Metal-free Trans-imination Using Iminoiodane

A Thesis

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# ABSTRACT

Imino-$\lambda^3$-iodanes are useful nitrene precursors and effective oxidants in the reactions with various organic substrates. Most of the known reactions of imino-$\lambda^3$-iodanes are carried in the presence of transition metal catalysts, required for the in-situ generation of active metal-nitrenoid species. Recently, several groups have reported the aziridination of olefines, C-H amination of alkanes, and imination of aldehydes using imino-$\lambda^3$-iodanes under metal-free conditions. However, the imination of sulfides using imino-$\lambda^3$-iodanes under metal-free condition is still unknown. Herein, we report the new reaction of metal-free trans-imination reaction of sulfides using imino-$\lambda^3$-iodanes in the presence of catalytic amounts of elemental iodine. The trans-imination reactions of various alkyl or aryl sulfides proceed at room temperature to give the corresponding sulfilimines in low to good yields. The reaction of allyl sulfides under similar conditions proceeds as [2,3]-sigmatropic rearrangement to give the corresponding allyl sulfonamides in good yields. The same condition using triphenyl phosphine instead of sulfides produced iminophosphorane in good yield, and the product was confirmed by X-ray crystallography.

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# Chapter 1

## 1.1 Introduction

Sulfur compounds including sulfur-heteroatom ylides are well known for many

reactions as important reagents[1-5].  Hypervalent iodine (III) compounds are

commonly known to be strong oxidants due to their high leaving group ability and

also their high electron-withdrawing ability.  The basic reaction involves the I(III)

reacting with a substrate to oxidize the compound to the product while reducing

down to I(I) compound.  Another type of reaction involves ligand transfer which is

the focus on this thesis.  Some common iodine (III) reagents include (diacetoxyiodo)

benzene, hydroxy(tosyloxy) iodobenzene, diphenyliodonium salt, aziodobenz

iodoxole, and phenyl(N-tosyl) imino-$\lambda^3$-iodane.

The first synthetic procedure for imino-iodane was introduced in 1974 by

Abramovitch reacting DIB, $MeSO_2NH_2$ with pyridine to produce the respective

product[6].  One year later Yamada introduced the most common synthetic procedure

by reacting p-toluene sulfonamide with DIB in the presence of KOH to generate the

iminoiodane[7].  Many reactions have been explored with imino-iodane to do

aziridination reactions, α-aminations, sulfoximination, intermolecular C-H

amination, and intramolecular C-H amination[8].

## 1.2 Metal and Metal-free reactions of Imino-$\lambda^3$-iodane

Metal reactions with imino-iodane have been reported for the reactions

with copper to create a metal nitrenoid intermediate species[7].  Recently, several of

the same products have been able to be synthesized in the presence of $I_2$ as

catalyst generating an N,N-diiodo intermediate[9].  Uemura reported the reaction of

thioanisole in the presence of CuOTf and imino-$\lambda^3$-iodane to create the respective

sulfilimine product in good yields[10]. Previously reported, many reactions using

hypervalent halogen reagents for trans-imination under harsh or metal-catalyzed

conditions[11-13]. We have created a metal free, safe reaction for trans-imination

which will be discussed in greater detail to follow[9]. Sulifilimines have many

applications as they can be used in aza-Wittig reaction, used as metal catalyst

ligands as sulfilimine palladacycles, N-sulfoximines, and in aziridination and

epoxidation reactions[14].

# Chapter 2

## 2.1 Optimization of Sulfilimine Synthesis

Thioanisole was reacted with imino-$\lambda^3$-iodane in the presence of $I_2$ as

catalyst and TBAI as an iodine additive to generate the sulfilimine product in

moderate to good yields shown in scheme 1. The mount of $I_2$, necessity of TBAI,

best solvent, and reaction time were all investigated shown in Table 1.

**Table 1.** Optimization of trans-imination.

| Entry | Time (h) | Solvent | $I_2$ (mol%) | TBAI (mol%) | Product (%) $^{a,b}$ |
|-------|----------|---------|--------------|-------------|----------------------|
| 1 | 3 | MeCN | 20 | 10 | 81 (80) |
| 2 | 3 | Hexane | 20 | 10 | 15 |
| 3 | 3 | AcOEt | 20 | 10 | 49 |
| 4 | 3 | MeOH | 20 | 10 | 77 |
| 5 | 3 | THF | 20 | 10 | 4 |
| 6 | 3 | Et$_2$O | 20 | 10 | trace |
| 7 | 3 | PhH | 20 | 10 | 47 |
| 8 | 3 | CCl$_4$ | 20 | 10 | 7 |
| 9 | 3 | CH$_2$Cl$_2$ | 20 | 10 | 83 (83) |
| 10 | 3 | CH$_2$Cl$_2$ | 20 | none | 84 |
| 11 | 3 | CH$_2$Cl$_2$ | none | 10 | 7 |
| 12 | 3 | CH$_2$Cl$_2$ | none | none | 5 |
| 13 | 3 | CH$_2$Cl$_2$ | 10 | none | 72 |
| 14 | 24 | CH$_2$Cl$_2$ | 10 | none | 87 |
| 15 | 24 | CH$_2$Cl$_2$ | 5 | none | 91 |
| 16 | 24 | CH$_2$Cl$_2$ | 2 | none | 92 (88) |
| 17 | 24 | CH$_2$Cl$_2$ | 1 | none | 68 |
| 18 | 48 | CH$_2$Cl$_2$ | 1 | none | 66 |
| 19 | 24 | CH$_2$Cl$_2$ (dark) | 2 | none | 77 |

2

Ph–S–Me + PhINTs $\xrightarrow[\text{rt, solvent, time}]{\substack{\text{I}_2\text{ (catalytic amount)} \\ \text{TBAI (Additive)}}}$ Ph–S(=NTs)–Me
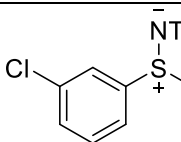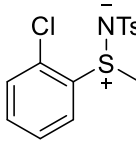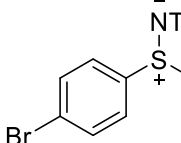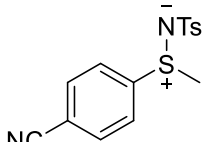
(1 equiv)        (1.2 equiv)
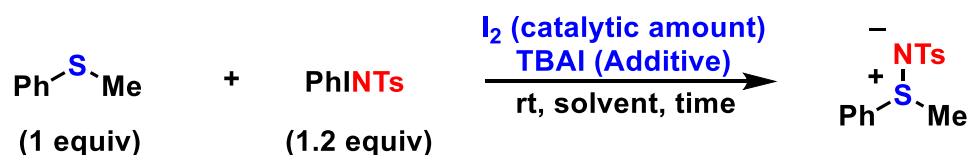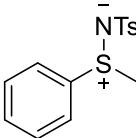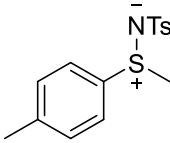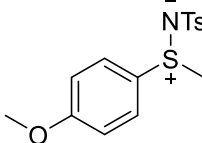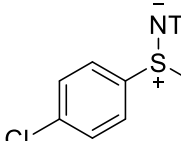
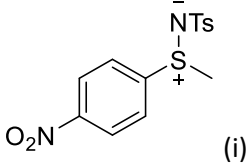**Scheme 1.** Optimization of trans-imination reaction conditions.

Throughout the testing, the solvent choice of dichloromethane was the best solvent due to high solubility of reagents and product for the reaction to proceed (entry 9). Nonpolar solvents, such as hexane lacked high solubility (entry 2). The amount of $I_2$ was found to be most effective at 2 mol% (entry 16). TBAI additive was not necessary for the reaction to occur. This is supported for reaction conditions with $I_2$ present reacting without TBAI (entry 10). However, the reaction did not occur when TBAI was present with the absence of $I_2$ indicating the necessity of $I_2$ (entry 11). Finally, the reaction occurred best at 24 hours (entry 14). This allowed the reaction to go to completion with increased time from 3 hours. The reaction, when under dark conditions, suppressed the yield slightly which indicates that the reaction mechanism is possibly radical in nature due to light not being able to aid in catalysis (entry 19).

## 2.2 Reactions with Substituted Thioanisoles Using Imino-$\lambda^3$-iodanes

When different substituted thioanisoles were reacted in the presence of PhINTs and $I_2$ (according to scheme 1), the respective products (a-i) were produced in moderate to good yields (59-88%) shown in Table 2. The main inhibiting factor for the reactions was strong electron withdrawing groups (product i), which tend to deactivate the reaction site, as well as steric hindrance as ortho-substituted thioanisoles (product f) tended to have lower yields when compared to the respective para-substituted thioanisole.
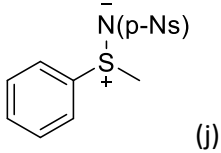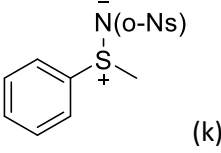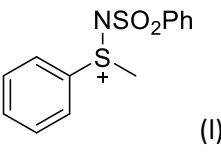
**Table 2.** Products of suliflimines with substituted thioanisoles.

| Product | Yield (%) |
|---|---|
| (a) | 88 |
| (b) | 72 |
| (c) | 78 |
| (d) | 79 |
| (e) | 80 |
| (f) | 68 |
| (g) | 70 |
| (h) | 86 |

|  | 59 |
|---|---|
|  | |

Reactions with thioanisole have also been used in the presence of different imino-$\lambda^3$-iodanes synthesize the respective products (j-l) in moderate to good yields (51-92%) shown in Table 3.  Steric hindrance inhibits the reaction greatly as product k has lower yields than products j and l.  This is due to the nitro group blocking the reaction site on the imino-$\lambda^3$-iodane.
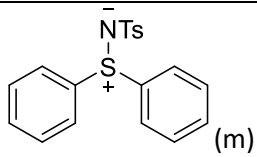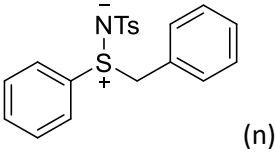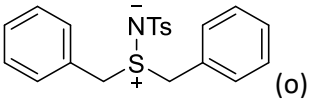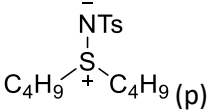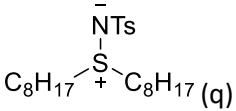
**Table 3.** Reactions of other imino-$\lambda^3$-iodanes and thioanisole.
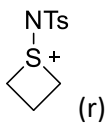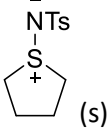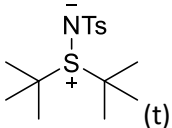
| Product | Yield (%) |
|---|---|
|  | 92 |
|  | 51 |
|  | 67 |

## 2.3 Reaction of Substituted Sulfides Using PhINTs

Reactions under the optimized conditions according to scheme 1 were done with substituted sulfides and PhINTs to create the products (m-t) in low to good yields (8-97%) shown in Table 4.  Steric hindrance is the main inhibiting factor, as the greater the steric hindrance of the sulfide, the lower the yield of the respective product (product t). Strong electron donating derivatives (product q) and strained sulfide rings (product r) helped to increase the reaction site, thus increasing the yield of the respective products.

**Table 4.** Reaction of substituted sulfides using PhINTs.

| Product | Yield (%) |
|---|---|
| NTs S+ (m) | 56 |
| NTs S+ (n) | 65 |
| NTs S+ (o) | 66 |
| NTs S+ $C_4H_9$ $C_4H_9$ (p) | 79 |
| NTs S+ $C_8H_{17}$ $C_8H_{17}$ (q) | 90 |

| | |
|---|---|
| NTs (r) (strained thietane with S+) | 97 |
| NTs (s) (thiolane with S+) | 76 |
| NTs (t) (di-tert-butyl sulfilimine with S+) | 8 |

## 2.4 Reaction of Triphenylphosphine Under Optimized Condition

The reaction of triphenylphosphine analogue in place of the respective sulfide produced the respective iminophosphorane product (u) in great yield (92%). The structure of the product was confirmed by x-ray crystallography shown in Scheme 2.
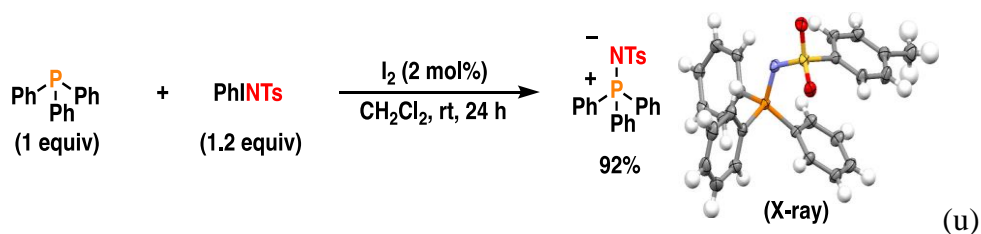


**Scheme 2.** Reaction of triphenylphosphine and PhINTs.

## Chapter 3

## 3.1 Mechanistic Studies

Many blank experiments were run to check the reaction type, which has been inferred to be radical in nature. The amidyl radical generation during the reaction, as previously reported, was further investigated[14]. To check if the

amidyl radical was generated, the reaction was done in the presence of two radical scavenger molecules, BHT and TEMPO. When the reaction occured in the presence of the radical scavengers, the yields drop to 11% yield indicating the intermediate is radical in nature. The next step was to check if the reaction generated nitrene intermediate species. This was done by reacting excess $I_2$ and benzene. No nitrene species were generated, indicating the reaction was radical in nature. The blank experiments are shown in Scheme 3.
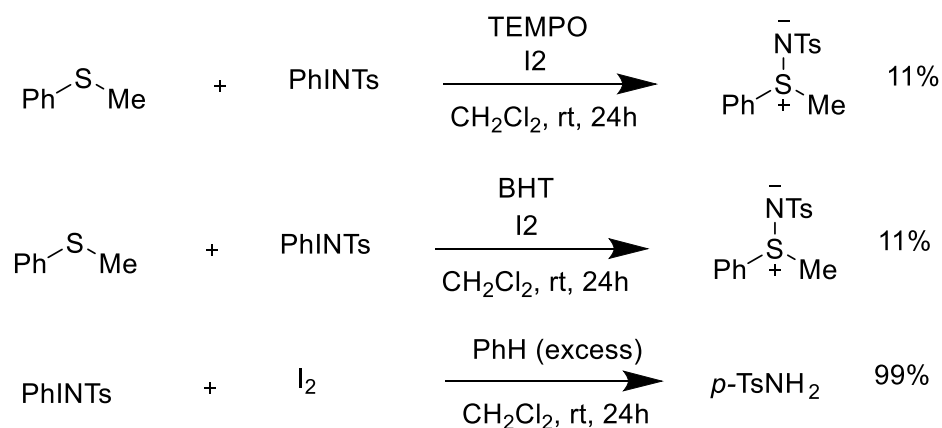


**Scheme 3.** Blank experiment for mechanistic studies.

The proposed mechanism involves the generation of the amidyl radical from the reaction of PhINTs and $I_2$. The amidyl radical then reacts with the sulfide to form the radical intermediate followed by the regeneration of $I_2$ catalyst. Finally, the formation of the sulfilimine product is generated in the last step. The proposed mechanism can be seen in Scheme 4.

8
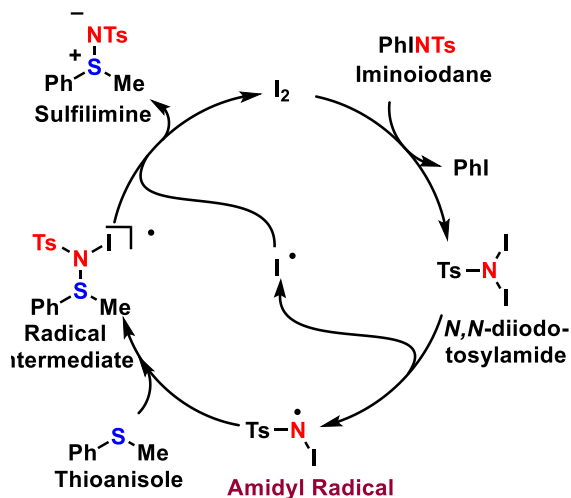
**Scheme 4.** Proposed radical mechanism.

# Chapter 4

## 4.1 [2,3] – Sigmatropic Rearrangement of Sulfilimine

Under the optimized reaction conditions, allylic sulfides undergo [2,3] –
sigmatropic rearrangement of the product shown in Scheme 5. Previously
reported by Uemura, allylic sulfides react to form the sulfilimine intermediate, but
then undergo [2,3]-sigmatropic rearrangement[10]. Investigation of metal-free
conditions were performed and the respective products were isolated.
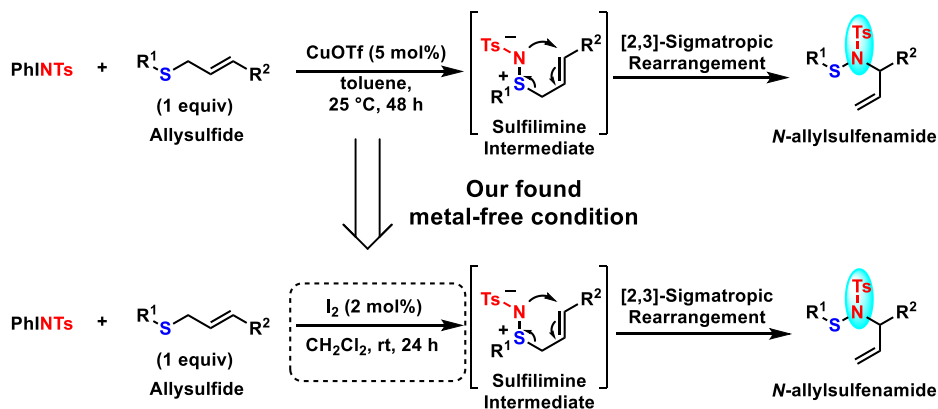


**Scheme 5**. [2,3] – sigmatropic rearrangement of allylic sulfilimines.

## 4.2 Optimization of [2,3] – Sigmatropic Rearrangement

Multiple solvents were tested with dichloromethane as the best solvent (entry 9). The reaction time was changed to shorter than 24 hours and the yield decreased , indicating that the reaction occurs further to completion upon increased time (entry 10). The amount of $I_2$ is still essential to maintain high yields (entry 11-13). The rearrangement product was again confirmed by x-ray crystallography. Optimization table can be found in table 5.
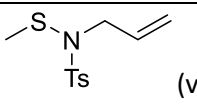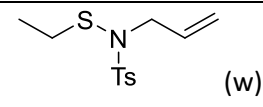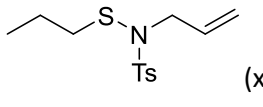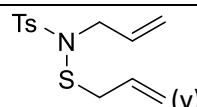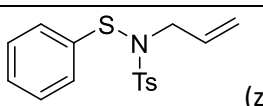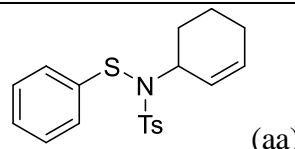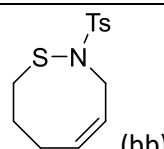
**Table 5**. Optimization of [2,3] – sigmatropic rearrangement reaction.

| Entry | Time (h) | Solvent | $I_2$ (mol%) | Product (%) [a,b] |
|-------|----------|---------|--------------|-------------------|
| 1 | 24 | MeCN | 2 | (93) |
| 2 | 24 | AcOEt | 2 | (92) |
| 3 | 24 | $CHCl_3$ | 2 | (94) |
| 4 | 24 | MeOH | 2 | (40) |
| 5 | 24 | Heptane | 2 | (14) |
| 6 | 24 | $ClCH_2CH_2Cl$ | 2 | (96) |
| 7 | 24 | PhH | 2 | (55) |
| 8 | 24 | Ether | 2 | (32) |
| 9 | 24 | $CH_2Cl_2$ | 2 | (97) 97 |
| 10 | 12 | $CH_2Cl_2$ | 2 | 78 |
| 11 | 24 | $CH_2Cl_2$ | 1 | 77 |
| 12 | 48 | $CH_2Cl_2$ | 0.5 | 73 |
| 13 | 24 | $CH_2Cl_2$ | none | 65 |
| 14 | 24 | $CH_2Cl_2$ (dark) | 2 | 91 |

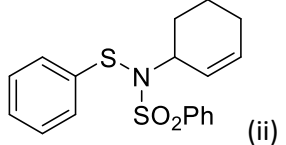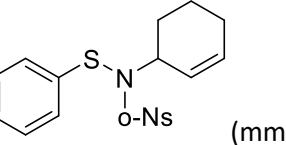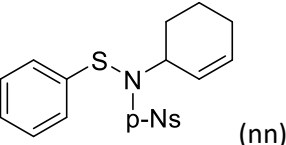## 4.3 [2,3] – Sigmatropic Rearrangement Metal-free Products
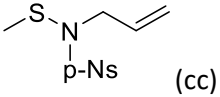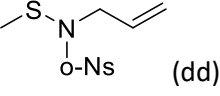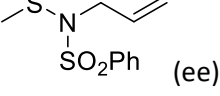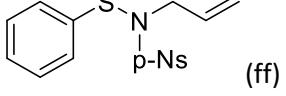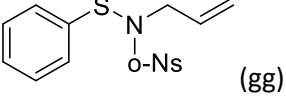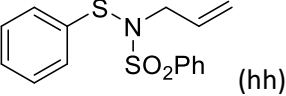
Many allylic sulfides were reacted with PhINTs to produce the respective allylsulfenamide products (v-bb) in moderate to good yields (20-99%) shown in Table 6. The main inhibiting factor of the reaction was steric hindrance of the allylic sulfide (product aa).
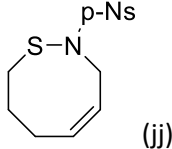
**Table 6**. [2,3] – sigmatropic rearrangement of allylsulfide with PhINTs.

| Product | Yield (%) |
|---------|-----------|
| (v) | 97 |
| (w) | 99 |
| (x) | 70 |
| (y) | 82 |
| (z) | 80 |
| (aa) | 53 |
| (bb) | 20 |

When the reactions were run with different allylic sulfides and different imino-$\lambda^3$-iodanes, the respective products (cc-jj) were isolated in low to good yields (3-92%) shown in Table 7. Steric hindrance of the allylic sulfides inhibited the reaction much more than the hindrance (products ff-nn) of the imino-$\lambda$3-iodane as products dd was unaffected by the ortho-substituted derivative. Large ring opening reaction occurred at a low rate as well (product jj).

**Table 7.** [2,3] – sigmatropic rearrangement of allylsulfide with $PhINSO_2Ar$.

| Product | Yield (%) |
|---|---|
|  (cc) | 92 |
|  (dd) | 89 |
|  (ee) | 89 |
|  (ff) | 50 |
|  (gg) | 18 |
|  (hh) | 53 |
|  (ii) | 24 |
|  (mm) | 24 |
|  (nn) | 53 |

| | |
|---|---|
|   (jj) | 3 |

## 4.4 Application of Allylsulfenamide

Reactions of allylsulfenamide were investigated in order to synthesize an allylic amine derivative. The reaction is shown in Scheme 6. The allylsulfenamide was reacted in mild basic conditions (10% KOH in MeOH) overnight to create S-N bond cleavage and the product (kk) was isolated at 81% yield.
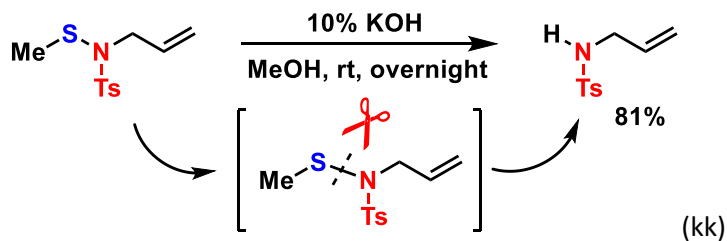


**Scheme 6.** S-N bond cleavage of allylsulfenamide in mild basic condition.

## 4.5 [2,3] – Sigmatropic Rearrangement of Diphenylallylphosphine with PhINTs

Under the optimized reaction conditions, diphenylallylphosphine reacted with PhINTs and $I_2$ produce the respective rearrangement phosphine derivatized product (ll) in good yield (89%). The reaction shows an application of the investigated [2,3] – sigmatropic rearrangement reaction. The reaction is shown Scheme 7.
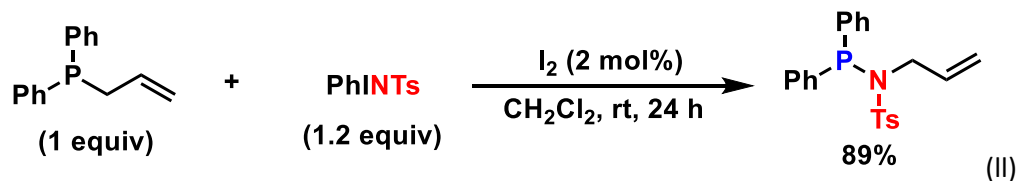
**Scheme 7.** Reaction of diphenylallylphosphine with PhINTs.

# Chapter 5

## 5.1 General Experimental Remarks

All reactions were done under argon atmosphere and flame-dried glassware. All reagents were ACS grade and used without any further purification. Dichloromethane was distilled over $CaH_2$ prior to use. Melting points were obtained in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrophotometer, and peaks were measured in wavenumbers $(cm^{-1})$. $^1H$ NMR were measured using a Varian Inova 500 and 300 MHz NMR spectrometer. $^{13}C$ were also measuring using a Varian Inova 500 and 300 MHz NMR spectrometers at 125 and 75 MHz, respectively. Chemical shifts were measured in parts per million (ppm). $^1H$ and $^{13}C$ chemical shifts were referenced relative to tetramethylsilane. X-ray crystal analysis was performed by Rigaku RAPID II XRD Image Plate using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 173 K.

## 5.2 General Procedure for Imination of Sulfides

Imino-$\lambda^3$-iodane (0.12-0.24 mmol) was added at room temperature with a mixture of sulfide (0.10-.020 mmol) and $I_2$ (0.02-0.004 mmol) in dichloromethane (1.0-2.0 mL). The reaction was stirred at room temperature for 24 h. After the reaction, 5% aqueous $Na_2S_2O_3$ (2.5-5.0 mL) quenched the reaction and the solution was extracted with ethyl acetate. The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under

reduced pressure. The residue was then isolated through column chromatography with Hexane-AcOEt (1:1 to 0:100) to obtain pure product.



(a) [15].
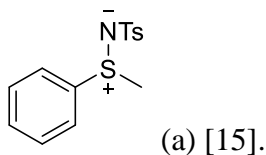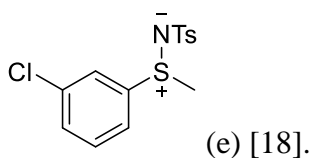
Reaction of thioanisole (25 mg, 0.20 mmol) according to the general procedure afforded 52 mg (88%) of product, isolated as a white solid: mp 129–130 ∘C (lit. [15]; mp 131.5–132 ∘C); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.73 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.56–7.46 (m, 3H), 7.16 (d, J = 8.5 Hz, 2H), 2.84 (s, 3H), 2.37 (s, 3H).



(b) [16].
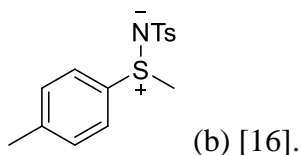
Reaction of methyl(4-tolyl) sulfide (28 mg, 0.20 mmol) according to the general procedure afforded 44 mg (72%) of product, isolated as a light brown oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.28 (d, J =8.3 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 2.82 (s, 3H), 2.39 (s, 3H), 2.35 (s, 3H).
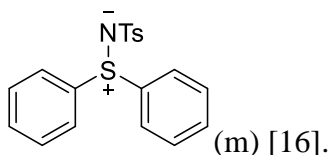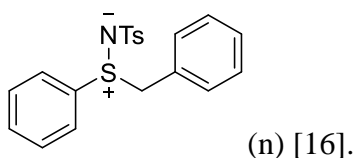


(c) [17].
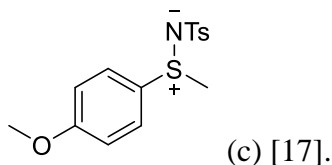
Reaction of 4-methoxyphenyl(methyl)sulfide (31 mg, 0.20 mmol) according to the general procedure afforded 51 mg (78%) of product, isolated as a white solid: mp 147 ∘C (lit. [17]; mp 146–147 ∘C); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.68 (d, J = 7.3 Hz, 2H),

7.59 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 7.3 Hz, 2H), 6.94 (d, J = 8.3 Hz, 2H), 3.81 (s, 3H),

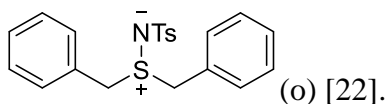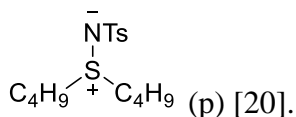2.80 (s, 3H), 2.33 (s, 3H).



(d) [17].
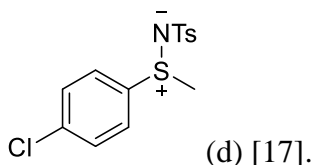
Reaction of 4-chlorophenyl(methyl)sulfide (32 mg, 0.20 mmol) according to the

general procedure afforded 52 mg (79%) of product, isolated as a light yellow solid: mp

111–112 °C (lit. [17]; mp 112–113 °C); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.71 (d, J = 8.0

Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.84

(s, 3H), 2.36 (s, 3H).



(e) [18].

Reaction of 3-chlorophenyl(methyl)sulfide (32 mg, 0.20 mmol) according to the

general procedure afforded 53 mg (80%) of product, isolated as a white solid: mp 137–

138 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.68 (d, J = 8.0 Hz, 2H), 7.61 (s, 1H), 7.53 (d, J =

7.8 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H),

2.83 (s, 3H), 2.33 (s, 3H).



(f) [19].
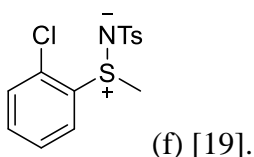
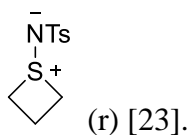Reaction of 2-chlorophenyl(methyl)sulfide (32 mg, 0.20 mmol) according to the

general procedure afforded 45 mg (68%) of product, isolated as a white solid: mp 149–

150 ∘C; 1H NMR (500 MHz, CDCl$_3$): δ8.12 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 7.52–7.41 (m, 3H), 7.20 (d, J = 8.3 Hz, 2H), 2.87 (s, 3H), 2.36 (s, 3H).



(g) [20].
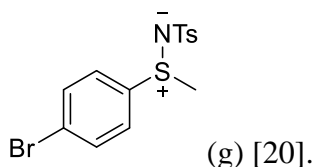
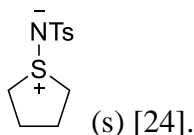Reaction of 4-bromophenyl(methyl)sulfide  (41 mg, 0.20 mmol) according to the general procedure afforded 52 mg (70%) of product, isolated as a white solid: mp 110–111 ∘C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.70 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 2H), 7.55 (d, J = 9.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 2.83 (s, 3H), 2.35 (s, 3H).



(h).
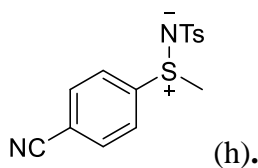
Reaction of 4-cyanophenyl(methyl)sulfide (30mg, 0.20mmol) according to the general procedure afforded 55mg (86%) of product, isolated as a light brown solid: mp 159–160 ∘C; IR (neat) cm−1: 3096, 3035, 2929, 2856, 2234, 1400, 1144, 758; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.83 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.17(d, J =8.3Hz, 2H), 2.87 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (75MHz, CDCl$_3$): δ 142.3, 141.6,140.7, 133.5, 129.4, 126.6, 126.2, 117.1, 116.1, 38.8, 21.4; HRMS (ESI-TOF-positive mode): calculated for C$_{15}$H$_{14}$N$_2$NaO$_2$S$_2$ ([M + Na])+: 341.0394, found: 341.0382.

(i) [21].
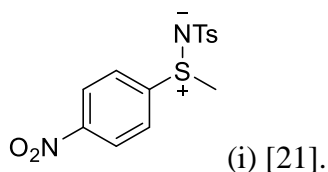
Reaction of 4-nitrophenyl(methyl)sulfide (34 mg, 0.20 mmol) according to the general procedure afforded 40 mg (59%) of product, isolated as a yellow solid: mp 161–163◦C (lit. [21]; mp150◦C); $^1$H NMR(500MHz, CDCl$_3$): δ 8.33(d, J =9.0Hz, 2H), 7.93 (d, J = 9.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.92 (s, 3H), 2.37 (s, 3H).



(m) [16].

Reaction of diphenylsulfide (37 mg, 0.20 mmol) according to the general procedure afforded 40 mg (56%) of product, isolated as a white solid: mp 108–109 ◦C (lit. [16]; mp 109.0–109.5 ◦C); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.74 (d, J = 9.0 Hz, 2H), 7.64–7.59 (m, 4H), 7.52–7.41 (m, 6H), 7.14 (d, J = 8.5 Hz, 2H), 2.33 (s, 3H).



(n) [16].

Reaction of benzyl(phenyl)sulfide (20 mg, 0.1 mmol) according to the general procedure afforded 24 mg (65%) of product, isolated as a white solid: mp 149–150◦C (lit. [16]; mp 147–148◦C); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.62 (d, J = 8.0 Hz, 2H), 7.55–7.48 (m, 3H), 7.45–7.38 (m, 2H), 7.31–7.25 (m, 1H), 7.18 (t, J = 7.5 Hz, 2H), 7.07 (d, J = 8.0

Hz, 2H), 6.98 (d, J = 7.5 Hz, 2H), 4.34 (d, J = 12.8 Hz, 1H), 4.13 (d, J = 12.8 Hz, 1H),

2.32 (s, 3H).


(o) [22].

Reaction of dibenzylsulfide (43 mg, 0.20 mmol) according to the general

procedure afforded 51 mg (66%) of product, isolated as a white solid: mp 187–189 ∘C

(lit. [22]; mp 191–193 ∘C); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.43 (d, J = 8.0 Hz, 2H), 7.36–

7.26 (m, 6H), 7.22 (d, J = 7.5 Hz, 4H), 6.97 (d, J = 8.0 Hz, 2H), 4.14 (d, J = 13.0 Hz, 2H),

4.06 (d, J = 13.0 Hz, 1H), 2.32 (s, 3H).


(p) [20].

Reaction of dibutylsulfide (29 mg, 0.20 mmol) according to the general procedure

afforded 52 mg (79%) of product, isolated as a white solid: mp 64–65 ∘C (lit. [20]; mp

77.5–78.5 ∘C); ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5

Hz, 2H), 2.88-2.78 (m, 2H), 2.77–2.68 (m, 2H), 2.38 (s, 3H), 1.59–1.46 (m, 4H), 1.36–

1.22 (m, 4H), 0.82 (t, J = 7.0 Hz, 6H).


(q).
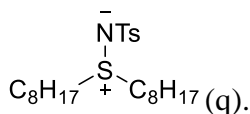
Reaction of dioctylsulfide (52 mg, 0.20 mmol) according to the general procedure

afforded 77 mg (90%) of product, isolated as a white solid: mp 82∘C; IR (neat) cm−1:

2918, 2858, 1384, 1139, 716; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.79 (d, J = 8.3 Hz, 2H),

7.22 (d, J = 8.3 Hz, 2H), 2.89–2.80 (m, 2H), 2.73–2.64 (m, 2H), 2.39 (s, 3H), 1.64–1.58

(m, 4H), 1.34–1.12 (m, 20H), 0.88 (t, J = 7.3 Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 141.6, 141.5, 129.1, 126.3, 49.0, 31.7, 28.9, 28.9, 28.3, 22.8, 22.6, 14.1; HRMS (ESI-TOF-positive mode): calculated for C$_{23}$H$_{42}$NO$_2$S$_2$ ([M + H])+: 428.2657, found: 428.2665.



(r) [23].

Reaction of thietane (15 mg, 0.20 mmol) according to the general procedure afforded 47 mg (97%) of product, isolated as a white solid: mp 103–104 ∘C (lit. [23]; mp 98 ∘C); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.76 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 4.26–4.08 (m, 2H), 3.70–3.57 (m, 2H), 2.62–2.16 (m, 5H).



(s) [24].

Reaction of tetrahydrothiophene (18 mg, 0.20 mmol) according to the general procedure afforded 45 mg (76%) of product, isolated as a white solid: mp131–133 ∘C (lit. [24]; mp 132–134 ∘C); $^1$H NMR (300 MHz, CDCl$_3$): δ 7.79 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz,2H), 3.19–3.00 (m, 4H), 2.58–2.42 (m, 2H), 2.40 (s, 3H), 2.11–1.93 (m, 2H); 13CNMR (75MHz, CDCl$_3$): δ 143.6, 139.1, 129.5, 126.5, 54.5, 25.6, 21.5.



(t) [25].
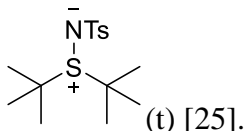
Reaction of di-tert-butylsulfide (29mg, 0.20mmol) according to the general procedure afforded 5mg (8%) of product, isolated as a colorless oil; $^1$H NMR (500 MHz,

CDCl$_3$): δ 7.86 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 2.46 (s, 3H), 1.43 (s, 18H);

13C NMR (75 MHz, CDCl$_3$): δ 144.5, 129.8, 129.5, 128.8, 49.6, 30.6, 21.7.
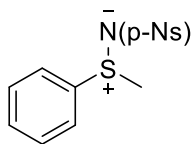
N(p-Ns) structure (j) [26].

Reaction of thioanisole (25 mg, 0.20 mmol) with imino-λ3-iodane (97 mg, 0.24 mmol) according to the general procedure afforded 61 mg (92%) of product, isolated as a white solid: mp 167 ◦C (lit. [26]; mp 164–165 ◦C); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.20 (d, J = 8.7 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H), 7.70 (d, J = 8.1 Hz, 2H), 7.62-7.46 (m, 3H), 2.93 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 149.8, 149.2, 135.1, 133.1, 130.3, 127.4, 125.9, 124.0, 39.2.
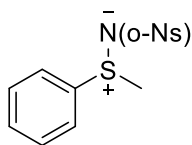
N(o-Ns) structure (k).

Reaction of thioanisole (25 mg, 0.20 mmol) with imino-λ3-iodane (97mg, 0.24 mmol) according to the general procedure afforded 33 mg (51%) of product, isolated as a colorless oil; IR (neat) cm−1: 3096, 3065, 3023, 2926, 1540, 1370, 1305, 1149, 1124, 852, 766; $^1$H NMR (300 MHz, CDCl$_3$): δ 8.16 (d, J = 6.0 Hz, 1H), 7.79 (d, J = 8.1 Hz, 2H), 7.66–7.49 (m, 6H), 2.95 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 147.5, 137.1, 136.2, 132.6, 132.2, 131.8, 130.3, 130.1, 125.8, 123.7, 39.1; HRMS (ESI-TOF-positive mode): calculated for C$_{13}$H$_{13}$N$_2$O$_4$S$_2$ ([M + H])+: 325.0317, found: 325.0319.

(l) [27].
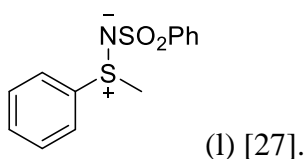
Reaction of thioanisole (25 mg, 0.20 mmol) with imino-λ3-iodane (86 mg, 0.24 mmol) according to the general procedure afforded 38 mg (67%) of product, isolated as a white solid: mp 89–90∘C; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.85 (d, J = 7.8 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.57-7.32 (m, 6H), 2.85 (s, 3H).

## 5.3. Large Scale Reaction

Imino-λ$^3$-iodane (448 mg, 1.20 mmol) was added at room temperature to a stirred mixture of thioanisole (124 mg, 1.00 mmol) and I$_2$ (5 mg, 0.02 mmol) in dichloromethane (10.0mL). The reaction was stirred at room temperature for 24 h. After reaction, 5% aqueous Na$_2$S$_2$O$_3$ (25 mL) was added to the mixture and the solution was extracted with ethyl acetate. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was separated by column chromatography using the Hexane-EtOAc (1:1) to afford the pure product a in 76% (223 mg).



(u) [28].
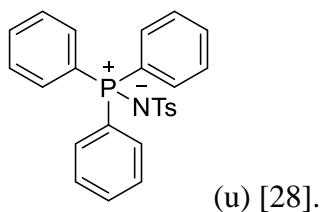
Isolated as a white solid: mp 190 ∘C (lit. [28]; mp 185.5–186.2 ∘C); $^1$H NMR (500 MHz, CDCl$_3$): δ 7.44 (dd, J = 12.3 Hz, 7.8 Hz, 2H), 7.57 (t, J = 7.8 Hz, 3H), 7.50 (d, J = 7.8 Hz, 2H), 7.46 (dt, J = 7.8 Hz, 3.0 Hz, 6H), 7.00 (d, J = 7.8 Hz, 2H), 2.23 (s, 3H).

(aa) [29]
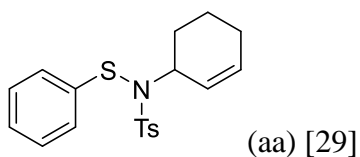
Isolated as a light yellow oil at 38 mg (53%): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.85 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.36-7.27 (m, 4H), 7.19 (t, 7.1 Hz, 1H), 5.79-5.69 (m, 1H), 4.98-4.76 (m, 2H), 2.43 (s, 3H), 1.98-1.52 (m, 6H).



(jj)
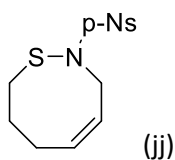
Isolated as a colorless oil at 2 mg (3%):  IR (neat) cm−1: 3106, 2924, 2883, 1606, 1526, 1381, 1146,854, 746; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.15 (d, 8.8 Hz, 2H), 8.07 (d, 8.8 Hz, 2H), 5.77-5.68 (m, 1H), 5.39-5.33 (m, 2H), 4.05 (dd, 15.0 Hz, 2.0 Hz, 1H), 3.25-3.17 (m, 1H) 3.18-3.06 (m, 1H), 2.65-2.50 (m, 2H), 2.32-2.23 (m, 1H), 2.00-1.92 (m, 1H).



(bb) [30]
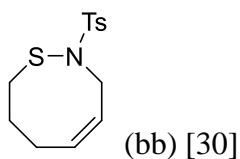
Isolated as white powder: mp 62.9-64.4˚C (lit 68-69˚C); IR (neat) cm−1: 3026, 2932, 2853, 1652, 1599, 1351, 1162, 937, 747; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.79 (d, 8.5 Hz, 2H), 7.30 (d, 8.5 Hz, 2H), 6.02-5.83 (m, 2H), 4.36-4.02 (m, 2H), 2.92-2.82 (m, 2H), 2.62-2.36 ( m, 5H) 1.88 (quint, 6.0 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 143.7, 136.5, 135.5, 129.5, 128.1, 128.0, 51.0, 38.4, 30.3, 24.4, 21.6.

(kk) [31]
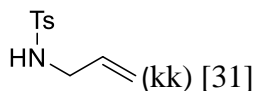
Isolated as yellow oil at 35 mg (81%): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76 (d, 8.5 Hz, 2H), 7.31 (d, 8.5 Hz, 2H), 5.77-5.67 (m, 1H), 5.17 (dd, 15.5 Hz, 1.3 Hz, 1H), 5.09 (dd, 10.5 Hz, 1.3 Hz, 1H), 4.71 (s, 1H), 3.61-3.55 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 143.5, 136.9, 132.0, 129.7, 127.1, 117.7, 45.8, 21.5.


(mm)
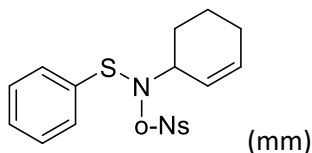
Isolated as light yellow oil at 19 mg (24%): ^{1}H NMR (500 MHz, CDCl$_3$): δ8.19 (d, 25 Hz, 1H), 7.69-7.55 (m, 3H), 7.36 (d, 8.0 Hz, 2H), 7.22 (t, 7.5 Hz, 1H), 7.18-7.11 (m, 2H), 5.91-5.84 (m, 1H), 5.44-5.38 (m, 1H), 5.07-5.00 (m, 1H), 2.06-1.89 (m, 3H), 1.81-1.59 (m, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 147.8, 138.1, 132.9, 132.6, 131.5, 128.7, 127.5, 125.5, 124.0, 60.2, 29.1, 24.3, 21.2.


(nn)
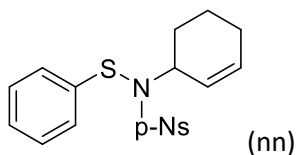
Isolated as light yellow oil at 41 mg (53%): ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.36 (d, 8.3 Hz, 2H), 8.17 (d, 8.3 Hz, 2H), 7.47 (d, 8.2 Hz, 2H), 7.37-7.31 (m, 2H), 7.24 (d, 7.5 Hz, 1H), 5.84-5.79 (m, 1H), 5.01-4.95 (m, 2H), 2.01-1.87 (m, 3H), 1.79-1.71 (m, 1H), 1.69-1.52 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 150.3, 145.5, 138.1, 133.4, 129.0, 128.9, 127.4, 126.3, 124.3, 60.5, 28.7, 24.2, 21.1.

(gg)
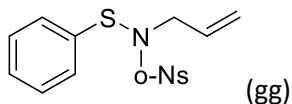
Isolated as light yellow oil at 8 mg (11%): IR (neat) cm−1: 3090, 2929, 2856, 1641, 1540, 1365, 1348, 1169, 929, 854, 742: $^1$H NMR (500 MHz, CDCl$_3$): δ 8.20 (d, 6.9 Hz, 1H), 7.72-7.58 (m, 3H), 7.37-7.29 (m, 3H), 7.28-7.16 (m, 2H), 5.95-5.78 (m, 1H), 5.32-5.18 (m, 2H), 4.34 (d, 6.6 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): 147.8, 135.7, 134.1, 132.9, 132.6, 131.6, 129.1, 129.0, 128.0, 127.0, 124.2, 12.2, 57.2; HRMS (ESI-TOF-positive mode): calculated for C$_{15}$H$_{16}$N$_2$O$_4$S$_2$ ([M + H])+: 351.0473, found: 3513.0485.



(ii)
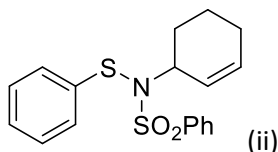
Isolated as light yellow oil at 17 mg (24%): $^1$H NMR (500 MHz, CDCl$_3$): δ 7.98 (d, 8.0 Hz, 2H), 7.60 (t, 7.5 Hz, 1H), 7.55-7.49 (m, 2H), 7.45 (d, 7.5 Hz, 2H), 7.35-7.23 (m, 2H), 7.20 (t, 7.3 Hz, 1H), 5.78-5.71 (m, 1H), 4.99-4.90 (m, 2H), 2.00-1.84 (m, 3H), 1.75-1.68 (m, 1H), 166-1.50 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 140.0, 139.3, 133.1, 132.6, 129.1, 128.8, 127.7, 126.9, 126.7, 60.0, 28.6, 24.2, 21.2.



(ff)
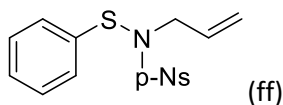
Isolated as white solid at 35 mg (50%): mp 104.5-105.8˚C (lit 107.0-109.0˚C); IR (neat) cm$^{−1}$: 3112, 3070, 2923, 1531, 1350, 1312, 1169, 929, 857, 739; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.35 (d, 8.9 Hz, 2H), 8.11 (d, 8.9 Hz, 2H), 7.46-7.40 (m, 2H), 7.39-7.28 (m, 3H), 5.82-5.65 (m, 1H), 5.28-5.16 (m, 2H), 4.23 (d, 6.6 Hz, 2H); $^{13}$C NMR (150

MHz, CDCl$_3$): δ 150.3, 144.9, 135.8, 131.7, 129.2, 128.3, 127.3, 124.2, 120.4, 57.4;

HRMS (ESI-TOF-positive mode): calculated for C$_{15}$H$_{15}$N$_2$O$_4$S ([M + H])+: 351.0473,

found: 351.0475.


(hh)
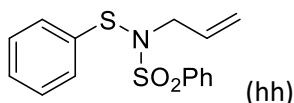
Isolated as light brown oil at 29 mg (47%): IR (neat) cm−1: 3066, 3020, 2987,

2923, 2859, 1643, 1349, 1169, 930, 738; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.93 (d, 6.9 Hz,

2H), 7.64-7.56 (m, 1H), 7.55-7.47 (m, 2H), 7.39 (d, 6.9 Hz, 2H) 7.35-7.28 (m, 2H), 7.27-

7.20 (m, 1H), 5.82-5.64 (m, 1H), 5.18 (dd, 13.8 Hz, 1.3 Hz, 1H), 5.13 (dd, 6.5 Hz, 1.3

Hz, 1H), 4.17 (dd, 6.5 Hz, 1.3 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 139.2, 136.9,

133.1, 132.2, 129.1, 129.0, 127.8, 127.6, 126.5, 119.8, 56.9; HRMS (ESI-TOF-positive

mode): calculated for C$_{15}$H$_{15}$NO$_2$S$_2$ + Na ([M + Na])+:328.0442, found: 328.0450.


(y) [32]
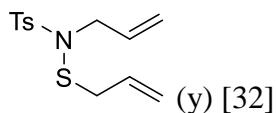
Isolated as amorphous brown oil at 47 mg (82%): $^1$H NMR (500 MHz, CDCl$_3$): δ

7.79 (d, 7.5 Hz, 2H), 7.30 (d, 7.5 Hz, 2H), 5.90-5.67 (m, 2H) 5.26-5.12 (m, 4H), 4.07 (d,

6.0 Hz, 2H), 3.52 (d, 7.5 Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): 143.8,

136.2, 133.1, 131.4, 129.5, 127.9, 119.9, 119.1, 57.8, 43.7, 21.6; HRMS (ESI-TOF-

positive mode): calculated for C$_{13}$H$_{17}$NO$_2$S$_3$ ([M + H])+: 284.0779, found: 284.0787.

(v) [32]
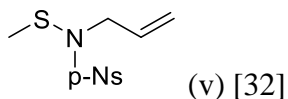
Isolated as white solid at 53 mg (92%): mp 111.2-112.7°C; $^1$H NMR (500 MHz, CDCl$_3$): δ 8.37 (d, 7.5 Hz, 2H), 8.11 (d, 7.5 Hz, 2H), 5.86-5.76 (m, 1H), 5.27 (dd, 18.0 Hz, 1.0 Hz, 1H), 5.25 (d, 11.0 Hz, 1H), 4.27 (dd, 6.5 Hz, 1.0 Hz, 2H), 2.57 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 150.2, 144.6, 132.4, 129.1, 124.1, 120.0, 57.1, 24.2; HRMS (ESI-TOF-positive mode): calculated for C$_{10}$H$_{12}$N$_2$O$_4$S$_2$ ([M])+: 288.0238, found: 288.0245.



(dd)
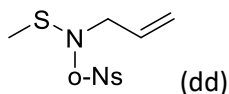
Isolated as a colorless oil: at 52 mg (89%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.25 (d, 8.0 Hz, 1H), 7.77-7.66 (m, 3H), 6.00-5.89 (m, 1H), 5.37 (d, 17.0 Hz, 1H), 5.29 (d, 10.0 Hz, 1H), 4.22 (d, 6.5 Hz, 2H), 2.44 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 147.8, 134.0, 133.5, 132.8, 131.9, 131.5, 124.2, 120.0, 57.0, 23.0.



(ee)
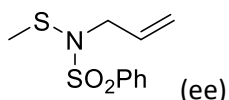
Isolated as light yellow oil at 43 mg (89%): $^1$H NMR (500 MHz, CDCl$_3$): δ 7.92 (d, 8.5 Hz, 2H), 7.60 (t, 7.8 Hz, 1H), 7.55-7.49 (m, 2H), 5.88-5.77 (m, 1H), 5.25 (d, 17.0 Hz, 1H), 5.22 (d, 10.5 Hz, 1H), 4.08 (d, 6.5 Hz, 2H), 2.46 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 139.0, 133.1, 133.0, 128.9, 127.7, 119.3, 56.5, 23.7.

(z) [29]
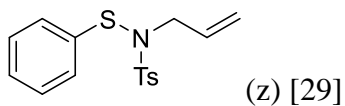
Isolated as a light yellow oil at 51 mg (80%): $^1$H NMR (500 MHz, CDCl$_3$): δ 7.81 (d, 8.0 Hz, 2H), 7.39 (d, 9.0 Hz, 2H), 7.35-7.25 (m, 4H), 7.26-7.20 (m, 1H), 5.76-5.65 (m, 1H), 5.17 (dd, 17 Hz, 1.3 Hz, 1H), 5.13 (dd, 11.5 Hz, 1.3 Hz, 1H), 4.15 (d, 6.3 Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ 144.0, 137.1, 136.2, 132.4, 129.6, 128.9, 127.8, 127.4, 126.3, 59.7, 56.9, 21.6.



(x)
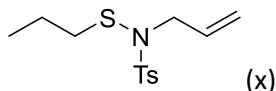
Isolated as yellow oil at 40 mg (70%): IR (neat) cm−1: 3087, 2971, 2935, 2877, 1649, 1340, 1155, 928, 707; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.80 (d, 7.5 Hz, 2H), 7.30 (d, 7.5 Hz, 2H), 5.82-5.70 (m, 1H), 5.24-5.12 (m, 2H), 4.04 (d, 6.5 Hz, 2H), 2.86 (t, 7.5 Hz, 2H), 2.43 (s, 3H), 1.68-1.56 (m, 2H), 0.98 (t, 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): 143.8, 136.0, 133.1, 128.4, 127.9, 119.2, 57.7, 42.2, 21.6, 20.6, 13.3; HRMS (ESI-TOF-positive mode): calculated for C$_{13}$H$_{19}$NO$_2$S$_2$ + H ([M + H])+: 286.0935, found: 286.0944.



(w)
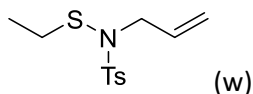
Isolated as brown oil at 53 mg (99%): IR (neat) cm−1: 3093, 2978, 2929, 2871, 1647, 1329, 1159, 925, 712; $^1$H NMR (300 MHz, CDCl$_3$): δ 7.79 (d, 8.5 Hz, 2H), 7.29 (d, 8.5 Hz, 2H), 5.82-5.68 (m, 1H), 5.24-5.12 (m, 2H) 4.04 (d, 6.5 Hz, 2H), 2.90 (q, 8.0 Hz, 2H), 2.42 (s, 3H), 1.22 (t, 25 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 143.8, 136.0, 133.1,

129.4, 127.8, 119.2, 52.8, 34.0, 21.5, 12.2; HRMS (ESI-TOF-positive mode): calculated

for $C_{12}H_{18}NO_2S_2$ ([M + H])+: 272.0779, found: 272.0789.



(v) [32]
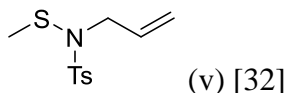
Isolated as a brown solid at 41 mg (80%): mp 65.5-66.5° (lit [32] 68.5-69.5°C); [1]H

NMR (300 MHz, CDCl$_3$): δ 7.79 (d, 8.3 Hz, 2H), 7.31 (d, 8.3 Hz, 2H), 5.88-5.77 (m,

1H), 5.25 (dd, 17.5 Hz, 10.5 Hz, 1H), 5.21 (d, 10.5 Hz, 1H), 4.06 (d, 6.0 Hz, 2H), 2.44 (s,

3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 143.8, 136.1, 133.2, 129.5, 127.8,

119.2, 56.4, 23.6, 21.6.

# Chapter 6

## 6.1 Conclusion

In conclusion, a new metal-free method for trans-imination has been created for

reactions of sulfides, triphenylphosphine, allylic sulfides, and allylic phosphines in the

presence of catalytic amount of I$_2$ using imino-$\lambda^3$-iodanes. The general procedure gives

the respective products in moderate to good yields. The reaction mechanism most likely

involves the amidyl radical species, which is supported through the blank reaction studies

with radical scavengers. Allylic sulfides and phosphines can also react under [2,3] –

sigmatropic rearrangement to give the rearranged final products as well.

# References

1. Aggarwal, V.K.; Winn, C.L. Catalytic, Asymmetric Sulfur Ylide-Mediated Epoxidation of Carbonyl Compounds: Scope, Selectivity, and Applications in Synthesis. *Acc. Chem. Res.* **2004**, *37*, 611–620.

2. Aggarwal, V.K. Catalytic asymmetric epoxidation and aziridination mediated by sulfur ylides. Evolution of a project. *Synlett* **1998**, 329–336.

3. Lu, L.-Q.; Li, T.-R.; Wang, Q.; Xiao, W.-J. Beyond sulfide-centric catalysis: Recent advances in the catalytic cyclization reactions of sulfur ylides. *Chem. Soc. Rev.* **2017**, *46*, 4135–4149.

4. Sun, X.-L.; Tang, Y. Ylide-Initiated Michael Addition-Cyclization Reactions beyond Cyclopropanes. *Acc. Chem. Res.* **2008**, *41*, 937–948.

5. Aggarwal, V.; Richardson, J. Product class 1: Sulfur ylides. *Sci. Synth.* **2004**, *27*, 21–104.

6. Abramovitch, R. A.; Bailey, T. D.; Takaya, T.; Uma, V. *J.* The Reaction of Methanesulfonyl Nitrene with Benzene. Attempts to Generate Sulfonyl Nitrenes from Sources Other than the Azides *Org. Chem.* **1974**, *39*, 340–345.

7. Yamada, Y.; Yamamoto,T.; Okawara, M.; Synthesis and reaction of new type I-N Ylide, N-tosyliminoiodane. *Chem. Lett.* **1975.** *4,* 361-362.

8. Gilchrist, T. L.; Moody, C. J.; The chemistry of sulfilimines. *Chem. Rev.,* **1977.** *77*, 409-435.

9. Yoshimura, A.; Makitalo, C. L.; Jarvi, M. E.; Shea, M. T.; Postnikov, P. S.; Rohde, G. T.; Zhdankin, V. V.,; Saito, A.; Yusubov, M. S., Sulfonylimino Group

Transfer Reaction Using Imino-$\lambda^3$-iodanes with I$_2$ as Catalyst Under Metal-free

Condition. *Molecules.* **2019.** *24,* 979-990.

10. Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, C. P.; Sparey, T. J.;

Taylor, P. C. Catalytic Asymmetric Sulfimidation. *J. Org. Chem.* **1997.** *62*, 6512-6518.

11. Cho, Y. C.; Bolm, C. Metal-free imination of sulfoxides and sulfides.

*Tetrahedron Lett.* **2005.** *46,* 8007-8008.

12. Ochiai, M.; Naito, M.; Miyamoto, K.; Hayashi, S.; Nakanishi, W. Imination of

Sulfides and Sulfoxides with Sulfonylimino-$\lambda^3$-bromane under Mild, Metal-Free

Conditions. *Chem. Eur. J.* **2010***. 10,* 8713-8718.

13. Nicolaou, K. C.; Nilewski, C.; Hale, C. R. H.; Ioannidou, H. A.; ElMarrouni,

A.; Koch, L. G. Total Synthesis and Structural Revision of Viridicatumtoxin B. **2013.** *52,*
8661-8665.

14. Lamar, A.A.; Nicholas, K.M. Iodine-Catalyzed Aminosulfonation of

Hydrocarbons by Imidoiodinanes. a Synthetic and Mechanistic Investigation. *J. Org.*

*Chem.* **2010**, *75*, 7644–7650.

15. Hong, S.; Sutherlin, K.D.; Vardhaman, A.K.; Yan, J.J.; Park, S.; Lee, Y.-M.;

Jang, S.; Lu, X.; Ohta, T.; Ogura, T.; et al. A Mononuclear Nonheme Iron(V)-Imido

Complex. *J. Am. Chem. Soc.* **2017**, *139*, 8800–8803.

16. Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, C.P.; Sparey, T.J.;

Taylor, P.C. Catalytic Asymmetric Sulfimidation. *J. Org. Chem.* **1997**, *62*, 6512–6518.

17. Morita, H.; Tatami, A.; Maeda, T.; Ju Kim, B.; Kawashima, W.; Yoshimura,

T.; Abe, H.; Akasaka, T. Generation of Nitrene by the Photolysis of N-Substituted

Iminodibenzothiophene. *J. Org. Chem.* **2008**, *73*, 7159–7163.

18. Kapovits, I.; Ruff, F.; Kucsman, A. Basicity of sulfur(IV)-nitrogen(sp2) sulfur(VI) group in N-sulfonyl sulfilimines. *Tetrahedron* **1972**, *28*, 4413–4417.

19. Aida, T.; Furukawa, N.; Oae, S. Mechanism of the reaction of N-arylsulfonylsulfimides with trivalent phosphorus compounds. *J. Chem. Soc. Perkin Trans. 2* **1976**, 1438–1444.

20. Giribabu, L.; Singh, S.P.; Patil, N.M.; Kantam, M.L.; Gupte, S.P.; Chaudhari, R.V. Highly Efficient Sulfimidation of 1,3-Dithianes by Cu(I) Complexes. *Synth. Commun.* **2008**, *38*, 619–625.

21. Marzinzik, A.L.; Sharpless, K.B. A simple method for the preparation of N-sulfonylsulfilimines from sulfides. *J. Org. Chem.* **2001**, *66*, 594–596.

22. Ou, W.; Chen, Z.-C. Hypervalent iodine in synthesis XXXII: A novel way for the synthesis of N-sulfonylsulfilimines from sulfides and sulfonamides using iodosobenzene diacetate. *Synth. Commun.* **1999**, *29*, 4443–4449.

23. Ruff, F.; Komoto, K.; Furukawa, N.; Oae, S. Steric effects in the reaction of alkylphenyl and dialkylsulfides with chloramine-T. *Tetrahedron* **1976**, *32*, 2763–2767.

24. Yamamoto, T.; Yoshida, D.; Hojyo, J.; Terauchi, H. Preparation of tetraalkylammonium N-chloro-p-toluenesulfonamides and their application to imination of phosphorus compounds and sulfides. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3341–3342.

25. Hopper, R.J. N-Sulfonyl-sulfilimines as premature vulcanization inhibitors. *RubberChem. Technol.* **1980**, *53*, 1106–1116.

26. Okamura, H.; Bolm, C. Rhodium-Catalyzed Imination of Sulfoxides and Sulfides: Efficient Preparation of N-Unsubstituted Sulfoximines and Sulfilimines. *Org. Lett.* **2004**, *6*, 1305–1307.

27. Akutagawa, K.; Furukawa, N.; Oae, S. Preparation of N-(arylsulfonyl)sulfoximines by oxidation of N-(arylsulfonyl)sulfilimines with sodium hypochlorite in a two-phase system. *J. Org. Chem.* **1984**, *49*, 2282–2284.

28. Yoshimura, A.; Nemykin, V.N.; Zhdankin, V.V. o-Alkoxyphenyliminoiodanes: Highly Efficient Reagents for the Catalytic Aziridination of Alkenes and the Metal-Free Amination of Organic Substrates. *Chem. Eur. J.* **2011**, *17*, 10538–10541.

29. Jiang, Y.; Mo, F.; Qui, D.; Kuang, C.; Zhang, Y.; Wang, J. Catalyst-Free Imidation of Allyl Sulfides with Chloramine-T and Subsequent [2,3]-Sigmatropic Rearrangement. *Chin. J. Chem.* **2012**, 30, 2029–2035.

30. Sashida, H.; Tsuchiya, T. Thermal Ring Expansion of 2-Vinylthiacycloalkane N-Imides by [2,3]-Sigmatropic Rearrangement. *Heterocycles* **1984**, *22*, 1303–1306.

31. Zhou, Y.; Nikbakht, A.; Bauer, F.; Breit, B. A Rhodium Catalyzed Cycloisomerization and Tandem Diels–Alder Reaction for Facile Access to Diverse Bicyclic and Tricyclic Heterocycles. *Chem. Sci.* **2019**, *10*, 4805–4810.

32. Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, C. P.; Sparey, T. J.; Taylor, P. C. Catalytic Asymmetric Sulfimidation. *J. Org. Chem.* **1997**, *62*, 6512–6518.

# Appendix

$^1$H NMR (500 MHz, CDCl$_3$)
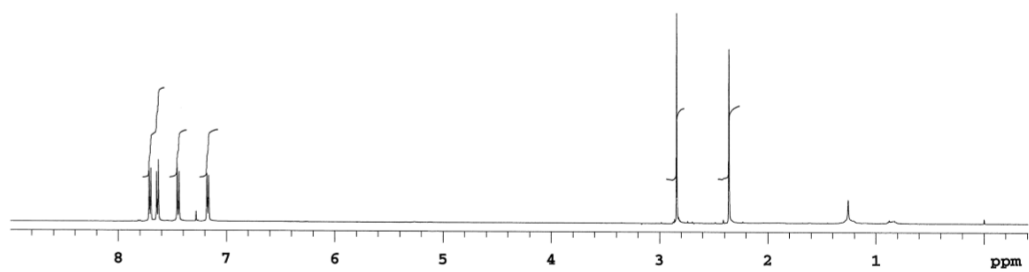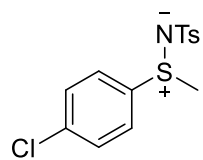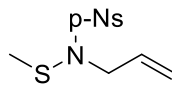
35

¹H NMR (500 MHz, CDCl₃)

$^1$H NMR (500 MHz, CDCl$_3$)
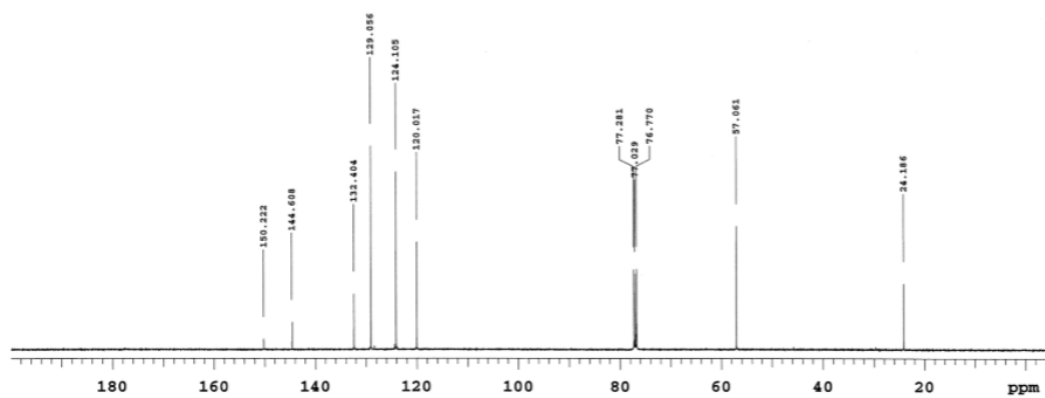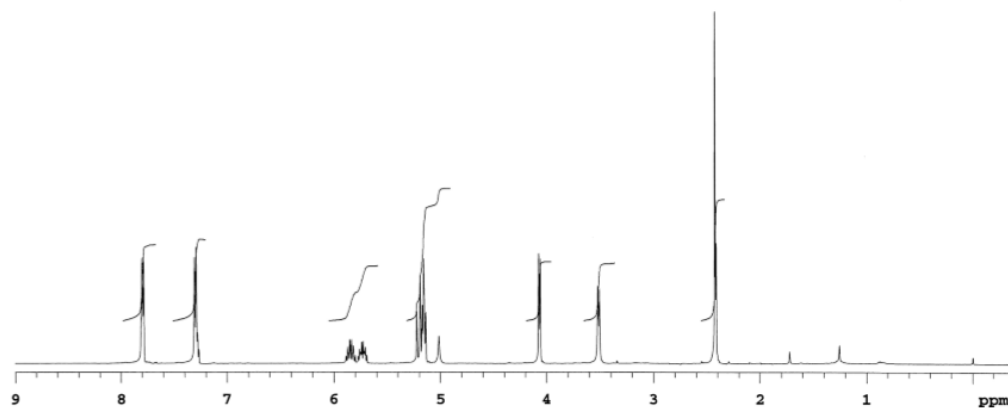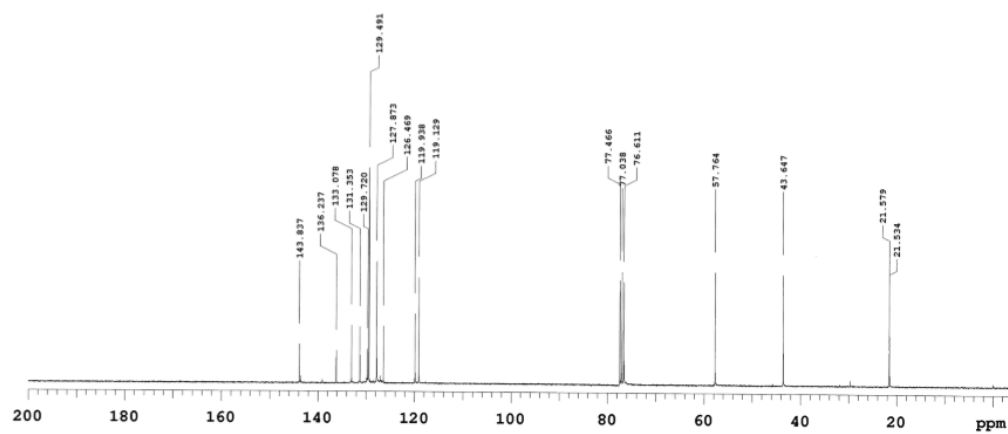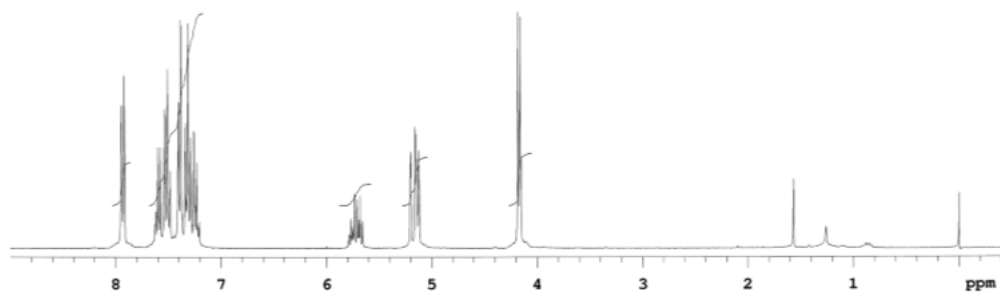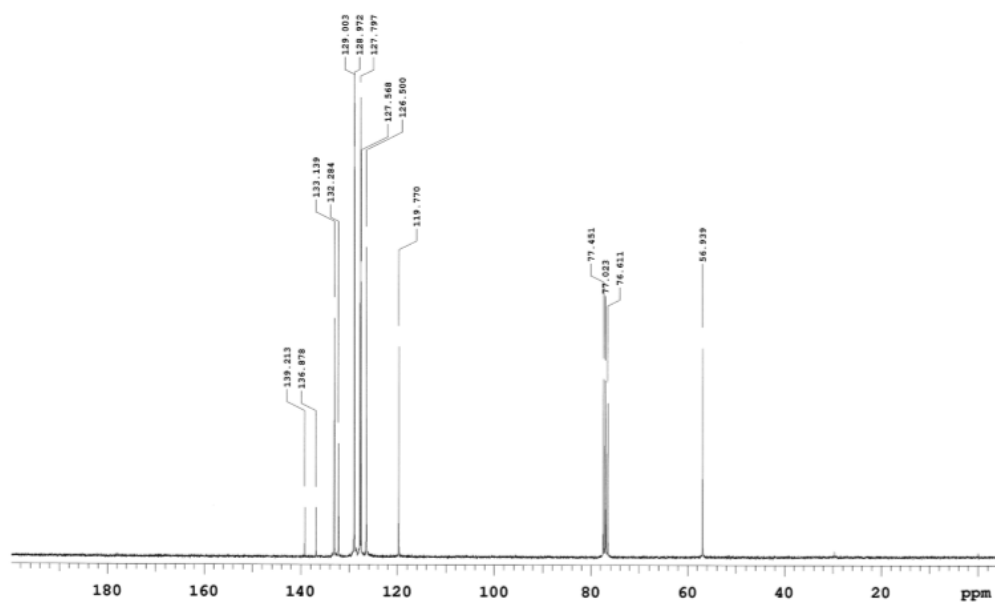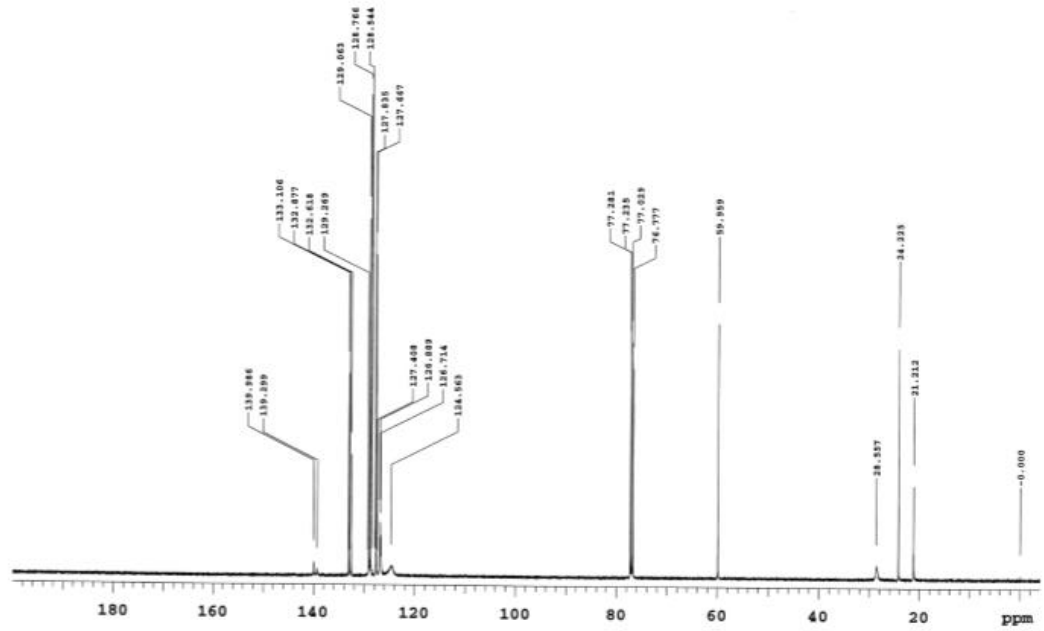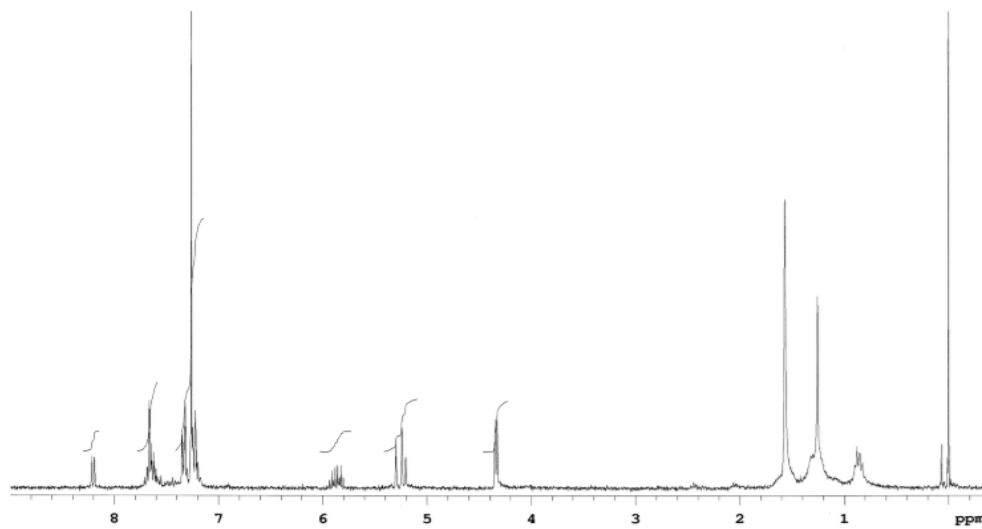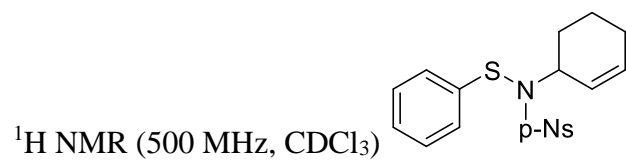


$^{13}$C NMR (75 MHz, CDCl$_3$)



40

$^1$H NMR (500 MHz, CDCl$_3$)

¹H NMR (500 MHz, CDCl₃)

$$\underset{C_4H_9 \overset{+}{\underset{}{S}} C_4H_9}{\overset{\overset{-}{NTs}}{|}}$$

$$\overset{\overline{\text{NTs}}}{\underset{\text{C}_8\text{H}_{17}}{\overset{|}{\underset{+}{\text{S}}}}\text{C}_8\text{H}_{17}}$$



¹³C NMR (75 MHz, CDCl₃)

$$\begin{array}{c} \overline{\text{NTs}} \\ | \\ \text{S} \\ + \end{array}$$
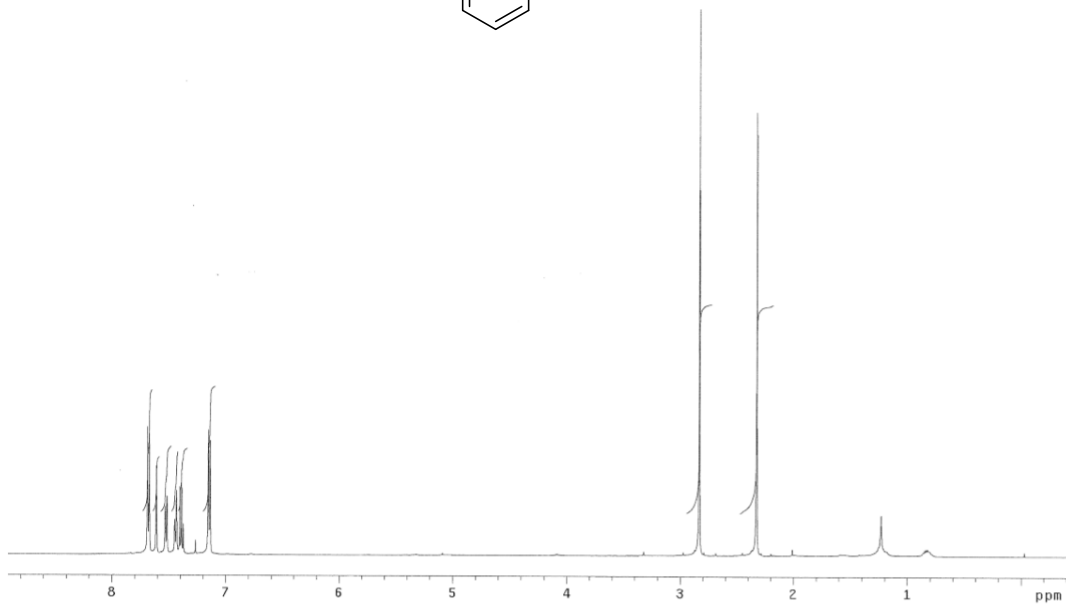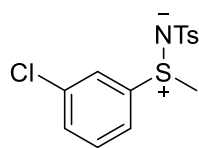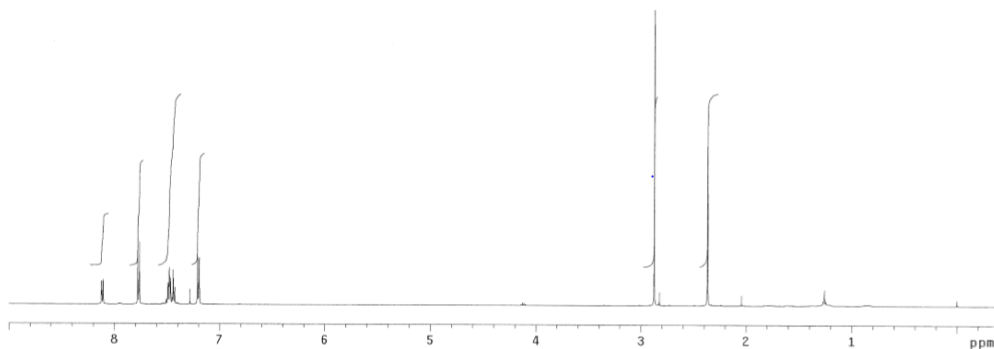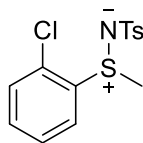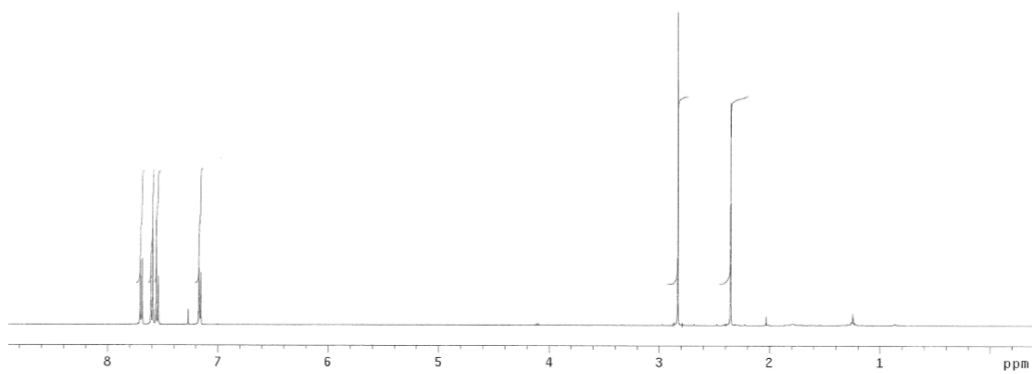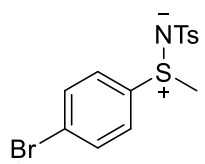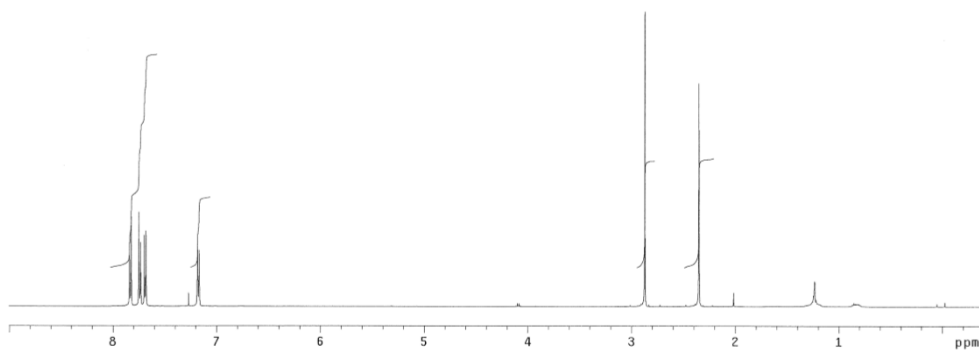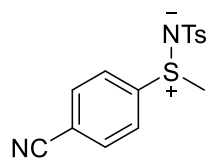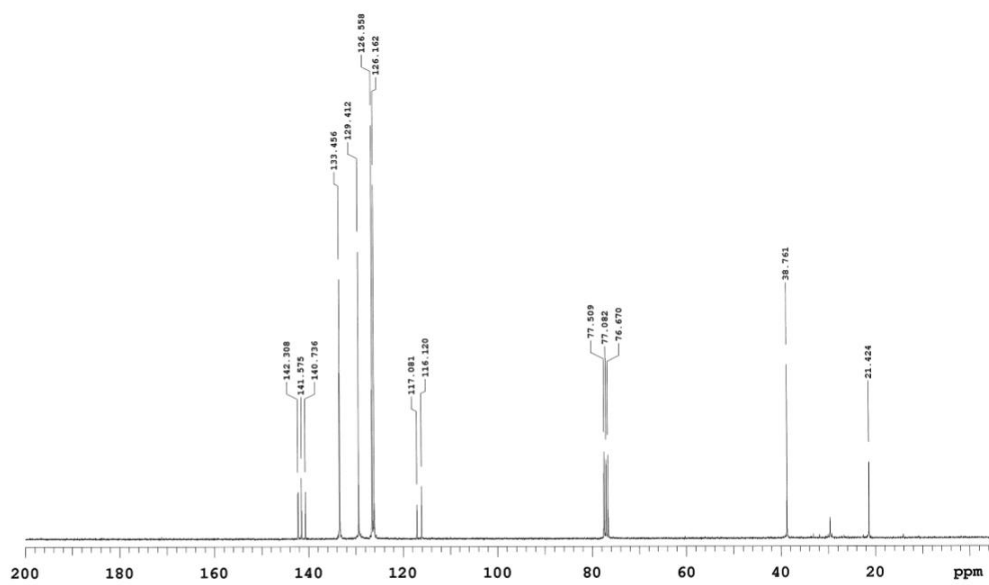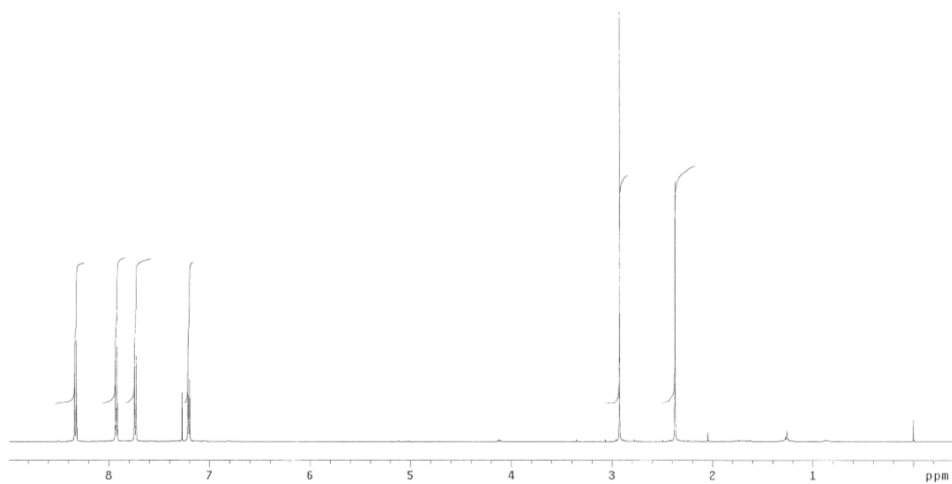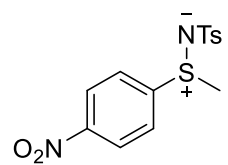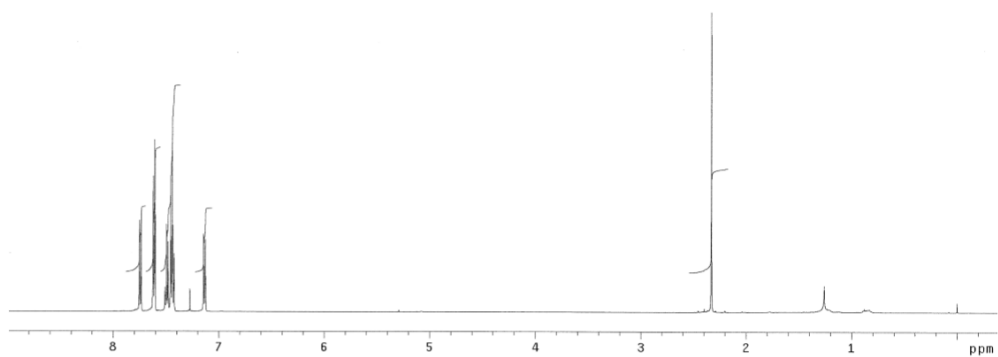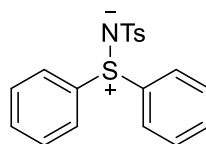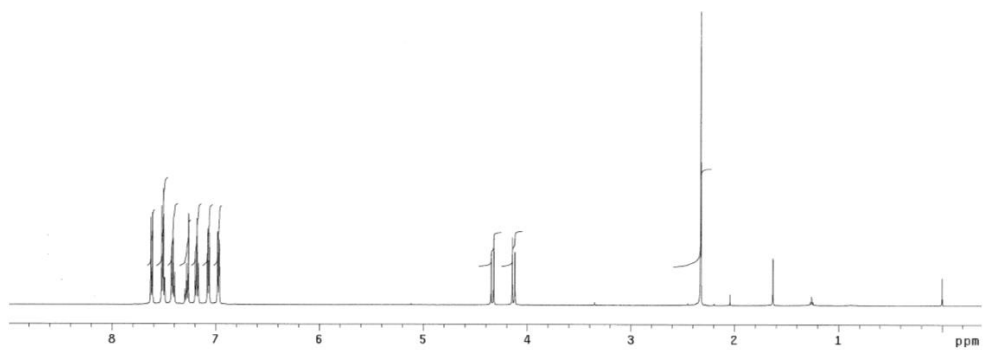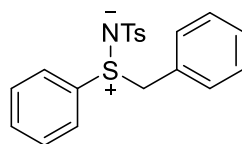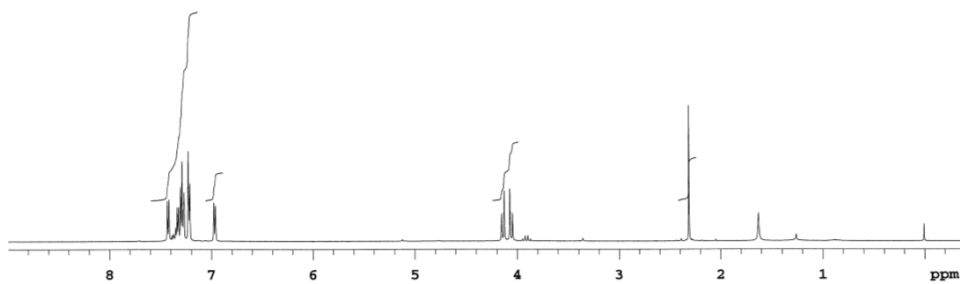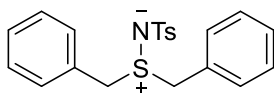
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)

$^{1}$H NMR (300 MHz, CDCl$_3$)



$^{13}$C NMR (75 MHz, CDCl$_3$)



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<sup>1</sup>H NMR (500 MHz, CDCl₃)
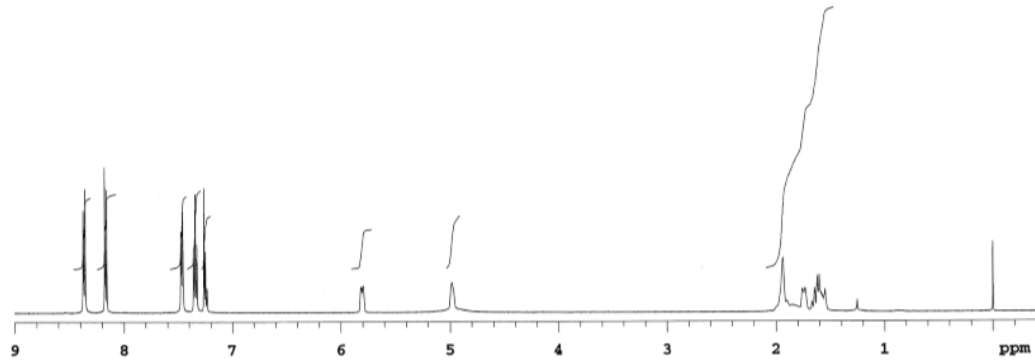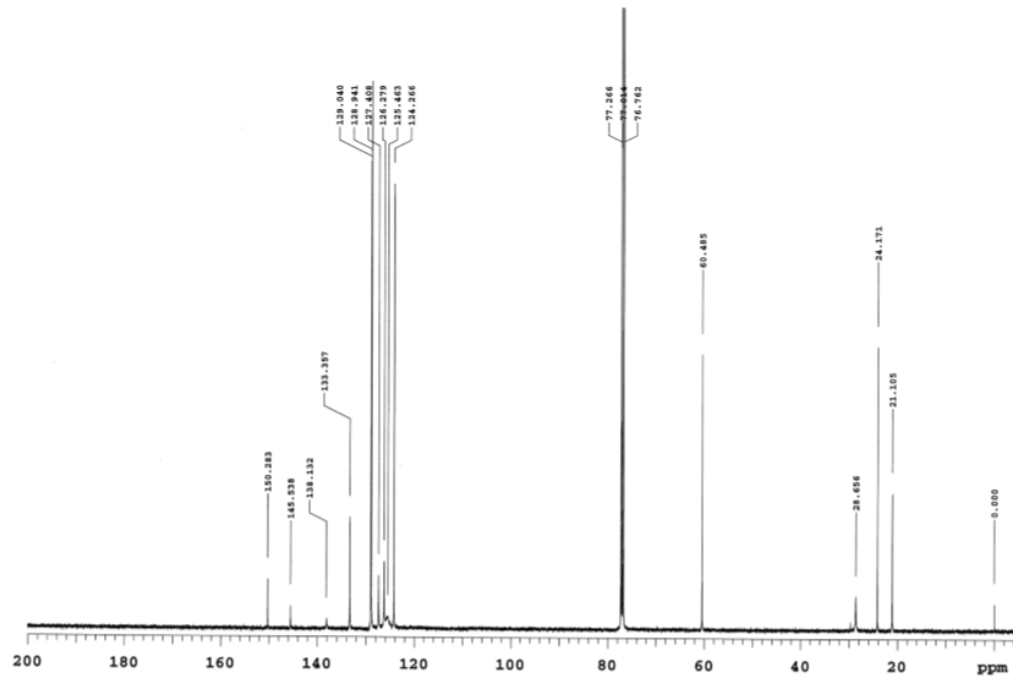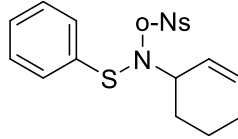


<sup>13</sup>C NMR (75 MHz, CDCl₃)

<sup>1</sup>H NMR (300 MHz, CDCl₃)



<sup>13</sup>C NMR (75 MHz, CDCl₃)



50

$^{1}$H NMR (300 MHz, CDCl$_3$)

S$^{+}$(Ph)(CH$_3$)—N$^{-}$(o-Ns)

$^{13}$C NMR (75 MHz, CDCl$_3$)

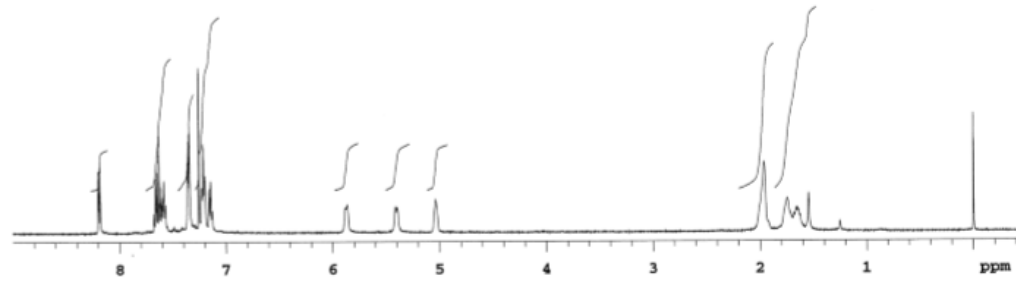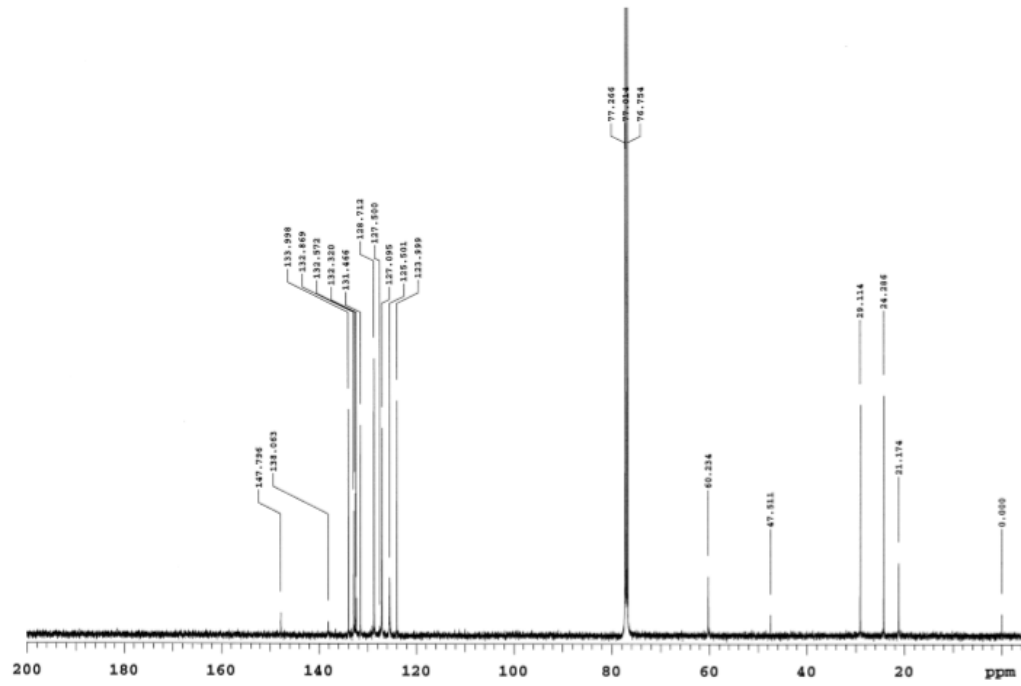$$\overset{\displaystyle \overline{\phantom{N}}}{\underset{+}{\overset{N SO_2Ph}{S}}} \!\!-\!CH_3$$

<sup>1</sup>H NMR (500 MHz, CDCl₃)

$^1$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (75 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (75 MHz, CDCl$_3$)
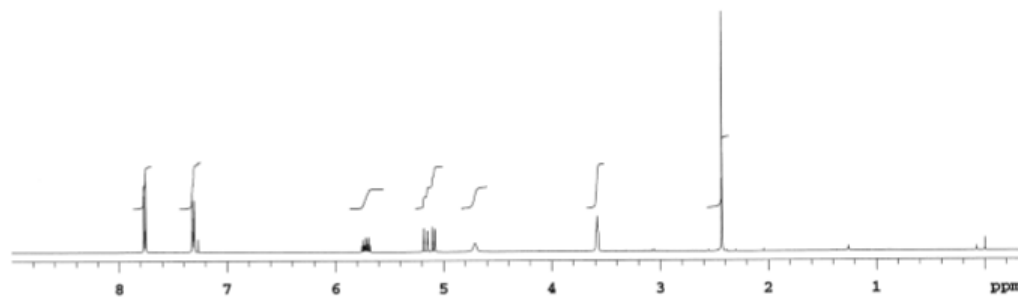
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

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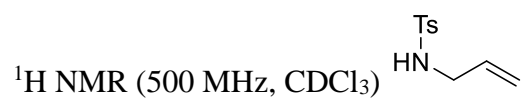$^1$H NMR (500 MHz, CDCl$_3$)
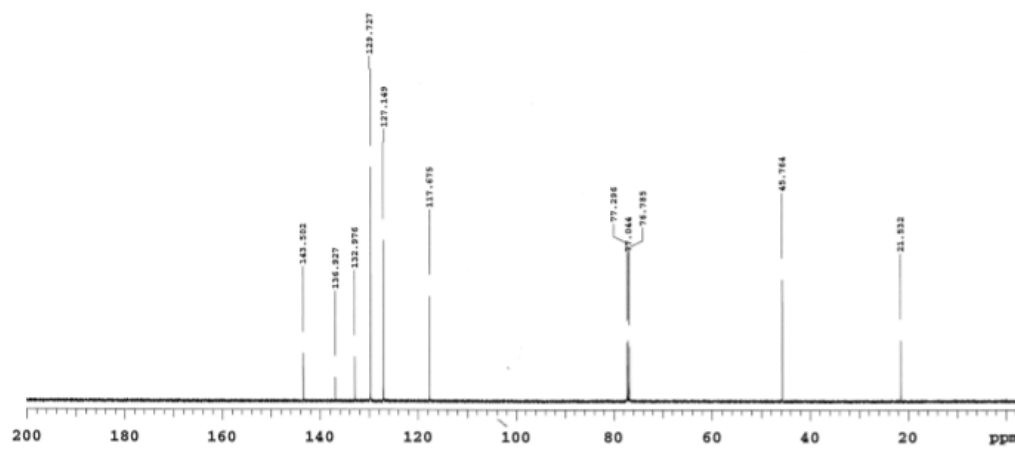


$^{13}$C NMR (75 MHz, CDCl$_3$)



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<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

<sup>1</sup>H NMR (500 MHz, CDCl₃)
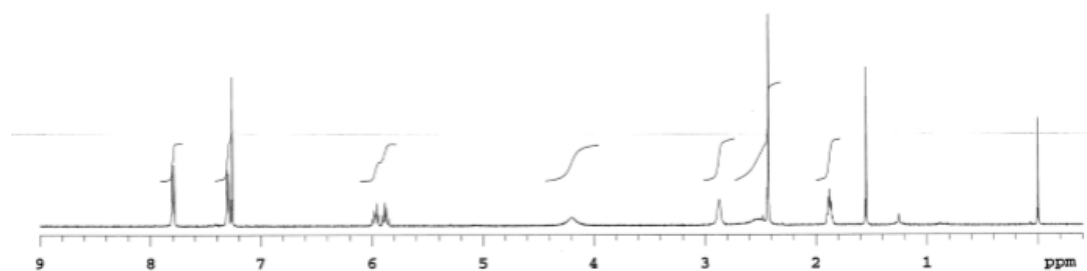
$^{1}$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (75 MHz, CDCl$_3$)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

p-Ns



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)



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$^1$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (75 MHz, CDCl$_3$)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

$^1$H NMR (500 MHz, CDCl$_3$)



$^{13}$C NMR (75 MHz, CDCl$_3$)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)



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<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



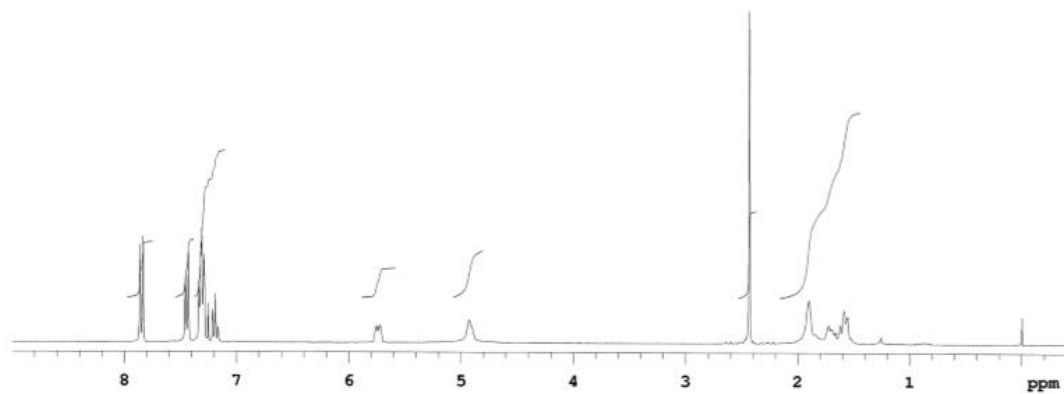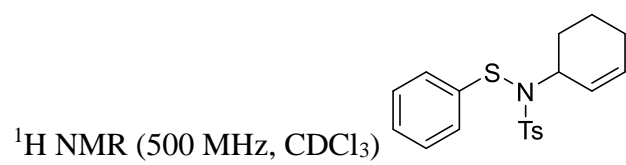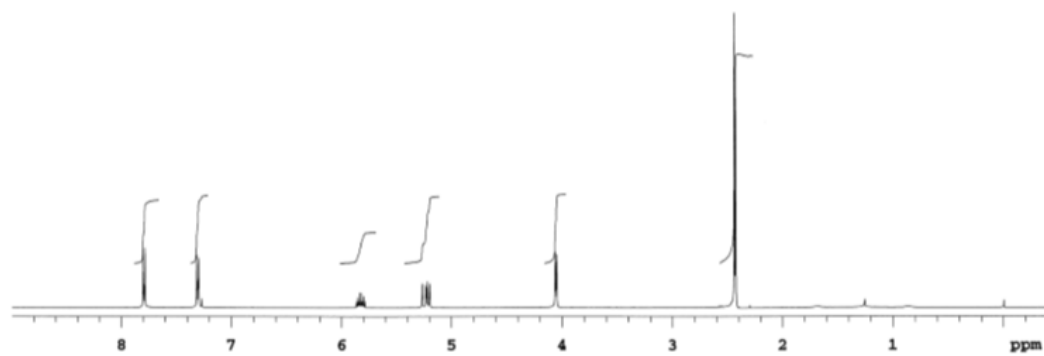<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)
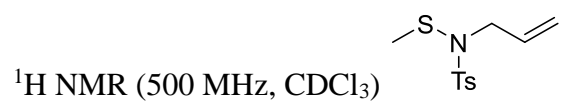
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

¹H NMR (500 MHz, CDCl₃)



¹³C NMR (75 MHz, CDCl₃)