MILD SYNTHESIS OF SULPHONIUM SALTS FROM HYPERVALENT IODINE BENZYNE PRECURSORS

BY

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I am eternally grateful for the friendships that I have made along the way. To quote Ging Freecss: “You should enjoy the little detours to the fullest, because that’s where you’ll find the things more important than what you want.” I appreciate the friends I have made for your unconditionally protection, support, and love-Anh C., Greeshma P., Nathan D., Adeesha

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My family has been a loving support although young me has often failed to realize. Without the fights, the flaws, we wouldn’t stand here stronger as ever. You have been where I return in times of hardships but now, I realize that you are who I want to be around during easy times as well. Cám ơn bố mẹ rất nhiều. Nhờ bố mẹ mà con có được ngày hôm nay. Con thương bố mẹ lắm!

To my new family, Naoto, Meatball & Baby, I have never truly understood the phrase “unwavering love and support” until you have loved me.

Dedicated to my family, bố mẹ, chi Sa & Na, & my Naoto

For your unconditional love

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1. PREFACE:

Interest in efficient protocols for obtaining sulfonium salts are stemmed from their tremendous applications. Arylsulfonium salts are highly photosensitive and are well known for their ability of releasing protons under UV conditions. Thus, they are widely used as photoinitiators applied in the fields of coatings and materials. From the synthetic standpoint, they can serve as aryl or alkyl donation sources, forming interesting organic frameworks. Therefore, access to these compounds is highly desired. Recently, our group reported an efficient benzyne precursor, pseudocyclic arylbenziodoxaboroles, that can be generated in mild conditions: treatment with water or weak base at room temperature. Reactions of such benzyne precursor with various sulfide substrates allow for diverse functionalized sulfonium salts obtained in moderate to excellent yield.

2. BACKGROUND INFORMATION

2.1. General hypervalent iodine compounds

Elemental iodine is among the heaviest non-metal and non-radioactive elements. Iodine was first isolated from the ash of seaweed by Bernard Courtois in 1811. Since the beginning of the 19th century, many derivatives of polyvalent iodine inorganic compounds with oxidation states of +3, +5 and +7 were prepared. The formation of iodine organic and inorganic derivatives in various oxidation states (-1, 0, +1, +3, +5, +7) was also found.

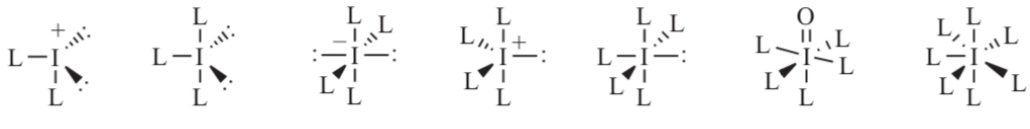
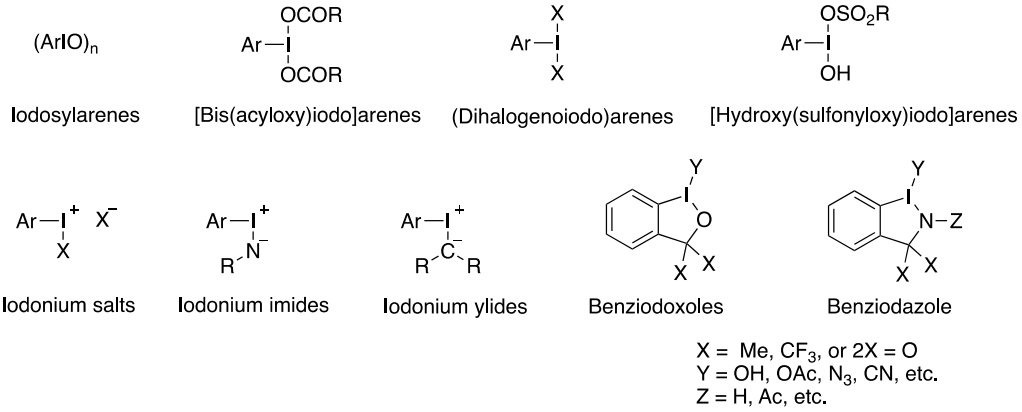


Figure 1. Martin-Arduengo classification for hypervalent iodine compounds.

In organic chemistry, iodine and its compounds in higher oxidation states have emerged as versatile and environmentally friendly reagents in the field. An attractive feature of iodine is its similar reactivity to that of a heavy metal counterpart. Iodine compounds are often used for oxidative addition, ligand exchange, and reductive elimination, which are commonly discussed in the field of transition metal chemistry. In contrast to its transition metal competitor, iodine is more environmentally friendly and can be obtained at a low cost. A large variety of trivalent and pentavalent iodine have been prepared, characterized and tested for various applications. Lesser examples of heptavalent iodine compounds were studied[1,2].

Common examples of trivalent iodine compounds:



Common examples of pentavalent iodine compounds:

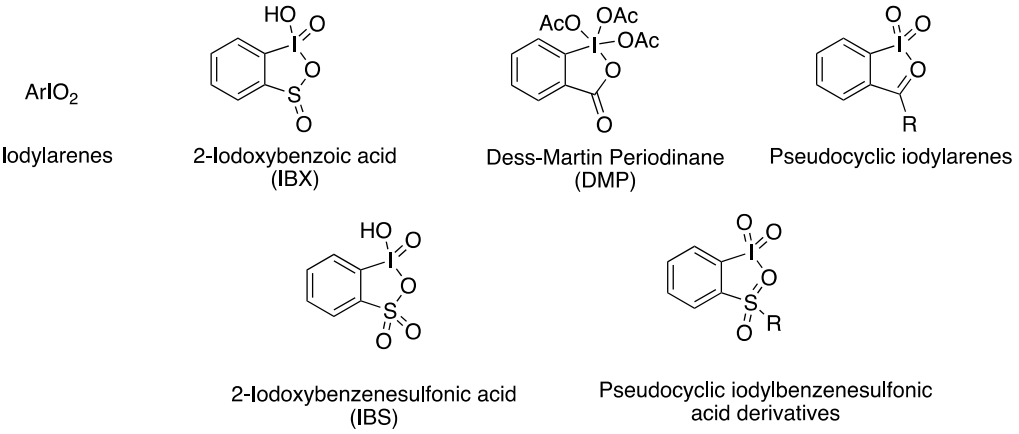
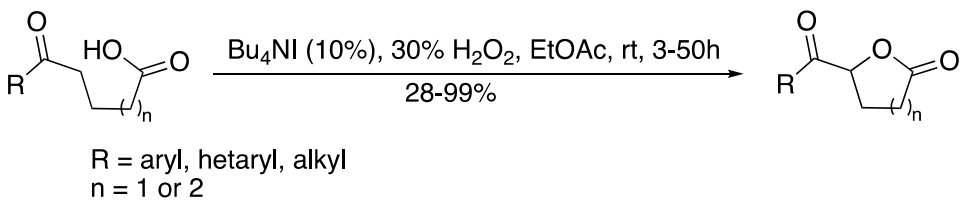


Figure 2. Examples of common iodine oxidation agents in each oxidation state

2.2. Examples of new bond transformations using iodine compound catalysts

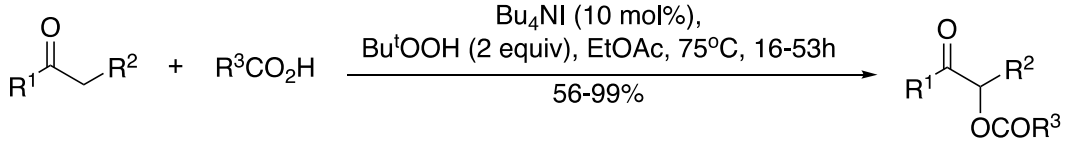
Ishihara and co-workers reported a first case of obtaining lactones from oxocarboxylic acids using tetrabulammonium iodide and aqueous hydrogen peroxide at room temperature[3]. The approach is simple and environmentally friendly while allows for obtaining lactones in moderate to excellent yield in both large and small scale synthesis. An important advantage of this approach is that it allows for the conversion to lactones without the Baeyer-Villiger byproducts which potentially complicate the purification process.



Scheme 1. Oxylactonization from oxocarboxylic acids using tetrabutylammonium iodide as a

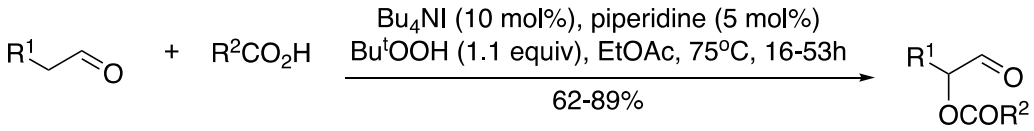
pre-catalyst.

This procedure inspires further oxidative applications to obtain carbonyl compounds from carboxylic acids and ketones or 1,3-dicarbonyl compounds. *Tert*-butylhydroperoxide (TBHP) is used as terminal oxidant instead of hydrogen peroxide. Similarly, aldehydes can be α-oxyacylated using Bu_4NI with piperidine and TBHP as terminal oxidant. Both processes allow for the desired products to be obtained in good to excellent yields. Various functional groups such as terminal or internal alkenyl, benzyloxy, silyloxy, acetal, halogen, and ester are reported to be stable under the conditions[4].



R^1 = aryl, hetaryl, alkyl
R^2 = H, alkyl, COMe, COPh, etc.
R^3 = aryl, Me, CH_2=CH, CH_2C(Me)

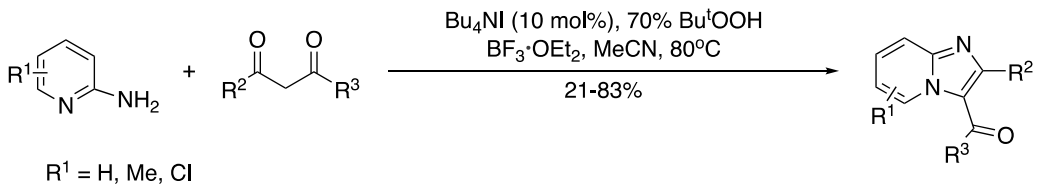
Scheme 2. α-Oxyacylation of ketones using tetrabutulammonium iodide as a pre-catalyst.



R^1 = aryl, hetaryl, alkyl
R^2 = aryl, Me, CH_2=CH, CH_2C(Me)

Scheme 3. α-Oxyacylation of aldehydes using tetrabutylammonium iodide as a pre-catalyst.

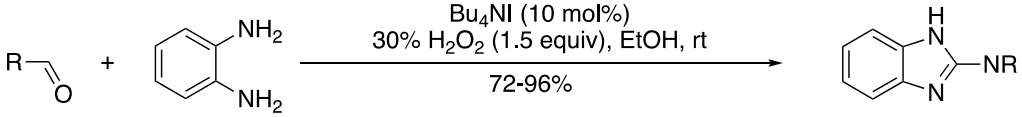
In 2011, Nachtsheim and coworkers first reported that Bu_4NI-H_2O_2 or Bu_4NI-TBHP catalyst system can be used to obtain C-N bonds coupling. Reactions of benzoxazoles with various amines under the said conditions affords the corresponding coupling products in moderate to high yields. The Bu_4NI-TBHP catalyst system is found to generate products faster and in higher yields[5].



R^1 = H, Me, Cl
R^2 = aryl, alkyl
R^3 = Me, OMe, OEt

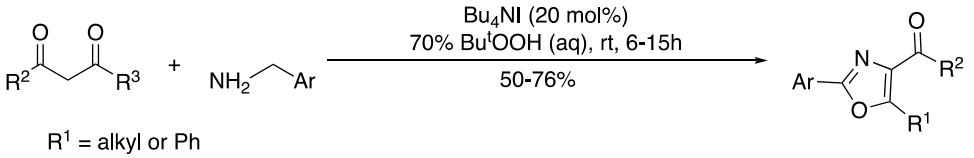
Scheme 4. Oxidative coupling of 2-aminopyridines with β-ketoesters and 1,3-diones using tetrabutylammonium iodide as a pre-catalyst.

Similarly, the same catalytic system is found useful in synthesizing benzimidazoles by a similar coupling reactions between phenylenediamines with aromatic or aliphatic aldehydes. The method allows for the corresponding product yield to be obtained in good to excellent yields (Scheme 5)[6]. Another useful application of Bu_4NI-H_2O_2 catalyst system is the couplings of β-ketoesters with benzylamines to obtain oxazoles and imidazoles in moderate to good yields (Scheme 6)[7].



R = alkyl or Ph

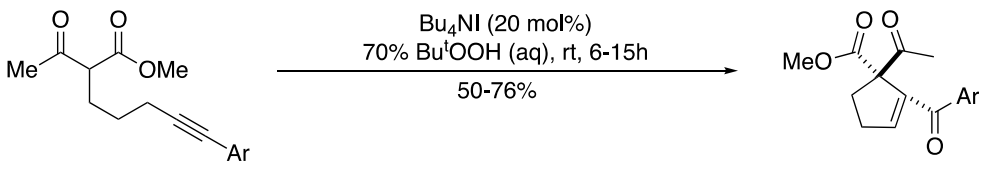
Scheme 5. Oxidative coupling of phenylenediamines with aldehydes and using tetrabutylammonium iodide as a pre-catalyst.



R^1 = alkyl or Ph
R^2 = OMe, OEt, OBu^t, Me, Ph
Ar = Ph, 4-ClC_6H_4, 2-ClC_6H_4, 4-MeC_6H_4, 2-furyl

Scheme 6. Oxidative coupling of β-ketoesters with benzylamines using tetrabutylammonium iodide as a pre-catalyst.

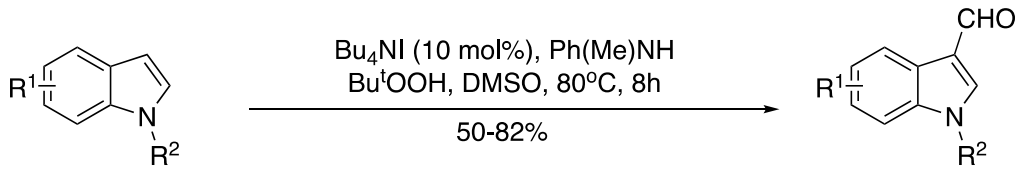
In 2011, Moran and co-workers discovered that the same of Bu_4NI-H_2O_2 catalyst system oxidizes cyclization of δ-alkynyl β-ketoesters[8]. This is the first example of C-C bond formation achievement using an iodine catalyst source. The cyclopentane products containing adjacent quaternary and tertiary stereocenters were formed diastereoselectively and in good yield.



Ar = Ph, 4-ClC_6H_4, 2-ClC_6H_4, 4-MeC_6H_4, 2-furyl

Scheme 7. Oxidative cyclization of δ-alkynyl β-ketoesters using tetrabutylammonium iodide as a pre-catalyst.

Another example of successful C-C bond formation from using an iodine sourced catalyst is the formylation of N-H and N-substituted indoles by using *N*-methylaniline as a carbonyl source. Bu_4NI-catalysed system allows for C3-selective formylation under metal-free conditions. From the screening study, pivalic acid was chosen to be an additive because of its ability to suppress the decomposition of indoles under most oxidative conditions. The conversion is obtained in good yield. This is especially important considering the desired products are present in many bioactive molecules[9].



R^1 = H, F, Cl, Et, Br, I, OCH_2, OMe, CN, Me, CO_2Me in various ring positions
R^2 = H, Me, CH_2Ph, Ph

Scheme 8. Oxidative cyclization of indoles using tetrabutylammonium iodide as a pre-catalyst.

2.3. Reactions using trivalent iodine species

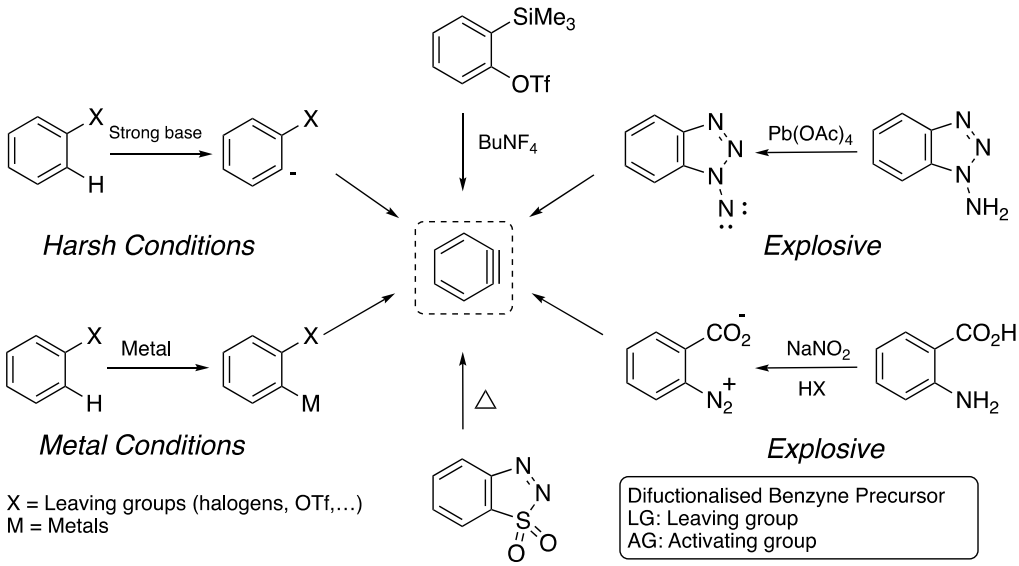
Trivalent iodine compounds are amongst the most well studied class of hypervalent iodines. In fact, a moderate amount of this species is commercially available to purchase. An important class of trivalent iodine compounds are diaryl iodonium species. Cyclic trivalent compounds exhibit better stability than their acyclic analogues. This can be attributed to the effective overlapping of two sp^2-hybridized lone pairs between iodine and the aromatic system. However, because of this stability, poor reactivity in most organic solvents remains a challenge. This can be overcome by conversion of these compounds to their corresponding pseudocyclic iodonium salts that have slightly poorer moisture stability. However, they display much better reactivity and have also been found to be useful for new bond forming transformations while being easy to handle. They are known for their strong electrophilic characteristics and consequently high leaving group ability. Okuyama and Ochiai have

calculated that the leaving group ability of iodobenzene is approximately million times higher than the leaving ability of the triflate group. Iodonium ylides have found broad application in alkylation, alkenylation, alkynylation as well as arylations. Their high reactivity allows for reactions to be carried out in mild conditions[10, 11].

2.4. Evolution of benzyne precursors

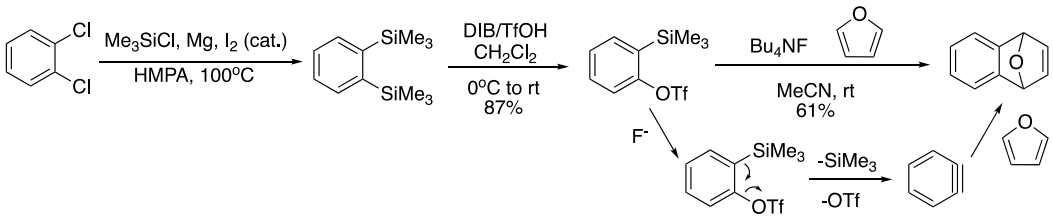
2.4.1. Introduction to benzyne: preparation, characterization and application

Arynes are valuable species in organic chemistry. They have been found useful in the construction of heterocyclic compounds, natural products, polycyclic aromatics and polysubstituted aromatic compounds. Due to their high bond and angle strains, arynes can only be generated *in situ* under suitable conditions summarized in Scheme 9. Treatment of aryl halides with strong base is found to be effective. However, this method suffers from an unavoidable drawback where the strong base competes with the nucleophile yielding a considerable amount of side products. Active metals (lithium or magnesium) may be used to generate metal-halogen exchange. Upon reaction with a nucleophile, benzyne is generated. Oxidation of benzyne precursors such as 1-aminobenzotriazole, anthranilic acid and 1,2,3-benzothiadiazole 1,1-dioxide also produces benzyne. However, these methods should be avoided due to the starting materials explosive nature. Decarboxylation of arene-diazonium-2-carboxylates works effectively but with relatively harsh conditions that requires extreme high temperature[12].



Scheme 9. General methods for benzyne preparations[12].

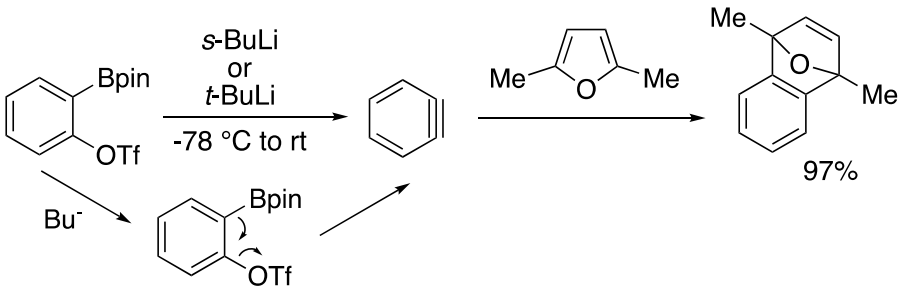
In 1983, Kobayashi and co-workers reported 2-(trimethylsilyl)phenyl triflates as an alternative benzyne precursor that is activated under mild conditions. Benzyne is obtained by treating the precursor with a fluorine source (tetrabutylammonium fluoride, Bu_4NF) at room temperature. Due to their high affinity, the fluorine acts as a nucleophile attacking the silicone, followed by reductive elimination of the triflate leaving group, forming the desired benzyne in situ. Because of the mild conditions required to induce the benzyne formation, 2-(trimethylsilyl)phenyl triflates is made available for purchase commercially and consequently been applied in many new molecule synthesis[13, 14].



Scheme 10. Preparation of Kobayashi benzyne reagent and its cycloaddition application with tetrahydrofuran.

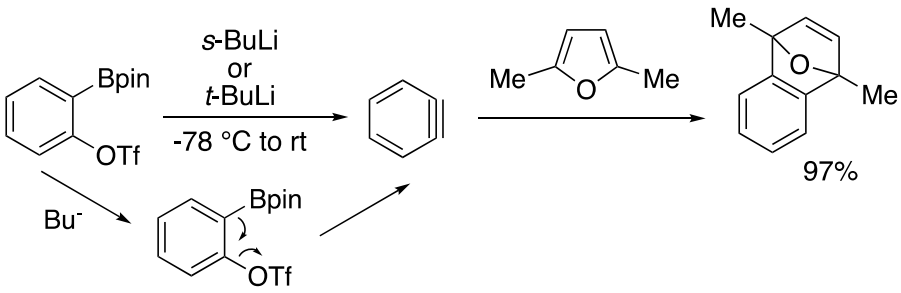
2.4.2. Arylboronic acid as benzyne precursor

The first evidence of phenylboronic acid being used as an benzyne precursor dates back to 1964 by Morrocchi and coworkers[16]. Treatment of 2-chlorophenylboronic acid in ether with *n*-butyllithium in the presence of furan at rt, followed by acidic workup afforded various cycloaddition products in 55-60% yield. This reaction template was then screened for optimal conditions by Hosoya and co-workers in 2013[17]. Treatment of 2-(trifluoromethanesulfonyloxy)arylboronic acid with *t*-BuLi in diethyl ether with 2,5-dimethylfuran afforded cycloaddition product at 97%. The reaction suffers the drawback of using strong base. However, this can be overcome by adding the base-sensitive nucleophiles after boron-ate complex formations.



Scheme 11. Preparation of arylboronic benzyne reagent and its cycloaddition application with 2,5-dimethylfuran.

Ikawa and coworkers introduced an approach to obtain benzyne from 2-[neopentyl glycolato)boryl]phenyl triflates at 120°C in the presence of a fluoride ion[18]. The advantageous feature of this approach is that it allows for the generation of benzynes bearing functionalized groups such as carbonyl, cyano, bromo, and primary amino groups. The activation with mild fluorine source instead of strong base such as *t*-BuLi allows for functionalized benzyne generation. Cycloaddition of precursor with 2,5-dimethylfuran afforded cycloaddition product at 85%. Moreover, the precursor is easily made through Miyaura borylation of iodophenyl derivatives followed by triflation without the need of using protection group for the case of synthesising functionalized benzyne precursor. However, this approach suffers the drawback of needing elevated temperature to generate benzyne.

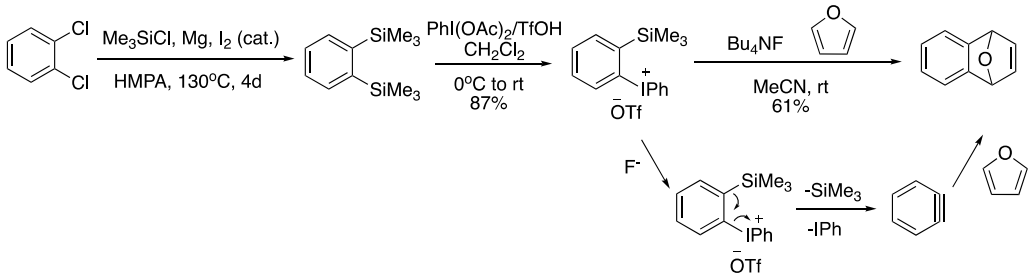


Scheme 12. Preparation of arylboronic benzyne reagent and its cycloaddition application with 2,5-dimethylfuran.

Despite the drawbacks of harsh conditions to generate benzyne from arylboronic acids, these examples set forth the concept of utilising boronic acid functional group as the trigger point.

2.4.3. Hypervalent iodine as benzyne precursor

Organohypervalent iodine compounds are efficient, versatile reagents that generate benzyne quantitatively under mild conditions. The first hypervalent iodine benzyne precursor, 2-(trimethylsilyl)phenyl triflate, was introduced by Kitamura and co-workers in 1995. The high efficiency of Kitamura reagent can be attributed to the hypervalent iodine functional group. The leaving ability of the phenyliodanyl group is approximately ~10^6 times greater than the trifluoromethylsulfonyloxy group of the Kobayashi reagent. This is the advantageous of hypervalent iodine compound that allows for benzyne to be generated extremely efficiently in milder conditions. This can be seen in Scheme 11, the cycloaddition with furan gives the product higher yield in a shorter amount of time[13, 14, 15]. Another advantage of this method is that it allows for benzynes to be generated from a mild source, in this case, a fluorine source from Bu_4NF. By taking advantage of the affinity of fluorine to silicone, Bu_4NF is mild yet effective in triggering the $SiMe_3$ activator group. This approach expands the utilisation of base sensitive nucleophiles.



Scheme 13. Preparation of Kitamura benzyne reagent and its cycloaddition application with tetrahydrofuran.

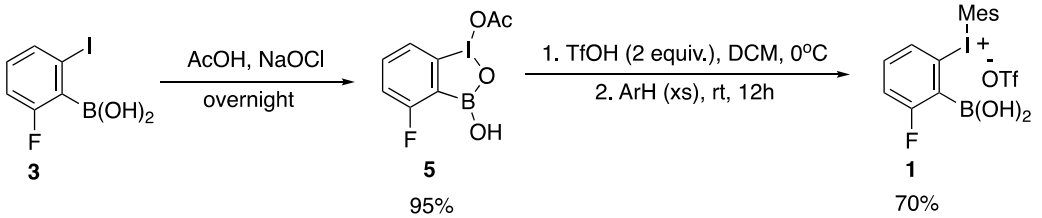
In previous research published in 2017, our group reported the preparation, structural identification, and reactivity via aryne adduct reactions with various benzyne trapping substrates of the precursor mesityl-2-fluoro-1-phenyboronic acid-6-iodonium triflate. The precursor is prepared by the ligand exchange reaction between the corresponding hypervalent iodine heterocycles **3** (1-acetoxybenziodoxaboroles) and arenes in the presence of strong acid TfOH. The reaction of 1-acetoxy-4-fluorobenziodoxaborole (1 equiv.) with mesitylene in the presence of triflic acid (2 equiv.) under mild conditions afforded the corresponding 1-

mesitylbenziodoxaborole triflate **1** in 95% yield[22].

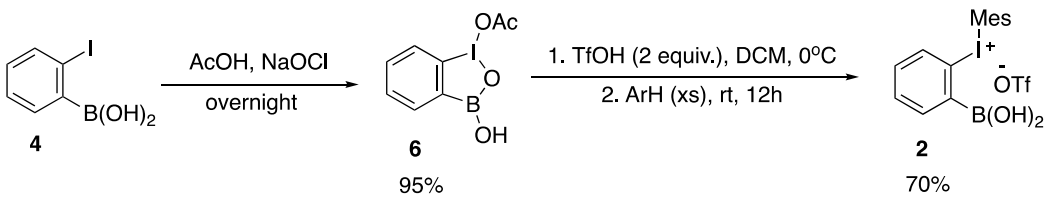
The pseudocyclic structure of 1-phenyl-4fluorobenziodoxaborole triflate is confirmed by x-ray analysis. The structure reveals a short intramolecular interaction of 2.698 to 2.717 Å between the oxygen and iodine atoms in the benziodoxaborole ring. An additional interaction of triflate oxygen and the iodine centre results in the overall pseudo square planar geometry.

It is expected that the pseudocyclic salt performs as a benzyne precursor similarly to common ortho functionalized groups benzyne reagents. Similar to Kitamura and Kobayashi reagents' trigger group tetramethylsilane, *ortho*-$B(OH)_2$ of our compound is easily activated by hard bases. The boric acid group may also be activated using a fluorine source at room temperature. This is important because unlike strong bases, mild fluorine anion does not compete in a nucleophilic reaction. Interestingly, it is found that upon aqueous workup, in the absence of a fluorine source, the desired adduct product is isolated in good yield. This suggests that water is the main trigger source of boric acid. Subsequent elimination of the boric acid group leads to the nucleofugic group iodomesitylene leaving, forming the desired benzyne intermediate in situ. Optimization of reaction reveals optimal yield is obtained with dichlomethane/water (9:1) as solvent at room temperature for 3 hours.

Various reactions with benzyne trapping agents affords desired products in good to excellent yield. Such promising results encourage us to develop an inspired protocol to synthesize a diversely functionalized sulfonium salts.



Scheme 12. Synthesis of fluorinated hypervalent iodine benzyne precursor.



Scheme 14. Synthesis of hypervalent iodine benzyne precursor.

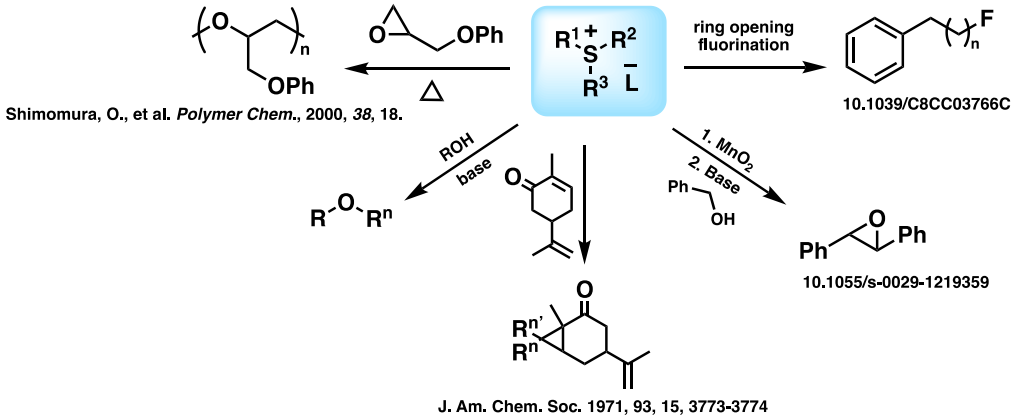
2.5. Sulfonium Salts from Hypervalent Iodine Benzyne Precursors

Interest in sulfonium compounds has been stimulated by their useful application as raw materials for the synthesis of drugs and sulfur containing natural compounds. In addition, sulfonium salts are desired for their high photosensitivity and therefore useful as efficient photochemical catalyst for cationic polymerization. Ultraviolet (UV) curing of polymeric materials quickly become of the most popular techniques used in the paints and coatings industry owing to its efficient and low energy consumption because curing can typically take place in matter of minutes; UV cured coatings are also one of the most environmental friendly coating solutions because it contains and emits essentially no volatile organic compounds while maintaining outstanding performance delivered by traditional or powder coatings such as abrasion and chemical resistance, and customization of hardness and flexibility[19].

An important class of UV cure coating system is living cationic photoinitiating system. Compared to traditional free radical polymerization system, cationic initiated polymers have many advantages such as rapid and selective polymerization without oxygen inhibition; its physical performance also exceeds radical initiated polymers in terms of abrasion, resistance and hardness. However, there are a few disadvantages when utilizing this system. The polymer relies on the photoinitiator as it plays an important role in curing and polymerization. Physical characteristics also depend on the initiator used. Low solubility of photoinitiator inhibits effective polymerization for it does not activate the monomer of interest. Resin mixture also takes a long time to cure because of the lack of effective photoinitiator contribution. Therefore, a great demand of effective cationic polymer photoinitiators rizes. Several groups have reported the use of diphenyliodonium salts/metal halides, radical photoinitiators/metal halides, zinc salts, and dimanganese decacarbonyl/alkyl bromide as catalytic source for cationic photoinitiators. However, the use of non-metal initiator was limited because of its incompatibility with the resin. Most importantly, metal system has sufficient Lewis acidity level that activates the propagating cation end. Recently, Nishikawa and coworkers published the use of diaryliodonium salt as non-metal catalyst.

Degradation of diaryliodonium under UV light generates hydroiodic acid that subsequently reacts with nBu_4NI to generate initiating and propagating species with C-I bonds to achieve monomer conversion of 95% with high polymer weight[20].

Sulfonium salts demonstrate as a competitive photoinitiator for its excellent solubility in common organic solvents. Depending on the substituent placed on the aromatic groups, desirable properties of end polymer film can be fine-tuned. For example, dibenzothiophene moieties improve hardness of the coatings; benzoyl moieties provide excellent in monomer conversion due to its high photoinitiation efficiency. Pappas et al. reported the synthesis and photoactivity of anthracene bound sulfonium salts, which absorb longer wavelengths between 330 and 410 nm due to the strong absorptivity of anthracene in this region. Zhang et al. reported a novel class of triarylsulfonium salts with competitive hardness, cure time with glossy and transparent cured film.

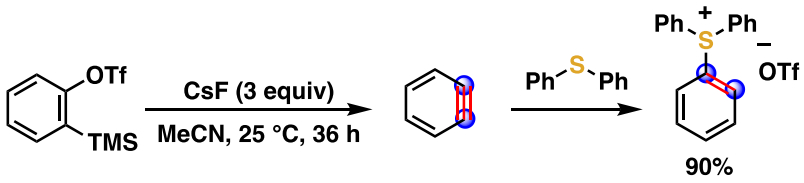


Scheme 15. Examples of sulfonium salts applications.

Among several synthetic methods reported to obtain sulfonium salts, the direct synthesis from the corresponding sulfides is most preferred due to its direct and relatively simpler procedure. Alkylation or arylating agents for reactions with such sulfides have been reported such as alkyl iodides, diaryliodonium salts, triaryloxonium salts, and strongly acidic alcohols or ethers.

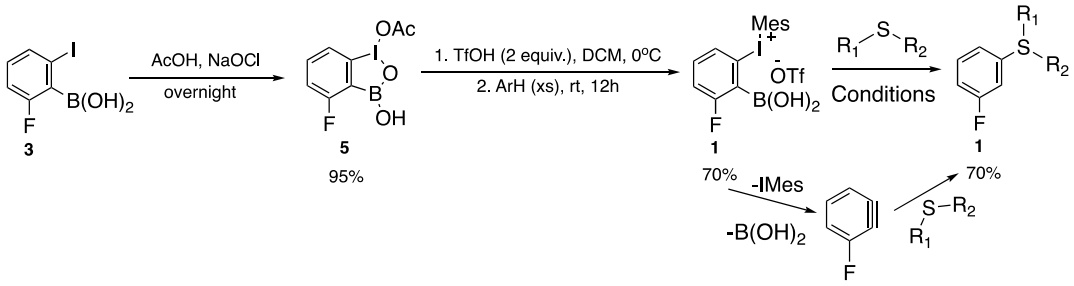
Zhang et al. recently provided a mild approach to synthesize triarylsulfonium salts using the Kobayashi benzyne precursor. This precursor needs a mild fluorine source to activate at room temperature. Reaction of such precursor to a variety of aromatic sulfides yield triarylsulfonium salts with moderate to good yield. This route however lack of

application to unsymmetrical and alkyl sulfonium products and requires tedious long reaction time[21].

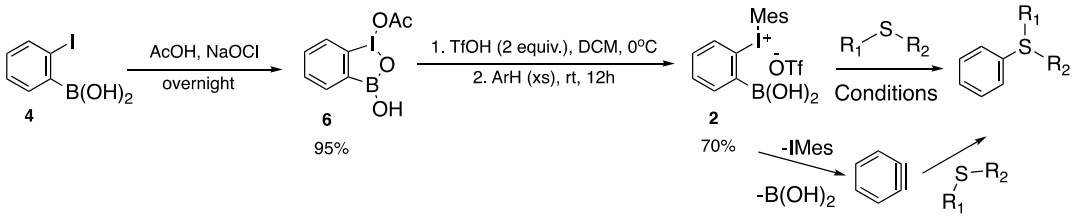


Scheme 16. Sulfonium salts from Kobayashi's benzyne precursor[21]

Herein, we report a mild and effective approach to synthesize sulfonium salt from our benzyne precursors (**1** and **2**) and sulfides. This method provides a library of sulfonium products with symmetrical and unsymmetrical alkyl and aryl groups with plethora of applications. Because the benzyne precursor used efficiently can be activated by water or weak base at room temperature, desired salts can be obtained in good to excellent yield in less reaction time.



Scheme 17. Sulfonium salts from hypervalent fluorinated iodine benzyne precursor



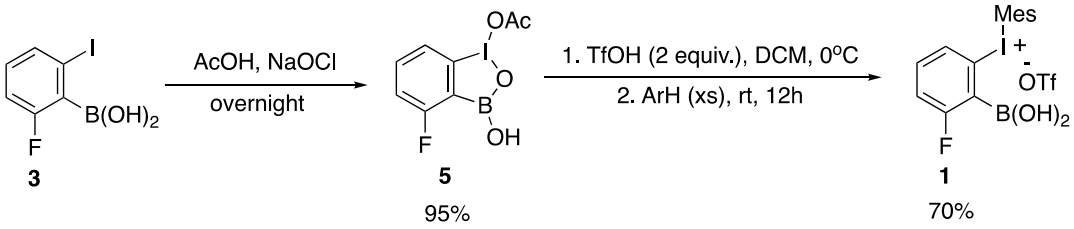
Scheme 18. Sulfonium salts from hypervalent iodine benzyne precursor.

RESULTS AND DISCUSSION

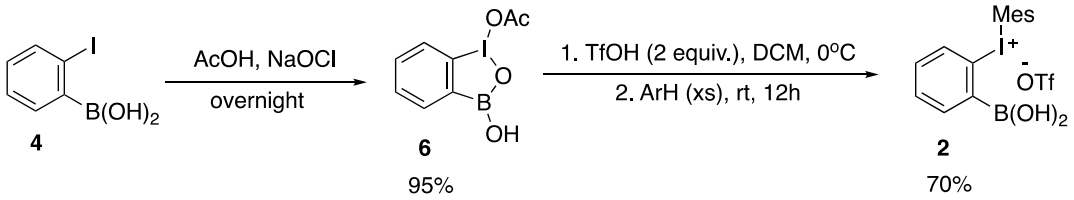
3.1. Synthesis of hypervalent iodine starting materials

The synthesis and optimization of the benzyne precursors **1** and **2** have been described in

detail elsewhere[22]. Commercially available 2-iodophenyl boronic acid is oxidized with acetic acid and bleach. The resulting white solids **5** and **6** are filtered and washed with water. To achieve the final acyclic product **1** and **2**, **5** and **6** are treated with triflic acid. Mesitylene is then added to achieve the corresponding ligand.



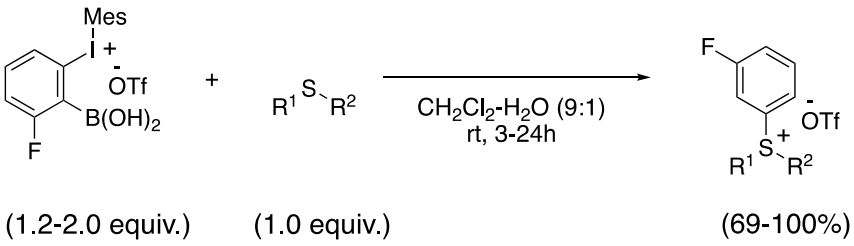
Scheme 19. Synthesis of fluorinated hypervalent iodine benzyne precursor.



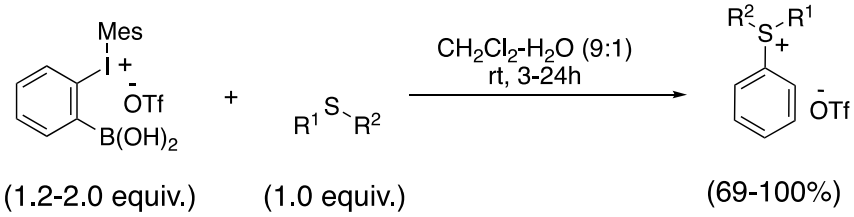
Scheme 20. Synthesis of hypervalent iodine benzyne precursor.

3.2. The aim of this research

The aim of this research is to synthesize a library of sulfonium salts from the hypervalent iodine benzyne precursor **1** and commercially available disulfides. The library consists of sulfonium salts with symmetrical and asymmetrical ligands. Sulfonium salts with both aliphatic and aromatic side chains are successfully synthesized. The hypervalent iodine species: mesityl-2-fluoro-1-phenyboronic acid-6-iodonium triflate (**1**) and mesityl-1-phenyboronic acid-2-iodonium triflate (**2**) were used to introduce fluorophenyl or phenyl functional group to commercially purchased sulfides (Schemes 19 and 20). Because of its higher cost, 10 representative examples with mesityl-1-phenyboronic acid-2-iodonium triflateare chosen to demonstrate feasibility. Both benzyne precursors are activated using water. Non-fluorinated precursor requires slightly more basic media to achieve excellent yield. Therefore, sodium bicarbonate is added to raize the reaction's pH (Scheme 20). Iodomesitylene bi-product can be easily washed off using either ether or hexane, no column chromatography is necessary.



Scheme 21. Sulfonium salts synthesized from fluorinated benzyne precursor **1**.



Scheme 22. Sulfonium salts synthesized from benzyne precursor **2**.

3.3. Structural study of benzyne precursor mesityl-2-fluoro-1-phenyboronic acid-6-iodonium triflate

In previous research published in 2017, our group reported the preparation, structural identification, and reactivity via aryne adduct reactions with various benzyne trapping substrates of the precursor mesityl-2-fluoro-1-phenyboronic acid-6-iodonium triflate. The precursor is prepared by the ligand exchange reaction between the corresponding hypervalent iodine heterocycles **3** (1-acetoxybenziodoxaboroles) and arenes in the presence of strong acid TfOH. The reaction of 1-acetoxy-4-fluorobenziodoxaborole (1 equiv) with mesitylene in the presence of triflic acid (2 equiv) under mild conditions afforded the corresponding 1-mesitylbenziodoxaborole triflate **1** in 95% yield[22].

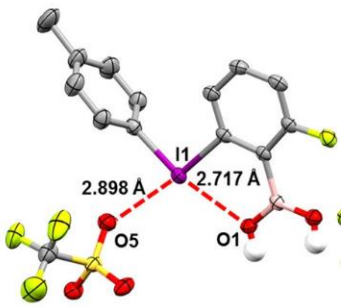


Figure 3. X-ray analysis of acyclic 1-mesitylbenziodoxaborole triflate[21]

The pseudocyclic structure of 1-phenyl-4fluorobenziodoxaborole triflate is confirmed

by x-ray analysis. The structure reveals a short intramolecular interaction of 2.698 to 2.717 Å between the oxygen and iodine atoms in the benziodoxaborole ring. An additional interaction of triflate oxygen and the iodine center results in the overall pseudo square planar geometry.

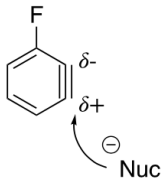
It is expected that the pseudocyclic salt performs as a benzyne precursor similarly to common ortho functionalized groups benzyne reagents. Similar to Kitamura and Kobayashi reagents' trigger group tetramethylsilane, *ortho*-$B(OH)_2$ of our compound is easily activated by hard bases. The boric acid group may also be activated using a fluorine source at room temperature. This is important because unlike strong bases, mild fluorine anion does not compete in a nucleophilic reaction. Interestingly, it is found that upon aqueous workup, in the absence of a fluorine source, the desired adduct product is isolated in good yield. This suggests that water is the main trigger source of boric acid. Subsequent elimination of the boric acid group leads to the nucleofugic group iodomesitylene leaving, forming the desired benzyne intermediate in situ. Optimization of reaction reveals optimal yield is obtained with dichlomethane/water (9:1) as solvent at room temperature for 3 hours.
Various reactions with benzyne trapping agents affords desired products in good to excellent yield. Such promising results encourage us to develop an inspired protocol to synthesize a diversely functionalized sulfonium salts.

Zhang and coworkers have performed extensive studies to synthesize aromatic sulfonium salts, but it lacks examples using asymmetrical alkyl/aromatic sulfides and alkyl sulfides. Therefore, this study begins with the simplest form of asymmetrical alkyl/aromatic sulfide, thioanisole. Reaction of benzyne precursor **1** with thioanisole using developed reaction condition yields successful results (100% isolated yield), and the sulfonium salt product is confirmed by x-ray analysis.

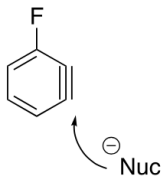
Figure 4. X-ray analysis of thioanisole sulfonium product.

3.4. Regioselectivity of fluorinated benzyne precursor

Benzyne's instability is attributed to the internal bond angle being strained to 120º. Alkyne bonds's angle are estimated about 180ºC. The angle difference accounts for arynes's high reactivity, thus challenging to isolate. Moreover, the decrease in bond angle also causes π orbitals distortion, which drives arynes to quickly re-aromitize. There are three models that can be used to explain the regioselectivity: the charge-controlled, steric, and aryne distortion models. The charge controlled-model predicts nucleophilic attack at the partial positive carbon. The steric model also predicts nucleophilic addition at the same carbon. Both models provide a good estimation to explain the regioselectivity outcome. However, they do not quantify the exclusivity of the meta product.

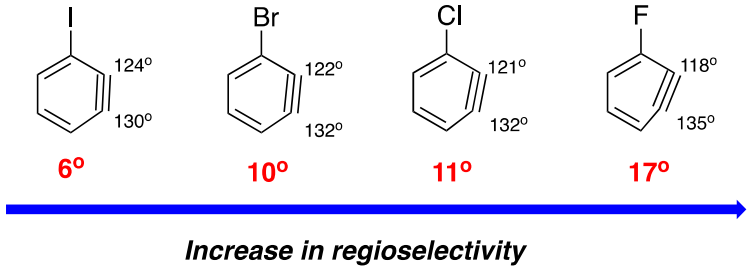


Scheme 24. Charge-controlled model



Scheme 25. Steric model

Computational study efforts have been made to elucidate decorated benzynes's electrophilicity via the aryne distortion model. The model compares halobenzynes and the effect of halogens on the benzyne carbons. Nucleophilic attack favors carbon that most resembles a linear angle. Halogens of smaller size are observed to distort the internal angle most thus providing a quantitative tool to explain the meta exclusive outcome. It is determined that fluorinated benzyne has 4 folds electrophilicity compared to undecorated benzynes. Therefore, meta adducts of fluorinated benzyne are exclusively achieved[23].



Scheme 26. Aryne distortion model[23]

3.5. Optimization study

Optimization studies were conducted on the model reaction between **1** and thioanisole. Table 1 summarizes all conditions screened. It is hypothesized that the sulfonium product is formed from the nucleophilic attack of sulfide to the benzyne intermediate. To verify the benzyne mechanism pathway, the optimized reaction is tested with and without water (conditions 1&2). In the absence of water, no desired product is achieved; the reaction does not homogenize and the starting materials are recovered at 100% NMR yield. By introducing water in catalytic amount (condition 2), the reaction mixture homogenizes. The desired product is obtained at 100% NMR and isolated yield.

Solvents of different polarities were screened to determine the effect on the reaction.

Entries 3-8 demonstrate that good to excellent yields can be achieved with acetonitrile, chloroform, dichloroethane, benzene, ethyl acetate, heptane. No noticeable trend is observed corresponding to solvent's polarity. Interestingly, product can be obtained in good yield using just water as a solvent (condition 11). Dichloromethane (condition 2) is found to achieve the best yield.

Conditions 9 & 10 explores different benzyne trigger agents. Methanol and *tert*-butoxide are added in lieu of water. Because methanol and *tert*-butoxide anions are stronger nucleophile than hydroxide generated by water, they compete with sulfide nucleophiles, thus decreasing overall yield.

Conditions 12 & 13 explore different ratio of dichloromethane to water. It is found that the 9:1 ratio of dichloromethane to water is best. Decreasing the water provides insufficient benzyne trigger amount while increasing water ratio provides more opportunity for more water nucleophiles competing with the sulfides.

Negative control experiments are performed to highlight the importance of using I(III) precursor **3** (entries 14 and 15). Benzyne formation could not be achieved without converting iodine of compound **3** to be a good leaving group (entry 14). It is also not possible to obtain benzyne with the proposed mild reaction condition while the compound is in cyclic form (entry 15).

Entry	Solvent	Solvent Ratio	ArI(III)	Isolated Yield (%)[a]
1	CH_2Cl_2	100%	**1**	0%
2	CH_2Cl_2-H_2O	9:1	**1**	100 %
3	MeCN-H_2O	9:1	**1**	94%
4	$C_2H_4Cl_2$- H_2O	9:1	**1**	60%
5	$CHCl_3$-H_2O	9:1	**1**	81%
6	PhH-H_2O	9:1	**1**	64%
7	AcOEt-H_2O	9:1	**1**	86%
8	Heptane-H_2O	9:1	**1**	63%

9	CH_2Cl_2-MeOH	9:1	**1**	48%
10	CH_2Cl_2-^{t}BuOH	9:1	**1**	<50% (impure)
11	H_2O	100%	**1**	75%
12	CH_2Cl_2-H_2O	7:3	**1**	93%
13	CH_2Cl_2-H_2O	95:5	**1**	79%
14	CH_2Cl_2-H_2O	9:1	**3**	0%
15	CH_2Cl_2-H_2O	9:1	**5**	0%
16	CH_2Cl_2-$NaHCO_3$ solid	9:1	**2**	0%

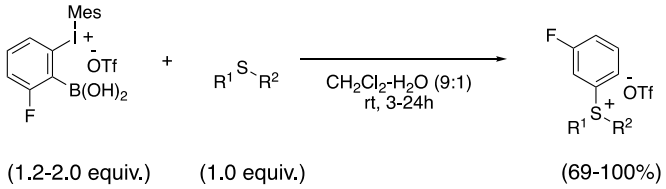
Table 1. Reaction optimization of benzyne **1** with thioanisole

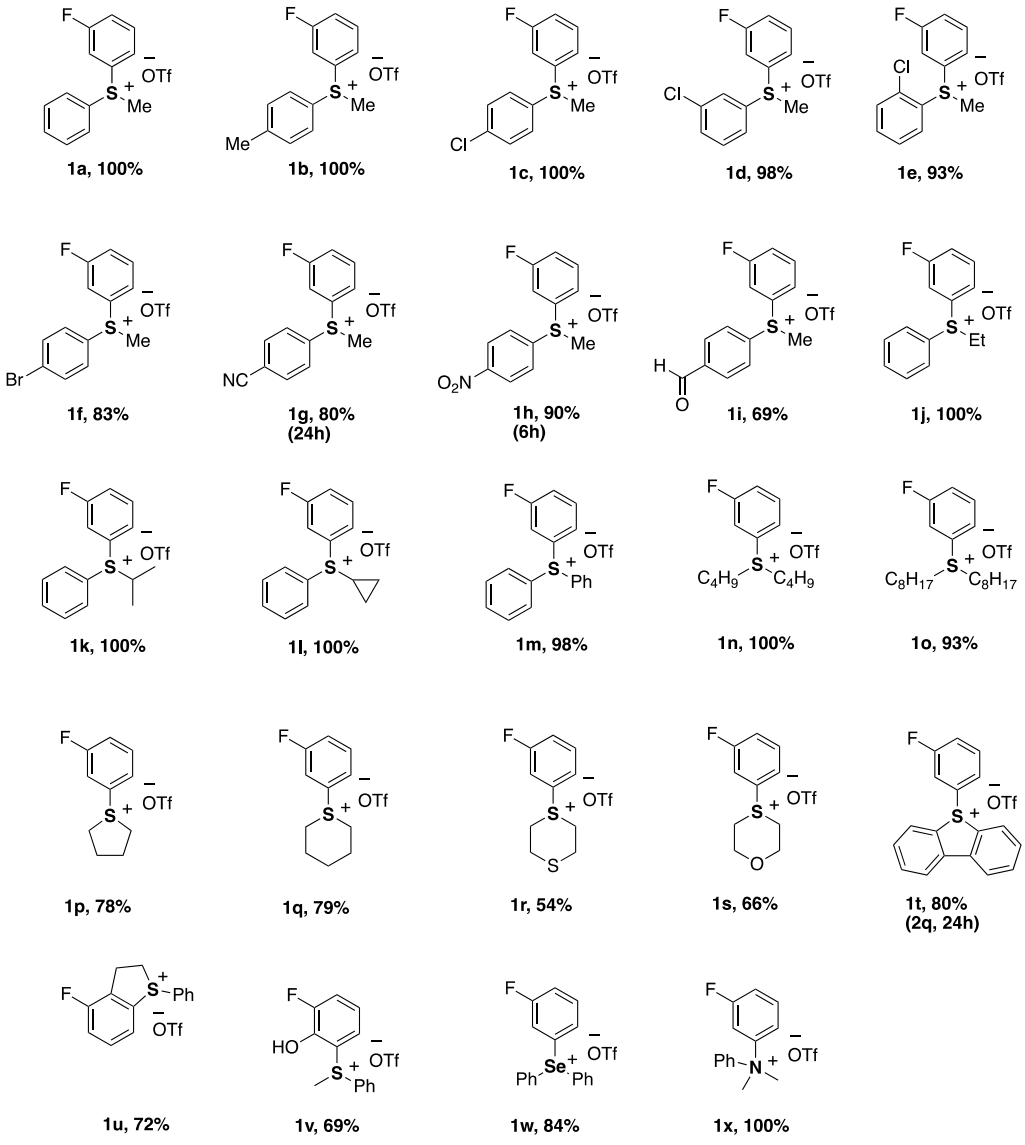
Non-fluorinated derivative **2** was also examined. Due to the high cost of the starting material, only a few representatives of sulfides and selenide were chosen. The non-fluorinated benzyne precursor **2** is less electrophilic than **1** due to the lack of fluorine on the 3rd carbon. Thus, there is a general drop of desired product yield observed. Although water was a sufficient base that can be used to activate the benzyne precursor, the overall reaction yield was extremely low (3% NMR yield, 0% isolated). Therefore, saturated solution of sodium bicarbonate is used as a mild base to activate the non-fluoronated benzyne precursor. A blank experiment was ran to determine the role of sodium bicarbonate (Entry 16). Without water, the reaction did not homogenize and no product is detected. This concluded that the benzyne precursor was activated by water. Sodium bicarbonate acted as a reaction catalyst. It did not participate in the reaction. Sodium bicarbonate only altered the pH to improve water nucleophilicity. Compared to the fluorinated analogue **1**, **2** is less electrophilic, thus requiring a basic medium[23].

3.6. Reaction with fluorinated benzyne precursors

A variety of types of sulfides were then evaluated., beginning with thioanisole derivatives bearing different benzene substitutions. The reaction conditions provide for nucleophilic sulfides to react with electronic benzyne precursor. Sulfides with electron rich

benzene rings inducted by electron donating groups (hydrogen, methyl, chlorine) provide for better nucleophilicity of sulfur, thereby having higher yield than analogues with electron withdrawing groups (cyano, nitro, aldehyde). Increasing in reaction time from the original time of 3 hours overcomes weak nucleophilicity, thus improving the overall yield of desired compounds.



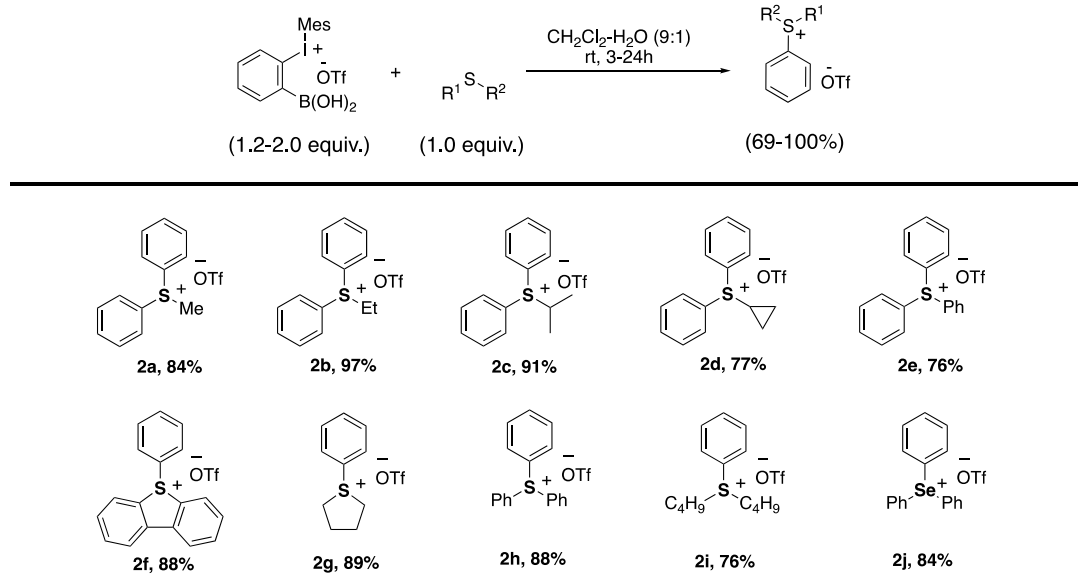


Scheme 27. Substituted thioanisole sulfonium salt products.

Other alkyl and aromatic substituted sulfides are investigated. All reactions provide good to excellent yield. Nucleophiles with simple alkyl substitutions render excellent yield due to maximized nucleophilicity of sulfur. Sulfide candidates with electron rich groups have decreased nucleophilicity thus lower yield. Increasing benzyne precursor concentration and/or reaction time are found to overcome low yield challenges.

3.7. Reactions with non-fluoronated benzyne precursors

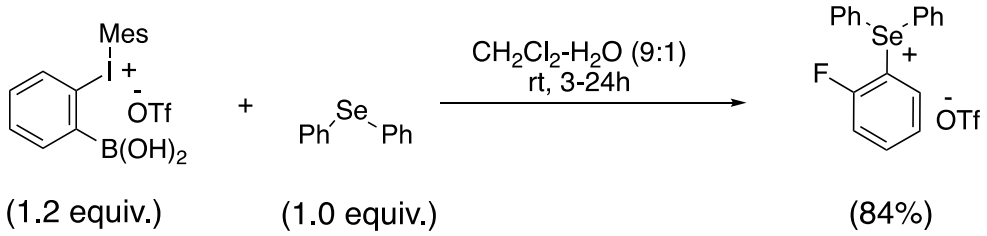
Excellent yields of sulfonium salts are achieved with benzyne precursor without fluorine. Without the fluorine inductive effect, mild base is needed to improve reaction's yield. It should be clarified that water is the benzyne activator source. Mild base (sodium bicarbonate) is added only to increase the pH which favours reaction's high yields.



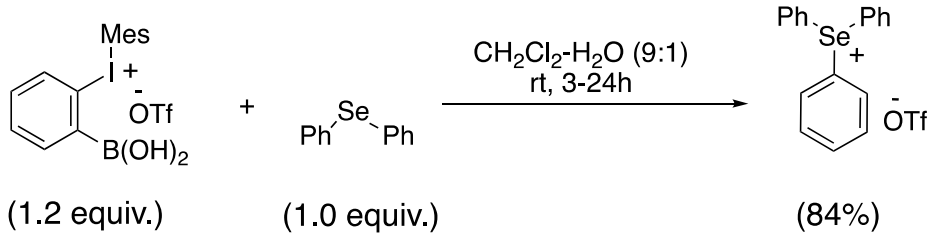
Scheme 28. Sulfonium salts from non-fluorinated benzyne precursors **2**

3.8. Reactions of benzyne with selenides

Selenium salts are achieved in excellent yields using the current reported methods. Only one derivative of selenide is evaluated to demonstrate feasibility. Reaction optimizations and limitation evaluation is not within the scope of this study.



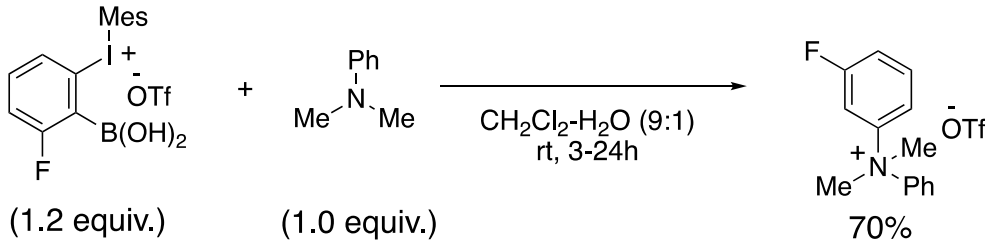
Scheme 29. Selenium salt from reaction of selenide and fluorinated benzyne precursor



Scheme 30. Selenium salt from reaction of selenide and benzyne precursor **1**

3.9. Reaction with amines

Ammonium salts are achieved in excellent yields using the current reported methods. Only one derivative of amine is evaluated to demonstrate feasibility. Reaction optimizations and limitation evaluation is not within the scope of this study.



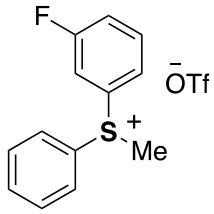
Scheme 31. Ammonium salt from reaction of amine and benzyne precursor **1**

4. EXPERIMENTAL PART

Reaction of mesityle-2-fluoro-1-phenylboronic acid-6-iodonium triflate with various substrates

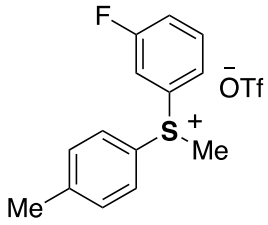
Sulfide or selenide was added to a solution of mesityle-arylboronic acid-iodonium triflate in methylene chloride (1.8 mL) and water (0.2 mL). The reaction was stirred at room temperature for 3-24 h. After completion of the reaction, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by extraction over diethyl ether afforded analytically pure products.

3-Fluorophenyl-methyl-phenylsulfonium triflate



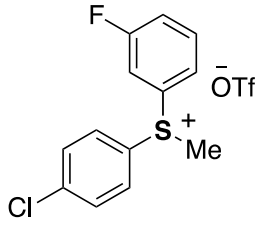
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and thioanisole (124 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (100%) of product, isolated as white solid: mp 118.8-119.3°C; IR (neat) cm^{-1} 3099, 3072, 3024, 2940, 1597, 1255, 1221, 1168, 1078, 1028, 686, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.3Hz, 2H), 7.83-7.68 (m, 5H), 7.53 (d, *J* = 7.6Hz, 1H), 7.42 (t, J = 7.5Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 253.0 Hz), 138.7 (d, ^{3}J = 8.0 Hz), 135.2, 131.8, 130.7, 128.6 (d, ^{3}J = 8.1 Hz), 126.8 (d, ^{4}J = 3.2 Hz), 126.2, 122.1 (d, ^{2}J = 22.0 Hz), 121.7 (q, ^{1}J = 319.0 Hz), 117.0, 28.2; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.7 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{12}FS$ $([M\text{-}OTf])^{+}$: 219.0644 found: 219.0633.

3-Fluorophenyl-methyl-4-phenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and methyl *p*-tolyl sulfide (138 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (100%) of product, isolated as white solid: mp 120.1-120.6°C; IR (neat) cm^{-1} 3071, 3031, 2940, 2879, 1596, 1479, 1258, 1222, 1163, 1084, 1030, 756, 676, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0Hz, 3H), 7.74-7.67 (m, 1H), 7.53-7.45 (m, 3H), 7.42 (t, J = 7.5Hz, 1H), 3.75 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 250.0 Hz), 147.0, 133.7 (d, ^{3}J = 8.1 Hz), 132.4, 130.7, 129.5 (d, ^{3}J = 8.1 Hz), 126.5 (d, ^{4}J = 3.2 Hz), 121.9 (d, ^{2}J = 22.0 Hz), 121.7 (q, ^{1}J = 317.9 Hz), 117.4, 28.3, 21.2 ^{19}F NMR (376 Hz, CD_3CN): δ -129.5 (s, 1F), -99.7 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{14}FS$ ([M-OTf])$^{+}$: 233.0795 found: 233.0793.

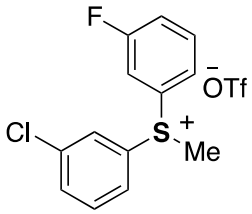
4-Chlorophenyl-3-fluorophenyl-methysulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 4-chlorothioanisole (159 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 40 mg (100%) of product, isolated as white solid: mp 99.3-100.5°C; IR (neat) cm^{-1} 3073, 3026, 2941, 2896, 1596, 1573, 1482, 1255, 1219, 1163, 1098, 1030, 821, 757, 681, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.9Hz, 2H), 7.82 (d, *J* = 8.1Hz, 1H), 7.77-7.72 (d, 1H), 7.69 (d, J = 7.9Hz, 2H), 7.52 (dt, J = 7.3Hz, 1H), 7.47 (td, J = 7.3Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 251.0 Hz), 141.3, 132.5, 131.9, 133.7 (d, ^{3}J = 8.6 Hz), 128.2 (d, ^{3}J = 8.1 Hz), 124.9 (d, ^{4}J = 3.0 Hz), 124.9, 122.3 (d, ^{2}J = 21.0 Hz), 121.7 (q, ^{1}J = 319.0 Hz), 117.6, 28.4; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.6 (s, 1F);

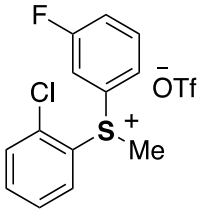
HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{11}ClFS$ ([M-OTf])$^+$: 253.0254 found: 253.0249.

3-Chlorophenyl-3-fluorophenyl-methysulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 3-chlorothioanisole (159 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 39 mg (98%) of product, isolated as white solid: mp 92.9-93.5°C; IR (neat) cm^{-1} 3071, 3034, 3022, 2936, 1596, 1581, 1479, 1269, 1250, 1222, 1164, 1085, 1028, 878, 757, 682, 635; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.3Hz, 1H), 7.84-7.64 (m, 5H), 7.58 (d, *J* = 7.3Hz, 1H), 7.45 (1, J = 7.4Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^1J = 251.0 Hz), 136.9, 135.2, 133.7 (d, ^3J = 8.6 Hz), 130.3, 129.3, 128.1, 127.1 (d, ^3J = 8.3 Hz), 127.9 (d, ^4J = 3.0 Hz), 122.4 (d, ^2J = 21.0 Hz), 121.7 (q, ^1J = 319.0 Hz), 117.8, 28.2; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.5 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{11}ClFS$ ([M-OTf])$^+$: 253.0254 found: 253.0249.

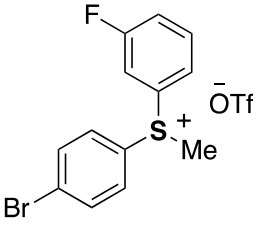
2-Chlorophenyl-3-fluorophenyl-methysulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 2-chlorothioanisole (159 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (94%) of product, isolated as white solid: mp 152.9-153.4°C; IR (neat) cm^{-1} 3078, 2939, 2367, 1596, 1481, 1248, 1224, 1166, 1028, 752, 679, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 7.7Hz, 1H), 7.88 (m, *J* = 7.7Hz, 1H), 7.83-7.69 (m, 4H), 7.67-7.63 (m,

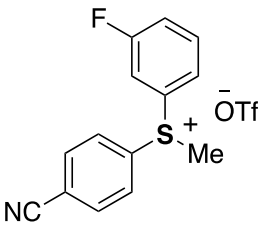
1H), 7.57 (dt, *J* = 7.7Hz, 1H), 7.45 (td, *J* = 7.7Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 251.0 Hz), 136.7, 135.9, 132.4, 130.8, 130.5, 133.8 (d, ^{3}J = 8.5 Hz), 127.0 (d, ^{3}J = 8.1 Hz), 127.5 (d, ^{4}J = 3.5 Hz), 122.6 (d, ^{2}J = 21.0 Hz), 122.0 (q, ^{1}J = 319.0 Hz), 118.4, 27.6; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.5 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{11}ClFS$ ([M-OTf])$^{+}$: 253.0254 found: 253.0249.

4-Bromophenyl-3-fluorophenyl-methysulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 4-bromothioanisole (203 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (83%) of product, isolated as white solid: mp 112.2-113.3°C; IR (neat) cm^{-1} 3072, 3025, 2917, 2849, 1596, 1479, 1256, 1479, 1256, 1164, 1031, 816, 757, 680, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.78 (m, *J* = 7.7Hz, 1H), 7.74-7.67 (m, 1H), 7.56 (d, *J* = 7.9Hz, 1H), 7.45 (t, *J* = 7.9Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 251.0 Hz), 134.9, 133.8 (d, ^{3}J = 8.2 Hz), 132.4, 129.8, 128.1 (d, ^{3}J = 8.2 Hz), 126.9 (d, ^{4}J = 3.5 Hz), 122.5, 122.3 (d, ^{2}J = 21.3 Hz), 121.8 (q, ^{1}J = 320.0 Hz), 117.6, 28.3; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.6 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{11}BrFS$ ([M-OTf])$^{+}$: 296.9749 found: 296.9743.

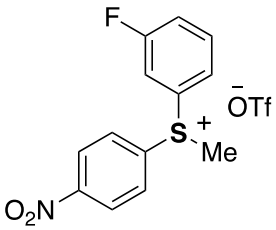
4-Cyanophenyl-3-fluorophenyl-methysulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 4-cyanothioanisole (149 mg, 0.10 mmol) according to the general procedure above for 3 hours

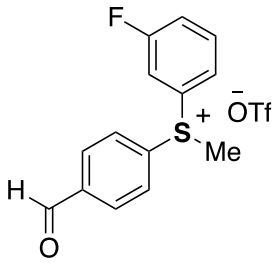
afforded 31 mg (90%) of product, isolated as white solid: mp 134.6-135.3°C; IR (neat) cm^{-1} 3108, 3066, 3036, 3019, 2934, 2237, 1594, 1479, 1430, 1277, 1253, 1223, 1152, 1078, 1028, 873, 835, 755, 674, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, J = 7.9Hz, 4H), 7.75-7.50 (m, 4H), 3..56 (s, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.6 (d, ^{1}J = 251.0 Hz), 135.2, 131.77, 133.9 (d, ^{3}J = 8.2 Hz), 127.6 (d, ^{4}J = 3.4 Hz), 127.2 (d, ^{3}J = 8.4 Hz), 122.7 (d, ^{2}J = 21.0 Hz), 121.6 (q, ^{1}J = 319.0 Hz), 118.1, 28.1; ^{19}F NMR (376 Hz, CD_3CN): δ -79.2 (s, 3F), -108.3 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{11}NO_2S$ ($[M\text{-}OTf]^+$): 244.0596 found: 244.0591

4-Nitrophenyl-3-fluorophenyl-methysulfonium triflate



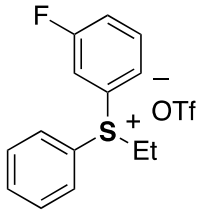
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 4-nitrothioanisole (203 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (90%) of product, isolated as white solid: mp 136.5-137.2°C; IR (neat) cm^{-1} 3108, 3067, 3031, 2931, 2917, 2849, 1607, 1595, 1524, 1348, 1281, 1223, 1150, 1092, 1030, 857, 743, 681, 640; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 9.0Hz, 2H), 8.06 (d, J = 9.0Hz, 2H), 7.77 (m, 3H), 7.61 (m, 1H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.4 (d, ^{1}J = 251.0 Hz), 151.5, 133.7 (d, ^{3}J = 8.5 Hz), 133.0, 131.9, 127.5 (d, ^{4}J = 3.5 Hz), 126.6 (d, ^{3}J = 8.2 Hz), 126.1, 122.6 (d, ^{2}J = 21.0 Hz), 121.6 (q, ^{1}J = 319.0 Hz), 118.3, 28.2; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.6 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{11}FNO_2S$ ($[M\text{-}OTf]^+$): 264.0495 found:

4-(3-fluorophenyl-methysulfonium)benzaldehyde triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 4-(methylthio)benzaldehyde (152 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 27 mg (67%) of product, isolated as white solid: mp 104.9-106.2°C; IR (neat) cm^{-1} 3093, 3067, 3026, 2930, 1698, 1594, 1577, 1481, 1254, 1224, 1178, 1156, 1027, 820, 788, 689, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 8.15 (dd, *J* = 8.5 Hz, 4H),7.84-7.82 (m, 1H), 7.74 (dd, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 192.0, 163.6 (d, ^{1}J = 251.0 Hz), 140.6, 133.9 (d, ^{3}J = 8.5 Hz), 132.0, 131.9, 131.3, 127.6 (d, ^{3}J = 8.2 Hz), 127.4 (d, ^{4}J = 3.5 Hz), 122.6 (d, ^{2}J = 21.0 Hz), 121.7 (q, ^{1}J = 318.4 Hz), 118.2, 28.2; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.4 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{12}FOS$ $([M\text{-}OTf])^{+}$: 247.0593 found: 247.0604.

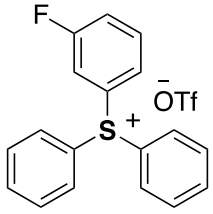
3-Fluorophenyl-ethyl-phenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and ethylthiobenzene (138 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 27 mg (67%) of product, isolated as white solid: mp 104.9-106.2°C; IR (neat) cm^{-1} 3067, 1593, 1480, 1448, 1259, 1225, 1158, 1029, 998, 755, 687, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.89 (m, 3H), 7.82-7.69 (m, 4H), 7.58 (d, *J* = 7.5 Hz, 1H) , 7.44 (t, *J* = 7.8 Hz, 1H), 4.41-4.27 (m, 2H), 1.52 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.6 (d, ^{1}J

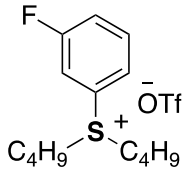
= 251.0 Hz), 135.5, 132.0, 133.9 (d, ^{3}J = 8.3 Hz), 126.7 (d, ^{3}J = 8.1 Hz), 127.5 (d, ^{4}J = 3.5 Hz), 124.2, 122.4 (d, ^{2}J = 21.0 Hz), 122.0 (q, ^{1}J = 319.0 Hz), 118.4, 40.8, 9.3; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.4 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{13}FS$ ([M-OTf])$^{+}$: 233.0800 found: 233.0795.

3-Fluorophenyl-diphenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and diphenyl sulfide (186 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 42 mg (98%) of product, isolated as white solid: mp 111.3-112.5°C; IR (neat) cm^{-1} 3093, 3066, 3031, 1591, 1477, 1263, 1150, 1064, 1032, 841, 754, 686, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.71 (m, 11H), 7.66 (d, *J* = 7.6 Hz, 1H) , 7.47 (t, *J* = 7.6 Hz, 1H), 7.34 (td, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.3 (d, ^{1}J = 254.0 Hz), 135.0, 133.5 (d, ^{3}J = 8.0 Hz), 131.8, 131.3, 126.3 (d, ^{3}J = 7.8 Hz), 127.3 (d, ^{4}J = 3.4 Hz), 123.8, 122.1 (d, ^{2}J = 21.0 Hz), 122.0 (q, ^{1}J = 319.0 Hz), 118.1 (d, ^{2}J = 25.6 Hz); ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.6 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{13}FS$ ([M-OTf])$^{+}$: 281.0800 found: 281.0795.

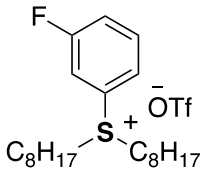
Dibutyl-3-fluorophenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and dibutyl sulfide (146 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (95%) of product, isolated as light yellow oil: IR (neat) cm^{-1} 2966, 2938, 2878, 1593, 1482, 1258, 1225, 1158, 1030, 755, 678, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 7.5 Hz, 1H), 7.81-7.73 (m, 1H), 7.68 (dt, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 4.00-3.81 (m, 4H),

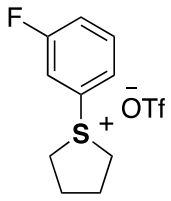
1.73-1.62 (m, 3H), 1.55-1.44 (m, 5H), 0.93 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.7 (d, ^{1}J = 250.0 Hz), 133.7 (d, ^{3}J = 8.4 Hz), 123.5 (d, ^{3}J = 8.3 Hz), 128.8 (d, ^{4}J = 3.2 Hz), 122.4 (d, ^{2}J = 21.1 Hz), 120.7 (q, ^{1}J = 319.0 Hz), 118.9 (d, ^{2}J = 25.2 Hz); ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.7 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{22}FS$ ([M-OTf])$^{+}$: 241.1426 found: 241.1421.

3-Fluorophenyl-dioctylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and dioctyl sulfide (258 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 50 mg (100%) of product, isolated as light yellow oil: IR (neat) cm^{-1} 3062, 2930, 2850, 1593, 1481, 1256, 1225, 1160, 1030, 756, 678, 638; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.8 Hz, 1H), 7.81-7.73 (m, 1H), 7.71-7.65 (m, 1H), 7.55-7.48 (m, 1H), 3.96-3.83 (m, 4H), 1.67-1.38 (m, overlap), 1.26-1.22 (m, 18H), 0.988-0.83 (m, 6H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.7 (d, ^{1}J = 250.0 Hz), 133.7 (d, ^{3}J = 8.2 Hz), 123.5 (d, ^{3}J = 8.1 Hz), 128.8 (d, ^{4}J = 3.3 Hz), 122.9 (d, ^{2}J = 21.1 Hz), 121.7 (q, ^{1}J = 319.0 Hz), 118.9 (d, ^{2}J = 25.2 Hz); 44.6, 31.9, 29.1, 28.9, 28.1, 24.6, 22.9, 13.9; ^{19}F NMR (376 Hz, CD_3CN): δ -79.2 (s, 3F), -108.6 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{22}H_{38}FS$ ([M-OTf])$^{+}$: 353.2678 found: 353.2673.

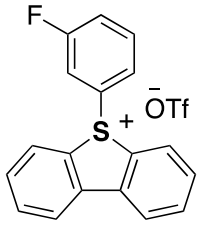
3-Fluorohenyl-tetrahydro-thiophenium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and thiolane (88 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 25 mg (81%) of product, isolated as white solid: mp 72.2-73.0°C; IR (neat) cm^{-1} 3075, 3031, 3004, 2974, 2956, 1596, 1587, 1483, 1260, 1221, 1167, 1154, 1094, 1028, 828, 757, 679, 635; ^{1}H NMR

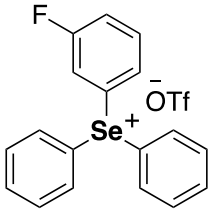
(400 MHz, $CDCl_3$): δ 7.74-7.60 (m, 3H), 7.51 (d, *J* = 8.0 Hz, 1H), 3.94 (quintet, *J* = 6.7 Hz, 2H), 3.70 (quintet, *J* = 6.7 Hz, 2H), 2.53-2.30 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.4 (d, ^{1}J = 250.0 Hz), 133.4 (d, ^{3}J = 8.4 Hz), 128.7 (d, ^{3}J = 8.1 Hz), 126.9 (d, ^{4}J = 3.4 Hz), 122.9 (d, ^{2}J = 21.1 Hz), 120.8 (q, ^{1}J = 319.0 Hz), 117.6; 49.0, 29.4; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.6 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{10}H_{12}FS$ ($[M\text{-}OTf]$)$^+$: 183.0644 found: 183.0638.

S-(3-Fluorophenyl)-dibenzothiophenium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (1280 mg, 0.12 mmol) and dibenzothiophene (184 mg, 0.10 mmol) according to the general procedure above for 24 hours afforded 34 mg (80%) of product, isolated as white solid: mp 169.8-170.5°C; IR (neat) cm^{-1} 3098, 3072, 3037, 11595, 1480, 1255, 1221, 1154, 1084, 1029, 868, 759, 670, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 7.8 Hz, 2H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.97 (t, *J* = 7.7 Hz, 2H), 7.74 (t, *J* = 7.7 Hz, 2H), 7.67-7.60 (m, 2H), 7.36 (dt, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 250.0 Hz), 135.3, 134.1 (d, ^{3}J = 8.2 Hz), 132.4, 131.9, 128.7, 127.4, 129.9 (d, ^{3}J = 8.2 Hz), 127.4 (d, ^{4}J = 3.2 Hz), 123.0 (d, ^{2}J = 21.2 Hz), 120.8 (q, ^{1}J = 319.0 Hz), 118.1; 49.0, 29.4; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -107.9 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{12}FS$ ($[M\text{-}OTf]$)$^+$: 279.0644 found: 279.0638.

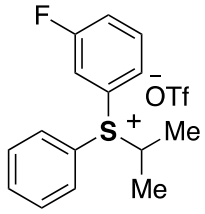
3-Fluorophenyl-diphenyselenium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and diphenyl selenide (233 mg, 0.10 mmol) according to the general procedure above for 3 hours

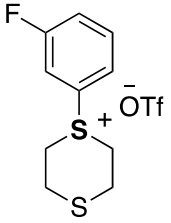
afforded 47 mg (100%) of product, isolated as dark yellow oil: IR (neat) cm^{-1} 3067, 1592, 1477, 1258, 1223, 1154, 1029, 743, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.54 (m, 11H), 7.45-7.39 (td, 2H, *J* = 8.4 Hz), 7.25-7.22 (m, 1H, overlap); ^{13}C NMR (100 MHz, CD_3CN): δ 163.7 (d, ^{1}J = 251.0 Hz), 134.4, 133.9 (d, ^{3}J = 8.1 Hz), 132.2, 132.0, 128.5 (d, ^{3}J = 7.9 Hz), 128.1 (d, ^{4}J = 3.5 Hz), 127.0, 121.5 (d, ^{2}J = 21.1 Hz), 121.7 (q, ^{1}J = 319.0 Hz), 119.1 (d, ^{2}J = 25 Hz); ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.7 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{14}FOSe$ $([M\text{-}OTf])^{+}$: 329.0245 found: 329.0239.

3-Fluorophenyl-isopropyl-phenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and isopropyl phenyl sulfide (152 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (94%) of product, isolated as colourless oil: IR (neat) cm^{-1} 3067, 2988, 1684, 1593, 1474, 1258, 1225, 1171, 1029, 750, 686, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20-8.12 (m, 3H), 7.82-7.70 (m, 5H), 7.46 (td, 1H, *J* = 8.0 Hz), 5.45 (septet, 1H, *J* = 6.7 Hz), 1.55-1.51 (m, 6H, overlap); ^{13}C NMR (100 MHz, CD_3CN): δ 163.6 (d, ^{1}J = 251.0 Hz), 135.7, 134.0 (d, ^{3}J = 8.5 Hz), 132.1, 132.1, 125.6 (d, ^{3}J = 8.1 Hz), 128.3 (d, ^{4}J = 3.5 Hz), 122.8 (d, ^{2}J = 21.2 Hz), 120.9 (q, ^{1}J = 319.0 Hz), 118.9), (d, ^{2}J = 25 Hz). 51.9, 18.3, 18.2; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.1 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{16}FS$ $([M\text{-}OTf])^{+}$: 247.0957 found: 297.0951.

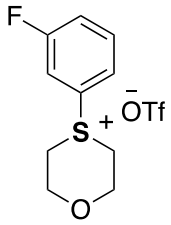
1-(3-Fluorophenyl)-1,4-dithianium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 1,4-

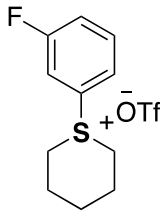
dithiane (120 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 19 mg (53%) of product, isolated as white solid: mp 98.0-99.2°C; IR (neat) cm^{-1} 3064, 3000, 2944, 2368, 1588, 1477, 1422, 1264, 1223, 1142, 1027, 909, 792, 754, 671, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 1H, *J* = 7.5 Hz), 7.75-7.68 (m, 2H), 7.48 (t, 1H, *J* = 8.3 Hz), 4.28 (d, 2H, *J* = 12.8 Hz), 3.80 (t, 2H, *J* = 11.6 Hz), 3.54 (t, 2H, *J* = 12.8 Hz), 3.19 (d, 2H, *J* = 11.3 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 251.0 Hz), 133.6 (d, ^{3}J = 8.5 Hz), 125.0 (d, ^{3}J = 8.2 Hz), 127.3 (d, ^{4}J = 3.5 Hz), 122.5 (d, ^{2}J = 21.0 Hz), 123.3 (q, ^{1}J = 313.0 Hz), 117.1 (d, ^{2}J = 23.5 Hz). 41.9, 25.1; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.9 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{10}H_{12}FS_2$ $([M\text{-}OTf])^+$: 215.0364 found: 215.0359.

1-(3-Fluorophenyl)-1,4-thioxanium triflate



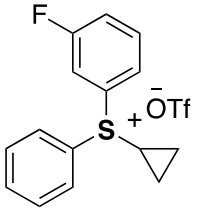
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and 1,4-thioxane (104 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 23 mg (53%) of product, isolated as white solid: mp 121.2-123.1°C; IR (neat) cm^{-1} 3079, 3065, 3014, 2912, 2887, 2862, 1587, 1478, 1264, 1223, 1162, 1071, 1032, 1104, 831, 755, 673, 642; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 1H, *J* = 7.5 Hz), 7.74-7.65 (m, 2H), 7.47 (t, 1H, *J* = 7.3 Hz), 4.41 (d, 2H, *J* = 13.2 Hz), 4.19 (t, 2H, *J* = 12.3 Hz), 4.07 (d, 2H, *J* = 13.2 Hz), 3.61 (t, 2H, *J* = 12.2 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ 163.6 (d, ^{1}J = 250.0 Hz), 133.6 (d, ^{3}J = 8.4 Hz), 124.8 (d, ^{3}J = 8.4 Hz), 127.0 (d, ^{4}J = 3.3 Hz), 122.1 (d, ^{2}J = 21.2 Hz), 121.7 (q, ^{1}J = 319.0 Hz), 117.7, 63.7, 38.5; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.9 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{10}H_{12}FOS$ $([M\text{-}OTf])^+$: 199.0593 found: 199.0587.

1-(3-Fluorophenyl)(pentamethylene)sulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and tetrahydrothiopyran (102 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 27 mg (79%) of product, isolated as white solid: mp 76.5-77.9°C; IR (neat) cm^{-1} 3086, 3074, 3007, 2952, 2912, 1596, 1482, 1448, 1437, 1282, 1260, 1225, 1153, 1083, 1028, 844, 755, 676, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 1H, *J* = 7.9 Hz), 7.76-7.69 (m, 2H), 7.45 (t, 1H, *J* = 7.9 Hz), 4.06 (t, 2H, *J* = 11.0 Hz), 3.77 (d, 2H, *J* = 11.0 Hz), 2.40 (m, 2H), 2.02 (m, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 250.0 Hz), 133.5 (d, ^{3}J = 8.5 Hz), 126.0 (d, ^{3}J = 8.1 Hz), 126.9 (d, ^{4}J = 3.4 Hz), 122.0 (d, ^{2}J = 21.0 Hz), 121.7 (q, ^{1}J = 319.0 Hz), 117.5, 41.2, 22.8, 22.7; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -109.2 (s, 1F); HRMS (ESI-TOF-positive mode): calcd for $C_{11}H_{14}FS$ $([M\text{-}OTf])^{+}$: 197.0800 found: 197.0795.

3-Fluorophenyl-cyclopropyl-phenylsulfonium triflate



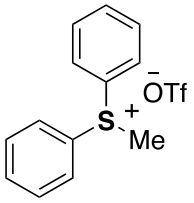
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (640 mg, 0.12 mmol) and cyclopropyl phenyl sulfide (150 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 32 mg (86%) of product, isolated as light yellow oil; IR (neat) cm^{-1} 3062, 1593, 1478, 1259, 1224, 1157, 1029, 754, 685, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 2H, *J* = 7.7 Hz), 7.94 (d, 1H, *J* = 7.8 Hz), 7.79-7.64 (m, 4H), 7.61 (dt, 1H, *J* = 7.7 Hz), 7.4 (t, 1H, *J* = 8.0 Hz), 4.03 (septet, 1H, *J* = 7.4 Hz), 31.77-1.66 (m, 2H), 1.55-1.44 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 163.5 (d, ^{1}J = 250.0 Hz), 133.5 (d, ^{3}J = 8.5 Hz), 126.0 (d, ^{3}J = 8.1 Hz), 126.9 (d, ^{4}J = 3.4 Hz), 122.0 (d, ^{2}J = 21.0 Hz), 121.7 (q, ^{1}J = 319.0 Hz), 117.5, 41.2, 22.8, 22.7; ^{19}F NMR (376 Hz, CD_3CN): δ -79.3 (s, 3F), -108.9 (s, 1F); HRMS (ESI-TOF-positive

mode): calcd for $C_{15}H_{15}FS$ ([M-OTf])$^{+}$: 245.0800 found: 245.0795.

Reaction of mesityle-1-phenylboronic acid-2-iodonium triflate with various substrates

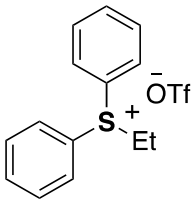
Sulfide or selenide was added to a solution of mesityle-arylboronic acid-iodonium triflate in methylene chloride (1.8 mL) and saturated $NaHCO_3$ (0.2 mL). The reaction was stirred at room temperature for 3-24 h. After completion of the reaction, and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by extraction over diethyl ether afforded analytically pure products.

Methyl-diphenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and methyl phenyl sulfide (124 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 28 mg (85%) of product, isolated as white solid: mp 95.1-96.8°C (lit.mp) ; IR (neat) cm^{-1} 3097, 3076, 3068, 3024, 2937, 1586, 1484, 1254, 1222, 1157, 1073, 1028, 824, 758, 690, 634; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.88 (m, 4H), 7.48-7.64 (m, 6H), 3.73 (s, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ 134.9, 131.8, 130.4, 126.8, 121.7 (q, ^{1}J = 319.0 Hz), 28.1; ^{19}F NMR (376 Hz, CD_3CN): δ -79.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{13}H_{13}S$ ([M-OTf])$^{+}$: 201.0732 found: 201.0732.

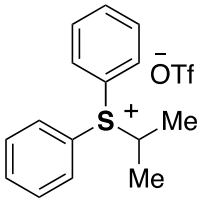
Ethyl-diphenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and ethyl phenyl sulfide (138 mg, 0.10 mmol) according to the general procedure above for 3 hours

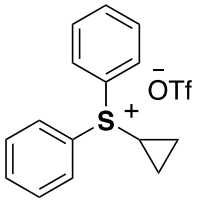
afforded 28 mg (85%) of product, isolated as colourless oil; IR (neat) cm^{-1} 3092, 3065, 2984, 2943, 1581, 1480, 1261, 1224, 1156, 1030, 839, 755, 685, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 4H, *J* = 7.2 Hz), 7.75-7.65 (m, 6H), 4.32 (quartet, 2H, *J* = 7.2 Hz), 1.50 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ 134.7, 131.6, 130.7, 124.1, 120.9 (q, ^{1}J = 318.5 Hz), 40.3, 9.7; ^{19}F NMR (376 Hz, CD_3CN): δ -79.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{15}S$ $([M\text{-}OTf])^{+}$: 215.0894 found: 215.0889.

Isopropyl-diphenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and ethyl phenyl sulfide (152 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 31 mg (83%) of product, isolated as colourless oil; IR (neat) cm^{-1} 3066, 2988, 1581, 1478, 1259, 1158, 1076, 1029, 756, 690, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-8.12 (m, 4H), 7.78-7.69 (m, 6H), 5.42 (septet, 1H, *J* = 6.5 Hz), 1.52 (d, 6H, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, CD_3CN): δ 135.5, 132.1, 131.9, 124.1, 120.6 (q, ^{1}J = 318.8 Hz), 51.5, 18.3; ^{19}F NMR (376 Hz, CD_3CN): δ -79.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{17}S$ $([M\text{-}OTf])^{+}$: 229.1051 found: 229.1045.

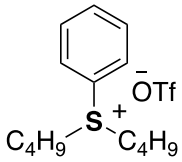
Cyclopropyl-diphenylsulfonium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and cyclopropyl phenyl sulfide (150 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 31 mg (83%) of product, isolated as colourless oil; IR (neat) cm^{-1} 3050, 1581, 1447, 1261, 1224, 1156, 1072, 1029, 827, 755, 684, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00-

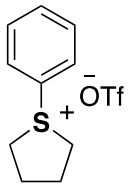
7.96 (m, 4H), 7.76-7.67 (m, 6H), 4.16-4.08 (m, 1H), 1.77-1.71 (m, 2H), 1.44-1.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 131.4, 130.2, 126.5, 120.9 (q, ^1J = 319.0 Hz), 22.5, 8.1; ^{19}F NMR (376 Hz, $CDCl_3$): δ -78.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{15}S$ $([M\text{-}OTf])^+$: 227.0894 found: 227.0889.

Dibutyl-phenylsulfonium triflate



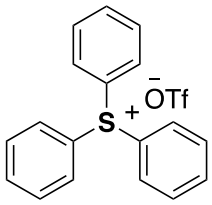
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and dibutyl sulfide (146 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 37 mg (100%) of product, isolated as light yellow oil; IR (neat) cm^{-1} 3065, 2964, 2937, 2877, 1467, 1259, 1224, 1156, 1030, 755, 687, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.90 (m, 2H), 7.84-7.69 (m, 3H), 3.94-3.79 (m, 4H), 1.71-1.60 (m, 2H), 1.53-1.43 (m, 4H), 0.94-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 132.0, 131.8, 121.8 (q, ^1J = 320.0 Hz), 121.7, 44.2, 26.6, 21.5, 13.1; ^{19}F NMR (376 Hz, $CDCl_3$): δ -79.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{14}H_{23}S$ $([M\text{-}OTf])^+$: 223.1520 found: 223.1515.

Tetrahydro-phenyl-thiophenium triflate



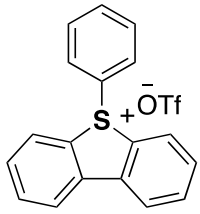
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and thiolane (88 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 28 mg (88%) of product, isolated as light yellow oil; IR (neat) cm^{-1} 3061, 2918, 2361, 2334, 1594, 1448, 1158, 1026, 684, 637; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.64 (m, 5H), 4.37-4.27 (m, 2H), 3.70-3.67 (m, 2H), 2.67-2.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.1, 131.4, 129.7, 125.0, 121.8 (q, ^1J = 320.0 Hz), 48.7, 29.2; ^{19}F NMR (376 Hz, $CDCl_3$): δ -79.3 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{15}H_{15}S$ $([M\text{-}OTf])^+$: 165.0738 found: 165.0732.

Triphenyl sulfonium triflate



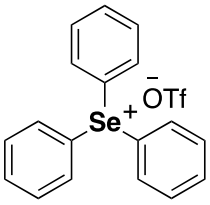
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and biphenyl sulfide (186 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 28 mg (88%) of product, isolated as white solid: mp 132.1-133.6°C (lit.[] mp); IR (neat) cm^{-1} 3090, 3062, 1581, 1551, 1477, 1274, 1224, 1155, 1066, 1029, 749, 685, 636; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 132.1, 131.7, 125.7, 121.8 (q, ^{1}J = 318.3 Hz), 48.7, 29.2; ^{19}F NMR (376 Hz, $CDCl_3$): δ -79.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{15}S$ ($[M\text{-}OTf]$)$^{+}$: 263.0894 found: 263.0882.

S-Phenyl-dibenzothiophenium triflate



Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and dibenzothiophene (184 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 28 mg (88%) of product, isolated as white solid: mp 187.0-188.1°C (lit. mp); IR (neat) cm^{-1} 3027, 2921, 2851, 1635, 1574, 1269, 1153, 1030, 827, 755, 667, 635; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.88 (t, *J* = 7.5 Hz, 1H), 7.74-7.64 (m, 5H), 7.54 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 3027, 2921, 2851, 1635, 1574, 1269, 1153, 1030, 827, 755, 667, 635; ^{19}F NMR (376 Hz, $CDCl_3$): δ -79.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{13}S$ ($[M\text{-}OTf]$)$^{+}$: 261.0732 found: 261.0732.

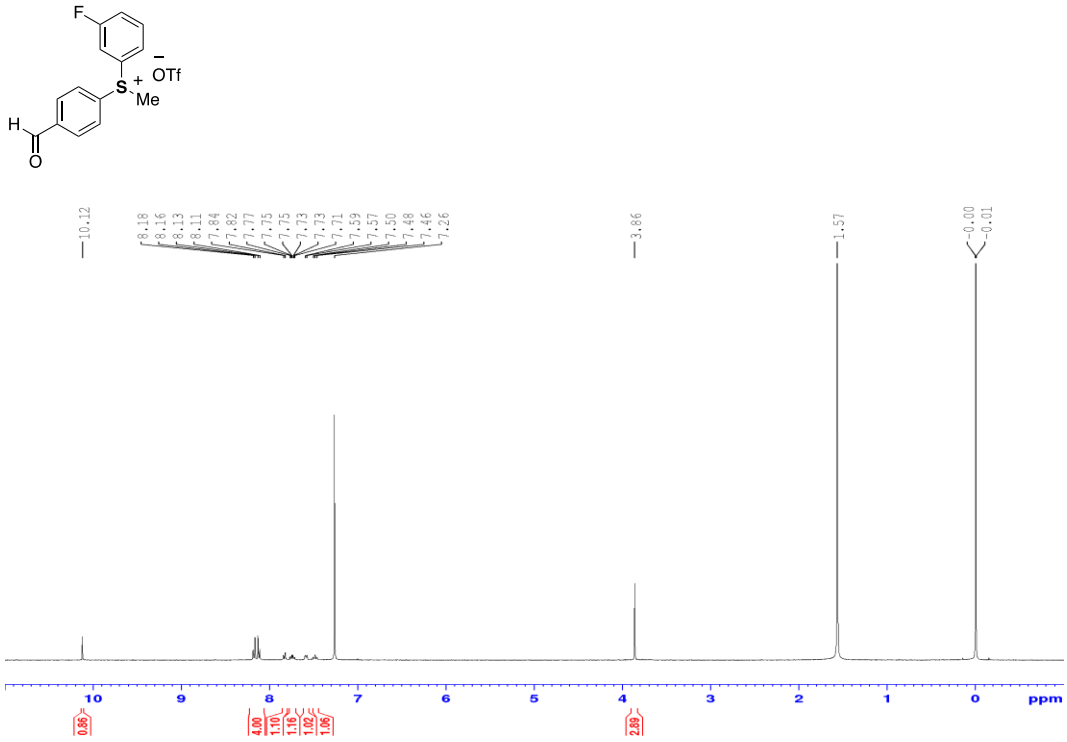
Triphenyl selenium triflate

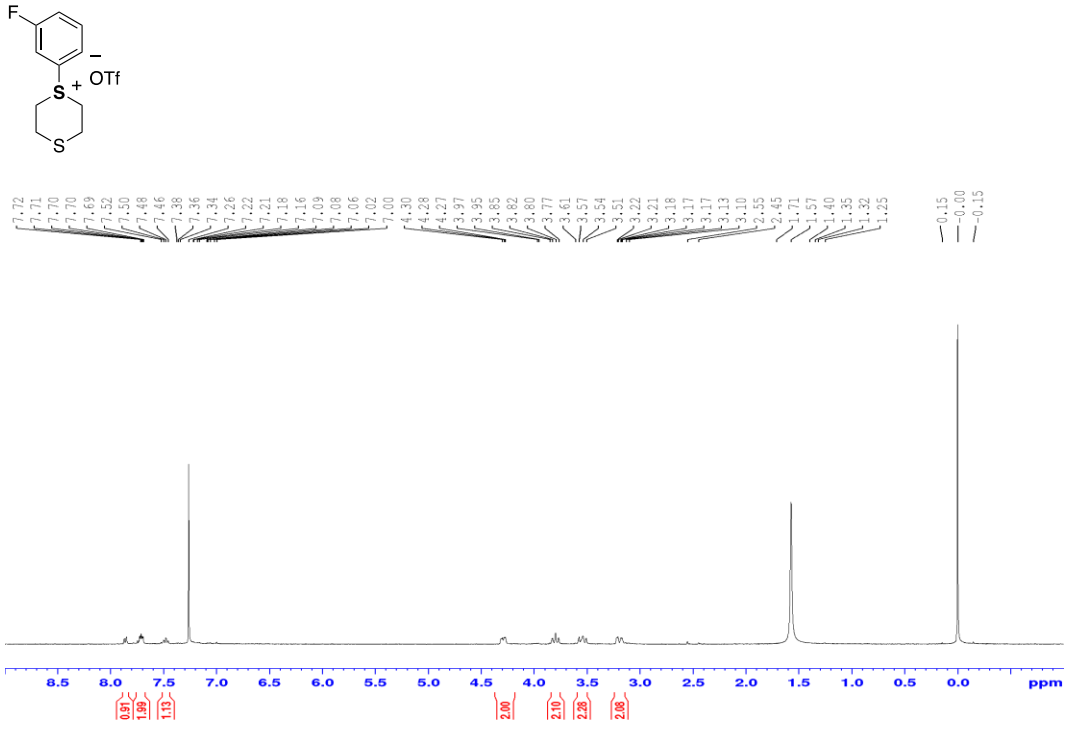


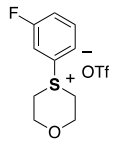
Reaction of mesityl-1-phenyboronic acid-2-iodonium triflate (619 mg, 0.12 mmol) and diphenyl selenide (233 mg, 0.10 mmol) according to the general procedure above for 3 hours afforded 32 mg (71%) of product, isolated as light yellow oil; IR (neat) cm^{-1} 3027, 2921, 2851, 1635, 1574, 1269, 1153, 1030, 827, 755, 667, 635; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.68 (m, 5H), 7.67-7.61 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8, 131.7, 131.2, 126.3, 120.8 (q, ^{1}J = 319.0 Hz); ^{19}F NMR (376 Hz, $CDCl_3$): δ -78.2 (s, 3F); HRMS (ESI-TOF-positive mode): calcd for $C_{18}H_{15}Se$ $([M\text{-}OTf])^{+}$: 311.0339 found: 311.0334.

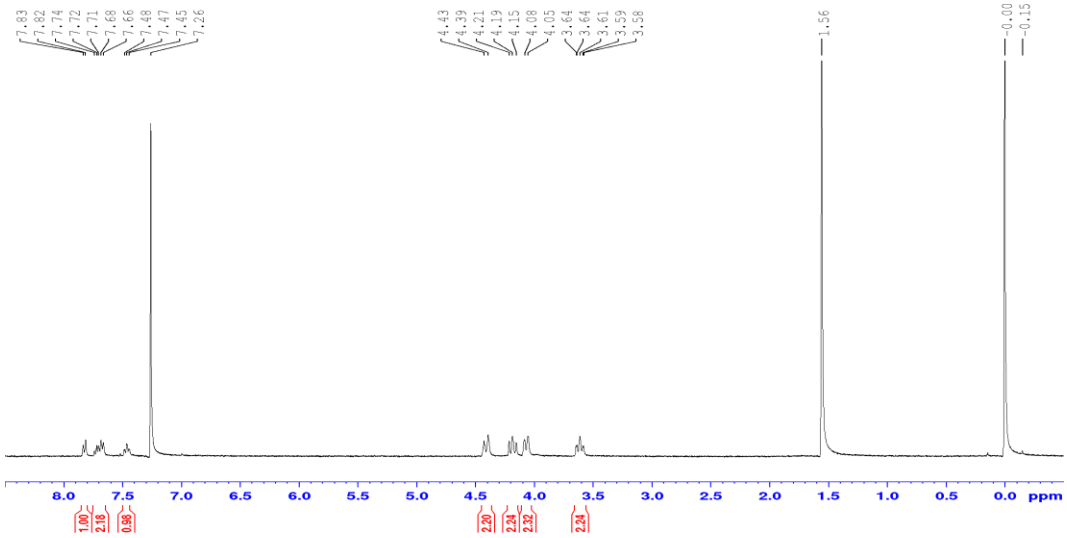
4. APPENDIX

4.1 Proton NMR:






F
OTf
S
O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7.68
7.66
7.48
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7.45
7.26
4.43
4.39
4.21
4.19
4.15
4.08
4.05
3.64
3.64
3.61
3.59
3.58
1.56
0.00
-0.15
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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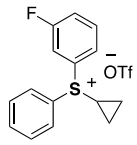
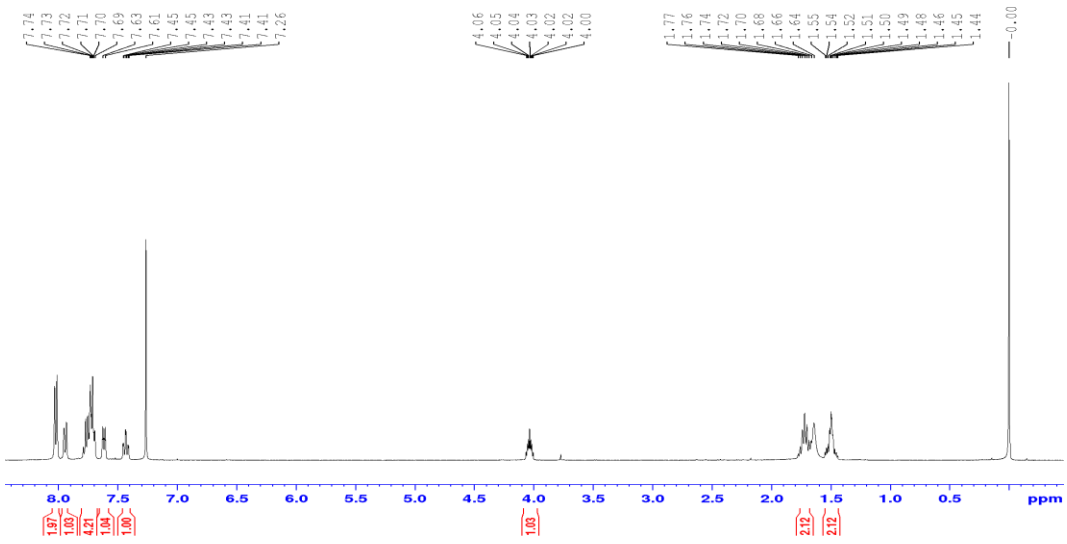

F
OTf
S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7.61
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7.45
7.43
7.43
7.41
7.41
7.26
4.06
4.05
4.04
4.03
4.02
4.02
4.00
1.77
1.76
1.74
1.72
1.70
1.68
1.66
1.64
1.55
1.54
1.52
1.51
1.50
1.49
1.48
1.46
1.45
1.44
0.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
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ppm
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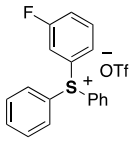
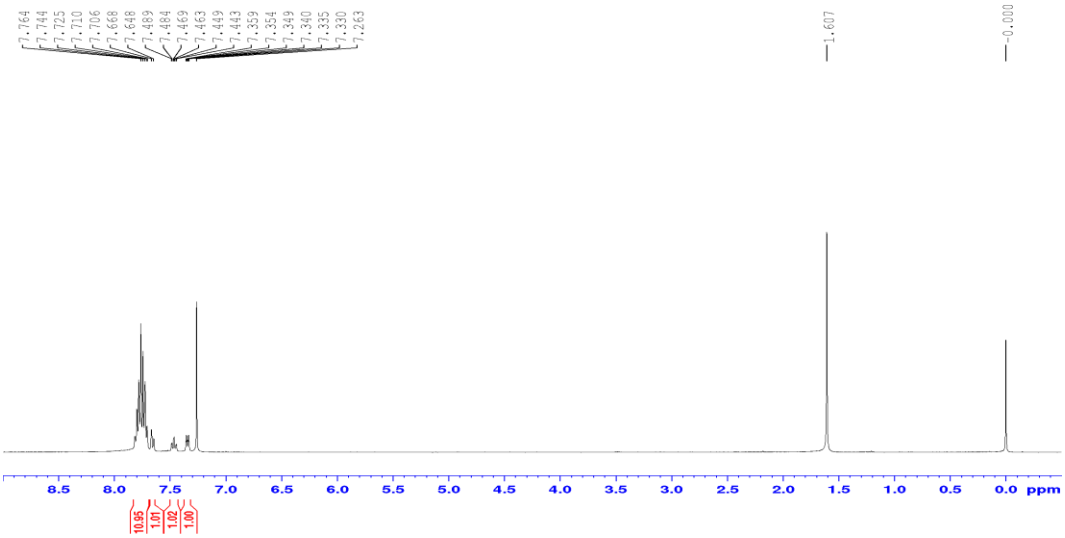
2.12


F
OTf
S
+
Ph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7.449
7.443
7.359
7.354
7.349
7.340
7.335
7.330
7.263
1.607
0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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ppm
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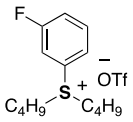
1.02
1.00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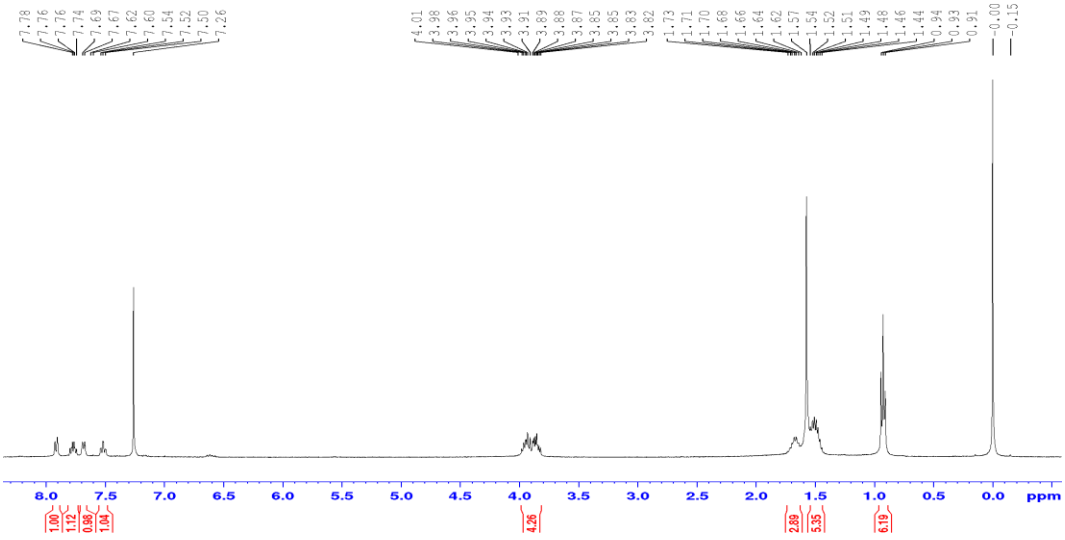
OTf
S
+
C4H9
C4H9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7.60
7.54
7.52
7.50
7.26
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3.98
3.96
3.95
3.94
3.93
3.91
3.89
3.88
3.87
3.85
3.85
3.83
3.82
1.73
1.71
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1.68
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1.57
1.54
1.52
1.51
1.49
1.48
1.46
1.44
0.94
0.93
0.91
0.000
0.15
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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
ppm
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0.98
1.04
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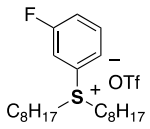
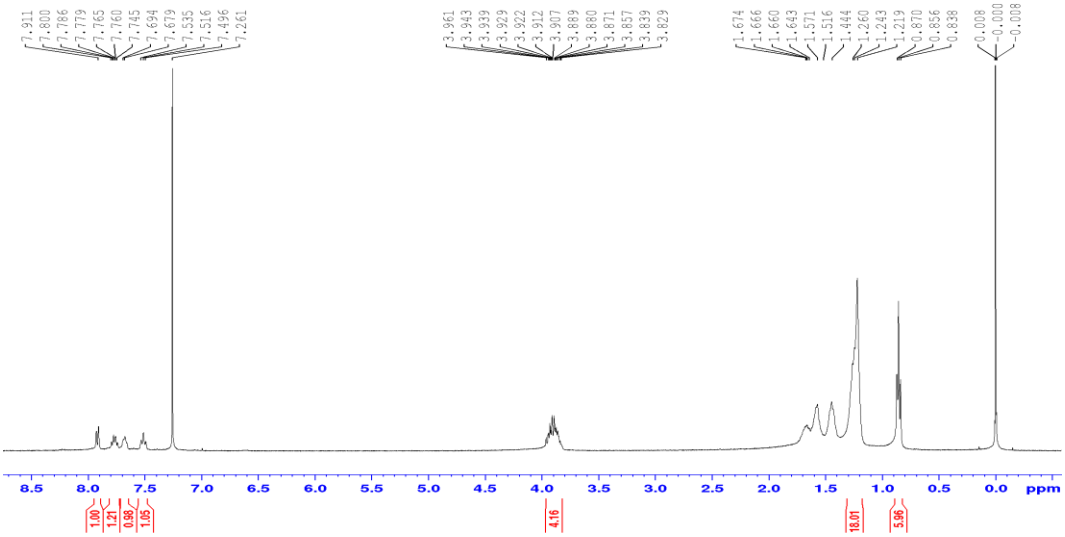
2.89
5.35
6.19


F
OTf
S
C8H17
C8H17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7.760
7.745
7.694
7.679
7.535
7.516
7.496
7.261
3.961
3.943
3.939
3.929
3.922
3.912
3.907
3.889
3.880
3.871
3.857
3.839
3.829
1.674
1.666
1.660
1.643
1.571
1.516
1.444
1.260
1.243
1.219
0.870
0.856
0.838
0.008
0.000
-0.008
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 ppm
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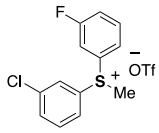
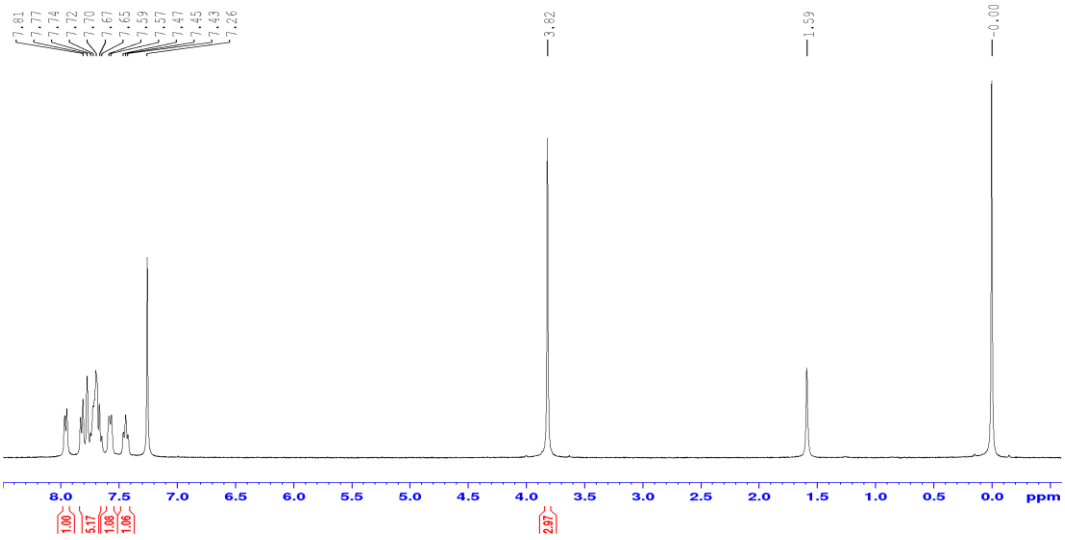
1.21
0.88
1.05
4.16
18.01
5.96


F
OTf
Cl
S
Me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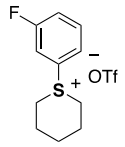
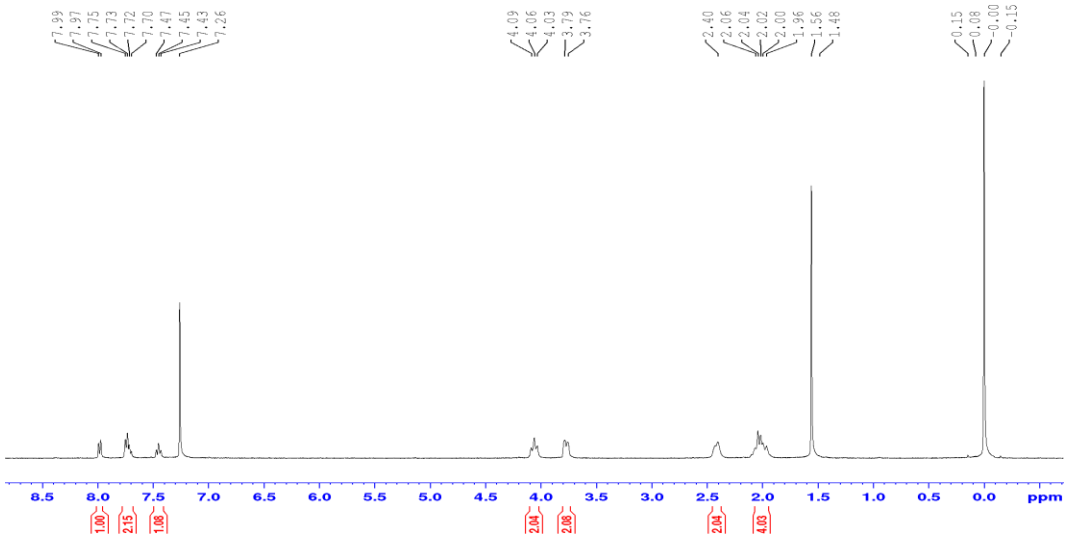
7.74
7.72
7.70
7.67
7.65
7.59
7.57
7.47
7.45
7.43
7.26
3.82
1.59
0.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
5.17
1.08
1.06
2.97


F
OTf
S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7.97
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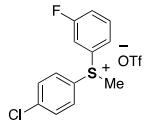
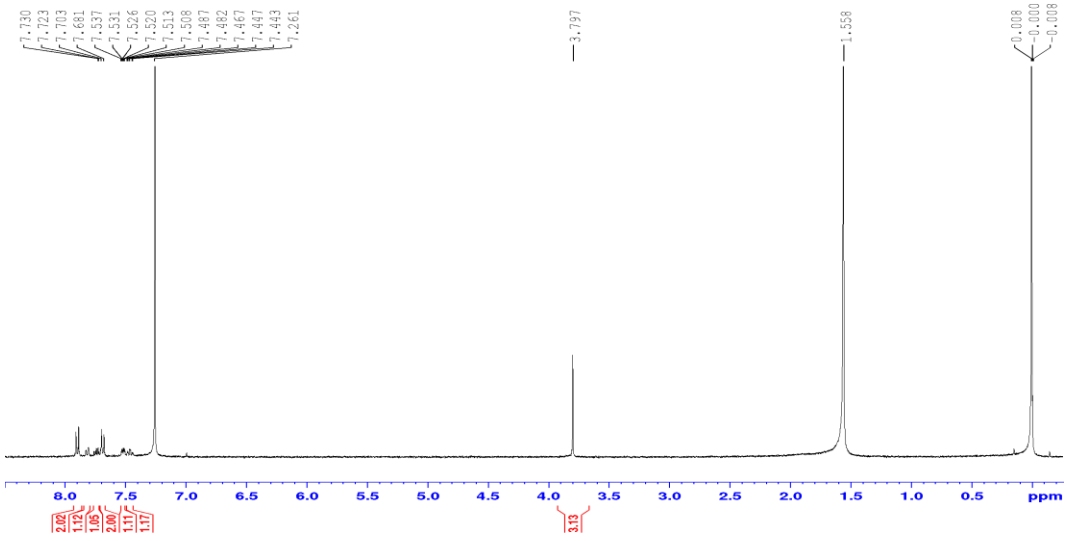
7.73
7.72
7.70
7.47
7.45
7.43
7.26
4.09
4.06
4.03
3.79
3.76
2.40
2.06
2.04
2.02
2.00
1.96
1.56
1.48
0.15
0.08
-0.00
-0.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.15
1.08
2.04
2.08
2.04
4.03


F
OTf
S
Me
Cl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7.520
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7.508
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7.482
7.467
7.447
7.443
7.261
3.797
1.558
0.008
0.000
-0.008
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
0.5
ppm
2.02
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1.85
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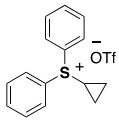
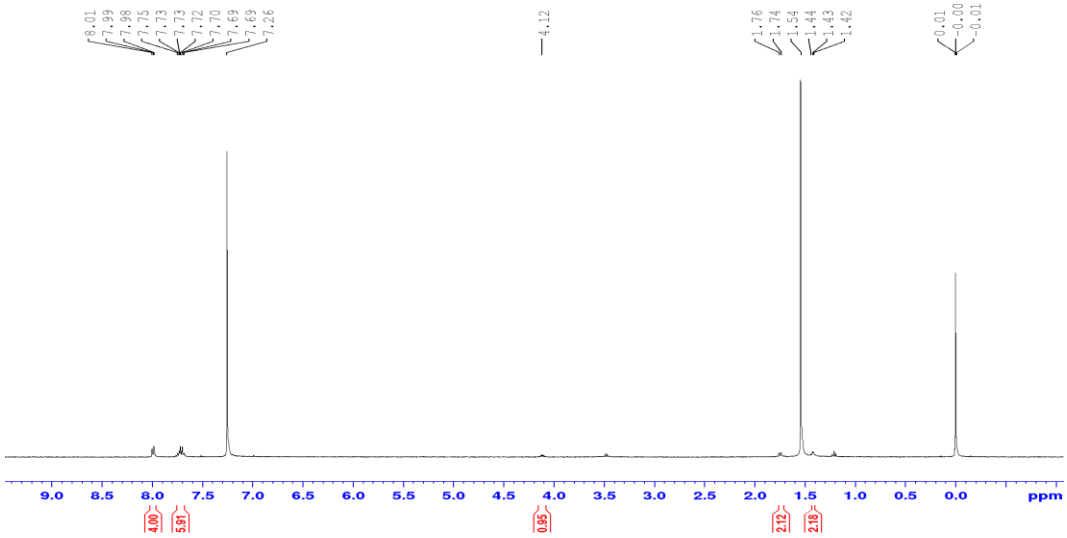
1.17
3.13


OTf
S
+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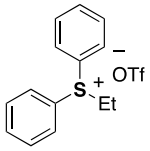
7.99
7.98
7.75
7.73
7.73
7.72
7.70
7.69
7.69
7.26
4.12
1.76
1.74
1.54
1.44
1.43
1.42
0.01
0.00
-0.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.00
5.97
0.95
2.12
2.18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+
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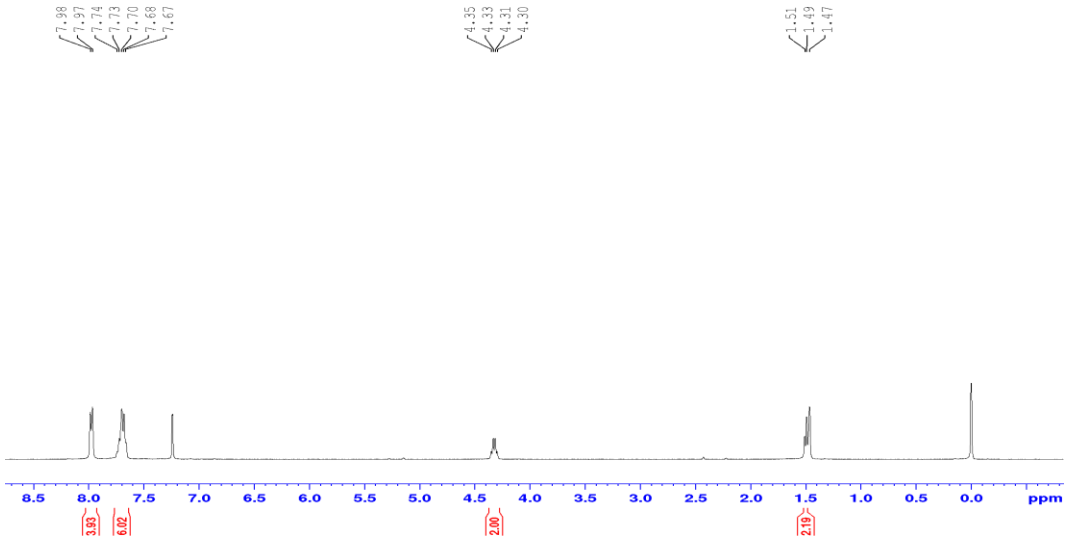
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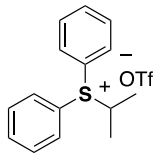
7.70
7.68
7.67
4.35
4.33
4.31
4.30
1.51
1.49
1.47
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.93
6.02
2.00
2.19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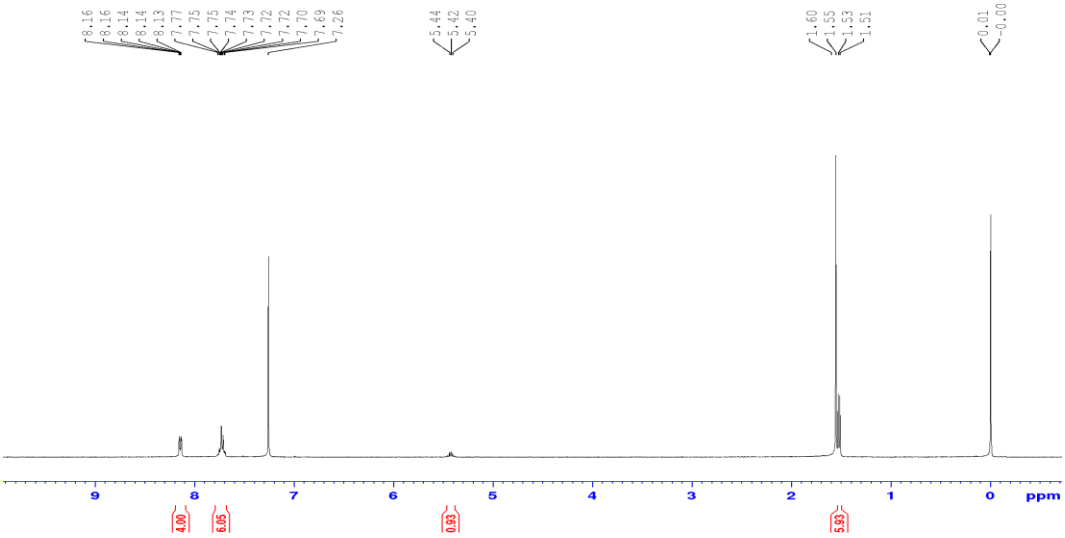
OTf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8.14
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7.75
7.75
7.74
7.73
7.72
7.72
7.70
7.69
7.26
5.44
5.42
5.40
1.60
1.55
1.53
1.51
0.01
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7
6
5
4
3
2
1
0
ppm
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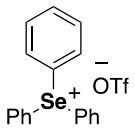
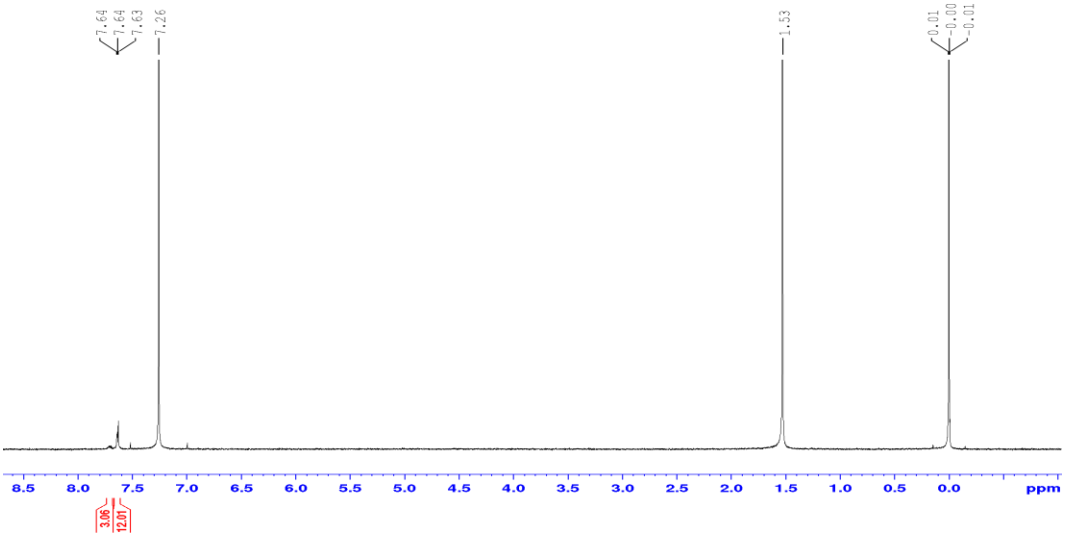
6.05
0.93
5.93


Se
+
OTf
Ph
Ph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0.00
-0.01
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8.0
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7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
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0.5
0.0
ppm
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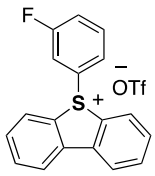
12.01


F
OTf
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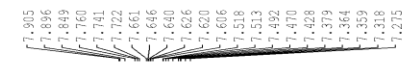
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7.606
7.518
7.513
7.492
7.470
7.428
7.379
7.364
7.359
7.318
7.275


2.606
2.513
2.417
2.379
2.179
1.955
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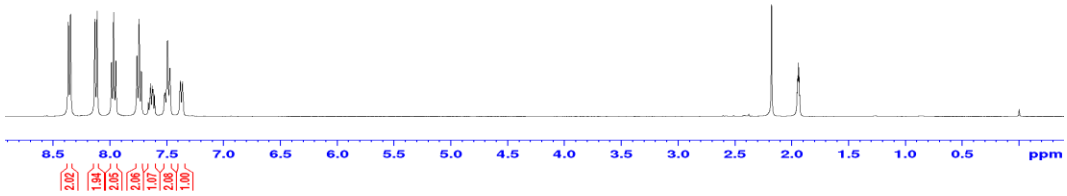
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4.0
3.5
3.0
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0.5
ppm
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2.05
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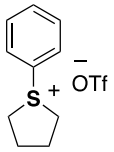
2.08
1.00


OTf
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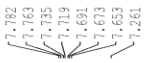
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7.735
7.719
7.691
7.673
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7.261


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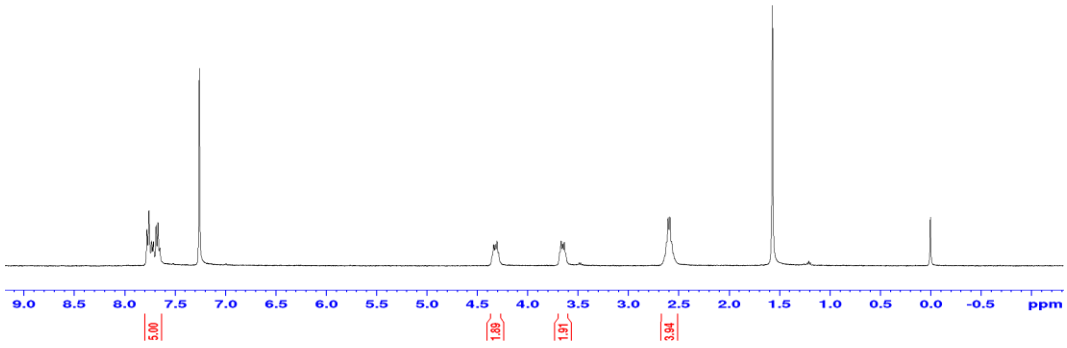
4.320
4.303

3.666
3.651
3.634


2.604
2.587


1.568


0.000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6.5
6.0
5.5
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4.5
4.0
3.5
3.0
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1.5
1.0
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0.0
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ppm
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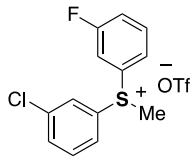
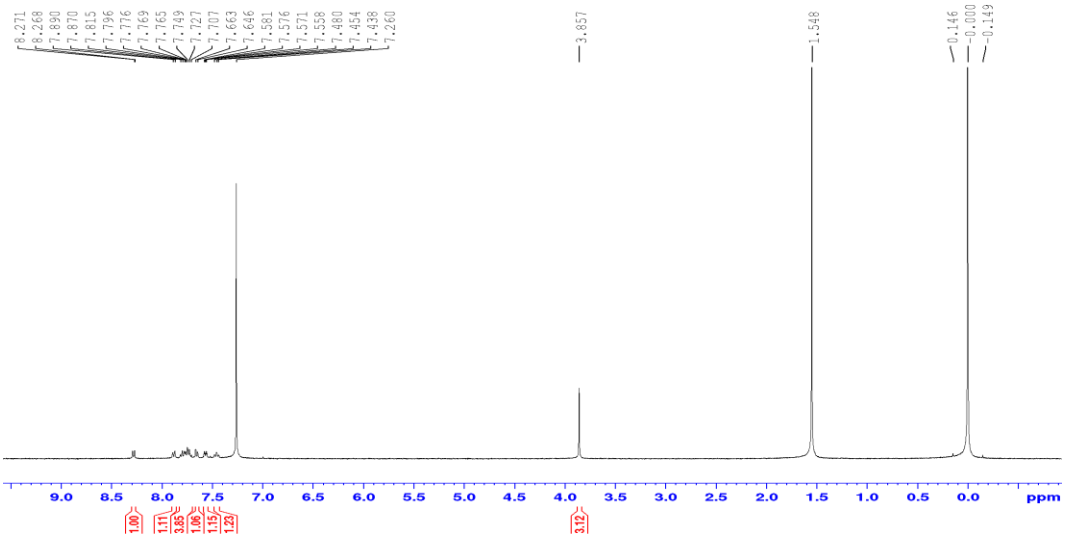
1.91
3.94


F
Cl
S
+
Me
OTf
−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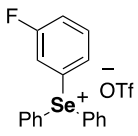
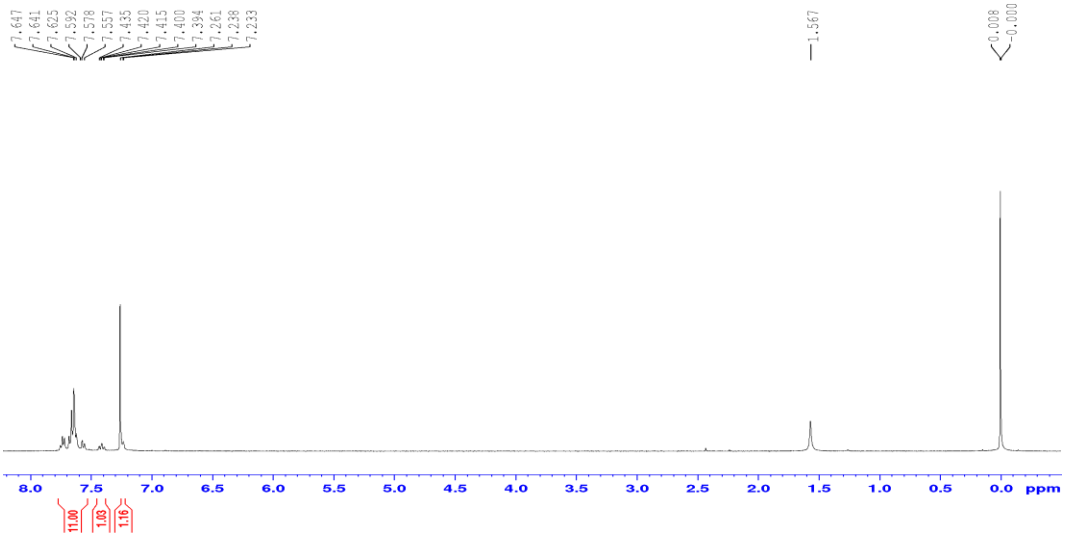
7.769
7.765
7.749
7.727
7.707
7.663
7.646
7.581
7.576
7.571
7.558
7.480
7.454
7.438
7.260
3.857
1.548
0.146
0.000
-0.149
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.11
3.85
1.06
1.15
1.23
3.12


F
Se
+
Ph
Ph
OTf
−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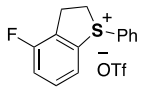
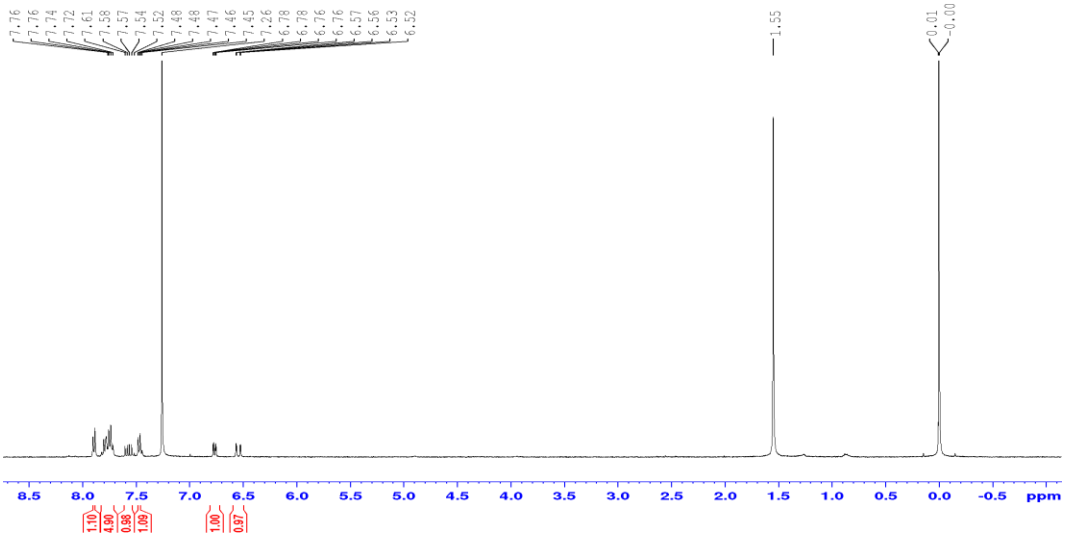
7.641
7.625
7.592
7.578
7.557
7.435
7.420
7.415
7.400
7.394
7.261
7.238
7.233
1.567
0.008
-0.000
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
11.00
1.03
1.16


F
S
+
Ph
–
OTf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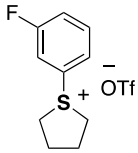
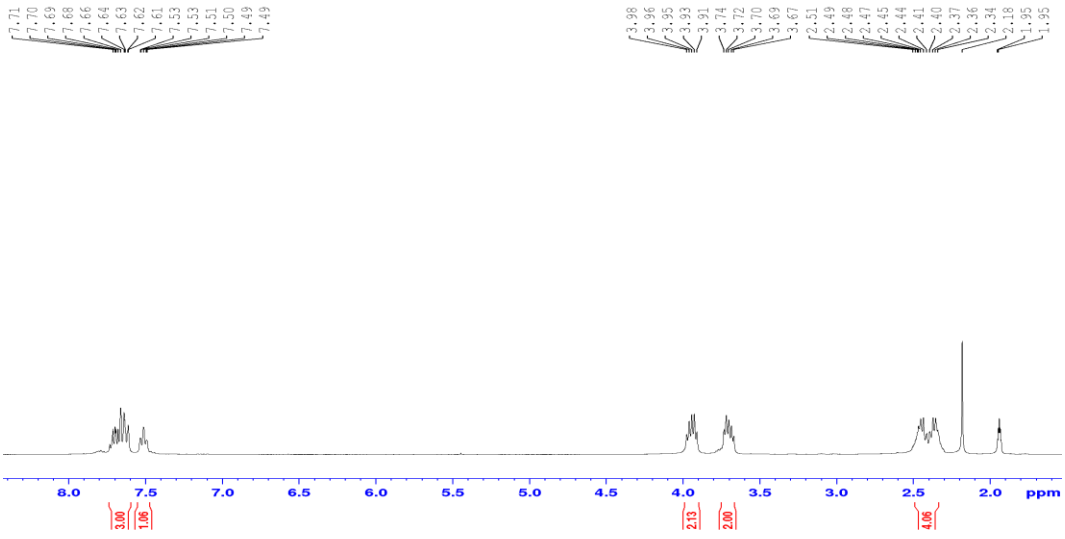
7.76
7.74
7.72
7.61
7.58
7.57
7.54
7.52
7.48
7.48
7.47
7.46
7.45
7.26
6.78
6.76
6.76
6.57
6.56
6.53
6.52
1.55
0.01
-0.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.10
4.99
0.98
1.09
1.00
0.97


F
–
OTf
S
+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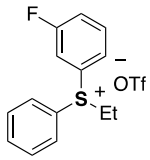
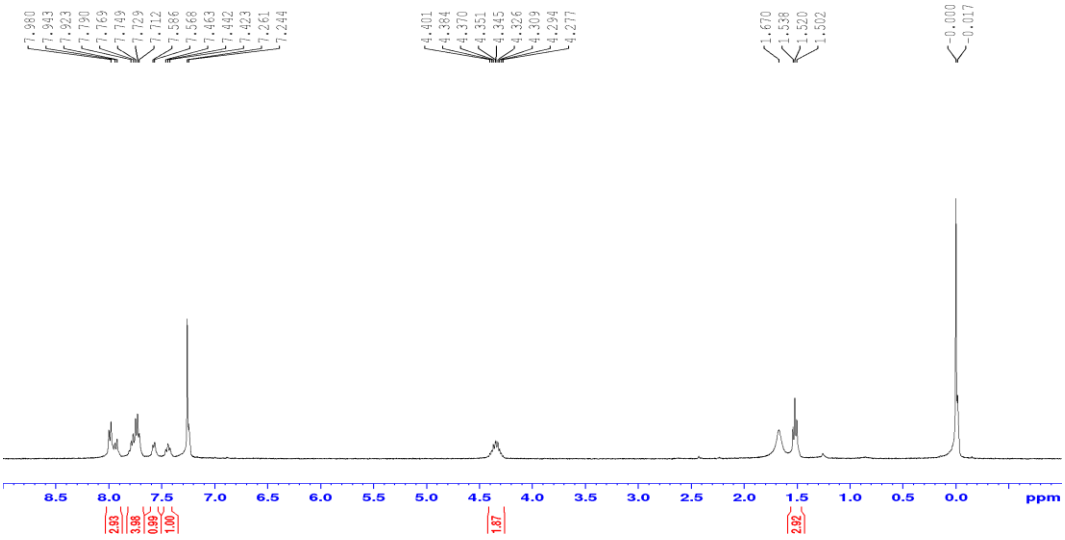
7.70
7.69
7.68
7.66
7.64
7.63
7.62
7.61
7.53
7.53
7.51
7.50
7.49
7.49
3.98
3.96
3.95
3.93
3.91
3.74
3.72
3.70
3.69
3.67
2.51
2.49
2.48
2.47
2.45
2.44
2.41
2.40
2.37
2.36
2.34
2.18
1.95
1.95
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
3.00
1.06
2.13
2.00
4.06


F
OTf
S
Et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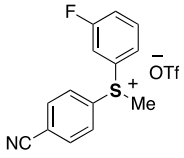
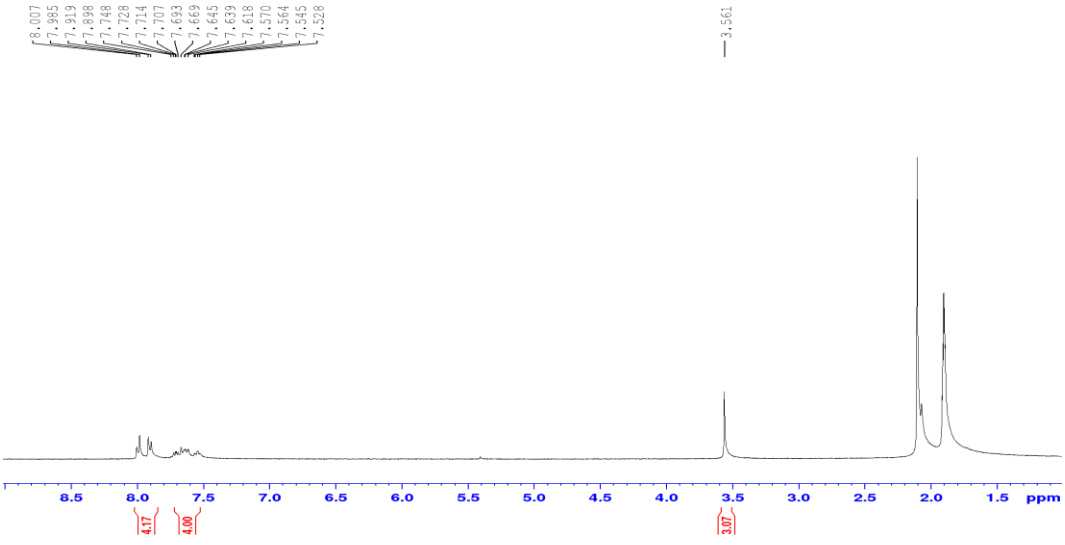
7.943
7.923
7.790
7.769
7.749
7.729
7.712
7.586
7.568
7.463
7.442
7.423
7.261
7.244
4.401
4.384
4.370
4.351
4.345
4.326
4.309
4.294
4.277
1.670
1.538
1.520
1.502
0.000
-0.017
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.93
3.88
0.99
1.00
1.87
2.92


F
OTf
S
Me
NC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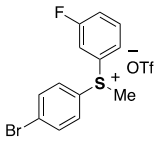
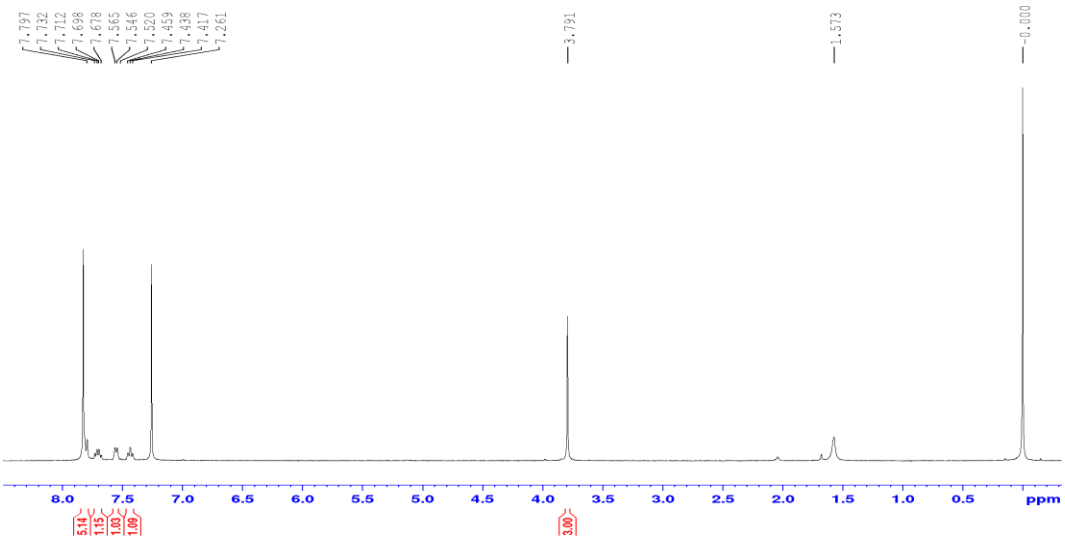
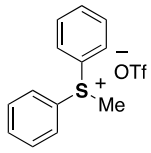
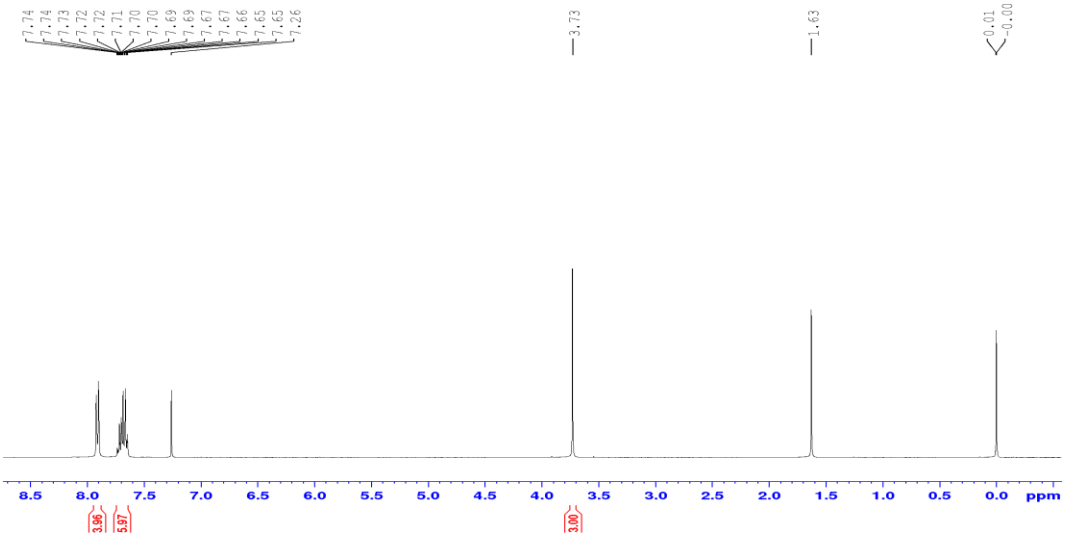
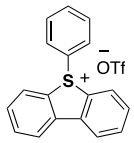
7.985
7.919
7.898
7.748
7.728
7.714
7.707
7.693
7.669
7.645
7.639
7.618
7.570
7.564
7.545
7.528
3.561
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
4.17
4.00
3.07

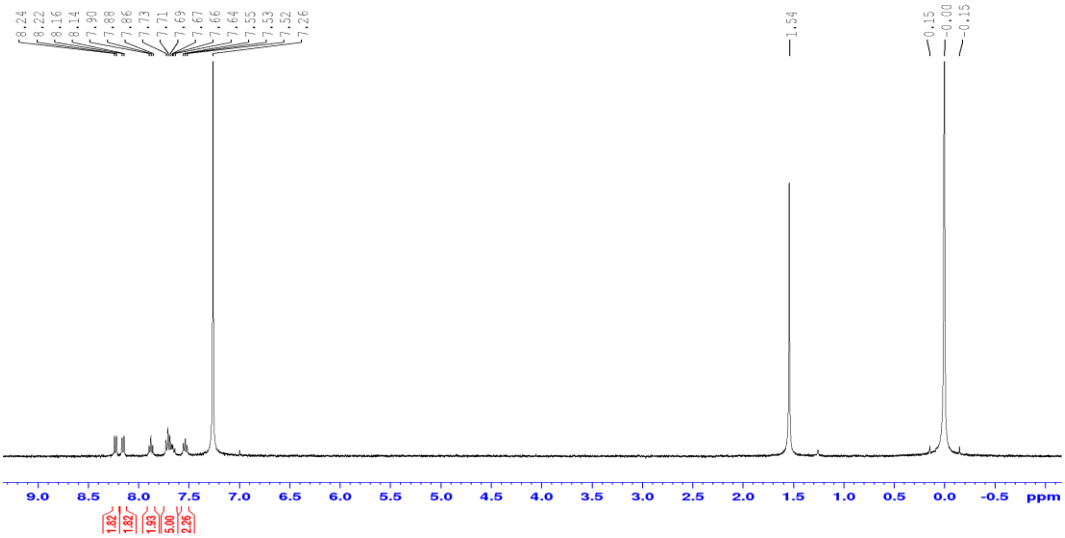

F
OTf
S
Me
Br

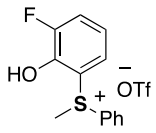

7.797
7.732
7.712
7.698
7.678
7.565
7.546
7.520
7.459
7.438
7.417
7.261
3.791
1.573
0.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.14
1.15
1.03
1.09
3.00

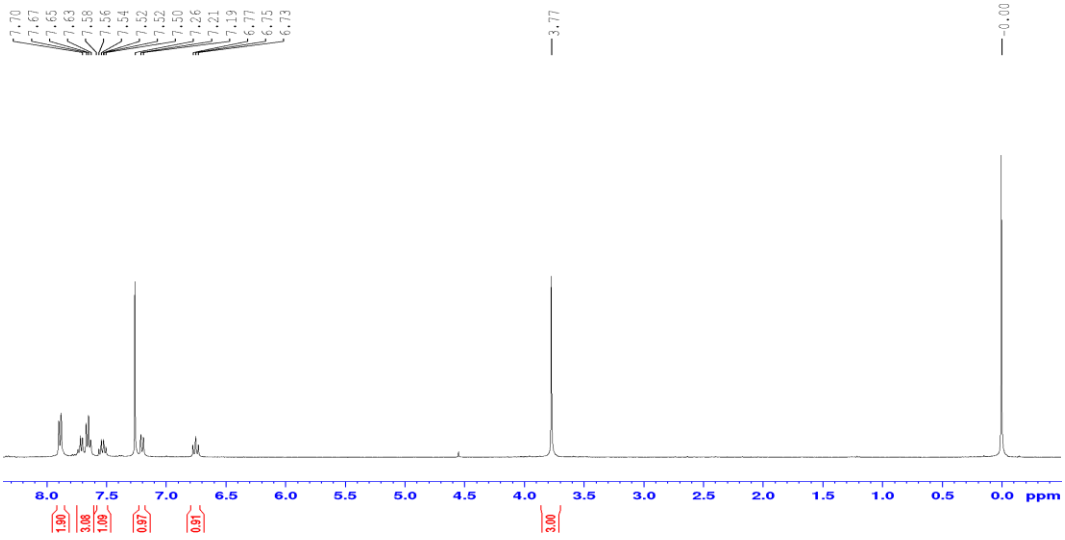

OTf
S
Me

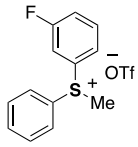

7.74
7.74
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.69
7.67
7.67
7.66
7.65
7.65
7.26
3.73
1.63
0.01
0.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.96
5.97
3.00

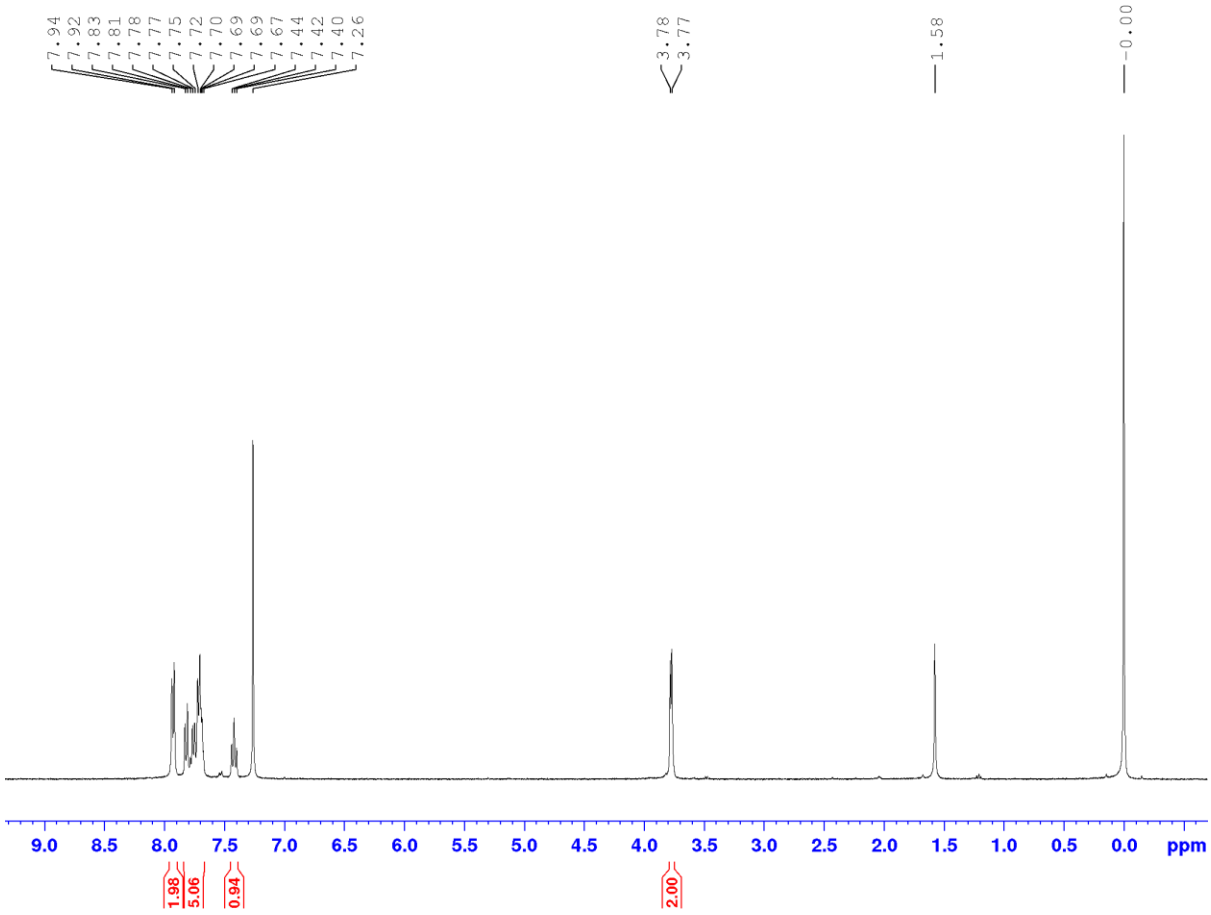

OTf

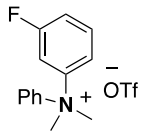

8.24
8.22
8.16
8.14
7.90
7.88
7.86
7.73
7.71
7.69
7.67
7.66
7.64
7.55
7.53
7.52
7.26
1.54
0.15
0.00
-0.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.82
1.82
1.93
5.00
2.98

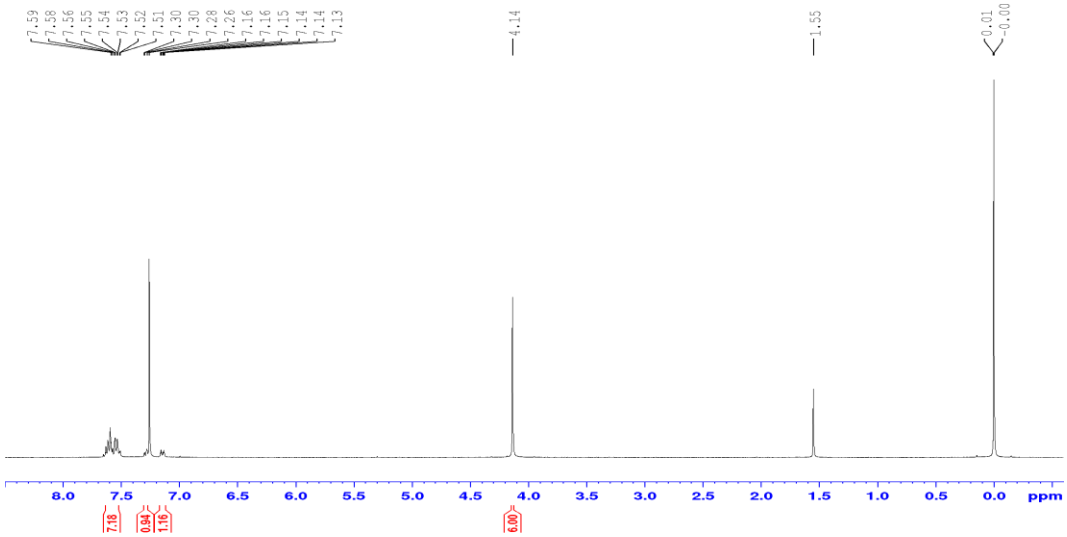

F
HO
OTf
Ph


7.70
7.67
7.65
7.63
7.58
7.56
7.54
7.52
7.52
7.50
7.26
7.21
7.19
6.77
6.75
6.73
3.77
0.00
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 ppm
1.90
3.08
1.09
0.97
0.91
3.00


F
OTf
S
Me


7.94
7.92
7.83
7.81
7.78
7.77
7.75
7.72
7.70
7.69
7.67
7.44
7.42
7.40
7.26
3.78
3.77
1.58
0.00
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
ppm
1.98
5.06
0.94
2.00


F
Ph
N
OTf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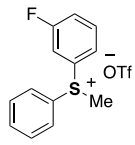
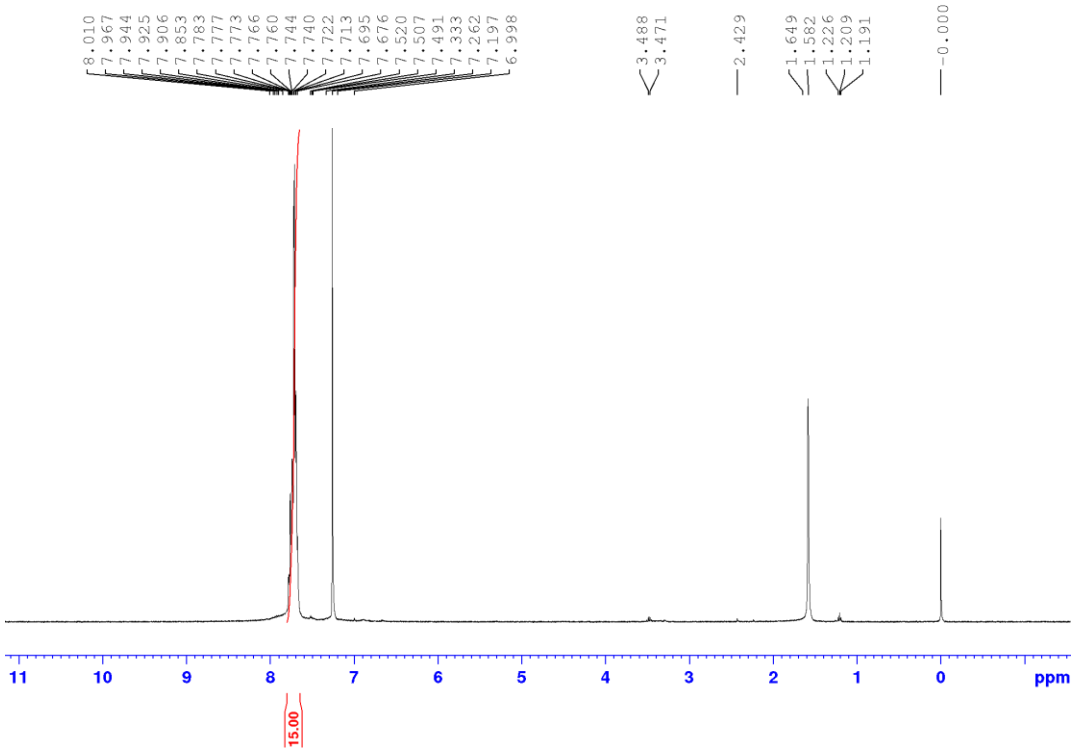
7.58
7.56
7.55
7.54
7.53
7.52
7.51
7.30
7.28
7.26
7.16
7.16
7.15
7.14
7.14
7.13
4.14
1.55
0.01
0.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
7.18
0.84
1.16
6.00


F
OTf
S
Me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7.944
7.925
7.906
7.853
7.783
7.777
7.773
7.766
7.760
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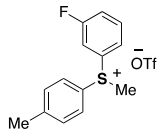
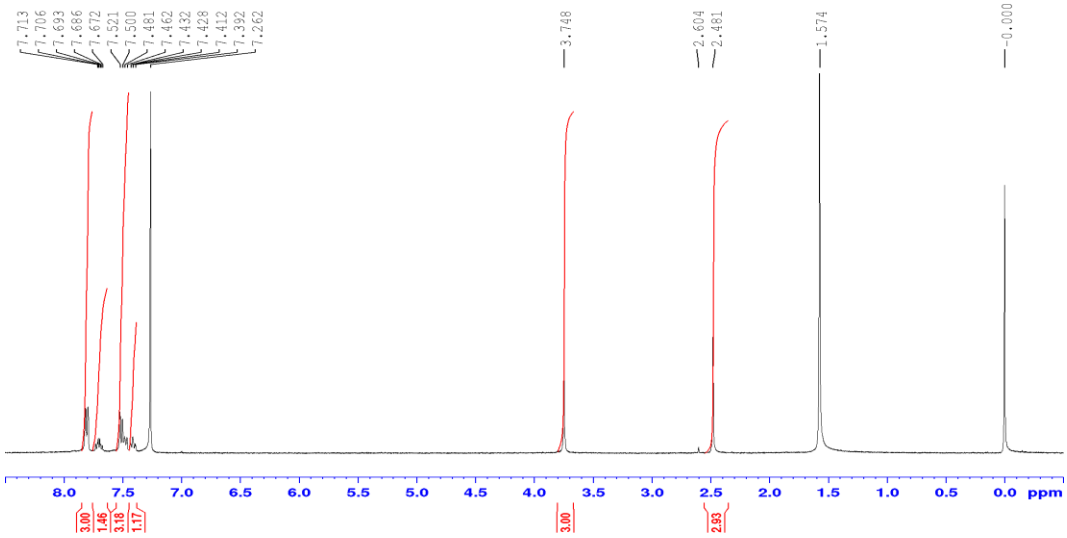
7.740
7.722
7.713
7.695
7.676
7.520
7.507
7.491
7.333
7.262
7.197
6.998
3.488
3.471
2.429
1.649
1.582
1.226
1.209
1.191
0.000
11
10
9
8
7
6
5
4
3
2
1
0
ppm
15.00


F
OTf
S
Me
Me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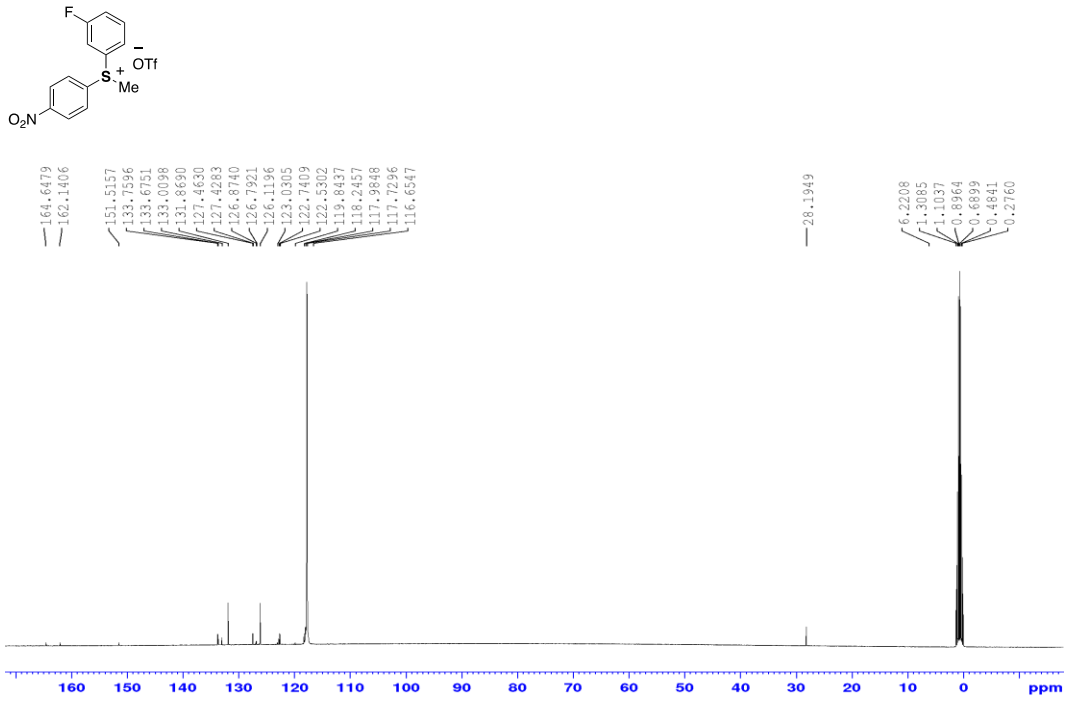
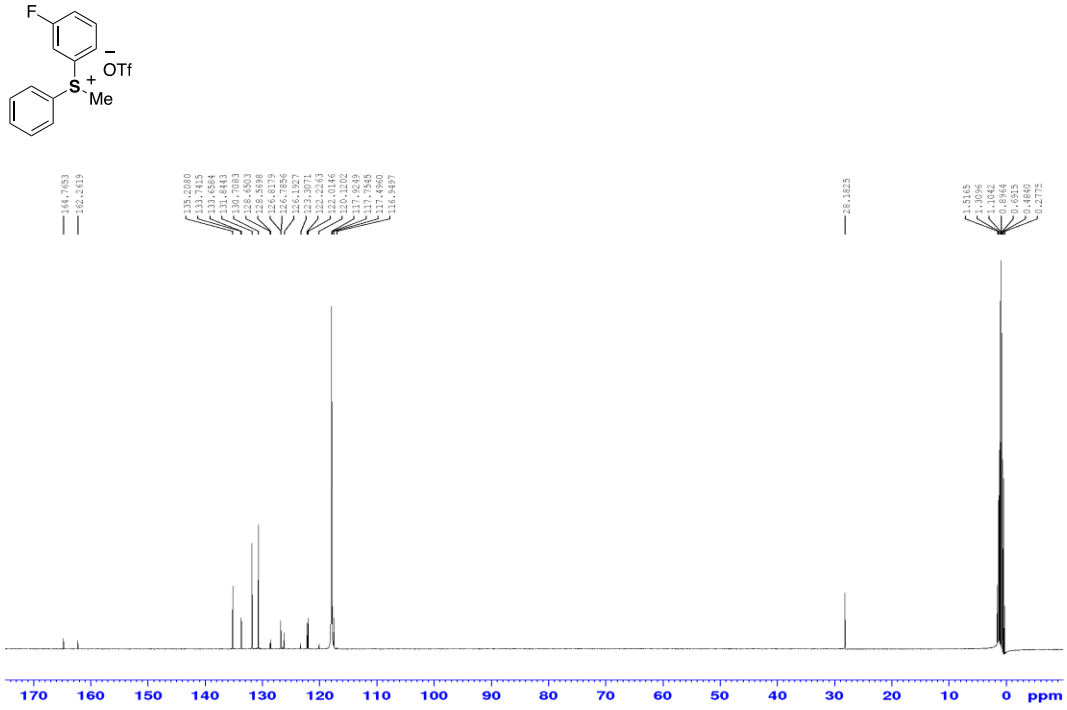
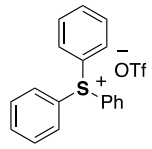
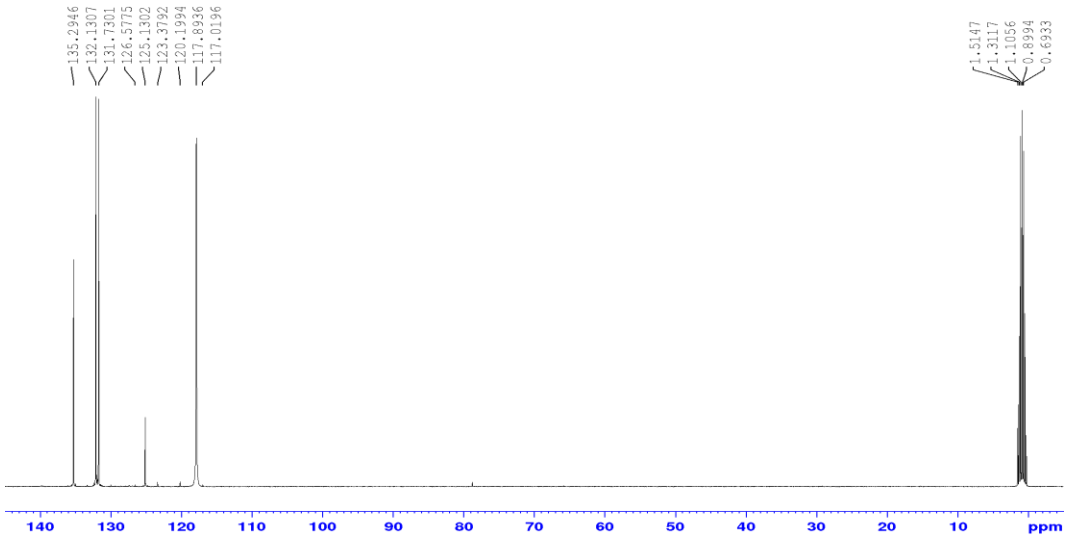
7.686
7.672
7.521
7.500
7.481
7.462
7.432
7.428
7.412
7.392
7.262
3.748
2.604
2.481
1.574
0.000
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.00
1.46
3.18
1.17
3.00
2.93

4.2. CNMR diagrams






OTf
S
+
Ph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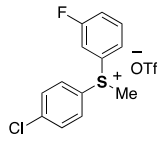
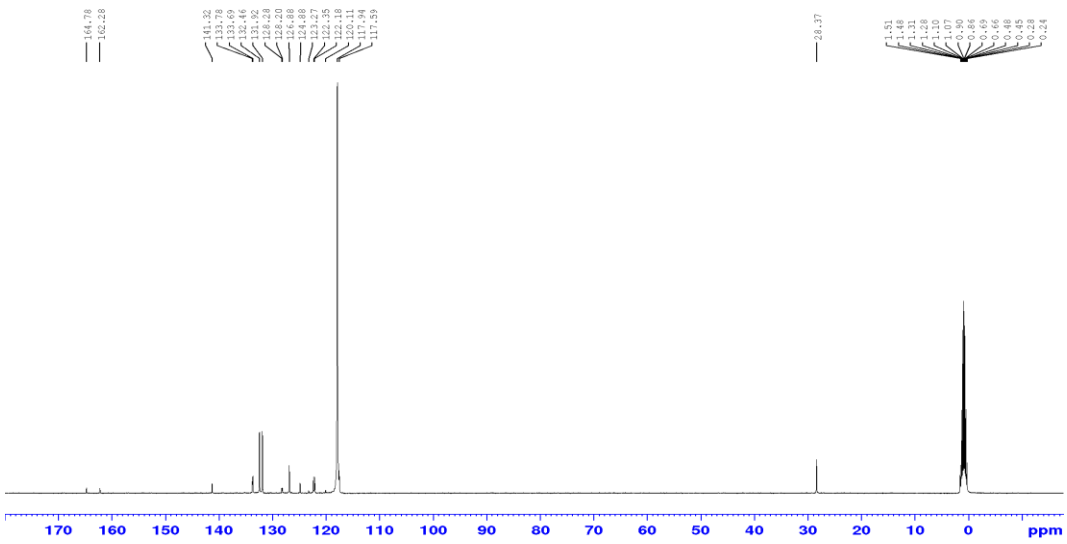
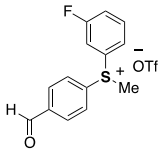
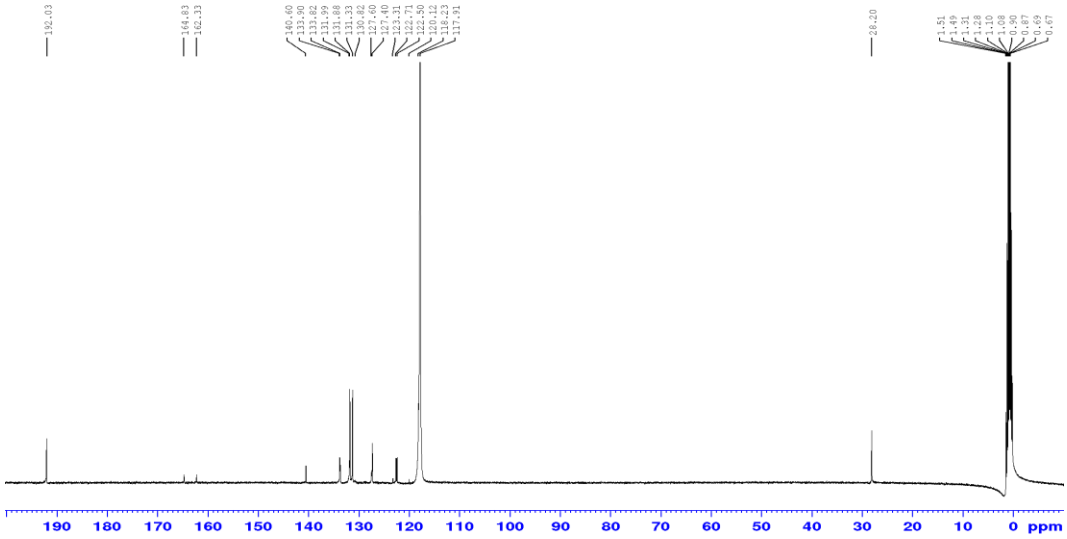
132.1307
131.7301
126.5775
125.1302
123.3792
120.1994
117.8936
117.0196
1.5147
1.3117
1.1056
0.8994
0.6933
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


F
OTf
S
+
Me
Cl


164.78
162.28
141.32
133.78
133.69
132.46
131.92
128.28
126.20
125.88
124.88
123.27
122.35
122.18
120.11
117.94
117.59
28.37
1.51
1.48
1.31
1.28
1.10
1.07
0.90
0.86
0.69
0.66
0.48
0.45
0.28
0.24
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


F
OTf
S
Me
H
O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162.33
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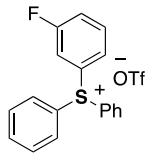
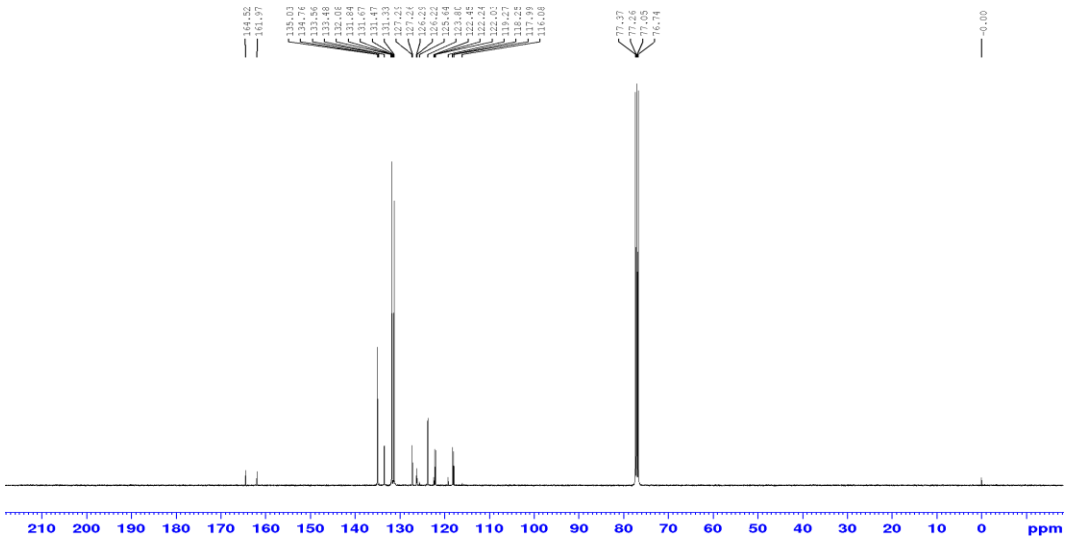
133.82
131.99
131.88
131.33
130.82
127.60
127.40
123.31
122.71
122.50
120.12
119.23
117.91
28.20
1.51
1.49
1.31
1.28
1.10
1.08
0.90
0.87
0.69
0.67
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


F
OTf
S
Ph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134.76
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133.48
132.06
131.64
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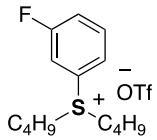
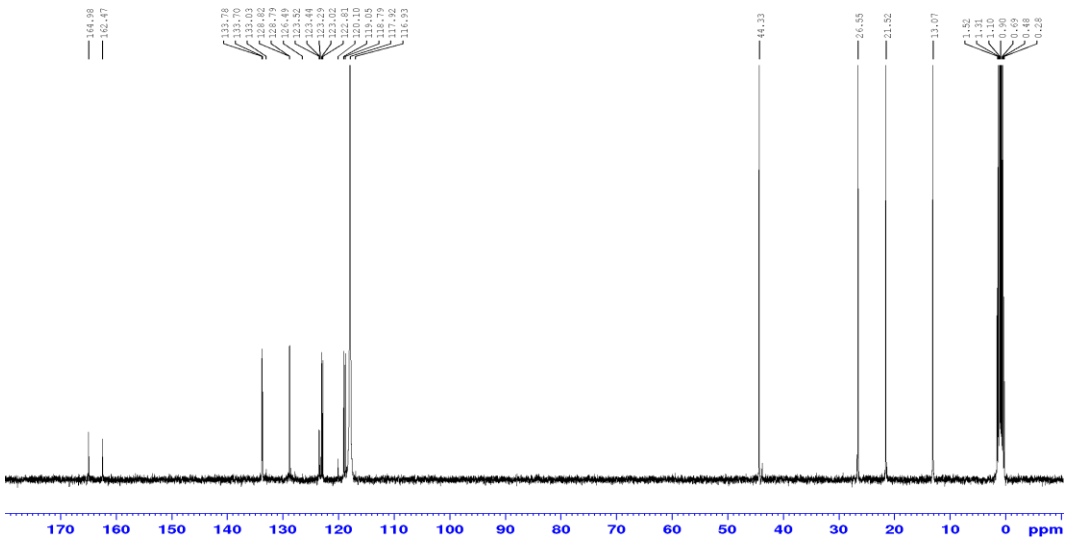
131.47
131.33
127.25
127.24
126.25
126.22
125.94
125.86
122.45
122.24
122.03
119.27
118.25
117.98
114.48
77.37
77.26
77.05
76.74
0.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


F
OTf
S
C4H9
C4H9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126.49
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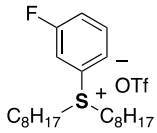
123.44
123.29
123.02
122.81
120.10
119.05
118.79
117.92
116.93
44.33
26.55
21.52
13.07
13.52
13.31
13.15
13.00
0.69
0.48
0.28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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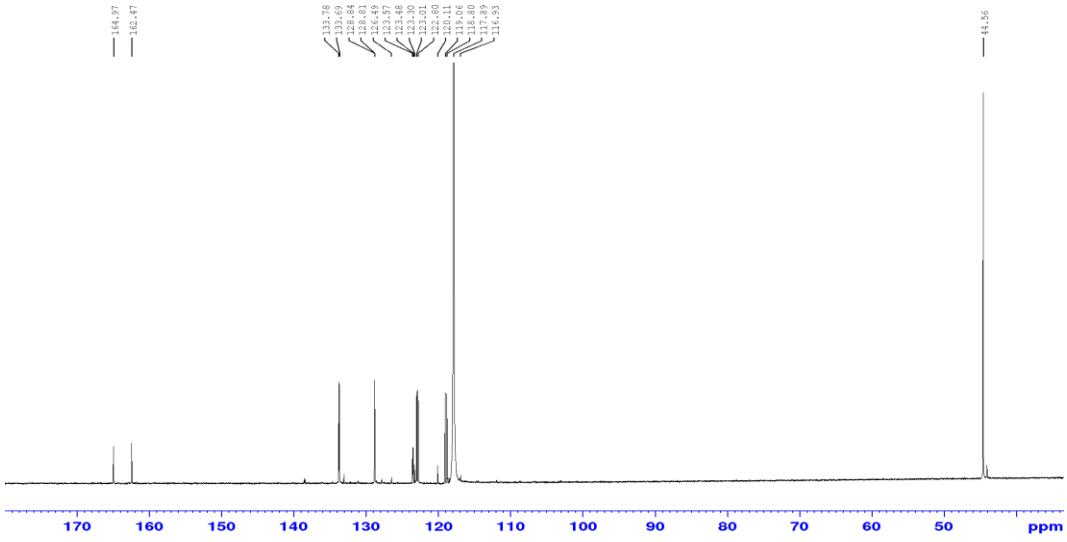
OTf
S
C8H17
C8H17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133.69
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128.81
126.49
123.57
123.48
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120.11
119.06
118.80
117.89
116.93
44.56
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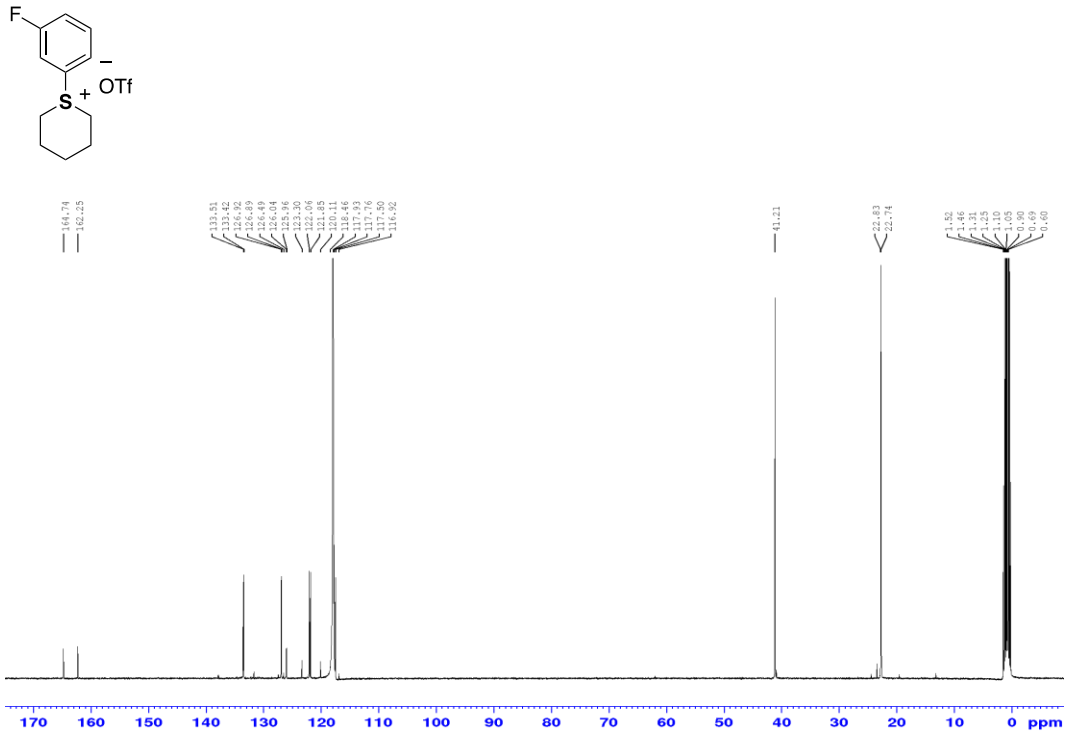
F
OTf
S
164.74
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133.51
133.42
126.92
126.89
126.69
126.04
125.96
123.30
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121.85
121.11
118.46
117.93
117.76
117.50
116.92
41.21
22.83
22.74
1.52
1.46
1.31
1.25
1.10
1.05
0.90
0.69
0.60
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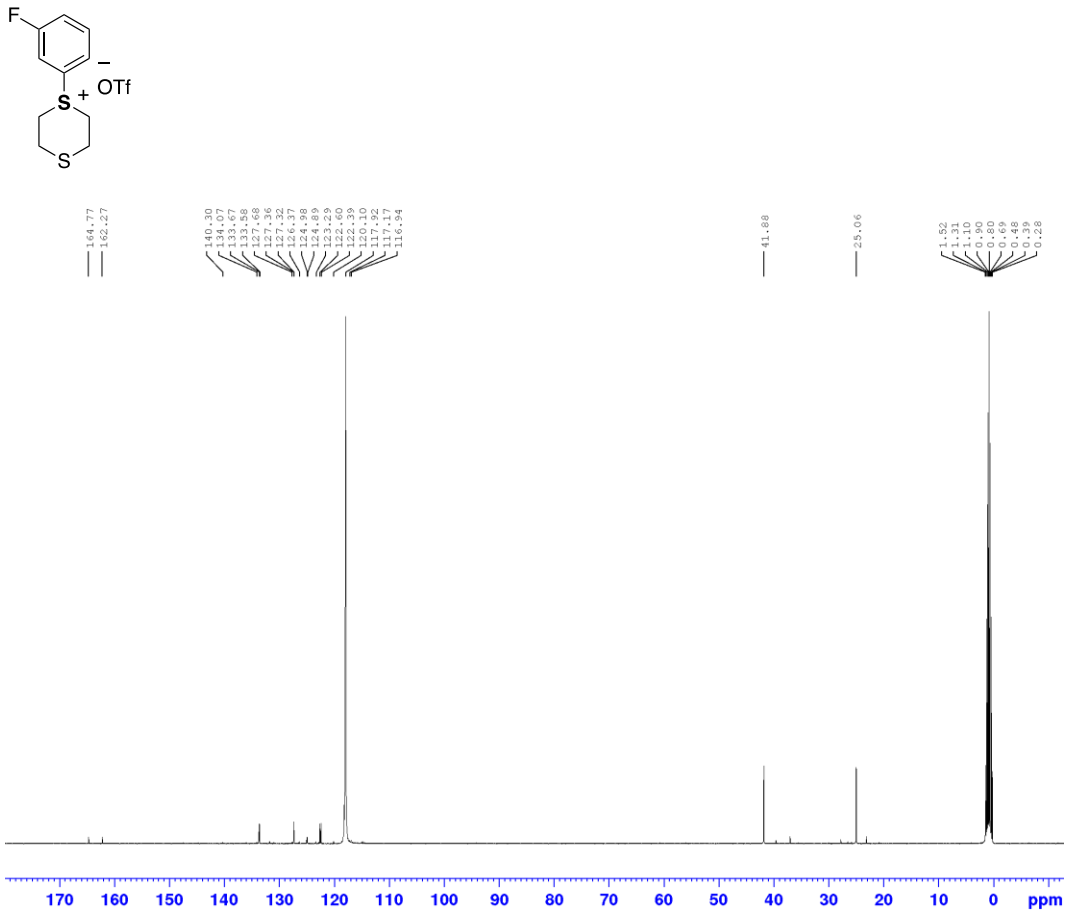
F
OTf
S
S
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140.30
134.07
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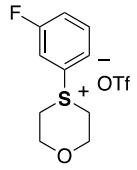
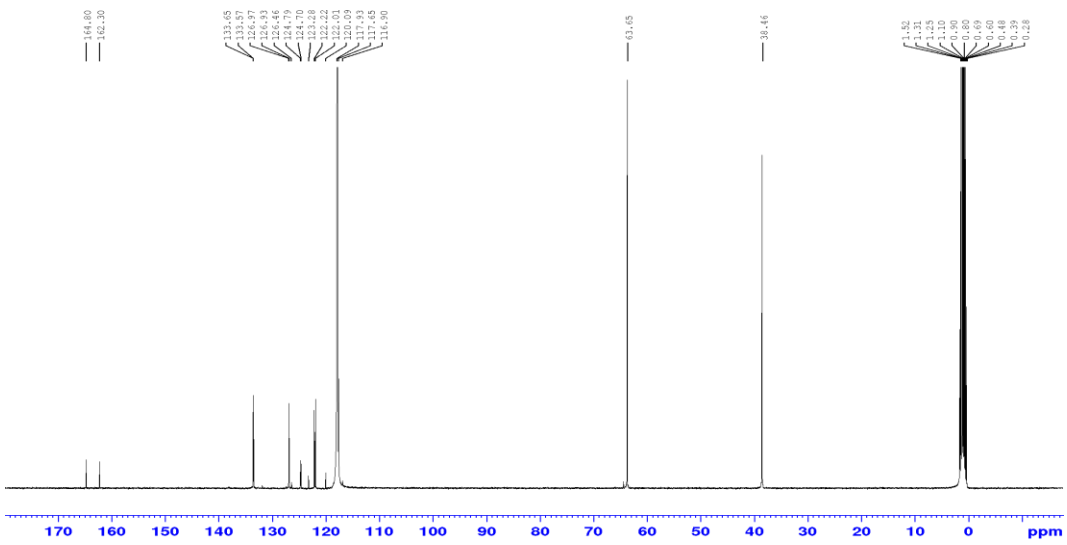
133.58
127.68
127.36
127.32
126.37
124.88
124.89
123.29
122.60
122.39
120.10
117.82
117.17
116.94
41.88
25.06
1.52
1.31
1.10
0.90
0.80
0.69
0.48
0.39
0.28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


F
OTf
S
O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126.93
126.46
124.79
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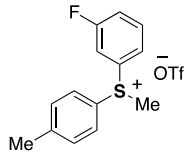
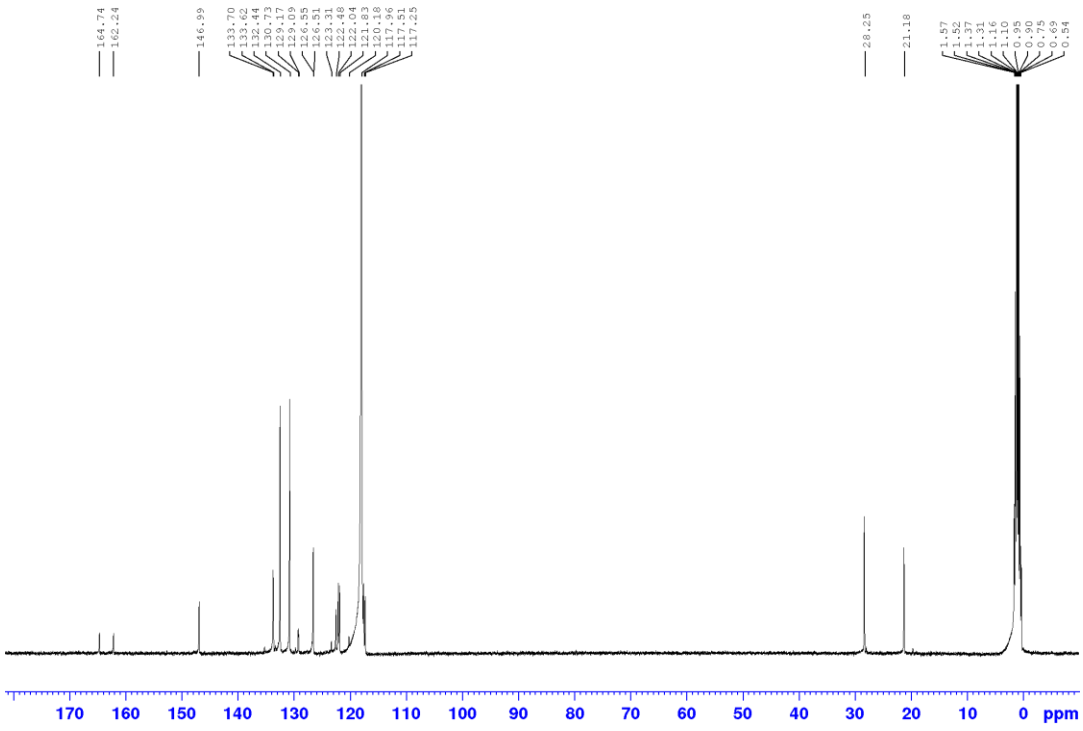
123.28
122.22
122.01
120.09
117.83
117.65
116.90
63.65
38.46
1.52
1.31
1.25
1.10
0.90
0.80
0.69
0.60
0.48
0.39
0.28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


F
OTf
S
Me
Me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129.17
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126.51
123.31
122.48
122.04
121.83
120.18
117.96
117.51
117.25
28.25
21.18
1.57
1.52
1.37
1.31
1.16
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0.95
0.90
0.75
0.69
0.54
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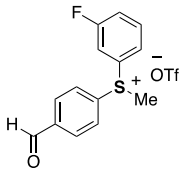
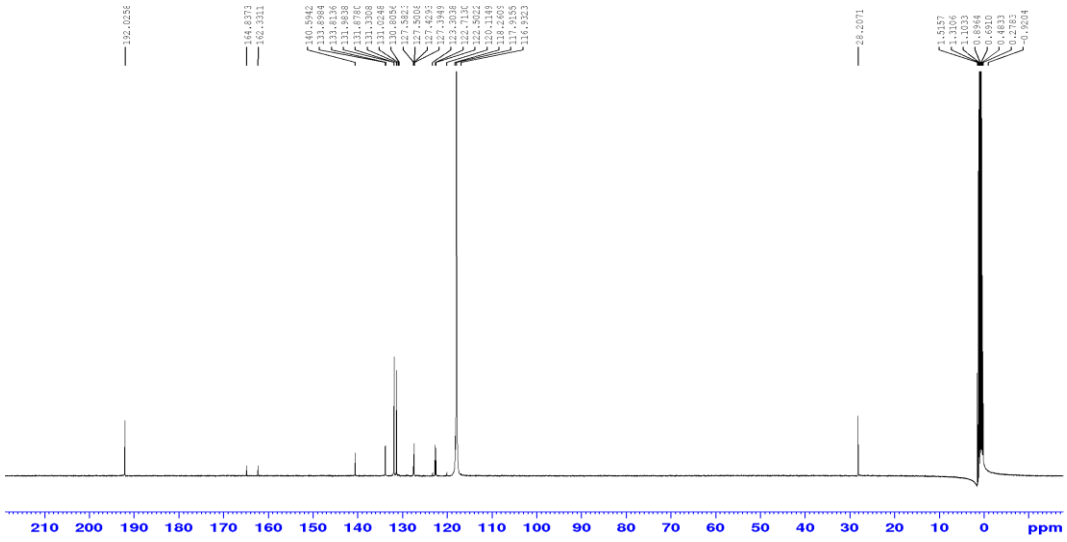

F
OTf
S
Me
H
O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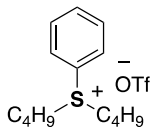
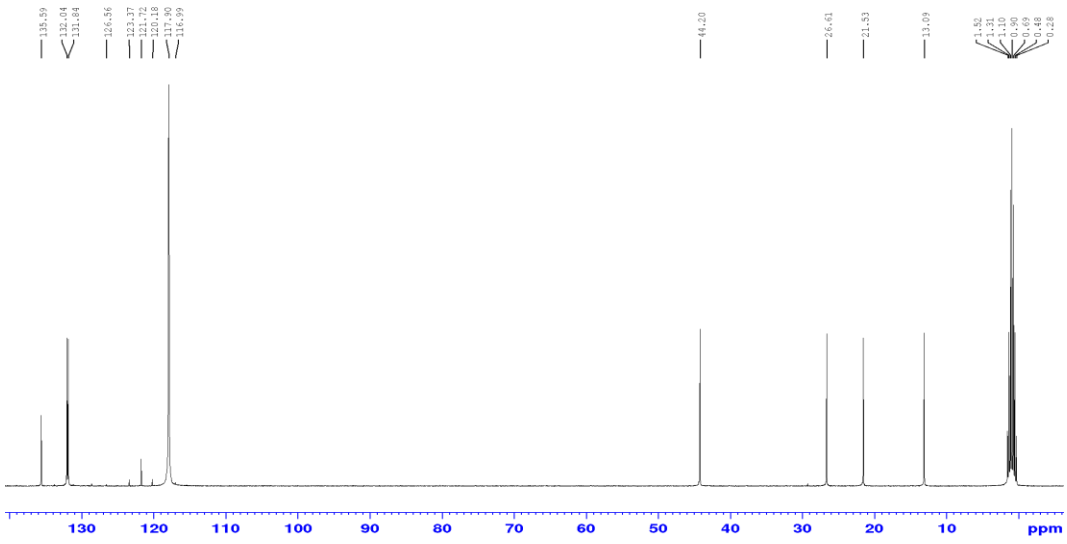

OTf
S
C4H9
C4H9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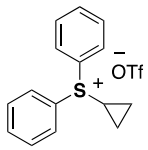
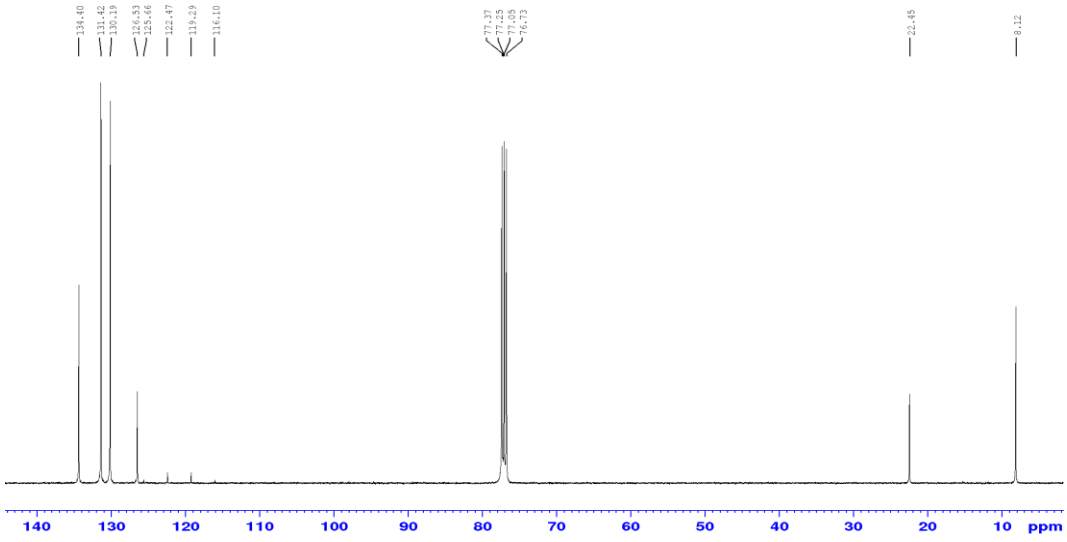

OTf
S
+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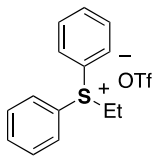
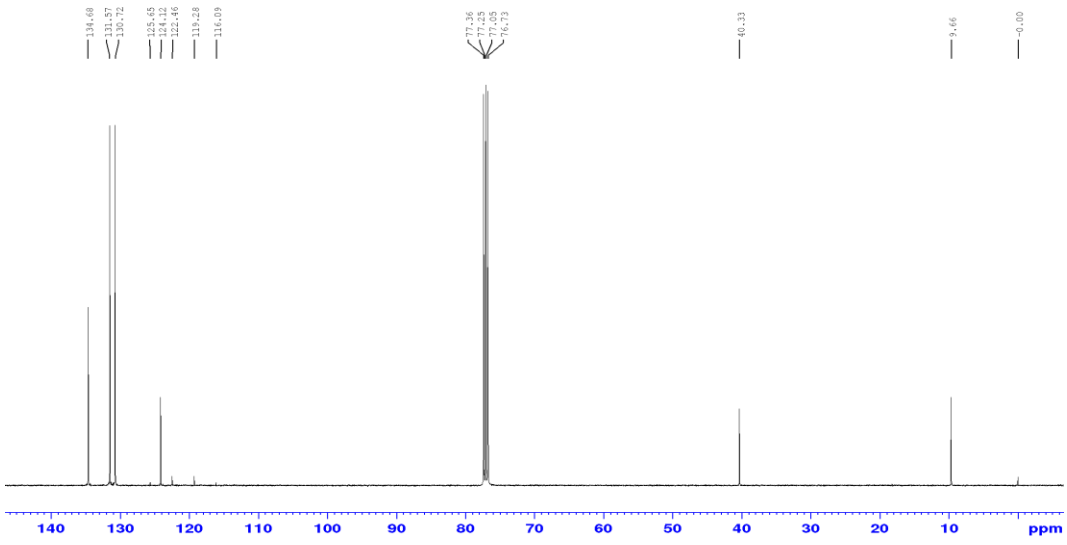
126.53
125.66
122.47
119.29
116.10
77.37
77.25
77.05
76.73
22.45
8.12
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OTf
S
+
Et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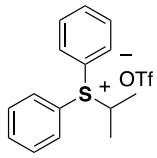
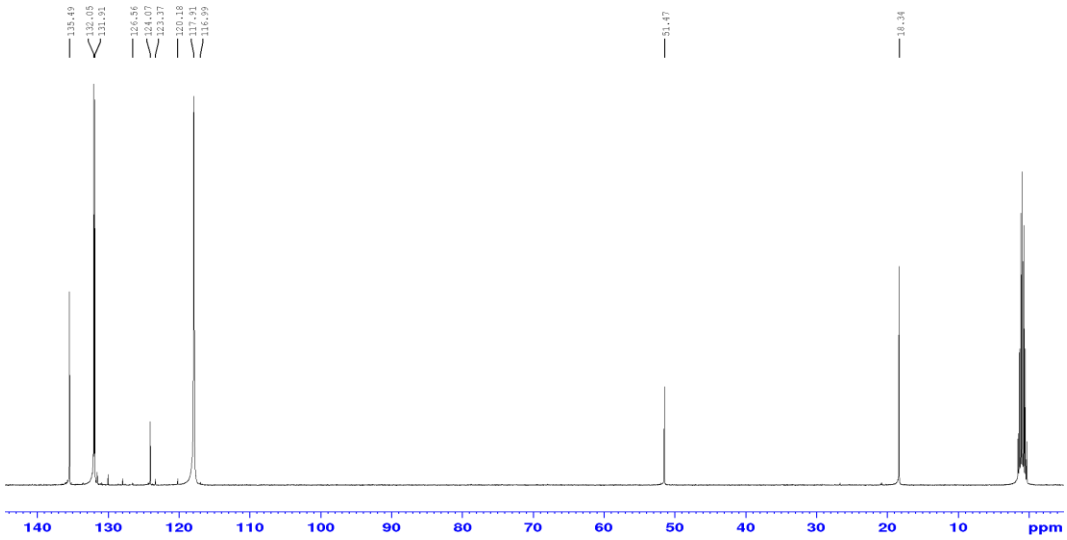
131.57
130.72
125.65
124.12
122.46
119.28
116.09
77.36
77.25
77.05
76.73
40.33
9.66
-0.00
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


S
+
OTf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120.18
117.91
116.99
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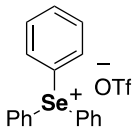
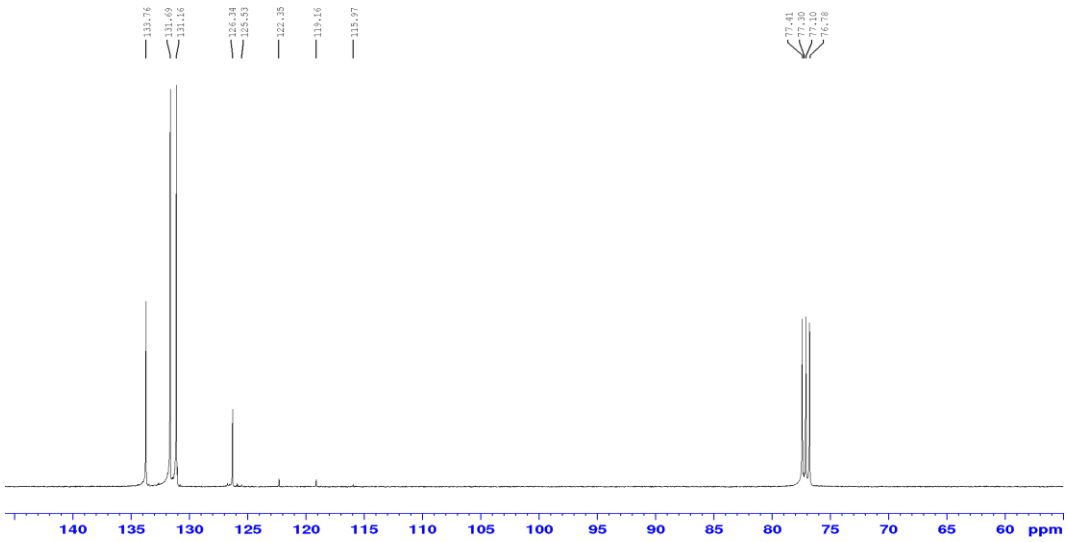
18.34
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Se
+
OTf
Ph
Ph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115.97
77.41
77.30
77.10
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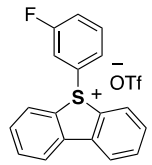
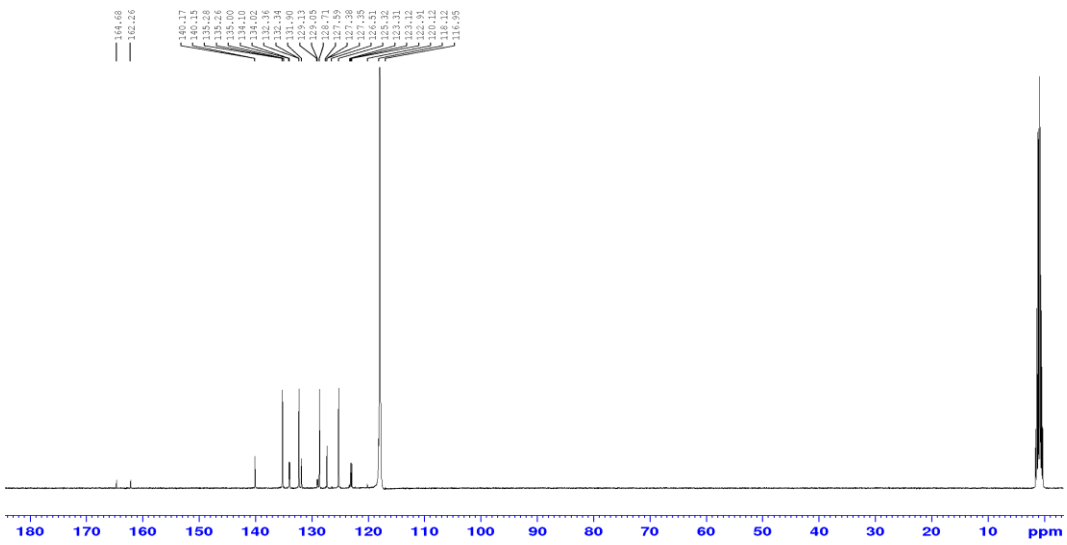
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
ppm


F
OTf
S +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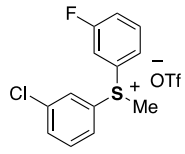
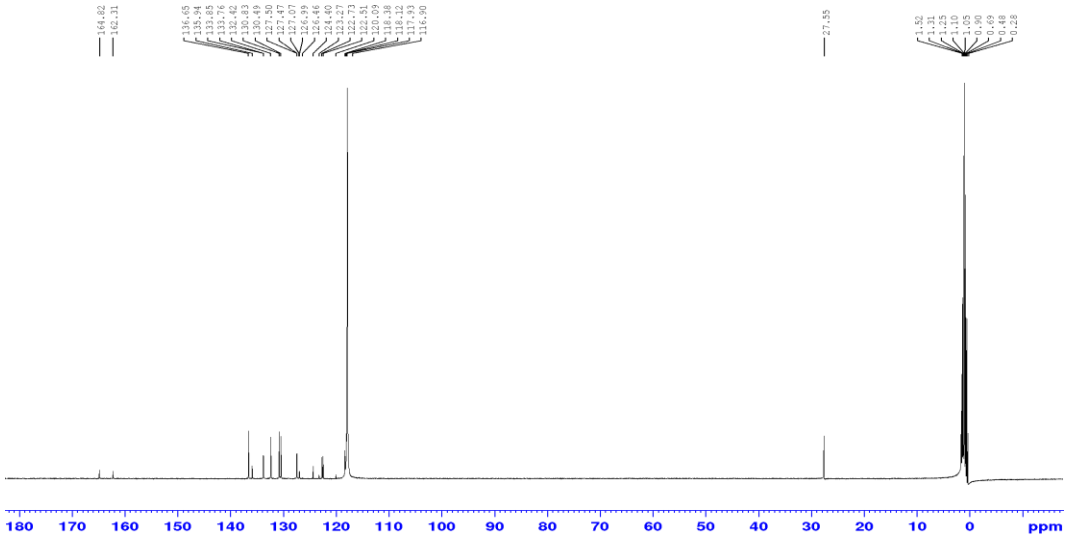

F
Cl
S +
Me
OTf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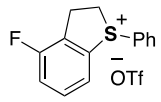
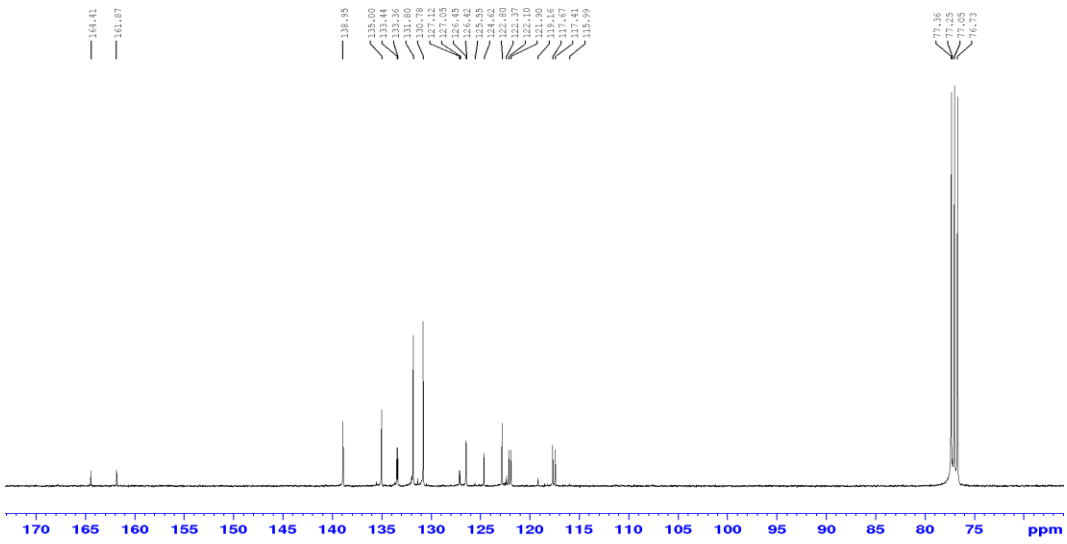

F
S
+
Ph
−
OTf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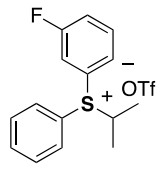
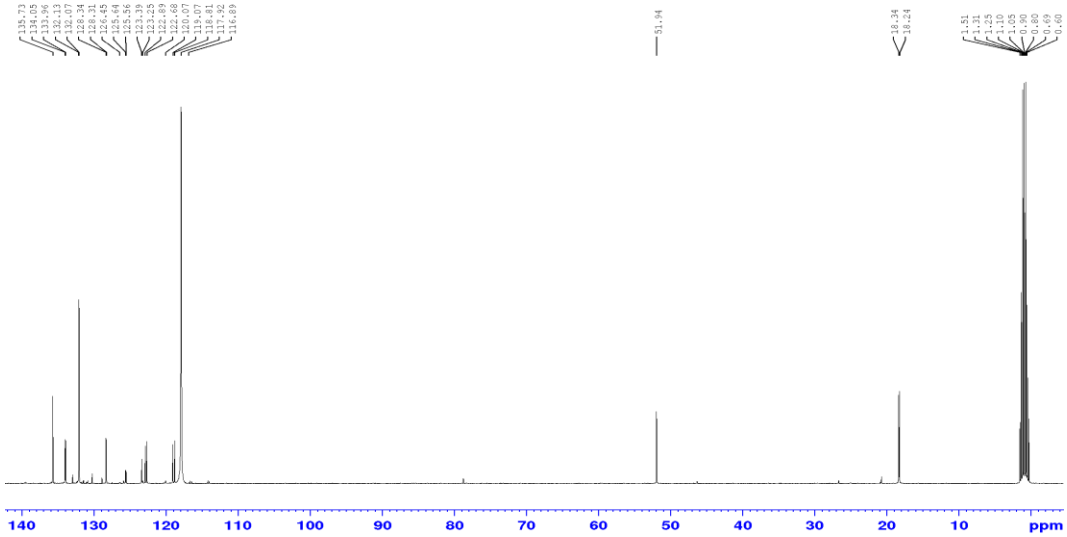
127.10
126.45
126.42
125.55
124.62
122.80
122.37
122.10
121.90
119.16
117.67
117.41
115.99
77.36
77.25
77.05
76.73
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 ppm


F
−
OTf
S
+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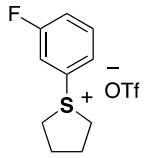
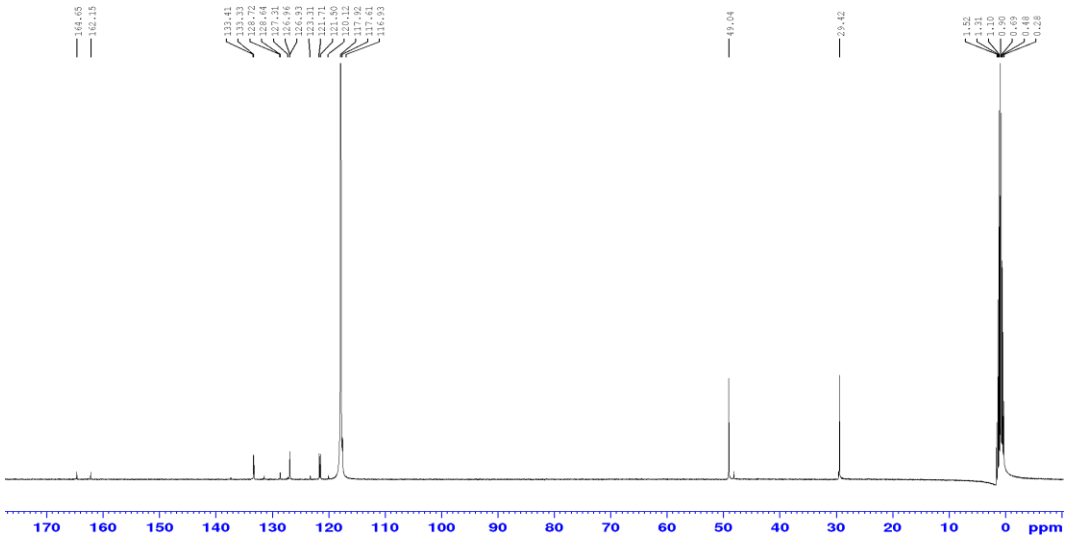
125.56
123.39
123.35
122.69
122.68
120.07
119.07
118.81
118.80
116.89
51.94
18.34
16.24
1.51
1.31
1.25
1.10
1.05
0.90
0.80
0.69
0.60
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


F
S
+
OTf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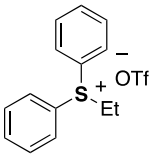
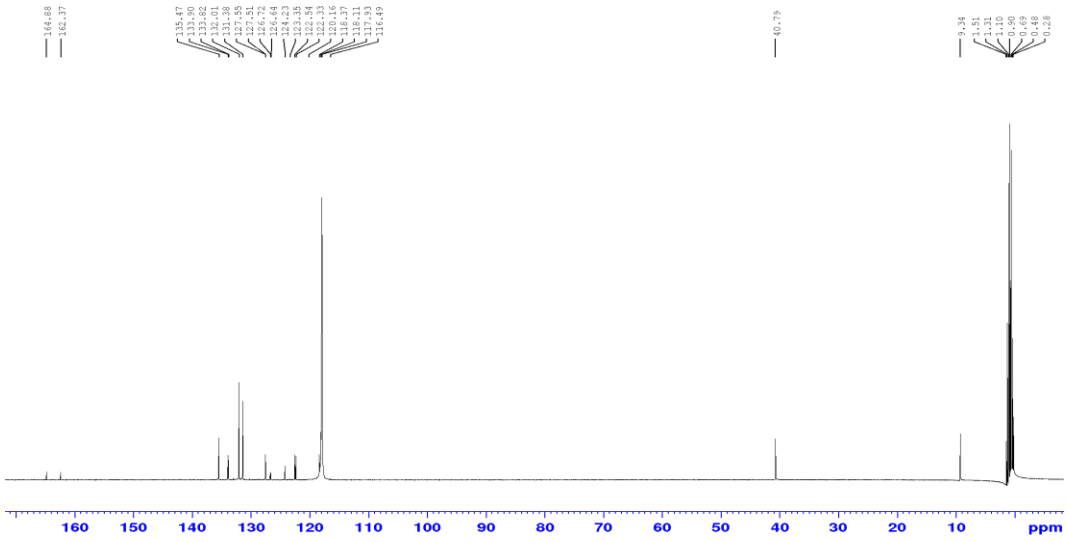
123.31
121.71
121.50
120.32
117.92
117.61
116.93
49.04
29.42
1.52
1.31
1.10
0.90
0.69
0.48
0.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


S
+
OTf
Et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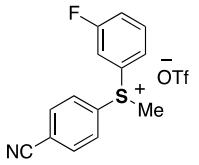
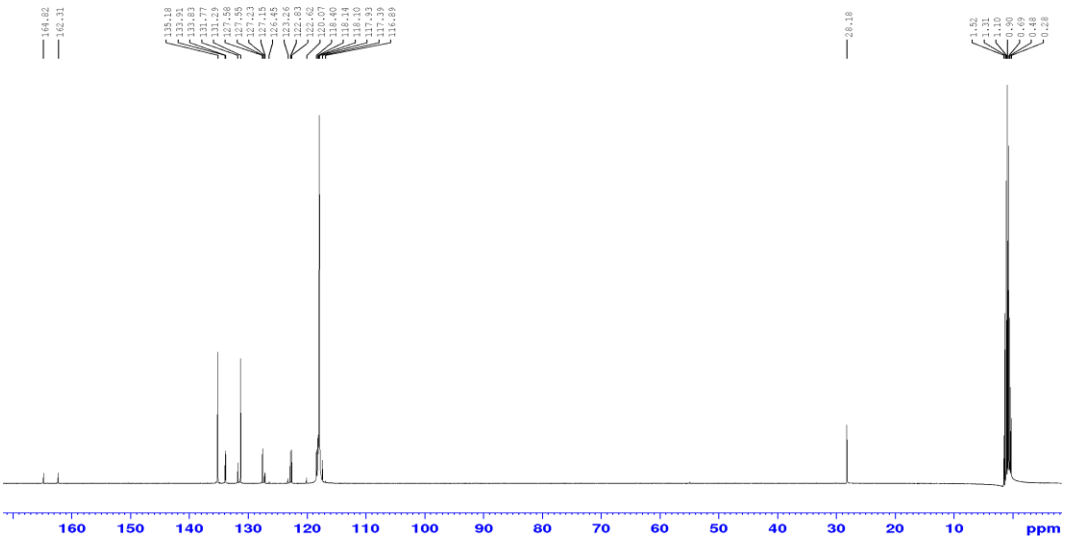
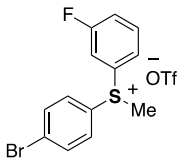
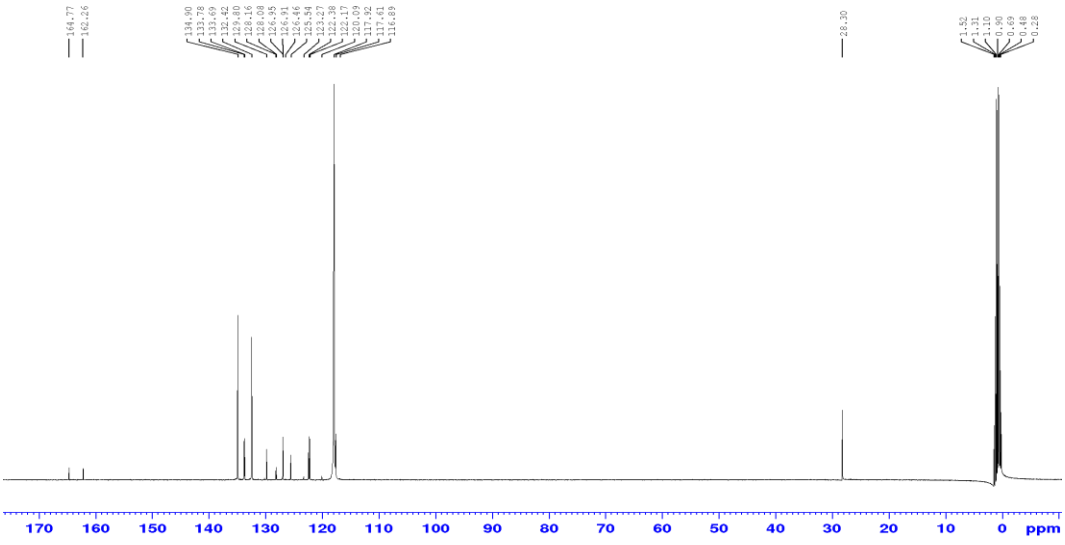
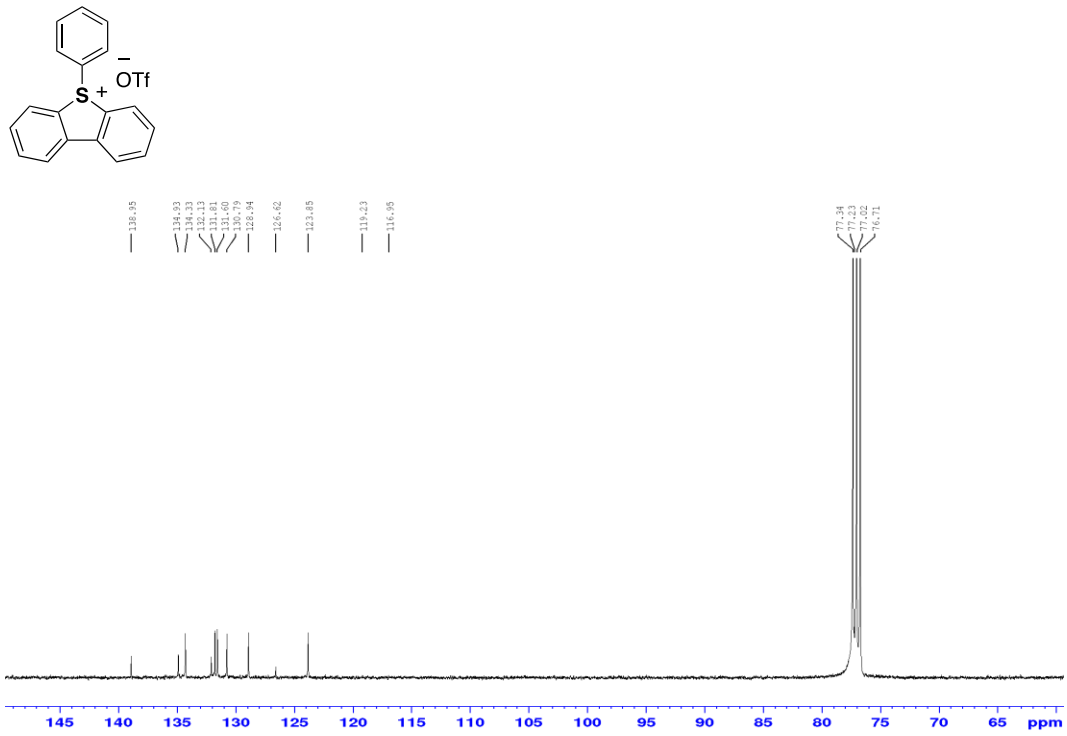
126.64
124.23
123.35
122.54
122.33
120.16
118.37
118.11
117.93
116.49
40.79
9.34
1.51
1.31
1.10
0.90
0.69
0.48
0.28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

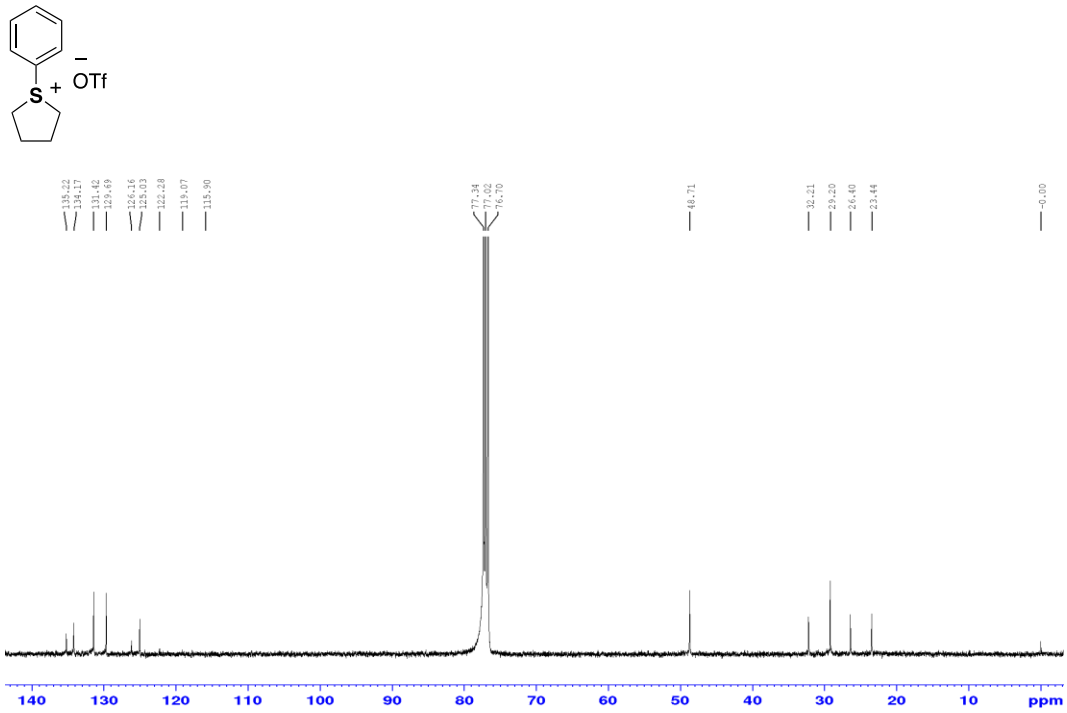

F
OTf
S
+
Me
NC

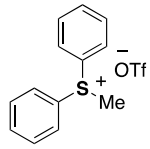

164.82
162.31
135.18
133.91
133.83
131.77
131.29
127.58
127.55
127.23
127.15
126.45
123.26
122.83
122.62
120.07
118.40
118.34
118.10
117.93
117.39
116.89
28.18
1.52
1.31
1.10
0.90
0.69
0.48
0.28
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

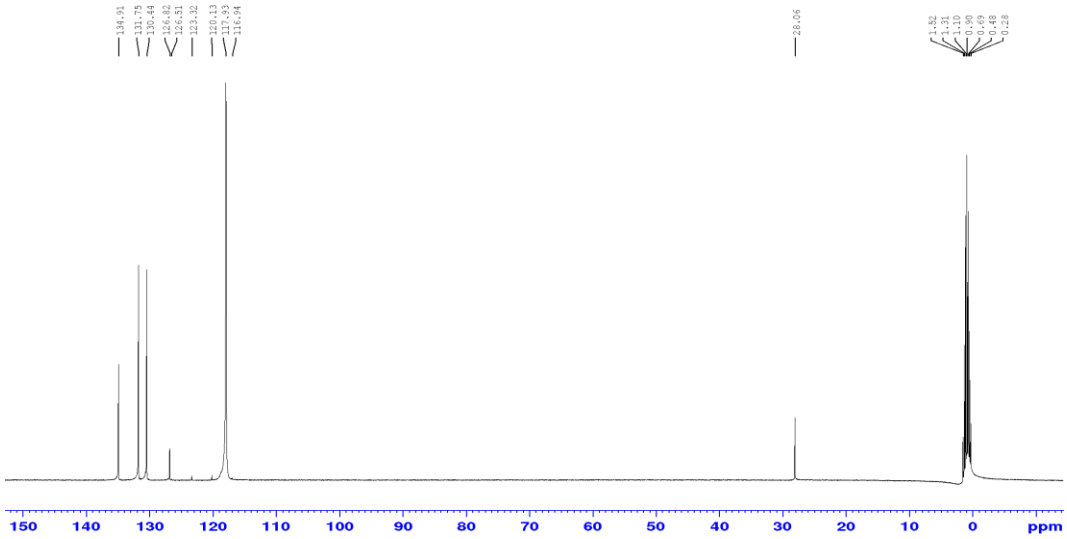

F
OTf
S
+
Me
Br

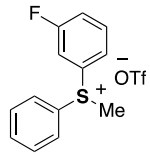

164.77
162.26
134.90
133.78
133.69
132.42
129.80
128.16
128.08
126.95
126.91
126.46
125.54
123.27
122.38
121.17
120.09
117.92
117.61
116.89
28.30
1.52
1.31
1.10
0.90
0.69
0.48
0.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

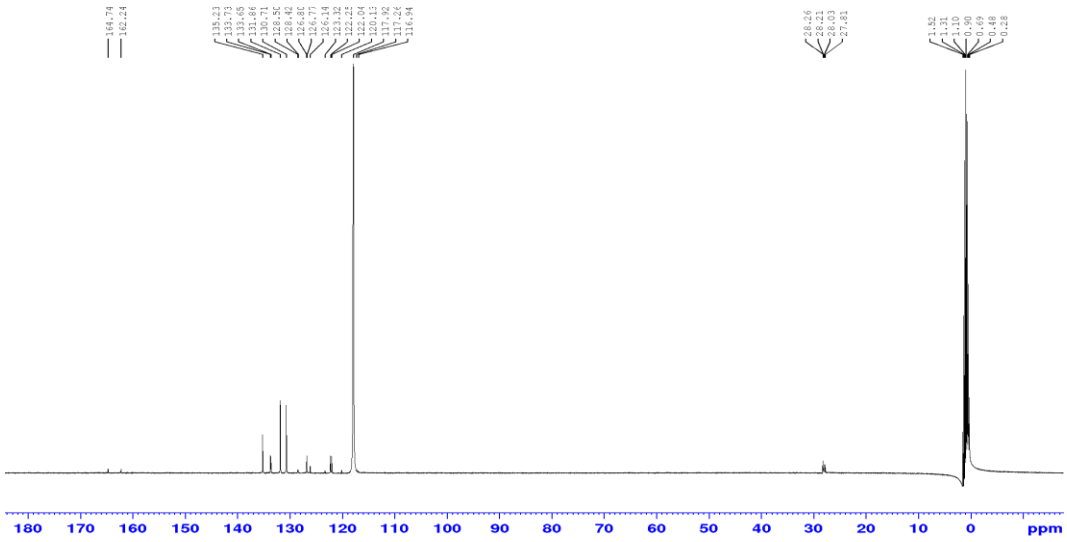

OTf
S
+
138.95
134.93
134.33
132.13
131.81
131.60
130.79
128.94
126.62
123.85
119.23
116.95
77.34
77.13
77.02
76.71
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
ppm

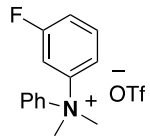

OTf
S
+
135.22
134.17
131.42
129.69
126.16
125.03
122.28
119.07
115.90
77.34
77.02
76.70
48.71
32.21
29.20
26.40
23.44
0.00
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

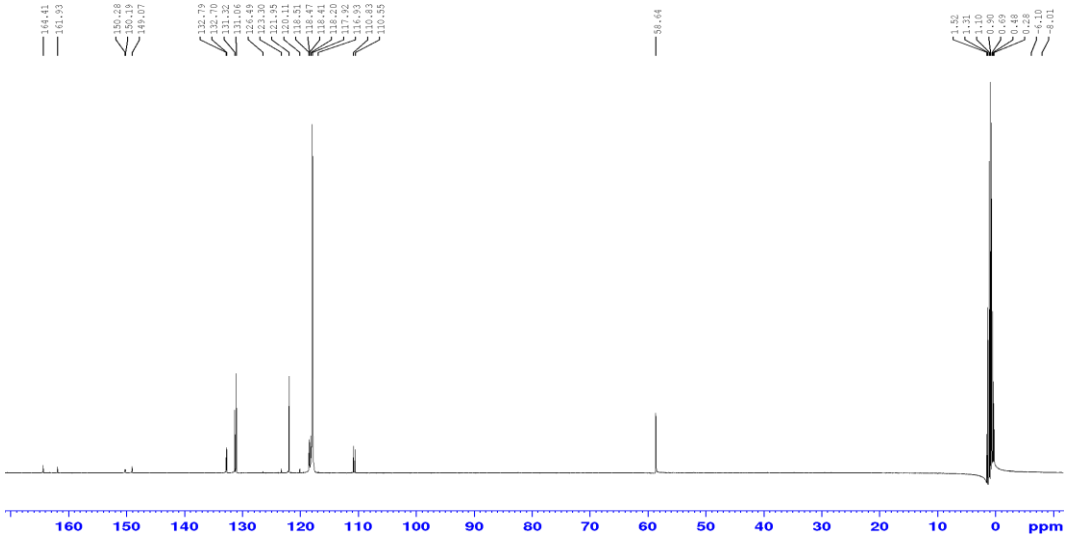

OTf
S
+
Me


134.91
131.75
130.44
126.82
126.51
123.32
120.13
117.93
116.94
28.06
1.52
1.31
1.10
0.90
0.69
0.48
0.28
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

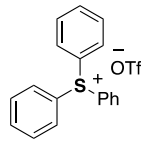

F
OTf
S
+
Me

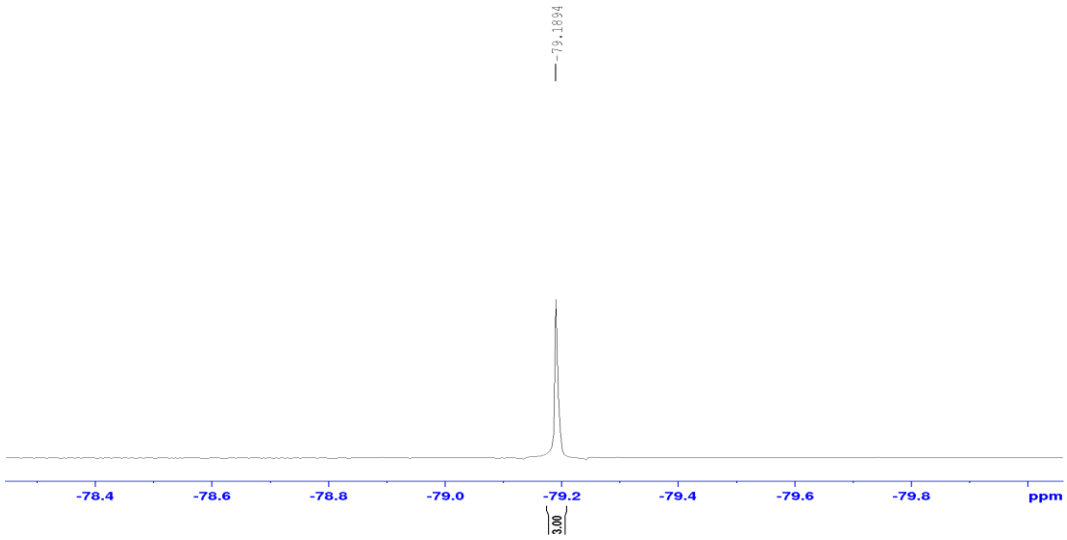

164.74
162.24
135.23
133.73
133.65
131.86
130.71
128.55
128.42
126.86
126.77
126.14
123.32
122.22
120.04
120.01
117.92
117.26
116.94
28.26
28.21
28.03
27.81
1.52
1.31
1.10
0.90
0.69
0.48
0.28
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

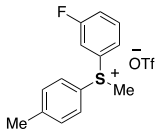


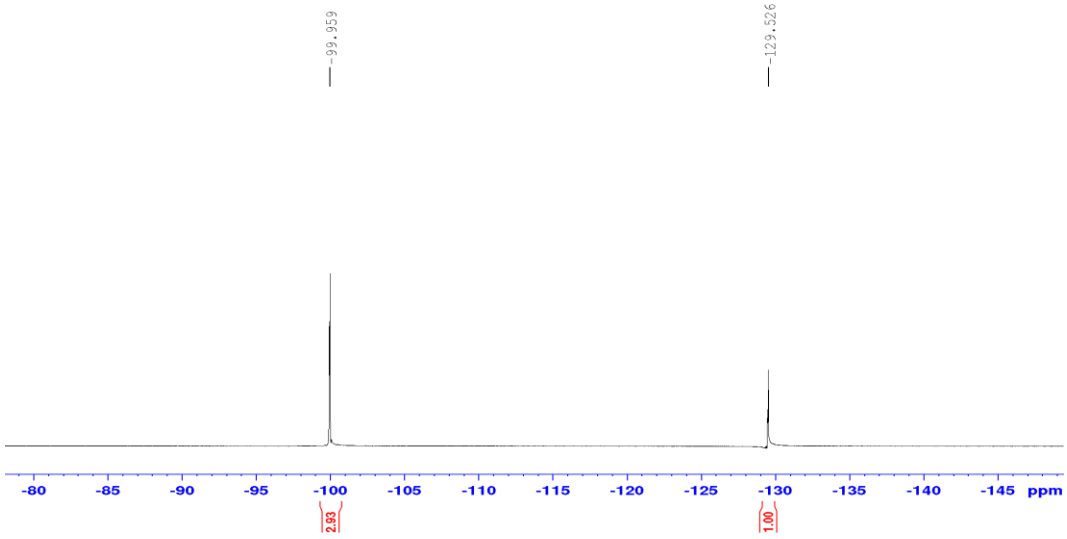


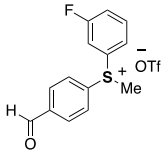
4.3. FNMR Spectra

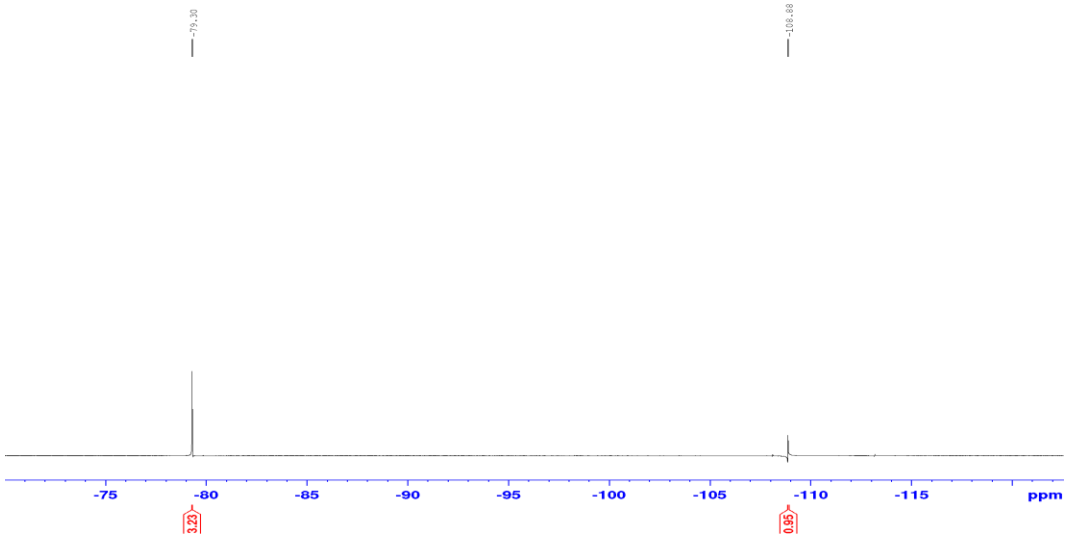


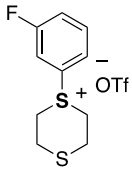


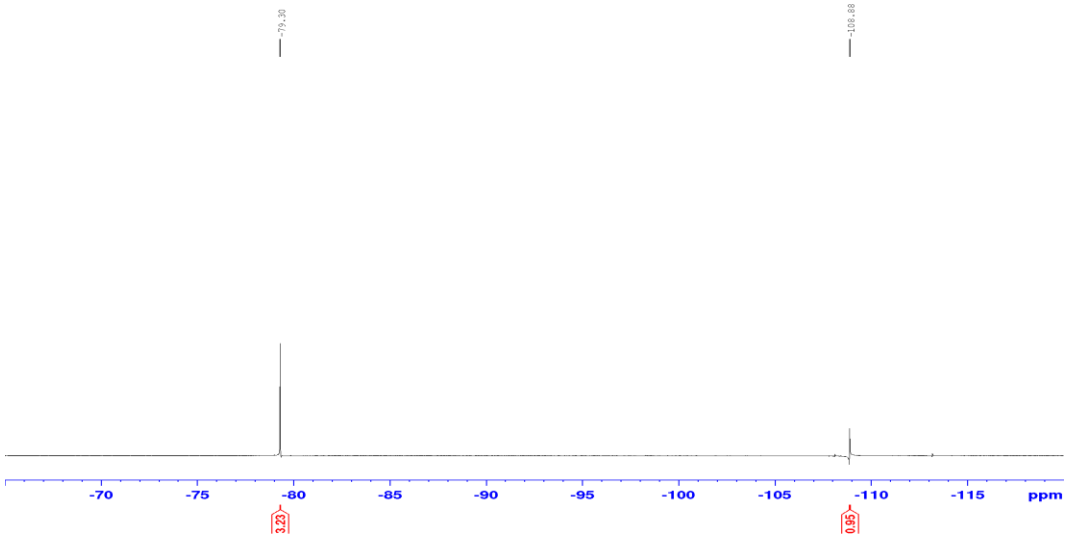

F
OTf
S
Me
Me

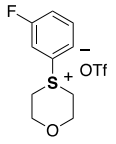

-99.959
-129.526
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
ppm
2.00
1.00

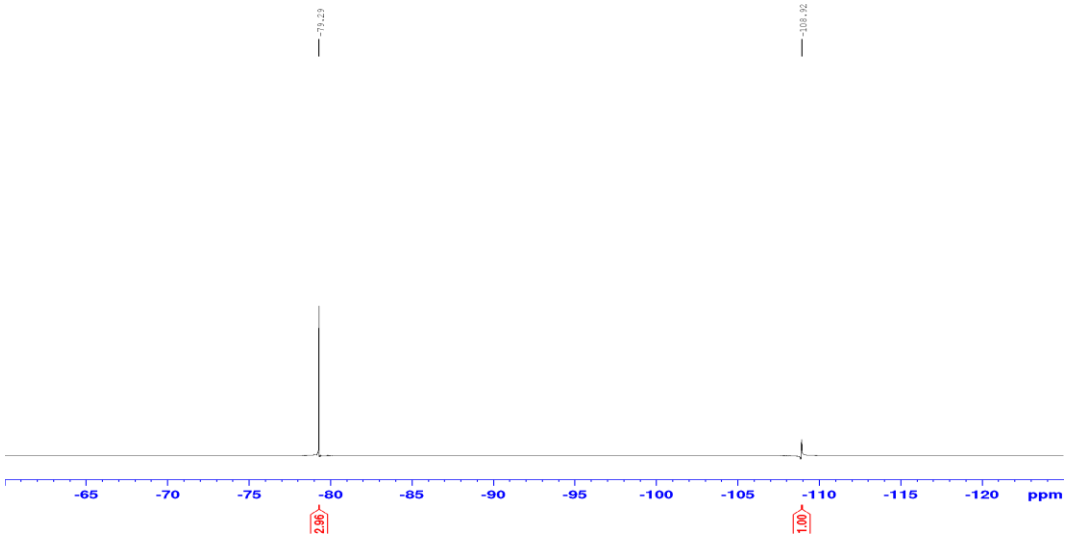

F
OTf
S
Me
H
O

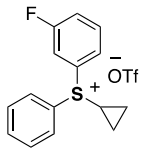

-79.30
-108.88
-75
-80
-85
-90
-95
-100
-105
-110
-115
ppm
3.23
0.85

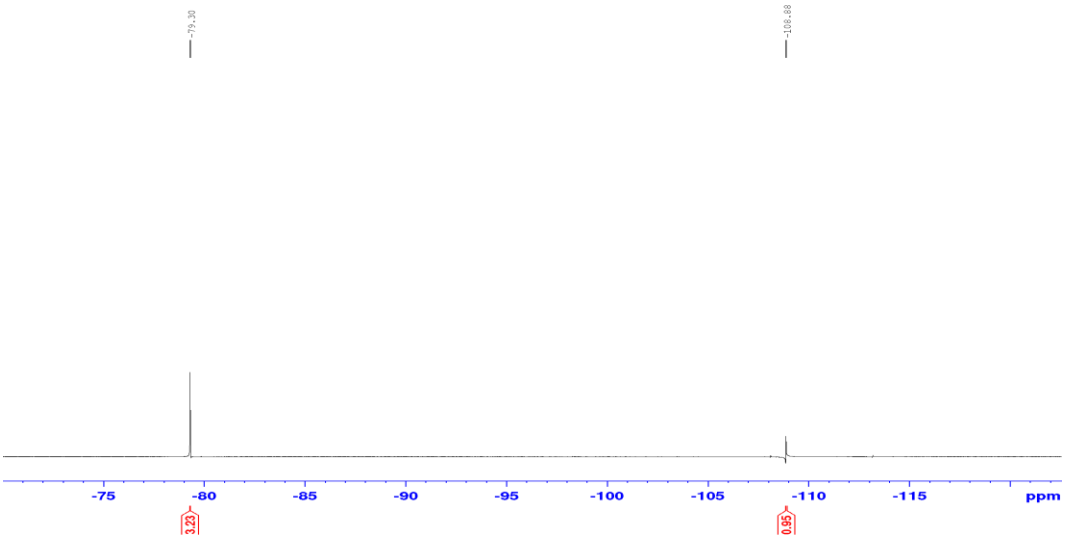

F
OTf
S
S

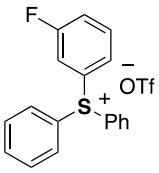

-79.30
-108.88
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
ppm
3.23
0.95

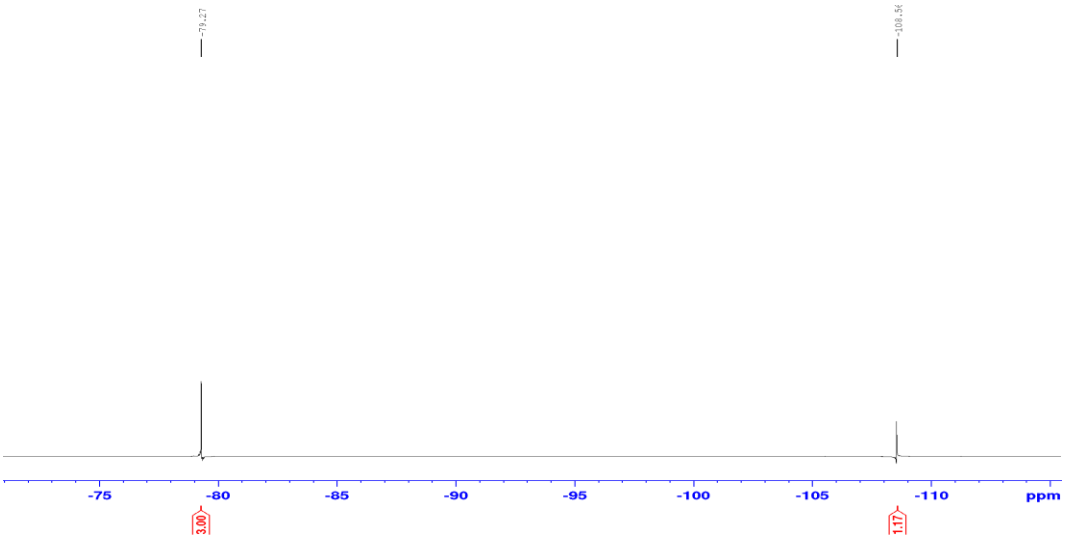

F
OTf
S
O


-79.29
-108.92
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
ppm
2.96
1.00


F
OTf
S
+


-79.30
-108.88
-75
-80
-85
-90
-95
-100
-105
-110
-115
ppm
3.23
0.95


F
OTf
S
+
Ph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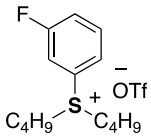
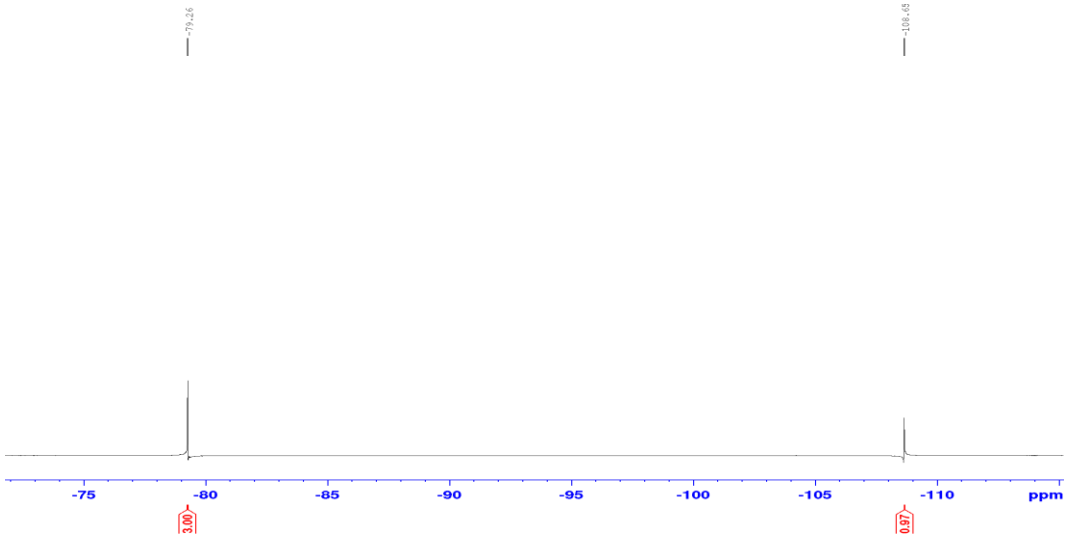
-108.54
-75
-80
-85
-90
-95
-100
-105
-110
ppm
3.00
1.17


F
OTf
S
+
C4H9
C4H9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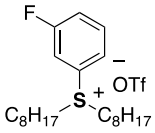
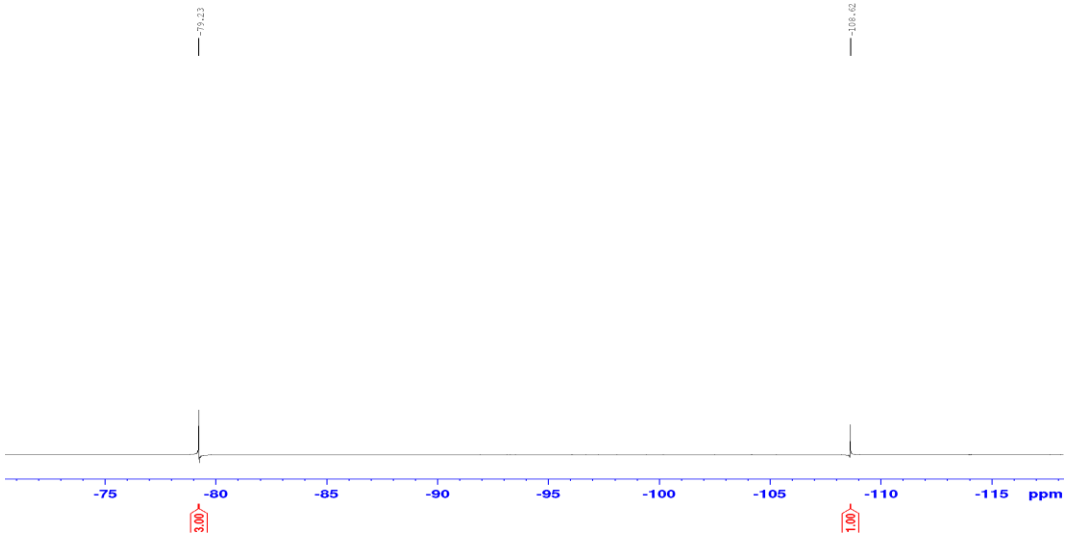
-106.45
-75
-80
-85
-90
-95
-100
-105
-110
ppm
3.00
0.97


F
OTf
S
+
C8H17
C8H17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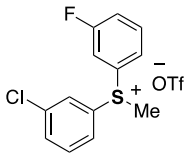
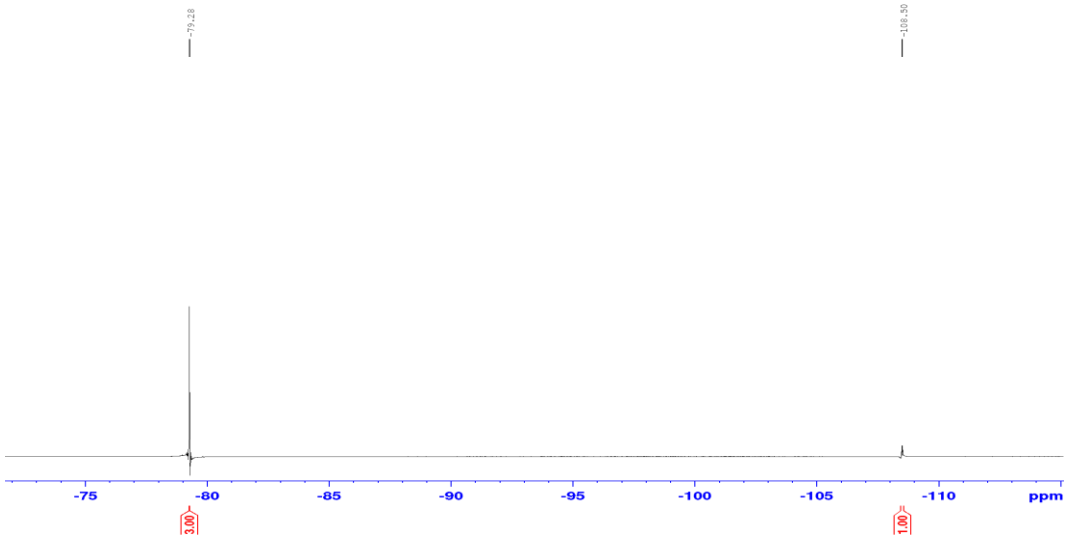
-75
-80
-85
-90
-95
-100
-105
-110
-115
ppm
3.00
1.00


F
Cl
S
+
Me
OTf
−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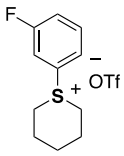
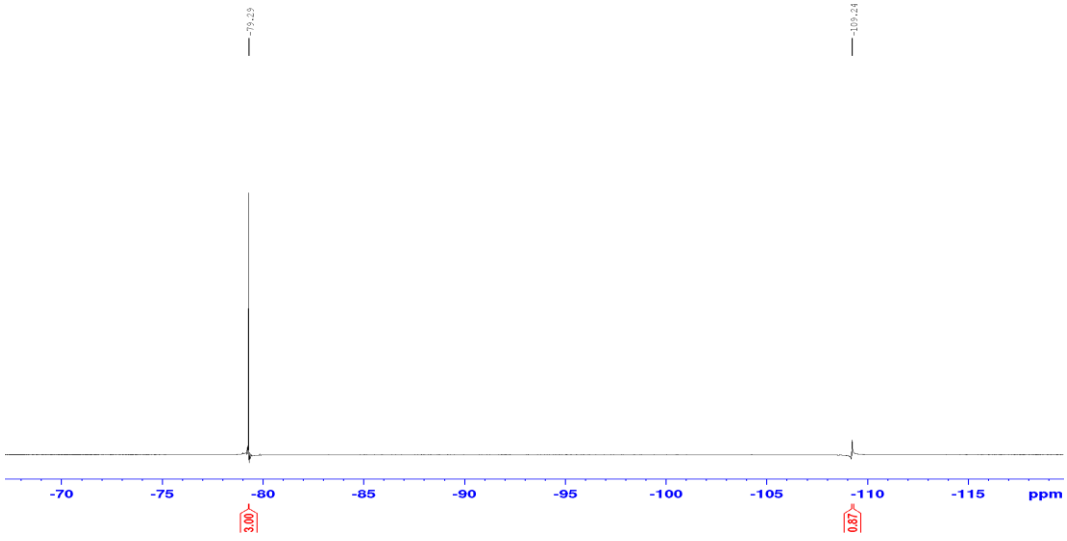
-90
-95
-100
-105
-110
ppm
3.00
1.00


F
S
+
OTf
−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-80
-85
-90
-95
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-105
-110
-115
ppm
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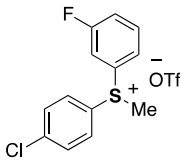
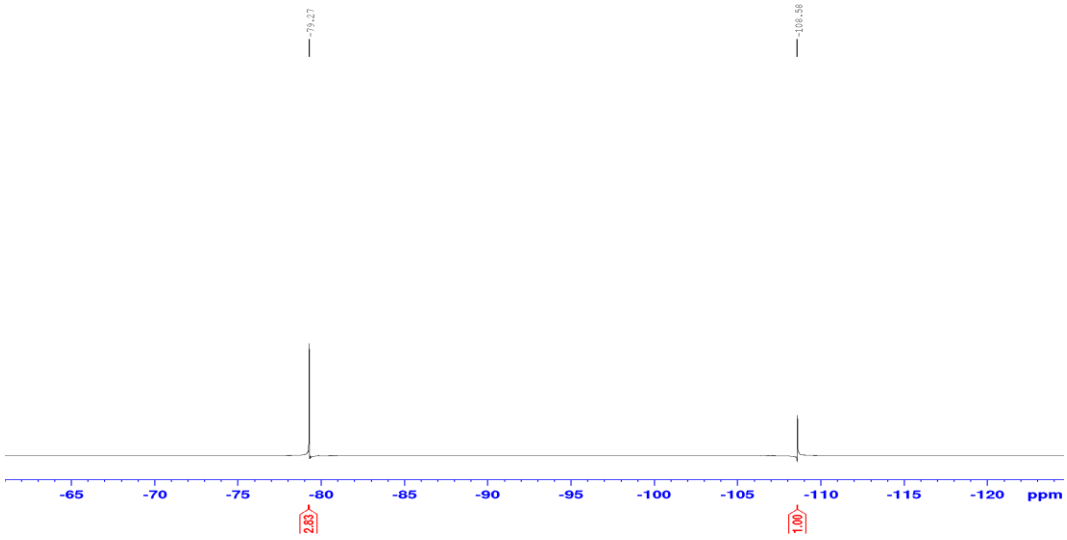
0.87


F
OTf
S
Me
Cl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-80
-85
-90
-95
-100
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-110
-115
-120
ppm
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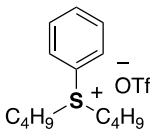
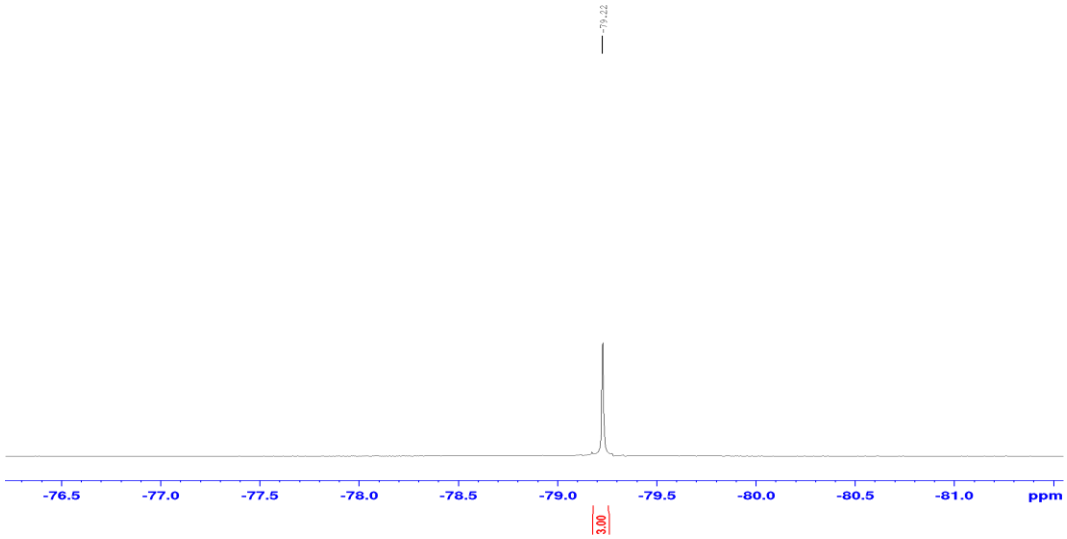
1.00


OTf
S
C4H9
C4H9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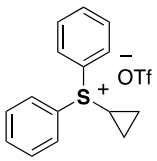
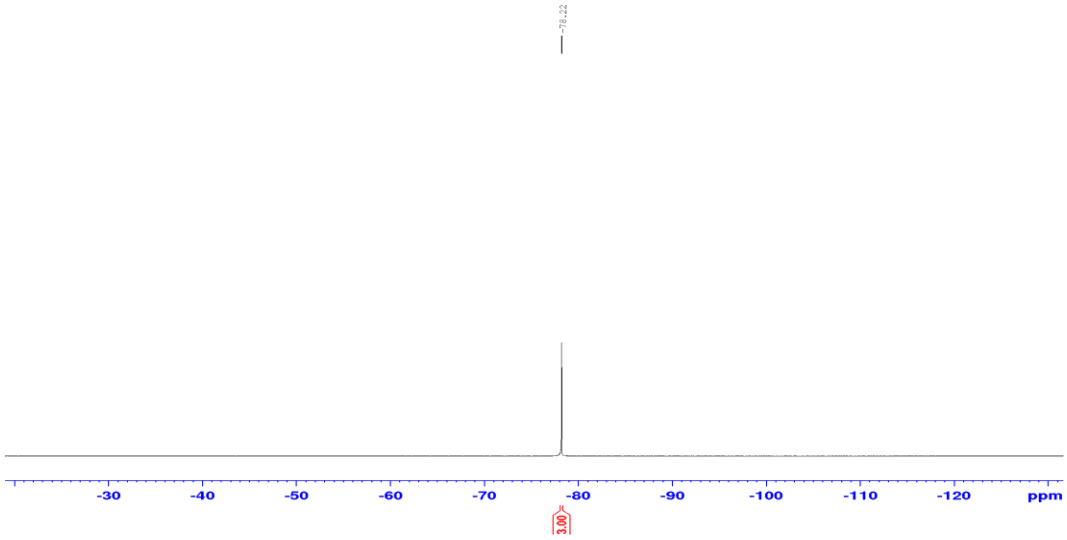
-76.5
-77.0
-77.5
-78.0
-78.5
-79.0
-79.5
-80.0
-80.5
-81.0
ppm
3.00


OTf
S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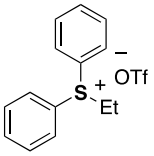
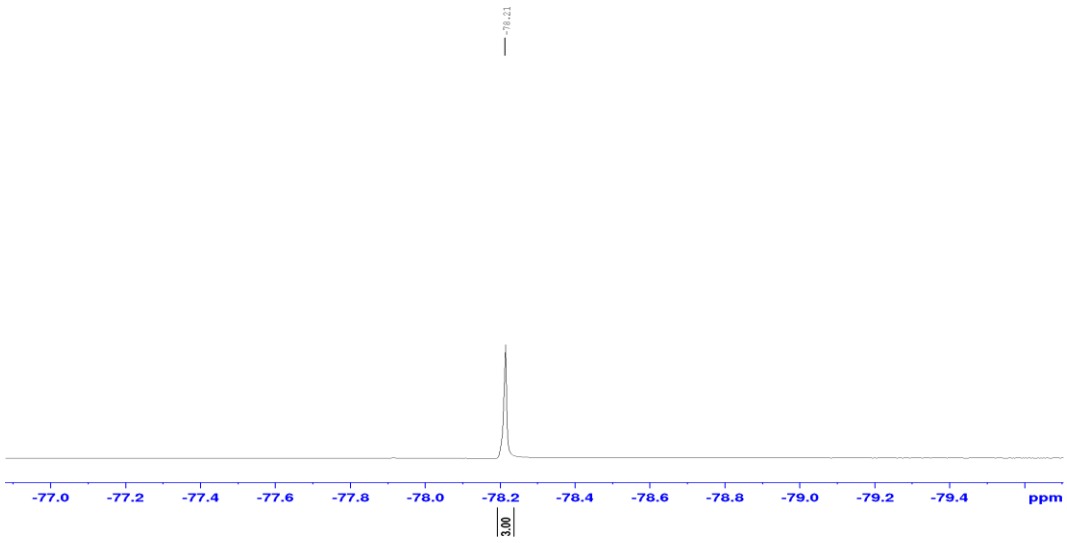
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
ppm
3.00


OTf
S
Et


-78.21
-77.0
-77.2
-77.4
-77.6
-77.8
-78.0
-78.2
-78.4
-78.6
-78.8
-79.0
-79.2
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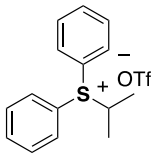
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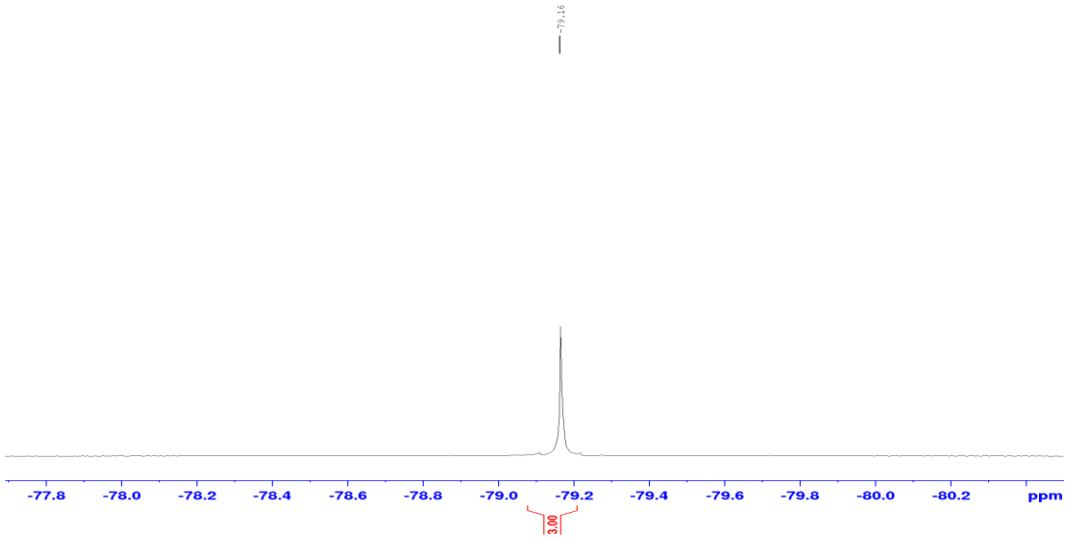
OTf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ppm
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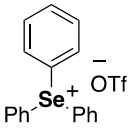
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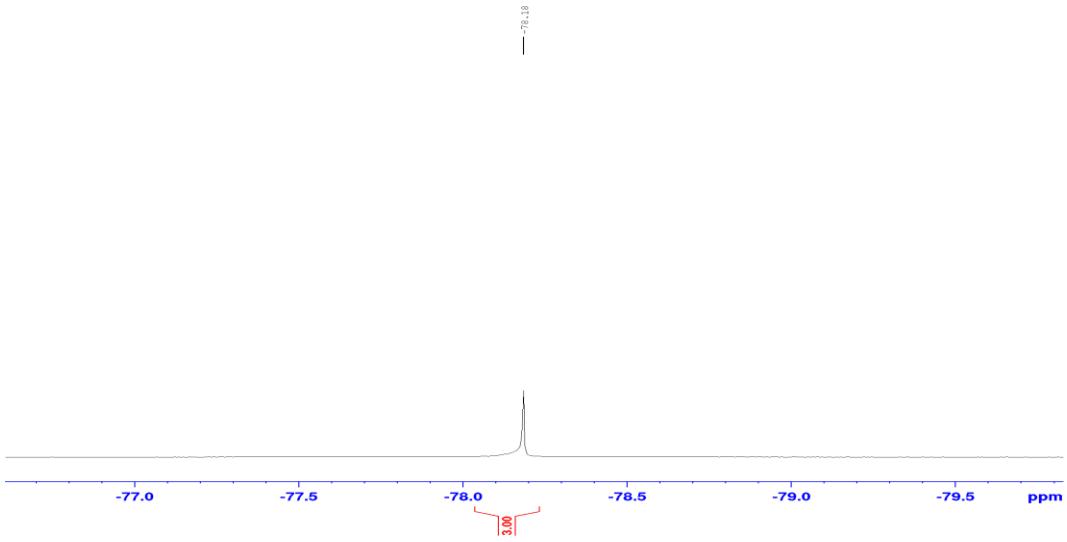
+
OTf
Ph
Ph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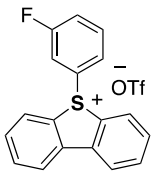
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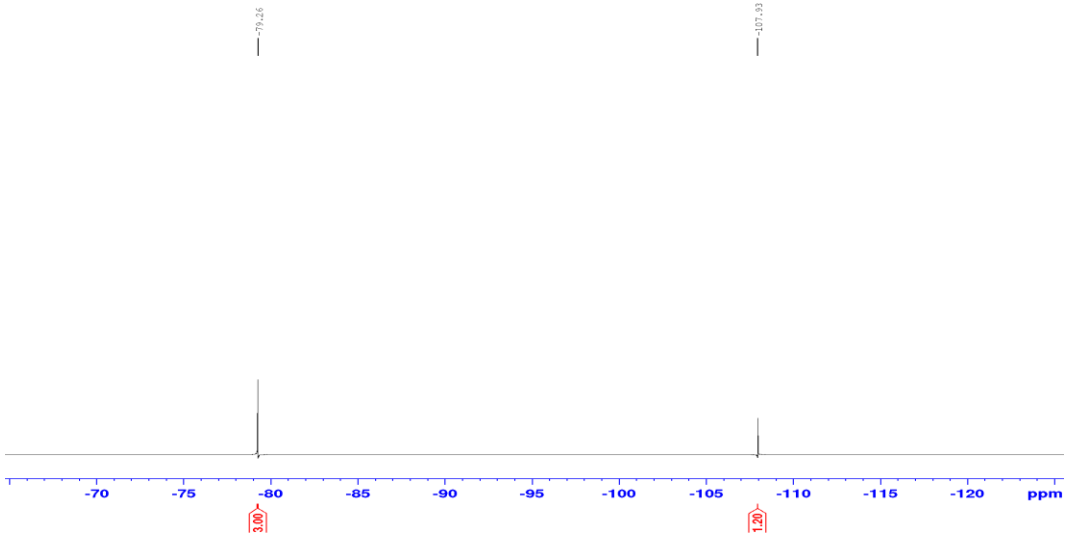
OTf
S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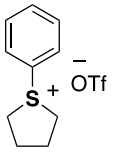
1.20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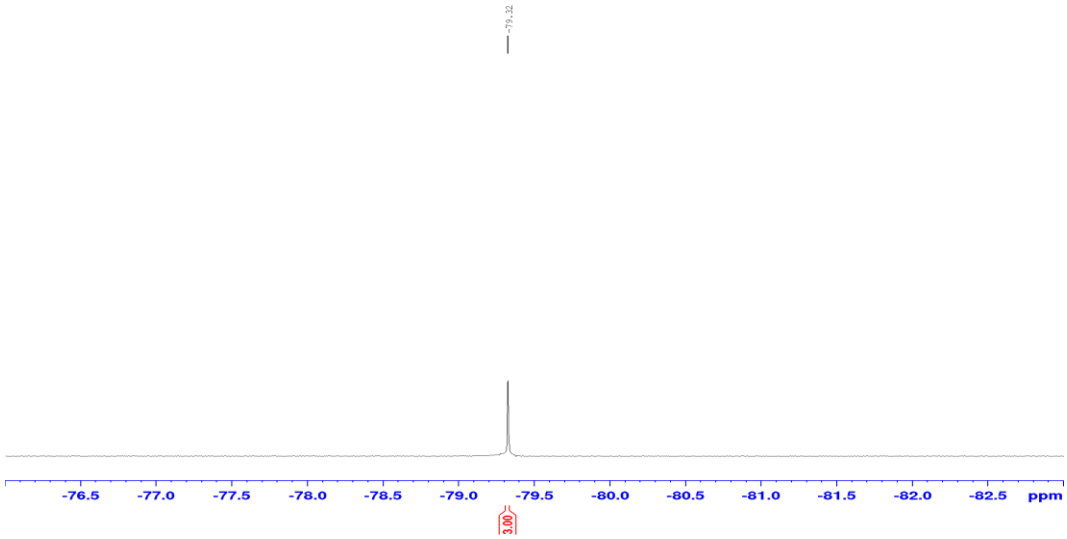
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ppm
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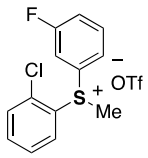
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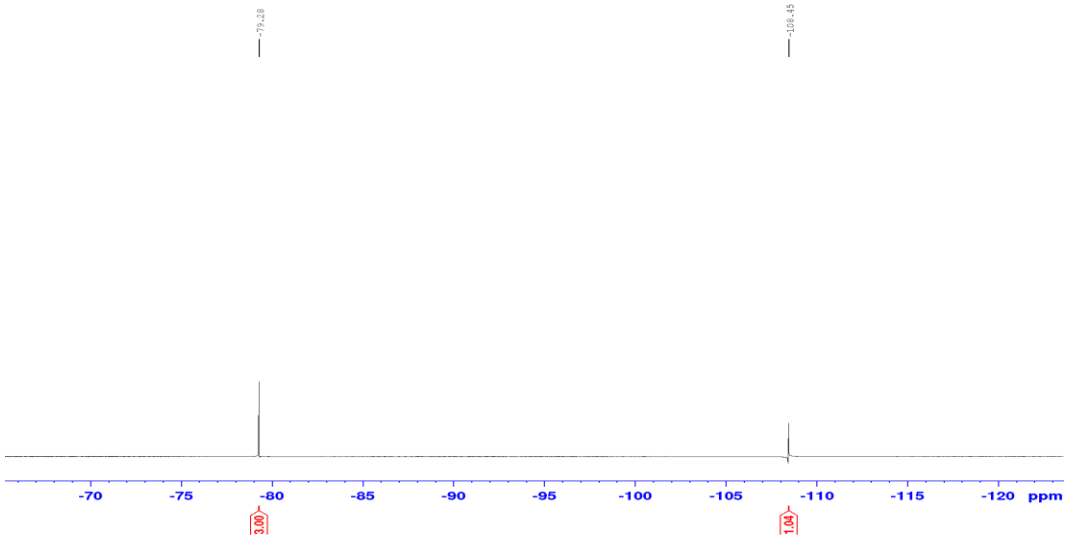
Cl
S
+
Me
OTf
−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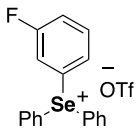
1.04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+
Ph
Ph
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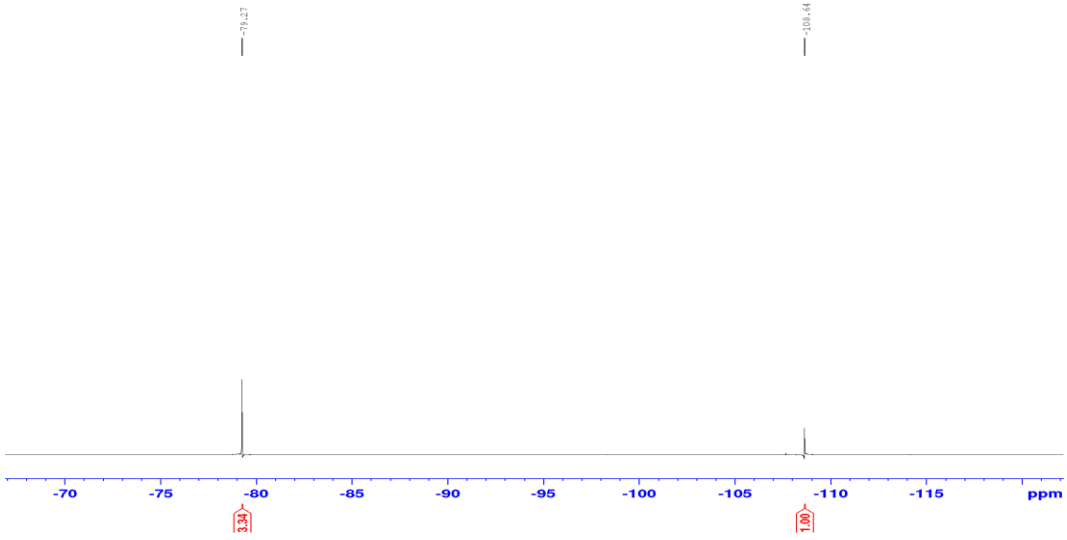
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-115
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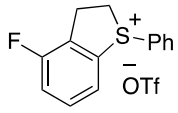
1.00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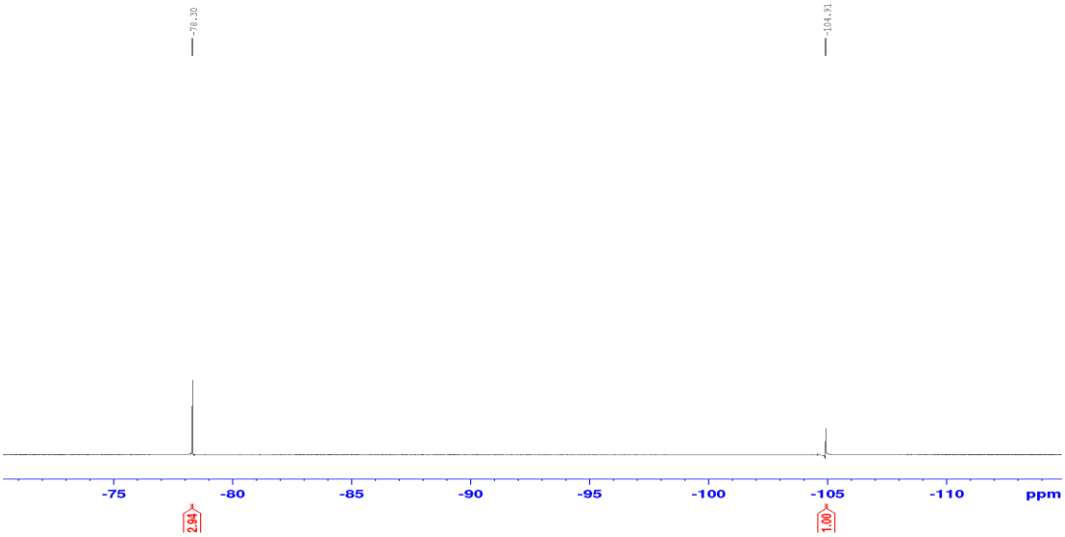
+
Ph
OTf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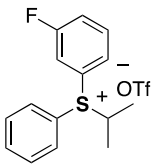
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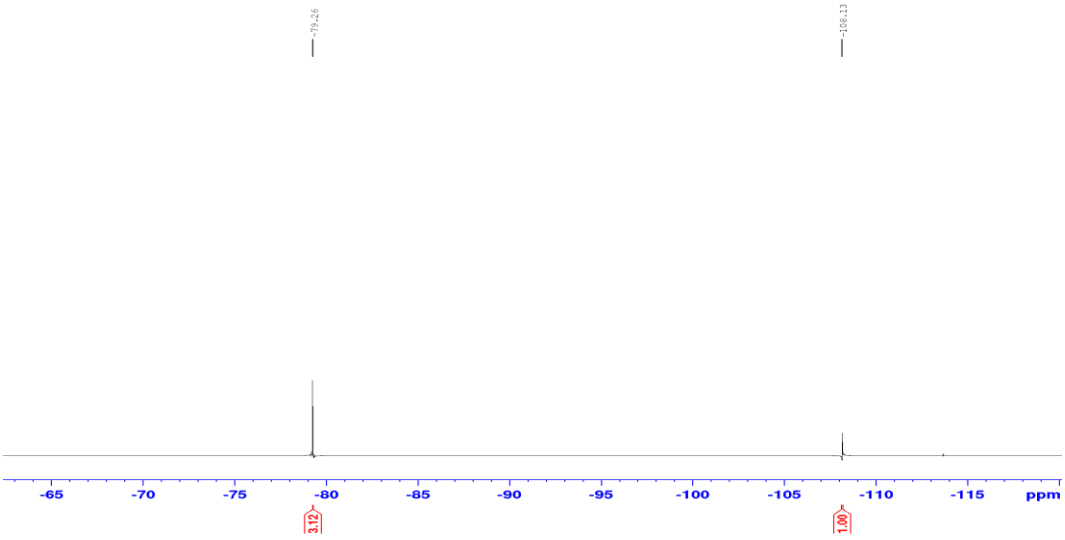
+
OTf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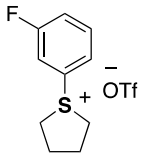
1.00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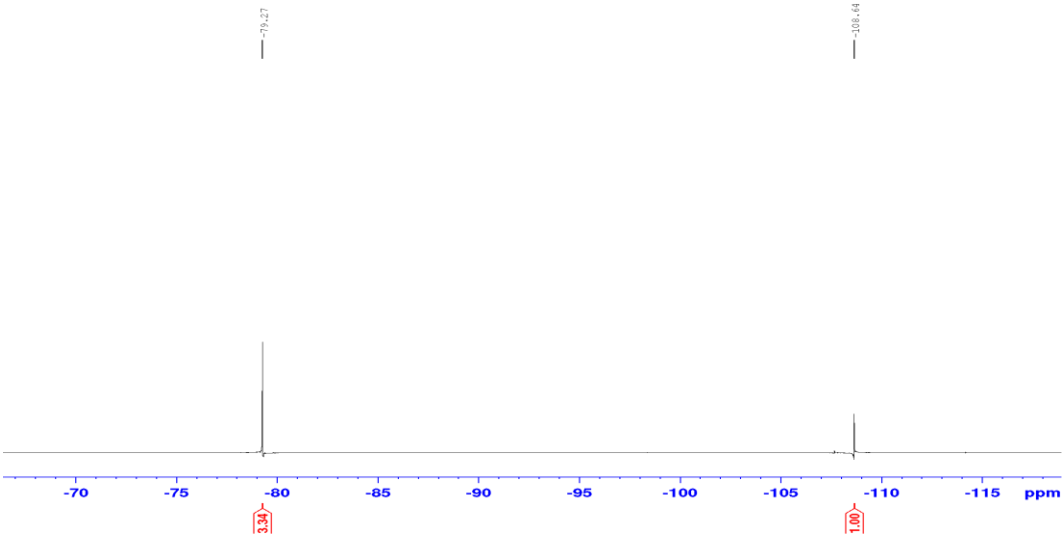
+
OTf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ppm
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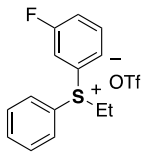
1.00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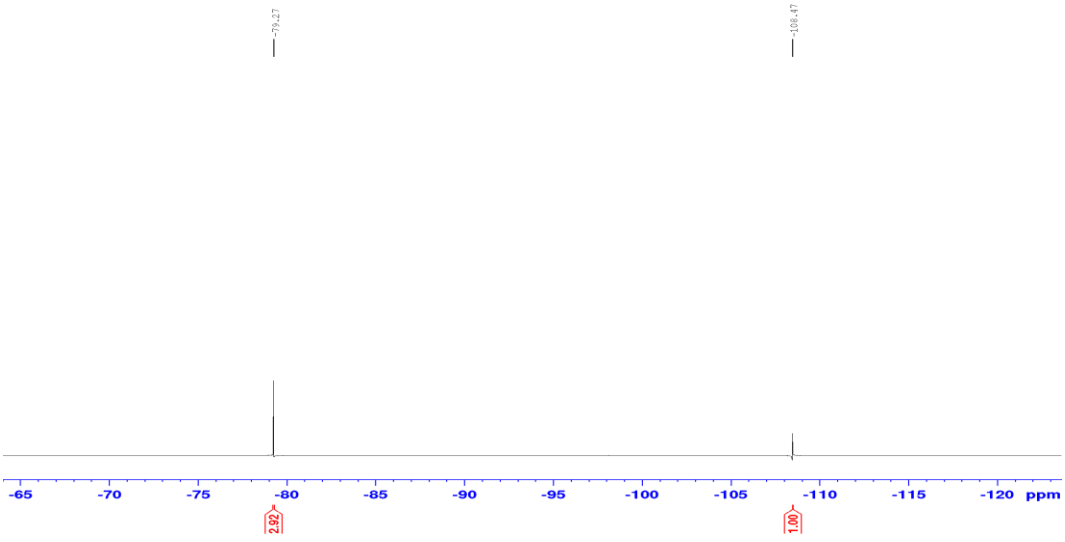
S
+
OTf
Et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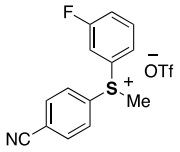
1.00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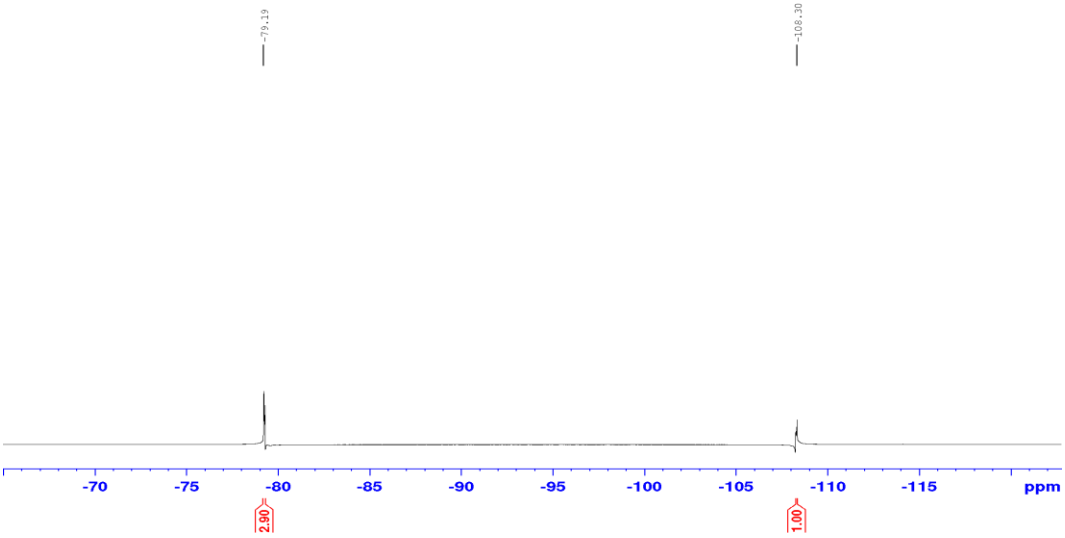
OTf
S
Me
NC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-100
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ppm
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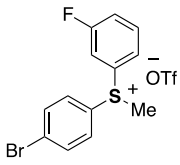
1.00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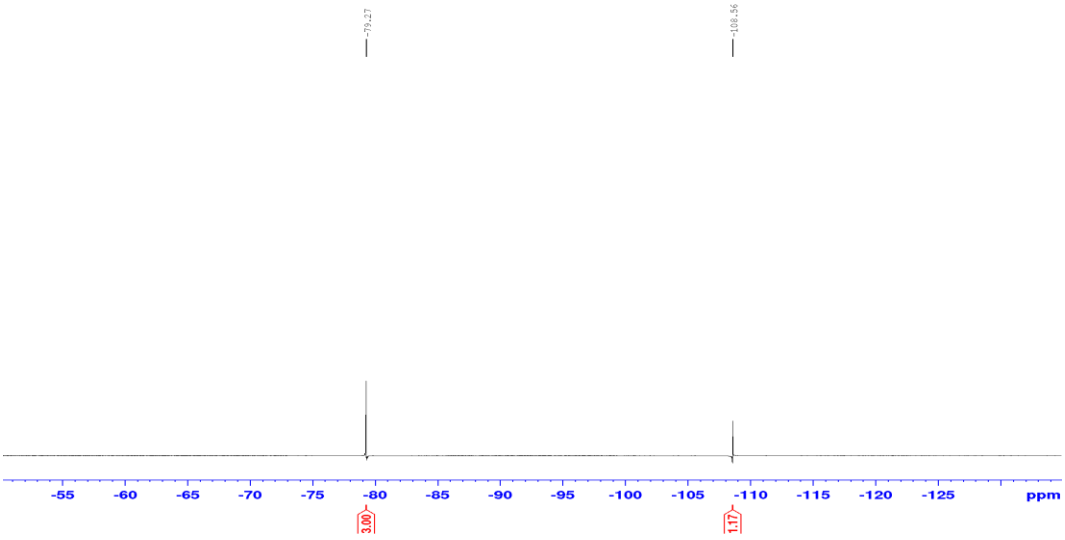
OTf
S
Me
Br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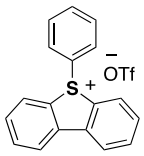
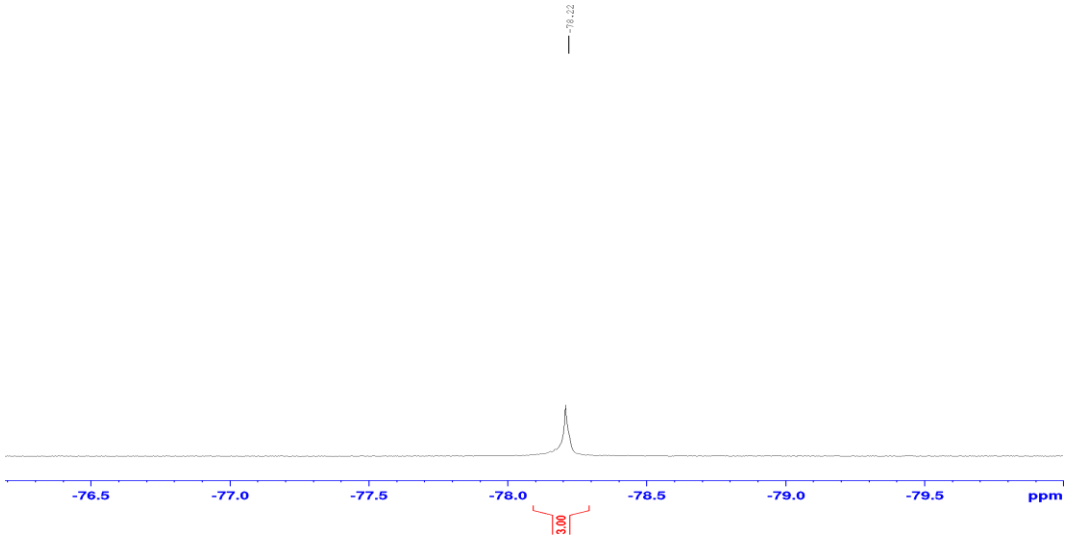
-125
ppm
3.00
1.17


OTf
S
+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ppm
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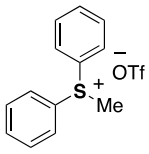
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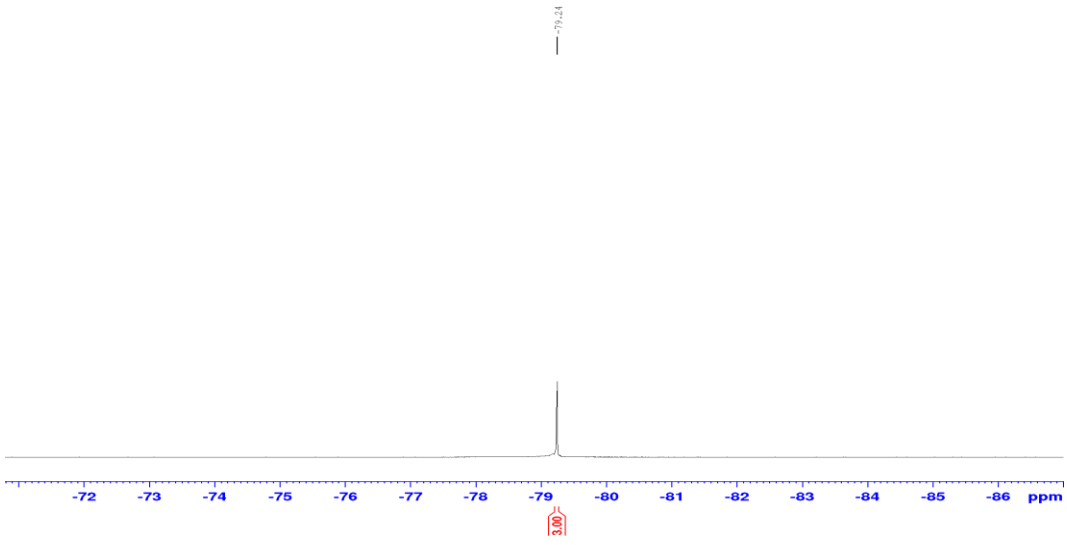
+
Me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-80
-81
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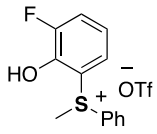
-86
ppm
3.00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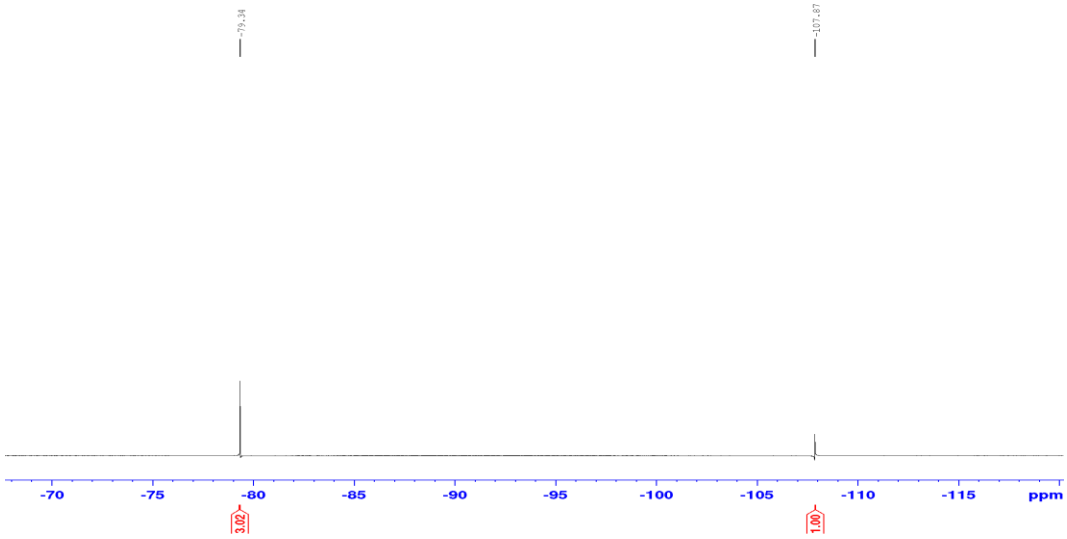
HO
S
+
Ph
OTf
−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-100
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-115
ppm
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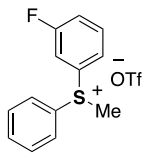
1.00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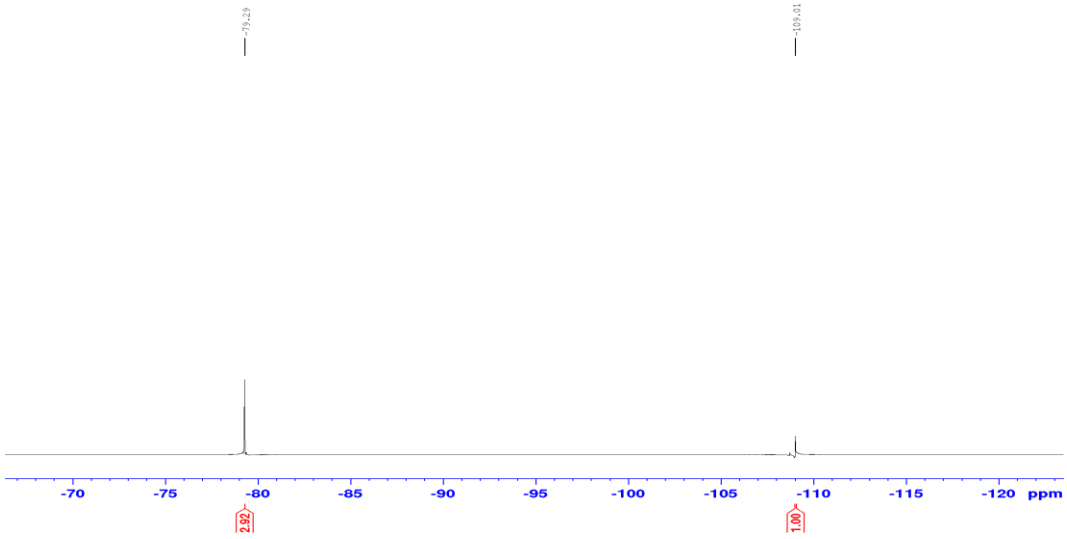
S
+
Me
OTf
−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-105
-110
-115
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ppm
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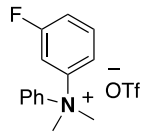
1.00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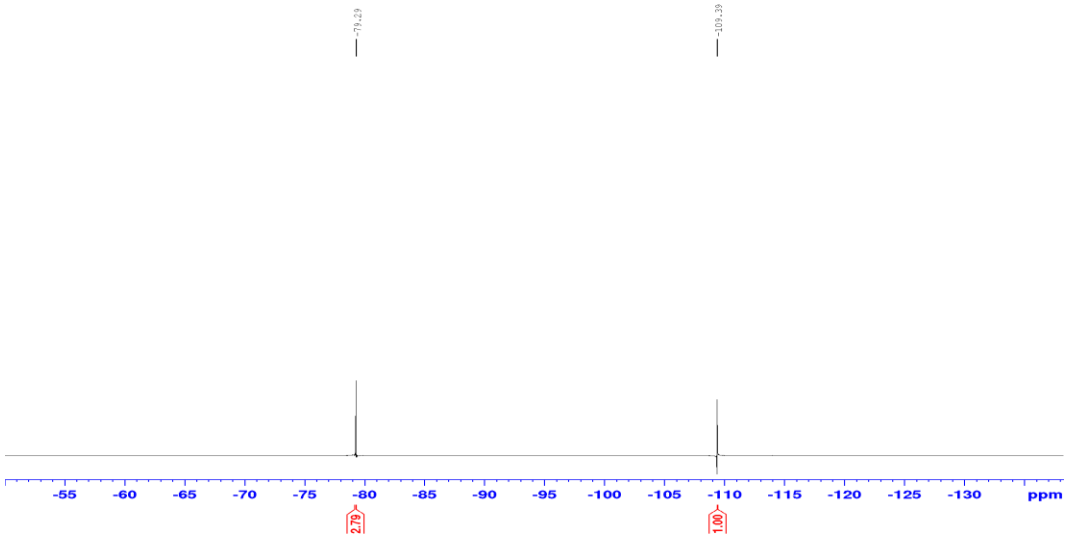
Ph
N
+
OTf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-75
-80
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-90
-95
-100
-105
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-115
-120
-125
-130
ppm
2.79
1.00

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