DEVELOPMENT OF NEW OXIDIZING SYSTEMS BASED ON HYPERVALENT IODINE

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LIST OF ABBREVIATIONS

Ac = acetate

Anal. Calcd = Analytically Calculated

Ar = aryl

Bn = benzyl

br = broad

t-Bu = *tert*-butyl

d = doublet

dec = decomposition

DIB = (Diacetoxyiodo)benzene

DMF = dimethylformamide

DMP = Dess-Martin periodinane

DMSO = dimethyl sulfoxide

ee % = enantiomeric excess

equiv = equivalent

ESI-MS = electrospray ionization mass spectroscopy

ESI-MS/MS = electrospray ionization mass spectroscopy/mass spectrometry

Et = ethyl

g = gram

GC = gas chromatography

GC-MS = gas chromatography mass spectrometry

h = hour

IBX = 2-iodobenzoic acid

IR – infrared

LC-MS = liquid chromatography mass spectrometry

lit = literature

m = multiplet

Me = methyl

min = minute

MHz = megahertz

ml = milliliter

µl = microliter

mmol = millimole

mol-equiv = mole equivalent

mp = melting point

NMR = nuclear magnetic resonance

Ph = phenyl

ppm = parts per million

i-Pr = isopropyl

q = quadruplet

rt = room temperature

s = singlet

t = triplet

TFA = trifluoroacetate

THF = tetrahydrofuran

TLC = thin layer chromatography

TMS = trimethylsilyl

Chapter 1

Review

1. Hypervalent Iodine in Organic Synthesis.

1.1 Introduction

Organohypervalent iodine reagents have attracted significant recent interest as versatile and environmentally benign oxidants with numerous applications in organic synthesis. Hypervalent iodine compounds are extensively employed in organic synthesis as highly selective and environmentally friendly oxidizing reagents. Hypervalent iodine compounds have been known since the late 19th century. Recently organic chemistry of hypervalent iodine compounds has experienced an immense development due to these properties and also commercial availability. Hypervalent iodine reagents are useful synthetic tools due to their low toxicity, ready availability, and ease of handling. Also, there is high interest for hypervalent iodine reagents because of high efficiency and very useful oxidizing properties of these reagents. There is considerable current interest and research activity in the development of new reagents and synthetic applications based on the organic chemistry of hypervalent iodine. Iodine forms stable polycoordinated compounds because it is the largest, most polarizable, and most electropositive element in its group. Mild reaction conditions and highly chemoselective oxidizing properties of polyvalent organic iodine reagents brought these reagents to the attention of modern synthetic chemists. A variety of new chemical transformations effected by hypervalent iodine reagents have recently been developed. These protocols include catalytic imidations with iodonium imides, hypervalent iodine mediated oxidative coupling of phenols and related compounds, applications of iodine(III) compounds as useful carbene and nitrene precursors and the broad synthetic applications of hypervalent iodine heterocycles derived from benziodoxoles and benziodazoles. [1-34]

Organic iodine(III) and iodine(V) derivatives are currently routinely employed in organic synthesis as reagents for various selective oxidative transformations of organic

compounds. They range from the formation of carbon-carbon and carbon-heteroatom bonds in oxidative coupling reactions to the activation of carbon-hydrogen bonds. Efficient and ecofriendly hypervalent iodine reagents and based on them catalytic systems are now widely used in organic synthesis for various oxidative transformations of organic substrates.

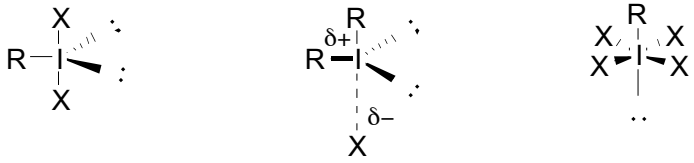
The fundamental feature of these compounds is the highly polarized three-center-four-electron (3c-4e) bond, in which the central atom bears a positive charge and two monovalent ligands share the corresponding negative charge. This type of bonding serves to distinguish hypervalent compounds from transition metal complexes in which *d*-orbital hybridization is invoked to account for bonding beyond the stable octet. Furthermore, hypervalent iodine compounds are versatile, selective oxidants that have the added advantage of being biodegradable and low in toxicity. Chemical properties and reactivity is similar to the heavy metal reagents such as Hg(II), Tl(III), Pb(IV) but without the toxicity and environmental issues. Therefore hypervalent iodine reagents are an excellent alternative to heavy metal reagents. The catalytic use of hypervalent iodine derivatives has also recently become known. A great number of reviews covered specific aspects of hypervalent organoiodide chemistry.[1-45] The understanding of iodine(III) reagents is more developed than for iodine (V) compounds, but nonetheless the chemistry of iodine(V) compounds (λ^5-iodanes) has also attracted substantial attention in recent years.

The purpose of this chapter is to summarize the recent literature data on the preparation and synthetic applications of selected classes of hypervalent iodine(III) and iodine(V) reagents, which are closely related to the reagents and methodologies designed and developed during our own research efforts.

1.2 Hypervalent iodine(III) and hypervalent iodine(V) reagents. Classification

Organic iodine(III) and iodine(V) compounds are commonly classified by the type of ligands attached to the iodine atom.[34,40,42,44-45]

Structural aspects of hypervalent iodine compounds have previously been discussed in the literature.[1,2,34,44-46] All known organic hypervalent iodine derivatives include two general structural types, according to IUPAC. First structural type is iodine(III) compounds **1** and **2**, also named λ^3-iodanes. The second structural type is iodine(V) compounds **3**, or λ^5-iodanes (Scheme1).



1 **2** **3**

R=carbon ligand; X=halogen, O-, or N-ligand.

Scheme 1

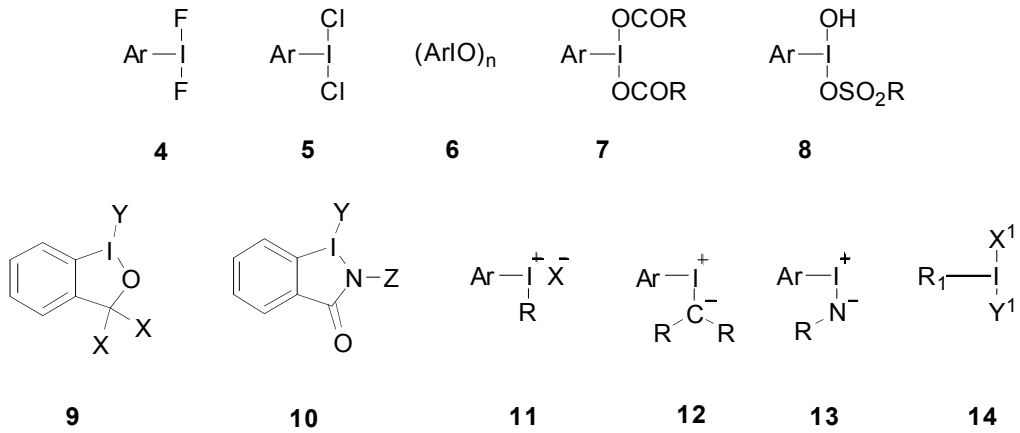
The iodine atom in λ^3-iodanes **1**and **2** has a total 10 electrons, and it forms distorted trigonal bipyramid geometry. The least electronegative carbon ligand R and both electron pairs reside in equatorial positions, and two heteroatom ligands X occupy the apical positions. This linear three-center, four-electron (3c–4e) bond is highly polarized and is longer and weaker than a regular covalent bond. The term "hypervalent" is accepted for this type of bond, and the presence of this bond in λ^3-iodanes is responsible for their electrophilic reactivity.

Organic λ^5-iodanes **3** have a distorted octahedral geometry. The electron pair and the organic group R, connected to iodine by a normal covalent bond using 5sp-hybridized orbitals, are in the apical positions. Two orthogonal hypervalent 3c–4e bonds accommodate four heteroatom ligands X.

Important spectroscopic (NMR, LC-MS, ESI-MS, ESI-MS/MS) structural studies, X-ray analysis,[62-66] and results of other general structural studies have been recently reported[67-86] for all main classes of organic hypervalent iodine compounds.

Also, various computational methods were used to investigate the structure and reactivity of several classes of hypervalent iodine compounds theoretically.[47-61]

The following general classes of iodine(III) and iodine(V) derivatives have great practical importance in many synthetic applications (Scheme 2 and Scheme 3).

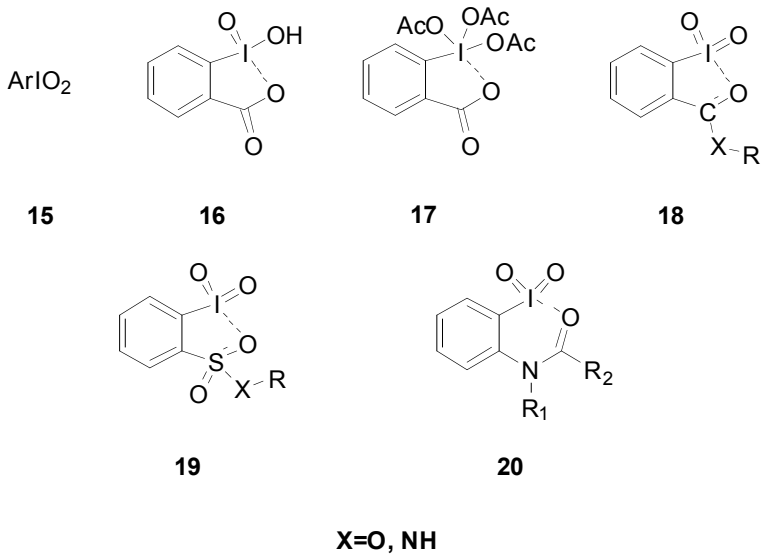


X=Me, CF_3 or 2X=O; Y=OH, OAc, CN, etc.; Z=H, Ac, etc.
R_1=C_nF_{2n+1}, $C_nF_{2n+1}CH_2$, $ArSO_2CH_2$
X^1=Y^1=Cl, $OCOCF_3$; X^1=OH; Y^1=OSO_2R

Scheme 2

(Difluoroiodo)arenes **4** and (dichloroiodo)arenes **5** are effectively used as fluorinating and chlorinating reagents. Iodosylarenes **6**, [bis(acyloxy)iodo]arenes **7**, aryliodine(III) organosulfonates **8** are generally powerful oxidizing agents, and have been widely applied as reagents for oxygenation and oxidative functionalization of organic substrates. Five-membered iodine(III) heterocycles[39] (benziodoxoles **9** and benziodazoles **10**) are more stable than their acyclic analogues; this allows the isolation and practical use of several unstable iodine(III) derivatives. Iodonium salts **11** in general do not possess any significant oxidizing properties, but have reactivity due to the ability of the -ArI fragment to be a good leaving group. Iodonium ylides **12** and imides **13** serve as carbene and nitrene precursors, respectively. The most practically useful representatives of stabilized alkyl substituted λ^3-iodanes **14** are [bis(trifluoroacetoxy)iodo]perfluoro-alkanes, $C_nF_{2n+1}I(OCOCF_3)_2$. They are relatively stable, serve as electrophilic

perfluoroalkylating agents, as precursors for (perfluoroalkyl)aryliodonium salts and applicable as effective and easily recyclable oxidative reagents.



Scheme 3

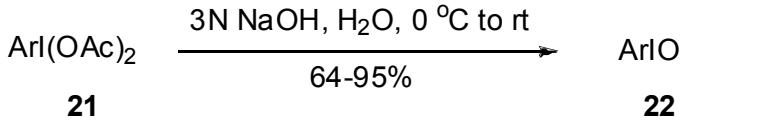
Among the iodylarenes **15**, only iodylbenzene, $PhIO_2$, has found relatively wide practical application in modern organic synthesis as an oxidizing agent. 2-Iodoxybenzoic acid (IBX) **16** and analogues and Dess-Martin periodinane (DMP) **17** are the most important representatives of five-membered iodine(V) heterocycles**.** Both IBX and DMP are highly efficient, chemoselective mild agents for the variety of synthetically useful oxidative transformations.

The main classes of pseudocyclic iodine(V) derivatives are pseudo-benziodoxoles **18**, **19** and pseudo-benziodoxazines **20,** which have found growing practical application as efficient oxidizing reagents, and they are now established reagents in modern organic synthesis.

1.3 Hypervalent iodine(III) and hypervalent iodine(V) reagents. Preparation and application

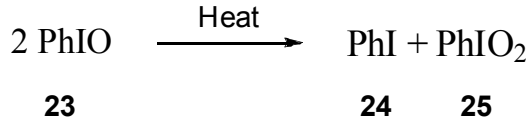
A. Iodosylarenes, Iodosobenzene, and Iodosylbenzene sulfate. Preparation and properties

Iodosobenzene **23** is the most important representative of iodosylarenes, and can be prepared by simple treatment of (diacetoxy)iodobenzene with sodium hydroxide by alkaline hydrolysis.[86] The same procedure can be used to prepare iodosylarenes **22** with different substituents (*ortho- metha- para*-substituted) from the respective (diacetoxy)iodoarenes **21** (Scheme 4).[68]



Scheme 4

For example, iodosobenzene **23** is a yellow amorphous powder, and it cannot be recrystallized due to its polymeric nature. Extended storage at room temperature or heating results in disproportionation reaction of iodosobenzene **23**. First time iodylbenzene $PhIO_2$ **25** was prepared by Willgerodt in the 19th century. Willgerodt observed that iodosobenzene **23** disproportionates under steam distillation afforded equal equivalents of iodobenzene **24** and colorless, explosive iodylbenzene, $PhIO_2$ **25** (Scheme 5).[87]

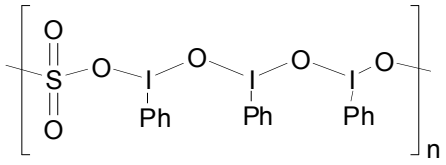


Scheme 5

Iodosobenzene **23** should not be dried at elevated temperatures because it has been reported that 3.0 g of PhIO **23** upon drying at 110 °C in vacuum exploded violently.[88] Iodosobenzene **23** dissolves in methanol with depolymerization affording $PhI(OMe)_2$.[89]

Iodosobenzene **23** is an effective oxidizing reagent, but it has some disadvantages as well. For instance, it is insoluble in most organic solvents because of the polymeric structure. This property of iodosobenzene **23** significantly restricts and decreases its practical usefulness and applications. The majority of the known reactions of iodosobenzene **23** require the presence of a definite solvent or a catalyst (Lewis acid, bromide or iodide anions, transition metal complex, etc.) that can depolymerize $(PhIO)_n$, generating the reactive monomeric species which in turn oxidize substrates.

Another hypervalent iodine(III) reagent is oligomeric iodosylbenzene sulfate $[(PhIO)_3SO_3]_n$ **26** (Scheme 6).

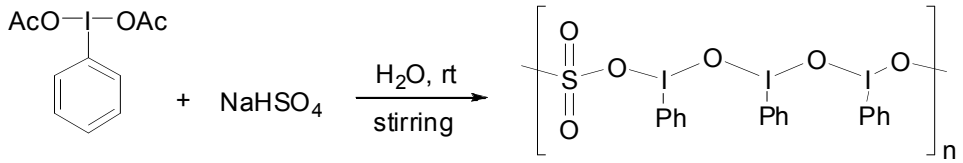


oligomeric iodosylbenzene sulfate

26

Scheme 6

It is a thermally stable yellow crystalline solid, and it can be prepared by treatment of commercially available (diacetoxyiodo)benzene **27** with aqueous sodium hydrogen sulfate (Scheme 7).



27 **26**

Scheme 7

Oligomeric iodosylbenzene sulfate **26** has been investigated in the biomimetic oxidation of anthracene to anthraquinone catalyzed by Fe(III) phthalocyanine complex, Co(II) tetraphenylporphyrin, and Ru(II) tetraphenylporphyrin. It has been reported that oligomeric iodosylbenzene sulfate **26** possesses high reactivity in catalytic oxidation reactions at room temperature in the presence of a catalyst, while the reaction in the absence of catalyst does not occur at room temperature under investigated reaction conditions.[90] This reagent can be used as an excellent alternative to the potentially explosive iodosobenzene **23** in transition metal phthalocyanine- and porphyrin-catalyzed reactions.[91]

B. Iodosobenzene. Applications and transition metal catalyzed reactions

Transition metal salts and complexes can effectively catalyze various oxidative transformations involving hypervalent iodine(III) reagents. It is generally thought that the intermediate highvalent oxo complexes are responsible for the oxygen transfer from iodosobenzene **23** to the organic substrate. However, the details of the initial interaction of iodosobenzene **23** with metal complex are still under consideration. In many biomimetic oxidations catalyzed by metalloporphyrins and other transition metal derivatives, iodosobenzene **23** is widely used as the most efficient terminal oxidant – source of oxygen. Many studies on the use of iodosobenzene **23** as an oxidant in transition metal catalyzed reactions have been published. Recently it was shown that iodosobenzene **23** reacts with metalloporphyrins and some other metal complexes with the formation of unstable adducts which can serve as the actual oxidizers in catalytic

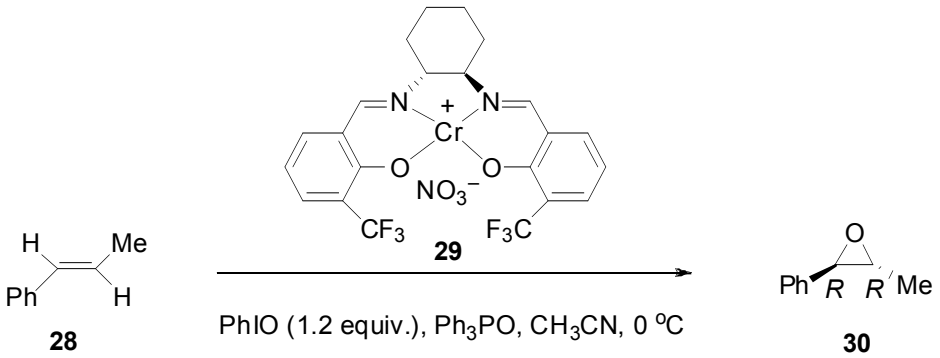
oxygenations.[92-96] The unique reactivity of iodosobenzene **23** as the source of oxygen in the catalytic oxygenation reactions can be explained by the intermediate formation of such highly reactive adducts.

Hydroxylation of hydrocarbons, the transition metal-mediated epoxidation of alkenes, oxidation of alcohols to carbonyl compounds, δ-sultone formation through Rh-catalyzed C-H insertion, and oxidation of organic sulfides to sulfoxides can be performed employing iodosobenzene **23**.

It was recently reported by two independent groups of Vinod and Giannis that oxone can be used as a stoichiometric oxidant in catalytic reactions of the iodine(V) species for the oxidation of alcohols. Later, Ishihara and coauthors have optimized the procedure for the catalytic oxidation of alcohols by using 2-iodobenzenesulfonic acid as an extremely active catalyst and Oxone® as terminal oxidant. The recent development in the field of organoiodine chemistry was the catalytic utilization of hypervalent iodine reagents. Recently, numerous examples of catalytic utilization of the iodine(III) species have been reported by several other groups.

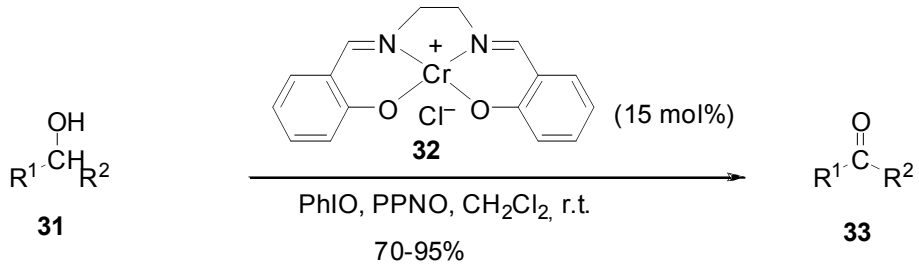
It was shown that the cytochrome P 450 model system forms different active oxidizing species from different iodosylarenes, which can be explained by the involvement of the corresponding catalyst-iodosylarene complexes.[93] Current mechanistic studies of cytochrome P-450, a heme-containing monooxygenase enzyme, and its synthetic models provoked significant interest in iodosobenzene **23** as an oxidant in the transition-metal-catalyzed oxygenations.[97] It was found in the presence of cytochrome P-450 or various transition metal complexes that iodosobenzene **23** converts alkanes to alcohols and alkenes to epoxides, often with high regioselectivity and stereoselectivity.[2] Gilheany and co-workers reported a highly enantioselective alkene epoxidation catalyzed by chiral nonracemic chromium salen complexes. They described asymmetric epoxidations of alkenes with iodosobenzene **23** in the presence of chiral complexes of transition metals.[98-119] Gilheany and co-workers showed that in these reactions iodosobenzene **23** is the only applicable oxidant, and 92% yield (the highest) was achieved in the epoxidation of (E)-β-methylstyrene **28** with Ph_3PO as a donor ligand in the presence of the chromium salen complex **29** (stoichiometric amounts).[103] This

reaction was performed as catalytic reaction with 5-10 mol % of chromium complex (Scheme 8).[101-103]



Scheme 8

Various carbonyl compounds **33** can be obtained by chemoselective oxidation from appropriate primary and secondary alcohols **31** by iodosobenzene **23** in the presence of a (salen)Cr(III) complex **32** as the catalyst (Scheme 9).[125,126]



R^1, R^2 = H, alkyl, alkenyl, aryl; PPNO = 4-phenylpyridine *N*-oxide

Scheme 9

It was found that the monomeric mono(iodosylbenzene)(tetraphenylporphinato)-manganese(IV) adducts are able to oxidize cyclohexane and styrene at room temperature with the formation of the respective oxidation products in high yields.[92] The monomeric mono(iodosylbenzene) (tetraphenylporphinato)manganese(IV) adducts, 4-ROC_6H_4-

OMn(IV)TPP(OIPh), were synthesized by the reaction of the corresponding (tetraphenylporphinato)manganese(III) derivatives with iodosobenzene **23**

Various iron(III) and manganese(III) porphyrin complexes can be used as catalysts in the hydroxylations of cyclohexane, cyclohexene, adamantane, and various aromatic hydrocarbons.[111,120,121] Recently, Breslow and co-workers have reported that iodosobenzene **23** can be used as an effective oxidant in metalloporhyrins-catalyzed regioselective hydroxylations of several steroidal derivatives.[111,120-125] The selective hydroxylation is explained by the geometry of the catalyst-substrate complex. In the presence of a manganese(III) porphyrin catalyst an androstanediol derivative **34** was hydroxylated at the 6α carbon with complete regioselectivity (Scheme 10).[122]

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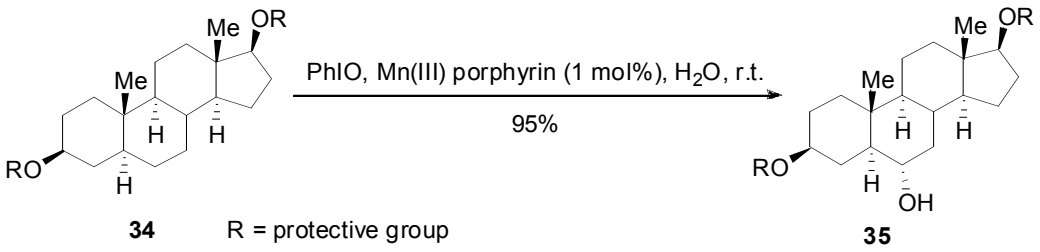
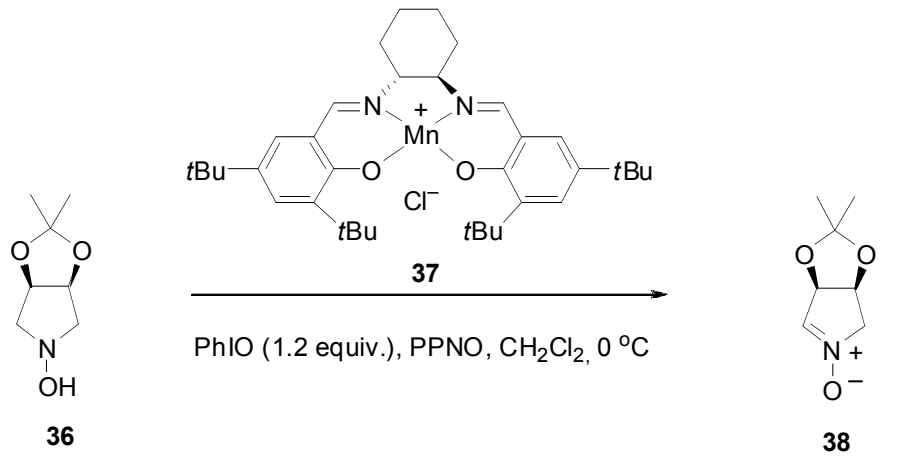


34 R = protective group **35**

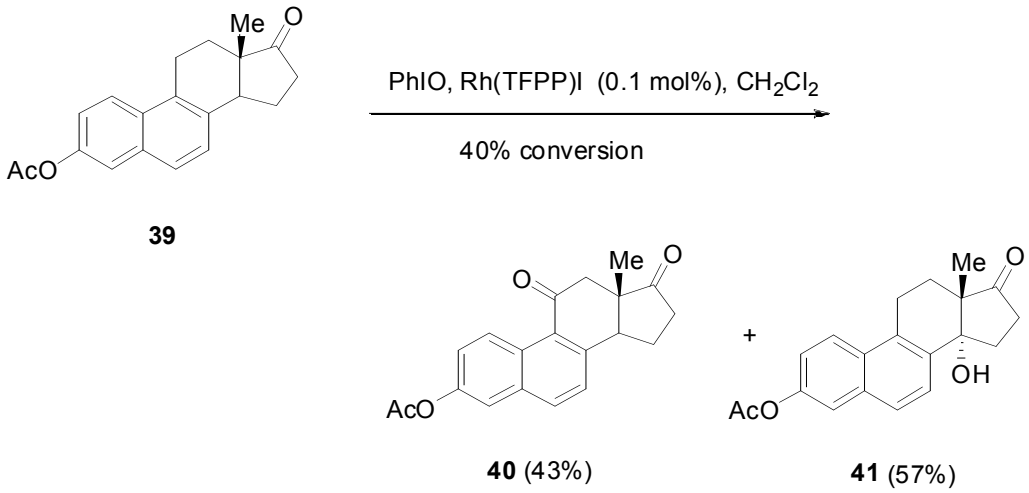
Scheme 10

N-oxides can be obtained by oxidation of *N,N*-disubstituted hydroxylamines with iodosobenzene **23** in the presence of catalytic amounts of the chiral (salen)Mn(III) complex **37** (Jacobsen catalyst).[127] Thus *meso-cis*-3,4-isopropylidenedioxy-1-hydroxypyrrolidine **36** affords the corresponding *N*-oxide **38** with moderate enantioselectivity (Scheme 11).[127]



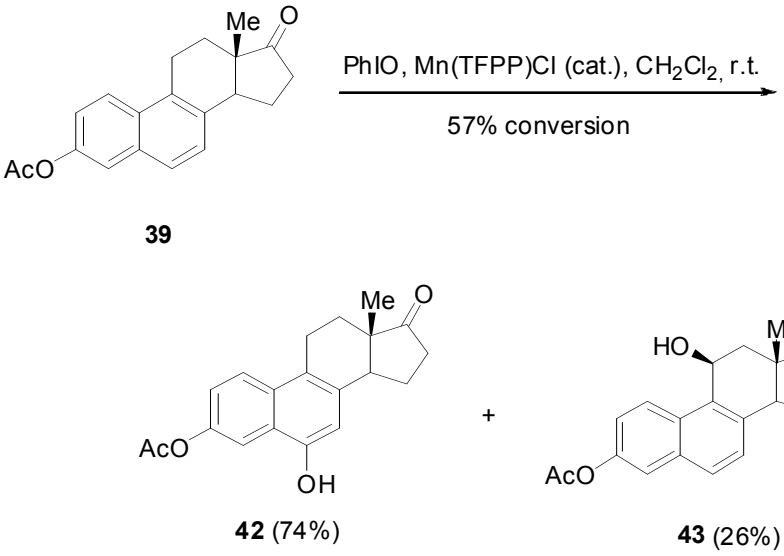
Scheme 11

Two products **40** and **41** form in the case when aromatic steroid equilenin acetate **39** undergoes regioiselective and stereoselective reaction catalyzed by rhodium(III) porphyrin using iodosobenzene **23** as an oxidant (Scheme 12).[124]



Scheme 12

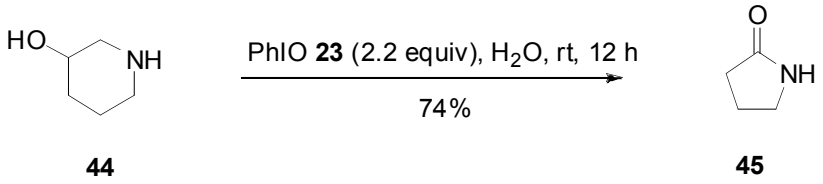
When manganese porphyrin is used as a catalyst then a different selectivity is observed in the hydroxylation reaction outcome (Scheme 13).[123]



Mn(TFPP)Cl = chloro[5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato] manganese(III)

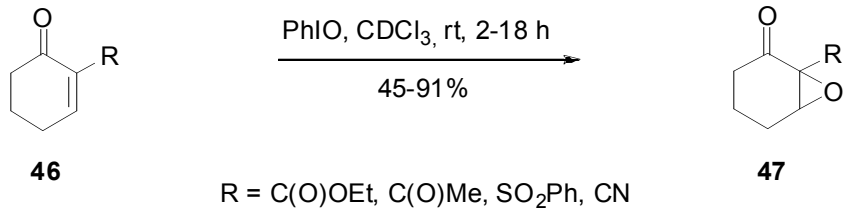
Scheme 13

Besides transition metal catalyzed reactions, iodosobenzene **23** can be employed for numerous other oxidation reactions. Recently, it has been reported that the oxidation of 3-hydroxypiperidine **44** with iodosobenzene **23** in water affords 2-pyrrolidinone **45** directly in good yield (Scheme 14).[129]



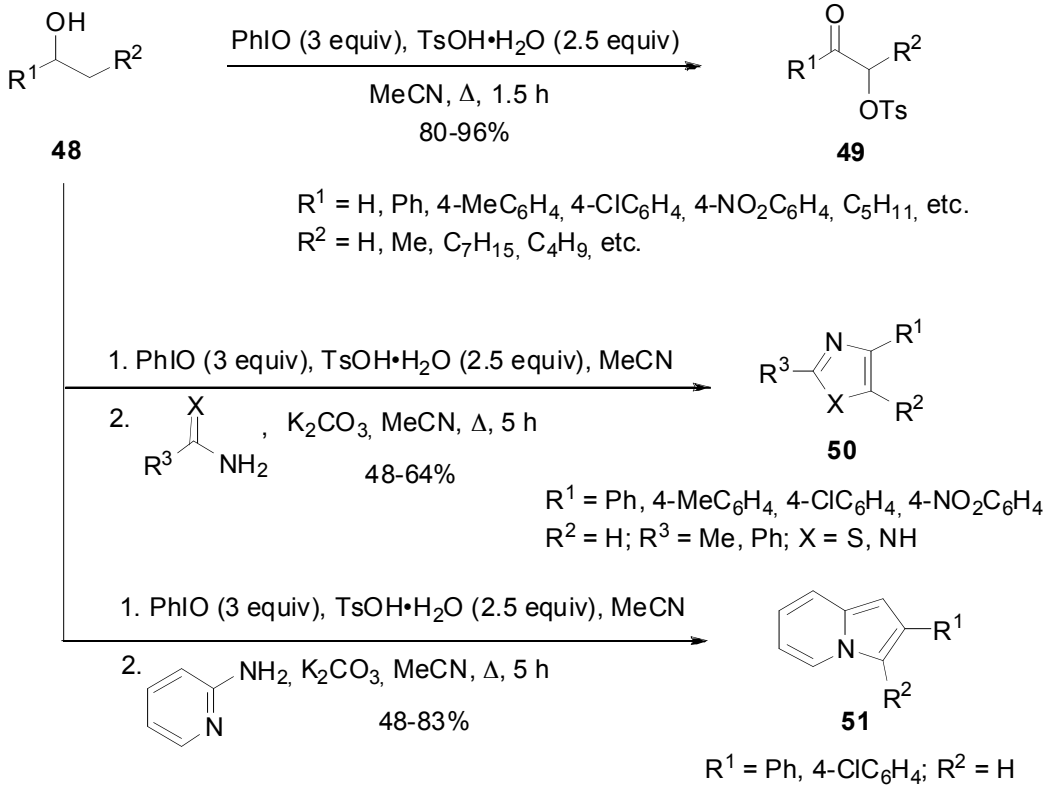
Scheme 14

Nucleophilic epoxidation of electron-deficient alkenes is another example to apply iodosobenzene **23** as an appropriate reagent. For instance, iodosobenzene **23** can react with enones **46** to afford the corresponding epoxides **47** usually with high yields (Scheme 15).[88]



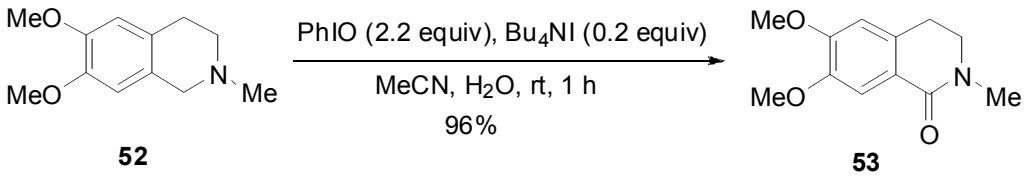
Scheme 15

It has been reported by Togo and co-workers[130] that the treatment of alcohols **48** with iodosobenzene **23** and *p*-toluenesulfonic acid monohydrate gives α-tosyloxy ketones and aldehydes **49**. Thiazoles (**50**, X = S), imidazoles (**50**, X = NH), and imidazopyridines **51** can be prepared from alcohols by treatment with iodosobenzene **23** and *p*-toluenesulfonic acid monohydrate, followed by thioamides, benzamidine, and 2-aminopyridine, respectively (Scheme 16).[130]



Scheme 16

Iodosobenzene **23** is a useful reagent for oxidation of tetrahydroisoquinolines **52** by $(PhIO)_n/Bu_4NI/H_2O$ to the respective lactams **53** (Scheme 17).[128]

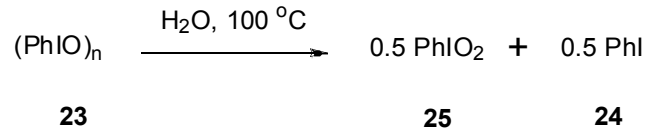


52 **53**

Scheme 17

C. Iodylarenes. Iodylbenzene

Iodoxy compounds or iodylarenes, $ArIO_2$, are noncyclic iodine(V) compounds that have been relatively well investigated. These compounds have a polymeric structure, and it is known that they are insoluble in the majority of organic solvents, except DMSO, and have an explosive character upon the heating or mechanical impact. Structural investigations of iodylarenes revealed infinite polymeric chains with strong I···O secondary intermolecular interactions.[132-133] The noncyclic iodyl compounds have found only very limited practical application due to their low stability. While the aryl derivatives, $ArIO_2$, can form relatively stable compounds, iodylalkanes can exist only at very low temperatures because these compounds are very unstable. However, iodylarenes have found some synthetic application as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds and other useful oxidative transformations. Iodylarenes can be prepared by the direct oxidation of iodoarenes with strong oxidants or by disproportionation of iodosylarenes. Among various $ArIO_2$ derivatives, iodylbenzene $PhIO_2$ **25** is the most popular and can be prepared accordingly to Scheme 16 [27] and, as it was mentioned above, Willgerodt first reported that the disproportionation of iodosobenzene **23** under steam distillation afforded iodylbenzene **25** and iodobenzene **24** (Scheme 18).

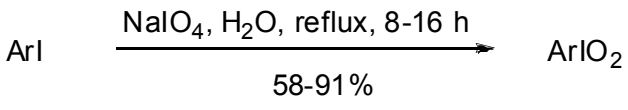


23 **25** **24**

Scheme 18

However, disproportionation is a less convenient approach to obtain iodylarenes than oxidation of iodoarenes. It is thought that the initial oxidation of ArI usually leads to iodosylarenes, which then slowly disproportionate to ArI and $ArIO_2$ upon gentle heating.[69,133,134]

Different methods have been reported for preparation of iodylarenes from iodoarenes, for example, the oxidation of iodoarenes with inorganic oxidants such as Caro's acid, potassium bromate[135], dimethyldioxirane[136], Oxone®[137], and sodium hypochlorite. [75,69,138] A new procedure has been developed by Skulski and coworkers for preparation of various iodylarenes from the corresponding iodoarenes **54** using sodium periodate as the oxidant.[133] The reaction was performed in boiling water[133](Scheme 19). Improved protocol has been reported by using boiling 30% aqueous acetic acid that allows shortening the time of reaction. Any further purification is not required and the iodylarenes **55** can be used directly in subsequent transformations.



54 **55**

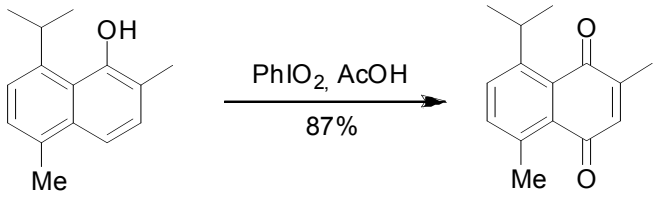
Ar = Ph, 3-$HO_2CC_6H_4$, 4-$MeOC_6H_4$, 4-MeC_6H_4, 3-MeC_6H_4,

2-MeC_6H_4, 4-FC_6H_4, 4-ClC_6H_4, 3-ClC_6H_4, 4-BrC_6H_4,

3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-$NaO_2CC_6H_4$, 2-$NaO_2CC_6H_4$

Scheme 19

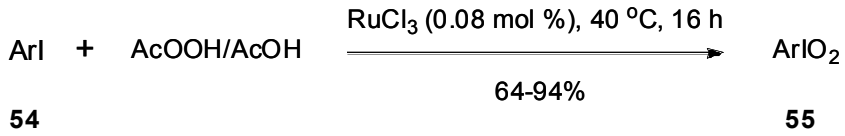
Activated aromatic ring can be oxidized by iodylbenzene **25** in aqueous acetonitrile or acetic acid media, yielding quinones or quinine imines.[139] Thus, naphthol **56** can be oxidized accordingly with this procedure and afforded cadalenquinone **57** (Scheme 20).[140]



56 **57**

Scheme 20

A new method has been reported for the preparation of iodylarenes **55** in the presence of catalytic amounts of ruthenium trichloride using peroxyacetic acid as an oxidant[141,142] (Scheme 21).

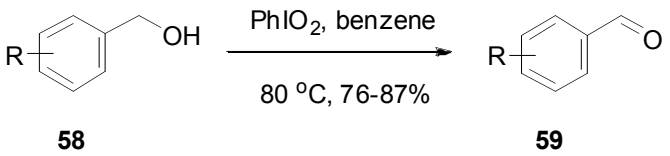


54 **55**

R=H; 4-CH_3; 2-CH_3; 2-iPr; 2-OCH_3; 4-Cl; 3-Cl; 2-Cl; 4-Br; 4-F; 4-CF_3; 3,5-CF_3

Scheme 21

Oxidation of benzylic alcohols **58** by iodylbenzene **25** in benzene at 80 °C afforded corresponding aldehydes **59** in good yield[143] (Scheme 22).

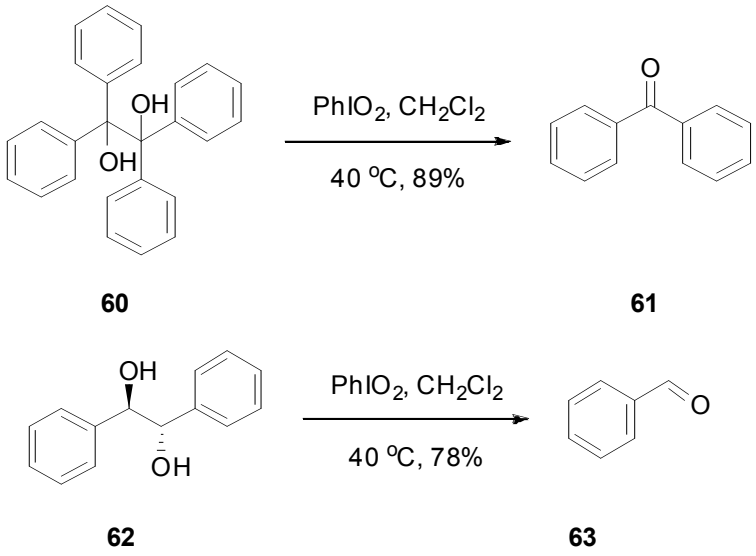


58 **59**

R=H, 4-NO_2, 4-t-Bu

Scheme 22

Oxidation of glycols **60** and **62** can be performed using iodylbenzene **25** as an oxidant, yielding the corresponding carbonyl derivatives **61** and **63**[143] (Scheme 23).

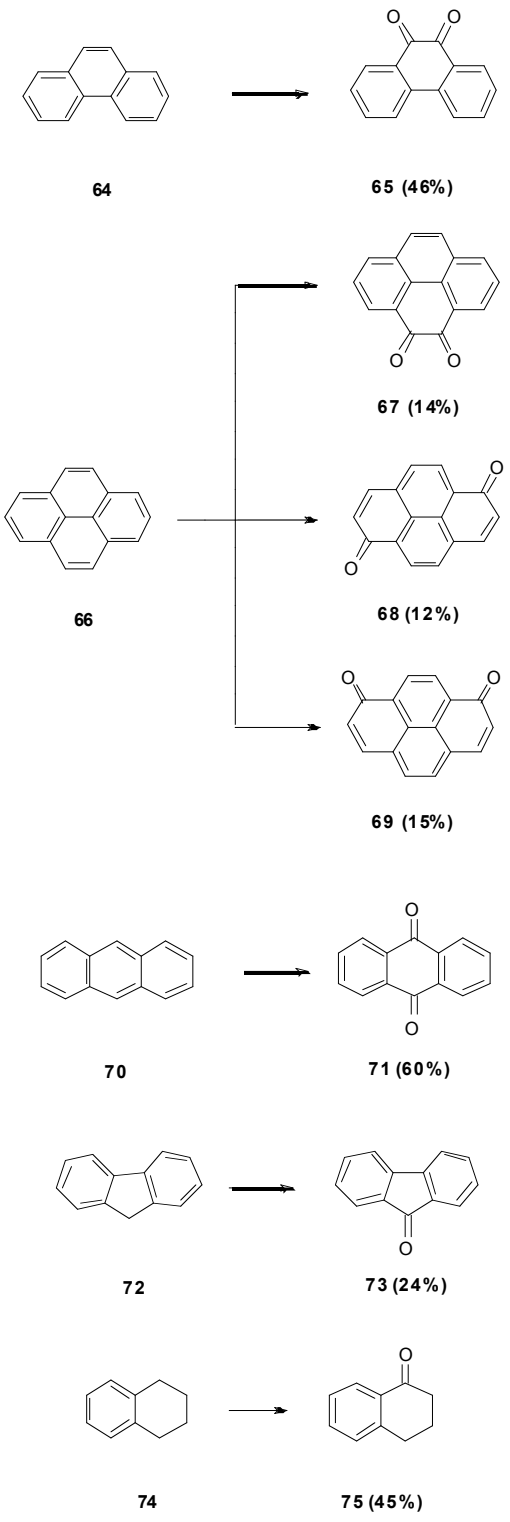


60 **61**

62 **63**

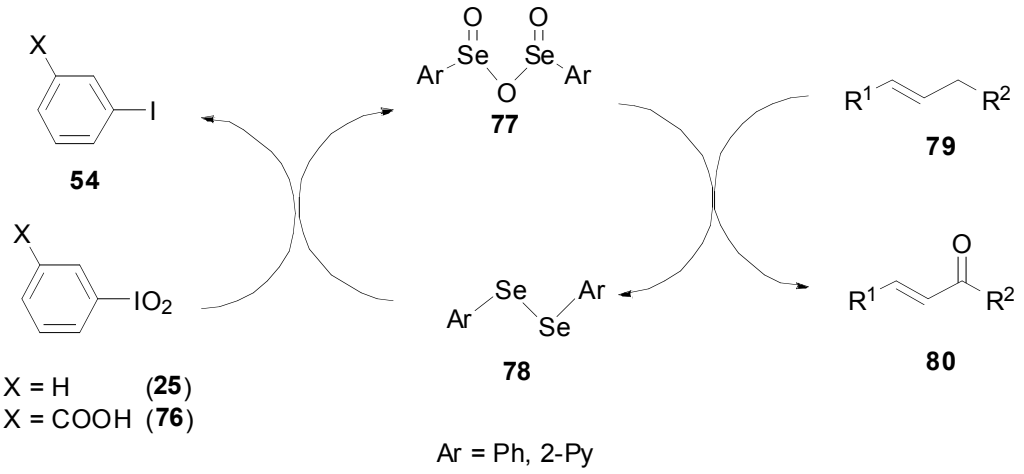
Scheme 23

Activated C–H bonds can be oxidized by iodylbenzene **25** in nitrobenzene at 170 °C.[144] This procedure is useful for preparation of benzophenone **61** from 1,1,4,4-tetraphenylbuta-1,3-diene and diphenylmethane; phenanthrenequinone **65** from phenanthrene **64**; pyrene-4,5-quinone **67**, pyrene-1,6-quinone **68** and pyrene-3,6-quinone **69** from pyrene **66**; anthraquinone **71** from anthracene **70**; fluorenone **73** from fluorene **72**, and tetralone **75** from tetralin **74** (Scheme 24).



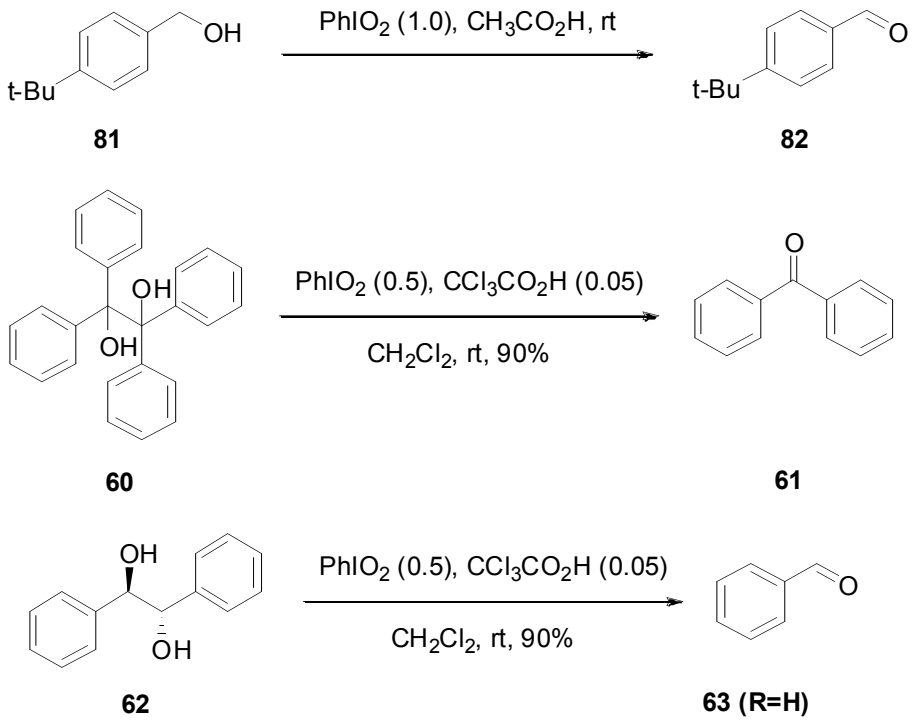
Scheme 24

Catalytic oxidative systems with iodylbenzene as a stoichiometric co-oxidant have been developed. Barton and coauthors reported an efficient allylic oxidation method with 2-pyridineseleninic anhydride **77** (Ar = 2-Py) as the principal oxidant, generated *in situ* by oxidation of the corresponding diselenide **78** with iodylbenzene **25** or 3-iodylbenzoic acid **76** (Scheme 25).[145]



Scheme 25

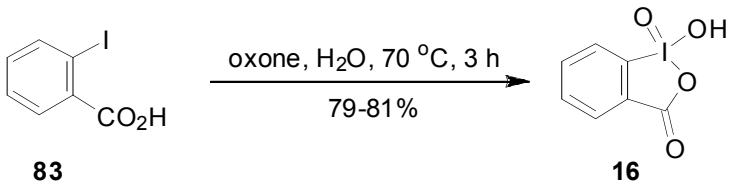
Several catalytic systems have been developed for the oxidation of alcohols using iodylbenzene **25** as an oxidant. The reactions are strongly catalyzed by acetic or trichloroacetic acid decreasing the time of reaction and inc reasing the yields (Scheme 26).[141,143,146]



Scheme 26

D. Five-membered Iodine(V) Heterocycles

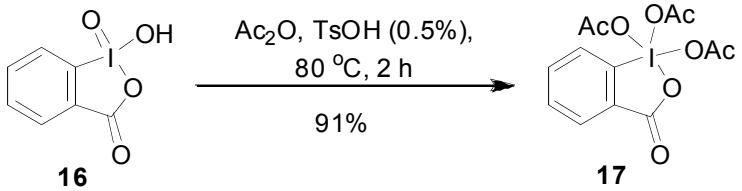
Among others five-membered iodine(V) heterocycles 2-iodoxybenzoic acid or IBX **16** is the most important reagent. IBX **16** is a cyclic benziodoxole oxide explosive under excessive heating or impact. IBX **16** is the DMP precursor and is insoluble in most organic solvents. The first time it was prepared in 1893. The preparation of IBX **16** involves oxidation of 2-iodobenzoic acid with potassium bromate in aqueous solution of sulfuric acid.[148] Also, IBX **16** can be prepared by oxidation of 2-iodobenzoic acid **83** with excess peracetic acid or aqueous sodium hypochlorite.[149] Santagostino and coworkers reported the convenient method for preparation of IBX **16** involving oxidation of 2-iodobenzoic acid **83** with Oxone (Scheme 27).[150]



83 **16**

Scheme 27

In 1983 Dess and Martin transformed IBX **16** to the soluble triacetoxybenziodoxole **17** by heating IBX **16** with acetic anhydride to 100 °C.[151] Now, this compound is commonly referred to as Dess-Martin periodinane (DMP) and used for the oxidation of alcohols to the respective carbonyl compounds.[84] To obtain DMP **17**, IBX **16** is treated with acetic anhydride in the presence of *p*-toluenesulfonic acid (TsOH) (Scheme 28).[152]



16 **17**

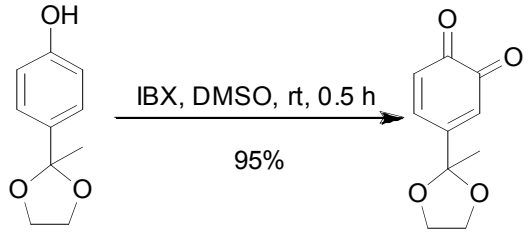
Scheme 28

The mild reaction conditions: room temperature, absence of acidic or basic additives, high chemoselectivity, and preparative convenience have made this reagent especially suitable for the oxidation of substrates containing sensitive functional groups such as unsaturated moieties, amino groups, silyl ethers, phosphine oxides, sulfides, selenides. DMP oxidation is accelerated by the addition of water to the reaction mixture immediately before or during the reaction.[153]

IBX **16** is useful for the oxidation reactions of 1,2-diols. In contrast to DMP **17**, which generally cleaves the glycol C–C bond, IBX **16** in DMSO oxidizes 1,2-diols to α-ketols[154,155] or α-diketones (1,2-diketones or 2-hydroxyketones), and no C-C bond

cleavage occurs.[156,157] But the use of IBX **16** extremely restricted by its low solubility in most organic solvents, except DMSO.

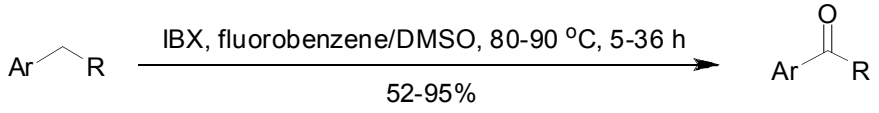
Various phenols were oxidized to *o*-quinones by IBX **16** (Scheme 29).[158]



84 **85**

Scheme 29

IBX **16** is an efficient and selective reagent for the oxidation of benzylic positions for variety of different substrates without overoxidation (Scheme 30).[159]

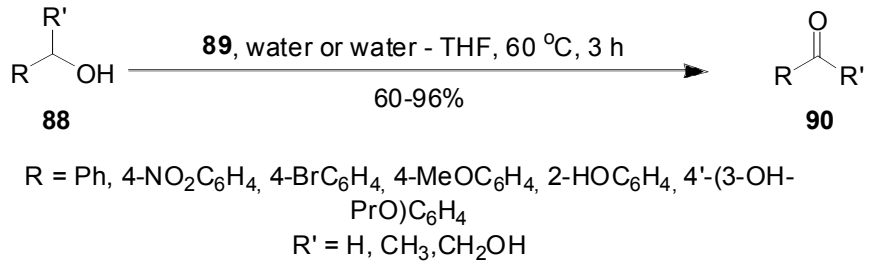


86 **87**

Ar = Ph, 4-*t*-BuC_6H_4, 2-MeC_6H_4, 3-IC_6H_4, 4-BrC_6H_4, 3,4-$(MeO)_2C_6H_3$, 2-PhC_6H_4, 4-(4-pyridyl)C_6H_4, etc.
R = H, C_3H_7, etc.

Scheme 30

Several IBX **16** analogs have been synthesized and reported in literature. For instance, Thottumkara and Vinod have reported the preparation of the water-soluble analog of IBX, *m*-iodoxyphthalic acid (mIBX) **89**, which oxidizes benzylic and allylic alcohols to carbonyl compounds in water (Scheme 31).[160]

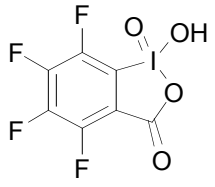


88 **90**

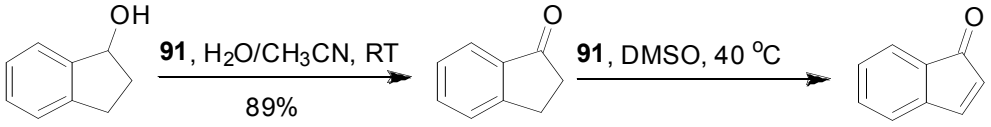
R = Ph, 4-$NO_2C_6H_4$, 4-BrC_6H_4, 4-$MeOC_6H_4$, 2-HOC_6H_4, 4'-(3-OH-PrO)C_6H_4
R' = H, CH_3,CH_2OH

Scheme 31

Wirth and coworkers have reported perfluorinated IBX or FIBA **91**. FIBA **91** showed similar reactivity to IBX **16** with alcohols, sulfides and unsaturated amides (Scheme 32).[161]



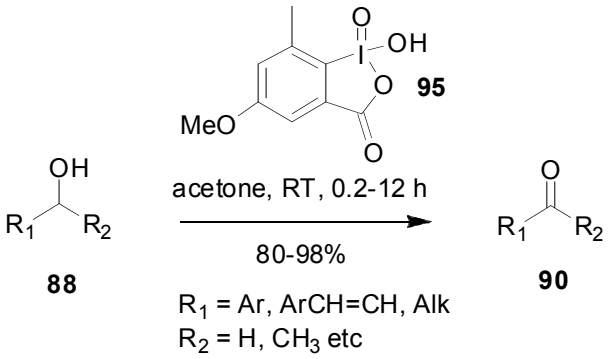
91



92 **93** **94**

Scheme 32

Preparation and reactivity of p-methoxy-o-methyl-IBX **95** have been reported by Moorthy and coworkers. They assumed that additional methoxy group increases solubility of IBX in organic solvents. For instance, this reagent can oxidize various alcohols (Scheme 33).

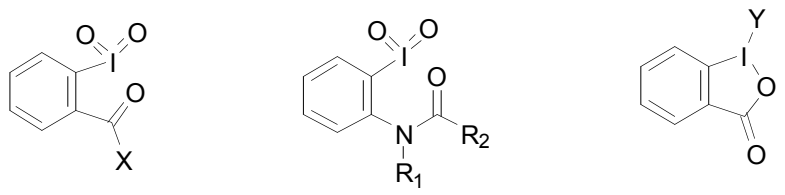


Scheme 33

E. Pseudocyclic Iodine(V) Reagents

Pseudocyclic iodine(V) compounds have much better solubility than non-cyclic aryliodyl derivatives, which is explained by a partial disruption of their polymeric nature due to the redirection of secondary bonding. Recently, pseudo-benziodoxoles and pseudo-benziodoxazines have found increasing practical application in organic synthesis as efficient oxidizing reagents.

Aryliodyl derivatives bearing an appropriate substituent in the *ortho*-position to the iodine, are characterized by the presence of a pseudocyclic structural moiety due to a strong intramolecular secondary bonding between the hypervalent iodine center and the oxygen atom in the *ortho*-substituent. When iodine(V) atom and the *ortho*-substituent's oxygen atom are located in 1,5-position, the planar, five-membered pseudo-benziodoxole structural moiety **18** arises. On the other hand, 1,6-arrangement of iodine and oxygen atoms results in a non-planar six-membered ring of pseudo-benziodoxazines. Generally, the distance between the iodine and oxygen atoms amounts to 2.6 - 2.7 Å in pseudo-benziodoxoles **18** and pseudo-benziodoxazines **20**,[72-76] which is comparable with the I-O bond length in benziodoxoles **96** from 2.2 Å to 2.5 Å (Scheme 34).

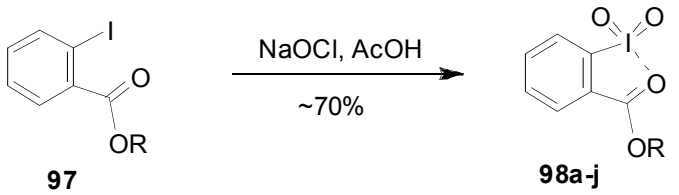


18 **20** **96**

X=OR, NHR, etc.; R_1,R_2 = H, alkyl, aryl; Y = OH, N_3, PH, etc.

Scheme 34

Esters of 2-iodoxybenzoic acid (IBX–esters) **98**, as an example of a new class of pentavalent iodine compounds with a pseudo-benziodoxole structure, can be conveniently prepared by hypochlorite oxidation of iodobenzoate esters **97** (Scheme 35).[74,75] This method allows to prepare reagents **98** derived from a wide variety of precursors. All products **98** have moderate to good solubility in common organic solvents.



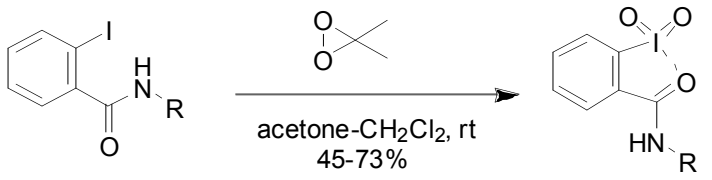
97 **98a-j**

a: R = Me; **b:** R = Et; **c:** R = *i*-Pr; **d:** R = *tert*-Bu;
e: R = (–)-menthyl; **f:** R = (+)-menthyl; **g:** R = (±)-menthyl;
h: R = [(1*S*)-*endo*]-(–)-bornyl; **i:** R = 2-adamantyl; **j:** R = 1-adamantyl

Scheme 35

Reagents **98a-j** can oxidize a range of alcohols to the respective carbonyl compounds under mild conditions.

The new 2–iodoxybenzamides (IBX-amides) **100** are stable and soluble compounds with unique and synthetically valuable oxidizing properties, they were prepared by our group[73] (Scheme 36). 2–Iodoxybenzamides **100** have increased solubility and stability in comparison to other I(V) reagents. 2–Iodoxybenzamides **100** are useful oxidizing reagents towards alcohols with a reactivity pattern similar to IBX. A wide range of alcohols can be oxidized by these reagents to the respective carbonyl compounds under mild conditions in chloroform.[75,162]

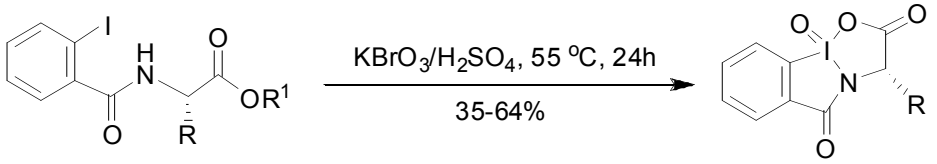


99 **100a-g**

a: R = (*S*)-CH(CH$_3$)CO$_2$CH$_3$; **b**: R = (*R*)-CH(CH$_3$)CO$_2$CH$_3$;
c: R = (*S*)-CH(CH$_2$Ph)CO$_2$CH$_3$; **d**: R = (*S*)-CH(*i*-Bu)CO$_2$CH$_3$;
e: R = CH$_2$CH$_2$CO$_2$H; **f**: R = CH(CH$_3$)CH$_2$CO$_2$H; **g**: R = (*R*)-CH(Ph)CH$_3$

Scheme 36

Benziodazole oxides **102** can be regarded as selective, chiral oxidizing reagents for organic synthesis, and can be prepared by oxidation of the readily available 2-iodobenzamides **101** with potassium bromate (Scheme 37).[163]

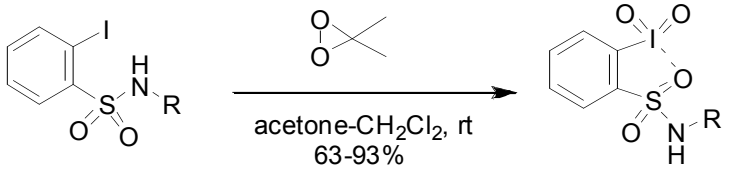


101 **102**

R = CH$_3$, *i*-Pr, *i*-Bu; R^1 = H or CH$_3$

Scheme 37

Amides of 2-iodoxybenzenesulfonic acid **104a-e** were recently prepared by the dioxirane oxidation of the corresponding 2-iodobenzenesulfamides **103** and isolated as stable, microcrystalline products (Scheme 38).[136]



103 **104a-e**

a: R = (*S*)-CH(CH$_3$)CO$_2$CH$_3$; **b**: R = (*S*)-CH(CH$_2$Ph)CO$_2$CH$_3$;
c: R = (*S*)-CH(*i*-Pr)CO$_2$CH$_3$; **d**: R = (*S*)-CH(*i*-Bu)CO$_2$CH$_3$;
e: R = (*R*)-CH(Ph)CH$_3$

Scheme 38

These representatives of the pseudocyclic hypervalent iodine compounds can selectively oxidize benzyl alcohols to aldehydes.

Chapter 2

Results and Discussion

2. Development of New Oxidizing Systems Based on Hypervalent Iodine.

2.1 Electrophilic iodination of aromatic compounds. Preparation of New Hypervalent Iodine(V) Oxidizing Reagent Potassium 4-Iodylbenzenesulfonate and its Application for Electrophilic Iodination of Aromatic Compounds.

A. Introduction

In recent years, iodoarenes have gained increasing importance because they are widely used as building blocks in organic synthesis. They are particularly important as indispensable substrates for numerous methods of C-C, C-N, and C-O bond formation, for the chemistry of heterocyclic and organometallic compounds, and for the synthesis of polyvalent iodine organic compounds. In addition, polyvalent organoiodine compounds have served as cooxidants in the iodination of arenes.

Aryl iodides are highly valuable compounds, particularly in the area of cross-coupling reactions. They are the most reactive of the aryl halides in cross-coupling reactions and thus have a very wide range of reactions and reaction conditions (many of which are extremely mild) to which they can be applied. At the same time, aryl iodides are generally more difficult to prepare and more expensive than the corresponding bromides or chlorides. In response to this situation, a tremendous amount of research has gone into developing more mild cross-coupling conditions for aryl bromides and chlorides.

Aryl iodides can easily be transformed into tritium labeled compounds by metal-mediated hydrodehalogenation and, thus, are important intermediates in medicinal chemistry.[164,165,166] The number of functional transformations, for example, Heck reactions as well as Stille and Negishi cross couplings, originating from aryl iodides also

make these compounds valuable synthetic intermediates.

We have developed a new efficient hypervalent iodine (V) oxidizing reagent potassium 4-iodylbenzenesulfonate **107** that has mild and chemoselective oxidizing properties, combined with benign environmental character. This water-soluble reagent can be used for oxidation of alcohols to carbonyl compounds and oxidative iodination of aromatic compounds under aqueous conditions. In particular electrophilic iodination of aromatic compounds gives many various aryl iodides which importance was discussed above. To obtain potassium 4-iodylbenzenesulfonate **107,** 4-iodobenzenesulfonic acid **105** was used as a starting material.

A keen interest in benzenesulfonic acids is aroused due to the presence of the sulfo-group in their structure that gives these iodoaromatic compounds an important property: to be water-soluble. This fact allows chemists to carry out reactions with such compounds and synthesize hypervalent iodine compounds and their derivatives in water media, and perform environmentally friendly green-chemistry reactions.

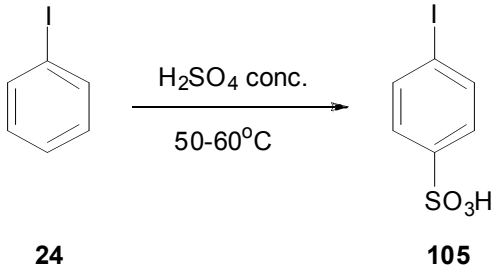
4-Iodobenzenesulfonic acid **105** was chosen as starting material because it is a convenient compound for synthesis of our target reagent, which meets the requirements and needs of our project: to prepare hypervalent iodine reagent that can be used in environmentally friendly conditions and to be water-soluble, while it is a powerful oxidizing reagent. Furthermore, it is easy to synthesize using common reagents and the preparation procedure of it does not involve complicated chemical operations.

Also, it should be mentioned that 4-iodobenzenesulfonic acid **105** is of interest by its own it is a starting material for preparation of pipsyl chloride that is widely used in biochemistry to analyze amino acids and steroid hormones.[167]

It is known that unlike the majority of electrophilic aromatic substitution reactions, the sulfonation reaction is reversible and requires thorough and specific selection of reaction conditions to obtain desired product. Moreover, aryl iodides, which contain electron-donating groups, in the presence of sulfuric acid undergo disproportionation reaction that gives polyiodoarenes as products. This reaction is known as Jacobsen reaction or Jacobsen rearrangement.

B. Results and Discussion

A convenient method to obtain 4-iodobenzenesulfonic acid **105** (starting material for our hypervalent iodine reagent) was developed by means of sulfonation of iodobenzene **24** in presence of 94-98% sulfuric acid under stirring at 50-60^{o}C. 4-Iodobenzenesulfonic acid was obtained with 90-95% yield after 30 hours of stirring, when 1 to 1.5 ratio (iodobenzene to sulfuric acid respectively) was used (Scheme 39). Precipitated crystals of 4-iodobenzenesulfonic acid **105** were filtered every 5 hours during the reaction progress or were extracted in hot chloroform. In case when the temperature of reaction mixture was higher than 50-60^{o}C, the percent yield of target product was lower, and did not exceed 60%. Furthermore, side products formed due to the disproportionation reaction (di- and tri-iodobenzenes).



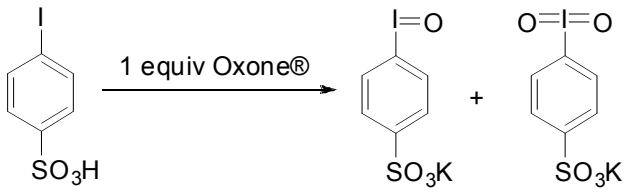
Scheme 39

It is important to emphasize that in given conditions the reaction is highly regioselective and as a result only para-substituted products were formed. While when oleum (fuming sulfuric acid) was used for this reaction ortho-substituted product (2-iodobenzenesulfonic acid) was formed as well (up to 5%).

4-Iodobenzenesulfonic acid **105** is highly hygroscopic and absorbs water easily. Therefore it must be stored in desiccator with calcium chloride or sulfuric acid. Chloroform or chloroform-hexanes mixture are good solvents for its recrystallization.

Oxidation of 4-iodobenzenesulfonic acid **105** in the presence of Oxone® (1:1 ratio) in water gave the mixture of potassium salts of 4-iodobenzenesulfonic acid **106** and **107** containing hypervalent iodine (III) and hypervalent iodine (V) in structure (1:1 ratio)

(Scheme 40). Potassium peroxymonosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, which is usually sold under the commercial name "Oxone®", is known as inexpensive and effective oxidant. It has been used in various synthetic applications, has relatively good storage ability and it is convenient reagent and safe to handle.

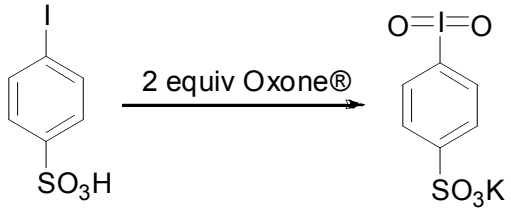


105 **106** **107**

Scheme 40

As it was expected, these salts are water-soluble and so of interest for "green" chemistry. However, the separation of these two salts was not achieved after many attempts.

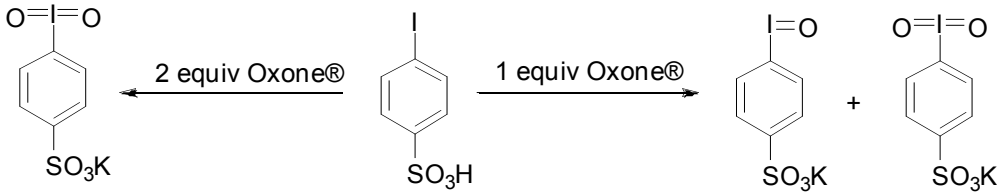
Later on, the amount of Oxone® was doubled, and target compound potassium 4-iodylbenzenesulfonate **107** was obtained by filtration with 94% yield as single product (Scheme 41).



105 **107**

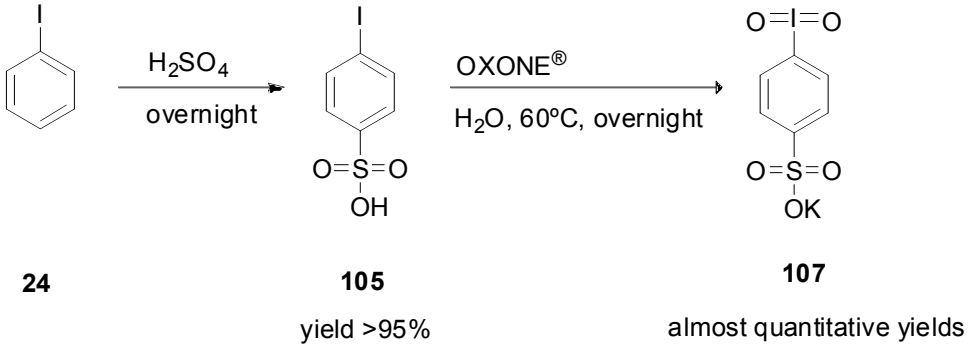
Scheme 41

So, amount of Oxone® used affects the product type and distribution (Scheme 42):



Scheme 42

Potassium 4-iodylbenzenesulfonate **107** was prepared using oxidation of 4-iodylbenzenesulfonic acid **105** as starting material within the scope of our goal to obtain recyclable hypervalent iodine compounds that can be employed in organic syntheses accordingly with environmentally friendly "green" chemistry conception. The scheme of preparation of potassium 4-iodylbenzenesulfonate **107** from starting material is given below (Scheme 43):



Scheme 43

This new hypervalent iodine (V) reagent can be heated up to 259 ^{o}C with further explosion. Also, potassium 4-iodylbenzenesulfonate **107** did not change its oxidizing properties even after 3 years of storage at room temperature.

The structure of the reagent **107** was confirmed by single crystal X-ray crystallography (CAMERON diagrams of reagent **107** are presented in Figures 1 and 2, and selected bond distances are listed in Table 1).

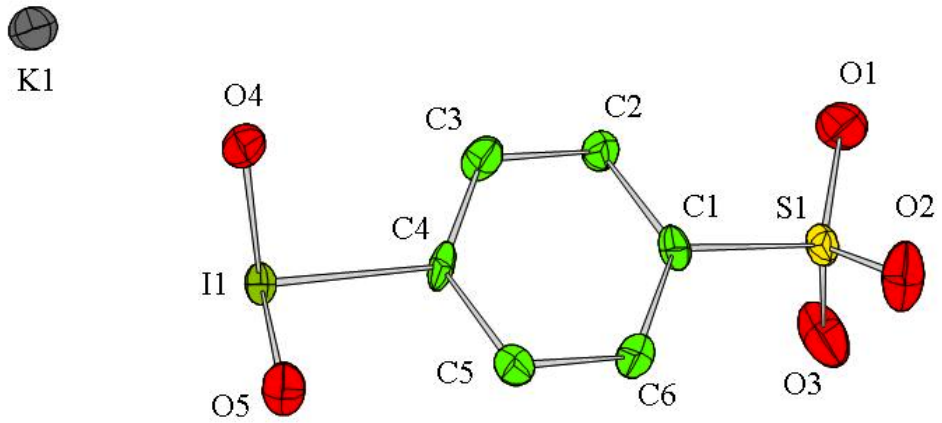


Figure 1. CAMERON drawing of potassium 4-iodylbenzenesulfonate **107**

Perspective view of potassium 4-iodylbenzenesulfonate **107** with 50% ellipsoid probability.

Table 1. Selected interatomic distances [Å] and angles [^{o}] in of potassium 4-iodylbenzenesulfonate **107**.

Bond	Distance, [Å]
I1 – O4	1.792(9)
I1 – O5	1.800(9)
I1 – C4	2.111(11)
C1 – S1	1.773(11)
S1 – O1	1.452(10)
S1 – O2	1.455(10)
S1 – O3	1.454(11)
O4-I1-O5	102.9(5)

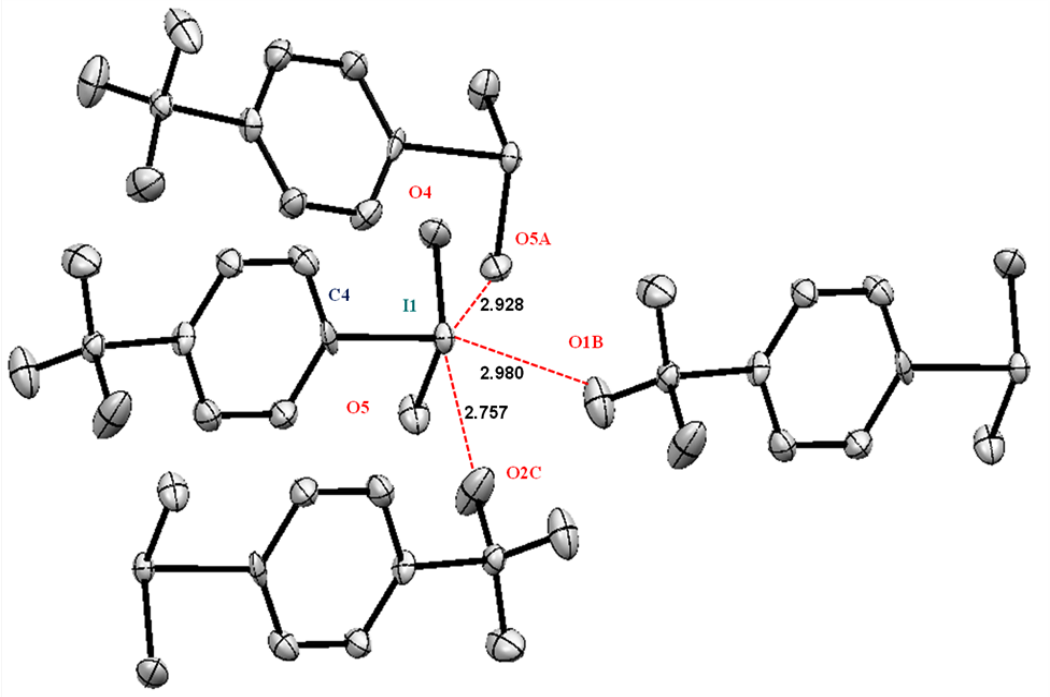


Figure 2. Intermolecular secondary bonding in X-ray structure of potassium 4-iodylbenzenesulfonate **107**.

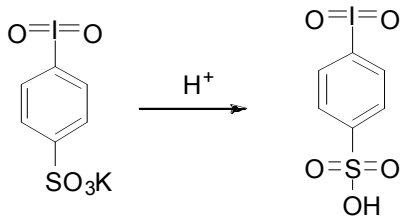
The X-ray data shows the structure of our reagent contains hypervalent iodine (V) which is bound with two oxygen atoms. Also, it shows that potassium 4-iodylbenzenesulfonate **107** contains the cation of potassium and a negatively charged sulfo-group that gives molecule ionic character and, as a consequence, the property of water-solubility. Intermolecular secondary bonding shows that hypervalent iodine (V) and oxygen atom from sulfo-group are attracted.

In comparison with the majority of known hypervalent iodine compounds, which are covalent, our reagent has ionic character: it is a potassium salt of arylsulfonic acid, so it has good solubility in water. This fact allows using it in water. Another advantage of our reagent is its accessibility. It can be very easily obtained from cheap starting materials and synthesized with good yields.

At the next step we have investigated the applicability, efficacy, and chemical properties of our newly developed hypervalent iodine (V) reagent for electrophilic iodination of aromatic compounds. We have proposed method for iodination of aromatic

compounds, which includes different protocols. The difference between these protocols is only in the solvent, temperature, and acid used. Solvent, temperature, and acid are varied depending on structure of substrate for iodination.

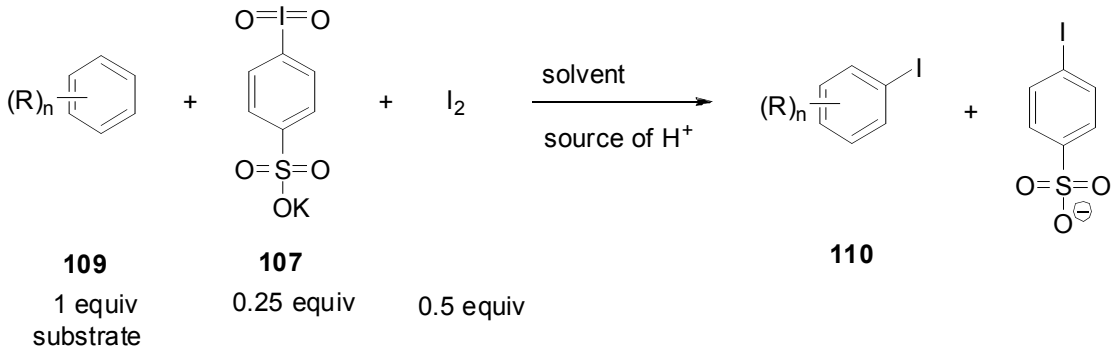
We have found that aryliodides can be obtained in a good yields by oxidation of wide range of appropriate arenes with potassium 4-iodylbenzenesulfonate **107**, only in presence of acid (in particular, 5% sulfuric acid or acetic acid), otherwise, in the absence of acid (protons) in the reaction mixture, potassium 4-iodylbenzenesulfonate does not interact with substrate. It was assumed, that indeed, potassium 4-iodylbenzenesulfonate **107** under aqueous conditions with Amberlyst 15 or Amberlite IRA 120 gives new reagent - 4-iodylbenzensulfonic acid **108**. This new reagent has better solubility in water than potassium 4-iodylbenzenesulfonate **107**, but at the same time is less stable. Thereby, we propose, that in acidic media the actual oxidant is not potassium 4-iodylbenzenesulfonate **107**, but 4-iodylbenzensulfonic acid **108** (Scheme 44).



107 **108**

Scheme 44

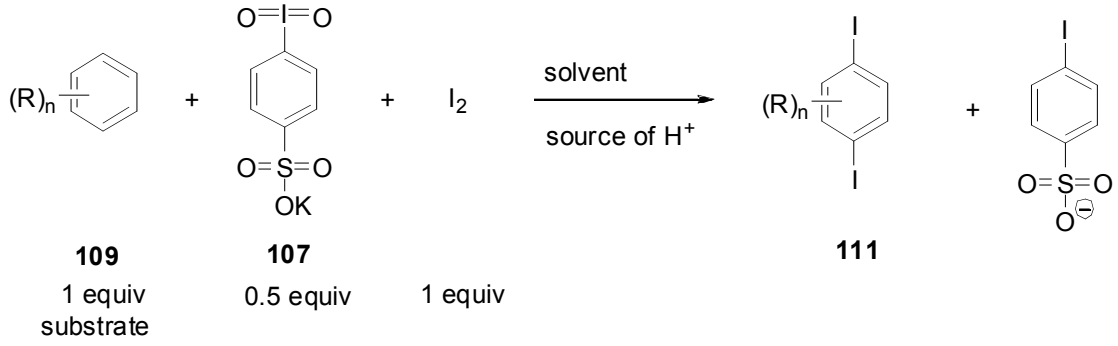
The common scheme of electrophilic iodination of aromatic compounds to obtain mono-iodo-substituted products is presented below (Scheme 45). To get mono-substituted product iodine should be used in stoichiometric amounts (without excess):



n=1,2,3,4

Scheme 45

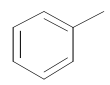
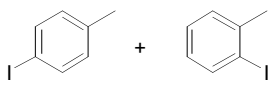
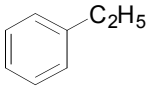
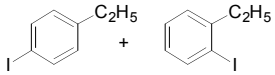
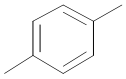
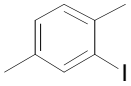
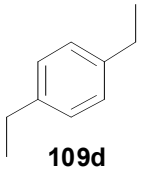
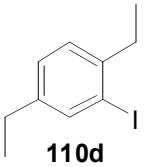
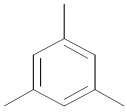
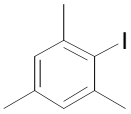
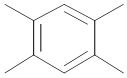
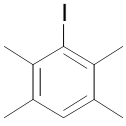
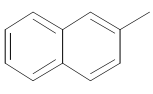
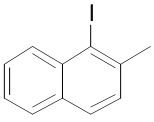
We have found that many practically useful aryl iodides can be obtained in a good yield by oxidation of appropriate arenes (0.2 mmol), iodine (0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (0.055-0.06 mmol) in aqueous conditions with source of protons (Scheme 45), as well as diiodinated products when amounts of iodine and reagent are doubled (Scheme 46).

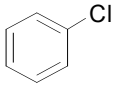
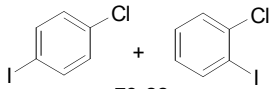
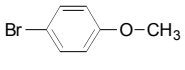
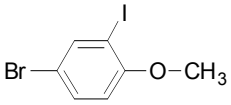
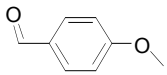
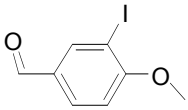
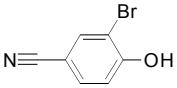
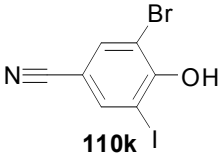
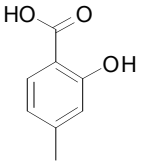
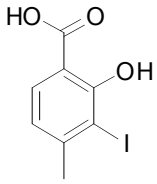
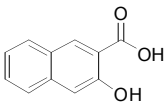
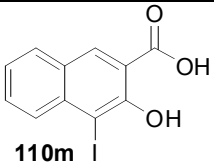
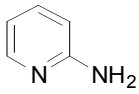
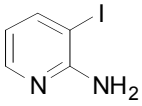


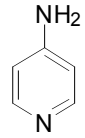
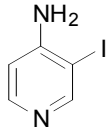
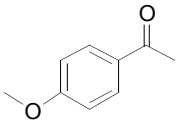
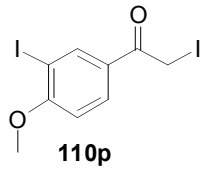
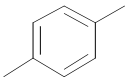
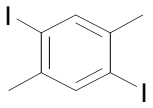
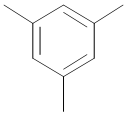
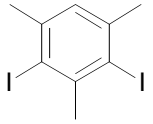
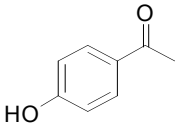
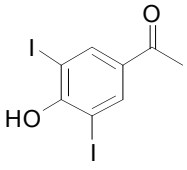
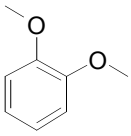
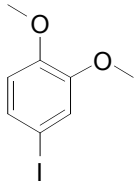
Scheme 46. Diiodination of arenes.

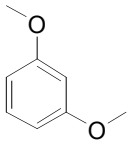
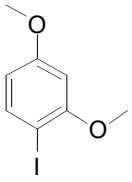
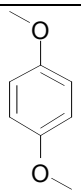
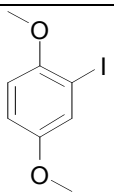
The preparative yields, structure of products, and reaction conditions are summarized in Table 2.

Table 2. Iodination of aromatic compounds using potassium 4-iodylbenzensulfonate **107**[a].

Entry	Substrate **109**	Product **110,111**	T, °C	Time, h	Yield, [%][b]		
					Method A	Method B	Method C
1	 **109a**	 **110a** 84:16 **110a'**	65	Over night	98[c]	-	
2	 **109b**	 **110b** 86:14 **110b'**	65	Over night	83[c]		
3	 **109c**	 **110c**	65	Over night	84[d]	-	
4	 **109d**	 **110d**	65	Over night	89[d]	-	
5	 **109e**	 **110e**	65	Over night	98[d]	-	
6	 **109f**	 **110f**	65	Over night	98[d]	-	
7	 **109g**	 **110g**	65	Over night	86	-	

8	 **109h**	 **110h** 78:22 **110h'**	65	48	99[c]	-	
9	 **109i**	 **110i**	65	Over night	90	-	
10	 **109j**	 **110j**	65	Over night	97	-	
11	 **109k**	 **110k**	RT	Over night	77	80[e]	
12	 **109l**	 **110l**	RT	Over night	84	87[e]	
13	 **109m**	 **110m**	RT	Over night	92	92[e]	
14	 **109n**	 **110n**	RT	24	51	50[e]	

15	 **109o**	 **110o**	RT	Over night	88	-	88
16	 **109p**	 **110p**	40	18	65	-	
17	 **109q**	 **111q**	65	Over night	92[f]	-	
18	 **109d**	 **111d**	65	Over night	99[f]	-	
19	 **109r**	 **111r**	RT	Over night	88[f]	94[e]	
20	 **109s**	 **110s**	80	1	-	-	96[g]

21	 **109t**	 **110t**	80	6	-	-	98[g]
22	 **109u**	 **110u**	80	11	-	-	90[g]

[a] Reaction conditions: Arenes (0.2 mmol), iodine (0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (0.05-0.06 mmol), MeCN (0.5 mL) and aq. H_2SO_4 (5%, 0.5 mL). [b] Isolated yield. [c] Determined by GC-analysis. [d] Reaction conditions as in protocol [a], but 0.1 mmol iodine was used. [e] Reaction conditions: Arenes (0.2 mmol), iodine (0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (0.05-0.06 mmol), MeCN (0.5 mL) and aq. H_2SO_4 (5%, 0.5 mL). [f] Di-iodination reaction conditions: Arenes (0.2 mmol), iodine (0.22 mmol) and potassium 4-iodylbenzenesulfonate **107** (0.12 mmol), MeCN (0.5 mL) and Amberlyst 15 (100 mg). [g] Dimethoxybenzene (1.0 mmol) in acetic acid (5 mL), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate **107** (106 mg, 0.3 mmol).

Only for iodination of toluene, ethylbenzene, and chlorobenzene we obtained mixture of para- and ortho-iodo-substituted products with para-product as a major product.

In order to achieve our goal we had to find and use different reaction conditions depending on the nature of substrate and effects of substituents in it. We changed temperature, solvent, and amount of iodine and reagent. When reaction did not occur at room temperature or the rate of reaction was slow, additional heat was applied to promote the reaction, increasing the temperature up to 80^{o}C. A solvent was chosen depending on substituent that starting arene has, taking into account stability and nature of compound, and sensitivity towards oxidation process and acid media. The crucial moment is amount of iodine and reagent used. If target product is mono-iodosubstituted product, then iodine should be used in stoichiometric amounts, if di-iodosubstituted product is a target product, then amount of iodine and reagent should be doubled.

It is crucially important to have source of protons in reaction mixture for iodination reaction to occur. Because reactions that were carried out in ethyl acetate without sulfuric acid or acetic acid at 65ºC did not occur even after amounts of hypervalent iodine (V) reagent and molecular iodine were doubled and quadrupled.

All previously reported aryl iodides were identified by comparison of their NMR spectra and melting points with literature data. New products were identified by ^{1}H, ^{13}C NMR spectra, GC-MS, and elemental analysis. The detailes are reported in the experimental section.

C. Summary

To summarize all mentioned above, we have developed a safe, convenient, efficient, and straightforward procedure for preparing new, effective, water-soluble, and environmentally friendly hypervalent iodine (V) reagent - potassium 4-iodylbenzenesulfonate **107**, useful for oxidative iodination of aromatic compounds. Potassium 4-iodylbenzenesulfonate was prepared and characterized. This reagent allows to obtain various aryl iodides that are highly valuable compounds, particularly in the area of cross-coupling reactions.

Potassium 4-iodylbenzenesulfonate **107** is an efficient green chemistry reagent for oxidative iodination of aromatic compounds. It is a water-soluble compound due to its ionic nature, and it is environmentally friendly reagent, which has great potential and high possibility of important application in organic syntheses.

Furthermore, iodination reactions were studied and investigated with wide range of different aromatic substrates in presence of newly developed hypervalent iodine (V) reagent.

All in all, by changing reaction conditions we confirmed that source of protons is required and necessary for iodination reaction to occur. Green chemistry synthesis can be performed with newly synthesized, effective hypervalent iodine (V) reagent giving many different and useful aryl iodides. And finally, by changing amounts of reagent and iodine we can control the product we obtain (mono- or di-substituted product).

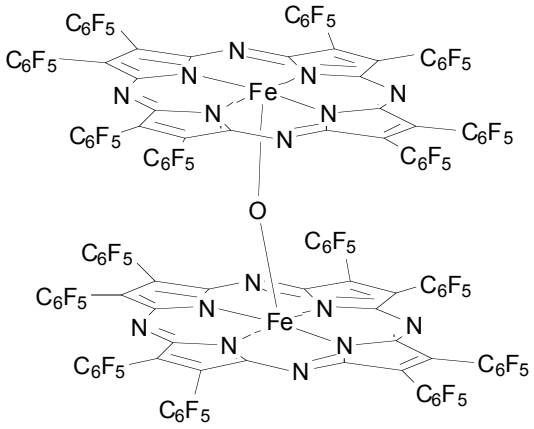
2.2 Oxidation Catalytic Reactions with Hypervalent Iodine Species

2.2.1 Reactivity Study of Newly Synthesized Metalloporphyrin Complex - Perfluoro-Iron(III) Tetraazaporphyrin (μ-oxodimer), and Influence of its Concentration on Catalytic Oxygenation Process. Method Optimization.

A. Introduction

Convenient hypervalent iodine reagent iodosobenzene **23**, (PhIO), is important as an efficient source of oxygen that has found widespread application in various oxygenation reactions. Traditionally, iodosobenzene **23** is the most common reagent for oxygenation reactions of organic substrates in presence of metalloporphyrin catalysts. This allows us to compare reactivity of newly synthesized metalloporphyrin catalysts with already known and previously investigated compounds. It helps researchers to have some kind of scale by which they can estimate the effectiveness of new metalloporphyrin catalysts. Iodosobenzene **23** is known to be an efficient source of oxygen for the oxygenation of hydrocarbons in the presence of Fe(III) porphyrin complexes. This property of PhIO **23** was first reported by Groves and co-workers in 1979. Since then, many studies were accomplished, that involved iodosobenzene **23** as an oxidant. It seems reasonable and rational to start investigation of properties and efficacy of a new catalyst under standard conditions, so we can compare its reactivity meaningfully. As iodosobenzene **23** is a standard oxidant in porphyrin catalytic oxidation, so, this compound allows us to compare catalytic activity of newly synthesized metal porphyrin complexes with already known catalysts in standard conditions. In other words, the goal of this part of our project was to investigate newly synthesized perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** as a new catalyst and compare its reactivity to previously synthesized and described metal porphyrin complexes. Also, it is important to mention that blank experiments are reported in literature, and were performed for iodosobenzene **23** and some organic substrates in dichloromethane, and the formation of products was not observed, even with low conversion.[168,169]

It is known that porphyrins are not very stable compounds and can undergo oxidation. But if fluorine atoms were introduced into the molecule, the stability upon oxidation increases. Therefore it is better to use fluorinated form of catalyst for oxidation reactions. The structure of catalyst is presented in Scheme 47 below.

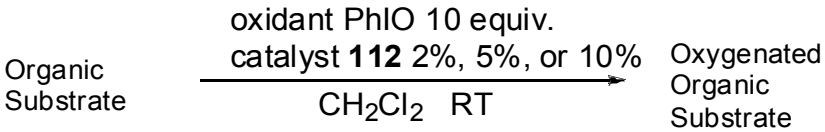


Scheme 47. Chemical structure of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**

B. Results and Discussion

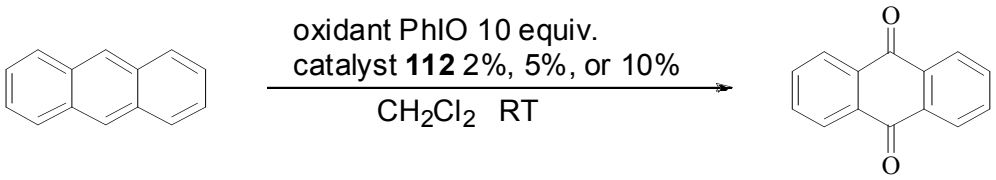
It was decided to start our investigation of reactivity of perfluoro-iron(III) tetraazaporphyrin (μ-oxodimer) **112** in oxidation reactions with most common and simple organic aromatic substrates. PhIO **23** represents iodine(III) species and was used as an oxidant in the reactions with : anthracene **70**, t-Bu-anthracene **115**, naphthalene **119**, phenanthrene **64**, adamantane **121**, and toluene **124**. These reactions mimic natural oxidations performed by the heme-containing cytochrome P-450 class of enzymes.

The common scheme for catalytic oxygenation reactions is presented below. (Scheme 48):



Scheme 48. Common scheme for catalytic oxygenation reactions

At first, a set of preliminary experiments was performed, to test the appropriate amount of catalyst needed for oxidation to be more efficient. The oxidation of anthracene **70** was carried out in dry dichloromethane with perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** and iodosobenzene **23** under stirring at room temperature. Samples of the reaction mixture were collected at first every 5 minutes, then every 30 minutes, filtered through silica gel, washed with a mixture of ethyl acetate and hexanes (2:3 v:v), and analyzed by GC-MS (Scheme 49).



70 **71**

Scheme 49. Oxygenation of anthracene **70** catalyzed by 2%, 5%, or 10% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112**

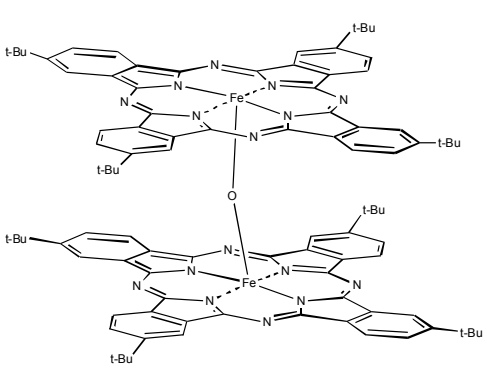
When 10 molar percent of catalyst was used, in 30 minutes we observed 100% conversion. For 5 molar percent of catalyst 100% conversion was achieved in 1 hour, and for 2 molar percent of catalyst 100% conversion was reached in 2 hours (Table 3). According to the GC-MS data, anthraquinone **71** and iodobenzene, resulting from the reduction of hypervalent iodine reagent, were the only products formed under these reaction conditions.

Table 3. Time for 100% conversion depending on concentration of catalyst **112** for anthracene **70**

Entry	Catalyst (mol%)	Conversion [%]	Time [h]
23	2	100	2
24	5	100	1
25	10	100	0.5

Our new catalyst perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112**

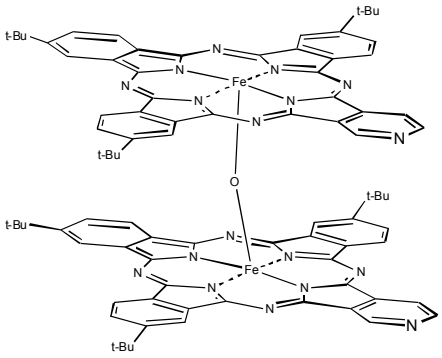
was compared with similar known metalloporphyrin complexes: iron(III) phthalocyanine-(μ-oxodimer) catalysts **113** and **114** that have been investigated in metal porphyrin-catalyzed oxygenation (Scheme 50).[170]



Catalyst 1

Iron(III) phthalocyanine-(μ-oxodimer)

113



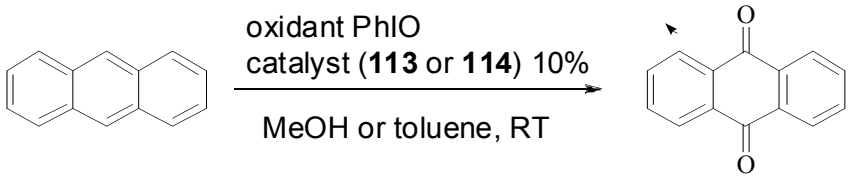
Catalyst 2

Iron(III) phtalocyanine-(μ-oxodimer)

114

Scheme 50. Iron(III) phthalocyanine-(μ-oxodimer) catalysts **113** and **114**[170].

These two catalyst **113** and **114** were investigated in binuclear iron(III) phthalocyanine(μ-oxodimer)-catalyzed oxygenation of anthracene **70** and results have been published (Scheme 51; Table 4).[170]



70 **71**

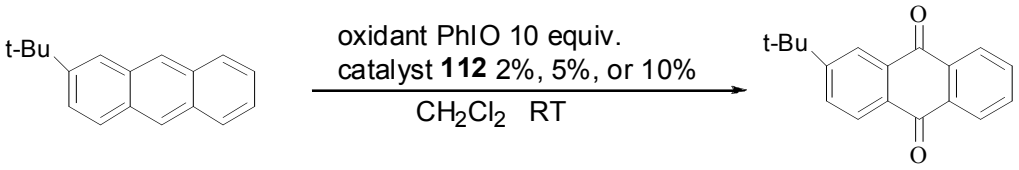
Scheme 51. Binuclear iron(III) phthalocyanine(μ-oxodimer)-catalyzed oxygenation using catalysts **113** and **114**[170].

Table 4. Binuclear iron(III) phthalocyanine (μ-oxodimer)-catalyzed oxygenation using catalysts **113** and **114**[170].

Catalyst	Catalyst (mol%)	Oxidant	Solvent	Conversion, %	Time, h
1	10	(PhIO)n	toluene	100	5
2	10	(PhIO)n	MeOH	100	2

The data presented in Scheme 51 and Table 4 clearly indicate that perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** is more efficient catalyst for oxygenation reaction than known catalyst **113** and catalyst **114**. It takes only 30 minutes for reaction to occur with 100% conversion for 10 mol% new catalyst versus 5 hours and 2 hours for catalyst **113** and catalyst **114** respactively in the same concentration.

In order to determine the scope of our procedure, we have performed a standard set of reactions. The same procedure was repeated for other different substrates. For example, in the case of 2-*tert*-butylanthracene **115** (Scheme 52) 10 mol% of catalyst, as well as 5 mol% gave 2-*tert*-butylanthraquinone **116** with 100% conversion in 1 hour. While in the case of 2 mol. % of catalyst just 98% conversion was achieved in 5 hours and did not change anymore (Table 5; Figure 3). Compared to the oxidation of anthracene **70**, the reaction of 2-*tert*-butylanthracene **115** was slower, probably due to steric hindrance caused by the *tert*-butyl group.



115 **116**

Scheme 52. Oxygenation of 2-*tert*-butylanthracene **115** catalyzed by 2%, 5%, or 10% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**

Table 5. Time for 100% conversion depending on concentration of catalyst **112** for 2-*tert*-butylanthracene **115.**

Entry	Catalyst (mol%)	Conversion [%]	Time [h]
26	2	98	5
27	5	100	1
28	10	100	1

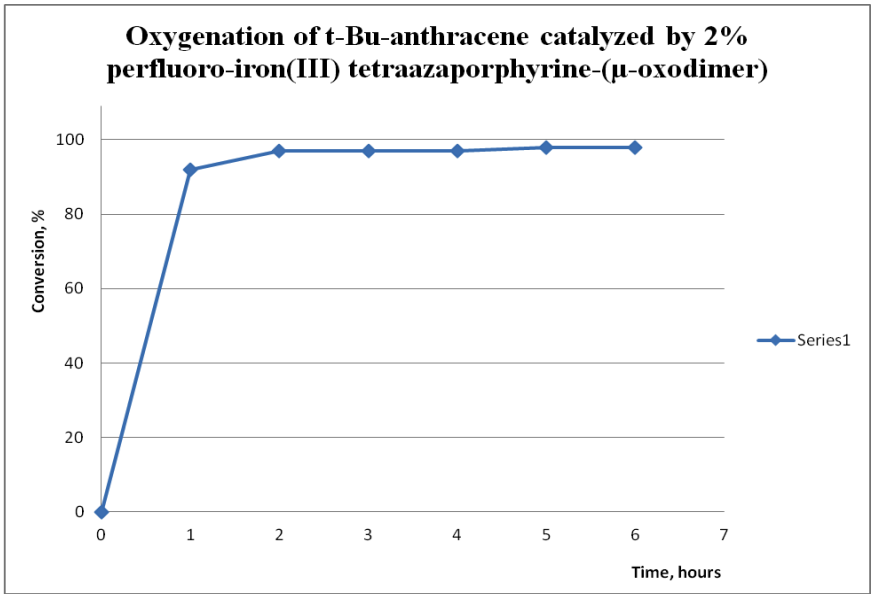
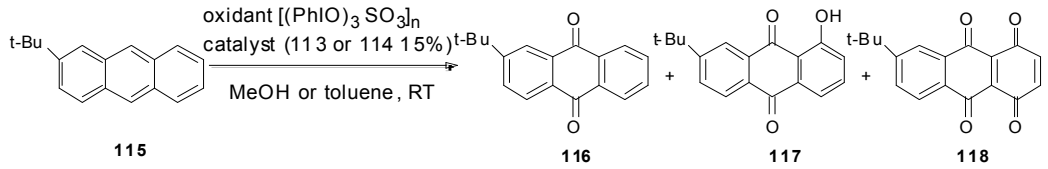


Figure 3. Characteristic curve of relationship between percent of conversion (%) and time (h) in catalytic oxidation of 2-*tert*-butylanthracene **115** to 2-*tert*-butylanthraquinone **116** using iodosobenzene **23** in dichloromethane at room temperature in the presence of 2% perfluoro-iron(III) tetraazaporphyrin-(µ-oxodimer) **112.**

Oxidation of 2-*tert*-butylanthracene **115** by perfluoro-iron(III) tetraazaporphyrin-(µ-oxodimer) **112** was compared with oxidation by known catalyst **113** and catalyst **114** (Scheme 53; Table 6).



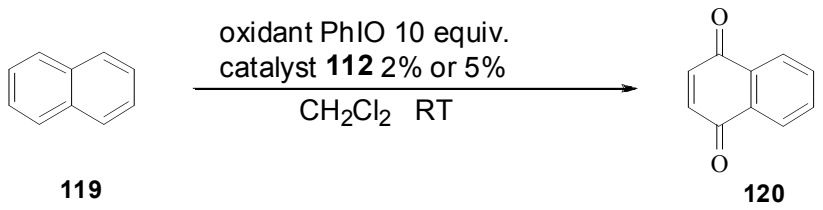
Scheme 53. Binuclear iron(III) phthalocyanine (μ-oxodimer)-catalyzed oxygenation using catalysts **113** and **114**[170]..

Table 6. Binuclear iron(III) phthalocyanine (μ-oxodimer)-catalyzed oxygenation using catalysts **113** and **114**[170].

Catalyst	Catalyst (mol%)	Oxidant	Solvent	Conversion, %	Time, h
1	15	[(PhIO)3 SO3]n	toluene	100 (quinone 1)	20
2	15	[(PhIO)3 SO3]n	MeOH	100 (76:13:11)	0.5

In the case of known catalyst **113** in amount of 15 mol% 100% conversion was achieved only in 20 hours giving 2-*tert*-butylanthraquinone **116**, while known catalyst **114** in amount of 15 mol% gave a mixture of three products **116**, **117**, and **118** in 30 minutes. The data presented in Scheme 53 and Table 6 undoubtedly shows that perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** is more reactive catalyst for oxygenation of 2-*tert*-butylanthracene **115** than catalyst **113** and **114**. Even 5 mol% of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** interconverts 2-*tert*-butylanthracene **115** to 2-*tert*-butylanthraquinone **116** in 1 hour with 100% conversion.

For naphthalene **119** as a substrate 100 % conversion was achieved in 1 hour in both cases 5 and 2 mol% of catalyst (Scheme 54; Table 7). GC-MS analysis of the reaction mixture indicated the presence of a single product of oxidation **120** along with iodobenzene, resulting from the reduction of reagent **23.**

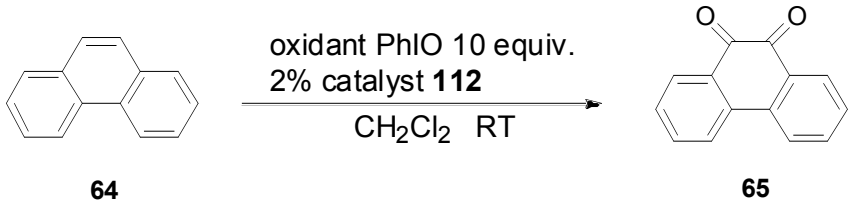


Scheme 54. Oxygenation of naphthalene **119** catalyzed by 2% or 5% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**

Table 7. Time for 100% conversion depending on concentration of catalyst **112** for naphthalene **119.**

Entry	Catalyst (mol%)	Conversion [%]	Time [h]
29	**2**	**100**	**1**
30	**5**	**100**	**1**

Oxygenation of phenanthrene **64** catalyzed by 2 mol% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** is presented below (Scheme 55; Table 8).



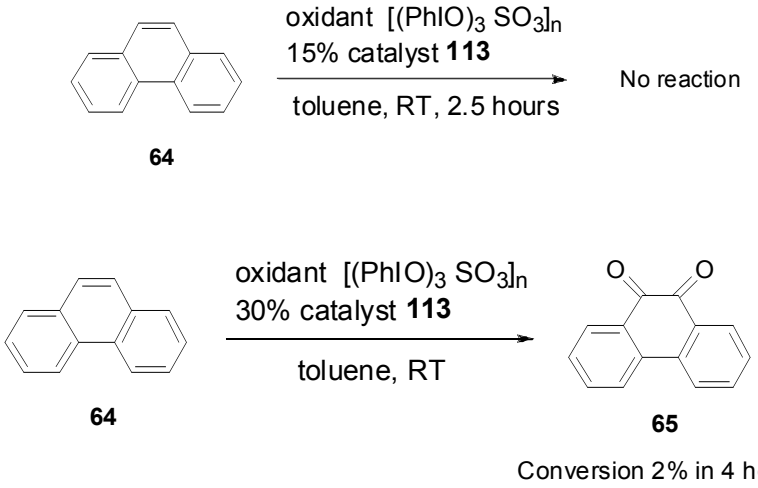
Scheme 55. Oxygenation of phenanthrene **64** catalyzed by 2% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**

Table 8. Time for 100% conversion depending on concentration of catalyst for phenanthrene **64.**

Entry	Catalyst (mol%)	Conversion [%]	Time [h]
31	2	100	2

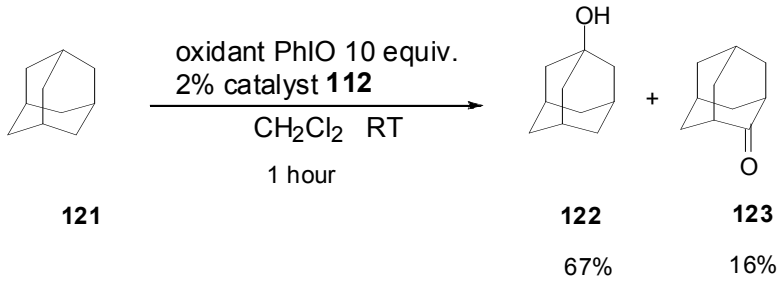
Again, the oxygenation of phenanthrene **64** by 2 mol% of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** occurs in 2 hours with 100% conversion, that

demonstrates obvious advantage of it over known catalyst **113** which did not give a product of oxygenation at all. And 30 mol% of known catalyst **114** gives the oxidized product in 4 hours with 2% conversion only (Scheme 56).

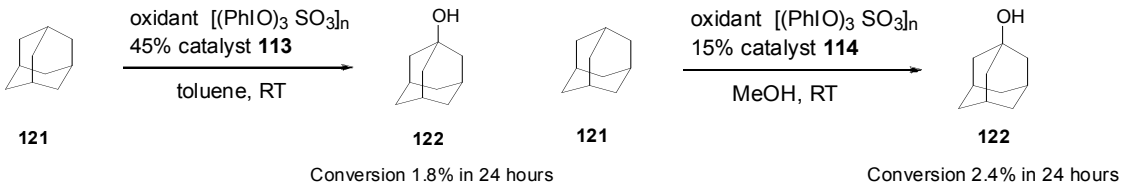


Scheme 56. Binuclear iron(III) phthalocyanine (μ-oxodimer)-catalyzed oxygenation of phenanthrene **64**[170].

When adamantane **121** was used as a substrate with 2 mol% of catalyst, the mixture of products 1-adamantanol **122** and 2-adamantanone **123** was obtained (67:16 respectively) (Scheme 57).



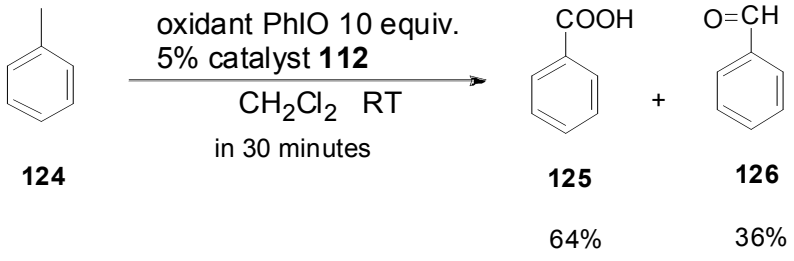
Scheme 57. Oxygenation of adamantane **121** catalyzed by 2% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**



Scheme 58. Binuclear iron(III) phthalocyanine (μ-oxodimer)-catalyzed oxygenation of adamantane **121**[170].

But when 45 mol% of known catalyst **113** was used, 1.8% conversion only was observed in 24 hours. 15 mol% of known catalyst **114** was used, and only 2.4% conversion was achieved in 24 hours giving 1-adamantanol as a product. So, these multiple comparisons and examples strongly prove the efficiency and high exceptional reactivity of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** in oxygenation reactions of different hydrocarbons.

As adamantane **121**, toluene **124** gave a mixture of products: benzoic acid **125** and benzaldehyde **126** (64:36 respectively) as a result of oxygenation reaction using 5 molar percent of catalyst (Scheme 59). This is an impressive proof of high reactivity of new catalyst, as toluene previously has been commonly used as nonreactive organic solvent for similar metalloporphyrin-catalyzed oxygenation reactions.



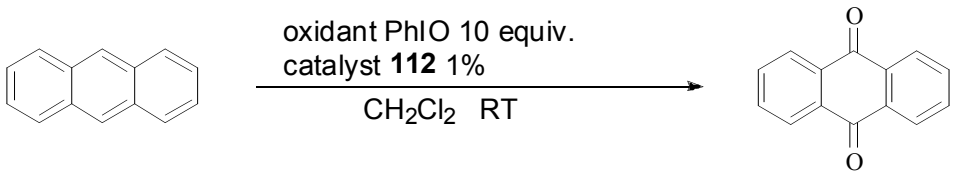
Scheme 59. Oxygenation of toluene **124** catalyzed by 5% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**

All oxygenation reactions performed during the first step of investigation of our new catalyst **112** were summarized in Table 9. On this step, we showed that perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** is an efficient and reactive catalyst for metalloporphyrin-mediated oxygenations, and has significant advantage over many known metalloporphyrin catalysts.

Table 9. Summary Table. Time for 100% conversion depending on concentration of catalyst **112** for different substrates.

Entry	Substrate	Catalyst, mol%	Conversion, %	Time, hours
24	anthracene	10	100	0.5
25	anthracene	5	100	1
26	anthracene	2	100	2
27	t-Bu-anthracene	5	100	1
28	t-Bu-anthracene	2	98	5
29	naphthalene	5	100	1
30	naphthalene	2	100	1
31	phenanthrene	2	100	2
32	adamantane	2	two products	1
33	toluene	5	two products	0.5

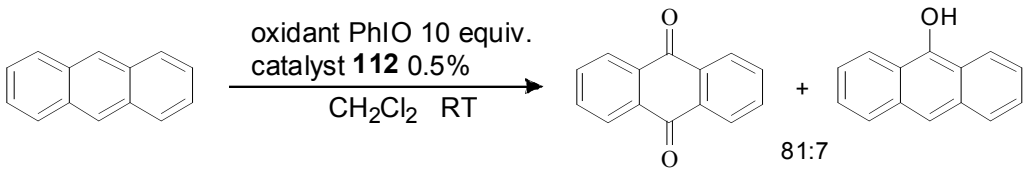
As a next step, it was decided to decrease the amount of catalyst used. At first, we used anthracene **70**, iodosobenzene **23**, and 1% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112**. Surprisingly, but in this case 100% conversion was achieved in 15 minutes with 90% yield (Scheme 60), while further decrease of amount perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** to 0.5 mol% gave in 30 minutes a mixture of two products: anthraquinone and anthracen-9-ol (81:7 respectively)(Scheme 61), (Table 10).



70 **71**

90% yield

Scheme 60. Oxygenation of anthracene **70** catalyzed by 1% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**



70 **71** **127**

Scheme 61. Oxygenation of anthracene **70** catalyzed by 0.5% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**

Optimization of reaction conditions has been carried out, varying the amount of catalyst we used.

On the one hand, these reactions illustrate that there is a specific concentration of catalyst that is the most effective for oxygenation reaction to occur in the shortest period of time. Based on the experiment, it was established that 1 mol% of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** is the most appropriate amount for oxidation reaction to take place effectively when iodosobenzene **23** is used as the oxidant in dichloromethane (Figure 4).

On the other hand, as a consequence of the results and data we collected, we can assume that alongside with the oxidation process, competitive reactions take place between catalyst and oxidant and partially "eat out" the catalyst. Probably, this is the reason why we observe at first acceleration of reaction rate (interval between 0.5 and 1 mol% of catalyst), and the reaction slows down dramatically in the interval between 1 and 2 mol%, and after that the rate of reaction increases again. The graphical

representation of relationship between required amount of time to achieve 100% conversion and catalyst concentration in reaction mixture is shown in Figure 4.

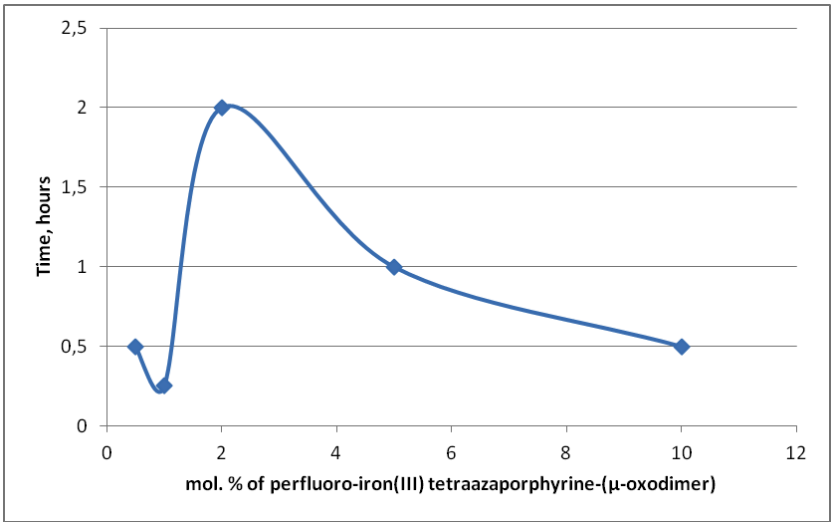
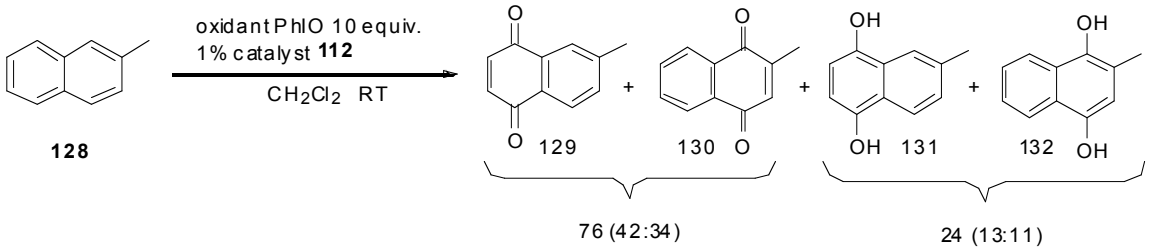


Figure 4. Reactivity curve. Illustration of required amount of time to achieve 100% conversion of anthracene **70** to anthraquinone **71** depending on catalyst **112** concentration in reaction mixture.

In order to demonstrate the general character of the optimized reaction conditions, we performed the oxidation of 2-methylnaphthalene. This reaction is important because can lead to provitamin K **130** as a product (Scheme 62).



Scheme 62. Oxygenation of 2-methylnaphthalene **128** catalyzed by 1% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.**

Mixture of 4 products **129**, **130**, **131**, **132** was obtained in 20 minutes, that, accordingly GC-MS analysis, contained two different quinones: 6-methylnaphthalene-

1,4-dione **129** and 2-methylnaphthalene-1,4-dione **130** (76% total) and two different alcohols: 6-methylnaphthalene-1,4-diol **131** and 2-methylnaphtalene-1,4-diol **132** (24% total) (Table 10).

Table 10. Summary Table. Time for 100% conversion depending on concentration of catalyst **112** for anthracene **70** and 2-methylnaphthalene **128**.

Entry	**Substrate**	**Catalyst, mol.%**	**Conversion, %**	**Time, h**
34	anthracene	1	100	0.25
35	anthracene	0.5	2 products (81:7)	0.5
36	2-methylnaphthalene	1	4 products (11:13:34:42)	0.3

C. Summary

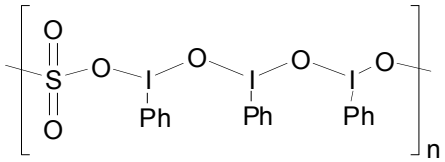
It has been shown that perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** is an efficient catalyst for oxygenation reactions that has greater stability toward oxidative degradation, due to fluorine atoms it contains. Obviously, it has significant advantage being way more efficient over known similar catalysts for oxygenation reactions with hypervalent iodine oxidant iodosobenzene **23**. Activity of new oxidizing system was compared for different substrates. Perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** is an efficient catalyst for the oxidation of a variety of aromatic compounds using iodosylbenzene as an standard oxidant.

2.2.2 Comparative Reactivity of Different Oxidants in Metalloporphyrin-Catalyzed Oxygenation of Hydrocarbons in Presence of Perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer): Iodosobenzene, Oligomeric Iodosylbenzene Sulfate, Isopropyl 2-Iodylbenzoate, Oxone®, Hydrogen Peroxide, and Peroxyacetic Acid

A. Introduction

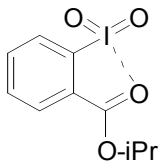
It was shown above that the most appropriate amount of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** to use for oxygenation reaction is 1 molar percent, with iodosobenzene as an oxidant in dichloromethane (anthracene as a substrate). After finding that perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** can be effectively used as a catalyst in biomimetic oxidations with iodosobenzene **23** and has obvious advantage over many known metalloporphyrin catalysts, we decided to compare the reactivity of this reagent with other oxidants, in particular with some hypervalent iodine oxidants as well. It was mentioned before, that iodosobenzene **23** is a standard oxidant, which allows us to compare the reactivity and effectiveness of newly synthesized catalyst with other known catalysts, as most of them were investigated in reactions with iodosobenzene **23**. But despite its usefulness as an oxidant, practical applications of iodosobenzene **23** are hampered by its low solubility in nonreactive media,[2,29,44] as well as low thermal stability and explosive properties upon moderate heating.[88] Therefore, we were investigating safe and convenient alternatives to iodosobenzene **23** and searching ways to increase the effectiveness of new oxidizing system through optimization.

We have investigated catalytic oxidation reactions with different substrates using following oxidants: oligomeric iodosylbenzene sulfate **26**, isopropyl 2-iodylbenzoate **98c**, Oxone®, hydrogen peroxide, and peroxyacetic acid (Scheme 63).



oligomeric iodosylbenzene sulfate

26



isopropyl 2-iodylbenzoate

98c

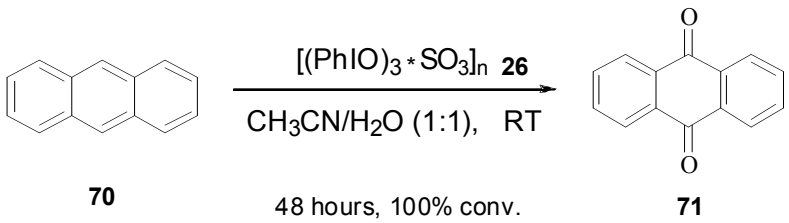
Scheme 63. Hypervalent iodine oxidants

B. Results and Discussion

As a next step, we decided to compare reactivity of different oxidants for oxygenation reactions with the novel catalyst, to find the best reagent for this reaction to be more effective, and continue with further method optimization.

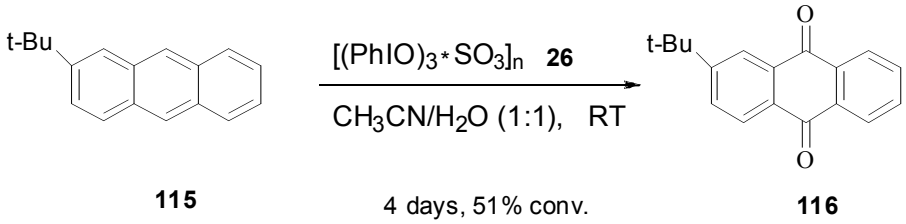
At this point, it was important to perform the blank experiments, as a preliminary experiment, for oligomeric iodosylbenzene sulfate **26** to ensure that this reagent alone cannot serve as a source of oxygen in the metalloporphyrin-mediated oxygenation under reaction condition we use (acetonitrile-water (1:1) mixture at room temperature). The term "blank experiment" implies the reaction of substrate with oxidant in the absence of catalyst. It is known in literature, that oligomeric iodosylbenzene sulfate **26** forms anthraquinone from anthracene in methanol in a blank experiment.[170] The ability of Oxone® to serve as a source of oxygen in the metalloporphyrin-mediated oxygenation, is also known in literature. But the treatment of anthracene with Oxone® in acetonitrile-water (1:1) mixture in blank experiment did not lead to oxidation of the substrate.[171] And, as it was already mentioned above, treatment of organic aromatic substrates with iodosobenzene **23** does not form any product as well.[168]

The oxidation of anthracene **70** with oligomeric iodosylbenzene sulfate **26** in the absence of catalyst at room temperature in acetonitrile-water (1:1) mixture proceeds extremely slow. And eventually 100% conversion is achieved in 48 hours (Scheme 64).



Scheme 64. Blank experiment

In case when 2-*tert*-butylanthracene **115** is treated with oligomeric iodosylbenzene sulfate **26** in the absence of catalyst at room temperature in acetonitrile-water (1:1) mixture, 51% conversion was achieved in 4 days, and 58% conversion was achieved in 10 days (Scheme 65).

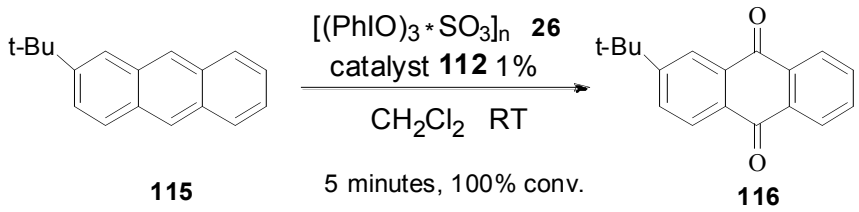


Scheme 65. Blank experiment.

The conclusion from the blank experiment is even the reaction in the absence of catalysts at room temperature occurs, the rate of reaction is extremely low. This fact demonstrates and proves ultimate reactivity of oligomeric iodosylbenzene sulfate **26** because it was the only oxidant that can oxidize substrate in the absence of catalyst under the reaction conditions we use.

At first, we decided to investigate oxidation of 2-*tert*-butylanthracene **115** with oligomeric iodosylbenzene sulfate **26**. The oligomeric iodosylbenzene sulfate $[(PhIO)_3 \bullet SO_3]_n$ **26** was prepared by simple treatment of commercially available (diacetoxyiodo)benzene with aqueous hydrogen sulfate and isolated as a thermally stable, yellow crystalline solid.[172] 2-*Tert*-butylanthracene **115** was chosen because, as it was shown in the part 2.2.1, in comparison with other substrates the oxidation reaction of 2-

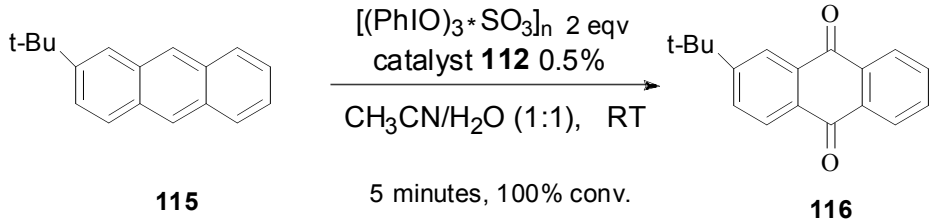
tert-butylanthracene **115** was slower, probably due to steric hindrance caused by the *tert*-butyl group. Reaction was carried out in dry dichloromethane with perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** (1 mol%) (Scheme 66), giving 100% conversion in 5 minutes.



115 **116**

Scheme 66

This result indicates that oligomeric iodosylbenzene sulfate **26** is more powerful reagent for this oxidation system than iodosobenzene **23**, and dramatically accelerates the rate of oxidation reaction. In comparison, when iodosobenzene **23** was used, 100% conversion was achieved in 15 minutes. Therefore, almost the same reaction was repeated with twice smaller concentration of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** (0.5 mol.%). Also, it was decided to change the solvent system for acetonitrile-water (1:1) mixture, as it is considered to be less harmful for environment than organic solvent dichloromethane (Scheme 67). In contrast to iodosobenzene **23**, the water-soluble oligomeric iodosylbenzene sulfate **26** shows very high reactivity in catalytic oxidations at room temperature in the presence of catalyst **112** (1% in dichloromethane and 0.5 mol% acetonitrile-water (1:1) mixture).



115 **116**

Scheme 67

When 100% conversion was observed in 5 minutes, it was decided to add only portions of substrate and oxidant - oligomeric iodosylbenzene sulfate **26** in the reaction mixture, in amounts they were added initially, until percent of conversion will be less than 100% and this value will not change anymore. This technique allows us to investigate number of cycles the catalyst can work in the oxidation system under given conditions (Table 11).

Table 11. Perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** cycles in oxygenation of 2-*tert*-butylanthracene **115** with oligomeric iodosylbenzene sulfate **26** in acetonitrile-water (1:1) solvent system.

Addition of substrate and oxidant	**Conversion, %**	**Time**
1st addition	100	5 minutes
2nd addition	100	5 minutes
3rd addition	100	10 minutes
4th addition	100	20 minutes
5th addition	100	20 minutes
6th addition	100	40 minutes
7th addition	100	1.5 hour
8th addition	99	4 hours

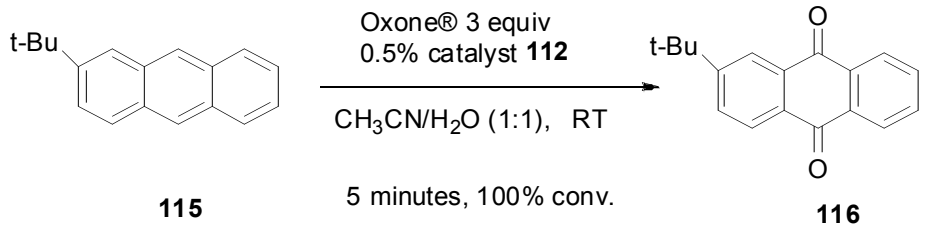
It was determined that perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** (0.5 mol.%) catalyst can work super-efficiently up to 8 cycles in oxidizing system 2-*tert*-butylanthracene **115** with oligomeric iodosylbenzene sulfate **26** in acetonitrile-water (1:1) solvent system.

Further investigation and optimization of factors for effectiveness of the oxidizing system was continued. And Oxone® was used as the next oxidant to be investigated.

Potassium peroxymonosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, which is usually sold under the commercial name ”Oxone®”, is known as inexpensive and effective oxidant. It

has been used in various synthetic applications, has relatively good storage ability and it's convenient and safe to handle.

Reaction was carried out in acetonitrile-water (1:1) mixture with perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** (0.5 mol%) and Oxone® (3 mol. eqv.) (Scheme 68). 100% conversion was observed in 5 minutes.



Scheme 68

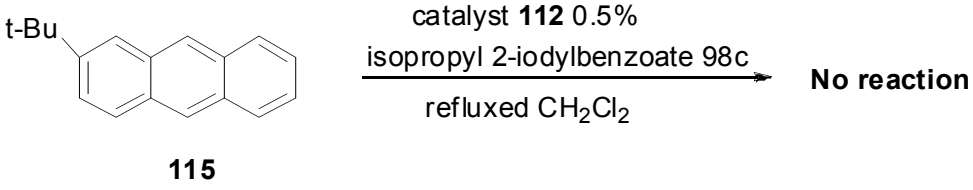
Because the result for oxidation reaction with Oxone® was similar to the result for oxidation reaction with oligomeric iodosylbenzene sulfate **26** (100% conversion in 5 minutes), we needed a way to compare reactivity of two oxidizing reagents: Oxone® and oligomeric iodosylbenzene sulfate **26**. It was decided to determine number of cycles the catalyst can handle in the case when Oxone® was used. Again, as it was described for oligomeric iodosylbenzene sulfate **26** oxidation procedure, portions of substrate and oxidant, Oxone® for this case, were added in the reaction mixture, in amounts they were added initially, until percent of conversion was less than 100% and this value would not change anymore (Table 12).

Table 12. Perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** cycles in oxygenation of 2-*tert*-butylanthracene **115** with Oxone® in acetonitrile-water (1:1) solvent system.

Addition of substrate and oxidant	**Catalyst, mol% in reaction mixture**	**Conversion, %**	**Time**
1st addition	0.5	100	5 minutes
2nd addition	0.25	100	30 minutes
3rd addition	0.17	75	24 hours

As it turned out, already after the third addition, only 75% conversion was achieved in 24 hours. This experiment clearly indicates that oligomeric iodosylbenzene sulfate **26** is at least twice more powerful oxidant than Oxone®, and has huge advantage over Oxone® for such oxidizing system.

To extend the whole picture of oxygenation reactions of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** with different oxidants, 2-*tert*-butylanthracene **115** was treated with isopropyl-2-iodylbenzoate **98c** in dichloromethane. But oxygenation reaction did not occur even after the reaction mixture was refluxed in dichloromethane (Scheme 69).

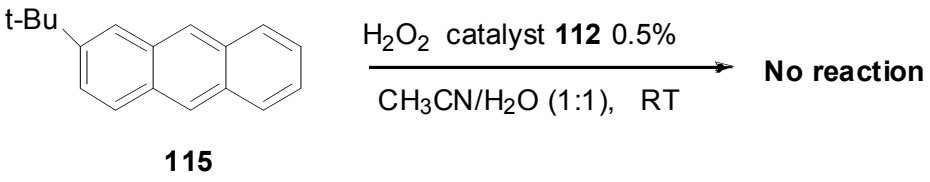


115

Scheme 69

In contrast to iodosobenzene **23** and oligomeric iodosylbenzene sulfate **26,** isopropyl-2-iodylbenzoate **98c** has not shown to be a suitable reagent for investigated oxidation transformations. The reaction did not occur, as the complicated mechanism of metalloporphyrin-mediated oxygenation may require hypervalent iodine(III) to be involved.

Hydrogen peroxide was used as a next oxidant in reaction with 0.5 mol% catalyst **112** and 2-*tert*-butylanthracene **115** in acetonitrile-water (1:1) solvent system (Scheme 70).

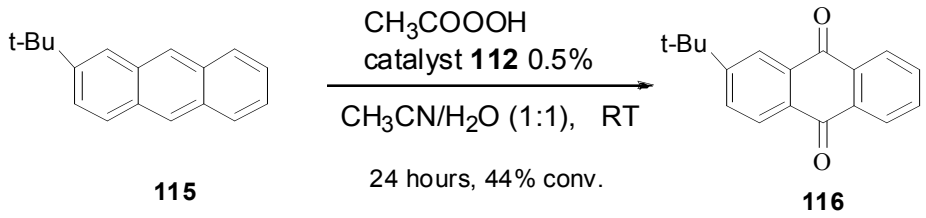


115

Scheme 70

Reaction did not occur as it was in case with isopropyl-2-iodylbenzoate **98c** even after many days.

At last, 2-*tert*-butylanthracene **115** was treated with peroxyacetic acid as an oxidant in presence of 0.5 mol% perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** in acetonitrile-water (1:1) solvent system (Scheme 71).



Scheme 71

The oxygenation of 2-*tert*-butylanthracene **115** was very slow, probably due to low reactivity of oxidant, with a 44% conversion reached only after 24 hours at room temperature.

All in all, it is clear that oligomeric iodosylbenzene sulfate **26** and Oxone® are the most reactive and efficient oxidants for the particular oxidizing system in presence of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** in acetonitrile-water (1:1) solvent system. Iodosobenzene **23** is less reactive, but still can be useful for oxygenation of aromatic compounds in dichloromethane. Peroxyacetic acid is too weak to compete with other oxidants we have investigated, while isopropyl 2-iodylbenzoate **98c** and hydrogen peroxide do not react with substrate at all (Table 13).

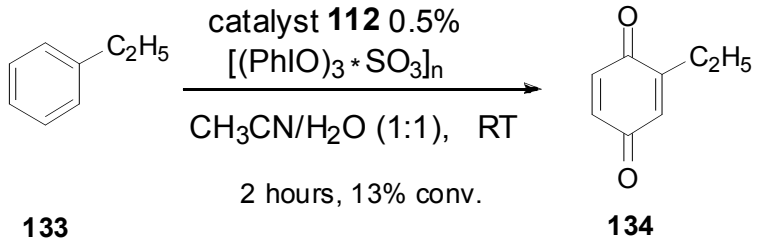
Table 13. Summary table.

Entry	Substrate	Reagent	Catalyst, mol%	Solvent	Conversion, %	Time
37	anthracene	$[(PhIO)_3SO_3]_n$	none	CH_3CN-H_2O (1:1)	100	48 hours
38	2-*tert*-butylanthracene	$[(PhIO)_3SO_3]_n$	none	CH_3CN-H_2O (1:1)	58	10 days
39	2-*tert*-butylanthracene	$[(PhIO)_3SO_3]_n$	1	DCM	100	5 minutes
40	2-*tert*-butylanthracene	$[(PhIO)_3SO_3]_n$	0.5	CH_3CN-H_2O (1:1)	100	5 minutes
41	2-*tert*-butylanthracene	Oxone®	0.5	CH_3CN-H_2O (1:1)	100	5 minutes
42	2-*tert*-butylanthracene	CH_3COOOH	0.5	CH_3CN-H_2O (1:1)	44	24 hours
43	2-*tert*-butylanthracene	H_2O_2	0.5	CH_3CN-H_2O (1:1)	0	3 days
44	2-*tert*-butylanthracene	isopropyl 2-iodylbenzoate	0.5	DCM	0	3 days

The best catalytic effect is observed for oxygenation with oligomeric iodosylbenzene sulfate **26** in the presence of 0.5 mol% of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** (entry 40; 100% conversion in 5 minutes with 8 possible cycles). The reactivity of Oxone® in the presence of 0.5 mol% catalyst is slightly lower (entry 41; 100% conversion 5 minutes with 3 possible cycles).

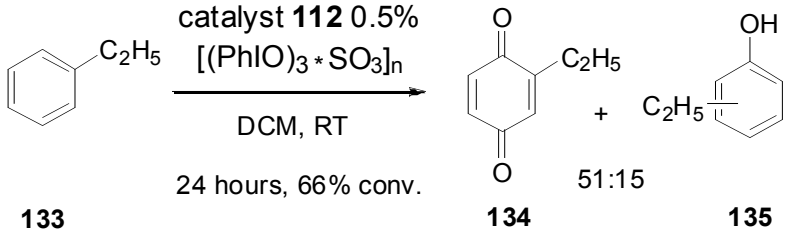
To expand the range of observations and investigate the effectiveness of new oxidizing system on different substrates, the oxygenation of ethylbenzene was performed in different solvent systems with most reactive reagents.

Ethylbenzene **133** was treated with oligomeric iodosylbenzene sulfate **26** in the presence of 0.5 mol% of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** in acetonitrile-water (1:1) solvent system (Scheme 72). In this reaction conditions oligomeric iodosylbenzene sulfate **26** slowly oxidizes ethylbenzene with 13% conversion after 2 hours.



Scheme 72

When DCM was used as a solvent instead of acetonitrile-water (1:1) mixture, two products **134** and **135** have formed and reached ratio 51:15 respectively after 24 hours (Scheme 73). This ratio was changing by time and was monitored by GC-MS analysis (Table 14).



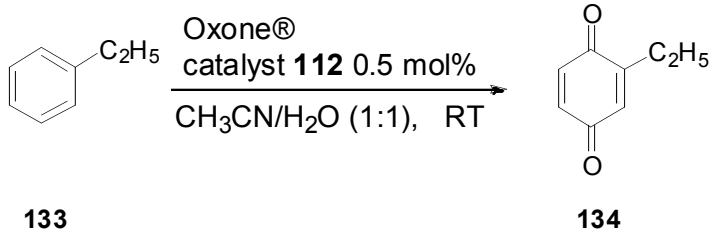
Scheme 73

Table 14. The progress of oxygenation reaction of ethylbenzene with oligomeric iodosylbenzene sulfate **26** in the presence of 0.5 mol% of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** in DCM.

Conversion, %	Ratio of products 134:135	Time, h
33	26:7	0.25
41	32:9	0.5
51	39:12	1
54	41:13	2
66	51:15	24

Further, we have investigated catalytic oxidation of ethylbenzene with Oxone® in the presence of 0.5 mol% of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** in

acetonitrile-water (1:1) solvent system (Scheme 74). Oxone® as an oxidant leads to a significant increase in the reaction rate in comparison with oligomeric iodosylbenzene sulfate **26** with a 100% conversion reached in 1 hour.



133 **134**

Scheme 74

Oxidation of tetralin in the presence of 0.5 mol% catalyst **112** and Oxone® as an oxidant proceeds with 100% conversion after 15 minutes, leading to a mixture of five different products. This result clearly shows that the given reaction is not selective.

C. Summary

We have investigated and compared reactivity of different oxidants for oxygenation reactions of organic substrates with the novel catalyst perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112.** Oligomeric iodosylbenzene sulfate **26**, isopropyl 2-iodylbenzoate **98c**, Oxone®, hydrogen peroxide, and peroxyacetic acid have been compared. It was found that oligomeric iodosylbenzene sulfate **26** and Oxone® are the most efficient oxygenating agents in the biomimetic catalytic oxidation of aromatic hydrocarbons in the presence of perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112**.

We have demonstrated the general character of the optimized reaction conditions for new catalytic oxidizing system on various substrates. It was shown in blank experiment that oligomeric iodosylbenzene sulfate **26** alone can serve as a source of oxygen in the metalloporphyrin-mediated oxygenation under reaction condition we used. However, reaction proceeds extremely slow in the absence of catalyst.

2.3 Conclusion

In conclusion, we have developed, prepared, and investigated a new efficient, highly selective, and water-soluble hypervalent iodine(V) reagent – potassium 4-iodylbenzenesulfonate. This new green-chemistry reagent was characterized by means of NMR, elemental analyses, and single crystal X-ray crystallography. Furthermore, iodination reaction were studied with potassium 4-iodylbenzenesulfonate as an oxidant, and specific reaction conditions were found, depending of the goal and desired target product. Also, many different and useful aryl iodides can be obtained from aromatic organic substrates treated with this new reagent. In summary, the design, preparation, structure and reactivity investigation of new 4-iodylbenzenesulfonate have been performed.

Moreover, the new, powerful, and effective oxidizing systems have been developed using new perfluoro-iron(III) tetraazaporphyrin-(μ-oxodimer) **112** in the biomimetic catalytic oxidations of aromatic hydrocarbons. Reactivity of different oxidants in metalloporphyrin-catalyzed oxygenation of hydrocarbons was compared. The general character of the optimized reaction conditions has been demonstrated for the new catalytic oxidizing system. This investigation has shown that perfluoro-iron(III) tetraazaporphyrine-(μ-oxodimer) **112**/ iodosobenzene, perfluoro-iron(III) tetraaza-porphyrin-(μ-oxodimer) **112**/ oligomeric iodosylbenzene sulfate **26**, and perfluoro-iron(III) tetraazaporphyrine-(μ-oxodimer) **112/** Oxone® catalytic systems can be effectively applied toward the oxidation of aromatic compounds and some hydrocarbons and have obvious advantage over many known metalloporphyrin-mediated oxidizing catalytic systems. However, in several cases, these reactions are not selective. For instance, the oxidation of tetralin in the presence of 0.5 mol% of Oxone® proceeds with 100% conversion after 15 minutes leading to a mixture five different products of oxidation.

Chapter 3

Experimental

3. Experimental Section

3.1 General Methods

All melting points were determined in an open capillary tube with a Mel-temp II® melting point apparatus and are uncorrected. NMR spectra were recorded at 500 MHz INOVA-500 (Varian) (^{1}H NMR), 125.6 MHz (^{13}C NMR) and at Bruker AM NMR spectrometers (400 MHz). Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to the tetramethylsilane. Analytical thin-layer chromatography was performed using precoated silica gel 60 F254 plates (MERCK, Darmstadt) and the spots were visualized with UV light at 254 nm. GC-MS analysis was carried out with HP 5890A gas chromatograph using a 5970 Series mass selective detector. Elemental analysis was conducted by the Atlantic Microlab, Inc., Norcross, GA.

3.2 Materials

All commercial reagents were ACS reagent grade and used without further purification. Methylene chloride was distilled from CaH_2 and stored over molecular sieves (4 Å). All other reagents and solvents were of commercial quality from freshly opened containers.

3.3 Synthesis and Characterization of Compounds

3.3.1 General Procedure for the preparation of reagents and iodoaromatic compounds

Preparation of 4-Iodobenzensulfonic acid 105

50 ml concentrated H_2SO_4 (27.2 g, 0.28 mol) was added to 20 ml of iodobenzene **24** (36.4 g, 0.178 mol) under stirring and heated up to 50^{o}C. The reaction mixture was stirred at 50-60^{o}C for 30 hours. In 3 hours reaction mixture obtained pink color. 20 ml hexanes was added to reaction mixture to get rid of the rest of iodobenzene and stirring for 5 more minutes. Product was extracted with small portions of boiling chloroform (100 ml) and the system of two clear layers was obtained. The top layer was carefully transferred using a Pasteur pipette into a round bottom flask and evaporated under reduced pressure followed by filtration. Crystals were collected by filtration under reduced pressure, washed with hexanes afforded **2** 48.0 g (95 %) of product, mp 66-68 °C, (lit.[173], mp 70 °C). ^{1}H NMR (500 MHz, D_2O): δ 7.90 (dd, $2H_{arom.}$, J = 2.0 Hz, 8.5 Hz), 7. 52 (dd, $2H_{arom.}$, J = 1.5 Hz, 8.5 Hz). ^{13}C NMR (125 MHz, D_2O) δ 142.0, 138.0, 127.0, 97.7.

Preparation of Potassium 4-iodylbenzenesulfonate 107

Method A.

4-iodobenzenesulfonic acid **105** (2.840 g, 10 mmol) was added to the Oxone® (2x6.14 g (2x10 mmol) solution in H_2O (20 ml) and the reaction mixture stirred at 60°C for 2 hours. After that reaction mixture was cooled to 5^{o}C and filtered. Precipitate was washed with water (3x10 ml) and dried under vacuum, affording 3.33 g (94%) of product. After recrystallization from water 2.6 g (80 %) of purified product were isolated as white flaky crystalline solid, mp 259°C (explodes). Anal. Calcd. for $C_6H_4IKO_5S$: C, 20.35; H, 1.14; I, 35.83; S, 9.05. Found: C, 20.26; H, 1.10; I, 36.07; S, 8.86. ^{1}H NMR (500 MHz, D_2O): δ: 8.14 (d, $4H_{arom.}$, J = 1.5 Hz) ppm. ^{13}C NMR (125 MHz, D_2O) δ: 152.0, 147.1, 127.6, 127.3.

Method B.

4-Iodobenzenesulfonic acid **105** (2.840 g, 10 mmol) was added to the Oxone® solution (2.5 equiv, 25 mmol) in water (10 ml) under stirring at 60°C. Reaction mixture was left overnight, then cooled down to room temperature. After the reaction mixture was left for

1 hour at RT the precipitate was filtered and washed 2 times with water (2 x 5 ml). Filtrate was dried under vacuum to give 3.400 g (96%) of white powder as final product. ^{1}H NMR (500 MHz, D_2O) δ: 8.14 (d, 4H, *J* = 1.5 Hz). ^{13}C NMR (125 MHz, D_2O) δ: 152.0, 147.1, 127.6, 127.3.

Preparation of 4-Iodylbenzenesulfonic acid 108

A solution of potassium 4-iodylbenzenesulfonate **107** (1.073 g, 3.03 mmol) in 30 mL H_2O was cooled down to 5^{o}C and Amberlyst 15 (10.0 g) was added under stirring for 30 min at room temperature. After that precipitate was filtered and washed with water (10 ml). Water was evaporated and crystals were dried under vacuum afforded 930 mg (97%) of product, mp 142-142.5^{o}C (explosion). Anal. Calcd for $C_6H_5IO_5S$ [M-H^{-}] 314.8824; found 314.8815 [M-H^{-}]. ^{1}H NMR (200 MHz, D_2O): δ 8.11 (m, 4$H_{arom.}$, *J* = 1.0 Hz)). δ: 151.7, 146.9, 127.4, 127.1 ppm.

General procedures for iodination and diiodination

Method A. Mono-iodination (at room temperature**).**

To a mixture of an appropriate arene **109** (0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 mL) was added aqueous H_2SO_4 (5%, 0.5 mL) and the reaction mixture was stirred at room temperature as indicated in the tables (the reactions were monitored by TLC and GC-MS). Then, 5% aqueous Na_2SO_3 (0.5 mL) and H_2O (5 ml) were added and the mixture was shaken for 5 minutes, was filtered and washed with water. The pure iodoarenes **110** were characterized by NMR-spectroscopy.

3-Bromo-4-hydroxy-5-iodobenzonitrile 110k

Reaction of 3-Bromo-4-hydroxy-benzonitrile **109k** (39.6 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 mL) according to the general procedure, mono-iodination method A **(**at

room temperature**)**, afforded 49.9 mg (77%) of product, isolated as microcrystalline solid, mp 188-190°C (from benzene-hexane 5:1) (lit. mp 190-191 °C).[183] Anal. Calcd for C_7H_2BrINO [M-H$^-$] 321.8365, found 321.8379. ^{1}H NMR (200 MHz, CD3OD): δ 8.11 (d, *J*=1.9 Hz, 1H), 7.94 (d, *J*=1.9 Hz, 1H), 8.11 (d, *J*=1.9 Hz, 1H) ppm.

2-Hydroxy-3-iodo-4-methylbenzoic acid 110l

Reaction of 2-Hydroxy-4-methylbenzoic acid **109l** (30.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at room temperature**)**, afforded 46.7 mg (84%) of product as white crystals, mp 217-219^{o}C (from hexane-EtOAc – 6:1), (lit.[174], mp 219-220^{o}C). Anal. Calcd for $C_8H_6IO_3$ [M-H$^-$] 276.9362, found 276.9364. ^{1}H NMR (200 MHz, CD_3OD): δ 7.82 (d, *J*=1.3 Hz, 1H), 7.71 (d, *J*=1.3 Hz, 1H), 2.29b (s, 3H) ppm.

3-Hydroxy-4-iodo-2-naphthoic acid 110m

Reaction of 3-Hydroxy-2-naphthoic acid **109m** (37.6 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at room temperature**)**, afforded 57.8 mg (92%) of product, isolated as yellow crystalline solid, mp 208-210^{o}C (decomposition) (lit.[175], mp 210^{o}C (dec.). Anal. Calcd for $C_{11}H_6IO_3$ [M-H$^-$] 312.9362, found 312.9377. ^{1}H NMR (200 MHz, CD_3OD): δ 8.62 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.43 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.0 Hz, 1.3 Hz, 1H) ppm.

2-Amino-3-iodopyridine 110n

Reaction of 2-amino-pyridin **109n** (18.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A (at room temperature), afforded 22.4 mg (51%) of product, isolated as white crystalline solid, mp 83-85^{o}C (from hexane-EtOAc – 3:1), (lit.[176], mp 86^{o}C). Anal. Calcd for $C_5H_6IN_2$ [M+H$^+$] 220.9576,

found 220.9583 or HRMS (FAB) *m/z* calcd for $C_5H_6IN_2$ (M+H) 220.9576, found 220.9583. ^{1}H NMR (200 MHz, CD_3OD): δ 8.07 (d, *J*=1.7 Hz, 1H), 7.67 (dd, *J* =8.8 Hz, 2.3 Hz, 1H), 6.47 (dd, *J* = 8.8 Hz, 0.6 Hz, 1H) ppm.

4-Amino-3-iodopyridine 110o

Reaction of 4-Amino-pyridin **109o** (18.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at room temperature**)**, afforded 38.7 mg (88%) of product, isolated as white needle-shaped crystals, mp 74-76^{o}C (lit.[177], mp 76-77^{o}C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.12 (d, 1H, *J* = 5.5 Hz), 6.60 (d, 1H, *J* = 5.5 Hz), 4.62 (br s, 2H, NH_2) ppm.

Method A. Di-iodination (at room temperature**).**

To a mixture of an appropriate arene **109** (0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate **107** (42.5 mg, 0.12 mmol) in MeCN (0.5 ml) and Amberlyst 15 (100 mg) was added aqueous H_2SO_4 (5%, 0.5 mL) and the reaction mixture was stirred at room temperature. The reactions were monitored by TLC and GC-MS. Then, 5% aqueous Na_2SO_3 (0.5 ml) and H_2O (5 ml) were added and the mixture was shaken for 5 minutes, was filtered and washed with water. The pure iodoarenes **111** were characterized by NMR-spectroscopy.

1-(4-Hydroxy-3,5-diiodophenyl)ethanone 111r

Reaction of 1-(4-Hydroxy-phenyl)ethanone **109r** (27.2 mg, 0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate **107** (42.5 mg, 0.12 mmol) in MeCN (0.5 ml) according to the general procedure, di-iodination method A **(**at room temperature**)**, afforded 68.3 mg (88%) of product, isolated as white crystalline solid. mp 159-160 °C (from MeOH-H_2O 1:1) (lit.[178], mp 158-160 °C). Anal. Calcd for $C_8H_5I_2O_2$ [M-H$^-$] 386.8379, found 386.8378. ^{1}H NMR (200 MHz, CD_3OD): δ 8.35 (s, 2H), 2.54 (s, 3H, CH_3), ppm.

Method A. Mono-iodination (at 40°C).

To a mixture of an appropriate arene **109** (0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) was added aqueous H_2SO_4 (5%, 0.5 ml) and the reaction mixture was stirred at 40°C (the reactions were monitored by TLC and GC-MS). Then, 5% aqueous Na_2SO_3 (0.5 ml) and H_2O (5 ml) were added and the mixture was shaken for 5 minutes, was filtered and washed with water. The pure iodoarenes **110** were characterized by NMR-spectroscopy.

2-Iodo-1-(3-iodo-4-methoxyphenyl)ethanone 110p

Reaction of 1-(4-methoxyphenyl)ethanone **109p** (30 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 40°C**)**, afforded 52.3 mg (65%) of product **110p**, isolated as white needle-shaped crystals, mp 116.5-117°C (from hexane-CH_2Cl_2 10:1) (lit.[179], mp 115-116°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, J = 2.0 Hz, 1H), 7.98 (dd, J = 8.5 Hz, 2 Hz, 1H), 6.86 (d, J = 9.0 Hz, 1H), 4.29 (s, 2H, CH_2-I), 3.97 (s, 3H, CH_3) ppm.

Method A. Mono-iodination (at 65°C**).**

To a mixture of an appropriate arene **109** (0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) was added aqueous H_2SO_4 (5%, 0.5 ml) and the reaction mixture was stirred at 65°C (the reactions were monitored by TLC and GC-MS). Then, 5% aqueous Na_2SO_3 (0.5 ml) and H_2O (5 ml) were added and the mixture was shaken for 5 minutes, was filtered and washed with water. The pure iodoarenes **110** were characterized by NMR-spectroscopy.

2-Iodo-1,4-dimethylbenzene 110c

Reaction of 1,4-dimethylbenzene **109c** (21.2 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded 39 mg (84%) of product as colorless liquid.[184] ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.66 (s,1H), 7.10 (d, J = 7.5 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 2.42 (s, 3H, CH_3), 2.25 (s, 3H, CH_3) ppm.

2-Iodo-1,4-diethylbenzene 110d

Reaction of 1,4-diethylbenzene **109d** (26.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded 46.3 mg (89%) of product as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.66 (s, 1H), 7.25 (s, 1H), 7.12 (s, 1H), 2.69 (q, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, CH_2), 2.56 (q, $^3J_{H\text{-}H}$ = 7.5 Hz, 2H, CH_2), 1.22-1.17 (m, 6H, CH_3) ppm.

2-Iodo-1,3,5-trimethylbenzene 110e

Reaction of 1,3,5-trimethylbenzene **109e** (24 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded 48.2 mg (98%) of product, isolated as microcrystalline white solid, mp 28-29.5 °C (lit.[178], mp 30-31 °C). ^{1}H NMR (500 MHz, $CDCl_3$): □δ 6.90 (s, $2H_{arom.}$) 2.44 (s, 6H, CH_3), 2.25 (s, 3H, CH_3) ppm.

3-Iodo-1,2,4,5-tetramethylbenzene 110f

Reaction of 1,2,4,5-tetramethylbenzene **109f** (26.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded 51 mg (98%) of product, isolated as microcrystalline white solid, mp 77-79°C (lit.[180], mp 78.5-79.53°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (s, $1H_{arom.}$), 2.44 (s, 6H,

CH_3), 2.31 (s, 6H, CH_3) ppm.

1-Iodo-2-methylnaphthalene 110g

Reaction of 2-methylnaphthalene **109g** (28.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded 46 mg (86%) of product as colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.5 Hz, 1H), □7.74 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.53-7.57 (m, 1H), 7.44-7.47 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 2.71 (s, 3H) ppm.

4-Bromo-2-iodo-1-methoxybenzene 110i

Reaction of 4-Bromo-1-methoxybenzene **109i** (37.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded 56.3 mg (90%) of product as pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, 1H, *J* = 2.5 Hz), 7.41 (dd, 1H, *J* = 9.0 Hz, 2.5 Hz), 6.69 (d, 1H, *J* = 9.0 Hz), 3.86 (s, 3H, CH_3) ppm.

2-iodo-1-methoxy-4-vinylbenzene 110j

Reaction of 1-methoxy-4-vinylbenzene **109j** (27.2 mg, 0.2 mmol), iodine (0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A (at 65°C), afforded 50.8 mg (97%) of product.

1-iodo-4-methylbenzene 110a and 1-iodo-2-methylbenzene 110a'

Reaction of methylbenzene **109a** (18.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A (at 65°C), afforded a

mixture (98%) of two products 1-iodo-4-methylbenzene **110a** and 1-iodo-2-methylbenzene **110a'** (84:16 respectively) accordingly GC-MS.

1-iodo-4-ethylbenzene 110b and 1-iodo-2-ethylbenzene 110b'

Reaction of ethylbenzene **109b** (21.2 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded a mixture (83%) of two products 1-iodo-4-ethylbenzene **110b** and 1-iodo-2-ethylbenzene **110b'** (86:14 respectively) accordingly GC-MS analysis.

1-chloro-4-iodobenzene 110h and 1-chloro-2-iodobenzene110h'

Reaction of chlorobenzene **109h** (22.5 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 mL) according to the general procedure, mono-iodination method A **(**at 65°C**)**, afforded a mixture (99%) of two products 1-chloro-4-iodobenzene **110h** and 1-chloro-2-iodobenzene **110h'** (78:22 respectively) accordingly GC-MS analysis.

Method A. Di-iodination (at 65°C**).**

To a mixture of an appropriate arene **109** (0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate **107** (42.5 mg, 0.12 mmol) in MeCN (0.5 ml) and Amberlyst 15 (100 mg) was added aqueous H_2SO_4 (5%, 0.5 mL) and the reaction mixture was stirred at 65°C as indicated in the tables (the reactions were monitored by TLC and GC-MS). Then, 5% aqueous Na_2SO_3 (0.5 ml) and H_2O (5 ml) were added and the mixture was shaken for 5 min, was filtered and washed with water. The pure iodoarenes **111** were characterized by NMR-spectroscopy.

2,5-Diiodo-1,4-dimethylbenzene 111q

Reaction of 1,4-dimethylbenzene **109q** (21.2 mg, 0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate **107** (42.5 mg, 0.12 mmol) in MeCN (0.5 ml) according to the general procedure, di-iodination method A **(**at 65°C**)** , afforded 65.8 mg (92%) of product, isolated as white needle-shaped crystals, mp 102.5-103.5°C (lit.[181], mp 103-104°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ .65 (s, 2H), 2.34 (s, 6H, CH_3) ppm.

2,4-Diiodo-1,3,5-trimethylbenzene 111d

Reaction of 1,3,5-trimethylbenzene **109d** (24 mg, 0.2 mmol), iodine (55.9 mg, 0.22 mmol) and potassium 4-iodylbenzenesulfonate **107** (42.5 mg, 0.12 mmol) in MeCN (0.5 ml) according to the general procedure, di-iodination method A **(**at 65°C**)** , afforded 73.6 mg (99%) of product, isolated as white needle-shaped crystals, mp 80-81.5°C (lit.[181], mp 82°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 (s, 1H), 2.93 (s, 3H, CH_3), 2.42 (s, 6H, CH_3) ppm.

Method B.

To a mixture of arenes **109** (0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055 mmol) in MeCN (0.5 ml) was added Amberlyst 15 (100 mg) and H_2O (0.5 ml). The reaction mixture was stirred at room temperature as indicated in the tables (the reactions were monitored by TLC). Then, 5% aqueous Na_2SO_3 (0.5 ml) and H_2O (5 ml) were added and the mixture was shaken for 5 minutes, then extracted by ethyl acetate (5 ml), washed with water, dried by Na_2SO_4. The pure iodoarenes **110** were characterized by NMR-spectroscopy after evaporation of solvent.

3-Bromo-4-hydroxy-5-iodobenzonitrile 110k

Reaction of 3-Bromo-4-hydroxy-benzonitrile **109k** (39.6 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method C,

afforded 51.8 mg (80%) of product, isolated as microcrystalline solid, mp 188-190°C (from benzene-hexane 5:1) (lit. mp 190-191 °C[183]). Anal. Calcd for C_7H_2BrINO [M-H$^-$] 321.8365, found 321.8379. ^{1}H NMR (200 MHz, CD3OD): δ 8.11 (d, *J*=1.9 Hz, 1H), 7.94 (d, *J*=1.9 Hz, 1H), 8.11 (d, *J*=1.9 Hz, 1H) ppm.

2-Hydroxy-3-iodo-4-methylbenzoic acid 110l

Reaction of 2-hydroxy-4-methylbenzoic acid **109l** (30.4 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method C, afforded 48.3 mg (87%) of product as white crystals, mp 217-219^{o}C (from hexane-EtOAc – 6:1), (lit.[174], mp 219-220^{o}C). Anal. Calcd for $C_8H_6IO_3$ [M-H$^-$] 276.9362, found 276.9364. ^{1}H NMR (200 MHz, CD_3OD): δ 7.82 (d, *J*=1.3 Hz, 1H), 7.71 (d, *J*=1.3 Hz, 1H), 2.29b (s, 3H) ppm.

3-Hydroxy-4-iodo-2-naphthoic acid 110m

Reaction of 3-hydroxy-2-naphthoic acid **109m** (37.6 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method C, afforded 57.7 mg (92%) of product, isolated as yellow crystalline solid, mp 208-210^{o}C (decomposition) (lit. mp 210^{o}C (dec)[175]). Anal. Calcd for $C_{11}H_6IO_3$ [M-H$^-$] 312.9362, found 312.9377. ^{1}H NMR (200 MHz, CD_3OD): δ 8.62 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.43 (td, *J* = 8.0 Hz, 1.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.0 Hz, 1.3 Hz, 1H) ppm.

2-Amino-3-iodopyridine 110n

Reaction of 2-amino-pyridine **109n** (18.8 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate **107** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method C, afforded 22 mg (50%) of product, isolated as white crystalline solid, mp 83-85^{o}C (from hexane-EtOAc – 3:1), (lit.[176], mp. 86^{o}C). Anal. calcd for $C_5H_6IN_2$ (M+H) 220.9576, found 220.9583. ^{1}H

NMR (200 MHz, CD_3OD): δ 8.07 (d, *J*=1.7 Hz, 1H), 7.67 (dd, *J* =8.8 Hz, 2.3 Hz, 1H), 6.47 (dd, *J* = 8.8 Hz, 0.6 Hz, 1H) ppm.

1-(4-Hydroxy-3,5-diiodophenyl)ethanone 111r

Reaction of 1-(4-hydroxy-phenyl)ethanone **109r** (27.2 mg, 0.2 mmol), iodine (27.9 mg, 0.11 mmol) and potassium 4-iodylbenzenesulfonate (**1)** (19.5 mg, 0.055-0.06 mmol) in MeCN (0.5 ml) according to the general procedure, mono-iodination method C, afforded 72.9 mg (94%) of product, isolated as white crystalline solid. mp 159-160 °C (from MeOH-H_2O 1:1) (lit.[178], mp 158-160 °C). Anal. Calcd for $C_8H_5I_2O_2$ [M-H^-] 386.8379, found 386.8378. ^{1}H NMR (200 MHz, CD_3OD): δ 8.35 (s, 2H), 2.54 (s, 3H, CH_3), ppm.

Metod C.

To a solution of dimethoxybenzene **109s-u, 109o** (1.0 mmol) in acetic acid (5 ml), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate **107** (106 mg, 0.3 mmol) were added under stirring at 80^{o}C. After stirring, the mixture was cooled down to room temperature and ice water was added. Product was extracted with dichloromethane (20 ml), washed with $NaHCO_3$ (10% in water) and dried over Na_2SO_4. Evaporation of dichloromethane gave the pure product.

4-Iodo-1,2-dimethoxy benzene 110s

To a solution of 1,2-dimethoxybenzene **109s** (138 mg, 1.0 mmol) in acetic acid (5 ml), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate **107** (106 mg, 0.3 mmol) were added under stirring at 80^{o}C for 1 hour, according to the general procedure, method E, afforded 253 mg (96%) of product, isolated as oil that can be crystallized in refrigirator.[186] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.5, 2 Hz, 1H), 7.11 (d, *J* = 2 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 4 Hz,1H), 3.85 (s, 3H, 2-OCH_3), 3.84 (s, 3H, 1-OCH_3) ppm.

4-Iodo-1,3-dimethoxy benzene 110t

To a solution of 1,3-dimethoxybenzene **109t** (138 mg, 1.0 mmol) in acetic acid (5 ml), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate **107** (106 mg, 0.3 mmol) were added under stirring at 80°C for 6 hours, according to the general procedure, method E, afforded 258 mg (98%) of product, isolated as oil that can be crystallized in refrigirator.[187] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.32 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.85 (s, 3H, 3-OCH_3), 3.80 (s, 3H, 1-OCH_3) ppm.

2-Iodo-1,4-dimethoxy benzene 110u

To a solution of 1,4-dimethoxybenzene **109u** (138 mg, 1.0 mmol) in acetic acid (5 ml), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate **107** (106 mg, 0.3 mmol) were added under stirring at 80°C for 11 hours, according to the general procedure, method E, afforded 237 mg (90%) of product, isolated as pink oil that can be crystallized in refrigirator.[188] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 3 Hz, 1H), 6.86 (dd, *J* = 9 Hz, 3 Hz, 1H), 6.75 (d, *J* = 9 Hz, 1H), 3.82 (s, 3H, 3-OCH_3), 3.750 (s, 3H, 1-OCH_3) ppm.

4-Amino-3-iodopyridine 110o

To a solution of 4-aminopyridine **109o** (94 mg, 1.0 mmol) in acetic acid (5 ml), iodine (127 mg, 0.5 mmol) and potassium 4-iodylbenzenesulfonate **107** (106 mg, 0.3 mmol) were added under stirring at 80°C for 1 hour, according to the general procedure, method E, afforded 193 mg (88%) of product, isolated as white needle-shaped crystals, mp 74-76°C (lit. mp 76-77°C).

Method D.

4-bromo-2-iodoanisole 110i

To a mixture of 4-bromoanisole **109i** (468 mg, 2.5 mmol), iodine (350 mg, 1.38 mmol) and potassium 4-iodylbenzenesulfonate **107** (347 mg, 0.98 mmol) in MeCN (3.0 ml) was added aqueous H_2SO_4 (5%, 3.0 ml) and the reaction mixture was stirred at 80°C for 12

hours (the reaction was monitored by TLC and GC-MS). After that the reaction mixture was cooled down to room temperature and extracted with hexanes (6.0 ml). Evaporation of hexanes layer gave 638 mg (81%) of 4-bromo-2-iodoanisole **110i**. 1.2 g Oxone® was added to the water layer after extraction. This mixture was stirred at 60°C for 2 hours. After reaction mixture was cooled down to 5°C and filtered, washed with water (3x1.0 ml), and dried. Potassium 4-iodylbenzenesulfonate **107** was obtained as solid 320 mg (92%).

3.3.2 General procedures for catalytic reactions with hypervalent iodine species and preparation of oxidants for these reactions.

Preparation of iodosobenzene 23.

Finely ground iodosobenzene diacetate **27** (32.2 g., 0.10 mole) is placed in a 250-ml. beaker, and 150 ml of 3*N* sodium hydroxide is added over a 5-minute period with vigorous stirring. The lumps of solid that form are triturated with a stirring rod or spatula for 15 minutes, and the reaction mixture stands for an additional 45 minutes to complete the reaction. One hundred milliliters of water is added, the mixture is stirred vigorously, and the crude, solid iodosobenzene is collected on a Büchner funnel. The wet solid is returned to the beaker and triturated in 200 ml of water. The solid is again collected on the Büchner funnel, washed there with 200 ml of water, and dried by maintaining suction. Final purification is effected by triturating the dried solid in 75 ml of chloroform in a beaker. The iodosobenzene **23** is separated by filtration and air-dried; weight 18.7–20.5 g. (85–93%); mp 210 °C *(Caution! Explodes!).* Iodometric titration[182] shows the product to be more than 99% pure.

Iodosylbenzene sulfate 26.

Solid (diacetoxy)iodobenzene **27** (322 mg, 1.00 mmol) was added to $NaHSO_4 \cdot H_2O$ (142 mg, 1.03 mmol) in a mortar. The mixture was ground for 5 min, and the resulting yellowish mass was transferred to a beaker and mixed with water (3 mL). A clear yellow

solution was formed after 1 min of stirring and then yellow crystals started to precipitate. After 1 hour, the precipitate was filtered, washed with cold water, and dried to afford 127 mg of a yellow crystalline solid. Additional product (71 mg) was obtained by slow evaporation of the mother liquor[172]. Overall combined yield: 198 mg (80 %); mp 143–145°C. ^{1}H NMR (300 MHz, D_2O): δ = 8.18 (d, J = 8.4 Hz, 2 H), 7.7 (t, J = 7.5 Hz, 1 H), 7.57 (t, J = 7.5 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 135.26, 134.49, 134.22, 133.84, 133.12, 132.78, 132.02, 131.62, 130.88 ppm. Anal. calcd. C 29.21, H 2.04, I 51.44, S 4.33; found C 29.22, H 2.08, I 51.06, S 4.32.

Preparation of isopropyl 2-iodoxybenzoate 98c.

To a vigorously stirred suspension of isopropyl ester of 2-iodobenzoic acid (1.45 g, 5 mmol) and sodium hypochlorite solution ("bleach", 5% NaOCl, 15 ml), 20 mL of dichloromethane was added and then excess dry ice over the course of 10 min. The reaction mixture was stirred overnight, the organic layer separated, and the aqueous layer extracted three times with dichloromethane (3 × 10 ml). The combined organic fractions were dried over anhydrous magnesium sulfate, and the solvent was evaporated in a vacuum to afford 1.43 g (89%) of product **98c**, mp 156 - 157°C (decomposition; recrystallized from CH_2Cl_2/ether). ^{1}H NMR ($CDCl_3$): δ 8.34 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 5.31 (m, 1H) 1.35 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (CDCl3): δ 167.5, 149.6, 134.9, 131.8, 130.2, 126.8, 124.8, 71.9, 21.8. Anal. Calcd for $C_{10}H_{11}IO_4$: C, 37.29; H, 3.44; I, 39.40. Found: C, 37.21; H, 3.49; I, 39.36.

Typical Procedure for Catalytic Oxidation of Organic Substrates with perfluoro-iron(III) tetraazaporphyrine-(μ-oxodimer) 112.

A solution of appropriate substrate (anthracene **70**, 2-tert-butylanthracene **115**, naphthalene **119**, phenanthrene **64**, adamantane **121**, toluene **124**, 2-methylnaphthalene **128**, ethylbenzene **133,** tetralin) in dichloromethane or in acetonitrile-water (1:1 v:v) mixture was mixed with 0.5%, 1%, 2%, 5%, or 10% perfluoro-iron(III) tetraazaporphyrine-(μ-oxodimer) **112** and appropriate oxidant (PhIO **23**, $[(PhIO)_3SO_3]$

26, Oxone®, isopropyl 2-iodoxybenzoate **98c,** H_2O_2, or CH_3COOOH) under stirring, at room temperature. Samples of the reaction mixture (15-40 μL) were collected every 5 (30) minutes, filtered through 2–3 cm of silica gel suspended in a Pasteur pipette, washed with a mixture of ethyl acetate and hexane (2:3 v:v), and analyzed using GC-MS.

Typical Procedure for Catalytic Oxidation of Anthracene 70 to Anthraquinone 71.

A solution of anthracene **70** (8.9 mg, 0.05 mmol) in dichloromethane (1 ml) or in acetonitrile-water (1:1 v:v) mixture (1 ml) was mixed with 0.5%, 1%, 2%, 5%, or 10% perfluoro-iron(III) tetraazaporphyrine-(μ-oxodimer) **112** and appropriate oxidant (PhIO **23**, $[(PhIO)_3SO_3]$ **26**, Oxone®, isopropyl 2-iodoxybenzoate **98c,** H_2O_2, or CH_3COOOH) under stirring, at room temperature. Samples of the reaction mixture (15-40 μL) were collected every 5 (30) minutes, filtered through 2–3 cm of silica gel suspended in a Pasteur pipette, washed with a mixture of ethyl acetate and hexane (2:3 v:v), and analyzed using GC-MS.

Typical Procedure for Catalytic Oxidation of 2-tert-butylanthracene 115.

A solution of 2-tert-butylanthracene **115** (11.7 mg, 0.05 mmol) in dichloromethane (1 ml) or in acetonitrile-water (1:1 v:v) mixture (1 ml) was mixed with 0.5%, 1%, 2%, 5%, or 10% perfluoro-iron(III) tetraazaporphyrine-(μ-oxodimer) **112** and appropriate hypervalent iodine oxidant (PhIO **23**, $[(PhIO)_3SO_3]$ **26**, Oxone®, isopropyl 2-iodoxybenzoate **98c,** H_2O_2, or CH_3COOOH) under stirring, at room temperature. Samples of the reaction mixture (15-40 μL) were collected every 5 (30) minutes, filtered through 2–3 cm of silica gel suspended in a Pasteur pipette, washed with a mixture of ethyl acetate and hexane (2:3 v:v), and analyzed using GC-MS.

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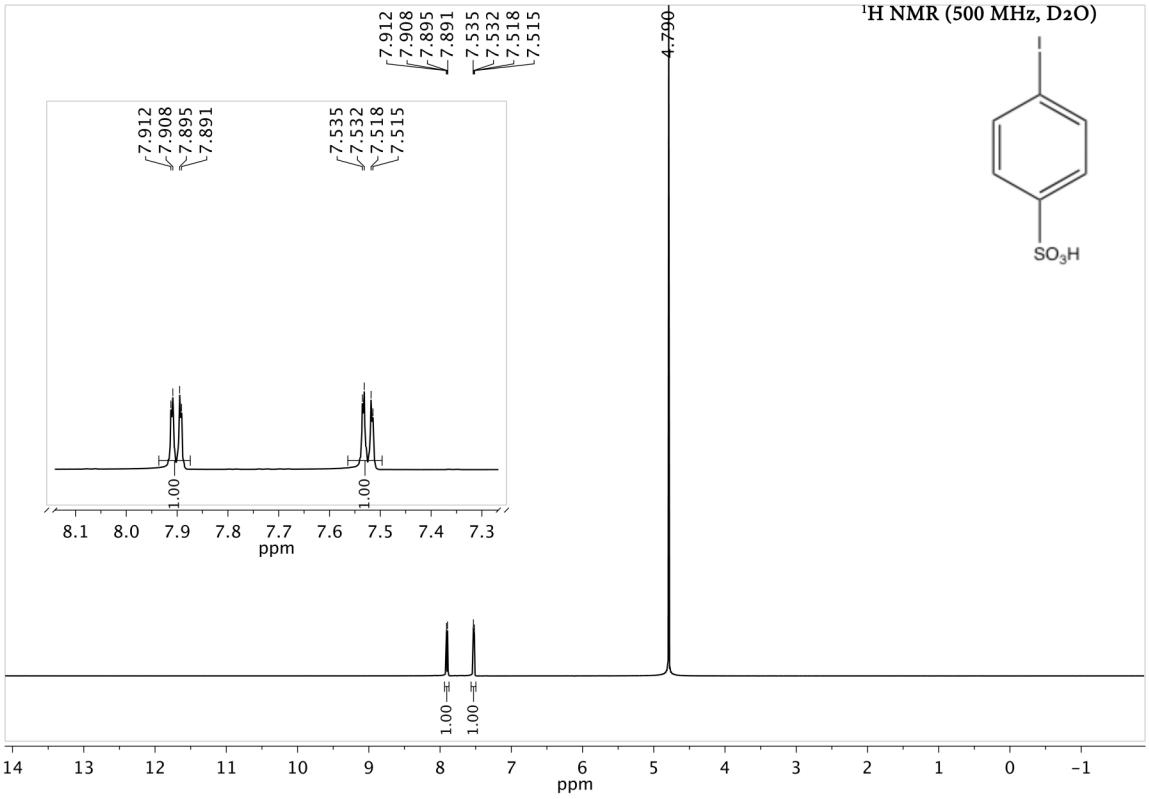
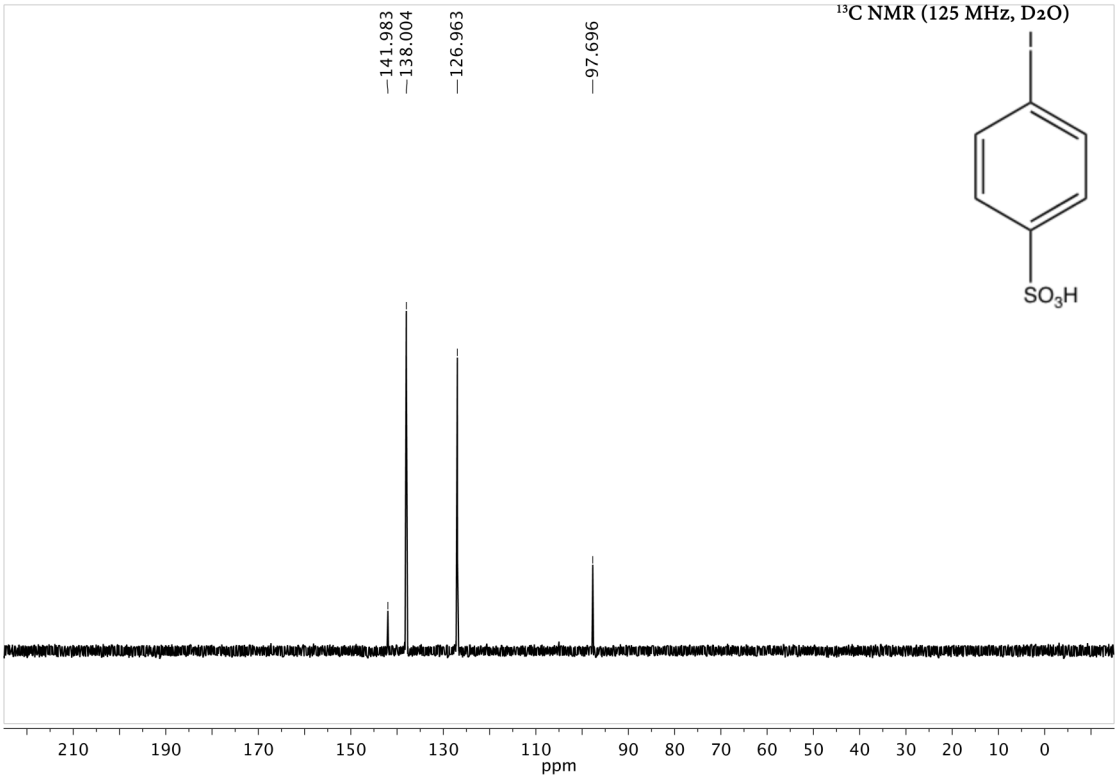
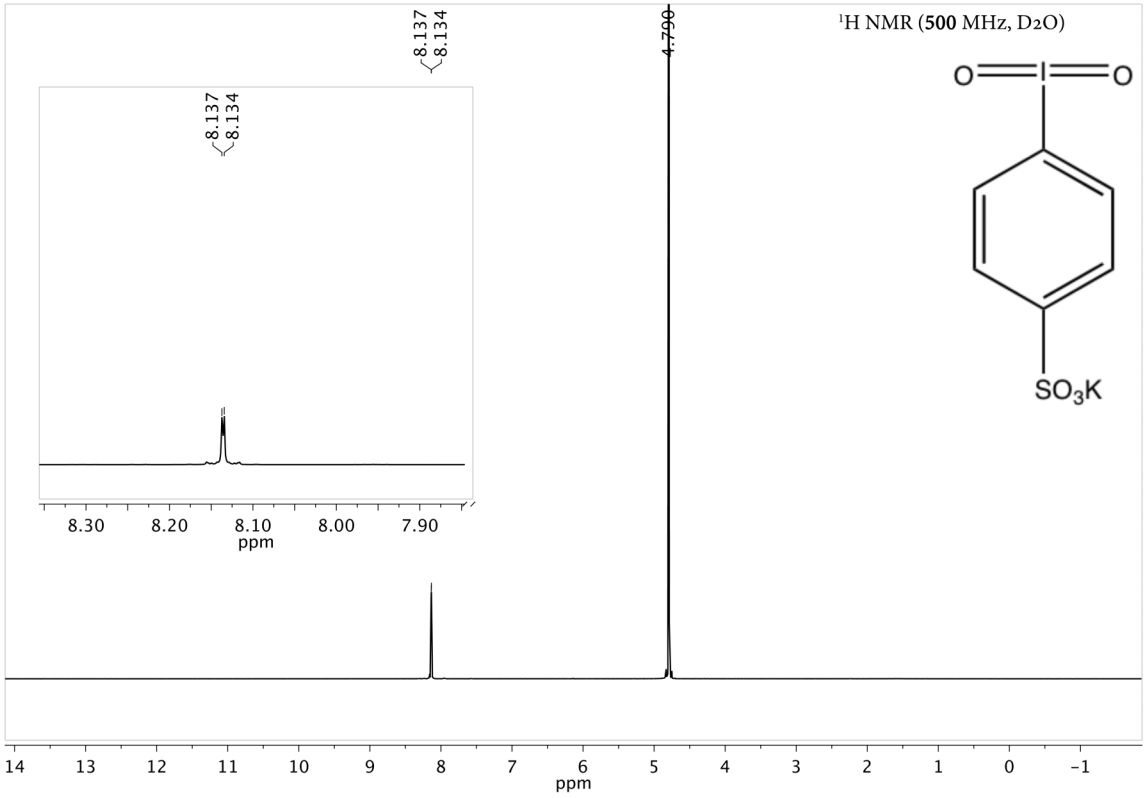
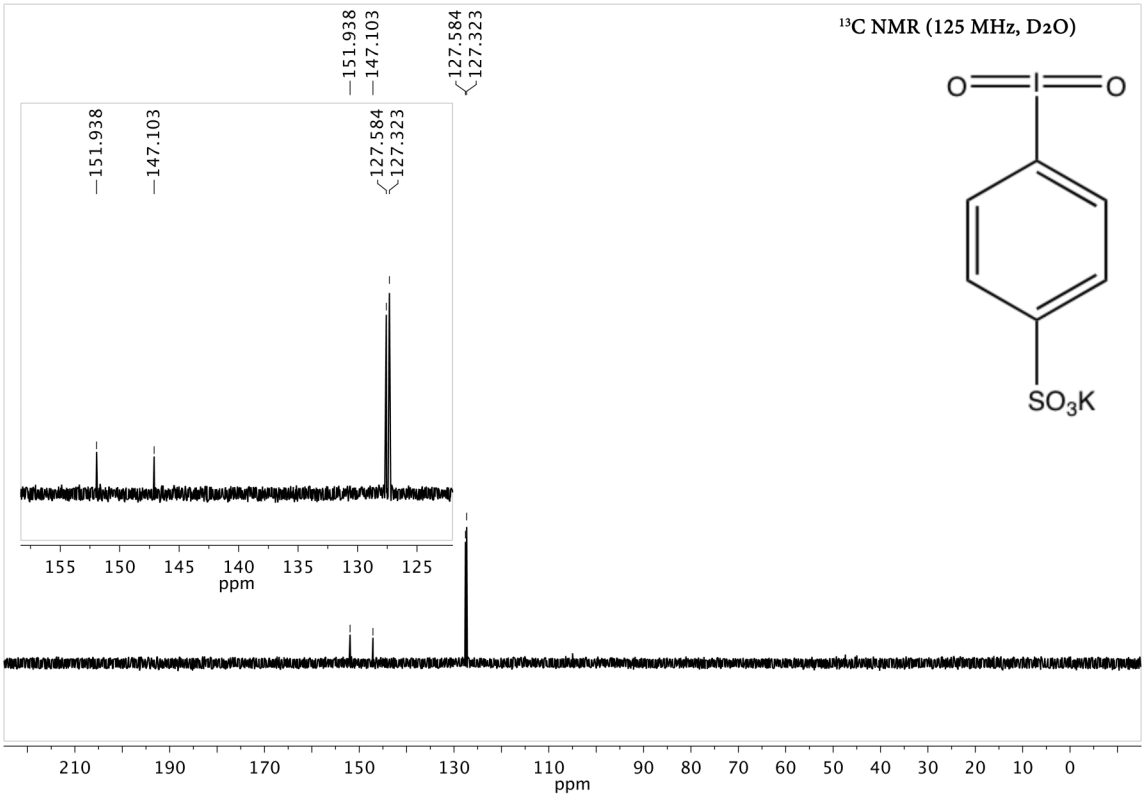
Appendices

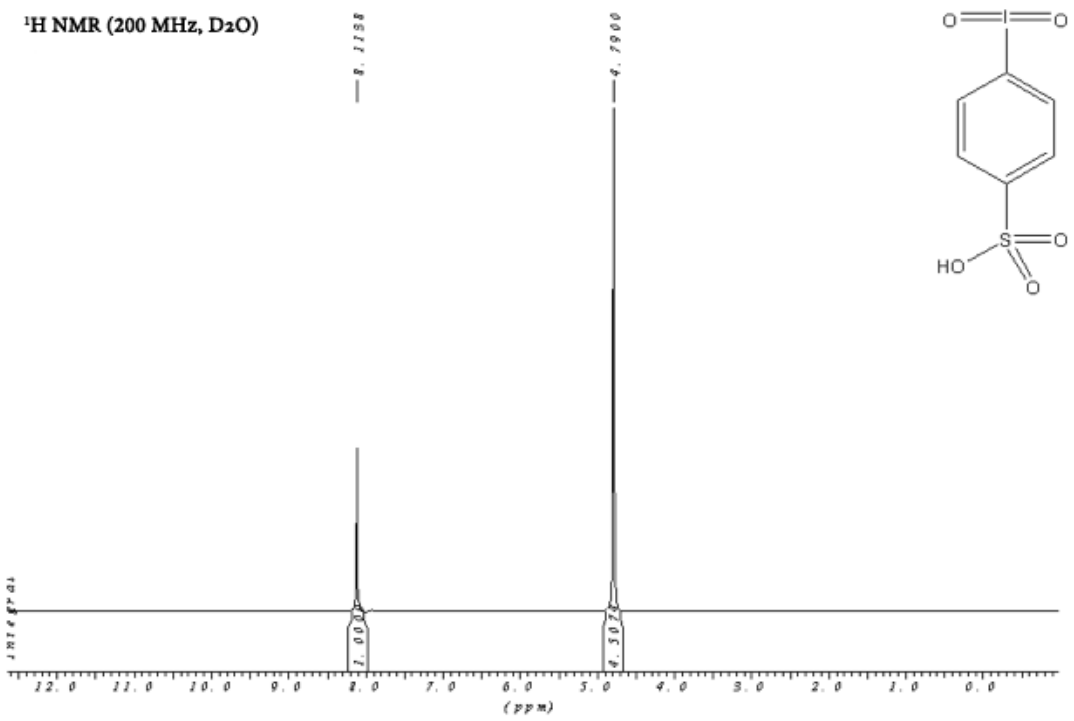
^{1}H-NMR and ^{13}C-NMR Spectra of Compounds

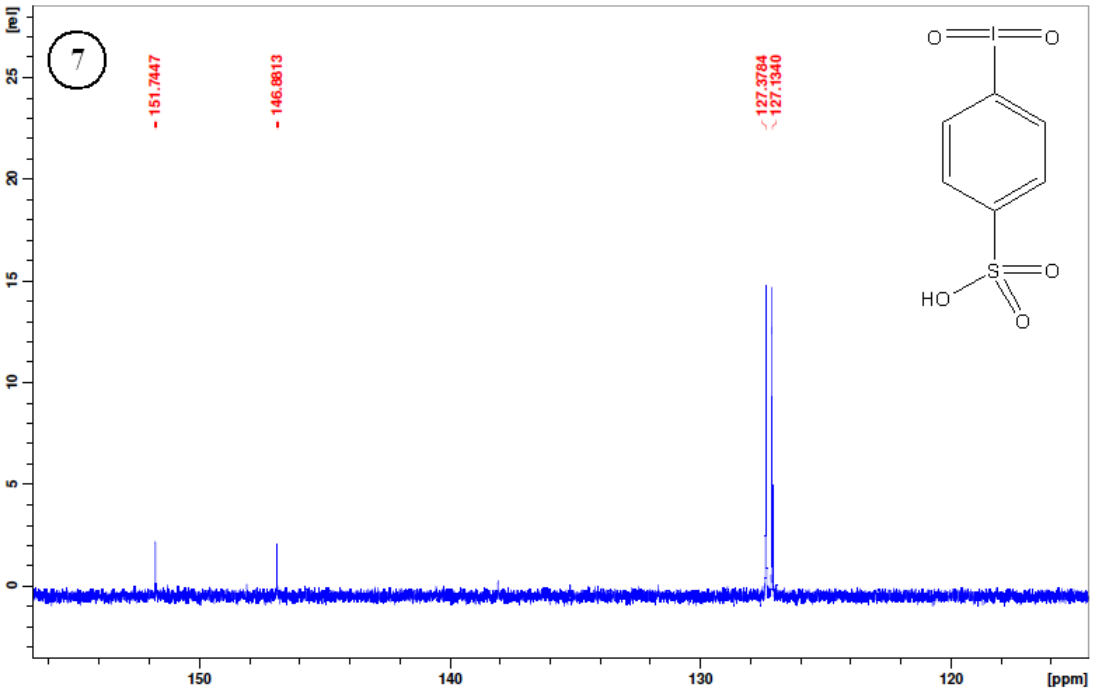


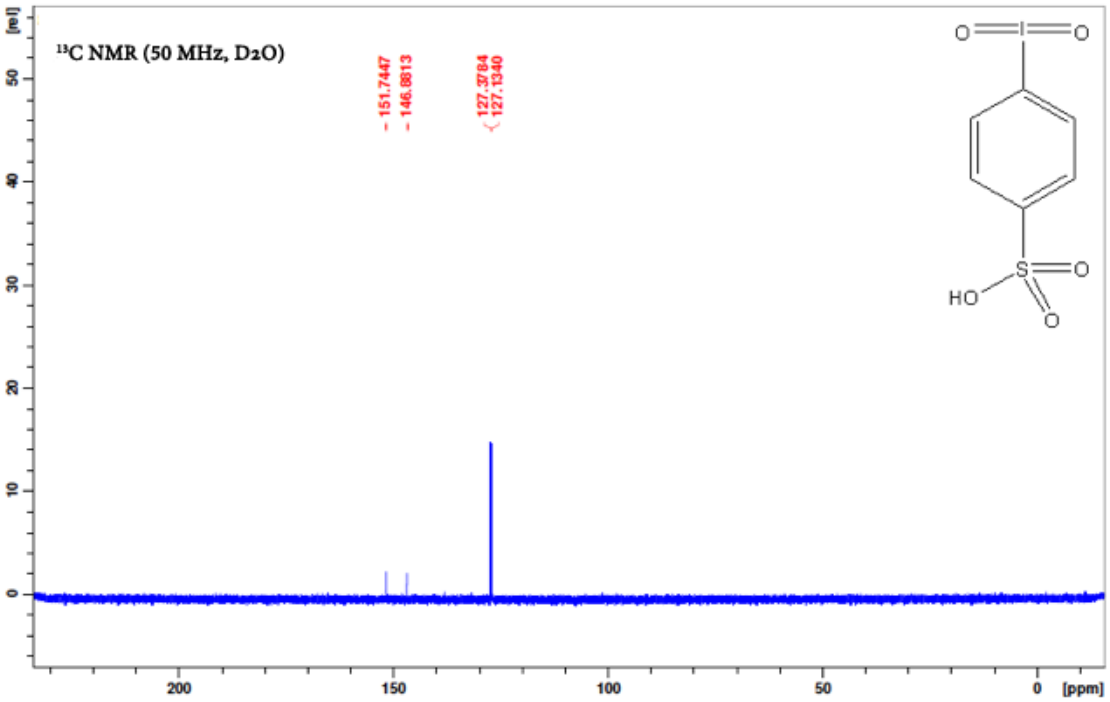

^{13}C NMR (125 MHz, D2O)
141.983
138.004
126.963
97.696
SO3H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
ppm

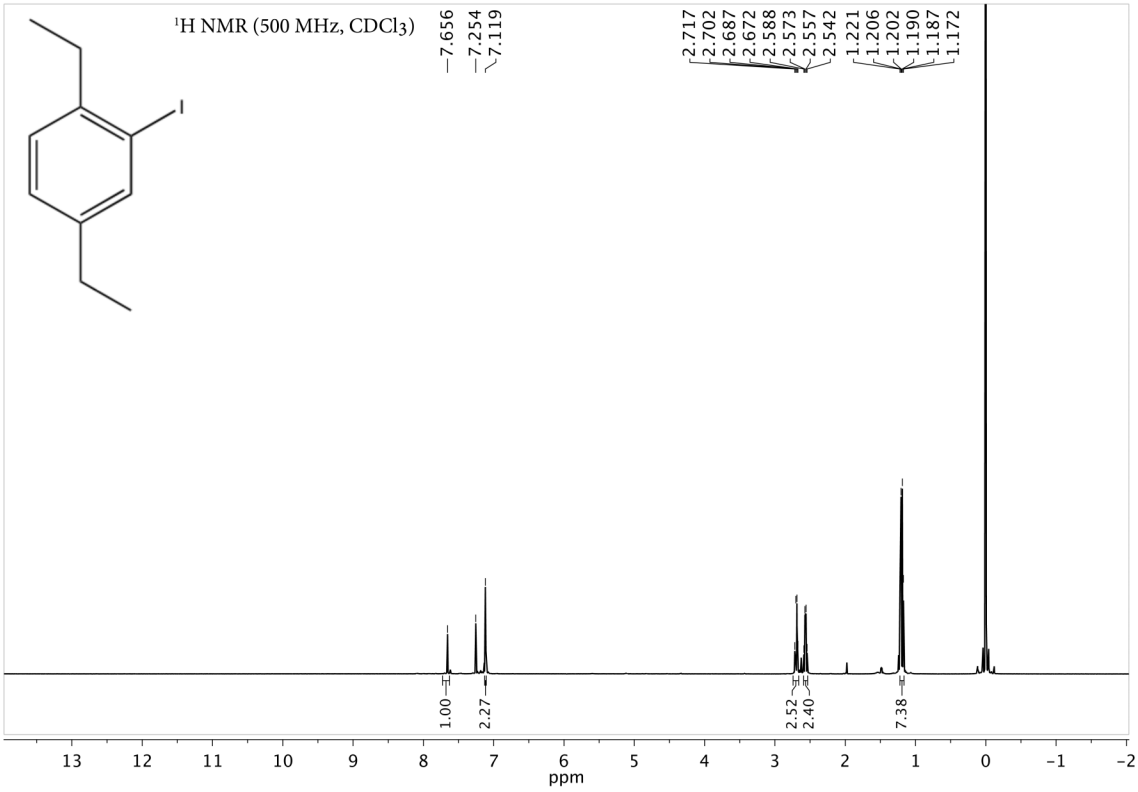

8.137
8.134
4.790
^{1}H NMR (**500** MHz, D_2O)
O
I
O
SO_3K
8.137
8.134
8.30
8.20
8.10
8.00
7.90
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm

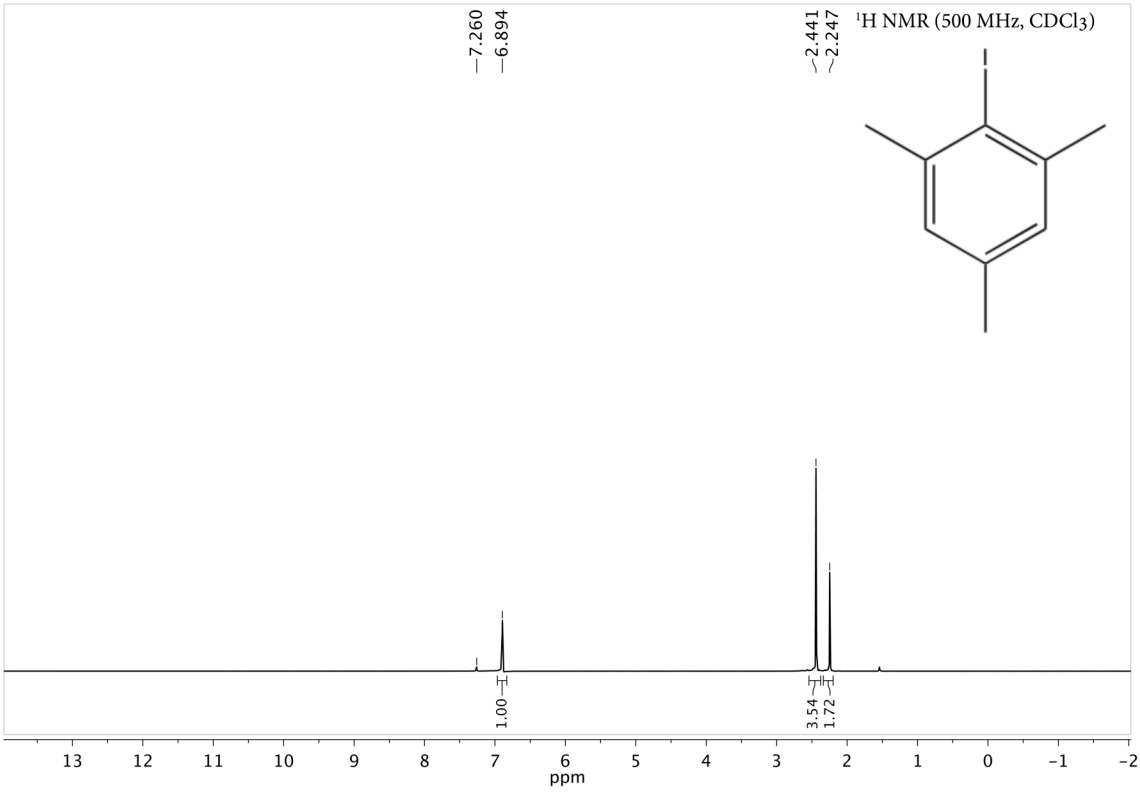

^{13}C NMR (125 MHz, D2O)
151.938
147.103
127.584
127.323
O
I
O
SO3K
155 150 145 140 135 130 125
ppm
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
ppm

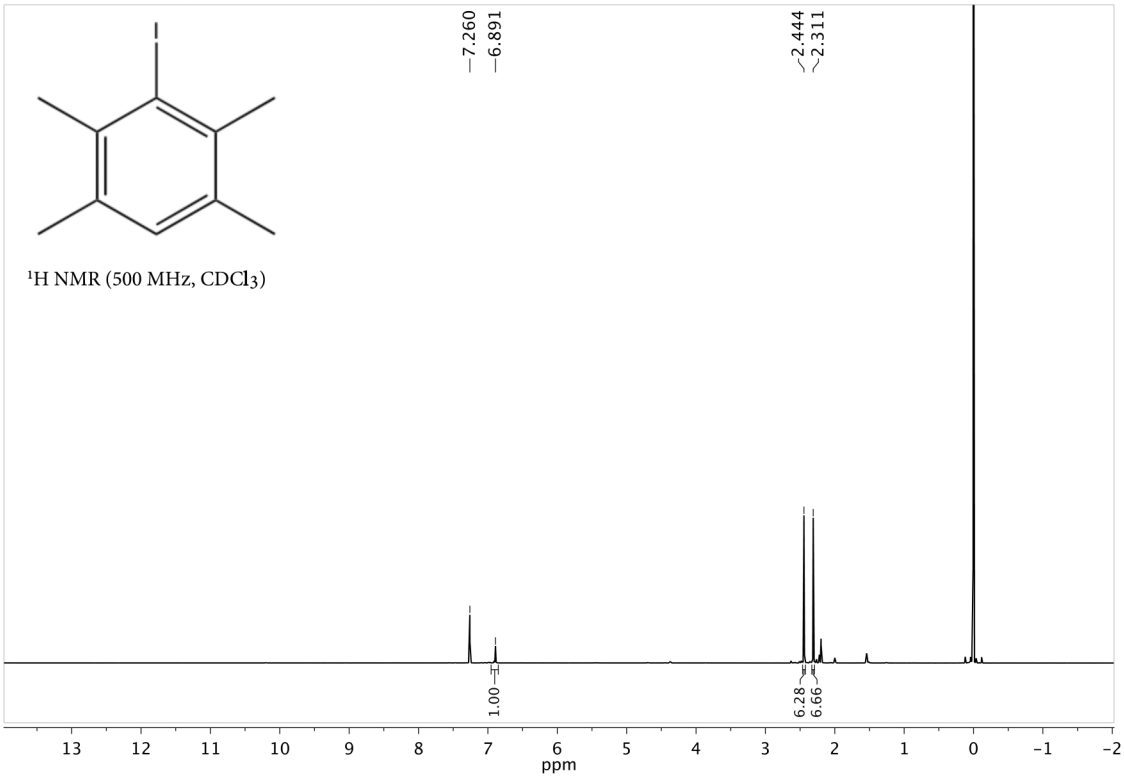

¹H NMR (200 MHz, D2O)
8.1198
4.7900
1.0000
4.3076
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)
O
I
O
S
O
HO
O


7
151.7447
146.8813
127.3784
127.1340
[rel]
25
20
15
10
5
0
150
140
130
120
[ppm]
O
I
O
S
O
HO
O

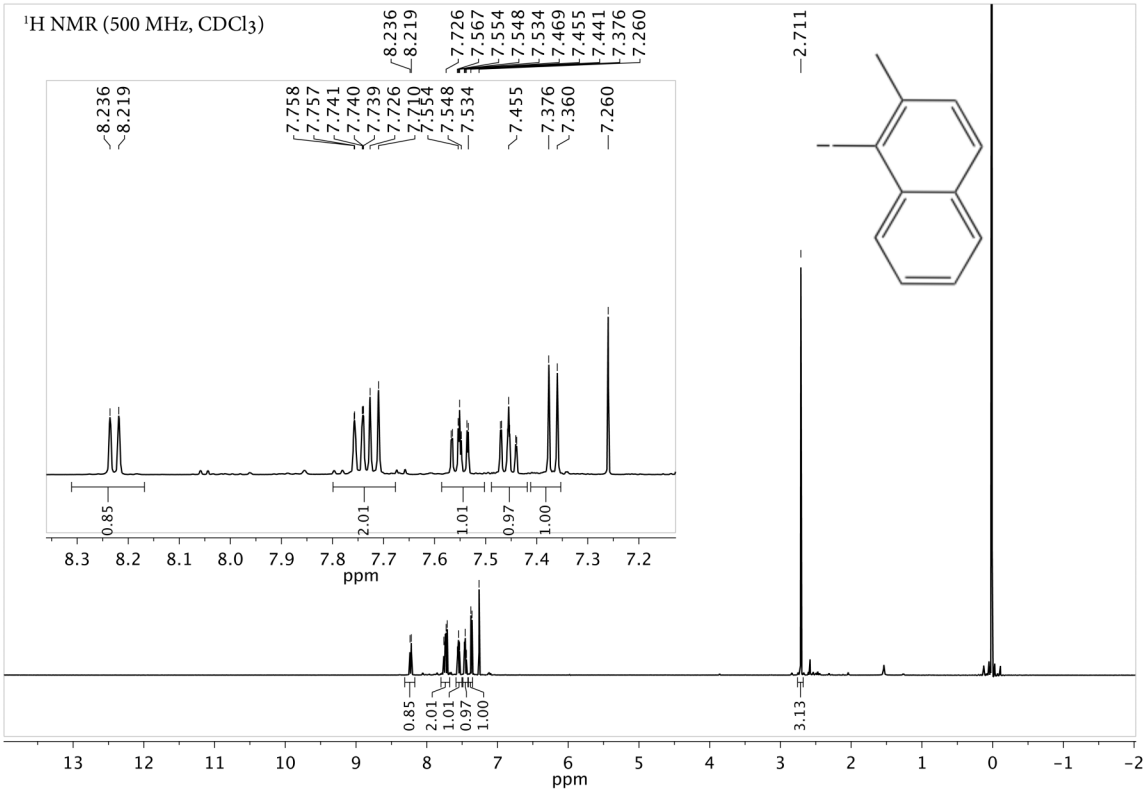

^{13}C NMR (50 MHz, D$_2$O)
151.7447
146.8813
127.3784
127.1340
[rel]
50
40
30
20
10
0
200
150
100
50
0
[ppm]
O
I
O
S
O
HO
O

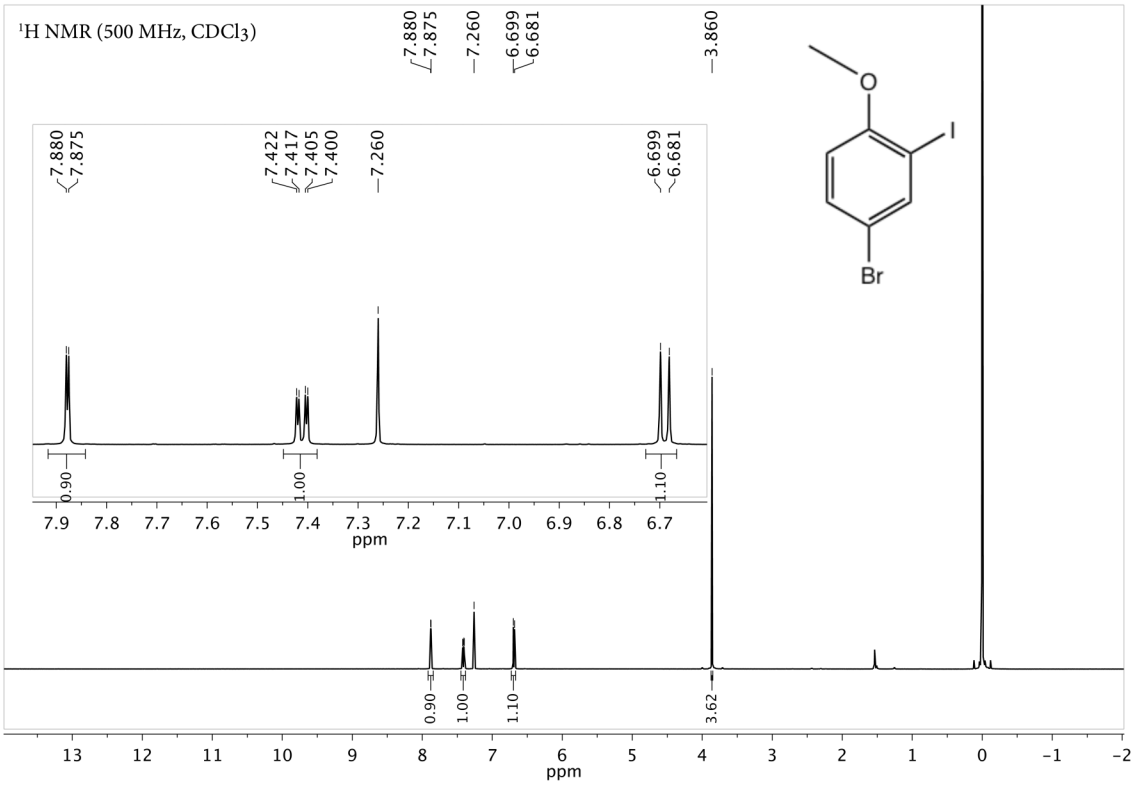

^{1}H NMR (500 MHz, $CDCl_3$)
I
7.656
7.254
7.119
2.717
2.702
2.687
2.672
2.588
2.573
2.557
2.542
1.221
1.206
1.202
1.190
1.187
1.172
1.00
2.27
2.52
2.40
7.38
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm

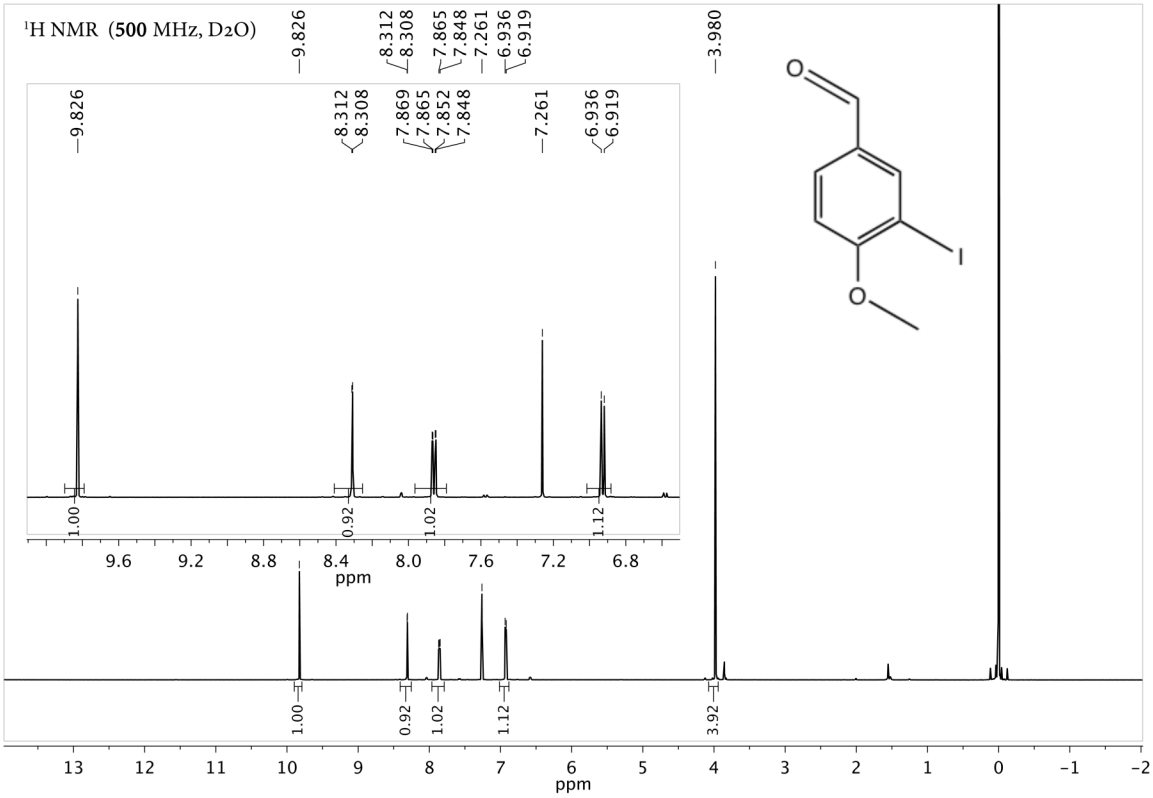

7.260
6.894
2.441
2.247
1H NMR (500 MHz, CDCl3)
1.00
3.54
1.72
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm



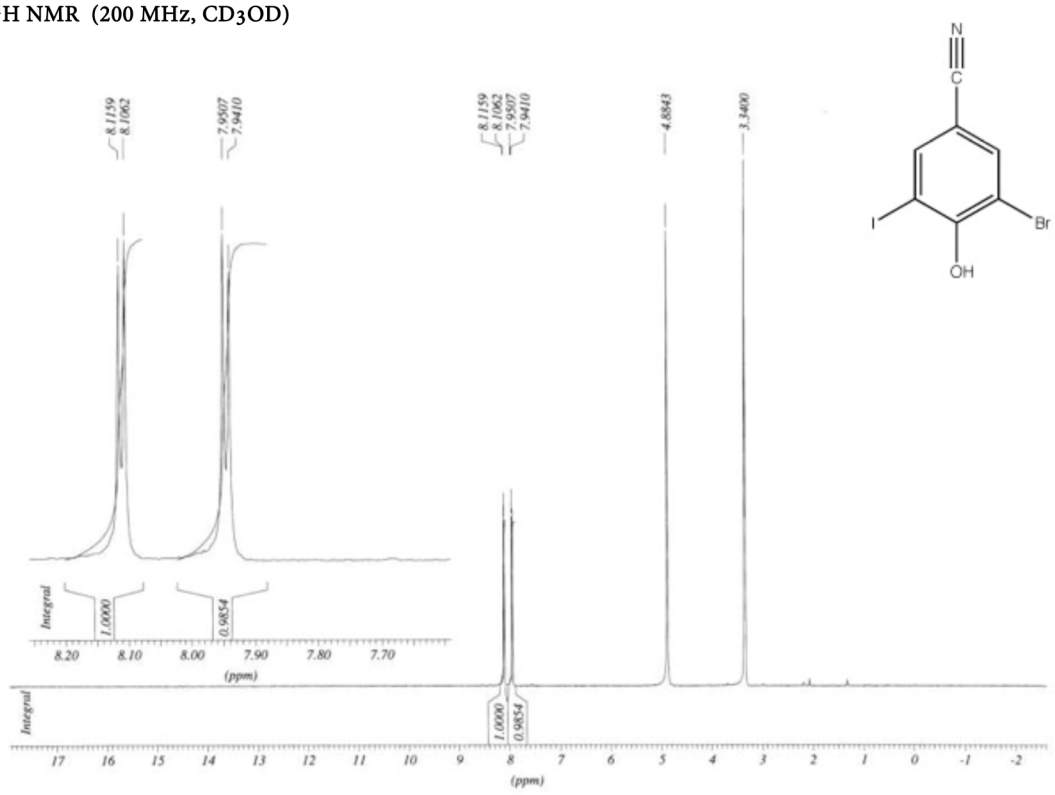
^{1}H NMR (500 MHz, $CDCl_3$)

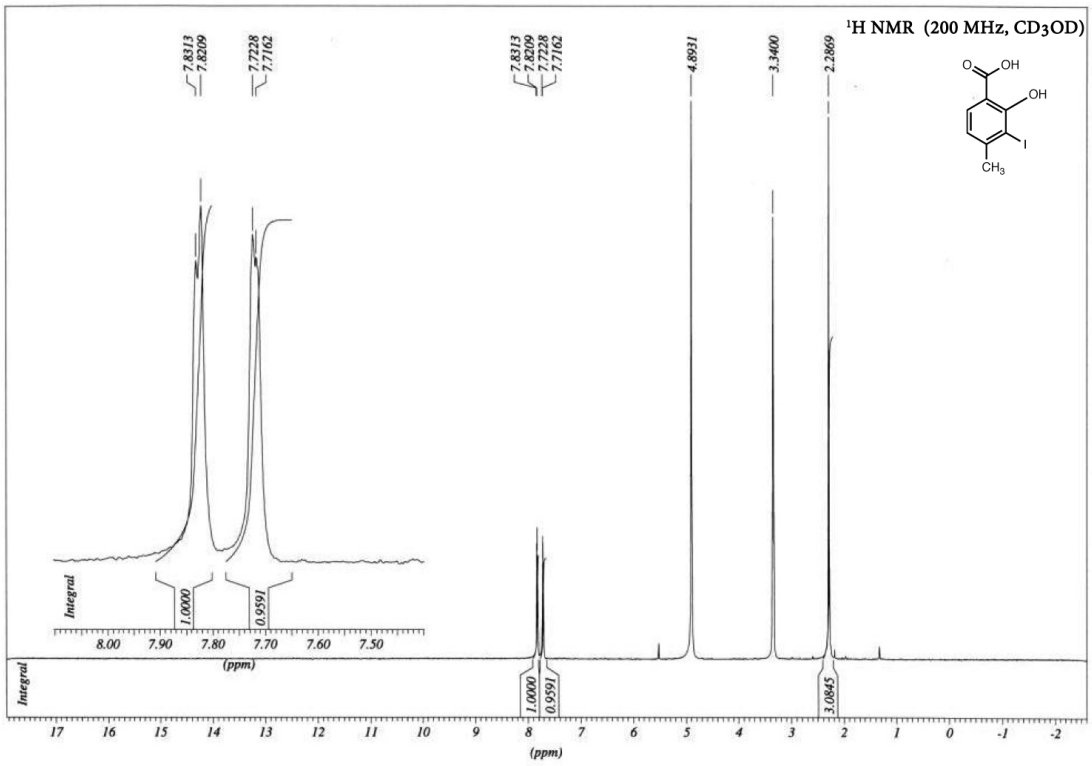

1H NMR (500 MHz, CDCl3)
8.236
8.219
7.726
7.567
7.554
7.548
7.534
7.469
7.455
7.441
7.376
7.260
2.711
7.758
7.757
7.741
7.740
7.739
7.726
7.710
7.554
7.548
7.534
7.455
7.376
7.360
7.260
0.85
2.01
1.01
0.97
1.00
3.13
ppm

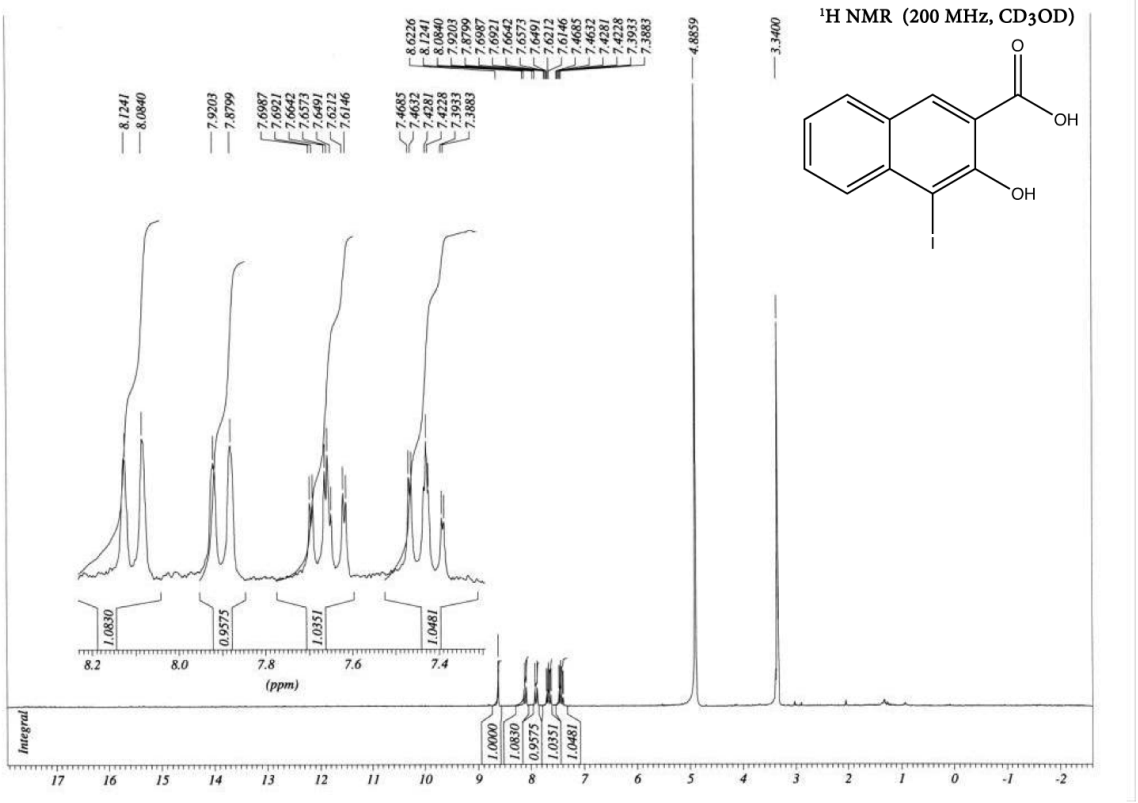

^{1}H NMR (500 MHz, $CDCl_3$)
7.880
7.875
7.260
6.699
6.681
3.860
O
I
Br
7.422
7.417
7.405
7.400
0.90
1.00
1.10
3.62
ppm

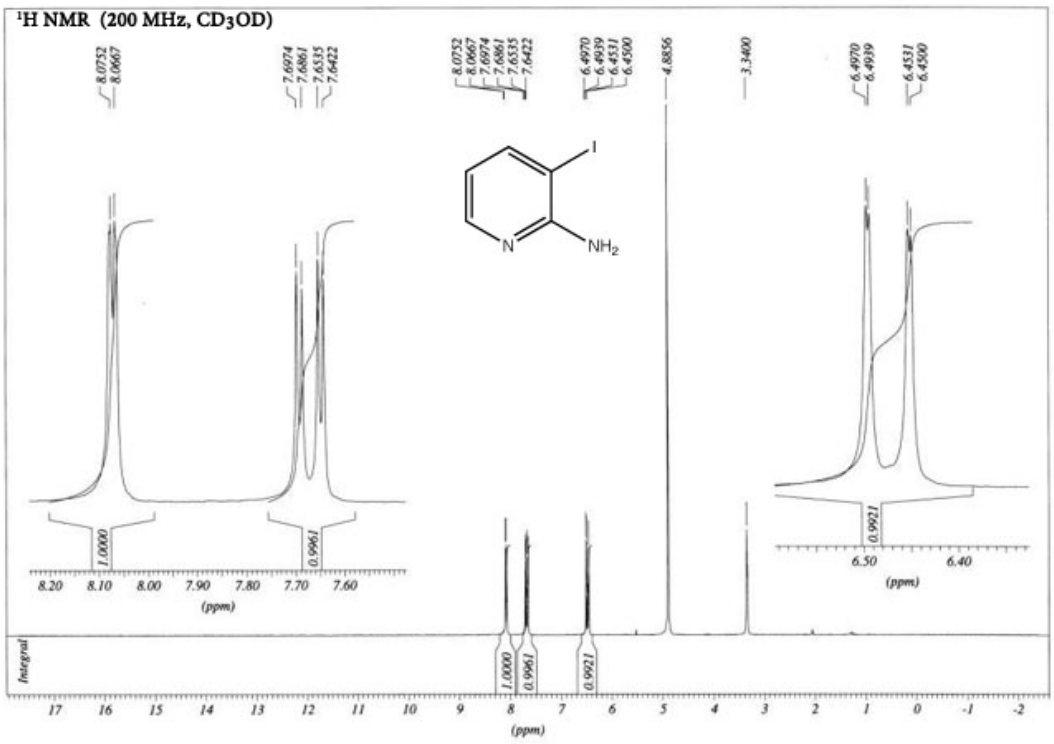

¹H NMR (500 MHz, D2O)
9.826
8.312
8.308
7.865
7.848
7.261
6.936
6.919
3.980
O
I
O
ppm

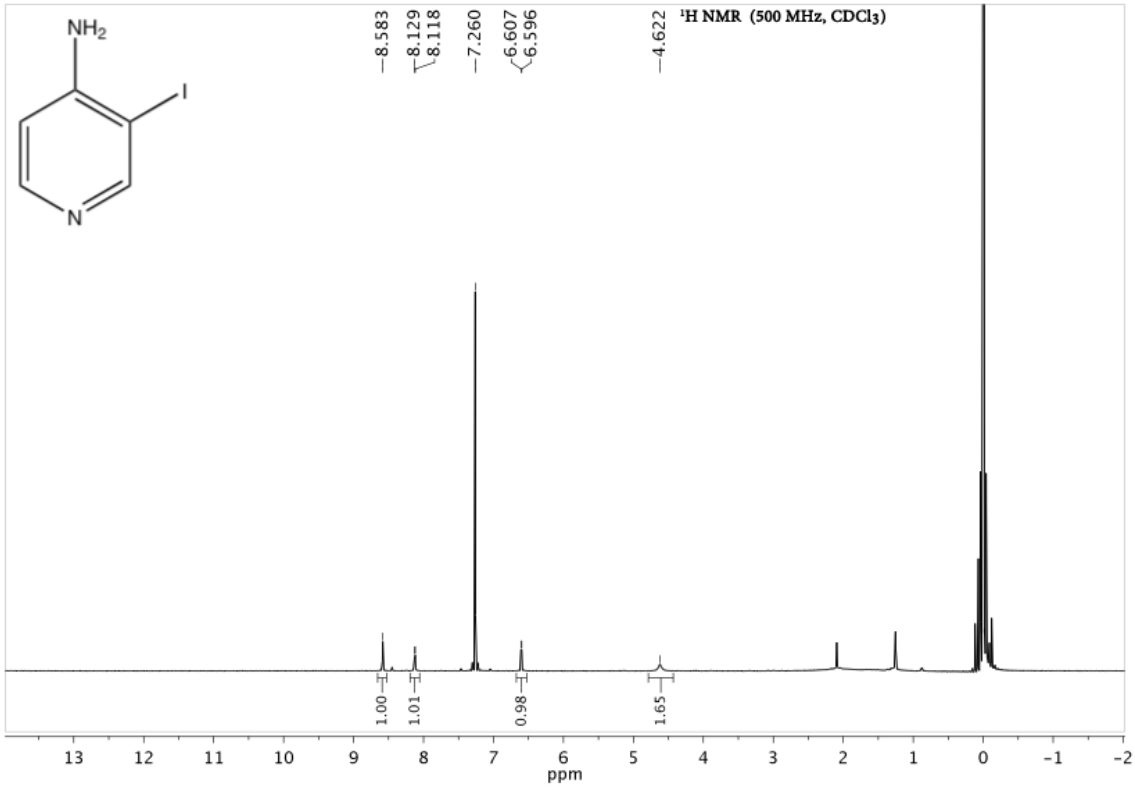
^{1}H NMR (200 MHz, CD_3OD)

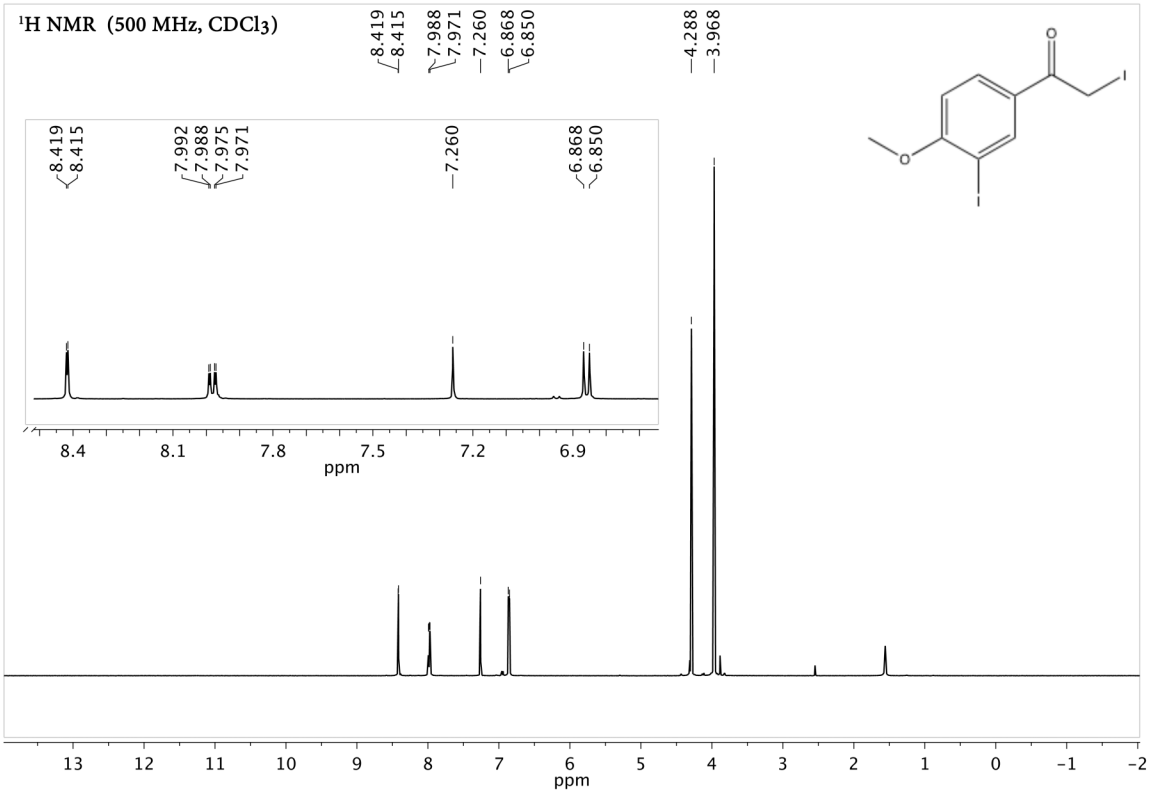


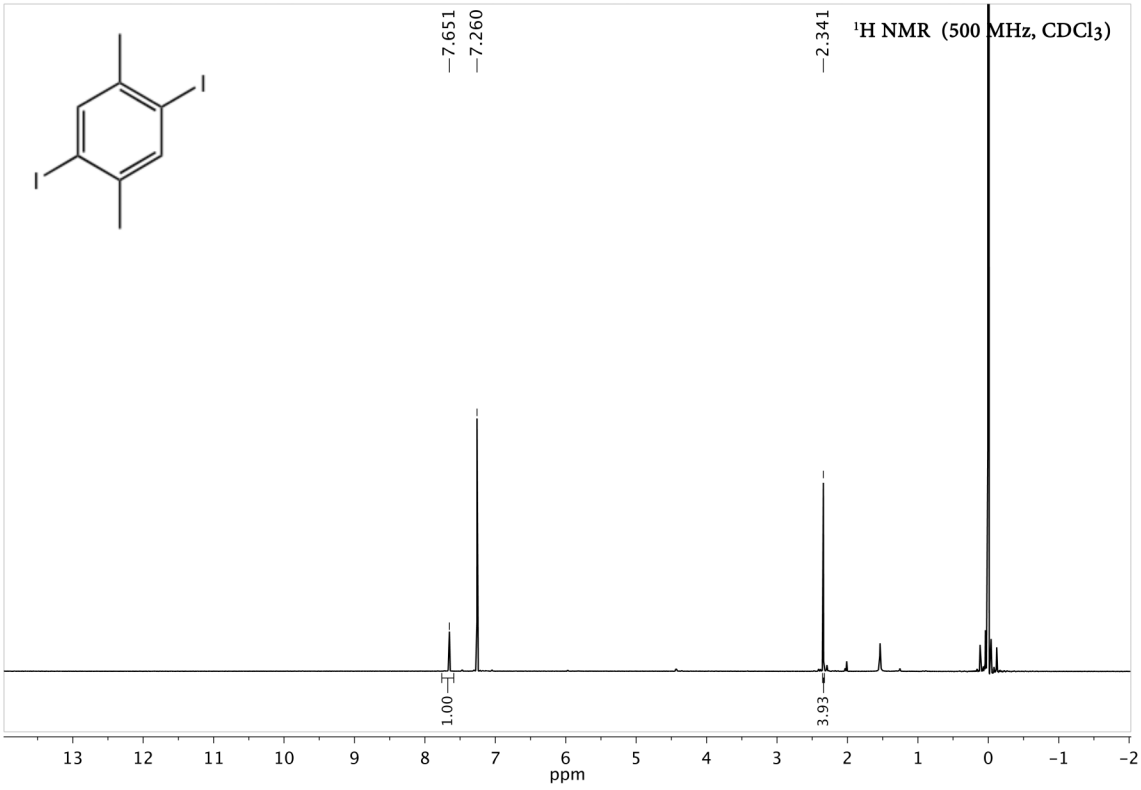

¹H NMR (200 MHz, CD3OD)
7.8313
7.8209
7.7228
7.7162
4.8931
3.3400
2.2869
OH
OH
I
CH3
Integral
1.0000
0.9591
3.0845
(ppm)

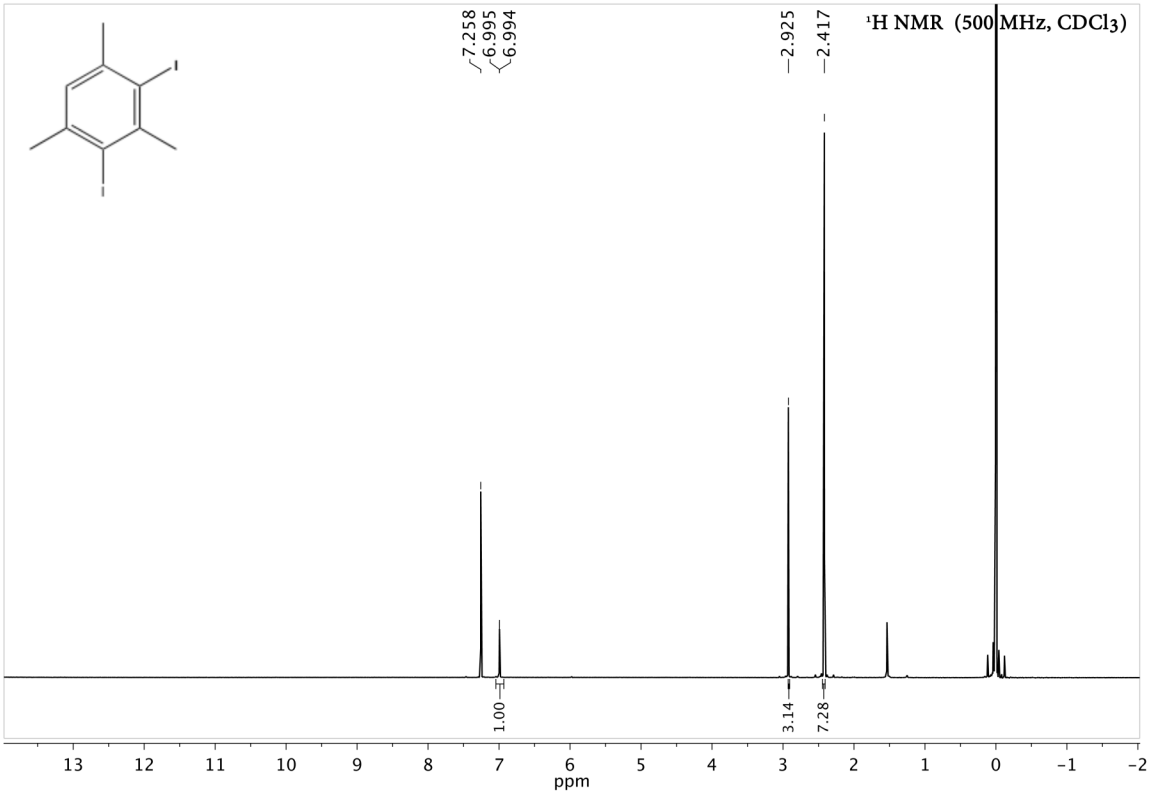

¹H NMR (200 MHz, CD3OD)
8.6226
8.1241
8.0840
7.9203
7.8799
7.6987
7.6921
7.6642
7.6573
7.6491
7.6212
7.6146
7.4685
7.4632
7.4281
7.4228
7.3933
7.3883
4.8859
3.3400
OH
OH
I
1.0830
0.9575
1.0351
1.0481
(ppm)
integral
1.0000
1.0830
0.9575
1.0351
1.0481

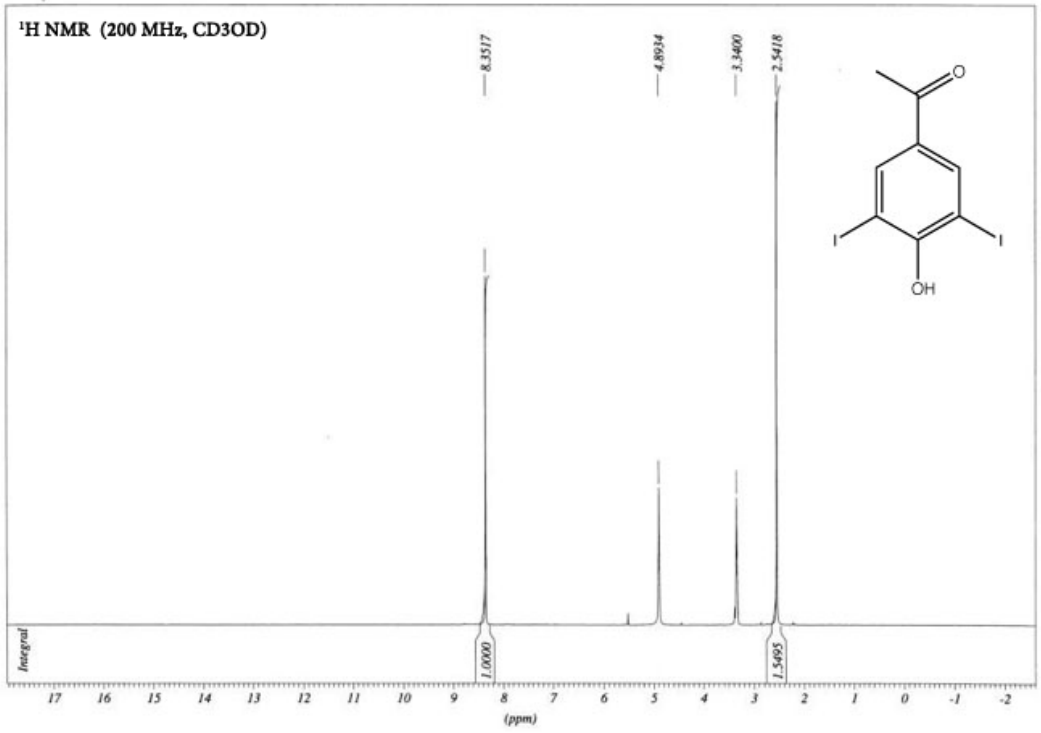

¹H NMR (200 MHz, CD3OD)
8.0752
8.0667
7.6974
7.6861
7.6535
7.6422
6.4970
6.4939
6.4531
6.4500
4.8856
3.3400
I
N
NH2
1.0000
0.9961
0.9921
Integral
(ppm)

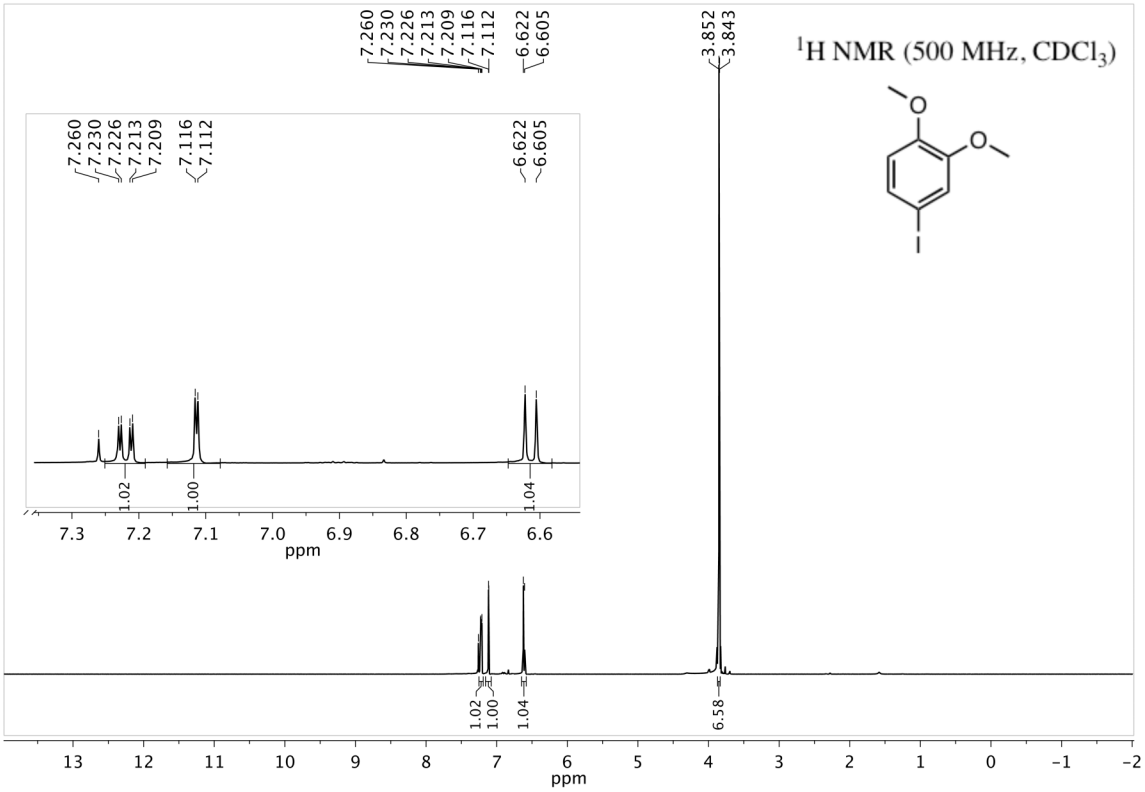

NH2
I
N
8.583
8.129
8.118
7.260
6.607
6.596
4.622
1H NMR (500 MHz, CDCl3)
1.00
1.01
0.98
1.65
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm

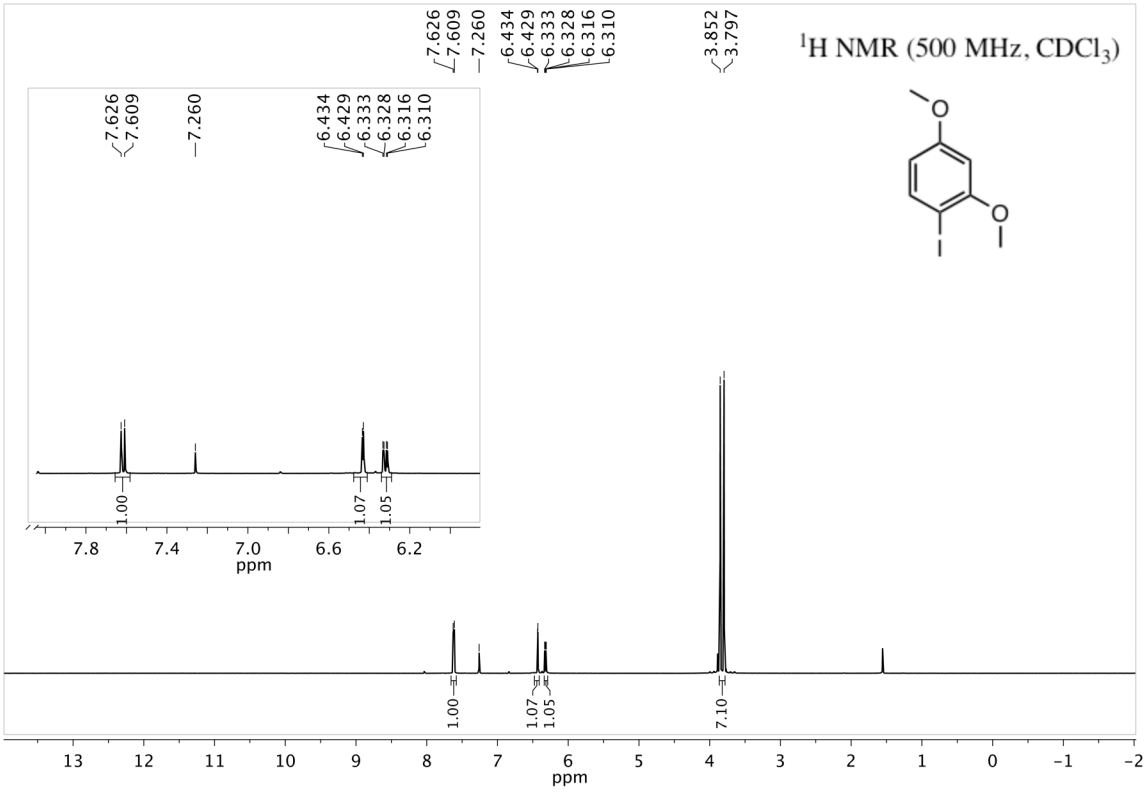

¹H NMR (500 MHz, CDCl3)
8.419
8.415
7.988
7.971
7.260
6.868
6.850
4.288
3.968
7.992
7.975
ppm
O
I

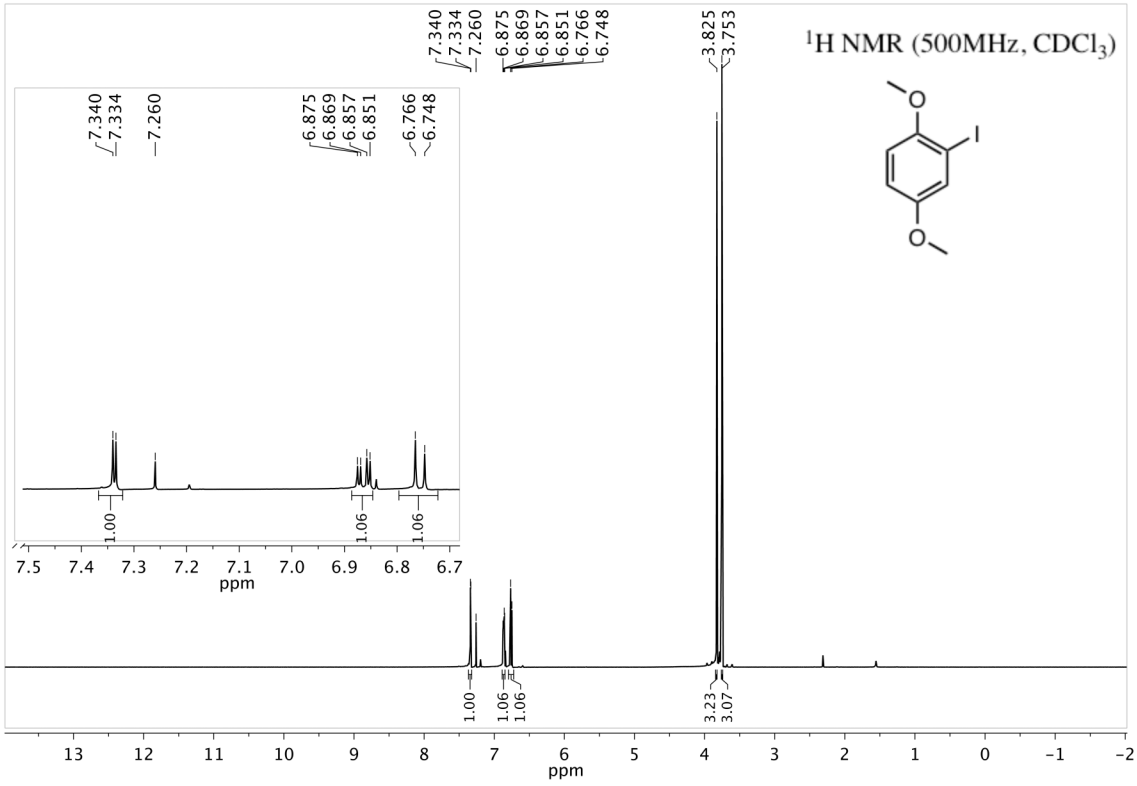

7.651
7.260
2.341
^{1}H NMR (500 MHz, $CDCl_3$)
I
I
1.00
3.93
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm


^{1}H NMR (500 MHz, CDCl$_3$)
7.258
6.995
6.994
2.925
2.417
1.00
3.14
7.28
13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2
ppm


¹H NMR (200 MHz, CD3OD)
8.3517
4.8934
3.3400
2.5418
O
I
I
OH
Integral
1.0000
1.5495
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
(ppm)


^{1}H NMR (500 MHz, $CDCl_3$)
7.260
7.230
7.226
7.213
7.209
7.116
7.112
6.622
6.605
3.852
3.843
1.02
1.00
1.04
6.58
ppm


^{1}H NMR (500 MHz, $CDCl_3$)
7.626
7.609
7.260
6.434
6.429
6.333
6.328
6.316
6.310
3.852
3.797
1.00
1.07
1.05
7.10
ppm


^{1}H NMR (500MHz, $CDCl_3$)
7.340
7.334
7.260
6.875
6.869
6.857
6.851
6.766
6.748
3.825
3.753
O
I
O
1.00
1.06
1.06
3.23
3.07
ppm