3, t = 60 min
19F
298.0

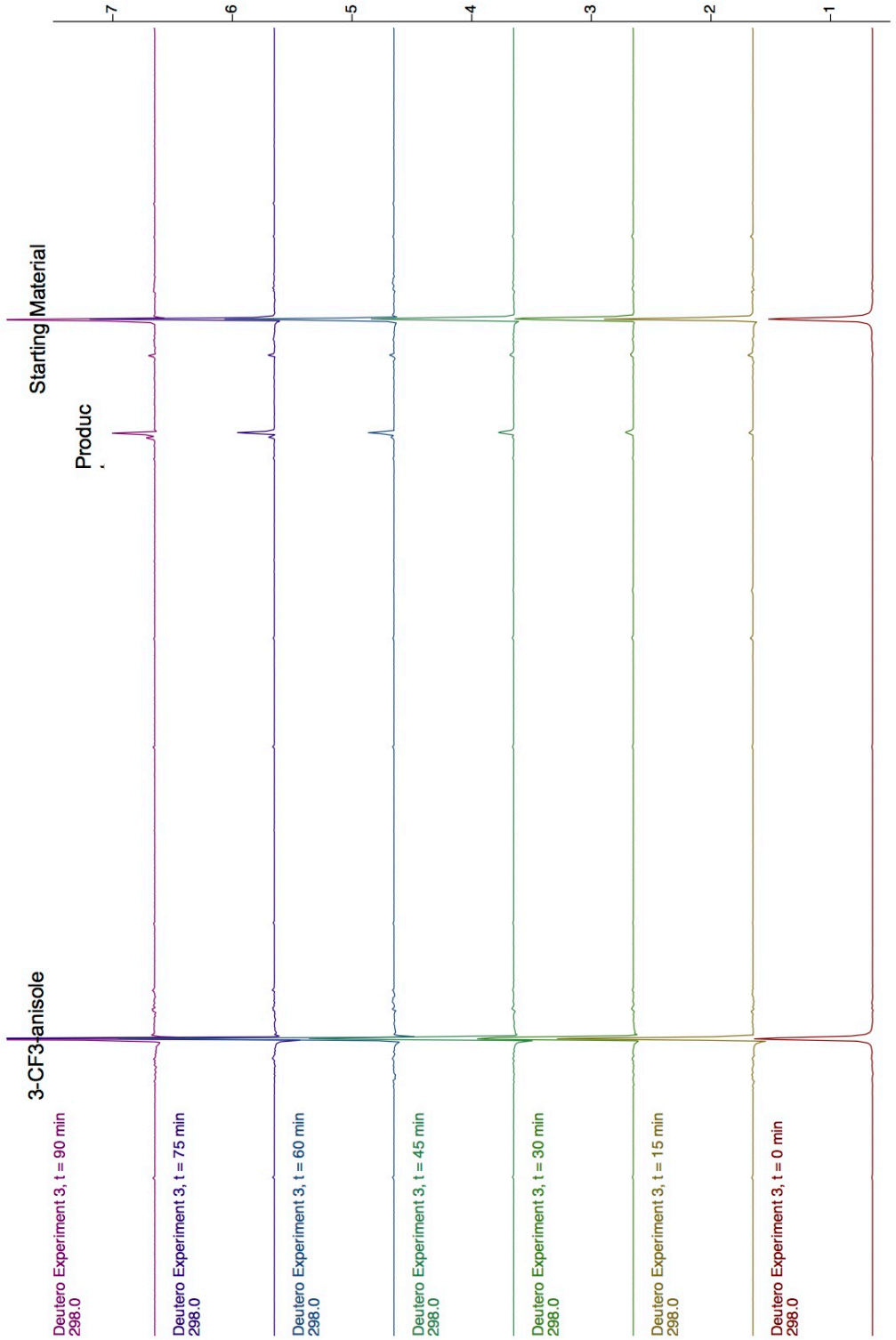


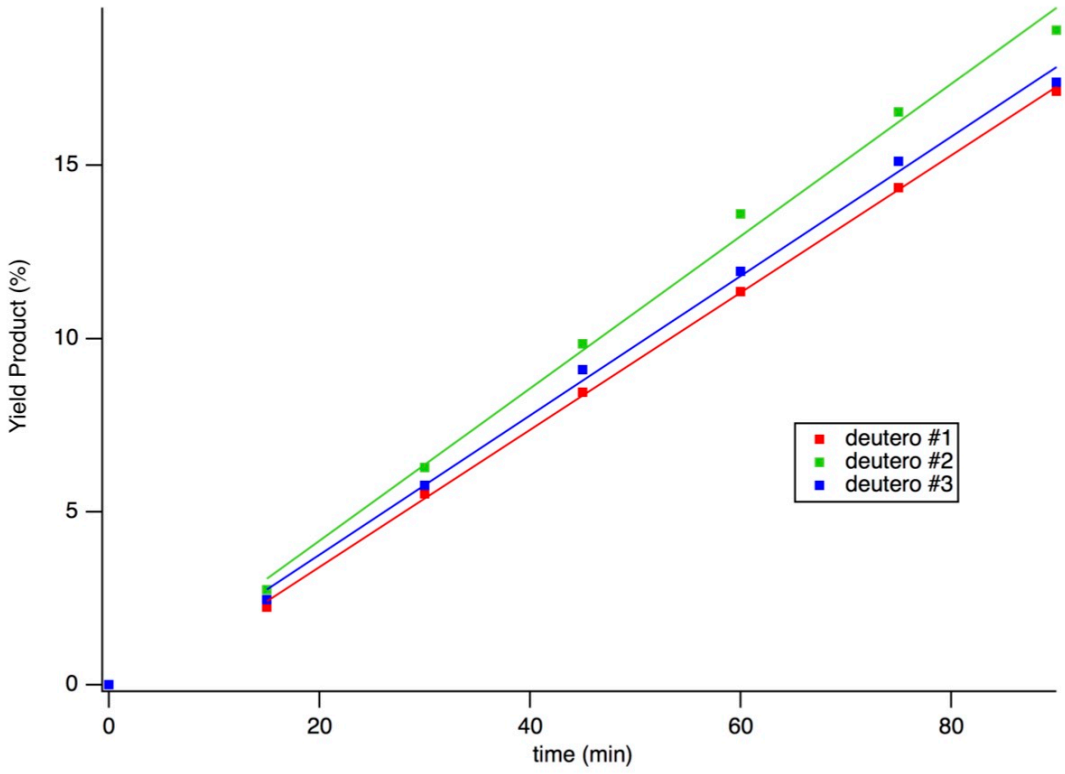
Deutero Experiment 3, t = 75 min
19F
298.0



Deutero Experiment 3, t = 90 min
19F
298.0




3-CF3-anisole
Starting Material
Produc
Deutero Experiment 3, t = 90 min
298.0
Deutero Experiment 3, t = 75 min
298.0
Deutero Experiment 3, t = 60 min
298.0
Deutero Experiment 3, t = 45 min
298.0
Deutero Experiment 3, t = 30 min
298.0
Deutero Experiment 3, t = 15 min
298.0
Deutero Experiment 3, t = 0 min
298.0
-62.1 -62.2 -62.3 -62.4 -62.5 -62.6 -62.7 -62.8 -62.9 -63.0 -63.1 -63.2 -63.3 -63.4 -63.5 -63.6 -63.7 -63.8 -63.9 -64.0 -64.1 -64.2
f1 (ppm)
7 6 5 4 3 2 1


Yield Product (%)
0
5
10
15
0
20
40
60
80
time (min)
deutero #1
deutero #2
deutero #3

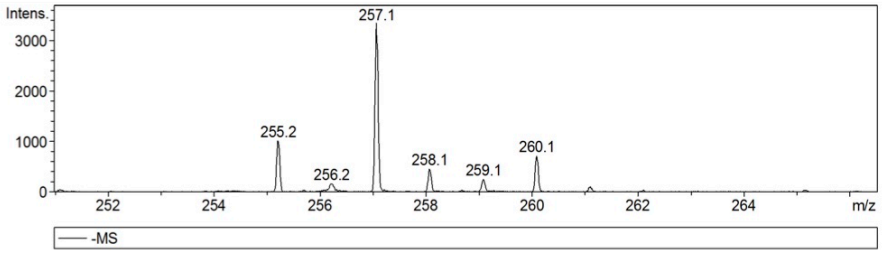
Mass Spectrum List Report

Analysis Info

Analysis Name	2LOW RES	Acquisition Date	4/20/2017 9:08:35 AM
Method	negative_010616.tofpar	Operator	operator name
Sample Name	NAS-2-63_4-1	Instrument	BioTOF II
	ESI NEGFree format commentsFree format comments		

Acquisition Parameter

n/a	n/a	n/a	n/a	detbias	1800 V
EndP	3000 V	n/a	n/a	n/a	n/a



#	m/z	I
1	145.0	1485
2	169.1	144
3	212.1	268
4	213.0	4652
5	214.1	811
6	215.1	112
7	241.0	141
8	255.2	1002
9	256.2	156
10	257.1	3332
11	258.1	450
12	259.1	249
13	260.1	704
14	283.2	1502
15	284.2	237

Intermolecular Competition 1

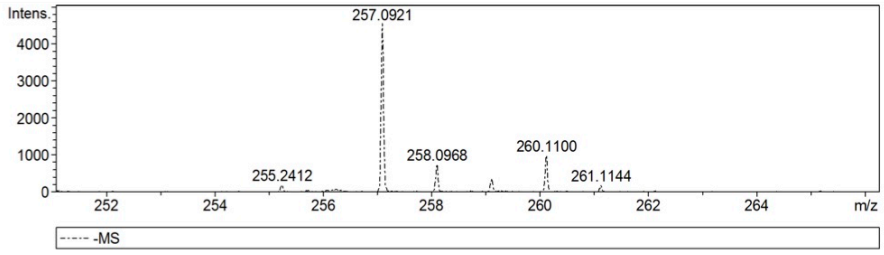
Mass Spectrum List Report

Analysis Info

Analysis Name	14-2 low res	Acquisition Date	4/21/2017 10:39:37 AM
Method	negative_010616.tofpar	Operator	operator name
Sample Name	NAS-2-63_4-2	Instrument	BioTOF II
	ESI NEGFree format commentsFree format comments		

Acquisition Parameter

n/a	n/a	n/a	n/a	detbias	1800 V
EndP	3000 V	n/a	n/a	n/a	n/a



#	m/z	I
1	137.0352	1272
2	138.0418	524
3	144.9769	273
4	169.0767	292
5	212.0851	1128
6	213.0673	7994
7	214.0718	1491
8	215.0769	204
9	229.0971	529
10	230.1012	218
11	232.1133	145
12	241.0612	174
13	242.0710	109
14	255.2412	185
15	257.0921	4546
16	258.0968	745
17	259.1042	358
18	260.1100	983
19	261.1144	176
20	283.0535	327
21	283.2723	175
22	284.0571	251
23	333.0851	110
24	339.0162	173
25	377.1115	675
26	378.1166	168
27	380.1266	165

Intermolecular Competition 2

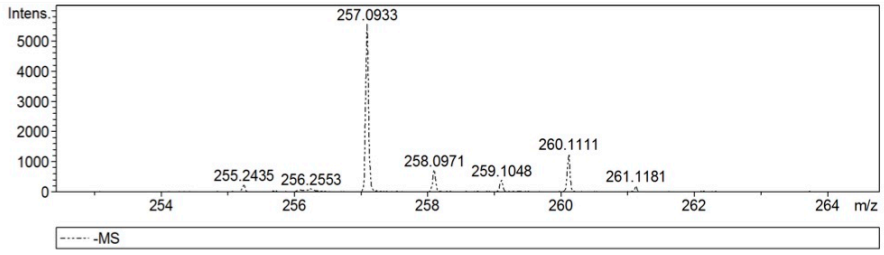
Mass Spectrum List Report

Analysis Info

Analysis Name	14-3 low res	Acquisition Date	4/21/2017 10:41:55 AM
Method	negative_010616.tofpar	Operator	operator name
Sample Name	NAS-2-63_4-3	Instrument	BioTOF II
	ESI NEGFree format commentsFree format comments		

Acquisition Parameter

n/a	n/a	n/a	n/a	detbias	1800 V
EndP	3000 V	n/a	n/a	n/a	n/a



#	m/z	I
1	137.0359	381
2	138.0422	134
3	144.9772	344
4	169.0771	335
5	211.9322	108
6	212.0862	1104
7	213.0690	9619
8	214.0733	2021
9	215.0787	235
10	227.0564	104
11	229.0974	429
12	230.1013	212
13	232.1144	152
14	241.0630	278
15	242.0707	111
16	255.2435	230
17	256.2553	103
18	257.0933	5577
19	258.0971	717
20	259.1048	376
21	260.1111	1259
22	261.1181	195
23	283.0545	187
24	283.2726	322
25	284.0579	154
26	333.0878	117
27	377.1130	747
28	378.1167	159
29	380.1296	193

Intermolecular Competition 3

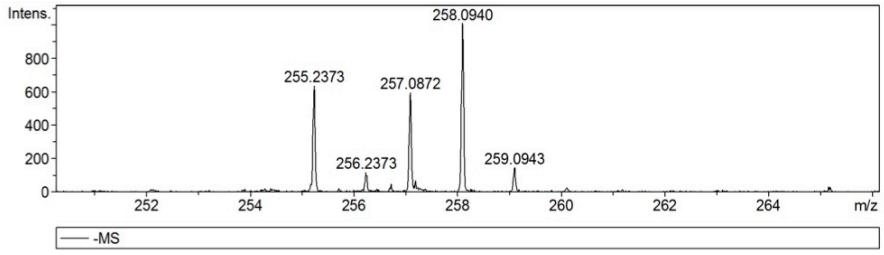
Mass Spectrum List Report

Analysis Info

Analysis Name	11-1 low res	Acquisition Date	4/21/2017 10:30:58 AM
Method	negative_010616.tofpar	Operator	operator name
Sample Name	NAS-2-63_1-1	Instrument	BioTOF II
	ESI NEGFree format commentsFree format comments		

Acquisition Parameter

n/a	n/a	n/a	n/a	detbias	1800 V
EndP	3000 V	n/a	n/a	n/a	n/a



#	m/z	I
1	137.0321	2104
2	138.0389	456
3	144.9732	3873
4	212.0814	693
5	213.0637	1525
6	214.0684	254
7	229.0890	131
8	230.0972	270
9	231.1001	101
10	243.0776	132
11	244.0814	189
12	255.2373	632
13	256.2373	114
14	257.0872	593
15	258.0940	1009
16	259.0943	143
17	282.0462	150
18	283.0469	811
19	283.2674	806
20	284.0531	351
21	284.2673	121
22	378.1092	105

Intramolecular Competition 1

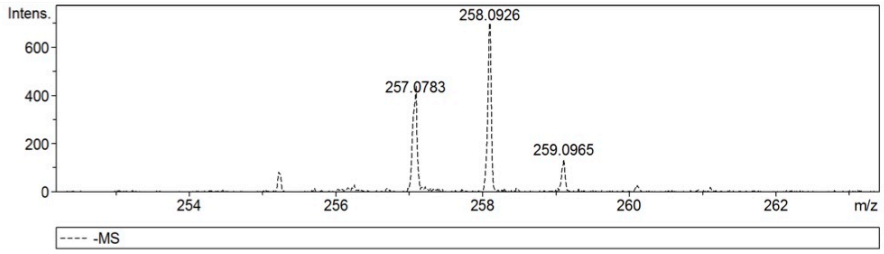
Mass Spectrum List Report

Analysis Info

Analysis Name	11-2 low res	Acquisition Date	4/21/2017 10:34:27 AM
Method	negative_010616.tofpar	Operator	operator name
Sample Name	NAS-2-63_1-2	Instrument	BioTOF II
	ESI NEGFree format commentsFree format comments		

Acquisition Parameter

n/a	n/a	n/a	n/a	detbias	1800 V
EndP	3000 V	n/a	n/a	n/a	n/a



#	m/z	I
1	137.0335	7775
2	138.0391	1620
3	139.0411	120
4	144.9737	1990
5	212.0817	436
6	213.0667	551
7	214.0708	177
8	230.1000	204
9	257.0783	394
10	258.0926	699
11	259.0965	134
12	273.0839	131
13	274.0908	207
14	282.0472	196
15	283.0490	999
16	283.2700	129
17	284.0519	404
18	297.0425	306
19	298.0456	181

Intramolecular Competition 2

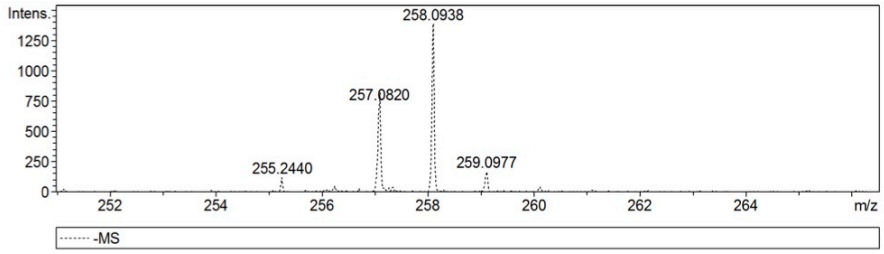
Mass Spectrum List Report

Analysis Info

Analysis Name	11-3 low res	Acquisition Date	4/21/2017 10:36:41 AM
Method	negative_010616.tofpar	Operator	operator name
Sample Name	NAS-2-63_1-3	Instrument	BioTOF II
	ESI NEGFree format commentsFree format comments		

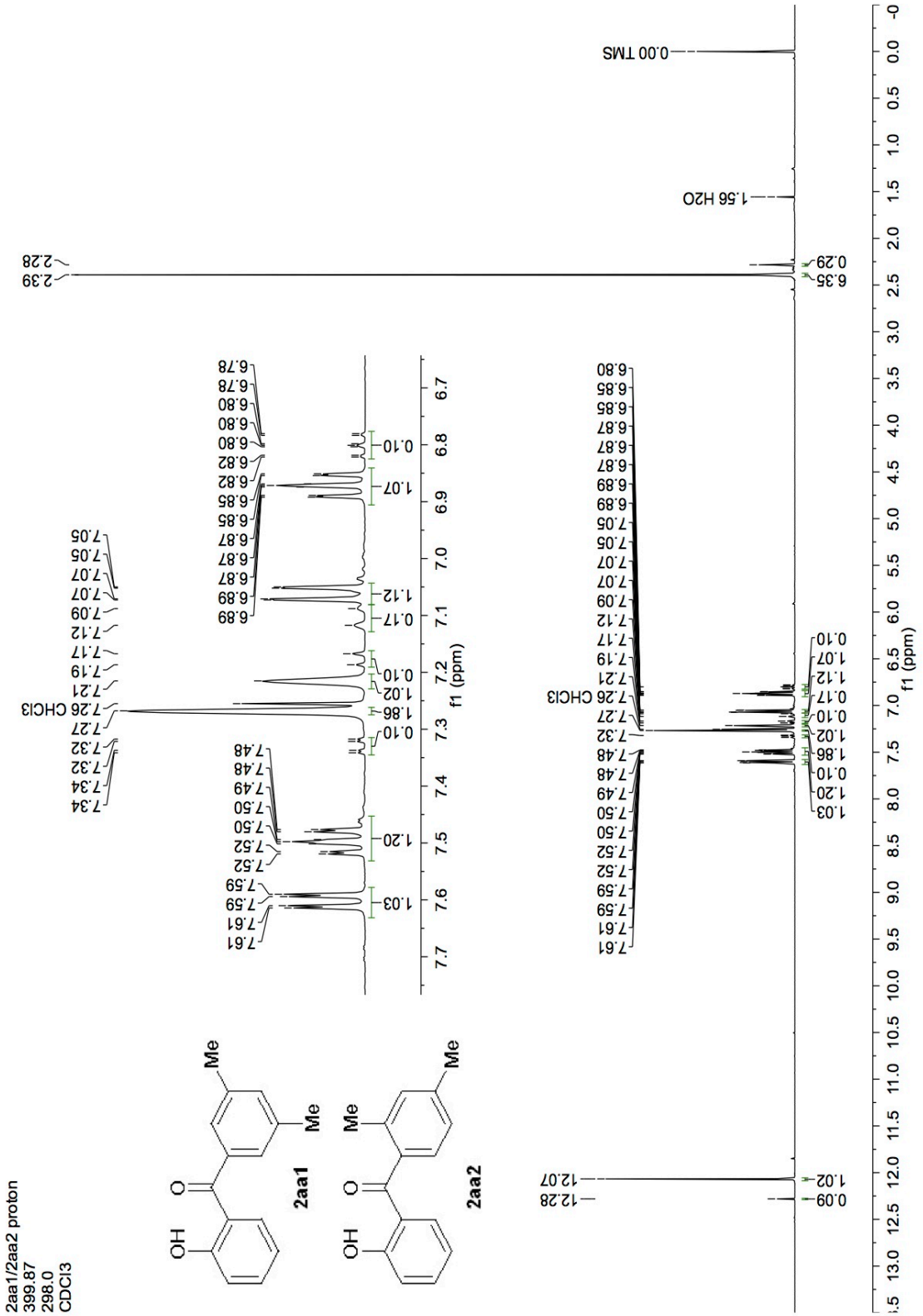
Acquisition Parameter

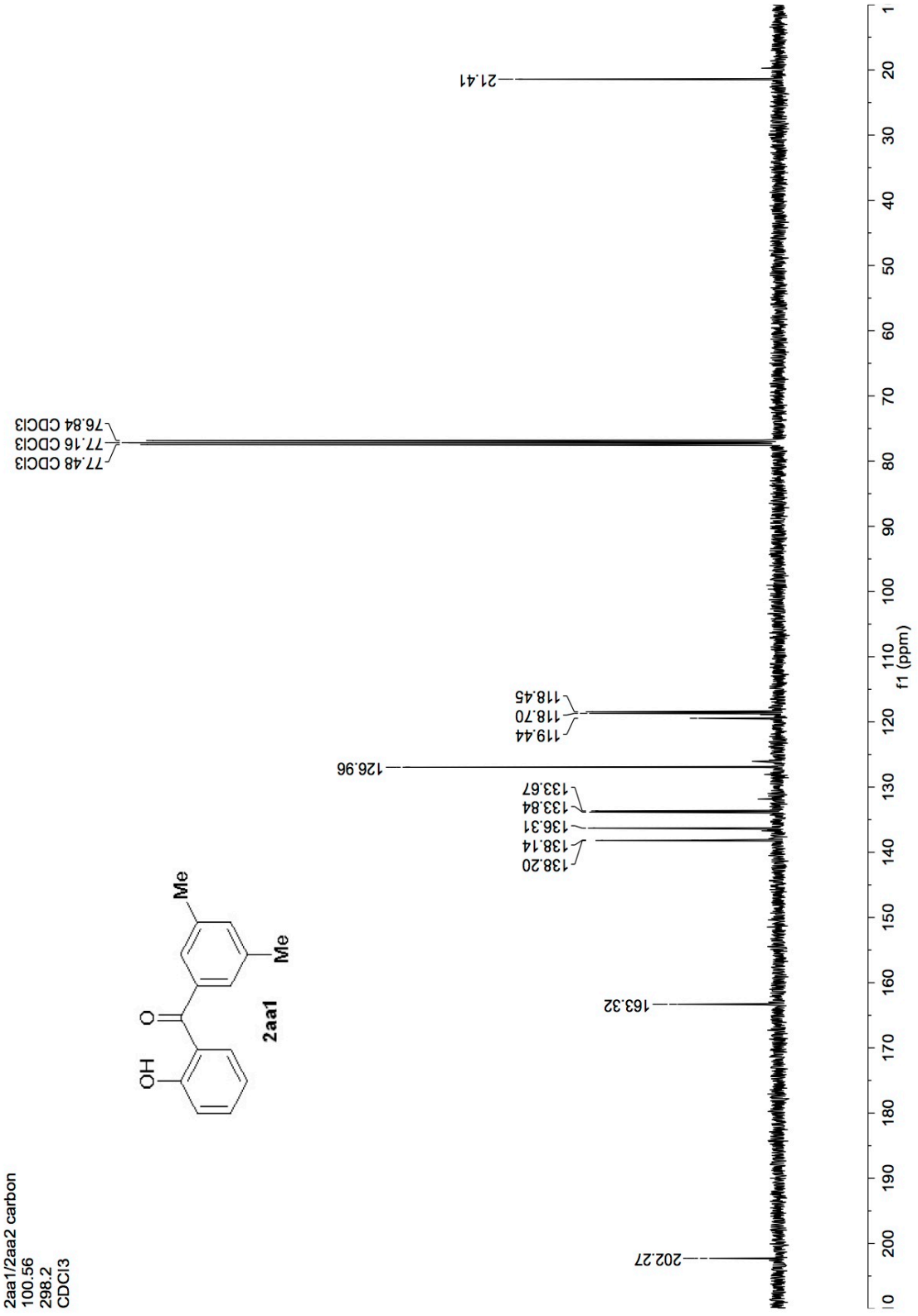
n/a	n/a	n/a	n/a	detbias	1800 V
EndP	3000 V	n/a	n/a	n/a	n/a



#	m/z	I
1	137.0338	6045
2	138.0388	1360
3	139.0431	104
4	144.9735	530
5	212.0826	655
6	213.0675	1163
7	214.0728	269
8	229.0926	126
9	230.0996	258
10	243.0836	111
11	244.0828	167
12	255.2440	119
13	257.0820	727
14	258.0938	1387
15	259.0977	166
16	273.0821	165
17	274.0870	316
18	282.0524	129
19	283.0495	662
20	283.2674	131
21	284.0532	321
22	297.0419	171
23	298.0507	122
24	378.1095	118

Intramolecular Competition 3


2aa1/2aa2 proton
399.87
298.0
CDCl3
Me
Me
O
OH
2aa1
Me
Me
O
OH
2aa2
0.00 TMS
1.56 H2O
2.39
2.28
6.35
0.29
12.28
12.07
1.02
0.09
7.26 CHCl3
f1 (ppm)


2aa1/2aa2 carbon
100.56
298.2
CDCl3
Me
Me
O
OH
2aa1
202.27
163.32
138.20
138.14
136.31
133.84
133.67
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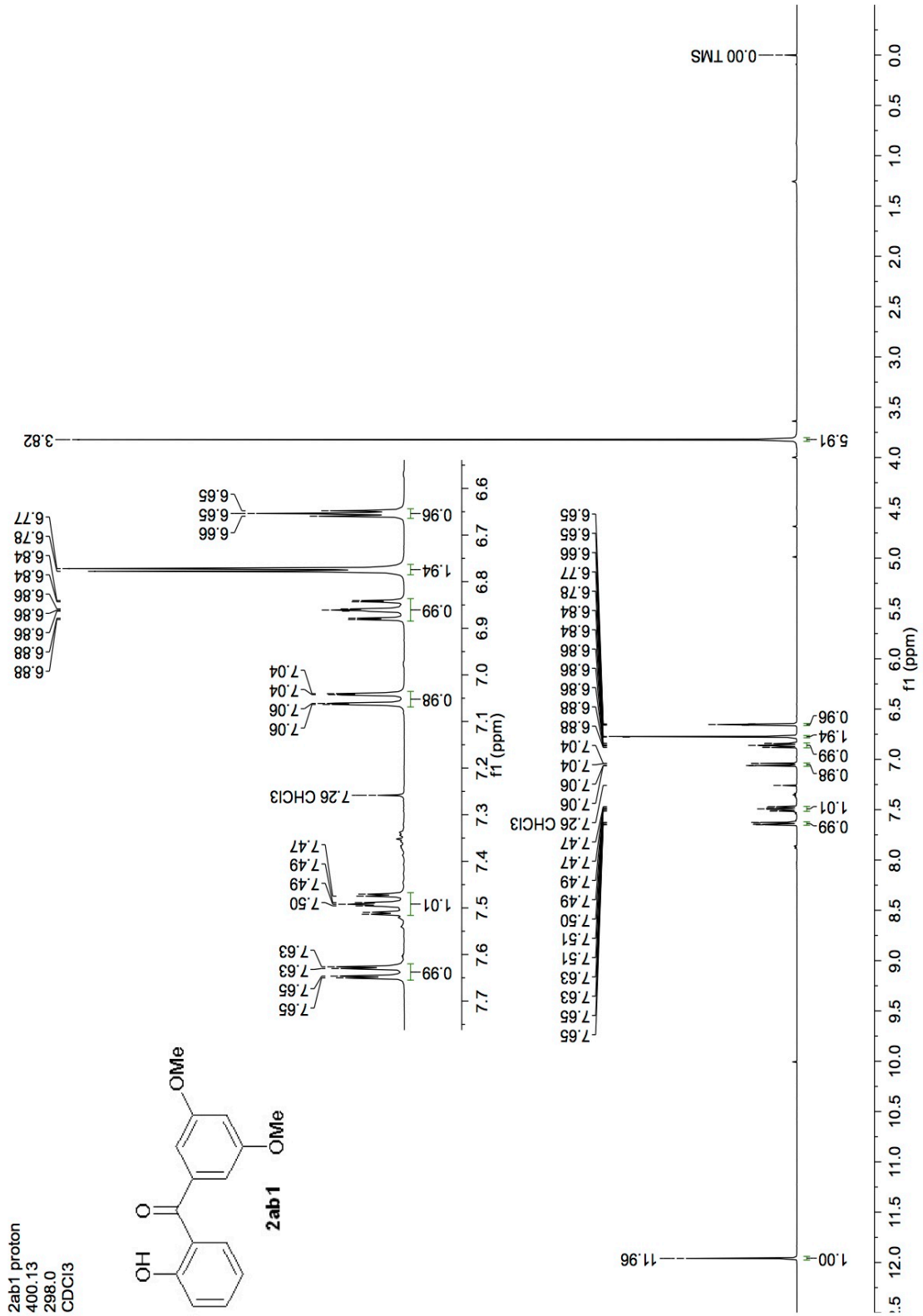
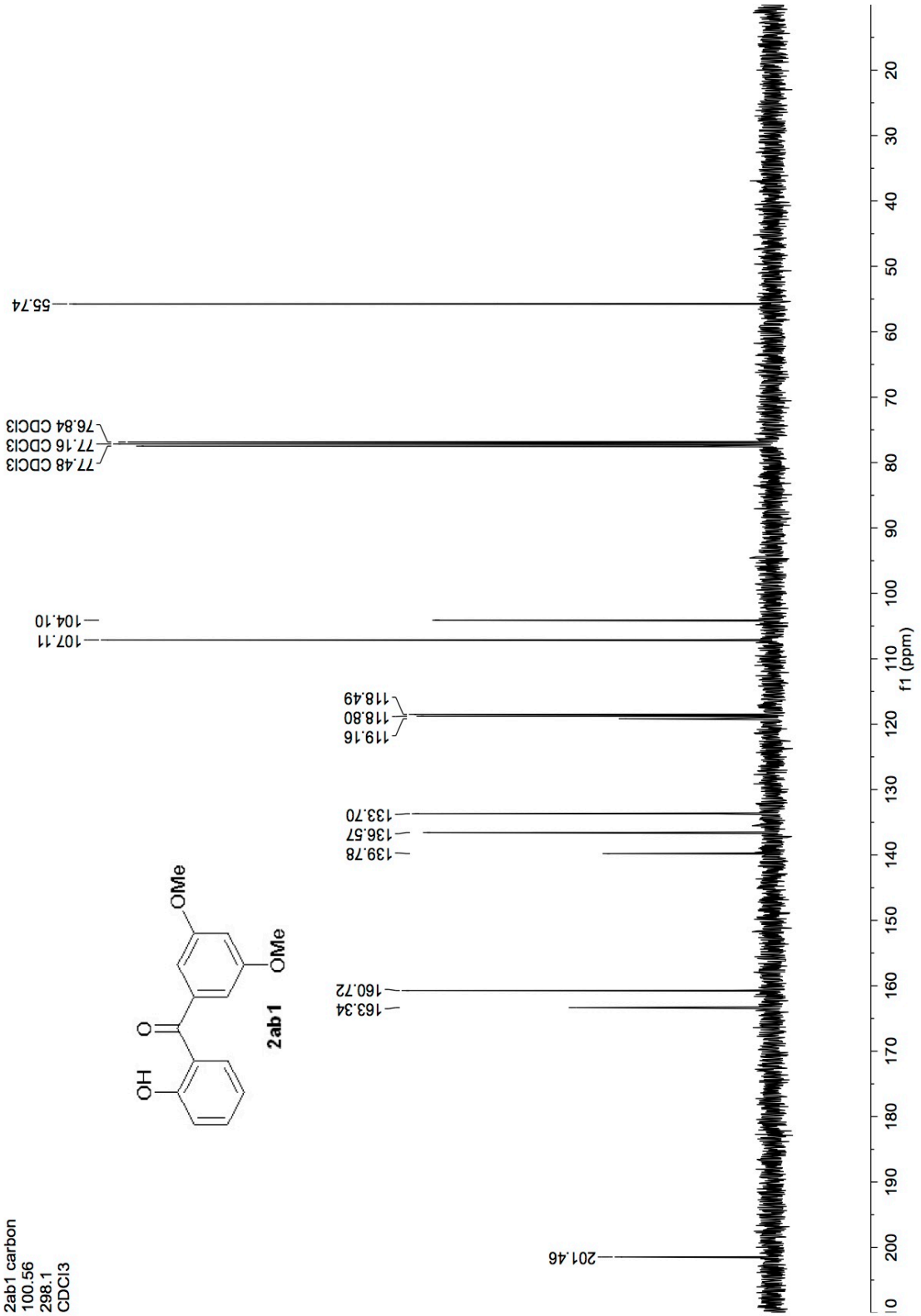
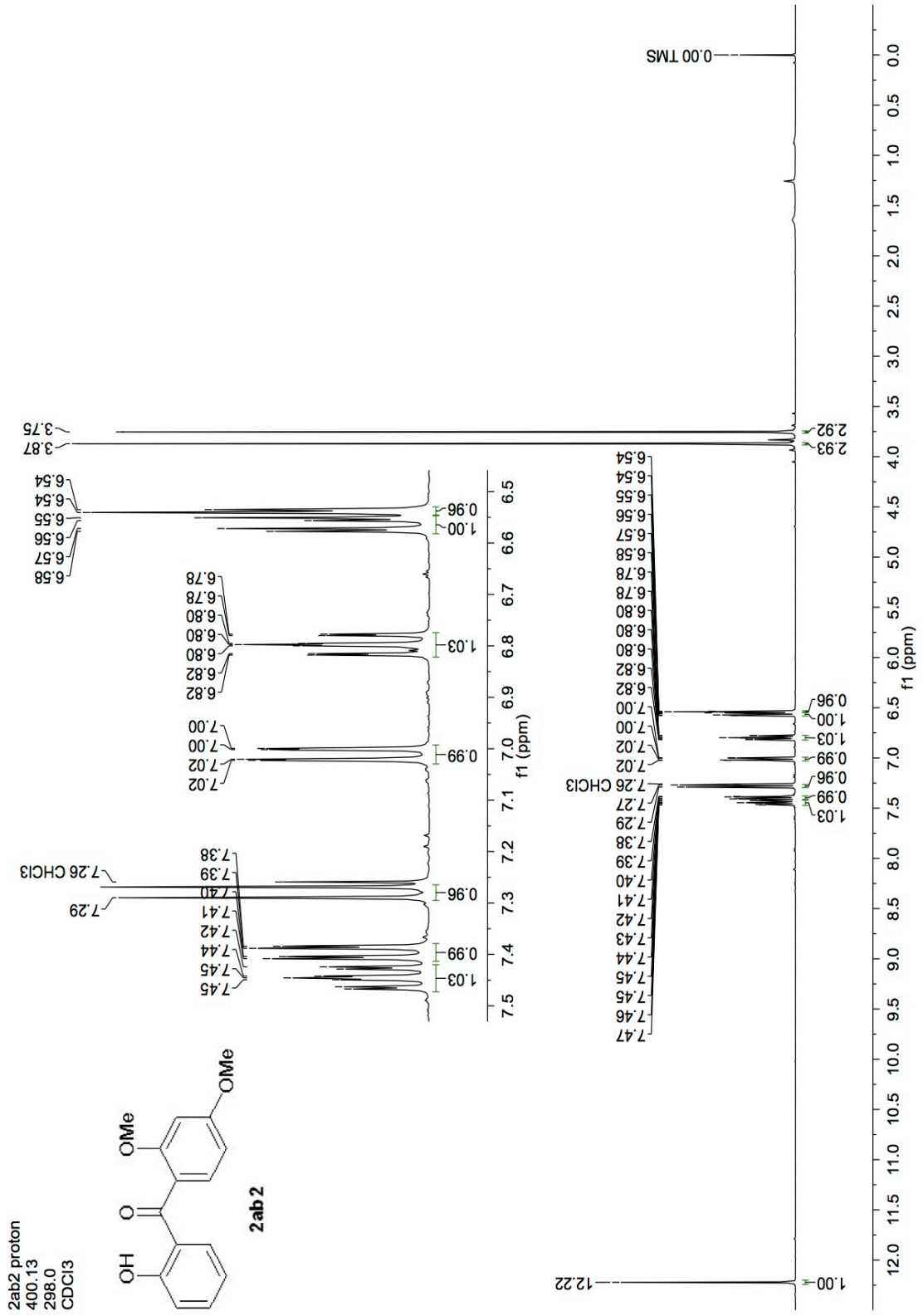
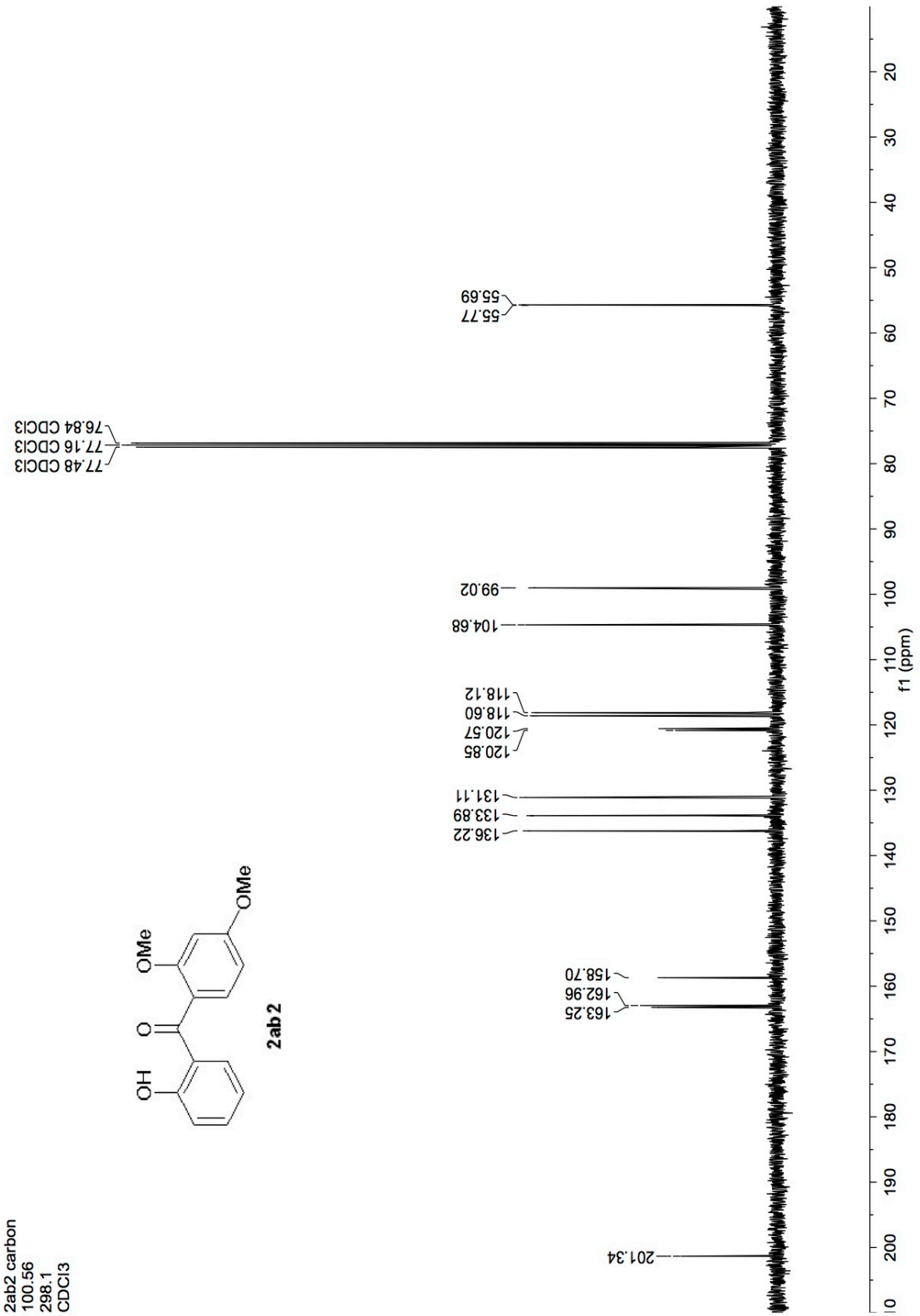
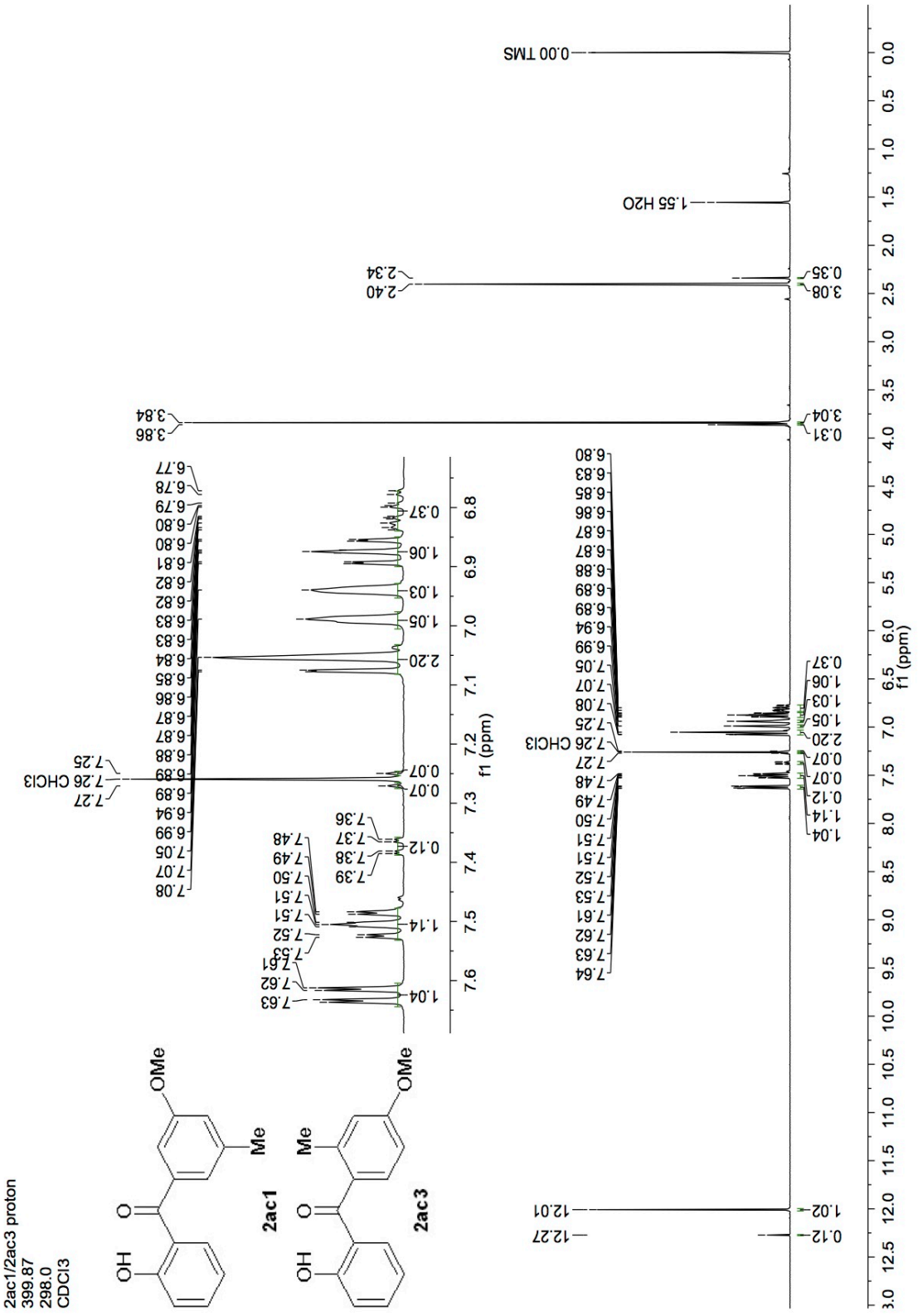
118.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.41
f1 (ppm)


2ab1 proton
400.13
298.0
CDCl3
OH
O
OMe
OMe
2ab1
0.00 TMS
7.26 CHCl3
f1 (ppm)

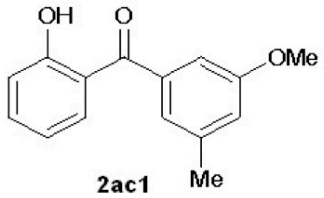

2ab1 carbon
100.56
298.1
CDCl3
OMe
OMe
O
OH
2ab1
201.46
163.34
160.72
139.78
136.57
133.70
119.16
118.80
118.49
107.11
104.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.74
f1 (ppm)


2ab2 proton
400.13
298.0
CDCl3
OH
O
OMe
OMe
2ab2
12.22
7.47
7.46
7.45
7.45
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.29
7.27
7.26 CHCl3
7.02
7.02
7.00
7.00
6.82
6.82
6.80
6.80
6.80
6.80
6.78
6.78
6.58
6.57
6.56
6.55
6.54
6.54
3.87
3.75
2.93
2.92
0.00 TMS
1.00
0.96
1.03
0.99
0.96
1.00
1.03
0.99
0.96
1.00
f1 (ppm)

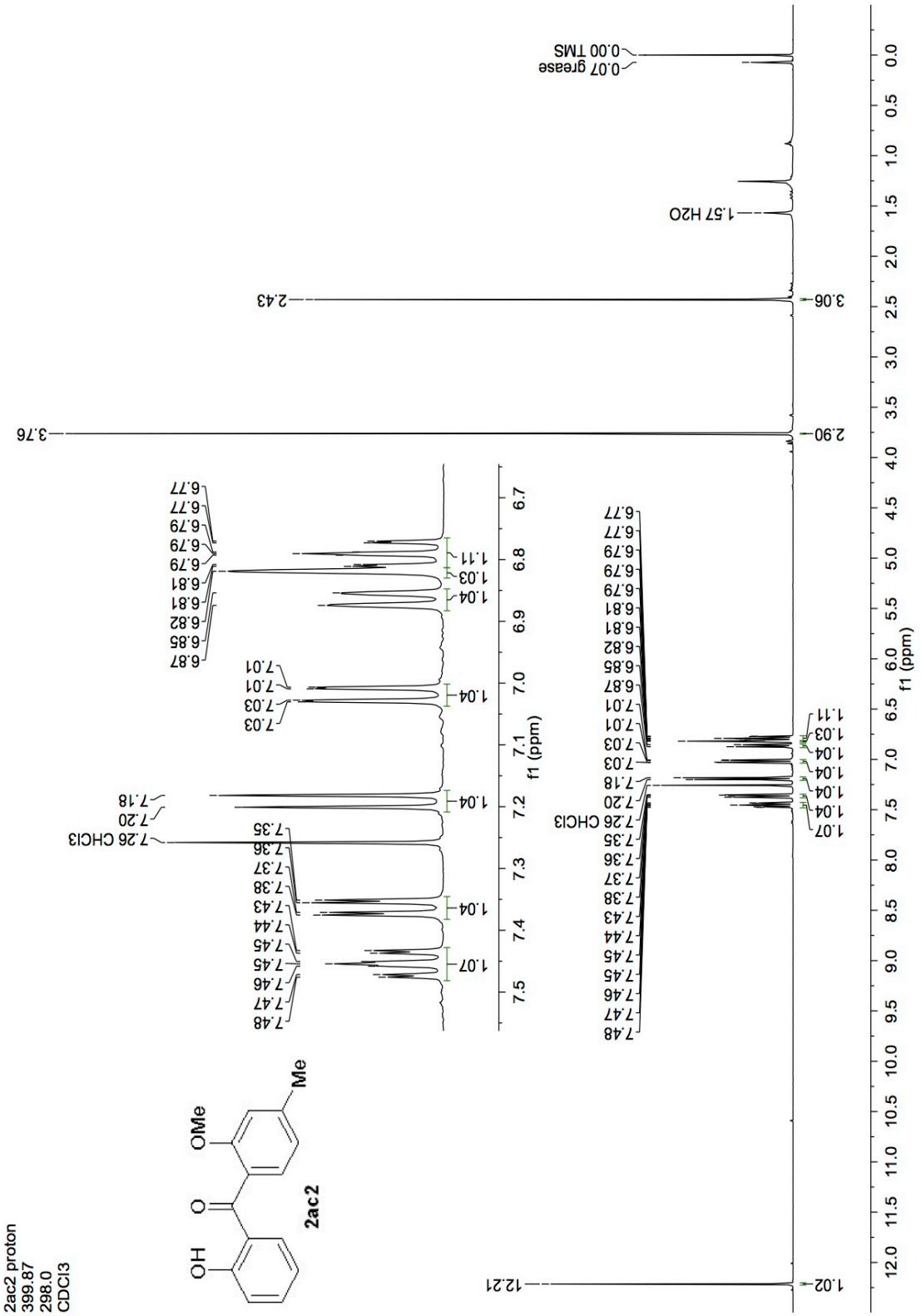

2ab2 carbon
100.56
298.1
CDCl3
2ab 2
OMe
OMe
O
OH
201.34
163.25
162.96
158.70
136.22
133.89
131.11
120.85
120.57
118.60
118.12
104.68
99.02
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.77
55.69
f1 (ppm)

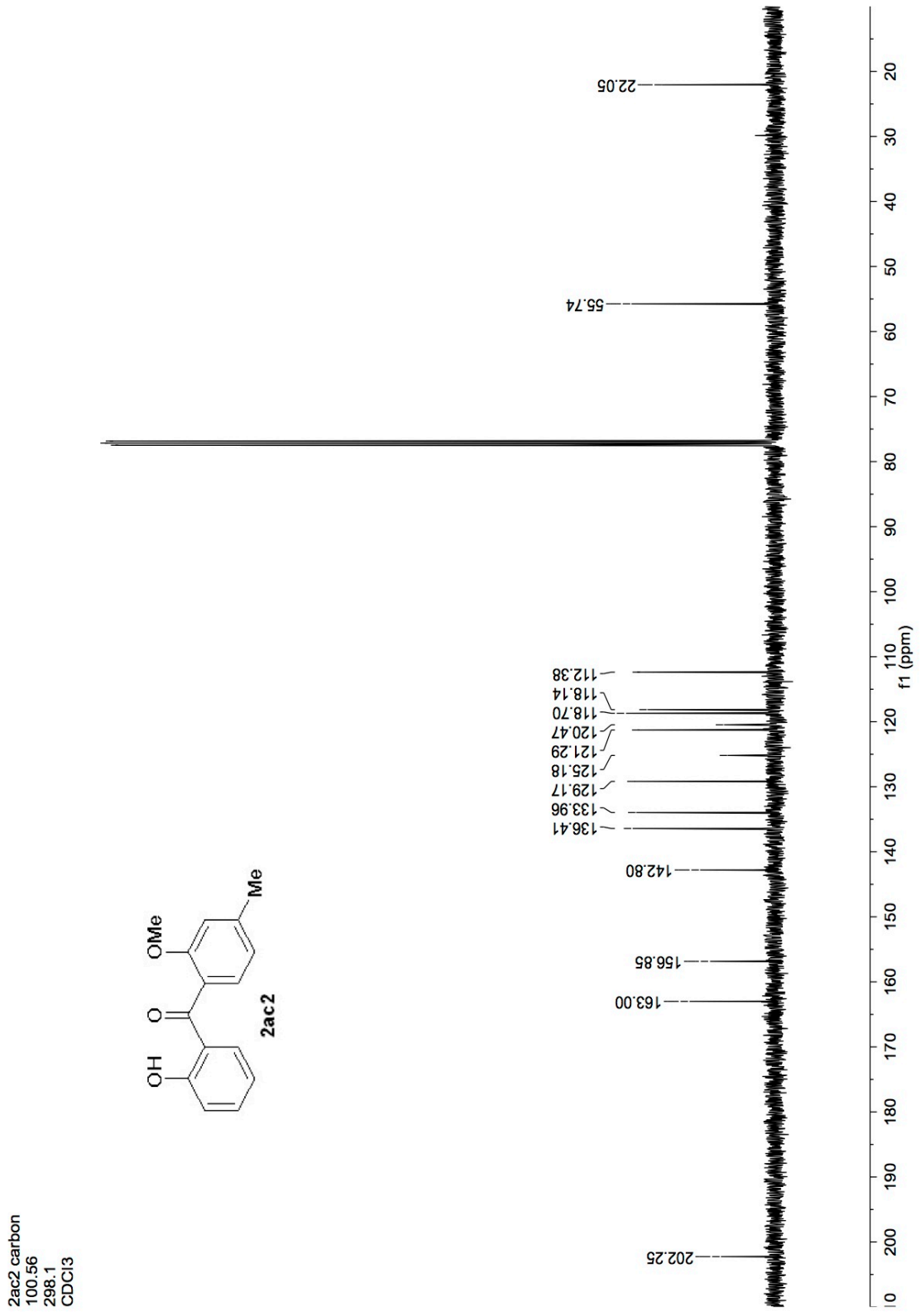

2ac1/2ac3 proton
399.87
298.0
CDCl3
OMe
Me
O
OH
2ac1
2ac3
f1 (ppm)
0.00 TMS
1.55 H2O
7.26 CHCl3

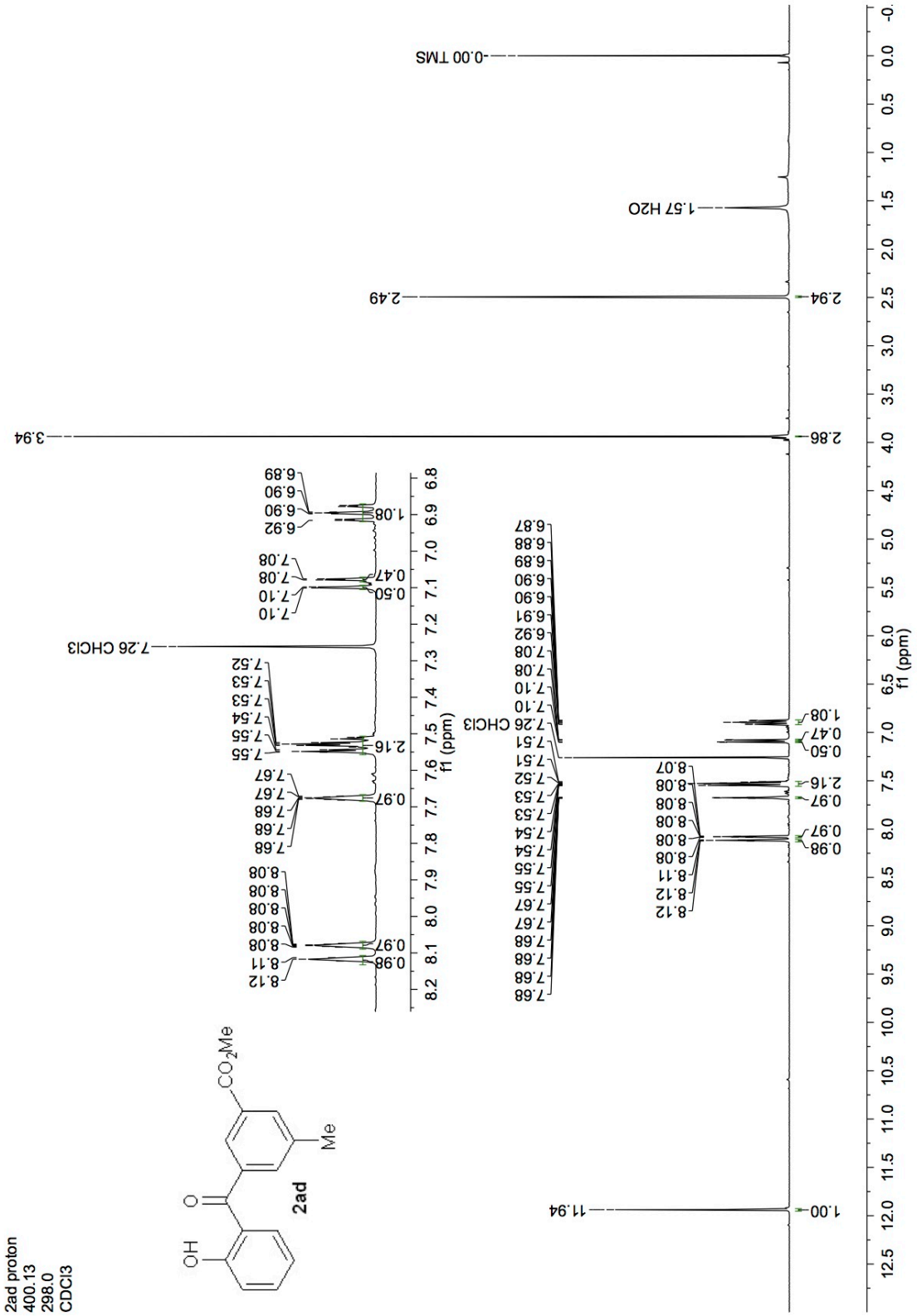
2ac1/2ac3 carbon
100.56
298.1
CDCl3

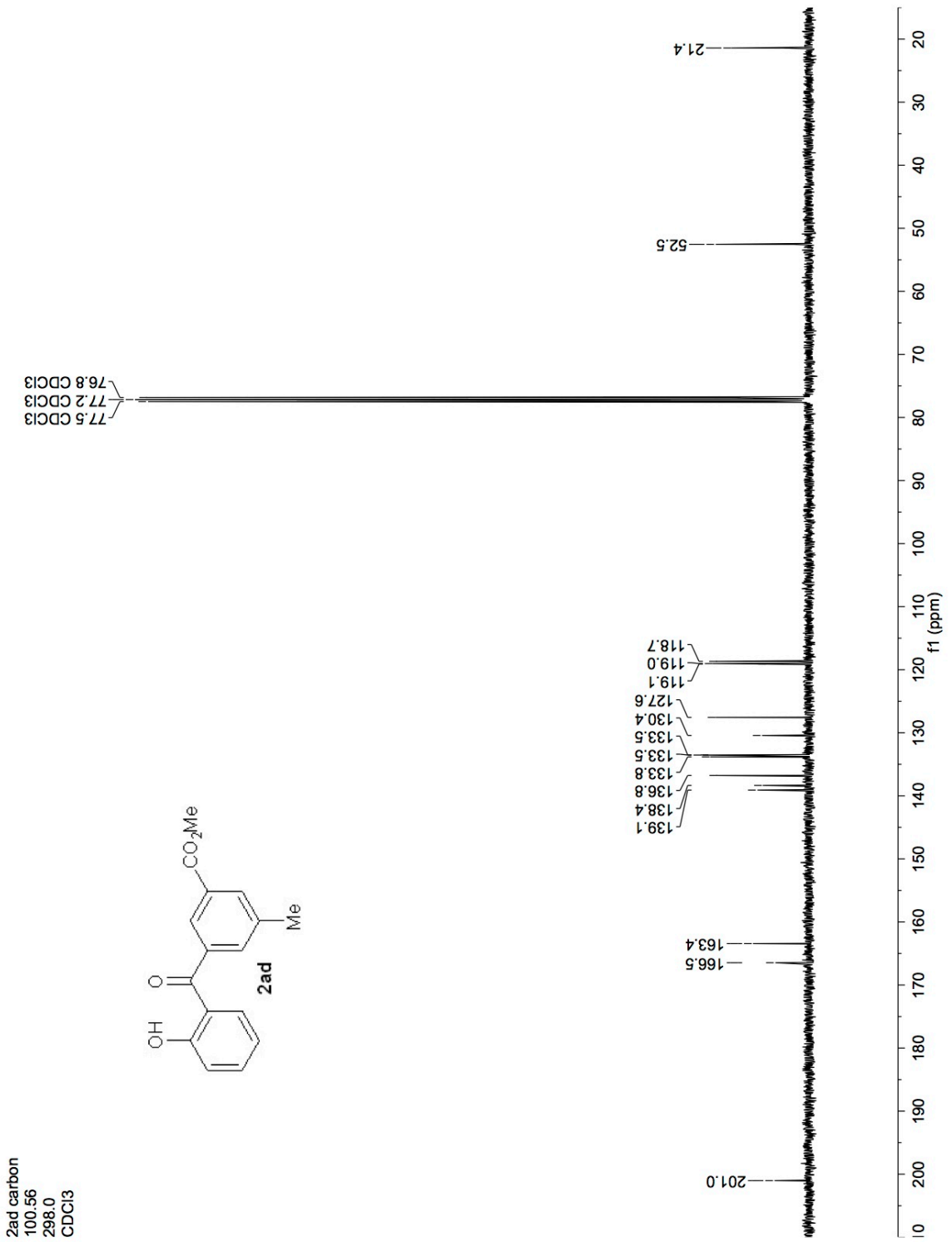


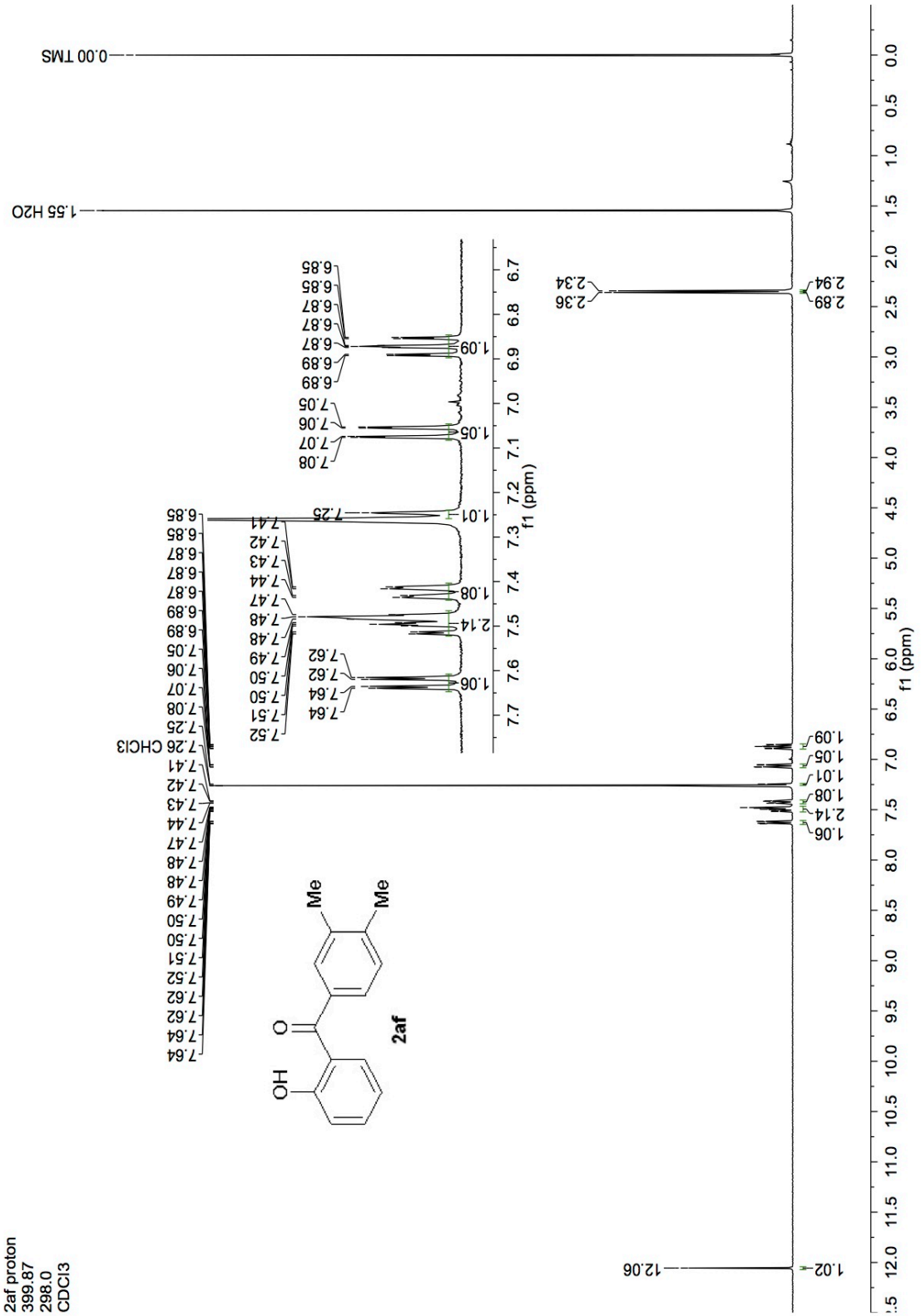
2ac1

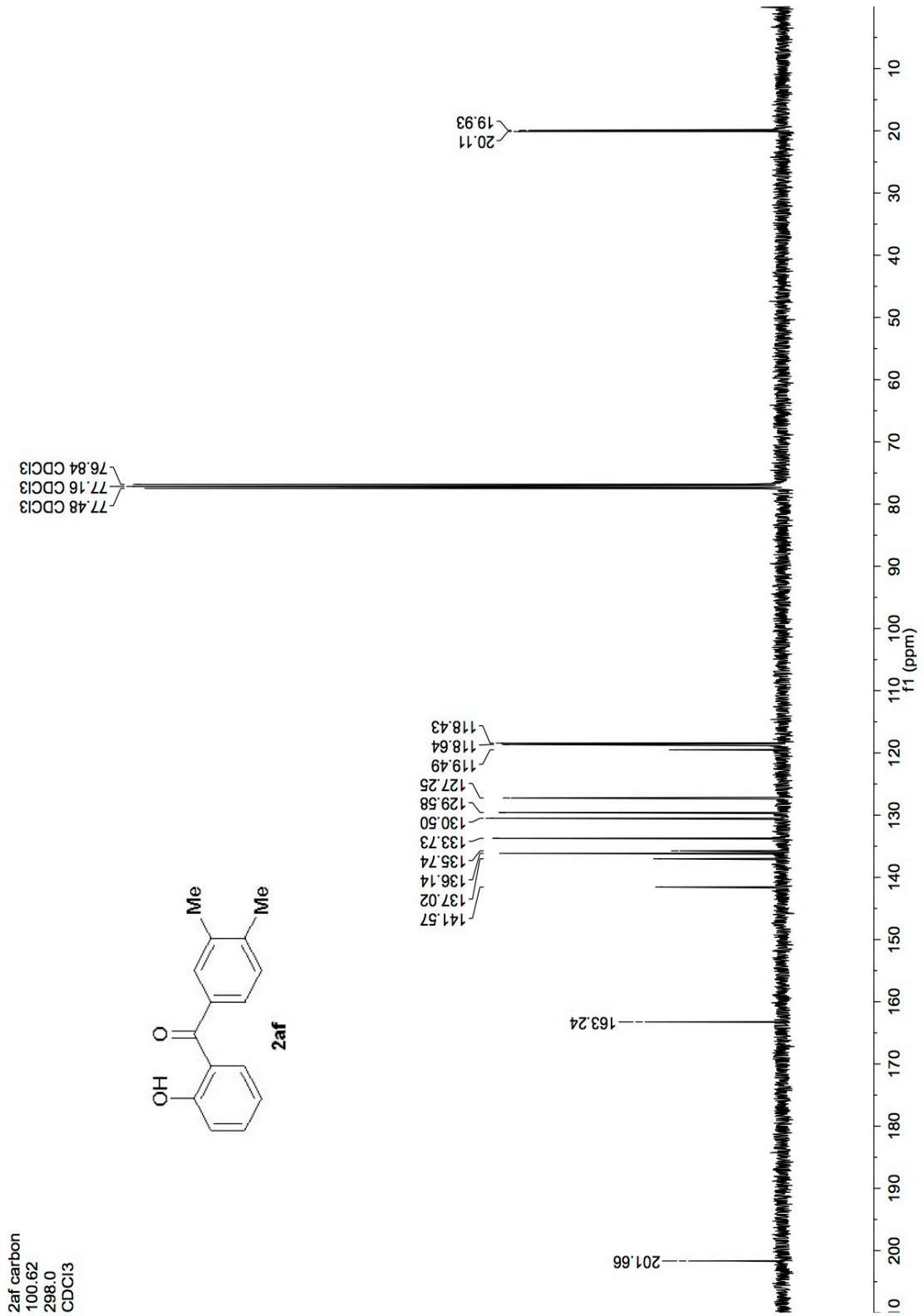

2ac2 proton
399.87
298.0
CDCl3
OH
O
OMe
Me
2ac2
12.21
7.76
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.38
7.37
7.36
7.35
7.26 CHCl3
7.20
7.18
7.03
7.01
7.01
6.87
6.85
6.82
6.81
6.81
6.79
6.79
6.79
6.77
6.77
2.43
1.57 H2O
0.07 grease
0.00 TMS
1.02
3.06
2.90
1.07
1.04
1.04
1.04
1.04
1.03
1.11
f1 (ppm)

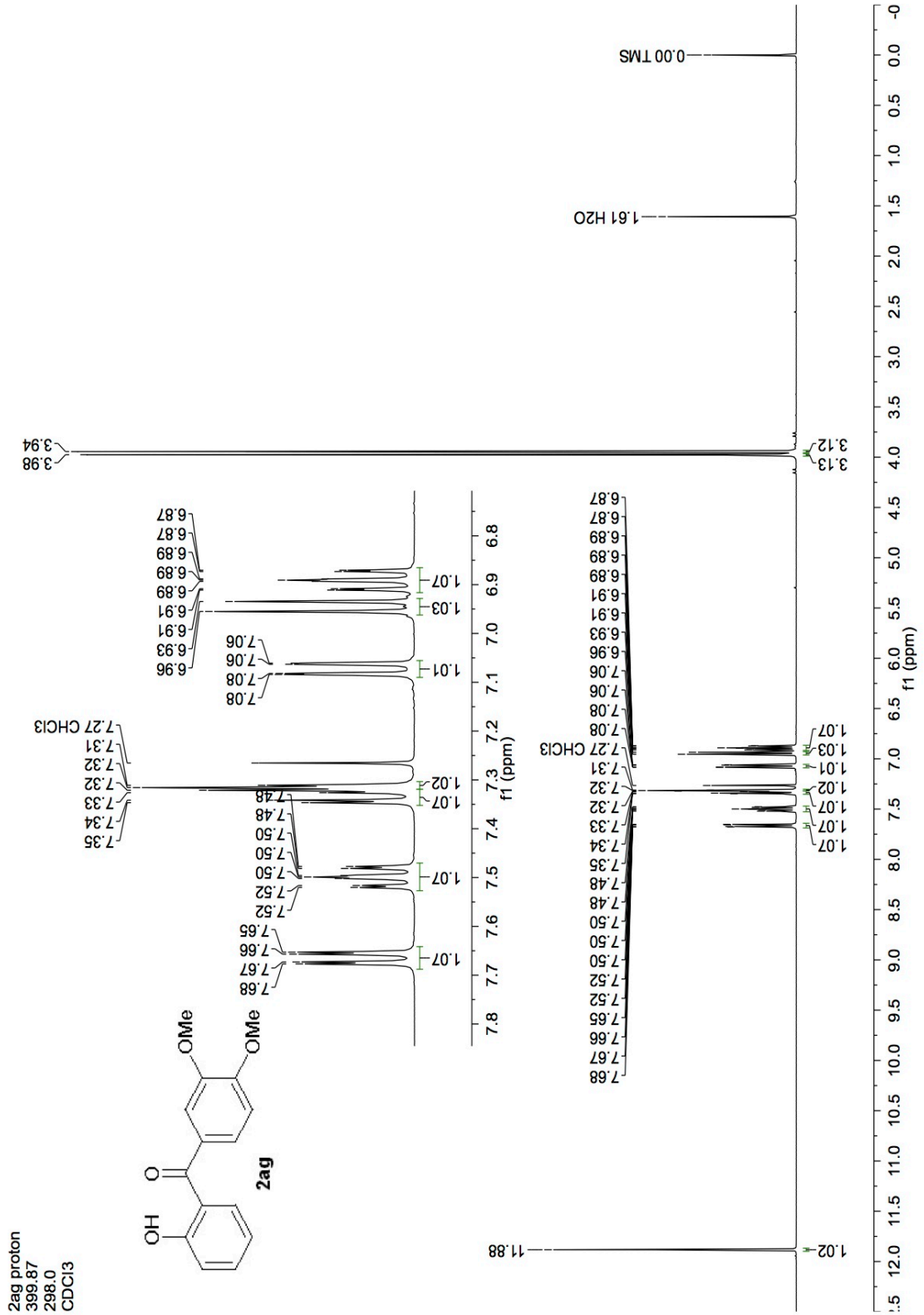

2ac2 carbon
100.56
298.1
CDCl3
OH
O
OMe
Me
2ac2
202.25
163.00
156.85
142.80
136.41
133.96
129.17
125.18
121.29
120.47
118.70
118.14
112.38
55.74
22.05
f1 (ppm)

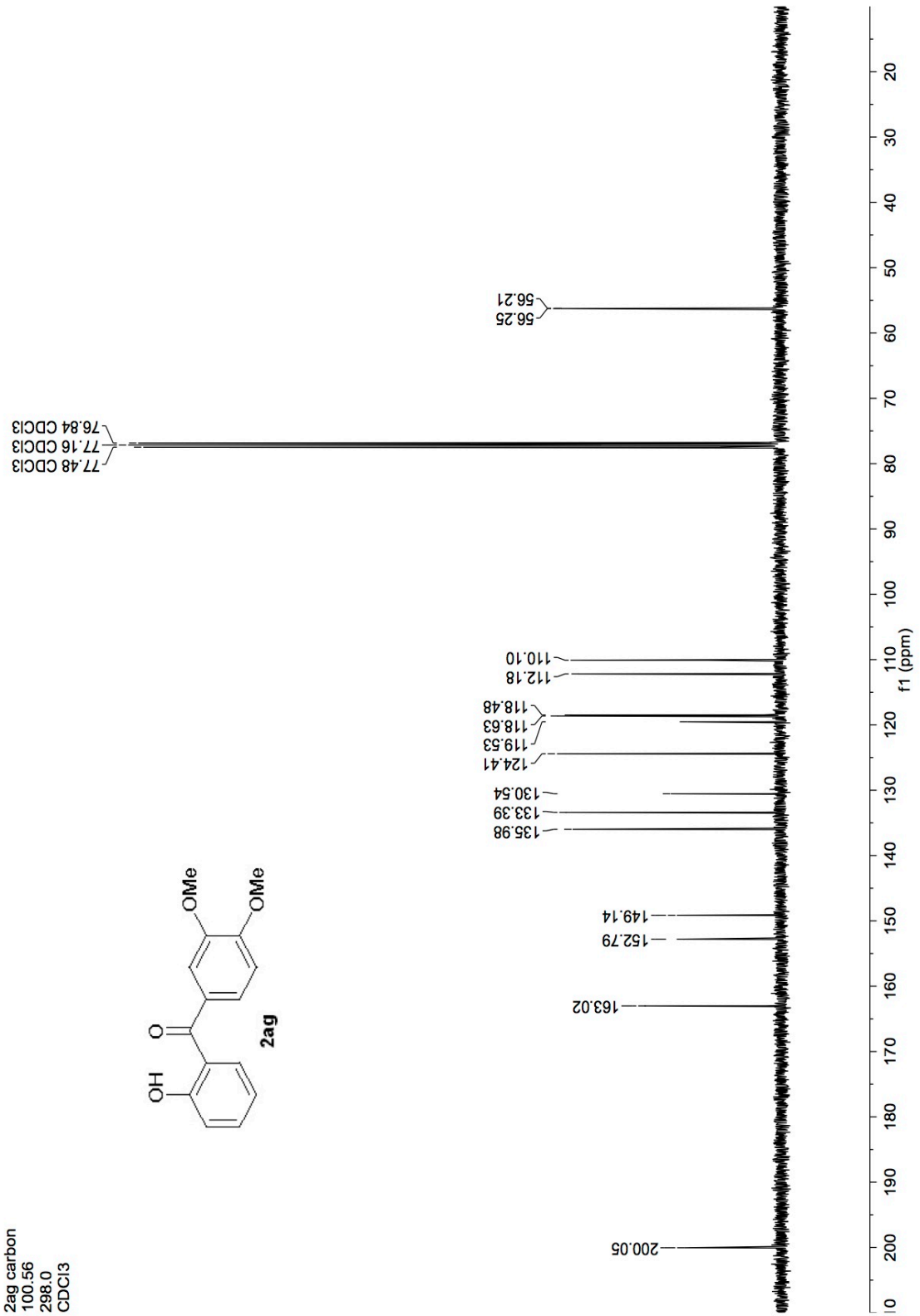

2ad proton
400.13
298.0
CDCl3
2ad
OH
O
CO2Me
Me
0.00 TMS
1.57 H2O
2.49
3.94
7.26 CHCl3
11.94
f1 (ppm)

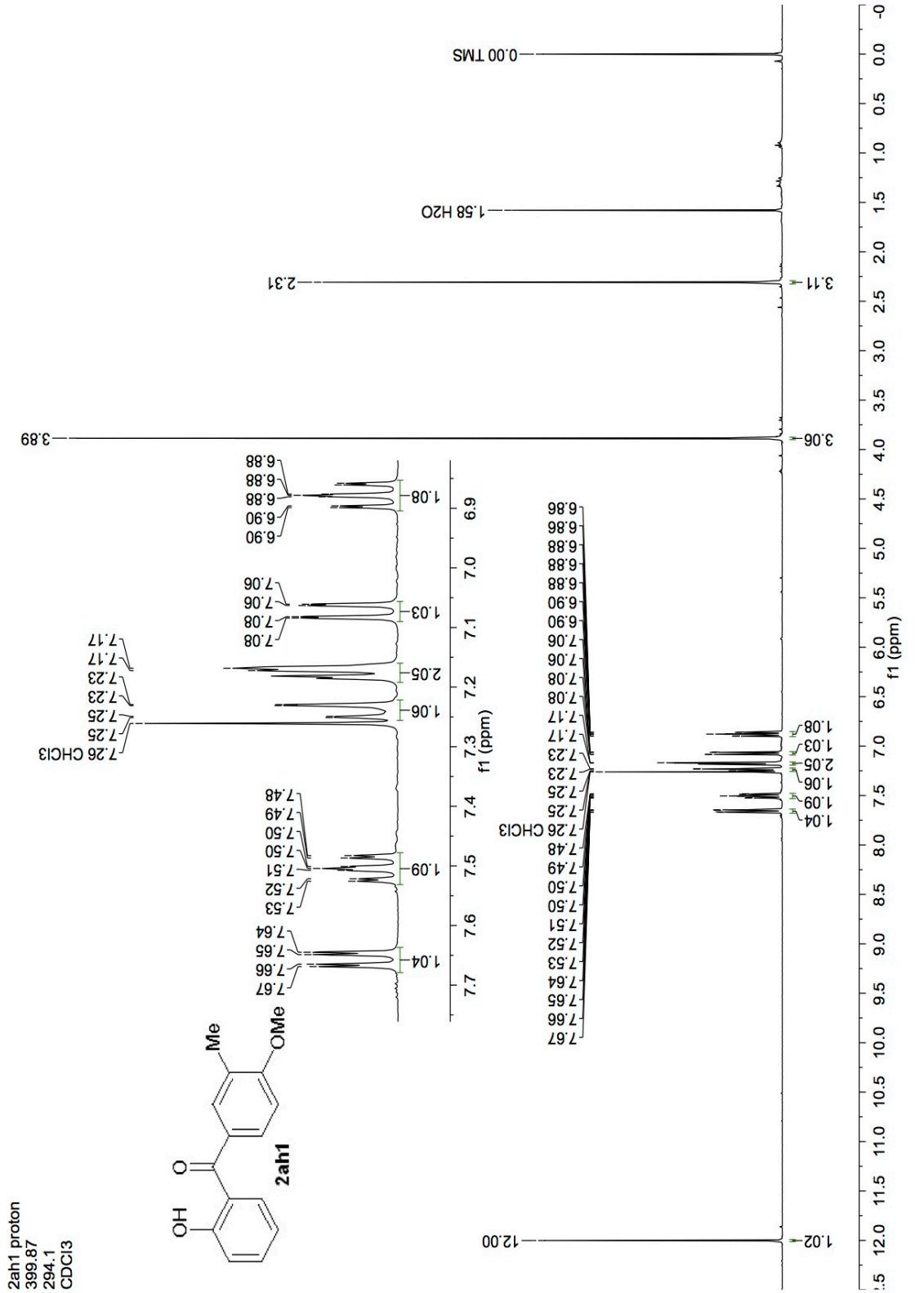

2ad carbon
100.56
298.0
CDCl3
2ad
CO2Me
Me
OH
O
201.0
166.5
163.4
139.1
138.4
136.8
133.8
133.5
133.5
130.4
127.6
119.1
119.0
118.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
52.5
21.4
f1 (ppm)


2af proton
399.87
298.0
CDCl3
0.00 TMS
1.55 H2O
7.26 CHCl3
Me
Me
O
OH
2af
f1 (ppm)

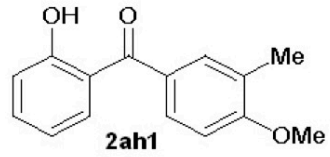

2af carbon
100.62
298.0
CDCl3
Me
Me
O
OH
2af
201.66
163.24
141.57
137.02
136.14
135.74
133.73
130.50
129.58
127.25
119.49
118.64
118.43
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.11
19.93
f1 (ppm)


2ag proton
399.87
298.0
CDCl3
OH
O
OMe
OMe
2ag
0.00 TMS
1.61 H2O
CHCl3
f1 (ppm)

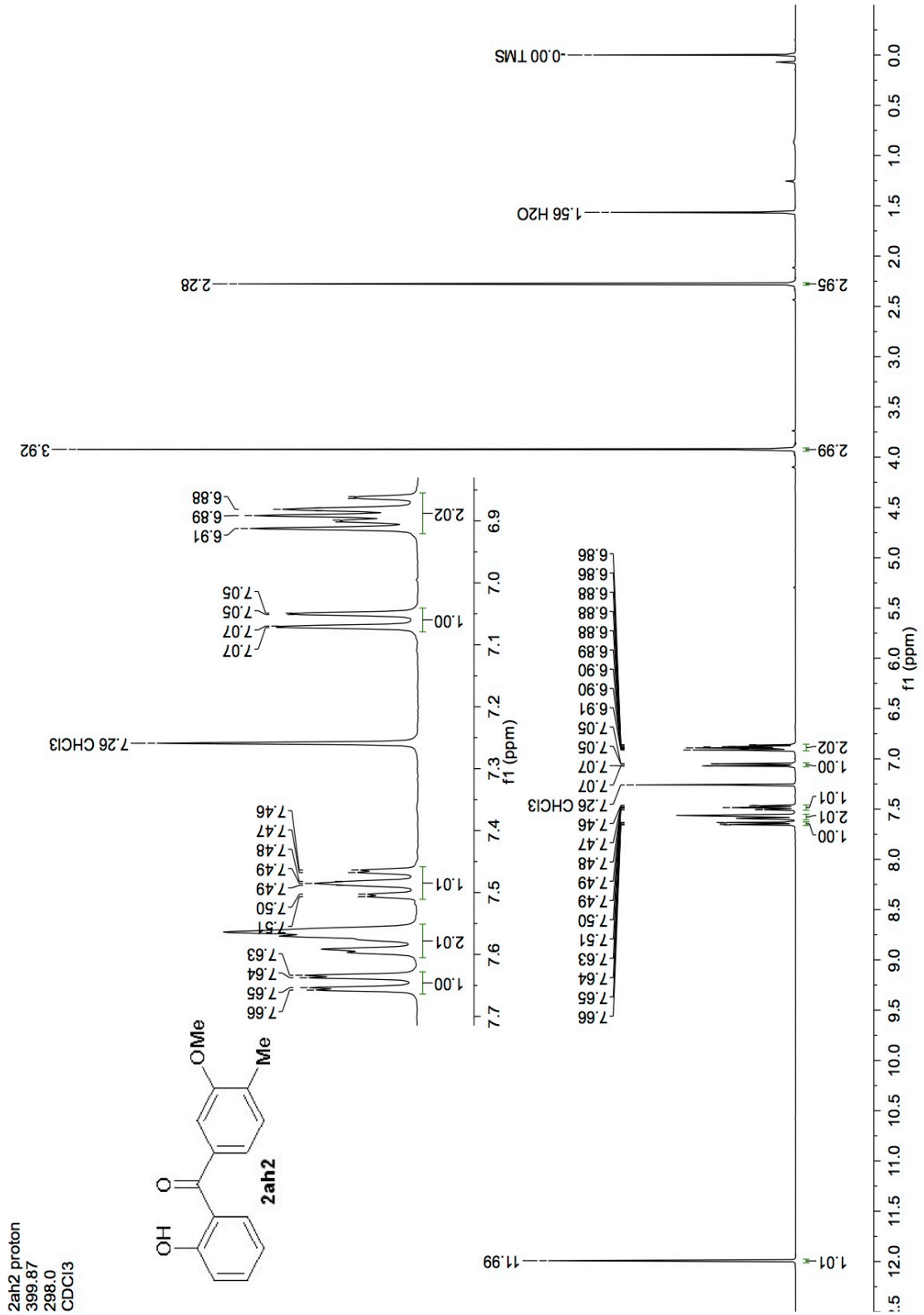

2ag carbon
100.56
298.0
CDCl3
OMe
OMe
O
OH
2ag
200.05
163.02
152.79
149.14
135.98
133.39
130.54
124.41
119.53
118.63
118.48
112.18
110.10
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.25
56.21
f1 (ppm)

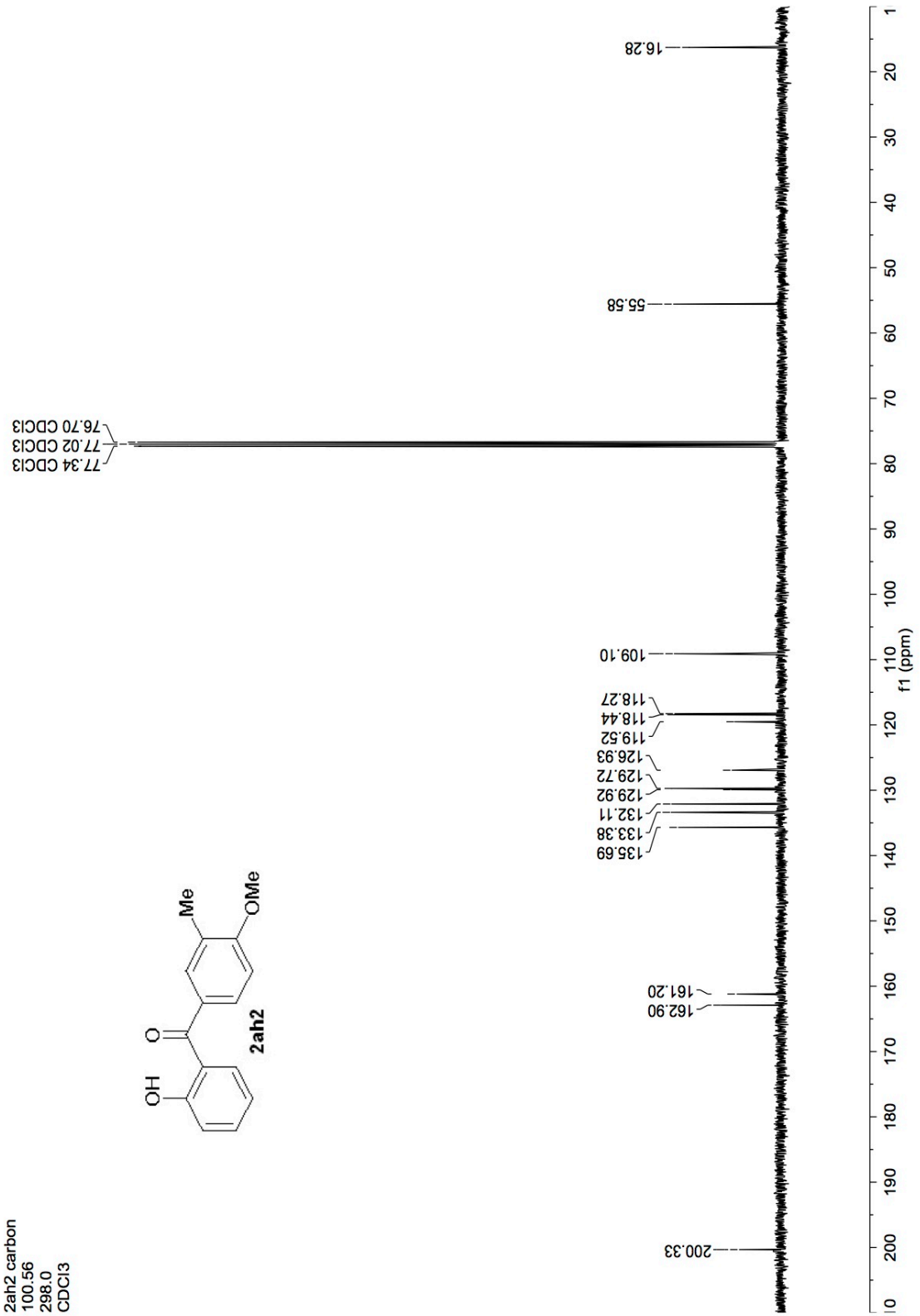

2ah1 proton
399.87
294.1
CDCl3
2ah1
OH
O
Me
OMe
0.00 TMS
1.58 H2O
2.31
3.89
7.26 CHCl3
f1 (ppm)

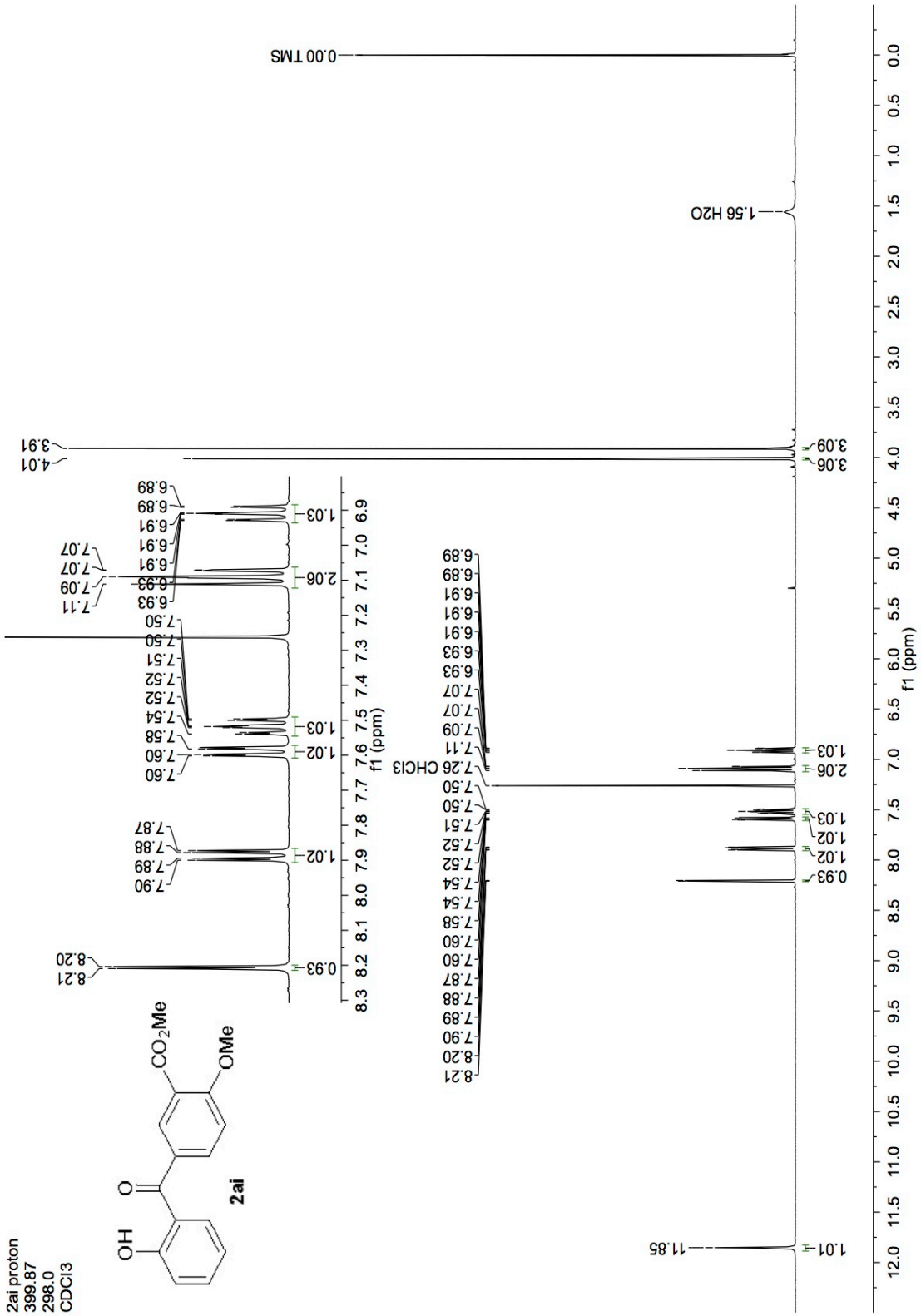
2ah1 carbon
100.56
294.7
CDCl3

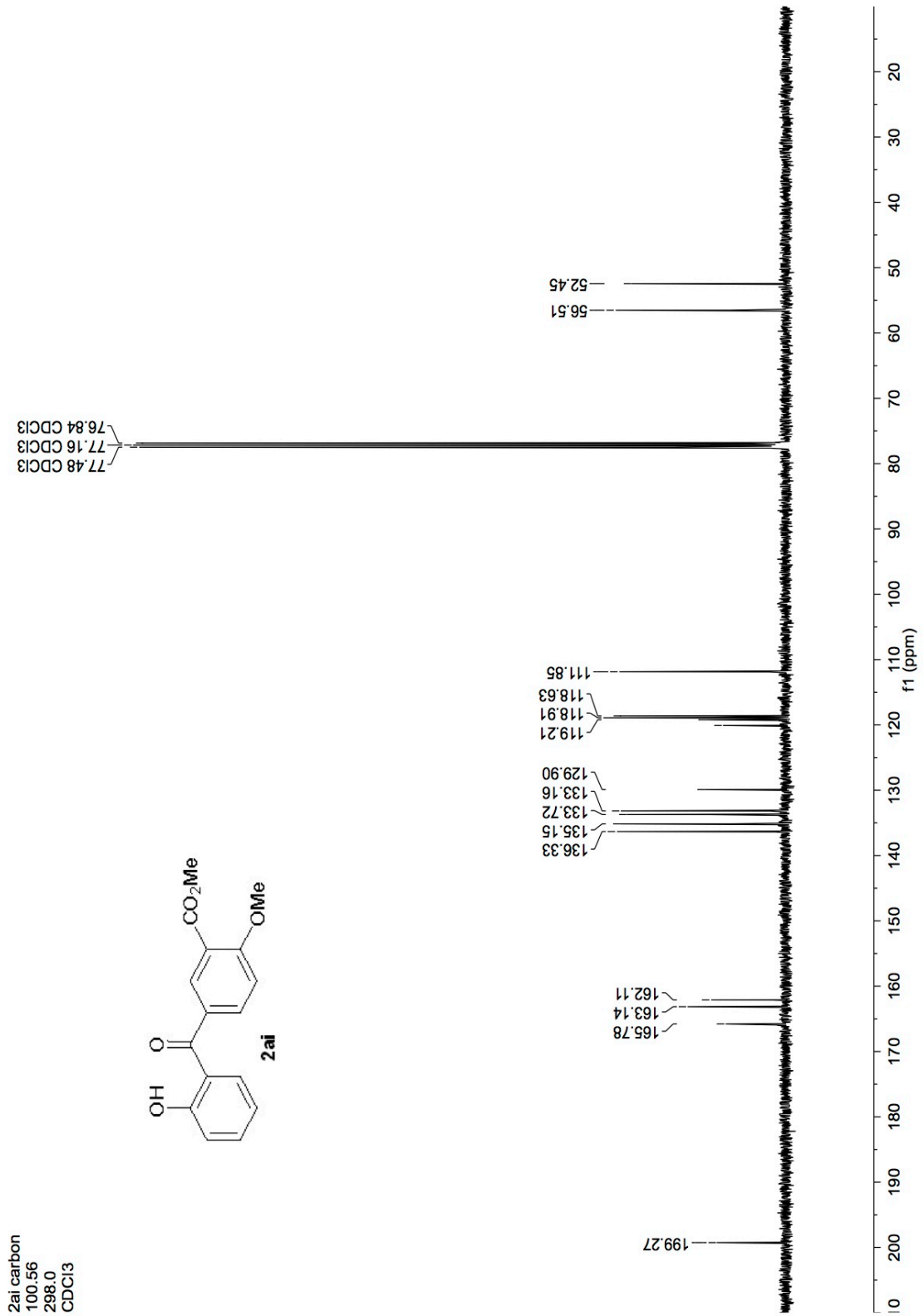


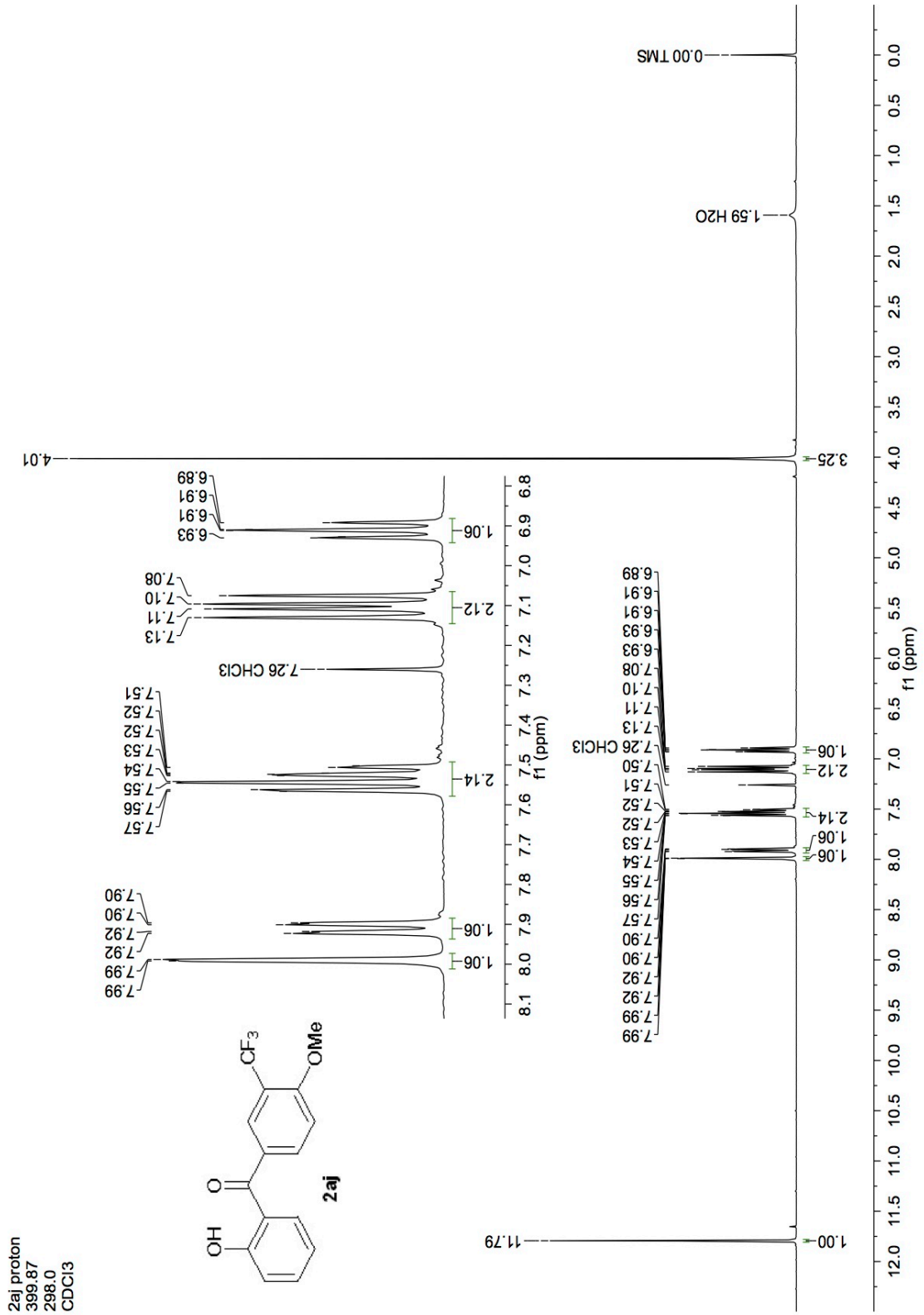
2ah1

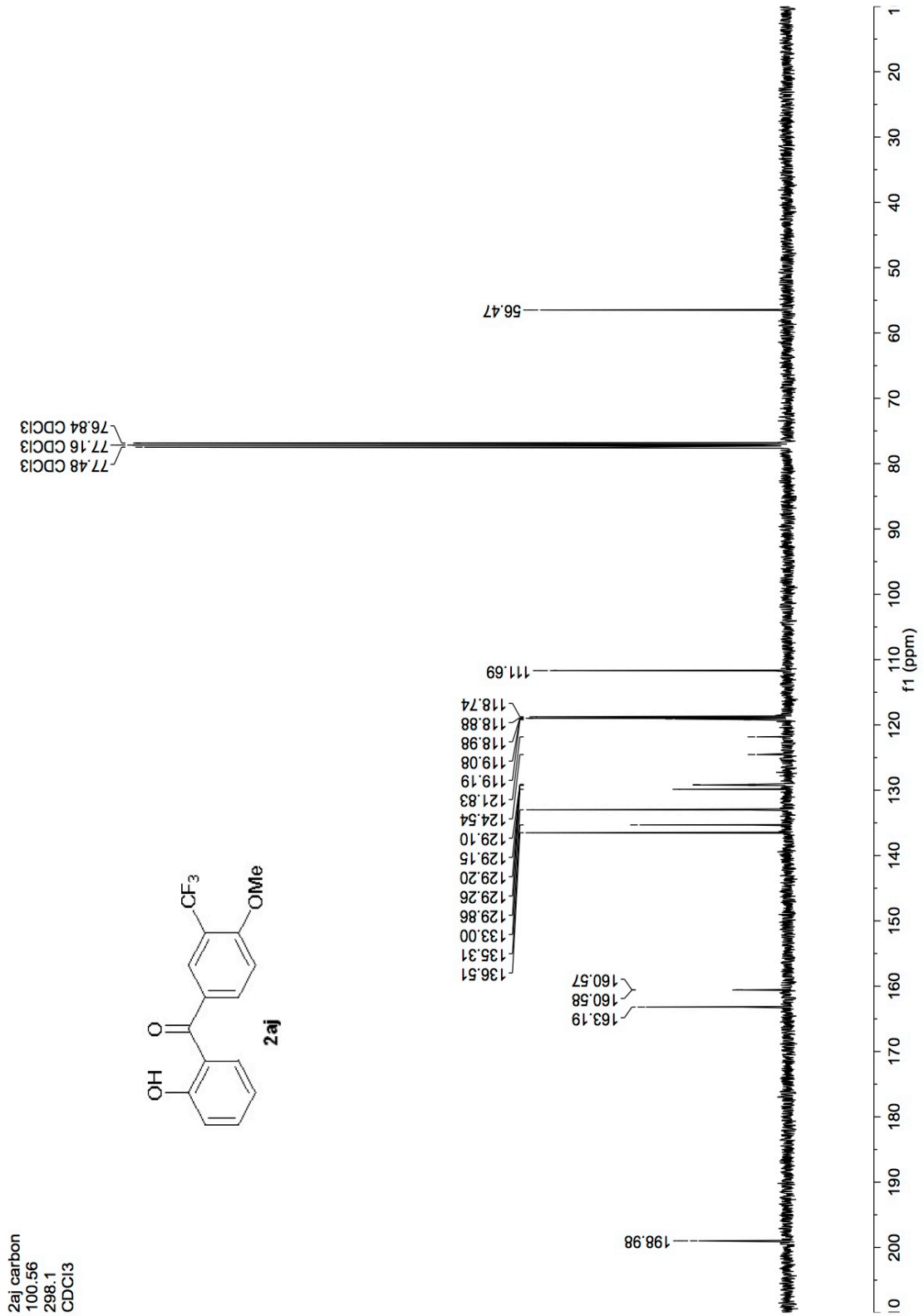

2ah2 proton
399.87
298.0
CDCl3
2ah2
OMe
Me
O
OH
11.99
7.66
7.65
7.64
7.63
7.51
7.50
7.49
7.49
7.48
7.47
7.46
7.26 CHCl3
7.07
7.07
7.05
7.05
6.91
6.89
6.88
3.92
2.28
1.56 H2O
0.00 TMS
1.01
2.01
1.00
2.02
1.00
2.99
2.95
f1 (ppm)

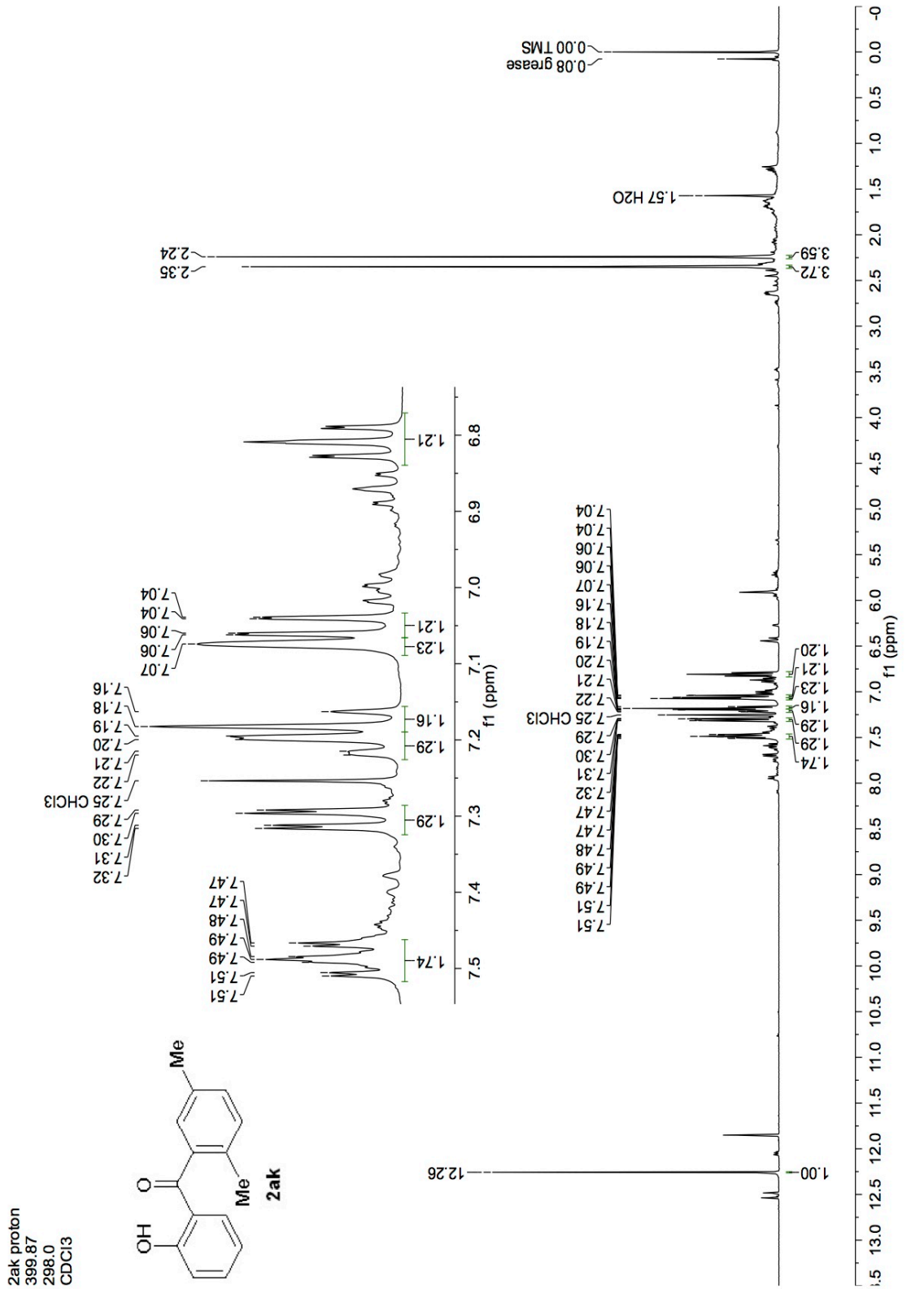

2ah2 carbon
100.56
298.0
CDCl3
Me
OMe
O
OH
2ah2
200.33
161.20
162.90
135.69
133.38
132.11
129.92
129.72
126.93
119.52
118.44
118.27
109.10
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
55.58
16.28
f1 (ppm)

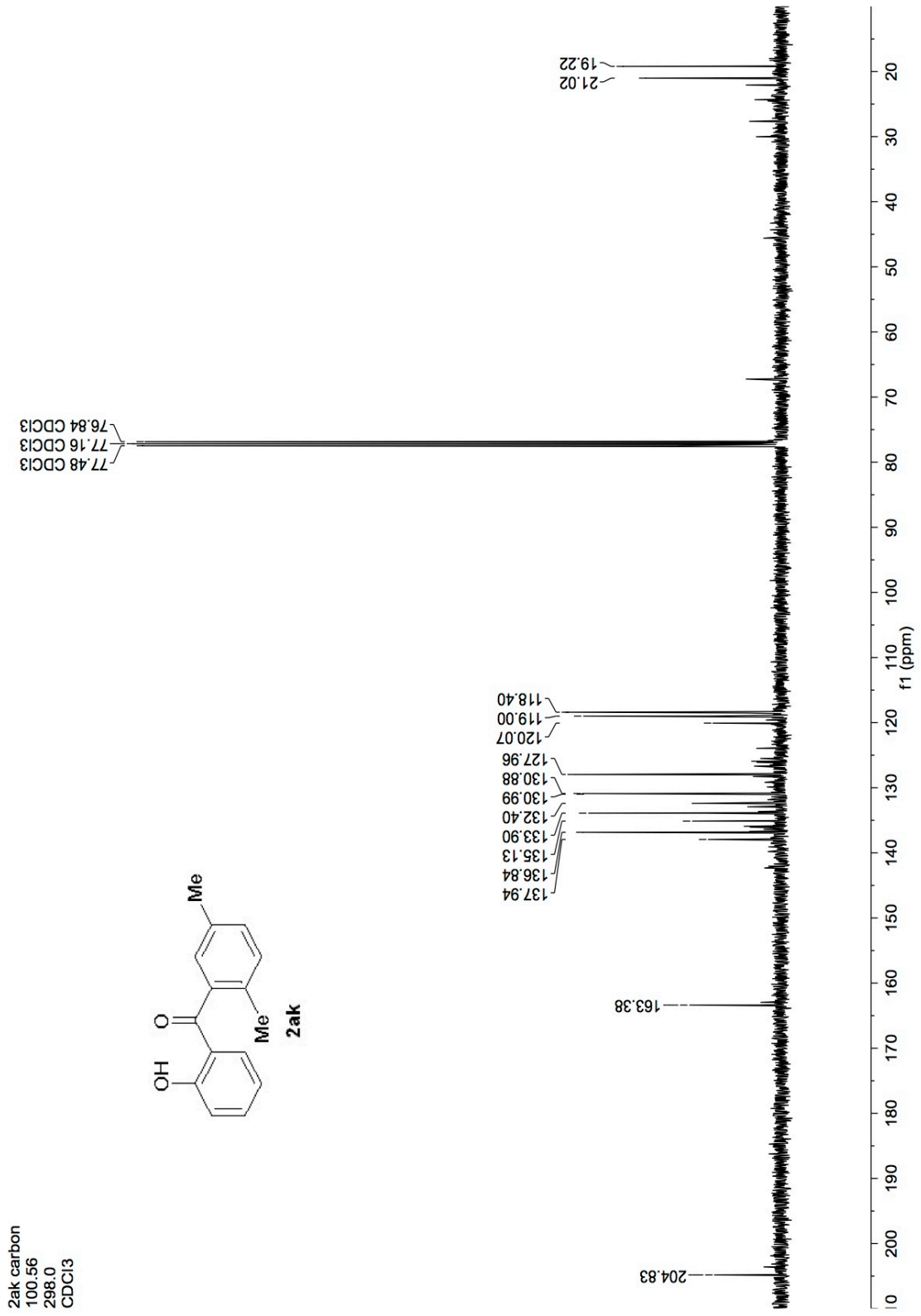

2ai proton
399.87
298.0
CDCl3
2ai
CO2Me
OMe
OH
O
0.00 TMS
1.56 H2O
7.26 CHCl3
f1 (ppm)

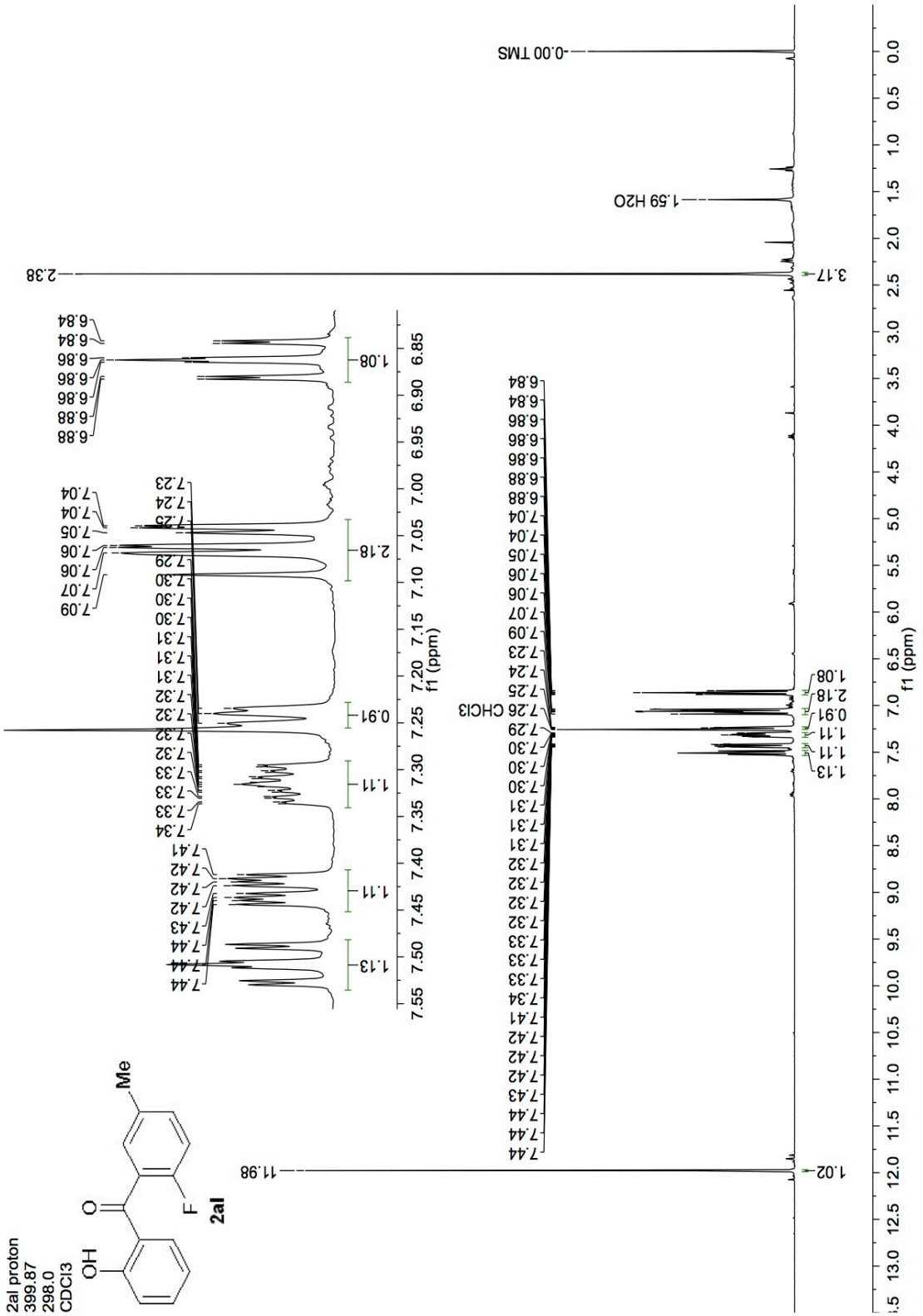

2ai carbon
100.56
298.0
CDCl3
199.27
165.78
163.14
162.11
136.33
135.15
133.72
133.16
129.90
119.21
118.91
118.63
111.85
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.51
52.45
OH
O
OMe
CO2Me
2ai
f1 (ppm)

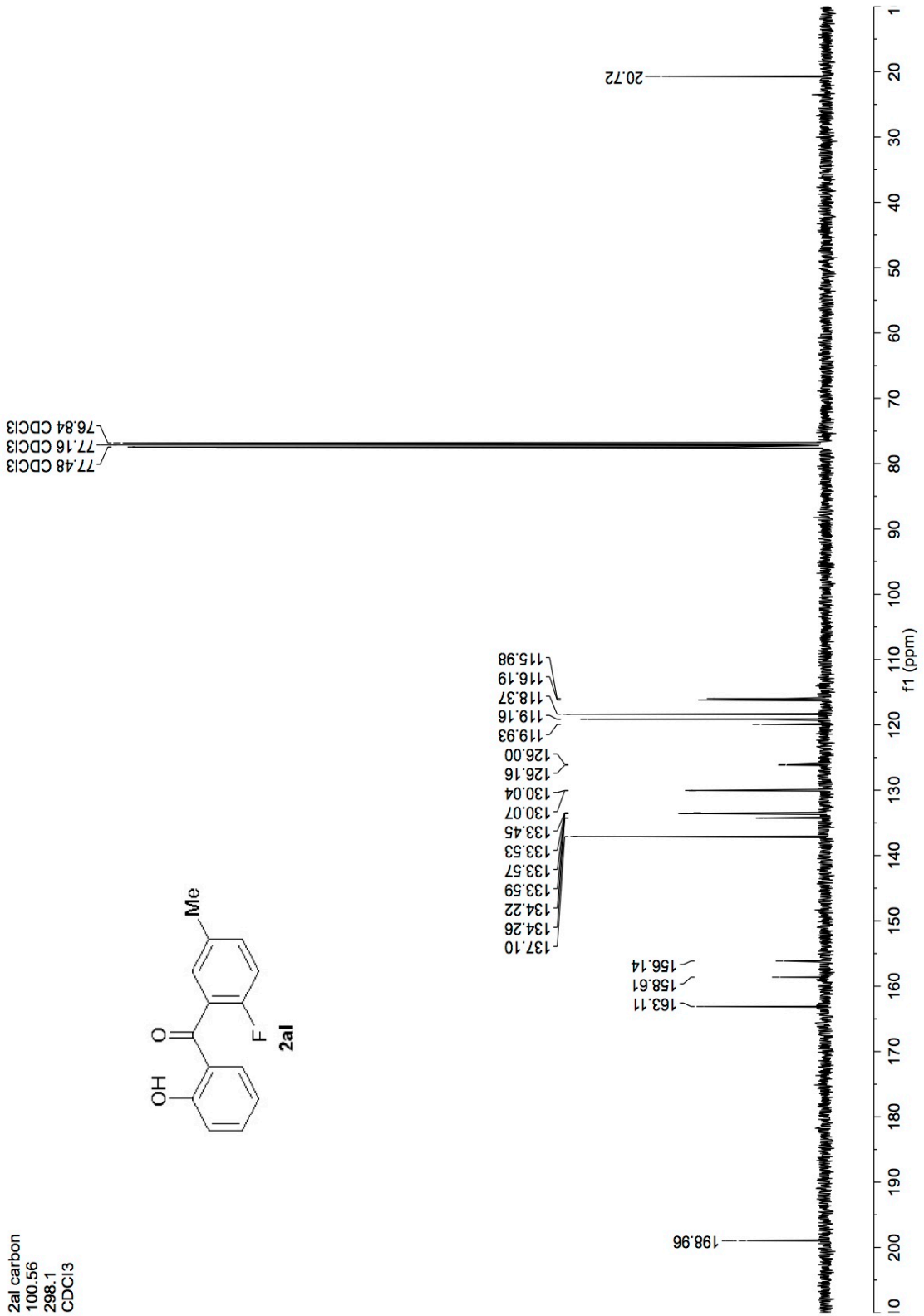

2aj proton
399.87
298.0
CDCl3
OH
O
CF3
OMe
2aj
0.00 TMS
1.59 H2O
7.26 CHCl3
f1 (ppm)


2aj carbon
100.56
298.1
CDCl3
2aj
CF3
OMe
O
OH
198.98
163.19
160.58
160.57
136.51
135.31
133.00
129.86
129.26
129.20
129.15
129.10
124.54
121.83
119.19
119.08
118.98
118.88
118.74
111.69
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.47
f1 (ppm)

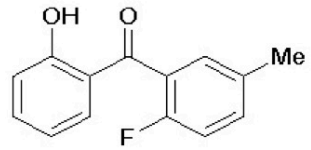

2ak proton
399.87
298.0
CDCl3
OH
O
Me
Me
2ak
12.26
7.51
7.49
7.49
7.48
7.47
7.47
7.32
7.31
7.30
7.29
7.25 CHCl3
7.22
7.21
7.20
7.19
7.18
7.16
7.07
7.06
7.06
7.04
7.04
2.35
2.24
1.57 H2O
0.08 grease
0.00 TMS
3.72
3.59
1.74
1.29
1.29
1.16
1.23
1.21
1.20
1.00
f1 (ppm)


2ak carbon
100.56
298.0
CDCl3
Me
O
OH
Me
2ak
204.83
163.38
137.94
136.84
135.13
133.90
132.40
130.99
130.88
127.96
120.07
119.00
118.40
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
21.02
19.22
f1 (ppm)


2al proton
399.87
298.0
CDCl3
OH
O
F
Me
2al
11.98
1.02
3.17
2.38
1.59 H2O
0.00 TMS
CHCl3
f1 (ppm)

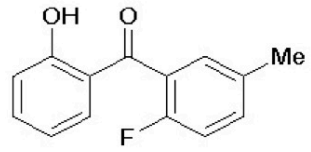

2al carbon
100.56
298.1
CDCl3
Me
O
F
OH
2al
198.96
163.11
158.61
156.14
137.10
134.26
134.22
133.59
133.57
133.53
133.45
130.07
130.04
126.16
126.00
119.93
119.16
118.37
116.19
115.98
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
20.72
f1 (ppm)

2al with {1H} decoupling 19F
376.22
298.1
CDCl3

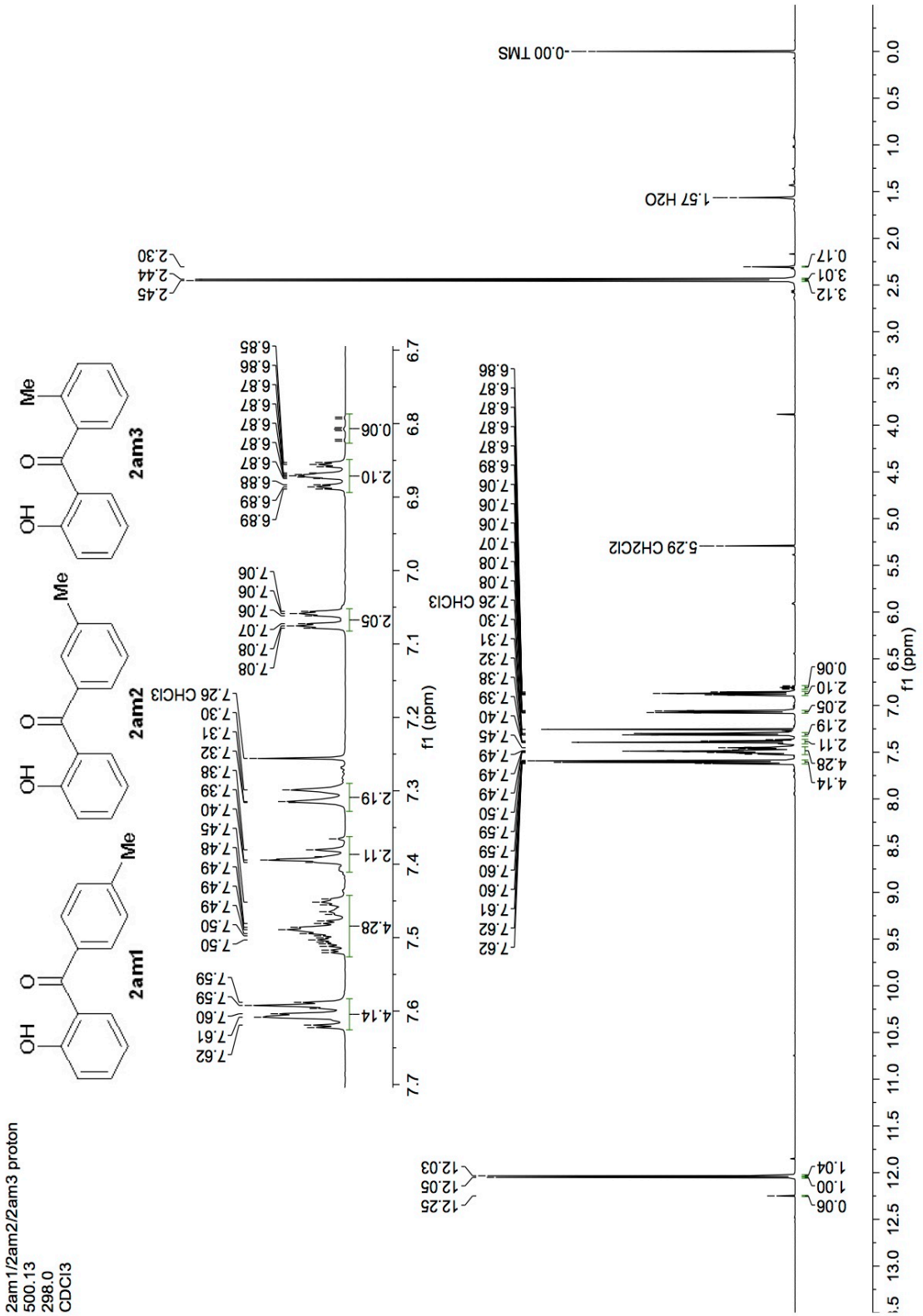


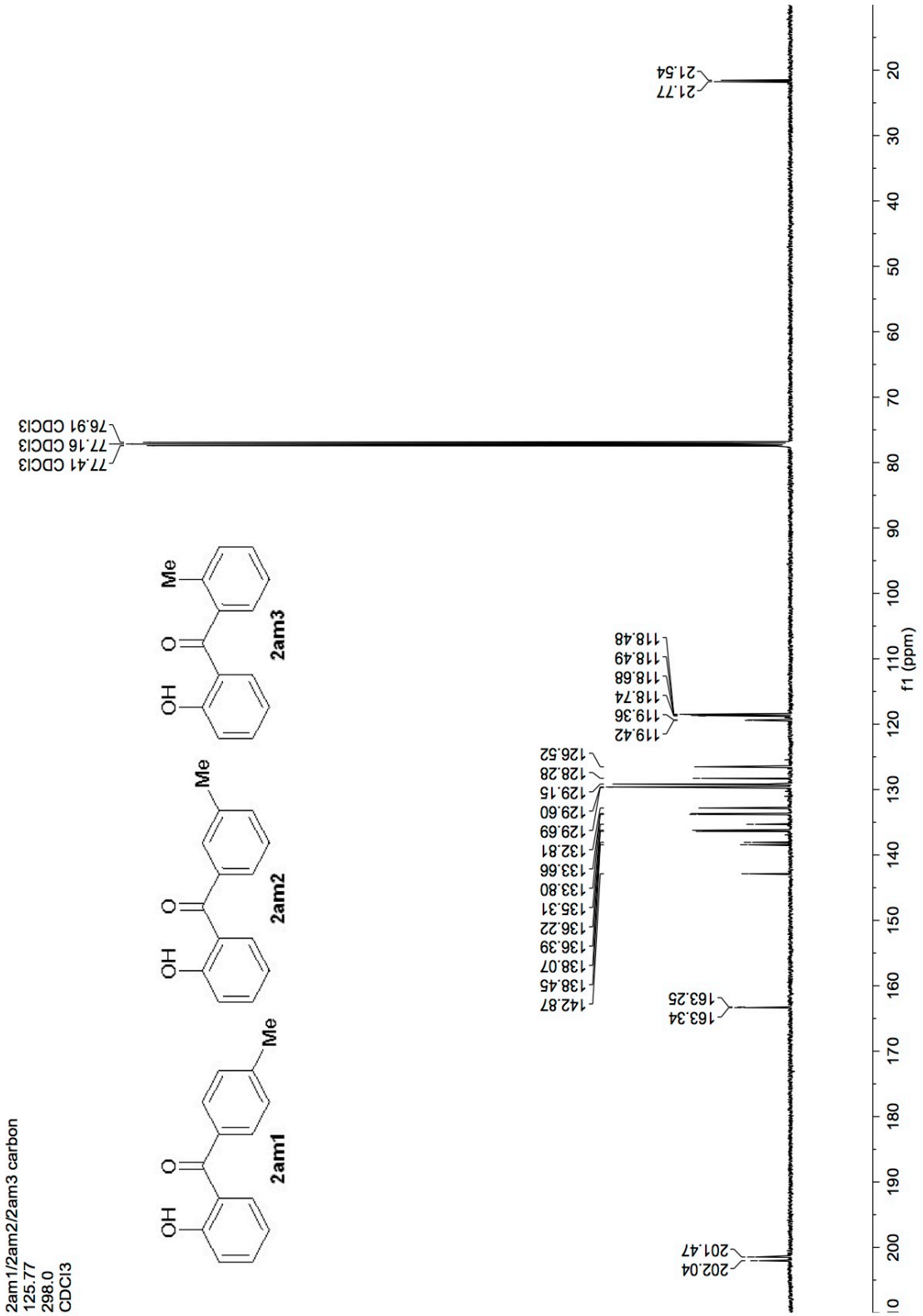
2al

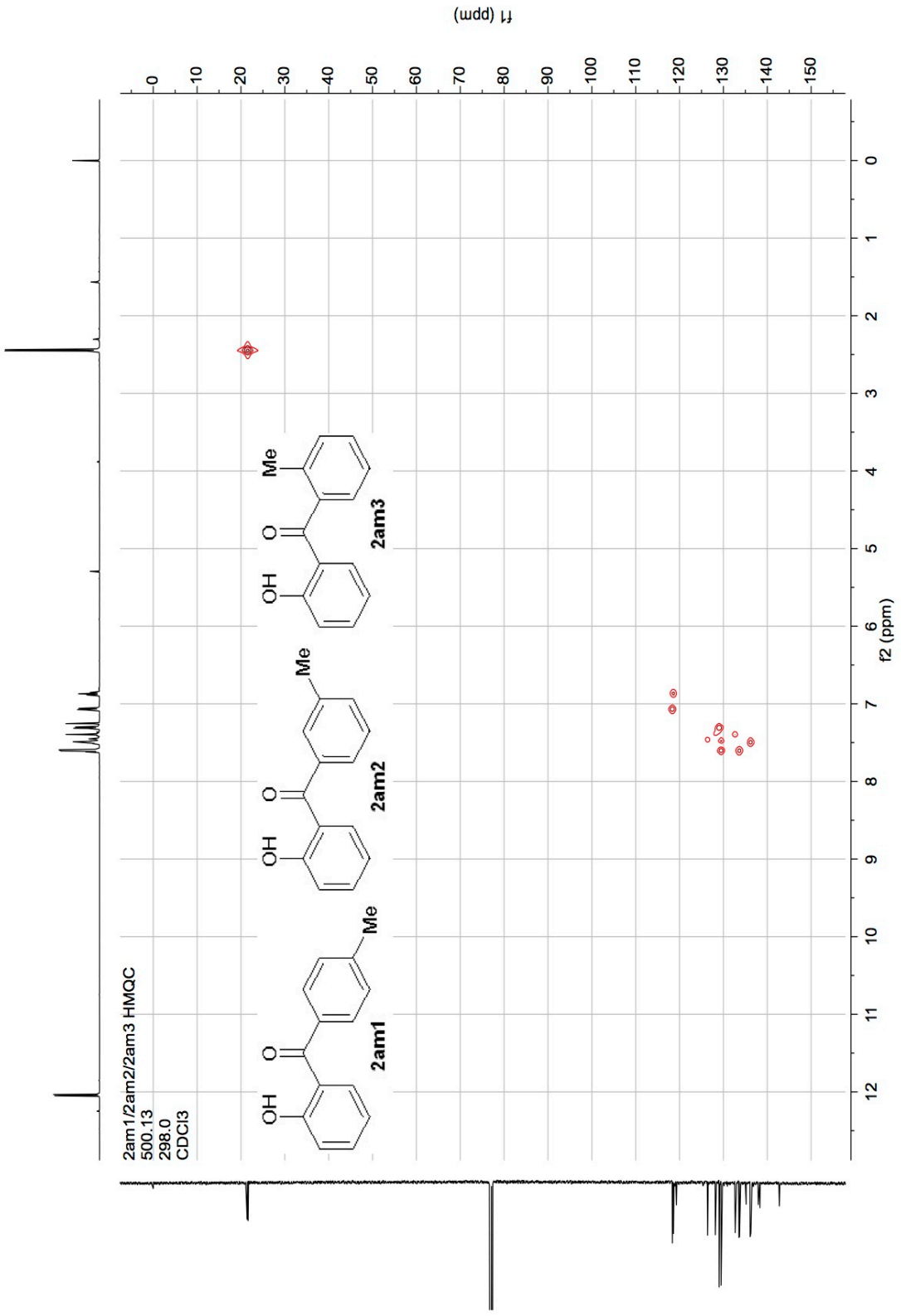
2al no decoupling 19F
376.22
298.0
CDCl3

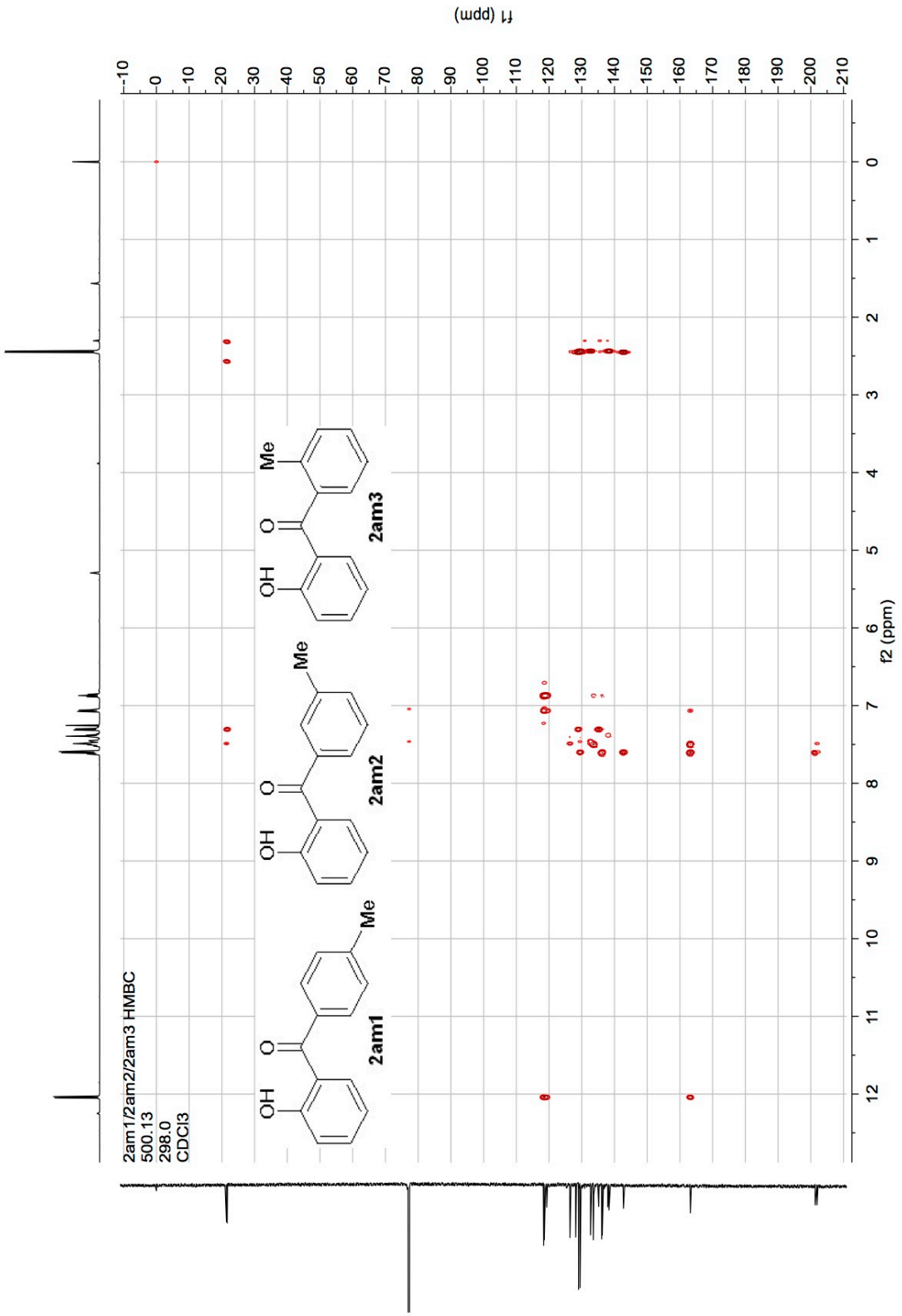


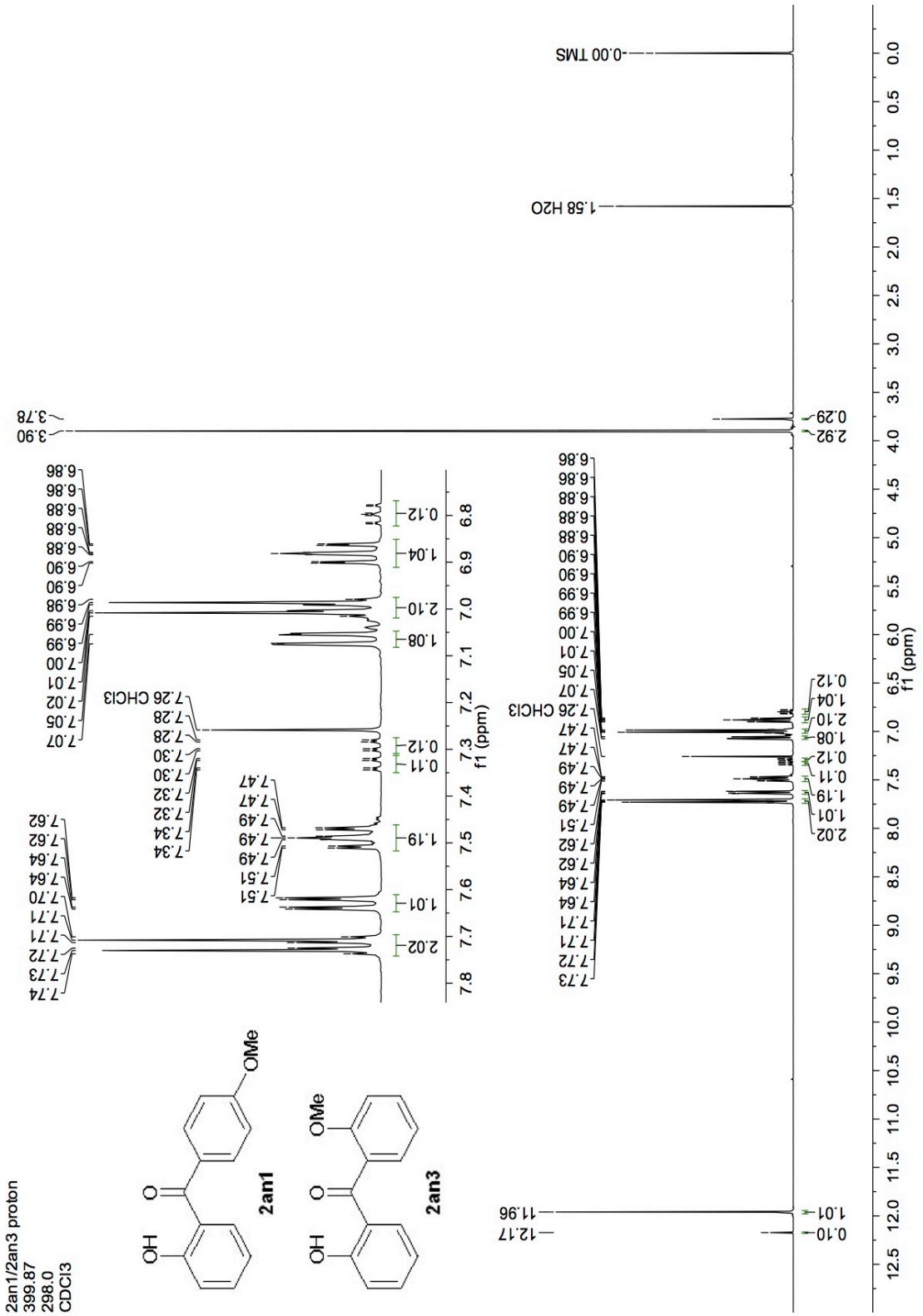
2al

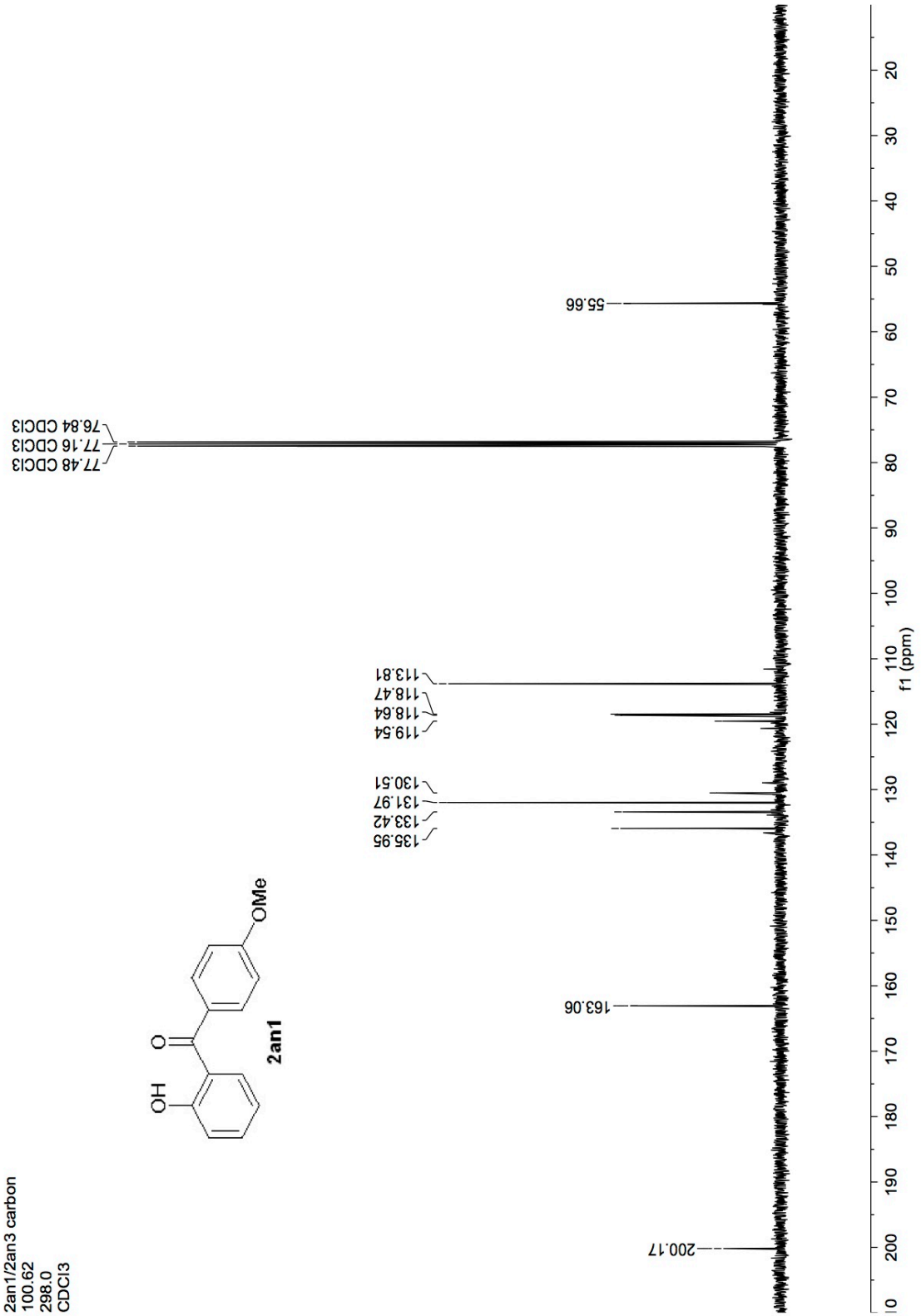

2am1/2am2/2am3 proton
500.13
298.0
CDCl3
2am1
2am2
2am3
OH
O
Me
0.00 TMS
1.57 H2O
5.29 CH2Cl2
7.26 CHCl3
f1 (ppm)

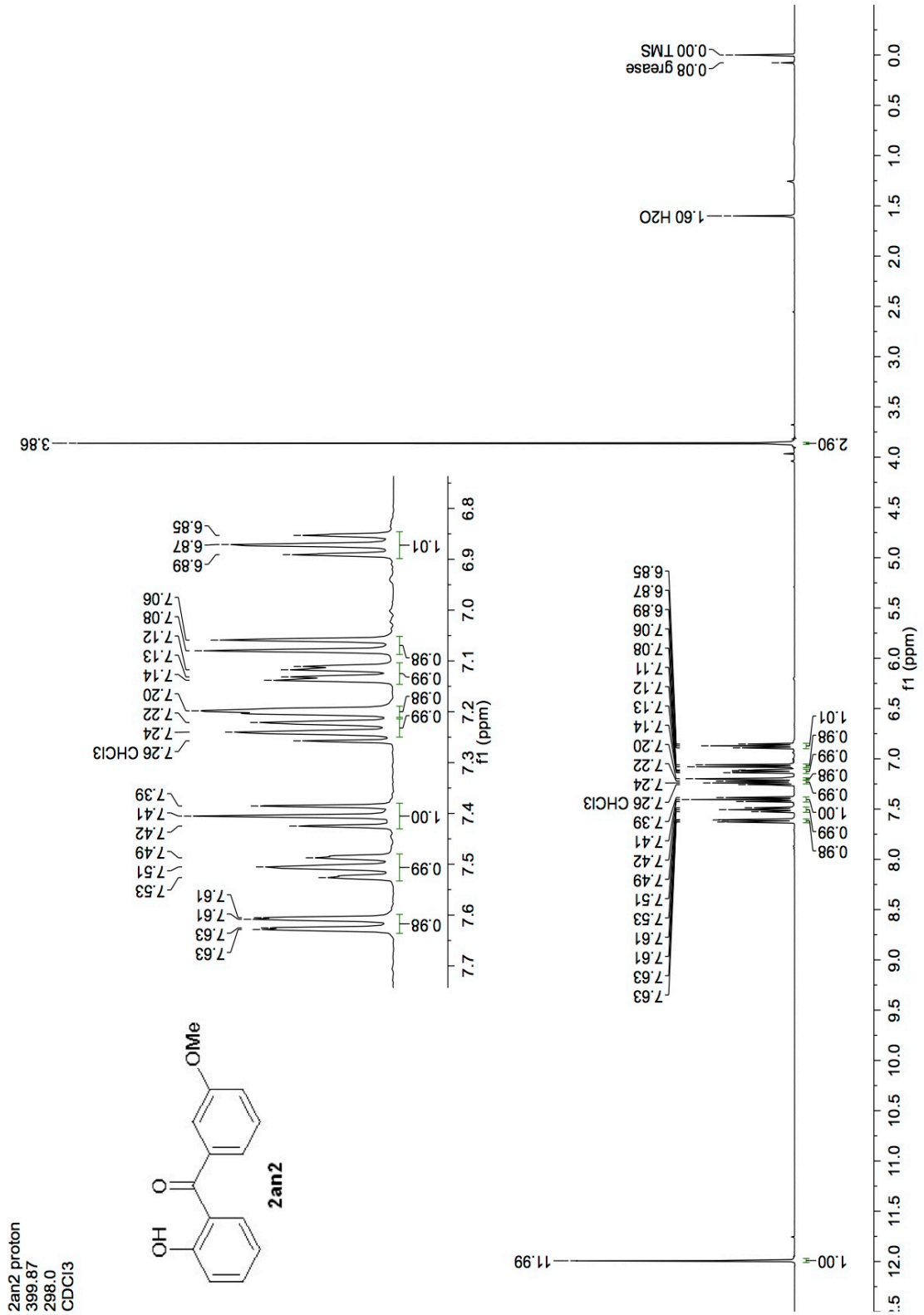

2am1/2am2/2am3 carbon
125.77
298.0
CDCl3
2am1
2am2
2am3
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
202.04
201.47
163.34
163.25
142.87
138.45
138.07
136.39
136.22
135.31
133.80
133.66
132.81
129.69
129.60
129.15
128.28
126.52
119.42
119.36
118.74
118.68
118.49
118.48
21.77
21.54
f1 (ppm)

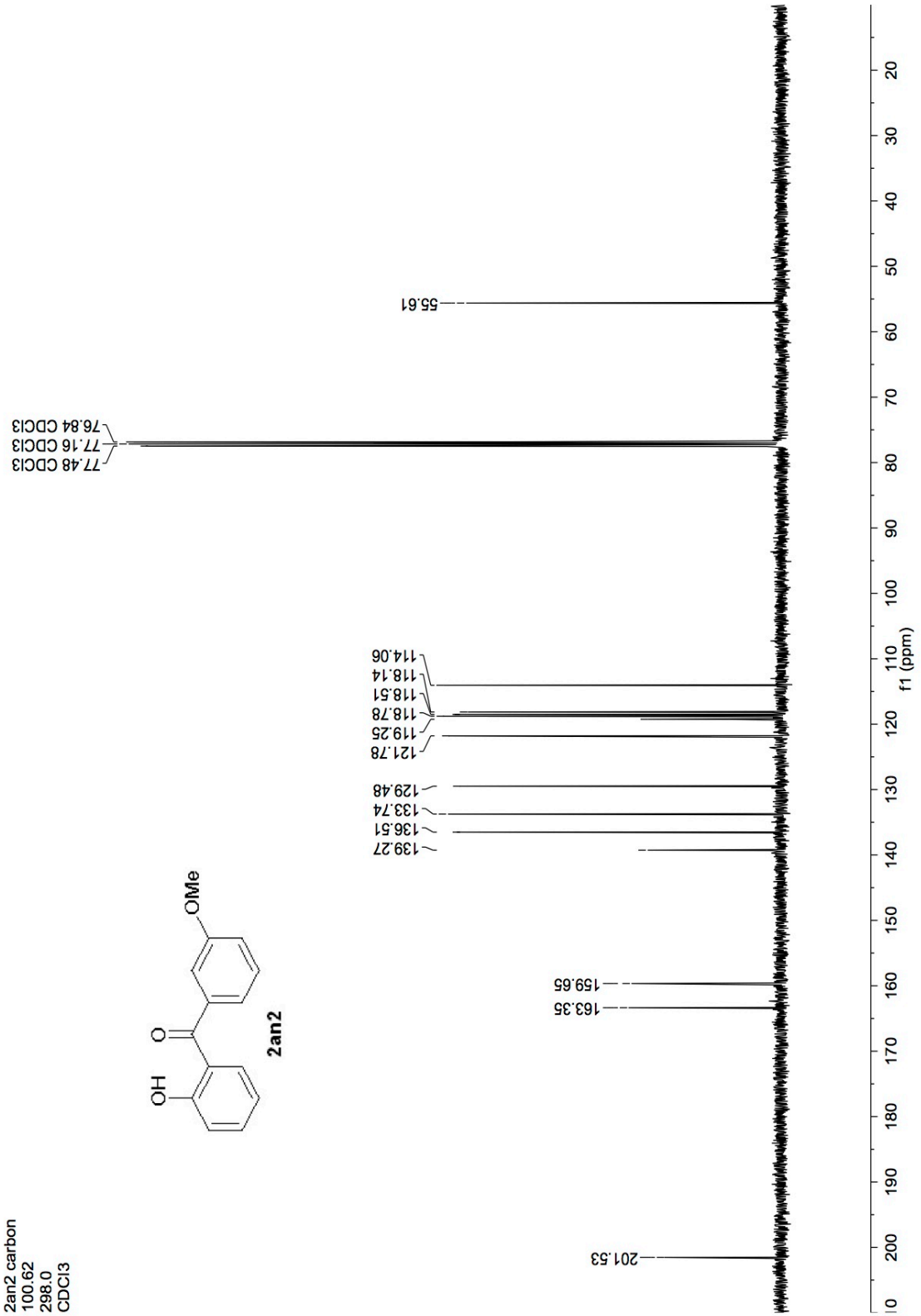

2am1/2am2/2am3 HMQC
500.13
298.0
CDCl3
f1 (ppm)
f2 (ppm)
2am1
2am2
2am3
OH
O
Me

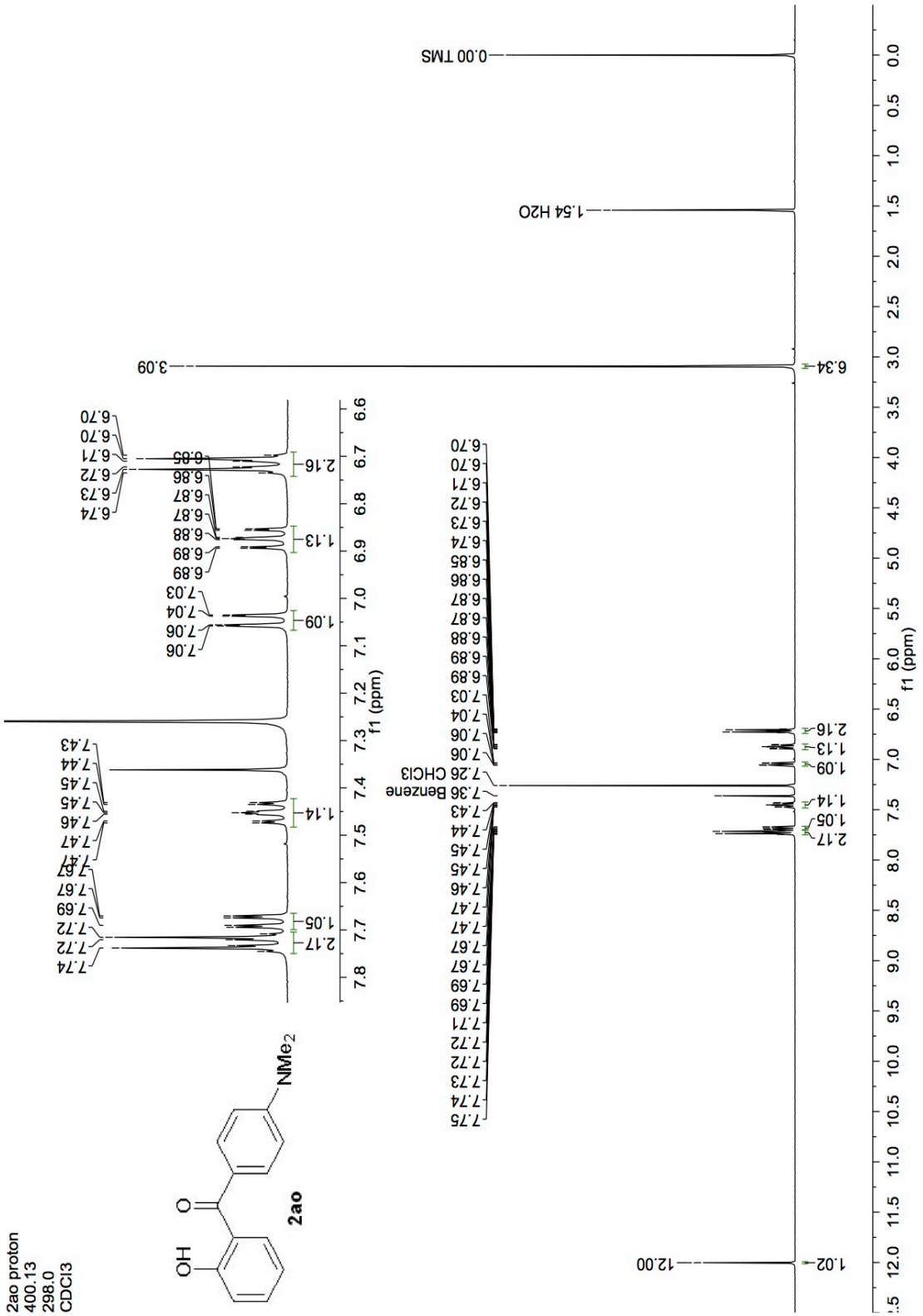

2am1/2am2/2am3 HMBC
500.13
298.0
CDCl3
2am1
2am2
2am3
OH
O
Me
f1 (ppm)
f2 (ppm)

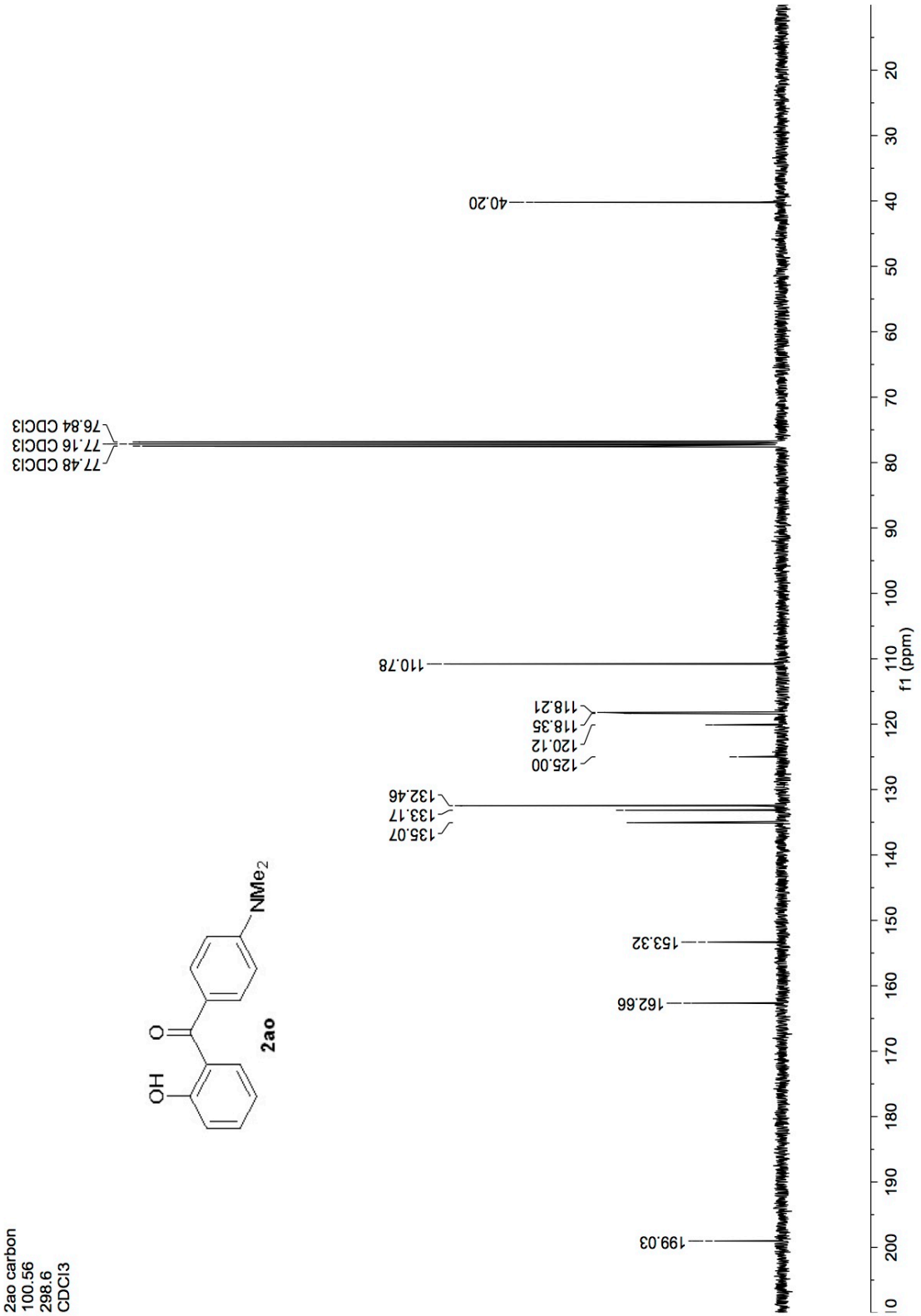

2an1/2an3 proton
399.87
298.0
CDCl3
2an1
2an3
OMe
OH
O
TMS
H2O
CHCl3
f1 (ppm)

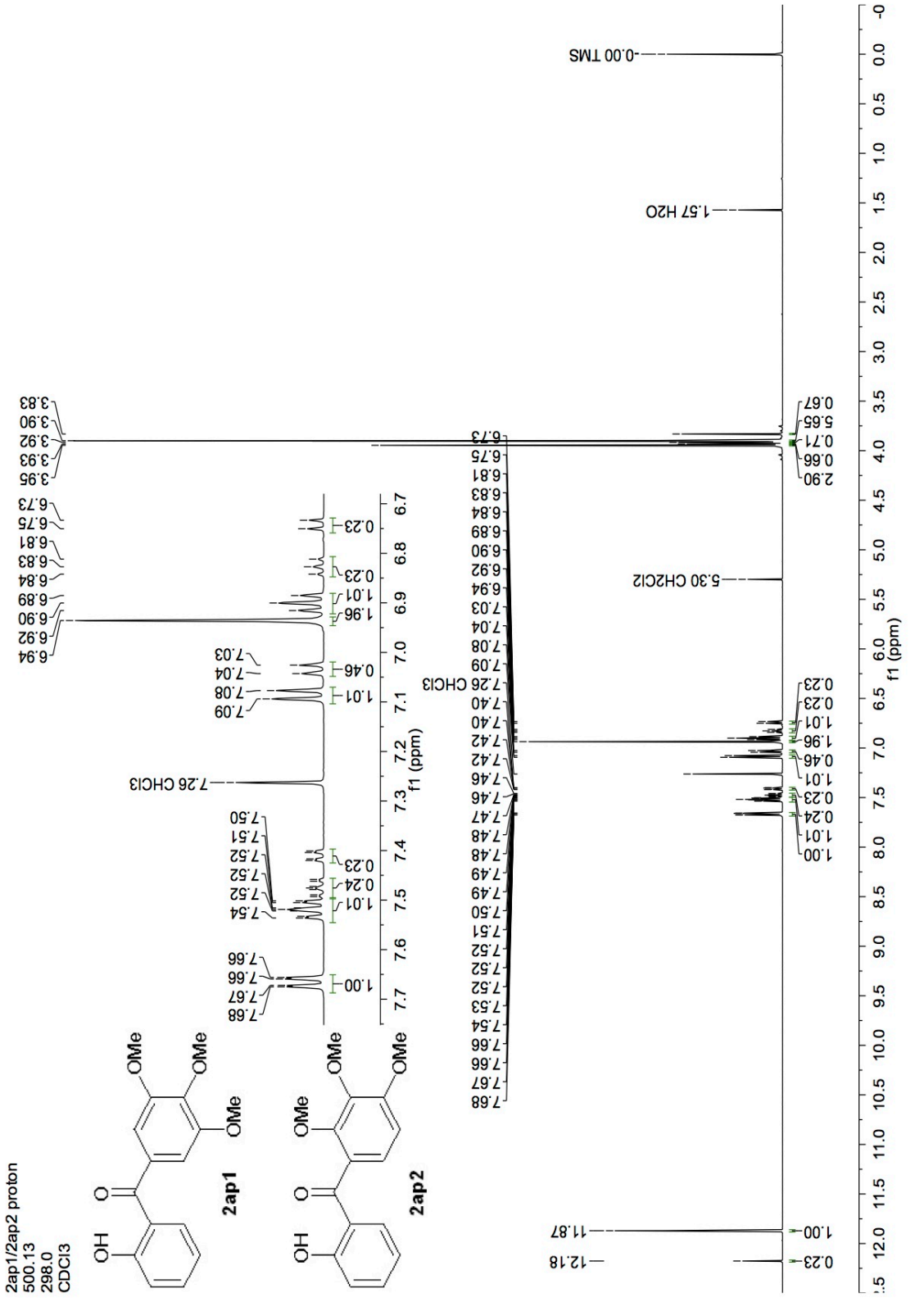

2an1/2an3 carbon
100.62
298.0
CDCl3
OMe
O
OH
2an1
200.17
163.06
135.95
133.42
131.97
130.51
119.54
118.64
118.47
113.81
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.66
f1 (ppm)

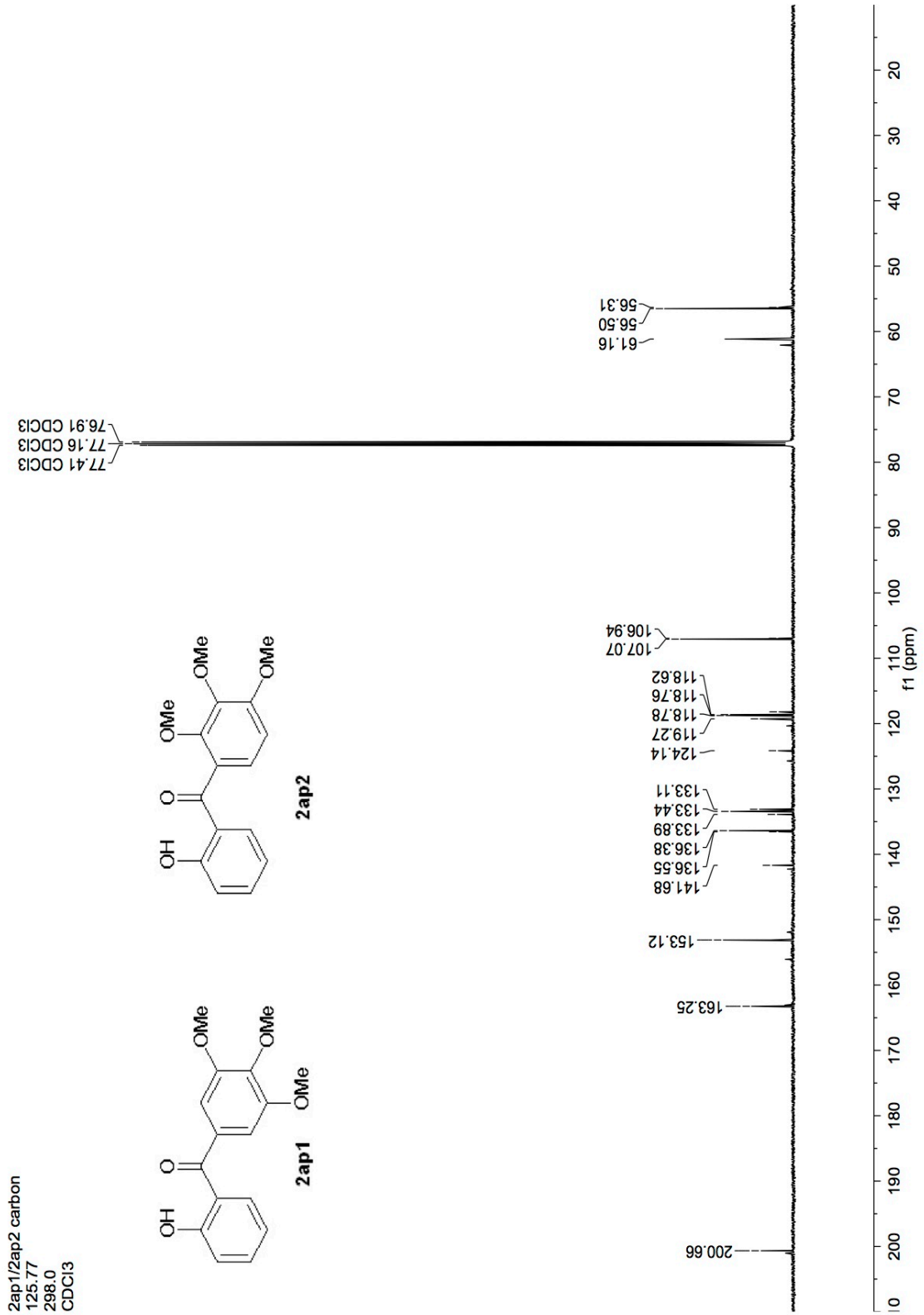

2an2 proton
399.87
298.0
CDCl3
OMe
O
OH
2an2
f1 (ppm)
11.99
1.00
2.90
3.86
1.60 H2O
0.08 grease
0.00 TMS
7.63
7.61
7.53
7.51
7.49
7.42
7.41
7.39
7.26 CHCl3
7.24
7.22
7.20
7.14
7.13
7.12
7.11
7.08
7.06
6.89
6.87
6.85
0.98
0.99
1.00
0.99
0.98
1.01

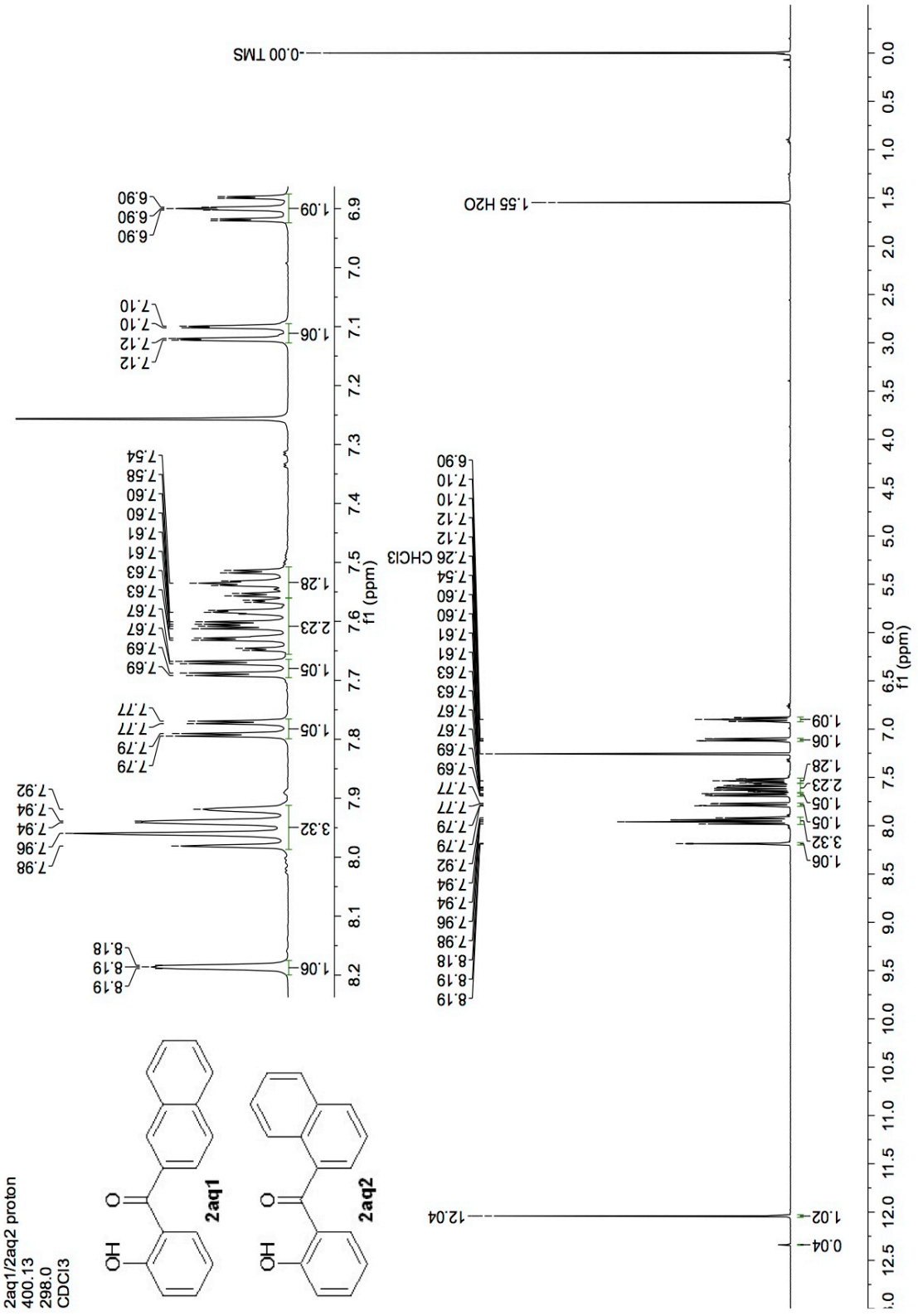

2an2 carbon
100.62
298.0
CDCl3
OMe
O
OH
2an2
201.53
163.35
159.65
139.27
136.51
133.74
129.48
121.78
119.25
118.78
118.51
118.14
114.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.61
f1 (ppm)

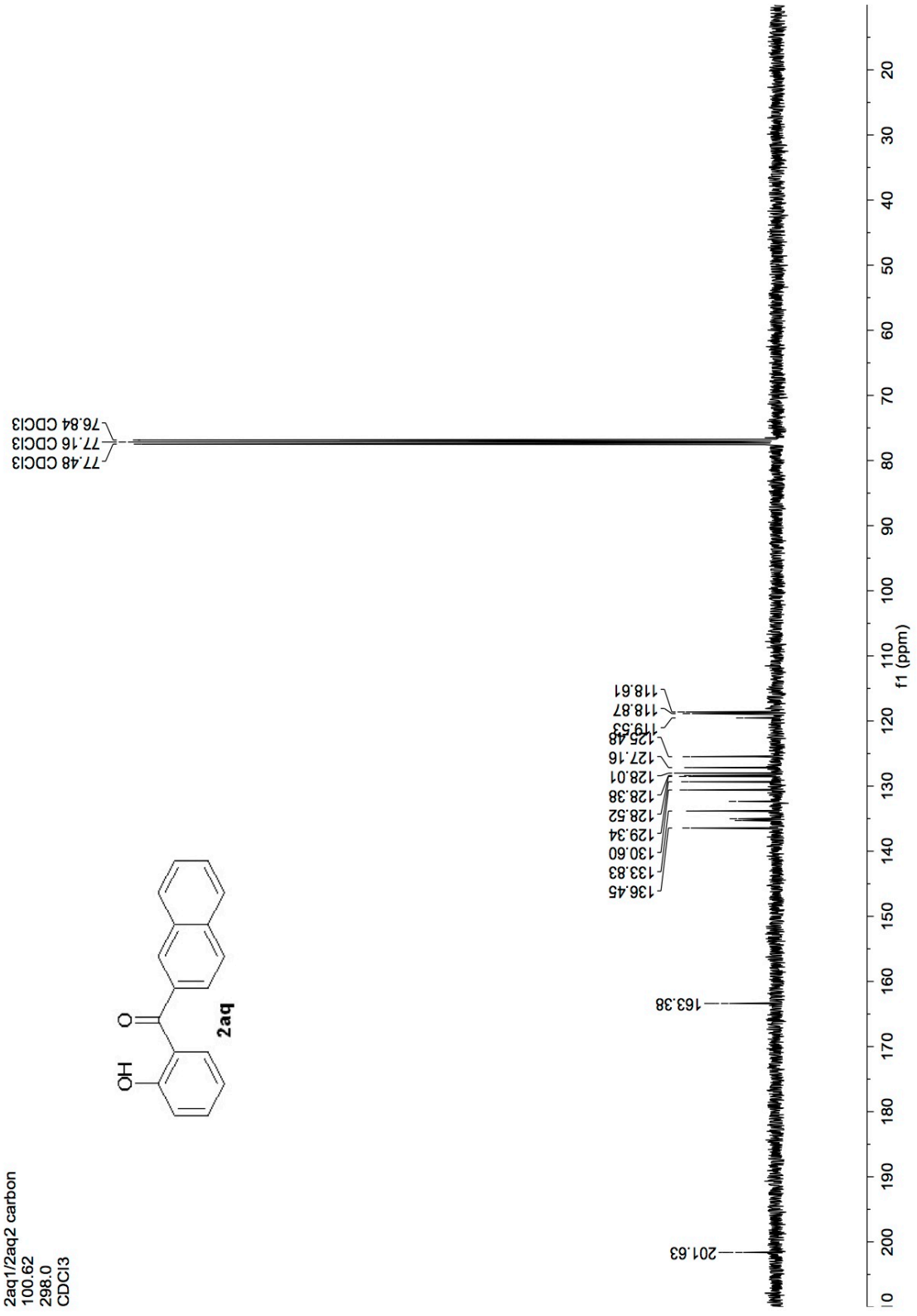

2ao proton
400.13
298.0
CDCl3
2ao
NMe2
OH
O
0.00 TMS
1.54 H2O
7.26 CHCl3
7.36 Benzene
f1 (ppm)

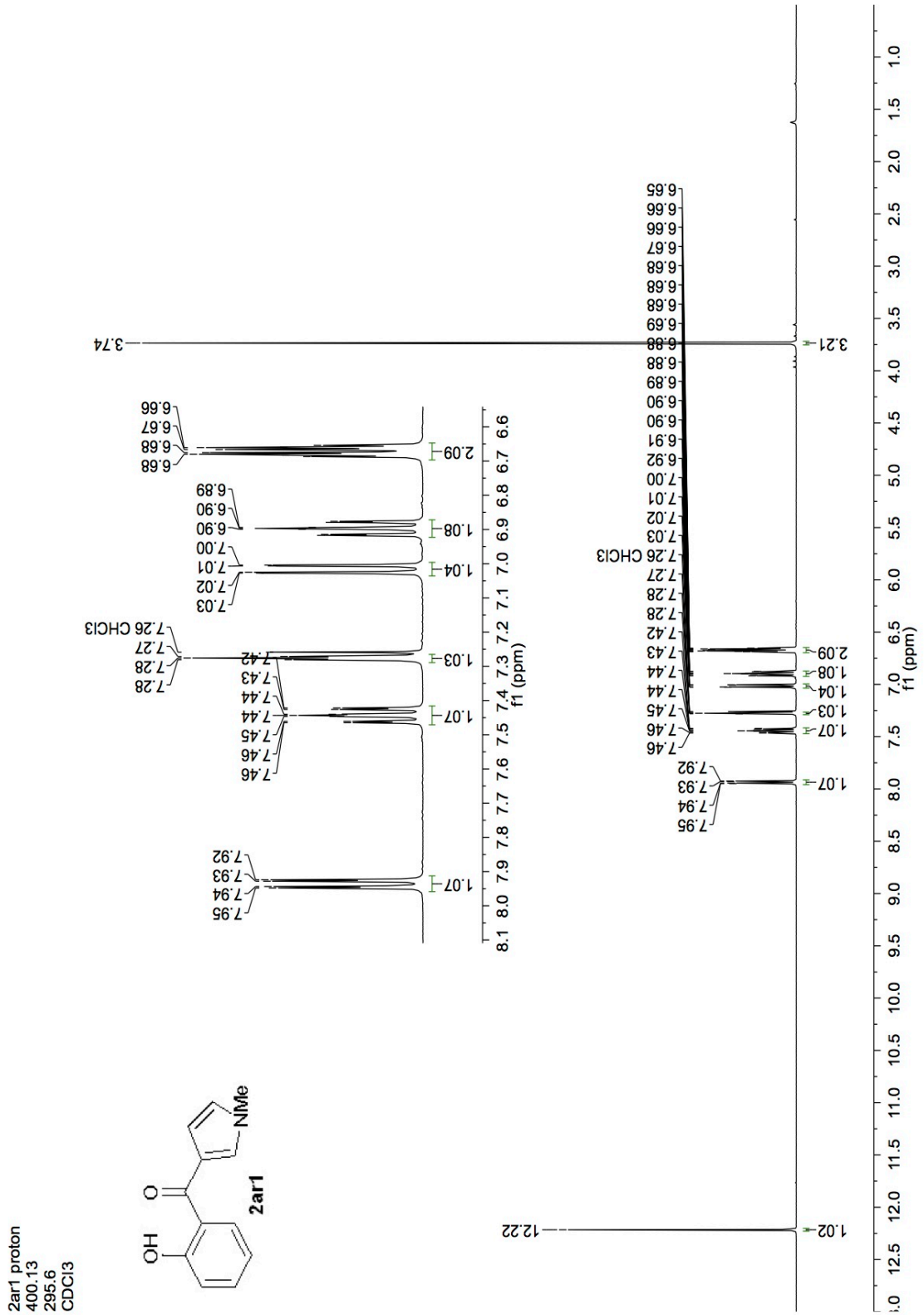

2ao carbon
100.56
298.6
CDCl3
199.03
162.66
153.32
135.07
133.17
132.46
125.00
120.12
118.35
118.21
110.78
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
40.20
OH
O
NMe2
2ao
f1 (ppm)

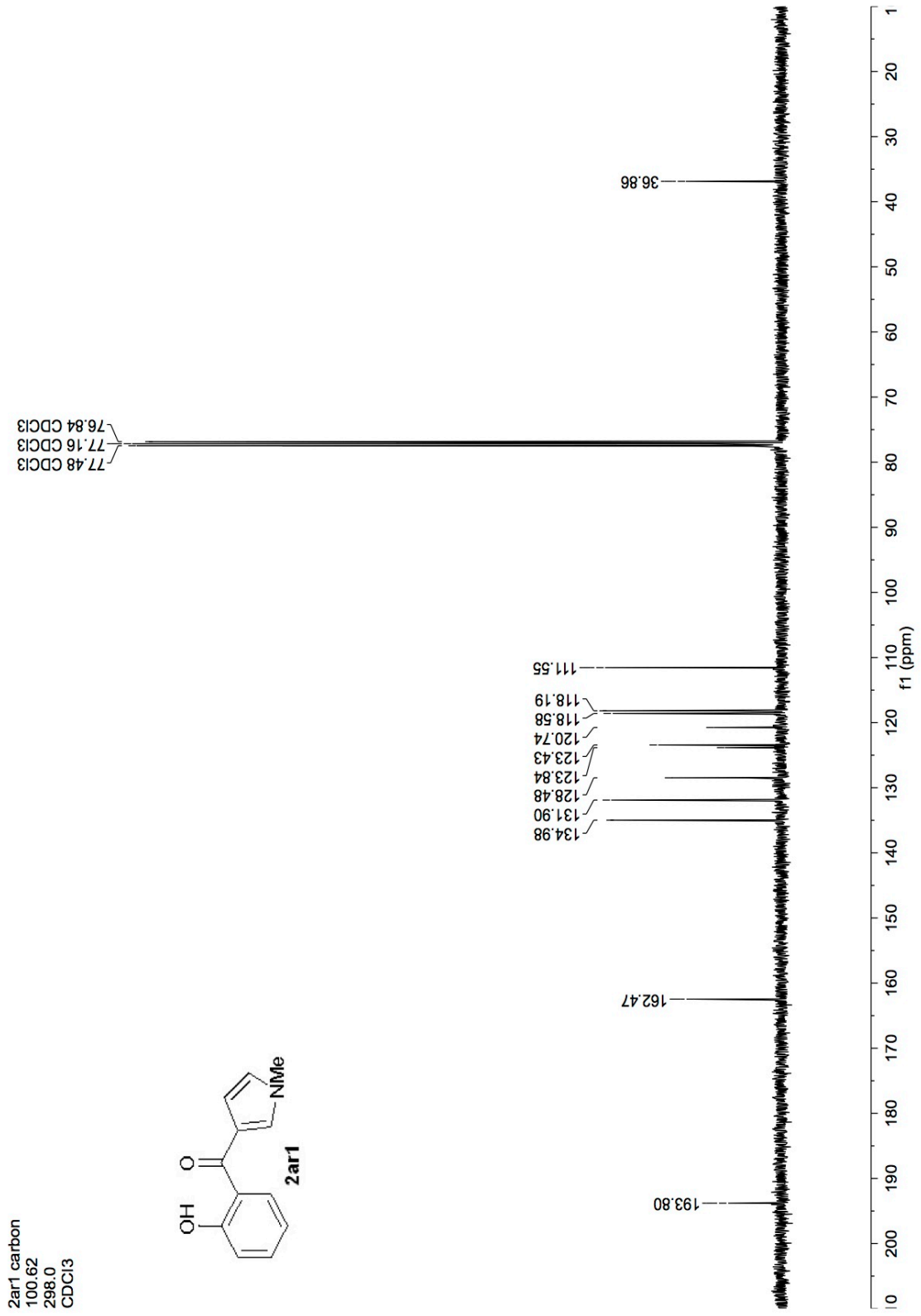

2ap1/2ap2 proton
500.13
298.0
CDCl3
2ap1
2ap2
OMe
OH
O
7.26 CHCl3
5.30 CH2Cl2
1.57 H2O
0.00 TMS
f1 (ppm)

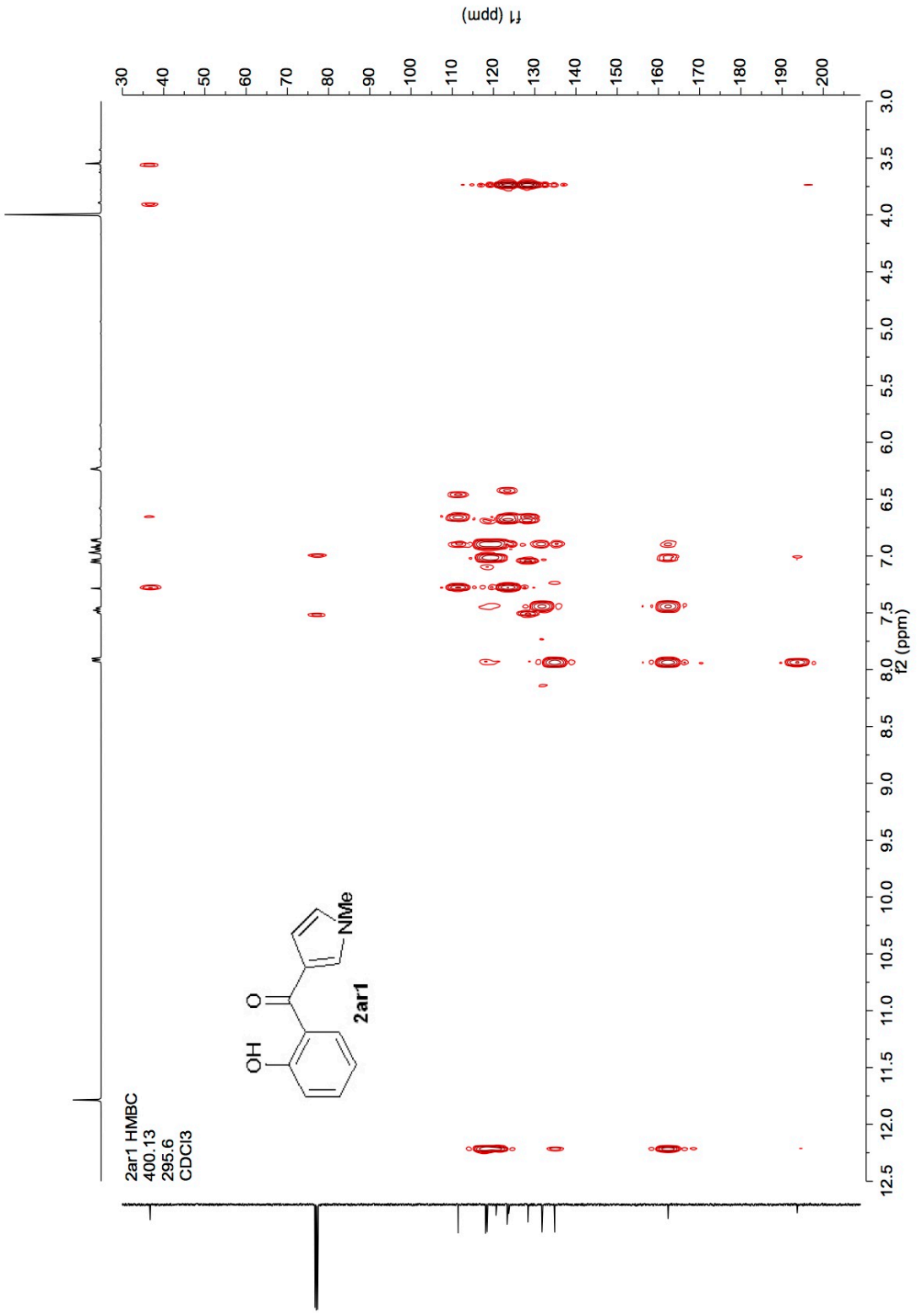

2ap1/2ap2 carbon
125.77
298.0
CDCl3
OMe
OMe
OMe
O
OH
2ap1
OMe
OMe
O
OH
2ap2
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
61.16
56.50
56.31
107.07
106.94
118.62
118.76
118.78
119.27
124.14
133.11
133.44
133.89
136.38
136.55
141.68
153.12
163.25
200.66
f1 (ppm)

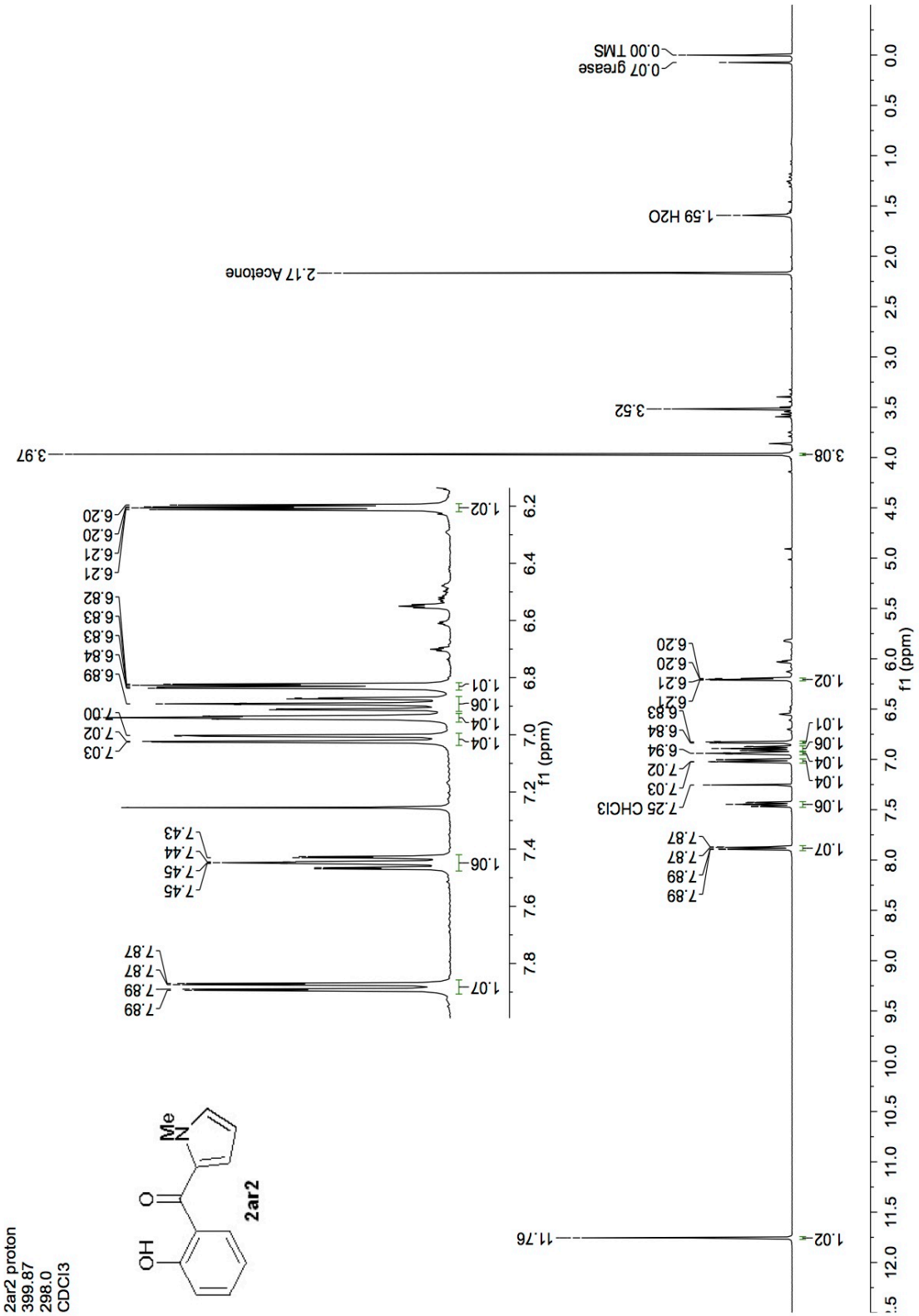

2aq1/2aq2 proton
400.13
298.0
CDCl3
2aq1
2aq2
OH
O
TMS
H2O
CHCl3
f1 (ppm)

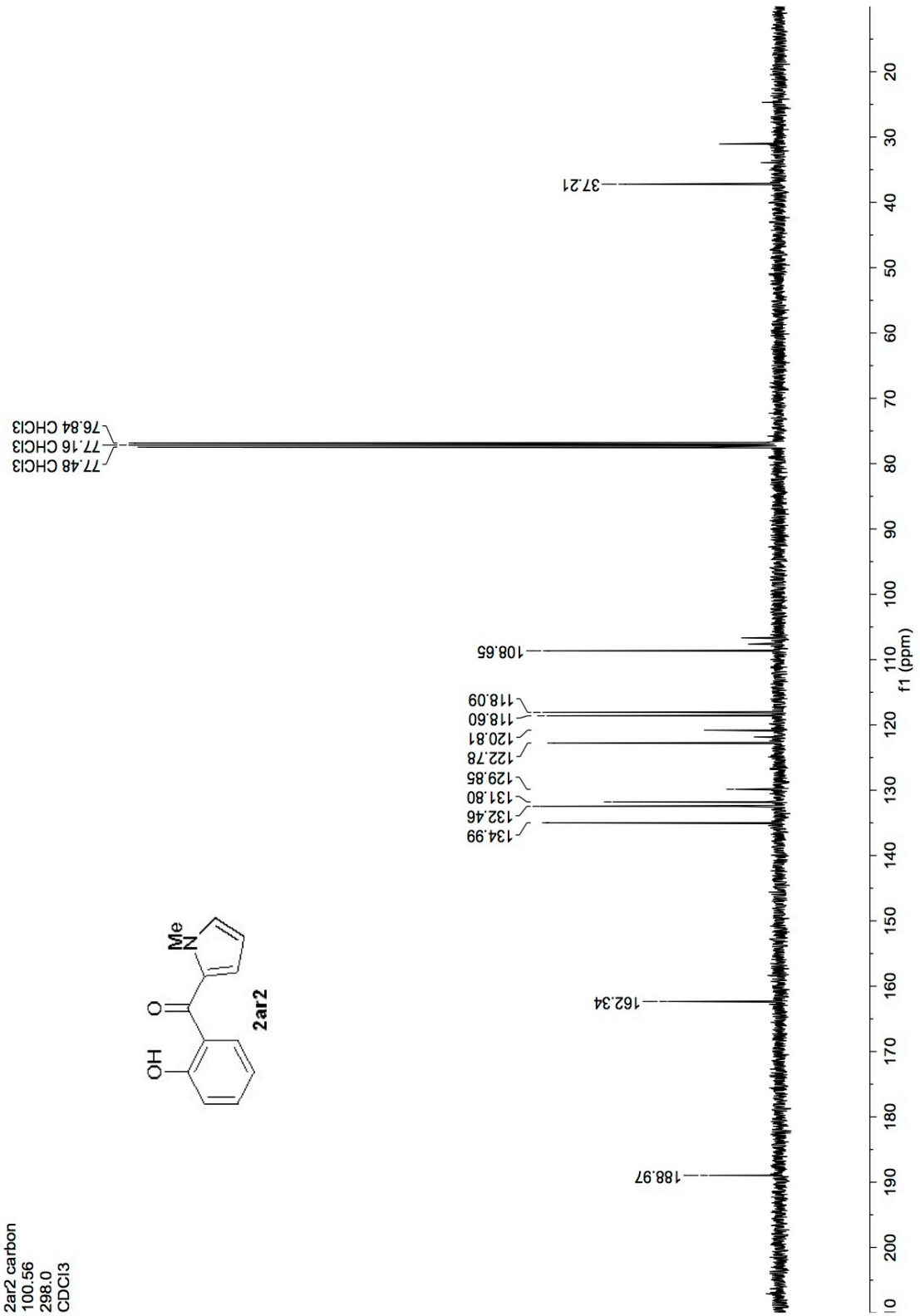

2aq1/2aq2 carbon
100.62
298.0
CDCl3
2aq
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
201.63
163.38
136.45
133.83
130.60
129.34
128.52
128.38
128.01
127.16
126.48
119.53
118.87
118.61
f1 (ppm)

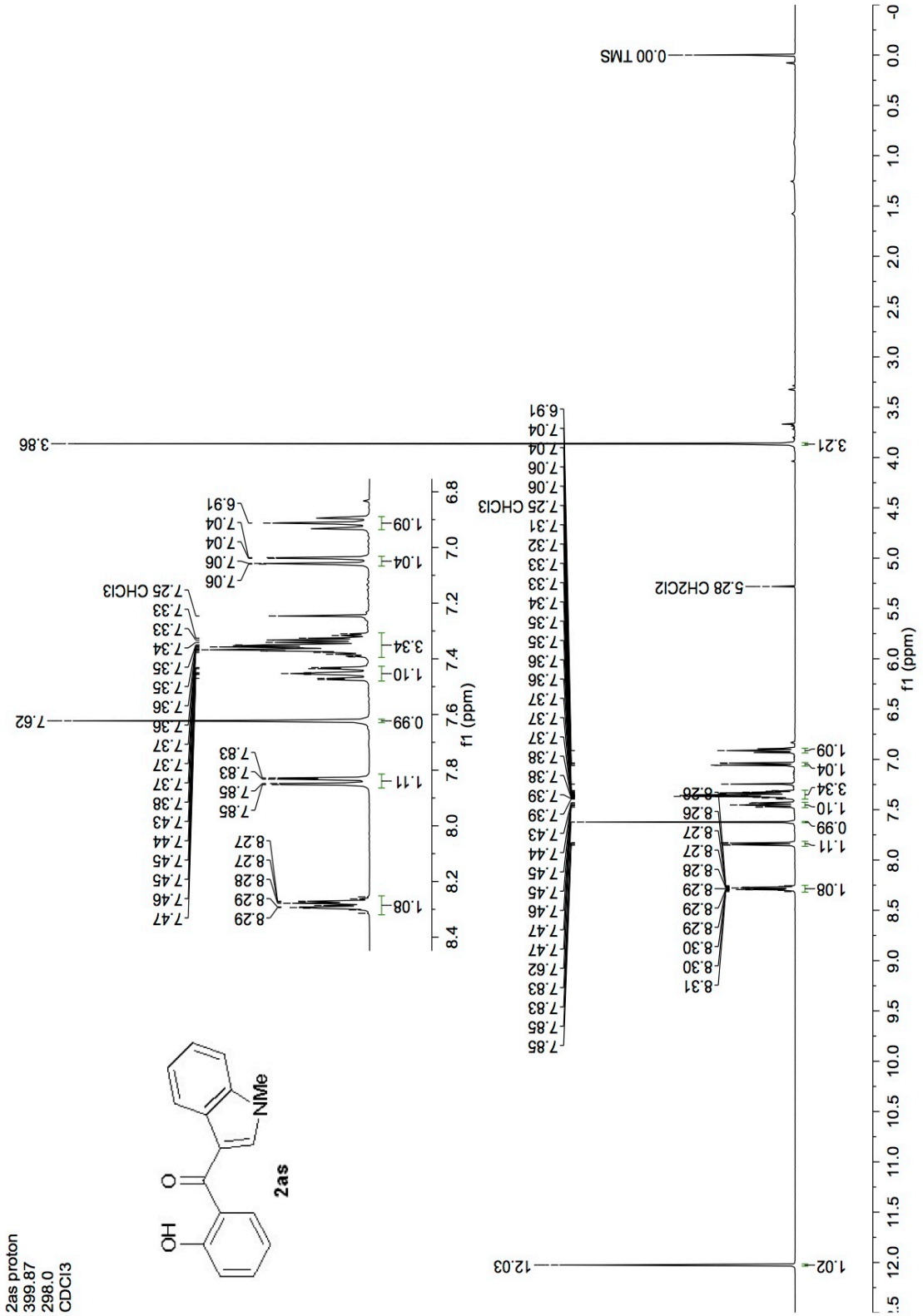

2ar1 proton
400.13
295.6
CDCl3
OH
O
NMe
2ar1
f1 (ppm)

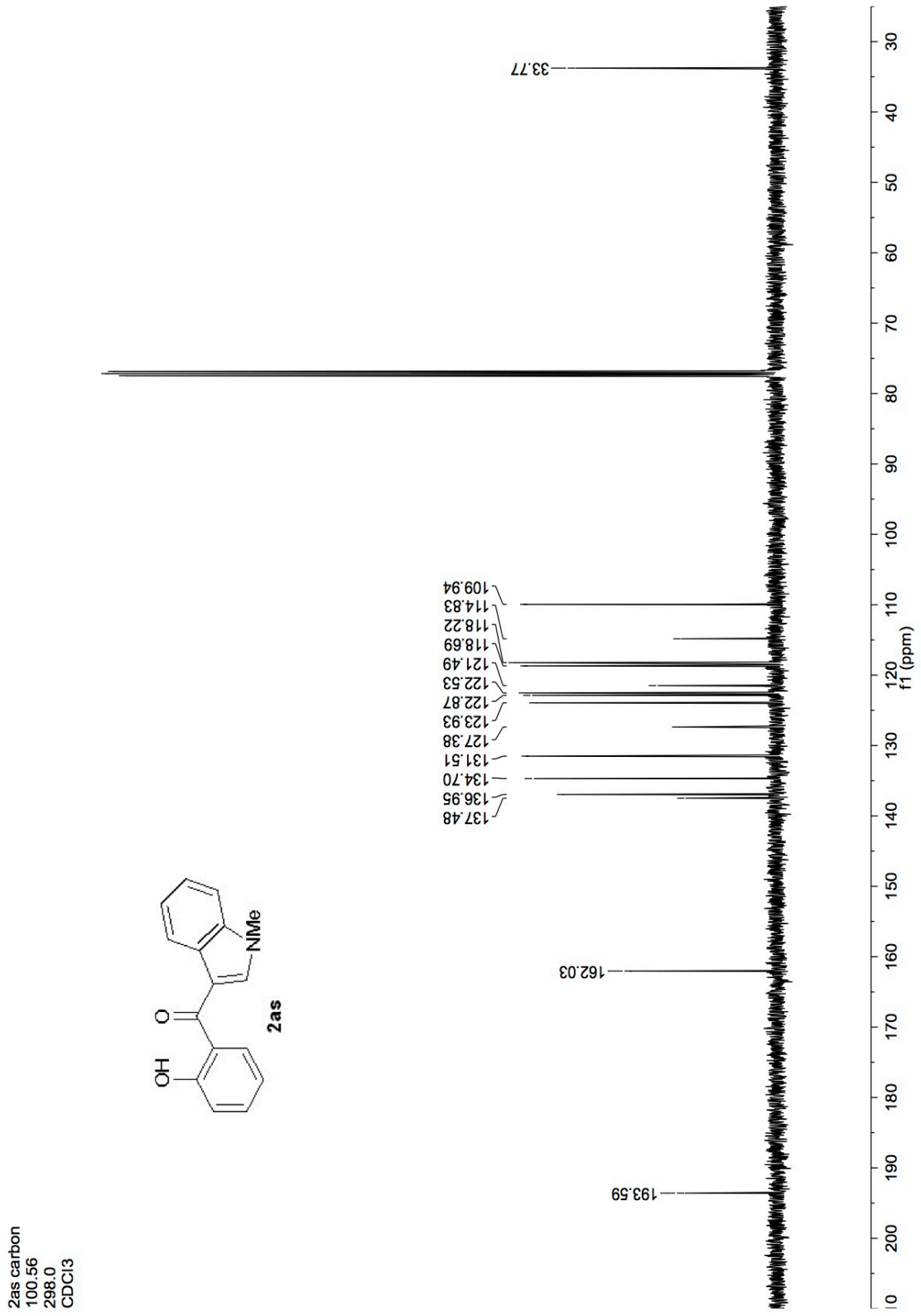

2ar1 carbon
100.62
298.0
CDCl3
OH
O
NMe
2ar1
193.80
162.47
134.98
131.90
128.48
123.84
123.43
120.74
118.58
118.19
111.55
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
36.86
f1 (ppm)

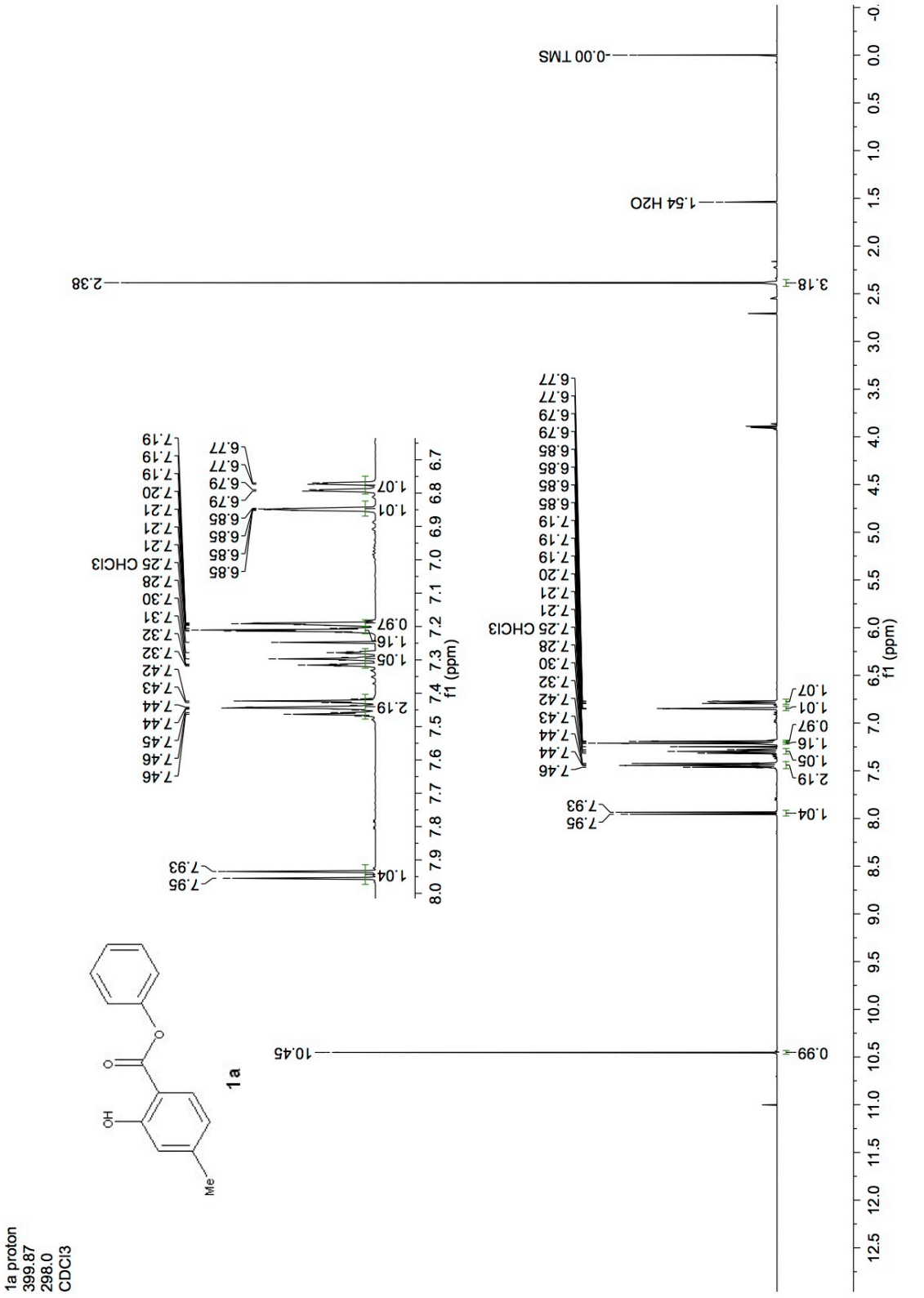

2ar1 HMBC
400.13
295.6
CDCl3
OH
O
NMe
2ar1
f1 (ppm)
f2 (ppm)

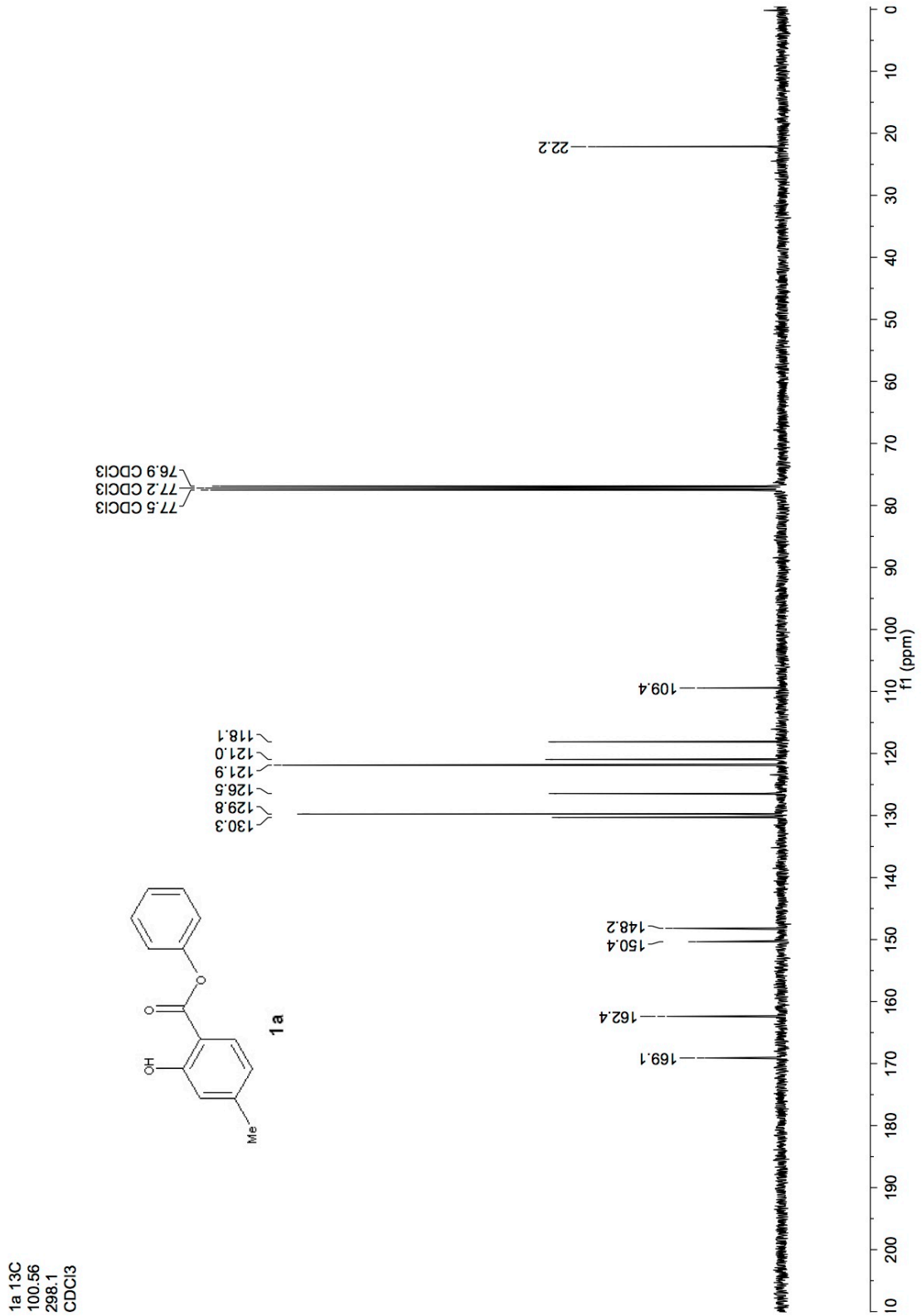

2ar2 proton
399.87
298.0
CDCl3
2ar2
Me
N
O
OH
11.76
1.02
7.89
7.89
7.87
7.87
1.07
7.45
7.45
7.44
7.43
1.06
7.03
7.02
7.00
6.89
6.84
6.83
6.83
6.82
6.21
6.21
6.20
6.20
1.02
1.04
1.06
1.01
3.97
3.08
3.52
2.17 Acetone
1.59 H2O
0.07 grease
0.00 TMS
7.25 CHCl3
f1 (ppm)

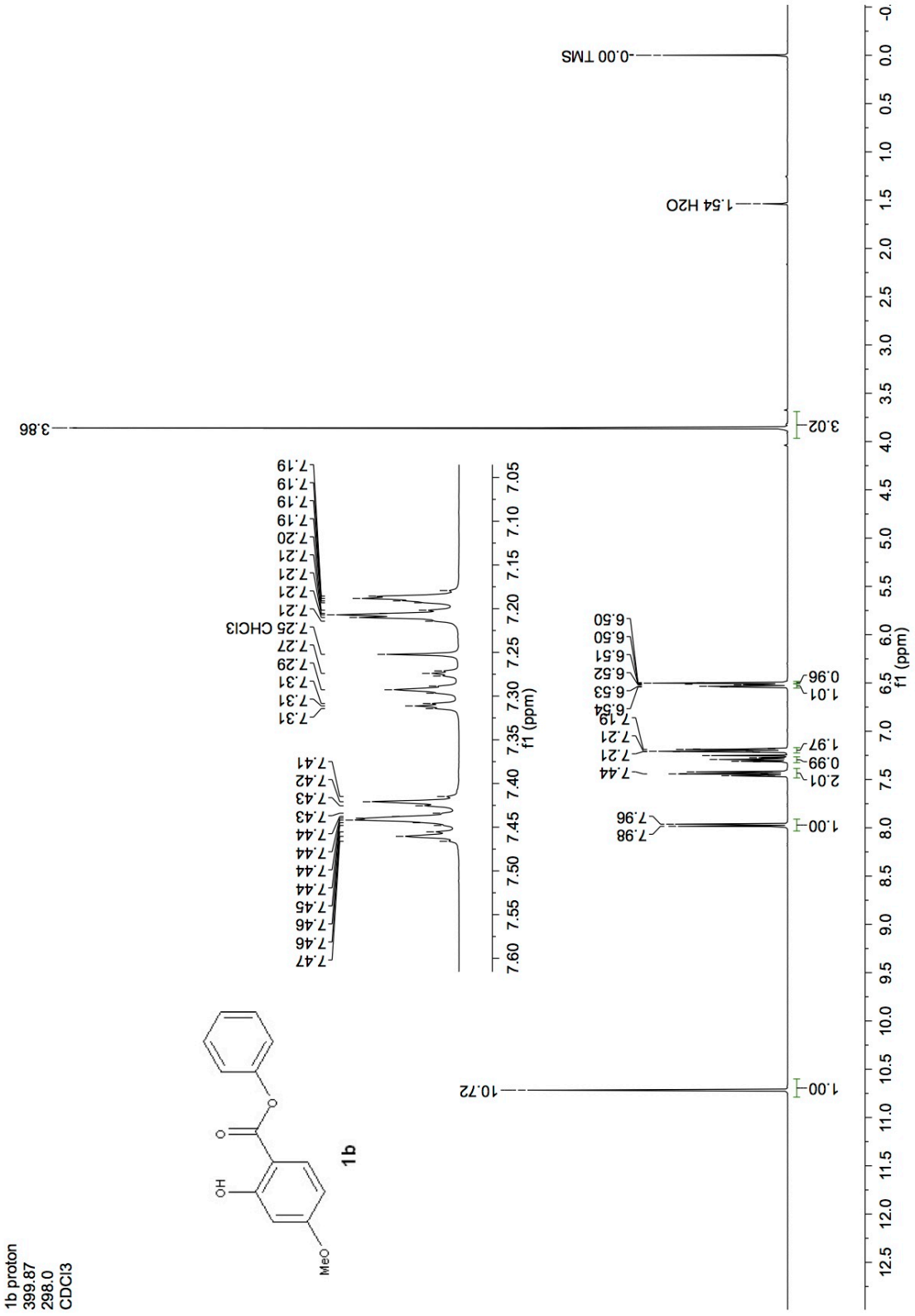

2ar2 carbon
100.56
298.0
CDCl3
2ar2
Me
N
O
OH
188.97
162.34
134.99
132.46
131.80
129.85
122.78
120.81
118.60
118.09
108.65
77.48 CHCl3
77.16 CHCl3
76.84 CHCl3
37.21
f1 (ppm)

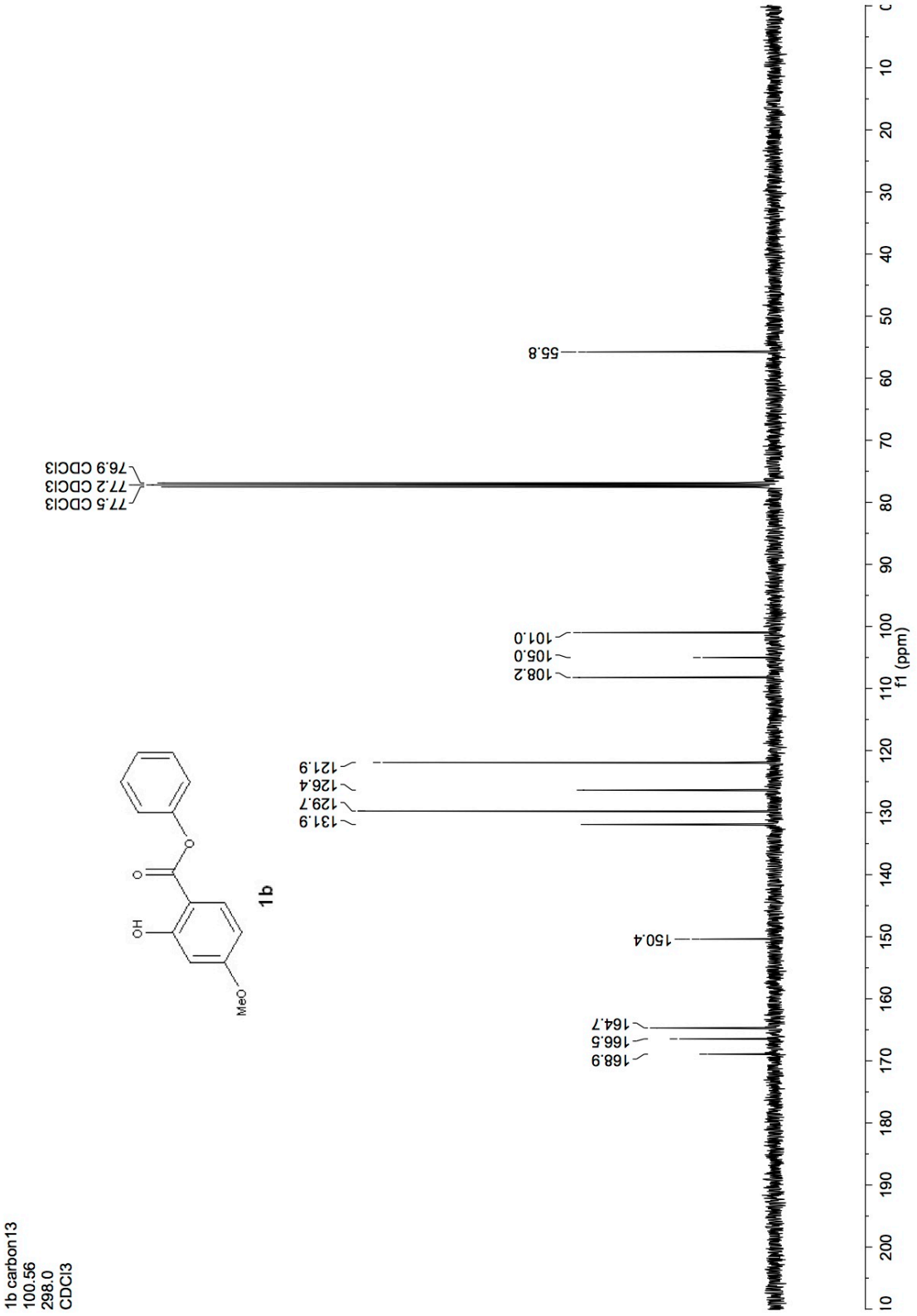

2as proton
399.87
298.0
CDCl3
2as
NMe
OH
O
0.00 TMS
3.21
5.28 CH2Cl2
12.03
1.02
1.08
1.11
0.99
1.10
3.34
1.04
1.09
3.86
7.62
7.25 CHCl3
f1 (ppm)

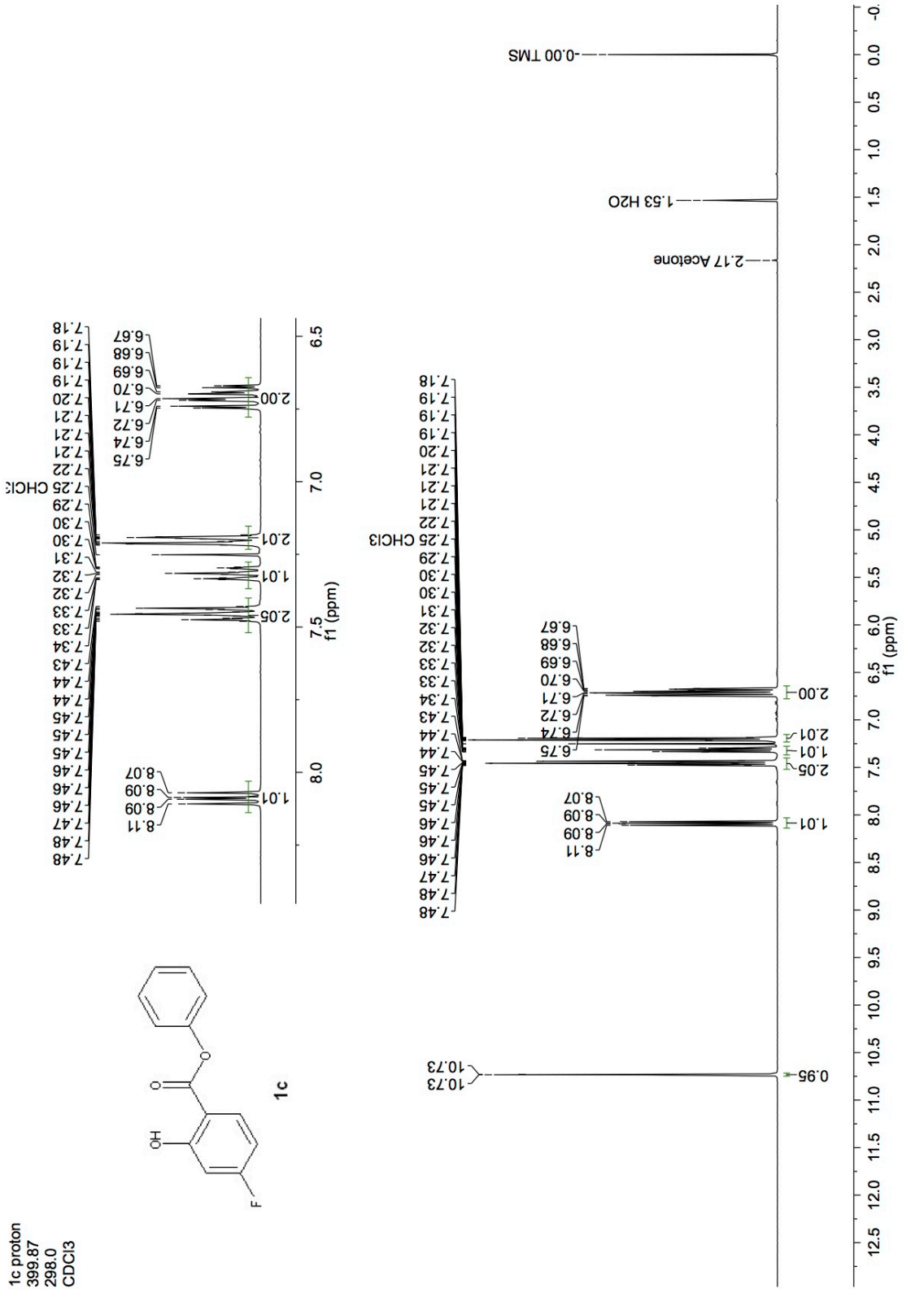

2as carbon
100.56
298.0
CDCl3
NMe
O
OH
2as
193.59
162.03
137.48
136.95
134.70
131.51
127.38
123.93
122.87
122.53
121.49
118.69
118.22
114.83
109.94
33.77
f1 (ppm)

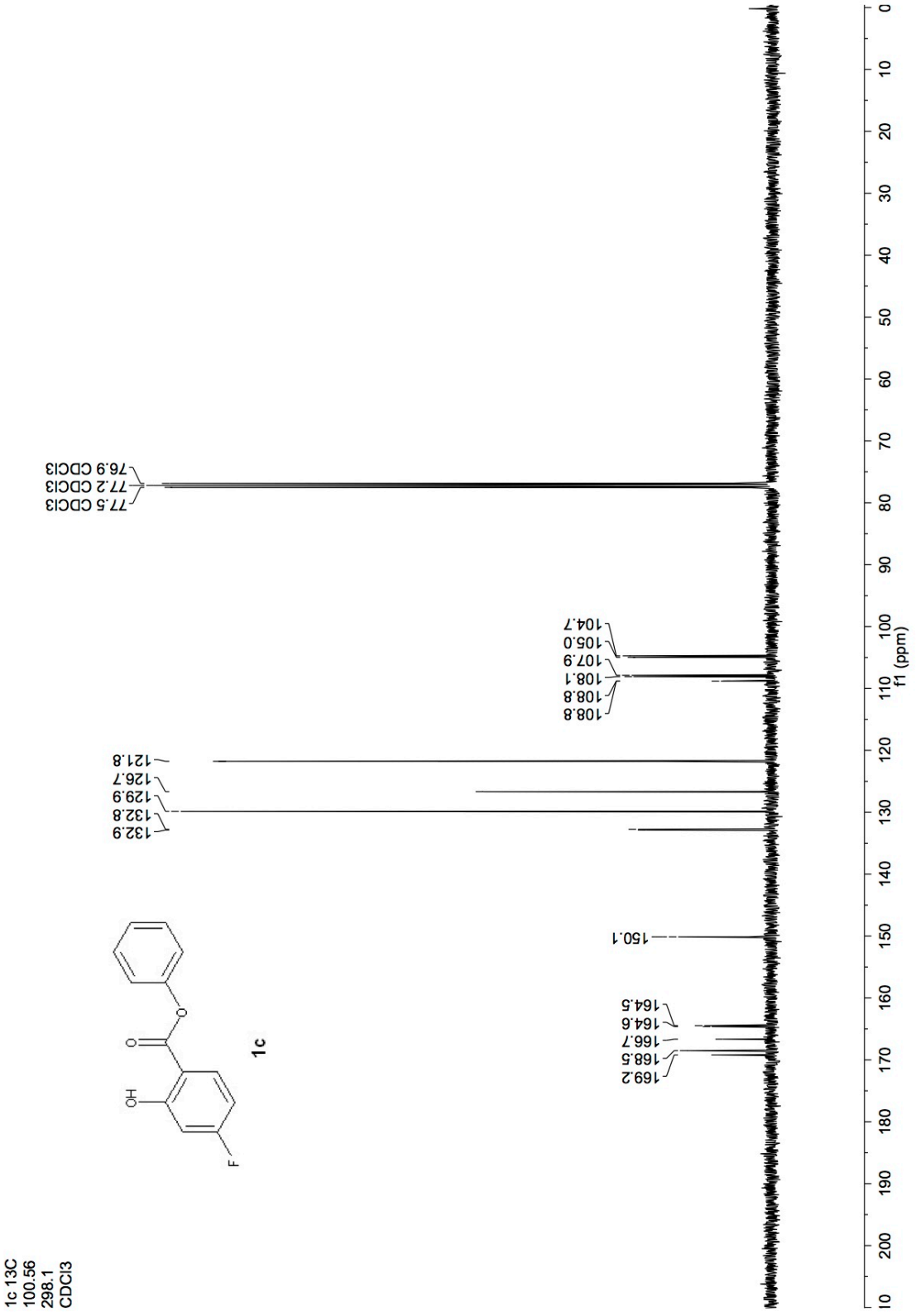

1a proton
399.87
298.0
CDCl3
1a
Me
OH
O
O
f1 (ppm)
-0.00 TMS
1.54 H2O
CHCl3
CHCl3


1a 13C
100.56
298.1
CDCl3
1a
Me
OH
O
O
22.2
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
109.4
118.1
121.0
121.9
126.5
129.8
130.3
148.2
150.4
162.4
169.1
f1 (ppm)

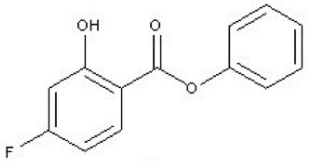

1b proton
399.87
298.0
CDCl3
1b
MeO
OH
O
O
10.72
1.00
7.98
7.96
7.47
7.46
7.46
7.45
7.44
7.44
7.44
7.44
7.44
7.43
7.43
7.42
7.41
7.44
7.21
7.21
1.97
0.99
2.01
7.31
7.31
7.29
7.27
7.25 CHCl3
7.21
7.21
7.21
7.21
7.20
7.19
7.19
7.19
7.19
7.19
6.54
6.53
6.52
6.51
6.50
6.50
1.01
0.96
3.02
3.86
1.54 H2O
0.00 TMS
f1 (ppm)
f1 (ppm)


1b carbon13
100.56
298.0
CDCl3
1b
MeO
OH
O
O
168.9
166.5
164.7
150.4
131.9
129.7
126.4
121.9
108.2
105.0
101.0
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
55.8
f1 (ppm)


1c proton
399.87
298.0
CDCl3
1c
f1 (ppm)
TMS
H2O
Acetone
CHCl3

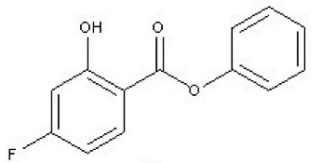

1c 13C
100.56
298.1
CDCl3
1c
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
132.9
132.8
129.9
126.7
121.8
108.8
108.8
108.1
107.9
105.0
104.7
150.1
169.2
168.5
166.7
164.6
164.5
f1 (ppm)

1c no decoupling 19F
376.46
298.0
CDCl3

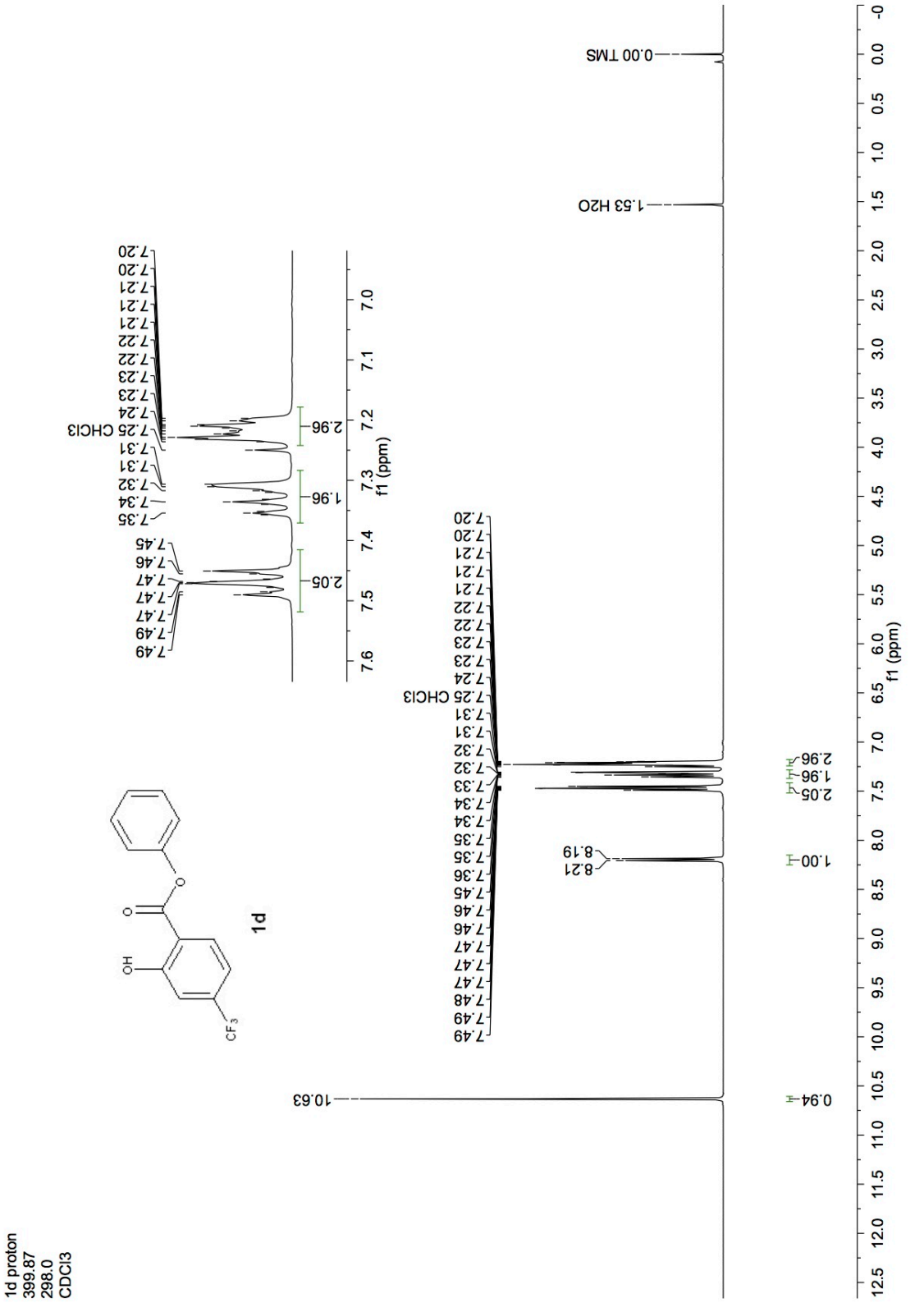


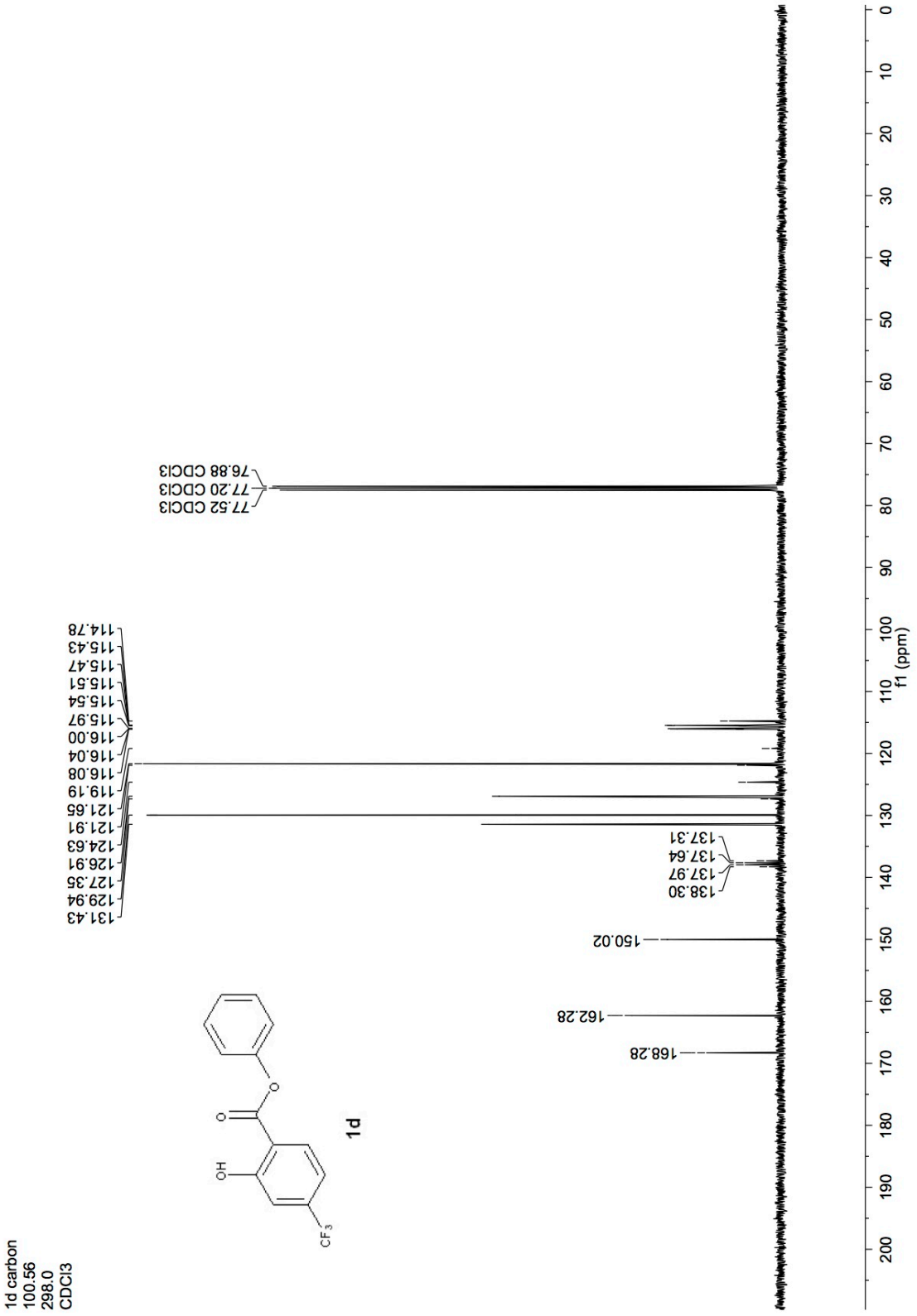
1c

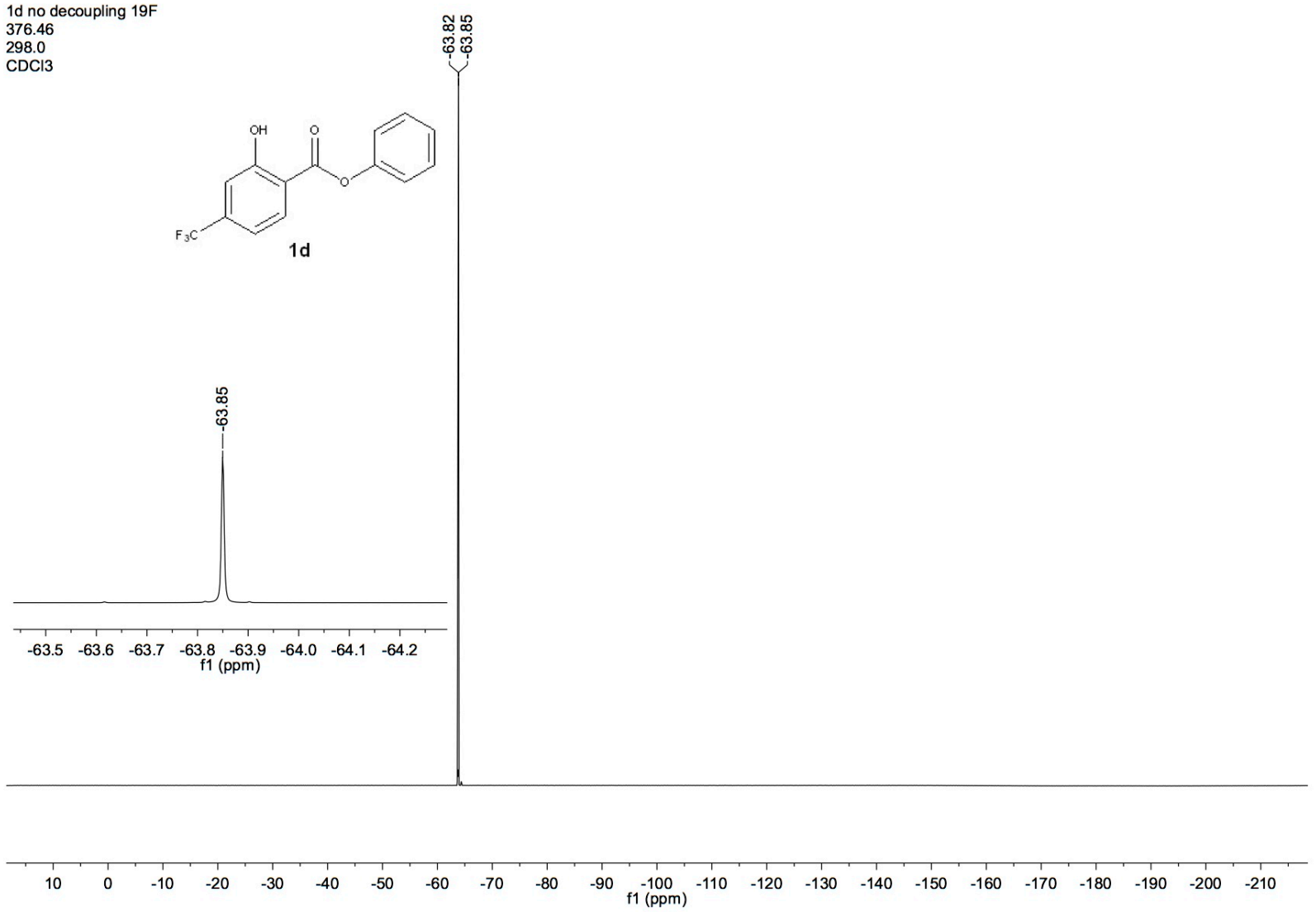
1c with {1H} decoupling 19F
376.46
298.0
CDCl3



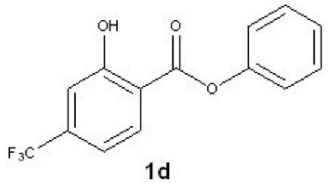
1c


1d proton
399.87
298.0
CDCl3
10.63
8.21
8.19
7.49
7.48
7.47
7.46
7.45
7.36
7.35
7.34
7.33
7.32
7.31
7.25 CHCl3
7.24
7.23
7.22
7.21
7.20
1.53 H2O
0.00 TMS
0.94
1.00
2.05
1.96
2.96
f1 (ppm)
1d
OH
O
O
CF3

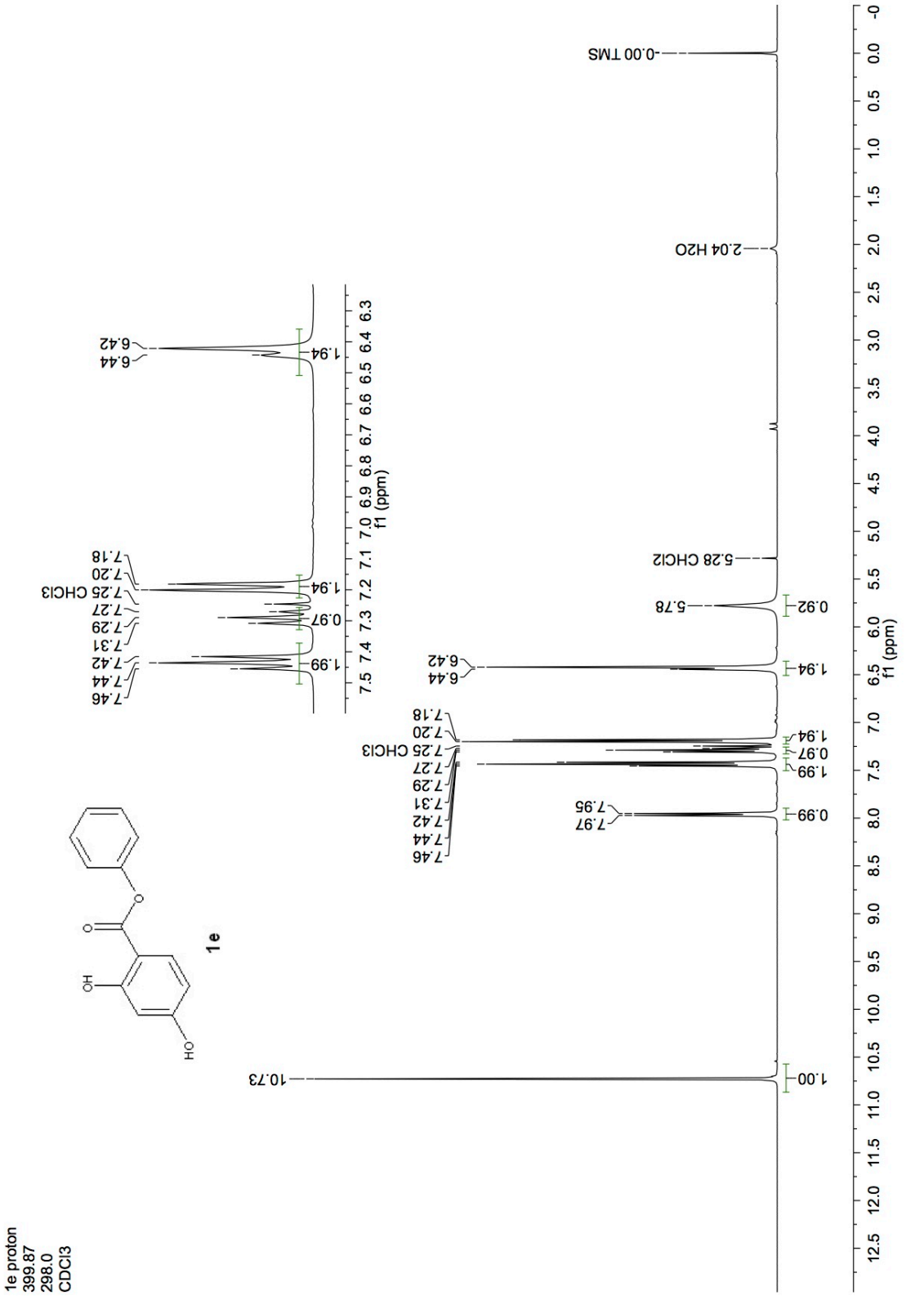

1d carbon
100.56
298.0
CDCl3
1d
f1 (ppm)
77.52 CDCl3
77.20 CDCl3
76.88 CDCl3
131.43
129.94
127.35
126.91
124.63
121.91
121.65
119.19
116.08
116.04
116.00
115.97
115.54
115.51
115.47
115.43
114.78
138.30
137.97
137.64
137.31
150.02
162.28
168.28

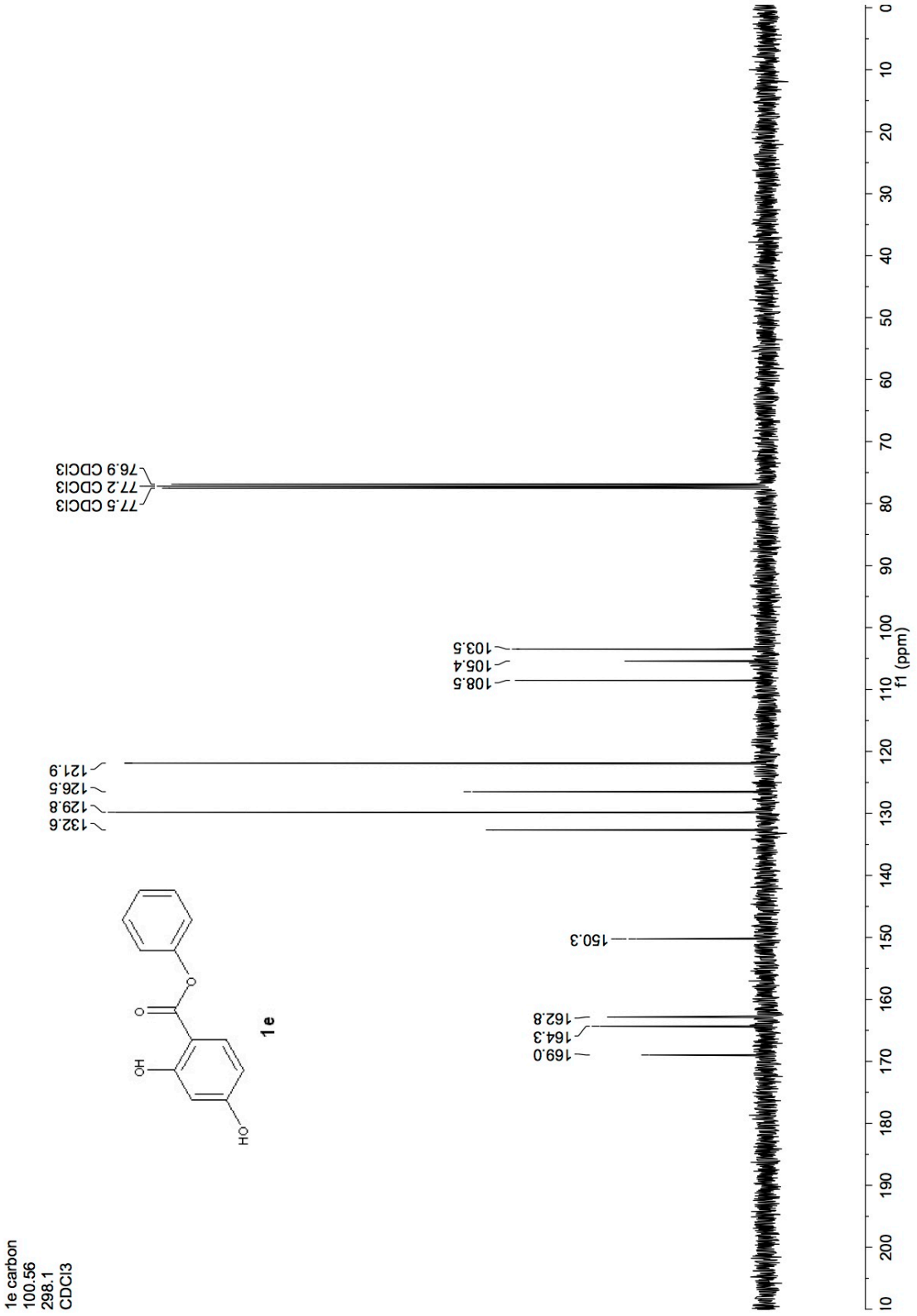

1d no decoupling 19F
376.46
298.0
CDCl3
-63.82
-63.85
OH
O
O
F3C
1d
-63.85
-63.5 -63.6 -63.7 -63.8 -63.9 -64.0 -64.1 -64.2
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

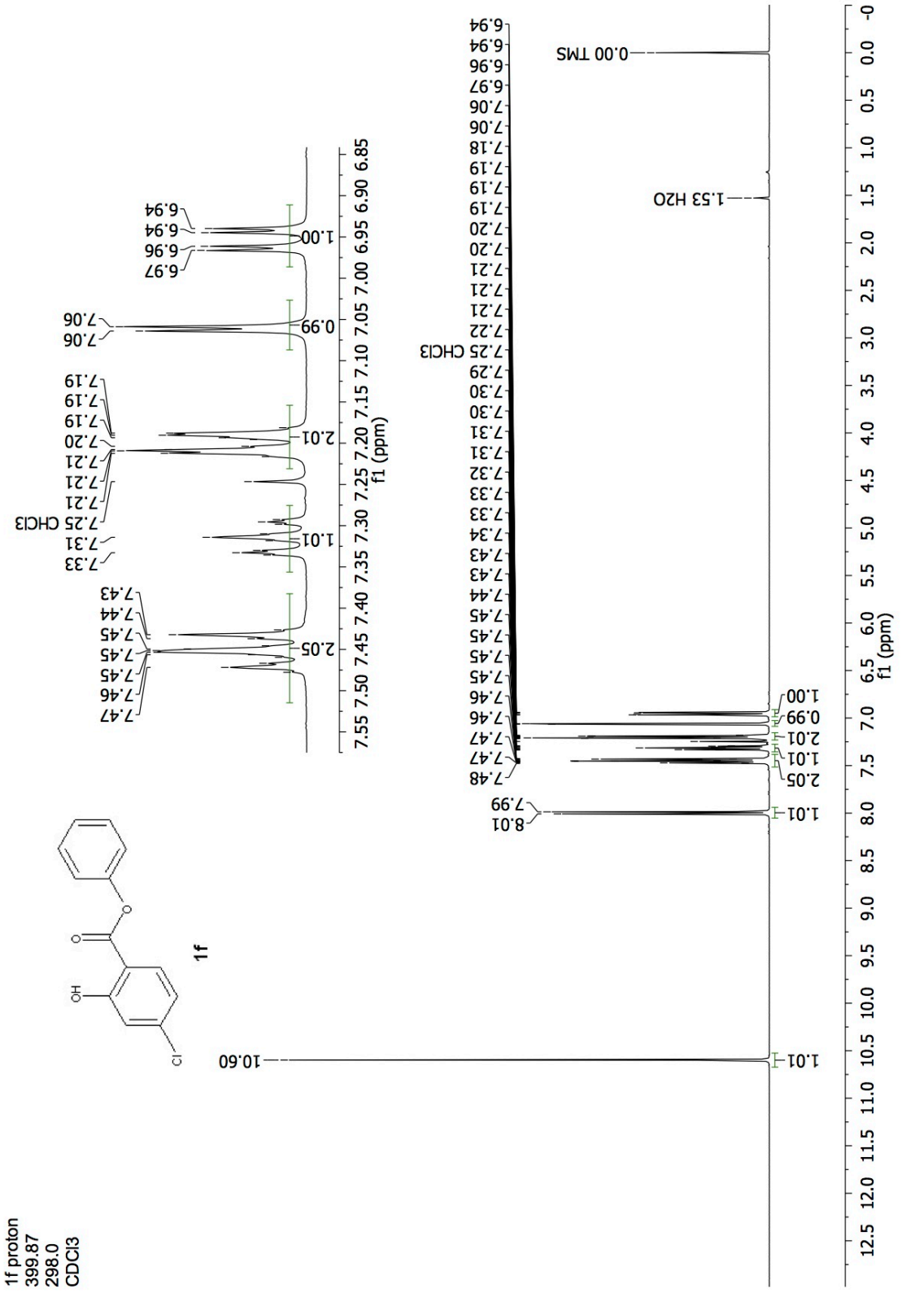
1d with {1H} decoupling 19F
376.46
298.1
CDCl3

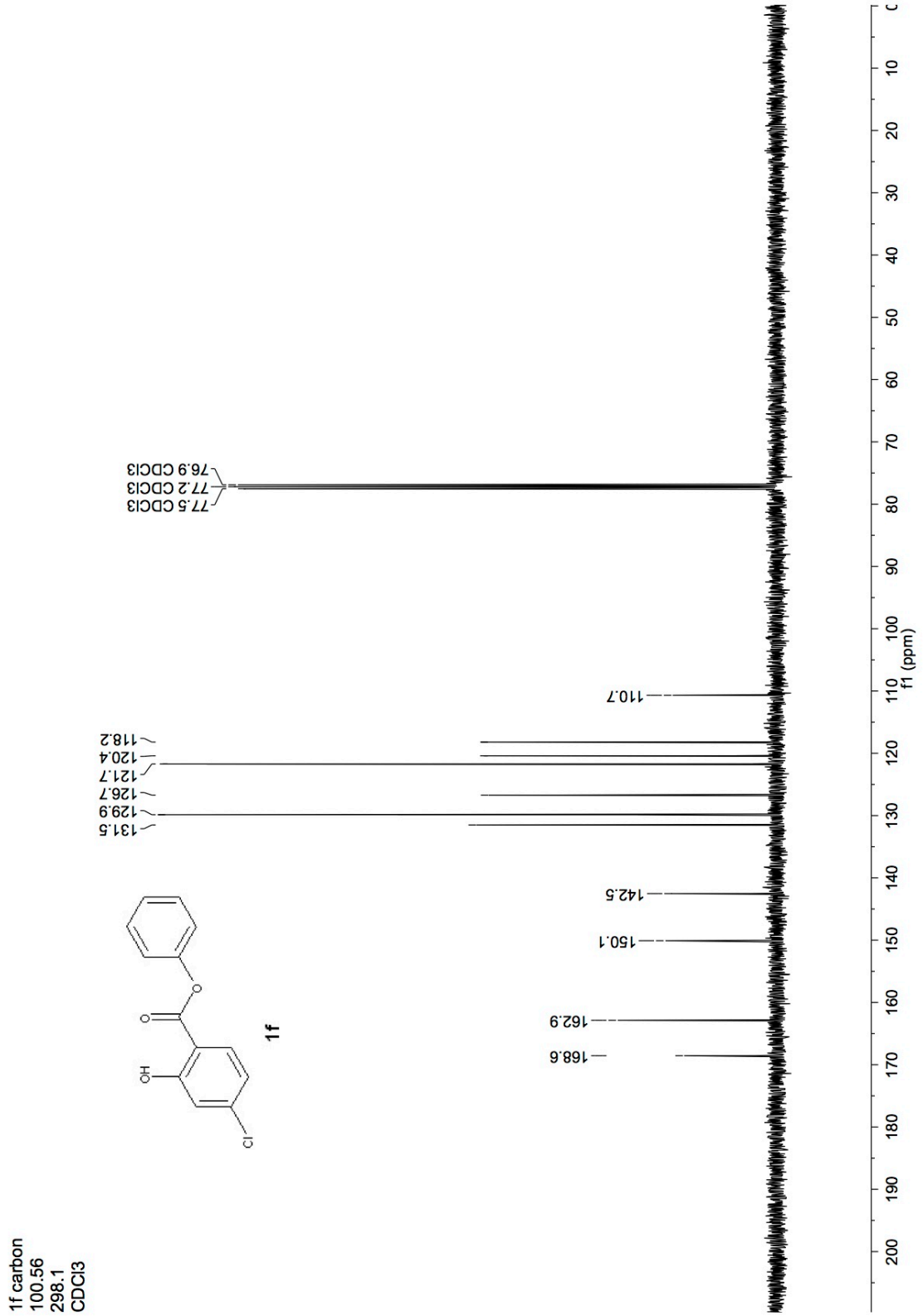


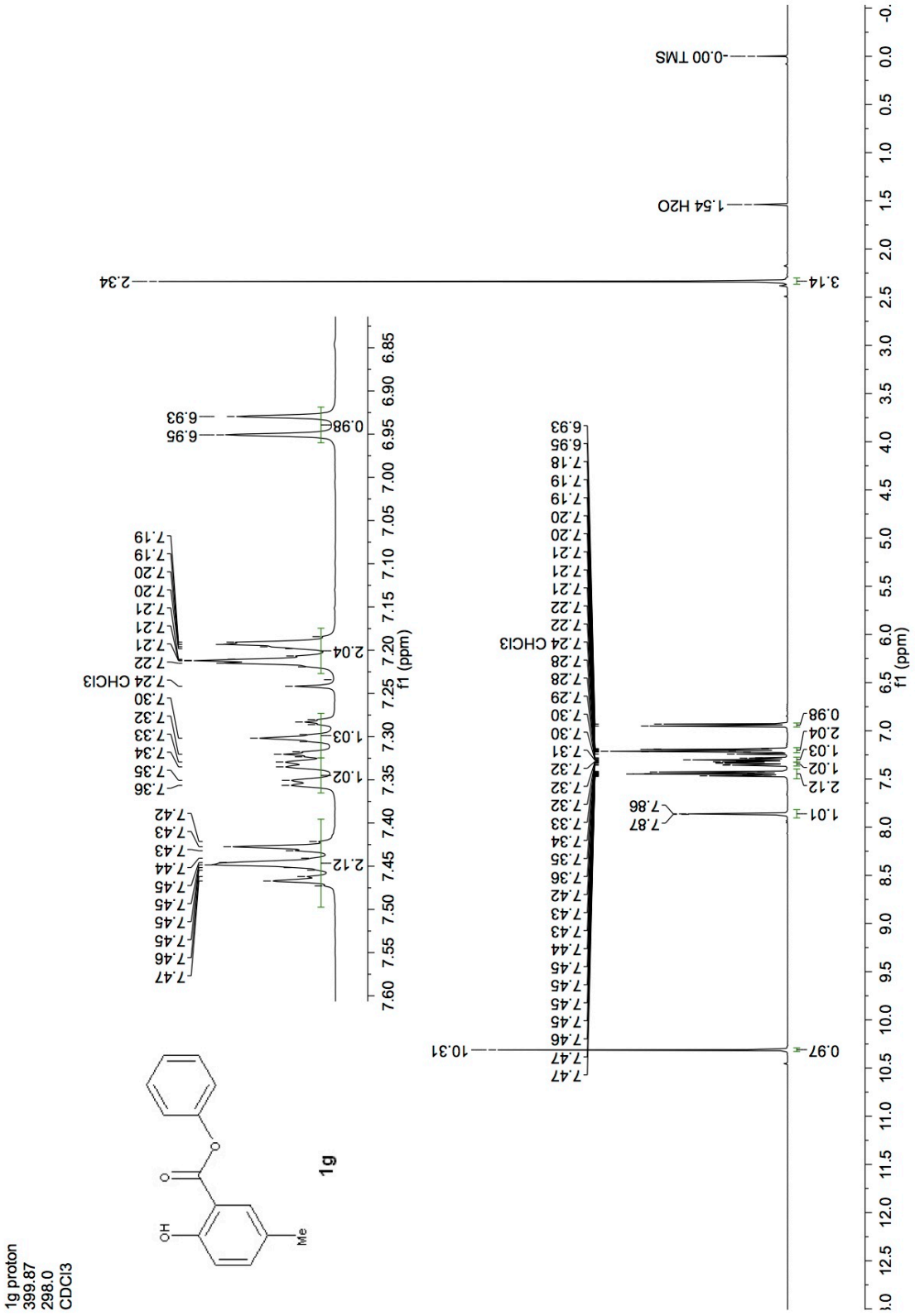
1d

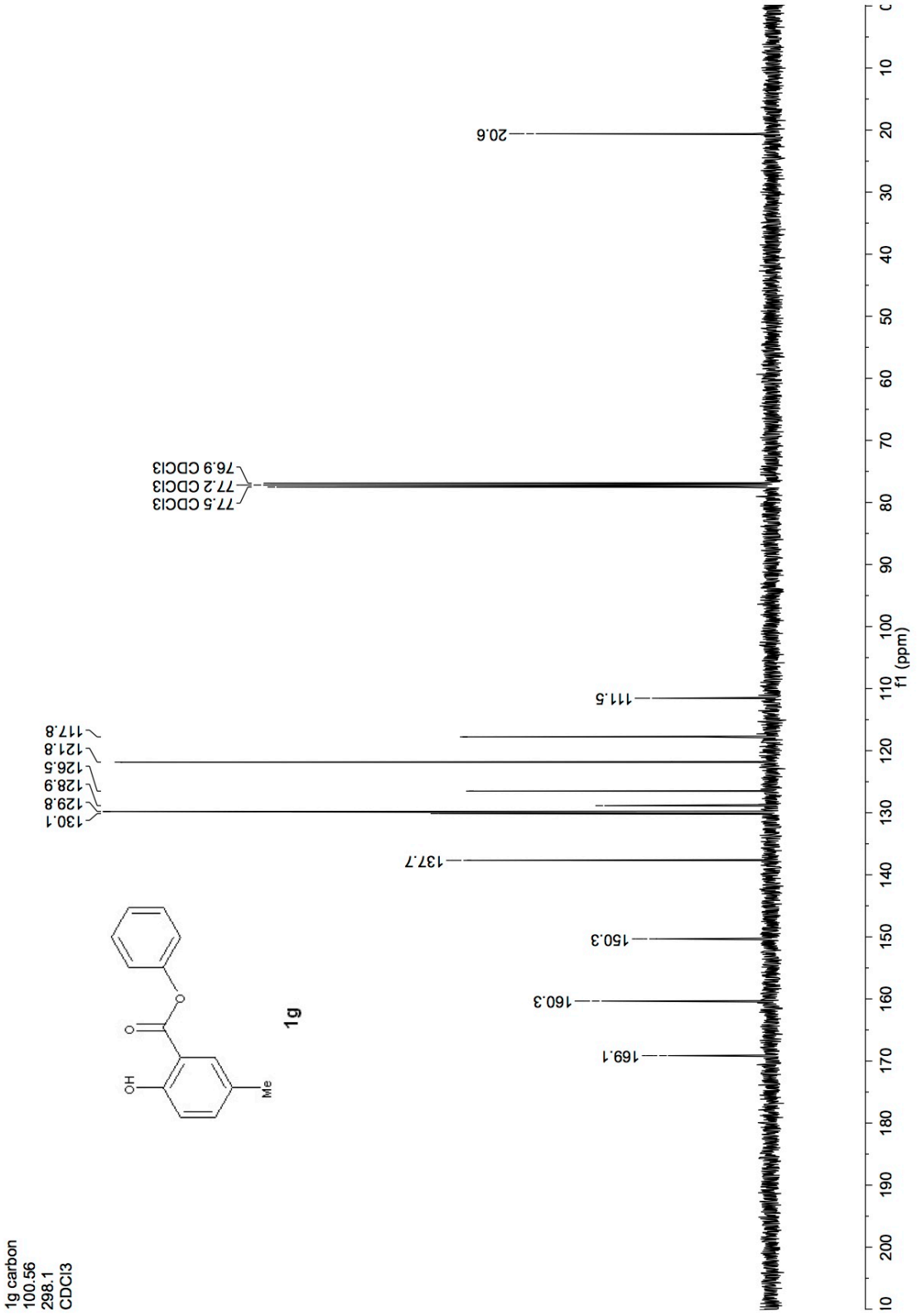

1e proton
399.87
298.0
CDCl3
1 e
10.73
7.97
7.95
7.46
7.44
7.42
7.31
7.29
7.27
7.25 CHCl3
7.20
7.18
6.44
6.42
5.78
5.28 CHCl2
2.04 H2O
0.00 TMS
1.00
0.99
1.99
0.97
1.94
0.92
f1 (ppm)

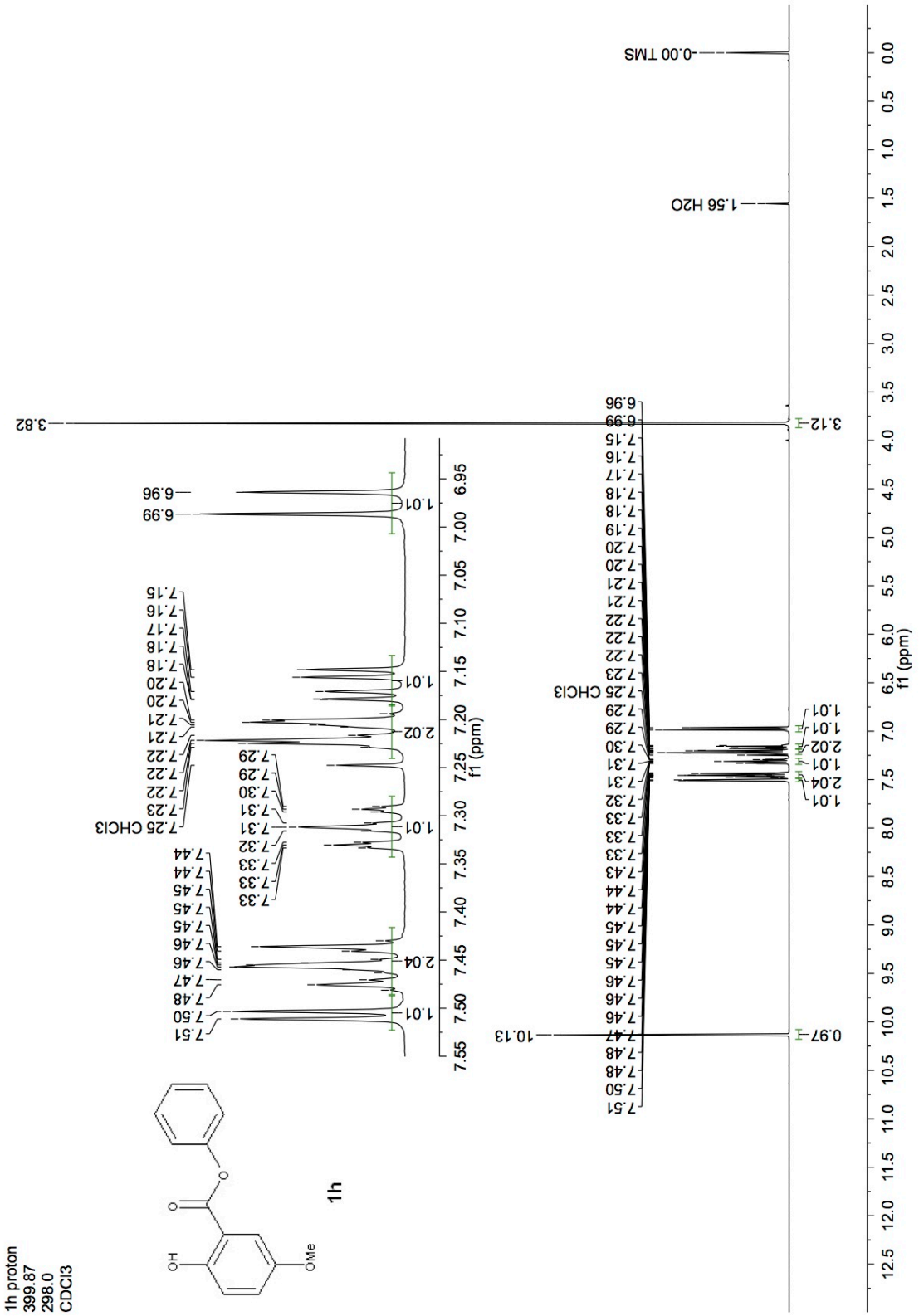

1e carbon
100.56
298.1
CDCl3
1e
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
132.6
129.8
126.5
121.9
108.5
105.4
103.5
150.3
169.0
164.3
162.8
f1 (ppm)

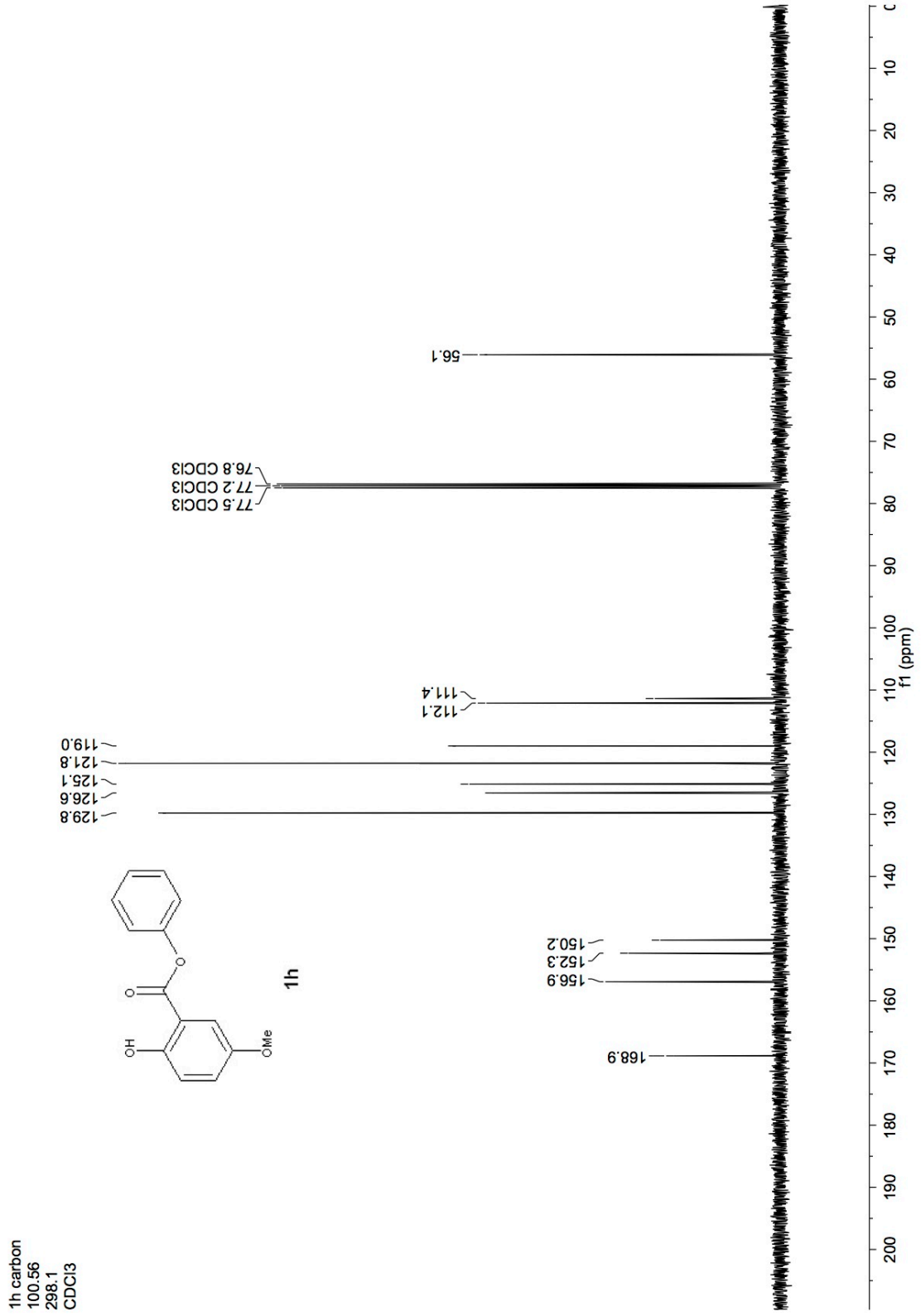

1f proton
399.87
298.0
CDCl3
1f
10.60
8.01
7.99
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.45
7.44
7.43
7.43
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.25 CHCl3
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.06
7.06
6.97
6.96
6.94
6.94
1.53 H2O
0.00 TMS
1.01
1.01
2.05
1.01
2.01
0.99
1.00
f1 (ppm)
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.33
7.31
7.25 CHCl3
7.21
7.21
7.20
7.19
7.19
7.19
7.06
7.06
6.97
6.96
6.94
6.94
2.05
1.01
2.01
0.99
1.00
f1 (ppm)


1f carbon
100.56
298.1
CDCl3
1f
168.6
162.9
150.1
142.5
131.5
129.9
126.7
121.7
120.4
118.2
110.7
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
f1 (ppm)

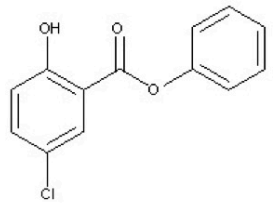

1g proton
399.87
298.0
CDCl3
1g
f1 (ppm)
CHCl3
TMS
H2O


1g carbon
100.56
298.1
CDCl3
1g
20.6
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
111.5
117.8
121.8
126.5
128.9
129.8
130.1
137.7
150.3
160.3
169.1
f1 (ppm)

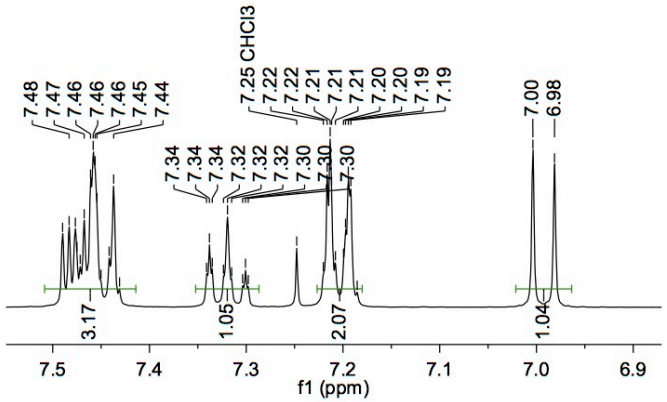

1h proton
399.87
298.0
CDCl3
1h
OH
OMe
0.00 TMS
1.56 H2O
CHCl3
f1 (ppm)

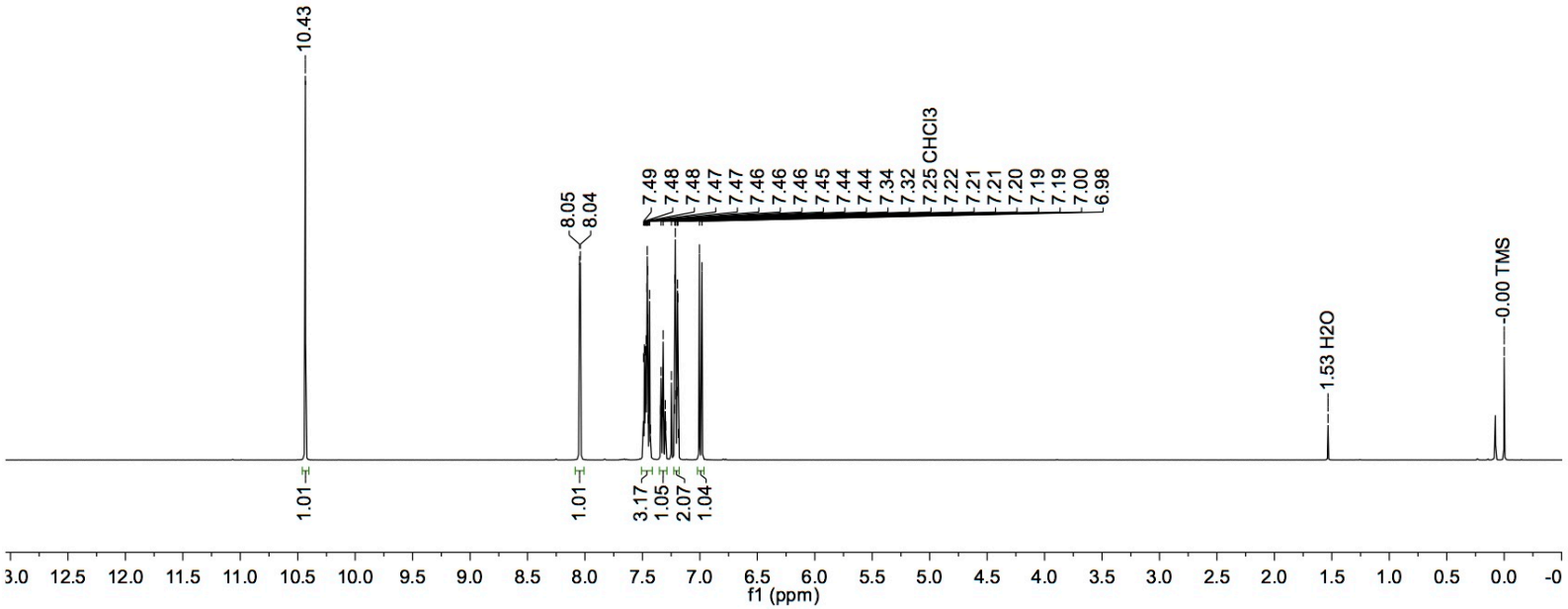

1h carbon
100.56
298.1
CDCl3
1h
OH
OMe
O
O
168.9
156.9
152.3
150.2
129.8
126.6
125.1
121.8
119.0
112.1
111.4
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.1
f1 (ppm)

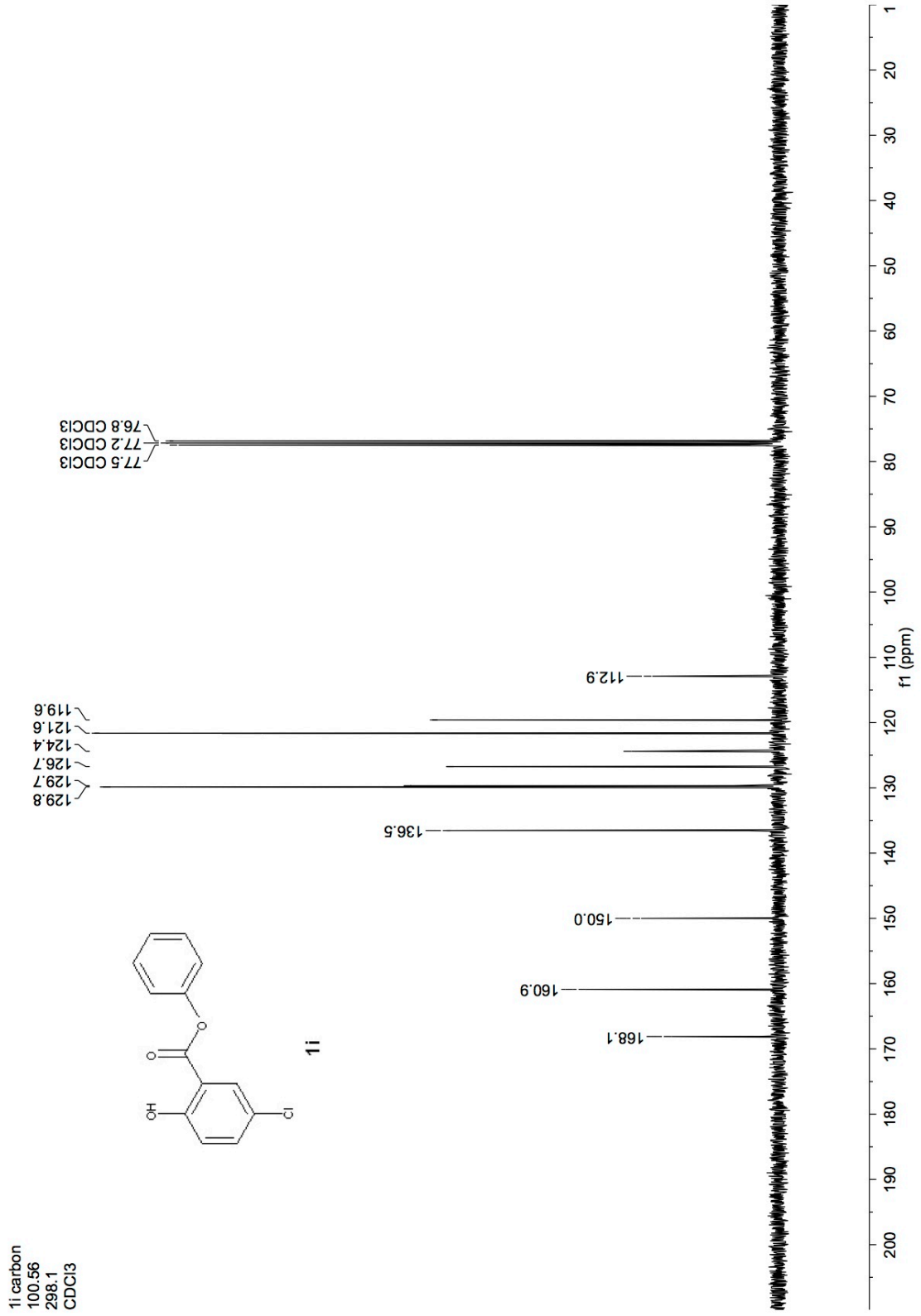
1i proton
399.87
298.0
CDCl3

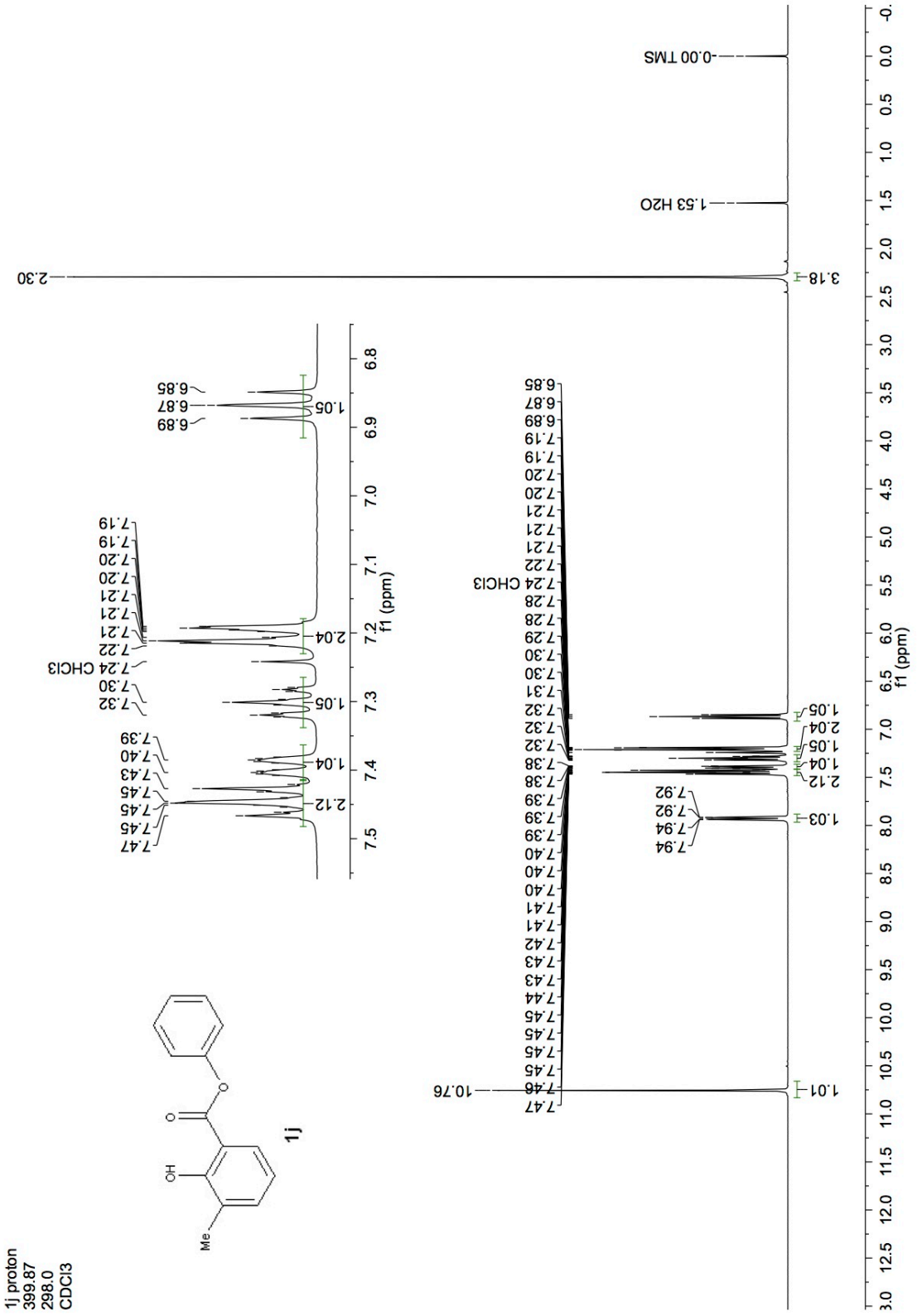


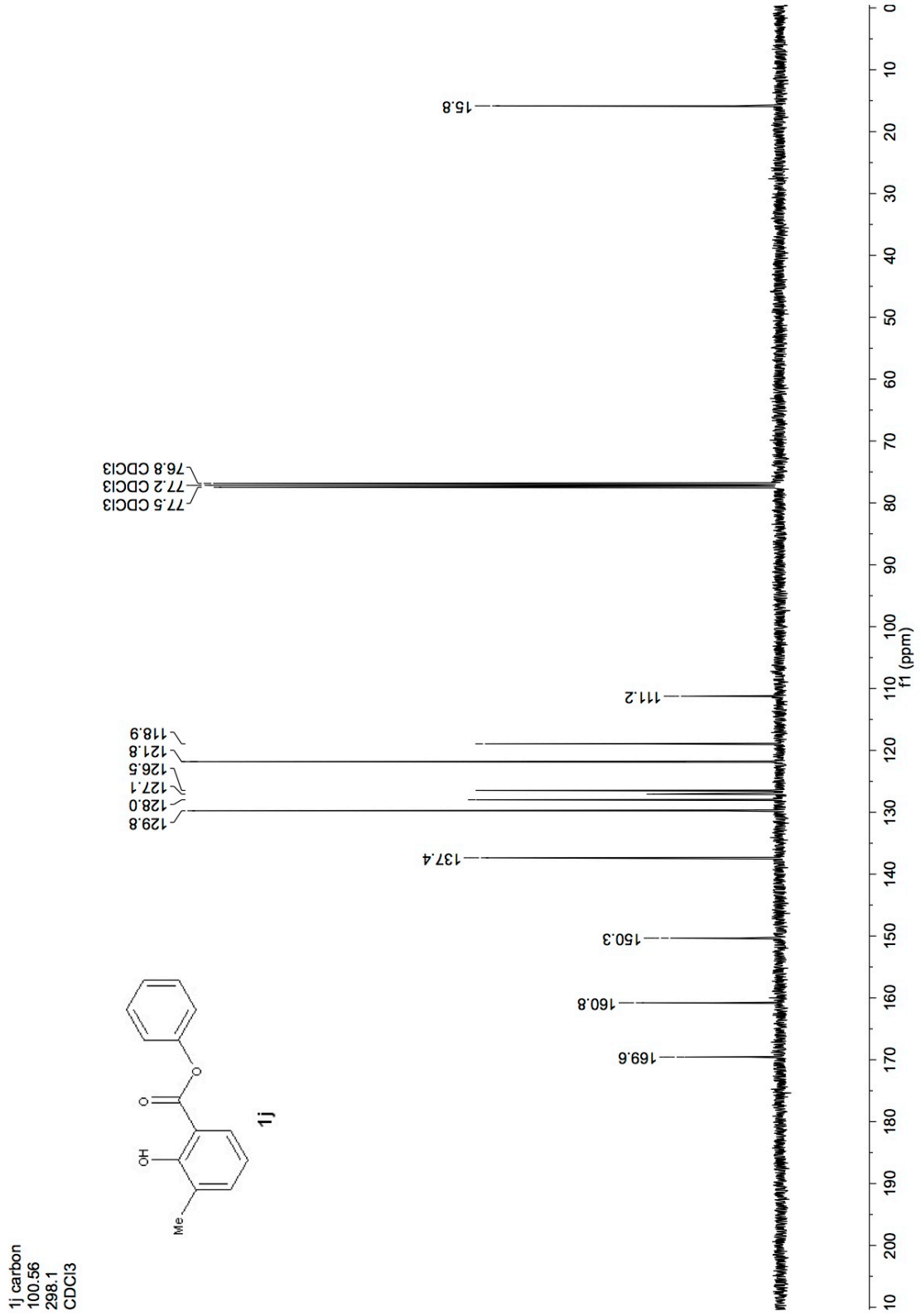
1i

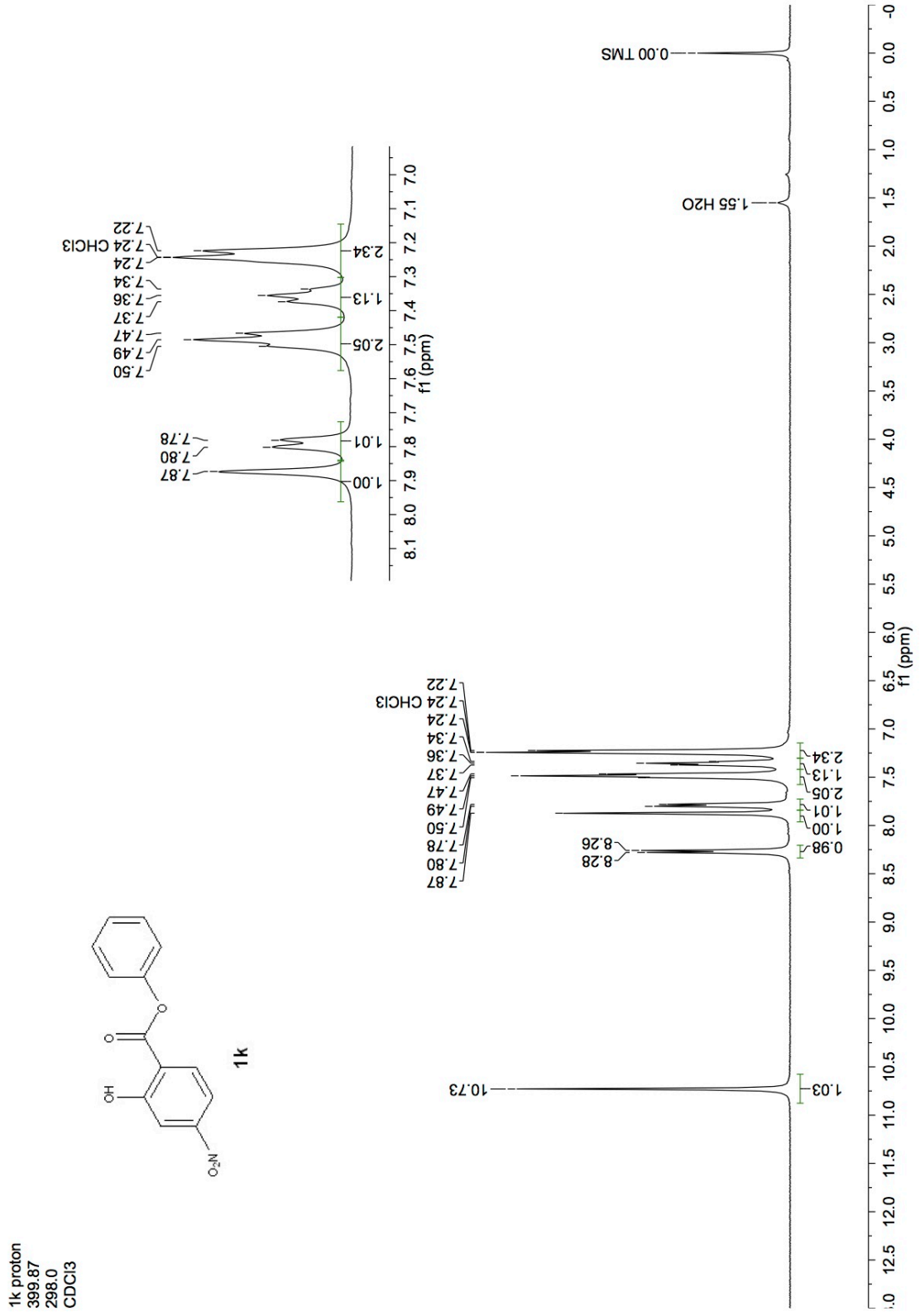


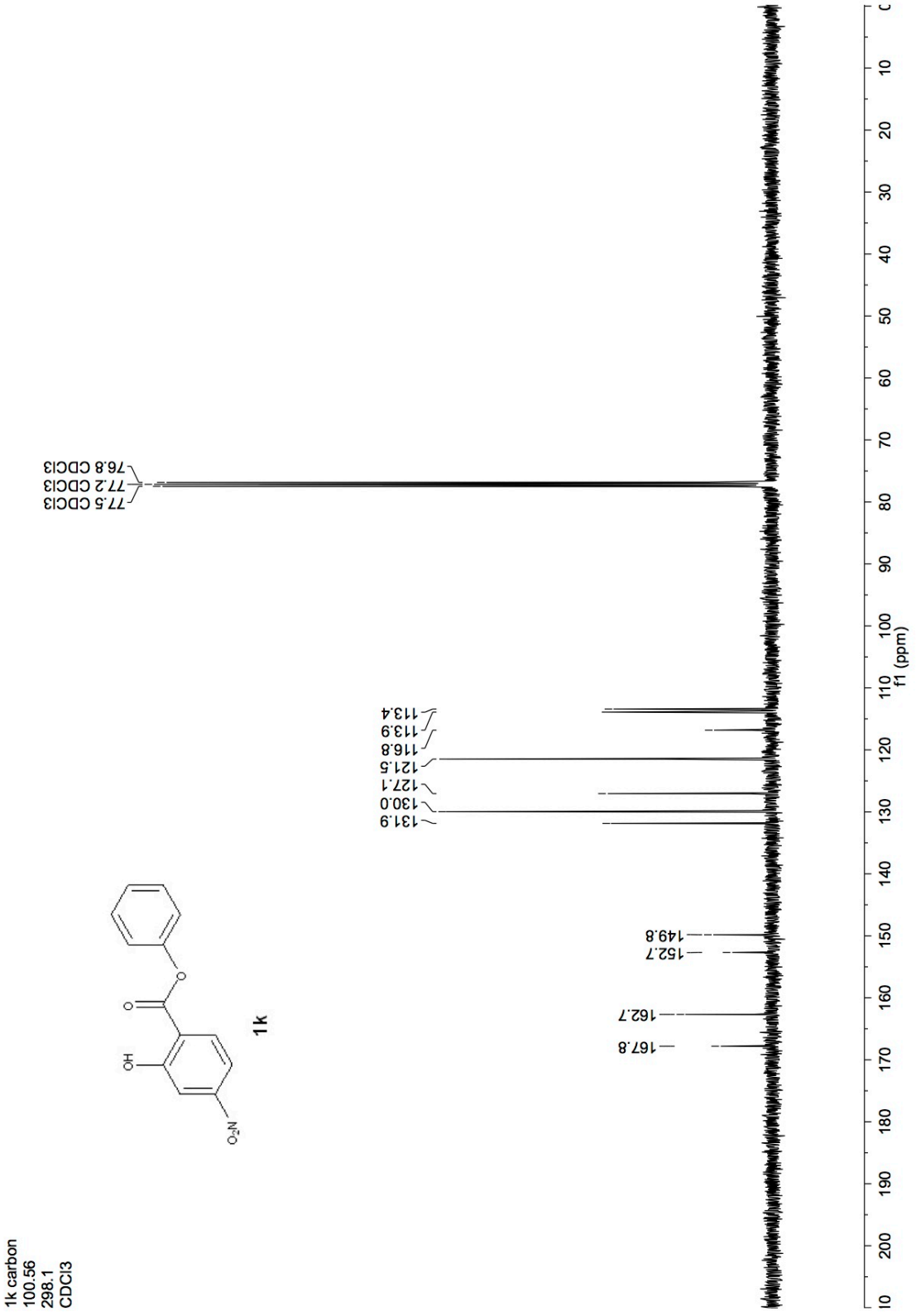


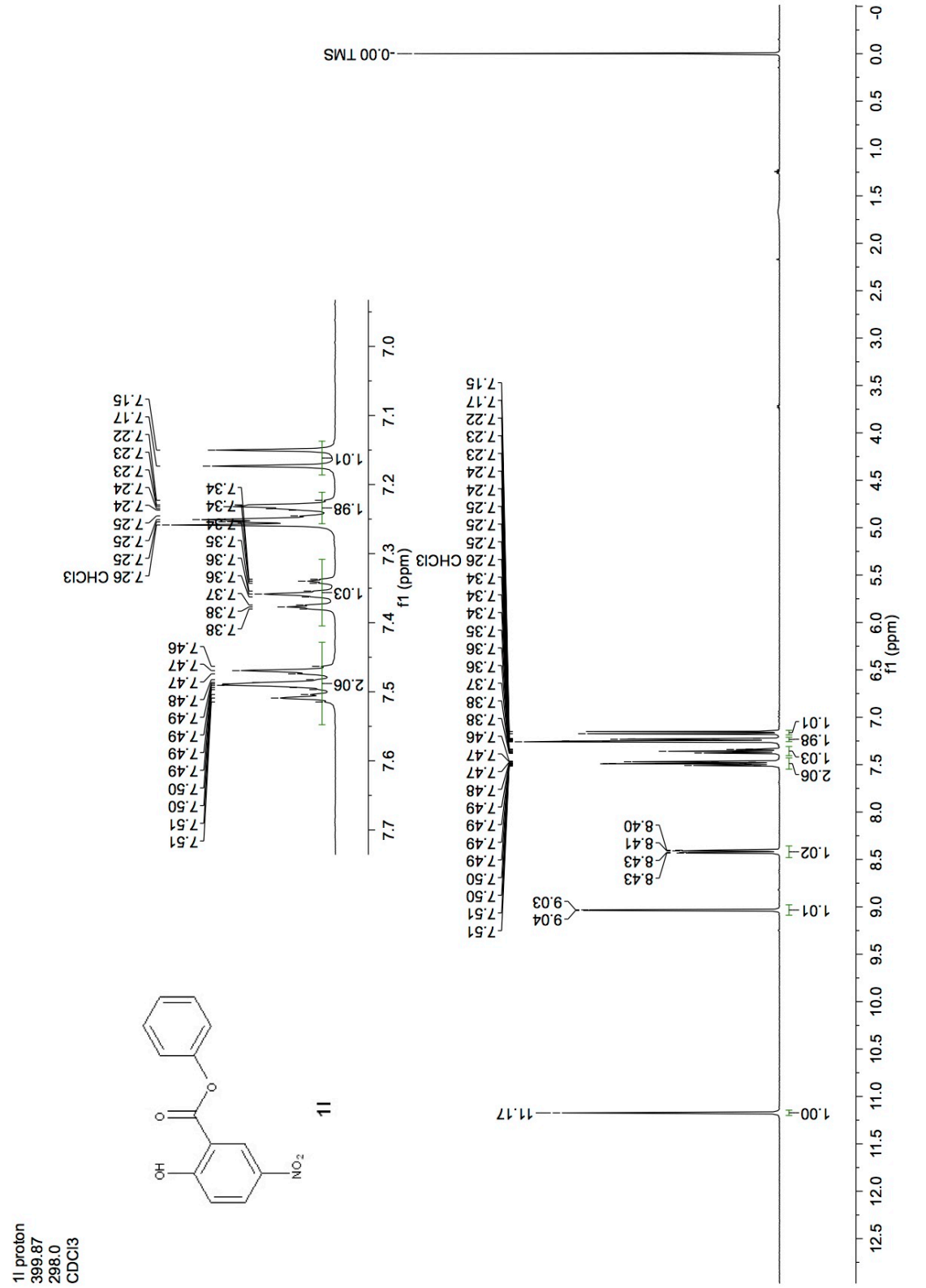

1i carbon
100.56
298.1
CDCl3
1i
168.1
160.9
150.0
136.5
129.8
129.7
126.7
124.4
121.6
119.6
112.9
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

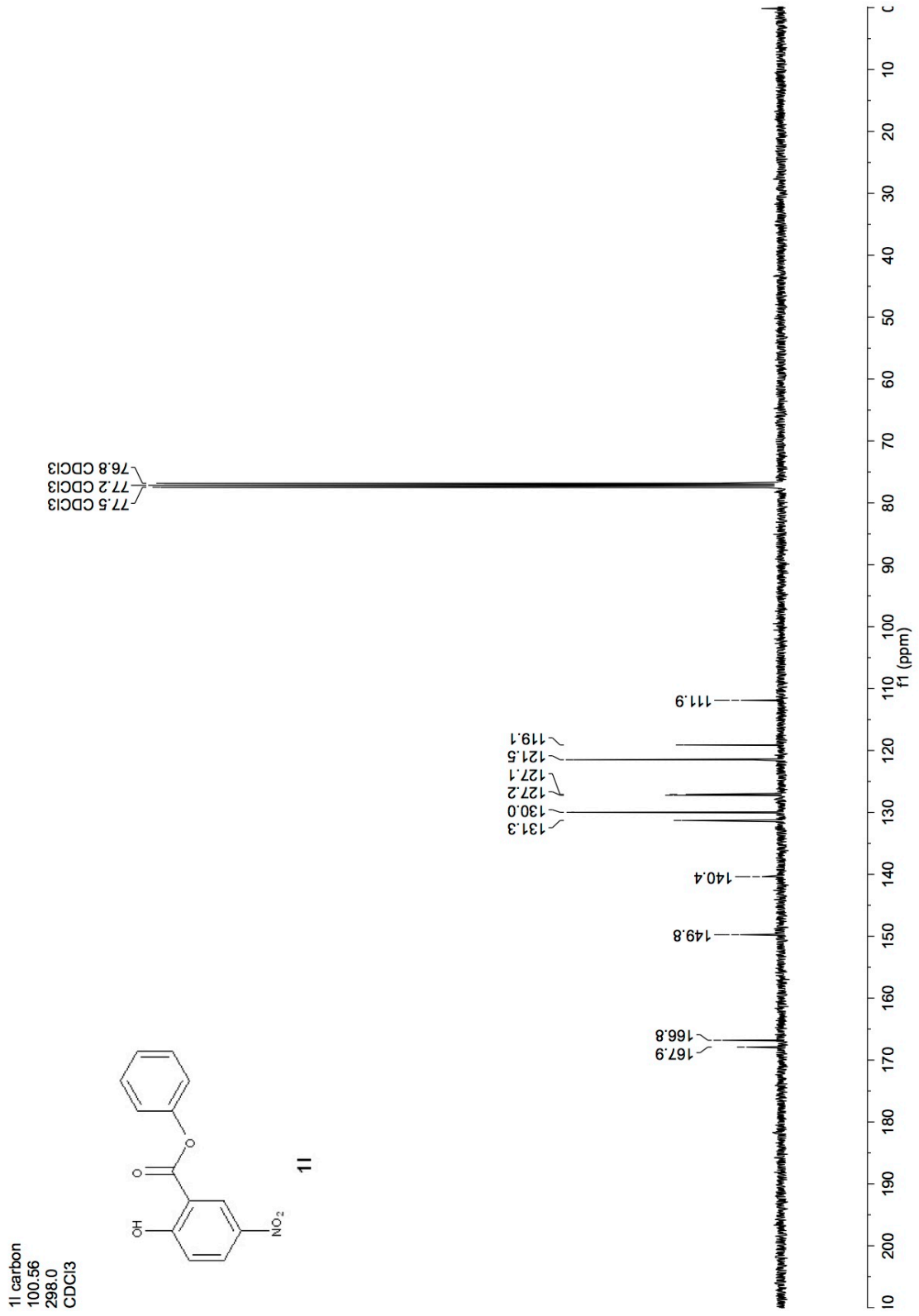

1j proton
399.87
298.0
CDCl3
1j
Me
OH
O
O
f1 (ppm)
-0.00 TMS
1.53 H2O
CHCl3
2.30
3.18
10.76
1.01
1.03
2.12
1.04
1.05
2.04
1.05
1.05

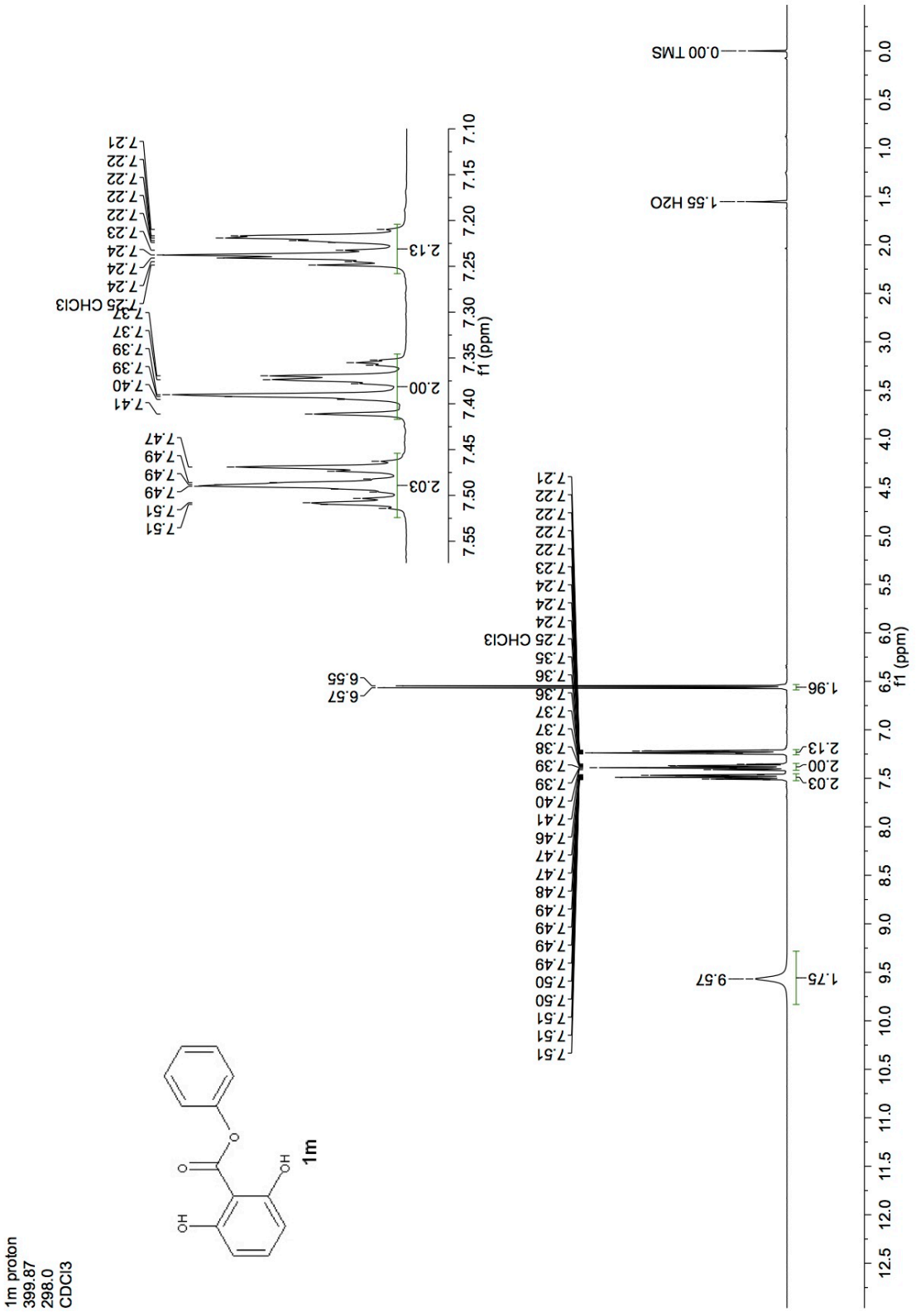

1j carbon
100.56
298.1
CDCl3
Me
OH
O
O
1j
169.6
160.8
150.3
137.4
129.8
128.0
127.1
126.5
121.8
118.9
111.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
15.8
f1 (ppm)

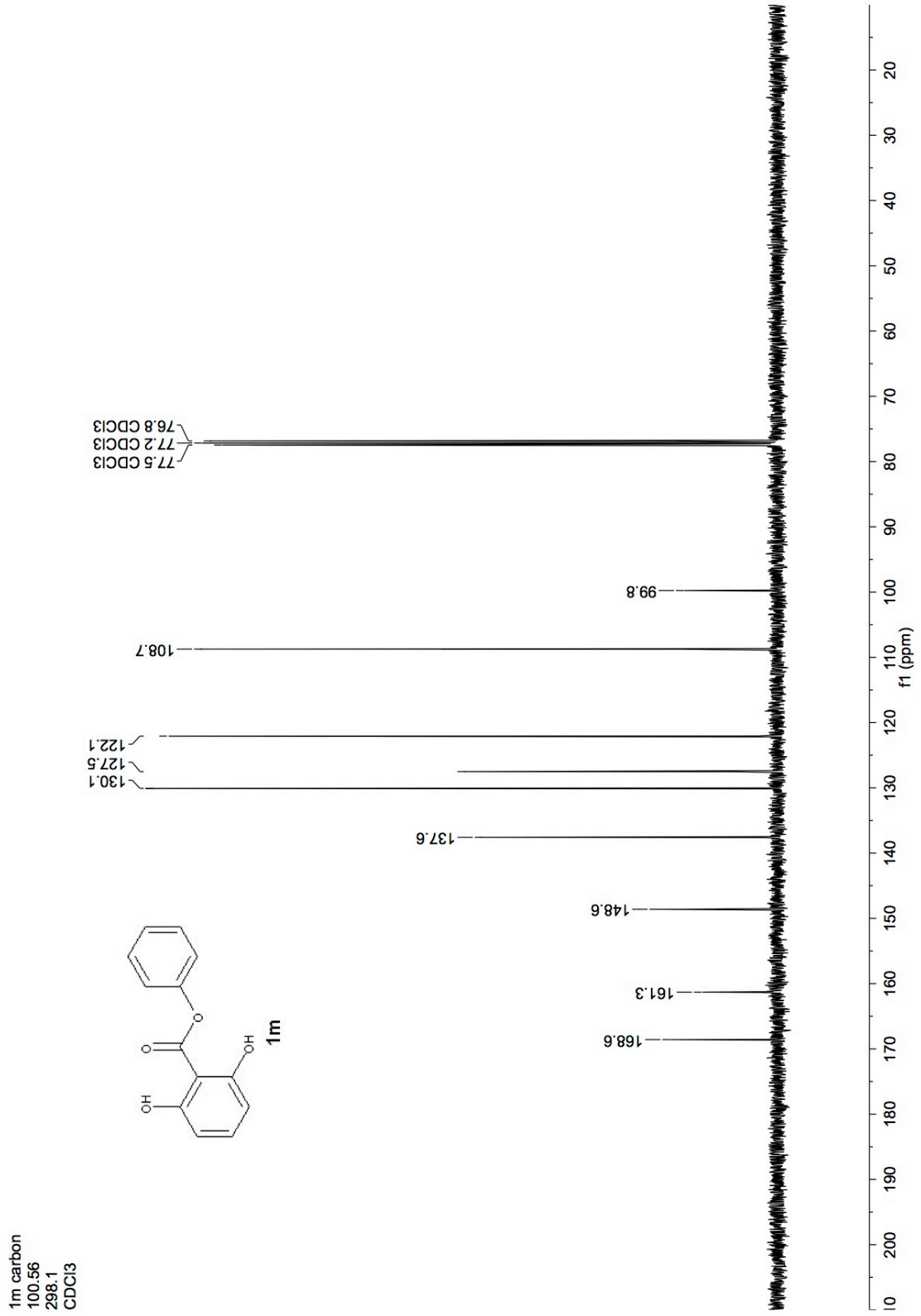

1k proton
399.87
298.0
CDCl3
1k
f1 (ppm)
0.00 TMS
1.55 H2O
CHCl3

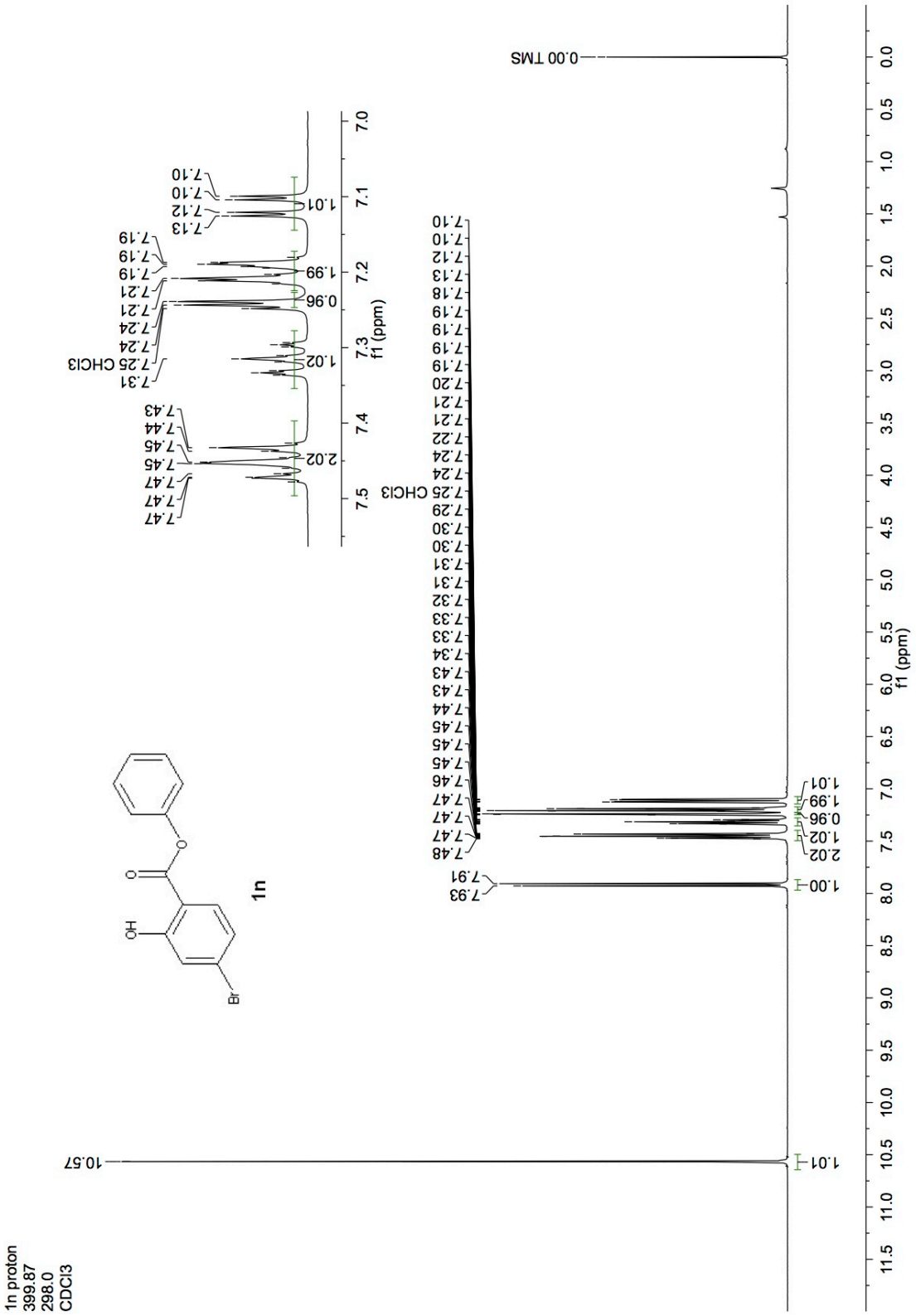

1k carbon
100.56
298.1
CDCl3
1k
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
131.9
130.0
127.1
121.5
116.8
113.9
113.4
167.8
162.7
152.7
149.8
f1 (ppm)

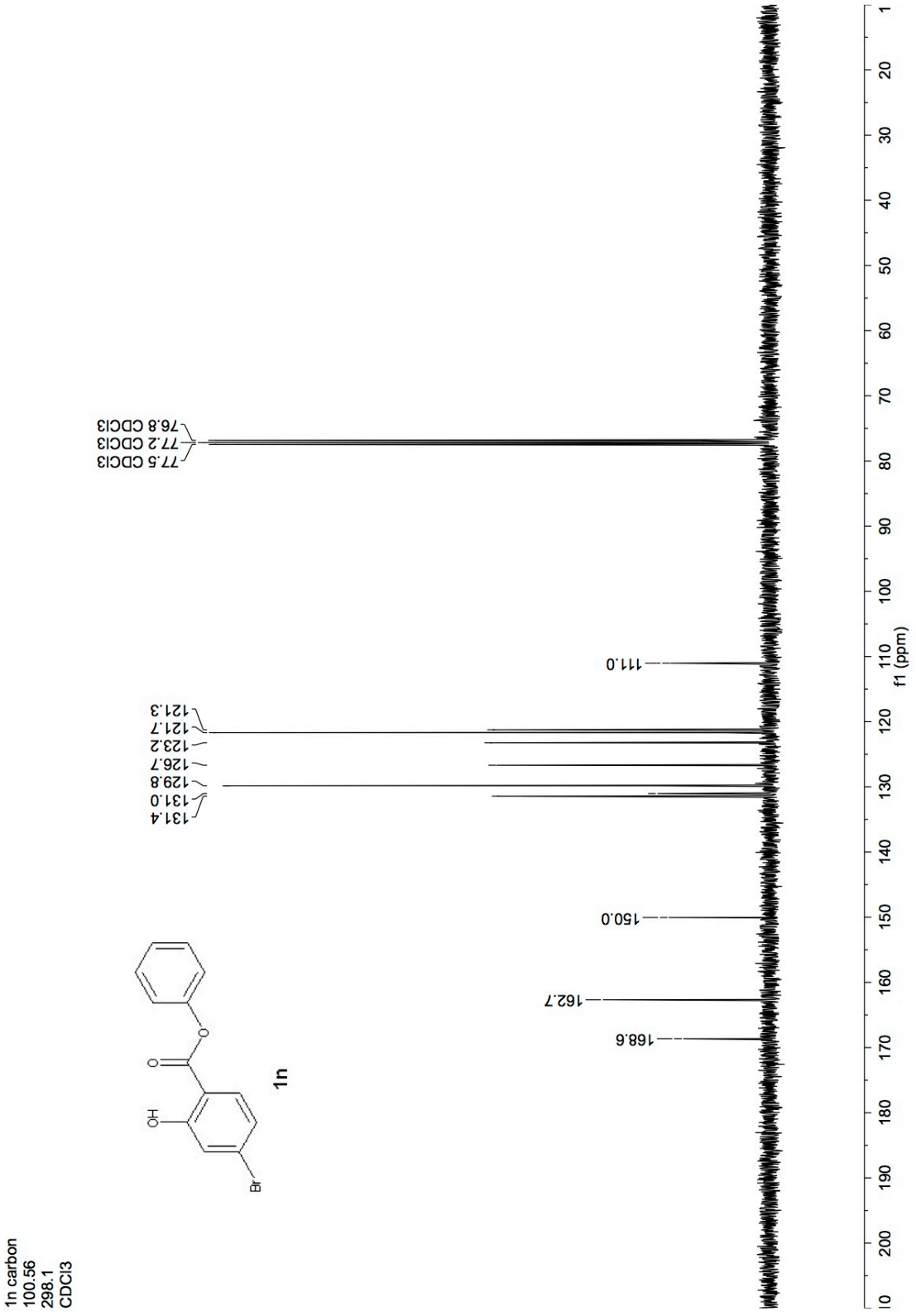

1l proton
399.87
298.0
CDCl3
1l
0.00 TMS
CHCl3
f1 (ppm)

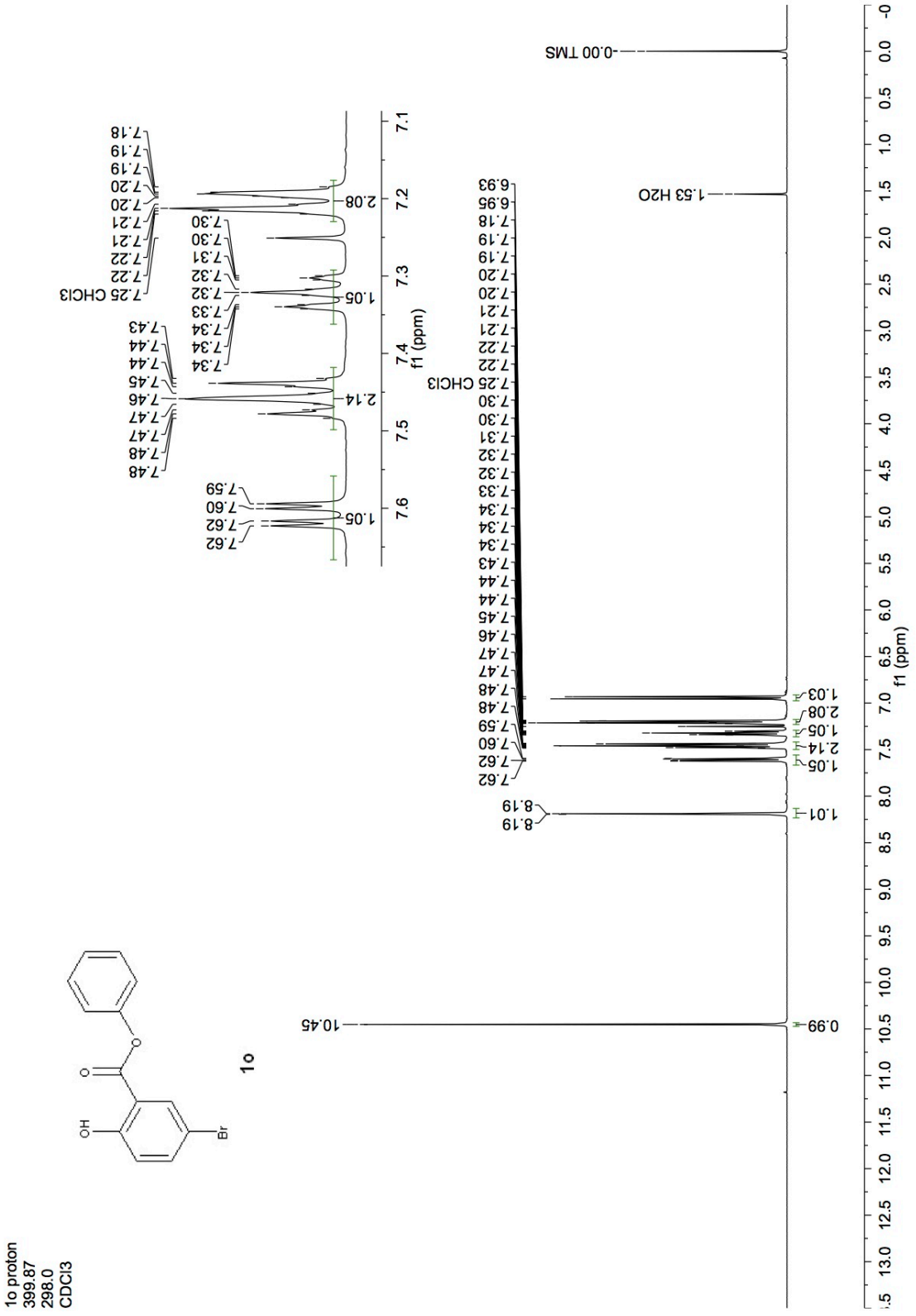

1l carbon
100.56
298.0
CDCl3
1l
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
111.9
119.1
121.5
127.1
127.2
130.0
131.3
140.4
149.8
166.8
167.9
f1 (ppm)

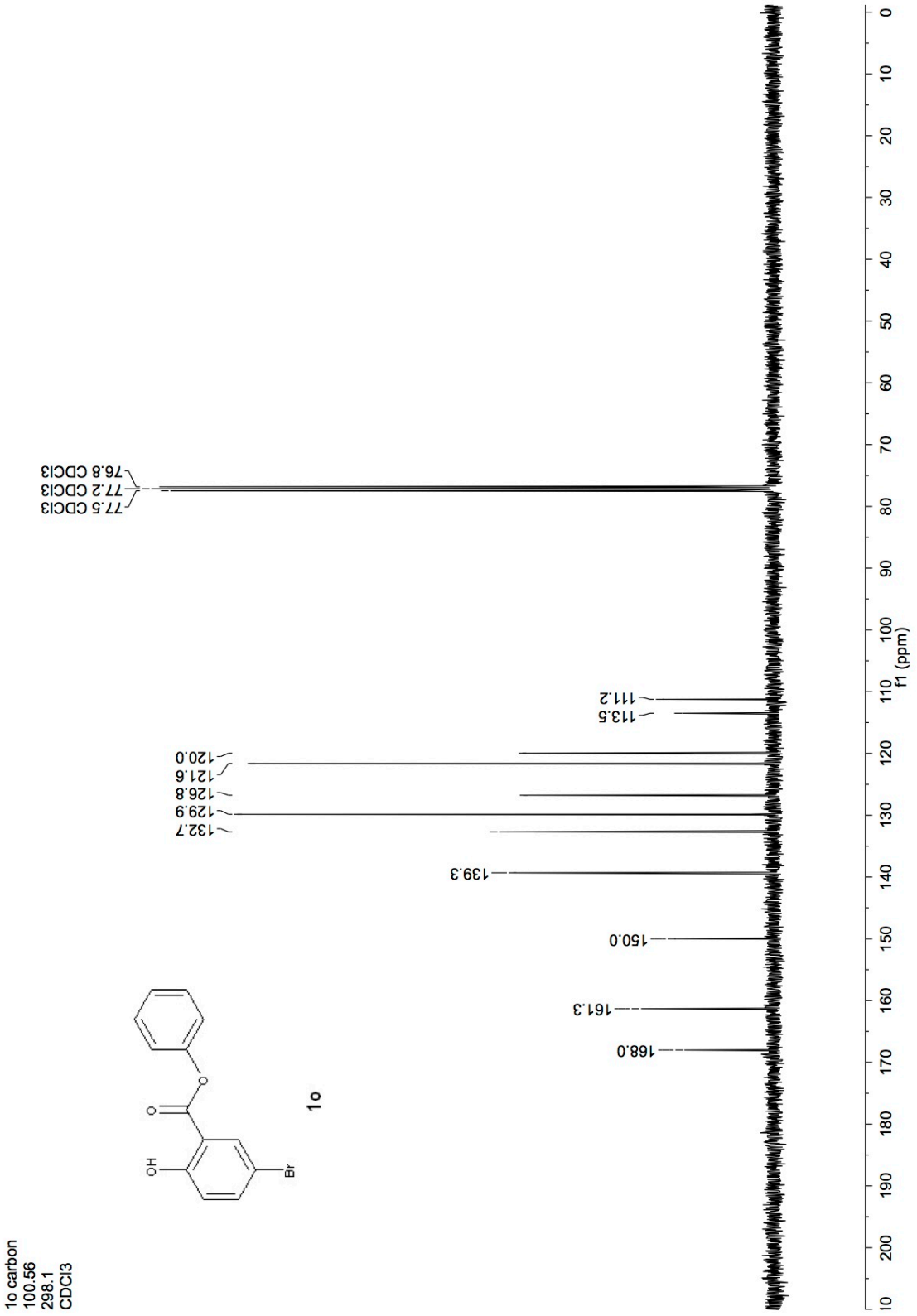

1m proton
399.87
298.0
CDCl3
1m
0.00 TMS
1.55 H2O
CHCl3
f1 (ppm)

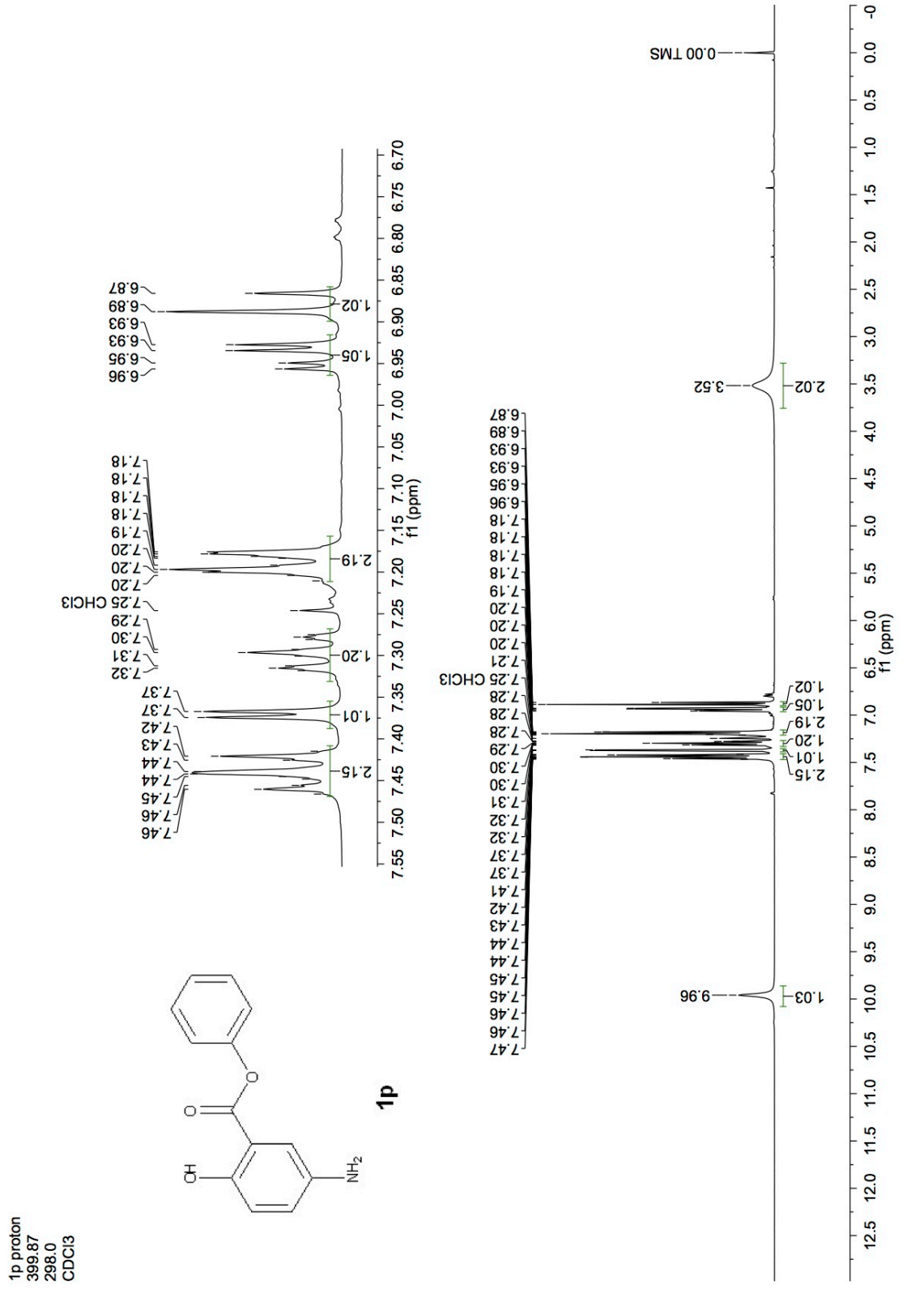

1m carbon
100.56
298.1
CDCl3
1m
168.6
161.3
148.6
137.6
130.1
127.5
122.1
108.7
99.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

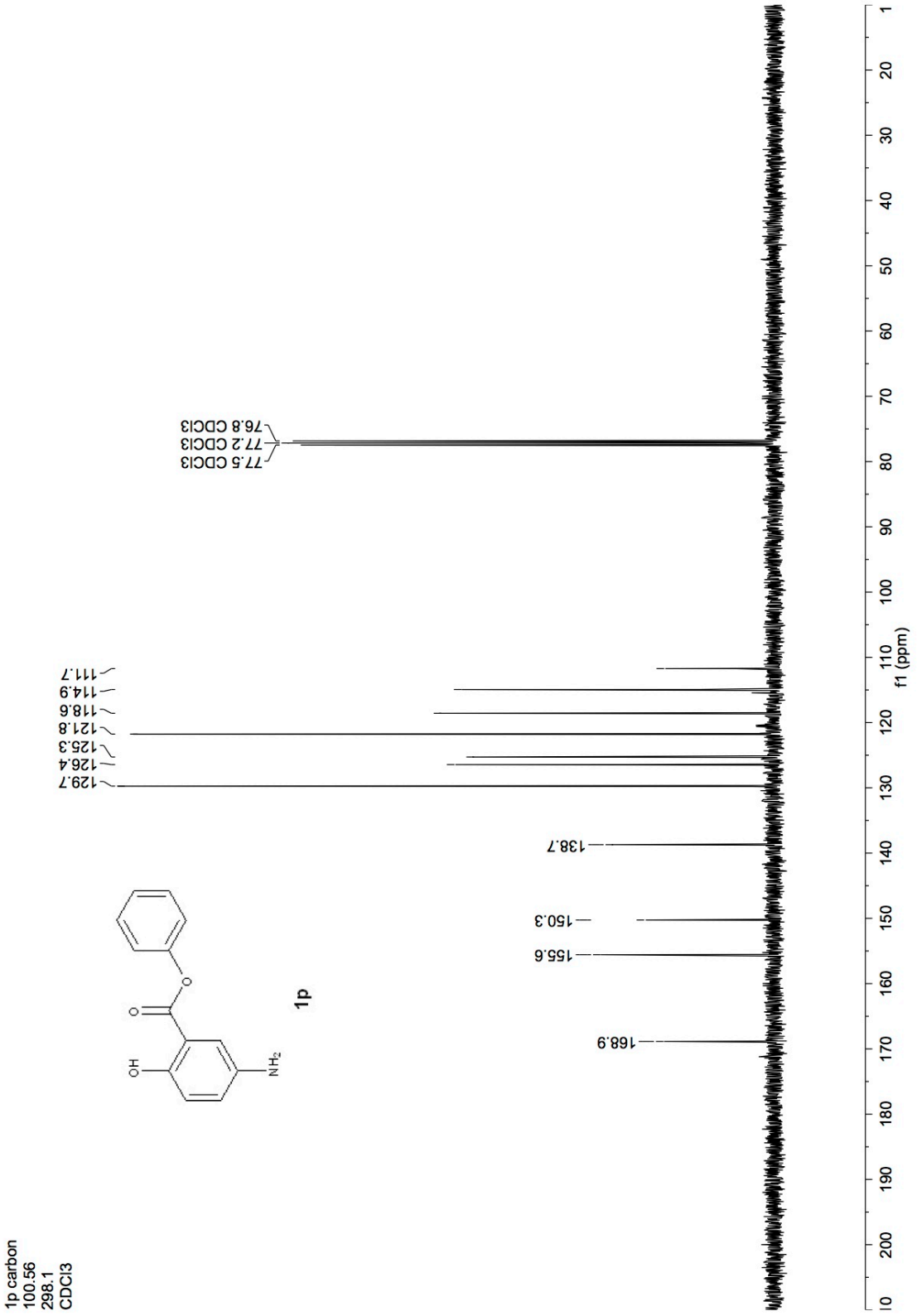

1n proton
399.87
298.0
CDCl3
10.57
1.01
7.93
7.91
7.48
7.47
7.47
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.25 CHCl3
7.24
7.24
7.22
7.21
7.21
7.20
7.19
7.19
7.19
7.19
7.18
7.13
7.12
7.10
7.10
2.02
1.02
0.96
1.99
1.01
1.00
0.00 TMS
f1 (ppm)
7.47
7.47
7.45
7.45
7.44
7.43
2.02
7.31
7.25 CHCl3
7.24
7.24
7.21
7.21
7.19
7.19
7.19
1.02
0.96
1.99
7.13
7.12
7.10
7.10
1.01
f1 (ppm)
1n
OH
O
O
Br

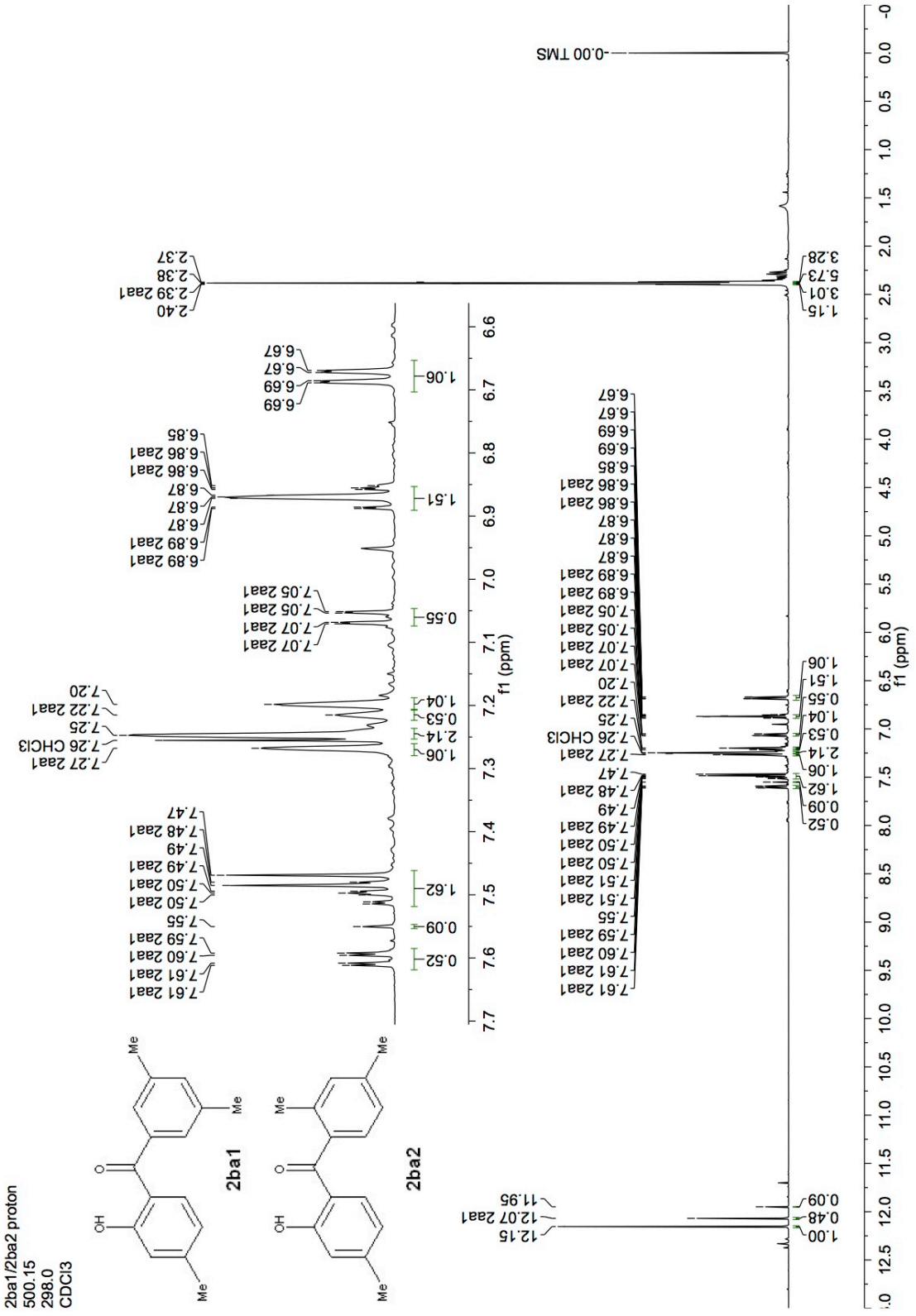

1n carbon
100.56
298.1
CDCl3
1n
Br
OH
O
O
168.6
162.7
150.0
131.4
131.0
129.8
126.7
123.2
121.7
121.3
111.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

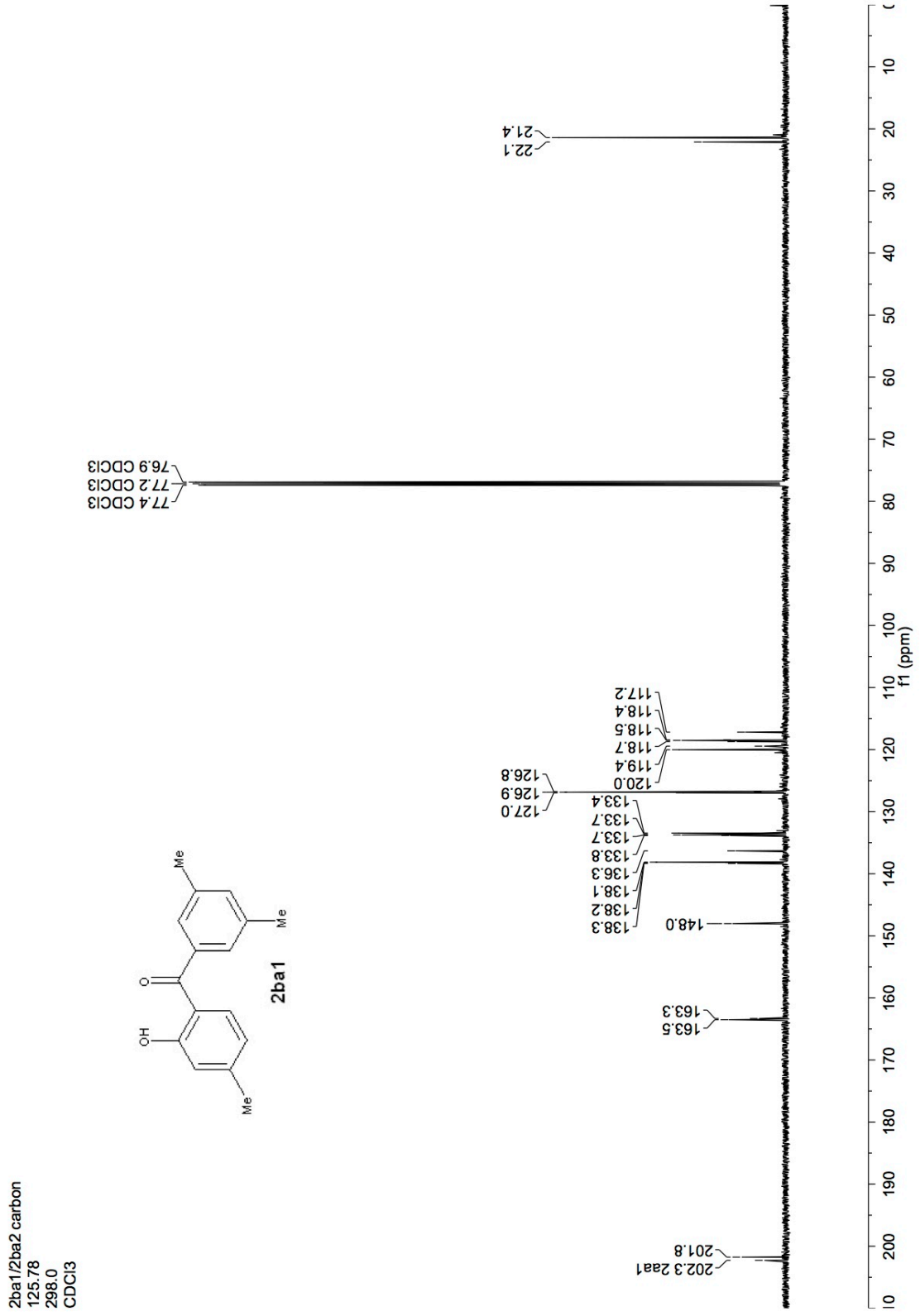

1o proton
399.87
298.0
CDCl3
1o
OH
O
O
Br
10.45
0.99
1.01
8.19
8.19
1.05
2.14
1.05
2.08
1.03
7.62
7.62
7.60
7.59
7.48
7.48
7.47
7.47
7.46
7.45
7.44
7.44
7.43
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.25 CHCl3
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
6.95
6.93
1.53 H2O
0.00 TMS
f1 (ppm)
7.62
7.62
1.05
7.59
7.60
7.48
7.48
2.14
7.47
7.47
7.46
7.45
7.44
7.44
7.43
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.25 CHCl3
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.19
7.18
2.08
1.05
f1 (ppm)

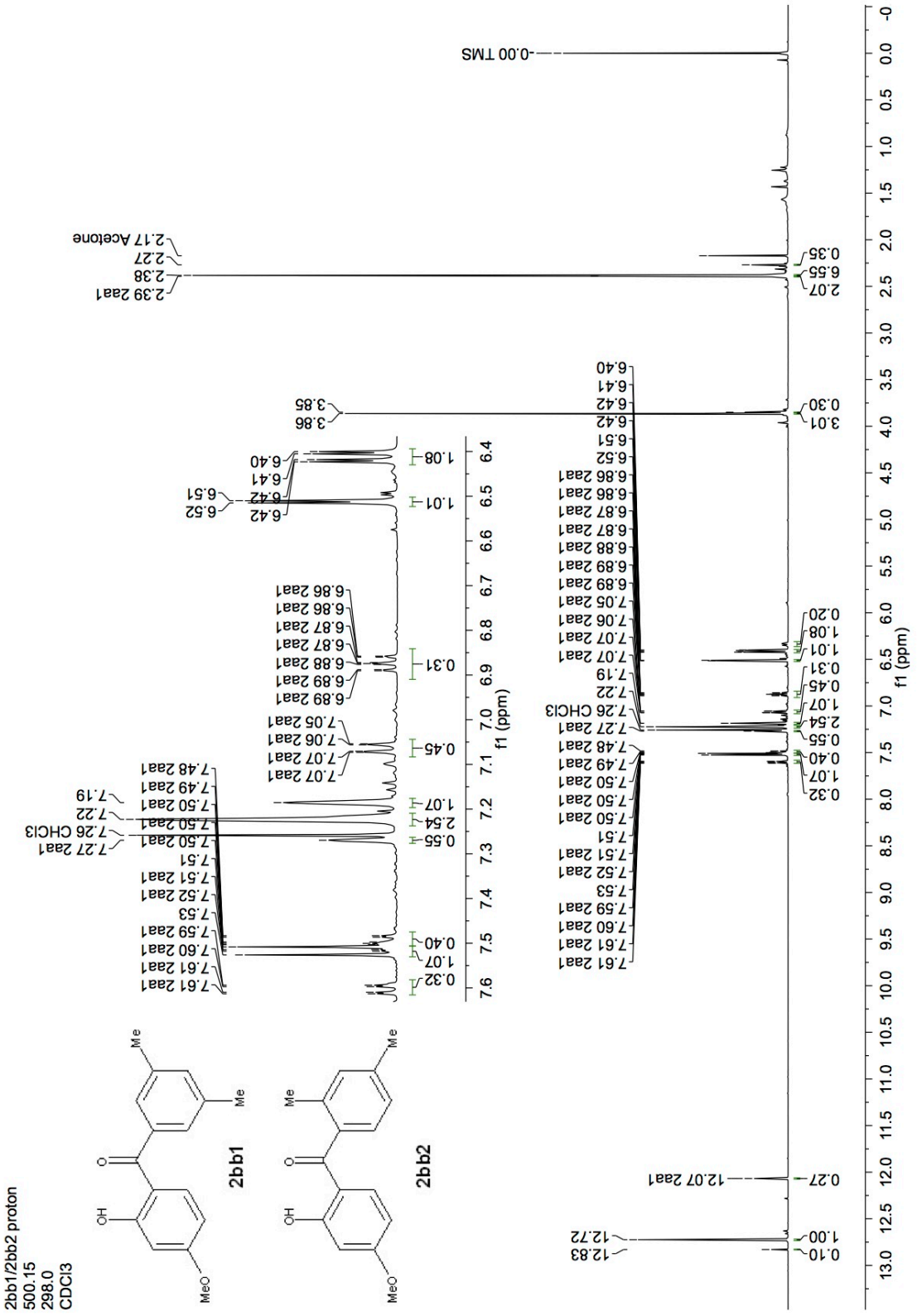

1o carbon
100.56
298.1
CDCl3
1o
168.0
161.3
150.0
139.3
132.7
129.9
126.8
121.6
120.0
113.5
111.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

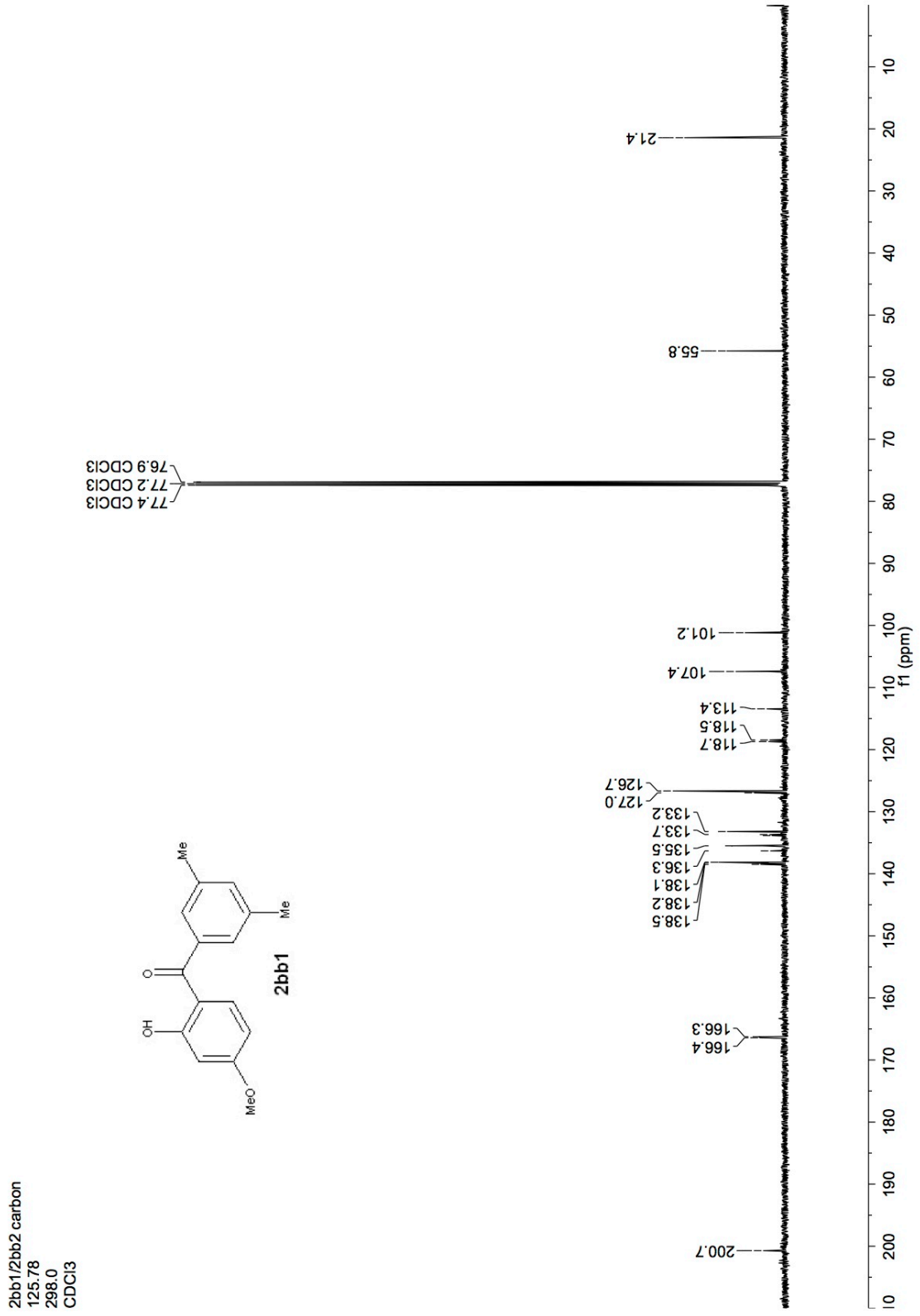

1p proton
399.87
298.0
CDCl3
1p
f1 (ppm)
CHCl3
TMS

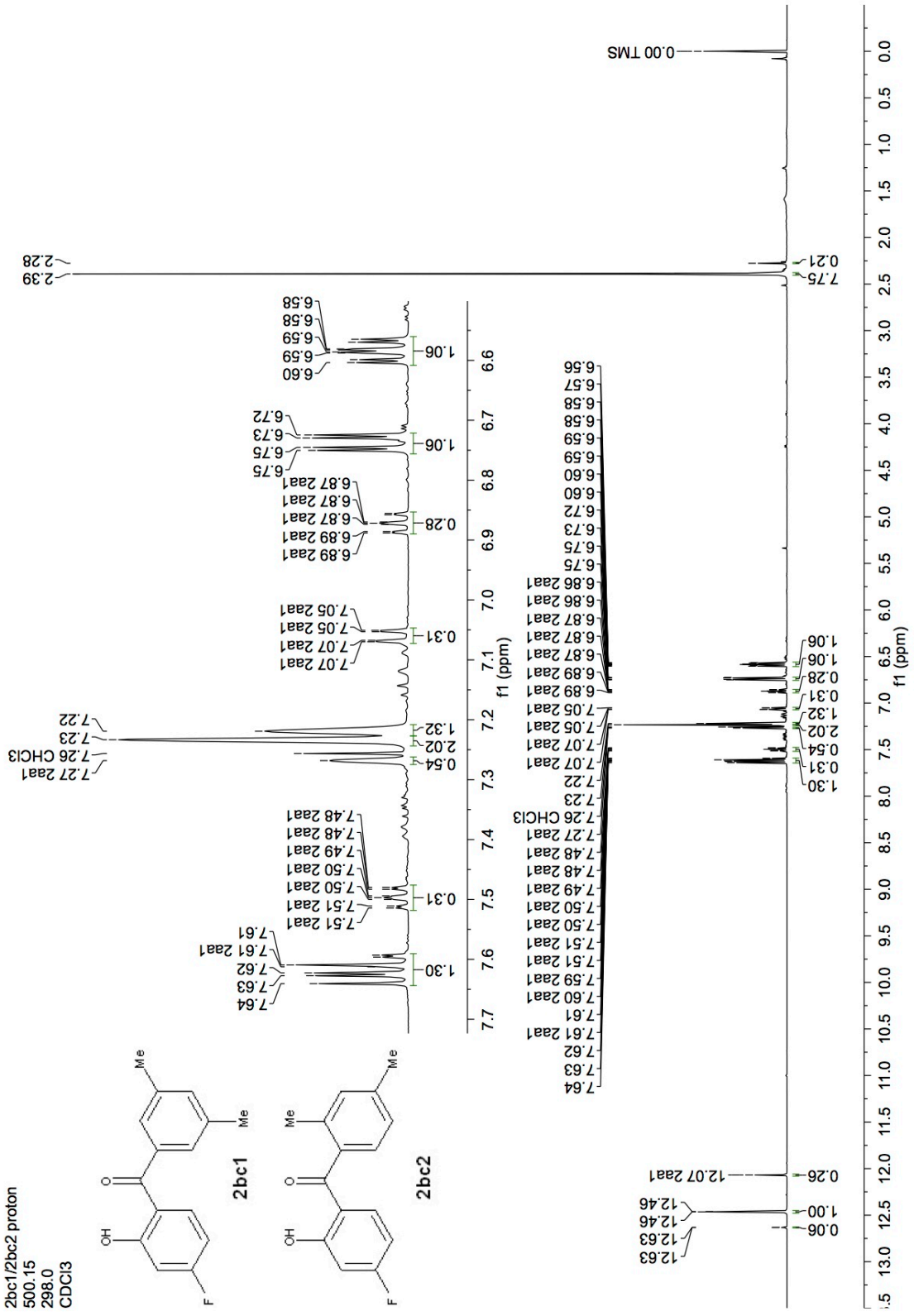

1p carbon
100.56
298.1
CDCl3
1p
168.9
155.6
150.3
138.7
129.7
126.4
125.3
121.8
118.6
114.9
111.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
f1 (ppm)

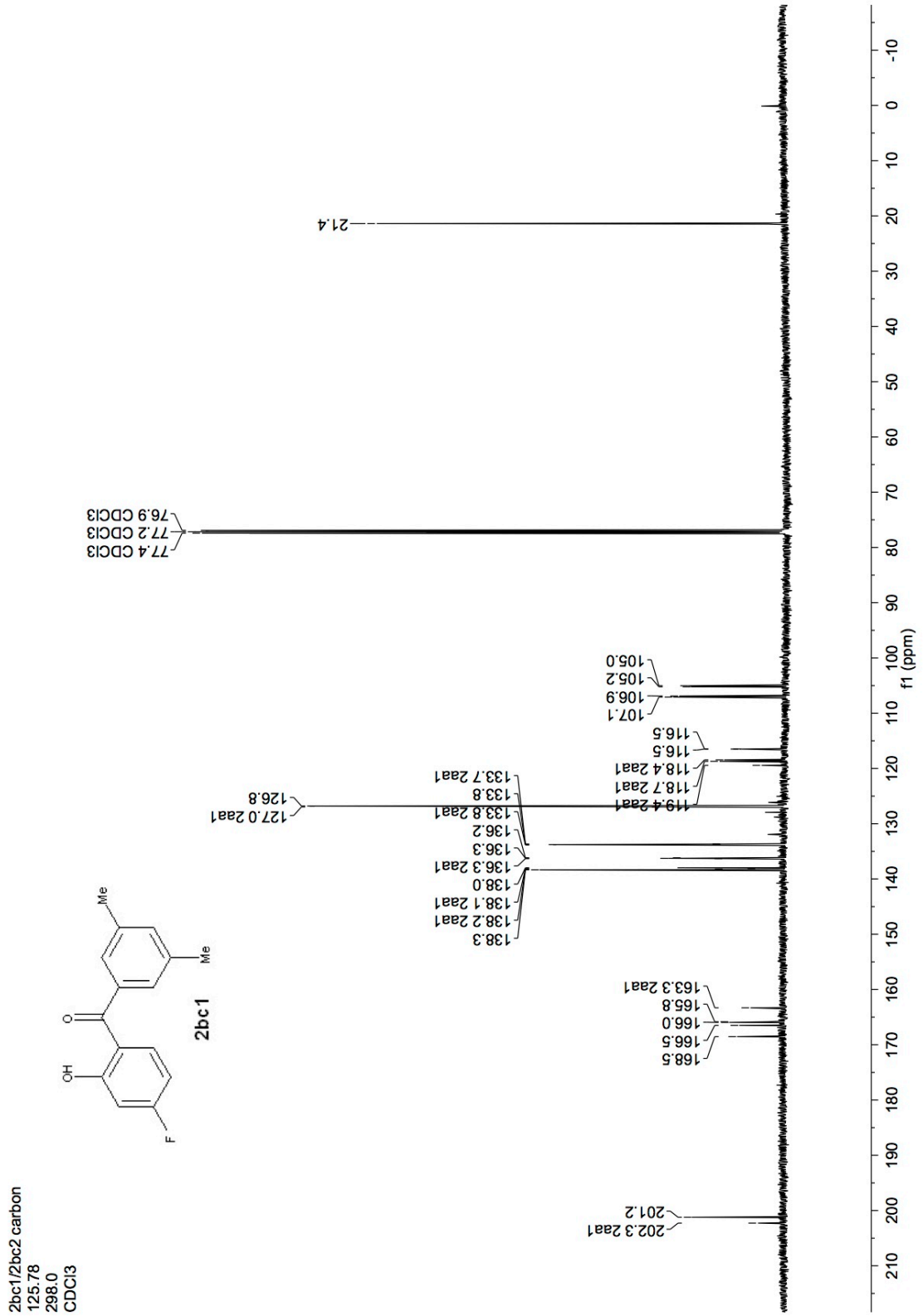

2ba1/2ba2 proton
500.15
298.0
CDCl3
2ba1
2ba2
Me
OH
O
f1 (ppm)
TMS


2ba1/2ba2 carbon
125.78
298.0
CDCl3
2ba1
Me
Me
Me
OH
O
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
201.8
202.3 2aa1
163.3
163.5
148.0
138.3
138.2
138.1
136.3
133.8
133.7
133.7
133.4
127.0
126.9
126.8
120.0
119.4
118.7
118.5
118.4
117.2
22.1
21.4
f1 (ppm)

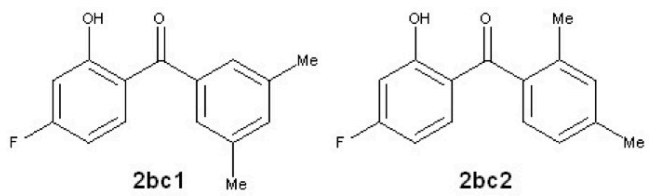

2bb1/2bb2 proton
500.15
298.0
CDCl3
2bb1
2bb2
Me
MeO
OH
O
f1 (ppm)
TMS
Acetone
CHCl3


2bb1/2bb2 carbon
125.78
298.0
CDCl3
Me
Me
O
OH
MeO
2bb1
200.7
166.4
166.3
138.5
138.2
138.1
136.3
135.5
133.7
133.2
127.0
126.7
118.7
118.5
113.4
107.4
101.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
55.8
21.4
f1 (ppm)


2bc1/2bc2 proton
500.15
298.0
CDCl3
2bc1
2bc2
Me
Me
O
OH
F
f1 (ppm)
0.00 TMS
7.27 2aa1
7.26 CHCl3
12.07 2aa1

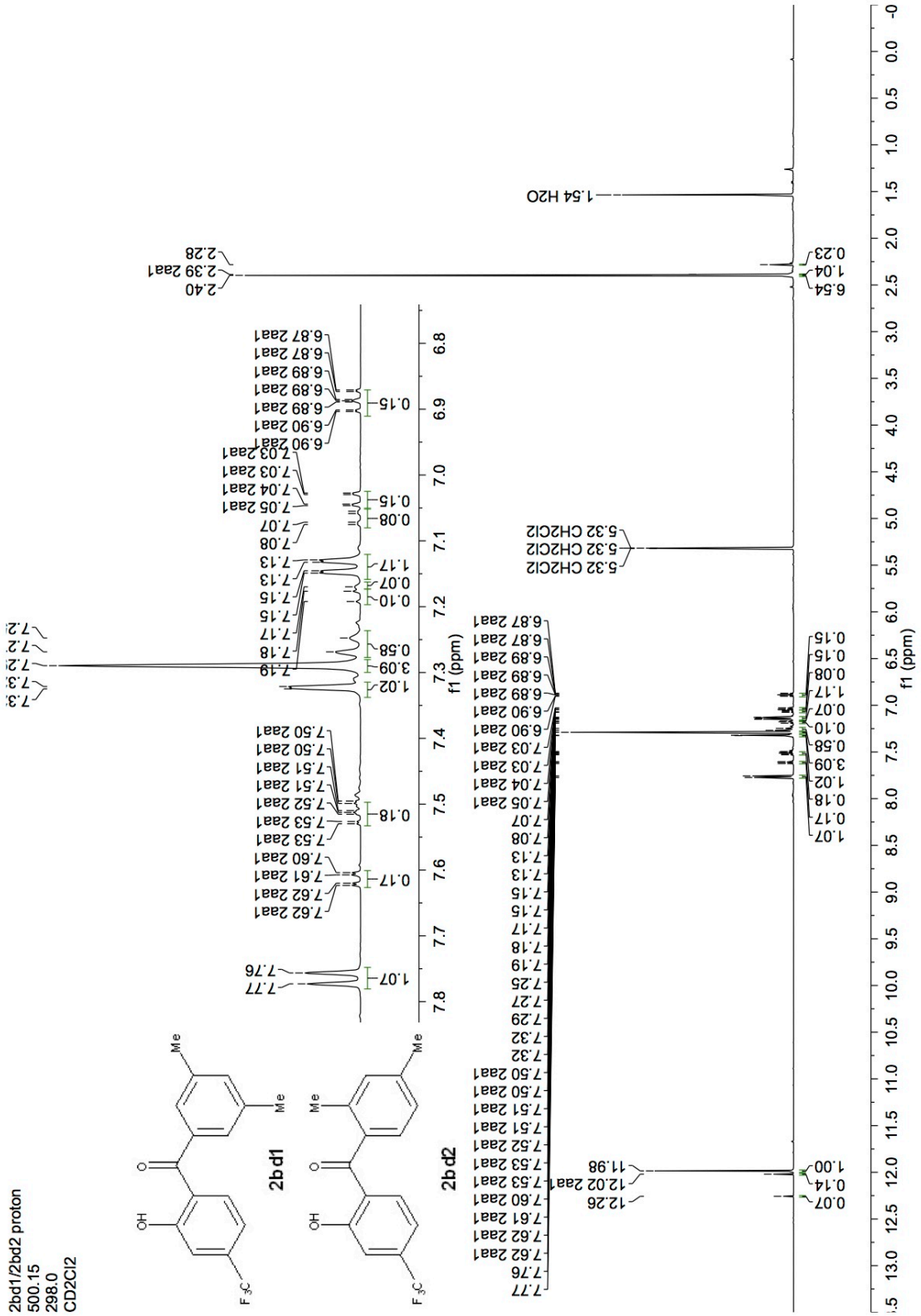

2bc1/2bc2 carbon
125.78
298.0
CDCl3
2bc1
Me
Me
O
OH
F
202.3 2aa1
201.2
168.5
166.5
166.0
165.8
163.3 2aa1
138.3
138.2 2aa1
138.1 2aa1
138.0
136.3 2aa1
136.3
136.2
133.8 2aa1
133.8
133.7 2aa1
127.0 2aa1
126.8
119.4 2aa1
118.7 2aa1
118.4 2aa1
116.5
116.5
107.1
106.9
105.2
105.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
21.4
f1 (ppm)

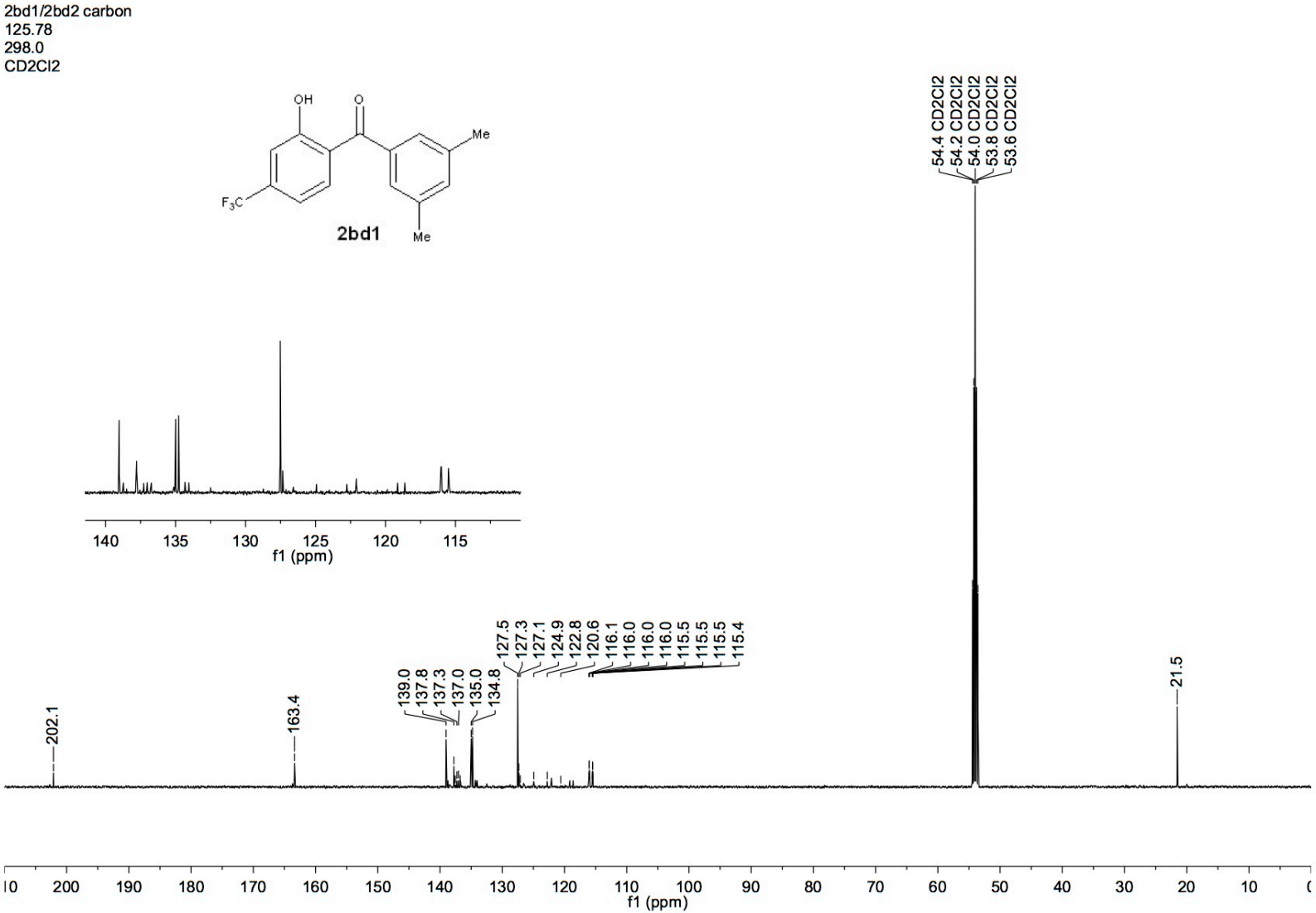
2bc1/2bc2 fluorine
470.56
298.0
CDCl3



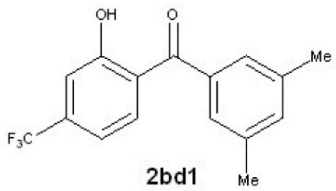
2bc1

2bc2

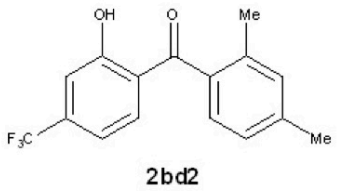

2bd1/2bd2 proton
500.15
298.0
CD2Cl2
2bd1
2bd2
f1 (ppm)


2bd1/2bd2 carbon
125.78
298.0
CD2Cl2
OH
O
Me
F3C
Me
2bd1
54.4 CD2Cl2
54.2 CD2Cl2
54.0 CD2Cl2
53.8 CD2Cl2
53.6 CD2Cl2
140
135
130
125
120
115
f1 (ppm)
127.5
127.3
127.1
124.9
122.8
120.6
116.1
116.0
116.0
116.0
115.5
115.5
115.4
139.0
137.8
137.3
137.0
135.0
134.8
202.1
163.4
21.5
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

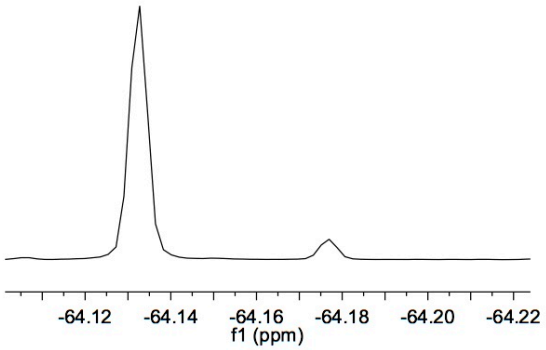
2bd1/2bd2 fluorine
470.56
298.0
CD2Cl2

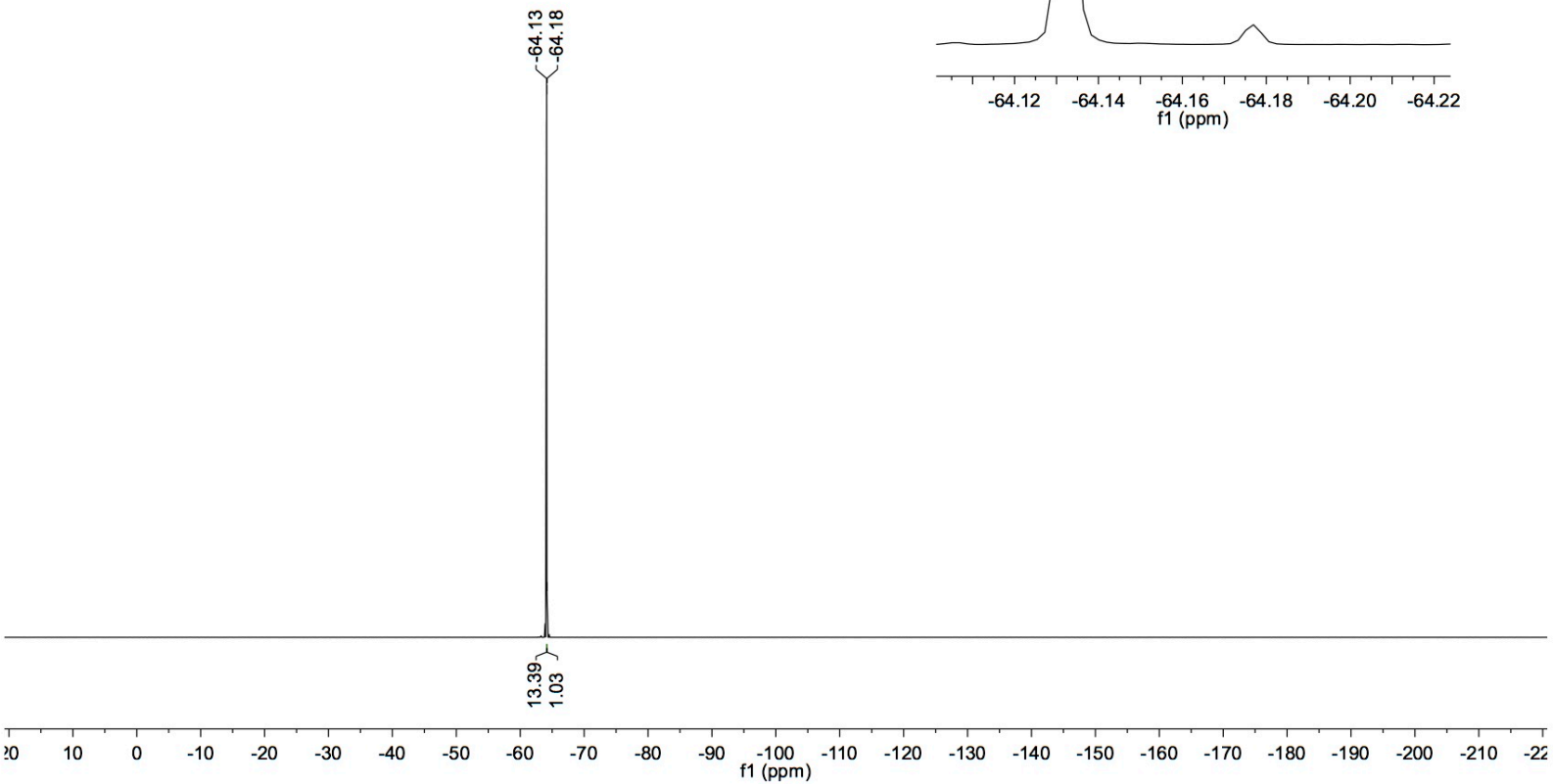


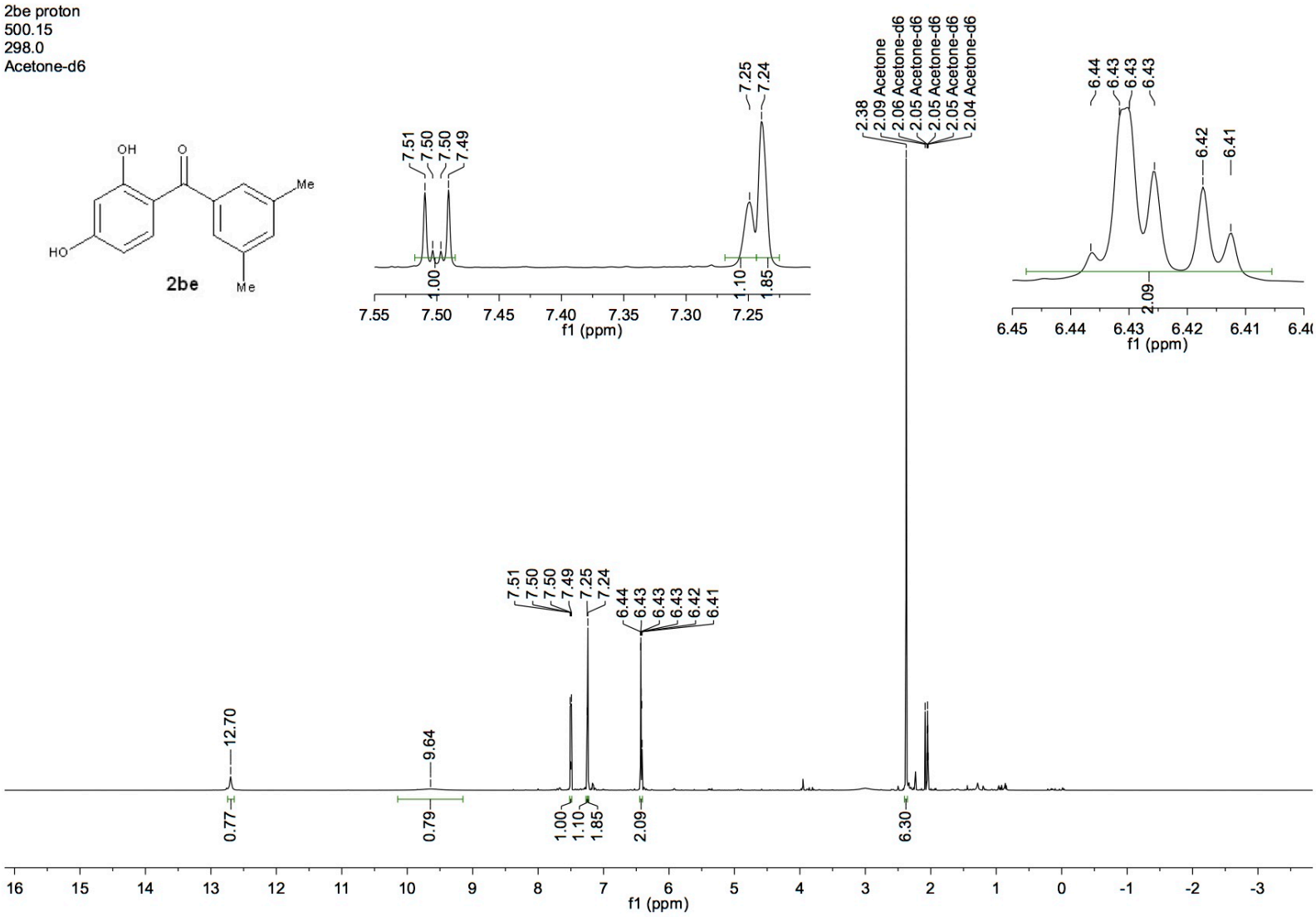
2bd1

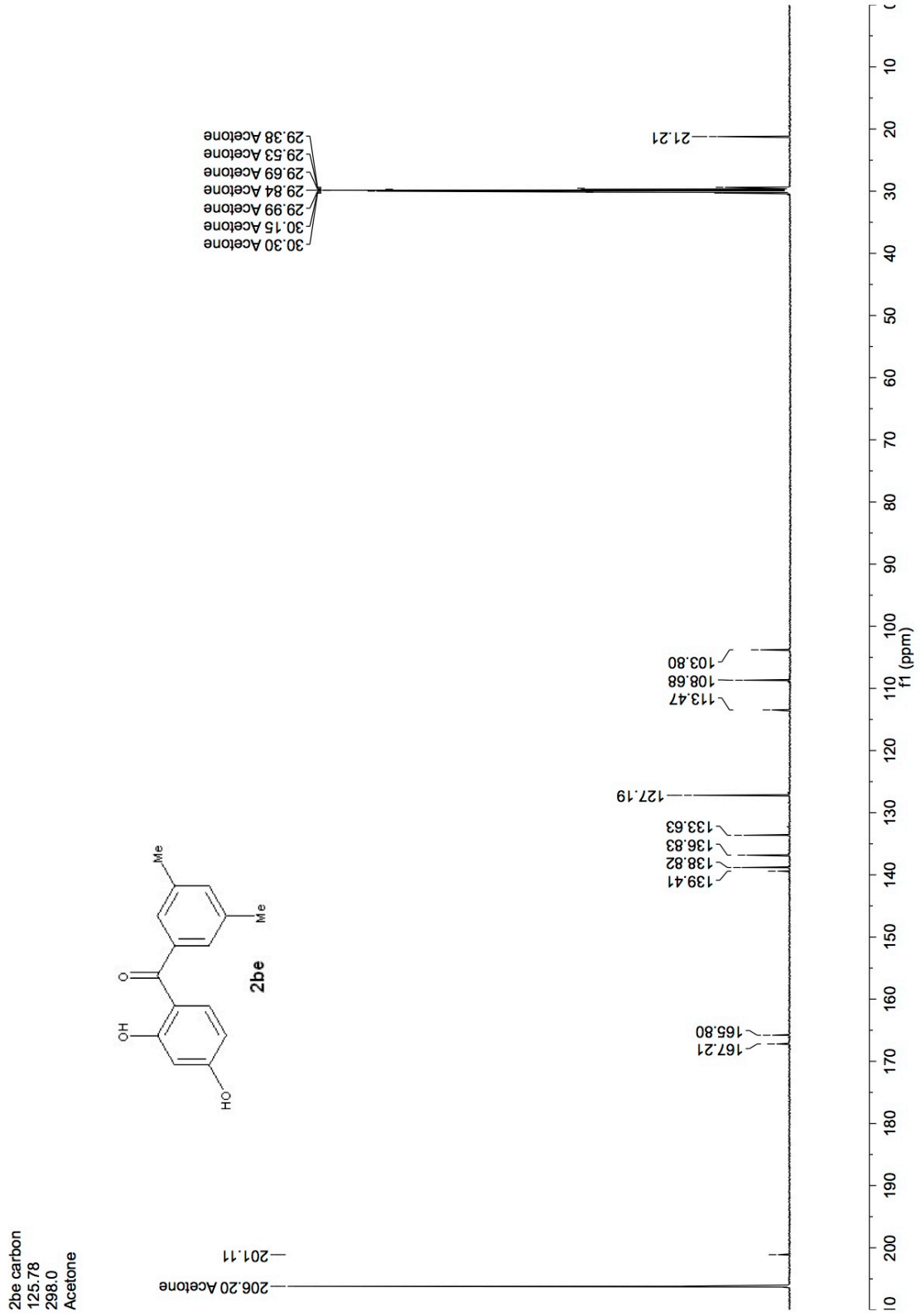


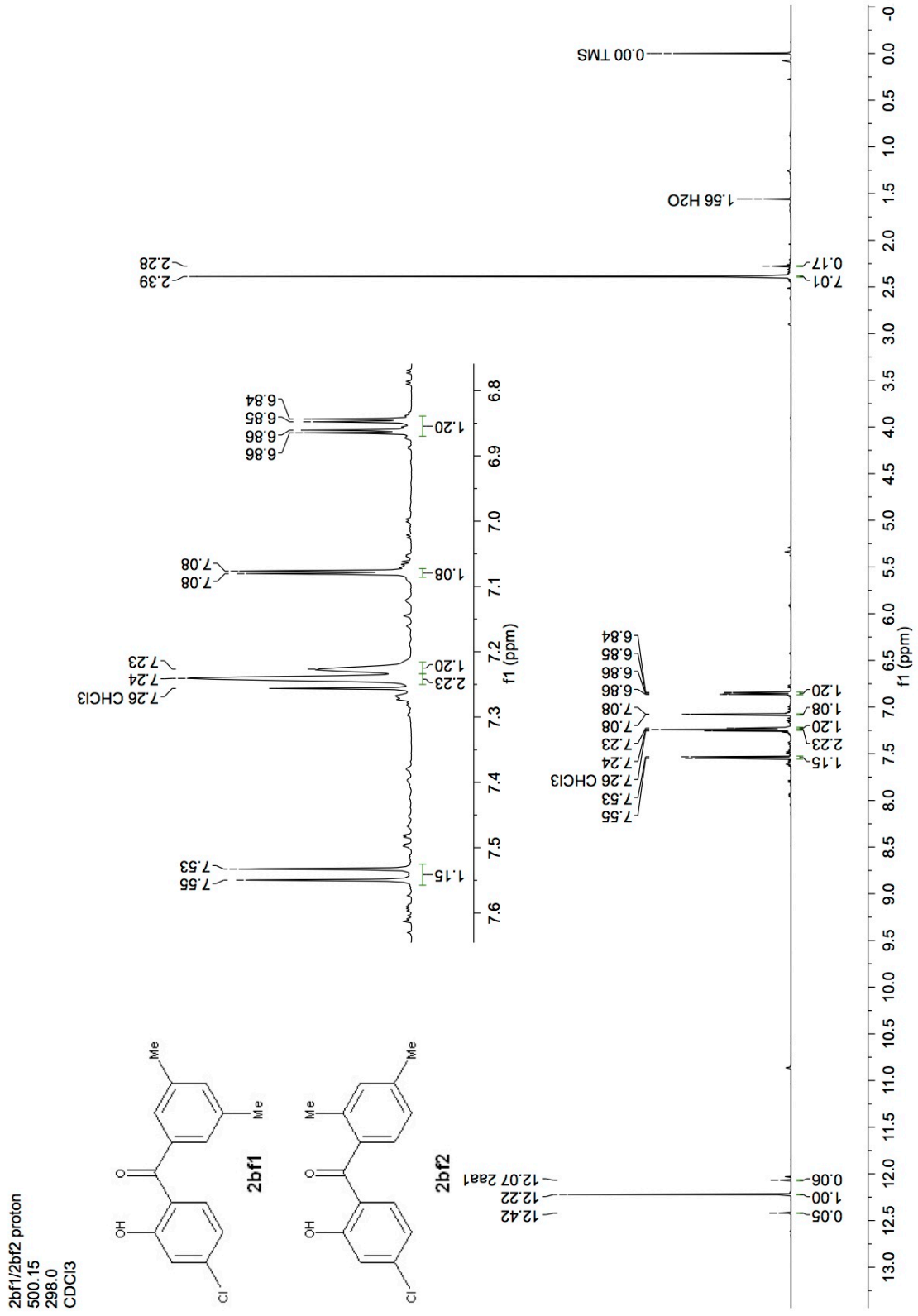
2bd2

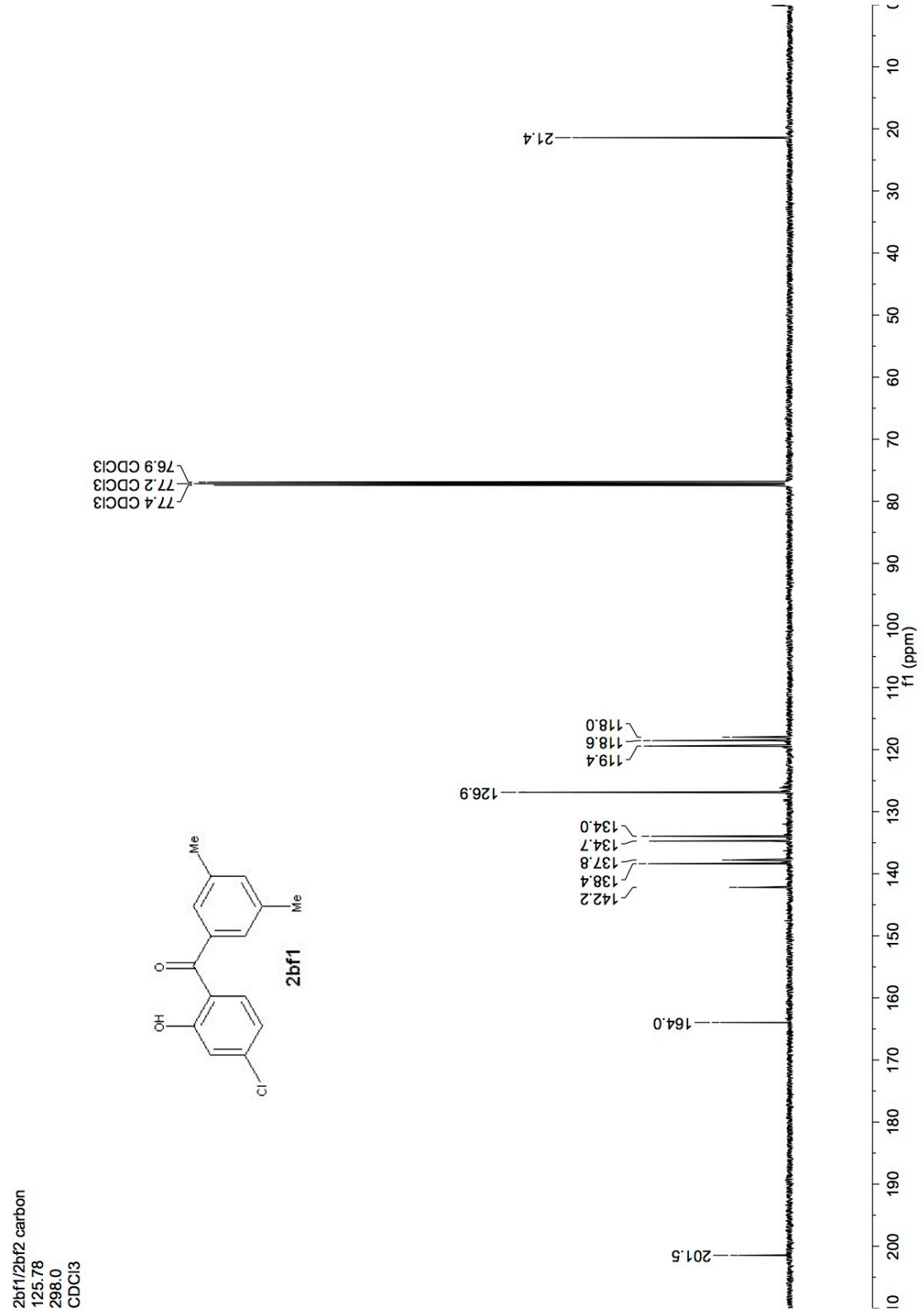


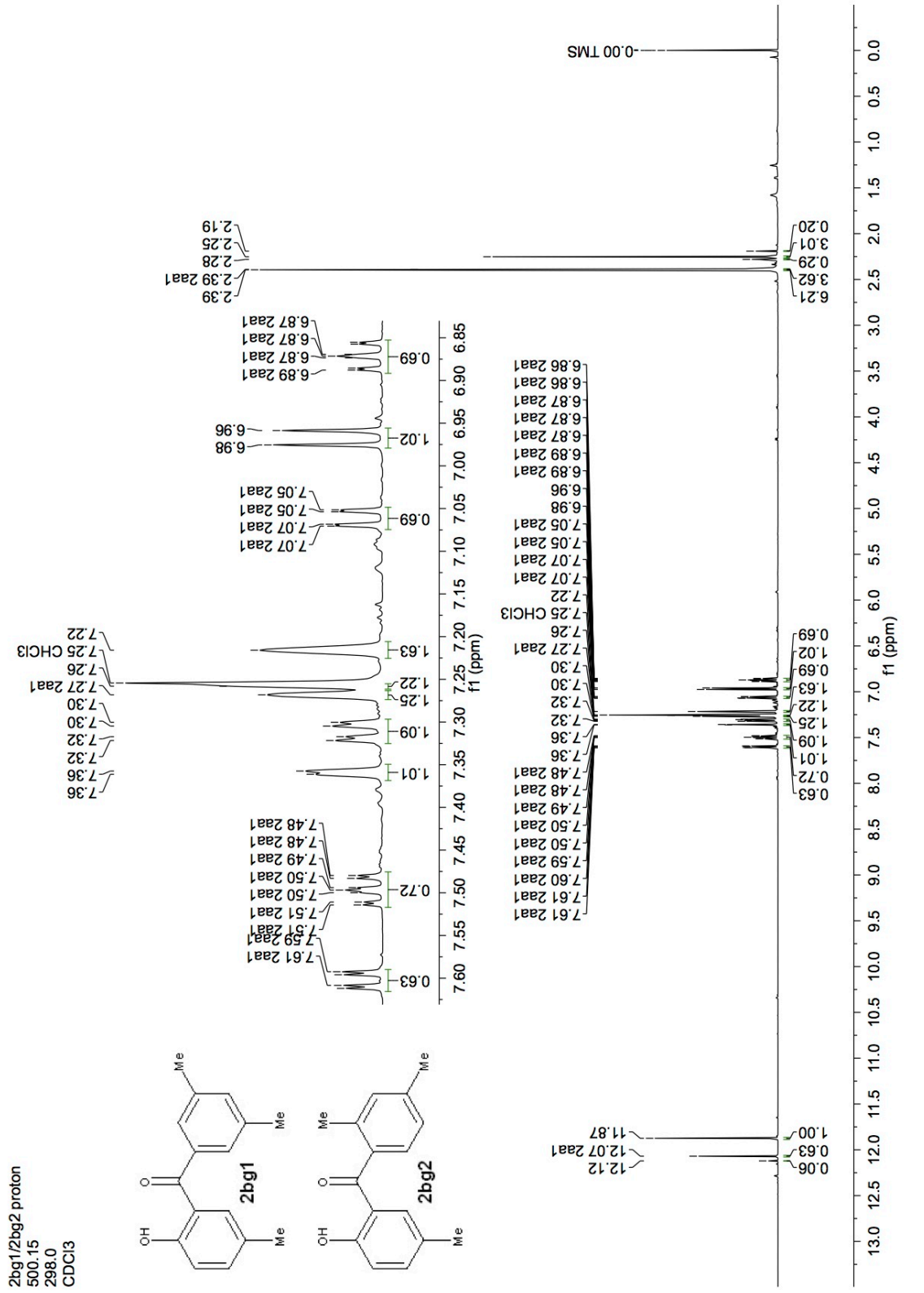


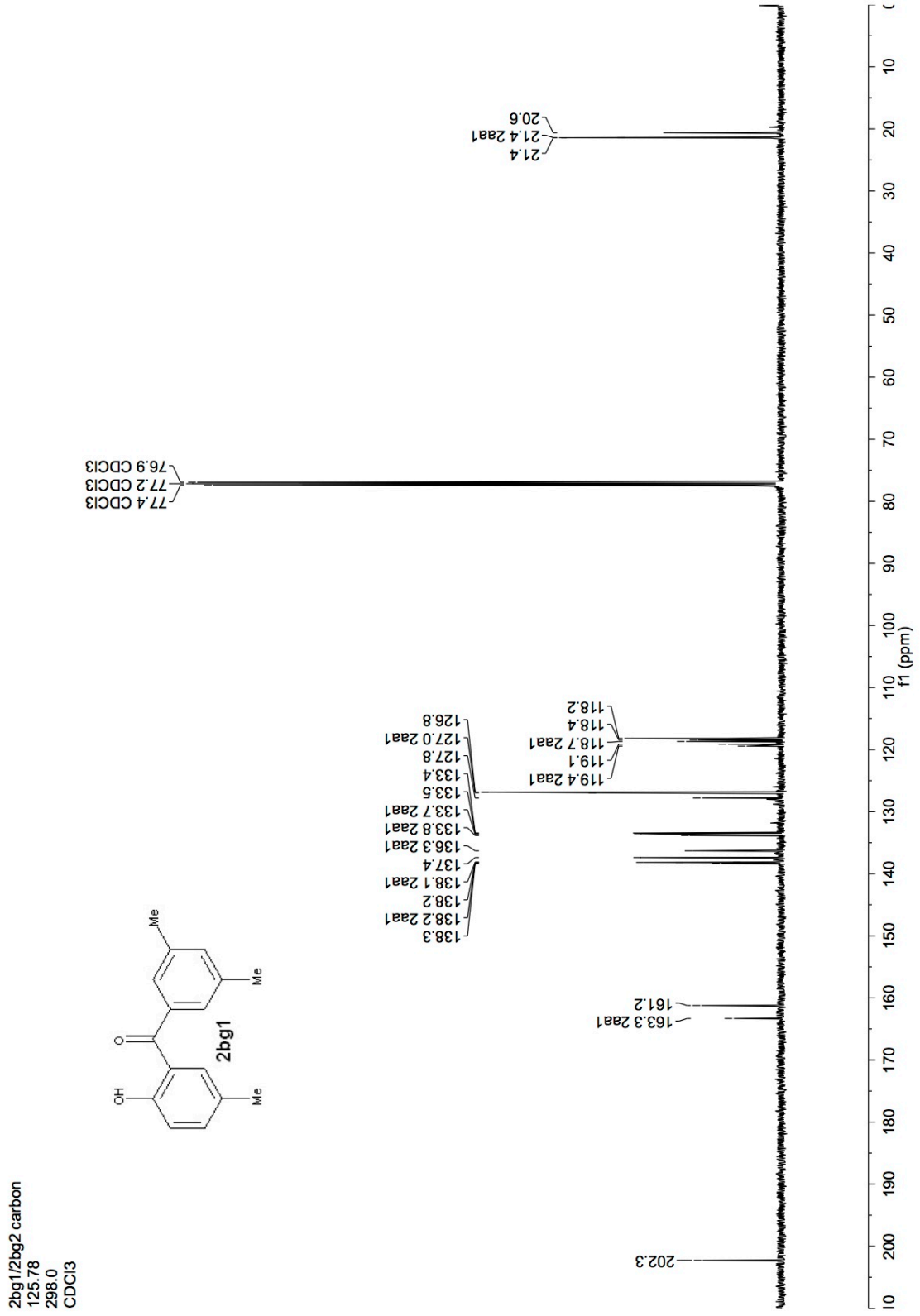

2be proton
500.15
298.0
Acetone-d6
OH
O
Me
HO
Me
2be
7.51
7.50
7.50
7.49
7.25
7.24
1.00
1.10
1.85
7.55
7.50
7.45
7.40
7.35
7.30
7.25
f1 (ppm)
2.38
2.09 Acetone
2.06 Acetone-d6
2.05 Acetone-d6
2.05 Acetone-d6
2.05 Acetone-d6
2.04 Acetone-d6
6.44
6.43
6.43
6.43
6.42
6.41
2.09
6.45
6.44
6.43
6.42
6.41
f1 (ppm)
12.70
9.64
7.51
7.50
7.50
7.49
7.25
7.24
6.44
6.43
6.43
6.43
6.42
6.41
0.77
0.79
1.00
1.10
1.85
2.09
6.30
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

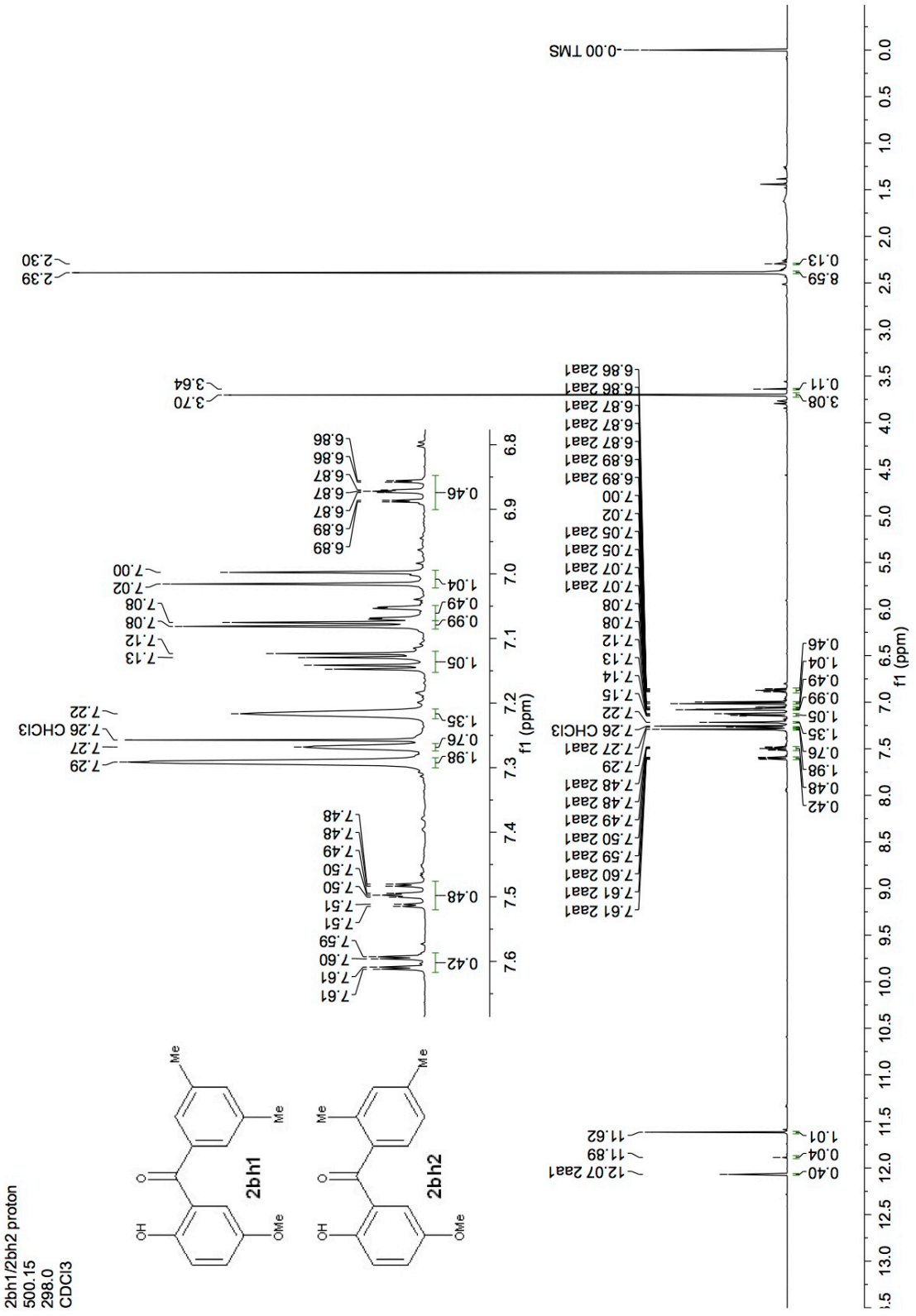

2be carbon
125.78
298.0
Acetone
206.20 Acetone
201.11
167.21
165.80
139.41
138.82
136.83
133.63
127.19
113.47
108.68
103.80
30.30 Acetone
30.15 Acetone
29.99 Acetone
29.84 Acetone
29.69 Acetone
29.53 Acetone
29.38 Acetone
21.21
2be
Me
Me
O
OH
HO
f1 (ppm)

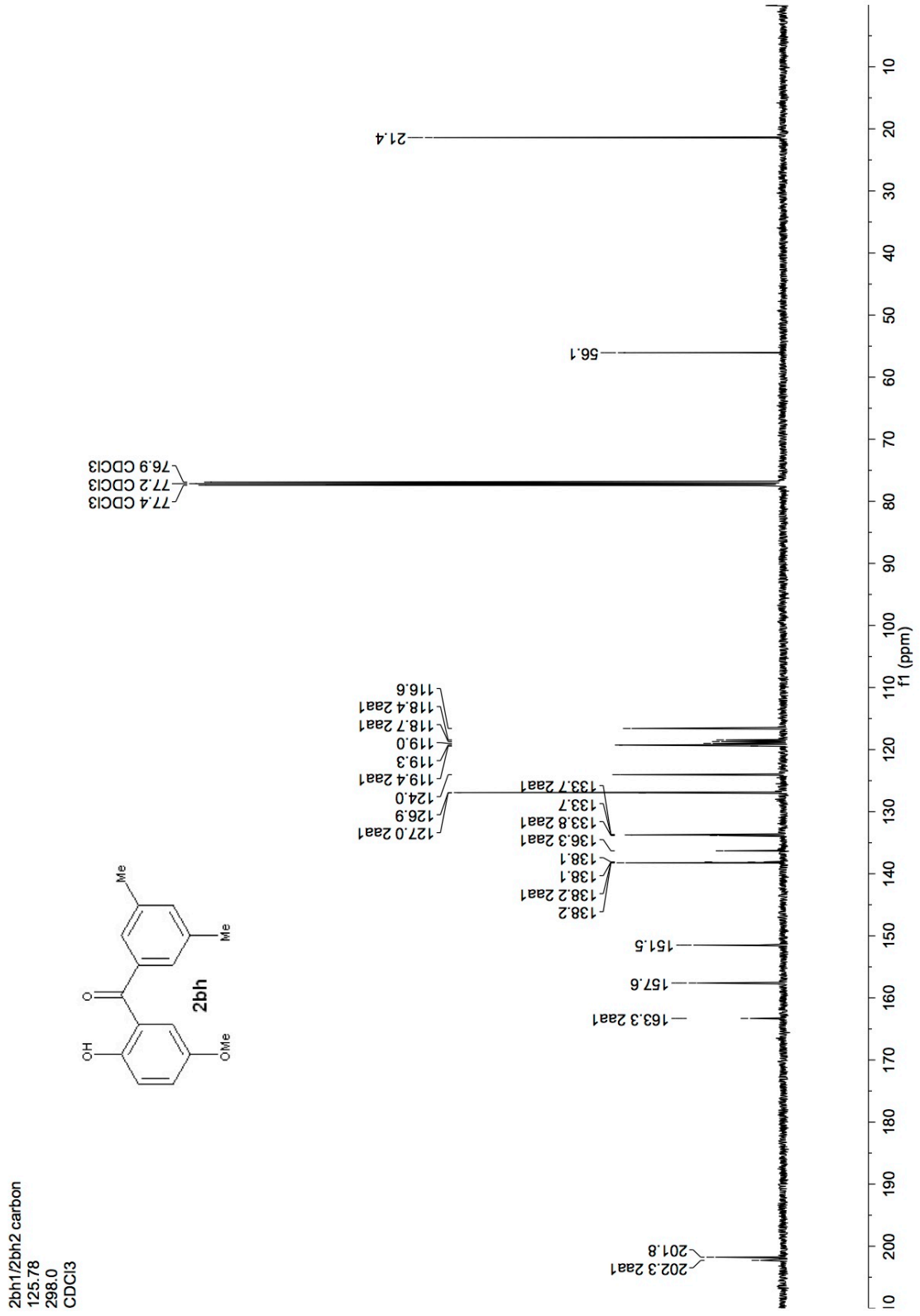

2bf1/2bf2 proton
500.15
298.0
CDCl3
2bf1
2bf2
Me
Me
OH
Cl
0.00 TMS
1.56 H2O
12.42
12.22
12.07 2aa1
7.55
7.53
7.26 CHCl3
7.24
7.23
6.86
6.85
6.84
2.39
2.28
f1 (ppm)

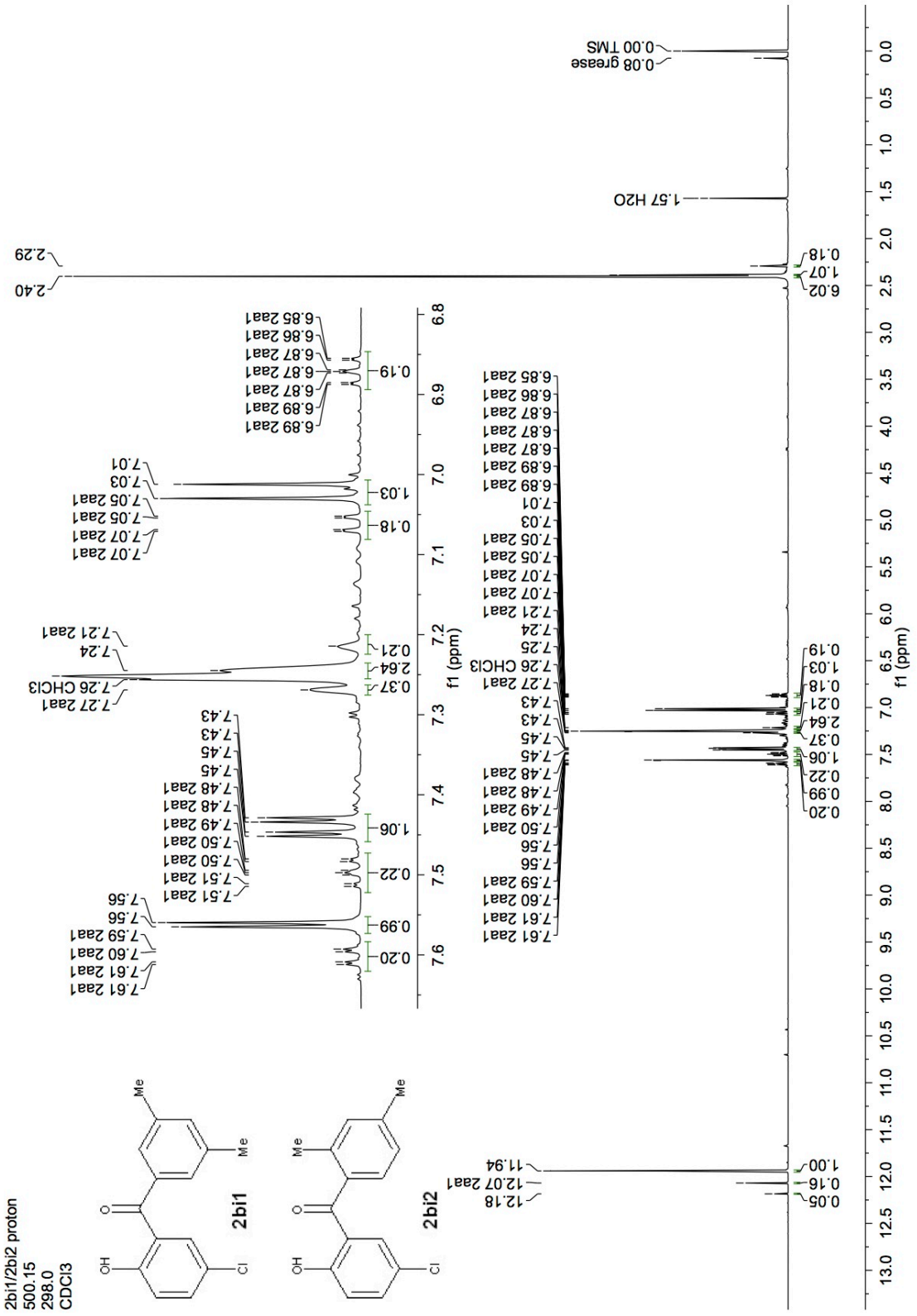

2bf1/2bf2 carbon
125.78
298.0
CDCl3
2bf1
Me
Me
O
OH
Cl
201.5
164.0
142.2
138.4
137.8
134.7
134.0
126.9
119.4
118.6
118.0
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
21.4
f1 (ppm)

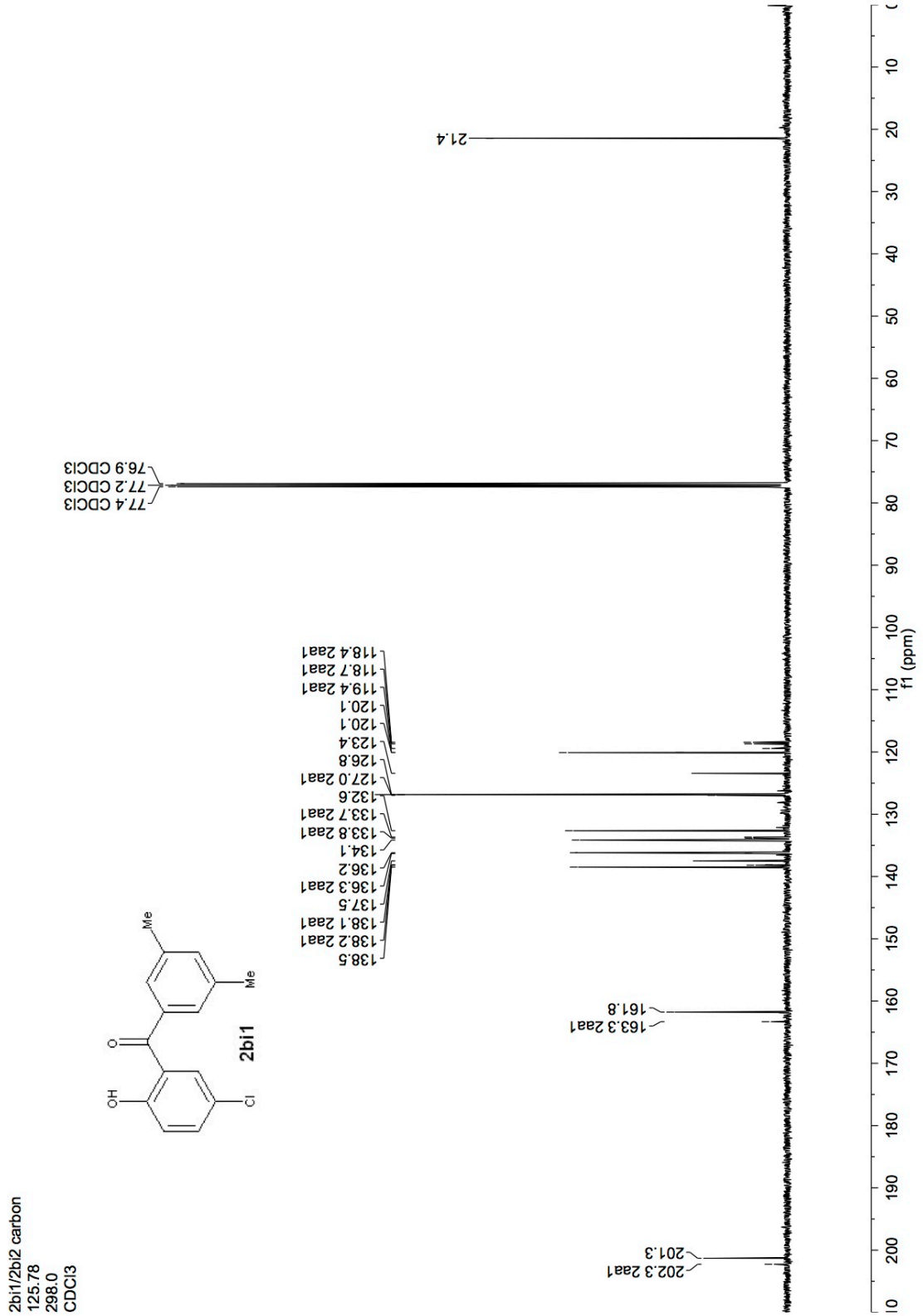

2bg1/2bg2 proton
500.15
298.0
CDCl3
2bg1
2bg2
Me
OH
O
TMS
CHCl3
f1 (ppm)

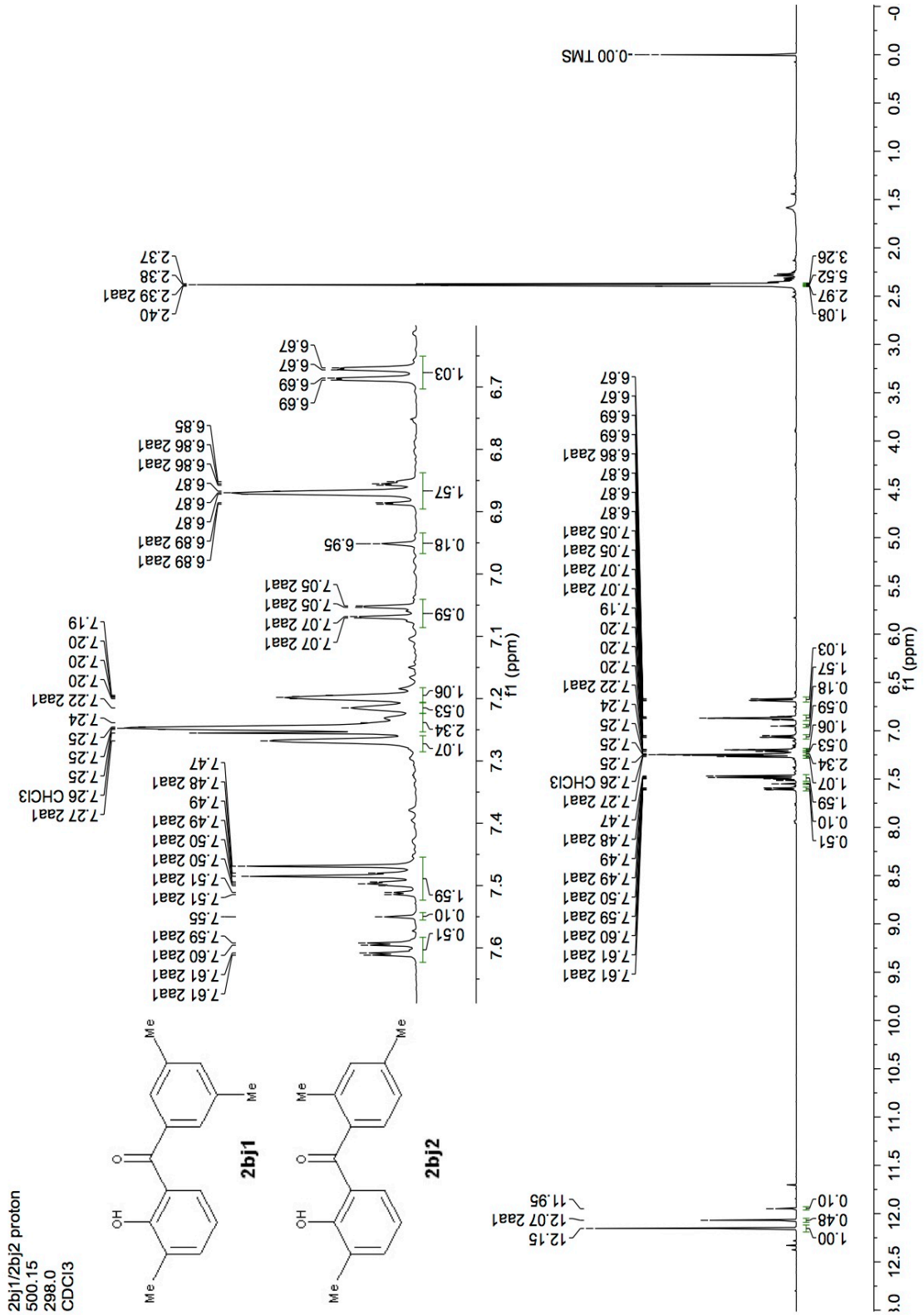

2bg1/2bg2 carbon
125.78
298.0
CDCl3
2bg1
Me
Me
Me
OH
O
202.3
163.3 2aa1
161.2
138.3
138.2 2aa1
138.2
138.1 2aa1
137.4
136.3 2aa1
133.8 2aa1
133.7 2aa1
133.5
133.4
127.8
127.0 2aa1
126.8
119.4 2aa1
119.1
118.7 2aa1
118.4
118.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
21.4
21.4 2aa1
20.6
f1 (ppm)

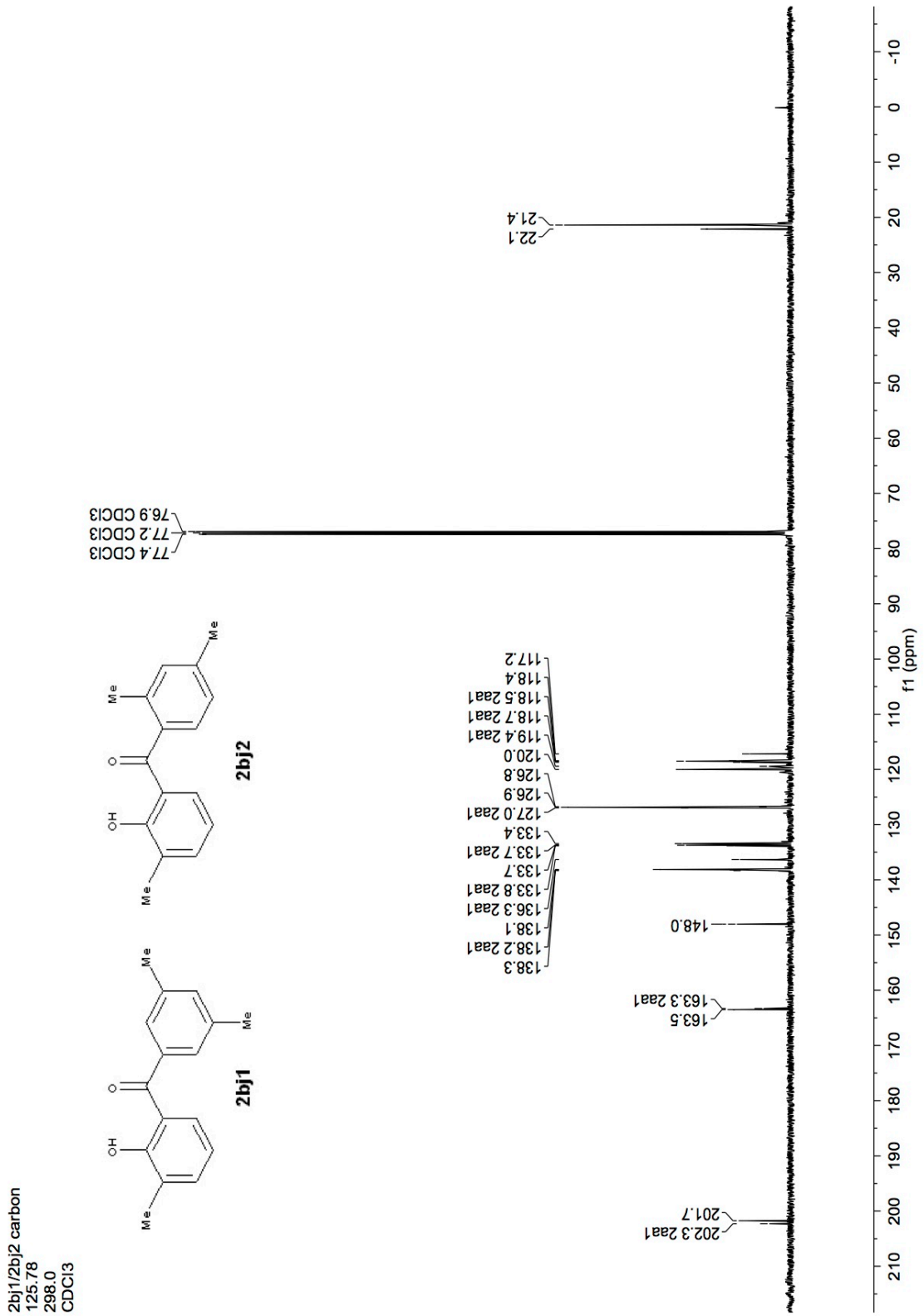

2bh1/2bh2 proton
500.15
298.0
CDCl3
2bh1
2bh2
Me
OH
OMe
O
f1 (ppm)
TMS
CHCl3

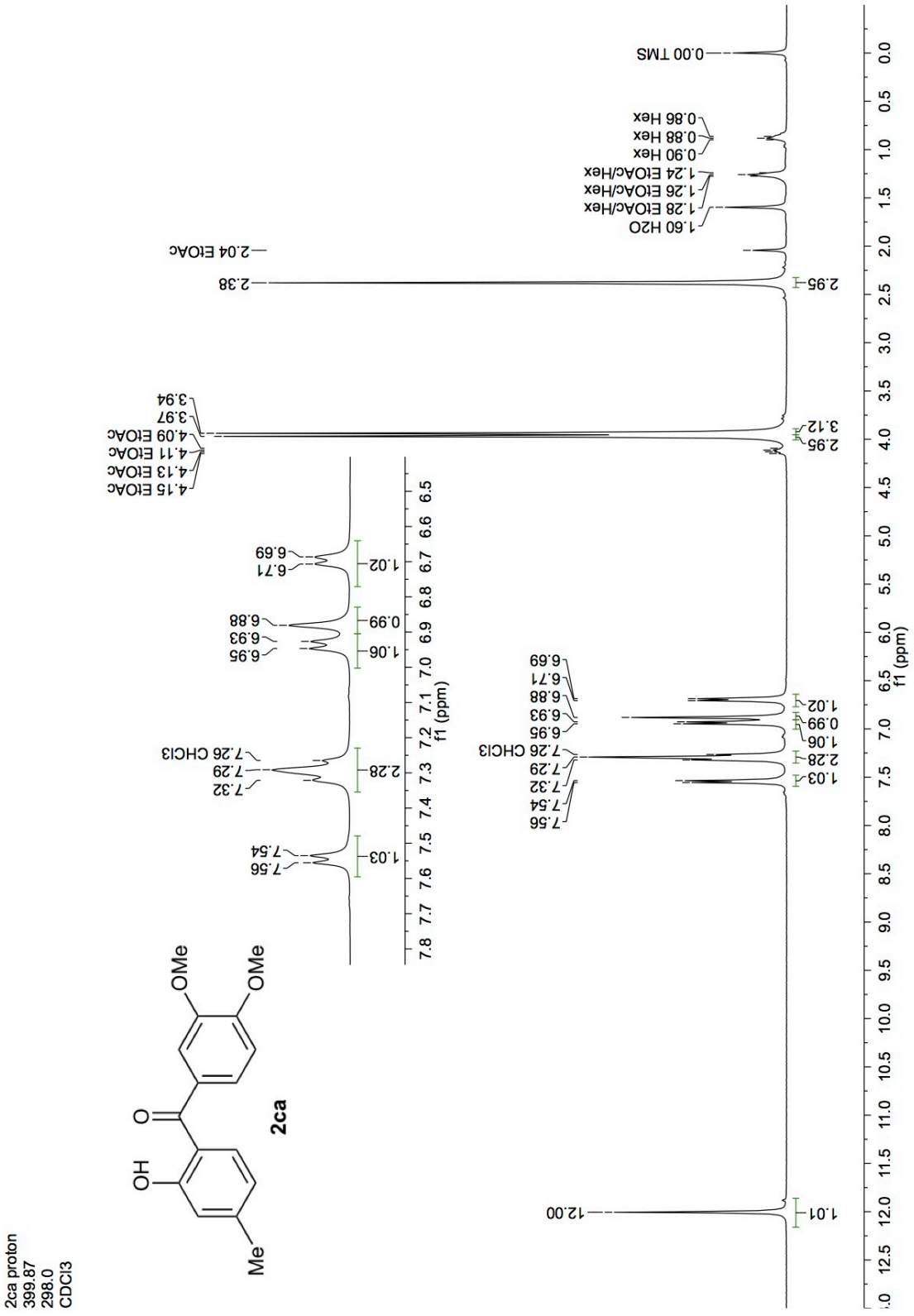

2bh1/2bh2 carbon
125.78
298.0
CDCl3
2bh
Me
Me
OMe
OH
O
202.3 2aa1
201.8
163.3 2aa1
157.6
151.5
138.2
138.2 2aa1
138.1
138.1 2aa1
138.1
136.3 2aa1
133.8 2aa1
133.7
133.7 2aa1
127.0 2aa1
126.9
124.0
119.4 2aa1
119.3
119.0
118.7 2aa1
118.4 2aa1
116.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
56.1
21.4
f1 (ppm)

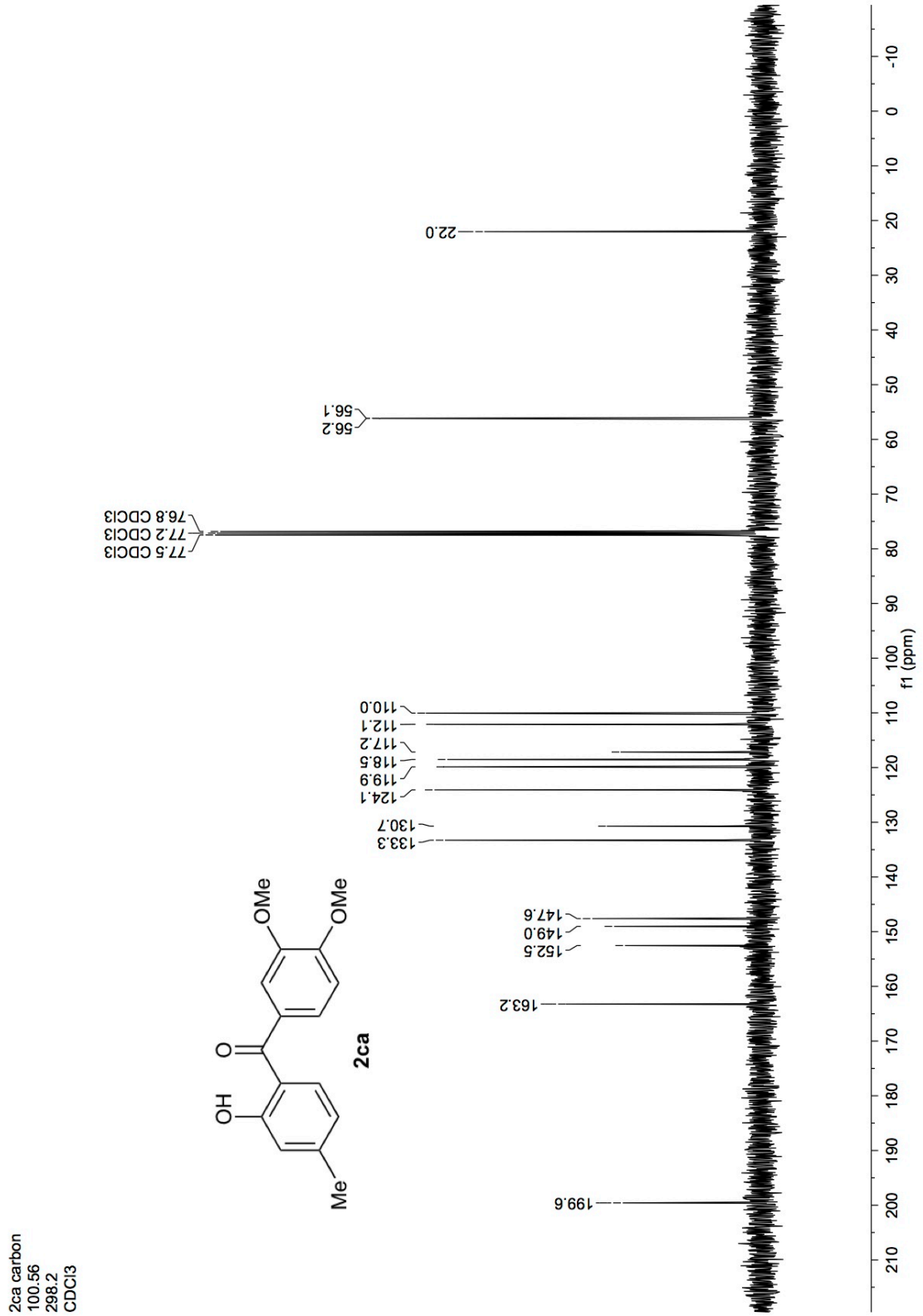

2bi1/2bi2 proton
500.15
298.0
CDCl3
2bi1
2bi2
f1 (ppm)

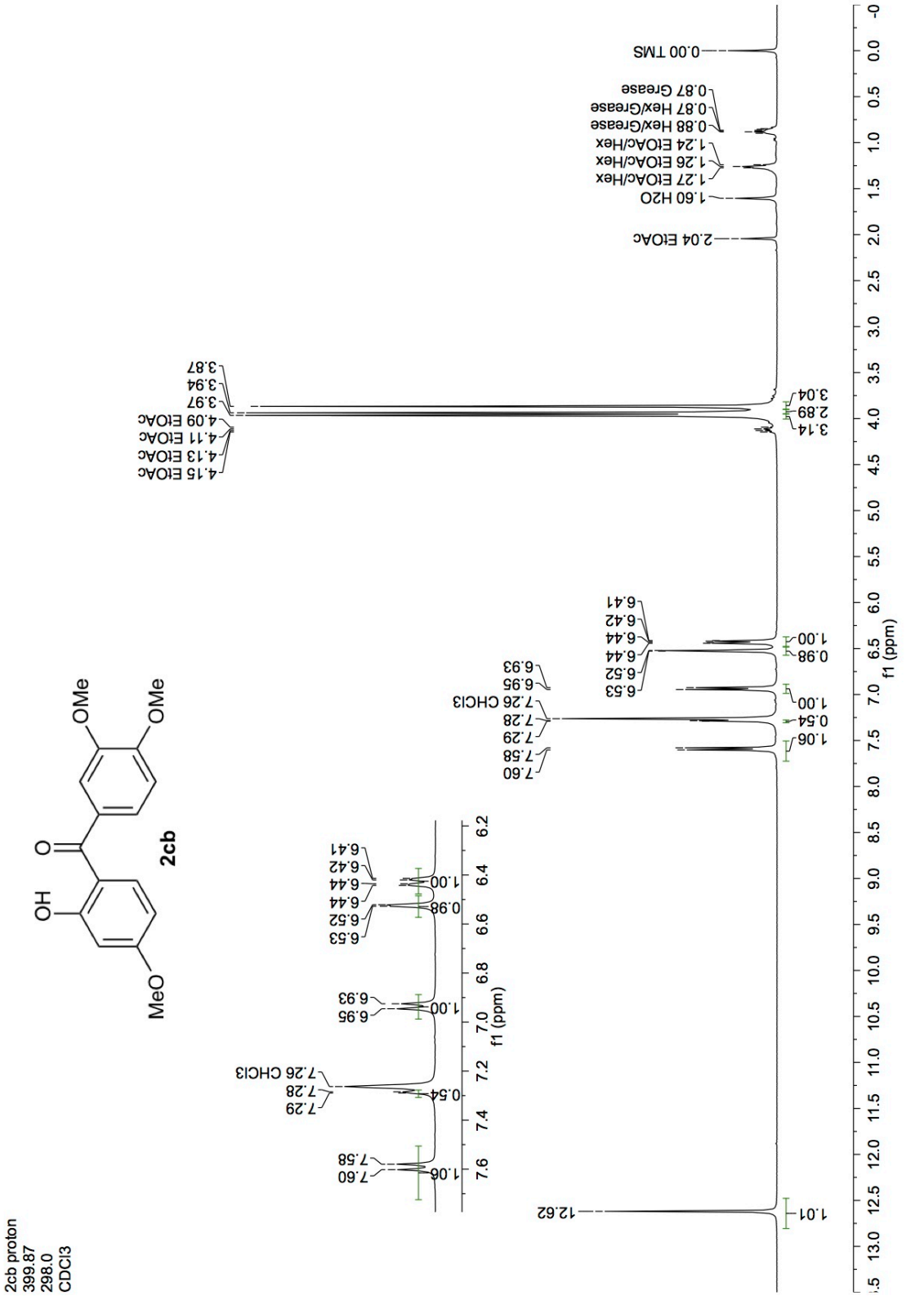

2bi1/2bi2 carbon
125.78
298.0
CDCl3
2bi1
Me
Me
O
OH
Cl
f1 (ppm)
202.3 2aa1
201.3
163.3 2aa1
161.8
138.5
138.2 2aa1
138.1 2aa1
137.5
136.3 2aa1
136.2
134.1
133.8 2aa1
133.7 2aa1
132.6
127.0 2aa1
126.8
123.4
120.1
120.1
119.4 2aa1
118.7 2aa1
118.4 2aa1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
21.4

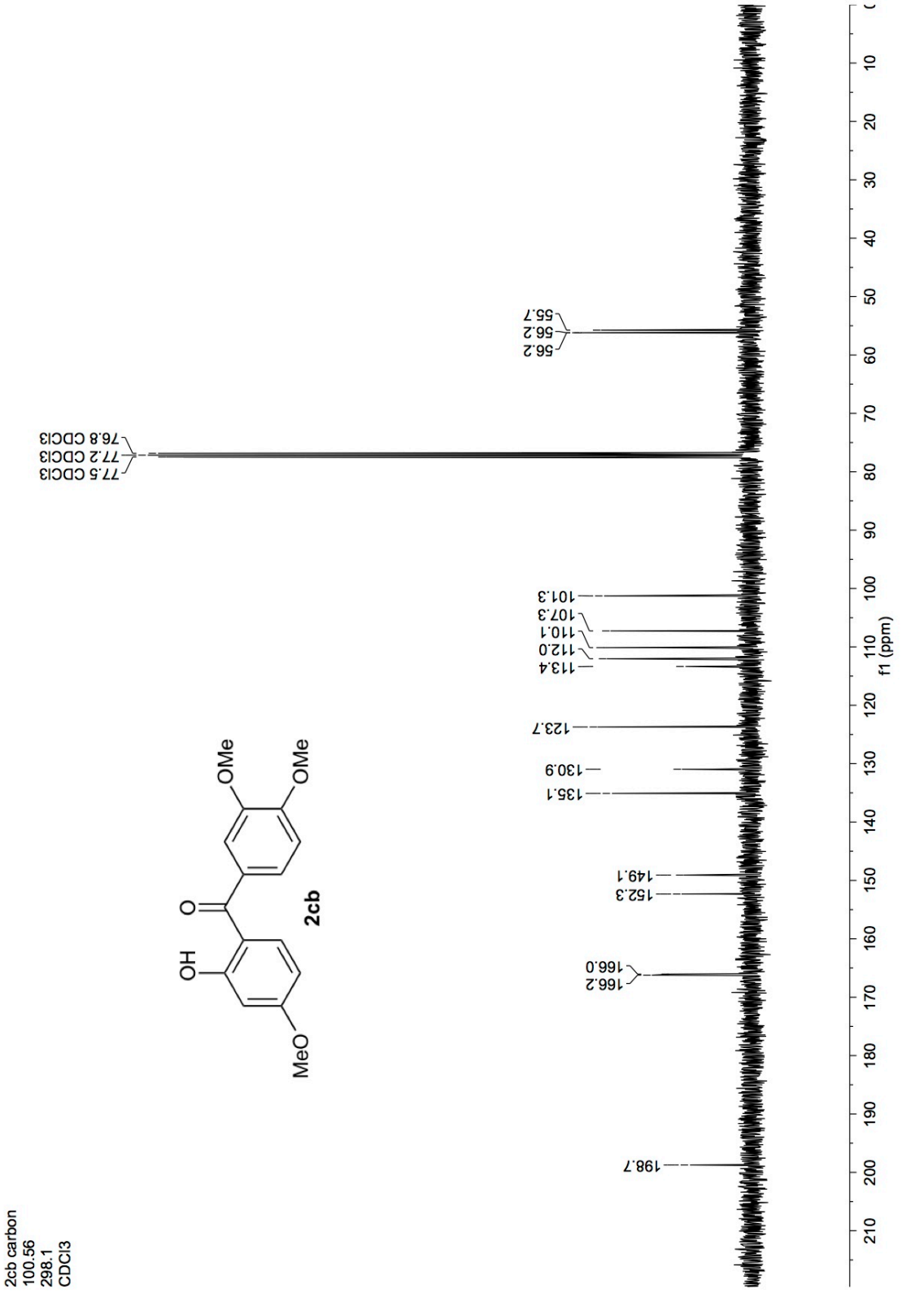

2bj1/2bj2 proton
500.15
298.0
CDCl3
2bj1
2bj2
f1 (ppm)

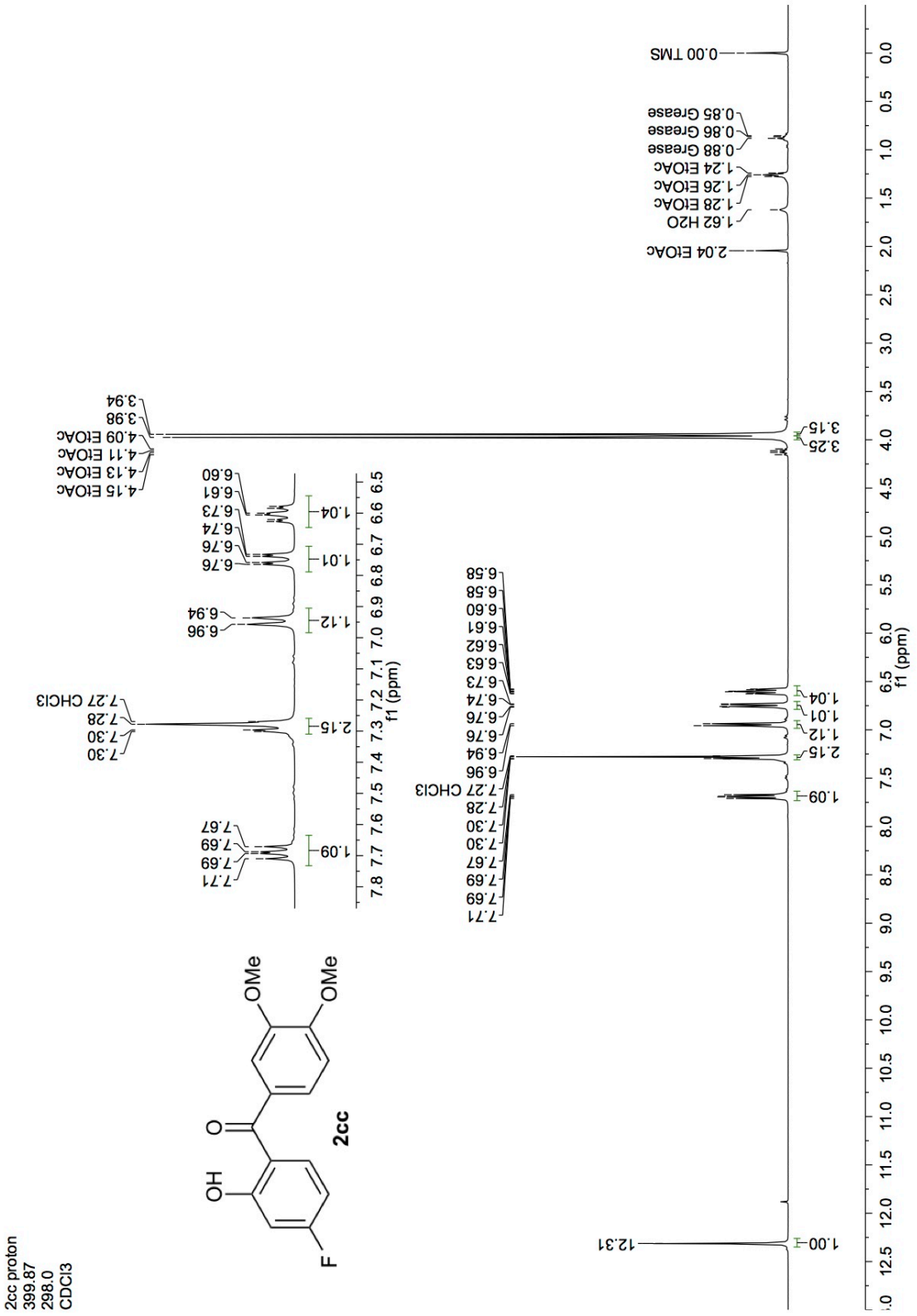

2bj1/2bj2 carbon
125.78
298.0
CDCl3
2bj1
2bj2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
202.3 2aa1
201.7
163.5
163.3 2aa1
148.0
138.3
138.2 2aa1
138.1
136.3 2aa1
133.8 2aa1
133.7
133.7 2aa1
133.4
127.0 2aa1
126.9
126.8
120.0
119.4 2aa1
118.7 2aa1
118.5 2aa1
118.4
117.2
22.1
21.4
f1 (ppm)

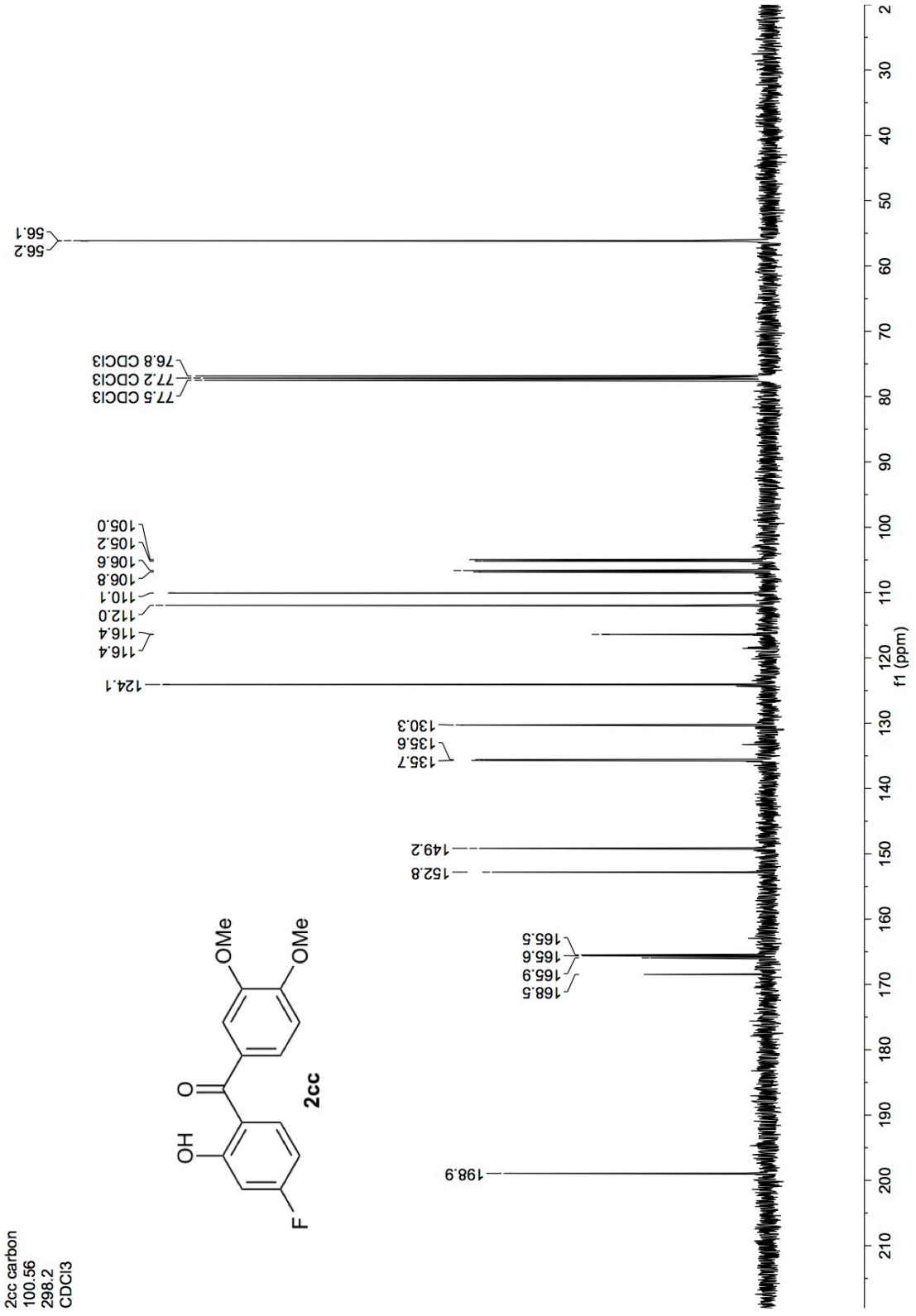

2ca proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
Me
2ca
0.00 TMS
0.86 Hex
0.88 Hex
0.90 Hex
1.24 EtOAc/Hex
1.26 EtOAc/Hex
1.28 EtOAc/Hex
1.60 H2O
2.04 EtOAc
2.38
2.95
3.12
4.15 EtOAc
4.13 EtOAc
4.11 EtOAc
4.09 EtOAc
3.97
3.94
6.69
6.71
6.88
6.93
6.95
7.26 CHCl3
7.29
7.32
7.54
7.56
12.00
1.01
1.03
2.28
1.06
0.99
1.02
f1 (ppm)


2ca carbon
100.56
298.2
CDCl3
OMe
OMe
O
OH
Me
2ca
199.6
163.2
152.5
149.0
147.6
133.3
130.7
124.1
119.9
118.5
117.2
112.1
110.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.2
56.1
22.0
f1 (ppm)

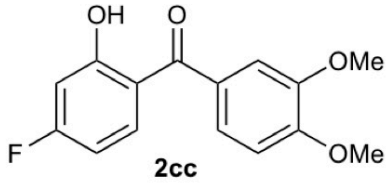

2cb proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
MeO
2cb
f1 (ppm)
0.00 TMS
0.87 Grease
0.87 Hex/Grease
0.88 Hex/Grease
1.24 EtOAc/Hex
1.26 EtOAc/Hex
1.27 EtOAc/Hex
1.60 H2O
2.04 EtOAc
3.14
2.89
3.04
4.15 EtOAc
4.13 EtOAc
4.11 EtOAc
4.09 EtOAc
3.97
3.94
3.87
6.41
6.42
6.44
6.44
6.52
6.53
0.98
1.00
7.26 CHCl3
7.28
7.29
7.58
7.60
1.06
0.54
1.00
6.93
6.95
12.62
1.01


2cb carbon
100.56
298.1
CDCl3
OMe
OMe
O
OH
MeO
2cb
198.7
166.2
166.0
152.3
149.1
135.1
130.9
123.7
113.4
112.0
110.1
107.3
101.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.2
56.2
55.7
f1 (ppm)


2cc proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
F
2cc
f1 (ppm)
0.00 TMS
0.85 Grease
0.86 Grease
0.88 Grease
1.24 EtOAc
1.26 EtOAc
1.28 EtOAc
1.62 H2O
2.04 EtOAc
3.15
3.25
4.15 EtOAc
4.13 EtOAc
4.11 EtOAc
4.09 EtOAc
3.98
3.94
6.58
6.60
6.61
6.62
6.63
6.73
6.74
6.76
6.94
6.96
7.27 CHCl3
7.28
7.30
7.67
7.69
7.71
12.31
1.00
1.09
2.15
1.12
1.01
1.04

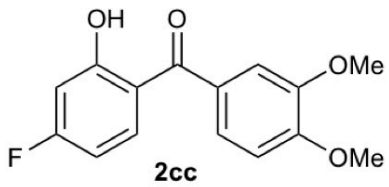

2cc carbon
100.56
298.2
CDCl3
OMe
OMe
O
OH
F
2cc
198.9
168.5
165.9
165.6
165.5
152.8
149.2
135.7
135.6
130.3
124.1
116.4
116.4
112.0
110.1
106.8
106.6
105.2
105.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.2
56.1
f1 (ppm)

2cc no decoupling 19F
376.46
298.0
CDCl3

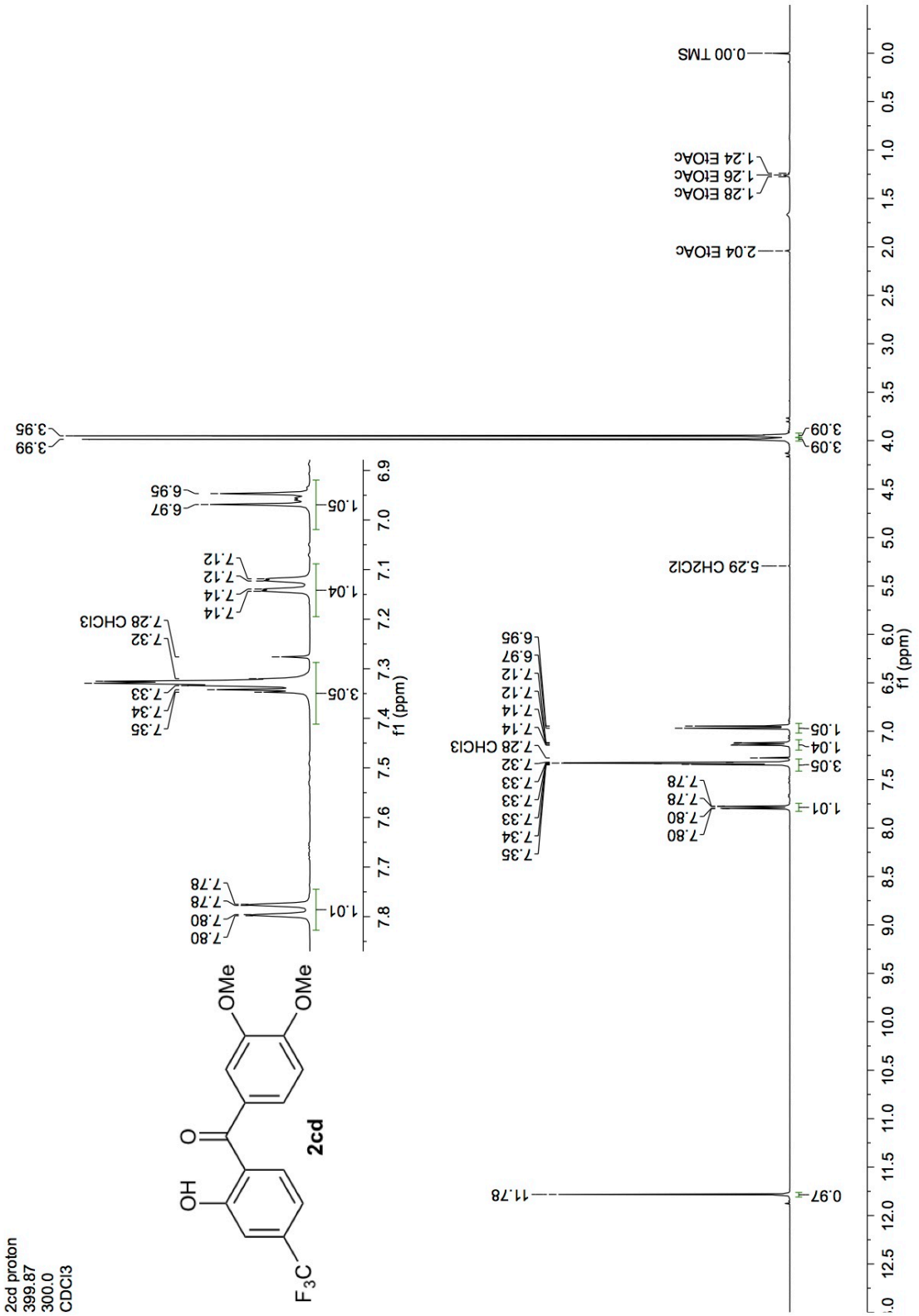


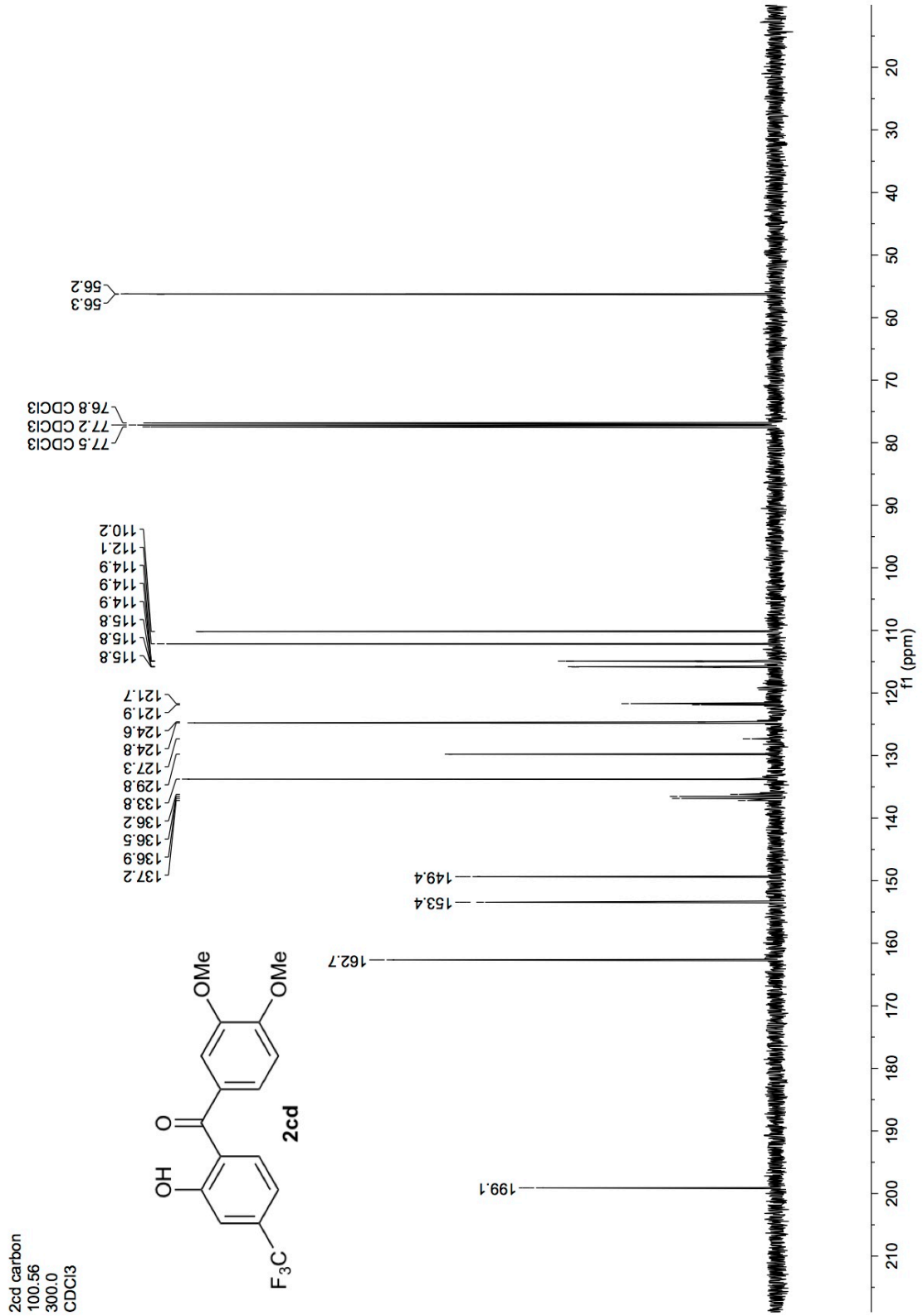
2cc

2cc with {1H} decoupling 19F
376.46
298.0
CDCl3

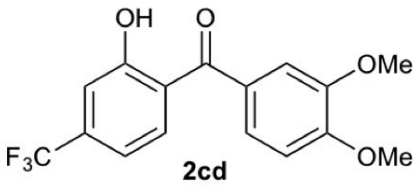


2cc


2cd proton
399.87
300.0
CDCl3
OMe
OMe
O
OH
F3C
2cd
f1 (ppm)
0.00 TMS
1.24 EtOAc
1.26 EtOAc
1.28 EtOAc
2.04 EtOAc
5.29 CH2Cl2
7.28 CHCl3

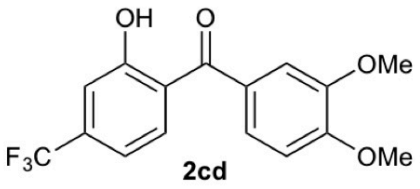

2cd carbon
100.56
300.0
CDCl3
OMe
OMe
O
OH
F3C
2cd
199.1
162.7
153.4
149.4
137.2
136.9
136.5
136.2
133.8
129.8
127.3
124.8
124.6
121.9
121.7
115.8
115.8
115.8
114.9
114.9
114.9
112.1
110.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.3
56.2
f1 (ppm)

2cd no decoupling 19F
376.46
298.0
CDCl3

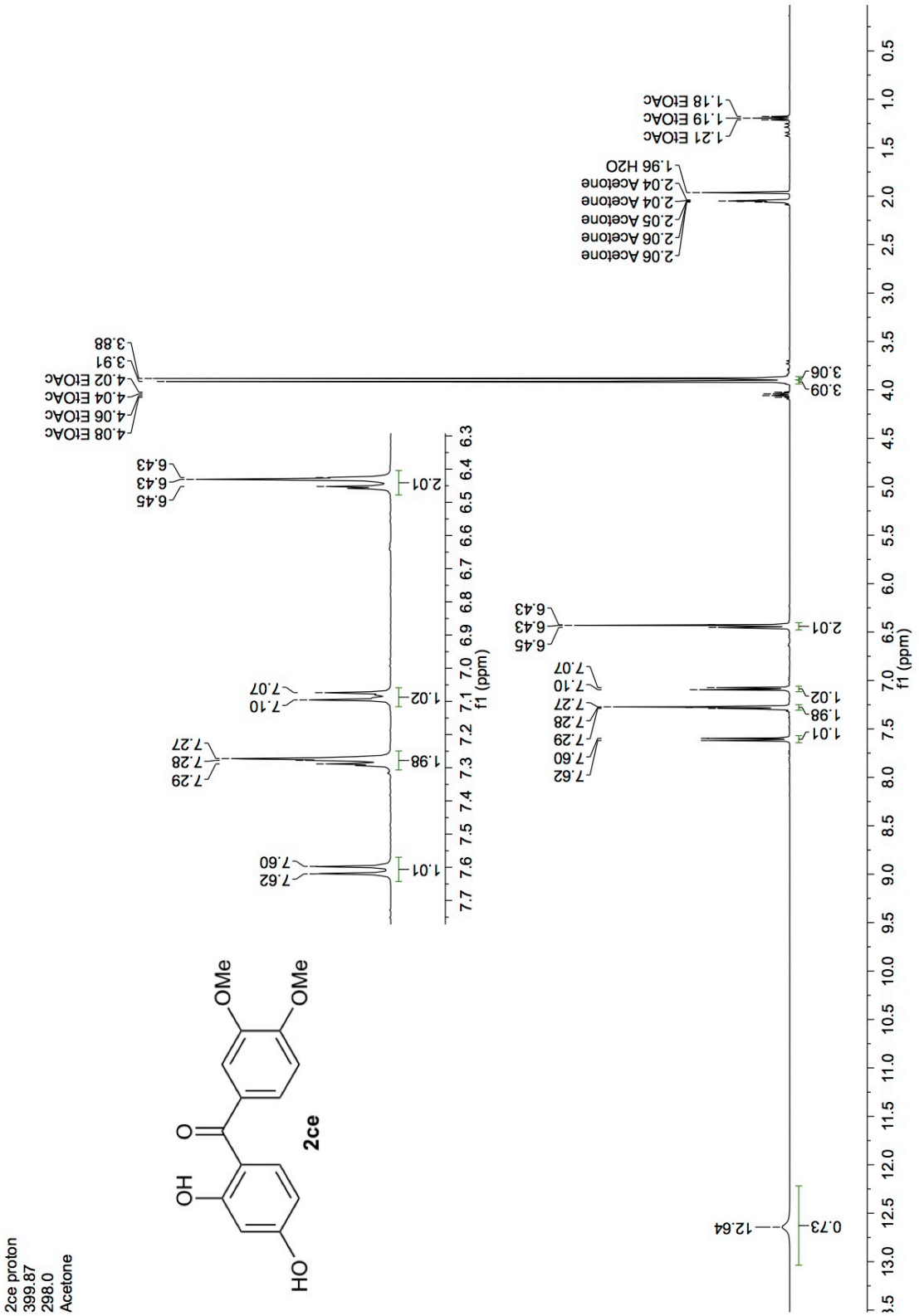


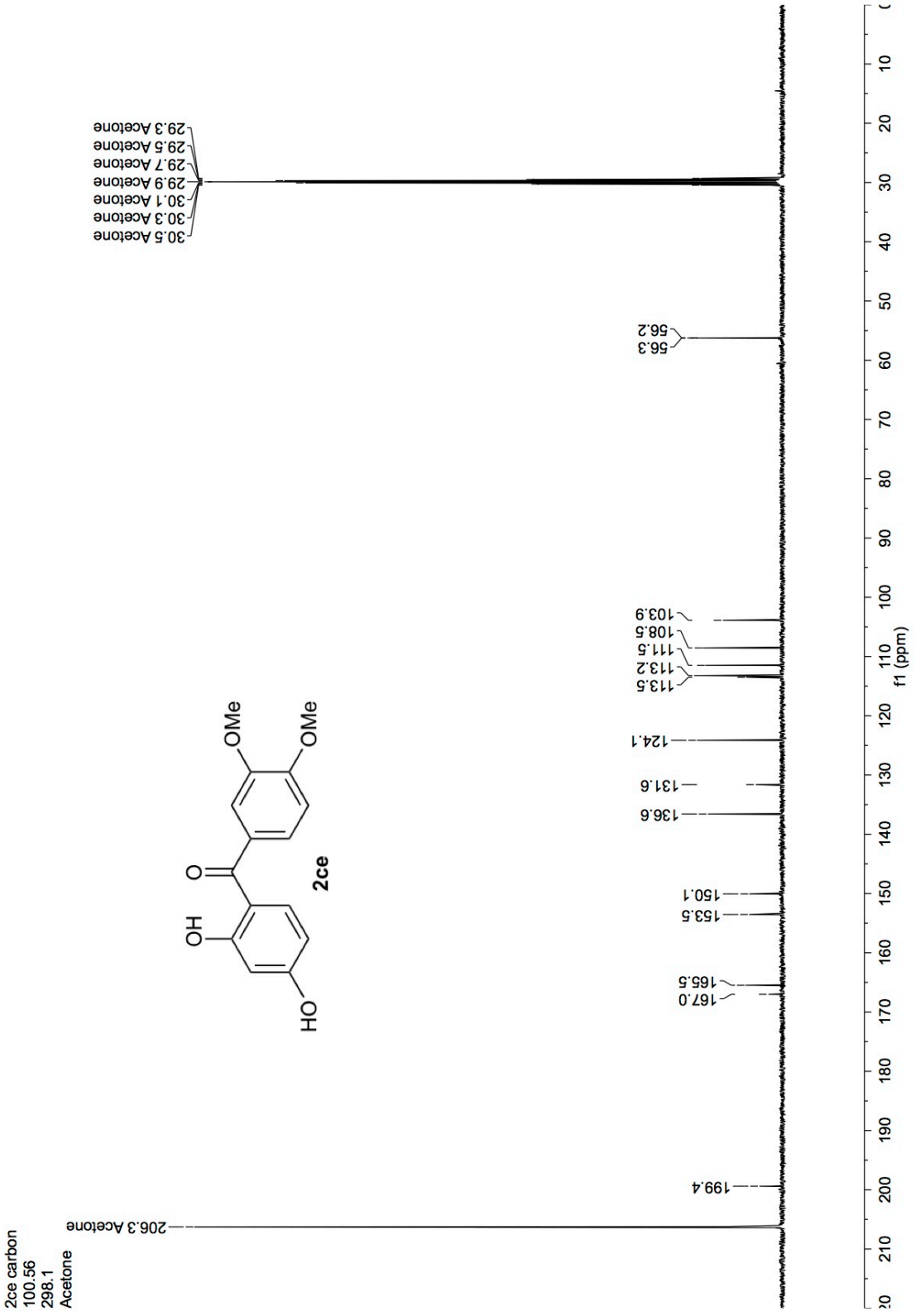
2cd

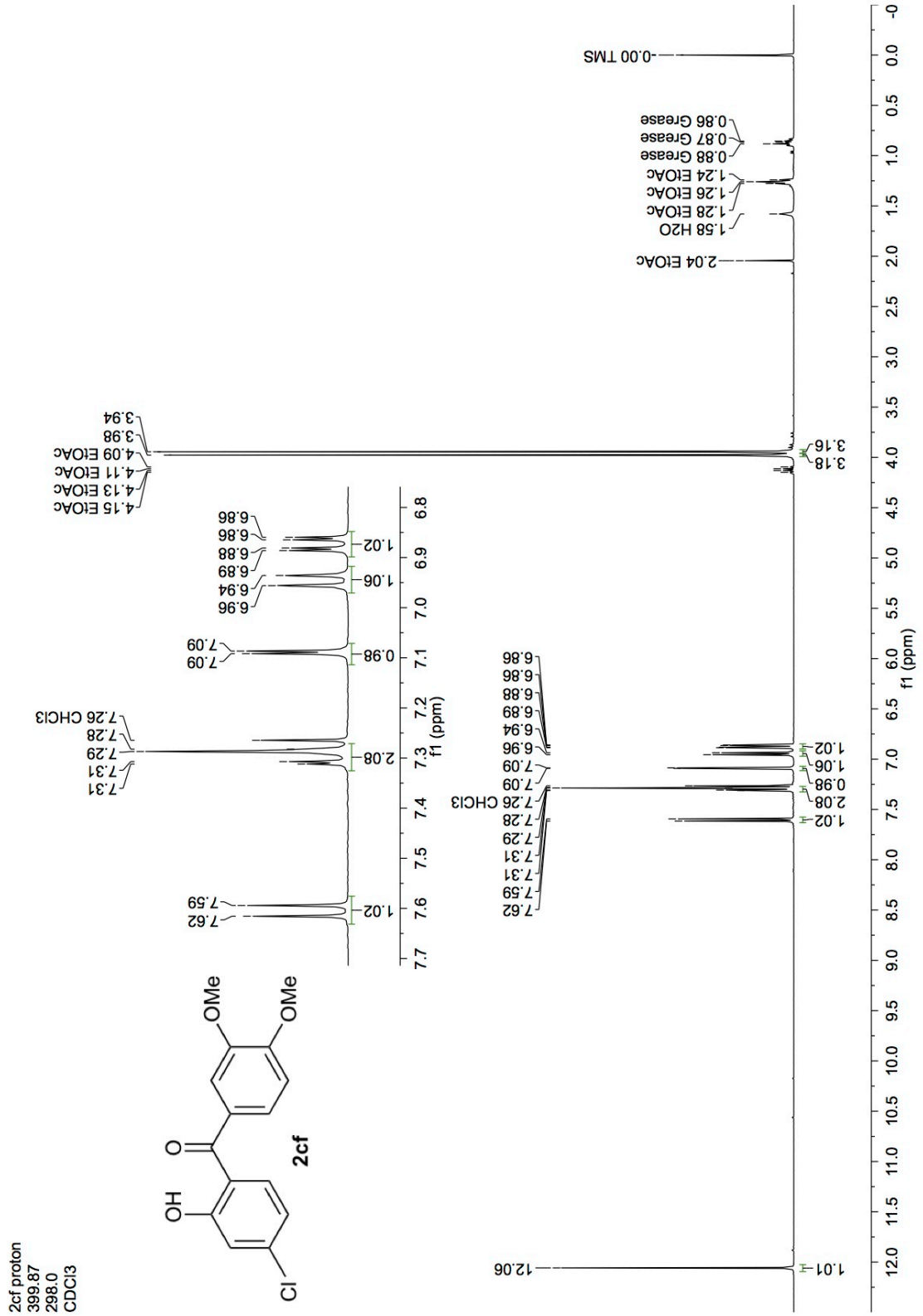
2cd with {1H} decoupling 19F
376.46
298.1
CDCl3

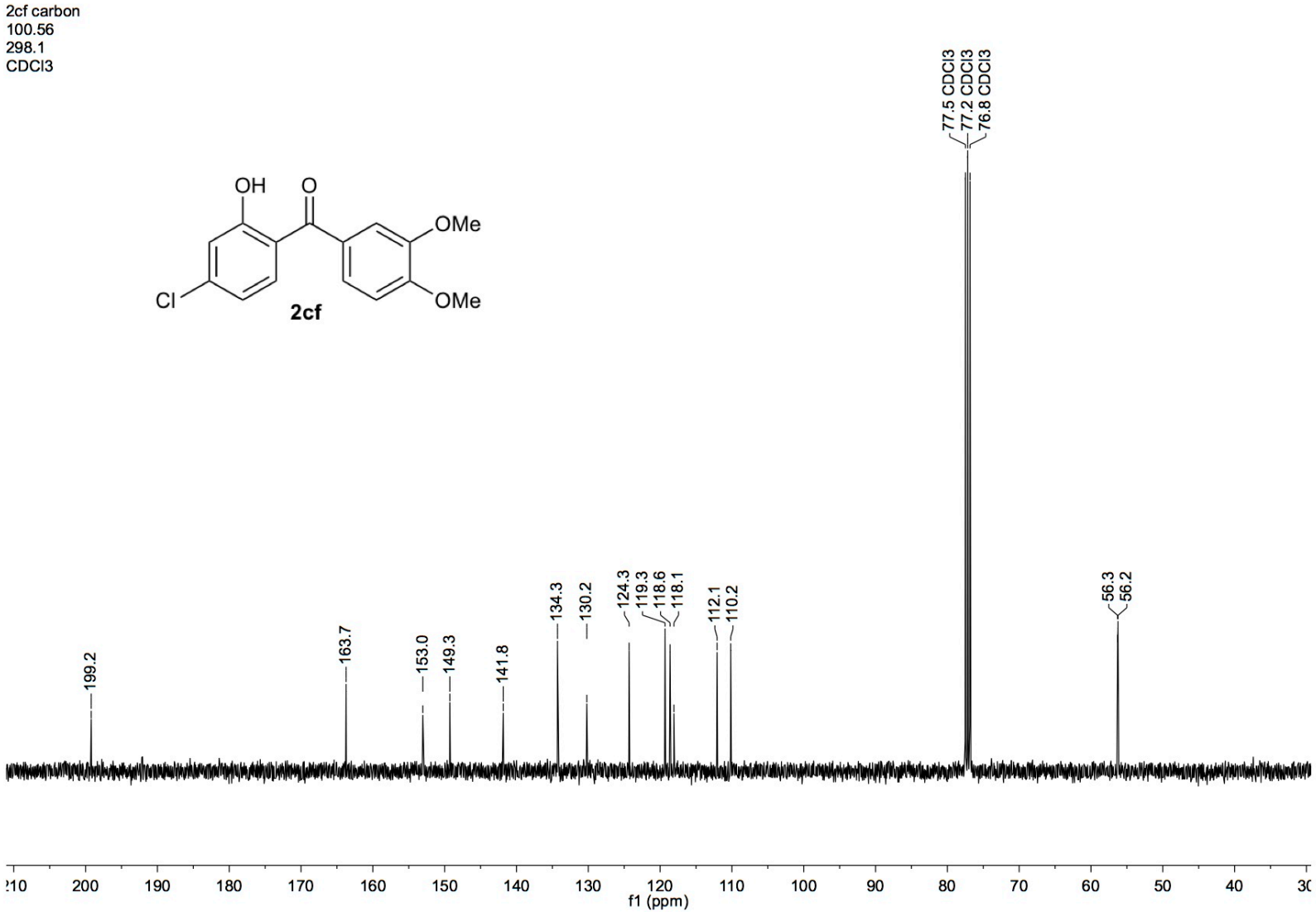


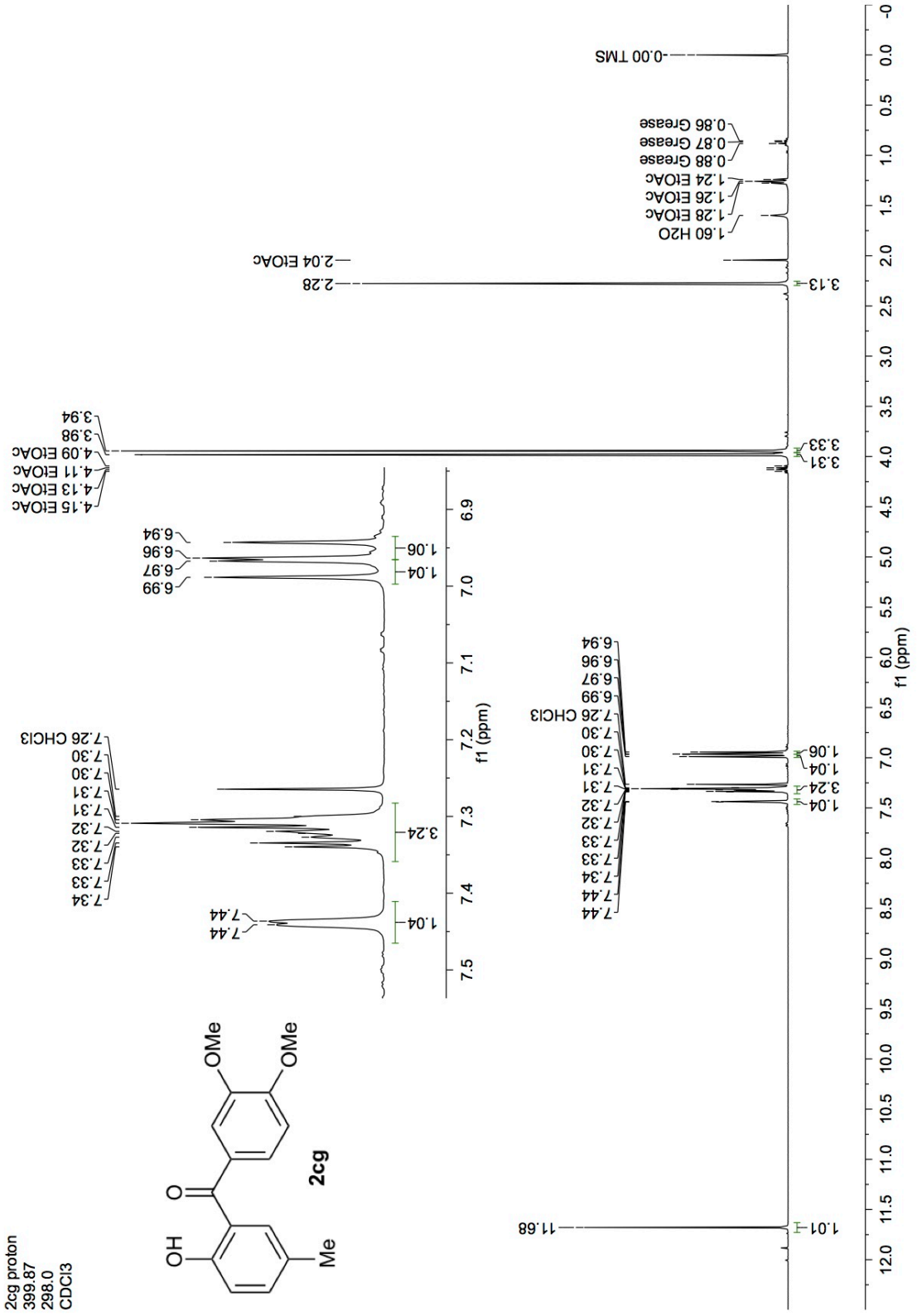
2cd

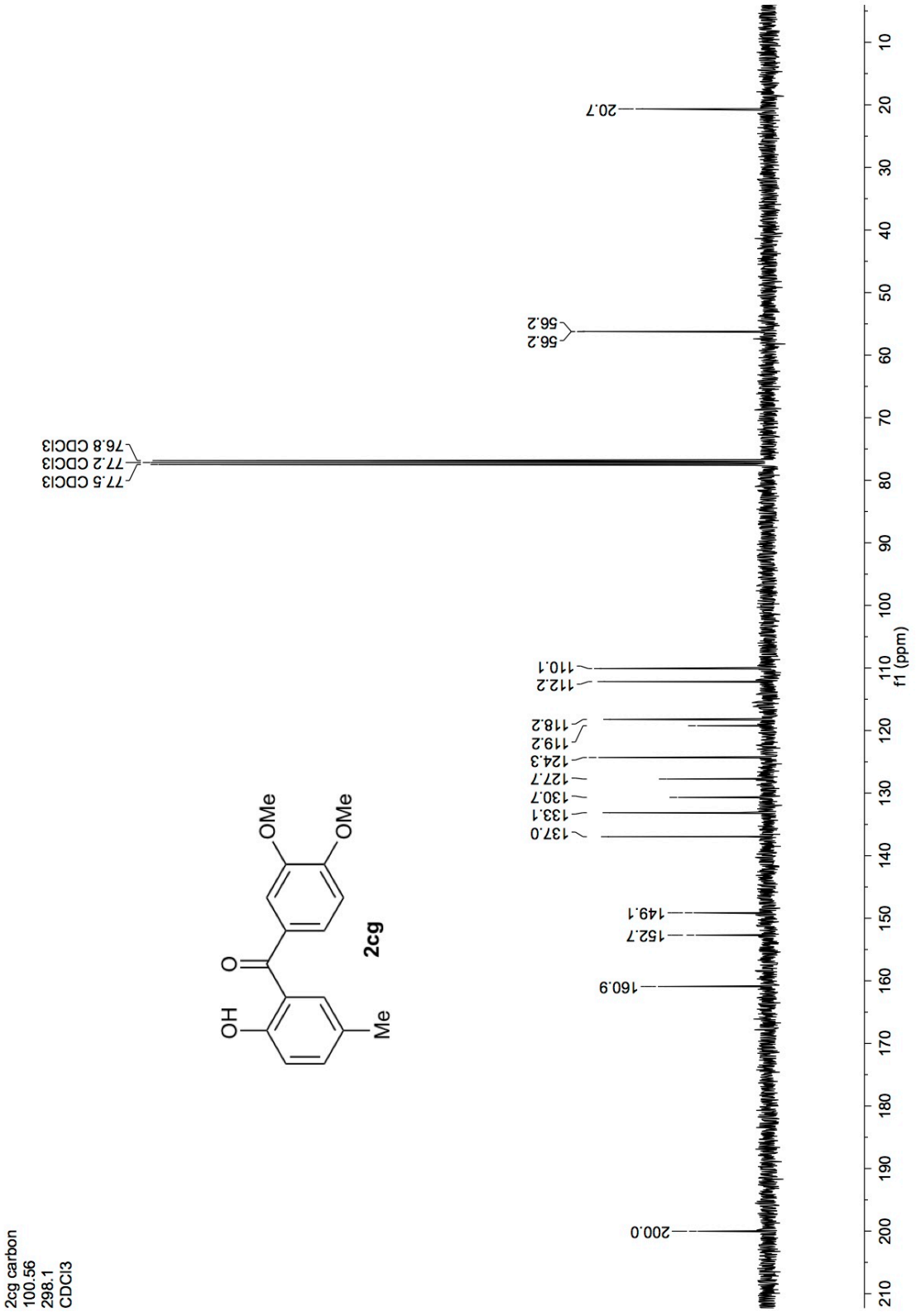

2ce proton
399.87
298.0
Acetone
OMe
OMe
O
OH
HO
2ce
f1 (ppm)

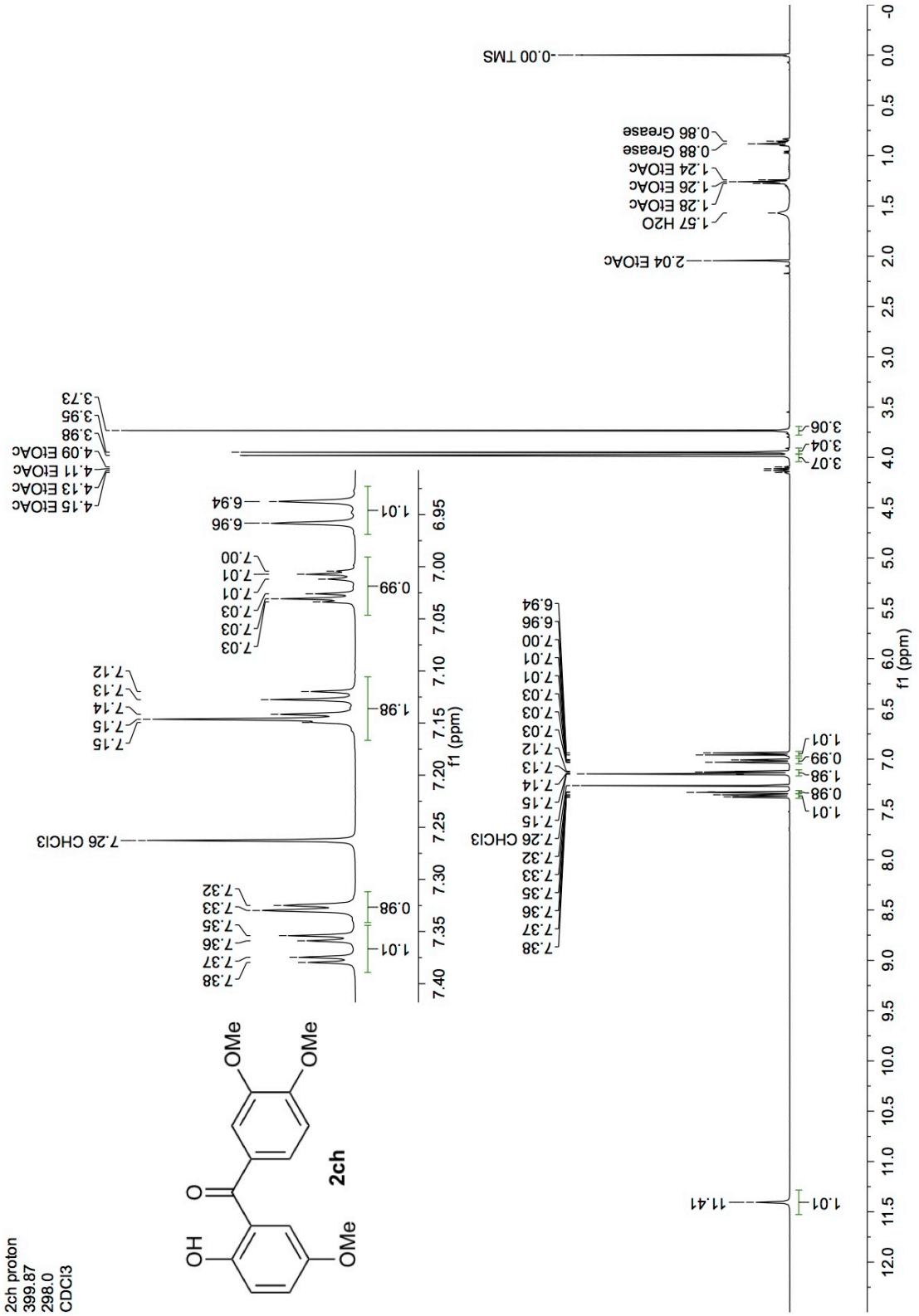

2ce carbon
100.56
298.1
Acetone
206.3 Acetone
199.4
167.0
165.5
153.5
150.1
136.6
131.6
124.1
113.5
113.2
111.5
108.5
103.9
56.3
56.2
30.5 Acetone
30.3 Acetone
30.1 Acetone
29.9 Acetone
29.7 Acetone
29.5 Acetone
29.3 Acetone
OMe
OMe
O
OH
HO
2ce
f1 (ppm)

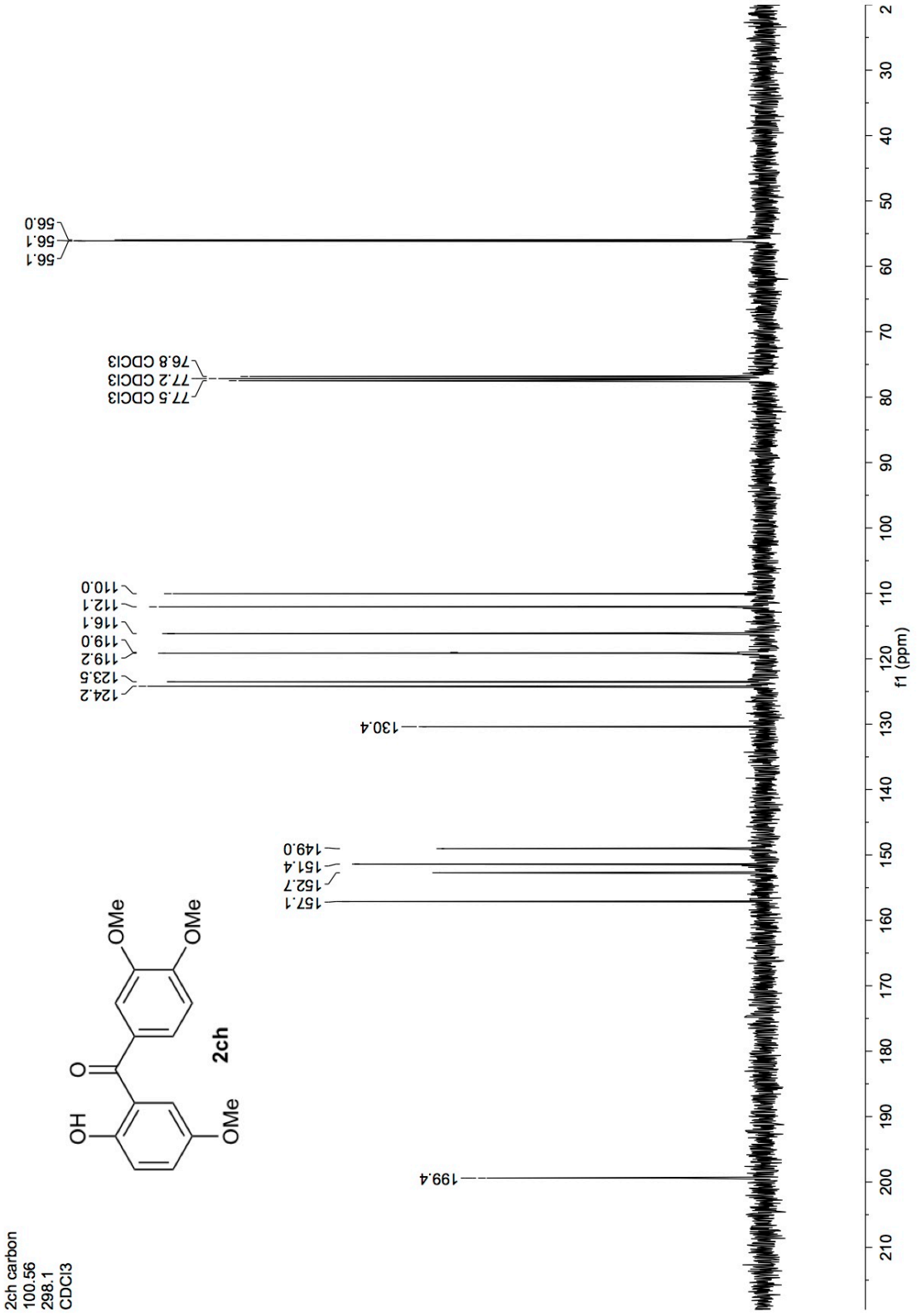

2cf proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
Cl
2cf
f1 (ppm)
-0.00 TMS
0.86 Grease
0.87 Grease
0.88 Grease
1.24 EtOAc
1.26 EtOAc
1.28 EtOAc
1.58 H2O
2.04 EtOAc
3.16
3.18
4.09 EtOAc
4.11 EtOAc
4.13 EtOAc
4.15 EtOAc
3.94
3.98
6.86
6.88
6.89
6.94
6.96
7.09
7.26 CHCl3
7.28
7.29
7.31
7.59
7.62
12.06
1.01
1.02
0.98
2.08
1.06
1.02

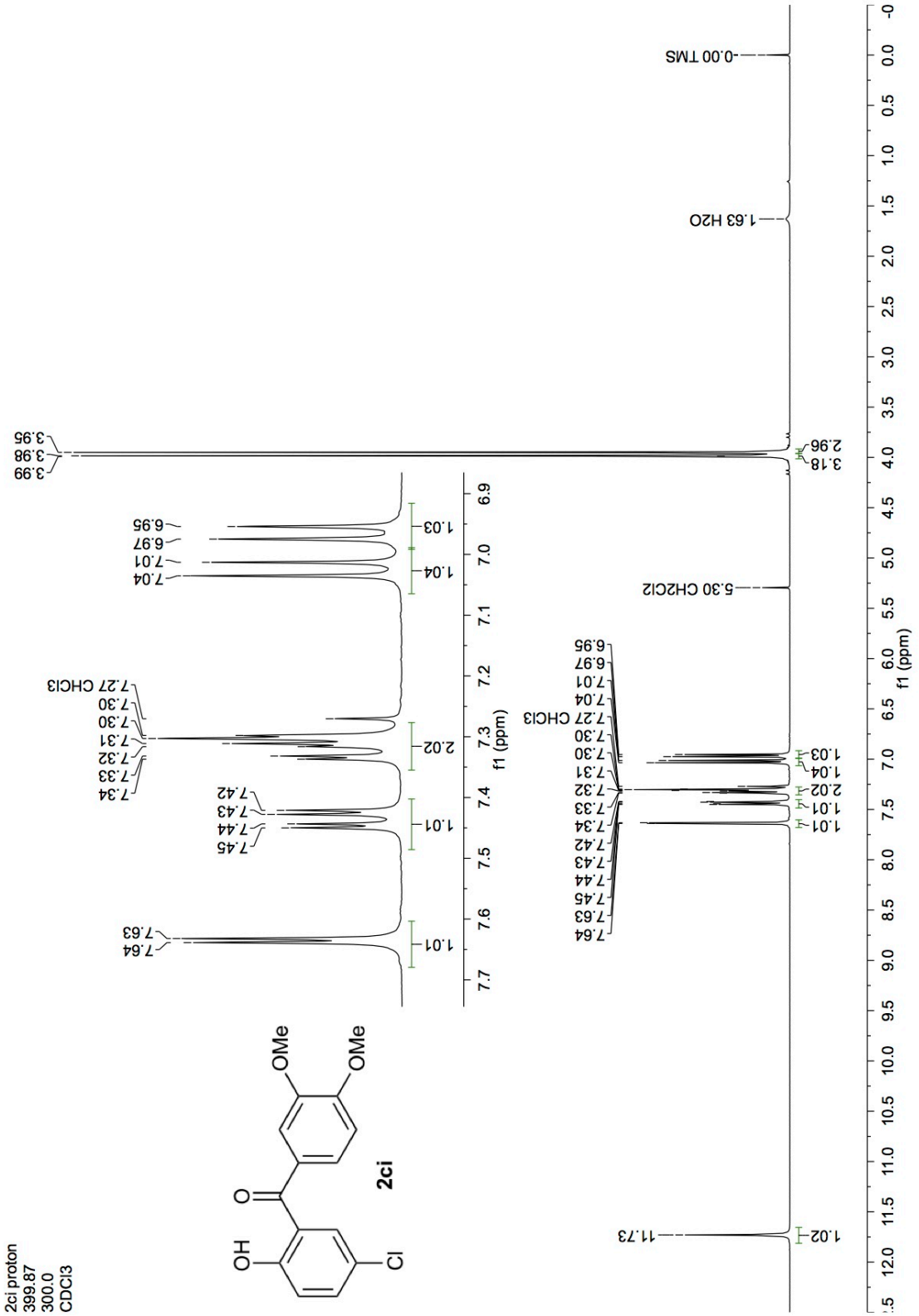

2cf carbon
100.56
298.1
CDCl3
OH
O
OMe
OMe
Cl
2cf
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
199.2
163.7
153.0
149.3
141.8
134.3
130.2
124.3
119.3
118.6
118.1
112.1
110.2
56.3
56.2
f1 (ppm)

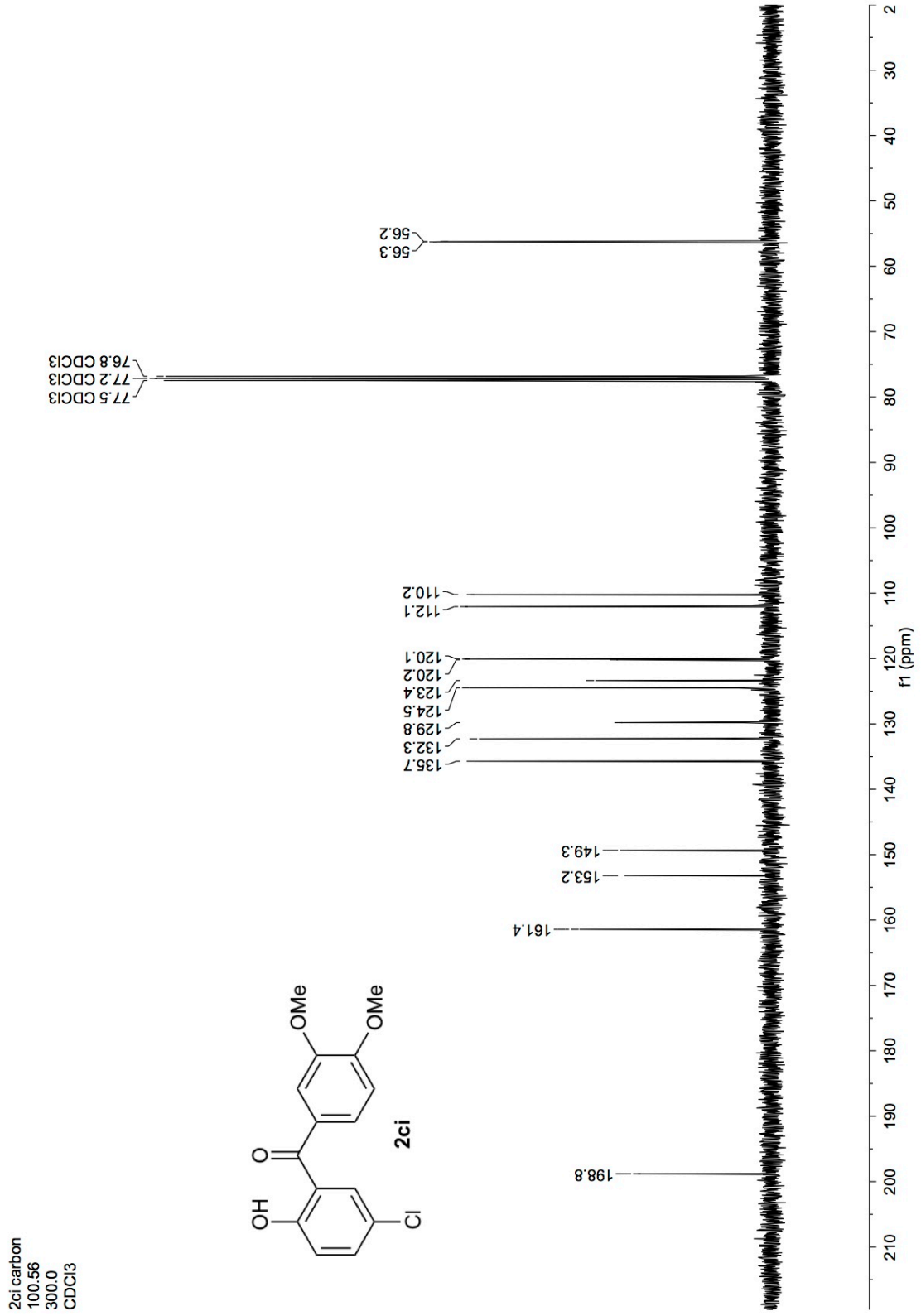

2cg proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
Me
2cg
-0.00 TMS
0.86 Grease
0.87 Grease
0.88 Grease
1.24 EtOAc
1.26 EtOAc
1.28 EtOAc
1.60 H2O
2.04 EtOAc
2.28
3.13
3.31
3.33
4.15 EtOAc
4.13 EtOAc
4.11 EtOAc
4.09 EtOAc
3.98
3.94
6.94
6.96
6.97
6.99
7.26 CHCl3
7.30
7.30
7.31
7.31
7.32
7.32
7.33
7.33
7.34
7.44
11.68
1.01
1.04
3.24
1.04
1.06
f1 (ppm)

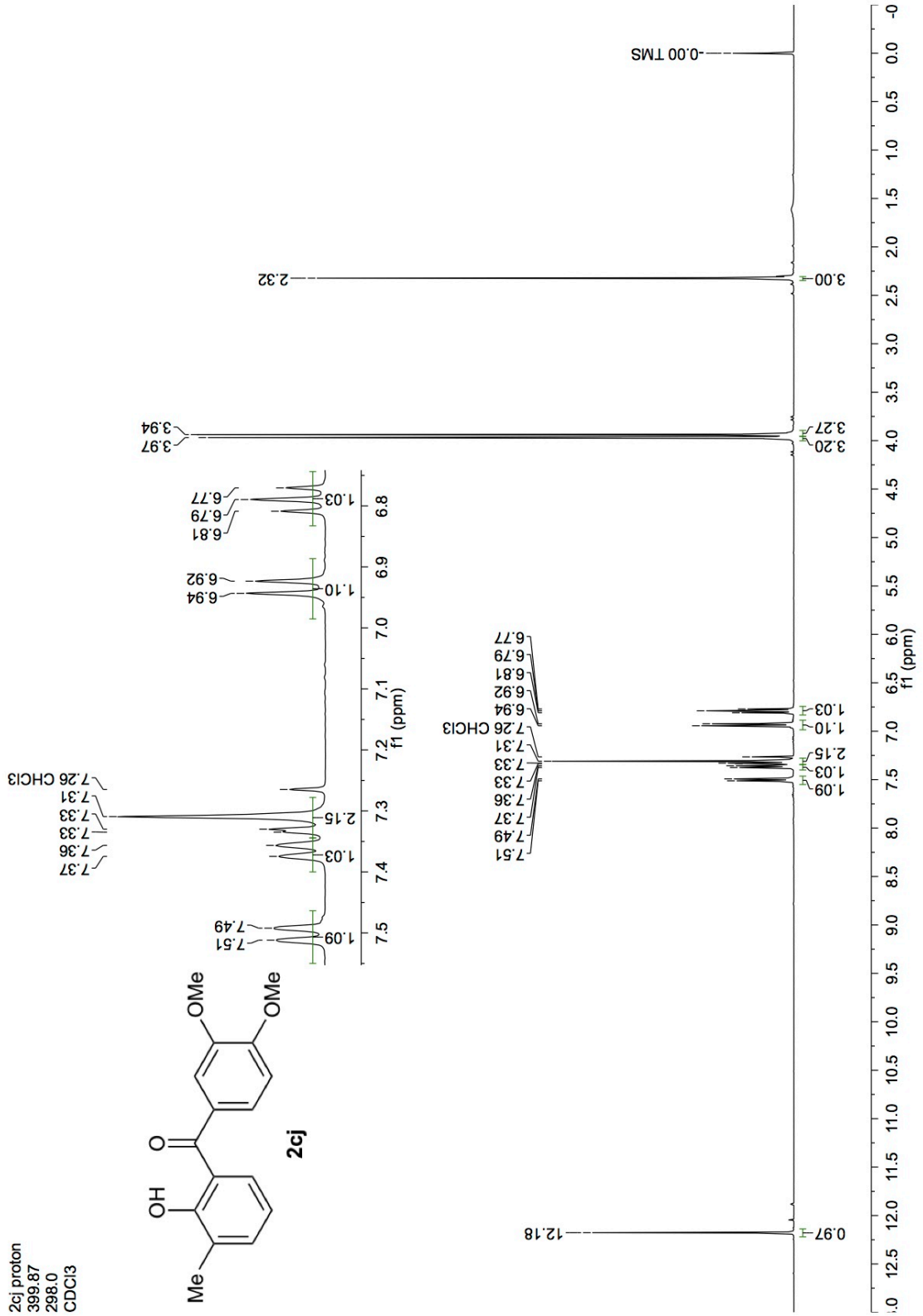

2cg carbon
100.56
298.1
CDCl3
OMe
OMe
O
OH
Me
2cg
200.0
160.9
152.7
149.1
137.0
133.1
130.7
127.7
124.3
119.2
118.2
112.2
110.1
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.2
56.2
20.7
f1 (ppm)

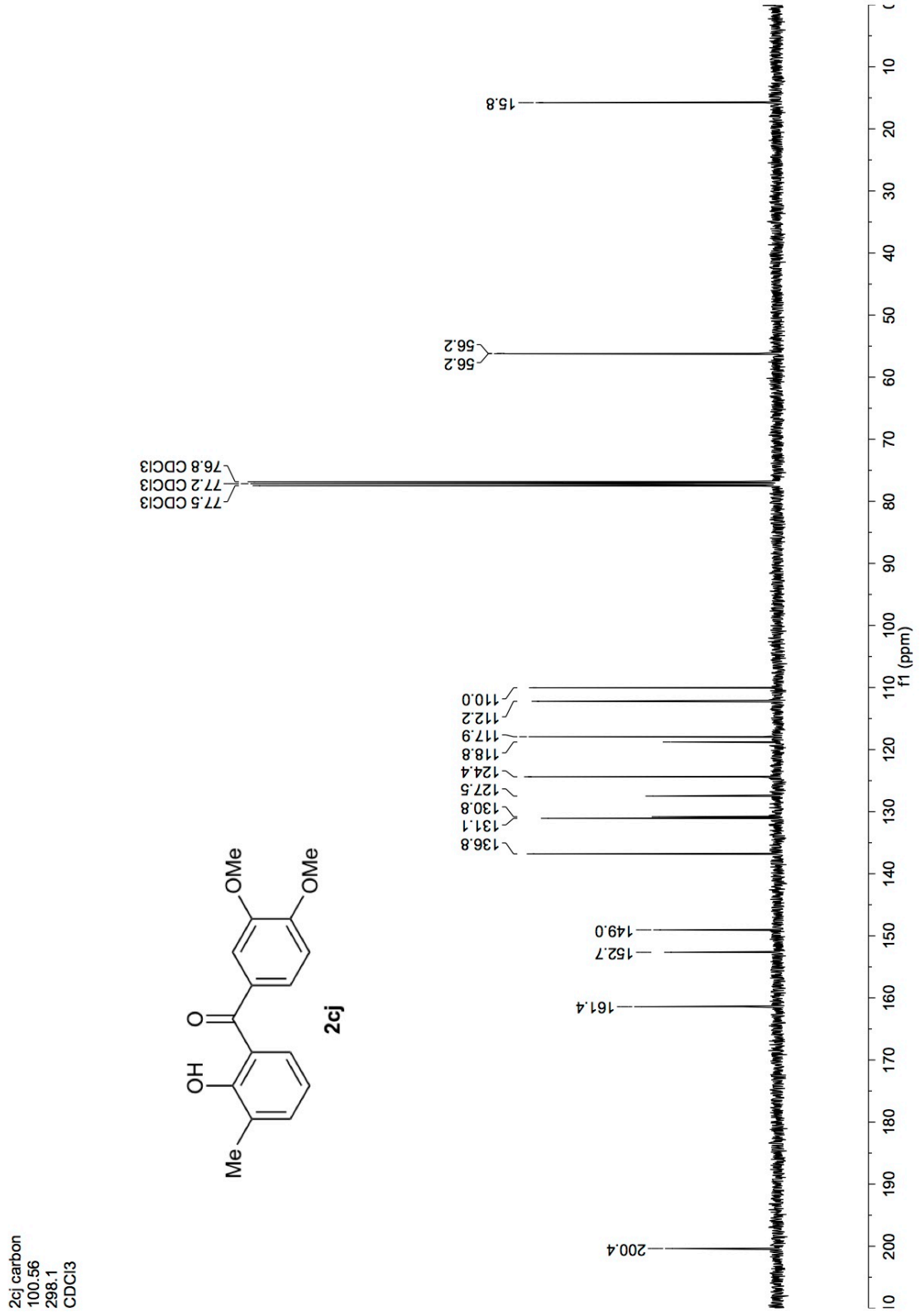

2ch proton
399.87
298.0
CDCl3
2ch
OMe
OMe
OMe
OH
O
f1 (ppm)
-0.00 TMS
0.86 Grease
0.88 Grease
1.24 EtOAc
1.26 EtOAc
1.28 EtOAc
1.57 H2O
2.04 EtOAc
3.06
3.04
3.07
4.15 EtOAc
4.13 EtOAc
4.11 EtOAc
4.09 EtOAc
3.98
3.95
3.73
7.26 CHCl3
11.41
1.01
0.98
1.98
0.99
1.01

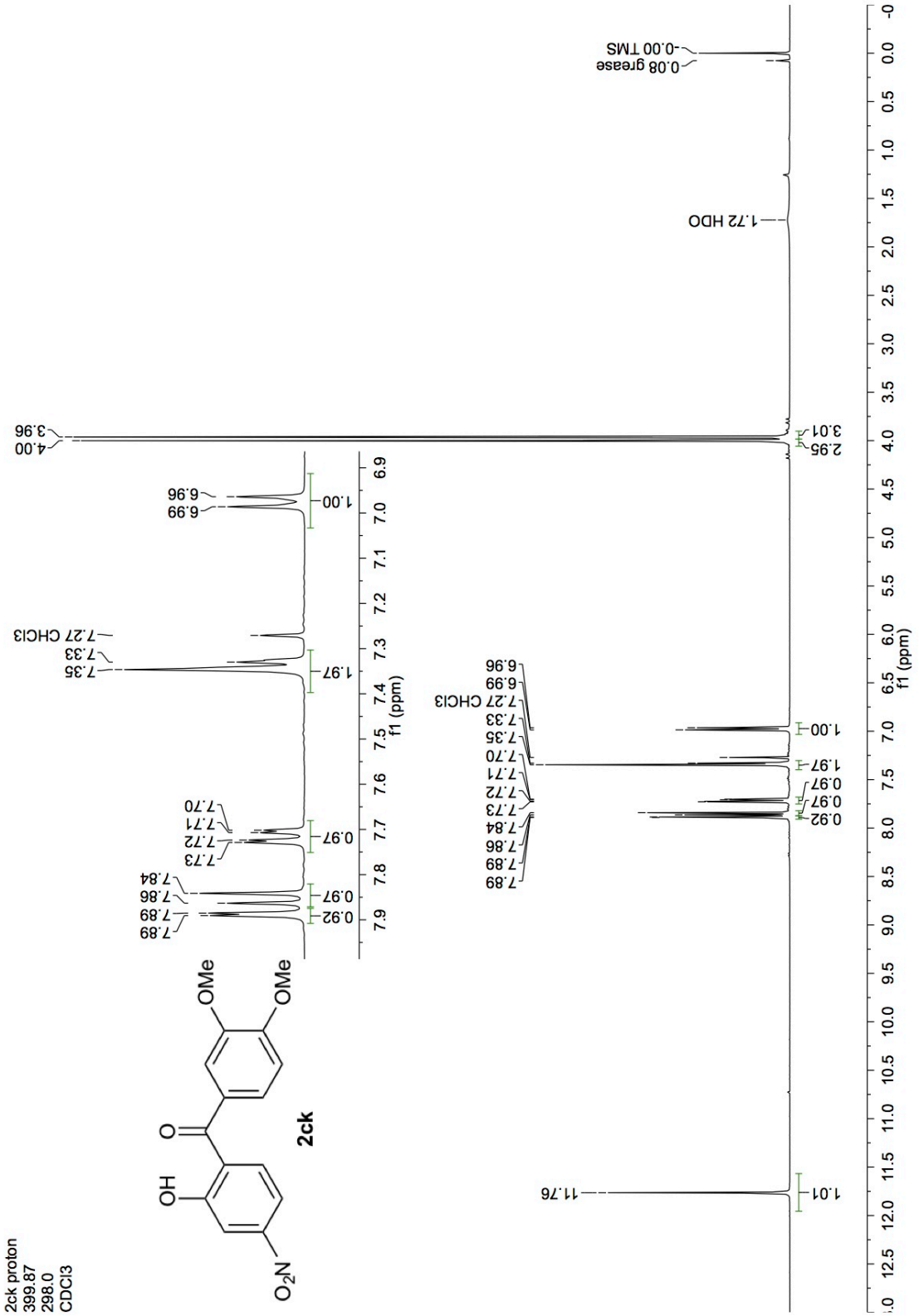

2ch carbon
100.56
298.1
CDCl3
OMe
OMe
OH
O
OMe
2ch
199.4
157.1
152.7
151.4
149.0
130.4
124.2
123.5
119.2
119.0
116.1
112.1
110.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.1
56.1
56.0
f1 (ppm)


2ci proton
399.87
300.0
CDCl3
OMe
OMe
O
OH
Cl
2ci
f1 (ppm)
-0.00 TMS
1.63 H2O
5.30 CH2Cl2
7.27 CHCl3
3.99
3.98
3.95
3.18
2.96
1.02
11.73
1.01
2.02
1.04
1.03
7.64
7.63
7.45
7.44
7.43
7.42
7.34
7.33
7.32
7.31
7.30
7.04
7.01
6.97
6.95

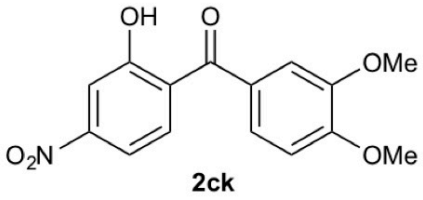

2ci carbon
100.56
300.0
CDCl3
OMe
OMe
O
OH
Cl
2ci
198.8
161.4
153.2
149.3
135.7
132.3
129.8
124.5
123.4
120.2
120.1
112.1
110.2
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.3
56.2
f1 (ppm)


2cj proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
Me
2cj
f1 (ppm)
-0.00 TMS
12.18
7.51
7.49
7.37
7.36
7.33
7.33
7.31
7.26 CHCl3
6.94
6.92
6.81
6.79
6.77
3.97
3.94
2.32
1.09
1.03
2.15
1.10
3.27
3.20
3.00
0.97

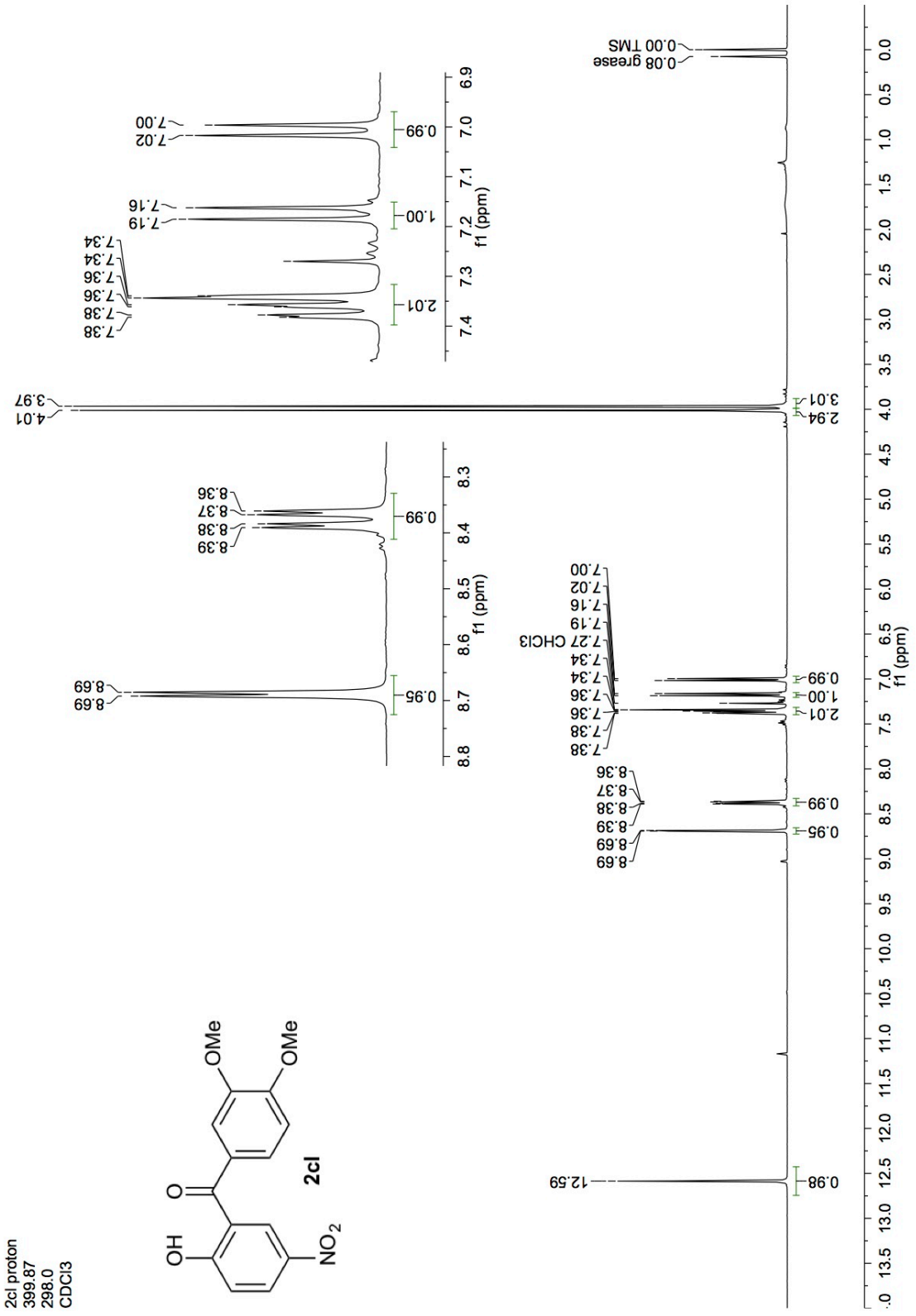

2cj carbon
100.56
298.1
CDCl3
OMe
OMe
O
OH
Me
2cj
200.4
161.4
152.7
149.0
136.8
131.1
130.8
127.5
124.4
118.8
117.9
112.2
110.0
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.2
56.2
15.8
f1 (ppm)

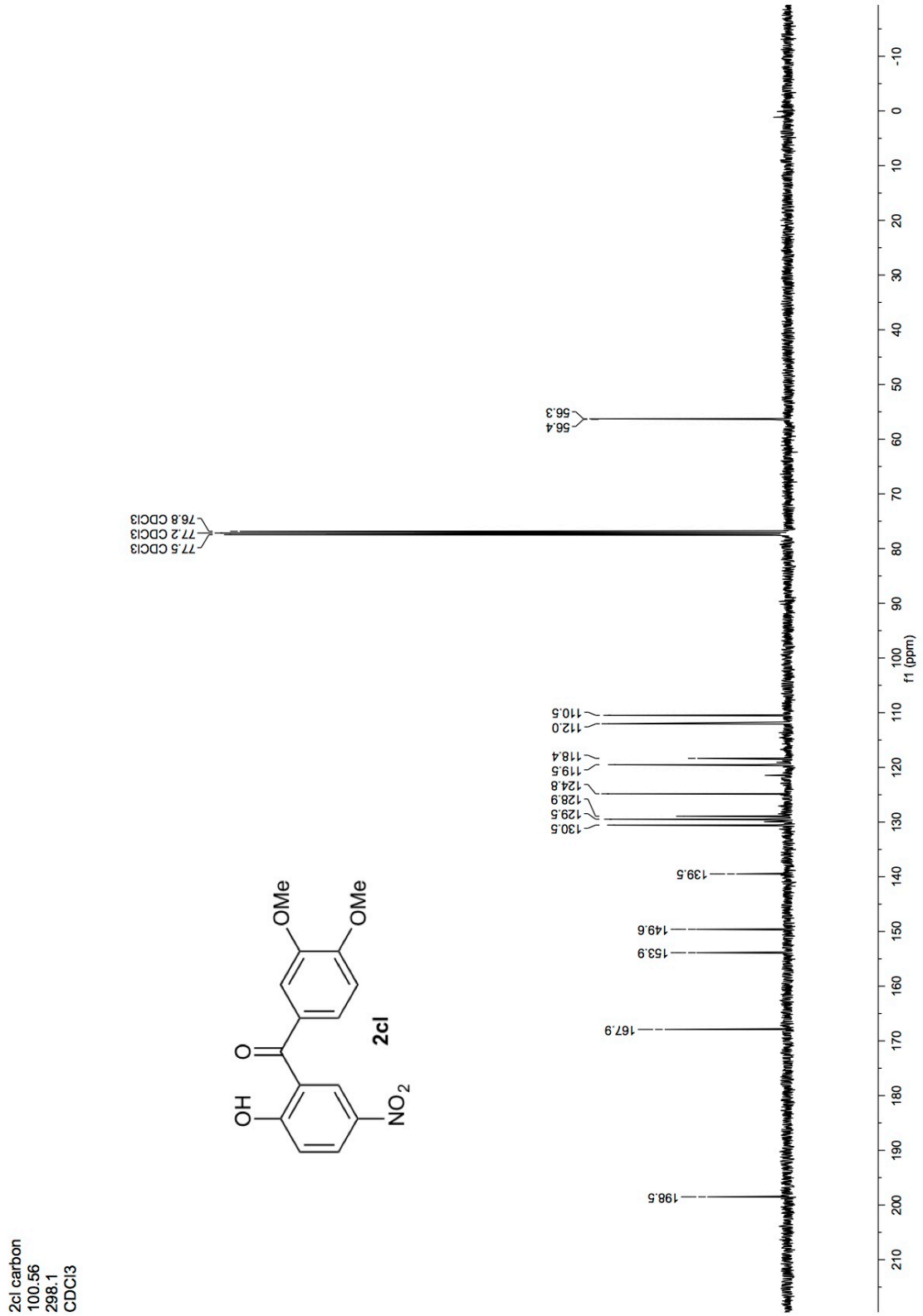

2ck proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
O_2N
2ck
f1 (ppm)
0.08 grease
-0.00 TMS
1.72 HDO
7.27 CHCl3

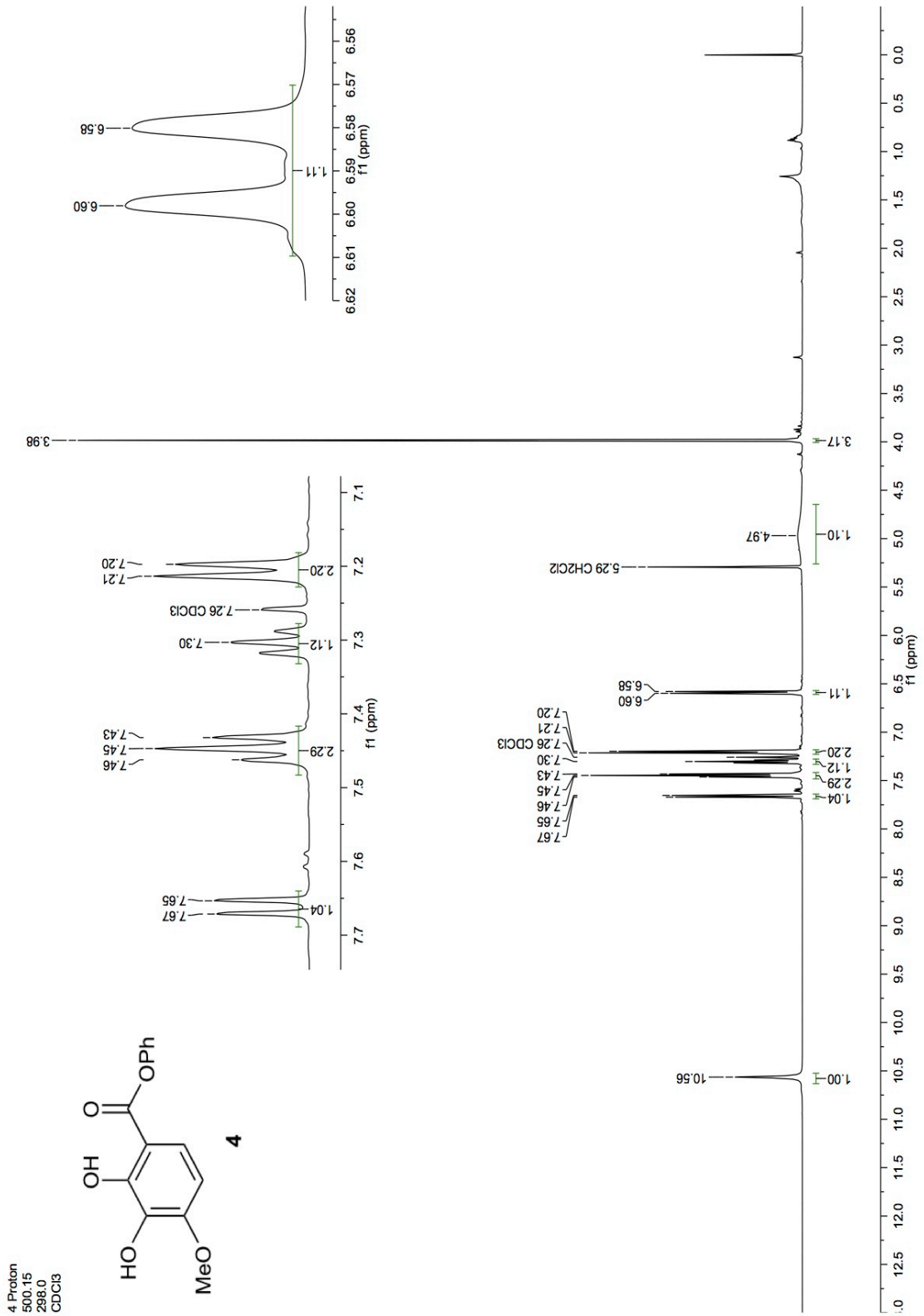
2ck carbon
100.56
298.1
CDCl3

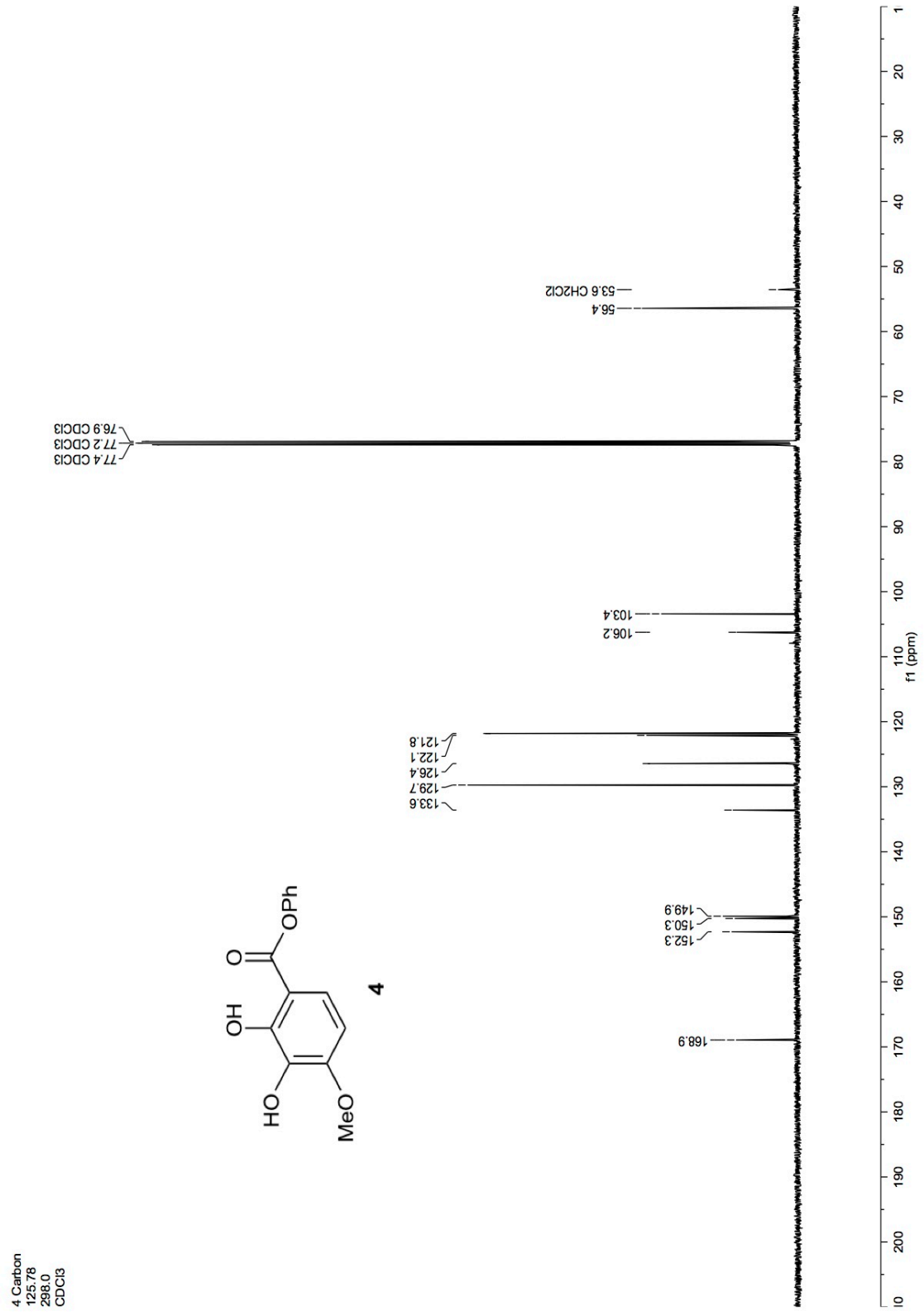


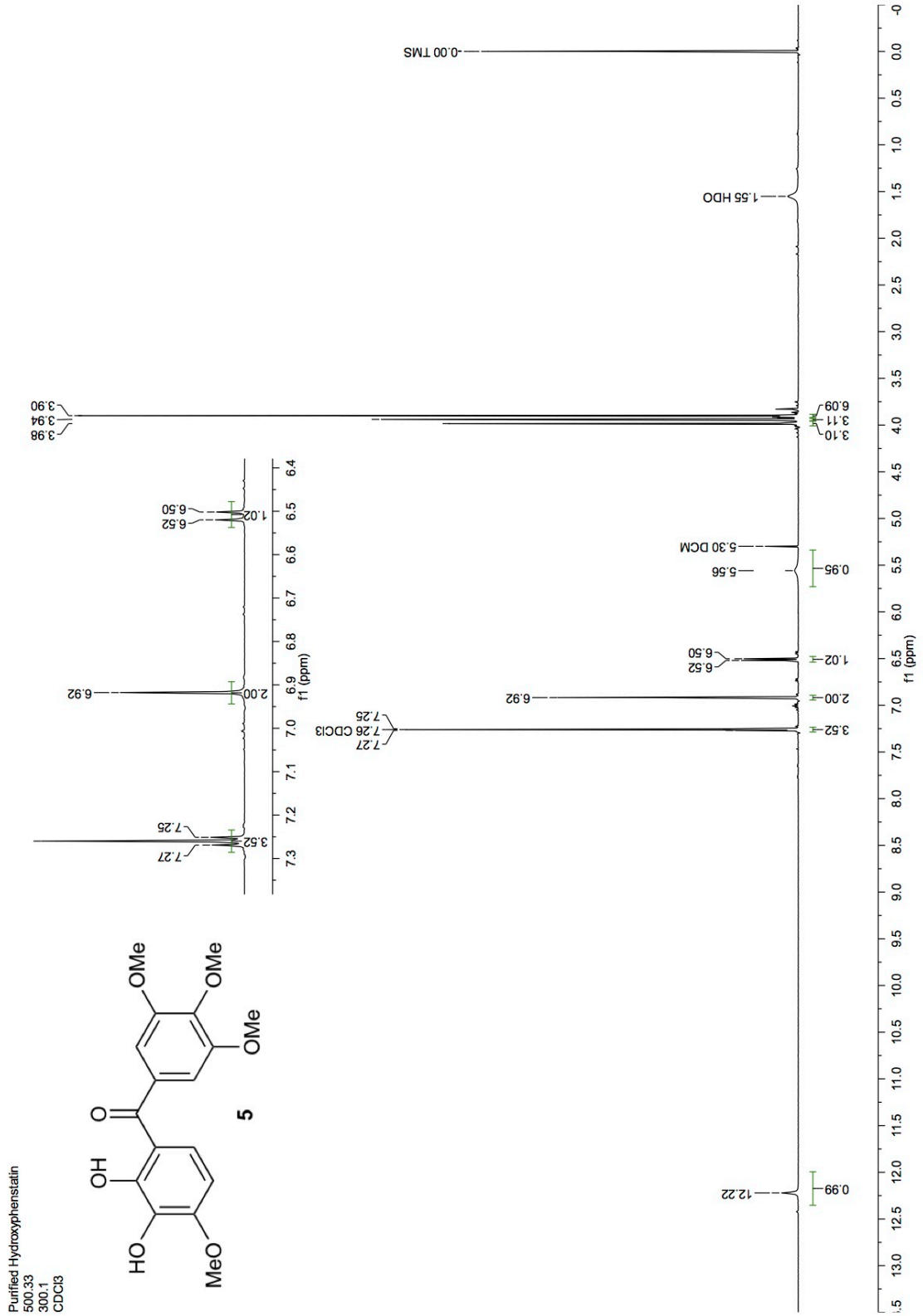
2ck


2cl proton
399.87
298.0
CDCl3
OMe
OMe
O
OH
NO2
2cl
f1 (ppm)
CHCl3
TMS
grease


2cl carbon
100.56
298.1
CDCl3
OMe
OMe
O
OH
NO2
2cl
198.5
167.9
153.9
149.6
139.5
130.5
129.5
128.9
124.8
119.5
118.4
112.0
110.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
56.4
56.3
f1 (ppm)


4 Proton
500.15
298.0
CDCl3
OPh
O
OH
HO
MeO
4
10.56
7.67
7.65
7.46
7.45
7.43
7.30
7.26 CDCl3
7.21
7.20
6.60
6.58
5.29 CH2Cl2
4.97
3.98
2.29
1.12
1.04
2.20
1.11
1.10
3.17
1.00
f1 (ppm)


4 Carbon
125.78
298.0
CDCl3
OPh
O
OH
HO
MeO
4
168.9
152.3
150.3
149.9
133.6
129.7
126.4
122.1
121.8
106.2
103.4
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
56.4
53.6 CH2Cl2
f1 (ppm)


Purified Hydroxyphenstatin
500.33
300.1
CDCl3
OMe
OMe
OMe
O
OH
HO
MeO
5
0.00 TMS
1.55 HDO
5.30 DCM
5.56
6.52
6.50
6.92
7.27
7.26 CDCl3
7.25
3.98
3.94
3.90
3.10
3.11
6.09
12.22
0.99
0.95
1.02
2.00
3.52
f1 (ppm)