SYNTHESIS OF PRECURSORS TO NON-ISOCYANATE POLYURETHANES

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Title

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

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ABSTRACT

Biobased diamines are excellent precursors for the synthesis of non-isocyanate polyurethanes (NIPUs). We have prepared several biobased diamines using three different reactions for their synthesis. In the first method, we have carried out chain elongation of cellulose-derived 2,5-diformylfuran by the Henry reaction followed by reduction of the nitroalkene. Yields of the key step: Hantzsch Ester reduction, were 70-80%. Method two involves the Friedel-Crafts alkylation of furfurylamine with different ketones under acidic conditions. Yields of large-scale alkylation reaction were 60-77%. In method three, we combined the Henry reaction and Friedel-Crafts alkylation techniques to access diamines from hemicellulose-derived furfural. These diamines can be reacted with carbonates to access hydroxyalkylcarbamates in good yields, around 80%. We have also developed a novel method for accessing biscarbamates directly from dialdehydes in good yields, 70-94%. The hydroxyalkylcarbamates and biscarbamates are valuable precursors to obtain polyurethanes via the phosgene-free route.

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DEDICATION

I would like to dedicate my work to my parents. Thank you for supporting and encouraging me all the time during my life in graduate school. Without your understanding and giving strong backing to me, I can hardly insist on my goal all the time when I am faced with difficulties. I want to express the gratitude for your love, which makes me stronger and better.

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LIST OF ABBREVIATIONS

Ac ..... acetyl

aq ..... aqueous

AMF 5-acetoxymethyl-2-furaldehyde

Bn ..... benzyl

BOMF ..... (5-Formylfuran-2-yl) methyl benzoate

Bu ..... butyl

Calcd. ..... calculated

$CDCl_3$ ..... chloroform-d

DCM ..... dichloromethane

DFF 2,5-Diformylfuran

DMAP 4-Dimethylaminopyridine

DMF ..... N, N-Dimethylmethanamide

DMSO ..... dimethyl sulfoxide

EA ..... ethyl acetate

eq ..... equivalent

Et ..... ethyl

EtOH ..... ethanol

FT-IR ..... Fourier-Transform Infrared Spectroscopy

GC-MS ..... Gas Chromatography–Mass Spectrometry

h ..... hours

HEH ..... Hantzsch ester

HMF 5-Hydroxymethylfurfural

HPLC ..... High Performance Liquid Chromatography

HRMS ..... High Resolution Mass Spectrometry

i-PrOH.....Isopropyl alcohol

Me .....methyl

MeOH .....methanol

min .....minutes

mp .....melting point

NIPU .....Non-isocyanate polyurethane

NMR .....Nuclear Magnetic Resonance

OBMF .....5,5'-(Oxybis(methylene))bis(furan-2-carbaldehyde)

OTf.....triflate

Ph .....phenyl

PU .....polyurethane

RBF .....round bottom flask

RT .....room temperature

TBDMS.....tert-butyldimethylsilyl

TESH.....triethylsilane

THF .....tetrahydrofuran

TLC .....Thin Layer Chromatography

wt.....weight

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CHAPTER 1. INTRODUCTION TO BIOMASS-DERIVED DIAMINES

1.1. Introduction

Amines play an important role in the chemical and biochemical industry and are widely applied in polymers, drugs, and agricultural products. Acting as excellent precursors for the synthesis of polyamide and polyurethane, amines recently have attracted increasing interest in the polymer industry[1]. These amine-derived polymers satisfy the growing demand for automotive, insulation and construction industries, which means the consumption of polymers is also increasing rapidly.

1.1.1. Categories and Nucleophilicity of Amines

Amines are generated from ammonia when the N-H bonds are replaced by substituents. They are divided into three categories: primary amines, secondary amines, and tertiary amines according to the number of replaced hydrogen atoms (Figure 1). Depending on the nitrogen substituents, tertiary amines are more nucleophilic than the others. However, its participation in reactions is hampered by the steric hindrance around the nitrogen. The nitrogen lone pair of primary amines is more accessible as there is little steric hindrance. The high reactivity of primary amines in several types of transformations makes them attractive as monomers in polymer chemistry. Huntsman's JEFFAMINE® is an example of a popular amine extensively used in polymer chemistry. This company supplies commercial amine monomers. Huntsman offers specialized polyether amines for polymer applications. However, almost all their products are linear amines and they do not offer bio-based primary amines.

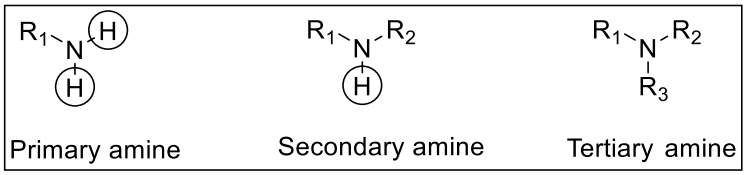


Figure 1. Structure of the primary amine, secondary amine, and tertiary amine.

Another way to categorize amines is by on the type of nitrogen substituent. If the substituent is an alkyl group, the compound is called an aliphatic amine. If the substituent is an aryl group, the compound is called an aromatic amine. We can analyze the reactivities of amines by the nucleophilicity of these two types of amines. There is no doubt that their reactivities have a large distinction; both substituent and reaction media also affect the reactivity of amines. Electron-donating substituents on the amine nitrogen result in greater basicity of the amine and correspond with enhanced nucleophilicity. It is reasonable to predict that the aliphatic amines are more nucleophilic and reactive than aromatic amines.

It is important to know that protic solvents will provide protons to amines and generate hydrogen bonds in solution. The formation of hydrogen bonds will then reduce the nucleophilicity of amine and depress the reaction progress.[2] Common ketones are poor solvents for amine reactions since there is potential for a background reaction between ketones and amines.

According to their nucleophilicity, both aromatic primary diamines and primary aliphatic diamines can react with carbonates and generate precursors of polyurethanes in an efficient and economical way. In summary, the biobased primary diamines potentially provide ideal precursors for polymers. Currently, most of the diamines used in polymer synthesis are derived from petroleum. With the projected rapid decline of fossil fuel resources, there is a need for replacement of fossil fuel derived chemicals with those from renewable resources. The three different types of biomass, oilseeds, carbohydrates, and lignin all have potential as the feedstock for diamine synthesis. However, the synthesis of primary amines is a challenge because the high reactivity of

diamines and also being polar, their isolation is often challenging. Our group is interested in exploring new methodologies for the synthesis of diamines because of their application for polymer synthesis and due to the limitation of commercially available primary diamines.

1.2. Synthesis of Amines

Very few amines are found in nature. The major two non-edible naturally occurring sources of amines are polylysine and chitosan. Polylysine can be produced by the *Streptomyces* microorganism. Chitosan can be obtained by deacetylation of insect chitin (Figure 2). [2,3]

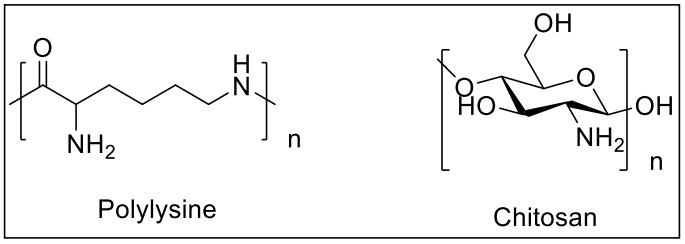


Figure 2. Structure of polylysine and chitosan.

Because there are few non-edible amine sources available in nature, we need to develop new synthetic methods to access amines for the increasing needs of chemical industries. There are three major ways to synthesize amines: nucleophilic substitution, reduction, and reductive amination. A brief description of each type is provided below.

1.2.1. Synthesis of Amines by Nucleophilic Substitution Reaction

The most commonly used methodology for the synthesis of amines is the reaction of ammonia with alcohols or alkyl halides.[4] Both of these reactants are inexpensive and available on a large scale, which benefits industrial preparation. The reaction using alcohol as an electrophile is environmentally friendly because water is the only byproduct. Although both reactions are inexpensive, they both require demanding conditions, such as specialized catalysts, reactors, and high temperatures. At the same time, these reactions also require special purification techniques,

such as fractional distillation since the selectivity is poor and there are primary, secondary and tertiary amines in the mixture (Scheme 1).

Alkylation Reaction with Alcohol:

$$ROH + NH_3 \rightarrow RNH_2 + H_2O$$

Ammonolysis Reaction of Halides:

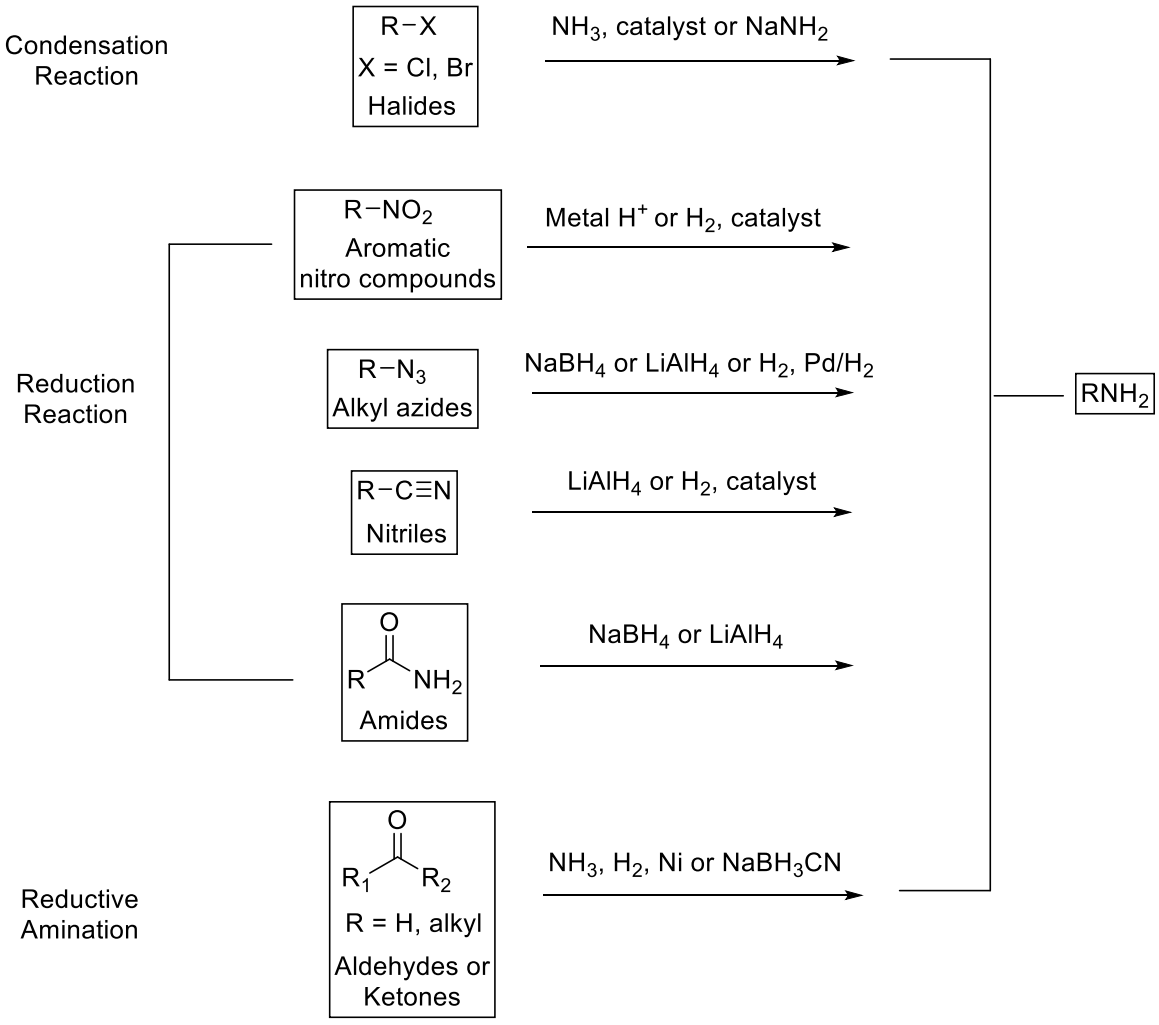
$$RX + NH_3 \rightarrow RNH_3^+ + X^-$$

$$RNH_3^+ + X^- + NH_3 \rightarrow RNH_2 + NH_4^+ + X^-$$

Scheme 1. Synthesis of amines in industry.

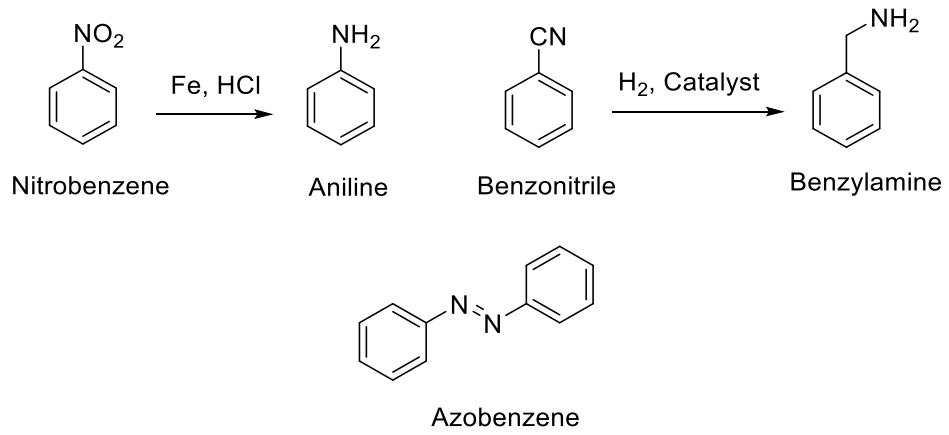
1.2.2. Synthesis of Amines by Reduction

To prepare pure amines for further research, both reduction and reductive amination are more widely applied in laboratories.[5] The reason is that these two methods have better selectivity than substitution reaction and provide access to pure amines. Reductions provide a wide range of amines from different substrates, such as nitro compounds, azides, nitriles, and amides (Scheme 2).[6–8] Most commonly used reagents for reductions are sodium borohydride, lithium aluminum hydride, and transition metal catalysis under hydrogen. We can access amines from aldehydes and ketones by reductive amination.



Scheme 2. Different methods for amine synthesis.

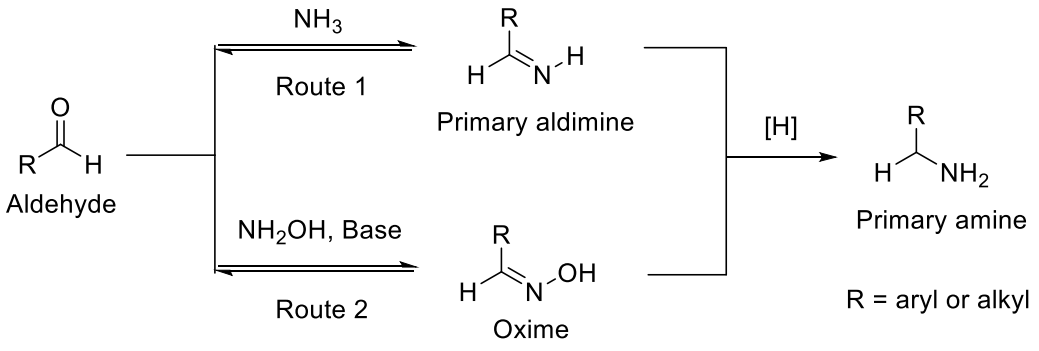
The first reduction of nitrobenzene to aniline was conducted by Bechamp in 1854. The reducing agent was acidic iron, which is inexpensive. This method is used to prepare aniline on a large scale for industry. However, the conversion of it is not so perfect. In addition, iron as a catalyst is consumed rapidly resulting in a slower rate of reaction. Thus, other catalysts are now used during the reaction protocol, such as Zinc and Raney nickel.[9,10,11] On the other hand, benzonitrile could be reduced to benzylamine by catalytic hydrogenation (Scheme 3). Although these amines are easy to prepare, aniline is easily oxidized and generates azobenzene, which is not a good platform for further polymer applications.



Scheme 3. Reduction of nitrobenzene and benzonitrile.

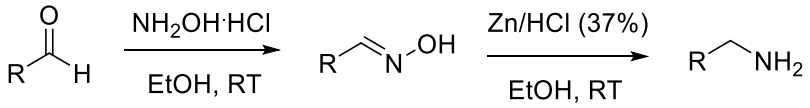
1.2.3. Synthesis of Amines by Reductive Amination

Reductive amination is a widely used method that can convert aldehydes to primary amines selectively without the formation of secondary and tertiary amine byproducts. There are two possible intermediates: aldimines and oximes (Scheme 4).[12] Beller's group using water-soluble Rh catalysts converted aldehydes to primary amines using ammonia (Route 1).[13] Oximes are more stable than aldimines. Furfural can be converted to solid 2-furfural oxime by reaction with hydroxylamine hydrochloride and sodium carbonate.[14] Then, we can obtain furfurylamine by reduction with Raney Ni under hydrogen (Route 2). Thus, oximes are the better precursor of pure primary amine because there is no side product even with simple protocols.



Scheme 4. Two routes for reductive amination of aldehydes.

Ayedi's group applied the reductive amination technique, developing a simple and low-cost synthesis route to primary amines.[12] The first step is treating aliphatic or aromatic aldehydes with hydroxylamine hydrochloride at room temperature in ethanol. Then the oxime intermediate is reduced by zinc with hydrochloric acid (Scheme 5). Actually, the selective hydrogenation reaction could occur with catalysis (such as Raney Ni) or hydride reagent (such as $NaBH_4$ and $LiAlH_4$).[15,16] However, the zinc-acid reaction condition is better because it is more safe and economical. Furthermore, ethanol, as the solvent, can improve conversion and decrease both the reaction time and the consumption of the reagent. At the same time, this method required short reaction time, low temperature, which satisfy the rules of green chemistry. The researchers applied the reaction condition to aldehydes such as benzaldehyde and furfural, obtaining excellent yields for all substrates. However, aliphatic substrates gave lower yields than aromatic substrates. One reason for lower yields with aliphatic substrates is due to the lower stability of aliphatic oximes.



Scheme 5. A simple protocol for the synthesis of the primary amine from the aldehyde.

In summary, the substitution reaction of alcohols or halides is economical and amenable for preparation on an industrial scale. However, its selectivity is poor for the synthesis of pure amines. Reduction and reductive amination have better selectivity than substitution reaction, which makes them more applicable to laboratory research. The reduction reaction is applicable to a large range of substrates than reductive amination. However, there are few studies on the reduction of aliphatic-nitro compounds because many byproducts are generated; mild reduction reaction conditions are required for this kind of substrate. In our research, we investigated the reduction of nitroalkane in depth and explored a way to selectively reduce aliphatic nitro compounds to amines.

1.3. Synthesis of Biomass-Derived Amines

Taking advantage of low cost and environmentally friendly procedures, we are interested in the synthesis of biomass-derived amines for preparing renewable polymeric materials. The major biomass feedstock includes carbohydrates, lignin, oil & fats, chitin, and protein (Figure 3).[2] Chitin and protein are nitrogen-containing compounds and the other biomass feedstock are non-nitrogen-containing compounds. Figure 3 shows examples of different categories of biomass materials. The alcohols and carbonyl compounds such as ethylene glycol and hydroxymethylfurfural (HMF) are derived from cellulosic biomass. An example of a phenolic carbonyl compound is 3-hydroxy-4-methoxybenzaldehyde, readily derived from lignin.

A major goal of our research group is the conversion of renewable biomass to diamines. We have developed new synthetic methodologies to convert lignocellulosic biomass to amines using different protocols and these will be discussed in the following chapters.

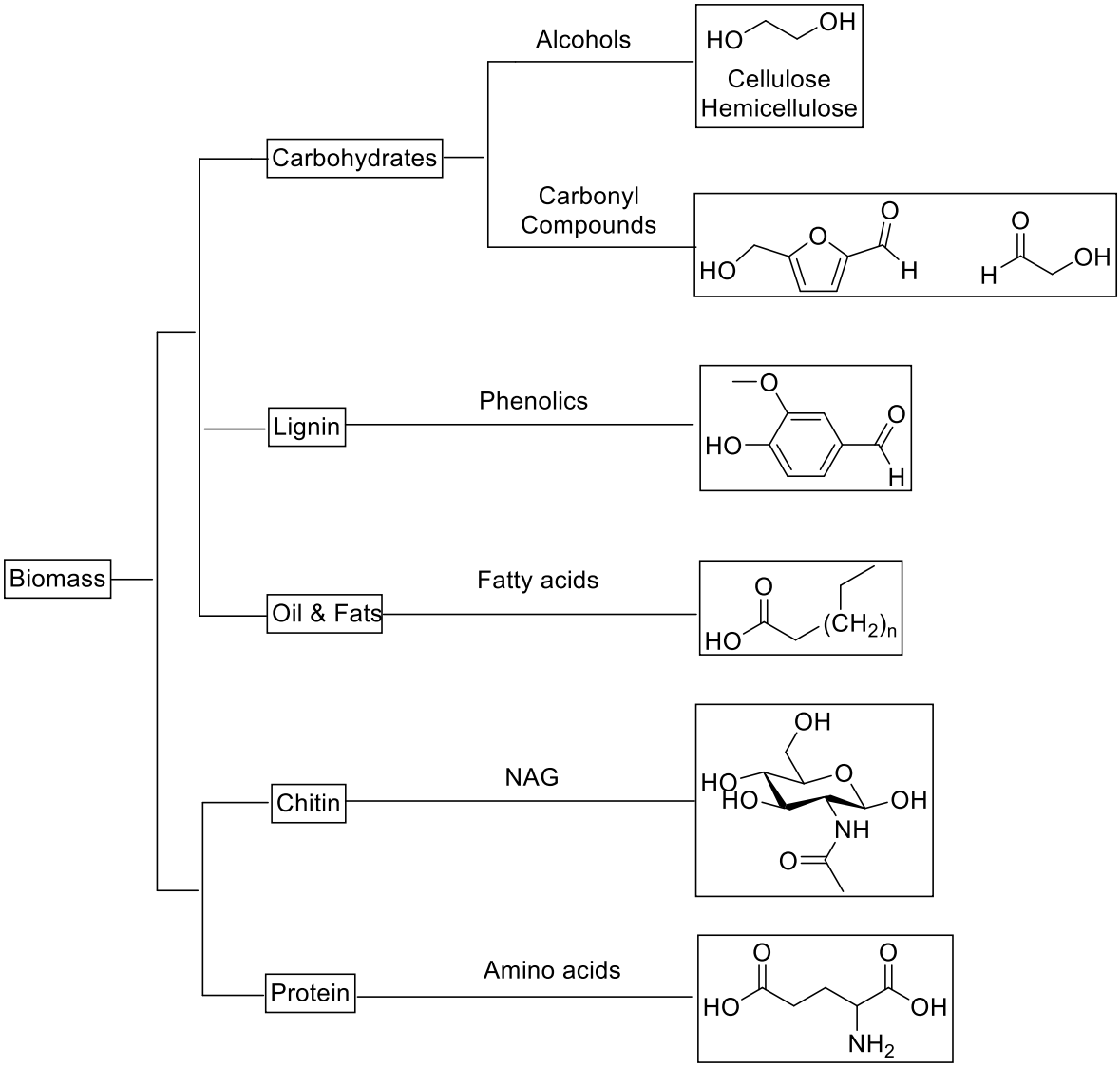
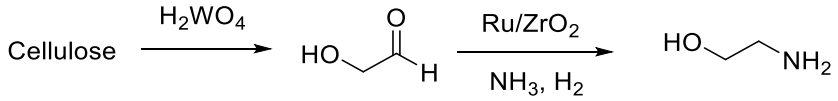


Figure 3. Summary of biomass platform molecules.

1.3.1. Synthesis of Biobased Amines by Reductive Amination

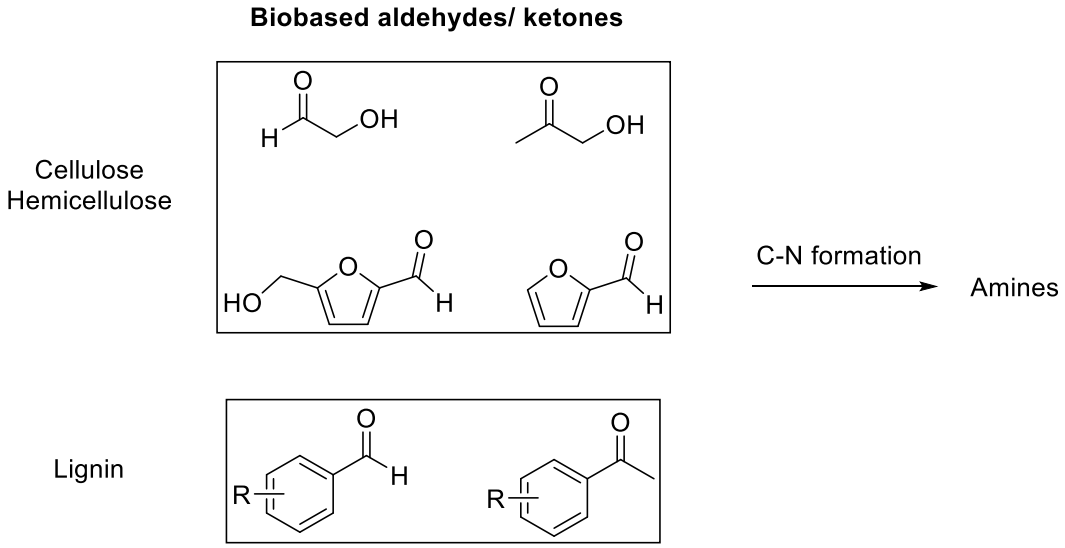
Liang's group developed a two-step route to convert cellulose to ethanolamine (Scheme 6).[17] The first step was to hydrolyze cellulose to glycolaldehyde using tungstic acid solution (H_2WO_4). The second step reduced the aldehyde functional group to the primary amine by ruthenium catalyst that was supported by zirconium dioxide (ZrO_2). They also conducted a series of optimization reactions including different metal catalysts, temperature, and pressure for hydrogenation. Finally, they concluded that the Ru/ZrO_2 catalyst should be pre-reduced at 150 °C.

The optimized reaction temperature was 75 °C and the pressure was 3.0 MPa H_2. Under these conditions, the yield of ethanolamine was 83%, which is 30% higher than the original yield.



Scheme 6. Direct conversion of cellulose to hydroxylamine.

They also applied the same method to other biomass substrates including aldehydes and ketones. Scheme 7 shows examples of aldehydes and ketones derived from cellulose, hemicellulose, and lignin and their conversion to amines.

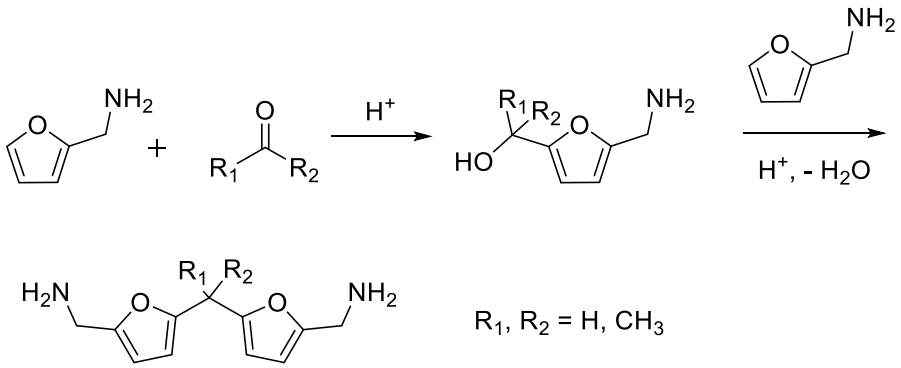


Scheme 7. Examples of primary amines from biobased aldehydes and ketones.

1.3.2. Synthesis of Biobased Diamines from Furfurylamine

Scheme 8 shows the reaction scheme for the synthesis of diamines from furfurylamine.[18] The condensation reaction occurs when furfurylamine is mixed with carbonyl compounds under acidic conditions. Furfurylamine is an electron-rich furan and undergoes Friedel-Crafts alkylation at C-5. The reported procedure involves the reaction of furfurylamine with carbonyl compounds in the presence of an acid catalyst. The reactions work well dialkyl ketones and are less effective

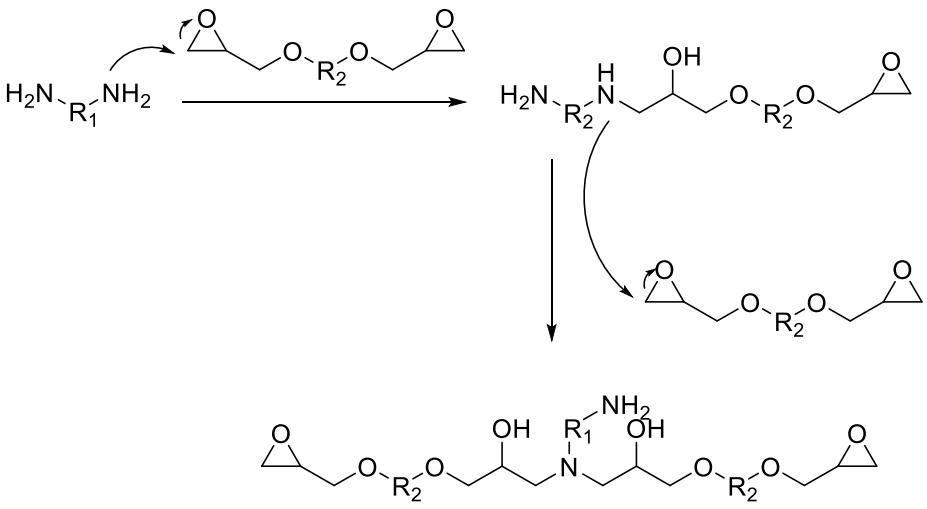
aromatic ketones. Reactions with aldehydes are low yielding but there are reports of successful reactions using alternative conditions.



Scheme 8. Synthesis of biobased diamines from furfurylamine.

1.4. Application of Diamines

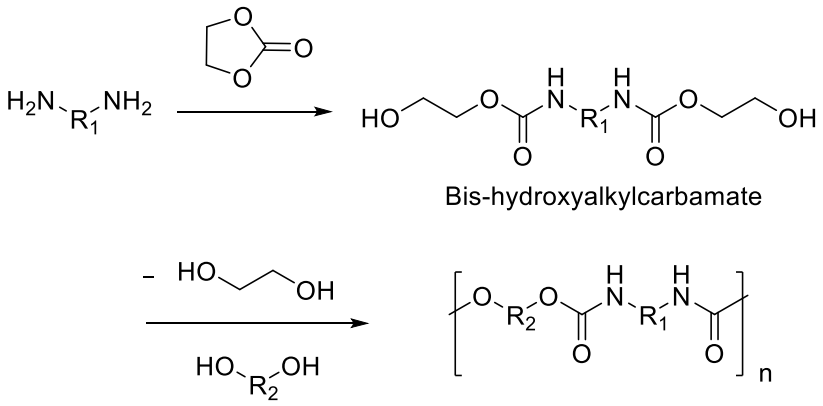
Diamines are excellent precursors for the synthesis of epoxy resins. Diamines are also useful components as hardeners for epoxy resins and could cure the epoxy precursor to generate epoxy-amine resins. The epoxy resin has good chemical and mechanical properties and it is good material for thermosets that makes it widely applicable in coatings. The mechanism for preparing epoxy resin is shown in Scheme 9.[19] At first, the amine group attacks the epoxy ring. A hydroxyl group is formed after the ring opening step. Secondly, the secondary amine formed in the first step attacks another epoxy ring and results in crosslinked compounds.



Scheme 9. Example of diamine application in epoxy resin.

Diamines are also good precursors for the synthesis of non-isocyanate polyurethanes (NIPUs). Polyurethanes (PUs) are used in our daily lives as raw materials for construction, insulation, and mattresses. PUs are commonly prepared from isocyanates and alcohols. However, the precursor of isocyanates, phosgene, is very harmful to both the environment and humans. Thus, the synthesis of NIPU has been investigated to solve the potential issue of using PUs.

Dyer and Scott reported a protocol for the synthesis of polyurethanes from ethylene carbonate and primary diamines in 1957 (Scheme 10).[20] The ring opening of the carbonate by the amine resulted in the formation of hydroxyalkylcarbamates. The hydroxyalkylcarbamates on heating with a polyol in the presence of barium oxide or zinc borate at 150 °C under vacuum, loses ethylene glycol to form polyurethanes. Thus, diamines are important in the synthesis of polymer compounds.



Scheme 10. Application of diamine in NIPU synthesis.

1.5. Objective

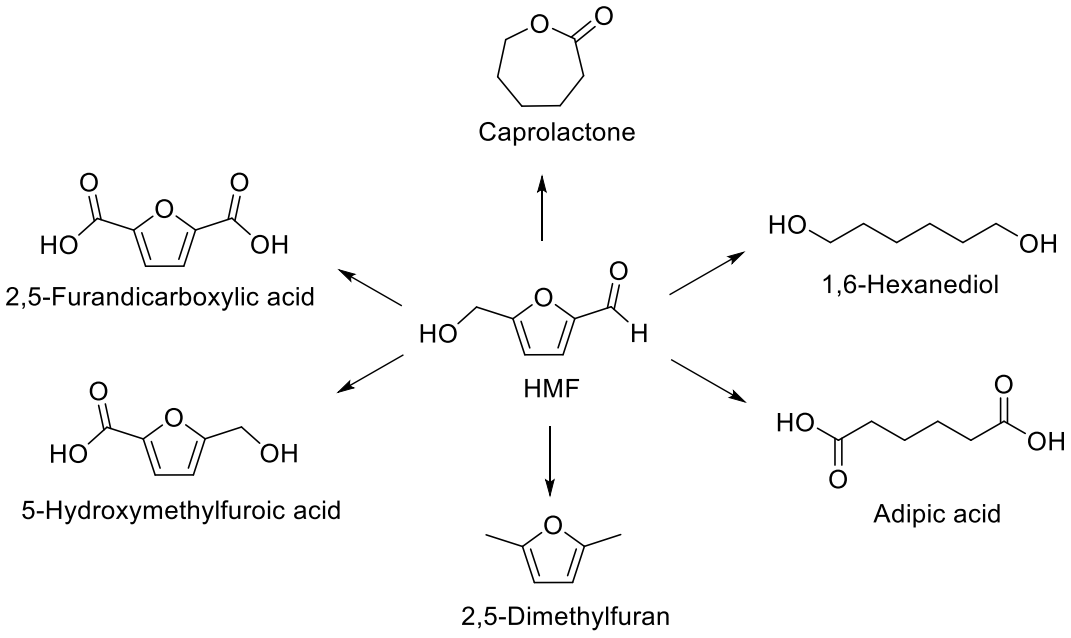
According to the United States Environmental Protection Agency, there are 12 principles of Green chemistry: prevent waste, maximize atom economy, design less hazardous chemical syntheses, design safer chemicals and products, use safer solvents and reaction conditions, increase energy efficiency, use renewable feedstocks, avoid chemical derivatives, use catalysts and not stoichiometric reagents, design chemicals and products to degrade after use, analyze in real time to prevent pollution, and minimize the potential for accidents.

To satisfy the requirements of green chemistry, our group focus is on the synthesis of biobased diamines and the application as excellent precursors of non-isocyanate polyurethanes (NIPUs). We have developed three different methods for accessing biobased NIPU precursors. In the first method, we have carried out chain elongation of 2,5-diformylfuran by the Henry reaction followed by reduction of the nitroalkene. Method two involved the condensation of furfurylamine with different ketones under acidic conditions. This protocol provides access to a series of bisfuran diamines in high yields. The diamines can be reacted with carbonates to access urethane diols, precursors of polyurethanes. We have also developed a novel method for accessing biscarbamates directly from dialdehydes, which is a key precursor for NIPU as well. Results from these studies will be discussed in the following chapter.

CHAPTER 2. SYNTHESIS OF AMINES FROM CELLULOSE AND HEMICELLULOSE-DERIVED MATERIALS

2.1. Introduction

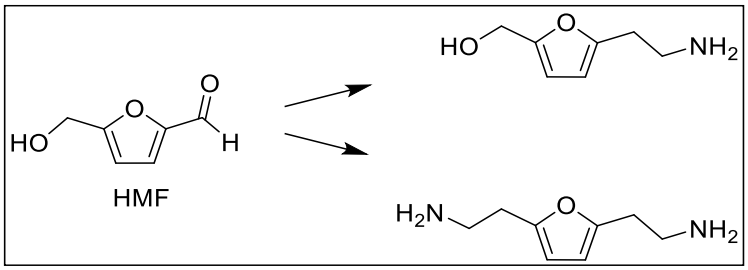
Our group's research focus is on developing new applications for biomass-derived monomers. A key feedstock material we have used extensively is 5-hydroxymethylfurfural (HMF), which is readily available from cellulose. Currently, there are several commercial sources for HMF. HMF is an important platform chemical for the industry because it affords access to many biomass molecules (Scheme 11). For example, HMF can be oxidized to 2,5-furandicarboxylic acid and 5-hydroxymethylfuroic acid. HMF can also be ring opened to generate adipic and levulinic acids.[21]



Scheme 11. Derivatives from HMF.

The work described in this chapter was designed to afford biobased amines from cellulose-derived aldehydes by environmentally friendly chemical methodologies. We chose selective reduction and reductive amination as the synthetic methods for the preparation of the desired amines. Scheme 12 shows the target amines. The Henry reaction and chemoselective

hydrogenation were applied to HMF as a technique for the preparation of amines. In a homologation reaction, one carbon was inserted between the aldehyde moiety and the furan ring. We also found that this technique was applicable to prepare diamines from diformylfuran (DFF), which is an excellent precursor for the preparation of non-isocyanate polyurethanes (NIPU).



Scheme 12. Target aminoalcohol and diamine from HMF.

In this chapter, three synthetic routes including the Henry reaction and Friedel-Crafts alkylation techniques to biobased diamines will be discussed in detail. The Henry reaction route to amines will be discussed in the beginning. Firstly, the Henry reaction was applied to symmetric, unsymmetrical and protected aldehyde substrates. Secondly, multiple reduction techniques were explored to improve the yield of amine products as well as decrease the expense of reagents. Optimization of the transfer hydrogenation methodology by Hantzsch ester reagent was also studied for understanding the reduction reaction. Finally, the synthesis of amines from nitroalkane was investigated.

2.2. Aldehyde Substrates for The Henry Reaction

The first step in the synthesis of amines is the conversion of the aldehydes to nitroalcohols by the Henry reaction followed by acid-mediated dehydration, following well-established literature protocols.[22] Both temperature and pH value had strong effects on the yields of products. The stoichiometric equivalent of nitromethane differed with the number of aldehyde moieties.

We designed a series of substrates to study the Henry reaction in depth. Figure 4 shows the structures of aldehyde substrates used in our study. Benzaldehyde (**1a**) and furfural (**1b**) were chosen to understand the influence exerted by the furan ring as in HMF (**1c**) versus the phenyl ring in benzaldehyde on the outcome of the reaction. We also designed HMF (**1c**) derivatives with hydroxyl group protected by benzoyl chloride (**1d**), acetic anhydride (**1e**), and tert-butyldimethylsilyl chloride (**1f**). Masking hydroxyl groups decreased the polarity of these substrates and facilitated purification. In addition, the protected HMF (**1d-f**) were much less water-soluble and resulted in improved yields. Finally, we investigated benzene dialdehydes and furan-based dialdehydes as substrates for the synthesis of diamines.

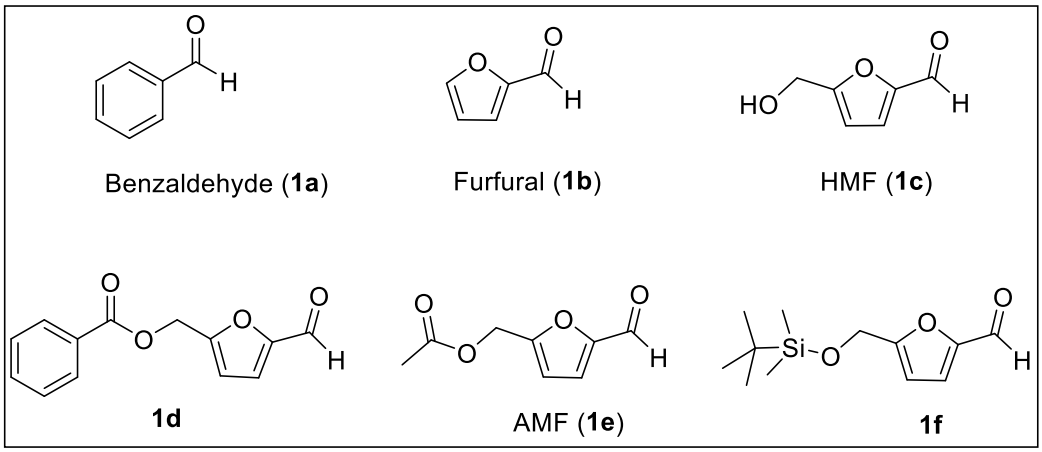
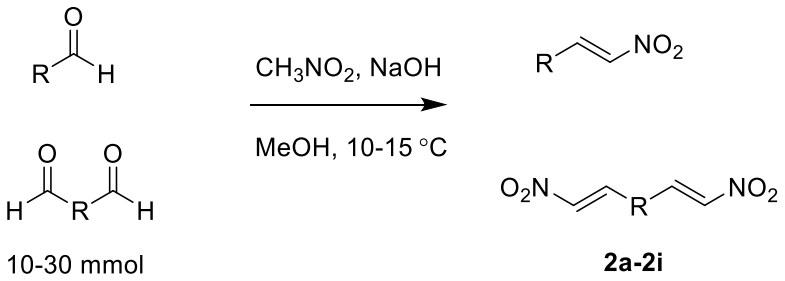


Figure 4. Structures of aldehyde substrates for the Henry reaction.

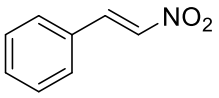
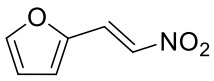
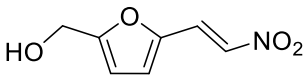
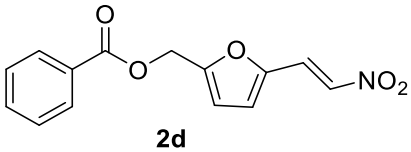
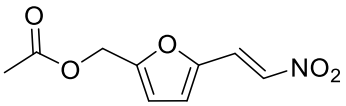
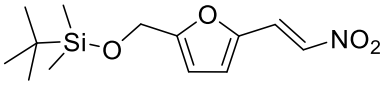
The Henry reaction is shown in Scheme 13 and involves the treatment of an aldehyde with nitromethane in the presence of a base. The reactions were carried out at below room temperature and monitored by thin layer chromatography. Pure products were isolated after column chromatography.



Scheme 13. Reaction condition of the Henry reaction.

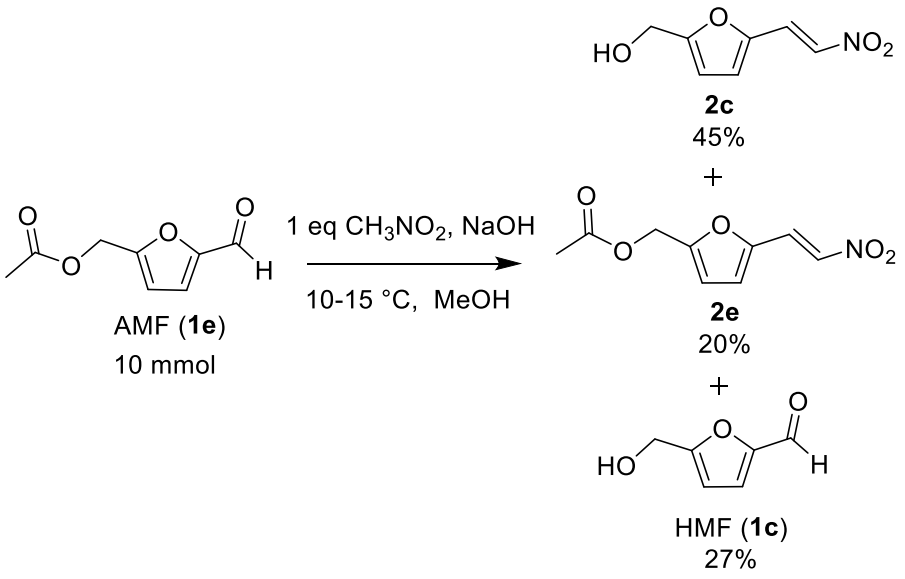
Table 1 provides details of the reaction outcome using various aldehydes in the Henry reaction. It includes the equivalents of nitromethane used and the isolated yield of nitroalkene products. Reaction with benzaldehyde (**1a**) gave the highest yield for an unsymmetrical nitroalkene product **2a** (entry 1, Table 1). This is most likely due to the stability of the phenyl ring as compared to the more reactive furan ring. The furan-based substrates are more sensitive to acid or base condition and decomposed. Reaction with furfural (**1b**) and HMF (**1c**) were also efficient and gave the products in good yield (entries 2 and 3, Table 1). Three hydroxyl protected HMF derivatives (acetate, benzoate and TBDMS ether) were also evaluated in the Henry reaction. Reaction with the benzoyl protected HMF derivative **1d** gave modest yield of **2d** (entry 4, Table 1). In contrast, both the acetate and silyl protected HMF derivatives **1e** and **1f** gave poor yields of **2e** and **2f** (entries 5 and 6, Table 1).

Table 1. Aldehyde substrates study for the Henry reaction.

Entry	Substrate	CH_3NO_2 (eq)	Product	Yield (%)[a]
1	Benzaldehyde (**1a**)	1.0	 **2a**	76
2	Furfural (**1b**)	1.0	 **2b**	68
3	HMF (**1c**)	1.0	 **2c**	70
4	**1d**	1.0	 **2d**	51
5	AMF (**1e**)	1.0	 **2e**	20
6	**1f**	1.0	 **2f**	10

[a] Yields are for the pure isolated product after column chromatography.

The acetate and silyl ether protecting groups in substrates **1e** and **1f** were incompatible with the reaction or work up conditions. For example, there were two byproducts using AMF (**1e**) as the starting aldehyde in the Henry reaction due to hydrolysis. The target product **2e** was produced in 20% yield, the deprotected nitroalkene in 45% yield, and 27% of HMF (Scheme 14).



Scheme 14. The result of the Henry reaction with acetylated HMF.

The Henry reaction of substrates **1d** and **1f** faced the same problem. Both the benzoate derivative of HMF **1d** as well as the product nitroalkene **2d** from the Henry reaction was base sensitive resulting in multiple products. During the Henry reaction, the base was added to the reaction while cooling the reaction vessel in an ice bath and keeping the reaction temperature under 0 °C. Even under these mild conditions, the reaction gave low yields. The Henry reaction with dialdehydes was examined next for the synthesis of diamines. Figure 5 shows the structure of the three dialdehyde substrates; terephthaldehyde (**1g**), diformylfuran (DFF, **1h**), and 5,5′(oxy-bis(methylene)) bis-2-furfural (OBMF, **1i**).

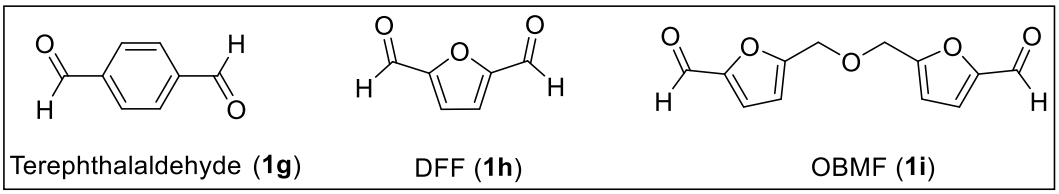
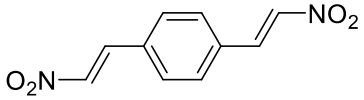
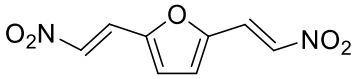
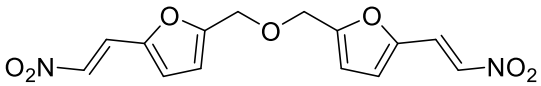


Figure 5. Structure of dialdehyde substrates for the Henry reaction.

These reactions used a slight excess of nitromethane for complete conversion. In general, the functionalization of both aldehyde groups was rather difficult. The desired product was

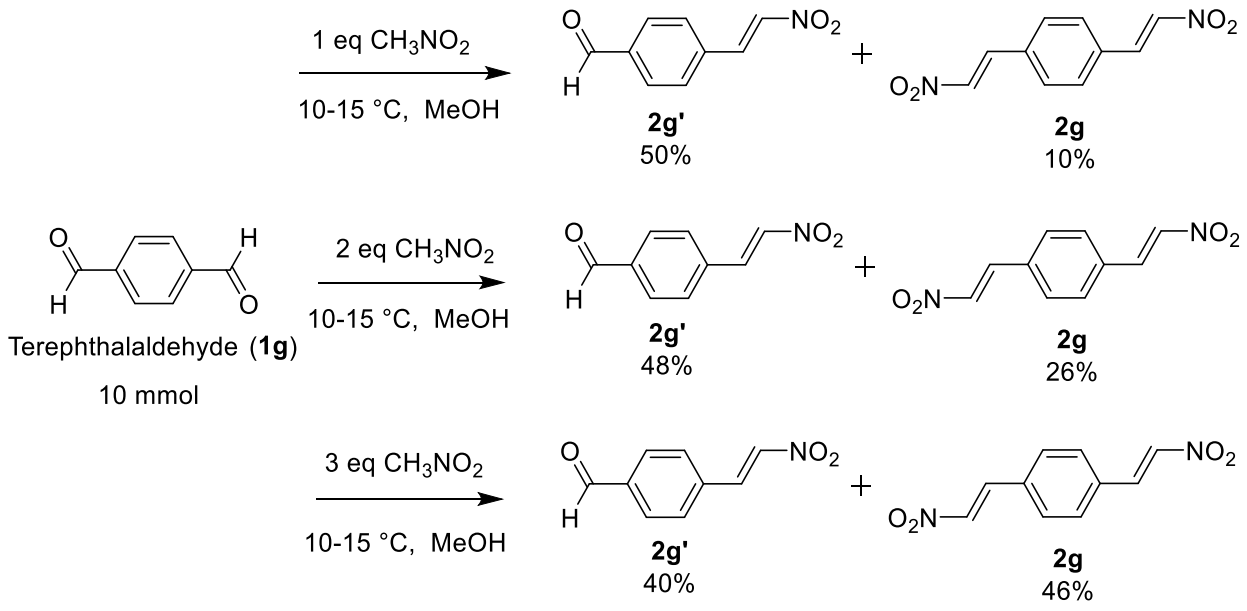
contaminated with the mono functionalized product as well as unreacted starting material. Of the three different dialdehydes investigated, DFF (**1h**) gave the highest yield for the bisnitroalkene (entry 2, Table 2). On the other hand, reaction with terephthaldehyde (**1g**) (entry 1, Table 2) and OBMF (**1i**) (entry 3, Table 2) were not efficient. The yields for the bisnitroalkenes were relatively low due to the poor selectivity in the Henry reaction of dialdehydes (46-50%).

Table 2. Dialdehyde substrates study for the Henry reaction.

Entry	Substrate	CH_3NO_2 (eq)	Product	Yield (%)[a]
7	Terephthalaldehyde (**1g**)	2.1	 **2g**	68
8	DFF (**1h**)	2.1	 **2h**	46
9	OBMF (**1i**)	2.1	 **2i**	50

[a] Yields are for the pure isolated product after column chromatography.

Scheme 15 shows the yields of the target product **2g** and byproduct **2g'** with 1-3 equivalents of nitromethane. The highest yield for product **2g** was 46% on a 2 g scale. The ratio of the two products was around 1:1 under the optimized condition (using 3 eq of nitromethane).



Scheme 15. Results from the Henry reaction with symmetric dialdehydes.

To carry out the Henry reaction effectively, we examined the solubility of the bisnitroalkene **2h** in different solvents at two different temperatures. Six different solvents were investigated: toluene, ethyl acetate, methanol, acetone, THF, and DMF. Nitroalkene **2h** was either insoluble or soluble to a limited extent at room temperature in all the six solvents. Compound **2h** was mostly insoluble in toluene, ethyl acetate and methanol at 60 °C but was soluble in Acetone, THF, and DMF at the same temperature. Based on these results we tried THF for the Henry reaction for DFF to improve the conversion by the better solubility of product **2h**. However, the nitro compound was hard to purify because the product emulsified with byproduct due to the interface between water and THF. In contrast, the product precipitates out during the Henry reaction with MeOH and results in higher yield.

In conclusion, we found that protection of the hydroxyl group was not preferable for the Henry reaction because hydrolysis was always observed. HMF (**1c**), DFF (**1h**), and furfural (**1b**) were the best substrates for the Henry reaction and gave good yields for the corresponding nitroalkenes.

2.3. Hydrogenation of Nitroalkene Substrates by Various Reagents

We have investigated the reduction of nitroalkenes to nitroalkanes using a wide range of reagents (Table 3). We tried multiple reducing agents such as zinc/acid, iron/acid, sodium borohydride and multiple catalysts for hydrogenation such as Pd/C, Raney Ni, and $RhCl(PPh_3)_3$.[23–27] However, these common procedures for reducing aromatic nitroalkenes did not work well for the furan containing substrates. Multiple products were generated making it difficult to purify and characterize. We identified and isolated nitroalkanes after reduction using a GC-MS technique.

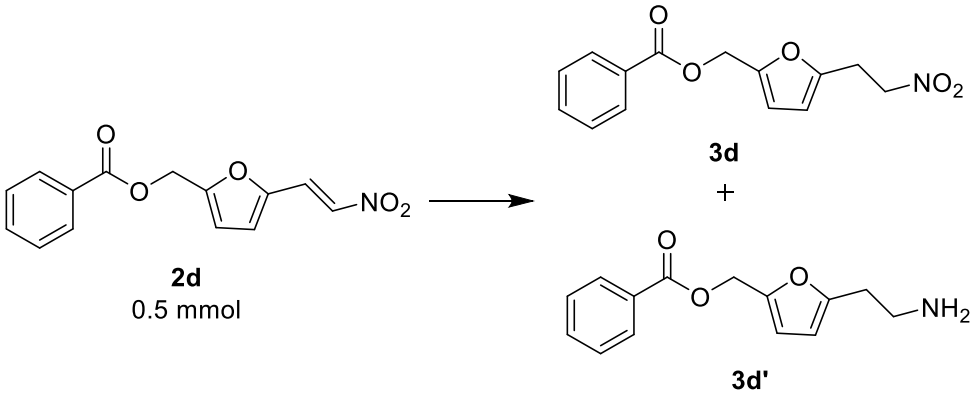
We used GC-MS to monitor the progress of reduction because it showed the conversion of substrates and products as the reaction proceeded. A thin layer chromatography (TLC) technique was problematic because amines decomposed on exposure to silica gel. Another problem was that the polarity of nitroalkanes and nitroalkenes were quite similar and the R_f values were indiscernible. Thus, it was necessary to track the progress of reduction by GC. We also applied GC-MS to analyze results because multiple products were generated after reduction and it was challenging to analyze by NMR. When using GC-MS, the compounds were separated by different boiling points and the retention times for different for easy analysis. The mass fragment was shown for different peaks. The mass of different products in the reaction mixture was also analyzed. In addition, it was convenient to make a comparison of the conversion for reaction optimization.

Iron and zinc metal combined with acids (such as hydrochloric acid, ammonium chloride or acetic acid) is a well-established procedure for the reduction of nitroalkenes. Reduction of **2d** under the above conditions led to more than four products. We also explored tin(II) chloride as a reducing agent which also gave mixtures consisting of amines, nitroalkanes, oximes, and imines.

After the failure of metal/acid conditions to provide a clean product, we investigated alternative mild methods for reduction and these results are shown in Table 3. Catalytic

hydrogenation of **2d** using Pd/C under 1 bar H_2 gave 30% yield of the desired nitroalkane product (entry 1, Table 3). Reduction using sodium borohydride gave **3d** in 11% yield (entry 2, Table 3). Other reductions under mild conditions, such as Raney Ni/HCOOH or 5% $RhCl(PPh_3)_3$ under 1 bar H_2 were not successful in providing the desired product (data not shown).

Table 3. Selective hydrogenation of substrate **2d**



Entry	Reagent	Solvent	Temperature (°C)	Conversion of **3d** (%)[a]
1	Pd/C, 1bar H_2	THF/EtOH	RT to 50	30
2	$NaBH_4$	THF/EtOH	RT	11

[a] Conversion is calculated by GC integration.

The most likely reason for the low yield under catalytic hydrogenation conditions was that the catalyst was poisoned. The failure to obtain even modest yields for the desired product under standard reaction conditions led us to consider alternate reductions using green chemical methods preferably amenable to recycling. Towards this end, we undertook a study to evaluate Hantzsch ester as a reducing agent for the conversion of nitroalkene to nitroalkane.

2.4. Introduction to Hantzsch Ethyl Ester (HEH)

Hantzsch ethyl ester (HEH) is a well-known biomimetic analog of NADH or NADPH, which are well known reducing reagents in biosynthetic reactions in plants and animals (Figure 6).[28] Hantzsch ethyl ester (HEH) as a reagent is stable, inexpensive, and has the potential for recycling.

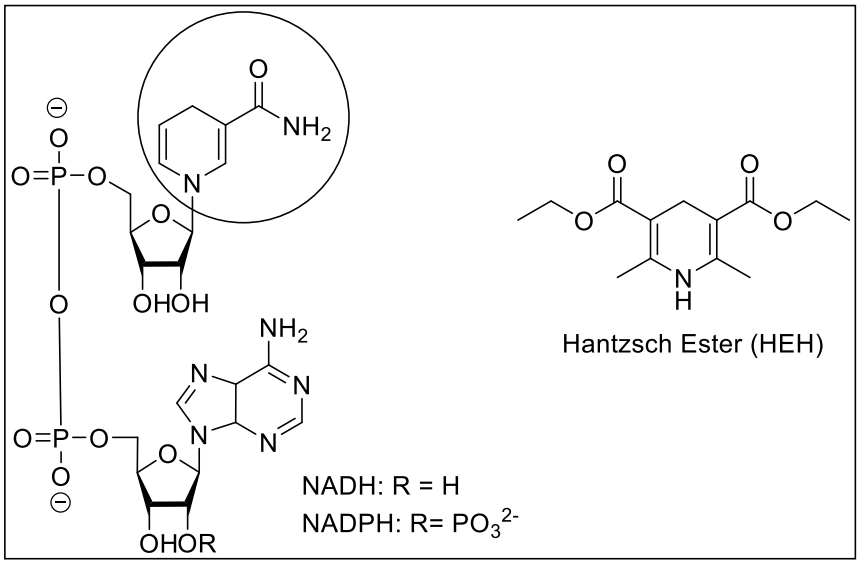


Figure 6. Structure of NADH, NADPH, and Hantzsch ester.

Hantzsch ester is an excellent reagent for the reduction of C-C double bonds.[29] It can selectively reduce carbon-carbon double bond in α,β-unsaturated aldehydes, ketones, esters as well as nitroalkenes. Furthermore, the carbonyl, nitro, cyanide, sulfonyl, and sulfinyl groups are inert to HEH.[30] Hantzsch ester is a simple and safe way to chemoselectively reduce nitroalkene without the need for expensive reagents and pressurized conditions.

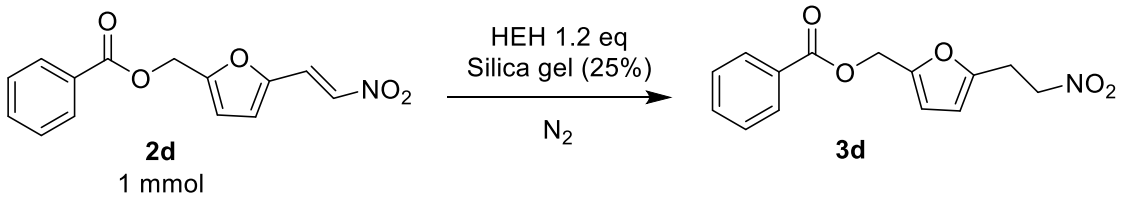
2.5. Hydrogenation of Nitroalkene to Nitroalkane by HEH

We have developed a protocol based on literature precedents and studied the selective hydrogenation of nitroalkenes by HEH in depth (Table 4).[31] The optimization of variables such as

solvent, temperature, and reaction time was investigated. Table 4 shows the conversion calculated by GC and the corresponding isolated yields.

Previous researchers used benzene as a solvent because most of the organic compounds dissolve well in it and the boiling point is relatively high. However, it is too hazardous to work with. We evaluated different solvents for the reduction of benzoate **2d** using 1.2 equivalents of HEH and silica gel and these results are shown in Table 4. Reduction with benzene as a solvent gave the reduced product in modest yield (entry 1, Table 4). Toluene was a better solvent for the reduction due to similarities with benzene and its low toxicity. Reduction in toluene at 70 °C gave the product in good yield (entry 3, Table 4). We investigated a combination of solvents as well because toluene was difficult to remove due to its high boiling point. A combination of toluene and ethyl acetate was a poor solvent because the conversion of the substrate was low at 40-50 °C (entry 4, Table 4). A combination of toluene and THF was the best solvent system for the reduction (entry 5, Table 4). The optimized temperature was 75 °C and the reaction time was 48 h since the substrate had not converted completely in 20 h. We tried to use 2M HCl to remove pyridine byproduct, however, the yield decreased due to hydrolysis.

Table 4. Optimization of selective hydrogenation of substrate **2d**.



2d
1 mmol

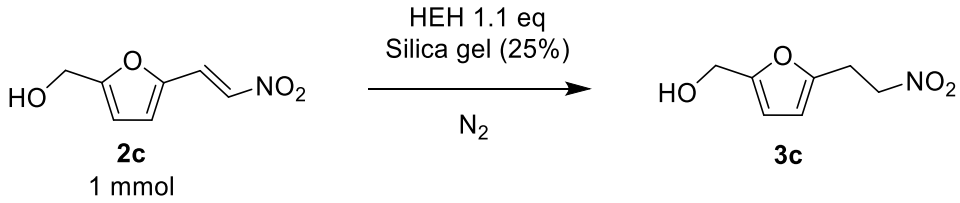
3d

Entry	Solvent [a]	Temperature (°C)	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	Benzene	60	20	87	58
2[d]	Toluene	60	48	98	37
3	Toluene	70	20	86	76
4	Toluene/EA	40-50	30	47	-
5	Toluene/THF	75	48	100	80

[a] The ratio of combine solvent is 1:1, the concentration of substrate is 0.1mmol/mL.
[b] Conversion is calculated by the percentage of integration in GC.
[c] Yield is for the pure isolated product after column chromatography.
[d] Use 2M HCl to remove byproduct.

We also investigated the HEH reduction in detail using substrate **2c,** a compound containing an unprotected hydroxyl group (entries 1-7, Table 5). Benzene (entry 1, Table 5) and toluene (entry 2, Table 5) as a solvent were both effective in the reduction. Reaction in the absence of silica gel was not effective (entry 3, Table 5). Silica gel acts as an acid catalyst and thus is essential for the reaction. If the temperature was 80 °C, the substrate decomposed (entry 5, Table 5). A mixed solvent system of toluene/THF at 75 °C was optimal for the reduction (entry 7, Table 5). The reaction time also impacted the efficiency of the reaction. If the reaction time was too short, leftover starting material made purification difficult. Thus, the optimized reaction time was 48 h.

Table 5. Optimization of selective hydrogenation of substrate **2c**.



2c
1 mmol

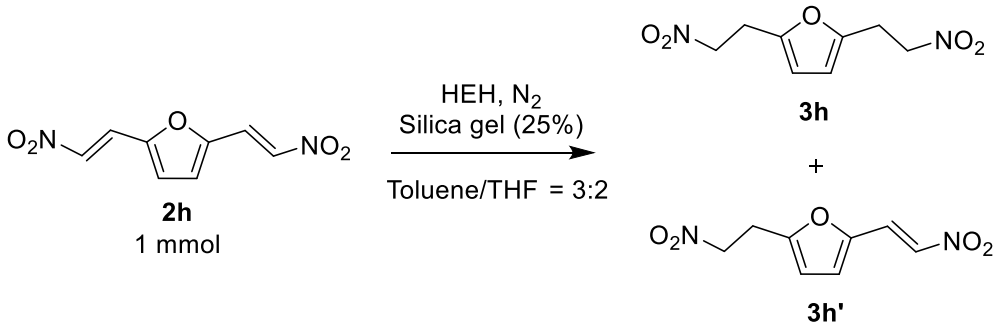
3c

Entry	Solvent [a]	Temperature (°C)	Time (h)	Conversion (%)[b]	Yield (%)[c]
1	Benzene	60	20	85	76
2	Toluene	60	20	80	76
3[d]	Toluene	60	30	16	-
4	Toluene	70	48	100	74
5	Toluene	80	48	100	70
6	Toluene/EA	50	30	79	72
7	Toluene/THF	75	48	100	78

[a] The ratio of combine solvent is 1:1, the concentration of substrate is 0.1mmol/mL.
[b] Conversion is calculated by the percentage of integration in GC.
[c] Yield is for the pure isolated product after column chromatography.
[d] This reaction conducted without Silica gel.

We also optimized the HEH reduction of bisnitroalkene **2h** and these results are presented in Table 6. For this reaction, we investigated the amount of HEH ester required for optimal conversion to the desired bisnitroalkane product using toluene/THF as the solvent (entries 1-4, Table 6). The optimal amount of HEH was 5 equivalents (entry 4, Table 6) and under these conditions, no mono reduction product was observed.

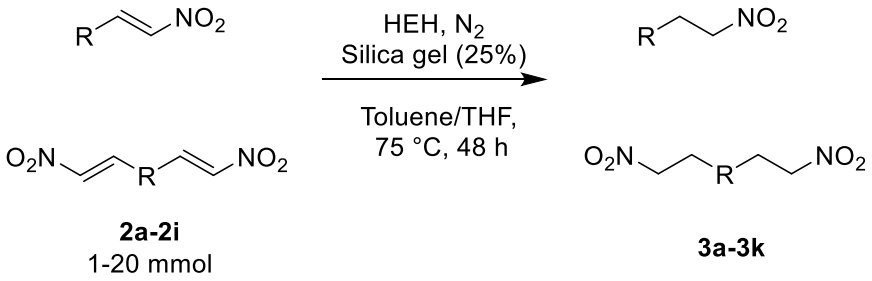
Table 6. Optimization of selective hydrogenation of substrate **2h**.



Entry	Amount of HEH (eq)	Temperature (°C)	Time (h)	Yield of **3h** (%)[a]	Yield of **3h'** (%)[a]
1	1.1	65	48	0	60
2	2.4	65	48	28	27
3	3.5	75	48	68	0
4	5.0	75	48	70	0

[a] Yields are for the pure isolated product after column chromatography.

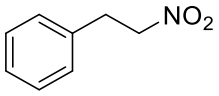
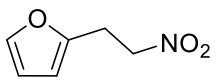
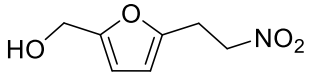
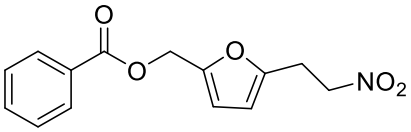
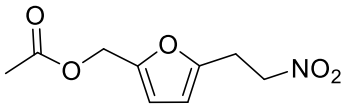
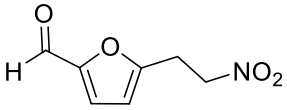
Scheme 16 shows details of the HEH reduction. The nitroalkene was treated with HEH reducing reagent in the presence of silica gel. The stoichiometric equivalent of HEH differed with the number of nitroalkene moieties. The reactions were carried out at 75 °C and monitored by thin layer chromatography as well as GC-MS. Pure products were isolated after column chromatography.



Scheme 16. The HEH reduction reaction.

The HEH reduction has a broad substrate scope and is very chemoselective. Table 7 shows the structures of nitroalkane products, the amount of HEH and the isolated yields of the reduced products. Almost all the substrates gave excellent yield in the reduction (entries 1-6, Table 7). The conversion of the substrates was nearly 100% as shown by GC-MS. The isolated yields were slightly lower than 100% after purification. We also investigated the selectivity of HEH reduction in the formation of **3j**. The starting material **2j** containing a nitroalkene and an aldehyde was obtained by the oxidation of the primary hydroxyl group in **2c** by MnO_2 (entry 6, Table 7). Overall, these experiments clearly demonstrate that HEH reductions are chemoselective and proceed in good yields.

Table 7. Synthesis of nitroalkanes by selective hydrogenation.

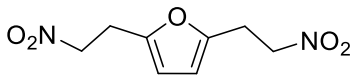
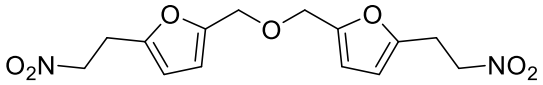
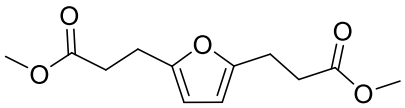
Entry	Substrate	HEH (eq)	Product	Yield (%)[a]
1	**2a**	1.1	 **3a**	83
2	**2b**	1.1	 **3b**	85
3	**2c**	1.1	 **3c**	78
4	**2d**	1.1	 **3d**	80
5	**2e**	1.1	 **3e**	83
6	**2j**	1.1	 **3j**	72

[a] Yields are for the pure isolated product after column chromatography.

Since one of the goals for the thesis is the synthesis of biobased diamines, we next examined the reduction of bisnitroalkenes and these results are shown in Table 8. Reduction of bis-nitroalkenes was less efficient than reactions of mononitroalkenes (entries 1 and 2, Table 8). Lower yields were obtained because reaction times were longer than 48 h and also because of decomposition of the substrate. The yield for **3i** (entry 2, Table 8) is relatively low because the ether function group is not stable under high-temperature conditions. The HEH reductions are quite chemoselective. The double bond in substrate **2k**, an unsaturated ester could not be reduced by

HEH (entry 3, Table 8), which suggests that alkene attached to an ester has lower reduction potential than nitroalkenes.

Table 8. Selective hydrogenation with different dinitroalkanes.

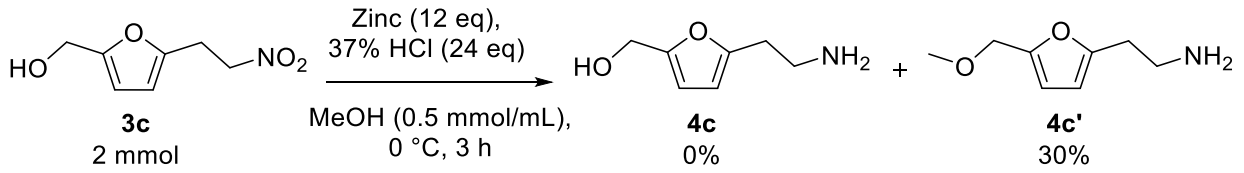
Entry	Substrate	HEH (eq)	Product	Yield (%)[a]
1	**2h**	3.5	 **3h**	70
2	**2i**	3.5	 **3i**	62
3	**2k**	3.5	 **3k**	0

[a] Yields are for the pure isolated product after column chromatography.

We also studied conjugate reduction using CuCl/$NaBH_4$ at 0 °C which gave the desired product **3c** in 37% yield. Compared to sodium borohydride, the HEH was a better reagent for selective reducing nitroalkenes to nitroalkanes efficiently and economically.

2.6. Reduction of Nitroalkanes to Amines

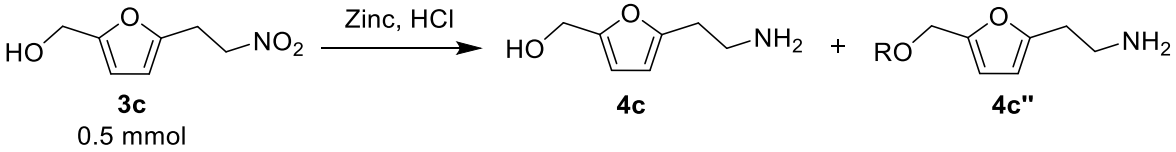
We examined different methods to reduce both furan-based nitroalkanes and phenyl nitroalkanes to amines. Catalytic hydrogenation using Pd/C and Raney Ni were not optimal with furan substrates. These methods generated multiple products, and which could not be identified. A report from Maresh's group, which reduced phenyl aliphatic nitroalkane to the amine was investigated.[32] Scheme 17 shows the reaction conditions for the reduction. Interestingly, the amine methyl ether **4c'** was formed in low yield and the desired amino alcohol **4c** was not formed because the solvent methanol was involved in the side reaction.



Scheme 17. Zinc reduction of nitroalkane in MeOH.

To avoid methylation, we tried many other solvents which are miscible with water (entries 1-7, Table 9). At first, we examined alternative alcohol solvents which are similar to methanol. Reactions with other alcohol solvents also gave ether products and the amount of the byproduct was dependent on the size of the alkyl group. Thus, linear primary alcohols gave more ether byproduct (entries 1-4, Table 9). In contrast, the reaction using i-PrOH as a solvent gave the desired product in good yield and lower amounts of the ether (entry 5, Table 9). Separation of the desired product from the ether byproduct was difficult. The amines decomposed during column chromatography on silica gel. We also investigated other solvents to replace alcohol, such as H_2O (entry 6, Table 9), and THF (entry 7, Table 9). THF was better than H_2O because it was easier to remove although the product was formed at a slightly lower yield.

Table 9. Optimization of solvent for zinc reduction.



3c
0.5 mmol

4c

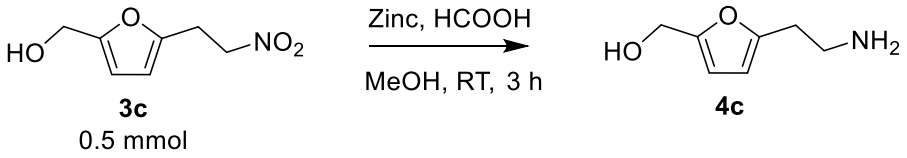
4c"

Entry	Solvent	Conversion of **4c** (%)[a]	Conversion of **4c''** (%)[a]
1	Methanol	0	R = CH_3 (90)
2	Ethanol	0	R = Et (80)
3	1-propanol	40	R = $CH_3(CH_2)_2$ (28)
4	Butanol	0	R = $CH_3(CH_2)_3$ (34)
5	i-PrOH	64	R = $(CH_3)_2CH$ (16)
6	H_2O	72	0
7	THF	58	0

[a] Conversion is calculated by the percentage of integration in GC.

Gowda's group reported a mild Zn/HCOOH procedure for the reduction of nitrobenzene to aniline.[33] Thus, we explored the use of HCOOH instead of HCl to improve the yield of desired amine product (Table 10). Under this condition, methylation not observed in methanol. Our results on the optimization of the amount of zinc and HCOOH is shown in Table 10. When a slight excess of zinc was used (1.2 eq), we recovered high yield of the starting material **3c**, and the yield of product **4c** was low (entry 1, Table 10). This suggests that the conversion was low when there was not enough reducing reagent zinc. The yield of the product improved with the use of excess zinc (entry 2, Table 10). The isolated yield of crude amine **4c** was 60% under optimized conditions (6 eq Zinc and 12 eq HCOOH) (entry 3, Table 10).

Table 10. Optimization of the zinc-acid amount.



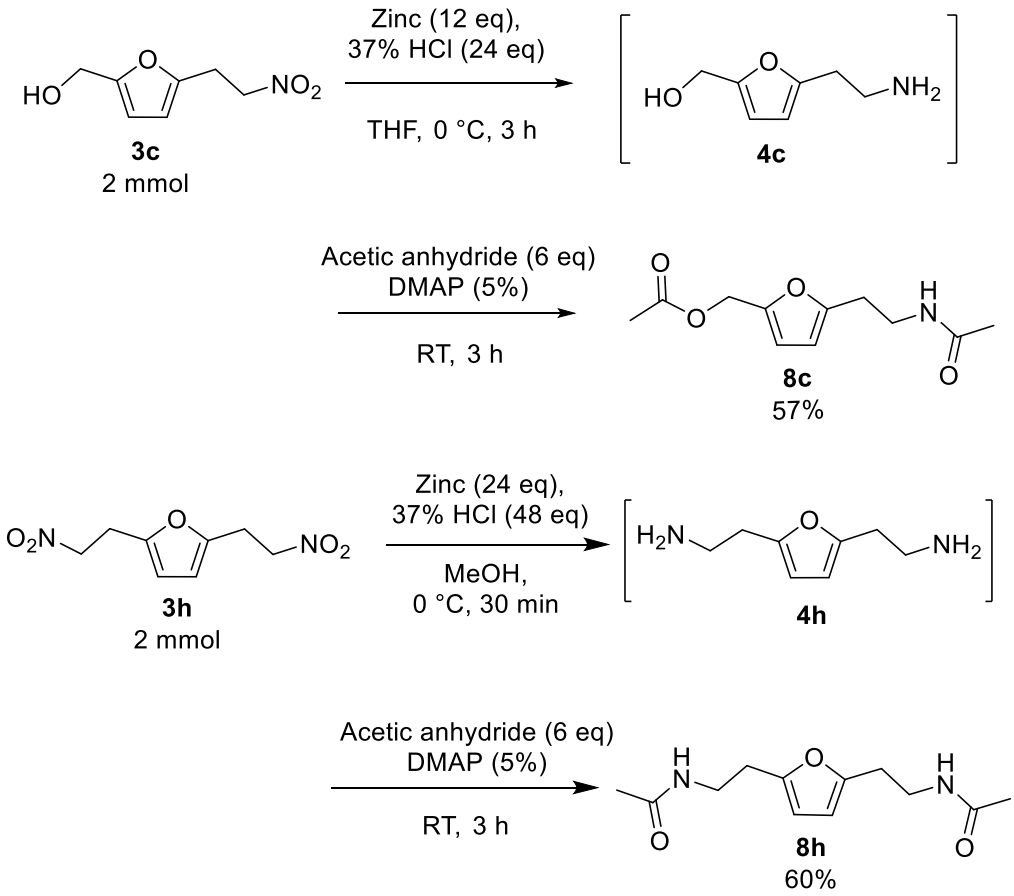
3c
0.5 mmol

4c

Entry	Amount of Zinc (eq)	Amount of HCOOH (eq)	Conversion of Product **4c** (%)[a]	Conversion of Substrate **3c** (%)[a]
1	1.2	12	16	65
2	6.0	12	72	3
3	12	24	60	0

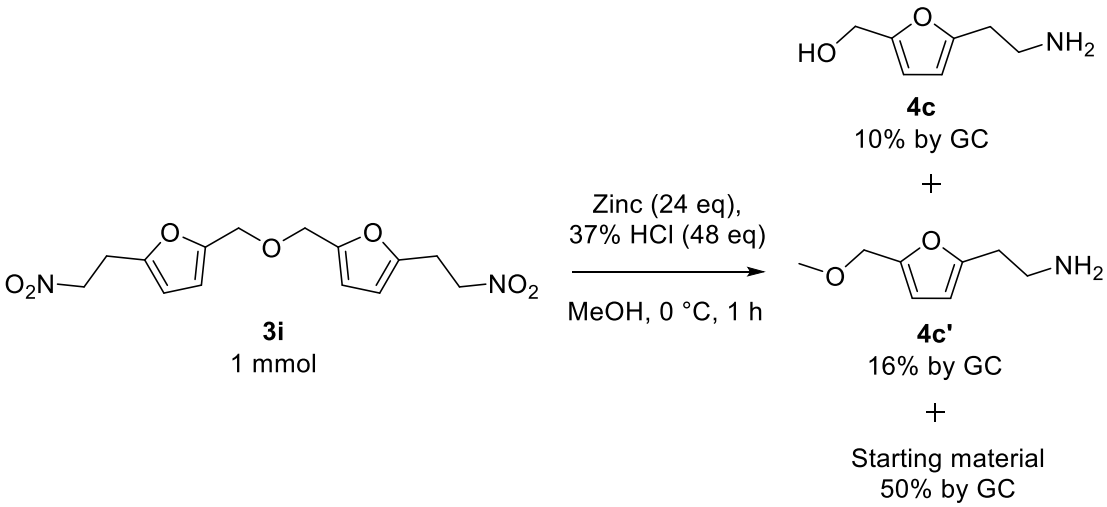
[a] Conversion is calculated by the percentage of integration in GC.

The optimized condition was also applicable to dinitro-compound **3h** (Scheme 18). Isolation and purification of the amino alcohol and the diamine were difficult. Thus, the crude reduction product was treated with acetic anhydride to form amides. Amides **8c** and **8h** were readily purified and isolated.



Scheme 18. Reaction conditions for amines synthesis.

The zinc reduction was not applicable to substrate **3i** because the ether functionality was acid sensitive and resulted in hydrolysis. In addition, most of the starting material was not converted (Scheme 19).



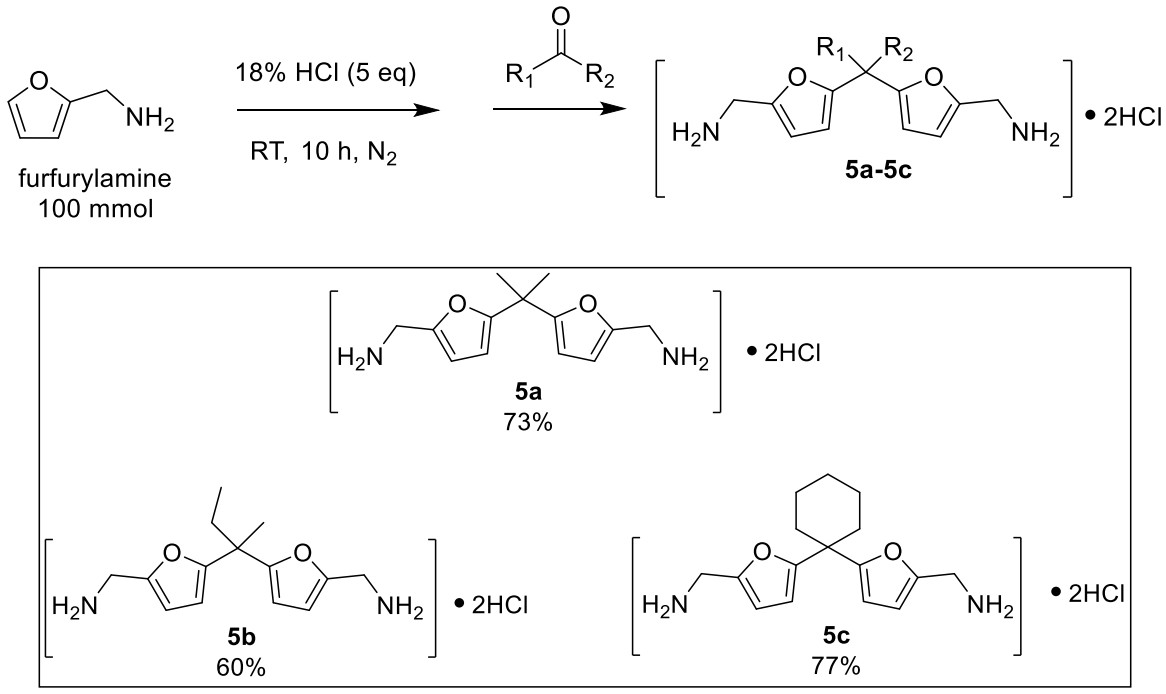
Scheme 19. Zinc reduction of substrate **3i**.

2.7. One-Step Synthesis of Diamines from Hemicellulose-Derived Aldehydes

To access bisfuran diamines with potential for varying the bridge substituents, we used another non-edible biomass source, such as hemicellulose-derived aldehydes. We applied Friedel -Crafts alkylation of furfurylamine, a kind of electrophilic aromatic substitution. Furfurylamine can be obtained from furfural by treatment with hydroxylammonium chloride followed by reduction.[12] The reagents for alkylation were hydrochloric acid and ketones which are inexpensive. In addition, the only byproduct was water which is environmentally friendly.

The direct application of literature protocols for diamine synthesis was unsatisfactory.[34] Ketones reacted rapidly with furfurylamine and competitive imine generation was a challenge. In addition, both the diamine products and corresponding chloride salt were very soluble in water. A modification of the reported procedure involved the conversion of amine to amine hydrochloride salt by the dropwise addition of HCl to amine under nitrogen and stirring for 10 h at room temperature. Then ketones were added to the reaction stirred for 3 days to complete the reaction. The diamine chloride salt precipitated from aqueous solution and was easy to purify by washing the solid. We could obtain pure diamine products by basification of the salt followed by extraction.

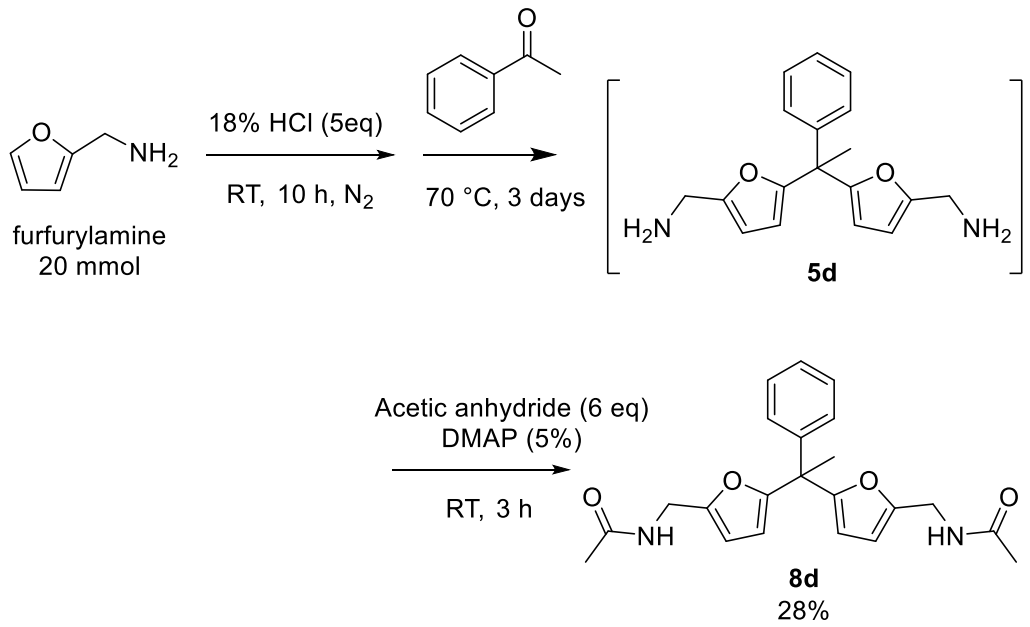
Scheme 20 shows the reaction conditions, structures of diamine products, and yields. We used acetone, 2-butanone, and cyclohexanone to prepare diamines for further research. We carried out the reaction on 100 mmol scale using optimized conditions and obtained fair to good yields for all diamine products (60-77%).



Scheme 20. One-step synthesis of symmetric and unsymmetrical diamines.

We applied the above condition to acetophenone and 5-nonanone in an effort to diversify the desired diamines. However, these reactions did not work out well due to the water solubility of the product and lower reactivity of the ketones. For example, reaction with acetophenone did not proceed at room temperature. If the reaction temperature was lower than 60 °C, there was no condensation observed even after 3 days. If the temperature was higher than 80 °C, the starting material decomposed in one day. The optimized condition was conducting the reaction for 3 days below 70 °C. We observed target diamine by GC, however, the concentration was not high enough for it to precipitates from the aqueous solution. Furthermore, the diamine could not be isolated by column chromatography. Thus, we treated the diamine with acetic anhydrides to generate the

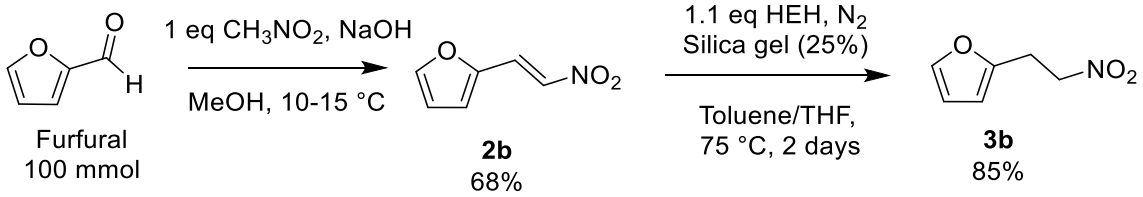
bisamide which was easier to purify and characterize. We obtained 28 % yield of amide **8d** under the optimal condition (Scheme 21). Reaction with 5-nonanone was also problematic.



Scheme 21. One-step synthesis of unsymmetrical diamine **5d**.

2.8. The Henry Reaction-Route to Amines Followed by Condensation

We applied the Henry reaction technique to hemicellulose-derived aldehydes to expand the routes to prepare biobased diamines. Firstly, we converted furfural to nitroalkene **2b** and reduced it to nitroalkane **3b** under optimized HEH reduction (Scheme 22).

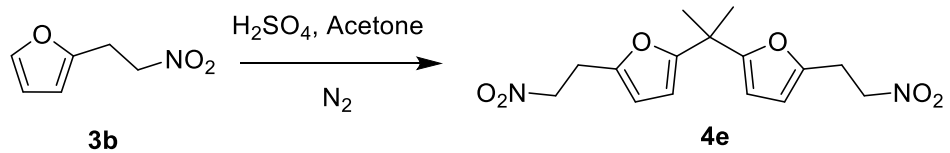


Scheme 22. Application of the Henry reaction to furfural.

Secondly, we carried out Friedel-Crafts alkylation with nitroalkane **3b**, a reaction similar to that described above for furfurylamine. We did not obtain a good yield of the bis-nitroalkane by the direct application of the protocol used with furfurylamine. The nucleophilicity of nitroalkane

3b is lower than furfurylamine and thus alkylations are more difficult. We replaced HCl with sulfuric acid developed from another literature protocol.[35] Then, we tried a series of reaction conditions to obtain a better yield of product **4e** (entries 1-5, Table 11) At first, we raised the reaction temperature to facilitate the consumption of starting material. However, the furan ring decomposed at high temperatures like 80 °C and the yield was unsatisfactory (entry 3, Table 11). Then we increased the amount of sulfuric acid and acetone. The yield of product **4e** was increased to 62% under the optimized condition. (entry 5, Table 11).

Table 11. Optimization of reaction conditions for Friedel-Crafts alkylation of nitroalkane **3b**.



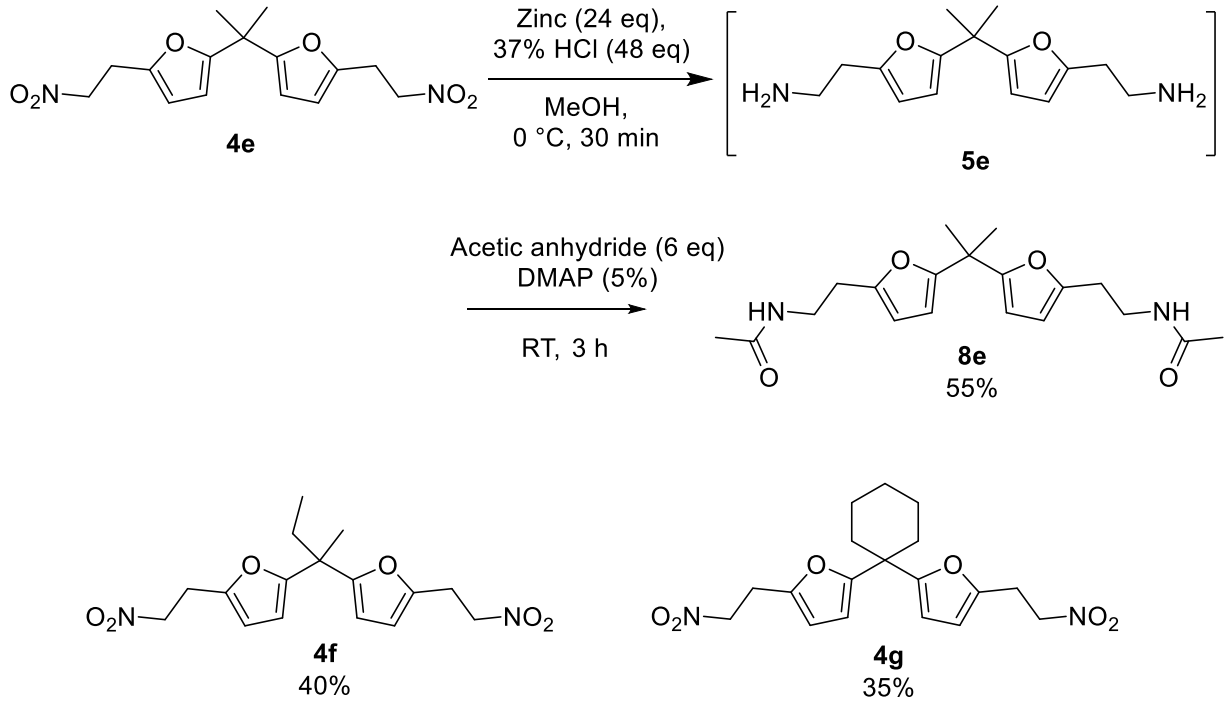
3b
2 mmol

4e

Entry	Amount of H_2SO_4 (eq)	Amount of Acetone (eq)	Temperature (°C)	Time (h)	Conversion (%)[a]	Yield (%)[b]
1	0.05	0.6	70	24	10	-
2	0.05	0.6	70	48	19	-
3	0.05	0.6	80	24	45	40
4	2	2	60	24	-	58
5	2	2	70	24	-	62

[a] Conversion is calculated by the percentage of integration in GC
[b] Yield is for the pure isolated product after column chromatography.

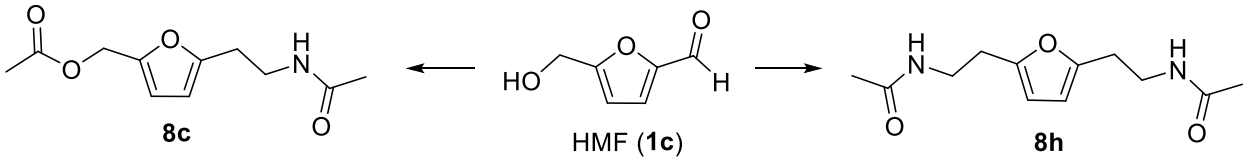
Thirdly, compound **4e** was reduced by acidic zinc to diamine (Scheme 23). Finally, we treated diamine with acetic anhydride and obtained amide **8e** to isolate and characterize. In addition, this Friedel-Crafts alkylation also works for the synthesis of dinitroalkane **4f** and **4g**. The yields were 40% and 35%.



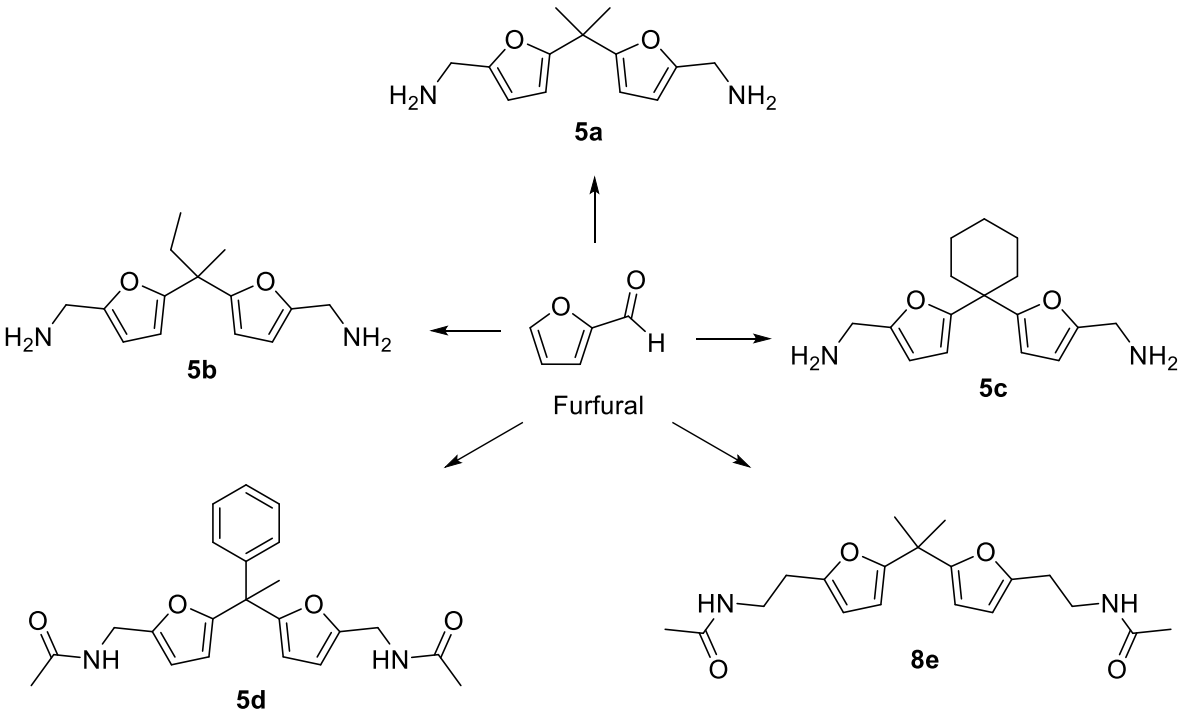
Scheme 23. Reduction of dinitro compound **4e** to diamine and the structure of **4f** and **4g**.

2.9. Conclusion

Our group has successfully explored ways to synthesize amines from biobased aldehydes including cellulose and hemicellulose (Scheme 24 and 25). The first method involved the conversion of HMF to nitroalkene by the Henry reaction. Selective hydrogenation by HEH converted nitroalkenes to nitroalkanes. Finally, we reduced nitroalkanes to amines using zinc under acidic conditions. The second method involved the application of Friedel-Crafts alkylation of furfurylamine (derived from furfural) to obtain diamines. The third method involved a combination of the Henry reaction and Friedel-Crafts alkylation techniques to generate diamine from furfural. Future experiments with **3b** will involve the use of different ketones to prepare a series of homologated diamines. The diamines described in this chapter show potential as precursors for NIPU, which will be the subject of discussion in the next chapter.



Scheme 24. Amines from HMF.



Scheme 25. Diamines from furfural.

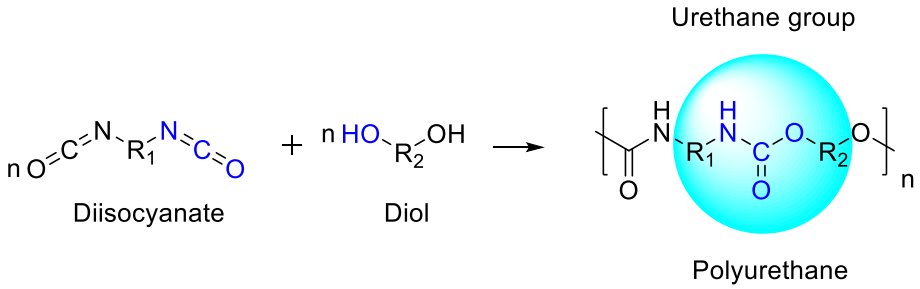
CHAPTER 3. CARBAMATE SYNTHESIS FROM NON-EDIBLE BIOMASS MATERIALS

3.1. Introduction

In the previous chapter, we discussed the development of methods to synthesize biomass-derived diamines from both cellulose and hemicellulose. In this chapter, we detail ways to take advantage of the potential of biomass diamines for the synthesis of NIPU monomers.

Polyurethanes (PUs) are widely used polymers in industry. They are good raw materials for construction, automobile, electronics, coatings, insulation, and mattresses, all of which support our daily lives. According to *Plastics Europe*, the worldwide production of PUs is 18Mt, ranking 5th by polymer types in 2016.[36]

Polyurethanes (PUs) are polymer compounds containing the urethane group. Most of them are made by reactions between isocyanates and alcohols containing two or more hydroxyl groups, such as diols and polyols. Scheme 26 shows the structure of polyurethane, which is generated by a reaction between diisocyanate and diol. The urethane group is highlighted. Physical and chemical properties of PUs depend on their structures, especially the R_1 and R_2 groups.[37]



Scheme 26. Synthesis of PU from diisocyanate and diol.

PUs products are divided into three categories based on their properties of density and rigidity. The three categories are flexible foams, rigid foams, and non-porous PUs.[36] Flexible foams are low density and more flexible than the other two types and are applied to cushions and

mattresses. Rigid foams have more strength and thermal insulation and are applied to construction and insulation. Non-porous PUs have special structures that are applied to coating, adhesives, and elastomers. We can expand the applications of PUs by controlling their properties, such as masking their structures and changing their densities. Our group focuses on synthesizing a series of carbamates to provide access to various PU precursors.

However, the related issues cannot be ignored because the increased production of PUs has long-lasting damage on both human beings and the environment. One problem is that isocyanates are prepared by the reaction of phosgene with amines. For example, phosgene, a starting material of PU, is a harmful chemical to human beings. In addition, about 95% of PUs comes from two potentially carcinogenic and mutagenic compounds: 2,4-toluene diisocyanate (MDI) and 4,4'-diphenylmethane diisocyanate (TDI) (Figure 7).[38,39]Another problem is that PUs can decompose to toxic amines by hydrolysis when discarded to landfill. European countries are considering forbidding isocyanates with REACH regulation. Thus, it is vital to develop more methods to provide non-isocyanate polyurethanes (NIPUs).

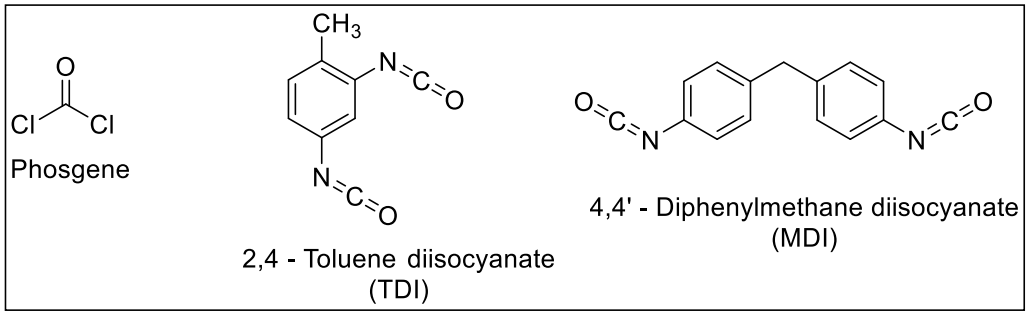
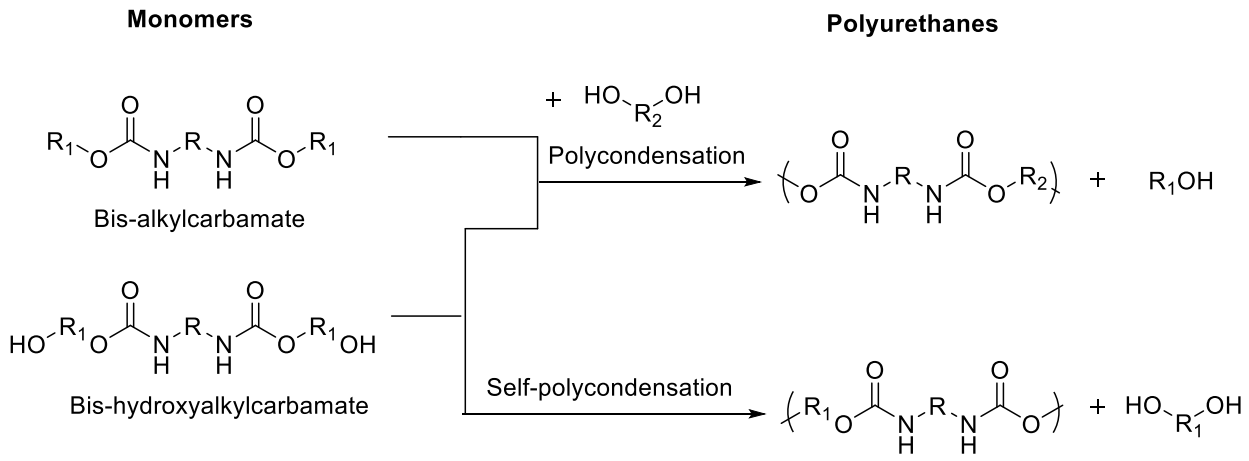


Figure 7. Structure of phosgene, TDI, and MDI.

Two techniques are widely used for the synthesis of NIPUs: polycondensation between diols and bis-carbamates; polyaddition between carbonates and amines followed by self-polycondensation.[40] Phosgene-free carbamates as the monomer can be precursors of NIPUs by these two routes (Scheme 27).[41] Our group focuses on the synthesis of phosgene-free carbamates.

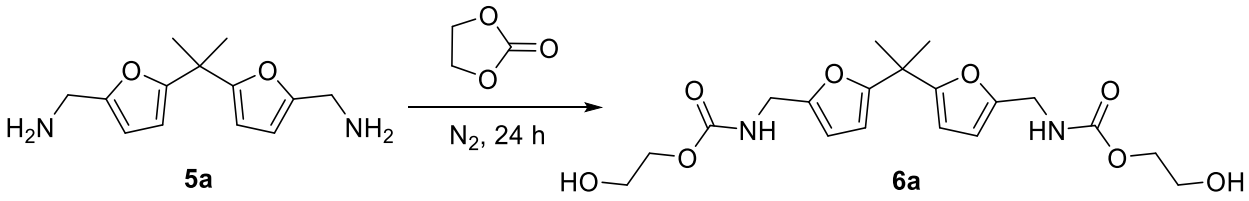


Scheme 27. Two routes to PUs from monomers.

3.2. Synthesis of Hydroxyalkylcarbamates from Diamines

In chapter 2, we discussed the synthesis of a series of diamines. Then, we prepared hydroxyalkylcarbamates from diamine **5a** using a protocol from literature (Table 12).[42] The reported procedure involved the reaction between ethylene carbonate and diamine at room temperature for 24 h in DCM. However, a simple application of literature protocol to diamine **5a** was unsatisfactory. Although we increased the reaction time to 48 h at room temperature, the conversation was low, and the isolated yield was 39% (entry 1, Table 12). The yield increased to 50% when we conducted the reaction 40 °C for 48 h (entry 2, Table 12). Then, we replaced the solvent DCM with EtOH and increased the reaction temperature (entries 3 and 4, Table 12). The best reaction temperature was 80 °C and the corresponding yield was 85% (entry 4, Table 12). The improved condition was better because EtOH is an environmentally benign solvent and can be made from biomass materials.

Table 12. Synthesis of hydroxyalkylcarbamates from diamine **5a**.



Entry	Solvent	Temperature (°C)	Time (h)	Yield of **6a** (%)[a]
1	DCM	RT	48	39
2	DCM	40	48	50
3	EtOH	70	24	80
4	EtOH	80	24	85

[a] Yields are for the pure isolated product after column chromatography.

We applied the optimized condition for substrates **5b** and **5c**. Figure 8 shows the structures of diamine substrates.

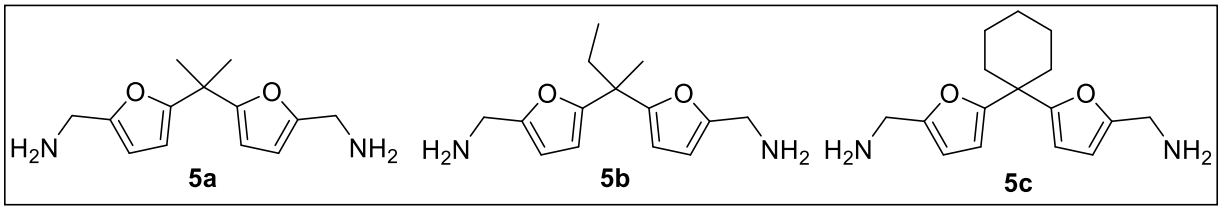
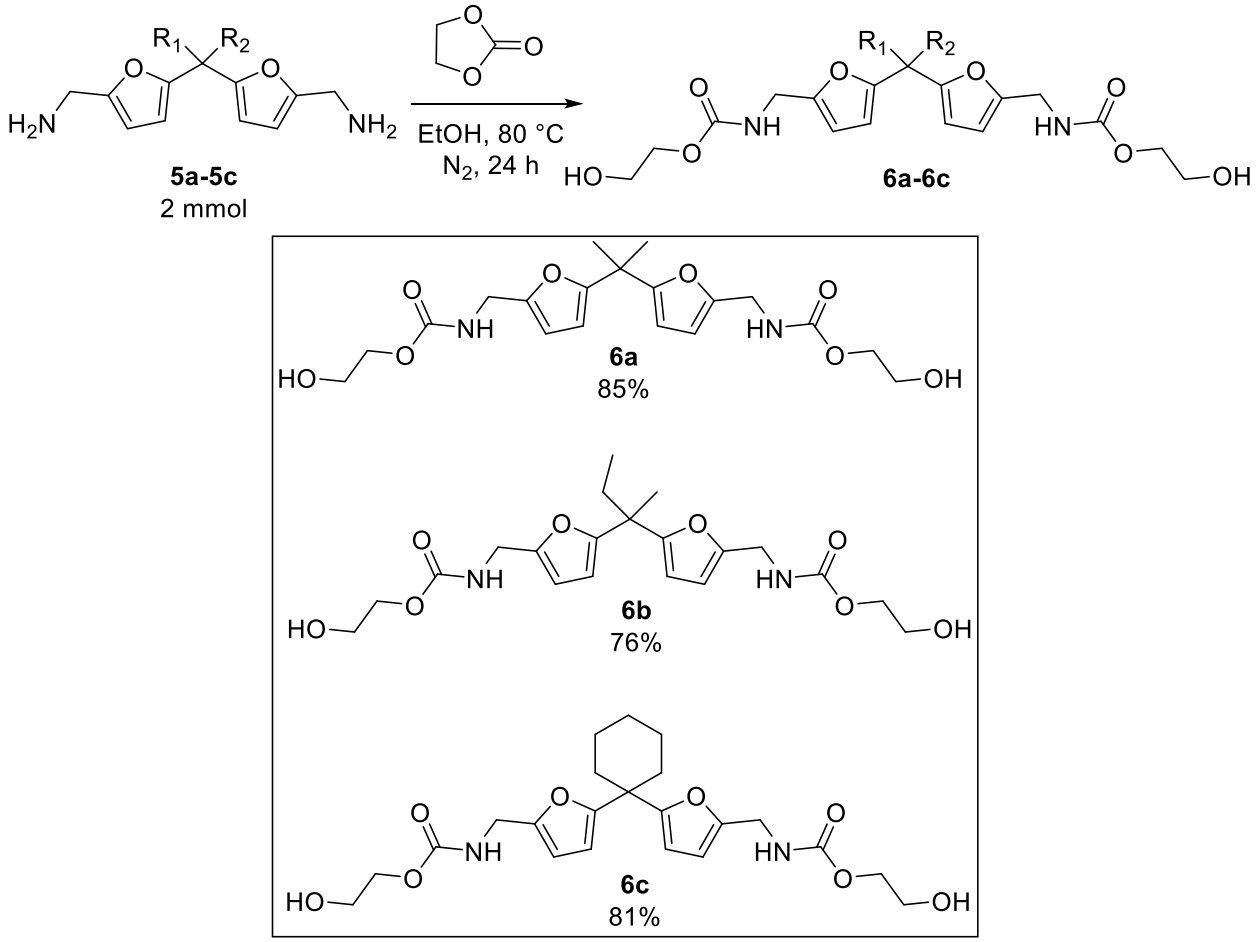


Figure 8. Structures of diamine substrates.

Scheme 28 summarizes the reaction, structures of products and their yields. All the three products are produced in good yield. Product **6a** and **6c** are symmetric diols, whereas product **6b** is an unsymmetrical diol.



Scheme 28. Synthesis of hydroxyalkylcarbamates from different diamines.

We also investigated the chain extended diamines **4h** and **5e** under the optimized condition for hydroxyalkylcarbamate synthesis (Figure 9). Unfortunately, these reactions were not clean and gave multiple products (reaction analyzed by GC-MS and TLC). We could not isolate target diols under our reaction conditions. One reason for the lack of success could be attributed to higher polarity of the products which led to difficulty in isolation. Although this protocol was not applicable to chain extended diamines, we will investigate alternate reaction conditions and isolation procedures in the future.

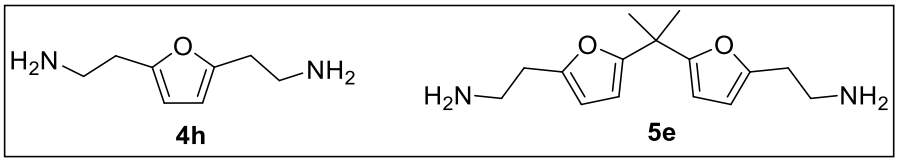


Figure 9. Chain extended diamines.

3.3. Synthesis of Carbamates Directly from Aldehydes

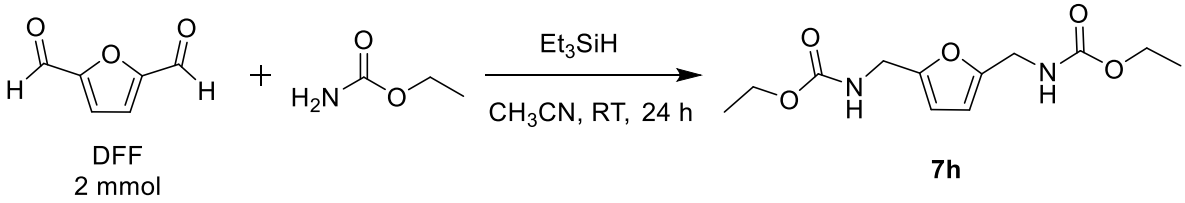
As we discussed before, our group successfully synthesized biobased diamines and corresponding hydroxyalkylcarbamates. Friedel-Crafts reaction of furan with different aldehydes and ketones furnish bridged bisfurans and trisfurans.[43–46] Dialdehydes can be readily prepared from the corresponding bisfurans by Vilsmeier-Haack formylation.[47,48] The ready availability of different furan dialdehydes led us to think if we could directly convert them to biscarbamates. If such a process could be developed, it will provide an alternate route for the synthesis of NIPUs. A recent report from the Nakada's group on the functional group interconversion of an aldehyde to a methyl group was well suited for our work. The extension of Nakada's protocol to dialdehydes will provide direct access to biscarbamates and thus avoid the need for diisocyanates.

Nakada's method involves the treatment of an aldehyde in the presence a Lewis acid catalyst, organosilane, solvent, and methyl or ethyl carbamate. The optimized condition for the reaction was aldehyde (1 eq), carbamate (1.05 eq), triethylsilane (3 eq), a catalytic amount of bismuth (III) chloride (10%) in acetonitrile at room temperature. Ethyl carbamate was optimal in the reaction.

We began our work using diformylfuran (DFF) as the starting material to optimize reaction conditions for reductive carbamoylation. These results are shown in Table 13. The variables we evaluated were the amount of Lewis acid, the nature of the Lewis acid, and the amount of the reducing agent. Reaction under Nakada's condition (10% catalyst, 6 eq triethylsilane, and 1.05 eq of ethyl carbamate) gave the product **7h** in 85% yield (entry 1, Table 13). Under these conditions,

we noticed that there was leftover triethylsilane. Increasing the amount of $BiCl_3$ to 20 and 30% gave lower yields of **7h** (entries 2 and 3, Table 13). We carried out several experiments using 5 mol% $BiCl_3$ while varying the amount of triethylsilane (entries 4-6, Table 13). The optimal conditions were using 4 equivalents of triethylsilane and 5% $BiCl_3$ which gave the product in 83% yield (entry 6, Table 13). We also evaluated $Bi(OTf)_3$ as a Lewis acid in the carbamoylation reaction (entries 7-9, Table 13). The yields were lower than 50% regardless of the amount of the catalyst and triethylsilane.

Table 13. Synthesis of biscarbamate **7h** directly from DFF.



Entry	Lewis acid	Amount of Lewis acid (%)	Amount of Et_3SiH (%)	Yield (%)[a]
1	$BiCl_3$	10	4	85
2	$BiCl_3$	20	6	68
3	$BiCl_3$	30	4	63
4	$BiCl_3$	5	2	60
5	$BiCl_3$	5	3	78
6	$BiCl_3$	5	4	83
7	$Bi(OTf)_3$	5	2	40
8	$Bi(OTf)_3$	5	4	46
9	$Bi(OTf)_3$	10	2	43

[a] Yields are for the pure isolated product after column chromatography.

We applied the optimized condition for biscarbamoylation to other dialdehyde substrates. Figure 10 shows structures of aldehyde substrates used for the study. Aromatic dialdehydes were studied for comparing their reactivity with DFF. Terephthaldehyde (**1g**) is similar to DFF (**1h**) in electron distribution although DFF is less aromatic. Isophthaldehyde (**1n**) is similar to DFF in

chemical structure. We also studied the reductive amination of the bis-furan dialdehyde (**1m-1q)** and the tri-furan dialdehyde (**1r** and **1s**) made by our group, which also worked well.

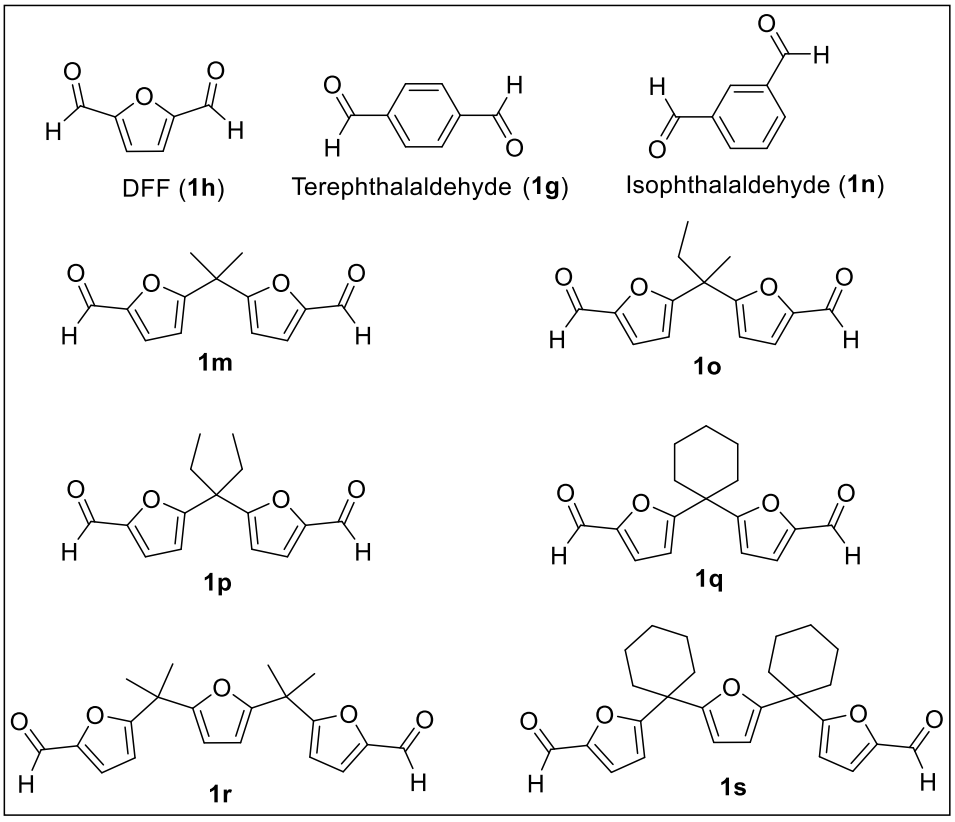
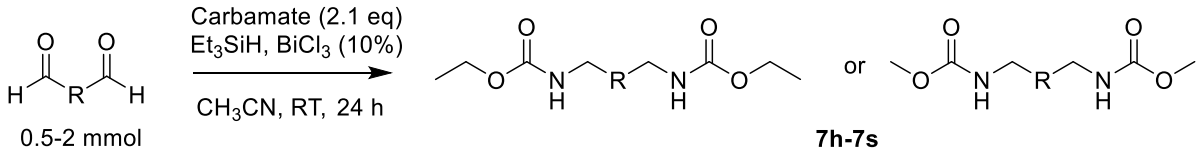
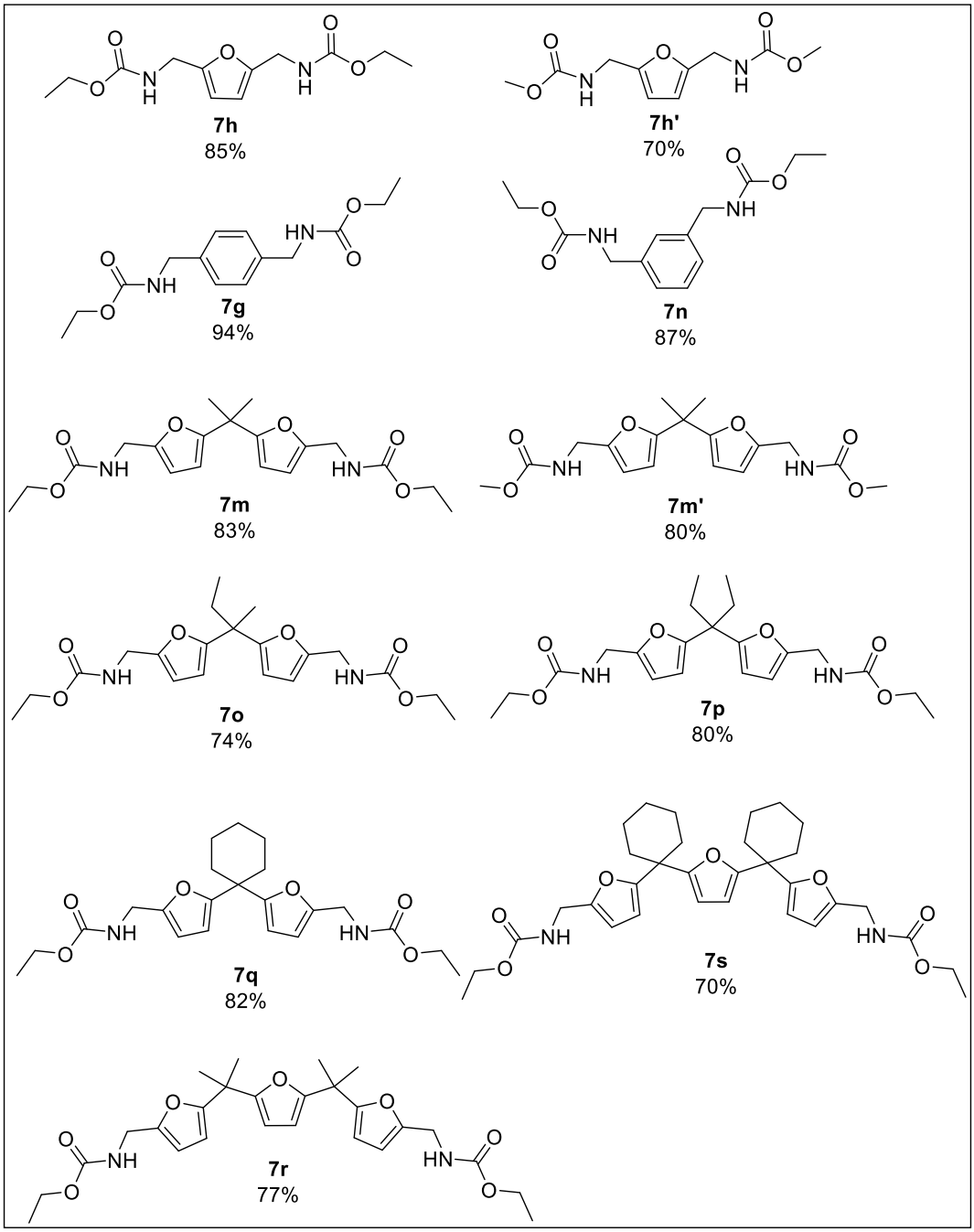


Figure 10. Structures of aldehyde substrates.

Scheme 29 shows the optimized reaction condition for synthesizing biscarbamates from different substrates, the structures of carbamate products and corresponding yields. As noted before, DFF gave 85 % of **7h**. The reaction of DFF using methyl carbamate as the reagent gave product **7h'** in a slightly lower yield of 70%. Thus, ethyl carbamate was a better reagent in the biscarbamoylation reaction. Aromatic substrates also gave high yields of the carbamoylated products **7g** and **7n**. The yield of product **7g** was 94% and the yield of product **7n** was 87%. Bisfurandialdehyde **1m-1q** were also competent substrates in the reaction and gave **7m-7q** in around 80% yield. In addition, trisfurandialdehyde **1r-1s** gave slightly lower yield of **7r** and **7s** which were 77% and 70%. These results show that both aromatic dialdehydes and furan-based

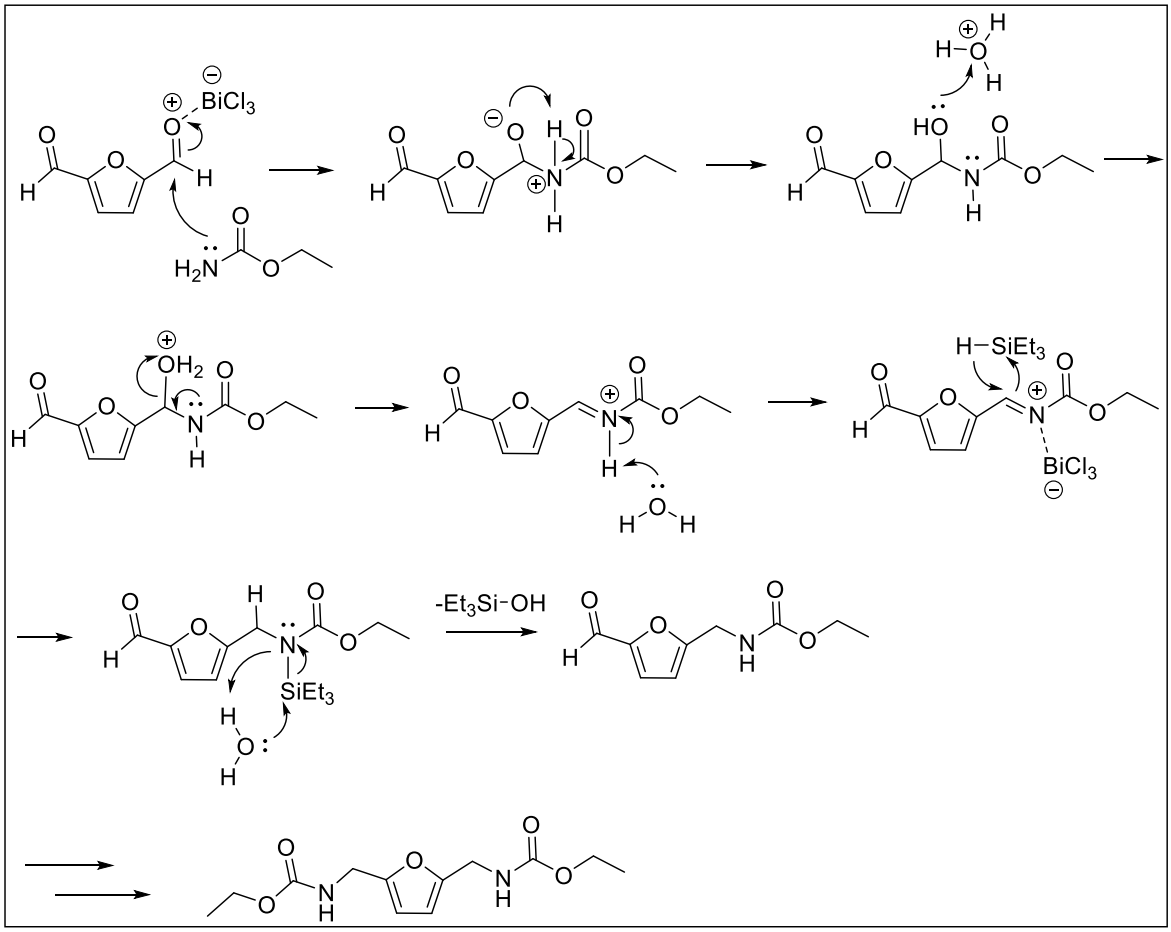
dialdehydes are equally effective in the biscarbamoylation. This simple and green carbonylation protocol are applicable to both bis and trisfuran derived dialdehydes.





Scheme 29. Synthesis of carbamates directly from aldehydes.

We also rationalized the mechanism of carbonylation of DFF. (Scheme 30) At first, the Lewis acid catalyst $BiCl_3$ actived the reactivity of aldehyde functional group in DFF. The primary amine nucleophilic attacked the carbonyl group. Then, proton transfer happened and generated the carbinolamine intermediate. The hydroxyl group was protonated and removed by dehydration. Deprotonation of the iminium ion generated imine intermediate. Triethylsilane reduced the imine intermediate to secondary amine as an hydrosilane reducing reagent. The hydride transfer occurs in a four-center arrangement between the hydrosilane and the actived amine center. The silyl group was removed as alcohol. The silyl alcohol was converted to silyl ether after dehydration, which was detected by GC-MS. This mechanism explained that the amount of TESH have effect on the result of the carbonylation reaction. [49,50]



Scheme 30. Mechanism of carbonylation of DFF.

3.4. Conclusion

In this chapter, we discussed how we developed a new method to access to biobased carbamates in two ways. The first method was the synthesis of hydroxyalkylcarbamates from various biobased diamines, which are available using the Henry reaction or a one-step condensation. The second method was the synthesis of biscarbamates directly from dialdehydes, which was very simple and economic. The starting materials in both methods are derived from non-edible biomass. In addition, the product carbamates are excellent precursors for accessing different biomass-derived NIPUs.

3.5. Future Plan

Firstly, we plan to synthesize more bisfuran diamines and dinitroalkanes with varying bridge substituents by Friedel-Crafts alkylation. We can obtain more biobased diamines which have the potential to be the precursor of polyurethanes by the substrate scope study. The challenge was the purification of furan-based amines due to their polarity and stability. We are working on a non-water solvent system for reduction conditions recently.

Secondly, we will synthesis of various hydroxyalkylcarbamates from all the biobased diamines that we have. The challenge for this plan was converting chain extended diamines to corresponding hydroxyalkylcarbamates, which did not work out well in previous experiments.

In addition, polymer synthesis is also attractive to our group. We can access biobased polyurethanes polymers directly by dicarbamate compounds. What's more, our group has techniques to access the biobased epoxy compounds. Then, we can synthesis of biobased epoxy resins by reactions between epoxy compounds and diamines.

CHAPTER 4. EXPERIMENTAL SECTION

4.1. General

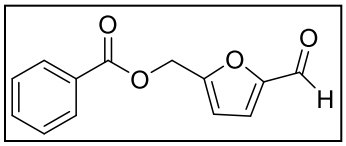
All solvents were HPLC grade. Flash chromatography was performed using Sorbtech silica gel 60 (230-400 mesh). Thin layer chromatographic analyses were performed on silica gel Whatmann-60F glass plates and components.

Melting points were measured with a REACH melting points determination apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Ascend^{TM} 400 Bruker (400 MHz) Spectrometer. ^{13}C NMR spectra were recorded on Ascend^{TM} 400 Bruker (100 MHz) Spectrometer. FT-IR spectra were recorded on a Nicolet iS 10 FT-IR Spectrometer. High resolution mass spectra were obtained at a SYNAPT G2-Si High Definition Mass Spectrometer.

4.2. Materials and Methods

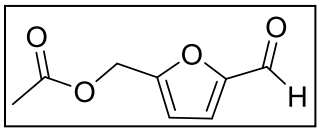
Furfurylamine, benzaldehyde, and 2-furaldehyde were purchased from Sigma-Aldrich. Terephthaldehyde (1,4-benzenedicarboxaldehyde) was purchased from Acros Organics. Isophthalaldehyde (1,3-benzenedicarboxaldehyde) was purchased from TCI Chemicals. 5-Hydroxymethylfurfural (HMF) and 5,5'-(oxybis(methylene)) bis(furan-2-carbaldehyde) (OBMF) were synthesized by Eric Serum following literature procedures. Furan-based dialdehyde substrates **1m-1s** were prepared by Krystal Grieger following literature procedures.[47,48,51,52,53,54]

4.3. Synthesis of HMF-derived Substrates

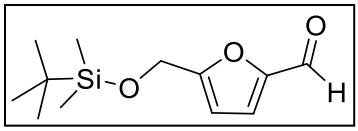


(5-Formylfuran-2-yl) methyl benzoate (1d): 5-Hydroxymethylfurfural (0.03 mol, 1 eq) and 5 % DMAP were dissolved in 10 mL THF in 100 mL 2 necked round bottom flask. Then pyridine (4.2 mmol, 1.4 eq) and benzoyl chloride (4.2 mmol, 1.4 eq) in 3 mL THF was added

dropwise to the reaction. The reaction was protected by N_2. The temperature was increased to 75 °C for 3 h and then allowed to cool down to RT overnight. A yellow solid precipitated after cooling. The mixture was extracted thrice with ethyl acetate and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography on silica gel (elution with EA: Hexane = 1:10).[55] Yield: 80 %; Light yellow solid, mp. 55-57 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.61 (s, 1H), 8.03-8.00 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 2H), 7.21 (d, J = 4 Hz, 1H), 6.65 (d, J = 4 Hz, 1H), 5.34 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 177.8, 165.9, 155.5, 152.9, 133.4, 129.8, 129.3, 128.5, 121.9, 112.8, 58.2; IR (ATR) ν 2850, 1708, 1671, 1252 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{10}O_4Na)^+$ 253.0477; found 253.0482.

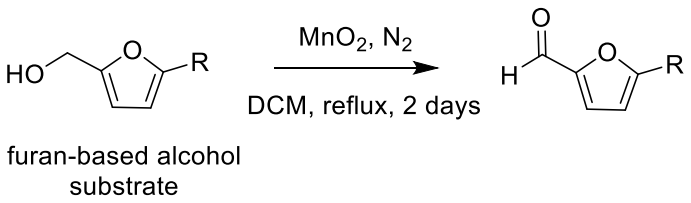


5-Acetoxymethyl-2-furaldehyde (AMF, 1e): 5-Hydroxy-methylfurfural (0.06 mol, 1 eq) was dissolved in acetic anhydride (0.18 mol, 3 eq) at room temperature. Then 5 % DMAP was added and the reaction mixture stirred for 3 h. After the reaction was complete (TLC), the reaction was poured into 500 mL ice water. The mixture was extracted thrice with ethyl acetate and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with EA: Hexane = 1:10). Yield: 80 %; Light yellow solid, mp. 55-57 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.61 (t, J = 1.4 Hz, 1H), 7.19 (d, J = 4 Hz, 1H), 6.57 (d, J = 4 Hz, 1H), 5.10 (s, 2H), 2.08 (t, J = 1.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 177.9, 170.4, 155.5, 152.9, 121.8, 112.7, 57.9, 20.7. IR (ATR) ν 2846, 1728, 1670, 1225 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_8H_9O_4)^+$ 169.147, found 169.045.[56]

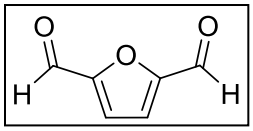


5-[[(tert-Butyldimethylsilyl)oxy]methyl]-2-furaldehyde (1f): 5-Hydroxymethylfurfural (0.015 mol, 1 eq) and imidazole (0.037 mol, 2.5 eq) were mixed in round bottle flask in 20 mL DMF under argon. tert-Butyldimethylsilyl chloride (0.019 mol, 1.3 eq) was then added to the reaction vessel. The reaction was stirred for 18h at room temperature. After reaction was complete (TLC analysis), the mixture was extracted thrice with hexane and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with Hexane).[57] Yield: 90 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.47-9.45 (m, 1H), 7.10 (d, J = 4 Hz, 1H), 6.35 (d, J = 4 Hz, 1H), 4.62-4.60 (m, 2H), 0.81-0.79 (m, 9H), 0.00-(-0.02) (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 177.2, 161.1, 152.1, 122.3, 109.3, 58.4, 25.6, 18.1, -5.6; IR (ATR) ν 2857, 1679 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{12}H_{21}O_3Si)^+$ 241.1260, found 241.1263.[58]

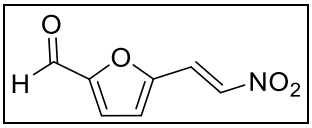
The alcohol substrate (0.01 mol, 1 eq) was dissolved in 20 mL DCM and (0.05 mol, 5 eq) MnO_2 was added in as a catalyst. The reaction was protected by N_2 and was stirred for 2 days under reflux (Scheme 31). If the substrate wasn't complete (TLC analysis), more MnO_2 was added. After the reaction was complete, MnO_2 was removed by filtration. The solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with EA: Hexane = 1:5).



Scheme 31. Oxidation condition for aldehydes.



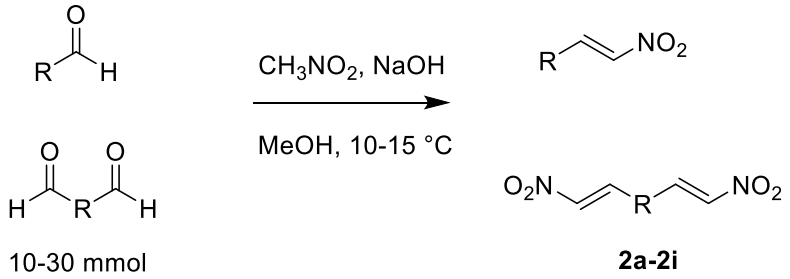
2,5-Diformylfuran (DFF, 1h): Yield: 80 %; Light yellow solid, mp. 110-112 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.83 (s, 2H), 7.32 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 179.3, 154.3, 119.5; IR (ATR) ν 2748, 1664 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_6H_5O_3)^+$ 125.0239, found 125.0241.



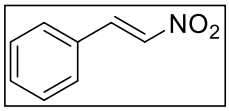
5-(2-Nitrovinyl)furan-2-carbaldehyde (2j): Yield: 55 %; Orange solid, mp. 174-176 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.75 (s, 1H), 7.80 (d, *J* = 12 Hz, 1H), 7.72 (d, *J* = 12 Hz, 1H), 7.32 (d, *J* = 4 Hz, 1H), 7.00 (d, *J* = 4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 178.0, 154.1, 150.6, 138.7, 124.4, 121.5, 119.9; IR (ATR) ν 2852, 1662, 1510, 1331 cm^{-1}; ESI-HRMS: m/z calcd. For $(C_7H_6NO_4)^+$ 168.0297, found 168.0303.

4.4. Synthesis of Nitroalkenes by the Henry Reaction

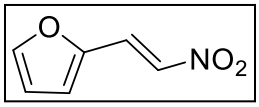
General procedure: The aldehyde substrate (10-30 mmol, 1 eq) was dissolved in 15 mL MeOH and cooled in an ice bath. CH_3NO_2 (1 eq or 2.1 eq) was added dropwise (Scheme 32). Then 25 wt. % aqueous NaOH (1.1 eq or 2.2 eq) was added dropwise slowly and the temperature maintained at 10-15 °C. The reaction mixture was stirred for 10 min after the addition was complete. 15 wt. % aqueous solution of HCl (2.2 eq or 4.4 eq) was prepared in a beaker. Then the reaction mixture was added into the HCl aqueous solution. Yellow solid precipitated out directly. The mixture was extracted thrice with ethyl acetate and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with EA: Hexane = 1:5).



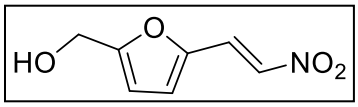
Scheme 32. The Henry reaction condition.



ß-Nitrostyrene (2a): Yield: 76 %; Yellow solid, mp. 55-57 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, *J* = 13.6 Hz, 1H), 7.59 (d, *J* = 13.6 Hz, 1H), 7.56-7.54 (m, 2H), 7.50-7.45 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 139.2, 137.2, 132.3, 130.2, 129.5, 129.3; IR (ATR) ν 1511, 1339 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_8H_7NO_2Na)^+$ 172.0374; found 172.0378.

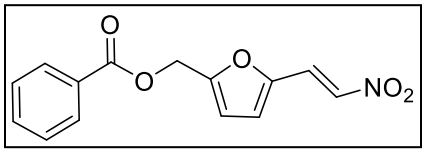


2-(2-Nitrovinyl)furan (2b): Yield: 68 %; Yellow solid, mp. 74-76 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, *J* = 13.6 Hz, 1H), 7.59 (d, *J* = 1.2 Hz, 1H), 7.52 (d, *J* = 13.6 Hz, 1H), 6.89 (d, *J* = 3.6 Hz, 1H), 6.57 (dd, *J* = 3.6 Hz, *J* = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.0, 146.8, 135.1, 125.6, 120.1, 113.5; IR (ATR) ν 1493, 1307 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_6H_5NO_3Na)^+$ 162.0167; found 162.0170.

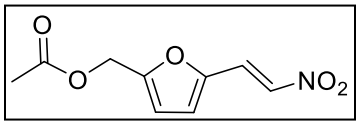


(5-(2-Nitrovinyl)furan-2-yl)methanol (2c): Yield: 70 %; Yellow solid, mp. 83-85 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, *J* = 12 Hz, 1H), 7.51 (d, *J* = 12 Hz, 1H), 6.85 (d, *J* = 4 Hz, 1H), 6.48 (d, *J* = 4 Hz, 1H), 4.68 (d, *J* = 4 Hz, 2H), 2.16 (t, *J* = 4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101

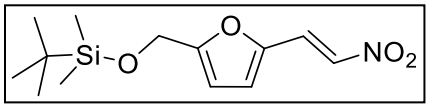
MHz) δ 159.0, 146.6, 134.9, 125.5, 121.1, 111.2, 57.7; IR (ATR) ν 3345, 1494, 1327, 1181 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_7H_7NO_4Na)^+$ 192.0273, found 192.0277.



(5-(2-Nitrovinyl)furan-2-yl)methyl benzoate (2d): Yield: 51 %; Yellow solid, mp. 78-80 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.07-8.05 (m, 2H), 7.75 (d, *J* = 13.2 Hz, 1H), 7.59-7.53 (m, 2H), 7.47-7.44 (m, 2H), 6.86 (d, *J* = 3.2 Hz, 1H), 6.65 (d, *J* = 3.2 Hz, 1H), 5.34 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 166.0, 154.3, 147.1, 135.4, 133.5, 130.3, 129.9, 129.4, 128.6, 125.2, 120.8, 113.8, 58.2; IR (ATR) ν 1717, 1533, 1329, 1267 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{11}NO_5Na)^+$ 296.0535; found 296.0543.

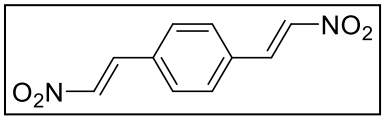


(5-(2-Nitrovinyl)furan-2-yl)methyl acetate (2e): Yield: 20 %; Yellow solid, mp. 39-41 ºC; ^1H NMR ($CDCl_3$, 400MHz) δ 7.75-7.71 (m, 1H), 7.55-7.50 (m, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.55 (d, *J* = 3.2 Hz, 1H), 5.07 (s, 2H), 2.12-2.10 (m, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.4, 154.3, 147.1, 135.4, 125.2, 120.7, 113.7, 57.8, 20.8; IR (ATR) ν 1741, 1493, 1324, 1220 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_9H_9NO_5Na)^+$ 234.0378; found 234.0385.

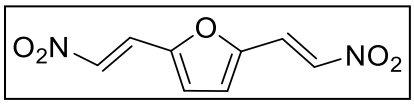


tert-Butyldimethyl((5-(2-nitrovinyl)furan-2-yl)methoxy) silane (2f): Yield: 10 %; Yellow solid, mp. 44-46 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, *J* = 13.2 Hz, 1H), 7.48 (d, *J* = 13.2 Hz, 1H), 6.84 (d, *J* = 3.6 Hz, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 4.69 (s, 2H), 0.92 (s, 9H), 0.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 155.1, 150.5, 108.9, 108.3, 78.6, 65.0, 58.2, 25.9, 18.5, -5.2;

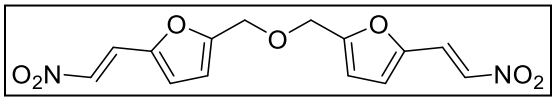
IR (ATR) ν 1528, 1324 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{13}H_{21}NO_4SiNa)^+$ 306.1138; found 306.1145.



1,4-Bis(2-nitrovinyl)benzene (2g): Yield: 46 %; Yellow solid, mp. 200-202 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.02 (s, 1H), 7.98 (s, 1H), 7.64 (s, 1H), 7.64 (s, 4H), 7.61 (s, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 138.7, 137.4, 133.5, 130.0; IR (ATR) ν 1538, 1340 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{10}H_8N_2O_4Na)^+$ 243.0374; found 243.0382.



2,5-Bis(2-nitrovinyl)furan (2h): Yield: 68 %; Yellow solid, mp. 164-166 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, J = 13.2 Hz, 2H), 6.61 (d, J = 13.2 Hz, 2H), 7.00 (s, 2H); ^{13}C NMR (DMSO-d_6, 101 MHz) δ 149.9, 137.8, 125.1, 122.8; IR (ATR) ν 1520, 1324 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_8H_5N_2O_5)^-$ 209.0199; found 209.0228.

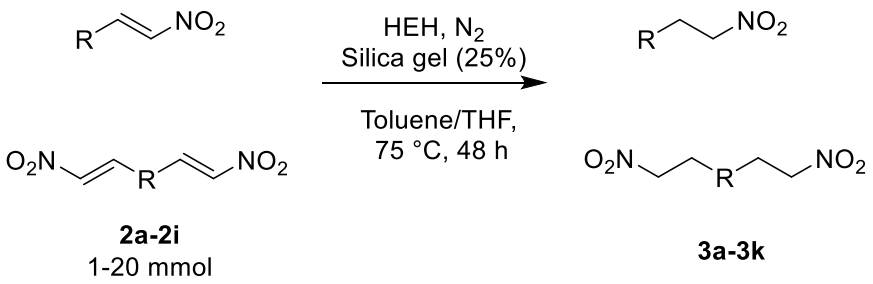


5,5'-(Oxybis(methylene))bis(2-(2-nitrovinyl) furan) (2i): Yield: 50 %; Yellow solid, mp. 99-101 ºC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, J = 12 Hz, 2H), 7.52 (d, J = 12 Hz, 2H), 6.86 (d, J = 4 Hz, 2H), 6.53 (d, J = 4 Hz, 2H), 4.57 (s, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 155.9, 147.0, 135.3, 125.3, 120.8, 113.1, 64.5; IR (ATR) ν 1491, 1320, 1069 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{12}N_2O_7Na)^+$ 343.0542; found 343.0538.

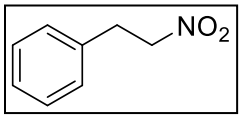
4.5. Synthesis of Nitroalkanes by Selective Hydrogenation

General procedure: Nitroalkene substrate (1-20 mmol, 1 eq), Hantzsch ester (1.1 eq or 3.5 eq) and silica gel (25 %) were mixed in a round bottom flask. Under argon atmosphere, the

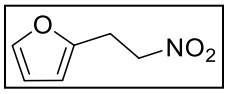
reaction mixture was stirred at 75 °C in 30 mL toluene/THF for 2 days (Scheme 33). After the completion of the reaction, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with EA: Hexane = 1:5).[31]



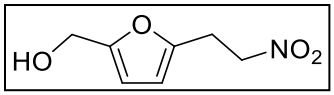
Scheme 33. Selective hydrogenation condition.



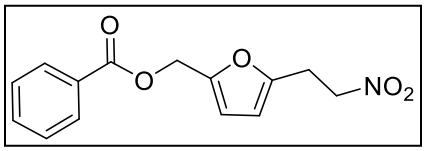
Nitro-2-phenylethane (3a): Yield: 83 %; Light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.21 (m, 5H), 4.61 (t, *J* = 7.6 Hz, 2H), 3.32 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.8, 128.9, 128.5, 127.3, 76.2, 33.3; IR (ATR) ν 1511, 1339 cm^{-1}; ESI-HRMS: m/z calcd. for ($C_8H_9NO_2$) 151.0631, found:151.0629.[59]



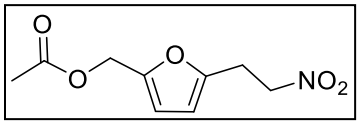
2-(2-Nitroethyl)furan (3b): Yield: 85 %; Light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30-7.35 (m, 1H), 6.30 (dd, *J* = 3.2 Hz, *J* = 2 Hz, 1H), 6.13 (dd, *J* = 3.2 Hz, *J* = 0.8 Hz, 1H), 4.63 (t, *J* = 6.8 Hz, 2H), 3.35 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.5, 142.3, 110.6, 107.4, 73.4, 26.1; IR (ATR) ν 1549, 1376 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_6H_7NO_3Na)^+$ 164.0324; found 164.0338.



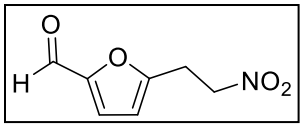
(5-(2-Nitroethyl)furan-2-yl)methanol (3c): Yield: 78 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.04 (d, *J* = 3.2 Hz, 1H), 5.95 (d, *J* = 3.2 Hz, 1H), 4.51 (t, *J* = 7.2 Hz, 2H), 4.32 (s, 2H), 3.81 (br. s, 1H), 3.16 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 153.4, 149.3, 108.2, 107.6, 72.9, 56.3, 25.5; IR (ATR) ν 3356, 1547, 1377, 1171 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_7H_9NO_4Na)^+$ 194.0429, found 194.0433.



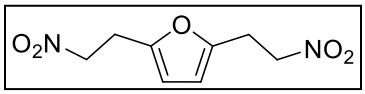
(5-(2-Nitroethyl)furan-2-yl)methyl benzoate (3d): Yield: 80 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02-7.99 (m, 2H), 7.51-7.47 (m, 1H), 7.39-7.35 (m, 2H), 6.38 (d, *J* = 3.2 Hz, 1H), 6.10 (d, *J* = 3.2 Hz, 1H), 5.22 (s, 2H), 4.60 (t, *J* = 7.2 Hz, 2H), 3.29 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 165.9, 150.4, 149.1, 133.0, 129.7, 129.5, 128.2, 111.7, 108.2, 72.9, 58.2, 25.8; IR (ATR) ν 1716, 1552, 1373, 1265 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{13}NO_5Na)^+$ 298.0692; found 298.0697.



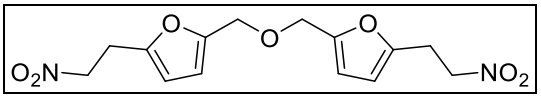
(5-(2-Nitroethyl)furan-2-yl)methyl acetate (3e): Yield: 83 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.29-6.28 (m, 1H), 6.09 (s, 1H), 4.95 (d, *J* = 2 Hz, 2H), 4.62 (td, *J* = 7.2 Hz, *J* = 2 Hz, 2H), 3.32 (td, *J* = 7.2 Hz, *J* = 2 Hz, 2H), 2.04 (d, *J* = 2.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.6, 150.3, 149.3, 111.7, 108.4, 73.1, 57.9, 26.1, 20.8; IR (ATR) ν 1738, 1552, 1376, 1230 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_9H_{11}NO_5Na)^+$ 236.0535; found 236.0537.



(2-Nitroethyl)furan-2-carbaldehyde (3j): Yield: 72 %; Yellow solid, mp. 37-39 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.50 (s, 1H), 7.15 (d, *J* = 3.6 Hz, 1H), 6.37 (d, *J* = 3.6 Hz, 1H), 4.71 (t, *J* = 6.8 Hz, 2H), 3.42 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 177.2, 156.4, 152.5, 123.1, 110.8, 72.3, 26.1; IR (ATR) ν 2977, 1716, 1552, 1367 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_7H_7NO_4Na)^+$ 192.0273, found 192.0279.

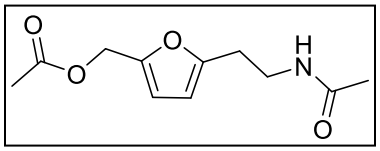


2,5-Bis(2-nitroethyl)furan (3h): Yield: 70 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.04 (s, 2H), 4.60 (t, *J* = 7.2 Hz, 4H), 3.29 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 149.3, 108.4, 73.3, 26.1; IR (ATR) ν 1547, 1377 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_8H_{10}N_2O_5Na)^+$ 237.0487; found 237.0500.

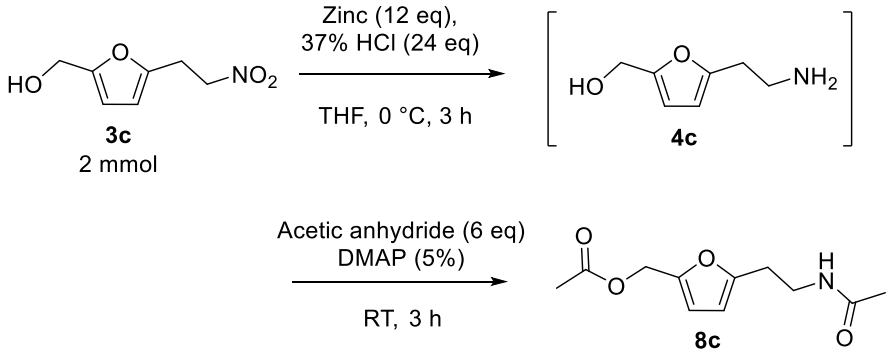


5,5'-(Oxybis(methylene))bis(2-(2-nitroethyl) furan) (3i): Yield: 62 %; White solid, mp. 45-47 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.21(d, *J* = 3.2 Hz, 2H), 6.06 (d, *J* = 3.2 Hz, 2H), 4.61 (t, *J* = 7.2 Hz, 4H), 4.36 (s, 4H), 3.30 (t, *J* = 7.2 Hz, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 151.0, 150.0, 110.7, 108.1, 73.2, 63.4, 26.0; IR (ATR) ν 1547, 1376, 1058 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{16}N_2O_7Na)^+$ 347.0855; found 347.0854.

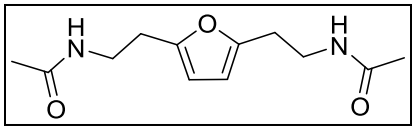
4.6. The Henry Reaction-Route to Amines



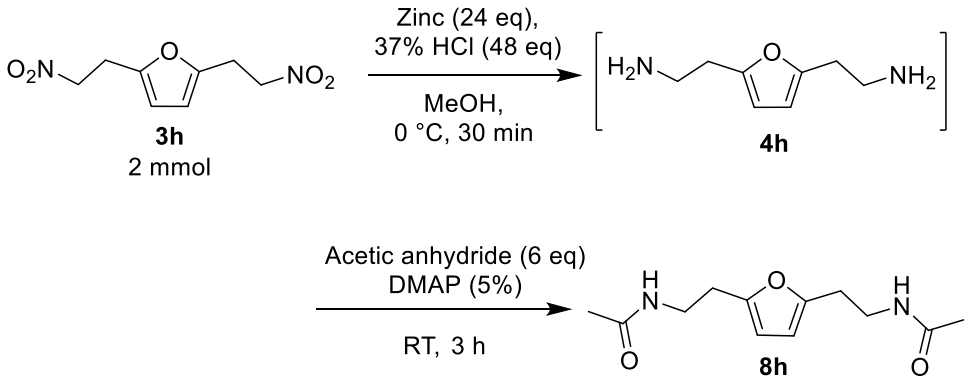
(5-(2-Acetamidoethyl)furan-2-yl)methyl acetate (8c): Nitroalkane substrate (2 mmol, 1 eq) and active Zn dust (12 mmol, 6 eq) were added in a vial in 2 mL THF. HCOOH (24 mmol, 12 eq) was then added to the mixture and the reaction was stirred for 3 h at room temperature (Scheme 34). After the reaction was complete, the zinc was removed by filtration. The mixture was extracted thrice with DCM. Crude amine product was obtained after the solvent was removed under reduced pressure. Acetic anhydride (6 eq) was added to the crude amine in an ice bath. The mixture was stirred for 3 h at room temperature. The mixture was extracted thrice with ethyl acetate and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with MeOH: DCM = 1:50).[33] Yield: 57 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.31 (d, *J* = 4 Hz, 1H), 6.04 (d, *J* = 4 Hz, 1H), 5.73 (br. s, 1H), 4.99 (s, 2H), 3.53 (dd, *J* = 12.8 Hz, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 8 Hz, 2H), 2.07 (s, 3H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.8, 170.3, 154.2, 148.6, 111.7, 107.5, 58.3, 38.1, 28.4, 23.4, 21.1; IR (ATR) ν 3291, 1738, 1650, 1549, 1229 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{11}H_{15}NO_4Na)^+$ 248.0899; found 248.0901.



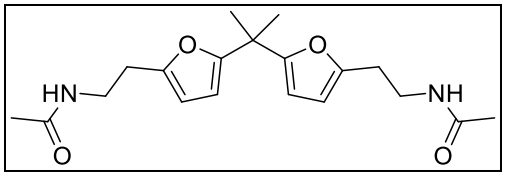
Scheme 34. Reduction condition for amine **4c**.



(Furan-2,5-diylbis(ethane-2,1-diyl))diacetamide (8h): Nitroalkane substrate (2 mmol, 1 eq) was dissolved in 2 mL MeOH in an ice bath. Zn dust (12 mmol, 6 eq) and 37% HCl (96 mmol, 48 eq) were slowly added alternatively and the temperature was maintained below 0 °C (Scheme 35). After 30 min when the reaction was complete, Zinc was removed by filtration. NaOH solution was added dropwise to filtrate kept in an ice bath and the pH was adjusted to 10. White zinc salt precipitated out and was removed by filtration. The mixture was extracted thrice with DCM. The crude amine product was obtained after the solvent was removed under reduced pressure. Acetic anhydride (6 eq) was added to the crude amine in an ice bath. The mixture was stirred for 3 h at room temperature. The mixture was extracted thrice with ethyl acetate and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with MeOH: DCM = 1:50).[32] Yield: 60 %; Pink solid, mp. 135-137 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.23 (br. s, 2H), 5.90 (s, 2H), 3.51 (q, *J* = 6.4 Hz, 4H), 2.73 (t, *J* = 6.4 Hz, 4H), 1.92 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.4, 152.0, 107.4, 38.1, 28.8, 23.3; IR (ATR) ν 3279, 1638, 1550 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{12}H_{18}N_2O_3Na)^+$ 261.1215; found 261.1226.



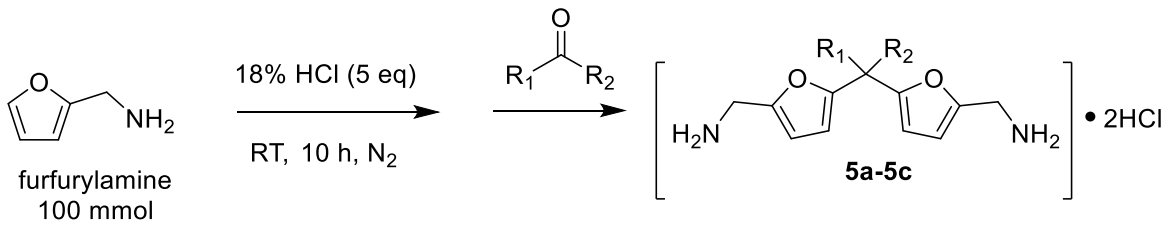
Scheme 35. Reduction condition for diamine **4h**.



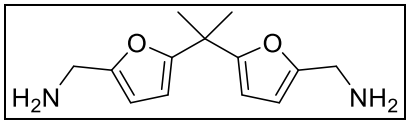
N, N'-((propane-2,2-diylbis(furan-5,2-diyl))bis(ethane-2,1-diyl))diacetamide (8e): Yield: 55 %; Light yellow solid, mp. 105-107 ºC; ^{1}H NMR ($CDCl_3$, 400MHz) δ 6.27 (br. s, 2H), 5.90 (d, *J* = 2.8 Hz, 2H), 5.86 (d, *J* = 2.8 Hz, 2H), 3.41 (q, *J* = 6.4 Hz, 4H), 2.73 (t, *J* = 6.4 Hz, 4H), 1.88 (s, 6H), 1.54 (s, 6H); ^{13}C NMR ($CDCl_3$, 101MHz) δ 170.3, 159.0, 151.7, 106.5, 104.5, 38.4, 37.2, 28.2, 26.2, 23.2; IR (ATR) ν 3279.75, 1636.74, 1556.37 cm^{-1};

4.7. One-Step Synthesis of Symmetric and Unsymmetrical Diamines and Dinitroalkanes

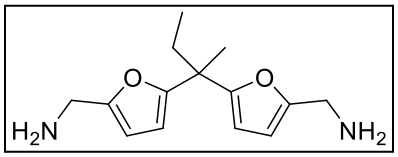
General procedure: Furfurylamine (100 mmol, 2.1 eq) was placed in a 2 necked round bottom flask fitted with a reflux condenser under argon. The reaction vessel was cooled in an ice bath and 18 wt. % aqueous solution of HCl (0.25 mol, 5 eq) was added dropwise into the flask. Then the mixture was stirred for 10 h at room temperature (Scheme 36). Ketone (0.049 mol, 1 eq) was then added to the mixture. The reaction was heated to 40 °C for 2-3 days until the reaction was complete. Then the reaction mixture was cooled in the refrigerator for 2 h. The pink solid precipitate and was collected by filtration. NaOH solution was added to the solid and the pH was adjusted to 10. The mixture was extracted thrice with DCM and the combined extracts were dried over sodium sulfate. After filtration, the pure amine product was obtained after the solvent was removed under reduced pressure.[34]



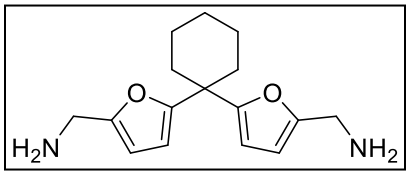
Scheme 36. Condition for one-step synthesis of diamines.



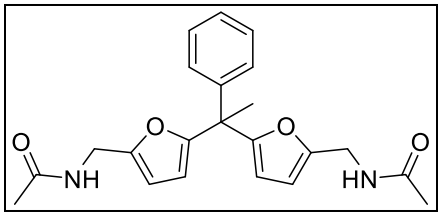
2-Furanmethanamine (5a): Yield: 73 %; Brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.90-5.82 (m, 2H), 5.80-5.70 (m, 2H), 3.58 (t, *J* = 3.6 Hz, 4H), 1.47 (d, *J* = 3.6 Hz, 6H), 1.29 (d, *J* = 3.6 Hz, 4H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.1, 155.4, 105.3, 104.6, 39.5, 37.4, 26.4; IR (ATR) ν 3365, 3284, 1552, 1015, 783 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{13}H_{18}N_2O_2Na)^+$ 257.1266; found 257.1273.[35]



(Butane-2,2-diylbis(furan-5,2-diyl))dimethanamine (5b): Yield: 60 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.01 (d, *J* = 4 Hz, 2H), 5.93 (d, *J* = 4 Hz, 2H), 3.74 (s, 4H), 2.01 (q, *J* = 8 Hz, 2H), 1.56 (s, 4H), 1.54 (s, 3H), 0.77 (t, *J* = 8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 158.5, 155.4, 105.6, 105.4, 41.6, 39.6, 31.8, 22.4, 9.0; IR (ATR) ν 3367, 3274, 1552, 1015, 780 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{20}N_2O_2Na)^+$ 271.1422; found 271.1424.

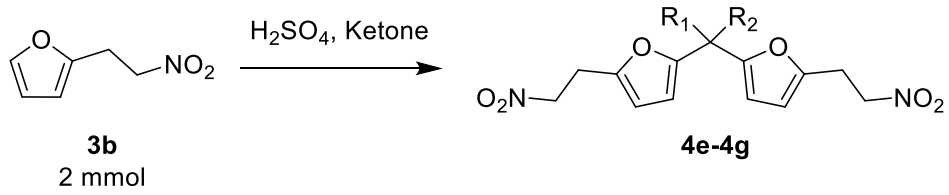


(Cyclohexane-1,1-diylbis(furan-5,2-diyl))dimethanamine (5c): Yield: 77 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.00 (d, *J* = 4 Hz, 2H), 5.87 (d, *J* = 4 Hz, 2H), 3.73 (s, 4H), 2.18-2.06 (m, 4H), 1.60-1.40 (m, 10H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 158.3, 155.2, 105.7, 105.5, 41.9, 39.6, 34.0, 25.9, 22.6; IR (ATR) ν 3366, 3285, 1549, 1014, 777 cm^{-1}; HRMS calculated for $(C_{16}H_{22}N_2O_2Na)^+$: m/z = 297.1579, found: 297.1573.[35]

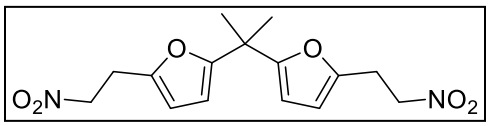


(((1-Phenylethane-1,1-diyl) bis(furan-5,2-diyl))bis (methylene))diacetamide (8d): Acetic anhydride (6 eq) was added to the crude diamine (synthesized by the general procedure described above) in an ice bath. The mixture was stirred for 3 h at room temperature. Water was added when the reaction was complete. The mixture was extracted thrice with ethyl acetate and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with MeOH: DCM = 1:50). Yield: 28 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20-7.30 (m, 3H), 7.69-7.10 (m, 2H), 6.14 (d, J = 3.2 Hz, 4H), 5.95 (d, J = 3.2 Hz, 2H), 4.25-4.45 (m, 4H), 1.95 (s, 9H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.1, 157.7, 150.9, 145.1, 128.3, 127.0, 126.9, 108.1, 107.8, 46.4, 36.8, 26.0, 23.2; IR (ATR) ν 3280, 1650, 1544, 725 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{22}H_{24}N_2O_4Na)^+$ 403.1634; found 403.1640.

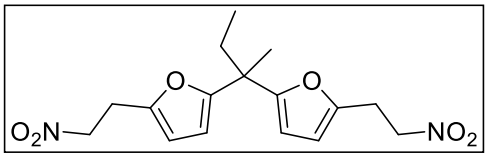
General procedure: Nitroalkanes (2 mmol, 1 eq) and ketones (4 mmol, 2 eq) were dissolved in 5 mL EtOH under argon. A 50 wt. % aqueous solution of H_2SO_4 (2 eq) was added slowly at 0 °C under nitrogen. The reaction mixture was stirred for 24 h at 60-70 °C (Scheme 37). The reaction was washed with saturated aqueous $NaHCO_3$ and extracted thrice with ethyl acetate and the combined extracts were dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure. The pure product was isolated by column chromatography with silica gel (elution with EA: Hexane = 1:20).[35]



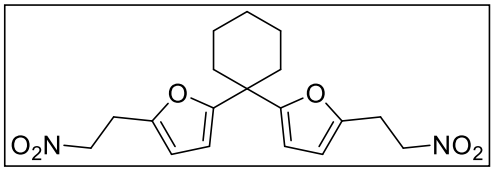
Scheme 37. Synthesis of dinitroalkane**s** by Friedel Crafts alkylation.



5,5'-(Propane-2,2-diyl)bis(2-(2-nitroethyl)furan) (4e): Yield: 62 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.02 (d, *J* = 3.2 Hz, 2H), 5.90 (d, *J* = 3.2 Hz, 2H), 4.60 (t, *J* = 6.8 Hz, 4H), 3.31 (t, *J* = 6.8 Hz, 4H), 1.57 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.7, 148.0, 107.9, 105.0, 73.7, 37.5, 26.3, 26.2; IR (ATR) ν 1547, 1378 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{15}H_{18}N_2O_6Na)^+$ 345.1063; found 345.1073.



5,5'-(Butane-2,2-diyl) bis (2-(2-nitroethyl)furan) (4f): Yield: 40 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.02 (d, *J* = 3.2 Hz, 2H), 5.93 (d, *J* = 3.2 Hz, 2H), 4.60 (t, *J* = 6.8 Hz, 4H), 3.30 (t, *J* = 6.8 Hz, 4H), 1.98 (q, *J* = 7.6 Hz, 2H), 1.51 (s, 3H), 0.76 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 158.9, 147.9, 107.8, 105.9, 41.5, 31.7, 26.3, 22.1, 8.8; IR (ATR) ν 1548.35, 1378.02 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{16}H_{20}N_2O_6Na)^+$ 359.1219; found 359.1229.

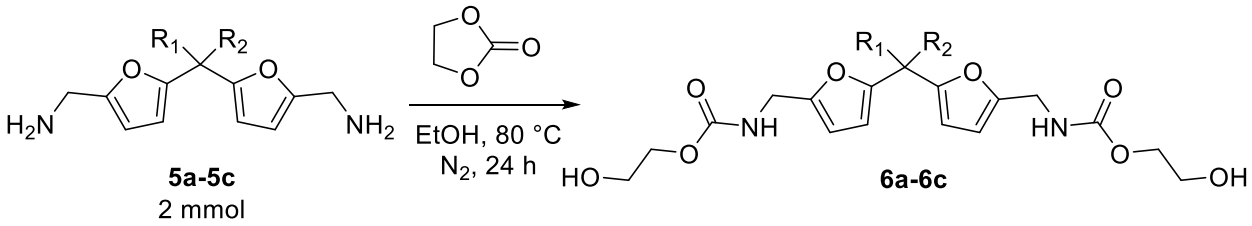


5,5'-(Cyclohexane-1,1-diyl)bis(2-(2-nitroethyl)furan) (4g): Yield: 35 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.02 (d, *J* = 3.2 Hz, 2H), 5.88 (d, *J* = 3.2 Hz, 2H), 4.59 (t, *J* = 6.8 Hz,

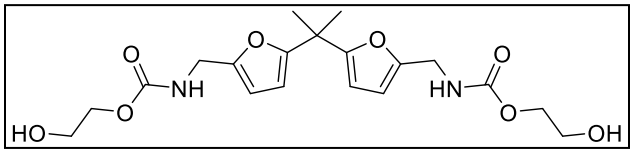
4H), 2.05-2.15 (m, 4H), 1.40-1.55 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 158.7, 147.7, 107.9, 106.0, 73.7, 41.8, 33.8, 26.3, 25.8, 22.4; IR (ATR) ν 1548.52, 1378.30 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{18}H_{22}N_2O_6Na)^+$ 385.1375; found 385.1377.

4.8. Synthesis of Hydroxyalkylcarbamates from Diamines

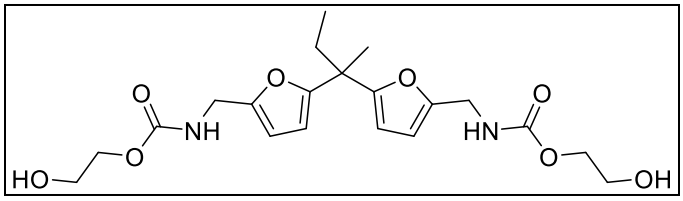
General procedure: Diamine (2 mmol, 1 eq) and ethylene carbonate (4.2 mmol, 2.1 eq) were dissolved in 4 mL EtOH under argon (Scheme 38). The starting material was not converted completely at room temperature. The temperature was increased to 80 °C. After 24 h, the reaction was complete. The mixture was extracted thrice with DCM and the combined extracts were dried over sodium sulfate. After filtration, the pure product was obtained after the solvent was removed under reduced pressure.[42]



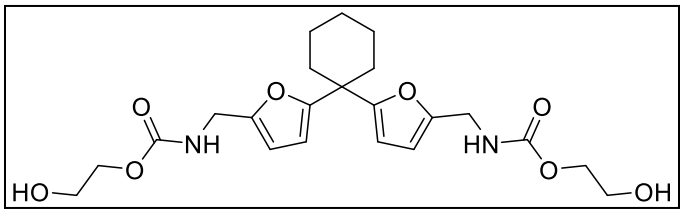
Scheme 38. Synthesis of hydroxyalkylcarbamates from different diamines.



Bis (2-hydroxyethyl) ((propane-2,2-diylbis(furan-5,2-diyl)) bis(methylene)) dicarbamate (6a): Yield: 80 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.08 (d, J = 2.8 Hz, 2H), 5.92 (d, J = 2.8 Hz, 2H), 5.56 (br. s, 2H), 4.24 (d, J = 5.2 Hz, 4H), 4.14 (s, 4H), 3.65-3.75 (m, 4H), 3.16 (s, 2H), 1.57 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.7, 156.9, 150.1, 107.8, 104.9, 66.9, 61.5, 38.3, 37.3, 26.3; IR (ATR) ν 3317, 1694, 1524, 1247 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{19}H_{25}N_2O_8)^-$ 409.1611; found 409.1613.



Bis(2-hydroxyethyl)((butane-2,2-diylbis(furan-5,2-diyl))bis(methylene)) dicarbamate (6b): Yield: 76 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ 6.06 (d, *J* = 3.2 Hz, 2H), 5.92 (d, *J* = 3.2 Hz, 2H), 5.72 (br. s, 2H), 4.20 (d, *J* = 5.6 Hz, 4H), 4.10 (s, 4H), 3.67 (s, 4H), 3.49 (br. s, 2H), 1.95 (q, *J* = 7.2 Hz, 2H), 1.48 (s, 3H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101MHz) δ 158.8, 156.9, 150.1, 107.6, 105.8, 66.7, 61.2, 41.3, 38.2, 31.6, 22.0, 8.8; IR (ATR) ν 3316.61, 1693.52, 1526.03, 1247.12 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{20}H_{28}N_2O_8Na)^+$ 447.1743; found 447.1740.

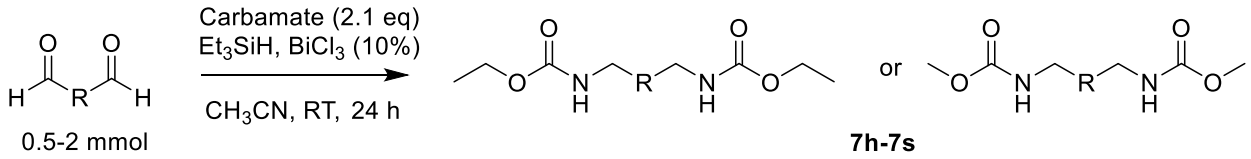


Bis(2-hydroxyethyl) ((cyclohexane-1,1-diylbis(furan-5,2diyl)) bis(methylene)) dicarbamate (6c): Yield: 81 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ 6.04 (d, *J* = 4 Hz, 2H), 5.86 (d, *J* = 4 Hz, 2H), 5.80 (br. s, 2H), 4.17 (d, *J* = 5.6 Hz, 4H), 4.06 (s, 4H), 3.69 (br. s, 2H), 3.63 (s, 4H), 2.05 (s, 4H), 1.60-1.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 101MHz) δ 158.6, 156.8, 149.9, 107.6, 105.8, 66.6, 61.0, 41.6, 38.1, 33.7, 25.7, 22.3; IR (ATR) ν 3316.84, 1693.91, 1526.56, 1247.89 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{22}H_{30}N_2O_8Na)^+$ 473.1900; found 473.1894.

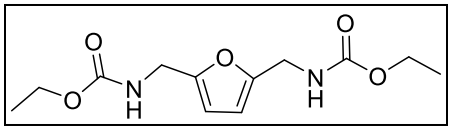
4.9. Synthesis of Carbamates Directly from Aldehydes

General procedure: Dialdehyde substrate (2 mmol, 1 eq), triethylsilane (8 mmol, 4 eq), ethyl carbamate or methyl carbamate (4.2 mmol, 2.1 eq) and $BiCl_3$ (10 mol %) were mixed in a round bottle flask under argon (Scheme 39). Dry acetonitrile (5 mL) was then added and the

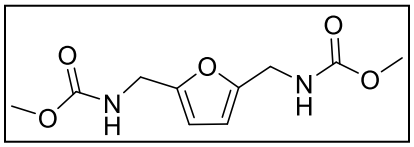
reaction was stirred for 24 h at room temperature. The catalyst was removed by filtration and then the solvent was removed under reduced pressure. The remaining triethylsilane was removed by washing with hexane. The pure product was obtained after recrystallization with hexane and DCM.[60]



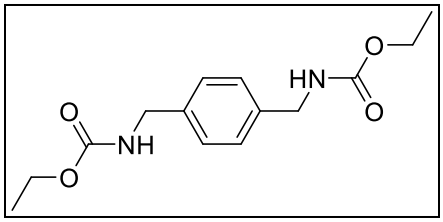
Scheme 39. Condition for carbamates synthesis from aldehydes.



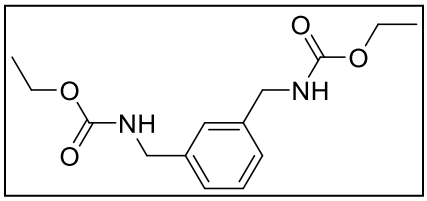
Diethyl(furan-2,5-diylbis(methylene))dicarbamate (7h): Yield: 85 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.11 (s, 2H), 5.14 (br. s, 2H), 4.26 (d, J = 5.6 Hz, 4H), 4.10 (q, J = 6.8 Hz, 4H), 1.21 (t, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 156.5, 151.5, 108.1, 61.2, 38.2, 14.7; IR (ATR) ν 3316, 1693, 1526, 1249 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{12}H_{18}N_2O_5Na)^+$ 293.1113; found 293.1113.



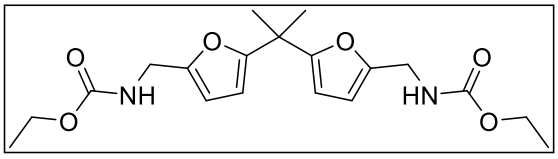
Dimethyl(furan-2,5-diylbis(methylene))dicarbamate (7h'): Yield: 70 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.14 (s, 2H), 5.00 (br. s, 2H), 4.31 (s, 4H), 4.13 (d, J = 5.6 Hz, 4H), 3.69 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 156.9, 151.5, 108.2, 52.5, 38.3; IR (ATR) ν 3322, 1694, 1519, 1244 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{10}H_{14}N_2O_5Na)^+$ 265.0800; found 265.0803.



Diethyl(1,4-phenylenebis(methylene))dicarbamate (7g): Yield: 90 %; White solid, mp. 135-137 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (s, 4H), 5.03 (br. s, 2H), 4.33 (s, 4H), 4.13 (d, *J* = 5.6 Hz, 4H), 1.24 (t, *J* = 6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 156.8, 138.0, 127.9, 61.2, 44.8, 14.8; IR (ATR) ν 3307, 1685, 1526, 1246 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{20}N_2O_4Na)^+$ 303.1321; found 303.1331.

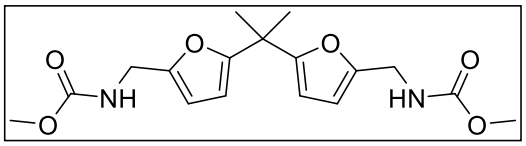


Diethyl (1,3-phenylenebis(methylene))dicarbamate (7n): Yield: 85 %; Light yellow solid, mp. 136-138 ºC; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 (s, 1H), 7.21 (s, 3H), 4.99 (br. s, 2H), 4.36 (s, 4H), 4.16 (s, 4H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 157.0, 139.2, 129.1, 126.7, 61.2, 45.0, 14.8; IR (ATR) ν 3309, 1684, 1530, 1250 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{14}H_{20}N_2O_4Na)^+$ 303.1333; found 303.1321.

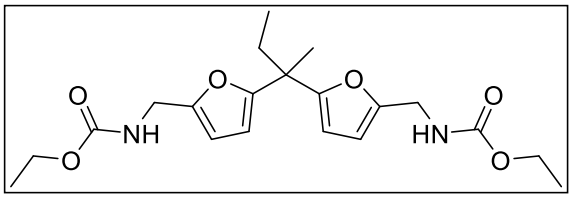


Diethyl((propane-2,2-diylbis(furan-5,2-diyl)) bis(methylene))dicarbamate (7m): Yield: 83 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.06 (s, 2H), 5.88 (s, 2H), 5.15 (br. s, 2H), 4.24 (s, 4H), 4.09 (d, *J* = 6.4 Hz, 4H), 1.56 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ

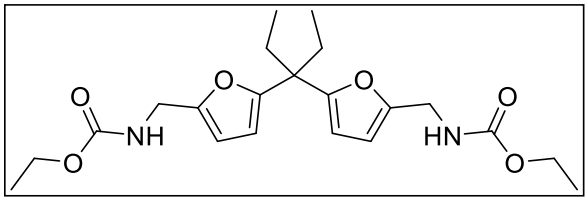
159.5, 156.4, 150.3, 107.5, 104.9, 60.9, 38.2, 37.3, 26.3, 14.6; IR (ATR) ν 3296, 1688, 1535, 1251 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{19}H_{26}N_2O_4Na)^+$ 369.1790; found 369.1803.



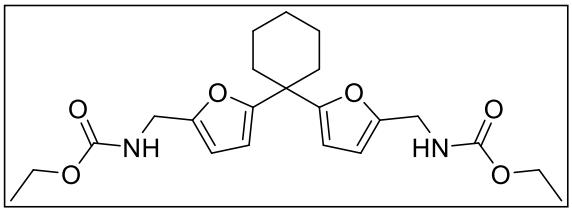
Dimethyl ((propane-2,2-diylbis (furan-5,2-diyl))bis(methylene))dicarbamate (7m'): Yield: 80 %; Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.06 (s, 2H), 5.88 (s, 2H), 5.34 (br. s, 2H), 4.24 (s, 4H), 3.62 (s, 6H), 1.55 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.1, 156.7, 150.0, 107.3, 104.6, 52.1, 38.0, 37.0, 26.0; IR (ATR) ν 3326.10, 1698.15, 1520.25, 1248.38 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{17}H_{22}N_2O_6Na)^+$ 373.1375; found 373.1377.



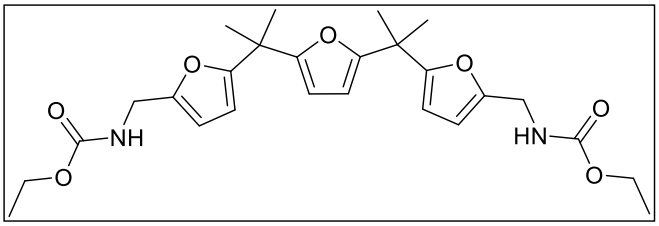
Diethyl ((butane-2,2-diylbis(furan-5,2-diyl)) bis(methylene))dicarbamate (7o): Yield: 74 %; Yellow oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.09 (s, 2H), 5.93 (s, 2H), 5.26 (br. s, 2H), 4.28 (s, 4H), 4.11 (s, 4H), 1.99 (s, 2H), 1.52 (s, 3H), 1.22 (s, 6H), 0.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 157.6, 155.8, 149.3, 106.5, 104.8, 60.1, 40.3, 37.3, 30.7, 21.2, 13.8, 7.9; IR (ATR) ν 3324.67, 1694.18, 1520.36, 1244.54 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{20}H_{28}N_2O_6Na)^+$ 415.1845; found 415.1847.



Diethyl ((pentane-3,3-diylbis (furan-5,2-diyl)) bis(methylene))dicarbamate (7p): Yield: 80 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.11 (s, 2H), 6.00 (s, 2H), 5.18 (br. s, 2H), 4.27 (s, 4H), 4.11 (s, 4H), 1.97 (s, 4H), 1.22 (s, 6H), 0.70 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 156.2, 155.4, 149.0, 106.2, 105.9, 59.9, 44.4, 37.2, 26.6, 13.7, 7.3; IR (ATR) ν 3325.95, 1694.67, 1519.60, 1246.24 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{21}H_{30}N_2O_6Na)^+$ 429.2002; found 429.2007.

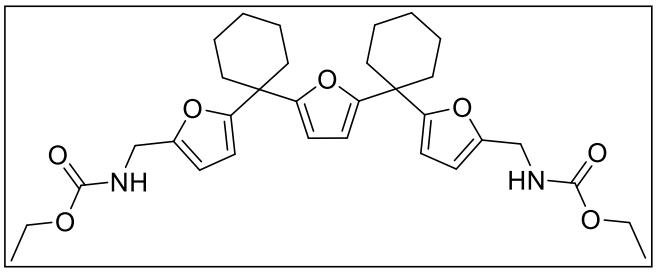


Diethyl ((cyclohexane-1,1-diylbis(furan-5,2-diyl)) bis(methylene))dicarbamate (7q): Yield: 82 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.08 (s, 2H), 5.87 (s, 2H), 5.07 (br. s, 2H), 4.25 (s, 4H), 4.10 (s, 4H), 2.09 (s, 4H), 1.48 (s, 6H), 1.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 158.7, 156.4, 150.0, 107.6, 105.9, 61.0, 41.8, 38.2, 33.8, 25.7, 22.4, 14.6; IR (ATR) ν 3323.54, 1694.20, 1520.44, 1243.96 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{22}H_{30}N_2O_6Na)^+$ 441.2002; found 441.1997.



Diethyl (((furan-2,5-diylbis(propane-2,2-diyl))bis(furan-5,2-diyl)) bis(methylene)) dicarbamate (7r): Yield: 77 %; Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.08 (s, 2H), 5.88 (s,

2H), 5.84 (s, 2H), 5.01 (br. s. 2H), 4.28 (s, 4H), 4.12 (s, 4H), 1.57 (s, 12H), 1.23 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.9, 158.3, 149.9, 107.5, 104.7, 104.2, 61.0, 38.2, 37.4, 26.2, 14.6; IR (ATR) ν 3327.29, 1694.29, 1519.51, 1243.04 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{26}H_{34}N_2O_7Na)^+$ 509.2264; found 509.2267.



Diethyl(((furan-2,5-diylbis(cyclohexane-1,1-diyl))bis(furan-5,2-diyl)) bis(methylene)) dicarbamate (7s): Yield: 68 %; Orange oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.08 (d, *J* = 3.2 Hz, 2H), 5.88 (s, 2H), 5.79 (d, *J* = 3.2 Hz, 2H), 4.97 (br. s. 2H), 4.27 (d, *J* = 4.4 Hz, 4H), 4.11 (q, *J* = 6.4 Hz, 4H), 2.00-2.25 (m, 8H), 1.35-1.55 (m, 12H), 1.15-1.30 (m, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.1, 156.2, 156.1, 149.3, 107.3, 105.3, 105.0, 60.8, 41.4, 38.0, 33.4, 25.4, 22.0, 14.4; IR (ATR) ν 3328.53, 1698.69, 1514.75, 1245.42 cm^{-1}; ESI-HRMS: m/z calcd. for $(C_{32}H_{42}N_2O_7Na)^+$ 589.2890; found 589.2890.

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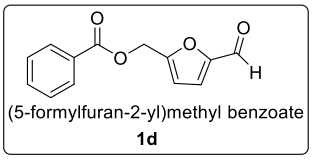
APPENDIX. NMR SPECTRAL DATA



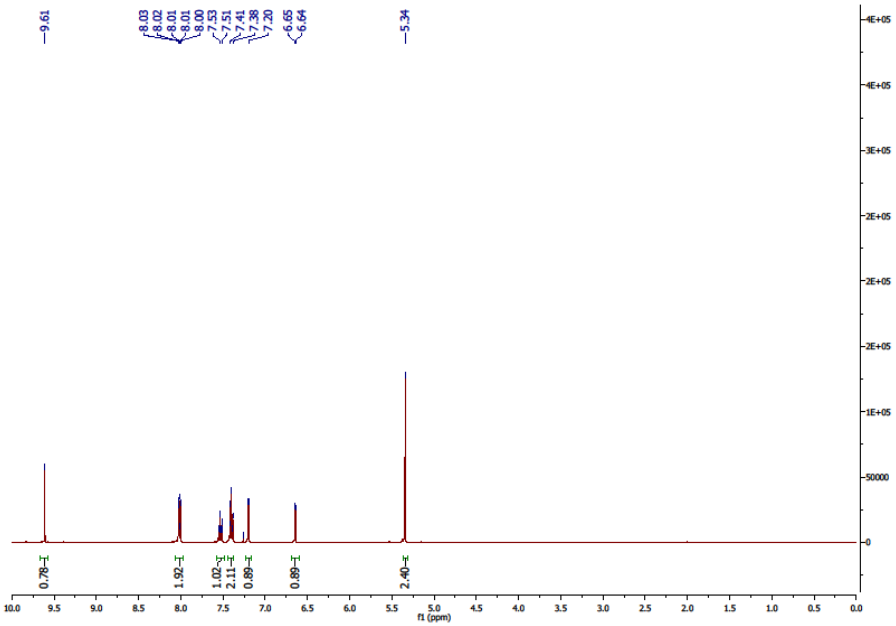


Figure A1. ^{1}H-NMR spectrum for compound **1d**

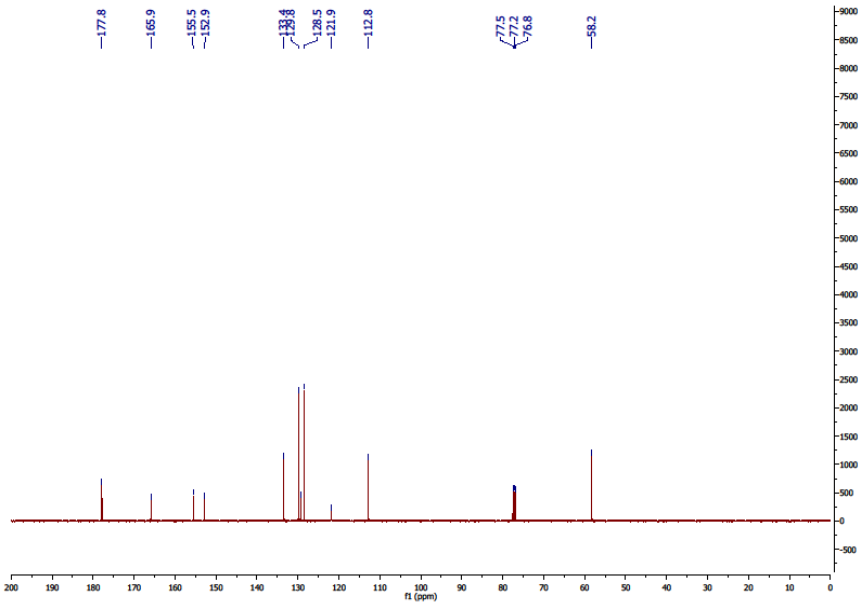
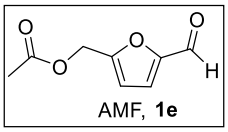


Figure A2. ^{13}C-NMR spectrum for compound **1d**



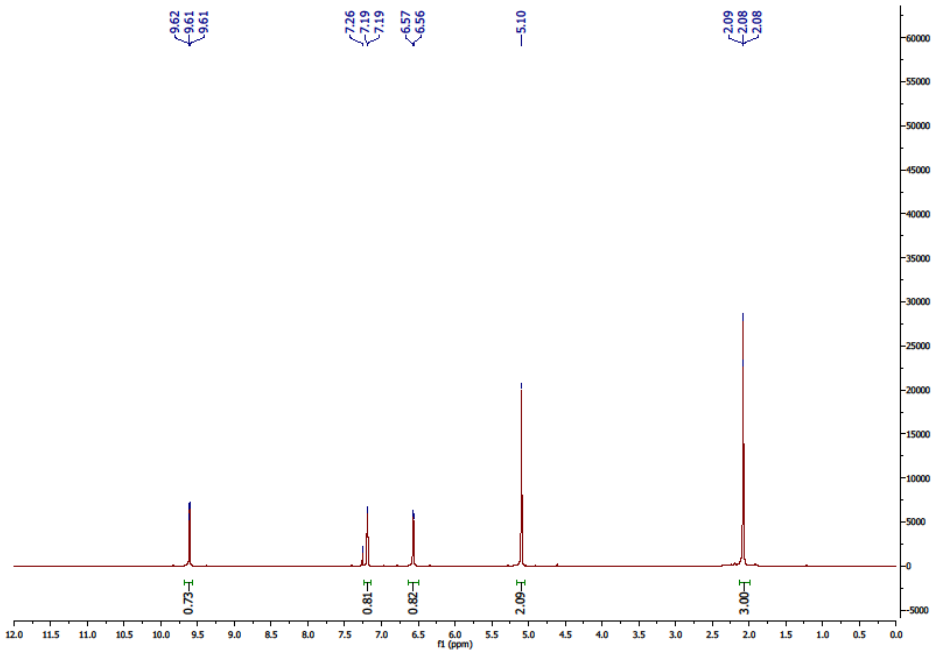


Figure A3. [1]H-NMR spectrum for compound **1e**

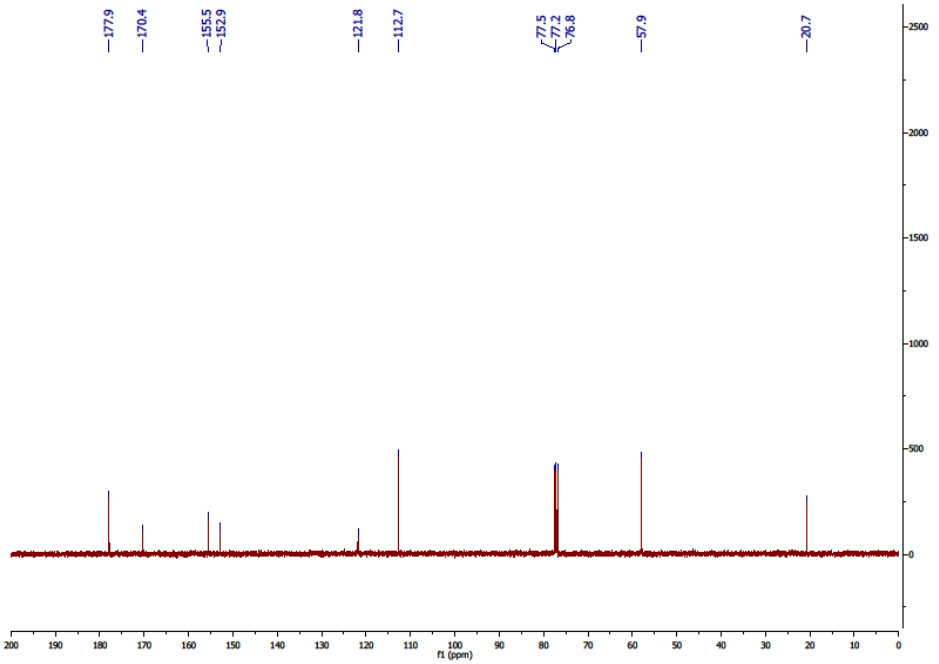
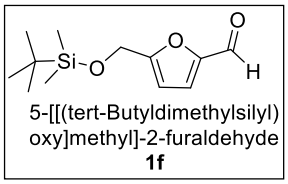


Figure A4. [13]C-NMR spectrum for compound **1e**



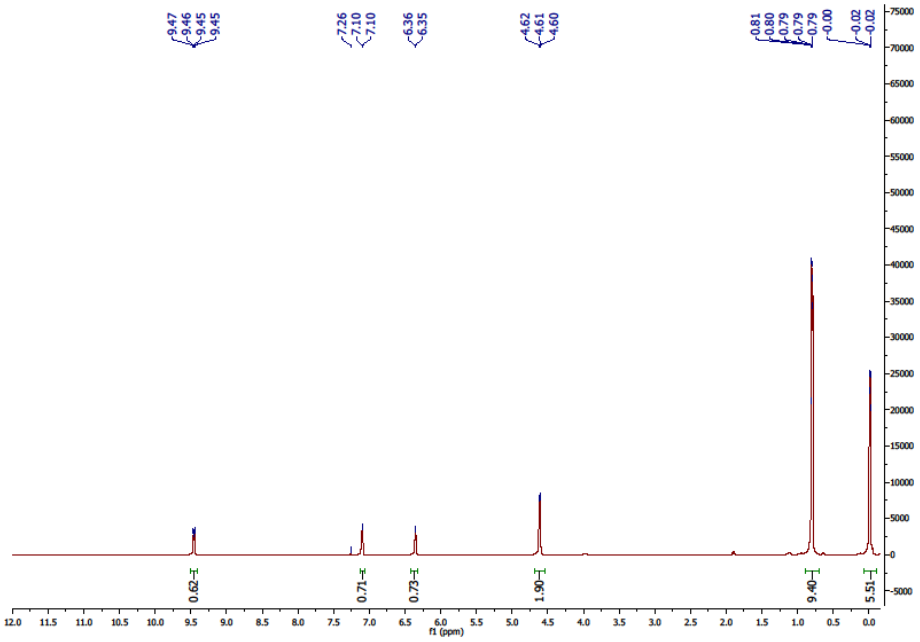


Figure A5. ^{1}H-NMR spectrum for compound **1f**

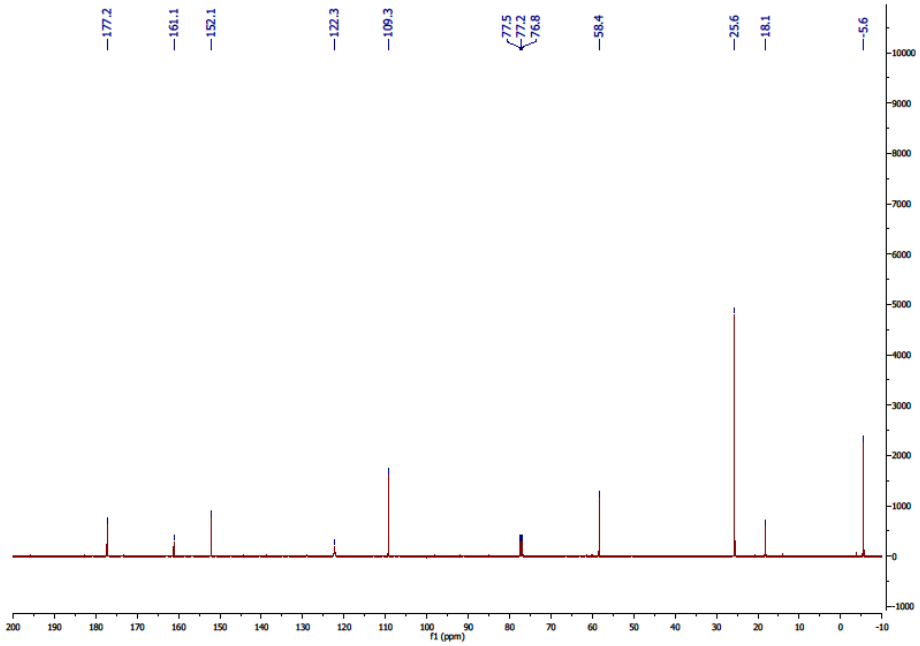
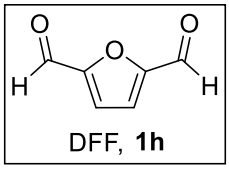


Figure A6. ^{13}C-NMR spectrum for compound **1f**



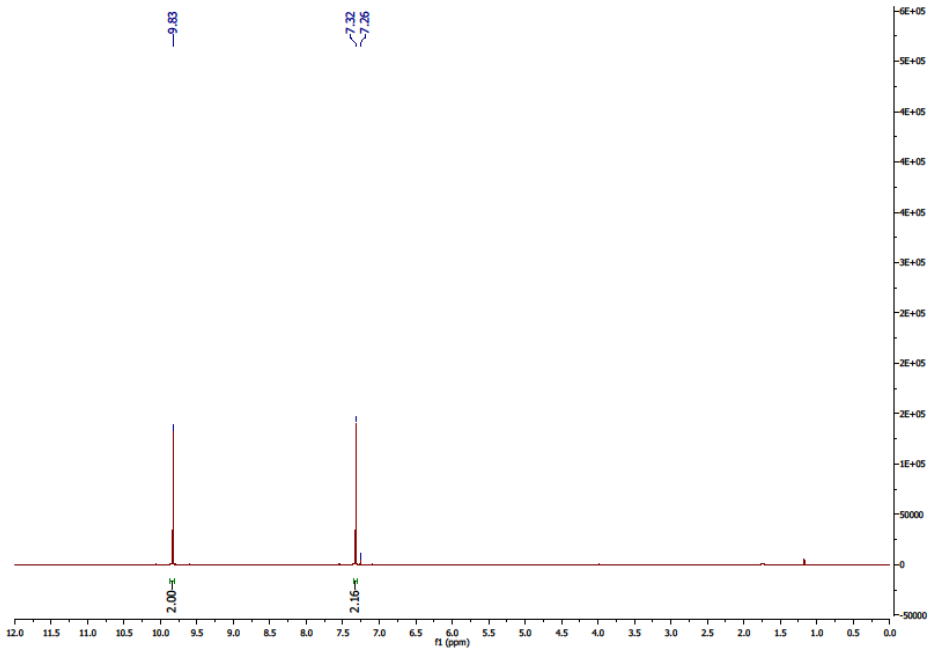


Figure A7. [1]H-NMR spectrum for compound **1h**

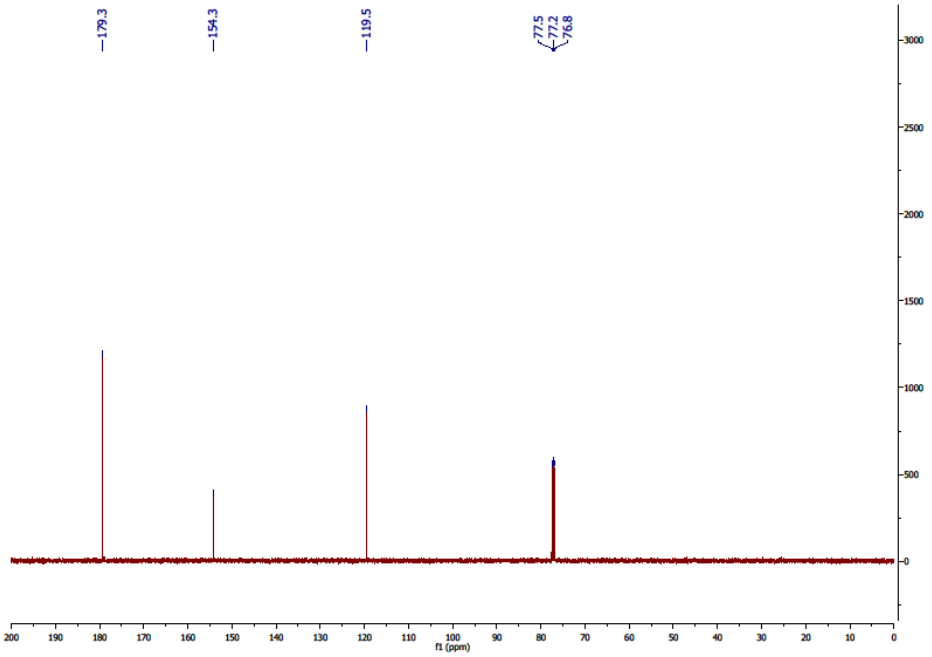
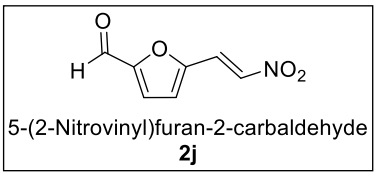


Figure A8. [13]C-NMR spectrum for compound **1h**



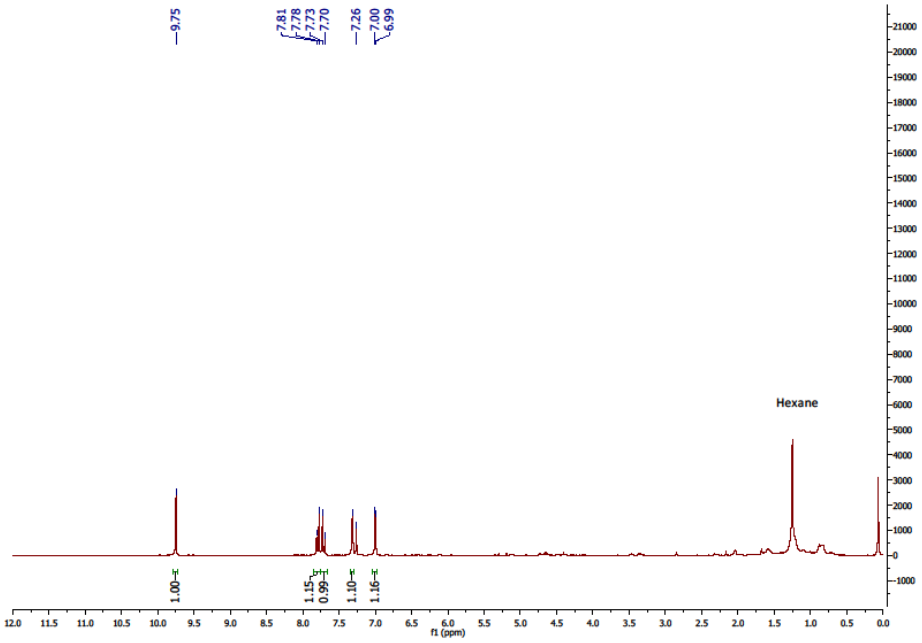


Figure A9. [1]H-NMR spectrum for compound **2j**

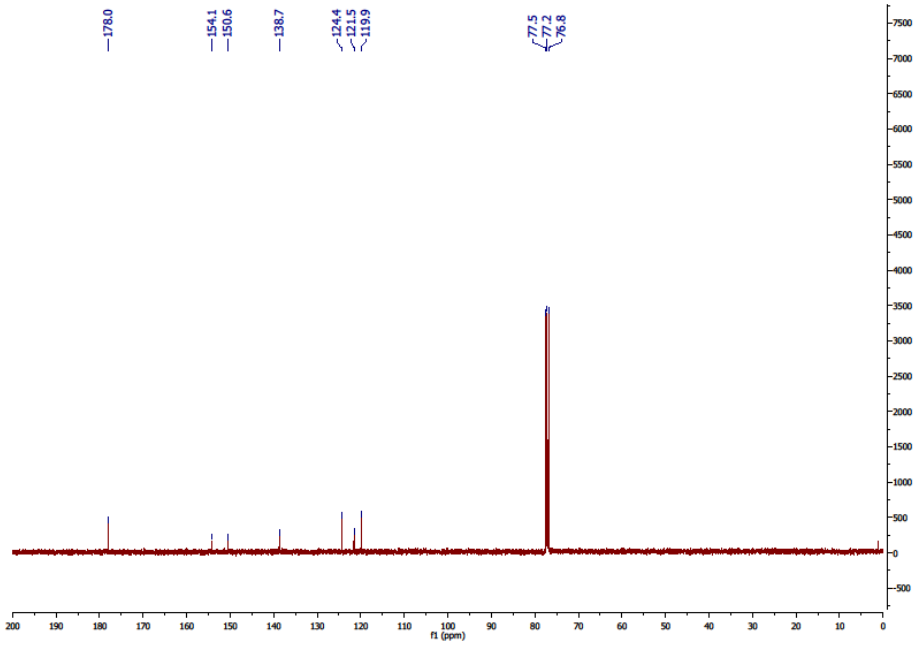
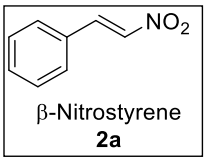


Figure A10. [13]C-NMR spectrum for compound **2j**



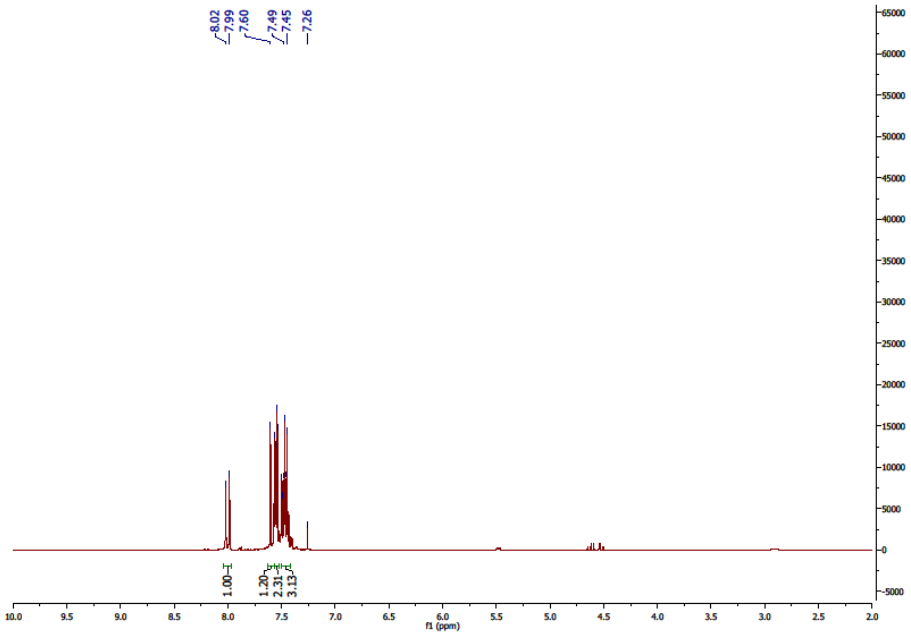


Figure A11. [1]H-NMR spectrum for compound **2a**

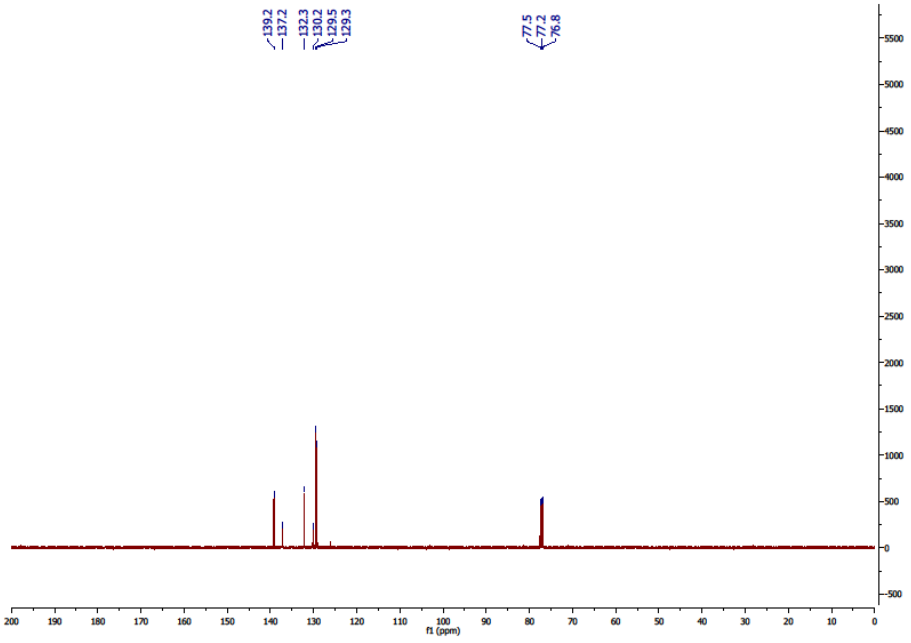
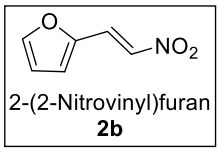


Figure A12. [13]C-NMR spectrum for compound **2a**



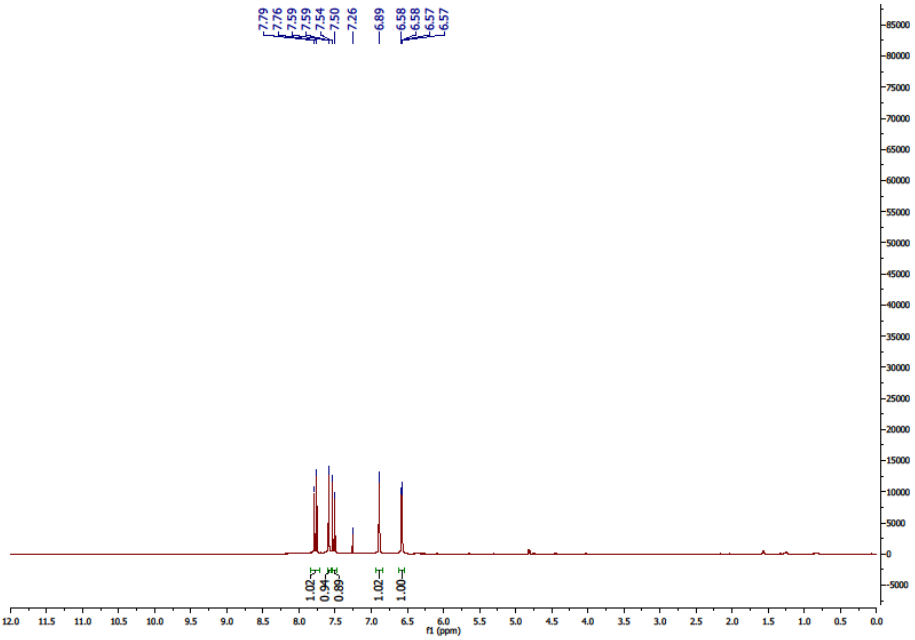


Figure A13. [1]H-NMR spectrum for compound **2b**

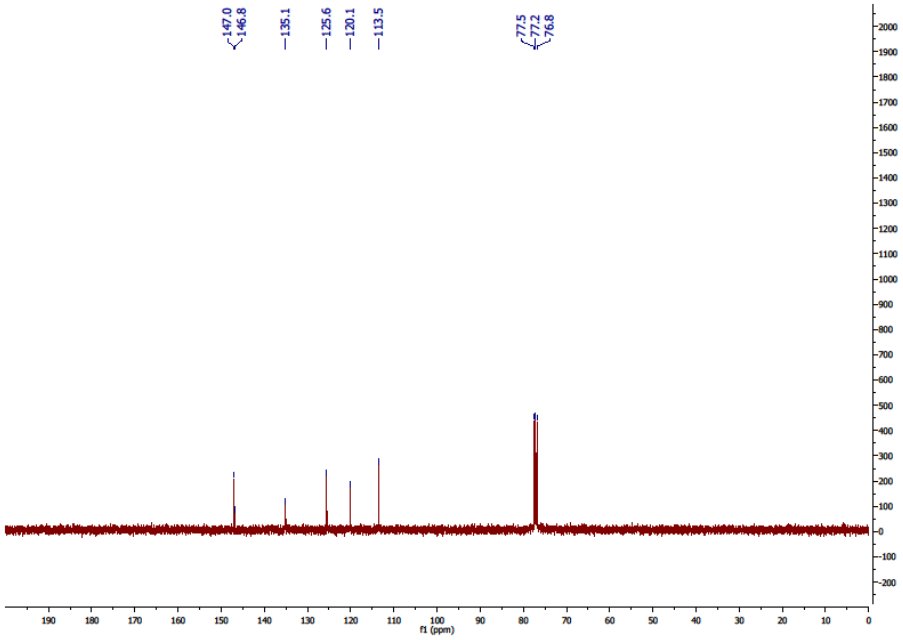
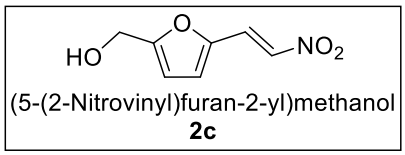


Figure A14. [13]C-NMR spectrum for compound **2b**



(5-(2-Nitrovinyl)furan-2-yl)methanol
2c

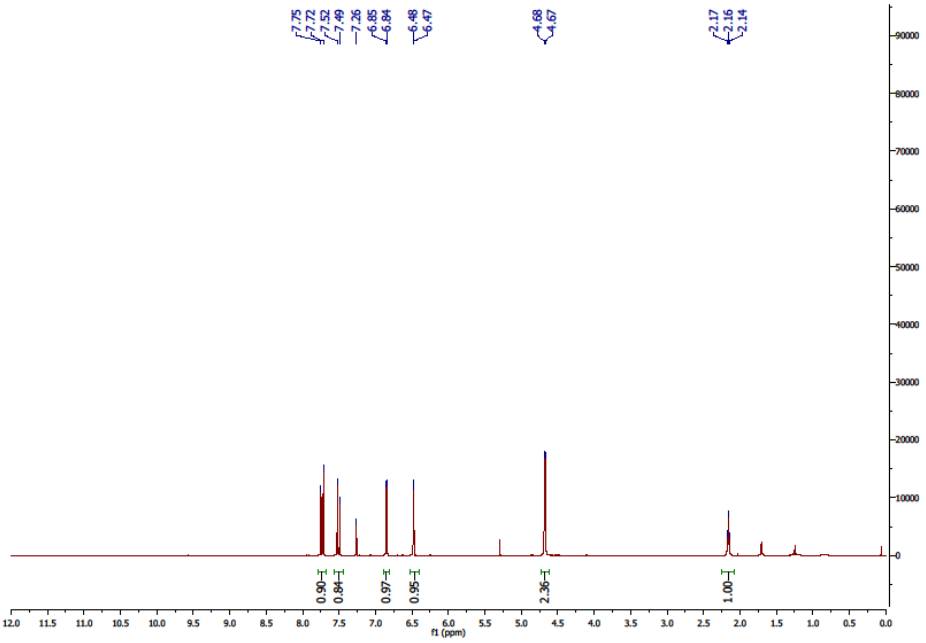


Figure A15. [1]H-NMR spectrum for compound **2c**

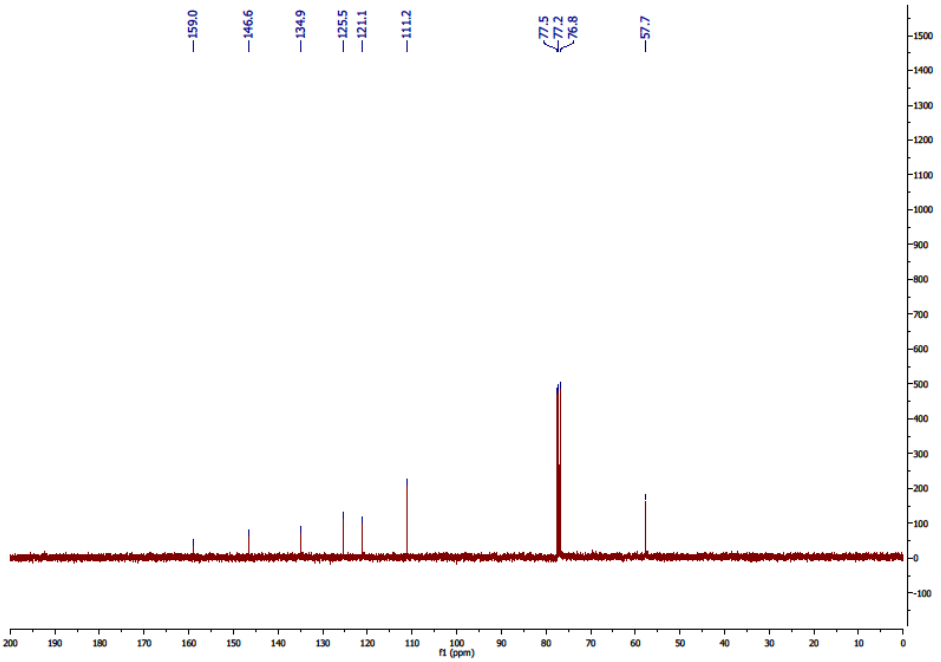
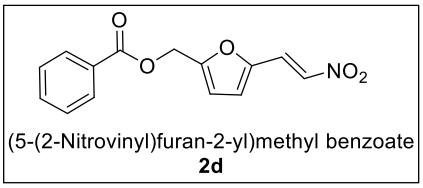


Figure A16. [13]C-NMR spectrum for compound **2c**



(5-(2-Nitrovinyl)furan-2-yl)methyl benzoate
2d

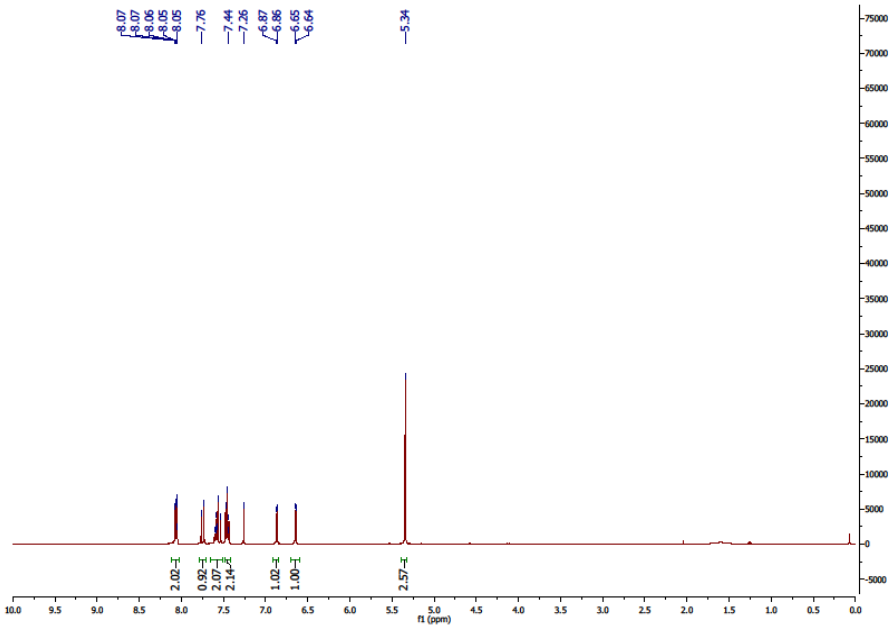


Figure A17. [1]H-NMR spectrum for compound **2d**

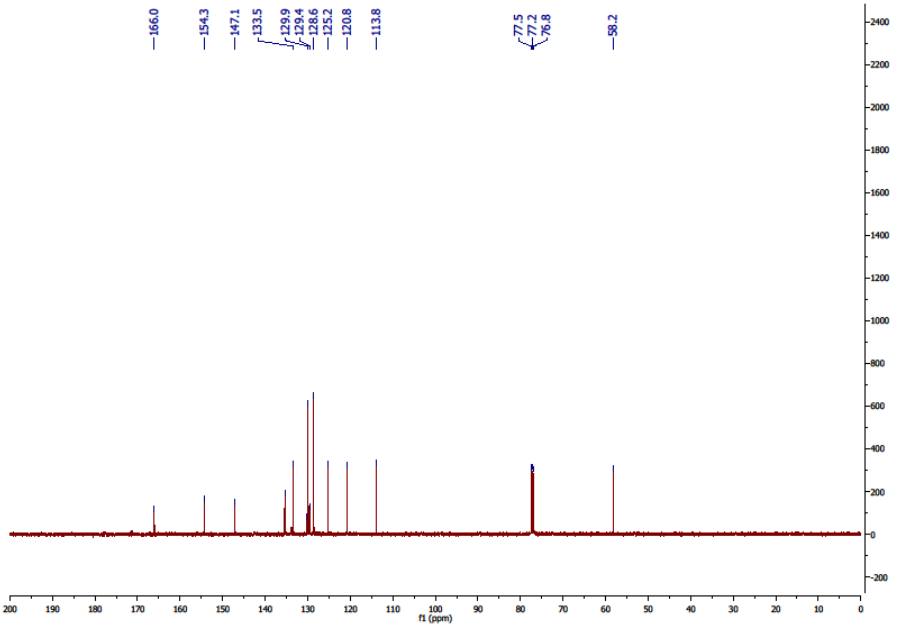
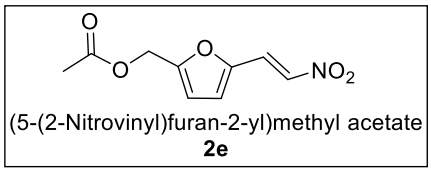


Figure A18. [13]C-NMR spectrum for compound **2d**



(5-(2-Nitrovinyl)furan-2-yl)methyl acetate
2e

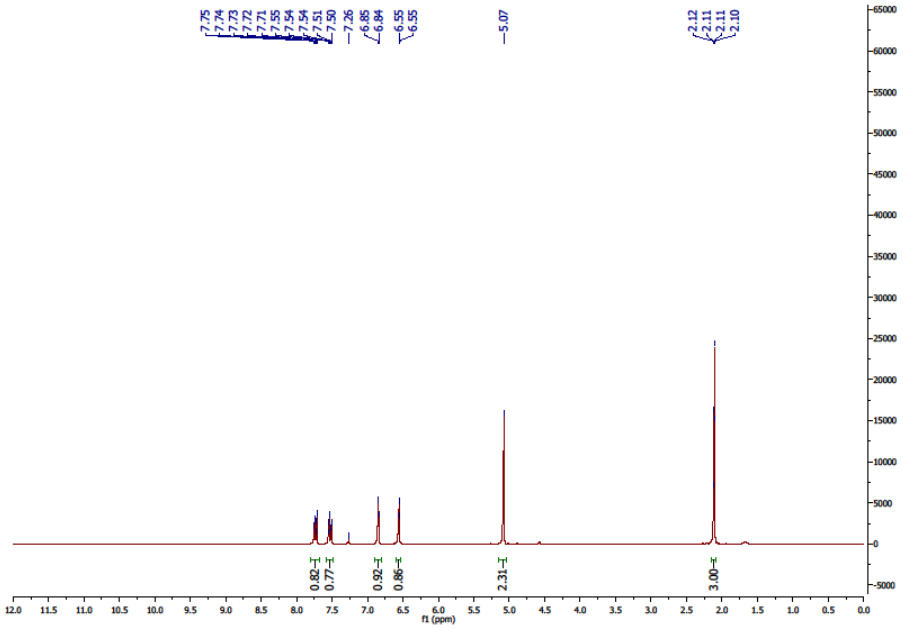


Figure A19. [1]H-NMR spectrum for compound **2e**

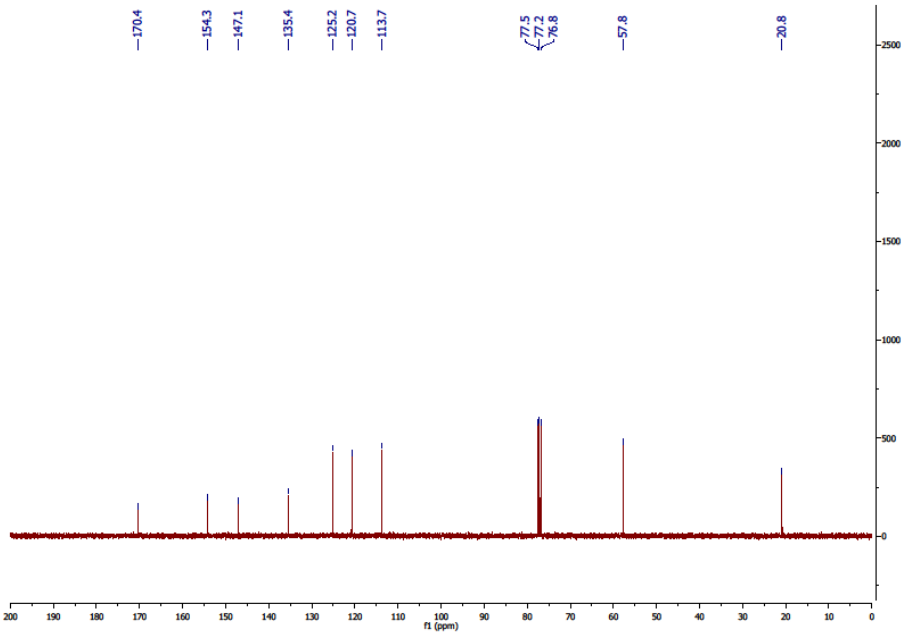
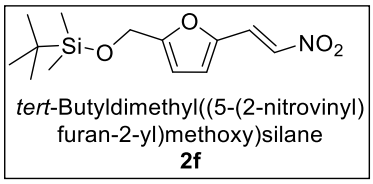


Figure A20. [13]C-NMR spectrum for compound **2e**



tert-Butyldimethyl((5-(2-nitrovinyl) furan-2-yl)methoxy)silane
2f

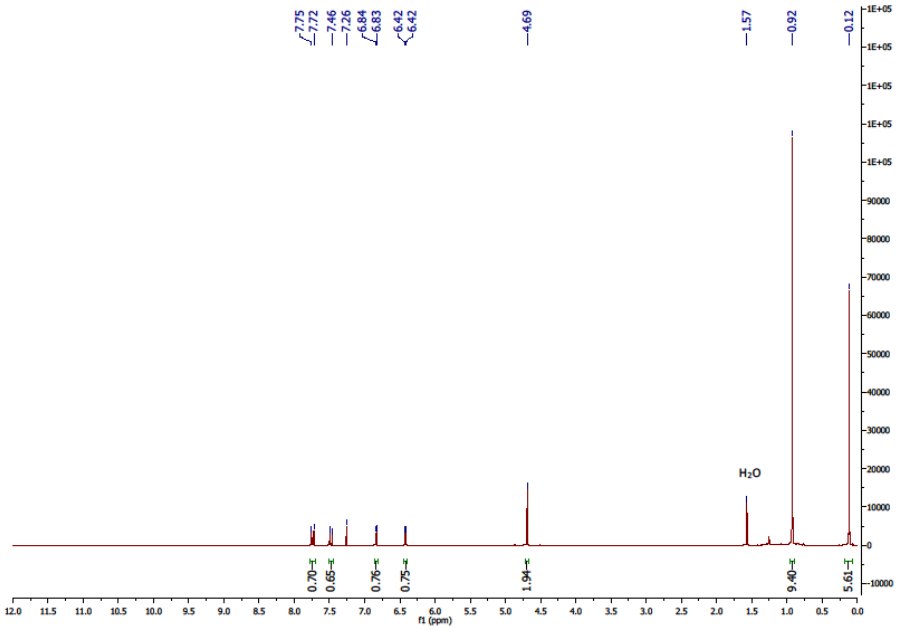


Figure A21. [1]H-NMR spectrum for compound **2f**

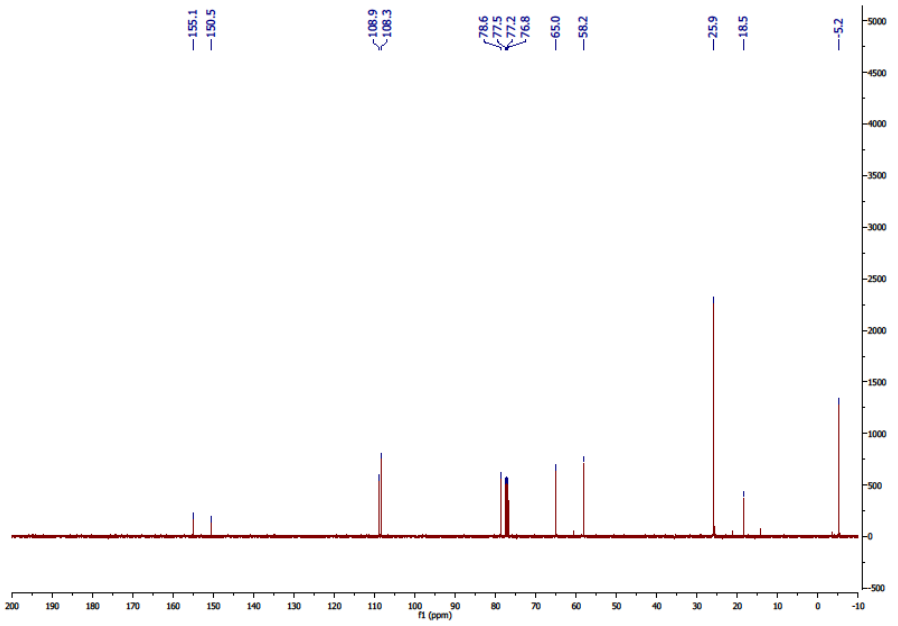
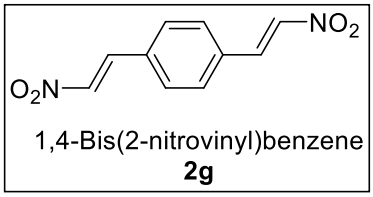


Figure A22. [13]C-NMR spectrum for compound **2f**



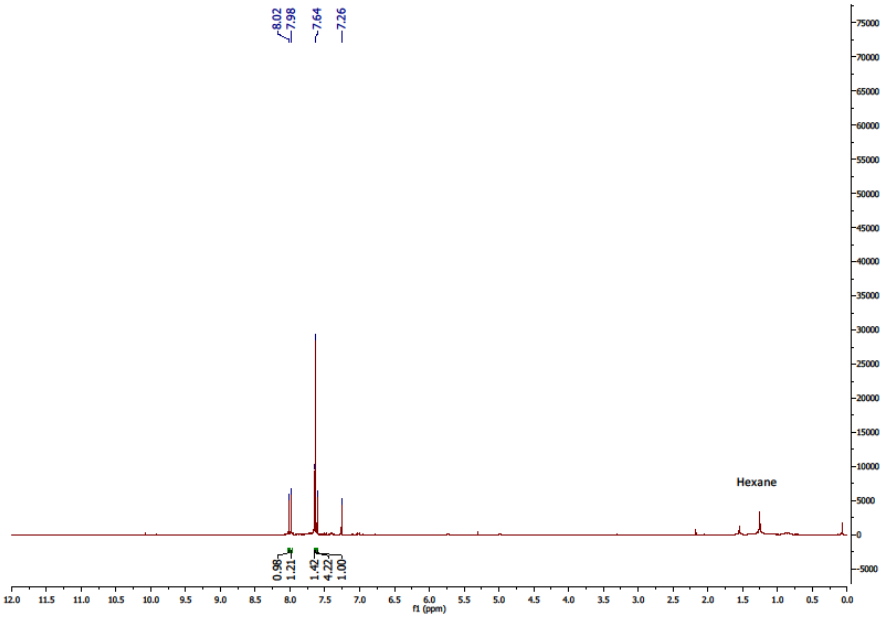


Figure A23. [1]H-NMR spectrum for compound **2g**

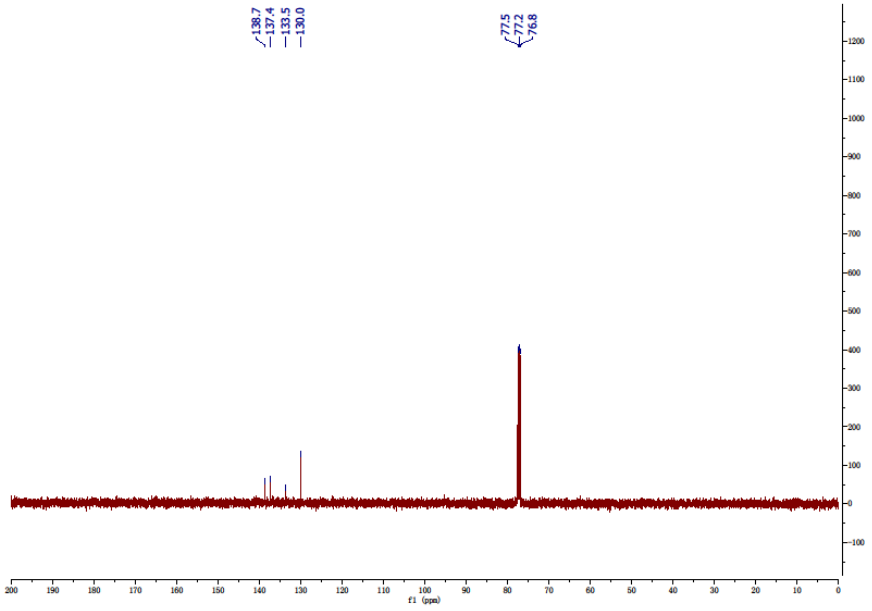
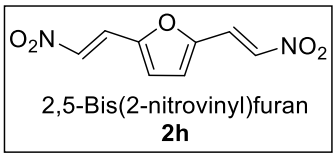


Figure A24. [13]C-NMR spectrum for compound **2g**



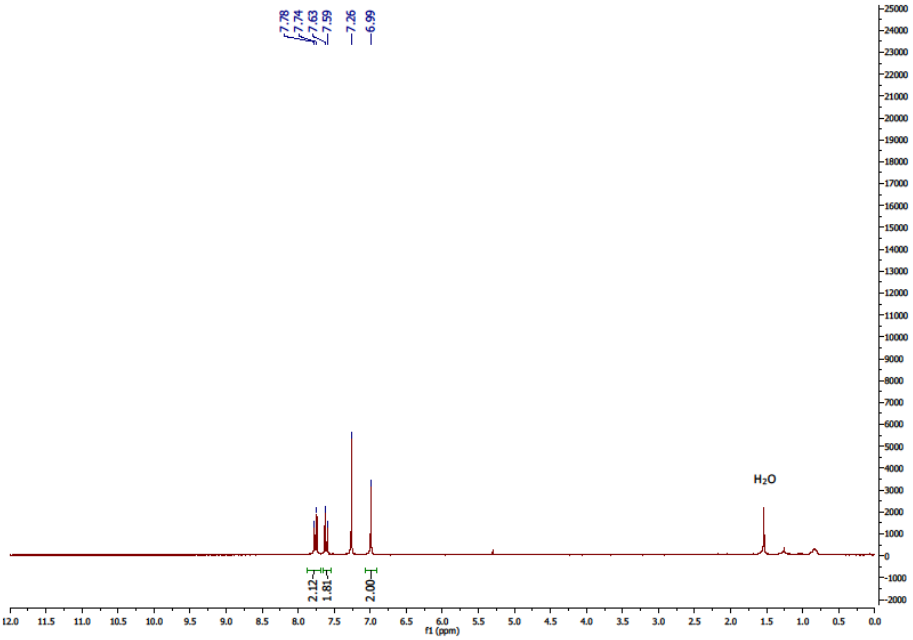


Figure A25. [1]H-NMR spectrum for compound **2h**

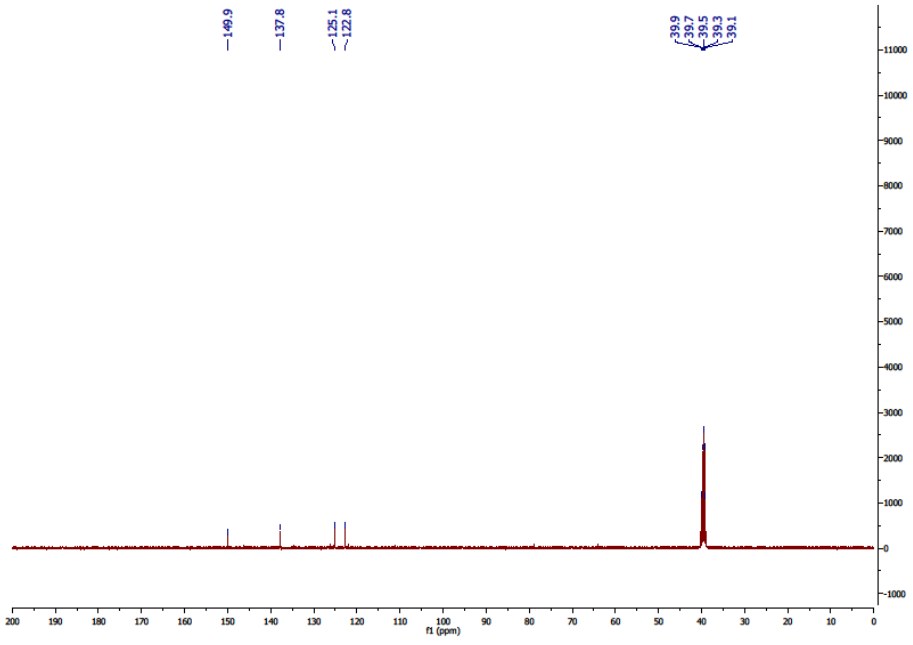
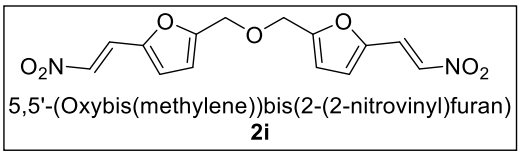


Figure A26. [13]C-NMR spectrum for compound **2h**



5,5'-(Oxybis(methylene))bis(2-(2-nitrovinyl)furan)

2i

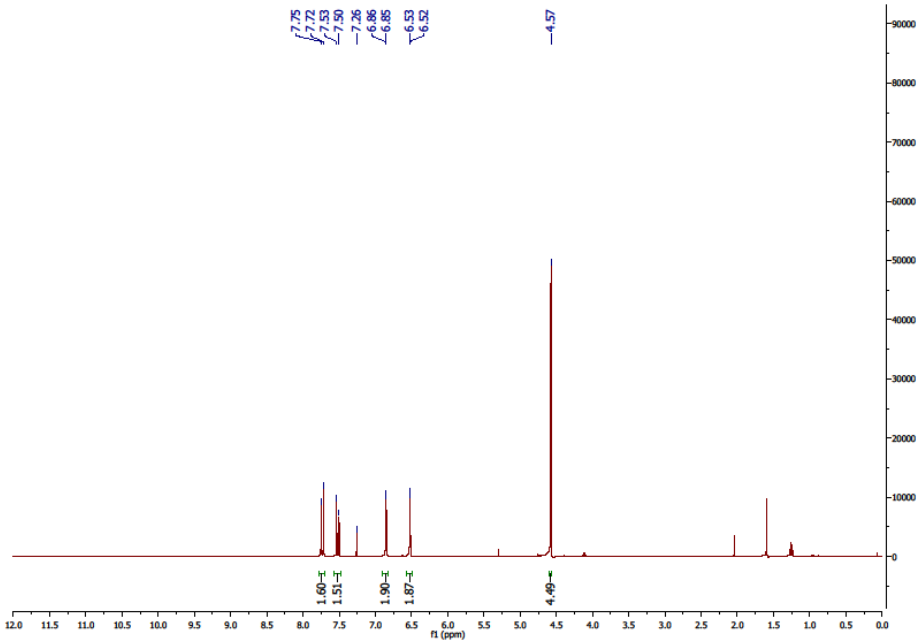


Figure A27. [1]H-NMR spectrum for compound **2i**

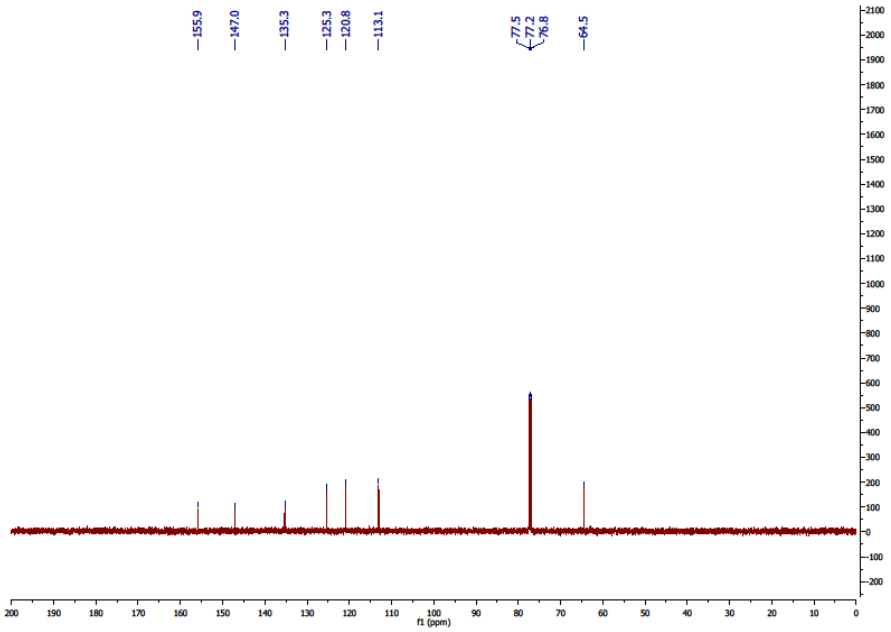
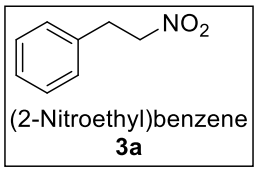


Figure A28. [13]C-NMR spectrum for compound **2i**



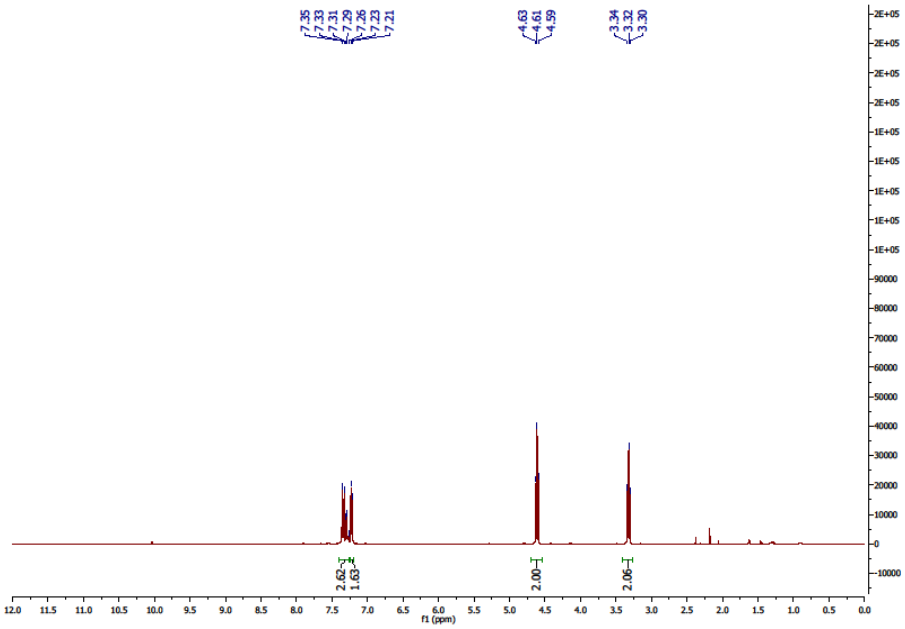


Figure A29. [1]H-NMR spectrum for compound **3a**

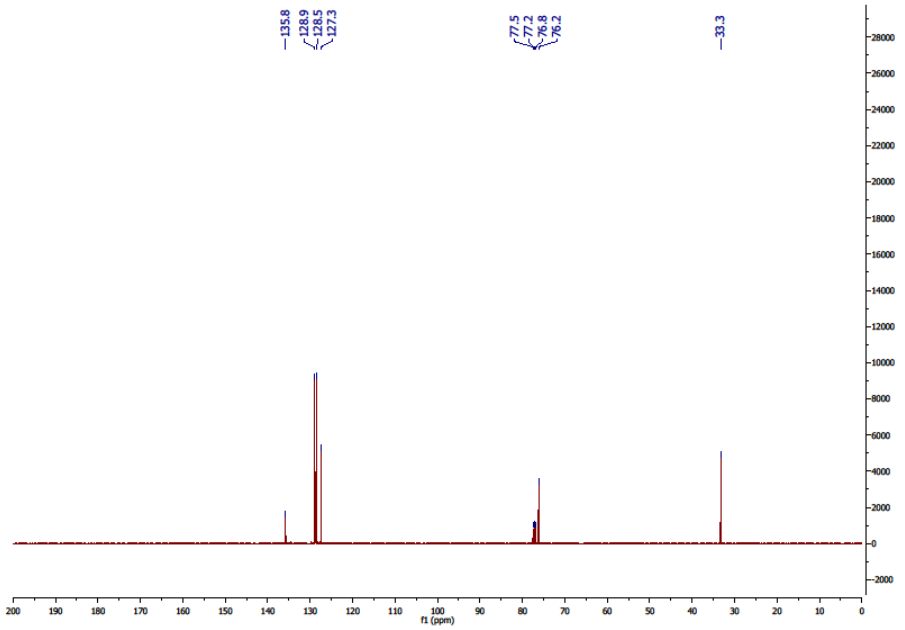
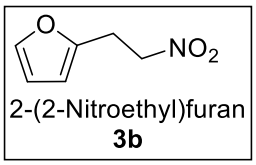


Figure A30. [13]C-NMR spectrum for compound **3a**



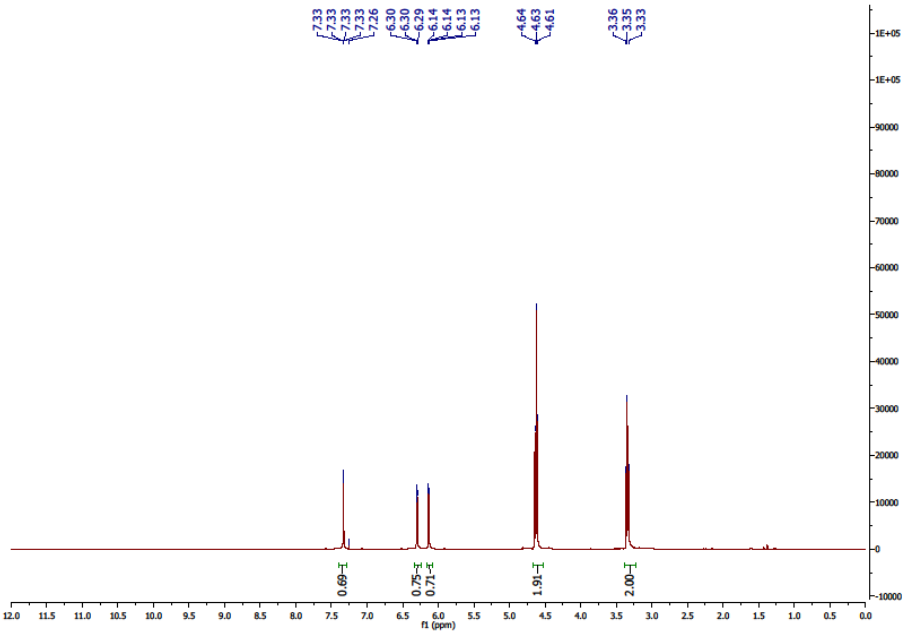


Figure A31. [1]H-NMR spectrum for compound **3b**

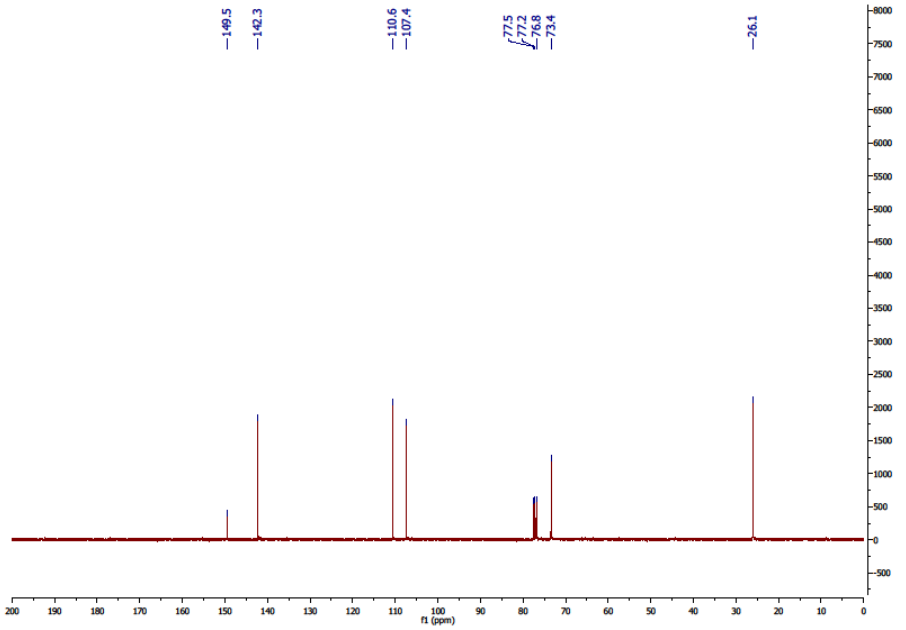
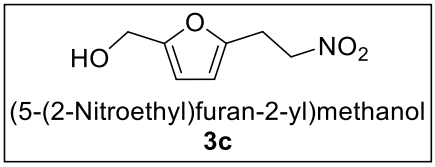


Figure A32. [13]C-NMR spectrum for compound **3b**



(5-(2-Nitroethyl)furan-2-yl)methanol
3c

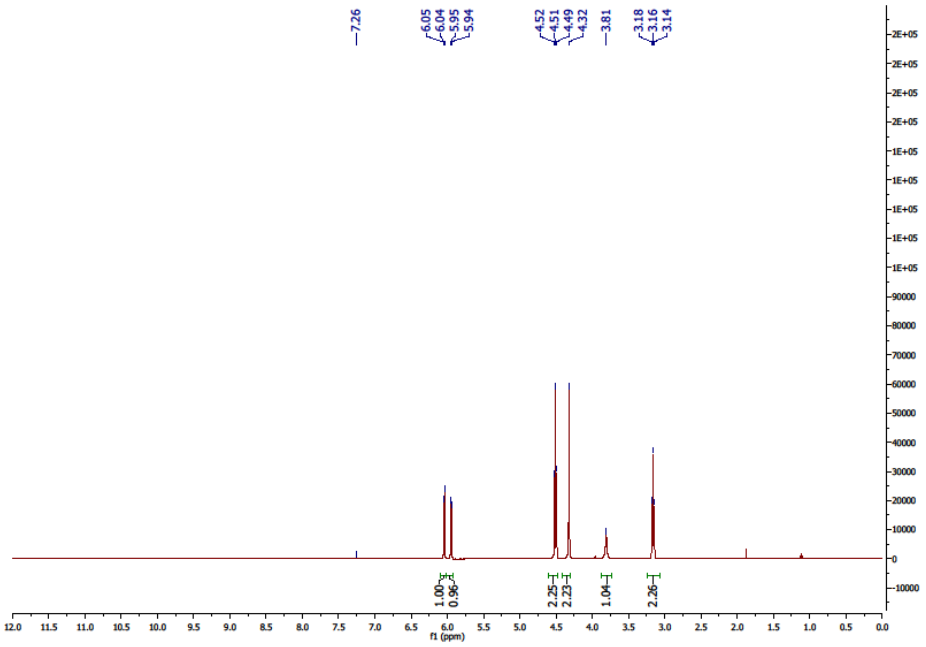


Figure A33. ^{1}H-NMR spectrum for compound **3c**

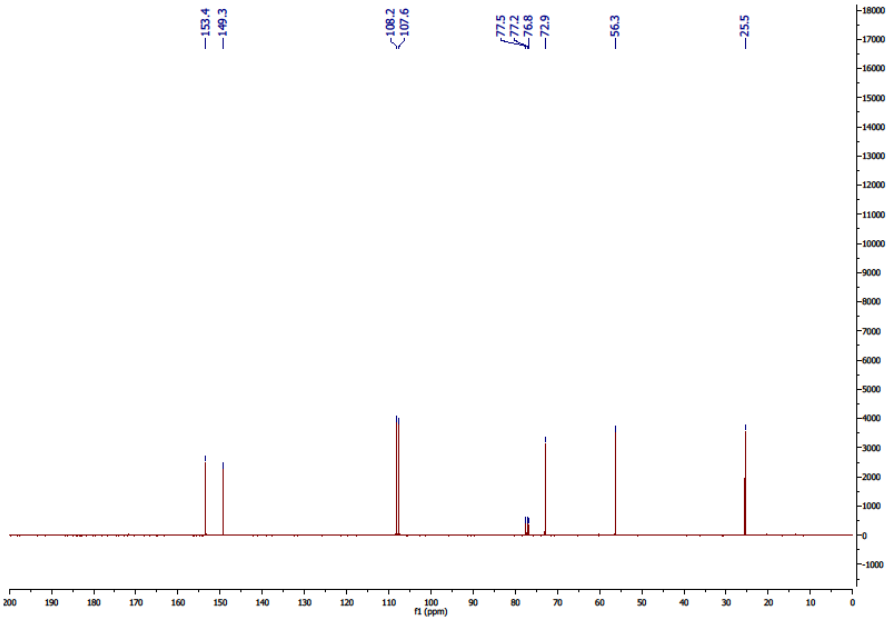
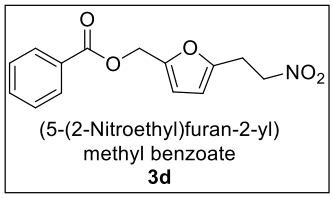


Figure A34. ^{13}C-NMR spectrum for compound **3c**



(5-(2-Nitroethyl)furan-2-yl)
methyl benzoate
3d

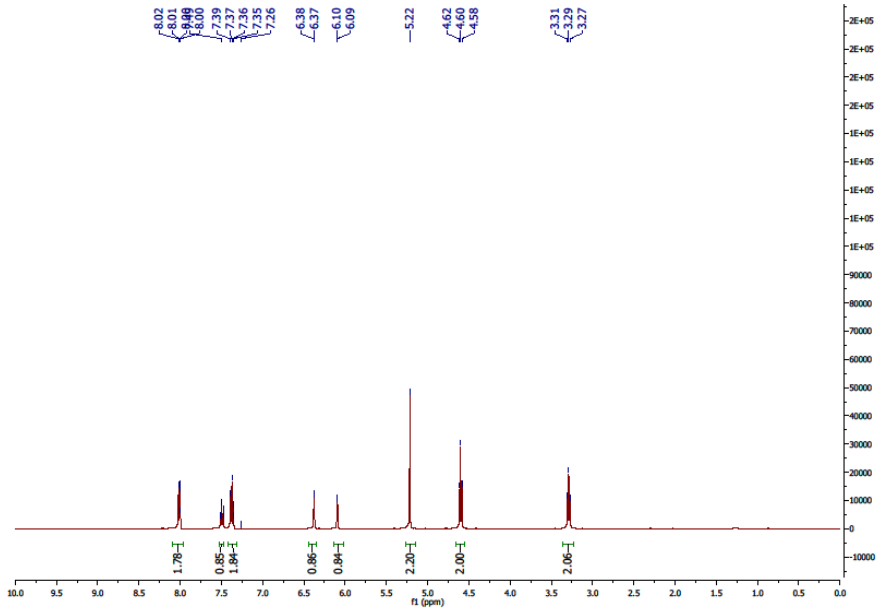


Figure A35. [1]H-NMR spectrum for compound **3d**

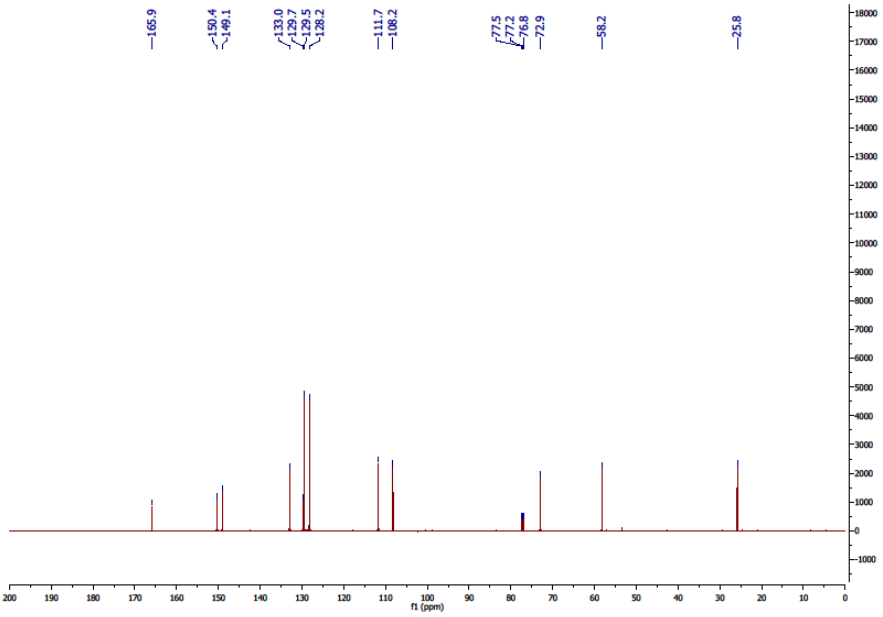
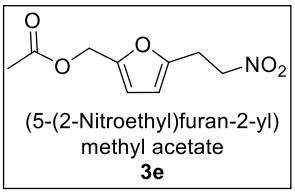


Figure A36. [13]C-NMR spectrum for compound **3d**



(5-(2-Nitroethyl)furan-2-yl) methyl acetate

3e

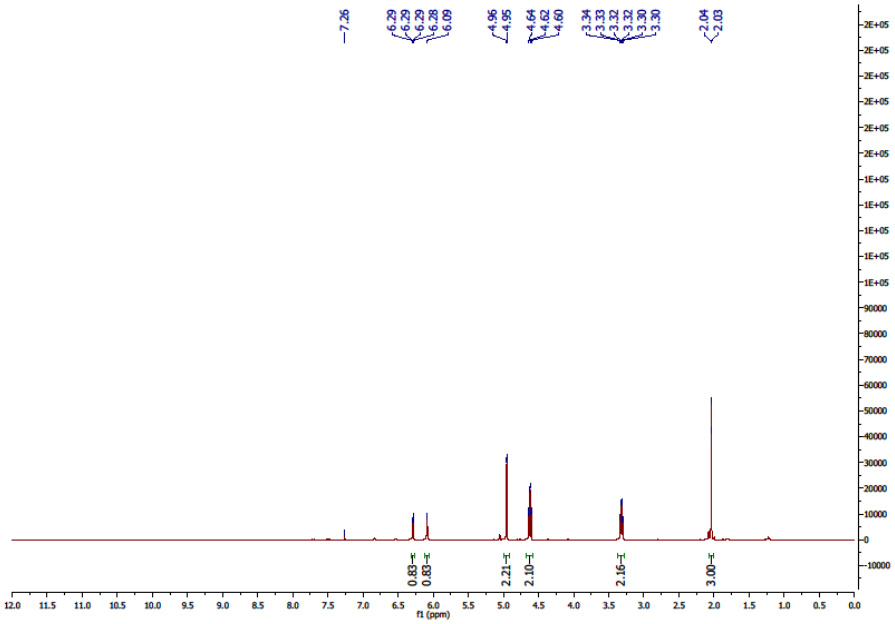


Figure A37. [1]H-NMR spectrum for compound **3e**

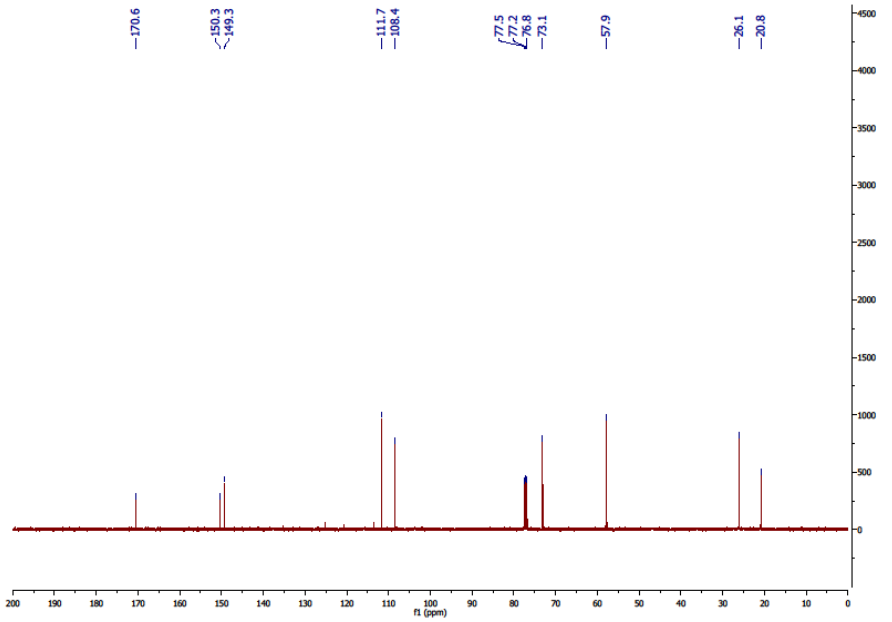
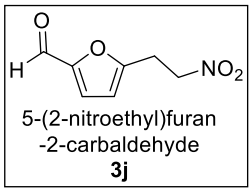


Figure A38. [13]C-NMR spectrum for compound **3e**



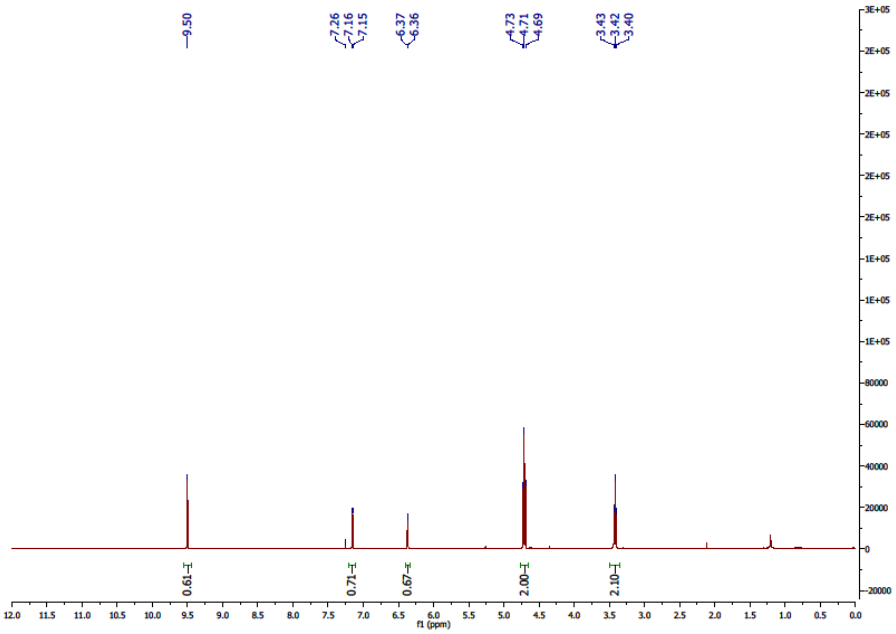


Figure A39. [1]H-NMR spectrum for compound **3j**

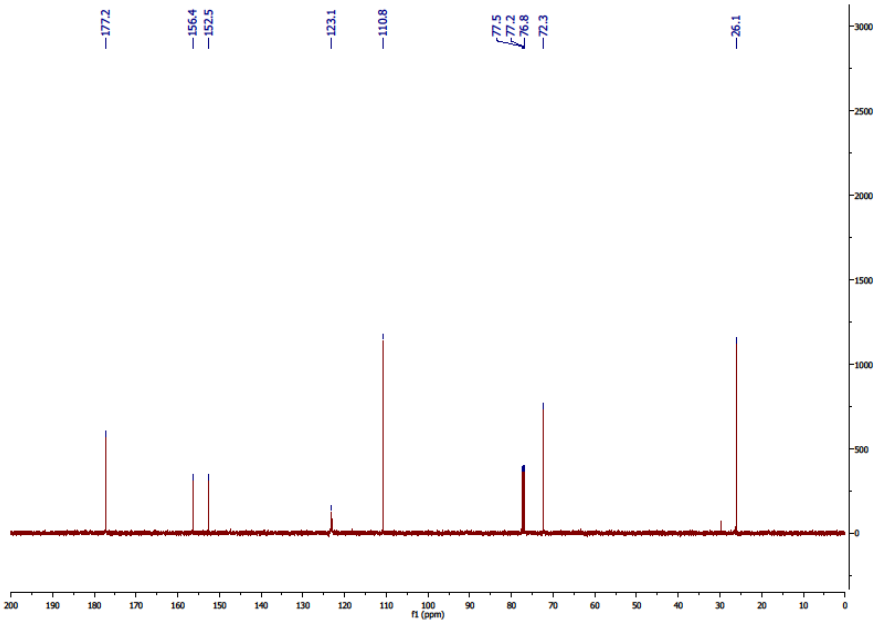
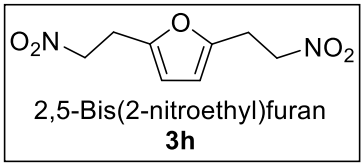


Figure A40. [13]C-NMR spectrum for compound **3j**



2,5-Bis(2-nitroethyl)furan
3h

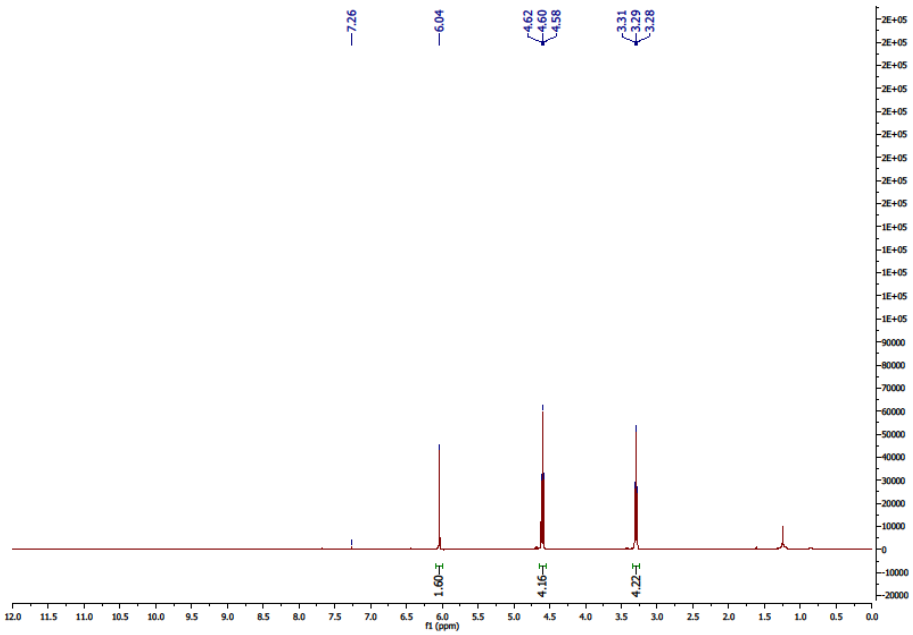


Figure A41. ^{1}H-NMR spectrum for compound **3h**

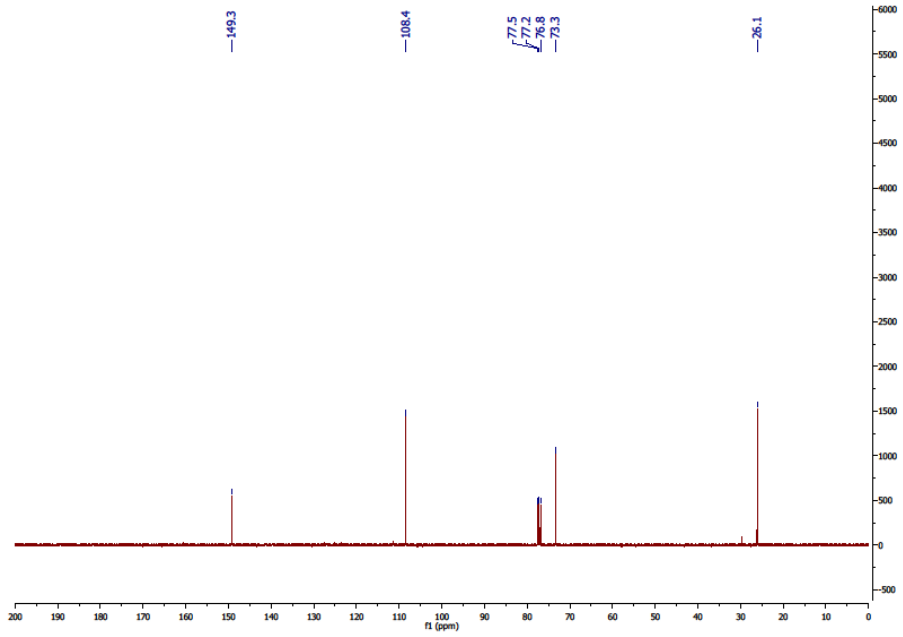
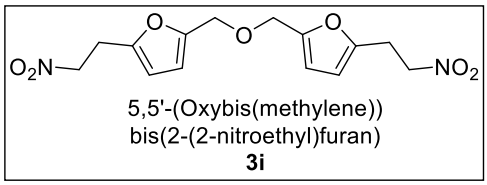


Figure A42. ^{13}C-NMR spectrum for compound **3h**



5,5'-(Oxybis(methylene))
bis(2-(2-nitroethyl)furan)
3i

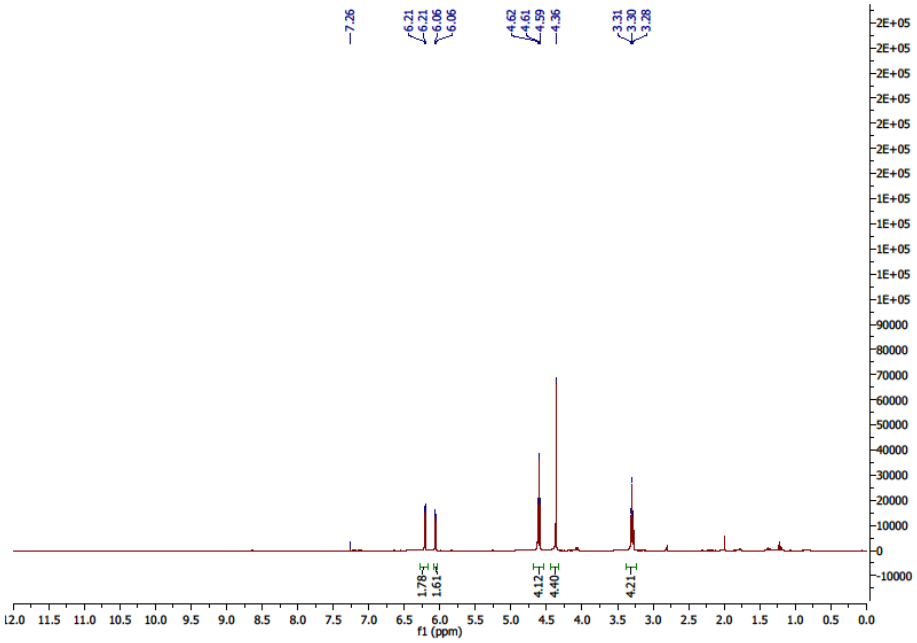


Figure A43. [1]H-NMR spectrum for compound **3i**

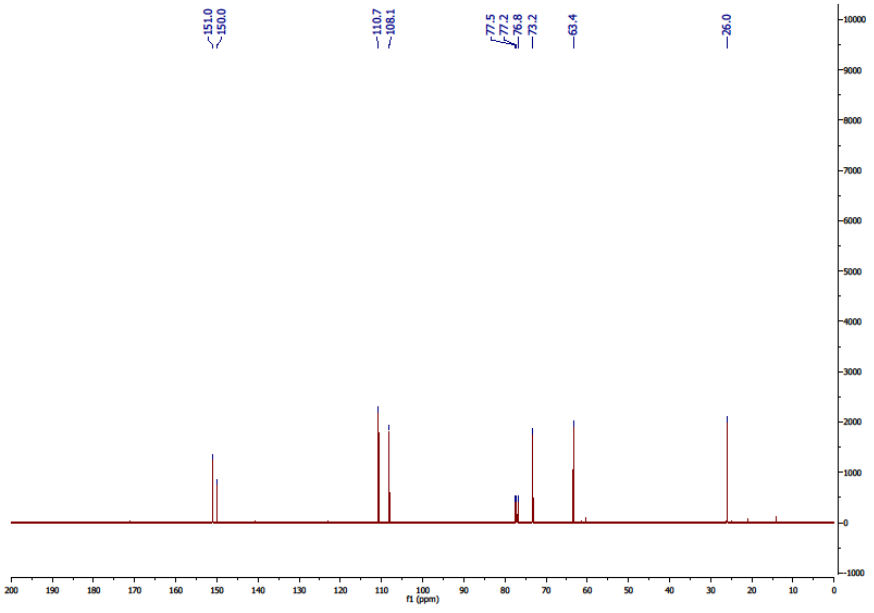
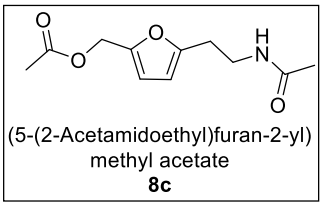


Figure A44. [13]C-NMR spectrum for compound **3i**



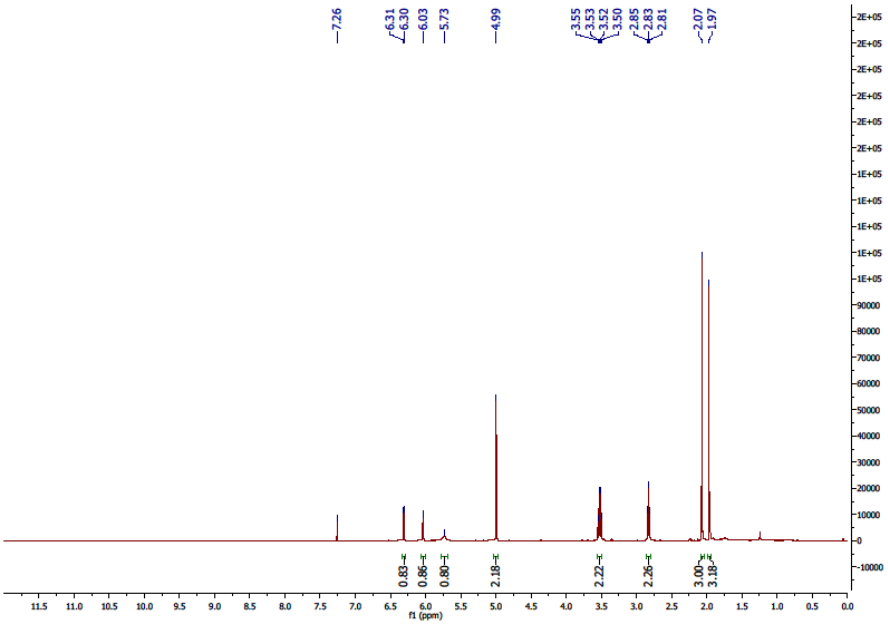


Figure A45. [1]H-NMR spectrum for compound **8c**

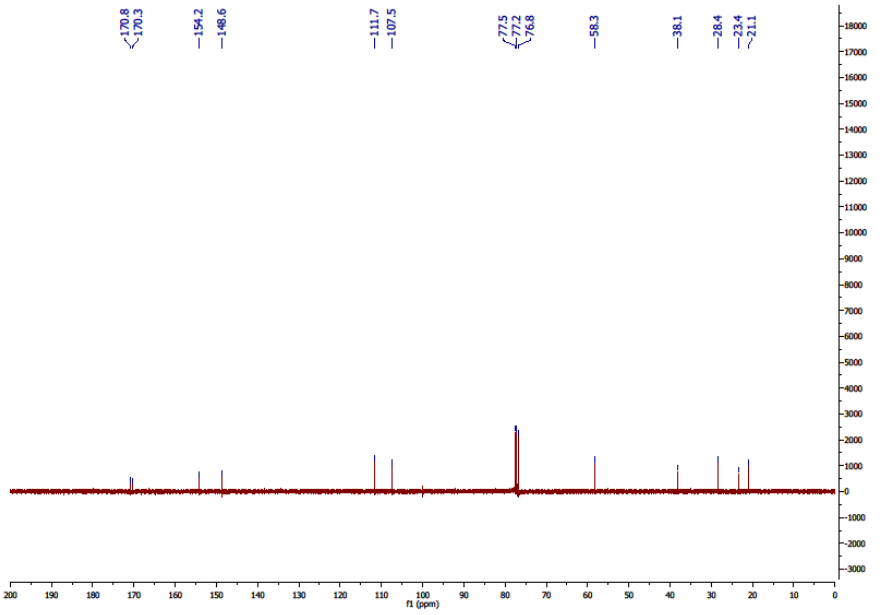
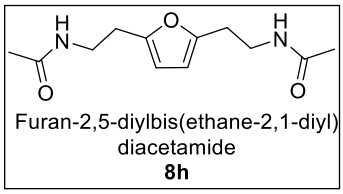


Figure A46. [13]C-NMR spectrum for compound **8c**



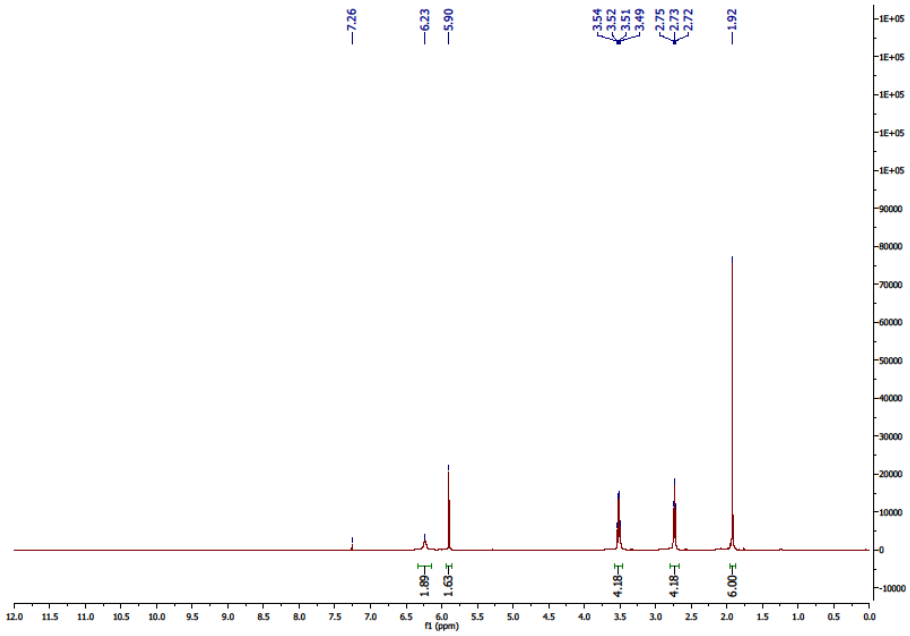


Figure A47. [1]H-NMR spectrum for compound **8h**

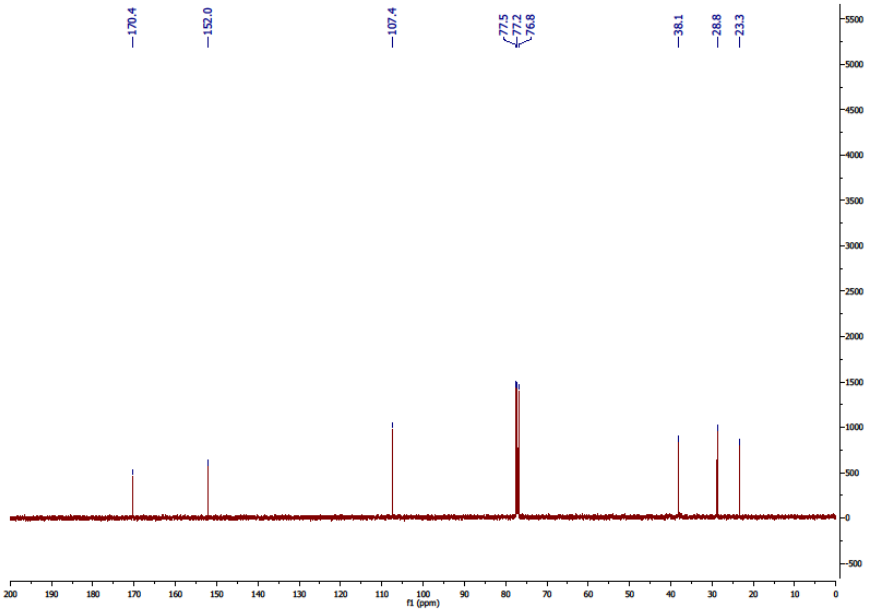
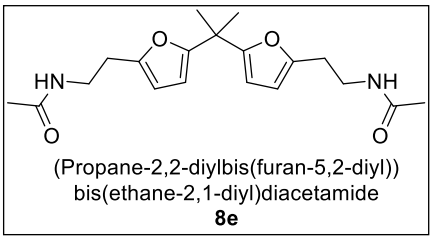


Figure A48. [13]C-NMR spectrum for compound **8h**



(Propane-2,2-diylbis(furan-5,2-diyl))
bis(ethane-2,1-diyl)diacetamide
8e

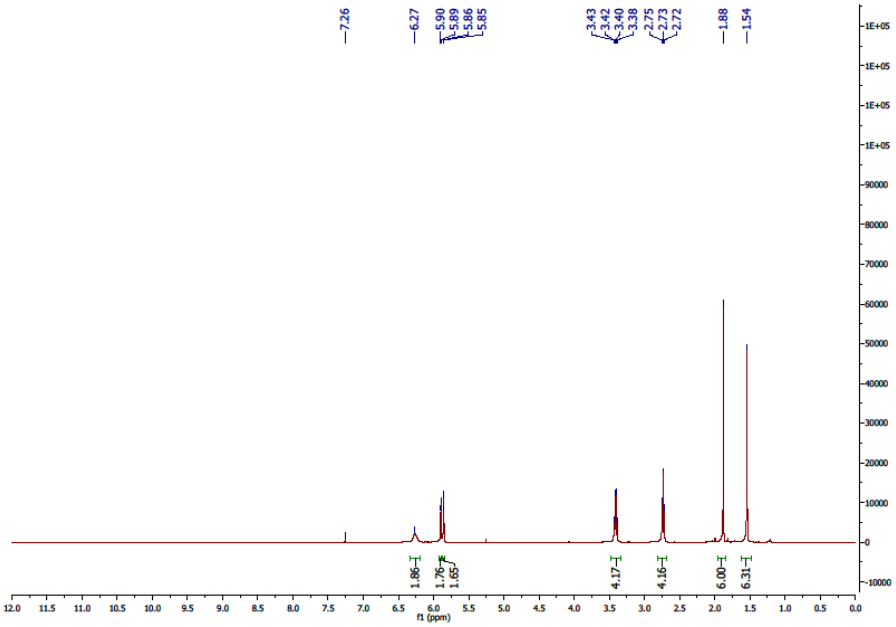


Figure A49. ^{1}H-NMR spectrum for compound **8e**

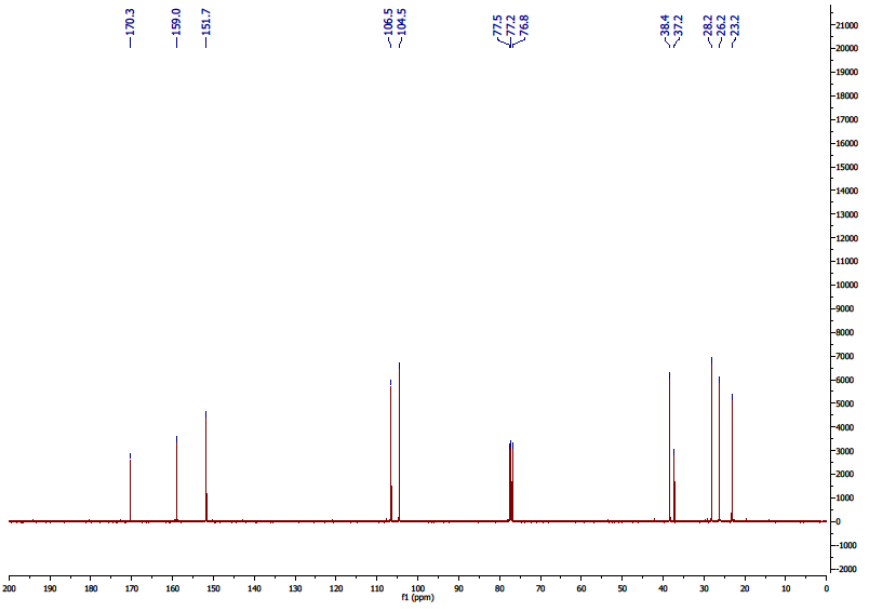
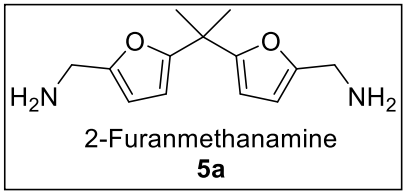


Figure A50. ^{13}C-NMR spectrum for compound **8e**



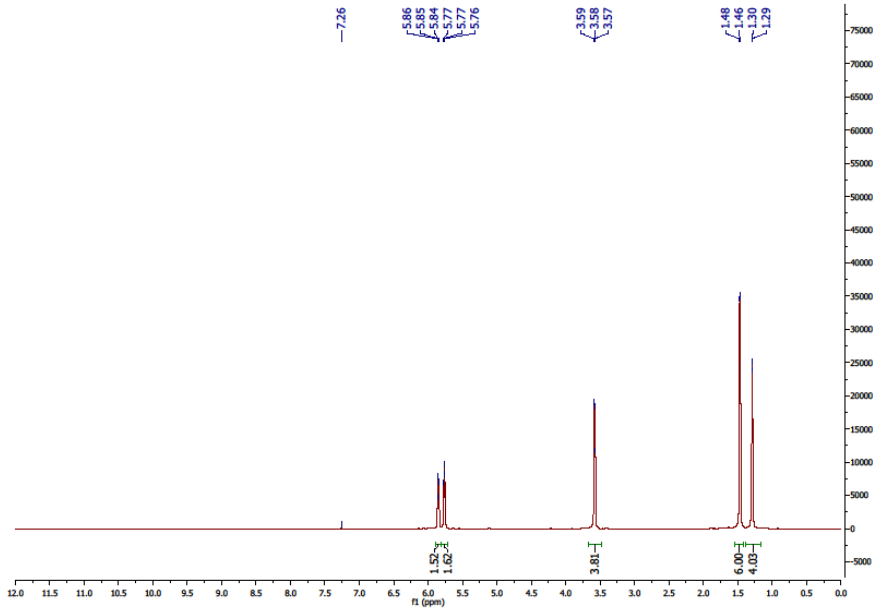


Figure A51. [1]H-NMR spectrum for compound **5a**

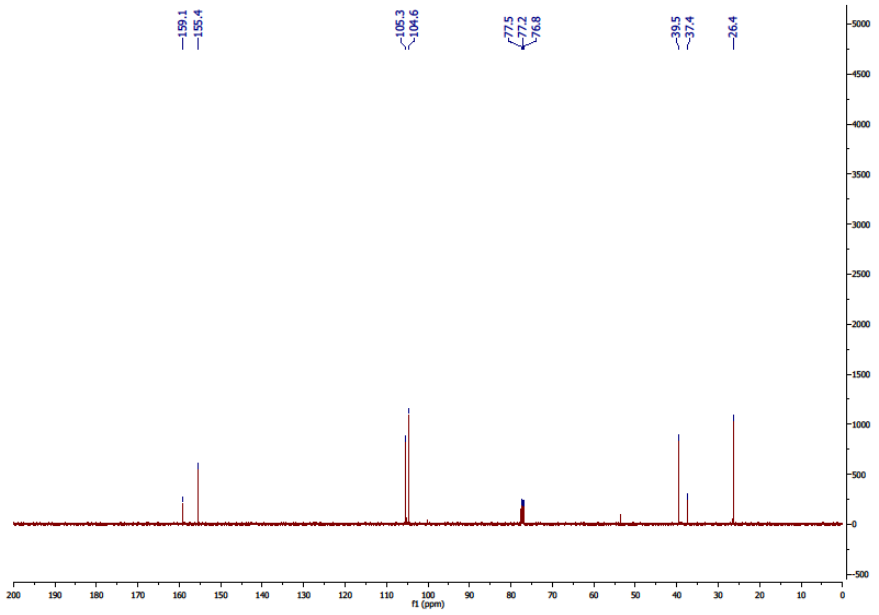
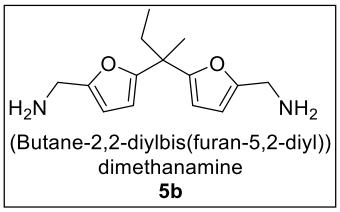


Figure A52. [13]C-NMR spectrum for compound **5a**



(Butane-2,2-diylbis(furan-5,2-diyl))
dimethanamine
5b

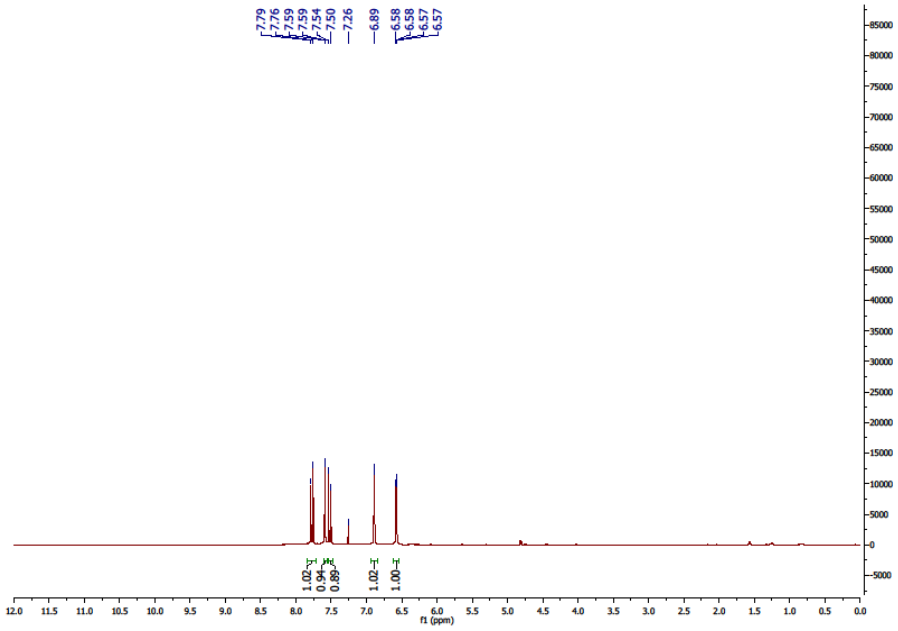


Figure A53. [1]H-NMR spectrum for compound **5b**

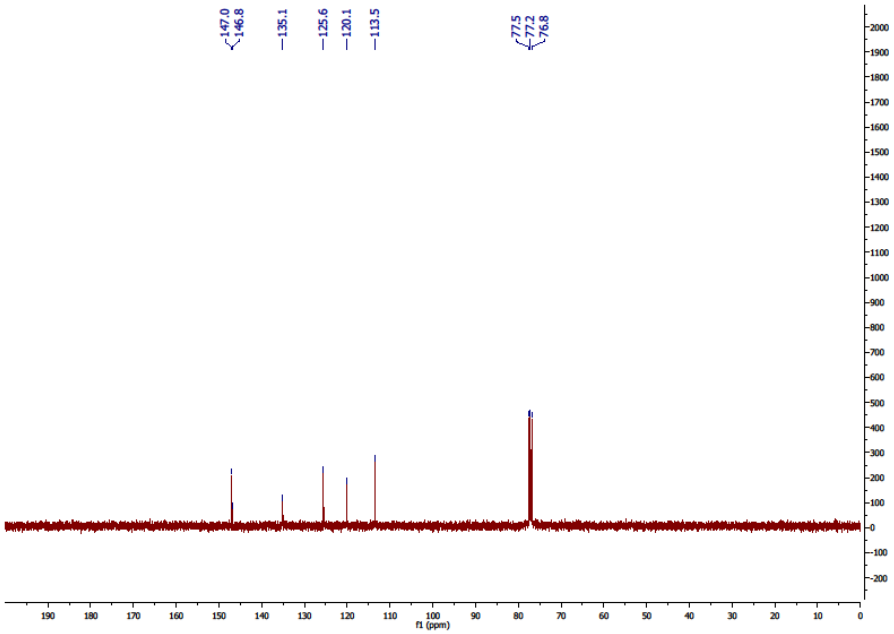
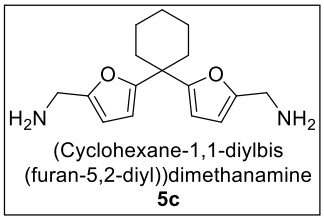


Figure A54. [13]C-NMR spectrum for compound **5b**



(Cyclohexane-1,1-diylbis
(furan-5,2-diyl))dimethanamine
5c

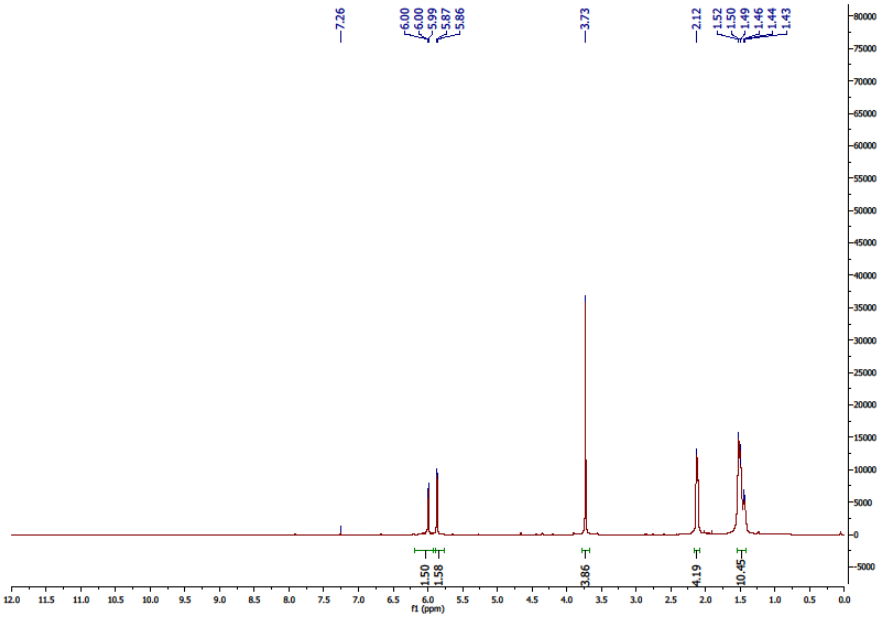


Figure A55. ^{1}H-NMR spectrum for compound **5c**

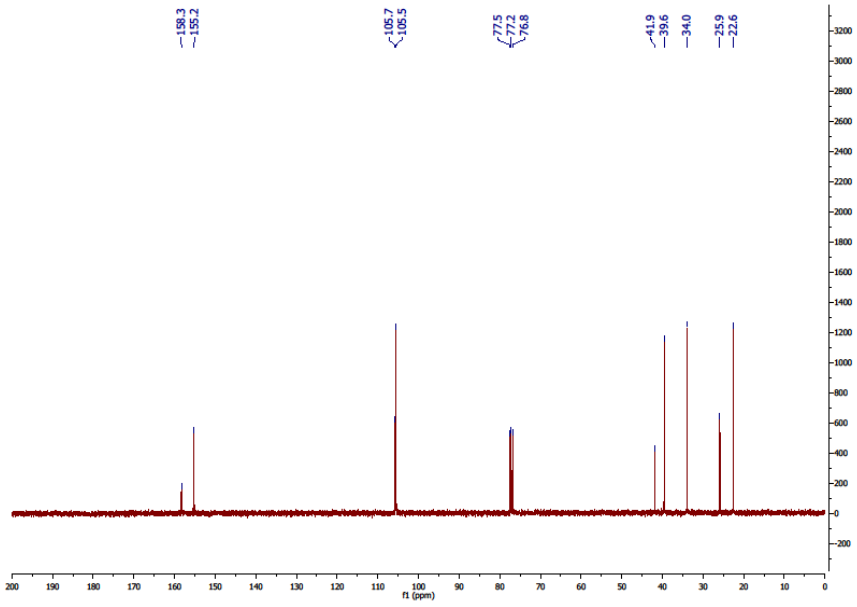
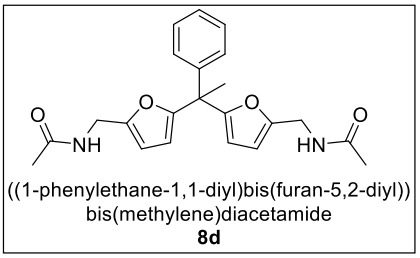


Figure A56. ^{13}C-NMR spectrum for compound **5c**



((1-phenylethane-1,1-diyl)bis(furan-5,2-diyl))
bis(methylene)diacetamide
8d

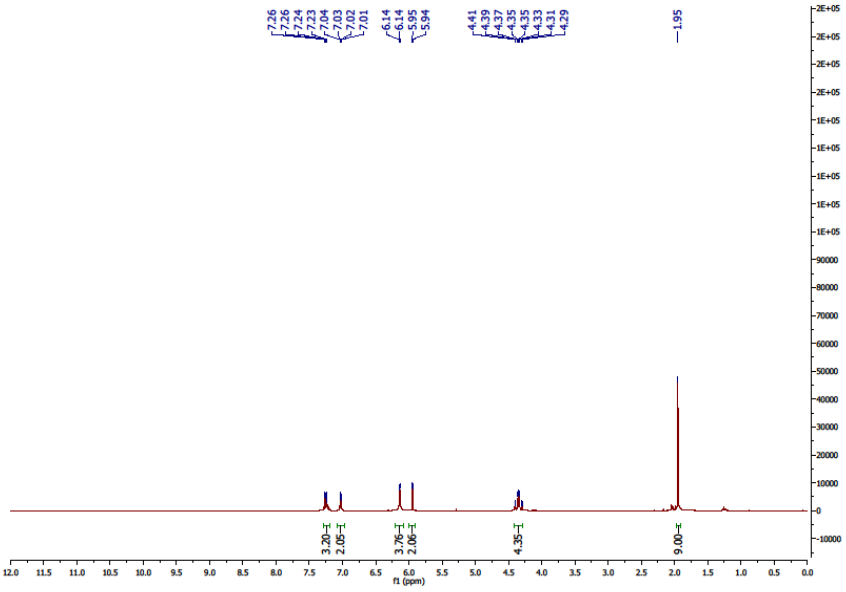


Figure A57. ^{1}H-NMR spectrum for compound **8d**

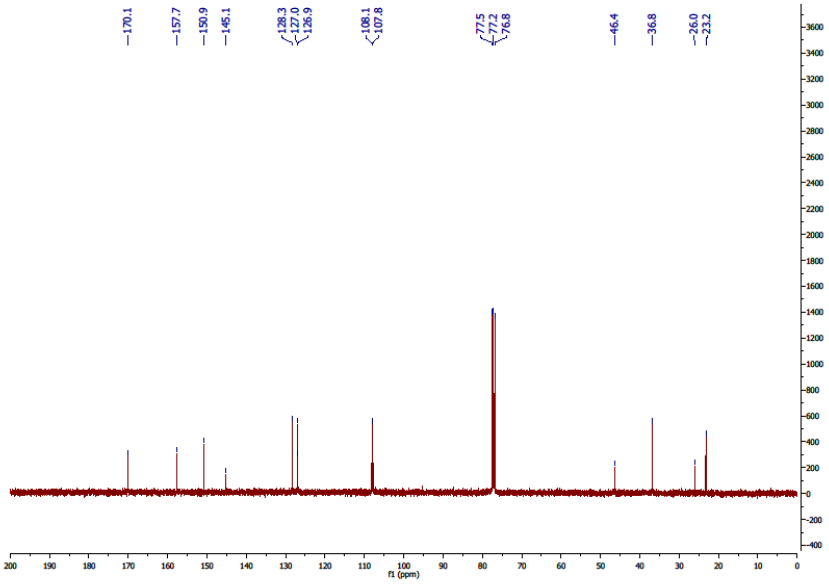
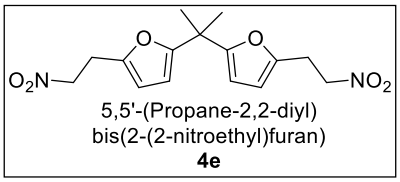


Figure A58. ^{13}C-NMR spectrum for compound **8d**



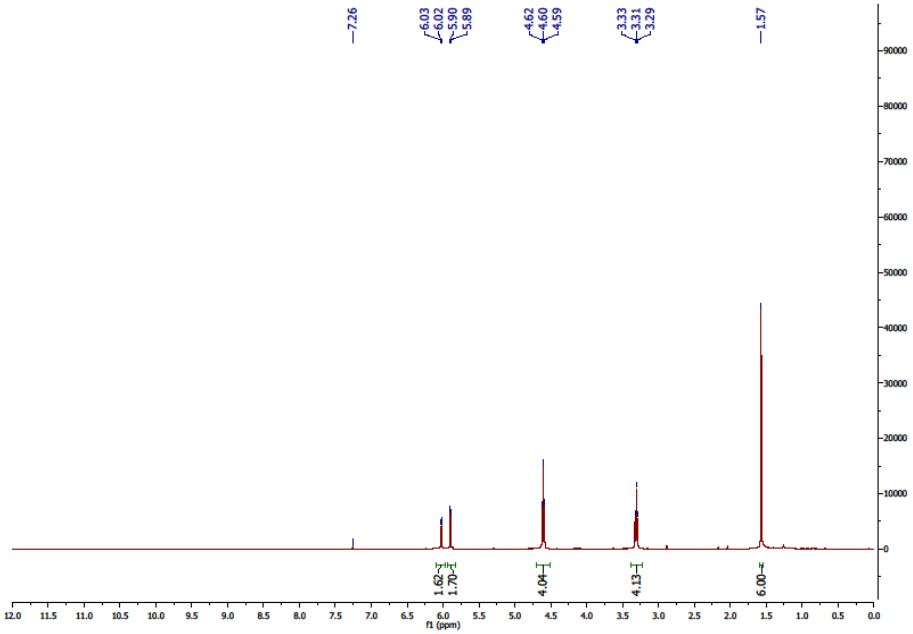


Figure A59. [1]H-NMR spectrum for compound **4e**

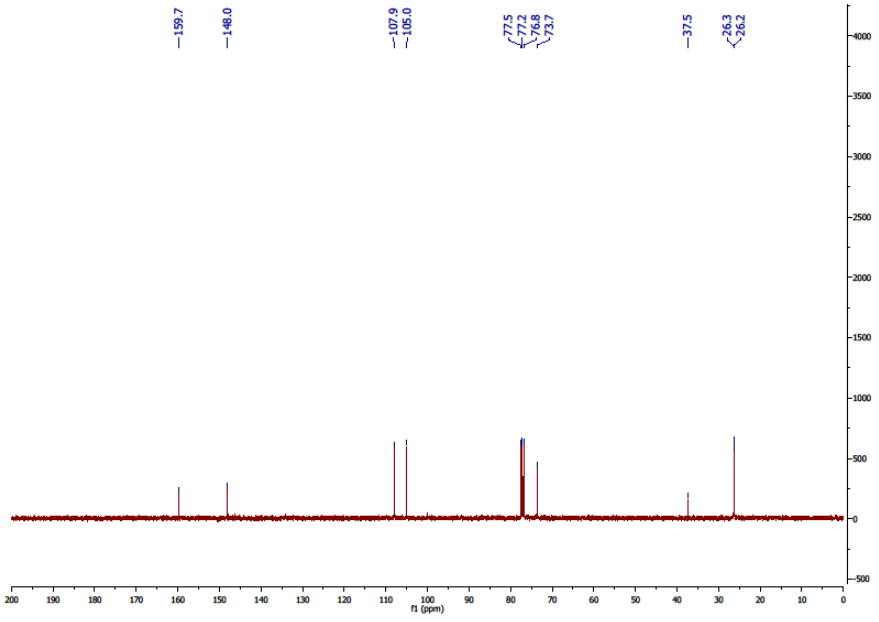
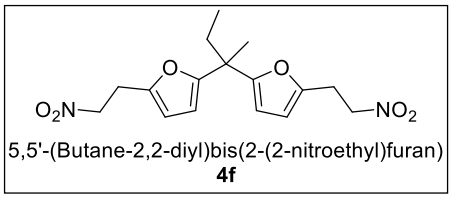


Figure A60. [13]C-NMR spectrum for compound **4e**



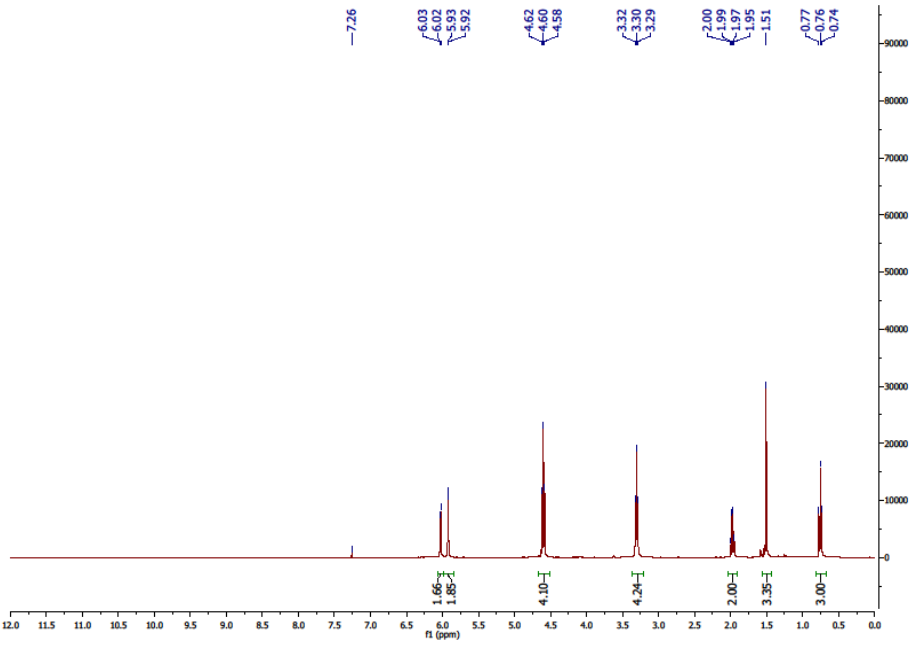


Figure A61. [1]H-NMR spectrum for compound **4f**

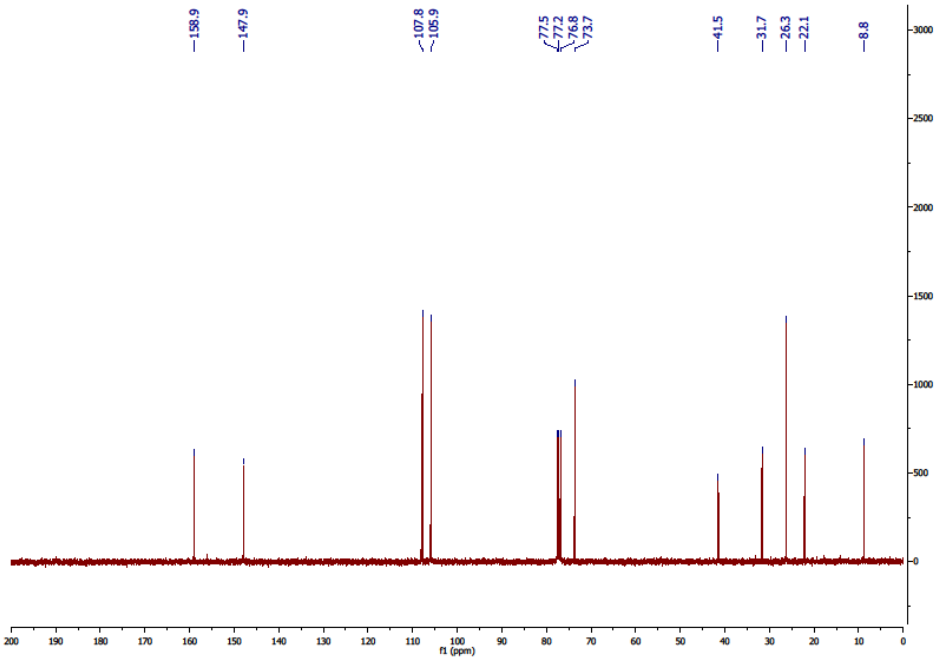
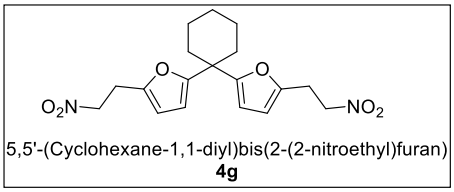


Figure A62. [13]C-NMR spectrum for compound **4f**



5,5'-(Cyclohexane-1,1-diyl)bis(2-(2-nitroethyl)furan)
4g

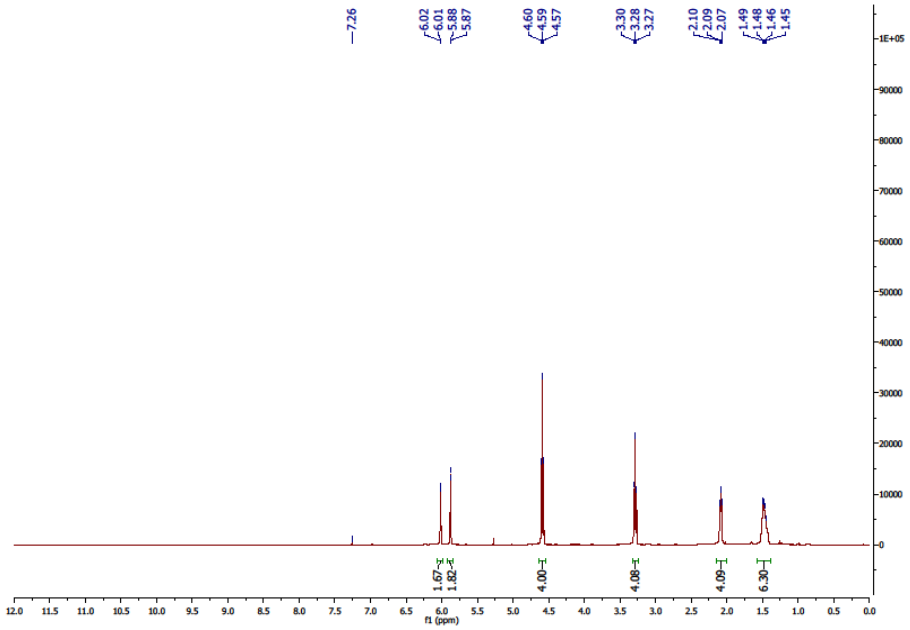


Figure A63. ^{1}H-NMR spectrum for compound **4g**

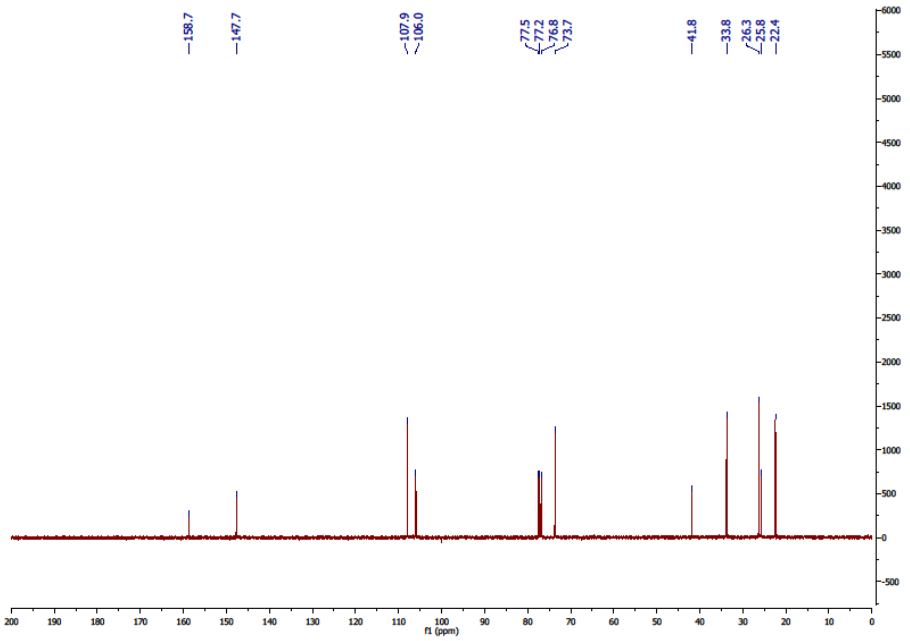
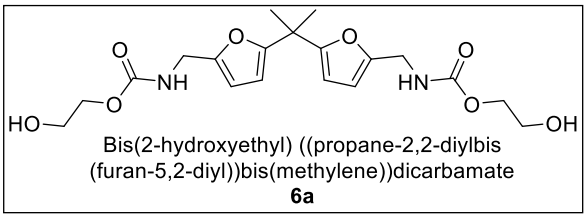


Figure A64. ^{13}C-NMR spectrum for compound **4g**



Bis(2-hydroxyethyl) ((propane-2,2-diylbis (furan-5,2-diyl))bis(methylene))dicarbamate

6a

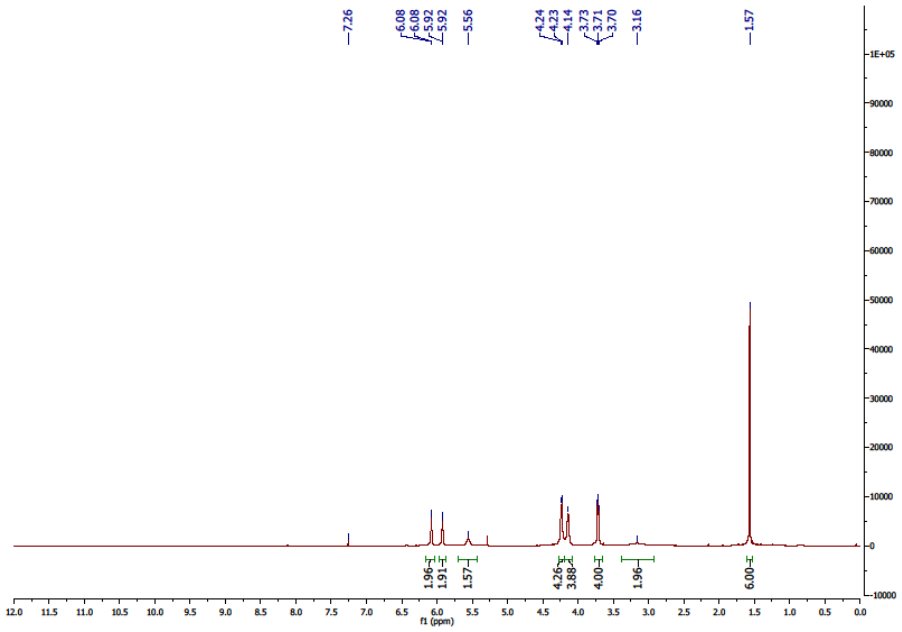


Figure A65. [1]H-NMR spectrum for compound **6a**

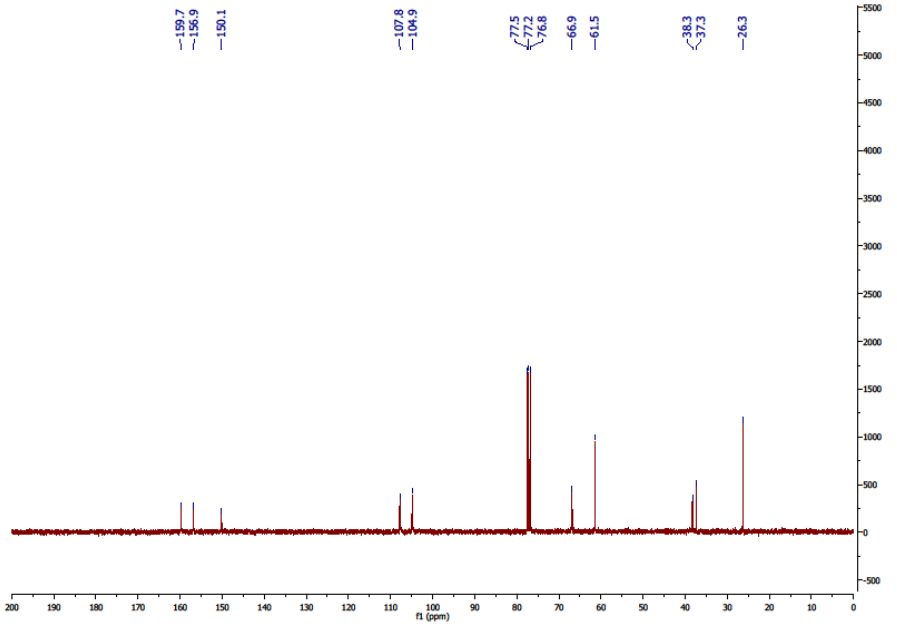
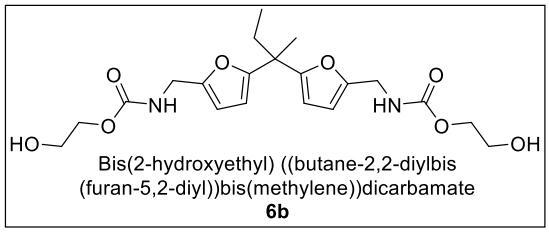


Figure A66. [13]C-NMR spectrum for compound **6a**



Bis(2-hydroxyethyl) ((butane-2,2-diylbis (furan-5,2-diyl))bis(methylene))dicarbamate

6b

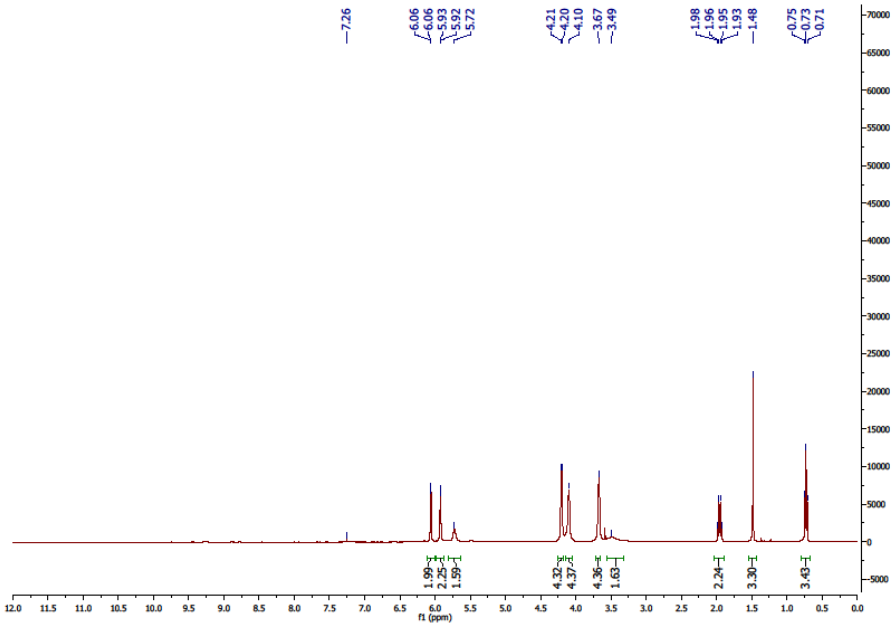


Figure A67. [1]H-NMR spectrum for compound **6b**

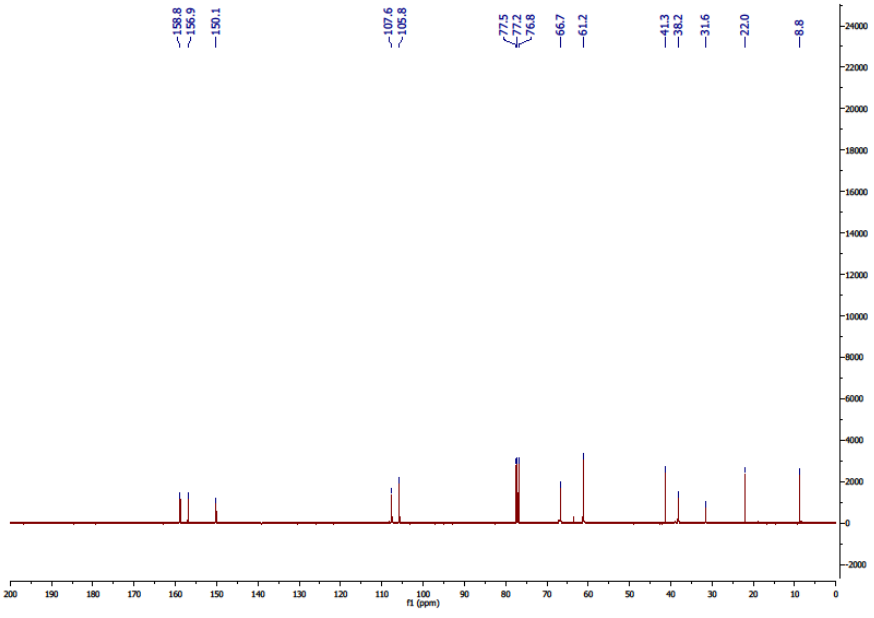
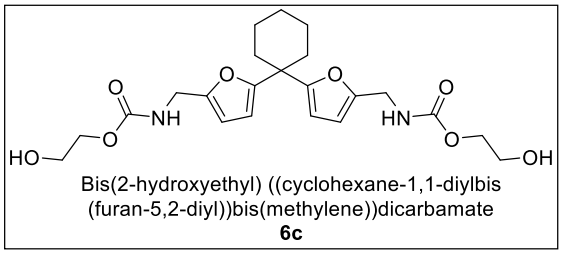


Figure A68. [13]C-NMR spectrum for compound **6b**



Bis(2-hydroxyethyl) ((cyclohexane-1,1-diylbis (furan-5,2-diyl))bis(methylene))dicarbamate

6c

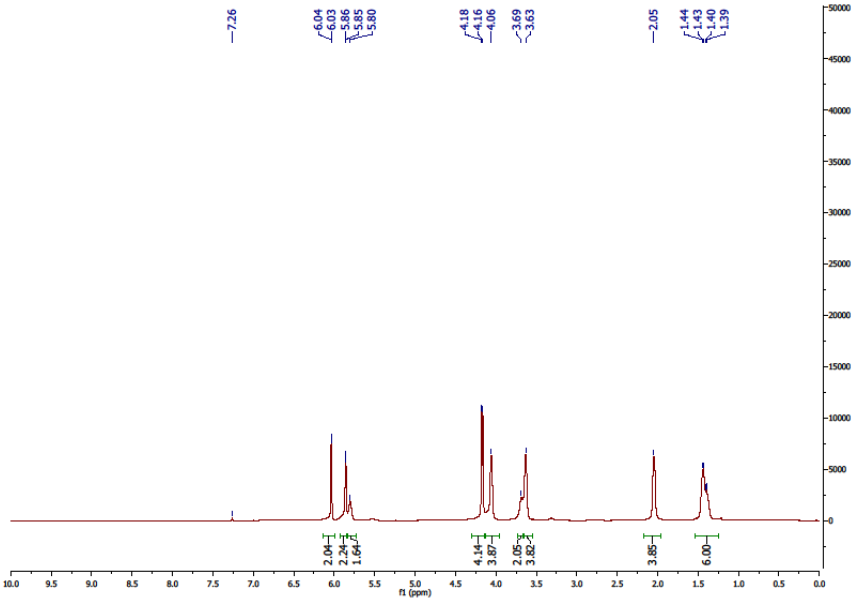


Figure A69. ^{1}H-NMR spectrum for compound **6c**

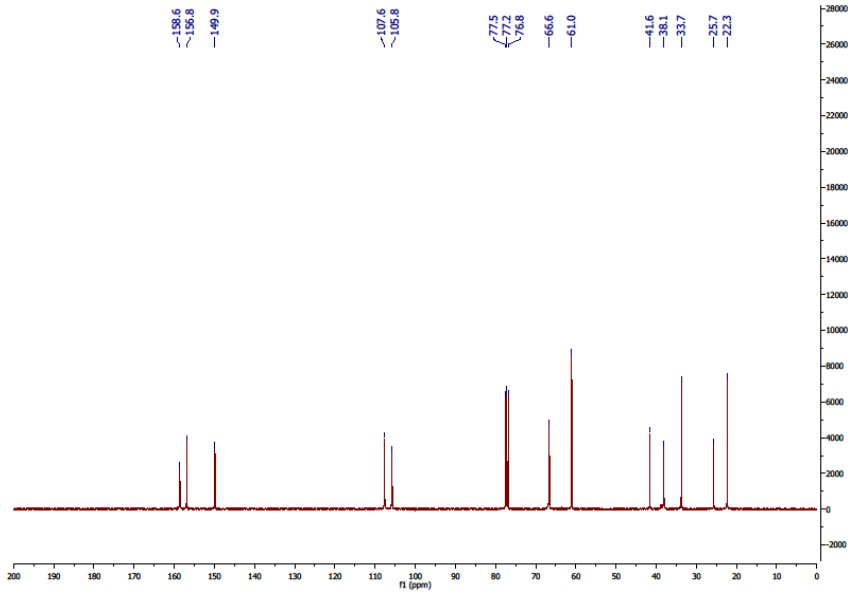
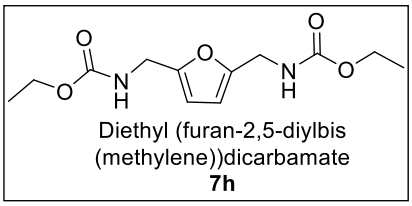


Figure A70. ^{13}C-NMR spectrum for compound **6c**



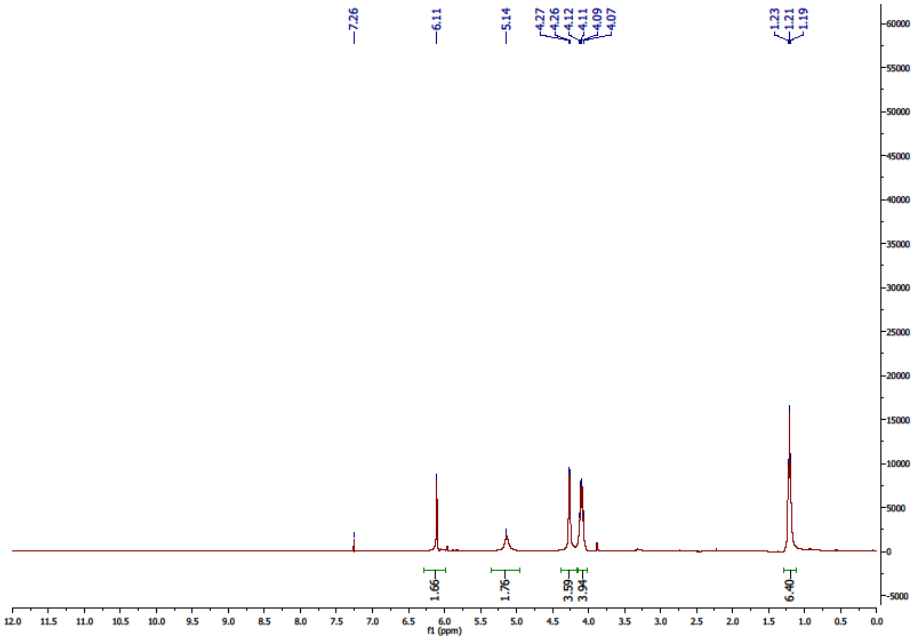


Figure A71. [1]H-NMR spectrum for compound **7h**

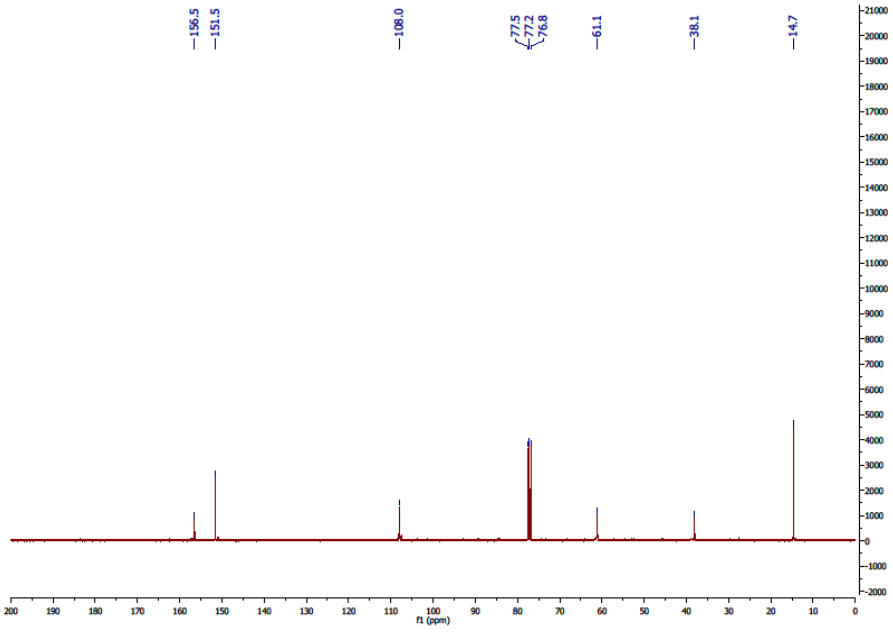
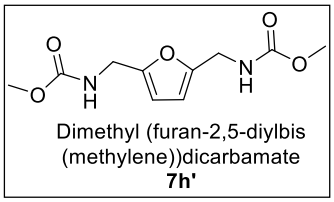


Figure A72. [13]C-NMR spectrum for compound **7h**



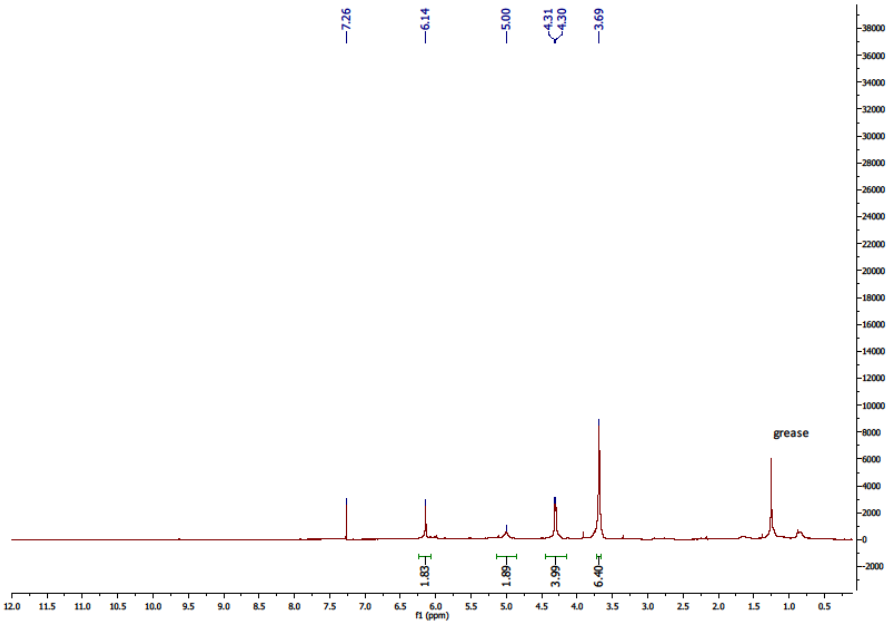


Figure A73. [1]H-NMR spectrum for compound **7h'**

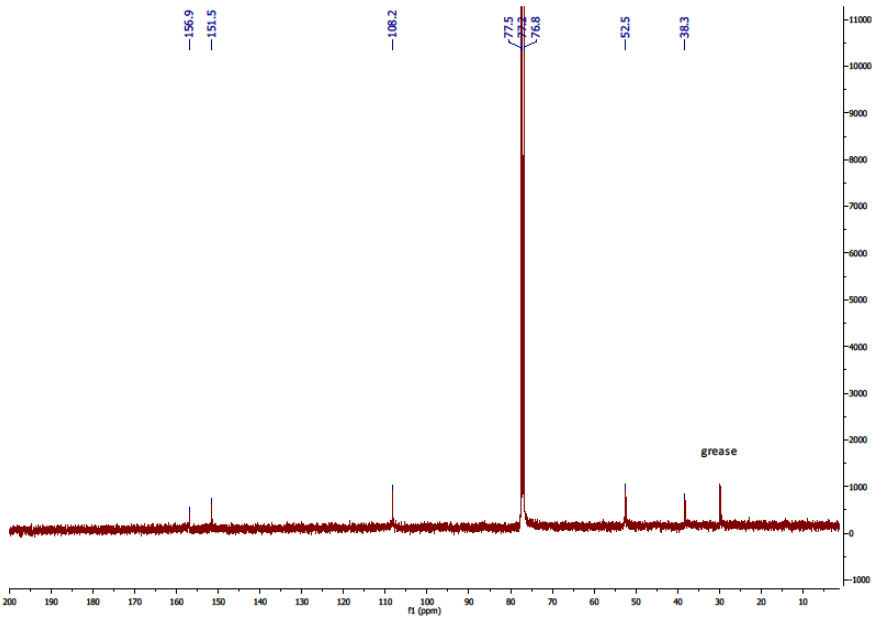
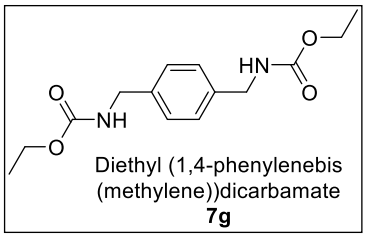


Figure A74. [13]C-NMR spectrum for compound **7h'**



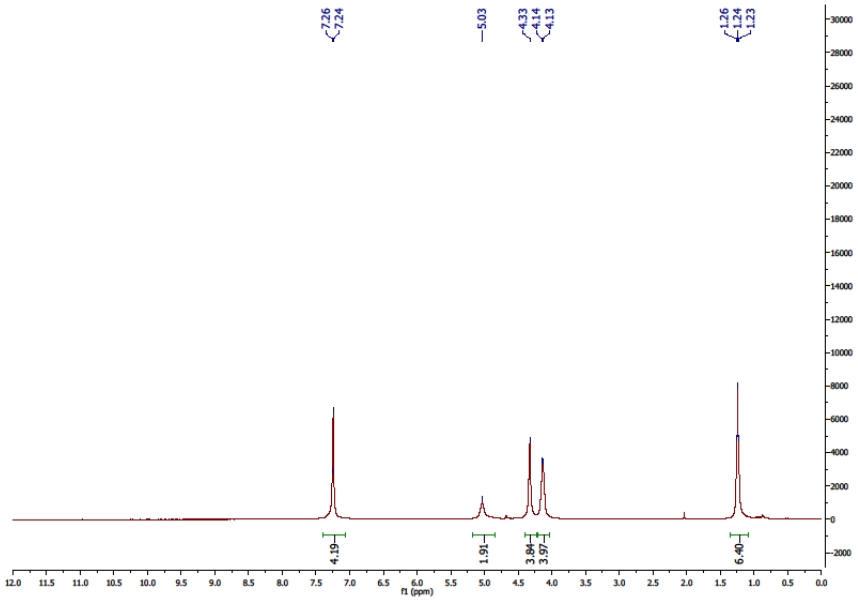


Figure A75. [1]H-NMR spectrum for compound **7g**

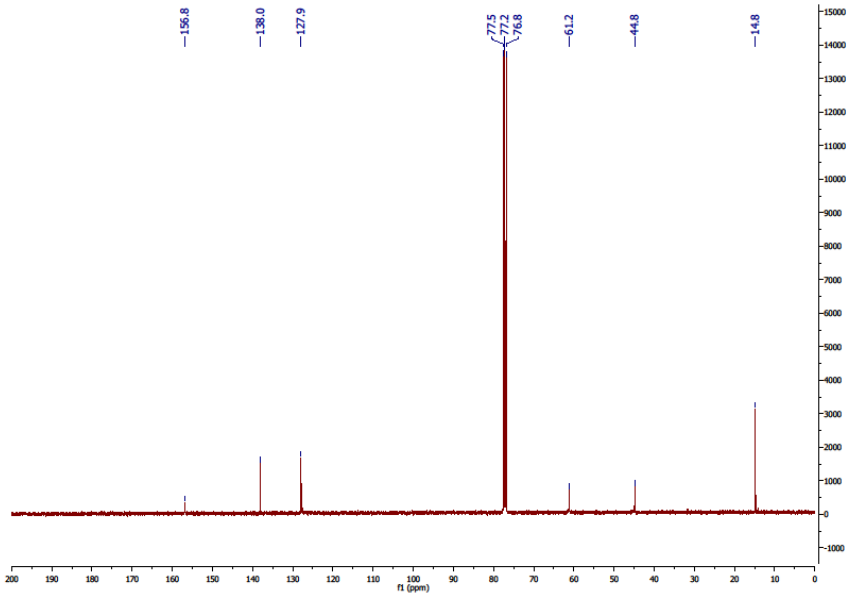
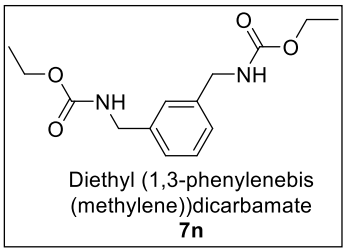


Figure A76. [13]C-NMR spectrum for compound **7g**



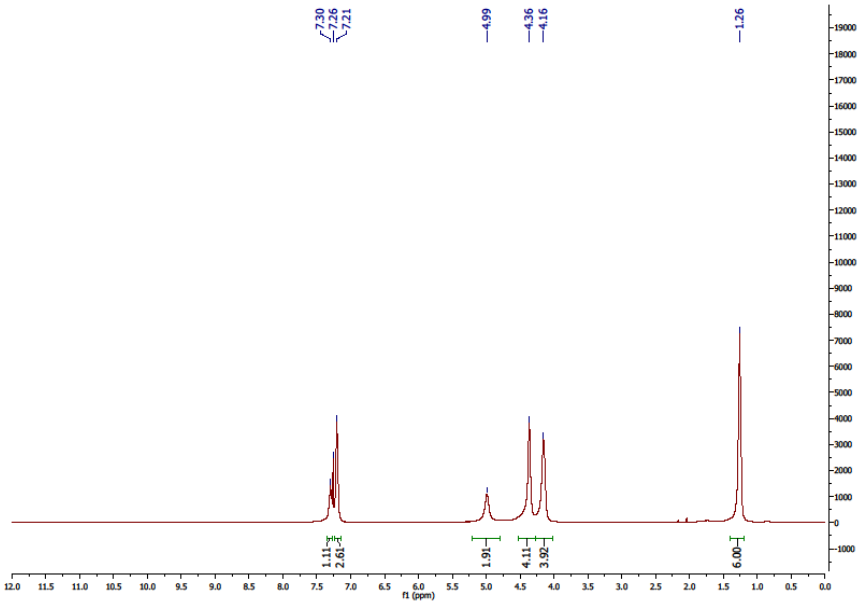


Figure A77. [1]H-NMR spectrum for compound **7n**

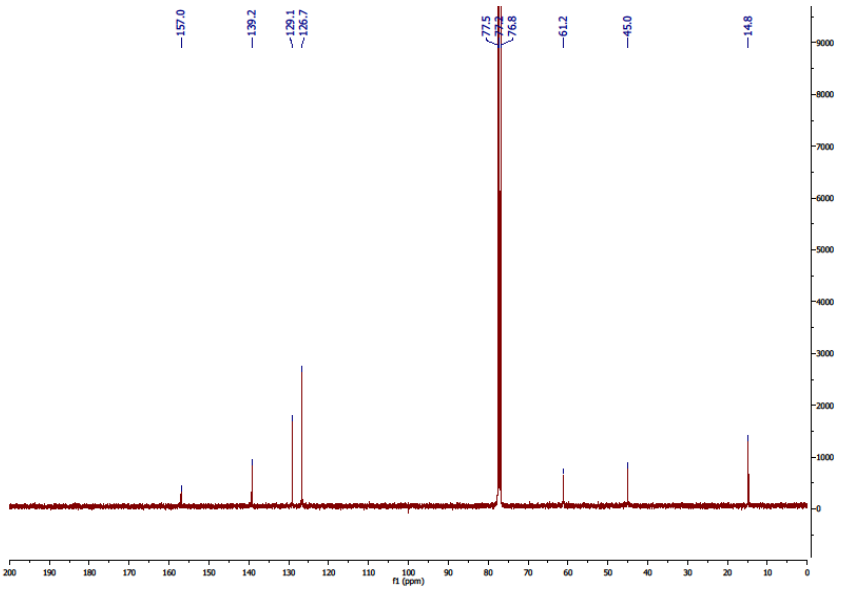
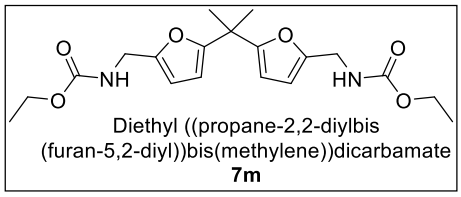


Figure A78. [13]C-NMR spectrum for compound **7n**



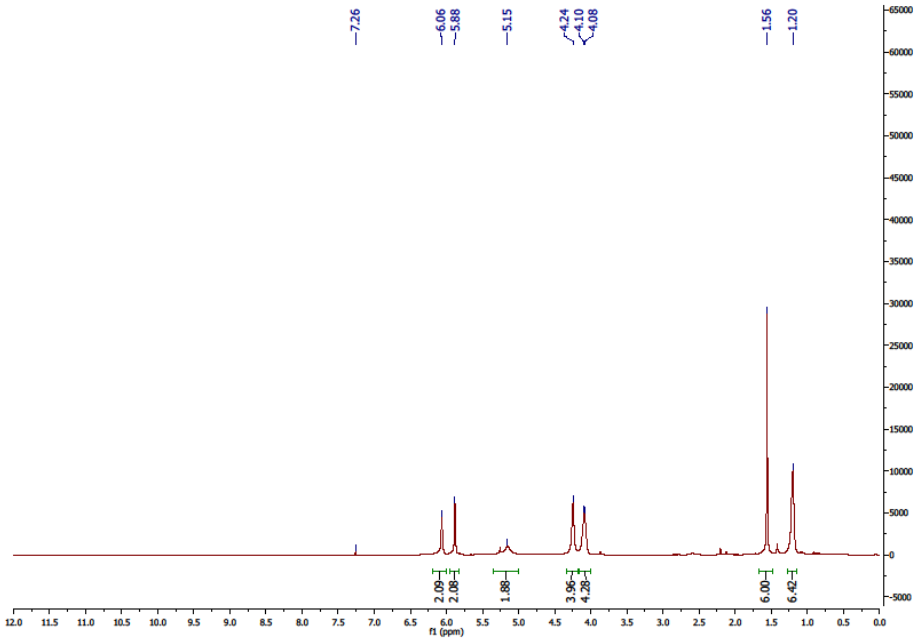


Figure A79. [1]H-NMR spectrum for compound **7m**

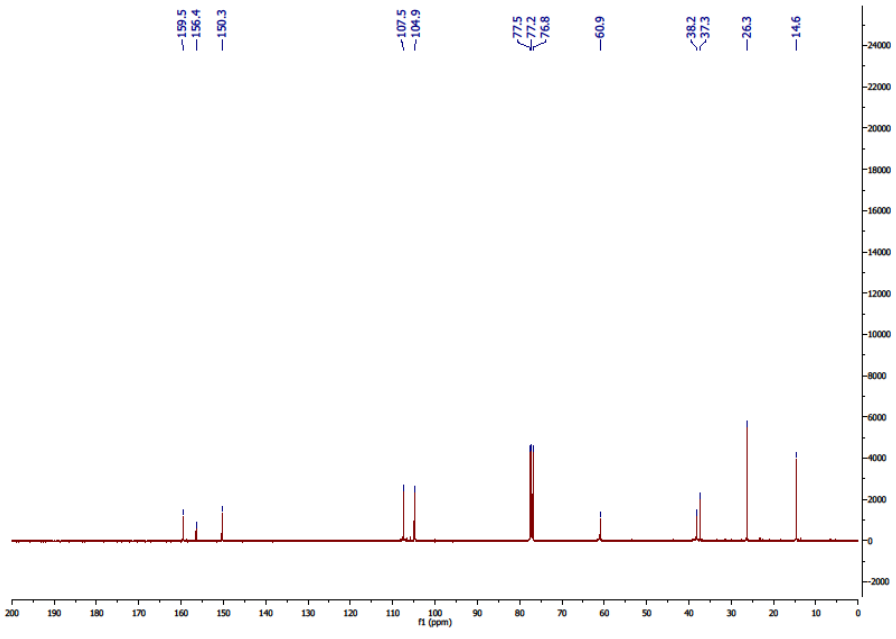
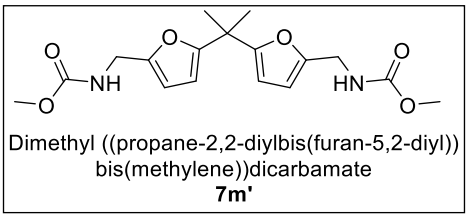


Figure A80. [13]C-NMR spectrum for compound **7m**



Dimethyl ((propane-2,2-diylbis(furan-5,2-diyl)) bis(methylene))dicarbamate

7m'

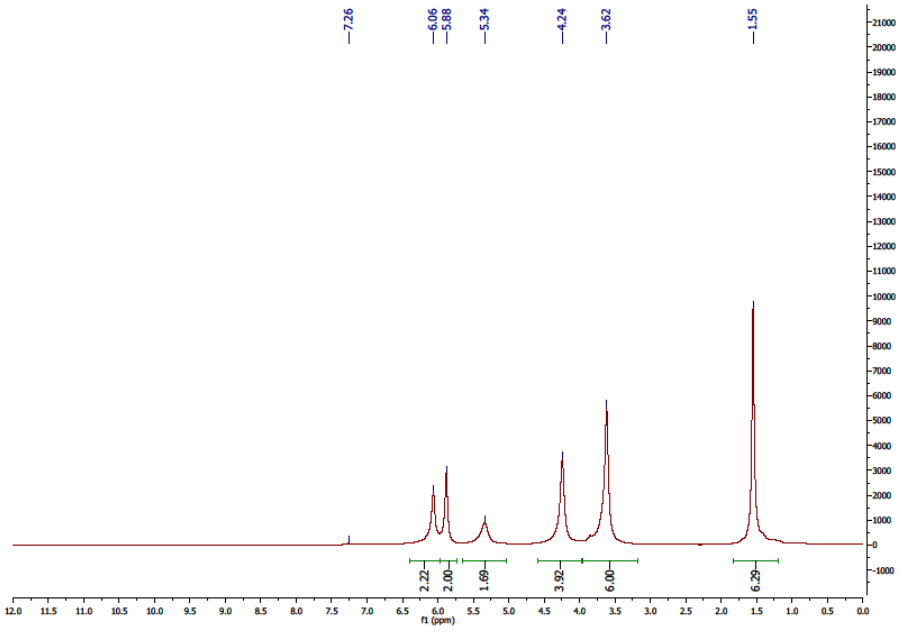


Figure A81. [1]H-NMR spectrum for compound **7m'**

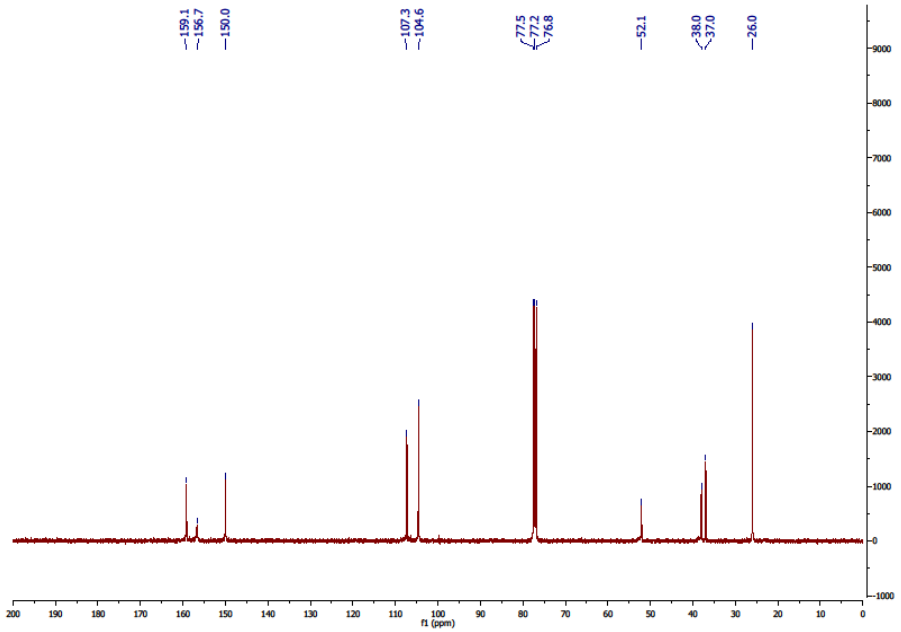
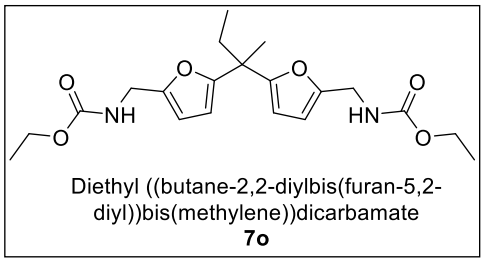


Figure A82. [13]C-NMR spectrum for compound **7m'**



Diethyl ((butane-2,2-diylbis(furan-5,2-diyl))bis(methylene))dicarbamate
7o

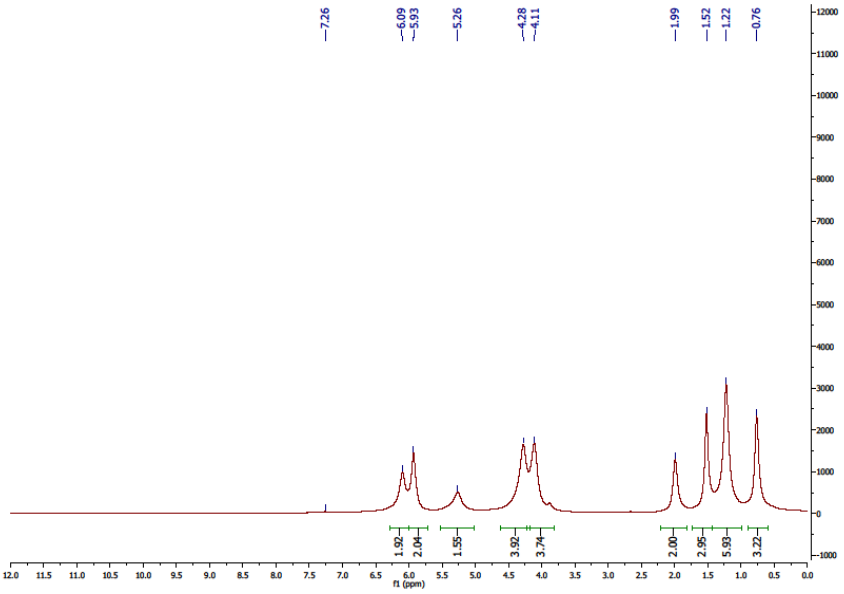


Figure A83. ^{1}H-NMR spectrum for compound **7o**

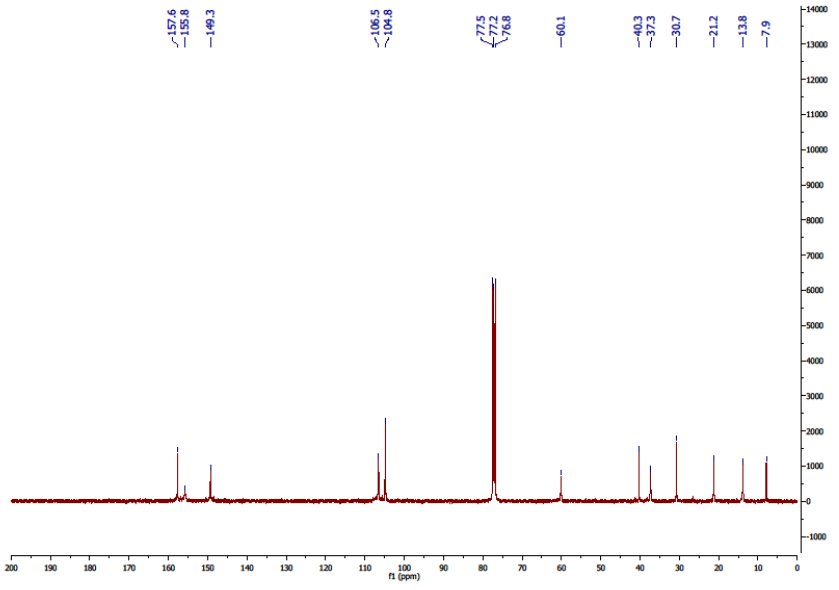
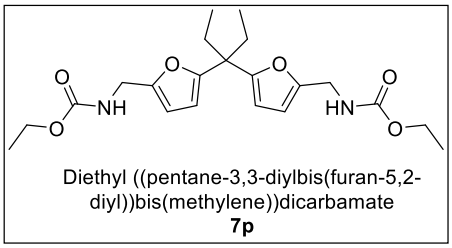


Figure A84. ^{13}C-NMR spectrum for compound **7o**



Diethyl ((pentane-3,3-diylbis(furan-5,2-diyl))bis(methylene))dicarbamate

7p

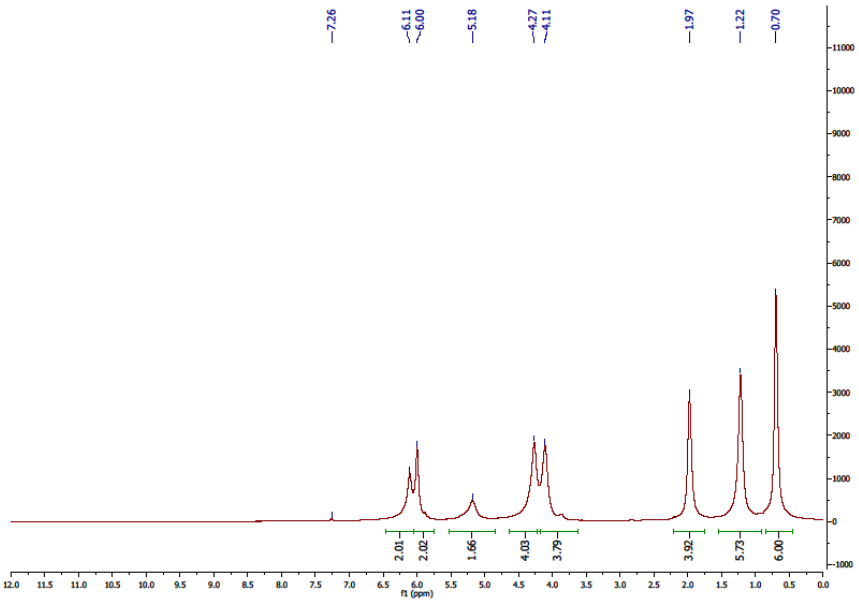


Figure A85. ^{1}H-NMR spectrum for compound **7p**

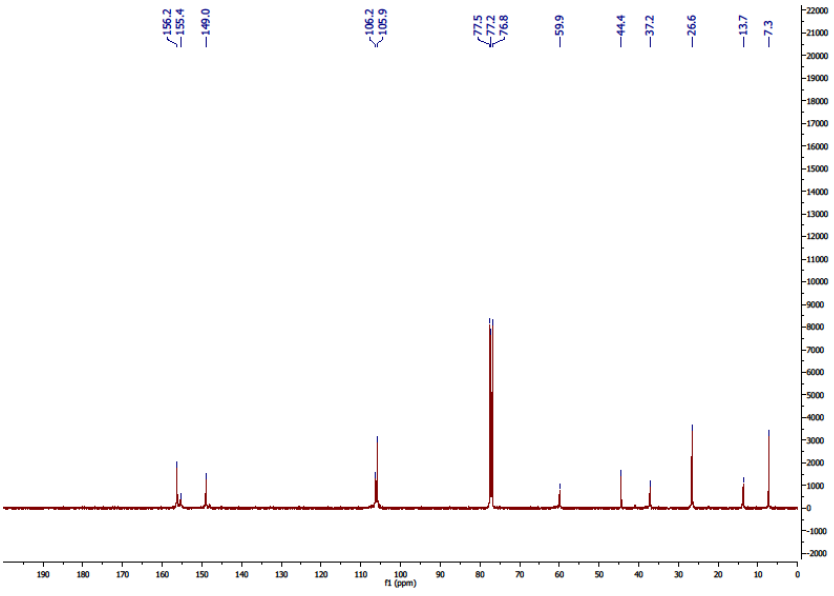
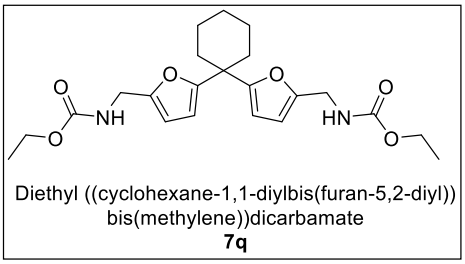


Figure A86. ^{13}C-NMR spectrum for compound **7p**



Diethyl ((cyclohexane-1,1-diylbis(furan-5,2-diyl))
bis(methylene))dicarbamate
7q

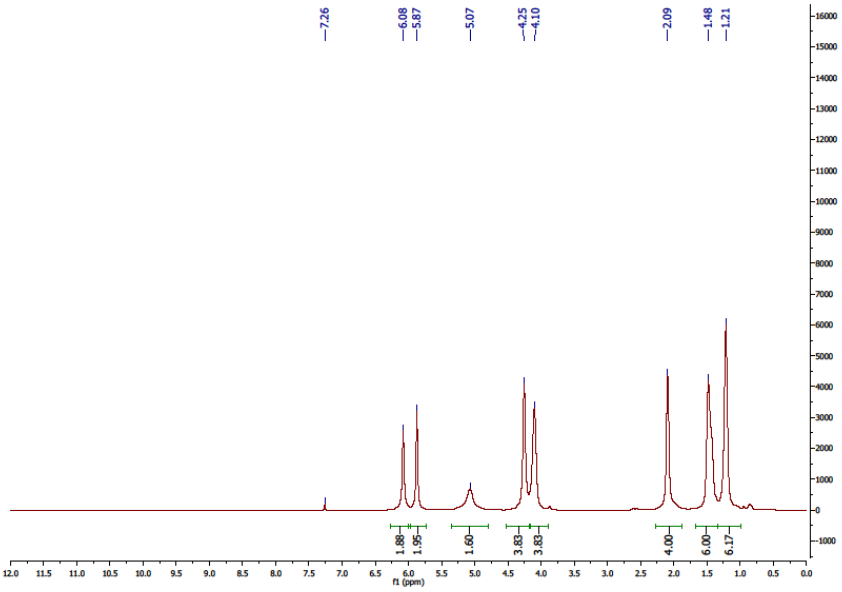


Figure A87. [1]H-NMR spectrum for compound **7q**

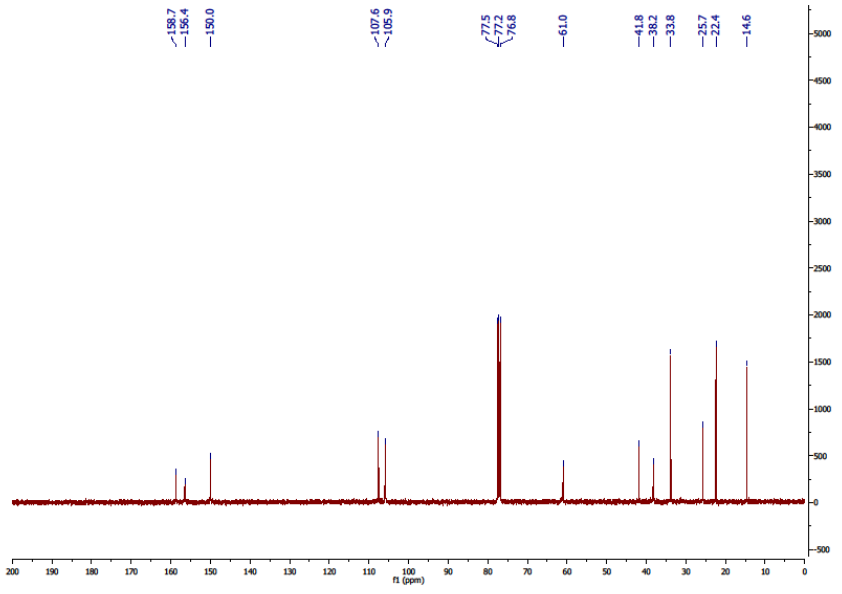
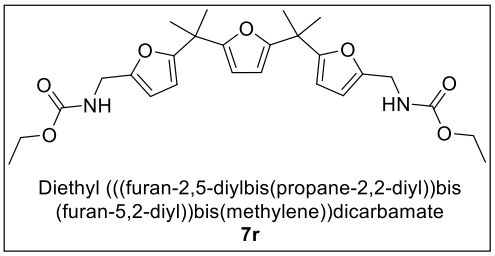


Figure A88. [13]C-NMR spectrum for compound **7q**



Diethyl (((furan-2,5-diylbis(propane-2,2-diyl))bis
(furan-5,2-diyl))bis(methylene))dicarbamate
7r

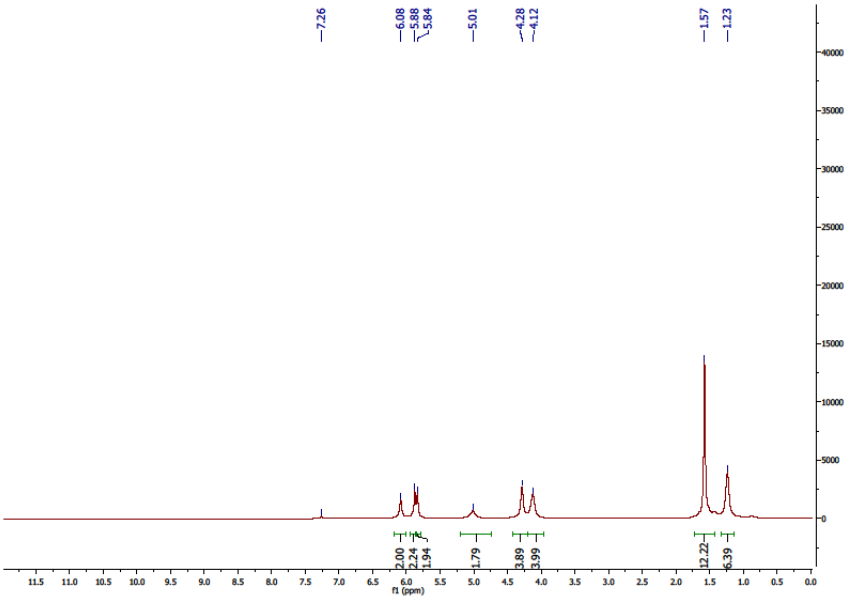


Figure A89. ^{1}H-NMR spectrum for compound **7r**

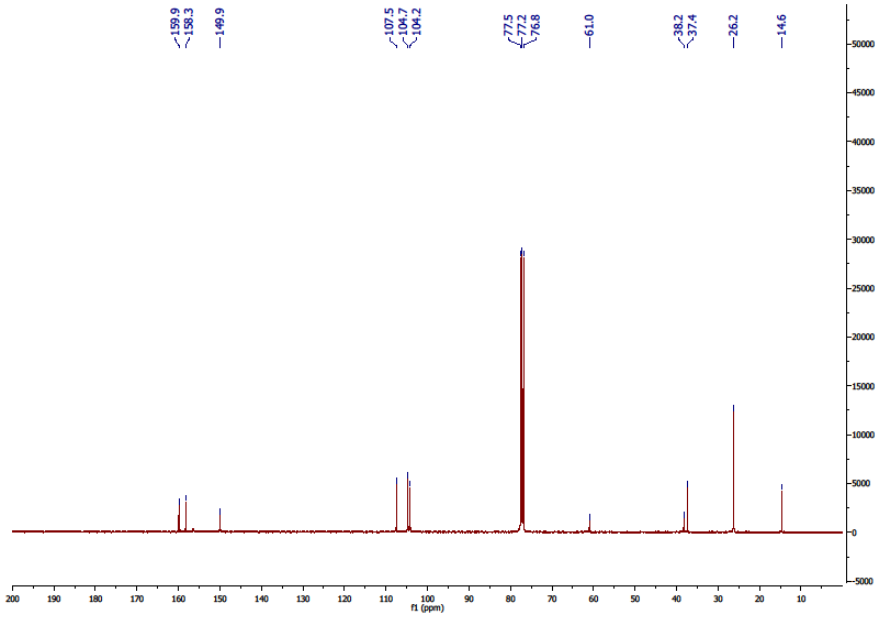
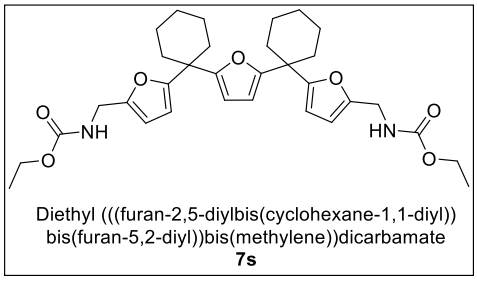


Figure A90. ^{13}C-NMR spectrum for compound **7r**



Diethyl (((furan-2,5-diylbis(cyclohexane-1,1-diyl)) bis(furan-5,2-diyl))bis(methylene))dicarbamate

7s

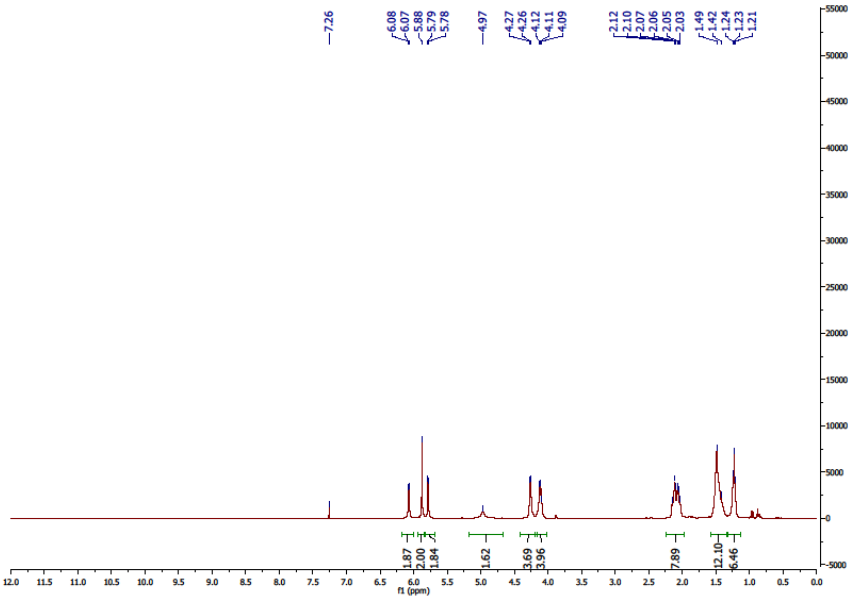


Figure A91. ^{1}H-NMR spectrum for compound **7s**

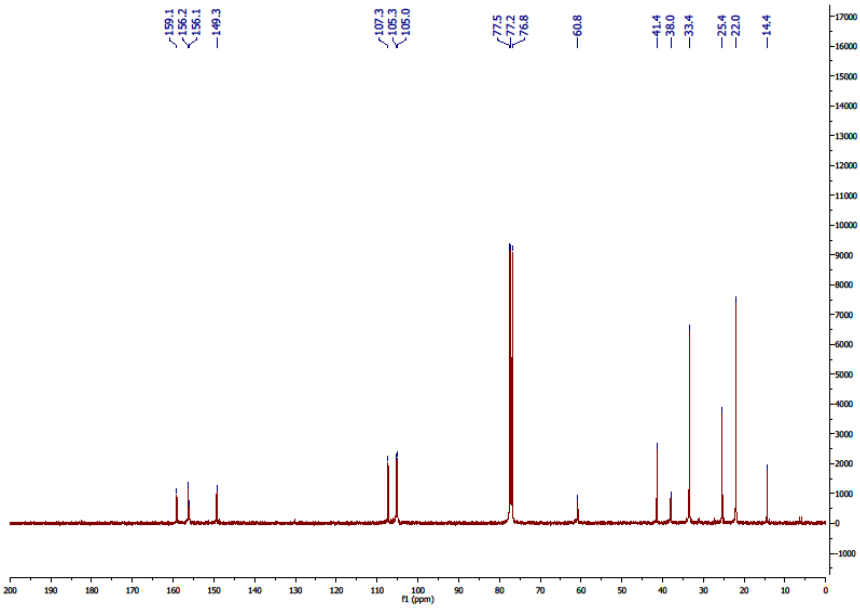


Figure A92. ^{13}C-NMR spectrum for compound **7s**