TRANSTION METAL MEDIATED CARBON-HETEROATOM AND CARBON-CARBON BOND FORMATION: STUDIES IN MULTICOMPONENT COUPLING REACTIONS AND RING-CLOSING METATHESIS

by

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$Pd(PPh_3)_4$ catalytically assembles sulfenamide ($PhS\text{-}NR_2$), alkyne, carbon monoxide and diphenyl diselenide in a one-pot four component coupling reaction to yield (Z)-β-selenyl acrylamides. The reaction proceeds in good to excellent yield (60-95%) and is tolerant of a wide range of functional groups on both the nitrogen of the sulfenamide and the alkyne. Moderate selectivities ranging from 4:1 to 7:1 β-selenyl to β-sulfenyl acrylamide have been observed despite the initial concentration of 2:1 selenium to sulfur in the reaction. The chalcogeno selectivity was found to depend directly on CO pressure; increased CO pressure decreased selectivity for selenium over sulfur.

The azaselenolation of carbon monoxide by sulfenamide is catalyzed by $RhCl(CO)(PPh_3)_2$ to give Se-aryl selenocarbamates. The reaction proceeds in moderate to good yield (71-89%) and exhibits a 9:1 selectivity for the formation of seleno- over thiocarbamate despite the initial 1.4:1 concentration of selenium to sulfur in the reaction. Selectivity is postulated to arise from the more favorable oxidative addition of diphenyl diselenide to rhodium relative to diphenyl disulfide. Also discussed is the effect of several transition metal complexes on the yield and selectivity of the azaselenolation

reaction and our attempts to develop a transition metal catalyzed olefin azasulfenylation reaction.

Imine-olefin ring-closing metathesis of α,ω imino-olefins with Schrock-type alkylidene complexes, $Mo(=CHR)(=NAr)(OR')_2$ is discussed. Ring-closing proceeded to yield the target substrate 2H-chromene in 63% yield. Mechanistically, it was determined that the reaction operates under kinetic control via initial alkylidene-olefin metathesis followed by ring-closing alkylidene-imine metathesis.

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SYMBOLS AND ABBREVIATIONS

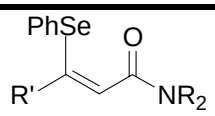
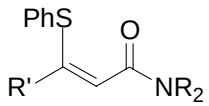
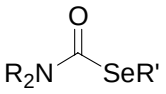
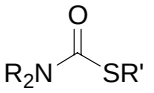
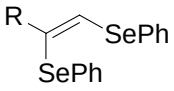
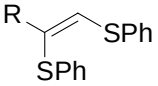
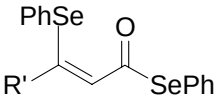
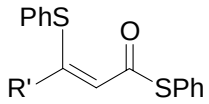
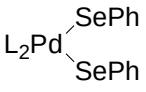
ac	acetylacetonato
ADMET	acyclic diene metathesis
ARCM	asymmetric ring-closing metathesis
Bn	benzyl
Bz	benzene
br	broad (NMR signal)
Bu^n	*n*-butyl
Bu^t	tertiary butyl
°C	degrees Celcius
COD	cyclooctadiene
Cp	cyclopentadienyl
Cp^*	pentamethyl cyclopentadienyl
Cy	cyclohexyl
d	doublet (NMR signal)
dd	doublet of doublets (NMR signal)
dt	doublet of triplets (NMR signal)
dba	dibenzylideneacetone

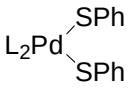
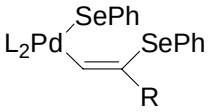
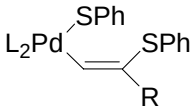
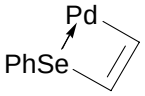
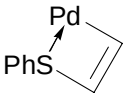
dtd	doublet of triplets of doublets (NMR signal)
dppf	diphosphinoferrocene
EI	electron ionization
Et	ethyl
FT-IR	Fourier transform infra-red
δ	chemical shift
g	gram
GC	gas chromatography
GC/MS	gas chromatography/mass spectroscopy
h	hour
HRMS	high resolution mass spectroscopy
hpt	heptet (NMR signal)
Hz	hertz
^{i}Pr	isopropyl
J	coupling constant (NMR signal)
K	Kelvin
L	ligand

m	multiplet (NMR signal)
MAO	methyl aluminum oxide
mg	milligram
MHz	megahertz
min	minutes
mL	milliliter
mmol	millimole
m/z	mass/charge
Me	methyl
noe	nuclear Overhauser effect
Ph	phenyl
p	para
ppm	parts per million (NMR signal)
Pr	propyl
pyr	pyridine
q	quartet (NMR signal)
RCM	ring-closing metathesis

ROM	ring-opening metathesis
ROMP	ring-opening metathesis polymerization
RT	room temperature
s	singlet (NMR signal)
t	triplet (NMR signal)
TMS	trimethylsilyl
tol	toluene
Ts	tosyl
μmol	micromole

NOMENCLATURE FOR SELENIUM AND SULFUR CONTAINING COMPOUNDS

Name	Structure
(*Z*)-β-selenyl acrylamide	
(*Z*)-β-sulfenyl acrylamide	
selenocarbamate	
thiocarbamate	
(*Z*)-1,2-bis(arylseleno)-1-alkene	
(*Z*)-1,2-bis(arylthio)-1-alkene	
(*Z*)-1,3-bis(arylseleno)-2-alken-1-one	
(*Z*)-1,3-bis(arylthio)-2-alken-1-one	
Pd (II) diselenolate	

Pd (II) dithiolate	
vinyl palladium selenolate	
vinyl palladium thiolate	
palladium selenoether	
palladium sulfidoether	

PREFACE

“Only a ditch digger starts on top.”
Unknown.

I have so many people that I would like to thank for helping me through these last five years of graduate school. I am afraid though that I can’t thank everyone as I just don’t have the space. If I left you off my list, you have my sincerest apologies. First and foremost I must thank my advisor Tara Meyer for being so patient with me and my somewhat independent spirit. I can not recall a time when Dr. Meyer wouldn’t sit down with me to discuss chemistry or just plain old science. She has always provided me with guidance and advice and for that I am eternally grateful.

A supporting and loving family is a blessing that I have had the fortune to enjoy. My mother and father have always been there when I needed them the most. They are the ones who taught me what it means to respect yourself, your profession and to work hard. In the words of my father, “If you aren’t going to do it right, then don’t do it all.” I have lived by this mantra my whole life, so thanks Dad. To my brother the engineer, thanks for the beers at Ryans and for keeping my head straight as to what really matters most in life.

The supporting cast at the University of Pittsburgh is fantastic. I would like to thank Dr. Fu-Tyan Lin and his wife for teaching me the often frustrating art of NMR spectroscopy and Dr. Kasi Somayajula for always fixing the GC-MS. The office staff has always been very helpful especially Fran Nagy who without I feel the department doings would grind to halt. Dr. George Bandik, thanks for always being a friendly ear to my problems.

Where would I be without the cast and crew of the Meyer group? I will really miss catching football on the fifth floor and venturing into Oakland for lunch or a beer. Jim, Kenny, Ryan, Robbyn, Doreen, Rachel, Steve, Matt, Pat, Jo-Jo, Carol and Ona thanks for putting up with me and the often horrible smells emanating from my hood. I should also thank my good friends Bird, Chuck, Mnion, Jason, Kurtis P. and Megan for the many good time together.

Thank you Professors Chapman, Petoud and d'Itri for serving on my dissertation defense committee. A final and special thanks to the late Dr. Shepard for serving on my Comprehensive Exam Committee and for teaching me so much.

Daniel Jason Knapton

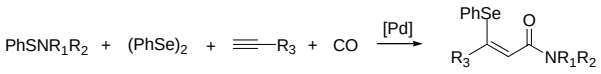
CHAPTER 1. A PALLADIUM CATALYZED REGIO- AND STEREOSELECTIVE FOUR COMPONENT COUPLING REACTION.

1.1. Introduction.

The development of one-pot multi-component coupling reactions has provided a rapid and elegant means for the preparation of complex molecular architectures from simple and diverse building blocks.[1-3] The attraction to the synthetic chemist lies in the multitude of advantages that include higher yields than almost any sequential synthesis to the same target, a single purification step, and easy adaptation to combinatorial synthetic schemes.[4-6] Well-known examples include the Ugi 4-component reaction,[7] as well as the Hantzch,[8] Biginelli,[9] Mannich,[10] Passerini,[11] and Bucherer-Bergs[12] 3-component reactions. These assembly processes have several common aspects that enhance their utility: 1) high selectivity for the synthesis of one isomeric form of a single product; 2) tolerance of structural diversity on one or more of the reagents; 3) the formation of at least one C-C bond.

We have developed a new palladium mediated 4-component coupling reaction for the synthesis of β-selenyl acrylamides (Scheme 1).[13a,b] This reaction satisfies the above mentioned criteria in that it produces high yields of a single regio- and stereoisomer; there is considerable diversity available in both the alkyne and sulfenamide ($PhS\text{-}NR_2$) reagents; and one C-C bond, as well as two C-heteroatom bonds (C-N, C-Se), are formed. In addition, the reaction yields a product with two reactive functionalities available for subsequent modification: an α,β-

unsaturated amide and a vinylic pseudohalide group, PhSe-.[14] It should be noted that few multi-component couplings give products with more than one reactive functionality and, although metal-catalyzed multi-component coupling reactions[1,2,15] are well known, they are generally limited to 3-components with the corresponding 4-component reactions[16] being far more rare.



Scheme 1. The preparation of β-selenyl acrylamides

An unusual pair of heteroatom delivery agents are used in our system, PhS-NR_2 and $(PhSe)_2$. Sulfenamides represent an alternative to the traditional NR_2 delivery agents, namely amines and silylamines. Despite the need for their preparation, sulfenamides are easily synthesized in one step from commercially available starting materials, and neither they nor their starting materials are noxious.[17] Although not commonly encountered, sulfenamides have found some synthetic utility. For example, Kuniyasu and coworkers found them to be quite useful in the production of thiocarbamates in the palladium catalyzed azathiolation of carbon monoxide,[18a] and more recently, Kondo and coworkers have prepared polyfunctionalized alkenes via the ruthenium mediated addition of sulfenamides to alkynes.[18b] In addition, a specific class of sulfenamide, 4'-nitrobenzenesulfenanalide (NBSA), has been found to be an effective reagent for the amidino- and amido-sulphenylation,[19] aminosulfenylation[20,21] and bromosulfenylation[22] of alkenes. The introduction of the PhSe group is more highly precedented using the easily handled $(PhSe)_2$.[23] The PhSe-SePh bond is easily cleaved by palladium, and it is known that Pd-SePh groups are

capable of migratory insertion, a key reaction in our system.[15h] It is important to note that the reactions mixtures do not contain significant quantities of thiols or selenols, and therefore, are not particularly odiferous.

No simple or general methodology exists for the synthesis of the β-selenyl acrylamides despite the wealth of knowledge regarding the preparation and reactivity of the corresponding vinyl chalcogenides.[14e, 23, 24] The most common preparation of β-selenyl acrylamides involves the initial synthesis of β-functionalized acrylates from the hydrochalcogenation of pre-formed alkynoic esters. The acrylamide derivatives are then prepared in subsequent steps by simple condensation methods. This approach, though effective, requires several steps and generally involves the use of the noxious chalcogenols.[25]

Recently, new methodology for the preparation of the related β-sulfenyl acrylates and β-telluryl acrylamides has been reported.[26, 27] The former has been prepared via the palladium catalyzed thioesterification alkynes and the later via the photoinduced group transfer radical addition of tellurylcarbamates to aromatic acetylenes. Neither has yet to be extended to include β-selenyl acrylamides. Other less common methods for the preparation of β-chalcogenyl acrylamides exist but are limited by low yield, substrate specificity and α rather than β substitution of the chalcogen.[15e, 25, 28]

1.2. Overview.

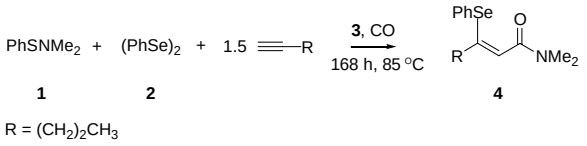
In this chapter we present a full study of the β-selenyl acrylamide forming reaction including reactant generality, mechanism and the selective partitioning of selenium and sulfur in the reaction products. The effect of 2- and 3-component side reactions on the overall formation of

the β-selenyl acrylamides is also considered. Finally, our attempts to extend the reaction methodology to include β-sulfenyl acrylamides is discussed.

1.3. Results and Discussion.

1.3.1. Reaction Optimization.

The reaction of S-phenyl-*N*-dimethyl sulfenamide, $PhSNMe_2$ (**1**), with 1-pentyne, CO and diphenyl diselenide (**2**) was catalyzed by 4.0% $Pd(PPh_3)_4$ (**3**) in benzene at 85 ºC for 168 h to yield the β-selenyl acrylamide (Z)-3-phenylselenyl-hex-2-enoic acid dimethylamide (**4**) in 84% isolated yield based on sulfenamide (Scheme 2). As previously reported,[13a] the reaction proceeded with 100% regiospecificity for placing selenium in the β-position and 100% stereoselectivity for yielding only the Z isomer as determined by both ^1H NMR and noe difference spectroscopy.



Scheme 2. The preparation of acrylamide **4**

Optimization experiments were carried out to determine the ideal catalyst and solvent system for the reaction. For aliphatic alkynes, $Pd(PPh_3)_4$ was identified as the only active catalyst as Pd_2dba_3, $(dppf)_2PdCl_2$, $(PPh_3)_2PdCl_2$, $(AsPh_3)_2PdCl_2$, $Pd(OAc)_2$, $PdCl_2$, $Pt(PPh_3)_4$ and $ClRh(PPh_3)_3$ produced only trace or no β-selenyl acrylamide. Interestingly, for phenyl acetylene, only $(PPh_3)_2PdCl_2$ was found to be active;[29] The use of $Pd(PPh_3)_4$, $(AsPh_3)_2PdCl_2$, $(dppf)_2PdCl_2$, and $((o\text{-}toly)_3P)_2PdCl_2$ resulted in trace or no β-selenyl acrylamide product. Benzene was found to be the solvent of choice, but only a moderate decrease in yield was observed in toluene, acetonitrile and methylene chloride.

The best yields of acrylamide were obtained at 150-170 h of reaction at 80-85 ºC in the presence of 3-5% of palladium with an optimal stoichiometry of one equivalent of sulfenamide and $(PhSe)_2$ to 1.5 equivalents of alkyne. The long reaction times were found to be necessary to obtain the highest yields of β-selenyl acrylamide as, for example, an increase in isolated yield of 55% to 84% was observed upon increasing the reaction time from 68 h to 168 h for the preparation of acrylamide **4**. Attempts to reduce the reaction time by either increasing temperature or CO pressure resulted in a decreased yield of β-selenyl acrylamide with a concomitant increase in undesired by-products.

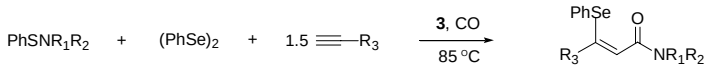
1.3.2. Reaction Generality.

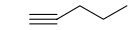
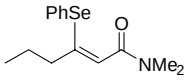
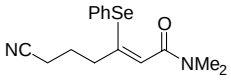
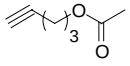
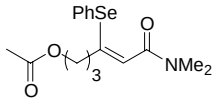
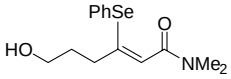
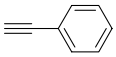
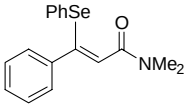
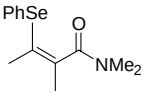
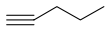
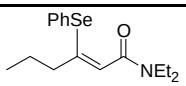
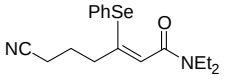
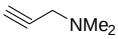
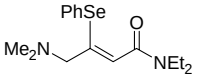
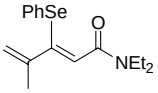
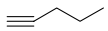
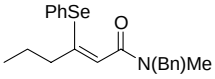
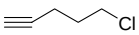
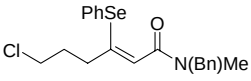
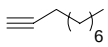
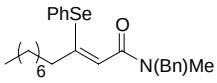
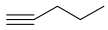
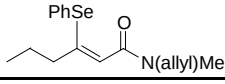
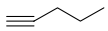
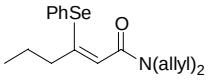
As can be seen in Table 1, the reaction can deliver a variety of NR_2 groups to the product. Both simple dialkyl and allyl functionalized sulfenamides, $PhSNEt_2$ (**5**) and PhSN(allyl)Me (**6**), were found to react with 1-pentyne to give β-selenyl acrylamides in 70% and 82% isolated yields, respectively (entries 7 & 14). An increase in catalyst loading to 8% palladium was necessary for

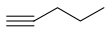
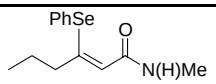
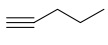
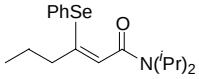
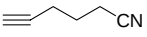
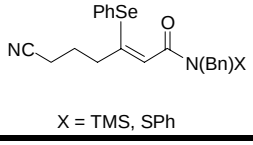
reactions with benzyl and diallyl functionalized sulfenamides, PhSN(Bn)Me (**7**) and $PhSN(allyl)_2$ (**8**), to obtain excellent GC yields of acrylamide, 95% and 85% in the case of 1-pentyne, respectively (entries 11 & 15). *N*-benzyl functionalized sulfenamides can be used with a lower catalyst loading, but such reactions were observed to proceed in lower yields in some cases (entries 12 & 13). Not surprisingly, neither a primary sulfenamide, PhSN(H)Me (**9**), nor a sterically encumbered sulfenamide, $PhSN(^iPr)_2$ (**10**), yielded acrylamide (entries 16 & 17) as both have been reported to be inactive towards the related palladium catalyzed azathiolation of CO.[18] Attempts to prepare a primary β-selenyl acrylamide via TMS protection of a sulfenamide also failed; couplings attempted with PhSN(Bn)TMS (**11)** resulted in a complex mixture of products (entry 18).

With respect to a variety of functionalized alkynes, the reaction proceeded in good to excellent yields (Table 1). Simple aliphatic alkynes such as 1-pentyne and 1-decyne reacted to yield acrylamide as well as alkynes substituted with cyano, halogen, ester, and dialkyl amine functionalities. Internal alkynes as well as hydroxy-substituted alkynes were found to be unreactive (entries 6 & 4). Propargyl alcohols have been reported to undergo intramolecular lactonization under similar conditions but no lactone product was observed upon workup of the reaction involving 5-hydroxy-1-pentyne.[15o] Notably, phenyl acetylene was found to be unreactive for acrylamide formation with catalyst **3** but was partially converted to acrylamide in low yield with $(PPh_3)_2PdCl_2$ (entry 5). In addition, the conjugated alkyne, 3-methyl-butyn-3-ene, was also found to be unreactive under Pd(0) catalysis but was observed in trace quantities under $(PPh_3)_2PdCl_2$ catalysis (entry 10).

Table 1. The palladium catalyzed preparation of β-selenyl acrylamides



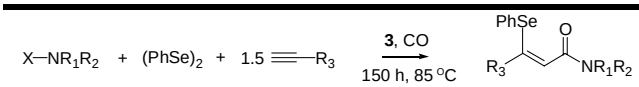
entry	**PhS−NR$_1$R$_2$**	**−R$_3$**	product	compound	yield,%
1	PhS−NMe$_2$			**4**	84
2				**12**	70
3				**13**	72
4				**14**	0
5				**15**	30[a]
6				**16**	0
7	PhS−NEt$_2$			**17**	70
8				**18**	80
9				**19**	85[b]
10				**20**	trace[a]
11	PhS−N(Bn)Me			**21**	95[b,c]
12				**22**	60
13				**23**	60
14	PhS−N(allyl)Me			**24**	82
15	PhS−N(allyl)$_2$			**25**	85[b,c]

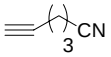
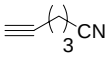
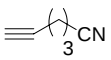
16	PhS−N(Me)H			**26**	0
17	PhS−N(^{i}Pr)$_2$			**27**	0
18	PhS−N(Bn)TMS		 X = TMS, SPh	**28a,b**	trace

a: $(PPh_3)_2PdCl_2$; b: GC yield; c: 8% $Pd(PPh_3)_4$

One of the more surprising aspects of this reaction is that sulfenamide proved to be a better source of the NR_2 group than the more traditional sources, simple amines and silyl amines. Both diethyl amine (**29**) and *N*,*N*-dimethyltrimethylsilylamine (**30**) were found to produce β-selenyl acrylamide under typical reaction conditions but in significantly reduced yields relative to sulfenamide (Table 2).

Table 2. The effect of the NR_2 source on the preparation of β-selenyl acrylamides



entry	**X-NR$_1$R$_2$**	—**R$_3$**	product	yield, %[a]
1	$PhSNEt_2$ **5**		**18**	85
2	$HNEt_2$ **29**		**18**	40
3	$TMSNMe_2$ **30**		**12**	40

a: GC yield

1.3.3. Mechanism.

Coupling the mechanistic work on the reactivity of transition metals with diaryl dichalcogenides published by others with our own observations, it seems reasonable to propose that the formation of β-selenyl acrylamides proceeds according to the following catalytic cycle (Figure 1):[13, 15h, 15o, 18, 30, 31] The loss of phosphine to give a coordinatively unsaturated Pd species is followed by oxidative addition (I) of $(PhSe)_2$ to generate a Pd(II) diselenolate species that stereoselectively inserts alkyne via cis-selenopalladation (II) to yield a vinyl palladium selenolate. Selective CO insertion into the palladium carbon bond (III) gives a transient palladium acyl intermediate which can then react with sulfenamide via σ-bond metathesis (IV)[18] to yield β-selenyl acrylamide and a mixed palladium thiolate selenolate species. The catalyst can then re-enter the cycle either by reductive elimination (V) or by direct insertion of alkyne (VI) into either the Pd-SPh or Pd-SePh bond.

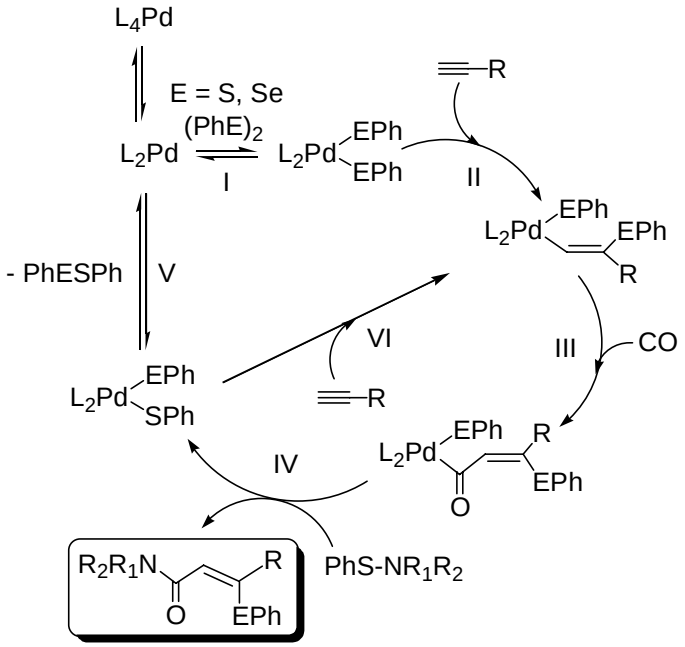
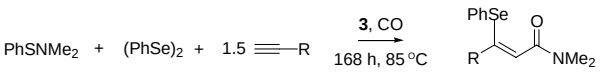


Figure 1. The initially proposed catalytic cycle

As this reaction involves the assembly of 4-components, we were particularly interested in determining the degree to which 2- and 3-component side reactions were contributing to the overall reaction mixture and if any of the resulting byproducts were, in fact, mechanistically relevant. As such, a detailed analysis of the reaction mixture resulting from the preparation of acrylamide **4** was undertaken. Although acrylamide **4** was isolated in 84% yield based on sulfenamide, it was found to comprise only 47.5% of the final reaction mixture. A complete analysis of all products is presented in Table 3. Before discussing the byproducts arising from the 2- and 3-component reactions, it must be emphasized that since, under the reaction conditions, all three diaryl dichalcogenides are present (**2**, **31** and **32**) one might expect that *all* classes of products would be present as both S and Se derivatives. Particularly important to the understanding of the reaction mechanism is not only the presence of the sulfur analog (**33**) of the

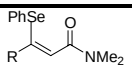
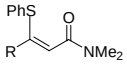
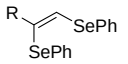
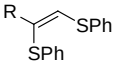
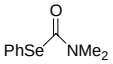
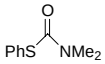
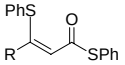
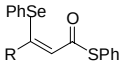
major product **4** but also the relative ratio of these two products. Selectivity is discussed later in the paper.

Table 3. Complete product distribution for the 4-component coupling reaction



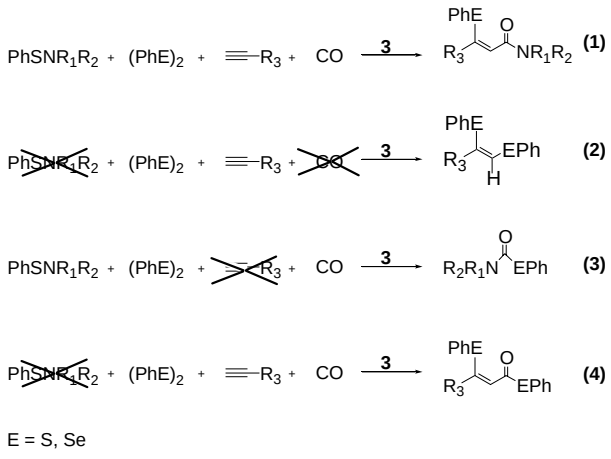
1 **2** **4**

$R = (CH_2)_2CH_3$

PhSe-SePh		PhS-SPh	PhSe-SPh
17.0%	47.5%	0.3%	trace
2	**4**	**31**	**32**
			
6.8%	2.7%	trace	3.4%
33	**34**	**35**	**36**
			SePPh3
0.1%	10.3%	11.1%	trace
37	**38**	**39**	**40**
PhSePh			
trace			
41			

Not surprisingly, evidence was found for the 2- and 3-component side reactions shown in Scheme 3. These reactions have been reported and studied extensively by Kuniyasu, Ogawa, Sonoda and Kurosawa.[15h, 18] By-products **34** and **35** are indicative of simple dichalcogenation of

alkyne (eq 2, Scheme 3). The presence of by-products **36** and **37** is consistent with azaselenolation and azathiolation of CO (eq 3, Scheme 3). The by-products (**38**, **39**) present in the largest quantities are those resulting from the carbonylative addition of the diaryl dichalcogenides to alkyne (eq 4, Scheme 3). Although these two by-products comprise nearly 20% of the reaction mixture, it must be remembered that sulfenamide is the limiting reagent under the optimized reaction conditions and that the reactions described by eq. 2 and 4 will continue to occur after all sulfenamide has been consumed. As a result, compounds **38** and **39** are expected byproducts even in high yielding reactions. Trace selenium triphenyl phosphine (**40**) and diphenyl selenide (**41**) were also observed in the final reaction mixture with the latter most likely arising from the aryl group exchange between phosphine and diphenyl diselenide.[32]

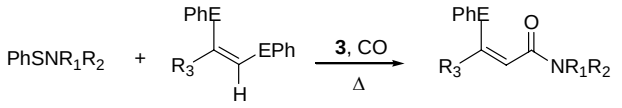


Scheme 3. The competing 3- and 4-component coupling reactions

Given that the 2- and 3-component by-products were present in the reaction mixtures, we thought it important to determine if any of them could be intermediates in the production of the

4-component product. Both selenium and sulfur addition products **34** and **35** were prepared and reacted under 0.5 atm of initial CO pressure with sulfenamide **1** in the presence of catalytic amounts of palladium to determine if the products of dichalcogenation (eq 2, Scheme 3) lay along the reaction pathway towards acrylamide formation. GC analysis of the final reaction mixtures showed no acrylamide products, even in the presence of 50% catalyst **3** (Table 4). It can be concluded then that the formation of addition products like **34** and **35** is essentially irreversible and that they do not contribute to acrylamide formation.

Table 4. The reactivity of the dichalcogenated by-products towards acrylamide formation

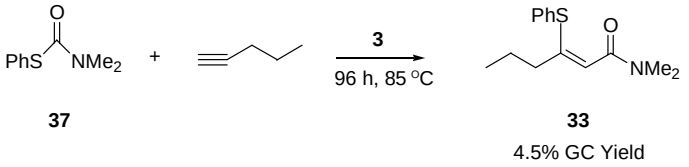


PhSNR$_1$R$_2$	**PhE / R$_3$ / EPh / H**	% Pd	product	yield, %[a]
PhSNMe$_2$	E = Se R$_3$ = (CH$_2$)$_2$CH$_3$	5	**4**	0
1	**34**			
PhSNMe$_2$	E = S R$_3$ = (CH$_2$)$_2$CH$_3$	5	**33**	0
1	**35**			
PhSNEt$_2$	E = Se R$_3$ = (CH$_2$)$_3$CN	50	**18**	0
5	**42**			

a: GC yield

With respect to the reactivity of the 2-component products arising from azathiolation and azaselenolation towards acrylamide formation (Scheme 3, eq. 3), we have found that a small percentage of thiocarbamate **37** can be converted to β-sulfenyl acrylamide **33** upon reaction with

alkyne in the presence of catalytic amounts of catalyst **3** (Scheme 4). Based upon this finding, it seems likely then that selenocarbamate **36** is also active to a small degree for producing β-selenyl acrylamide **4**. The most likely explanation is that the chalcogenocarbamates can oxidatively re-add to palladium, insert alkyne, and reductively eliminate to give the 4-component product. A radical type mechanism similar to the one encountered in the photoinduced preparation of β-telluryl acrylamides can be envisioned but is unlikely based upon the fact that only the *Z* isomer of the 4-component product is produced.[27]

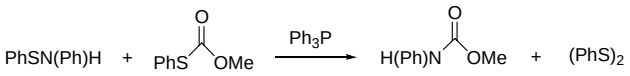


37 **33**

4.5% GC Yield

Scheme 4. The preparation of acrylamide **33** from thiocarbamate

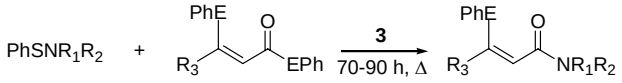
The final class of by-products, those that arise from the carbonylative addition of the dichalcogenides to the alkyne (eq.4, Scheme 3) do appear to have a potentially significant role in the overall 4-component reaction. We suspected that this might be the case based on the previously reported reactivity of sulfenamides with thioesters (Scheme 5).[33]

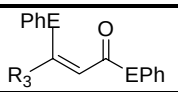


Scheme 5. The reaction of sulfenamide with thioester

Selenium carbonylative addition product (**43**) was prepared and reacted with sulfenamides **1** and **5** in the presence and absence of catalyst **3**. In all cases, complete conversion to the β-selenyl acrylamides **4** and **17** was observed. In addition, the reaction of sulfenamide **5** with the cyano functionalized sulfur carbonylative addition product (**44**) also yielded β-sulfenyl acrylamide (**45**) quantitatively in the absence of catalyst **3** (Table 5). It can be concluded then that the reaction of the carbonylative addition by-products with sulfenamide is facile and a contributing factor to the production of acrylamide in the reaction.

Table 5. The reactivity of the carbonylative addition by-products towards acrylamide formation



PhS-NR$_1$R$_2$		% Pd	product	yield, %[a]
PhSNMe$_2$	E = Se R$_3$ = (CH$_2$)$_2$CH$_3$	4	**4**	100
1	**43**			
PhSNEt$_2$	E = Se R$_3$ = (CH$_2$)$_2$CH$_3$	0	**17**	100
5	**43**			
PhSNEt$_2$	E = S R$_3$ = (CH$_2$)$_3$CN	0	**45**	100
5	**44**			

a: GC yield

Based on these mechanistic studies, we propose the following revision of the catalytic cycle (Figure 2). We have added steps VII and VIII to acknowledge the fact that significant product formation may arise from this alternative pathway. The key factor, which we have not been able

to determine unequivocally, is the relative rates of reductive elimination (VII) of the palladium acyl intermediate vs. the proposed σ-bond metathesis (IV) of sulfenamide with the palladium acyl intermediate. We have chosen not to include the pathway that involves the initial formation of selenocarbamate (eq. 3, Scheme 3) since the low yields obtained under the control conditions (Scheme 4) suggest that this is not a significant pathway in the overall 4-component reaction.

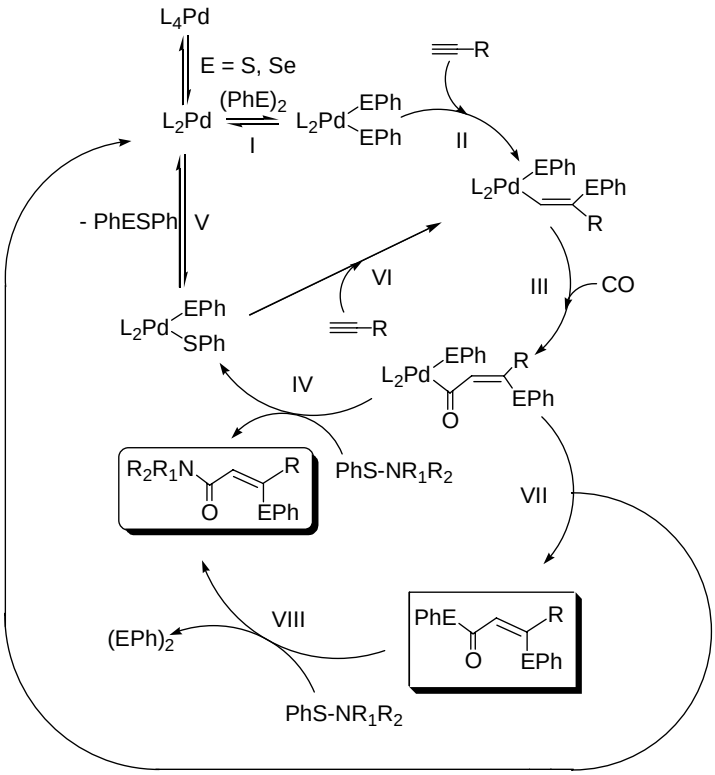


Figure 2. The revised catalytic cycle

1.3.4. Selectivity.

One of the more fascinating aspects of the reaction is the selective formation of β-selenyl acrylamide over β-sulfenyl acrylamide. Analysis of several reaction mixtures arising from the synthesis of β-selenyl acrylamide **4** yielded selectivities ranging from 4:1 to 7:1 selenium to sulfur acrylamide product **33**. Significantly, these observed selectivities were much larger than we expected based upon the initial 2:1 ratio of selenium to sulfur in the reaction mixture.

We have determined that the observed selectivity is *not* due to a difference in the insertion rate of alkyne into the Pd-SePh and Pd-SPh bonds. We had initially suspected this possibility as it would be consistent with our observation that, while the reaction mixture contained the mixed chalcogeno carbonylative addition product **39**, we never observed the reverse substituted regioisomer (**46**) (Figure 3). Such a distribution of products would be expected if alkyne preferentially inserted into Pd-SePh whenever the catalyst bore both SePh and SPh groups.

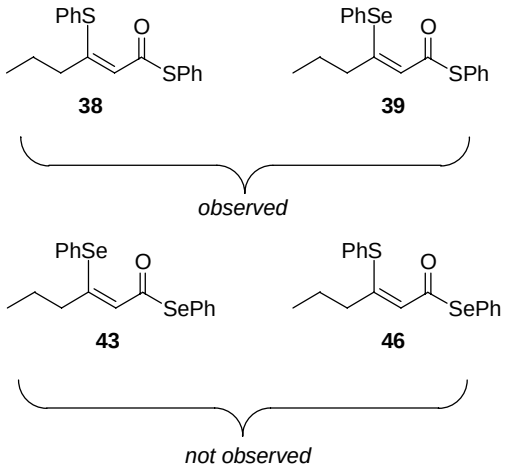
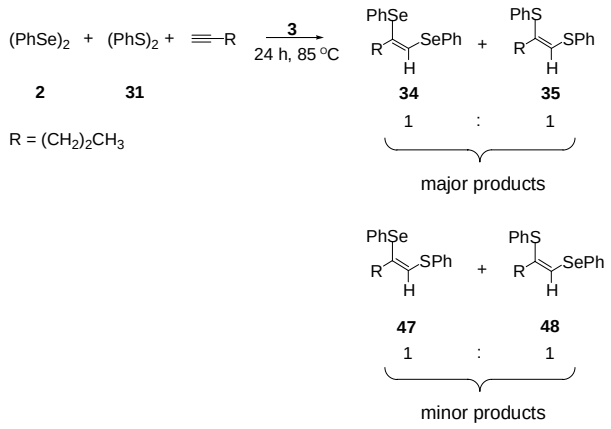


Figure 3. Potential carbonylative addition by-products

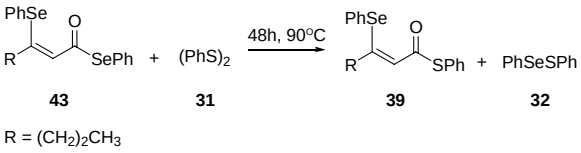
To address this question of selective selenopalladation versus thiopalladation of the alkyne, a competition experiment involving the reaction of stoichiometric amounts of 1-pentyne, $(PhSe)_2$, and $(PhS)_2$ in the presence of catalytic palladium was conducted for one day at 85 ºC. GC analysis of the final reaction mixture showed that the all selenium and sulfur dichalcogenated products, **34** and **35**, were formed in a 1:1 ratio. Small amounts of the mixed selenium and sulfur addition products, (**47**) and (**48**), were also observed, again in a 1:1 ratio. These results strongly indicate that there is no kinetic preference for alkyne insertion into Pd-SePh over Pd-SPh bonds.



Scheme 6. Seleno- vs. thiopalladation

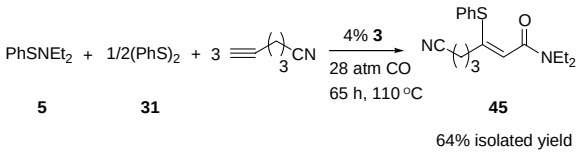
We have identified an alternative explanation for the absence of the mixed carbonylative addition regioisomer **46**. It appears that the selenium carbonylative addition products such as **43** are preferentially converted into their corresponding thioesters in the presence of $(PhS)_2$. For example, the mixed byproduct **39** can be produced in amounts similar to those encountered in the preparation of β-selenyl acrylamide **4** by the simple reaction of $(PhS)_2$ with the selenium carbonylative addition product **43** (Scheme 7). This reaction also explains the absence of

derivative **43**, which to this point was not satisfactorily accounted for based upon our revised mechanistic proposal (Figure 2).



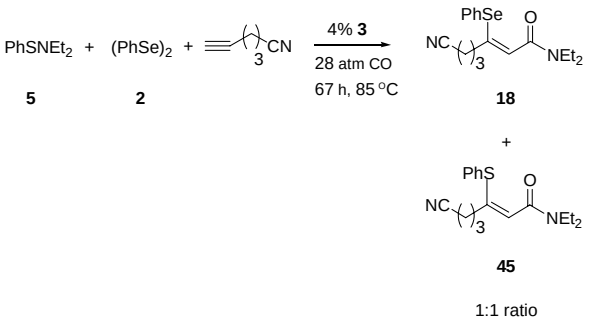
Scheme 7. The preparation of the mixed carbonylative addition regioisomer **39**

An intriguing result relevant to the discussion of selectivity was obtained when attempts were made to extend the methodology to give the related β-sulfenyl acrylamides. Surprisingly, we found that the acrylamide products could not be produced in significant yield by repeating the reactions with added $(PhS)_2$ in place of $(PhSe)_2$. Only upon increasing the initial CO pressure from 0.5 atm to 28 atm and by adding excess alkyne were we able to obtain good yields of β-sulfenyl acrylamide relative to sulfenamide (Scheme 8).



Scheme 8. The high pressure preparation of β-sulfenyl acrylamide **45**

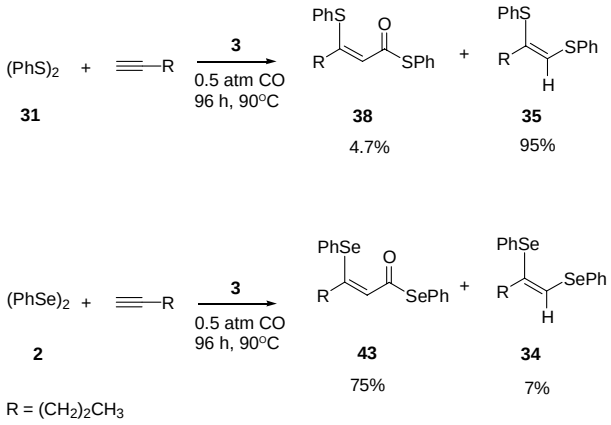
This unexpected difference in reactivity between sulfur and selenium led us to examine the potential effect of CO pressure on acrylamide reaction selectivity. *Increasing the CO pressure in reactions that previously gave at least 4:1 selectivity for β-selenyl acrylamides to β-sulfenyl acrylamides resulted in a complete loss of selectivity* (Scheme 9). Presumably, at this higher pressure, the CO insertion step ceases to be rate determining and, therefore, any inherent rate differences between the Se and S derivatives become irrelevant to product distribution.



Scheme 9. The effect of CO pressure on acrylamide reaction selectivity

It seemed logical to hypothesize that the variation between the sulfur and selenium acrylamide forming reactions at low CO pressure could be due to the differential activity of the chalcogens towards carbonylative addition. This idea was tested further by examining the carbonylative addition of $(PhS)_2$ and $(PhSe)_2$ to 1-pentyne under conditions similar to those of the acrylamide producing reactions (Scheme 10). The carbonylative addition of $(PhS)_2$ to 1-pentyne was found to produce a near quantitative yield of only the simple addition product **35**; only trace amounts of the carbonylative addition product **38** were present. In contrast, the selenium carbonylative addition product **43** was the major product obtained with only small amounts of the addition

product **34** present under the same reaction conditions. It thus appears that the carbonylative addition of $(PhS)_2$ to the alkyne is less favored than the corresponding carbonylative addition of $(PhSe)_2$ at low CO pressure.



Scheme 10. The differential activity of the chalcogens towards carbonylative addition

We believe that the difference in rates likely corresponds to the differences in chelation strengths of the seleno- and sulfidoethers. Selenoethers exhibit much higher binding constants to mid-valent metals than sulfidoethers due both to selenium's lower electronegativity and to its larger, more diffuse valence orbitals. Thus, selenium is more likely to bind to palladium to form a 4-membered and/or a 5-membered-ring chelate than is sulfur (Figure 4).[34] Chelation may facilitate the rate of formation of carbonylated product either by creating a crowded coordination sphere or by inhibiting the deinsertion of CO. In any case, the seleno-favoring effect must be significant, given that the vinyl sulfidoether would ordinarily be expected to be faster at migratory insertion based on simple nucleophilicity arguments. Negative hyperconjugation with

selenium would be expected to more effectively delocalize the negative charge on the anionic vinyl ligand, disfavoring migration to CO relative to the sulfur analog.[35]

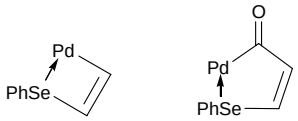
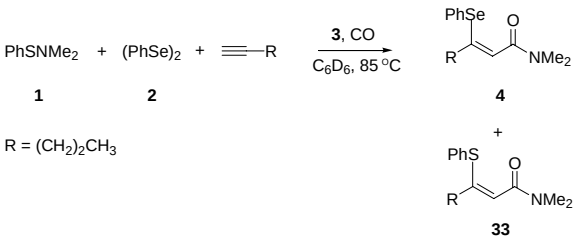


Figure 4. Potential chelation of the vinyl selenoether intermediates

Finally, in addition to the effect of CO pressure on determining reaction selectivity, the concentrations of both $(PhS)_2$ and $(PhSe)_2$ in the reaction mixture should also play an important role as the concentration of $(PhS)_2$ is expected to increase and the concentration of $(PhSe)_2$ expected to decrease with reaction time. To address this effect of chalcogen concentration, a detailed ^1H NMR experiment in which the concentrations of both selenium and sulfur containing acrylamides **4** and **33** were measured as a function of time (Scheme 11). As expected, the best selectivity for the formation of **4** over **33** was observed early in the reaction, but this selectivity was observed to decrease slowly over time as the reaction progressed to consume sulfenamide **1** and consequently produce $(PhS)_2$ and acrylamide **33**.



Scheme 11. The ^{1}H NMR analysis of reaction selectivity

Based then upon our findings, we believe that two major factors contribute to the observed selective formation of β-selenyl acrylamides over β-sulfenyl acrylamides: 1) an initially small concentration of $(PhS)_2$ (or PhS-SePh); 2) the favorable insertion of CO into vinyl β-selenoethers relative to vinyl β-sulfidoethers at low CO pressure.

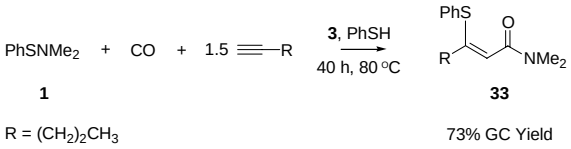
1.4. Miscellaneous Observations: The Preparation of β-Sulfenyl Acrylamides from Thiophenol.

In our investigations regarding the synthesis of β-sulfenyl acrylamides, we have found that such compounds can also be prepared by the simple replacement of $(PhS)_2$ with thiophenol. In contrast to the above mentioned preparations of β-sulfenyl acrylamides using $(PhS)_2$, this reaction proceeds under mild conditions, i.e. low initial CO pressure and short reaction times.

The reaction of one equivalent of both sulfenamide **1** and PhSH (**49**) with 1.5 equivalents of 1-pentyne for 40 h at 80 °C under 0.5 atm of initial CO pressure in the presence of 2.5% catalyst **3** resulted in a 73% GC yield of acrylamide **33** based on sulfenamide **1**. A detailed analysis of the reaction mixture resulting from the preparation of acrylamide **33** was undertaken, and unlike its β-selenyl acrylamide counterpart, a majority, 71.1%, of the final reaction mixture was composed

of acrylamide **33**. A complete analysis of all products is presented in Table 6. Not surprisingly, evidence was found for the 2- and 3-component side reactions (Scheme 3). The presence of by-products **35** and **37** are indicative of simple dithiolation of the alkyne and the azathiolation of CO respectively. As expected, $(PhS)_2$ **31** was also observed as its presence is necessary for the formation of both by-products **35** and **37**. Unlike the prior reactions performed with $(PhS)_2$, we believe we have observed for the first time the formation of the (*E*)-β-sulfenyl acrylamide (**50**).

Table 6. Complete product distribution for the thiophenol based preparation of acrylamide **33**

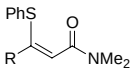
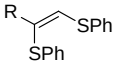
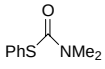
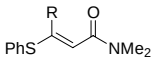


1

R = $(CH_2)_2CH_3$

33

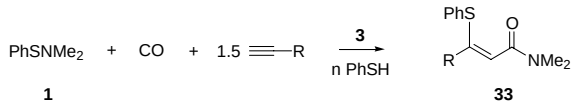
73% GC Yield

PhS-SPh				
1.9%	71.1%	5.7%	7.4%	13.7%
31	**33**	**35**	**37**	**50**

In an attempt to optimize the reaction conditions, temperature, time and the number of equivalents of PhSH **49** were altered, but the yields of acrylamide **33** were not improved (Table 7). We observed that increasing the temperature while decreasing the reaction time produced a poor yield of acrylamide **33** (entry 1). Also, reducing the number of equivalents of PhSH relative

to sulfenamide **1** produced a low yield of acrylamide **33** (entry 2). By increasing the reaction time, a moderate 65% of acrylamide **33** was obtained (entry 3).

Table 7. The thiophenol based preparation of acrylamide **33**



1

33

R = $(CH_2)_2CH_3$

Entry	Eq. PhSH[a]	Time, h	Temperature, °C	% Yield, **33**[b]
1	1	16	90	50
2	0.5	20	90	40
3	1	63	75	65

a: Number of equivalents relative to sulfenamide **1**. b: GC yield.

Based on our own observations coupled with that of Sonoda and co-workers,[15n] we believe that the formation of acrylamide **33** in the presence of PhSH proceeds according to the catalytic cycle shown in Figure 5: The loss of phosphine to give a coordinatively unsaturated Pd species is followed by oxidative addition (A) of PhSH to generate a Pd(II) hydride thiolate species. This then regio- and stereospecifically inserts alkyne via *cis*-thiopalladation (B) to yield a vinyl palladium hydride. It should be noted at this point that *trans*-thiopalladation of the alkyne would result in the formation of the (*E*)-β-sulfenyl acrylamide **50**. Regioselective CO insertion into the palladium carbon bond (C) gives a transient palladium acyl intermediate which can then react with sulfenamide via σ-bond metathesis (D) to yield β-sulfenyl acrylamide and a Pd(II) hydride thiolate species.

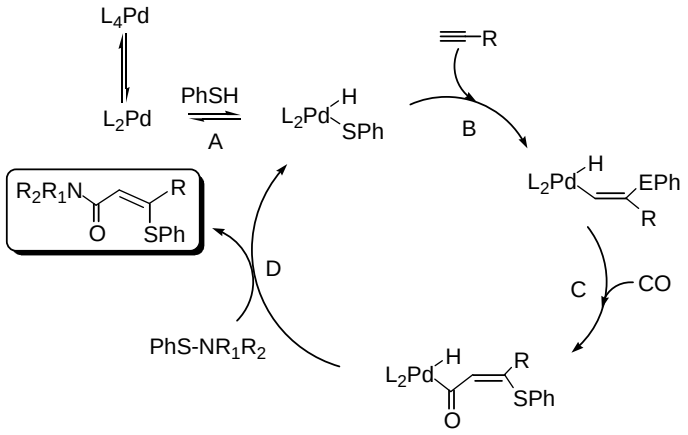


Figure 5. Proposed thioformylation catalytic cycle

In this proposed catalytic cycle, we make no reference to a palladium dithiolate mediated mechanism as we have observed that β-sulfenyl acrylamides can not be produced in significant yields under low CO pressure. Nevertheless, the presence of by-products **35** and **37** do indicate that palladium dithiolate is present in the reaction mixture, and thus, it is likely that some (*Z*)-β-sulfenyl acrylamide is being produced according to a mechanism similar to the one found in Figure 2.

As illustrated in Figure 5, the reaction should be catalytic in PhSH. However, we have observed that reducing the number of equivalents of PhSH decreases the yield of acrylamide **33** (Table 7, entries 1 & 2). This apparent discrepancy in proposed mechanism and observation appears to indicate that PhSH is being removed from the catalytic cycle most likely by its oxidation to $(PhS)_2$. It should be noted that we have neither fully investigated this reaction nor its catalytic cycle as, despite the milder reaction conditions, the use of the noxious PhSH renders it less desirable than our previously stated methods.

1.5. Conclusions.

In conclusion, we have developed a high yielding method for the formation of regio- and stereodefined β-selenyl and β-sulfenyl acrylamides via a palladium catalyzed four-component coupling reaction in which one C-C bond and two carbon-heteroatom bonds are formed. From a synthetic standpoint, the reaction exhibits excellent tolerance for a wide variety of substituents on both the nitrogen of the sulfenamide and alkyne. In addition, the versatility of the chalcogens as pseudo halides coupled with the presence of the α,β-unsaturated amide functionality make the β-chalcogenyl acrylamides synthetically attractive targets.[14]

1.6. Experimental Section.

1.6.1. General Methods.

Benzene, toluene, xylenes and anisole were distilled under nitrogen from sodium. Methylene chloride, acetonitrile, diethlyamine, *N*,*N*-dimethyltrimethylsilylamine and pyridine were distilled under nitrogen from calcium hydride. Amines were purchased and used without further purification. All transition metal catalysts were commercially obtained from Strem and stored in a nitrogen filled glovebox. Carbon monoxide and diphenyl diselenide were purchased and used without further purification. Diphenyl disulfide was recrystallized from methanol and dried at 30 °C under vacuum. Thiophenol was dried over $CaCl_2$ and stored at 0 °C under N_2. Acetylenes were commercially obtained, dried under nitrogen with CaH_2, P_2O_5 or molecular sieves, and

distilled prior to use. ^{1}H-, ^{13}C-NMR, 300 and 75 MHz, respectively, were recorded with Bruker spectrometers. Chemical shifts were referenced to residual ^{1}H or ^{13}C signals in deuterated solvents. Column chromatography was performed using Sorbent 60 32-60 standard grade silica gel and/or activated neutral Brockmann I alumina standard grade gel. Gas chromatography-mass spectrometry (GC/MS) was performed on a Hewlett Packard Series 5980 GC/5971 A MS with a Hewlett Packard Series 1 capillary column. Gas chromatography (GC) was performed on a Hewlett Packard Series 6850 GC with a Hewlett Packard Series 1 methyl siloxane column. IR spectra were obtained on a Perkin Elmer Spectrum BX FT-IR system. High-resolution mass spectra (HRMS) were obtained on a Fison VG Autospec in the Mass Spectral Facility of the University of Pittsburgh. Elemental analysis was performed independently by Desert Analytics, Tucson, Arizona.

1.6.2. The Preparation of Sulfenamides.

General procedure for the preparation of sulfenamides. According to the method of Davis *et al*.,[17] in a 250 mL round bottom flask was placed silver nitrate (780.0 mg, 4.60 mmol) in 70 mL of methanol. After dissolution had taken place, an equivalent of $(PhS)_2$ was added, and the reaction mixture was immediately cooled in an ice bath. Five equivalents of the appropriate amine were added, and the reaction was stirred overnight. The silver mercaptide salt was filtered off, and the solvent removed *in vacuo*. The resulting residue was dissolved in ether, washed with water (4 x 50 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. The sulfenamide was then purified by column chromatography on alumina (5% ethyl acetate/hexanes).

S-Phenyl-*N*-dimethyl-sulfenamide (1): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. To the solution, 11.5 mL of a 2.0 M solution of dimethyl amine in THF (23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **1** (400 mg, 2.60 mmol) in 57% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.53 (s, 6 H), 6.93-7.37 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 48.3, 127.1, 128.8, 129.9, 137.2; MS (EI), *m/z* 153 (M^+), 138, 109, 77, 65.

S-Phenyl-*N*-diethyl-sulfenamide (5): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. Diethylamine (1.2 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **5** (507 mg, 2.80 mmol) in 60% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 1.08 (t, *J = 7.0 Hz*, 6 H), 2.79 (q, *J = 7.0 Hz*, 4 H), 6.92-7.35 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.8, 53.4, 125.0, 125.5, 128.8, 142.1; MS (EI), *m/z* 181 (M^+), 166, 109, 77, 65.

S-Phenyl-*N*-allyl-*N*-methyl-sulfenamide (6): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. *N*-allyl-*N*-methyl

amine (1.6 g, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **6** (519 mg, 2.90 mmol) in 63% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.59 (s, 3), 3.34 (d, *J = 6.4 Hz*, 2 H), 4.98 (m, 2 H), 5.79 (dtd, *J = 10.0, 7.0, 2.4 Hz*, 1 H), 6.93-7.36 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 45.2, 63.3, 117.1, 126.4, 127.6, 128.7, 135.4; MS (EI), *m/z* 179 (M^+), 138, 109, 77, 65.

S-Phenyl-*N*-benzyl-*N*-methyl-sulfenamide (7): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. *N*-benzyl-*N*-methyl amine (3.0 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **7** (209 mg, 2.0 mmol) in 43% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.51 (s, 3 H), 3.87 (s, 2 H), 6.95-7.35 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 45.2, 65.1, 127.0, 128.6, 128.7, 128.9, 138.2, 138.8; MS (EI), *m/z* 229 (M^+), 138, 109, 91, 77, 65.

S-Phenyl-*N*-diallyl-sulfenamide (8): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. *N*-diallyl amine (2.2 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether,

washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **8** (574 mg, 2.80 mmol) in 60% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 3.44 (d, *J = 6.4 Hz*, 4 H), 5.04 (m, 4 H), 5.83 (dtd, *J = 10.5, 6.4, 2.6 Hz*, 2 H), 6.92-7.35 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 60.9, 117.5, 126.1, 128.9, 135.6, 140.6; MS (EI), *m/z* 205 (M^+), 164, 109, 77, 65, 41.

S-Phenyl-*N*-methyl-sulfenamide (9): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. To the solution, 11.5 mL of a 2.0 M solution of *N*-methyl amine in THF (23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **9** (458 mg, 3.30 mmol) in 73% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.24 (br.s, 1 H), 2.42 (d, *J = 17.4 Hz*, 3 H), 6.93-7.35 (m, 5); ^{13}C NMR (75 MHz, C_6D_6) δ 38.4, 123.8, 125.2, 128.8, 129.1, 141.7; MS (EI), *m/z* 139 (M^+), 124, 109, 97, 65.

S-Phenyl-*N*-diisopropyl-sulfenamide (10): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. *N*-diisopropyl amine (3.3 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **10** (668 mg, 3.20 mmol) in 70% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 1.07 (d, *J* =

6.4 Hz, 12 H), 3.12 (hpt, *J = 6.5 Hz*, 2 H), 6.89-7.36 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 21.9, 55.8, 122.1, 124.4, 128.6, 146.4; MS (EI), *m/z* 209 (M^+), 194, 152, 109, 77, 65.

S-Phenyl-*N*-trimethylsilyl-*N*-benzyl-sulfenamide (11): Silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, **31** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. *N*-trimethylsilyl-*N*-benzyl amine (4.6 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **11** (502 mg, 1.80 mmol) in 40% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 0.80 (s, 9 H), 3.55 (s, 2 H), 7.07-7.19 (m, 10 H). MS (EI), *m/z* 215 (M^+- TMS), 109, 91 (base), 77, 65, 51.

1.6.3. The Preparation of the (Z)-1,2-Bis(Arylchalcogeno)-1-Alkenes.

General procedure for the preparation of the (Z)-1,2-bis(arylchalcogeno)-1-alkenes: According to the method of Kuniyasu *et al.*,[15h] to a glass bomb in a nitrogen filled glovebox were added an equivalent of diphenyl dichalcogenide (**2** or **31**), alkyne and 5% catalyst **3**. The reaction was heated for 24 h at 85 ºC with stirring. The resultant solutions were filtered through celite, reduced *in vacuo*, and used without further purification.

(*Z*)-1,2-Bis(phenylseleno)-1-pentene (34): To a glass bomb in a nitrogen filled glovebox were added **2** (64.5 mg, 0.20 mmol), 1-pentyne (20.0 μL, 0.20 mmol) and 5% catalyst **3** (13.4 mg, 10.0 μmol). The reaction was heated for 24 h at 85 ºC with stirring. The resultant solution was

filtered through celite, reduced *in vacuo*, and used without further purification. Compound **34** was prepared in 60% GC yield ^{1}H NMR (300 MHz, C_6D_6) δ 0.69 (t, *J = 7.3 Hz*, 3 H), 1.41 (m, $J_1 = J_2 = 7.4$ *Hz*, 2 H), 2.14 (t, *J = 7.2 Hz*, 2 H), 6.86-7.75 (m, 11 H); MS (EI), *m/z* 382 (M^+), 314, 183, 157, 143, 129, 115, 91, 77 (base), 65.

(*Z*)-1,2-Bis(phenylthio)-1-pentene (35): To a glass bomb in a nitrogen filled glovebox were added **31** (44.0 mg, 0.20 mmol), 1-pentyne (20.0 μL, 0.20 mmol) and 5% catalyst **3** (12.0 mg, 10.0 μmol). The reaction was heated for 24 h at 85 ºC with stirring. The resultant solution was filtered through celite, reduced *in vacuo*, and used without further purification. Compound **35** was prepared in 88% GC yield. ^{1}H NMR (300 MHz, C_6D_6) δ 0.70 (t, *J = 7.3 Hz*, 3 H), 1.43 (m, $J_1 = J_2 = 7.4$ *Hz*, 2 H), 2.10 (t, *J = 7.5 Hz*, 2 H), 6.49 (s, 1 H), 6.85-7.73 (m, 10 H); MS (EI), *m/z* 286 (M^+) (base), 177, 167, 147, 135, 109, 91, 77, 65.

6-cyano-(*Z*)-1,2-bis(phenylseleno)-1-pentene (42): To a glass bomb in a nitrogen filled glovebox were added **2** (64.0 mg, 0.20 mmol), 5-cyano-1-pentyne (21.0 μL, 0.20 mmol) and 5% catalyst **3** (12.0 mg, 10.0 μmol). The reaction was heated for 24 h at 85 ºC with stirring. The resultant solution was filtered through celite, reduced *in vacuo*, and used without further purification. Compound **42** was prepared in 90% GC yield. ^{1}H NMR (300 MHz, C_6D_6) δ 0.97 (m, $J_1 = J_2 = 7.0$ *Hz*, 2 H), 1.51 (t, *J = 7.0 Hz*, 2 H), 1.98 (t, *J = 7.0 Hz*, 2 H), 6.88-7.88 (m, 11 H); MS (EI), *m/z* 407 (M^+), 314, 250, 233, 157, 129, 115, 77 (base).

1.6.4. The Preparation of the (Z)-1,3-Bis(arylchalcogeno)-2-Alken-1-Ones.

General procedure for the preparation of (Z)-1,3-bis(arylchalcogeno)-2-alken-1-ones: Based on the method of Kuniyasu *et al*.,[15h] to a glass bomb in a nitrogen filled glovebox were added an equivalent of diphenyl dichalcogenide (**2** or **31**), alkyne, and 5.0% catalyst **3**. The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h for the sulfur derivatives and 72 h for the selenium derivatives at 85 ºC with stirring. The resultant solutions were filtered through celite, reduced *in vacuo*, and used without further purification.

(*Z*)-1,3-Bis(phenylthio)-2-hexen-1-one (38): To a glass bomb in a nitrogen filled glovebox were added **31** (44.0 mg, 0.20 mmol), 1-pentyne (20.0 μL, 0.20 mmol) and 5% catalyst **3** (12.0 mg, 10.0 μmol). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 85 ºC with stirring. The resultant solution was filtered through celite, reduced *in vacuo*, and used without further purification. Compound **38** was prepared in 65% GC yield. ^{1}H NMR (300 MHz, C_6D_6) δ 0.46 (t, $J = 7.3$ *Hz*, 3 H), 1.09 (m, $J_1 = J_2 = 7.6$ *Hz*, 2 H), 1.81 (t, $J = 7.4$ *Hz*, 2 H), 6.22 (s, 1 H), 6.83-7.73 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.3, 22.8, 38.4, 117.9, 127.2, 128.7, 129.1, 129.2, 129.3, 135.1, 135.9, 137.4, 160.9, 183.5; MS (EI), *m/z* 314 (M^+), 205 (base), 176, 109, 91, 77, 65.

(*Z*)-1,3-Bis(phenylseleno)-2-hexen-1-one (43): To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.19 mmol), 1-pentyne (20.0 μL, 0.20 mmol) and 5.2% catalyst **3** (12.0 mg, 10.0 μmol). The reaction mixture was charged with 0.5 atm of CO gas and heated for 72 h at 85 ºC with stirring. The resultant solution was filtered through celite, reduced *in vacuo*, and used without further purification. Compound **43** was prepared in 75% GC yield. ^{1}H NMR (300 MHz, C_6D_6) δ 0.43 (t, $J = 7.3$ *Hz*, 3 H), 1.06 (m, $J_1 = J_2 = 7.6$ *Hz*, 2 H), 1.84 (t, $J = 7.5$ *Hz*, 2 H),

6.53 (s, 1 H), 6.86-7.76 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.3, 23.2, 39.6, 122.6, 129.6, 131.3, 132.5, 133.1, 133.3, 133.5, 136.2, 137.5, 162.2, 186.3; MS (EI), *m/z* 253 (M^+-SePh) (base), 157, 91, 77, 65.

6-Cyano-(*Z*)-1,3-bis(phenylthio)-2-hexen-1-one (44): To a glass bomb in a nitrogen filled glovebox were added **31** (43.6 mg, 0.20 mmol), 5-cyano-1-pentyne (21.0 μL, 0.20 mmol) and 5% catalyst **3** (12.0 mg, 10.0 μmol). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 85 ºC with stirring. The resultant solution was filtered through celite, reduced *in vacuo*, and used without further purification. Compound **44** was prepared in 60% GC yield. ^{1}H NMR (300 MHz, C_6D_6) δ 0.95 (m, $J_1 = J_2 = 6.9$ *Hz*, 2 H), 1.20 (t, $J = 6.9$ *Hz*, 2 H), 1.76 (t, $J = 6.8$ *Hz*, 2 H), 6.07 (s, 1 H), 6.90-7.73 (m, 10 H); MS (EI), *m/z* 230 (M^+-SPh)(base), 189, 109, 77, 65, 51.

1.6.5. The Preparation of the Chalcogenocarbamates.

***N*-Dimethyl phenyl selenocarbamate (36):** To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (43.0 mg, 0.28 mmol), **2** (64.0 mg, 0.20 mmol), 5.5 % $RhCl(CO)(PPh_3)_2$ (8.0 mg, 11.0 μmol) and benzene (4.0 mL).[13b,c] The reaction mixture was charged with 0.5 atm of CO gas and heated for 64 h at 85 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. The following molar amounts of carbamates and yields based on sulfenamide were determined by GC: **36** (0.20 mmol, 71%); **37** (0.022 mmol, 7.8%). Also observed by GC were the following species with their corresponding molar amounts: $(PhSe)_2$ **2** (0.06 mmol), $(PhS)_2$ **31** (0.14 mmol), and PhSSePh **32** (0.015 mmol). The crude reaction mixture was partially purified by column chromatography (5% ethyl acetate/hexanes,

methanol) to yield a mixture of carbamates **36** and **37**. **36:** ^{1}H NMR (300 MHz, C_6D_6) δ 2.44 (br.s, 6 H), 6.83-7.75 (m, 5 H); MS (EI), *m/z* 229 (M^+), 157, 77, 72 (base), 65. **37**: ^{1}H NMR (300 MHz, C_6C_6) δ 2.27 (br.s, 6 H), 6.83-7.75 (m, 5 H); MS (EI), *m/z* 181 (M^+), 109, 77, 72 (base), 65.

***N*-Dimethyl phenyl thiocarbamate (37):** According to the method of Kuniyasu *et al*.,[18] to a stainless steel reaction vessel with glass insert in a nitrogen filled glovebox were added sulfenamide **1** (40.0 mg, 0.26 mmol), 5.6% catalyst **3** (13.0 mg, 11.2 μmol) and pyridine (2 mL). The reaction mixture was charged with 28 atm of carbon monoxide gas and heated for 24 h at 90 ˚C with stirring. The resultant solution was degassed, filtered through celite and reduced *in vacuo*. The crude reaction mixture was purified by column chromatography using hexanes, methanol to yield the red oil (**37**) (38.0 mg, 0.21 mmol) in 80% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.27 (br.s, 6 H), 6.83-7.75 (m, 5 H); MS (EI), *m/z* 181 (M^+), 109, 77, 72 (base), 65.

1.6.6. The Effect of Catalyst on the Preparation of Aliphatic β-Selenyl Acrylamides.

a) Pd_2dba_3: To a glass bomb in a nitrogen filled glovebox were added **2** (65.0 mg, 0.20 mmol), sulfenamide **1** (33.0 mg, 0.21 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 7.6% Pd_2dba_3 (14.0 mg, 15.0 μmol) and benzene (1.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 65 h at 90 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was not detected by GC or GC/MS.

b) $(dppf)_2PdCl_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (65.8 mg, 0.21 mmol), sulfenamide **1** (33.0 mg, 0.21 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 5.0%

$(dppf)_2PdCl_2$ (11.7 mg, 10.0 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 65 h at 80 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was not detected by GC or GC/MS.

c) $(PPh_3)_2PdCl_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (65.8 mg, 0.21 mmol), sulfenamide **1** (33.0 mg, 0.21 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 5.0% $(PPh_3)_2PdCl_2$ (8.5 mg, 10.0 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 65 h at 80 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was detected in trace amounts by GC and GC/MS.

d) $(AsPh_3)_2PdCl_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.20 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 6.3% $(AsPh_3)_2PdCl_2$ (10.0 mg, 12.6 μmol) and benzene (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 144 h at 90 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was not detected by GC or GC/MS.

e) $Pd(OAc)_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 9.0% $Pd(OAc)_2$ (4.0 mg, 17.8 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 65 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was not detected by GC or GC/MS.

f) $PdCl_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (62.4 mg, 0.19 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), 1-decyne, (54.0 μL, 0.30 mmol), 10.0% $PdCl_2$ (10.0 mg, 20.0 μmol) and toluene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 94 h at 78 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **100** was not detected by GC or GC/MS.

g): $Pt(PPh_3)_4$: To a glass bomb in a nitrogen filled glovebox were added **2** (62.6 mg, 0.20 mmol), sulfenamide **1** (31.5 mg, 0.20 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 10.0% $Pt(PPh_3)_4$ (25.0 mg, 10.0 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 46 h at 80 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was detected in trace amounts by GC and GC/MS.

h) $ClRh(PPh_3)_3$: To a glass bomb in a nitrogen filled glovebox were added **2** (62.4 mg, 0.19 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), 1-decyne, (54.0 μL, 0.30 mmol), 10.0% $ClRh(PPh_3)_3$ (20.0 mg, 20.0 μmol) and toluene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 94 h at 78 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide was not detected by GC or GC/MS.

1.6.7. The Effect of Catalyst on the Preparation of Aromatic β-Selenyl Acrylamides.

a) $Pd(PPh_3)_4$: To a glass bomb in a nitrogen filled glovebox were added **2** (64.5 mg, 0.20 mmol), sulfenamide **1** (32.0 mg, 0.20 mmol), phenyl acetylene, (32.0 μL, 0.30 mmol), 3.2% $Pd(PPh_3)_4$ (7.5 mg, 6.5 μmol) and benzene (2.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 66 h at 75 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **15** was not detected by GC or GC/MS.

b) $(AsPh_3)_2PdCl_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), phenyl acetylene, (32.0 μL, 0.30 mmol), 5.2% $(AsPh_3)_2PdCl_2$ (8.2 mg, 10.4 μmol) and benzene (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 140 h at 91 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **15** was not detected by GC or GC/MS.

c) $(dppf)_2PdCl_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (64.0 mg, 0.20 mmol), sulfenamide **1** (30.0 mg, 0.19 mmol), phenyl acetylene, (32.0 μL, 0.30 mmol), 5.5% $(dppf)_2PdCl_2$ (9.0 mg, 11.0 μmol) and benzene (2.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 163 h at 90 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **15** was detected in trace amounts by GC and GC/MS.

d) $((o\text{-}toly)_3P)_2PdCl_2$: To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.20 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), phenyl acetylene, (32.0 μL, 0.30 mmol), 5.5% $((o\text{-}toly)_3P)_2PdCl_2$ (8.7 mg, 11.0 μmol) and benzene (3.0 mL). The reaction mixture was charged

with 0.5 atm of CO gas and heated for 120 h at 90 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **15** was not detected by GC or GC/MS.

1.6.8. The Effect of Solvent on the Preparation of β-Selenyl Acrylamides.

a) $C_6H_5CH_3$: To a glass bomb in a nitrogen filled glovebox were added **2** (62.7 mg, 0.20 mmol), sulfenamide **1** (32.4 mg, 0.21 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 3.5% $Pd(PPh_3)_4$ (8.4 mg, 7.2 μmol) and toluene (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 63 h at 80 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was observed in 53% GC yield.

b) CH_3CN: To a glass bomb in a nitrogen filled glovebox were added **2** (64.9 mg, 0.20 mmol), sulfenamide **1** (34.5 mg, 0.22 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 3.4% $Pd(PPh_3)_4$ (8.0 mg, 6.9 μmol) and CH_3CN (3.2 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 63 h at 83 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was observed in 59% GC yield.

c) CH_2Cl_2: To a glass bomb in a nitrogen filled glovebox were added **2** (63.4 mg, 0.20 mmol), sulfenamide **1** (31.5 mg, 0.20 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 3.0% $Pd(PPh_3)_4$ (9.4 mg, 6.0 μmol) and CH_2Cl_2 (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 50 h at 80 ºC with stirring. The resultant orange solution was degassed, filtered

through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide **4** was observed in 48% GC yield.

1.6.9. The Preparation of β-Selenyl Acrylamides.

(*Z*)-3-Phenylselenyl-hex-2-enoic acid dimethylamide (4): To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **1** (29.0 mg, 0.19 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 4.5% catalyst **3** (10.0 mg, 8.6 μmol) and benzene (1.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 168 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield the orange oil (**4**) (47.5 mg, 0.16 mmol) in 84% yield. The following percentages of byproducts in the final reaction mixture were determined by GC using the internal standards method (hexamethylbenzene) and identified either by comparison to independently prepared standards or by isolation from column chromatography: $(PhSe)_2$, **2**, 17.0%; (*Z*)-3-phenylselenyl-hex-2-enoic acid dimethylamide, **4**, 47.5%; $(PhS)_2$, **31**, 0.3%; PhS-SePh, **32**, trace; (*Z*)-3-phenylsulfenyl-hex-2-enoic acid dimethylamide, **33**, 6.8%; (*Z*)-1,2-bis(phenylseleno)-1-pentene, **34**, 2.7%; (*Z*)-1,2-bis(phenylthio)-1-pentene, **35**, trace; *N*-dimethyl phenyl selenocarbamate, **36**, 3.4%; *N*-dimethyl phenyl thiocarbamate, **37**, 0.1%; (*Z*)-1,3-bis(phenylthio)-2-hexen-1-one, **38**, 10.3%; 3-phenylselenyl-hex-2-enoic acid S-phenyl ester, **39**, 11.1%; $SePPh_3$, **40**, trace; PhSePh, **41**, trace. The *E/Z* ratio was determined by noe difference and ^{1}H NMR spectroscopy (*E/Z* = 0/100). **4:** ^{1}H NMR (300 MHz, C_6D_6) δ 0.61 (t, *J = 7.3 Hz*, 3 H), 1.34 (m, $J_1 = J_2 = 7.5$ *Hz*, 2 H), 2.16 (t, *J* =

7.4 Hz, 2 H), 2.31 (s, 3 H), 2.69 (s, 3 H), 6.29 (s, 1 H), 6.92-7.62 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.4, 23.5, 34.9, 36.5, 40.1, 114.3, 128.5, 128.9, 130.6, 137.7, 157.5, 166.6; IR (NaCl) 3070, 2887, 2325, 1960, 1815, 1633 (C=O), 1438, 1034, 674 cm^{-1}; MS (EI), *m/z* 297 (M^+), 253, 157, 140 (base), 72. HRMS calcd for $C_{14}H_{19}NOSe$: 297.0639. Found 297.0631. Anal. Calcd for $C_{14}H_{19}NOSe$: C, 56.55; H, 6.39; N, 4.71. Found: C, 56.90; H, 6.44; N, 4.67. **33:** ^{1}H NMR (300 MHz, C_6D_6) δ 0.65 (t, *J = 7.4 Hz*, 3 H), 1.36 (m, $J_1 = J_2 = 7.4$ *Hz*, 2 H), 2.03 (t, *J = 7.3 Hz*, 2 H), 2.44 (s, 3 H), 2.71 (s, 3 H), 5.98 (s, 1 H), 6.90-7.42 (m, 5 H); MS (EI), *m/z* 249 (M^+), 205, 176, 140 (base), 109, 72. **39**: ^{1}H NMR (300 MHz, C_6D_6) δ 0.45 (t, *J = 7.3 Hz*, 2 H), 1.10 (m, $J_1 = J_2 = 7.5$ *Hz*, 2 H), 1.92 (t, *J = 7.4 Hz*, 2 H), 6.55 (s, 1 H), 6.89-7.56 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.3, 23.5, 39.7, 120.1, 127.4, 128.8, 129.1, 129.4, 131.2, 133.3, 135.9, 137.1, 163.0, 184.7; MS (EI), *m/z* 362 (M^+), 253 (base), 157, 109, 91, 77, 65.

(*Z*)-3-Phenylsulfenyl-hex-2-enoic acid dimethylamide (33): Acrylamide **33** was isolated by column chromatography in the preparation of acrylamide **4**. ^{1}H NMR (300 MHz, C_6D_6) δ 0.65 (t, *J = 7.4 Hz*, 3 H), 1.36 (m, $J_1 = J_2 = 7.4$ *Hz*, 2 H), 2.03 (t, *J = 7.3 Hz*, 2 H), 2.44 (s, 3 H), 2.71 (s, 3 H), 5.98 (s, 1 H), 6.90-7.42 (m, 5 H); MS (EI), *m/z* 249 (M^+), 205, 176, 140 (base), 109, 72.

3-Phenylselenyl-hex-2-enoic acid S-phenyl ester (39): Compound **39** was isolated by column chromatography in the preparation of acrylamide **4**. ^{1}H NMR (300 MHz, C_6D_6) δ 0.45 (t, *J = 7.3 Hz*, 2 H), 1.10 (m, $J_1 = J_2 = 7.5$ *Hz*, 2 H), 1.92 (t, *J = 7.4 Hz*, 2 H), 6.55 (s, 1 H), 6.89-7.56 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.3, 23.5, 39.7, 120.1, 127.4, 128.8, 129.1, 129.4, 131.2, 133.3, 135.9, 137.1, 163.0, 184.7; MS (EI), *m/z* 362 (M^+), 253 (base), 157, 109, 91, 77, 65.

6-Cyano-(*Z*)-3-phenylselenyl-hex-2-enoic acid dimethylamide (12): To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **1** (31.0 mg, 0.20

mmol), 5-cyano-1-pentyne, (32.0 μL, 0.30 mmol), 3.8% catalyst **3** (9.0 mg, 7.7 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 144 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield the orange oil (**12**) (45.0 mg, 0.14 mmol) in 70% yield. The *E/Z* ratio was determined by noe and ^{1}H NMR difference spectroscopy (*E/Z* = 0/100). ^{1}H NMR (300 MHz, C_6D_6) δ 1.15 (m, $J_1 = J_2 = 7.2$ *Hz*, 2 H), 1.34 (t, $J = 7.0$ *Hz*, 2 H), 2.15 (t, $J = 7.2$ *Hz*, 2 H), 2.36 (s, 3 H), 2.68 (s, 3 H), 6.34 (s, 1 H), 6.93-7.07 (m, 3 H), 7.46-7.48 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 15.3, 25.0, 34.9, 36.3, 36.6, 116.0, 119.0, 129.2, 130.0, 137.3, 154.3, 166.3; MS (EI), *m/z* 322 (M^+), 278, 165 (base), 157, 77, 72. HRMS calcd for $C_{15}H_{18}N_2OSe$: 322.0585. Found 322.0584.

Acetic acid 5-dimethylcarbamoyl-(*Z*)-4-phenylselenyl-pent-4-enyl ester (13): To a glass bomb in a nitrogen filled glovebox were added **2** (61.2 mg, 0.19 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), acetic acid pent-4-ynyl ester (40.0 μL, 0.30 mmol), 3.5% catalyst **3** (8.6 mg, 7.4 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 144 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield the orange oil (**13**) (53.3 mg, 0.15 mmol) in 72% yield. The *E/Z* ratio was determined by noe and ^{1}H NMR difference spectroscopy (*E/Z* = 0/100). ^{1}H NMR (300 MHz, C_6D_6) δ 1.54 (m, $J_1 = J_2 = 7.1$ *Hz*, 2 H), 1.58 (s, 3 H), 2.21 (t, $J = 7.3$ *Hz*, 2 H), 2.35 (s, 3 H), 2.68 (s, 3 H), 3.73 (t, $J = 6.4$ *Hz*, 2 H), 6.33 (s, 1 H), 6.93-6.99 (m, 3 H), 7.55-7.57 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 20.5, 29.3, 34.6, 35.0, 36.5, 63.1, 114.8, 129.0, 130.3, 137.7, 156.3,

166.6, 170.0; MS (EI), *m/z* 355 (M^+), 269, 198 (base), 157, 138, 111, 72, 43. HRMS calcd for $C_{16}H_{21}NO_3Se$: 355.0698. Found 355.0686.

6-Hydroxy-(Z)-3-phenylselenyl-hex-2-enoic acid dimethylamide (14): To a glass bomb in a nitrogen filled glovebox were added **2** (65.0 mg, 0.21 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), 5-hydroxy-1-pentyne, (28.0 μL, 0.30 mmol), 3.0% catalyst **3** (6.5 mg, 5.6 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 48 h at 80 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The formation of (**14**) was not detected by GC-MS.

***N,N*-Dimethyl-3-phenyl-3-phenylselenyl-acrylamide (15):** To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **1** (30.2 mg, 0.19 mmol), phenyl acetylene, (35.0 μL, 0.30 mmol), 6.0% $(PPh_3)_2PdCl_2$ (9.0 mg, 11.4 μmol) and benzene (2.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 168 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield the orange oil (**15**) (12.0 mg, 0.04 mmol) in 30% yield. The E/Z ratio was determined by ^{1}H NMR spectroscopy (*E/Z* = 100). ^{1}H NMR (300 MHz, C_6D_6) δ 2.34 (s, 3 H), 2.70 (s, 3 H), 6.48 (s, 1 H), 6.74-7.27 (m, 10 H); MS (EI), *m/z* 331 (M^+), 287, 254, 157, 72 (base).

(Z)-2-Methyl-3-phenylselenyl-but-2-enoic acid dimethylamide (16): To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **1** (32.5 mg, 0.21 mmol), 2-butyne, (25.0 μL, 0.30 mmol), 2.5% catalyst **3** (6.3 mg, 5.4 μmol) and benzene (1.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 50 h at 80 ºC

with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide (**16**) was not detected by GC-MS.

(*Z*)-3-Phenylselenyl-hex-2-enoic acid diethylamide (17): To a glass bomb in a nitrogen filled glovebox were added **2** (64.0 mg, 0.20 mmol), sulfenamide **5** (36.5 mg, 0.20 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 3.8% catalyst **3** (9.0 mg, 7.7 μmol) and benzene (1.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 140 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield (**17**) (46.0 mg, 0.14 mmol) in 70% yield. The *E/Z* ratio was determined by noe difference and ^{1}H NMR spectroscopy (*E/Z* = 0/100). ^{1}H NMR (300 MHz, C_6D_6) δ 0.59 (t, *J = 7.3 Hz*, 3 H), 0.77 (br.s, 3 H), 0.99 (br.s, 3 H), 1.33 (m, $J_1 = J_2 = 7.3$ *Hz*, 2 H), 2.18 (t, *J = 7.0 Hz*, 2 H), 2.84 (br.s, 2 H), 3.26 (br.s, 2 H), 6.37 (s, 1 H), 6.94-7.00 (m, 3 H), 7.61-7.63 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.4, 13.6, 14.8, 23.6, 40.1, 40.7, 42.1, 114.0, 128.5, 128.9, 130.8, 137.8, 157.8, 166.0; MS (EI), *m/z* 325 (M^+), 253, 168 (base), 157, 100. HRMS calcd for $C_{16}H_{23}NOSe$: 325.0945. Found 325.0944.

6-Cyano-(*Z*)-3-phenylselenyl-hex-2-enoic acid diethylamide (18): To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.20 mmol), sulfenamide **5** (36.3 mg, 0.20 mmol), 5-cyano-1-pentyne, (32.0 μL, 0.30 mmol), 5.1% catalyst **3** (11.8 mg, 10.2 μmol) and benzene (1.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 165 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield (**18**) (55.0 mg, 0.16 mmol) in 80% yield. The *E/Z* ratio was determined by noe difference

and ^{1}H NMR spectroscopy (*E/Z* = 0/100). ^{1}H NMR (300 MHz, C_6D_6) δ 0.83 (t, *J = 6.9 Hz,* 3 H), 0.98 (t, *J = 6.9 Hz,* 3 H), 1.09 (m, $J_1 = J_2 = 7.0$ *Hz*, 2 H), 1.30 (t, *J = 7.0 Hz,* 2 H), 2.17 (t, *J = 7.1 Hz,* 2 H), 2.85 (q, *J = 6.9 Hz*, 2 H), 3.24 (q, *J = 6.9 Hz,* 2 H), 6.41 (s, 1 H), 6.90-7.03 (m, 3 H), 7.45-7.47 (m, 2 H). ^{13}C NMR (75 MHz, C_6D_6) δ 13.5, 14.8, 15.2, 24.8, 36.2, 40.7, 42.1, 115.9, 118.9, 129.1, 130.2, 137.4, 154.5, 165.5. MS (EI), *m/z* 350 (M^+), 278, 193 (base), 157, 77, 72. HRMS calcd for $C_{17}H_{22}N_2OSe$: 350.0890. Found 350.0897.

4-Dimethylamino-(Z)-3-phenylselenyl-hex-2-enoic acid diethylamide (19): To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **5** (35.7 mg, 0.20 mmol), dimethyl-prop-ynyl amine, (33.0 μL, 0.30 mmol), 4.5% catalyst **3** (10.5 mg, 9.0 μmol) and benzene (1.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 162 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. An 85% GC yield of (**19**) was observed. The *E/Z* ratio was determined ^{1}H NMR (*E/Z* = 0/100). ^{1}H NMR (300 MHz, C6D6) δ 0.79 (t, *J = 6.7* Hz, 3 H), 0.99 (t, *J = 6.7* Hz, 3 H), 1.87 (s, 6 H), 2.35 (s, 1 H), 2.68 (s, 1 H), 2.90 (q, 2 H), 3.27 (q, 2 H), 6.87 (s, 1 H) 6.90-7.08 (m, 3 H), 7.68-7.77 (m, 2 H); MS (EI), *m/z* 340 (M^+), 219, 183, 157, 82, 72, 58 (base).

(Z)-4-Methyl-3-phenylselenyl-penta-2,4-dienoic acid diethylamide (20): To a glass bomb in a nitrogen filled glovebox were added **2** (61.5 mg, 0.19 mmol), sulfenamide **5** (35.4 mg, 0.19 mmol), 3-methyl-butyn-3-ene, (29.0 μL, 0.30 mmol), 6.0% $(PPh_3)_2PdCl_2$ (8.0 mg, 11.7 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 168 h at 90 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. Acrylamide (**20**) was detected in trace amounts by GC and GC-MS.

(*Z*)-3-Phenylselenyl-hex-2-enoic acid methyl-benzyl-amide (21): To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **7** (46.0 mg, 0.20 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 8.6% catalyst **3** (21.0 mg, 17.3 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 138 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. A 95% GC yield of (**21**) was observed. The *E/Z* ratio was determined by ^{1}H NMR (*E/Z* = 0/100). Two distinct rotamers were observed by ^{1}H and ^{13}C NMR at room temperature. ^{1}H NMR (300 MHz, C_6D_6) δ 0.49 (t, *J = 7.1 Hz*, 3 H), 0.60 (t, *J = 7.0 Hz*, 3 H), 1.34 (m, 4 H), 2.07 (t, *J = 7.1 Hz*, 2 H), 2.19 (t, *J = 7.2 Hz*, 2 H), 2.39 (s, 3 H), 2.81 (s, 3 H), 4.06 (s, 2 H), 4.51 (s, 2 H), 6.35 (s, 1 H), 6.42 (s, 1 H), 6.95-7.69 (m, 20 H). ^{13}C NMR (75 MHz, C_6D_6) δ 13.3, 13.4, 23.5, 23.6, 33.6, 34.2, 39.9, 40.2, 50.8, 53.2, 113.9, 130.5, 132.3, 132.4, 134.5, 137.7, 138.4, 158.9, 159.1, 166.8, 167.2; MS (EI), *m/z* 373 (M^+), 296, 253, 216 (base), 157, 120, 91, 77, 65.

6-Chloro-(*Z*)-3-phenylselenyl-hex-2-enoic acid benzyl-methyl-amide (22): To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.19 mmol), sulfenamide **7** (46.0 mg, 0.20 mmol), 5-chloro-1-pentyne, (38.0 μL, 0.30 mmol), 4.6% catalyst **3** (10.8 mg, 9.3 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of carbon monoxide gas and heated for 64 h at 78 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using hexanes, 20% ethyl acetate/hexanes, methanol to yield the orange oil (**22**) (50.0 mg, 0.12 mmol) in 60% yield. The *E/Z* ratio was determined by noe difference and ^{1}H NMR spectroscopy (*E/Z* = 0/100). Two distinct rotamers were observed by ^{1}H and ^{13}C NMR at room temperature. ^{1}H NMR (300 MHz, C_6D_6) δ 1.44 (m, $J_1 = J_2 = 7.5$

Hz, 2 H), 1.54 (m, $J_1 = J_2 = 7.1$ *Hz*, 2 H), 2.19 (t, $J = 7.0$ *Hz*, 2 H), 2.30 (t, $J = 7.3$ *Hz*, 2 H), 2.38 (s, 3 H), 2.80 (m, 5 H), 2.91 (t, $J = 7.0$ *Hz*, 2 H), 4.05 (s, 2 H), 4.50 (s, 2 H), 6.38 (s, 1 H), 6.46 (s, 1 H), 6.94-7.55 (m, 20 H). ^{13}C NMR (75 MHz, C_6D_6) δ 32.2, 32.4, 33.7, 34.2, 34.9, 35.1, 43.4, 43.7, 50.8, 53.3, 115.1, 115.2, 126.6, 130.1, 137.5, 138.2, 156.5, 156.8, 166.5, 167.1; MS (EI), *m/z* 407 (M^+), 287, 250 (base), 157, 91, 77, 65. HRMS calcd for $C_{20}H_{22}NOClSe$: 407.0572. Found 407.0555.

(*Z*)-3-Phenylselenyl-undec-2-enoic acid benzyl-methyl-amide (23): To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.19 mmol), sulfenamide **7** (45.0 mg, 0.19 mmol), 1-decyne, (54.0 μL, 0.30 mmol), 4.5% catalyst **3** (10.0 mg, 8.6 μmol) and benzene (3 mL). The reaction mixture was charged with 0.5 atm of carbon monoxide gas and heated for 64 h at 78 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The crude reaction mixture was purified via column chromatography using hexanes, 20% ethyl acetate/hexanes, methanol to yield the orange oil (**12**) (50.5 mg, 0.11 mmol) in 60% yield. The *E/Z* ratio was determined by ^{1}H NMR spectroscopy (*E/Z* = 0/100). Two distinct rotamers were observed by ^{1}H and ^{13}C NMR at room temperature. The rotamers resolved into one species when the sample was heated to 75 ºC. ^{1}H NMR (300 MHz, C_6D_6) δ 0.87 (t, $J = 6.9$ *Hz*, 6 H), 1.03-1.40 (m, 24 H), 2.19 (t, $J = 7.1$ *Hz*, 2 H), 2.28 (t, $J = 7.3$ *Hz*, 2 H), 2.41 (s, 3 H), 2.81 (s, 3 H), 4.09 (s, 2 H), 4.52 (s, 2 H), 6.42 (s, 1 H), 6.48 (s, 1 H), 6.94-7.73 (m, 20 H); ^{13}C NMR (75 MHz, d_8-tol) δ 14.4, 23.1, 29.6, 30.5, 30.7, 32.3, 33.6, 34.2, 38.3, 38.5, 50.8, 53.4, 113.6, 113.7, 130.7, 131.6, 132.3, 132.5, 133.6, 133.9, 134.6, 135.0, 138.5, 159.2, 159.6, 167.1, 167.7; MS (EI), *m/z* 443 (M^+), 323, 286 (base), 157, 120, 91, 77, 65.

(*Z*)-3-Phenylselenyl-hex-2-enoic acid allyl-methyl-amide (24): To a glass bomb in a nitrogen filled glovebox were added **2** (66.0 mg, 0.21 mmol), sulfenamide **9** (40.0 mg, 0.22 mmol), 1-

pentyne, (30.0 μL, 0.30 mmol), 4.5% catalyst **3** (12.7 mg, 10.9 μmol) and benzene (1.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 136 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield (**24**) (57.0 mg, 0.18 mmol) in 82% yield. The *E/Z* ratio was determined by noe difference and ^{1}H NMR spectroscopy (*E/Z* = 0/100). Two distinct rotamers were observed by ^{1}H and ^{13}C NMR at room temperature. ^{1}H NMR (300 MHz, C_6D_6) δ 0.59 (m, 6 H), 1.22 (br.s, 4 H), 2.16 (m, 4 H), 2.45 (s, 3 H), 2.78 (s, 3 H), 3.40 (m, 2 H), 3.92 (m, 2 H), 4.91 (m, 4 H), 5.40 (m, 1 H), 5.60 (m, 1 H), 6.35 (s, 2 H), 6.88-6.99 (m, 6 H), 7.58-7.62 (m, 4 H); ^{13}C NMR (75 MHz, C_6D_6) 13.4, 23.6, 33.5, 34.2, 40.1, 50.0, 52.0, 114.0, 116.0, 116.9, 130.5, 133.5, 134.1, 137.8, 158.0, 158.6, 166.4, 166.9; MS (EI), *m/z* 323 (M^+), 253, 166 (base), 157, 77, 41. HRMS calcd for $C_{16}H_{21}NOSe$: 323.0798. Found 323.0788.

(*Z*)-3-Phenylselenyl-hex-2-enoic acid diallylamide (25): To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **8** (41.0 mg, 0.20 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 10.0% catalyst **3** (24.0 mg, 20.0 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 138 h at 85 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield the viscous oil. An 85% GC yield of (**25**) was observed. The *E/Z* ratio was determined by noe and ^{1}H NMR difference spectroscopy (*E/Z* = 0/100). ^{1}H NMR (300 MHz, C_6D_6) δ 0.57 (t, J = *7.3 Hz*, 3 H), 1.31 (m, $J_1 = J_2$ = *7.4 Hz*, 2 H), 2.15 (t, J = *7.4 Hz*, 2 H), 3.55 (s, 2 H), 4.00 (d, J = *5.3 Hz*, 2 H), 4.94 (m, 4 H), 5.44 (m, 1 H), 5.73 (m, 1 H), 6.38 (s, 1 H), 6.95-7.81 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.4, 21.4, 23.5, 40.1, 48.4, 49.1, 113.8, 116.1, 117.1, 130.5, 131.7,

132.3, 133.5, 133.9, 137.8, 159.2, 166.7; MS (EI), *m/z* 349 (M^+), 272, 253, 192 (base), 157, 77, 41. HRMS calcd for $C_{18}H_{23}NOSe$: 349.0931. Found 349.0944.

(Z)-3-Phenylselenyl-hex-2-enoic acid methylamide (26): To a glass bomb in a nitrogen filled glovebox were added **2** (61.5 mg, 0.19 mmol), sulfenamide **9** (29.5 mg, 0.21 mmol), 1-pentyne (30.0 μL, 0.30 mmol), 3.3% catalyst **3** (7.6 mg, 6.5 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 70 h at 75 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. Acrylamide (**26**) was not detected by GC-MS.

(Z)-3-Phenylselenyl-hex-2-enoic acid diisopropylamide (27): To a glass bomb in a nitrogen filled glovebox were added **2** (64.2 mg, 0.20 mmol), sulfenamide **10** (43.8 mg, 0.21 mmol), 1-pentyne, (30.0 μL, 0.30 mmol), 3.2% catalyst **3** (7.7 mg, 6.6 μmol) and benzene (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 43 h at 80 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. Acrylamide (**27**) was not detected by GC-MS.

6-cyano-3-phenylselenyl-hex-2-enoic acid phenylsulfanyl-ethyl-amide (28a) and 6-cyano-3-phenylselenyl-hex-2-enoic acid trimethylsilylamine-ethyl-amide (28b): To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.20 mmol), sulfenamide **11** (60.0 mg, 0.21 mmol), 5-cyano-1-pentyne, (32.0 μL, 0.30 mmol), 4.1% catalyst **3** (10.0 mg, 8.6 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 165 h at 95 ºC with stirring. The resultant orange solution was degassed, filtered through celite and reduced *in vacuo* to yield a red, viscous oil. The formation of (**28a**) and (**28b**) was observed by GC-MS. **28a:** MS (EI), *m/z* 384 (M^+-SPh), 278, 227, 157, 91, 77, 65, 51. **28b:** MS (EI), *m/z* 384 (M^+-TMS), 342, 278, 227, 157, 91, 77, 65, 51.

1.6.10. The Effect of NR_2 Source on the Preparation of β-Selenyl Acrylamides.

The preparation of acrylamide 18 from amine 29: To a glass bomb in a nitrogen filled glovebox were added **2** (65.0 mg, 0.21 mmol), 5-cyano-1-pentyne (32.0 μL, 0.30 mmol), 4.7% of catalyst **3** (11.5 mg, 9.9 μmol), and benzene (2.5 mL). The glass bomb was sealed, transferred to a vacuum line, and placed under nitrogen where amine **29** (21.0 μL, 0.20 mmol) was added. The reaction mixture was charged with 0.5 atm of CO gas and heated for 138 h at 90 ºC with stirring. The resultant solution was degassed, filtered through celite and analyzed by GC, GC-MS. The GC yield of **18** was determined to be 40%.

The preparation of acrylamide 12 from amine 30: To a glass bomb in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), 5-cyano-1-pentyne (32.0 μL, 0.30 mmol), 4.1% of catalyst **3** (9.5 mg, 8.2 μmol), and benzene (2.5 mL). The glass bomb was sealed, transferred to a vacuum line, and placed under nitrogen where amine **30** (32.0 μL, 0.20 mmol) was added. The reaction mixture was charged with 0.5 atm of CO gas and heated for 138 h at 90 ºC with stirring. The resultant solution was degassed, filtered through celite and analyzed by GC, GC-MS. The GC yield of **12** was determined to be 40%.

1.6.11. The Reactivity of the Dichalcogenated Byproducts Towards Acrylamide Formation.

The attempted preparation of acrylamide 4 from bis(arylseleno)-1-alkene 34 and sulfenamide 1: To a glass bomb in a nitrogen filled glovebox were added **34** (45.8 mg, 0.12 mmol), sulfenamide **1** (19.1 mg, 0.12 mmol), 9.0% of catalyst **3** (12.5 mg, 10.8 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 72 h

at 90 ºC with stirring. The resultant solution was degassed, filtered through celite and analyzed by GC, GC-MS. Acrylamide **4** was not detected.

The attempted preparation of acrylamide 33 from bis(phenylthio)-1-alkene 35 and sulfenamide 1: To a glass bomb in a nitrogen filled glovebox were added **35** (57.2 mg, 0.20 mmol), sulfenamide **1** (31.0 mg, 0.20 mmol), 5.4% of catalyst **3** (12.5 mg, 10.8 μmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 48 h at 80 ºC with stirring. The resultant solution was degassed, filtered through celite and analyzed by GC, GC-MS. The formation of acrylamide **35** was not detected.

The attempted preparation of acrylamide 18 from bis(phenylseleno)-1-alkene 42 and sulfenamide 5 in the presence of substoichiometric Pd: To a glass bomb in a nitrogen filled glovebox were added **42** (81.0 mg, 0.19 mmol), sulfenamide **5** (37.0 mg, 0.20 mmol), 50% of catalyst **3** (115.6 mg, 0.1 mmol) and benzene (2.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 144 h at 80 ºC with stirring. The resultant solution was degassed, filtered through celite and analyzed by GC, GC-MS. The formation of acrylamide **18** was not detected.

1.6.12. The Preparation of Acrylamide 33 from Thiocarbamate.

a) To a glass bomb in a nitrogen filled glovebox were added thiocarbamate **37** (38.0 mg, 0.21 mmol), 1-pentyne (20.0 μL, 0.20 mmol), 5% of catalyst **3** (12.1 mg, 10.5 μmol) and benzene (2.0 mL). The reaction was heated for 96 h at 85 ˚C with stirring. The resultant solution was filtered through celite and analyzed by GC-MS and GC. A 4.5% GC yield of acrylamide **33** was observed.

1.6.13. The Reactivity of the Carbonylative Addition Byproducts Towards Acrylamide Formation.

The preparation of acrylamide 4 from phenylseleno-2-alken-1-one 43 and sulfenamide 1 in the presence of catalytic Pd: To a glass bomb in a nitrogen filled glovebox were added **43** (73.8 mg, 0.18 mmol), sulfenamide **1** (28.0 mg, 0.18 mmol), 4.0% of catalyst **3** (8.3 mg, 7.2 μmol) and benzene (2.5 mL). The reaction was heated for 96 h at 75 ºC with stirring. The reaction was filtered through celite and analyzed by GC-MS and GC. A 100% GC yield of acrylamide **4** was observed.

The preparation of acrylamide 17 from phenylseleno-2-alken-1-one 43 and sulfenamide 5 in the absence of catalyst: To a glass bomb in a nitrogen filled glove box were added **43** (74.0 mg, 0.18 mmol), sulfenamide **5** (33.0 mg, 0.18 mmol) and benzene (2.5 mL). The reaction was heated for 96 h at 75 ºC with stirring. The reaction was filtered through celite and analyzed by GC-MS and GC. A 100% GC yield of acrylamide **17** was observed.

The preparation of acrylamide 45 from phenylthio-2-alken-1-one 44 and sulfenamide 5 in the absence of catalyst: To a glass bomb in a nitrogen filled glovebox were added **44** (27.6 mg, 0.12 mmol), sulfenamide **5** (23.0 mg, 0.12 mmol) and benzene (2.5 mL). The reaction was heated for 70 h at 90 ºC with stirring. The resultant orange solution was filtered through celite and reduced *in vacuo* to yield a viscous oil. GC analysis showed the yield of acrylamide (**45**) to be 100%. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes, ethyl acetate to yield the orange oil **45** (37.0 mg, 0.11 mmol) in 92% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 0.82 (t, *J = 6.7 Hz*, 3 H), 1.01 (t, *J = 6.7 Hz*, 3 H), 1.12 (m, $J_1 = J_2 = 7.0$ *Hz*, 2 H), 1.33 (t, *J = 7.0 Hz*, 2 H), 2.00 (t, *J = 7.0 Hz*, 2 H), 2.91

(q, *J = 6.9 Hz*, 2 H), 3.27 (q, *J = 6.8 Hz*, 2 H), 6.07 (s, 1 H), 6.90-6.93 (m, 3 H), 7.28-7.30 (m, 2 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.4, 14.7, 15.2, 24.0, 34.9, 39.9, 42.3, 118.9, 121.3, 129.2, 133.4, 134.1, 146.2, 165.0; MS (EI), *m/z* 302 (M^+), 230, 193 (base), 109, 100, 77, 65, 51.

1.6.14. Selectivity.

The palladium catalyzed reaction of 1-pentyne with $(PhS)_2$ and $(PhSe)_2$: To a glass bomb in a nitrogen filled glovebox were added $(PhS)_2$ **31** (65.4 mg, 0.30 mmol), $(PhSe)_2$ **2** (94.2 mg, 0.30 mmol), 1-pentyne (30.0 μL, 0.30 mmol), 4.5 % of catalyst **3** (17.0 mg, 14.7 μmol) and benzene (3 mL). The reaction was heated for 24 h at 90 ºC with stirring. The resultant solution was filtered through celite and analyzed by GC-MS, GC. (*Z*)-1,2-bis(phenylseleno)-1-pentene **34** and (*Z*)-1,2-bis(phenylthio)-1-pentene **35** were both detected in 27.0 % GC yield. (*Z*)-1-phenylthio-2-phenylseleno-1-pentene (**47**) and (*Z*)-1-phenylseleno-2-phenylthio-1-pentene (**48**) were also observed in 17 and 20 % yields, respectively, by GC.

The reaction of phenylseleno-2-hexen-1-one 43 with $(PhS)_2$: To a glass bomb were added **43** (61.5 mg, 0.15 mmol), **31** (34.5 mg, 0.16 mmol) and benzene (2 mL). The reaction was heated for 48 h at 90 ºC with stirring. The reaction was filtered through celite and analyzed by GC-MS and GC. A 5.3% GC yield of **39** (0.008 mmol) was observed. Trace amounts of diaryl dichalcogenide **32** were also observed.

6-Cyano-(*Z*)-3-phenylsulfenyl-hex-2-enoic acid diethylamide (45): To a stainless steel reaction vessel with glass insert in a nitrogen filled glovebox were added **31** (13.0 mg, 0.06 mmol), sulfenamide **5** (18.5 mg, 0.11 mmol), 5-cyano-1-pentyne (32.0 μL, 0.30 mmol), 4.0% of catalyst **3** (5.0 mg, 4.3 μmol) and benzene (2.0 mL). The reaction mixture was charged with 28

atm of CO gas and heated for 65 h at 110 ˚C with stirring. The resultant solution was degassed, filtered through celite and reduced *in vacuo* to yield a viscous oil. The crude reaction mixture was purified via column chromatography using 5% ethyl acetate/hexanes, 20% ethyl acetate/hexanes and ethyl acetate to yield the orange oil (**45**) (20.0 mg, 0.07 mmol) in 64% yield. Spectral data matches those obtained in prior experiments.

The high pressure preparation of acrylamides 18 and 45 from 5-cyano-1-pentyne and sulfenamide 5: To a stainless steel reaction vessel with glass insert in a nitrogen filled glovebox were added **2** (63.0 mg, 0.20 mmol), sulfenamide **5** (36.7 mg, 0.20 mmol), 5-cyano-1-pentyne (32.0 μL, 0.30 mmol), 4.9% of catalyst **3** (11.5 mg, 9.9 μmol) and xylenes (2.5 mL). The reaction mixture was charged with 28 atm of CO gas and heated for 67 h at 85 ˚C with stirring. The resultant solution was degassed, filtered through celite and analyzed by GC. A 25% GC yield of both acrylamides **18** and **45** was observed.

The comparative carbonylative additions of $(PhS)_2$ and $(PhSe)_2$ to 1-pentyne:

(a): To a glass bomb in a nitrogen filled glovebox were added **31** (43.0 mg, 0.20 mmol), 1-pentyne (25.0 μL, 0.25 mmol), 6.2% of catalyst **3** (14.5 mg, 12.5 μmol) and benzene (2.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 94 h at 90 ˚C with stirring. The resultant solution was degassed, filtered through celite, and analyzed by GC-MS and GC. Compounds **35** and **38** were detected in GC yields of 95 and 4.7%, respectively.

(b): To a glass bomb in a nitrogen filled glovebox were added **2** (62.0 mg, 0.19 mmol), 1-pentyne (25.0 μL, 0.25 mmol), 5.8% of catalyst **3** (12.5 mg, 11.0 μmol) and benzene (2.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 94 h at 90 ˚C with stirring. The resultant solution was degassed, filtered through celite, and analyzed by GC-MS and GC. Compounds **34** and **43** and were detected in GC yields of 7 and 75%, respectively.

The ^{1}H NMR analysis of reaction selectivity: To a screw-top NMR tube in a nitrogen filled glovebox were added 0.1 mL of a 0.0203 M C_6D_6 solution of sulfenamide **1**; 0.1 mL of a 0.02 M C_6D_6 solution of **2**; 0.15 mL of a 0.02 M C_6D_6 solution of 1-pentyne; 0.1 mL of a 0.01 M C_6D_6 solution of catalyst **3** and 0.1 mL of a 0.115 M C_6D_6 solution of anisole standard. The reaction mixture was charged with CO gas and heated to 80 ˚C. The reaction was monitored by ^{1}H NMR every 24 h for 6 days. Integrated areas were used to determine the relative amounts of both selenium and sulfur acrylamide products **4** and **33**. The product ratio of **4**:**33** after 3 h reaction and every 24 h is as follows: 100:1; 6:1; 4.5:1; 3.3:1; 3.2:1; 4:1; 3.5:1.

1.6.15. The Preparation of β-Sulfenyl Acrylamides from Thiophenol.

a) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (33.6 mg, 0.22 mmol), 2.5% catalyst **3** (6.4 mg, 5.5 μmol) and 1-pentyne (30.0 μL, 0.30 mmol). The glass bomb was sealed, transferred to a vacuum line, and placed under nitrogen where **49** (20.0 μL, 0.20 mmol) was added. The reaction mixture was charged with 0.5 atm of CO gas and heated for 41 h at 80 °C. The resultant solution was degassed, filtered through celite, and analyzed by GC-MS and GC. A 73% GC yield of acrylamide **33** was observed. The following %'s of products and by-products in the final reaction mixture were determined by GC using the internal standards method (hexamethylbenzene) and identified either by comparison to independently prepared standards or by isolation from column chromatography. $(PhS)_2$, **31**, 1.9%; (*Z*)-3-phenylsulfenyl-hex-2-enoic acid dimethylamide **33**, 71.1%; (*Z*)-1,2-bis(phenylthio)-1-pentene, **35**, 5.7%.; *N*-dimethyl phenyl thiocarbamate, **37**, 7.4%; (*E*)-3-phenylsulfenyl-hex-2-enoic acid dimethylamide

50, 13.7%; **50**: MS (EI), *m/z* 249 (M^+), 205 (M^+- NMe_2), 176, 140 (M^+- SPh) (base), 109 (PhS^+), 72 (Me_2NCO^+).

b) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (31.8 mg, 0.20 mmol), 2.9% catalyst **3** (6.8 mg, 5.8 μmol) and 1-pentyne (30.0 μL, 0.30 mmol). The glass bomb was sealed, transferred to a vacuum line, and placed under nitrogen where **49** (20.0 μL, 0.20 mmol) was added. The reaction mixture was charged with 0.5 atm of CO gas and heated for 16 h at 90 °C. The resultant solution was degassed, filtered through celite, and analyzed by GC-MS and GC. A 50% GC yield of acrylamide **33** was observed.

c) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (31.3 mg, 0.20 mmol), 3.3% catalyst **3** (6.8 mg, 6.6 μmol) and 1-pentyne (30.0 μL, 0.30 mmol). The glass bomb was sealed, transferred to a vacuum line, and placed under nitrogen where **49** (10.0 μL, 0.10 mmol) was added. The reaction mixture was charged with 0.5 atm of CO gas and heated for 20 h at 90 °C. The resultant solution was degassed, filtered through celite, and analyzed by GC-MS and GC. A 40% GC yield of acrylamide **33** was observed.

d) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (31.0 mg, 0.20 mmol), 3.0% catalyst **3** (7.0 mg, 6.0 μmol) and 1-pentyne (30.0 μL, 0.30 mmol). The glass bomb was sealed, transferred to a vacuum line, and placed under nitrogen where **49** (20.0 μL, 0.20 mmol) was added. The reaction mixture was charged with 0.5 atm of CO gas and heated for 63 h at 75 °C. The resultant solution was degassed, filtered through celite, and analyzed by GC-MS and GC. A 65% GC yield of acrylamide **33** was observed.

1.7. References.

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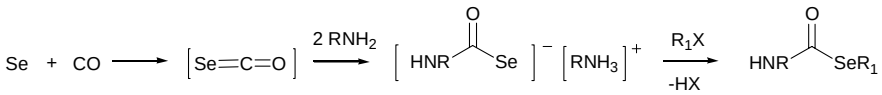
CHAPTER 2. THE TRANSITION METAL CATALYZED AZASELENOLATION OF CARBON MONOXIDE

2.1. Introduction.

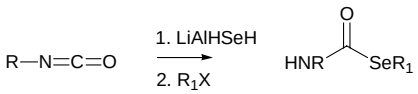
Due to the potential of Se-aryl selenocarbamates both as antiviral agents and as precursors for carbamoyl radicals, the development of new and simple methodology for their preparation is an important endeavor.[1,2] The synthetic applications of carbamoyl radicals is wide ranging. They have been used in the preparation of β-, γ-, and δ-lactams,[1,3,4] oxazolidine-2,4-diones,[5] and they have been shown to add to both aromatic rings[6-8] and to olefinic carbons.[9] They also have been used in the carbotelluration of acetylenes[10] and in the preparation of isocyanates.[11]

Previously unknown prior to 1979, Sonoda and co-workers reported the first preparation of Se-alkyl selenocarbamates.[12] The reaction was reported to proceed via the initial carbonylation of selenium followed by nucleophilic attack on the resulting carbonyl selenide by amine generating a carbamate ammonium salt; the salt was then alkylated at selenium with alkyl halide (Scheme 1). Although the reaction yields were moderate to excellent, 72-100%, only Se-alkyl selenocarbamates could be synthesized due to the dependence on alkylation as the final step. A second route to Se-alkyl selenocarbamates via the reaction of lithium alkyl selenides with amide chlorides was investigated, but the authors found that the carbamates were produced in poor yields.



Scheme 1. The first preparation of selenocarbamates

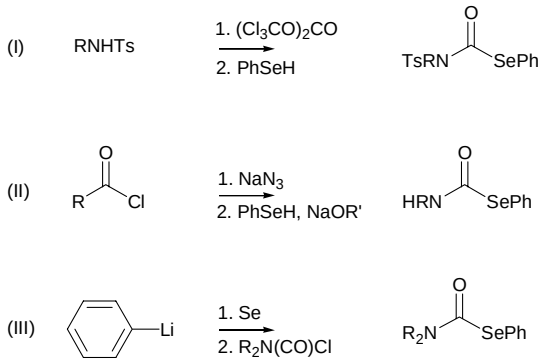
More recently, selenocarbamates have been accessed via the reductive selenylation of aromatic isocyanates by LiAlHSeH followed by alkylation of nucleophilic selenium with alkyl halide (Scheme 2).[13] Reaction yields are reported as high as 73%, but again, dependence upon alkylation as the final step limits the reaction to producing only Se-alkyl selenocarbamates.



Scheme 2. The reductive selenylation of aromatic isocyanates

The need for a final alkylation step as discussed in the previous methods has precluded the preparation of Se-aryl selenocarbamates, and only three methods have been reported for their synthesis, each suffering its own significant drawbacks. Rigby and co-workers have prepared such compounds by the *in-situ* formation of carbamoyl chloride from triphosgene and amine followed by reaction with selenophenol.[1] Although high yielding, the reaction conditions are less than desirable (Scheme 3, I). Barrett and co-workers have reported the synthesis of Se-aryl

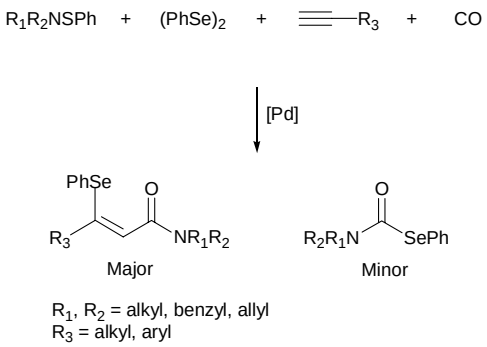
selenocarbamates based on the rearrangements of acyl azides in the presence of selenophenol.[14] Nevertheless, the reaction proceeds only in moderate 60-65% yield and requires the use of the noxious selenophenol (Scheme 3, II). Similar to the methodology first reported by Sonoda, Tour and co-workers were able to prepare Se-aryl selenocarbamates from the reaction of lithium aryl selenides with carbamoyl chlorides (Scheme 3, III).[15] Although Tour has avoided the toxic reagents encountered in the first two methods, reaction yields were unsatisfactorily low at 45%.



Scheme 3. Various methods for the synthesis of Se-aryl selenocarbamates

Given the synthetic utility of Se-aryl selenocarbamates coupled with the fact that few methods exist for their synthesis, it would be highly advantageous to develop new catalytic means for their preparation from simple and easily handled starting materials. As we have previously observed the production of Se-aryl selenocarbmates as byproducts in the synthesis of β-chalcogenyl acrylamides coupled with the selective incorporation of selenium over sulfur into

the β-chalcogenyl acrylamides (Scheme 4), we were confident that new catalytic methodology could be developed for their preparation.[16,17]



Scheme 4. The synthesis of β-selenyl acrylamides

2.2. Overview.

Herein, we report a new and chalcogenoselective rhodium catalyzed synthesis of Se-aryl selenocarbamates from $(PhSe)_2$, sulfenamide, and carbon monoxide. A catalytic cycle and the potential source of chalcogenoselectivity is proposed. Also discussed is the effect of several transition metal complexes on the azaselenolation and azatellurolation of carbon monoxide by sulfenamide. Finally, our attempts to develop a novel catalytic azasulfenylation of olefins is discussed.

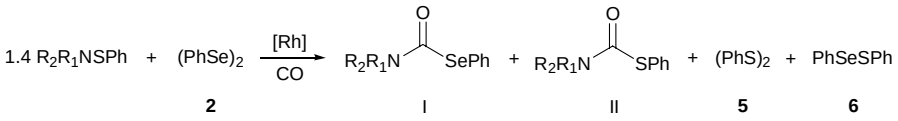
2.3 Results and Discussion.

2.3.1. The $RhCl(CO)(PPh_3)_2$ Catalyzed Azachalcogenation of Carbon Monoxide.

The reaction of 1.4 equivalents of S-phenyl-*N*-dimethyl sulfenamide, $PhSNMe_2$, (**1**) with one equivalent of $(PhSe)_2$ (**2**) in benzene under 0.5 atm of initial CO pressure at 80 °C in the presence of 5.5% Rh resulted in a modest 71 % GC yield of *N*-dimethyl phenyl selenocarbamate (**3**) based on sulfenamide **1** (Table 1). It should be noted that *N*-dimethyl phenyl thiocarbamate (**4**), $(PhS)_2$ (**5**), and the mixed diary dichalcogenide PhSSePh (**6**) were observed by GC/MS and GC as reaction byproducts. Based on the initial amounts of selenium and sulfur in the reaction mixture, a 1.4:1 product ratio of seleno- to thiocarbamate **3**:**4** was expected, but a dramatic increase in reaction selectivity to 9.1:1 seleno- to thiocarbamate **3**:**4** was observed.[18]

With the modest yield and favorable selenium selectivity obtained above, the tolerance of the reaction for different NR_2 groups was examined (Table 1). The reaction of 1.4 equivalents of S-phenyl-*N*-benzyl-*N*-methyl sulfenamide, PhSN(Bn)Me, (**7**) with one equivalent of $(PhSe)_2$ **2** in benzene under 0.5 atm of initial CO pressure at 80 °C in the presence of 6.8% Rh resulted in an excellent 89% GC yield of *N*-benzyl-*N*-methyl phenyl selenocarbamate (**8**) based on sulfenamide **7**. As in the previous experiment, a 9:1 product ratio of seleno- to thiocarbamate **8**:**9** was observed despite the initial 1.4:1 ratio of selenium and sulfur in the reaction mixture. Attempts to extend the reaction to include S-phenyl-*N*-diethyl sulfenamide, $PhSNEt_2$, (**10**) surprisingly produced only a 31% yield of selenocarbamate (**11**), but complete selectivity for the formation of selenocarbamate **11** was observed.

Table 1. The $RhCl(CO)(PPh_3)_2$ catalyzed azachalcogenation of carbon monoxide

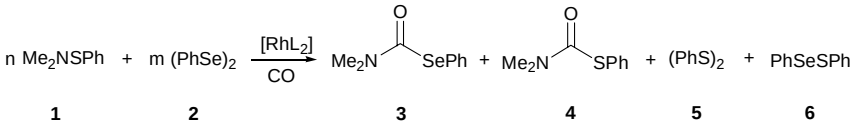


$PhSNR_1R_2$	Time, h	Solvent	Temperature, °C	% Yield, I[a]	% Yield, II[a]	Predicted Ratio I:II[b]	Observed Ratio I:II
$PhSNMe_2$	64	Bz	80	71	7.8	1.4:1	9.1:1
PhSN(Bn)Me	48	Bz	80	89	10.8	1.4:1	9:1
$PhSNEt_2$	64	Bz	85	31	0	1.4:1	----

a: Yields were determined by GC using the internal standards method (hexamethylbenzene). b: Predicted ratio was determined from the initial amounts of selenium and sulfur in the reaction mixture.

Having partially tested the reaction generality, the effects of altering the ligand sphere on yield and selectivity were then examined under nonoptimized reaction conditions. In order to achieve this goal, $RhCl(CO)(PCy_3)_2$ (**12**) was prepared and used in the azaselenolation of carbon monoxide by sulfenamide **1**.[19] Slightly higher yield and better selectivity was obtained in the synthesis of selenocarbamate **3** using $RhCl(CO)(PPh_3)_2$ (Table 2).

Table 2. The effect of phosphine ligand on the $RhCl(CO)L_2$ catalyzed azaselenolation of CO.



L	Temperature, °C	Time, h	% Yield, **3**[a]	% Yield, **4**[a]	Predicted Ratio **3**:**4**[b]	Observed Ratio **3**:**4**
PPh_3	105	6	28	3.7	1:1	7:1
PCy_3	105	6	20	3.5	1:1	5.7:1

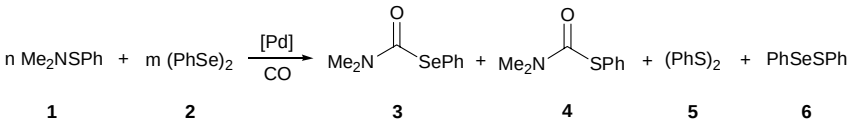
a: Yields were determined by GC using the internal standard method (hexamethylbenzene). b: Predicted ratios were determined from the initial amounts of selenium and sulfur in the reaction mixture.

2.3.2. The Palladium Catalyzed Azachalcogenation of Carbon Monoxide.

Both $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ were found to be poor catalysts for the azaselenolation of carbon monoxide. The reaction of one equivalent of *N*-dimethyl-S-phenyl sulfenamide, Me_2NSPh, **1** with one equivalent of $(PhSe)_2$ **2** in pyridine under 0.5 atm of initial CO pressure at 65 °C resulted in poor yields of both *N*-dimethyl phenyl selenocarbamate **3** and *N*-dimethyl thiocarbamate **4** based on sulfenamide **1**, 6 and 12% respectively (Table 3, entry 1). It should be noted that both $(PhS)_2$ **5** and the mixed diaryl dichalcogenide PhSSePh **6** were observed by GC/MS and GC as reaction byproducts. Based on the initial amounts of selenium and sulfur in the reaction mixture, a 2:1 product ratio of seleno- to thiocarbamate **3**:**4** was expected, but the reverse chalcogeno selectivity was observed. Such selectivity for the formation of thiocarbamate **4** is not surprising when it is considered that the related palladium catalyzed azathiolation of carbon monoxide is known to proceed efficiently *only* in pyridine.[20] An improved 45% yield of carbamate **3** was obtained by performing the reaction in benzene, an azathiolation suppressing

solvent, at 85 °C. Nevertheless, slight chalcogeno selectivity for thiocarbamate **4** was still observed (entry 2). In another azathiolation suppressing solvent, toluene, at 80 °C, favorable formation of carbamate **3** was observed but in only a 35% yield (entry 3). Upon increasing the reaction temperature to 105-110 °C in benzene or toluene, poor yields of carbamate **3** were encountered (entries 4-7). In all cases, large catalyst loadings were necessary to achieve even modest yields and selectivities, and thus, $Pd(PPh_3)_4$ was found to be an unacceptable catalyst for the desired transformation. In addition, $Pd_2(dba)_3$ also failed to produce useful results (entry 8).

Table 3. The Pd catalyzed azachalcogenation of carbon monoxide



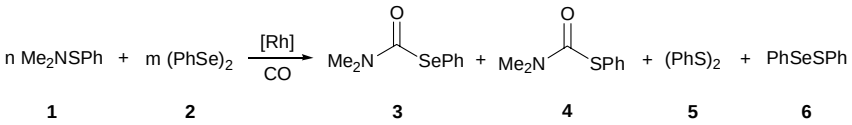
Entry[a]	Solvent	Temperature, °C	% Yield, **3**[b]	% Yield, **4**[b]	Predicted Ratio **3**:**4**[c]	Observed Ratio **3**:**4**
1	Pyr	65	6	12	2:1	1:2
2	Bz	80	45	15	4:1	3:1
3	Tol	80	35	12.5	2:1	2.8:1
4	Bz	105	22	22	4:1	1:1
5	Bz	105	22	8.7	2:1	2.5:1
6	Bz	110	30	15	1:1	2:1
7	Tol	110	25	20	1:1	1.3:1
8[d]	Pyr	70	7.5	15	2:1	1:2

a: All reactions run for 24 h unless otherwise indicated. b: Yields were determined by GC using the internal standards method (hexamethylbenzene). c: Predicted ratios were determined from the initial amounts of selenium and sulfur in the reaction mixture. d: $Pd_2(dba)_3$.

2.3.3. The $[Cl(COD)Rh]_2$ Catalyzed Azachalcogenation of Carbon Monoxide.

$[Cl(COD)Rh]_2$ was found to be a poor catalyst for the azaselenolation of carbon monoxide. The reaction of two equivalents of sulfenamide **1** with one equivalent of $(PhSe)_2$ **2** in benzene under 0.5 atm of initial CO pressure at 25 °C resulted in low yields of *N*-dimethyl phenyl selenocarbamate **3** and *N*-dimethyl thiocarbamate **4** based on sulfenamide **1**, 32.5 and 16%, respectively (Table 4, entry 1). It should be noted that both $(PhS)_2$ **5** and the mixed diary dichalcogenide PhSSePh **6** were observed by GC/MS and GC as reaction byproducts. Based on the initial amounts of selenium and sulfur in the reaction mixture, a 1:1 product ratio of seleno- to thiocarbamate **3**:**4** was expected, but in this case, the formation of selenocarbamate **3** was slightly favored. Similar results were obtained upon repeating this experiment (entry 2). Reducing the number of equivalents of sulfenamide **1** and the reaction time resulted in a slight improvement in both yield and selectivity for the formation selenocarbamate **3** (entry 3) whereas increasing the reaction temperature from 25 °C to 55-65 °C produced low 25-26% yields of carbamate **3** (entries 4 & 5). Lowering the reaction temperature below 25 °C provided moderate selectivity for selenocarbamate formation, but poor yields, 9.5-12.5%, were encountered (entries 6 & 7). The best yield of carbamate **3**, 40%, was obtained at short reaction time at higher temperatures, but both this yield and the observed selectivity were not satisfactory (entry 8). In the hopes of removing $(PhS)_2$ from the reaction and hence reduce the likelihood of the formation of thiocarbamate **4**, $AgNO_3$ was added to the reaction mixture.[21] No effect on reaction selectivity was observed (entry 9). In all cases, large catalyst loadings were necessary to achieve even modest yields and selectivities, and thus, $[Cl(COD)Rh]_2$ was found to be an unacceptable catalyst for the desired transformation.

Table 4. The $[Cl(COD)Rh]_2$ catalyzed azachalcogenation of carbon monoxide



Entry[a]	Time, h	Temperature, °C	% Yield, **3**[b]	% Yield, **4**[b]	Predicted Ratio **3**:**4**[c]	Observed Ratio **3**:**4**
1	24	25	32.5	16	1:1	2:1
2	24	25	30	15	1:1	2:1
3	17	25	38	14	2:1	2.7:1
4	17	65	26.3	17.5	1:1	1.5:1
5	19	55	25	14.1	1:1	1.8:1
6	17	10	9.5	2.7	1:1	3.5:1
7	19	19	12.5	5.8	1:1	2.1:1
8	3	87	40	15	2:1	2.7:1
9[d]	22	25	20	10	1:1	2:1

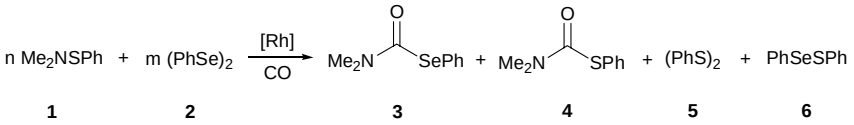
a: All reactions run in benzene unless otherwise indicated. b: Yields were determined by GC using the internal standards method (hexamethylbenzene). c: Predicted ratios were determined from the initial amounts of selenium and sulfur in the reaction mixture. d: Run in the presence of $AgNO_3$.

2.3.4. The $RhCl(PPh_3)_3$ Catalyzed Azachalcogenation of Carbon Monoxide.

$RhCl(PPh_3)_3$ was found to be a poor catalyst for the azaselenolation of carbon monoxide. The reaction of one equivalent of sulfenamide **1** with one equivalent of $(PhSe)_2$ **2** in pyridine under 0.5 atm of initial CO pressure at 70 °C in the presence of 20% Rh resulted in low yields of both *N*-dimethyl phenyl selenocarbamate **3** and *N*-dimethyl thiocarbamate **4** based upon sulfenamide **1**, 20 and 15% respectively (Table 5, entry 1). It should be noted that both $(PhS)_2$ **5** and the mixed diary dichalcogenide PhSSePh **6** were observed by GC/MS and GC as reaction byproducts. Based on the initial amounts of selenium and sulfur in the reaction mixture, a 2:1 product ratio of seleno- to thiocarbamate **3**:**4** was expected, but in this case, only a 1.3:1 ratio was observed. By reducing the amount of catalyst to 10%, an increase in yield to 30% of

carbamate **3** was observed with a concomitant increase in the reaction selectivity for selenocarbamate **3** (entry 2). With 20% catalyst in benzene at 70 °C, yields were halved relative to pyridine but reaction selectivities were similar (entries 3 & 4). The mixing of pyridine and benzene with variable amounts of catalyst failed to produce significant results (entries 5-7); in addition, performing the reaction at room temperature in pyridine yielded only trace amounts of carbamate **3** (entry 8). A dramatic increase in the selectivity for the formation of selenocarbamate **3** was observed in benzene at higher temperatures with 6% catalyst (entries 9 & 10). Nonetheless, yields were still unacceptably low, 23 and 5% respectively. Based upon these findings, $RhCl(PPh_3)_3$ was found to be a poor catalyst for the desired transformation.

Table 5. The $RhCl(PPh_3)_3$ catalyzed azachalcogenation of carbon monoxide.



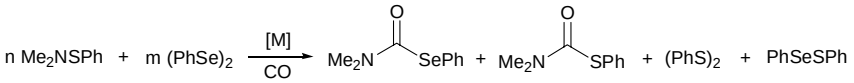
Entry[a]	Solvent	Temperature, °C	% Yield, **3**[b]	% Yield, **4**[b]	Predicted Ratio **3**:**4**[c]	Observed Ratio **3**:**4**
1[d]	Pyr	70	20	15	2:1	1.3:1
2[e]	Pyr	70	31	13	2:1	2.4:1
3	Bz	70	9.5	8	2:1	1.2:1
4	Bz	70	8	6	2:1	1.3:1
5[d]	Bz/Pyr	70	14	4.5	2:1	3.1:1
6[e]	Bz/Pyr	70	12.5	5	2:1	1.3:1
7[f]	Bz/Pyr	50	10	4.5	2:1	2.2:1
8	Pyr	25	3	3	2:1	1:1
9	Bz	110	23	2.3	1:1	10:1
10	Bz	110	5.1	0.4	1:1	13:1

a: All reactions run for 24 h unless otherwise indicated. b: Yields were determined by GC using the internal standards method (hexamethylbenzene). c: Predicted ratios were determined from the initial amounts of selenium and sulfur in the reaction mixture. d: 20% Rh. e: 10% Rh. f: 2.5% Rh.

2.3.5. The Miscellaneous Transition Metal Catalyzed Azachalcogenation of Carbon Monoxide.

The azaselenolation of carbon monoxide by sulfenamide **1** was tested using various Pt, Ir, and Rh complexes (Table 6). In all cases, $Pt(PPh_3)_4$, $[Cp^*IrCl_2]_2$, and $Cp^*Ir(CO)_2$ (**13**) produced only trace or no selenocarbamate **3**. Interestingly, thiocarbamate **4** was not detected in any of the reactions. $(CO)_2Rh(acac)$ also failed to produce significant yields of either carbamate **3** or **4**.

Table 6. The miscellaneous transition metal catalyzed azachalcogenation of carbon monoxide



1 2 3 4 5 6

Entry[a]	[M]	Temperature, °C	Time, h	% Yield, **3**[b]	% Yield, **4**[b]
1	$Pt(PPh_3)_4$	110	1	trace	0
2	$Pt(PPh_3)_4$	110	24	trace	0
3	$[Cp^*IrCl_2]_2$	70	24	0	0
4	$Cp^*Ir(CO)_2$	70	24	trace	0
5	$(CO)_2Rh(acac)$	127	20	12.5	4.2

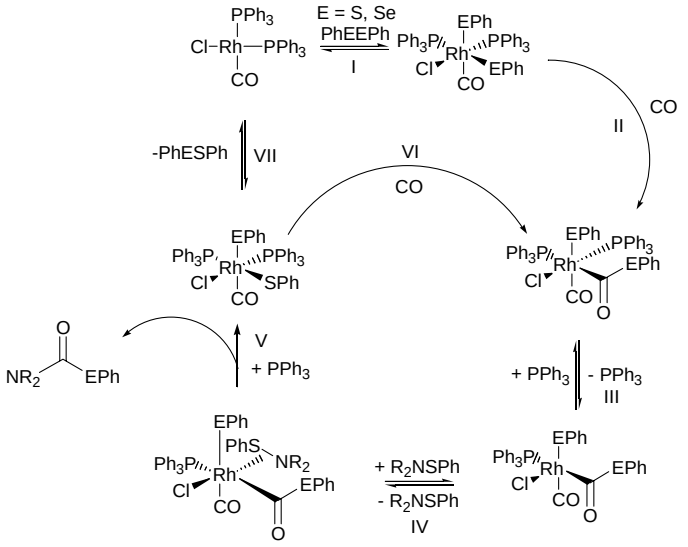
a: All reactions run in benzene unless otherwise indicated. b: Yields were determined by GC using the internal standards method (hexamethylbenzene).

2.3.6. Catalytic Cycle and Reaction Selectivity.

Based upon mechanistic work previously reported on the reactivity of the transition metals with diaryl dichalcogenides coupled with our own observations,[17,22-25] it is reasonable to propose that the formation of selenocarbamates proceeds according to the following catalytic cycle (Scheme 6): oxidative addition (I) of $(PhSe)_2$ generates a Rh(IV) diselenolate species that inserts CO via

selenorhodation (II) to yield a transient rhodium acyl intermediate. This intermediate then undergoes the loss of phosphine (III) to give a coordinatively unsaturated rhodium species. Coordination of sulfenamide (IV) in the appropriate geometry followed by σ-bond metathesis (V)[20] then proceeds to yield both selenocarbamate and a mixed rhodium thiolate selenolate species. The catalyst can then re-enter the cycle by either reductive elimination (VII) or by direct insertion of CO (VI) into either the Rh-SPh or Rh-SePh bond. Species **3**, **4**, **5** and **6** encountered in the workup of reactions involving sulfenamide **1** are accounted for in this proposed catalytic cycle.

Some insight into the catalytic cycle was obtained by changing the ligand from PPh_3 to larger and better σ-donor PCy_3. This change would be expected to both facilitate the oxidative addition of $(PhSe)_2$ (I) and the migratory insertion of CO (II). However, only a slight difference in yield was observed after 6 h thus suggesting that neither of the above steps are rate limiting in the formation of selenocarbamate. This result is in contrast to our findings that migratory CO insertion is the rate limiting step in the palladium catalyzed synthesis of β-selenyl acrylamides.



Scheme 5. The proposed catalytic cycle for the $RhCl(CO)(PPh_3)_2$ catalyzed preparation of selenocarbamates

The most favorable aspect of the $RhCl(CO)(PPh_3)_2$ as a catalyst is the selective formation of seleno- over thiocarbamate. This observed selectivity most likely arises from either the selective oxidative addition of $(PhSe)_2$ over $(PhS)_2$ to rhodium or the favorable insertion of CO into Rh-SePh bonds over that of Rh-SPh bonds with the later being comparable to the selective insertion of alkyne into the Pd-SePh over Pd-SPh bonds.[16,17, 26]

As with the preparation of β-selenyl acrylamides, the concentrations of both $(PhS)_2$ and $(PhSe)_2$ possibly play an important role in reaction selectivity as the concentration of $(PhSe)_2$ is expected to decrease and the concentration of $(PhS)_2$ to increase with reaction time. It should be noted though that this type of selectivity dependence would only be observed if both dichalcogenides were to equally oxidatively add to the rhodium catalyst. In order to address this effect of chalcogeno concentration, a ^1H NMR experiment was conducted in which the

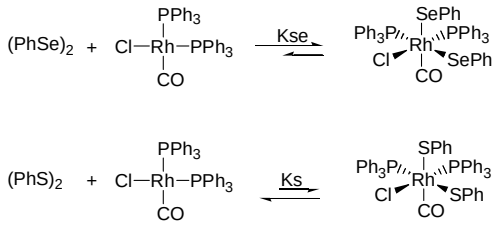
concentrations of seleno- and thiocarbamates **3** and **4** were measured as a function of time. In contrast to our previous findings with β-selenyl acrylamides, we observed the reaction selectivity for the formation of selenocarbamate **3** to increase with reaction time even though $(PhS)_2$ concentration was concomitantly increasing. This most likely indicates that the rhodium catalyst selectively oxidatively adds $(PhSe)_2$ over $(PhS)_2$. To address this question of selective oxidative addition, the azaselenolation of CO by sulfenamide **1** was performed under nonoptimized reaction conditions in the presence of 0.5 equivalents of $(PhS)_2$, and the reaction selectivity was compared to a control experiment run in the absence of $(PhS)_2$. *The same selective formation of selenocarbamate **3** was observed in the presence and absence of excess $(PhS)_2$* (Table 7).

Table 7 The effect of $(PhS)_2$ concentration on the selective formation of selenocarbamate **3**

Additive	Solvent	Temperature, °C	% Yield, **3**[a]	% Yield, **4**[a]	Observed Ratio **3**:**4**
none	Bz	110	36.3	9.1	4:1
$(PhS)_2$	Bz	110	44.4	11.1	4:1

a: Yields were determined by GC using the internal standards method (hexamethylbenzene).

The results discussed above suggest that the equilibrium describing the oxidative addition of $(PhSe)_2$ to $RhCl(CO)(PPh_3)_2$ (K_{se}) lies towards the formation of the catalytically active rhodium diselenolate whereas the related sulfur based equilibrium (K_s) favors starting $RhCl(CO)(PPh_3)_2$ and $(PhS)_2$ (Scheme 6). Thus, if Kse >> Ks, the selective formation of selenocarbamate over thiocarbamate would be expected even in the presence of excess $(PhS)_2$.



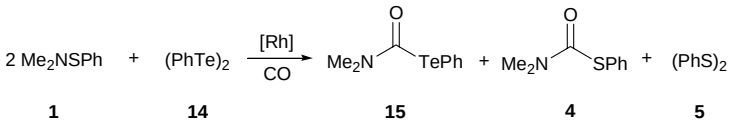
Scheme 6. Equilibrium for the oxidative addition of the diaryl dichalcogenides to $RhCl(CO)(PPh_3)_2$

Given our previous findings that CO insertion into vinyl palladium chalcogenates plays a key role in the reaction selectivity for the formation of β-selenyl over β-sulfenyl acrylamides coupled with the work of Arisawa on the differing insertion rates of alkynes into rhodium selenolate and thiolate bonds, a difference in the insertion rates of CO into the Rh-SePh and Rh-SPh bonds may exist.[17,26] Favorable selenorhodation of CO would be expected to result in a greater concentration of rhodium acyl selenolate relative to rhodium acyl thiolate thus leading to the observed selective formation of seleno- over thiocarbamate provided that the rates of σ-bond metathesis are the same for both rhodium acyl chalcogenates. A more detailed investigation into the role of CO in determining reaction selectivity must be carried in order to address these questions.

2.3.7. Tellurocarbamates.

In an attempt to extend the reaction methodology to include tellurocarbamates,[27-29] $(PhTe)_2$ (**14**) was substituted for $(PhSe)_2$ **2**. The reaction of two equivalents of sulfenamide **1** and one

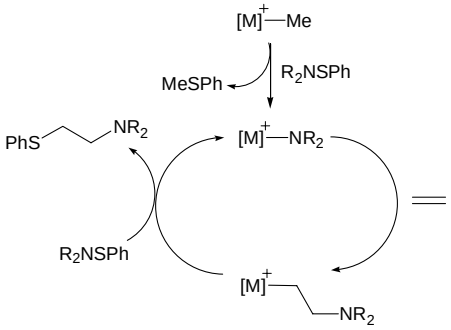
equivalent of $(PhTe)_2$ **14** in benzene under 0.5 atm of CO pressure at 85 °C for 24 h in the presence of 5% $ClRh(PPh_3)_3$ failed to produce either thiocarbamate **4** or telluryl carbamate **15** (Scheme 7). The failure to produce any product most likely is the result of the formation of rhodium telluride catenates as evidenced by the presence of an insoluble metallic coating on the reaction vessel.



Scheme 7. The attempted preparation of tellurocarbamate **15**

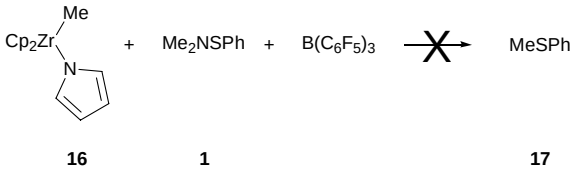
2.3.8. Miscellaneous Observations: Transition Metal Catalyzed Olefin Azasulfenylation.

As sulfenamides have been used in the Lewis acid mediated azasulfenylation of olefins, we were interested in developing a metal catalyzed version of such a reaction. [30-33] We envisioned the reaction proceeding according to the following catalytic cycle (Scheme 8):[34]



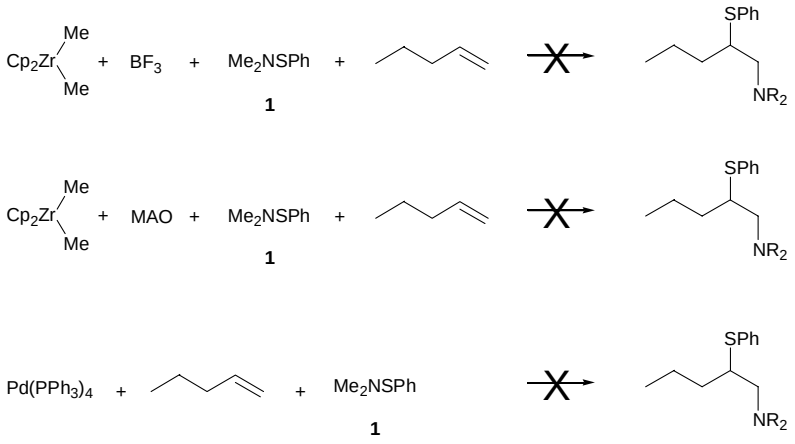
Scheme 8. The proposed catalytic cycle for olefin azasulfenylation

Our initial hopes were to utilize thorium cations derived from thorocenes but concerns over radioactivity precluded their use. Instead the more commonly encountered zirconocene catalysts were employed. Methyl(*N*-pyrrole)zirconocene (**16**) was prepared and reacted with $B(C_6F_5)_3$ in the presence of sulfenamide **1** to determine if initiation into the catalytic cycle was possible. (Scheme 9). Unfortunately, MeSPh (**17**) was not detected by either ^1H NMR or GC-MS.



Scheme 9. The reaction of zirconocene **16** with sulfenamide **1** in the presence of $B(C_6F_5)_3$

Even though initiation into the proposed catalytic cycle was not observed with zirconocene **16**, we next proceeded to the test the azasulfenylation of 1-pentene with the cations derived from $Cp_2Zr(Me)_2$ as well as with $Pd(PPh_3)_4$. Under no conditions were the azasulfenylated products detected by either ^1H NMR or GC-MS (Scheme 10).



Scheme 10. The attempted catalytic azasulfenylation of 1-pentene by sulfenamide **1**

2.4. Experimental Section.

General Methods: Benzene, toluene, ethanol, benzene-d_6 and toluene-d_8 were distilled under nitrogen from sodium. Pyridine, $CHCl_3$, *n*-pentane, Et_2O, diethyl amine, and *N*-benzyl-*N*-methyl amine were distilled under nitrogen from calcium hydride. All transition metal catalysts were commercially obtained from Strem and stored in a nitrogen filled glovebox save for $Cp^*Ir(CO)_2$ **7** and $RhCl(CO)(PCy_3)_2$ **13**. Carbon monoxide and $(PhSe)_2$ **2** were purchased and used without further purification. $(PhS)_2$ **5** was recrystallized from methanol and dried at 30 °C.

^{1}H-, ^{13}C- and ^{31}P NMR (300, 75 and 17.2 MHz) were recorded with Bruker spectrometers. Chemical shifts were referenced to residual ^{1}H or ^{13}C signals in deuterated solvents. IR spectra were obtained on a Perkin Elmer Spectrum BX FT-IR system. Column chromatography was performed using Sorbent 60 32-60 standard grade silica gel and/or activated neutral Brockmann I alumina standard grade gel. Gas chromatography-mass spectrometry (GC/MS) was performed on a Hewlett Packard Series 5980 GC/5971 A MS with a Hewlett Packard Series 1 capillary column. Gas chromatography (GC) was performed on a Hewlett Packard Series 6850 GC with a Hewlett Packard Series 1 methyl siloxane column.

2.4.1. The Synthesis of Sulfenamides and Thiocarbamate 4.

S-Phenyl-*N*-dimethyl-sulfenamide (1): According to the method of Davis *et al*.,[21] silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, $(PhS)_2$ **5** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. Dimethyl amine (11.5 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **1** (400 mg, 2.60 mmol) in 57% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.53 (s, 6 H), 6.93-7.37 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 48.3, 127.1, 128.8, 129.9, 137.2; MS (EI), *m/z* 153 (M^+), 138, 109, 77, 65.

S-Phenyl-*N*-benzyl-*N*-methyl-sulfenamide (7): According to the method of Davis *et al*.,[21] silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom

flask. Upon dissolution, $(PhS)_2$ **5** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. *N*-benzyl-*N*-methyl amine (3.0 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **7** (209 mg, 2.0 mmol) in 43% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.51 (s, 3 H), 3.87 (s, 2 H), 6.95-7.35 (m, 10 H); ^{13}C NMR (75 MHz, C_6D_6) δ 45.2, 65.1, 127.0, 128.6, 128.7, 128.9, 138.2, 138.8; MS (EI), *m/z* 229 (M^+), 138, 109, 91, 77, 65.

S-Phenyl-*N*-diethyl-sulfenamide (10): According to the method of Davis *et al*.,[21] silver nitrate (780 mg, 4.60 mmol) in 70 mL methanol was placed in a 250 mL round bottom flask. Upon dissolution, $(PhS)_2$ **5** (1.0 g, 4.6 mmol) was added, and the reaction mixture was immediately cooled in an ice bath. Diethylamine (1.2 mL, 23.0 mmol) was added and the reaction stirred overnight. The silver mercaptide salt was removed by filtration and the solvent removed *in vacuo*. The resulting orange residue was dissolved in ether, washed with water (4 x 25 mL), dried over $MgSO_4$, and the solvent removed *in vacuo*. Column chromatography on alumina (5% ethyl acetate/hexanes) yielded pure sulfenamide **10** (507 mg, 2.80 mmol) in 60% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 1.08 (t, *J = 7.0 Hz*, 6 H), 2.79 (q, *J = 7.0 Hz*, 4 H), 6.92-7.35 (m, 5 H); ^{13}C NMR (75 MHz, C_6D_6) δ 13.8, 53.4, 125.0, 125.5, 128.8, 142.1; MS (EI), *m/z* 181 (M^+), 166, 109, 77, 65.

***N*-Dimethyl phenyl thiocarbamate (4):** According to the method of Kuniyasu and co-workers,[20] to a stainless steel reaction vessel with glass insert in a nitrogen filled glovebox were added S-phenyl-*N*-dimethyl sulfenamide **1** (40.0 mg, 0.26 mmol), 5.6% $Pd(PPh_3)_4$ (13.0 mg, 11.2

μmol) and pyridine (2 mL). The reaction mixture was charged with 28 atm of carbon monoxide gas and heated for 24 h at 90 ˚C with stirring. The resultant solution was degassed, filtered through celite, and reduced *in vacuo*. The crude reaction mixture was purified by column chromatography using hexanes, methanol to yield the red oil (**4**) (38.0 mg, 0.21 mmol) in 80% yield. ^{1}H NMR (300 MHz, C_6D_6) δ 2.27 (bs., 6 H), 6.83-7.75 (m, 5 H); MS (EI), *m/z* 181 (M^+), 109, 77, 72 (base), 65.

2.4.2. The Synthesis of Transition Metal Complexes 12 and 13.

Chlorocarbonylrhodiumbis(tricyclohexylphosphine) (12): According to the method of Uson *et al*.,[19] PCy_3 (149.0 mg, 0.53 mmol) in 5 mL $CHCl_3$ was added to a 10 mL $CHCl_3$ solution of $RhCl(CO)(PPh_3)_2$ (171.0 mg, 0.25 mmol). The mixture was refluxed under nitrogen for 2 h and then concentrated to an oil. The addition of *n*-pentane precipitated the yellow complex which was filtered, washed with *n*-pentane and Et_2O, and air dried to give catalyst **13** in both *cis* and *trans* isomers (79.0 mg, 0.11 mmol) in 44% yield. ^{31}P NMR (C_6D_6) δ 37.6, 38.6, 40.0, 41.0.

Dicarbonyl(pentamethylcyclopentadienyl)iridium (13): According to the method of Kang *et al*.,[35] carbon monoxide was bubbled into a suspension of $[Cp^*IrCl_2]_2$ (100.0 mg, 0.13 mmol), $Fe_2(CO)_9$ (68.0 mg, 0.19 mmol) and Na_2CO_3 (50.0 mg, 0.5 mmol) in 30 mL ethanol at 70 °C for 3 h. The yellow, orange solution was filtered and reduced *in vacuo* yielding a dark red oil. The residue was extracted with benzene and the solvent removed *in vacuo*. The residue was purified by column chromatography on silica (benzene) yielding catalyst **7** (26 mg, 0.07 mmol) in 59% yield. IR (υ_{CO}) 1925, 2000 cm^{-1}.

2.4.3. The Azachalcogenation of Carbon Monoxide.

General procedure for the azaselenolation of carbon monoxide: To a glass bomb in a nitrogen filled glovebox were added varying equivalents of sulfenamide, $(PhSe)_2$ and catalyst in benzene, toluene or pyridine. The reaction mixture was charged with 0.5 atm of CO gas and heated for 40-60 h at the desired temperature with stirring. The resultant solution was degassed, filtered through celite and analyzed by GC/MS and GC. The amounts of seleno- and thiocarbamate were determined using the internal standards method (hexamethylbenzene).

2.4.3.a The $RhCl(CO)(PPh_3)_2$ Catalyzed Azachalcogenation of Carbon Monoxide.

1) *N*-Dimethyl phenyl selenocarbamate (3): To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (43 mg, 0.28 mmol), **2** (64 mg, 0.20 mmol) 5.5% $RhCl(CO)(PPh_3)_2$ (8.0 mg, 11.0 μmol) and benzene (4.0 mL).[17,18] The reaction mixture was charged with 0.5 atm of CO gas and heated for 64 h at 85 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. The following molar amounts of carbamates and yields based on sulfenamide were determined by GC: **3** (0.20 mmol, 71%); **4** (0.022 mmol, 7.8%). Also observed by GC were the following species with their corresponding molar amounts: $(PhSe)_2$ **2** (0.06 mmol), $(PhS)_2$ **5** (0.14 mmol), and PhSSePh **6** (0.015 mmol). The crude reaction mixture was partially purified via column chromatography (5% ethyl acetate/hexanes, methanol) to yield a mixture of carbamates **3** and **4**. **3:** ^{1}H NMR (300 MHz, C_6D_6) δ 2.44 (br.s, 6 H), 6.83-7.75 (m, 5 H); MS (EI), *m/z* 229 (M^+), 157, 77, 72 (base), 65. **4**: ^{1}H NMR (300 MHz, C_6C_6) δ 2.27 (br.s, 6 H), 6.83-7.75 (m, 5 H); MS (EI), *m/z* 181 (M^+), 109, 77, 72 (base), 65.

2) *N*-Benzyl-*N*-methyl phenyl selenocarbamate (8): To a glass bomb in a nitrogen filled glovebox were added sulfenamide **7** (46.6 mg, 0.203 mmol), **2** (45.9 mg, 0.146 mmol), 6.8% $RhCl(CO)(PPh_3)_2$ (9.7 mg, 14.0 μmol) and benzene (3.0 mL).[18] The reaction mixture was charged with 0.5 atm of CO gas and heated for 42 h at 80 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. The following molar amounts of carbamates and yields based on sulfenamide were determined by GC: **8** (0.181 mmol, 89.1 %); **9** (0.022 mmol, 10.8%). Also observed by GC were the following species with their corresponding molar amounts: $(PhSe)_2$ **2** (0.075 mmol) and $(PhS)_2$ **5** (0.09 mmol). The crude reaction mixture was partially purified via column chromatography (hexanes, methanol) to yield a mixture of carbamates **8** and **9**. Two isomers of each carbamate were observed at room temperature, but coalesced above 80 °C. ^{1}H NMR data is reported at 80 °C. **8**: ^{1}H NMR (300 MHz, d_8-tol, 353 K) 2.56 (s, 3 H), 4.23 (s, 2 H), 7.03-7.64 (m, 10 H); MS (EI), *m/z* 305 (M^+), 157, 148, 91 (base), 77, 65, 51. **9**: ^{1}H NMR (300 MHz, d_8-tol) 2.68 (s, 3 H), 4.31 (s, 2 H), 7.03-7.64 (m, 10 H); MS (EI), *m/z* 305 (M^+), 248, 157, 148, 91 (base), 77, 65, 51.

3) *N*-Diethyl phenyl selenocarbamate (11): To a glass bomb in a nitrogen filled glovebox were added sulfenamide **10** (52.7 mg, 0.291 mmol), **2** (67.0 mg, 0.21 mmol), 3.8% $RhCl(CO)(PPh_3)_2$ (8.0 mg, 11.0 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 64 h at 85 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. A 31% GC yield of carbamate **11** (0.09 mmol) was observed. Also observed by GC were the following species with their corresponding molar amounts: $(PhSe)_2$ **2** (0.16 mmol); $(PhS)_2$ **5** (0.08 mmol); PhSSePh **6** (0.02 mmol); Et_2NSPh **10** (0.12 mmol).

2.4.3.b The Comparative Azachalcogenation of Carbon Monoxide by Sulfenamide 1 Catalyzed by $RhCl(CO)(PPh_3)_2$ and $RhCl(CO)(PCy_3)_2$:

1) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (29.0 mg, 0.19 mmol), **2** (30.0 mg, 0.10 mmol) 3.4% $RhCl(CO)(PPh_3)_2$ (4.5 mg, 6.5 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 6 h at 105 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. A 28% GC yield of carbamate **3** (0.05 mmol) was observed. Carbamate **4** was observed in a 3.7% GC yield (0.007 mmol).

2) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (31.0 mg, 0.20 mmol), **2** (30.7 mg, 0.10 mmol) 2.6% $RhCl(CO)(PCy_3)_2$ **12** (4.5 mg, 5.0 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 6 h at 105 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. A 20% GC yield of carbamate **3** (0.04 mmol) was observed. Carbamate **4** was observed a in 3.5% GC yield (0.007 mmol).

2.4.3.c The Palladium Catalyzed Azachalcogenation of Carbon Monoxide.

1) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 10% $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 65 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.012 mmol, 6%); **4**: (0.024 mmol, 12%).

2) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (131.8 mg, 0.42 mmol), 10% $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and benzene (3.2 mL). The reaction

mixture was charged with 0.5 atm of CO gas and heated for 24 h at 80 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.09 mmol, 45%); **4**: (0.03 mmol, 15%).

3) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (69.1 mg, 0.22 mmol), 10% $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and toluene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 80 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.07 mmol, 35%); **4**: (0.025 mmol, 12.5%).

4) To a glass bomb in a nitrogen filled glovebox were added **1** (35.2 mg, 0.23 mmol), **2** (125.6 mg, 0.4 mmol), 10% $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and benzene (3.3 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 105 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.05 mmol, 22%); **4**: (0.05 mmol, 22%).

5) To a glass bomb in a nitrogen filled glovebox were added **1** (35.2 mg, 0.23 mmol), **2** (62.8 mg, 0.2 mmol), 10% $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and benzene (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 105 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.05 mmol, 22%); **4**: (0.02 mmol, 8.7%).

6) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (37.7 mg, 0.12 mmol), 10% $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 110 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.06 mmol, 30%); **4**: (0.03 mmol, 15%).

7) To a glass bomb in a nitrogen filled glovebox were added **1** (35.2 mg, 0.23 mmol), **2** (31.4 mg, 0.1 mmol), 10% $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and toluene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 110 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.05 mmol, 25%); **4**: (0.04 mmol, 20%).

8) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 20% Pd_2dba_3 (36.6 mg, 0.04 mmol) and pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.015 mmol, 7.5%); **4**: (0.03 mmol, 15%).

2.4.3.d The $[Cl(COD)Rh]_2$ Catalyzed Azachalcogenation of Carbon Monoxide.

1) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (31.4 mg, 0.1 mmol), 9% $[Cl(COD)Rh]_2$ (8.87 mg, 0.018 mmol) and benzene (3.0 mL). The reaction

mixture was charged with 0.5 atm of CO gas and stirred at 25 °C for 22.5 h. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.065 mmol, 32.5%); **4**: (0.032 mmol, 16%).

2) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (31.4 mg, 0.1 mmol), 8.7% $[Cl(COD)Rh]_2$ (8.5 mg, 0.017 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 25 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.06 mmol, 30%); **4**: (0.03 mmol, 15%).

3) To a glass bomb in a nitrogen filled glovebox were added **1** (15.3 mg, 0.1 mmol), **2** (31.4 mg, 0.1 mmol), 19% $[Cl(COD)Rh]_2$ (9.4 mg, 0.019 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and stirred at 25 °C for 17 h. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.038 mmol, 38%); **4**: (0.014 mmol, 14%).

4) To a glass bomb in a nitrogen filled glovebox were added **1** (36.7 mg, 0.24 mmol), **2** (31.4 mg, 0.1 mmol), 10% $[Cl(COD)Rh]_2$ (11.8 mg, 0.024 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 17 h at 65 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.063 mmol, 26.3%); **4**: (0.042 mmol, 17.5%).

5) To a glass bomb in a nitrogen filled glovebox were added **1** (36.7 mg, 0.24 mmol), **2** (31.4 mg, 0.1 mmol), 14.4% $[Cl(COD)Rh]_2$ (17.0 mg, 0.034 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 19 h at 55 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.06 mmol, 25%); **4**: (0.034 mmol, 14.1%).

6) To a glass bomb in a nitrogen filled glovebox were added **1** (33.6 mg, 0.22 mmol), **2** (31.4 mg, 0.1 mmol), 12% $[Cl(COD)Rh]_2$ (13.0 mg, 0.026 mmol) and benzene (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and stirred at 10 °C for 17 h. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.021 mmol, 9.5%); **4**: (0.006 mmol, 2.7%).

7) To a glass bomb in a nitrogen filled glovebox were added **1** (36.7 mg, 0.24 mmol), **2** (31.4 mg, 0.1 mmol), 14.4% $[Cl(COD)Rh]_2$ (17.0 mg, 0.034 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and stirred for 19 h at 19 °C. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.03 mmol, 12.5%); **4**: (0.014 mmol, 5.8%).

8) To a glass bomb in a nitrogen filled glovebox were added **1** (15.3 mg, 0.1 mmol), **2** (31.4 mg, 0.1 mmol), 18% $[Cl(COD)Rh]_2$ (17.8 mg,0.036 mmol) and benzene (3.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 3 h at 87 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts

of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.04 mmol, 40%); **4**: (0.015 mmol, 15%).

9) To a glass bomb in a nitrogen filled glovebox were added **1** (27.5 mg, 0.18 mmol), **2** (31.4 mg, 0.1 mmol), 8.7% $[Cl(COD)Rh]_2$ (11.8 mg, 0.024 mmol), $AgNO_3$ (40.7 mg, 0.24 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 25 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.04 mmol, 20%); **4**: (0.02 mmol, 10%).

2.4.3.e The $ClRh(PPh_3)_3$ Catalyzed Azachalcogenation of Carbon Monoxide.

1) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 20% $ClRh(PPh_3)_3$ (37.0 mg, 0.04 mmol) and pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.04 mmol, 20%); **4**: (0.03 mmol, 15%).

2) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 10% $ClRh(PPh_3)_3$ (18.5 mg, 0.02 mmol) and pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.062 mmol, 31%); **4**: (0.026 mmol, 13%).

3) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 20% $ClRh(PPh_3)_3$ (37.0 mg, 0.04 mmol) and benzene (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.019 mmol, 9.5%); **4**: (0.016 mmol, 8.0%).

4) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 20% $ClRh(PPh_3)_3$ (37.0 mg, 0.04 mmol) and benzene (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.016 mmol, 8%); **4**: (0.012 mmol, 6%).

5) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 20% $ClRh(PPh_3)_3$ (37.0 mg, 0.04 mmol) and a 50/50 mixture of benzene/pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.028 mmol, 14%); **4**: (0.009 mmol, 4.5%).

6) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 10% $ClRh(PPh_3)_3$ (37.0 mg, 0.04 mmol) and a 50/50 mixture of benzene/pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The

following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.025 mmol, 12.5%); **4**: (0.01, mmol, 5%).

7) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 2.5% $ClRh(PPh_3)_3$ (37.0 mg, 5.0 μmol) and a 50/50 mixture of benzene/pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 50 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.02 mmol, 10%); **4**: (0.009 mmol, 4.5%).

8) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 20% $ClRh(PPh_3)_3$ (37.0 mg, 0.04 mmol) and pyridine (1.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 25 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.006 mmol, 3%); **4**: (0.006 mmol, 3%).

9) To a glass bomb in a nitrogen filled glovebox were added **1** (33.6 mg, 0.22 mmol), **2** (31.4 mg, 0.1 mmol), 6% $ClRh(PPh_3)_3$ (12.0 mg, 0.013 mmol) and benzene (4 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 110 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.046 mmol, 23%); **4**: (0.0045 mmol, 2.3%).

10) To a glass bomb in a nitrogen filled glovebox were added **1** (13.7 mg, 0.09 mmol), **2** (15.7 mg, 0.05 mmol), 6% $ClRh(PPh_3)_3$ (4.9 mg, 5.4 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 110 °C with stirring. The

solution was degassed, filtered through celite and analyzed by GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (5.0 μmol, 5.1%); **4**: (0.4 μmol, 0.4%).

2.4.3.f The Miscellaneous Transition Metal Catalyzed Azachalcogenation of Carbon Monoxide.

1) To a glass bomb in a nitrogen filled glovebox were added **1** (33.6 mg, 0.22 mmol), **2** (31.4 mg, 0.1 mmol), 10% $Pt(PPh_3)_4$ (27.4 mg, 0.022 mmol) and benzene (3.5 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 1 h at 110 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. Carbamate **3** was observed in trace amounts.

2) To a glass bomb in a nitrogen filled glovebox were added **1** (33.6 mg, 0.22 mmol), **2** (31.4 mg, 0.1 mmol), 10% $Pt(PPh_3)_4$ (27.4 mg, 0.022 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 110 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. Carbamate **3** was observed in trace amounts.

3) To a glass bomb in a nitrogen filled glovebox were added **1** (33.6 mg, 0.22 mmol), **2** (31.4 mg, 0.1 mmol), 20% $[Cp^*IrCl_2]_2$ (35.1 mg, 0.044 mmol) and benzene (5.6 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. Neither Carbamate **3** or **4** was observed.

4) To a glass bomb in a nitrogen filled glovebox were added **1** (30.6 mg, 0.2 mmol), **2** (62.8 mg, 0.2 mmol), 15% $Cp^*Ir(CO)_2$ **7** (16.9 mg, 0.044 mmol) and benzene (4.0 mL). The reaction

mixture was charged with 0.5 atm of CO gas and heated for 24 h at 70 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC. Carbamate **3** was observed in trace amounts.

5) To a glass bomb in a nitrogen filled glovebox were added **1** (36.0 mg, 0.24 mmol), **2** (32.0 mg, 0.1 mmol), 10.5% $(CO)_2Rh(acac)$ (6.5 mg, 0.03 mmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 127 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC and GC-MS. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.03 mmol, 12.5%); **4**: (0.01 mmol, 4.2%).

2.4.4. The Effect of $(PhS)_2$ on Reaction Selectivity.

1) The ^{1}H NMR analysis of reaction selectivity.

a) To a screw-top NMR tube in a nitrogen filled glove were added sulfenamide **1** (19.7 mg, 0.13 mmol), **2** (16.3 mg, 0.05 mmol), 4.4% $RhCl(CO)(PPh_3)_2$ (4.0 mg, 6.0 μmol), and 0.15 mL of a 0.175 mM solution of hexamethylbenzene. The reaction mixture was charged with 0. 5 atm of CO gas and heated to 75 °C. The reaction was monitored at 4.5 h and then at 24 h of reaction. Integrated areas were used to determine the relative amounts of both seleno- and thiocarbamates **3** and **4**. The observed product ratios of compounds **3**:**4** are as follows: 1:1 and 2:1.

2) The analysis of reaction selectivity in the presence of excess $(PhS)_2$.

a) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (18.0 mg, 0.11 mmol), **2** (32.0 mg, 0.10 mmol) 7.8% $RhCl(CO)(PPh_3)_2$ (6.0 mg, 8.6 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 110 °C

with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.04 mmol, 36.3 %); **4**: (0.01 mmol, 9.1%).

b) To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (34.0 mg, 0.18 mmol), $(PhSe)_2$ **2** (32.0 mg, 0.10 mmol), $(PhS)_2$ **5** (14.0 mg, 0.06 mmol) 7.8% $RhCl(CO)(PPh_3)_2$ (6.0 mg, 8.6 μmol) and benzene (5.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 110 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. The following molar amounts of carbamates **3** and **4** and corresponding yields based on sulfenamide were determined by GC: **3**: (0.08 mmol, 44.4 %); **4**: (0.02 mmol, 11.1%).

2.4.5. Tellurocarbamates.

***N*-Dimethyl phenyl tellurocarbamate (15):** To a glass bomb in a nitrogen filled glovebox were added sulfenamide **1** (31.0 mg, 0.20 mmol), $(PhTe)_2$ **14** (41.0 mg, 0.10 mmol), 5.0% $ClRh(PPh_3)_3$ (15.0 mg, 10.0 μmol) and benzene (4.0 mL). The reaction mixture was charged with 0.5 atm of CO gas and heated for 24 h at 85 °C with stirring. The solution was degassed, filtered through celite and analyzed by GC/MS and GC. Neither tellurocarbamate **15** nor thiocarbamate **4** were detected.

2.5. Experimental Section: Transition Metal Catalyzed Olefin Azasulfenylation.

General Methods: Et_2O, toluene, THF, benzene-d_6 and CD_2Cl_2 were distilled under nitrogen from sodium. 1-pentene and pyrrole were distilled under nitrogen from calcium hydride.

$Pd(PPh_3)_4$ and Cp^*ZrCl_2 were obtained from Strem and stored in a nitrogen filled glovebox. Methyl lithium, MAO, BF_3 and $B(C_6F_5)_3$ were purchased and used without further purification. Dimethyl zirconocene was prepared according to the method of Samuel et al.[36] *N*-pyrrole lithium was prepared according to the method of Temme et al.[37] Sulfenamides were prepared according to the method of Davis et al.[21] ^1H NMR, 300 MHz, was recorded with Bruker spectrometers. Chemical shifts were referenced to residual ^1H signals in deuterated solvents. Gas chromatography-mass spectrometry (GC/MS) was performed on a Hewlett Packard Series 5980 GC/5971 A MS with a Hewlett Packard Series 1 capillary column.

1) Methylzirconocene chloride: According to the method of Jordon,[38] in a nitrogen filled glovebox Cp_2ZrMe_2 (100.0 mg, 0.4 mmol) in 5 mL toluene was mixed with a solution of Cp_2ZrCl_2 (117.0 mg, 0.4 mmol). The resultant solution was refluxed under N_2 at 130 °C with stirring for 30 h. The solution was cooled to room temperature and the solvent removed *en vacuo*. $Cp_2Zr(Me)(Cl)$ was collected in 64% yield (70.0 mg, 0.25 mmol) from recrystallization (hexanes). ^1H NMR (300 MHz, THF-d_8) δ 6.23 (10 H, s), 0.21 (3 H, s).

2) Methyl(*N*-pyrrole)zirconocene (16): According to the method of Temme *et al*.[37], in a nitrogen filled glovebox, $Cp_2Zr(Me)(Cl)$ (98.1 mg, 0.34 mmol) and *N*-pyrrole lithium (28.0 mg, 0.38 mmol) were dissolved in dry THF. After 4 h of stirring at room temperature, the solvent was removed *en vacuo*. The resulting solids were dissolved in toluene and LiCl was removed by filtration. The resulting solution was reduced *en vacuo* and methyl(*N*-pyrrole)zirconocene (**16**) was collected in 24% yield (24.0 mg, 0.08 mmol) from recrystallization (hexanes/toluene). ^1H NMR (300 MHz, C_6D_6) δ 0.41 (s, 3 H), 5.66 (s, 10 H), 6.57 (m, 2 H), 6.62 (m, 2 H). ^{13}C NMR (75 MHz, C_6D_6) δ 30.2, 109.4, 110.3, 112.8.

3) The reaction of zirconocene 16 with sulfenamide 1 in the presence of $B(C_6F_5)_3$: To a screw-top NMR tube in a nitrogen filled glove were added **16** (50.0 mg, 0.16 mmol) and $B(C_6F_5)_3$ (82.0 mg, 0.16 mmol) in C_6D_6. Sulfenamide **1** (25.0 mg, 0.16 mmol) was then added to the NMR tube. The ^1H NMR of the reaction mixture showed the consumption of both sulfenamide **1** and cation, but the production of MeSPh (**17**) was not observed.

4) The attempted catalytic azasulfenylation of 1-pentene by sulfenamide 1.

a) In a nitrogen filled glovebox, Cp_2ZrMe_2 (50.0 mg, 0.19 mmol), **1** (31.0 mg, 0.2 mmol), 0.2 mL of a 1.0 mM solution of 1-pentene, and $B(C_6F_5)_3$ (102.0 mg, 0.2 mmol) were mixed in CD_2Cl_2 in a Schlenk flask and let stir for 24 h at 25 °C. The reaction was filtered through celite and analyzed by GC-MS and ^1H NMR. No azasulfenylation product was detected.

b) In a nitrogen filled glovebox, Cp_2ZrMe_2 (50.0 mg, 0.19 mmol), **1** (31.0 mg, 0.2 mmol), 0.2 mL of a 1.0 mM solution of 1-pentene and 0.5 mL of a 1.0 mM solution of MAO were mixed in toluene in a Schlenk flask and let stir for 24 h at room temperature. The reaction was filtered through celite and analyzed by GC-MS and ^1H NMR. No azasulfenylation product was detected.

c) To a screw-top NMR tube in a nitrogen filled glovebox were added in C_6D_6, 10% $Pd(PPh_3)_4$ (24.0 mg, 0.02 mmol), **1** (31.0 mg, 0.2 mmol), and 0.2 mL of a 1.0 mM solution of 1-pentene. The reaction was heated at 75 °C and monitored for product formation every 24 h for 4 days. No azasulfenylation product was detected.

2.6. References.

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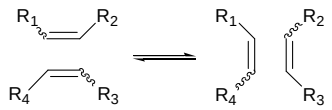
CHAPTER 3. IMINE-OLEFIN RING-CLOSING METATHESIS

3.1. Introduction

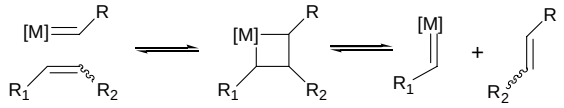
3.1.1. General Aspects.

Olefin metathesis is a transition metal catalyzed reaction that transposes the alkylidene groups of two substituted alkenes (Scheme 1).[1]



Scheme 1. General principle of olefin metathesis

The mechanism for olefin metathesis was first reported by Chauvin and Herisson and involves a [2+2] cycloaddition that generates an unstable intermediate metallacyclobutane.[2] Cleavage of the metallacyclobutane can occur either in a non-productive fashion yielding initial olefin and alkylidene or in a productive fashion yielding new olefin and alkylidene (Scheme 2).[1]



Scheme 2. The Chauvin mechanism for olefin metathesis

First generation olefin-metathesis catalysts were ill-defined mixtures of transition metal salts (WCl_6, $MoCl_6$, $ReCl_5$, etc.) and their complexes with main group organometallic compounds such as $EtAlCl_2$ and $Sn(CH_3)_4$. These catalysts were only capable of polymerizing strained cyclic olefins in a non-living fashion. In addition, the poorly defined nature of the catalysts prevented control of activity and selectivity. Over the past 15 years, a series of new, well-defined catalyst systems has been developed that selectively catalyze a variety of organic transformations and polymerizations (Figure 1).[3-7]

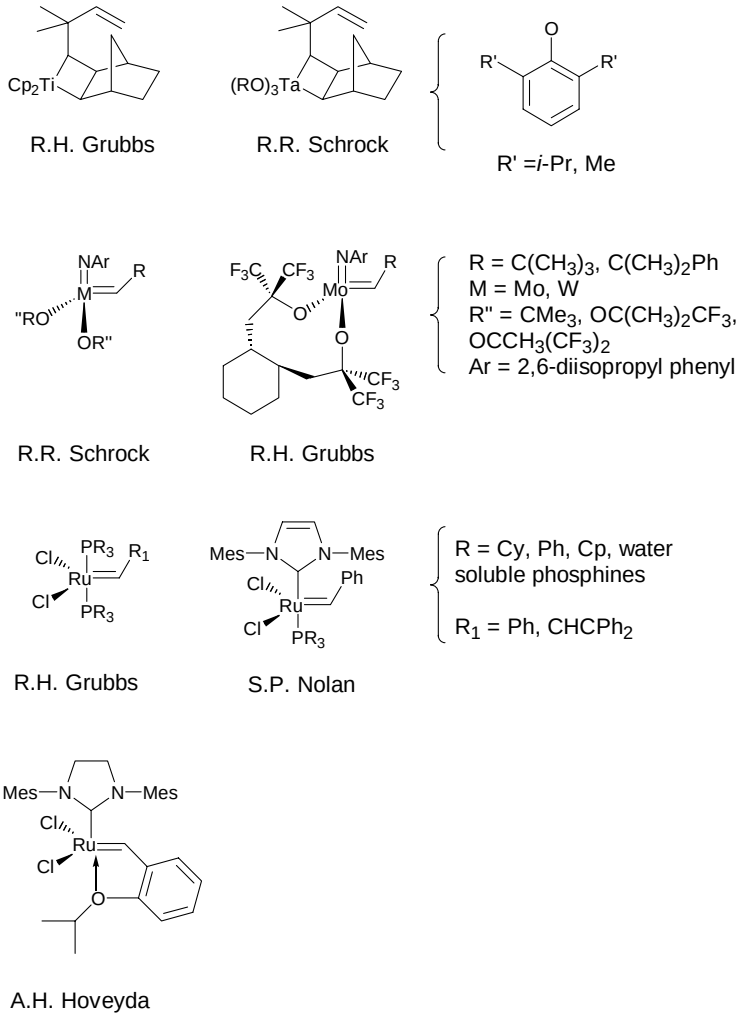


Figure 1. Single-component transition metal catalysts for olefin metathesis

Grubbs reported the titanocyclobutane complex in Figure 1 as the first well-defined olefin metathesis catalyst. The titanocyclobutane was shown to polymerize norbornenes in a living fashion, but the general utility of the system was limited by its instability in the presence of Lewis basic functionalities.[8] Further single component alkylidene catalysts based on Ta and Re then followed (Figure 1).

In 1990, Schrock and co-workers reported new molybdenum and tungsten alkylidene catalysts capable of polymerizing a variety of monomers such as norbornenes and barrelenes (Figure 1).[9,10] The molybdenum catalysts have also found use in ring-closing metathesis (RCM),[5] carbonyl-olefin ring-closing metathesis,[8,11,12] imine metathesis,[13] ring-opening of cyclic imines (ROM)[14] and asymmetric ring-closing metathesis (ARCM).[15,16,17,18]

In 1992, Grubbs and co-workers reported a new class of ruthenium carbene catalysts (Figure 1).[19,20] These catalysts have found more wide spread use than their molybdenum counterparts in synthetic application such as RCM, ring-opening metathesis polymerization (ROMP), ARCM and cross metathesis because, in contrast to the Schrock alkylidene catalysts, they are stable to a large variety of Lewis basic functional groups and conditions including air, water and temperature.[8,21-24]

More recently, a new generation of ruthenium catalysts containing imidazolylidene carbene ligands have been developed by both Nolan and Hoveyda. These catalysts show better reactivity and functional group compatibility than all previously reported metathesis catalysts (Figure 1).[4,6,7,25,26]

In general, olefin metathesis can be used in four closely related reactions: (A) ring-opening metathesis polymerization; (B) ring-closing metathesis and its asymmetric counterpart, ARCM; (D) acyclic diene metathesis (ADMET) and (E) carbonyl-olefin ring-closing metathesis (Figure 2).[15,16,27-29]

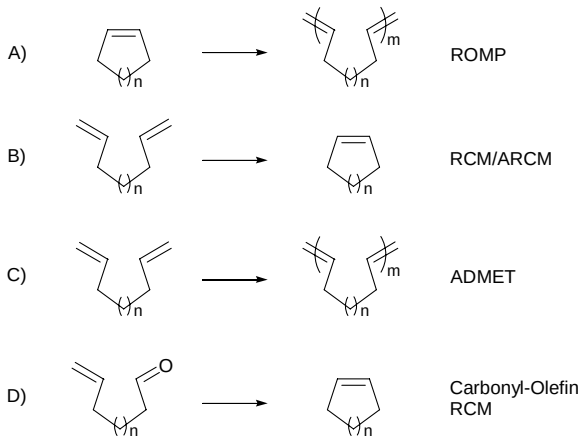


Figure 2. General overview of metathesis reactions

3.1.2. Ring-Opening Metathesis Polymerization.

ROMP, the oldest of the five applications shown in Figure 2, is a reaction in which strained cycloalkenes are polymerized to yield a polymer with olefins in the backbone. The driving force for the reaction lies in the release of the monomer's strain energy. Hence, low strain cyclic alkenes such as cyclopentene are difficult to polymerize. However, more highly strained cyclic olefins such as norbornenes,[30] barrelenes,[31] cyclobutenes[32] and cyclooctenes[33] are readily polymerized (Figure 3).

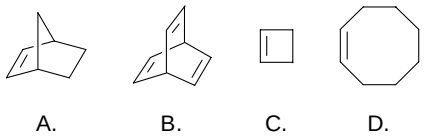


Figure 3. Common monomers used in ROMP

With regard to polymer microstructure, ROMP results in good polydispersity although bimodal distribution sometimes is observed. In addition, high polymer tacticity is obtained for some monomers such as 1,7,7 trimethyl-norbornene, and well-defined chain lengths are also obtained with the use of chain termination agents such as generic aldehydes. Block copolymers can also be prepared by the sequential addition of different monomers, although generally with low polydispersity.[22,27]

The modern metathesis catalysts have provided a means for the construction of a variety of interesting polymers. For example, the redox polymer[34] and amine scavenger polymer[35] shown in Figure 4 are easily prepared by ROMP with either the Schrock or Grubbs catalyst.

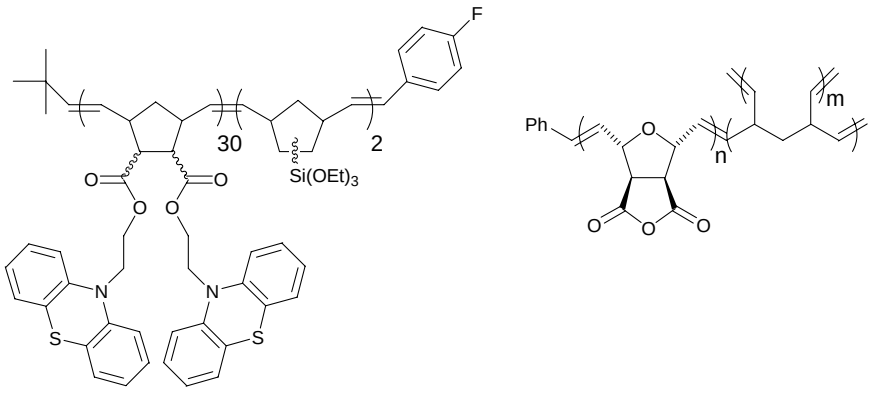
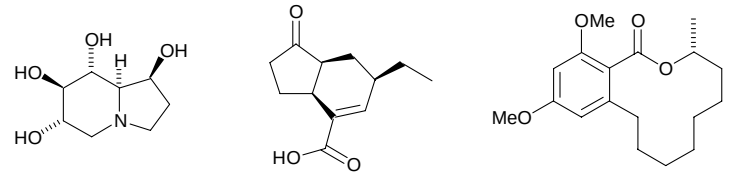


Figure 4. Redox and amine scavenger polymers prepared by ROMP

3.1.3. Ring-Closing Metathesis.

In recent years, ring-closing metathesis has evolved into an efficient and powerful method for the formation of C-C bonds. In contrast to ROMP, ring-closing metathesis is enthalpically disfavored, but the release of small volatile olefins provides enough entropic driving force to overcome this initial enthalpic barrier.[36]

With respect to the preparation of natural products, RCM has evolved into a valuable synthetic tool. For example, Blechert and co-workers utilized RCM as the key step in their synthesis of castanospermin and coronafacinic acid.[1,37] In addition, macrocyclic natural products have also been prepared via RCM as in Furstner's synthesis of (+)-lasiodiplodine (Figure 5).[38] An abundance of reports regarding the use of RCM in the synthesis of natural products exists and are too many to list here.[28,29,39,40]



castanospermin coronafacinic acid (+) lasiodiplodin

Figure 5. Natural products prepared by RCM

RCM has also been successfully applied in the field of peptide chemistry. For example, highly functionalized 6- and 7-membered amino esters or acrylic amides have been prepared by Shoemaker and Rutjes, and RCM has been shown to be an efficient method for the functionalization of monocyclic β-lactams and for the preparation of bicyclic β-lactams.[41,42] In addition, the RCM of dienic amides has provided dehydro lactams that are direct precursors of the Z-ethylenic dipeptide isosteres (Figure 6).[43]

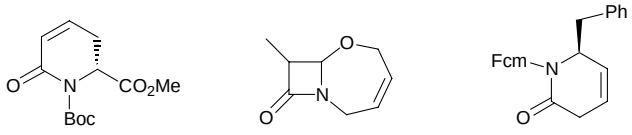


Figure 6. Compounds prepared by RCM in peptide chemistry

3.1.4. Acyclic Diene Metathesis Polymerization.

ADMET is not as common as ROMP or RCM, but the thermodynamics of ADMET are similar to RCM. The formation of small, volatile molecules is the driving force for the cross-metathesis reaction.[2] Recent advances in ADMET include the synthesis of alcohol functionalized polymers and highly conjugated polymers (Figure 7).[27]

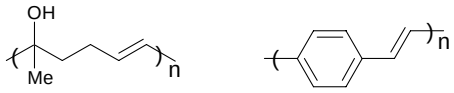


Figure 7. Recent examples of polymers synthesized by ADMET

3.1.5. Heteroatom Metathesis Reactions.

Heteroatom metathesis reactions are amongst the least studied transformations available to the metathesis catalysts.[3,22,44] Among the reasons for this lack of study has been the incompatibility of the catalyst systems with polar functional groups encountered in organic synthesis coupled with the overwhelming success of olefin metathesis. In addition, olefin metathesis can be carried out catalytically whereas heteroatom metathesis must usually be carried out stoichiometrically.[8]

Nevertheless, several heteroatom metathesis reactions have been developed using carbonyl- and imine-containing compounds (Figure 8). For example, the Tebbe or Tebbe-Petasis olefination is one of the most widely employed means for the installation of a terminal olefin

(I).[45] Similarly, although less commonly encountered, tantalum alkylidenes are capable of installing a *t*-butyl terminated olefin in a manner similar to the Tebbe reaction (II).[46] With regard to imine-containing compounds, Bergman and co-workers have developed both stoichiometric and semi-catalytic zirconium imido based processes for imine-metathesis (III).[44] Mountford has also shown that titanium imido compounds can stoichiometrically metathesize imines as well as a α,α diimines (IV).[47] Most relevant to this chapter is the carbonyl-olefin ring-closing reaction reported by Grubb's and co-workers (V) as it represents the only example, save for those included in this chapter, of heteroatom ring-closing metathesis.[8,11,12,48]

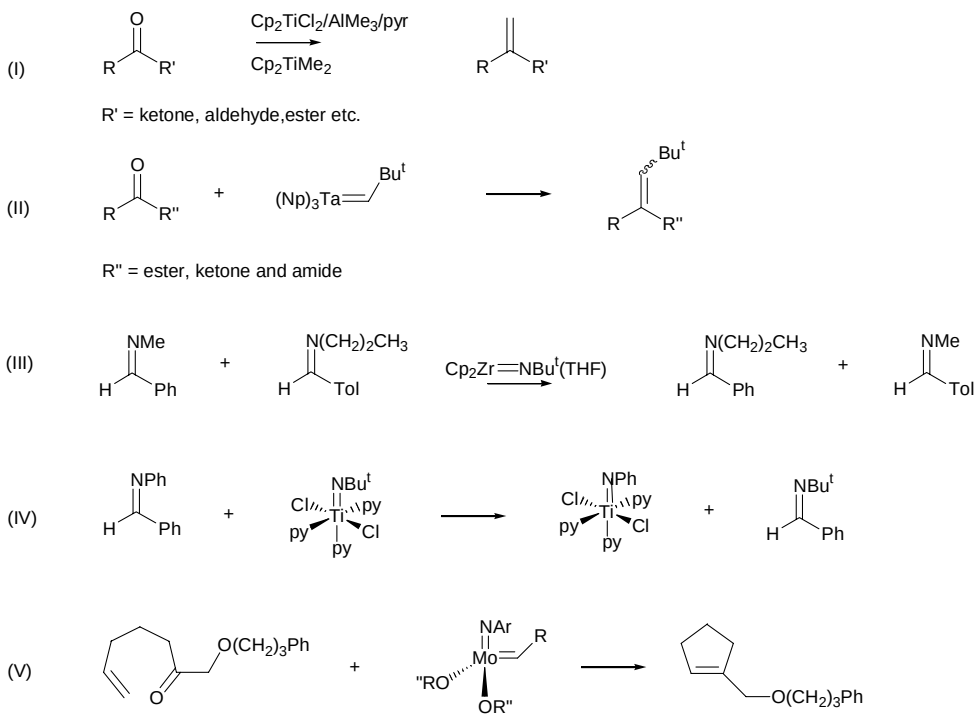
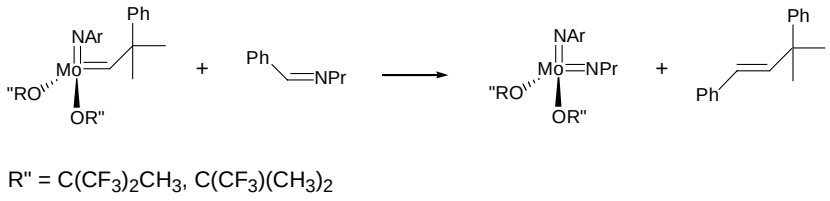


Figure 8. Heteroatom metathesis reactions

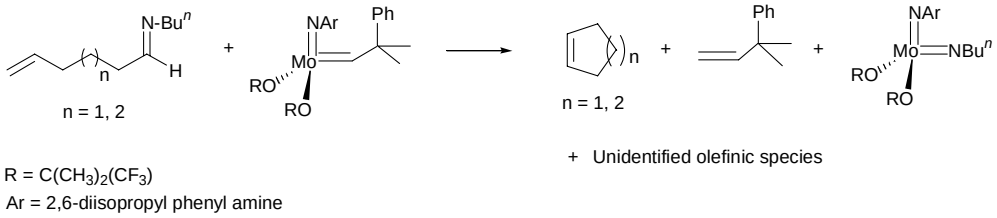
3.1.6. Molybdenum Based Imine Metathesis Reactions.

One of our major research goals is to examine the metathesis activity of Schrock-type alkylidenes with imines in order to expand the scope of heteroatom metathesis. During the course of their studies in this field, Cantrell and Meyer discovered that the molybdenum bis(imide) complexes $(DME)Cl_2Mo(=NR)_2$ (R = *t*-Bu, 2,6-diisopropylphenyl) are capable of catalyzing imine metathesis (Scheme 3).[13,49] In addition, they discovered the first ring-opening metathesis of a cyclic imine, pyrroline, with the Schrock catalyst.[14]



Scheme 3. Imine-alkylidene metathesis with the Schrock catalyst

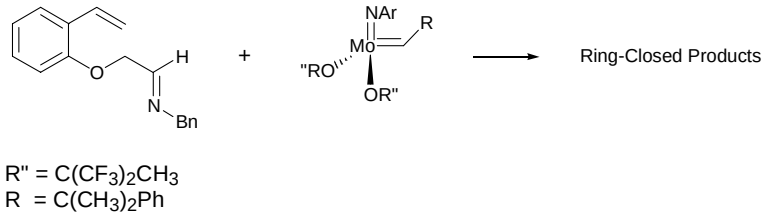
Based on these observations, Badawood and Meyer sought to examine the final piece of the metathesis study: imine-olefin ring-closing metathesis. They were successful in producing both cyclopentene and cyclohexene from α,ω imino-olefins, but several side reactions were observed to be in competition with the ring-closing reaction. The identity of the side products could not though be determined due presumably to their low yield and high volatility (Scheme 4).[50,51]



Scheme 4. The first example of imine-olefin ring-closing metathesis

3.2. Overview.

Presently our work on imine-olefin ring-closing metathesis focuses on developing new methods for C-C bond formation, determining the kinetic and thermodynamic preferences of the reaction, and elucidating the secondary pathways in competition with the reaction. In order to accomplish these goals, an α,ω imino-olefin was designed based on the following requirements: a six-membered ring-forms upon ring-closing and competitive byproducts are of significant molecular weight to be analyzed chromatographically. According to the above criteria, benzyl-[2-(2-vinyl)-phenoxy) ethylidene] amine was chosen as a suitable substrate for this study (Scheme 5).



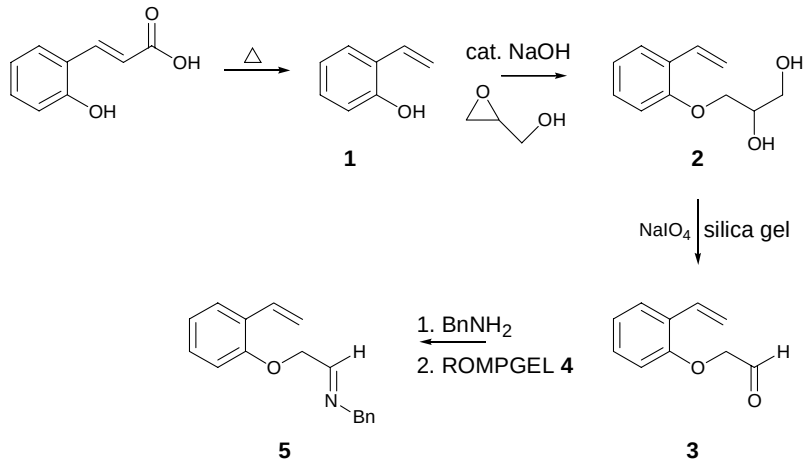
Scheme 5. Ring-closing metathesis of benzyl-[2-(2-vinyl)-phenoxy) ethylidene] amine.

Herein, we report the Schrock catalyst, $Mo(=CHC(Me)_2Ph)(=NAr)[OC(CH_3)(CF_3)_2]$, is capable of stoichiometric imine-olefin ring-closing metathesis with the designed substrate. The identity and amounts of the major species and a portion of the byproducts has been determined. In this chapter, we present the results of our studies and discuss the mechanistic implications of the heteroatom metathesis reaction.

3.3. Results.

3.3.1. Substrate Synthesis.

In order to achieve the above stated goals, benzyl-[2-(2-vinyl)-phenoxy) ethylidene] amine (**5**) was prepared according to Scheme 6.



Scheme 6. Synthesis of substrate **5**

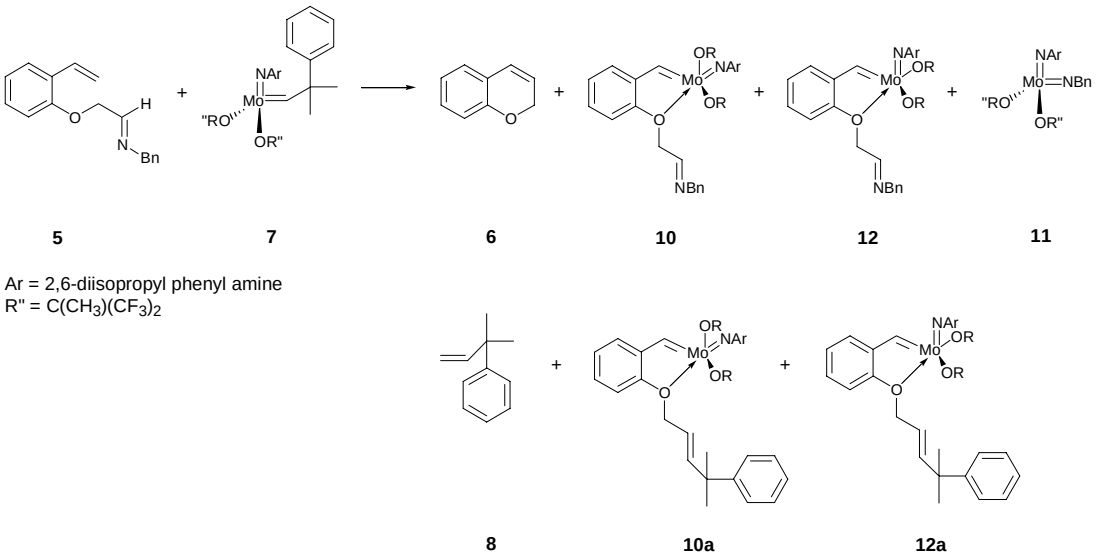
Alcohol (**1**) was prepared in yields of 40-45% by the vacuum decarboxylation of 2-hydroxy cinnamic acid and was used without further purification. It is important to note that 2-hydroxy cinnamic acid must be pretreated by slow evaporation from acetone in order to obtain acceptable yields of **1** by decarboxylation. Attempts to prepare alcohol **1** in better yield via the Wittig reaction between salicylaldehyde and methyl triphenyl phosphorane bromide were unsuccessful.

Diol (**2**) was obtained in 27-95% yield by the base-catalyzed ring opening of the epoxide glycidol, and the purification of **2** was unnecessary as it directly crystallized from the reaction mixture. Reaction time, temperature, and ratio of base to alcohol **1** were adjusted, but yields considered to vary considerably and no one ideal set of reaction conditions was found.

Aldehyde (**3**) was prepared in yields greater than 70% via the oxidative cleavage of diol **2** by $NaIO_4$ over silica gel. Further purification of **3** was unnecessary as determined by ^1H NMR spectroscopy. Other methods of oxidative cleavage were attempted. Neither MnO_2 nor $NaIO_4$ in ether or in ethanol were successful in yielding pure **3** in comparable yields. Imine **5** was then prepared by the condensation of benzyl amine with aldehyde **3**. Excess contaminating amine was successfully removed by ROMPGEL (**4**) as evidenced by ^1H NMR spectroscopy.

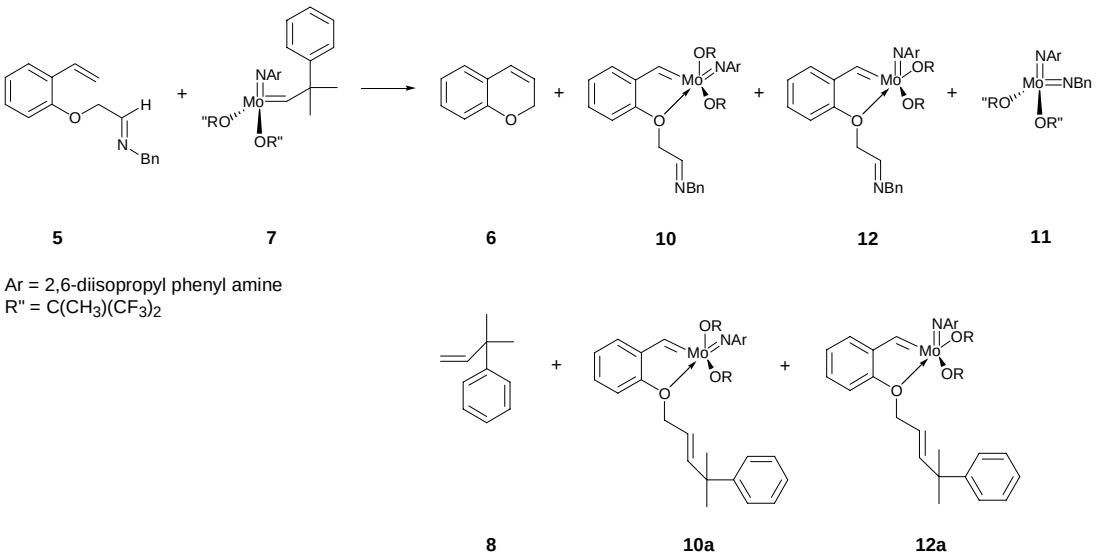
3.3.2. Overview of the Imine-Olefin Ring-Closing Metathesis Reaction.

With substrate **5** in hand, an *in situ* examination of the ring-closing metathesis reaction of imino-olefin **5** and alkylidene **7** was undertaken. Treatment of imino-olefin **5** with varying amounts of alkylidene **7** gave the ring closed product chromene (**6**), neophylene (**8**), mixed bis(imide) (**11**), and chelate complexes (**10**) and (**12**). In addition, the neophylene capped chelates (**10a**) and (**12a**) were also observed (Scheme 7).



Scheme 7. Overview of the ring-closing metathesis reaction of imino-olefin **5** and alkylidene **7**

3.3.3. The Stoichiometric Reaction of Imino-Olefin 5 and Alkylidene 7.

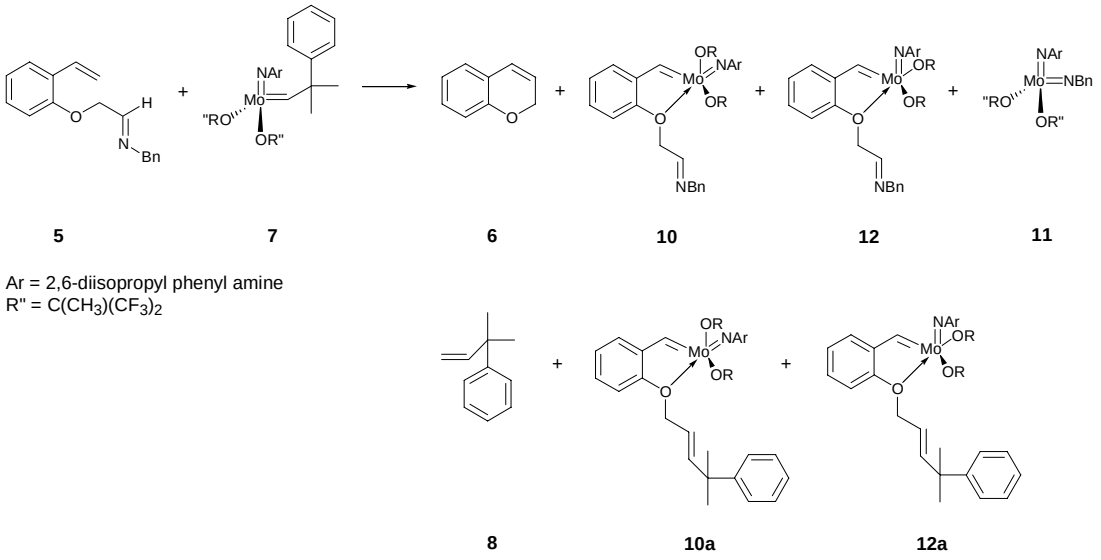


Equimolar amounts of imino-olefin **5**, alkylidene **7**, and anisole were combined in a screw-top NMR tube in order to determine the feasibility of the heteroatom metathesis reaction. Five hours after mixing, new olefin resonances corresponding to the formation of the ring-closed product **6** were observed in the ^{1}H NMR spectrum. Resonances corresponding to neophylene **8** and mixed bis(imide) **11**, the expected byproducts of ring-closing, were also detected. Unexpectedly, alkylidene resonances at δ 13.4 and 12.9 were detected and assigned to that of chelate **10** and its geometrical isomer **12** based upon arguments presented in the Discussion section of this report.

After one day, imino-olefin **5** was completely consumed as indicated by the disappearance of the -OCH_2- resonance at δ 4.7, and the growth of the resonances corresponding to chromene **6** and byproducts **8** and **11** was observed. In addition, we believe that chelates **10** and **12** have undergone alkylidene-imine metathesis to form the neophylene capped chelates **10a** and **12a**. Their potential presence in the reaction mixture is indicated by the vinylic doublet of triplets at ~ δ 4.5.

After four days, the yield of chromene **6** was determined to be 43%, and the reaction was halted. Purification of the reaction mixture by column chromatography yielded a mixture of chromene **6**, neophylene **8**, 2,6-diisopropyl phenyl amine (**9**), and small quantities of other unidentifiable olefin species as indicated by ^{1}H NMR spectroscopy and GC/MS analysis. Structural assignments of species **8** and **9** were made by comparison to standard spectra, and ring-closed product **6** was identified by comparison to an independently prepared sample of 2H-chromene.

3.3.4. The Reaction of Imino-Olefin 5 and Excess Alkylidene 7.



To gain insight into the heteroatom ring-closing metathesis reaction, excess alkylidene **7**, imino-olefin **5** and anisole were mixed in a screw-top NMR tube. Shortly after mixing, new resonances were detected for the formation of chromene **6** and neophylene **8**. After one day, chelates **10** and **12**, mixed bis(imide) **11** and other secondary molybdenum species (**13**) were detected by ^{1}H NMR spectroscopy. In addition, trace amounts of neophylene capped chelates **10a** and **12a** were observed as in the prior experiment with their CH_{α} resonances most likely corresponding to those of the secondary molybdenum species **13**. Over the next six days, the growth of resonances corresponding to chromene **6** and byproducts **8** and **11** was observed. The millimolar amounts of each major species present in solution after 6 days are provided in Table 1. It should be noted that mass balance was examined and the partitioning of molybdenum and substrate functionalities was strictly monitored. The total molar amount of ring-closed product **6**

combined with that of chelates **10** and **12** were in good accord with total molar amount of neophylene **8** produced by alkylidene-olefin metathesis. Furthermore, the total molar amount of molybdenum containing species present upon reaction completion is in good agreement with the starting molar amount of alkylidene **7**.

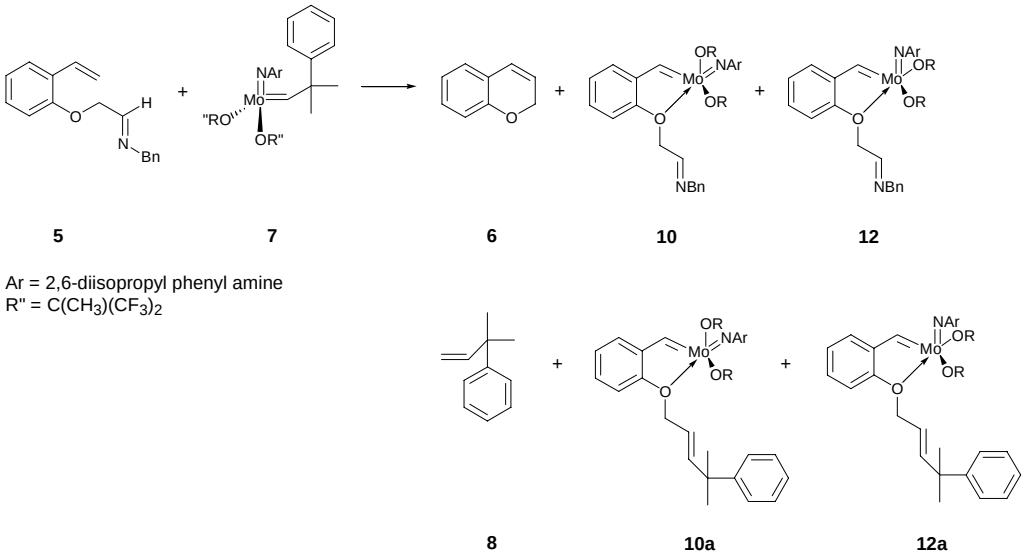
Table 1. The millimolar amounts of the major species present after 6 days

Compound	Integrated Resonance (δ)	mmol(s)
6	6.7	0.08
7	12.3	0.05
8	6.1	0.14
10	13.4	0.07
11	5.1	< 0.2[a]
12	12.9	0.02
13	12.9-13.0	0.01

a: Estimated value is larger than the actual value due to peak overlap in ^{1}H NMR spectrum.

After six days, the yield of chromene **6** was determined to be approximately 63%, and the reaction was halted. In an attempt to induce crystallization of the chelates, the reaction was layered with hexanes and cooled to –35 °C. Unfortunately, crystallization of said species was not observed. Column chromatography of the reaction mixture yielded two notable fractions. The second fraction was found to contain the expected species **6**, **8** and **9** as indicated by both ^{1}H NMR spectroscopy and GC/MS analysis, but the first fraction contained an unidentified alkylidene species. To the best of our knowledge, no molybdenum alkylidene capable of surviving chromatography has been reported to exist.

3.3.5. The Reaction of Excess Imino-Olefin 5 and Alkylidene 7.



To further probe the ring-closing reaction, excess imino-olefin **5**, alkylidene **7** and hexamethylbenzene were combined in screw-top NMR tube. Immediately after mixing, new olefin resonances were detected by ^{1}H NMR spectroscopy for the formation of chromene **6** and neophylene **8**. After one day, chelates **10** and **12** as well as several new olefinic resonances were observed by ^{1}H NMR spectroscopy, but, interestingly, mixed bis(imide) **11** was not detected. Again, neophylene capped chelates **10a** and **12a** were observed in trace amounts.

After one day, alkylidene **7** was completely consumed as indicated by the disappearance of the CHα resonance at δ 12.3; the reaction was halted, and the yield of chromene **6** was determined to be 36%. The millimolar amounts of the major species present in solution after one day are provided in Table 2. Mass balance was examined and the partitioning of molybdenum and

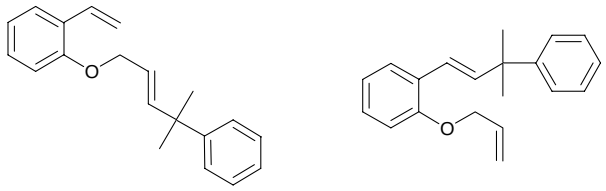
substrate functionalities was strictly monitored. As in the previous experiment, similar results were obtained.

Table 2. The millimolar amounts of the major species present after 1 day

Compound	Integrated Resonance (δ)	mmol(s)
6	6.25	0.09
8	6.1	0.12
10	13.4	0.05
12	12.9	0.01

Column chromatography of the reaction mixture yielded several notable fractions. ^{1}H NMR spectroscopy and GC/MS analysis of combined fractions indicated the presence of the expected species **6**, **8** and **9** as well as three other unidentified compounds *a*, *b* and *c* comprising approximately 10.5% of the mixture. According to the mass spectral traces, two of the unknown compounds *a* and *b* exhibited not only nearly equal retention times but also the exact same mass spectral fragmentation patterns with potential mass ion peaks at *m/z* 278, base peaks at *m/z* 117 and the characteristic fragmentation pattern of a substituted aromatic compound (*m/z* 91, 77, 65, 51). In addition, the first fragmentations of their potential mass ions correspond to the loss of neophylene thus indicating that these species are directly related to the ring-closing reaction. ^{1}H NMR spectral data supports the presence of a neophylene capped type byproduct in the reaction mixture as evidenced by the presence of a downfield doublet for the -OCH_2- unit and a characteristic doublet of triplets with a chemical shift similar to that of the doublet of triplets for chromene **6**. It should be noted that several overlapping peaks are present in the olefin region for

these compounds and thus complete assignment is impossible. Based on this data, the possible structures of byproducts *a* and *b* are shown in Figure 9.



14 **15**

Figure 9. Possible structures for byproducts *a* and *b*

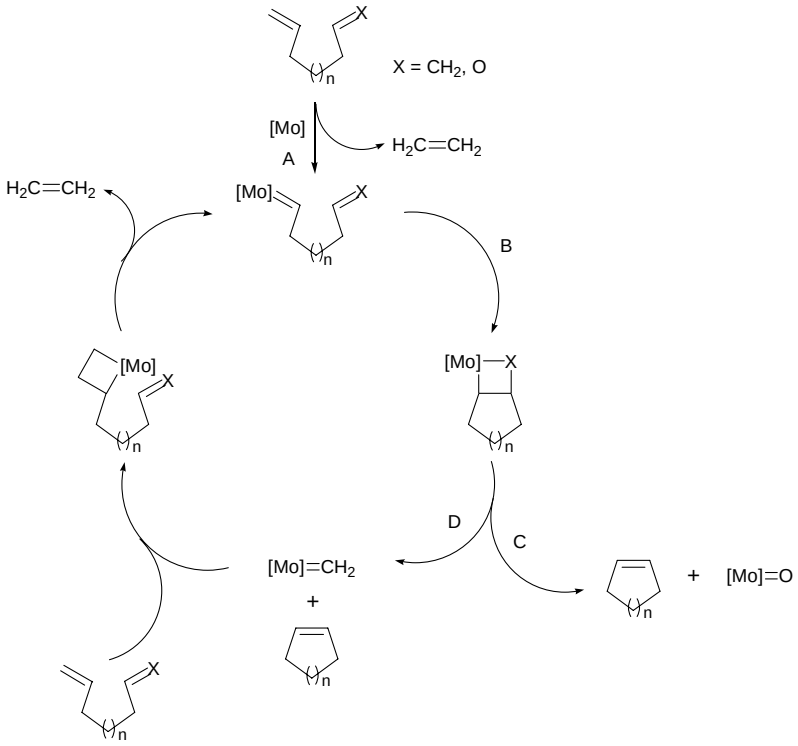
The identity of the third species detected by GC/MS analysis remains unclear at this time. Mass spectral data suggests that it is not closely related to byproducts *a* and *b* due to the differing mass ion peaks, but it can at least be concluded that it is a high molecular weight aromatic olefin. The origin of this species is unknown at this time, but it may be the degradation product of chelates **10a** and **12a**.

3.4. Discussion.

3.4.1. Mechanism.

Previous mechanistic studies on olefin and carbonyl-olefin ring-closing metathesis catalyzed by molybdenum alkylidenes provide a comparative viewpoint from which to consider the

mechanism of imine-olefin ring-closing metathesis. It is now accepted that both reactions proceed via the initial coordination of olefin to the alkylidene catalyst followed by [2+2] cycloaddition. This addition generates an unstable metallacycle that productively cleaves to yield a new substrate terminated with alkylidene functionality (Scheme 8, A). The new alkylidene reacts in [2+2] fashion (B) with the second reactive functionality of the substrate, olefin or carbonyl, producing a new metallacycle that cleaves (C,D) yielding the ring-closed product.[8,11]



Scheme 8. The mechanism of olefin and carbonyl-olefin ring-closing metathesis

It is important to note that olefin ring-closing metathesis is a catalytic process in which a new reactive alkylidene is generated upon ring closure (D). In contrast, carbonyl-olefin ring closing metathesis is inherently a stoichiometric process as unreactive molybdenum oxide is produced in the ring-closing step (C). In addition, it is also important to note that the initial [2+2] cycloaddition of the carbonyl-olefin ring-closing reaction proceeds under kinetic control, alkylidene-olefin metathesis, rather than thermodynamic control, alkylidene-carbonyl metathesis.

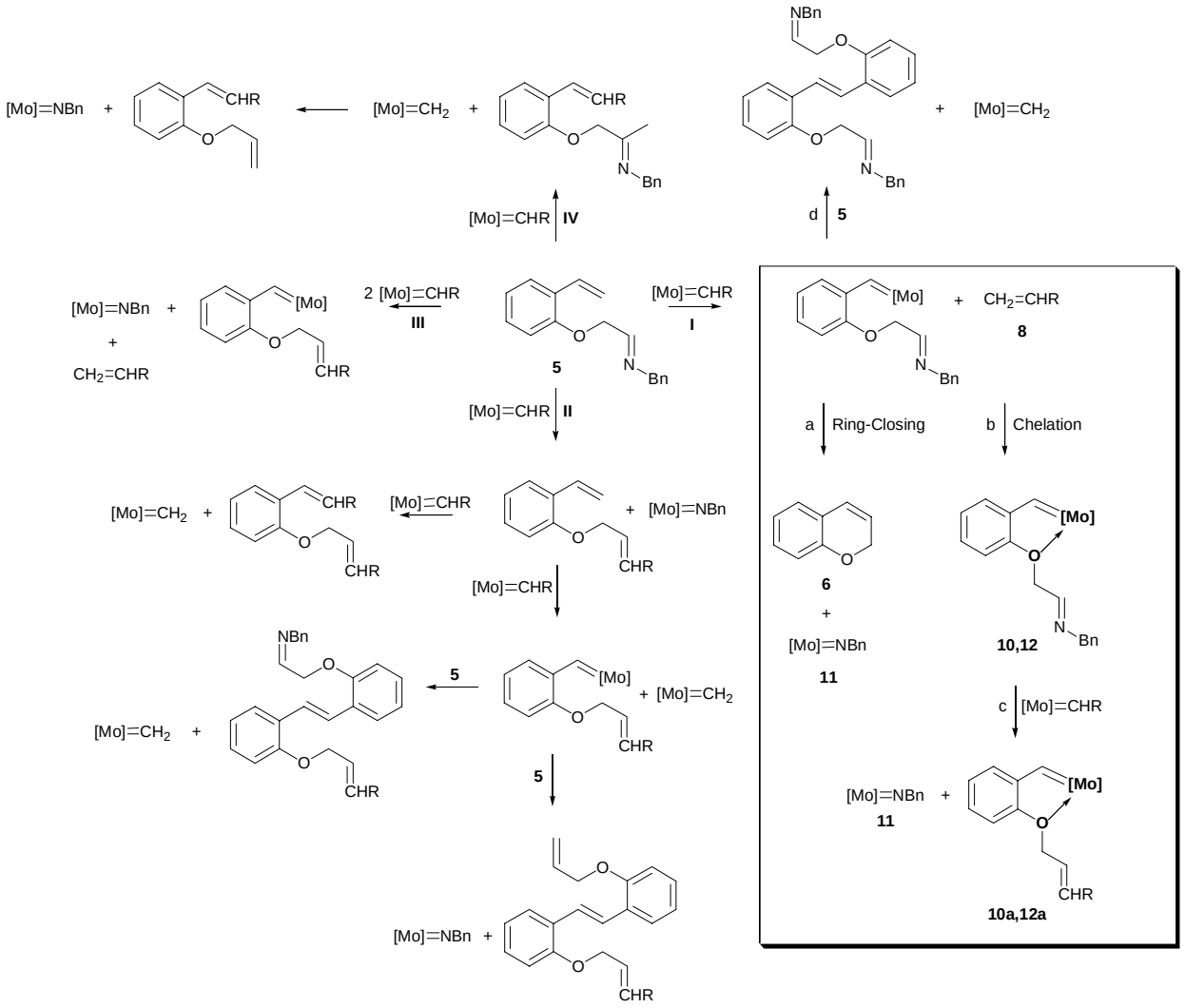
3.4.2. The Imine-Olefin Ring-Closing Metathesis Reaction.

It is reasonable to assume that the imine-olefin ring-closing metathesis reaction proceeds along an analogous pathway to both olefin and carbonyl-olefin ring-closing metathesis. Upon closer examination of the imine metathesis reaction though, one can envision several competing pathways. A complete mechanistic proposal is presented in Scheme 9.

Focusing on the route to ring-closed product (Scheme 9, I), we believe the reaction initially proceeds with the kinetically favored alkylidene-olefin metathesis yielding a transient iminoalkylidene and neophylene **8**. The iminoalkylidene then undergoes ring-closing via alkylidene-imine metathesis (Ia) to produce chromene **6** and mixed bis(imide) **11**. The iminoalkylidene can also be chelated (Ib) by oxygen yielding chelates **10** and **12**. We were not able to unambiguously determine the ring-closing potential of chelates **10** and **12** due to their low concentration in solution. Nevertheless, we believe that these chelates are capable of further alkylidene-imine metathesis (Ic) thus forming the neophylene capped species **10a**, **12a** and the

mixed bis(imide) **11**. It should be noted that no ADMET reaction (Id) of imino-olefin **5** was observed in any reaction.

Based upon our observations, it appears that some of the secondary reactions illustrated in Scheme 9 are in active competition with the ring-closing metathesis reaction. Pathway II, although kinetically unfavored, would be expected to yield the neophylene-capped olefin **14**, and Pathway IV olefin **15**. The isolation of both of these byproducts from the reaction mixture strongly suggests that both Pathways II and IV are proceeding.



Scheme 9. A mechanistic proposal for the heteroatom metathesis reaction

Having explored the potential mechanistic pathways of the reaction, we believed it pertinent to also examine the transition state structure of the alkylidene-imine ring-closing step. The ring-closing step must proceed through an eight membered intermediate or transition state that partially reflects the formation of the six-membered ring in chromene **6**. Based upon the rules

governing the formation of six-membered rings as established by Zimmerman and Traxler coupled with the necessary co-planarity of the imine and alkylidene function over the CNO face of the alkylidene,[52] we hypothesize that the imine-alkylidene ring-closing step proceeds through the state shown in Figure 10.[53]

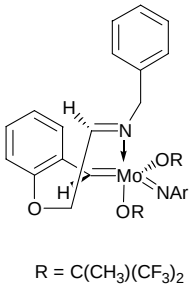
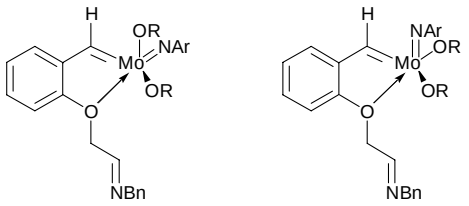


Figure 10. A potential intermediate or transition state in the alkylidene-imine ring- closing step of substrate **5**

In each of the ring-closing reactions, an unexpected chelation of the reactive iminoalkylidene by oxygen was observed from the presence of the downfield alkylidene signals at δ 13.5 and 12.9. Such chelation was postulated to form structures **10** and **12** (Figure 11). We believe these species are formed immediately following alkylidene-olefin metathesis of imino-olefin **5** and alkylidene **7**. The alkylidene signals for each species fall within the region observed for chelated molybdenum alkylidenes in trigonal-bypyramidal geometries as reported by Schrock and co-workers.[52] In addition, the CH_α coupling constants of the chelates were determined to be 142 Hz and 148 Hz respectively. These large coupling constants correspond to a decreased interaction of the alkylidene CH_α bond with molybdenum center leading to weaker C-Mo bonding and stronger

CHα bonding. We believe these structures to be geometrical isomers of one another via ligand rearrangement although the potential equilibrium for such a rearrangement is unknown at this time.



10 **12**

Figure 11. Tentative structures of the chelates observed in the ring-closing of substrate **5**

Although we were unable to determine the ring-closing potential of chelates **10** and **12**, we believe that they are thermodynamic sinks incapable of further ring-closing metathesis. The strength of the Mo-O bond should provide not only the stabilizing force to create the chelate but also an enthalpic barrier to dissociation. Furthermore, the chelate species exist in the wrong geometrical orientation for alkylidene-imine ring-closing metathesis. However, we do feel that chelates **10** and **12** are susceptible to further reactions with alkylidene **7**. In all of the ring-closing reactions, a doublet of triplets at ~δ 4.5 was observed in the ^{1}H NMR spectra. This resonance is characteristic of neophylene-capped substrates such as species **10a** and **12a** (Scheme 7) that is produced by alkylidene-imine metathesis. It is tempting to conclude that alkylidene-imine metathesis is occurring not with the chelates but with the starting imino-olefin **5** to produce a species such as byproduct **14**. This can be ruled out based on the neophylene

capping observed during the reaction of excess alkylidene **7** with imino-olefin **5** as no starting material **5** was observed to be available for such a reaction.

Based upon our observations, it can be concluded that the imine-olefin ring-closing metathesis reaction operates under kinetic control via initial alkylidene-olefin metathesis followed by the more thermodynamically favored alkylidene-imine metathesis. Support for this conclusion lies in the immediate formation of the kinetic products **6**, **8**, and **10** as observed by ^{1}H NMR spectroscopy. The presence of chelates **10** and **12** is particularly diagnostic in that they represent a "trapping" of the kinetically formed iminoalkylidene. This conclusion is in good agreement with the mechanism for the carbonyl-olefin ring-closing metathesis and the observation by Cantrell and Meyer that alkylidene-imine metathesis is slow in comparison to alkylidene-olefin metathesis.[49]

3.5. Conclusion.

Despite the complexity of these systems we have established that the kinetic preference of Schrock-type alkylidenes for terminal olefins over imines is sufficiently large to allow for heteroatom ring-closing metathesis. In addition, we have potentially elucidated some of the secondary pathways that are competitive with the reaction as well as developed a new means for C-C bond formation.

3.6. Experimental Section.

General Considerations.

All manipulations of air- and/or water-sensitive compounds were performed in a nitrogen filled drybox or by standard high vacuum techniques. Solid organometallic compounds were transferred in a nitrogen filled drybox and stored at–35 °C, unless otherwise stated. ^{1}H, ^{13}C-NMR spectra were recorded with Bruker spectrometers at 300 and 75 MHz, respectively. Chemical shifts were referenced to residual ^{1}H signals in deuterated solvents. Significant ^{1}H NMR data are tabulated in the order: multiplicity, number of protons, coupling constant (s) in hertz. Gas chromatography-mass spectrometry (GC/MS) was performed on a Hewlett Packard Series 5980 GC/5971 A MS with a Hewlett Packard Series 1 capillary column. Column Chromatography was performed using Sorbent 60 32-60 standard grade silica gel.

Materials.

Unless otherwise indicated, materials were obtained from commercial suppliers and used without further purification. Methylene chloride, anisole and benzyl amine were distilled under nitrogen from calcium hydride. Benzene was distilled under nitrogen from sodium and benzophenone. Benzene-d_6 was dried over sodium and benzophenone, degassed by repeated freeze-pump-thaw cycles, vacuum transferred, and stored in a nitrogen drybox.

General Procedure for The Ring-Closing Metathesis Reactions. $Mo(=CHCMe_2Ph)(=NAr)[OC(CH_3)(CF_3)_2]_2$ (**7**) was purchased from Strem and used without further purification. Separate stock solutions of alkylidene, imine, and standard in the stated molar amount were prepared in benzene-d_6. An internal standard was added to the noted

experiments. The alkylidene and imine were mixed in a screw-top NMR tube. A ^{1}H NMR spectrum was acquired after mixing and every 24 hours thereafter until the concentration of the alkylidene remained constant or reached zero. Integrated areas were used to determine the relative stoichiometries of reagents and products.

2-Vinyl-phenol (1): After 2-hydroxycinnamic acid was pretreated by slow evaporation from acetone, the acid (7.16 g, 43.7 mmol) was decarboxylated according to the method of Hansen under vacuum yielding the white oil **1** (2.36 g, 45%).[54] ^{1}H NMR ($CDCl_3$) δ 5.10 (s, OH), 5.41 (dd, 1, *J = 11.0, 1.0*), 5.80 (dd, 1, *J = 16.0, 1.0*), 7.15 (dd, 1, *J = 17.4, 11.1*), 6.72-7.44 (m, 4).

3-(2-Vinyl-phenoxy)-propane-1,2-diol (2). Using the method of Palermo *et al.*,[55] **1** (2.36 g, 19.6 mmol) in 30 mL of water was heated to 75-80 °C, and a solution of sodium hydroxide (100.0 mg, 2.5 mmol) was added over a period of five minutes. An aqueous solution of racemic glycidol (1.45 g, 19.6 mmol) was added over a period of two hours, and the reaction was stirred for four hours. After dilution with water, heptane was added, and the reaction was allowed to cool to room temperature. Further cooling to 0 ºC gave two crops of solid. Recrystallization from heptane/water gave pure **2** (720.0 mg, 20%). Mp 83-85 °C. ^{1}H NMR ($CDCl_3$) δ 2.31 (br s, 1), 2.76 (br s, 1), 3.99 (m, 2), 4.24-4.26 (m, 1), 4.33 (m, 2), 5.45 (dd, 1, *J = 11.0, 1.0*), 5.91 (dd, 1, *J = 17.2, 1.0*), 7.16 (dd, 1, *J = 17.4, 11.1*), 6.75-7.65 (m, 4). ^{13}C NMR ($CDCl_3$) δ 63.7, 69.5, 70.4, 112.1, 114.9, 121.3, 126.6, 126.9, 128.9, 131.2, 155.3.

(2-Vinyl-phenoxy)-acetaldehyde (3). Based on the method of Lodge *et al.*,[56] 8.5 mL of a 0.308 M solution of sodium periodate (2.6 mmol) was added dropwise over a period of five minutes to a vigorously stirred suspension of silica gel (8.0 g) in methylene chloride (70 mL). Compound **2** (250.0 mg, 1.28 mmol) in methylene chloride was added dropwise, and the reaction was monitored by thin layer chromatography (1:1 ethyl acetate/hexanes). Upon the disappearance of

2 from TLC, the mixture was filtered through celite to remove solids. The solvent was removed *in vacuo* yielding the white solid **3** (147.0 mg, 70%). ^{1}H NMR ($CDCl_3$) δ 4.58 (s, 2), 5.34 (dd, 1, *J = 11.0, 1.0*), 5.81 (dd, 1, *J = 17.3, 1.0*), 7.17 (dd, 1, *J = 17.6, 11.1*), 7.00-7.56 (m, 4), 9.91 (s, 1).

ROMPGEL (4). Based on the method of Arnauld *et al*.,[35] to a stirred solution of 3,6-epoxy-1,2,3,6-tetrahydrophthalicanhydride (1.5 g, 9.0 mmol), norbornadiene (0.1 mL, 1.8 mmol), and bis(tricyclohexylphosphine) benzylideneruthenium(IV) dichloride (111.0 mg, 0.14 mmol) was added. After stirring for two hours, ethyl vinyl ether (1.5 mL) was added, and the reaction was further stirred for one hour. The insoluble tan solid was removed by filtration and washed with methylene chloride (5 ml), ethyl acetate (5 ml), ether (5 ml), and methylene chloride (5 ml). The solid was dried under vacuum at room temperature yielding **4**.

Benzyl-[2-(2-vinyl)-phenoxy) ethylidene] amine (5). To a solution of **3** (191.0 mg, 1.17 mmol) in 10 mL of benzene under nitrogen, benzyl amine (0.12 mL, 1.11 mmol) was added. Molecular sieves (4 Å, 3.0 g) were added over a period of one hour, and the reaction was further stirred for one hour. The reaction mixture was filtered, added to **4** (140.0 mg), and stirred under nitrogen for 10 hours. ROMPGEL **4** was then removed by filtration and washed with benzene. The solvent was removed *in vacuo* from the combined filtrates to yield the orange oil **5** (93.0 mg, 32%).[50] ^{1}H NMR ($CDCl_3$) δ 3.99 (m, 2), 4.79 (m, 2), 5.35 (dd, 1, *J = 11.0, 1.0*), 5.84 (dd, 1, *J = 17.0, 1.0*), 7.14 (dd, 1, *J = 17.6, 11.2*), 6.93-7.57 (m, 9), 8.02 (br s, 1). ^{13}C NMR ($CDCl_3$) 64.6, 70.3, 112.4, 114.6, 121.3, 126.5, 127.3, 128.1, 128.3, 128.8, 131.5, 138.4, 155.4, 162.0.

2H-Chromene (6). Based on the method of Boyd *et al*.,[57] a benzene solution of racemic chroman-4-ol (300.0 mg, 1.99 mmol) containing toluene *p*-sulfonic acid (1.14 mg, 5.9 μmol) and hydroquinone (0.2 mg, 1.8 μmol) was heated under reflux using a Dean-Stark trap for 1.5 hours.

The cooled benzene solution was washed with water, dried (Na_2SO_4) and reduced *in vacuo*. The residue was partially purified by column chromatography on silica gel (methylene chloride) yielding a mixture of **6** and chroman-4-ol. ^{1}H NMR (C_6D_6) δ 4.47 (m, 2, 2-H), 5.26 (dt, 1, J_1 = *13.4*, J_2 = *4.4*), 6.17 (dtd, 1, J_1 = *8.5*, J_2 = *3.4*, J_3 = *0.5*), 6.90-7.45 (m, 4 H). MS(EI), *m/z* 133, 132, 131 (base), 103, 77, 51.

The stoichiometric reaction of imino-olefin 5 and alkylidene 7. The following stock solutions were prepared in benzene-d_6: 0.065 M alkylidene **7**, 0.144 M imine **5**, and 0.131 M anisole. Imine **5** (0.09 mL, 0.01 mmol), alkylidene **7** (0.2 mL, 0.01 mmol) and anisole (0.1 mL, 0.01 mmol) were added to a screw-top NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy for four days, and a 43% yield of chromene **6** was observed. In addition, neophylene **8**, mixed bis(imide) **11**, chelate **10**, and chelate isomer **12** were detected. The dark red reaction mixture was flashed through a silica column (methylene chloride). The solvent was removed *in vacuo* yielding a light green oil containing **6**, **8**, **9**, and other unidentified olefin products.[50] **6**: ^{1}H NMR (C_6D_6) δ 4.45 (m, 2, 2-H), 5.24 (dt, 1, J_1 = *10.0*, J_2 = *3.6*), 6.17 (dtd, 1, J = *9.8*), 6.90-7.45 (m, 4 H). MS(EI), *m/z* 133 (M^++1), 132 (M^+), 131 (M^+-1) (base), 103 (M^+ - CO), 77, 51. **8**: ^{1}H NMR (C_6D_6) 1.37 (s, 6), 5.04 (dd, 1, J_1 = *4.2*, J_2 = *1.3*), 5.08 (dd, 1, J_1 = *11.0*, J_2 = *1.3*), 7.05-8.00 (m, 5 H). MS(EI), *m/z* 147 (M^++1), 146 (M^+), 131 (M^+ - CH_3) (base), 91, 77, 51. **9**: ^{1}H NMR (C_6D_6) δ 1.22 (d, 12, J = *6.7*), 2.72 (hpt, 2, J = *6.8*), 7.10-7.55 (m, 4 H). MS(EI), *m/z* 177 (M^+),162 (M^+-CH_3), 120. **10**: ^{1}H NMR (C_6D_6) δ 6.60 (m, 2), 13.5 (s, 1). ^{13}C NMR (C_6D_6) δ(C_α) 303.6, J_{CH} = *142.0 Hz*. **11**: ^{1}H NMR (C_6D_6) δ 5.15 (s,2) (other resonances not observable due to overlap). **12**: ^{1}H NMR (C_6D_6) δ 6.56 (m, 2), 12.9 (s,1). ^{13}C NMR (C_6D_6) δ(C_α) 266.4, J_{CH} = *148.0 Hz*.

The reaction of imino-olefin 5 and excess alkylidene 7. Imine **5** (34.5 mg, 0.13 mmol) in 0.45 mL benzene-d_6, excess alkylidene **7** (200.0 mg, 0.26 mmol) in 2.5 mL benzene-d_6 and anisole (0.04 mL, 0.36 mmol) were added to a screw-top NMR tube. The reaction was monitored for six days by ^{1}H NMR spectroscopy, and a 64 % yield of chromene **6** was observed; in addition, neophylene **8**, chelate **10**, chelate isomer **12** and bis(imide) **11** were detected. The reaction was reduced *in vacuo* yielding a dark green oil and flashed through a silica column (methylene chloride). The solvent was removed *in vacuo* yielding a light green oil containing compounds **6**, **8**, and **9**. **6**: ^{1}H NMR (C_6D_6) δ 4.45 (m, 2, 2-H), 5.24 (dt, 1, J_1 = *10.0,* J_2 = *3.6*), 6.17 (dtd, 1, J = *9.8*), 6.90-7.45 (m, 4 H). MS(EI), *m/z* 133 (M^++1), 132 (M^+), 131 (M^+-1) (base), 103 (M^+ - CO), 77, 51. **8**: ^{1}H NMR (C_6D_6) 1.37 (s, 6), 5.04 (dd, 1, J_1 = *4.2,* J_2 = *1.3*), 5.08 (dd, 1, J_1 = *11.0,* J_2 = *1.3*), 7.05-8.00 (m, 5 H). MS(EI), *m/z* 147 (M^++1), 146 (M^+), 131 (M^+ - CH_3) (base), 91, 77, 51. **9**: ^{1}H NMR (C_6D_6) δ 1.22 (d, 12, J = *6.7*), 2.72 (hpt, 2, J = *6.8*), 7.10-7.55 (m, 4 H). MS(EI), *m/z* 177 (M^+),162 (M^+-CH_3), 120. **10**: ^{1}H NMR (C_6D_6) δ 6.60 (m, 2), 13.5 (s, 1). ^{13}C NMR (C_6D_6) δ(C_α) 303.6, J_{CH} = *142.0 Hz*. **11**: ^{1}H NMR (C_6D_6) δ 5.15 (s, 2) (other resonances not observable due to overlap). **12**: ^{1}H NMR (C_6D_6) δ 6.56 (m, 2), 12.9 (s,1). ^{13}C NMR (C_6D_6) δ(C_α) 266.4, J_{CH} = *148.0 Hz*.

The reaction of excess imino-olefin 5 and alkylidene 7. Excess imine **5** (93.5 mg, 0.37 mmol) in 0.55 mL benzene-d_6, alkylidene **7** (203.0 mg, 0.25 mmol) in 1.5 mL benzene-d_6 and hexamethyl benzene standard (0.65 mL, 0.2 mmol) were added to a screw-top NMR tube. Immediately after mixing, the formation of chromene **6** and neophylene **8** was detected. The reaction was monitored for one day by ^{1}H NMR spectroscopy, and a 36% yield of chromene **6** was observed; in addition, chelate **10**, chelate isomer **12**, and secondary olefinic species were detected. The dark red solution was flashed through a silica column (methylene chloride). The

solvent was removed *in vacuo* yielding a light green oil containing compounds **6**, **8**, and **9**. **6**: ^{1}H NMR (C_6D_6) δ 4.45 (m, 2, 2-H), 5.24 (dt, 1, $J_1 = 10.0$, $J_2 = 3.6$), 6.17 (dtd, 1, $J = 9.8$), 6.90-7.45 (m, 4 H). MS(EI), *m/z* 133 (M^++1), 132 (M^+), 131 (M^+-1) (base), 103 (M^+ - CO), 77, 51. **8**: ^{1}H NMR (C_6D_6) 1.37 (s, 6), 5.04 (dd, 1, $J_1 = 4.2$, $J_2 = 1.3$), 5.08 (dd, 1, $J_1 = 11.0$, $J_2 = 1.3$), 7.05-8.00 (m, 5 H). MS(EI), *m/z* 147 (M^++1), 146 (M^+), 131 (M^+ - CH_3) (base), 91, 77, 51. **9**: ^{1}H NMR (C_6D_6) δ 1.22 (d, 12, $J = 6.7$), 2.72 (hpt, 2, $J = 6.8$), 7.10-7.55 (m, 4 H). MS(EI), *m/z* 177 (M^+),162 (M^+-CH_3), 120. **10**: ^{1}H NMR (C_6D_6) δ 6.60 (m, 2), 13.5 (s, 1). ^{13}C NMR (C_6D_6) δ(C_α) 303.6, $J_{CH} = 142.0$ Hz. **12**: ^{1}H NMR (C_6D_6) δ 6.56 (m, 2), 12.9 (s,1). ^{13}C NMR (C_6D_6) δ(C_α) 266.4, $J_{CH} = 148.0$ Hz.

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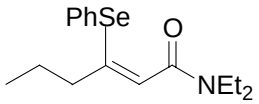
Appendix A.

Chapter 1

Figure A.1. The 300 and 75 MHz ^{1}H and ^{13}C NMR spectra of (*Z*)-3-phenylselenyl-hex-2-enoic acid diethylamide.



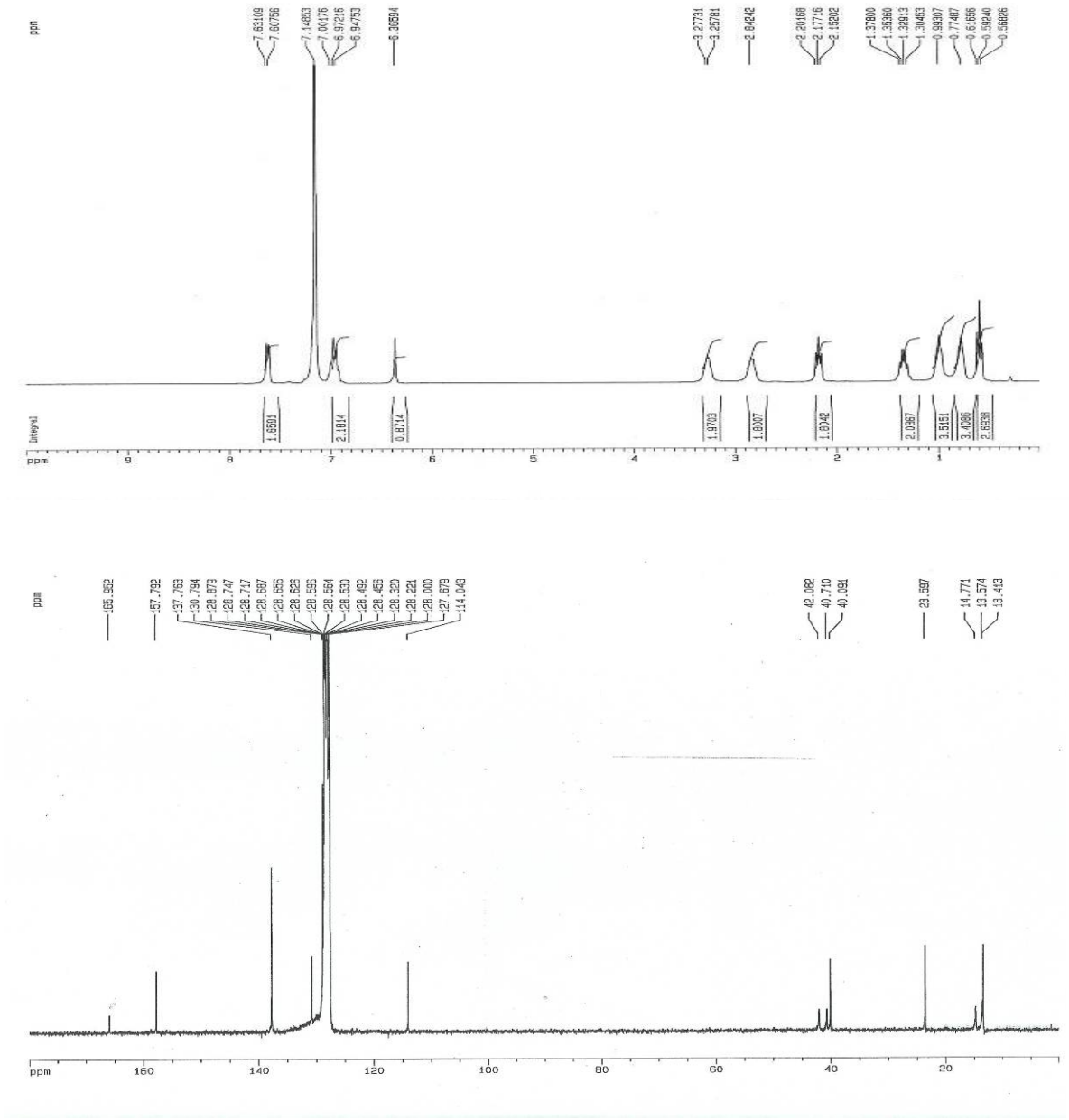
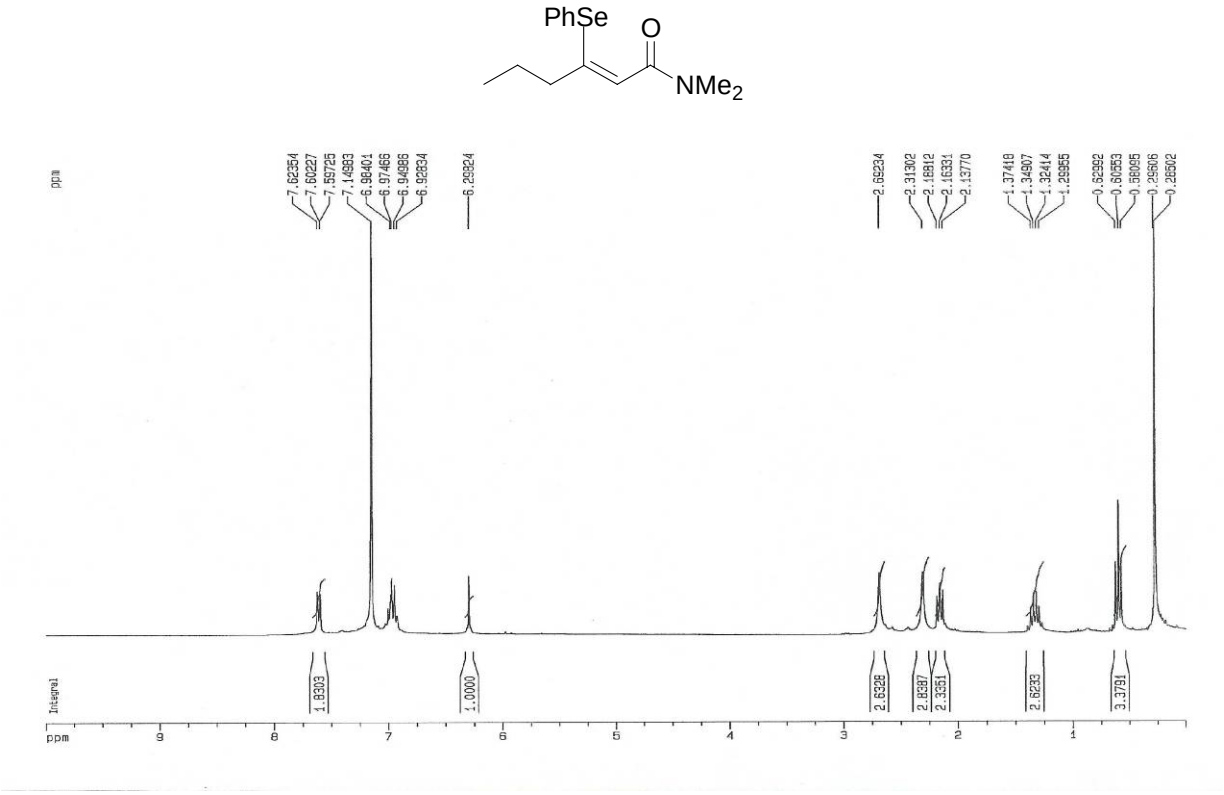


Figure A.2. The 300 MHz ^{1}H NMR spectrum and IR trace of (*Z*)-3-phenylselenyl-hex-2-enoic acid dimethylamide.



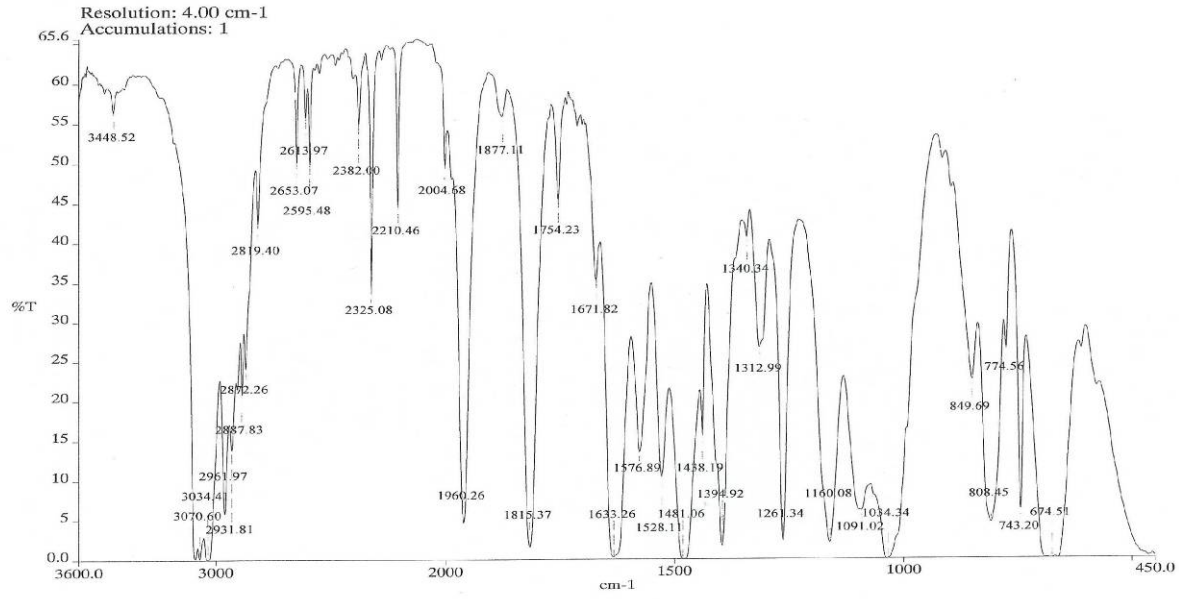


Figure A.3. The noe spectra of (*Z*)-3-phenylselenyl-hex-2-enoic acid dimethylamide.

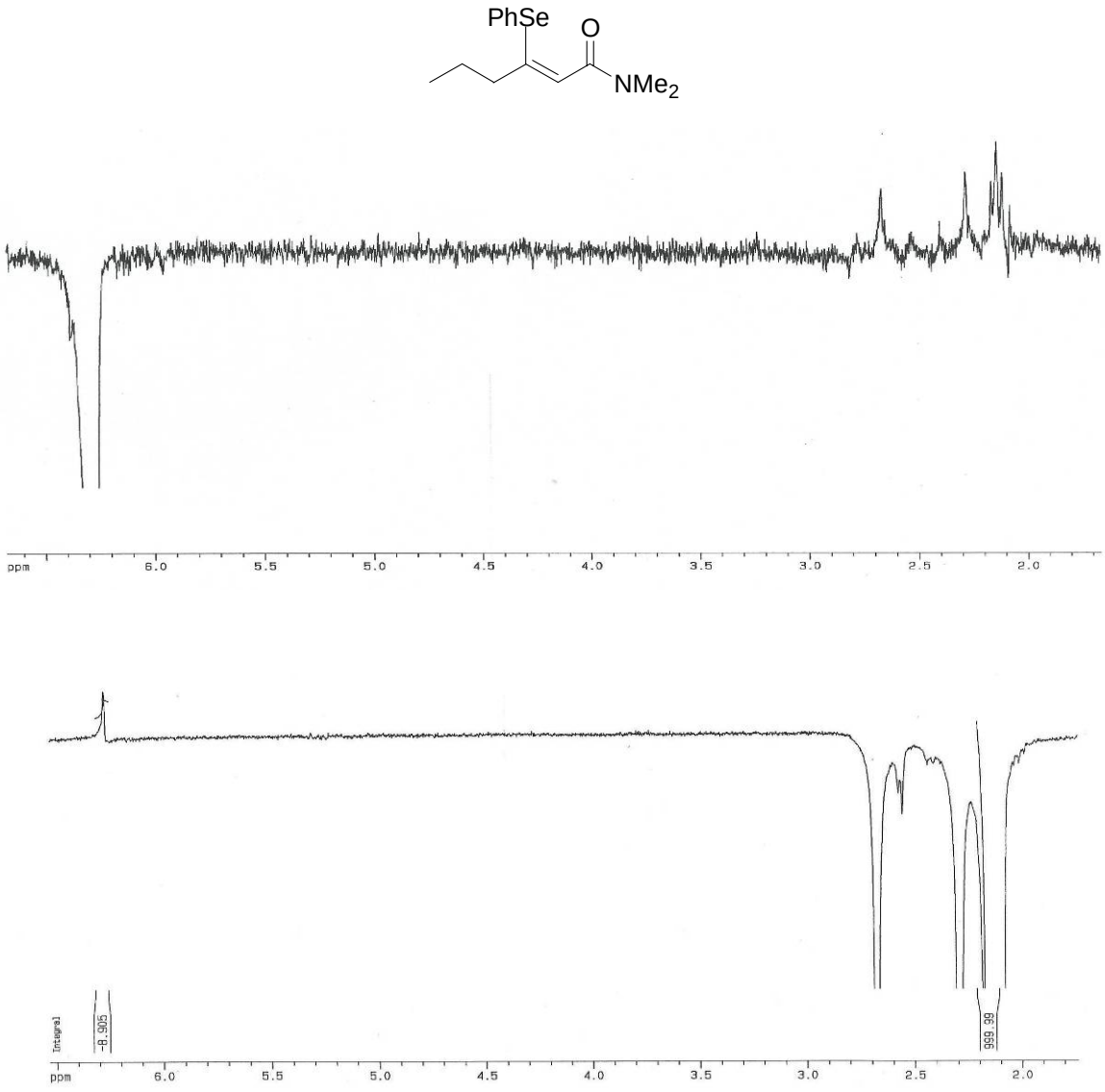
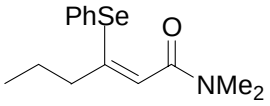


Figure A.4. The MS trace of (*Z*)-3-phenylselenyl-hex-2-enoic acid dimethylamide.



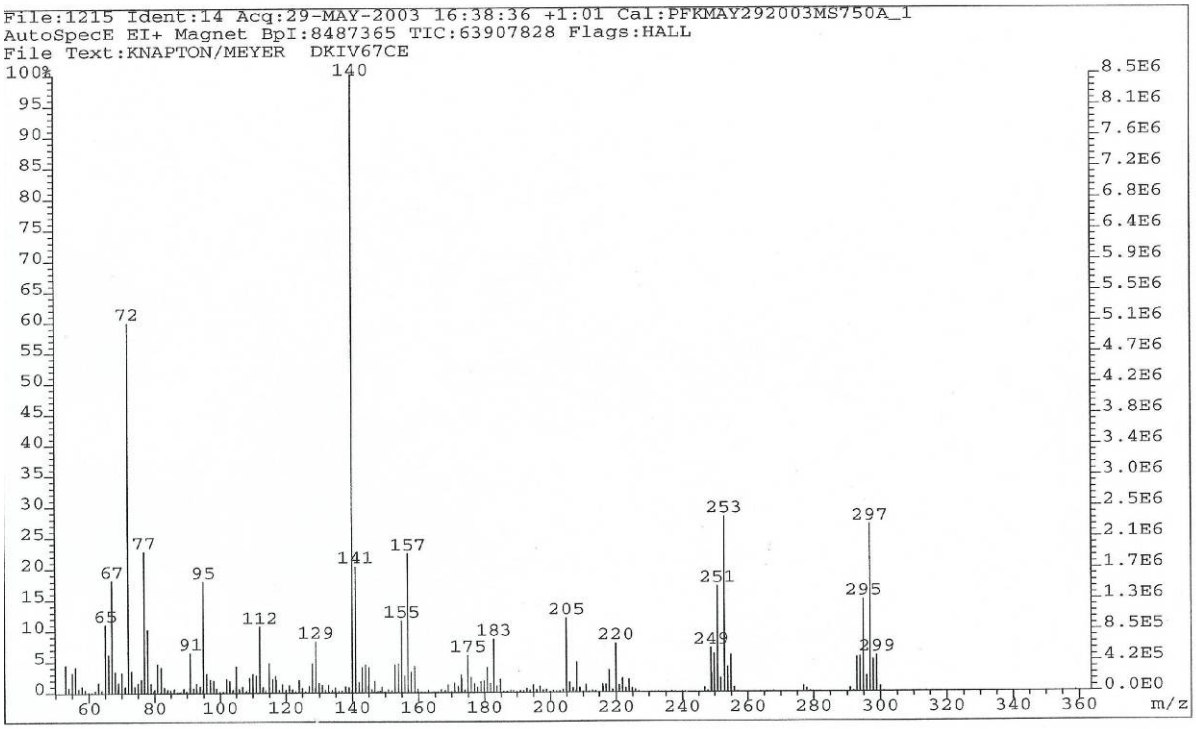
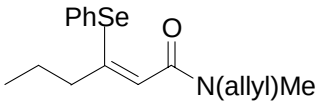


Figure A.5. The 600 and 150 MHz ^{1}H and ^{13}C NMR spectra of (*Z*)-3-phenylselenyl-hex-2-enoic acid allyl-methyl-amide.



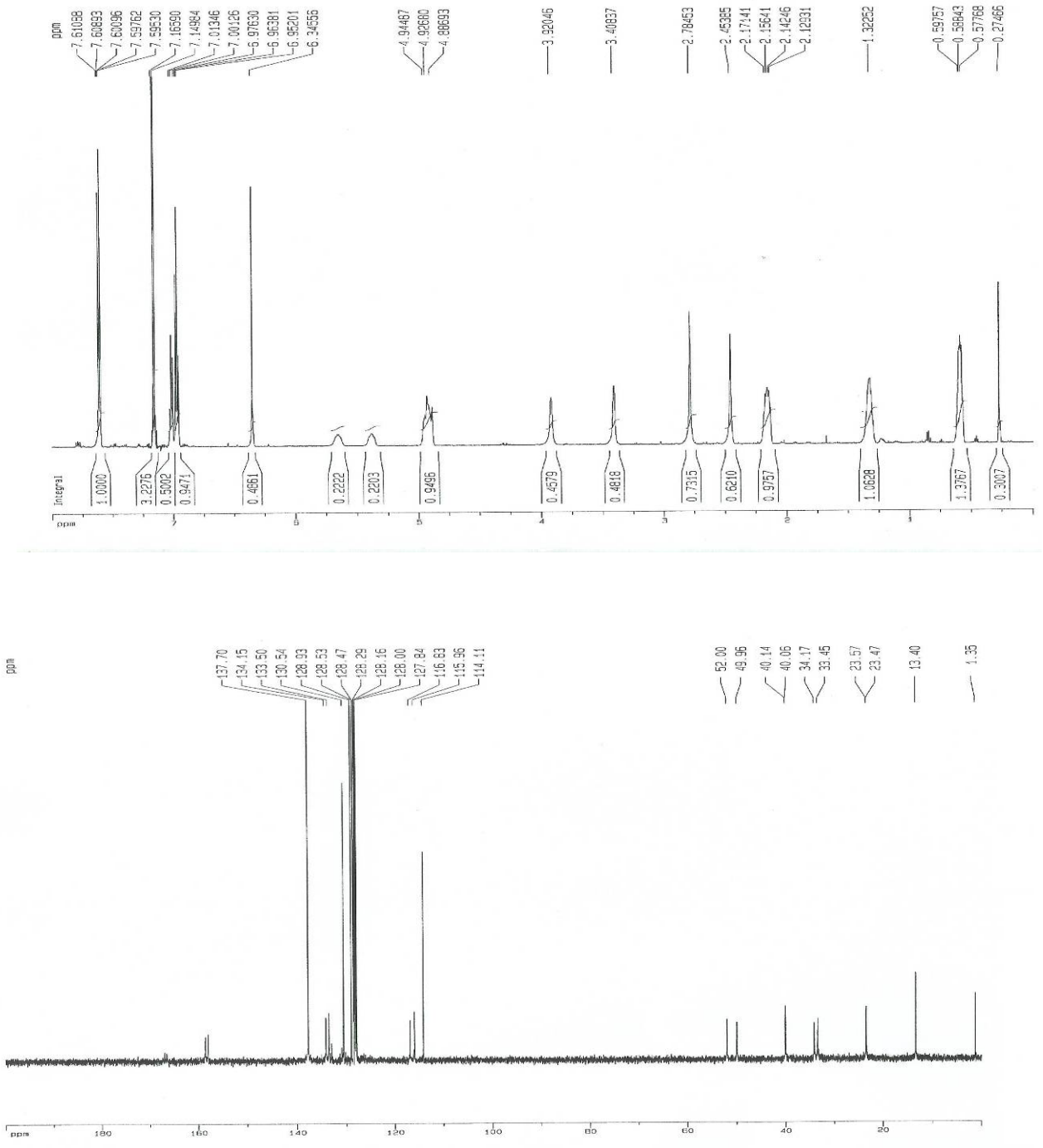
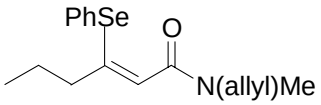
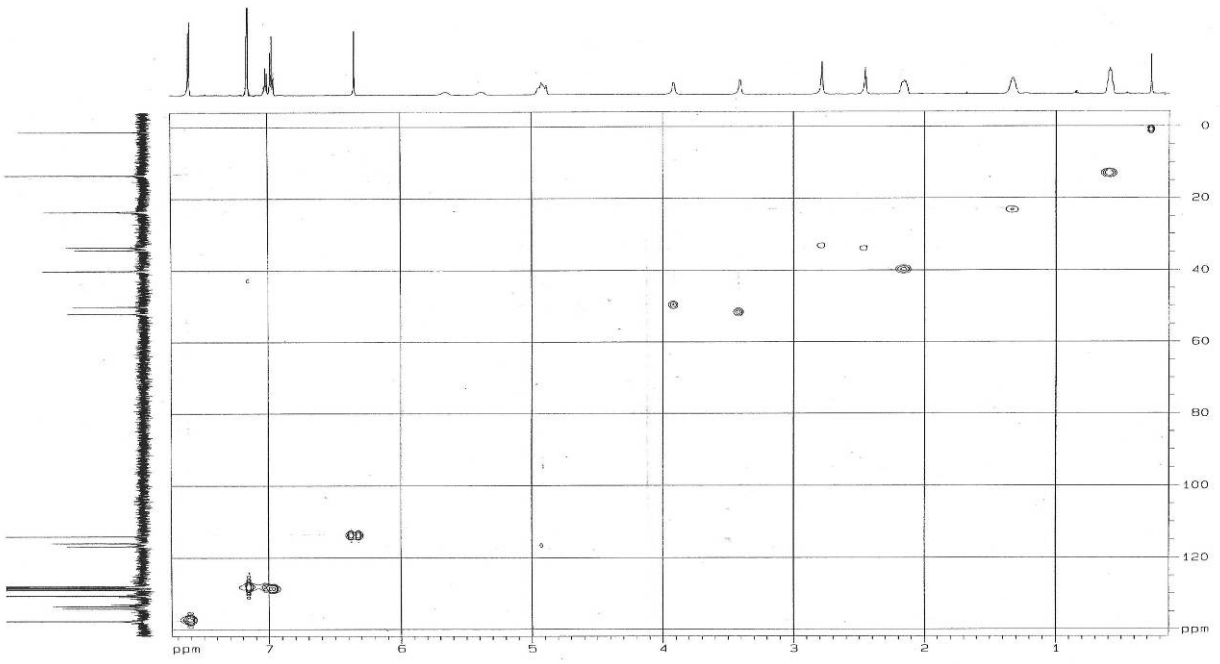


Figure A.6. The 600 MHz/150 MHz HMQC and HMBC spectra of (*Z*)-3-phenylselenyl-hex-2-enoic acid allyl-methyl-amide.





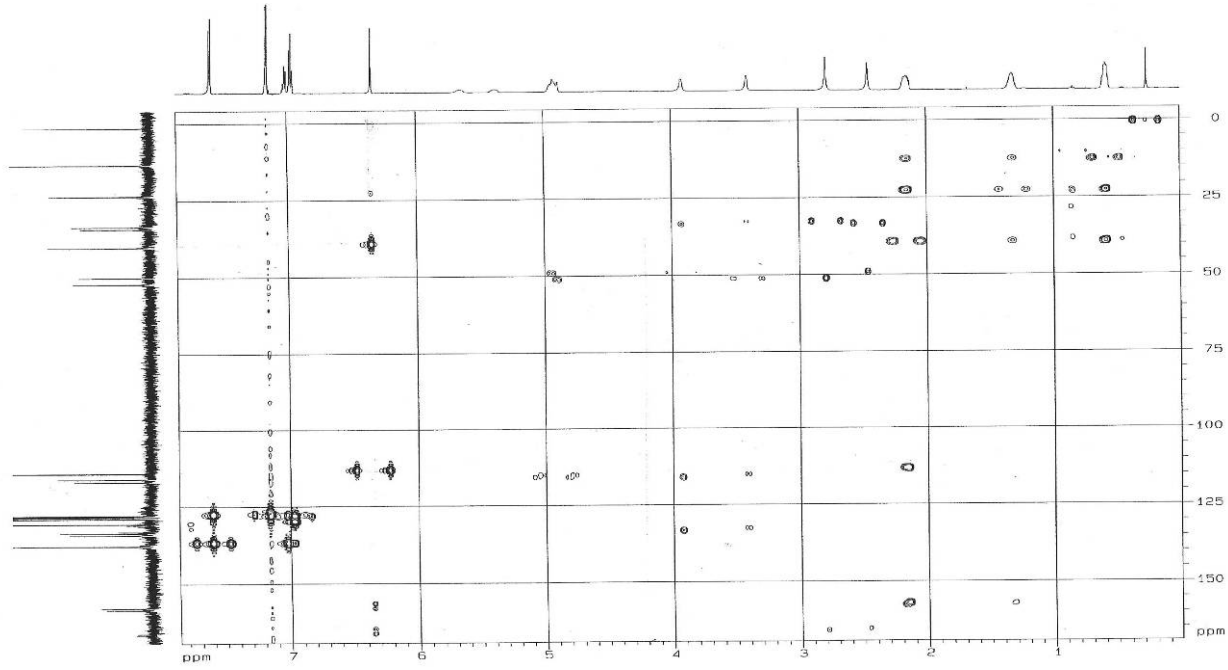
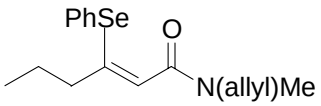


Figure A.7. The MS trace of (*Z*)-3-phenylselenyl-hex-2-enoic acid allyl-methyl-amide.



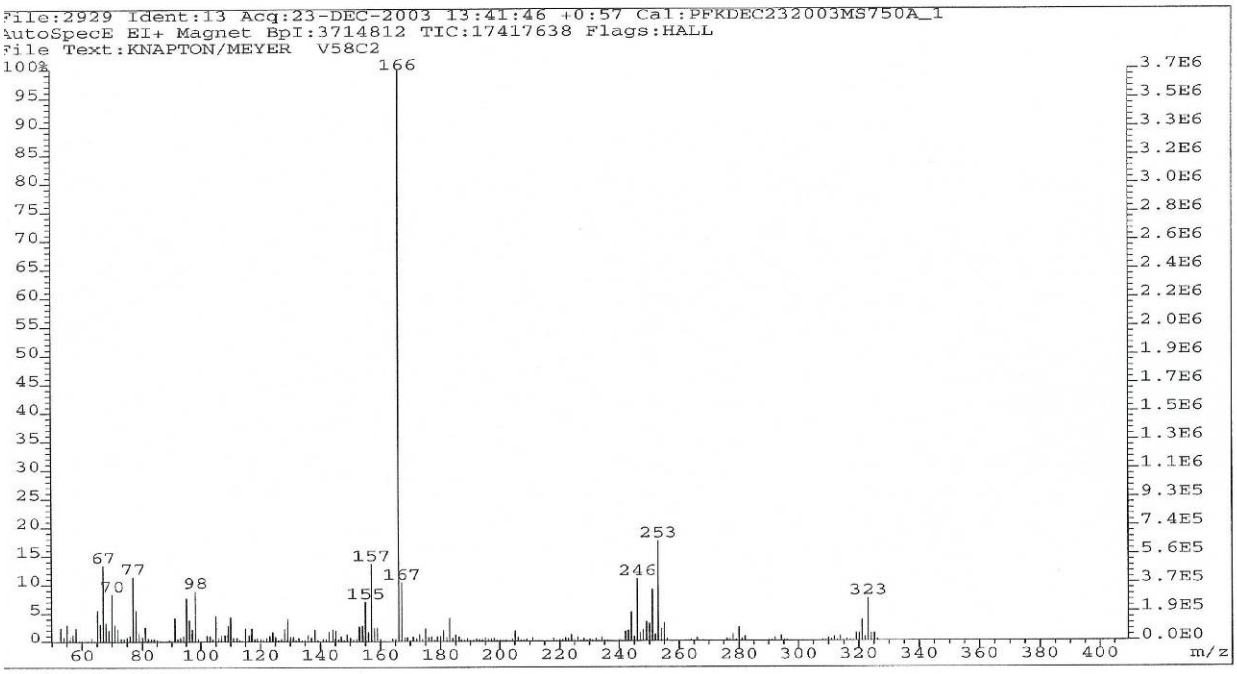
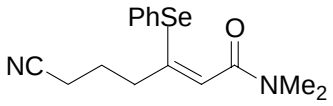
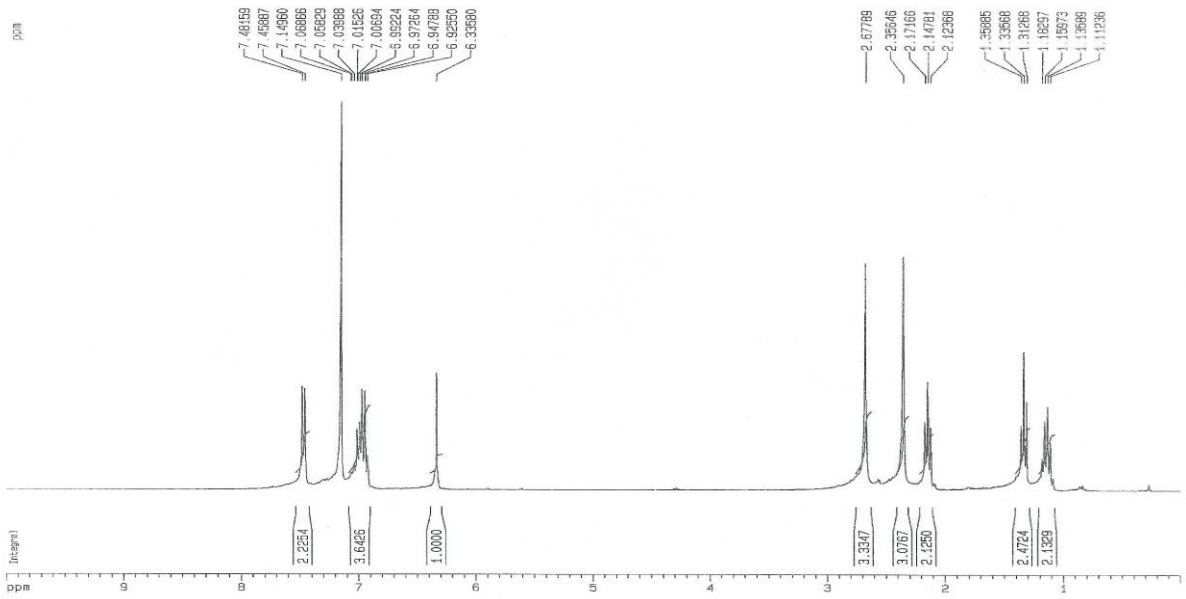


Figure A.8. The 300 MHz ^{1}H NMR spectrum and MS trace of 6-cyano-(*Z*)-3-phenylselenyl-hex-2-enoic acid dimethylamide.





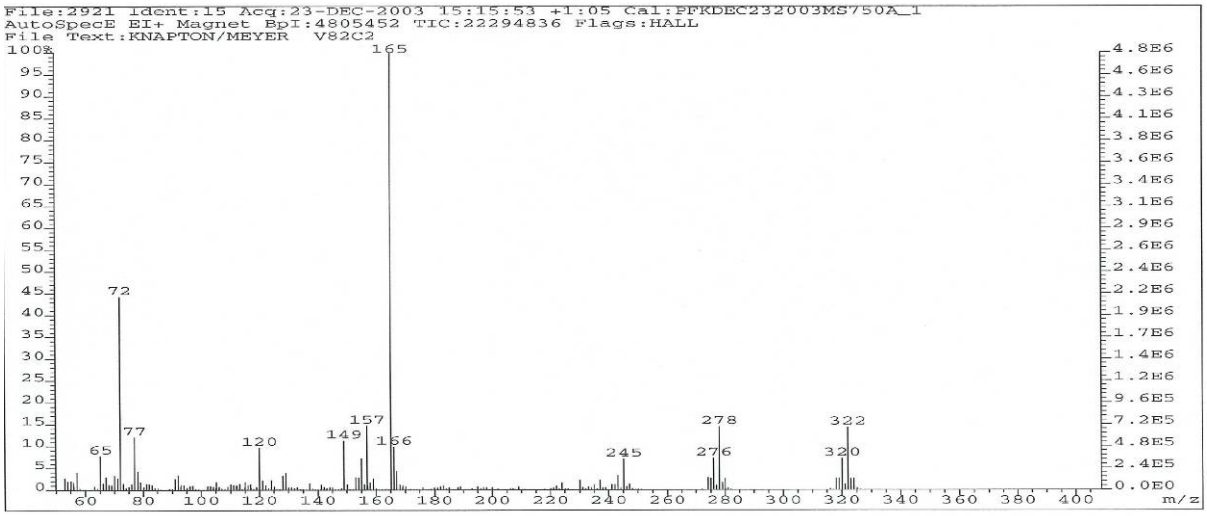
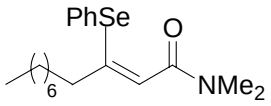
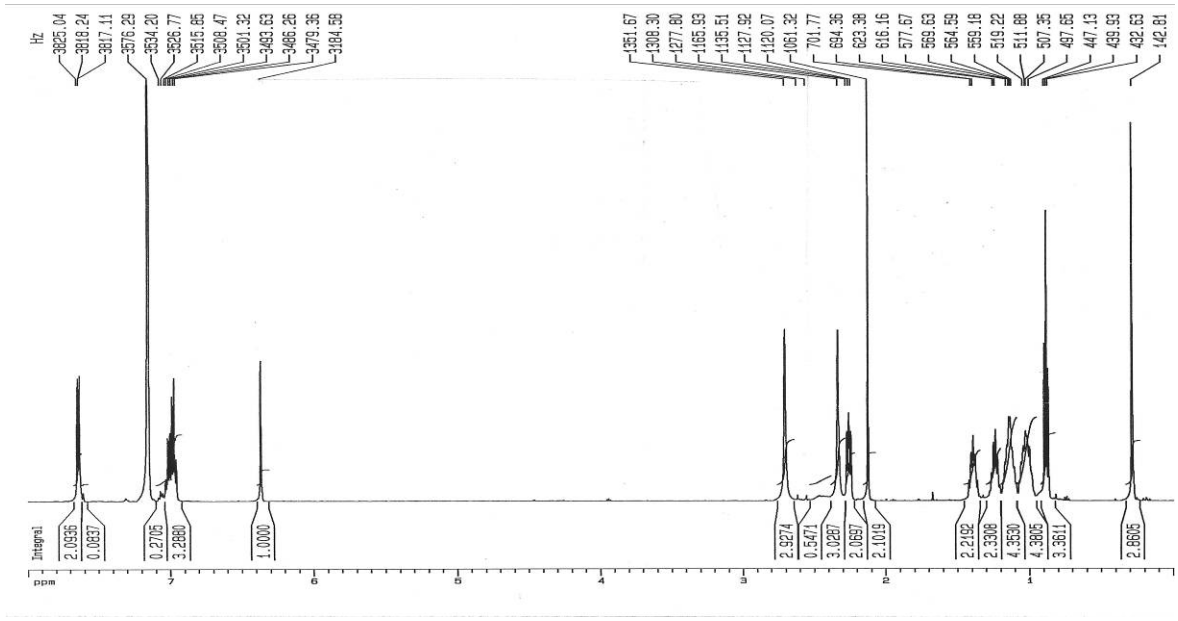


Figure A.9. The 500 and 125 MHz ^{1}H and ^{13}C NMR spectra of (*Z*)-3-phenylselenyl-undec-2-enoic acid dimethylamide.





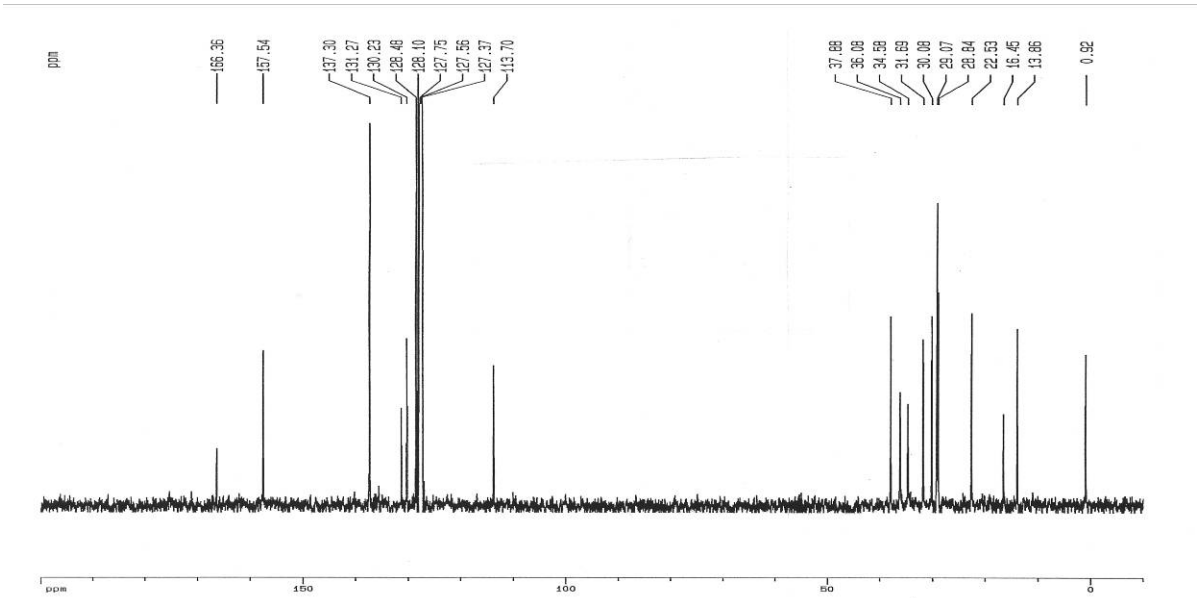


Figure A.10. The 300 and 75 MHz ^{1}H and ^{13}C NMR spectra of (*Z*)-1,3-bis(phenylthio)-2-hexen-1-one.

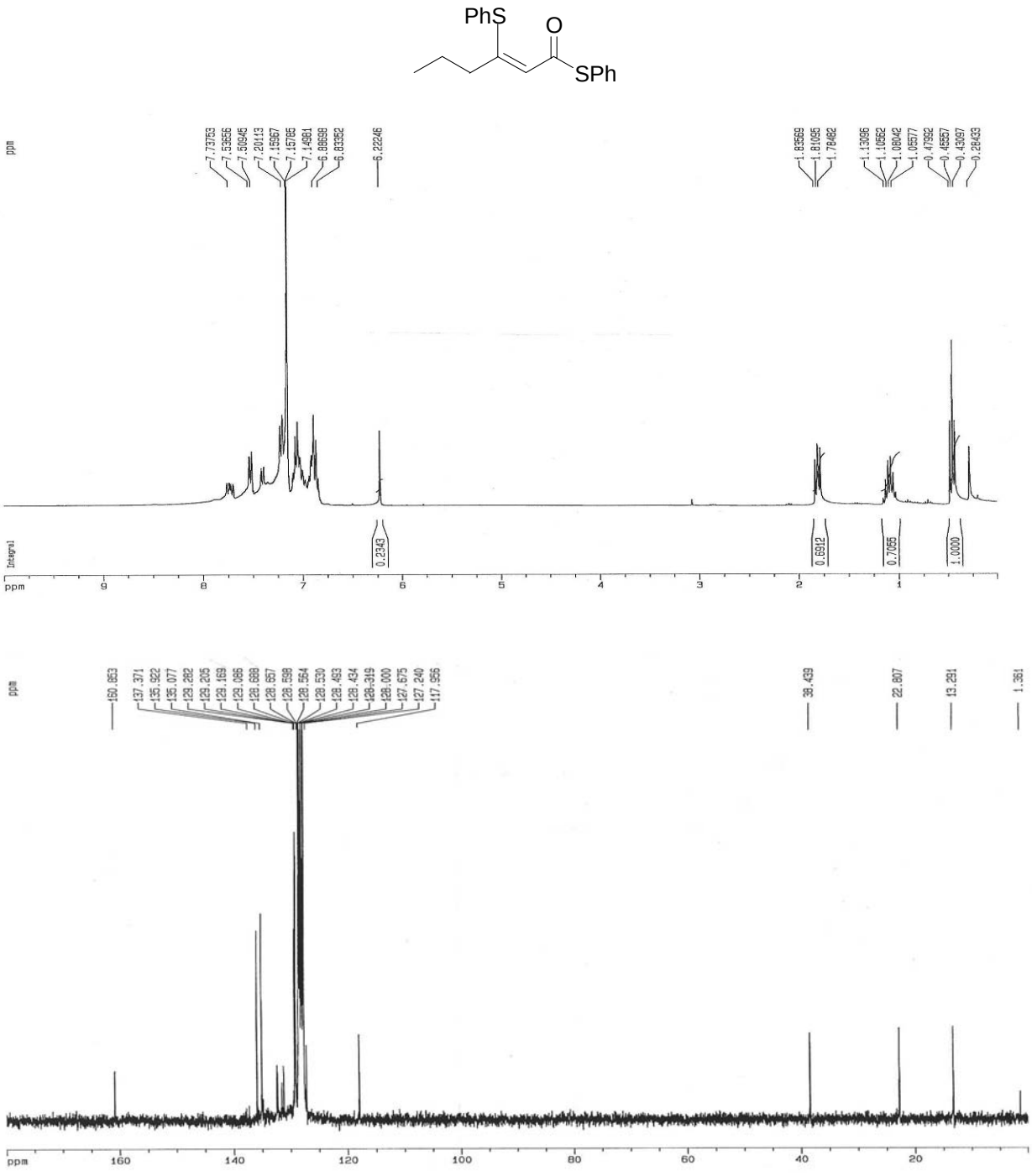


Figure A.11. The 300 and 75 MHz ^{1}H and ^{13}C NMR spectra of (*Z*)-1,3-bis(phenylseleno)-2-hexen-1-one.

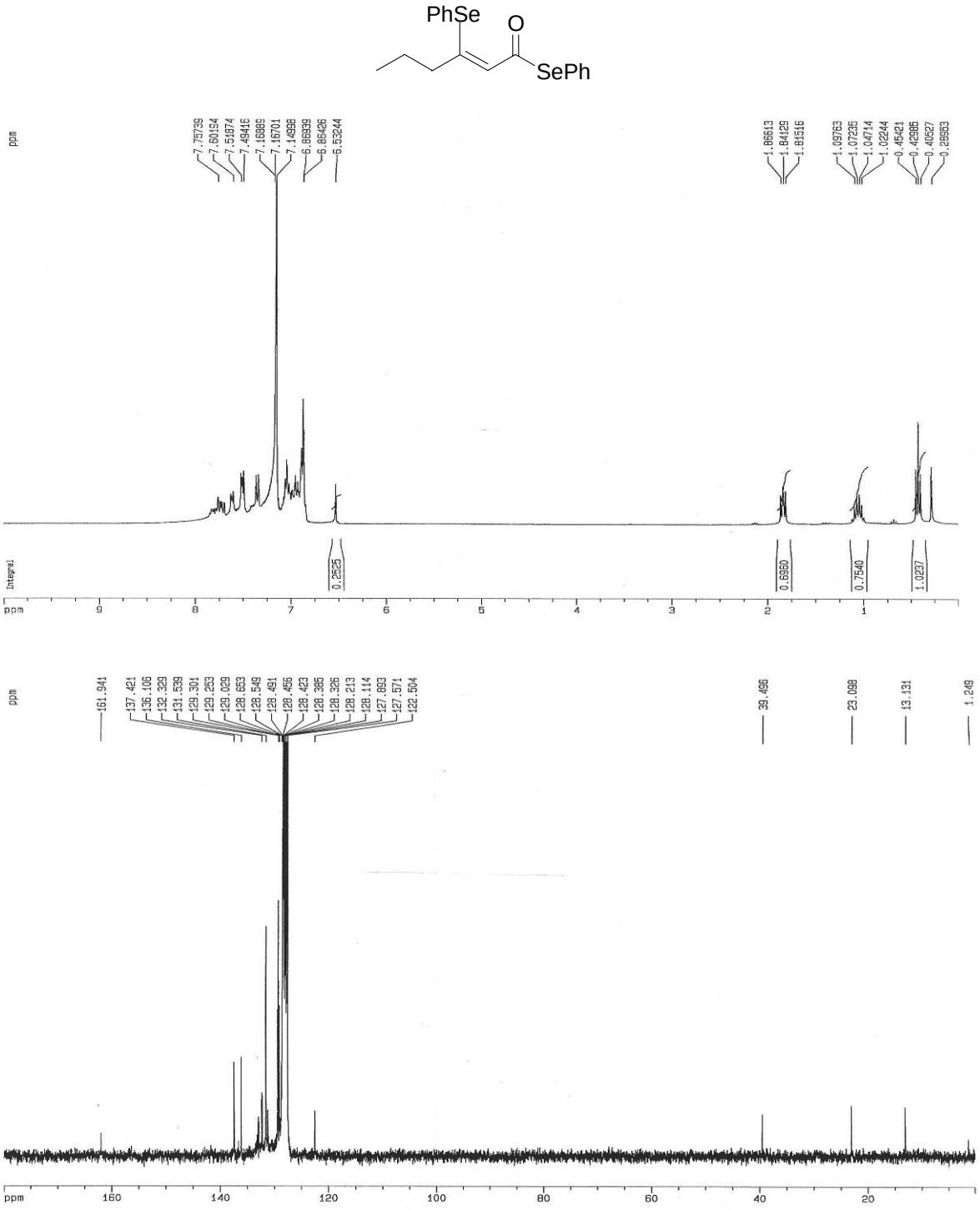


Figure A.12. The 300 and 75 MHz ^{1}H and ^{13}C NMR spectra of S-phenyl-*N*-diethyl-sulfenamide.

$PhS-NEt_2$

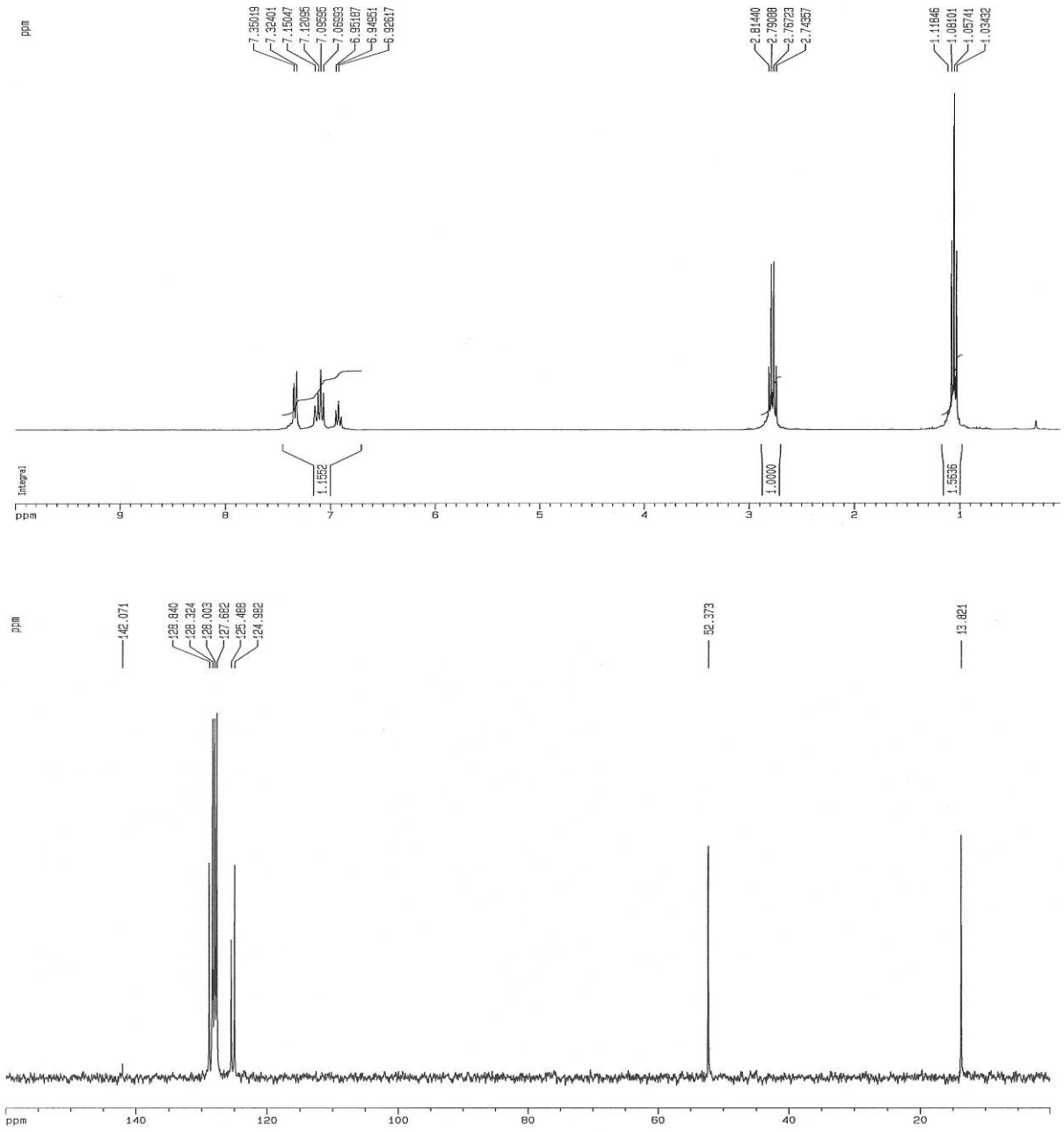
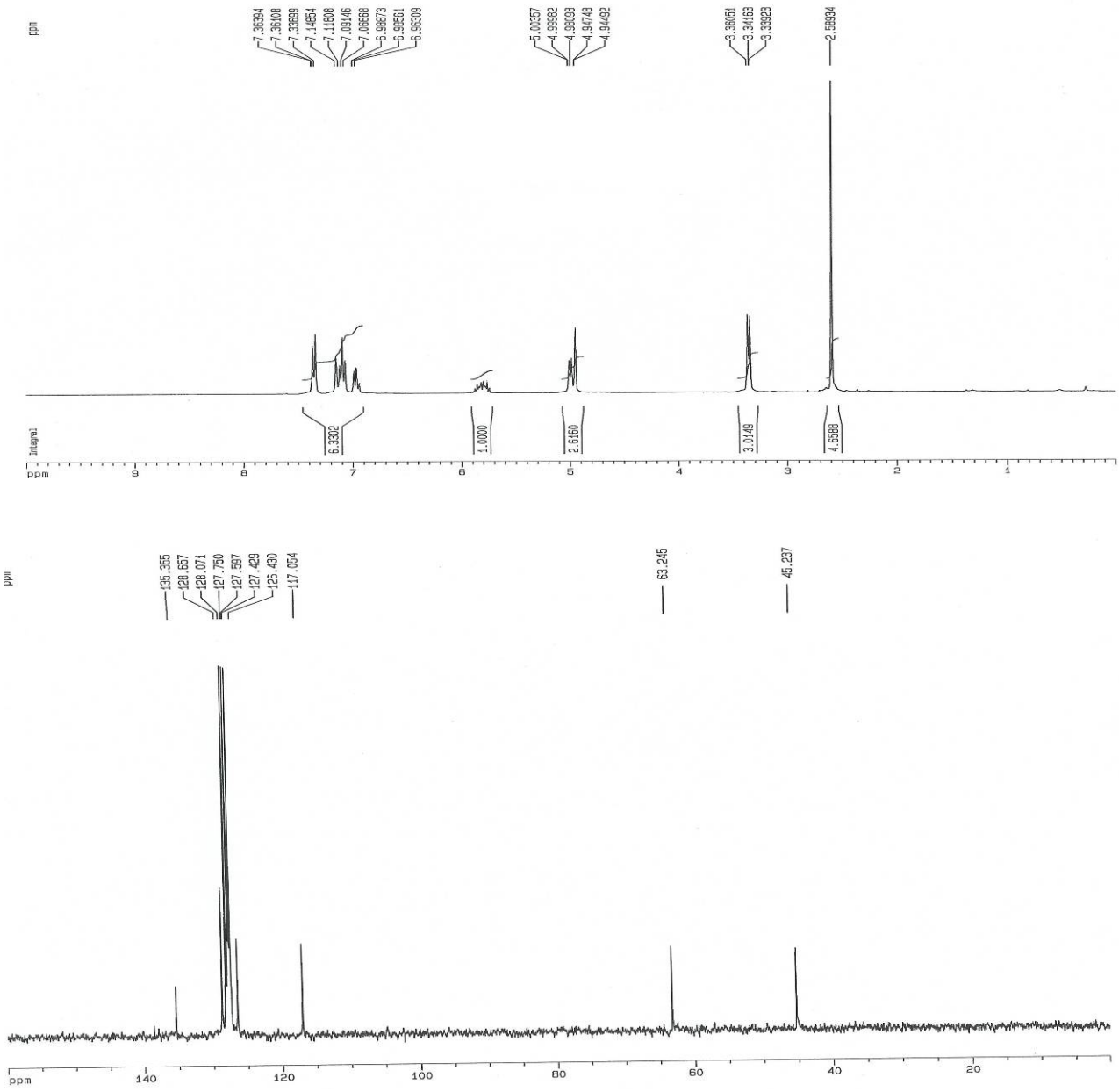


Figure A.13. The 300 and 75 MHz ^{1}H and ^{13}C NMR spectra S-phenyl-*N*-allyl-*N*-methyl sulfenamide.

PhS—N(allyl)Me



Appendix B.

Chapter 2

Figure B.1. A typical GC trace for the preparation of *N*-benzyl-*N*-methyl phenyl selenocarbamate with corresponding MS trace of title product.

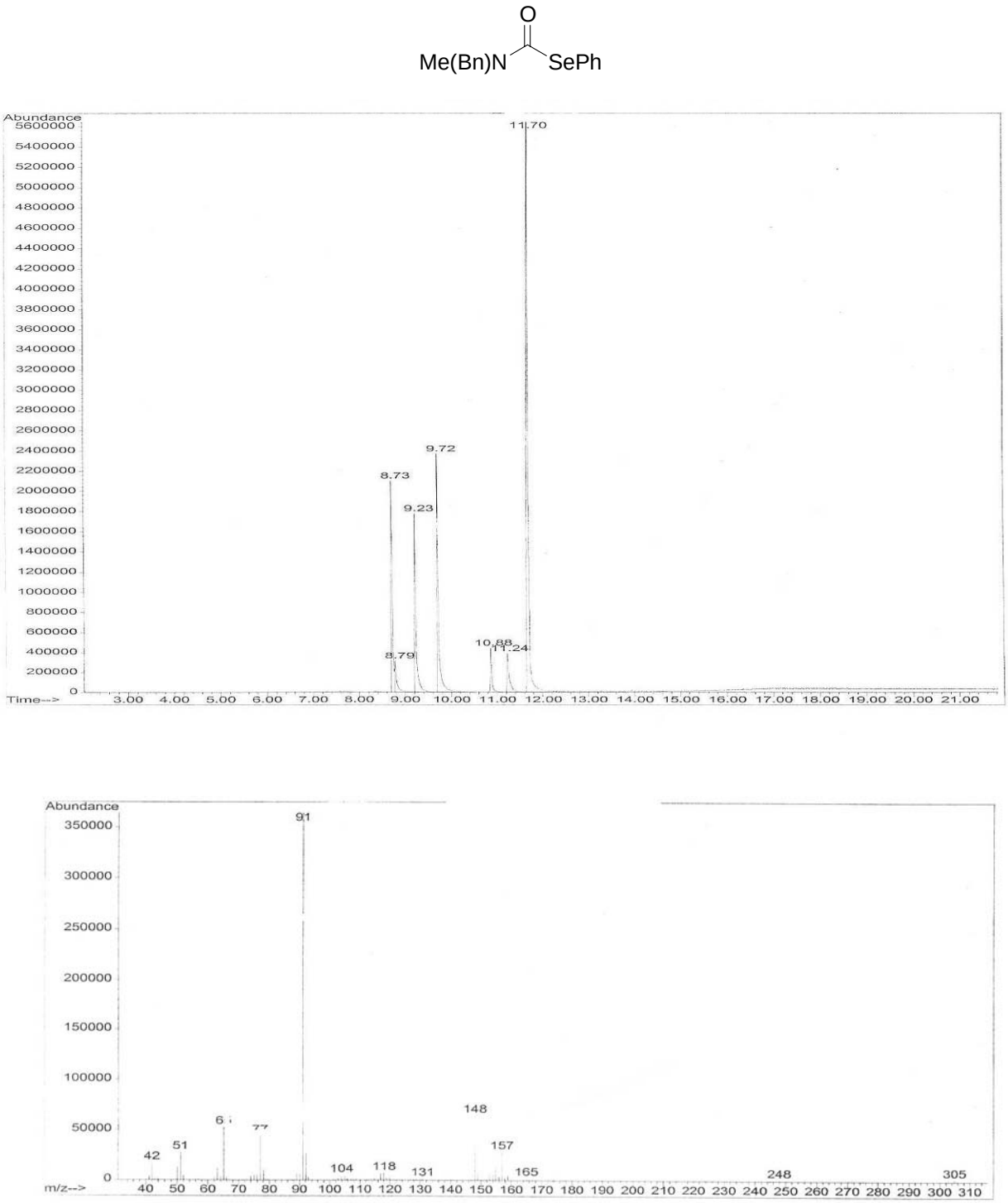


Figure B.2. The high temperature 300 MHz ^{1}H NMR of a 9:1 mixture of *N*-benzyl-*N*-methyl phenyl selenocarbamate and *N*-benzyl-*N*-methyl phenyl thiocarbamate.

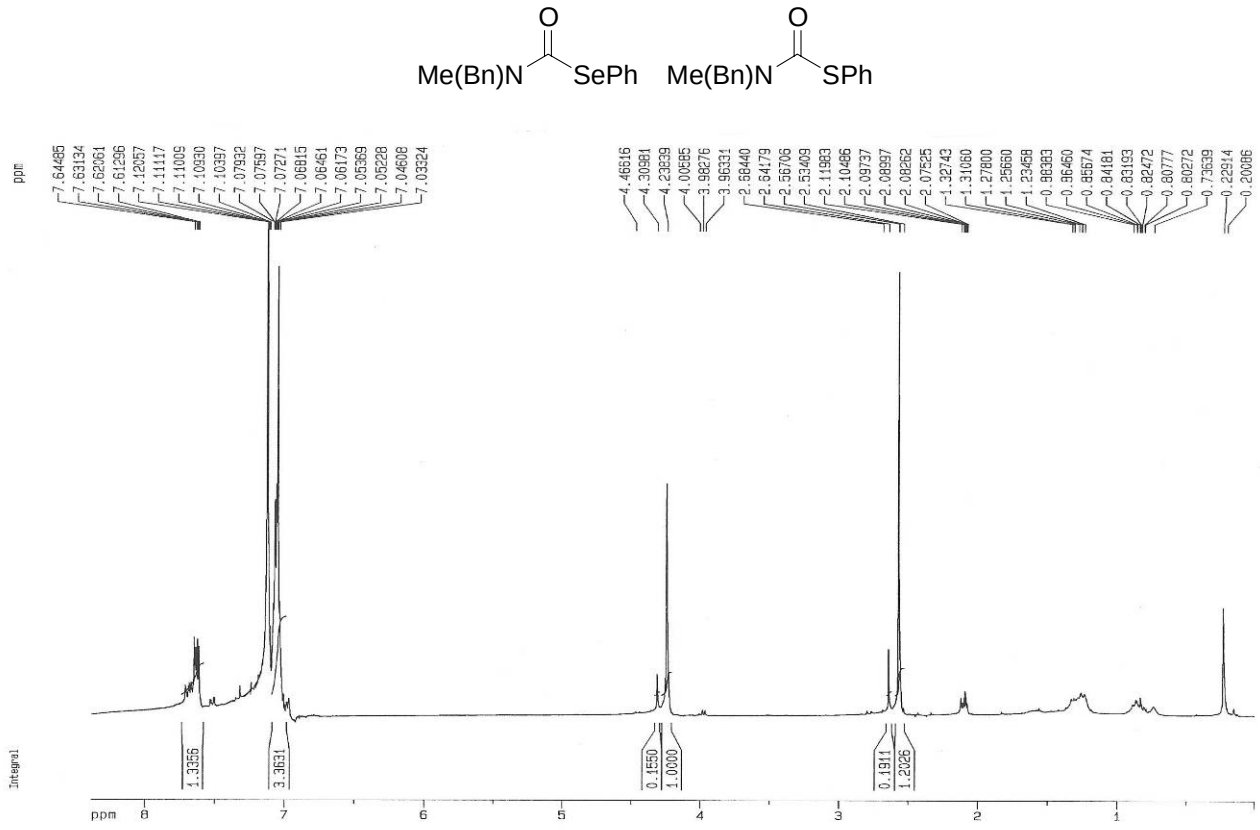
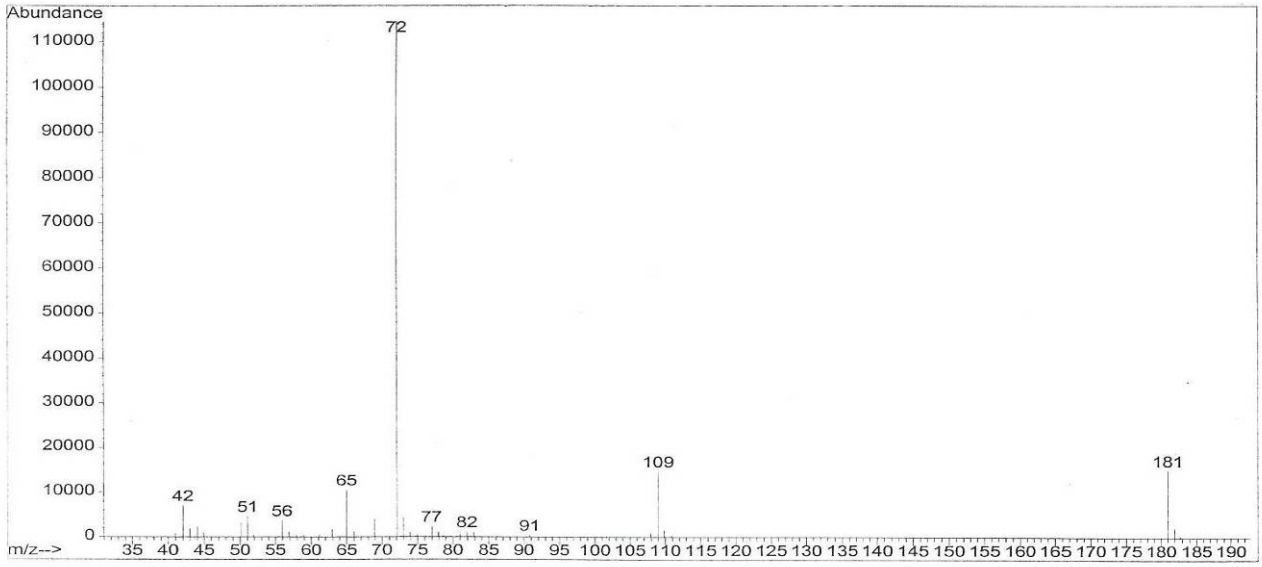
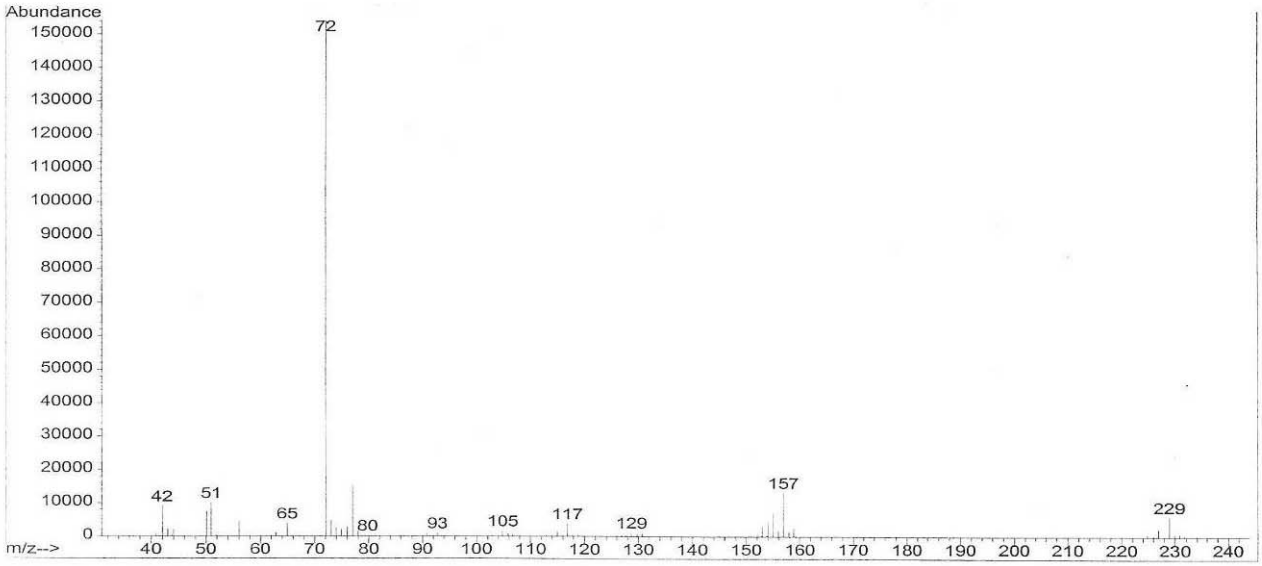


Figure B.3. The MS traces for *N*-dimethyl phenyl thiocarbamate and *N*-dimethyl phenyl selenocarbamate.

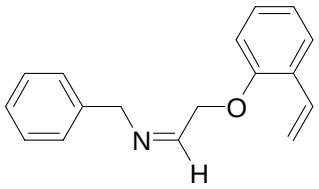


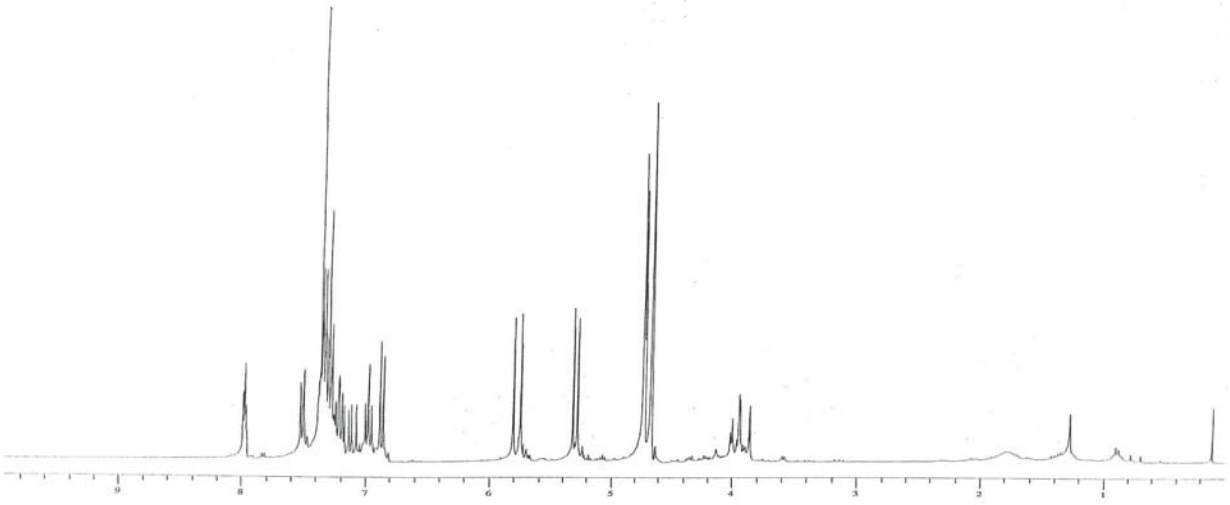


Appendix C.

Chapter 3

Figure C.1. The 300 and 75 MHz ^{1}H and ^{13}C NMR spectra of benzyl-[2-(2-vinyl)-phenoxy) ethylidene] amine.





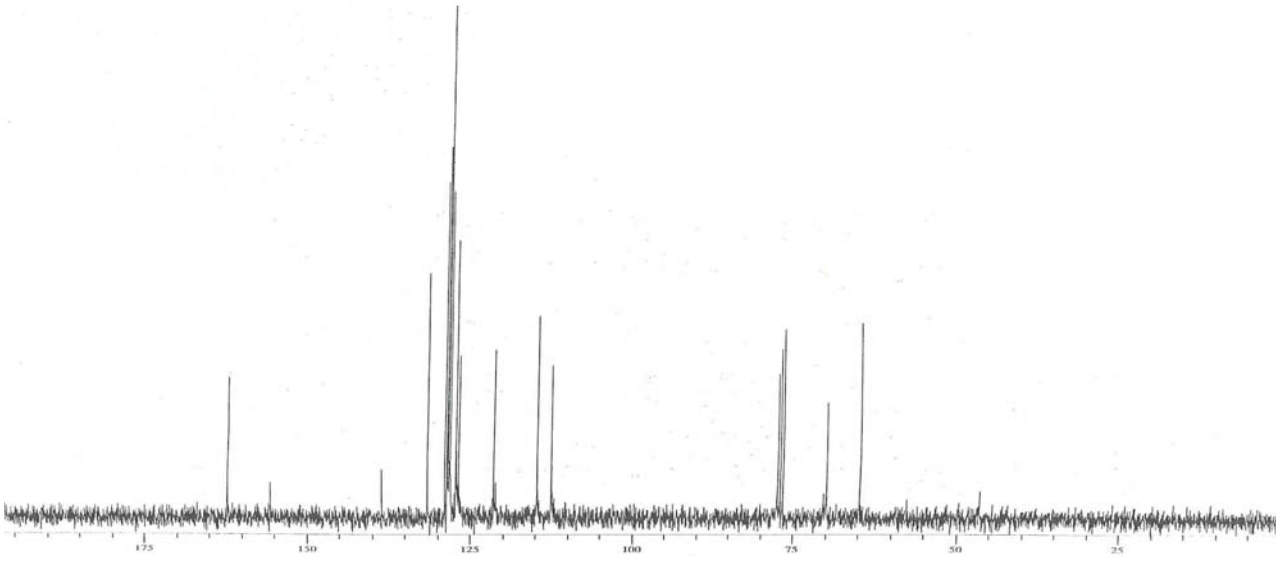


Figure C.2. The 300 MHz ^{1}H NMR spectrum of a mixture of neophylene and 2H-chromene.