SYNTHESIS OF 1,1-DISUBSTITUTED ALKYL VINYL SULFIDES VIA
RHODIUM-CATALYZED ALKYNE HYDROTHIOLATION:
SCOPE AND LIMITATIONS

by

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# Abstract

Tp*Rh(PPh$_3$)$_2$ is a useful catalyst for alkyne hydrothiolation. Vinyl sulfides, the products of this reaction, are useful synthetic intermediates. The goal of this thesis project was to explore the scope and limitations of alkyne hydrothiolation with alkyl thiols catalyzed by Tp*Rh(PPh$_3$)$_2$. A variety of thiols and alkynes successfully undergo catalytic hydrothiolation. In general, the branched isomer was formed in good-to-excellent yields and with high selectivity. Electron rich phenylacetylenes were more reactive than electron deficient ones, and provided higher yields. Aliphatic alkynes need longer reaction times than aromatic alkynes in order to reach complete conversion. A broad range of functional groups were well tolerated, including halides, amines, nitriles, amines, ethers, esters and silanes. Alkoxy groups with the ability to coordinate with rhodium slowed down the catalytic turnover and lowered the yields. Strongly coordinating groups, such as pyridine, precluded catalysis. Alkynes that are Michael acceptors react with reversed regioselectivity. Hydrothiolation using internal alkynes was successful, although the reaction times were longer and temperatures are higher than that needed for terminal alkynes. Overall, the work presented in this thesis provides a general method in construction of branched alkyl vinyl sulfides from alkynes.

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| | |
|---|---|
| Å | angstroms ($10^{-10}$ meters) |
| μ | mu, micro |
| br | broad |
| calcd | calculated |
| cat. | catalyst |
| cm | centimeters |
| *J* | coupling constant |
| ° | degrees |
| °C | degrees Celcius |
| *d* | deuterium |
| DCE | 1,2-dichloroethane |
| Bp | dihydrobis(pyrazolyl)borate |
| d | doublet |
| EI | electron impact |
| equiv. | equivalents |
| Et | ethyl |
| ν | frequency |
| δ | gamma |
| GC-MS | gas chromatography-mass spectroscopy |
| g | gram |
| Hz | hertz |
| HRMS | high resolution mass spectroscopy |
| h | hours |
| Tp | hydrotris(pyrazolyl)borate |
| *i* | iso |
| *i*-Pr | isopropyl |
| κ | kappa |
| K | kelvin |
| kcal | kilocalorie |
| L | liter |
| LRMS | low resolution mass spectroscopy |
| m/z | mass/charge |
| MALDI | matrix-assisted laser desorption/ionization |
| MHz | mega hertz |
| Me | methyl |
| DCM | dichloromethane |
| μL | microliter |
| mg | milligram |

| | |
|---|---|
| mL | milliliter |
| mmol | millimole |
| min | minutes |
| M | molar (mol $L^{-1}$) |
| mol | mole |
| m | multiplet |
| *n* | normal |
| NMR | nuclear magnetic resonance |
| ORTEP | Oakridge Thermal Ellipsoid Plot |
| ppm | parts per million |
| Ph | phenyl |
| $\pi$ | pi |
| q | quartet |
| rt | room temperature |
| SEM | scanning electron microscopy |
| s | singlet |
| *t* | tertiary |
| t | triplet |
| THF | tetrahydrofuran |
| TEMPO | 2,2,6,6-tetramethylpiperidine-*N*-oxyl |
| $PMe_3$ | trimethylphosphine |
| $PPh_3$ | triphenylphosphine |
| UV | ultra violet |
| *Z* | zusammen |
| *E* | entgegen |
| DBU | 1,8-Diazabicyclo[5.4.0]undec-7-ene |
| Tp* | tris(3,5-dimethylpyrazolyl)borate |
| $Tp^{Ph,Me}$ | tris(3-phenyl,5-methylpyrazolyl)borate |

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# Chapter 1 – Introduction

## 1.1 Background

Sulfur is a very important element in nature. It is used in many industrial products such as rubber, detergents, fungicides, dyestuffs, agrichemicals, and medicines.[1] Many natural products also contain C-S bonds. Griseoviridin, a broad spectrum streptogramin antibiotic, is only one of many examples.[2]
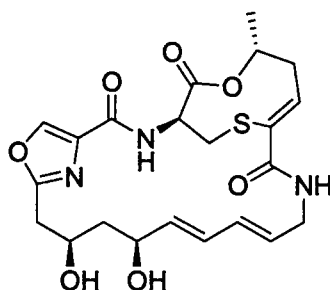


**Figure 1.1. Griseoviridin**

Vinyl sulfides are important synthetic intermediates and powerful building blocks for many natural and synthetic molecules.[3] Cross coupling of vinyl halides and thiols is a viable method to obtain vinyl sulfides.[4] However, alkyne hydrothiolation, the addition of a thiol to the π-bond of an acetylene, is a more atom-economical method to gain vinyl sulfide products, by converting all of the atoms in the starting materials into the products, thereby limiting waste production.

Generally, in alkyne hydrothiolation of terminal alkynes, there are three potential products: branched, *E*-linear, and *Z*-linear isomers (eq **1.1**). Free radical[5] and nucleophilic[6] hydrothiolation have been applied for making vinyl sulfides, but these

methodologies are generally limited to aryl thiols. Another significant disadvantage is that neither method can give branched products: free radical reactions only give the linear isomer without selectivity and nucleophilic reactions preferentially generate the Z-linear isomer.

$$RSH \ + \ R^1\text{---}\equiv\quad\longrightarrow\quad \underset{\text{branched}}{R^1\overset{SR}{\diagup}\diagdown} \ + \ \underset{E\text{-linear}}{R^1\diagup\diagdown SR} \ + \ \underset{Z\text{-linear}}{R^1\diagdown\diagup_{SR}} \quad (1.1)$$
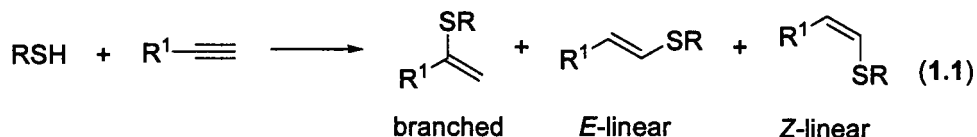
Transition metal catalyzed cross coupling reactions are widely used in the construction of carbon-heteroatom bonds. The use of amines,[7] alcohols[8] and phosphines[9] in cross coupling reactions with suitable substrates is well documented in the literature. However, because of the widespread prejudice that thiols are considered as catalyst poisons,[10] the transition metal catalyzed addition of thiols to alkynes has not received as much attention. Moreover, the cases of synthesizing branched alkyl vinyl sulfides using transition metal are even scarce. Therefore, there is a great demand to find a general synthetic method towards the branched alkyl vinyl sulfides selectively.

## 1.2 Hydrothiolation Reactions

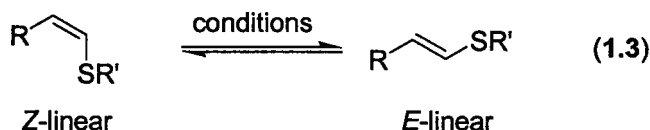As shown before, there are three major products in the hydrothiolation of alkynes. The branched isomer is formed from Markovnikov addition, whereas the $E$-linear and $Z$-linear isomers are formed from anti-Markovnikov addition. Comparing the two linear products, the $Z$-linear isomer is kinetically favored while the $E$-linear isomer is thermodynamically more stable. In this section, the methods to form the linear and branched isomers will be discussed in detail.

### 1.2.1 Linear Isomers

The first publication in this field was by H. Bader and co-workers in 1949.[11] In this paper, 1-hexyne was treated with thioacetic acid and was heated for 10 min to give 1-hexenyl thioacetate in 53% yield (eq **1.2**). The mechanism and stereoselectivity of this reaction were not mentioned.

$$CH_3COSH \quad + \quad n\text{-}C_4H_9 \equiv \quad \xrightarrow{\text{heat}} \quad \underset{H \quad\quad H}{\overset{n\text{-}C_4H_9 \quad SCOCH_3}{>=<}} \quad\quad (1.2)$$

$$53\%$$
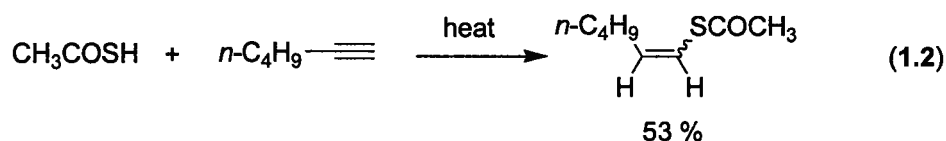
Isomerization between $E$- and $Z$-linear adducts often accompanies the reaction (eq **1.3**). Based on Truce and co-workers' publication in 1972, the equilibrium could be achieved in 15 min under dilute acidic conditions, while under basic condition it needed hours or days.[6c] The ratio of the $E$- and $Z$-linear isomers was approximately 3:1.[6c]

$$\underset{\text{Z-linear}}{R\diagup\diagdown\underset{SR'}{\big|}} \quad \underset{\xleftarrow{\hspace{2cm}}}{\overset{\text{conditions}}{\xrightarrow{\hspace{2cm}}}} \quad \underset{\text{E-linear}}{R\diagdown\diagup\diagdown SR'} \quad\quad (1.3)$$

## 1.2.1.1 Free Radical Hydrothiolation

Free radical reactions were versatile in the synthesis of organic molecules, and free radical hydrothiolation has been under investigation since the 1960s. Usually this type of reaction was induced by either UV radiation or chemical initiators.[5b] However, the ratio of the E- and Z-linear isomers was often hard to control.[5a,b] Generally, the Z-linear isomer was formed preferentially. In some cases, the ratio of the products depended on the ratio of thiol to alkyne. For example, in the free radical addition of benzenethiol to phenylacetylene, when the ratio of thiol to alkyne was 20:1, the Z-linear isomer was formed in 16% yield. When the ratio was changed to 1:1, the yield of the Z-linear isomer was 56%. In comparison, when the ratio was 1:20, the Z-linear isomer was formed in over 95% yield.[5a,b]

In 1987, Oshima and co-workers reported the free radical hydrothiolation reaction catalyzed by Et$_3$B. The yields for aromatic thiol were good-to-excellent (70-91%), but for aliphatic thiols, the yields were low even after prolonged reaction time. This problem can be solved by adding 4 equivalents of methanol. However, this reaction showed no stereoselectivity between the E and Z-linear isomers (see Scheme 1.1).[5d]
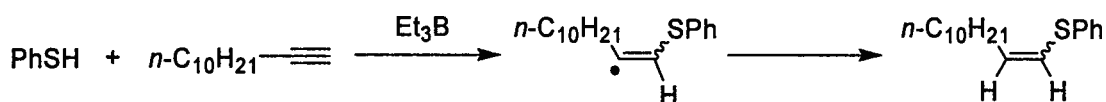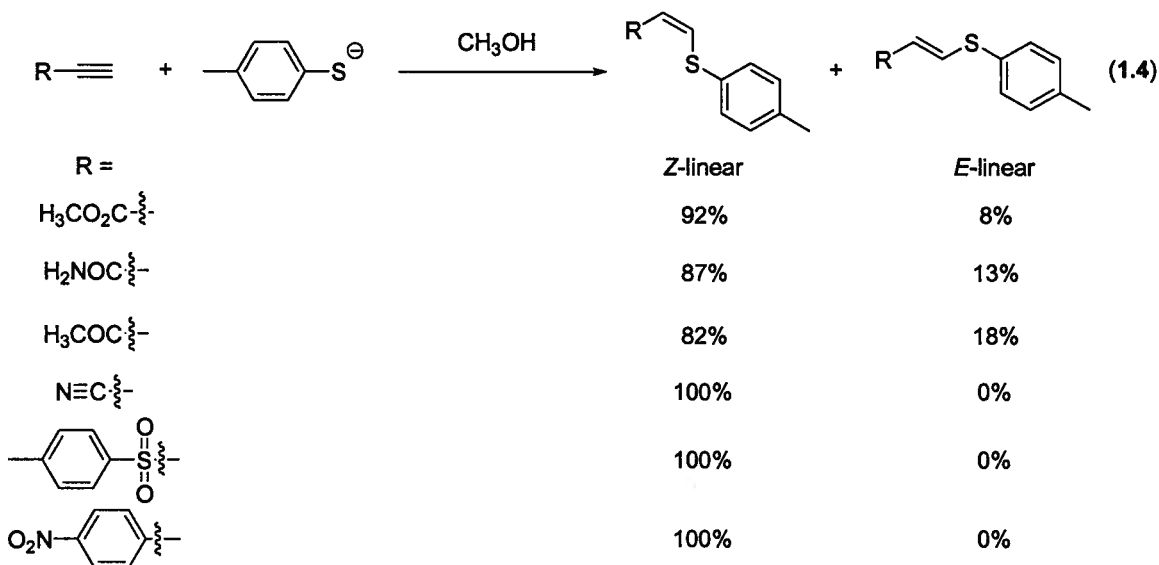


**Scheme 1.1**

## 1.2.1.2 Nucleophilic Hydrothiolation

Nnucleophilic hydrothiolation favored the Z-linear product via *trans*-addition of thiol to alkyne.[6a,c-e] In the early stage of nucleophilic hydrothiolation, thiols were

deprotonated to the thiolate first and then reacted with acetylenes in ethanol to produce Z-linear isomers in moderate to good yields (65-87%).[6a] The reaction between p-toluenethiolate and acetylenes containing carbonyl groups, such as amide and acetyl, gave high degree of Z-adducts, but also had some E-adducts (about 10-20%). However the other activating groups such as p-tolysulfonyl, cyano, and p-nitrophenyl gave the Z-adducts exclusively (eq 1.4).[6c]



| R = | Z-linear | E-linear |
|---|---|---|
| $H_3CO_2C$- | 92% | 8% |
| $H_2NOC$- | 87% | 13% |
| $H_3COC$- | 82% | 18% |
| $N\equiv C$- | 100% | 0% |
| (p-tolylsulfonyl)- | 100% | 0% |
| $O_2N$-(phenyl)- | 100% | 0% |

In 2005, Oshima and co-workers reported stereoselective hydrothiolation catalyzed by cesium carbonate. Aryl alkynes and alkyl thiols were used in this reaction and the Z-linear isomer was found to be preferred.[6e] A free radical pathway was completely inhibited by the radical inhibitor (TEMPO), so only nucleophilic hydrothiolation occurred. The electronic effect of the arylacetylenes had been examined: electron donating groups gave the Z-isomer exclusively but higher temperature was needed in order to get high yields; the electron withdrawing groups could help the reaction occur even at room temperature but without selectivity, and E-linear isomer was favored at high
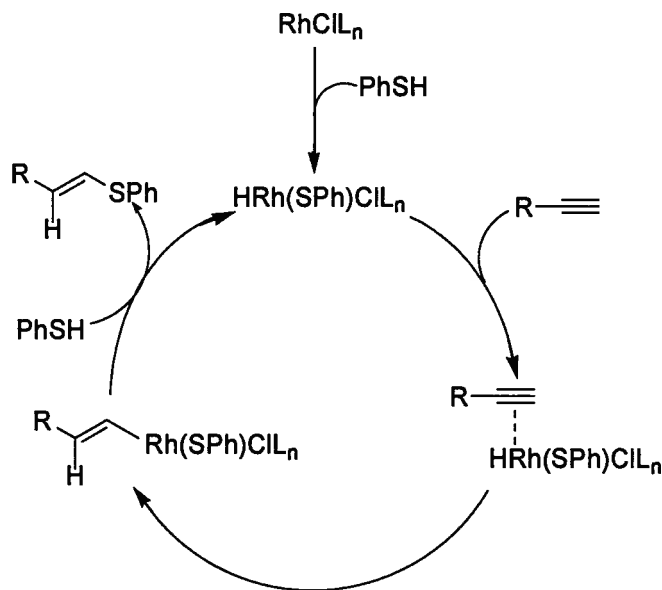
reaction temperature. A limitation of this methodology was that aryl thiols were found to give poor yield even at high temperature.

### 1.2.1.3 Transition Metal-Catalyzed Hydrothiolation

In 1976, Newton and co-workers discovered the first hydrothiolation reaction, catalyzed by molybdenum. Thiols were treated as both the electron and proton donor in the reaction.[12a] The molybdenum catalyst facilitated the reaction between benzenethiol and dimethyl acetylenedicarboxylate in 25% yield with over 95% of the $E$-isomer (eq 1.5).
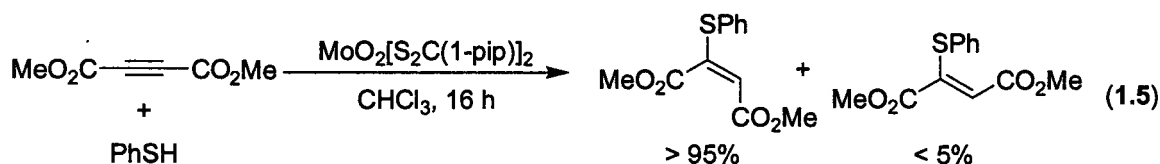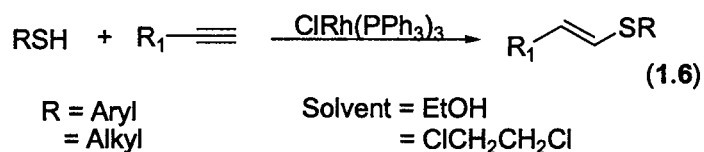


The methodology for selectively synthesizing the $E$-linear isomer was greatly improved by Ogawa and co-workers in 1999.[12b] They discovered that Wilkinson's catalyst, $ClRh(PPh_3)_3$, catalyzed the hydrothiolation of 1-octyne and benzene thiol in good yield (62-97%). EtOH was found to be the best solvent and the reaction was completed after 20 hours at 20-40 °C with the $E$-linear isomer formed preferentially. Some mechanistic data had been obtained and the key step of the catalytic cycle was postulated to be migratory insertion of the alkyne into the Rh-H bond (see Scheme 1.2).[12b]

RhClL$_n$

PhSH

R$\diagdown$  
$\quad\diagup$SPh  
H

HRh(SPh)ClL$_n$

R$\longrightarrow\!\!\!\equiv$

PhSH

R$\diagdown$  
$\quad\diagup\diagdown$Rh(SPh)ClL$_n$  
H

R$\longrightarrow\!\!\!\equiv$  
$\;\vdots$  
HRh(SPh)ClL$_n$

**Scheme 1.2**

The problem with this methodology was only benzene thiol was investigated as the thiol source and the author indicated that alkyl thiols did not work under the same conditions.[12b,c] Our research group has recently reported that Wilkinson's catalyst did catalyze hydrothiolation reaction using alkyl thiols with good regioselectivity of the *E*-linear isomer, when the solvent was changed from ethanol to 1,2-dichloroethane (eq 1.6).[12d]

$$\text{RSH} + \text{R}_1\!\!\longrightarrow\!\!\!\equiv \xrightarrow{\text{ClRh(PPh}_3)_3} \text{R}_1\diagup\!\!\diagdown\!\!\diagup\text{SR} \quad \text{(1.6)}$$

R = Aryl  
   = Alkyl

Solvent = EtOH  
          = ClCH$_2$CH$_2$Cl

In 2007, Yadav and co-workers reported InBr$_3$ to be an efficient catalyst in hydrothiolation using aryl thiols.[12e] Aryl alkynes gave a mixture of linear products in excellent yield with the *E*-linear isomer favored. However, when aliphatic alkynes were

used, the product was the corresponding thioacetal (see Scheme 1.3). All the reactions were completed in less than 30 minutes, but no mechanistic data were provided.
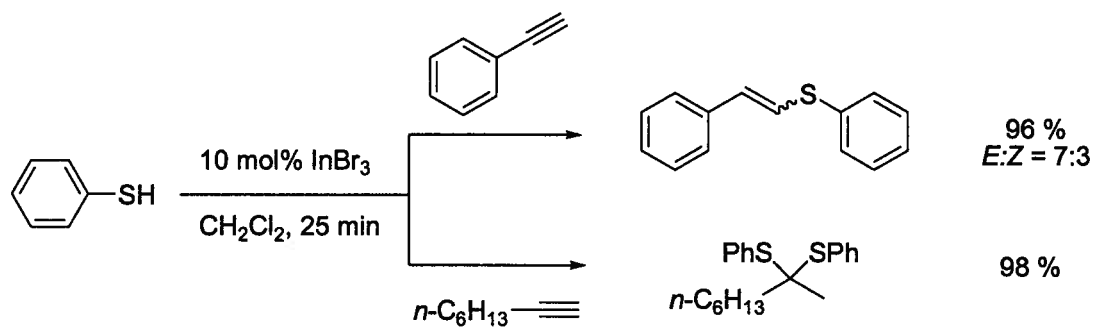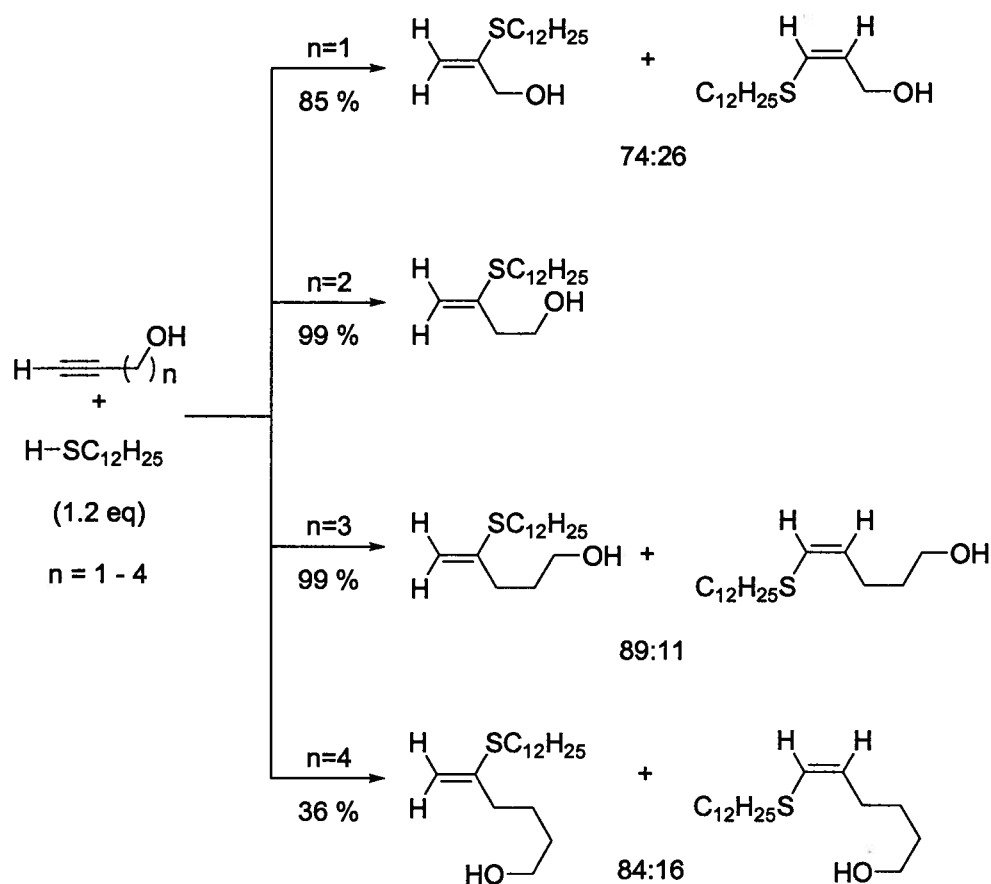


**Scheme 1.3**

## 1.2.2 Branched Isomer

Compared with the linear adducts, the branched product is much more difficult to access, and the examples of using alkyl thiols are uncommon. In Truce's 1956 paper, some branched product was obtained together with the linear adducts using nucleophilic sodium p-toluenethiolate, but no selectivity was reported.[6a]

## 1.2.2.1 Nucleophilic Hydrothiolation

The few examples of hydrothiolation using aliphatic thiols that form the branched isomer regioselectively employ nucleophilic conditions. In 2005, Oshima and co-workers found terminal alkynes with a hydroxyl group can give the branched isomer in cesium carbonate mediated hydrothiolation (see Scheme 1.4).[6e] 3-butyn-1-ol gave 99% of branched product exclusively (n=2). Propargyl alcohol (n=1) and 4-pentyn-1-ol (n=3) gave a mixture of Z-linear and branched adducts in good and excellent yields respectively,

with the branched isomer favored. However, if n=4, the yield decreased significantly, but the stereoselectivity was still the same. No reasonable explanation was given in the paper.
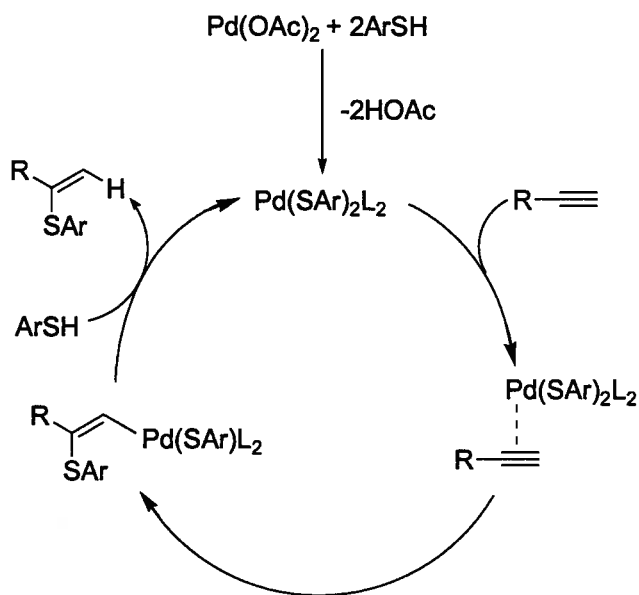


**Scheme 1.4**

### 1.2.2.2 Transition Metal-Catalyzed Hydrothiolation

The first work of synthesizing branched vinyl sulfides was performed by Ogawa and co-workers in 1992.[12c] They discovered $Pd(OAc)_2$ catalyzed hydrothiolation and provided the branched isomer as the major adduct. However, only aryl thiols and a few alkynes were investigated, no alkyl thiol was employed, and the reactions needed high temperature and prolonged reaction times. A plausible reaction mechanism was also

provided. Migratory insertion of alkynes into Pd-S bond was considered as the key step of the reaction (see Scheme 1.5).

$$Pd(OAc)_2 + 2ArSH$$

$$\downarrow -2HOAc$$

Pd(SAr)$_2$L$_2$

R—≡≡

R—≡≡  Pd(SAr)$_2$L$_2$

ArSH

R \ / H
  \=/
  SAr

R \ / Pd(SAr)L$_2$
  \=/
  SAr

**Scheme 1.5**

Hydrothiolation of benzenethiol and conjugated terminal enynes with a terminal triple bond was achieved by Bäckvall and co-workers in 1994. In each case, the triple bond was found more reactive than the double bond, and the branched diene was formed in moderate yield (41-75%).[12f] However, the reaction of internal enynes was not successful and only benzenethiol was used as a thiol source. Those products can be oxidized to the sulfoxide derivatives by oxone. Furthermore, those conjugated dienes could be further functionalized by Michael addition of a nucleophile, followed by [2,3] sigmatropic rearrangement to generate the allylic alcohol (see Scheme 1.6).
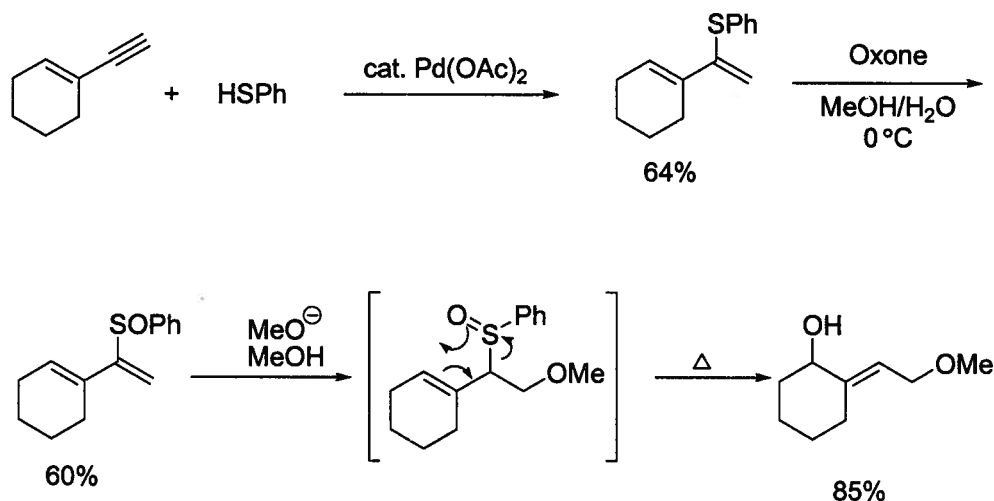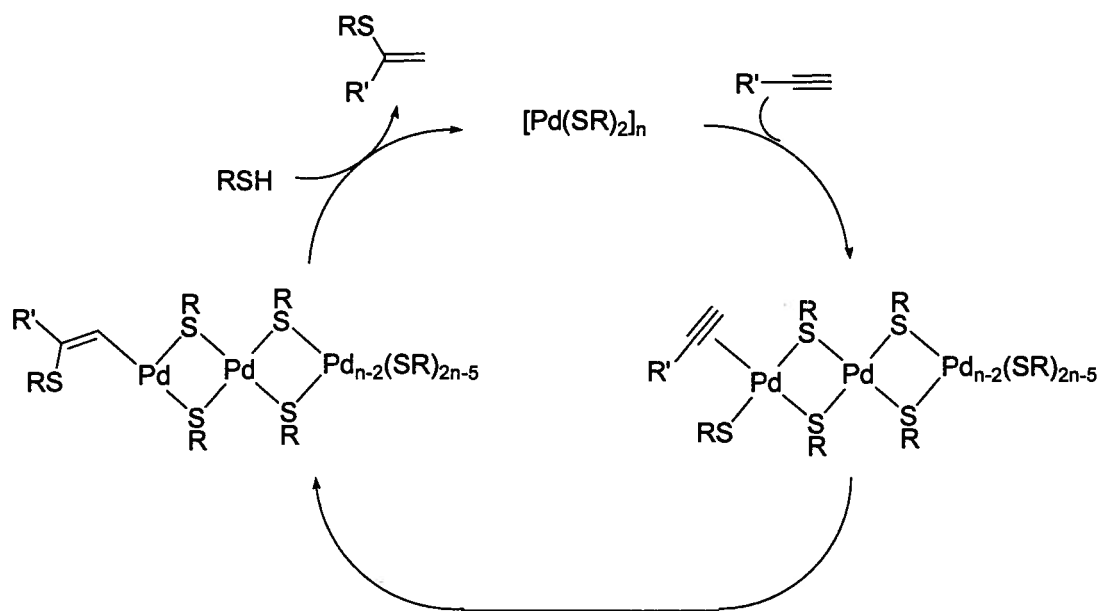
**Scheme 1.6**

In 2007, Beletskaya and co-workers reported a novel approach for the preparation of one dimensional Pd nanoparticles with organic ligands.[12g] In this approach, Pd(OAc)$_2$ dissolved in alkyne, reacted with thiol and generated nanostructured Pd species in 85% yield at room temperature (see Scheme 1.7). Both nm- and $\mu$m-scale Pd species could be prepared depending on different reaction conditions, but only nm-scale Pd nanoparticles had high efficiency and regioselectivity for the branched isomer in hydrothiolation reactions.
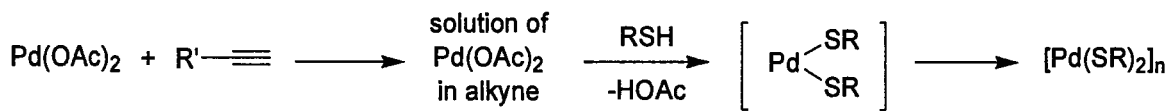


**Scheme 1.7**

The hydrothiolation reaction occurred at 80-100 °C or under microwave heating. Cyclohexanethiol reacted with different terminal alkynes in good to excellent yields (75-92%) with great regioselectivity for the branched isomer. Benzene thiol was less reactive but the regioselectivity was still good. A postulated reaction mechanism was also

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provided. Alkyne coordinated to palladium, migratory inserted into the Pd-S bond and trapped by thiol to generate the product (see Scheme 1.8). This is the second report about synthesizing the branched alkyl vinyl sulfide in hydrothiolation reaction.



**Scheme 1.8**

## 1.3 Previous work of our group

The first example of synthesizing the branched alkyl vinyl sulfide via transition metal catalyzed hydrothiolation was reported by our group in 2005.[12h] Tp*Rh(PPh3)2 (I, Tp* = tris(3,5-dimethylpyrazolyl)-borate, Figure 1.2) was an efficient catalyst to give the branched isomer predominantly in good to excellent yields and selectivity. Ten examples using alkyl thiols were given. Aryl thiols were also found to generate the branched isomer preferentially, but the selectivity was lower. Because the products of the reactions using aryl thiols are readily available using other means, these reactions were not studied further. Instead, we chose to explore the use of alkyl thiols because the vinyl sulfide products are not readily available.
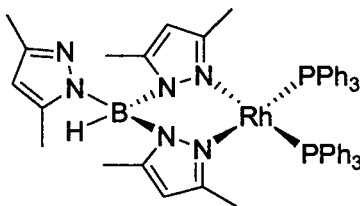


**Figure 1.2. Tp*Rh(PPh3)2 Complex (I)**

A series of pyrazolylborate ligands, such as Tp* (tris(3,5-dimethylpyrazolyl)borate), Bp* (bis(3,5-dimethylpyrazolyl)borate), Tp (trispyrazolylborate), Tp^Ph (tris(3-phenylpyrazolyl)borate), and Tp^Ph,Me (tris(3-phenyl,5-methylpyrazolyl)borate), were used to synthesize different kinds of rhodium complexes.[12j] For the catalytic activity, Bp* < Tp < Tp^Ph < Tp^Ph,Me ~ Tp*. Since the synthesis and purification of Tp^Ph,Me rhodium complex was more difficult, Tp*Rh(PPh3)2 was chosen for scope and limitation investigations.

A previous undergraduate student (Baldip Kang) had performed some preliminary mechanistic investigations using labeling studies.[13a] The reaction was believed to

proceed via oxidative addition of the thiol, ligand exchange of triphenylphosphine for the alkyne, alkyne insertion into Rh-S bond, and reductive elimination to form the branched product and regenerate the catalyst (see Scheme 1.9). Further exploration of the reaction mechanism is underway.[13b]
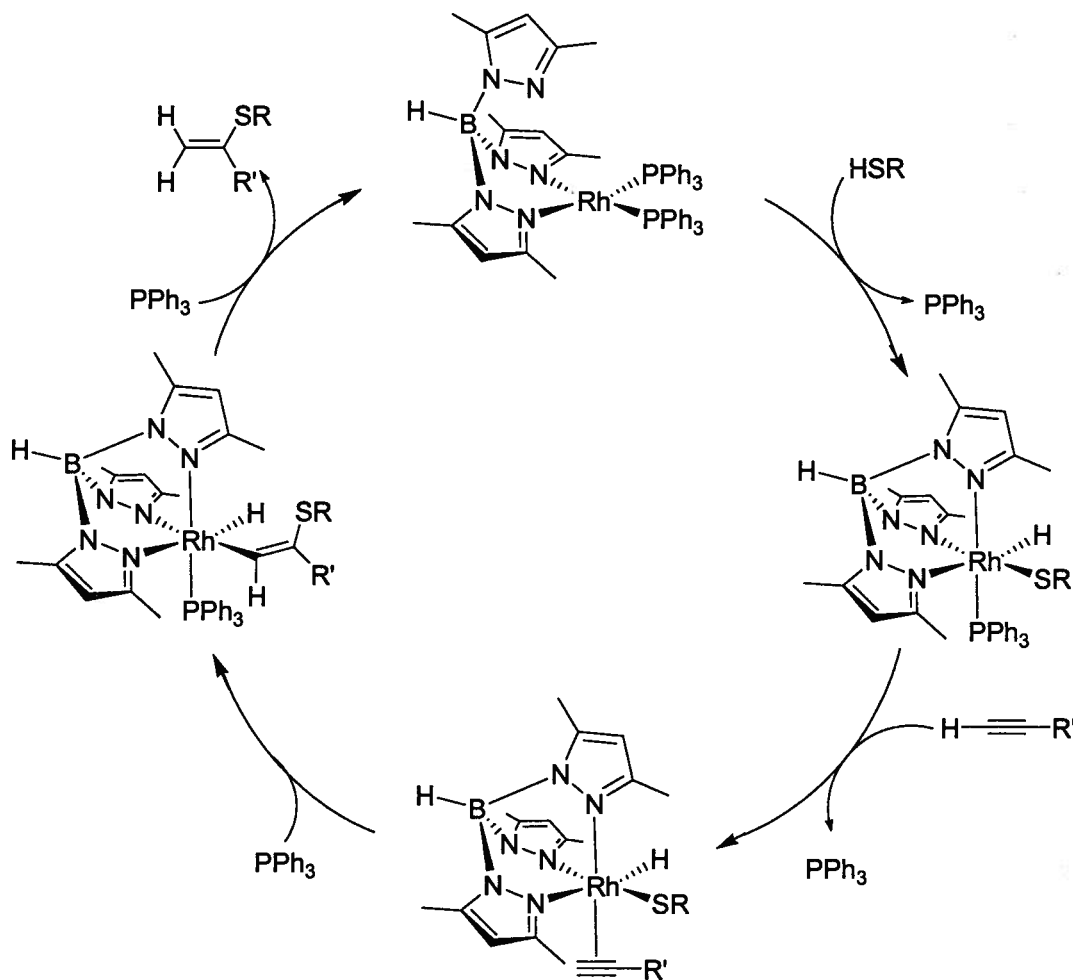


**Scheme 1.9**

Another important observation is that Tp*Rh(PPh₃)₂ was found to decompose in THF and DCE if left for prolonged time, producing a complex via orthometalation of one of the phosphine ligands (eq **1.7**).[14] Although it formed a strained four-membered ring, this process was determined to be irreversible. This would be detrimental to a catalytic

reaction, as it would remove the active catalyst. The cyclometalation could be avoided once some nonpolar solvents were used, such as benzene and toluene. For hydrothiolation, slightly polar solvents are needed. Thus, a 1:1 ratio of toluene and DCE was found to be optimal for hydrothiolation and would preclude catalyst decomposition even if prolonged reaction times were needed.



$$\xrightarrow[\substack{\text{rt, 12 h} \\ (73\%)}]{\text{DCE}}$$

(1.7)
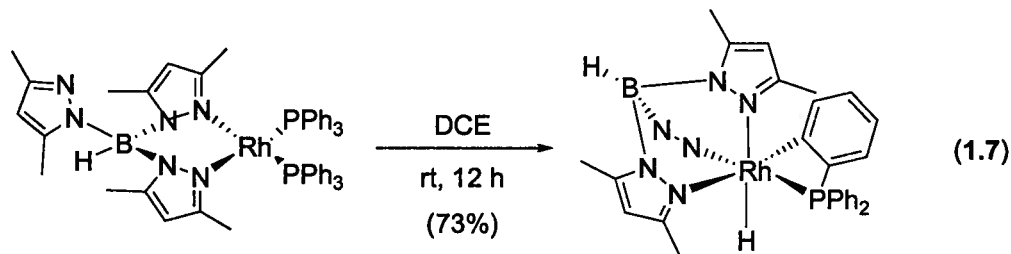
Tp*Rh(PPh$_3$)$_2$ was demonstrated to not only work in alkyne hydrothiolation, but also catalyze alkyne hydrophosphinylation (eq **1.8**).[15] Compared with hydrothiolation, in which the branched isomer was formed predominantly, it was expected to produce the same isomer for hydrophosphinylation. Upon investigation of this hypothesis, it was found that Tp*Rh(PPh$_3$)$_2$ did catalyze alkyne hydrophosphinylation, although not as well as Wilkinson's catalyst. In addition, the product was not the branched isomer, but the *E*-linear adducts. It was postulated that both Wilkinson's catalyst and Tp*Rh(PPh$_3$) reacted with Ph$_2$P(O)H to generate the active catalytic species and that this process was more efficient with Wilkinson's catalyst.



$$Ph_2P(O)H + R\text{---}\equiv \longrightarrow$$

branched     *E*-linear     *Z*-linear

(1.8)

15
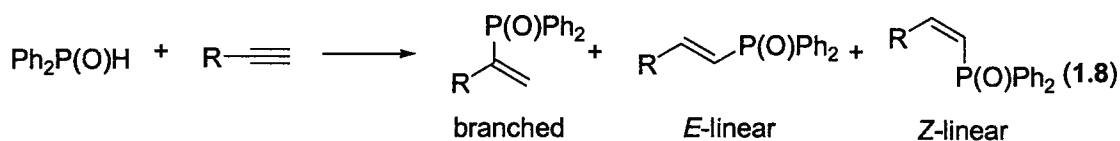
## 1.4 Summary

Vinyl sulfides are important synthetic intermediates in total synthesis and useful building blocks for many highly functionalized molecules. Transition metal catalyzed alkyne hydrothiolation is an efficient method to produce vinyl sulfides. Methods of forming the *E*- and *Z*- linear adducts have been investigated widely. However, most methods of making branched isomer are limited to aryl thiols. Tp*Rh(PPh$_3$)$_2$ is a promising catalyst for alkyne hydrothiolation reaction, giving branched alkyl vinyl sulfides predominantly. Given that this process provides a useful strategy for the formation of branched alkyl vinyl sulfides, we wanted to explore the substrate scope and limitations of this catalyst. As such, the goals of this research project were to evaluate functional group tolerance, as well as steric and electronic effects in alkyne hydrothiolation catalyzed by Tp*Rh(PPh$_3$)$_2$ .

# Chapter 2 –Substrate Scope and Limitations of

# Tp*Rh(PPh₃)₂ Catalyzing Alkyne Hydrothiolation

## 2.1 Introduction

Alkyne hydrothiolation, as discussed in chapter 1, is the addition of an S-H bond

across an alkynyl π-bond and is a very efficient method for the synthesis of vinyl sulfides

(eq 2.1). Although aryl vinyl sulfides can be made by radical,[5] nucleophilic,[6] and metal-

catalyzed[12] reactions, a general synthetic method of the branched alkyl vinyl sulfides is

still not well developed.



$$\text{branched (a)} \quad E\text{-linear (b)} \quad Z\text{-linear (c)}$$
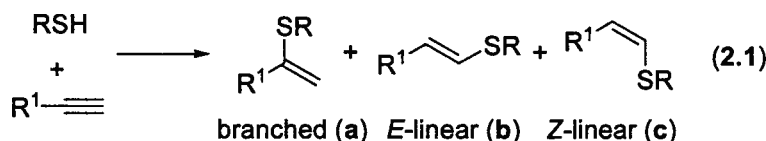
Our group has recently reported that Tp*Rh(PPh₃)₂ (I, Figure 1.2)[12h] and Tp$^{Ph,Me}$

Rh(PPh₃)₂ are excellent catalysts for alkyne hydrothiolation using alkyl thiols to generate

branched alkyl vinyl sulfides.[12h,j] In our early work, we reported ten examples of alkyne

hydrothiolation. We wanted to explore the scope in greater detail. Since the synthesis and

purification of the Tp$^{Ph,Me}$ rhodium complex was difficult and time consuming,

Tp*Rh(PPh₃)₂ was chosen for the scope and limitations investigation.

## 2.2 Results and Discussion

A broad range of thiols and alkynes were selected for investigation. The reactions are classified into five parts: (1) hydrothiolation of benzylthiol and aryl alkynes, (2) hydrothiolation of benzylthiol and aliphatic alkynes, (3) hydrothiolation of phenylacetylene with different thiols, (4) hydrothiolation of different alkynes and $n$-propanethiol, and (5) hydrothiolation of internal alkynes and other cases. The hydrothiolation using $n$-propanethiol was done by another group member (Anthony Sabarre), and some reactions from this previous work will be cited.
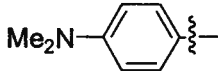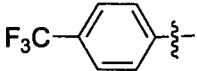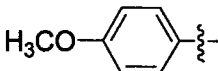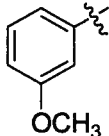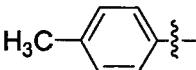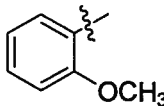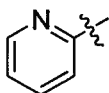
In a typical experiment, PhCH₃ (2 mL), 1,2-dichloroethane (DCE, 2 mL) and Tp*Rh(PPh₃)₂ (280 mg, 0.30 mmol, 3 mol %) were combined in a 20 mL vial equipped with a magnetic stir bar and a screw cap. Thiol (11 mmol, 1.1 equiv relative to alkyne) and alkyne (10 mmol) were then added and the solution was stirred at room temperature for 2 hours. In some cases longer reaction times and higher temperatures were needed; these conditions will be noted in the text and in the experimental section.

### 2.2.1 Hydrothiolation of Benzylthiol and Aryl Alkynes

We first examined the electronic effect of *para*-substituted phenylacetylenes (Table 2.1, entries 1-6). The electronic modifications at the *para*- position did not influence the reaction regioselectivity, but h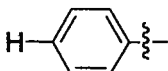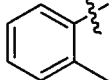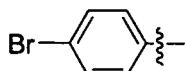ad a significant effect on the reaction efficiency and yield. The branched isomers were the only product of these reactions. Alkynes with electron-donating groups (entries 1-4) gave excellent yields, but those with electron-withdrawing groups (entries 5 and 6) gave lower yields. The methoxy group at *meta*- position (entry 7) also gave a very good isolated yield, however the yield of the reaction of *ortho*-methoxyphenylacetylene (entry 8) was much lower even after 24 hours. There are two

potential explanations for these results: the methoxy group at the *ortho-* position could be too bulky and/or the oxygen of the ether could coordinate to rhodium. Both scenarios would lead to slower catalysis. We chose a more sterically demanding *ortho-*methylphenylacetylene (entry 9) for further investigation and found that the yield was still good. Since the methyl group cannot coordinate to rhodium easily, we concluded that the coordination of oxygen to rhodium was the reason for the low reaction efficiency and yield indicated in entry 8. An alkyne with a strongly coordinating group, 2-pyridylacetylene (entry 10), showed no reactivity at all.

**Table 2.1.** Scope of Hydrothiolation of Aryl Alkynes with Benzylthiol Catalyzed by **I**.

$$Ph\text{-}SH + Ar\text{---}\equiv \xrightarrow[\text{2 h, rt}]{\substack{\text{3 mol\% I} \\ \text{DCE:PhCH}_3\ (1:1)}} Ar\text{-}C(=CH_2)\text{-}S\text{-}CH_2Ph$$

| entry[a] | Ar | product, yield[b] | entry[a] | Ar | product, yield[b] |
|---|---|---|---|---|---|
| 1 | Me₂N–C₆H₄– | **1a**, 90% | 6[d] | F₃C–C₆H₄– | **6a**, 40% |
| 2[c] | H₃CO–C₆H₄– | **2a**, 93% | 7 | (3-OCH₃-phenyl) | **7a**, 83% |
| 3 | H₃C–C₆H₄– | **3a**, 91% | 8[e] | (2-OCH₃-phenyl) | **8a**, 55% |
| 4[c] | H–C₆H₄– | **4a**, 90% | 9 | (2-CH₃-phenyl) | **9a**, 85% |
| 5[d] | Br–C₆H₄– | **5a**, 67% | 10 | (2-pyridyl) | 0% |

[a] Reaction conditions: 10 mmol alkyne, 11 mmol thiol, 4 mL of 1:1 DCE:PhCH₃, and 0.3 mmol (3 mol %) catalyst, at room temperature for 2 h, unless otherwise noted. [b] Isolated yields. [c] Ref 12h. [d] An additional ~5-10% of an unidentified byproduct was observed. [e] Reaction time 24 h.

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In order to get more information about why 2-pyridylacetylene did not react, we conducted the following reaction: Tp*Rh(PPh₃)₂ (93 mg, 0.1 mmol) was dissolved in $d_8$-toluene (1 mL), and 2-pyridylacetylene (0.1 mL, 1.0 mmol) was then added. After 30 minutes, the color of the solution changed from orange to black, and the $^{31}$P NMR spectrum showed that the PPh₃ signal Tp*Rh(PPh₃)₂ (δ 42.92, d, $J$ = 175.6 Hz) had vanished and both a new doublet (δ 45.90, $J_{Rh-P}$ = 124.7 Hz) and new singlet (δ -4.56) appeared. A rhodium hydride species (δ -14.68, $J_{Rh-H}$ = 20.5 Hz, $J_{P-H}$ = 17.6 Hz) was also detected in the $^1$H NMR spectrum. The solution was transferred to a 5 mL vial, layered with 2 mL of hexanes; crystals suitable for X-ray diffraction formed after 2 days at room temperature. The ORTEP diagram (Figure 2.1) indicated that the terminal C-H bond of alkyne was activated and a rhodium hydridoacetylide (complex II) was generated. The bond lengths and angles of complex II was very similar to other reported rhodium hydridoacetylieds.[14]

We have previously reported that such a C-H activation process irreversible and that the resulting complex has no reactivity in alkyne hydrothiolation reactions.[14] In addition, we have found that hydrothiolation proceeds by S-H activation, followed by alkyne migratory insertion.[13a] In other words, S-H activation must be faster than C-H activation.

The same phenomenon was also observed in the catalytic reaction. Thus, we thought since that binding of pyridine suppresses thiol coordination. As a result, 2-pyridylacetylene is in close proximity to the metal center, which facilitates C-H activation, thereby suppressing catalysis.
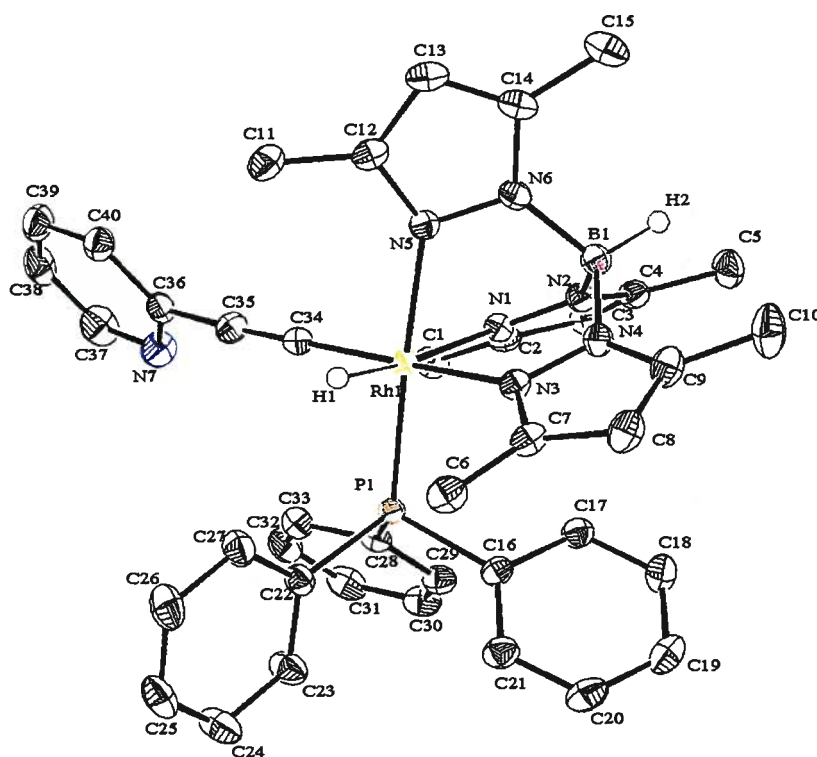
**Figure 2.1.** ORTEP diagram of complex **II**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for the B-H hydrogen and the phenyl groups of PPh₃, are excluded for clarity. Selected bond lengths (Å), angles (deg): Rh-P = 2.2732(5), Rh-C(34) = 1.9627(17), Rh-H = 1.46(2), C(34)-C(35) = 1.212(2), C(34)-Rh(1)-P(1) = 88.72(5), C(34)-Rh(1)-H(1) = 83.8(9), P(1)-Rh(1)-H(1) = 88.1(8).

## 2.2.2 Hydrothiolation of Benzylthiol and Aliphatic Alkynes

Hydrothiolation of aliphatic alkynes was studied next. Compared to aromatic alkynes, the reactions of aliphatic alkynes need longer time to complete, but the yields and selectivities were still very good. 3-Phenyl-1-propyne (Table 2.2, entry 1), 5-hexynenitrile (entry 2), 5-chloro-1-pentyne (entry 3), and 1-octyne (entry 4) reacted with benzyl thiol in good-to-excellent yields. The lower yield of phenyl propargyl ether (entry
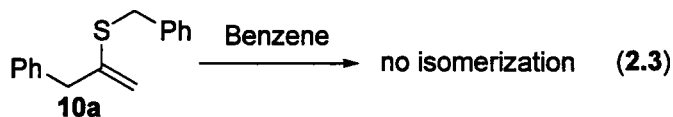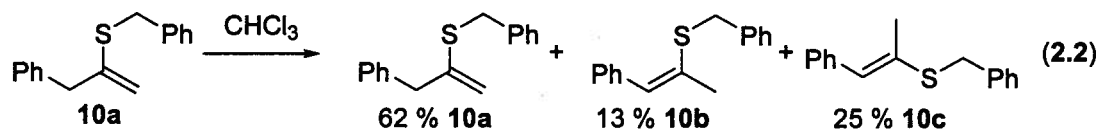
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5) could also be attributed to the coordination of oxygen to rhodium. In addition, the product of entry 6 and its oxidized derivatives may be suitable for Diels-Alder reactions.

**Table 2.2.** Scope of Hydrothiolation of Aliphatic Alkynes with Benzylthiol Catalyzed by I.

$$Ph\overset{}{\frown}SH \quad + \quad R\!-\!\!\!\equiv\!\!\! \quad \xrightarrow[\text{rt}]{\begin{array}{c}\text{3 mol\% I}\\ \text{DCE:PhCH}_3\ (1:1)\end{array}} \quad R\overset{S\overset{}{\frown}Ph}{\diagup}$$

| entry[a] | R | time (h) | product, yield[b] | entry[a] | R | time (h) | product, yield[b] |
|---|---|---|---|---|---|---|---|
| 1 | Ph\~\~ | 24 | **10a**, 85% | 6[c] | cyclohexenyl | 10 | **15a**, 81% |
| 2 | NC\~\~\~ | 48 | **11a**, 88% | 7[c] | t-Bu- | 24 | **16a**, 63% |
| 3 | Cl\~\~\~ | 24 | **12a**, 90% | | | | |
| 4 | n-C$_6$H$_{13}$- | 16 | **13a**, 92% | 8 | TMS- | 2 | **17a:17b:17c**<br>= 6:3:2, 88% |
| 5 | PhO\~\~ | 24 | **14a**, 33% | 9 | EtO$_2$C- | 2 | **18b:18c**<br>= 2:1, 68% |

[a] Reaction conditions: 10 mmol alkyne, 11 mmol thiol, 4 mL of 1:1 DCE:PhCH$_3$, and 0.3 mmol (3 mol %) catalyst, rt. [b] Isolated yields. [c] Ref 12h.

The products of the alkynes containing propargylic protons (entries 1-4) can isomerize under acidic conditions. For example, when benzyl(1-benzylvinyl)sulfane (**10a**) was let to stand in chloroform overnight, 13% of Z- and 25% of E- internal vinyl sulfide were found (eq **2.2**).[12h] This phenomenon could be avoided if less acidic solvents were used for chromatography and NMR spectroscopic studies (eq **2.3**).

S^Ph  CHCl₃ → ... Ph ... + Ph ... + Ph ...  (2.2)
**10a**   **62 % 10a**   **13 % 10b**   **25 % 10c**

Ph ... S^Ph  Benzene ——→ no isomerization   (2.3)
**10a**

The effect of sterics was also investigated. The reaction of 3,3-dimethyl-1-butyne (entry 7) took 24 hours to go to completion and formed the branched isomer in moderate yield, indicating that sterically bulky groups can somewhat slow catalysis. If trimethylsilyl acetylene (entry 9) was used, the reaction was complete in 2 hours, but the regioselectivity was lowered, with 40% of the the linear isomers being formed. It is not clear why the selectivity was lowered, but could be due to the beta-silicon effect. Trimethylsilyl groups are useful functional groups that can be easily deprotected or further functionalized in Hiyama[16] cross-coupling. The hydrothiolation of ethyl propiolate gave a mixture of *E*- and *Z*-linear isomers in a 2:1 ratio.[17] No branched product was formed in this case. This result was likely due to the strongly electron withdrawing ester group, which activates the beta-position of the alkene toward nucleophilic attack. The use of DBU generates a 1:2 ratio of *E*- and *Z*-linear isomers after 2 h at room temperature. Therefore, the result using Tp*Rh(PPh₃)₂ is not simply due to competing Michael addition. Several competing mechanisms are possible.

### 2.2.3 Hydrothiolation of Phenylacetylene with Different Thiols

Given that a variety of alkynes were found to be effective in hydrothiolation, we next examined the substrate scope of thiols that participate in this reaction. Besides benzyl thiol (Table 2.3, entry 1), a variety of alkyl thiols reacted with phenylacetylene in good yields, including both unhindered (entry 2) and sterically bulky (entry 3) groups. Many functional groups were well tolerated, such as heteroaromatic rings (entry 4), ethers (entry 5), esters (entry 6) and amines (entry 7). However, the reaction of thiols with a carboxylic acid (entry 8) or allyl group (entry 9) failed. In the latter case, since the *n*-propanethiol (entry 2) reacted with phenylacetylene successfully, we thought the double bond should play an important role in this process. This was disappointing, because if the allyl mercaptan (entry 9) reacted successfully, the product could undergo several transformations, such as thio-Cope[18] and Mislow-Evans[19] rearrangements (upon oxidation to the sulfoxide).

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**Table 2.3.** Scope of Hydrothiolation of Phenylacetylene with Different Thiols Catalyzed by **I.**

$$\text{RSH} + \text{Ph}\!-\!\!\!\equiv \xrightarrow[\substack{\text{2 h, rt}}]{\substack{\text{3 mol\% I} \\ \text{DCE:PhCH}_3\ (1:1)}} \text{Ph}\overset{\text{SR}}{=}$$

| entry[a] | R | product, yield[b] | entry[a] | R | product, yield[b] |
|---|---|---|---|---|---|
| 1[c] | Ph | 1a, 90% | 6 | BuO(C=O)~~ | 23a, 80% |
| 2[d] | ~~ | 19a, 74% | | | |
| 3[c] | cyclopentyl | 20a, 78% | 7[e] | Me₂N~~ | 24a, 65% |
| 4 | furan-CH₂ | 21a, 75% | 8[e] | HO₂C~~ | 0% |
| 5 | PhO~~ | 22a, 70% | 9[e] | allyl | 0% |

[a] Reaction conditions: 10 mmol alkyne, 11 mmol thiol, 4 mL of 1:1 DCE:PhCH₃, and 0.3 mmol (3 mol %) catalyst, at rt for 2 h, unless otherwise noted. [b] Isolated yields. [c] Ref 12h. [d] Ref 3f. [e] Reaction time: 24 h.

Further insight was obtained from the following stoichiometric reaction. A $d_8$-toluene (1 mL) solution of Tp*Rh(PPh₃)₂ (93 mg, 0.1 mmol) was placed in a NMR tube, and allyl mercaptan (0.08 mL, 1.0 mmol) was added by syringe. After 30 minutes, the $^{31}$P NMR spectrum showed that the PPh₃ signal Tp*Rh(PPh₃)₂ ($\delta$ 42.92, d, $J$ = 175.6 Hz) disappeared and a new singlet ($\delta$ -4.56) appeared, which indicated that both of the PPh₃ ligands had dissociated. However, no rhodium hydride species were found in the $^1$H NMR spectrum, although the methylene resonance of thiol changed from a doublet of

doublets ($\delta$ 3.16, $J$ = 7.0 Hz, $J$ = 7.0 Hz) to a doublet ($\delta$ 2.78, $J$ = 6.9 Hz). This data could indicate that diallyl sulfide formed in this process, but no further information can be provided from GC-MS analysis. Nonetheless, the data showed that the allyl mercaptan did react with Tp*Rh(PPh$_3$)$_2$, but not in the same way that other thiols react.

### 2.2.4 Hydrothiolation of Different Alkynes and *n*-Propanethiol

The catalytic hydrothiolation of *n*-propanethiol and various alkynes was investigated by Anthony Sabarre.[3f] Similar to the reactions of benzyl thiol, all reactions proceeded with high selectivity of branched products. Likewise, the reactions of *para*-substituted phenylacetylenes with benzyl thiol followed the same trends. All the hydrothiolation products proved to be suitable for Kumada-type cross-coupling to generate 1,1-disubstituted olefins.[3d,20]

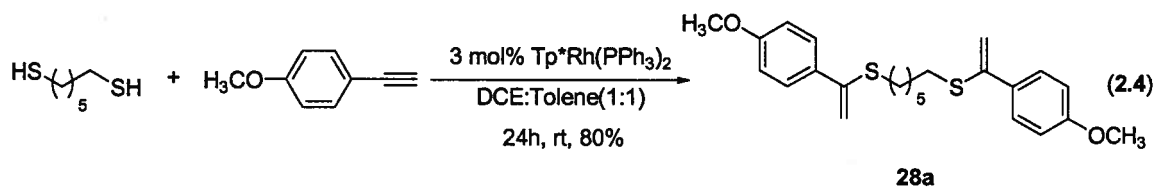### 2.2.5 Hydrothiolation of Internal Alkynes and Other Cases

The catalytic hydrothiolation reactions of internal alkynes were found to be much more difficult to achieve than with terminal alkynes. Longer reaction times were always needed and sometimes high temperature was necessary (Table 2.4). While the reaction between cyclopentylthiol and diphenylacetylene proceeded in excellent yield providing a single isomer (entry 1), only a trace of the desired product can be found in the reaction using benzyl thiol (entry 2). Cyclotrimerization[21] occurred when 3-hexyne was used, and the yield of expected product was only 32 % (entry 3). The reaction of 1-phenyl-1-propyne gave a moderate yield and favored the less-hindered isomer as product (entry 4).

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**Table 2.4.** Scope of Hydrothiolation of Internal Alkynes Catalyzed by **I**

$$\text{RSH} \quad + \quad \text{R}_1\text{---}\!\!\equiv\!\!\text{---}\text{R}_2 \quad \xrightarrow[\text{DCE:PhCH}_3\,(1:1)]{3\text{ mol\% I}} \quad \text{product}$$

| entry[a] | R | alkyne | temperature, time | product | yield[b] |
|---|---|---|---|---|---|
| 1[c] | cyclopentyl | Ph—≡—Ph | 80 °C, 24 h | **25a**, 94% |  |
| 2 | Ph | Ph—≡—Ph | rt, 24 h | trace |  |
| 3 | Ph | Et—≡—Et | rt, 24 h | **26a**, 32%[d] |  |
| 4[c] | Ph | Ph—≡—Me | 50 °C, 4 h | **27a:27b**= 1:3.5, 70%[d] |  |

[a] Reaction conditions: 10 mmol alkyne, 11 mmol thiol, 4 mL of 1:1 DCE:PhCH$_3$, and 0.3 mmol (3 mol %) catalyst. [b] Isolated yields. [c] Ref 12h [d] Yield based on 1H NMR analysis.

Finally we achieved a successful hydrothiolation of 1,6-hexanedithiol and 2.2 equivalents of 4-methoxyphenylacetylene and obtained 80% of desired product after 24 hours at room temperature (eq **2.4**). None of the mono-addition product was detected, although this species is likely an intermediate in the formation of **28a** .

$$\text{HS}\!-\!(\text{CH}_2)_5\!-\!\text{SH} \quad + \quad \text{H}_3\text{CO}-\!\!\diamondsuit\!\!-\!\!\equiv \quad \xrightarrow[\substack{\text{DCE:Tolene(1:1)} \\ 24\text{h, rt, }80\%}]{3\text{ mol\% Tp*Rh(PPh}_3)_2} \quad \text{28a} \qquad (2.4)$$

**28a**

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## 2.3 Experimental Procedures

### 2.4.1 General Methods

Manipulation of organometallic compounds was performed in a nitrogen-filled Vacuum Atmospheres drybox ($O_2$ < 2 ppm). NMR spectra were recorded on Bruker Avance 300 or Bruker Avance 400 spectrometers. $^1$H, $^{13}$C and $^{31}$P chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constant values were extracted assuming first-order coupling. The multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, quin = quintet, m = multiplet). $^{31}$P{1H} NMR spectra were referenced to an external 85% $H_3PO_4$ standard, and $^{19}$F NMR spectra were referenced to $CFCl_3$ standard. All spectra were obtained at 25 °C. Elemental analyses were performed using a Carlo Erba Elemental Analyzer EA 1108. Mass spectra were recorded on a Kratos MS-50 mass spectrometer.

### 2.4.2 Materials and Methods.

Hexanes (boiling range 68.3-69.6 °C), $CH_2Cl_2$, $Et_2O$, THF, benzene, $PhCH_3$ and DCE (1,2-dichloroethane) were dried by passage through solvent purification columns.[22] $CDCl_3$ was distilled from $P_2O_5$ and was degassed prior to use. $C_6D_6$ was purified by vacuum transfer from Na/benzophenone. All organic reagents were obtained from commercial sources and used as received. Wilkinson Catalyst was purchased from Strem Chemicals and was used without further purification. Tp*Rh(PPh$_3$)$_2$ (I)[23] was prepared as previously reported.[12j]

### 2.4.3 General experimental procedure for hydrothiolation.

Tp*Rh(PPh₃)₂ (280 mg, 0.30 mmol, 3 mol %), PhCH₃ (2 mL), DCE (2 mL) were combined in the glove box in a 20 mL vial equipped with a magnetic stir bar and a screw cap. Thiol (11 mmol) and alkyne (10 mmol) were added sequentially. The vial was removed from the glove box. The vial was then wrapped in aluminum foil and the solution was stirred at the indicated temperature and monitored by TLC. After the reaction was completed, the resulting mixture was filtered through silica gel, washed by hexanes, concentrated under vacuum. Flash chromatography (SiO₂, hexanes or a mixture of hexanes: EtOAc as eluent) provided the product. Note: The reactions proceed very slowly in the absence of the catalyst, indicating that background reactions are minimal. The addition of a non-nucleophilic base (2,2-lutidine) does not impede or improve the reaction.[12h] Analytical data for **2a, 4a, 13a, 15a, 16a, 19a, 20a, 25a,** and **27a,b** were previously reported.[12h]
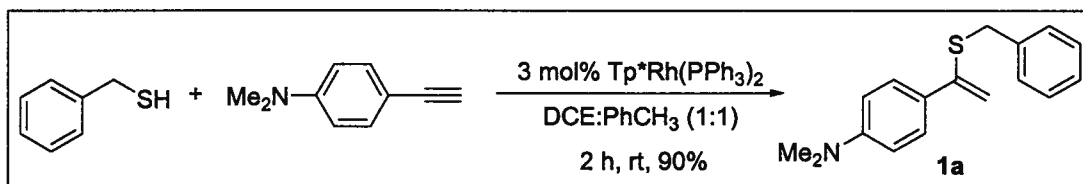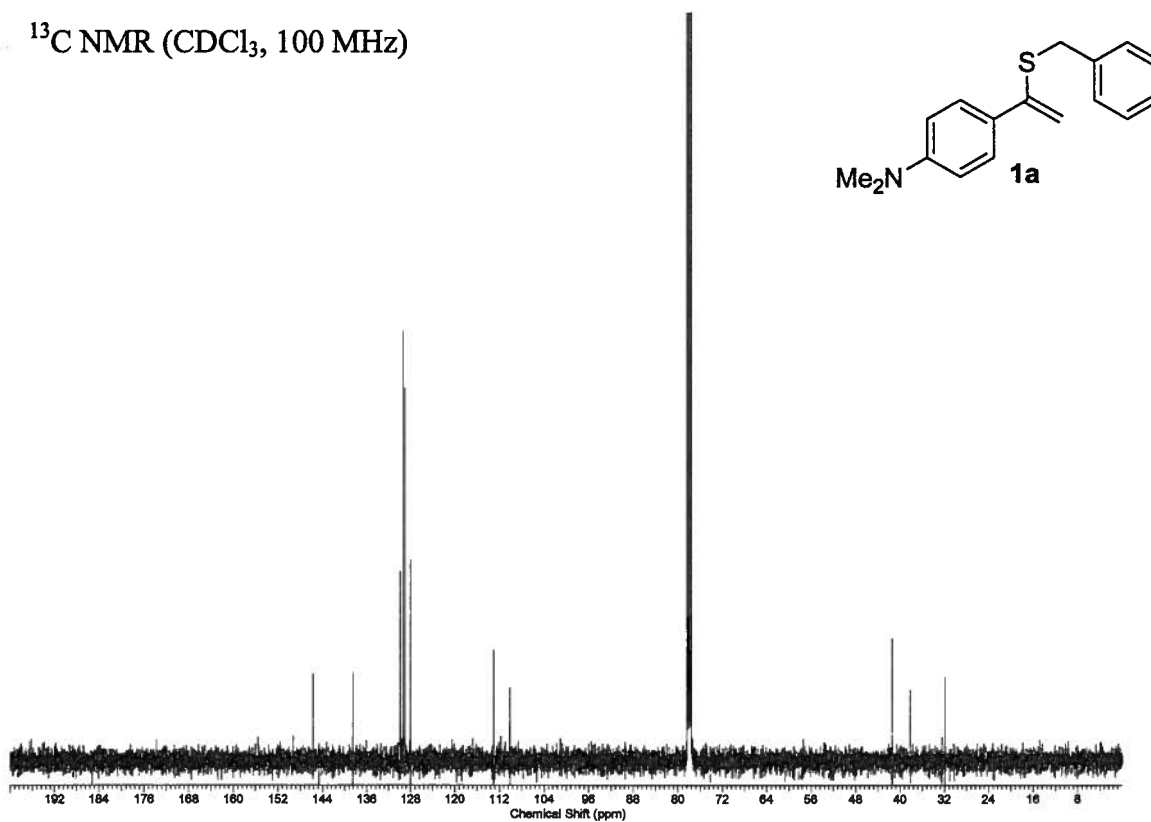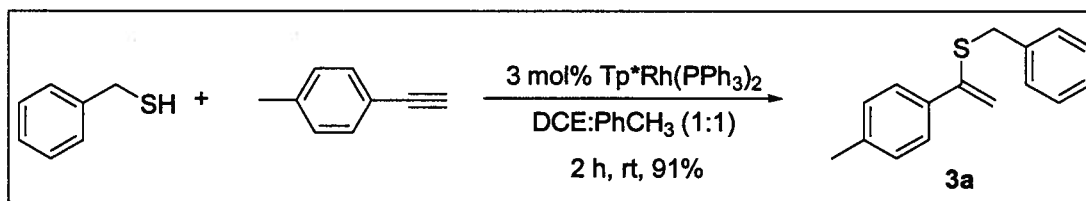
**Benzyl(1-(4-*N*,*N*-dimethyphenylvinyl)sulfane** **(1a):** Yellow oil, 90% yield. Column chromatography conditions: 20:1 hexanes:EtOAc and 3 % Et$_3$N. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.47 (d, 2H, $J$ = 8.7 Hz), 7.31 − 7.23 (m, 5H), 6.71 ( d, 2H, $J$ = 9.1 Hz), 5.36 (s, 1H), 5.08 (s, 1H), 3.90 (s, 2H), 2.99 (s, 6H), 1.55 (H$_2$O). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz): δ 149.3, 145.7, 138.5, 129.9, 129.4, 129.1, 128.2, 128.0, 113.0, 110.1, 41.5, 38.2. HRMS (EI) m/z calcd for C$_{17}$H$_{19}$SN: 269.1238; found: 269.1236. Anal. calcd for C$_{17}$H$_{19}$SN: C, 75.79; H, 7.11; N, 5.20; found: C, 75.72; H, 7.16; N, 5.53.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)
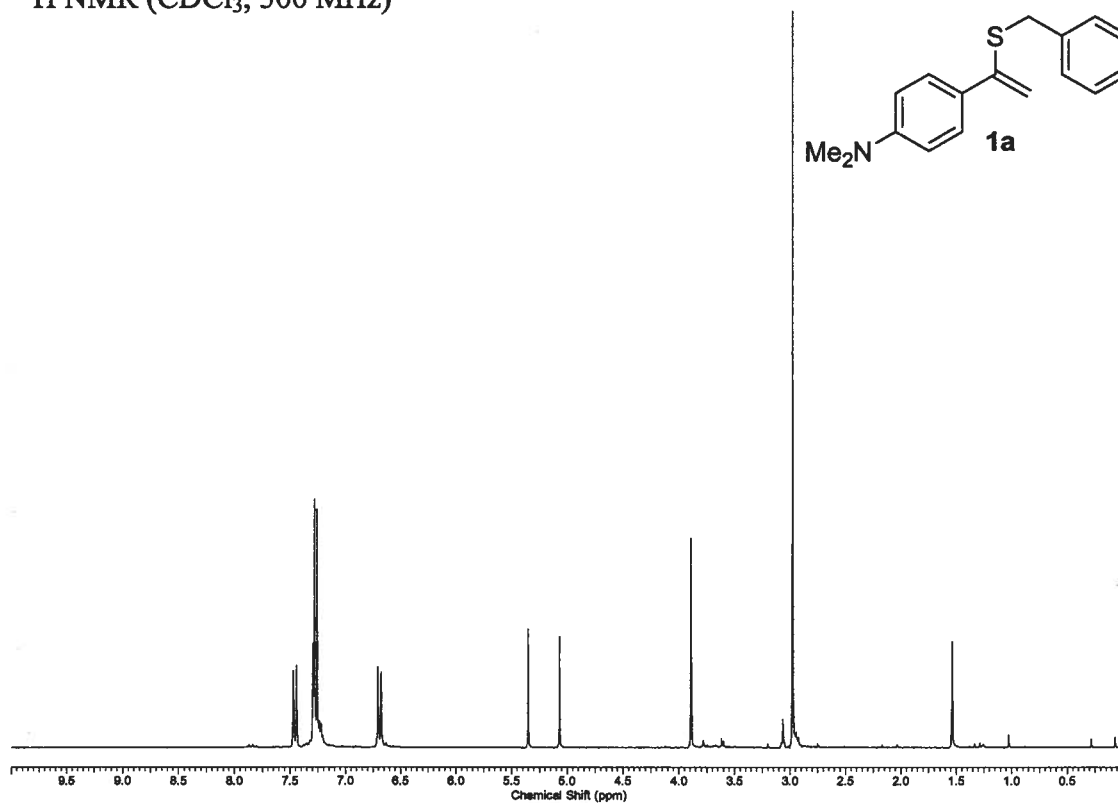


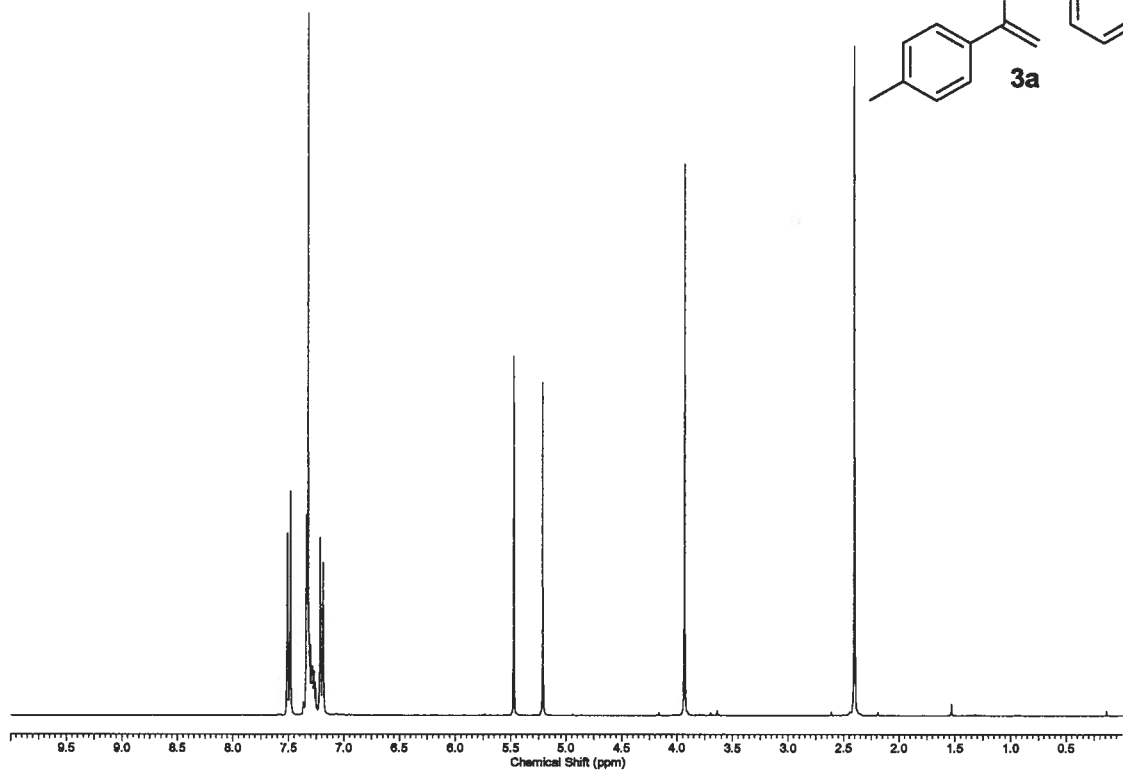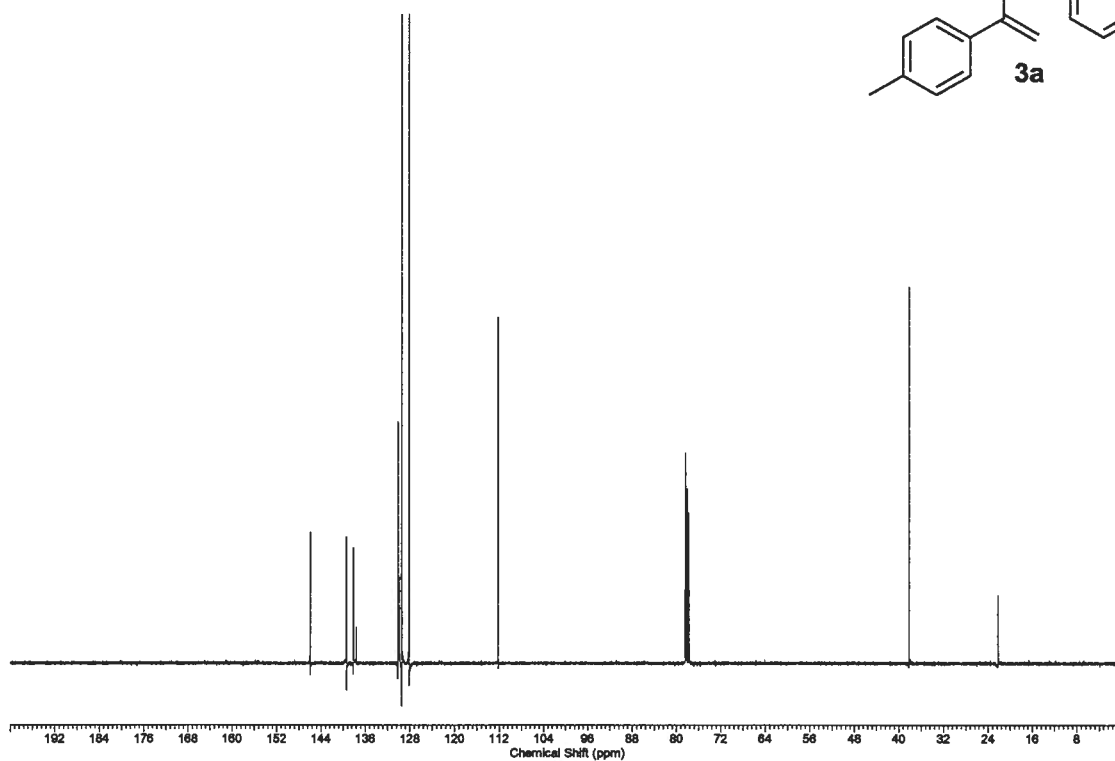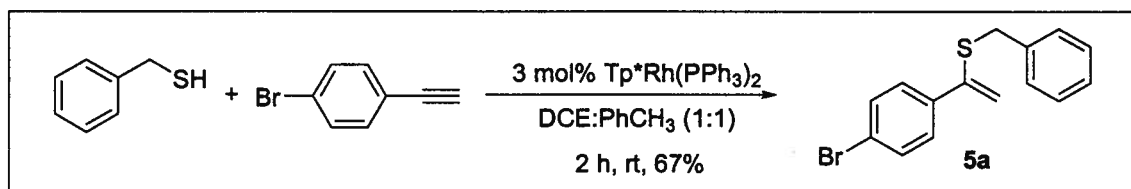<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)

**Benzyl(1-*p*-tolylvinyl)sulfane** (**3a**): Yellow oil, 91% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.47 (d, 2H, $J$ = 8.2 Hz), 7.34 – 7.27 (m, 5H), 7.20 (d, 2H, $J$ = 7.8 Hz), 5.47 (s, 1H), 5.21 (s, 1H), 3.93 (s, 2H), 2.40 (s, 3H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz): δ 145.9, 139.4, 138.1, 137.6, 130.1, 130.0, 129.5, 128.2, 128.1, 112.2, 38.2, 22.2. HRMS (EI) m/z calcd for C$_{16}$H$_{16}$S: 240.0967; found: 240.0973. Anal. calcd for C$_{17}$H$_2$SN: C, 79.95; H, 6.71; found: C, 79.73; H, 6.62.

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



Chemical Shift (ppm)
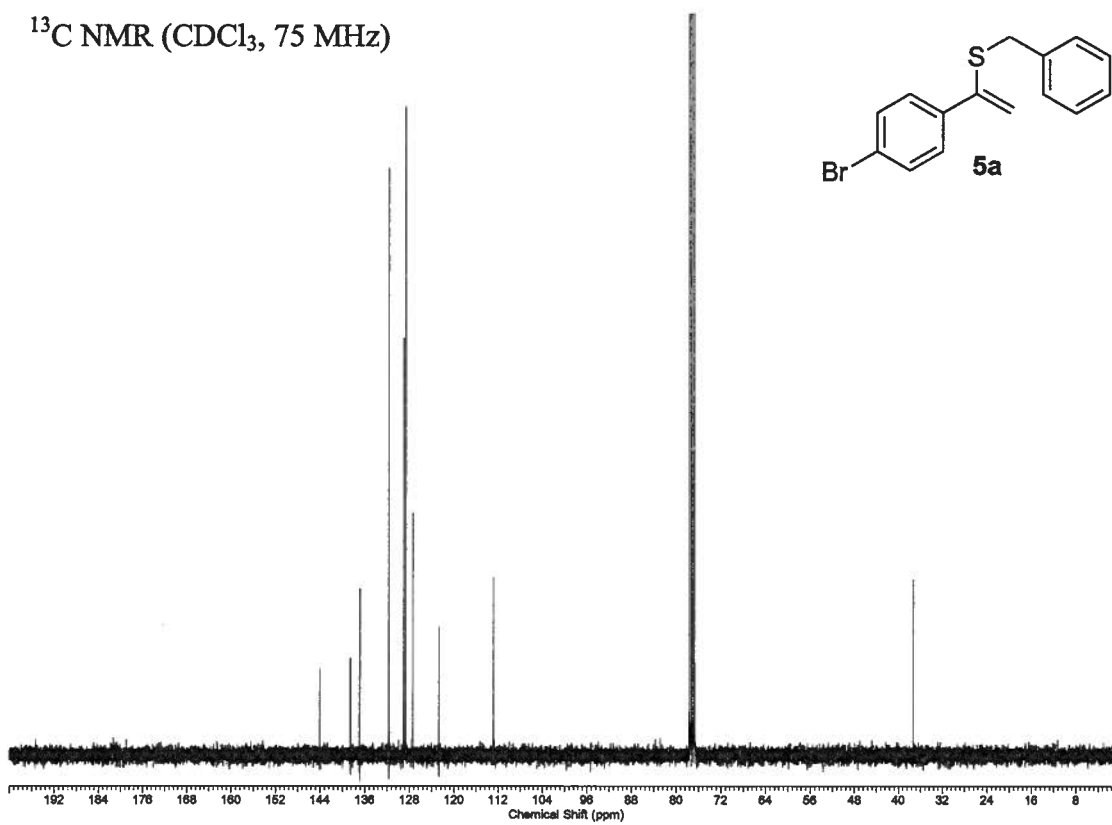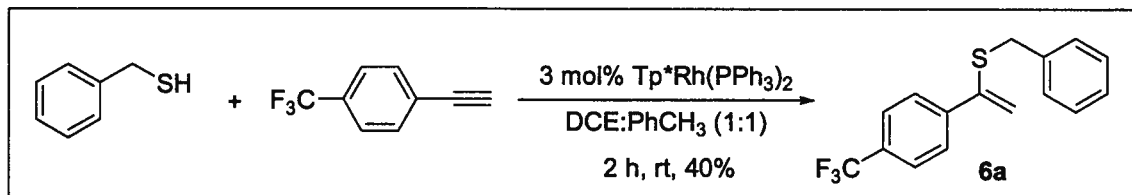
# $^{13}$C NMR (CDCl$_3$, 100 MHz)



Chemical Shift (ppm)

33

**Benzyl(1-(4-bromophenyl)vinyl)sulfane (5a)**: Pale yellow oil, 67% yield. Column

chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz):

δ 7.48 (d, 2H, $J$ = 8.7 Hz), 7.41 (d, 2H, $J$ = 8.7 Hz), 7.32 – 7.22 (m, 5H), 5.44 (s, 1H),

5.23 (s, 1H), 3.88 (s, 2H), 1.54 (H$_2$O). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ 144.0, 138.5,

136.9, 131.7, 129.0 (two peaks overlaping), 128.7, 127.4, 122.6, 112.9, 37.3. HRMS (EI)

m/z calcd for C$_{15}$H$_{13}$S$^{79}$Br: 303.9921; found: 303.9919. Anal. calcd for C$_{15}$H$_{13}$S$^{79}$Br: C,

59.02; H, 4.29; found: C, 58.64; H, 4.40.

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



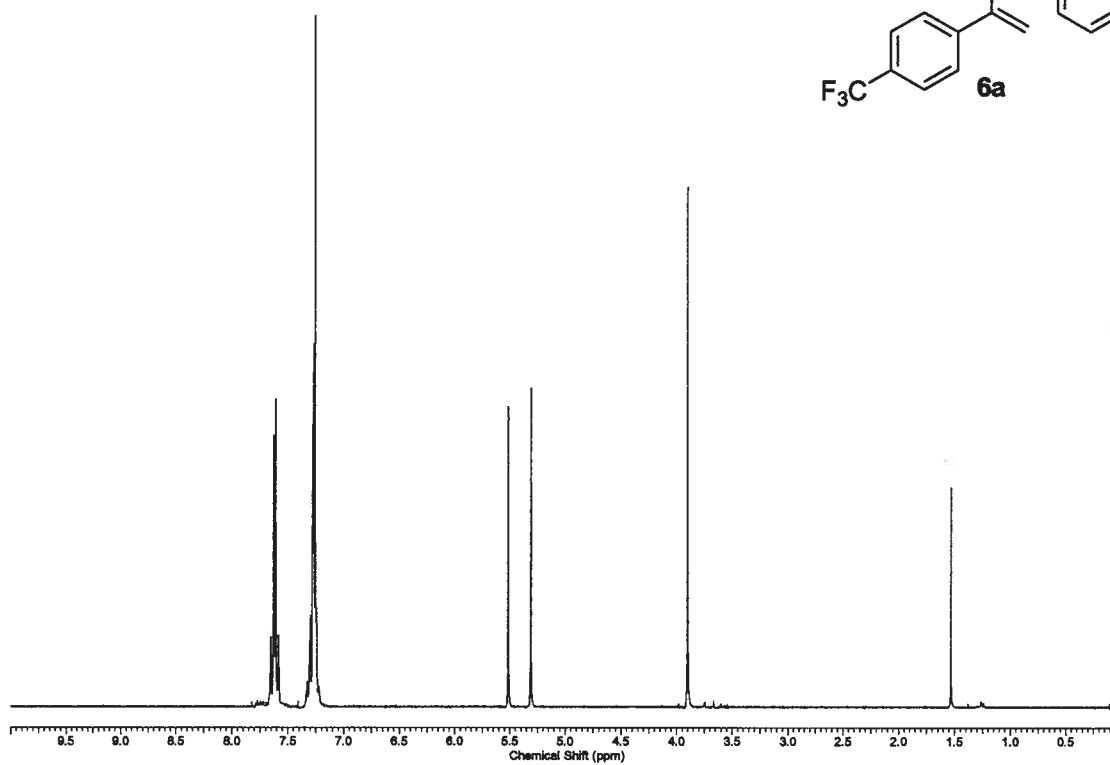# $^{13}$C NMR (CDCl$_3$, 75 MHz)



35

**Benzyl(1-(4-(trifluoromethyl)phenyl)vinyl)sulfane (6a)**: Yellow oil, 40% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.65 – 7.58 (m, 4H), 7.33 – 7.23 (m, 5H), 5.52 (s, 1H), 5.31 (s, 1H), 3.90 (s, 2H), 1.53 (H$_2$O). $^{19}$F NMR (CDCl$_3$, 282 MHz): δ -63.1 (d, $J$ = 4.2 Hz). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz): δ 143.8, 143.0, 136.6, 130.4 (q, $J$ = 33.0 Hz), 128.8, 128.5, 127. 5, 127.3, 125.4 (q, $J$ = 3.8 Hz), 124.1 (q, $J$ = 272.2 Hz), 113.9, 37.3. HRMS (EI) m/z calcd for C$_{16}$H$_{13}$SF$_3$: 294.0690; found: 294.0702. Anal. calcd for C$_{16}$H$_{13}$SF$_3$: C, 65.29; H, 4.45; found: C, 64.94; H, 4.36.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)
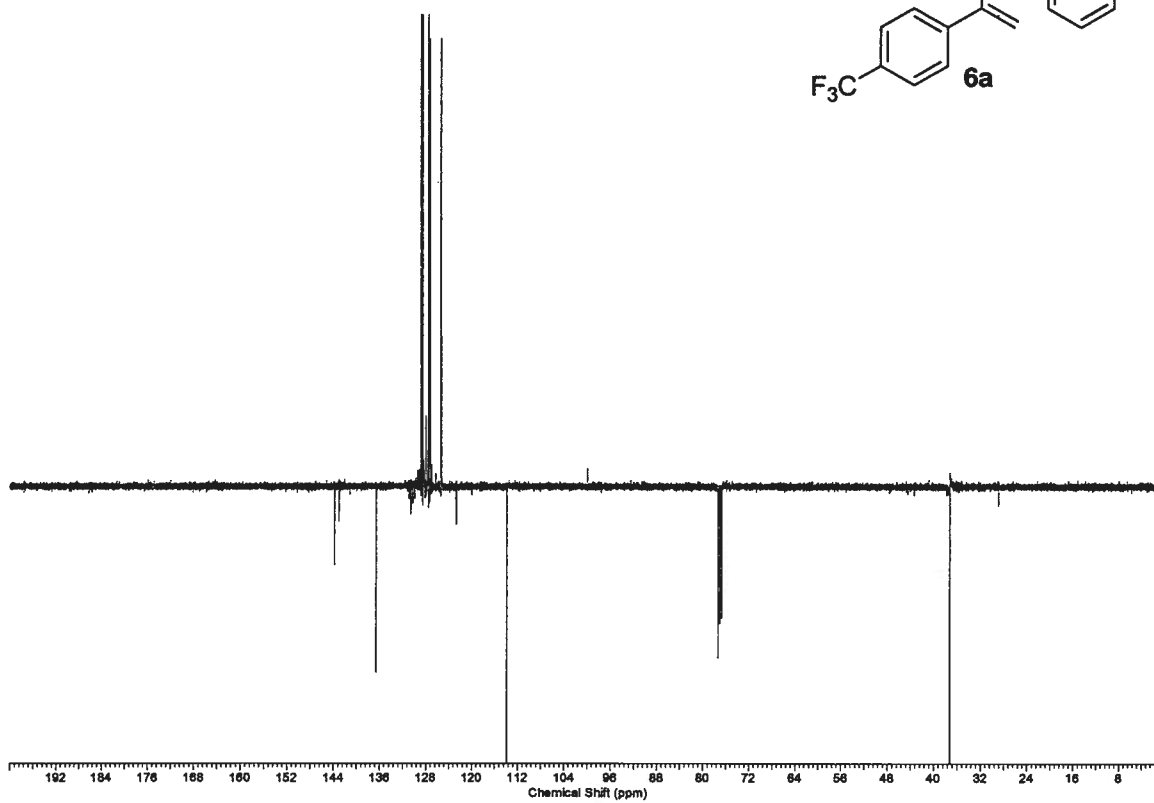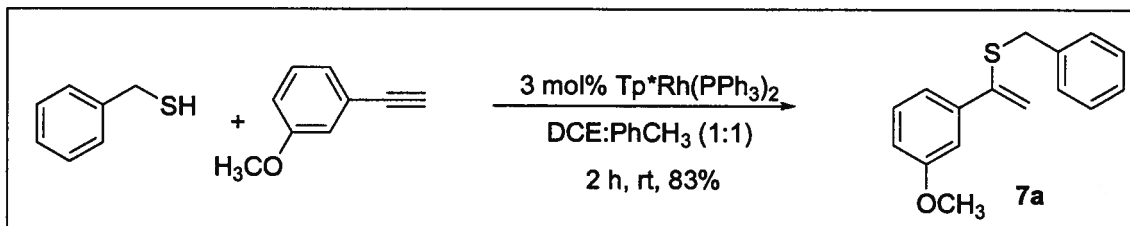


<sup>13</sup>C APT NMR (CDCl<sub>3</sub>, 100 MHz)

**Benzyl(1-(3-methoxyphenyl)vinyl)sulfane (7a):** Yellow oil, 83% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.32 – 6.90 (m, 9H), 5.50 (s, 1H), 5.25 (s, 1H), 3.93 (s, 2H), 3.84 (s, 3H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ 159.8, 145.1, 141.0, 137.2, 129.6, 129.1, 128.7, 127.3, 119.9, 114.4, 112.9, 112.2, 55.5, 37.4. HRMS (EI) m/z calcd for C$_{16}$H$_{16}$SO: 256.0922; found: 256.0921. Anal. calcd for C$_{16}$H$_{16}$SO: C, 74.96; H, 6.27; found: C, 74.59; H, 6.27.

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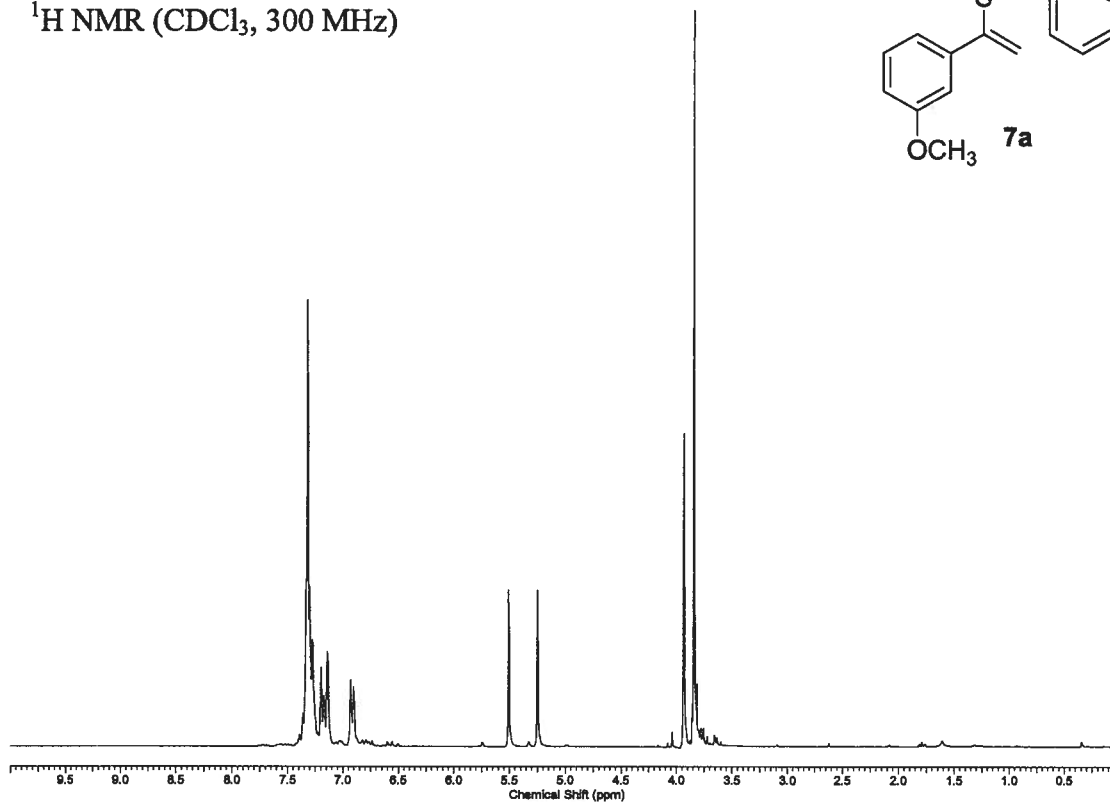


$^{13}$C NMR (CDCl$_3$, 75 MHz)

**Benzyl(1-(2-methoxyphenyl)vinyl)sulfane** (**8a**): Pale yellow oil, 55% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.31 – 7.21 (m, 7H), 6.96 – 6.90 (m, 2H), 5.37 (s, 1H), 5.34 (s, 1H), 3.90 (s, 2H), 3.84 (s, 3H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz): δ 157.1, 142.7, 138.1, 131.5, 130.4, 129.9, 129.4, 128.0, 121.6, 121.5, 114.4, 112.29, 56.8, 38.2. HRMS (EI) m/z calcd for C$_{16}$H$_{16}$SO: 256.0922; found: 256.0923. Anal. calcd for C$_{16}$H$_{16}$SO: C, 74.96; H, 6.27; found: C, 74.79; H, 6.35.

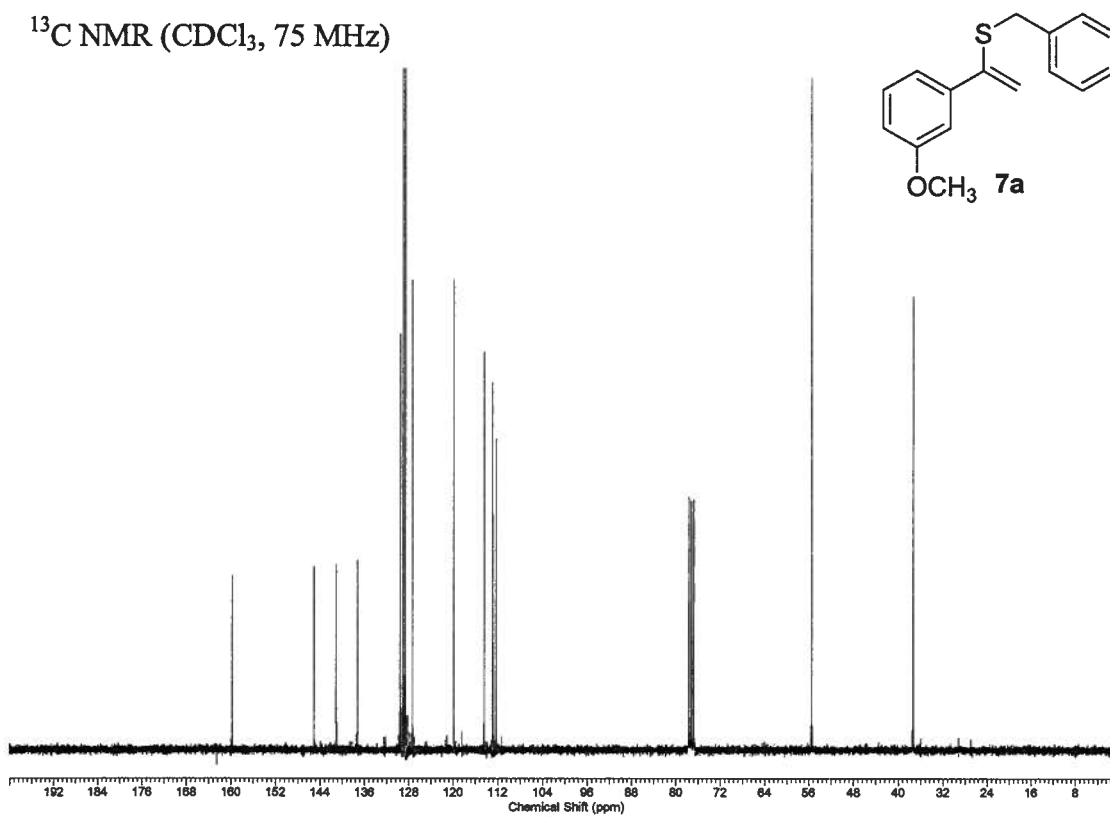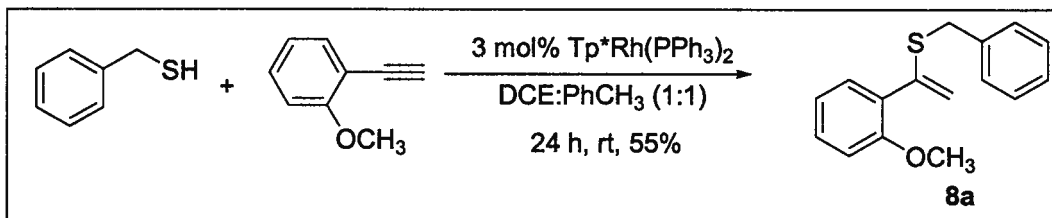¹H NMR (CDCl₃, 400 MHz)



**8a**

¹³C NMR (CDCl₃, 100 MHz)



**8a**

41
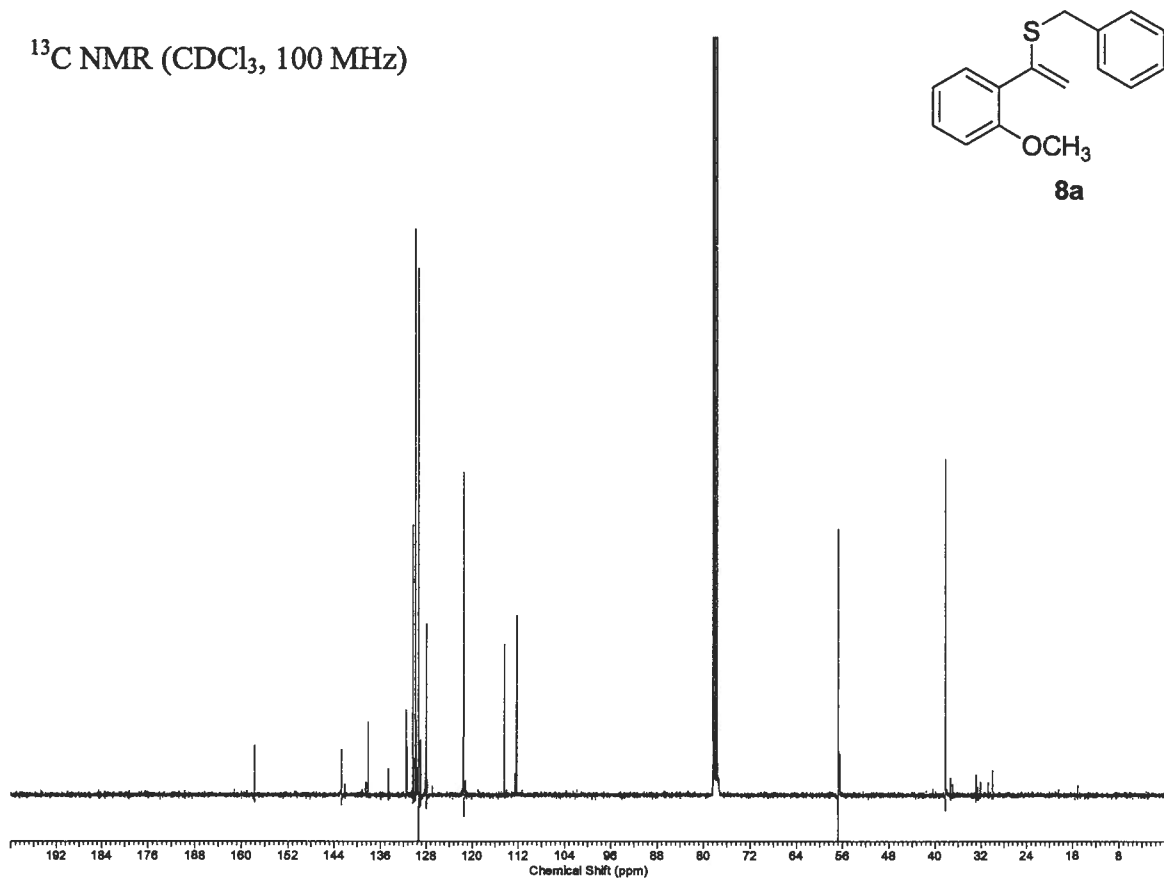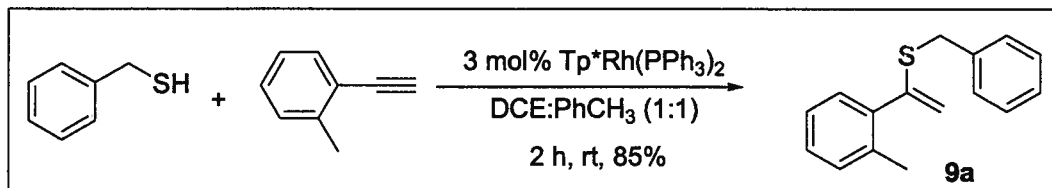
**Benzyl(1-*o*-tolylvinyl)sulfane (9a):** Pale yellow oil, 85% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.36 – 7.22 (m, 9H), 5.34 (s, 1H), 5.15 (s, 1H), 3.91 (s, 2H), 2.38 (s, 3H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz): δ 145.9, 140.4, 138.0, 137.1, 131.3, 130.5, 129.9, 129.5, 129.1, 128.2, 126.6, 112.5, 37.9, 20.7. HRMS (EI) m/z calcd for C$_{16}$H$_{16}$S: 240.0973; found: 240.0976. Anal. calcd for C$_{16}$H$_{16}$S: C, 79.95; H, 6.71; found: C, 80.32; H, 6.77.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)
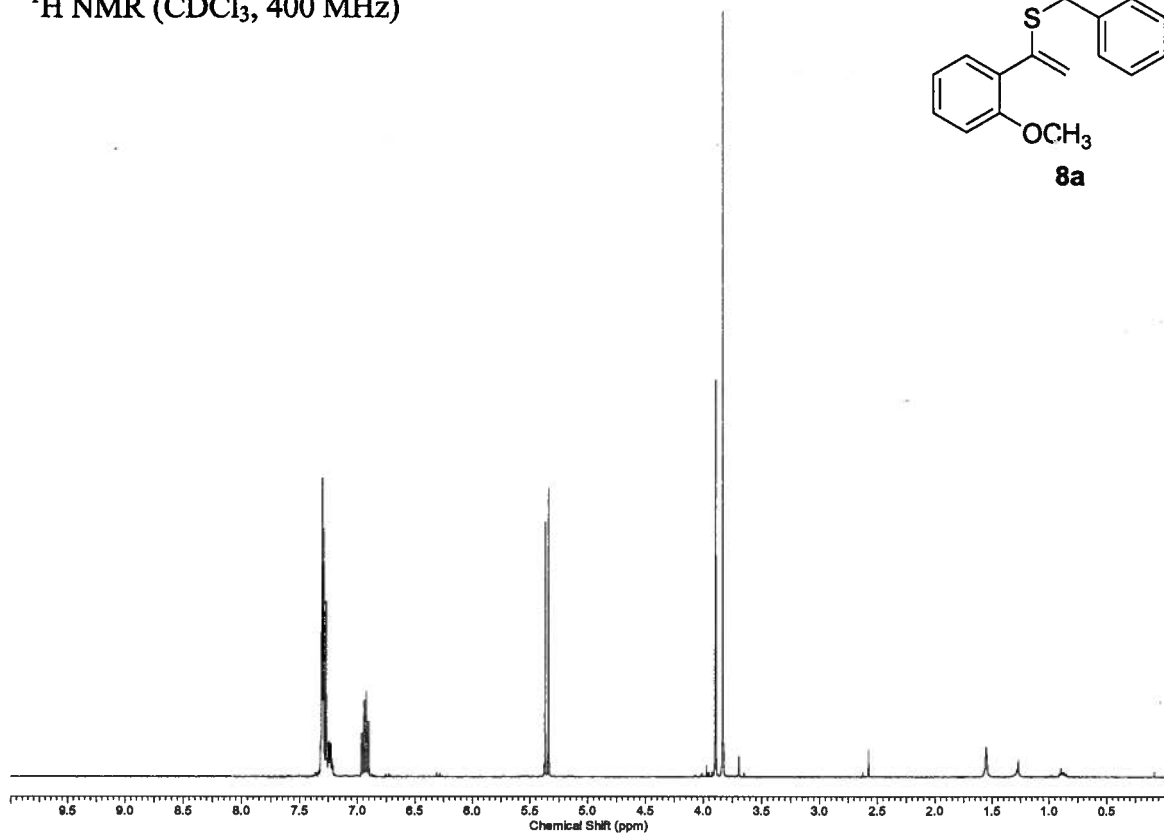
**9a**



<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)

**9a**
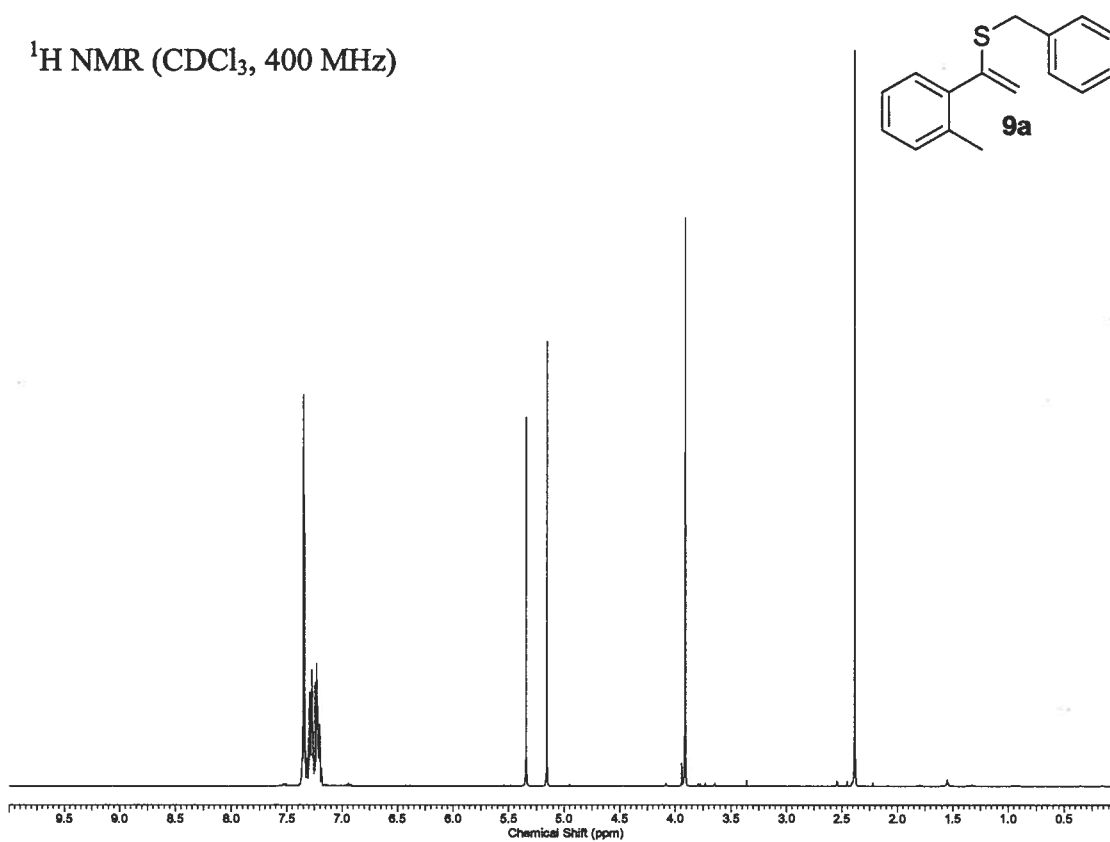
**Benzyl(1-benzylvinyl)sulfane (10a):** Pale yellow oil, 85% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (C$_6$D$_6$, 400 MHz): δ 7.27 – 7.10 (m, 10H), 5.06 (s, 1H), 4.89 (s, 1H), 3.73 (s, 2H), 3.52 (s, 2H). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 100 MHz): δ 146.1, 139.2, 137.3, 129.7, 129.5, 129.0, 128.9, 127.6, 127.1, 108.5, 44.3, 37.0. HRMS (EI) m/z calcd for C$_{16}$H$_{16}$S: 240.0973; found: 240.0967. Anal. calcd for C$_{16}$H$_{16}$S: C, 79.95; H, 6.71; found: C, 79.83; H, 6.71.

<sup>1</sup>H NMR (C₆D₆, 400 MHz)

$^{1}$H NMR (C$_6$D$_6$, 400 MHz)



**10a**

Chemical Shift (ppm)

$^{13}$C NMR (C$_6$D$_6$, 100 MHz)



**10a**

Chemical Shift (ppm)

45
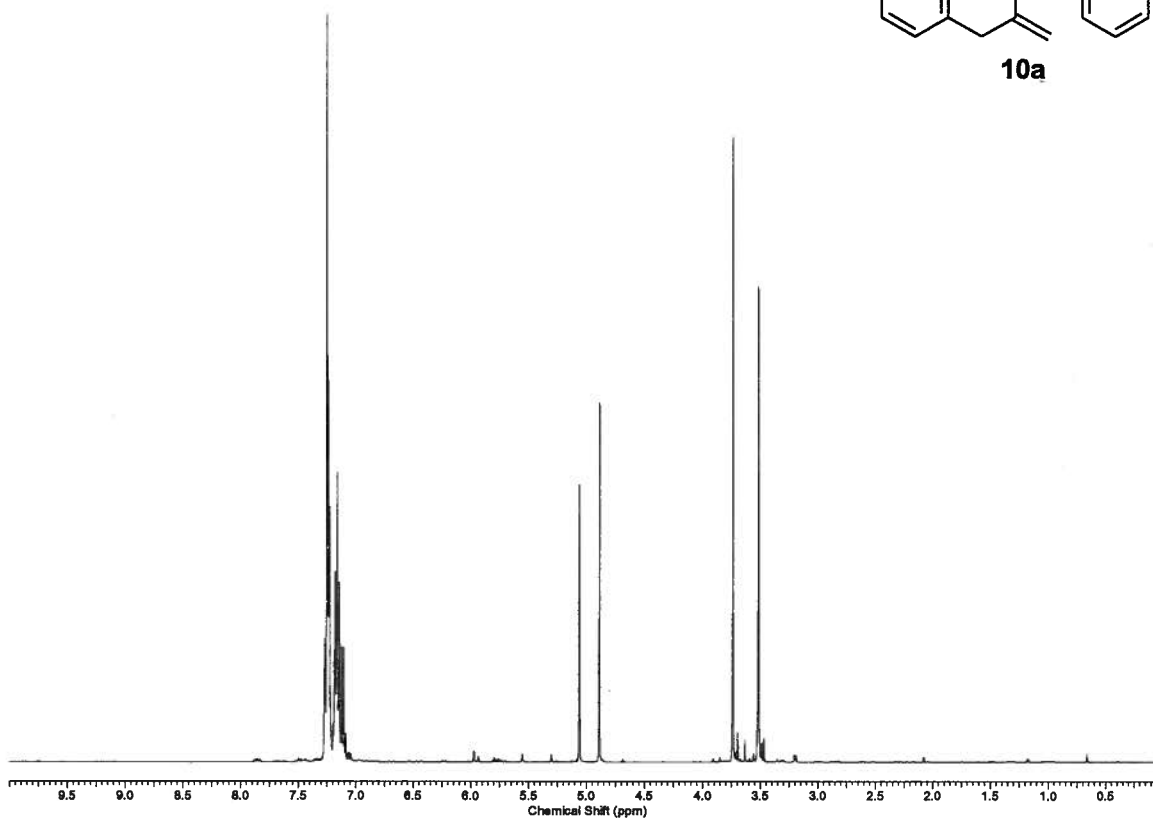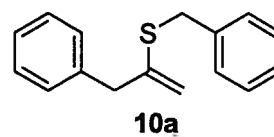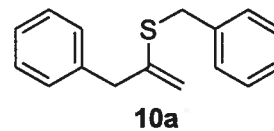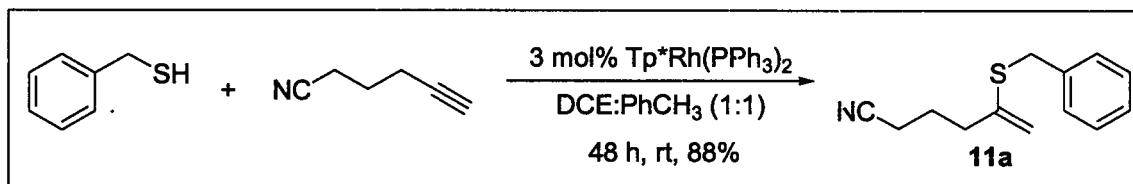
**Benzyl(3-cyanopropylvinyl)sulfane (11a)**: Pale yellow oil, 88% yield. Column chromatography conditions: 10:1 hexanes:EtOAc. $^1$H NMR ($C_6D_6$, 400 MHz): $\delta$ 7.24 – 7.09 (m, 5H), 4.90 (s, 1H), 4.71 (s, 1H), 3.64 (s, 2H), 2.01 (t, 2H, $J$ = 7.1 Hz), 1.48 (t, 2H, $J$ = 7.1 Hz), 1.35 (m, 2H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 100 MHz): $\delta$ 144.1, 137.3, 129.4, 129.1, 127.8, 108.7, 36.7, 36.4, 38.7, 24.7, 15.9. HRMS (EI) m/z calcd for $C_{13}H_{15}SN$: 217.0925; found: 217.0926. Anal. calcd for $C_{13}H_{15}SN$: C, 71.84; H, 6.96; found: C, 71.87; H, 7.12.

$^1$H NMR (C$_6$D$_6$, 400 MHz)



Chemical Shift (ppm)
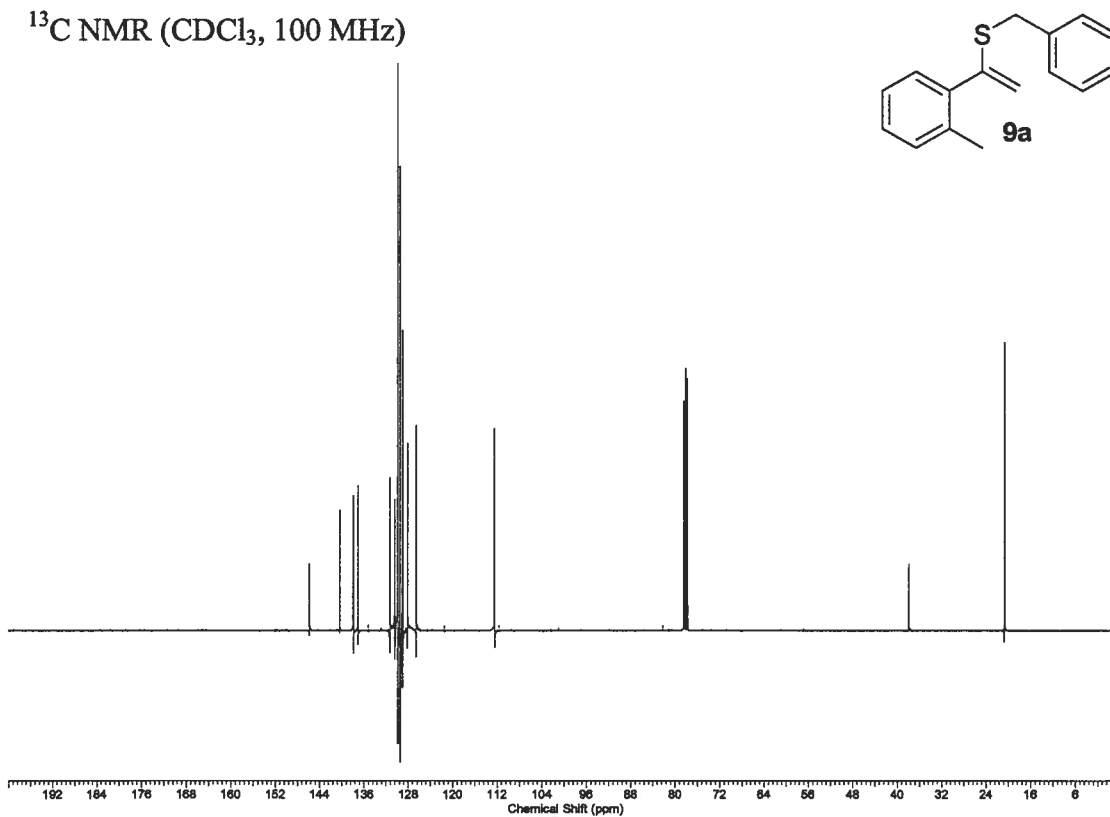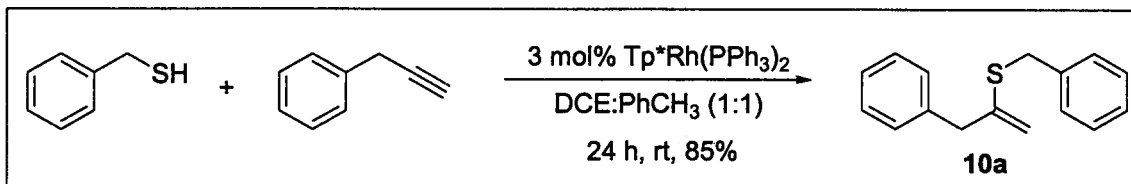
$^{13}$C NMR (C$_6$D$_6$, 100 MHz)



Chemical Shift (ppm)

47
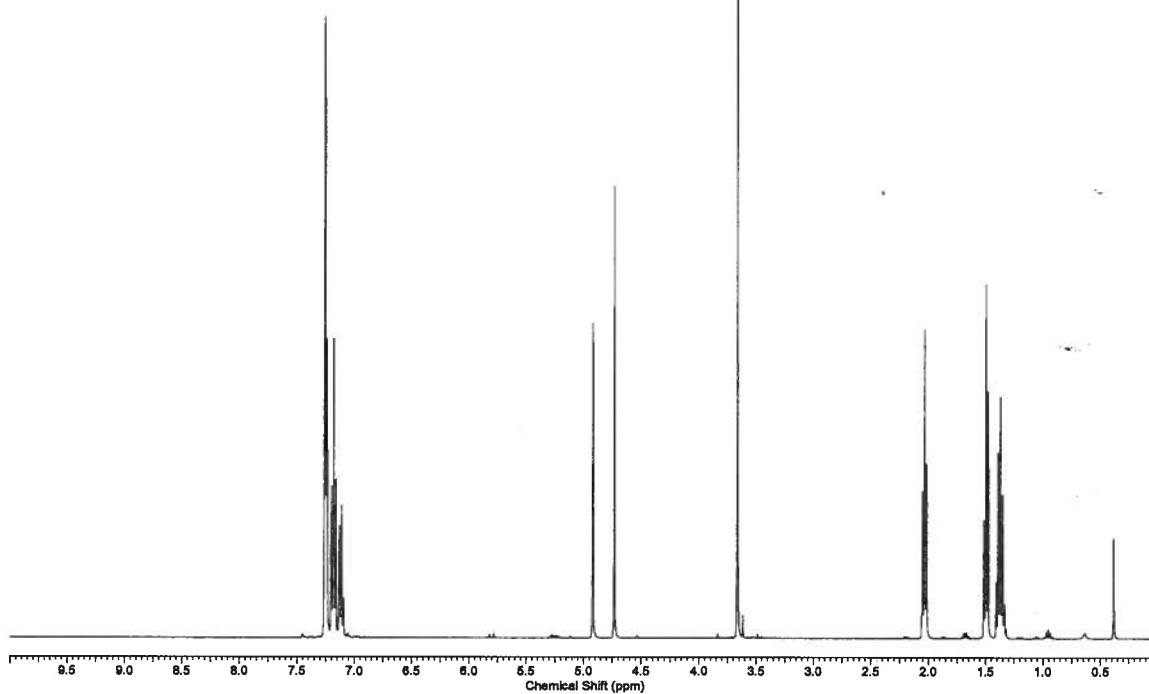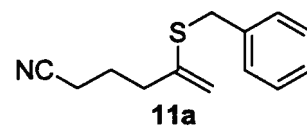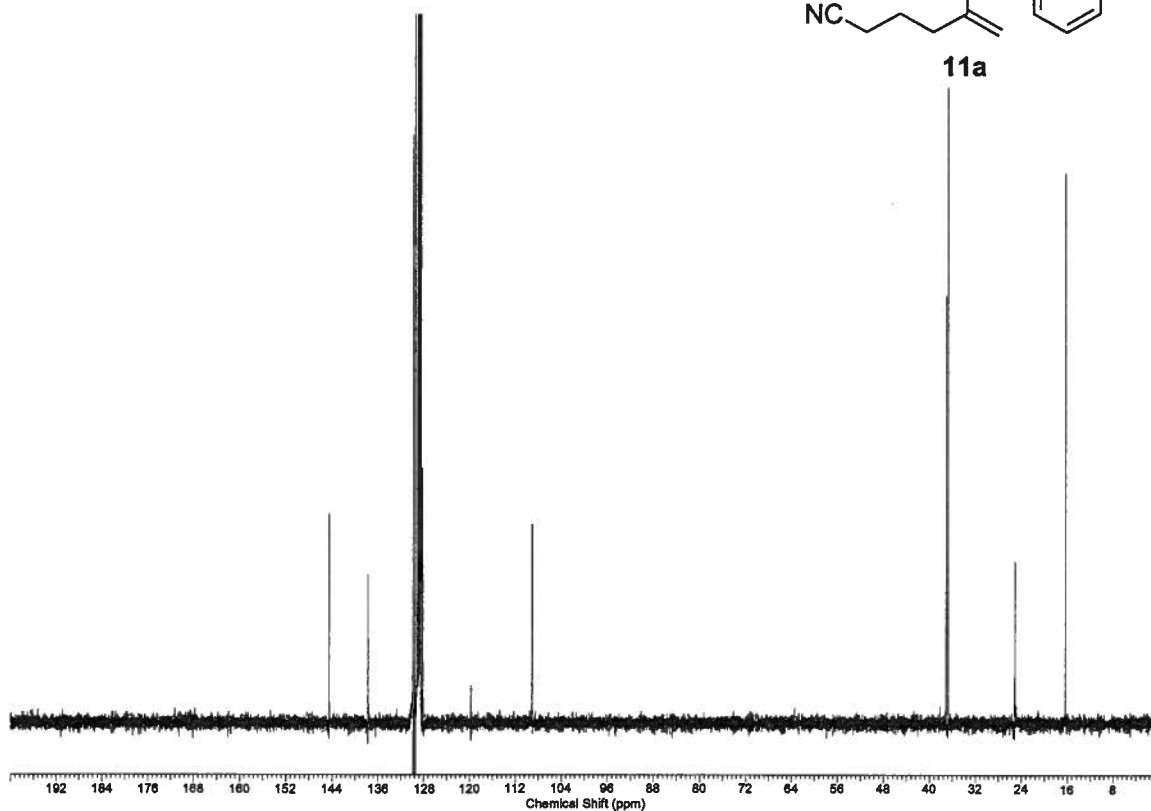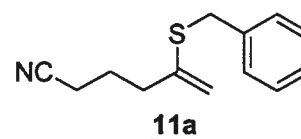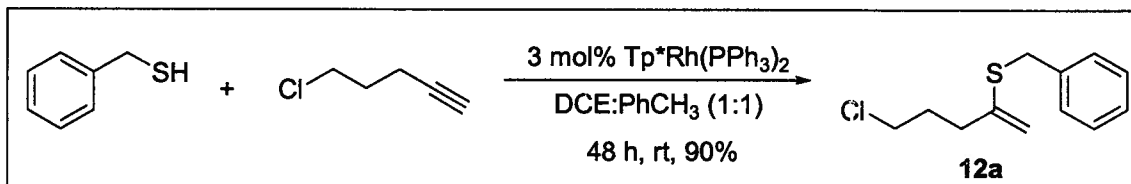
**Benzyl(3-chloropropylvinyl)sulfane (12a)**: Pale yellow oil, 90% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR ($C_6D_6$, 400 MHz): δ 7.25 – 7.07 (m, 5H), 4.99 (s, 1H), 4.76 (s, 1H), 3.69 (s, 2H), 3.17 (t, 2H, $J$ = 6.5 Hz), 2.24 (t, 2H, $J$ = 7.4 Hz), 1.79 (m, 2H). $^{13}$C{$^1$H} NMR ($C_6D_6$, 100 MHz): δ 145.3, 137.8, 129.9, 129.5, 128.2, 108.5, 44.6, 37.2, 35.4, 32.4. HRMS (EI) m/z calcd for $C_{12}H_{15}S^{37}Cl$: 228.0554; found: 228.0552. Anal. calcd for $C_{12}H_{15}SCl$: C, 63.56; H, 6.67; found: C, 63.90; H, 6.69.

## ¹H NMR (C₆D₆, 400 MHz)



## ¹³C NMR (C₆D₆, 100 MHz)



49
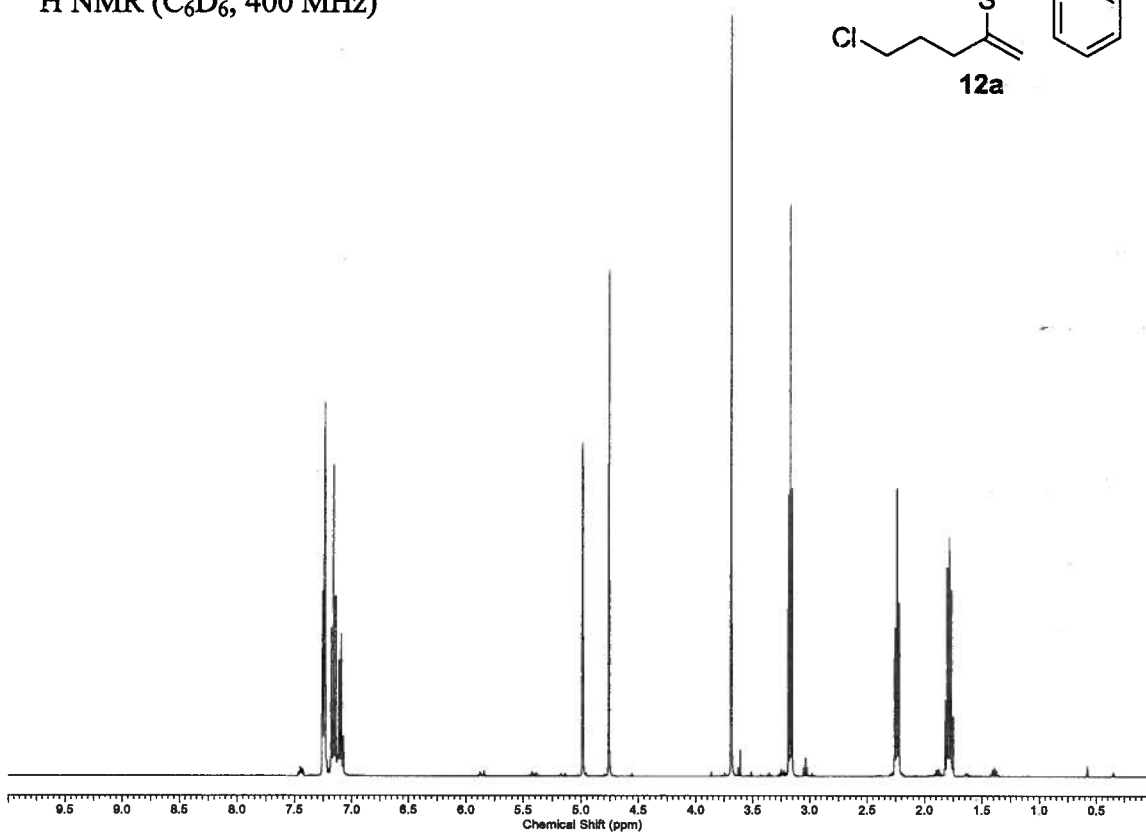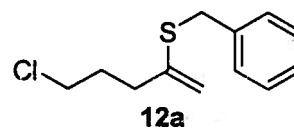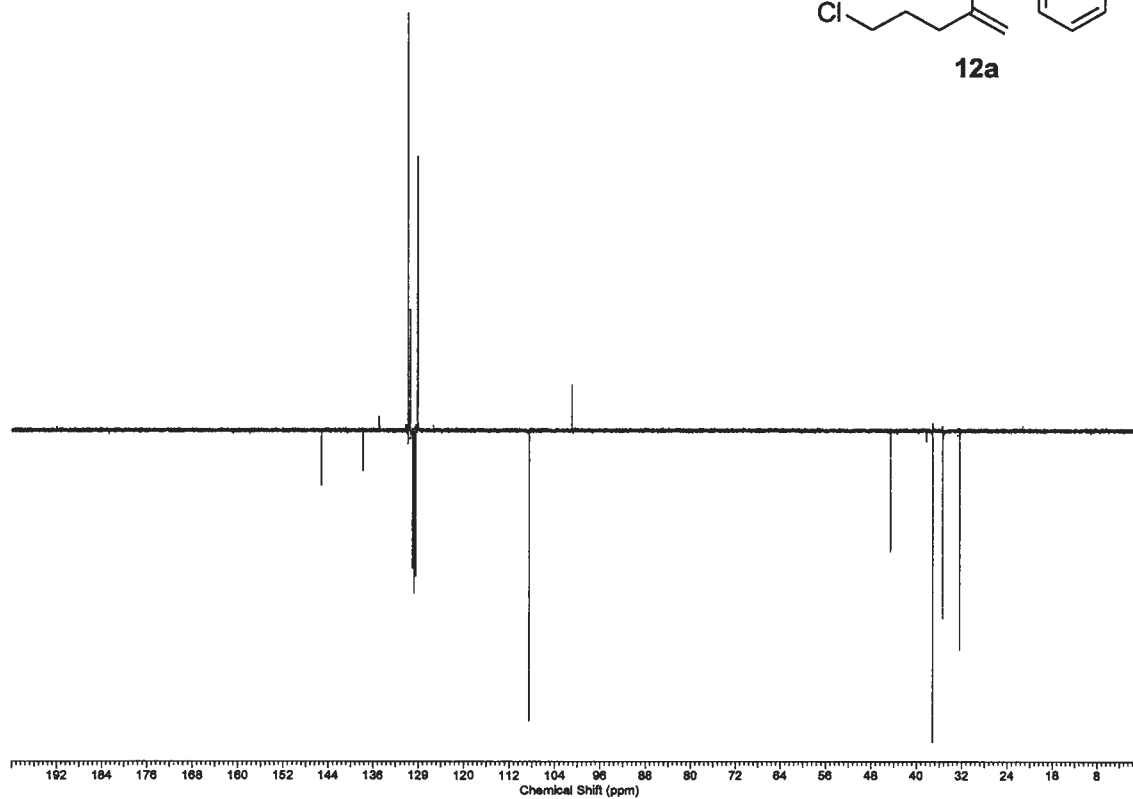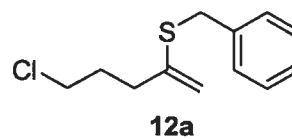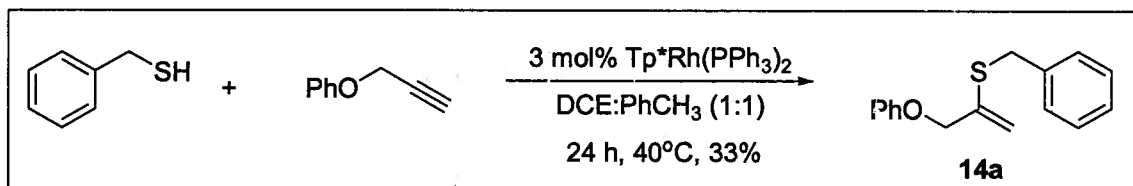
**Benzyl(phenoxymethylvinyl)sulfane (14a):** Pale yellow oil, 33% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.39 – 7.24 (m, 7H), 6.99 – 6.89 (m, 3H), 5.48 (s, 1H), 5.12 (s, 1H), 4.58 (s, 2H), 4.01 (s, 2H), 1.55 (H$_2$O). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz): δ 159.3, 141.9, 137.6, 130.4, 129.9, 129.6, 128.3, 122.2, 115.6, 112.2, 71.6, 37.5. HRMS (ESI) m/z calcd for C$_{16}$H$_{16}$SO: 257.1000; found: 257.0992. Anal. calcd for C$_{16}$H$_{16}$SO: C, 74.96; H, 6.29; found: C, 75.13; H, 6.36.
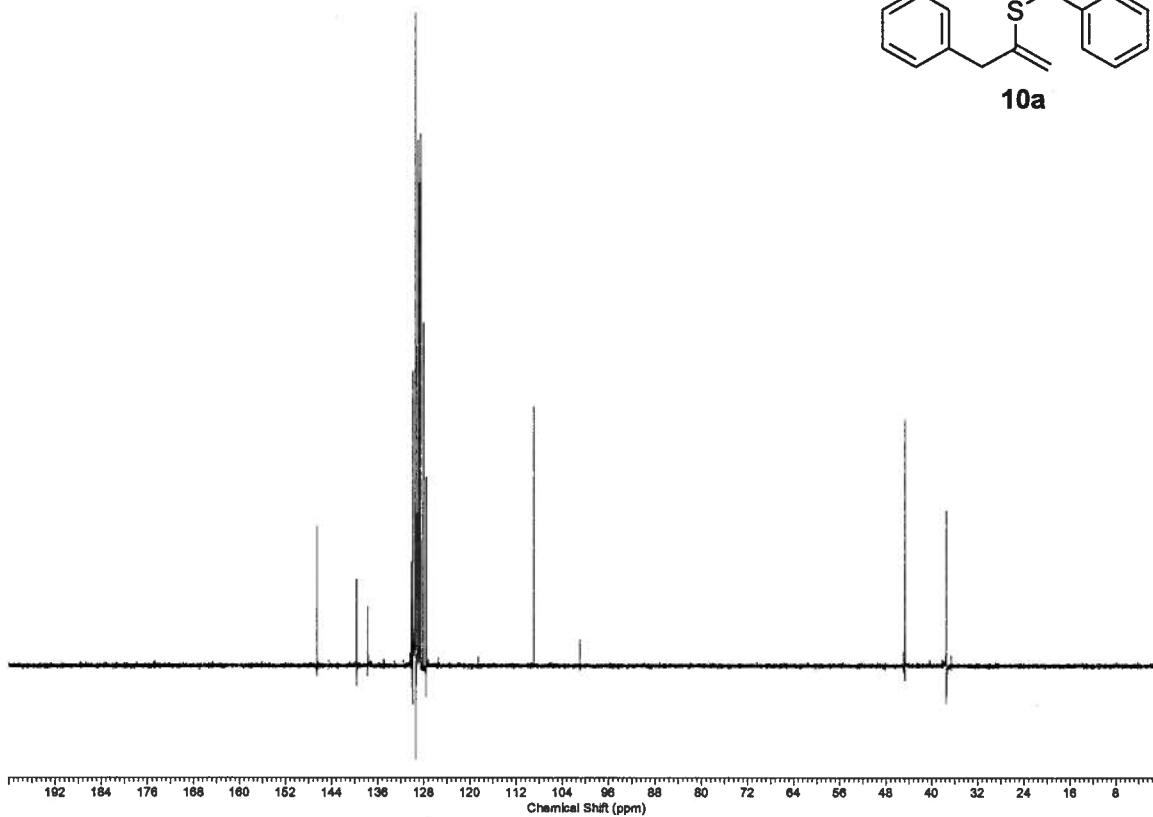
## $^{1}$H NMR (CDCl$_3$, 300 MHz)



14a

## $^{13}$C APT NMR (CDCl$_3$, 100 MHz)



14a
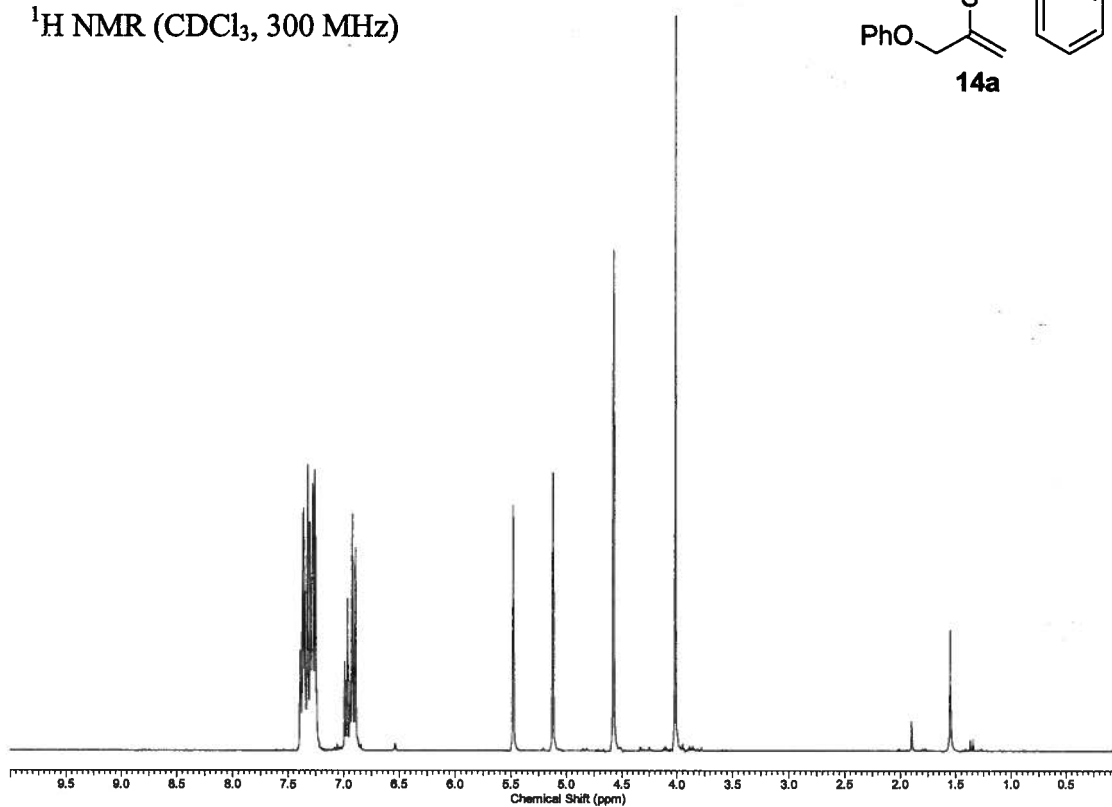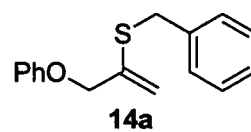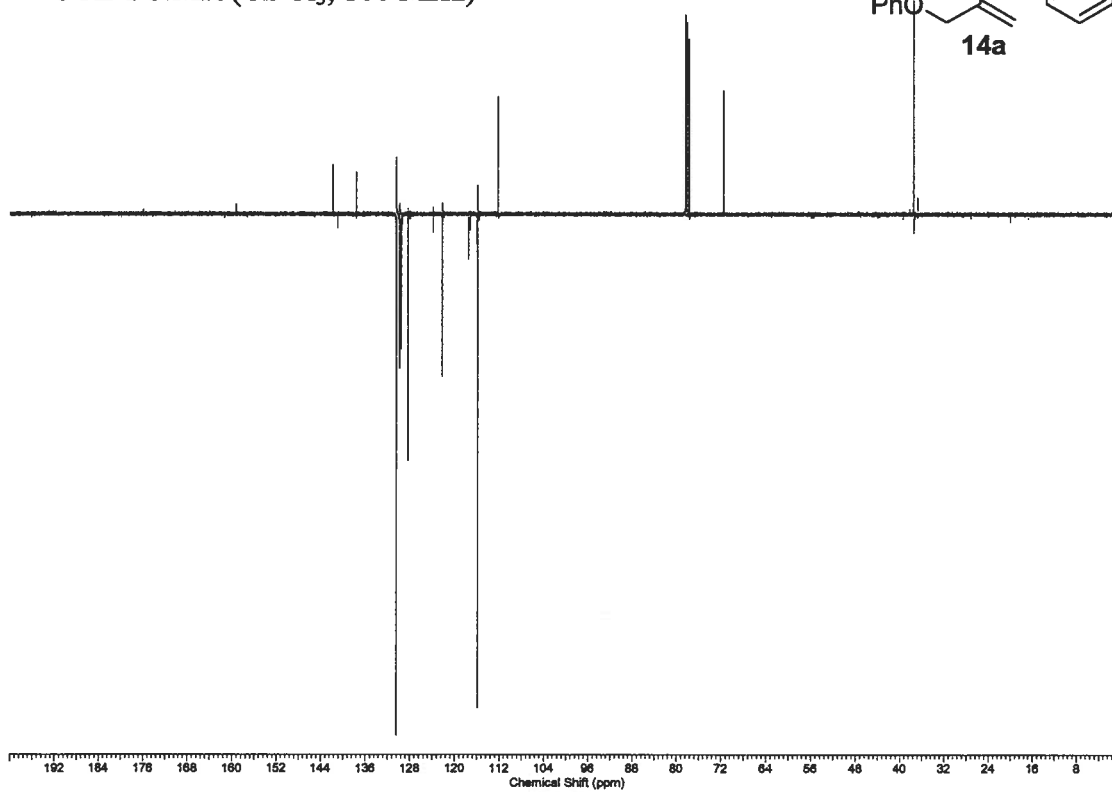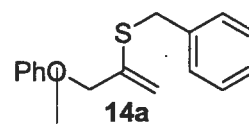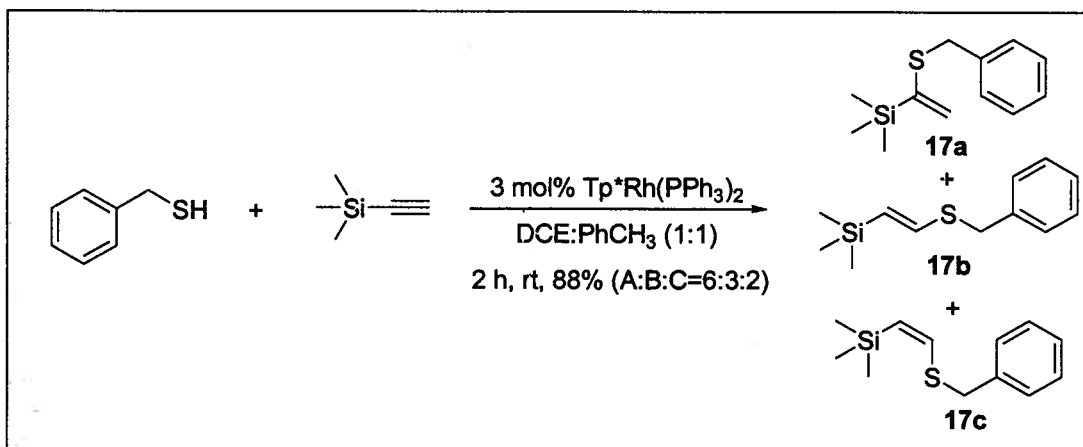
Mixture of benzyl(1-trimethylsilylvinyl)sulfane (17a), (E)-benzyl(2-trimethylsilylvinyl)sulfane (17b), and (Z)-benzyl(2-trimethylsilylvinyl)sulfane (17c): Yellow oil, 88% yield, 6:3:2 mixture of 17a and 17b and 17c. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.38–7.23 (m, 27.5H: 15H: 5H 17a, 7.5H: 5H 17b and 5H: 5H 17c), 6.85 (d, 1H: 1H 17c, $J$ = 13.25 Hz), 6.55 (d, 1.5H: 1H 17b, $J$ = 17.8 Hz), 5.79 (d, 1.5H: 1H 17b, $J$ = 17.8 Hz), 5.62 (d, 1H: 1H 17c, $J$ = 13.3 Hz), 5.45 (s, 3H: 1H 17a), 5.44 (s, 3H: 1H 17a), 3.96 (s, 9H: 6H: 2H 17a and 3H: 2H 17b), 3.90 (s, 2H: 2H 17c), 0.19 (s, 27H: 9H 17a), 0.14 (s, 9H: 9H 17c), 0.06 (s, 13.5H: 9H, 17b), 1.54 (H$_2$O). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ 147.7, 136.8, 129.1, 128.7, 127.3, 115.1, 35.6, -1.4. HRMS (EI) m/z calcd for C$_{12}$H$_{17}$SSi (mixture of isomers): 222.0899; found: 222.0896. Anal. calcd for C$_{12}$H$_{18}$SSi (mixture of isomers): C, 64.80; H, 8.16; found: C, 65.05; H, 8.21.

## ¹H NMR (CDCl₃, 300 MHz)



**17a** + **17b** + **17c**

## ¹³C NMR (CDCl₃, 75 MHz)



**17a** + **17b** + **17c**

53
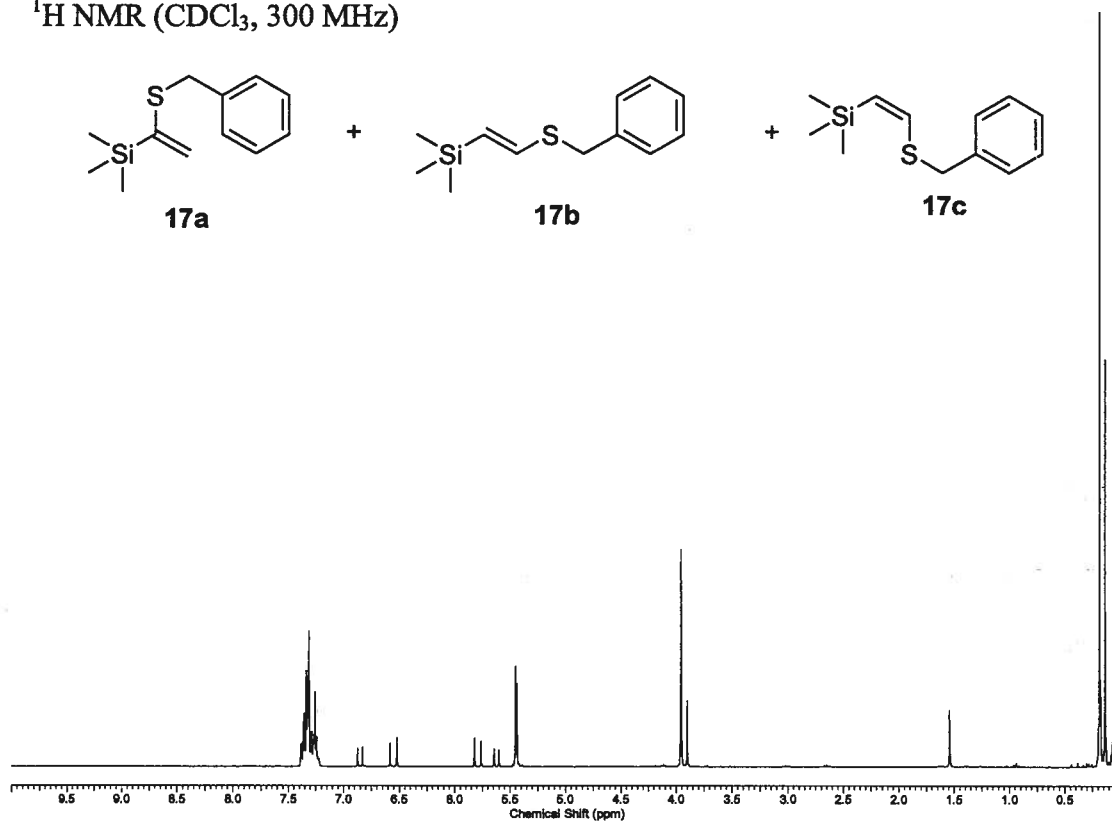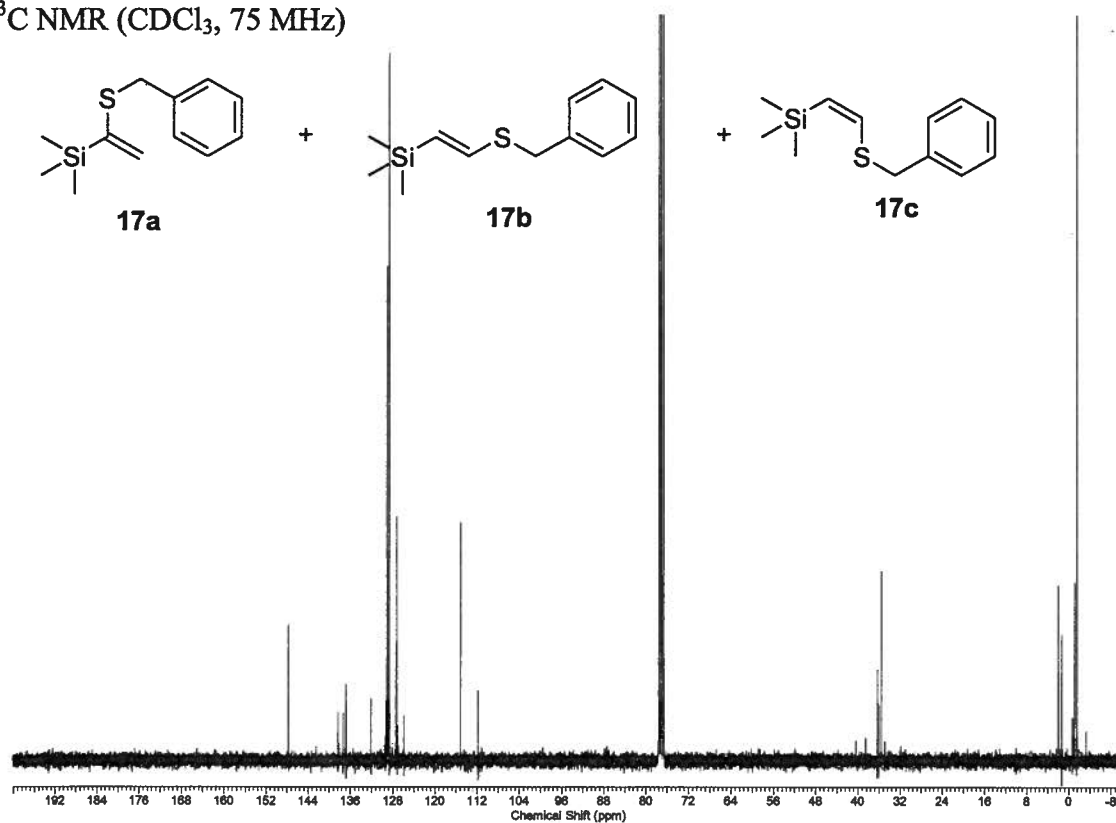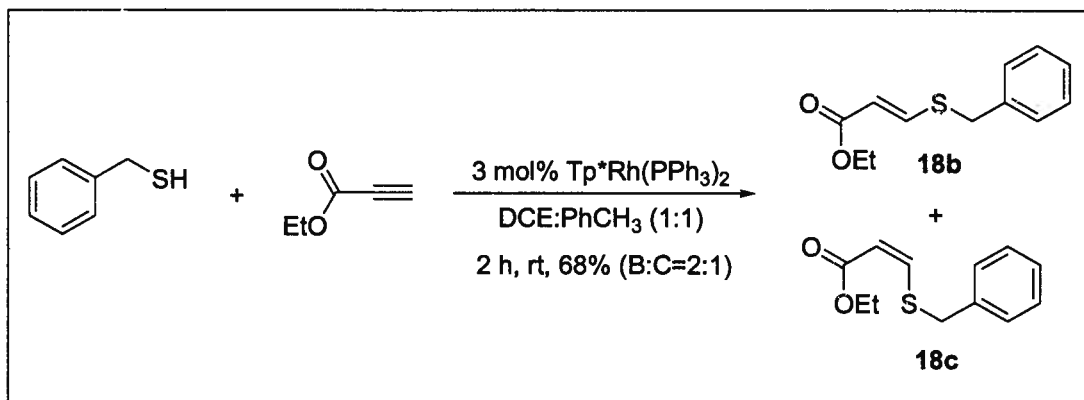
**(*E*)-benzyl(2-ethyl carbonovinyl)sulfane (18b)** Yellow oil, 40% yield. Column

chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz):

δ 7.68 (d, 1H, $J$ = 15.1 Hz), 7.35 – 7.31 (m, 5H), 5.79 (d, 1H, $J$ = 15.5 Hz), 4.17 (q, 2H,

$J$ = 7.3 Hz), 4.02 (s, 2H), 1.27 (t, 3H, $J$ = 7.3 Hz), 1.54 (H$_2$O). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75

MHz): δ 165.37, 146.07, 135.63, 129.0, 128.94, 127.90, 114.63, 60.41, 36.75,

14.47. HRMS (EI) m/s calcd for C$_{12}$H$_{14}$SO$_2$: 222.0715; found: 222.0719. Anal. calcd for

C$_{12}$H$_{14}$SO$_2$: C, 64.83; H, 6.35; found: C, 64.94; H, 6.42.

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



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



55
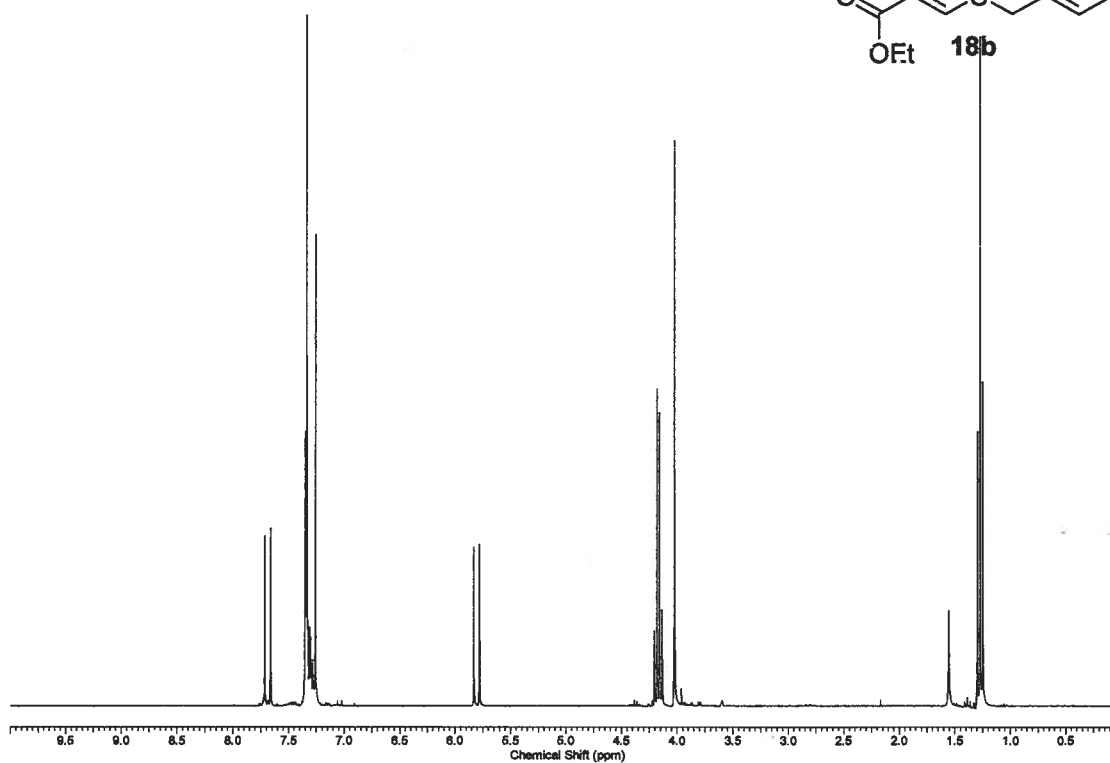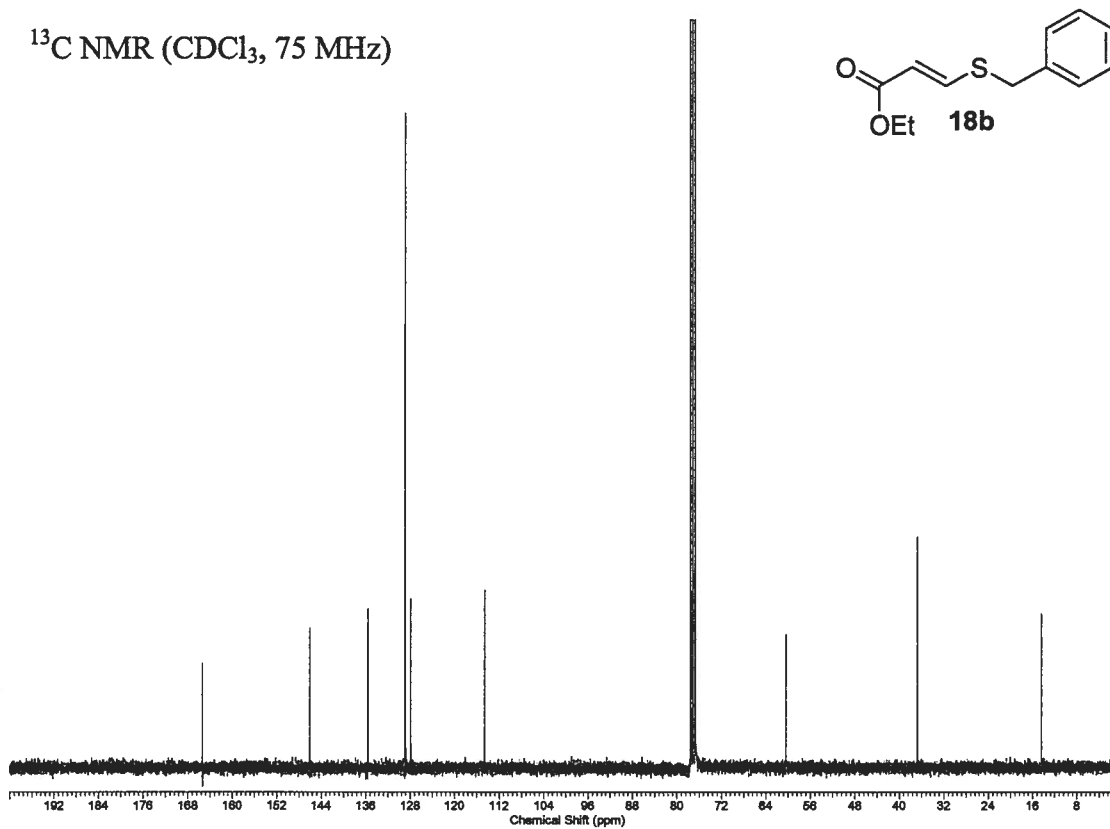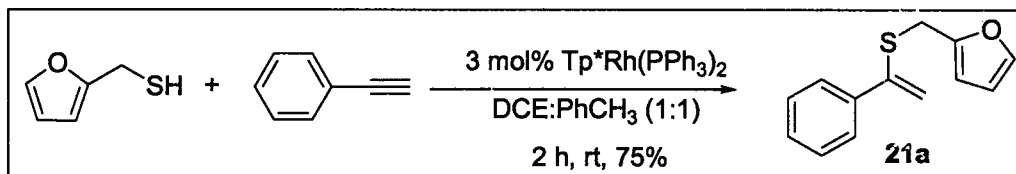
**2-((1-Phenylvinylthio)methyl)furan (21a):** Yellow oil, 75% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.56 – 7.53 (m, 2H), 7.39 – 7.33 (m, 4H), 6.29 – 6.27 (m, 1H), 6.10 – 6.09 (m, 1H), 5.49 (s, 1H), 5.31 (s, 1H), 3.88 (s, 2H), 1.54 (H$_2$O). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ 150.8, 144.4, 142.2, 139.2, 128.6, 128.5, 127.5, 113.5, 110.6, 107.8, 31.1. HRMS (EI) m/z calcd for C$_{13}$H$_{12}$SO: 216.0609; found: 216.0606. Anal. calcd for C$_{13}$H$_{12}$SO: C, 72.19; H, 5.59; found: C, 72.45; H, 5.60.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



**21a**
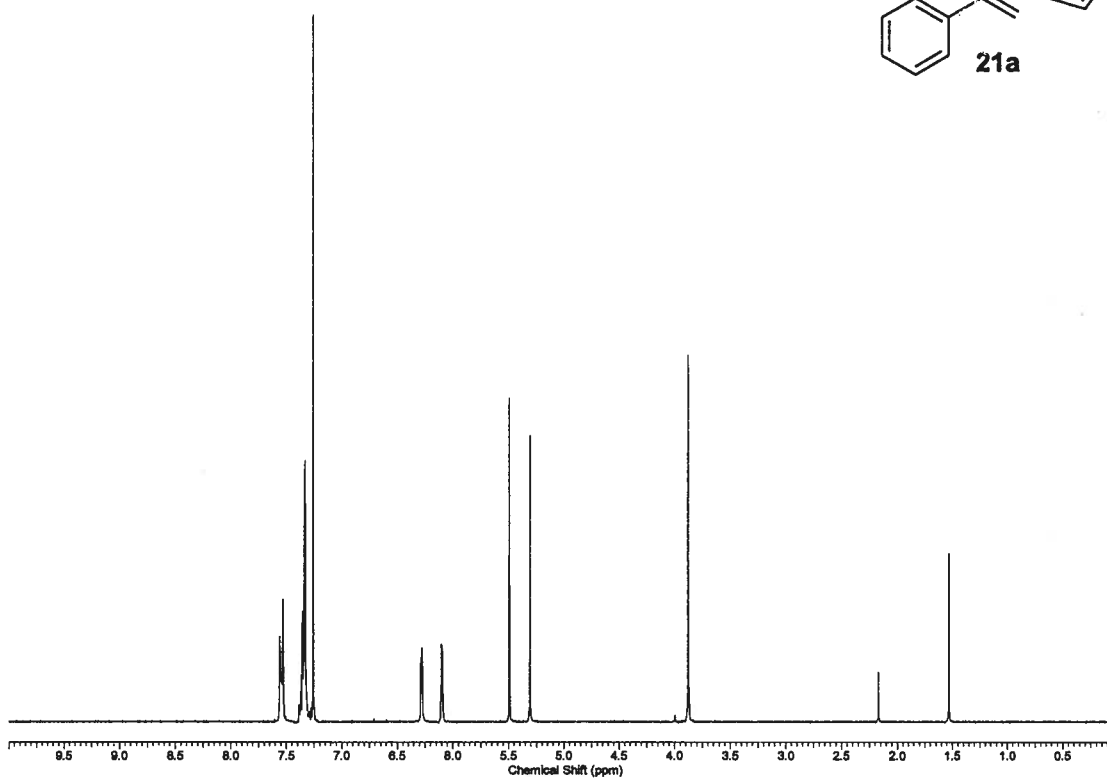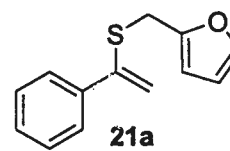
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)



**21a**
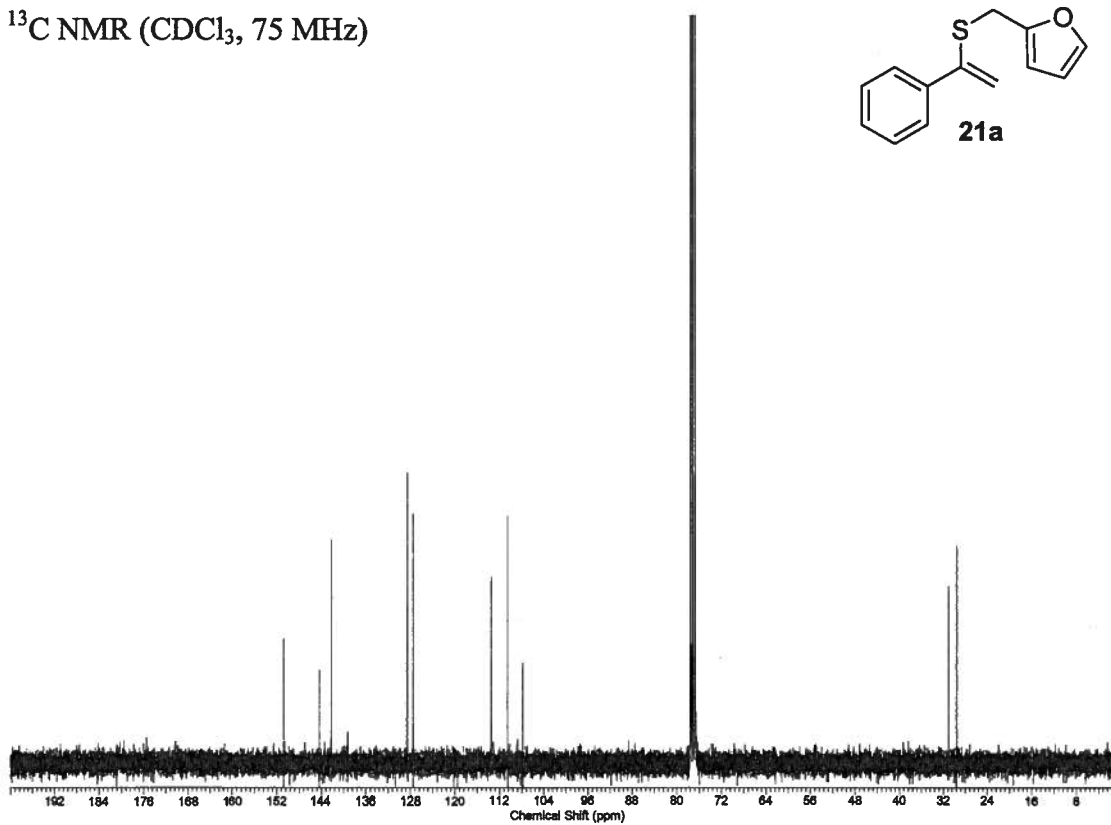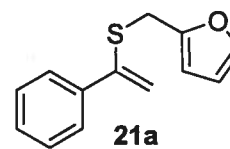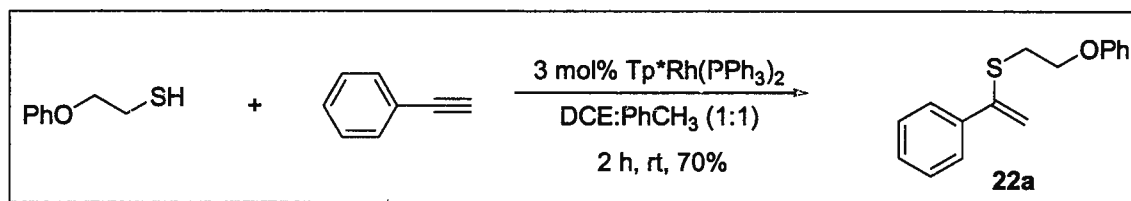
**(2-Phenoxyethyl)(1-phenylvinyl)sulfane (22a)**: White solid, 70% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.58 – 7.55 (m, 2H), 7.38 – 7.34 (m, 2H), 7.28 – 7.23 (m, 3H), 6.96 – 6.92 (m, 1H), 6.84 – 6.81 (m, 2H), 5.51 (s, 1H), 5.36 (s, 1H), 4.12 (t, 2H, $J$ = 7.1 Hz), 3.03 (t, 2H, $J$ = 7.1 Hz), 1.54 (H$_2$O). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): δ 158.5, 144.1, 139.3, 129.6, 128.8, 128.6, 127.5, 121.2, 114.7, 113.0, 66.4, 30.9. HRMS (EI) m/z calcd for C$_{16}$H$_{16}$SO: 256.0922; found: 256.0921. Anal. calcd for C$_{16}$H$_{16}$SO: C, 74.96; H, 6.29; found: C, 74.58; H, 6.52.

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

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

59
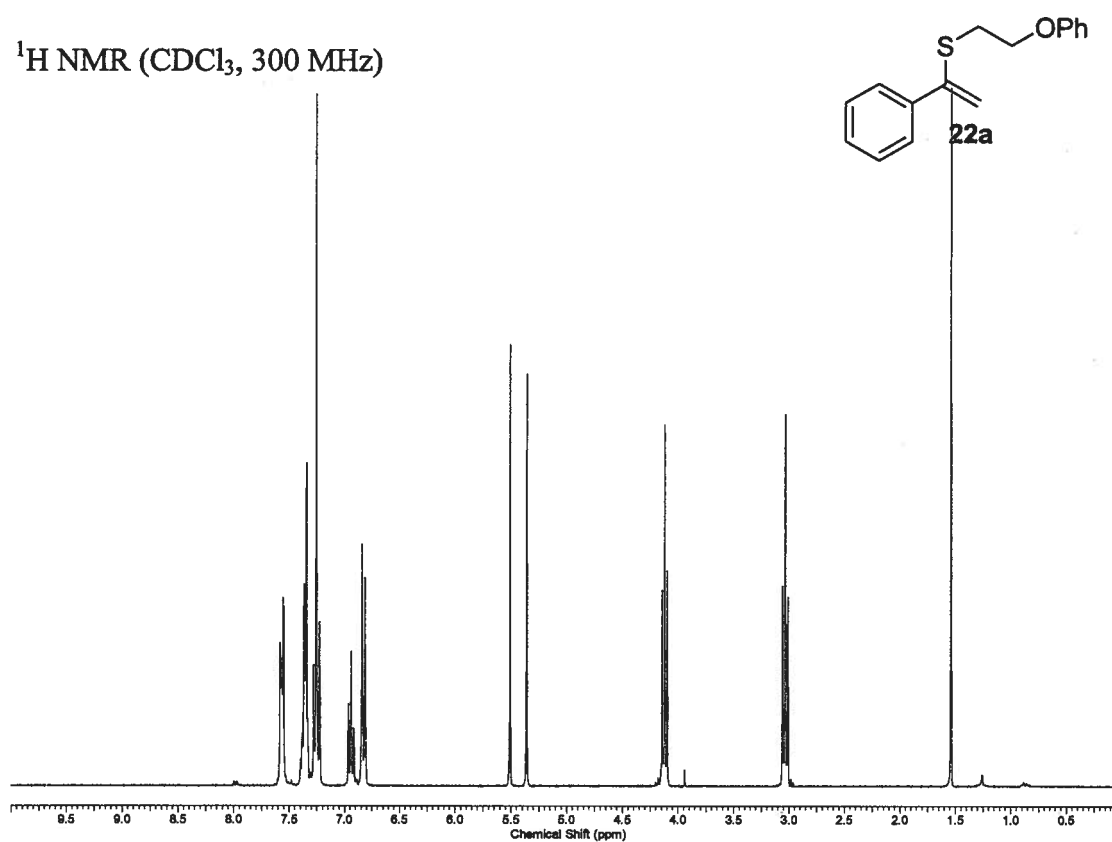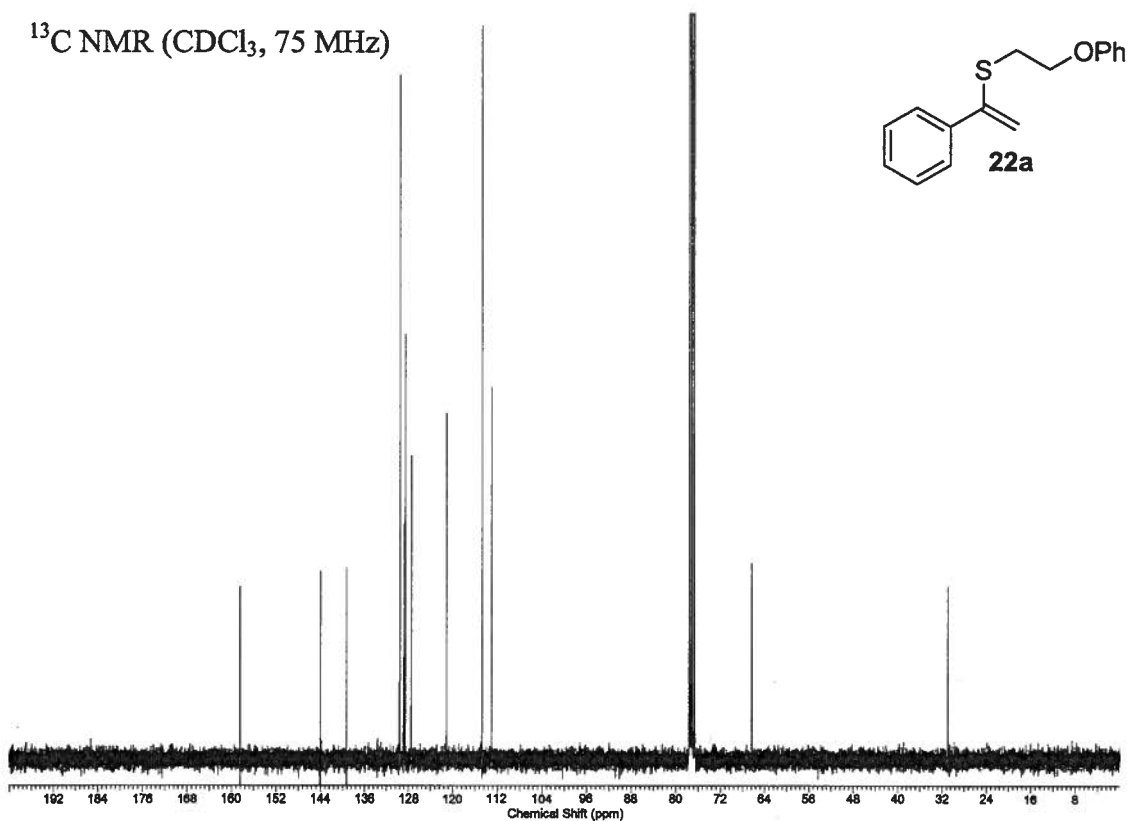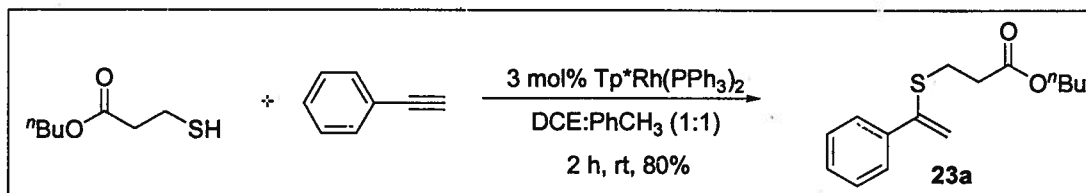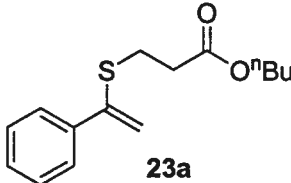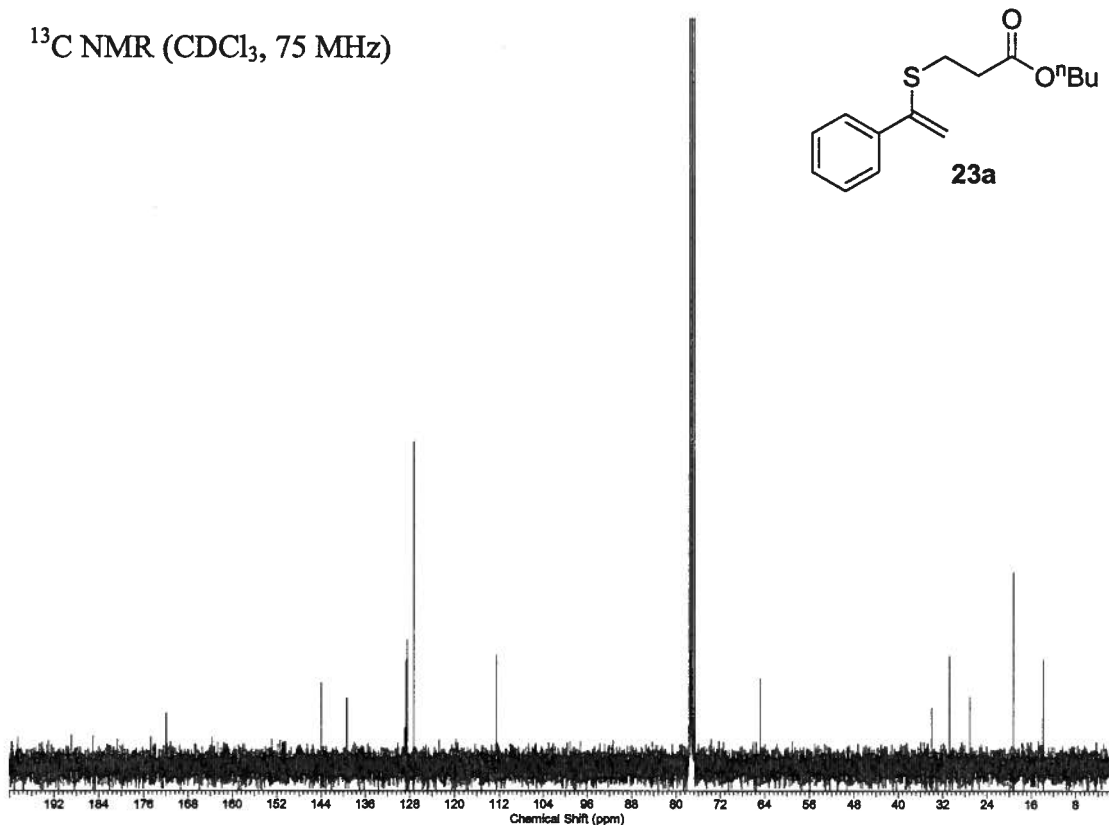
**Butyl 3-(1-phenylvinylthio)propanoate (23a):** Yellow oil, 80% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.55 – 7.32 (m, 5H), 5.51 (s, 1H), 5.27 (s, 1H), 4.09 (t, 2H, $J$ = 6.6 Hz), 2.93 (t, 2H, $J$ = 7.3 Hz) , 2.61 (t, 2H, $J$ = 7.3 Hz), 1.61 (m, 2H), 1.54 (H$_2$O), 1.37 (m, 2H), 0.93 (m, 3H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 75 MHz): $\delta$ 172.0, 144.1, 139.4, 128.7, 128.6, 127.4, 112.5, 64.8, 33.9, 30.8, 27.1, 19.3, 13.9. HRMS (EI) m/z calcd for C$_{15}$H$_{20}$SO$_2$: 264.1184; found: 264.1185. Anal. calcd for C$_{15}$H$_{20}$SO$_2$: C, 68.14; H, 7.62; found: C, 68.00; H, 7.36.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)



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

**N,N-dimethyl-2-(1-phenylvinylthio)ethanamine (24a):** Yellow oil, 65% yield. Column chromatography conditions: 20:1 hexanes:EtOAc and 3 % Et$_3$N. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.56 – 7.33 (m, 5H), 5.47 (s, 1H), 5.23 (s, 1H), 2.81 (t, 2H, $J$ = 7.4 Hz), 2.57 (t, 2H, $J$ = 7.4 Hz) , 2.25 (s, 6H). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100 MHz): $\delta$ 145.8, 140.5, 129.5, 129.3, 128.2, 112.1, 59.1, 46.2, 30.8. HRMS (EI) m/z calcd for C$_{12}$H$_{17}$NS: 207.1082; found: 207.1078.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)

**24a**

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)

**24a**

63
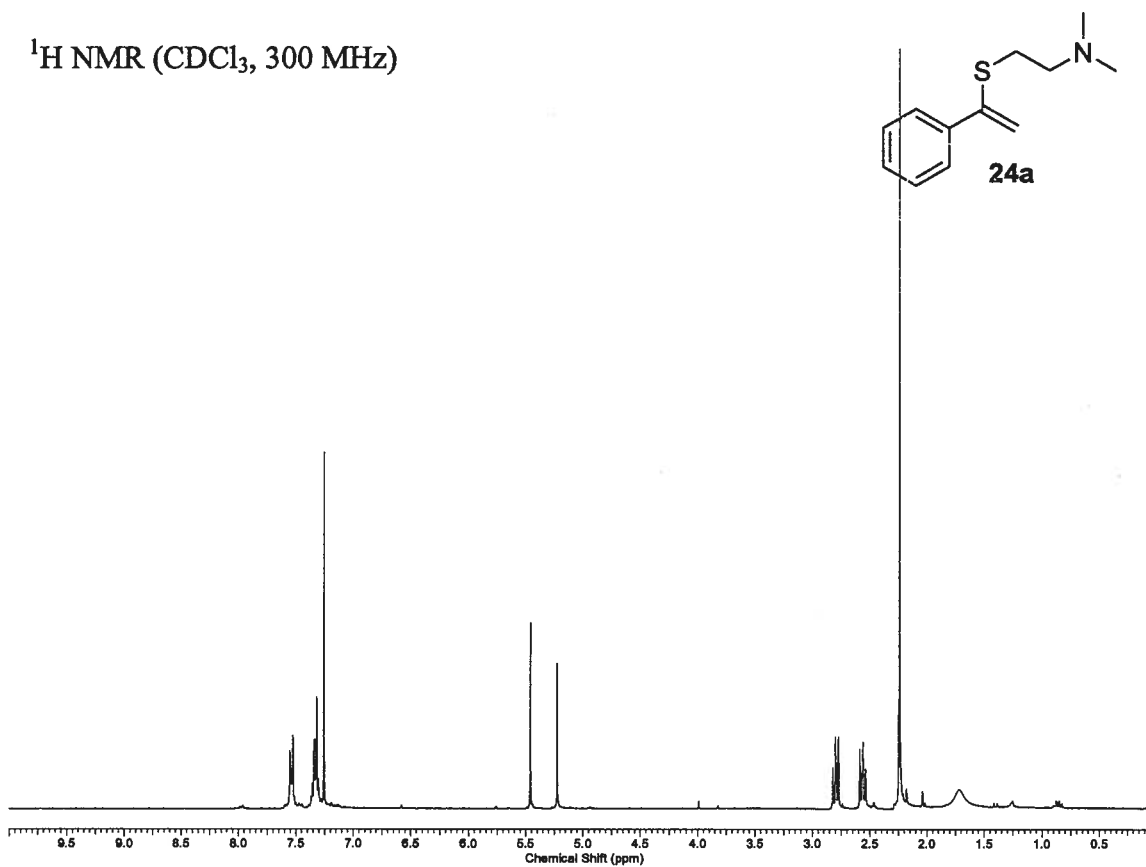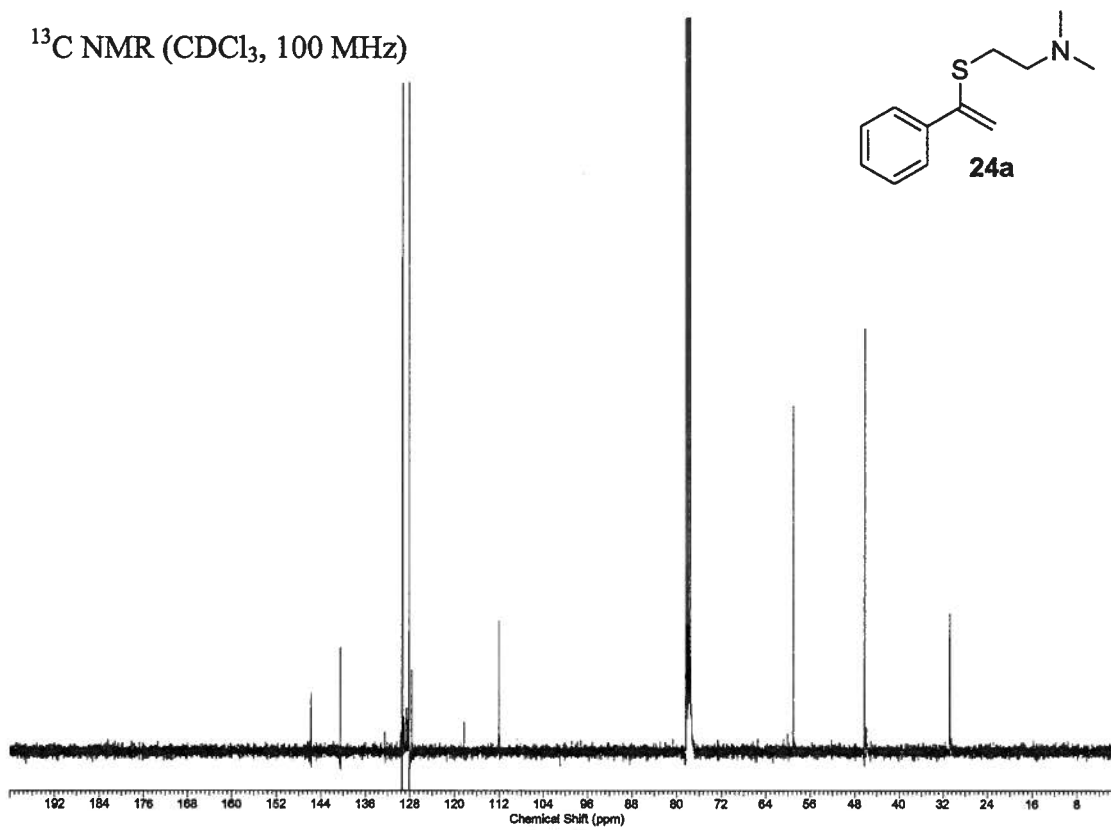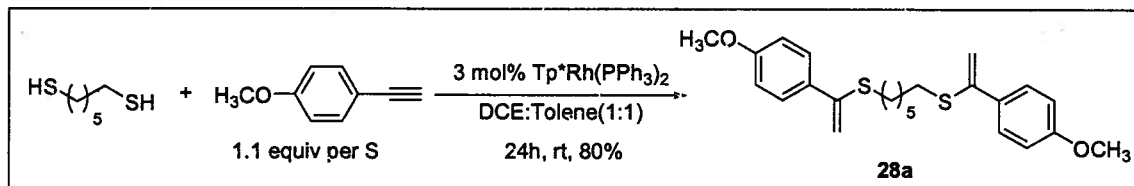
**1,2-Bis(1-(4-methoxyphenyl)vinylthio)hexane (34a)**: Yellow oil, 80% yield. Column chromatography conditions: 20:1 hexanes:EtOAc. $^1H$ NMR ($C_6D_6$, 400 MHz): δ 7.60 – 7.56 (m, 4H), 6.76 – 6.73 (m, 4H), 5.41 (s, 2H), 5.13 (s, 2H), 3.30 (s, 6H), 2.50 (t, 4H, $J$ = 7.3 Hz), 1.45 (quin, 4H, $J$ = 7.3 Hz), 1.13 (quin, 4H, $J$ = 3.7 Hz). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 100 MHz): δ 160.8, 145.9, 133.1, 129.1, 114.5, 109.6, 55.2, 32.6, 29.1, 29.0. HRMS (EI) m/z calcd for $C_{24}H_{30}S_2O_2$: 414.1686; found: 414.1687. Anal. calcd for $C_{24}H_{30}S_2O_2$: C, 69.52; H, 7.29; found: C, 69.20; H, 7.31.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz)
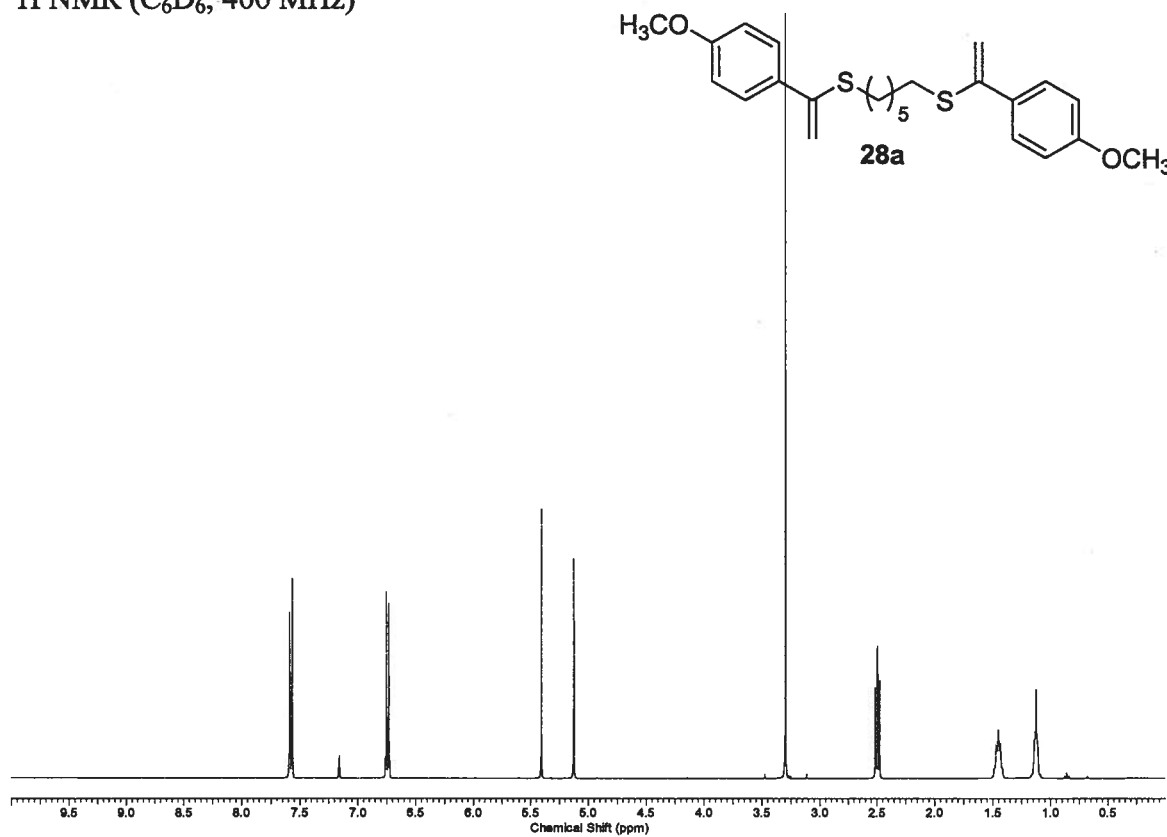


<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz)
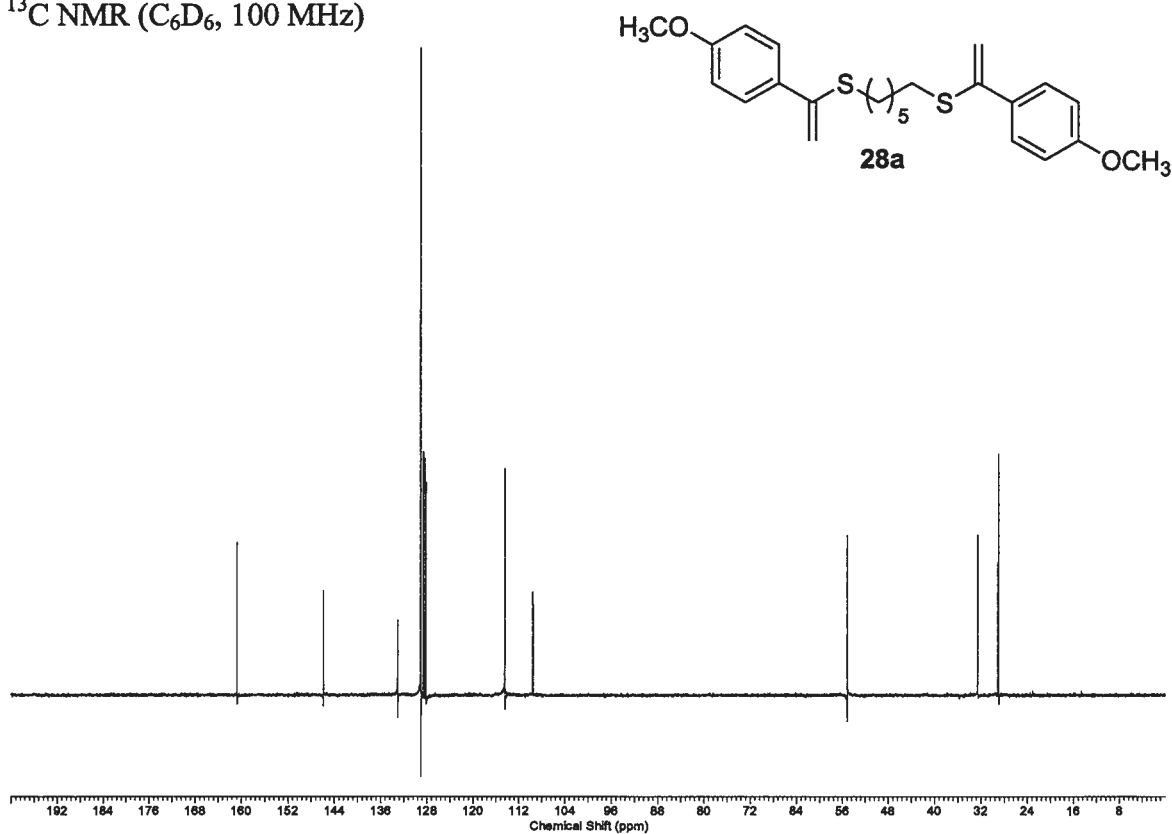
**Synthesis of complex II.** In glove box, a solution of Tp*Rh(PPh$_3$)$_2$ (93 mg, 0.1 mmol) in toluene (1 mL) were combined in the glove box in a 5 mL vial equipped with a screw cap and a magnetic stir bar. 2-pyridylacetylene (0.1 mL, 1.0 mmol) was added by syringe to the solution. The mixture was stirred for 2 h at room temperature, followed by layering with 2 mL hexanes. After 2 days, brown crystals formed. The solution was decanted, and the crystals were washed with 2 × 1 mL of hexanes. The product was dried under reduced pressure to give 50 mg (65 %) of an brown crystalline solid. $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) at 25 °C: δ 8.19 (d, 1H, $J$ = 3.9 Hz) 7.60 (m, 6H),7.42 – 7.33 (m, 4H), 7.24 – 7.20 (m, 6H), 7.70 – 6.90 (m, 2H), 5.71 (d, 2H, $J$ = 8.8 Hz), 5.17 (s, 1H), 2.72 (s, 3H), 2.50 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H), 1.44 (s, 3H), 1.37 (s, 3H), δ -14.68 (q, 1H, $J_{Rh-H}$ = 20.5 Hz, $J_{P-H}$ = 17.6 Hz), B-H not observed. $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 100 MHz): δ 154.5, 150.8, 149.8, 147.8, 145.5, 144.5, 135.9, 135.8, 135.6, 133.8, 133.4, 130.5, 128.2, 128.1, 126.1, 119.7, 107.5, 106.3, 106.1, 16.5, 13.2, 12.9, 12.1. $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 121 MHz): δ 37.69 ($J_{Rh-P}$ = 130.8 Hz). HRMS (EI) m/z calcd for C$_{40}$H$_{42}$BN$_7$PRh: 765.2387; found: 765.2389.

**X-Ray crystal structure of complex II:** Measurement for complexes **II** was made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K$\alpha$ radiation. Data were collected in a series of $\varnothing$ and $\omega$ scans and subsequently processed with the Bruker SAINT[24] software package. Data were corrected for absorption effects using the multiscan technique (SADABS).[25] Data were corrected for by Lorentz and polarization effects. The structure was solved using direct methods[26] and refined using SHELXTL.[27] For complexe **II** all non-hydrogen atoms were refined anisotropically, whereas all hydrogen atoms were placed in calculated positions and not refined, except for B-H

hydrogen which was located in difference maps and refined isotropically. The material crystallizes with both toluene and hexane in the lattice. In this case, there was a 1:2 mixture of toluene and hexane occupying the same space in the asymmetric unit. Mild restraints were employed to maintain reasonable geometries for both solvent molecules. Full details for complex **II** are presented in the Appendix.

<sup>y</sup> <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz)

Complex **II**
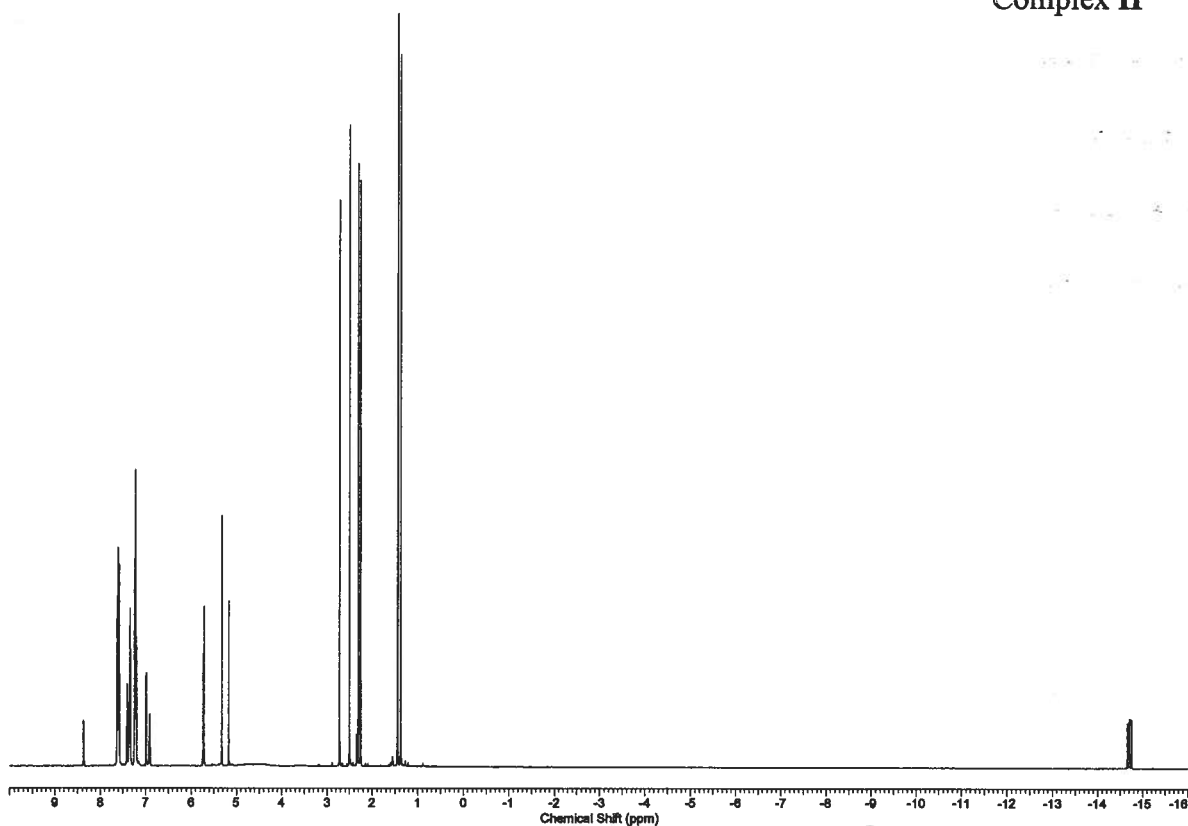
<sup>y</sup> <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz)

Complex **II**

68
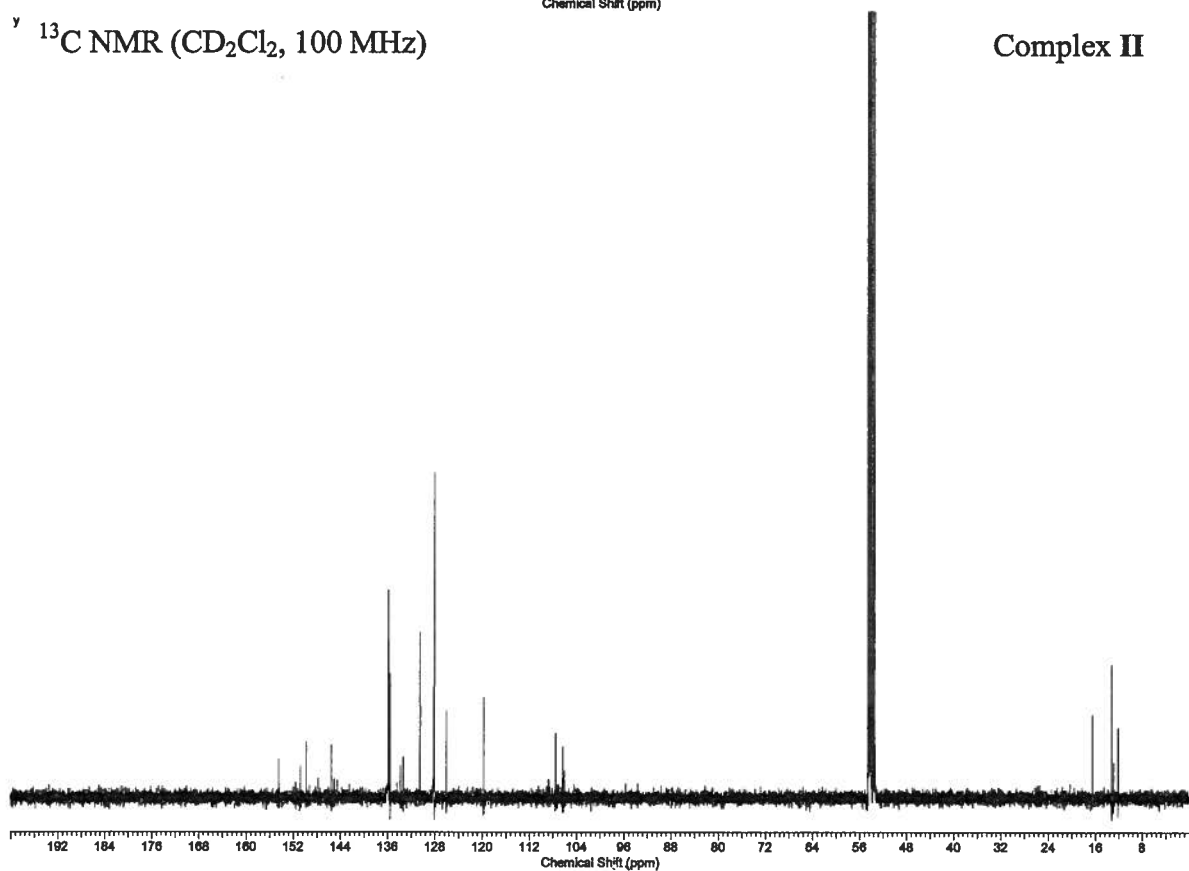
# Chapter 3 – Summary, Conclusions and Future Work

## 3.1 Summary and Conclusions

The goal of this thesis project was to explore the substrate scope and limitations of alkyne hydrothiolation using Tp*Rh(PPh₃)₂ as the catalyst. Tp*Rh(PPh₃)₂ was found to be effective for a variety of thiols and alkynes, including both terminal and internal alkynes. Most of the reactions gave good-to-excellent yields, and the branched isomer was favored in most cases. Electronic substitution of substituted phenyl acetylenes had little influence on regioselectivity, but had a great impact on the reaction efficiency and yields. Aliphatic alkynes need longer reaction time to complete reaction compared to aryl alkynes. A wide range of functional groups were tolerated, including halides, amines, nitriles, amines, ethers, esters and silanes. Alkoxy groups with the ability to coordinate with rhodium slowed down the catalytic turnover and lower the yield. Strongly coordinating groups, such as pyridine, totally precluded catalysis. The regioselectivity of the catalyst was reversed when electronically activated alkynes, i.e., those that undergo Michael addition, were used. Hydrothiolation using internal alkynes was much more difficult and needed longer reaction time and higher reaction temperature for completion.

## 3.2 Future Work

Further attention is warranted in several areas. In a few reactions, some byproducts were formed (about 5-10%). Although efforts to date have been unsuccessful in unequivocally determining the identity of the byproducts, larger scale reactions could provide sufficient material for isolation and characterization. Moreover, the product identity could provide some mechanistic clues. On the other hand, a detailed mechanistic picture could point out how to minimize the byproduct and also give more information about the scope and limitation. Such mechanistic work is currently underway.[13b]

We have demonstrated that the products of the hydrothiolation using *n*-propanethiol are suitable for Kumada cross-coupling to generate 1,1-disubstituted olefins. Other functionalization of 1,1-disubstituted vinyl sulfide could also be studied, such as Diels-Alder reactions. In addition, hydrothiolation could be used as a key step in the synthesis of some sulfur containing natural products and drug molecules[28], such as Emtricitabine, Eletriptan, and Ertapenem (see Figure 3.1).
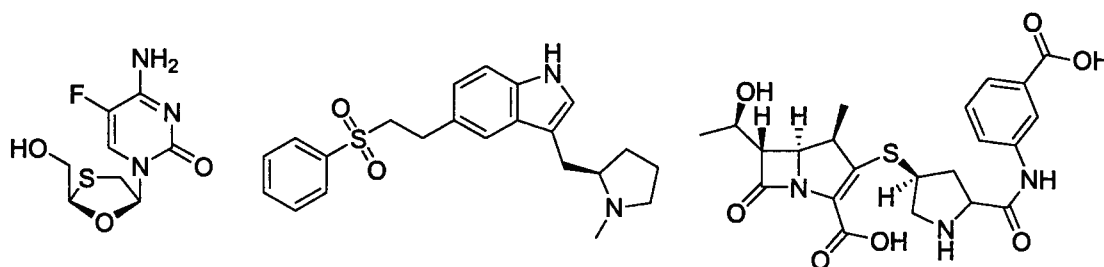
**Figure 3.1.** Emtricitabine, Eletriptan, and Ertapenem

The Tp* ligand has shown unique properties in rhodium catalyzed alkyne hydrothiolation. It would be interesting to synthesize other metal complexes with this ligand. These new complexes may have different reactivity in hydrothiolation, as well as

other reactions, such as asymmetric hydrogenation, cyclotrimerization and Diels-Alder reactions. In addition, other bidentate or tridentate ligands can also be used to form new rhodium complexes. Those new ligands may provide new selectivities in hydrothiolations.

After having demonstrated the use of Tp*Rh(PPh$_3$)$_2$ in S-H and P-H bond activation reactions, activation of H-X bonds (such as X = O) could be paid more attention. For example, the intermolecular alkyne hydroalkoxylation using rhodium complex could be an interesting research topic. On the other hand, after investigating alkyne hydrothiolation, the stereoselective alkene hydrothiolation reactions also have a good potential to study.

# References

(1) For examples of sulfur compounds as synthetic precursors or reagents for methodology, see: (a) Metzner, P.; Thuillier, A. In *Sulfur Reagents in Organic Synthesis;* Academic Press: London, 1994, 200. (b) Bratz, M.; Bullock, W. H.; Overman, L. E.; Takemoto, T. *J. Am. Chem. Soc.* **1995**, *117*, 5958-5966. (c) Stiefel, E. I.; Matsumoto, K., Eds.; In *Transition Metal Sulfur Chemistry: Biological and Industrial Significance;* ACS Symposium Series 653; ACS: Washington, DC, 1996, 358. (d) Vedula, M. S.; Pulipaka, A. B.; Venna, C.; Chintakunta, V. K.; Jinnapally, S.; Kattuboina, V. A.; Vallakati, R. K.; Basetti, V.; Akella, V.; Rajgopal, S.; Reka, A. K.; Teepireddy, S. K.; Mamnoor, P. R.; Rajagopalan, R.; Bulusu, G.; Khandelwal, A.; Upreti, V. V.; Mamidi, S. R. *Eur. J. Med. Chem.* **2003**, *38*, 811-824. (e) Chen, M. S.; White, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 1346-1347. (f) Farhat, S.; Zouev, I.; Marek, I. *Tetrahedron* **2004**, *60*, 1329-1337. (g) Sharma, V. M.; Seshu, K. V. A.; Sekhar, V. C.; Madan, S.; Vishnu, B.; Babu, P. A.; Krishna, C. V.; Sreenu, J.; Krishna, V. R.; Venkateswarlu, A.; Rajagopal, S.; Ajaykumarb, R.; Kumarb, T. S. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 67-71.

(2) (a) Paris, J. M.; Barriere, J. C.; Smith, C.; Bost, P. E. In *Recent Progress in the Chemical Synthesis of Antibiotics*; Lucas, G.; Ohno, M., Eds.; Springer-Verlag: Berlin, 1990; pp 183-248. (b) Di Giambattista, M.; Chinali, G.; Cocito, C. *J. Antimicrob. Chemother.* **1989**, *24*, 485-488. (c) Cocito, C. *Microbiol. Rev.* **1979**, 43, 145-169.

(3) For examples of vinyl sulfides as synthetic intermediates or precursors to functionalized molecules, see: (a) Parham, W. E.; Motter, R. F. *J. Am. Chem. Soc.*

1958, *81*, 2146-2148. (b) Mukaiyama, T.; Kamio, K.; Kobayashi, S.; Takei, H. *Bull. Chem. Soc. Jpn.* **1972**, *4*, 193-202. (c) McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 548-551. (d) Wenkert, E.; Ferreira, T. W.; Michelotti, E. L. *J. Chem. Soc. , Chem. Commun.* **1979**, *6*, 637-638. (e) Trost, B. M.; Lavoie, A. C. *J. Am. Chem. Soc.* **1983**, *105*, 5075-5090. (f) Sabarre, A.; Love. J. A. *Org. Lett.* **2008**, *submitted.*

(4)   (a) Bates, C. G.; Saejueng, P.; Doherty, M. Q.; Venkataraman, D. *Org. Lett.*, **2004**, *6*, 5005-5008. (b) Wang, Z.; Mo, H.; Bao, W. *Synlett*, **2007**, 91-94.

(5)   Radical reactions: (a) Oswald, A. A.; Griesbaum, K.; Hudson, B. E.; Bregman, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 2877-2884. (b) Griesbaum, K. *Angew. Chem. Int. Ed.* **1970**, *9*, 270. (c) Patai, S., Ed.; In *The Chemistry of the Thiol Group;* John Wiley & Sons, Ltd.: London, 1974, *2.* (d) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J. L.; Oshima, K.; Utimoto, K. *Chem. Lett.* **1987**, 1647-1650. (e) Capella, L.; Montevecchi, P. C.; Navacchia, M. L. *J. Org. Chem.* **1996**, *61*, 6783-6789.

(6)   Nucleophilic reactions: (a) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756-2759. (b) Carson, J. F.; Boggs, L. E. *J. Org. Chem.* **1966**, *31*, 2862-2864. (c) Truce, W.; Tichenor, G. J. W. *J. Organomet. Chem.* **1972**, *37*, 2391-2396. (d) Katritzky, A. R.; Ramer, W. H.; Ossana, A. *J. Org. Chem.* **1985**, *50*, 847-852. (e) Kondoh, A.; Takami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2005**, *70*, 6468-6473.

(7)   For recent reviews, see: (a) Andrea, T.; Eisen, M. S. *Chem. Soc. Rev.* **2008**, *37*, 550-567. (b) Hultzsch, K. C.; Gribkov, D. V.; Hampel, F. *J. Organomet. Chem.* **2005**, *690*, 4441-4452. (c) Nobis, M.; Driessen-Holscher, B. *Angew. Chem. Int. Ed.* **2001**, *40*, 3983-3985.

(8) For recent reviews, see: (a) Chianese, A. R.; Lee, S. J.; Gagne, M. R. *Angew. Chem. Int. Ed.* **2007**, *46*, 4042-4059. (b) Messerle, B. A.; Vuong, K. Q. *Pure Appl. Chem.* **2006**, *78*, 385-390.

(9) For recent reviews, see: (a) Li, C. J. *Chem. Rev.* **2005**, *105*, 3095-3165. (b) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161-2185.

(10) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205-3220.

(11) Bader, H.; Cross, L. C.; Heilbron, Ian; Jones, E. R. H. *J. Chem. Soc.* **1949**, 619-623

(12) Metal-catalyzed reactions: (a) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2056-2061. (b) Ogawa, A.; Ikeda, T.; Kimura, K.; Hirao, T. *J. Am. Chem. Soc.* **1999**, *121*, 5108-5114. (c) Kuniyasu, H.; Ogawa, A.; Sato, K. I.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902-5903. (d) Shoai, S.; Bichler, P.; Kang, B.; Buckley, H.; Love, J. A. *Organometallics* **2007**, *26*, 5778-5781. (e) Yadav, J. S.; Subba Reddy, B. V.; Raju, A.; Ravindar, K.; Gakul Baishya *Chem. Lett.* **2007**, *36*, 1474-1475. (f) Bäckvall, J. E.; Ericsson, A. *J. Org. Chem.* **1994**, *59*, 5850-5851. (g) Ananikov, V. P.; Orlov, N. V.; Beletskaya, I. P.; Khrustalev, V. N.; Antipin, M. Y.; Timofeeva, T. V. *J. Am. Chem. Soc.* **2007**, *129*, 7252-7253. (h) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614-17615. (j) Fraser, L. R.; Bird, J.; Wu, Q.; Cao, C.; Patrick, B. O.; Love, J. A. *Organometallics* **2007**, *26*, 5602-5611.

(13) (a) Kang, B. Mechanistic and Structural Investigation of Rhodium-Catalyzed Alkyne Hydrothiolation with Alkyl and Arylthiols, *B. Sc. Thesis*, 2006. (b) Shoai, S.; Kang, B.; Love, J. A. manuscript in preparation.

(14) Cao, C.; Wang, T.; Patrick, B. O.; Love, J. A. *Organometallics* **2006**, *25*, 1321-1324.

(15) Van Rooy, S.; Cao, C.; Patrick, B. O.; Lam, A.; Love, J. A. *Inorg. Chim. Acta* **2006**, *359*, 2918-2923.

(16) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918-920.

(17) No reaction occurs in the absence of catalyst.

(18) Yoshinao, T.; Toshiro, H.; Zenichi, Y. *J. Am. Chem. Soc.* **1980**, *102*, 2392-2398.

(19) (a) Deborah, K.J.H.; William, L.J. *J. Am. Chem. Soc.* **1995**, *117*, 9077-9078. (b) Bickart, P.; Carson, F.W.; Jacobus, J.: Miller, E.G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869-4876. (c) Evans, D.A.; Andrew, G.C.; Simis, C.L. *J. Am. Chem. Soc.* **1971**, *93*, 4956-4957.

(20) (a) Wenkert, E.; Fernandes, J. B.; Michelotti, E. L.; Swindell, C. S. *Synthesis,* **1981**, 701-703. (b) Wenkert, E.; Shepard, M. E.; Mcphail, A. T. *J. Chem. Soc. Chem. Commun.* **1986**, *13*, 1390-1391. (c) Okamura, H.; Miura, M.; Takei, H. *Tetrahedron Lett.* **1979**, *1*, 43-46.

(21) (a) Amer, I.; Bernstein, T.; Eisen, M.; Blum, J.; Vollhardt, K.P.C. *J. Mol. Catal.* **1990**, *60*, 313-321. (b) Agenet, N.; Gandon, V.; Vollhardt, K.P.C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860-8871.

(22) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.

(23) (a) Connelly, N. G.; Emslie, D. J. H.; Geiger, W. E.; Hayward, O. D.; Linehan, E. B.; Orpen, A. G.; Quayle, M. J.; Rieger, P. H. *J. Chem. Soc., Dalton Trans* **2001**,

670- 683. (b) Cîrcu, V.; Fernandes, M. A.; Carlton, L. *Inorg. Chem.* **2002**, *41*, 3859-3865.

(24) *Bruker SAINT software package*, version 7.03A; Bruker AXS Inc.: Madison, WI, 1997-2003.

(25) *Bruker SAINT software package*, Version 2.10; Bruker AXS Inc.: Madison, WI, 2003.

(26) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.

(27) *Bruker SAINT software package*, Version 5.1; Bruker AXS Inc.: Madison, WI, 1997.

(28) Fernández, F.; Khiar, N. *Chem. Rev.* **2003**, *103*, 3651-3705.

# Appendix: X-ray Crystallographic Data for Complex II

## A. Crystal Data

| | |
|---|---|
| Empirical Formula | $C_{40}H_{42}BN_7PRh$ |
| Formula Weight | 765.50 |
| Crystal Color, Habit | yellow, prism |
| Crystal Dimensions | 0.26 X 0.44 X 0.50 mm |
| Crystal System | orthrhombic |
| Lattice Type | primitive |
| Lattice Parameters | $a = 15.851(2)$ Å $\alpha = 90.0°$ |
| | $b = 19.184(3)$ Å $\beta = 90.0°$ |
| | $c = 23.951(4)$ Å $\gamma = 90.0°$ |
| | $V = 4667.9(8)$ Å$^3$ |
| Space Group | *P bca* (#61) |
| Z value | 8 |
| Dcalc | 1.396 g/cm$^3$ |
| F000 | 3168.00 |
| $\mu$ (MoK$\alpha$) | 5.53 cm$^{-1}$ |

## B. Intensity Measurements

| | |
|---|---|
| Diffractometer | Bruker X8 APEX II |
| Radiation | MoK$\alpha$ ($\lambda = 0.71073$ Å) |
| | graphite monochromated |
| Data Images | 1071 exposures @ 5.0 seconds |
| Detector Position | 36.00 mm |
| $2\theta$max | 56.0° |
| No. of Reflections Measured | Total: 67640 |
| | Unique: 8786 ($R_{int} = 0.025$) |
| Corrections | Absorption ($T_{min} = 0.803$, $T_{max} = 0.866$); Lorentz-polarization |

## C. Structure Solution and Refinement

| | |
|---|---|
| Structure Solution | Direct Methods (SIR97) |
| Refinement | Full-matrix least-squares on $F^2$ |
| Function Minimized | $\Sigma \, w \, (Fo^2 - Fc^2)^2$ |
| Least Squares Weights | $w=1/(\sigma^2(Fo^2)+(0.0252P)^2 + 6.3229P)$ |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (I>0.00$\sigma$(I)) | 8786 |
| No. Variables | 465 |
| Reflection/Parameter Ratio | 18.89 |

| | |
|---|---|
| Residuals (refined on $F^2$, all data): R1; wR2 | 0.034; 0.066 |
| Goodness of Fit Indicator | 1.08 |
| No. Observations ($I > 2.00\sigma(I)$) | 8528 |
| Residuals (refined on F): R1; wR2 | 0.024; 0.058 |
| Max Shift/Error in Final Cycle | 0.00 |
| Maximum peak in Final Diff. Map | 0.37 e$^-$/Å$^3$ |
| Minimum peak in Final Diff. Map | -0.45 e$^-$/Å$^3$ |

# Table 1. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$)

| Atom | X | Y | Z | U(eq) |
|------|------|------|------|-------|
| C(1) | 3595(1) | 1859(1) | 6238(1) | 26(1) |
| C(2) | 3929(1) | 1913(1) | 6819(1) | 21(1) |
| C(3) | 3465(1) | 1887(1) | 7317(1) | 25(1) |
| C(4) | 4042(1) | 1909(1) | 7743(1) | 23(1) |
| C(5) | 3909(1) | 1919(1) | 8362(1) | 32(1) |
| C(6) | 7592(1) | 3523(1) | 6858(1) | 26(1) |
| C(7) | 7058(1) | 3235(1) | 7313(1) | 22(1) |
| C(8) | 7088(1) | 3391(1) | 7883(1) | 28(1) |
| C(9) | 6529(1) | 2945(1) | 8142(1) | 26(1) |
| C(10) | 6290(1) | 2875(1) | 8746(1) | 40(1) |
| C(11) | 7217(1) | 661(1) | 6221(1) | 29(1) |
| C(12) | 6883(1) | 779(1) | 6797(1) | 23(1) |
| C(13) | 7009(1) | 381(1) | 7278(1) | 28(1) |
| C(14) | 6576(1) | 707(1) | 7700(1) | 24(1) |
| C(15) | 6504(1) | 504(1) | 8301(1) | 35(1) |
| C(16) | 5451(1) | 3915(1) | 6643(1) | 20(1) |
| C(17) | 4991(1) | 3753(1) | 7125(1) | 23(1) |
| C(18) | 4926(1) | 4232(1) | 7557(1) | 30(1) |
| C(19) | 5326(1) | 4875(1) | 7518(1) | 33(1) |
| C(20) | 5784(1) | 5037(1) | 7047(1) | 31(1) |
| C(21) | 5845(1) | 4562(1) | 6608(1) | 26(1) |
| C(22) | 6200(1) | 3632(1) | 5559(1) | 21(1) |
| C(23) | 5907(1) | 4228(1) | 5282(1) | 30(1) |
| C(24) | 6402(1) | 4560(1) | 4888(1) | 36(1) |
| C(25) | 7189(1) | 4299(1) | 4758(1) | 34(1) |
| C(26) | 7481(1) | 3703(1) | 5016(1) | 33(1) |
| C(27) | 6985(1) | 3370(1) | 5414(1) | 26(1) |
| C(28) | 4519(1) | 3282(1) | 5750(1) | 20(1) |
| C(29) | 3845(1) | 3669(1) | 5962(1) | 24(1) |
| C(30) | 3094(1) | 3715(1) | 5664(1) | 29(1) |
| C(31) | 3002(1) | 3375(1) | 5157(1) | 32(1) |
| C(32) | 3671(1) | 2993(1) | 4944(1) | 30(1) |
| C(33) | 4428(1) | 2948(1) | 5234(1) | 25(1) |
| C(34) | 5683(1) | 1740(1) | 5812(1) | 19(1) |
| C(35) | 5547(1) | 1443(1) | 5374(1) | 23(1) |
| C(36) | 5323(1) | 1054(1) | 4883(1) | 22(1) |
| C(37) | 4368(1) | 825(1) | 4190(1) | 37(1) |
| C(38) | 4811(1) | 261(1) | 3996(1) | 35(1) |
| C(39) | 5562(1) | 98(1) | 4256(1) | 33(1) |
| C(40) | 5827(1) | 500(1) | 4703(1) | 27(1) |
| N(1) | 4756(1) | 1961(1) | 6936(1) | 19(1) |

| | | | | |
|---|---|---|---|---|
| N(2) | 4819(1) | 1941(1) | 7510(1) | 20(1) |
| N(3) | 6490(1) | 2726(1) | 7228(1) | 19(1) |
| N(4) | 6183(1) | 2542(1) | 7741(1) | 21(1) |
| N(5) | 6393(1) | 1324(1) | 6923(1) | 19(1) |
| N(6) | 6199(1) | 1281(1) | 7483(1) | 20(1) |
| N(7) | 4598(1) | 1226(1) | 4623(1) | 31(1) |
| Rh(1) | 5973(1) | 2226(1) | 6507(1) | 15(1) |
| B(1) | 5683(1) | 1856(1) | 7788(1) | 21(1) |
| P(1) | 5545(1) | 3240(1) | 6105(1) | 17(1) |

## Table 2. Bond Lengths (Å)

| Atoms | Length (Å) | Atoms | Length (Å) |
|---|---|---|---|
| C(1)-C(2) | 1.492(2) | C(21)-H(21) | 0.95 |
| C(1)-H(1A) | 0.98 | C(22)-C(27) | 1.385(2) |
| C(1)-H(1B) | 0.98 | C(22)-C(23) | 1.401(2) |
| C(1)-H(1C) | 0.98 | C(22)-P(1) | 1.8334(17) |
| C(2)-N(1) | 1.343(2) | C(23)-C(24) | 1.382(3) |
| C(2)-C(3) | 1.401(2) | C(23)-H(23) | 0.95 |
| C(3)-C(4) | 1.371(3) | C(24)-C(25) | 1.380(3) |
| C(3)-H(3) | 0.95 | C(24)-H(24) | 0.95 |
| C(4)-N(2) | 1.354(2) | C(25)-C(26) | 1.378(3) |
| C(4)-C(5) | 1.497(3) | C(25)-H(25) | 0.95 |
| C(5)-H(5A) | 0.98 | C(26)-C(27) | 1.393(3) |
| C(5)-H(5B) | 0.98 | C(26)-H(26) | 0.95 |
| C(5)-H(5C) | 0.98 | C(27)-H(27) | 0.95 |
| C(6)-C(7) | 1.488(2) | C(28)-C(29) | 1.396(2) |
| C(6)-H(6A) | 0.98 | C(28)-C(33) | 1.398(2) |
| C(6)-H(6B) | 0.98 | C(28)-P(1) | 1.8374(17) |
| C(6)-H(6C) | 0.98 | C(29)-C(30) | 1.392(2) |
| C(7)-N(3) | 1.343(2) | C(29)-H(29) | 0.95 |
| C(7)-C(8) | 1.399(3) | C(30)-C(31) | 1.386(3) |
| C(8)-C(9) | 1.379(3) | C(30)-H(30) | 0.95 |
| C(8)-H(8) | 0.95 | C(31)-C(32) | 1.387(3) |
| C(9)-N(4) | 1.351(2) | C(31)-H(31) | 0.95 |
| C(9)-C(10) | 1.501(3) | C(32)-C(33) | 1.389(3) |
| C(10)-H(10A) | 0.98 | C(32)-H(32) | 0.95 |
| C(10)-H(10B) | 0.98 | C(33)-H(33) | 0.95 |
| C(10)-H(10C) | 0.98 | C(34)-C(35) | 1.212(2) |
| C(11)-C(12) | 1.494(3) | C(34)-Rh(1) | 1.9627(17) |
| C(11)-H(11A) | 0.98 | C(35)-C(36) | 1.437(2) |
| C(11)-H(11B) | 0.98 | C(36)-N(7) | 1.348(2) |
| C(11)-H(11C) | 0.98 | C(36)-C(40) | 1.398(2) |
| C(12)-N(5) | 1.338(2) | C(37)-N(7) | 1.342(3) |
| C(12)-C(13) | 1.397(2) | C(37)-C(38) | 1.371(3) |
| C(13)-C(14) | 1.372(3) | C(37)-H(37) | 0.95 |
| C(13)-H(13) | 0.95 | C(38)-C(39) | 1.380(3) |
| C(14)-N(6) | 1.355(2) | C(38)-H(38) | 0.95 |
| C(14)-C(15) | 1.497(3) | C(39)-C(40) | 1.383(3) |
| C(15)-H(15A) | 0.98 | C(39)-H(39) | 0.95 |
| C(15)-H(15B) | 0.98 | C(40)-H(40) | 0.95 |
| C(15)-H(15C) | 0.98 | N(1)-N(2) | 1.3773(19) |
| C(16)-C(21) | 1.392(2) | N(1)-Rh(1) | 2.2448(14) |
| C(16)-C(17) | 1.399(2) | N(2)-B(1) | 1.531(2) |
| C(16)-P(1) | 1.8330(17) | N(3)-N(4) | 1.368(2) |

| | | | |
|---|---|---|---|
| C(17)-C(18) | 1.388(2) | N(3)-Rh(1) | 2.1386(14) |
| C(17)-H(17) | 0.95 | N(4)-B(1) | 1.541(2) |
| C(18)-C(19) | 1.391(3) | N(5)-N(6) | 1.379(2) |
| C(18)-H(18) | 0.95 | N(5)-Rh(1) | 2.1037(14) |
| C(19)-C(20) | 1.375(3) | N(6)-B(1) | 1.555(2) |
| C(19)-H(19) | 0.95 | Rh(1)-P(1) | 2.2732(5) |
| C(20)-C(21) | 1.395(3) | Rh(1)-H(1) | 1.46(2) |
| C(20)-H(20) | 0.95 | B(1)-H(2) | 1.068(19) |

**Table 3. Bond Angles (°)**

| Atoms | Angle (°) | Atoms | Angle (°) |
|---|---|---|---|
| C(2)-C(1)-H(1A) | 109.5 | C(26)-C(25)-C(24) | 120.18(18) |
| C(2)-C(1)-H(1B) | 109.5 | C(26)-C(25)-H(25) | 119.9 |
| H(1A)-C(1)-H(1B) | 109.5 | C(24)-C(25)-H(25) | 119.9 |
| C(2)-C(1)-H(1C) | 109.5 | C(25)-C(26)-C(27) | 119.88(18) |
| H(1A)-C(1)-H(1C) | 109.5 | C(25)-C(26)-H(26) | 120.1 |
| H(1B)-C(1)-H(1C) | 109.5 | C(27)-C(26)-H(26) | 120.1 |
| N(1)-C(2)-C(3) | 109.71(15) | C(22)-C(27)-C(26) | 120.72(17) |
| N(1)-C(2)-C(1) | 123.06(16) | C(22)-C(27)-H(27) | 119.6 |
| C(3)-C(2)-C(1) | 127.16(15) | C(26)-C(27)-H(27) | 119.6 |
| C(4)-C(3)-C(2) | 106.39(15) | C(29)-C(28)-C(33) | 119.08(16) |
| C(4)-C(3)-H(3) | 126.8 | C(29)-C(28)-P(1) | 122.12(13) |
| C(2)-C(3)-H(3) | 126.8 | C(33)-C(28)-P(1) | 118.70(13) |
| N(2)-C(4)-C(3) | 107.48(15) | C(30)-C(29)-C(28) | 120.09(17) |
| N(2)-C(4)-C(5) | 122.46(16) | C(30)-C(29)-H(29) | 120 |
| C(3)-C(4)-C(5) | 130.04(16) | C(28)-C(29)-H(29) | 120 |
| C(4)-C(5)-H(5A) | 109.5 | C(31)-C(30)-C(29) | 120.64(18) |
| C(4)-C(5)-H(5B) | 109.5 | C(31)-C(30)-H(30) | 119.7 |
| H(5A)-C(5)-H(5B) | 109.5 | C(29)-C(30)-H(30) | 119.7 |
| C(4)-C(5)-H(5C) | 109.5 | C(30)-C(31)-C(32) | 119.37(17) |
| H(5A)-C(5)-H(5C) | 109.5 | C(30)-C(31)-H(31) | 120.3 |
| H(5B)-C(5)-H(5C) | 109.5 | C(32)-C(31)-H(31) | 120.3 |
| C(7)-C(6)-H(6A) | 109.5 | C(31)-C(32)-C(33) | 120.58(18) |
| C(7)-C(6)-H(6B) | 109.5 | C(31)-C(32)-H(32) | 119.7 |
| H(6A)-C(6)-H(6B) | 109.5 | C(33)-C(32)-H(32) | 119.7 |
| C(7)-C(6)-H(6C) | 109.5 | C(32)-C(33)-C(28) | 120.21(17) |
| H(6A)-C(6)-H(6C) | 109.5 | C(32)-C(33)-H(33) | 119.9 |
| H(6B)-C(6)-H(6C) | 109.5 | C(28)-C(33)-H(33) | 119.9 |
| N(3)-C(7)-C(8) | 109.13(16) | C(35)-C(34)-Rh(1) | 176.59(15) |
| N(3)-C(7)-C(6) | 122.66(15) | C(34)-C(35)-C(36) | 174.47(18) |
| C(8)-C(7)-C(6) | 128.07(16) | N(7)-C(36)-C(40) | 121.96(16) |
| C(9)-C(8)-C(7) | 106.49(15) | N(7)-C(36)-C(35) | 117.47(16) |
| C(9)-C(8)-H(8) | 126.8 | C(40)-C(36)-C(35) | 120.51(16) |
| C(7)-C(8)-H(8) | 126.8 | N(7)-C(37)-C(38) | 125.08(19) |
| N(4)-C(9)-C(8) | 107.22(16) | N(7)-C(37)-H(37) | 117.5 |
| N(4)-C(9)-C(10) | 122.18(17) | C(38)-C(37)-H(37) | 117.5 |
| C(8)-C(9)-C(10) | 130.60(17) | C(37)-C(38)-C(39) | 117.89(18) |
| C(9)-C(10)-H(10A) | 109.5 | C(37)-C(38)-H(38) | 121.1 |
| C(9)-C(10)-H(10B) | 109.5 | C(39)-C(38)-H(38) | 121.1 |
| H(10A)-C(10)-H(10B) | 109.5 | C(38)-C(39)-C(40) | 118.96(19) |
| C(9)-C(10)-H(10C) | 109.5 | C(38)-C(39)-H(39) | 120.5 |
| H(10A)-C(10)-H(10C) | 109.5 | C(40)-C(39)-H(39) | 120.5 |

| | | | |
|---|---|---|---|
| H(10B)-C(10)-H(10C) | 109.5 | C(39)-C(40)-C(36) | 119.37(18) |
| C(12)-C(11)-H(11A) | 109.5 | C(39)-C(40)-H(40) | 120.3 |
| C(12)-C(11)-H(11B) | 109.5 | C(36)-C(40)-H(40) | 120.3 |
| H(11A)-C(11)-H(11B) | 109.5 | C(2)-N(1)-N(2) | 106.12(13) |
| C(12)-C(11)-H(11C) | 109.5 | C(2)-N(1)-Rh(1) | 139.34(12) |
| H(11A)-C(11)-H(11C) | 109.5 | N(2)-N(1)-Rh(1) | 113.58(10) |
| H(11B)-C(11)-H(11C) | 109.5 | C(4)-N(2)-N(1) | 110.25(14) |
| N(5)-C(12)-C(13) | 108.94(16) | C(4)-N(2)-B(1) | 128.97(15) |
| N(5)-C(12)-C(11) | 122.16(16) | N(1)-N(2)-B(1) | 120.13(13) |
| C(13)-C(12)-C(11) | 128.89(16) | C(7)-N(3)-N(4) | 106.80(13) |
| C(14)-C(13)-C(12) | 106.61(15) | C(7)-N(3)-Rh(1) | 134.92(12) |
| C(14)-C(13)-H(13) | 126.7 | N(4)-N(3)-Rh(1) | 118.21(10) |
| C(12)-C(13)-H(13) | 126.7 | C(9)-N(4)-N(3) | 110.32(14) |
| N(6)-C(14)-C(13) | 108.03(16) | C(9)-N(4)-B(1) | 130.27(15) |
| N(6)-C(14)-C(15) | 123.13(17) | N(3)-N(4)-B(1) | 117.97(13) |
| C(13)-C(14)-C(15) | 128.84(17) | C(12)-N(5)-N(6) | 107.51(13) |
| C(14)-C(15)-H(15A) | 109.5 | C(12)-N(5)-Rh(1) | 136.08(12) |
| C(14)-C(15)-H(15B) | 109.5 | N(6)-N(5)-Rh(1) | 116.10(10) |
| H(15A)-C(15)-H(15B) | 109.5 | C(14)-N(6)-N(5) | 108.90(14) |
| C(14)-C(15)-H(15C) | 109.5 | C(14)-N(6)-B(1) | 128.90(15) |
| H(15A)-C(15)-H(15C) | 109.5 | N(5)-N(6)-B(1) | 122.05(13) |
| H(15B)-C(15)-H(15C) | 109.5 | C(37)-N(7)-C(36) | 116.69(17) |
| C(21)-C(16)-C(17) | 118.74(16) | C(34)-Rh(1)-N(5) | 94.85(6) |
| C(21)-C(16)-P(1) | 123.47(13) | C(34)-Rh(1)-N(3) | 171.02(6) |
| C(17)-C(16)-P(1) | 117.72(12) | N(5)-Rh(1)-N(3) | 82.29(5) |
| C(18)-C(17)-C(16) | 120.46(16) | C(34)-Rh(1)-N(1) | 94.55(6) |
| C(18)-C(17)-H(17) | 119.8 | N(5)-Rh(1)-N(1) | 82.46(5) |
| C(16)-C(17)-H(17) | 119.8 | N(3)-Rh(1)-N(1) | 93.52(5) |
| C(17)-C(18)-C(19) | 120.20(18) | C(34)-Rh(1)-P(1) | 88.72(5) |
| C(17)-C(18)-H(18) | 119.9 | N(5)-Rh(1)-P(1) | 176.42(4) |
| C(19)-C(18)-H(18) | 119.9 | N(3)-Rh(1)-P(1) | 94.14(4) |
| C(20)-C(19)-C(18) | 119.73(17) | N(1)-Rh(1)-P(1) | 97.51(4) |
| C(20)-C(19)-H(19) | 120.1 | C(34)-Rh(1)-H(1) | 83.8(9) |

| | | | |
|---|---|---|---|
| C(18)-C(19)-H(19) | 120.1 | N(5)-Rh(1)-H(1) | 92.1(8) |
| C(19)-C(20)-C(21) | 120.45(17) | N(3)-Rh(1)-H(1) | 87.8(9) |
| C(19)-C(20)-H(20) | 119.8 | N(1)-Rh(1)-H(1) | 174.1(8) |
| C(21)-C(20)-H(20) | 119.8 | P(1)-Rh(1)-H(1) | 88.1(8) |
| C(16)-C(21)-C(20) | 120.40(17) | N(2)-B(1)-N(4) | 109.69(14) |
| C(16)-C(21)-H(21) | 119.8 | N(2)-B(1)-N(6) | 110.01(14) |
| C(20)-C(21)-H(21) | 119.8 | N(4)-B(1)-N(6) | 107.54(14) |
| C(27)-C(22)-C(23) | 118.48(16) | N(2)-B(1)-H(2) | 111.2(10) |
| C(27)-C(22)-P(1) | 122.53(13) | N(4)-B(1)-H(2) | 109.8(10) |
| C(23)-C(22)-P(1) | 118.97(13) | N(6)-B(1)-H(2) | 108.5(10) |
| C(24)-C(23)-C(22) | 120.63(18) | C(16)-P(1)-C(22) | 104.94(8) |
| C(24)-C(23)-H(23) | 119.7 | C(16)-P(1)-C(28) | 102.88(8) |
| C(22)-C(23)-H(23) | 119.7 | C(22)-P(1)-C(28) | 98.75(8) |
| C(25)-C(24)-C(23) | 120.06(19) | C(16)-P(1)-Rh(1) | 109.33(6) |
| C(25)-C(24)-H(24) | 120 | C(22)-P(1)-Rh(1) | 118.96(6) |
| C(23)-C(24)-H(24) | 120 | C(28)-P(1)-Rh(1) | 119.92(5) |

**Table 4. Anisotropic Displacement Parameters (Å x $10^3$)**

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|------|------|------|------|------|------|------|
| C(1) | 21(1) | 27(1) | 29(1) | 2(1) | -4(1) | -5(1) |
| C(2) | 18(1) | 16(1) | 28(1) | 1(1) | -2(1) | -2(1) |
| C(3) | 18(1) | 24(1) | 32(1) | 2(1) | 3(1) | -1(1) |
| C(4) | 22(1) | 19(1) | 27(1) | 1(1) | 5(1) | 1(1) |
| C(5) | 30(1) | 37(1) | 27(1) | 0(1) | 9(1) | 1(1) |
| C(6) | 22(1) | 24(1) | 33(1) | -2(1) | -1(1) | -5(1) |
| C(7) | 19(1) | 20(1) | 28(1) | -4(1) | -4(1) | 1(1) |
| C(8) | 26(1) | 30(1) | 29(1) | -10(1) | -4(1) | -5(1) |
| C(9) | 24(1) | 31(1) | 24(1) | -8(1) | -5(1) | -1(1) |
| C(10) | 40(1) | 54(1) | 26(1) | -13(1) | 1(1) | -11(1) |
| C(11) | 26(1) | 27(1) | 32(1) | -4(1) | 0(1) | 6(1) |
| C(12) | 19(1) | 19(1) | 30(1) | -2(1) | -3(1) | 0(1) |
| C(13) | 25(1) | 19(1) | 38(1) | 3(1) | -5(1) | 3(1) |
| C(14) | 22(1) | 21(1) | 30(1) | 7(1) | -6(1) | -2(1) |
| C(15) | 39(1) | 34(1) | 33(1) | 13(1) | -5(1) | 3(1) |
| C(16) | 17(1) | 19(1) | 24(1) | -1(1) | 0(1) | 2(1) |
| C(17) | 24(1) | 20(1) | 25(1) | 0(1) | 1(1) | -1(1) |
| C(18) | 32(1) | 32(1) | 25(1) | -6(1) | 4(1) | 1(1) |
| C(19) | 37(1) | 28(1) | 33(1) | -12(1) | -1(1) | 3(1) |
| C(20) | 31(1) | 20(1) | 42(1) | -6(1) | -1(1) | -3(1) |
| C(21) | 24(1) | 21(1) | 32(1) | 0(1) | 3(1) | -2(1) |
| C(22) | 21(1) | 22(1) | 20(1) | 2(1) | 2(1) | -3(1) |
| C(23) | 24(1) | 31(1) | 35(1) | 11(1) | 7(1) | 3(1) |
| C(24) | 35(1) | 35(1) | 38(1) | 16(1) | 4(1) | -3(1) |
| C(25) | 32(1) | 43(1) | 26(1) | 7(1) | 7(1) | -11(1) |
| C(26) | 24(1) | 47(1) | 29(1) | 3(1) | 8(1) | 0(1) |
| C(27) | 25(1) | 31(1) | 23(1) | 3(1) | 3(1) | 2(1) |
| C(28) | 18(1) | 19(1) | 22(1) | 5(1) | -1(1) | -1(1) |
| C(29) | 21(1) | 22(1) | 29(1) | 2(1) | 0(1) | -1(1) |
| C(30) | 20(1) | 28(1) | 39(1) | 5(1) | -1(1) | 3(1) |
| C(31) | 24(1) | 38(1) | 35(1) | 12(1) | -9(1) | -2(1) |
| C(32) | 31(1) | 35(1) | 24(1) | 3(1) | -6(1) | -4(1) |
| C(33) | 25(1) | 27(1) | 23(1) | 2(1) | 0(1) | 0(1) |
| C(34) | 18(1) | 18(1) | 21(1) | 1(1) | -1(1) | 0(1) |
| C(35) | 23(1) | 22(1) | 25(1) | -2(1) | -1(1) | 0(1) |
| C(36) | 25(1) | 23(1) | 19(1) | 0(1) | 1(1) | -4(1) |
| C(37) | 37(1) | 45(1) | 28(1) | -1(1) | -11(1) | -5(1) |
| C(38) | 47(1) | 38(1) | 20(1) | -6(1) | 0(1) | -15(1) |
| C(39) | 42(1) | 29(1) | 29(1) | -8(1) | 8(1) | -4(1) |
| C(40) | 28(1) | 27(1) | 24(1) | -3(1) | 1(1) | -1(1) |
| N(1) | 18(1) | 20(1) | 19(1) | 1(1) | -1(1) | -1(1) |
| N(2) | 20(1) | 20(1) | 19(1) | 1(1) | 1(1) | -1(1) |

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|---|---|---|---|---|---|---|
| N(3) | 18(1) | 18(1) | 20(1) | -1(1) | -2(1) | -1(1) |
| N(4) | 21(1) | 23(1) | 19(1) | -2(1) | -2(1) | -1(1) |
| N(5) | 19(1) | 19(1) | 20(1) | 0(1) | -1(1) | 0(1) |
| N(6) | 19(1) | 21(1) | 21(1) | 3(1) | -2(1) | -1(1) |
| N(7) | 31(1) | 34(1) | 29(1) | -4(1) | -7(1) | 2(1) |
| Rh(1) | 14(1) | 14(1) | 16(1) | -1(1) | -1(1) | -1(1) |
| B(1) | 21(1) | 23(1) | 20(1) | 1(1) | -2(1) | 0(1) |
| P(1) | 16(1) | 16(1) | 18(1) | 0(1) | 2(1) | 0(1) |

# Table 5. Torsional Angles (°)

| Atoms | Angle | Atoms | Angle |
|---|---|---|---|
| N(1)-C(2)-C(3)-C(4) | -1.04(19) | Rh(1)-N(5)-N(6)-C(14) | -174.44(11) |
| C(1)-C(2)-C(3)-C(4) | 175.87(16) | C(12)-N(5)-N(6)-B(1) | 176.02(14) |
| C(2)-C(3)-C(4)-N(2) | -0.43(19) | Rh(1)-N(5)-N(6)-B(1) | 1.37(18) |
| C(2)-C(3)-C(4)-C(5) | 177.82(18) | C(38)-C(37)-N(7)-C(36) | -0.1(3) |
| N(3)-C(7)-C(8)-C(9) | 1.3(2) | C(40)-C(36)-N(7)-C(37) | 2.0(3) |
| C(6)-C(7)-C(8)-C(9) | -174.33(17) | C(35)-C(36)-N(7)-C(37) | -175.23(17) |
| C(7)-C(8)-C(9)-N(4) | 0.0(2) | C(35)-C(34)-Rh(1)-N(5) | -85(2) |
| C(7)-C(8)-C(9)-C(10) | -179.5(2) | C(35)-C(34)-Rh(1)-N(3) | -14(3) |
| N(5)-C(12)-C(13)-C(14) | 0.0(2) | C(35)-C(34)-Rh(1)-N(1) | -168(2) |
| C(11)-C(12)-C(13)-C(14) | 179.58(17) | C(35)-C(34)-Rh(1)-P(1) | 95(2) |
| C(12)-C(13)-C(14)-N(6) | 0.1(2) | C(12)-N(5)-Rh(1)-C(34) | 45.16(17) |
| C(12)-C(13)-C(14)-C(15) | -179.57(18) | N(6)-N(5)-Rh(1)-C(34) | -142.20(11) |
| C(21)-C(16)-C(17)-C(18) | 0.3(3) | C(12)-N(5)-Rh(1)-N(3) | -126.27(17) |
| P(1)-C(16)-C(17)-C(18) | 177.40(14) | N(6)-N(5)-Rh(1)-N(3) | 46.37(11) |
| C(16)-C(17)-C(18)-C(19) | -0.7(3) | C(12)-N(5)-Rh(1)-N(1) | 139.12(17) |
| C(17)-C(18)-C(19)-C(20) | 0.4(3) | N(6)-N(5)-Rh(1)-N(1) | -48.24(11) |
| C(18)-C(19)-C(20)-C(21) | 0.3(3) | C(12)-N(5)-Rh(1)-P(1) | -131.1(6) |
| C(17)-C(16)-C(21)-C(20) | 0.4(3) | N(6)-N(5)-Rh(1)-P(1) | 41.6(7) |
| P(1)-C(16)-C(21)-C(20) | -176.52(14) | C(7)-N(3)-Rh(1)-C(34) | 53.6(4) |
| C(19)-C(20)-C(21)-C(16) | -0.7(3) | N(4)-N(3)-Rh(1)-C(34) | -130.0(4) |
| C(27)-C(22)-C(23)-C(24) | -2.1(3) | C(7)-N(3)-Rh(1)-N(5) | 125.56(16) |
| P(1)-C(22)-C(23)-C(24) | 176.69(16) | N(4)-N(3)-Rh(1)-N(5) | -58.09(11) |
| C(22)-C(23)-C(24)-C(25) | 0.7(3) | C(7)-N(3)-Rh(1)-N(1) | -152.55(16) |
| C(23)-C(24)-C(25)-C(26) | 0.8(3) | N(4)-N(3)-Rh(1)-N(1) | 23.81(12) |
| C(24)-C(25)-C(26)-C(27) | -1.0(3) | C(7)-N(3)-Rh(1)-P(1) | -54.75(16) |
| C(23)-C(22)-C(27)-C(26) | 1.9(3) | N(4)-N(3)-Rh(1)-P(1) | 121.61(11) |
| P(1)-C(22)-C(27)-C(26) | -176.85(15) | C(2)-N(1)-Rh(1)-C(34) | -39.85(18) |
| C(25)-C(26)-C(27)-C(22) | -0.3(3) | N(2)-N(1)-Rh(1)-C(34) | 153.51(11) |
| C(33)-C(28)-C(29)-C(30) | 0.4(2) | C(2)-N(1)-Rh(1)-N(5) | -134.16(18) |
| P(1)-C(28)-C(29)-C(30) | 176.73(13) | N(2)-N(1)-Rh(1)-N(5) | 59.20(11) |
| C(28)-C(29)-C(30)-C(31) | 0.5(3) | C(2)-N(1)-Rh(1)-N(3) | 144.10(17) |
| C(29)-C(30)-C(31)-C(32) | -0.8(3) | N(2)-N(1)-Rh(1)-N(3) | -22.54(11) |
| C(30)-C(31)-C(32)-C(33) | 0.1(3) | C(2)-N(1)-Rh(1)-P(1) | 49.46(17) |
| C(31)-C(32)-C(33)-C(28) | 0.8(3) | N(2)-N(1)-Rh(1)-P(1) | -117.18(10) |
| C(29)-C(28)-C(33)-C(32) | -1.0(3) | C(4)-N(2)-B(1)-N(4) | -116.39(18) |
| P(1)-C(28)-C(33)-C(32) | -177.50(14) | N(1)-N(2)-B(1)-N(4) | 73.77(18) |
| Rh(1)-C(34)-C(35)-C(36) | 149.7(18) | C(4)-N(2)-B(1)-N(6) | 125.50(17) |
| C(34)-C(35)-C(36)-N(7) | 75(2) | N(1)-N(2)-B(1)-N(6) | -44.33(19) |
| C(34)-C(35)-C(36)-C(40) | -103(2) | C(9)-N(4)-B(1)-N(2) | 123.19(19) |
| N(7)-C(37)-C(38)-C(39) | -1.4(3) | N(3)-N(4)-B(1)-N(2) | -71.92(18) |
| C(37)-C(38)-C(39)-C(40) | 0.9(3) | C(9)-N(4)-B(1)-N(6) | -117.19(19) |
| C(38)-C(39)-C(40)-C(36) | 0.8(3) | N(3)-N(4)-B(1)-N(6) | 47.71(19) |

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|---|---|---|---|
| N(7)-C(36)-C(40)-C(39) | -2.4(3) | C(14)-N(6)-B(1)-N(2) | -126.28(17) |
| C(35)-C(36)-C(40)-C(39) | 174.74(17) | N(5)-N(6)-B(1)-N(2) | 58.82(19) |
| C(3)-C(2)-N(1)-N(2) | 2.05(18) | C(14)-N(6)-B(1)-N(4) | 114.30(18) |
| C(1)-C(2)-N(1)-N(2) | -175.01(15) | N(5)-N(6)-B(1)-N(4) | -60.59(19) |
| C(3)-C(2)-N(1)-Rh(1) | -165.22(13) | C(21)-C(16)-P(1)-C(22) | -1.79(17) |
| C(1)-C(2)-N(1)-Rh(1) | 17.7(3) | C(17)-C(16)-P(1)-C(22) | -178.73(13) |
| C(3)-C(4)-N(2)-N(1) | 1.72(19) | C(21)-C(16)-P(1)-C(28) | -104.65(15) |
| C(5)-C(4)-N(2)-N(1) | -176.69(16) | C(17)-C(16)-P(1)-C(28) | 78.41(14) |
| C(3)-C(4)-N(2)-B(1) | -168.91(16) | C(21)-C(16)-P(1)-Rh(1) | 126.86(14) |
| C(5)-C(4)-N(2)-B(1) | 12.7(3) | C(17)-C(16)-P(1)-Rh(1) | -50.08(14) |
| C(2)-N(1)-N(2)-C(4) | -2.35(18) | C(27)-C(22)-P(1)-C(16) | 116.69(16) |
| Rh(1)-N(1)-N(2)-C(4) | 168.64(10) | C(23)-C(22)-P(1)-C(16) | -62.02(16) |
| C(2)-N(1)-N(2)-B(1) | 169.24(14) | C(27)-C(22)-P(1)-C(28) | -137.38(15) |
| Rh(1)-N(1)-N(2)-B(1) | -19.78(17) | C(23)-C(22)-P(1)-C(28) | 43.91(16) |
| C(8)-C(7)-N(3)-N(4) | -2.15(19) | C(27)-C(22)-P(1)-Rh(1) | -5.93(17) |
| C(6)-C(7)-N(3)-N(4) | 173.80(15) | C(23)-C(22)-P(1)-Rh(1) | 175.35(13) |
| C(8)-C(7)-N(3)-Rh(1) | 174.50(13) | C(29)-C(28)-P(1)-C(16) | -10.51(16) |
| C(6)-C(7)-N(3)-Rh(1) | -9.5(3) | C(33)-C(28)-P(1)-C(16) | 165.86(13) |
| C(8)-C(9)-N(4)-N(3) | -1.4(2) | C(29)-C(28)-P(1)-C(22) | -118.13(14) |
| C(10)-C(9)-N(4)-N(3) | 178.16(17) | C(33)-C(28)-P(1)-C(22) | 58.24(14) |
| C(8)-C(9)-N(4)-B(1) | 164.43(17) | C(29)-C(28)-P(1)-Rh(1) | 111.04(13) |
| C(10)-C(9)-N(4)-B(1) | -16.0(3) | C(33)-C(28)-P(1)-Rh(1) | -72.59(14) |
| C(7)-N(3)-N(4)-C(9) | 2.20(18) | C(34)-Rh(1)-P(1)-C(16) | 167.32(7) |
| Rh(1)-N(3)-N(4)-C(9) | -175.10(11) | N(5)-Rh(1)-P(1)-C(16) | -16.4(6) |
| C(7)-N(3)-N(4)-B(1) | -165.56(14) | N(3)-Rh(1)-P(1)-C(16) | -21.20(7) |
| Rh(1)-N(3)-N(4)-B(1) | 17.14(18) | N(1)-Rh(1)-P(1)-C(16) | 72.91(7) |
| C(13)-C(12)-N(5)-N(6) | -0.13(18) | C(34)-Rh(1)-P(1)-C(22) | -72.26(8) |
| C(11)-C(12)-N(5)-N(6) | -179.74(15) | N(5)-Rh(1)-P(1)-C(22) | 104.0(6) |
| C(13)-C(12)-N(5)-Rh(1) | 172.94(12) | N(3)-Rh(1)-P(1)-C(22) | 99.22(7) |
| C(11)-C(12)-N(5)-Rh(1) | -6.7(3) | N(1)-Rh(1)-P(1)-C(22) | -166.68(7) |
| C(13)-C(14)-N(6)-N(5) | -0.22(19) | C(34)-Rh(1)-P(1)-C(28) | 49.01(8) |
| C(15)-C(14)-N(6)-N(5) | 179.51(16) | N(5)-Rh(1)-P(1)-C(28) | -134.7(6) |
| C(13)-C(14)-N(6)-B(1) | -175.65(16) | N(3)-Rh(1)-P(1)-C(28) | -139.51(7) |
| C(15)-C(14)-N(6)-B(1) | 4.1(3) | N(1)-Rh(1)-P(1)-C(28) | -45.41(7) |
| C(12)-N(5)-N(6)-C(14) | 0.21(18) | Rh(1)-N(5)-N(6)-C(14) | -174.44(11) |