Studies Toward C-N, C-O, C-S and C-Se Bonds Formations for the Construction of Five Membered Heterocycles

A Thesis Submitted

in Partial Fulfilment of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

by

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August 2016

Dedicated To

My Family Members and

Teachers

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, India under the supervision of Prof. Tharmalingam Punniyamurthy.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Guwahati — M. Sengoden

August 2016

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

CERTIFICATE

This is to certify that Mr. M. Sengoden has been working under my supervision since December 2010. I am forwarding his thesis entitled "*Studies Toward C-N, C-O, C-S and C-Se Bonds Formations for the Construction of Five Membered Heterocycles*" being submitted for the Ph.D. degree of this institute. I certify that he has fulfilled all the requirements according to the rules of this institute, and regarding the investigations embodied in his thesis and this work has not been submitted elsewhere for a degree.

Guwahati

August 2016

Prof. Tharmalingam Punniyamurthy

Supervisor

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M. Sengoden

List of Abbreviations

Ac	acetyl
Bz	benzoyl
Bn	benzyl
BQ	benzoquinone
Bu	butyl
Boc	*tert*-butoxycarbonyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	dichloromethane
DMSO	dimethylsulfoxide
DME	dimethoxyethane
DMAP	dimethylaminopyridine
dr	diastereomeric ratio
equiv	equivalent
ESI	electrospray ionization
Et	ethyl
ee	enantiomeric excess
EWG	electron wthdrawing group
EDG	electron donating group
FT-IR	Fourier transform infrared spectroscopy
HRMS	high-resolution mass spectrometry
HPLC	high performance liquid chromatography
m/z	mass to charge ratio
mp	melting point
Me	methyl
NMR	nuclear magnetic resonance
Pr	propyl
Ph	phenyl
Ts	*p*-toluenesulfonyl

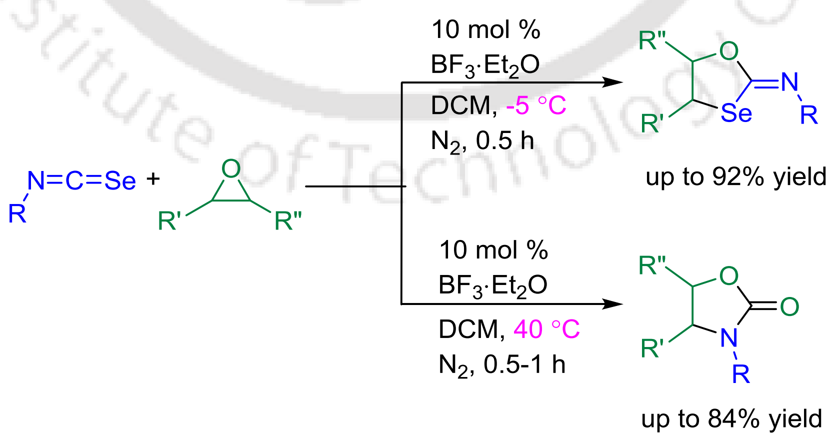
rt	room temperature
Boc	*tert*-butoxycarbonyl
Bu_4NI	tetrabutylammonium iodide
HBF_4	tetrafluoroboric acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
NEt_3	triethylamine
TMS	trimethylsilyl
PPh_3	triphenyphosphine

Abstract

The thesis contains five chapters. The first chapter describes the cycloaddition of oxiranes with isoselenocyanates using $BF_3 \cdot Et_2O$. In the second chapter, the cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates and carbodiimides is demonstrated using $Fe(NO_3)_3 \cdot 9H_2O$ on water. The third chapter focuses on pyrrolidine catalyzed cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide in aqueous medium. The fourth chapter contains Al(salen)-catalyzed cycloaddition of optically active aziridines with isothiocyanates. The final chapter deals with Cu-catalyzed synthesis of substituted imidazolidines *via* $C(sp^3)$–H activation.

Chapter I. Cycloaddition of Oxiranes with Isoselenocyanates Using $BF_3 \cdot Et_2O$

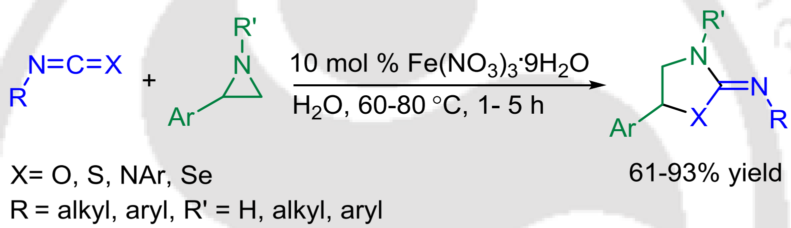
The cycloaddition of isocyanates, isothiocyanates, isoselenocyanates and carbodiimides with three-membered ring heterocycles affords a powerful synthetic tool for the construction of five-membered heterocycles. In addition, the construction of C-Se bonds has received considerable attention due to their presence in many molecules that are of biological, pharmaceutical and material interest. This chapter describes, Lewis acid catalyzed cycloaddition of oxirane with isoselenocyanate (Scheme 1). This protocol is general and regeoselective to access 2-imino-1,3-oxaselenolanes and 2-oxazolidinones in good to high yields with wide variety of substrate scope and functional group tolerance.



Scheme 1. (3+2)-Cycloaddition Reactions of Oxiranes with Isoselenocyanates

Chapter II. Fe-Catalyzed Cycloaddition of Aziridines with Isocyanates, Isothiocyanates, Isoselenocyanates and Carbodiimides

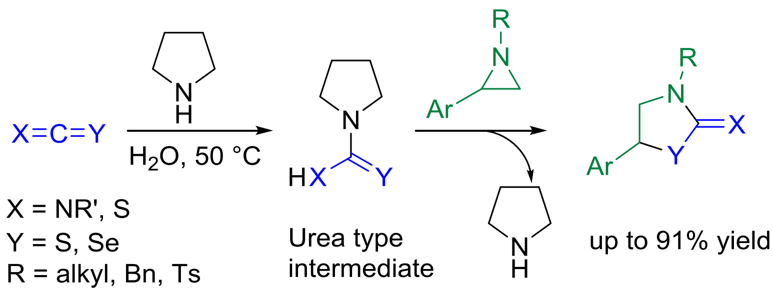
The use of water as a reaction medium for organic synthesis has attracted much interest in recent years because it is the most abundant liquid on the planet, cheap, readily available, non-toxic and non-flammable. The functionalized nitrogen containing five-membered heterocycles are important structural scaffolds exhibiting interesting biological and medicinal properties, which can be accessed using the cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates and carbodiimides. This chapter reports Fe-catalyzed cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates and carbodiimides that takes place in aqueous suspension (Scheme 2). The protocol is simple and uses non-toxic and cheap iron salt as the catalyst and water as a reaction medium under air.



Scheme 2. "On Water" Fe-Catalyzed Cycloaddition of Aziridines with Isocyanates, Isothiocyanates, Isoselenocyanates and Carbodiimides

Chapter III. Pyrrolidine-Catalyzed Cycloaddition of Aziridines with Isothiocyanates, Isoselenocyanates and Carbon Disulfide "On Water"

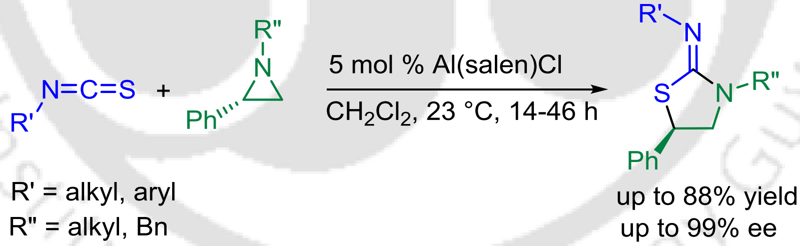
The use of organocatalysis has attracted considerable attention in recent years. In this chapter, we present the synthesis of azolidines from the cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide using pyrrolidine as a catalyst on water at moderate temperature under air (Scheme 3). The reaction occurs in aqueous suspension *via* a urea type intermediate affording a potential route for the construction of five membered heterocycles under mild reaction conditions. This protocol is attractive from atom economical, functional group tolerance and easy access of starting materials.



Scheme 3. Pyrrolidine Catalyzed Synthesis of Substituted Azolidines

Chapter IV. Al(salen)-Catalyzed Cycloaddition of Aziridines with Isothiocyanates

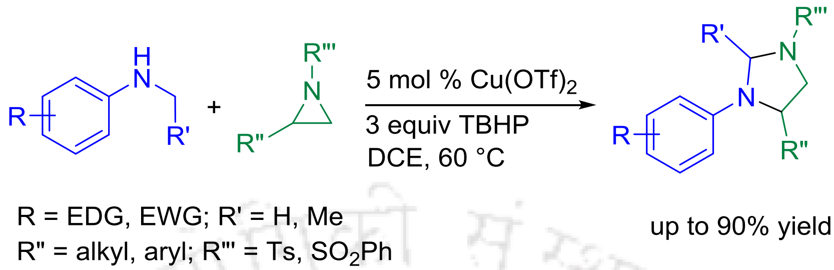
Iminothiazolidines are important heterocyclic motifs of numerous pharmaceuticals. They also find wide applications as catalysts for asymmetric transformations. The development of enantiospecific approaches is thus highly desirable. The chapter presents the stereospecific Al(salen)-catalyzed cycloaddition of enantioenriched aziridines with isothiocyanates at room temperature under air (Scheme 4). The protocol provides a potential route for the synthesis of enantioenriched iminothiazolidines in good yields. The reaction of a series of substituted isothiocyanates with aziridines has been accomplished to afford the target enantioenriched iminothiazolidines in excellent yields and high optical purities.



Scheme 4. Stereospecific Al(salen)-Catalyzed Cycloaddition of Aziridines with Isothiocyanates

Chapter V. Cu-Catalyzed Synthesis of Substituted Imidazolidines *via* Regioselective C(sp^3)–H Functionalization

Imidazolidines are important structural units that are found in various bioactive compounds and also used as catalysts and ligands in synthetic chemistry. The chapter covers Cu-catalyzed domino synthesis of substituted imidazolidines from *N*-alkyl anilines and aziridines in presence of ^{t}BuOOH at 60 °C (Scheme 5). This process involves a ring opening followed by C-N bond formation *via* C(sp^3)–H functionalization. This process is efficient, selective and provides the target heterocycles in good yield.



Scheme 5. Cu-Catalyzed Domino Synthesis of Substituted Imidazolidines

Contents

Cycloaddition of Oxiranes with Isoselenocyanates Using $BF_3{\cdot}Et_2O$

Five-membered heterocycles have been widely studied in synthetic organic chemistry for its importance in biological and pharmaceutical studies[1-3] and can be easily constructed by the cycloaddition of cumulene with three-membered heterocycles.[4] Cumulenes are a highly varied class of compounds, including species such as ketenes, allenes, ketenimines and isocyanates, as well as isothiocyanates, isoselenocyanates, carbon dioxide and carbon disulfide.[5] Three-membered heterocyclic compounds are highly reactive due to their molecular strain and have thus received much attention in synthetic chemistry. In addition, their structural scaffolds often have been encountered in pharmaceuticals such as antitumor agents and antibiotics.[6] In addition, the synthesis of selenium containing compounds has received considerable attention due to their interesting biological, pharmaceutical and material properties.[7,8] For examples, 2-imino-1,3-oxaselenolanes and 2-oxazolidinones are found in a wide variety of natural products and exhibit antioxidant, antimicrobial, antiviral and anticancer activities.[9] Furthermore, substituted 2-oxazolidinones and their analogues such

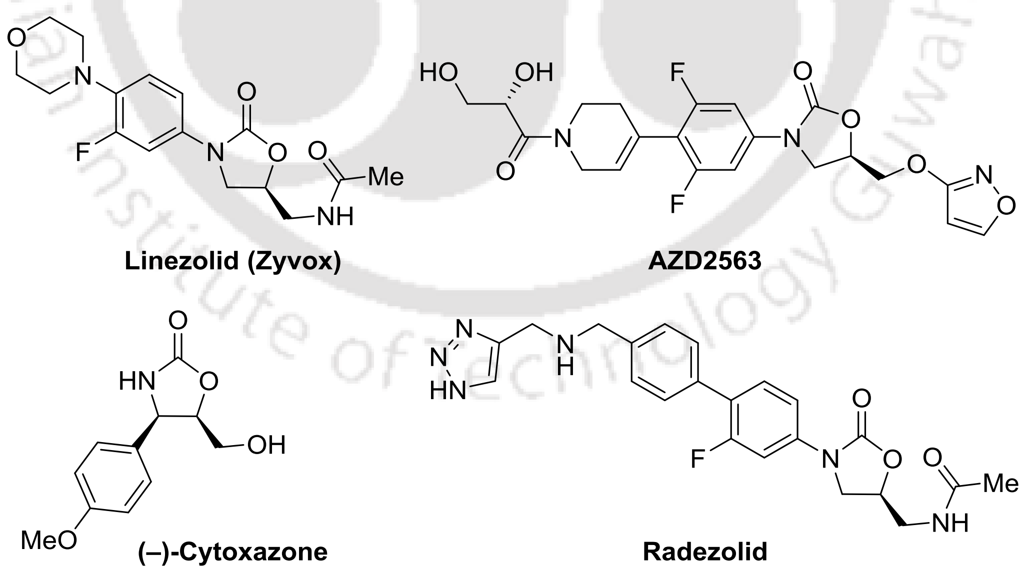
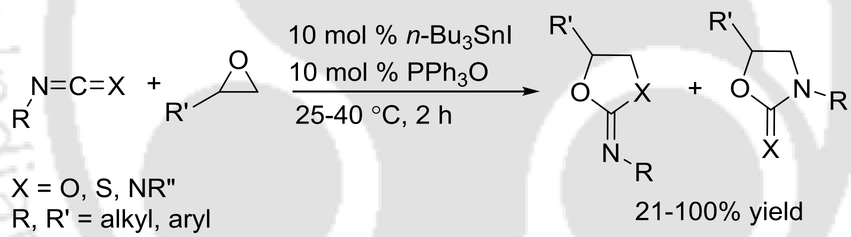


Figure 1. Examples of medicinally significant five membered heterocyclic compounds

as, linezolid,[9c] AZD2563,[9d] DuP 105, DuP 721[9e] and radezolid[9f] are used as antibiotics and (–)-cytoxazone[9g] used as cytokine modulator (Figure 1). In this chapter, we describe the cycloaddition of oxiranes with isoselenocyanates using $BF_3 \cdot Et_2O$ for the synthesis of functionalized 2-imino-1,3-oxaselenolanes and 2-oxazolidinones.

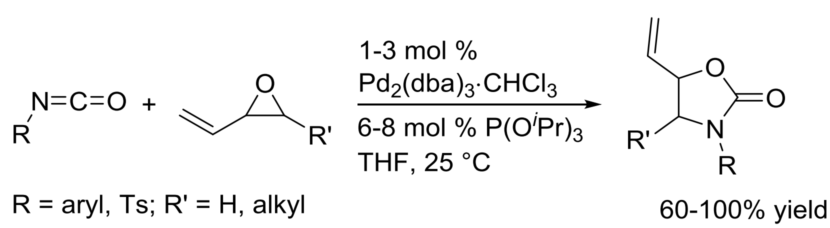
1.1 Cycloaddition of Isocyanates, Isothiocyanates and Carbodiimides with Oxiranes

The cycloaddition of isocyanates, isothiocyanates, and carbodiimides with oxiranes has been considerably studied. For examples, Shibata and co-workers reported the cycloaddition reaction of isocyanates, isothiocyanates, and carbodiimides with oxiranes using organotin halides-Lewis base complexes for the synthesis of 2-dioxolanimines, 2-oxathiolanimines and 2-oxazolidinimines (Scheme 1).[10] A combination of 10 mol % Bu_3SnI and 10 mol % PPh_3O gave the best results. Under this condition, disubstituted oxiranes showed poor reactivity, however, the use of Me_2SnI_2-HMPA afforded good yields.



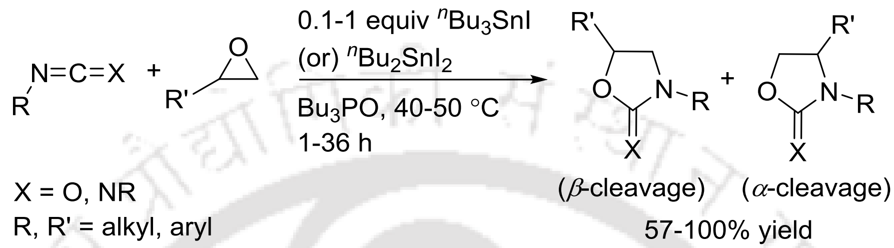
Scheme 1. Organotin Iodide Catalyzed Synthesis of Oxazolidines and Analogues

Trost and co-workers studied Pd-catalyzed cycloaddition of vinyl epoxide with nitrogen nucleophiles using 1-3 mol % of $(dba)_3Pd_2CHCl_3$ and 6-8 mol % of $P(O^iPr)_3$ in THF at room temperature (Scheme 2).[11] These reaction conditions are also suitable for the reactions of enantiomerically pure epoxides with isocyanates to obtain optically active oxazolidines.



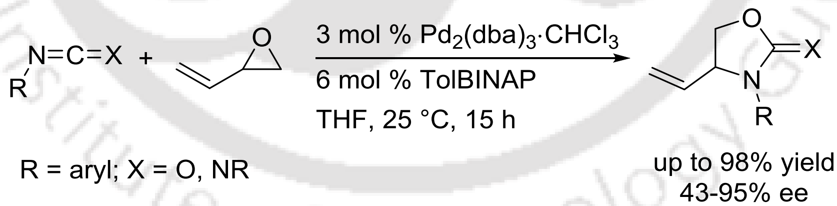
Scheme 2. Pd-Catalyzed Cycloaddition of Isocyanates with Oxiranes

Baba and co-workers showed the cycloaddition of isocyanates and carbodiimides with oxiranes using trialkyltin iodides and phosphine oxides at moderate temperature (Scheme 3).[12] The formation of the heterocycles depends strongly on the Sn-complex, $^{n}Bu_3SnI$ promoted selective *α*-cleavage of the oxirane ring, while the other types, $^{n}Bu_2SnI_2$ produced selective *β*-cleavage cycloaddition product.



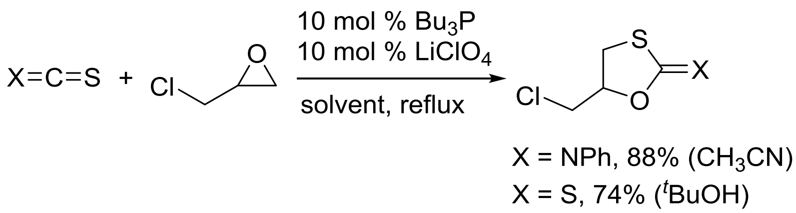
Scheme 3. Cycloaddition of Oxiranes with Isocyanates and Carbodiimides

Larksarp and Alper demonstrated Pd(0)-catalyzed asymmetric cycloaddition of vinyloxiranes with isocyanates and carbodiimides using chiral phosphine ligands such as, (*S*)- or (*R*)-TolBINAP for the synthesis of enantioselective vinyloxazolidine (Scheme 4).[13] The active Pd(0)-TolBINAP catalyst has been generated *in situ* by the reaction of 3 mol % of $Pd_2(dba)_3{\cdot}CHCl_3$ with 2 equiv of the ligand. The same catalytic system was successfully applied to the reaction of unsymmetrical carbodiimides with vinyloxiranes to provide the corresponding 1,3-oxazolidin-2-imine in 88-99% ee.



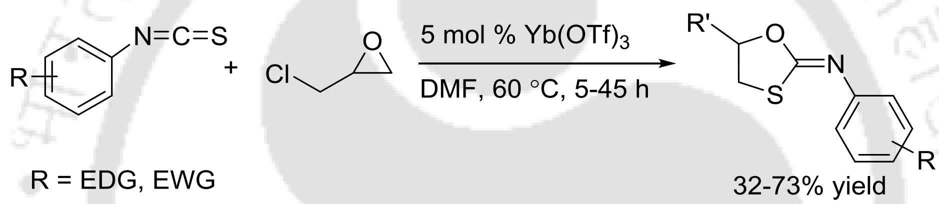
Scheme 4. Asymmetric Cycloaddition of Isocyanates and Carbodiimides with Vinyloxiranes

Organophosphine-catalyzed cycloaddition of isothiocyanates and carbon disulfide with epichlorohydrin provided 1,3-oxathiolanes in good yields in the presence of $LiClO_4$ (Scheme 5).[14]



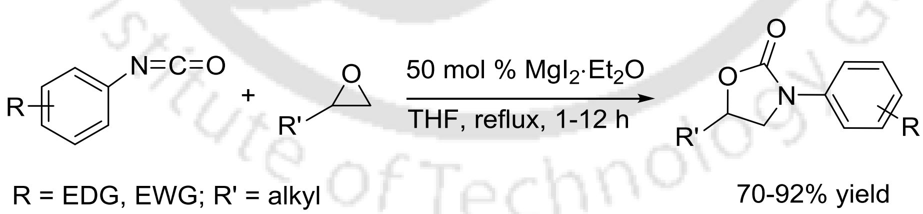
Scheme 5. PBu_3-Catalyzed Synthesis of 1,3-Oxathiolanes

$Yb(OTf)_3$ catalyzed the cycloaddition of isothiocyanates with epichlorohydrin to yield *N*-(5-(chloromethyl)-1,3-oxathiolan-2-ylidene)anilines in DMF at 60 °C (Scheme 6).[15] In case of aryl oxiranes and alkyl isothiocyantes, the reaction has been failed. The reaction of (*R*)-epichlorohydrin has been demonstrated and the configuration is retained at the chiral centers of the epoxide.



Scheme 6. Yb-Catalyzed Cycloaddition of Isothiocyanates with Epichlorohydrin

Zhang and Chen utilized $MgI_2{\cdot}Et_2O$ for the cycloaddition of various aryl isocyanates with oxiranes in THF under reflux (Scheme 7).[16] The corresponding 3-aryloxazolidin-2-ones have been obtained in highly regioselective manner with good to high yields.



Scheme 7. Mg-Catalyzed Cycloaddition of Isocyanates with Oxiranes

1.2 Present Study

We present here the cycloaddition of oxiranes with isoselenocyanates using $BF_3{\cdot}Et_2O$ to afford 1,3-oxaselenolane and 1,3-oxazolidinone. The standardization of the protocol was carried out with phenyl isoselenocyanate **1a** and styrene oxide **2a** as the model substrates using different Lewis acids and solvents at varied temperature (Table 1). As expected, the protocol was effective, and interestingly, afforded selectively either *Z*-phenyl-2-imino-1,3-oxaselenolane **3a** (-5 °C) or 3,4-diphenyl-oxazolidin-2-one **4a** (40 °C) as sole product depend on the temperature with excellent regioselectivity. Recrystallization of **4a** in hexane gave crystals whose structure was confirmed by single crtystal X-ray analysis (Figure 2). In a set of screened Lewis acids such as, $BF_3{\cdot}Et_2O$, $SnCl_4$, $InCl_3$ and $FeCl_3$, all were active, and $BF_3{\cdot}Et_2O$ afforded the best results. CH_2Cl_2 was found to be the solvent of choice, while toluene and CH_3CN exhibited moderate to good results. In contrast, THF and 1,4-dioxane yielded inferior results. Using 10 mol % of $BF_3{\cdot}Et_2O$ the target molecules could be obtained in quantitative yield. The reaction at -5 °C gave the complete conversion with 1.5 equiv of styrene oxide, while the process at 40 °C required 2 equiv of styrene oxide to provide the best results. Control experiments of both the processes confirmed that no reaction was observed without the Lewis acid.

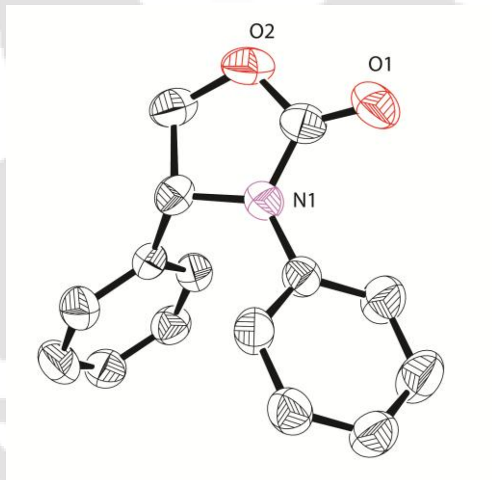
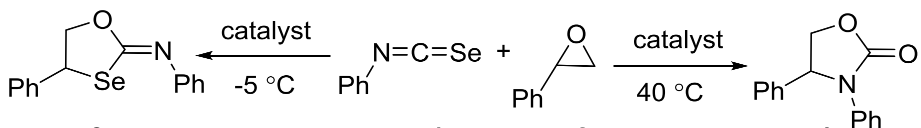


Figure 2. ORTEP diagram of 3,4-diphenyloxazolidin-2-one **4a**. Thermal ellipsoids are drawn at a 40% probability level. Hydrogen atoms have been omitted for clarity.

Having the optimized conditions in hand, the scope of the procedure was pursued. The reactions of a series of aryl and cyclohexyl isoselenocyanates **1b-l** with oxirane **2a** was examined (Table 2). Aryl isoselenocyanates having electron donating as well as -withdrawing substitutents in the aromatic ring readily proceeded the reactions to give the corresponding

Table 1. Optimization of the Reaction Conditions



Entry	Catalyst	Solvent	Time (h)	Conversion (%)[a]	
				3a[b]	**4a**[c]
1	**$BF_3 \cdot Et_2O$**	**CH_2Cl_2**	**0.5**	**98**	**92**
2	$SnCl_4$	CH_2Cl_2	3	60	53
3	$Cu(OTf)_2$	CH_2Cl_2	8	n.d.	-
4	$Sc(OTf)_3$	CH_2Cl_2	18	70	68
5	$InCl_3$	CH_2Cl_2	3	65	52
6	$FeCl_3$	CH_2Cl_2	3	<5	-
7	$BF_3 \cdot Et_2O$	$CHCl_3$	0.5	90	85
8	$BF_3 \cdot Et_2O$	THF	1	<3	-
9	$BF_3 \cdot Et_2O$	toluene	1	55	41
10	$BF_3 \cdot Et_2O$	CH_3CN	1	90	79
11	$BF_3 \cdot Et_2O$	1,4-dioxane	1	<3	-
12[d]	$BF_3 \cdot Et_2O$	CH_2Cl_2	0.5	78	71
13[e]	$BF_3 \cdot Et_2O$	CH_2Cl_2	0.5	80	-
14	-	CH_2Cl_2	24	n.d.	n.d.

[a] Determined by 400 MHz ^{1}H NMR spectroscopy. [b] Reaction conditions: Isoselenocyanate **1a** (0.5 mmol), oxirane **2a** (0.75 mmol) and catalyst (10 mol %) were stirred at -5 °C in solvent (1 mL) under N_2 balloon. [c] Reaction was carried out with 2 equiv of oxirane at 40 °C. [d] $BF_3 \cdot Et_2O$ (5 mol %) was used. [e] 1 Equiv of oxirane was used.

target heterocycles in good to high yields. For examples, aryl isoselenocyanates **1b-h** having 2-chloro, 3-fluoro, 4-chloro, 4-fluoro, 4-iodo, 4-methoxy and 4-methyl groups in the phenyl ring proceeded the cycloaddition with **2a** to give the heterocyclic compounds **3b-h** in 42-92% yields (-5 °C) and **4b-h** in 61-84% yields (40 °C). Recrystallization of **3f** in hexane gave crystals whose structure was confirmed by single crystal X-ray analysis (Figure 3). Under these conditions, aryl isoselenocyanate **1i** with 4-nitro group showed no reaction and the starting material was recovered intact. However, the disubstituted aryl isoselenocyanate **1j** with 3,4-dimethyl group underwent reaction with **2a** to provide the heterocycles **3i** and **4i** in 83 and 78% yield, respectively. Similarly, 1-naphthyl isoselenocyanate **1k** proceeded reaction with **2a** to afford the heterocycles **3k** and **4k** in 87 and 71% yield, respectively. In contrast, cyclohexyl isoselenocyanate **1l** at both the reaction temperatures (-5 and 40 °C) gave **3l** as the sole product.

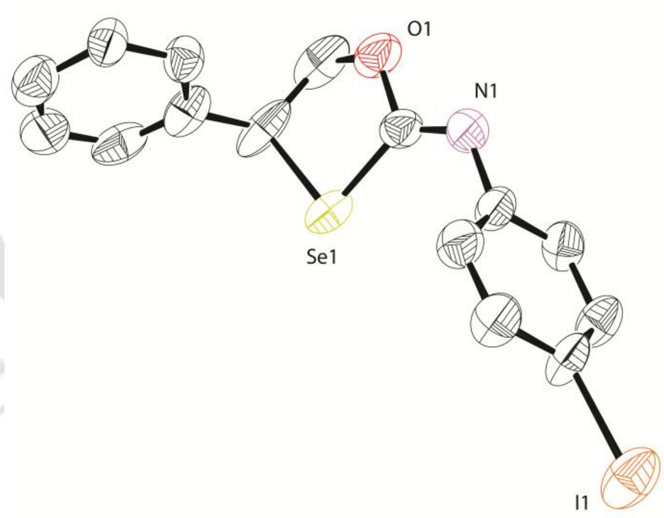
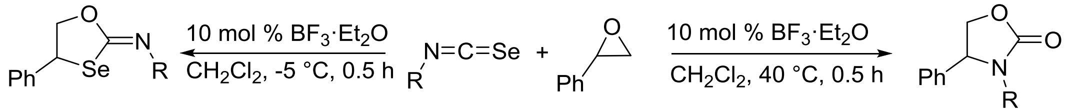


Figure 3. ORTEP diagram of (*Z*)-4-iodo-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzene-amine **3f**. Thermal ellipsoids are drawn at a 40% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Reactions of Substituted Isoselenocyanates with Styrene Oxide



3a-l **1a-l** **2a** **4a-k**

R = alkyl, aryl

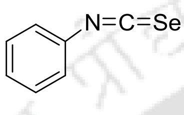
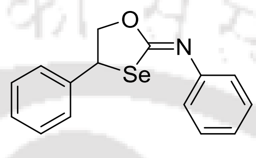
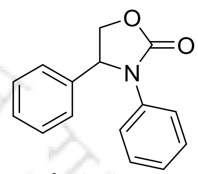
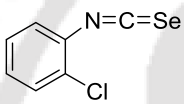
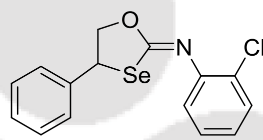
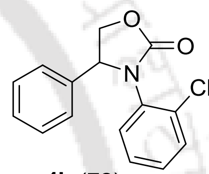
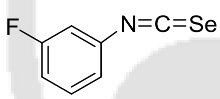
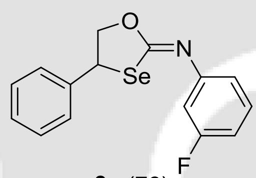
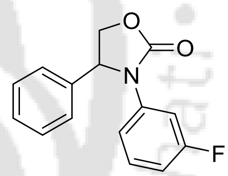
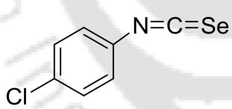
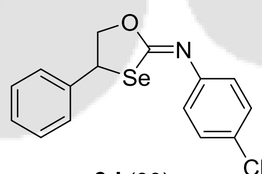
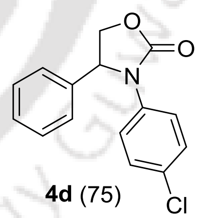
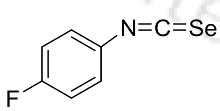
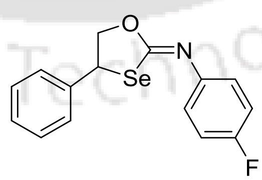
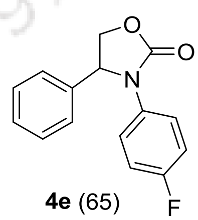
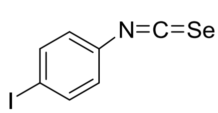
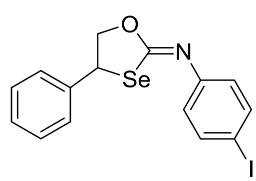
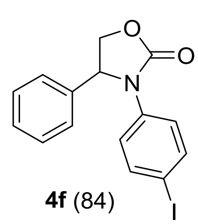
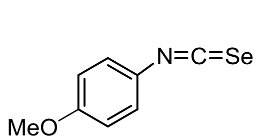
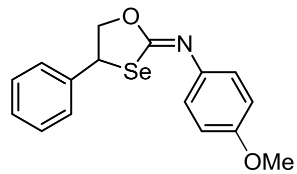
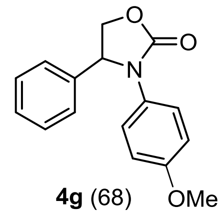
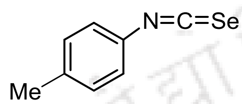
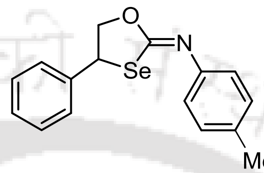
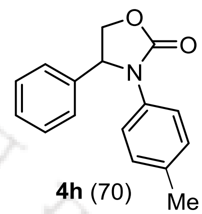
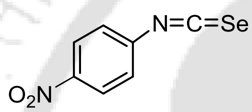
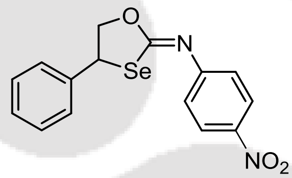
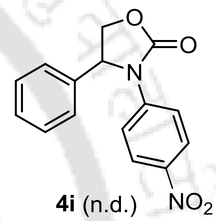
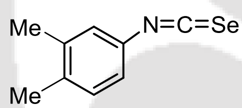
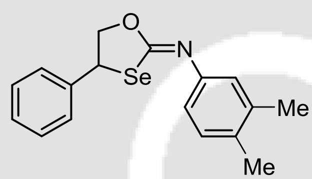
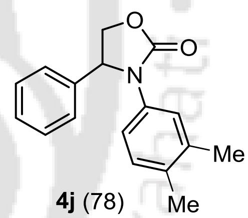
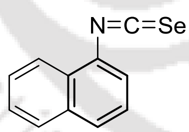
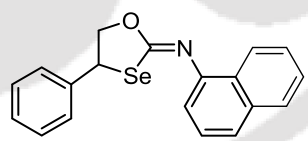
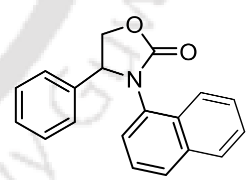
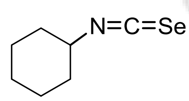
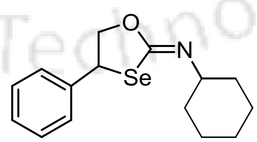
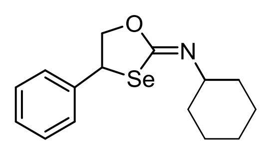
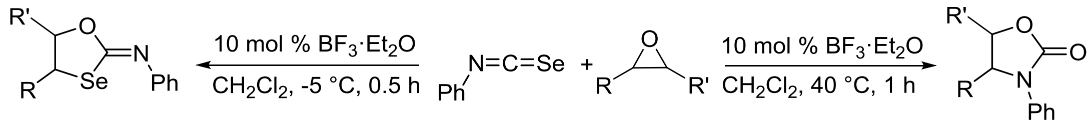
Entry	Isoselenocyanates	Product (Yield, %) -5 °C[a]	40 °C[b]
1	 **1a**	 **3a** (86)	 **4a** (73)
2	 **1b**	 **3b** (42)	 **4b** (72)
3	 **1c**	 **3c** (76)	 **4c** (61)
4	 **1d**	 **3d** (90)	 **4d** (75)
5	 **1e**	 **3e** (92)	 **4e** (65)
6	 **1f**	 **3f** (85)	 **4f** (84)

Table 2 continued........

7	 **1g**	 **3g** (88)	 **4g** (68)
8	 **1h**	 **3h** (78)	 **4h** (70)
9	 **1i**	 **3i** (n.d.)	 **4i** (n.d.)
10	 **1j**	 **3j** (83)	 **4j** (78)
11	 **1k**	 **3k** (87)	 **4k** (71)
12			

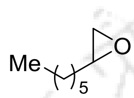
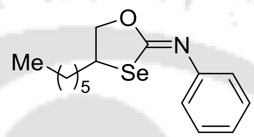
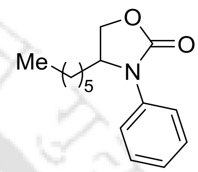
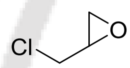
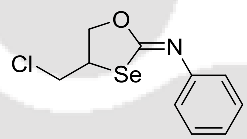
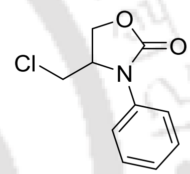
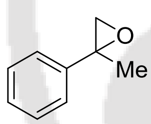
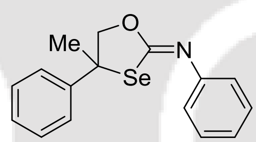
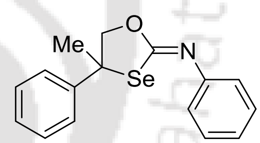
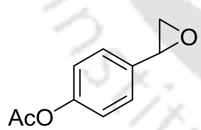
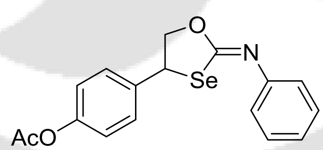
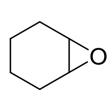
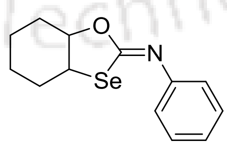
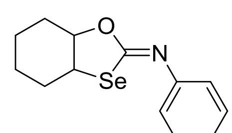
Reaction conditions: [a] Isoselenocyanate **1a-l** (0. 5 mmol), oxirane **2a** (0.75 mmol) and $BF_3{\cdot}Et_2O$ (10 mol %) were stirred in CH_2Cl_2 at -5 °C for 0.5 h under N_2. [b] Reaction was performed at 40 °C for 0.5 h.

Table 3. Reactions of Substituted Oxiranes with Phenyl Isoselenocyanate



3m-q **1a** **2b-f** **4l-m**

R = alkyl, aryl; R' = H, alkyl

Entry	Oxirane	Product (Yield, %)	
		-5 °C[a]	40 °C[b]
1	 **2b**	 **3m** (79)	 **4l** (68)
2	 **2c**	 **3n** (86)	 **4m** (73)
3	 **2d**	 **3o** (72)	 **3o** (76)
4	 **2e**	 **3p** (65)	 **3p** (70)
5	 **2f**	 **3q** (62)	 **3q** (68)

Reaction conditions: [a] Isoselenocyanate **1a** (0. 5 mmol), oxirane **2b-f** (0.75 mmol) and $BF_3 \cdot Et_2O$ (10 mol %) were stirred in CH_2Cl_2 at -5 °C for 0.5 h under N_2. [b] Reaction was performed at 40 °C for 1 h.

Finally, the reaction of substituted oxiranes **2b-f** with phenyl isoselenocyanate **1a** was investigated (Table 3). As above, the reaction efficiently occurred and the product formation was dependent on the nature of the oxirane. For examples, *n*-octene-1,2-oxide **2b** and epichlorohydrin **2c** proceeded reaction with **1a** to give the heterocylic compounds **3m-n** in 79-86% yield (-5 °C) and **4l-m** in 71-73% yield (40 °C). In contrast, the reactions of *α*-methylstyrene oxide **2d,** 4-acetoxystyrene oxide **2e** and cyclohexene oxide **2f** with **1a** at both the reactions temperatures (-5 and 40 °C) afforded selectively heterocycles **3o-q** in 62-76% yield. Among them, the compound **3q** afforded single crystals in hexane whose structure was determined by X-ray analysis (Figure 4). These results suggest that the reactions of isoselenocyanates with oxiranes are regioselective and the product formation depends on the reaction temperature and nature of the oxirane.

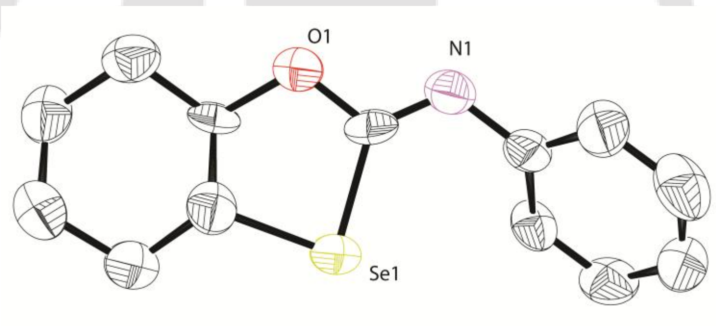
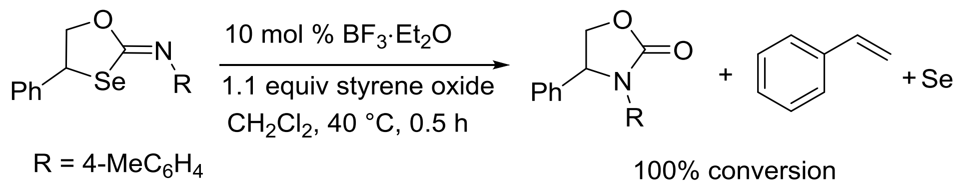
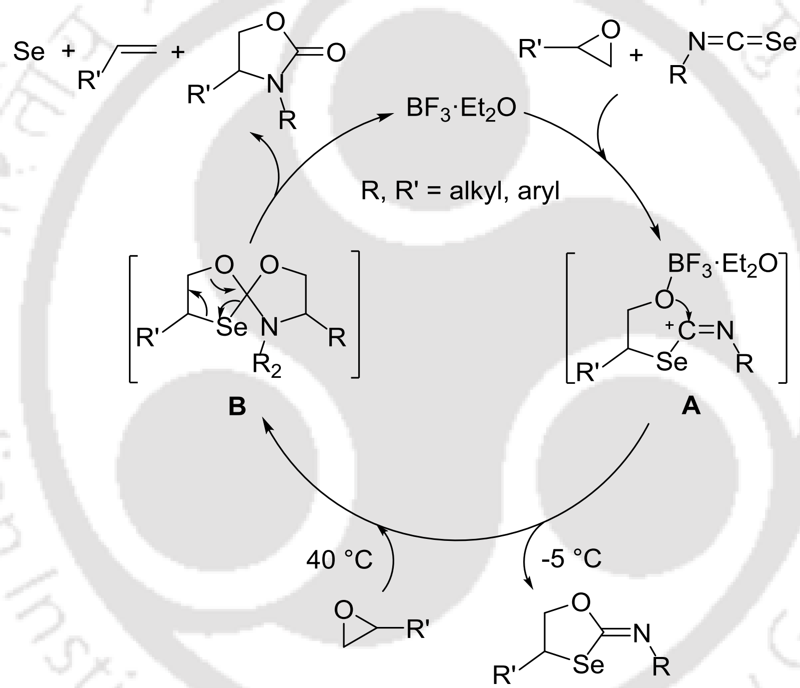


Figure 4. ORTEP diagram of (*Z*)-*N*-(Hexahydrobenzo[*d*][1,3]oxaselenol-2-ylidene)benzene-amine **3q**. Thermal ellipsoids are drawn at a 85% probability level. Hydrogen atoms have been omitted for clarity.

To reveal the mechanism, the compound **3h** was reacted with 1.1 equiv of **2a** and the heterocycle **4h**, styrene and Se were obtained in 100% converison along with a trace of phenyl acetaldehyde[17] (Scheme 8). These results suggest that the oxirane **2** first undergoes reaction with isoselenocyanate **1** in the presence of the Lewis acid to give the heterocycle **3** (at -5 °C) that could further react with oxirane **2** at 40 °C to provide **4** along with alkene and Se. Thus, the reaction of the Lewis acid with oxirane **2** can lead to the formation of a secondary carbocation that could undergo reaction with Se of isoselenocyante to afford the intermediate **A** (Scheme 9). The intramolecular cyclization of **A** could lead to the formation of the heterocycle **3**. At 40 °C, the compound **3** may undergo further reaction with oxirane **2** to give the intermediate **B** which could give the heterocycle **4**, alkene and Se.



Scheme 8. Mechanistic Studies



Scheme 9. Plausible Reaction Mechanism

In summary, the cycloaddition of isoselenocyanate with oxirane has been developed. The process is efficient, regioselective, temperature dependent providing a potential route for the synthesis of 2-imino-1,3-oxaselenolanes and 2-oxazolidinones in short reaction time.

1.3 Experimental Section

General Information. Anilines, oxiranes, alkenes, *m*-CPBA (77%), $BF_3{\cdot}Et_2O$, $SnCl_4$ (1.0 M solution in DCM), $Cu(OTf)_2$ (98%) and $Sc(OTf)_3$ (99.99%) were purchased from Aldrich. $InCl_3$ (98%) was purchased from Lancaster. $FeCl_3$ (96%) was purchased from Rankem. Selenium (99.9%) was purchased from SRL. The column chromatography was performed with Rankem silica gel (60-120 mesh). NMR (^1H and ^{13}C) spectra were recorded with a Varian 400 spectrometer. Melting points were determined with a Büchi B-545 apparatus and are uncorrected. FT-IR spectra were recorded using Perkin Elmer IR spectrometer. Elemental analyses were recorded using Perkin Elmer CHNS analyzer. X-Ray data were collected on a Bruker SMART APEX equipped with a CCD area detector using Mo Kα radiation. The structures were solved by direct method using *SHELXL-97* (Göttingen, Germany).

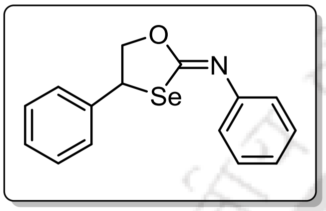
General Procedure for Preparation of Isoselenocyanates.[18] To a stirred solution of the isocyanide (2 mmol) in $CHCl_3$ (1 mL) were added selenium powder (3 mmol) and NEt_3 (2 mmol) at room temperature (26 °C) under nitrogen balloon and the mixture was stirred for 7 h. Progress of the reaction was monitored by TLC using hexane as eluent. The suspension was then passed through a celite bed and the solvent was removed by evaporation on a rotary evaporator. The residue was purified on a silica gel column chromatography using hexane as eluent.

General Procedure for Synthesis of Substituted 2-Imino-1,3-oxaselenolanes 3a-q. A mixture of isoselenocyanate **1a-l** (0.5 mmol), oxirane **2a-f** (0.75 mmol) and $BF_3{\cdot}Et_2O$ (0.05 mmol) were stirred at -5 °C in CH_2Cl_2 under nitrogen balloon. The progress of reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and the solution was washed with 5% $NaHCO_3$ solution (5 mL), brine (1 x 3 mL) and water (3 x 5 mL) and. Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate (8:2) as eluent.

General Procedure for Synthesis of 1,3-Oxazolidinones 4a-m. A mixture of isoselenocyanate **1a-l** (0.5 mmol), oxirane **2a-f** (1 mmol) and $BF_3{\cdot}Et_2O$ (0.05 mmol) were stirred at 40 °C in CH_2Cl_2 under nitrogen balloon. The progress of reaction was monitored by

TLC using ethyl acetate and hexane. The reaction mixture was filtered. The solution was diluted with CH_2Cl_2 (15 mL) and washed with 5% $NaHCO_3$ solution (5 mL), brine (1 x 3 mL) and water (3 x 5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified on silica gel column chromatography using hexane and ethyl acetate (8:2) as eluent.

1.4 Characterization Data of Products



(*Z*)-*N*-(4-Phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3a.

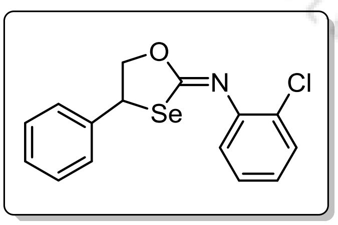
Yellow liquid; yield 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.34-7.26 (m, 5H), 7.11 (t, *J* = 6.8 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.10 (t, *J* = 7.2 Hz, 1H), 4.67 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.51 (dd, *J* = 10.0, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 150.3, 137.8, 129.4, 129.2, 128.5, 127.8, 124.8, 121.0, 76.8, 48.8.

FT-IR (neat) 3059, 3030, 2936, 2887, 1732, 1651, 1592, 1488, 1454, 1244, 1116, 1091, 1044, 1017 cm^{-1}.

Anal. Calcd. for $C_{15}H_{13}NOSe$: C, 59.61; H, 4.34; N, 4.63. Found: C, 59.70; H, 4.33; N, 4.59.



(*Z*)-2-Chloro-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3b.

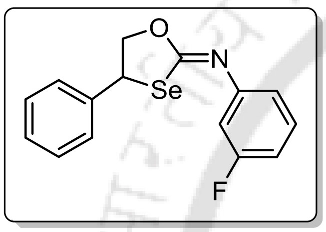
Yellow liquid; yield 42%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.36-7.26 (m, 3H), 7.19 (td, J = 7.6, 1.6 Hz, 2H), 7.04 (td, J = 8.0, 1.6 Hz, 1H), 6.96 (dd, J = 7.6, 1.2 Hz, 1H), 5.16 (t, J = 6.8 Hz, 1H), 4.73 (dd, J = 10.0, 6.0 Hz, 1H), 4.58 (dd, J = 10.0, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 147.3, 137.7, 130.2, 129.5, 129.2, 128.6, 127.8, 126.7, 125.7, 121.9, 49.3.

FT-IR (neat) 3029, 2924, 1651, 1585, 1494, 1471, 1451, 1280, 1245, 1101, 1059, 1042, 1017 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}ClNOSe$: C, 53.51; H, 3.59; N, 4.16. Found: C, 53.59; H, 3.57; N, 4.12.



(*Z*)-3-Fluoro-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3c.

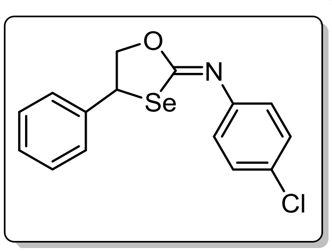
Yellow liquid; yield 76%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.21 (m, 6H), 6.85-6.71 (m, 3H), 5.14 (t, J = 6.8 Hz, 1H), 4.70 (dd, J = 10.0, 6.0 Hz, 1H), 4.54 (dd, J = 10.0, 7.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (d, J_{C-F} = 245.6 Hz), 163.5, 151.9 (d, J_{C-F} = 9.9 Hz), 137.6, 130.6 (d, J_{C-F} = 9.0 Hz), 129.2, 128.6, 127.7, 116.7, 111.7 (d, J_{C-F} = 20.6 Hz), 108.6 (d, J_{C-F} = 22.1 Hz), 77.0, 49.0.

FT-IR (neat) 3063, 3030, 2928, 1652, 1604, 1582, 1480, 1454, 1262, 1092, 1044, 1022 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}FNOSe$: C, 56.26; H, 3.78; N, 4.37. Found: C, 56.36; H, 3.77; N, 4.34.



(*Z*)-4-Chloro-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3d.

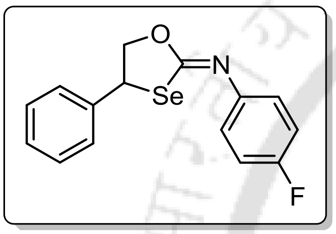
Yellow liquid; yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.12 (t, *J* = 7.2 Hz, 1H), 4.67 (dd, *J* = 9.6, 6.0 Hz, 1H), 4.51 (dd, *J* = 9.6, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 148.7, 137.6, 130.6, 130.0, 129.4, 129.2, 128.6, 127.7, 122.3, 76.9, 49.0.

FT-IR (neat) 3061, 3030, 2928, 1651, 1590, 1485, 1455, 1245, 1091, 1044, 1020, 1010, 945 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}ClNOSe$: C, 53.51; H, 3.59; N, 4.16. Found: C, 53.59; H, 3.57; N, 4.14.



(*Z*)-4-Fluoro-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3e.

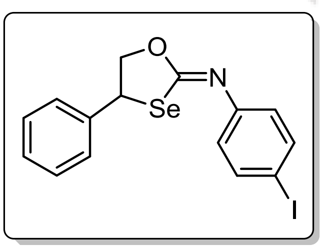
Yellow liquid; yield 92%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.34-7.27 (m, 3H), 7.00-6.91 (m, 4H), 5.9 (t, *J* = 7.2 Hz, 1H), 4.66 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.19 (dd, *J* = 10.0, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.2 (d, J_{C-F} = 241.8 Hz), 146.3, 137.7, 129.1, 128.5, 127.7, 122.3 (d, J_{C-F} = 8.4 Hz), 116.1 (d, J_{C-F} = 22.1 Hz), 76.8, 48.8.

FT-IR (neat) 3062, 3031, 2928, 1658, 1601, 1501, 1454, 1214, 1091, 1044, 1020 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}FNOSe$: C, 56.26; H, 3.78; N, 4.37. Found: C, 56.34; H, 3.76; N, 4.33.



(*Z*)-4-Iodo-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3f.

Colorless solid; yield 85%.

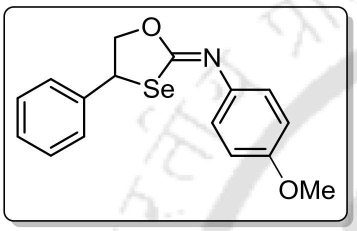
Mp: 161-162 °C.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.38-7.28 (m, 5H), 6.73 (d, *J* = 8.4 Hz, 2H), 5.11 (t, *J* = 6.8 Hz, 1H), 4.67 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.50 (dd, *J* = 9.6, 7.6 Hz, 1H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 163.1, 149.8, 138.4, 137.6, 129.3, 128.6, 127.8, 123.2, 88.7, 76.9, 49.1.

FT-IR (KBr) 2943, 1652, 1576, 1473, 1462, 1244, 1202, 1115, 1093, 1079, 1041, 1003, 948 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}INOSe$: C, 42.08; H, 2.83; N, 3.27. Found: C, 42.15; H, 2.81; N, 3.24.



(*Z*)-4-Methoxy-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3g.

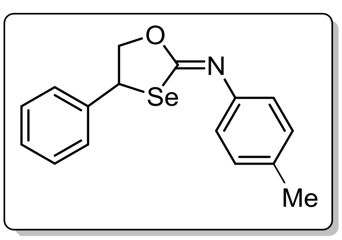
Yellow liquid; yield 88%.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, *J* = 6.8 Hz, 2H), 7.34-7.25 (m, 3H), 6.91 (d, *J* = 6.8 Hz, 2H), 6.84 (t, *J* = 6.8 Hz, 2H), 5.90 (dd, *J* = 7.2, 6.0 Hz, 1H), 4.66 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.49 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.76 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 162.4, 156.8, 143.6, 137.9, 129.1, 128.4, 127.7, 121.9, 114.5, 76.6, 55.4, 48.6.

FT-IR (neat) 3060, 3031, 2933, 2835, 1651, 1505, 1463, 1455, 1290, 1243, 1091, 1033, 945 cm^{-1}.

Anal. Calcd. for $C_{16}H_{15}NO_2Se$: C, 57.84; H, 4.55; N, 4.22. Found: C, 57.96; H, 4.53; N, 4.18.



(*Z*)-4-Methyl-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3h.

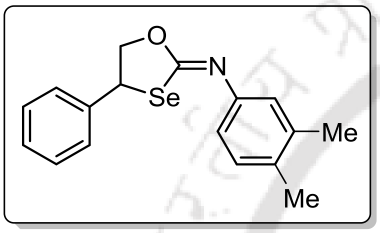
Yellow liquid; yield 78%.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.32-7.25 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 5.06 (t, *J* = 6.4 Hz, 1H), 4.61 (dd, *J* = 10.0, 5.6 Hz, 1H), 4.46 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.29 (s, 3H).

[13]C NMR (100 MHz, $CDCl_3$) δ 162.1, 147.7, 137.9, 134.1, 129.8, 129.0, 128.3, 127.6, 120.6, 76.5, 48.5, 20.9.

FT-IR (neat) 3060, 3028, 2942, 2887, 1651, 1505, 1454, 1370, 1282, 1244, 1173, 1089, 1043, 1014, 945 cm^{-1}.

Anal. Calcd. for $C_{16}H_{15}NOSe$: C, 60.76; H, 4.78; N, 5.06. Found: C, 60.82; H, 4.77; N, 5.02.



(*Z*)-3,4-Dimethyl-*N*-(4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3j.

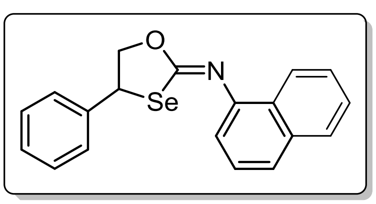
Yellow liquid; yield 83%.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.35-7.25 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.80 (s, 1H), 6.75 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.06 (dd, *J* = 7.2, 6.4 Hz, 1H), 4.63 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.48 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.23 (s, 3H), 2.22 (s, 3H).

[13]C NMR (100 MHz, $CDCl_3$) δ 161.9, 148.0, 137.9, 137.5, 132.8, 130.3, 129.0, 128.3, 127.7, 122.1, 117.8, 76.5, 48.4, 19.8, 19.2.

FT-IR (neat) 3060, 3027, 2938, 2885, 1654, 1603, 1496, 1453, 1371, 1281, 1244, 1120, 1089, 1044, 1025, 1000 cm^{-1}.

Anal. Calcd. for $C_{17}H_{17}NOSe$: C, 61.82; H, 5.19; N, 4.24. Found: C, 61.91; H, 5.16; N, 4.21.



(*Z*)-*N*-(4-Phenyl-1,3-oxaselenolan-2-ylidene)naphthalen-1-amine 3k.

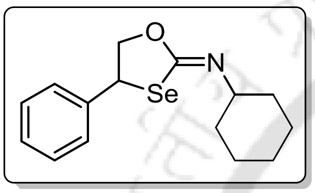
Yellow liquid; yield 87%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, *J* = 4.8 Hz, 1H), 7.83 (t, *J* = 4.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.52-7.47 (m, 2H), 7.42-7.37 (m, 3H), 7.35-7.24 (m, 3H), 7.05 (d, *J* = 6.8 Hz, 1H), 5.07 (t, *J* = 6.8 Hz, 1H), 4.73 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.57 (dd, *J* = 10.0, 7.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 147.2, 137.8, 134.3, 129.2, 128.5, 127.9, 127.8, 127.6, 126.5, 126.0, 125.8, 125.0, 123.7, 115.0, 77.1, 48.6.

FT-IR (neat) 3059, 2927, 1651, 1574, 1494, 1454, 1393, 1270, 1245, 1113, 1073, 1045, 1013 cm^{-1}.

Anal. Calcd. for $C_{19}H_{15}NOSe$: C, 64.78; H, 4.29; N, 3.98. Found: C, 64.86; H, 4.28; N, 3.95.



(*Z*)-*N*-(4-Phenyl-1,3-oxaselenolan-2-ylidene)cyclohexanamine 3l.

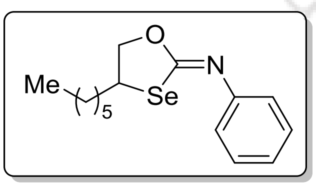
Colorless liquid; yield 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.23 (m, 5H), 5.06 (dd, *J* = 6.8, 6.0 Hz, 1H), 4.45 (dd, *J* = 10.0, 6.0 Hz, 1H), 4.29 (dd, *J* = 10.0, 6.8 Hz, 1H), 2.53 (m, 1H), 1.78-1.75 (m, 3H), 1.61-1.58 (m, 1H), 1.48-1.40 (m, 2H), 1.35-1.19 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 138.2, 129.0, 128.4, 128.2, 127.7, 75.2, 48.5, 33.8, 33.7, 25.5, 24.6.

FT-IR (neat) 3061, 3030, 2928, 2854, 1728, 1660, 1493, 1451, 1369, 1348, 1243, 1129, 1059, 1040, 1014 cm^{-1}.

Anal. Calcd. for $C_{15}H_{19}NOSe$: C, 58.44; H, 6.21; N, 4.54. Found: C, 58.51; H, 6.19; N, 4.50.



(*Z*)-*N*-(4-Hexyl-1,3-oxaselenolan-2-ylidene)benzenamine 3m.

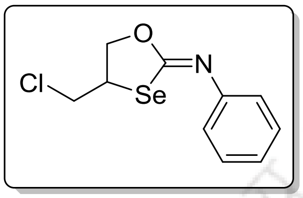
Yellow liquid; yield 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 4.57-4.50 (m, 1H), 3.35 (dd, *J* = 10.0, 4.8 Hz, 1H), 3.13 (t, *J* = 10.0 Hz, 1H), 1.97-1.88 (m, 1H), 1.75-1.67 (m, 1H), 1.58-1.52 (m, 1H), 1.51-1.40 (m, 1H), 1.39-1.29 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 150.3, 129.3, 124.5, 121.0, 84.4, 34.1, 31.7, 31.2, 29.1, 26.0, 22.6, 14.1.

FT-IR (neat) 3060, 3027, 2927, 2856, 1658, 1593, 1488, 1458, 1221, 1146, 1090, 1020 cm^{-1}.

Anal. Calcd. for $C_{15}H_{21}NOSe$: C, 58.06; H, 6.82; N, 4.51. Found: C, 58.15; H, 6.81; N, 4.47.



(*Z*)-*N*-(4-(Chloromethyl)-1,3-oxaselenolan-2-ylidene)benzenamine 3n.

Colorless solid; yield 86%.

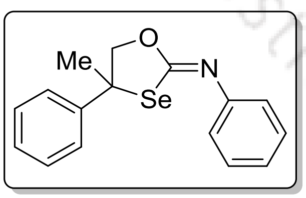
Mp: 53-54 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 2H), 4.80-4.74 (m, 1H), 3.79 (qd, *J* = 11.2, 4.8 Hz, 2H), 3.47 (dd, *J* = 10.4, 5.6 Hz, 1H), 3.43 (dd, *J* = 10.4, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 149.9, 129.4, 124.9, 120.8, 81.5, 43.2, 28.5.

FT-IR (KBr) 3062, 3031, 2928, 1637, 1551, 14841, 1454, 1214, 1095, 1024, 1020 cm^{-1}.

Anal. Calcd. for $C_{10}H_{10}ClNOSe$: C, 43.74; H, 3.67; N, 5.10. Found: C, 43.81; H, 3.66; N, 5.07.



(*Z*)-*N*-(4-Methyl-4-phenyl-1,3-oxaselenolan-2-ylidene)benzenamine 3o.

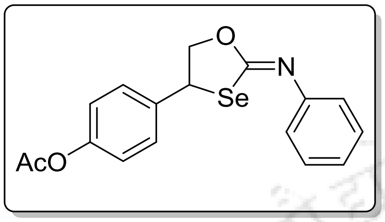
Colorless liquid; yield 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 6.8 Hz, 3H), 7.29 (t, *J* = 7.6 Hz, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.66 (d, *J* = 10.0 Hz, 1H), 4.41 (d, *J* = 9.6 Hz, 1H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 150.1, 141.7, 129.4, 129.0, 127.9, 126.6, 124.8, 121.1, 81.5, 59.2, 29.4.

FT-IR (neat) 2926, 1644, 1489, 1446, 1384, 1260, 1087, 1019, 912 cm^{-1}.

Anal. Calcd. for $C_{16}H_{15}NOSe$: C, 60.76; H, 4.78; N, 4.43. Found: C, 60.83; H, 4.76; N, 4.40.



4-((*Z*)-2-(Phenylimino)-1,3-oxaselenolan-4-yl)phenyl acetate 3p.

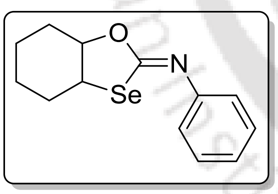
Yellow liquid; yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 4H), 7.11-6.92 (m, 4H), 5.05 (t, *J* = 7.2 Hz, 1H), 4.61 (dd, *J* = 10.4, 6.4 Hz, 1H), 4.45 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 162.4, 150.6, 150.1, 135.5, 129.4, 128.9, 124.8, 122.4, 120.9, 76.7, 48.1, 21.1.

FT-IR (neat) 3061, 3032, 3001, 2930, 2840, 1755, 1643, 1506, 1462, 1369, 1201, 1167, 1090, 1046, 1018 cm^{-1}.

Anal. Calcd. for $C_{17}H_{15}NO_3Se$: C, 56.68; H, 4.20; N, 3.89. Found: C, 56.77; H, 4.18; N, 3.91.



(*Z*)-*N*-(Hexahydrobenzo[*d*][1,3]oxaselenol-2-ylidene)benzenamine 3q.

Colorless solid; yield 62%.

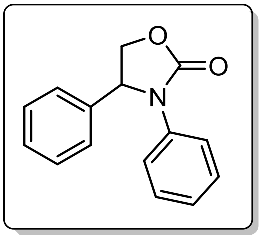
Mp: 102-103 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.4 Hz, 2H), 7.09 (t, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.00 (td, *J* = 11.2, 4.0 Hz, 1H), 3.56 (td, *J* = 10.8, 3.6 Hz, 1H), 2.38-2.34 (m, 1H), 2.17-2.13 (m, 1H), 1.95-1.82 (m, 1H), 1.80-1.78 (m, 1H), 1.68-1.58 (m, 2H), 1.48-1.32 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 150.1, 129.3, 124.6, 121.1, 88.5, 49.6, 30.4, 29.8, 26.1, 24.1.

FT-IR (KBr) 3069, 2937, 2861, 1645, 1588, 1484, 1445, 1361, 1257, 1194, 1145, 1116, 1086, 1039 cm^{-1}.

Anal. Calcd. for $C_{13}H_{15}NOSe$: C, 55.72; H, 5.40; N, 5.00. Found: C, 55.78; H, 5.39; N, 4.98.



3,4-Diphenyloxazolidin-2-one 4a.[10]

Colorless solid; yield 73%.

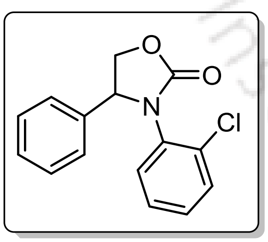
Mp: 119-120 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.35-7.29 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* =7.2 Hz, 1H), 5.39 (dd, *J* = 8.4, 6.4 Hz, 1H), 4.77 (t, *J* = 8.0 Hz, 1H), 4.19 (dd, *J* = 8.0, 6.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 138.4, 137.2, 129.5, 129.1, 129.0, 126.4, 124.8, 121.0, 69.9, 60.8.

FT-IR (KBr) 3062, 3001, 2971, 2911, 1754, 1597, 1499, 1401, 1367, 1222, 1202, 1127, 1042 cm^{-1}.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48; N, 5.85. Found: C, 75.39; H, 5.45; N, 5.81.



3-(2-Chlorophenyl)-4-phenyloxazolidin-2-one 4b.

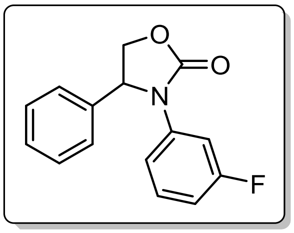
Yellow liquid; yield 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.32-7.25 (m, 5H), 7.15 (td, *J* = 7.2, 1.6 Hz, 1H), 7.10 (td, *J* = 7.2, 1.6 Hz, 1H), 7.03 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.37 (dd, *J* = 8.8, 6.8 Hz, 1H), 4.84 (t, *J* = 8.8 Hz, 1H), 4.39 (dd, *J* = 8.8, 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 137.4, 133.5, 132.6, 130.6, 130.2, 129.7, 129.4, 129.2, 127.6, 127.5, 70.5, 62.0.

FT-IR (neat) 3063, 3031, 2922, 1760, 1693, 1524, 1485, 1455, 1401, 1366, 1212, 1120, 1067, 1036 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.91; H, 4.40; N, 5.09.



3-(3-Fluorophenyl)-4-phenyloxazolidin-2-one 4c.

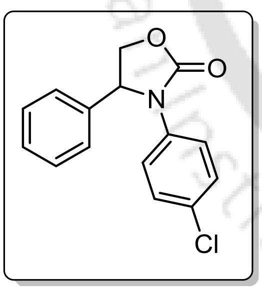
Yellow liquid; yield 61%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.05 (m, 7H), 6.74 (td, *J* = 8.4, 2.4 Hz, 1H), 5.34 (dd, *J* = 8.4, 5.6 Hz, 1H), 4.75 (t, *J* = 8.4 Hz, 1H), 4.17 (dd, *J* = 8.8, 5.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (d, J_{C-F} = 244.1 Hz), 155.7, 138.8 (d, J_{C-F} = 10.7 Hz), 138.0, 130.2 (d, J_{C-F} = 9.2 Hz), 129.6, 129.1, 126.2, 115.8, 111.5 (d, J_{C-F} = 20.6 Hz), 108.3 (d, J_{C-F} = 25.2 Hz), 69.9, 60.6.

FT-IR (neat) 3062, 3032, 2912, 1755, 1614, 1494, 1455, 1397, 1357, 1206, 1117, 1080, 1049 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}FNO_2$: C, 70.03; H, 4.70; N, 5.44. Found: C, 70.10; H, 4.67; N, 5.41.



3-(4-Chlorophenyl)-4-phenyloxazolidin-2-one 4d.

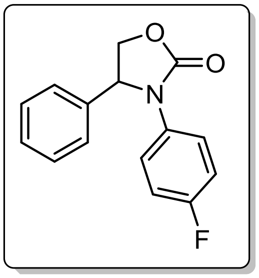
Yellow liquid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 7.26-7.16 (m, 4H), 5.34 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.75 (t, *J* = 8.8 Hz, 1H), 4.16 (dd, *J* = 8.8, 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 137.8, 135.7, 130.0, 129.6, 129.1, 129.0, 126.3, 122.0, 69.9, 60.6.

FT-IR (neat) 3027, 2961, 2919, 1755, 1747, 1637, 1495, 1455, 1396, 1354, 1292, 1211, 1129, 1096, 1047 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.42; N, 5.12. Found: C, 65.90; H, 4.40; N, 5.08.



3-(4-Fluorophenyl)-4-phenyloxazolidin-2-one 4e.

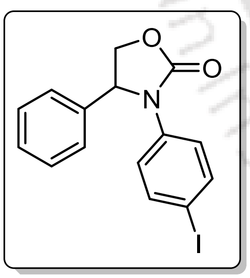
Yellow liquid; yield 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 7H), 6.94-6.89 (m, 2H), 5.32 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.75 (t, *J* = 8.8 Hz, 1H), 4.18 (dd, *J* = 8.8, 6.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, $J_{C\text{-}F}$ = 243.6 Hz), 156.1, 137.8, 133.0, 129.3, 128.9, 126.3, 123.0 (d, $J_{C\text{-}F}$ = 7.6 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22.7 Hz), 69.7, 60.9.

FT-IR (neat) 3062, 3030, 2919, 1754, 1510, 1455, 1400, 1358, 1228, 1159, 1126, 1081, 1047 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}FNO_2$: C, 70.03; H, 4.70; N, 5.44. Found: C, 70.09; H, 4.71; N, 5.39.



3-(4-Iodophenyl)-4-phenyloxazolidin-2-one 4f.

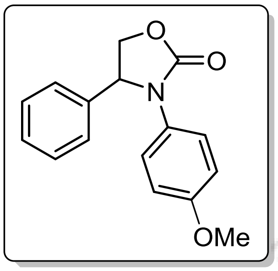
Yellow liquid; yield 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.8 Hz, 2H), 7.39-7.31 (m, 3H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.19 (d, *J* = 9.2 Hz, 2H), 5.36 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.77 (t, *J* = 8.8 Hz, 1H), 4.19 (dd, *J* = 8.4, 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 137.9, 137.0, 129.6, 129.1, 128.6, 126.2, 122.5, 88.5, 69.9, 60.4.

FT-IR (neat) 3063, 3031, 2917, 1755, 1585, 1489, 1455, 1409, 1393, 1350, 1287, 1210, 1129, 1047 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}INO_2$: C, 49.34; H, 3.31; N, 3.84. Found: C, 49.41; H, 3.30; N, 3.81.



3-(4-Methoxyphenyl)-4-phenyloxazolidin-2-one 4g.[19a]

Colorless solid; yield 68%.

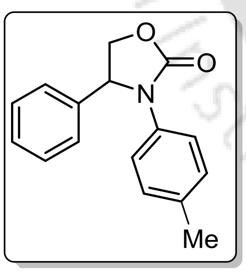
Mp: 136-137 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (m, 7H), 6.77 (d, *J* = 7.2 Hz, 2H), 5.30 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.75 (t, *J* = 8.8 Hz, 1H), 4.19 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 156.4, 138.3, 129.9, 129.2, 128.7, 126.5, 123.3, 114.1, 69.7, 61.2, 55.2.

FT-IR (KBr) 3065, 3032, 3003, 2912, 2836, 1751, 1611, 1514, 1457, 1427, 1400, 1297, 1249, 1181, 1126, 1081, 1034 cm^{-1}.

Anal. Calcd. for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.47; H, 5.58; N, 5.18.



4-Phenyl-3-*p*-tolyloxazolidin-2-one 4h.[19b]

Yellow solid; yield 70%.

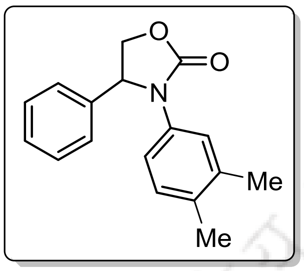
Mp: 105-106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 7H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.33 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.72 (t, *J* = 8.8 Hz, 1H), 4.14 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 138.5, 134.5, 129.5, 129.4, 128.8, 126.4, 121.2, 69.9, 60.9, 20.8.

FT-IR (KBr) 3071, 3032, 2922, 2861, 1743, 1732, 1515, 1457, 1401, 1349, 1227, 1130, 1044 cm^{-1}.

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.96; H, 5.95; N, 5.50.



3-(3,4-Dimethylphenyl)-4-phenyloxazolidin-2-one 4j.

Colorless solid; yield 78%.

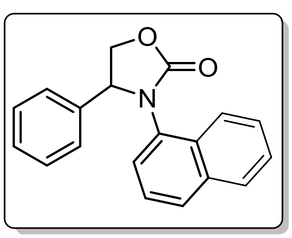
Mp: 130-131 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 7.22 (s, 1H), 6.96 (s, 2H), 5.33 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.75 (t, *J* = 8.8 Hz, 1H), 4.16 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.15 (s, 3H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 138.6, 137.2, 134.7, 133.3, 129.9, 129.3, 128.7, 126.4, 122.7, 118.6, 69.8, 60.8, 20.0, 19.1.

FT-IR (KBr) 3062, 3032, 2970, 2938, 2920, 1746, 1615, 1506, 1455, 1398, 1356, 1222, 1211, 1135, 1112, 1050 cm^{-1}.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.3; H, 6.41; N, 5.24. Found: C, 76.44; H, 6.39; N, 5.26.



3-(Naphthalen-1-yl)-4-phenyloxazolidin-2-one 4k.

Colorless solid; yield 71%.

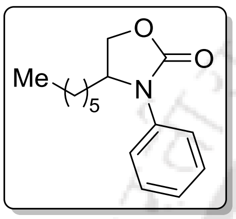
Mp: 152-153 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.47 (t, *J* = 8.4 Hz, 1H), 7.31-7.21 (m, 6H), 7.12 (s, 1H), 5.36 (s, 1H), 4.93 (t, *J* = 8.8 Hz, 1H), 4.49 (dd, *J* = 8.8, 6.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 137.7, 134.6, 132.5, 130.1, 129.1, 128.6, 127.3, 126.9, 126.4, 125.3, 122.6, 70.3, 63.5.

FT-IR (KBr) 3062, 3031, 2927, 1741, 1601, 1501, 1459, 1411, 1376, 1300, 1256, 1215, 1135, 1089, 1052, 1026 cm^{-1}.

Anal. Calcd. for $C_{19}H_{15}NO_2$: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.96; H, 5.21; N, 4.81.



4-Hexyl-3-phenyloxazolidin-2-one 4l.

Pale yellow solid; yield 71%.

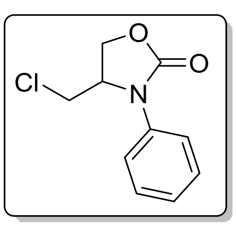
Mp: 78-79 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.60 (q, *J* = 6.0 Hz, 1H), 4.05 (t, *J* = 8.4 Hz, 1H), 3.63 (dd, *J* = 8.8, 7.6 Hz, 1H), 1.88-1.79 (m, 1H), 1.74-1.65 (m, 1H), 1.50-1.46 (m, 1H), 1.42-1.17 (m, 7H), 0.87 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 138.4, 128.9, 123.8, 118.1, 73.1, 50.4, 34.9, 31.6, 28.9, 24.4, 22.5, 22.4, 14.0.

FT-IR (KBr) 3061, 2961, 2930, 2858, 1750, 1602, 1503, 1486, 1407, 1380, 1311, 1220, 1126, 1082 cm^{-1}.

Anal. Calcd. $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.97; H, 8.55; N, 5.63.



4-(Chloromethyl)-3-phenyloxazolidin-2-one 4m.

Colorless solid; yield 73%.

Mp: 98-99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 4.85-4.80 (m, 1H), 4.13 (t, *J* = 9.2 Hz, 1H), 3.93 (dd, *J* = 9.2, 6.0 Hz, 1H), 3.78-3.69 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 137.9, 129.3, 124.5, 118.5, 71.0, 48.2, 44.7.

FT-IR (KBr) 2947, 2862, 1747, 1611, 1504, 1466, 1385, 1065 cm^{-1}.

Anal. Calcd. for $C_{10}H_{10}ClNO_2$: C, 56.75; H, 4.76; N, 6.62. Found: C, 56.85; H, 4.77; N, 6.59.

Crystal Data and Structure Refinement for 3f at 296(2) K

Identification code	3f	
CCDC number	843128	
Empirical formula	$C_{15}H_{12}INOSe$	
Formula weight	428.12	
Temperature	296 (2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
	Loop xyz 'x, y, z' '-x, y+1/2, -z+1/2' '-x, -y, -z' 'x, -y-1/2, z-1/2'	
Unit cell dimensions	*a* = 12.7577 (7) Å	α(°) = 90.00
	b = 10.0993 (6) Å	β(°) = 94.400 (3)
	c = 11.6512 (7) Å	γ(°) = 90.00
Volume	1496.76 (15) $Å^3$	
Z	4	
Density (calculated)	1.904 Mg/m^3	
Absorption coefficient	4.563 mm^{-1}	
F(000)	816.0	
Crystal size	0.34 x 0.30 x 0.27 mm	
Theta range for data collection	1.60 to 28.54°	
Index ranges	-17<=h<=14, -13<=k<=13, -13<=l<=15	
Reflections collected	3709	
Independent reflections	3585 [R (int) = 0.0532]	
Completeness to theta = 28.54°	97.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.292 and 0.231	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3398 / 0 /172	
Goodness-of-fit on F^2	1.420	
Final R indices [I>2sigma (I)]	*R1* = 0.0532, *wR2* = 0.1609	
R indices (all data)	*R1* = 0.1363, *wR2* = 0.2460	

Crystal Data and Structure Refinement for 3q at 296(2) K

Identification code	3q
CCDC number	843126
Empirical formula	$C_{13}H_{15}NOSe$
Formula weight	280.22
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
	Loop xyz
	'x, y, z' '-x, y+1/2, -z+1/2' '-x, -y, -z' 'x, -y-1/2, z-1/2'
Unit cell dimensions	*a* = 6.7304 (4) Å α(°)=90.00
	b = 7.6804 (4) Å β(°)= 92.209 (4)
	c = 23.0785 (13) Å γ(°)=90.00
Volume	1192.09 (12) $Å^3$
Z	4
Density (calculated)	1.561 Mg/m^3
Absorption coefficient	3.128 mm^{-1}
F(000)	568.0
Crystal size	0.40 x 0.35 x 0.30 mm
Theta range for data collection	1.77 to 19.98°
Index ranges	-6<=h<=6, -7<=k<=7, -21<=l<=21
Reflections collected	1084
Independent reflections	1022 [R (int) = 0.0515]
Completeness to theta = 19.98°	97.2%
Absorption correction	multi-scan
Max. and min. transmission	0.391 and 0.298
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1084 / 0 /145
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma (I)]	*R1* = 0.0515, *wR2* = 0.1110
R indices (all data)	*R1* = 0.0596, *wR2* = 0.1223

Crystal Data and Structure Refinement for 4a at 296(2) K

Identification code	4a
CCDC number	843127
Empirical formula	$C_{15}H_{13}NO_2$
Formula weight	239.26
Temperature	296 (2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
	Loop xyz
	‘x, y, z’ ‘-x+1/2, y+1/2, -z+1/2’ ‘-x, -y, -z’ ‘x-1/2, -y-1/2, z-1/2’
Unit cell dimensions	*a* = 10.4808 (9) Å α(°)=90.00
	b = 8.9744 (8) Å β(°)=91.143 (5)
	c = 13.0800 (12) Å γ(°)=90.00
Volume	1230.05 (19) $Å^3$
Z	4
Density (calculated)	1.292 Mg/m^3
Absorption coefficient	0.086 mm^{-1}
F(000)	504.0
Crystal size	0.33 x 0.29 x 0.26 mm
Theta range for data collection	2.47 to 26.14°
Index ranges	-12<=h<=12, -10<=k<=10, -16<=l<=16
Reflections collected	2401
Independent reflections	1779 [R (int) = 0.0515]
Completeness to theta = 26.14°	97.8 %
Absorption correction	multi-scan
Max. and min. transmission	0.978 and 0.972
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2401 / 0 /164
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma (I)]	*R1* = 0.0515, *wR2* = 0.1412
R indices (all data)	*R1* = 0.0654, *wR2* = 0.1508

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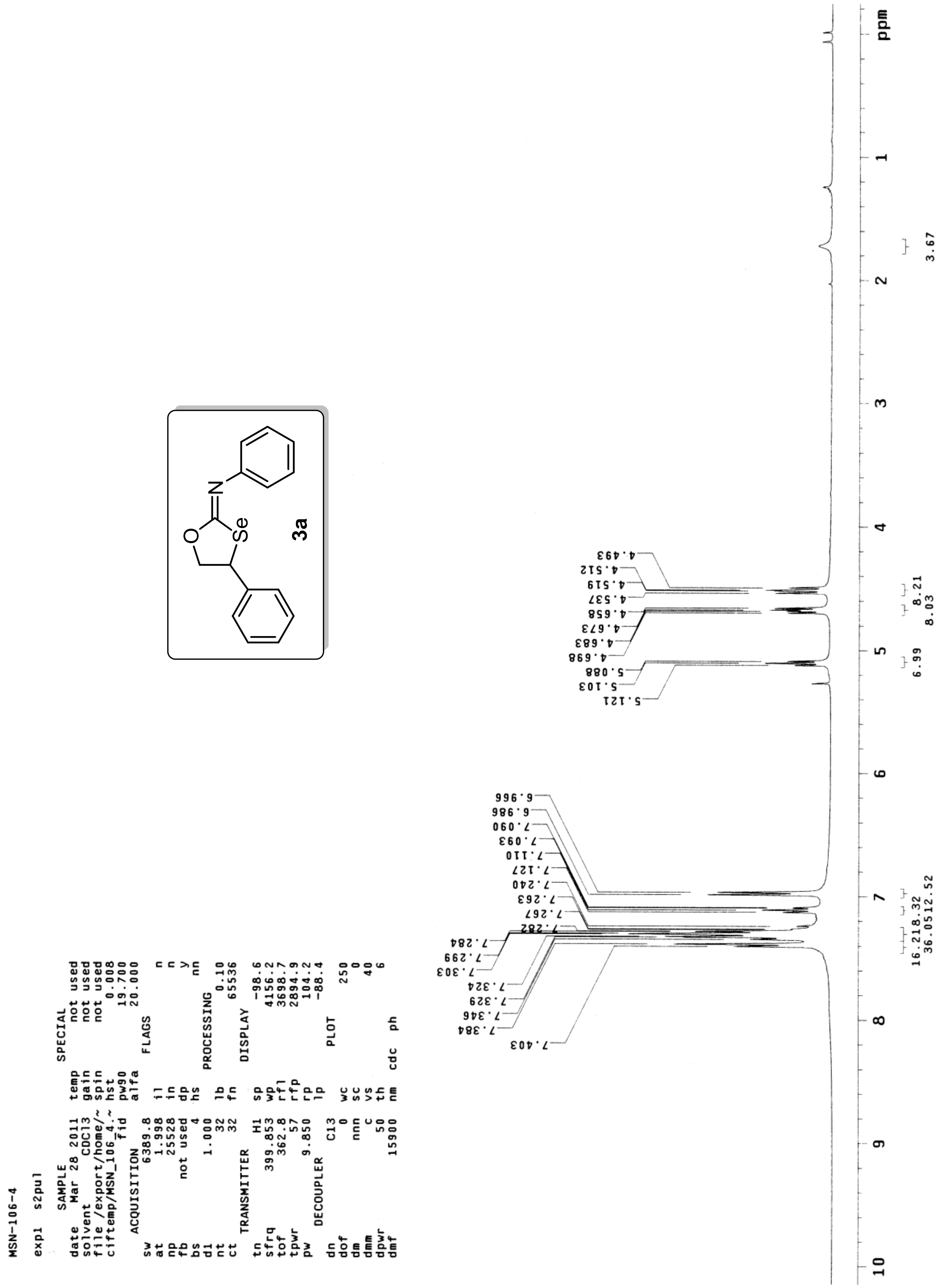
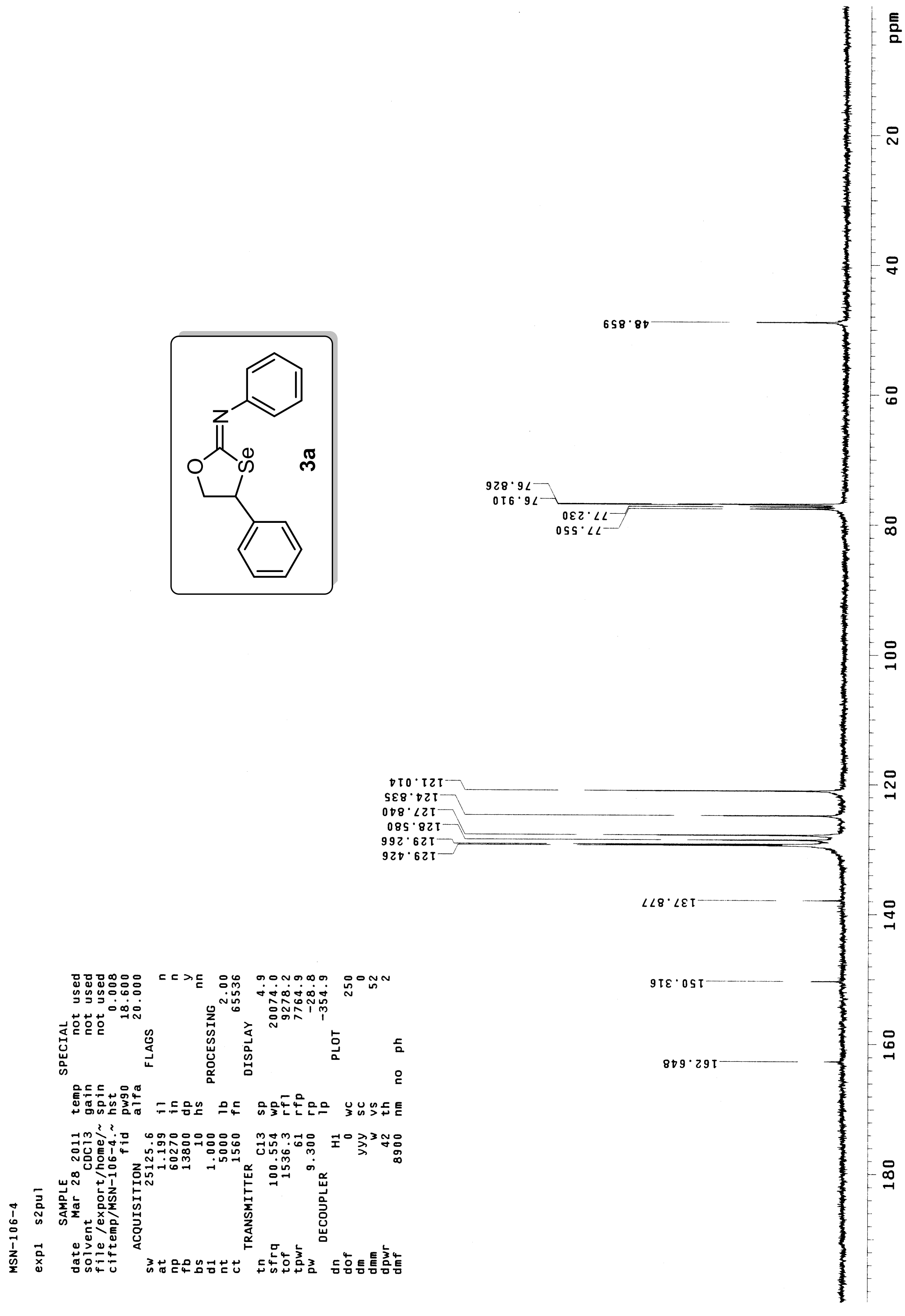
1.6 Selected NMR (^{1}H and ^{13}C) Spectra

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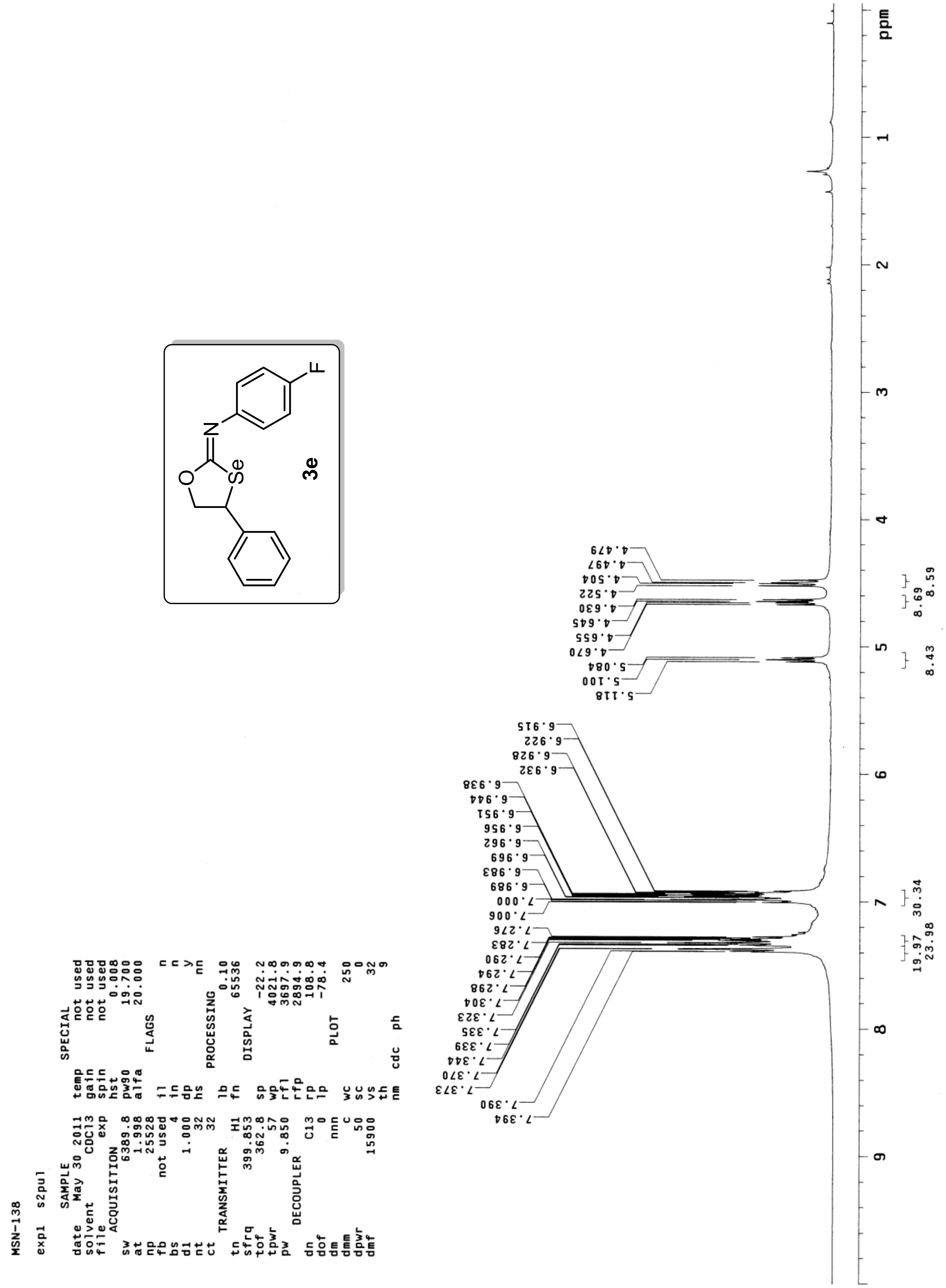
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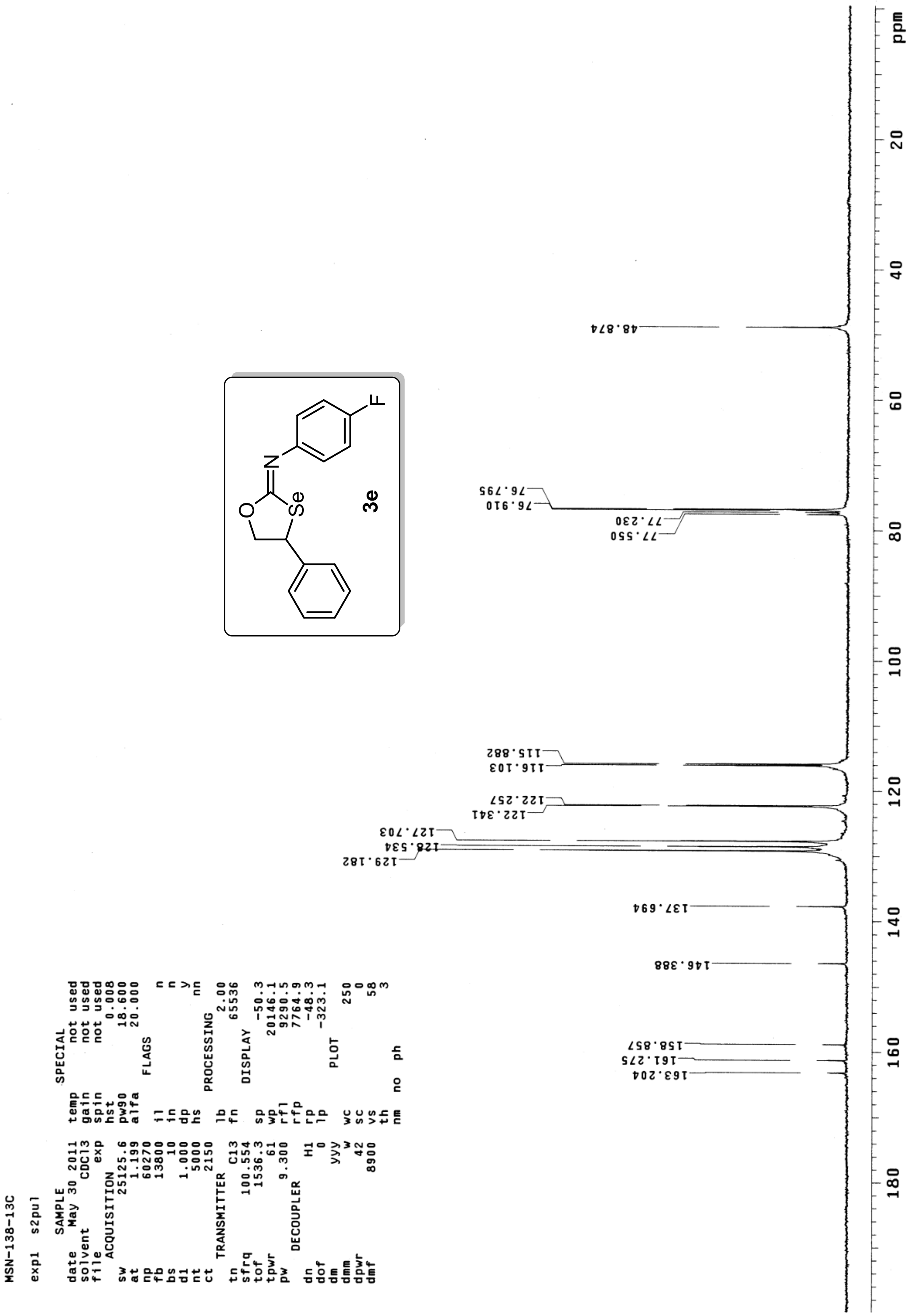
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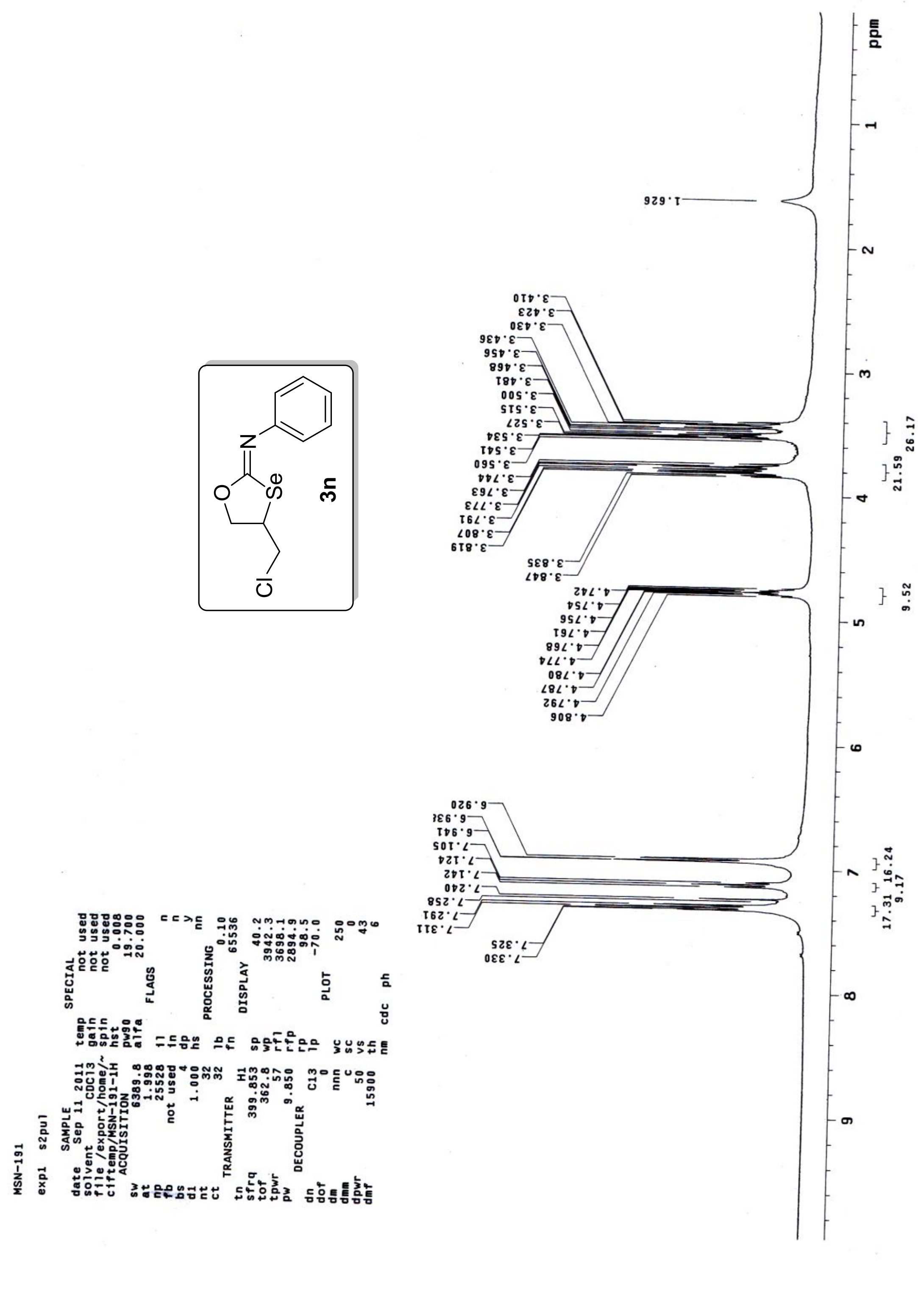
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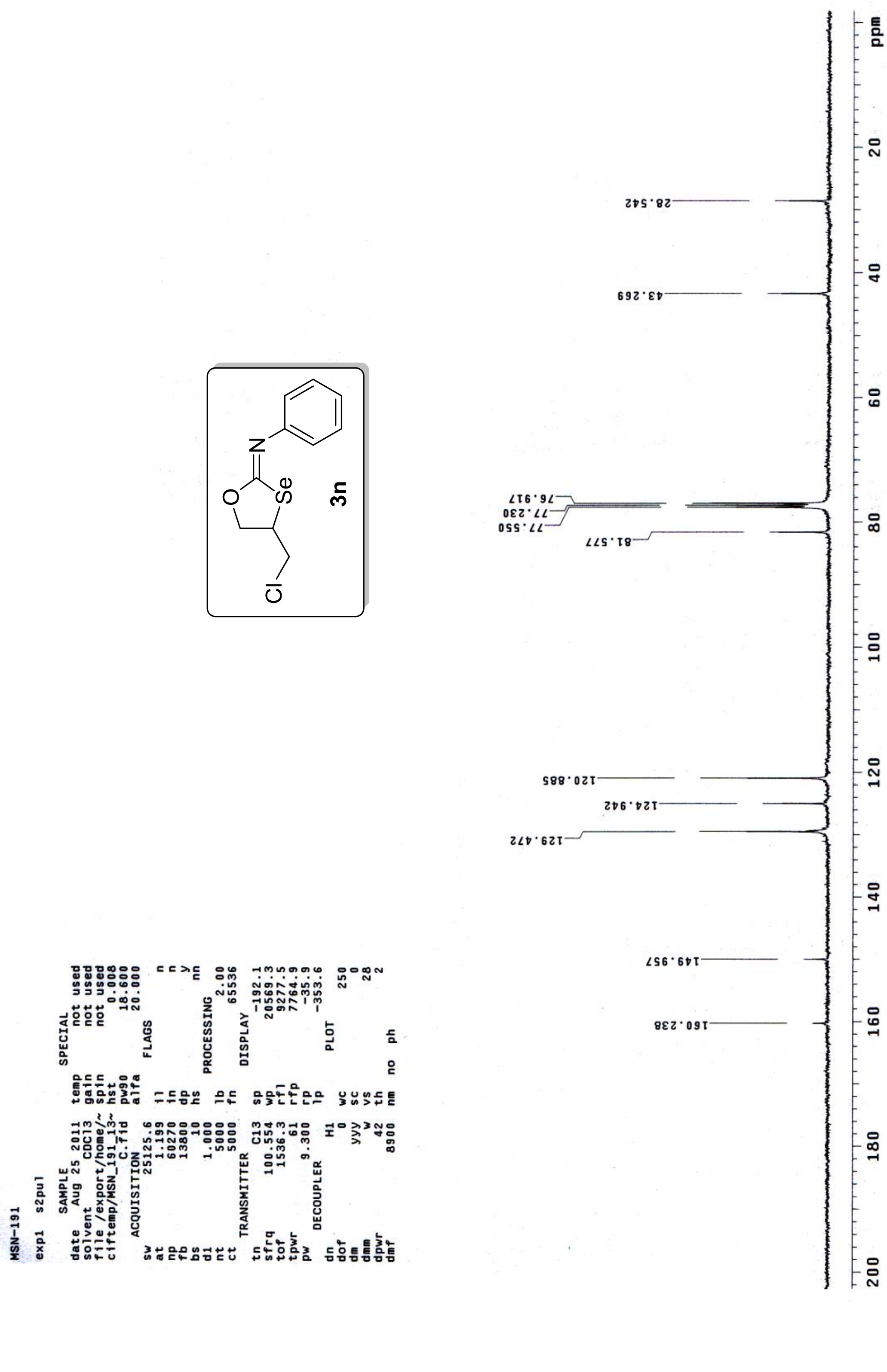
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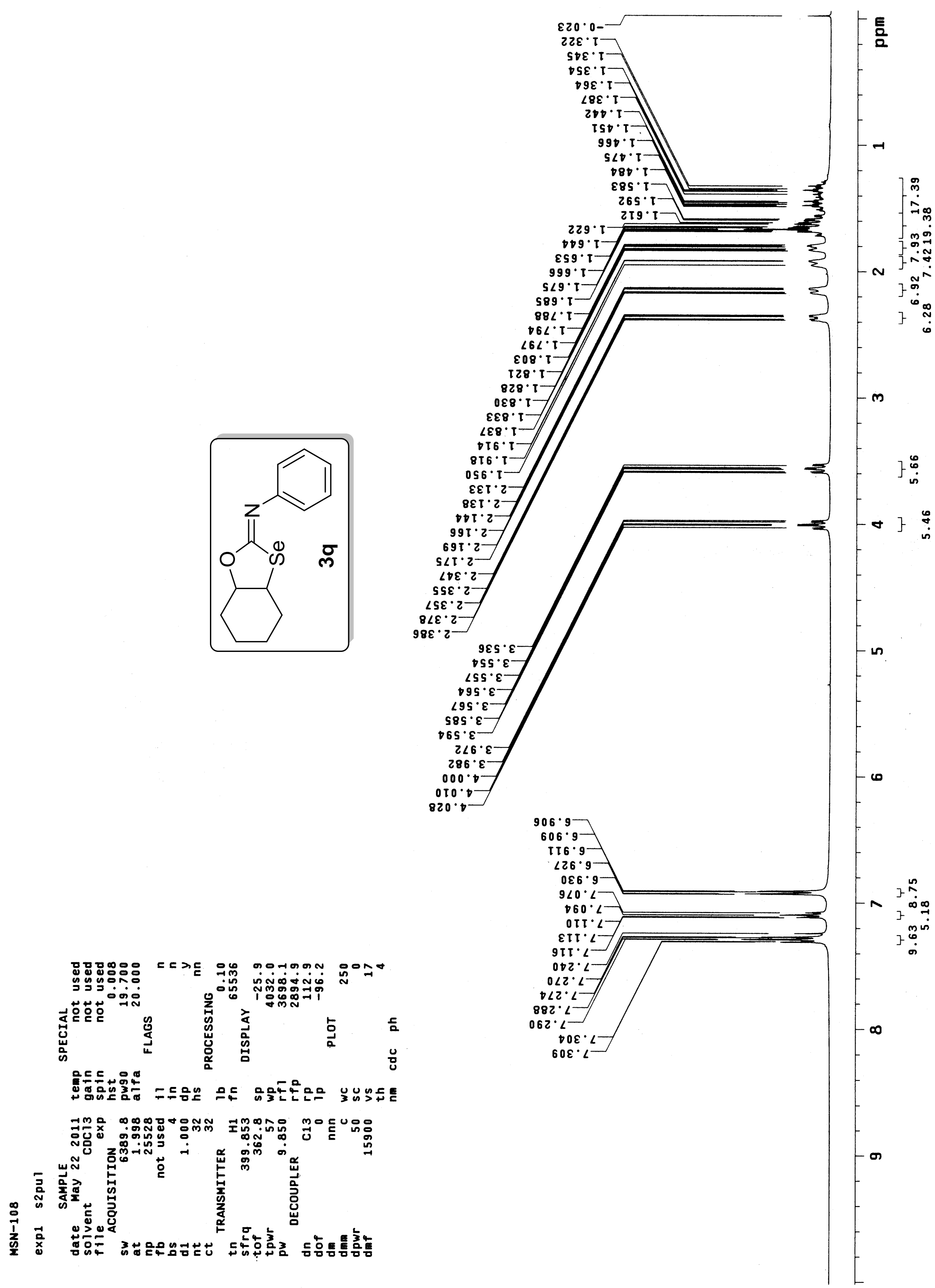
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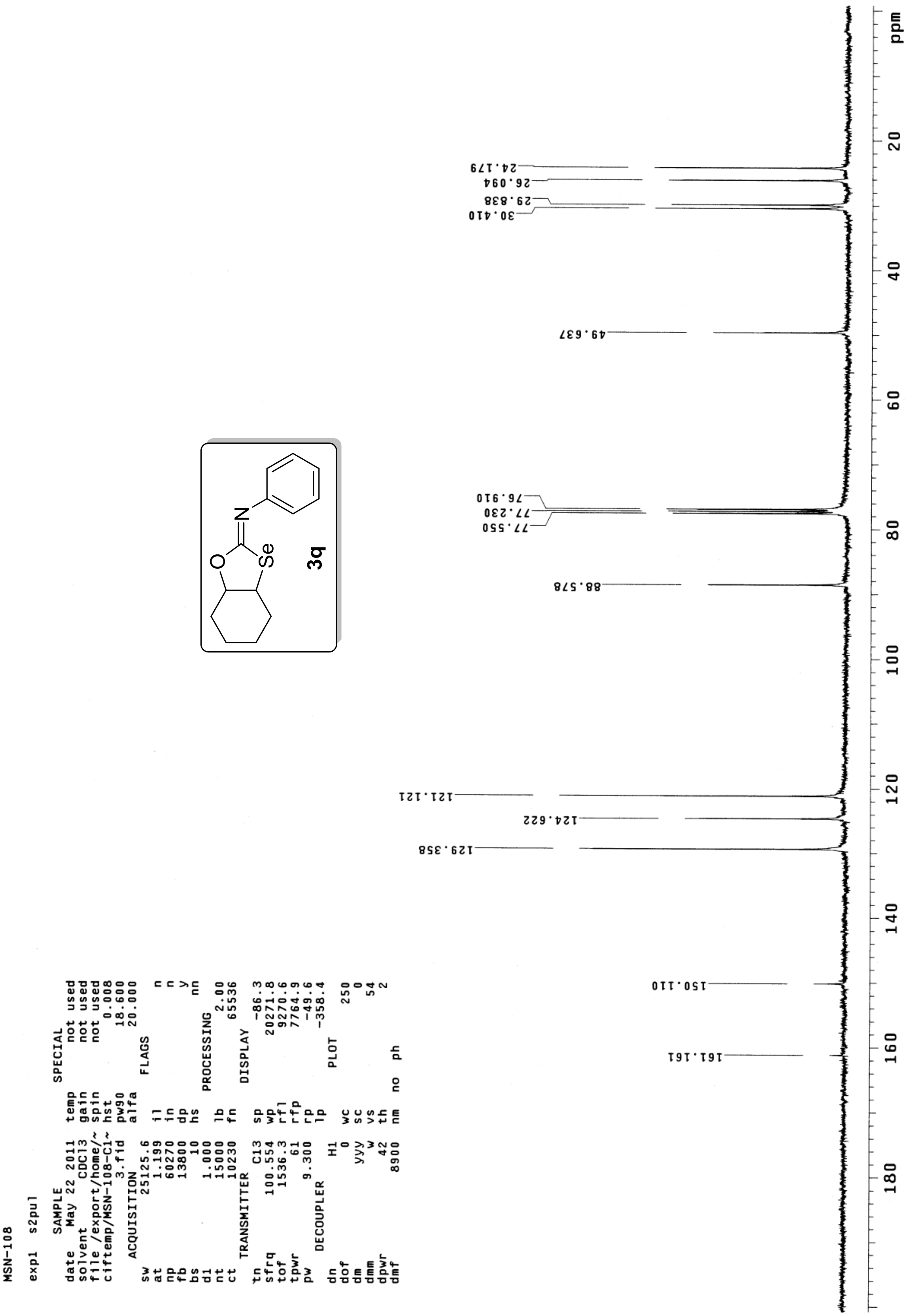
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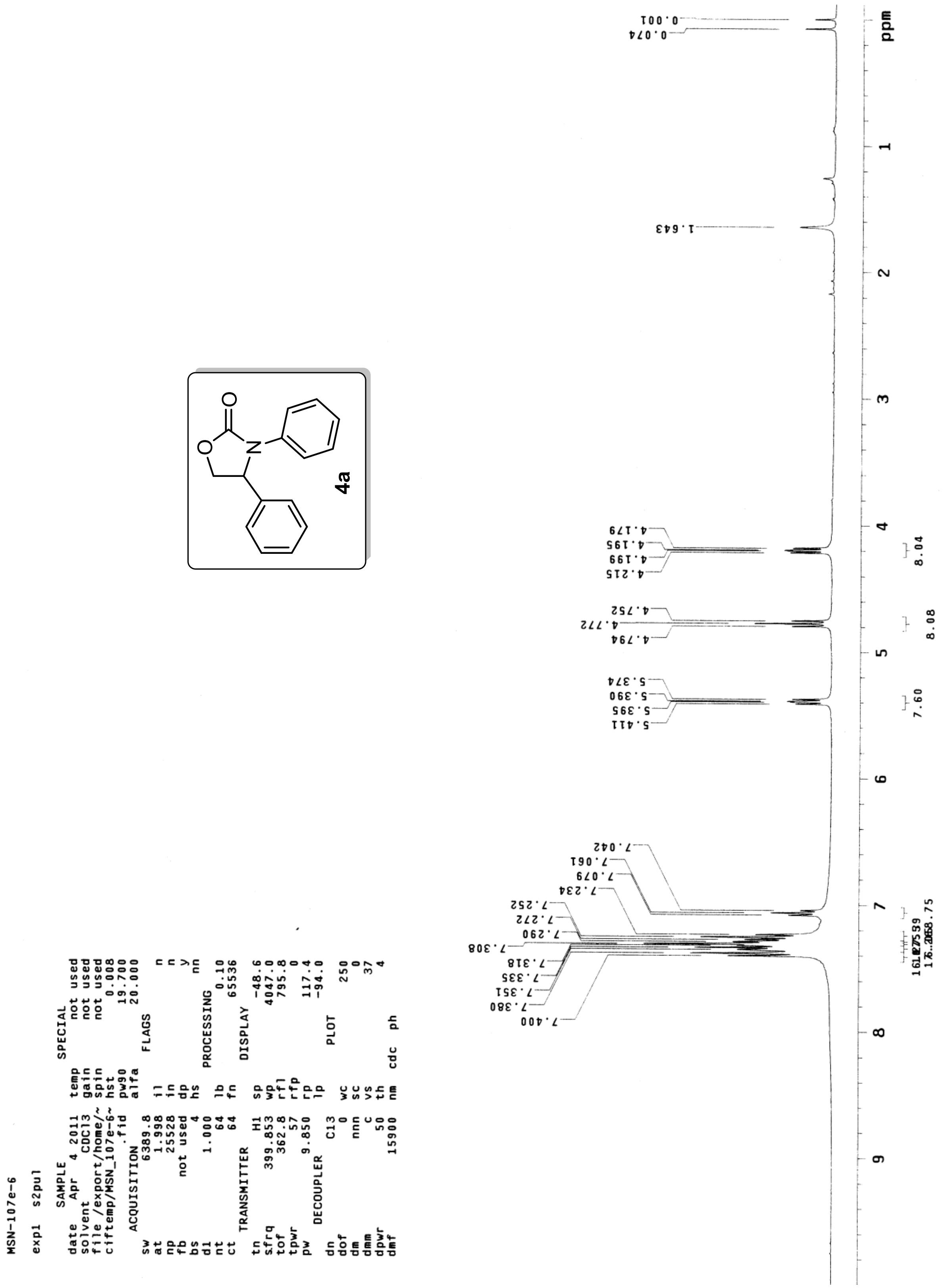
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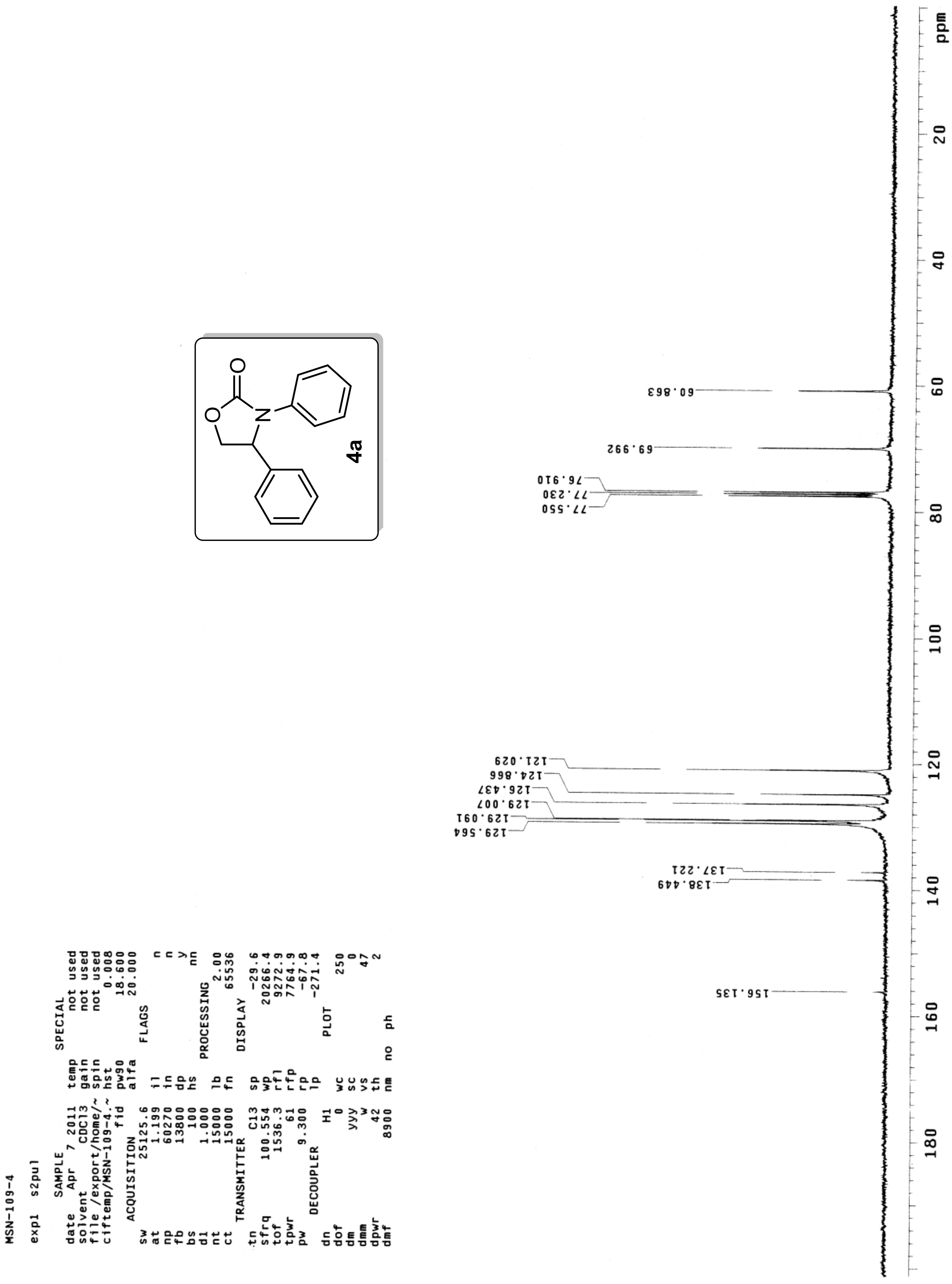
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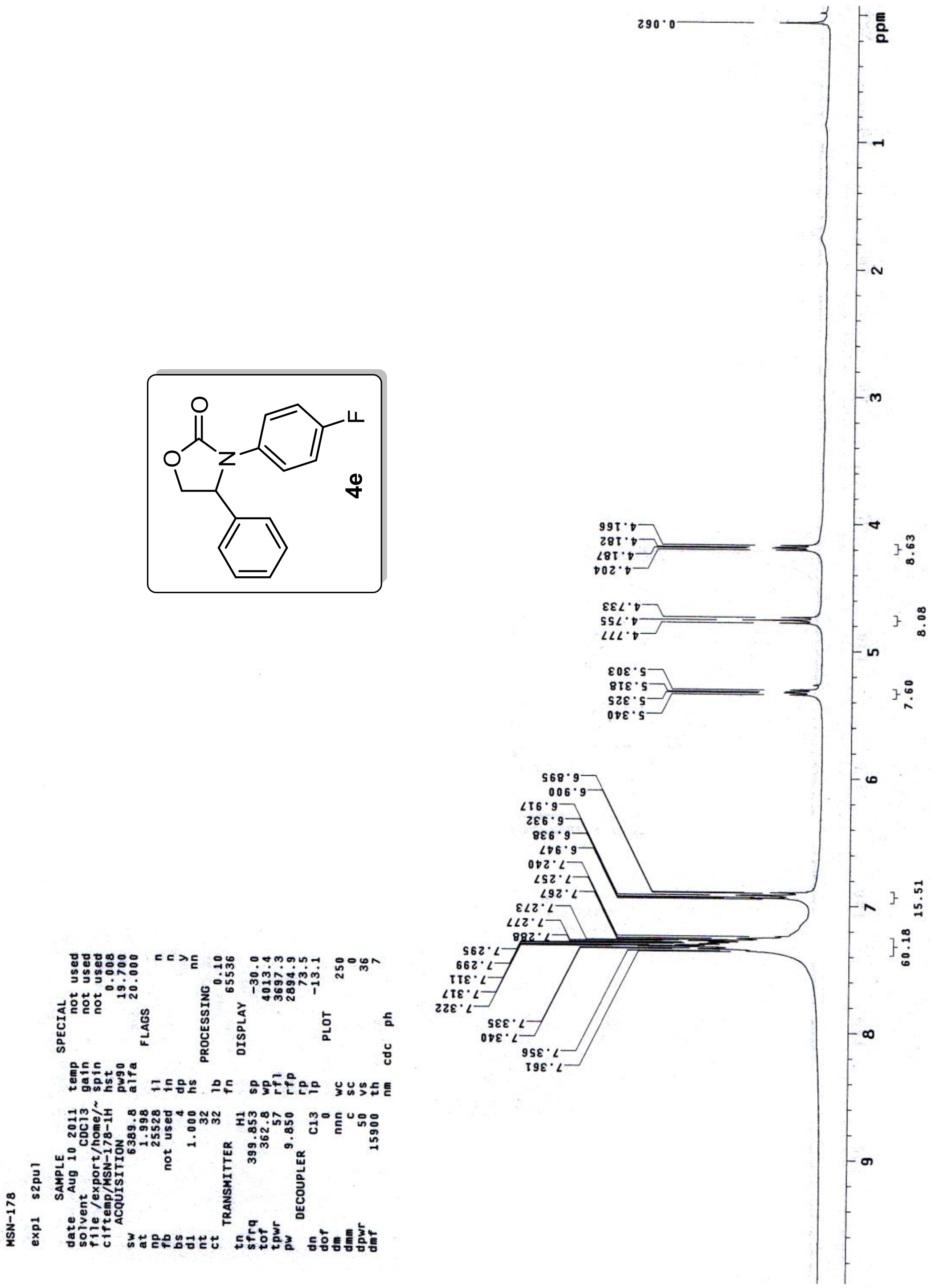
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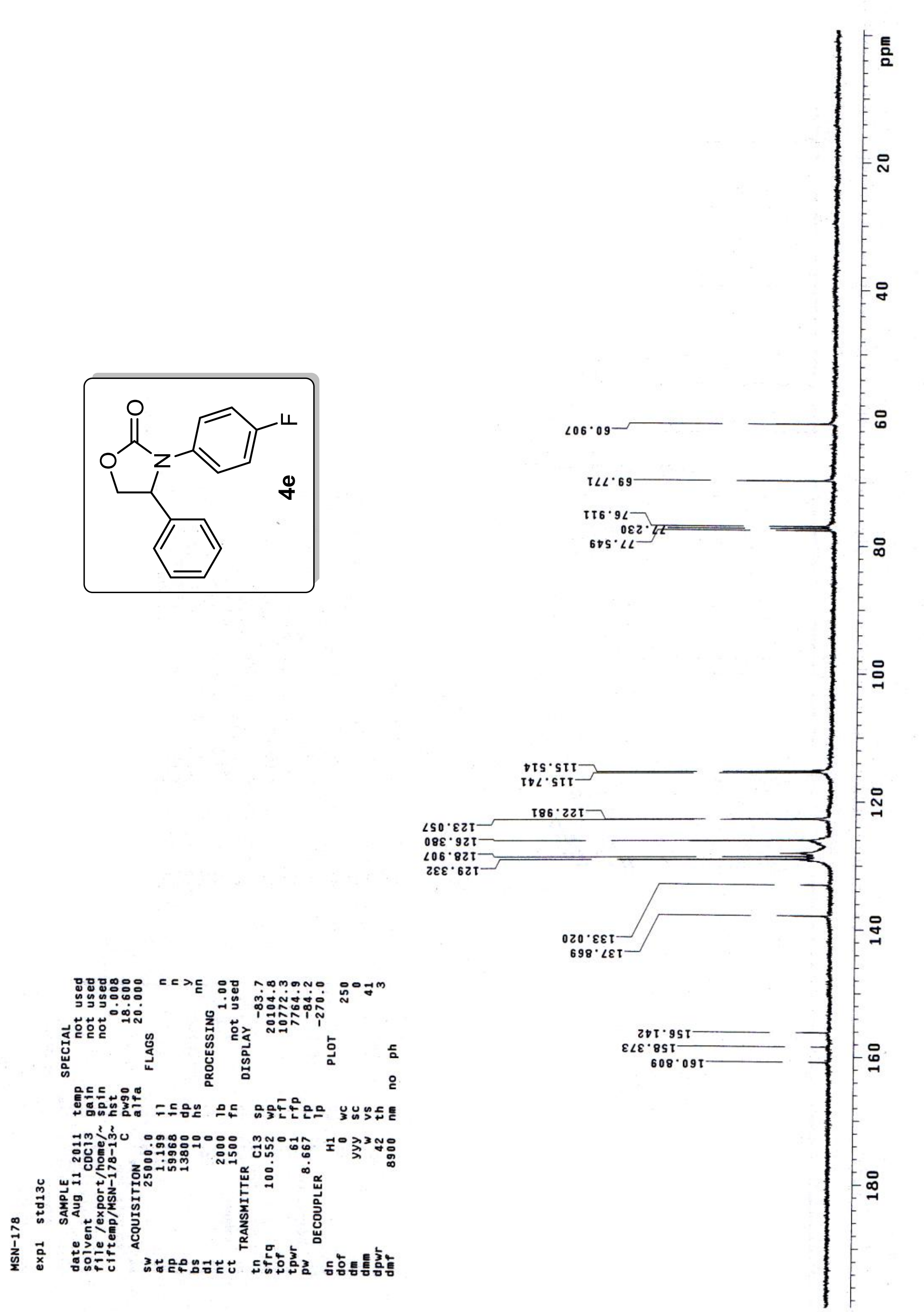

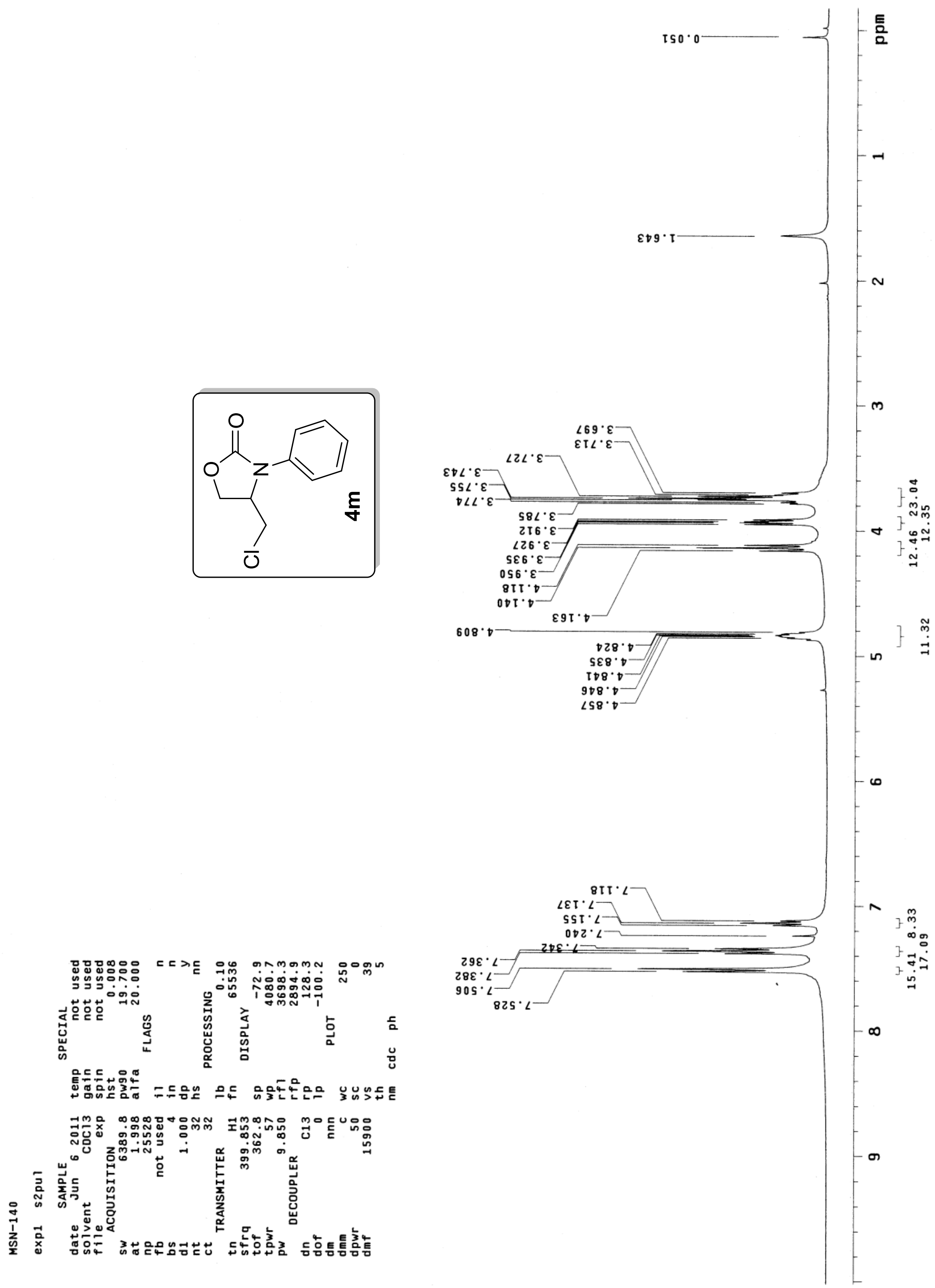
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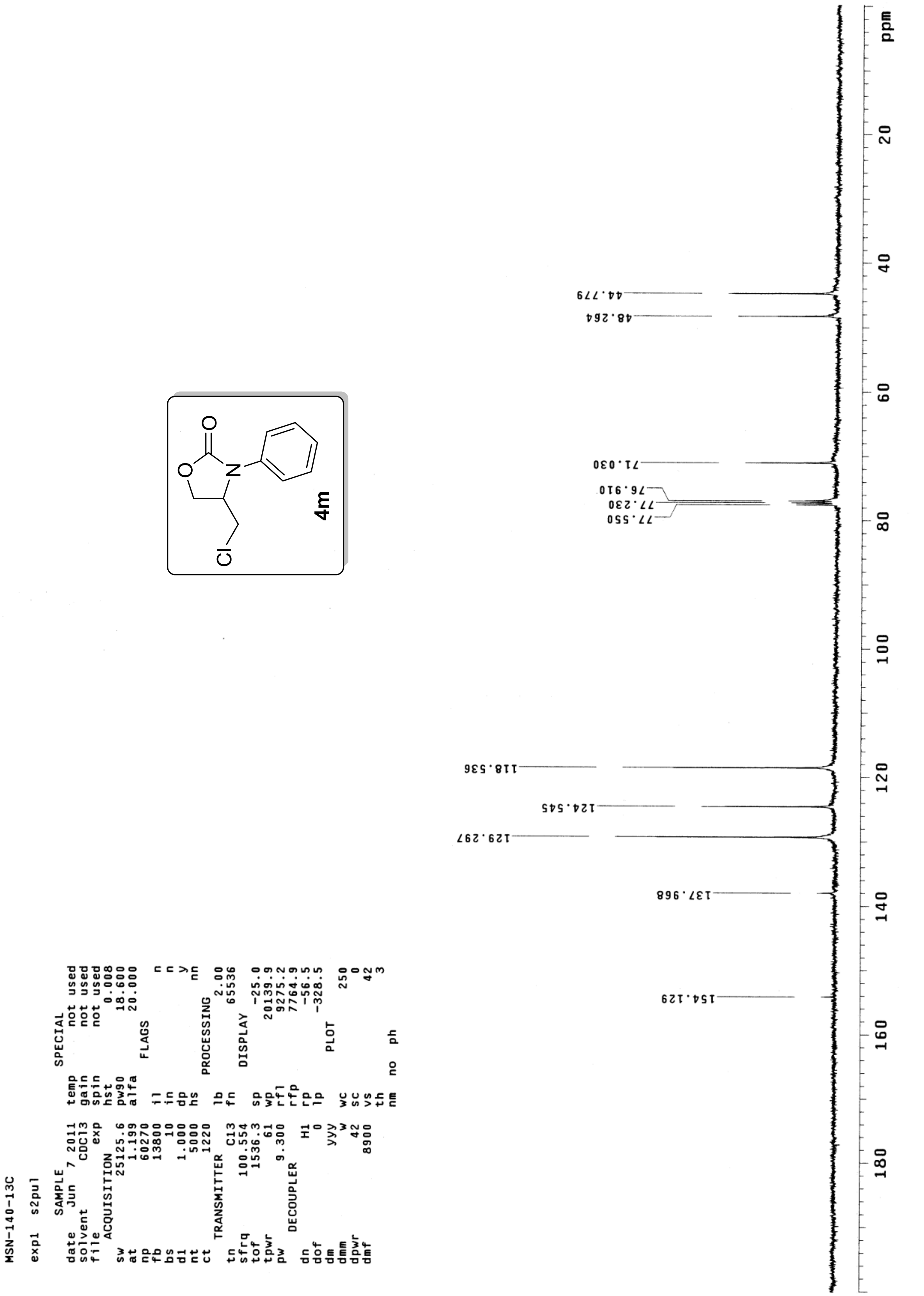
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Chapter II

Fe-Catalyzed Cycloaddition of Aziridines with Isocyanates, Isothiocyanates, Isoselenocyanates and Carbodiimides

The use of water as a reaction medium for organic synthesis has attracted much interest in recent years, in both academia and industry, because it is the most abundant liquid on the planet, cheap, readily available, non-toxic and non-flammable.[1,2] The reactions of water-insoluble organic compounds that take place in aqueous suspensions ("on water") are attactive due to their high efficiency.[3] The functionalized nitrogen containing five-membered heterocycles are important structural scaffolds exhibiting interesting biological and medicinal properties, which can be accessed using the cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates and carbodiimides (Figure 1).[4] The reaction of aziridines with carbodiimides, isocyanates, and isothiocyanates has been studied employing HBF_4,[5] Ph_4SbBr,[6] NaI,[7] Pd,[8] Ni,[9] PBu_3,[10] or Zn[11] as either the catalyst or reagent. These reactions are effective in an organic medium and generally involve an inert atmosphere. Development of eco-friendly cycloaddition of isoseleonocyanates and its analogues with aziridines would thus

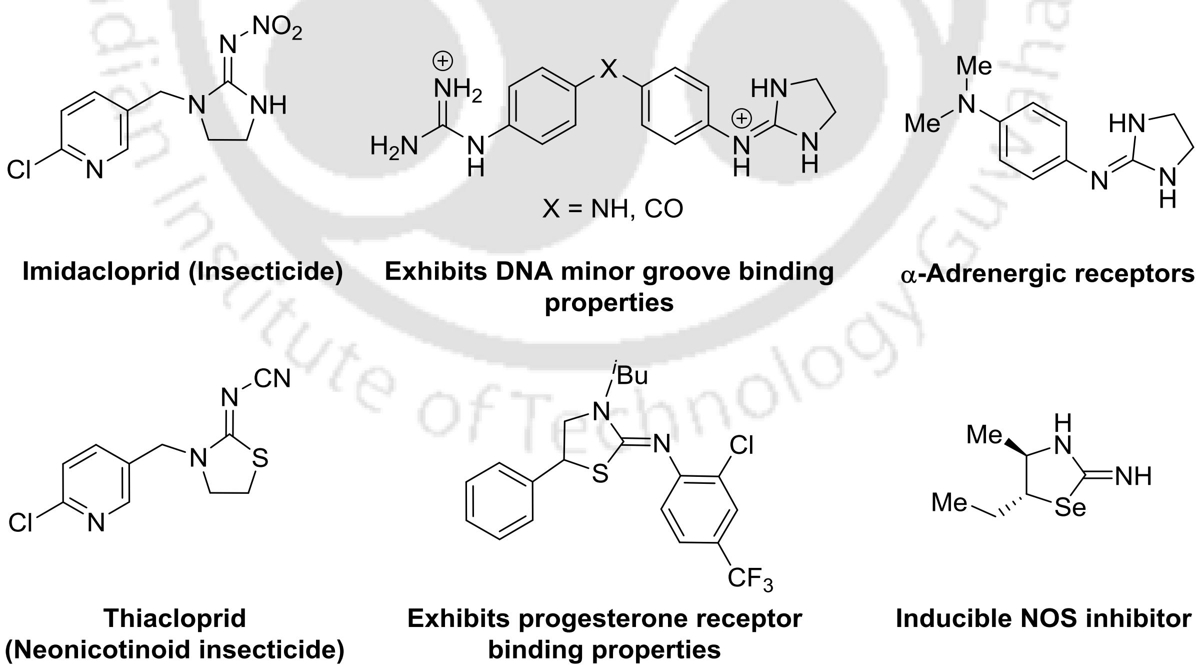
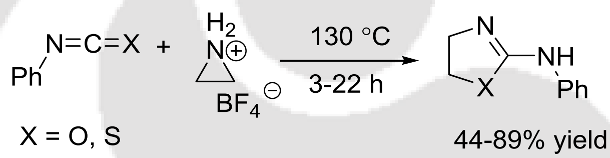


Figure 1. Examples of some biologically active and medicinally significant compounds

be valuable. In this chapter, we report Fe-catalyzed cycloaddition of aziridines with isoseleonocyanates and its analogues in aqueous suspension at moderate temperature. The use of $Fe(NO_3)_3 \cdot 9H_2O$ as the catalyst and water as the solvent are the significant practical advantages.[12]

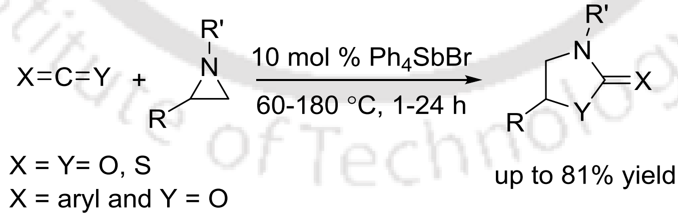
2.1 Cycloaddition of Aziridines with Isocyanates, Isothiocyanates and Carbodiimides

The cycloaddition of aziridine with isocyanates and its analogues has been disclosed for the synthesis of substituted azolidines. For example, Pfeil and Milzner reported the cycloaddition of aziridinium tetrafluoroborate with isocyanate or isothiocyanate to give the corresponding oxazolidines or thiazolidines (Scheme 1).[5]



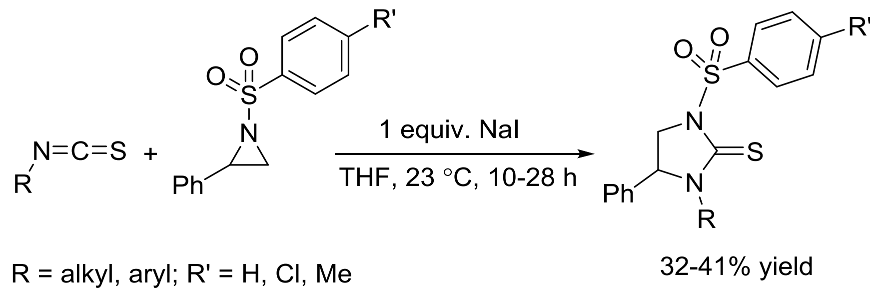
Scheme 1. Cycloaddition of Aziridinium Tetrafluoroborate with Isocyanates and Isothiocyanate

Organo-antimony halides have been employed for the cycloaddition of 1,2-disubstituted aziridines with isocyanates, carbon disulfide and carbon dioxide (Scheme 2).[6] The reaction selectively promoted by *α*-cleavage of aziridine to afford cycloadducts in moderate to good yields.



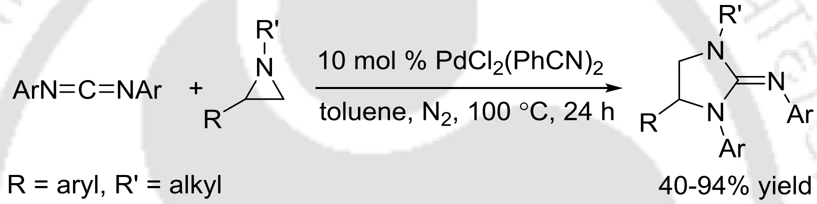
Scheme 2. Ph_4SbBr-Catalyzed Synthesis of Azolidines

Reaction of *N*-sulfonyl aziridines with alkyl and aryl isothiocyantes has been reported for the synthesis of 2-imidazolidinethione using 1 equiv of NaI in THF at room temperature (Scheme 3).[7]



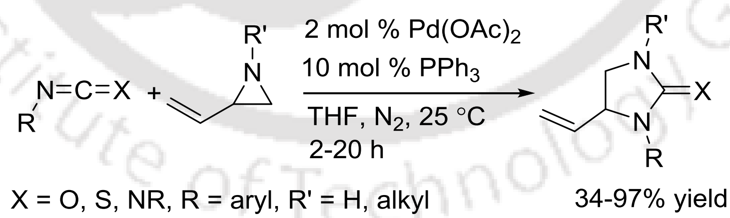
Scheme 3. NaI Promoted Synthesis of 2-Imidazolidinethione

Baeg and Alper explored the synthesis of imidazolidenimines by the cycloaddition of aziridines with carbodiimides using 10 mol % $PdCl_2(PhCN)_2$ in toluene at 100 °C (Scheme 4).[8a] The process is a regiospecific, involving selective cleavage of the more substituted aziridine ring carbon-nitrogen bond to afford the desired heterocycles in 40-94% yields.



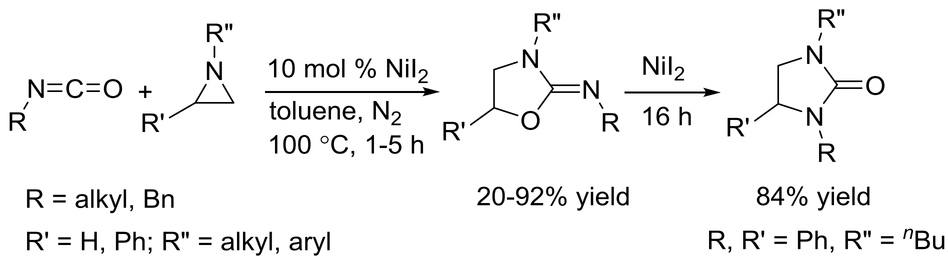
Scheme 4. Pd-Catalyzed Cycloaddition of Aziridines with Carbodiimides

The same group established an efficient protocol for the synthesis of imidazolidinones, imidazolidinethones and imidazolidineimines by the cycloaddition 2-vinylaziridines with isocyanates, isothiocyanates, and carbodiimides in the presence of $Pd(OAc)_2$ and PPh_3, at room temperature (Scheme 5).[8b]



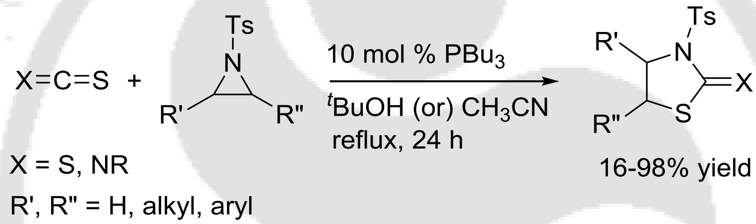
Scheme 5. Pd-Catalyzed Synthesis of Imidazolidines Using PPh_3

Saito and co-worker accomplished Ni-catalyzed synthesis of iminooxazolidines from aziridines with isocyanates using 10 mol % NiI_2 in toluene at 100 °C (Scheme 6).[9] In longer reaction, the isomerization of the iminooxazolidine to the corresponding imidazolidinone was observed.



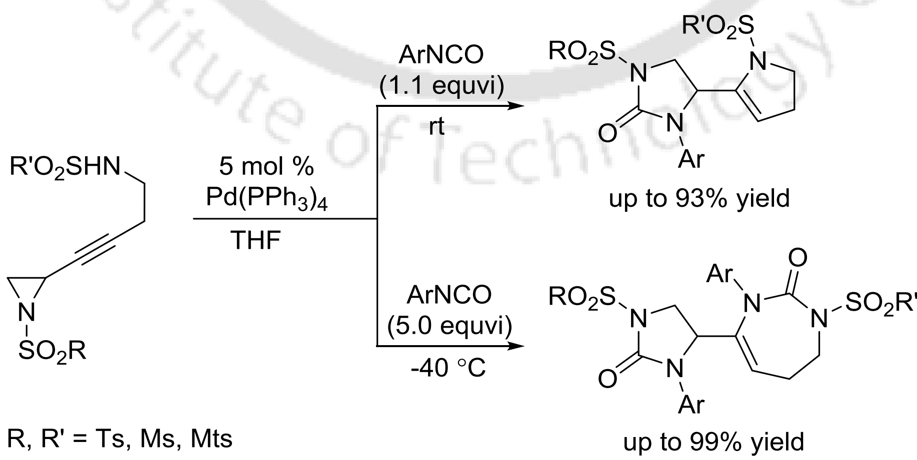
Scheme 6. Ni-Catalyzed Cycloaddition of Aziridines with Isocyanates

PBu_3-catalyzed cycloaddition of isothiocyanates and carbon disulfide with *N*-(*p*-toluenesulfonyl) aziridines provided the 1,3-thiazolidines (Scheme 7).[10] In this reaction, the solvent plays an important role, for example, the cycloaddition takes place efficiently with isothiocyanates or carbon disulfide in CH_3CN or ^{t}BuOH, respectively, to give the corresponding heterocycles in good yields.



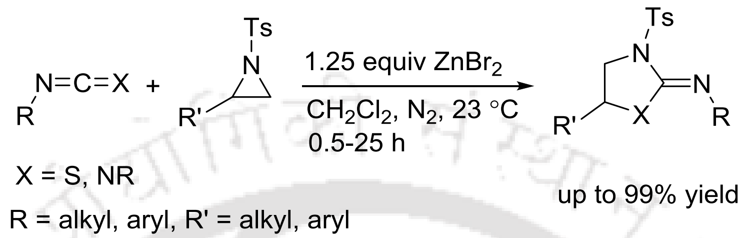
Scheme 7. PBu_3-Catalyzed Synthesis of 2-Thiazolidinethiones

Ohno and co-workers developed a domino cyclization of 2-alkylaziridines with isocyanates through ring expansion to the synthesis of imidazolidin-2-ones using 5 mol % $Pd(PPh_3)_4$ in THF (Scheme 8).[8c] This reaction selectively provides mono- and bis-adduct by changing the isocyanate equivalent and reaction temperature.



Scheme 8. Pd-Catalyzed Domino Synthesis of 2-Imidazolidinones

Zn(II)-mediated cycloaddition of alkyl and aryl isothiocyanates and carbodiimides with *N*-sulfonyl-2-substituted aziridines and 2-phenylaziridine provided iminothiazolidines and iminoimidazolidines in CH_2Cl_2 at room temperature under inert atmosphere (Scheme 9).[11] Using this protocol, the synthesis of enantioenriched iminothiazolidines can be accomplished by reaction of enantiopure *N*-H- and *N*-sulfonylaziridines with isothiocyanates.

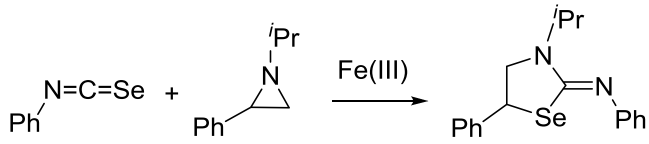


Scheme 9. Zn(II)-mediated Cycloaddition of Aziridines with Isothiocyanates and Carbodiimides

2.2 Present Study

Herin we decribe Fe-catalyzed cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates and carbodiimides that takes place in aqueous suspension at moderate temperature. The optimization of the reaction conditions was carried out using phenyl isoselenocyanate **1a** and 1-isopropyl-2-phenylaziridine **2a** as model substrates in the presence of 10 mol % $Fe(NO_3)_3{\cdot}9H_2O$ on water at various temperatures (Table 1). Gratifyingly, the reaction proceeded to afford selectively the target iminoazoselenolidine **3a** at 5 h in 80% conversion at room temperature when the suspension of the soluble $Fe(NO_3)_3{\cdot}9H_2O$ and the insoluble substrates **1a** and 2**a** was stirred on water (entry 1). Increase of the reaction temperature to 60 $^\circ$C led to completion the process in 1 h with 100% conversion (entry 3). In a set of Fe(III) salts screened, $Fe(NO_3)_3{\cdot}9H_2O$, $Fe_2(SO_4)_3{\cdot}5H_2O$, $FeCl_3{\cdot}6H_2O$, and $Fe(acac)_3$, all were active, and the former afforded the best results (entries 5-8). The effect of the organic medium such as toluene, CH_2Cl_2 and $(CH_2Cl)_2$ was examined, but no reaction was observed (entries 9-11). Lowering the amount of the iron(III)-catalyst (5 mol %) or the quantity of the aziridine (1 equiv) led to the formation of **3a** in <91% conversion (entries 4 and 5). Control experiments confirmed that without the iron(III)-catalyst the reaction led to produce **3a** after 8 h in 12% conversion (entry 12).

Table 1. Optimization of Reaction Conditions[a]

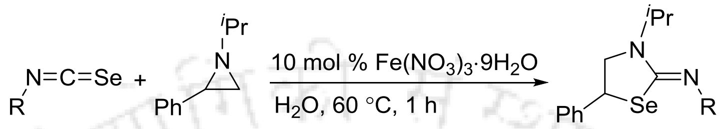


Entry	Catalyst	Solvent	Temp (°C)	Time (h)	Conversion **3a** (%)[b]
1	$Fe(NO_3)_3{\cdot}9H_2O$	H_2O	25	5	80
2	$Fe(NO_3)_3{\cdot}9H_2O$	H_2O	40	3	87
3	$\mathbf{Fe(NO_3)_3{\cdot}9H_2O}$	$\mathbf{H_2O}$	**60**	**1**	**100**
4	$Fe(NO_3)_3{\cdot}9H_2O$	H_2O	60	2	82[c]
5	$Fe(NO_3)_3{\cdot}9H_2O$	H_2O	60	1	91[d]
6	$FeCl_3{\cdot}6H_2O$	H_2O	60	1	87
7	$Fe_2(SO_4)_3{\cdot}5H_2O$	H_2O	60	1	58
8	$Fe(acac)_3$	H_2O	60	1	47
9	$Fe(NO_3)_3{\cdot}9H_2O$	toluene	60	1	n.d.
10	$Fe(NO_3)_3{\cdot}9H_2O$	CH_2Cl_2	40	1	n.d.
11	$Fe(NO_3)_3{\cdot}9H_2O$	$(CH_2Cl)_2$	60	1	n.d.
12	-	H_2O	60	8	12

[a] Reaction condition: Isoselenocyanate (0.5 mmol), aziridine (0.6 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (10 mol %) and water (1 mL) were stirred under air. [b] Determined by 400 MHz ^{1}H NMR. [c] Catalyst 5 mol % used. [d] 1 equiv of aziridine used.

Next, the scope of the procedure was studied for the reaction of a series of substituted isoselenocyanates (Table 2). The substrates **1a-l** having both the electron withdrawing and -donating groups in the phenyl ring readily proceeded reactions with aziridine **2a** to give the target products in good to high yields. For examples, aryl isoselenocyanates containing 2-methoxy-, 3-methyl-, 4-chloro-, 4-iodo-, 4-methoxy-, 4-methyl- and 4-nitro- substituents in the phenyl ring underwent reactions to give the target products **3b-h** in 61-90% yield. Recrystallization of **3b** in hexane gave crystals whose structure was confirmed by single crystal X-ray analysis (Figure 2). The reaction of aryl isoselenocyanate bearing 3,4-dimethyl substituents in the phenyl ring furnished **3i** in 93% yield, whereas naphthyl **1j** and fluorene **1k** isoselenocyanates underwent reactions to afford **3j** and **3k** in 85% and 75% yield, respectively. A similar result was observed with cyclohexyl isoselenocyanate **1l** affording **3l** in 72% yield.

Table 2. Reaction of Substituted Isoselenocyanates with Aziridine[a]



1a-l **2a** **3a-l**

R = alkyl, aryl

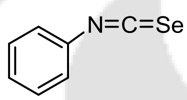
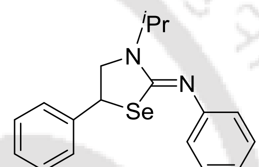
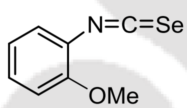
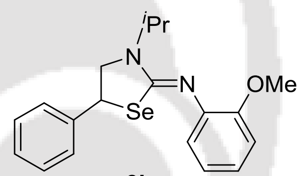
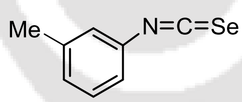
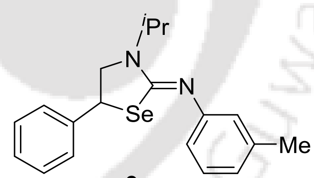
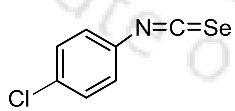
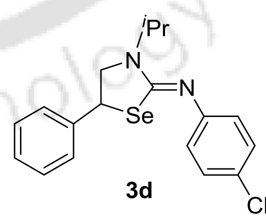
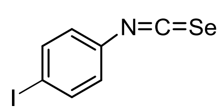
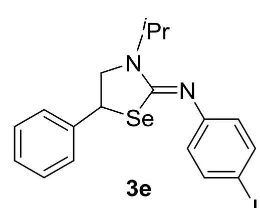
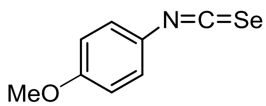
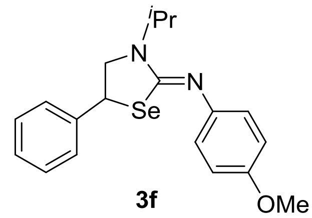
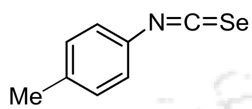
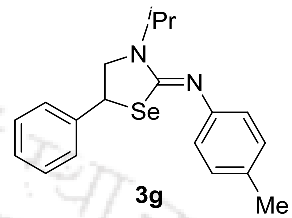
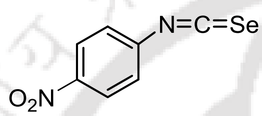
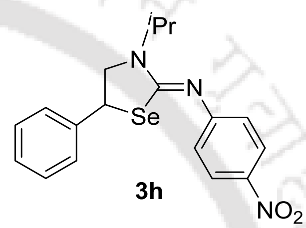
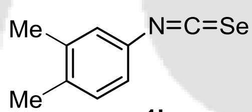
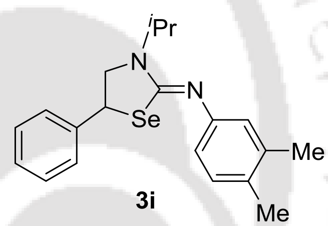
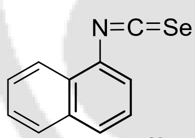
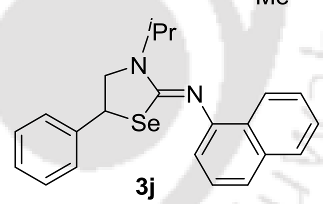
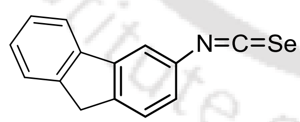
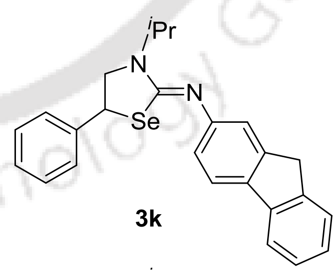
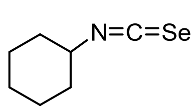
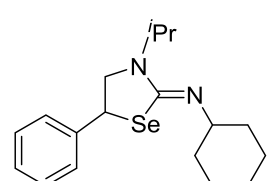
Entry	Isoselenocyanates	Time (h)	Product	Yield (%)[b]
1	 **1a**	1	 **3a**	88
2	 **1b**	1	 **3b**	90
3	 **1c**	1	 **3c**	85
4	 **1d**	1	 **3d**	86
5	 **1e**	1	 **3e**	89

Table 2 continued.....

6	 **1f**	1	 **3f**	82
7	 **1g**	1	 **3g**	79
8	 **1h**	1	 **3h**	61
9	 **1i**	1	 **3i**	93
10	 **1j**	1	 **3j**	85
11	 **1k**	1	 **3k**	75
12	 **1l**	1	 **3l**	72

[a] Reaction conditions: Isoselenocyanate **1a-l** (0.5 mmol), aziridine **2a** (0.6 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (10 mol %) and water (1 mL) were stirred at 60 °C for 1 h under air. [b] Isolated yield.

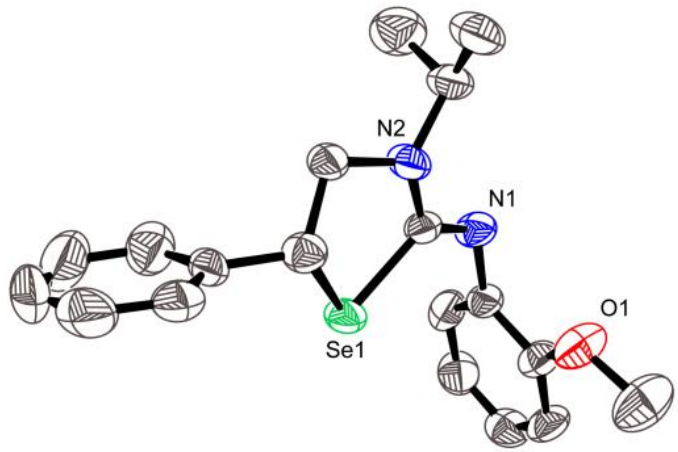
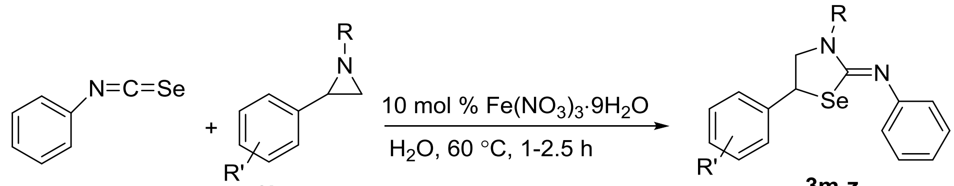


Figure 2. ORTEP diagram of ((*Z*)-*N*-(3-isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-2-methoxybenzenamine **3b** with 40% ellipsoid. H-Atoms are omitted for clarity (CCDC 899302).

The reactions of a series of aziridines were further studied with phenyl isoselenocyanate (Table 3). As above, the reactions took place efficiently to afford the target molecules in good to high yields. For examples, aryl aziridines **2b-o** having unsubstituted, benzyl, *n*-butyl, cyclohexyl and phenyl substituents on the nitrogen atom proceeded reaction to give the target iminoazoselenolidines **3m-q** in 61-91% yields. In addition, both the substrates bearing electron donating and -withdrawing groups in the phenyl ring of the aziridines were compatible, and the cycloaddition products were obtained in high yields. For examples, the substrates having 2-chloro, 3-nitro, 4-bromo, 4-chloro, 4-fluoro, 4-methoxy and 4-methyl substituents in the phenyl ring proceeded reactions to give the target molecules **3r-x** in 66-88% yields. Aryl aziridine **2n** having 3,4-dimethyl substituent in the phenyl ring underwent reaction with 87% yield. A similar result was observed with aziridine **2o** giving **3z** in 71% yield. Under these conditions, *N*-benzoyl-2-phenyl aziridine **2p** proceeded intramolecular cyclization to afford 4,5-dihydro-2,5-diphenyloxazole **10** in 78% yield as a sole product, whereas the aziridine **2q** underwent decomposition and no cycloaddition was obtained.

Table 3. Reaction of Substituted Aziridines with Phenyl Isoselenocyanate[a]



1a + **2b-q** → **3m-z**

R = H, alkyl, aryl, Bz, Boc; R' = EDG, EWG

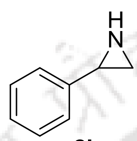
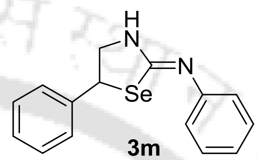
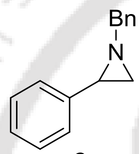
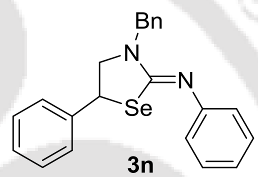
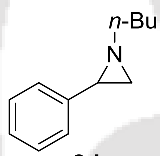
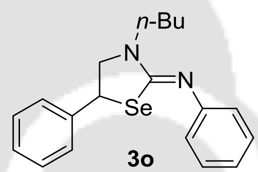
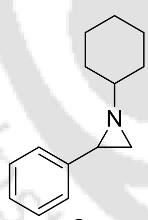
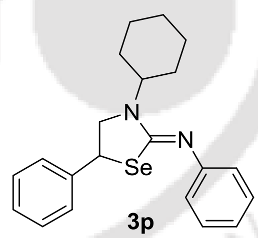
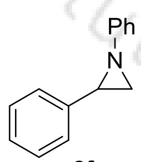
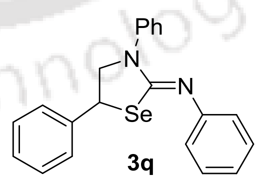
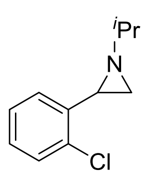
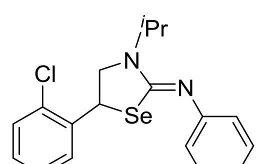
Entry	Aziridine	Time (h)	Product	Yield (%)[b]
1	 **2b**	1	 **3m**	81
2	 **2c**	1	 **3n**	75
3	 **2d**	1	 **3o**	91
4	 **2e**	1	 **3p**	79
5	 **2f**	1	 **3q**	61
6	 **2g**	2.5	 **3r**	78

Table 3 continued.....

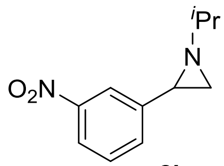
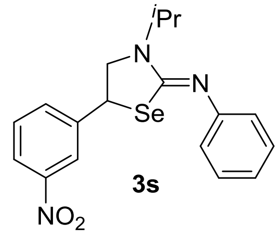
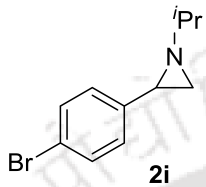
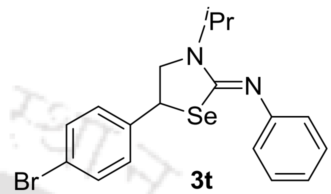
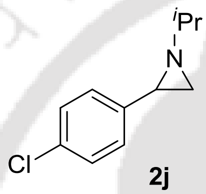
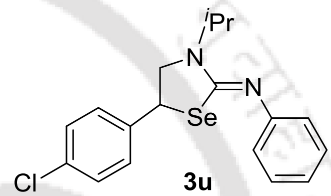
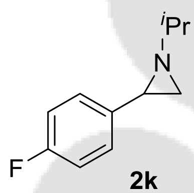
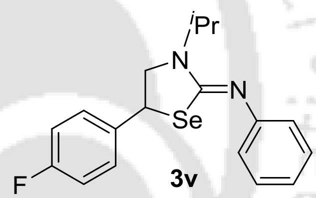
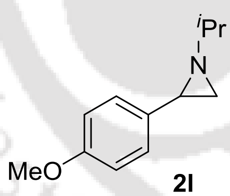
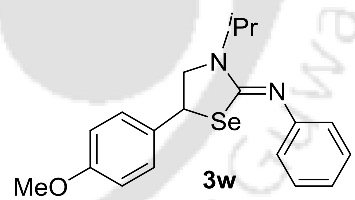
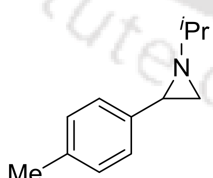
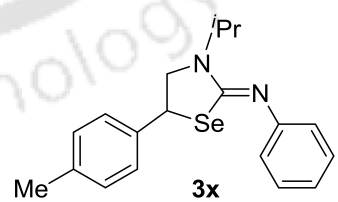
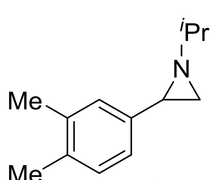
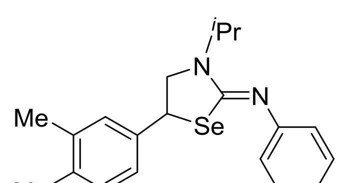
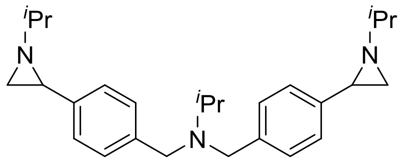
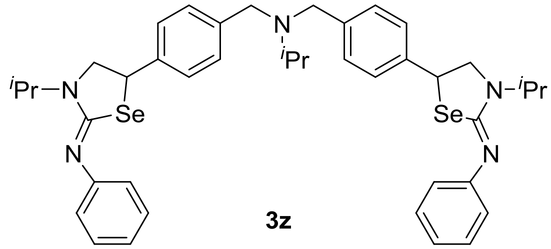
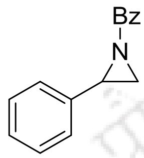
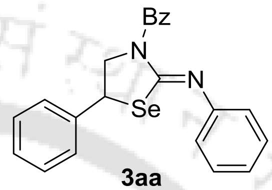
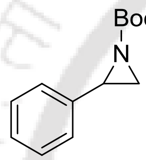
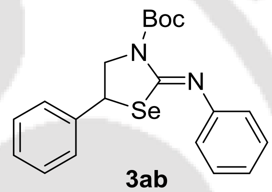
7	 **2h**	1	 **3s**	66
8	 **2i**	1	 **3t**	74
9	 **2j**	1	 **3u**	86
10	 **2k**	1	 **3v**	71
11	 **2l**	1	 **3w**	88
12	 **2m**	1	 **3x**	82
13	 **2n**	1	 **3y**	87

Table 3 continued.....

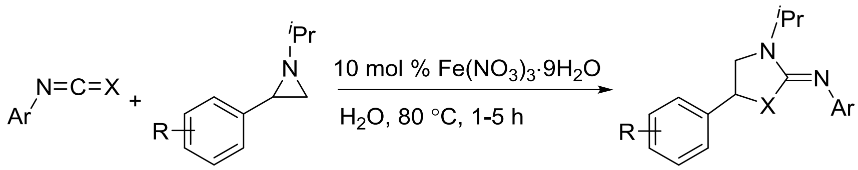
14	 **2o**	1	 **3z**	71
15	 **2p**	1	 **3aa**	n.d.
16	 **2q**	1	 **3ab**	n.d.

[a] Reaction conditions: Isoselenocyanate **1a** (0.5 mmol), aziridine **2b-q** (0.6 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (10 mol %) and water (1 mL) were stirred at 60 °C for 1 h under air. [b] Isolated yield.

Finally, to reveal the generality of the protocol, the reaction of **2** was studied with carbodiimides **4**, isocyanates **5** and isothiocyanates **6**, as representative examples (Table 4). The reactions occurred efficiently at 80 °C to provide the target molecules **7-9** in 65-79% yields. Isothiocyanates **6** exhibited greater reactivity compared to carbodiimides **4** and isocyanates **5**. These observed results suggest that the procedure affords a general method for the cycloaddition of aziridines with heterocumulenes to afford the target heterocycles in good to high yields.

To reveal the scale up of the protocol, the reaction of **1b** with **2a** was examined for gram scale synthesis (Scheme 10). As above, the reaction readily proceeded to afford **3b** in 91% yield. This result clearly suggests that the protocol may be used for the gram scale synthesis. The proposed catalytic cycle is shown in Scheme 12. Iron salts are soluble in water, while the aziridines and heterocumulenes float on the surface of water as either oil or a mixture of oil and solid. The resulting suspension proceeds reaction on stirring to give the target molecules

Table 4. Reaction of Isocyanates, Isothiocyanates and Carbodiimides with Aziridines[a]



4-6 2 7-9

X= O, S, NAr

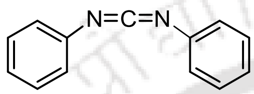
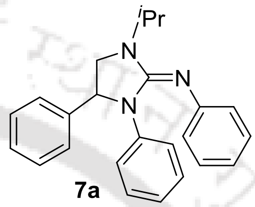
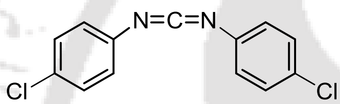
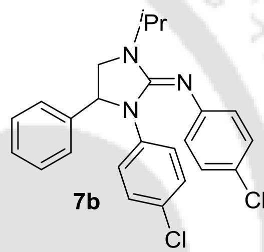
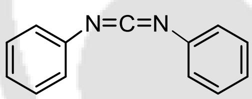
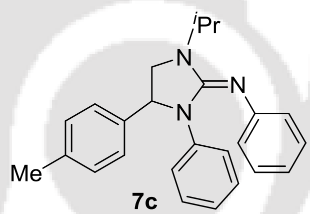
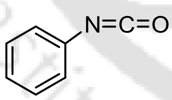
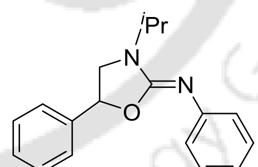
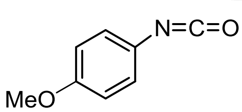
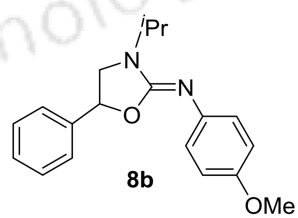
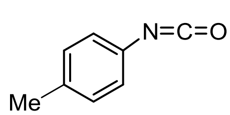
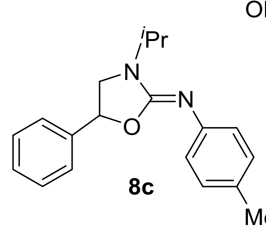
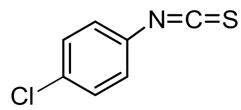
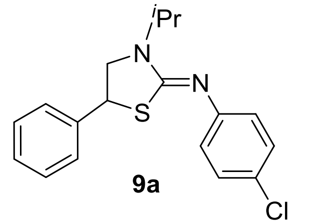
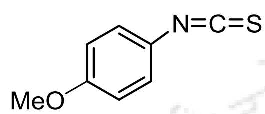
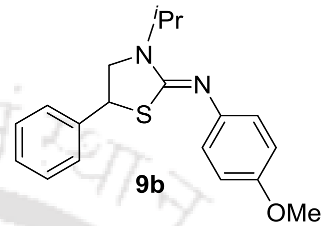
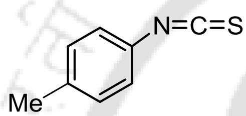
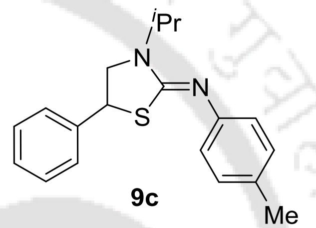
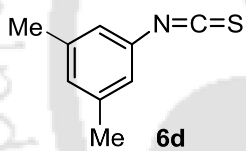
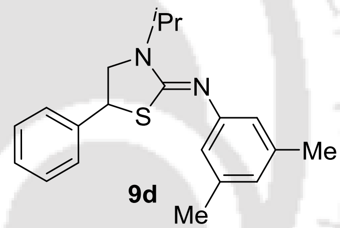
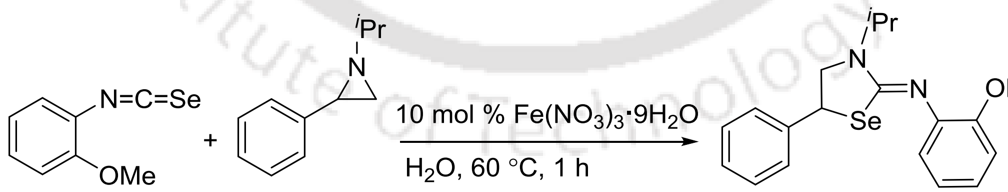
Entry	Substrate	Time (h)	Product	Yield (%)[b]
1	 **4a**	2	 **7a**	79
2	 **4b**	3	 **7b**	75
3	 **4a**	1.5	 **7c**	68
4	 **5a**	3.5	 **8a**	65
5	 **5b**	3	 **8b**	71
6	 **5c**	5	 **8c**	67

Table 4 continued.....

7	 **6a**	1	 **9a**	76
8	 **6b**	1	 **9b**	78
9	 **6c**	1	 **9c**	71
10	 **6d**	1	 **9d**	74

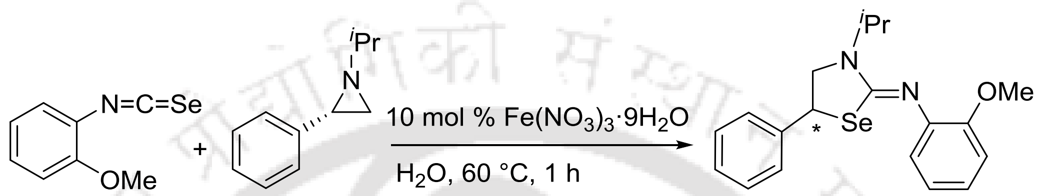
[a] Reaction conditions: **4-6** (0.5 mmol), aziridine **2** (0.6 mmol), $Fe(NO_3)_3 \cdot 9H_2O$ (10 mol %) and water (1 mL) were stirred at 80 °C. [b] Isolated yield.



1b 7 mmol, 1.5 g — **2a** 7.7 mmol, 1.25 g — **3b** 2.3 g, 91%

Scheme 10. Gram Scale Synthesis

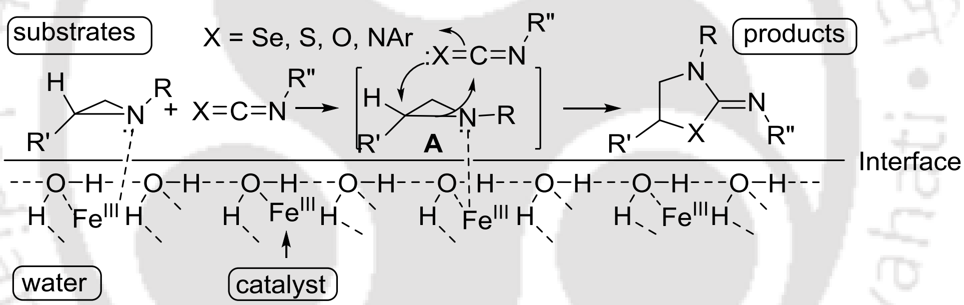
as water insoluble oil or solid. These results suggest that the reaction may take place on the water-oil interface. Furthermore, (*S*)-**2a** proceeded reaction with **1b** to give optically active **3b**, which suggests that the reaction may not involve the carbocation intermediate (Scheme 11). Thus, chelation of the iron species with nitrogen of the aziridines may lead to the formation of the intermediate **A** that could cyclize to complete the catalytic cycle giving the target products.



1b (*S*)-**2a** **3b**

$[\alpha]_D^{20}$ + 21 (c= 0.16, $CHCl_3$)

Scheme 11. Reaction with Optically Active Aziridine



Scheme 12. Plausible Reaction Mechanism

In summary, an efficient, simple and general route for the cycloaddition of aziridines with heterocumulenes on water has been described using Fe(III) catalysis under air. The procedure will be attractive from economical and environmental points of view to access the target heterocycles in good to high yields.

2.3 Experimental Section

General Information. All reactions were performed in pure water (>5 MΩ cm @ 25 °C, total organic content < 30 ppb) obtained from Elix water purification system. Amines and alkenes were purchased from Aldrich and used as received. $Fe(NO_3)_3 \cdot 9H_2O$ (98%) was purchased from Merck. $Fe_2(SO_4)_3 \cdot 5H_2O$ (97%) and $FeCl_3 \cdot 6H_2O$ (99%) were obtained from

Otto Chemie. Selenium (99.9%) and L-Phenylglycine (99%) were purchased from SRL. The aziridines were prepared according to the reported procedure.[13] The reactions were monitored by analytical TLC on Merck silica gel G/GF 254 plates. The column chromatography was performed with Rankem silica gel (60-120 mesh). Optical rotation were determined by using Perkin Elmer-343 Polarimeter. NMR (^{1}H and ^{13}C) spectra were recorded on DRX-400 Varian spectrometer and the data are accounted as follows: chemical shifts (δ ppm) (multiplicity, coupling constant (Hz), integration).The abbreviations for multiplicity are as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets. Melting points were determined with a Büchi B-545 apparatus and are uncorrected. FT-IR spectra were recorded using Perkin Elmer IR spectrometer. Elemental analyses were recorded using Perkin Elmer CHNS analyzer. For single crystal X-ray analysis the intensity data were collected using Bruker SMART APEX-II CCD diffractometer, equipped with 1.75 kW sealed-tube Mo-Kα irradiation (λ = 0.71073 Å) at 298(2) K and the structures were solved by direct methods using *SHELLX-97* (Göttingen, Germany) and refined with full-matrix least squares on F^2 using SHELXL-97.

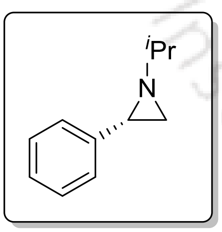
General Procedure for Preparation of Isoselenocyanates. To a solution of the isocyanide (2 mmol) in $CHCl_3$ (1 mL) were added selenium powder (3 mmol) and NEt_3 (2 mmol) at room temperature (26 °C) under nitrogen balloon and the mixture was stirred for 7 h. Progress of the reaction was monitored by TLC using hexane as eluent. The suspension was then passed through a celite bed and the solvent was removed by evaporation on a rotary evaporator. The residue was purified on a silica gel column chromatography using hexane as eluent.

General Procedure for Preparation of *N,N'*-Diarylcarbodiimides 4a-b. *N,N'*-Diarylthiourea (1.0 mmol), mercury oxide (1.0 mmol) and Na_2SO_4 (1.2 mmol) were stirred in dry CH_2Cl_2 (10 mL) at room temperature for 2-5 h. The resulting black reaction mixture was filtered off over a sintered funnel and the precipitate was rinsed with CH_2Cl_2 (10 mL) and the solvent was removed by evaporation on a rotary evaporator. The residue was purified on a silica gel column chromatography using hexane as eluent.

General Procedure for Preparation of Isocyanates 5a-c. To a stirred solution of aniline (1 mmol) and NEt_3 (5 mmol) in CH_2Cl_2 (5 mL) at 0 ^oC under N_2 atmosphere was added triphosgene (1 mmol) in dry CH_2Cl_2 (2 mL). The progress of the reaction was monitored by TLC using hexane as eluent. After 2 h, the reaction mixture was filtered and the solvent was removed by evaporation on a rotary evaporator. The residue was purified on a silica gel column chromatography using hexane as eluent.

General Procedure for Preparation of Isothiocyanates 6a-d. To a stirred solution of the CS_2 (2.5 mmol) and NEt_3 (3 mmol) was added aniline (1 mmol) in EtOAc (10 mL) at room temperature (26 °C) and the mixture was stirred for 1 h to give the triethylammonium dithiocarbamate salt. The mixture was then treated with $FeSO_4 \cdot 7H_2O$ (20 mol %) and NEt_3 (1 mmol), and the stirring was continued for an additional 5 h. Progress of the reaction was monitored by TLC using hexane as eluent. The reaction mixture was then washed with water (3 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a residue that was purified on a silica gel column chromatography using hexane as eluent.

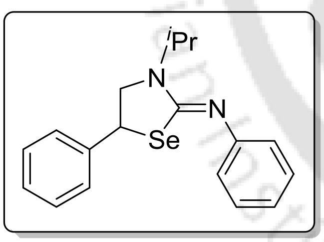
Preparation of (*S*)-2-(Isopropylamino)-2-Phenylethanol.[14] To a solution of L-phenylglycinol (5.1 mmol) in ethanol (5 mL), acetone (10.2 mmol) was added and the solution was stirred for 2 h at room temperature, and then $NaBH_4$ (15.3 mmol) was added at 0 °C. After being stirred for 4 h, the solvent was removed on a rotary evaporator. The residue was dissolved in water and extracted with CH_2Cl_2 (3×10 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a the residue, which was recrystallized from hexane to give the titled compoound as a colorless solid in 63% yield.



Procedure for Preparation of (*S*)-1-Isopropyl-2-phenylaziridine 2a.[15] To a stirred solution of (*S*)-2-(isopropylamino)-2-phenylethanol (1.0 mmol), TsCl (1.2 mmol) and DMAP (10 mg) in dry CH_2Cl_2 (20 mL) at 0 °C were added a solution of Et_3N (1.5 mmol) in dry CH_2Cl_2 (5 mL). Then the mixture was allowed to reach to room temperature and stirring was continued for 24 h. The mixture was then treated with a saturated NH_4Cl solution (20 mL), and extracted with CH_2Cl_2 (3×10 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a residue, that was purified on a silica gel column chromatography using hexane and ethyl acetate (19:1) as eluent to afford (*S*)-**2a** as a colorless liquid; yield 67%; $[\alpha]_D^{20}$ = +139.9 (c= 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 5H), 2.37 (dd, *J* = 6.4, 3.2 Hz, 1H), 1.92 (d, *J* = 3.2 Hz, 1H), 1.68 (d, *J* = 6.8 Hz, 1H), 1.66-1.61 (m, 1H), 1.23 (d, *J* = 2.4 Hz, 3H), 1.22 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 127.8, 126.8, 126.3, 126.0, 61.3, 40.4, 36.3, 22.0, 21.5; Anal. Calcd. for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 82.09; H, 9.33; N, 8.58.

General Procedure for Cycloaddition Reaction of Aziridines with Isocyanates, Isothiocyanates, Isoselenocyanates and Carbodiimides. A suspension of isocyanates, isothiocyanates, isoselenocyanates, carbodiimides (0.5 mmol), aziridine **2a-o** (0.6 mmol), $Fe(NO_3)_3·9H_2O$ (0.05 mmol) and water (1 mL) was stirred for appropriate time and temperature. The progress of reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was cooled to room temperature and extracted with diethyl ether (3 × 10 mL). The organic layer was washed with water (1 x 5 mL) and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified on silica gel column chromatography using hexane and ethyl acetate (19:1) as eluent.

2.4 Characterization Data of Products



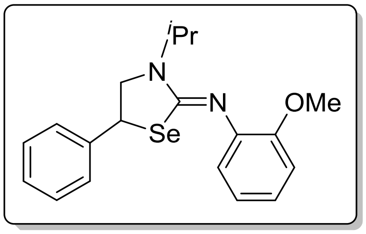
(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 3a.
Yellow liquid; yield 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.31-7.22 (m, 5H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 2H), 4.78-4.72 (m, 2H), 3.85 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.65 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.26 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.1, 140.0, 128.5, 128.3, 127.4, 127.2, 122.8, 121.3, 53.4, 46.8, 41.6, 19.6, 19.0.

FT-IR (neat) 3058, 3027, 2971, 2929, 2869, 1614, 1590, 1489, 1454, 1402, 1363, 1243, 1205, 1185, 1163, 1126, 1069, 1024 cm^{-1}.

Anal. Calcd. for $C_{18}H_{20}N_2Se$: C, 62.97; H, 5.87; N, 8.16. Found: C, 63.08; H, 5.83; N, 8.13.



((*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-2-methoxybenzenamine 3b.

Colorless solid; yield 90%.

Mp: 107-108 °C.

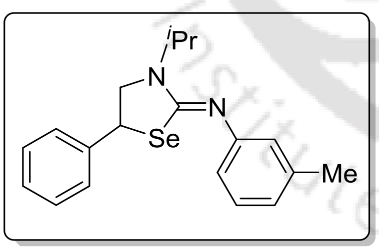
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.27-7.18 (m, 3H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 2H), 4.83-4.80 (m, 1H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.83 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.76 (s, 3H), 3.63 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.26 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 151.6, 142.7, 140.2, 128.4, 127.5, 127.4, 123.9, 122.0, 120.6, 111.5, 55.6, 54.0, 47.1, 41.8, 19.8, 19.1.

FT-IR (KBr) 3026, 2970, 2923, 2870, 1623, 1586, 1493, 1464, 1400, 1363, 1236, 1204, 1184, 1112, 1047, 1027 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2OSe$: C, 61.12; H, 5.94; N, 7.50. Found: C, 61.18; H, 5.91; N, 7.46.

$[\alpha]_D^{20}$ = + 21 (c= 0.16, $CHCl_3$).



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-3-methylbenzenamine 3c.

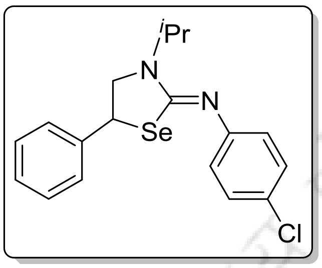
Colorless liquid; yield 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.29-7.19 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.85-6.80 (m, 3H), 4.81-4.77 (m, 1H), 4.72 (t, *J* = 6.8 Hz, 1H), 3.80 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.62 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.30 (s, 3H), 1.28 (d, *J* = 4.8 Hz, 3H), 1.26 (d, *J* = 4.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.2, 140.1, 138.3, 128.5, 127.6, 127.5, 123.8, 122.3, 118.3, 53.6, 47.0, 41.8, 21.3, 19.9, 19.2.

FT-IR (neat) 3030, 2971, 2927, 2862, 1613, 1593, 1455, 1400, 1362, 1282, 1207, 1185, 1069 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2Se$: C, 63.86; H, 6.21; N, 7.84. Found: C, 63.96; H, 6.19; N, 7.80.



(*Z*)-4-Chloro-*N*-(3-isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 3d.

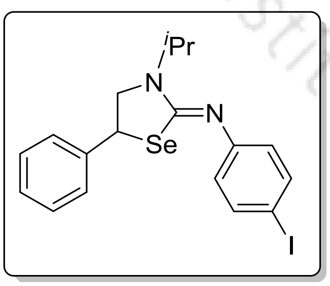
Yellow liquid; yield 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.78-4.68 (m, 2H), 3.84 (dd, *J* = 10.4, 6.8 Hz, 1H), 3.65 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.24 (t, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 151.8, 139.8, 128.7, 128.6, 128.0, 127.8, 127.4, 123.0, 53.8, 47.2, 42.2, 19.8, 19.2.

FT-IR (neat) 3061, 3029, 2972, 2930, 2870, 1614, 1585, 1485, 1404, 1364, 1274, 1243, 1205, 1185, 1162, 1088, 1068, 1009 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}ClN_2Se$: C, 57.23; H, 5.07; N, 7.42. Found: C, 57.32; H, 5.06; N, 7.40.



(*Z*)-4-Iodo-*N*-(3-isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 3e.

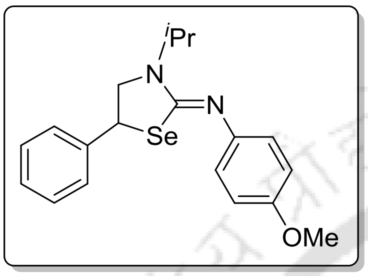
Colorless liquid; yield 89%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.40-7.25 (m, 3H), 6.77 (d, *J* = 8.4 Hz, 2H), 4.80-4.75 (m, 2H), 3.86 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.66 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.27 (t, *J* = 6.4 Hz, 6H).

[13]C NMR (100 MHz, $CDCl_3$) δ 156.6, 152.8, 139.8, 137.6, 128.7, 127.8, 127.5, 123.9, 86.6, 53.8, 47.2, 42.2, 20.0, 19.3.

FT-IR (neat) 3059, 3027, 2971, 2928, 2869, 1614, 1573, 1479, 1403, 1363, 1274, 1243, 1205, 1185, 1125, 1067, 1002 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}IN_2Se$: C, 46.07; H, 4.08; N, 5.97. Found: C, 46.17; H, 4.05; N, 5.94.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-4-methoxybenzenamine 3f.

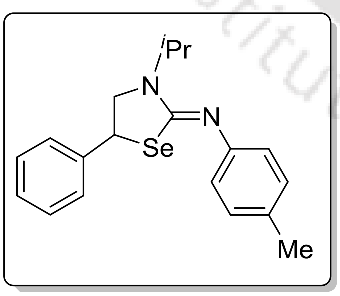
Yellow liquid; yield 82%.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33-7.25 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.82-4.75 (m, 2H), 3.86 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.73 (s, 3H), 3.67 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.31 (d, *J* = 4.8 Hz, 3H), 1.29 (d, *J* = 4.4 Hz, 3H).

[13]C NMR (100 MHz, $CDCl_3$) δ 156.8, 155.7, 146.8, 140.2, 128.6, 127.6, 127.5, 122.3, 113.9, 55.1, 53.7, 47.1, 41.8, 19.8, 19.2.

FT-IR (neat) 3031, 2971, 2870, 2833, 1614, 1504, 1464, 1401, 1363, 1294, 1239, 1205, 1185, 1067, 1035, 981 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2OSe$: C, 61.12; H, 5.94; N, 7.50. Found: C, 61.20; H, 5.91; N, 7.45.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-4-methylbenzenamine 3g.

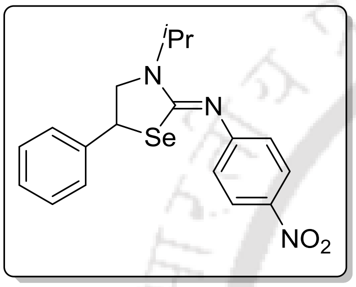
Yellow liquid; yield 79%.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.47-7.28 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.81-4.77 (m, 2H), 3.90 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.71 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.31 (s, 3H), 1.30 (t, *J* = 6.8 Hz, 6H).

[13]C NMR (100 MHz, $CDCl_3$) δ 156.3, 150.8, 140.1, 132.2, 129.3, 128.5, 127.5, 127.4, 121.3, 53.7, 47.0, 41.8, 20.8, 19.8, 19.2.

FT-IR (neat) 3024, 2971, 2928, 2868, 2124, 1622, 1602, 1505, 1454, 1401, 1363, 1205, 1185, 1068, 924 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2Se$: C, 63.86; H, 6.21; N, 7.84. Found: C, 63.95; H, 6.18; N, 7.80.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-4-nitrobenzenamine 3h.

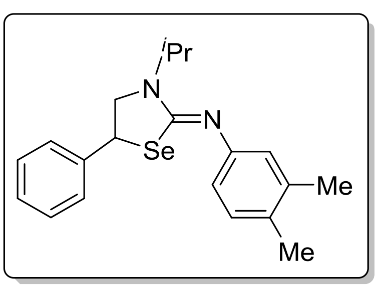
Reddish yellow liquid; yield 61%.

[1]H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.30-7.23 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.84 (t, *J* = 7.6 Hz, 1H), 4.75-4.71 (m, 1H), 3.91 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.71 (dd, *J* = 11.2, 8.0 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 6H).

[13]C NMR (100 MHz, $CDCl_3$) δ 159.1, 157.0, 143.0, 139.4, 128.9, 128.1, 127.5, 124.9, 122.0, 54.0, 47.7, 42.8, 20.0, 19.4.

FT-IR (neat) 3064, 3029, 2973, 2929, 2872, 1614, 1574, 1463, 1405, 1332, 1280, 1244, 1207, 1185, 1108, 1067 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}N_3O_2Se$: C, 55.67; H, 4.93; N, 10.82. Found: C, 55.79; H, 4.90; N, 10.80.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-3,4-dimethylbenzenamine 3i.

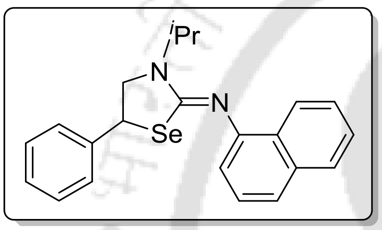
Yellow liquid; yield 93%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.35-7.25 (m, 3H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.85-4.77 (m, 2H), 3.89 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.69 (dd, *J* = 10.4, 8.4 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 1.31 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 151.1, 140.1, 136.4, 130.7, 129.7, 128.4, 127.4, 127.3, 122.6, 118.3, 53.5, 46.9, 41.6, 19.7, 19.6, 19.0, 18.9.

FT-IR (neat) 3026, 2970, 2931, 2867, 1618, 1598, 1496, 1453, 1396, 1363, 1285, 1243, 1203, 1184, 1068, 1002 cm^{-1}.

Anal. Calcd. for $C_{20}H_{24}N_2Se$: C, 64.68; H, 6.51; N, 7.54. Found: C, 64.78; H, 6.50; N, 7.50.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)naphthalen-1-amine 3j.

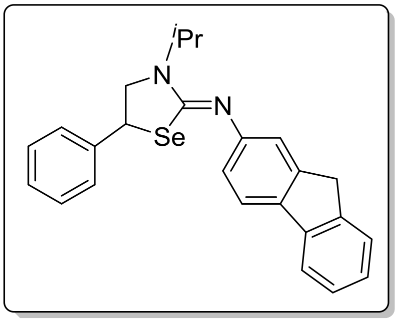
Yellow liquid; yield 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.8 Hz, 1H), 7.91 (d, *J* = 5.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.61-7.50 (m, 3H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.36-7.29 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 1H), 5.12-5.10 (m, 1H), 4.81 (t, *J* = 7.6 Hz, 1H), 3.95 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.77 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.47 (d, *J* = 4.4 Hz, 3H), 1.45 (d, *J* = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 150.1, 140.2, 134.2, 128.8, 128.6, 127.7, 127.5, 126.0, 125.0, 124.0, 123.2, 115.0, 54.0, 47.5, 41.9, 20.1, 19.5.

FT-IR (neat) 3056, 2971, 2869, 1614, 1563, 1504, 1455, 1389, 1363, 1245, 1208, 1185, 1066, 1040, 1014 cm^{-1}.

Anal. Calcd. for $C_{22}H_{22}N_2Se$: C, 67.17; H, 5.64; N, 7.12. Found: C, 67.28; H, 5.61; N, 7.09.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-9H-fluoren-2-amine 3k.

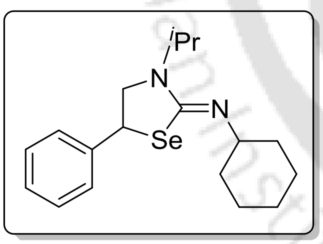
Yellow liquid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.37-7.20 (m, 6H), 7.05 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.87-4.79 (m, 2H), 3.90 (dd, *J* = 10.8, 6.8 Hz, 1H), 3.88 (s, 2H), 3.71 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.33 (d, *J* = 4.8 Hz, 3H), 1.32 (d, *J* = 4.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 152.7, 144.4, 143.1, 142.0, 140.3, 137.1, 128.8, 127.9, 127.7, 126.7, 125.8, 124.9, 120.5, 120.2, 119.3, 118.4, 54.0, 47.4, 42.2, 37.0, 20.1, 19.4.

FT-IR (neat) 3060, 3029, 2970, 2928, 2869, 1621, 1598, 1454, 1402, 1364, 1280, 1244, 1207, 1184, 1125, 1110, 1067, 1026, 981 cm^{-1}.

Anal. Calcd. for $C_{25}H_{24}N_2Se$: C, 69.60; H, 5.61; N, 6.49. Found: C, 69.70; H, 5.58; N, 6.46.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)cyclohexanamine 3l.

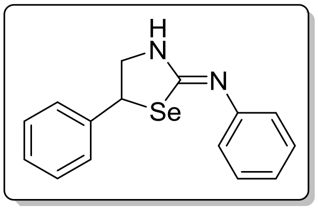
Colorless liquid; yield 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.29-7.21 (m, 3H), 4.73 (t, *J* = 7.6 Hz, 1H), 4.50-4.47 (m, 1H), 3.67 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.45 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.56-2.50 (m, 1H), 1.72-1.21 (m, 10H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 5.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 140.7, 128.6, 127.7, 127.6, 68.8, 53.4, 47.1, 42.0, 34.9, 34.7, 25.8, 25.0, 19.7, 18.7.

FT-IR (neat) 3029, 2968, 2926, 2852, 1634, 1492, 1450, 1363, 1289, 1234, 1204, 1183, 1155, 1059, 968 cm^{-1}.

Anal. Calcd. for $C_{18}H_{26}N_2Se$: C, 61.88; H, 7.50; N, 8.02. Found: C, 61.97; H. 7.48; N, 7.99.



(*Z*)-*N*-(5-Phenyl-1,3-selenazolidin-2-ylidene)benzenamine 3m.

Pale yellow solid; yield 81%.

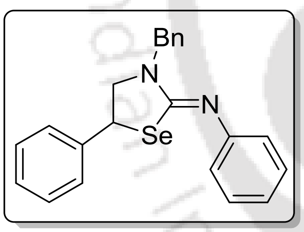
Mp: 113-114 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.39-7.71 (m, 5H), 7.09-7.04 (m, 3H), 5.05 (t, *J* = 7.6 Hz, 1H), 3.97 (dd, *J* = 11.6, 6.4 Hz, 1H), 3.85 (dd, *J* = 11.6, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 149.9, 140.1, 129.0, 128.7, 127.8, 127.6, 123.5, 121.2, 56.6, 48.0.

FT-IR (KBr) 3049, 3029, 2917, 2858, 1633, 1588, 1489, 1451, 1312, 1258, 1183, 1074, 1025, 908 cm^{-1}.

Anal. Calcd. for $C_{15}H_{14}N_2Se$: C, 59.81; H, 4.68; N, 9.30. Found: C, 59.93; H, 4.66; N, 9.27.



(*Z*)-*N*-(3-Benzyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 3n.

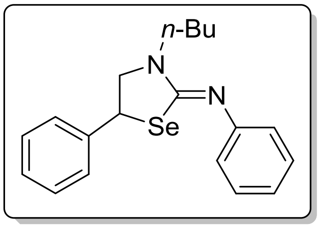
Yellow liquid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.29 (m, 12H), 7.17-7.15 (m, 3H), 5.00 (d, *J* = 14.8, 1H), 4.88 (t, *J* = 7.2, 1H), 4.86 (d, *J* = 14.8, 1H), 3.83 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.71 (dd, *J* = 10.4, 8.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 153.2, 139.6, 137.1, 128.9, 128.6, 128.5, 128.3, 127.7, 127.6, 127.4, 123.3, 121.5, 58.6, 50.8, 42.2.

FT-IR (neat) 3060, 3021, 2901, 2846, 1626, 1588, 1490, 1448, 1395, 1355, 1264, 1207, 1181, 1076, 1027, 909 cm^{-1}.

Anal. Calcd. for $C_{22}H_{20}N_2Se$: C, 67.52; H, 5.15; N, 7.16. Found: C, 67.60; H, 5.14; N, 7.14.



(*Z*)-*N*-(3-Butyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 3o.

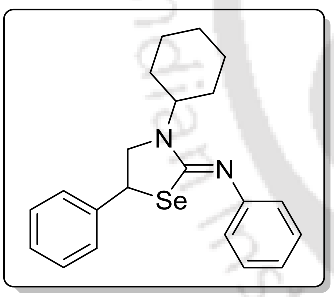
Yellow liquid; yield 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 3H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.81 (t, *J* = 7.6 Hz, 1H), 3.89 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.74 (dd, *J* = 10.4, 8.0 Hz, 1H), 3.61-3.56 (m, 2H), 1.70-1.62 (m, 2H), 1.42-1.37 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 153.5, 140.1, 128.8, 128.7, 127.7, 127.5, 123.1, 121.6, 59.4, 47.0, 42.1, 29.3, 20.2, 13.9.

FT-IR (neat) 3058, 3028, 2956, 2929, 2860, 1618, 1590, 1489, 1465, 1404, 1289, 1244, 1207, 1185, 1104, 1071, 1024 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2Se$: C, 63.86; H, 6.21; N, 7.84. Found: C, 63.96; H, 6.20; N, 7.81.



(*Z*)-*N*-(3-Cyclohexyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 3p.

Colorless solid; yield 79%.

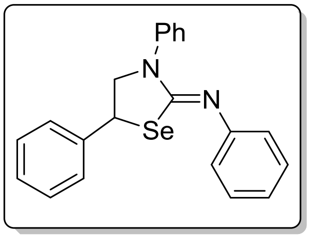
Mp: 98-99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.34-7.26 (m, 5H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.77 (t, *J* = 7.2 Hz, 1H), 4.41 (m, 1H), 3.93 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.74 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.05-2.00 (m, 2H), 1.85-1.83 (m, 2H), 1.72-1.69 (m, 1H), 1.53-1.39 (m, 4H), 1.13-1.10 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 153.4, 140.3, 128.6, 128.5, 127.5, 127.4, 122.9, 121.5, 55.3, 54.9, 41.9, 30.4, 29.8, 25.8, 25.7, 25.5.

FT-IR (KBr) 3058, 3027, 2929, 2854, 1615, 1591, 1489, 1463, 1400, 1262, 1240, 1205, 1182, 1134, 1072, 1024, 1009 cm^{-1}.

Anal. Calcd. for $C_{21}H_{24}N_2Se$: C, 65.79; H, 6.31; N, 7.31. Found: C, 65.88; H, 6.29; N, 7.27.



(*Z*)-*N*-(3,5-Diphenyl-1,3-selenazolidin-2-ylidene)benzenamine 3q.

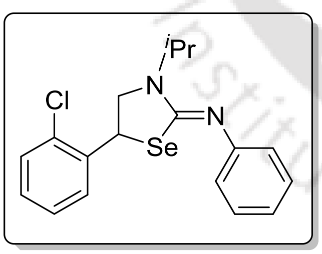
Yellow liquid; yield 61%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.48-7.44 (m, 2H), 7.43-7.37 (m, 2H), 7.36-7.31 (m, 2H), 7.29-7.26 (m, 3H), 7.19-7.15 (m, 1H), 7.08-7.04 (m, 1H), 7.00-6.98 (m, 2H), 4.96 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.40 (dd, *J* = 10.8, 6.4 Hz, 1H), 4.30 (dd, *J* = 10.8, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 153.2, 141.8, 139.6, 132.0, 129.1, 128.1, 127.8, 125.1, 123.9, 121.6, 61.7, 42.1.

FT-IR (neat) 3058, 3027, 2917, 2857, 1627, 1585, 1491, 1459, 1383, 1347, 1307, 1267, 1160, 1082 cm^{-1}.

Anal. Calcd. for $C_{21}H_{18}N_2Se$: C, 66.84; H, 4.81; N, 7.42. Found: C, 66.93; H, 4.80; N, 7.39.



(*Z*)-*N*-(5-(2-Chlorophenyl)-3-isopropyl-1,3-selenazolidin-2-ylidene)benzenamine 3r.

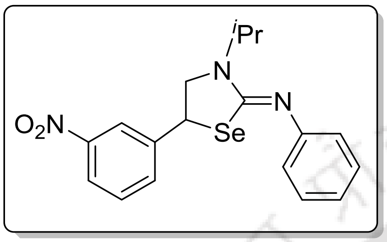
Colorless liquid; yield 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.38-7.32 (m, 1H), 7.30-7.15 (m, 4H), 7.06-7.02 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 2H), 5.20 (t, *J* = 6.0 Hz, 1H), 4.84-4.77 (m, 1H), 3.93 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.77 (dd, *J* = 10.8, 5.2 Hz, 1H), 1.33 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 153.3, 138.9, 133.1, 129.4, 128.8, 128.5, 127.7, 127.3, 123.2, 121.5, 51.7, 47.3, 38.2, 19.8, 19.2.

FT-IR (neat) 3059, 2970, 2928, 2869, 1621, 1588, 1488, 1474, 1442, 1401, 1364, 1205, 1184, 1166, 1071, 1051, 1037, 995 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}N_2Se$: C, 57.23; H, 5.07; N, 7.42. Found: C, 57.33; H, 5.04; N, 7.40.



(*Z*)-*N*-(3-Isopropyl-5-(3-nitrophenyl)-1,3-selenazolidin-2-ylidene)benzenamine 3s.

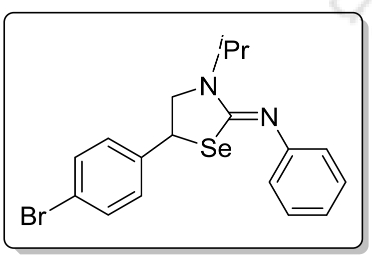
Yellow liquid; yield 61%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.07-8.01 (m, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 4.79-4.72 (m, 2H), 3.90 (dd, J = 10.8, 6.4 Hz, 1H), 3.67 (dd, J = 10.8, 6.0 Hz, 1H), 1.28 (d, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 153.1, 148.1, 143.4, 133.6, 129.7, 128.8, 123.3, 122.4, 122.1, 121.4, 53.3, 47.4, 40.1, 19.6, 19.5.

FT-IR (neat) 3076, 3034, 2972, 2929, 2870, 1621, 1588, 1531, 1488, 1402, 1349, 1271, 1244, 1208, 1187, 1166, 1126, 1070, 1024, 982 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}N_3O_2Se$: C, 55.67; H, 4.93; N, 10.82. Found: C, 55.74; H, 4.90; N, 10.80.



(*Z*)-*N*-(5-(4-Bromophenyl)-3-isopropyl-1,3-selenazolidin-2-ylidene)benzenamine 3t.

Colorless solid; yield 74%.

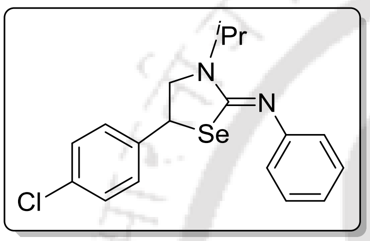
Mp: 125-126 °C.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.30-7.25 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 4.84-4.74 (m, 1H), 4.66 (t, *J* = 6.4 Hz, 1H), 3.83 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.60 (dd, *J* = 10.0, 7.6 Hz, 1H), 1.28 (t, *J* = 6.4 Hz, 6H).

[13]C NMR (100 MHz, $CDCl_3$) δ 155.9, 153.2, 139.6, 131.7, 129.2, 128.8, 123.2, 121.5, 121.3, 53.5, 47.2, 40.9, 19.8, 19.4.

FT-IR (KBr) 3024, 2971, 2928, 2869, 1621, 1588, 1487, 1399, 1364, 1242, 1204, 1183, 1070, 1010 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}BrN_2Se$: C, 51.20; H, 4.54; N, 6.63. Found: C, 51.29; H, 4.52; N, 6.60.



(*Z*)-*N*-(5-(4-Chlorophenyl)-3-isopropyl-1,3-selenazolidin-2-ylidene)benzenamine 3u.

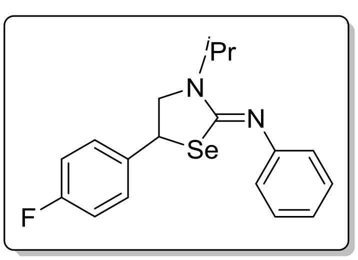
Yellow liquid; yield 86%.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.33-7.20 (m, 6H), 7.06-7.01 (m, 3H), 4.83-4.77 (m, 1H), 4.66 (t, *J* = 6.8 Hz, 1H), 3.80 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.58 (dd, *J* = 10.0, 8.0 Hz, 1H), 1.27 (t, *J* = 6.8 Hz, 6H).

[13]C NMR (100 MHz, $CDCl_3$) δ 155.7, 153.1, 139.0, 133.0, 128.8, 128.7, 128.5, 123.0, 121.4, 53.4, 47.1, 40.7, 19.6, 19.2.

FT-IR (neat) 3053, 3028, 2971, 2929, 2869, 1614, 1590, 1489, 1468, 1399, 1363, 1271, 1241, 1204, 1185, 1126, 1091, 1070, 1014, 981 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}ClN_2Se$: C, 57.23; H, 5.07; N, 7.42. Found: C, 57.33; H, 5.05; N, 7.39.



(*Z*)-*N*-(5-(4-Fluorophenyl)-3-isopropyl-1,3-selenazolidin-2-ylidene)benzenamine 3v.

Colorless solid; yield 71%.

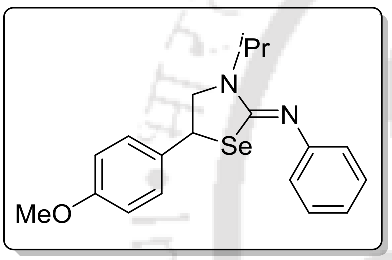
Mp: 91-92 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.06-6.96 (m, 5H), 4.82-4.77 (m, 1H), 4.73 (t, J = 6.8 Hz, 1H), 3.85 (dd, J = 10.4, 6.4 Hz, 1H), 3.61 (dd, J = 10.4, 7.6 Hz, 1H), 1.28 (t, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J_{C-F} = 244.8 Hz), 156.2, 153.4, 136.2, 129.3 (d, J_{C-F} = 8.4 Hz), 128.9, 123.3, 121.6, 115.7 (d, J_{C-F} = 21.1 Hz), 54.0, 47.3, 41.2, 19.9, 19.4.

FT-IR (KBr) 3054, 2971, 2928, 2870, 1618, 1589, 1508, 1489, 1400, 1364, 1226, 1205, 1185, 1159, 1070, 1015, 981 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}FN_2Se$: C, 59.83; H, 5.30; N, 7.75. Found: C, 59.91; H, 5.28; N, 7.71.



(*Z*)-*N*-(3-Isopropyl-5-(4-methoxyphenyl)-1,3-selenazolidin-2-ylidene)benzenamine 3w.

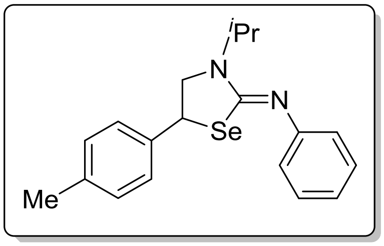
Colorless liquid; yield 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.27 (t, J = 7.2 Hz, 2H), 7.05-7.01 (m, 3H), 6.85 (d, J = 8.8 Hz, 2H), 4.84-4.78 (m, 1H), 4.74 (t, J = 6.8 Hz, 1H), 3.82 (dd, J = 10.4, 6.4 Hz, 1H), 3.62 (dd, J = 10.4, 8.4 Hz, 1H), 1.30 (d, J = 4.0 Hz, 3H), 1.28 (d, J = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 156.4, 153.3, 131.8, 128.7, 128.6, 122.9, 121.5, 113.9, 55.0, 53.9, 47.0, 41.6, 19.9, 19.1.

FT-IR (neat) 3024, 2971, 2923, 2869, 1615, 1588, 1511, 1488, 1461, 1400, 1363, 1302, 1252, 1206, 1181, 1070, 1033, 981 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2OSe$: C, 61.12; H, 5.94; N, 7.50. Found: C, 61.22; H, 5.91; N, 7.47.



(*Z*)-*N*-(3-Isopropyl-5-*p*-tolyl-1,3-selenazolidin-2-ylidene)benzenamine 3x.

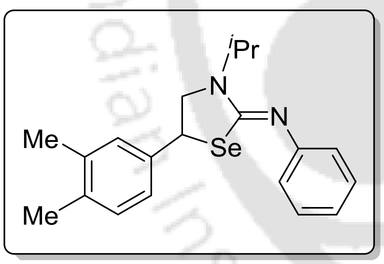
Yellow liquid; yield 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.10-7.04 (m, 3H), 4.88-4.83 (m, 1H), 4.80 (t, *J* = 7.6 Hz, 1H), 3.88 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.70 (dd, *J* = 10.4, 8.4 Hz, 1H), 2.36 (s, 3H), 1.35 (d, *J* = 4.4 Hz, 3H), 1.33 (d, *J* = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 153.3, 137.4, 137.0, 129.3, 128.7, 127.4, 123.1, 121.6, 53.9, 47.1, 41.9, 21.0, 20.0, 19.2.

FT-IR (neat) 3026, 2971, 2925, 2868, 1914, 1589, 1513, 1488, 1466, 1401, 1363, 1272, 1244, 1205, 1186, 1162, 1070, 1023, 981 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2Se$: C, 63.86; H, 6.21; N, 7.84. Found: C, 63.93; H, 6.20; N, 7.80.



(*Z*)-*N*-(3-Isopropyl-5-(3,4-dimethylphenyl)-1,3-selenazolidin-2-ylidene)benzenamine 3y.

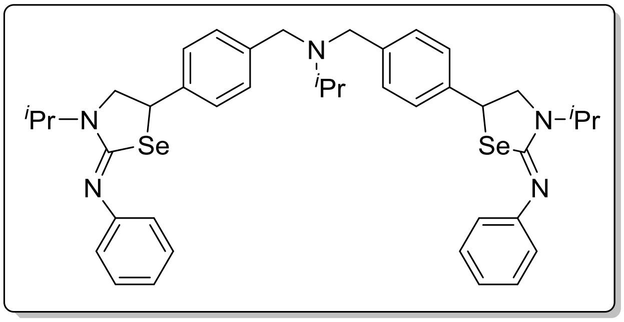
Colorless liquid; yield 87%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.11-7.02 (m, 5H), 5.03 (t, *J* = 6.8 Hz, 1H), 4.93-4.87 (m, 1H), 3.91-3.81 (m, 2H), 2.36 (s, 3H), 2.34 (s, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 153.4, 136.9, 135.3, 135.1, 131.2, 128.7, 127.2, 126.2, 123.0, 121.6, 52.4, 47.2, 37.6, 20.9, 19.8, 19.5, 19.3.

FT-IR (neat) 3024, 2971, 2928, 2869, 1620, 1588, 1446, 1402, 1363, 1255, 1236, 1188, 1164, 1126, 1069, 1024, 982 cm^{-1}.

Anal. Calcd. for $C_{20}H_{24}N_2Se$: C, 64.68; H, 6.51; N, 7.54. Found: C, 64.77; H, 6.48; N, 7.50.



(*Z*)-*N*,*N*-Bis(3-isopropyl-5-(4-((isopropylamino)methyl)phenyl)-1,3-selenazolidin-2-ylidene) benzeneamine 3z.

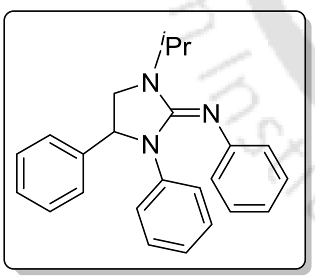
Colorless liquid; yield 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 8H), 7.30 (t, *J* = 7.2 Hz, 4H), 7.08-7.02 (m, 6H), 4.86-4.79 (m, 4H), 3.89 (dd, *J* = 10.4, 6.4 Hz, 2H), 3.70 (t, *J* = 10.4, 8.4 Hz, 2H), 3.57 (s, 4H), 2.97-2.94 (m, 1H), 1.34 (d, *J* = 4 Hz, 6H), 1.33 (d, *J* = 4 Hz, 6H), 1.11 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 153.5, 140.6, 138.3, 128.8, 128.7, 127.4, 123.2, 121.7, 53.9, 52.9, 48.4, 47.2, 42.0, 20.1, 19.3, 17.6.

FT-IR (neat) 3058, 3026, 2968, 2929, 2869, 1621, 1589, 1488, 1462, 1400, 1400, 1363, 1272, 1244, 1205, 1184, 1163, 1125, 1070, 1019 cm^{-1}.

Anal. Calcd. for $C_{41}H_{49}N_5Se_2$: C, 63.97; H, 6.42; N, 9.10. Found: C, 64.08; H, 6.40; N, 9.06.



(*Z*)-*N*-(1-Isopropyl-3,4-diphenylimidazolidin-2-ylidene)benzenamine 7a.

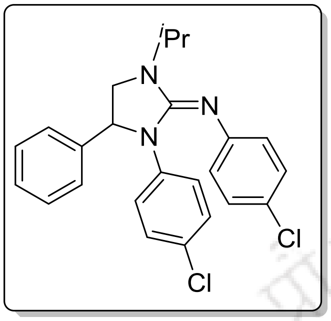
Yellow liquid; yield 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H), 6.95-6.90 (m, 5H), 6.87-6.78 (m, 4H), 6.61 (t, *J* = 7.2 Hz, 1H), 4.77 (dd, *J* = 8.8, 6.8 Hz, 1H) 4.51-4.44 (m, 1H), 3.89 (t, *J* = 8.8 Hz, 1H), 3.29 (dd, *J* = 8.8, 6.8 Hz, 1H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 149.2, 142.1, 142.0, 128.8, 127.9, 127.8, 126.6, 124.3, 124.2, 122.2, 119.8, 64.8, 47.9, 44.7, 19.3, 18.4.

FT-IR (neat) 3061, 3021, 2927, 2935, 2872, 1633, 1587, 1487, 1416, 1365, 1252, 1124, 1070, 1027, 997 cm^{-1}.

Anal. Calcd. for $C_{24}H_{25}N_3$: C, 81.09; H, 7.09; N, 11.82. Found: C, 81.19; H, 7.06; N, 11.75.



(_Z_)-4-Chloro-_N_-(3-(4-chlorophenyl)-1-isopropyl-4-phenylimidazolidin-2-ylidene)benzenamine 7b.

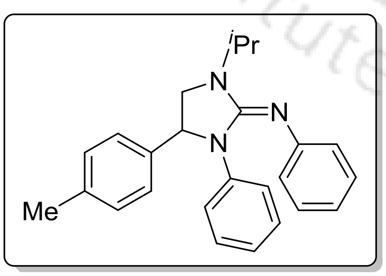
Yellow liquid; yield 75%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 5H), 6.88 (d, _J_ = 8.8 Hz, 2H), 6.86 (d, _J_ = 7.6 Hz, 2H), 6.72 (d, _J_ = 8.8 Hz, 2H), 6.62 (d, _J_ = 8.8 Hz, 2H), 4.68 (dd, _J_ = 8.4, 6.8 Hz, 1H) 4.37-4.31 (m, 1H), 3.84 (t, _J_ = 8.8 Hz, 1H), 3.26 (dd, _J_ = 9.2, 6.8 Hz, 1H), 1.20 (d, _J_ = 6.8 Hz, 3H), 1.12 (d, _J_ = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 147.8, 141.2, 140.6, 130.1, 129.0, 128.4, 128.3, 128.0, 126.7, 126.0, 125.0, 123.5, 65.1, 48.1, 45.1, 19.4, 18.5.

FT-IR (neat) 3033, 2972, 2873, 2249, 1884, 1633, 1583, 1487, 1416, 1366, 1251, 1119, 1090, 1013, 909 cm^{-1}.

Anal. Calcd. for $C_{24}H_{23}Cl_2N_3$: C, 67.93; H, 5.46; N, 9.90. Found: C, 68.02; H, 5.44; N, 9.86.



(_Z_)-_N_-(1-Isopropyl-3-phenyl-4-_p_-tolylimidazolidin-2-ylidene)benzenamine 7c.

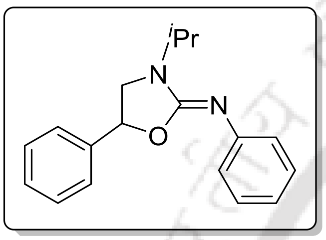
Yellow liquid; yield 68%.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 4H), 7.08-6.81 (m, 9H), 6.61 (t, *J* = 7.6 Hz, 1H), 4.77 (dd, *J* = 8.4, 6.8 Hz, 1H), 4.50-4.47 (m, 1H), 3.88 (t, *J* = 8.8 Hz, 1H), 3.27 (dd, *J* = 8.6, 6.8 Hz, 1H), 2.42 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.27 (d, *J* = 6.4 Hz, 3H).

[13]C NMR (100 MHz, $CDCl_3$) δ 152.2, 149.1, 142.2, 142.0, 130.1, 129.0, 128.4, 128.3, 128.0, 125.2, 124.2, 120.8, 64.8, 47.9, 44.7, 21.1, 19.6, 18.8.

FT-IR (neat) 3059, 3027, 2972, 2939, 2879, 1652, 1589, 1550, 1488, 1445, 1366, 1325, 1241, 1071, 1025, 908 cm^{-1}.

Anal. Calcd. $C_{25}H_{27}N_3$: C, 81.26; H, 7.37; N, 11.37. Found: C, 81.35; H, 7.34; N, 11.31.



(*Z*)-*N*-(3-Isopropyl-5-phenyloxazolidin-2-ylidene)benzenamine 8a.

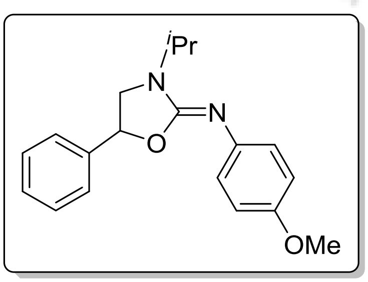
Yellow liquid; yield 65%.

[1]H NMR (400 MHz, $CDCl_3$) δ 7.45-7.33 (m, 5H), 7.31-7.18 (m, 4H), 7.01-6.97 (m, 1H), 5.46 (t, *J* = 7.6 Hz, 1H), 4.46-4.30 (m, 1H), 3.82 (t, *J* = 8.4 Hz, 1H), 3.36 (dd, *J* = 8.4, 7.6 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.4 Hz, 3H).

[13]C NMR (100 MHz, $CDCl_3$) δ 152.2, 147.9, 139.1, 128.8, 128.7, 128.5, 125.8, 123.7, 121.9, 77.3, 47.9, 45.0, 19.7, 18.9.

FT-IR (neat) 3059, 3026, 2972, 2921, 2872, 1670, 1591, 1493, 1451, 1424, 1365, 1244, 1214, 1127, 1060, 1021, 999 cm^{-1}.

Anal. Calcd. for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19; N, 9.99. Found: C, 77.20; H, 7.16; N, 9.95.



(*Z*)-*N*-(3-Isopropyl-5-phenyloxazolidin-2-ylidene)-4-methoxybenzenamine 8b.

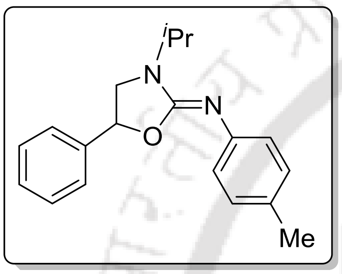
Yellow liquid; yield 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.31 (m, 5H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.41 (t, *J* = 8.0 Hz, 1H), 4.36-4.33 (m, 1H), 3.78 (t, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.30 (t, *J* = 8.4 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 152.0, 141.2, 139.3, 128.9, 128.7, 125.9, 124.4, 113.9, 77.3, 55.5, 48.1, 45.0, 19.8, 19.0.

FT-IR (neat) 3035, 2972, 2920, 2834, 1668, 1505, 1459, 1427, 1365, 1283, 1238, 1209, 1178, 1127, 1103, 1060, 1028, 910 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2O$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.61; H, 7.11; N, 9.00.



(*Z*)-*N*-(3-Isopropyl-5-phenyloxazolidin-2-ylidene)-4-methylbenzenamine 8c.

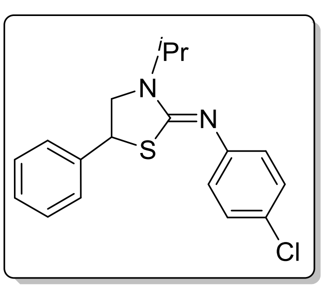
Yellow liquid; yield 67%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 7.12-6.96 (m, 4H), 5.42 (t, *J* = 7.6 Hz, 1H), 4.40-4.33 (m, 1H), 3.80 (t, *J* = 8.4 Hz, 1H), 3.32 (dd, *J* = 8.4, 7.2 Hz, 1H), 2.26 (s, 3H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 145.3, 139.2, 130.9, 129.1, 128.8, 128.6, 125.7, 123.4, 77.2, 48.0, 44.9, 20.8, 19.7, 18.9.

FT-IR (neat) 3026, 2972, 2921, 2870, 2110, 1889, 1668, 1605, 1508, 1417, 1366, 1331, 1291, 1239, 1126, 1107, 1060, 1018, 1000, 910 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.63; H, 7.51; N, 9.48.



(*Z*)-4-Chloro-*N*-(3-isopropyl-5-phenylthiazolidin-2-ylidene)benzenamine 9a.

Colorless solid; yield 76%.

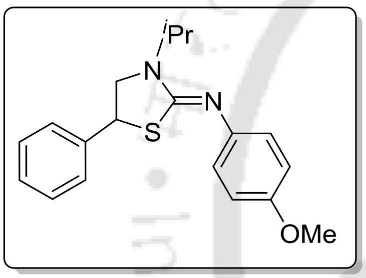
Mp: 92-93 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.32-7.25 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.67-4.61 (m, 2H), 3.83 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.53 (dd, *J* = 10.0, 7.6 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.7, 139.0, 128.8, 128.7, 128.2, 127.9, 127.3, 123.6, 52.9, 46.7, 46.3, 19.9, 19.0.

FT-IR (KBr) 3061, 3030, 2972, 2931, 2871, 2127, 1882, 1606, 1586, 1485, 1455, 1364, 1272, 1242, 1211, 1190, 1163, 1126, 1089, 1067, 1031, 1009, 937 cm^{-1}.

Anal. Calcd. for $C_{18}H_{19}ClN_2S$: C, 65.34; H, 5.79; N, 8.47; S, 9.69. Found: C, 65.46; H, 5.76; N, 8.42; S, 9.66.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-methoxybenzenamine 9b.

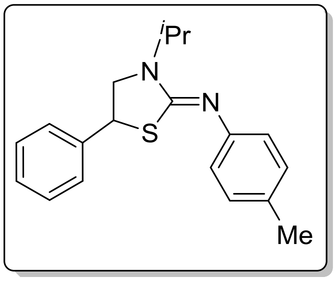
Colorless liquid; yield 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.31-7.22 (m, 3H), 6.91 (d, *J* = 9.2 Hz, 2H), 6.79 (d, *J* = 9.2 Hz, 2H), 4.68-4.60 (m, 2H), 3.83 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.71 (s, 3H), 3.52 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 155.7, 145.4, 139.2, 128.8, 128.1, 127.5, 123.1, 114.1, 55.4, 53.0, 46.7, 46.4, 20.0, 19.1.

FT-IR (neat) 3032, 2970, 2934, 2871, 2059, 1870, 1614, 1504, 1455, 1402, 1364, 1290, 1237, 1179, 1126, 1103, 1066, 1035, 937 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2OS$: C, 69.90; H, 6.79; N, 8.58; S, 9.82. Found: C, 69.99; H, 6.77; N, 8.54; S, 9.78.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-methylbenzenamine 9c.

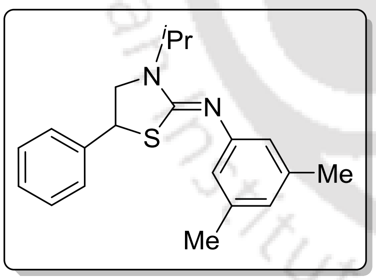
Colorless liquid; yield 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.31-7.22 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 4.78-4.71 (m, 1H), 4.58 (t, *J* = 7.2 Hz, 1H), 3.76 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.48 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.30 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.4, 139.1, 131.6, 129.1, 128.4, 127.7, 127.1, 121.6, 52.4, 46.1, 46.0, 45.9, 20.6, 19.5, 18.7.

FT-IR (neat) 3025, 2971, 2928, 2870, 1624, 1602, 1505, 1470, 1454, 1402, 1363, 1270, 1242, 1212, 1191, 1126, 1106, 1066, 1030, 938 cm^{-1}.

Anal. Calcd. for $C_{19}H_{22}N_2S$: C, 73.51; H, 7.14; N, 9.02; S, 10.33. Found: C, 73.61; H, 7.12;, N, 8.97; S, 10.30.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-3,5-dimethylbenzenamine 9d.

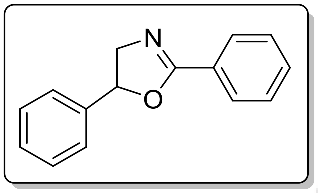
Colorless liquid; yield 74%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.34 (m, 1H), 7.38-7.31 (m, 5H), 6.27 (d, *J* = 8.4 Hz, 1H), 6.70 (s, 1H), 4.78-4.71 (m, 1H), 4.68 (t, *J* = 7.6 Hz, 1H), 3.87 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.57 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.33 (s, 6H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.29 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 152.0, 139.0, 138.1, 128.7, 128.0, 127.4, 124.6, 119.8, 52.8, 46.6, 46.2, 21.3, 19.9, 18.9.

FT-IR (neat) 3029, 2971, 2927, 2867, 1614, 1455, 1402, 1362, 1289, 1240, 1210, 1143, 1068, 1027, 953 cm^{-1}.

Anal. Calcd. for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 74.14; H, 7.43; N, 8.59; S, 9.84.



4,5-Dihydro-2,5-diphenyloxazole 10.[16]

Yellow liquid; yield 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.39-7.26 (m, 5H), 5.62 (dd, *J* = 10.0, 8.0 Hz, 1H), 4.44 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.97 (dd, *J* = 14.8, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 140.9, 131.4, 128.7, 128.4, 128.3, 127.5, 125.6, 80.9, 62.9.

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.81; H, 5.81; N, 6.35.

Crystal Data and Structure Refinement for 3b at 296(2) K

Identification code	MSN-293	
CCDC number	899302	
Empirical formula	$C_{19}H_{22}N_2OSe$	
Formula weight	373.35	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
	Loop xyz	
	'x, y, z' '-x+1/2, -y, z+1/2' '-x, y+1/2, -z+1/2' 'x+1/2, -y+1/2, -z'	
Unit cell dimensions	*a* = 9.5405 (7) Å	α(°)= 90.00
	b = 12.1915 (8) Å	β(°)= 90.00
	c = 15.6390 (11) Å	γ(°)= 90.00
Volume	1819.0 (2) $Å^3$	
Z	4	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	2.070 mm^{-1}	
F(000)	768.0	
Crystal size	0.35 x 0.25 x 0.20 mm	
Theta range for data collection	2.12 to 31.02°	
Index ranges	-13<=h<=12, -16<=k<=17, -22<=l<=22	
Reflections collected	3249	
Independent reflections	3003 [R (int) = 0.0339]	
Completeness to theta = 24.99°	98.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.661 and 0.543	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5701 / 0 / 208	
Goodness-of-fit on F^2	0.806	
Final R indices [I>2sigma (I)]	*R1* = 0.0414, *wR2* = 0.0878	
R indices (all data)	*R1* = 0.0921, *wR2* = 0.0979	

2.5 References

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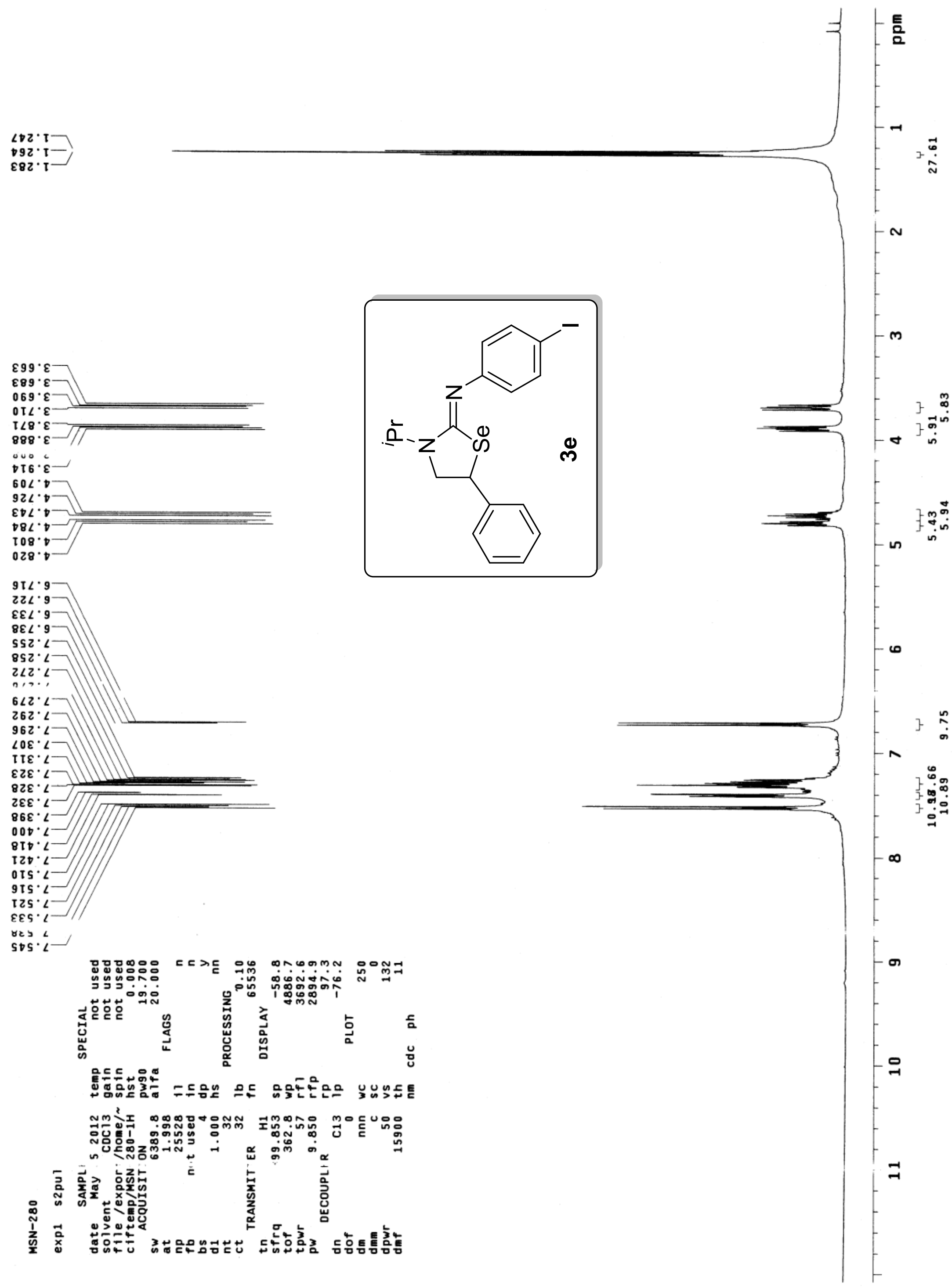
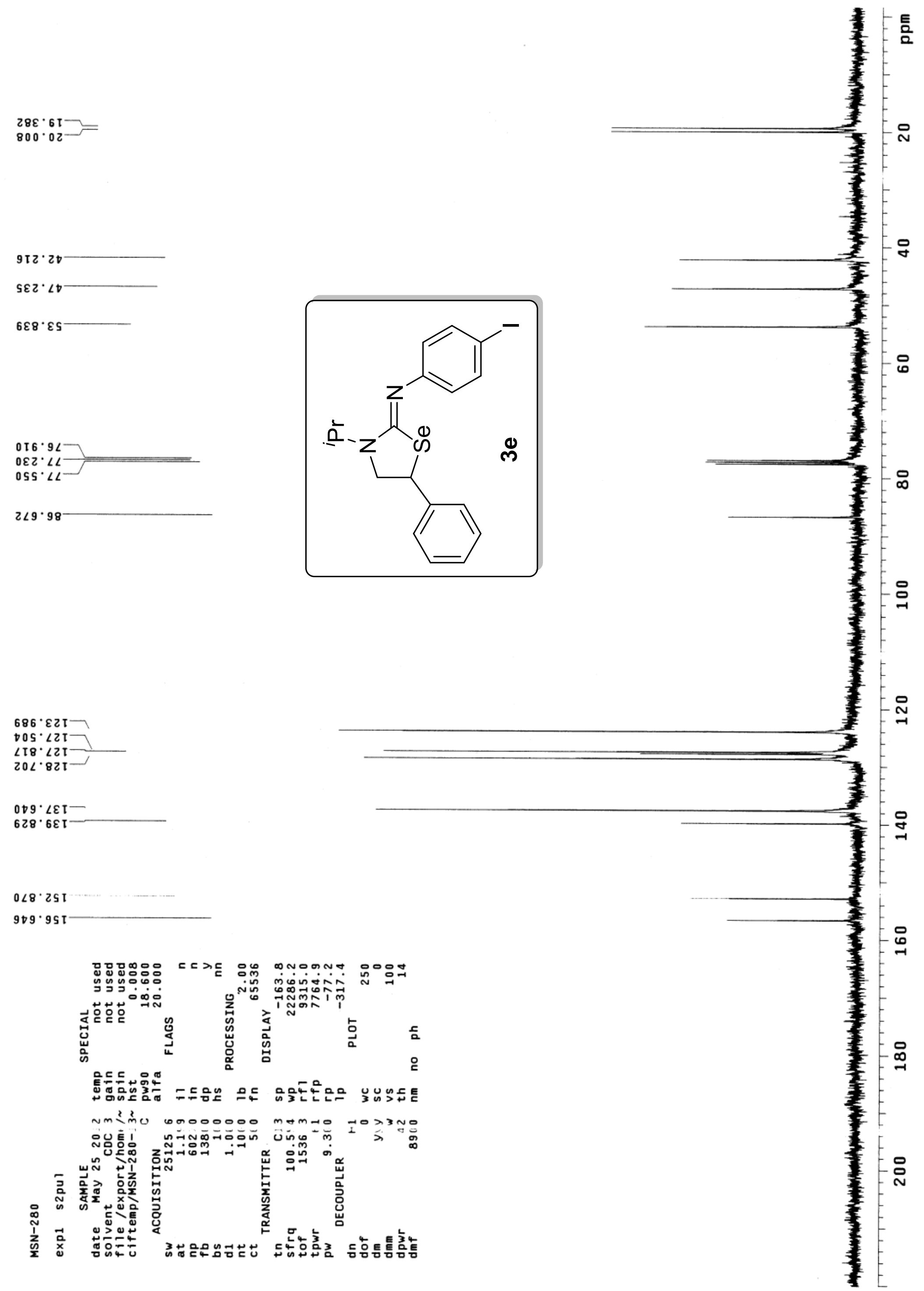
2.6 Selected NMR (^{1}H and ^{13}C) Spectra

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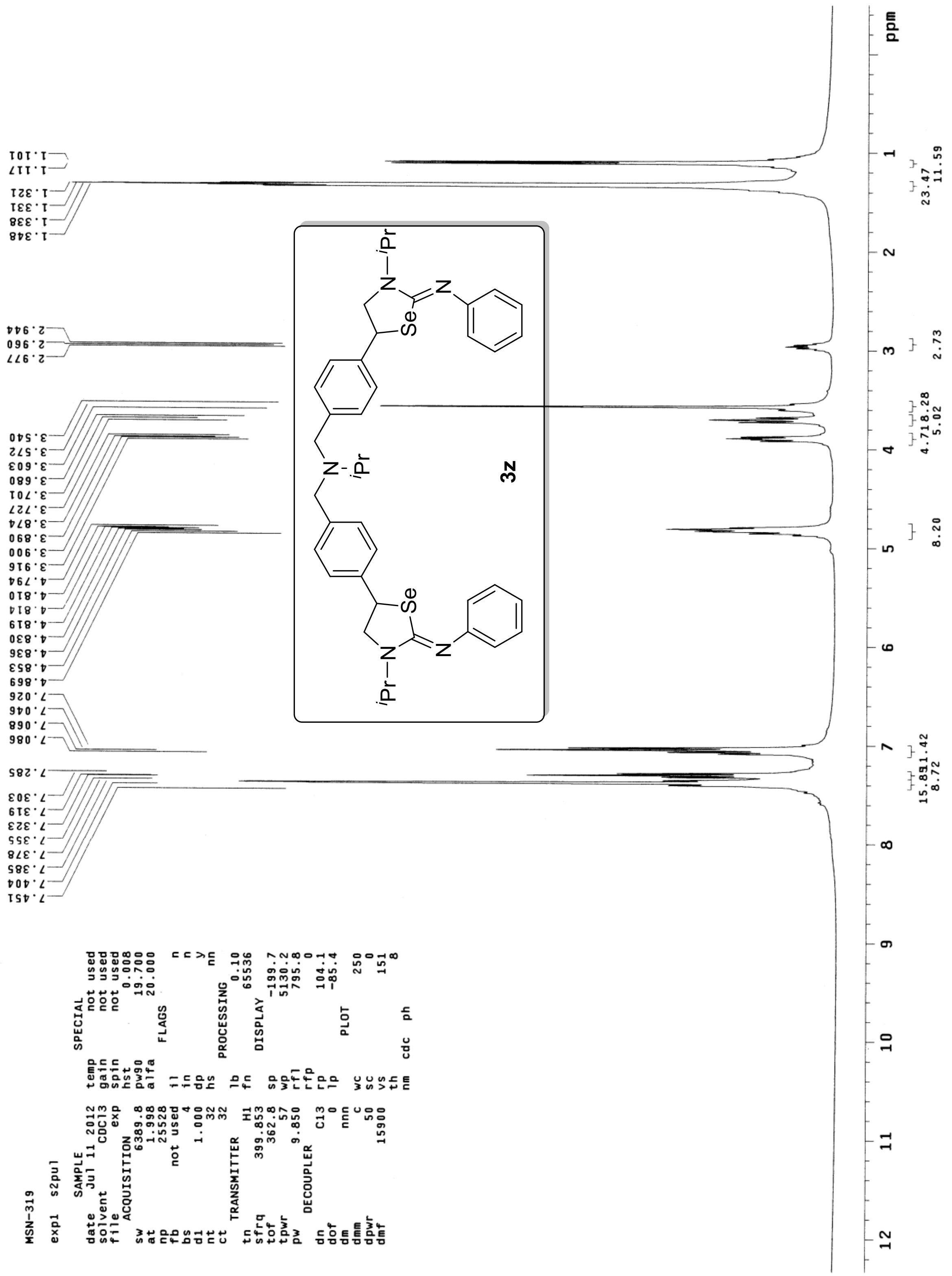
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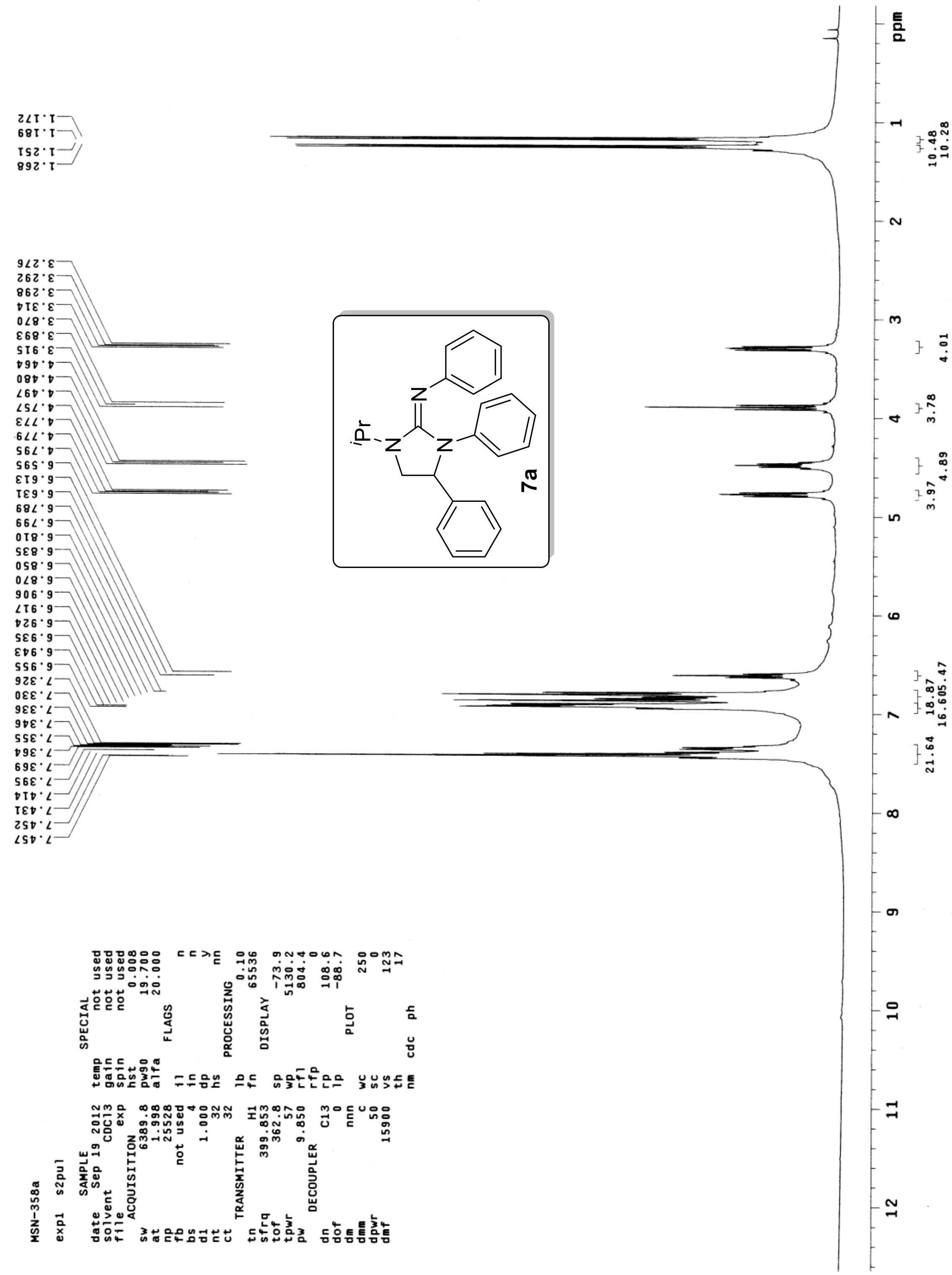
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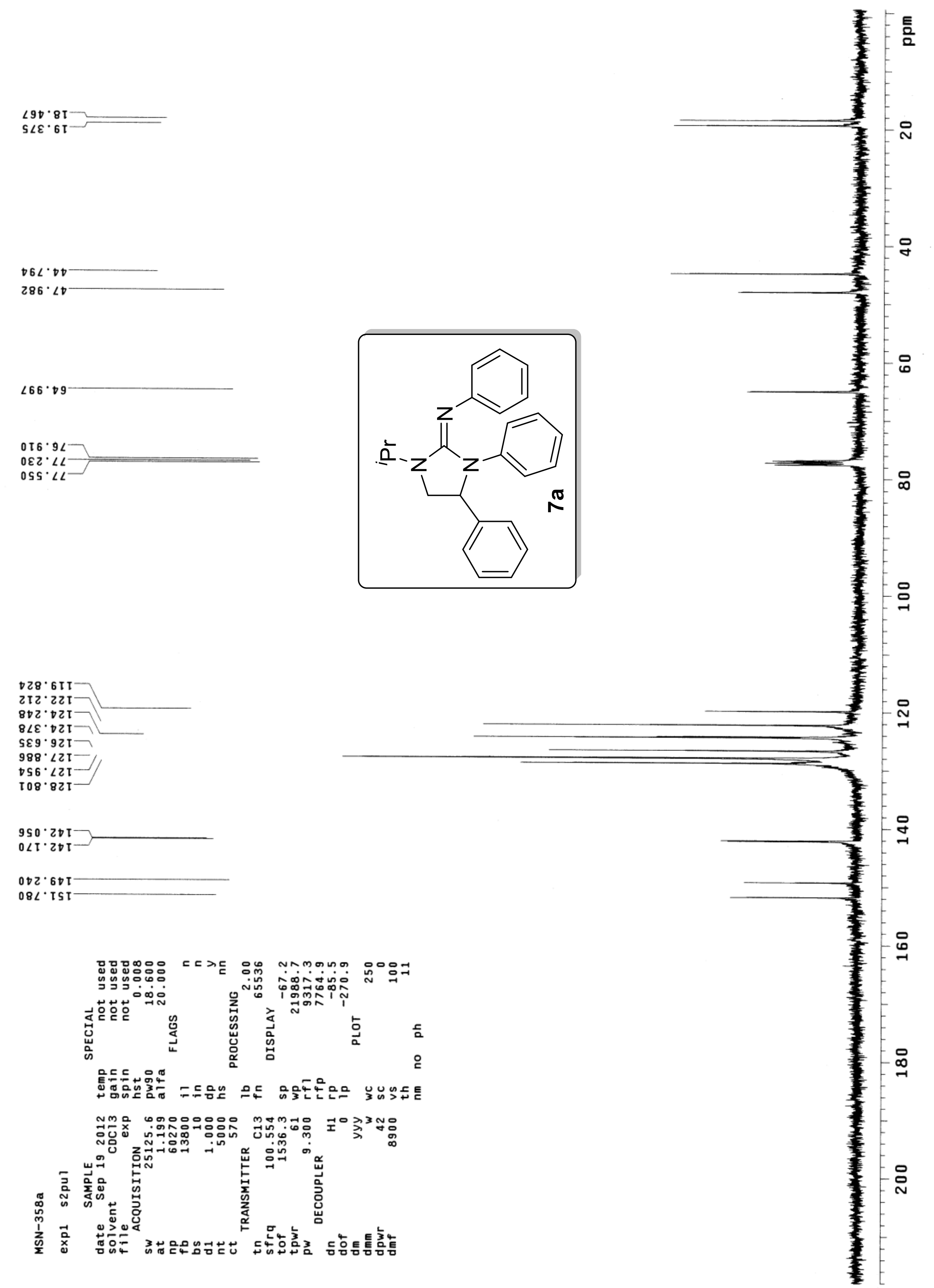
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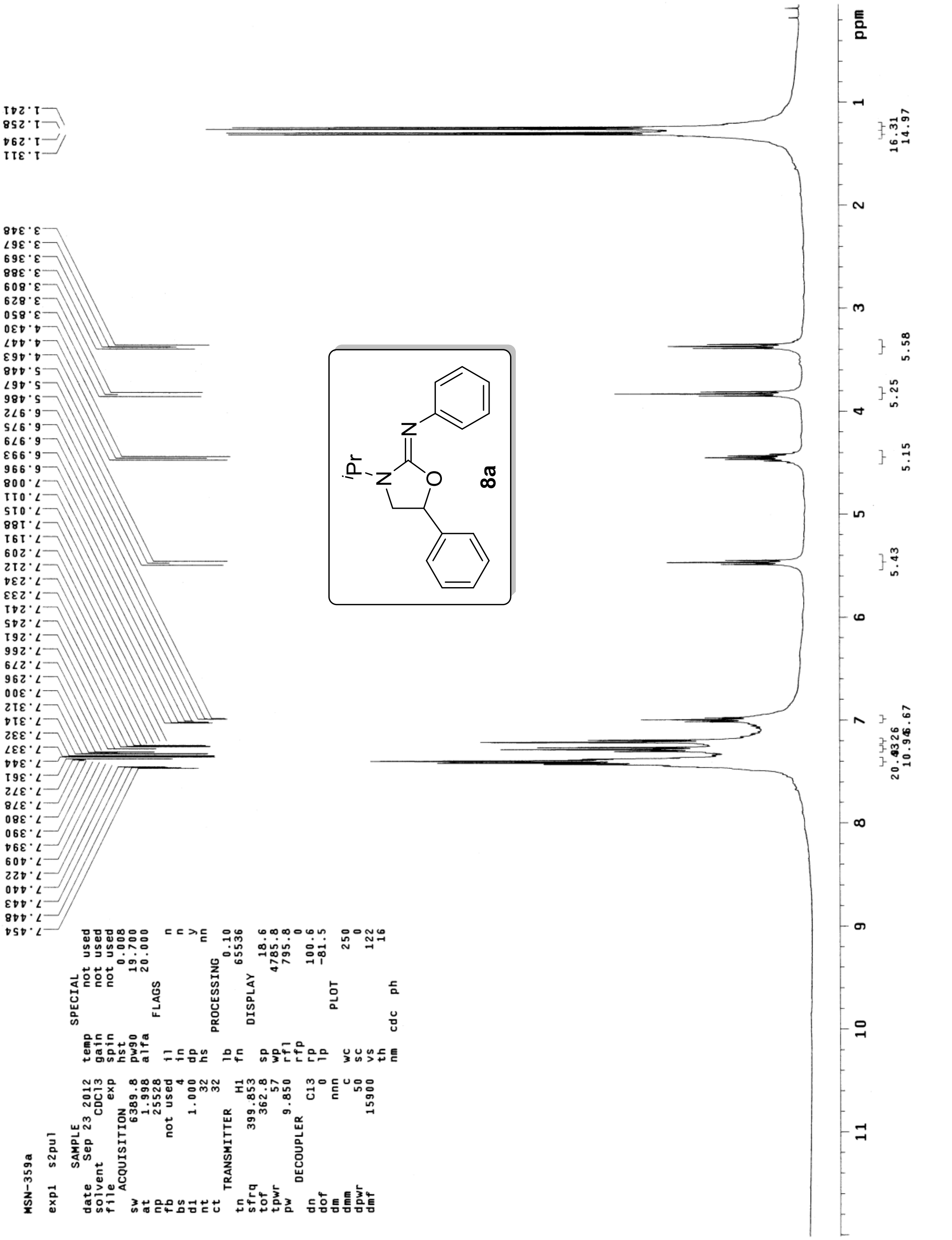

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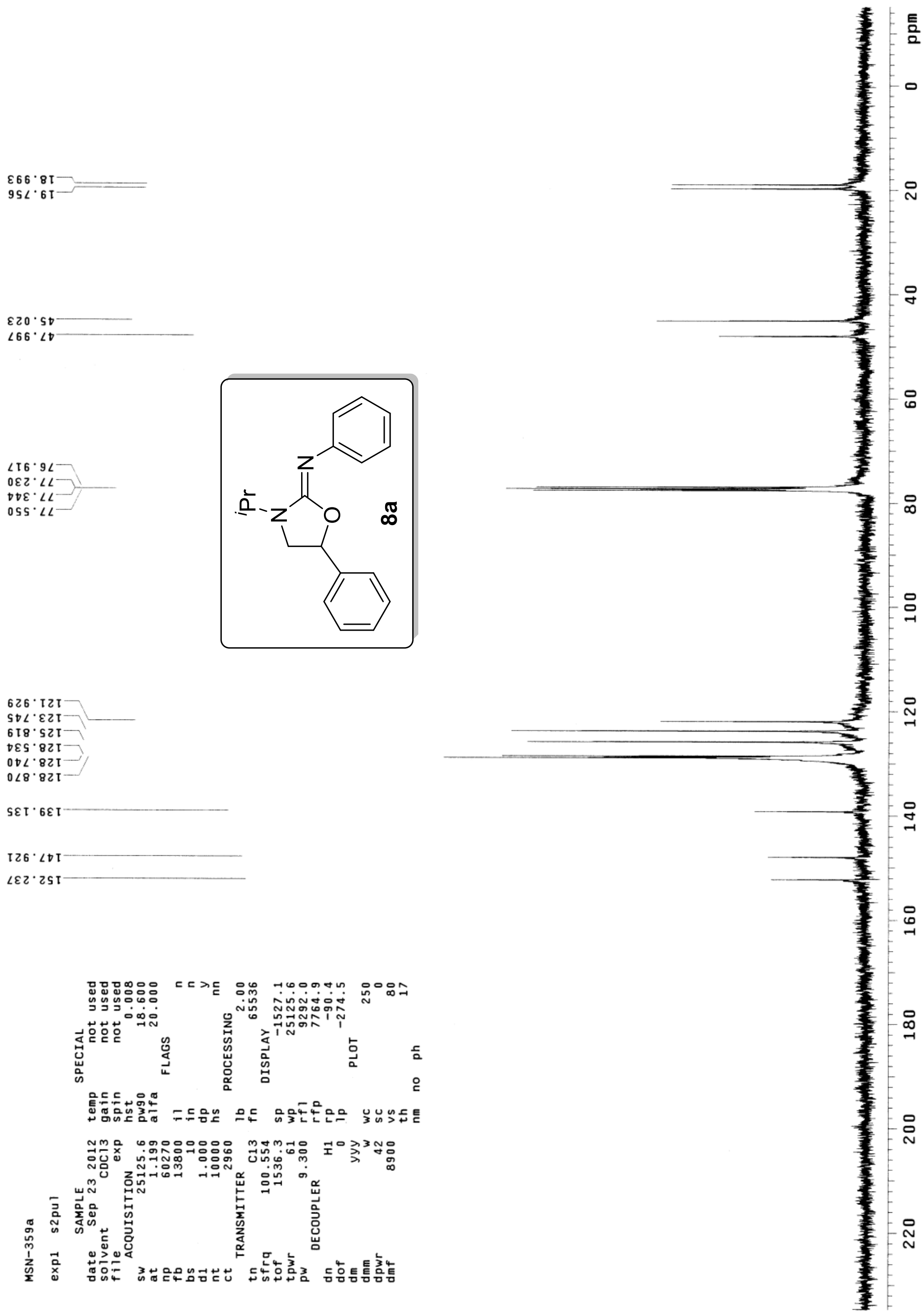
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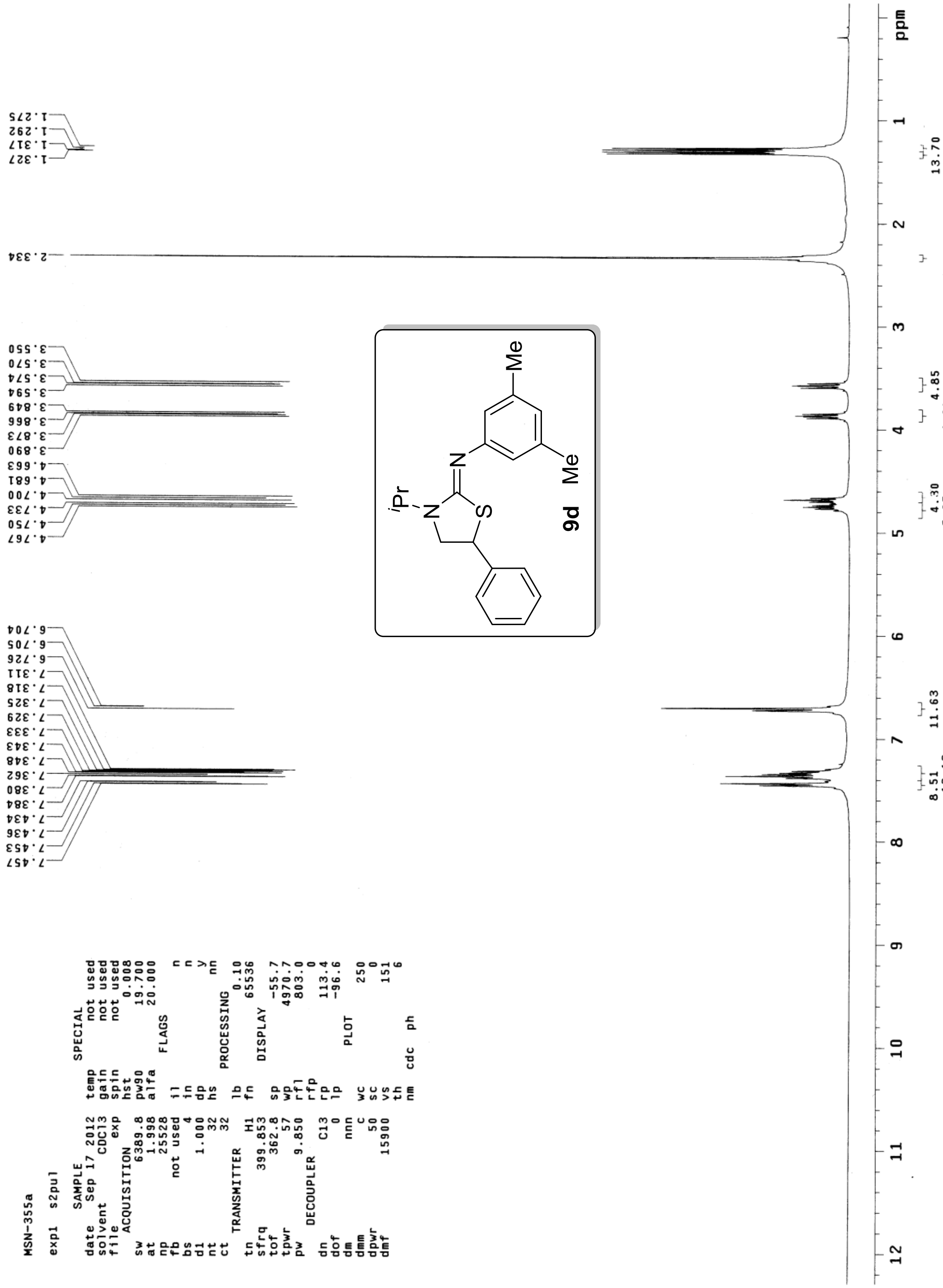
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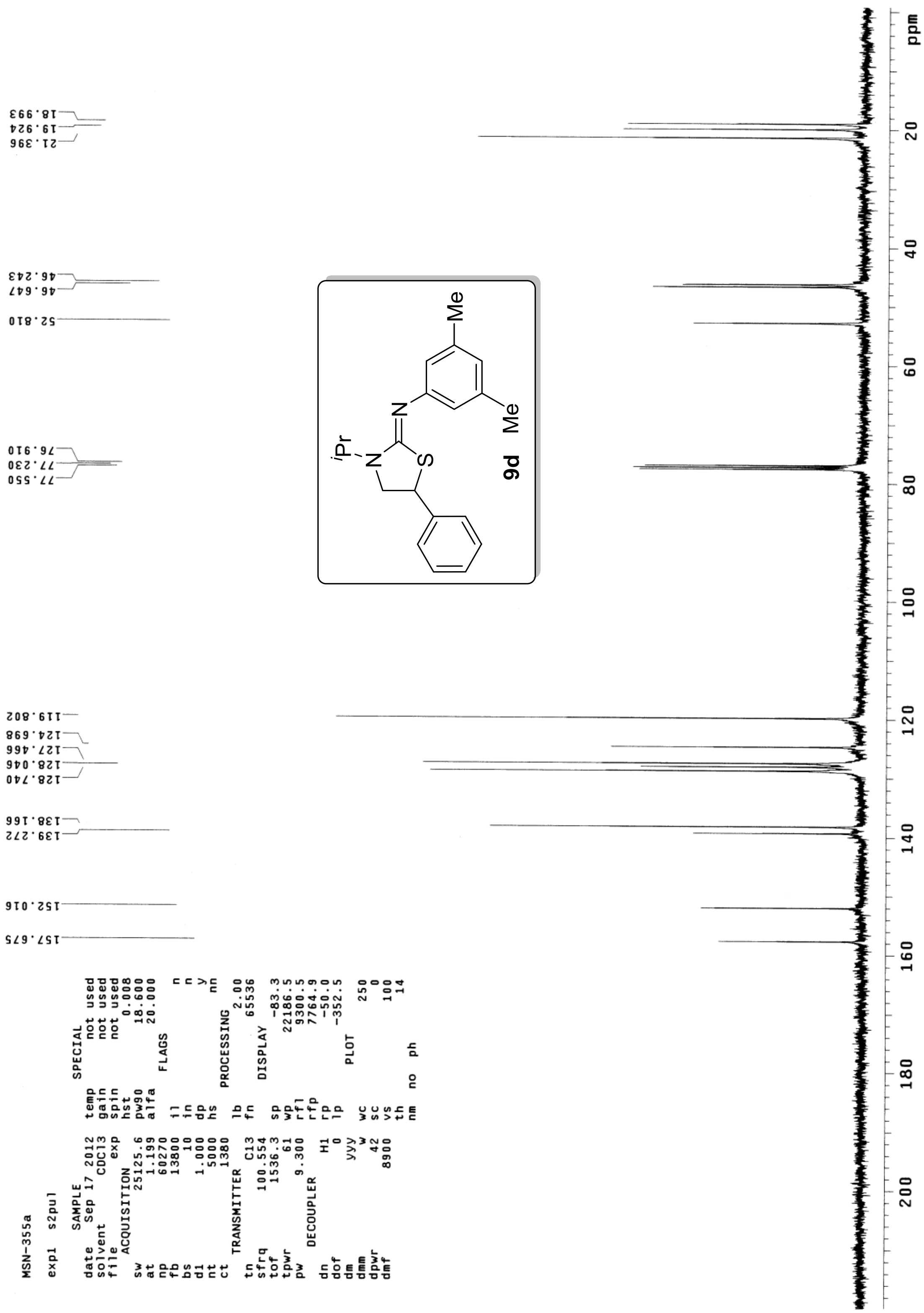
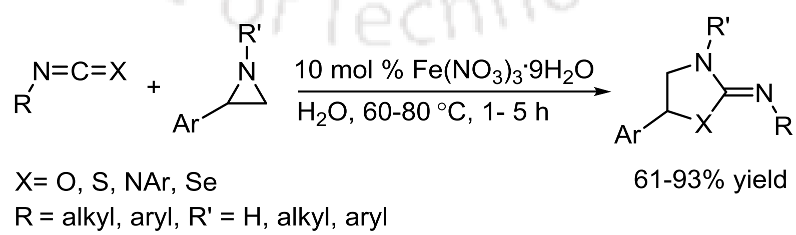


Chapter III

Pyrrolidine-Catalyzed Cycloaddition of Aziridines with Isothiocyanates, Isoselenocyanates and Carbon Disulfide "On Water"

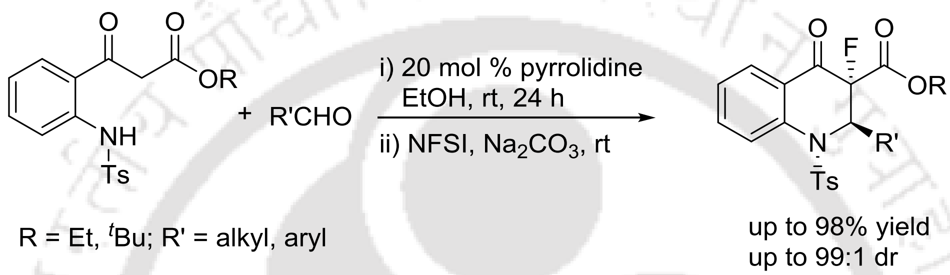
Organocatalysis has recently emerged as a powerful synthetic tool for the construction of diverse biologically active building blocks.[1,2] Because organocatalysts are relatively stable, less toxic, readily accessible, inexpensive, environmentally benign and simple to use compared to the conventional transition metal catalysts. They can be classified by the variety of their modes of activation as amine catalysts,[3] hydrogen-bonding catalysts,[4] phase-transfer catalysts,[5] etc. Among them, amine catalysis has received much attention in synthetic chemistry.[3] Water is the most abundant, cheap, safe and environmentally benign solvent in nature. Development of effective methods for the use of water as a reaction medium for organic synthesis has thus received much attention in recent years.[6-8] The cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide is a powerful way to access a wide variety of functionalized five membered heterocycles in synthetic organic chemistry, that are found in a wide range of products possessing biological activities.[9] In chapter II, we described Fe-catalyzed cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates and carbodiimides that takes place in aqueous suspension (Scheme 1).[10] In this chapter, we report pyrrolidine-catalyzed cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide in aqueous medium at moderate temperature. This reaction involves a urea type intermediate and the target heterocycles are formed in good yields.



Scheme 1. Fe-Catalyzed Cycloaddition of Aziridines with Isocyanates, Isothiocyanates, Isoselenocyanates and Carbodiimides

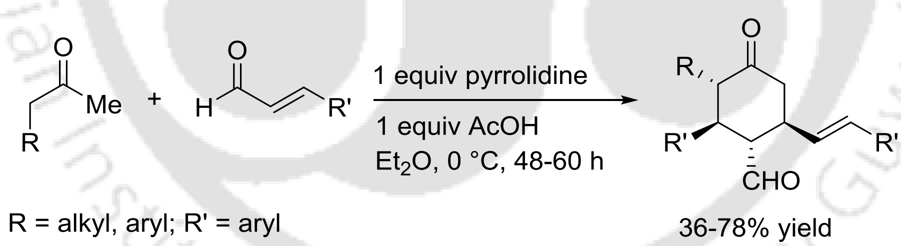
3.1 Pyrrolidine Catalyzed Reactions

Pyrrolidine catalyzed reactions represent an important approach for the construction of carbon-carbon and carbon-heteroatom bonds. For example, Ma and co-workers reported the synthesis fluorinated 2,3-dihydroquinolin-4(1*H*)-one from *β*-(2′-anilino)-*β*-ketoesters and aldehydes using pyrrolidine as a catalyst and *N*-fluorobenzenesulfonimide (NFSI) as a fluorinating agent (Scheme 2).[11] The reaction takes place via a sequence of Knoevenagel condensation/aza-Michael addition/electrophilic fluorination.



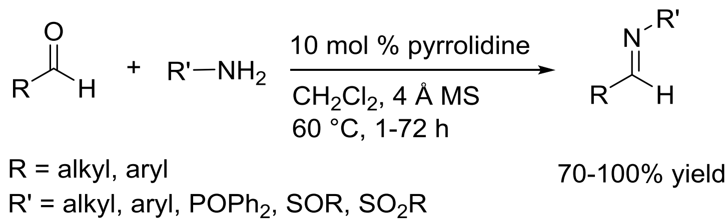
Scheme 2. Synthesis Fluorinated 2,3-Dihydroquinolin-4(1*H*)-one

Pyrrolidine mediated domino reaction of methylethylketones and *α,β*-unsaturated aromatic aldehydes afforded 4-oxocyclohexanecarbaldehydes *via* aldol condensation followed by a tandem inter- and intra-Michael addition (Scheme 3).[12]



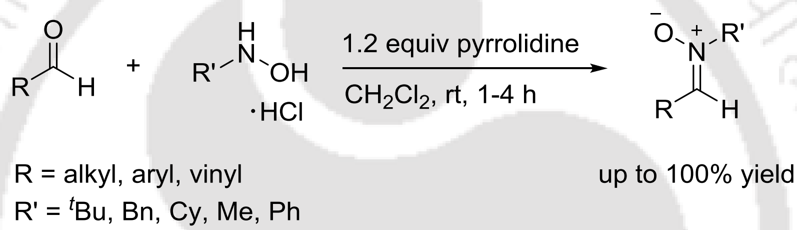
Scheme 3. Domino Synthesis of Substituted 4-Oxocyclohexanecarbaldehyde

Cid and co-workers described the synthesis of aldimines from aldehydes and primary amines using 10 mol % pyrrolidine in CH_2Cl_2 (Scheme 4).[13] The process can be applied for the synthesis of *N*-alkyl, *N*-aryl, *N*-phosphinoyl, *N*-sulfinyl and *N*-sulfonyl imines in good yields.



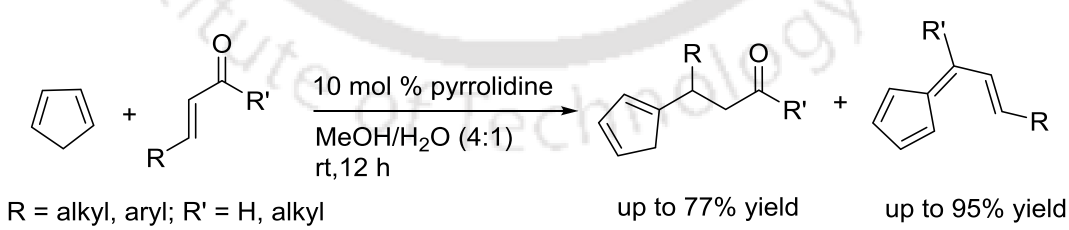
Scheme 4. Pyrrolidine Catalyzed Synthesis of Imines

The same group accomplished pyrrolidine mediated synthesis of nitrone by condensation of *N*-substituted hydroxylamine hydrochlorides with aldehydes (Scheme 5).[14] Mechanistic studies suggest that the cooperative pyrrolidine/pyrrolidinium chloride increases the nucleophilicity of the hydroxylamine and electrophilicity of the carbonyl group *via* iminium ion formation to provide nitrone in good yields.



Scheme 5. Synthesis of Imidazolidines from Hydroxylamine Hydrochlorides and Aldehydes

The reactions of cyclopentadiene with *α,β*-unsaturated carbonyl compounds furnished 4-cyclopentadienyl-2-butanones or 6-vinylfulvenes using 10 mol % pyrrolidine in MeOH/H_2O (Scheme 6).[15] The reaction takes place *via* Michael addition at the *β*-carbon of enone, or 1,2-addition to the carbonyl compound to provide corresponding 4-cyclopentadienyl-2-butanones and 6-vinylfulvenes, respectively.

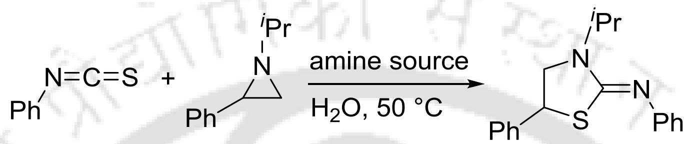


Scheme 6. Synthesis of Imidazolidines from Hydroxylamine Hydrochlorides and Aldehydes

3.2 Present Study

We present here the cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide using pyrrolidine as a catalyst. The reaction occurs in aqueous medium *via* a urea type intermediate affording a potential route for the construction of five membered heterocycles in high yields under mild reaction conditions.

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

Entry	Catalyst	Temp. (°C)	Time (h)	Conv. (%)[a,b]
1	pyrrolidine	28	12	46
2	**pyrrolidine**	**50**	**6**	**97**
3	morpholine	50	6	36
4	piperidine	50	6	38
5	L-proline	50	6	75
6	*N*-methylaniline	50	6	25
7	diisopropylamine	50	6	20
8	*N*-Boc-pyrrolidine	50	6	9
9	triethylamine	50	6	9
10	DBU	50	6	15
11	$NaHCO_3$	50	6	12
12	K_2CO_3	50	6	13
13	pyrrolidine	50	10	86[c]
14	-	50	12	9
15	-	28	12	4

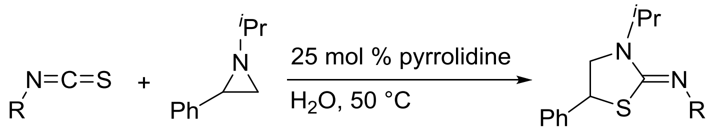
[a] Reaction conditions: Isothiocyanate (0.5 mmol), aziridine (0.5 mmol), catalyst (25 mol %), H_2O (1.0 mL), 50 °C, air. [b] Determined by 400 MHz 1H NMR. [c] 20 mol % of catalyst used.

First, the reaction conditions were optimized employing phenyl isothiocyanate (**1a**) and 1-isopropyl-2-phenylaziridine (**2a**) as model substrates in the presence of various amine catalysts on water (Table 1). Gratifyingly, the reaction occurred to give the desired thiazolidin-2-ylidene (**3a**) in 46% yield when the substrates **1a** and **2a** were stirred with 25 mol % pyrrolidine for 12 h on water at ambient conditions (entry 1). Increasing the reaction temperature to 50 °C led to completion of the process in 6 h with 97% yield (entry 2). In a set of screened amine catalysts, pyrrolidine, morpholine, piperidine, L-proline, *N*-methylaniline, diisopropylamine, *N*-Boc pyrrolidine, triethylamine, DBU, $NaHCO_3$ and K_2CO_3, the former afforded the superior results (entries 2-13). Control experiments confirmed that without the amine catalyst the reaction produced **3a** after 12 h in <9% yield (entry 14 and 15).

With the optimal conditions in hand, the generality of the protocol was studied for the reactions of a series of substituted isothiocyanates with aziridine **2a** (Table 2). The reactions were efficient to afford the target products in high yields. For examples, isothiocyanates **1b-h** having 2-methoxy, 2-methyl, 3-fluoro, 4-ethyl, 4-methoxy, 4-methyl and 4-nitro substituents in the phenyl ring underwent reaction to give the heterocycles **3b-h** in 69-88% yields. Likewise, the substrates **1i-k** bearing 2,4-, 3,4- and 3,5-dimethyl substituents readily underwent reaction to provide the target products **3i-k** in 79-85% yields. Furthermore, aliphatic isothiocyanate **1l** was compatible affording the target heterocycle **3l** in 70% yield. Similarly, 1-naphthyl isothiocyanate **1m** underwent reaction to give the desired **3m** in 82% yield.

Next, the reactions of substituted aziridines **2b-k** with isothiocyanate **1b** were examined and the results are summarized in table 3. For examples, aryl aziridines **2b-e** having allyl, benzyl, *n*-butyl and cyclohexyl substituents on the nitrogen atom underwent reaction to give the cycloaddition products **3n-q** in 69-83% yields, whereas 1-tosyl-2-phenyl-aziridine **2f** showed no reaction and the starting materials were recovered intact. Furthermore, the substrates **2g-k** having electrons donating and -withdrawing substituents such as 4-bromo, 4-fluoro, 4-methoxy, 4-methyl and 2,4-dimethyl groups readily underwent reaction to furnish the thiazolidin-2-ylidenes **3s-w** in 73-89% yields.

Table 2. Pyrrolidine-Catalyzed Cycloaddition of Substituted Isothiocyanates with Aziridine[a]



1b-m **2a** R = alkyl, aryl **3b-m**

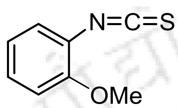
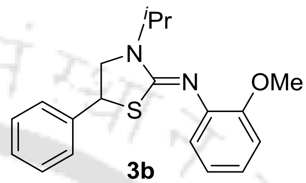
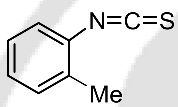
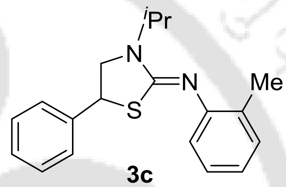
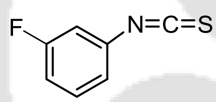
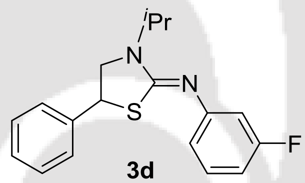
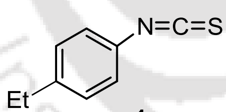
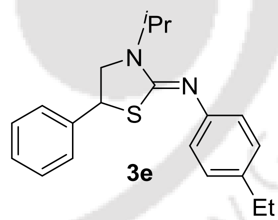
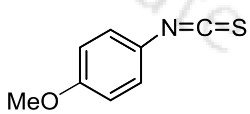
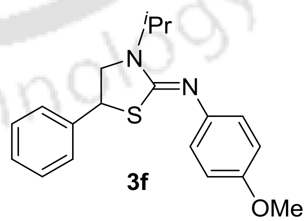
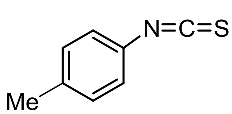
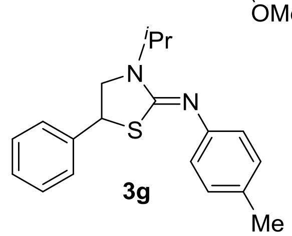
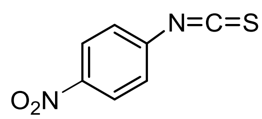
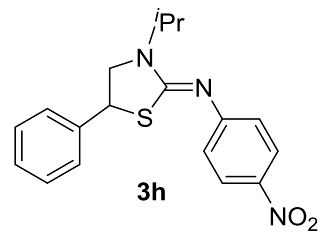
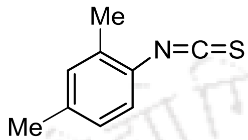
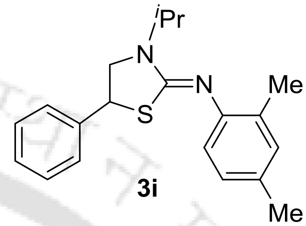
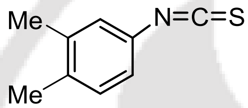
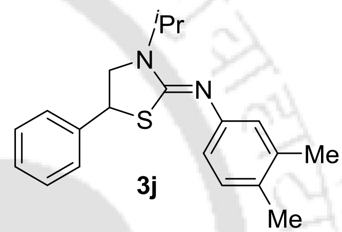
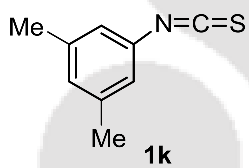
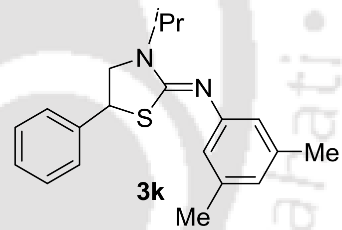
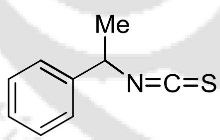
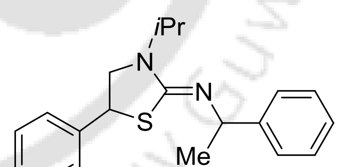
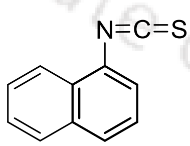
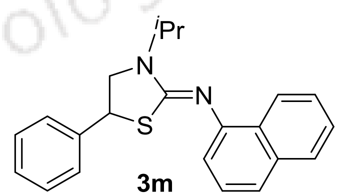
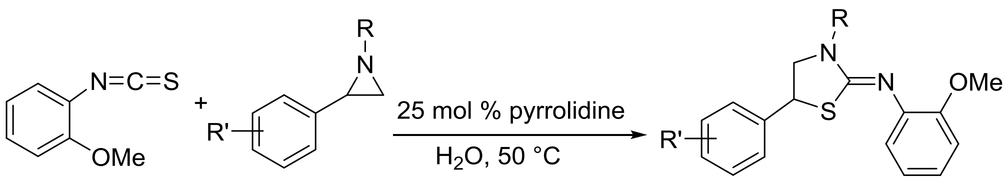
Entry	Isothiocyanates	Time (h)	Product	Yield (%)[b]
1	 **1b**	7.0	 **3b**	73
2	 **1c**	8.5	 **3c**	71
3	 **1d**	5.5	 **3d**	69
4	 **1e**	9.5	 **3e**	80
5	 **1f**	10.5	 **3f**	88
6	 **1g**	9.5	 **3g**	82

Table 2 continued.....

7	 **1h**	10.0	 **3h**	75
8	 **1i**	10.0	 **3i**	79
9	 **1j**	10.5	 **3j**	81
10	 **1k**	9.0	 **3k**	85
11	 **1l**	9.5	 **3l**	70
12	 **1m**	9.0	 **3m**	82

[a] Reaction conditions: Isothiocyanate **1a-m** (0.5 mmol), aziridine **2a** (0.5 mmol), pyrrolidine (25 mol %), H_2O (1.0 mL), 50 °C, air. [b] Yield of isolated product.

Table 3. Pyrrolidine-Catalyzed Cycloaddition of Isothiocyanate **1b** with Substituted Aziridine[a]



1b **2b-k** **3n-w**

R = alkyl, Bn, Ts; R' = EDG, EWG

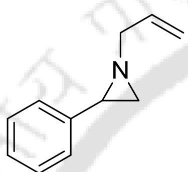
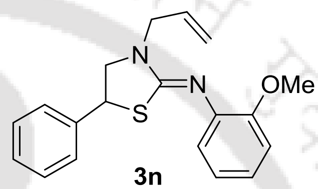
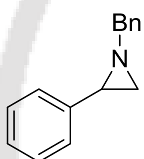
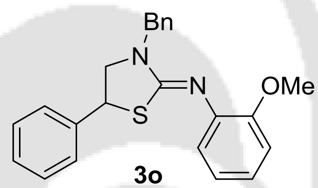
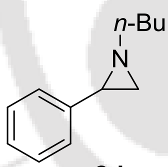
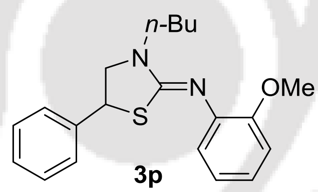
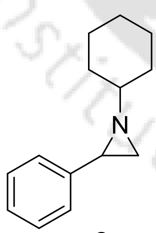
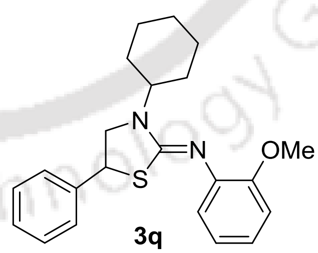
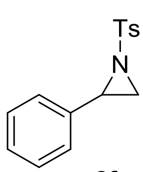
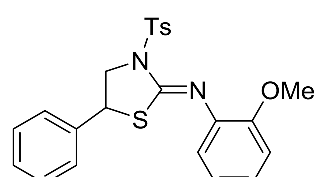
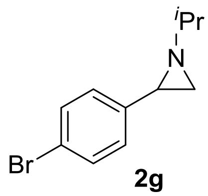
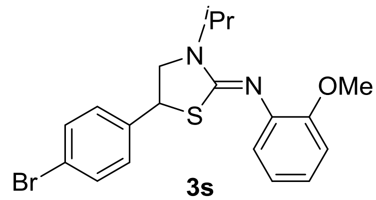
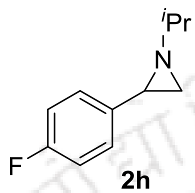
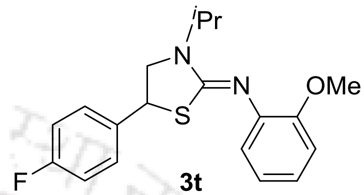
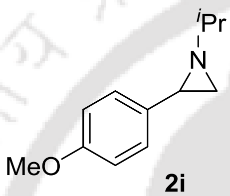
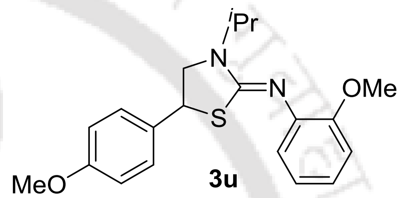
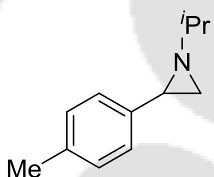
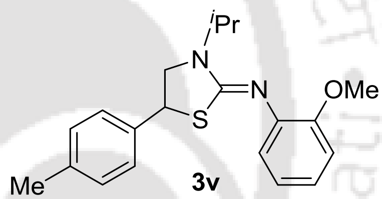
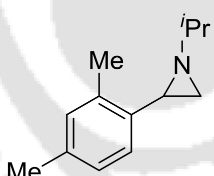
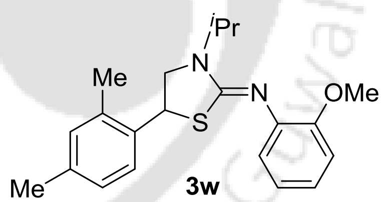
Entry	Aziridine	Time (h)	Product	Yield (%)[b]
1	 **2b**	9.5	 **3n**	70
2	 **2c**	10.5	 **3o**	78
3	 **2d**	6.5	 **3p**	83
4	 **2e**	8.5	 **3q**	69
5	 **2f**	12.0	 **3r**	n.d.

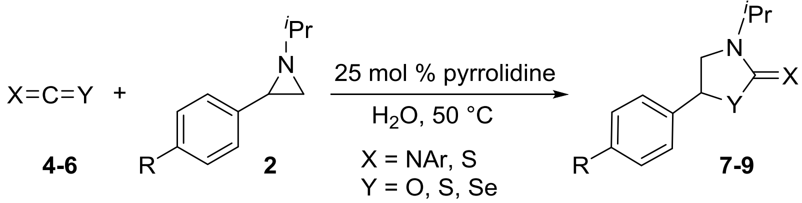
Table 3 continued.....

6	 **2g**	9.0	 **3s**	85
7	 **2h**	10.5	 **3t**	74
8	 **2i**	5.0	 **3u**	89
9	 **2j**	6.0	 **3v**	77
10	 **2k**	8.5	 **3w**	73

[a] Reaction conditions: Isoselenocyanate **1b** (0.5 mmol), **2b-k** (0.5 mmol), pyrrolidine (25 mol %), H_2O (1.0 mL), 50 °C, air. [b] Yield of isolated product. n.d. = not detected.

Finally, the reactions of other heterocumulenes, isocyanate **4**, isoselenocyanates **5a-e** and carbon disulfide **6** with aziridines, were investigated (Table 4). However, isocyanate **4** showed no reaction and the starting material was recovered intact (entry 1). In contrast, isoselenocyanates **5a-e** readily underwent reaction with aziridine **2a** to afford the target products **8a-e** in 80-91% yield. Likewise, carbon disulfide **6** underwent reaction with aziridines **2a**, **2g**, **2i** and **2j** to furnish the heterocycles **9a-d** in 73-85% yields.

Table 4. Pyrrolidine-Catalyzed Cycloaddition of Isoselenocyanates and Carbon Disulfide with Substituted Aziridines[a]



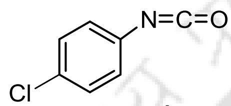
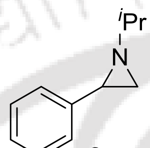
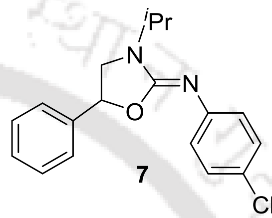
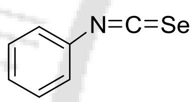
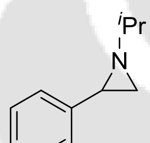
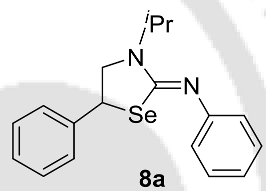
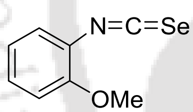
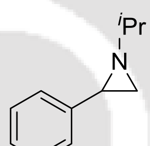
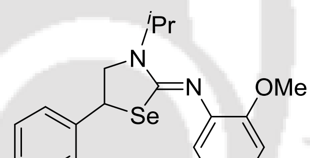
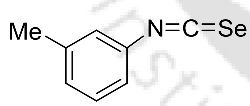
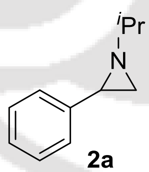
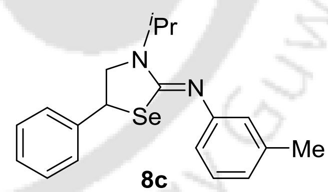
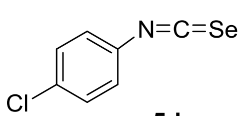
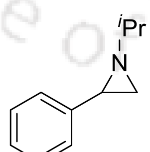
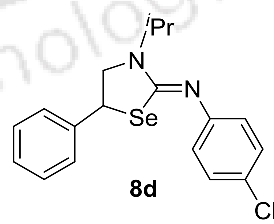
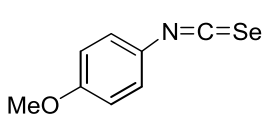
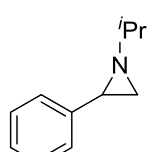
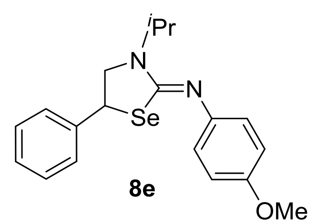
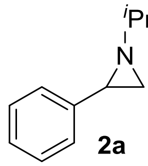
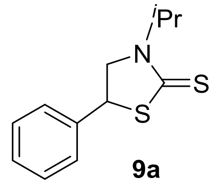
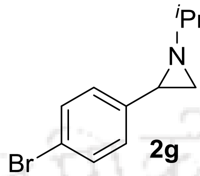
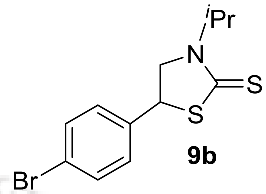
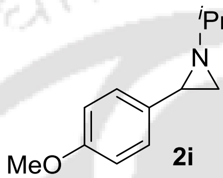
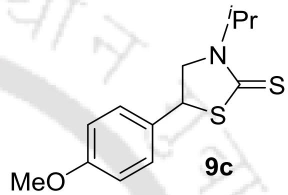
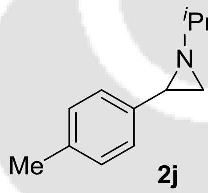
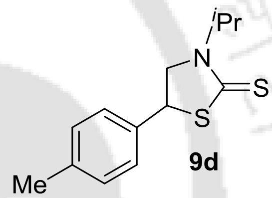
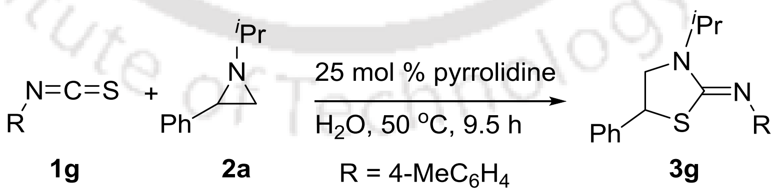
Entry	Substrate	Aziridine	Time (h)	Product	Yield (%)[b]
1	 **4**	 **2a**	3.5	 **7**	n.d.
2	 **5a**	 **2a**	4.0	 **8a**	91
3	 **5b**	 **2a**	2.5	 **8b**	80
4	 **5c**	 **2a**	4.5	 **8c**	83
5	 **5d**	 **2a**	3.5	 **8d**	89
6	 **5e**	 **2a**	6.0	 **8e**	85

Table 4 continued.....

7	S=C=S **6**	 **2a**	8.0	 **9a**	73
8	S=C=S **6**	 **2g**	9.5	 **9b**	85
9	S=C=S **6**	 **2i**	5.5	 **9c**	81
10	S=C=S **6**	 **2j**	7.0	 **9d**	77

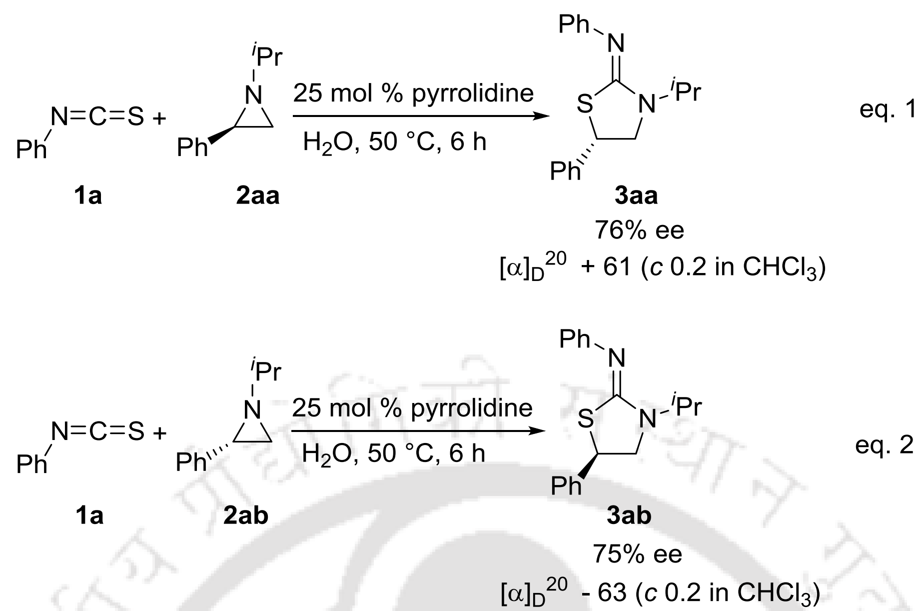
[a] Reaction conditions: **4-5** (0.5 mmol) or **6** (2.5 mmol), **2** (0.5 mmol), pyrrolidine (25 mol %), H_2O (1.0 mL), 50 °C, air. [b] Yield of isolated product. n.d. = not detected.

To reveal the scale up of the process, the reaction of **1g** with **2a** was studied (Scheme 7). As above, the reaction occurred to afford **3g** in 81% yield. This result clearly suggests that the protocol may be employed on the gram scale synthesis of the target heterocycles.

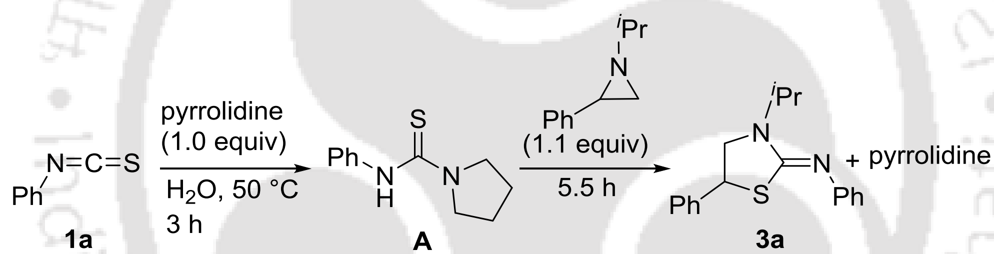


1g 10 mmol 1.49 g; **2a** 10 mmol 1.61 g; **3g** 2.51 g (81%)

Scheme 7. Gram Scale Synthesis



Scheme 8. Reaction of Chiral Aziridines



Scheme 9. Urea Type Intermediate

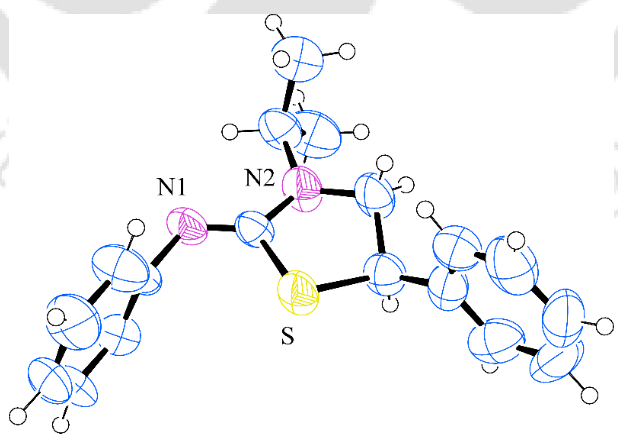
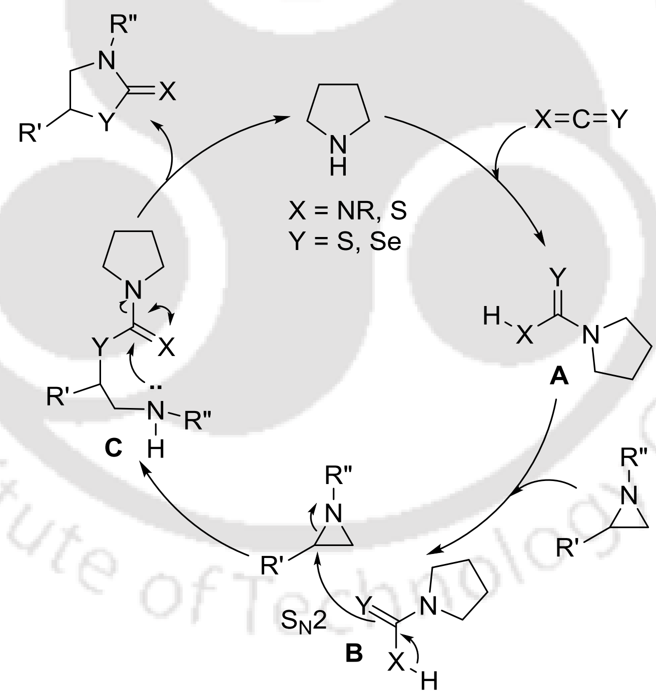


Figure 1. ORTEP diagram of (*R*)-(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)aniline **3ab**. Thermal ellipsoids are drawn at a 50% probability level (CCDC 1025804).

To gain insight into mechanism, optically active aziridines **2aa** and **2ab** having opposite configurations were reacted with heterocumulene **1a** under the optimized reaction conditions (eq. 1 and 2). The reactions proceeded readily to yield the target heterocycles with inverted configurations (Scheme 8). These results suggest that the reaction involves S_N2 pathway. Compound **3ab** in hexane gave crystals whose structure was determined by X-ray analysis and the compound to be of *R* configuration (Figure 1). Furthermore, we were able to isolate and characterize the reactive urea type intermediate **A** when a 1:1 mixture of heterocumulene **1a** and pyrrolidine were reacted (Scheme 9). The isolated intermediate **A** readily underwent reaction with aziridine **2a** to give the target product **3a**. These results suggest that the reaction of pyrrolidine with heterocumulene can yield the reactive urea type intermediate **A** that may proceed reaction with aziridine via intermediate **B** (S_N2) to afford **C**. The intramolecular cyclization of **C** may then give the target heterocycles and the catalyst to complete the catalytic cycle (Scheme 10).



Shcheme 10. Proposed Catalytic Cycle

In conclusion, we have developed an efficient and simple organocatalytic protocol for the (3+2)-cycloaddition reaction of isothiocyanates, isoselenocyanates and carbon disulfide with aziridines under mild conditions. The features of this process include the use of commercial pyrrolidine as the catalyst and involvement of urea type intermediate. These studies can open a new further development of the cycloaddition of isothiocyanates, isoselenocyanates and carbon disulfide with a variety of substrates.

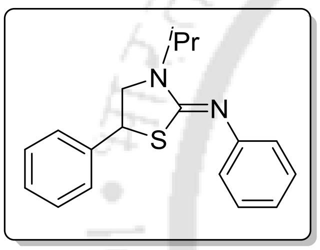
3.3 Experimental Section

General Information. All reactions were performed in pure water (>5 MΩ cm @ 25 °C, total organic content < 30 ppb) obtained from Elix water purification system. Amines and alkenes were purchased from Aldrich and used as received. Selenium (99.9%) and amino acids were purchased from SRL. Aziridines[13] and heterocumulenes[3t] were prepared according to the reported procedure. The reactions were monitored by analytical TLC on Merck silica gel G/GF 254 plates. The column chromatography was performed with Rankem silica gel (60-120 mesh). NMR (^{1}H and ^{13}C) spectra were recorded on DRX-400 Varian and Bruker Avance III 600 spectrometers. The data have been accounted as follows: chemical shifts (δ ppm) (multiplicity, coupling constant (Hz), integration). The abbreviations for multiplicity are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. Chemical shifts (δ) are reported relative to residual solvent signals ($CHCl_3$, 7.24 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR). Melting points were determined with a Büchi B-545 apparatus and are uncorrected. Elemental analyses were recorded using Perkin Elmer CHNS analyzer. Optical rotation was determined by using Perkin Elmer-343 Polarimeter. FT-IR spectra were recorded using Perkin Elmer IR spectrometer. HPLC analysis was carried out using Waters-2489 with Daicel Chiralcel OJ, OJ-H columns using isopropanol and hexane as eluent.

General Procedure for the Cycloaddition of Aziridines with Isothiocyanates and Isoselenocyanates. Isothiocyanate or isoselenocyanate (0.5 mmol), aziridine (0.5 mmol) and pyrrolidine (0.125 mmol) were stirred in H_2O (1 mL) at 50 °C under air (Table 1-4). The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. The reaction mixture was then cooled to room temperature and extracted with diethyl ether (3 x 10 mL). The organic layer was washed with water (5 mL). Drying (Na_2SO_4) and evaporation of the solvent on a rotary evaporator gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as eluent.

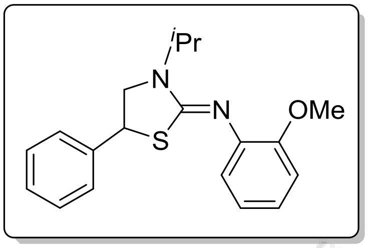
General Procedure for the Cycloaddition of Aziridines with Carbon Disulfide. Carbon disulfide (2.5 mmol) was added portion wise for 0.5 h to a stirred solution of aziridine (0.5 mmol) and pyrrolidine (0.125 mmol) were stirred in H_2O (1 mL) at 50 °C under air and the stirring continued for the appropriate time (Table 4). The progress of the reaction was monitored by TLC using ethyl acetate and hexane as eluent. The reaction mixture was then cooled to room temperature and extracted with diethyl ether (3 x 10 mL). The organic layer was washed with water (5 mL). Drying (Na_2SO_4) and evaporated on a rotary evaporator to give a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as eluent.

3.4 Characterization Data of Products



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3a.
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; colorless solid; yield 86%.
Mp: 108-109 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.32-7.22 (m, 5H), 7.02-6.96 (m, 3H), 4.69-4.64 (m, 2H), 3.86 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.54 (dd, *J* = 10.0, 7.6 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 152.3, 139.3, 128.8, 128.2, 127.5, 123.0, 122.2, 52.9, 46.7, 46.3, 20.0, 19.1.
FT-IR (KBr) 3075, 3034, 2964, 2934, 2856, 1613, 1584, 1178, 1061, 855, 766 cm^{-1}.
Anal. Calcd for $C_{18}H_{20}N_2S$: C, 72.93; H, 6.80; N, 9.45; S, 10.82. Found: C, 72.85; H, 6.82; N, 9.48; S, 10.85.
Compound **3aa**: $[\alpha]_D^{20}$ = + 61.0 (*c* 0.2 in $CHCl_3$); HPLC analysis: 76% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL min^{-1}, λ = 215 nm, t_R = 12.69 min (minor), 18.29 min (major)].

Compound **3ab**: $[\alpha]_D^{20}$ = - 63.0 (*c* 0.2 in $CHCl_3$); HPLC analysis: 75% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL min^{-1}, λ = 215 nm, t_R = 12.58 min (major), 18.79 min (minor)].



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-2 methoxyaniline 3b.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; yield 73%.

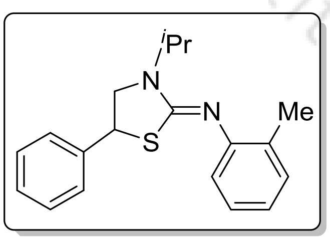
Mp: 107-108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.32-7.23 (m, 3H), 7.00-6.96 (m, 1H), 6.92-6.90 (m, 1H), 6.86-6.82 (m, 2H), 4.75-4.68 (m, 1H), 4.64 (t, *J* = 7.2 Hz, 1H), 3.87 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.80 (s, 3H), 3.54 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 151.8, 141.7, 139.6, 128.7, 128.0, 127.5, 123.9, 123.0, 120.7, 111.6, 55.8, 53.2, 46.5, 46.4, 19.9, 19.1.

FT-IR (KBr) 3056, 3032, 2973, 2947, 2926, 2867, 1623, 1585, 1493, 1187, 1064, 1024, 747 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2OS$: C, 69.90; H, 6.79; N, 8.58; S, 9.82. Found: C, 69.98; H, 6.77; N, 8.55; S, 9.84.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-2-methylaniline 3c.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 71%.

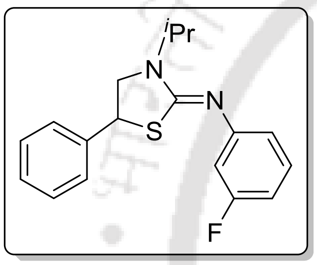
Mp: 74-75 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32-7.25 (m, 3H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.68-4.62 (m, 2H), 3.86 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.54 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.20 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.25 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7, 151.1, 139.6, 130.6, 130.2, 128.9, 128.2, 127.5, 126.4, 123.2, 121.4, 53.3, 46.7, 46.5, 20.0, 19.1, 18.2.

FT-IR (KBr) 3058, 3023, 2971, 2929, 2870, 1626, 1591, 1488, 1456, 1401, 1362, 1243, 1212, 1179, 1110, 1066, 939 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2S$: C, 73.51; H, 7.14; N, 9.02; S, 10.33. Found: C, 73.59; H, 7.13; N, 8.99; S, 10.29.



(*Z*)-3-Fluoro-*N*-(3-isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3d.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; colorless solid; yield 69%.

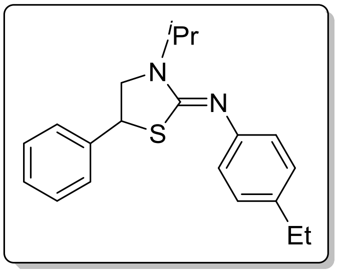
Mp: 91-92 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.36 (m, 2H), 7.32-7.23 (m, 3H), 7.17-7.13 (m, 1H), 6.77-6.74 (m, 1H), 6.72-6.65 (m, 2H), 4.68-4.61 (m, 2H), 3.84 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.53 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, J_{C-F} = 243.4 Hz), 158.5, 154.1 (d, J_{C-F} = 9.9 Hz), 139.0, 129.9 (d, J_{C-F} = 9.9 Hz), 128.9, 128.3, 127.5, 118.0, 109.7 (d, J_{C-F} = 16.8 Hz), 109.5 (d, J_{C-F} = 17.5 Hz) , 52.9, 46.8, 46.4, 20.0, 19.1.

FT-IR (KBr) 3061, 3028, 2975, 2925, 2856, 1618, 1588, 1482, 1402, 1254, 1228, 1182, 1126, 1057, 963 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}FN_2S$: C, 68.76; H, 6.09; N, 8.91; S, 10.20. Found: C, 68.86; H, 6.07; N, 8.89; S, 10.23.



(*Z*)-4-Ethyl-*N*-(3-isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3e.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 80%.

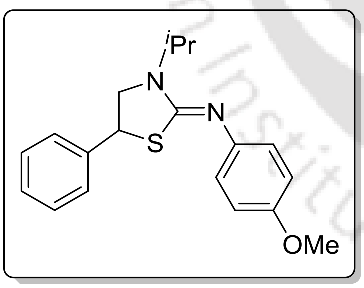
Mp: 63-64 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.33-7.26 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.70-4.63 (m, 2H), 3.85 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.54 (dd, *J* = 10.0, 7.6 Hz, 1H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23-1.18 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.9, 139.3, 138.6, 128.8, 128.2, 128.1, 127.5, 121.9, 52.9, 46.6, 46.2, 28.3, 20.0, 19.0, 15.7.

FT-IR (KBr) 3067, 3020, 2964, 2923, 2861, 1618, 1594, 1504, 1474, 1453, 1404, 1244, 1208, 1194, 1066, 848 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 73.93; H, 7.49; N, 8.67; S, 9.91.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-methoxybenzenamine 3f.[3t]

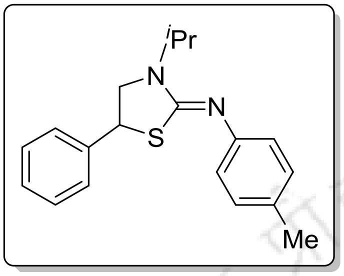
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.53; colorless liquid; yield 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 2H), 7.31-7.22 (m, 3H), 6.91 (d, *J* = 9.2 Hz, 2H), 6.79 (d, *J* = 9.2 Hz, 2H), 4.68-4.60 (m, 2H), 3.83 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.71 (s, 3H), 3.52 (dd, *J* = 9.6, 7.6 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 155.7, 145.4, 139.2, 128.8, 128.1, 127.5, 123.1, 114.1, 55.4, 53.0, 46.7, 46.4, 20.0, 19.1.

FT-IR (neat) 3032, 2970, 2934, 2871, 2059, 1870, 1614, 1504, 1455, 1402, 1364, 1290, 1237, 1179, 1126, 1103, 1066, 1035, 937 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2OS$: C, 69.90; H, 6.79; N, 8.58; S, 9.82. Found: C, 69.98; H, 6.77; N, 8.55; S, 9.84.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-methylbenzenamine 3g.[3t]

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.55; colorless solid; yield 82%.

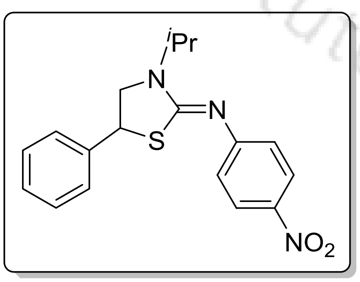
Mp: 89-90 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.33-7.26 (m, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 4.69-4.62 (m, 2H), 3.84 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.53 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.27 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 149.8, 139.3, 132.2, 129.4, 128.8, 128.1, 127.5, 121.9, 52.9, 46.7, 46.3, 21.0, 20.0, 19.1.

FT-IR (KBr) 3025, 2971, 2928, 2870, 1624, 1602, 1505, 1470, 1454, 1402, 1363, 1270, 1242, 1212, 1191, 1126, 1106, 1066, 1030, 938 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2S$: C, 73.51; H, 7.14; N, 9.02; S, 10.33. Found: C, 73.62; H, 7.11; N, 8.98; S, 10.29.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-nitroaniline 3h.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.45; yellow solid; yield 75%.

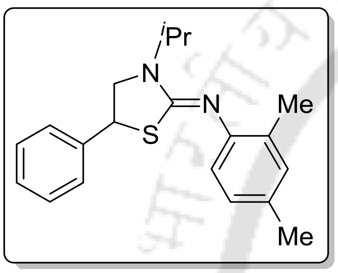
Mp: 68-69 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.39-7.28 (m, 5H), 7.04 (d, *J* = 8.8 Hz, 2H), 4.72 (t, *J* = 7.6 Hz, 1H), 4.70-4.63 (m, 1H), 3.91 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.60 (dd, *J* = 10.0, 8.0 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 158.3, 142.6, 138.5, 128.8, 128.3, 127.2, 124.8, 122.4, 52.8, 46.8, 46.6, 19.7, 19.1.

FT-IR (KBr) 3063, 3038, 2973, 2926, 2869, 2852, 1614, 1571, 1498, 1328, 1218, 1185, 1162, 1108, 1066, 850 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}N_3O_2S$: C, 63.32; H, 5.61; N, 12.31; S, 9.39. Found: C, 63.40; H, 5.60; N, 12.34; S, 9.36.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-2,4-dimethylaniline 3i.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 79%.

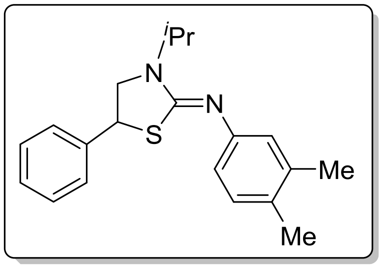
Mp: 69-70 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32-7.25 (m, 3H), 6.94 (s, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 4.68-4.61 (m, 2H), 3.85 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.52 (t, *J* = 8.4 Hz, 1H), 2.24 (s, 3H), 2.17 (s, 3H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.24 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 148.5, 139.7, 132.4, 131.0, 130.2, 128.8, 128.1, 127.5, 126.9, 121.2, 53.2, 46.6, 46.5, 21.0, 19.9, 19.1, 18.1.

FT-IR (KBr) 3063, 2967, 2926, 2844, 1626, 1605, 1492, 1470, 1397, 1242, 1206, 1192, 1166, 1117, 1064, 929 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 74.13; H, 7.44; N, 8.59; S, 9.84.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-3,4-dimethylaniline 3j.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 81%.

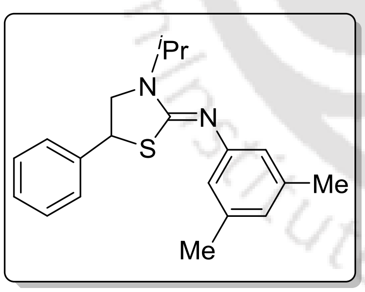
Mp: 96-97 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.34-7.27 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.71-4.63 (m, 2H), 3.84 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.53 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.21 (s, 3H), 2.19 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 150.0, 139.3, 136.8, 130.8, 129.9, 128.7, 128.0, 127.5, 123.4, 119.1, 52.8, 46.6, 46.2, 20.0, 19.9, 19.2, 19.0.

FT-IR (KBr) 3060, 3025, 2973, 2852, 1618, 1594, 1493, 1467, 1454, 1234, 1180, 1149, 1060, 966, 827 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 74.11; H, 7.44; N, 8.60; S, 9.85.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-3,5-dimethylbenzenamine 3k.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 85%.

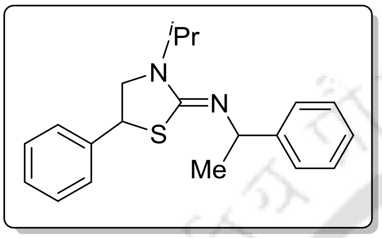
Mp: 74-75 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.34 (m, 1H), 7.38-7.31 (m, 5H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.68 (s, 1H), 4.78-4.71 (m, 1H), 4.68 (t, *J* = 7.6 Hz, 1H), 3.87 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.57 (dd, *J* = 9.6, 8.0 Hz, 1H), 2.33 (s, 6H), 1.32 (d, *J* = 6.8 Hz, 3H), 1.29 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 152.0, 139.2, 138.1, 128.7, 128.0, 127.4, 124.6, 119.7, 52.7, 46.6, 46.2, 21.3, 19.9, 18.9.

FT-IR (KBr) 3029, 2971, 2927, 2867, 1614, 1455, 1402, 1362, 1289, 1240, 1210, 1143, 1068, 1027, 953 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 73.95; H, 7.45; N, 8.67; S, 9.93.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-1-phenylethanamine 3l.

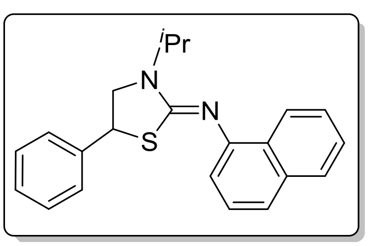
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.49; pale yellow liquid; yield 70%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (m, 4H), 7.35-7.25 (m, 5H), 7.21-7.16 (m, 1H), 4.63-4.56 (m, 2H), 4.29 (q, *J* = 6.4 Hz, 1H), 3.69 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.41 (dd, *J* = 9.6, 7.2 Hz, 1H), 1.46 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 147.2, 140.1, 128.8, 128.1, 128.0, 127.5, 126.5, 126.3, 64.1, 52.7, 46.6, 46.2, 25.9, 19.7, 18.9.

FT-IR (neat) 3049, 3029, 2917, 2858, 1633, 1588, 1489, 1451, 1312, 1258, 1183, 1074, 1025, 908 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2S$: C, 74.03; H, 7.46; N, 8.63; S, 9.88. Found: C, 74.14; H, 7.44; N, 8.59; S, 9.83.



(*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3m.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 82%.

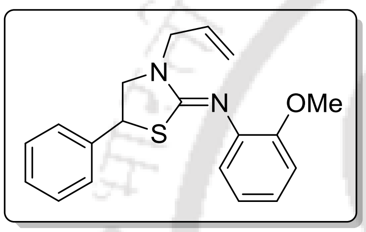
Mp: 102-103 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 3.6 Hz, 1H), 7.69-7.68 (m, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.35-7.33 (m, 2H), 7.28-7.25 (m, 3H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.15-7.12 (m, 1H), 6.95 (d, *J* = 6.6 Hz, 2H), 4.80-4.78 (m, 1H), 4.55 (t, *J* = 7.2 Hz, 1H), 3.81 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.49 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 148.9, 139.4, 134.5, 128.9, 128.2, 127.9, 127.5, 126.0, 125.1, 124.1, 123.0, 116.2, 53.2, 46.8, 46.6, 20.2, 19.4.

FT-IR (KBr) 3050, 3020, 2969, 2916, 2870, 2848, 1604, 1568, 1501, 1456, 1386, 1276, 1242, 1215, 1174, 1063, 1038, 926 cm^{-1}.

Anal. Calcd for $C_{22}H_{22}N_2S$: C, 76.26; H, 6.40; N, 8.08; S, 9.26. Found: C, 76.20; H, 6.41; N, 8.11; S, 9.28.



(*Z*)-*N*-(3-Allyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3n.

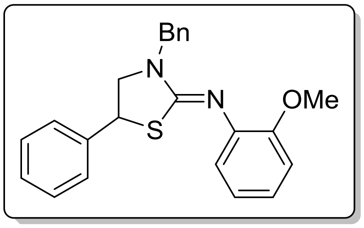
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.54; yellow liquid; yield 70%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 3H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 6.4 Hz, 2H), 5.99-5.89 (m, 1H), 5.27-5.19 (m, 2H), 4.71 (t, *J* = 7.2 Hz, 1H), 4.21-4.18 (m, 2H), 3.86-3.84 (m, 1H), 3.81 (s, 3H), 3.57 (t, *J* = 8.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 151.8, 141.4, 139.2, 133.0, 128.7, 128.1, 127.6, 124.1, 122.9, 120.8, 118.0, 111.8, 58.2, 55.9, 49.3, 46.7.

FT-IR (neat) 3064, 3025, 3006, 2952, 2924, 2832, 1627, 1586, 1493, 1466, 1453, 1399, 1247, 1173, 1110, 1046, 1027, 1005, 927 cm^{-1}.

Anal. Calcd for $C_{19}H_{20}N_2OS$: C, 70.34; H, 6.21; N, 8.63; S, 9.88. Found: C, 70.42; H, 6.19; N, 8.60; S, 9.85.



(*Z*)-*N*-(3-Benzyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3o.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; colorless solid; yield 78%.

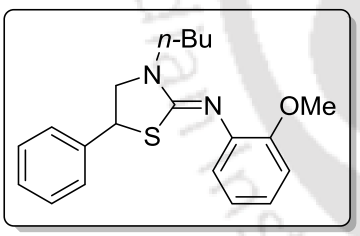
Mp: 87-88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.38-7.35 (m, 4H), 7.31-7.25 (m, 4H), 7.05-7.02 (m, 2H), 7.00-6.91(m, 2H), 4.90 (d, *J* = 14.8, 1H), 4.80 (d, *J* = 14.8, 1H), 4.70 (t, *J* = 7.6, 1H), 3.88 (s, 3H), 3.78 (dd, *J* = 10.0, 7.6 Hz, 1H), 3.52 (dd, *J* = 10.0, 8.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 151.9, 141.5, 139.1, 137.2, 128.8, 128.7, 128.6, 128.1, 127.6, 127.5, 124.1, 122.9, 120.9, 111.8, 57.9, 56.0, 50.2, 46.8.

FT-IR (KBr) 3080, 3061, 3025, 2990, 2960, 2916, 2867, 1624, 1585, 1493, 1452, 1407, 1360, 1240, 1213, 1152, 1110, 1023, 920 cm^{-1}.

Anal. Calcd for $C_{23}H_{22}N_2OS$: C, 73.76; H, 5.92; N, 7.48; S, 8.56. Found: C, 73.69; H, 5.94; N, 7.51; S, 8.53.



(*Z*)-*N*-(3-Butyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3p.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.61; colorless solid; yield 83%.

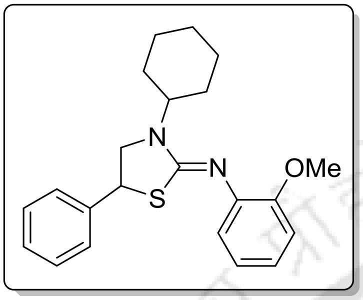
Mp: 71-72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.33-7.26 (m, 3H), 7.02-6.98 (m, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.87 (t, *J* = 6.4 Hz, 2H), 4.67 (t, *J* = 7.6 Hz, 1H), 3.88 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.81 (s, 3H), 3.63-3.57 (m, 3H), 1.68-1.63 (m, 2H), 1.42 (q, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 151.8, 141.8, 139.5, 128.7, 128.0, 127.5, 123.9, 123.0, 120.7, 111.7, 58.6, 55.8, 46.7, 46.2, 29.3, 20.2, 14.0.

FT-IR (KBr) 3064, 3001, 2956, 2924, 2857, 2829, 1628, 1582, 1495, 1457, 1403, 1293, 1248, 1225, 1176, 1101, 1046, 1027, 988 cm^{-1}.

Anal Calcd for $C_{20}H_{24}N_2OS$: C, 70.55; H, 7.10; N, 8.23; S, 9.42. Found: C, 70.65; H, 7.09; N, 8.20; S, 9.38.



(*Z*)-*N*-(3-Cyclohexyl-5-phenylthiazolidin-2-ylidene)-2-methoxyaniline 3q.

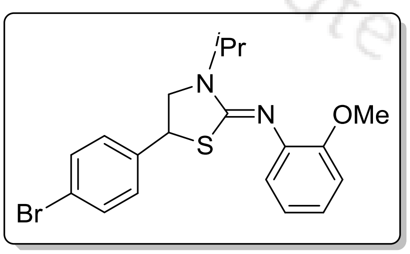
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.59; yellow liquid; yield 69%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 3H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.88-6.85 (m, 2H), 4.61 (t, *J* = 6.8 Hz, 1H), 4.36-4.31 (m, 1H), 3.91 (t, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.59 (t, *J* = 8.0 Hz, 1H), 2.03-1.65 (m, 5H), 1.48-1.06 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 151.8, 141.8, 139.8, 128.7, 128.0, 127.4, 123.9, 123.3, 120.8, 111.8, 55.9, 54.5, 54.3, 46.6, 30.5, 29.7, 25.8, 25.7, 25.6.

FT-IR (neat) 3060, 3020, 2937, 2851, 2829, 1628, 1583, 1493, 1466, 1401, 1302, 1231, 1173, 1111, 1046, 1028, 910, 891, 806 cm^{-1}.

Anal. Calcd for $C_{22}H_{26}N_2OS$: C, 72.09; H, 7.15; N, 7.64; S, 8.75. Found: C, 72.00; H, 7.13; N, 7.66; S, 8.71.



(*Z*)-*N*-(5-(4-Bromophenyl)-3-isopropylthiazolidin-2-ylidene)-2-methoxyaniline 3s.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; colorless solid; yield 85%.

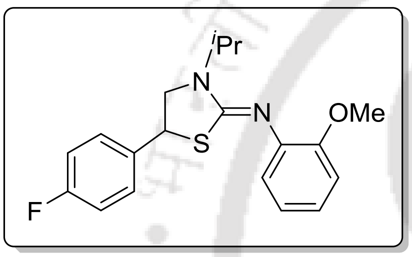
Mp: 79-80 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.01-6.98 (m, 1H), 6.92-6.85 (m, 3H), 4.73-4.70 (m, 1H), 4.56 (t, *J* = 6.8 Hz, 1H), 3.87 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.81 (s, 3H), 3.50 (dd, *J* = 9.2, 6.4 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 151.7, 141.6, 139.1, 131.8, 129.2, 124.1, 123.0, 121.9, 120.8, 111.7, 55.9, 53.2, 46.5, 45.8, 19.7, 19.3.

FT-IR (KBr) 3050, 3004, 2968, 2927, 2845, 2823, 1627, 1585, 1490, 1467, 1399, 1275, 1260, 1235, 1177, 1110, 1061, 934 cm^{-1}.

Anal. Calcd for $C_{19}H_{21}BrN_2OS$: C, 56.30; H, 5.22; N, 6.91; S, 7.91. Found: C, 56.38; H, 5.20; N, 6.89; S, 7.87.



(*Z*)-*N*-(5-(4-Fluorophenyl)-3-isopropylthiazolidin-2-ylidene)-2-methoxyaniline 3t.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.55; colorless solid; yield 74%.

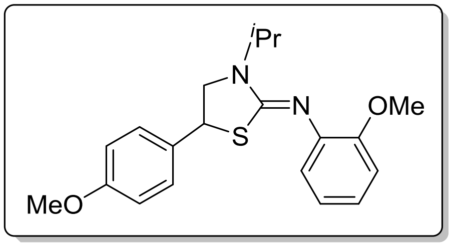
Mp: 120-121 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.02-6.99 (m, 3H), 6.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.87-6.85 (m, 2H), 4.74-4.72 (m, 1H), 4.62 (t, *J* = 6.6 Hz, 1H), 3.87 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.82 (s, 3H), 3.51 (dd, *J* = 9.6, 7.2 Hz, 1H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.23 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.2 ((d, J_{C-F} = 215.3 Hz), 151.8, 141.6, 135.7, 135.6, 129.3 (d, J_{C-F} = 8.0 Hz), 124.1, 123.1, 120.9, 115.8 (d, J_{C-F} = 21.3 Hz), 111.8, 56.0, 53.5, 46.5, 45.9, 19.9, 19.3.

FT-IR (KBr) 3053, 3034, 2965, 2927, 2861, 2834, 1625, 1585, 1510, 1493, 1466, 1240, 1224, 1174, 1114, 1026, 939 cm^{-1}.

Anal. Calcd for $C_{19}H_{21}FN_2OS$: C, 66.25; H, 6.15; N, 8.13; S, 9.31. Found: C, 66.32; H, 6.13; N, 8.16; S, 9.35.



(*Z*)-*N*-(3-Isopropyl-5-(4-methoxyphenyl)thiazolidin-2-ylidene)-2-methoxyaniline 3u.

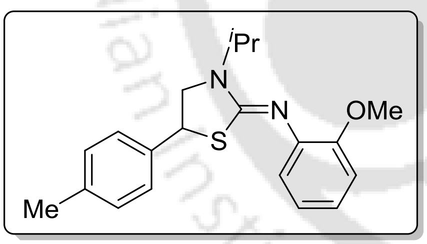
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.51; yellow liquid; yield 89%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.87-6.83 (m, 4H), 4.76-4.72 (m, 1H), 4.64 (t, *J* = 7.2 Hz, 1H), 3.86 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.54 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 152.1, 131.4, 128.8, 124.3, 123.4, 120.9, 120.8, 114.2, 111.9, 56.1, 55.5, 53.8, 46.7, 46.4, 20.1, 19.2.

FT-IR (neat) 3061, 2969, 2932, 2834, 1623, 1585, 1512, 1493, 1463, 1355, 1254, 1177, 1029, 928 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.79; N, 7.86; S, 8.99. Found: C, 67.30; H, 6.81; N, 7.83; S, 9.03.



(*Z*)-*N*-(3-Isopropyl-5-(*p*-tolyl)thiazolidin-2-ylidene)-2-methoxyaniline 3v.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless solid; yield 77%.

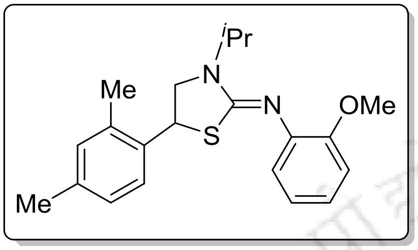
Mp: 117-118 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 6.8 Hz, 1H), 6.91 (d, *J* = 6.8 Hz, 1H), 6.85 (d, *J* = 6.8 Hz, 2H), 4.72-4.69 (m, 1H), 4.61 (t, *J* = 6.8 Hz, 1H), 3.84 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.80 (s, 3H), 3.51 (dd, *J* = 9.2, 8.0 Hz, 1H), 2.30 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 151.9, 141.7, 137.9, 136.5, 129.5, 127.5, 124.0, 123.1, 120.8, 111.8, 56.0, 53.5, 46.6, 46.5, 21.2, 20.0, 19.2.

FT-IR (KBr) 3040, 3009, 2973, 2923, 2848, 2834, 1629, 1586, 1492, 1469, 1450, 1402, 1260, 1236, 1220, 1180, 1158, 1111, 1062, 1045, 1025, 820 cm^{-1}.

Anal. Calcd for $C_{20}H_{24}N_2OS$: C, 70.55; H, 7.10; N, 8.23; S, 9.42. Found: C, 70.65; H, 7.09; N, 8.20; S, 9.38.



(*Z*)-*N*-(5-(2,4-Dimethylphenyl)-3-isopropylthiazolidin-2-ylidene)-2-methoxyaniline 3w.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; colorless solid; yield 73%.

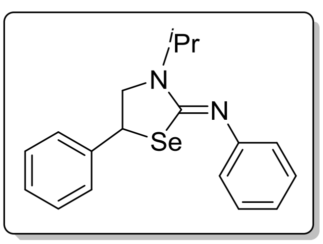
Mp: 84-85 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.03-6.98 (m, 2H), 6.95 (s, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.76-4.74 (m, 1H), 3.85 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.82 (s, 3H), 3.57 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.29 (s, 3H), 2.28 (s, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.27 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 151.9, 141.7, 137.5, 135.5, 134.4, 131.3, 127.3, 126.7, 123.9, 123.1, 120.8, 111.7, 55.9, 52.1, 46.5, 42.3, 21.1, 19.9, 19.6, 19.2.

FT-IR (KBr) 3058, 2970, 2924, 2859, 2831, 1624, 1585, 1493, 1464, 1402, 1362, 1257, 1236, 1177, 1113, 1046, 1028, 934 cm^{-1}.

Anal. Calcd for $C_{21}H_{26}N_2OS$: C, 71.15; H, 7.39; N, 7.90; S, 9.04. Found: C, 71.22; H, 7.37; N, 7.93; S, 9.00.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 8a.[3t]

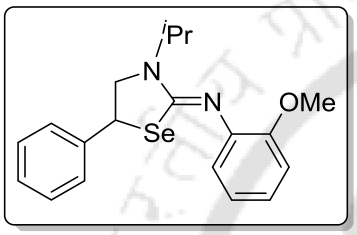
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.67; yellow liquid; yield 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.31-7.22 (m, 5H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 2H), 4.78-4.72 (m, 2H), 3.85 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.65 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.26 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.1, 140.0, 128.5, 128.3, 127.4, 127.2, 122.8, 121.3, 53.4, 46.8, 41.6, 19.6, 19.0.

FT-IR (neat) 3058, 3027, 2971, 2929, 2869, 1614, 1590, 1489, 1454, 1402, 1363, 1243, 1205, 1185, 1163, 1126, 1069, 1024 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}N_2Se$: C, 62.97; H, 5.87; N 8.16. Found: C, 63.07; H, 5.83; N, 8.19.



((*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-2-methoxybenzenamine 8b.[3t]

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.60; colorless solid; yield 80%.

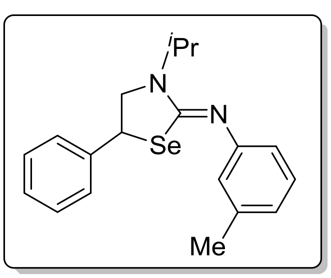
Mp: 107-108 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.27-7.18 (m, 3H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 2H), 4.83-4.80 (m, 1H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.83 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.76 (s, 3H), 3.63 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.26 (t, *J* = 7.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 151.6, 142.7, 140.2, 128.4, 127.5, 127.4, 123.9, 122.0, 120.6, 111.5, 55.6, 54.0, 47.1, 41.8, 19.8, 19.1.

FT-IR (KBr) 3026, 2970, 2923, 2870, 1623, 1586, 1493, 1464, 1400, 1363, 1236, 1204, 1184, 1112, 1047, 1027 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2OSe$: C, 61.12; H, 5.94; N, 7.50. Found: C, 61.19; H, 5.90; N, 7.47.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-3-methylbenzenamine 8c.[3t]

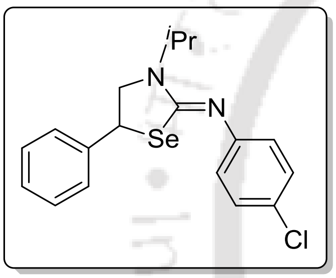
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.62; colorless liquid; yield 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.29-7.19 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.85-6.80 (m, 3H), 4.81-4.77 (m, 1H), 4.72 (t, *J* = 6.8 Hz, 1H), 3.80 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.62 (dd, *J* = 10.4, 8.0 Hz, 1H), 2.30 (s, 3H), 1.28 (d, *J* = 4.8 Hz, 3H), 1.26 (d, *J* = 4.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.2, 140.1, 138.3, 128.5, 127.6, 127.5, 123.8, 122.3, 118.3, 53.6, 47.0, 41.8, 21.3, 19.9, 19.2.

FT-IR (neat) 3030, 2971, 2927, 2862, 1613, 1593, 1455, 1400, 1362, 1282, 1207, 1185, 1069 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2Se$: C, 63.86; H, 6.21; N, 7.84. Found: C, 63.87; H, 6.23; N, 7.80.



(*Z*)-4-Chloro-*N*-(3-isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)benzenamine 8d.[3t]

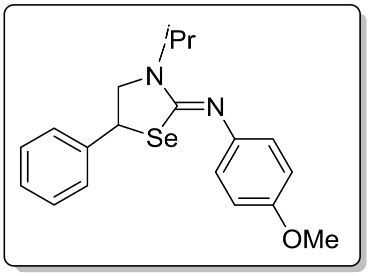
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.58; yellow liquid; yield 89%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.30-7.22 (m, 3H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.78-4.68 (m, 2H), 3.84 (dd, *J* = 10.4, 6.8 Hz, 1H), 3.65 (dd, *J* = 10.4, 8.0 Hz, 1H), 1.24 (t, *J* = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 151.8, 139.8, 128.7, 128.6, 128.0, 127.8, 127.4, 123.0, 53.8, 47.2, 42.2, 19.8, 19.2.

FT-IR (neat) 3061, 3029, 2972, 2930, 2870, 1614, 1585, 1485, 1404, 1364, 1274, 1243, 1205, 1185, 1162, 1088, 1068, 1009 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}ClN_2Se$: C, 57.23; H, 5.07; N, 7.42. Found: C, 57.31; H, 5.08; N, 7.39.



(*Z*)-*N*-(3-Isopropyl-5-phenyl-1,3-selenazolidin-2-ylidene)-4-methoxybenzenamine 8e.[3t]

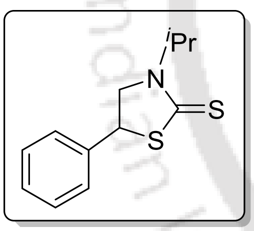
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.57; yellow liquid; yield 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.33-7.25 (m, 3H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.82-4.75 (m, 2H), 3.86 (dd, *J* = 10.4, 6.4 Hz, 1H), 3.73 (s, 3H), 3.67 (dd, *J* = 10.4, 7.6 Hz, 1H), 1.31 (d, *J* = 4.8 Hz, 3H), 1.29 (d, *J* = 4.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 155.7, 146.8, 140.2, 128.6, 127.6, 127.5, 122.3, 113.9, 55.1, 53.7, 47.1, 41.8, 19.8, 19.2.

FT-IR (neat) 3031, 2971, 2870, 2833, 1614, 1504, 1464, 1401, 1363, 1294, 1239, 1205, 1185, 1067, 1035, 981 cm^{-1}.

Anal. Calcd for $C_{19}H_{22}N_2OSe$: C, 61.12; H, 5.94; N, 7.50. Found: C, 61.05; H, 5.96; N, 7.54.



3-Isopropyl-5-phenylthiazolidine-2-thione 9a.

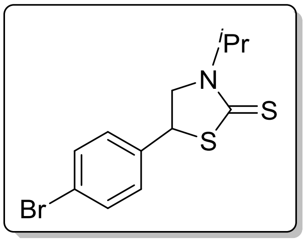
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.56; colorless liquid; yield 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 5H), 5.21-5.14 (m, 1H), 4.79 (dd, *J* = 7.6, 6.8 Hz, 1H), 4.28 (dd, *J* = 11.6, 8.4 Hz, 1H), 3.94 (dd, *J* = 11.6, 6.8 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 138.9, 129.1, 128.5, 127.2, 58.4, 49.6, 47.2, 19.6, 19.2.

FT-IR (neat) 3056, 3031, 2972, 2930, 2873, 1668, 1601, 1472, 1430, 1367, 1300, 1275, 1239, 1201, 1184, 1076, 1029, 973 cm^{-1}.

Anal. Calcd for $C_{12}H_{15}NS_2$: C, 60.72; H, 6.37; N, 5.90; S, 27.02. Found: C, 60.63; H, 6.38; N, 5.93; S, 27.06.



5-(4-Bromophenyl)-3-isopropylthiazolidine-2-thione 9b.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.52; colorless solid; yield 85%.

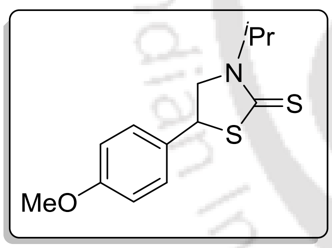
Mp: 69-70 °C.

^{1}H NMR (400 MHz, $CDCl_3$) 7.46 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.18-5.11 (m, 1H), 4.71 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.26 (dd, *J* = 11.6, 8.4 Hz, 1H), 3.87 (dd, *J* = 11.6, 6.4 Hz, 1H), 1.23 (d, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 138.1, 132.1, 128.8, 122.3, 58.2, 49.6, 46.4, 19.4, 19.2.

FT-IR (KBr) 3042, 2970, 2923, 2867, 1663, 1610, 1582, 1510, 1481, 1432, 1369, 1301, 1241, 1199, 1182, 1072, 1029, 1008, 823 cm^{-1}.

Anal. Calcd for $C_{12}H_{14}BrNS_2$: C, 45.57; H, 4.46; N, 4.43; S, 20.28. Found: C, 45.65; H, 4.44; N, 4.40; S, 20.32.



3-Isopropyl-5-(4-methoxyphenyl)thiazolidine-2-thione 9c.

Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.40; colorless solid; yield 81%.

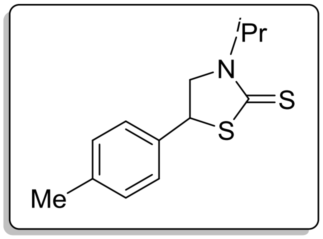
Mp: 62-63 °C.

^{1}H NMR (400 MHz, $CDCl_3$) 7.27 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.23-5.13 (m, 1H), 4.74 (t, *J* = 8.0 Hz, 1H), 4.22 (dd, *J* = 11.6, 8.0 Hz, 1H), 3.88 (dd, *J* = 11.6, 6.8 Hz, 1H), 3.77 (s, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.3, 130.5, 128.2, 114.7, 58.3, 55.1, 49.3, 46.5, 19.3, 19.0.

FT-IR (KBr) 3009, 2975, 2948, 2925, 2898, 2828, 1662, 1607, 1509, 1480, 1465, 1433, 1369, 1303, 1280, 1250, 1200, 1175, 1075, 1033, 831 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}NOS_2$: C, 58.39; H, 6.41; N, 5.24; S, 23.98. Found: C, 58.50; H, 6.40; N, 5.21; S, 23.94.



3-Isopropyl-5-(*p*-tolyl)thiazolidine-2-thione 9d.

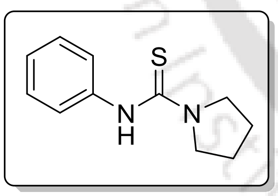
Analytical TLC on silica gel, 1:9 ethyl acetate/hexane R_f = 0.49; colorless liquid; yield 77%.

^{1}H NMR (400 MHz, $CDCl_3$) 7.25 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 5.20-5.13 (m, 1H), 4.77 (t, *J* = 8.0 Hz, 1H), 4.26 (dd, *J* = 11.6, 8.4 Hz, 1H), 3.91 (dd, *J* = 11.6, 6.8 Hz, 1H), 2.31 (s, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 138.2, 135.7, 129.6, 127.0, 58.3, 49.5, 46.9, 21.0, 19.5, 19.1.

FT-IR (neat) 3017, 2972, 2927, 2873, 1654, 1610, 1512, 1472, 1431, 1360, 1297, 1239, 1185, 1076, 1036, 816 cm^{-1}.

Anal. Calcd for $C_{13}H_{17}NS_2$: C, 62.11; H, 6.82; N, 5.57; S, 25.50. Found: C, 62.21; H, 6.80; N, 5.54; S, 25.45.



***N*-Phenylpyrrolidine-1-carbothioamide A.**

Phenyl isothiocyanate (0.5 mmol) and pyrrolidine (0.5 mmol) were stirred in H_2O (1 mL) for 3 h at 50 ºC under air. Then, the reaction mixture was then cooled to room temperature and extracted with dichloromethane (3 x 10 mL). The organic layer was washed with water (5 mL). Drying (Na_2SO_4) and evaporated on a rotary evaporator to give a colorless solid; yield 95% (98 mg).

Mp: 121-122 °C.

^{1}H NMR (400 MHz, $CDCl_3$) 7.34-7.30 (m, 4H), 7.19-7.16 (m, 1H), 6.91(s, 1H), 3.66 (s, 4H), 2.01 (s, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 139.4, 128.4, 125.8, 125.6, 52.2, 25.7

FT-IR (KBr) 3249, 3038, 2953, 2933, 2867, 1593, 1538, 1496, 1459, 1407, 1342, 1356, 1302, 1291, 1222, 949, 854, 725, 696 cm^{-1}

Anal. Calcd for $C_{18}H_{20}N_2S$: C, 64.04; H, 6.84; N, 13.58; S, 15.54. Found: C, 64.12; H, 6.82; N, 13.55; S, 15.51.

Crystal Data and Structure Refinement for 3ab at 296(2) K

Identification code	MSN-3ab
CCDC number	1025804
Empirical formula	$C_{18}H_{20}N_2S$
Formula weight	296.42
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2(1)
	Loop xyz
	'x, y, z' '-x, y+1/2, -z'
Unit cell dimensions	*a* = 10.2531 (3) Å α(°)= 90.00
	b = 9.5647 (3) Å β(°)=104.131 (2)
	c = 17.4780 (6) Å γ(°)= 90.00
Volume	1662.16 (9) $Å^3$
Z	4
Density (calculated)	1.184 Mg/m^3
Absorption coefficient	0.190 mm^{-1}
F(000)	632.0
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	1.20 to 27.05°
Index ranges	-10<=h<=13, -10<=k<=12, -18<=l<=22
Reflections collected	7283
Independent reflections	3247 [R (int) = 0.0464]
Completeness to theta = 27.05°	99%
Absorption correction	Multi-scan
Max. and min. transmission	0.963 and 0.934
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7283/ 1 /383
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma (I)]	*R1* = 0.0464, *wR2* = 0.1370
R indices (all data)	*R1* = 0.0584, *wR2* = 0.1486

3.5 References

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4. For example, see (a) Albrecht, Ł.; Dickmeiss, G.; Cruz Acosta, F.; Rodríguez-Escrich, C.; Davis, R. L.; Jørgensen, K. A. *J. Am. Chem. Soc*. **2012**, *134*, 2543. (b) Albrecht, Ł.; Dickmeiss, G.; Weise, C. F.; Rodríguez-Escrich, C.; Jørgensen, K. A. *Angew. Chem., Int. Ed*. **2012**, *51*, 13109. (c) Jiang, X.-X.; Zhang, Y.-F.; Chan, A. S. C.; Wang, R. *Org. Lett.* **2009**, *11*, 153.
5. (a) Xue, F.; Zhang, S.; Duan, W.; Wang, W. *Adv. Synth. Catal.* **2008**, *350*, 2194. (b) Rasappan, R.; Reiser, O. *Eur. J. Org. Chem.* **2009**, 1305.
6. (a) Grieco, P. A. *Organic Synthesis in Water*, Springer, New York, 1997. (b) Hailes, H. C. *Org. Process Res. Dev.* **2007**, *11*, 114. (c) Lindstroem, U. M. *Organic Reactions in Water*, Blackwell, Oxford, UK, 2007. (d) Anastas, P. T. *Handbook of Green Chemistry*, Wiley-VCH, Weinheim, 2010.

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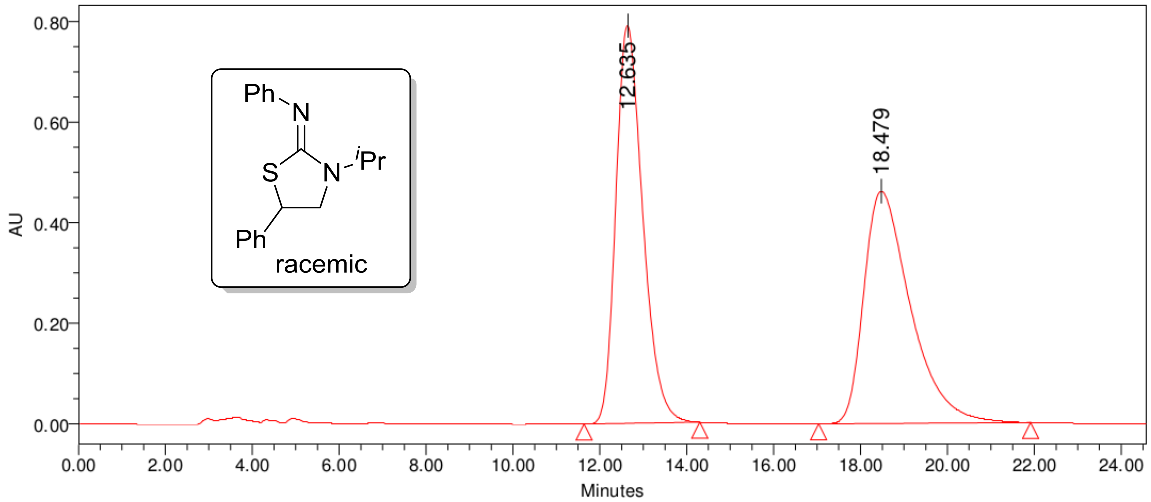
15. Coskun, N.; Cetin, M.; Gronert, S.; Ma, J.; Erden, I. *Tetrahedron* **2005**, *71*, 2636.

3.6 HPLC Chromatogram



Peak Results

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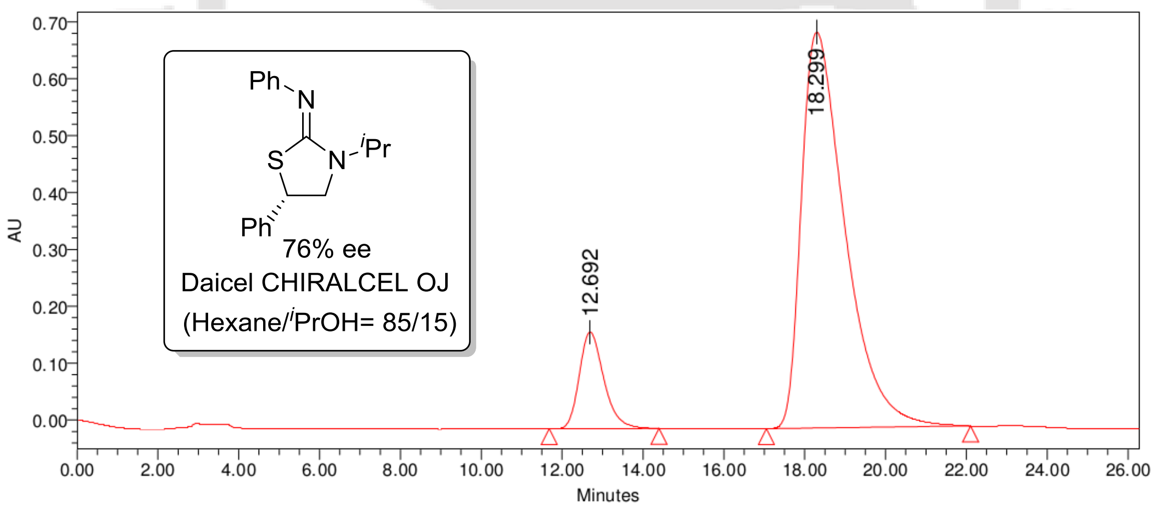

Peak Results

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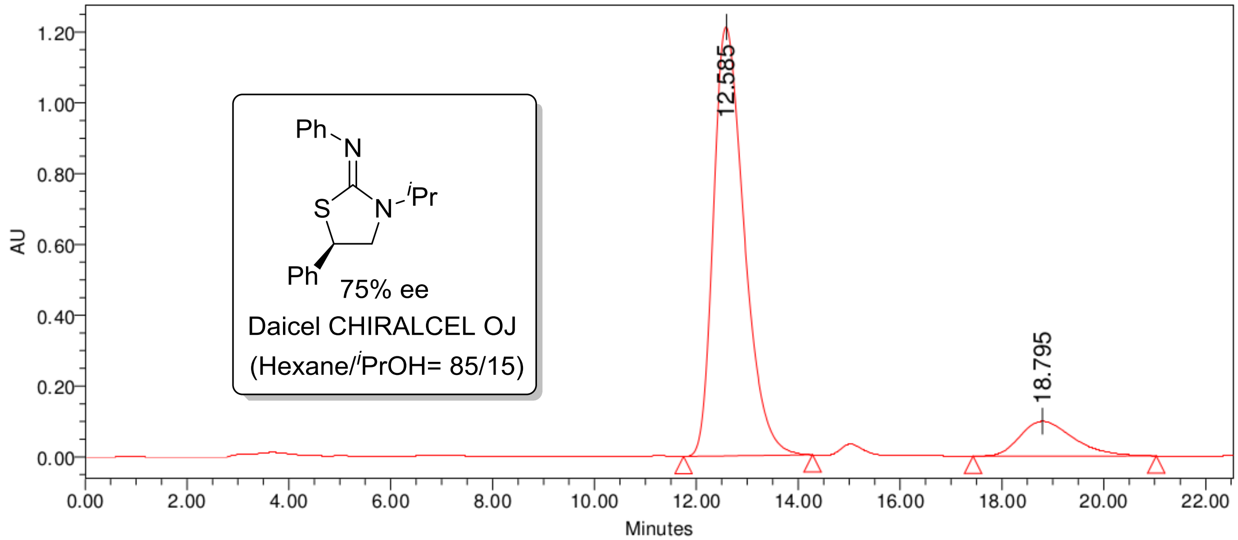

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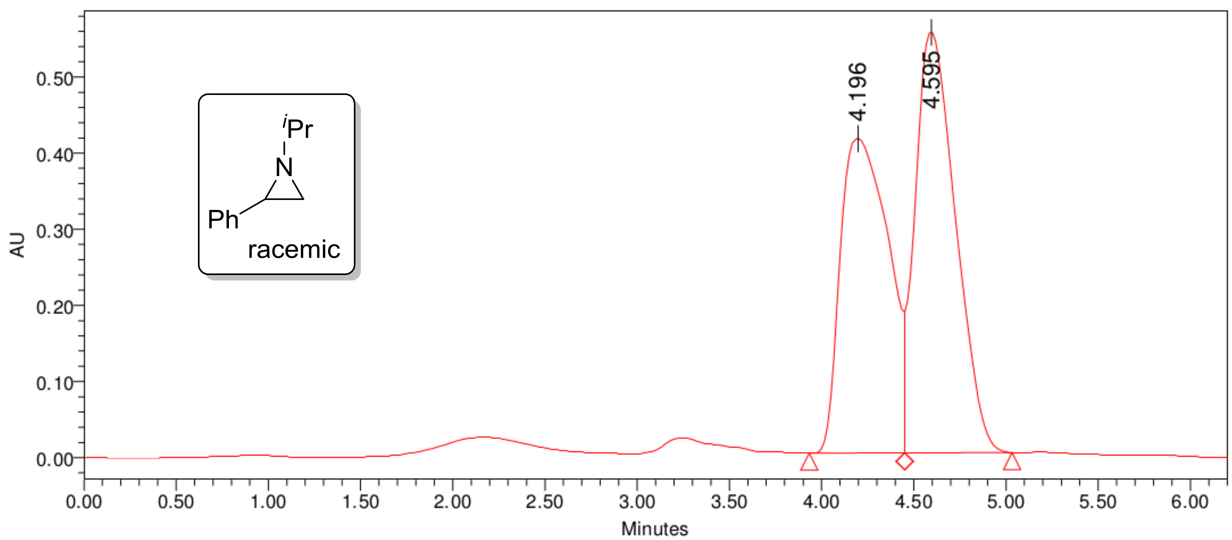

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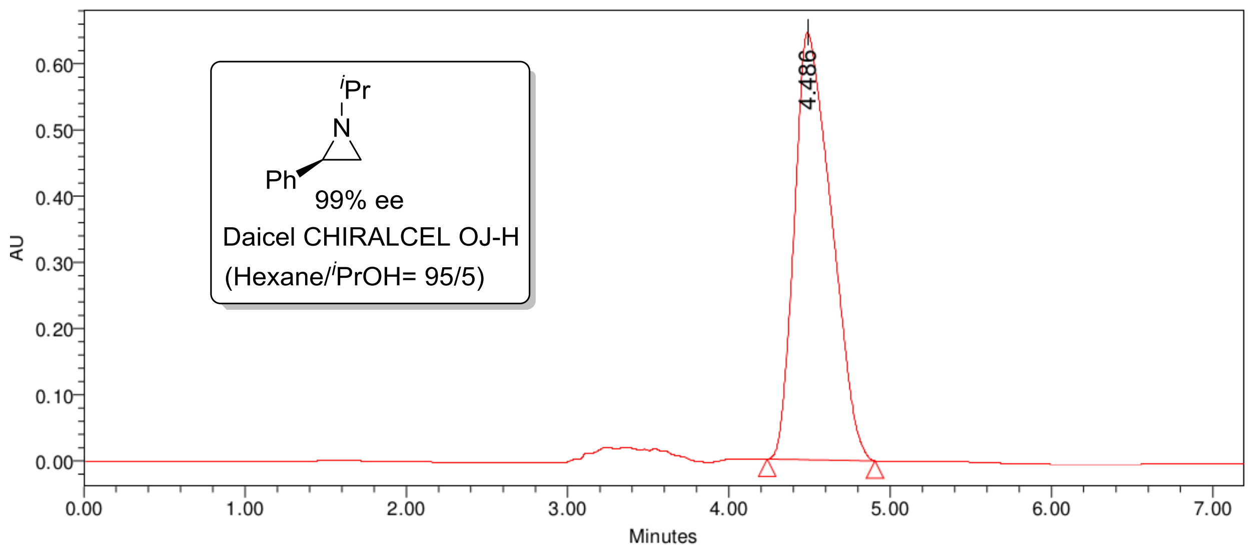

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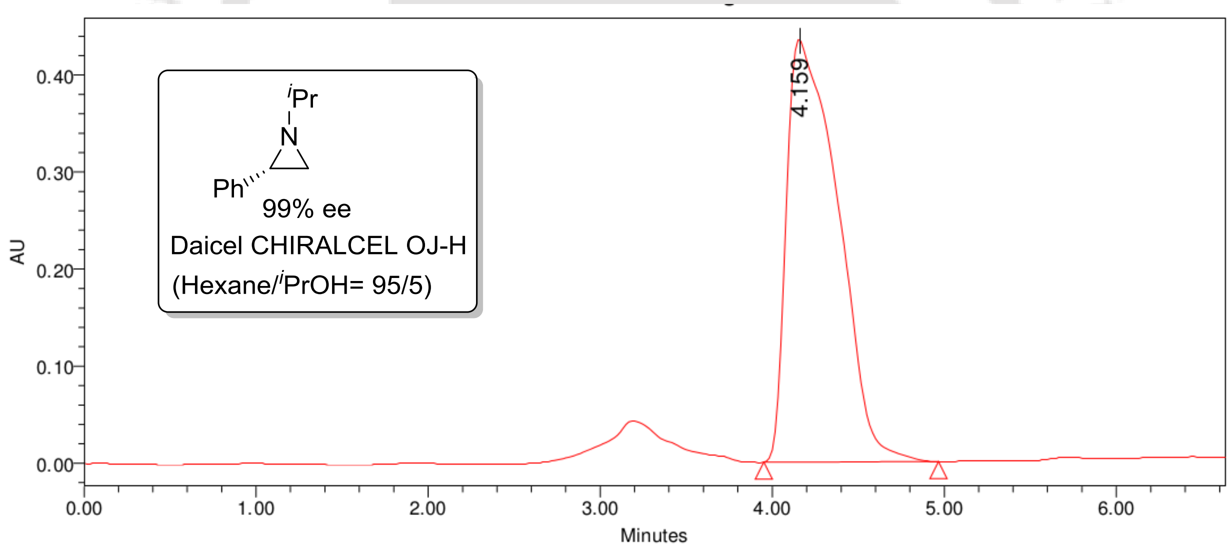

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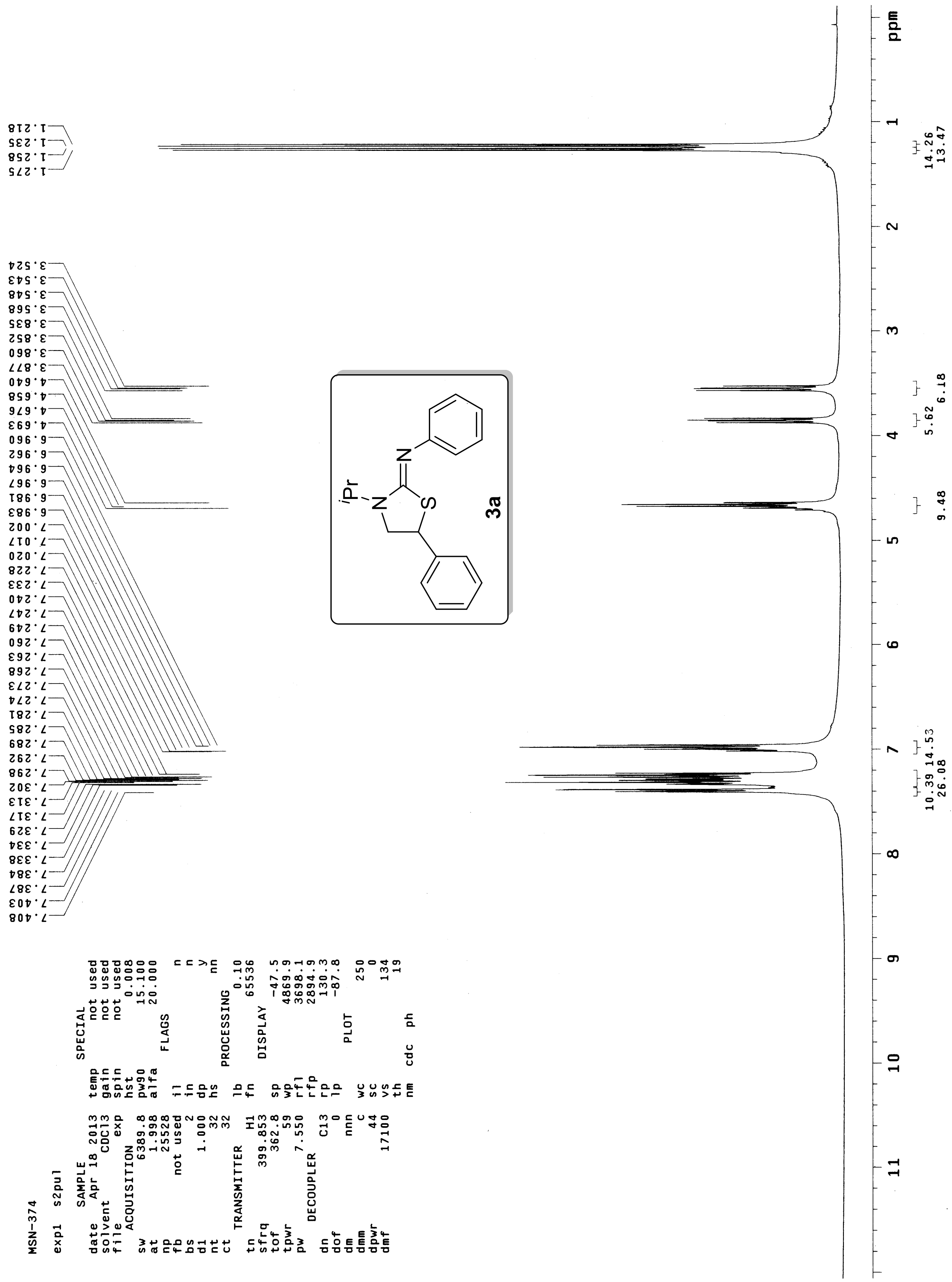
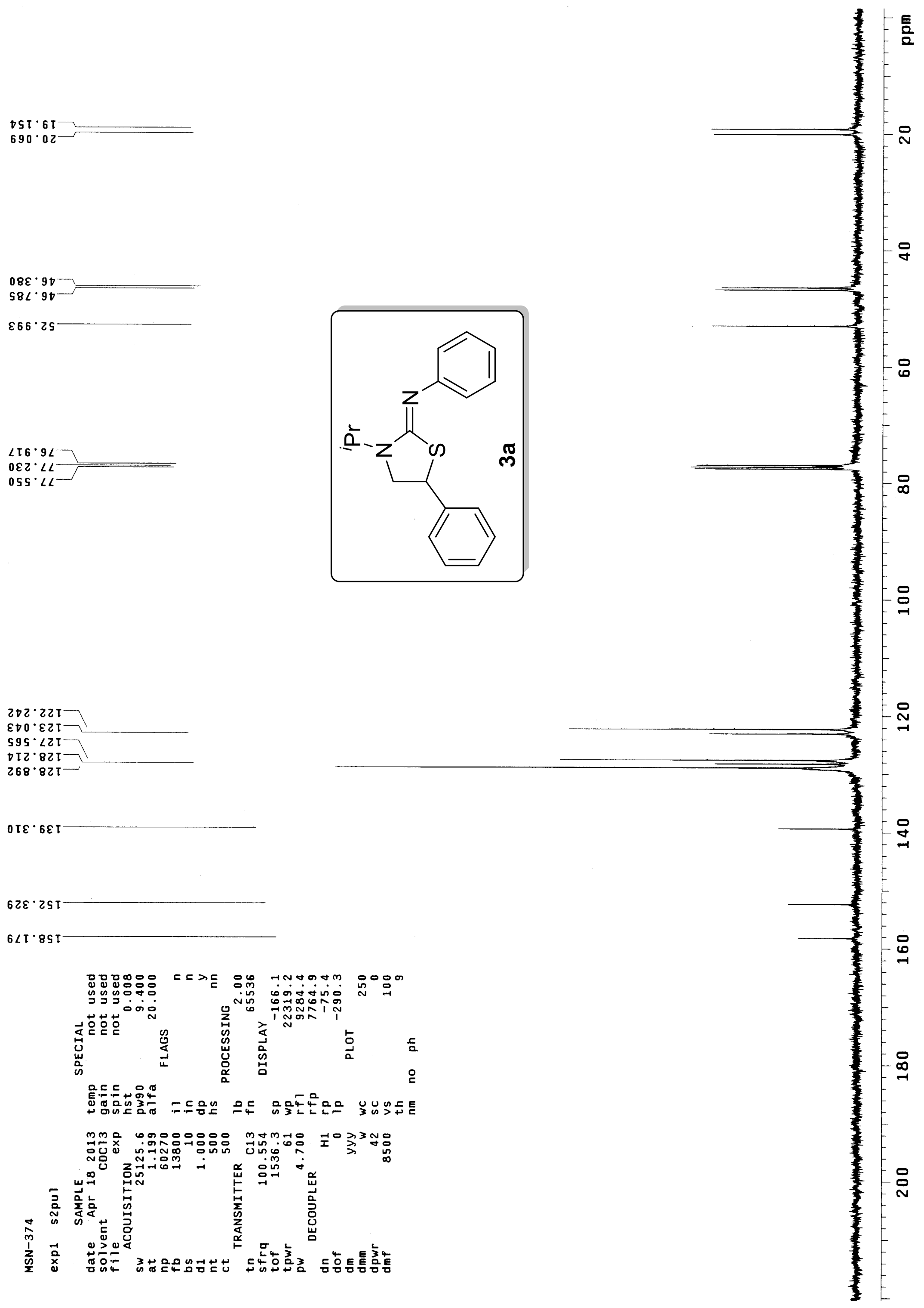
3.7 Selected NMR (^{1}H and ^{13}C) Spectra

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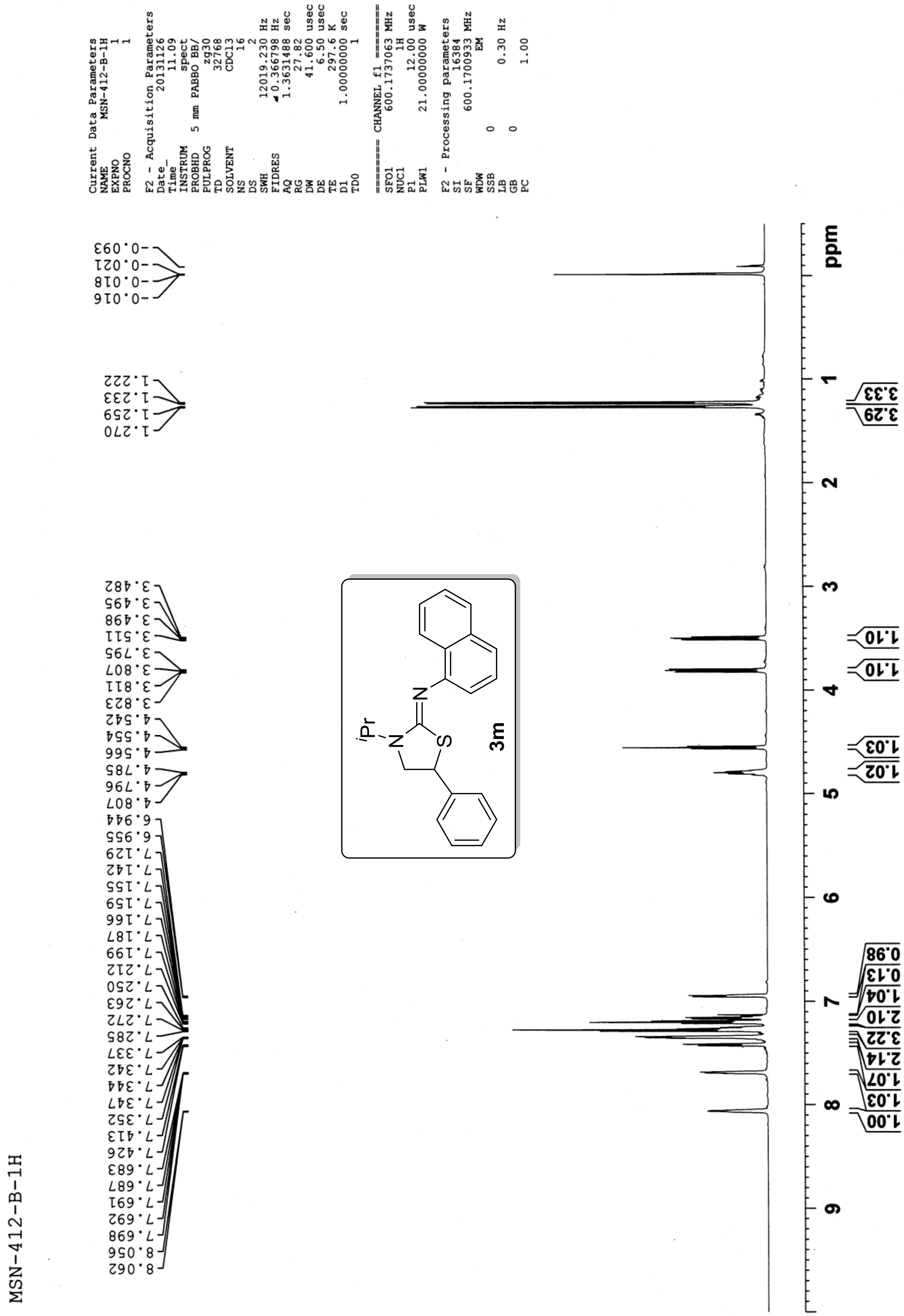

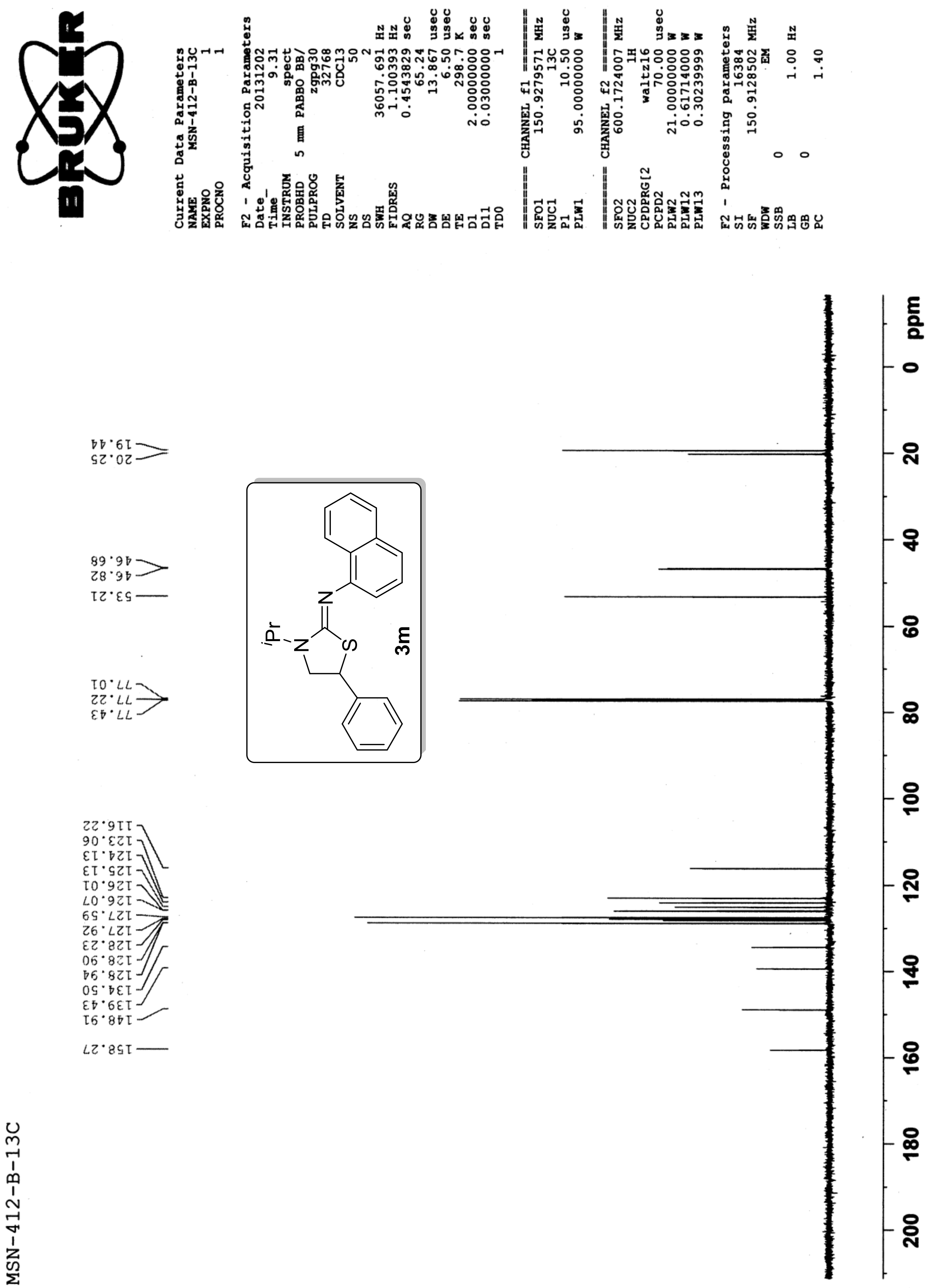
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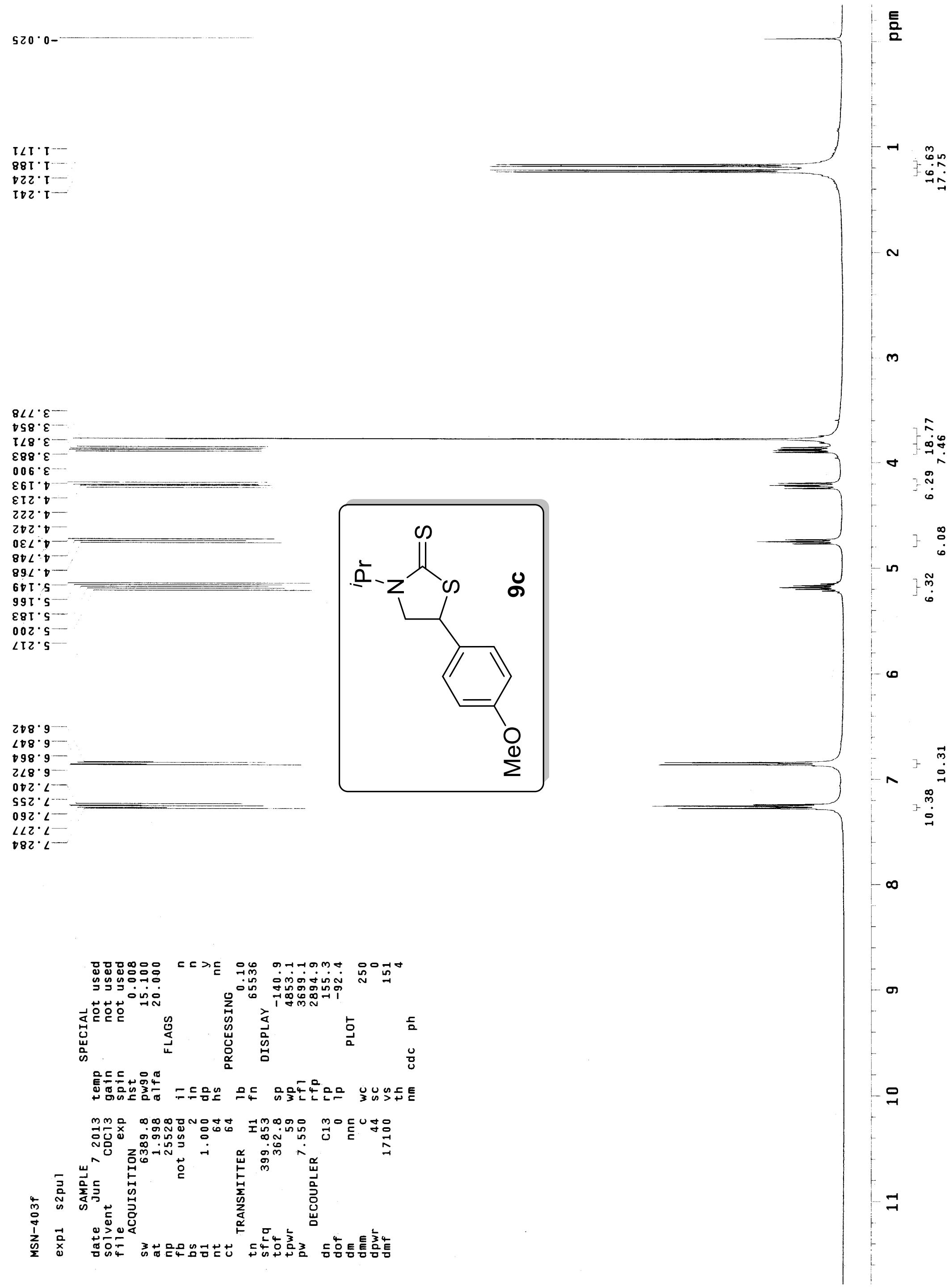
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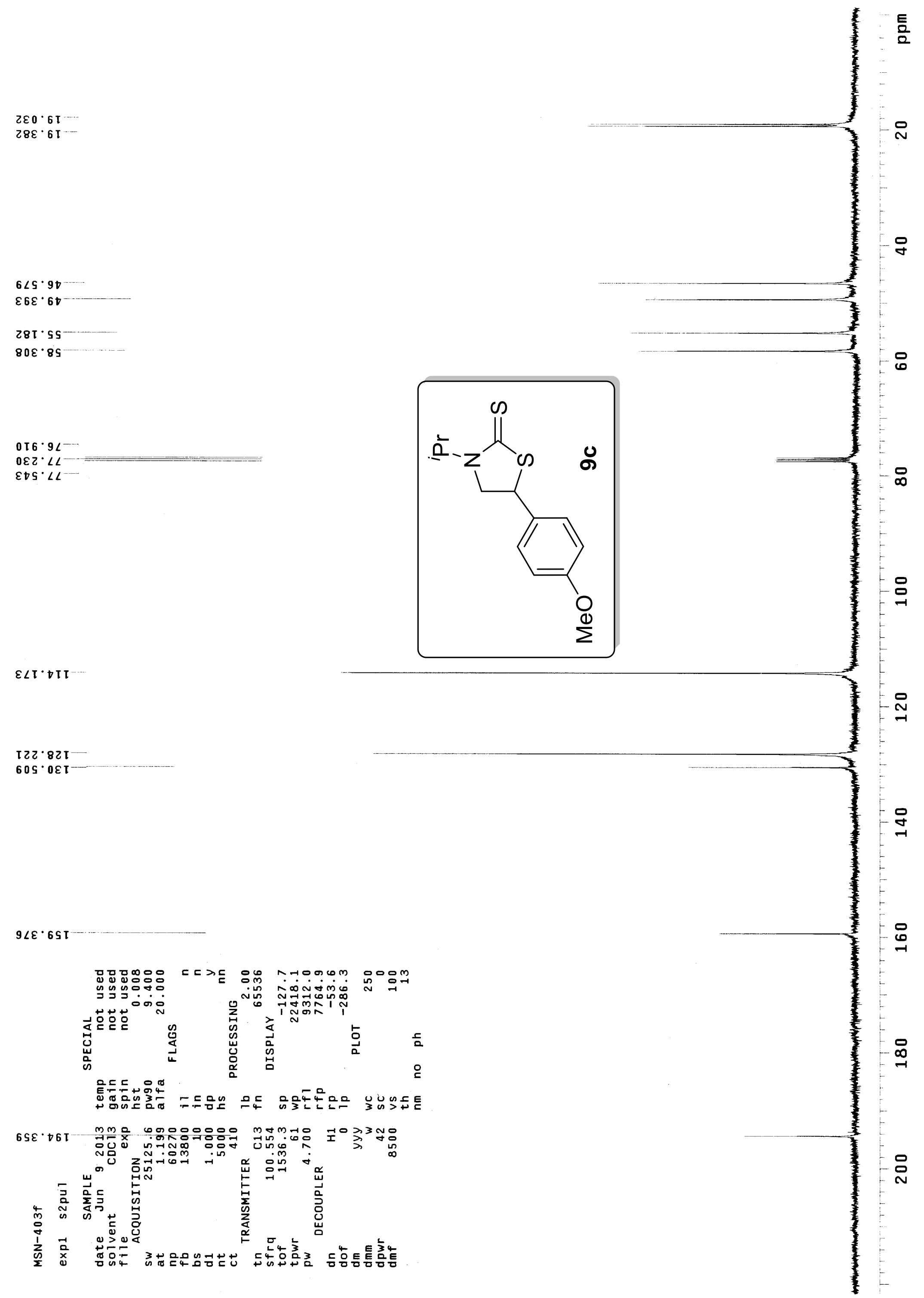
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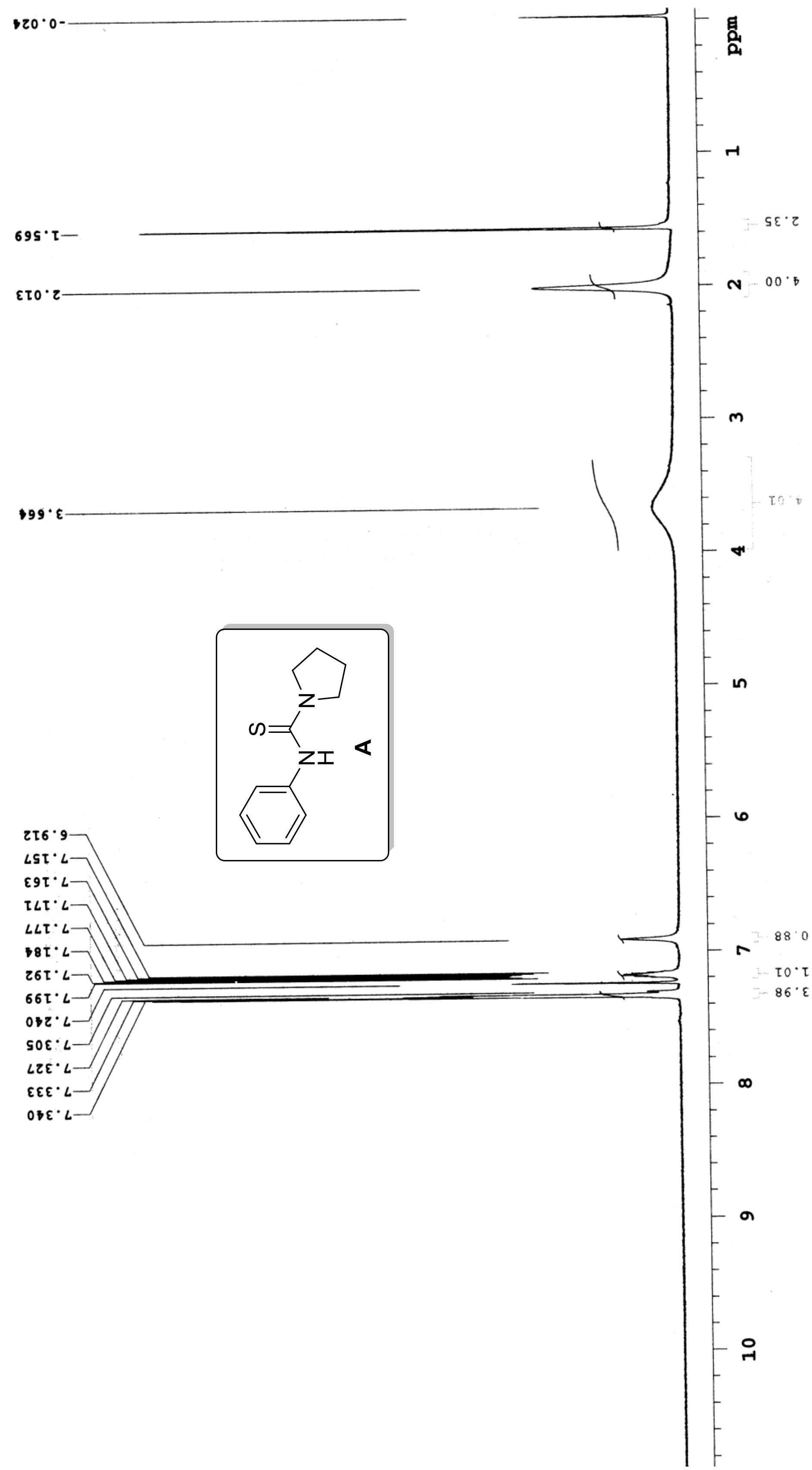
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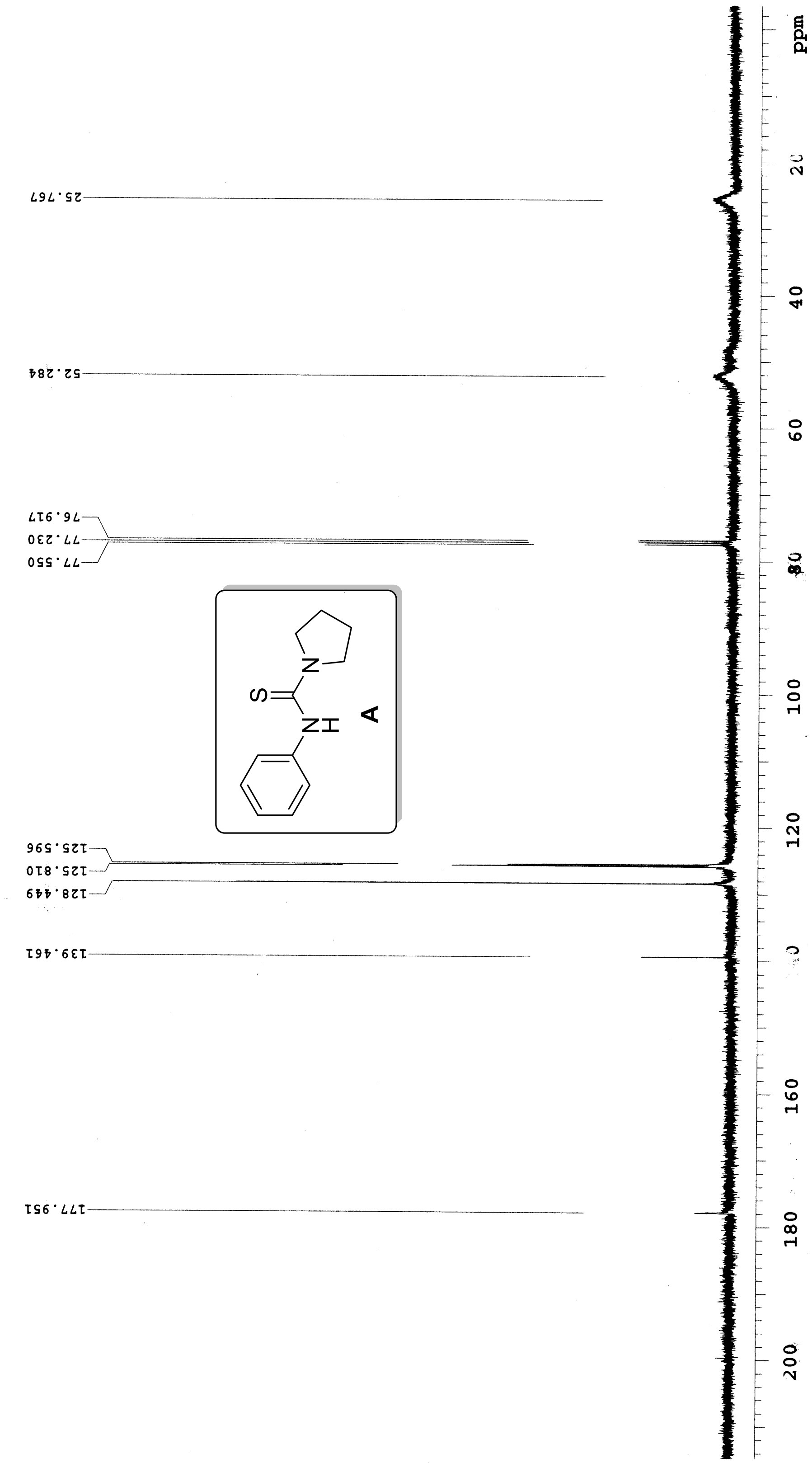
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Al(salen)-Catalyzed Cycloaddition of Aziridines with Isothiocyanates

The cycloaddition of aziridines with isocyanates, isothiocyanates, carbodiimides and analogues affords efficient approach for the construction of functionalized five membered nitrogen containing heterocycles that are important in biological and medicinal sciences.[1] Iminothiazolidines are important heterocyclic motifs used as effective organic catalysts in asymmetric transformations and found in numerous pharmaceuticals.[2] For examples, the compounds having iminothiazolidine scaffold is found in a range of medicinal chemistry applications such as progesterone receptor binding agents,[3] anti-depressant,[4] anti-inflammatory agent[5] and inducible nitric oxide synthase inhibitors.[6] In addition, they could be used as radio-protector agents.[7] As a result, the development of enantiospecific approaches for the synthesis of five membered heterocycles under relatively milder reaction conditions are highly desirable.

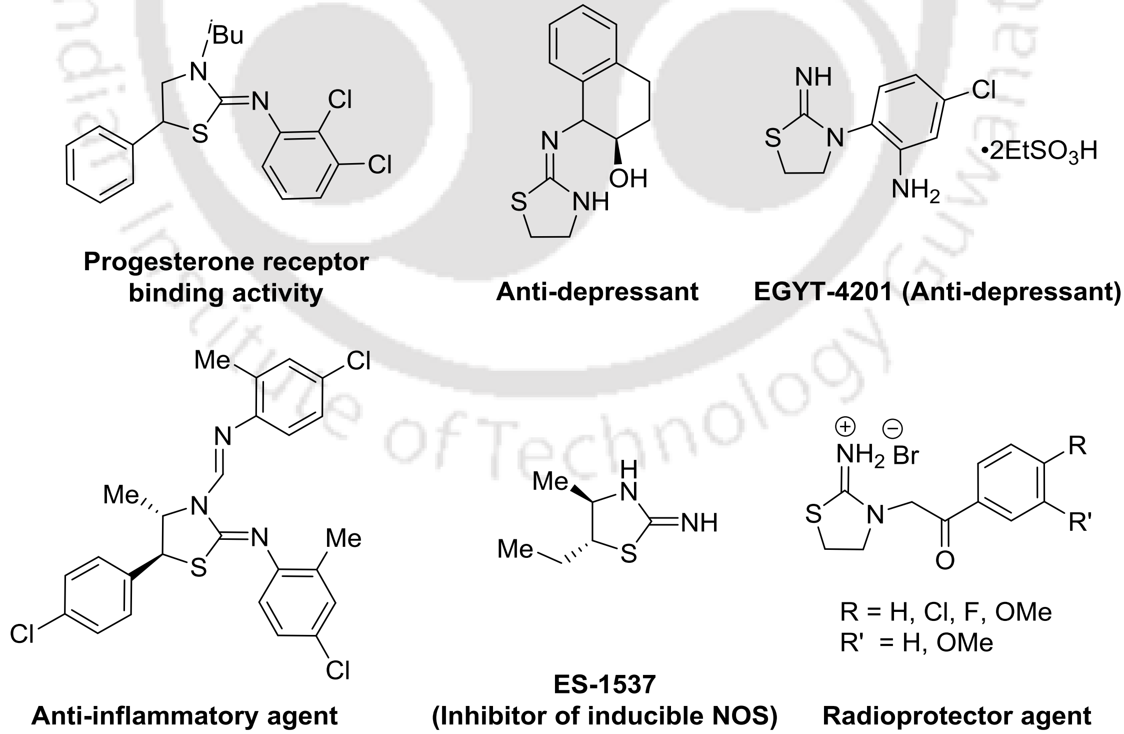
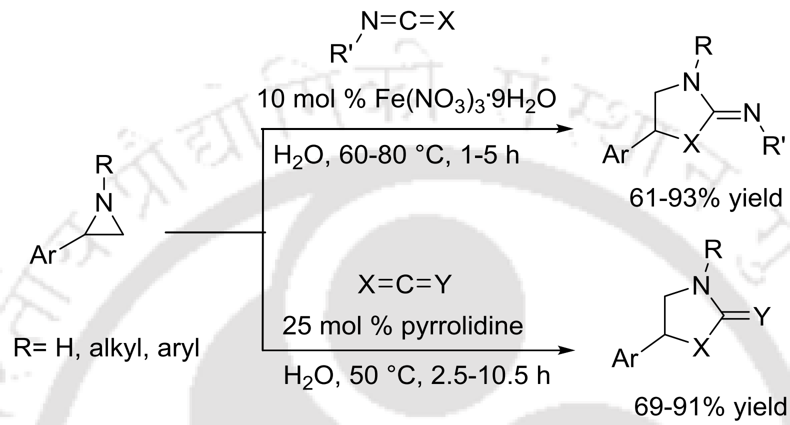


Figure 1. Examples of Some Biologically Active Iminothiazolidines

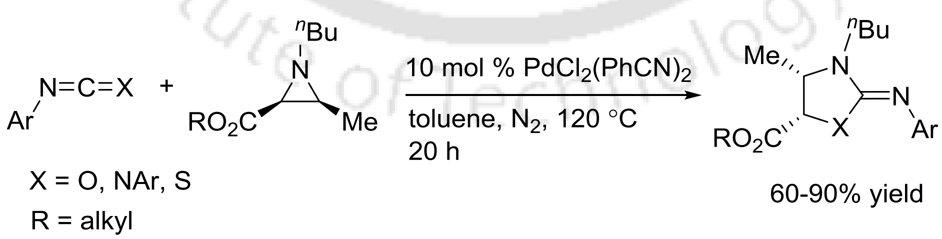
4.1 Synthesis of Enantioenriched Iminothiazolidines

In chapters 2 and 3, we described Fe and pyrrolidine-catalyzed cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates, carbodiimides and cabon disulfide those take place in aqueous suspension at moderate temperature (Scheme 1).[8,9] The protocol is simple and utilizes environmentally benign non-toxic water as a reaction medium under air.



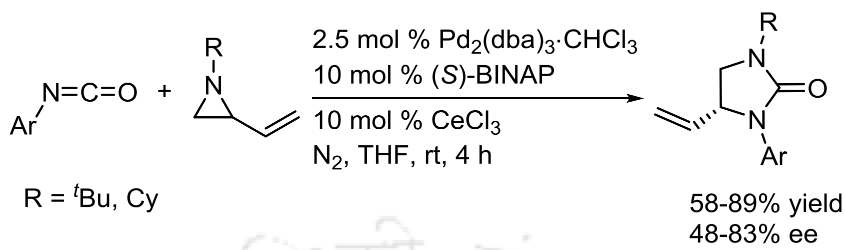
Scheme 1. Fe and pyrrolidine-catalyzed cycloaddition of aziridines with isocyanates and analogues

Alper and co-workers chiral Pd-catalyzed cycloaddition of aziridines with isocyanate, isothocyanates and carbodiimides to afford enantioenriched 2-iminoazolidines (Scheme 2).[10] These reactions occur both regio- and stereospecifically with retention of the stereochemistry of substituents in the aziridine ring. Further, they extended the substrate scope using enantiomerically pure 1,2-disubstituted aziridines to provide the corresponding chiral five-membered ring heterocycles.



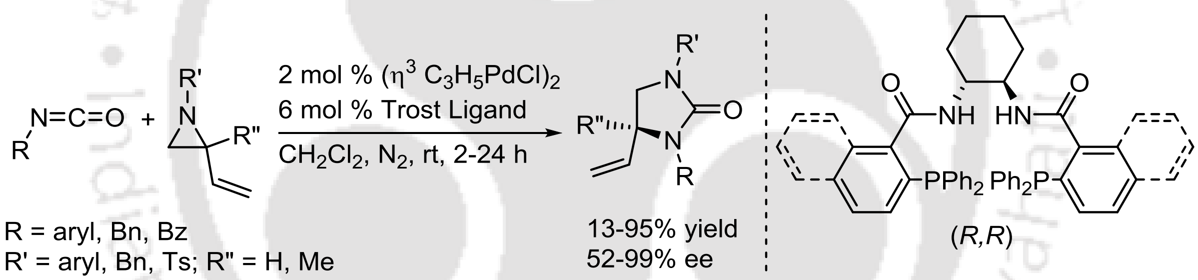
Scheme 2. Stereospecific Pd-Catalyzed Synthesis of Enantioenriched 2-Iminoazolidines

The same group disclosed $CeCl_3$ promoted enantioselective cycloaddition of *N*-alkyl-2-vinylaziridines with aryl isocyanates using a combination of $Pd_2(dba)_3CHCl_3$ and (*S*)-BINAP in THF at room temperature (Scheme 3).[11] The corresponding imidazolidin-2-ones have been obtained in high yield with up to 83% enantiomeric excess.



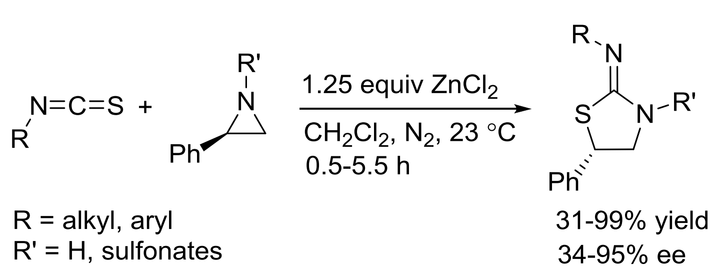
Scheme 3. Asymmetric Cycloaddition of Vinylaziridines with Isocyanates Using (*S*)-BINAP

Trost and co-workers described the asymmetric cycloaddition of 2-vinylaziridines with isocyanates using (η^3-$C_3H_5PdCl)_2$ and Trost ligand (Scheme 4).[12] Using this procedure, the imidazolidin-2-ones can be obtained in high yield and enantioselectivity with wide substrate scope. Additionally, the authors have demonstrated the synthesis of chiral diamines from the imidazolidin-2-ones.



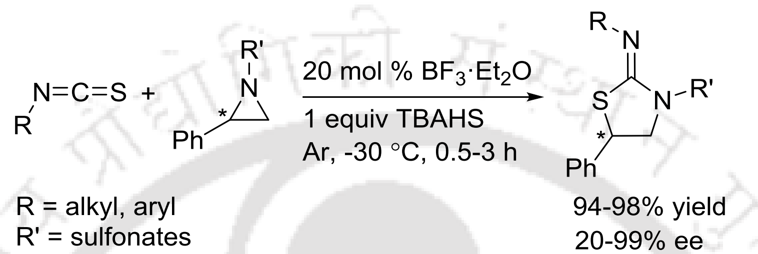
Scheme 4. Pd-Catalyzed Enantioselective Cycloaddition of Vinylaziridines with Isocyanates Using Trost Ligand

Stereospecific Zn(II)-mediated (3+2)-cycloadditions of alkyl and aryl isothiocyanates with of chiral *N*-H- and *N*-sulfonylaziridines has been shown for the synthesis of highly enantioenriched iminothiazolidines at room temperature (Scheme 5).[13]



Scheme 5. Stereospecific Zn(II)-Mediated Reaction of Chiral Aziridines with Isothiocyanates

Ghorai and co-workers reported the stereospecific synthesis of 2-iminothiazolidines from aryl- and alkyl isothiocyanates with *N*-sulfonylaziridines using $BF_3 \cdot Et_2O$ at -30 °C (Scheme 6).[14] Also, the *trans*-2,3-disubstituted *N*-tosylaziridines can be used to provide 2-iminothiazolidines with 99% diastereomeric ratio. The use of isothocyanates as solvent and stoichiometric amount of tetrabutylammonium hydrogen sulfate (TBAHS) as an additive was required to obtain the 2-iminothiazolidines in high enantiomeric excess.

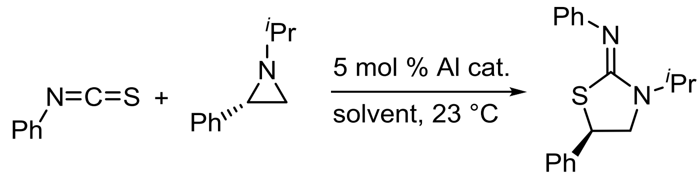


Scheme 6. $BF_3 \cdot Et_2O$-Catalyzed Stereospecific Synthesis of 2-Iminothiazolidines

4.2 Present Study

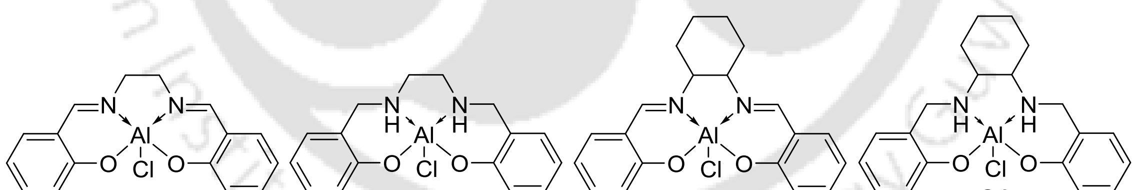
In continuation of our studies on cycloaddition reactions, we have developed a stereospecific Al(salen)-catalyzed cycloaddition of isothiocyanates with enantioenriched aziridines at room temperature under air. The protocol provides a potential route for the synthesis of enantioenriched iminothiazolidines in good yields. First, the reaction conditions were optimized employing phenyl isothiocyanate (**1a**) and 1-isopropyl-2-phenylaziridine (**2a**) as model substrates in the presence of various Al-complexes in CH_2Cl_2 at ambient conditions (Table 1). Gratifyingly, the reaction occurred to give the desired thiazolidin-2-ylidene (**3a**) in 87% yield and 97% ee when the substrates **1a** and **2a** were stirred with 5 mol % Al catalyst **C1** for 18 h in CH_2Cl_2 (entry 1). In a set of screened Al-catalysts **C1-C4**, the complex **C1** afforded the best results (entries 1-4). Next, the effect of a series of solvents was screened, MeOH, CH_3CN, toluene, THF, $CHCl_3$ and $(CH_2Cl)_2$, the reactions occurred efficiently to afforded with 27-89% yields and 80-96% ee (entries 6-11). A control experiment confirmed that without the catalyst the reaction was not observed (entry12).

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

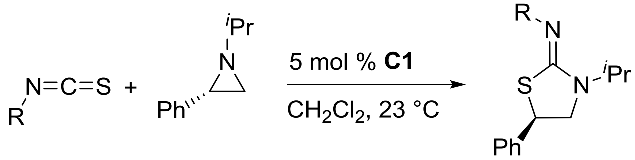
Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]	ee (%)[c]
1	**C1**	**CH_2Cl_2**	**18**	**87**	**97**
2	**C2**	CH_2Cl_2	8	88	91
3	**C3**	CH_2Cl_2	12	85	89
4	**C4**	CH_2Cl_2	9	88	86
5[d]	**C1**	CH_2Cl_2	18	78	95
6	**C1**	MeOH	5	86	85
7	**C1**	CH_3CN	8	89	93
8	**C1**	toluene	18	27	95
9	**C1**	THF	18	69	80
10	**C1**	$CHCl_3$	18	86	96
11	**C1**	$(CH_2Cl)_2$	18	81	96
12	-	CH_2Cl_2	18	n.d.	-



C1 **C2** **C3** **C4**

[a] Reaction conditions: Isothiocyanate **1a** (0.25 mmol), aziridine **2a** (0.25 mmol), catalyst (5 mol %), solvent (1.0 mL), 23 °C, air. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] 10 mol % TBAI used. n.d. = not detected.

Table 2. Reaction of Substituted Isothiocyanates with Aziridine **2a**[a]



1b-i **2a** R = alkyl, aryl **3b-i**

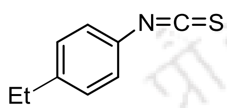
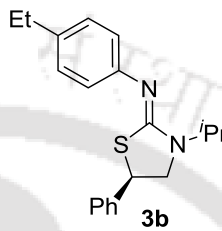
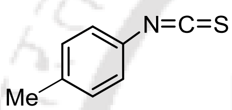
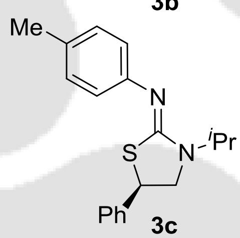
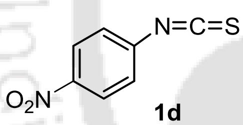
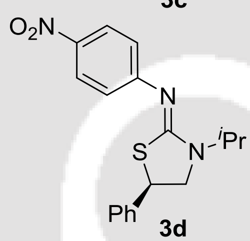
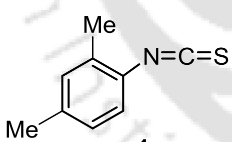
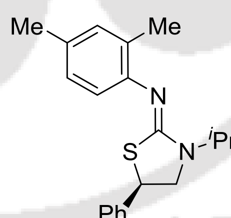
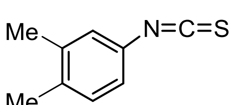
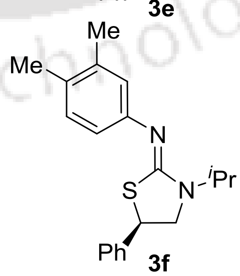
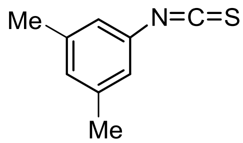
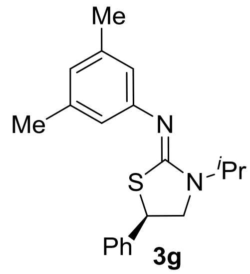
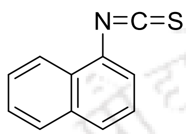
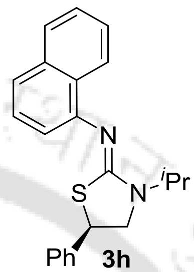
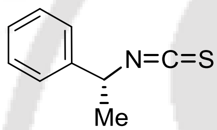
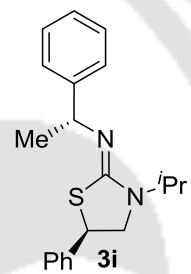
Entry	Isothiocyanates	Time (h)	Product	Yield (%)[b]	ee (%)[c]
1	 **1b**	27	 **3b**	76	96
2	 **1c**	26	 **3c**	83	97
3	 **1d**	14	 **3d**	87	97
4	 **1e**	36	 **3e**	83	96
5	 **1f**	40	 **3f**	75	94

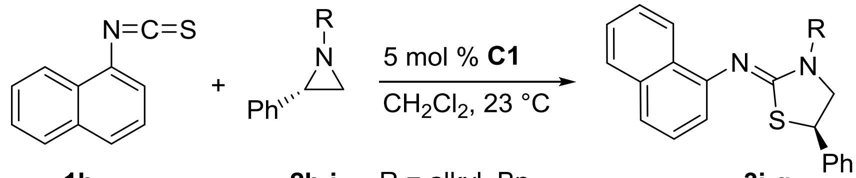
Table 2 continued.....

6	 **1g**	46	 **3g**	85	98
7	 **1h**	21	 **3h**	82	97
8	 **1i**	42	 **3i**	70	94

[a] Reaction conditions: Isothiocyanate **1b-i** (0.25 mmol), aziridine **2a** (0.25 mmol), catalyst (5 mol %), CH_2Cl_2 (1.0 mL), 23 °C, air. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

To explore the scope this protocol, a series of alkyl/aryl isothiocyanates **1** with aziridine **2a** were subjected to the optimized reaction conditions (Table 2). The reactions efficiently occurred to afford the target enantioenriched iminothiazolidines **3** in excellent yields and enantiomeric excess. For examples, isothiocyanates **1b-d** bearing ethyl, methyl and nitro groups in the phenyl rings proceeded reaction smoothly to provide the corresponding target heterocycles in **3b-d** in 76-87% yields and 96-97% ee. Likewise, 2,4-, 3,4- and 3,5-dimethyl substituted isothiocyanates **1e-g** underwent reaction with aziridine **1a** to give the desired iminothiazolidines **3e-g** in 75-85% yield with 94-98% ee. Furthermore, the reactions of 1-naphthyl isothiocyanate **1h** and α-methyl benzyl isothiocyanate **1i** afforded the desired **3h-i** in 82% and 70% yield with 97% and 94% ee, respectively.

Table 3. Reaction of Isothiocyanate **1h** with Substituted Aziridine[a]



1h + **2b-i** → **3j-q**; R = alkyl, Bn

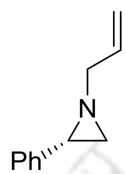
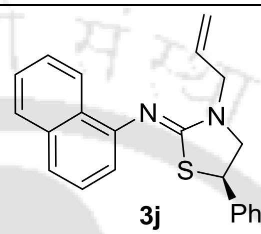
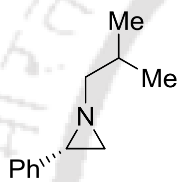
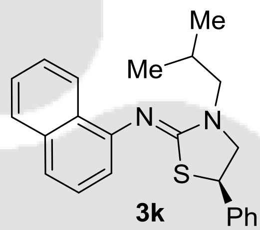
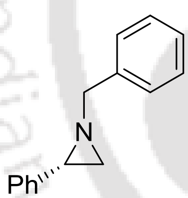
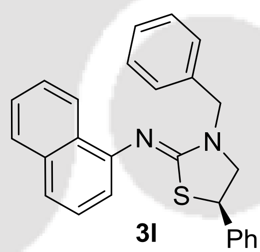
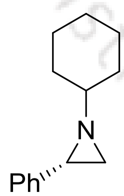
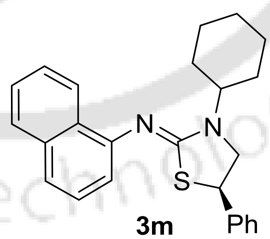
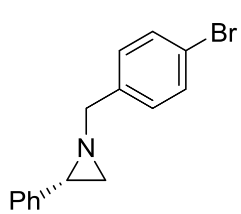
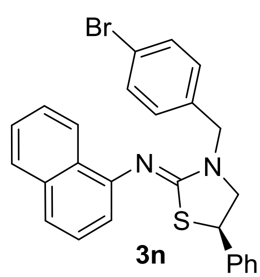
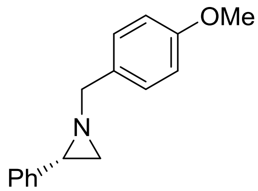
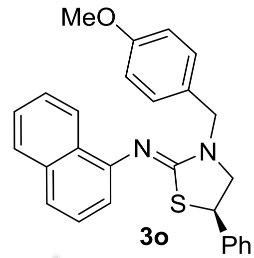
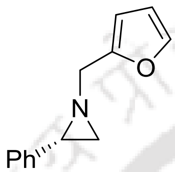
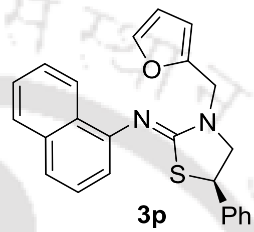
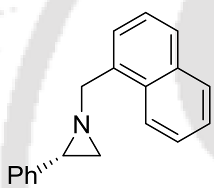
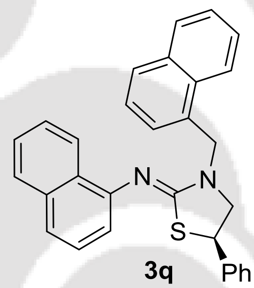
Entry	Aziridines	Time (h)	Product	Yield (%)[b]	ee (%)[c]
1	 **2b**	20	 **3j**	84	99
2	 **2c**	21	 **3k**	73	99
3	 **2d**	28	 **3l**	86	99
4	 **2e**	26	 **3m**	70	>99
5	 **2f**	24	 **3n**	84	99

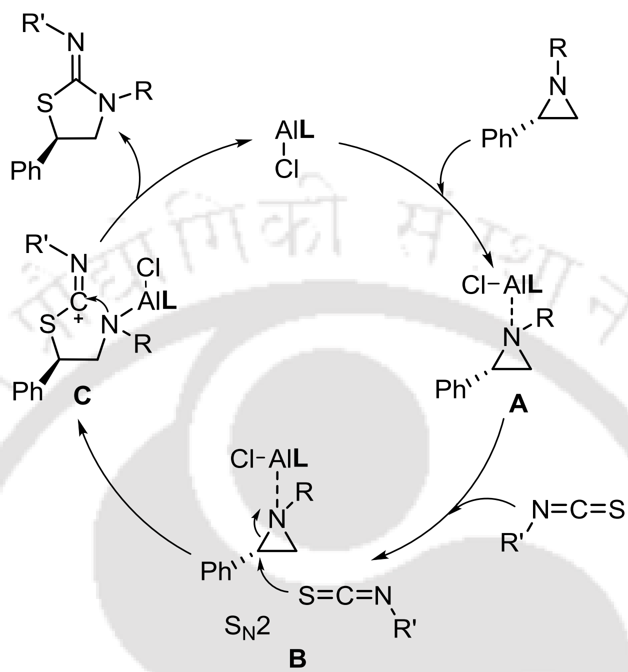
Table 3 continued.....

6	 **2g**	26	 **3o**	79	98
7	 **2h**	28	 **3p**	77	98
8	 **2i**	28	 **3q**	88	>99

[a] Reaction conditions: Isothiocyanate **1h** (0.25 mmol), aziridine **2b-i** (0.25 mmol), catalyst (5 mol %), CH_2Cl_2 (1.0 mL), 23 °C, air. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Next, the reactions of the substituted aziridines **2b-i** with isothiocyanate **1h** were examined and the results are summarized in table 3. For examples, aryl aziridines **2b-e** having allyl, benzyl, *n*-butyl and cyclohexyl substituents on the nitrogen atom underwent reaction to give the corresponding iminothiazolidines **3j-m** in 69-83% yields and 99% ee. Likewise, the substrates **2f-g** having electrons withdrawing and donating substituents such as 4-bromo and 4-methoxy groups readily underwent reaction to furnish the iminothiazolidines **3n-o** in 79-84% yields and 98-99% ee. Furthermore, the cycloaddition of the substrates **2h-i** having 2-furyl and 1-naphthyl substituents could be carried out with isothiocyanate **1h** to provide the desired iminothiazolidines **3p** and **3q** in 63 and 88% yields and 98 and 99% ee, respectively.

A plausible reaction mechanism is shown in scheme 7. The reaction of the Al-complex with aziridine can lead to the formation of the intermediate **A** that may undergo S_N2 nucleophilic opening (S_N2) with isothiocyanates to give the intermediate **C** *via* intermediate **B**. The intramolecular cyclization of **C** offers the desired enantioenriched iminothiazolidines to complete the catalytic cycle.



Scheme 7. Proposed Catalytic Cycle.

In conclusion, we have developed the stereospecific cycloaddition of enantiopure aziridines with isothiocyanates using Al(salen)Cl as catalyst at ambient conditions. This protocol provides an efficient and regioselective route to the construction of iminothiazolidines in high yields with excellent optical purity.

4.3 Experimental Section

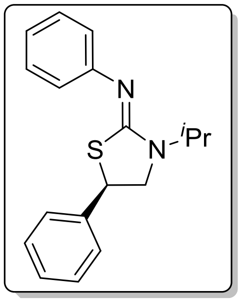
General Information. Amines and alkenes were purchased from Aldrich and used as received. All aminoacids were purchased from SRL. The reactions were monitored by analytical TLC on Merck silica gel G/GF 254 plates. The column chromatography was performed with Rankem silica gel (60-120 mesh). NMR (^{1}H and ^{13}C) spectra were recorded on DRX-400 Varian spectrometer, Bruker Avance III 600 using and the data are accounted as follows: chemical shifts (δ ppm) (multiplicity, coupling constant (Hz), integration). The abbreviations for multiplicity are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. Chemical shifts (δ) are reported relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^1H NMR and 77.23 ppm for ^{13}C NMR). Melting points were determined with a Büchi B-545 apparatus and are uncorrected. Optical rotation were determined by using Rudolph Research Analytical, Autopol II. FT-IR spectra were recorded using Theromo Fischer Scientific IR spectrometer. Mass spectra were recorded on a ESI-MS TOF Instrument. HPLC analysis was carried out using Waters-2489 equipped with Daicel Chiralcel OD/Chiralcel OJ column.

Procedure for the Preparation of L-Phenylglycinol. To a suspension of $LiAlH_4$ (2.2 mmol) in dry THF (10 mL) was added portion wise L-(+)-α-phenylglycine (1.0 mmol) at 0 °C. The mixture was allowed to reach to room temperature and stirring was continued for 1 h then refluxed for 24 h. After completion, the reaction mixture was quenched with EtOAc (50 mL), H_2O (1 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a (*S*)-(+)-2-phenylglycinol as pale yellow solid.

General Procedure for the Preparation of Chiral Aziridines. To a solution of L-phenylglycinol (1.1 mmol) in ethanol (5 mL), aldehyde (2.2 mmol) was added and the solution was stirred for 2 h at room temperature, and then $NaBH_4$ (3.3 mmol) was added at 0 °C. After being stirred for 4 h, the solvent was removed on a rotary evaporator. The residue was dissolved in water and extracted with CH_2Cl_2 (3×10 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a the residue, which was further reacted with TsCl (1.2 mmol) and DMAP (10 mg) in dry CH_2Cl_2 (20 mL) at 0 °C were added a solution of Et_3N (1.5 mmol) in dry CH_2Cl_2 (5 mL). Then the mixture was allowed to reach to room temperature and stirring was continued for 24 h. The mixture was then treated with a saturated NH_4Cl solution (20 mL), and extracted with CH_2Cl_2 (3×10 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a residue, that was purified on a silica gel column chromatography using hexane and ethyl acetate as eluent.

General Procedure for the Cycloaddition of Isothiocyanates with Chiral Aziridines. A mixture of isothiocyanates (0.25 mmol), aziridine (0.25 mmol) and catalyst (5 mol %) were stirred in CH_2Cl_2 (1 mL) for appropriate time at room temperature. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was then evaporated on a rotary evaporator to give a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate (19:1) as eluent.

4.4 Characterization Data of Products



(*R*,*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3a.

Colorless solid; yield 87%.

Mp: 109-110 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 6.6 Hz, 2H), 7.30-7.25 (m, 3H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 4.71-4.66 (m, 2H), 3.88 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.56 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H).

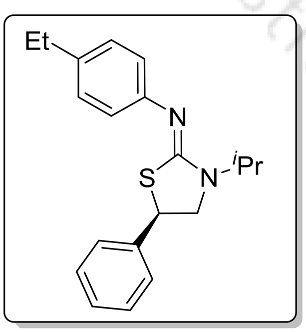
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 152.4, 139.4, 129.0, 128.3, 127.7, 123.1, 122.3, 53.1, 46.9, 46.5, 20.2, 19.2.

FT-IR (KBr) 3059, 3029, 2971, 2929, 2869, 1619, 1587, 1490, 1212, 1068, 936, 856 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}N_2S$ 297.1420, found 297.1426.

$[\alpha]_D^{20}$ = +70 (c= 0.2, $CHCl_3$).

HPLC analysis: 97% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 13.53 min (major), 20.66 min (minor)].



(*R*,*Z*)-4-Ethyl-*N*-(3-isopropyl-5-phenylthiazolidin-2-ylidene)aniline 3b.

Colorless liquid; yield 76%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.70-4.50 (m, 2H), 3.86 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.55 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.60 (q, *J* = 7.8 Hz, 2H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.24 (d, *J* = 6.6 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H).;

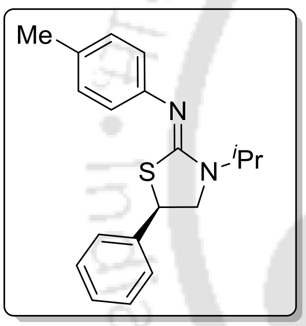
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 150.0, 139.5, 138.9, 129.0, 128.3, 128.2, 127.7, 122.1, 53.1, 46.9, 46.5, 28.5, 20.2, 19.2, 15.8.

FT-IR (neat) 3061, 3025, 2966, 2929, 2870, 1622, 1598, 1504, 1455, 1243, 1212, 1066, 935, 861 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}N_2S$ 325.1733, found 325.1733.

$[\alpha]_D^{20}$ = +244 (c= 0.2, $CHCl_3$).

HPLC analysis: 96% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 8.35 min (major), 12.82 min (minor)].



(*R*,*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-methylaniline 3c.

Colorless solid; yield 83%.

Mp: 88-89 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.88 (dd, *J* = 8.4, 2.4 Hz, 2H), 4.70-4.65 (m, 2H), 3.87 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.55 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.30 (s, 3H), 1.28 (d, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 6.6 Hz, 3H).

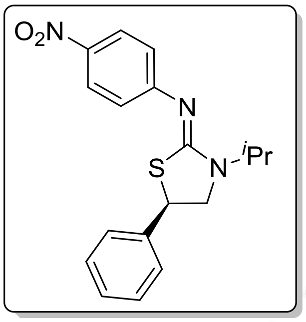
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 149.9, 139.4, 132.4, 129.6, 128.9, 128.3, 127.7, 122.0, 53.1, 46.9, 46.4, 21.1, 20.1, 19.2.

FT-IR (KBr) 3025, 2970, 2920, 2859, 1618, 1597, 1504, 1403, 1236, 1213, 1178, 1061, 949, 861 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{22}N_2S$ 311.1576, found 311.1588.

$[\alpha]_D^{20}$ = +85 (c= 0.2, $CHCl_3$).

HPLC analysis: 97% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 12.92 min (major), 18.91 min (minor)].



(*R*,*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-4-nitroaniline 3d.

Yellow solid; yield 87%.

Mp: 70-71 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.75 (t, *J* = 7.2 Hz, 1H), 4.71-4.67 (m, 1H), 3.94 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.63 (dd, *J* = 10.2, 7.8 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H).

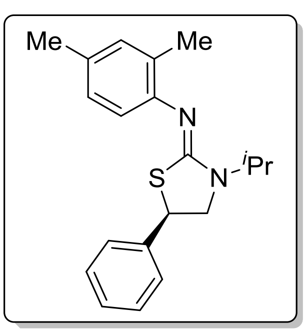
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 158.5, 143.1, 138.7, 129.2, 128.6, 127.6, 125.1, 122.7, 53.2, 47.2, 46.8, 20.1, 19.4.

FT-IR (KBr) 3061, 3029, 2967, 2925, 2853, 1612, 1571, 1502, 1330, 1271, 1218, 1065, 1018, 941, 856 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{19}N_3O_2S$ 342.1276, found 342.1284.

$[\alpha]_D^{20}$ = +297 (c= 0.2, $CHCl_3$).

HPLC analysis: 97% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 27.65 min (minor), 30.77 min (major)].



(*R*,*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-2,4-dimethylaniline 3e.

Colorless solid; yield 83%.

Mp: 69-70 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.97 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 4.71-4.65 (m, 2H), 3.88 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.55 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.27 (s, 3H), 2.20 (s, 3H), 1.30 (d, *J* = 6.6 Hz, 3H), 1.27 (d, *J* = 6.6 Hz, 3H).

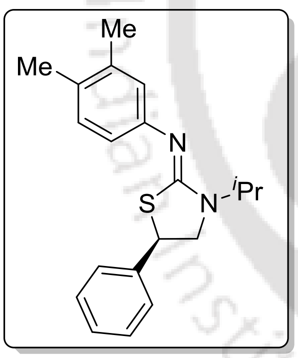
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 148.6, 139.7, 132.5, 131.1, 130.2, 128.9, 128.2, 127.6, 127.0, 121.2, 53.3, 46.7, 46.6, 21.1, 20.1, 19.2, 18.2.

FT-IR (KBr) 3056, 3020, 2969, 2929, 2866, 1622, 1597, 1495, 1453, 1242, 1209, 1067, 1022, 953, 874 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}N_2S$ 325.1733, found 325.1735.

$[\alpha]_D^{20}$ = +162 (c= 0.2, $CHCl_3$).

HPLC analysis: 94% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 11.95 min (major), 15.40 min (minor)].



(*R*,*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-3,4-dimethylaniline 3f.

Colorless liquid; yield 75%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 4.70-4.66 (m, 2H), 3.87 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.56 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.23 (s, 3H), 2.21 (s, 3H), 1.29 (d, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H).

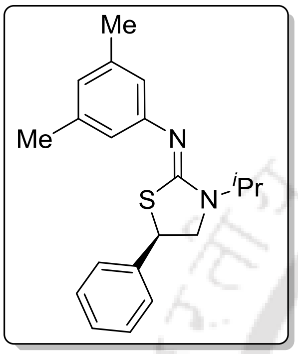
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 150.1, 139.4, 137.0, 131.1, 130.1, 128.9, 128.2, 127.7, 123.5, 119.2, 53.0, 46.9, 46.4, 20.2, 20.1, 19.4, 19.2.

FT-IR (neat) 3056, 3028, 2970, 2922, 2870, 1629, 1596, 1494, 1455, 1243, 1211, 1122, 1066, 938, 841 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}N_2S$ 325.1733, found 325.1729.

$[\alpha]_D^{20}$ = +112 (c= 0.2, $CHCl_3$).

HPLC analysis: 96% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 9.47 min (major), 12.82 min (minor)].



(*R*,*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)-3,5-dimethylaniline 3g.

Colorless solid; yield 85%.

Mp: 72-73 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 6.67 (s, 1H), 6.62 (s, 2H), 4.70-4.66 (m, 2H), 3.86 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.55 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.30 (s, 6H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.24 (d, *J* = 6.6 Hz, 3H).

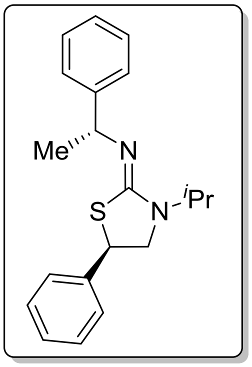
^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8, 152.2, 139.4, 138.4, 128.9, 128.3, 127.7, 124.9, 119.9, 53.0, 46.9, 46.4, 21.6, 20.2, 19.2.

FT-IR (KBr) 3056, 3028, 2970, 2925, 2865, 1622, 1587, 1469, 1401, 1241, 1210, 1069, 1026, 957, 844 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}N_2S$ 325.1733, found 325.1734.

$[\alpha]_D^{20}$ = +141 (c= 0.2, $CHCl_3$).

HPLC analysis: 98% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 6.99 min (major), 10.43 min (minor)].



(*R*,*Z*)-*N*-((*R*)-3-Isopropyl-5-phenylthiazolidin-2-ylidene)-1-phenylethanamine 3h.

Pale yellow liquid; yield 70%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 731-7.29 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 1H), 4.62-4.59 (m, 2H), 4.29 (q, *J* = 6.6 Hz, 1H), 3.72 (dd, *J* = 9.6, 6.6 Hz, 1H), 3.43 (dd, *J* = 9.6, 8.4 Hz, 1H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.19 (d, *J* = 7.2 Hz, 6H).

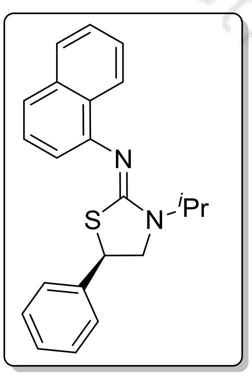
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.2, 147.4, 140.3, 128.9, 128.3, 128.2, 127.7, 126.7, 126.4, 64.2, 52.9, 46.8, 46.4, 26.0, 19.8, 19.0.

FT-IR (neat) 3060, 3027, 2969, 2925, 2865, 1629, 1492, 1396, 1241, 1208, 1178, 1063, 1013, 817 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}N_2S$ 325.1733, found 325.1732.

$[\alpha]_D^{20}$ = -20.0 (c= 0.2, $CHCl_3$).

HPLC analysis: 94% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 9.58 min (major), 20.85 min (minor)].



(*R*,*Z*)-*N*-(3-Isopropyl-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3i.

Colorless liquid; yield 82%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21-8.20 (m, 1H), 7.83-7.82 (m, 1H), 7.57-7.55 (m, 1H), 7.49-7.48 (m, 2H), 7.42-7.40 (m, 3H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.10-7.08 (m, 1H), 4.96-4.91 (m, 1H), 4.69 (t, *J* = 7.8 Hz, 1H), 3.94 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.63 (dd, *J* = 10.2, 7.8 Hz, 1H), 1.40 (d, *J* = 6.6 Hz, 3H), 1.37 (d, *J* = 6.6 Hz, 3H).

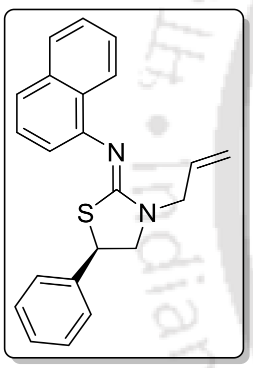
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 148.9, 139.4, 134.5, 128.9, 128.2, 127.9, 127.6, 126.1, 126.0, 125.2, 124.1, 123.1, 116.3, 53.2, 46.8, 46.7, 20.3, 19.5.

FT-IR (neat) 3058, 2969, 2929, 2869, 1613, 1571, 1501, 1456, 1388, 1245, 1213, 1181, 1065, 1039, 997 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}N_2S$ 347.1576, found 347.1589.

$[\alpha]_D^{20}$ = +154 (c= 0.2, $CHCl_3$).

HPLC analysis: 97% ee [Daicel CHIRALCEL OD column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL /min, λ = 215 nm, t_R = 12.89 min (major), 22.52 min (minor)].



(*R*,*Z*)-*N*-(3-Allyl-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3j.

Pale yellow liquid; yield 84%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20-8.18 (m, 1H), 7.83-7.81 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.48-7.47 (m, 2H), 7.41-7.38 (m, 3H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.10-6.03 (m, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 4.76 (t, *J* = 7.8 Hz, 1H), 4.41 (dd, *J* = 15.0, 6.0 Hz, 1H), 4.32 (dd, *J* = 15.0, 6.0 Hz, 1H), 3.92 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.66 (dd, *J* = 10.2, 8.4 Hz, 1H).

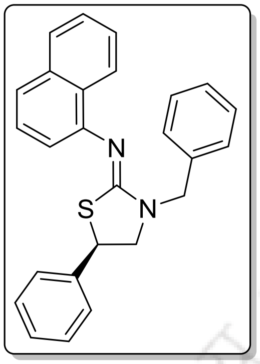
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.5, 148.7, 139.0, 134.5, 133.1, 129.0, 128.9, 128.3, 127.9, 127.7, 126.1, 126.0, 125.2, 124.1, 123.3, 118.2, 116.1, 58.1, 49.5, 47.0.

FT-IR (neat) 3058, 2921, 2854, 1618, 1571, 1502, 1386, 1347, 1246, 1183, 1158, 1079, 1014, 928 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{20}N_2S$ 345.1420, found 345.1416.

$[\alpha]_D^{20}$ = +35 (c= 0.2, $CHCl_3$).

HPLC analysis: 99% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 16.70 min (major), 25.07 min (minor)].



(*R*,*Z*)-*N*-(3-Benzyl-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3k.

Colorless liquid; yield 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.22 (m, 1H), 7.87-7.84 (m, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.51-7.49 (m, 4H), 7.46-7.42 (m, 3H), 7.37-7.35 (m, 3H), 7.31-7.29 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 5.09 (d, *J* = 15.2, 1H), 4.88 (d, *J* = 14.8, 1H), 4.76 (t, *J* = 7.2, 1H), 3.87 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.62 (dd, *J* = 10.0, 8.0 Hz, 1H).

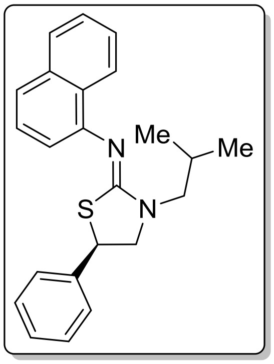
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.7, 138.8, 137.3, 134.5, 128.9, 128.8, 128.5, 128.3, 127.9, 127.7, 127.6, 126.1, 125.2, 124.2, 123.3, 116.0, 58.0, 50.5, 47.0.

FT-IR (neat) 3058, 3022, 2919, 2856, 1615, 1571, 1495, 1453, 1386, 1246, 1158, 1078, 1014, 928, 850 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{22}N_2S$ 395.1576, found 395.1574.

$[\alpha]_D^{20}$ = +86 (c= 0.2, $CHCl_3$).

HPLC analysis: 99% ee [Daicel CHIRALCEL OD column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL /min, λ = 215 nm, t_R = 9.32 min (major), 13.16 min (minor)].



(*R*,*Z*)-*N*-(3-Isobutyl-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3l.

Colorless liquid; yield 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.18 (m, 1H), 7.84-7.81 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.50-7.47 (m, 2H), 7.43-7.38 (m, 3H), 7.36-7.32 (m, 3H), 7.08 (dd, *J* = 7.2, 1.2 Hz, 1H), 4.73 (t, *J* = 7.2 Hz, 1H), 3.97 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.71(dd, *J* = 10.0, 7.6 Hz, 1H), 3.64 (dd, *J* = 13.6, 7.6 Hz, 1H), 3.48 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.19-2.14 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 6H).

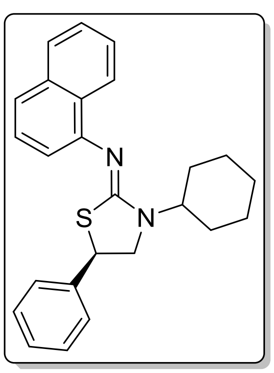
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 149.1, 139.2, 134.5, 129.0, 128.9, 128.3, 127.9, 127.7, 126.1, 126.0, 125.2, 124.1, 123.1, 116.2, 59.4, 54.3, 47.0, 27.7, 20.6.

FT-IR (neat) 3056, 2958, 2926, 2868, 1617, 1571, 1503, 1468, 1387, 1248, 1220, 1118, 1078, 1014, 962 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_2S$ 361.1733, found 361.1732.

$[\alpha]_D^{20}$ = +73 (c= 0.2, $CHCl_3$).

HPLC analysis: 99% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 7.59 min (major), 12.48 min (minor)].



(*R*,*Z*)-*N*-(3-Cyclohexyl-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3m.

Pale yellow liquid; yield 70%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22-8.21 (m, 1H), 7.85-7.84 (m, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.51-7.50 (m, 2H), 7.42-7.40 (m, 3H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.12-7.10 (m, 1H), 4.67 (t, *J* = 7.2 Hz, 1H), 4.56-4.54 (m, 1H), 3.98 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.67 (dd, *J* = 10.2, 7.2 Hz, 1H), 2.14-2.13 (m, 2H), 1.92-1.90 (m, 2H), 1.77-1.75 (m, 1H), 1.56-1.50 (m, 3H), 1.33-1.29 (m, 1H), 1.19-1.15 (m, 1H).

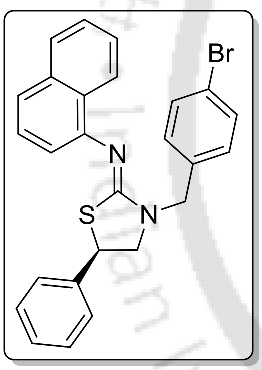
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.2, 149.0, 139.6, 134.5, 128.9, 128.8, 128.1, 127.9, 127.5, 126.1, 126.0, 125.1, 124.1, 123.0, 116.3, 54.8, 54.3, 46.8, 30.8, 30.1, 26.0, 25.9.

FT-IR (neat) 3057, 2930, 2854, 1611, 1571, 1503, 1450, 1387, 1245, 1215, 1176, 1078, 1012, 945 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{26}N_2S$ 387.1889, found 387.1889.

$[\alpha]_D^{20}$ = +123 (c= 0.2, $CHCl_3$).

HPLC analysis: 99% ee [Daicel CHIRALCEL OJ column, hexane/^{i}PrOH = 85:15, flow rate: 1 mL /min, λ = 215 nm, t_R = 7.10 min (major), 13.19 min (minor)].



(*R*,*Z*)-*N*-(3-(4-Bromobenzyl)-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3n.

Colorless liquid; yield 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.15 (m, 1H), 7.86-7.83 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.51-7.49 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.37-7.28 (m, 7H), 7.14 (d, *J* = 7.2 Hz, 1H), 4.97 (d, *J* = 15.2, 1H), 4.82 (d, *J* = 15.2, 1H), 4.74 (t, *J* = 7.2, 1H), 3.83 (dd, *J* = 10.0, 6.8 Hz, 1H), 3.59 (dd, *J* = 10.0, 8.0 Hz, 1H).

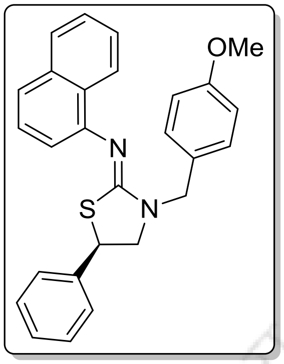
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.5, 138.6, 136.4, 134.5, 132.0, 130.2, 128.9, 128.8, 128.4, 128.0, 127.6, 126.2, 126.1, 125.3, 124.0, 123.4, 121.6, 116.0, 58.1, 49.8, 47.0.

FT-IR (neat) 3057, 3003, 2921, 2856, 1630, 1587, 1488, 1386, 1217, 1174, 1144, 1073, 1012, 949, 797, 776 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{21}BrN_2S$ 475.0664, found 475.0668.

$[\alpha]_D^{20}$ = +268 (c= 0.2, $CHCl_3$).

HPLC analysis: 99% ee [Daicel CHIRALCEL OD column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL /min, λ = 215 nm, t_R = 12.96 min (major), 15.63 min (minor)].



(*R*,*Z*)-*N*-(3-(4-Methoxybenzyl)-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3o.

Colorless liquid; yield 79%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21-8.19 (m, 1H), 7.83-7.81 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.48-7.47 (m, 2H), 7.41-7.39 (m, 3H), 7.35-7.33 (m, 2H), 7.30-7.25 (m, 3H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 4.97 (d, *J* = 14.4, 1H), 4.80 (d, *J* = 14.4, 1H), 4.71 (t, *J* = 7.2, 1H), 3.85-3.82 (m, 4H), 3.58 (dd, *J* = 10.2, 8.4 Hz, 1H).

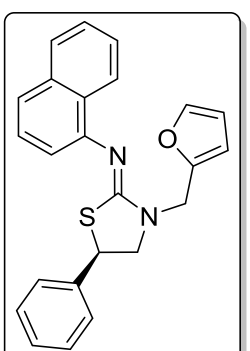
^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 158.7, 148.8, 139.0, 134.5, 130.0, 129.4, 128.9, 128.3, 128.0, 127.7, 125.2, 124.2, 123.3, 116.1, 114.3, 58.0, 55.5, 50.0, 47.0.

FT-IR (neat) 3057, 3006, 2954, 2930, 2835, 1629, 1571, 1510, 1467, 1282, 1245, 1173, 1078, 1035, 908 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}N_2OS$ 425.1682, found 425.1688.

$[\alpha]_D^{20}$ = +99 (c= 0.2, $CHCl_3$).

HPLC analysis: 98% ee [Daicel CHIRALCEL OD column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL /min, λ = 215 nm, t_R = 11.95 min (major), 17.82 min (minor)].



(*R*,*Z*)-*N*-(3-(Furan-2-ylmethyl)-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3p.

Pale yellow liquid; yield 77%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25-8.24 (m, 1H), 7.85-7.84 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.51-7.48 (m, 3H), 7.44-7.43 (m, 1H), 7.38-7.36 (m, 2H), 7.33-7.28 (m, 3H), 7.13-7.11 (m, 1H), 6.45-6.44 (m, 2H), 4.97 (d, *J* = 15.6, 1H), 4.92 (d, *J* = 15.6, 1H), 4.74 (t, *J* = 7.8, 1H), 3.95 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.69 (dd, *J* = 9.6, 7.8 Hz, 1H).

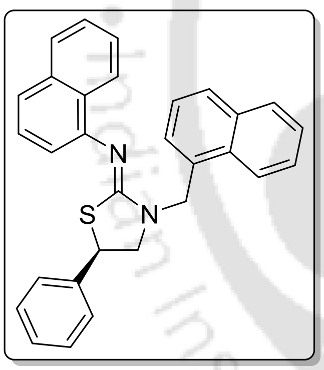
^{13}C NMR (150 MHz, $CDCl_3$) δ 158.4, 151.0, 148.6, 142.5, 138.9, 134.4, 128.9, 128.8, 128.3, 127.9, 127.6, 126.1, 126.0, 125.2, 124.2, 123.3, 116.0, 110.6, 109.0, 58.1, 47.0, 43.1.

FT-IR (neat) 3056, 2922, 2856, 1622, 1571, 1503, 1386, 1350, 1246, 1224, 1183, 1143, 1076, 1013, 933 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{20}N_2OS$ 385.1369, found 385.1368.

$[\alpha]_D^{20}$ = +50 (c= 0.2, $CHCl_3$).

HPLC analysis: 98% ee [Daicel CHIRALCEL OD column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL /min, λ = 215 nm, t_R = 8.84 min (major), 11.63 min (minor)].



(*R*,*Z*)-*N*-(3-(Naphthalen-1-ylmethyl)-5-phenylthiazolidin-2-ylidene)naphthalen-1-amine 3q.

Colorless liquid; yield 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.43-8.40 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.89-7.85 (m, 2H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.62-7.54 (m, 2H), 7.53-7.44 (m, 5H), 7.23-7.17 (m, 6H), 5.65 (d, *J* = 14.8, 1H), 5.17 (d, *J* = 14.8, 1H), 4.60 (t, *J* = 7.6, 1H), 3.75 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.54 (dd, *J* = 10.0, 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 148.7, 138.8, 134.6, 134.1, 133.2, 132.1, 129.0, 128.9, 128.85, 128.81, 128.2, 128.1, 127.6, 126.8, 126.4, 126.2, 125.4, 125.37, 125.33, 124.7, 124.2, 123.4, 116.2, 57.7, 49.3, 46.8.

FT-IR (neat) 3047, 2998, 2950, 2922, 2856, 1618, 1571, 1506, 1496, 1387, 1246, 1217, 1181, 1078, 1041, 1016, 934 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{24}N_2S$ 445.1733, found 445.1738.

$[\alpha]_D^{20}$ = +134 (c= 0.2, $CHCl_3$).

HPLC analysis: 99% ee [Daicel CHIRALCEL OD column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL /min, λ = 215 nm, t_R = 10.79 min (major), 16.42 min (minor)].

4.5 References

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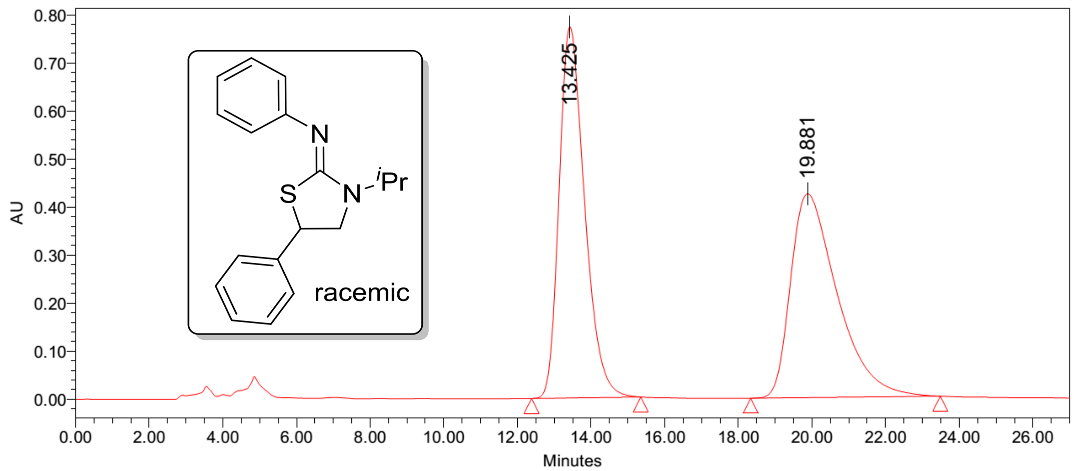
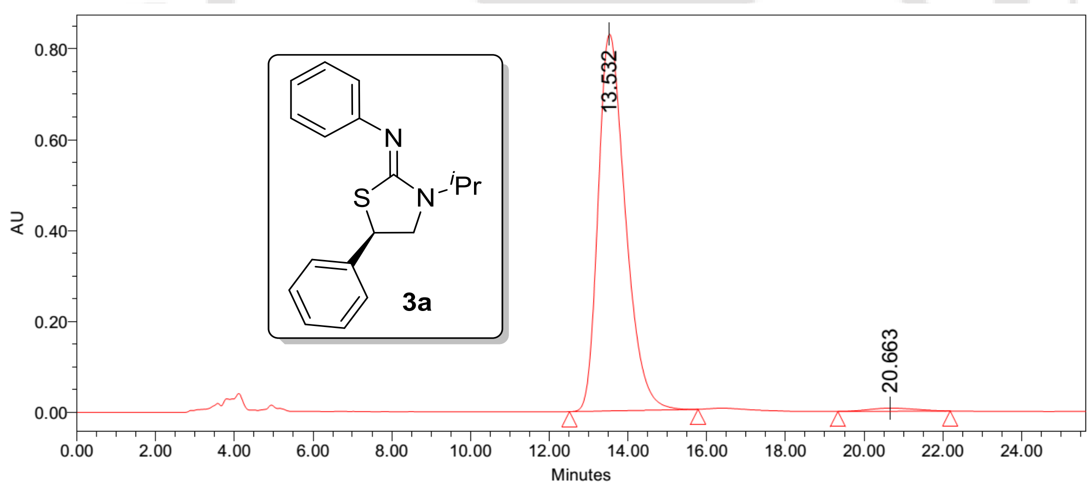
4.6 Selected HPLC Chromatograms



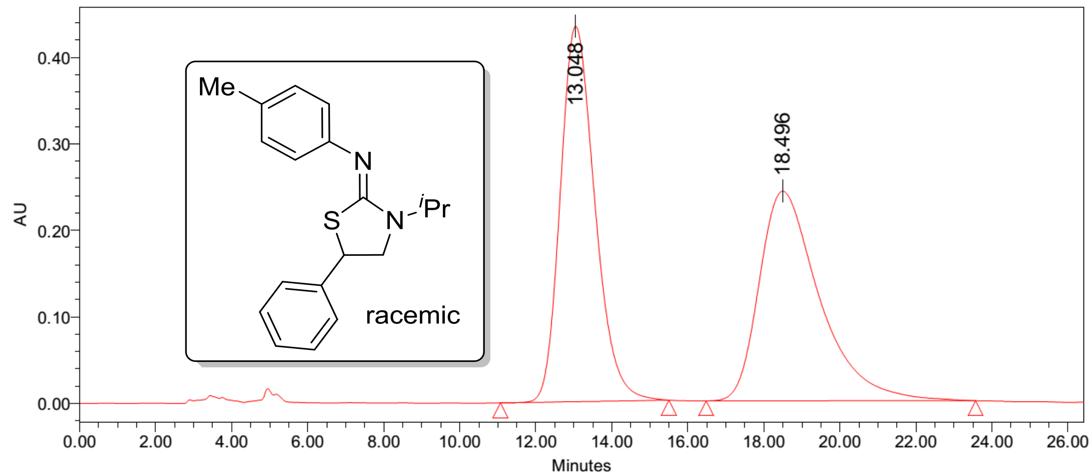
Peak Results

	RT	Height (µV)	% Area
1	13.425	772170	49.89
2	19.881	424100	50.11



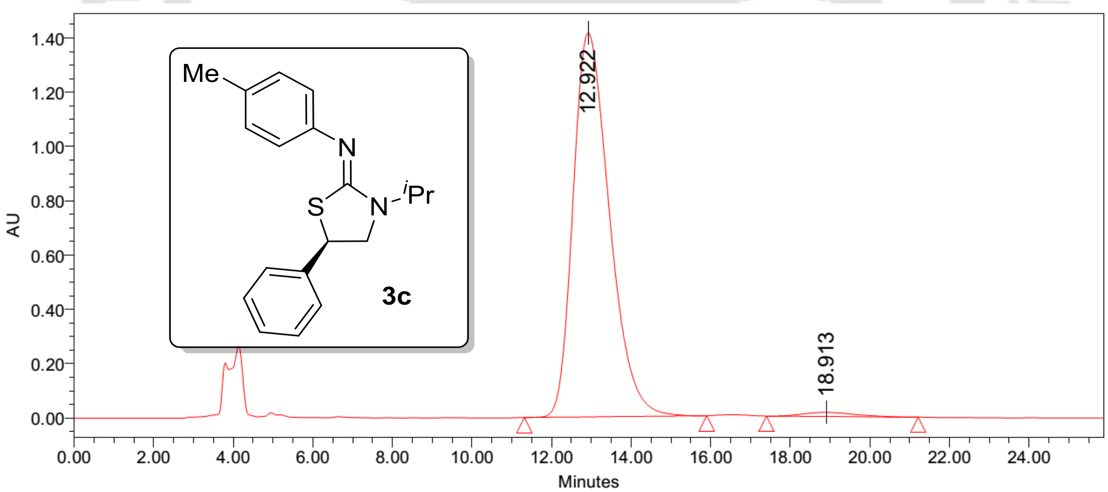
Peak Results

	RT	Height (µV)	% Area
1	13.532	829540	98.61
2	20.663	6742	1.39



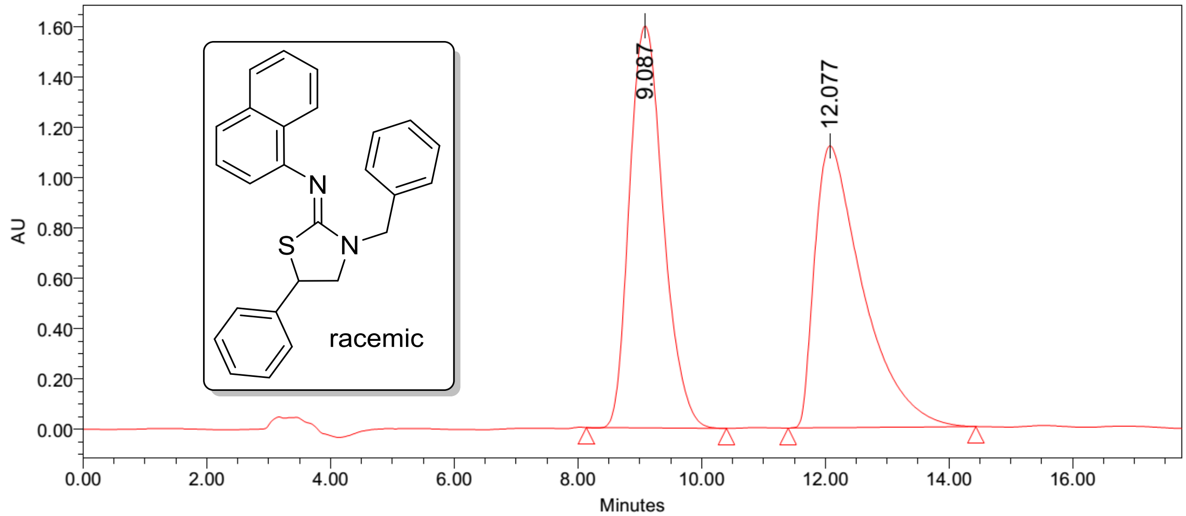
Peak Results

	RT	Height (μV)	% Area
1	13.048	434084	50.65
2	18.496	242256	49.35



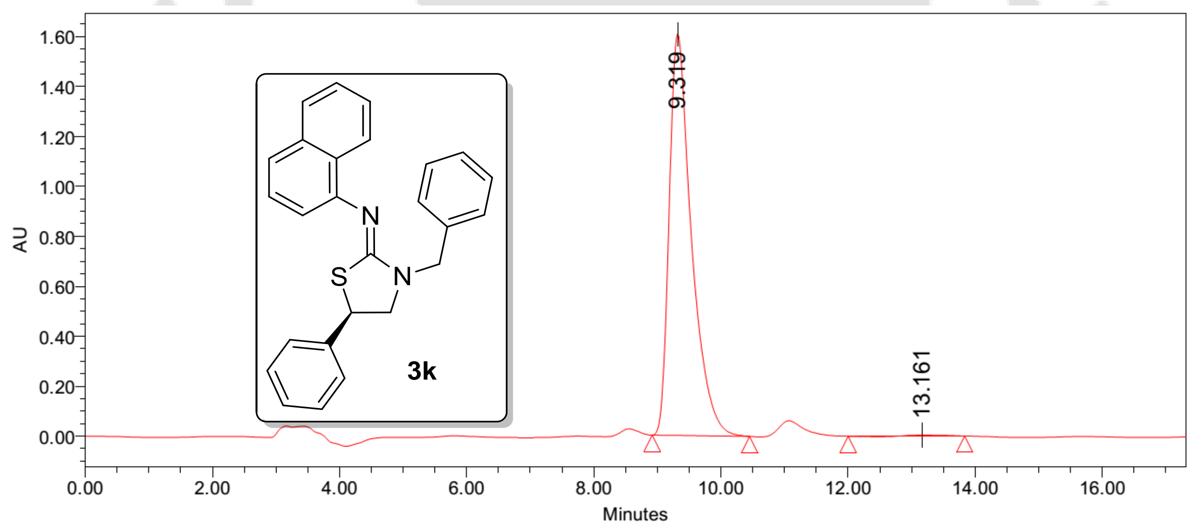
Peak Results

	RT	Height (μV)	% Area
1	12.922	1414254	98.45
2	18.913	15230	1.55



Peak Results

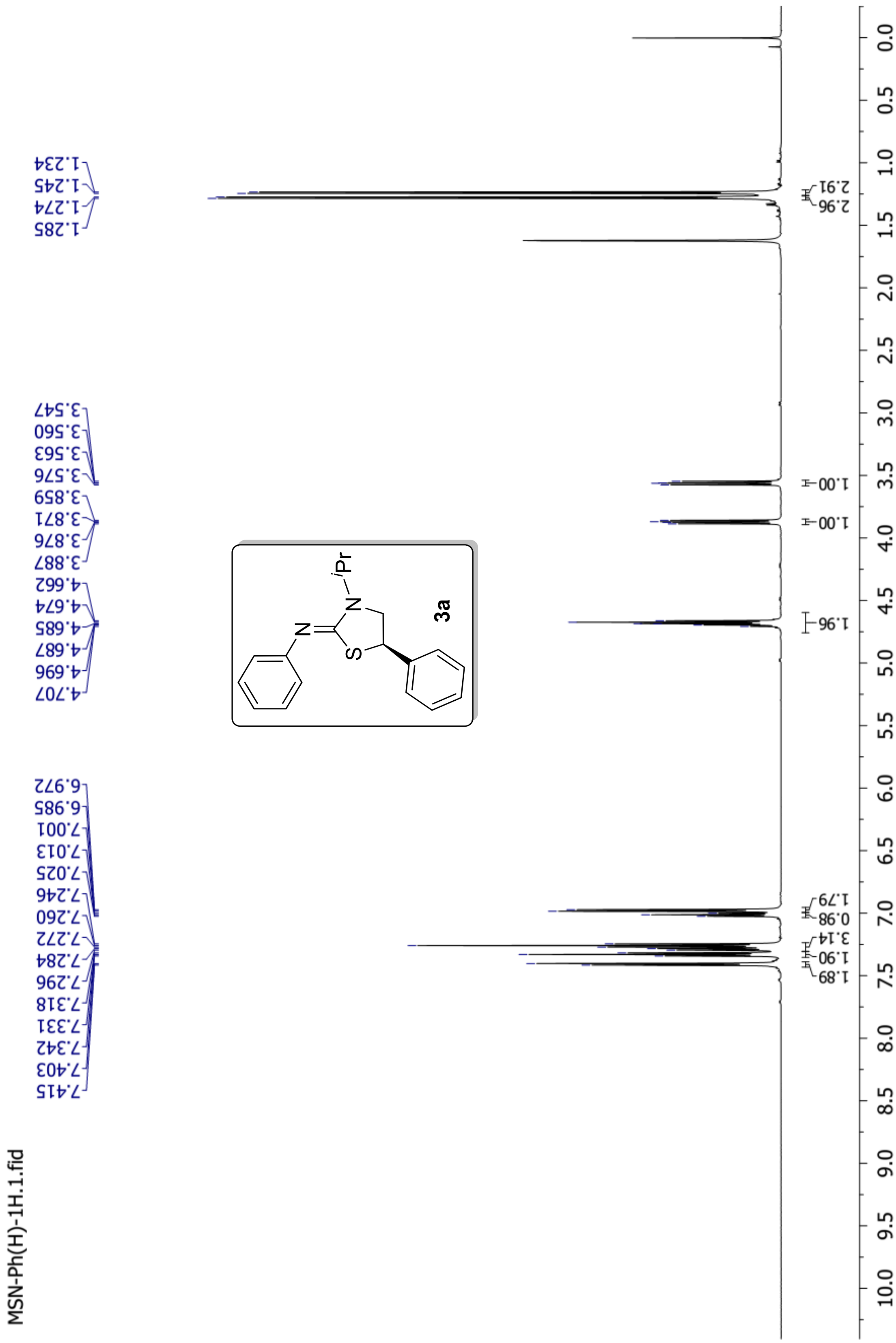
	RT	Height (μV)	% Area
1	9.087	1599531	50.05
2	12.077	1121581	49.95

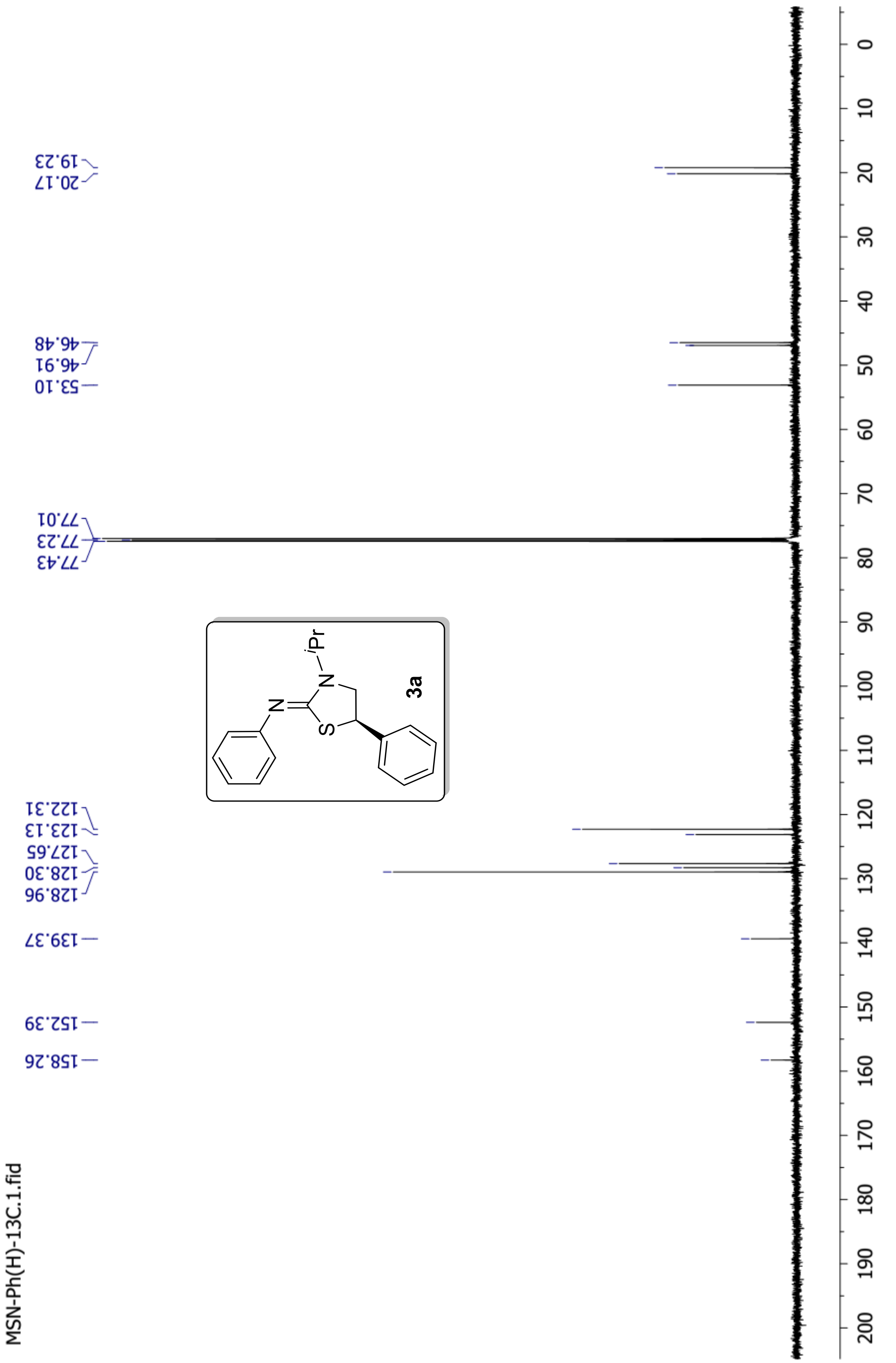


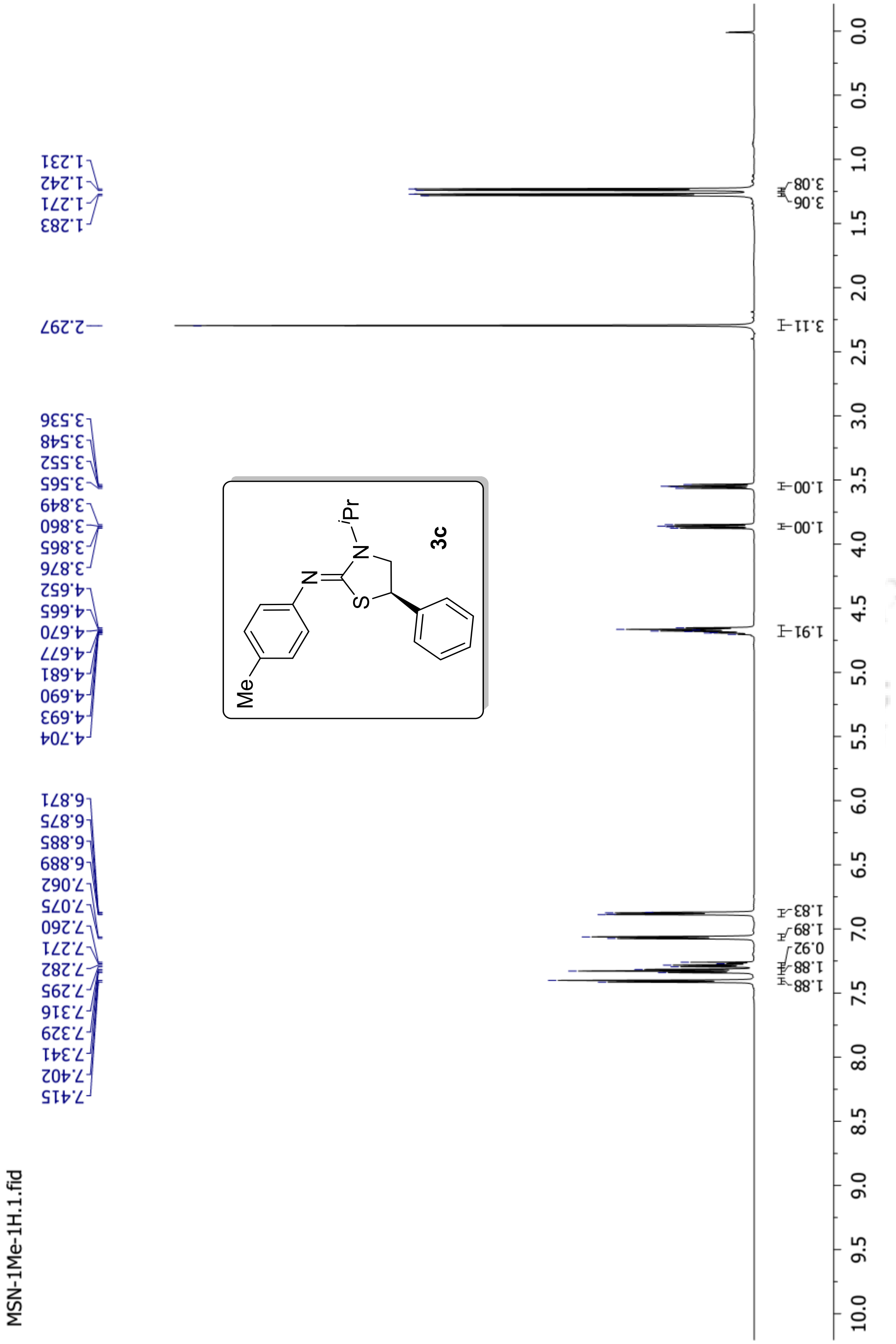
Peak Results

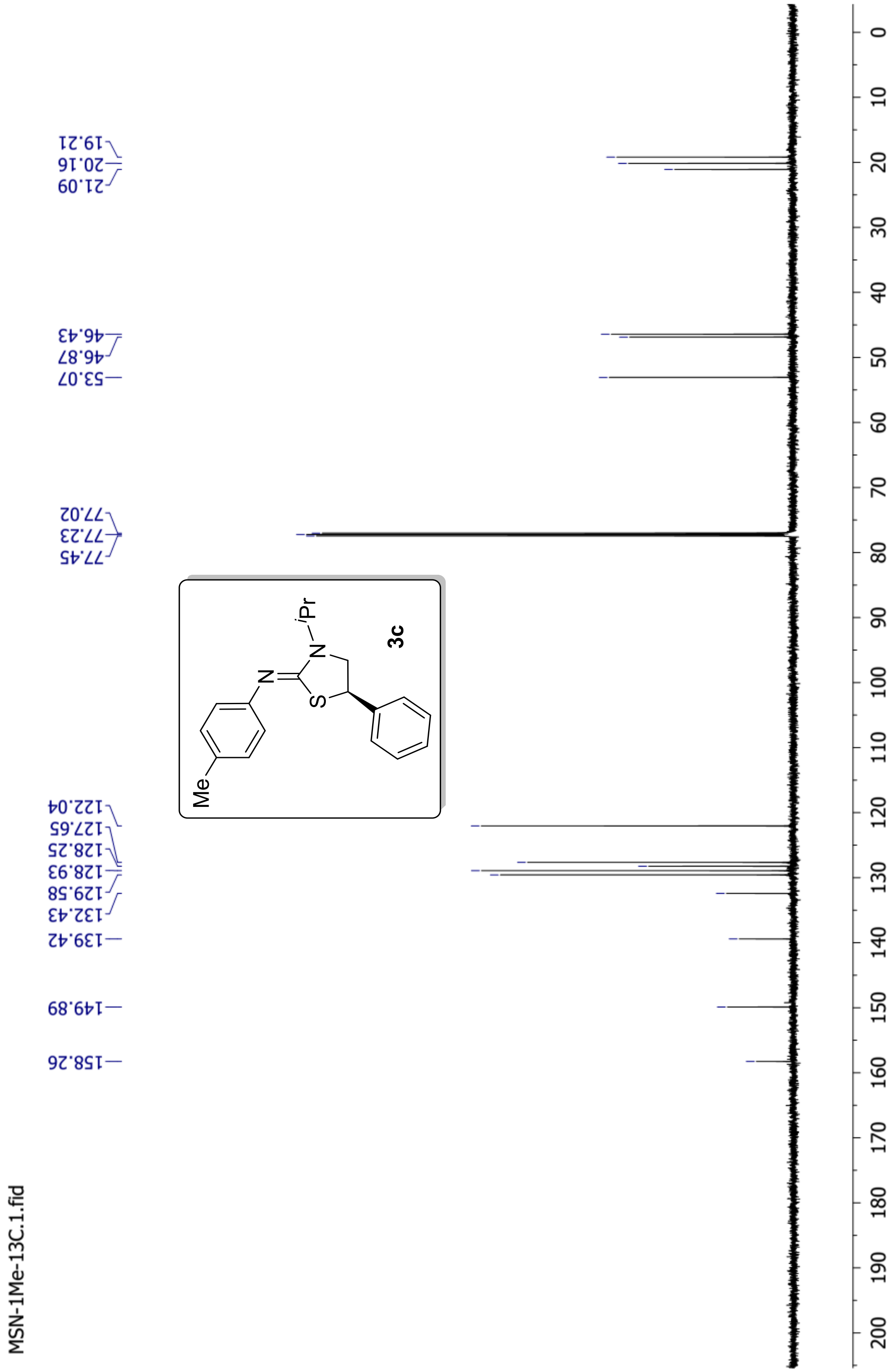
	RT	Height (μV)	% Area
1	9.319	1607702	99.46
2	13.161	3874	0.54

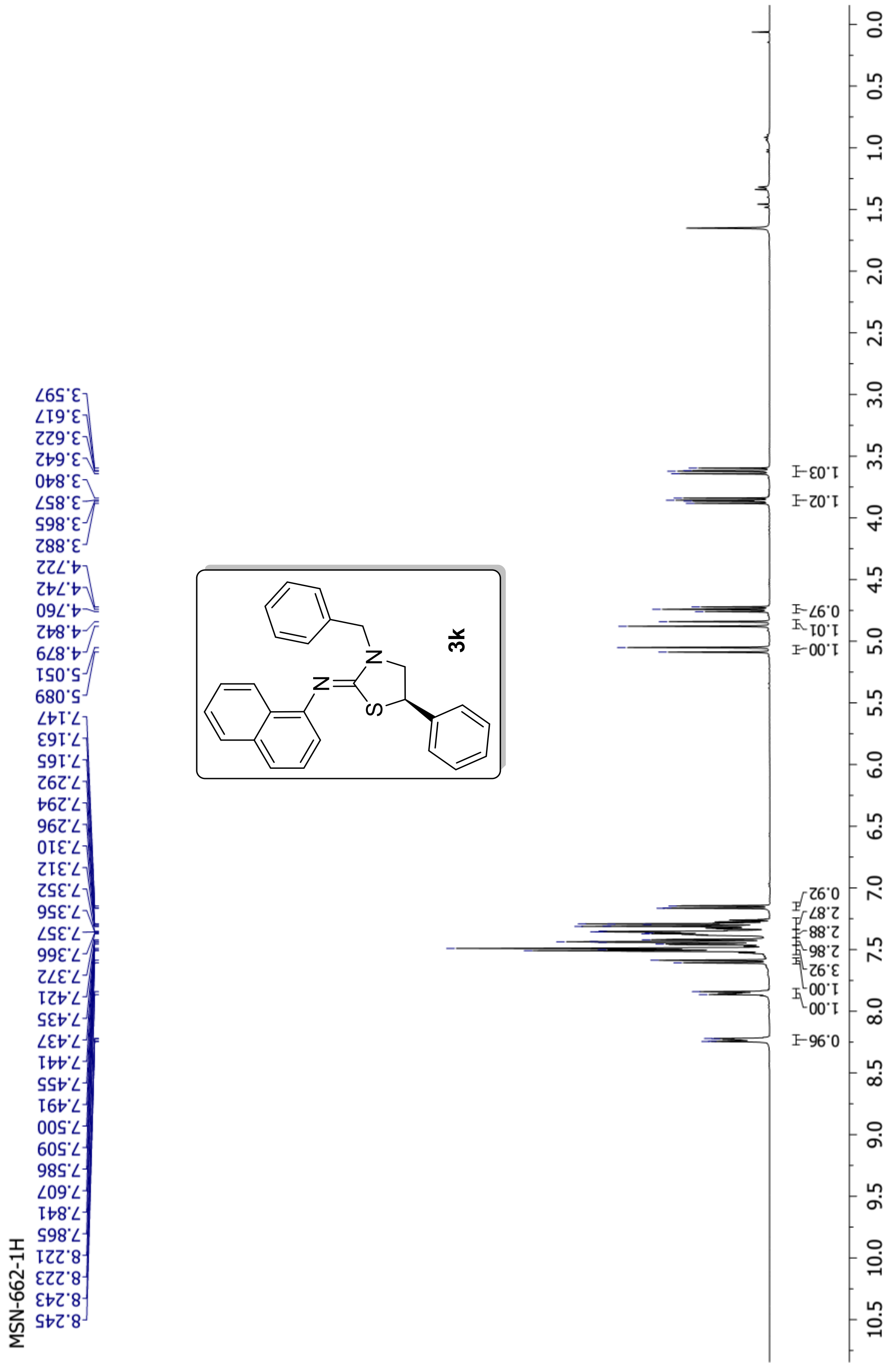
4.7 Selected NMR (^{1}H and ^{13}C) Spectra




19.23
20.17
46.48
46.91
53.10
77.01
77.23
77.43
122.31
123.13
127.65
128.30
128.96
139.37
152.39
158.26
MSN-Ph(H)-13C.1.fid
N
S
N
*i*Pr
3a
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200


MSN-1Me-1H.1.fid
3c
Me
iPr


19.21
20.16
21.09
46.43
46.87
53.07
77.02
77.23
77.45
122.04
127.65
128.25
128.93
129.58
132.43
139.42
149.89
158.26
MSN-1Me-13C.1.fid
3c
Me
N
S
N
iPr
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200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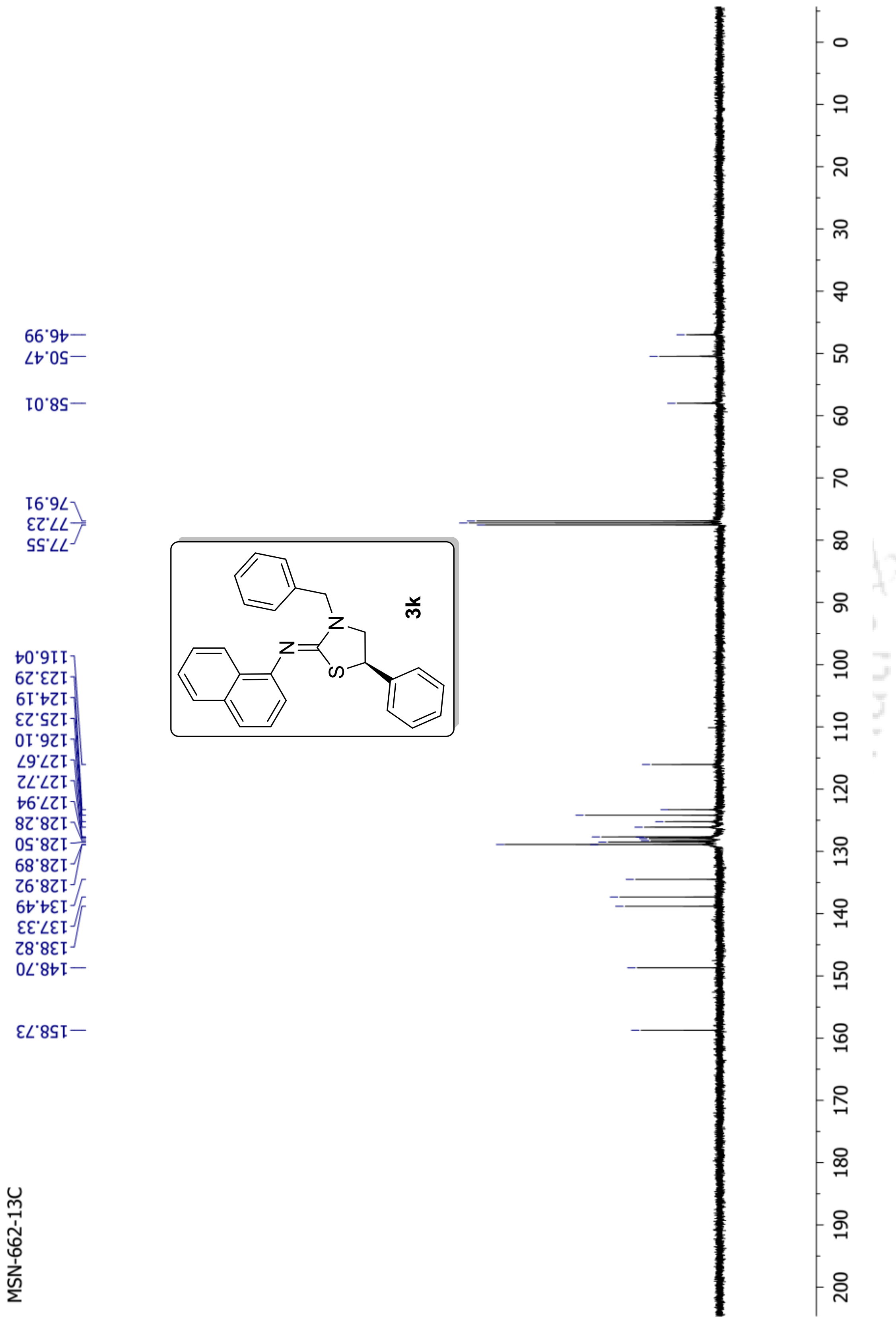
3k


MSN-662-13C
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138.82
137.33
134.49
128.92
128.89
128.50
128.28
127.94
127.72
127.67
126.10
125.23
124.19
123.29
116.04
77.55
77.23
76.91
58.01
50.47
46.99
N
S
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

Chapter V

Cu-Catalyzed Synthesis of Imidazolidines *via* Regioselective $C(sp^3)$–H Functionalization

The formation of C-N bonds has attracted considerable attention in synthetic chemistry due to presence of this moiety in many compounds that are important in pharmaceutical and biological sciences.[1] Transition-metal-catalyzed C-H functionalizations and subsequent C-N bond formations are particularly attractive because they are atom economical with braod substrate scope.[2] The catalytic oxidative transformation of the tertiary amines to generate iminium intermediate, as pioneered by Murahashi, Li and other groups has received much interest for $C(sp^3)$-H bond functionalization.[3] In this chapter, we report a simple Cu-catalyzed domino synthesis of substituted 1,3-imidazolidines from *N*-alkyl aniline and *N*-sulfonyl aziridines using *tert*-butyl hydroperoxide (TBHP) as an oxidant at moderate temperature.[4] This process involves C-N bonds formations *via* S_N2 nucleophilic ring opening and $C(sp^3)$–H functionalization.

Imidazolidines are important structural units that are found in natural products such as, (-)-aplaminal, chaetominine and (-)-dysibetaine PP.[5] Various bioactive compounds having imidazolidine scaffold exhibit a range of biological activities including anti-Trypanosoma cruzi agents, anti-inflammatory as well as widely used as central nervous system depressants, sedatives, and anticonvulsants.[6] They also find wide applications as catalysts and ligands in synthetic chemistry.[7] Therefore, the development of various synthetic strategies to access these class of compounds are highly desirable.

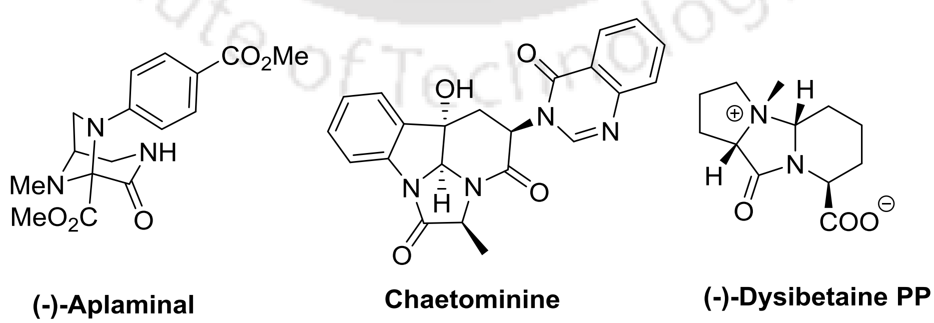
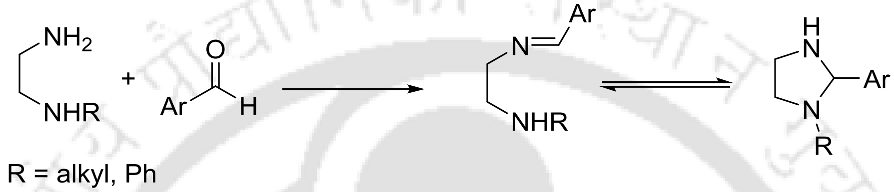


Figure 1. Examples of natural products contaning imidazolidines motifs

5.1 Strategies for Synthesis of Imidazolidines

5.1.1 Classical Method

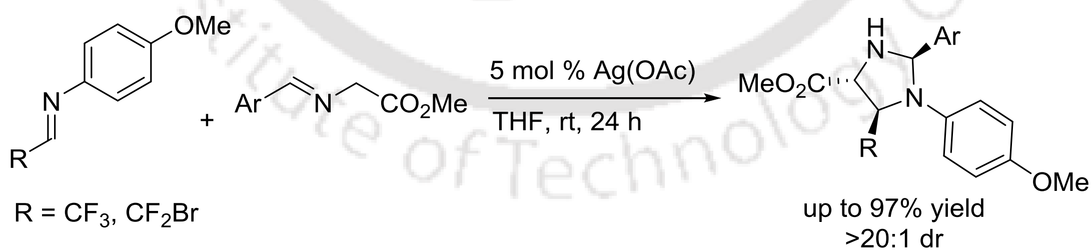
Generally, the classical method for the construction of substituted imidazolidines starts from the condensation of 1,2-diamine with aldehydes (Scheme 1).[8] However, *in situ* removal of water is needed to increase the reaction efficiency and unavailability of suitably substituted starting precursors limits these reactions for synthesizing different substituted imidazolidines.



Scheme 1. Classical Method for the Synthesis of Imidazolidines

5.1.2 Modern Methods

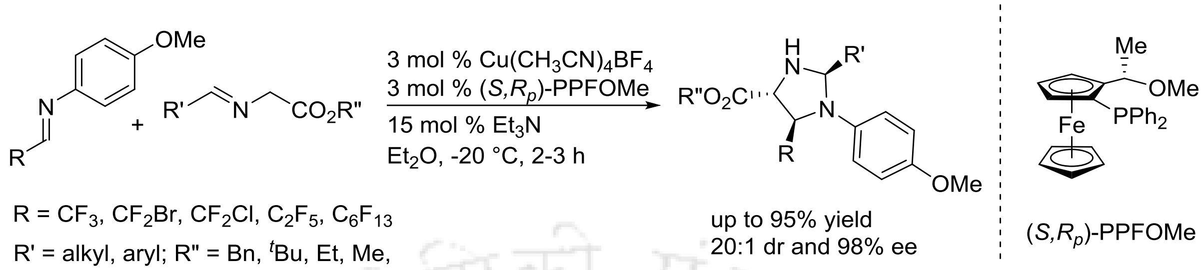
To overcome the limitations of traditional synthesis, considerable efforts are made on the development of new methods for the construction of substituted imidazolidines. For example, Wu and co-workers described diastereoselective synthesis of substituted imidazolidines from imines with azomethine ylides by Ag-catalyzed 1,3-dipolar cycloaddition (Scheme 2).[9] The reaction has been carried out using 5 mol % Ag(OAc) in THF at room temperature and imidazolidines have been obtained in good yields and diastereoselectivity.



Scheme 2. Ag-Catalyzed 1,3-Dipolar Cycloaddition of Imines with Azomethine Ylides

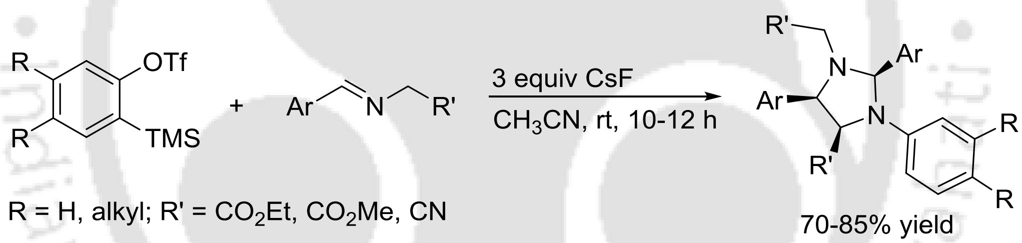
Cu-catalyzed asymmetric 1,3-diploar cycloaddition of azomethine ylides with fluorinated imines is reported to the synthesis of optically active fluorinated imidazolidines (Scheme 3).[10]

Using chiral ferrocene phosphine (S,R_p)-PPFOMe, the imidazolidine derivatives have been obtained in excellent diastereo and enantioselectivity.



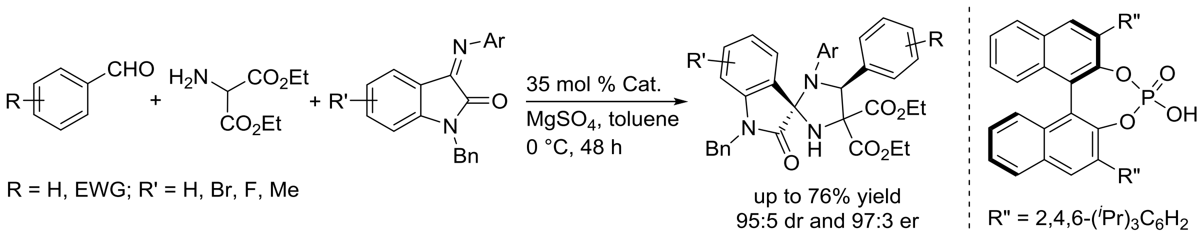
Scheme 3. Cu-Catalyzed Synthesis of Optically Active Imidazolidines Using (S,R_p)-PPFOMe

Hwu and co-workers reported a domino synthesis of imidazolidines from 2-(trimethylsilyl)aryl triflates and Schiff bases using an equivalent amount of CsF in CH_3CN (Scheme 4).[11] In this reaction, the azomethine ylides are generated *in situ* from aryne and Schiff base and followed by cycloaddition with another Schiff base to provide the desired imidazolidines in good yields.



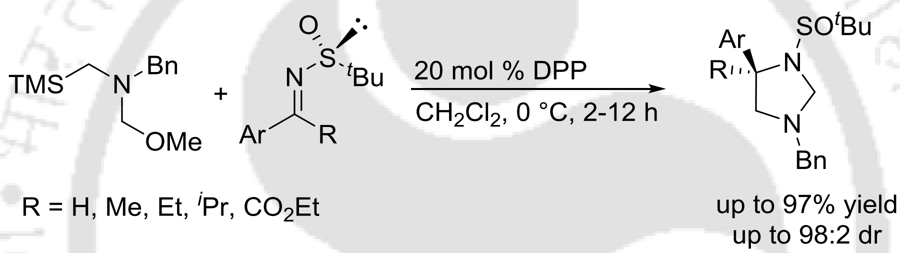
Scheme 4. CsF-Mediated Domino Synthesis of Highly Substituted Imidazolidines.

Shi group reported three component procedure for the construction of spiro[imidazolidine-2,3'-oxindole] in the presence of chiral phosphoric acid (Scheme 5).[12] This protocol involves the reaction of isatin-derived imines, aldehydes and diethyl 2-aminomalonate involving the azomethine ylides formation with subsequent 1,3-dipolar cycloadditions to afford spiro-derivated imidazolidines in good yields with high diastereo and enantioselectivities.



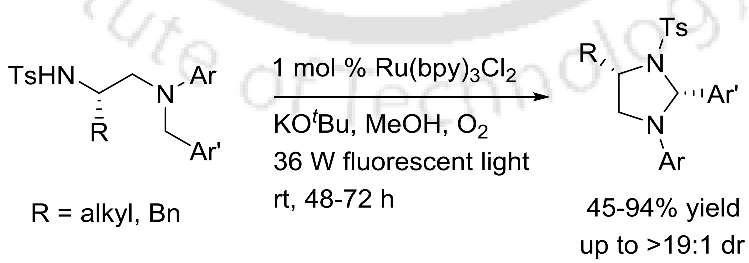
Scheme 5. Three-Component Synthesis of Imidazolidine Derivatives Using Chiral Phosphoric Acid

Asymmetric cycloaddition of *N*-sulfinylimines reported with non-stabilized azomethine ylide for the synthesis of 2-arylbenzothiazoles using diphenyl phosphate (DPP) in CH_2Cl_2 at 0 °C (Scheme 6).[13] The conversion of imidazolidines into the corresponding diamine was described in the presence of acidic medium.



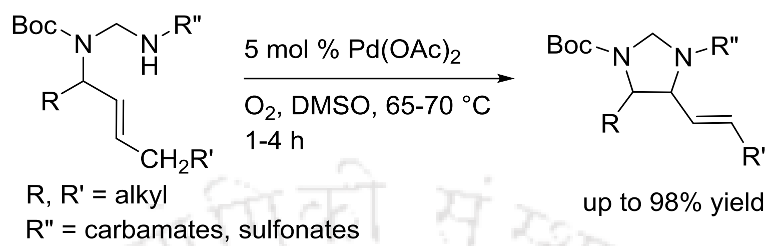
Scheme 6. Asymmetric Cycloaddition of *N*-Sulfinylimines with Azomethine Ylide

Ru-catalyzed visible light-induced intramolecular cyclization of diamines reported to the synthesis of imidazolidines (Scheme 6).[14] Using a combination of 1 mol % $Ru(bpy)_3Cl_2$ and KO^{t}Bu in MeOH under visible light, intramolecular cyclization gave the desired imidazolidines in 45-94% yield with 19:1 diastereoselectivity.



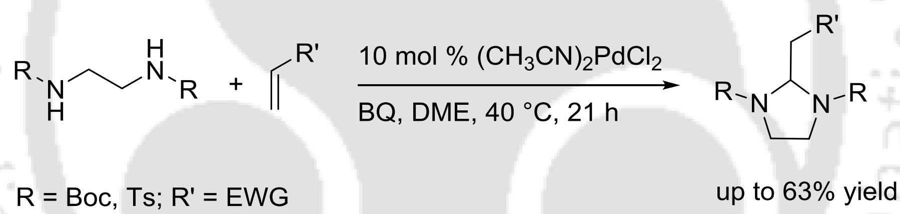
Scheme 7. Ru-Catalyzed Intramolecular Cyclization of Diamines

Hiemstra and co-workers reported Pd-catalyzed oxidative cyclization of aminals for the synthesis of imidazolidines (Scheme 8).[15] The authors described the synthesis of 1,2-diamines from corresponding imidazolidines in good yields.



Scheme 8. Synthesis of Imidazolidines Using Molecular Oxygen as Oxidant

Pd-catalyzed aza-Wacker reaction of *N*-tosyl and *N*-Boc derived 1,2-diamines with electron deficient alkenes using $(CH_3CN)_2PdCl_2$ and benzoquinone as an oxidant (Scheme 9).[16] The reaction takes place *via* sequence of enamine formation followed by cyclization to give the corresponding imidazolidines in 10-63% yields.

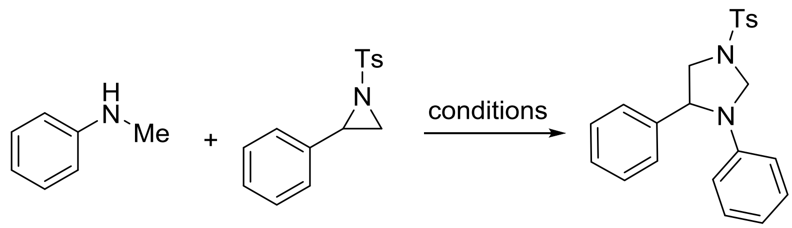


Scheme 9. Synthesis of Imidazolidines from 1,2-Diamines with Alkenes

5.2 Present Study

Herein we present Cu-catalyzed synthesis of imidazolidines in presence of ^{t}BuOOH at moderate temperature under air. This process involves a ring opening followed by C-N bond formation *via* C(sp^3)–H functionalization. First, optimization of the reaction conditions was performed using *N*-methylaniline **1a** and 2-phenyl-1-tosylaziridine **2a** as standard substrates employing different Cu-sources, oxidants and solvents (Table 1). Gratifyingly, the reaction occurred to furnish the target 3,4-diphenyl-1-tosylimidazolidine **3a** with 53% conversion when the substrates **1a** and **2a** were stirred at 60 °C for 6 h with 10 mol % of $Cu(OTf)_2$ and 3.0 equiv of TBHP in toluene (entry 1). Subsequent screening of the Cu sources, such as,

Table 1. Optimization of Reaction Conditions[a]

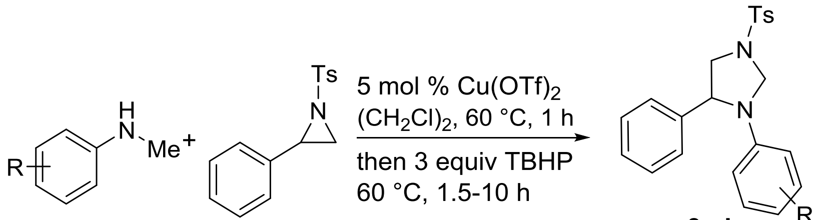


Entry	Catalyst (mol %)	Oxidant (equiv)	Solvent	*t* (h)	Conv. (%)[b]
1	$Cu(OTf)_2$ (10)	TBHP (3)	toluene	6	53
2	$Cu(OAc)_2$ (10)	TBHP (3)	toluene	6	18
3	$CuCl_2$ (10)	TBHP (3)	toluene	6	23
4	$Cu(NO_3)_2{\cdot}6H_2O$ (10)	TBHP (3)	toluene	6	39
5	$Cu(OTf)_2$ (10)	TBHP (3)	$(CH_2Cl)_2$	1	100
6	$Cu(OTf)_2$ (10)	TBHP (3)	THF	1	66
7	$Cu(OTf)_2$ (10)	TBHP (3)	DMSO	1	72
8	$Cu(OTf)_2$ (10)	TBHP (3)	$CHCl_3$	1	85
9	$Cu(OTf)_2$ (10)	TBHP (2.5)	$(CH_2Cl)_2$	5	89
10	**$Cu(OTf)_2$ (5)**	**TBHP (3)**	**$(CH_2Cl)_2$**	**1.5**	**100**
11	$Cu(OTf)_2$ (5)	DTBP (3)	$(CH_2Cl)_2$	1.5	n.d.
12	$Cu(OTf)_2$ (5)	O_2	$(CH_2Cl)_2$	1.5	9
13	$Cu(OTf)_2$ (5)	urea·H_2O_2 (3)	$(CH_2Cl)_2$	1.5	8
14	-	TBHP (3)	$(CH_2Cl)_2$	1.5	n.r.

[a] Reaction conditions: **1a** (0.55 mmol), **2a** (0. 5 mmol), Cu-catalyst, solvent (1 mL) were stirred at 60 °C for 1 h then oxidant was added. [b] Determined by 400 MHz ^{1}H NMR spectroscopy. n.d. = not detected. n.r. = no reaction

$Cu(OAc)_2$, $CuCl_2$ and $Cu(NO_3)_2{\cdot}3H_2O$ showed moderate catalytic activity (entries 2-4). The use of $(CH_2Cl)_2$ as the solvent led to completion of the process in 1 h with 100% conversion (entry 5), while THF, DMSO and $CHCl_3$ produced **3a** in 66–85% conversions (entries 6-8). Furthermore, a decrease in the amount of TBHP (2.5 equiv) led to prolonged reaction with

Table 2. Reaction of Substituted *N*-Methylanilines with Aziridine **2a**[a]



1a-l **2a** **3a-l**

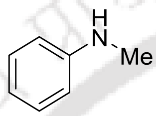
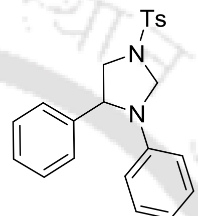
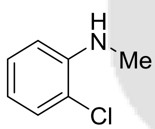
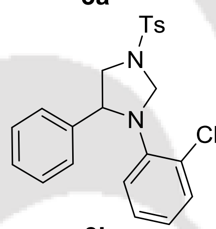
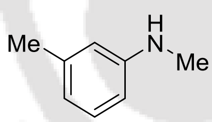
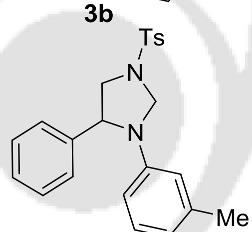
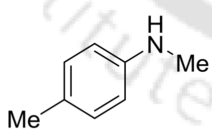
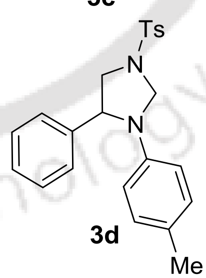
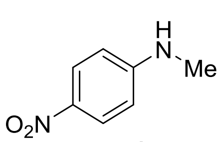
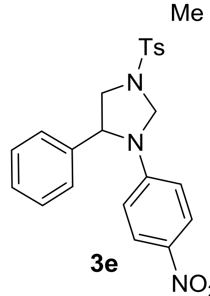
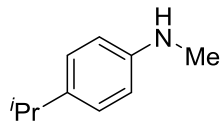
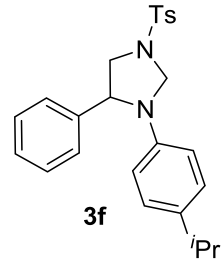
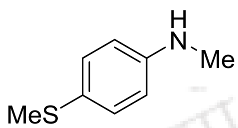
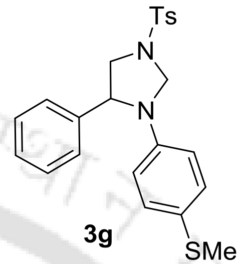
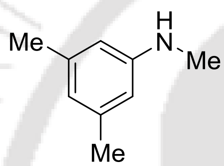
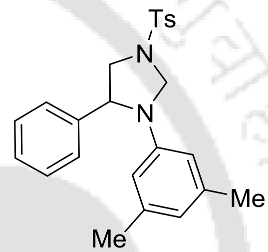
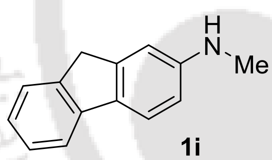
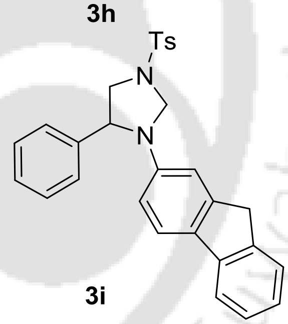
Entry	*N*-Methylanilines	Time (h)	Product	Yield (%)
1	 **1a**	1.5	 **3a**	86
2	 **1b**	5.0	 **3b**	55
3	 **1c**	1.5	 **3c**	66
4	 **1d**	1.5	 **3d**	77
5	 **1e**	10.0	 **3e**	52

Table 2 continued....

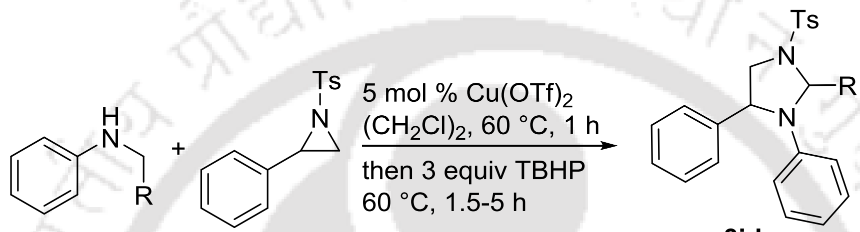
6	 **1f**	1.5	 **3f**	72
7	 **1g**	1.5	 **3g**	79
8	 **1h**	1.5	 **3h**	71
9	 **1i**	1.5	 **3i**	59

[a] Reaction conditions: **1a-l** (0.55 mmol), **2a** (0. 5 mmol), $Cu(OTf)_2$ (5 mol %), $(CH_2Cl)_2$ (1 mL) were stirred at 60 °C for 1 h then oxidant was added. [b] Isolated yield.

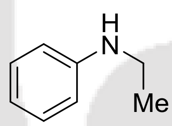
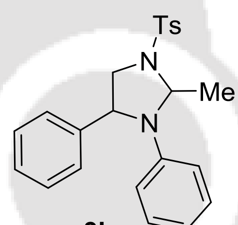
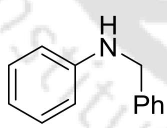
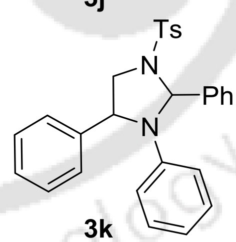
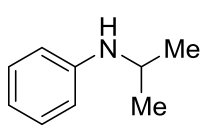
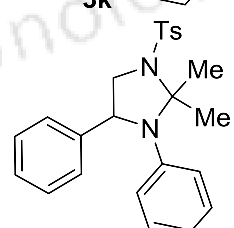
reduced conversion (entry 9). More favorably, we found that 100% conversion of **3a** could be obtained when this reaction was carried out with 5 mol % $Cu(OTf)_2$ in $(CH_2Cl)_2$ after 1.5 h (entry 10). Other oxidants such as DTBP, O_2 and urea·H_2O_2 produced inferior results (entries 11-13). A control experiment confirmed that without $Cu(OTf)_2$ the formation of **3a** was not observed and the starting material was recovered intact.

Having the optimal conditions in hand, the generality of this reaction was examined using a variety of substituted anilines **1a-i** (Table 2). A series of substitution at different position of the aromatic ring of the *N*-methylaniline **1a-h** containing both electron-rich and -poor groups underwent reaction with aziridine **2a** to give the target products in good to high yields. For instance, *N*-methylanilines having 2-chloro, 3-methyl, 4-methyl, 4-nitro, 4-isopropyl and 4-thiomethyl substituent in the phenyl ring reacted to furnish imidazolidines **3b-g** in 52-79% yields. Besides, the 3,5-dimethyl substituted aniline readily proceeded reaction with aziridine **2a** to provide **3h** in 71% yield. Similarly, *N*-methylaminofluorene **1i** produced the target imidazilidine **3i** in 59% yield.

Table 3. Reaction of Different *N*-Alkyl Anilines with Aziridine **1a**[a]

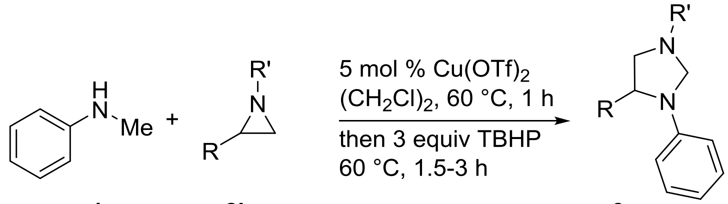


1j-l **2a** **3j-l**

Entry	*N*-Alkyl anilines	Time (h)	Product	Yield (%)
1	 **1j**	5.0	 **3j**	42
2	 **1k**	1.5	 **3k**	n.d.
3	 **1l**	5.0	 **3l**	n.d.

[a] Reaction conditions: **1j-l** (0.55 mmol), **2a** (0. 5 mmol), $Cu(OTf)_2$ (5 mol %), $(CH_2Cl)_2$ (1 mL) were stirred at 60 °C for 1 h then oxidant was added. [b] Isolated yield. n.d. = not detected.

Table 4. Reaction of Aniline **1a** with Substituted Aziridines[a]



1a **2b-p** **3m-aa**

R = alkyl, aryl; R' = Ts, SO_2Ph

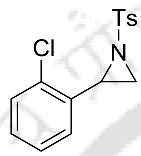
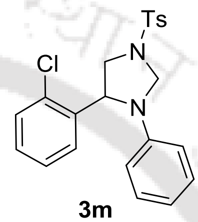
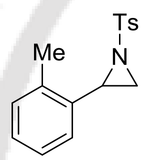
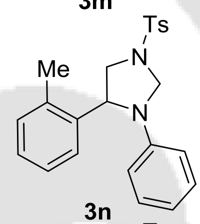
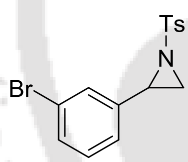
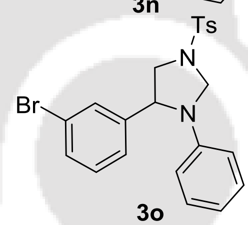
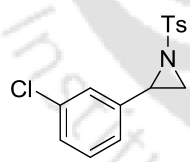
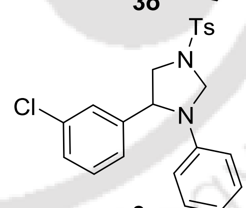
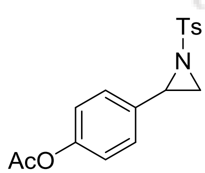
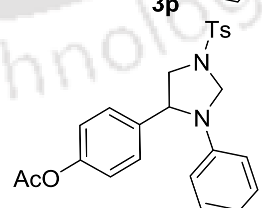
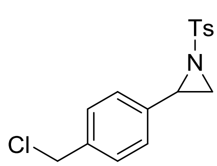
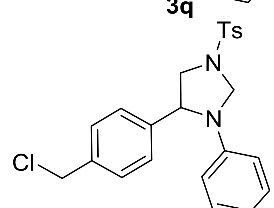
Entry	Aziridine	Time (h)	Product	Yield (%)
1	 **2b**	1.5	 **3m**	69
2	 **2c**	1.5	 **3n**	73
3	 **2d**	1.5	 **3o**	71
4	 **2e**	1.5	 **3p**	74
5	 **2f**	1.5	 **3q**	72
6	 **2g**	1.5	 **3r**	76

Table 4 continued.....

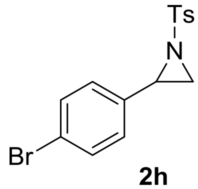
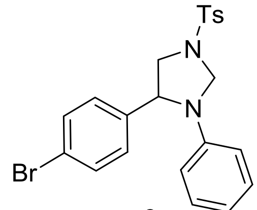
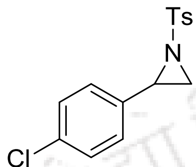
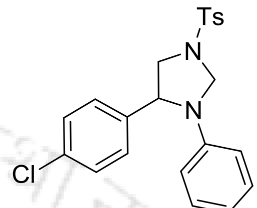
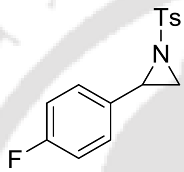
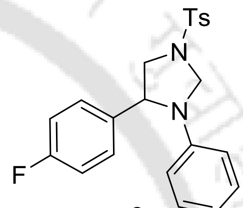
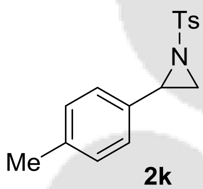
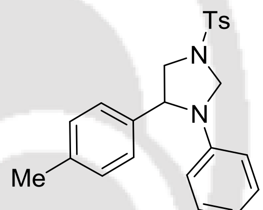
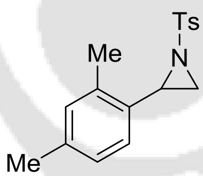
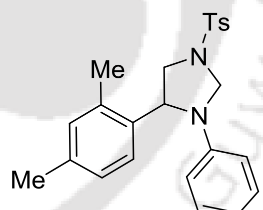
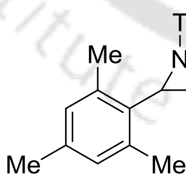
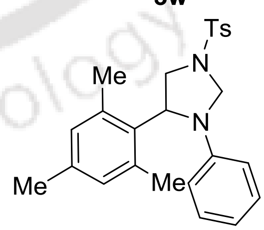
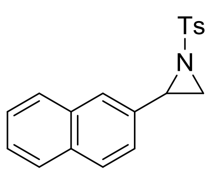
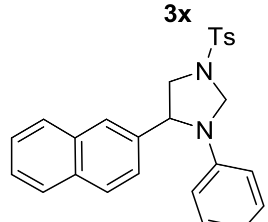
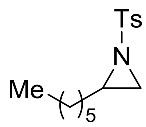
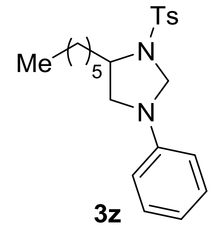
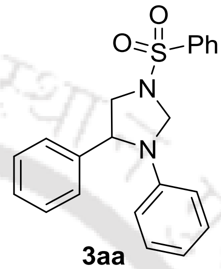
7	 **2h**	1.5	 **3s**	83
8	 **2i**	1.5	 **3t**	89
9	 **2j**	1.5	 **3u**	73
10	 **2k**	1.5	 **3v**	88
11	 **2l**	1.5	 **3w**	80
12	 **2m**	3.0	 **3x**	63
13	 **2n**	2.5	 **3y**	61

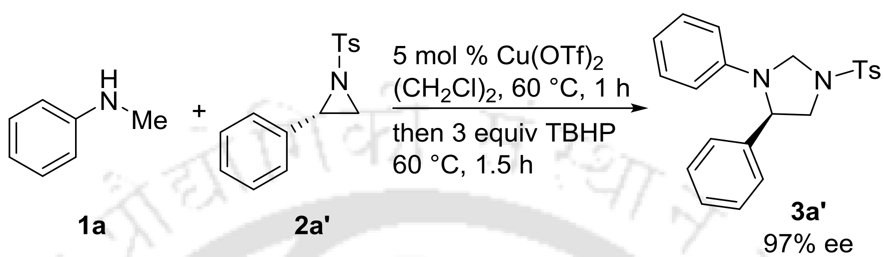
Table 4 continued.....

14	 **2o**	2.5	 **3z**	70
15	 **2p**	1.5	 **3aa**	82

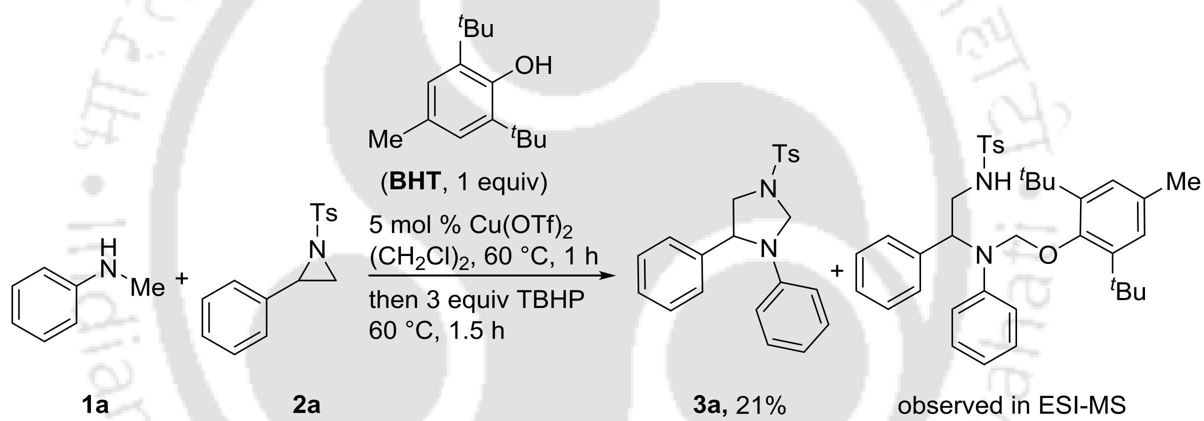
[a] Reaction conditions: amine **1a** (0.55 mmol), aziridine **2b-p** (0. 5 mmol), $Cu(OTf)_2$ (5 mol %), $(CH_2Cl)_2$ (1 mL) were stirred at 60 °C for 1 h then oxidant was added. [b] Isolated yield.

Further, the reaction of anilines bearing other *N*-alkyl substituents was studied (Table 3). *N*-Ethylaniline **1j** underwent reaction to give imidazolidine **3m** in 42% yield. In contrast, benzyl and isopropyl substituted anilines **1k-l** failed to produce the desired products **3n-o**, which may be due to steric hindrance of the alkyl groups. The substrate scope was further studied for the reaction of a series of *N*-tosyl aziridines with *N*-methylaniline as a standard substrate (Table 4). As above, the reaction efficiently occurred in high yields. 2-Aryl aziridines **2b-k** having 2-chloro, 2-methyl, 3-bromo, 3-chloro, 4-acetoxy, 4-CH_2Cl, 4-bromo, 4-chloro, 4-fluoro and 4-methyl functional groups in the aryl ring underwent reaction to furnish the imidazolidines **3m-v** in 69-89% yields. The reaction of 2-aryl aziridines bearing 2,4-dimethyl **2l** and 2,4,6-trimethyl **2m** substituents produced imidazolidines **3w-x** in 63-80% yields. Similar results were observed with 2-naphthyl **2n** and *n*-hexyl **2o** aziridines affording **3y** and **3z** in 61 and 70% yield, respectively. In addition, *N*-(phenylsulfonyl)aziridine **2p** underwent reaction to give imidazolidine **3aa** in 82% yield.

Next, the reaction of chiral aziridine **2a'** was investigated with **1a**. The reaction readily proceeded to give optically active **3a'** in 97% ee, suggesting that the radical formation in the reaction may not involve at benzylic position (Scheme 10). Our attempt to trap the radical intermediate using TEMPO or 1,1-diphenylethene was unsuccessful. There was no significant change in the yield of the product formation. However, the use of 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a radical scavenger in the reaction of *N*-methyl aniline **1a** with 2-phenyl-1-tosylaziridine **2a** dramatically decreases the product formation from 100 to 21% (Scheme 11). We observed the formation of BHT adduct using ESI-MS analysis.[17] These results suggest that the reaction proceeds *via* the radical pathway.

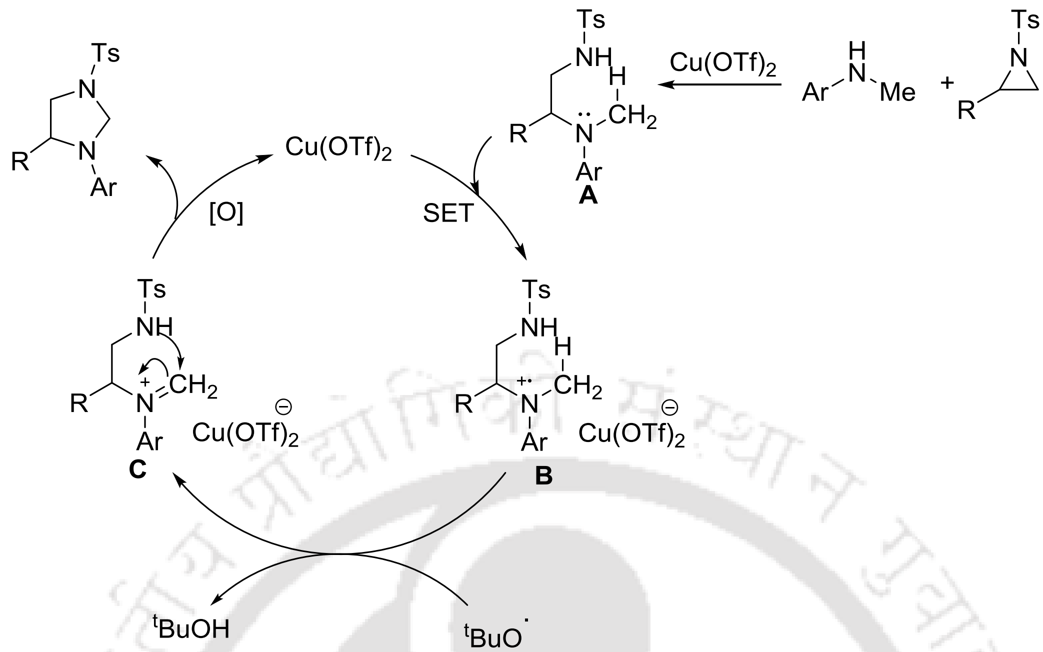


Scheme 10. Reaction with Chiral Aziridine



Scheme 11. Radical Scavenger Experiment

The proposed catalytic cycle is shown in Scheme 12. $Cu(OTf)_2$-catalyzed S_N2 nucleophilic opening of the aziridine with *N*-alkyl aniline can give the intermediate **A** that may convert into the radical cation **B** and $Cu(OTf)_2^-$ via single electron transfer (SET). Abstraction of *N*-methyl hydrogen by *tert*-butoxy radical can generate iminium cation **C** that may lead to cyclization to produce the target imidazolidines. Oxidation of the reduced $Cu(OTf)_2^-$ using TBHP may regenerate $Cu(OTf)_2$ to complete the catalytic cycle.



Scheme 12. Proposed Catalytic Cycle

In conclusion, a Cu-catalyzed domino synthesis of 1,3-imidazolidines is described from the readily accessible aziridines and *N*-alkyl anilines *via* a selective S_N2 nucleophilic ring opening and C(sp^3)–H functionalization using TBHP as an oxidant. This process is selective and provides the target imidazolidines in high yields. Chiral aziridine can be converted into the respective imidazolidine in high optical purity with opposite configuration.

5.3 Experimental Section

General Information. Amines, alkenes, $Cu(OTf)_2$ (98%), $Cu(OAc)_2$ (98%), $CuCl_2$ (99%) and oxidants [TBHP (5.5 M in decane), DTBP (98%), urea·H_2O_2 (97%)] were purchased from Aldrich and used as received. $Cu(NO_3)_2 \cdot 3H_2O$ (99%) was purchased from Merck. The reactions were monitored by analytical TLC on Merck silica gel G/GF 254 plates. The column chromatography was performed with Rankem silica gel (60-120 mesh). NMR (^{1}H and ^{13}C) spectra were recorded on DRX-400 Varian spectrometer, Bruker Avance III 600 spectrometer using and the data are accounted as follows: chemical shifts (δ ppm) (multiplicity, coupling constant (Hz), integration). The abbreviations for multiplicity are as follows: s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. Chemical shifts (δ) are reported relative to residual solvent signals

($CHCl_3$, 7.26 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR). Melting points were determined with a Büchi B-545 apparatus and are uncorrected. Optical rotation was determined by using Rudolph Research Analytical, Autopol II using a 50 mm path length cell at 589 nm at 23 °C. FT-IR spectra were recorded using Theromo Fischer Scientific IR spectrometer. Mass spectra were recorded on a ESI-MS TOF Instrument. HPLC analysis was carried out using Waters-2489 equipped with Daicel Chiralcel OD column.

General Procedure for Preparation of *N*-Methylanilines.[18] Sodium metal (5 mmol) was added portion wise in dry MeOH (20 mL) at 0 ºC. After complete consumption of sodium metal were added aniline (1 mmol) and paraformaldehyde (5 mmol) at room temperature (26 °C) and the mixture was stirred for 2 h at reflux to give the imine intermediate. The mixture was then reacted with $NaBH_4$ (1.5 mmol) at 0 ºC and the mixture was refluxed for an additional 2 h. The reaction mixture was then cooled to room temperature and the solvent was evaporated on a rotary evaporator to give a residue that was diluted with CH_2Cl_2 (15 mL) then washed with water (5 mL), dried (Na_2SO_4) and evaporated to give a residue which was purified on a silica gel column chromatography using hexane as an eluent.

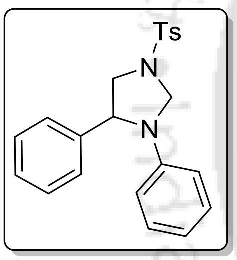
General Procedure for Preparation of Aziridines.[19] To a stirred solution of alkenes (1.0 mmol) and benzyltriethylammonium chloride (0.05 mmol) in CH_2Cl_2/H_2O (2:1, 15 mL) were added a solution of chloramine-T (1.1 mmol) and iodine (0.10 mmol) at room temperature under N_2. The stirring was continued for 24 h, then treated with a saturated $Na_2S_2O_3$ solution (2 mL) and extracted with CH_2Cl_2 (3×10 mL). Drying (Na_2SO_4) and evaporation of the solvent on a rotary evaporator gave a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate as an eluent.

Procedure for Preparation of Aminoalcohol. To a suspension of $LiAlH_4$ (2.2 mmol) in dry THF (10 mL) was added portionwise L-(+)-*α*-phenylglycine (1.0 mmol) at 0 °C. The mixture was allowed to reach to room temperature and stirring was continued for 1 h then refluxed for 24 h. The mixture quenched with EtOAc (50 mL), H_2O (1 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a (*S*)-(+)-2-phenylglycinol as pale yellow solid.

Procedure for Preparation of Chiral Aziridine. To a stirred solution of (*S*)-(+)-2-phenylglycinol (1.0 mmol), TsCl (2.5 mmol) and DMAP (0.05 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C were added a solution of Et_3N (3.0 mmol) in dry CH_2Cl_2 (5 mL). Then the mixture was allowed to reach to room temperature and stirring was continued for 24 h. The mixture was then treated with a saturated NH_4Cl solution (20 mL), and extracted with CH_2Cl_2 (3×10 mL), dried (Na_2SO_4) and evaporated on a rotary evaporator to give a residue, that was purified on a silica gel column chromatography using hexane and ethyl acetate as eluent.

General Procedure for the Synthesis of Imidazolidines. A mixture of aziridine (0.5 mmol), amine (0.55 mmol), $Cu(OTf)_2$ (0.025 mmol) and DCE (1 mL) were stirred for 1 h then, TBHP (1.5 mmol) was added, and then the stirring continued for appropriate time at 60 °C. The progress of the reaction was monitored by TLC using ethyl acetate and hexane. The reaction mixture was then evaporated on a rotary evaporator to give a residue that was purified on a silica gel column chromatography using hexane and ethyl acetate (9:1) as an eluent.

5.4 Characterization Data of Substituted Imidazolidines.



3,4-Diphenyl-1-tosylimidazolidine 3a.

Colorless solid; yield 86%.

Mp: 125-126 °C.

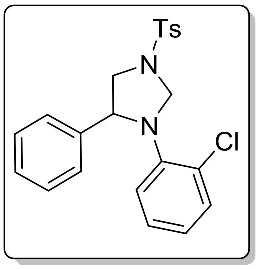
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.24-7.22 (m, 5H), 7.12-7.10 (m, 4H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 7.8 Hz, 2H), 5.03 (d, *J* = 6.0 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.53 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.92 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.46 (dd, *J* = 10.2, 4.8 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.0, 144.5, 140.6, 133.0, 130.0, 129.3, 129.1, 128.0, 127.8, 126.1, 118.4, 113.2, 66.2, 61.7, 55.7, 21.7.

FT-IR (KBr) 3060, 3025, 2923, 2803, 1599, 1508, 1491, 1345, 1158, 1087, 1029, 849, 746, 668 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}N_2O_2S$ 379.1475, found 379.1476.

3a': $[\alpha]_D^{20}$ = -26.0 (c= 0.2, $CHCl_3$).

HPLC analysis: 97% ee [Daicel CHIRALCEL OD column, hexane/^{i}PrOH = 90:10, flow rate: 1 mL /min, λ = 215 nm, t_R = 10.82 min (major), 20.02 min (minor)].



3-(2-Chlorophenyl)-4-phenyl-1-tosylimidazolidine 3b.

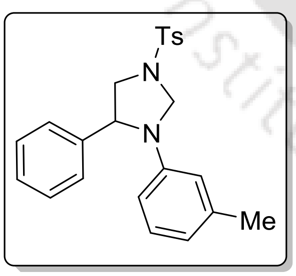
Colorless liquid; yield 52%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.20-7.17 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.87 (t, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.8 Hz, 1H), 5.29 (d, *J* = 7.2 Hz, 1H), 4.71 (t, *J* = 8.4 Hz, 1H), 4.46 (d, *J* = 7.2 Hz, 1H), 4.08 (dd, *J* = 10.8, 6.6 Hz, 1H), 3.24 (dd, *J* = 10.2, 8.4 Hz, 1H), 2.45 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.3, 142.9, 137.8, 133.8, 130.9, 130.3, 128.9, 128.2, 128.1, 127.4, 126.9, 124.2, 120.6, 68.5, 63.1, 55.0, 21.8.

FT-IR (neat) 3057, 3030, 2854, 1697, 1596, 1480, 1451, 1347, 1162, 1095, 935, 814, 756, 666 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}ClN_2O_2S$ 413.1085, found 413.1090.



4-Phenyl-3-*m*-tolyl-1-tosylimidazolidine 3c.

Colorless solid; yield 66%.

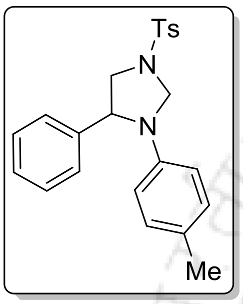
Mp: 133-134 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.25-7.23 (m, 5H), 7.12-7.10 (m, 2H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.22 (s, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 5.04 (d, *J* = 5.6 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 1H), 4.54 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.89 (dd, *J* = 10.4, 7.6 Hz, 1H), 3.46 (dd, *J* = 10.4, 5.2 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.4, 140.7, 139.1, 133.0, 130.0, 129.1, 129.0, 128.0, 127.8, 126.1, 119.4, 113.9, 110.5, 66.3, 61.6, 55.7, 21.9, 21.7.

FT-IR (KBr) 3025, 2960, 2921, 2853, 2812, 1603, 1585, 1491, 1453, 1343, 1158, 1088, 1029, 851, 801, 761, 668 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_2S$ 393.1631, found 393.1633.



4-Phenyl-3-*p*-tolyl-1-tosylimidazolidine 3d.

Colorless solid; yield 77%.

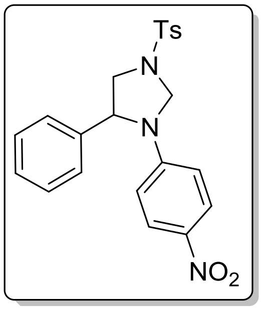
Mp: 141-142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.25-7.22 (m, 5H), 7.11-7.09 (m, 2H), 6.93 (dd, *J* = 8.8, 0.8 Hz, 2H), 6.31 (d, *J* = 8.8 Hz, 2H), 5.04 (d, *J* = 6.0 Hz, 1H), 4.70 (d, *J* = 5.6 Hz, 1H), 4.51 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.92 (dd, *J* = 10.4, 7.2 Hz, 1H), 3.43 (dd, *J* = 10.4, 5.2 Hz, 1H), 2.41 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 142.9, 140.7, 133.1, 130.0, 129.8, 129.0, 128.0, 127.8, 126.1, 113.5, 66.6, 61.9, 55.7, 21.7, 20.5.

FT-IR (KBr) 3028, 2920, 2853, 2817, 1619, 1600, 1523, 1492, 1347, 1184, 1162, 1099, 1027, 974, 814, 760, 668 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_2S$ 393.1631, found 393.1630.



3-(4-Nitrophenyl)-4-phenyl-1-tosylimidazolidine 3e.

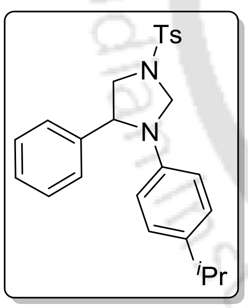
Yellow liquid; yield 52%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.6 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.29-7.27 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 2H), 6.32 (d, *J* = 9.6 Hz, 2H), 5.03 (d, *J* = 6.6 Hz, 1H), 4.91 (d, *J* = 6.6 Hz, 1H), 4.60 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.00 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.53 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 145.0, 138.9, 138.8, 132.6, 130.2, 129.4, 128.5, 127.9, 126.0, 125.8, 111.8, 65.4, 61.5, 55.7, 21.8.

FT-IR (neat) 3065, 3028, 2923, 1601, 1496, 1392, 1329, 1162, 1112, 1029, 950, 828, 667 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}N_3O_4S$ 424.1326, found 424.1321.



3-(4-Isopropylphenyl)-4-phenyl-1-tosylimidazolidine 3f.

Colorless solid; yield 72%.

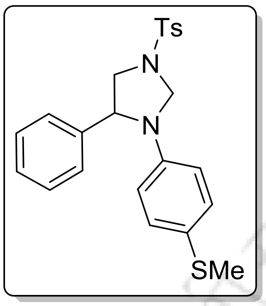
Mp: 138-139 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.27-7.31 (m, 5H), 7.15 (d, *J* = 6.6 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.37 (d, *J* = 8.4 Hz, 2H), 5.07 (d, *J* = 6.0 Hz, 1H), 4.73 (d, *J* = 6.0 Hz, 1H), 4.53 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.92 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.46 (dd, *J* = 10.2, 5.4 Hz, 1H), 2.80-2.76 (m, 1H), 2.41 (s, 3H), 1.18 (d, *J* = 3.6 Hz, 3H), 1.17 (d, *J* = 3.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.4, 143.2, 140.8, 138.9, 132.9, 130.0, 129.0, 128.0, 127.8, 127.1, 126.1, 113.3, 66.5, 62.0, 55.7, 33.2, 24.31, 24.3, 21.7.

FT-IR (KBr) 3036, 2954, 2939, 2859, 1617, 1601, 1522, 1349, 1186, 1162, 1098, 1031, 850, 813, 668 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{28}N_2O_2S$ 421.1944, found 421.1944.



3-(4-(Methylthio)phenyl)-4-phenyl-1-tosylimidazolidine 3g.

Colorless solid; yield 79%.

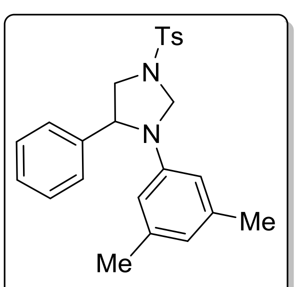
Mp: 77-78 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.25-7.22 (m, 5H), 7.12-7.09 (m, 4H), 6.32 (d, *J* = 9.0 Hz, 2H), 5.01 (d, *J* = 6.0 Hz, 1H), 4.75 (d, *J* = 6.0 Hz, 1H), 4.49 (dd, *J* = 7.2, 5.4 Hz, 1H), 3.94 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.44 (dd, *J* = 10.2, 5.4 Hz, 1H), 2.40 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.5, 143.5, 140.2, 132.9, 130.6, 130.1, 129.1, 128.0, 126.0, 113.9, 66.2, 61.7, 55.7, 21.7, 18.6.

FT-IR (KBr) 3064, 3025, 2919, 2859, 2806, 1597, 1502, 1351, 1164, 1093, 1028, 910, 850, 804, 667 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_2S_2$ 425.1352, found 425.1352.



3-(3,5-Dimethylphenyl)-4-phenyl-1-tosylimidazolidine 3h.

Colorless solid; yield 71%.

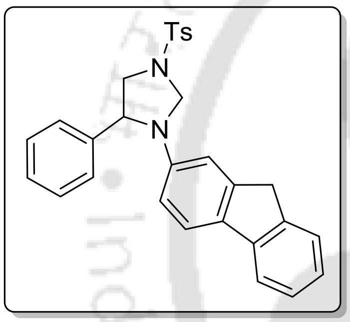
Mp: 166-167 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.25-7.24 (m, 5H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.42 (s, 1H), 6.05 (s, 2H), 5.05 (d, *J* = 5.4 Hz, 1H), 4.75 (d, *J* = 5.4 Hz, 1H), 4.58 (dd, *J* = 7.8, 5.4 Hz, 1H), 3.89 (dd, *J* = 10.2, 7.8 Hz, 1H), 3.48 (dd, *J* = 10.2, 4.8 Hz, 1H), 2.42 (s, 3H), 2.19 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.0, 144.3, 140.8, 138.9, 132.7, 130.0, 128.9, 128.0, 127.6, 126.0, 120.4, 111.1, 66.2, 61.4, 55.6, 21.7.

FT-IR (KBr) 3020, 2914, 2864, 1600, 1482, 1389, 1353, 1222, 1165, 1092, 1044, 851, 665 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{26}N_2O_2S$ 407.1788, found 407.1795.



3-(9H-Fluoren-2-yl)-4-phenyl-1-tosylimidazolidine 3i.

Colorless solid; yield 59%.

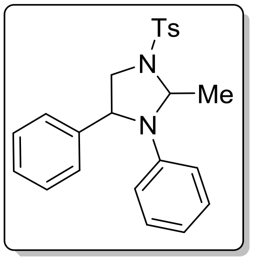
Mp: 233-234 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.31-7.22 (m, 6H), 7.20-7.13 (m, 3H), 6.59 (d, *J* = 1.6 Hz, 1H), 6.38 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.10 (d, *J* = 6.0 Hz, 1H), 4.84 (d, *J* = 6.0 Hz, 1H), 4.60 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.95 (dd, *J* = 10.4, 7.2 Hz, 1H), 3.74 (s, 2H), 3.49 (dd, *J* = 10.4, 5.2 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.5, 144.3, 142.4, 142.0, 140.6, 132.9, 132.8, 130.1, 129.1, 128.0, 127.9, 126.9, 126.1, 125.4, 124.9, 120.6, 118.9, 112.2, 109.9, 66.5, 61.7, 55.8, 37.2, 21.8.

FT-IR (KBr) 3055, 3024, 2917, 2816, 1616, 1575, 1489, 1456, 1343, 1161, 1100, 1030, 851, 762, 669 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{26}N_2O_2S$ 467.1788, found 467.1792.



2-Methyl-3,4-diphenyl-1-tosylimidazolidine 3j.

Colorless solid; yield 42%.

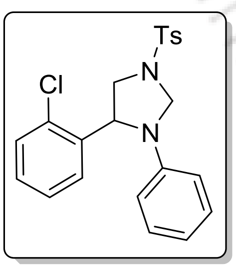
Mp: 146-147 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.29-7.23 (m, 3H), 7.16 (d, *J* = 6.8 Hz, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 8.0 Hz, 2H), 5.60 (q, *J* = 6.0 Hz, 1H), 4.27 (dd, *J* = 13.6, 7.6 Hz, 1H), 3.77 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.44 (dd, *J* = 13.2, 9.6 Hz, 1H), 2.27 (s, 3H), 1.71 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.6, 144.4, 140.4, 134.6, 129.9, 129.2, 129.0, 128.0, 127.6, 125.8, 118.0, 112.4, 74.7, 62.2, 54.1, 23.1, 21.6.

FT-IR (KBr) 3060, 3033, 2980, 2950, 2925, 2889, 1599, 1501, 1455, 1347, 1158, 1088, 1013, 916, 810, 751, 671 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_2S$ 393.1631, found 393.1644.



4-(2-Chlorophenyl)-3-phenyl-1-tosylimidazolidine 3m.

Colorless solid; yield 69%.

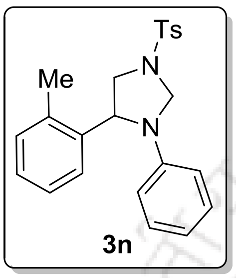
Mp: 122-123 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.20-7.16 (m, 3H), 7.13 (t, *J* = 7.2 Hz, 2H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.28 (d, *J* = 7.8 Hz, 2H), 5.09 (d, *J* = 6.0 Hz, 1H), 4.84 (dd, *J* = 7.8, 4.8 Hz, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 3.99 (dd, *J* = 10.8, 7.2 Hz, 1H), 3.54 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.52, 144.5, 137.6, 132.9, 132.3, 130.1, 129.9, 129.4, 129.0, 128.0, 127.5, 127.4, 118.6, 112.9, 66.0, 59.0, 54.1, 21.7.

FT-IR (KBr) 3064, 2925, 2823, 1657, 1599, 1508, 1350, 1159, 1088, 1033, 844, 747, 667 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}ClN_2O_2S$ 413.1085, found 413.1085.



3-Phenyl-4-(*o*-tolyl)-1-tosylimidazolidine 3n.

Colorless solid; yield 73%.

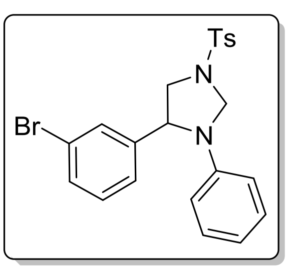
Mp: 144-145 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 3H), 7.00-6.96 (m, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 8.4 Hz, 2H), 5.07 (d, *J* = 6.0 Hz, 1H), 4.84 (d, *J* = 6.0 Hz, 1H), 4.61 (dd, *J* = 7.8, 5.4 Hz, 1H), 4.01 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.39 (dd, *J* = 10.8, 6.0 Hz, 1H), 2.40 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.9, 144.5, 137.9, 134.2, 132.9, 130.9, 130.0, 129.2, 127.9, 127.5, 126.8, 125.4, 118.2, 112.9, 66.2, 58.8, 54.2, 21.7, 19.4.

FT-IR (KBr) 3059, 2920, 2823, 1599, 1509, 1488, 1346, 1158, 1098, 1032, 846, 744, 667 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_2S$ 393.1631, found 393.1632.



4-(3-Bromophenyl)-3-phenyl-1-tosylimidazolidine 3o.

Colorless solid; yield 71%.

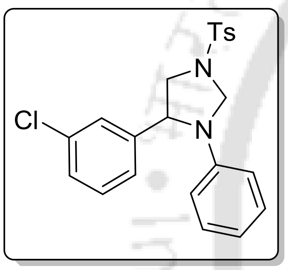
Mp: 131-132 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.24-7.23 (m, 3H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 2H), 5.04 (d, *J* = 6.0 Hz, 1H), 4.72 (d, *J* = 6.0 Hz, 1H), 4.49 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.90 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.46 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 144.6, 143.1, 132.8, 131.1, 130.7, 130.1, 129.4, 129.0, 127.9, 124.7, 123.2, 118.8, 113.2, 66.2, 61.2, 55.5, 21.8.

FT-IR (KBr) 3070, 3022, 2920, 2817, 1600, 1571, 1507, 1346, 1161, 1088, 1024, 847, 747, 665 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}BrN_2O_2S$ 459.0561, found 459.0571.



4-(3-Chlorophenyl)-3-phenyl-1-tosylimidazolidine 3p.

Colorless solid; yield 74%.

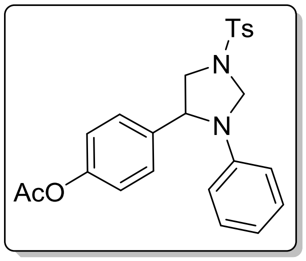
Mp: 141-142 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.24-7.17 (m, 4H), 7.15 (t, *J* = 8.4 Hz, 2H), 7.08 (s, 1H), 7.04 (d, *J* = 6.6 Hz, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 2H), 5.07 (d, *J* = 6.0 Hz, 1H), 4.75 (d, *J* = 6.0 Hz, 1H), 4.52 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.93 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.48 (dd, *J* = 10.2, 4.8 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.63, 144.6, 142.9, 134.9, 132.7, 130.3, 130.0, 129.3, 128.0, 127.9, 126.1, 124.3, 118.7, 113.2, 66.1, 61.2, 55.4, 21.7.

FT-IR (KBr) 3064, 3036, 2928, 2824, 1600, 1576, 1508, 1346, 1161, 1090, 1027, 848, 748, 668 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}ClN_2O_2S$ 413.1085, found 413.1087.



4-(3-Phenyl-1-tosylimidazolidin-4-yl)phenyl acetate 3q.

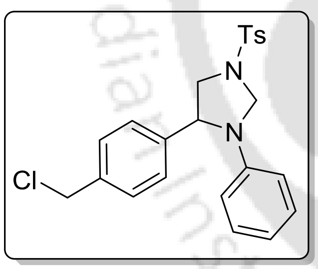
Colorless liquid; yield 72%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.14-7.11 (m, 4H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 7.8 Hz, 2H), 5.02 (d, *J* = 6.0 Hz, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 4.54 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.91 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.44 (dd, *J* = 10.2, 5.4 Hz, 1H), 2.40 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.5, 150.2, 144.8, 144.6, 138.0, 132.8, 130.1, 129.3, 128.0, 127.1, 122.2, 118.6, 113.3, 66.2, 61.2, 55.6, 21.7, 21.3.

FT-IR (neat) 3028, 2923, 2854, 1756, 1662, 1600, 1504, 1351, 1210, 1197, 1163, 1093, 1015, 912, 814, 752, 666 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{24}N_2O_4S$ 437.1530, found 437.1540.



4-(4-(Chloromethyl)phenyl)-3-phenyl-1-tosylimidazolidine 3r.

Colorless solid; yield 76%.

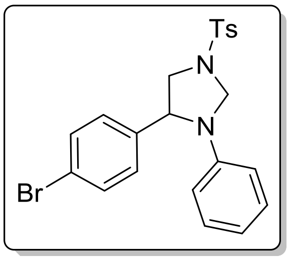
Mp: 175-176 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.13-7.09 (m, 4H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 7.8 Hz, 2H), 5.04 (d, *J* = 6.0 Hz, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 4.56-4.54 (m, 3H), 3.91 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.46 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 144.5, 141.0, 137.1, 132.9, 130.1, 129.4, 128.0, 126.5, 118.6, 113.2, 66.2, 61.4, 55.6, 46.0, 21.8.

FT-IR (KBr) 3053, 2965, 2921, 2822, 1600, 1508, 1347, 1161, 1092, 1028, 816, 744, 667 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}ClN_2O_2S$ 427.1242, found 427.1257.



4-(4-Bromophenyl)-3-phenyl-1-tosylimidazolidine 3s.

Colorless solid; yield 83%.

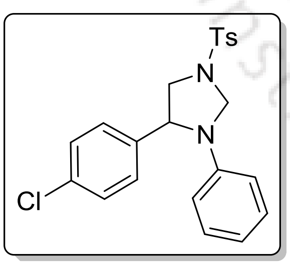
Mp: 179-180 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 8.4 Hz, 2H), 5.04 (d, *J* = 6.0 Hz, 1H), 4.73 (d, *J* = 5.4 Hz, 1H), 4.52 (dd, *J* = 7.2, 4.2 Hz, 1H), 3.91 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.47 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.63, 144.6, 139.7, 133.0, 132.1, 130.0, 129.4, 127.9, 127.8, 121.6, 118.7, 113.1, 66.0, 61.1, 55.5, 21.8.

FT-IR (KBr) 3075, 3019, 2897, 2812, 1600, 1504, 1485, 1381, 1343, 1158, 1054, 1029, 855, 748, 667 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}BrN_2O_2S$ 459.0561, found 459.0561.



4-(4-Chlorophenyl)-3-phenyl-1-tosylimidazolidine 3t.

Colorless solid; yield 89%.

Mp: 168-169 °C.

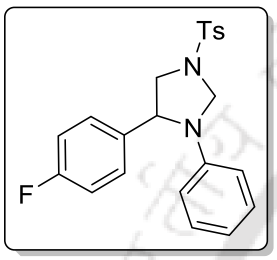
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.36

(d, *J* = 8.0 Hz, 2H), 5.04 (d, *J* = 6.0 Hz, 1H), 4.73 (d, *J* = 6.0 Hz, 1H), 4.53 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.91 (dd, *J* = 10.8, 7.6 Hz, 1H), 3.46 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.6, 139.2, 133.6, 133.1, 130.1, 129.4, 129.2, 127.9, 127.5, 118.7, 113.2, 66.1, 61.1, 55.6, 21.8.

FT-IR (KBr) 3067, 3024, 2926, 2889, 2811, 1600, 1505, 1487, 1343, 1158, 1088, 1029, 820, 749, 666 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}ClN_2O_2S$ 413.1085, found 413.1085.



4-(4-Fluorophenyl)-3-phenyl-1-tosylimidazolidine 3u.

Colorless solid; yield 73%.

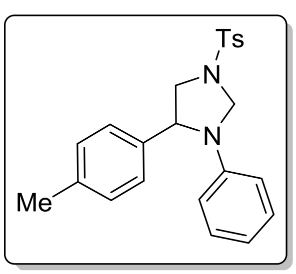
Mp: 179-180 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 2H), 7.09 (dd, *J* = 9.0, 5.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.75 (t, *J* = 7.8 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 2H), 5.05 (d, *J* = 6.0 Hz, 1H), 4.72 (d, *J* = 5.4 Hz, 1H), 4.54 (dd, *J* = 7.8, 4.8 Hz, 1H), 3.89 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.45 (dd, *J* = 10.2, 4.8 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$ = 244.5 Hz), 144.7, 144.6, 136.3, 132.9, 130.0, 129.4, 128.0, 127.7 (d, $J_{C\text{-}F}$ = 9.0 Hz), 118.6, 116.0 (d, $J_{C\text{-}F}$ = 21.0 Hz), 113.2, 66.1, 61.0, 55.7, 21.7.

FT-IR (KBr) 3058, 2923, 2892, 2821, 1601, 1508, 1346, 1223, 1161, 1088, 1028, 829, 750, 666 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{21}FN_2O_2S$ 397.1381, found 397.1381.



3-Phenyl-4-(*p*-tolyl)-1-tosylimidazolidine 3v.

Colorless solid; yield 88%.

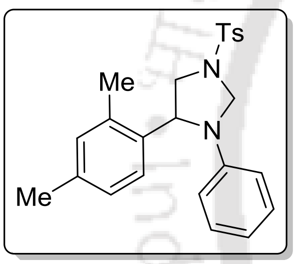
Mp: 147-148 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 5.02 (d, *J* = 6.0 Hz, 1H), 4.75 (d, *J* = 6.0 Hz, 1H), 4.50 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.90 (dd, *J* = 10.4, 7.6 Hz, 1H), 3.43 (dd, *J* = 10.4, 5.2 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.4, 137.6, 137.5, 133.0, 130.0, 129.7, 129.3, 128.0, 126.0, 118.4, 113.2, 66.2, 61.4, 55.9, 21.8, 21.3.

FT-IR (KBr) 3060, 2928, 2881, 2819, 1598, 1508, 1349, 1162, 1094, 1024, 812, 743, 666 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_2O_2S$ 393.1631, found 393.1632.



4-(2,4-Dimethylphenyl)-3-phenyl-1-tosylimidazolidine 3w.

Colorless solid; yield 80%.

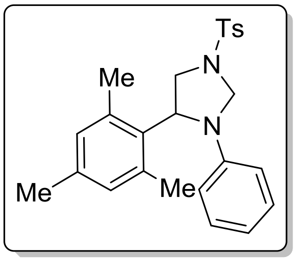
Mp: 162-163 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 2H), 6.97 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 2H), 5.02 (d, *J* = 6.0 Hz, 1H), 4.82 (d, *J* = 6.4 Hz, 1H), 4.56 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.97 (dd, *J* = 10.8, 7.6 Hz, 1H), 3.33 (dd, *J* = 10.8, 5.6 Hz, 1H), 2.39 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 144.5, 137.2, 134.9, 134.1, 133.2, 131.7, 130.0, 129.3, 128.0, 127.5, 125.5, 118.3,113.0, 66.3, 58.8, 54.5, 21.8, 21.2, 19.4.

FT-IR (KBr) 3061, 3028, 2911, 2792, 1599, 1506, 1464, 1380, 1354, 1165, 1096, 1029, 811, 749, 662 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{26}N_2O_2S$ 407.1788, found 407.1788.



4-Mesityl-3-phenyl-1-tosylimidazolidine 3x.

Colorless solid; yield 63%.

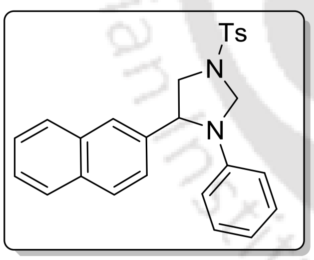
Mp: 171-172 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.76 (br s, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.17 (d, *J* = 8.4 Hz, 2H), 4.98 (d, *J* = 7.2 Hz, 1H), 4.85 (d, *J* = 7.2 Hz, 1H), 4.57 (t, *J* = 7.8 Hz, 1H), 4.06 (dd, *J* = 11.4, 7.8 Hz, 1H), 3.32 (dd, *J* = 11.4, 9.6 Hz, 1H), 2.40 (s, 3H), 2.21 (s, 3H), 2.14 (br s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 144.6, 137.2, 135.7, 133.0, 131.2, 130.0, 129.2, 128.0, 118.0, 112.2, 66.1, 57.8, 52.4, 21.7, 20.9, 20.7 (br s).

FT-IR (KBr) 3027, 2968, 2917, 2855, 1599, 1507, 1345, 1166, 1091, 1034, 970, 806, 750, 665 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{28}N_2O_2S$ 421.1944, found 421.1957.



4-(Naphthalen-2-yl)-3-phenyl-1-tosylimidazolidine 3y.

Colorless solid; yield 61%.

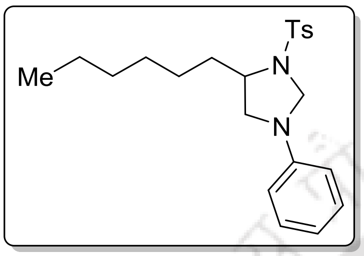
Mp: 167-168 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.70-7.68 (m, 3H), 7.53 (s, 1H), 7.48-7.46 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 2H), 5.16 (d, *J* = 6.0 Hz, 1H), 4.86 (d, *J* = 6.0 Hz, 1H), 4.73 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.04 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.60 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.0, 144.4, 138.0, 133.4, 133.1, 129.9, 129.3, 129.1, 128.0, 127.9, 127.8, 126.4, 126.1, 125.0, 123.8, 118.5, 113.2, 66.2, 61.8, 55.6, 21.7.

FT-IR (KBr) 3058, 3047, 2928, 2810, 1599, 1506, 1383, 1343, 1158, 1087, 1030, 815, 745, 666 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{24}N_2O_2S$ 429.1631, found 429.1641.



4-Hexyl-1-phenyl-3-tosylimidazolidine 3z.

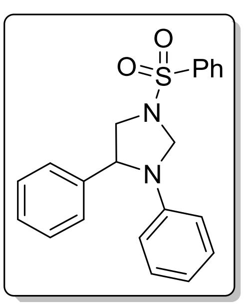
Colorless liquid; yield 70%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 4H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 2H), 4.87 (d, *J* = 7.8 Hz, 1H), 4.59 (d, *J* = 7.2 Hz, 1H), 4.02-3.98 (m, 1H), 3.01 (dd, *J* = 9.0, 7.2 Hz, 1H), 2.96 (dd, *J* = 9.0, 3.6 Hz, 1H), 2.37 (s, 3H), 1.82-1.77 (m, 1H), 1.62-1.57 (m, 1H), 1.48-1.21 (m, 8H), 0.91 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.6, 144.0, 134.6, 129.9, 129.3, 127.6, 118.1, 112.8, 64.2, 59.4, 51.3, 35.0, 31.8, 29.2, 25.8, 22.7, 21.6, 14.2.

FT-IR (neat) 3063, 3031, 2927, 2856, 1712, 1600, 1507, 1381, 1161, 1093, 1032, 995, 814, 749, 666 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{30}N_2O_2S$ 387.2101, found 387.2124.



3,4-Diphenyl-1-(phenylsulfonyl)imidazolidine 3aa.

Colorless solid; yield 82%.

Mp: 123-124 °C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.27-7.22 (m, 3H), 7.14-7.12 (m, 4H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 7.8 Hz, 2H), 5.08 (d, *J* = 6.0 Hz, 1H), 4.80 (d, *J* = 5.4 Hz, 1H), 4.53 (dd, *J* = 7.8, 5.4 Hz, 1H), 3.94 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.49 (dd, *J* = 10.8, 5.4 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 140.5, 136.0, 133.5, 129.4, 129.3, 129.1, 127.93, 127.9, 126.0, 118.5, 113.2, 66.2, 61.6, 55.7.

FT-IR (KBr) 3060, 3030, 2921, 2809, 1599, 1507, 1489, 1346, 1162, 1100, 1027, 851, 745, 688 cm^{-1}.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}N_2O_2S$ 365.1318, found 365.1333.

5.5 References

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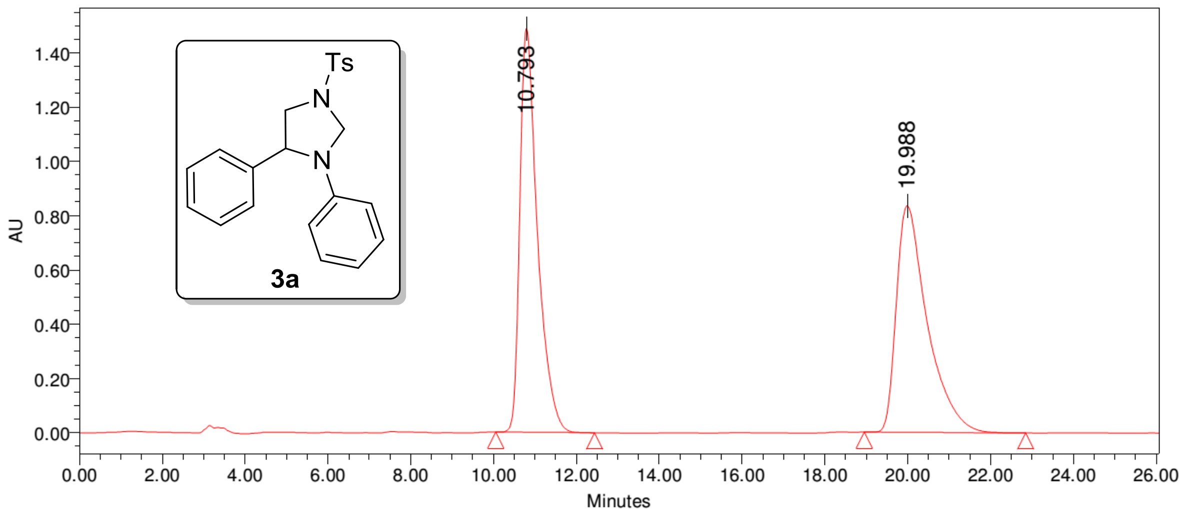
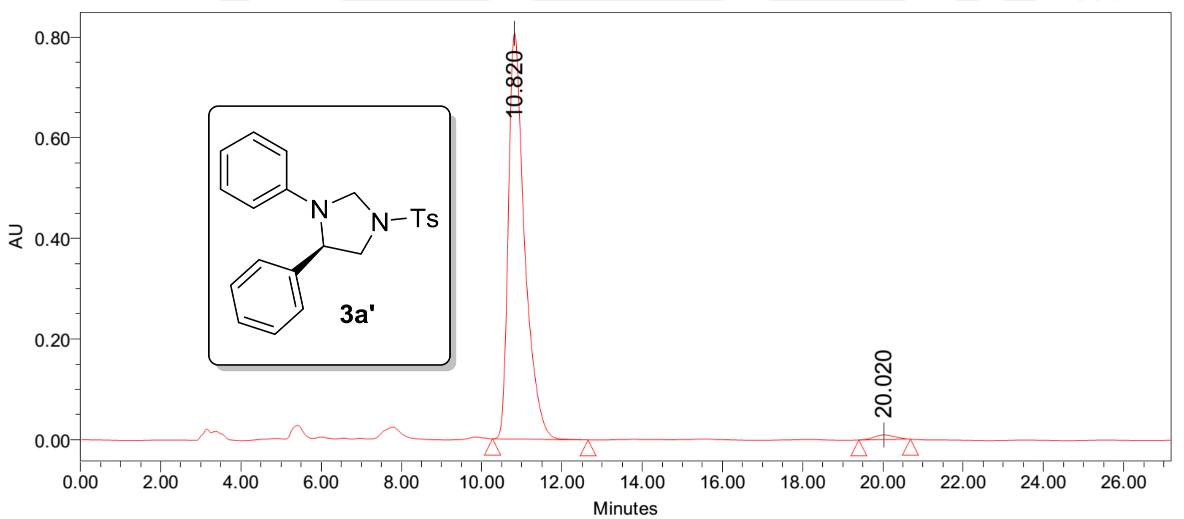
5.6 HPLC Chromatogram



Peak Results

	RT	Height (μV)	% Area
1	10.793	1489390	50.38
2	19.988	835441	49.62



Peak Results

	RT	Height (μV)	% Area
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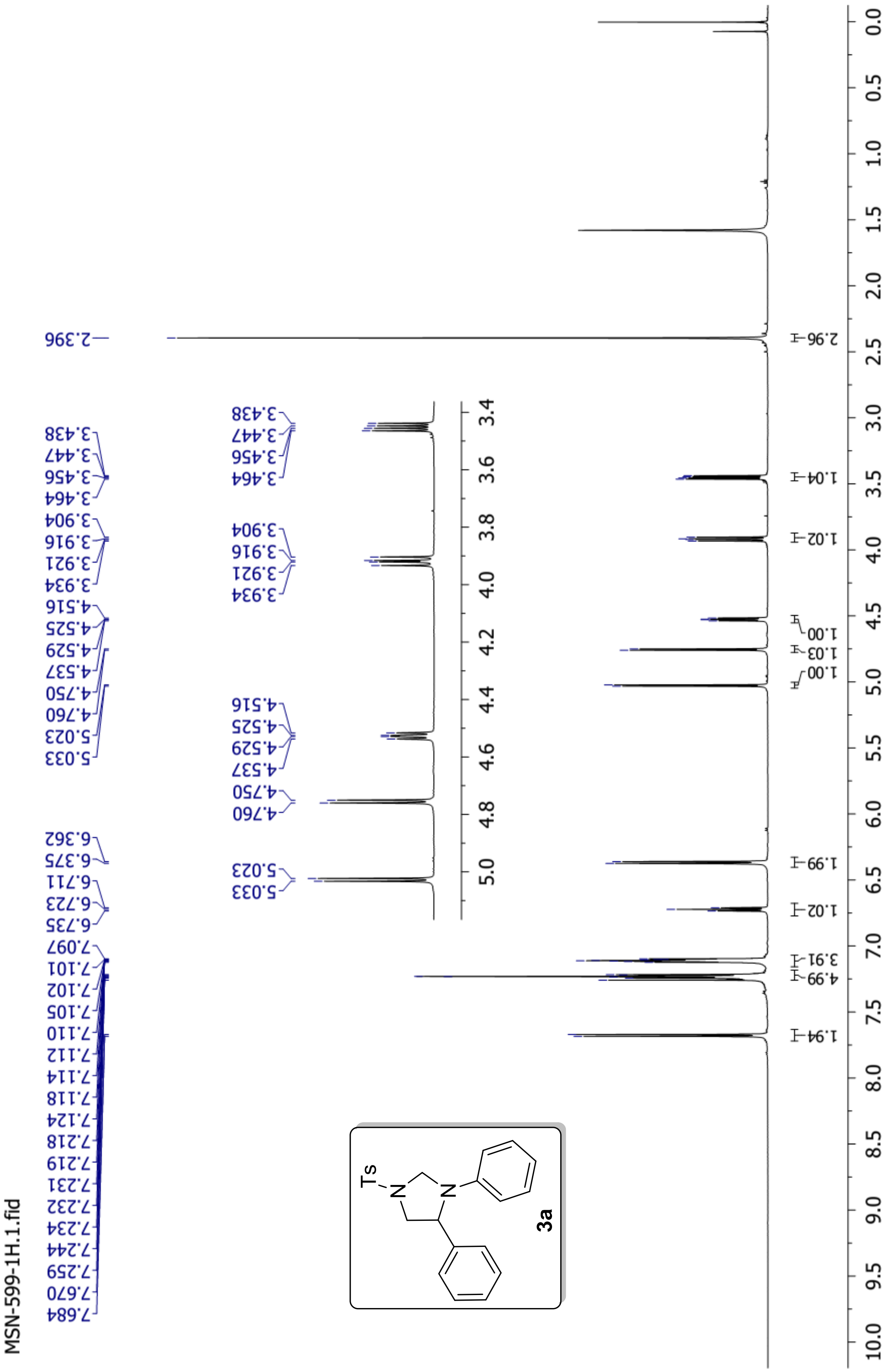
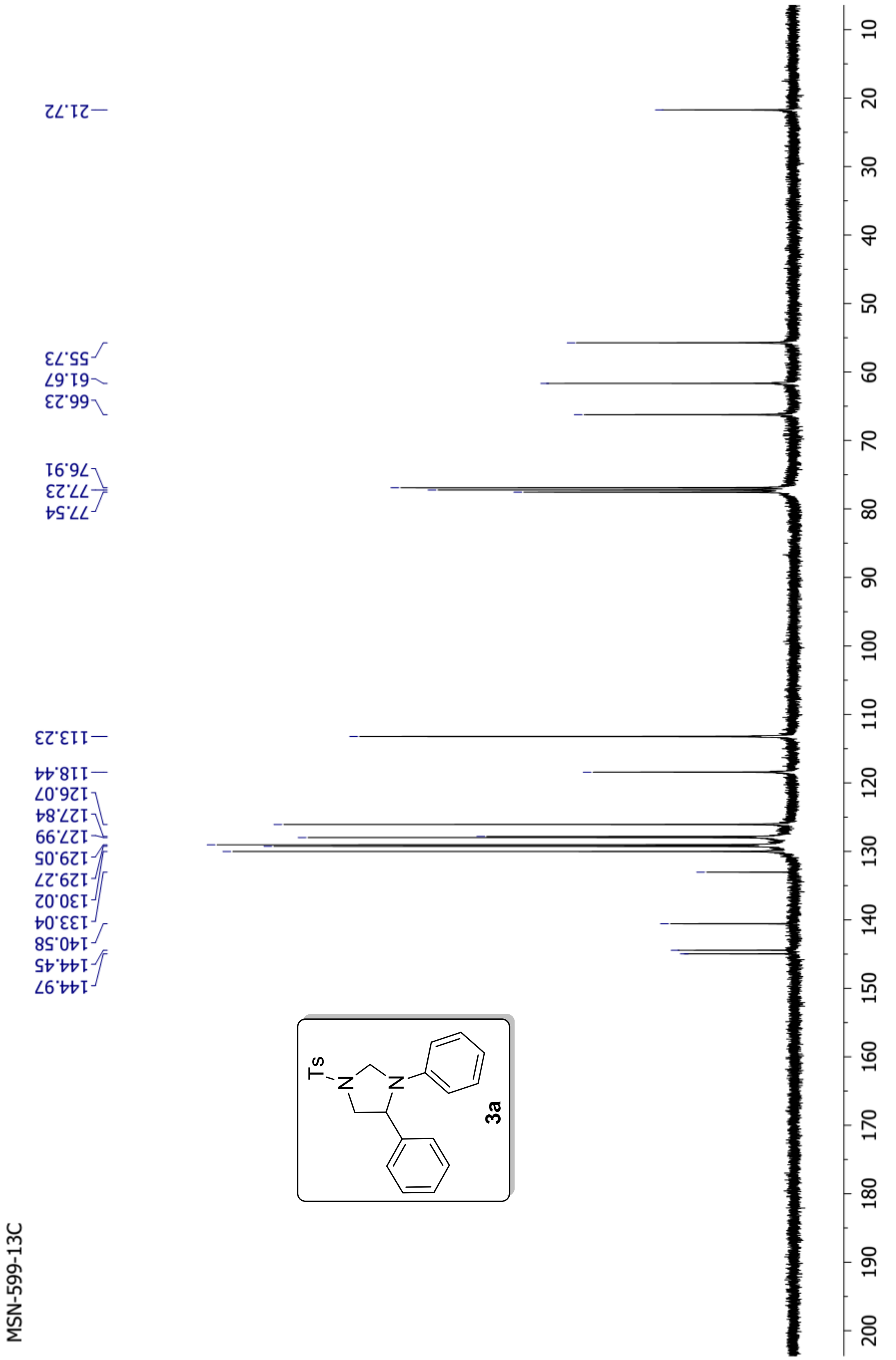
5.7 Selected NMR (^{1}H and ^{13}C) Spectra

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129.27
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133.04
140.58
144.45
144.97
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N
N
3a
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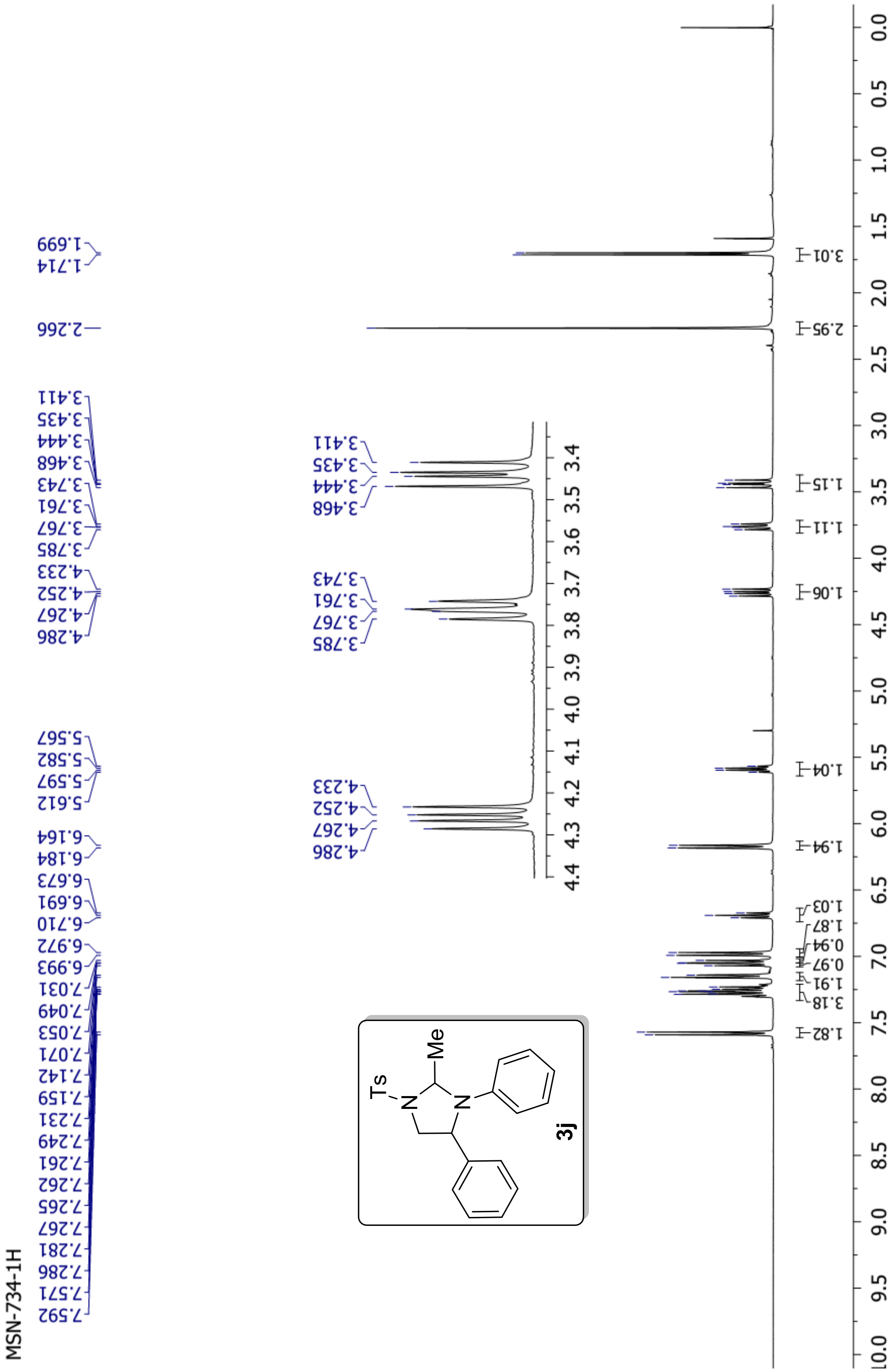
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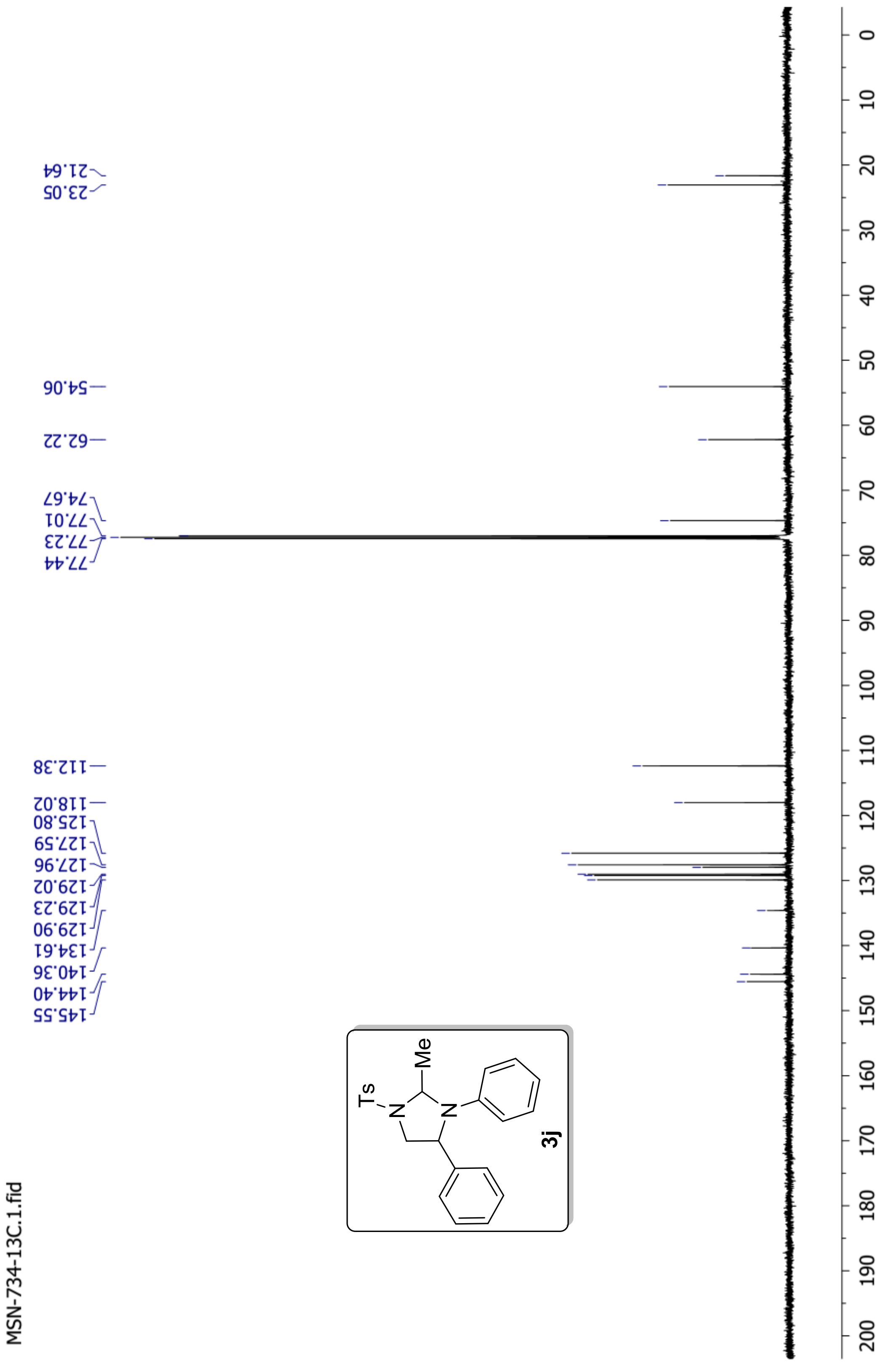
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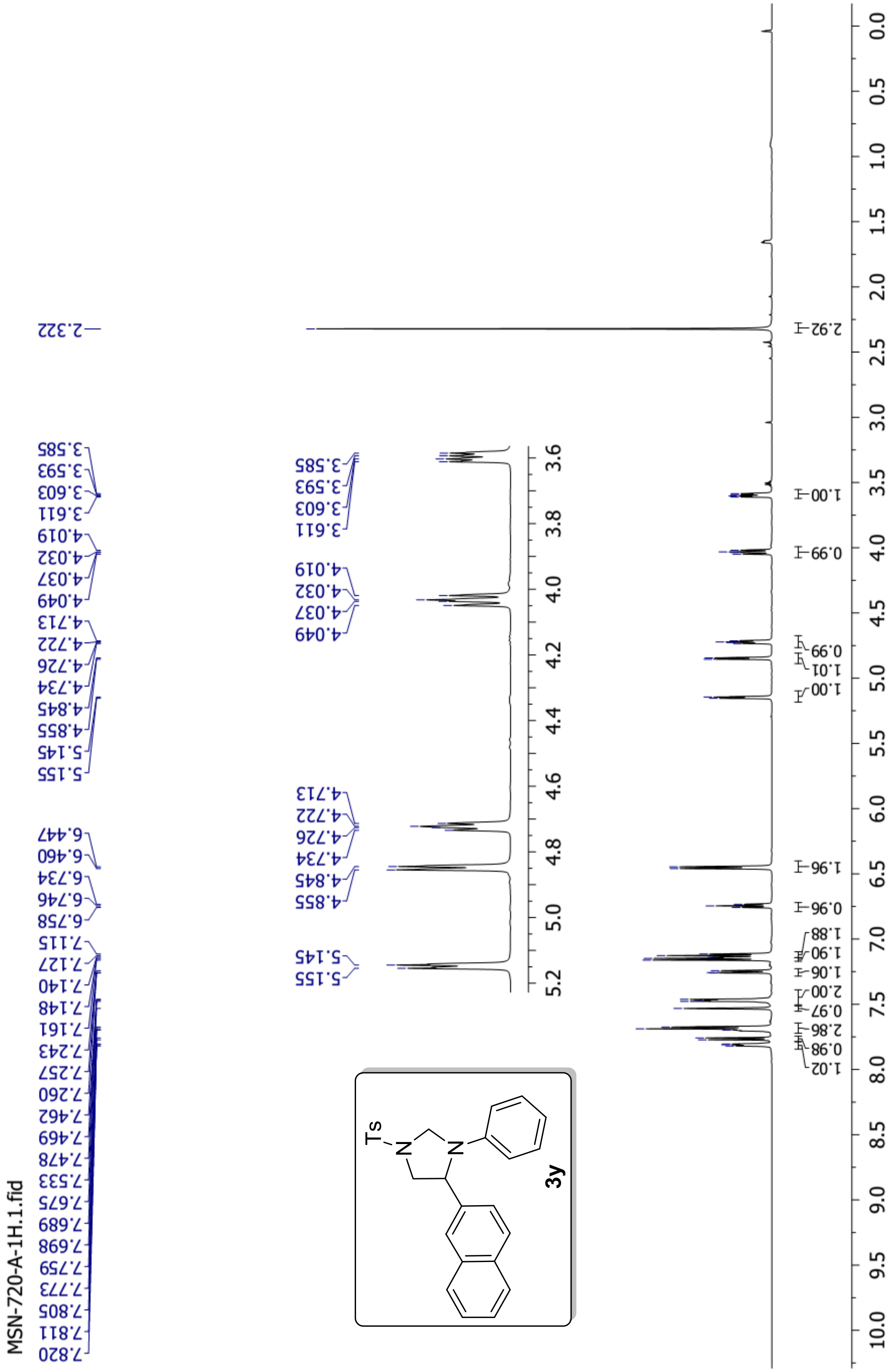
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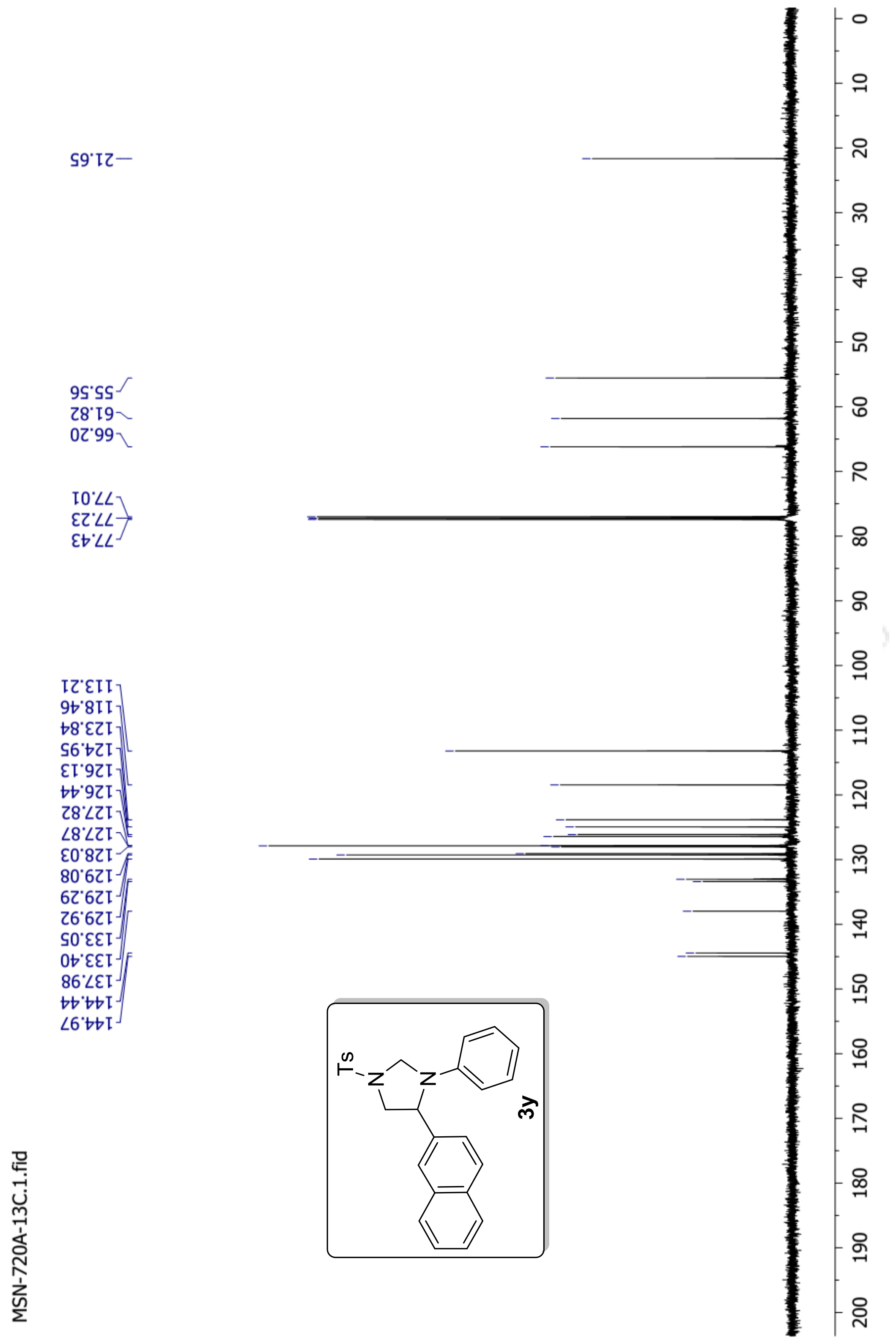
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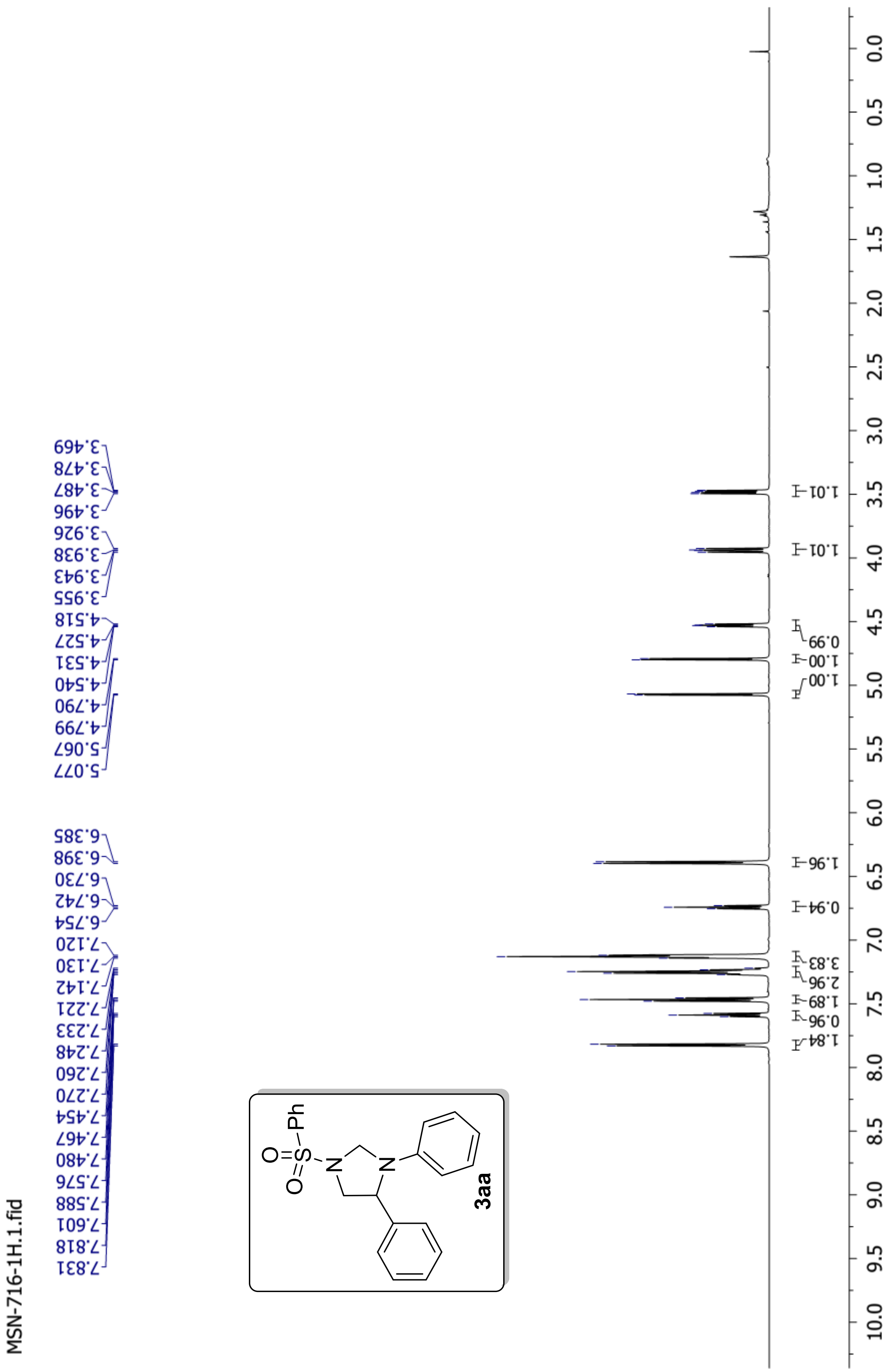
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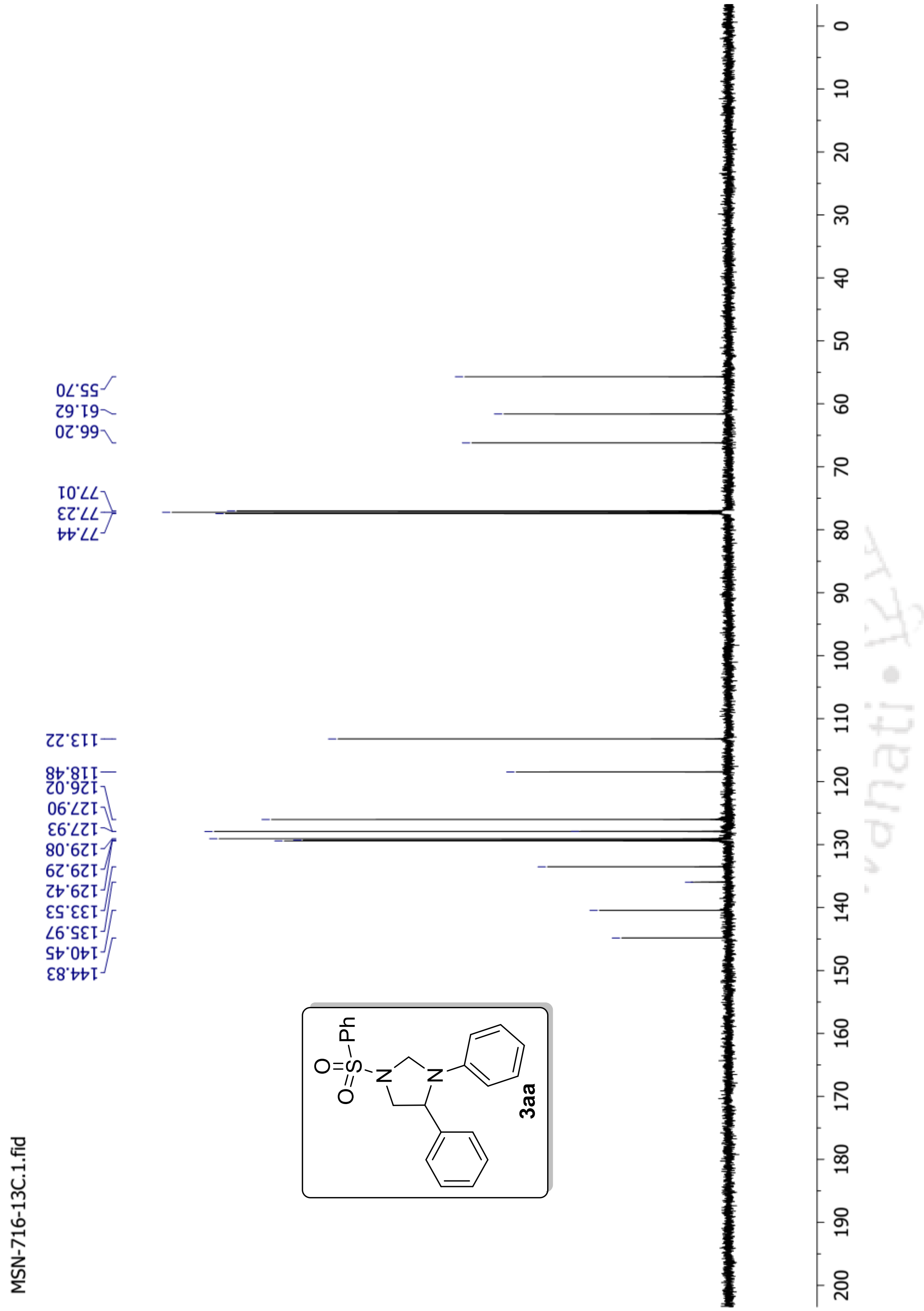
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Conclusions

In chapter 1, we presented $BF_3 \cdot Et_2O$ catalyzed the (3+2)-cycloaddition of oxiranes with isoselenocyanate for the synthesis of 2-imino-1,3-oxaselenolanes and 2-oxazolidinones. The process is efficient, regioselective, temperature dependent and affords the products in good yields. The experimental results suggest that the reactions involve a second cycloaddition depends on the reaction temperature and nature of the substrates.

In chapter 2, Fe-catalyzed cycloaddition of aziridines with isocyanates, isothiocyanates, isoselenocyanates and carbodiimides on water has been described using $Fe(NO_3)_3 \cdot 9H_2O$ as catalyst. The procedure is attractive from both economic and environmental point of view to access the target five-membered heterocycles in high yields.

In chapter 3, we described the cycloaddition of aziridines with isothiocyanates, isoselenocyanates and carbon disulfide to the synthesis of substituted azolidines using pyrrolidine as catalyst at moderate temperature. Wide substrate scope, atom economy, eco-friendliness are the significant practical advantages. This procedure can be utilized for large scale synthesis of five-membered heterocycles from readily available starting precursors.

In chapter 4, the stereospecific cycloaddition of chiral aziridines with isothiocyanates is described using Al(salen)Cl at room temperature under air. This reaction provides an effective and regioselective route for the synthesis of iminothiazolidines in high yields with excellent optical purity.

In chapter 5, Cu-catalyzed domino synthesis of substituted imidazolidines is presented from readily available *N*-alkyl anilines and aziridines using TBHP as an oxidant at moderate temperature. The reaction involves ring opening of aziridine followed by C-N bond formation *via* $C(sp^3)$–H functionalization. The scope of the reaction was carried out with different substituted anilines and aziridines, the desired products have been obtained in moderate to high yields.

List of Publications

1 Role of Temperature in (3+2)-Cycloaddition of Isoselenocyanates with Oxiranes Using $BF_3{\cdot}Et_2O$

Sengoden, M.; Punniyamurthy, T. *RSC Adv.* **2012**, *2*, 2736.

2 "On Water": Efficient Iron-Catalyzed Cycloaddition of Aziridines with Heterocumulenes

Sengoden, M.; Punniyamurthy, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 572.

3 A Novel Tandem Sequence to Pyrrole Syntheses by 5-*endo*-dig Cyclization of 1,3-Enynes with Amines

Bharathiraja, G.; Sakthivel, S.; **Sengoden, M.**; Punniyamurthy, T. *Org. Lett.* **2013**, *15*, 4996.

4 Synthesis of Substituted Pyrazoles from Vinylhydrozones *via* Bromoamination and Hydroamination with 2,2,6,6-Tetramethylpiperidine-1-oxyl and *N*-Bromosuccinimide

Sar, D.; Paul, R.; **Sengoden, M.**; Punniyamurthy, T. *Asian J. Org. Chem.* **2014**, *3*, 638.

5 Efficient Pyrrolidine Catalyzed Cycloaddition of Aziridines with Isothiocyanates, Isoselenocyanates and Carbon Disulfide "On Water"

Sengoden, M.; Vijay, M.; Balakumar, E.; Punniyamurthy, T. *RSC Adv*. **2014**, *4*, 97, 54149.

6 Expedient Synthesis of Tetrasubstituted Pyrroles *via* Copper-Catalyzed Cascade Inter-/Intramolecular Cyclization of 1,3-Enynes Carry a Nitro Group with Amines

Bharathiraja, G.; **Sengoden, M.**; Kannan, M.; Punniyamurthy, T. *Org. Biomol. Chem.* **2015**, *13*, 2786.

7 Transition-Metal-Mediated Carbon-Heteroatom Cross-Coupling. An Overview; in Arene Chemistry: Reaction Mechanisms and Methods for Aromatic Compounds; Kannan, M.; **Sengoden M.**; Punniyamurthy, T. (Mortier, J. Ed.) Wiley, Hoboken, NJ. 2015, pp. 547-586.

Conferences

1 (3+2)-Cycloaddition of Heterocumulenes with Aziridines On Water. **Sengoden, M.**; Punniyamurthy, T. *National Conference on Frontiers in Chemical Sciences,* organized by IIT Guwahati, December 02-03, 2012.

2 Role of Temperature in (3+2)-Cycloaddition of Isoselenocyanates with Oxiranes using $BF_3 \cdot Et_2O$. **Sengoden, M.**; Punniyamurthy, T. *8th J-NOST Conference*, organized by IIT Guwahati, December 15-17, 2012.

3 "On Water": Efficient Iron-Catalyzed Cycloaddition of Aziridines with Heterocumulenes. **Sengoden, M.**; Punniyamurthy, T. *International Symposium on Nature Inspired Initiatives in Chemical Trends*, organized by IICT Hyderabad, March 02-05, 2014.

4 "On Water": Efficient Pyrrolidine Catalyzed (3+2)-Cycloaddition of Aziridines with Isothiocyanates, Isoselenocyanates and Carbon Disulfide. **Sengoden, M.**; Vijay, M.; Balakumar, E.; Punniyamurthy, T. *International Conference on Nascent Developments in Chemical Sciences: Opportunities for Academia-Industry Collaboration,* organized by BITS Pilani, October 16-18, 2015.