Investigation of Iodonium Salts: Synthesis, Stability and Reactivity

Department of Chemical Sciences

Eman Saleh Zawia

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Contents

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Finally, special thanks go to my country for allowing me to have this opportunity to study a PhD degree.

Abbreviations

Bpy: 2.2-bipyridine.

Boc: *tert*-butyloxycarbonyl.

BINAP: 2.2-bis(diphenylphosphino)-1,1-binaphthyl.

Cbz: benzyloxycarbonyl.

Cp: cyclopentadienyl complex.

m-CPBA: m-chloroperoxybenzoic acid.

Cy: cyclohexyl.

CH_2Cl_2: dichloromethane.

CTAB: cetyltrimethylammonium bromide.

DCE: 1,2-dichloroethane.

DIAD: diisopropyl azodicarboxylate.

DEPEA: *N*,α-Diethylphenylethylamine.

Dppe: 1,2-bis(diphenylphosphino)ethane

Dibmim BF_4: 1-(4-acetoxyiodobenzyl)-*N*-methylimidazolium tetrafluoroborate.

DMF: *N*,*N*-dimethylformamide.

DMP: Dess–Martin periodinane.

DMSO: dimethylsulfoxide.

DIC: diisopropyl carbodiimide.

DMAP: *N*,*N*-dimethyl-4-aminopyridine.

Emin BF_4: 1-ethyl-*N*-methylimidazolium tetrafluoroborate hydroxyl(tosyl)iodobenzene.

HTIB: hydroxyl(tosyl)iodobenzene.

HRMS: high resolution mass spectrometry.

h: hour.

IBX: 2-iodoxybenzoic acid.

IMC: isothermal microcalorimetry.

KHMDS: potassium bis(trimethylsilyl)amide.

LED: light emitting diode.

IR: Infrared

MS: mass spectrometry.

NMR: nuclear magnetic resonance spectroscopy.

PIDA: phenyliodine(III) diacetate.

PIFA: [Bis(trifluoroacetoxy)iodo]benzene.

PTSA: *p*-toluenesulfonic acid monohydrate.

TBAF: tetra-*n*-butylammonium fluoride.

TFA: trifluoroacetic anhydride.

TFAA: trifluoroacetetic anhydride.

TFE: trifluoroethanol.

THF: tetrahydrofuran.

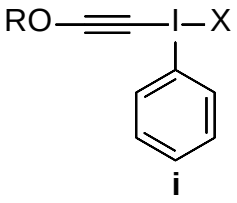
TIPS-EBX: triisopropylsilylethynylbenziodoxole.

TMS: trimethylsilane.

rt: room temperature.

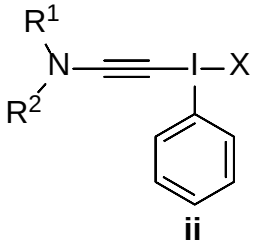
Abstract

This thesis describes several approaches to the synthesis of novel iodonium salts. Firstly, attempts to synthesise a variety of novel alkynyl(aryl)iodonium salts (**i-iii**) is discussed. Most of these attempts were unsuccessful, however, useful information for future work was obtaine. The synthesis of iodonium salt (**iii**) was successful and this compound displayed some unusual reactivity.



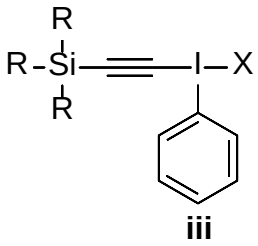
i

R = Et or Ph



ii

R^1 = Ts, R^2 = Ph



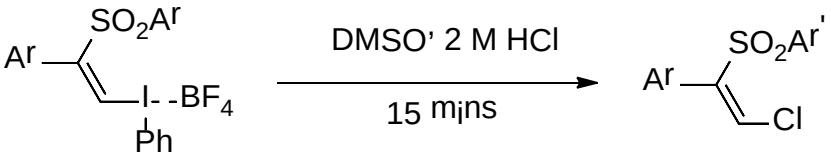
iii

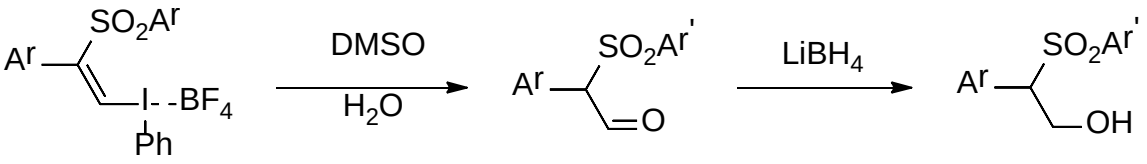
R = Me or *i*-Pr

X = BF_4, OTs, OTf

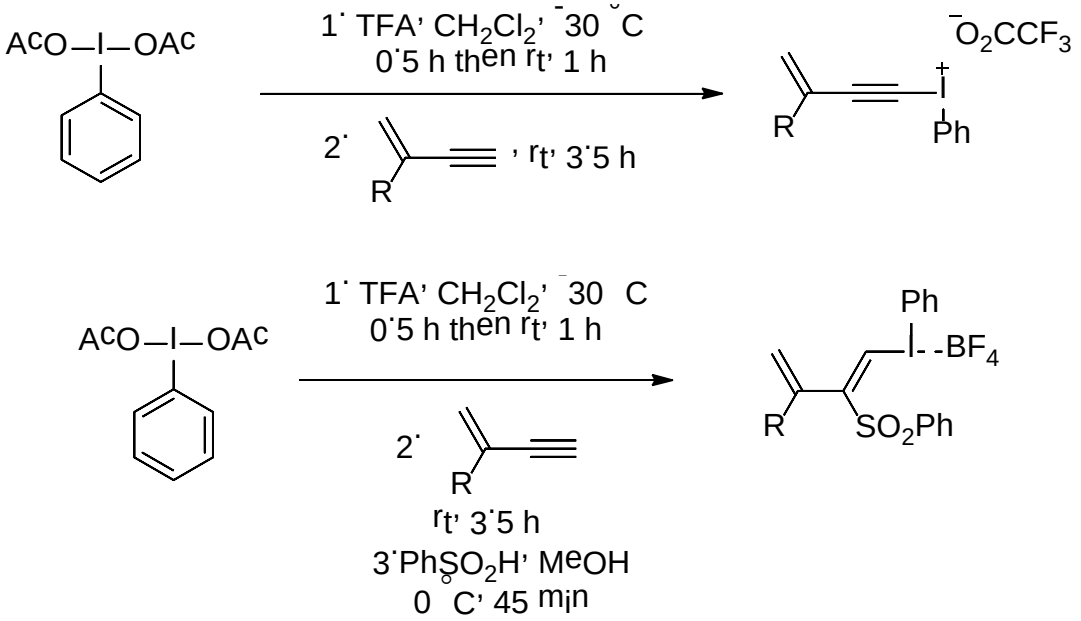
Several alkynyl(phenyl)iodonium trifluoroacetates were synthesised directly from commercially available iodobenzene diacetate and terminal acetylenes precursors with a range of substitution patterns in one step in excellent yields. These species were converted into alkenyl(arylsulfonyl)iodonium tetrafluoroborates in excellent yields by stereoselective Michael-type addition of arylsulfinic acids under protic conditions.

Secondly, new reactivity of alkenyl(arylsulfonyl)iodonium tetrafluoroborates was investigated. Specially, the conversion of these selectively into aldehydes and vinyl chlorides using aqueous DMSO was achieved.





Thirdly, two examples of stable enynyl(phenyl)iodonium trifluoroacetates were synthesised in excellent yields. These were converted into a new range of dienyl(aryl)iodonium salts.



Finally, a computational study of alkynyl(aryl)iodonium salts was undertaken in an attempt to rationalise our experimental data on reactivity and stability.

Chapter 1

1. Introduction

The element of iodine was discovered unexpectedly in 1811 by Courtois as a result of the addition of a large excess of sulfuric acid to the ash of kelp during the production of saltpetre, a critical ingredient of gunpowder. Courtois noted the production of a violet vapour upon the addition of excess sulfuric acid, and that a graphite like solid was produced upon its condensation. Courtois was unable to research the matter further due to financial restraints; however samples were supplied to others for further study. Iodine is the most electropositive of the halogen group as a result of its large atom. The most common oxidation states of iodine are +1 and -1. However, it forms multivalent compounds with other oxidation states + 3, + 5 and + 7.[1]

1.1 Hypervalent iodine chemistry.

During the last three decades hypervalent iodine chemistry has attracted much interest in the literature and has become a mainstay of organic chemistry. The benefits of hypervalent iodine species include their ease of preparation, their low environmental impact, low toxicity and the fact that they are easy to handle. [2,3]

A. General structure and bonding of hypervalent iodine compounds.

The structure of hypervalent iodine has been presented in reviews that have been published by Zhdankin *et al* and Varvoglis.[4,5] It is known that all hypervalent iodine compounds contain 3-center-4-electron bonds: one in the case of iodine(III) compounds, two in the case of iodine(V) compounds and three in the case of iodine(VII) compounds. In the case of iodine(III) species, there is one bonding orbital, a non-bonding orbital and an anti-bonding

orbital. The four electrons involved in the new bond doubly occupy both the bonding and non-bonding orbitals, leaving the anti-bonding orbital unoccupied (Figure 1). As the HOMO is localised around the two ligand groups bound to the iodine, the iodine centre itself is left highly electron deficient, whereas the molecule in general is electron rich. These facts inform much of the chemistry that hypervalent iodine compounds demonstrate. The iodine centre acts as a soft electron acceptor with the ligands able to rapidly exchange in solution. This allows attack at the iodine centre with loss of a ligand, followed by reductive elimination, furnishing an oxidised product and iodine(I) species.[4a,b]

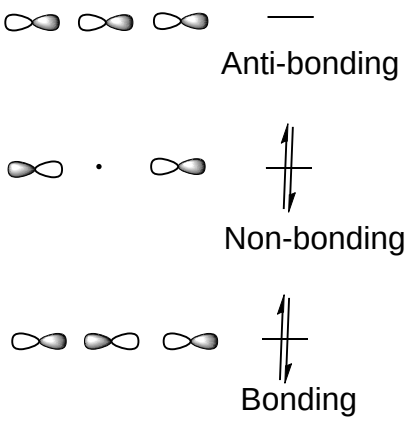
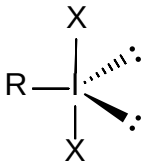


Figure 1

As mentioned above, all known compounds of hypervalent iodine are one of three types: iodine(III) (λ^3-iodanes), where the central iodine atom has 10 valence electrons, iodine (V) (λ^5-iodanes), where the central iodine atom has 12 valence electrons and iodine (VII) (λ^7-iodanes), where the central iodine atom has 14 valence electrons.

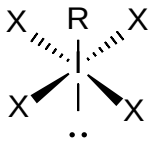
With respect to the central iodine, iodine(III) compounds have a distorted trigonal pyramidal geometry, with two heteroatom ligands in apical positions and with the least electronegative carbon ligand R and both electron pairs in equatorial positions (Figure 2).



R = Aryl group
X = Ligand e.g. Cl, OAc, ..

Figure 2

Bonding in this system is *via* a linear 3-centre, 4-electron bond. With respect to the central iodine, iodine(V) compounds have a distorted octahedral structure (Figure. 3). The electron pair and organic group are housed in the apical positions, with the four heteroatom ligands occupying the basal positions. These ligands are accommodated by two 3-centre 4-electron bonds. The organic apical group, however, is bonded *via* a standard covalent bond, utilising a 5sp orbital. [4b,c]



R = Aryl group
X = Ligand e.g. Cl, OAc, ..

Figure 3

Iodine(VII) compounds are rare, although the heptafluoroiodane is known. It adopts an unusual pentagonal pyramidal conformation and, unusually for a stable hypervalent iodine compound, contains no aromatic group or, indeed, no carbon ligands at all (Figure 4)

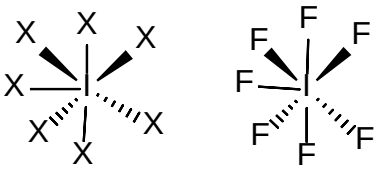


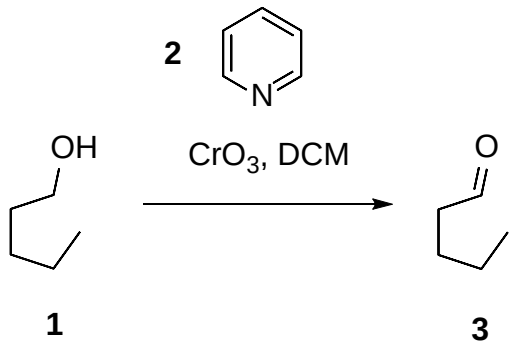
Figure 4

B. Reactions of hypervalent iodine compounds.

Many hypervalent iodine compounds with one carbon ligand are oxidants, and they undergo reactions typical of oxidants. These include oxidations of alcohols to ketones, α-oxygenations

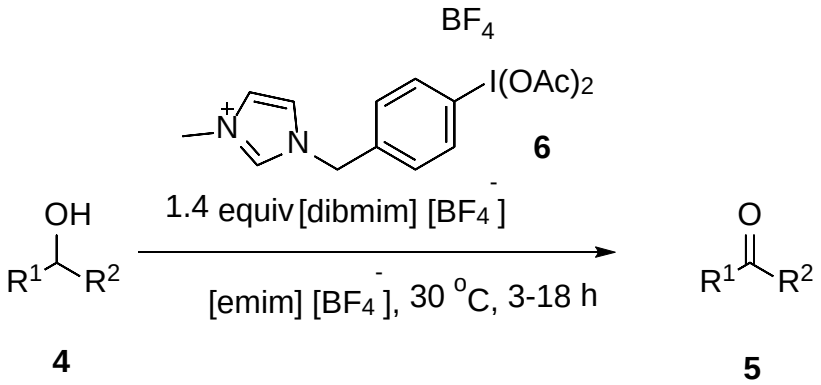
of carbonyl compounds and conversions of quinols to quinones.[4b,5] These compounds show similar reactivity to heavy metal oxidants, such as Ti(III), Hg(II) and Pd(IV) derivatives. However, as has been previously stated, they are far less toxic and environmentally damaging than heavy metal based reagents. Numerous papers have been published detailing the reactions of hypervalent iodine compounds and there are different classes of reactions possible. However, only a few of these will be considered here. One particular reaction of hypervalent iodine compounds is the oxidation of primary and secondary alcohols to aldehydes and ketones respectively. Historically, these types of transformations have been achieved by the use of CrO_3 based reagents such as the Collins reagent.[6]

For example, aldehyde **3** is generated upon treatment of alcohol **1** with CrO_3 in the presence of pyridine **2** in DCM (Scheme 1).



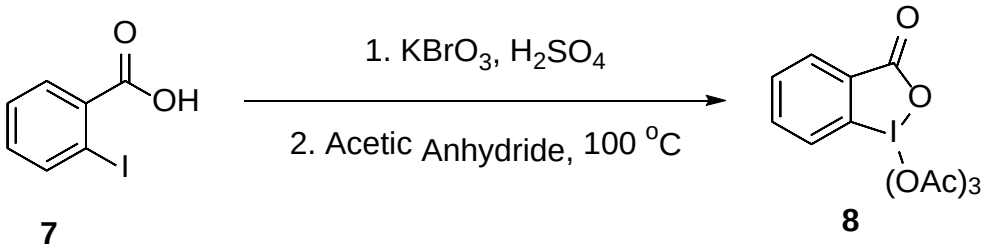
Scheme 1

However, these reactions require toxic chromium reagents which are difficult to handle and dispose of. These issues can be avoided by the use of hypervalent iodine compounds.[7] In 2005, Zhang reported the oxidation of various alcohols **4** to ketones **5** by treatment with an ionic hypervalent iodine species [dibmim] [BF_4^-] **6** in an ionic liquid solvent emim (Scheme 2). This process is highly selective for the oxidation of primary alcohols.[8]

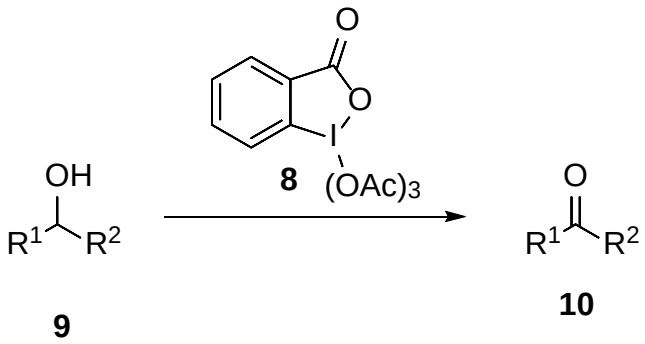


Scheme 2

A popular modern method for the oxidisation of alcohols **9** under mild conditions is the use of the hypervalent iodine compound Dess-Martin periodinane (DMP) **8** which is prepared by treatment of 2-iodobenzenzoic acid **7** with $KBrO_3$ in sulfuric acid, followed by heating to 100 ^oC with acetic anhydride (Scheme 3 and 4).[8,9]

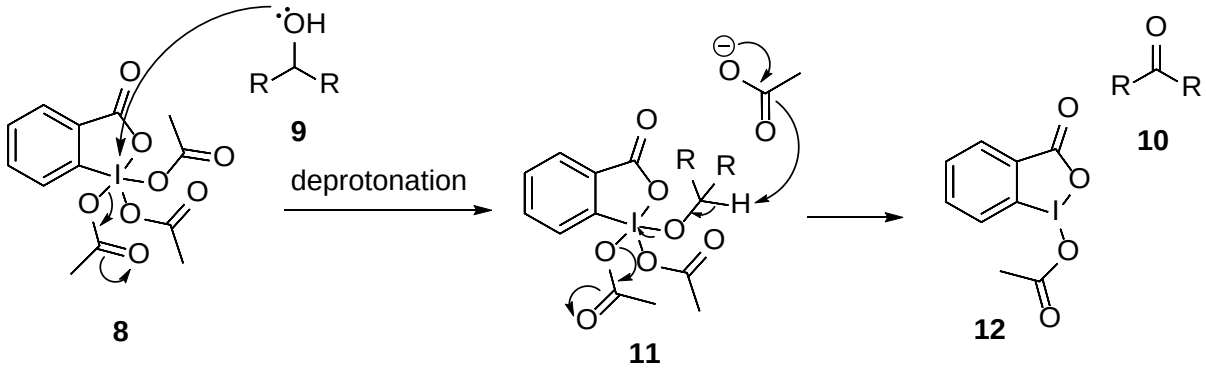


Scheme 3



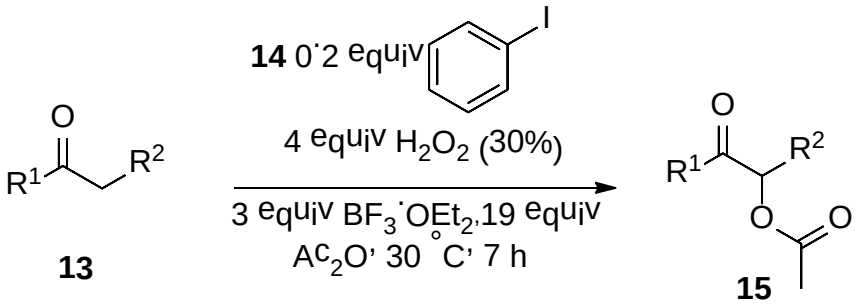
Scheme 4

The mechanism of this reaction has been studied and is believed to proceed by attack at the DMP iodine(V) centre **8** by the alcohol **9** leading to displacement of an acetate group and generation of diacetoxyalkoxy periodinane intermediate **11** upon deprotonation. Following a hypervalent twist the liberated acetate group then attacks the diacetoxyalkoxy periodinane complex **11** by deprotonating at the α-H to the alcohol, generating the carbonyl product **10**, acetic acid and an iodine(III) species (Scheme 5).[10]



Scheme 5

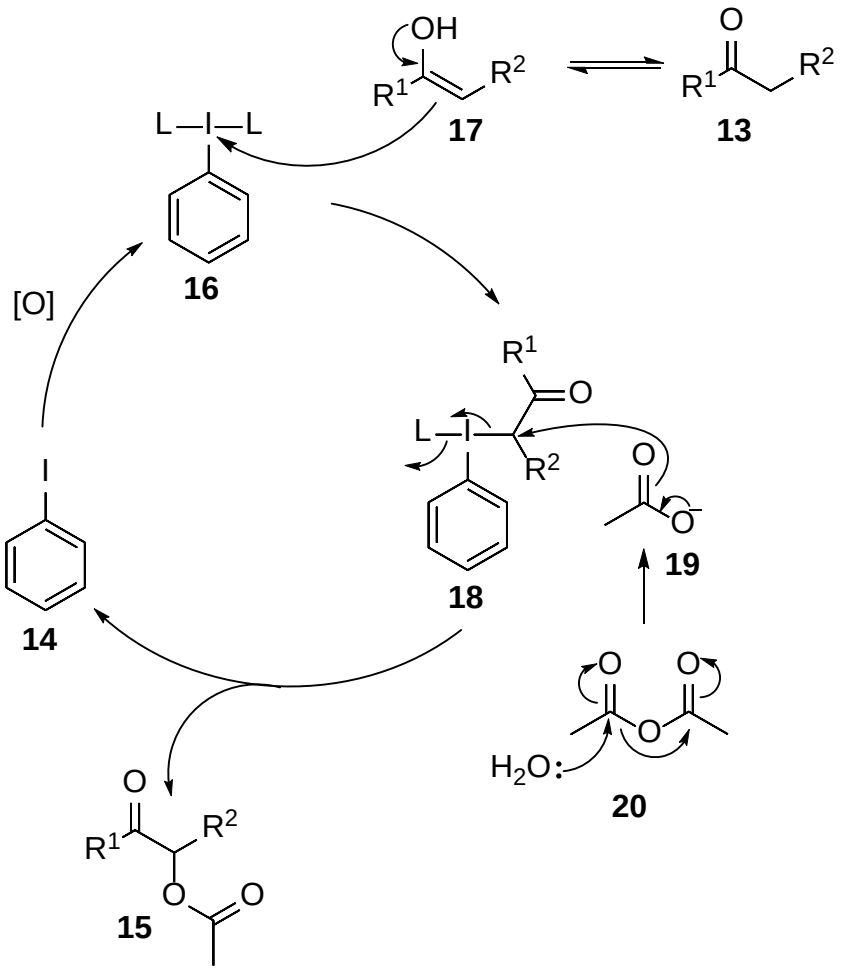
Huang *et al* reported an α-acetoxylaton of ketones **13** catalysed by iodobenzene **14**. Treatment with hydrogen peroxide and acetic anhydride in the presence of $BF_3.OEt_2$ generates the α-acetoxy ketone products **15** in moderate to good yields (Scheme 6).[11]



Scheme 6

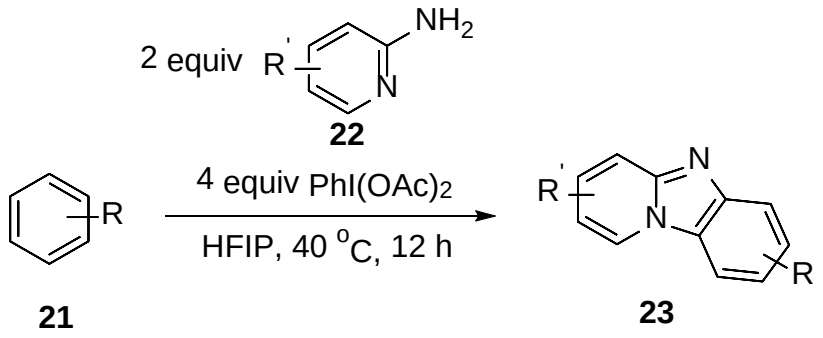
This reaction proceeds via nucleophilic attack of an *in-situ* generated iodine(III) species **16** by the ketone enol **17** generating a transient alkyl(phenyl)iodonium salt **18** which in turn is

attacked by an acetate, furnishing the product **15** and regenerating iodobenzene **14** (Scheme 7).[11]



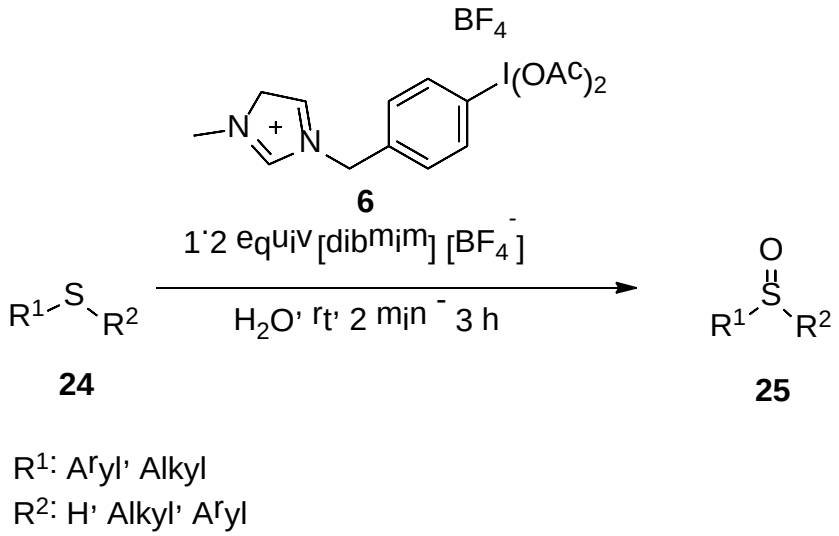
Scheme 7

A metal free iodobenzene diacetate mediated anulation of 2-aminopyridines with arenes has been developed by Antonchick and co-workers in HFIP (hexafluoroisopropanol). The group reported moderate to good yields for this process (up to 80%), with halides and esters shown to be compatible with the reported procedure (Scheme 8).[12]



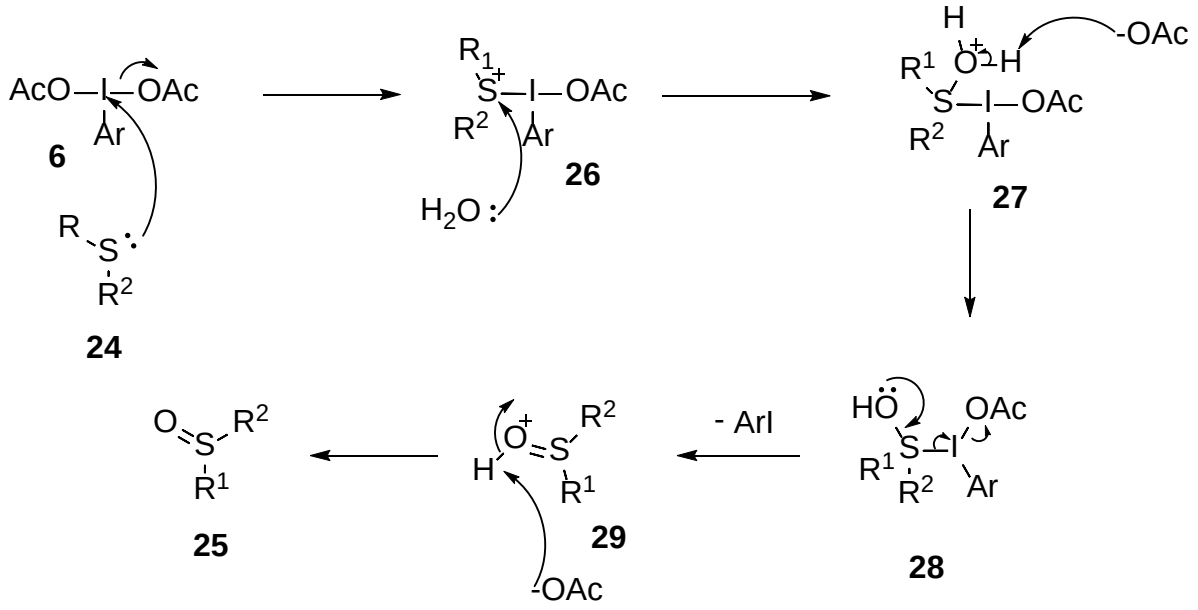
Scheme 8

Utilising Zhang's ion-supported hypervalent iodine species, [dibmim] [BF_4^-] **6**, Pei *et al* were able to create a selective oxidation of sulfides **24** to sulfoxides **25**. The reagent reportedly tolerates hydroxyl, nitrile, methoxy, alkene and ester functionalities. The group reports further that this reaction produces no over-oxidation of the substrate and, as with previous communications by the Zhang group, the environmental credentials of this process are cited (Scheme 9).[13]



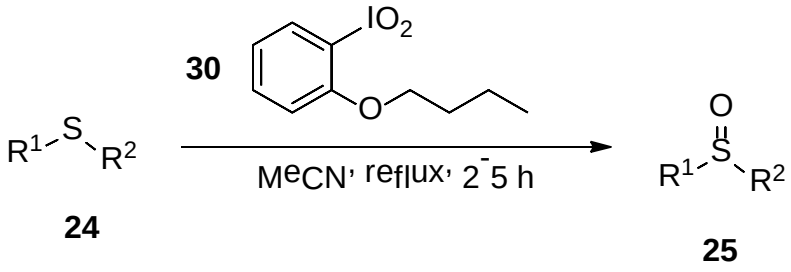
Scheme 9

This type of oxidation proceeds by ligand exchange at the iodine(III) centre **6**, generating a sulfide –iodine(III) complex **26**. This species is attacked by water **27**, followed by deprotonation and reductive elimination of iodine(III), affording the product sulfoxide **25** and an iodoarene (Scheme 10).[13]



Scheme 10

The Zhdankin group, utilising a different reagent **30**, were able to do the same transformation. This reaction requires slightly harsher conditions than those employed by the Pei group outlined above, sulfides **24** are treated with 1-butoxy-2-iodyl-benzene in refluxing acetonitrile, generating the equivalent sulfoxides **25** (Scheme 11). The hypervalent iodine reagent **30** was also found to be effective at oxidising alcohols to their equivalent carbonyls.[14]



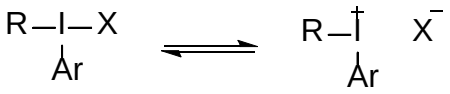
R^1: Aryl, Alkyl
R^2: H, Alkyl, Aryl

Scheme 11

1.2 Iodonium Salts.

In their seminal reviews, Zadankin and Stang define iodonium salts as any iodine(III) species with two carbon ligands.[4] In almost all cases (exceptions do exist), this can be generalised as

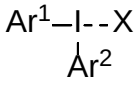
ligand(aryl)iodonium X where ligand is one of several possible carbon ligands, aryl is an aromatic ring and X is a counterion See (Figure 5) . The IUPAC name is λ^3-iodane.[15]



R: Arene, Alkene, Alkyne, Fluoroalkane, Nitrile.
Ar: Arenes, in rare cases other sp^2 or sp^3 Ligands.
X: counterion e.g. OTs, OTf, BF_4, ...

Figure 5

For the sake of this work, the same definitions shall be used, as will the term salt though in many cases this is misleading as the extent to which the bond between the iodine(III) centre and the counterion is covalent or ionic and the corresponding degree of interaction between the two varies dramatically between species. In general, the more non-coordinating the more ionic in character the species will be. Iodonium salts act as electrophilic equivalents of R, where R is a carbon ligand. Their rich chemistry has led to much interest in the literature. The most widely utilised species of iodonium salts in the literature are diaryliodonium salts. In the case of these species, both the carbon ligands are arenes, which may be either the same (symmetrical diaryliodonium salts) or different (asymmetrical diaryliodonium salts) (Figure 6).[15]



X can be any one of a number of counter ions

Figure 6

Unsymmetrical diaryliodonium salts are theoretically capable of transferring either of their aryl groups. However, selectivity is often observed. In general, in non-metal catalysed processes, the most electron rich arene is transferred. In metal catalysed processes, the least

hindered arene is transferred (Figure 7). With alkenyl-and alkynyl(aryl)iodonium salts, the alkene or alkyne ligand is invariably transferred.[16]

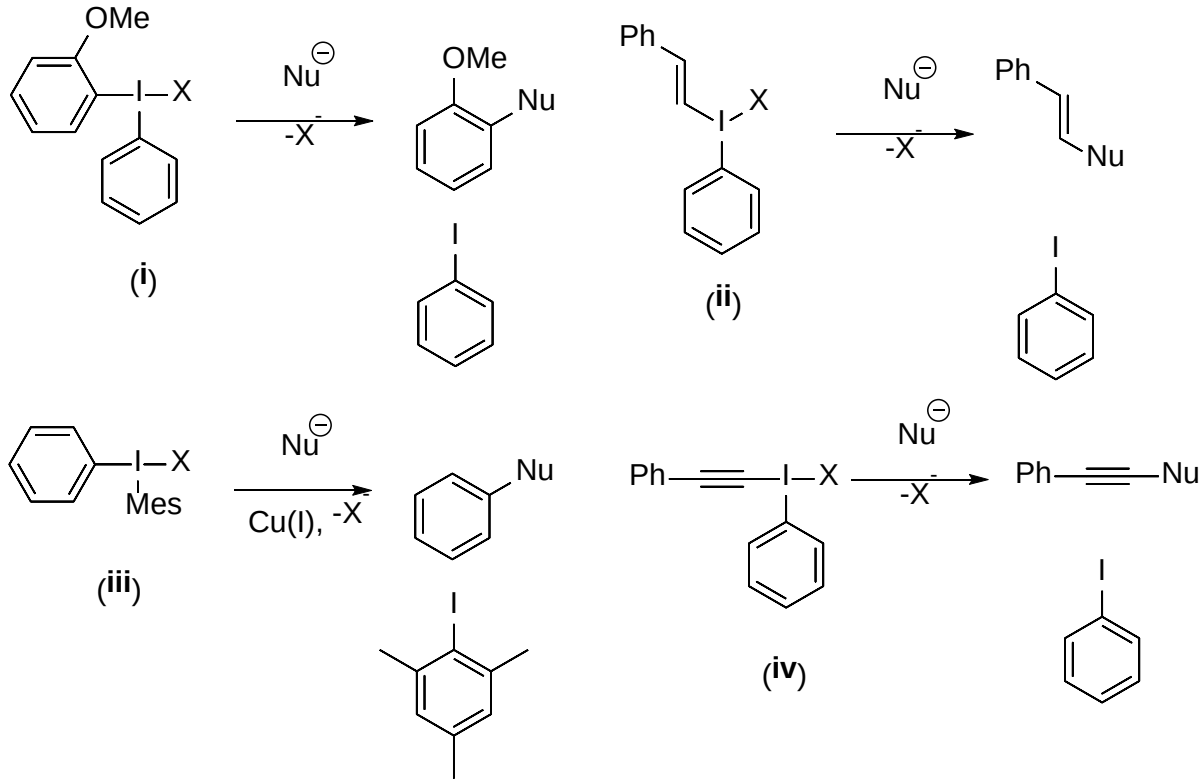
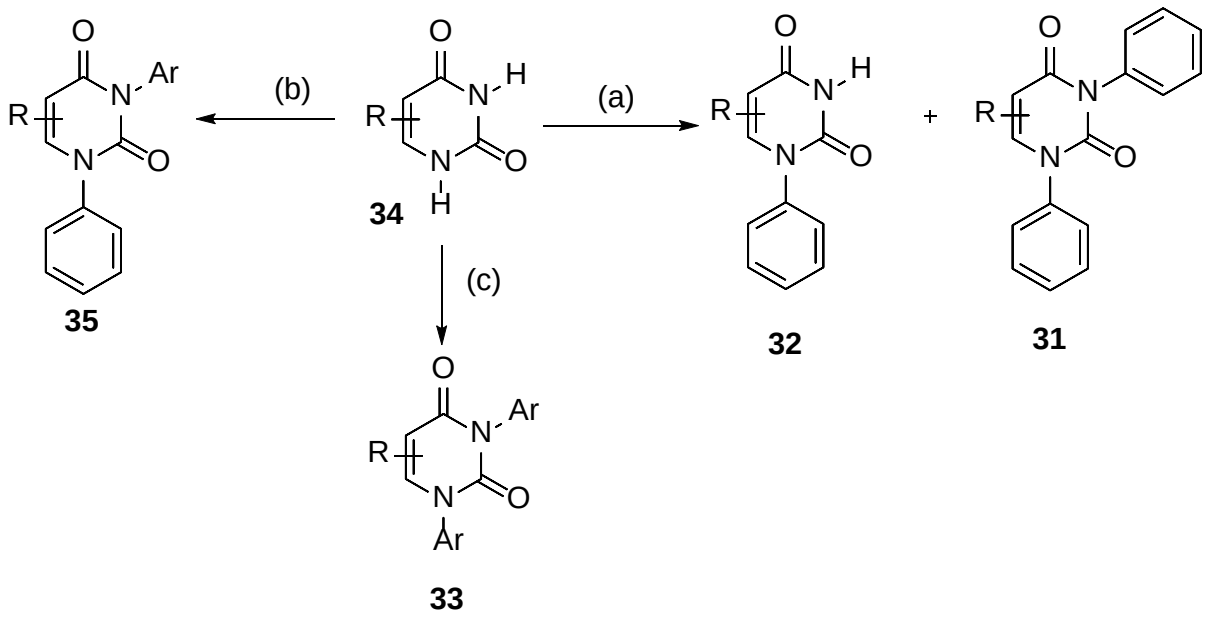


Figure 7

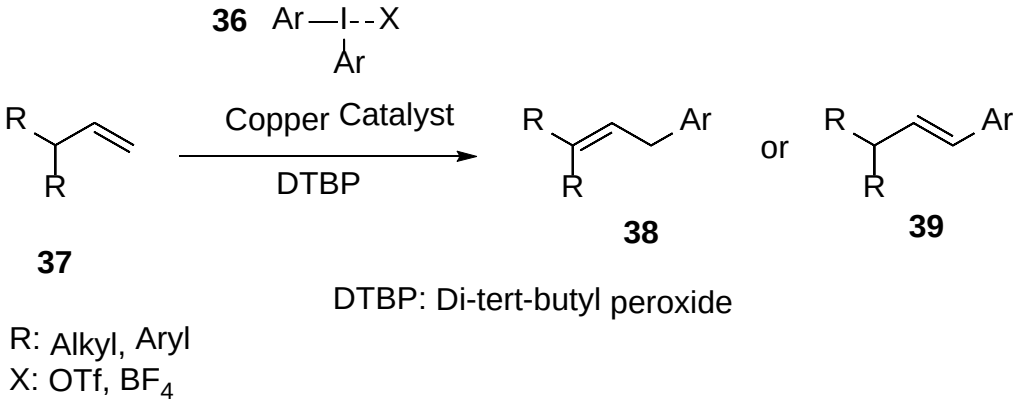
Diaryliodonium salts have been successfully utilised as arylating reagents by a number of groups. For example, Chen *et al*, have used these species to enable mono- and di-*N*-arylations of uracil and thymine. The group reports selective mono- *N*-arylation of uracil and its derivatives with diaryliodonium salts under CuI catalysis. In the presence of K_2CO_3, the copper-catalysed arylation gave N^1,N^3-diarylation products (59% yield of **31** and 5% of **32**). However, the use of NaOAc as the base in the copper-catalysed arylation of 6-methyluracil resulted in N^3-arylation products, (59% of **32** and trace amounts of **31**) and, in the copper-catalysed arylation of uracil or 5-methyluracil, N^1-arylation products were selectively produced (Scheme 12).[17]



Scheme 12

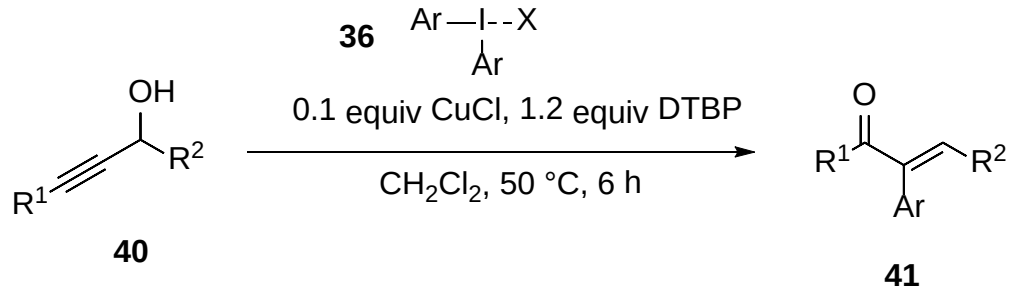
(a) **34** (1 mmol), $Ph_2I^+BF_4^-$ (1 mmol), CuI (10 mol%), base (2 mmol), DMF (5 mL), 40 ^oC, 6h; (b) **34** (0.5 mmol) $Ar_2I^+BF_4^-$ (1.2 mmol), CuI (10 mol%), K_2CO_3 (2 mmol), DMF (5 mL), 40 ^oC, 3-4 h; Ar = Ph, 4-Me-C_6H_4, 4-Cl-C_6H_4; (c) **34** (1 mmol), $Ar_2I^+BF_4^-$ (1.2 mmol), CuI (10 mol%), NaOAc (2 mmol), DMF (5 mL), 40 ^oC, 10 h; Ar = Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-Cl-C6H4, 4-Br-C_6H_4.

Gaunt *et al* have recently reported an alkene arylation reaction catalysed by Cu(I) and Cu(II) salts, utilising diaryliodonium salts **36** as both an oxidant, to generate the reactive Cu(III) species, and as a source of arenes. The Cu(III) species Gaunt proposes acts as an electrophilic arene transfer reagent, the equivalent of phenyl cation; it is subsequently attacked by the alkene. Interestingly, the major product differs from what would be obtained via a Heck reaction. The group reports excellent yields (up to 94%) and reasonable selectivity (up to 11:1) (Scheme 13).[18]



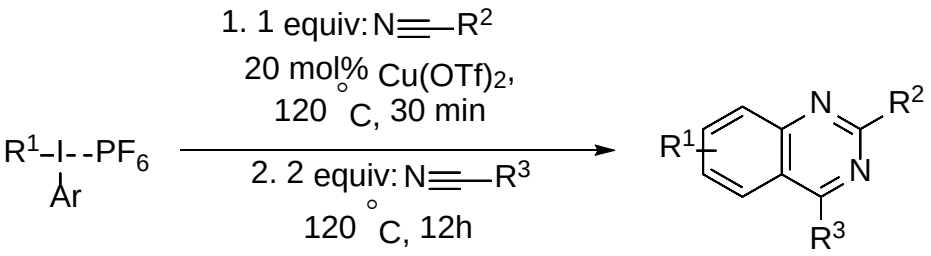
Scheme 13

Gaunt and co-workers have continued their excellent work with Cu(III) species generated from iodonium salts with a copper catalysed Meyer-Schüster rearrangement of propargylic alcohols **40** (Scheme 14). The group reported moderate to good yields for this process (38-86%), and demonstrated a wide substrate scope with the reported reaction conditions.[19]



Scheme 14

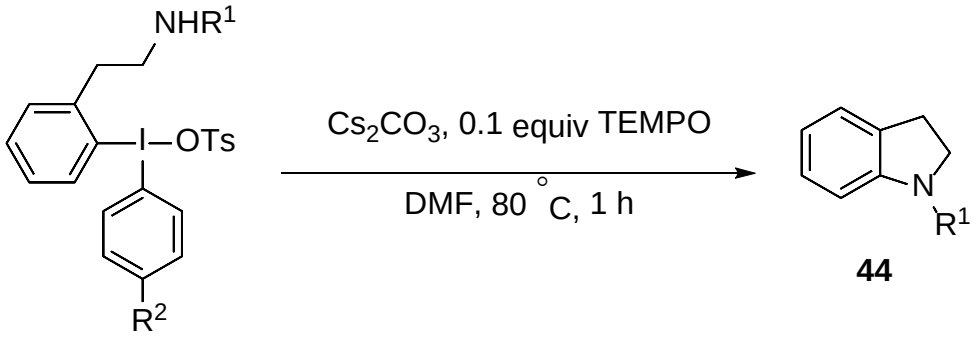
Li *et al* reported the synthesis of various quinazoline derivatives **42** from diaryliodonium hexafluorophosphates **43** via Cu(I) catalysis.[20] As with the processes reported by Gaunt, this reaction proceeds via a transient Cu(III) intermediate (Scheme 15).



43 **42**

Scheme 15

The Chi group reported interesting results in their synthesis of indolines **44** via the reactions of novel diaryliodonium salts **45** (Scheme 16). Of the two possible outcomes of this reaction, only the indolines **44** were isolated, the possible aryl substituted tertiary amine product was not detected. In order to study the influence of different arenes on this reaction, Chi and co-workers prepared a selection of diaryliodonium salts with *para*-substituted stabilising arenes. In the case of this reaction, they found little impact upon reactivity.[21]



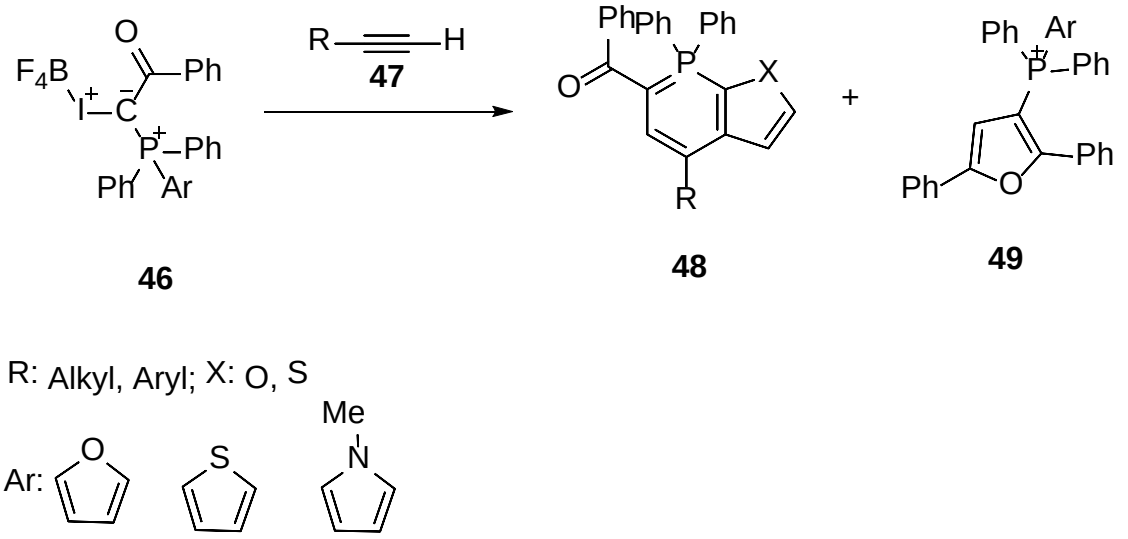
45 **44**

R^1: Boc, Cbz, Ac, CONEt
R^2: F, Cl, Br, Me, OMe

Scheme: **16**

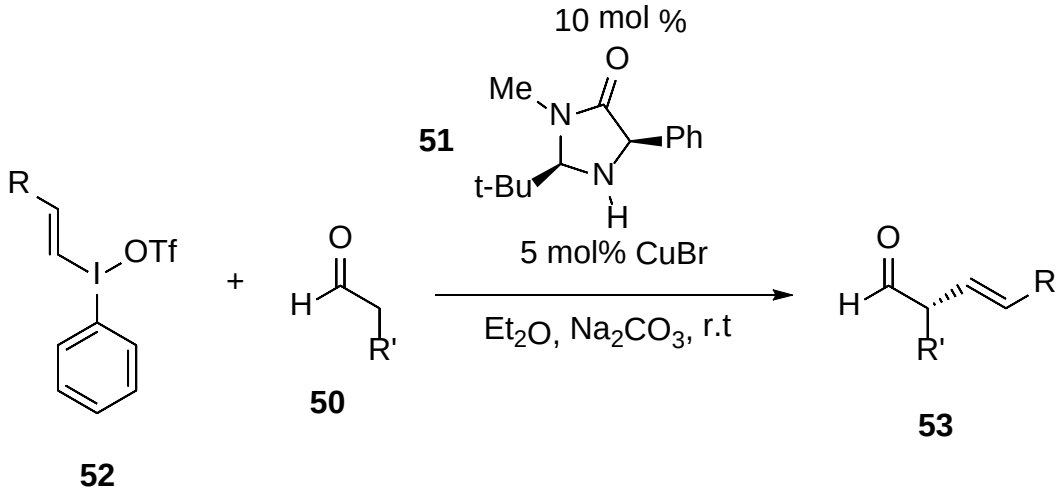
Matveeva and co-workers reported the synthesis of a series of novel heteroaryl substituted (in the phosphonium part) phosphonium-iodonium ylides **46** which, through their reactions with alkynes **47** allow the synthesis of phosphinolines **48** or phosphininofurans **49** (Scheme 17). This work is of particular interest as the phosphonium-iodonium ylides documented in this

paper represent an entirely new branch of hypervalent iodine reagents. The availability of these other similar mixed iodonium ylides represents an exciting opportunity to explore new chemistry.[22]



Scheme 17

Furthering their work in the field of enantioselective synthesis employing hypervalent iodine reagents, the MacMillan group have reported an interesting new methodology for α-vinylation of aldehydes **50**. Utilising two simultaneous catalytic systems, one using chiral cyclic secondary amines **51** and the second copper salts, MacMillan *et al* were able to employ alkenyliodonium salts **52** to generate enolisable α-formyl vinylic stereocentres without racemisation or olefin transposition, with both excellent yields (up to 98% and enantioselectivity (up to 97%) (Scheme 19).[23]



Scheme 19

1.3 Benziodoxole and benziodoxolone Reagents.

Benziodoxole and benziodoxolone are cyclic λ^3-iodanes that do not consist of a separate counterion (Figure 8).[24]

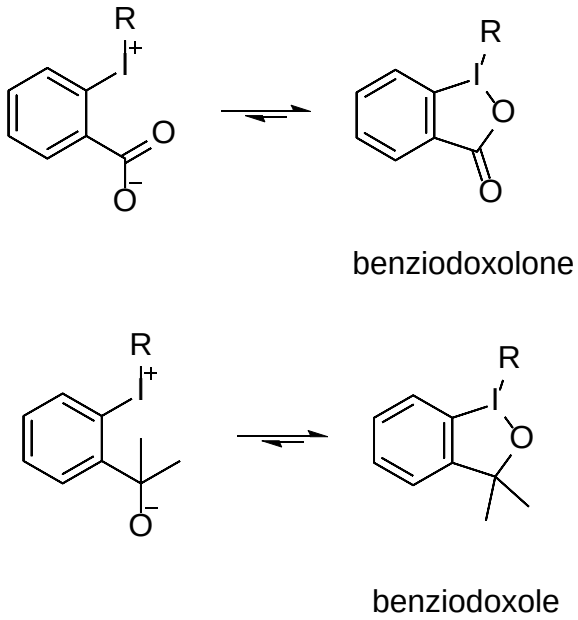


Figure 8

Numerous derivatives of benziodoxolone have been reported, generally derived from chloro-benziodoxole (Figure 9).[25]

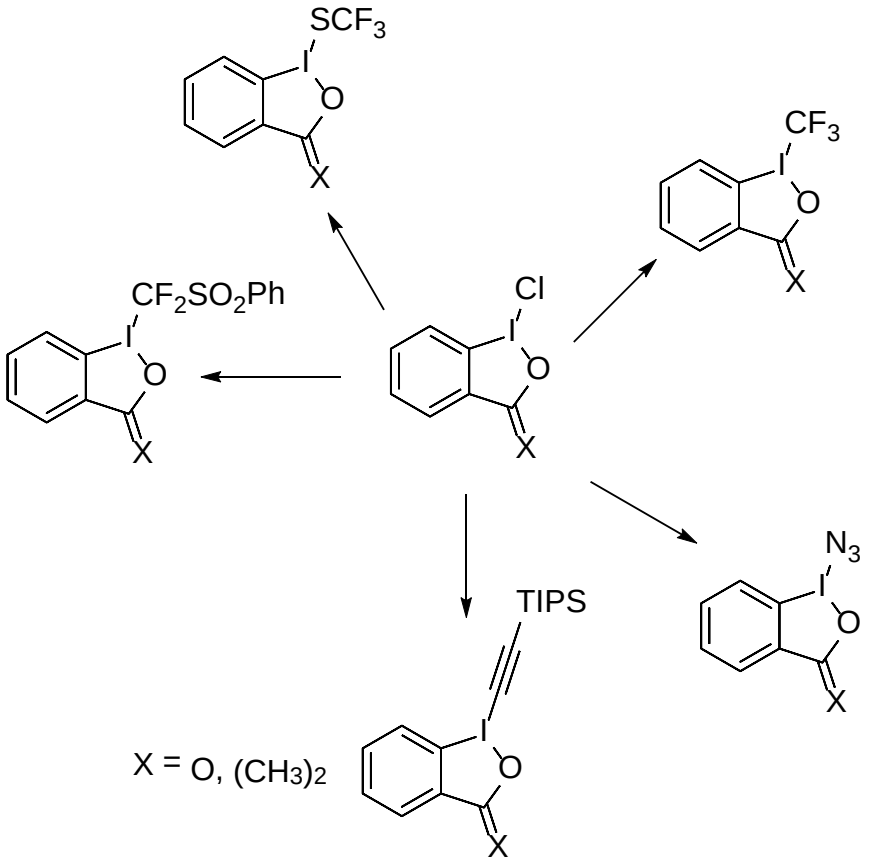


Figure 9

These species are typically more stable than their non-cyclic analogues, and generally undergo reactions with nucleophiles (Figure 10).

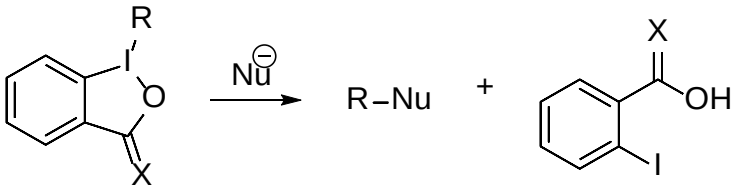
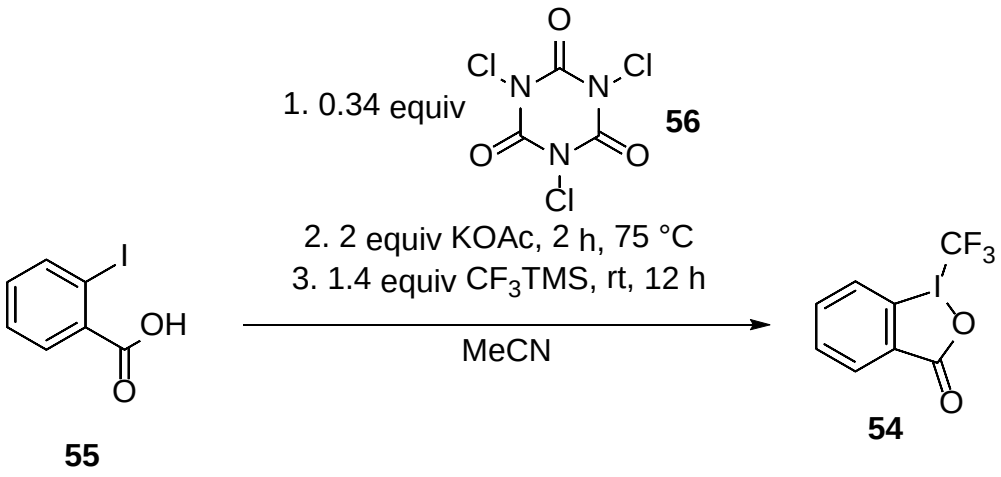


Figure 10

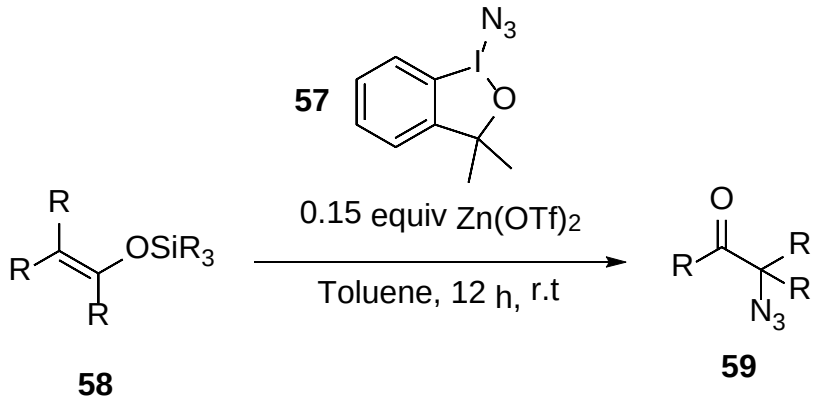
The most investigated of these species is Togni's reagent. This reagent function as electrophilic sources of trifluoromethane, a group of great importance in pharmaceuticals, which is generally added to increase lipophilicity of the target compound. Togni and co-workers have recently reported a general one pot synthesis of this reagent from 2-iodobenzoic acid **55** utilising trichloroisocyanuric acid (TCICA, **56**) as the primary oxidant. Togni states

that the 0.34 equivalents of TCICA used is approximately equal to 1.02 equivalents of Cl^+ (Scheme 20).[26]



Scheme 20

Waser and co-worker reported the synthesis and reactivity of an azide derivative of benziodoxole, which the group utilised in a zinc catalysed azidation of silyl enol ethers **59** in good yield (up to 82%) (Scheme 21).[21]

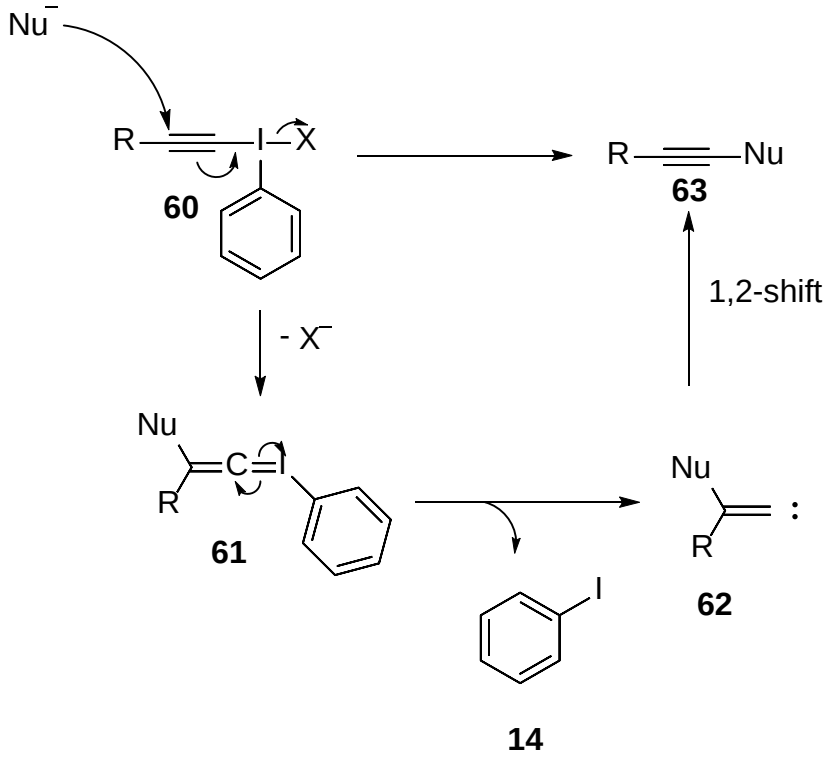


Scheme 21

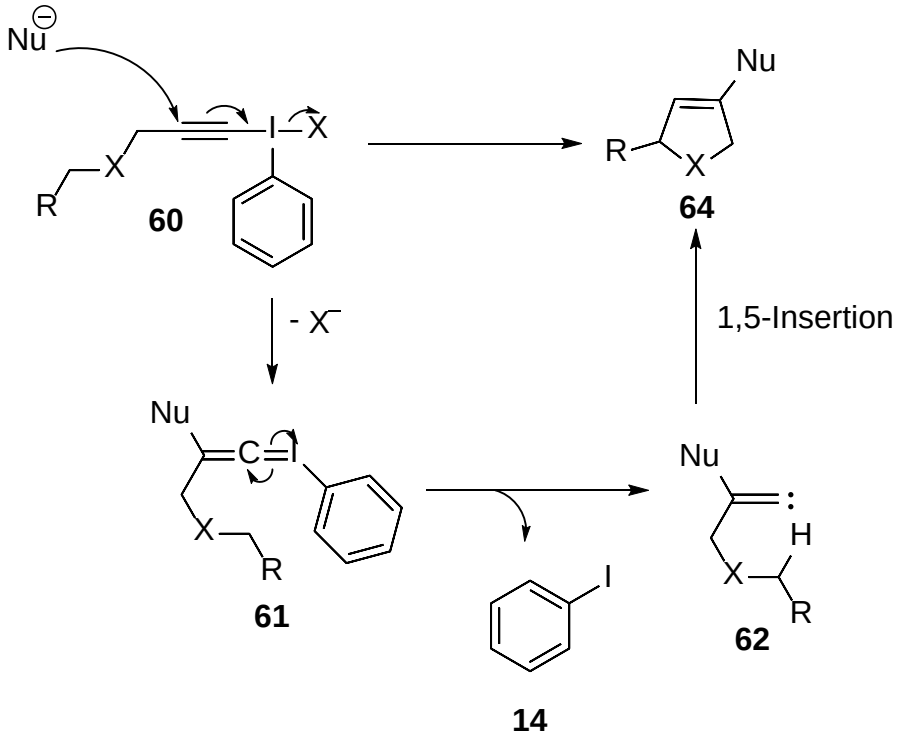
1.4 Alkynyl(aryl)iodonium Salts.

Alkynyl(aryl)iodonium salts represent a comparatively recent branch of hypervalent iodine chemistry, with the first documented synthesis performed by Beringer and Galton published in 1965.[27] For comparison, diaryliodonium salts have been known since the 19th century.[4]

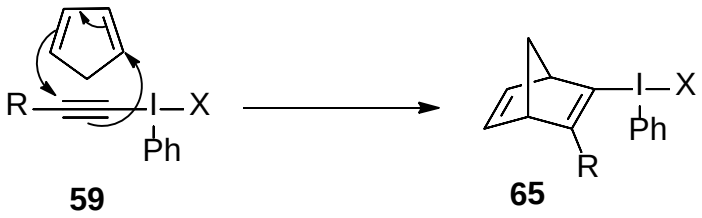
These species participate in many types of reactions; however particular interest has focused on three areas:(**i**) the generation of mixed acetylenes **63** via carbene rearrangement through attack of a soft nucleophile on the *β*-carbon, (hard nucleophiles lead only to decomposition products) (Scheme 22) (**ii**), the creation of 5-membered rings **64** via a carbene 1,5-insertion, again through attack of a soft nucleophile on the *β*-carbon (Scheme 23) and (**iii**) use of these salts as dieneophiles in cycloaddition reactions generating alkenyl(aryl)iodonium salts **65** (Scheme 24) .[28-30]



Scheme 22



Scheme 23

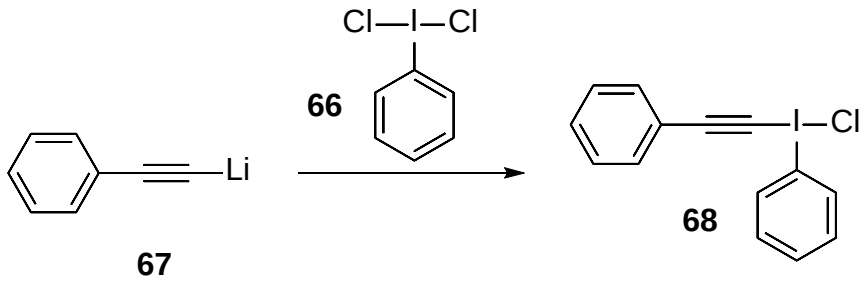


Scheme 24

A. Synthesis of alkynyl(aryl)iodonium salts.

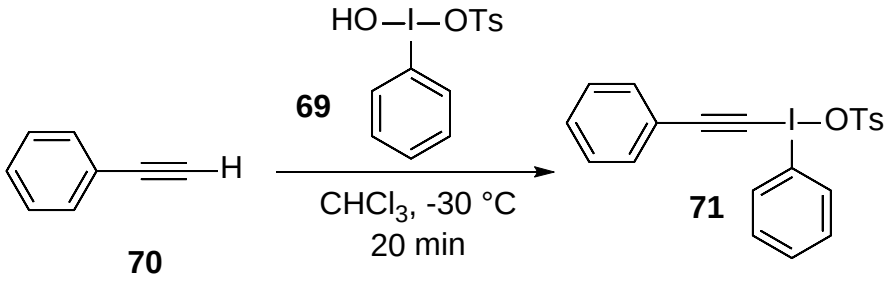
Beringer and Galton, as stated above, reported the first synthesis of an alkynyl(phenyl) iodonium salt, a chloride, through the treatment of dichloroiodobenzene **66** with lithium phenylacetylide **67** (Scheme 25). Unfortunately this species proved unstable and it decomposed to iodobenzene and phenylchloroacetylene over a period of a few hours. This can occur by nucleophilic attack on the *β*-carbon by the chloride counterion, which generates

a carbene intermediate with loss of iodobenzene which can rapidly undergo a 1,2-shift (Scheme 25).[27]



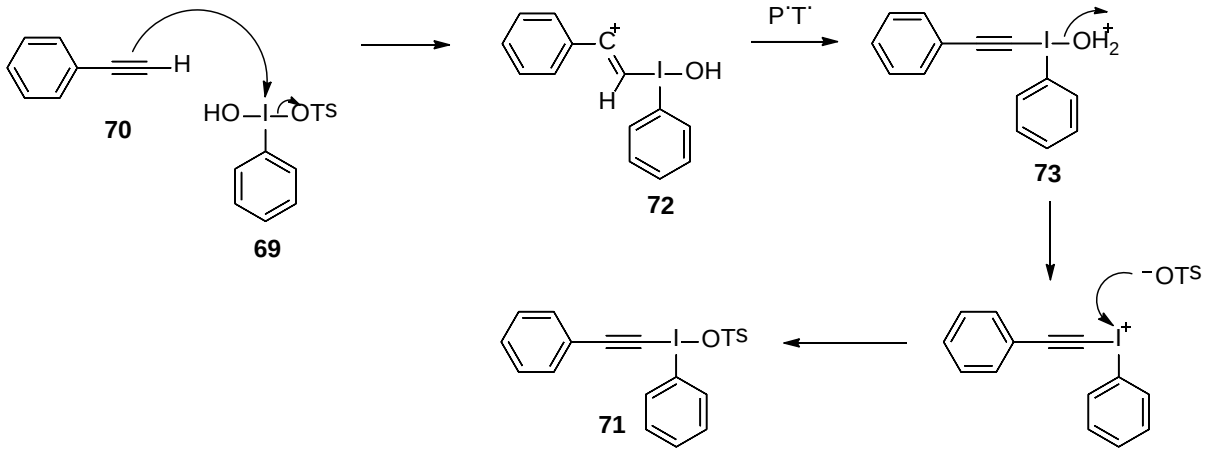
Scheme 25

The first synthesis of a stable, fully characterised alkynyl(phenyl)iodonium salt was reported by Koser *et al* who found that hydroxyl(tosyl)iodobenzene (HTIB, Koser's reagent, **69**) will react with terminal alkynes. In particular, HTIB **69** will react with phenylacetylene **70** to form phenylethynyl(phenyl)iodonium tosylate **71** exclusively. When HTIB was reacted with other terminal acetylenes, either a mixture of an alkenyl and alkynyl(phenyl)iodonium salt is formed, or the alkenyl(phenyl)salt is formed exclusively (Scheme 26).[31]



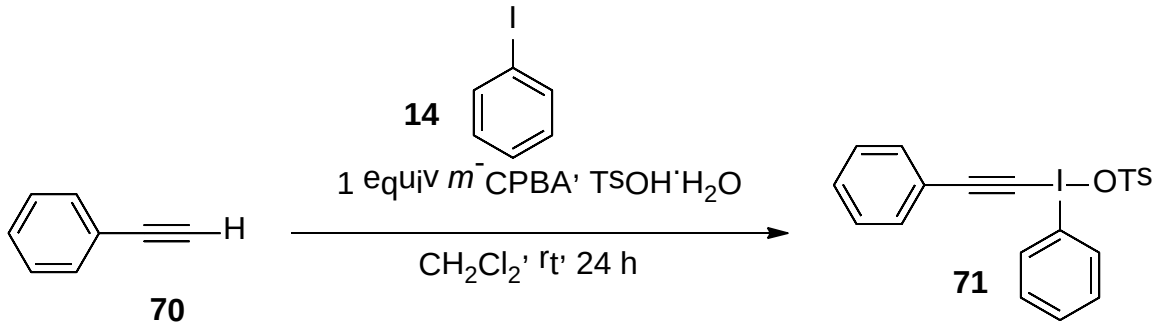
Scheme 26

In terms of the mechanism, this reaction is initiated by nucleophilic attack of the alkyne π cloud on HTIB **69** generating a carbocation alkenyl iodane intermediate **72.** Proton transfer followed by loss of water generates the alkynyl(phenyl)iodonium tosylate **71** (Scheme 27).[32]



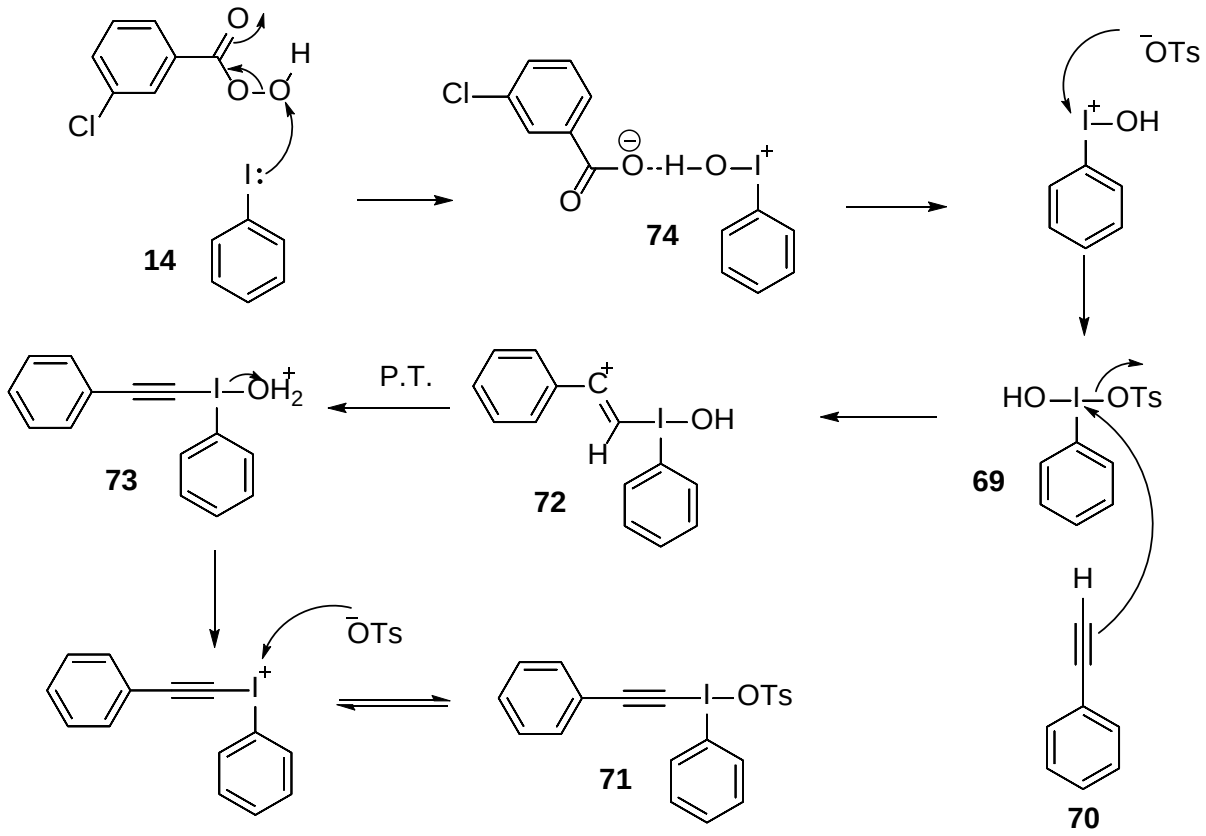
Scheme 27

Since the original report of this reaction by Koser, others have reported improved procedures. However, the most interesting synthesis of alkynyl(phenyl)iodonium tosylates was reported by Merrit and Olofsson, who have synthesised phenylethynyl(phenyl)iodonium tosylate from phenylacetylene **70** and iodobenzene using *m*-CPBA as the principle oxidant (Scheme 28). The group reported a 63% yield of the above compound; however, no other examples were reported. In spite of that, this paper is of particular interest, as it suggests an easy access to numerous phenylethynyl(aryl)iodonium tosylates, starting with the iodoarene. To access these compounds via previous routes, multistep synthesis of iodine(III) species are required.[32,33]



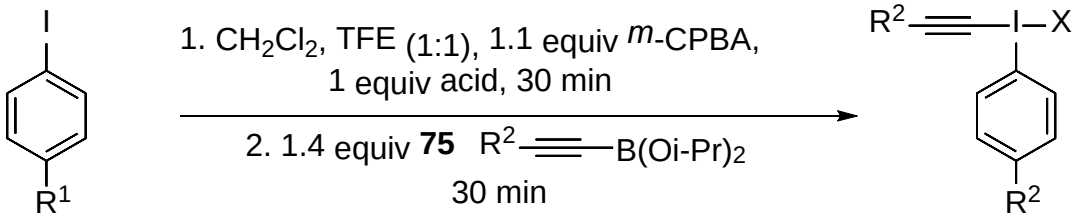
Scheme 28

In terms of mechanism, the initial attack is by an iodine lone pair on *m*-CPBA generating *m*-CBA (intermediate) **74**. This species is attacked by *para*-toluensulfonic acid, resulting in formation of HTIB **69** (Scheme 29). The mechanism then proceeds as for Koser's method.[33]



Scheme 29

Further to this work Olofsson and co-workers recently synthesised a selection of alkynyl(aryl)iodonium salts **77** in high yield (up to 100%) giving access to both tosylates and triflates. They utilised boronic esters **75** and aryl iodides **76** (Scheme 30).[34]

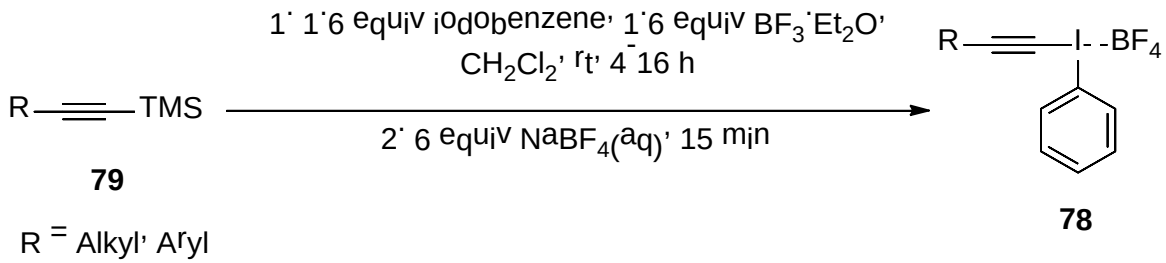


76 **77**

R^1: Me, H; R^2: Alkyl, Aryl; X: OTs, OTf

Scheme 30

Alkynyl(phenyl)iodonium tetrafluoroborates **78** may be prepared through treatment of iodosilbenzene with boron trifluoride etherate in the presence of trimethylsilylalkynes **79** followed by aqueous sodium tetrafluoroborate in moderate to good yields (Scheme 31).[35]



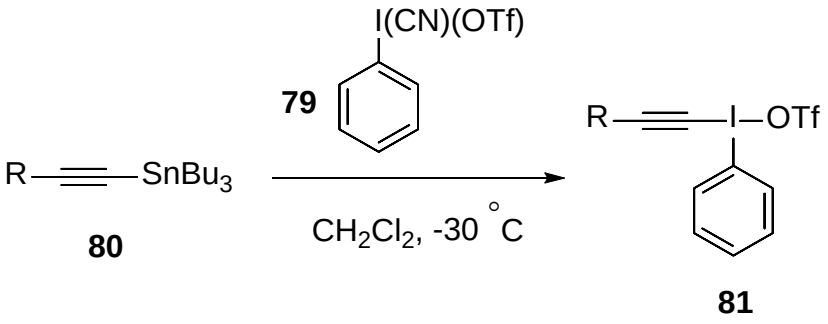
79

R = Alkyl, Aryl

78

Scheme 31

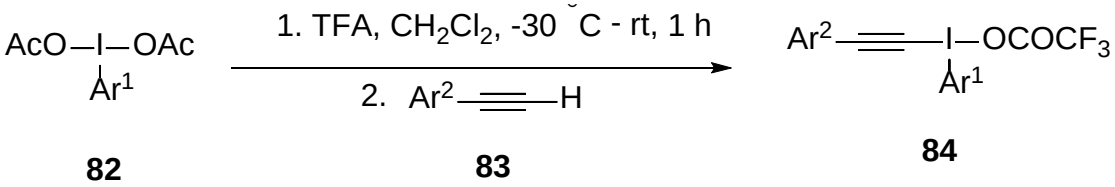
Another method for preparing alkynyl(phenyl)iodonium salts is an iodonium transfer reaction between cyano(phenyl)iodonium triflate(Stang's reagent, **79**) and alkynyl stannanes **80**, which generates the corresponding alkynyl(phenyl)iodonium triflates **81** in high yields (Scheme 32).[36] The reaction is particularly useful as, unlike the procedures outlined above, it is tolerant of many functional groups, and allows for the synthesis of complex, highly functionalised alkynyl(phenyl)odonium salts, thereby greatly extending the synthetic usefulness of these compounds. This procedure is highly selective and tolerant of many functional groups. The downside is the necessity for stannanes and a difficult to handle λ^3-iodane.[37]



R= Aryl, Alkyl, Carbonyl
many functional groups tolerated

Scheme 32

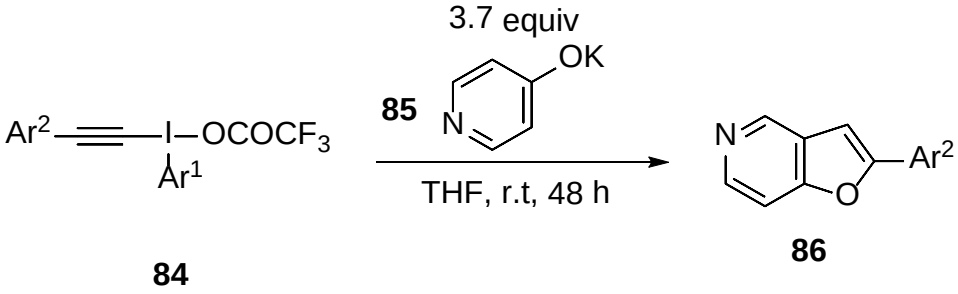
Carroll and co-workers reported a synthesis of various alkynyl(aryl)iodonium trifluoracetates **84** from readily available iodoarene diacetates **82** in good yields (48-85 %) (Scheme 33).[38]



Ar[1]: Ph, *p*-Tol, *p*-ClC$_6$H$_4$, Mes, *p*-ansyl , 2-thienyl
Ar[2]: Ph, *p*-BrC$_6$H$_4$, Mes, *p*-anisyl, *o*-anisyl, 3-thienyl

Scheme 33

As with Olofsson and co-workers, Carroll *et al* have synthesised alkynyl(aryl)iodonium trifloroacetates derived from a selection of iodoarenes, rather than just iodobenzene. The group utilised these salts in the synthesis of various 2-arylfuropyridines **84** and report a 12% variation in yield depending upon the iodoarene used (Scheme 34).[38]

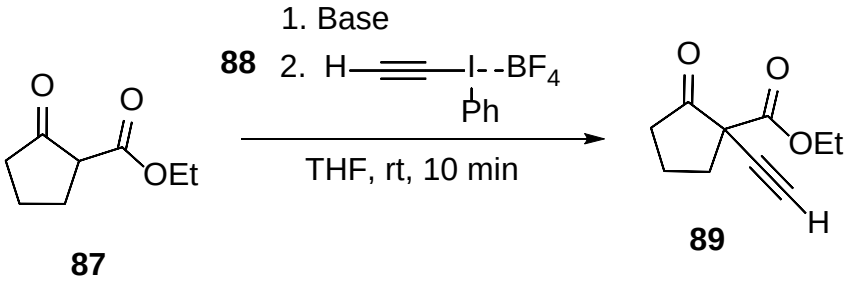


Ar^1: Ph, *p*-Tol, *p*-ClC_6H_4, Mes, *p*-Anisyl, 2-thienyl.
Ar^2: Ph, *p*-BrC_6H_4, Mes, *p*-Anisyl, *o*-Anisyl, 3-thienyl.

Scheme 34

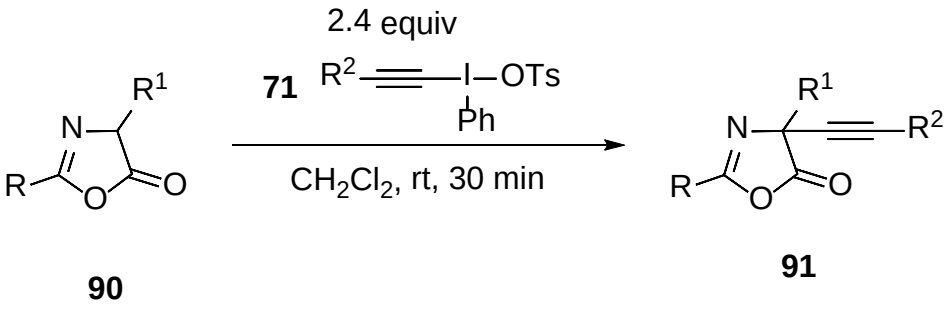
B. Chemistry of alkynyl(aryl)iodonium Salts.

Alkynyl(phenyl)iodonium salts are excellent alkynylating reagents towards soft nucleophiles, generating substituted alkynes via an addition elimination rearrangement sequence, often in high yields. This sequence generally occurs in where the nucleophile or another group bond to the alkyne which has good migratory aptitude. Simple enolates act as hard nucleophiles towards alkynyl(phenyl)iodonium salts, leading only to decomposition products; however Ochiai and co-workers have found that 1,3-dicarbonyl enolates **87** may be alkynylated under mild conditions in good yield (Scheme 35).[39]



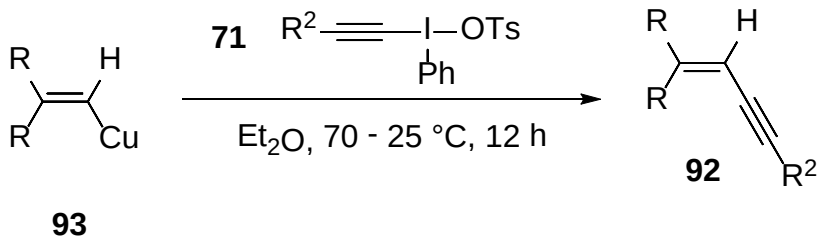
Scheme 35

Nachtsheim and co-workers developed an electrophilic alkynylation of azalactones **90** utilising alkynyl(phenyl)iodonium tosylates **71** in the presence of N,α-diethylphenylethylamine (DEPEA) in excellent yields (up to 97%) (Scheme 36).[40]



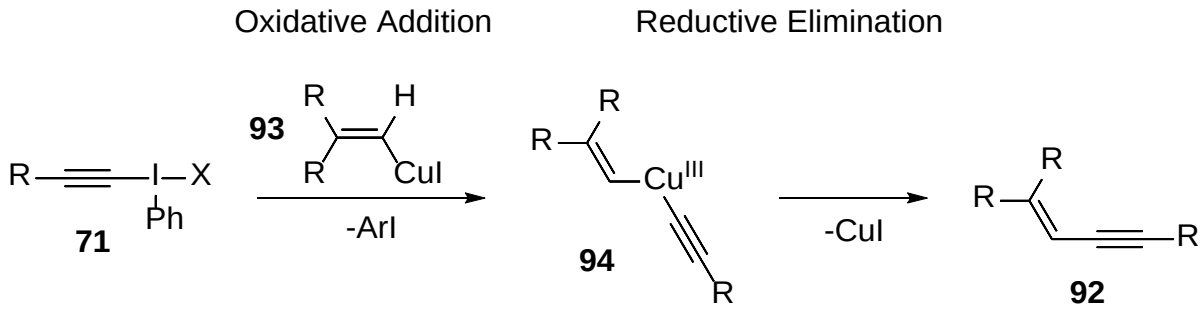
Scheme 36

Stang and Kitamura have reported a procedure for the synthesis of conjugated enynes **92** via the coupling of alkynyl(phenyl)iodonium tosylates **71** with vinylcopper reagents **93**. This complements the existing Sonogashira reaction, but without the need for expensive palladium based catalysts (Scheme 37).[41]



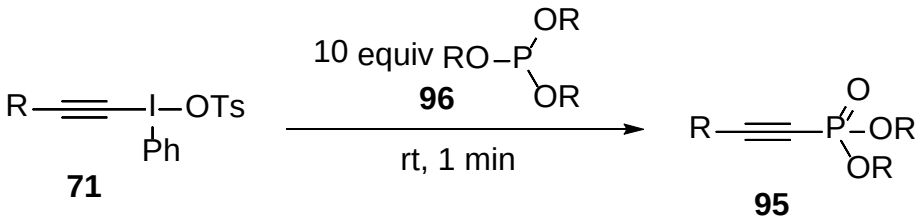
Scheme 37

They report good to excellent yields with complete retention of alkene stereochemistry. As Stang speculates, this reaction almost certainly proceeds via oxidative addition of copper to the alkynyl(phenyl)iodonium salt generating a copper(III) intermediate **94**, followed by reductive elimination of copper to generate the product **92** (Scheme 38).[41]



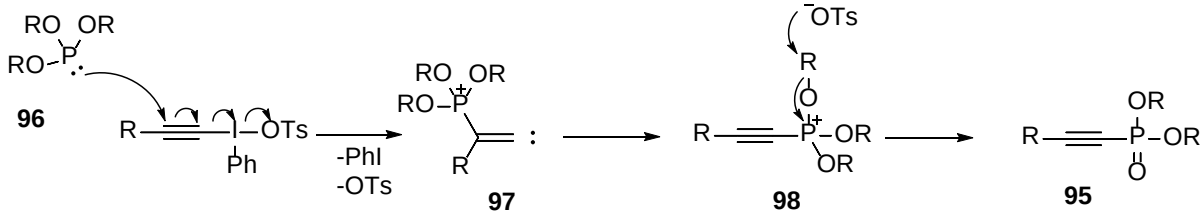
Scheme 38

Koser *et al* have reported a solvent free synthesis of alkynylphosphonate **95** from alkynyl(phenyl)iodonium tosylates **71** and trialkyl phosphites **96** in moderate to execellent yields (Scheme 39).[42]



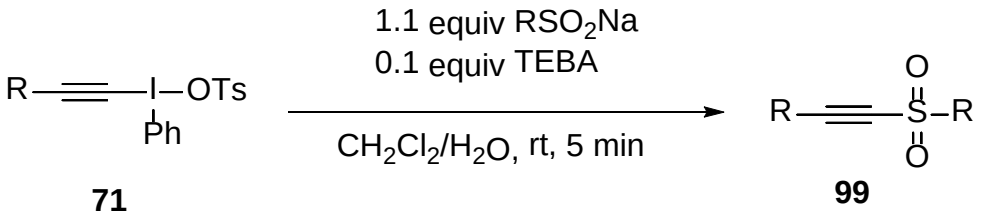
Scheme 39

The reaction proceeds via a typical addition elimination rearrangement sequence, followed by an Arbuzov-type process (Scheme 40).



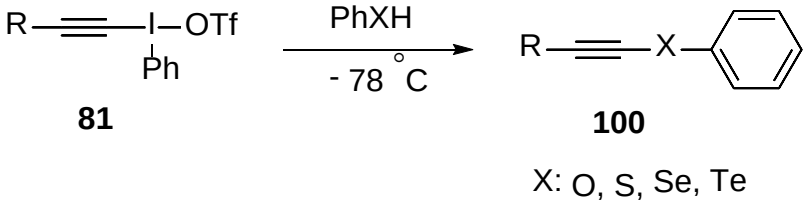
Scheme 40

Alkynyl sulfones **99** may be synthesised from alkynyl(phenyl)iodonium salts **71** by treatment with an aqueous solution of the appropriate sulfinic acid salt and a phase transfer catalyst rapidly and in moderate to good yield (Scheme 41).[43]



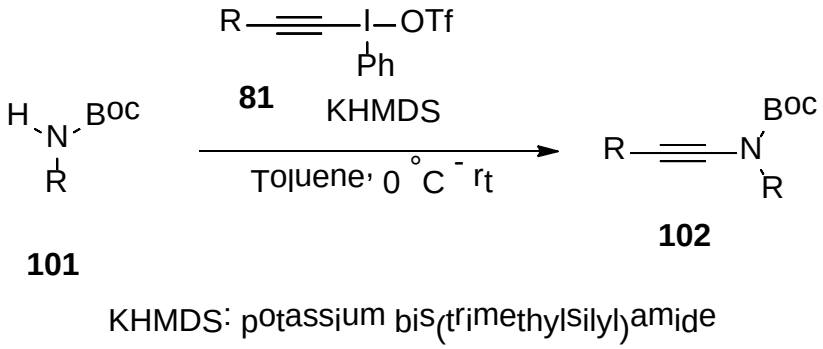
Scheme 41

Acetylenic ethers, thioethers, selenides, and tellurides **100** can be prepared by treatment of alkynyl(phenyl)iodonium salts **81** with appropriate nucleophiles in moderate to good yields (Scheme 42). Conditions vary depending on X.[44]



Scheme 42

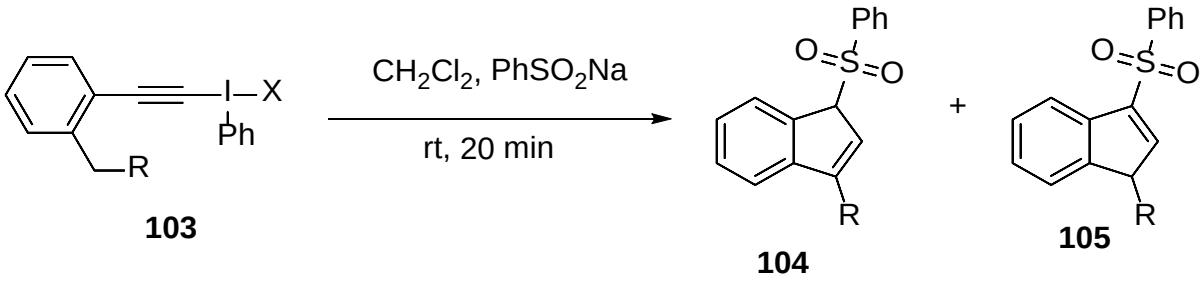
Nitrogen nucleophiles, provided they are sufficiently stabilised and softened may react with alkynyliodonium salts to generate *N*-alkynes.[45] For example various *N*-Boc alkynes were synthesised by Hashmi *et al* in low to moderate yield (Scheme 43). Lithium diphenylamide and lithium sulfonamide have also been proven useful nucleophiles in reactions with alkynyliodonium salts.[46]



KHMDS: potassium bis(trimethylsilyl)amide

Scheme 43

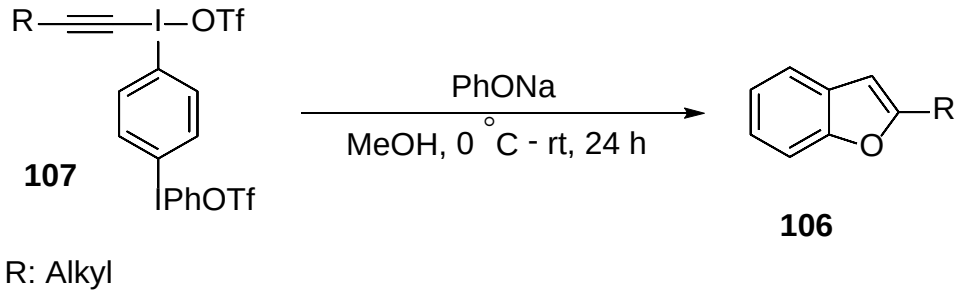
Varvoglis and co-workers used the same chemistry in the synthesis of phenylsulfonyl indenes and acetylenes via the appropriate alkynyliodonium triflates and tetrafluoroborates (Scheme 44).[47]



R: H or Me
X: OTf, BF_4

Scheme 44

A synthesis of 2-substituted benzofurans **106** has been reported by Kitamura et al, through treatment of alkynyliodonium salts **107** with phenoxide in methanol, leading to 1,5-insertion into the aromatic C-H bond (Scheme 45).[48]

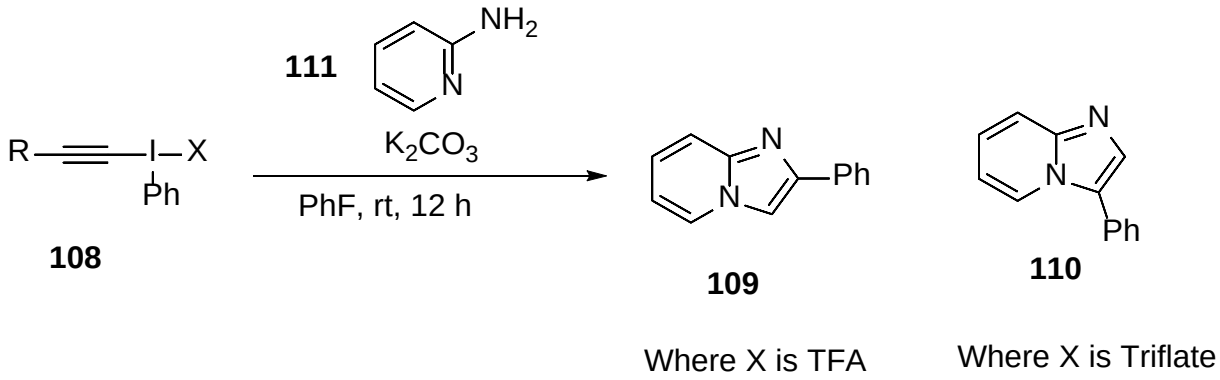


107 **106**

R: Alkyl

Scheme 45

Carroll and co-workers documented the first example of counterion dependency in observed regioselectivity in a reaction of alkynyl(phenyl)iodonium salts **108**. Carroll observed that if alkynyl(phenyl)iodonium trifluoroacetates were employed in the synthesis of aryl[1,2 *a*]imidazopyridines **109, 110**, then the major product (7:3) was 2-phenylimidazo[1,2-*a*]pyridine **109**. If alkynyl(phenyl)iodonium triflates were used, the only product was 3-phenylimidazo[1,2-*a*]pyridine **110** (Scheme 46).[49]

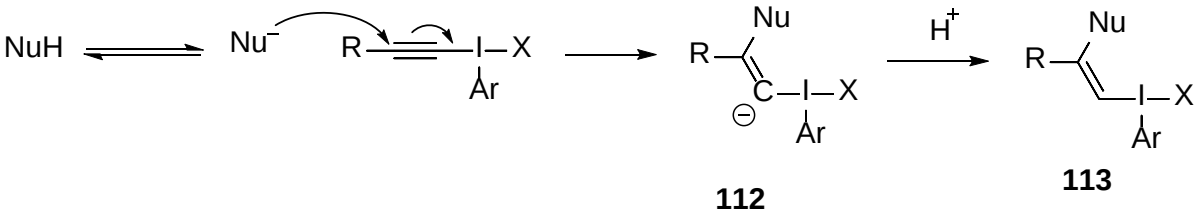


111 **108** **109** **110**

Where X is TFA Where X is Triflate

Scheme 46

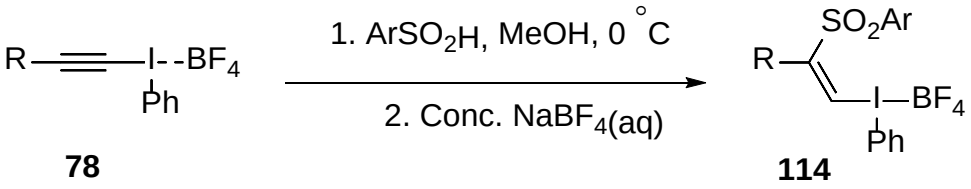
Upon treatment with an appropriate nucleophile, alkynyl(phenyl)iodonium salts initially form an iodonium ylide **112** which can be protonated under appropriate reaction conditions to generate an alkenyl(phenyl)iodonium salt **113** (Scheme 47).[49]



112 **113**

Scheme 47

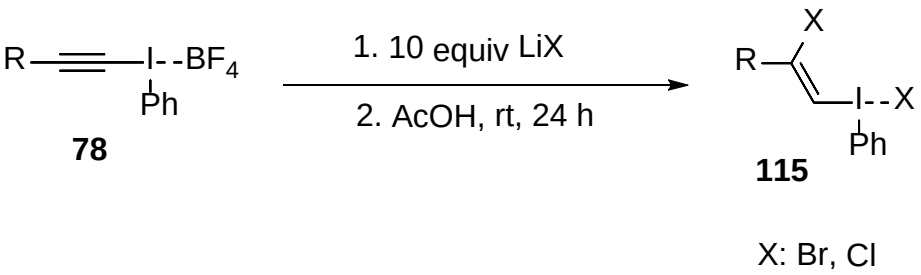
Ochiai and co-workers found that treatment of alkynyl(phenyl)iodonium tetrafluoroborates with arylsulfinic acids in methanol produce (*Z*-2-(benzenesulfonyl)-2-vinyl(phenyl)iodonium tetrafluoroborates **114** in good yields (Scheme 48). In the case of this reaction, methanol proved to be the best of the protic solvents tested.[50]



78 **114**

Scheme 48

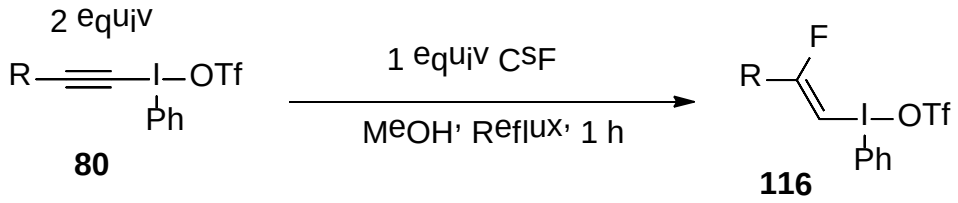
Ochiai and co-workers reported the synthesis of *Z*-chloro and bromosalkenyl(phenyl)iodonium chlorides and bromides **115**. In all cases, the alkenyl(phenyl)iodonium salts formed in the *Z* configuration, with no trace of the E isomer found (Scheme 49).[51]



78 **115**

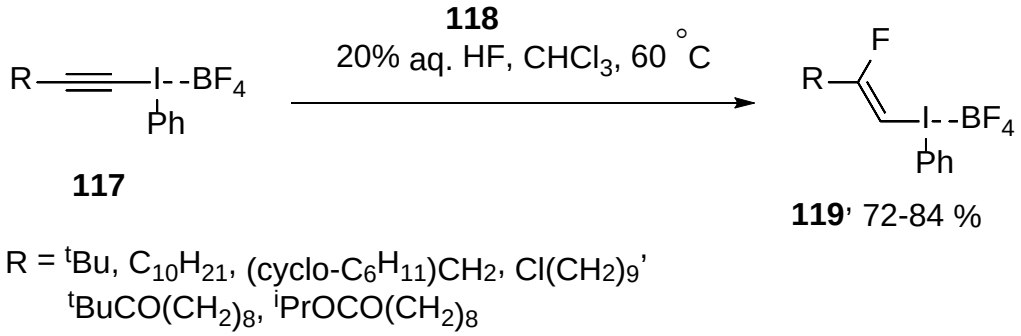
Scheme 49

Recently, Emond and co-workers reported the synthesis of fluoroalkenyl(phenyl)iodonium salts **116** from alkynyl(phenyl) iodonium triflates and tosylates. After a methodical screening of conditions, the group found that a one hour reflux in either methanol or wet acetonitrile, with two equivalents of alkynyl(phenyl)iodonium salt led to high yields of desired alkenyl(phenyl)iodonium salts (Scheme 50).[52]



Scheme 50

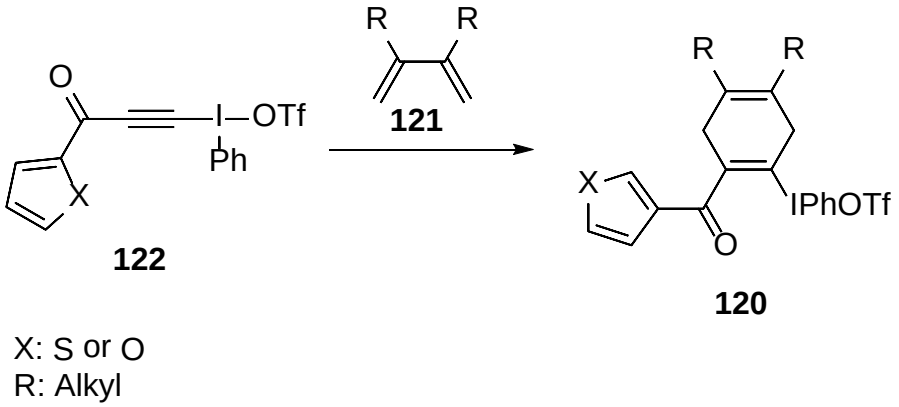
As has been outlined above alkenyliodonium salts can be obtained from alkynyliodonium salts. Yoshida and co-workers prepared fluoroalkenyliodonium salts **119** in high yields by the addition of aqueous HF to alkynyl(phenyl)iodonium salts (Scheme 51). The group was able to synthesise these salts having functional groups such as chloride ester and ketone.[53]



Scheme 51

Alkynyl(phenyl)iodonium salts, as highly electron deficient acetylenes, make excellent cycloaddition partners and have been utilised to this effect to generate new alkenyl- or

diaryliodonium salts. Their utility in the Diels-Alder reaction has been explored by Stang, and synthesis of numerous hexadiene products **120** has been reported (scheme 52).[54]



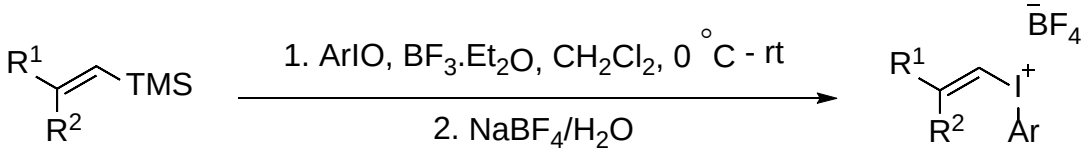
Scheme 52

1.5 Alkenyl iodonium salts their synthesis and application.

Alkenyliodonium salts have been known for many years and in the last two decades many new preparations and reactions have been reported.

A. Synthesise of alkenyl(aryl)iodonim salts.

The first general synthesis of these compounds was reported by Ochiai and co-workers via treatment of alkenylsilanes **123** with iodosobenzene and triethyloxonium tetrafluoroborate then followed by aqueous $NaBF_4$ solution (Scheme 53). The reaction proceeds via retention of the organosilane geometry.[55,56]



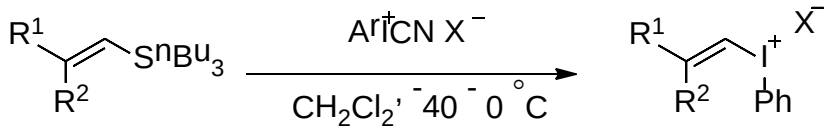
123

124, 72-92%

R^1 = 4-$BrC_6H_4OCH_2$, $PhCH_2CH_2$, 4-$ClC_6H_4OCH_2$, *n*-C_8H_{17}, etc.
R^2 = H, Me; Ar = Ph, 2,4,6-$Me_3C_6H_2$, etc.

Scheme 53

In a similar manner, alkenyliodonium salts **125** can be synthesised by treatment of stannylated alkenes **126** with aryl(cyano)iodonium triflate as an iodonium-transfer reagent (scheme 54).[57] This stereospecific synthesis is very general and mild condition.



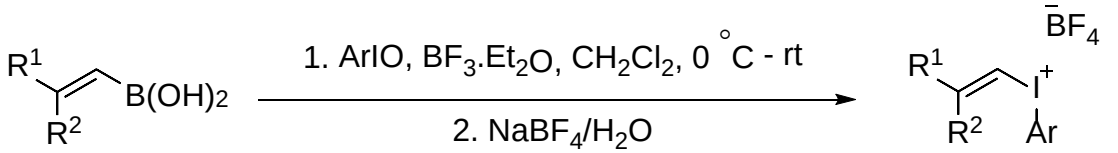
126

125, 49-86 %

R^1 = Me, Et, Bu, Ph; R^2 = Me, Et, Bu
Ar = Ph, 4-$CF_3C_6H_4$, 3,5-$(CF_3)_2C_6H_2$; X = OTf, OTs

Scheme 54

Ochiai reported that the alkenyliodonium salts **124** can be obtained in excellent yields by the reaction of vinylboronic acids **127** with $PhI(OAc)_2$ or PhIO and boron trifluoride etherate then followed by aqueous $NaBF_4$ solution (Scheme 55). [58] This reaction proceeds by borane-iodine(III) exchange.



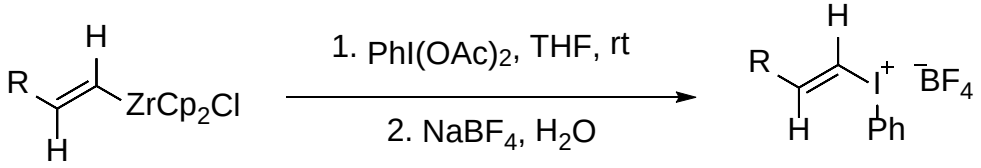
127

124, 82-96%

R^1 = Bu, ^{t}Bu, $Ph(CH_2)_3$, $(CH_3)_2CH(CH_2)_2$, etc.
R^2 = H, Me

Scheme 55

In the similar manner, Huang and co-workers isolated alkenyliodonium salts **128** by the reaction of vinylzirconium derivatives **129** with $PhI(OAc)_2$ then followed by aqueous $NaBF_4$ solution (scheme 56).[59]

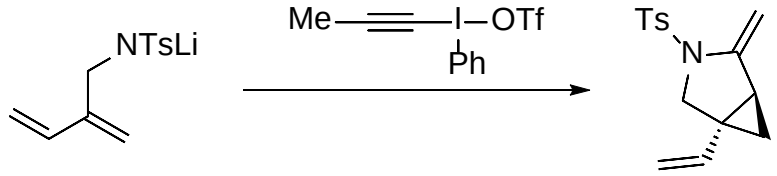


129

128

Scheme 56

Feldman and co-workers prepared the azabicyclo[3.1.0]hexane **130** in which alkynyliodonium salt where used. Where an alkene is present in the 5-position upon formation of alkylidene carbene, either through the nucleophile or the salt itself, the carbene can insert into it, forming a 3-membered ring used to a 5-membered ring, with migration of the alkene (Schem 57).[60]

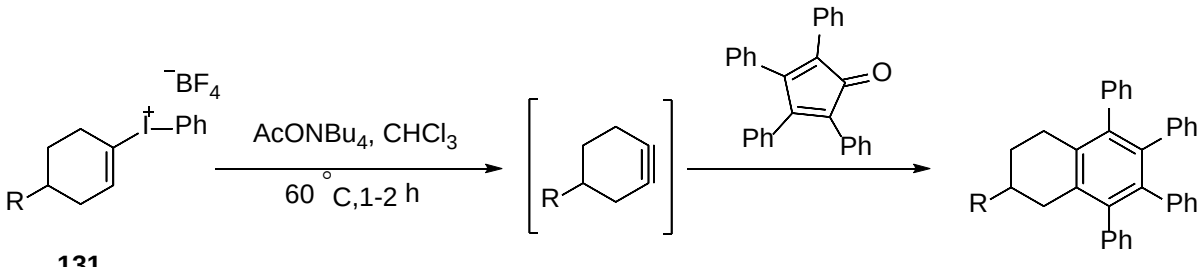


130

Scheme 57

B. Application of alkenyl iodonium salts.

Alkenyl(phenyl)iodonium salts are highly reactive compounds due to the excellent leaving ability of PhI. It has been shown to be 10^{12} times greater than iodine at leaving and a million times better than triflate.[61] Several research groups have studied the mechanisms of various reactions with alkenyl iodonium salts including Michael addition-elimination, ligand coupling and SN^1 and SN^2 processes with various nucleophiles.[62] Okuyama and Ochiai reviewed the reactions of alkenyliodonium salts with nucleophiles.[63,64] Okuyama and co-workers reported that the treatment of 1-cyclohexenyl(phenyl)iodonium salts **131** with base (including tetrabutylammonium acetate, fluoride ion, amines and alkoxides) in aprotic solvents led to cyclohexyne **132** formation intermediate. This was successfully trapped with tetraphenylcyclopentadienone to generate [4+2] cycloaddition products **133** in excellent yields (Scheme 58).[61,62]



131

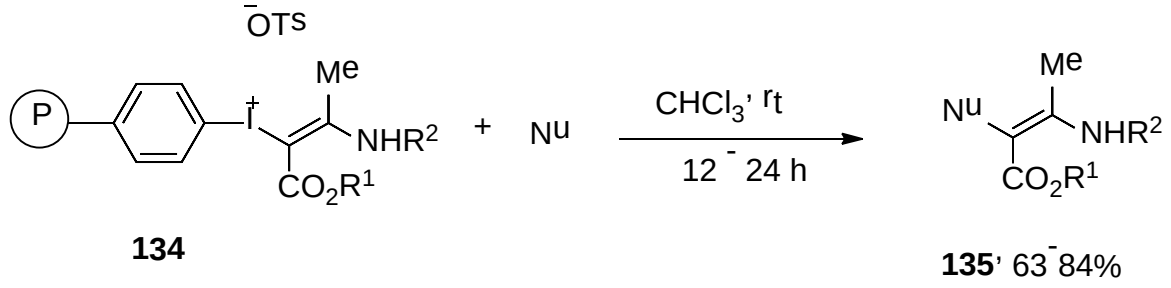
R = H, Me, Et, ^{t}Bu, Ph, CN

132

133, 64-93%

Scheme 58

Yan and Zhang found that alkenyl(phenyl)iodonium salts are good alkenylating reagents for several nucleophilic substrates. They demonstrated that these reactions proceed with predominant retention of geometry via the addition-elimination mechanism or ligand coupling on-+ iodine. For example, stereoselective reactions of alkenyliodonium salts with sodium selenide, sodium azide, sodium sulfide, potassium thiocyanate and with benzotriazole have been demonstrated by Zhang. In a specific example, the reaction of polymer-supported alkenyliodonium tosylates **134** and nucleophiles proceeds to generate functionalized beta-enamines **135** (scheme 59).[65]

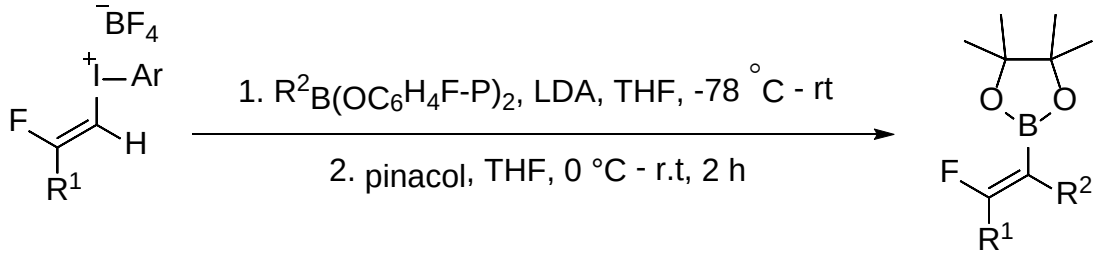


134 **135**, 63-84%

R^1 = H, Bn; R^2 = Me, Et
Nu = CN, Br, SO_2Tol, $SC(S)N(CH_3)CH_2Ph$, $SP(O)(OEt)_2$

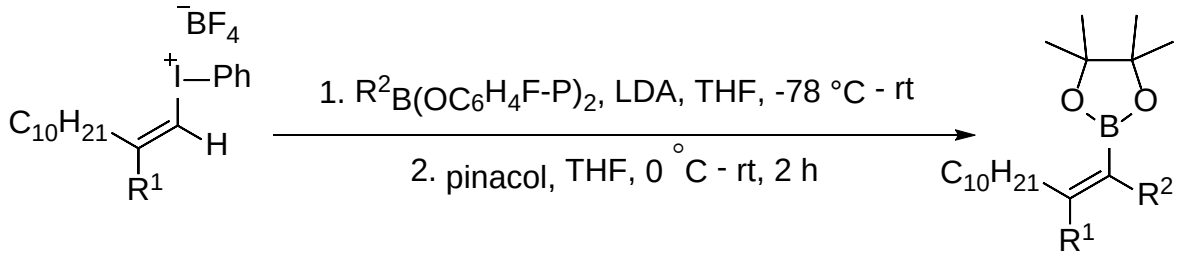
Scheme 59

Guan and co-workers reported that the preparation of (*E*)- and (*Z*)-(fluoroalkenyl)boronates can be achieved by the reaction of (*E*)- and (*Z*)-(2-fluoroalkenyl)iodonium salts **136, 138** with di(*p*-fluorophenoxy)alkylboranes **137, 139** followed by transesterification to the pinacol esters (Scheme 60).[66]



136

137, 50-72%



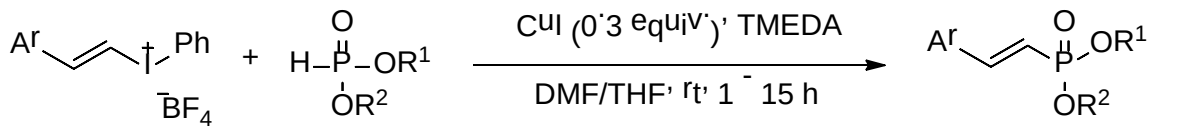
138

139, 63%

R^1 = $C_{10}H_{21}$, $AcO(CH_2)_9$, $BnO(CH_2)_3$, $BnO_2C(CH_2)_3$, etc.
Ar = Ph or Tol; R^2 = C_6H_{13}, BuCH=CH, $Br(CH_2)_3$

Scheme 60

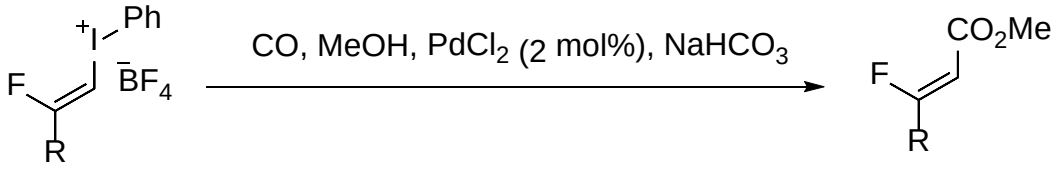
Kang and Huang improved the reaction of alkenyliodonium salts with carbon nucleophiles in stoichiometric or catalytic transition metal mediated processes. They established that alkenyliodonium salts undergo cross-coupling products when they react with organoborates via treatment with a copper(I) catalyst, terminal alkynes and Grignard reagents.[59] In a specific example, the copper-catalysed reaction of vinyliodoium salts **140** with H-phosphonates **141** generated the 2-arylvinylphosphonates **142** in moderate to good yields (scheme 61).[67]



Ar = Ph, 2-FC_6H_4, 2-MeC_6H_4, 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$NO_2C_6H_4$, etc.
R^1, R^2 = Me, Et, Bu, Bn, Ph, etc.

Scheme 61

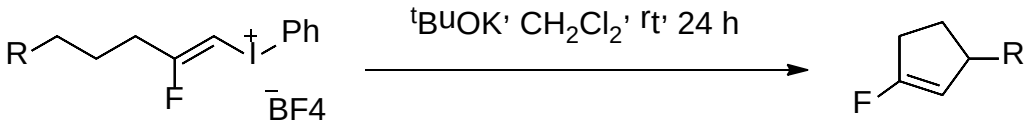
Moreover alkenyliodonium salts have been found to be highly reactive reagents for other cross-coupling reactions such as palladium-catalyzed cross-couplings e.g. Heck-type olefination and Sonogashira-type reactions. Yoshikawa and co-workers synthesised (*Z*)-β-fluoro-λ,β-unsaturated esters **144** stereoselectively from (*Z*)-2-fluoro-1-alkenyliodonium salts **143** via Pd-catalyzed methoxycarbonylation at room temperature (Scheme 62).[68]



R = $C_{10}H_{21}$, (*cyclo*-C_6H_{11})CH_2, Ph, $Cl(CH_2)_9$, $^iPrO_2C(CH_2)_8$

Scheme 62

Yoshida and co-workers deprotonated alkenyliodonium salts with strong base to generate alkylidenecarbenes by a base-induced α-elimination. The alkylidenecarbenes undergo 1,5-carbon-hydrogen insertion to generate substituted cyclopentenes.[69a] Guan and co-workers illustrated this reaction as with (*Z*)-(2-fluoroalkenyl)iodonium salts **145** and potassium *tert*-butoxide affording fluorocyclopentenes **146** (Scheme 63).[69a-c]

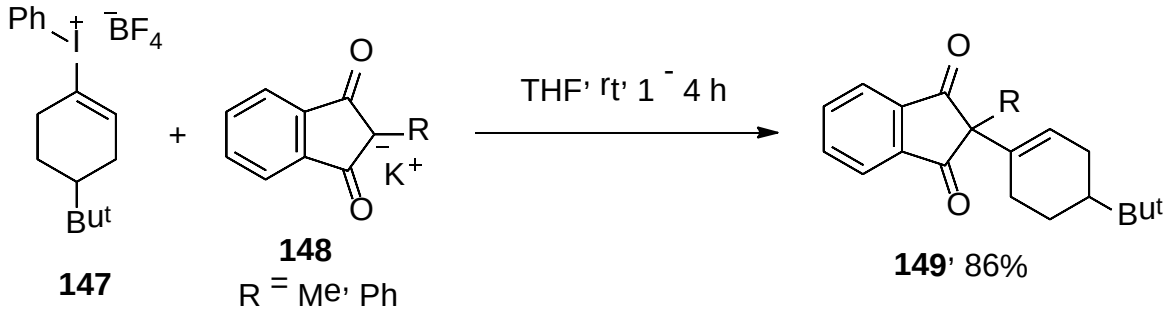


145 **146**, 68-71%

R = AcO(CH2)6, Cl(CH2)6, tBuCO(CH2)5, etc

Scheme 63

Ochiai and co-workers reported the reaction of alkenyliodonium salts **147** with enolates leading to alkylation. This type of process is difficult to achieve by other means and can lead to quaternary centre formation (Scheme 64).[70]



147

148
R = Me, Ph

149, 86%

Scheme 64

2. Aims and objectives.

The overall aim of this project was to synthesise novel iodonium salts and demonstrate their synthetic utility.

Objective 1: Formation of novel iodonium salts.

Y = OR, NR_2, SiR_3

Objective 2: To Investigate stabilities and properties of these salts by testing them in known literature reactions.

Objective 3: To investigate and develop new reactivity of these salts.

3. Results and Discussion.

Our initial proposal for this project was to synthesise a set of new alkynyl(aryl)iodonium salts with heteroatom substituents on the alkyne as these are not known in many cases and investigate their formation, stability and reactivity (Figure 11).

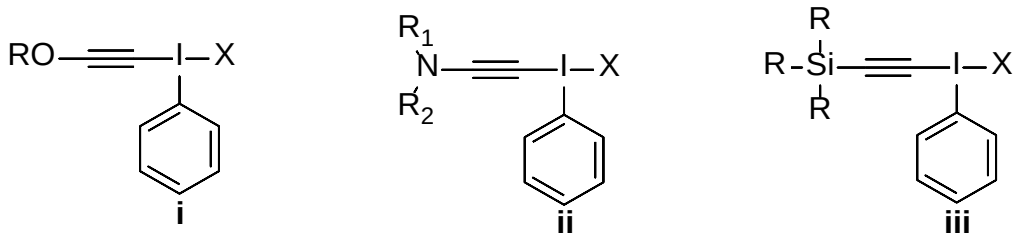


Figure 11

There many examples of stable alkynyl(aryl)iodonium (Figure 12).

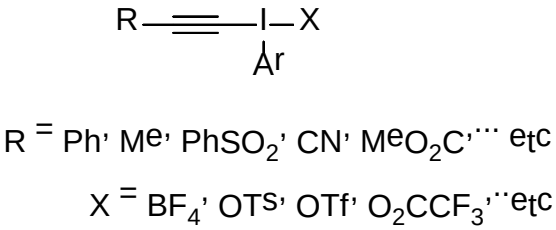
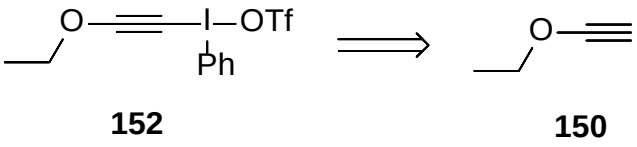


Figure 12

3.1. Attempted synthesis of β-ethoxyethynyl-λ^3-iodane.

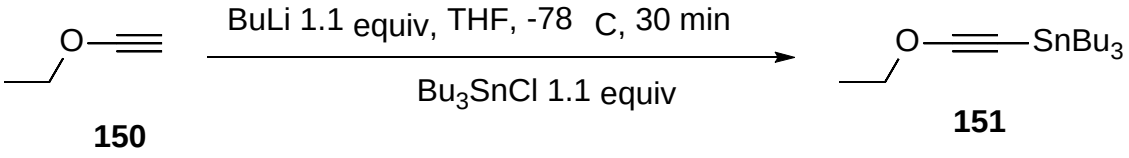
The initial plan was to prepare the β-ethoxyalkynyliodonium salt derivative from commercially available ethoxyacetylene **150** (Figure 13). The effect on stability of the iodonium salt by the alkoxy group was unknown. Known examples of iodonium salts shown above mostly contain electron-withdrawing substituents on the alkyne.



152 **150**

Figure 13

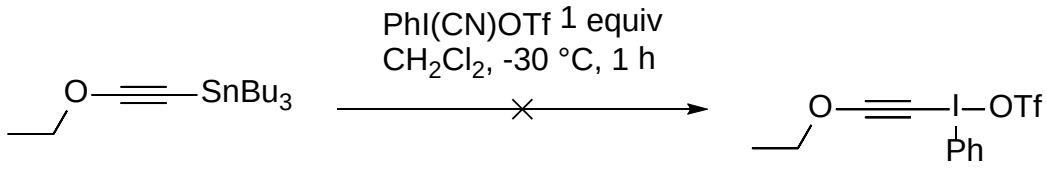
In order to prepare our target iodonium salt, first ethoxyacetylene **150** was deprotonated with BuLi and quenched with Bu_3SnCl to generate the alkynyl stannane **151** (Scheme 65).[71]



150 **151**

Scheme 65

The preparation of β-ethoxy ethynyl-λ^3-iodane **152** was attempted by treatment of 2-ethoxyethynyl(tributyl) stannane **151** with Stang's reagent (cyano(trifluoromethanesulfonyloxy) iodobenzene) in CH_2Cl_2 at -30 ºC for 1 hour. However, the reaction was unsuccessful after many attempts (Scheme 66).[36] Typically, precipitation of iodonium salt occurs upon addition of Stang's reagent.

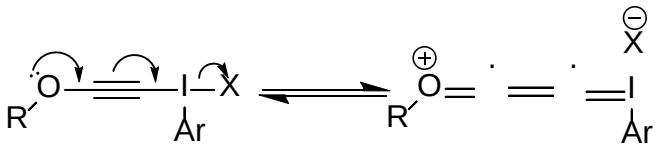


151 **152,** 0%

Scheme 66

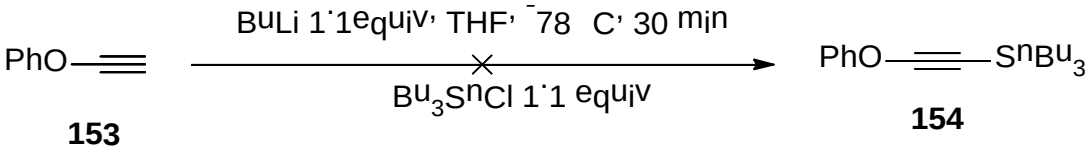
A possible reason for this failure can be understood by considering the resonance structure of this substrate which shows that the OR group is strongly electron-donating (Scheme 67). This

must affect the stability of these compounds and it is possible that decomposition occurs rapidly upon formation.



Scheme 67

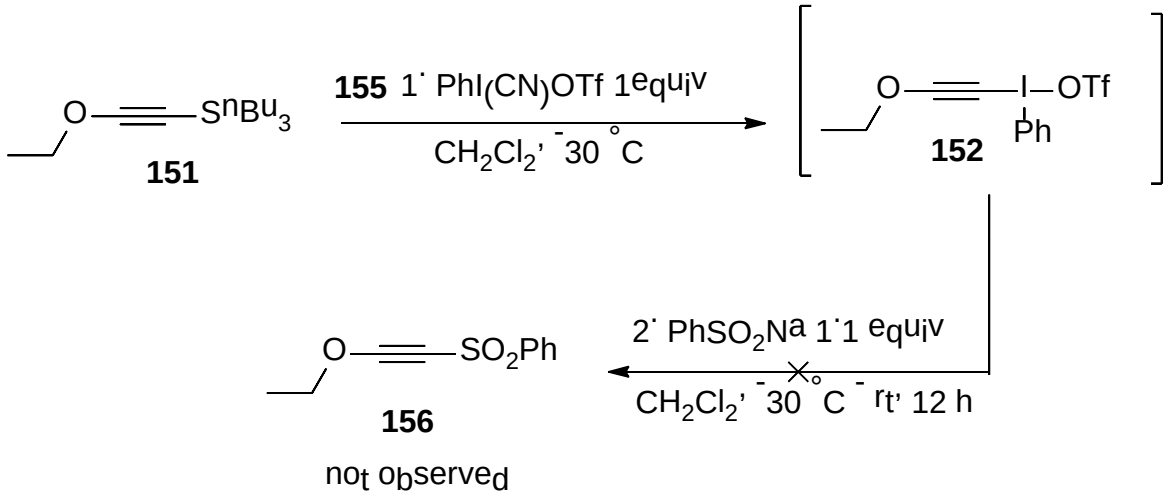
The presence of a phenoxy group in place of the ethoxy was considered in order to reduce the electron-donating ability and increase the stability of the iodonium salt. Phenoxyacetylene **153** was converted to alkynyl stannane **154** by the same procedure reported above (Scheme 65). However, the attempt to isolate the product **154** was unsuccessful (Scheme 68). Therefore it seemed likely that the desired stannane was unstable and decomposed rapidly.



Scheme 68

3.2. Attempted synthesis of 2-ethoxy ethynylbenzene.

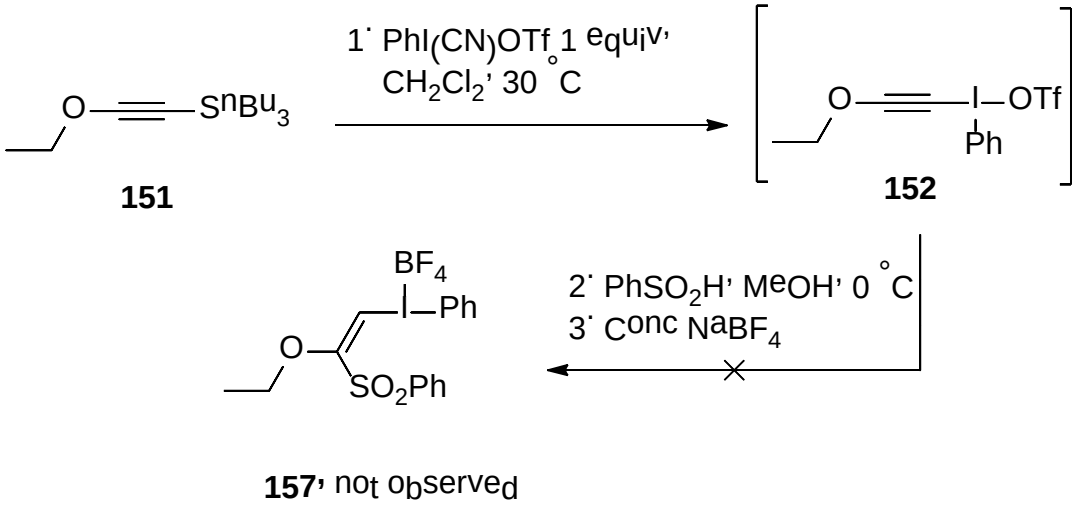
Because of the difficulties experienced in trying to isolate these β-oxyethynyl iodonium salts and on the assumption that the iodonium salts were formed but decomposed rapidly, the decision was made to attempt to react the iodonium salt immediately upon formation. In this regard the 1.2-shift reaction reported by Liu and Chen was attempted.[43] After repeating the procedure above, the solution was treated immediately with an aqueous solution of benzenesulfinic acid sodium salt in the presence of 10 mol% triethylbenzylammonium chloride. Unfortunately, we were not able to isolate the sulfone **156** either (Scheme 69).



Scheme 69

3.3. Attempted synthesis of β-ethoxy-β-acyloxyvinyl-λ^3-iodane.

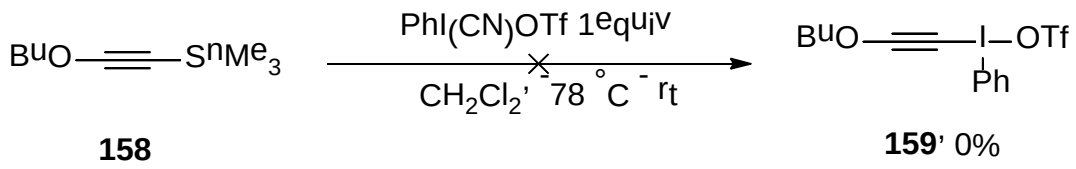
In another attempt to react the unstable β-oxyethynyliodonium salt **152** before it decomposed, its formation was attempted followed by addition of benzenesulfonic acid in methanol at 0 °C (Scheme 70). Unfortunately, the desired product **157** was not observed.



Scheme 70

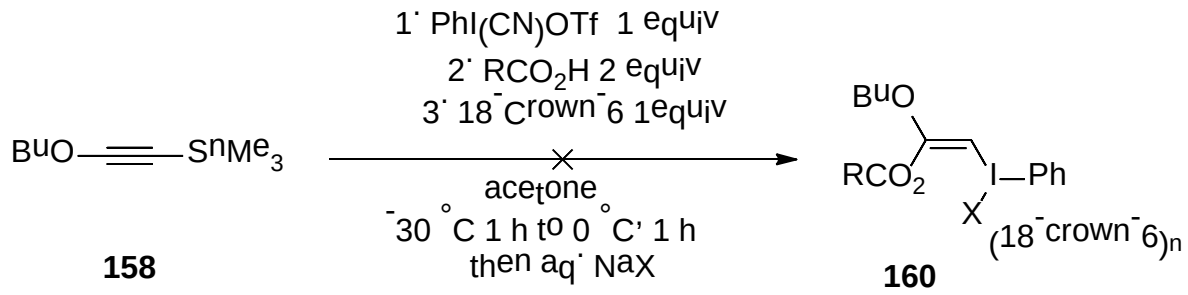
During the course of our studies, Miyamoto and co-workers reported their efforts to prepare a butoxyethynyl iodonium salt. In accordance with our study, all their attempts to isolate the β-

butoxyethynyl-$^{3}\lambda$-iodane were unsuccessful (Scheme 71). They reported that the reason is likely to be the strongly electron-donating ability of the β-butoxy group. Michael addition of the cyanide ion to **158** to afford the alkylidenecarbene may partially account for the high labiality of iodine **159**. However, when they attempted to trap iodonium salts *in-situ* with carboxylic acids in the presence of 18-crown-6 at -30 ºC to 0 ºC, the β-butoxy-β-acyloxyvinyl-$^{3}\lambda$-iodanes **160** were formed in good yields. However, the products were too labile to isolate and gradually decomposed even at -30 ºC (Scheme 72). [72]



158 **159**, 0%

Scheme 71

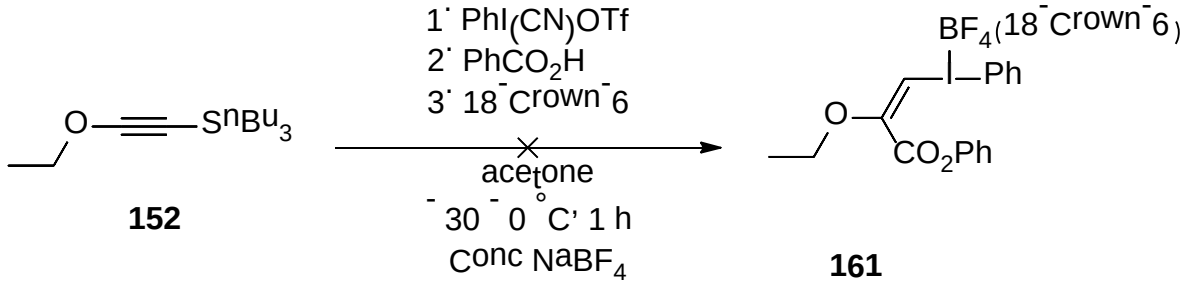


158 **160**

160a: R = Me, X = BF_4, n = 1 (74%); **158b**: R = Ph, X = BF_4, n = 1 (70%)
160c: R = Me, X = Br, n = 0 (66%); **158d**: R = Me, X = I, n = 0 (57%)
160e: R = Ph, X = Br, n = 0 (74%); **158f**: R = p-$CF_3C_6H_4$, X = Br, n = 0 (83%)
160g: R = p-MeC_6H_4, X = Br, n = 0 (61%)

Scheme 72

We attempted to repeat this procedure with our stannane **157**, using benzoic acid and 18-crown-6. In our hands, this procedure did not lead to iodonium salt **161** formation. (Scheme 73).



Scheme 73

3.4. Synthesis of ((phenylsulfonyl)ethynyl) triisopropylsilane.

We were also interested in preparing a β-silylethynyliodonium salt to investigate the effect of the silyl group on its reactions. It was envisaged that such a salt could be prepared from triisopropyl acetylene (Figure 14).

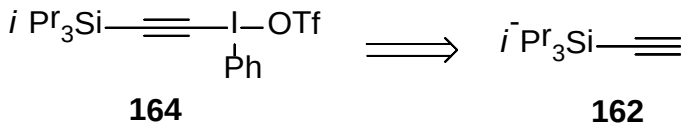
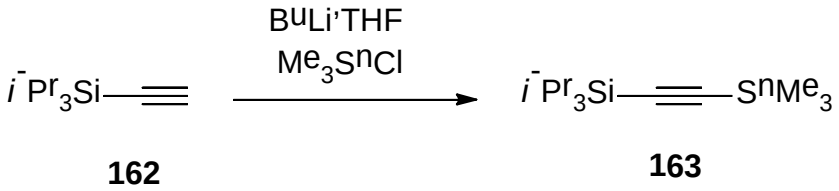


Figure 14

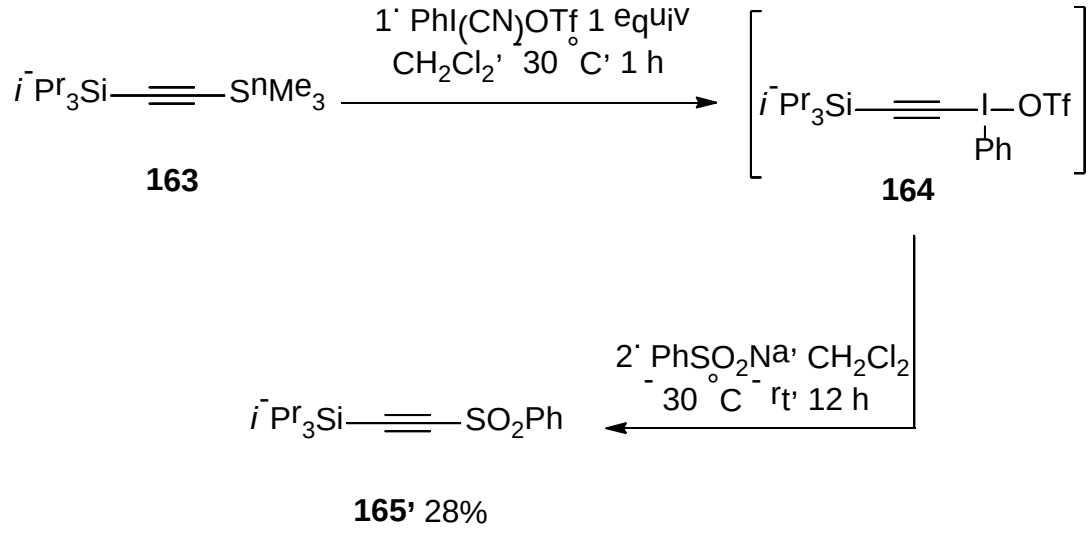
Accordingly the alkynyl stannane **163** was prepared by deprotonation of triisopropyl acetylene with *n*-BuLi followed by addition of Me_3SnCl (Scheme 74).[73]



Scheme 74

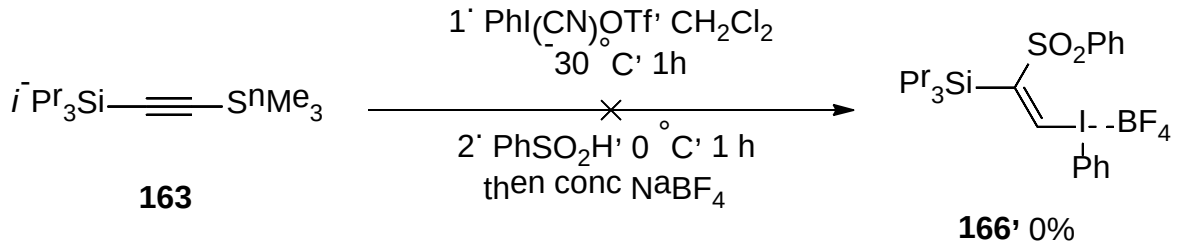
The preparation of silylethynyl(phenyl)iodonium salt was attempted by treatment of triisopropyl((trimethylstannyl)ethynyl)silane **163** with Stang's reagent (cyano(trifluoromethylsulfonyloxy)iodobenzene) in CH_2Cl_2 at - 30 ºC for 1 h.[36]

Unfortunately, we were not able to isolate the salt this time either. Despite this failure, we attempted to form the iodonium salt and react it *in-situ* like before just in case there were any stability issues. This involved treatment of the alkynyl(aryl)iodonium salt with 1.1 equiv of solid benzenesulfinic acid sodium salt. Pleasingly, the product (phenylsulfonyl)ethynyl)tripropylsilane **165** was isolated in 28% yield via the addition elimination 1,2-shift sequence (Scheme 75).



Scheme 75

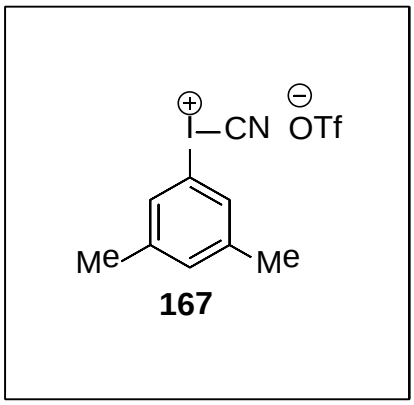
Surprisingly, conversion to the alkenyl(aryl)iodonium salt **166** via treatment of the alkynyl(aryl)iodonium salt **164** with benzenesulfinic acid in methanol was unsuccessful (Scheme 76).



Scheme 76

3.5. Synthesis of cyano(3,5-xylyl)iodonium trifluoromethanesulfonate 167.

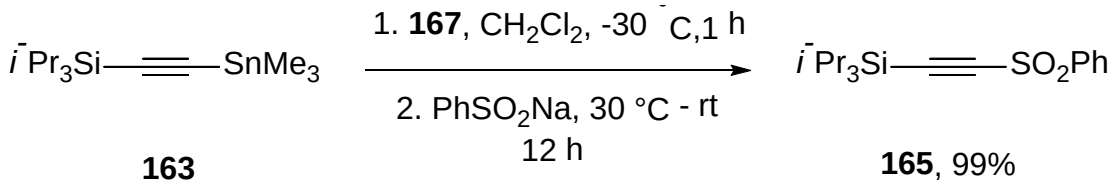
Due to improved yields reported by previous Moran group member David Hamnett in the synthesis of alkynyliodonium salts using modified Stang reagent **167** cyano(3,5-xylyl)iodonium trifluoromethanesulfonate (Scheme 77).[37] We decided to use this λ^3-iodane in place of the original Stang reagent and repeat the reactions with silane **163**.



167

Scheme 77

The reaction was carried out using exactly the same procedure as for Stang's reagent , however, this time the reaction worked much better. The (phenylsulfonyl)ethynyltripropylsilane **165** was obtained in an excellent 99% yield (Scheme 59).

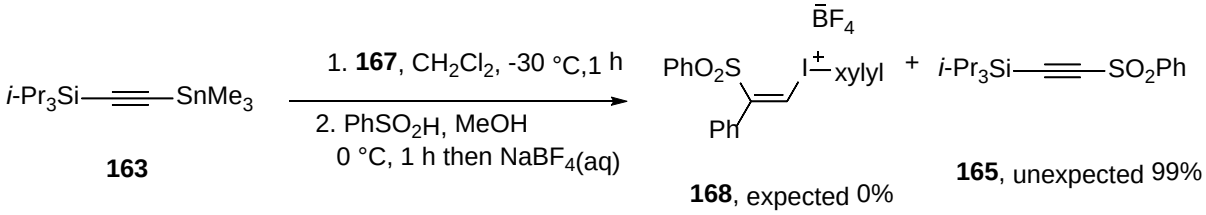


163 **165**, 99%

Scheme 78

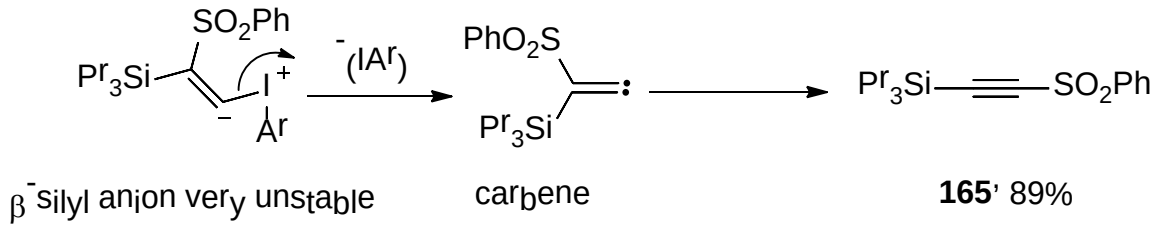
The second process with benzenesulfinic acid in MeOH was also repeated. Complete conversion of starting material was evident however, none of the expected alkenyliodonium

salt was isolated. Surprisingly, formation of alkyne **165** was observed in 89% yield (Scheme 79).



Scheme 79

Si stabilises positive charges on the β-carbon but in this case, the intermediate has a β-anion. A β-anion to a Si atom is very unstable and this intermediate breaks down rapidly before protonation can occur. Loss of IAr then 1,2-rearrangement leads to formation of **16**5 (Scheme 80).

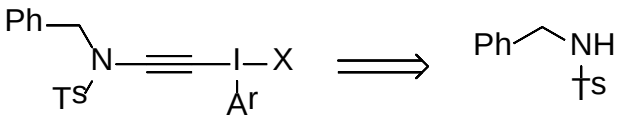


Scheme 80

3.6. Synthesis of alkynyl(aryl)iodonium salts with β-nitrogen substitution.

Next, we turned our attention to the formation of β-nitrogen containing alkynyliodonium salts. Ynamides are useful functional groups and the development of ynamideiodonium salts would enable a new synthetic route into derivatives. The rationale being that the electronic properties of nitrogen can be moderated by two substituents and more stable structures than the oxygen analogues can be made.

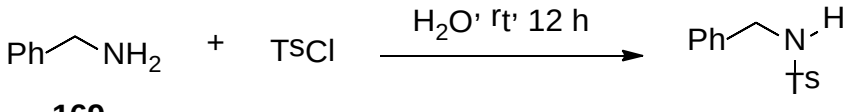
The structure of the initial target salt was envisaged to be prepared from benzyltosylamide (Figure 15).



176 **169**

Figure 15

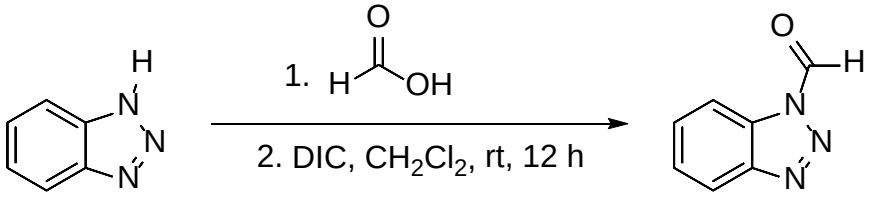
The preparation of this ynamide alkynyliodonium salt was attempted next, starting from benzyltosylamide. We started by combining dissolved benzylamine **171** with TsCl in water at room temperature and the desired product **172** was formed in moderate yield (Scheme 81)



169 **170**, 37%

Scheme 81

Then *n*-formylbenzotriazole (BtCHO) **172** was prepared by addition of DIC to a mixture of benzotriazole **171** and formic acid in CH_2Cl_2 (Scheme 82).[74]

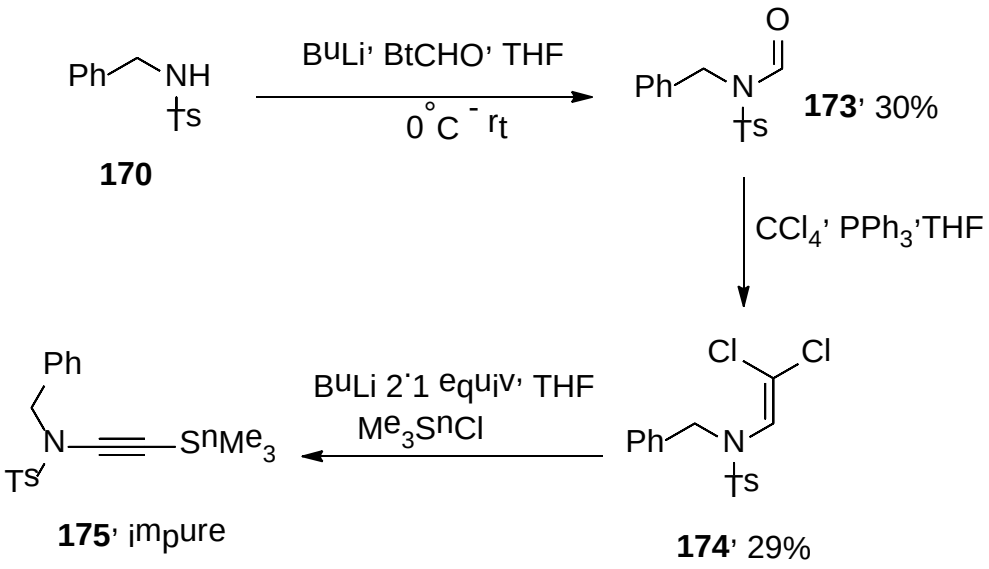


171 DIC: 1.3-dicyclohexylcarbodiimide **172**

Scheme 82

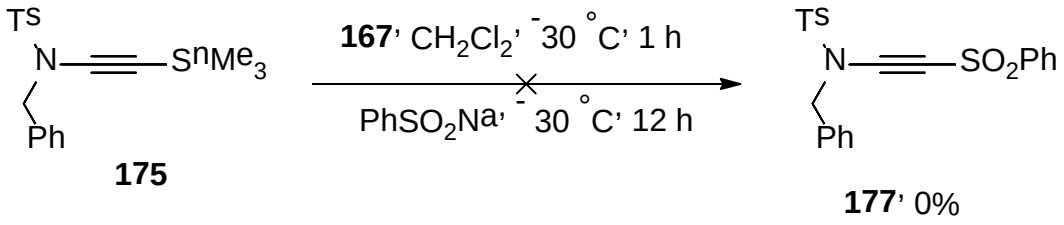
Next, benzyl-4-methyl benzenesulfonamide was deprotonated with BuLi and quenched with *n*-formylbenzotriazole (BtCHO) to generate benzyltosylformamide **173**. This was treated with

CCl_4 and PPh_3 to afford *n*-benzyl-*n*-(2,2-dichlorovinyl)-4-methylbenzenesulfonamide **174**. This was deprotonated with BuLi and quenched with Me_3SnCl to generate the alkynyl stannane **175** (Scheme 83).[75]



Scheme 83

The impure stannane **175** was treated with Stang reagent **167** in order to prepare the iodonium salt, but unfortunately, the salt was not obtained (Scheme 84).



Scheme 84

The difficulties in synthesising this compound are probably due to the same reason as for the alkoxy version, i.e. electron-donating nitrogen is responsible for reducing the stability. Therefore, formation of the bis-tosylamide derivative was envisaged to reduce the electron density on nitrogen further (Figure 16).

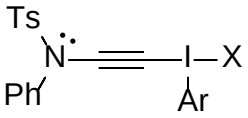
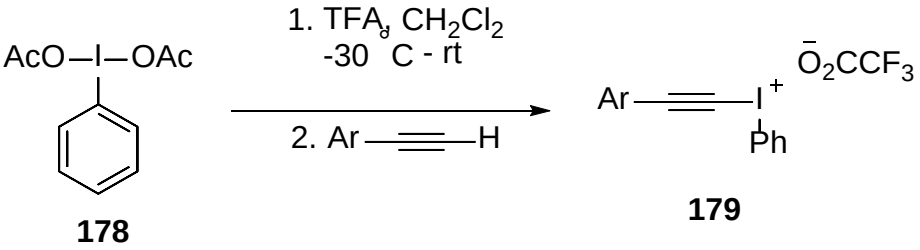


Figure 16

3.7. Synthesis of alkynyl(phenyl)iodonium trifluoroacetates.

In order to develop new reactivity with alkynyl(phenyl)iodonium salts we followed the procedure reported by Carroll, who was able to directly prepare (phenylethynyl)phenyliodonium trifluoroacetate from phenylacetylene.[38] This pathway held some advantage over others such as pure samples can be obtained in high yields in one step. The results for the synthesis of alkynyl(phenyl)iodonium trifluoroacetates by this method are summarised in Table 1.



178 **179**

Scheme 85

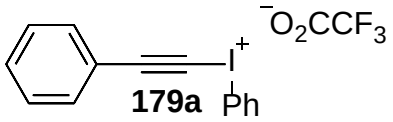
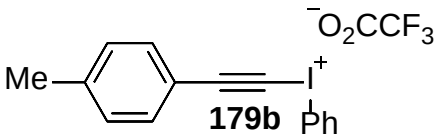
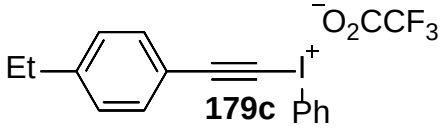
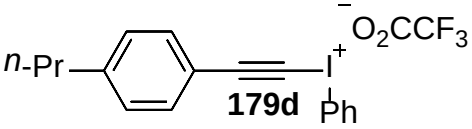
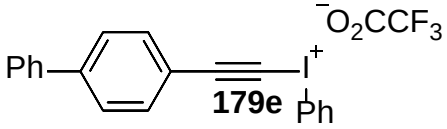
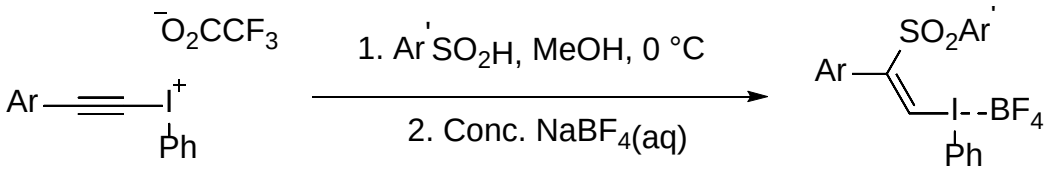
entry	product	yield %
1	 **179a**	95
2	 **179b**	98
3	 **179c**	93
4	 **179d**	84
5	 **179e**	78

Table 1

Commercially available iodobenzene diacetate was treated with trifluoroacetic acid and five different phenylacetylenes were added. The products were then crystallised from diethyl ether and petroleum ether and isolated in high yields, apart from **179e** which appeared to be somewhat unstable. Compound **179e** was taken forward to the next step immediately before further decomposition could occur.

3.8. Synthesis of (*Z*)(β-(aryl sulfonyl)alkenyl iodonium tetrafluoroborates.

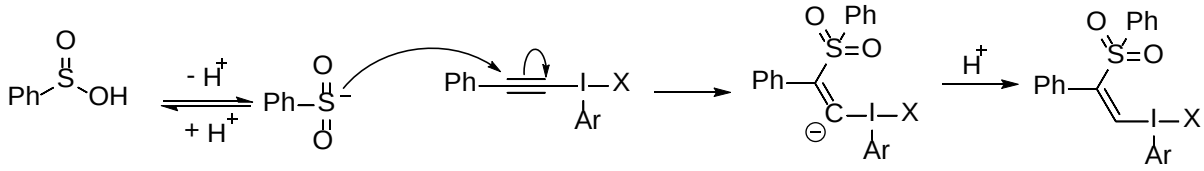
A series of alkenyl(arylsulfonyl)iodonium tetrafluoroborates **180** were synthesised by stereoselective Michael-type addition of arylsulfinic acids to the corresponding alkynyl(phenyl)iodonium trifluoroacetates **179** in methanol (Scheme 86).[50]



179 **180**

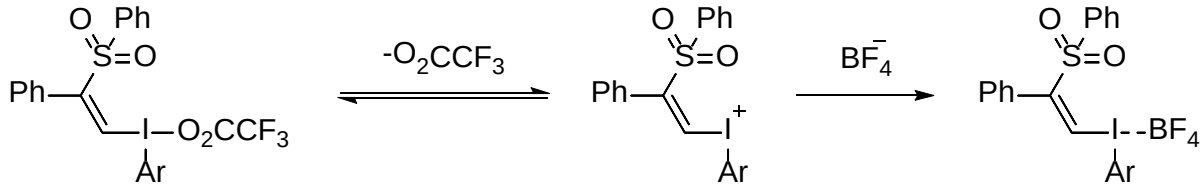
Scheme 86

As Ochiai reported, this reaction proceeds by addition of the nucleophile to the β-carbon, followed by rapid protonation of the resulting ylide intermediate (Scheme 87).[49]



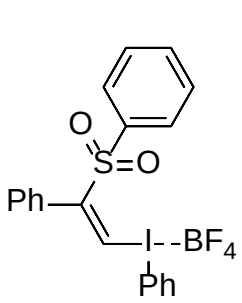
Scheme 87

The trifluoroacetate counterion was then replaced by tetrafluoroborate via an anion metathesis process (Scheme 88)

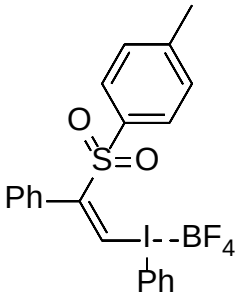


Scheme 88

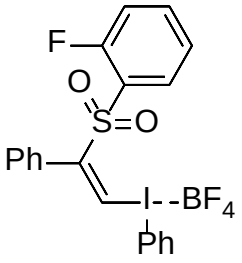
The results of alkeny(aryl)iodonium tetrafluoroborates is summarised in Table 2:



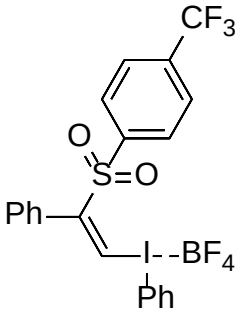
180a, 74%



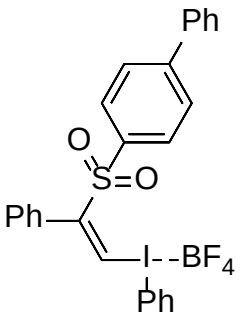
180b, 83%



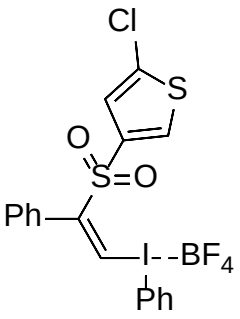
180c, 66%



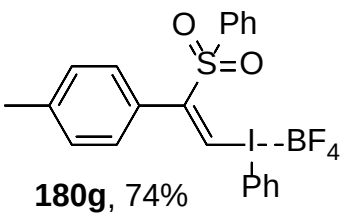
180d, 71%



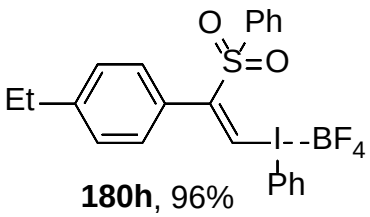
180e, 98%



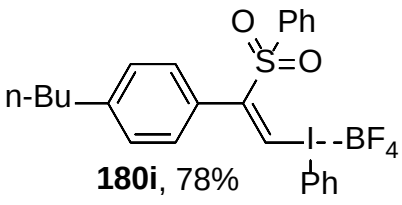
180f, 59%



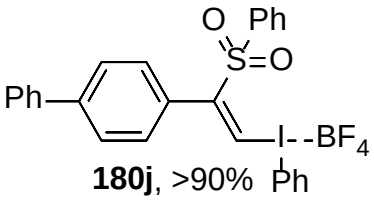
180g, 74%



180h, 96%



180i, 78%



180j, >90%

Table 2

The results obtained here were really encouraging, with all analogues performing well. All of the examples were obtained in good to excellent yields after crystallisation from diethyl ether and petrol via repeated washings and decantation, then recrystallization by slow addition of diethyl ether to a solution of each product in CH_2Cl_2.

As we obtained crystals of these compounds we were able to get a good quality X-ray crystal structure of the salt **180a** (Figure 17)

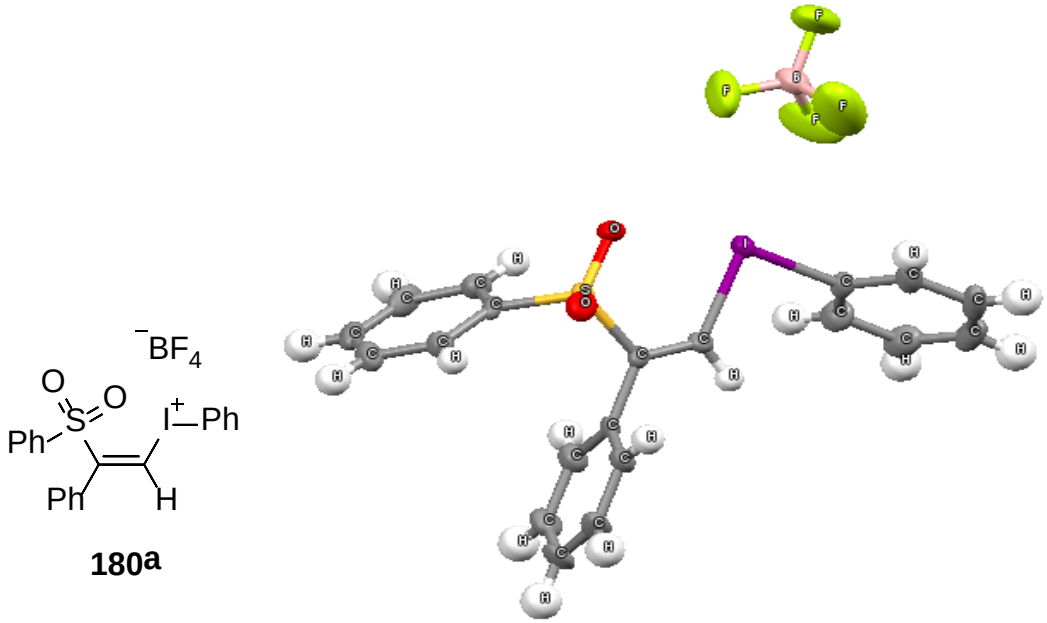
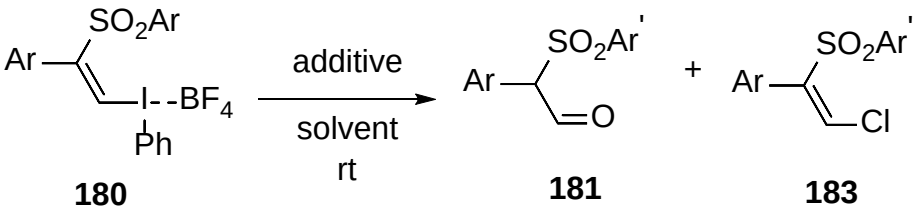


Figure 17

These salts were white microcrystalline solids in all cases and were insoluble in $CDCl_3$. Therefore, DMSO-d^6 was used as solvent for obtaining NMR spectra. However, we observed some changes in the NMR spectrum after one day. We decided to investigate this decomposition, identify the products and develop optimised conditions. Iodonium salt **180a** was stirred in anhydrous DMSO at room temperature overnight, however no change occurred (entry 1**)**. After addition of water to the solution the iodonium salt completely disappeared and a mixture of unknown compounds was formed (entry 2). We investigated the use of several different solvents but no conversion of **180a** occurred in all cases (entries 3-6). We returned to using DMSO as solvent and added acid and base to see the effect on this process. With the addition of 2 M NaOH solution complete conversion to one compound was observed which was identified as aldehyde **181a** (entry 7). Afterwards, it was determined that complete conversion to the aldehyde **181a** was possible with vigorous shaking in DMSO/H_2O

without any base (entry 8). We believe that the unknown compounds observed in (entry 2) are intermediates en route to **181a** and the increased agitation completes the solvolysis process. Adding hydrochloric acid led to conversion of the iodonium salt to the vinyl chloride **183a** with complete retention of stereochemistry Table 3.[76]



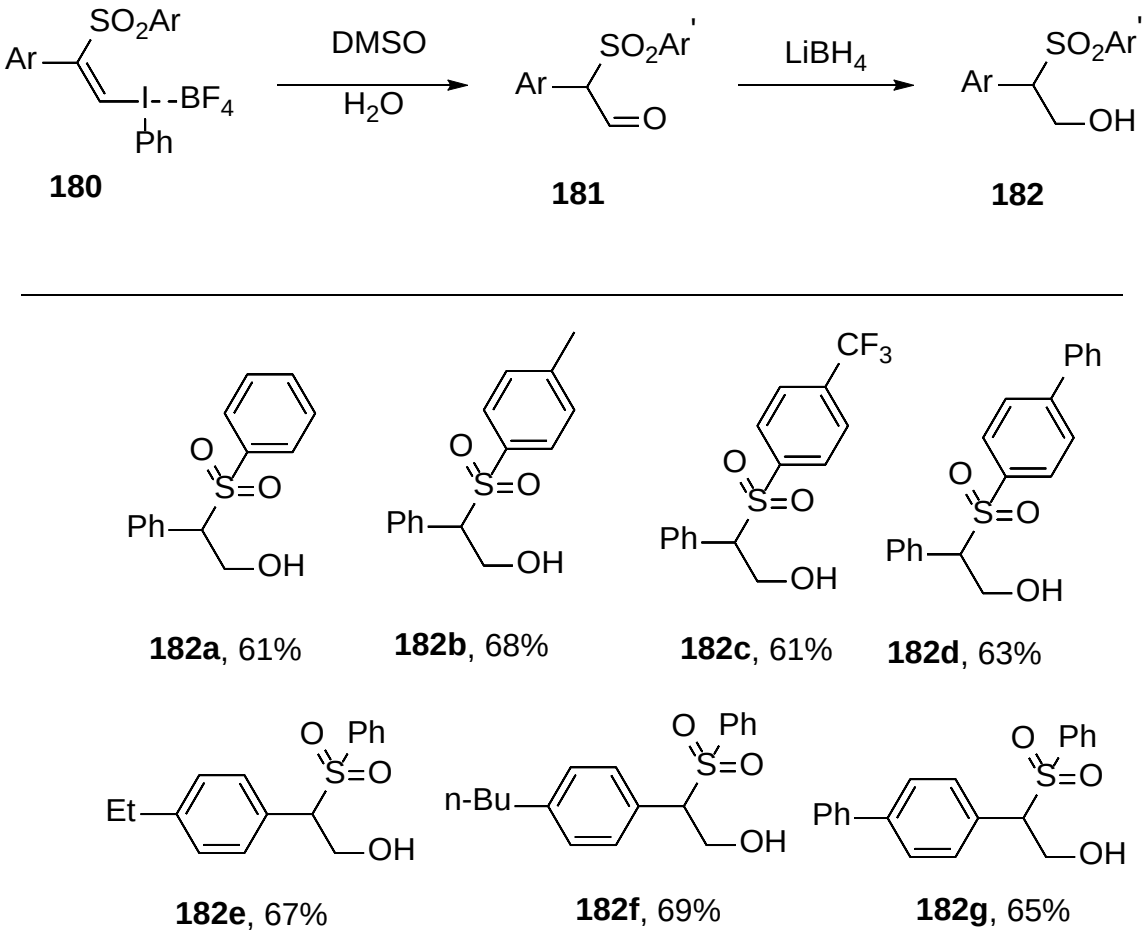
180 **181** **183**

entry	additive	solvent	Conversion/%
1	None	DMSO	0
2	2 equiv H_2O	DMSO	100 (mixture of products)
3	2 equiv H2O	MeCN	0
4	2 equiv H2O	$MeNO_2$	0
5	2 equiv H2O	EtOAc	0
6	2 equiv H2O	Et_2O	0
7	2 equiv 2 M NaOH	DMSO	100 (aldehyde)
8	2 equiv H2O	DMSO	100 (aldehyde)
9	2 equiv 2 M HCl	DMSO	100 (vinyl chloride)

Table 3

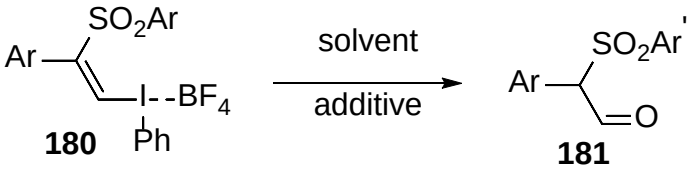
3.8.1. Synthesis of aldehydes and reduction to alcohols.

We then looked at the scope of the aldehyde conversion but it became apparent that purification of the aldehydes **181** was problematic. Therefore, reduction to the alcohol **182** was effected and these could be easily purified. The reaction was successful with different aromatic substituents on the alkene and the sulfone (Scheme 89).



Scheme 89

We repeated the experimental procedure using different solvents and stirred the mixtures overnight. No conversion of starting material was observed in all cases Table 4.

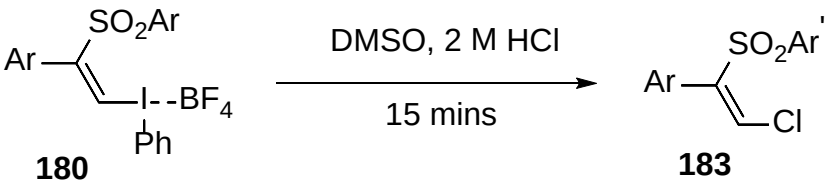


entry	ArI	additive	solvent	yield %
1	PhI	NaOH	DMSO	43
2	-	H_2O	DMSO	61
3	-	-	MeCN	0
4	-	-	$MeNO_2$	-
5	-	-	EtOAc	-
6	-	-	Et_2O	-
7	-	-	CH_2Cl_2	-

Table 4

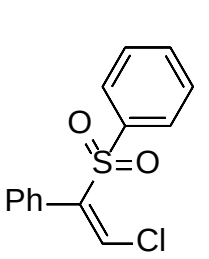
3.8.2. Synthesis of (*Z*)-(arylsulfonyl)vinylchloride.

Utilising our procedure, a series of (*Z*)-(phenylsulfonyl)vinyl chlorides **183** was synthesised from the corresponding alkenyl(aryl)iodonium tetrafluoroborates **180** by treatment with 2 M HCl in DMSO at room temperature for 15 minutes (Scheme 90).

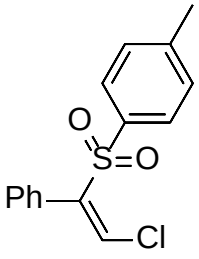


Scheme 90

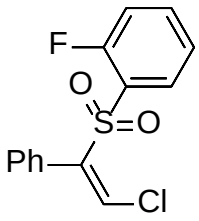
The reaction was suitable for a range of aromatic substituents on both the alkene and sulfone leading to excellent yields in all cases Table 5. The alkene stereochemistry was confirmed by comparison to literature data for the *Z* stereoisomer.[86]



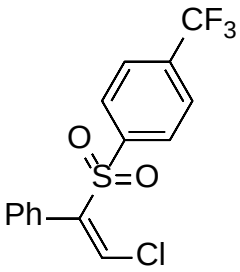
183a, 80%



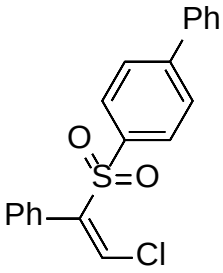
183b, 84%



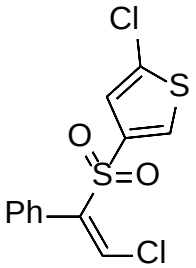
183c, 86%



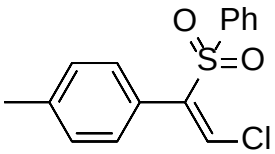
183d, 93%



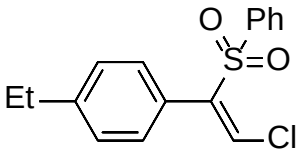
183e, 91%



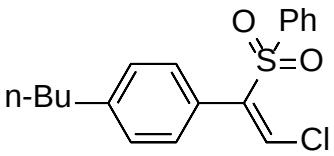
183f, 98%



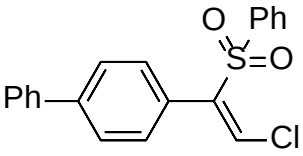
183g, 98%



183h, 77%



183i, 84%



183j, 89%

Table 5

Crystals suitable for X-ray crystallography were grown for vinyl chloride **183c** that is shown the *Z* stereoisomer of our product (Figure 18).

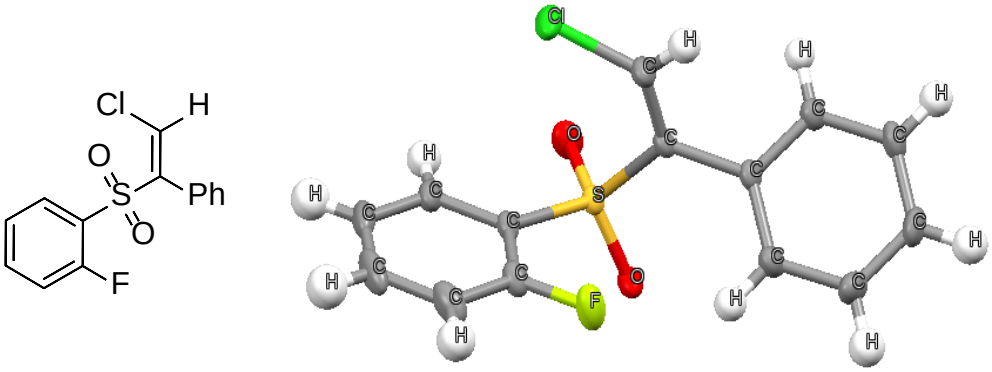
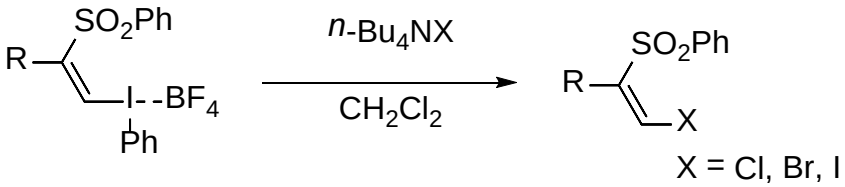


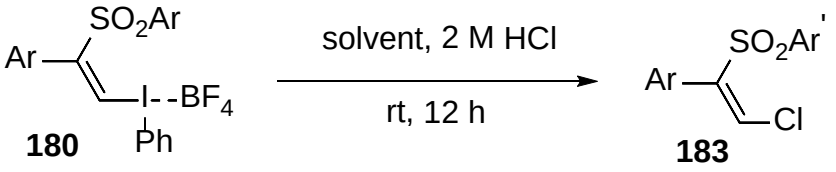
Figure 18

Ochiai and co-workers reported this same transformation but using different conditions. Namely, heating (*E*)-(β-alkylvinyl)iodonium tetrafluoroborates with *n*-Bu_4NX (X = Cl, Br, and I) in CH_2Cl_2 at room for temperature between 1 and 10 hours with yields of 75-100 % (Scheme 91).[50]



Scheme 91

When we varied the solvent from DMSO to other solvents in our procedure the chlorination reaction was very inefficient and low conversion was seen even after stirring overnight (Table 6). This demonstrates the unique properties of DMSO on the decomposition of vinyliodonium salts.

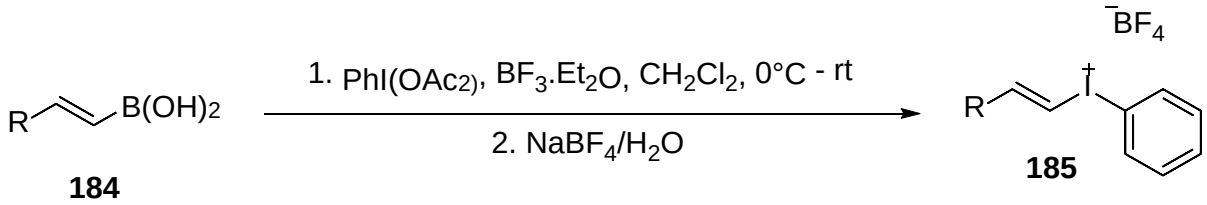


entry	ArI	Acid	solvent	yield %
1	PhI	HCl	DMSO	80
2	-	-	CH_2Cl_2	40
3	-	-	MeCN	32
4	-	-	$MeNO_2$	5
5	-	-	EtOAc	19
6	-	-	Et_2O	11

Table 6

3.9. Synthesis of alkenyl(phenyl)iodonium tetrafluoroborates.

Having studied the effects of water and acid on (*Z*)(β-(arylsulfonyl)alkenyliodonium tetrafluoroborates, it was decided to study the same effects in the case of alkenyl (phenyl)iodonium salts that do not contain the sulfonyl group. Utilising the procedure reported by Ochiai and co-workers (i.e. borane-iodine(III) exchange), some examples of alkenyl(phenyl)iodonium salts were synthesised from the commercially available vinyl boronic acids by treatment with BF_3-Et_2O and $PhI(OAc_2)$ in CH_2Cl_2 (Scheme 92).[58]



Scheme 92

Results of the synthesis of alkenyl(phenyl)iodonium tetrafluoroborates are shown below.

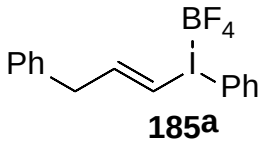
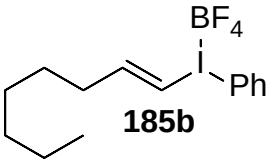
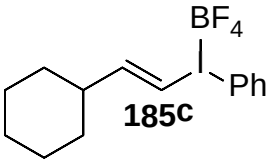
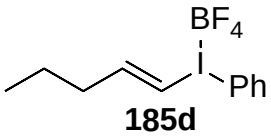
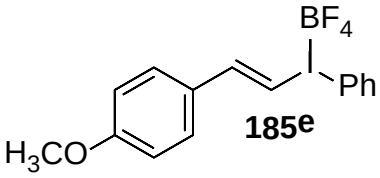
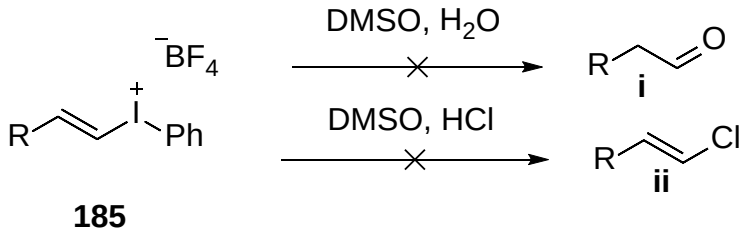
entry	product	yield %
1	 **185a**	56
2	 **185b**	69
3	 **185c**	49
4	 **185d**	44
5	 **185e**	0

Table 7

Four compounds were obtained in moderate yields using this method number of compounds obtained, apart from **185e** utilised (E)-(4-methoxystyryl)boronic acid (entry 5). Subjecting these iodonium salts to DMSO/H_2O did not lead to aldehyde **i** formation. We were also not able to convert these into the vinyl chlorides **ii**. (Scheme 93)



Scheme 93

It seems that the sulfonyl group is crucial for reaction to occur. The reason for this may can be explained by consideration of the resonance structures of the phenylsulfonyl group showing that the increasing stability of these compounds is due to the negative charge on sulfur being delocalized (Figure 19).

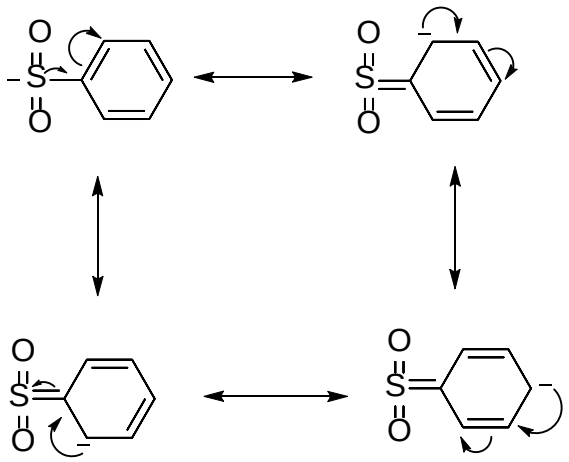


Figure 19

3.9. Synthesis of enynyl and dienyl(aryl)iodonium salts.

Building on the goal of this study to synthesise a new range of iodonium salts the next goal was the preparation of enynyl(aryl)iodonium salts. We suggested that these compounds would be useful in organic synthesis but they have two possible electrophilic sites i.e. the alkyne and the alkene (Figure 20). Possibly, 1,3-dienyl(aryl)iodonium could be prepared by conjugate addition of a nucleophile to the alkyne of enynyl(aryl)iodonium salts.

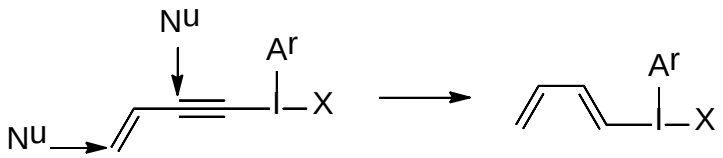


Figure 20

There is only one known example of a 1,3-enynyl salt (Figure 21) in the literature, reported by Stang and co-workers and it is unstable.[30]

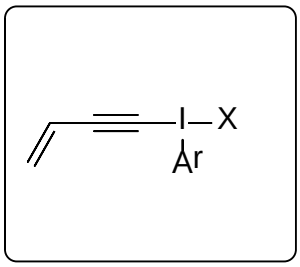


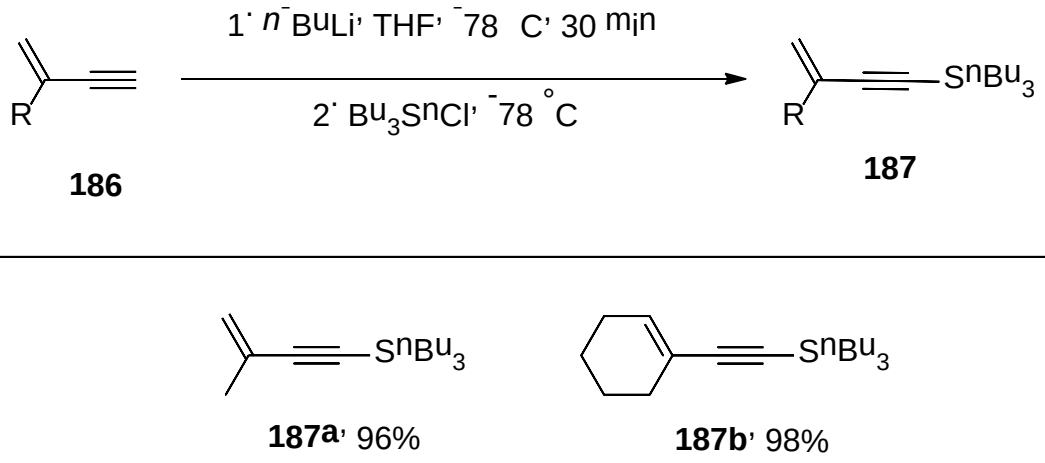
Figure 21

In order to prepare the enynyl(aryl)iodonium salts, we decided to utilize the general method that has been reported by Stang and co-workers i.e. treatment of stannanes with the Stang reagent.

The first step of this process was the synthesis of the enynyl stannanes:

3.9.1. Synthesis of enynyl stannane.

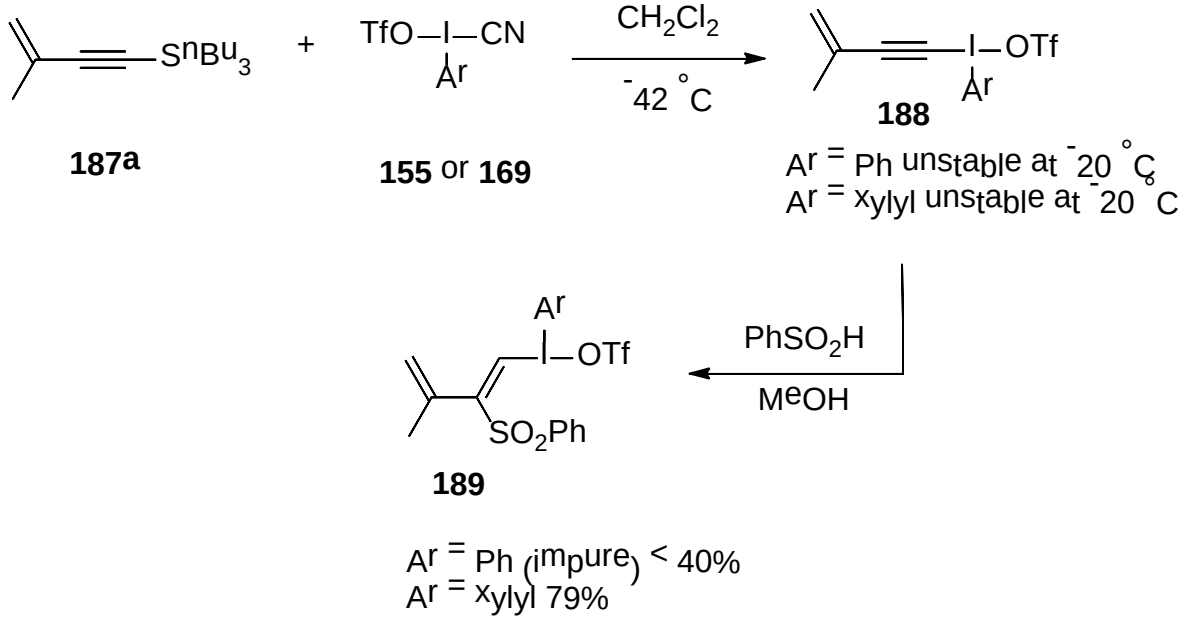
These compounds were synthesised by deprotonation of commercially available enyne by addition of butyl lithium followed by tin-lithium exchange by treatment with tri-*n*-butyltin chloride in THF (Scheme 94).[77] The crude products required no purification and the yields were excellent for these two examples.



Scheme 94

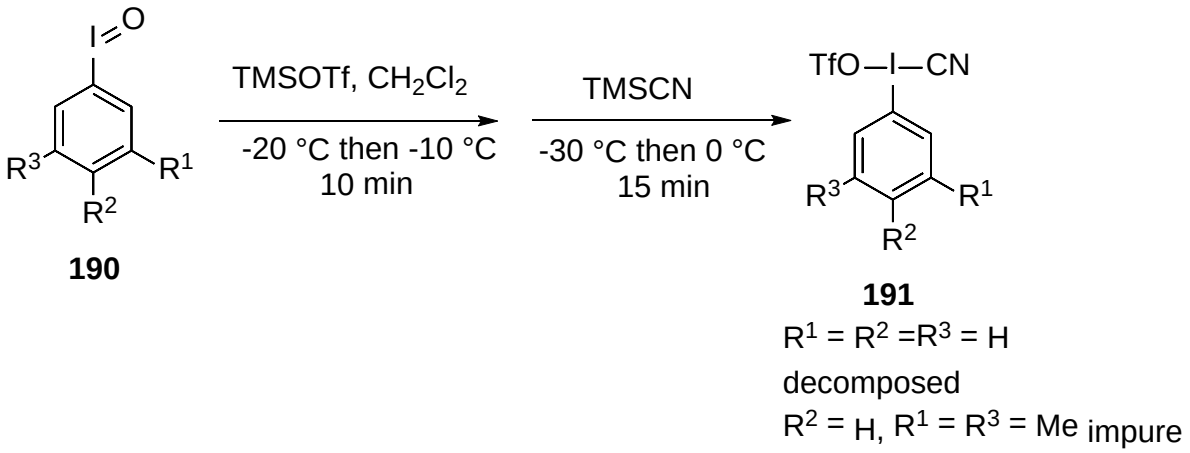
3.9.2. Synthesis of enynyl(aryl)iodonium salts.

As outlined above we decided to use Stang and co-workers procedure to convert the enynyl stannane into the enynyliodonium salt.[36] Previous work in this regard by previous Moran group member David Hamnett led to the preparation of two examples of enynyl(aryl)iodonium triflates **188** but these decomposed within minutes at room temperature or even at -20 °C. However, they could be converted directly to the dienyl(aryl)iodonium triflates **189** by addition of phenylsulfinic acid (scheme 95) .



Scheme 95

Similar to previous work by Hamnett the original Stang reagent provided a low yield of impure product. Whereas the xylyl Stang derivative led to a superior 79% yield of dienyl(xylyl)iodonium triflate over the two steps. Preparation of the Stang reagents **191** is relatively laborious because of the reactive species involved and the different temperatures required through the procedure (Scheme 96). Moreover, preparation of a pure sample of the xylyl derivative proved impossible. It seemed prudent at this point to investigate an alternative approach.[78,79]



190

191

$R^1 = R^2 = R^3 = H$ decomposed

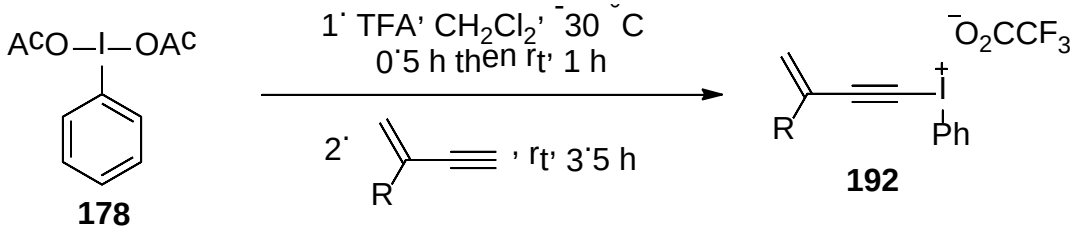
$R^2 = H$, $R^1 = R^3 = Me$ impure

Scheme 96

As has been outlined above alkynyl(aryl)iodonium trifluoroacetates can be easly prepared by the Carroll method and they are stable compounds compared to salts with other counterions. We decided to use this method to prepare the enynyliodonium salts via the terminal alkyne as we would not need to prepare more of the stannane compounds.

3.9.3. Synthesis of enynyl(phenyl) iodonium trifluoroacetates.

Following Carroll's general method iodobenzene diacetate was treated with TFA in CH_2Cl_2 followed by addition of the terminal alkyne (Scheme 97).[38] Gratifyingly, this method worked and trifluoroacetates **192a** and **192b** were isolated in quantitative yields after crystallisation from the crude reaction mixture Table 8. Surprisingly these trifluoroacetate salts were completely stable at room temperature for several days.



Scheme 97

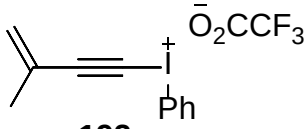
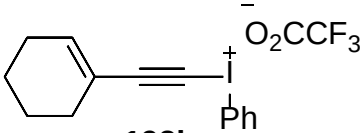
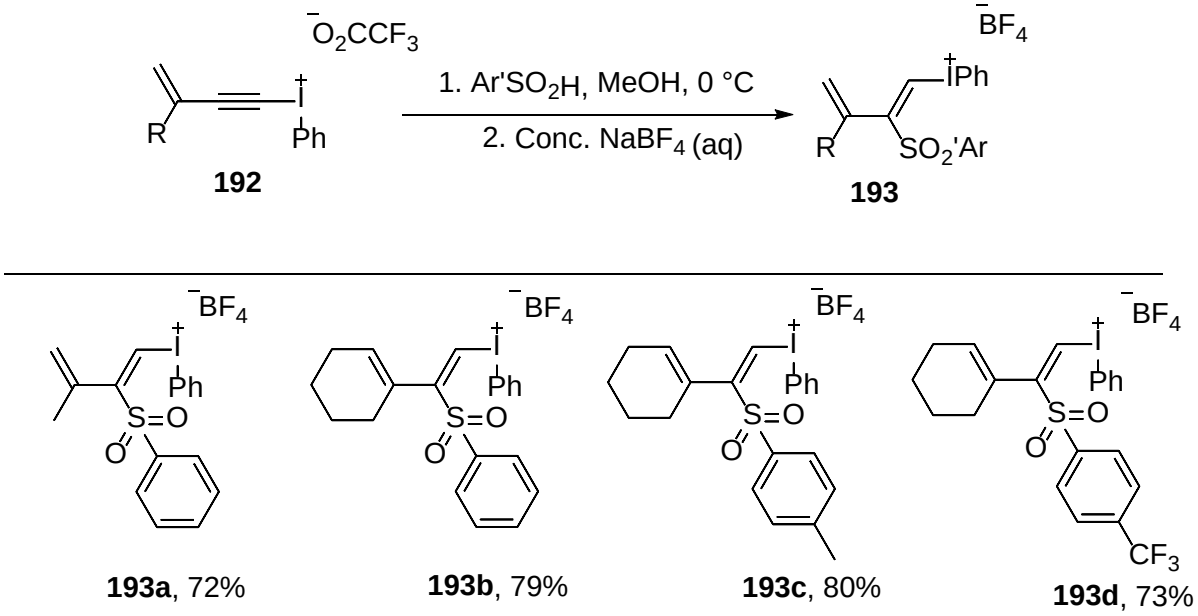
entry	product	yield %
1	 **192a**	98
2	 **192b**	99

Table 8

3.9.4. Synthesis of dienyl(phenyl)iodonium trifluoroacetatees.

These enynyliodonium trifluoroacetates **192** were converted into the corresponding dienyl(phenyl)iodonium tetrafluoroborates **193** by addition of phenylsulfinic acid in methanol, followed by conc $NaBF_4$ solution. The salts were obtained in good yields. In the case of the cyclohexyl analogue we prepared derivatives by addition of different arylsulfinic acids (Scheme 98). These λ^3-iodanes are crystalline solids and stable at room temperature under air indefinitely.

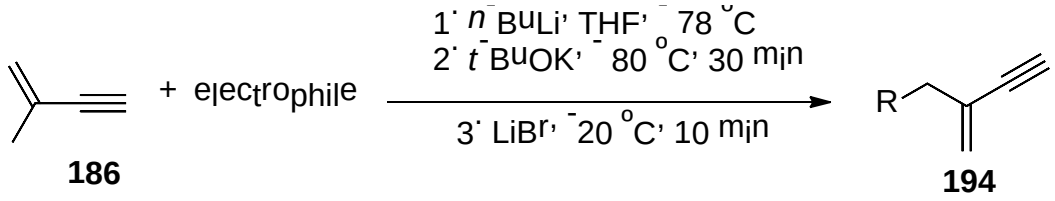


Scheme 98

At this point, we wished to investigate the scope of this process and prepare a range of dienyl(phenyl)iodonium tetrafluoroborates. Ultimately, we aimed to utilise these new salts in future synthetic transformations to illustrate their uses.

3.9.5. Synthesis of enynes.

Utilising the procedure reported by Brandsma and co-workers three new examples of enynes **194** were synthesised from commercially available 2-methylbut-1-en-3-yne **186** by treatment with *n*-butyl lithium in THF, followed by a solution *t*-BuOK in THF. After that was added a solution of lithium bromide in THF and finally an electrophile was added (Scheme 99).[80] The reaction worked well with a primary and secondary alkyl bromide as well as oxirane Table 9.



Scheme 99

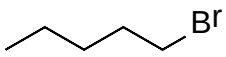
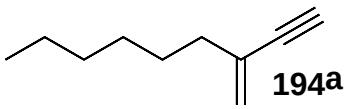
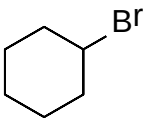
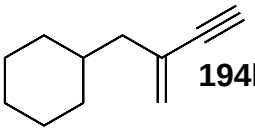
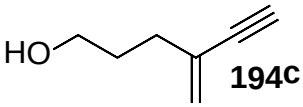
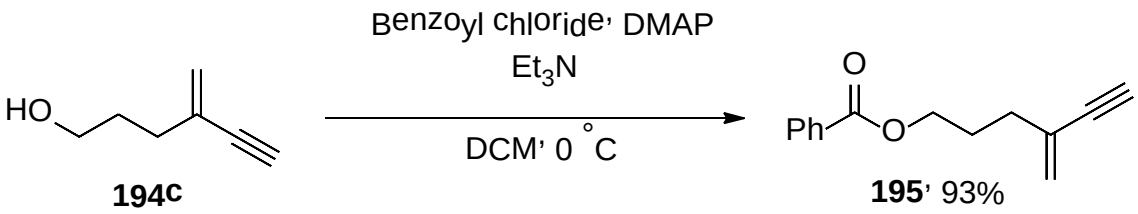
entry	electrophile	product	yield %
1		 **194a**	81
2		 **194b**	70
3		 **194c**	90

Table 9

All of the enynes were stored at - 20 ^{o}C to minimise any decomposition. It was anticipated that the presence of the primary alcohol (intry 3) could impact on the subsequent attempt to prepare the iodonium salt. Therefore, some of this material was converted into the benzoyl ester.

3.9.6. Synthesis of 4-methylenehex-5-yn-1-yl benzoate.

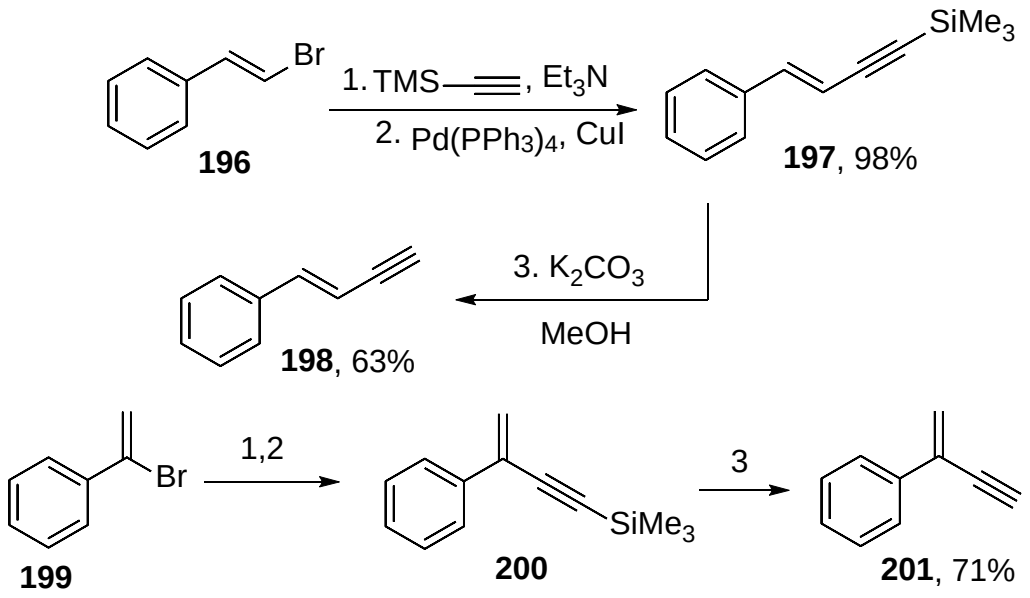
Utilising the procedure reported by Harrid and co-workers 4-methylenehex-5-yn-1-yl benzoate **195** was prepared from the corresponding alcohol (4-methylenehex-5-yn-1-ol) **194c** by treatment with benzoyl chloride.[81]The product was isolated in excellent yield (Scheme 100).



Scheme100

3.9.7. Synthesis of *(E)*-but-1-en-3-yn-1-ylbenzene.

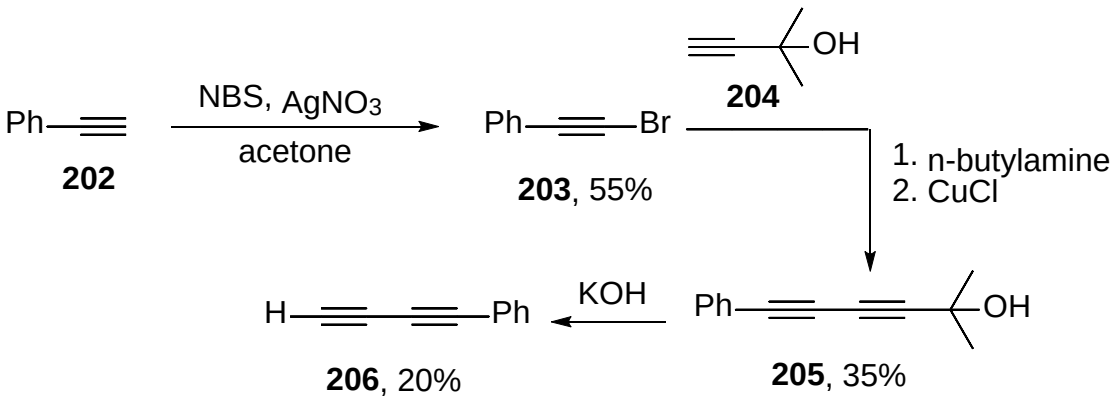
The results above show that the formation of iodonium salts from terminal alkynes is successful with alkyl enynes. We wondered if the use of aryl enynes would be successful. The synthesis of alkynyliodonium salts is successful from terminal arylacetylenes but not alkylacetylenes. Therefore, we could not take anything for granted. We prepared (*E)*-but-1-en-3-yn-1-ylbenzene **198** and (*Z*)-but-1-en-3-yn-2-ylbenzene from α- and β-bromostyrenes by Sonogashira a coupling with TMS-acetylene followed by treatment with K_2CO_3 to remove the TMS group (Scheme 101).[82]



Scheme 101

3.9.8. Synthesis of buta-1,3-diyn-1-ylbenzene.

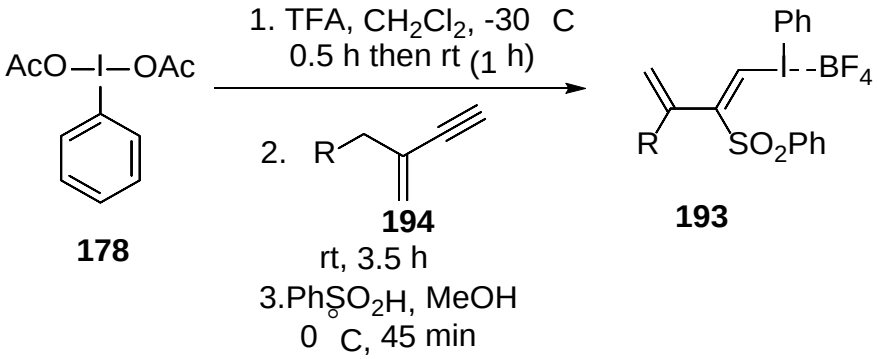
Utilised the procedure reported by Wulff and co-workers, NBS and $AgNO_3$ were added to ethynylbenzene in acetone which generated (bromoethynyl)benzene **202**. The (bromoethynyl) benzene **203**was quenched with 2-methyl buta-3-yn-2-ol **204** to afford 2-methyl-6-phenylhexa-3, 5-diyn-2-ol **205** which was treated with base (KOH) to afford buta-1,3-diyn-1-ylbenzene **206** in 20% yield (Scheme 102).[83]



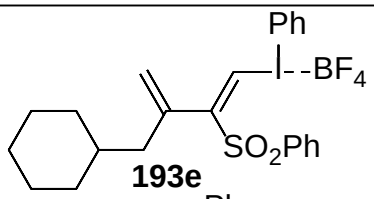
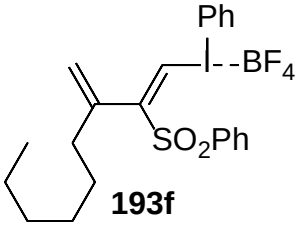
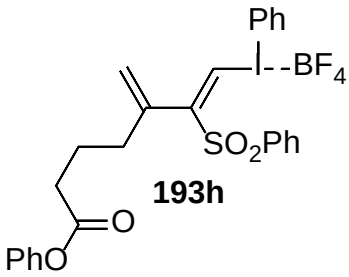
Scheme 102

3.9.9. Synthesis of dienyl iodonium tetrafluoroborates.

With the enynes in hand, we decided to convert these directly to the dienyliodonium salts **193** without crystallising and isolating the enynyliodonium salts (Scheme 103). The results for the synthesis of the dienyliodonium tetrafluoroborates is summarised in Table 10.



Scheme 103

entry	R	product	yield%
1	CH_2Cy	 **193e**	84
2	*n*-hexyl	 **193f**	56
3	$(CH_2)_3OH$	no desired product **193g**	n.r.
4	$(CH_2)_3OCOPh$	 **193h**	69
5	Ph	no desired product **193i**	n.r.
6	Ph	no desired product **193j**	n.r.
7	Ph	no desired product **193k**	n.r.

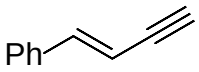
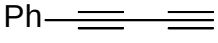
enyne 6 =  7 =  n.r = no reaction

Table 10

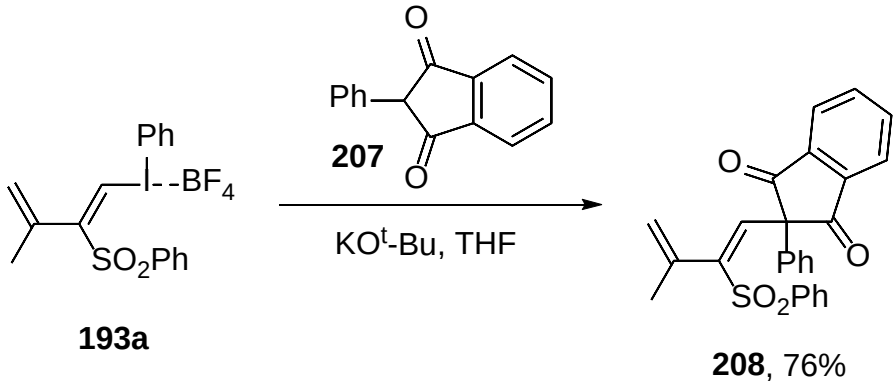
First, when the R was CH_2Cy the desired product was obtained in very good yield 84% (entry 1). However the yield dropped to 56% when the R was n-hexyl (entry 2). On the other hand, the expected product was not obtained when R was the alcohol analogue and the product could not be isolated as significant decomposition occurred. We suggest that the reason may be the free pendent alcohol. To overcome this problem an attempt has been made to convert

the alcohol function to an ester (entry 3 → 4), as a result the yield of our target product was significantly improved (entry 4). However phenyl analogues were not obtained (entries 5-7) due to the occurrence of decomposition before salts formation.

Next, we turned our attention to performing some reactions with these λ^3-iodanes. There are a range of transformations known for vinyliodonium salts and we chose to screen a few of these with our dienyliodonium salts.

3.9.10. Alkyenlation of an enolate.

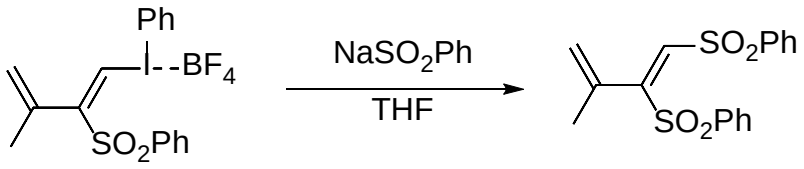
The first transformation investigated was alkylation of an enolate reaction as reported by Ochiai and co-workers. Ochiai found that alkenylphenyliodonium salts with a hydrogen atom attached to the α-vinylic carbon atom undergo a facile α-elimination by the reaction with weak base to generate alkylidenecarbenes. These can undergo 1,5-carbon-hydrogen insertions, providing a useful route for the construction of substituted cyclopentenes. We applied this process using our iodonium salt, by treatment with potassium *t*-butoxide and 2-phenyl-1*H*-indene-1,3(2*H*)-dione **207** in THF and the product **208** was obtained in good yield (Scheme 104).[70]



Scheme 104

3.9.11. Nucleophilic vinylic substitution.

Another interesting reaction that has been reported by Ochiai and co-workers is the nucleophilic vinylic substitution of iodonium salts. Utilising Ochiai's procedure, dienyliodonium tetrafluoroborate **193a** was treated with sodium benzenesulfinate in THF which generated bis-sulfone analogue **209** in excellent yield (Scheme 105).[84]



193a **209**, 98%

Scheme 105

We obtained high quality crystals of this compound after stirring the solid in petroleum ether. They were suitable for X-ray crystallography (Figure 22)

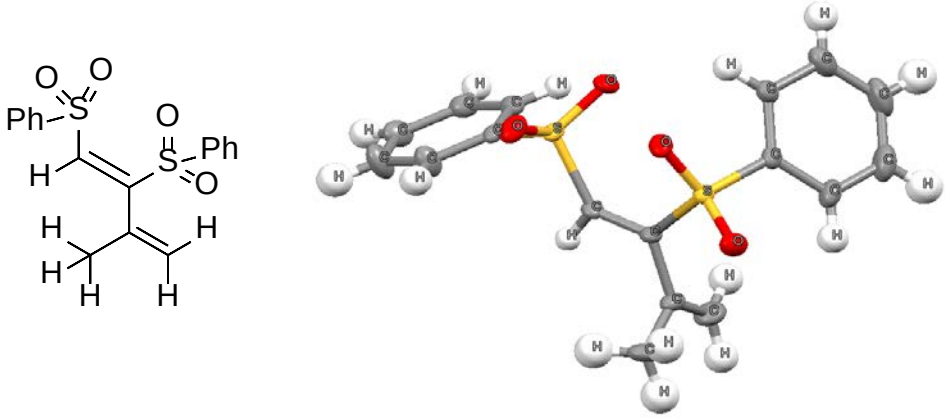


Figure 22

3.9.12. Chlorination of dienyliodonium salts.

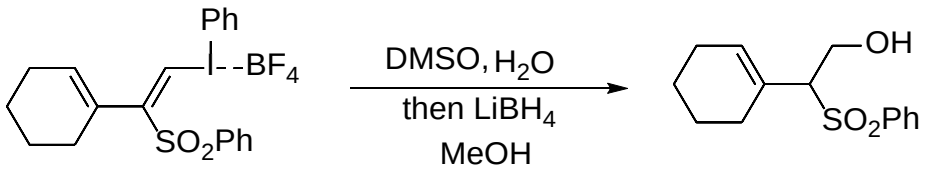
Having studied the effect of treatment of alkenyl(phenyl)iodonium salts with HCl in DMSO, it was decided to study the same effect in the case of dienyliodonium salts. Utilising our reported procedure, **210** was synthesised from **193a** by treatment with 2 M HCl in DMSO (Scheme 106). The product was obtained in excellent yield.

193a **210**, 91%

Scheme 106

3.9.13. 2-Oxidation of dienyl(phenyl)iodonium salt.

Similarly treatment with aqueous DMSO converted dienyl(phenyl)iodonium salt into the corresponding aldehyde which was reduced to the alcohol in good overall yield (Scheme 107)



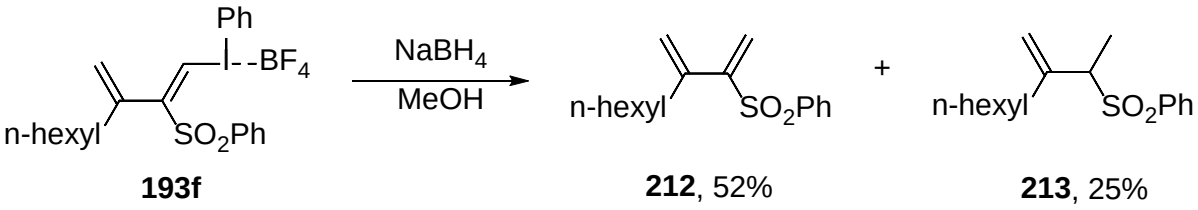
193b **211**, 66%

Scheme 107

3.9.14. Reduction of dienyl(phenyl)iodonium salt.

Reduction of dienyl(phenyl)iodonium salt with $NaBH_4$ provided direct access to diene **212** in moderate yield. The remainder of the mass balance was over-reduced products such as **213**

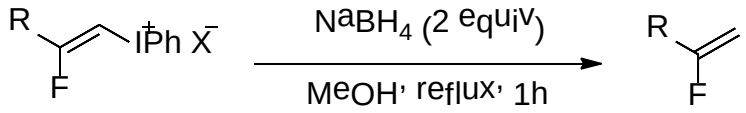
which was obtained in 25% yield (Scheme 108).[52] Presumably, the presence of the sulfone group makes over-reaction likely. No attempt to optimise this process was undertaken.



193f **212**, 52% **213**, 25%

Scheme 108

Nguyen and co-workers reported that this reaction proceeds by an S_N2 mechanism.[52] They carried out the reaction between alkenyliodonium salts and $NaBH_4$ in refluxing methanol for one hour. The products were obtained in moderates to excellent yields (Scheme 109)



R = Cyclohexyl-CH_2, X = BF_4 51%
R = $C_{10}H_{21}$, X = BF_4 86%
R = Ph, X = BF_4 61%
R = $PhCH_2CH_2$, X = BF_4 87%
R = Ph, X = OTs 67%

Scheme 109

4. Conclusions

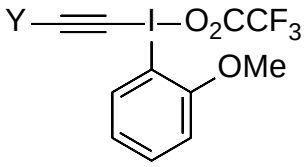
As was anticipated at the start of this project, it was found that alkynyl(aryl)iodonium salts with an alkoxy group (OR) or a nitrogen (NR_2) alkyne substituent were unstable. A possible reason for this is the electron-donating group of oxygen and nitrogen atoms. On the other hand, alkynyl(aryl)iodonium salts with a silicon (SiR_3) substituent was isolated and tested with a 1,2-shift reaction which lead to alkynyliodonium as aresult. Same compound was obtained in excellent yield by stereoselective Michael-type addition of phenylsulfinic acid.

The preparation of alkynyl(phenyl)iodonium trifluoroacetates has been demonstrated. These compounds were converted in to alkenyl(phenyl)iodonium tetrafluoroborates which were solvolysed in aqueous DMSO leading to selective aldehyde formation. In addition, the vinyl chloride formation was effected by addition of aqueous HCl to the DMSO solution.

The preparation of stable enynyliodonium salts has been achieved through a direct method from terminal alkynes. Moreover, dienyliodonium salts have been prepared and their reactivity and structural peculiarities investigated by a range of processes. In the literature, no previous studies were found regarding these compounds, therefore the published results from this work could shed further light upon and attract the attention to this interesting area of iodonium salt studies.[87]

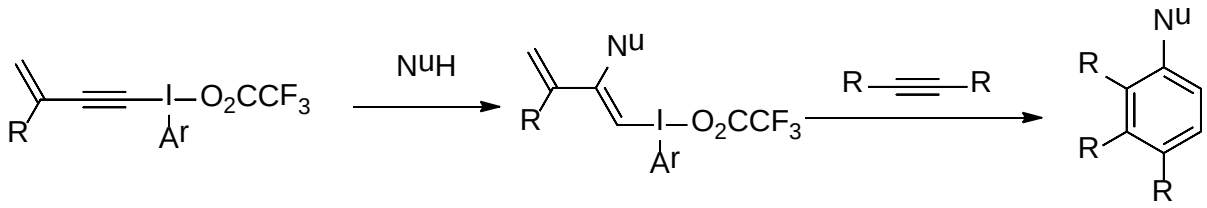
5. Future work

The future work will focus to improving this area by attempting to prepare iodonium salts with trifluoroacetate conterion and studying their reactivity and stability.



Y = OR, NR_2' Ph

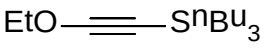
The dienyliodonium salts could be utilised in Diels-Alder reactions to prepare substituted benzene rings:



6. Experimental part

General. ^{1}H NMR spectra were recorded at 400 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm) and (DMSO-d^6: 2.52 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: 77.4 ppm) and (DMSO-d^6: 40.8 ppm). Mass spectrometry (m/z) was performed in ESI mode, with only molecular ions being reported. Infrared (IR) spectra νmax are reported in cm^{-1}. Bands are characterised as broad (br), strong (s), medium (m) and weak (w). A half of grade sizes of silica gel were used in column chromatography (35-75 μm, 63-200 μm).

Tributyl(ethoxyethynyl)stannane, 151:



According to the procedure reported by DeCicco and co-workers, to stirred solution of ethoxyacetylene (0.4 g, 30 mmol) in THF (20 mL) at -78 ºC under a N_2 atmosphere was added *n*-butyllithium (2.4 mL, 60 mmol). After 30 min Bu_3SnCl (3.2 mL, 60 mmol) was added. The reaction was stirred at room temperature overnight. Saturated NH_4Cl solution (50 mL) was added to the reaction mixture, which was extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with water (15 mL), dried over magnesium sulfate, filtered and concentrated in vacuo, giving the product as a yellow oil (0.4 g, 45%) a viscous brown oil (0.6 g, 30%).[71,73]

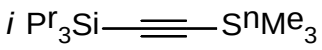
IR $_{(neat)}$: 2560 (w), 1190 (m), 980 (s), 660 (m), 546 (s).

^{1}H NMR: δ 0.94 (9H, t, *J* = 7.9 Hz), 1.10 (2H, t, *J* = 7.1 Hz), 1.33-1.40 (6H, m), 1.58-1.63 (12H, m), 3.60 (2H,q, *J* = 6.2 Hz).

^{13}C NMR: δ 10.8 (3C), 18.3 (6C), 100.5, 101.0, 127.2 (2C), 129.3 (2C), 134.1, 142.1.

HRMS: *m*/*z* calc'd for $[M]^+$ $C_{16}H_{32}OSn^+$ 360.1457 found 360.1458

Ethynyltriisopropylsilane, 163:



Synthesised according to the representative procedure for formation of **151** using (triisopropylsily)acetylene (500 mg, 27 mmol) instead of ethoxyaceylene and Me_3SnCl (2.97 mL, 30 mmol) instead of Bu3SnCl.was added (0.4 g, 45%).[73]

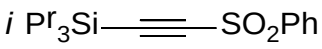
IR $_{(neat):}$ 2870 (w), 2100 (m), 1695 (s), 1150 (s), 760 (m).

^{1}H NMR: δ 0.71 (9H, s), 0.96 (18H, d, *J* = 8.4 Hz), 1.44-1.50 (3H, m).

^{13}C NMR: δ 11.5 (3C), 19.0 (9C), 114.0, 115.5.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{14}H_{31}SiSn^+$ 347.1139 found 347.1141

(Phenylsulfonyl)ethynyltripropylsilane, 165:



According to the procedure reported by Liu and Chen, to a stirred solution of *m*-xylyl(cyano)iodonium triflate (0.230 g, 61 mmol) in CH_2Cl_2 (2 mL) at -30 ^{o}C was added ethynyltriisopropylsilane (0.2 g, 61 mmol) after 30 min. Benzenesulfinic acid sodium salt (0.1 g, 67 mmol) was then added and the reaction mixture was stirred overnight. The reaction was quenched by addition of distilled water (2 mL) stirred for 1 h then extracted with DCM (2 x 5m L). The combined organic layers were washed with water (10 mL), dried over

magnesium sulfate, filtered and concentrated in vacuo yielding a viscous yellow oil (50 mg, 28%).[43]

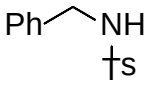
IR $_{(neat):}$ 2870 (w), 2100 (m), 1695 (s), 1150 (s), 760 (m).

^{1}H NMR: δ 0.91 (18H, m), 1.45 (3H, m), 7.59 (2H, t, *J* = 7.8 Hz), 7.68 (1H, t, *J* = 7.4 Hz), 8.03 (2H, d, *J* = 7.9 Hz).

^{13}C NMR: δ 10.8 (3C), 18.3 (6C), 100.5, 101.0, 127.2 (2C), 129.3 (2C), 134.1, 142.1.

HRMS: *m*/*z* calc'd for $[M]^{+}$ $C_{17}H_{26}O_2SSi^{+}$ 322.1423 found 322.1423

***N*-Benzyl-4-methylbenzenesulfonamide, 169:**



To stirred solution of benzylamine (3g, 30 mmol) in deionised water (20 mL), TsCl (6.8g, 36 mmol) was added. The reaction was stirred at room temperature overnight. The resulting mixture was extracted with ethylacetate, dried over $MgSO_4$ filtered and concentrated in vacuo yielding a white solid (2.7g, 37%).

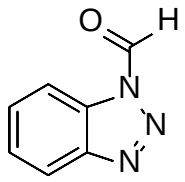
IR $_{(neat):}$ 3777 (w), 2987 (m), 1621 (w), 1245 (s), 688 (s).

^{1}H NMR: δ 2.44 (3H, s), 4.10 (2H, d, *J* = 6.4 Hz), 4.88 (1H, t, *J* = 6.3 Hz), 7.17-7.20 (2H, m), 7.23-7.30 (5H, m), 7.73-7.79 (2H, m).

^{13}C NMR: δ 21.7, 47.3, 127.1 (2C), 127.9 (2C), 128.0 (2C), 128.7 (2C), 129.8, 136.3, 136.8, 143.7.

HRMS: *m*/*z* calc'd for $[M]^{+}$ $C_{14}H_{15}NO_2S^{+}$ 261.0823 found 261.0824

***N*-Formylbenzotriazole (BtCHO), 172:**[74]



Following the procedure reported by Clavier and co-workers to mixture of benzotriazole (2.4 g, 20 mmol) and formic acid (0.9 mL, 24 mmol) in CH_2Cl_2 (40 mL) was added 1.3-dicyclohexylcarbodiimide (DIC) (5.8 g, 28 mmol). Then the mixture was stirred at room temperature overnight. The precipitate was filtered and the solvent removed in vacuo. The product was isolated as white needles (1.8 g, 80%).

Melting point: 95-96 ºC.

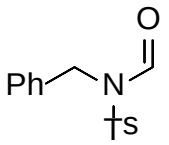
IR $_{(neat):}$ 3109 (m), 1729 (w), 1610 (m), 1596 (s), 588 (s).

^{1}H: δ 7.57 (1 H, ddd, *J* = 8.3, 7.2, 1.1 Hz), 7.70 (1 H, ddd, *J* = 8.2, 7.2, 1.0 Hz), 8.14 (1 H, t, *J* = 8.3, 1.0 Hz), 8.24 (1 H, d, *J* = 8.3 Hz), 9.87 (1H, s).

^{13}C: δ 113.7, 120.2, 127.1, 130.0, 130.7, 146.6, 160.0.

HRMS: *m*/*z* calc'd for $[M]^+$ $C_7H_5N_3O^+$ 147.0433, found 147.0434.

***N*-Formyl-*N*-phenyl-4-methyl-benzenesulfonamide, 173:**



Following the procedure reported by Bruckner, a solution of benzyl-4-methyl benzenesulfonamide **172** (1.3 g, 4.9 mmol) in THF (10 mL) at 0 °C was treated with *n*-BuLi (0.2 mL, 1.1 mmol). After five minute, a solution of formylbenzotriazole (1 g, 6.2 mmol) in

THF (12 mL) was added and the mixture stirred for two housr at room temperature.[75] Dilution with *tert*-butyl methyl ether (600 mL) and work up with saturated $NaHCO_3$ (60 mL)and the product was isolated as a white solid (0.4 g, 30%).

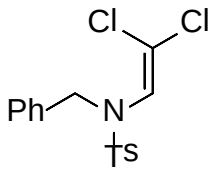
Melting point: 118-120 ºC.

IR $_{(neat):}$ 3604 (w), 2111 (m), 1567 (m), 1230 (s), 651 (m).

^{1}H NMR: δ 2.43 (3H, s), 4.46 (2H, s), 7.11-7.18 (2H, m), 7.24-7.41 (5H, m), 7.52-7.59 (2H, m), 9.29 (1H, s).

^{13}C NMR: δ 21.2, 47.3, 128.1 (2C), 127.9 (2C), 128.0 (2C), 128.7 (2C), 129.8, 134.3, 136.8, 143.7, 160.4.

***N*-Benzyl-*N*-(2,2-dichlorovinyl)-4-methylbenzenesulfonamide, 174:**



Following the procedure reported by Bruckne, [75] formamide **173** (344 mg, 1.42 mmol) and PPh_3 (995 mg, 4.26 mmol) were dissolved in THF (14 mL). CCl4 (1 mg, 7.1 mmol) was added at 60 °C. After stirring for one hour the mixture was diluted with methyl *tert*-butyl ether (TBME) (20 mL) and extracted with saturated $NaHCO_3$ solution (30 mL). The residue was purified by flash chromatography (5:1 petroleum ether/EtOAc) which furnished a white solid (176 mg, 35%).

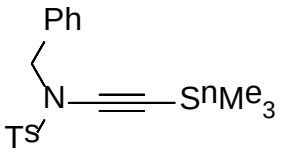
Melting point: 114-115 ºC.

IR $_{(neat):}$ 3700 (w), 2341 (w), 1742 (s), 1216 (m), 851 (s).

^{1}H NMR: δ 2.42 (3H, s), 4.43 (2H, s), 6.95 (1H, s), 7.05-7.19 (2H, m), 7.27-7.38 (5H, m), 7.40-7.48 (2H, m).

^{13}C NMR: δ δ 21.2, 54.3, 109.0, 128.1 (2C), 127.9 (2C), 128.0 (2C), 128.7 (2C), 129.8, 130.0, 134.3, 136.8, 143.7.

_N_-Benzyl-4-methyl-_N_-((trimethylstannyl)ethynyl)benzenesulfonamide, 175:



Prepared according to the representative procedure for **151** using *N*-benzyl-*N*-(2,2-dichlorovinyl)-4-methylbenzenesulfonamide (150 mg, 42 mmol), instead of ethoxyacetylene and the product isolated as a viscous dark brown oil. The product was impure and instable was taken forward for next step.

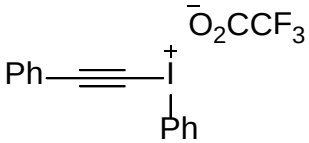
IR $_{(neat):}$ 3180 (w), 2960 (w), 1595 (s), 1490(s), 755 (s).

^{1}H NMR: δ 0.05 (9H, s), 2.44 (3H, s), 4.53 (2H, s), 7.28-7.41 (7H, m), 7.87 (2H, d, *J* = 8.4 Hz).

^{13}C NMR: δ -0.5 (3C), 22.0, 43.1, 92.2, 97.3, 127.9 (2C), 128.3 (2C), 128.4 (2C), 129.0, 129.7 (2C), 134.4, 134.7, 144.

HRMS: *m*/*z* calc'd for $[M]^{+}$ $C_{19}H_{23}NO_2SSn^{+}$ 449.0471 found 449.0476

Phenyl (phenylethynyl)iodonium 2,2,2-trifluoroacetate, 179a:[38,76]



Following the procedure reported by Carrol and co-workers, to a stirred solution of diacetoxyiodobenzene (3g, 9.3 mmol) in CH_2Cl_2 (60 mL) at -30 ^oC was added trifluoroacetic acid (1.4 ml, 19 mmol, 2 equiv) dropwise. The mixture was stirred for 30 min then was warmed to room temperature and stirred for a further hour. Phenylacetylene (1 mL, 9.3 mmol, 1 equiv) was added and the resulting mixture was stirred in darkness at room temperature for 3.5 h. The solution concentrated in vacuo to around 30 mL then diethyl ether (20 mL) was added and petroleum ether (40 mL) which initiated crystallisation of the product. After being placed in the freezer (-20 ^oC) for 48 h. The product was filtered and dried in vacuum to provide a white crystalline solid (3.7 g, 95%).

Melting point: 89-91 ^oC.

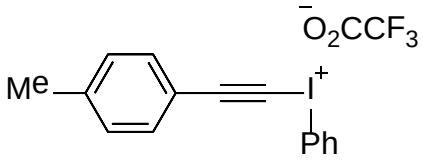
IR $_{(neat):}$ 3075 (w), 2168 (m), 1377 (s), 1187 (w), 1120 (s)

^1H NMR: δ 7.36 (2H, t, *J* = 7.5 Hz), 7.42 (1H, t, *J* = 7.5 Hz), 7.45-7.52 (4H, m), 7.59 (1H, t, *J* = 7.4 Hz) 8.16 (2H, d, *J* = 8.1 Hz).

^{13}C NMR: δ 45.6, 104.1, 116.0 (1C, q, *J* = 293 Hz), 120.7, 120.9, 128.9 (2C), 131.0, 132.1, 132.3 (2C), 133.1 (2C), 133.8 (2C), 162.8 (1C, q, *J* = 36 Hz).

HRMS: *m*/*z* calc'd for $[M\text{-}O_2CCF_3]^+$ $C_{14}H_{10}I^+$ 304.9822 found 304.9827.

Phenyl (p-tolylethynyl)-λ^3-iodanyl 2, 2, 2-trifluoroacetate, 179b:[76]



Prepared according to the representative procedure using 4-ethynyltoluene (1.1 ml, 9.3 aquiv), instead of phenylacetylene giving the product as a white crystalline solid (4 g, 98%).

Melting point: 80-81 ºC.

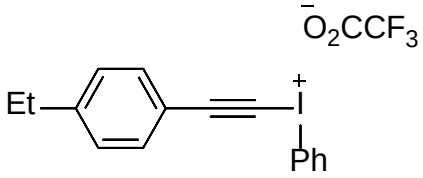
IR $_{(neat):}$ 1661 (w), 1422 (m), 1310 (s), 1013 (w), 721 (s)

^{1}H NMR: δ 2.38 (3H, s), 7.17 (2H, d, *J* = 7.7 Hz), 7.37 (2H, d, *J* = 7.7 Hz), 7.49 (2H, t, *J* = 7.8 Hz), 7.60 (1H, t, *J* = 7.4 Hz) 8.16 (2H, d, *J* =8.2 Hz).

^{13}C NMR: δ 22.1, 44.9, 105.0, 115.0 (1C, q, *J* = 296 Hz), 117.6, 121.1, 129.8 (2C), 132.2, 132.4 (2C), 133.1 (2C), 133.7 (2C), 141.9, 162.9 (1C, q, *J* = 36 Hz).

HRMS: *m*/*z* calc'd for [M- O_2CCF_3] $^{+}$ $C_{15}H_{12}I^{+}$ 318.9980 found 318.9985.

[((4-Ethylphenyl)]ethynyl)(phenyl)iodonium 2,2,2-trifluoroacetate, 179c:



Prepared according to the representative procedure using 1-ethyl-4-ethynyl benzene (1.3 mL, 9.3 equiv), instead of phenylacetylene giving the product as a white crystalline solid (3.8 g, 93%).

Melting point: 81-83 ºC.

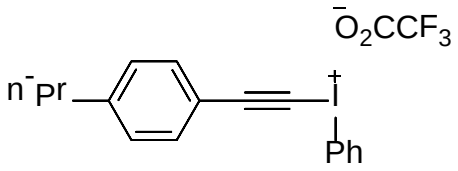
IR $_{(neat):}$ 1656 (s), 1417 (m), 1124 (s), 989 (m), 720 (s)

^{1}H NMR: δ 1.22 (3H, t, *J* = 7.7 Hz), 2.67 (2H, q, *J* = 7.6 Hz), 7.20 (2H, d, *J* = 8.1 Hz), 7.39 (2H, d, *J* = 8.1 Hz), 7.49 (2H, t, *J* = 7.9 Hz), 7.60 (1H, t, *J* = 7.5 Hz) 8.15 (2H, d, *J* = 8.0 Hz).

^{13}C NMR: δ 15.5, 29.3, 44.8, 105.0, 115.8 (1C, q, *J* = 292), 114.4, 117.3, 117.7, 121.1, 128.6 (2C), 132.2, 132.4 (2C), 133.3 (2C), 133.7 (2C), 148.1, 162.9 (1C, q, *J* = 38).

HRMS: *m*/*z* calc'd for [M- O_2CCF_3] $^{+}$ $C_{18}H_{18}I^{+}$ 333.0135 found 333.0140.

[((4-butylphenyl)ethynyl)](phenyl)iodonium 2,2,2-trifluoroacetate, 170d:



Prepared according to the representative procedure using 1-butyl-4-ethynylbenzene (1.6 ml, 9.3 aquiv), instead of phenylacetylene giving the product as a white crystalline solid (3.7 g, 84%).

Melting point: 83-85 ºC.

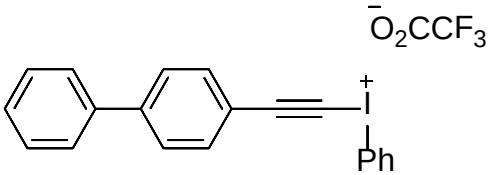
IR: 1665 (s), 1417 (m), 1183 (s), 991.2 (m), 721 (s) cm^{-1}.

^{1}H NMR: δ 0.91 (3H, t, *J* = 7.3 Hz), 1.33 (2H, hex, *J* = 7.3 Hz), 1.57 (2H, pen, *J* = 7.7 Hz), 2.63 (2H, t, *J* = 7.6 Hz), 7.18 (2H, d, *J* = 7.9 Hz), 7.39 (2H, d, *J* = 7.9 Hz), 7.50 (2H, t, *J* = 7.9Hz), 7.60 (1H, t, *J* = 7.4 Hz), 8.16 (2H, d, *J* = 8.4 Hz).

^{13}C NMR: δ 14.2, 22.6, 33.6, 36.0, 44.9, 105.0, 115.7 (1C, q, *J* = 291 Hz), 117.7, 121.0, 129.1 (2C), 132.1 (2C), 132.1 (2C), 132.4, 133.1 (2C), 133.6 (2C), 146.8, 162.9 (1C, q, *J* = 38 Hz).

HRMS: *m*/*z* calc'd for $[M- OCOCF_3]^+$ $C_{16}H_{14}I^+$ 361.448 found 361.01463.

([1,1'-Biphenyl]-4-ylethynyl)(phenyl)iodonium 2,2,2-trifluoroacetate, 179e:

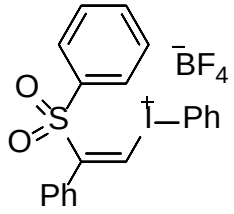


Prepared according to the representative procedure using 4-ethynyl-1,1'-biphenyl (1.6 ml, 9.3 aquiv), instead of phenylacetylene giving the product as a white crystalline solid (3.7 g, 84%). This compound is unstable and complete characterization could not be obtained.

^{1}H NMR: δ (2H, d, *J* = 6.9 Hz), 7.33-7.61 (5H, m), 7.62-7.89 (5H, m), 8.17 (2H, d, *J* = 7.7 Hz).

HRMS: m/z calc'd for $[M\text{-}OCOCF_3]^+$ $C_{20}H_{14}I^+$ 381.0135 found 381.0132

***(Z)*-Phenyl (2-phenyl-2-(phenylsulfonyl)vinyl)iodonium tetrafluoroborate, 180a:**[49,76]



Following the procedure reported by Ochiai and co-workers, Phenyl(phenylethynyl)iodonium trifluoroacetate, **179a** (0.50 g, 1.2 mmol, 1 equiv) dissolved in MeOH (5 mL) was added to a solution of phenylsulfinic acid (0.190 g, 1.3 mmol, 1.1 equiv) in MeOH (2 mL) at 0 ºC under N_2 atmosphere. The reaction mixture was stirred for 45 minutes then poured into saturated aqueous sodium tetrafluoroborate solution (5 mL). A white precipitate was formed which was filtered off and washed with CH_2Cl_2 (2 x 8 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was a clear, colourless, viscous oil. A 1:1 mixture of diethyl ether and petroleum ether (5 + 5 mL) was added to the residue, the mixture was swirled and the solvent removed by decantation. This was repeated until a white solid was formed. The crude solid product was recrystallised from the minimum amount of CH_2Cl_2 with slow addition of petroleum ether. (*Z*)-Phenyl(2-phenyl-2-(phenylsulfonyl)vinyl)iodonium tetrafluoroborate, **180a** was isolated as a white microcrystalline solid (0.47 g, 74%).

Melting point: 186-188 ºC.

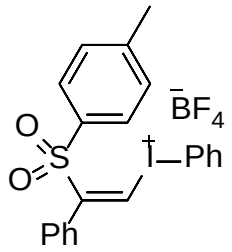
IR $_{(neat)}$: 1446 (m), 1304 (m), 1138 (m), 1059 (s), 623(s)

^{1}H NMR: δ 7.26 (2H, d, *J* = 7.6 Hz), 7.36 (2H, t, *J* = 7.4 Hz), 7.43 (1H, t, *J* = 7.5 Hz), 7.61-7.73 (4H, m), 7.78-7.88 (4H, m), 8.38(1H, s), 8.41 (2H, d, *J* = 7.8 Hz).

^{13}C NMR: δ 116.9, 117.6, 129.6 (2C), 129.9 (2C), 130.6 (2C), 131.2 (2C), 131.7, 131.8, 133.1 (2C), 134.1, 136.6, 137.0, 137.6 (2C), 146.7

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{20}H_{16}IO_2S^+$ 466.9910 found 446.9913.

***(Z)*-Phenyl(2-phenyl-2-tosylvinyl)iodonium tetrafluoroborate, 180b:**



Prepared according to the representative procedure using 4-methylbenzenesulfinic acid (1.1 aquiv) instead of phenylsulfinic acid and (phenylethynyl)iodonium trifluoroacetate, **179a** (0.5 g, 1 equiv) giving the product as a white solid (0.54 g, 83%).

Melting point: 125-127 ºC.

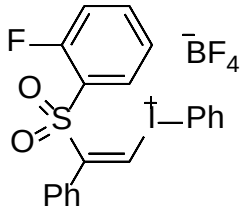
IR: 1535 (w), 1294 (m), 1135 (m), 1076 (s), 627 (s) cm^{-1}.

^{1}H NMR: δ 2.40 (3H, s), 7.28 (2H, d, *J* = 7.9 Hz), 7.36 (2H, t, *J* = 7.6 Hz), 7.40-7.49 (3H, m), 7.63-7.73 (4H, m), 7.82 (1H, t, *J* = 7.6 Hz), 8.33 (1H, s), 8.40 (2H, d, *J* = 7.9 Hz).

^{13}C NMR: δ 22.5, 116.9, 117.1, 129.7 (2C), 129.9 (2C), 130.5 (2C), 131.7 (2C), 131.8 (2C), 133.1 (2C), 133.7, 134.1 (2C), 137.6, 146.9, 148.1.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{21}H_{18}IO_2S^+$ 461.0067 found 461.0079.

***(Z)*- {(2-[(2-Fluorophenyl)sulfonyl]-2-phenylvinyl}(phenyl)iodonium tetrafluoroborate, 180c:**



Prepared according to the representative procedure using 2-fluorobenzenesulfinic acid (1.1 aquiv) instead of phenyl sulfinic acid and (phenylethynyl)iodonium trifluoroacetate, **179a** (0.43 g, 1 aquiv) giving the product as a white solid (0.37 g, 68%).

Melting point: 186-188 ºC.

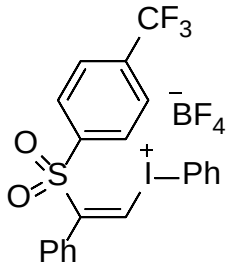
IR: 1597 (w), 1474 (m), 1317 (m), 1022 (m), 522 (s) cm^{-1}.

^1H NMR: δ 7.29-7.38 (4H, m), 7.40-7.46 (2H, t, m), 7.59 (1H, t, *J* = 9.6 Hz), 7.67 (2H, t, *J* = 7.8 Hz), 7.74-7.93(3H, m), 8.40 (2H, d, *J* = 7.8 Hz), 8.55 (1H, s).

^{13}C NMR: δ 116.9, 118.4, 119.1 (1C, d, *J* = 20 Hz), 124.4 (1C, d, *J* = 13 Hz), 127.2, 130.1 (2C), 130.4 (2C), 131.3, 132.1 (1C, d, *J* = 5.4 Hz), 133.2 (2C), 134.2, 137.7 (2C), 140.5 (1C, d, *J* = 9.8 Hz), 146.6, 162.0 (1C, d, *J* = 256 Hz).

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{20}H_{15}FIO_2S^+$ 464.9816 found 464.9826.

***(Z)*-Phenyl (2-phenyl-2-[(4-(trifluoromethyl) phenyl]sulfonyl)vinyl)iodonium tetrafluoroborate, 180d:**



Prepared according to the representative procedure using 4-(trifluoromethyl) benzenesulfinic acid (1.1 aquiv) instead of phenyl sulfinic acid and (phenylethynyl)iodonium trifluoroacetate, **179a** (0.5 g, 1 aquiv) giving the product as a white solid (0.51 g, 71%).

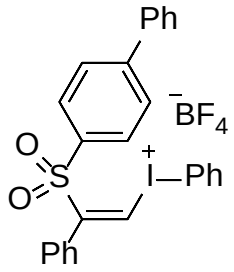
Melting point: 184-186 ºC.

IR: 1317 (s), 1129 (s), 1117 (m), 1059 (s), 641 (s) cm-1. ^{1}H NMR: δ 7.29 (2H, d, J = 7.8 Hz), 7.38 (2H, t, J = 7.6 Hz), 7.46 (1H, t, J = 7.6 Hz), 7.68 (2H, t, J = 7.8 Hz), 7.82 (1H, t, J = 7.4 Hz), 8.1 (4H, S), 8.39 (2H, d, J = 8.6 Hz), 8.50 (1H, s).

^{13}C NMR: 117.1, 119.2, 124.3 (1C, q, J = 274.2 Hz), 128.3 (1C, d, J = 3.3 Hz), 130.1 (2C), 130.7 (2C), 130.8 (2C), 131.3. 131.9, 133.0 (2C), 134.3 (2C), 136.1 (1C, q, J = 33 Hz), 137.6 (2C), 140.6, 145.8.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{21}H_{15}F_3IO_2S^+$ 514.9784 found 514.9807

***(Z)*- (2-([1, 1'-Biphenyl]-4-ylsulfonyl)-2-phenylvinyl) (phenyl)iodonium tetrafluoroborate, 180e:**



Prepared according to the representative procedure using 1, 1'-biphenyl]-4-sulfinic acid (1.1 aquiv) instead of phenyl sulfinic acid and (phenylethynyl)iodonium trifluoroacetate, **179a** (0.2g, 1 aquiv) giving the product as a white solid (0.29 g, 98%).

Melting point: 162-164 ºC.

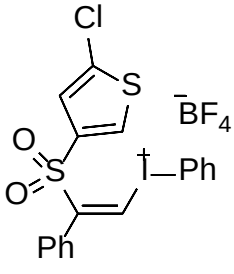
IR: 1596 (w), 1484 (m), 1289 (m), 1050 (m), 674 (s) cm^{-1}.

^{1}H NMR: δ 7.33 (2H, d, *J* = 7.2 Hz), 7.38 (2H, t, *J* = 7.5 Hz), 7.42-7.58 (4H, m), 7.67 (2H, t, *J* = 7.9 Hz), 7.77 (2H, d, *J* = 7.8 Hz), 7.82 (1H, t, *J* = 7.5 Hz), 7.88 (2H, d, *J* = 8.2 Hz), 7.96 (2H, d, *J* = 8.5 Hz), 8.39 (1H, s), 8.41(2H, d, *J* = 7.8 Hz).

^{13}C NMR: δ 116.9, 117.7, 128.6 (2C), 129.1 (2C), 130.0 (2C), 130.4 (2C), 130.5 (2C), 130.6 (2C), 131.8 (2C), 131.9, 133.1, 134.1(2C), 135.3, 137.6(2C), 138.7, 146.7, 148.1.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{26}H_{20}IO_2S^+$ 523.0223 found 523.0236.

***(Z)*- (2-((5-Chlorothiophen-2-yl) sulfonyl)-2-phenylvinyl) (phenyl)iodonium tetrafluoroborate, 190f:**



Prepared according to the representative procedure using 5-chlorothiophene-2-sulfinic acid (1.1 aquiv) instead of phenyl sulfinic acid and (phenylethynyl)iodonium trifluoroacetate, **179a** (0.4 g, 1 aquiv) giving the product as a white solid (0.32 g, 59%).

Melting point: 187-189 ºC.

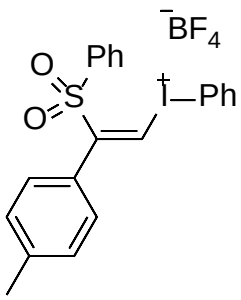
IR: 1399 (w), 1310 (w), 639 (s), 628 (m), 523 (m) cm^{-1}.

^{1}H NMR: δ 7.35 (2H, d, *J* = 7.6 Hz), 7.39-7.46 (3H, m), 7.51 (1H, t, *J* = 7.4 Hz), 7.65 (2H, t, *J* = 7.8 Hz), 7.73-7.83 (2H, m), 8.36 (3H, d, *J* = 9.4 Hz).

^{13}C NMR: 116.9, 117.2, 130.2 (2C), 130.9 (2C), 131.6, 131.9, 132.2, 133.2 (2C), 134.2, 134.6, 137.6 (2C), 139.0, 142.4, 147.3.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{18}H_{13}ClIO_2S_2^+$ 486.9085 found 486.9091.

***(Z)*-Phenyl (2-(phenylsulfonyl)-2-(p-tolyl)vinyl)iodonium, 180g:**



Prepared according to the representative procedure using (p-tolylethynyl)-l3-iodanyl 2, 2, 2-trifluoroacetate, **179b** (0.5 g) instead of Phenyl(phenylethynyl)iodonium giving the product as a white solid (0.47 g, 74%).

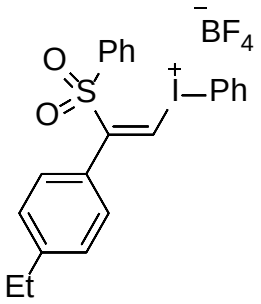
Melting point: 125-127 ºC.

IR: 1535 (m), 1303 (m), 1136 (m), 1059 (s), 651 (s) cm^{-1}. ^{1}H NMR: δ 2.26 (3H, s), 7.17 (4H, t, *J* = 6.9 Hz), 7.61-7.72 (4H, m), 7.77-7.89 (4H, m), 8.29 (1H, S), 8.39 (2H, d, *J* = 7.8 Hz).

^{13}C NMR: δ 22.07, 116.9, 128.9, 129.6 (2C), 130.4 (2C), 130.5 (2C), 131.2 (2C), 133.1(2C), 134.1, 136.8 (3C), 136.9, 137.6, 141.8, 146.7.

HRMS: *m/z* calc'd for $[M\text{-}BF_4]^+$ $C_{21}H_{18}IO_2S^+$ 461.0067 found 461.0082.

***(Z)*- (2-(4-Ethylphenyl)-2-(phenylsulfonyl)vinyl)(phenyl)iodonium, 180h:**



Prepared according to the representative procedure using ((4-ethylphenyl) ethynyl) (phenyl)-l3-iodanyl 2, 2, 2-trifluoroacetate, **179c** (0.5 g) instead of Phenyl (phenylethynyl)iodonium giving the product as a white solid (0.61 g, 96%).

Melting point: 122-124 ºC.

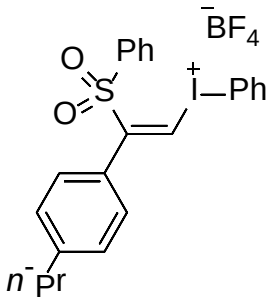
IR: 1526 (m), 1299 (m), 1134 (m), 1060 (s), 620 (s) cm^{-1}.

^{1}H NMR: δ 1.10 (3H, t, *J* = 7.5 Hz), 2.56 (2H, q, *J* = 7.8 Hz), 7.20 (4H, s), 7.67 (4H, t, *J* = 7.6 Hz), 7.85-7.97 (4H, m), 8.31 (1H, S), 8.39 (2H, d, *J* = 3.8 Hz).

^{13}C NMR: δ 16.4, 29.1, 116.9, 117.0, 129.1, 129.3 (2C), 129.5 (2C), 130.5 (2C), 131.2 (2C), 133.1 (2C), 134.1, 136.7, 136.9, 137.6 (2C), 146.7, 147.9.

HRMS: *m/z* calc'd for $[M\text{-}BF_4]^+$ $C_{22}H_{20}IO_2S^+$ 475.0223 found 475.0247.

***(Z)*-(2-(4-Butylphenyl)-2-(phenylsulfonyl)vinyl)(phenyl)iodonium tetrafluoroborate, 180i:**



Prepared according to the representative procedure using ((4-butylphenyl)ethynyl)(phenyl)-l3-iodanyl 2,2,2-trifluoroacetate, **179d** (0.5 g) instead of Phenyl(phenylethynyl)iodonium giving the product as a white solid (0.49 g, 78%).

Melting point: 120-122 ºC.

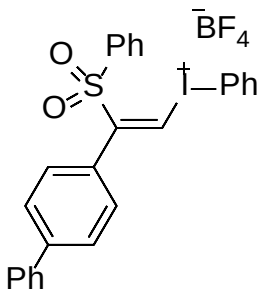
IR: 1526 (m), 1293 (m), 1130 (s), 1048 (s), 569 (s) cm^{-1}.

^{1}H NMR: δ 0.84 (3H, t, *J* = 7.5 Hz), 1.21 (2H, hex, *J* = 7.5 Hz), 1.77 (2H, pen, *J* = 7.5 Hz), 2.49-2.55 (2H, m), 7.18 (4H, s), 7.66 (4H, q, *J* = 7.2 Hz), 7.81 (4H, t, *J* = 8.6 Hz) 8.31 (1H, S), 8.39 (2H, d, *J* = 3.9 Hz).

^{13}C NMR: δ 14.9, 22.7, 33.9, 35.6, 116.8, 116.9, 129.01, 129.5, 129.8 (2C), 130.4 (2C), 131.1 (2C), 133.03 (2C), 134.1, 136.7 (2C), 136.9, 137.6 (2C), 146.5, 146.7.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{24}H_{24}IO_2S^+$ 503.0536 found 503.0549.

***(Z)-(*2-([1,1'-Biphenyl]-4-yl)-2-(phenylsulfonyl)vinyl)(phenyl)iodonium, 180j:**



Prepared according to the representative procedure using ([1, 1'-biphenyl]-4-ylethynyl)(phenyl)-l3-iodanyl 2,2,2-trifluoroacetate, **179e** (0.5 g) instead of Phenyl(phenylethynyl)iodonium trifluoroacetate giving the product as a white solid (0.55 g, 91%).

Melting point: 164-166 ºC.

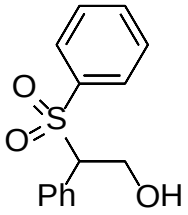
IR: 1501 (w), 1310 (m), 1132 (m), 1073 (m), 533 (s) cm^{-1}.

^{1}H NMR: δ 7.40 (3H, t, *J* = 8.5 Hz), 7.47 (2H, t, *J* = 7.6 Hz), 7.62-7.73 (8H, m), 7.83 (2H, t, *J* = 7.2 Hz), 7.80 (2H, d, *J* = 7.8 Hz), 8.41 (3H, t, *J* = 7.3 Hz).

^{13}C NMR: δ 117.0, 117.8, 127.9 (2C), 128.0 (2C), 129.5, 129.6 (2C), 130.3 (2C), 130.7, 131.13 (2C), 131.3 (2C), 131.9, 133.1 (2C), 134.1, 136.8, 137.1, 137.6, 139.7, 143.2, 146.3.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{26}H_{20}IO_2S^+$ 523.0223 found 523.0207.

2-Phenyl-2-(phenylsulfonyl) ethan-1-ol, 182a:[85]



(Z)-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl) iodonium tetrafluoroborate , **180a** (50 mg, 0.094 mmol, 1 equiv) was dissolved in DMSO (0.5 mL) at room temperature. Deionized water (20 µL) was added and the mixture was stirred overnight. Water (2.5 mL) was added to the mixture and the solution was shaken. This was extracted with ethyl acetate (5 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum. The product was used in next step as dissolved in methanol (2 ml), $LiBH_4$ (2 mg, 0.094 mmol, 1 equiv) was added in one portion and the the mixture was stirred overnight. The resulting was extracted with diethyl ether (5 mL) and washed with water (5 mL). The residue was purified by flash chromatography (5:1 petrolem ether/EtOAc) which furnished a colorless oil (0.015 g, 61%).[76]

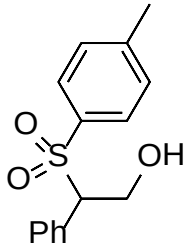
IR $_{(neat):}$ 3521 (w), 2428 (s), 1235 (m), 567 (w) cm^{-1}.

^{1}H NMR: δ 2.77 (OH, dd, *J* = 7.8, 4.8 Hz), 4.16 (1H, ddd, *J* = 13, 8.7, 4.5 Hz), 4.38 (1H, dd, *J* = 7.9, 4.7 Hz), 4.66 (1H, ddd, *J* = 12, 7.9, 4.5 Hz), 7.06 (2H, d, *J* = 7.4 Hz), 7.22-7.30 (3H, m), 7.34 (1H, t, *J* = 7.4 Hz), 7.59-7.70 (4H, m).

^{13}C NMR: δ 61.5, 73.3, 126.1, 126.2, 129.2 (2C), 129.8 (2C), 129.9 (2C), 130.0 (2C), 130.6, 140.7.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{14}H_{15}O_3S^+$ 263.0736 found 263.0701.

2-Phenyl-2-tosylethan-1-ol, 182b:



Prepared according to the representative procedure using *(Z)*-phenyl (2-phenyl-2-tosylvinyl)iodonium tetrafluoroborate, **180b** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate **180a** giving the product as a colorless oil (0.024 g, 68%).

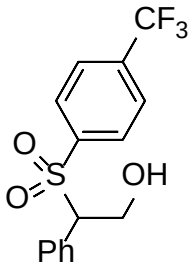
IR $_{(neat)}$: 3521 (w), 2428 (s), 1235 (m), 567 (w) cm^{-1}.

^{1}H NMR: δ 2.40 (3H, s), 2.99 (OH, br), 4.08 (1H, ddd, *J* = 13, 7.8, 4.9 Hz), 4.33 (1H, dd, *J* = 8.2, 4.5 Hz), 4.61 (1H, t, *J* = 10 Hz), 7.03 (2H, d, *J* = 7.9 Hz), 7.19 (2H, d, *J* = 7.4 Hz), 7.21-7.27 (2H, m), 7.38 (2H, d, *J* = 8.2 Hz).

^{13}C NMR: δ 21.9, 61.7, 73.0, 128.9 (2C), 129.3 (2C), 129.4 (2C), 129.7 (2C), 129.9 (2C), 131.3, 134.0, 145.4.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{15}H_{17}O_3S^+$ 277.0893 found 277.0876.

.**2-Phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-o, 182c:**



Prepared according to the representative procedure using *(Z)*-phenyl (2-phenyl-2-((4-(trifluoromethyl) phenyl)sulfonyl)vinyl)iodonium tetrafluoroborate, **180d** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.02 g, 61%).

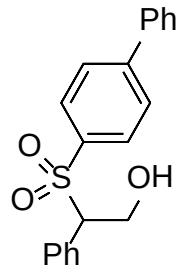
IR $_{(neat)}$: 2359 (w), 1319 (s), 1172 (s), 712 (m) cm^{-1}.

^{1}H NMR: δ 2.79 (OH, br), 4.16 (1H, d, *J* = 12 Hz), 4.38 (1H, dd, *J* = 7.9, 4.7 Hz), 4.66 (1H, dd, *J* = 12, 7.9 Hz), 7.06 (2H, d, *J* = 7.5 Hz), 7.27 (2H, t, *J* = 7.4), 7.34 (1H, t, *J* = 7.4 Hz), 7.61-7.70 (4H, m).

^{13}C NMR: δ61.4, 73.3, 123.4 (1C, q, *J* = 271.4 Hz), 126.2 (1C, d, *J* = 3.4 Hz), 129.2 (2C), 129.8 (2C), 129.9 (2C), 130.0 (2C), 130.6, 135.7, 136.0, 140.8.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{15}H_{17}F_3NO_3S^+$ 348.0876 found 348.0877.

2-([1,1'-Biphenyl]-4-ylsulfonyl)-2-phenylethan-1-ol, 182d:



Prepared according to the representative procedure using *(Z)* - (2-([1, 1'-biphenyl]-4-ylsulfonyl)-2-phenylvinyl) (phenyl)iodonium tetrafluoroborate, **180e** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.022 g, 63%).

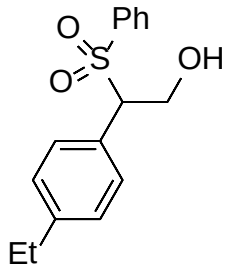
IR $_{(neat):}$ 3565 (w), 2359 (s), 2250 (m), 650 (w) cm^{-1}.

^{1}H NMR: δ 2.92-3.00 (OH, m), 4.10 (1H, m), 4.39 (1H, dd, *J* = 8.3, 4.8 Hz), 4.66 (1H, dd, *J* = 12, 8.2 Hz), 7.08 (1H, d, *J* = 7.5 Hz), 7.26 (4H, t, *J* = 7.2 Hz), 7.33 (1H, t, J = 7.2), 7.38-7.52 (3H, m), 7.53-7.65 (5H, m).

^{13}C NMR: δ 61.7, 73.2, 127.6 (2C), 127.7 (2C), 129.0 (2C), 129.1, 129.4 (2C), 129.6, 129.9 (2C), 130.0 (2C), 131.2, 135.5, 139.2, 147.2.

HRMS: m/z calcd. for $[M + H]^+$ $C_{20}H_{22}O_3S^+$ 356.1315 found 356.1322.

2-(4-Ethylphenyl)-2-(phenylsulfonyl)ethan-1-ol, 182e:



Prepared according to the representative procedure using *(Z)*-(2-(4-ethylphenyl)-2-(phenylsulfonyl) vinyl) (phenyl) iodonium, **180h** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.026 g, 67%).

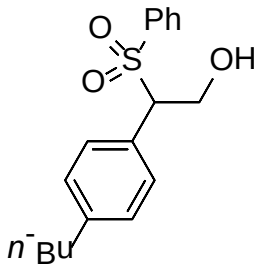
IR $_{(neat)}$: 2561 (s), 1345 (m), 1227 (m), 1162 (s), 767 (m) cm^{-1}.

^{1}H NMR: δ 1.19 (3H, t, *J* = 7.7), 2.61 (2H, q, *J* = 7.7), 2.91 (OH, dd, *J* = 9.0, 4.7 Hz), 4.09 (1H, ddd, *J* = 13, 9, 5 Hz), 4.33 (1H, dd, *J* = 8.2, 4.3 Hz), 4.59 (1H, ddd, *J* = 12, 8.0, 4.0 Hz), 6.94 (2H, d, *J* = 8.1 Hz), 7.07 (2H, d, *J* = 7.8), 7.41 (2H, t, *J* = 7.8), 7.53 (2H, d, *J* = 7.6 Hz), 7.59 (1H, t, *J* = 7.4 Hz).

^{13}C NMR: δ 15.8, 28.9, 61.7, 72.9, 128.2, 128.5 (2C), 129.1 (2C), 129.4 (2C), 129.8 (2C), 134.3 (2C), 137.1, 145.9.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{16}H_{18}NO_3S^+$ 308.1315 found 308.1318.

2-(4-Butylphenyl)-2-(phenylsulfonyl) ethan-1-ol, 182f:



Prepared according to the representative procedure using *(Z)*-(2-(4-butylphenyl)-2-(phenylsulfonyl) vinyl) (phenyl)iodonium tetrafluoroborate, **180j** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.026 g, 69%).

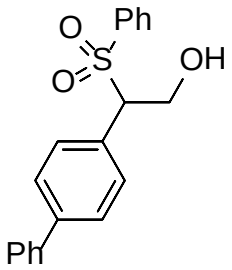
IR $_{(neat):}$ 2341 (s), 1446 (m), 1304 (m), 1142 (s), 687.6 (m) cm^{-1}.

^{1}H NMR: δ 0.91 (3H, t, *J* = 7.3 Hz), 1.24-1.35 (2H, m), 1.54 (2H, pent, *J* = 7.4 Hz), 2.56 (2H, t, *J* = 7.6 Hz), 2.99 (OH, br), 4.09 (1H, dd, *J* = 8.1, 4.4 Hz), 4.33 (1H, dd, *J* = 7.9, 4.6 Hz), 4.59 (1H, dd, *J* = 12, 8.1 Hz), 6.92 (2H, d, *J* = 7.9 Hz), 7.04 (2H, d, *J* = 7.4 Hz), 7.39 (2H, t, *J* = 7.8 Hz), 7.51 (2H, d, *J* = 3.8 Hz), 7.60 (1H, t, *J* = 7.4 Hz).

^{13}C NMR: δ 14.2, 22.5, 33.7, 35.6, 61.6, 72.8 128.1, 129.0 (3C), 128.9, 129.4, 130.4, 129.7, 134.2, 137.1, 144.5.

HRMS: *m/z* calc'd for $[M+NH_4]^+$ $C_{18}H_{26}NO_3S^+$ 336.1601 found 336.1630.

2-([1, 1-Biphenyl]-4-yl)-2-(phenylsulfonyl)ethan-1-ol, 182g :



Prepared according to the representative procedure using *(Z)-(*2-([1, 1'-biphenyl]-4-yl)-2-(phenylsulfonyl) vinyl) (phenyl) iodonium tetrafluoroborate, **180k** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.025 g, 65%).

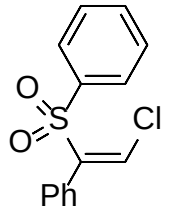
IR $_{(neat):}$ 3568 (w), 2358 (s), 2248 (m), 647 (w) cm^{-1}.

^{1}H NMR: δ 4.1-4.2 (1H, m), 4.40 (1H, dd, *J* = 8.1, 4.5 Hz), 4.65 (1H, dd, *J* = 12, 8.1 Hz), 7.11 (2H, d, *J* = 7.7 Hz), 7.37 (1H, t, *J* = 7.3 Hz), 7.40-7.51 (6H, m), 7.52-7.64 (5H, m).

^{13}C NMR: δ 61.6, 72.8, 127.4 (2C), 127.6 (2C), 128.2, 129.2 (2C), 129.3 (2C), 129.4 (2C), 130.1 (2C), 130.4, 134.4, 137.2, 140.4, 142.4.

HRMS: *m/z* calc'd for $[M+Na]^+$ $C_{20}H_{18}NaO_3S^+$ 361.0869 found 361.0869.

***(Z)*- (2-Chloro-1-(phenylsulfonyl)vinyl)benzene, 183a:**[76,86]



(Z)-Phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate,**180a** (0.050 g, mmol, equiv) was dissolved in DMSO (0.5 mL) at room temperature. HCl (2 N, 50 µL) was added and the mixture was stirred for 15 min. Brine (5 mL) was added to the mixture and the solution was shaken. This was extracted with ethyl acetate (10 mL) and washed with water (5 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by flash chromatography (20:1 petrolem ether/EtOAc) which furnished colorless oil (0.026 g, 80%).

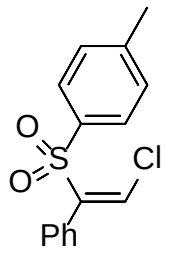
IR: 1586 (w), 1444 (m), 1320 (m), 1147 (s), 628 (s) cm^{-1}.

^{1}H NMR: δ 6.73 (1H, s), 7.26 (2H, d, *J* = 7.3 Hz), 7.34 (2H, t, *J* = 7.2 Hz), 7.41 (1H, t, *J* = 7.2 Hz), 7.49 (2H, t, *J* =7.8 Hz), 7.62 (1H, t, *J* = 7.4 Hz), 7.83 (2H, d, *J* = 7.6 Hz).

^{13}C NMR: δ 128.7 (2C), 128.8 (2C), 129.2, 129.4 (2C), 130.0, 130.5, 133.2 (2C), 134.2, 140.5, 145.6.

HRMS: m/z calc'd for $[M+H]^+$ $C_{14}H_{11}ClO_2S^+$ 279.0232 found 279.0241.

***(Z)*-1-[(2-Chloro-1-phenylvinyl)sulfonyl]-4-methylbenzene, 183b:**



Prepared according to the representative procedure using *(Z)*-phenyl (2-phenyl-2-tosylvinyl)iodonium tetrafluoroborate, **180b** (1 Equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.022 g, 84%).

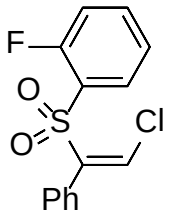
IR: 1578 (m), 1443 (m), 1146 (s), 1083 (m), 754 (s) cm^{-1}.

^{1}H NMR: δ 2.42 (3H, s), 6.69 (1H, s), 7.26 (4H, d, *J* = 16 Hz), 7.33 (2H, t, *J* =7.4 Hz), 7.35 (1H, t, *J* = 7.4 Hz), 7.70 (2H, d, *J* = 7.7 Hz).

^{13}C NMR: δ 22.7, 128.7 (2C), 128.8, 128.9 (2C), 129.9 (3C), 130.5, 133.3 (2C), 137.5, 145.2, 145.7.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{15}H_{14}ClO_2S^+$ 293.0388 found 293.0390.

***(Z)*-1-[(2-Chloro-1-phenylvinyl)sulfonyl]-2-fluorobenzene, 183c:**



Prepared according to the representative procedure using *(Z)*- (2-((2-Fluorophenyl) sulfonyl)-2-phenylvinyl) (phenyl) iodonium tetrafluoroborate, **180c** (1 equiv) instead of (*Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.023 g, 86%).

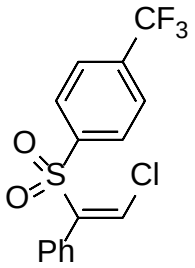
IR: 1599 (w), 1264 (m), 1146 (m), 1076 (s), 770 (m) cm^{-1}.

^{1}H NMR: δ 6.82 (1H, s), 7.16 (1H, t, *J* = 9.0 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 7.32-7.43 (5H, m), 7.56-7.65 (1H, m), 7.99 (1H, dd, *J* = 7.5, 1.6 Hz).

^{13}C NMR: δ 117.2 (1C, d, *J* = 20 Hz), 124.7 (1C, d, *J* = 3.8 Hz), 128.8 (2C), 129.4 (1C, d, *J* = 1.2 Hz), 130.1 (2C), 130.4 (1C, d, *J* = 1.2 Hz), 131.3, 132.5, 136 (1C, d, *J* = 8.5 Hz), 145.9, 160.0 (1C, d, *J* = 256 Hz).

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{14}H_{14}ClFNO_2S^+$ 314.0140 found 314.0140.

***(Z)*-1-[(2-Chloro-1-phenylvinyl) sulfonyl]-4-(trifluoromethyl) benzene, 183d:**



Prepared according to the representative procedure using *(Z)*-phenyl (2-phenyl-2-((4-(trifluoromethyl) phenyl) sulfonyl) vinyl) iodonium tetrafluoroborate, **180d** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.027 g, 93%).

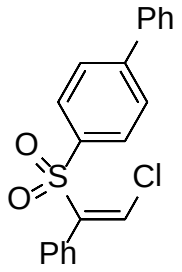
IR: 1591 (m), 1320 (s), 1125 (s), 1085 (s), 714 (m) cm^{-1}.

^{1}H NMR: δ 6.80 (1H, s), 7.27 (2H, d, *J* = 8.5 Hz), 7.33-7.47 (3H, m), 7.76 (2H, d, *J* = 7.9 Hz), 7.96 (2H, d, *J* = 7.97 Hz).

^{13}C NMR: δ 123.5 (1C, q, *J* = 274 Hz), 126.4, 128.9 (2C), 129.1 (2C), 130.3 (2C), 130.5 (2C), 132.6, 135.8 (1C, q, *J* = 33 Hz), 143.9, 144.9.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{15}H_{11}ClF_3O_2S^+$ 347.0010 found 347.0110.

***(Z)*-4-[(2-Chloro-1-phenylvinyl)sulfonyl)]-1,1'-biphenyl, 183e:**



Prepared according to the representative procedure using *(Z)* - (2-([1, 1'-biphenyl]-4-ylsulfonyl)-2-phenylvinyl) (phenyl)iodonium tetrafluoroborate, **180e** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.026 g, 91%).

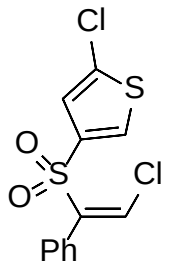
IR: 1592 (w), 1329 (m), 1148 (m), 1085 (w), 581 (m) cm^{-1}.

^{1}H NMR: δ 6.75 (1H, s), 7.30 (2H, d, *J* = 3.7 Hz), 7.36 (2H, t, *J* = 7.6 Hz), 7.42 (2H, t, *J* = 7.8 Hz), 7.48 (2H, t, *J* = 7.6 Hz), 7.60 (2H, d, *J* = 7.6 Hz), 7.70 (2H, d, *J* = 8.3 Hz), 7.88 (2H, d, *J* = 8.3 Hz).

^{13}C NMR: δ 127.7(2C), 127.9(2C), 128.8(2C), 129.1, 129.2(2C), 129.4, 129.5(2C), 130.0, 130.6(2C), 133.2, 138.9, 139.4, 145.6, 147.1.

HRMS: *m/z* calc'd for $[M+NH_4]^+$ $C_{20}H_{19}ClNO_2S^+$ 372.0820 found 372.0816.

***(Z)*-2-Chloro-5-[(2-chloro-1-phenylvinyl)sulfonyl)]thiophene, 183f:**



Prepared according to the representative procedure using *(Z)* - (2-((5-chlorothiophen-2-yl) sulfonyl)-2-phenylvinyl) (phenyl)iodonium tetrafluoroborate, **180f** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colourless oil (0.033g, 98%).

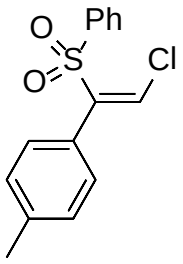
IR: 1402 (m), 1332 (s), 1146 (s), 990 (m), 605 (s) cm^{-1}.

^{1}H NMR: δ 6.78 (1H, s), 6.93 (1H, d, *J* = 3.9 Hz), 7.29 (2H, d, *J* = 7.9 Hz), 7.38 (2H, t, *J* = 7.7) 7.40-7.46 (2H, m).

^{13}C NMR: δ 127.4, 128.8(2C), 129.8, 130.2, 130.5(2C), 132.6, 134.6, 138.9, 140.5, 145.2.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{12}H_{12}Cl_2NO_2S_2$ 335.9681 found 335.9684.

***(Z)*-1-[(2-Chloro-1-(phenylsulfonyl) vinyl)]-4-methylbenzene, 183g:**



Prepared according to the representative procedure using *(Z)*-phenyl (2-(phenylsulfonyl)-2-(p-tolyl) vinyl) iodonium, **180g** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.026 g, 98%).

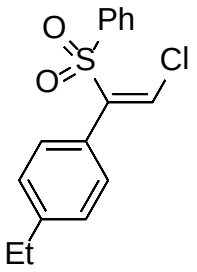
IR: 1578 (m), 1443 (m), 1146 (s), 1083 (m), 754 (s) cm^{-1}.

^{1}H NMR: δ 2.36 (3H, s), 6.70 (1H, s), 7.15 (4H, s), 7.49 (2H, t, *J* = 7.5 Hz), 7.61(1H, t, *J* = 7.5 Hz), 7.83 (2H, d, *J* = 7.5 Hz).

^{13}C NMR: δ 21.7, 128.6 (2C), 128.9, 129.3 (2C), 129.5 (2C), 130.3, 130.4 (2C), 134.1, 140.2, 140.6, 145.5.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{15}H_{17}ClNO_2S^+$ 310.0663 found 310.0663.

***(Z)*-1-(2-Chloro-1-(phenylsulfonyl) vinyl)-4-ethylbenzene, 183h:**



Prepared according to the representative procedure using *(Z)*-(2-(4-ethylphenyl)-2-(phenylsulfonyl) vinyl) (phenyl) iodonium, **180h** (1 equiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180h** giving the product as a colorless oil (0.021 g, 77%).

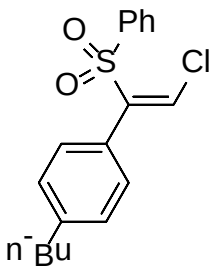
IR: 2359 (s), 1709 (m), 1332 (m), 1149 (s), 1084 (m), 722 (m) cm^{-1}.

^{1}H NMR: δ 1.23 (3H, t, *J* = 7.7 Hz), 2.65 (2H, q, *J* = 7.6 Hz), 6.70 (1H, s), 7.18 (4H, s), 7.49 (2H, t, *J* = 7.7 Hz), 7.61(1H, t, *J* = 7.6 Hz), 7.83 (2H, d, *J* = 7.7 Hz).

^{13}C NMR: δ 15.6, 28.9, 128.3 (2C), 128.6 (2C), 128.9, 129.2 (2C), 130.4, 130.5 (2C), 134.1, 140.6, 145.6, 146.4.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{16}H_{19}ClNO_2S^+$ 324.0820 found 324.0822.

***(Z)*-1-(2-Chloro-1-(phenylsulfonyl) vinyl)-4-propylbenzene, 183i:**



Prepared according to the representative procedure using *(Z)*-(2-(4-butylphenyl)-2-(phenylsulfonyl) vinyl) (phenyl) iodonium tetrafluoroborate, **180i** (1 equiv) instead of *(Z)*-

phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.024 g, 84%).

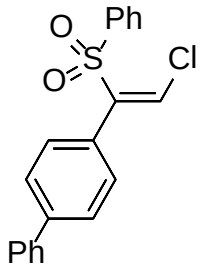
IR $_{(neat):}$ 2359 (s), 1709 (m), 1332 (m), 1149 (s), 1084 (m), 722 (m) cm^{-1}.

^{1}H NMR: δ 0.93 (3H, t, *J* = 7.3 Hz), 1.34 (2H, hex, *J* = 7.3 Hz), 1.59 (2H, q, *J* = 7.6 Hz), 2.61 (2H, t, *J* = 7.9 Hz), 6.70 (1H, s), 7.10-7.20 (4H, m), 7.48 (2H, t, *J* = 7.6 Hz), 7.60 (1H, t, *J* = 7.4 Hz), 7.83 (2H, d, *J* = 8.1 Hz).

^{13}C NMR: δ 15.6, 28.9, 128.3 (2C), 128.6 (2C), 128.9, 129.2 (2C), 130.4, 130.5 (2C), 134.1, 140.6, 145.6, 146.4.

HRMS: *m/z* calc'd for $[M+H]^+$ $C_{18}H_{20}ClO_2S$ 335.0910 found 335.0866.

(Z)-4-[2-Chloro-1-(phenylsulfonyl) vinyl]-1, 1'-biphenyl, 183j:



Prepared according to the representative procedure using *(Z)-(*2-([1, 1'-biphenyl]-4-yl)-2-(phenylsulfonyl) vinyl) (phenyl)iodonium, **180j** (1 aquiv) instead of *(Z)*-phenyl (2-phenyl-2-(phenylsulfonyl) vinyl)iodonium tetrafluoroborate, **180a** giving the product as a colorless oil (0.026 g, 83%).

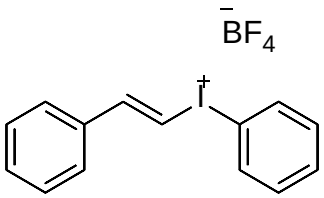
IR $_{(neat):}$ 1481 (w), 1318 (m), 1180 (m), 1004 (w), 648 (s) cm^{-1}.

^{1}H NMR: δ 6.78 (1H, s), 7.32-7.41 (3H, m), 7.42-7.54 (4H, m), 7.55-7.67 (5H, m), 7.88 (2H, d, *J* = 7.6 Hz).

^{13}C NMR: δ 127.4 (2C), 127.5 (2C), 128.2, 128.6 (2C), 129.3 (2C), 129.3 (2C), 129.4, 130.9 (2C), 132.0, 134.2, 140.3, 140.5, 142.9, 145.3.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{20}H_{19}ClNO_2S^+$ 372.0820 found 372.0821.

(E)- **Phenyl(styryl)iodonium tetrafluoroborate, 185a:**



Following the procedure reported by Fujita, to a solution of phenylvinyl boronic acid (1 g, 6.8 mmol) in CH_2Cl_2 (10 mL) at 0 ºC under a N_2 atmosphere was added BF_3-Et_2O (1mL, 8.1 mmol). The reaction mixture was stirred for 15 minutes, then solution of $PhI(OAc_2)$ (2.6 g, 8.1 mmol) in CH_2Cl_2 (10 ml) was added at 0 ºC. The reaction mixture was stirred for 1h then poured into saturated aqueous sodium tetrafluoroborate solution (5 mL). [58]A white precipitate was formed which was filtered off and washed with CH_2Cl_2 (2 x 10 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was clear, colourless, viscous oil which was washed several times with hexane the salt preiptated as a white solid (1.5 g, 56%).

Melting point: 150-151 ºC.

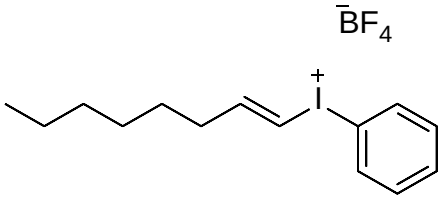
IR $_{(neat)}$: 3470 (w), 1442 (m), 1444 (m), 989 (s), 720 (s)

^{1}H NMR: δ 7.37-7.46 (3H, m), 7.48-7.57 (4H, m), 7.64 (1H, t, *J* = 7.5 Hz), 7.82 (1H, d, *J* = 15 Hz), 7.97 (1H, d, *J* = 15 Hz), 8.15 (2H, d, *J* = 7.8 Hz).

^{13}C NMR: δ 107.8, 120.1, 128.7 (2C), 130.3 (2C), 131.5, 132.4, 132.5 (2C), 136.1 (2C), 136.4, 147.5

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{14}H_{12}I^+$ 307.0120 found 307.0462.

***(E)*-Oct-1-en-1-yl(phenyl)iodonium tetrafluoroborate, 185b:**



Prepared according to the representative procedure using (*E*)-oct-1-en-1-ylboronic acid (0.5 g) instead of phenylvinylboronic giving the product as a brown viscous oil (0.9 g, 69%).

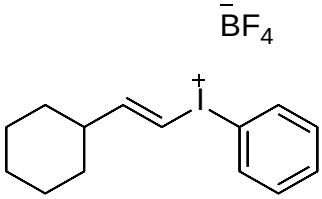
IR $_{(neat):}$ 3084 (w), 2928 (w), 1444 (m), 1444 (m), 987 (s), 737 (s).

^{1}H NMR: δ 0.80 (3H, t, *J* = 7.1 Hz), 1.12-1.31 (6H, m), 1.35-1.47 (2H, m), 2.29 (2H, q, *J* = 7.5 Hz), 6.76 (1H, d, *J* = 14 Hz), 6.97 (1H, ddd, *J* = 21, 14, 7.3 Hz), 7.45 (2H, t, *J* = 7.8 Hz) 7.60 (1H, t, *J* = 7.5 Hz), 7.97 (2H, d, *J* = 8.2 Hz).

^{13}C NMR: δ 14.2, 22.7, 27.8, 28.8, 31.6, 35.5, 96.6, 110.1, 132.6 (2C), 132.9, 135.9 (2C), 156.1.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{14}H_{20}I^+$ 315.0604 found 315.0614.

(*E*)-(2-Cyclohexylvinyl)(phenyl)iodonium tetrafluoroborate, 185c:



Prepared according to the representative procedure using (*E*)-(2-cyclohexylvinyl)boronic acid (0.5 g) instead of phenyl vinyl boronic giving the product as a brown viscous oil (1.5 g, 49%).

Melting point: 189-190 ºC.

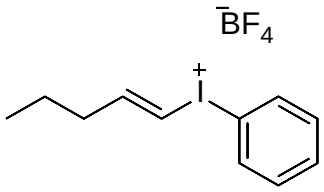
IR $_{(neat):}$ 3155 (w), 1515 (m), 1021 (s), 989 (s)

^{1}H NMR: δ 1.00-1.35 (5H, m), 1.51-1.77 (5H, m), 2.20-2.38 (1H, m), 7.05 (1H, dd, *J* = 14, 6.9 Hz), 7.16 (1H, d, *J* = 14 Hz), 7.58 (2H, t, *J* = 7.4 Hz) 7.70 (1H, t, *J* = 7.4 Hz), 8.10 (2H, d, *J* = 8.3 Hz).

^{13}C NMR: δ 26.1 (2C), 26.5, 32.2 (2C), 44.2, 102.5, 115.4, 132.9 (2C), 133.1, 136.2 (2C), 158.6.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{14}H_{18}I^+$ 313.0448 found 313.0447.

***(E)*-Pent-1-en-1-yl(phenyl)iodonium tetrafluoroborate, 185d:**



Prepared according to the representative procedure using (E)-pent-1-en-1-ylboronic acid (0.5 g) instead of phenylvinyl boronic giving the product as brown viscous oil (0.9 g, 44%).

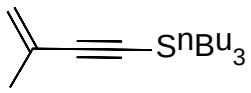
IR $_{(neat):}$ 3082 (w), 1444 (m), 987 (s), 737 (s)

^{1}H NMR: δ 0.77 (3H, t, *J* = 7.5 Hz), 1.38 (2H, hex, *J* = 7.2 Hz), 2.20 (2H, q, *J* = 6.9 Hz), 6.75 (1H, d, *J* = 14 Hz), 6.94 (1H, dt, *J* = 9.1, 7.2 Hz), 7.39 (2H, t, *J* = 7.8 Hz) 7.55 (1H, t, *J* = 7.5 Hz), 7.91 (2H, d, *J* = 8.2 Hz).

^{13}C NMR: δ 13.4, 21.0, 37.1, 96.7, 110.1, 132.5 (2C), 132.8, 135.6 (2C), 155.7.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{11}H_{14}I^+$ 273.0135 found 273.0130.

Tributyl(3-methylbut-3-en-1-yn-1-yl)stannane, 187a:



Following the procedure reported by Willis, to a stirred solution of 2-methylbut-1-en-3-yne (690 mg, 10.4 mmol) in THF (30 mL) at -78 °C under a N_2 atmosphere was added *n*-BuLi (11.7 ml, 18.7 mmol). The reaction mixture was warmed to 0 °C over 1h then recooled to -78°C and treated with tri-*n*-butyltin chloride (3.1 mL, 11.4 mmol). The reaction mixture was warmed to 20 °C over 1 h then filtered through a pad of silica gel.[77] The filtrate thus obtained was concentrated under reduced pressure to isolate the product as an orange oil (3.6 g, 98%).

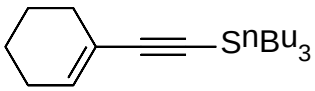
IR $_{(neat):}$ 2957 (s), 2852 (w), 1270 (m), 952 (s).

^{1}H NMR: δ 0.84 (9H, t, *J* = 7.7 Hz), 0.92 (6H, t, *J* = 8.7 Hz), 1.28 (6H, hex, *J* = 7.4 Hz) 1.44-1.57 (6H, m), 1.79 (3H, s), 5.06 (1H, s), 5.17 (1H, s).

^{13}C NMR: δ 11.2 (3C), 13.8 (3C), 23.8, 27.1 (3C), 29.1 (3C), 91.6, 111.6, 121.2, 127.6.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{17}H_{33}Sn^+$ 357.1526 found 357.1526.

(Cyclohex-1-en-1-ylethynyl)trimethylstannane, 187b:



Prepared according to the representative procedure using 1-ethynylcyclohex-1-ene (640 mg, 6.0 mmol) instead of 2-methylbut-1-en-3-yne giving the product as colourless oil (2.3 g, 96%).

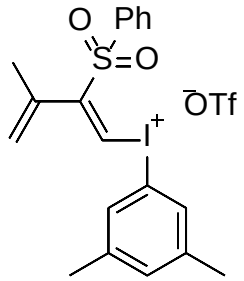
IR $_{(neat):}$ 2872 (s), 2855 (m), 1463 (m), 476 (w).

^{1}H NMR: δ 0.85 (10H, t, *J* = 7.4 Hz), 0.93 (5H, t, *J* = 8.3 Hz), 1.29 (6H, hex, *J* = 7.4 Hz) 1.45-1.63 (10H, m), 1.79 (4H, d, *J* = 22 Hz), 6.04 (1H, s).

^{13}C NMR: δ 11.3 (3C), 13.9 (3C), 21.8, 22.6, 25.9, 27.2 (3C), 29.0 (3C), 29.8, 89.2, 112.5, 121.7, 134.6.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{20}H_{37}Sn^+$ 397.1839 found 397.1842

(*Z*)-(3,5-dimethylphenyl)(3-methyl-2-(phenylsulfonyl)buta-1,3-dien-1-yl)iodonium trifluoromethanesulfonate, 189:



Tributyl(3-methylbut-3-en-1-yn-1-yl)stannane (1.9 g, 5.4 mmol) was added to a solution of *m*-xylyl (cyano) iodonium triflate (2.0 g, 4.9 mmol) in CH_2Cl_2 (20 mL) at 30 ºC under a N_2 atmosphere.[36] The reaction was stirred for 30 min then the solvent was removed under vacuum. The residue was dissolved in MeOH (5 mL) then added to a solution of phenylsulfinic acid (0.76 g, 5.4 mmol) in MeOH (20 mL) at 0 ºC under a N_2 atmosphere. The reaction mixture was stirred for 45 minutes then poured into saturated aqueous sodium tetrafluoroborate solution (15 mL). A white precipitate was formed which was filtered off and washed with CH_2Cl_2 (2 x 16 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered and concentrated in vacuum. The residue was a clear, colourless, viscous oil. A 1:1 mixture of diethyl ether and petroleum ether (20 + 20 mL) was added to the residue and the mixture swirled. The solvent was removed by decantation. This was repeated until a white solid was formed. The solid product was recrystallised from the

minimum amount of CH_2Cl_2 with slow addition of petroleum ether giving the product as a white microcrystalline solid (0.57 g, 79%).

Melting point: 157-159 ºC.

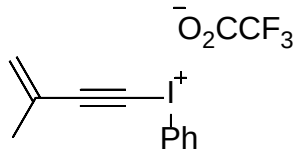
IR: 3046 (w), 1450 (m), 1288 (s), 1025 (s), 623 (w), 514 (m).

^{1}H NMR: δ 1.78 (3H, s), 2.40 (6H, s), 5.08 (1H, s), 5.25 (1H, s), 7.47 (1H, s), 7.78 (2H, t, *J* = 7.7 Hz), 7.91 (2H, t, *J* = 7.4 Hz), 7.95 (3H, d, *J* = 2.4 Hz), 8.11 (1H, s).

^{13}C NMR: δ 22.0 (2C), 24.1, 116.7 (q, *J* = 48 Hz), 124.2, 128.4, 129.6, 131.4 (2C), 134.7 (2C), 135.6, 135.8, 137.1 (2C), 138.2, 141.3, 142.8 (2C), 147.9.

HRMS: *m*/*z* calc'd for $[M\text{-}OTf]^+$ $C_{19}H_{20}IO_2S^+$ 439.0233 found 439.0233

(3-Methylbut-3-en-1-yn-1-yl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetate, 192a:



To a stirred solution of diacetoxy iodobenzene (3g, 9.3 mmol) in CH_2Cl_2 (60 mL) at -30 ºC was added trifluoroacetic acid (1.4 ml, 18.6 mmol) dropwise. The mixture was sttired 30 min then was warmed to room temperature and stirred for a further hour. Then 2-methylbut-1-en-3-ynee (0.88 ml, 9.3 mmol) was added and the resulting mixture was stirred in darkness at room temperature for 3.5 h. The solution was concentrated in vacuo to around 30 mL then diethyl ether (20 ml) and petroleum ether (40 ml) were added which initiated crystallisation of the product. After being placed in the freezer (-20 ºC) for 48 h, the product was filtered and dried in vacuum to provide a white crystalline solid (3.5 g, 98%).

Melting point: 40-42 ºC.

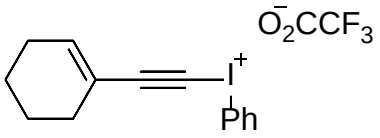
IR $_{(neat)}$: 3006 (w), 1661 (s), 1185 (s), 840 (w), 738 (m).

^{1}H NMR: 1.88 (3H, s), 5.43 (1H, s), 5.5 (1H, s), 7.50 (2H, t, *J* = 7.8 Hz), 7.61 (1H, t, *J* = 7.4 Hz), 8.11 (2H, d, *J* = 8.3 Hz).

^{13}C NMR: δ 22.1, 44.6, 105.4, 115.9 (1C, q, *J* = 298 Hz), 120.9, 125.4, 128.1, 132.2, 132.4 (2C), 133.7 (2C), 163.0 (1C, q, *J* = 37 Hz).

HRMS: *m*/*z* calc'd for $[M\text{-}O_2CCF_3]^+$ $C_{11}H_{10}I^+$ 268.9822 found 268.9817.

(Cyclohex-1-en-1-ylethynyl)(phenyl)-λ^3-iodanyl 2,2,2-trifluoroacetate, 192b:



Prepared according to the representative procedure using 1-ethynylcyclohex-1-ene (1.1 mL, 9.3 equiv) instead of 2-methylbut-1-en-3-yne giving the product as a white crystalline solid (4 g, 99%).

Melting point: 45-46 ºC.

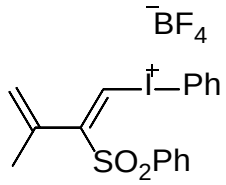
IR $_{(neat):}$ 3011 (w), 2256 (m), 1183 (s), 992 (w), 737 (s).

^{1}H NMR: 1.48-1.67 (4H, m), 2.02-2.11 (2H, m), 2.12-2.21 (2H, m), 6.29-6.35 (1H, m), 7.46 (2H, t, *J* = 7.7 Hz), 7.57 (1H, t, *J* = 7.4 Hz), 8.08 (2H, d, *J* = 8.3 Hz).

^{13}C NMR: δ 21.3, 22.1, 26.2, 28.7, 41.6, 107.2, 115.9 (1C, q, *J* = 291 Hz), 119.6, 120.8, 132.0, 132.3 (2C), 133.5 (2C), 142.7, 162.9 (1C, q, *J* = 39 Hz).

HRMS: *m*/*z* calc'd for $[M\text{-}OACF_3]^+$ $C_{14}H_{14}I^+$ 309.0135 found 309.0135.

[2-Methyl-1-(phenylsulfonyl)allyl](phenyl)iodonium tetrafluoroborate, 193a:



(3-Methylbut-3-en-1-yn-1-yl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetate, **192a** (0.50 g, 1.3 mmol, 1 equiv) dissolved in MeOH (5 mL) was added to a solution of phenylsulfinic acid (0.20 g, 1.4 mmol, 1.1 equiv) in MeOH (2 mL) at 0 ºC under a N_2 atmosphere. The reaction mixture was stirred for 45 minutes then poured into saturated aqueous sodium tetrafluoroborate solution (5 mL). A white precipitate was formed which was filtered off and washed with CH_2Cl_2 (2 x 8 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was a clear, colourless, viscous oil. A 1:1 mixture of diethyl ether and petroleum ether (5 + 5 mL) was added to the residue and the mixture was swirled. The solvent was removed by decantation. This process was repeated until a white solid was formed. The crude solid product was recrystallised from the minimum amount of CH_2Cl_2 with slow addition of petroleum ether. (2-Methyl-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate was isolated as a white microcrystalline solid (0.45 g, 72%).

Melting point: 150-152ºC.

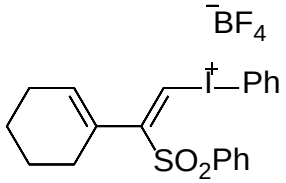
IR $_{(neat)}$: 1305 (m), 1135 (s), 1060 (s), 945 (w), 680 (m).

^{1}H NMR: δ 1.77 (3H, s), 5.08 (1H, s), 5.25 (1H, s), 7.68 (2H, d, *J* = 7.8 Hz), 7.78 (2H, t, *J* = 7.8 Hz), 7.83 (1H, t, *J* = 7.4 Hz), 7.91 (1H, t, *J* = 7.3 Hz), 8.02 (2H, d, *J* = 7.5 Hz), 8.16 (1H, s), 8.38 (2H, d, *J* = 7.9 Hz).

^{13}C NMR: δ 24.1, 116.9, 124.1, 129.6 (2C), 131.3 (2C), 133.1 (2C), 134.2, 137.0, 137.1, 137.2 (2C), 137.6, 138.4, 147.9

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{17}H_{16}IO_2S^+$ 410.991 found 410.9901.

[Cyclohex-1-en-1-yl(phenylsulfonyl]methyl)(phenyl)iodonium tetrafluoroborate, 193b:



Prepared according to the representative procedure using (cyclohex-1-en-ylethynyl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetaet, **192b** (0.5 g, 1.2 mmol), instead of (3-methylbut-3-en-1-yn-1-yl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetate, **192a** giving the product as white solid (0.5 g, 79%).

Melting point: 156-157 ºC.

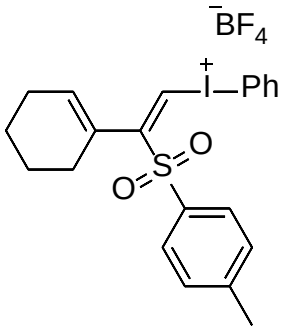
IR $_{(neat)}$: 1699 (s), 1417 (w), 1183 (s), 1124 (s), 720 (s).

^{1}H NMR: δ 1.34-1.41 (4H, m), 1.87-1.91 (4H, m), 5.79 (1H, s), 7.68 (2H, d, *J* = 7.7 Hz), 7.73-7.88 (3H, m), 7.91 (1H, t, *J* = 7.5 Hz), 7.98 (2H, d, *J* = 7.8 Hz), 8.04 (1H, s), 8.36 (2H, d, *J* = 7.9 Hz).

^{13}C NMR: δ 21.7, 23.1, 26.5, 29.8, 114.9, 116.8, 129.8 (2C), 130.6 (2C), 133.2 (2C), 133.1, 134.2, 136.5, 136.9 (2C), 137.0, 137.6, 149.1.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{20}H_{20}IO_2S^+$ 451.0223 found 451.0212.

(*Z*)-(2-(Cyclohex-1-en-1-yl)-2-tosylvinyl)(phenyl)iodonium tetrafluoroborate, 193c:



Prepared according to the representative procedure using (cyclohex-1-en-ylethynyl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetate, **192b** (0.1 g, 0.24 mmol), instead of (3-methylbut-3-en-1-yn-1-yl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetate, **192a** and 4-methylbenzenesulfinic acid instead of phenylsulfinic acid giving the product as a white solid (0.19 g, 80%).

Melting point: 160-161 ºC.

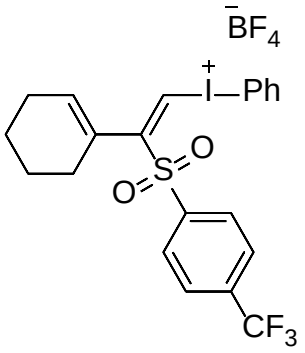
IR $_{(neat)}$: 2855 (w), 1471 (w), 1038 (s), 1003 (s), 723 (s).

^{1}H NMR: δ 1.35-1.51 (4H, m), 1.88-1.94 (4H, m), 2.48 (3H, s), 5.79 (1H, s), 7.58 (2H, d, *J* = 7.8 Hz), 7.67 (2H, t, *J* = 7.7 Hz), 7.79-7.89 (3H, m), 7.98 (1H, s), 8.36 (2H, d, *J* = 7.9 Hz).

^{13}C NMR: δ 22.6, 23.1, 26.5, 29.7, 114.5, 116.7, 129.8 (2C), 130.7, 131.6 (2C), 133.1 (2C), 134.1 (2C), 136.3, 137.6 (2C), 148.00, 149.3.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{21}H_{22}IO_2S^+$ 465.0385 found 465.0379.

(*Z*)-(2-(Cyclohex-1-en-1-yl)-2[4[(trifluoromethyl)phenyl)sulfonyl)vinyl)](phenyl)iodonium tetrafluoroborate, 193d:



Prepared according to the representative procedure using (cyclohex-1-en-ylethynyl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetate, **192b** (0.1 g, 0.24 mmol), instead of (3-methylbut-3-en-1-yn-1-yl)(phenyl)-λ3-iodanyl 2,2,2-trifluoroacetate, **192a** and 4-(trifluoromethyl)benzenesulfinic acid instead of phenylsulfinic acid giving the product as a white solid (0.09 g, 73%).

Melting point: 156-157 ºC.

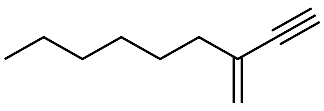
IR $_{(neat)}$: 2935 (w), 1447 (w), 1314 (s), 1012 (s), 740 (m).

^{1}H NMR: δ 1.30-1.40 (4H, m), 1.90-1.94 (4H, m), 5.80 (1H, s), 7.68 (2H, t, *J* = 7.4 Hz), 7.83 (1H, t, *J* = 7.5 Hz), 8.15 (3H, d, *J* = 7.1 Hz), 8.22 (2H, d, *J* = 8.3 Hz), 8.35 (2H, d, *J* = 8.1 Hz).

^{13}C NMR: δ 21.6, 23.1, 26.5, 29.7, 116.4, 116.8, 124.4 (1C, q, *J* = 274 Hz), 128.2, 128.3, 130.5, 130.9, 133.2, 134.2, 136.0 (1C, q, *J* = 32 Hz), 137.1, 137.5, 141.1, 148.3.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{21}H_{19}F_3IO_2S^+$ 519.0097 found 519.0098.

3-Methylenenon-1-yne, 194a:



To solution of 2-methylbut-1-en-3-yne (1.5 g, 30 mmol, 1 equiv) in THF (18 mL) at -78 ºC under a N_2 atmosphere was added *n*-butyllithium (26.6 ml, 2.2 aq). Then, *t*-BuOK (7.4 g, 66 mmol) in THF (10 mL) was added slowly. The resulting and mixture was stirred for 30 min. Then the reaction flask was transferred to an ice bath for 40 min, after which time it was cooled to -20 ºC lithium bromide (12 g, 66 mmol) in THF (10 ml) was added. After 10 min 1-bromo pentane (3.8 `mL, 1 equiv) was added. The reaction mixture was stirred overnight at -20 ºC. Saturated solution of ammonium chloride (40 ml) was added stirred at -40 ºC after 15 min, this was extracted with diethyl ether (30 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum.[80] The product was isolated as an orange oil (3.3 g, 81%)

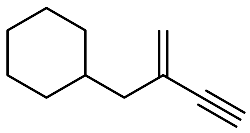
IR $_{(neat):}$ 3300 (w), 2927 (m), 2342 (s), 902 (m), 617 (m).

^{1}H NMR: δ 0.82-0.92 (3H, m), 1.22-1.36 (6H, m), 1.52 (2H, t, *J* = 7.5 Hz), 2.15 (2H, t, *J* = 7.5 Hz), 2.86 (1H, s), 5.28 (1H, s), 5.40 (1H, s).

^{13}C NMR: δ 14.1, 22.6, 27.9, 28.6, 31.6, 37.0, 76.7, 84.2, 122.5, 131.0

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C10H17^+$ 137.0930 found 137.1280.

(2-Methylenebut-3-yn-1-yl)cyclohexane, 194b:



Prepared according to the representative procedure using bromocyclohexane instead of 1-bromo pentane, giving the product as a brown oil (2.7 g, 70%).

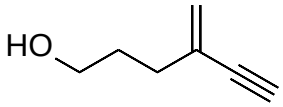
IR $_{(neat):}$ 3307 (w), 2928 (m), 1458 (w), 906 (s), 734 (s).

^{1}H NMR: δ 0.83-0.93 (3H, m), 1.23-1.34 (6H, m), 1.51 (2H, t, *J* = 7.2 Hz), 2.14 (2H, t, *J* = 7.2 Hz), 2.86 (1H, s), 5.27 (1H, s), 5.38 (1H, s).

^{13}C NMR: δ 14.0, 22.6, 27.9 (2C), 28.6, 31.6 (2C), 37.0, 84.2, 122.4, 131.0.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{11}H_{17}^+$ 149.1301 found 149.1260.

4-methylenehex-5-yn-1-ol, 194c:



Prepared according to the representative procedure using oxirane instead of 1-bromopentane, giving the product as a brown oil (2.9 g, 90%).

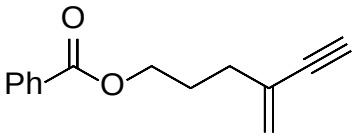
IR $_{(neat):}$ 3289 (w), 2924 (m), 2344 (2), 905 (m), 669 (m).

^{1}H NMR: δ 1.78 (2H, pentet, *J* = 7.1 Hz), 1.96 (1H, br), 2.24 (2H, t, *J* = 7.4 Hz), 2.89 (1H, s), 3.64 (2H, t, *J* = 6.4 Hz), 5.32 (1H, s), 5.42 (1H, s).

^{13}C NMR: δ 29.0, 33.2, 61.8, 76.8, 83.9, 123.2, 130.1.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_7H_{11}O^+$ 111.0732 found 111.0804.

4-methylenehex-5-yn-1-yl benzoate, 195:



According to the procedure reported by Harried and co-workers, to a solution of benzoyl chloride (0.74 mL, 6.4 mmol) and 4-(dimethylamino)pyridine (DMAP) (78 mg, 0.64 mmol, 0.1 equiv) in CH_2Cl_2 (20 mL), was added 4-methylenehex-5-yn-1-ol, **194c** (0.70 g, 6.4 mmol) and the mixture was cooled to 0 °C. Then, Et_3N (0.88 mL, 6.4 mmol) was added slowly to the

mixture. The resulting mixture was stirred at room temperature overnight. The resulting mixture was treated with 5% HCl solution (0.5 mL) and 0.5 M $NaHCO_3$ (0.6 mL) and washed with brine (10 mL) then extracted with CH_2Cl_2.[81] The organic layers were dried over anhydrous magnesium sulfate and the solvent removed under vacuum to give the product as yellow oil (1.3 g, 93% yield).

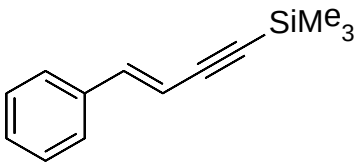
IR $_{(neat)}$: 3289 (w), 12924 (w), 2342 (s), 1053 (m), 615 (m).

^{1}H NMR: δ 2.00 (2H, pentet, *J* = 6.9 Hz), 2.31 (2H, t, *J* = 7.6 Hz), 2.93 (1H, s), 4.23 (2H, t, *J* = 6.5 Hz), 5.33 (1H, s), 5.44 (1H, s), 7.41 (2H, t, *J* = 7.7 Hz), 7.46-7.55 (1H, m), 8.03 (2H, d, *J* = 8.2 Hz).

^{13}C NMR: δ 27.2, 33.6, 64.1, 77.8, 83.8, 123.7, 128.5 (2C), 129.7 (2C), 130.5, 133.1, 134.7, 166.6.

HRMS: *m*/*z* calc'd for $[M]^+$ $C_{14}H_{14}O_2^+$ 215.1067 found 215.1066.

***(E)*-Trimethyl(4-phenylbut-3-en-1-yn-1-yl)silane, 197:**



To a solution of β-bromostyrene (2 g, 0.011 mol) and trimethylsilylacetylene (1.67 g, 0.011 mol) in Et_3N (25 mL) under a N_2 atmosphere was added $Pd(PPh_3)_4$ (0.063 g, 0.55mol) and CuI (0.021 g, 1.1 mol). This was stirred at room temperature for 12 h then filtered through a silica plug and concentrated in vacuo.[82] The residue was purified by flash chromatography (petroleum) which furnished a brown oil (2.2 g, 98%).

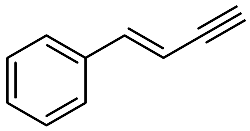
IR $_{(neat)}$: 2958 (w), 2359 (m), 1249 (s), 835 (s)

^{1}H NMR: δ 0.27 (9H, s), 6.20 (1H, d, *J* = 16 Hz), 7.04 (1H, d, *J* = 16 Hz), 7.24-7.42 (5H, m)

^{13}C NMR: δ 0.32 (2C), 97.2, 104.8, 108.4, 126.6 (2C), 128.4, 129.1 (2C), 136.4, 140.1, 142.7.

HRMS: *m*/*z* calc'd for $[M]^+$ $C_{13}H_{16}Si^+$ 200.1021 found 200.1026.

***(E)*-But-1-en-3-yn-1-ylbenzene, 198:**



To solution of *(E)*-trimethyl(4-phenylbut-3-en-1-yn-1-yl)silane (1 g, 4.99 mmol) in MeOH (15 mL), was added K_2CO_3 (0.8 g, 2 equiv) and the mixture was stirred at room temperature for 3 hours. The crude product was concentrated to the half by rotatory evaporator, quenched with water and the solution was extracted with Et_2O. The combined organic extracts was washed with brine and dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum.[82] The product was isolated as brown oil (0.4 g, 63%)

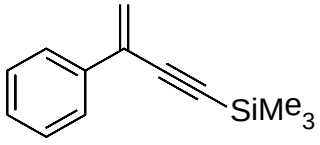
IR $_{(neat):}$ 2978 (w), 2242 (m), 905 (s), 726 (s)

^{1}H NMR: δ 3.11 (1H, s), 6.18 (1H, dd, *J* = 16, 2.3 Hz), 7.09 (1H, d, *J* = 16 Hz), 7.30-7.46 (5H, m)

^{13}C NMR: δ 79.5, 83.2, 107.3, 126.7 (2C), 128.6 (2C), 129.1, 136.1, 143.5.

HRMS: *m*/*z* calc'd for $[M]^+$ $C_{10}H_8^+$ 128.0626 found 128.0626.

Trimethyl(3-phenylbut-3-en-1-yn-1-yl)silane, 200:



Prepared according to the representative procedure for formation of **197** using α-bromostyrene (1 g) instead of β-bromo styrene giving the product as a brown viscous oil (1.1 g, 98%).

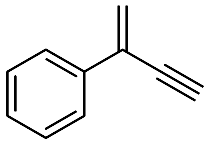
IR $_{(neat)}$: 2960 (w), 2400 (m), 1251 (s), 857 (s)

^{1}H NMR: δ 0.25 (9H, s), 5.7 (1H, s), 5.9 (1H, s), 7.26-7.41 (3H, m), 7.64 (2H, d, *J* = 7.8 Hz)

^{13}C NMR: δ 0.32 (3C), 96.3, 104.4, 121.8, 126.4 (2C), 128.7, 128.7 (2C), 130.9, 137.3.

HRMS: *m*/*z* calc'd for $[M]^+$ $C_{13}H_{16}Si^+$ 200.1021 found 200.1022.

But-1-en-3-yn-2-ylbenzene, 201:



Prepared according to the representative procedure for formation **198** using trimethyl(3-phenylbut-3-en-1-yn-1-yl)silane, **200** (1 g) instead of *(E)*-trimethyl(4-phenylbut-3-en-1-yn-1-yl)silane, **197** giving the product as a brown viscous oil (0.67 g, 71%).

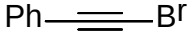
IR $_{(neat)}$: 2926 (w), 2164 (m), 1733 (s), 1050 (s), 730 (m).

^{1}H NMR: δ 3.10 (1H, s), 5.76 (1H, s), 5.98 (1H, s), 7.29-7.38 (3H, m), 7.09 (2H, d, *J* = 7.7 Hz).

^{13}C NMR: δ 78.9, 83.0, 122.5, 126.3 (2C), 128.6 (2C), 128.7, 130.0, 137.0.

HRMS: *m*/*z* calc'd for $[M]^+$ $C_{10}H_8^+$ 128. 0626 found 128.0626.

(Bromoethynyl) benzene, 203:



To a stirred solution of ethynylbenzene (20 mg, 20 mmol) in acetone (20 mL) were added *N*-bromosuccinnimde (62 mg, 35 mmol) and silver nitrate (50 mg, 3 mmol) in order. The mixture was stirred at room temperature overnight. Then poured into ice-water (15 mL), extracted with ether (10 mL) and washed with water (10 mL) and brine (10 mL) and the organic layer was dried with anhydrous magnesium sulfate filtered and concentrated in vacuo.[83] The product was isolated as a colourless oil (0.9g, 55%).

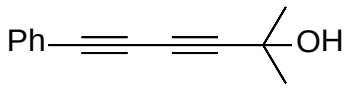
IR $_{(neat):}$ 2870 (w), 2100 (m), 1695 (s), 1150 (s), 760 (m).

^{1}H NMR: δ 7.28-7.41 (3H, m), 7.60 (2H, d, J = 7.8 Hz)

^{13}C NMR: δ 49.7, 80.4, 123.0, 128.1 (2C), 128.8, 131.9 (2C).

HRMS: m/z calc'd for $[M]^+$ $C_8H_5Br^+$ 179.9575 found 179.9601

2-Methyl-6-phenylhexa-3,5-diyn-2-ol, 205:



To the mixture of MeOH (10 mL) and H_2O (5 mL) were added *n*-butylamine (120 mg, 164 mmol), 2-methyl-3-butyn-2-ol (0.9 g, 11 mmol), copper(I) chloride (0.1 g, 101 mmol) and hydroxylaminehydrochloride (0.1 g, 144 mmol). (Bromoethynyl) benzene (1g, 55 mmole) in MeOH (5 mL) was added as dropwise to the mixture. The mixture was stirred at room temperature overnight. It was poured into ice-water (10 mL), extracted by ether (10 mL) and washed with water (5 mL) and brine (5 mL) and the organic layer was dried with anhydrous magnesium sulfate filtered and concentrated in vacuo.[83] The residue was purified by flash chromatography (10:1 petroleum ether/EtOAc) which furnished a white solid (0.6 g, 35%).

Melting point: 56-57 ºC.

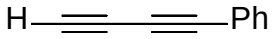
IR $_{(neat):}$ 2940 (m), 2133 (w), 1687 (s), 1090 (s), 880 (s).

^{1}H NMR: δ 1.55 (6H, s), 2.25 (1H, br), 7.28-7.33 (3H, m), 7.45-7.49 (2H, m).

^{13}C NMR: δ 30.9 (2C), 65.5, 67.0, 72.9, 78.7, 86.7, 121.4, 128.1 (2C), 128.9, 132.5 (2C).

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{13}H_{13}O^+$ 185.0888 found 185.0904

Synthesis of Buta-1, 3-diyn-1-ylbenzene, 206:



To solution of 2-methyl-6-phenylhexa-3, 5-diyn-2-ol (0.5 g, 27 mmol) in toluene (180 mL), was added KOH (0.3 g, 60 mmol) in one portion. The resulting mixture was refluxed under a N_2 atmosphere overnight. Then the reaction mixture was cooled to room temperature, filtered through celite and the filtrate concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether) which furnished a colourless oil (0.3 g, 20%).

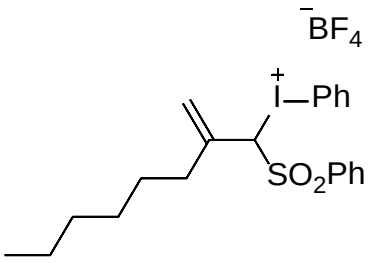
IR $_{(neat):}$ 2988 (m), 2222 (m), 1546 (s), 960 (s), 670 (s).

^{1}H NMR: δ 2.37 (1H, s), 7.30-7.48 (3H, m), 7.78 (2H, d, *J* = 7.7 Hz)

^{13}C NMR: δ 30.9, 65.5, 67.0, 72.9, 86.7, 121.4 (2C), 128.1 (2C), 128.9.

HRMS: *m*/*z* calc'd for $[M+H]^+$ C10H6$^+$ 127.0470 found 127.0470

(2-Methylene-1-(phenylsulfonyl)octyl)(phenyl)iodonium tetrafluoroborate, 193f:



To a stirred solution of diacetoxyiodobenzene (0.70 g, 2.2 mmol) in CH_2Cl_2 (20 ml) at -30 ºC was added trifluoroacetic acid (0.4 ml, 4.4 mmol) dropwise. The mixture was stirred for 30 min then warmed to room temperature and stirred for a further hour. After this it was cooled down to -30 ºC and 3-methylenenon-1-yne, **194a** (0.30 g, 2.2 mmol) was added slowly. The resulting mixture was stirred in darkness at the same temperature (-30 ºC) for 3.5 h then the solvent was removed under vacuum. The residue was dissolved in MeOH (5 mL) then added to a solution of phenylsulfinic acid (0.34 g, 2.4 mmol) in MeOH (2 mL) at 0 ºC under a N_2 atmosphere. The reaction mixture was stirred for 45 minutes then poured into saturated aqueous sodium tetrafluoroborate solution (5 mL). A white precipitate was formed which was filtered off and washed with CH_2Cl_2 (2 x 8 mL). The combined organic layers were washed with water, dried over magnesium sulfate, filtered and concentrated in vacuum. The residue was clear, colourless, viscous oil. A 1:1 mixture of diethyl ether and petroleum ether (5 + 5 mL) was added to the residue and the mixture was swirled and the solvent was removed by decantation. This process was repeated until a white solid was formed. The crude solid product was recrystallised from the minimum amount of CH_2Cl_2 with slow addition of petroleum ether. The product was isolated as a shiny grew solid (0.68 g, 56%).

Melting point: 140-141ºC.

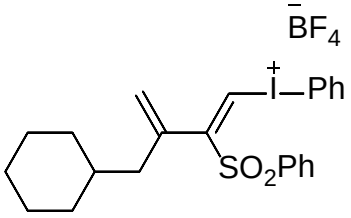
IR $_{(neat)}$: 2998 (w), 1446 (m), 1299 (s), 1077 (s), 624 (s).

^{1}H NMR: δ 0.81 (3H, t, J = 7.2 Hz), 0.92-1.27 (8H, m), 2.08 (2H, t, J = 7.5 Hz), 5.11 (1H, s), 5.21 (1H, s), 7.68 (2H, t, J = 7.7 Hz), 7.77 (2H, t, J = 7.7 Hz), 7.84 (1H, t, J = 7.6 Hz), 7.92 (1H, t, J = 7.6 Hz), 8.00 (2H, d, J = 7.8 Hz), 8.13 (1H, s), 8.38 (2H, d, J = 7.7 Hz).

^{13}C: δ 15.2, 23.2, 27.6, 29.1, 32.1, 36.6, 116.2, 116.9, 123.1, 129.9 (2C), 131.3 (2C), 133.2 (2C), 134.1, 136.8, 137.6 (2C), 137.5, 141.5, 148.0.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{22}H_{26}IO_2S^+$ 481.0698 found 481.0684.

2-(Cyclohexylmethyl)-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate, 193e:



Prepared according to the representative procedure using (2-methylenebut-3-yn-1-yl)cyclohexane, **194b** (0.33 g, 2.2 mmol), instead of 3-methylenenon-1-yne, **194a** giving the product as a white solid (1.1 g, 84%).

Melting point: 139-140 ºC.

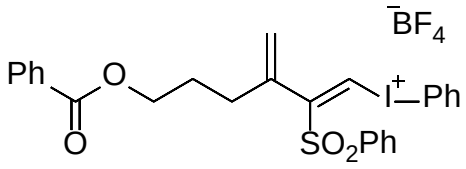
IR: 2999 (w), 1446 (m), 1305 (m), 627 (s).

^{1}H NMR: δ 0.61 (2H, q, *J* = 11 Hz), 0.93-1.15 (4H, m), 1.24 (2H, d, *J* = 13 Hz), 1.40-1.60 (3H, m), 2.02 (2H, d, *J* = 6.7 Hz), 5.18 (1H, s), 5.23 (1H, s), 7.69 (2H, t, *J* = 7.8 Hz), 7.77 (2H, t, *J* = 7.8 Hz), 7.84 (1H, t, *J* = 7.4 Hz), 7.91 (1H, t, *J* = 7.4 Hz), 8.02 (2H, d, *J* = 7.5 Hz), 8.15 (1H, S), 8.37 (2H, d, *J* = 7.5 Hz).

^{13}C NMR: δ 26.7 (2C), 27.1, 33.4, 35.5 (2C), 44.3, 116.3, 117.2, 124.5, 129.8 (2C), 131.3 (2C), 133.1 (2C), 134.1, 136.9, 137.0 (2C), 137.5, 139.8, 148.0.

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{23}H_{26}IO_2S^+$ 493.0693 found 493.0682.

(5-(Benzoyloxy)-2-methylene-1-(phenylsulfonyl)pentyl)(phenyl)iodonium tetrafluoroborate, 193h:



Prepared according to the representative procedure using (4-methylenehex-5-yn-1-yl benzoate, **195** (0.47 g, 2.2 mmol), instead of 3-methylenenon-1-yne, **194a** giving the product as a light brown wax (0.96 g, 69%).

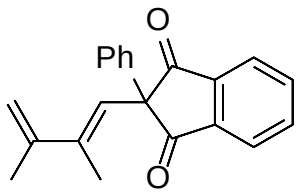
IR: 3010 (w), 1708 (m), 1052 (s), 712 (s), 449(w).

^{1}H NMR: δ 1.63 (2H, pentet, *J* = 6.6 Hz), 2.27 (2H, t, *J* = 7.2 Hz), 4.07 (2H, t, *J* = 6.0 Hz), 5.10 (1H, s), 5.30 (1H, s), 7.56 (2H, t, *J* = 7.4 Hz), 7.64-7.72 (3H, m), 7.75 (2H, t, *J* = 7.4 Hz), 7.80-7.90 (2H, m), 7.92 (2H, d, *J* = 3.7 Hz), 8.01 (2H, d, J = 3.7 Hz), 8.23 (1H, s), 8.38 (2H, d, *J* = 3.7 Hz).

^{13}C NMR : 27.0, 33.1, 65.0, 116.8, 117.0, 124.0, 130.0, 130.1 (2C), 130.4 (2C), 131.0, 131.3 (2C), 133.1 (2C), 134.2, 134.7 (2C), 136.5, 137.1, 137.6 (2C), 140.5, 147.6, 167.0

HRMS: *m*/*z* calc'd for $[M\text{-}BF_4]^+$ $C_{26}H_{24}IO_2S^+$ 559.0434 found 559.0424.

(*E*)-2-(2,3-dimethylbuta-1,3-dien-1-yl)-2-phenyl-1*H*-indene-1,3(2*H*)-dione, 208:



To stirred solution of potassium tetra-butoxide (13 mg, 0.12 mmol, 1.2 equiv) in THF (1.5 ml) was added 2-phenyl-1*H*-indene-1,3(2*H*)-dione (26 mg, 1.2 mmol, 1.2 equiv). The mixture was stirred under a N_2 atmosphere at room temperature for 1.5 h. A solution of (2-methyl-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate, **193a** (50 mg, 0.10 mmol,

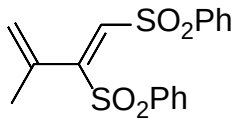
1 equiv) in THF (1.5 mL) was added to the mixture then stirred at room temperature for 24 h. Water (5 mL) was added and this was extracted with diethyl ether (3 x 5 mL) and the combined organic phase was washed with water (5 mL) and brine (4 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum.[70] The residue was purified by flash chromatography (5:1 petrolem ether/EtOAc) which furnished a colourless oil (23 mg, 76%).

IR: 2359 (s), 1221 (w), 1707 (s), 1306 (s), 528 (s).

^{1}H NMR: δ 1.83 (3H, s), 4.99 (1H, s), 5.03 (1H, s), 6.38 (1H, s), 7.23-7.37 (3H, m), 7.44-7.52 (4H, m), 7.58 (1H, t, *J* = 7.4 Hz), 7.73-7.82 (4H, m), 7.99-8.03 (2H, m).

^{13}C NMR: δ 24.3, 66.5, 121.7, 124.1, 127.8 (2C), 128.6 (2C), 128.8 (2C), 129.2, 129.8 (2C), 134.0, 135.5, 138.9 (2C), 139.2 (2C), 139.9 (2C), 140.2, 141.9, 145.8, 197.4 (2C). HRMS: *m*/*z* calc'd for $[M+Na]^+$ $C_{26}H_{20}NaO_4S^+$ 451.0975 found 451.0974.

(3-Methylbut-3-ene-1,2-diyldisulfonyl)dibenzene, 209:



To stirred solution of sodium benzenesulfinate (36 mg, 0.22 mmol, 1.1 equiv) in THF (5 mL) at 0 °C was added (2-methyl-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate, **193a** (0.10 g, 0.20 mmol, 1 equiv) then the mixture was stirred at 0 °C for 0.5 h. The resulting was extracted with diethyl ether (10 mL). The combined organic layers were washed with water (8 mL) dried over magnesium sulfate, filtered and concentrated in vacuum.[84] This was a clear, colourless, viscous oil. A 1:1 mixture of diethyl ether and petroleum ether (10 + 10 mL) was added to the residue and the mixture was swirled. The solvent was removed by decantation. This process was repeated until a white solid was formed. The crude solid

product was recrystallised from the minimum amount of CH_2Cl_2 with slow addition of petroleum ether. The product was isolated as a white solid (0.69 g, 98%).

Mp: 160-161 ^oC.

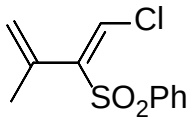
IR: 3068 (w), 1447 (m), 1149 (s), 1022 (w), 630 (s).

^1H NMR: δ 1.91 (3H, s), 4.86 (1H, s), 5.12 (1H, s), 6.81 (1H, s), 7.51-7.63 (4H, m), 7.63-7.71 (2H, m), 8.02 (2H, d, *J* = 7.8 Hz), 8.05 (2H, d, *J* = 7.8 Hz).

^{13}C NMR: δ 23.5, 123.1, 128.6 (2C), 129.6 (2C), 129.8 (2C), 129.9 (2C), 133.7, 134.9, 134.9, 136.1, 136.4, 139.8, 154.9.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{17}H_{17}O_4S_2^+$ 349.0563 found 349.0557.

(*Z*)- [(1-Chloro-3-methylbuta-1, 3-dien-2-yl)]sulfonyl)benzene, 210:



(2-Methyl-1-(phenylsulfonyl)allyl)(phenyl)iodonium tetrafluoroborate, **193a** (0.050 g, 0.10 mmol, equiv) was dissolved in DMSO (0.5 mL) at room temperature. HCl (2 N, 50 µL) was added and the mixture was stirred overnight. Brine (5 mL) was added to the mixture and the solution was shaken. This was extracted with ethyl acetate (10 mL) and washed with water (5 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by flash chromatography (20:1 petrolem ether/EtOAc) which furnished a colourless oil (0.023 g, 91%).

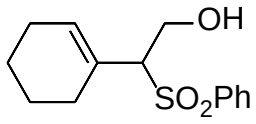
IR $_{(neat)}$: 1558 (s), 1221 (w), 1154 (s), 1120 (s), 862 (s).

^1H NMR: δ 2.07 (3H, s), 4.95 (1H, s), 5.18 (1H, s), 7.65 (1H, s), 7.54 (2H, t, *J* = 7.7 Hz), 7.65 (1H, t, *J* = 7.3 Hz), 7.98 (2H, d, *J* = 7.7 Hz).

^{13}C NMR: δ 23.5, 121.6, 127.6, 128.6 (2C), 129.2 (2C), 134.1, 140.1, 140.5, 148.1.

HRMS: *m*/*z* calc'd for $[M+H]^+$ $C_{11}H_{12}ClO_2S^+$ 243.0241 found 243.0240.

2-(Cyclohex-1-en-1-yl)-2-(phenylsulfonyl)ethan-1-ol, 211:



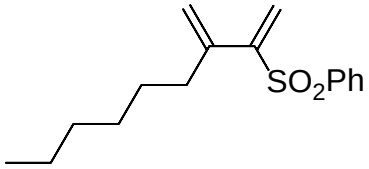
(Cyclohex-1-en-1-yl(phenylsulfonyl)methyl)(phenyl)iodonium tetrafluoroborate, **193b** (0.050 g, 0.10 mmol, 1 equiv) was dissolved in DMSO (0.5 mL) at room temperature. Deionised water (20 µL) was added and the mixture was stirred overnight. Water (2.5 mL) was added to the mixture and the solution was shaken. This was extracted with ethyl acetate (5 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum. The product was used in next step as dissolved in methanol (2 mL) and LiBH4 (2 mg, 0.1 mmol, 1 equiv) was added in one portion and the mixture was stirred overnight. The resulting was extracted with diethyl ether (5 mL) and washed with water (5 mL). The residue was purified by flash chromatography (5:1 petroluem ether/EtOAc) which furnished a colourless oil (0.018 g, 66%).

^{1}H NMR: δ 1.31-1.59 (4H, m), 1.72-1.89 (2H, m), 1.90-2.05 (2H, m), 2.79 (1H, dd, *J* = 9.0, 4.3 Hz), 3.69 (1H, dd, *J* = 8.0, 5.0 Hz), 3.90 (1H, ddd, *J* = 13, 9.2, 4.8 Hz), 4.30 (1H, ddd, *J* = 12, 8.0, 4.3 Hz), 5.36-5.38 (1H, s), 7.55 (2H, t, *J* = 7.5 Hz), 7.67 (1H, t, *J* = 7.2 Hz), 7.84 (2H, d, *J* = 7.5 Hz).

^{13}C NMR: δ 21.9, 22.9, 25.9, 27.8, 60.6, 128.9, 129.2 (2C), 129.5 (2C), 132.7, 134.2, 137.5.

HRMS: *m*/*z* calc'd for $[M+Na]^+$ $C_{14}H_{18}O_3SNa^+$ 289.0869 found 289.0870.

((3-methylenenon-1-en-2-yl)sulfonyl)benzene, 212:



To stirred solution of (2-methylene-1-(phenylsulfonyl)octyl)(phenyl)iodonium tetrafluoroborate, **207a** (70 mg, 0.12 mmol, 1 equiv) in methanol (5 mL) at room temperature was added sodium borohydried (0.09 g, 0.24 mmol, 2 equiv) in small portions. The mixture was reflux for 1 h after cooling to room temperature. Water (3 mL) was added and the mixture was stirred for further 10 min. This was extracted with CH_2Cl_2 (3 x 5 mL) and the organic layer was dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum.[52] The residue was purified by flash chromatography (5:1 petrolem ether/EtOAc) which furnished two compounds in different fractions. The first product was isolated as light brown oil (43 mg, 52%).

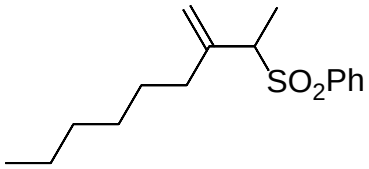
IR $_{(neat)}$: 3068 (w), 1447 (m), 1149 (s), 1022 (w), 630 (s).

^{1}H NMR: δ 0.83 (3H, t, *J* = 7.3 Hz), 1.04-1.30 (8H, m), 2.16 (2H, t, *J* = 7.3), 5.05 (1H, s), 5.15 (1H, s), 5.83 (1H, s), 6.47 (1H, s), 7.49 (2H, t, *J* = 7.4 Hz), 7.58 (1H, t, *J* = 7.4 Hz), 7.82 (2H, d, *J* = 7.7 Hz).

^{13}C NMR: δ 14.4, 22.9, 27.7, 28.9, 31.9, 36.4, 119.5, 125.3, 128.8 (2C), 129.2 (2C), 133.7, 139.4, 141.4, 151.3.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{16}H_{26}NO_2S^+$ 296.1679 found 296.1680.

[(3-Methylenenonan-2-yl)sulfonyl)]benzene, 213:



This compound was isolated as a colourless oil (11 mg, 25%)

IR $_{(neat):}$ 3111 (w), 1487 (m), 1150 (s), 1102 (w), 635 (s).

^{1}H NMR: δ 0.87 (3H, t, *J* = 7.3 Hz), 1.19-1.39 (8H, m), 1.47 (3H, d, *J* = 6.9 Hz), 2.03 (2H, t, *J* = 7.6 Hz), 3.67 (1H, q, *J* = 7.1 Hz), 4.94 (1H, s), 5.05 (1H, s), 7.52 (2H, t, *J* = 7.4 Hz), 7.63 (1H, t, *J* = 7.4 Hz), 7.84 (2H, d, *J* = 7.9 Hz).

^{13}C NMR: δ 14.4, 14.6, 22.9 (2C), 29.2, 32.0 (2C), 35.8, 66.0, 117.2, 129.1(2C), 129.8 (2C), 133.8, 143.4. 2.

HRMS: *m*/*z* calc'd for $[M+NH_4]^+$ $C_{16}H_{28}NO_2S^+$ 298.1835 found 298.1834.

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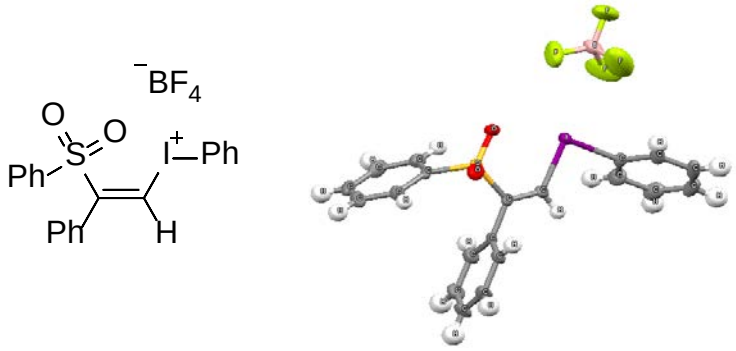
Appendix

X-Ray crystallographic data of 180a:



Bond precision: C-C = 0.0113 A Wavelength=0.71073

Cell: a=8.3212(5) b=12.9582(8) c=19.3261(13)

Alpha=90 beta=90 gamma=90

Temperature: 150 K

Calculated Reported

Volume 2083.9(2) 2083.9(2)

Space group P 21 21 21 P 21 21 21

Hall group P 2ac 2ab P 2ac 2ab

Moiety formula C20 H16 I O2 S, B F4?

Sum formula C20 H16 B F4 I O2 S C20 H16 B F4 I O2 S

Mr 534.10 534.10

Dx,g cm-3 1.702 1.702

Z 4 4

Mu (mm-1) 1.685 1.685

F000 1048.0 1048.0

F000’ 1047.17

h,k,lmax 12,19,29 12,19,29

Nref 7957[4443] 7472

Tmin,Tmax 0.721,0.845 0.770,0.880

Tmin’ 0.707

Correction method= # Reported T Limits: Tmin=0.770 Tmax=0.880

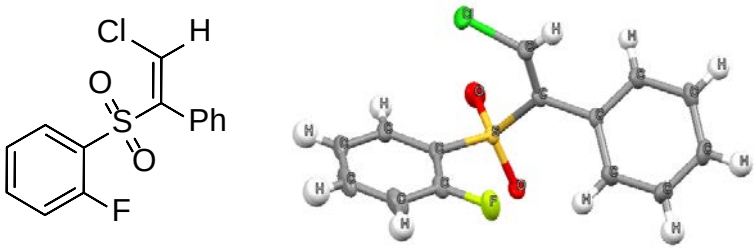
AbsCorr = MULTI-SCAN

Data completeness= 1.68/0.94 Theta (max) = 33.173

R (reflections) = 0.0585(5842) wR2 (reflections) = 0.1299(7472)

S = 1.046 Npar= 262

X-Ray crystallographic data of 183c:



No errors found in this datablock

Bond precision: C-C = 0.0032 A Wavelength=0.71073

Cell: a=6.7055(4) b=16.7598(10) c=11.9970(7)

Alpha=90 beta=105.0779(19) gamma=90

Temperature: 150 K

Calculated Reported

Volume 1301.84(13) 1301.84(13)

Space group P 21/n P 21/n

Hall group -P 2yn -P 2yn

Moiety formula C14 H10 Cl F O2 S?

Sum formula C14 H10 Cl F O2 S C14 H10 Cl F O2 S

Mr 296.73 296.73

Dx,g cm-3 1.514 1.514

Z 4 4

Mu (mm-1) 0.459 0.459

F000 608.0 608.0

F000’ 609.38

h,k,lmax 9,23,17 9,24,17

Nref 4008 3979

Tmin,Tmax 0.955,0.955 0.770,0.880

Tmin’ 0.955

Correction method= # Reported T Limits: Tmin=0.770 Tmax=0.880

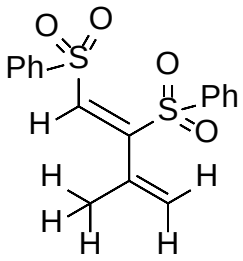
AbsCorr = MULTI-SCAN

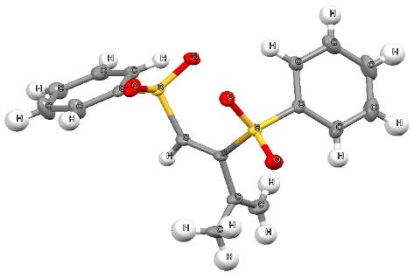
Data completeness= 0.993 Theta (max) = 30.589

R (reflections) = 0.0560(2974) wR2 (reflections) = 0.1284(3979)

S = 1.055 Npar= 172

X-Ray crystallographic data of 210:





Bond precision: C-C = 0.0041 A Wavelength=1.54178

Cell: a=8.3260(3) b=26.7042(9) c=15.1072(5)

Alpha=90 beta=103.7899(11) gamma=90

Temperature: 150 K

Calculated Reported

Volume 3262.11(19) 3262.11(19)

Space group C 2/c C 2/c

Hall group -C 2yc -C 2yc

Moiety formula C17 H16 O4 S2?

Sum formula C17 H16 O4 S2 C17 H16 F0 O4 S2

Mr 348.42 348.42

Dx,g cm-3 1.419 1.419

Z 8 8

Mu (mm-1) 3.113 3.113

F000 1456.0 1456.0

F000’ 1465.27

h,k,lmax 10,32,18 10,32,18

Nref 3226 3202

Tmin,Tmax 0.600,0.732 0.770,0.880

Tmin’ 0.511

Correction method= # Reported T Limits: Tmin=0.770 Tmax=0.880

AbsCorr = MULTI-SCAN

Data completeness= 0.993 Theta (max) = 72.119

R (reflections) = 0.0571(2913) wR2 (reflections) = 0.1594(3202)

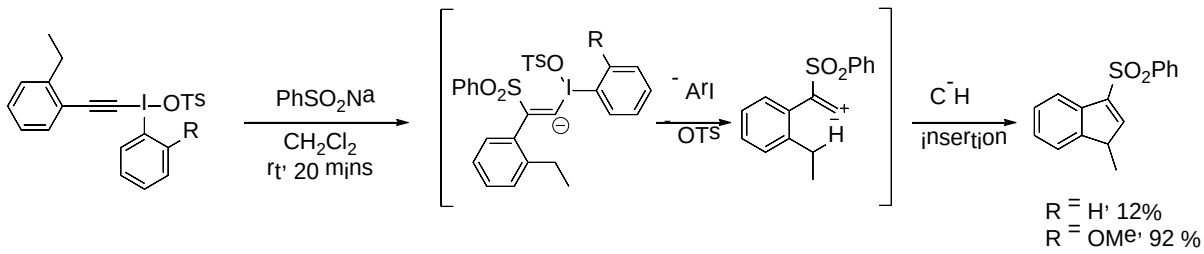
S = 1.054 Npar= 209

Chapter 2: Computational study

1. Computational study of alkynyl(aryl)iodonium salts.

As discussed in the previous chapter our initial aim for this study was to synthesise new alkynyl(aryl)iodonium salts bearing terminal heteroatom substituents on the alkynyl moiety as there are a lack of known examples which limits their synthetic applicability.

Hamnett and Moran,[1] investigated the difference in reactivity and stability of alkynyl(aryl)iodonium salts derived from different aryl iodoarenes. For example, the addition-C-H insertion reaction of benzenesulfinic sodium salt to 1-ethyl-2-ethynylbenzene(aryl)iodonium tosylate proceeds in excellent yield with the 2-anisyl derivative but in low yield using the phenyl analogue (Scheme 1).



Scheme 1

They obtained an X-ray crystal structure of 1-ethyl-2-ethynylbenzene(2-anisyl)iodonium tosylate which suggests that there is an interaction between the oxygen atom of the methoxy and the iodine(III) centre. They suggested that this increases the stability of the intermediate and reduces the probability of decomposition resulting in a higher yield of product .We were interested in investigating this assumption using computational chemistry techniques.

1.1 Computational details.

The *ab initio* computations for this work were performed using the quantum chemistry package Gaussian09 D. 01. which represents further development of the other types of Gaussian. All calculations were carried out with density functional theory (DFT) using 3-21G in dichloromethane as solvent. All compounds under study were fully optimized at the B3LYP/LANL2DZ level of theory utilizing Gaussian 09 suite of programs. A 3-21G basis set

was used for the iodine atom. Frequency calculations were carried out at the same level of theory.[2]

2. Aim

A computational study was proposed to help rationalise the different observed stabilities and reactivities of a range of λ^3-iodanes and to inform the structural and electronic requirements for the construction of new, stable salts.

Objective 1: Model several alkynyliodonium salts and compare their HOMO and LUMO orbital diagrams and the charge on the alkyne β-carbon

Objective 2: Correlate results with observed stability and reactivity

3. Results and discussion

As a consequence of our difficulties in preparing new alkynyl(aryl)ioddonium salts (detailed earlier) we decided to investigate the stability of known alkynyl(aryl)iodonium salts with computational chemistry. In this way we hoped to rationalise the different observed stabilities and reactivities of a range of alkynyl(aryl)iodonium salts in order to inform the structural and electronic requirements for the construction of new stable salts. Initially, we decided to model five λ^3-iodanes (i, ii, iii, iv and v): the phenyl, 2-anisyl, 4-anisyl, 4-nitrophenyl analogues and the cyclic benziodoxolone (Figure 1). We chose these salts to determine the effect of modifying the electronic properties of the aryl ring. Experimentally, we observed that the 4-anisyl derivative was unstable and led to low yields of products in several reactions, whereas the 2-anisyl salt was superior in every respect. Therefore, simple electronic arguments for stability are not valid. The 4-nitro analogue was chosen to see what effect an electron-

withdrawing group has compared to a methoxy. Benziodoxolones are more stable than acyclic salts, and we hoped to understand why this is the case.

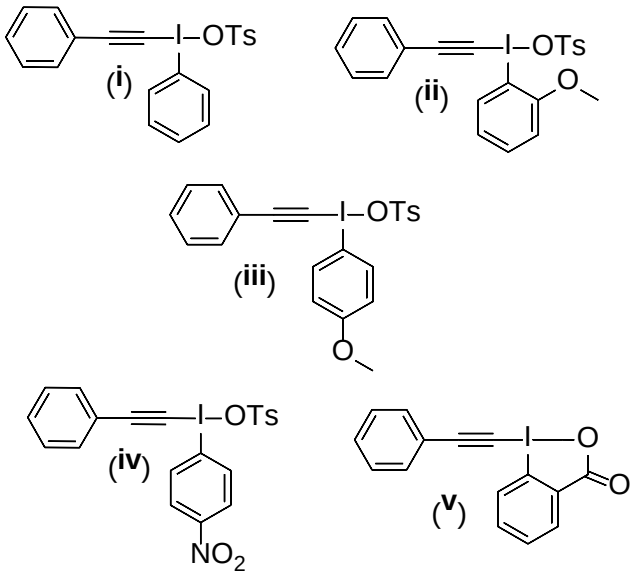
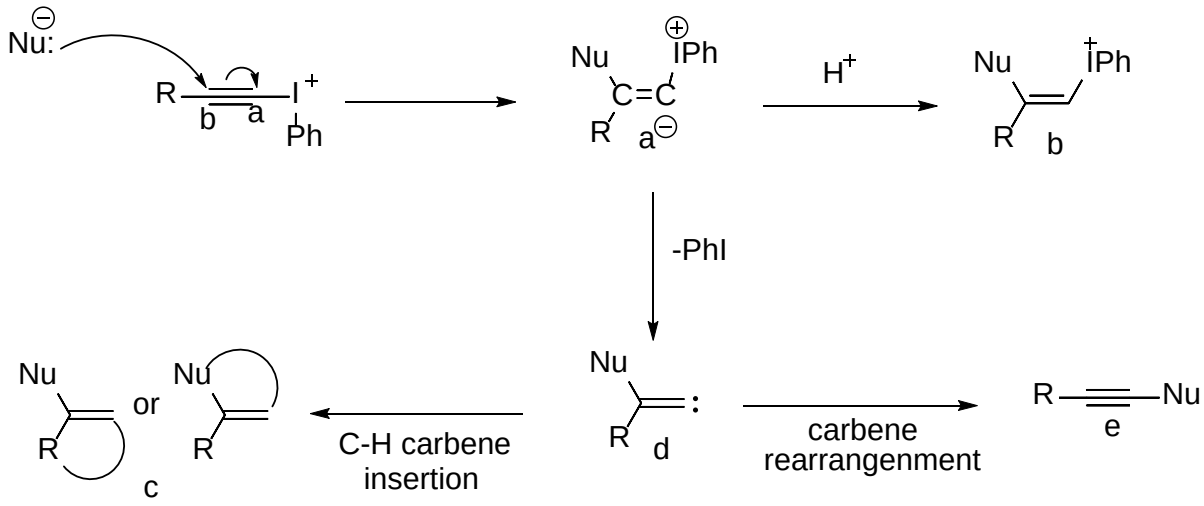


Figure 1

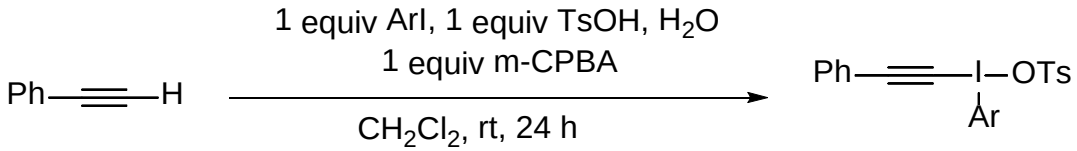
The reactivity patterns of alkynyliodonium salts are classified as electrophilic acetylenes in organic reactions. Due to the strong electron-withdrawing nature of the iodonium group these compounds are highly reactive in Diels-Alder cycloadditions and Michael-type conjugate addition. The different products obtained by attack of nucleophiles on alkynyliodonium salts are shown (Scheme 2).[3]



Scheme 2

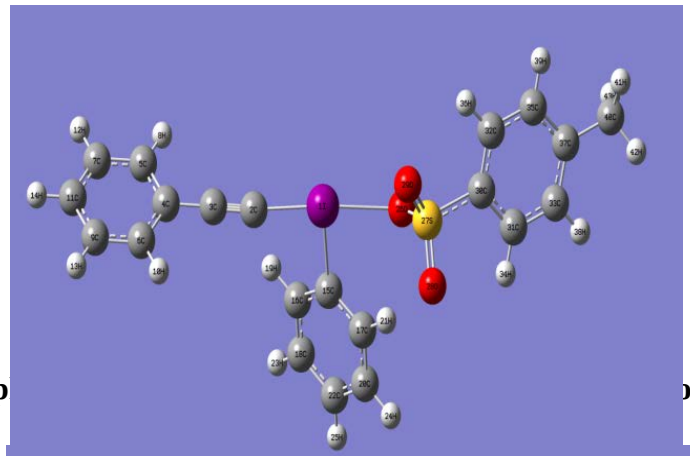
3.1 Phenylacetylene(aryl)iodonium tosylates.

Hamnett and Moran reported the preparation of several analogues of these salts based on the method reported by Olofsson. This involved their direct synthesis from terminal alkynes and aryl iodides using *m*-chloroperbenzoic acid and 4-toluenesulfonic acid in CH_2Cl_2 (Scheme 3).[4]

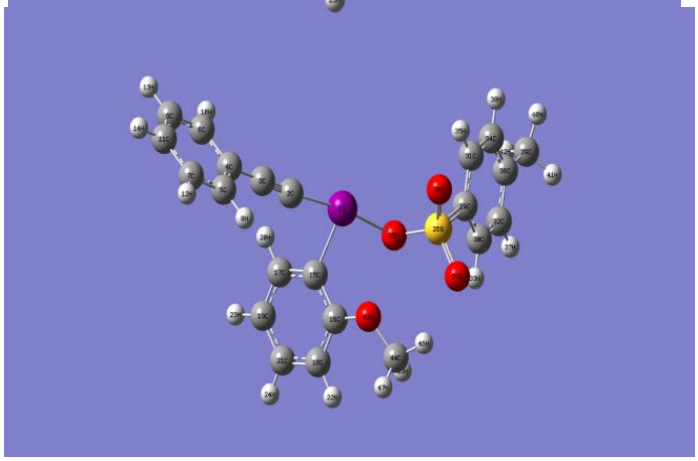


Scheme 3

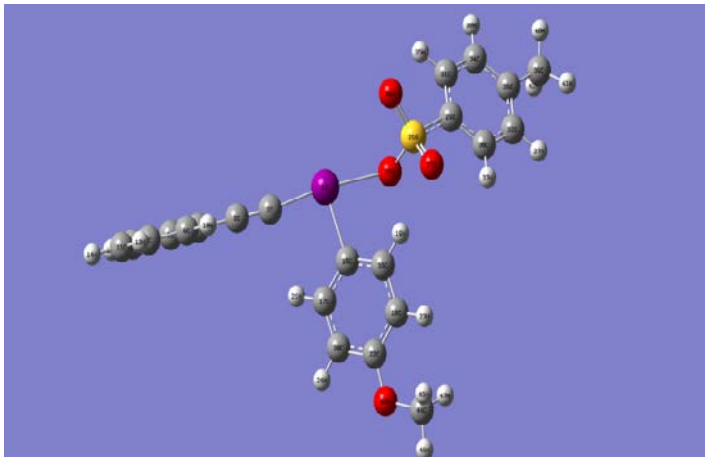
Phenyl(phenylethynyl)-iodanyl 4-methylbenzenesulfonate (i).



3.1.1 2-Methoxyp onate (ii).

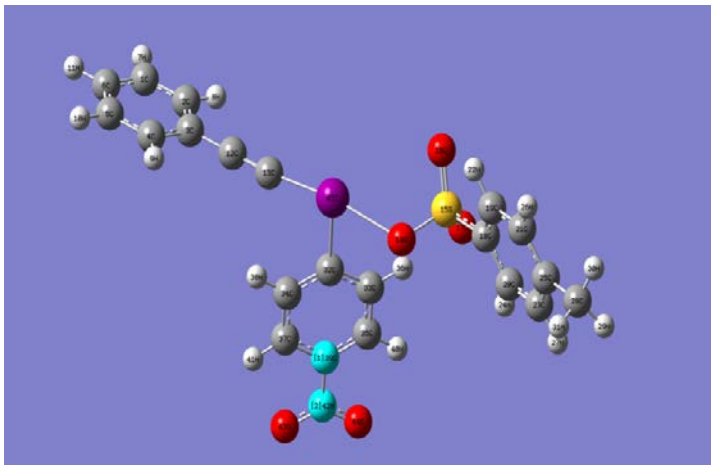


3.1.2 4-Methoxyphenyl)(phenylethynyl)-iodanyl 4-methylbenzenesulfonate (iii).



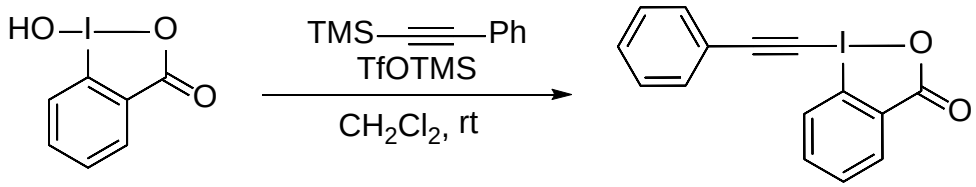
3.1.3 4-Nitrophenyl)(phenylethynyl)-l3-iodaneyl and 4-methylbenzenesulfonate (iv).

.

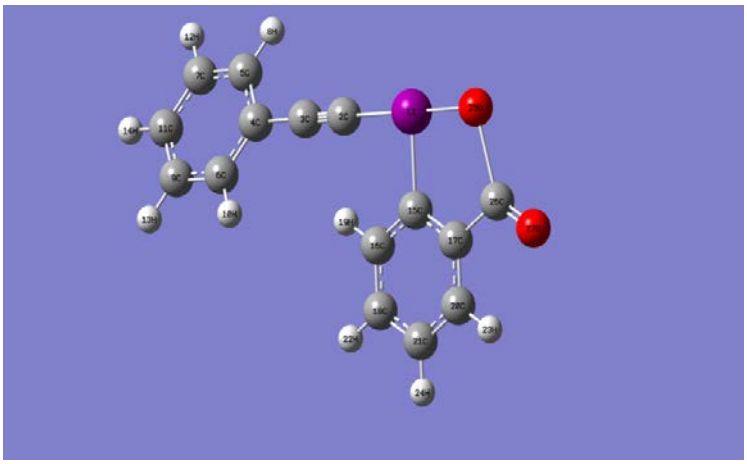


3.2 1-(Phenylethynyl)-λ^3-benzo[d][1,2]iodaoxol-3(1H)-one (v).

This type of λ^3-iodane generally can be synthesised by the method that is reported by Costanzo and co-workers, utilizing trimethylsilyl triflate and 2-iodosylbenzoic acid in CH_2Cl_2 at room temperature (Scheme 4).[5]

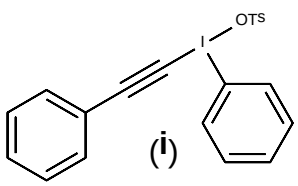


Scheme 4

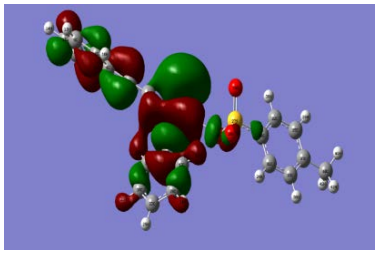


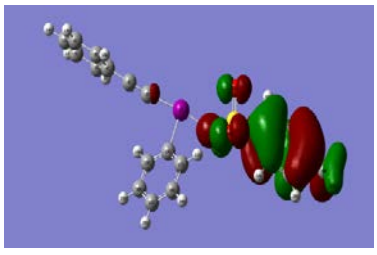
3.3 Comparison of the salts reactivity.

A. HOMO and LUMO orbitals:



(**i**)





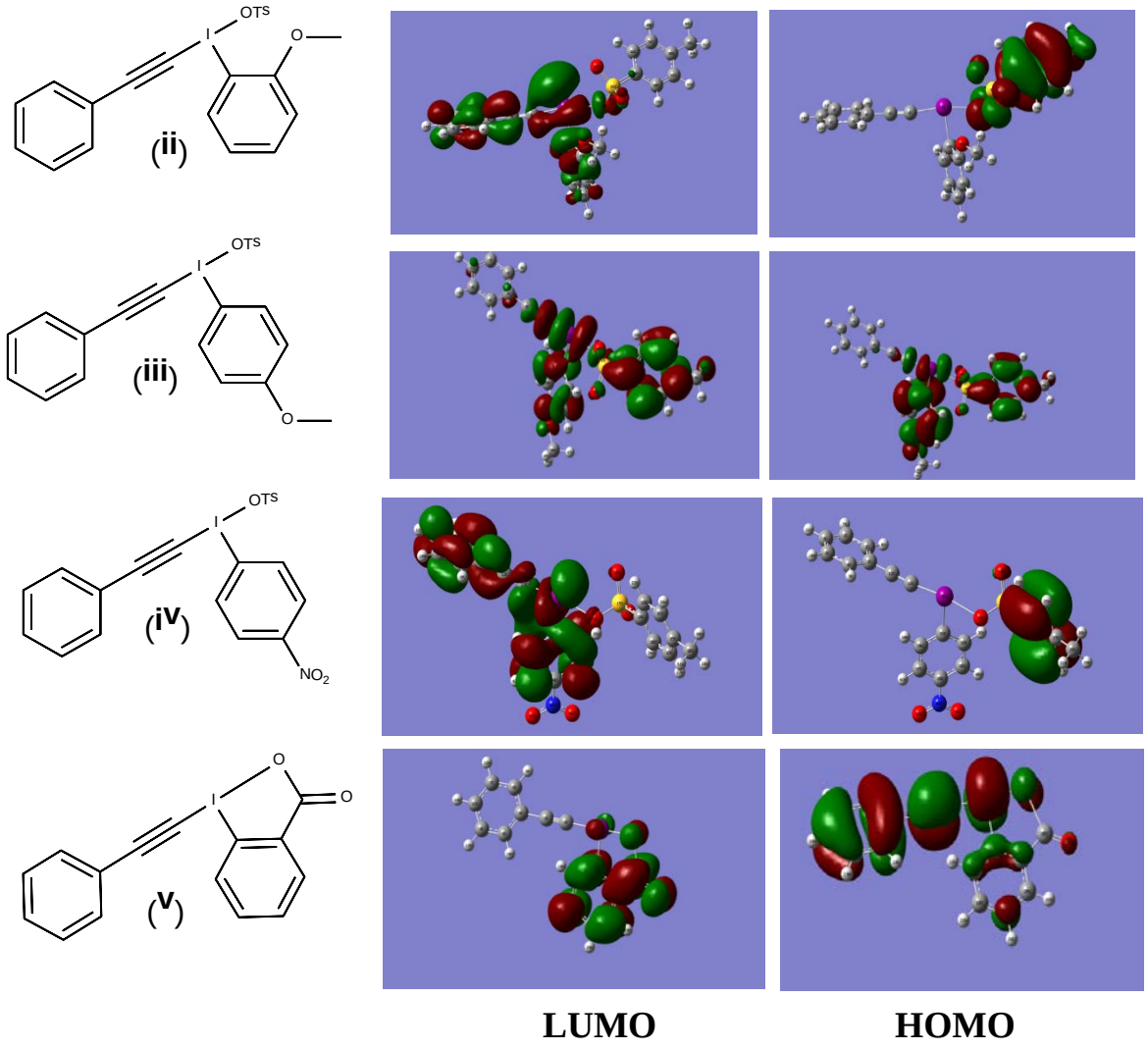


Figure 2

These results show the different HOMO and LUMO diagrams of the five λ^3-iodanes. It can be seen that the orbitals of iodonium salt (**i**) look very similar to (**ii**) but there is a big difference between salts (**i**) and (**iii**) and (**iv**) this may explain why salts (**iii**) and (**iv**) display poor reactivity. Iodane (**v**) also has completely different HOMO and LUMO orbitals to (**i**) and (**ii**) (Figure 2).

As mentioned above alkynyliodonium salts are electrophilic. In general a lower LUMO energy makes compounds more reactive toward nucleophiles. The results of this study show that the iodane with the lowest LUMO energy is 2-methoxyphenyl)(phenylethynyl)-iodany

methylbenzenesulfonate (**ii**). Next is phenyl(phenylethynyl)-iodanyl 4-methylbenzenesulfonate (**i**) then 4-methoxyphenyl)(phenylethynyl)-iodanyl 4-methylbenzenesulfonate (**iii**), 4-nitrophenyl)(phenylethynyl)-l3-iodaneyl and 4-methylbenzenesulfonate (**iv**) and iodane (**v**), Table 1.

Iodane	HOMO energy eV	LUMO energy eV
i	-6.326	-2.184
ii	-6.176	-2.306
iii	-6.288	-2.019
iv	-8.901	-1.419
V	-6.844	-1.483

Table 1

B. Atomic charge of *β*-carbon.

According to the postulated reaction mechanism with nucleophiles, nucleophiles must be able to attack the *β*-carbon atom to the iodine. It seems reasonable to assume that the larger the partial charge on the *β*-carbon, the more reactive it is towards nucleophiles. The result shows that iodane (**ii**) has the largest charge on the *β*-carbon, which is consistent with the observed reactivity, Table 2.

Iodane	Alkynyl *β*-carbon charge
ii	+0.096

i	+0.086
iii	+0.081
V	+0.061
iv	+0.060

Table 2

In summary, with this study we have shown that Gaussian 09 can be used to successfully model the types of compounds shown in Fig 1. Using DFT 3-21G in dichloromethane as solvent, the five λ^3-iodane in (Figure 1) were modelled. The atomic charge on the alkyne carbon beta to the iodine in the salts was interesting. This is the site where nucleophiles attack these salts and this relationship corresponds to the yields of several reactions that have been studied, i.e. greatest for 2-anisyl then phenyl then 4-anisyl. The HOMO and LUMO diagrams also show major differences. It seems that the LUMO must be similar to salt (**i**) for efficient reactions to occur.

4. Data

Cartesian Coordinates of all Stationary Points Found in the Potential Energy Surface of the Iodonium Ylides (B3LYP/LANL2DZ).

Iodane (**i**):

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	I	0	-0.531480	-0.024842	-0.459194
2	C	0	-2.555194	-0.330264	-0.089633
3	C	0	-3.706668	-0.684879	0.087589
4	C	0	-5.055421	-1.095174	0.302005
5	C	0	-5.525992	-1.343808	1.606546
6	C	0	-5.932011	-1.256691	-0.789213
7	C	0	-6.844265	-1.741529	1.809941
8	H	0	-4.849417	-1.222330	2.445999
9	C	0	-7.247779	-1.657472	-0.575263
10	H	0	-5.568459	-1.067542	-1.793783
11	C	0	-7.707065	-1.899038	0.722087
12	C	0	-7.199473	-1.930855	2.818295
13	H	0	-7.916392	-1.781733	-1.421590
14	H	0	-8.734305	-2.211108	0.884882
15	C	0	-0.699166	2.118360	0.083851
16	C	0	-1.970753	2.656292	0.206040
17	C	0	0.469355	2.839671	0.281659
18	C	0	-2.072313	4.007260	0.553031
19	H	0	-2.858741	2.055760	0.046679
20	C	0	0.335126	4.189112	0.627821

21	H	0	1.440303	2.379174	0.154759
22	C	0	-0.924690	4.771566	0.764320
23	H	0	-3.057665	4.452292	0.653451
24	H	0	1.233034	4.778045	0.788628
25	H	0	-1.012729	5.819735	1.032816
26	O	0	1.787081	0.537957	-0.775401
27	S	0	2.590399	-0.629332	-1.411398
28	O	0	3.141503	-0.249193	-2.718110
29	O	0	1.765770	-1.859354	-1.335546
30	C	0	3.976351	-0.836596	-0.288242
31	C	0	5.117049	-0.048785	-0.451925
32	C	0	3.902885	-1.774357	0.741560
33	C	0	6.181927	-0.196425	0.434293
34	H	0	5.170371	0.651192	-1.278660
35	C	0	4.978067	-1.912510	1.618871
36	H	0	3.021380	-2.399536	0.831760
37	C	0	6.129031	-1.124146	1.485103
38	H	0	7.074032	0.410998	0.302879
39	H	0	4.926288	-2.651067	2.415061
40	C	0	7.278366	-1.258309	2.456521
41	H	0	7.323719	-2.262761	2.887145
42	H	0	8.237753	-1.052255	1.972732
43	H	0	7.176480	-0.551033	3.289275

Iodane (**ii**):

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	I	0	-0.459299	-0.388162	-0.251132
2	C	0	-2.477436	-0.808281	-0.093352
3	C	0	-3.653206	-1.105857	-0.078522
4	C	0	-5.051626	-1.383372	0.033297
5	C	0	-5.966626	-0.867878	-0.911375
6	C	0	-5.553847	-2.174270	1.090497
7	C	0	-7.326061	-1.136047	-0.800866
8	H	0	-5.587757	-0.258747	-1.727241
9	C	0	-6.914737	-2.438447	1.193042
10	H	0	-4.856779	-2.573186	1.822098
11	C	0	-7.806065	-1.921714	0.249569
12	H	0	-8.013984	-0.731367	-1.538283
13	H	0	-7.282009	-3.050051	2.012704
14	H	0	-8.869034	-2.130282	0.332783
15	C	0	-0.659732	1.421091	0.870051
16	C	0	-0.852518	2.594272	0.129520
17	C	0	-0.560511	1.392092	2.249790
18	C	0	-0.964125	3.786274	0.871341
19	C	0	-0.678720	2.592889	2.962746

20	H	0	-0.390096	0.457904	2.772245
21	C	0	-0.879456	3.778889	2.265853
22	H	0	-1.110455	4.719329	0.344686
23	H	0	-0.605281	2.589018	4.045462
24	H	0	-0.966748	4.717097	2.808325
25	O	0	1.739662	0.472797	-0.231119
26	S	0	2.647785	-0.009645	-1.330937
27	O	0	3.182706	1.077123	-2.188205
28	O	0	2.071573	-1.220676	-1.991426
29	C	0	4.108361	-0.628403	-0.440081
30	C	0	5.112198	0.269057	-0.088712
31	C	0	4.188735	-1.979484	-0.124462
32	C	0	6.216423	-0.206989	0.617831
33	H	0	5.032514	1.312110	-0.379183
34	C	0	5.303055	-2.437286	0.581792
35	H	0	3.402955	-2.656163	-0.446389
36	C	0	6.325818	-1.560933	0.966881
37	H	0	7.010934	0.483738	0.894312
38	H	0	5.381385	-3.494798	0.827497
39	C	0	7.515246	-2.059405	1.752777
40	H	0	7.712983	-3.116632	1.547069
41	H	0	8.418185	-1.488310	1.511849
42	H	0	7.345589	-1.961498	2.833093
43	O	0	-0.917852	2.510036	-1.202761
44	C	0	-1.076259	3.723745	-1.926934

45	H	0	-0.221737	4.388304	-1.755720
46	H	0	-1.124771	3.469747	-2.984330
47	H	0	-1.999761	4.236786	-1.631993

Iodane (**iii**):

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	I	0	-0.541072	-0.744712	-0.254286
2	C	0	-2.603046	-0.897018	-0.012230
3	C	0	-3.795207	-1.088205	0.120609
4	C	0	-5.192325	-1.278632	0.295913
5	C	0	-5.671633	-2.393315	1.006175
6	C	0	-6.107106	-0.354544	-0.239363
7	C	0	-7.041265	-2.576638	1.174390
8	H	0	-4.964239	-3.106718	1.418382
9	C	0	-7.474714	-0.543853	-0.061755
10	H	0	-5.735195	0.504908	-0.789177
11	C	0	-7.945890	-1.653830	0.643575
12	H	0	-7.403204	-3.441867	1.722881
13	H	0	-8.174724	0.175917	-0.477058
14	H	0	-9.014138	-1.799621	0.778306

15	C	0	-0.642245	1.396355	-0.061244
16	C	0	-0.510076	2.164531	-1.212200
17	C	0	-0.814064	1.946427	1.202929
18	C	0	-0.563301	3.552203	-1.084638
19	H	0	-0.355090	1.708265	-2.183249
20	C	0	-0.864309	3.336117	1.314377
21	H	0	-0.904056	1.322981	2.085478
22	C	0	-0.742315	4.135972	0.174265
23	H	0	-0.476074	4.188336	-1.960454
24	H	0	-1.005220	3.808867	2.281682
25	O	0	1.678058	-0.093635	-0.797353
26	S	0	2.571977	-1.239959	-1.317981
27	O	0	3.009259	-0.991810	-2.702121
28	O	0	1.893727	-2.529840	-1.022272
29	C	0	4.035901	-1.147265	-0.270426
30	C	0	5.066186	-0.269237	-0.607125
31	C	0	4.124033	-1.943912	0.869738
32	C	0	6.185934	-0.181654	0.218305
33	H	0	4.993948	0.316452	-1.518151
34	C	0	5.251903	-1.847955	1.685415
35	H	0	3.327272	-2.646613	1.091800
36	C	0	6.294056	-0.962845	1.378075
37	H	0	6.994899	0.496121	-0.046384
38	H	0	5.328634	-2.477358	2.569609
39	C	0	7.498581	-0.842172	2.280516

40	H	0	7.681521	-1.771108	2.830750
41	H	0	8.402720	-0.600427	1.711559
42	H	0	7.357739	-0.044598	3.022686
43	O	0	-0.841759	5.499696	0.293599
44	C	0	0.408579	6.190882	0.325438
45	H	0	0.983736	6.022954	-0.592485
46	H	0	0.172948	7.251176	0.415071
47	H	0	1.013356	5.877653	1.184369

Iodane (**iv**):

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	C	0	7.248276	-1.807042	-1.181468
2	C	0	5.880774	-1.551122	-1.136967
3	C	0	5.178957	-1.669521	0.078780
4	C	0	5.874233	-2.051168	1.242685
5	C	0	7.241657	-2.306035	1.187342
6	C	0	7.931042	-2.183871	-0.021944
7	H	0	7.782527	-1.713109	-2.121889
8	H	0	5.343762	-1.259568	-2.033422
9	H	0	5.332898	-2.144689	2.178385

10	H	0	7.770936	-2.600409	2.088420
11	H	0	8.997764	-2.382977	-0.060768
12	C	0	3.778362	-1.407183	0.126389
13	C	0	2.584188	-1.174507	0.162993
14	O	0	-1.796521	-0.512716	0.253294
15	S	0	-2.659994	-0.833479	-1.001121
16	O	0	-2.310489	-2.160040	-1.533337
17	O	0	-2.623564	0.310946	-1.934848
18	C	0	-4.313735	-0.921138	-0.326128
19	C	0	-4.753082	-2.109822	0.260797
20	C	0	-5.151106	0.192294	-0.386858
21	C	0	-6.035522	-2.172546	0.799533
22	H	0	-4.102680	-2.977736	0.270585
23	C	0	-6.432915	0.113840	0.155345
24	H	0	-4.801412	1.096859	-0.872188
25	C	0	-6.893421	-1.063242	0.761451
26	H	0	-6.380836	-3.100395	1.248429
27	H	0	-7.089423	0.978358	0.099767
28	C	0	-8.272535	-1.132878	1.372872
29	H	0	-8.958398	-0.426694	0.896504
30	H	0	-8.700197	-2.135847	1.282897
31	H	0	-8.242333	-0.887820	2.441940
32	C	0	0.677685	1.160324	0.165489
33	C	0	-0.230168	1.894235	-0.583185
34	C	0	1.714289	1.714818	0.905052

35	C	0	-0.072785	3.282300	-0.594111
36	H	0	-1.041132	1.429611	-1.134911
37	C	0	1.852916	3.101835	0.894269
38	H	0	2.407506	1.099396	1.465309
39	C	0	0.958424	3.858203	0.141815
40	H	0	-0.740865	3.909891	-1.170400
41	H	0	2.636838	3.594533	1.455177
42	N	0	1.113784	5.325704	0.125872
43	O	0	2.038120	5.803716	0.780992
44	O	0	0.320233	5.970616	-0.554387
45	I	0	0.508170	-1.025103	0.167253

Iodane (**v**):

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	I	0	1.055080	-1.380800	-0.068716
2	C	0	-0.969684	-0.824182	-0.046188
3	C	0	-2.127849	-0.505797	-0.033302
4	C	0	-3.612676	-0.097611	-0.016781
5	C	0	-4.574353	-0.983897	0.469165
6	C	0	-3.996123	1.158148	-0.487512
7	C	0	-5.919229	-0.614683	0.483713

8	H	0	-4.271817	-1.974134	0.839496
9	C	0	-5.341254	1.528006	-0.472114
10	H	0	-3.238281	1.856871	-0.870383
11	C	0	-6.302811	0.641803	0.013261
12	H	0	-6.677363	-1.313451	0.866144
13	H	0	-5.643242	2.518339	-0.842947
14	H	0	-7.363250	0.932715	0.024885
15	C	0	1.612112	0.641128	0.038642
16	C	0	0.632143	1.632972	0.087374
17	C	0	2.961758	0.992539	0.061342
18	C	0	1.001829	2.975936	0.158109
19	H	0	-0.431802	1.355639	0.068685
20	C	0	3.331721	2.335815	0.133091
21	C	0	2.352043	3.327501	0.181337
22	H	0	0.229465	3.757807	0.195890
23	H	0	4.395933	2.612568	0.151389
24	H	0	2.643286	4.386442	0.237170
25	O	0	2.973785	-1.908261	-0.090064
26	C	0	4.043646	-0.102108	0.007812
27	O	0	5.262487	0.210282	0.028054

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