SYNTHESIS OF 5-SUBSTITUTED ISOXAZOLIDINES BY [3+2] CYCLOADDITION OF NITRONES GENERATED IN AN UNUSUAL WAY FROM NITROSOBENZENE AND STYRENE

A Thesis

by

JUN YONG KANG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2008

Major Subject: Chemistry

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Approved by:

Chair of Committee,	Brian T. Connell
Committee Members,	Daniel Romo
	Kevin Burgess
	Daniel Shantz
Head of Department,	David H. Russell

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ABSTRACT

Synthesis of 5-Substituted Isoxazolidines by [3+2]
Cycloaddition of Nitrones Generated in an Unusual
Way from Nitrosobenzene and Styrene. (December 2008)
Jun Yong Kang, B.S., Konyang University, Korea; M.S., San Francisco State University
Chair of Advisory Committee: Dr. Brian T. Connell

A new synthetic method toward 5-substituted isoxazolidines by [3+2] cycloaddition of nitrones generated from nitrosobenzene and styrene was discovered.

The formation of nitrones from nitrosobenzene and mono-substituted aromatic styrenes was demonstrated. The cycloaddition reactions between styrenes and nitrosobenzenes work well when a moderate excess of styrenes was employed. The labeling studies support that cleavage of the styrene double bond occurred and accounted for all the carbons in the starting materials and products.

A [3+2] dipolar cycloaddition is implicated by the available mechanistic data and allows for the rapid assembly of various substituted isoxazolidines directly from nitrosobenzenes, electron deficient alkenes, and styrene.

DEDICATION

To my parents

ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor Brian T. Connell for his concrete support and general concern for my development as an organic chemist. As an advisor, he has always encouraged me to explore new ideas, and he has guided me in the right direction. Brian's excellent teaching style, willingness, and openness to discussion in the classroom and in his office motivated me to join the group. It has been a pleasure to work under his guidance.

I would like to thank Dr. Daniel Romo, Dr. Kevin Burgess, and Dr. Daniel Shantz for their valuable time and suggestions over the years. I would especially like to thank Professor Romo for asking me critical and principal questions that expanded my view in chemistry during Friday meetings.

I would like to thank all Connell group members for their kind help and their friendship. I would especially like to thank Alejandro Bugarin for his help on this project. I would like to thank Dr. Daniel Singleton for his insight on this project, Dr. Joe Reibenspies for X-ray structure determination, and Dr. Shane Tichy for performing Mass Spectrometry.

Finally, I would like to take the opportunity to especially thank my mother, my father, and my family for their everlasting love and continual support.

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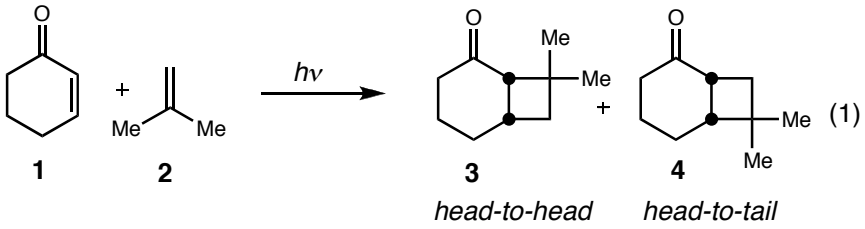
CHAPTER I

INTRODUCTION

1.1 Introduction of [2+2] Cycloadditions

Cycloaddition reactions have fascinated the chemical society for decades. Although cycloadditions have been extensively studied for generations, [2+2] cycloadditions have been less developed as either photo[1-4] or thermal[5-7] processes.

Photocycloaddition of olefins to carbon-carbon double bonds[4] is a well-known reaction often employed in a synthetic tool to synthesize cyclobutanes. Photocycloadditions of a,b-unsaturated ketones were explored by Corey[4] in 1964. When the unsaturated ketone **1** was added to an unsymmetrical olefin **2**, the two products were possible. If the larger end of the olefin forms a bond adjacent to the ketone, the *head-to-head* adduct **3** is formed. However, the opposite orientation produces the *head-to-tail* adduct **4** (eq 1).



In order to explain the orientation observed in several of these cycloadducts, Corey suggested that an initial complex was formed between an excited state of the ketone **1** and the substituted olefin **2**. The preferred orientation of the complex occurred when the oppositely charged ends of the olefins were closest to each other (Figure 1).

This thesis follows the style of *Journal of American Chemical Society.*

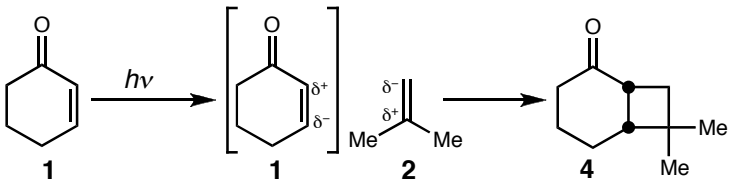
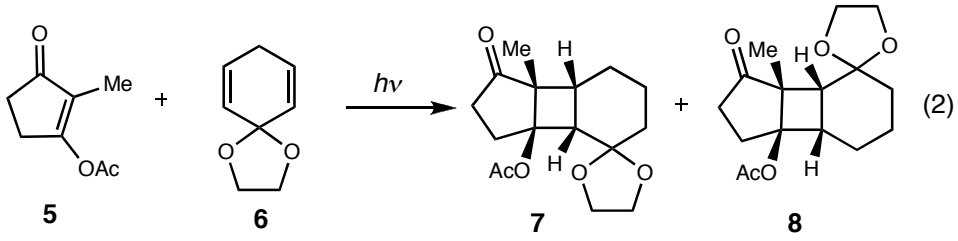


Figure 1. Electrostatic Interaction Driving a Photocycloaddition

Studying the addition of enone **5** to olefin **6**, Mayo and co-workers suggested that the solvent-dependent ratio of *head-to-tail* **7** and *head-to-head* **8** adducts was due to dipole interactions (eq 2).[3] The interaction of the dipoles could be reduced, but not eliminated completely by the use of a polar solvent.

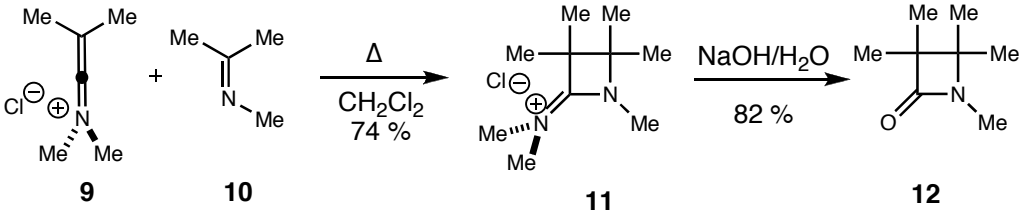


Although photocycloaddition of olefins to carbon-carbon double bonds[3,4] is a well-studied reaction, that of olefins to carbon-oxygen and carbon-nitrogen bonds are not well-documented. The thermal [2+2] cycloaddition reaction and mechanism have long been an issue at the core of theoretical and experimental organic chemistry and are probably the most complex transformations among the reactions classified by Woodward and Hoffmann as pericyclic.[8] One of the most studied reactions involved in thermal [2+2] cycloaddition reactions is cumulenes such as keteniminium salts. The mechanism of the reaction was considered to be either stepwise or concerted depending

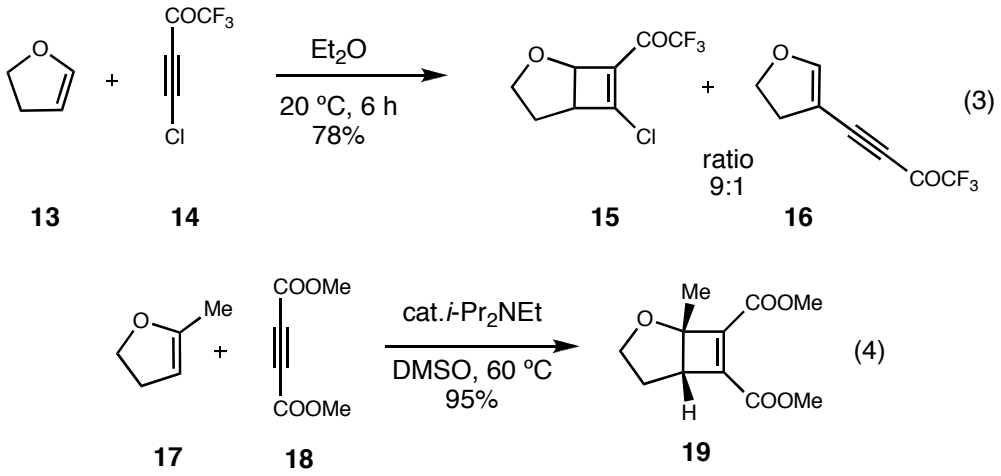
on bulkiness of the alkene and cumulene substituents and the electronic character.

The most studied [2+2] cycloaddition between aza cumulenes and imines involves keteniminium salts. In 1974, Ghosez and co-workers reported the reaction that led to the formation of 2-azetidinium salt **11** from cumulene **9** and imine **10**[9] (Scheme 1), which in turn was converted into beta-lactam **12**, an important substrate in the chemical synthesis of antibiotics and other biologically interesting compounds.

Scheme 1



Another [2+2] thermal cycloaddition which has been studied is the reaction of electron deficient acetylenes with vinyl ethers. This reaction is a highly promising synthetic approach that allows access to different carbocycles containing cyclobutene fragments. Tsvetkov and co-workers reported a reaction in which 1-trifloroacetyl-2-chloroacetylene **14** was treated with alkyl vinyl ether **13** to give [2+2] cycloadduct **15** (eq 3).[5] A competing reaction was electrophilic alkylation of the vinyl ether to give substituted vinylacetylene **16**, whose quantity was dependent on the nature of the ether. In 1987, Nicolaou and co-workers reported a thermal [2+2] cycloaddition[7] of dimethyl acetylenedicarboxylate **18** with cyclic enolether **17** in order to explore the oxocyclic product **19**, a structure present in a number of marine natural products (eq 4).



One of the most studied metal-catalyzed [2+2] cycloadditions is the transition metal-catalyzed dimerization of norbornadiene **20** (NBD), which was reported by Wittig in 1963.[10] Since then, various NBD dimerization reactions have been reported with Ni, Co, and Fe catalysts (Figure 2).[10-15]

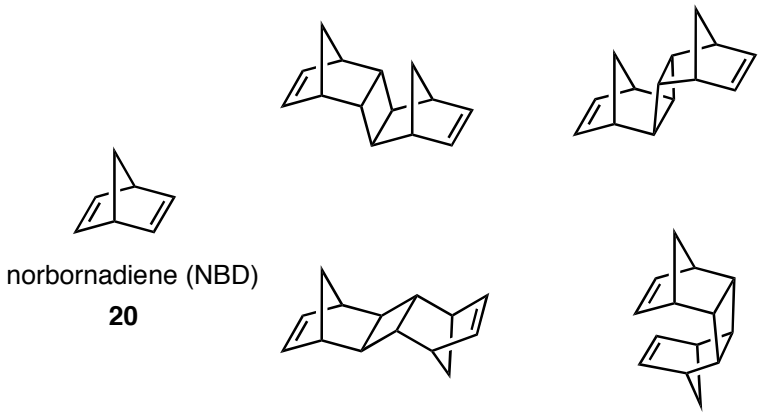
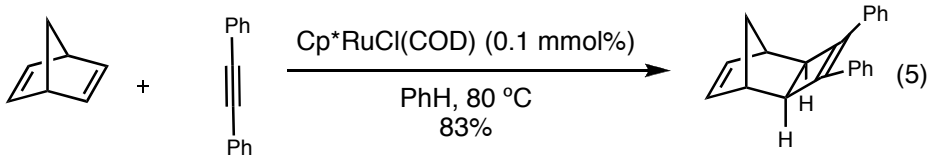


Figure 2. Various Norbornadiene Dimeric Structures

The [2+2] cycloaddition of olefins and/or alkynes is a versatile method for preparation of cyclobutane derivatives. Among them, ruthenium complex-catalyzed

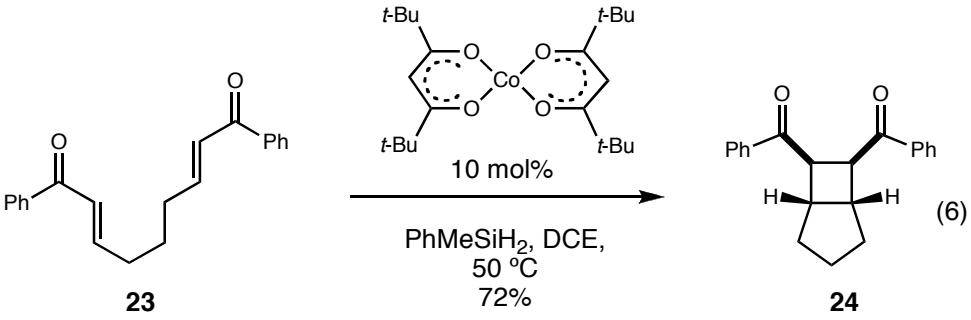
cycloaddition of norbornadienes (bicyclo-[2.2.1]heptene derivatives) with acetylenedicarboxylates is a general method. For instance, in 1994, Watanabe *et al.* reported a [2+2] cycloaddition of norbornadiene with diphenylacetylene catalyzed by a ruthenium complex (eq 5).[16]



20 **21** **22**

Watanabe and co-workers demonstrated that alkyne **21** was treated readily with norbornadiene **20** in the presence of a catalytic amount of $Cp^*RuCl(COD)$ at 80 ºC to give the corresponding *exo* [2+2] cycloadduct **22**. This was the first example of a carbon-carbon bond-forming reaction that was efficiently catalyzed by a neutral Cp^*-ruthenium complex. However, it still required the use of a strained alkene (norbornadiene) to produce the desired [2+2] cycloadduct.

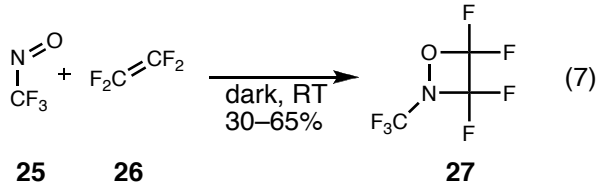
While the scope of the metal-catalyzed [2+2] cycloaddition has been restricted to the intermolecular reaction of strained alkene and electron-deficient alkenes and/or alkynes, the first intramolecular metal-catalyzed [2+2] cycloaddition of alkenes was reported by Krische and co-workers in 2001 (eq 6).[17] In this report, Krische *et al.* documented a metal-catalyzed [2+2] cycloaddition of tethered enone **23** that afforded the diastereomerically pure substituted [3.2.0] ring system **24**.



(6)

Considering the known [2+2] cycloaddition reactions, metal-catalyzed [2+2] cycloadditions are underdeveloped. In order to expand scope of substrates and develop enantioselective [2+2] cycloadditions,[18-21] metal-catalyzed conditions present an attractive opportunity. However, many metal-catalyzed [2+2] cycloadditions only proceed when alkynes with electron-withdrawing substituents and strained alkenes are used.[16,18,21] Thus, the scope of these reactions has been limited.

One of the least developed metal-catalyzed [2+2] cycloadditions is the process that allows to access saturated heterocyclic compounds. One early example of saturated heterocyclic compounds involved in [2+2] cycloadditions was reported by Haszeldine and co-workers. They showed that trifluoronitrosomethane **25** was treated with tetrafluoroethylene **26** to give 2-oxazetidine **27** in 1955 (eq 7).[22] We thus were intrigued by synthesis of saturated hetero [2+2] adducts, because hetero [2+2] cycloadducts could be useful building blocks in natural product synthesis or ligand synthesis for organometallic complex synthesis.

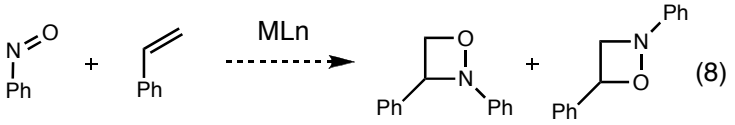


(7)

1.2 Specific Aim

The aim of this project is to develop a useful synthetic method toward hetero [2+2] cycloadducts based on a reaction of nitrosobenzenes and styrenes. In spite of their versatile importance, nitroso compounds have received little attention in cycloaddition reactions.[23] Among the alkene partners in [2+2] cycloadducts, nitrosobenzene **28** and styrene **29** were explored due to the well-known reactivity of nitroso compounds and biological potential of nitrogen containing heterocyclic compounds.[23]

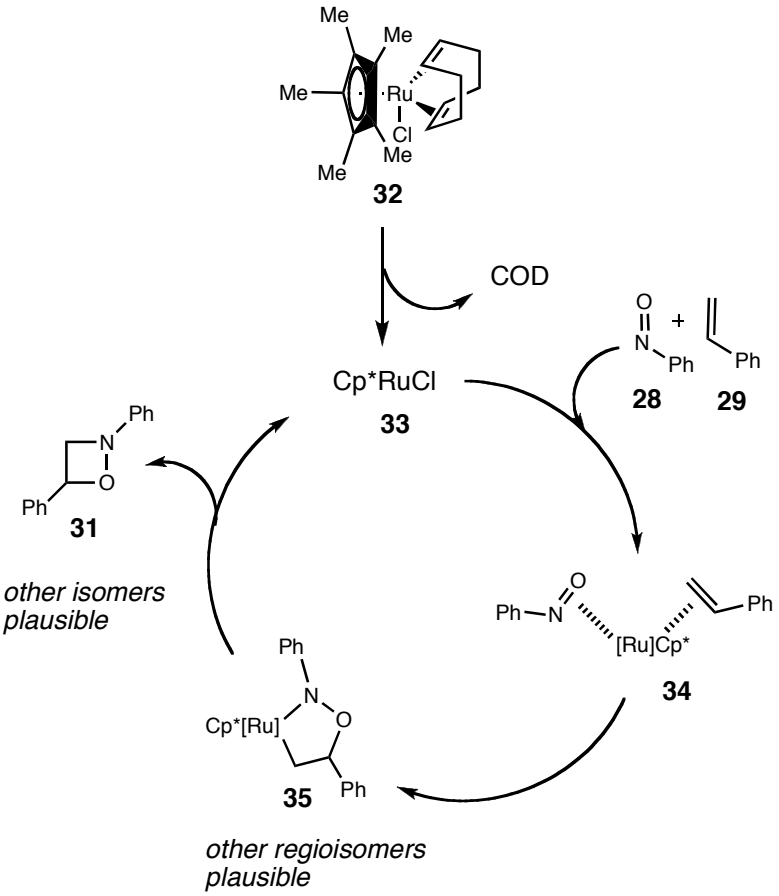
It was envisioned that the substituted oxazetidines **30** or **31** could be obtained by a transition metal-catalyzed [2+2] cycloaddition process (eq 8). $Ni(COD)_2$, $(COD)PdCl_2$, $RuCl(PPh)_3$, and $Cp^*RuCl(COD)$ were the first choice not only due to their commercial availability, but also because of their well-known catalysis of other cycloaddition reactions.



28 **29** **30** **31** (8)

One plausible mechanism is illustrated in Scheme 2. First, a unsaturated complex, Cp^*RuCl **33**, is formed by dissociation of COD (cyclooctadiene) from $Cp^*RuCl(COD)$ **32**. Then, nitrosobenzene **28** and styrene **29** coordinate at the unsaturated sites to form complex **34**. In the following step, a ruthenacyclopentane complex **35** is formed by oxidative cyclization. Another regioisomeric complex could also be formed at this stage. Finally, reductive elimination forms the [2+2] cycloadduct **31**.

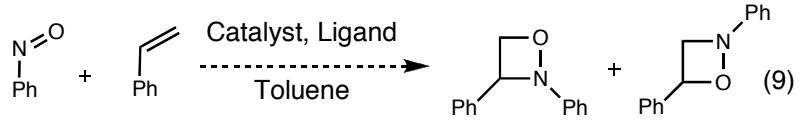
Scheme 2


Me
Me
Me
Ru
Cl
Me
Me
32
COD
Cp*RuCl
33
O
N
Ph
+
Ph
28
29
Ph
N
O
Ph
31
other isomers
plausible
Ph
N
O
Cp*[Ru]
Ph
35
other regioisomers
plausible
O
Ph
N
[Ru]Cp*
Ph
34

CHAPTER II

INVESTIGATION OF THE METAL CATALYZED [2+2] CYCLOADDITION WITH NITROSOBENZENE AND STYRENE

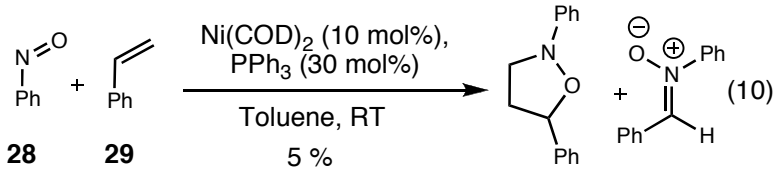
Our investigation of the metal-mediated hetero [2+2] cycloaddition began with an examination of reactions between nitrosobenzene **28** and styrene **29** with transition metal catalysts. It was expected that, utilizing reactive nitrosobenzene, these [2+2] cycloadditions could lead to four-membered heterocycles (eq 9).



28 **29** **30** **31**

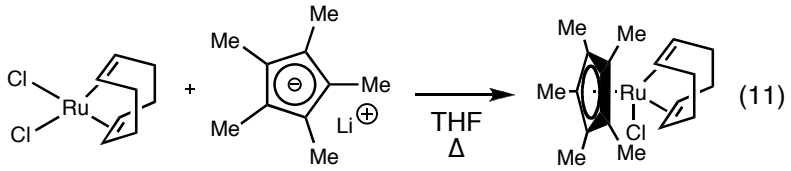
Catalyst = Cp*RuCl(COD), $Ni(COD)_2$, $RhCl(PPh_3)_3$, $CODPdCl_2$
Ligand = PPh_3
COD = 1,5cyclooctadiene, Cp*=η^5-C_5Me_5

Nitrosobenzene **28**, styrene **29**, and catalyst ($Ni(COD)_2$) were combined at room temperature in toluene (eq 10). After 48 h, solvent was evaporated and the reaction mixture was analyzed by ^1H NMR. The unpurified ^1H NMR spectrum revealed unexpected peaks but clear coupling patterns. Thorough analysis of the purified material by ^1H NMR, ^{13}C NMR, and mass spectroscopy indicated that the isolated product was 2,5-diphenylisoxazolidine **36**. Nitrone **37** was also observed.



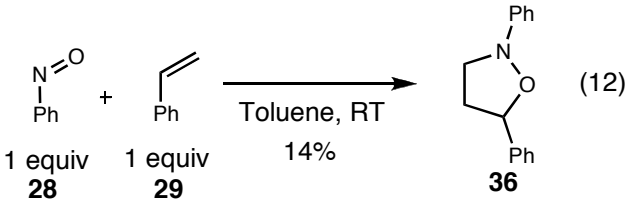
28 **29** **36** **37**

In an attempt to test the efficiency of various catalysts, $(COD)PdCl_2$, $RuCl(PPh)_3$, $Ni(COD)_2$, and $Cp^*RuCl(COD)$ **32** were tested. We attempted to prepare $Cp^*RuCl(COD)$ by the known method.[24] $RuCl_3 \bullet H_2O$ and Cp^* were combined in refluxing ethanol to generate $[Cp^*RuCl_2]_n$ and followed by treatment with COD (cyclooctadiene). However, mass analysis of the $[Cp^*RuCl_2]_n$ revealed that more than one Cp^* ligand on the ruthenium complex. Alternatively, a reaction with $RuCl_2(COD)$ **38** and C_5Me_5Li **39** was explored (eq 11). $RuCl_2(COD)$ and C_5Me_5Li were refluxed in THF, which provided the desired $Cp^*RuCl(COD)$ **32**.



38 **39** **32** (11)

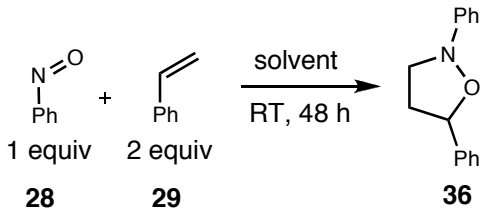
Unfortunately, complex **32** was not a catalyst for the desired [2+2] reaction. However, compound **36** was again observed. The other metal complexes produced similar results. A control experiment was performed to investigate the role of metal catalyst. Nitrosobenzene **28** and styrene **29** were treated in the absence of catalyst under the same reaction conditions. This reaction resulted in formation of the isoxazolidine **36** in higher yield than the reaction with catalysts, with no observation of other [2+2] cycloadducts (eq 12).



1 equiv **28** 1 equiv **29** **36** (12)

The conditions for this new transformation were then optimized. The solvent optimization results showed that the use of polar solvents such as DMF and MeCN increased the yield of product compared with less polar solvents such as toluene or benzene (Table 1).

Table 1. Solvent Optimization



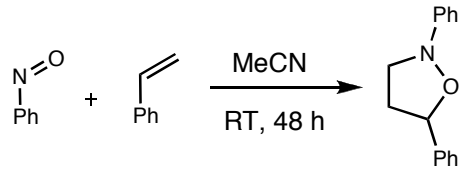
Entry	Solvent	Dielectric constant	Yield(%)[a]
1	$PhCH_3$	2.4	17 %
2	PhH	2.3	24 %
3	THF	7.5	26 %
4	MeOH	33.0	27 %
5	DMF	38.3	33 %
6	MeCN	36.6	33 %

[a] Isolated yields after chromatographic purification

Subsequently, the ratio of substrates was examined (Table 2). When the ratio of styrene to nitrosobenzene was doubled (entry 3), the yield of product was doubled (entry 3). The 1 : 3 ratio of **28** and **29** provided 46% of product. Finally, we found that the optimized ratio of substrates was 1 : 4 of **28** and **29**. When a 1 : 6 ratio of **28** and **29** was

employed (entry 6), the product yield was the same as the ratio of 1 : 4 (**28** : **29**). Conclusively, the yield of the isoxazolidine was best when a moderate excess of styrene (4 equiv) was employed (Table 2). However, using an excess of nitrosobenzene did not raise the product yield. The 2 : 1 ratio of **28** and **29** resulted in the same yield of 1 : 2 (**28** : **29**).

Table 2. Optimization of the Ratio of Substrates



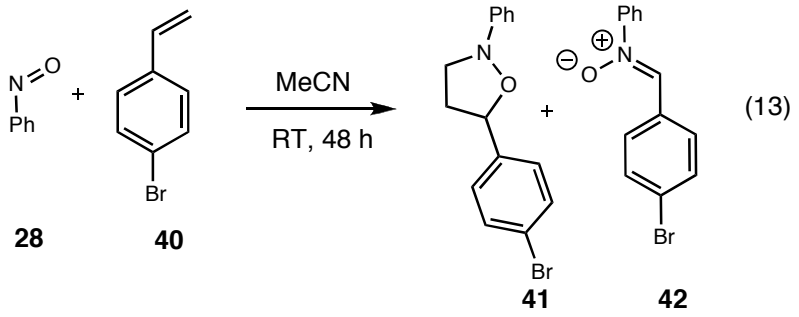
28 **29** **36**

Entry	**28** : **29**	Yield(%)[a]
1	1 : 1	15%
2	2 : 1	15%
3	1 : 2	33%
4	1 : 3	46%
5	1 : 4	49%
6	1 : 6	49%

[a] Isolated yields after chromatographic purification

With the complete optimization of solvents and ratio of substrates, it turned out that a polar solvent such as MeCN and a moderate excess of styrene (4 equiv) provided

the best yield. Having these optimization results in hand, we isolated all reaction products, because that could guide us for the next optimization and mechanism study. Thus, a reaction with 4-bromostyrene **40** and nitrosobenzene **28** was carefully monitored at room temperature and products were isolated by flash chromatography (eq 13).



4-Bromostyrene **40** was used because the bromide would potentially aid in obtaining suitable crystals for X-ray diffraction analysis. We observed that isoxazolidine **41** and (*Z*)-*N*-(4-bromobenzylidene) aniline oxide **42** were being formed. Nitrone **42** was confirmed by single crystal X-ray analysis (Figure 3). The observation of a nitrone in the reaction mixture suggests that the isoxazolidines may be forming by [3+2] cycloaddition reaction between the nitrone and styrene.[25]

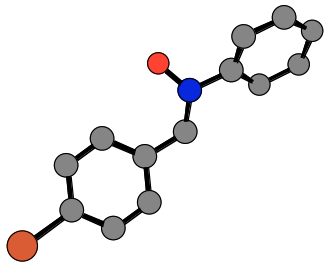


Figure. 3 X-Ray Structure of (*Z*)-*N*-(4-bromobenzylidene)aniline oxide **42**

CHAPTER III

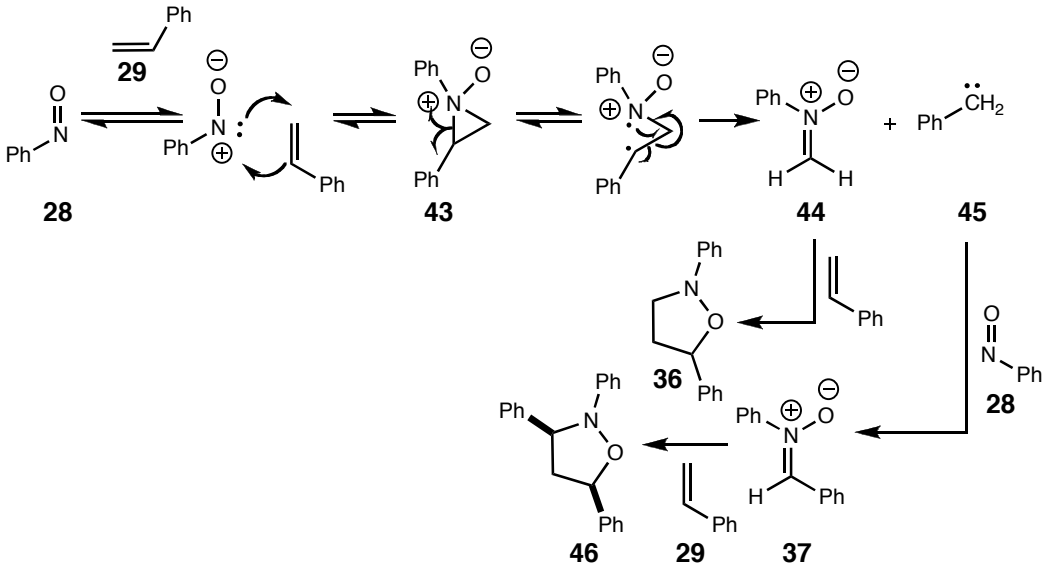
MECHANISTIC STUDIES

3.1 Aziridine Oxide Pathway

Although a wide variety of approaches toward nitrone synthesis have been reported,[26] this nitrone formation observed from nitrosobenzene and styrene is not precedented to date. Therefore, this mechanistic study will focus on the explanation of nitrone formation.

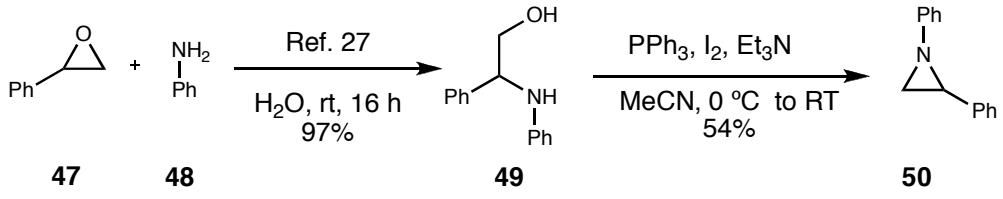
A proposed mechanism was designed based on the intermediacy of an aziridineoxide. Our initial hypothesis was that the formation of the unstable 1,2-diphenylaziridine 1-oxide **43** directly from nitrosobenzene **28** and styrene **29** could be followed by homolytic cleavage to generate unsubstituted nitrone **44**, which then undergoes [3+2] cycloaddition with styrene **29** to afford the isoxazolidine **36** (Scheme 3). It was hypothesized that the driving force of homolytic cleavage of nitrogen-carbon bond could be release of ring strain of aziridine oxide **43**. The proposed carbene intermediate **45** could react with nitrosobenzene **28** to generate the disubstituted nitrone **37**, which then reacts with styrene **29** to produce the isoxazolidine **46**.

Scheme 3



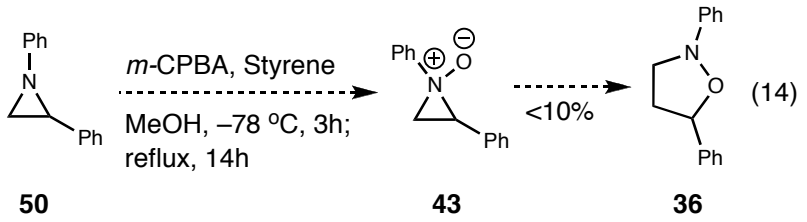
To investigate this proposed mechanism, we started with the aziridine **50**. Aminolysis of styrene oxide **47** and followed by intermolecular Mitsunobu type reaction afforded known aziridine **50** (Scheme 4).[27] Bromine rather than iodine was first employed in the conversion of **49** to **50**, but iodine led to a higher, albeit modest, yield of aziridine **50**.

Scheme 4



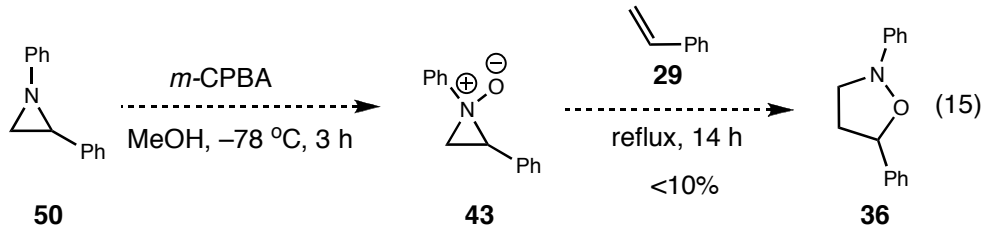
Aziridine **50** was oxidized with *m*-CPBA at –78 ºC to afford aziridine oxide[28] **43**

in situ (eq 14). This was then treated with styrene and production of **36** was monitored by ^{1}H NMR.



However, the yield of isoxazolidine was low (<10 %). This outcome could be explained by competing reaction (oxidation of styrene with *m*-CPBA) or the reaction pathway did not follow the speculative mechanism. In order to test the oxidation of styrene with *m*-CPBA, a reaction between styrene and *m*-CPBA was examined at –78 ºC. Indeed, oxidized styrenes were observed by ^{1}H NMR of the reaction.

To avoid oxidation of styrene before oxidation of aziridine, styrene was added at room temperature after oxidation of aziridine at –78 ºC. However, the yield of isoxazolidine was not significantly improved (eq 15). Styrene oxidation was observed at elevated temperature (–50 ºC). Therefore, temperatures higher than –50 ºC were excluded from this study to minimize formation of styrene oxide.

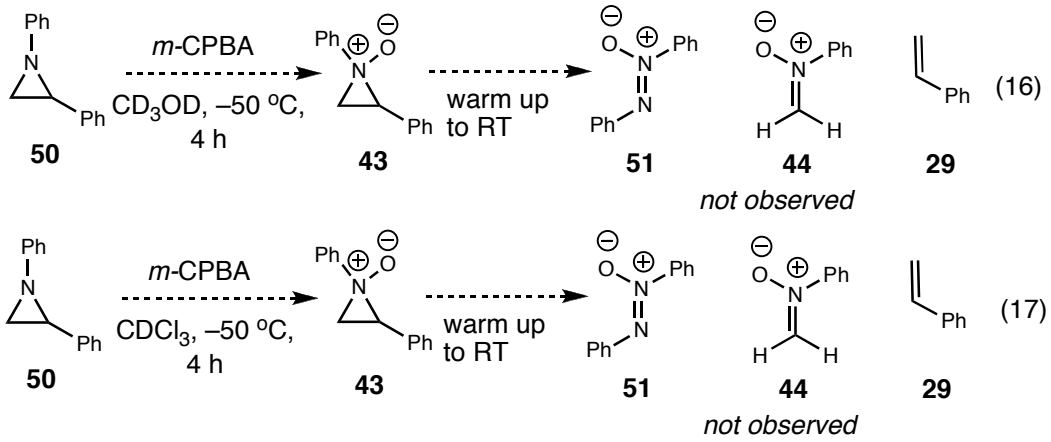


In an attempt to scrutinize any carbene-derived byproducts such as stilbene, ^{1}H NMR spectra of the reaction mixture and each fraction of flash column chromatography were carefully analyzed. We were not able to find any carbene related byproducts. From

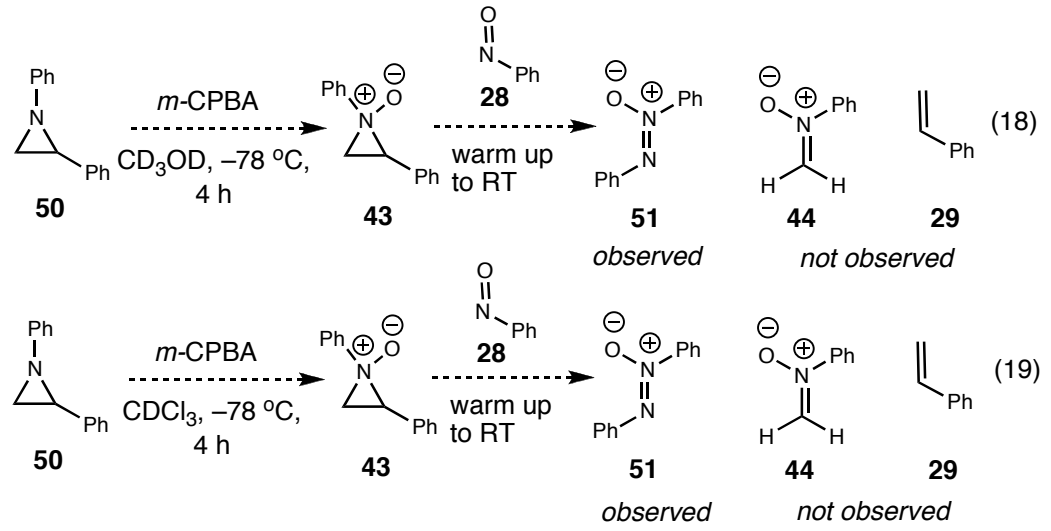
these results, no observation of carbene products and low yield of isoxazolidine (<10%), it was speculated that other mechanisms are more plausible.

Next, we examined whether radicals were involved in this reaction or not. Two reactions (one with light and the other one protected from light) were set up at room temperature. The result revealed that the reaction without light did not improve product yield. Therefore, it was implied that radical intermediates were not involved along the reaction pathway (Scheme 3). In addition, we used butylated hydroxytoluene (BHT) and galvinoxyl but the product yield was not improved. Any radical related byproduct from the proposed carbene intermediate was not observed. Therefore, another hypothesis was formulated. Aziridine oxide could generate unsubstituted nitrone, styrene, or azoxybenzene that could be proceeded by reduction of nitrosobenzene (eq 16).

In an attempt to investigate aziridine oxide **43** involved reaction, the aziridine **50** was dissolved in CD_3OD and followed by addition of *m*-CPBA in CD_3OD at –78 ºC. After 4 hours at –78 ºC, the reaction flask was warmed to room temperature (eq 16). Then, monitoring of the reaction by ^1H NMR showed none of the starting aziridine, unsubstituted nitrone **44**, styrene **29**, or azoxybenzene **51**. We also investigated the solvent effect on this reaction. When $CDCl_3$ was employed in the same reaction (eq 17), the results were identical.



Having found that no relevant reaction of aziridine oxide **50**, we further examined the reaction with nitrosobenzene to see if nitrosobenzene would initiate reaction with **50**. Nitrosobenzene **28** was added to the aziridine oxide at room temperature (eq 18,19). However, nitrone **44** or styrene **29** was not observed. These reactions resulted in formation of azoxybenzene **51**, derived from reduction of nitrosobenzene.

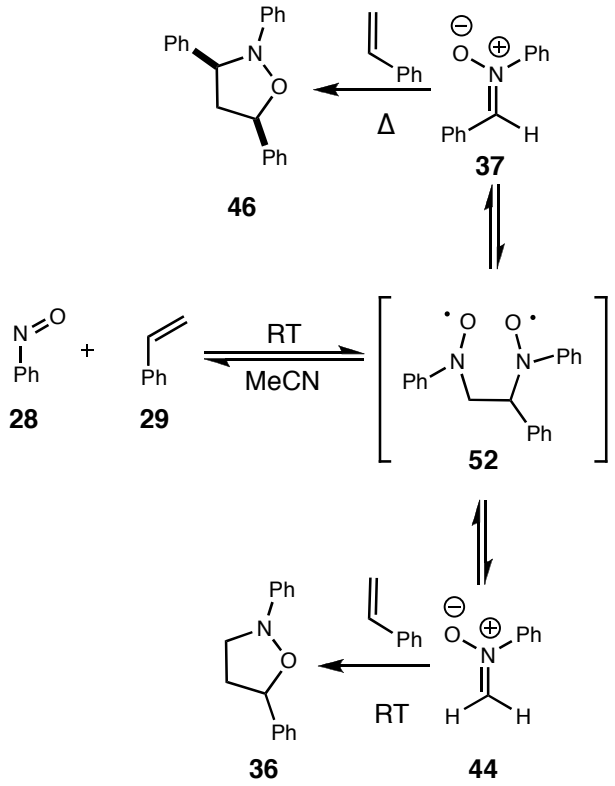


The experimental data did not fit well with the proposed mechanism (Scheme 3). Therefore, we examined other possibilities.

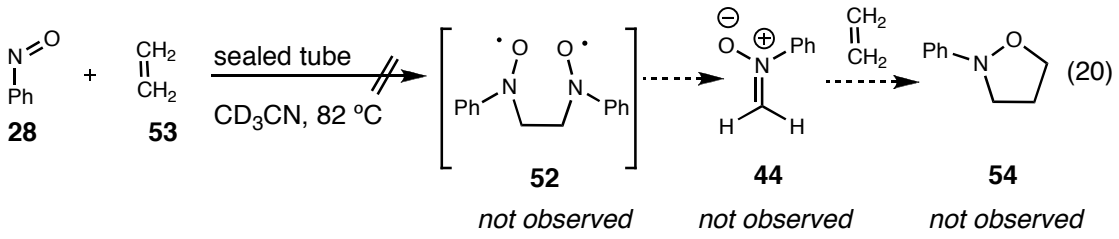
3.2 Nitroxide Pathway

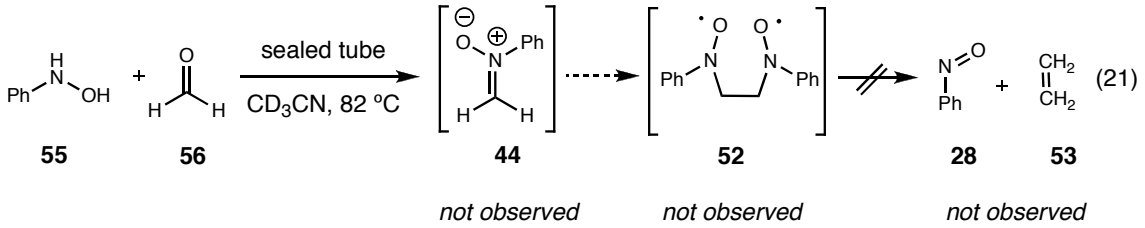
It was assumed that nitrosobenzene combines with styrene to produce bisnitroxide radical intermediate **52** in situ. Subsequently, this unstable intermediate undergoes decomposition. Therefore, it was hypothesized that C–C bond of **52** need to be cleaved to justify formation of the nitrones **37** and **44**. To investigate the formation of nitrones in the reaction mixture, it was necessary to determine the source of the methylene group on the nitrone. Therefore, we proposed a feasible but likely unstable intermediate such as a bisnitroxide radical intermediate **52**, formed by addition of two nitroso molecules to one styrene. Decomposition of **52** would yield unsubstituted nitrone **44** and substituted nitrone **37**. The two nitrones would then be available to undergo [3+2] cycloaddition with styrene to generate isoxazolidines **36** and **46** (Scheme 5). Substituted nitrone **37** would be less reactive than **44**, and likely not undergo cycloaddition without heating.

Scheme 5

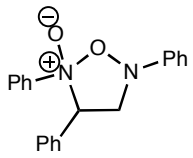


Compound **28** and **53** were combined in a sealed tube at 82 ºC, however, this reaction did not produce **54** (eq 20). In an attempt to determine if this reaction is reversible, *N*-phenylhydroxylamine **55** was treated with *p*-formaldehyde **56** in a sealed tube at 82 ºC to give **44**. Unsubstituted nitrone **44** was not directly observed, but was trapped by styrene to give isoxazolidine **36**. However, we were not able to observe **52**, nitrosobenzene **28**, or ethylene **53**. This result suggests the reaction is not reversible (eq 21).



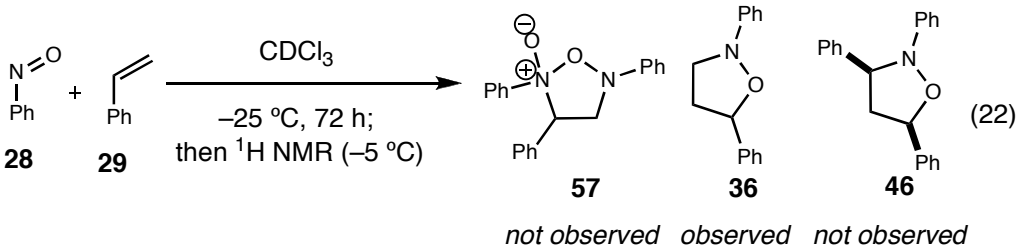


In 1963, Hepfinger and Griffin[29] suggested intermediate **57** that could be derived from reaction between nitrosobenzene and styrene. In an attempt to observe **57**, we ran reactions with nitrosobenzene and styrene at –25 ºC, with hope that **57** would be stable under the reaction conditions.



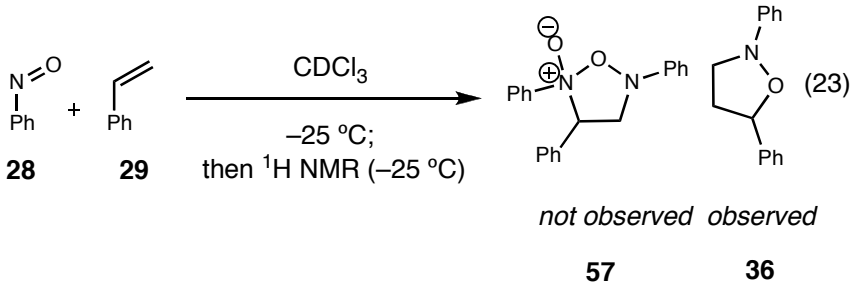
57

For the first reaction, nitrosobenzene **28** and styrene **29** were combined at –25 ºC in CD_3Cl for 72 hours and then the reaction mixture was monitored by ^1H NMR at –5 ºC. The reaction resulted in formation of the isoxazolidine **36** but the proposed intermediate **57** was not observed. It was possible that the intermediate **57** was being formed quickly even at low temperature (eq 22).



(22)

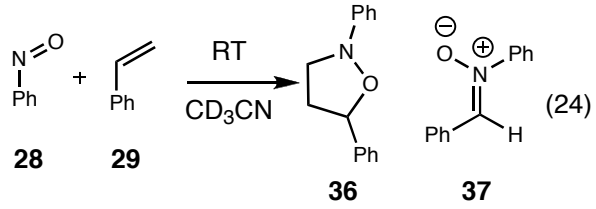
We found that the isoxazolidine **36** was formed after 30 hours at –25 ºC. However, compound **57** was not formed (eq 23). Because all attempts to this point to observe intermediate **57** were unsuccessful, other approaches were employed. We were not able to observe intermediate **57** when excess **28** was used. In addition, **28** was dissolved in neat styrene at –25 ºC and the reaction was monitored by ^{1}H NMR at –25 ºC. However, **57** was not observed. Unfortunately, all attempts to observe intermediate **57** were not successful.



(23)

3.3 Labeling Study

Our effort to explore the mechanism study was to determine the source of methylene and phenylmethine units on nitrones. The reaction of nitrosobenzene **28** and styrene **29** in CD_3CN as solvent produced **36** and **37** with no deuterium incorporation in either product (eq 24).

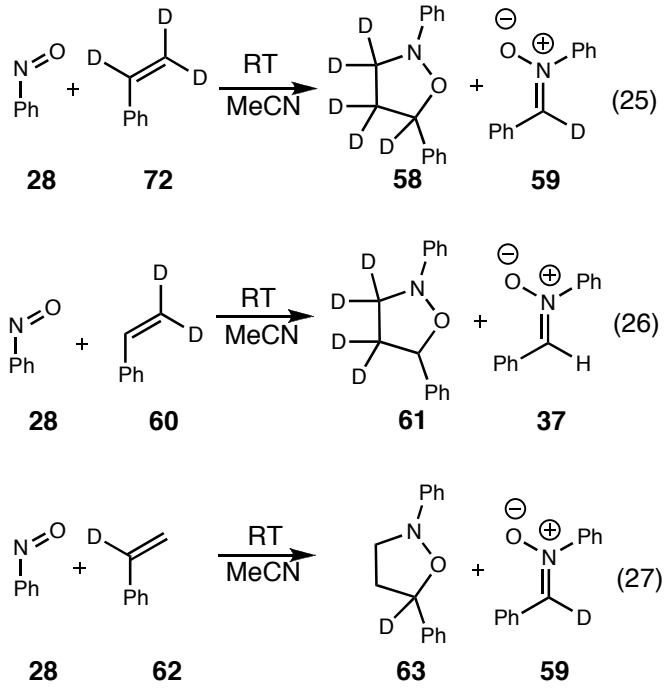


28 **29** **36** **37**

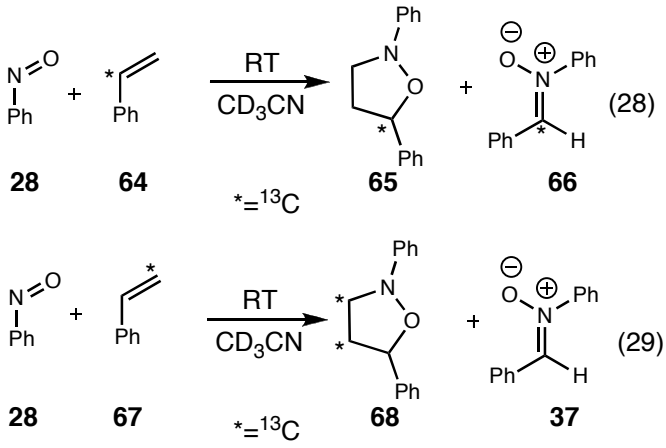
This reaction with deuterated solvent suggested that the methylenes on isoxazolidine **36** and phenylmethine on nitrone **37** was not derived from the solvent. Another possibility is that the methylene units are being donated by styrene, which would be supported by the requirement of excess styrene (4 equiv) to provide the best yield of isoxazolidine (Table 2).

Having this possibility in mind, we employed deuterium-labeled styrenes to verify source of the carbon on nitrone and isoxazolidine products. Three different deuterium-labeled styrenes were employed in the reactions (eq 25-27). When d_3 deuterated styrene **72** was subjected to the reaction conditions (PhNO, MeCN, RT), the products were the fully deuterated isoxazolidine **58** and nitrone **59** (eq 25). The reactions with b deuterated styrene **60** and a deuterated styrene **62** revealed the deuterium-incorporated nitrones and isoxazolidines as indicated in eq 26 and 27. These results strongly suggest that the extra carbons on nitrones and isoxazolidines result from

styrene. These data also pointed to cleavage of C=C bond of the styrene moiety as a key step in the mechanism.



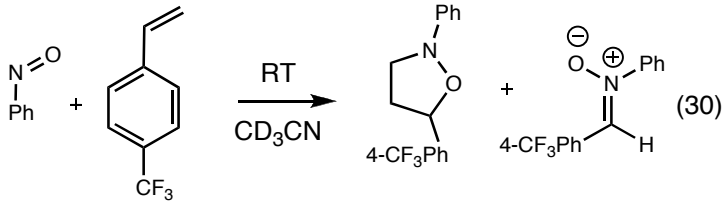
As additional confirmation of C=C bond cleavage of the styrene moiety, we utilized two ^{13}C labeled styrenes. The preparation of ^{13}C labeled styrenes was conducted as described in the reference.[30] The reaction of nitrosobenzene **28** with internal ^{13}C labeled styrene **64** in CD_3CN as solvent produced the isoxazolidine **65** with the ^{13}C labeled carbon and ^{13}C incorporated nitrone **66** (eq 28). On the other hand, the reaction of nitrosobenzene with the external ^{13}C labeled styrene **67** provided the isoxazolidine product **68** with two ^{13}C labeled carbons and no ^{13}C incorporated nitrone **37** (eq 29). These experiments support our hypothesis that cleavage of the styrene double bond occurred and accounted for all the carbons in the starting materials and products.



28 **64** **65** **66**

28 **67** **68** **37**

In an effort to find any carbon fragment of styrenes that would not be incorporated in products, 1-(trifluoromethyl)-4-vinylbenzene **69** was subjected to the standard reaction condition with nitrosobenzene **28** (PhNO, CD_3CN, RT). ^{19}F NMR was used to observe any carbon fragment that is not incorporated into the products. However, we were not able to observe any other carbon fragments containing F atoms (eq 30).



28 **69** **70** **71**

CHAPTER IV

APPLICATIONS

After optimization of the reaction and mechanistic studies, the scope of substrates was explored (Table 3). Styrenes with electron withdrawing substituents and electron donating substituents were subjected to the reaction conditions. The results of several cycloaddition reactions between styrenes and nitrosobenzenes in MeCN after 48 hours are summarized in Table 4. The isolated yields of isoxazolidines were best when a moderate excess of styrenes (4 equiv) was employed (Table 3, entry 1). Electron rich styrenes work better than electron deficient styrenes, but the unsubstituted parent styrene was the best substrate in this reaction, producing 49% of pure product of isoxazolidine **36** (Table 3, entry 1). Substituents at positions other than *para* lower the product yields. The structure of **36a** (entry 2) was confirmed by single crystal X-ray analysis (Figure 4), cementing our analysis and structural assignment.

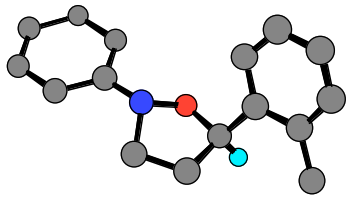
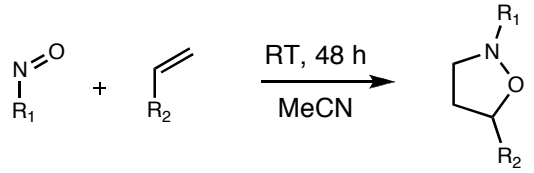


Figure 4. X-ray Structure of 2-phenyl-5-*o*-tolylisoxazolidine **36a**

Room temperature reactions between nitrosobenzenes and a variety of styrenes revealed that mono-substituted olefins either electron rich or deficient styrenes produced substituted nitrones and isoxazolidines. It is noteworthy that this reaction is very specific to mono substituted aromatic olefins.

Table 3. Room Temperature Cycloadditions[a]



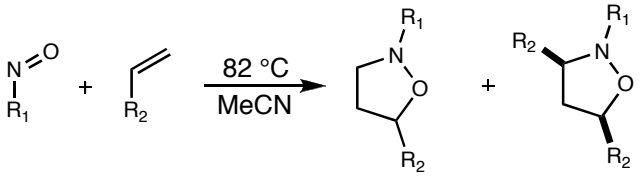
Entry	R_1	R_2	Product	Yield(%)[b]
1	Ph **28**	Ph **29**	**36**	49
2	Ph **28**	2-MePh **29a**	**36a**	48
3	Ph **28**	4-MeOPh **29b**	**36b**	48
4	Ph **28**	3-ClPh **29c**	**36c**	31
5	Ph **28**	4-*t*-BuPh **29d**	**36d**	30
6	Ph **28**	4-CF_3Ph **29e**	**36e**	40
7	Ph **28**	2-BrPh **29f**	**36f**	35
8	Ph **28**	4-BrPh **29g**	**36g**	48
9	4-BrPh **28a**	Ph **29**	**36h**	40

[a] R_1 (0.25 mmol), R_2 (1.0 mmol), and anhydrous MeCN (4 mL) were used. [b] Yield of isolated product.

Experiments to study the influence of temperature were undertaken in refluxing MeCN (82 ºC). The reaction at elevated temperature afforded the more hindered trisubstituted isoxazolidines in addition to the disubstituted isoxazolidines, which were

formed at room temperature (Table 4). When excess of parent styrene was combined with nitrosobenzene in refluxing MeCN, the best yield of isoxazolidines **36** and **46** was obtained. The product **46a (**entry 2) was also confirmed by single crystal X-ray analysis (Figure 5).

Table 4. Elevated Temperature Cycloadditions[a]



A *B*

Entry	R_1	R_2	Product(*A*/*B*)	Yield (%)[b]
1	Ph **28**	Ph **29**	**36/46**	49/40
2	Ph **28**	2-MePh **29a**	**36a/46a**	41/41
3	Ph **28**	4-MeOPh **29b**	**36b/46b**	48/39
4	Ph **28**	3-ClPh **29c**	**36c/46c**	30/32
5	Ph **28**	4-*t*-BuPh **29d**	**36d/46d**	33/30
6	Ph **28**	4-CF_3Ph **29e**	**36e/46e**	38/25
7	Ph **28**	2-BrPh **29f**	**36f/46f**	40/33
8	Ph **28**	4-BrPh **29g**	**36g/46g**	48/40
9	4-BrPh **28a**	Ph **29**	**36h/46h**	40/21

[a] R_1 (0.25 mmol), R_2 (1.0 mmol), and anhydrous MeCN (4 mL) were used. [b] Yield of isolated product.

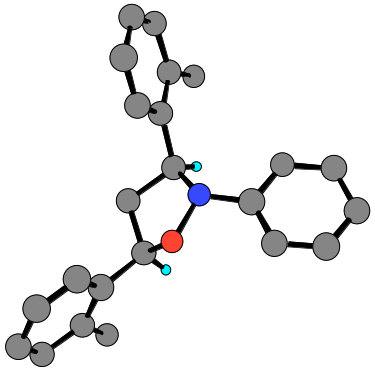
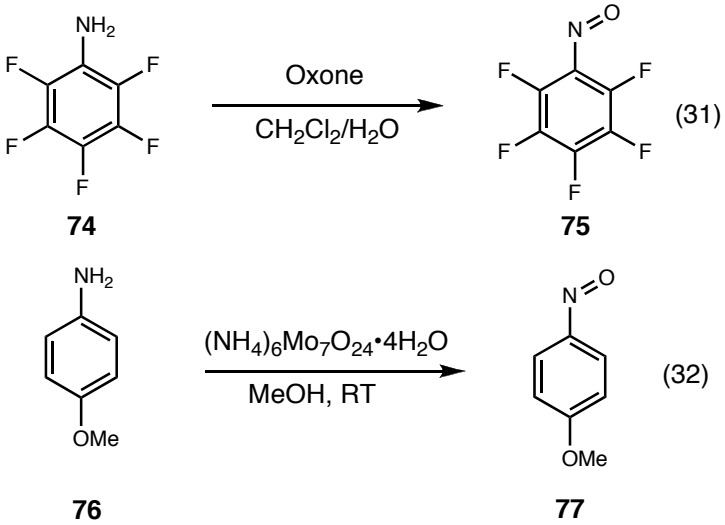


Figure 5. X-ray Structure of 2-phenyl-3,5-di*o*-tolylisoxazolidine **46a**

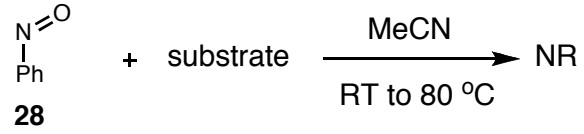
After several attempts to synthesize the pentafluoro nitrosobenzene **75**, oxidation of **74** with oxone ($2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$) gave the best yield. Oxidation of 4-methoxyaniline **76** was performed with $(NH_4)_6Mo_7O_{24} \bullet 4H_2O$ to afford 1-methoxy-4-nitrosobenzene **77** (eq 32). Oxidation with oxone was not successful in this case.

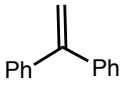
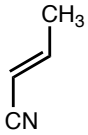
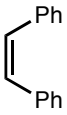
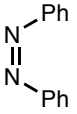
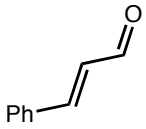
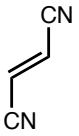


However, we were not able to observe any isoxazolidine products, when electron deficient **75** was employed. When the electron rich methoxy nitrosobenzene **77** was

tested under the same reaction conditions, traces of isoxazolidine product were observed. Having found that this transformation proceeds best when a moderate excess of styrene (4 equiv) and electron neutral styrene are employed, we investigated influence of substituents. When disubstituted olefins and mono and disubstituted alkynes were subjected to the reaction conditions, no cycloadducts were observed (Table 5). Subjection of azobenzene (entry 3) to styrene resulted in no formation of product. One of the plausible explanations of these results is that the relatively stable olefins do not react rapidly enough with nitrosobenzene. In addition, it seemed that disubstituted olefins were not favored in the transition state due to steric hindrance. However, the by-product was azoxybenzene. This result could be understood by the hypothesis that reduction of nitrosobenzene was faster than the reaction between nitrosobenzene and olefins. In addition to these observations, the desired cycloadducts were not observed even in refluxing MeCN.

Table 5. Reactions with Disubstituted Substrates and Alkynes

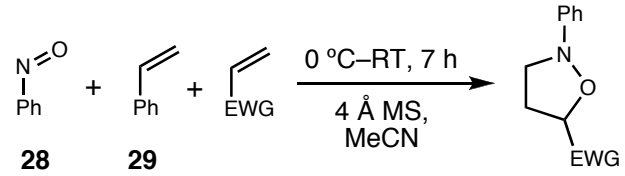


Entry	Substrate	Entry	Substrate
1		6	
2		7	
3		8	
4		9	
5			

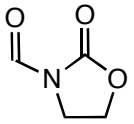
In order to understand the influence of electron stabilizing aromatic groups on olefines, we replaced the aromatic groups to alkoxides such as 2-methyl-2-(vinyloxy)propane, ethoxyethene, and 1-(vinyloxy)butane, and nitryl group such as prop-2-enenitrile. Interestingly, these reactions resulted in very low yields of isoxazolidines. These results indicate that the electron stabilizing aromatic substituent is crucial.

With these data in hand, we pursued the synthetically useful goal of trapping the reactive nitrone **44** in situ with a dipolarophile that is more reactive than the styrene employed for generation of the nitrone **44**. For instance, when nitrosobenzene **28**, acrylamide **78c**, and styrene **26** were combined at RT (Table 6 entry 4), the desired 5-substituted isoxazolidine **79c** was isolated in 82% yield in a single step from inexpensive, commercially available materials. No cycloadduct derived from the more plentiful, but less reactive dipolarophile styrene was observed when the reaction was started at 0 °C and allowed to warm to RT. Other cycloadducts were isolated as shown in Table 6 with use of an appropriate monosubstituted dipolarophile. The reactions were highly regioselective, with no evidence of formation of the 4-substituted products (^{1}H NMR spectroscopy). Methyl methacrylate, a disubstituted olefin, is also a suitable dipolarophile, yielding the expected cycloadduct in 52% yield. However, 1,2-substituted olefins, such as methyl crotonate, were unreactive in this cycloaddition at room temperature.

Table 6. An Efficient Cascade Process Utilizing Reactive Nitrone Intermediates[*a]



28 **29**

Entry	EWG	Product	Yield (%)[b]
1	CHO **78**	**79**	86[c]
2	CN **78a**	**79a**	65
3	CO_2Me **78b**	**79b**	78
4	$C(O)NMe_2$ **78c**	**79c**	82
5	C(O)Et **78d**	**79d**	74
6	 **78e**	**79e**	81

* These works were performed by Alejandro Bugarin. [a] **28** (1.0 mmol), **29** (2.0 mmol), EWG (0.5 mmol), and anhydrous MeCN (2 mL) were used. [b] Yield of isolated product. [c] Isolated as the primary alcohol after $NaCNBH_3$ reduction.

CHAPTER V

CONCLUSION

In conclusion, our initial studies toward [2+2] cycloaddition reactions have resulted in the discovery of a novel transformation. We have demonstrated the formation of nitrones from nitrosobenzene and mono-substituted aromatic styrenes, which can undergo a cyclization with electron-deficient alkenes to afford isoxazolidines in a single reaction flask. A [3+2] dipolar cycloaddition is clearly implicated by the available mechanistic data (Scheme 5). The reaction allows for the rapid assembly of various substituted isoxazolidines directly from nitrosobenzenes, electron deficient alkenes, and styrene. The synthetically useful reactions described in Table 3, 4, and 6 proceed in moderate to good yields and under convenient reaction conditions. In contrast to typical syntheses of isoxazolidines that require 3 or more total steps, this cascade provides direct access to 5-substituted isoxazolidines in a single step from commercially available starting materials.

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APPENDIX A

EXPERIMENTAL

A.1 General Information

All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Dry acetonitrile was obtained by distillation under argon. All commercially obtained reagents were used as received. 1-Bromo-4-nitrosobenzene was prepared by the known method.[1] Styrene-2-d1, Styrene-3,3-d2, and Styrene-2,3,3-d3 were purchased from Aldrich. Deionized water was used for all aqueous extractions and for obtaining all aqueous solutions.

Heating was accomplished by either a heating mantle or silicone oil bath. Temperature was controlled with a J-KEM temperature controller. Purification of reaction products was carried out by flash column chromatography using Silicycle silica gel 60 (230-400 mash). Analytical thin layer chromatography was performed on E. Merck 0.25 mm glass-backed silica gel 60-F plates. Visualization was accompanied with UV light and ceric ammonium molybdate staining. Concentration in vacuo refers to the removal of volatile solvent using a Buchi rotory evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr).

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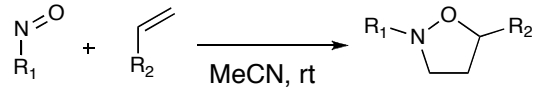
^{1}H NMR spectra were recorded on a Varian Inova 300 (at 300 MHz), or a Varian Mercury 300 (at 300 MHz), and are recorded relative to Me_4Si (δ 0.0). ^{1}H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet). Proton-decoupled ^{13}C NMR spectra were recorded on Varian Inova 300 (at 75 MHz), or a Varian Mercury 300 (at 75 MHz), and are reported relative to $CDCl_3$ (δ 77.16). High-resolution mass spectra (HRMS) were obtained at the center for Chemical Characterization and Analysis at TAMU. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer as thin film on NaCl plates.

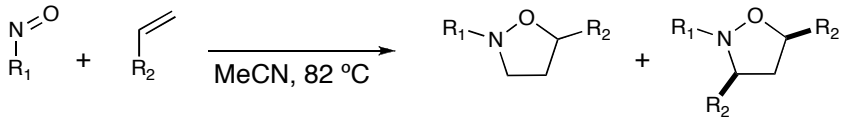
A.2 Procedures and Characterization Data.

A.2.1 General Procedure 1



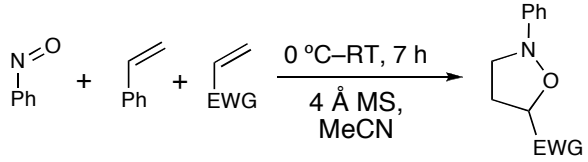
To a solution of appropriate nitrosobenzene (0.25 mmol, 1.0 equiv) in anhydrous acetonitrile (4 mL) under an argon atmosphere was added the corresponding olefin (1.0 mmol, 4.0 equiv). The solution was stirred at room temperature for 48 h unless otherwise stated. The solvent was evaporated under reduced pressure and the resulting brown residue was purified by flash column chromatography to give the corresponding isoxazolidine.

A.2.2 General Procedure 2

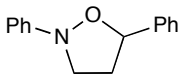


To a solution of appropriate nitrosobenzene (0.25 mmol, 1.0 equiv) in anhydrous acetonitrile (4 mL) under an argon atmosphere was added the corresponding olefin (1.0 mmol, 4.0 equiv). The solution was stirred at 82 ºC for 48 h unless otherwise stated. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography to give the corresponding isoxazolidine.

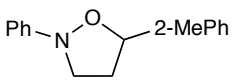
A.2.3 General Procedure 3



To a solution of nitrosobenzene (1.0 mmol, 2.0 equiv) in anhydrous acetonitrile (2 mL), and MS 4 Å under argon atmosphere was added styrene (2.0 mmol, 4.0 equiv) and the correspondent dipolarophile (0.5 mmol, 1.0 equiv). The solution was stirred at 0 ºC for two hours and additional 5 hours at room temperature. The solvent was evaporated under reduced pressure and the resulting residue was purified by flash column chromatography to give the corresponding isoxazolidine.

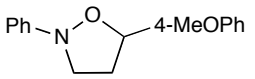


2,5-diphenylisoxazolidine (36): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and styrene **29** (1.0 mmol, 104 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a colorless oil **36** (28 mg, 49%). R_f = 0.15 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.25 (m, 7H), 7.11 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.97 (app tt, *J* = 6.8, 6.8, 2.0, 2.0 Hz, 1H), 5.16 (t, *J* = 7.5 Hz, 1H), 3.79-3.65 (m, 2H), 2.69-2.62 (m , 1H), 2.34-2.25 (m, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 140.3, 129.0, 128.6, 128.1, 126.6, 121.8, 115.1, 79.1, 54.3, 37.1; HRMS (ESI) calcd for $C_{15}H_{15}NO$ $[M+H]^+$: 226.1232; found: 226.1237.

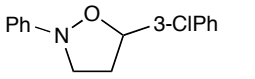


2-phenyl-5-*o*-tolylisoxazolidine (36a): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-methyl-2-vinylbenzene **29a** (1.0 mmol, 121 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **36a** (28 mg, 48%). R_f = 0.17 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-

7.58 (m, 1H), 7.34-7.10 (m, 7H), 7.0-6.96(m, 1H), 5.35 (t, J = 9 Hz, 1H), 3.79-3.73 (m, 1H), 3.69-3.63 (m, 1H), 2.74-2.62 (m, 1H), 2.38-2.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 138.7, 135.0, 130.4, 129.0, 127.6, 126.3, 125.3, 121.8, 115.1, 76.0, 54.0, 35.8, 19.5; HRMS (ESI) calcd for $C_{15}H_{17}NO$ $[M+H]^+$: 240.1388; found: 240.1389.

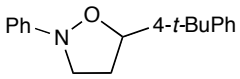


5-(4-methoxyphenyl)-2-phenylisoxazolidine (36b): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-methoxy-4-vinylbenzene **29b** (1.0 mmol, 134 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1 for 58 h. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **36b** (30 mg, 48%). R_f = 0.11 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.24 (m, 4H), 7.09 (d, J = 6 Hz, 2H), 6.98-6.88 (m, 3H), 5.09 (t, J = 9 Hz, 1H), 3.80 (s, 3H), 3.79-3.65 (m, 1H), 2.66-2.55 (m, 1H), 2.33-2.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 151.8, 131.9, 128.9, 128.1, 121.7, 115.0, 114.0, 78.9, 55.4, 54.4, 36.9; HRMS (ESI) calcd for $C_{16}H_{17}NO_2$ $[M+H]^+$: 256.1338; found: 256.1339.

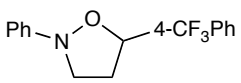


5-(3-chlorophenyl)-2-phenylisoxazolidine (36c): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-chloro-3-vinylbenzene **29c** (1.0 mmol, 138 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **36c** (20 mg, 31%). R_f = 0.18 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.33-7.25 (m, 5H), 7.11-7.08 (m, 2H), 7.02-6.97 (m, 1H), 5.15 (t, J = 6 Hz, 1H), 3.79-3.63 (m,

2H), 2.73-2.62 (m, 1H), 2.31-2.22 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 142.7, 134.5, 129.9, 129.0, 128.1, 126.7, 124.7, 122.1, 115.1, 78.3, 54.1, 37.0; HRMS (ESI) calcd for $C_{15}H_{14}ClNO$ $[M+H]^+$: 260.0842; found: 260.0841.

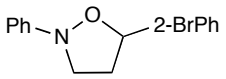


5-(4-tert-butylphenyl)-2-phenylisoxazolidien (36d): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-tert-butyl-4-vinylbenzene **29d** (1.0 mmol, 160 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **36d** (21 mg, 30%). R_f = 0.17 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.35 (m, 4H), 7.31-7.24 (m, 2H), 7.12-7.08 (m, 2H), 6.99-6.94 (m, 1H), 5.12 (t, *J* = 6 Hz, 1H), 3.79-3.68 (m, 2H), 2.66-2.59 (m, 1H), 2.34-2.28 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 151.2, 136.9, 129.0, 126.5, 125.6, 121.7, 115.0, 79.0, 54.4, 36.9, 34.7, 31.4; HRMS (ESI) calcd for $C_{19}H_{23}NO$ $[M+H]^+$: 282.1858; found: 282.1857.

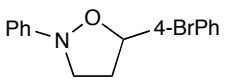


2-phenyl-5-(4-(trifluoromethyl)phenyl)isoxazolidines (36e): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-(trifluoromethyl)-4-vinylbenzene **29e** (1.0 mmol, 172 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **36e** (28 mg, 38%). R_f = 0.07 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.53 (m, 4H), 7.34-7.28 (m, 2H), 7.12-7.09 (m, 2H), 7.03-6.97 (m, 1H), 5.24 (t, *J* = 6Hz, 1H), 3.77-3.65 (m, 2H), 2,76-

2.69 (m, 1H), 2.30-2.23 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 144.8, 129.1, 126.7, 125.6 (2 C), 125.7 (2 C), 122.2, 115.2, 78.3, 54.0, 37.1; HRMS (ESI) calcd for $C_{16}H_{14}F_3NO$ $[M+H]^+$: 294.1106; found: 294.1019.

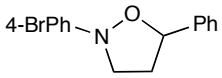


5-(2-bromophenyl)-2-phenylisoxazolidine (36f): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-bromo-2-vinylbenzene **29f** (1.0 mmol, 181 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **36f** (26.5 mg, 35%). R_f = 0.23 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 9, 3.61 Hz, 1H), 7.55 (dd, *J* = 8, 2.1 Hz, 1H), 7.36-7.29 (m, 3H), 7.18- 7.11 (m, 3H), 7.03-6.98 (m, 1H), 5.49 (dd, *J* = 9, 6 Hz, 1H), 3.70-3.57 (m, 2H), 2.91-2.79 (m, 1H), 2.21-2.11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 140.9, 132.7, 129.0, 127.7, 127.2, 122.1, 121.8, 115.3, 77.9, 53.7, 36.1; HRMS (ESI) calcd for $C_{15}H_{14}BrNO$ $[M+H]^+$: 304.0337; found: 304.0334.

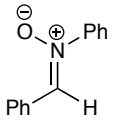


5-(4-bromophenyl)-2-phenylisoxazolidine (36g): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-bromo-4-vinylbenzene **29g** (1.0 mmol, 181 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **36g** (36 mg, 48%). R_f = 0.12 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.48 (m, 1H), 7.33-7.25 (m, 5H), 7.11-7.07 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.01-6.96 (m, 1H), 5.19 (t, 7.5 Hz, 1H), 3.78-3.68 (m, 2H), 2.73-2.66 (m, 1H), 2.29-2.25 (m, 1H); ^{13}C NMR

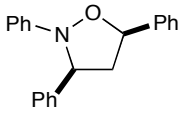
(75 MHz, $CDCl_3$) δ 151,5, 139.5, 131.7, 131.7, 130.9, 129.0, 128.2, 122., 121.8, 115.1, 78.4, 54.1, 37.0; HRMS (ESI) calcd for $C_{15}H_{14}BrNO$ $[M+H]^+$: 304.0337; found: 304.0339.



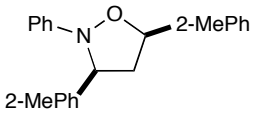
2-(4-bromophenyl)-5-phenylisoxazolidine (36h): 1-Bromo-4-nitrosobenzene **28a** (0.25 mmol, 47 mg, 1.0 equiv) and styrene **29** (1.0 mmol, 104 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **36h** (0.099 mmol, 30 mg, 40%). R_f = 0.22 (1:2 CH_2Cl_2:hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.29 (m, 9H), 6.97 (m, 2H), 5.14 (t, *J* = 9 Hz, 1H), 3.69 (m, 2H), 2.66 (m, 1H), 2.31 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.8, 139.8, 131.8, 128.7, 128.2, 126.6, 116.8, 114.2, 79.3, 54.2, 37.0; MS (ESI) 304 $[M+H]^+$; HRMS (ESI) calcd for $C_{15}H_{14}BrNO$ $[M+H]^+$ 304.0337 ; found 304.0336.



(*Z*)-*N*-benzylideneaniline oxide (37): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and styrene-3,3-d2 **60** (1.0 mmol, 106 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:1 EtOAc:hexane provided a pale brown solid **37** (18 mg, 36%). R_f = 0.425 (1:1 EtOAc:hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 8.41–8.32 (m, 2H), 7.92 (s, 1H), 7.79-7.75 (m, 2H), 7.51-7.44 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 134.8, 131.0, 130.7, 130.0, 129.2, 129.1, 128.9, 128.7; $C_{13}H_{11}NO$ $[M+H]^+$: 197.0841; found: 198.0918.

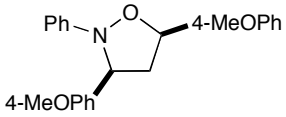


2,3,5-triphenylisoxazolidine (46): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and styrene **29** (1.0 mmol, 104 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a colorless oil **46** (22 mg, 40%). R_f = 0.32 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56–6.91 (m, 19H), 5.17 (dd, *J* = 9, 6 Hz, 1H), 4.92 (t, *J* = 6 Hz, 1H), 3.18 (ddd, *J* = 12, 9, 6 Hz, 1H), 2.47 (ddd, *J* = 12.3, 10.2, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 143.0, 137.9, 131.7, 129.7, 129.1, 128.9, 128.8, 128.7, 128.5, 127.4, 127.0, 126.8, 126.9, 126.4, 125.6, 122.4, 121.5, 114.0, 80.7, 71.6, 48.8; HRMS (ESI) calcd for $C_{21}H_{19}NO$ $[M+H]^+$:302.1545; found: 302.1553.

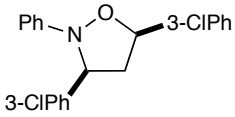


2-phenyl-3,5-di*o*-tolylisoxazolidine (46a): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-methyl-2-vinylbenzene **29a** (1.0 mmol, 121 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2 for 36 h. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **46a** (34 mg, 41%). R_f = 0.42 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6 Hz, 1H), 7.61-7.58 (m, 1H), 7.30-7.14 (m, 9H), 7.03-6.99 (m, 1H), 6.96-6.90 (m, 1H), 6.96-6.90 (m, 1H), 5.38 (dd, *J* = 9, 6 Hz, 1H), 5.10 (t, *J* = 9 Hz, 1H), 3.23 (ddd, *J* = 12, 9, 6 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H) 2.23 (ddd, *J* = 12, 10.2, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 140.9, 136.2, 135.6, 133.9, 130.7, 130.5,

128.7, 128.0, 127.2, 126.5, 126.3, 125.7, 121.2, 115.9, 113.8, 69.2, 46.2, 19.6; HRMS (ESI) calcd for $C_{23}H_{23}NO$ $[M+H]^+$: 330.1858; found: 330.1862.

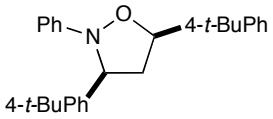


3,5-bis(4-methoxyphenyl)-2-phenylisoxazolidine (46b): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-methoxy-4-vinylbenzene **29b** (1.0 mmol, 134 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2 for 68 h. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **46b** (35 mg, 39%). R_f = 0.19 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, *J* = 9 Hz, 2H), 7.35 (d, *J* = 6 Hz, 2H), 7.27-7.22 (m, 2H), 7.06-7.03 (m, 2H), 6.94-6.87 (m, 5H), 5.11(dd, *J* = 9, 6 Hz, 1H), 4.86 (t, *J* = 9 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.08 (ddd, *J* = 12, 9, 6 Hz, 1H), 2.43 (ddd, *J* = 12, 10.2, 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 158.9, 152.8, 135.1, 129.7, 129.0, 128.6, 128.4, 128.3, 128.0, 127.5, 121.3, 116.0, 114.2, 114.0 (2C), 80.4, 71.2, 55.4, 48.7; HRMS (ESI) calcd for $C_{23}H_{23}NO_3$ $[M+H]^+$: 362.1678; found: 362.1699.

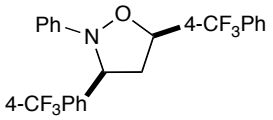


3-(2-chlorophenyl)-5-(3-chlorophenyl)-2-phenylisoxazolidine (46c): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-chloro-3-vinylbenzene **29c** (1.0 mmol, 138 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2 for 27 h. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **46c** (30 mg, 32%). R_f = 0.44 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.42-7.39 (m, 2H), 7.35-7.25 (m, 7H), 7.04-6.95 (m,

3H), 5.15 (dd, *J* = 9, 6 Hz, 1H), 4.89 (t, *J* = 6 Hz, 1H), 3.19 (ddd, *J* = 12, 9, 6 Hz, 1H), 2.40 (ddd, 12, 9.9, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 144.7, 140.0, 134.9, 134.6, 130.3, 130.0, 129.2, 128.6, 127.8, 127.0, 126.5, 124.9, 124.5, 122.0, 114.1, 79.8, 70.9, 48.4; HRMS (ESI) calcd for $C_{21}H_{17}Cl_2NO$ $[M+H]^+$: 370.0765; found: 370.0762.

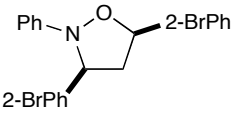


3,5-bis(4-tert-butylphenyl)-2-phenylisoxazolidine (46d): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-tert-butyl-4-vinylbenzene **29d** (1.0 mmol, 160 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2 for 68 h. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **46d** (31 mg, 30%). R_f = 0.47 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2 H), 7.43-7.36 (m, 6H), 7.28-7.22 (m, 2H), 7.08-7.04 (m, 2H), 6.93-6.90 (m, 1H), 5.13 (dd, *J* = 9, 6 Hz, 1H), 4.9 (t, 6 Hz, 1H), 3.13 (ddd, *J* = 12, 9, 6 Hz, 1H), 2.50 (ddd, *J* = 12, 10.5, 7.8 Hz, 1H), 1.34 (s, 9H), 1.32 (s, 9H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 151.6, 150.3, 140.1, 134.6, 129.0, 126.9, 126.1, 125.8, 125.6, 121.3, 113.9, 80.6, 71.6, 48.6, 34.7, 34.6, 31.5, 31.4; HRMS (ESI) calcd for $C_{29}H_{35}NO$ $[M+H]^+$: 414.2799; found: 414.2799.

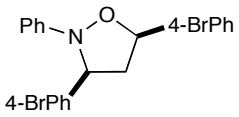


2-phenyl-3,5-bis(4-(trifluoromethyl)phenyl)isoxazolidines (46e): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-(trifluoromethyl)-4-vinylbenzene **29e** (1.0 mmol, 172 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2 for 36 h. Flash chromatography with 1:2

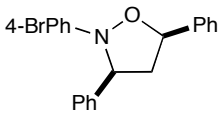
CH_2Cl_2:hexane provided a pale yellow oil **46e** (27 mg, 25%). R_f = 0.35 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.61 (m, 6H), 7.53-7.50 (m, 2H), 7.32-7.24 (m, 2H), 7.05-6.96 (m, 3H), 5.27 (dd, *J* = 9, 6 Hz, 1H), 5.00 (t, *J* = 6 Hz, 1H), 3.28 (ddd, *J* = 12, 9, 6 Hz, 1H), 2.40 (ddd, *J* = 12, 9.6, 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 146.6, 142.2, 129.3, 128.9, 127.2, 127.0, 126.9, 126.7, 126.1, 126.0 (2 C), 125.9, 125.8, 125.7 (2 C), 125.6, 122.6, 122.2, 116.0, 114.2, 79.7, 70.8, 48.4; HRMS (ESI) calcd for $C_{23}H_{17}F_6NO$ $[M+H]^+$: 438.1293; found: 438.1295.



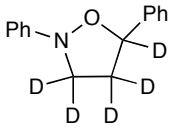
3,5-bis(2-bromophenyl)-2-phenylisoxazolidine (46f): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-bromo-2-vinylbenzene **29f** (1.0 mmol, 181 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2 for 27 h. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **46f** (38 mg, 33%). R_f = 0.52 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8, 1.5 Hz, 1H), 7.66 (dd, *J* = 6.7, 1.4 Hz, 1H), 7.58-7.52 (m, 2H), 7.38-7.26 (m, 6H), 7.18-7.12 (m, 2H), 7.06 (dd, *J* = 9, 1.2 Hz, 2H), 6.98-6.96 (m, 1H), 5.22 (dd, *J* = 9, 6.6 Hz, 1H), 5.30 (dd, *J* = 8.1, 6.6 Hz, 1H), 3.62 (ddd, *J* = 12.6, 8.4, 6.9 Hz, 1H), 2.09 (ddd, *J* = 12.3, 9, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 142.0, 138.4, 132.8 (2 C), 129.4, 129.2, 128.9, 128.2 (2 C), 127.8, 127.2, 122.5, 122.1, 121.9, 114.2, 79.1, 70.6, 46.1; HRMS (ESI) calcd for $C_{21}H_{17}Br_2NO$ $[M+H]^+$:457.9755; found: 457.9756.



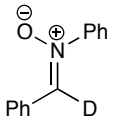
3,5-bis(4-bromophenyl)-2-phenylisoxazolidine (46g): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and 1-bromo-4-vinylbenzene **29g** (1.0 mmol, 181 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2 for 70 h. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **46g** (45 mg, 40%)). R_f = 0.37 (1:3 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.46 (m, 4H), 7.42-7.38 (m, 2H), 7.30-7.23 (m, 4H), 7.03-6.94 (m, 3H), 5.14 (dd, *J* = 9.6, 6 Hz, 1H), 4.87 (t, *J* = 7.8 Hz, 1H), 3.17 (ddd, *J* = 12.3, 8.1, 6 Hz, 1H), 2.35 (ddd, *J* = 12.3, 9.6, 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 141.7, 137.0, 132.0, 131.8, 129.2, 128.9, 128.8, 128.5, 128.1, 125.6, 122.4, 121.9, 121.3, 114.1, 79.8, 70.8, 48.5; HRMS (ESI) calcd for $C_{21}H_{17}Br_2NO$ $[M+H]^+$:457.9755; found: 457.9745.



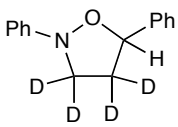
2-(4-bromophenyl)-3,5-diphenylisoxazolidine (46h): 1-Bromo-4-nitrosobenzene **28a** (0.25 mmol, 47mg, 1.0 equiv) and styrene **29** (1.0 mmol, 104 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP2. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow solid **46h** (0.052 mmol, 20 mg, 21%). R_f = 0.40 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.27-7.28 (m, 10H), 6.92 (m, 2H), 5.14 (dd, *J* = 9.0, 5.9 Hz, 1H), 4.85 (t, *J* = 6 Hz, 1H), 3.20 (ddd, *J* = 12, 9, 6 Hz, 1H), 2.49 (ddd, *J* = 12, 10.6, 9 Hz, 1H); 13C NMR (75 MHz, $CDCl_3$) δ 151.7, 142.4, 137.5, 131.9, 131.5, 129.1, 129.0, 128.7, 128.6, 127.6, 126.9, 126.8, 126.3, 117.6, 115.8, 113.8, 80.8, 71.7, 48.9; MS (ESI) 380 $[M+H]^+$; HRMS (ESI) calcd for $C_{21}H_{18}BrNO$ $[M+H]^+$: 380.0650; found: 380.0651.



2,5-diphenylisoxazolidine-3,3,4,4,5-d5 (58): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and styrene-2,3,3-d3 **72** (1.0 mmol, 107 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **58** (18 mg, 32%). R_f = 0.19 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.24 (m, 7H), 7.11 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.97 (app tt, *J* = 6.8, 6.8, 2.0, 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 140.2, 129.0, 128.6, 128.1, 126.7, 121.8, 115.1; $C_{15}H_{10}D_5NO$ $[M+H]^+$: 231.1493.

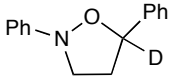


(*Z*)-*N*-benzylideneaniline oxide-d1 (59): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and styrene-2-d1 **62** (1.0 mmol, 105 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:1 EtOAc:hexane provided a pale brown solid **59** (20 mg, 41%). R_f = 0.45 (1:1 EtOAc:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41–8.38 (m, 2H), 7.79-7.76 (m, 2H), 7.51-7.47 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 134.8, 131.0, 130.7, 130.0, 129.2, 129.1, 128.9, 128.7; $C_{13}H_{11}NO$ $[M+H]^+$: 198.0903; found: 198.0918.

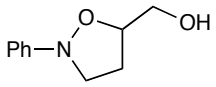


2,5-diphenylisoxazolidine-3,3,4,4-d4 (61): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and styrene-3,3-d2 **60** (1.0 mmol, 106 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **61** (15 mg, 27%). R_f

= 0.13 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.24 (m, 7H), 7.11 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.97 (app tt, *J* = 6.8, 6.8, 2.0, 2.0 Hz, 1H), 5.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 140.2, 129.0, 128.6, 128.1, 126.7, 121.8, 115.1, 79.0; $C_{15}H_{11}D_4NO$ $[M+H]^+$: 230.1518.

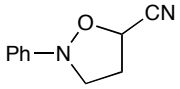


2,5-diphenylisoxazolidine-5-d1 (63): Nitrosobenzene **28** (0.25 mmol, 27 mg, 1.0 equiv) and styrene-2-d1 **62** (1.0 mmol, 105 mg, 4.0 equiv) were subjected to the reaction conditions described in the GP1. Flash chromatography with 1:2 CH_2Cl_2:hexane provided a pale yellow oil **63** (18 mg, 32%). R_f = 0.15 (1:2 CH_2Cl_2:hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.24 (m, 7H), 7.11 (dd, *J* = 8.7, 0.9 Hz, 2H), 6.97 (app tt, *J* = 6.8, 6.8, 2.0, 2.0 Hz, 1H), 3.81-3.65 (m, 2H), 2.70-2.61 (m , 1H), 2.33-2.24 (m, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.7, 140.2, 129.0, 128.6, 128.1, 126.7, 121.8, 115.1, 54.3, 36.9; $C_{15}H_{14}DNO$ $[M+H]^+$: 227.1318.

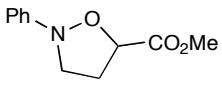


(2-phenylisoxazolidin-5-yl)methanol (79): To a solution of 2-phenylisoxazolidine-5-carbaldehyde (0.14 mmol, 25 mg, 1.0 equiv) in 5 mL of THF was added $NaCNBH_3$ (0.31 mmol, 19 mg, 2.2 equiv) in 2 mL of THF dropwise at 0 ºC, then stirred at room temperature for 2 hr. The solvent was removed under reduce pressure. Flash chromatography with 1:4 EtOAc:Hexanes provided a pale yellow oil **79** (21.7 mg, 86%). R_f = 0.55 (1:1 EtOAc:hexane); IR (thin film): 3382 (OH); 1598(CO); 1290 (NO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 4.42 (m, 1H), 3.84 (dd, *J* = 2.6, 9.2 Hz,

1H), 3.70 (dd, *J* = 5, 6.8 Hz, 1H), 3.59-3.52 (m, 2H), 2.26 (m, 1H), 2.18 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 128.8, 122.1, 115.2, 77.8, 64.1, 54.1, 29.7; MS (ESI) LRMS calcd for $C_{10}H_{13}NO_2$ $[M+H]^+$: *m/z* 180.1025, found 180.1029.

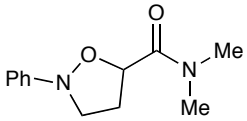


2-Phenyl-5-cyano-isoxazolidine (79a): Nitrosobenzene **28** (1.0 mmol, 107 mg, 2.0 equiv), styrene **29** (2.0 mmol, 208 mg, 4.0 equiv) and acrylonitrile **78a** (0.5 mmol, 26.5 mg, 1.0 equiv) were subjected to the reaction conditions described in the GP3. Flash chromatography with 1:4 EtOAc:hexane provided a pale yellow oil **79a** (56.5 mg, 65%). R_f = 0.55 (1:1 EtOAc:hexane); IR (thin film): 2242 (CN); 1716 (CO); 1279 (NO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 3H), 4.91 (dd, *J* = 5.1, 2.3 Hz, 1H), 3.80 (m, 1H), 3.48-3.45 (m, 1H), 2.63-2.69 (m , 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.41, 128.99, 123.26, 118.23, 115.67, 64.21, 52.21, 34.10; MS (CI) LRMS calcd for $C_{10}H_{10}N_2O$ $[M+H]^+$: *m/z* 175.07, found 175.2.

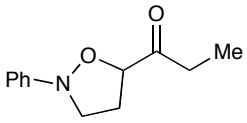


Methyl-2-phenylisoxazolidine-5-carboxylate (79b): Nitrosobenzene **28** (1.0 mmol, 107 mg, 2.0 equiv), styrene **29** (2.0 mmol, 208 mg, 4.0 equiv) and methyl acrylate **78b** (0.5 mmol, 43 mg, 1.0 equiv) were subjected to the reaction conditions described in the GP3. Flash chromatography with 1:4 EtOAc:hexane provided a pale yellow oil **79b** (81 mg, 78%). R_f = 0.6 (1:1 EtOAc:hexane); IR (thin film): 1737 (C=O); 1597(CO); 1209 (NO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8 Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H), 7.07 (t, *J* = 7 Hz, 1H),

4.75 (t, *J* = 7.3, 2.3 Hz, 1H), 3.80 (s, 3H), 3.60-3.55 (m, 2H), 2.54 (dd, *J* = 5.1, 2.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 151.6, 128.7, 122.4, 115.5, 75.1, 53.3, 52.4, 32.1; MS (CI) LRMS calcd for $C_{11}H_{13}NO_3$ $[M+H]^+$: *m/z* 208.09, found 208.2.

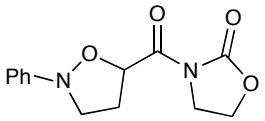


N,N-dimethyl-2-phenylisoxazolidine-5-carboxamide (79c): Nitrosobenzene **28** (1.0 mmol, 107 mg, 2.0 equiv), styrene **29** (2.0 mmol, 208 mg, 4.0 equiv) and N,N-dimethylacrylamide **78c** (0.5 mmol, 50 mg, 1.0 equiv) were subjected to the reaction conditions described in the GP3. Flash chromatography with 1:4 EtOAc:hexane provided a pale yellow oil **79c** (85 mg, 82%). R_f = 0.13 (1:1 EtOAc:hexane); IR (thin film): 1652 (C=O); 1598(CO); 1262 (NO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 4.93 (dd, *J* = 4.7, 4 Hz, 1H), 3.70-3.66 (m, 1H), 3.60-3.54 (m, 1H), 3.26 (s, 3H), 3.01 (s, 3H), 2.95-2.85 (m , 1H), 2.29-2.22 (m , 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.27, 150.8, 128.75, 122.18, 115.1, 74.9, 54.01, 37.1, 35.8, 29.9; MS (CI) LRMS calcd for $C_{12}H_{16}N_2O_2$ $[M+H]^+$: *m/z* 221.12, found 221.2.



1-(2-phenylisoxazolidin-5-yl)propan-1-one (79d): Nitrosobenzene **28** (1.0 mmol, 107 mg, 2.0 equiv), styrene **29** (2.0 mmol, 208 mg, 4.0 equiv) and ethyl vinyl ketone **78d** (0.5 mmol, 43 mg, 1.0 equiv) were subjected to the reaction conditions described in the GP3. Flash chromatography with 1:4 EtOAc:hexane provided a pale yellow oil **79d** (77 mg, 74%). R_f = 0.6 (1:1 EtOAc:hexane); IR (thin film): 1717 (C=O); 1598(CO); 1285 (NO) cm^{-1}. ^{1}H NMR (300

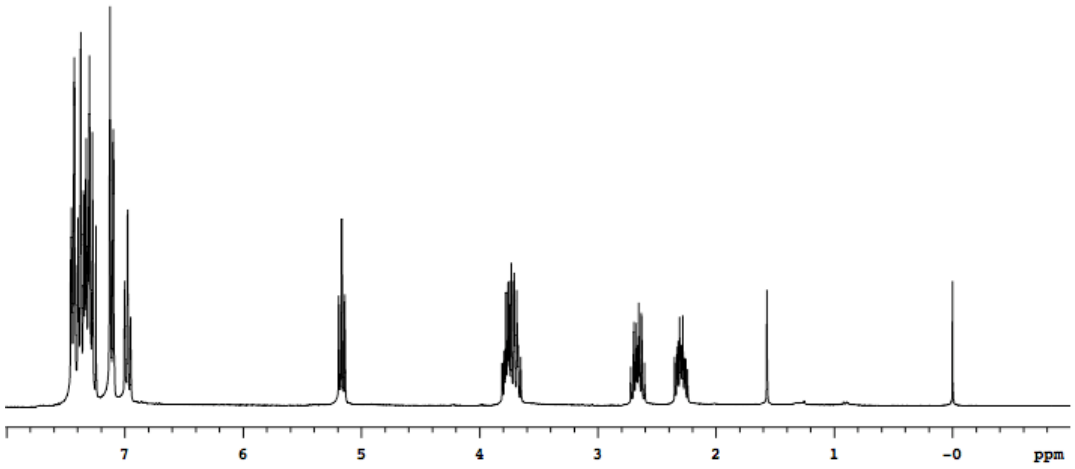
MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.02 (t, *J* = 7 Hz, 1H), 4.57 (dd, *J* = 5.5, 3 Hz, 1H), 3.59-3.54 (m, 1H), 3.36-3.28 (m, 1H), 2.78 (dd, *J* = 3, 3.7 Hz, 2H), 2.57-2.51 (m , 2H), 1.09 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.9, 150.2, 128.8, 122.4, 115.5, 81.0, 52.6, 31.6, 31.2, 7.1; MS (CI) LRMS calcd for $C_{12}H_{15}NO_2$ $[M+H]^+$: *m/z* 206.1, found 206.1.



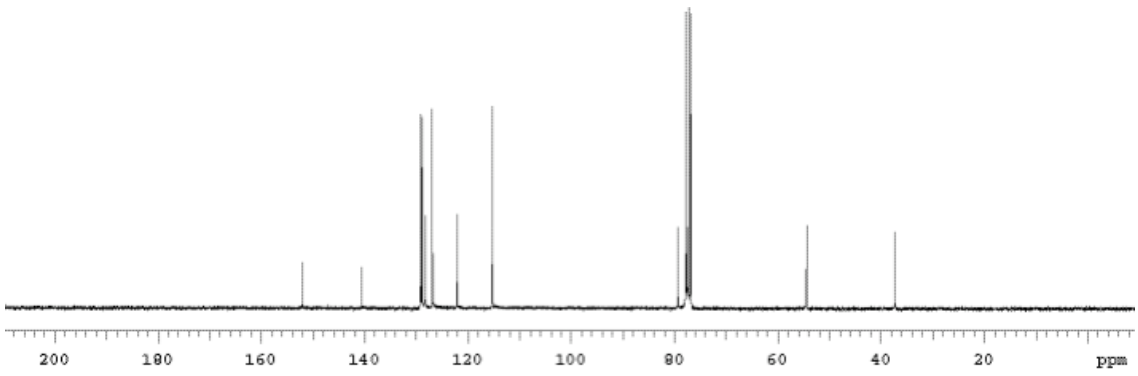
3-(2-phenylisoxazolidine-5-carbonyl)oxazolidin-2-one (79e): Nitrosobenzene **28** (1.0 mmol, 107 mg, 2.0 equiv), styrene **29** (2.0 mmol, 208 mg, 4.0 equiv) and 3-prop-2-enoyloxazolidin-2-one **78e** (0.5 mmol, 70.5 mg, 1.0 equiv) were subjected to the reaction conditions described in the GP3. Flash chromatography with 1:4 EtOAc:hexane provided a white solid **79e** (106 mg, 81%). R_f = 0.2 (1:1 EtOAc:hexane); IR (thin film): 1779 (C=O); 1704(CO); 1248 (NO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7 Hz, 1H), 5.68 (dd, *J* = 4.5, 4.8 Hz, 1H), 4.50 (t, *J* = 8 Hz, 2H), 4.10-4.03 (m, 2H), 3.63-3.56 (m, 2H), 2.64 (m, 1H), 2.55-2.47 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 153.1, 150.7, 128.7, 122.4, 115.5, 75.05, 62.8, 53.4, 42.5, 31.8; MS (CI) LRMS calcd for $C_{13}H_{14}N_2O_4$ $[M+H]^+$: *m/z* 263.1, found 263.2.

APPENDIX B

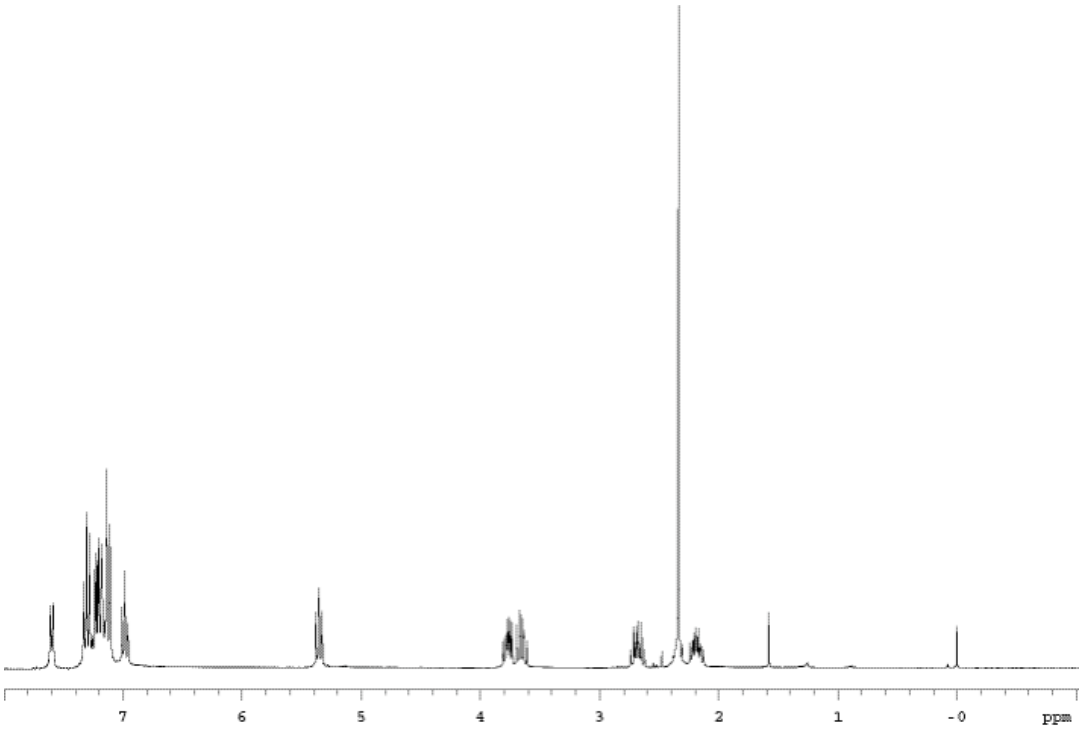
SELECTED SPECTRAL DATA



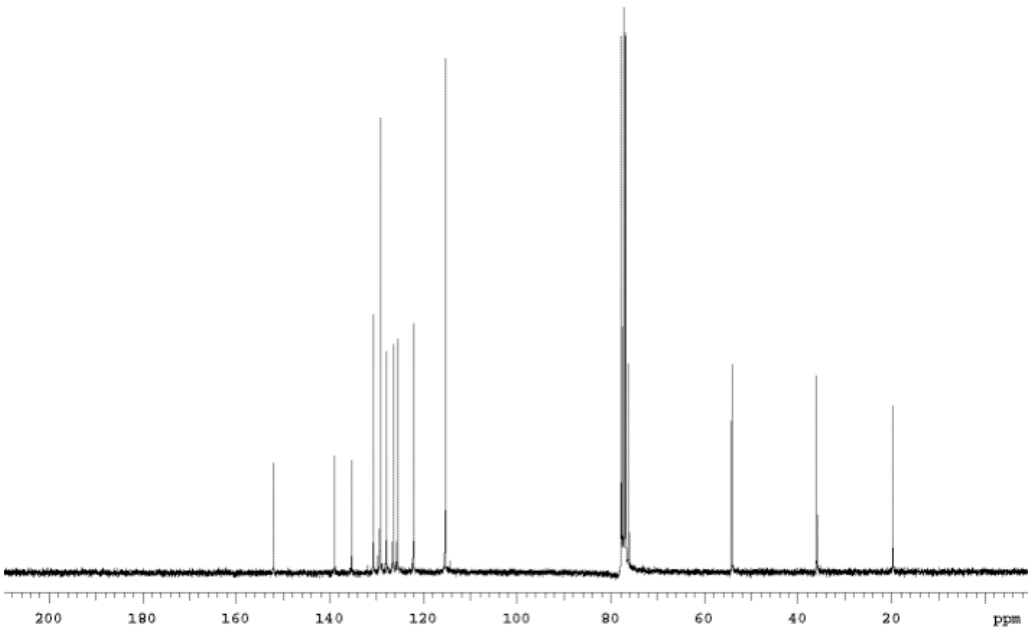
^{1}H NMR spectrum of **36**



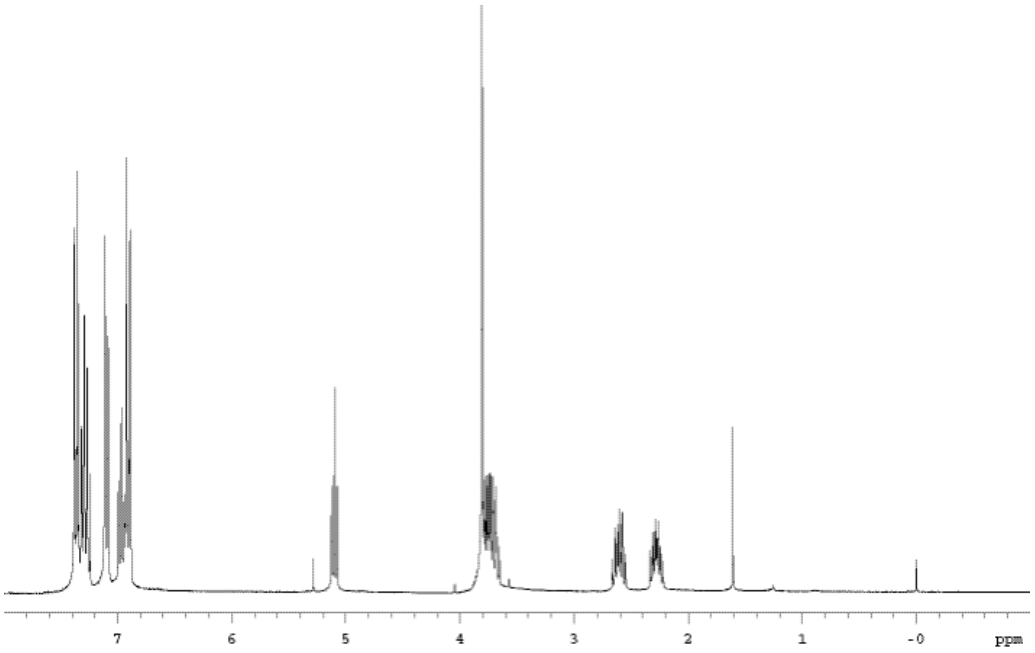
^{13}C NMR spectrum of **36**



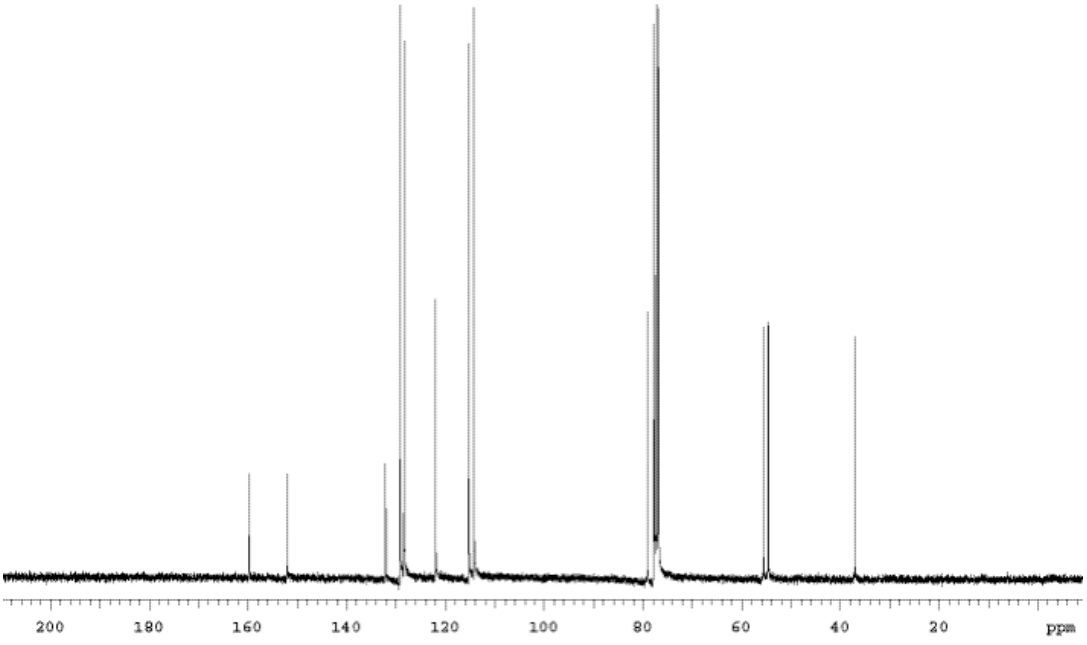
^{1}H NMR spectrum of **36a**



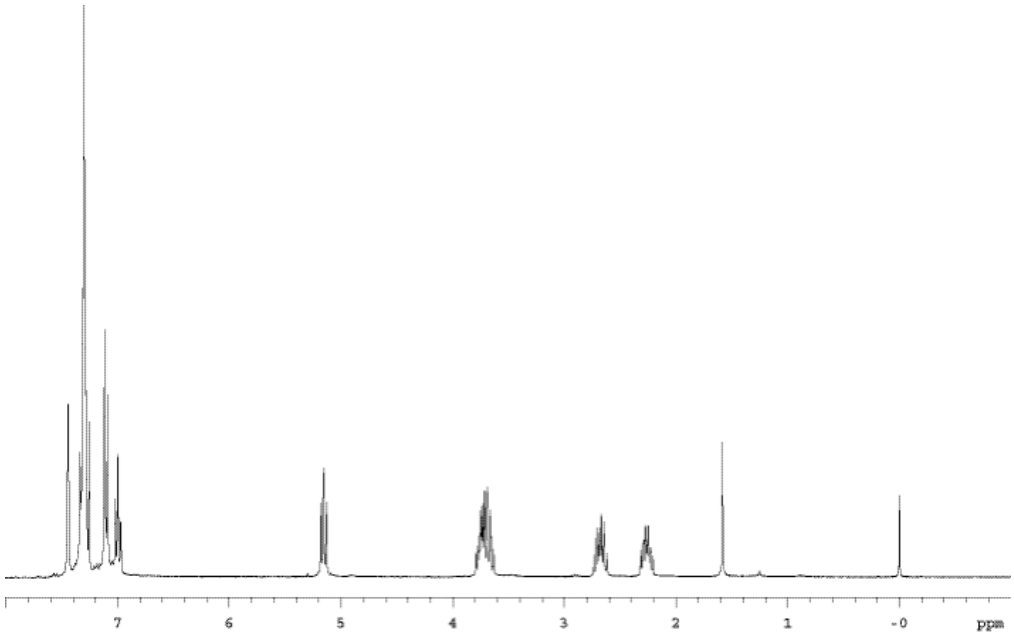
^{13}C NMR spectrum of **36a**



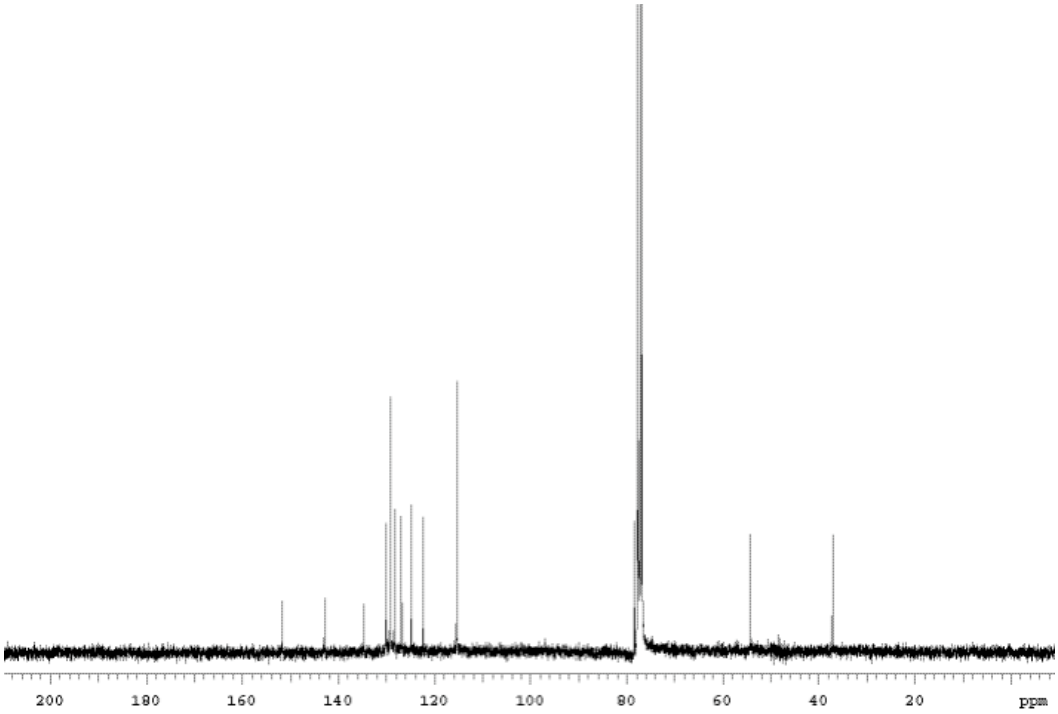
^{1}H NMR spectrum of **36b**



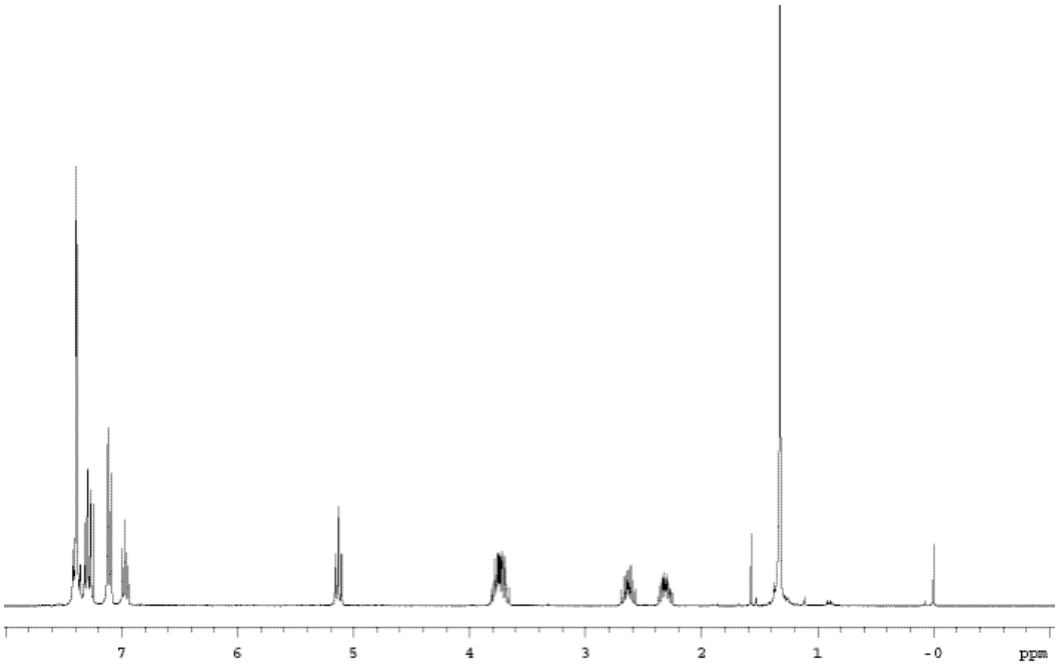
^{13}C NMR spectrum of **36b**



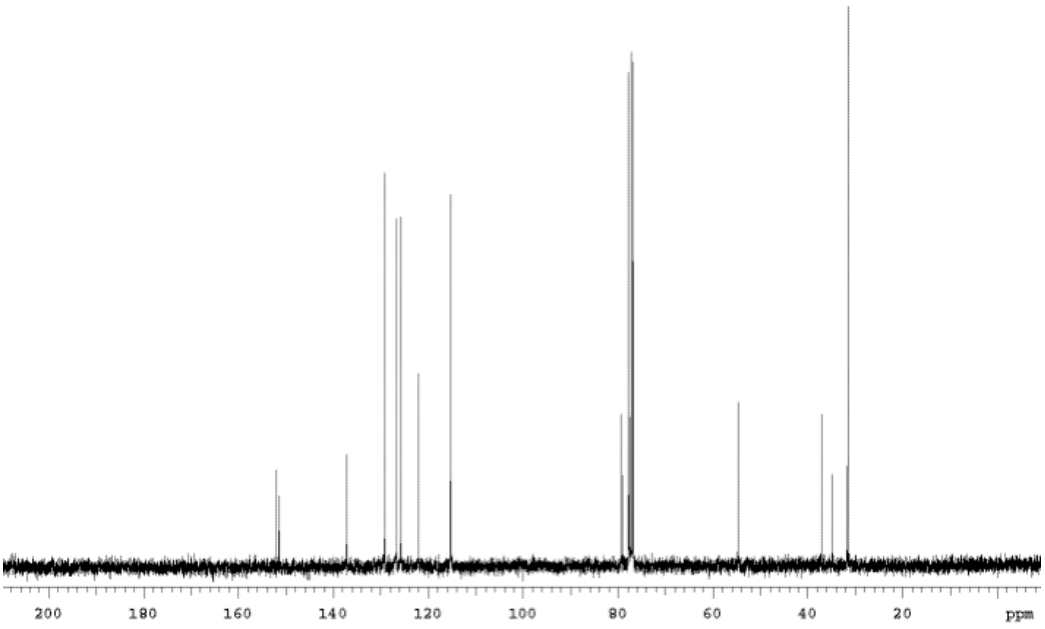
^{1}H NMR spectrum of **36c**



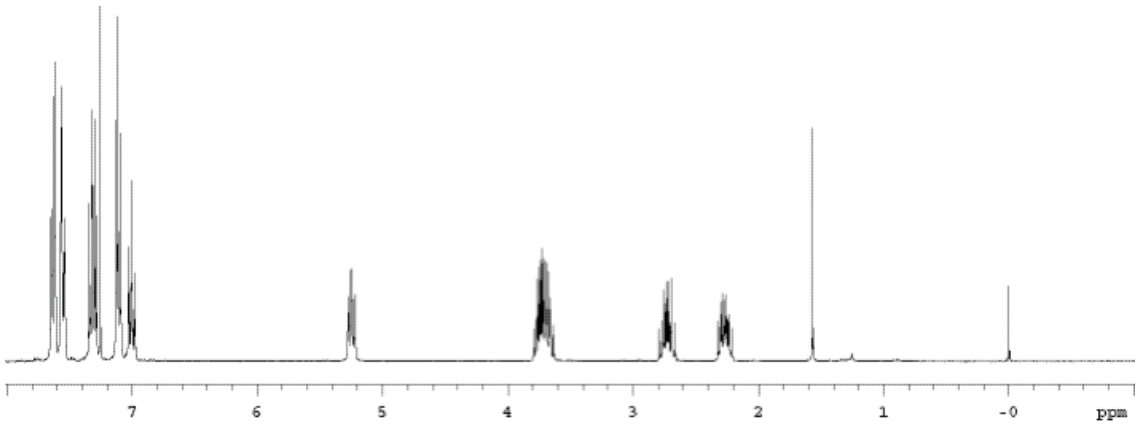
^{13}C NMR spectrum of **36c**



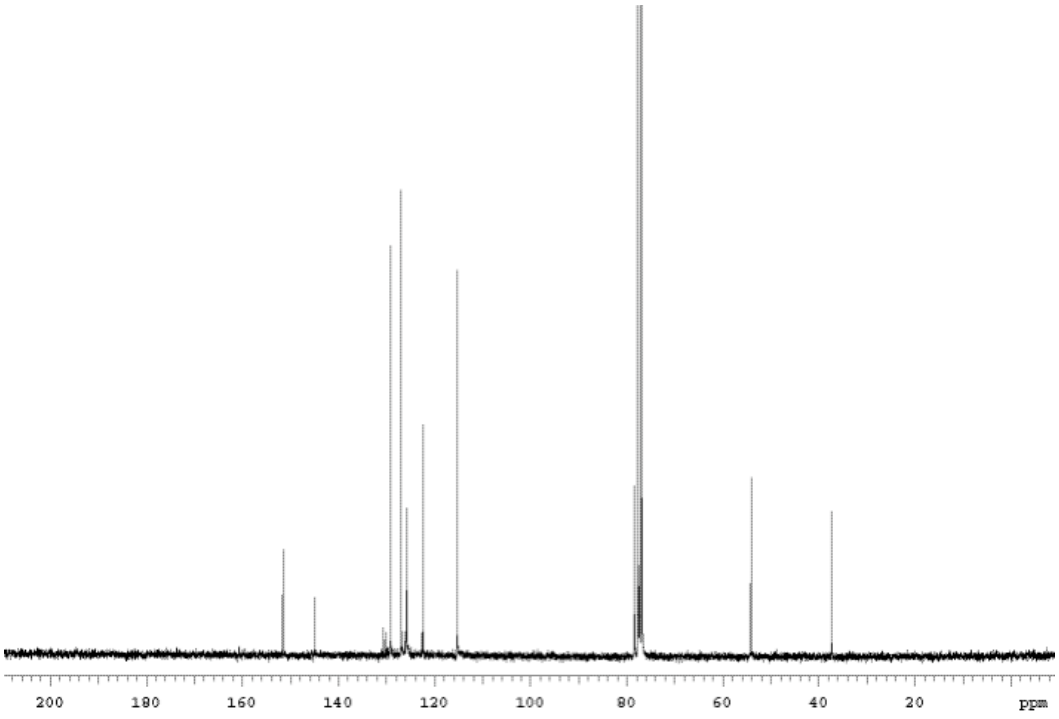
^{1}H NMR spectrum of **36d**



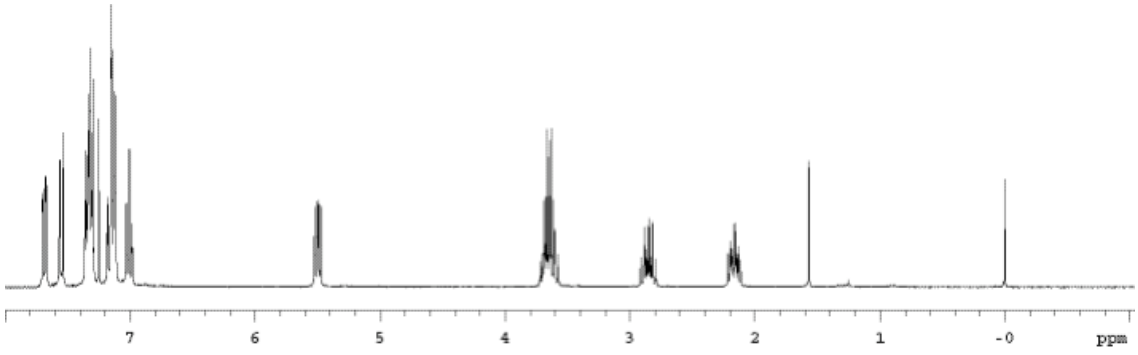
^{13}C NMR spectrum of **36d**



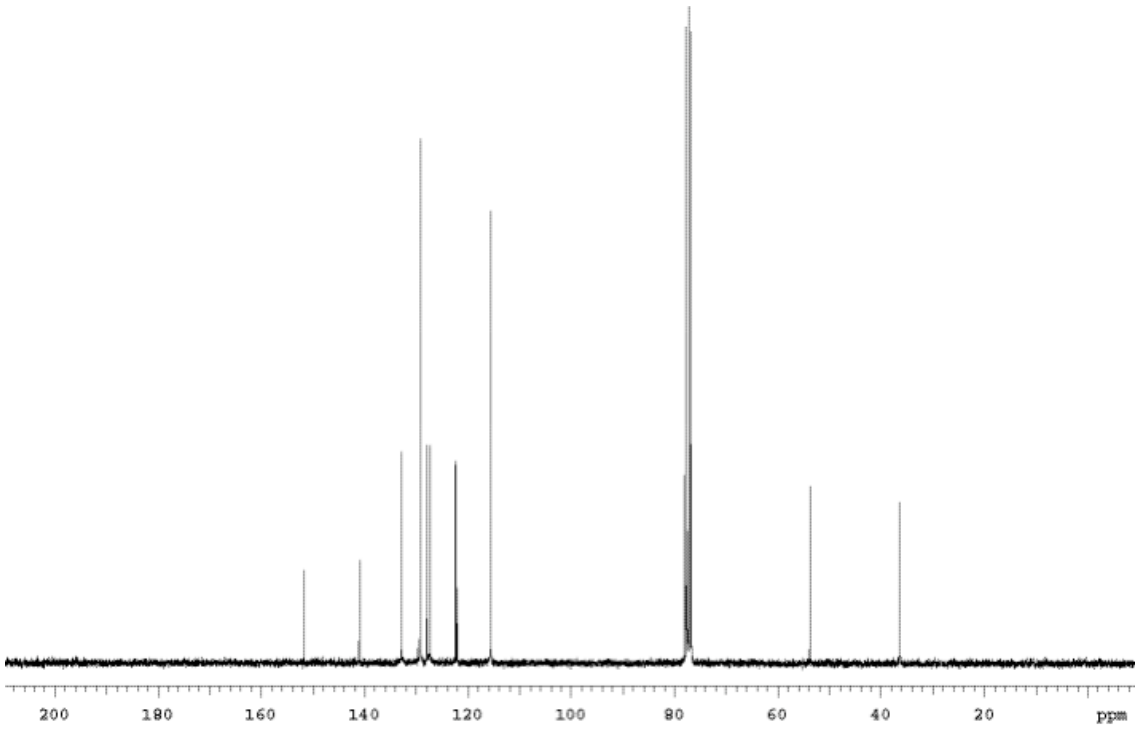
^{1}H NMR spectrum of **36e**



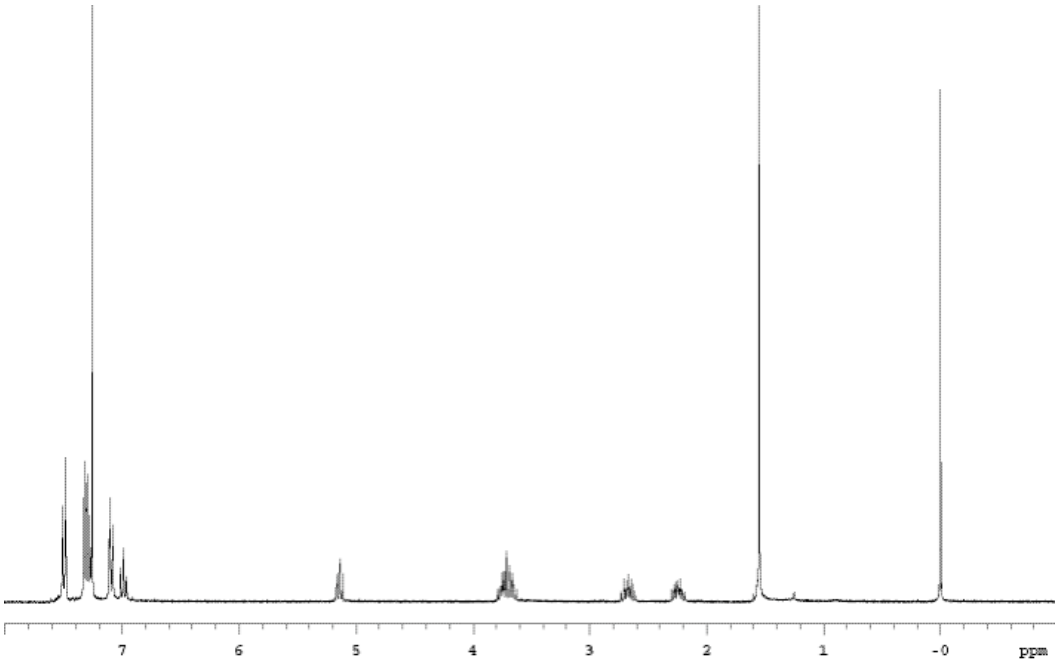
^{13}C NMR spectrum of **36e**



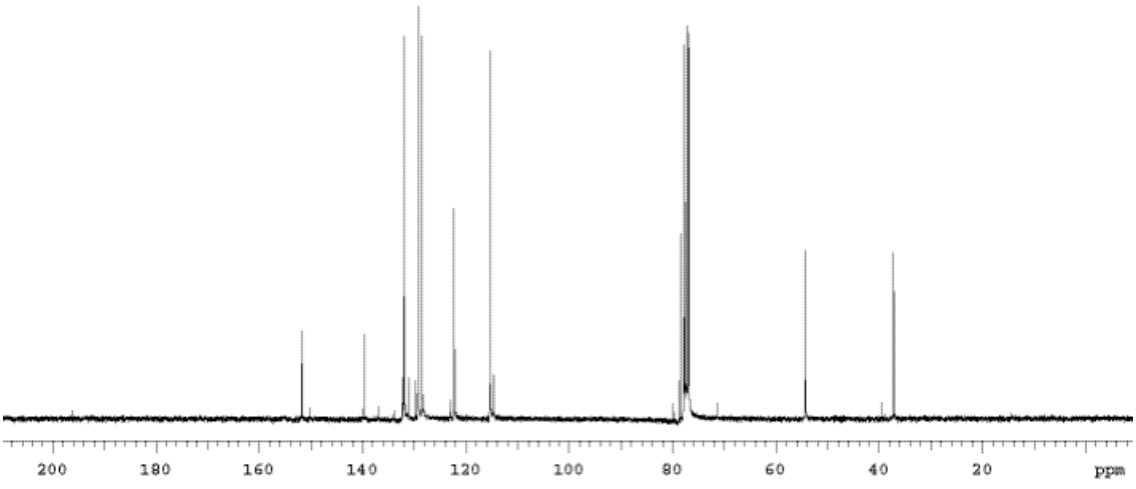
^{1}H NMR spectrum of **36f**



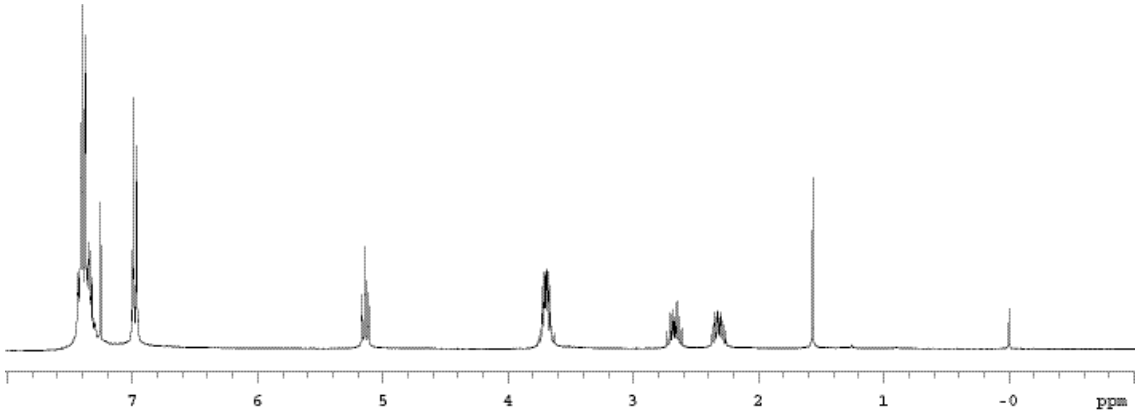
^{13}C NMR spectrum of **36f**



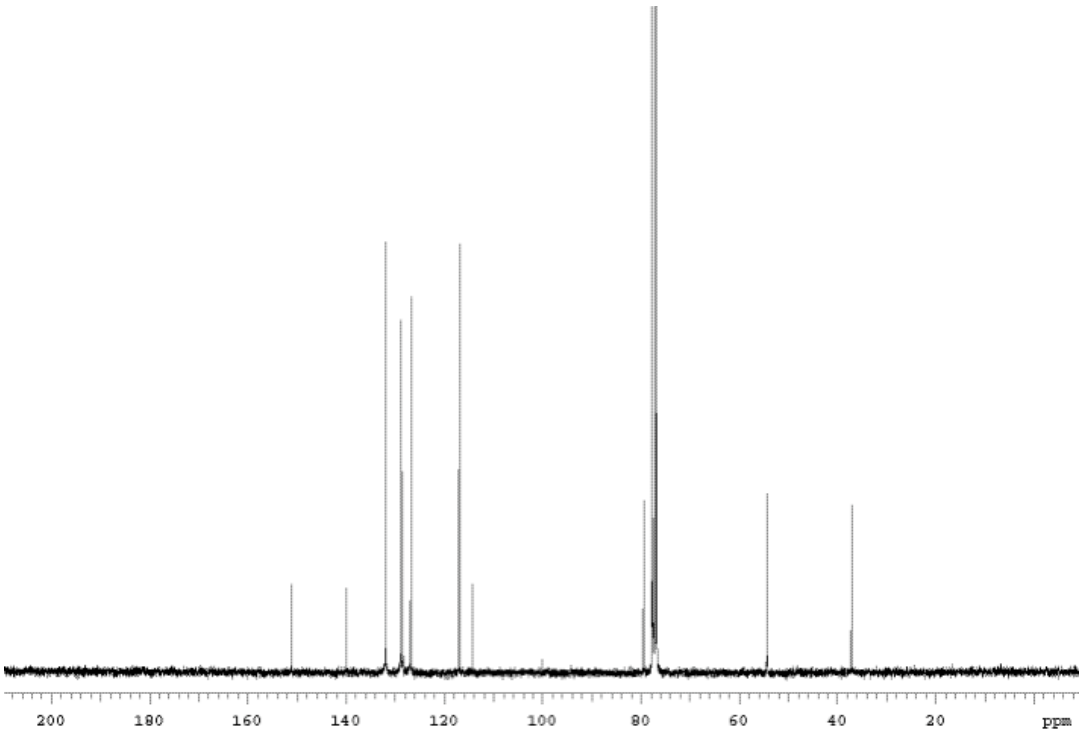
^{1}H NMR spectrum of **36g**



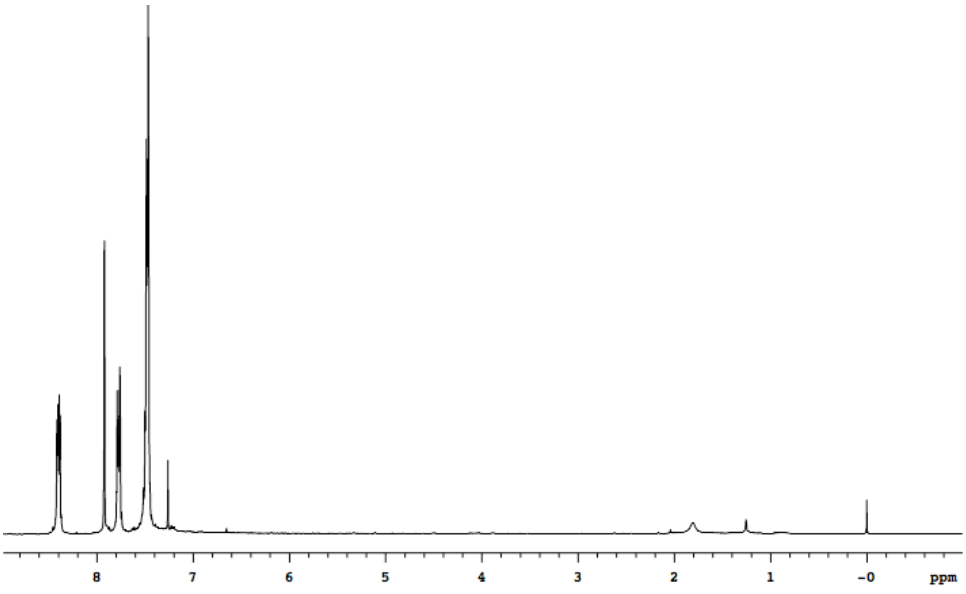
^{13}C NMR spectrum of **36g**



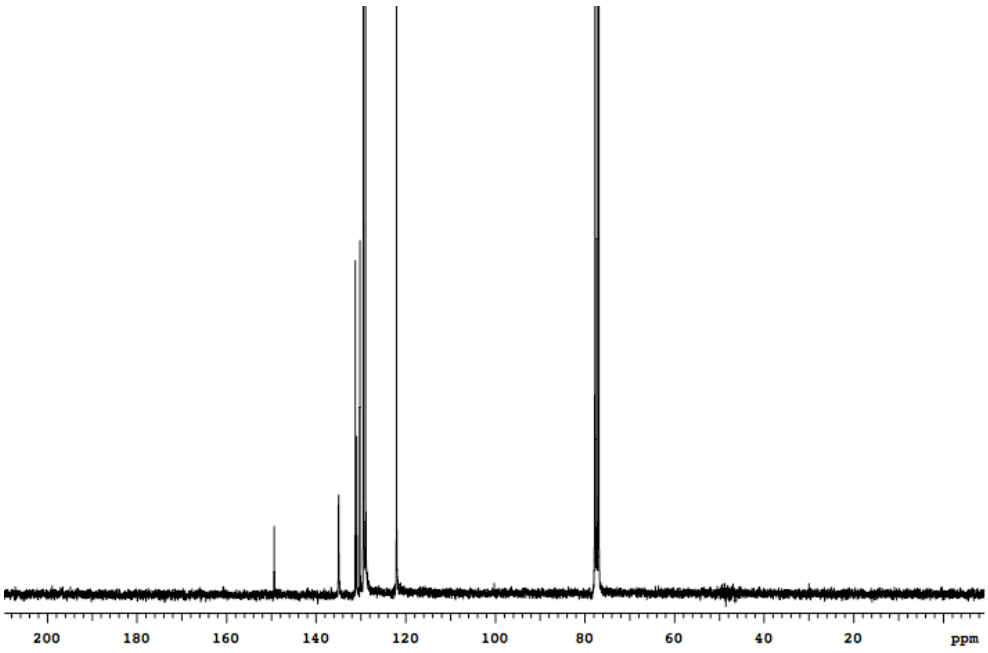
^{1}H NMR spectrum of **36h**



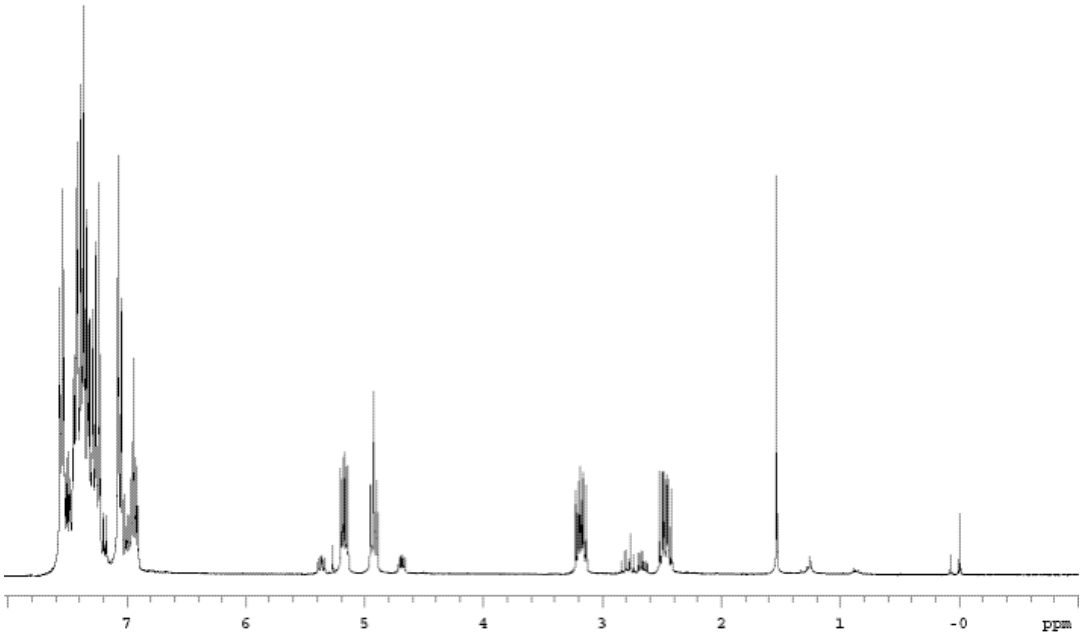
^{13}C NMR spectrum of **36h**



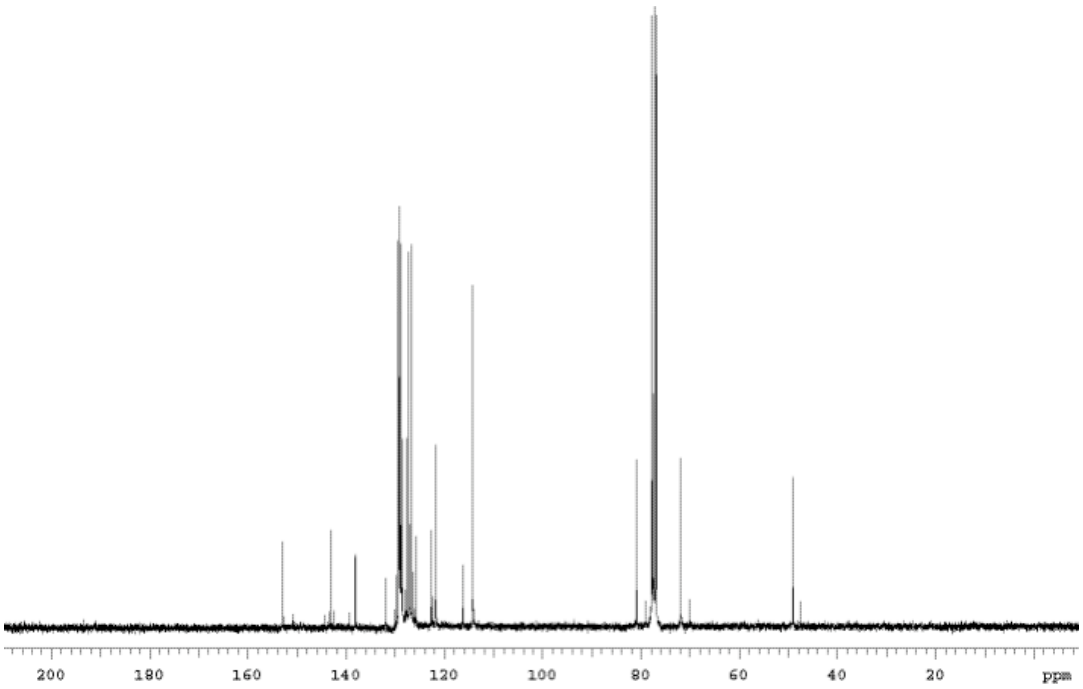
^{1}H NMR spectrum of **37**



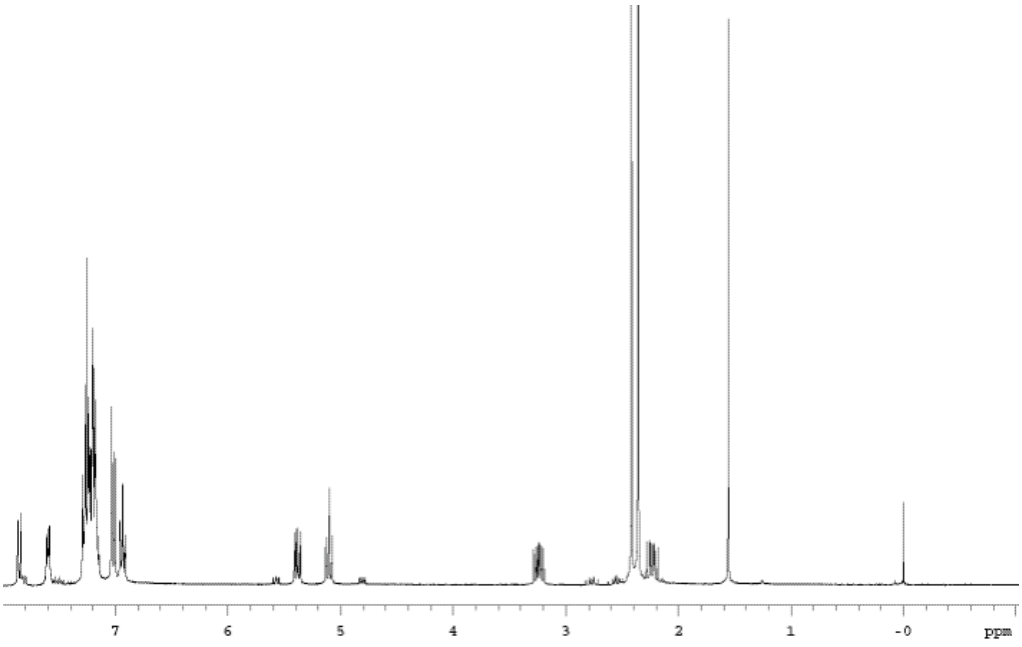
^{13}C NMR spectrum of **37**



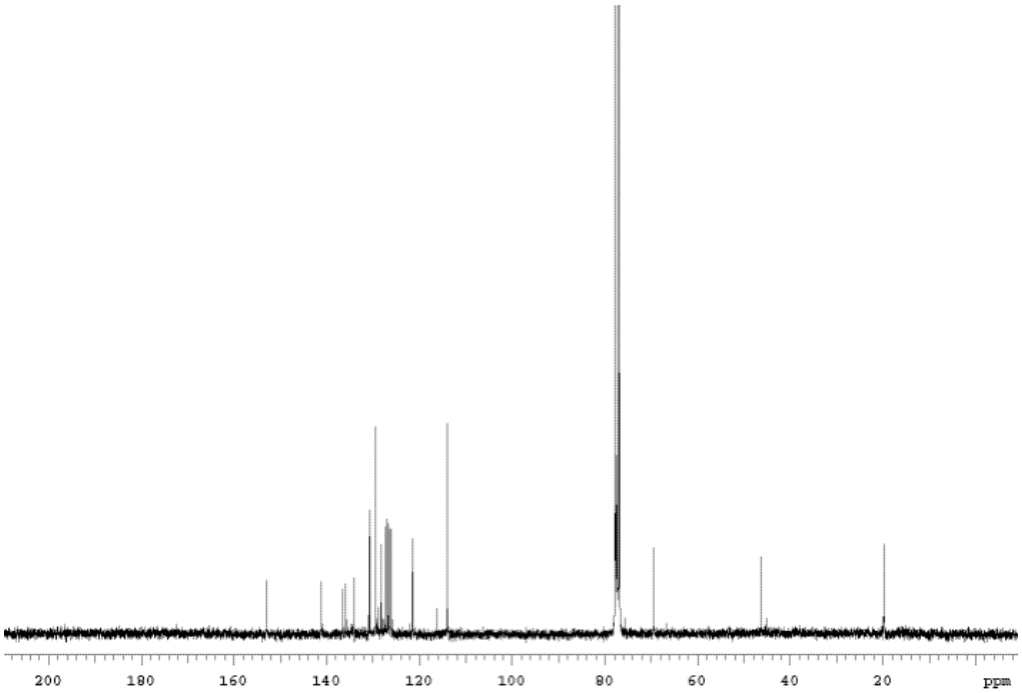
^{1}H NMR spectrum of **46**



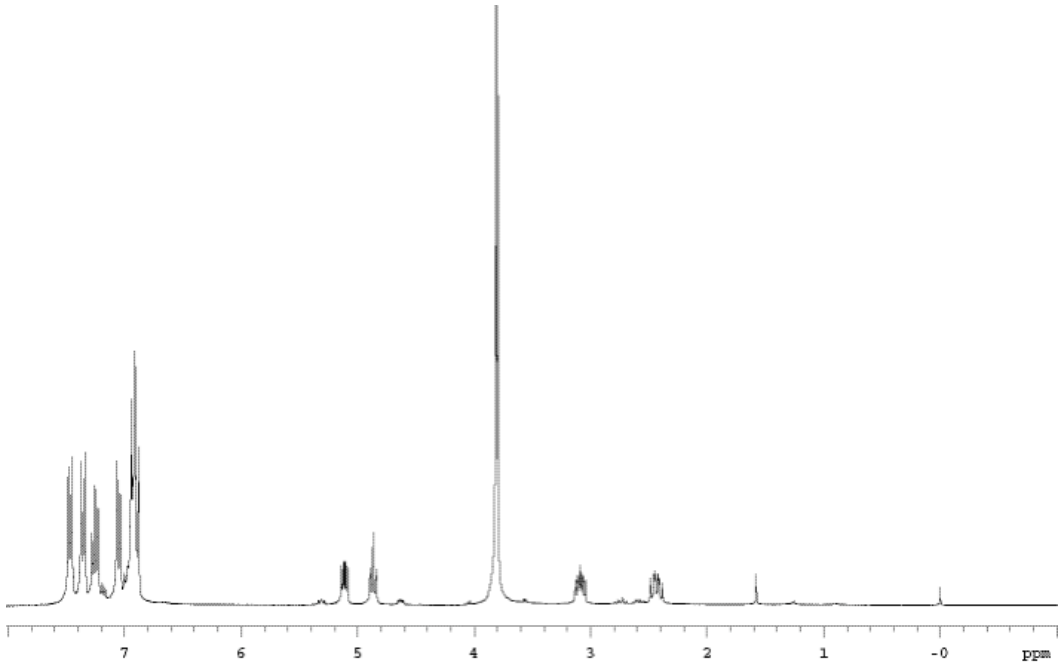
^{13}C NMR spectrum of **46**



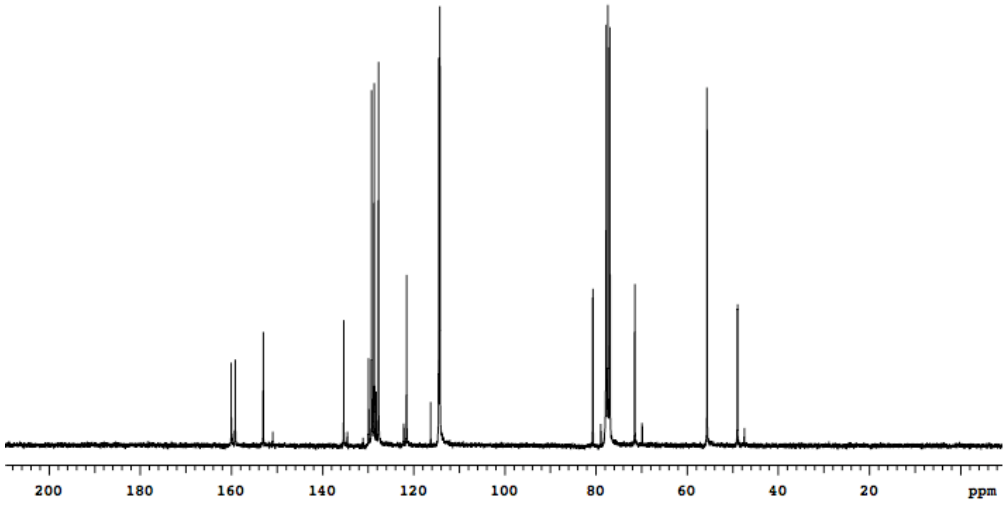
^{1}H NMR spectrum of **46a**



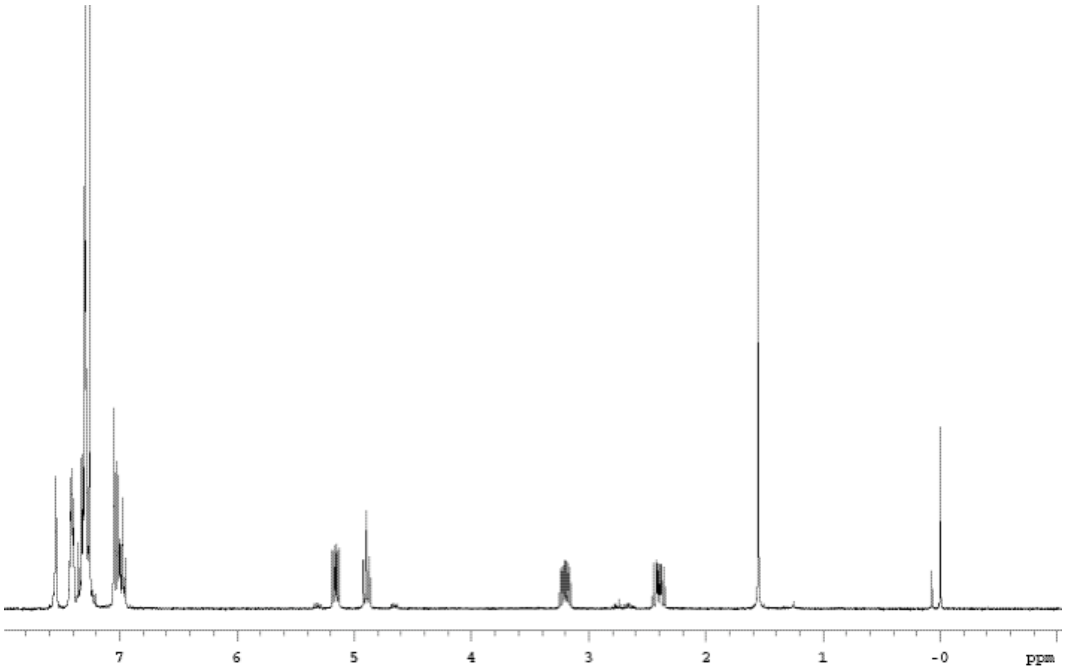
^{13}C NMR spectrum of **46a**



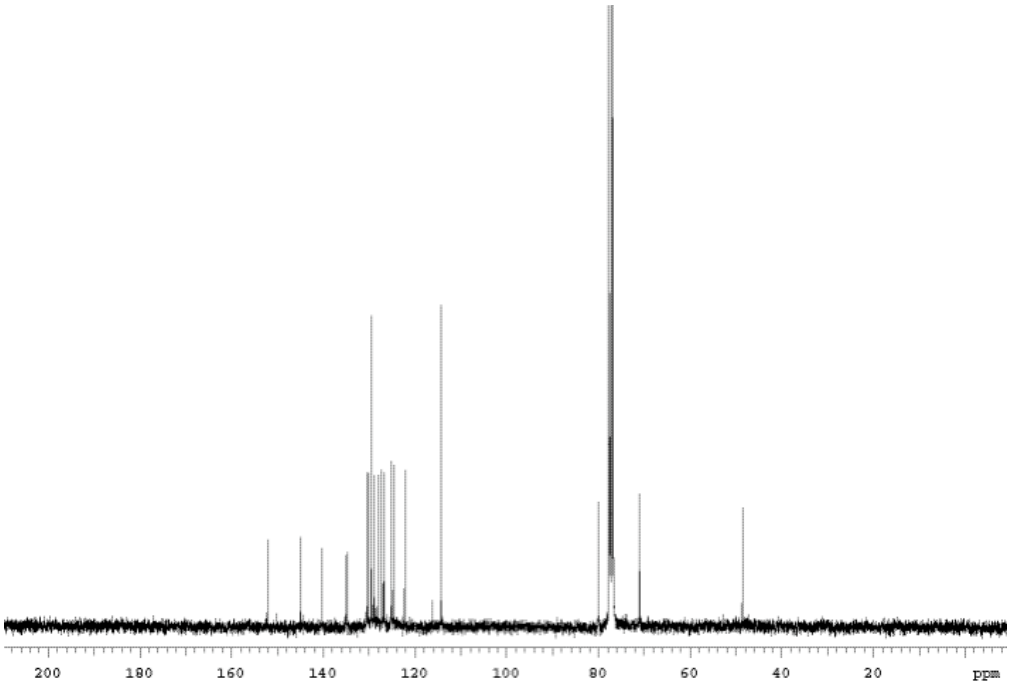
^{1}H NMR spectrum of **46b**



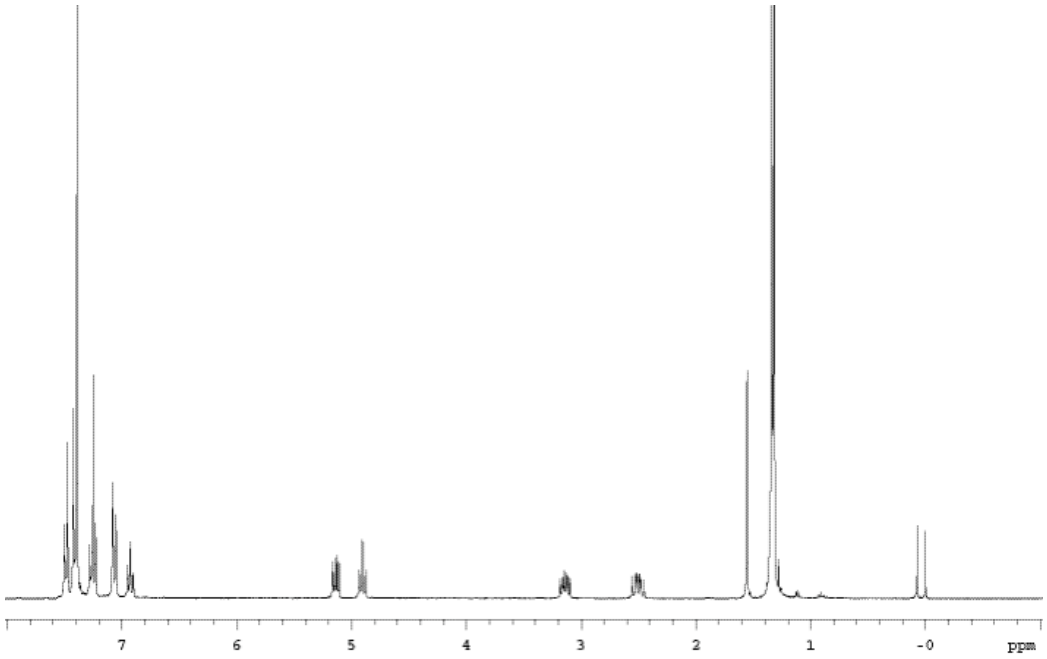
^{13}C NMR spectrum of **46b**



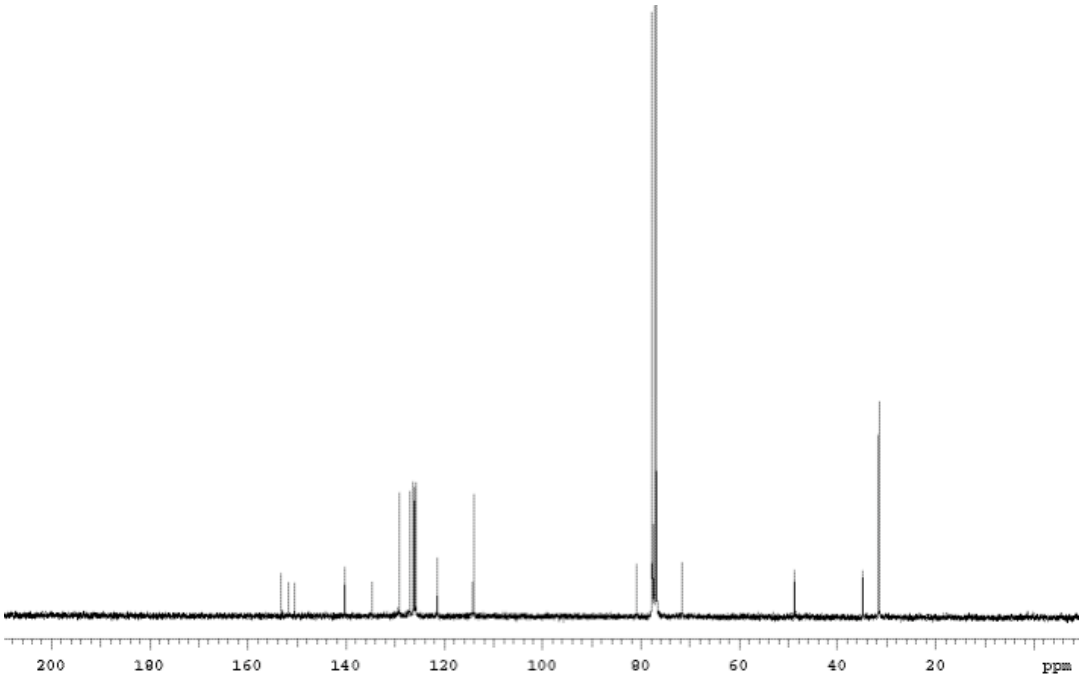
^{1}H NMR spectrum of **46c**



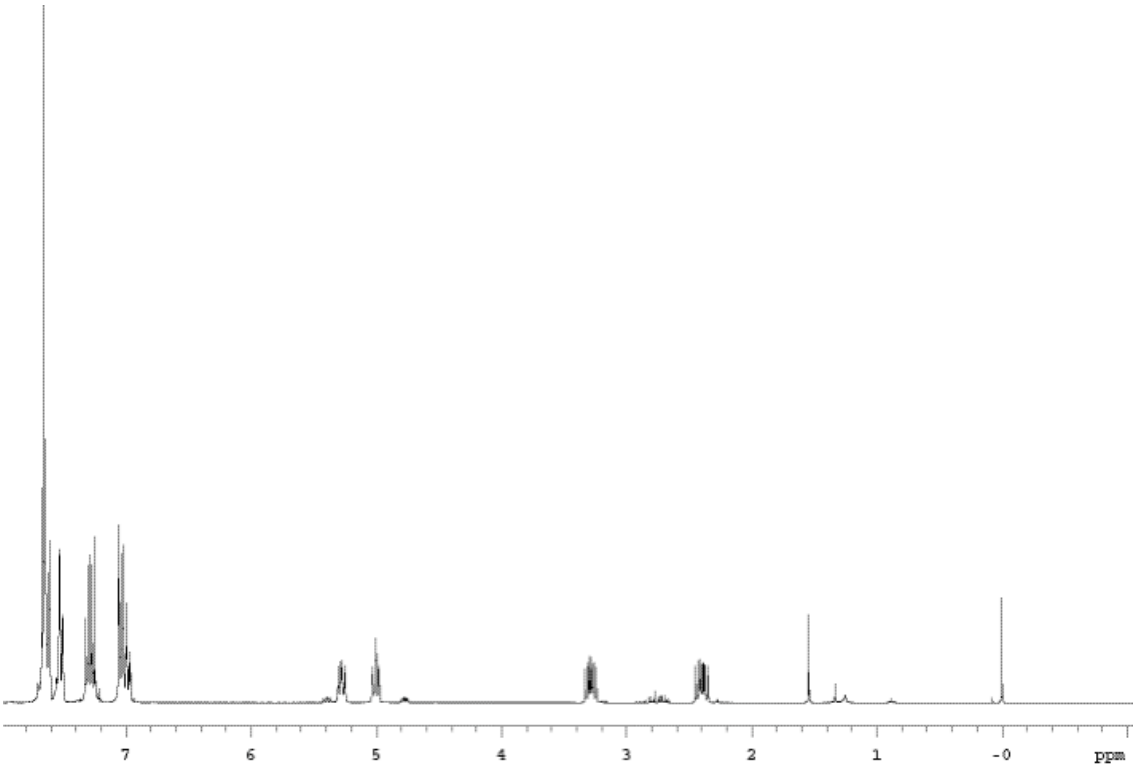
^{13}C NMR spectrum of **46c**



^{1}H NMR spectrum of **46d**



^{13}C NMR spectrum of **46d**



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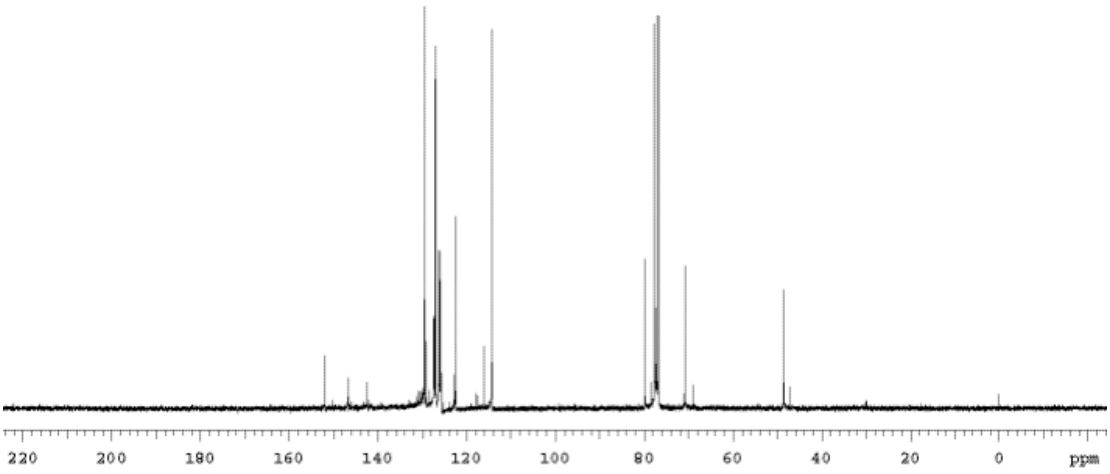
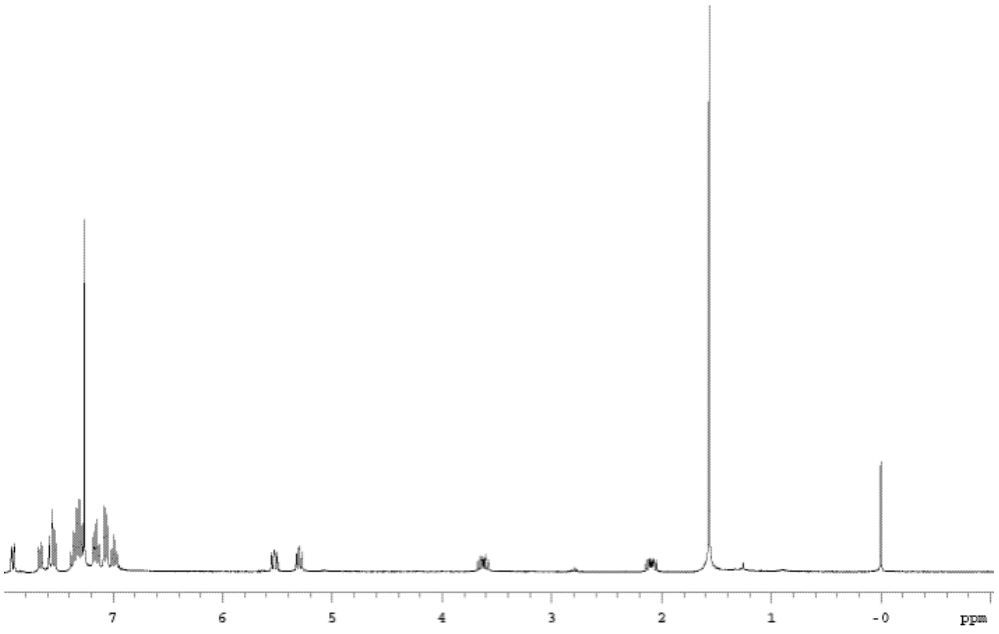


^{13}C NMR spectrum of **46e**



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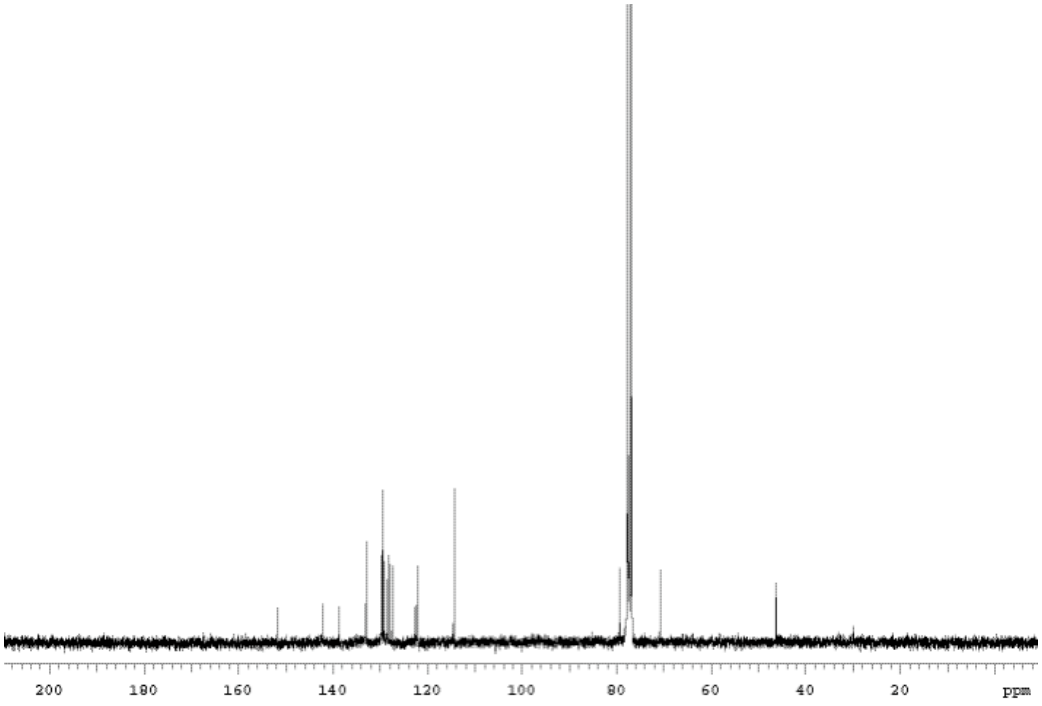

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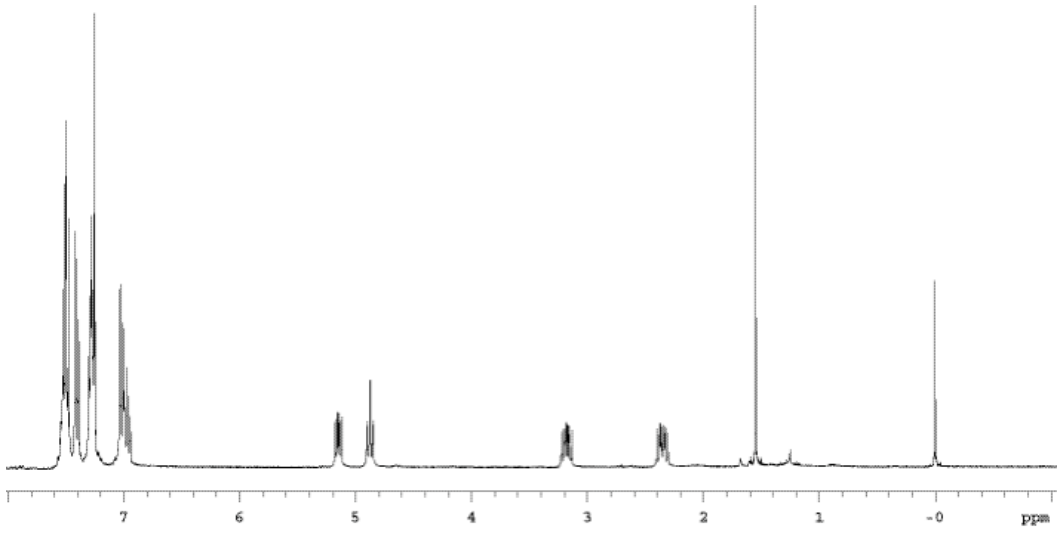
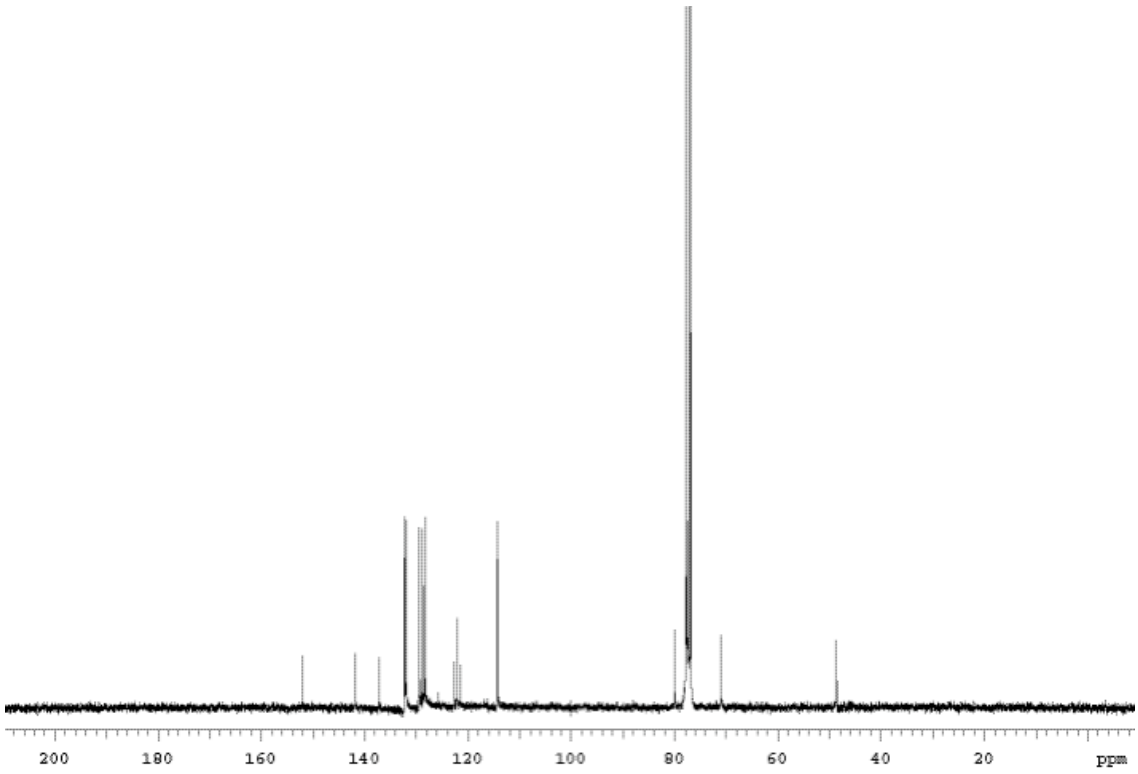
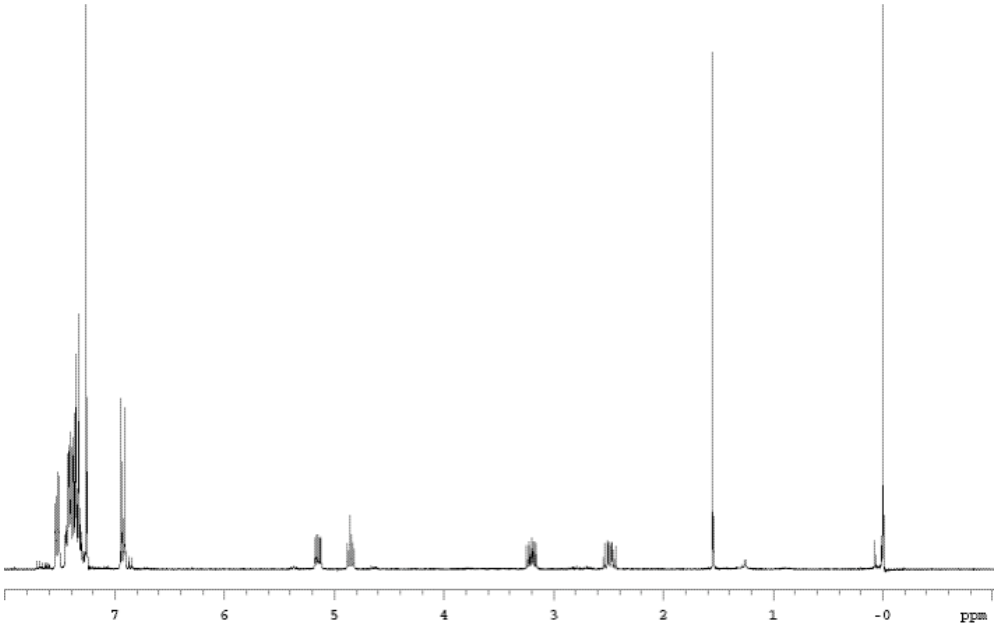


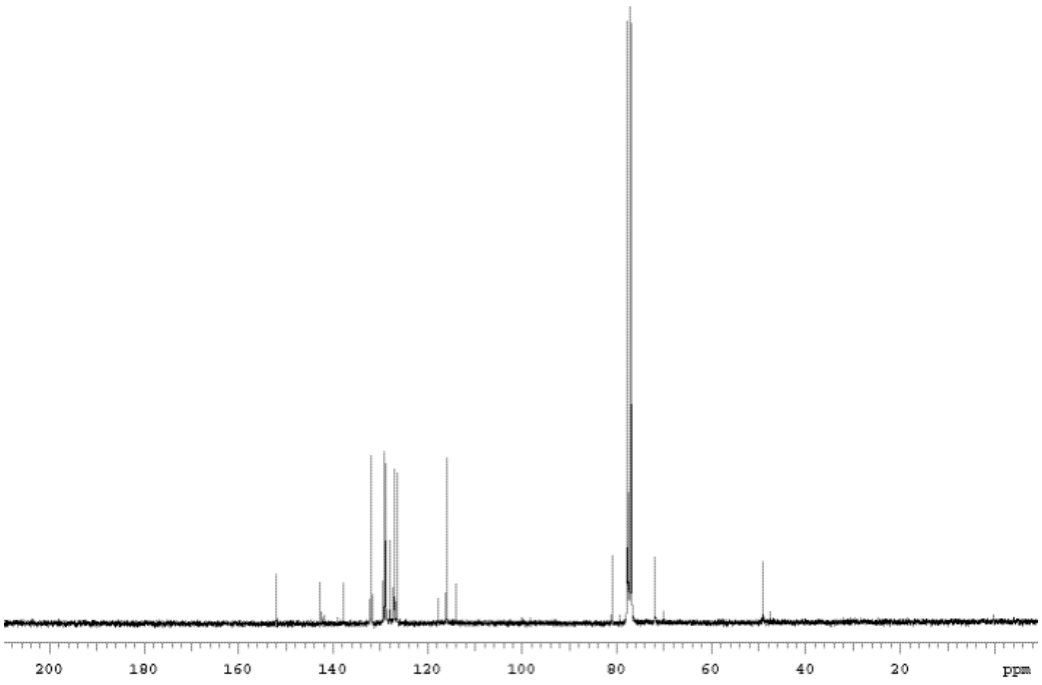
^{1}H NMR spectrum of **46g**



^{13}C NMR spectrum of **46g**



^{1}H NMR spectrum of **46h**



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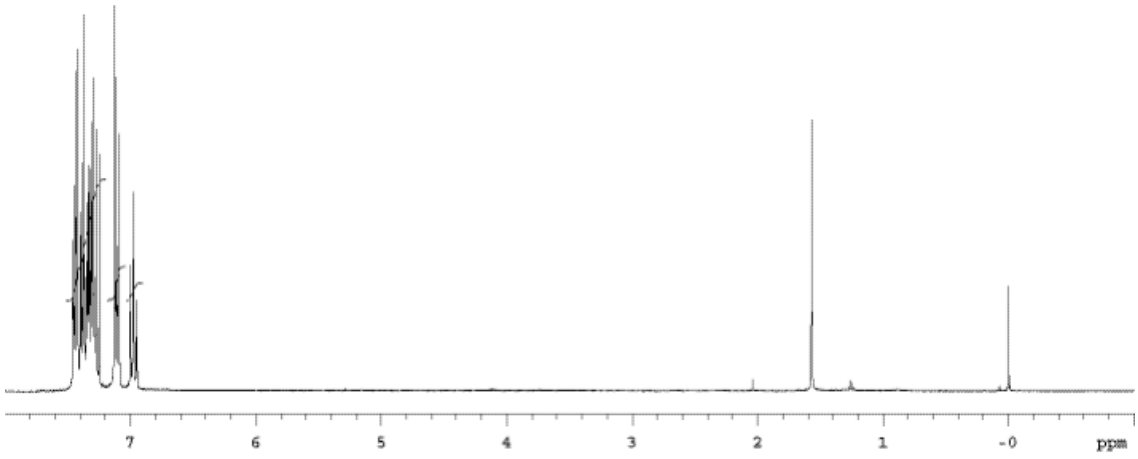
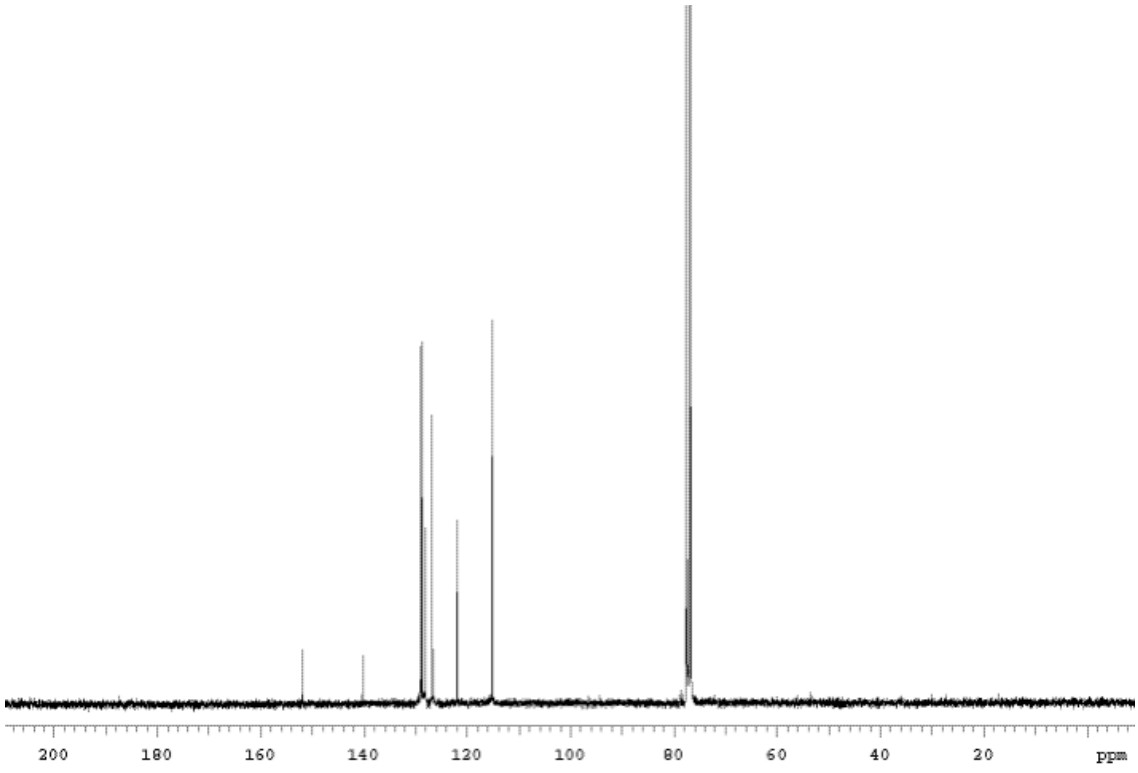
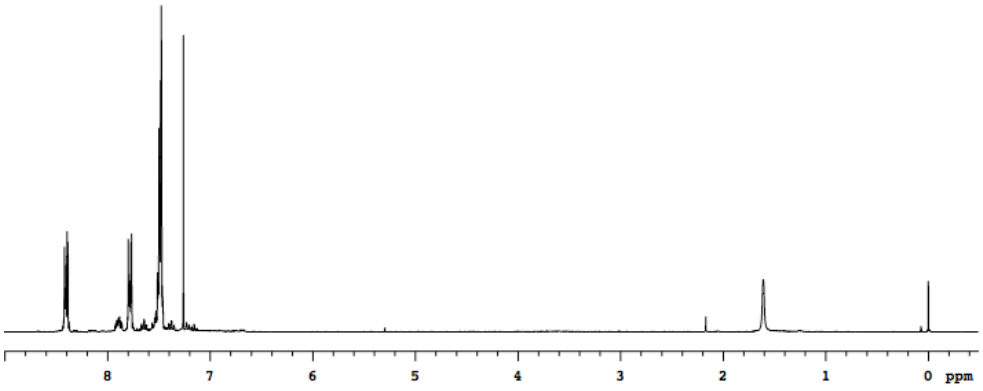


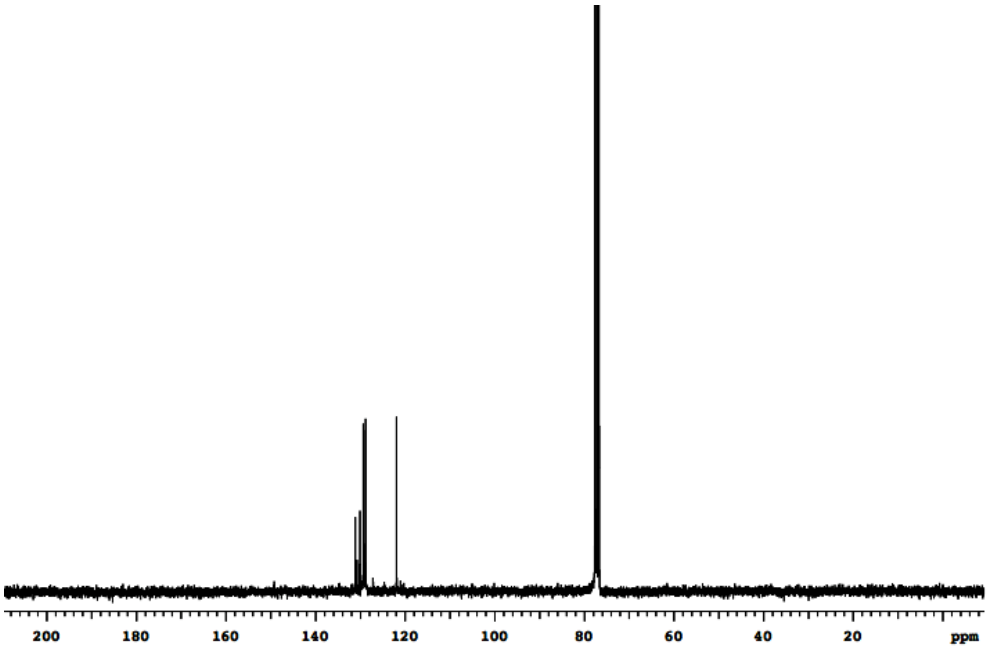
^{1}H NMR spectrum of **58**



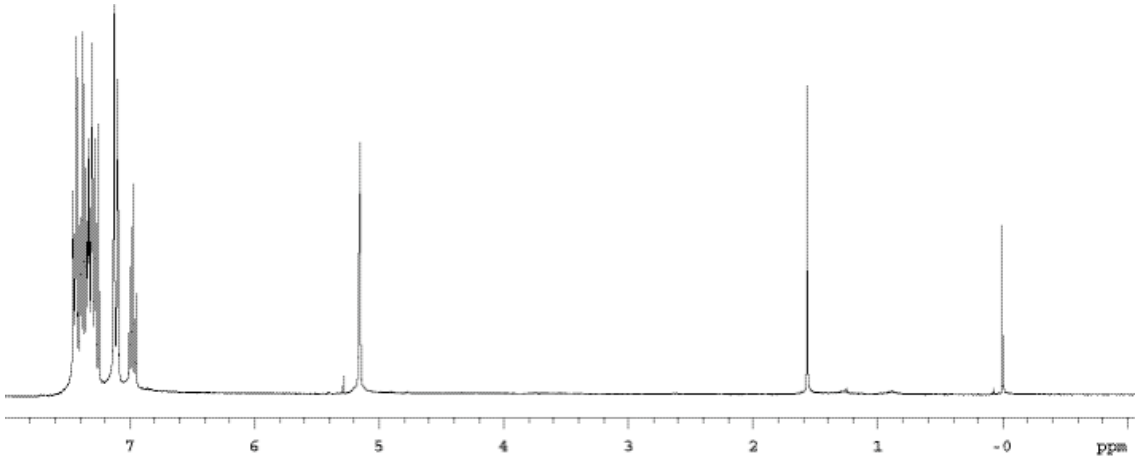
^{13}C NMR spectrum of **58**



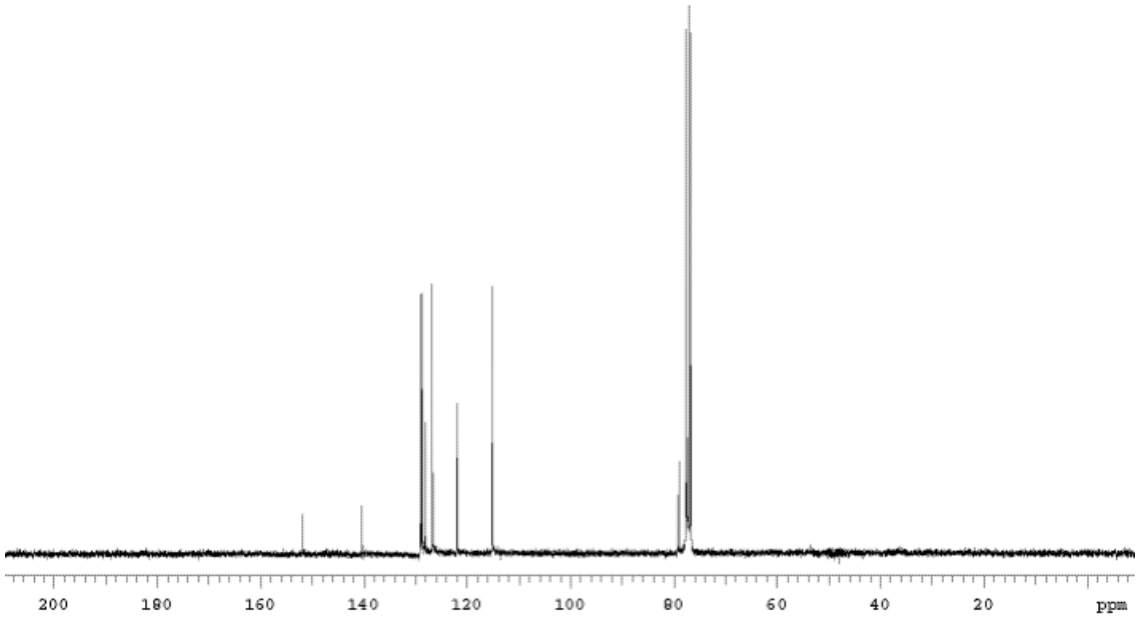
^{1}H NMR spectrum of **59**



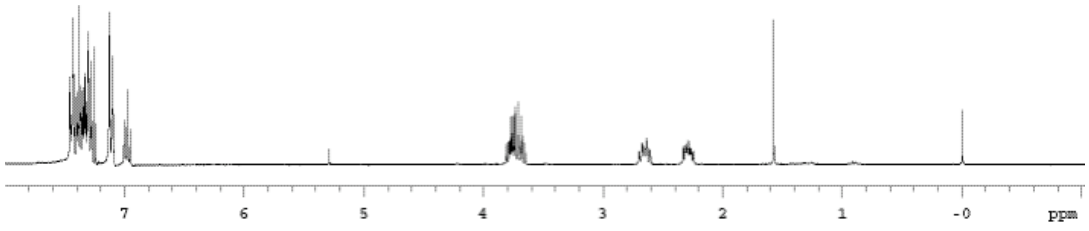
^{13}C NMR spectrum of **59**



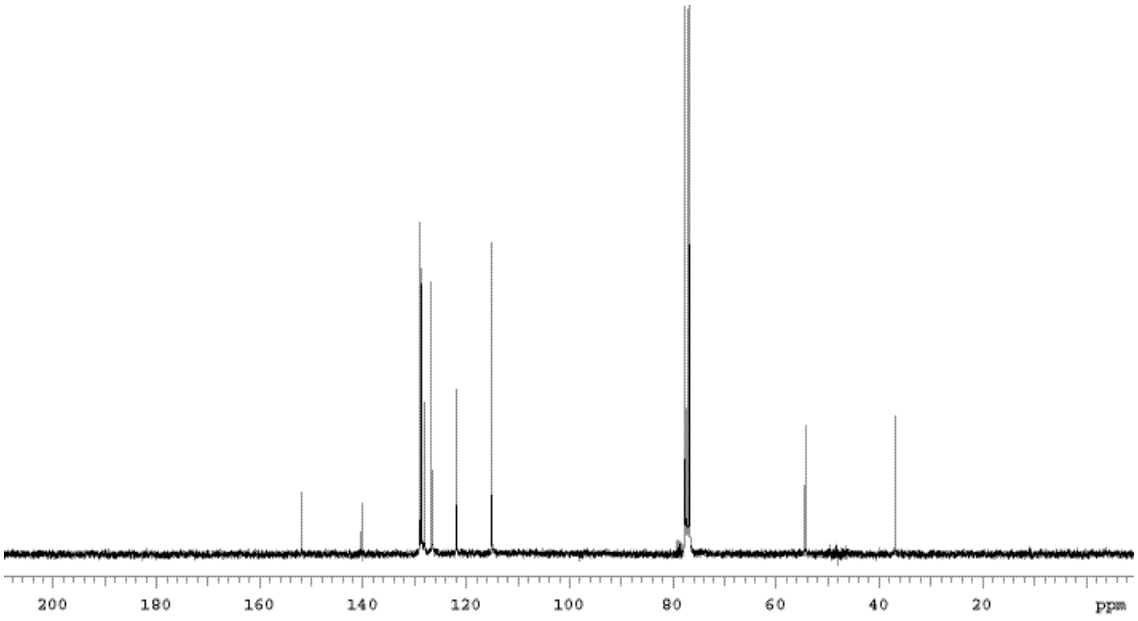
^{1}H NMR spectrum of **61**



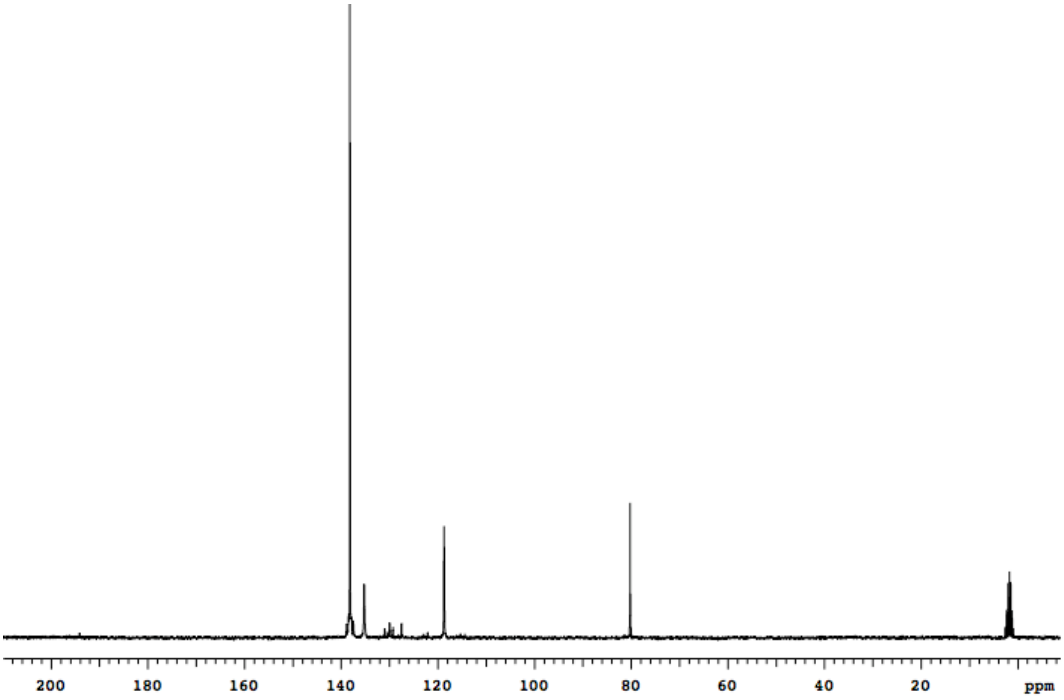
^{13}C NMR spectrum of **61**



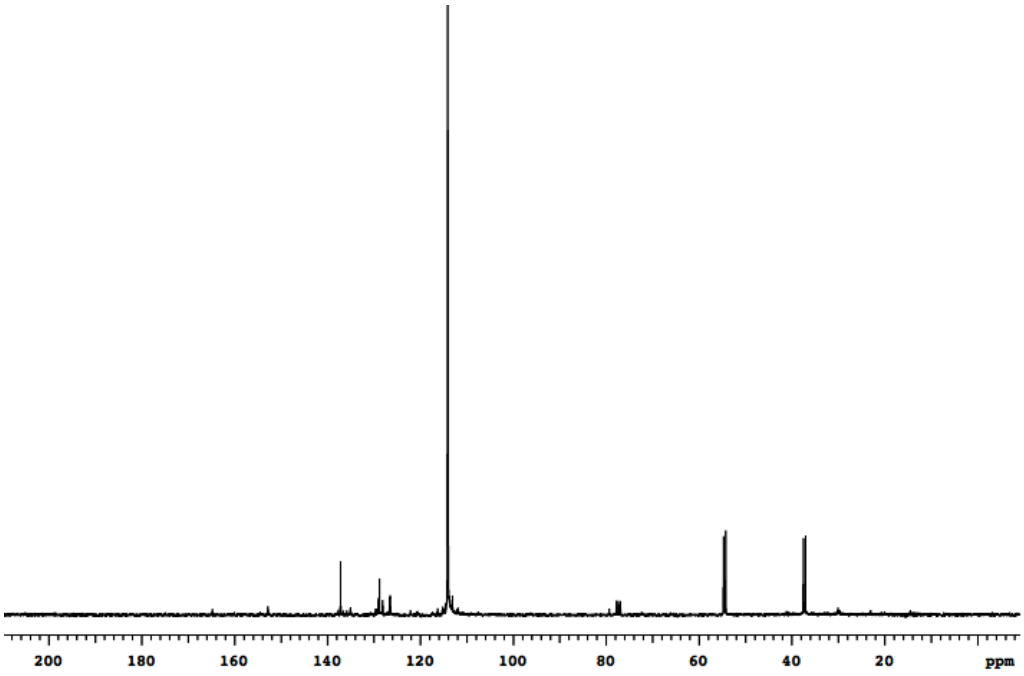
^{1}H NMR spectrum of **63**



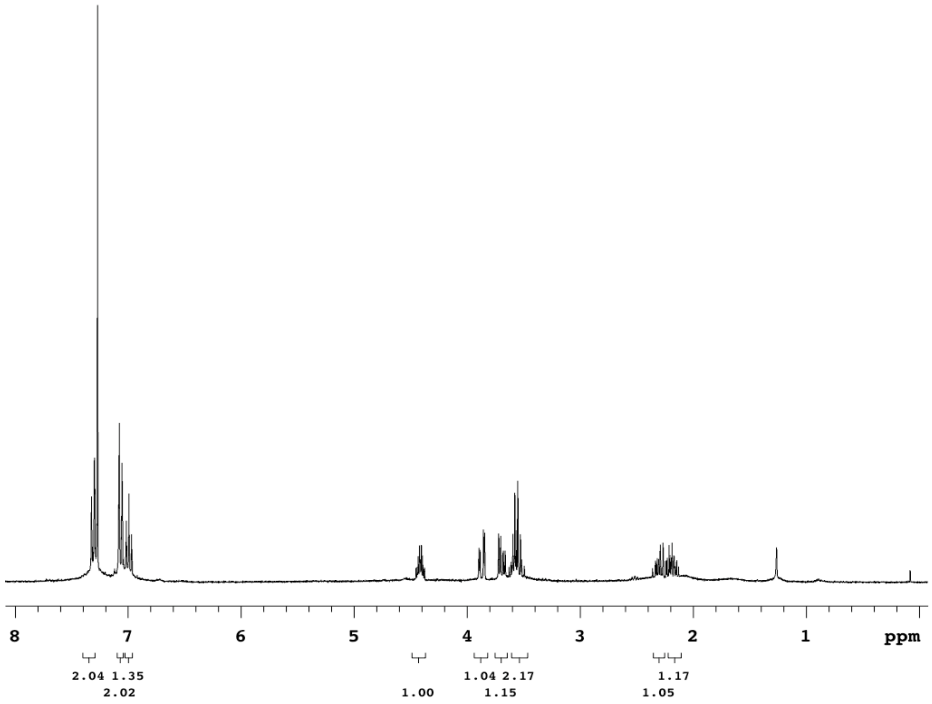
^{13}C NMR spectrum of **63**



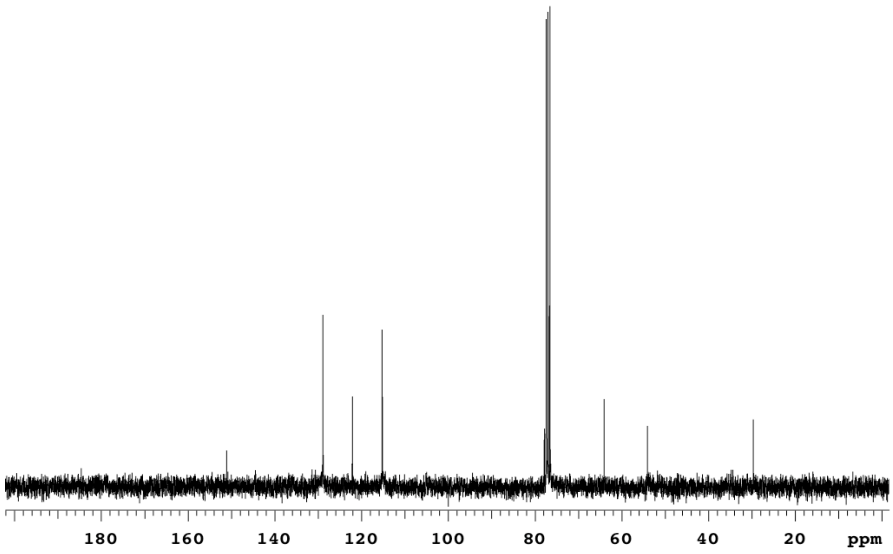
^{13}C NMR spectrum of **65**



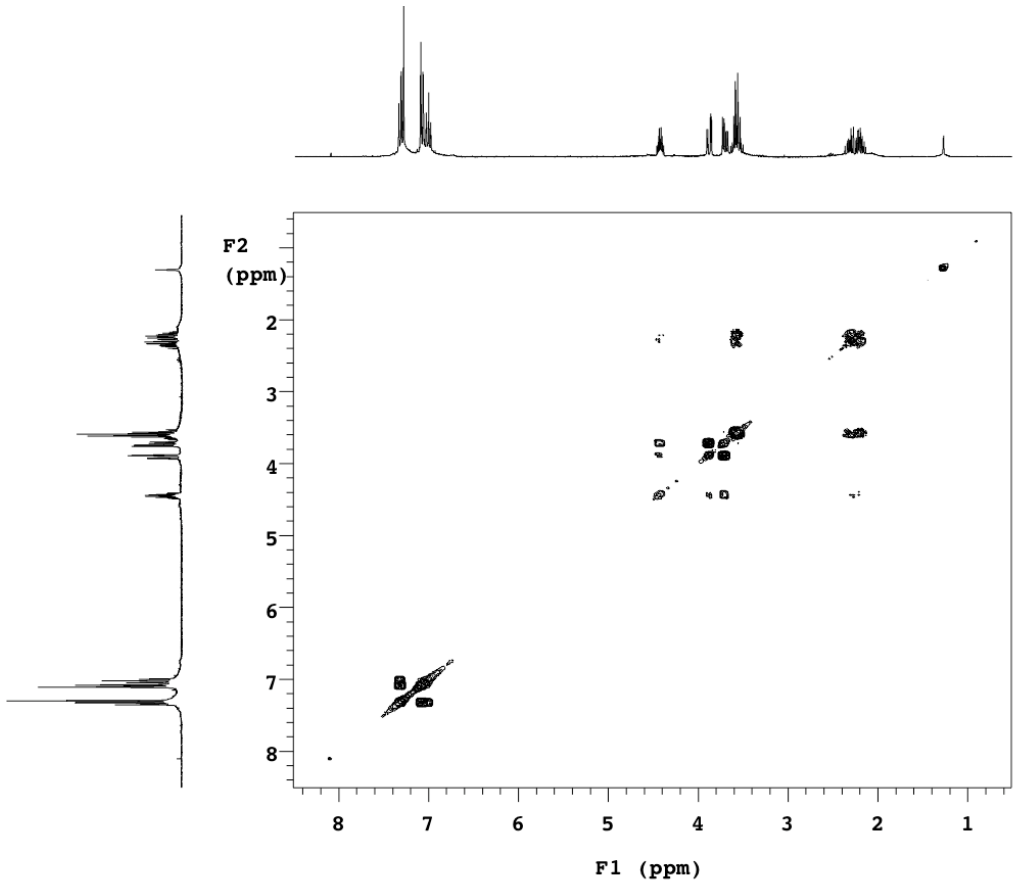
^{13}C NMR spectrum of **68**



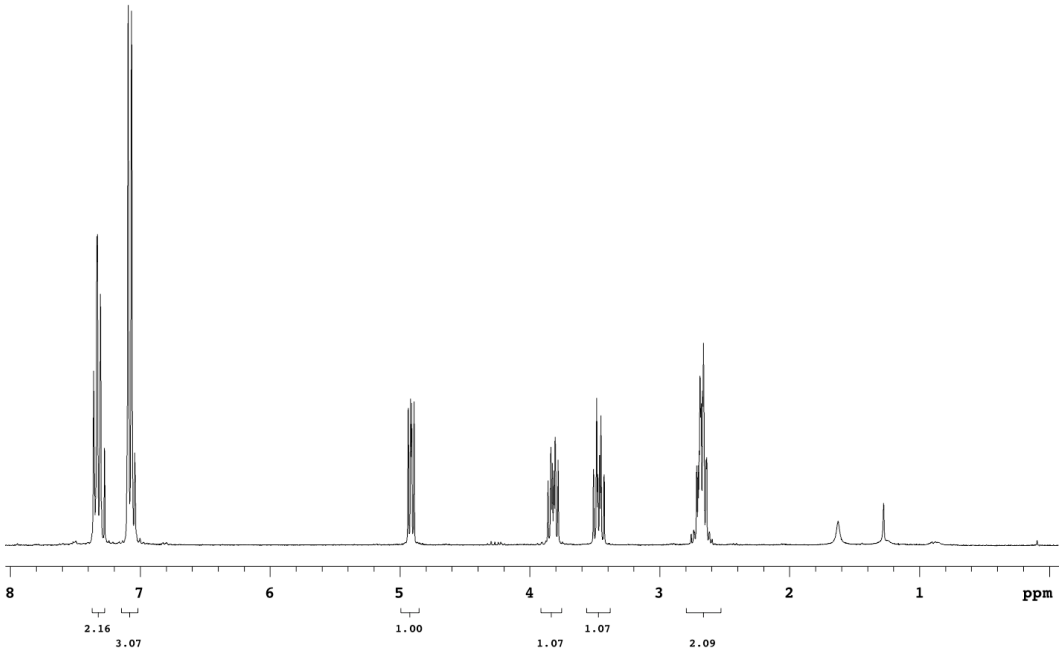
^{1}H NMR spectrum of **79**



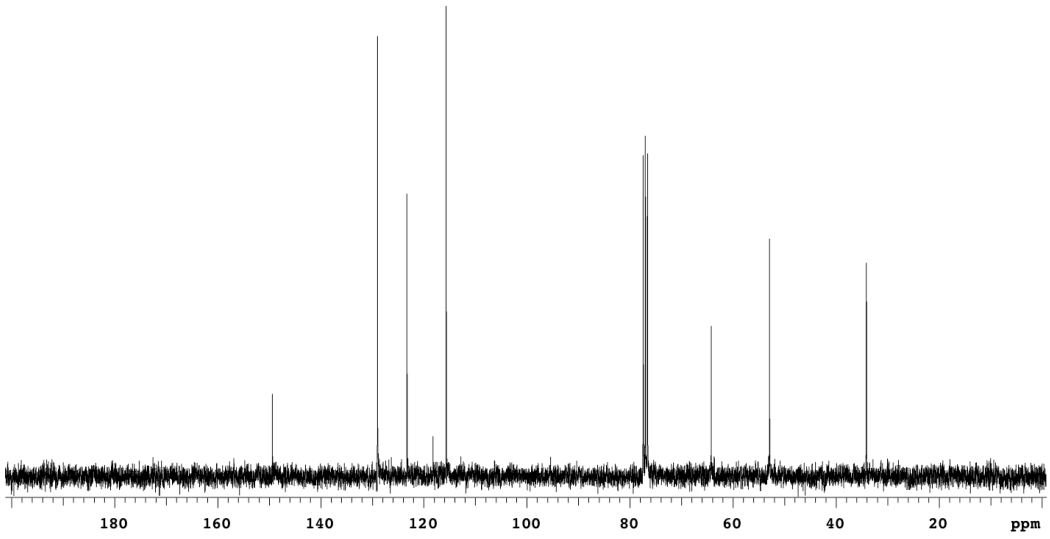
^{13}C NMR spectrum of **79**



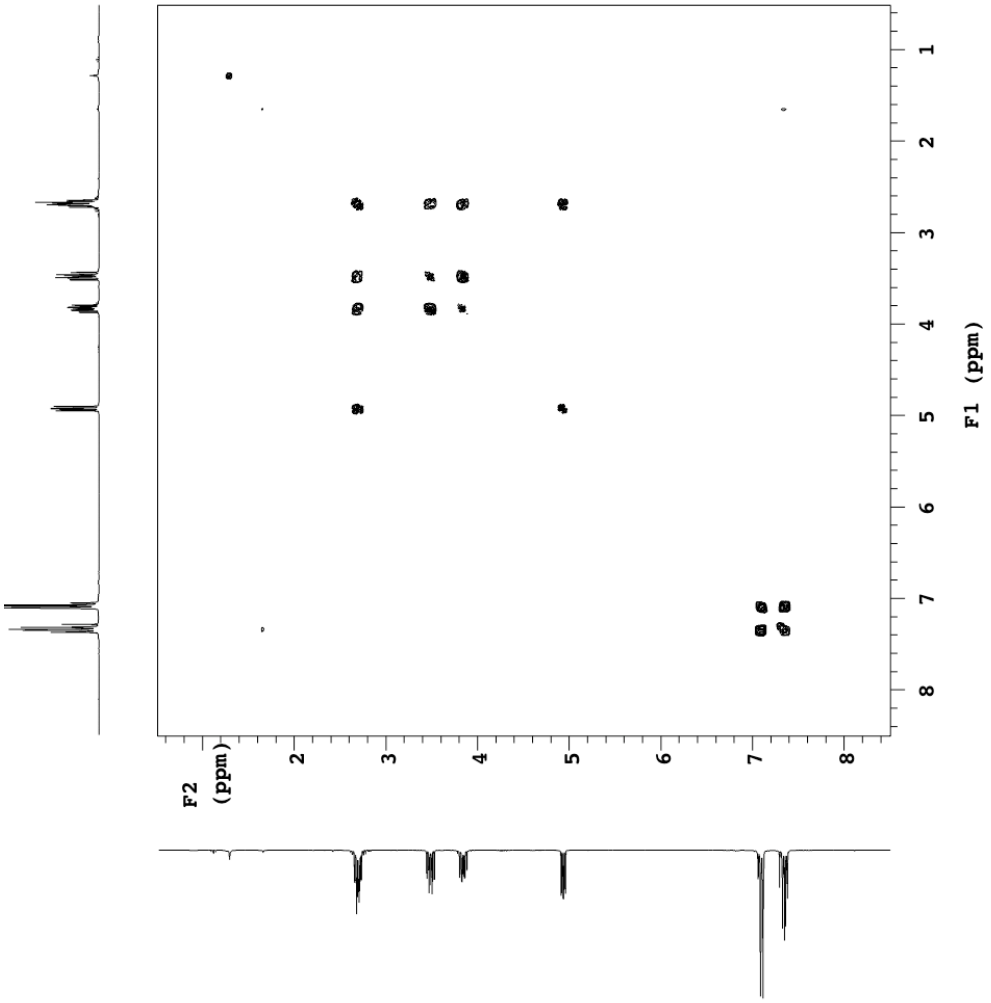
2D ^{1}H NMR spectrum of **79**



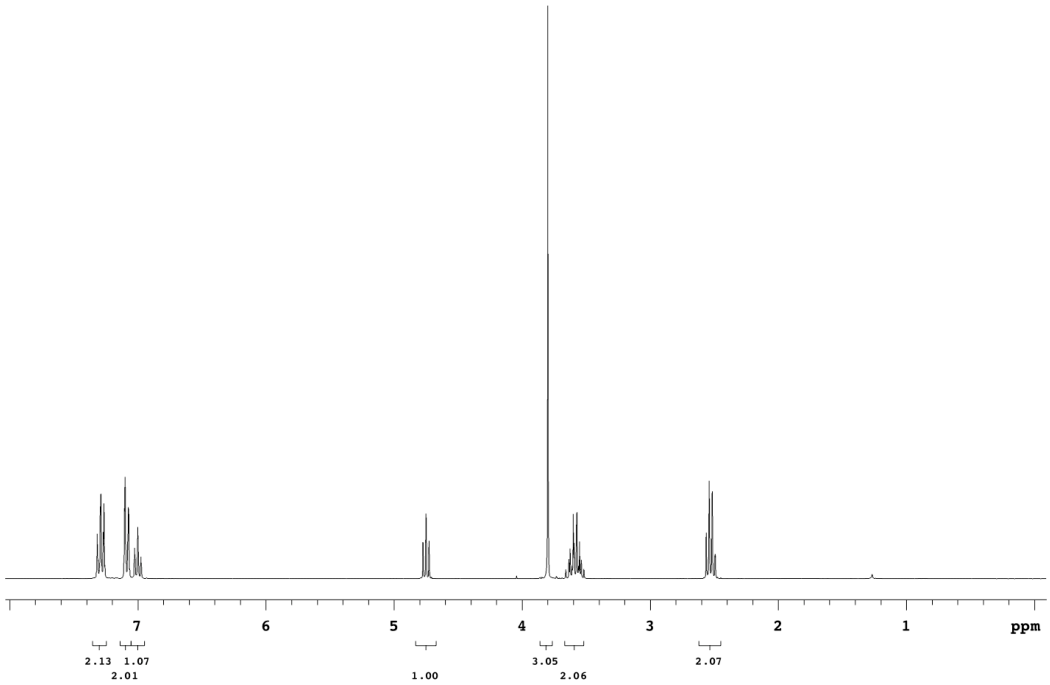
^{1}H NMR spectrum of **79a**



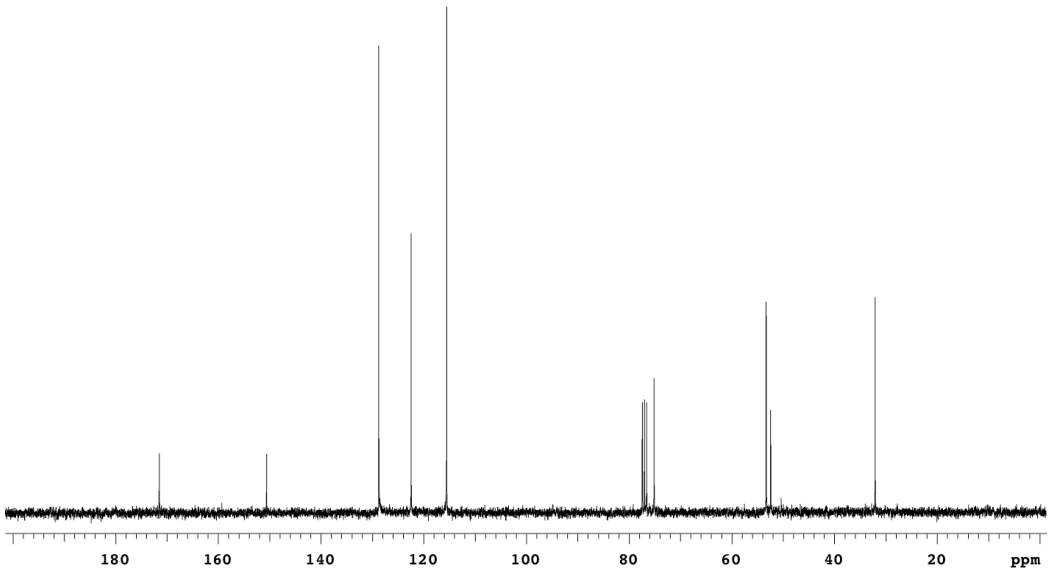
^{13}C NMR spectrum of **79a**



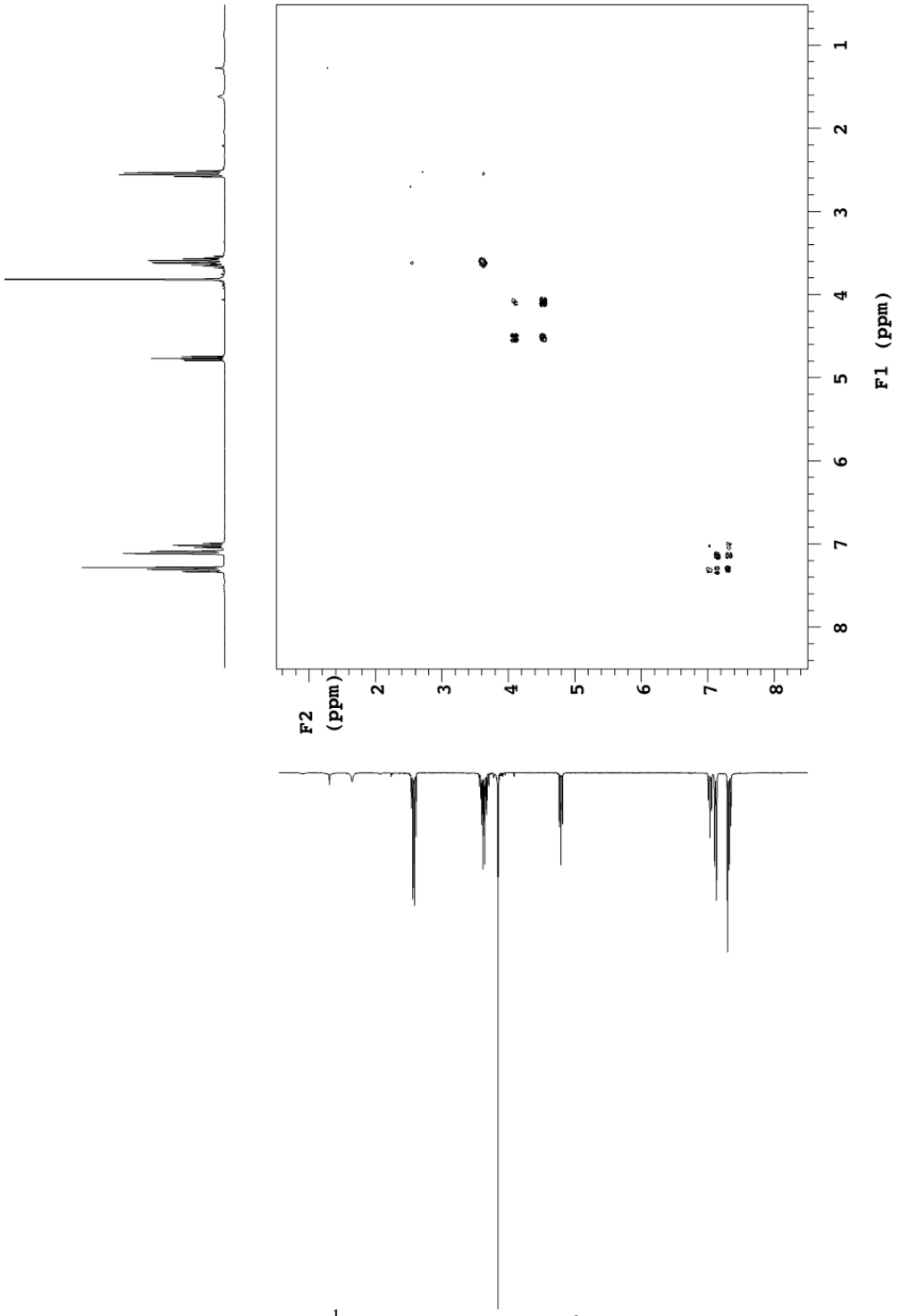
2D ^{1}H NMR spectrum of **79a**



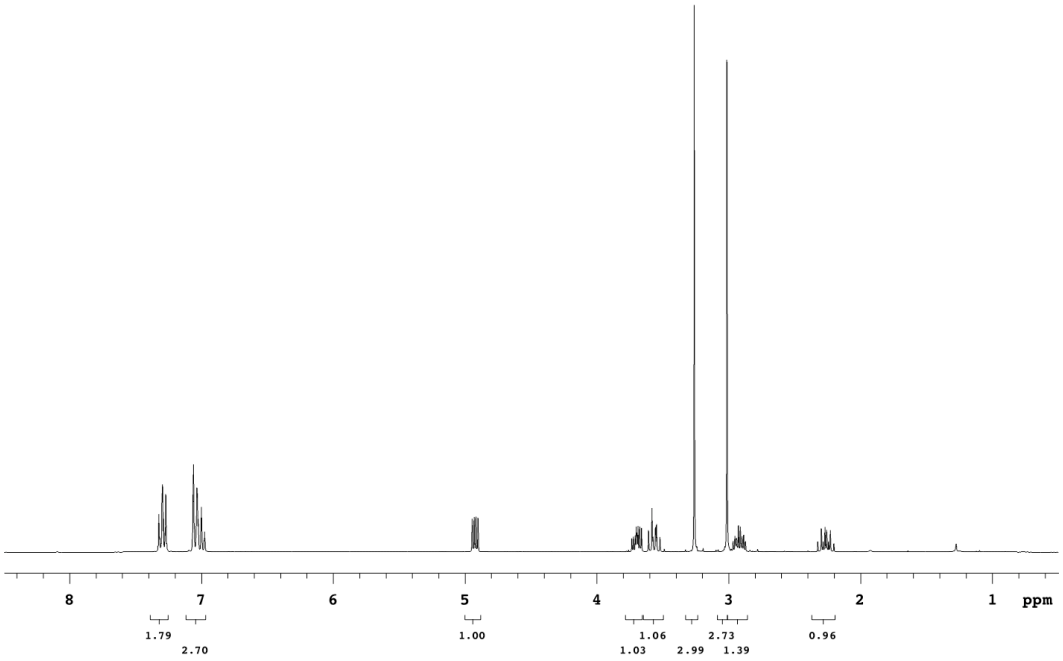
^{1}H NMR spectrum of **79b**



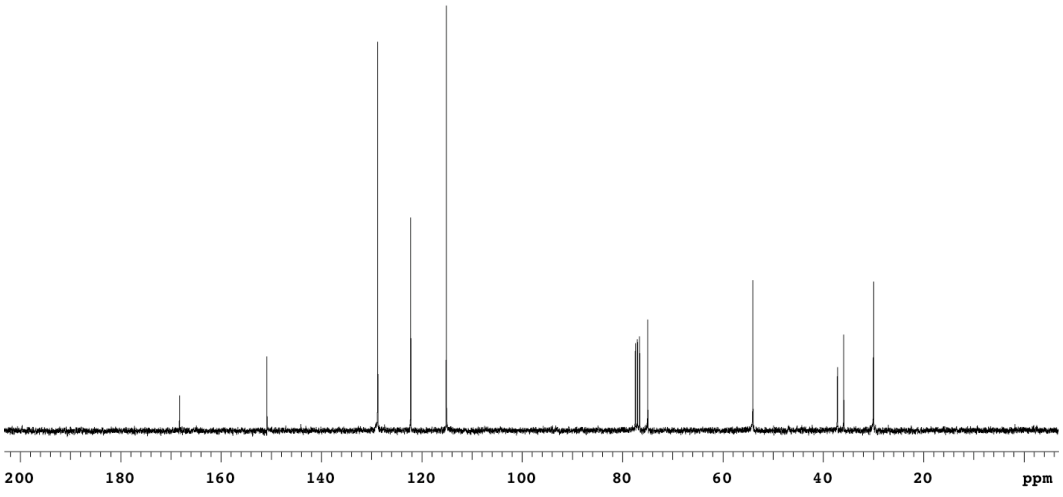
^{13}C NMR spectrum of **79b**



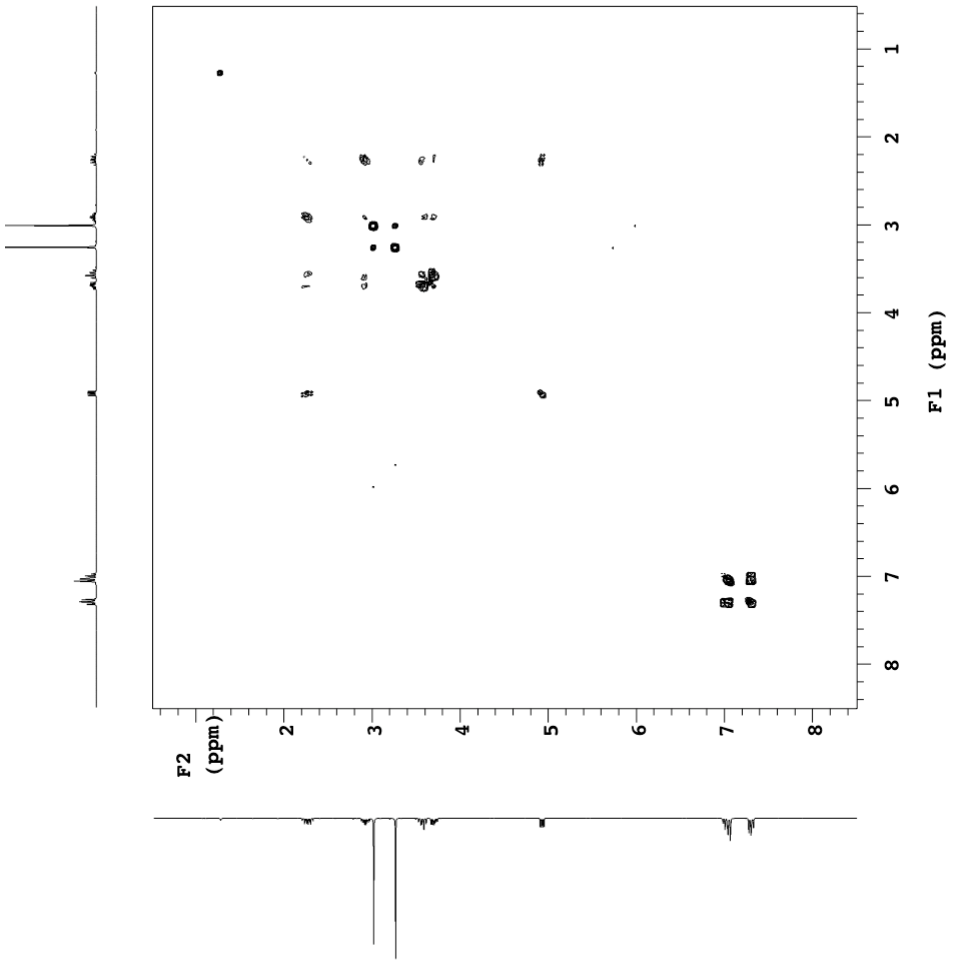
2D ^{1}H NMR spectrum of **79b**



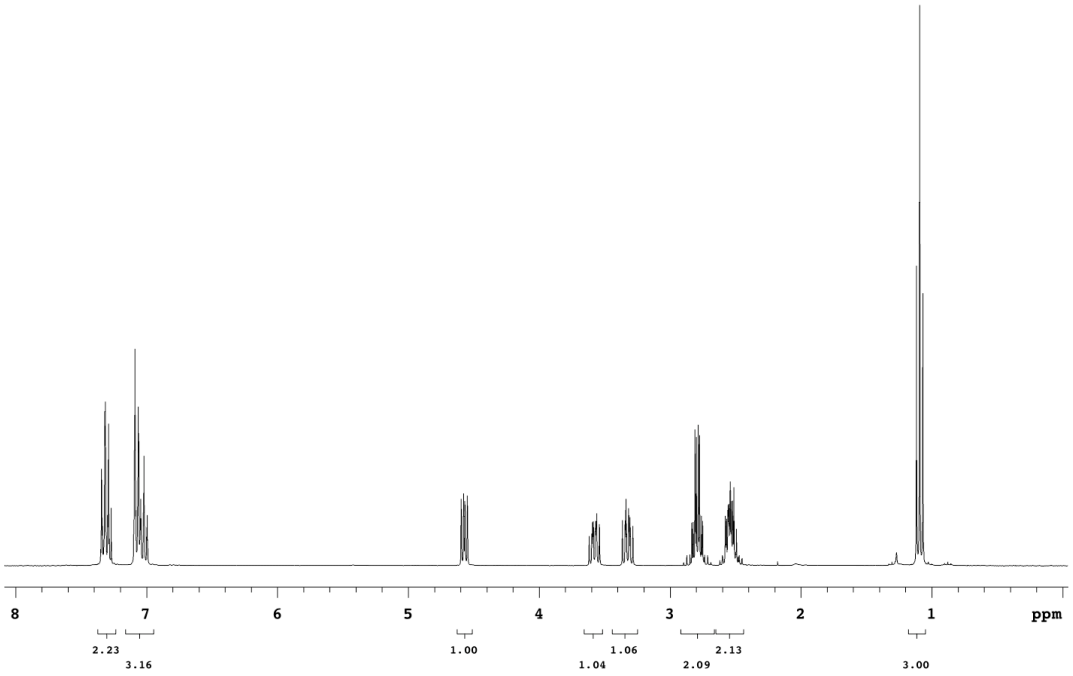
^{1}H NMR spectrum of **79c**



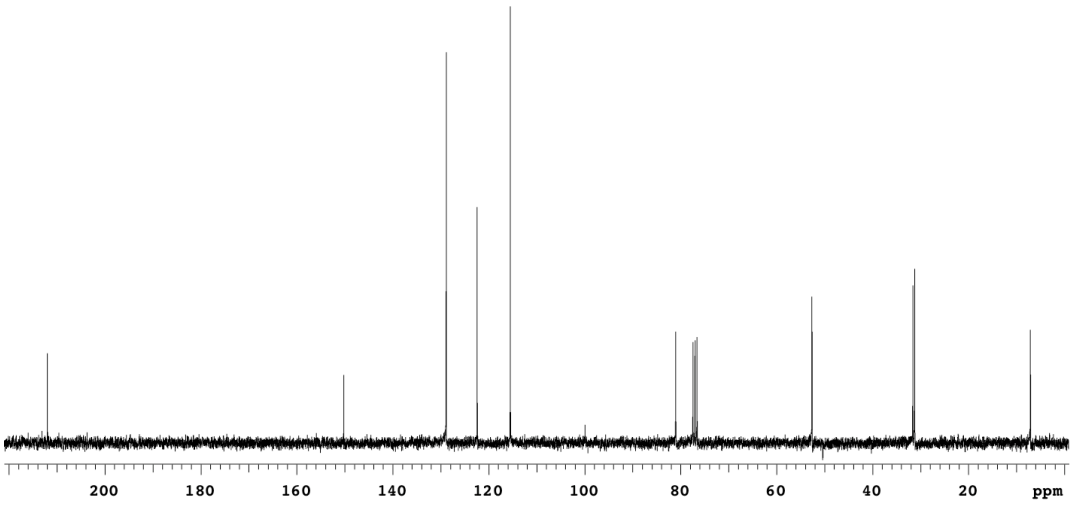
^{13}C NMR spectrum of **79c**



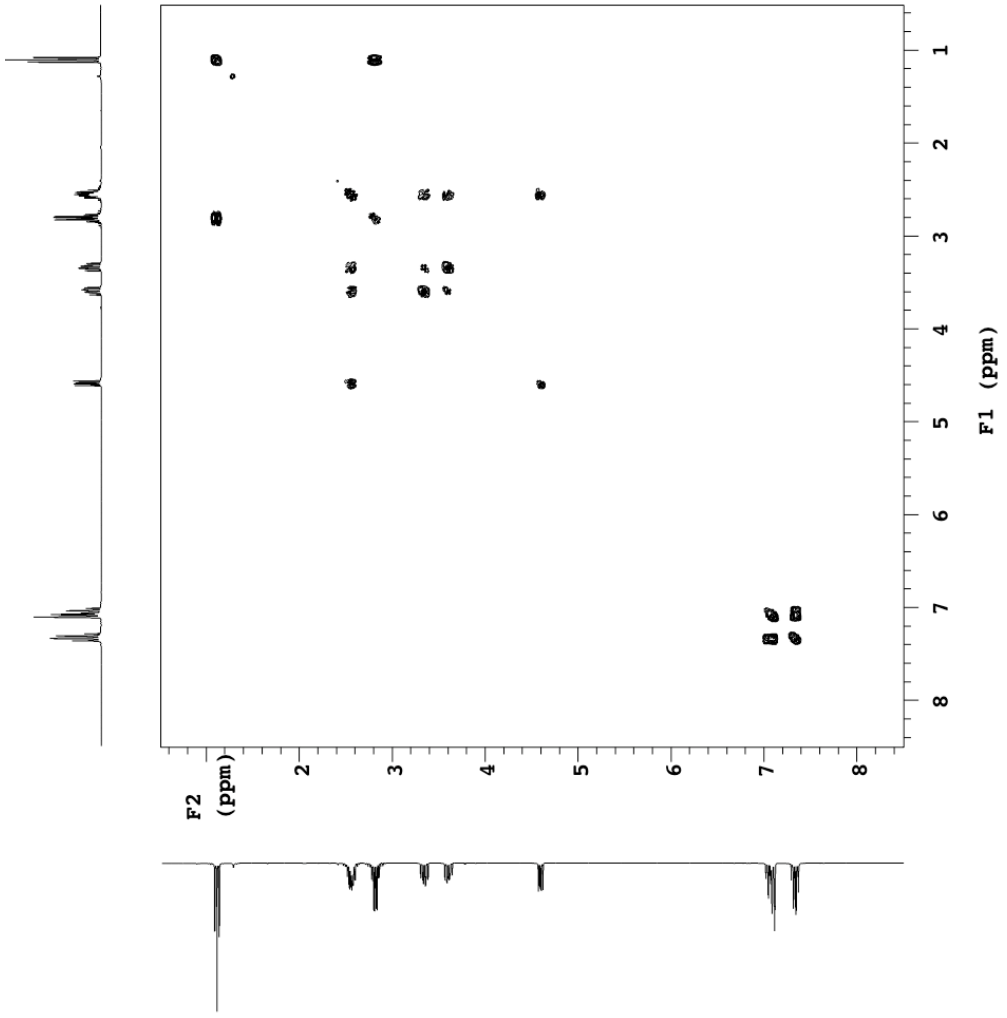
2D ^{1}H NMR spectrum of **79c**



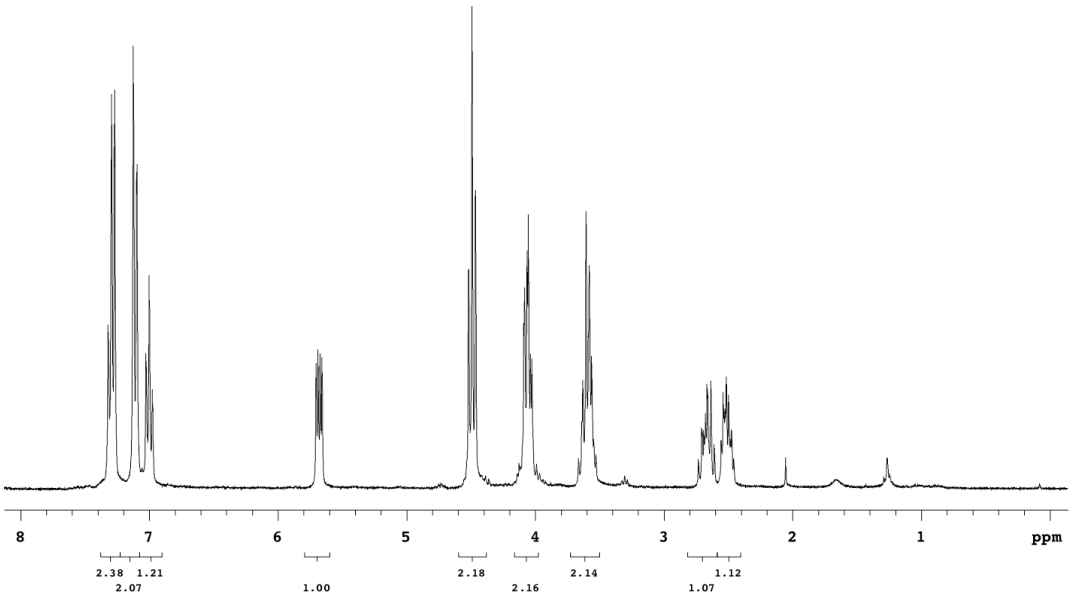
^{1}H NMR spectrum of **79d**



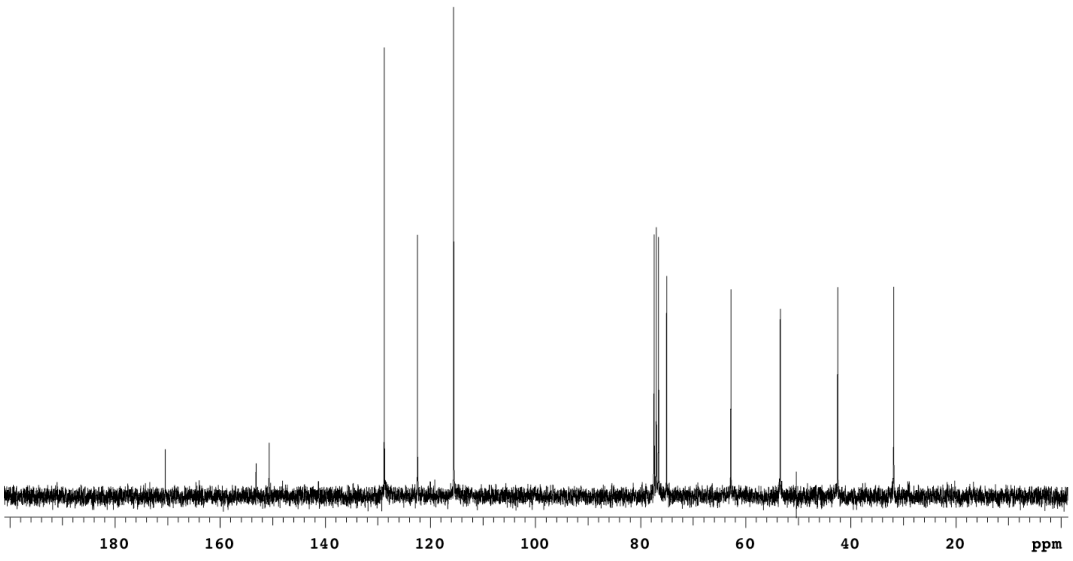
^{13}C NMR spectrum of **79d**



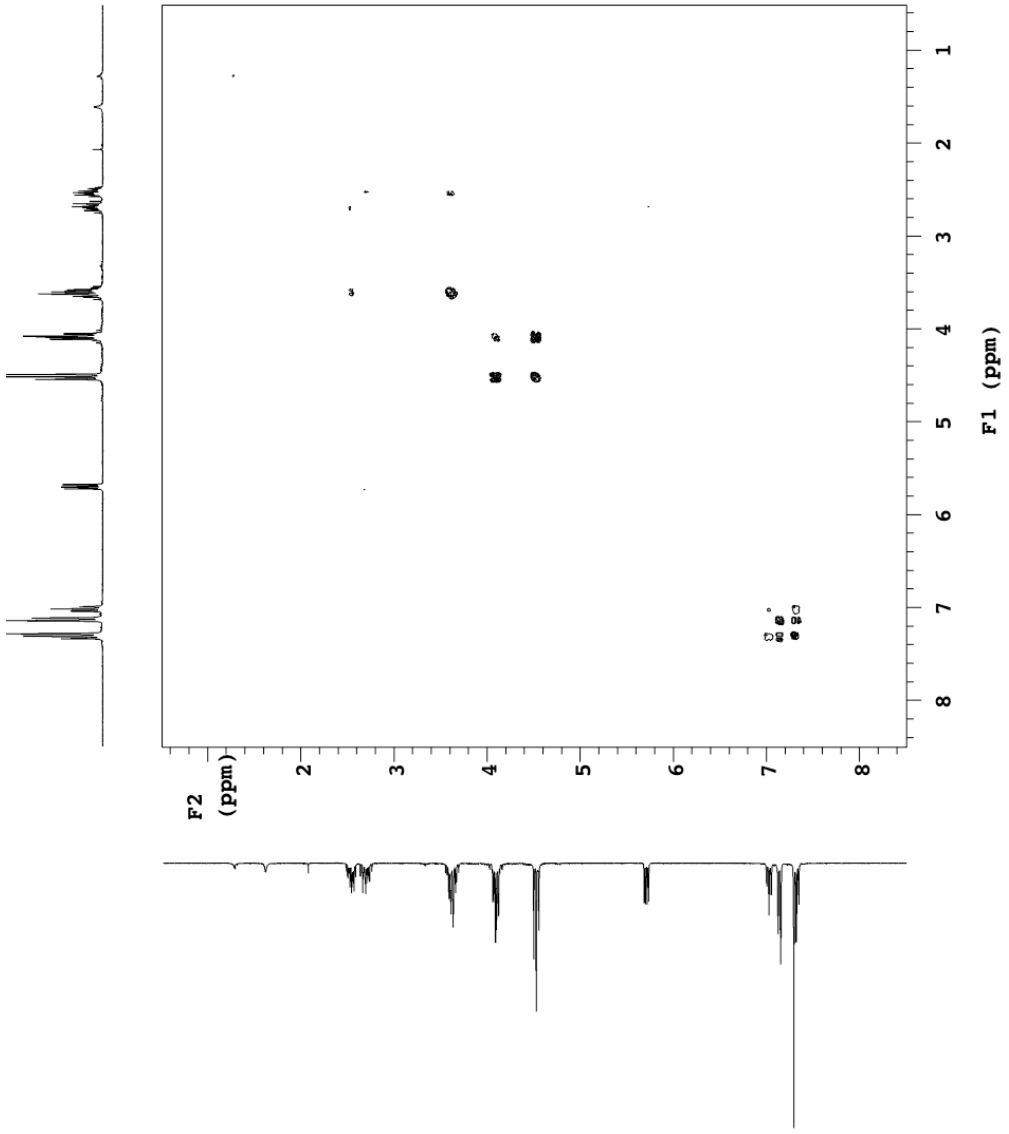
2D ^{1}H NMR spectrum of **79d**



^{1}H NMR spectrum of **79e**



^{13}C NMR spectrum of **79e**



2D ^{1}H NMR spectrum of **79e**

APPENDIX C

X-RAY STRUCTURE OF 42

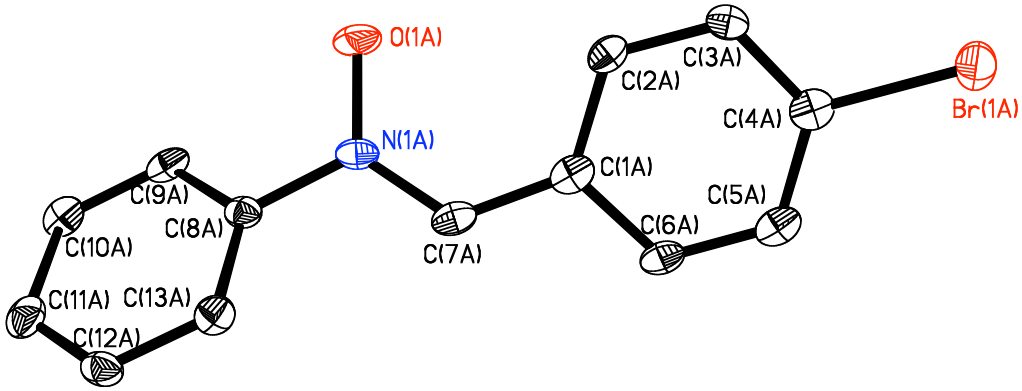


Table C.1. Crystal data and structure refinement for bc02

Identification code	bc02	
Empirical formula	C13 H10 Br N O	
Formula weight	276.13	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.581(4) Å	α= 96.601(16)°.
	b = 13.818(10) Å	β= 90.197(16)°.
	c = 14.582(10) Å	γ = 97.907(16)°.
Volume	1106.4(13) $Å^3$	
Z	4	
Density (calculated)	1.658 Mg/m^3	
Absorption coefficient	3.691 mm^{-1}	
F(000)	552	
Crystal size	0.50 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.41 to 25.00°.	
Index ranges	-6<=h<=6, -16<=k<=16, -17<=l<=15	
Reflections collected	5713	
Independent reflections	3683 [R(int) = 0.0509]	
Completeness to theta = 25.00°	94.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7092 and 0.2598	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3683 / 0 / 290	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1401	
R indices (all data)	R1 = 0.0701, wR2 = 0.1514	
Extinction coefficient	0.0044(14)	

Largest diff. peak and hole	0.955 and -0.957 e.Å^{-3}

Table C.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for bc02. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Br(1A)	10336(1)	9477(1)	6363(1)	28(1)
O(1A)	3926(6)	4764(3)	6391(3)	27(1)
N(1A)	6010(7)	4436(3)	6286(3)	18(1)
C(1A)	8437(8)	6054(4)	6244(3)	18(1)
C(2A)	6780(8)	6690(4)	6603(3)	18(1)
C(3A)	7354(8)	7695(4)	6645(3)	17(1)
C(4A)	9550(9)	8097(4)	6290(3)	18(1)
C(5A)	11205(8)	7497(4)	5919(3)	20(1)
C(6A)	10670(8)	6497(4)	5901(3)	20(1)
C(7A)	8102(9)	5006(4)	6204(3)	19(1)
C(8A)	5974(8)	3375(4)	6235(3)	16(1)
C(9A)	3976(8)	2784(4)	5815(3)	20(1)
C(10A)	3901(9)	1782(4)	5762(3)	20(1)
C(11A)	5768(9)	1357(5)	6123(4)	25(1)
C(12A)	7765(9)	1982(4)	6558(3)	20(1)
C(13A)	7875(9)	2990(4)	6615(3)	19(1)
Br(1B)	5074(1)	9183(1)	8733(1)	27(1)
O(1B)	-1091(6)	4450(3)	8644(3)	25(1)
N(2B)	1008(7)	4145(3)	8714(3)	17(1)
C(1B)	3411(9)	5780(4)	8763(3)	20(1)
C(2B)	1692(8)	6312(4)	8402(3)	17(1)
C(3B)	2197(8)	7306(4)	8385(3)	17(1)
C(4B)	4411(9)	7813(4)	8743(3)	18(1)
C(5B)	6119(9)	7309(4)	9109(3)	21(1)
C(6B)	5625(8)	6296(4)	9096(3)	19(1)
C(7B)	3098(9)	4732(4)	8787(3)	22(1)
C(8B)	963(8)	3099(4)	8741(3)	17(1)
C(9B)	-1041(8)	2600(4)	9151(3)	21(1)
C(10B)	-1152(9)	1607(4)	9175(3)	22(1)

C(11B)	663(9)	1094(4)	8796(3)	21(1)
C(12B)	2641(9)	1605(4)	8379(3)	21(1)
C(13B)	2794(8)	2605(4)	8346(3)	20(1)

Table C.3. Bond lengths [Å] and angles [°] for bc02

Br(1A)-C(4A)	1.888(6)
O(1A)-N(1A)	1.308(5)
N(1A)-C(7A)	1.329(7)
N(1A)-C(8A)	1.458(7)
C(1A)-C(2A)	1.422(7)
C(1A)-C(6A)	1.430(7)
C(1A)-C(7A)	1.428(8)
C(2A)-C(3A)	1.376(8)
C(3A)-C(4A)	1.400(7)
C(4A)-C(5A)	1.395(8)
C(5A)-C(6A)	1.369(8)
C(8A)-C(9A)	1.384(7)
C(8A)-C(13A)	1.390(7)
C(9A)-C(10A)	1.373(8)
C(10A)-C(11A)	1.394(7)
C(11A)-C(12A)	1.412(8)
C(12A)-C(13A)	1.379(8)
Br(1B)-C(4B)	1.880(6)
O(1B)-N(2B)	1.306(5)
N(2B)-C(7B)	1.322(7)
N(2B)-C(8B)	1.448(7)
C(1B)-C(6B)	1.395(7)
C(1B)-C(2B)	1.420(7)
C(1B)-C(7B)	1.440(8)
C(2B)-C(3B)	1.367(7)
C(3B)-C(4B)	1.402(7)
C(4B)-C(5B)	1.393(7)
C(5B)-C(6B)	1.388(8)
C(8B)-C(13B)	1.396(7)
C(8B)-C(9B)	1.404(7)
C(9B)-C(10B)	1.369(8)
C(10B)-C(11B)	1.394(8)

C(11B)-C(12B)	1.406(7)
C(12B)-C(13B)	1.379(8)

O(1A)-N(1A)-C(7A)	124.1(5)
O(1A)-N(1A)-C(8A)	116.7(4)
C(7A)-N(1A)-C(8A)	119.2(4)
C(2A)-C(1A)-C(6A)	117.5(5)
C(2A)-C(1A)-C(7A)	126.1(4)
C(6A)-C(1A)-C(7A)	116.4(5)
C(3A)-C(2A)-C(1A)	120.9(4)
C(2A)-C(3A)-C(4A)	119.6(5)
C(5A)-C(4A)-C(3A)	121.2(5)
C(5A)-C(4A)-Br(1A)	119.5(4)
C(3A)-C(4A)-Br(1A)	119.3(4)
C(6A)-C(5A)-C(4A)	119.4(5)
C(5A)-C(6A)-C(1A)	121.5(5)
N(1A)-C(7A)-C(1A)	125.9(5)
C(9A)-C(8A)-C(13A)	122.4(5)
C(9A)-C(8A)-N(1A)	117.3(4)
C(13A)-C(8A)-N(1A)	120.2(4)
C(10A)-C(9A)-C(8A)	118.3(5)
C(9A)-C(10A)-C(11A)	121.6(5)
C(10A)-C(11A)-C(12A)	118.5(5)
C(13A)-C(12A)-C(11A)	120.7(5)
C(12A)-C(13A)-C(8A)	118.4(5)
O(1B)-N(2B)-C(7B)	124.1(5)
O(1B)-N(2B)-C(8B)	116.1(4)
C(7B)-N(2B)-C(8B)	119.7(4)
C(6B)-C(1B)-C(2B)	118.5(5)
C(6B)-C(1B)-C(7B)	116.3(5)
C(2B)-C(1B)-C(7B)	125.2(5)
C(3B)-C(2B)-C(1B)	120.6(5)
C(2B)-C(3B)-C(4B)	119.9(5)
C(5B)-C(4B)-C(3B)	120.5(5)

C(5B)-C(4B)-Br(1B)	119.8(4)
C(3B)-C(4B)-Br(1B)	119.7(4)
C(6B)-C(5B)-C(4B)	119.2(5)
C(5B)-C(6B)-C(1B)	121.2(5)
N(2B)-C(7B)-C(1B)	125.6(5)
C(13B)-C(8B)-C(9B)	121.7(5)
C(13B)-C(8B)-N(2B)	121.1(4)
C(9B)-C(8B)-N(2B)	117.1(5)
C(10B)-C(9B)-C(8B)	118.4(5)
C(9B)-C(10B)-C(11B)	121.3(5)
C(10B)-C(11B)-C(12B)	119.4(5)
C(13B)-C(12B)-C(11B)	120.4(5)
C(12B)-C(13B)-C(8B)	118.7(5)

Symmetry transformations used to generate equivalent atoms:

Table C.4. Anisotropic displacement parameters ($Å^2$x 10^3) for bc02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1A)	27(1)	24(1)	32(1)	4(1)	-3(1)	0(1)
O(1A)	11(2)	31(3)	40(2)	2(2)	-1(2)	7(2)
N(1A)	13(2)	24(3)	17(2)	3(2)	-3(2)	7(2)
C(1A)	17(2)	29(3)	10(2)	7(2)	-2(2)	3(2)
C(2A)	14(2)	24(3)	14(2)	2(2)	-1(2)	0(2)
C(3A)	19(2)	21(3)	12(2)	0(2)	0(2)	6(2)
C(4A)	20(2)	28(3)	7(2)	2(2)	-6(2)	4(2)
C(5A)	16(2)	31(3)	13(2)	9(2)	-4(2)	3(2)
C(6A)	13(2)	28(3)	19(3)	4(2)	-3(2)	4(2)
C(7A)	14(2)	28(3)	13(2)	1(2)	1(2)	4(2)
C(8A)	16(2)	19(3)	14(2)	3(2)	3(2)	5(2)
C(9A)	12(2)	34(4)	14(2)	9(2)	0(2)	3(2)
C(10A)	18(2)	30(3)	13(2)	6(2)	-2(2)	1(2)
C(11A)	22(3)	29(3)	23(3)	10(2)	7(2)	1(2)
C(12A)	19(2)	24(3)	19(3)	7(2)	0(2)	8(2)
C(13A)	17(2)	23(3)	17(3)	4(2)	-3(2)	2(2)
Br(1B)	31(1)	23(1)	28(1)	4(1)	3(1)	3(1)
O(1B)	11(2)	31(2)	33(2)	6(2)	-5(1)	7(2)
N(2B)	17(2)	19(3)	17(2)	5(2)	-3(2)	3(2)
C(1B)	20(2)	34(3)	7(2)	9(2)	3(2)	1(2)
C(2B)	14(2)	26(3)	13(2)	5(2)	-4(2)	4(2)
C(3B)	21(2)	18(3)	14(2)	6(2)	1(2)	7(2)
C(4B)	20(2)	21(3)	12(2)	1(2)	-1(2)	6(2)
C(5B)	16(2)	29(3)	18(3)	5(2)	0(2)	1(2)
C(6B)	13(2)	30(3)	14(2)	6(2)	0(2)	5(2)
C(7B)	18(2)	33(4)	16(3)	7(2)	-5(2)	2(2)
C(8B)	19(2)	20(3)	12(2)	1(2)	-2(2)	2(2)
C(9B)	14(2)	30(4)	17(3)	3(2)	-3(2)	1(2)
C(10B)	20(2)	29(3)	17(3)	5(2)	-3(2)	0(2)

C(11B)	26(3)	20(3)	15(3)	-1(2)	-6(2)	1(2)
C(12B)	16(2)	26(3)	21(3)	1(2)	-3(2)	9(2)
C(13B)	18(2)	28(3)	12(2)	6(2)	-2(2)	1(2)

APPENDIX D

X-RAY STRUCTURE OF 36a

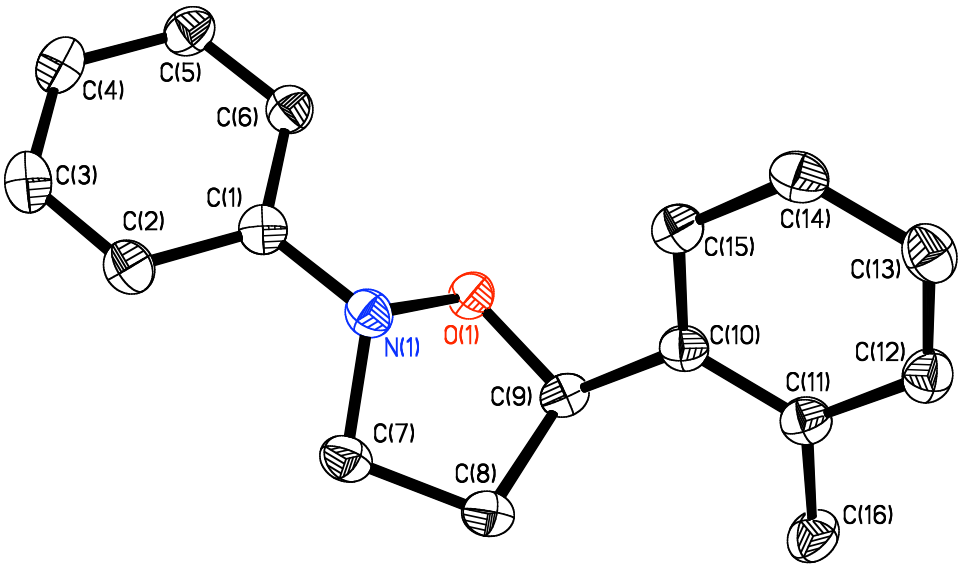


Table D.1. Crystal data and structure refinement for Pbcn

Identification code	pbcn	
Empirical formula	C16 H17 N O	
Formula weight	239.31	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 15.772(8) Å	α= 90°.
	b = 6.743(4) Å	β= 90°.
	c = 24.033(13) Å	γ = 90°.
Volume	2556(2) $Å^3$	
Z	8	
Density (calculated)	1.244 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	1024	
Crystal size	0.40 x 0.27 x 0.25 mm^3	
Theta range for data collection	1.69 to 27.55°.	
Index ranges	-20<=h<=20, -8<=k<=8, -31<=l<=30	
Reflections collected	26298	
Independent reflections	2941 [R(int) = 0.0399]	
Completeness to theta = 27.55°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9810 and 0.9698	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2941 / 0 / 164	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0705, wR2 = 0.1715	
R indices (all data)	R1 = 0.0804, wR2 = 0.1870	
Largest diff. peak and hole	0.695 and -0.292 $e.Å^{-3}$	

Table D.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Pbcn. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(1)	8718(1)	2305(2)	6252(1)	23(1)
C(2)	9053(1)	1415(2)	6729(1)	27(1)
C(3)	8939(1)	2311(3)	7243(1)	30(1)
C(4)	8492(1)	4089(3)	7291(1)	30(1)
C(5)	8173(1)	4993(3)	6816(1)	28(1)
C(6)	8283(1)	4123(2)	6297(1)	25(1)
C(7)	8943(1)	-723(2)	5691(1)	26(1)
C(8)	8805(1)	-1122(2)	5074(1)	26(1)
C(9)	8263(1)	689(2)	4880(1)	23(1)
C(10)	8684(1)	1879(2)	4423(1)	22(1)
C(11)	8646(1)	1201(2)	3870(1)	24(1)
C(12)	9054(1)	2311(2)	3458(1)	26(1)
C(13)	9494(1)	4049(2)	3583(1)	28(1)
C(14)	9522(1)	4712(2)	4128(1)	26(1)
C(15)	9115(1)	3632(2)	4546(1)	24(1)
C(16)	8153(1)	-647(2)	3717(1)	31(1)
N(1)	8867(1)	1447(2)	5724(1)	23(1)
O(1)	8120(1)	1857(2)	5373(1)	24(1)

Table D.3. Bond lengths [Å] and angles [°] for Pbcn

C(1)-C(2)	1.399(2)
C(1)-C(6)	1.409(2)
C(1)-N(1)	1.413(2)
C(2)-C(3)	1.387(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.395(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.389(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.389(2)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-N(1)	1.470(2)
C(7)-C(8)	1.524(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.561(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-O(1)	1.4392(18)
C(9)-C(10)	1.515(2)
C(9)-H(9)	1.0000
C(10)-C(15)	1.395(2)
C(10)-C(11)	1.405(2)
C(11)-C(12)	1.399(2)
C(11)-C(16)	1.515(2)
C(12)-C(13)	1.395(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.386(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.396(2)
C(14)-H(14)	0.9500

C(15)-H(15)	0.9500
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
N(1)-O(1)	1.4761(16)

C(2)-C(1)-C(6)	119.61(14)
C(2)-C(1)-N(1)	119.82(14)
C(6)-C(1)-N(1)	120.44(13)
C(3)-C(2)-C(1)	119.62(15)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	120.94(15)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	119.43(15)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(6)-C(5)-C(4)	120.52(16)
C(6)-C(5)-H(5)	119.7
C(4)-C(5)-H(5)	119.7
C(5)-C(6)-C(1)	119.85(14)
C(5)-C(6)-H(6)	120.1
C(1)-C(6)-H(6)	120.1
N(1)-C(7)-C(8)	102.49(12)
N(1)-C(7)-H(7A)	111.3
C(8)-C(7)-H(7A)	111.3
N(1)-C(7)-H(7B)	111.3
C(8)-C(7)-H(7B)	111.3
H(7A)-C(7)-H(7B)	109.2
C(7)-C(8)-C(9)	103.32(12)
C(7)-C(8)-H(8A)	111.1
C(9)-C(8)-H(8A)	111.1
C(7)-C(8)-H(8B)	111.1

C(9)-C(8)-H(8B)	111.1
H(8A)-C(8)-H(8B)	109.1
O(1)-C(9)-C(10)	112.07(12)
O(1)-C(9)-C(8)	105.60(12)
C(10)-C(9)-C(8)	113.01(12)
O(1)-C(9)-H(9)	108.7
C(10)-C(9)-H(9)	108.7
C(8)-C(9)-H(9)	108.7
C(15)-C(10)-C(11)	119.80(14)
C(15)-C(10)-C(9)	120.54(13)
C(11)-C(10)-C(9)	119.66(14)
C(12)-C(11)-C(10)	118.41(14)
C(12)-C(11)-C(16)	120.25(14)
C(10)-C(11)-C(16)	121.31(14)
C(13)-C(12)-C(11)	121.75(14)
C(13)-C(12)-H(12)	119.1
C(11)-C(12)-H(12)	119.1
C(14)-C(13)-C(12)	119.33(14)
C(14)-C(13)-H(13)	120.3
C(12)-C(13)-H(13)	120.3
C(13)-C(14)-C(15)	119.84(14)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(10)-C(15)-C(14)	120.86(14)
C(10)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(11)-C(16)-H(16A)	109.5
C(11)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(11)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(1)-N(1)-C(7)	118.00(12)
C(1)-N(1)-O(1)	107.70(11)

C(7)-N(1)-O(1)	102.77(11)
C(9)-O(1)-N(1)	104.09(10)

Symmetry transformations used to generate equivalent atoms:

Table D.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Pbcn. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(1)	26(1)	25(1)	1(1)	1(1)	-2(1)
C(2)	24(1)	30(1)	29(1)	3(1)	0(1)	1(1)
C(3)	27(1)	39(1)	25(1)	5(1)	-1(1)	-2(1)
C(4)	28(1)	38(1)	25(1)	-4(1)	-1(1)	-3(1)
C(5)	25(1)	30(1)	30(1)	-4(1)	-2(1)	0(1)
C(6)	23(1)	26(1)	26(1)	0(1)	-2(1)	-1(1)
C(7)	26(1)	23(1)	29(1)	2(1)	2(1)	4(1)
C(8)	26(1)	22(1)	29(1)	0(1)	2(1)	1(1)
C(9)	22(1)	23(1)	25(1)	-4(1)	1(1)	-1(1)
C(10)	20(1)	22(1)	25(1)	0(1)	0(1)	3(1)
C(11)	20(1)	25(1)	27(1)	-1(1)	-1(1)	3(1)
C(12)	25(1)	29(1)	24(1)	-1(1)	0(1)	4(1)
C(13)	25(1)	29(1)	29(1)	5(1)	1(1)	2(1)
C(14)	24(1)	23(1)	32(1)	1(1)	-2(1)	-1(1)
C(15)	22(1)	25(1)	25(1)	-2(1)	-2(1)	2(1)
C(16)	35(1)	32(1)	27(1)	-6(1)	-1(1)	-6(1)
N(1)	21(1)	24(1)	25(1)	2(1)	-2(1)	2(1)
O(1)	22(1)	27(1)	24(1)	-3(1)	-2(1)	4(1)

Table D.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Pbcn

	x	y	z	U(eq)
H(2)	9357	203	6702	33
H(3)	9167	1707	7567	36
H(4)	8406	4677	7646	36
H(5)	7878	6216	6845	34
H(6)	8065	4751	5973	30
H(7A)	8506	-1386	5921	31
H(7B)	9511	-1172	5813	31
H(8A)	8496	-2382	5015	31
H(8B)	9352	-1177	4872	31
H(9)	7705	193	4741	28
H(12)	9031	1868	3083	31
H(13)	9772	4772	3296	33
H(14)	9817	5898	4218	32
H(15)	9132	4097	4919	29
H(16A)	8166	-829	3312	47
H(16B)	7564	-507	3841	47
H(16C)	8410	-1802	3898	47

APPENDIX E

X-RAY STRUCTURE OF 46a

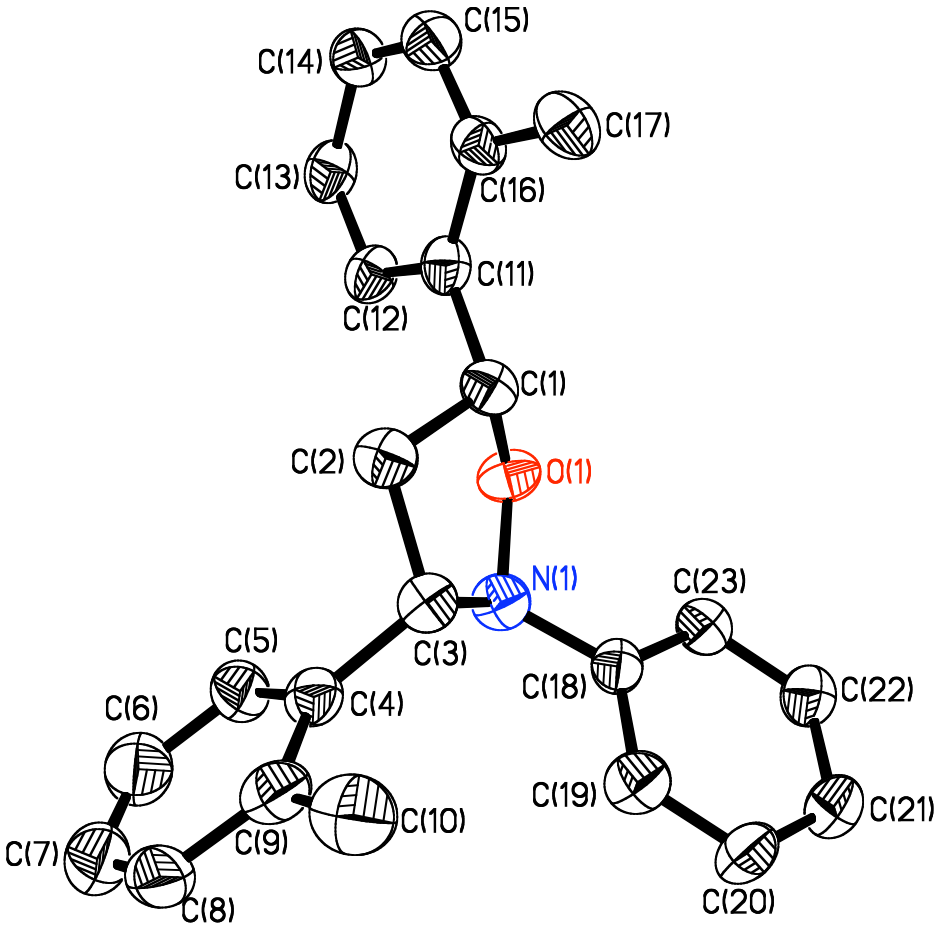


Table E.1. Crystal data and structure refinement for CcN

Identification code	ccn	
Empirical formula	C23 H23 N O	
Formula weight	329.42	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 11.227(7) Å	α= 90°.
	b = 32.76(2) Å	β= 115.235(8)°.
	c = 5.358(3) Å	γ = 90°.
Volume	1782(2) $Å^3$	
Z	4	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	704	
Crystal size	0.25 x 0.06 x 0.03 mm^3	
Theta range for data collection	2.10 to 24.99°.	
Index ranges	-13<=h<=13, -38<=k<=38, -6<=l<=6	
Reflections collected	8387	
Independent reflections	3136 [R(int) = 0.0714]	
Completeness to theta = 24.99°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9978 and 0.9817	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3136 / 2 / 229	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1174	
R indices (all data)	R1 = 0.0931, wR2 = 0.1358	
Absolute structure parameter	-3(2)	
Extinction coefficient	0.0133(16)	
Largest diff. peak and hole	0.282 and -0.177 $e.Å^{-3}$	

Table E.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for CcN. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(1)	2185(4)	1895(1)	9957(7)	34(1)
C(2)	1127(4)	1642(1)	10297(7)	38(1)
C(3)	1329(3)	1212(1)	9418(7)	36(1)
C(4)	70(4)	976(1)	7994(8)	38(1)
C(5)	-843(4)	1098(1)	5373(9)	50(1)
C(6)	-2019(5)	903(2)	3925(10)	62(1)
C(7)	-2337(4)	584(1)	5127(10)	58(1)
C(8)	-1503(4)	449(1)	7684(10)	54(1)
C(9)	-261(4)	642(1)	9231(8)	47(1)
C(10)	615(5)	483(1)	11940(10)	64(1)
C(11)	1873(3)	2345(1)	9450(7)	34(1)
C(12)	971(4)	2471(1)	6832(8)	38(1)
C(13)	630(4)	2879(1)	6335(8)	42(1)
C(14)	1163(4)	3161(1)	8411(8)	43(1)
C(15)	2056(4)	3037(1)	11007(8)	43(1)
C(16)	2425(4)	2628(1)	11598(7)	37(1)
C(17)	3393(4)	2507(1)	14426(7)	44(1)
C(18)	3055(3)	1054(1)	7775(7)	33(1)
C(19)	3129(4)	646(1)	8566(8)	44(1)
C(20)	4127(4)	403(1)	8571(8)	47(1)
C(21)	5090(4)	560(1)	7847(8)	47(1)
C(22)	5005(4)	962(1)	7047(8)	43(1)
C(23)	4000(3)	1212(1)	6982(7)	38(1)
N(1)	1953(3)	1291(1)	7496(6)	37(1)
O(1)	2182(2)	1724(1)	7452(4)	38(1)

Table E.3. Bond lengths [Å] and angles [°] for CcN

C(1)-O(1)	1.453(4)
C(1)-C(11)	1.512(5)
C(1)-C(2)	1.522(5)
C(1)-H(1)	1.0000
C(2)-C(3)	1.534(5)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-N(1)	1.494(4)
C(3)-C(4)	1.503(5)
C(3)-H(3)	1.0000
C(4)-C(5)	1.399(6)
C(4)-C(9)	1.408(5)
C(5)-C(6)	1.371(6)
C(5)-H(5)	0.9500
C(6)-C(7)	1.354(6)
C(6)-H(6)	0.9500
C(7)-C(8)	1.362(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.430(6)
C(8)-H(8)	0.9500
C(9)-C(10)	1.460(6)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.397(5)
C(11)-C(16)	1.399(5)
C(12)-C(13)	1.384(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.372(5)
C(13)-H(13)	0.9500
C(14)-C(15)	1.384(5)
C(14)-H(14)	0.9500

C(15)-C(16)	1.398(5)
C(15)-H(15)	0.9500
C(16)-C(17)	1.493(5)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.396(5)
C(18)-C(23)	1.400(5)
C(18)-N(1)	1.412(4)
C(19)-C(20)	1.373(5)
C(19)-H(19)	0.9500
C(20)-C(21)	1.394(5)
C(20)-H(20)	0.9500
C(21)-C(22)	1.374(5)
C(21)-H(21)	0.9500
C(22)-C(23)	1.383(5)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
N(1)-O(1)	1.443(4)

O(1)-C(1)-C(11)	107.6(3)
O(1)-C(1)-C(2)	101.8(3)
C(11)-C(1)-C(2)	114.8(3)
O(1)-C(1)-H(1)	110.7
C(11)-C(1)-H(1)	110.7
C(2)-C(1)-H(1)	110.7
C(1)-C(2)-C(3)	103.8(3)
C(1)-C(2)-H(2A)	111.0
C(3)-C(2)-H(2A)	111.0
C(1)-C(2)-H(2B)	111.0
C(3)-C(2)-H(2B)	111.0
H(2A)-C(2)-H(2B)	109.0
N(1)-C(3)-C(4)	110.8(3)
N(1)-C(3)-C(2)	103.1(3)

C(4)-C(3)-C(2)	113.5(3)
N(1)-C(3)-H(3)	109.7
C(4)-C(3)-H(3)	109.7
C(2)-C(3)-H(3)	109.7
C(5)-C(4)-C(9)	117.9(4)
C(5)-C(4)-C(3)	119.3(3)
C(9)-C(4)-C(3)	122.7(3)
C(6)-C(5)-C(4)	123.4(4)
C(6)-C(5)-H(5)	118.3
C(4)-C(5)-H(5)	118.3
C(7)-C(6)-C(5)	118.4(5)
C(7)-C(6)-H(6)	120.8
C(5)-C(6)-H(6)	120.8
C(6)-C(7)-C(8)	121.5(4)
C(6)-C(7)-H(7)	119.3
C(8)-C(7)-H(7)	119.3
C(7)-C(8)-C(9)	121.4(4)
C(7)-C(8)-H(8)	119.3
C(9)-C(8)-H(8)	119.3
C(4)-C(9)-C(8)	117.3(4)
C(4)-C(9)-C(10)	123.0(4)
C(8)-C(9)-C(10)	119.7(4)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	120.5(3)
C(12)-C(11)-C(1)	118.8(3)
C(16)-C(11)-C(1)	120.7(3)
C(13)-C(12)-C(11)	120.0(4)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0

C(14)-C(13)-C(12)	120.4(4)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(13)-C(14)-C(15)	119.7(4)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
C(14)-C(15)-C(16)	121.8(4)
C(14)-C(15)-H(15)	119.1
C(16)-C(15)-H(15)	119.1
C(15)-C(16)-C(11)	117.6(3)
C(15)-C(16)-C(17)	120.1(3)
C(11)-C(16)-C(17)	122.3(3)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-C(23)	119.4(3)
C(19)-C(18)-N(1)	119.6(3)
C(23)-C(18)-N(1)	120.6(3)
C(20)-C(19)-C(18)	119.9(4)
C(20)-C(19)-H(19)	120.0
C(18)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	121.0(4)
C(19)-C(20)-H(20)	119.5
C(21)-C(20)-H(20)	119.5
C(22)-C(21)-C(20)	118.8(3)
C(22)-C(21)-H(21)	120.6
C(20)-C(21)-H(21)	120.6
C(21)-C(22)-C(23)	121.5(4)
C(21)-C(22)-H(22)	119.2
C(23)-C(22)-H(22)	119.2
C(22)-C(23)-C(18)	119.4(4)

C(22)-C(23)-H(23)	120.3
C(18)-C(23)-H(23)	120.3
C(18)-N(1)-O(1)	112.7(3)
C(18)-N(1)-C(3)	118.6(3)
O(1)-N(1)-C(3)	108.7(2)
N(1)-O(1)-C(1)	107.2(2)

Symmetry transformations used to generate equivalent atoms:

Table E.4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for CcN. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(2)	36(2)	27(2)	0(2)	11(2)	-2(2)
C(2)	45(2)	41(2)	34(2)	-3(2)	22(2)	-3(2)
C(3)	40(2)	38(2)	31(2)	2(2)	17(2)	2(2)
C(4)	40(2)	37(2)	43(2)	0(2)	24(2)	1(2)
C(5)	39(2)	53(3)	52(3)	-17(2)	15(2)	-4(2)
C(6)	54(3)	68(3)	61(3)	-12(3)	22(2)	0(2)
C(7)	49(3)	61(3)	64(3)	-9(3)	25(3)	2(2)
C(8)	59(3)	41(2)	78(3)	-8(2)	46(3)	-7(2)
C(9)	56(3)	39(2)	53(3)	2(2)	30(2)	6(2)
C(10)	73(3)	62(3)	63(3)	-3(2)	36(3)	-6(2)
C(11)	30(2)	41(2)	32(2)	2(2)	15(2)	2(2)
C(12)	36(2)	42(2)	35(2)	3(2)	14(2)	7(2)
C(13)	36(2)	50(3)	34(2)	7(2)	10(2)	10(2)
C(14)	40(2)	44(2)	46(2)	-2(2)	19(2)	-3(2)
C(15)	43(2)	48(2)	40(2)	-6(2)	20(2)	-4(2)
C(16)	34(2)	41(2)	38(2)	-3(2)	19(2)	-7(2)
C(17)	43(2)	55(3)	31(2)	-3(2)	12(2)	-7(2)
C(18)	31(2)	39(2)	29(2)	-5(2)	12(2)	1(2)
C(19)	51(3)	42(2)	45(2)	6(2)	26(2)	1(2)
C(20)	49(2)	38(2)	55(3)	6(2)	24(2)	12(2)
C(21)	44(2)	47(2)	51(3)	1(2)	23(2)	8(2)
C(22)	40(2)	47(2)	43(2)	0(2)	19(2)	2(2)
C(23)	39(2)	40(2)	34(2)	1(2)	14(2)	-2(2)
N(1)	42(2)	36(2)	38(2)	4(1)	21(2)	-1(1)
O(1)	51(2)	33(1)	35(1)	0(1)	23(1)	2(1)

Table E.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for CcN

	x	y	z	U(eq)
H(1)	3060	1854	11557	41
H(2A)	237	1746	9100	46
H(2B)	1247	1644	12238	46
H(3)	1952	1056	11061	43
H(5)	-637	1329	4553	59
H(6)	-2597	990	2119	74
H(7)	-3160	451	4167	69
H(8)	-1752	221	8456	65
H(10A)	1436	388	11903	95
H(10B)	187	254	12412	95
H(10C)	811	698	13326	95
H(12)	592	2277	5391	46
H(13)	23	2964	4548	50
H(14)	921	3440	8068	52
H(15)	2427	3235	12427	51
H(17A)	3543	2738	15691	67
H(17B)	4226	2429	14381	67
H(17C)	3044	2275	15063	67
H(19)	2489	536	9100	53
H(20)	4162	124	9076	56
H(21)	5793	393	7905	56
H(22)	5651	1070	6526	52
H(23)	3952	1488	6405	45

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Publication Kang, J.-Y.; Bugarin, A.; Connell, B. T. Conversion of Nitrosobenzenes to Isoxazolidines: An Efficient Cascade Process Utilizing Reactive Nitrone Intermediates, *Chem. Commun*., **2008,** 3522-3524.