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## **Synthesis and Characterization of Furanic Compounds**

**by LaShonda T. Cureton and John J. La Scala**

**ARL-TR-6668**

**September 2013**

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**LaShonda T. Cureton and John J. La Scala**  
**Weapons and Materials Research Directorate, ARL**

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14. ABSTRACT Furans have been investigated in many chemical syntheses for specialty chemicals and polymers. Furans are attractive compounds because they are chemically obtainable through the catalytic decarbonylation of furfural, which is obtain through chemical modification of hemicelluloses (xylose). We seek to further develop biobased furanic materials with the goal of obtaining polymers with high $T_g$ and mechanical properties. This report details the synthesis of monomers necessary for the production of high-performance furan-based polymers analogous to Kevlar, nylon, epoxies, and other high-performance polymers. We used conventional synthetic organic chemistry to prepare monomers including furan-2-carbonyl azide; 2-furanamine; 2,2'-Methylenedifuran; di(2-furyl)methanone; 2,5-furan dicarboxylic acid; 2,5-furan dicarboxylic acid chloride; and 2,5-furan diamide. The monomers were purified using extraction methods and characterized using nuclear magnetic resonance spectroscopy. The monomers were produced at high purity and in good yields.					
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## 1. Introduction

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Production of polymeric materials derived from plants and other renewable resources has become a major research initiative in the last decade. The major driving force behind this research focus is primarily due to the rising costs of petroleum manufacturing—oil extraction and refining—and transportation to the United States and other countries (1). Additionally, there have been increased environmental concerns due to recent oil spills and seepage into the waterways and potable water systems (2). These issues present the need for developing high-strength and high-performance polymeric materials from sources other than petroleum chemicals. Kevlar and nylon are among the highest performing engineering polymeric materials, having good structural and thermal integrity, but are produced from and processed in petroleum-derived chemicals. The desire to develop materials that are derived from renewable resources, much like Kevlar and nylon and the properties thereof, is of great interest. We seek to further develop biobased furanic materials that are analogs to Kevlar and nylon with the goal of obtaining polymers with high  $T_g$  and mechanical properties. Furan has been investigated in many chemical syntheses for specialty chemicals and polymers (3, 4). Furan is an attractive compound because it is chemically obtainable through the catalytic decarbonylation of furfural, which is obtain through chemical modification of hemicelluloses (xylose) (4). Functional furan derivatives, such as 5-hydroxymethylfurfural, are prepared through the dehydration of glucose (5–7). The major source of glucose is in vegetable products like corn, an abundant renewable resource. The United States produced approximately 320 million tons of corn from 2010 to 2011 (8), so there should be no difficulty in obtaining furan and its derivatives for large- and small-scale resins and polymers. This research intends to develop a series of furanic monomers that can be used in the synthesis of high-performing polymers like Kevlar and nylon.

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## 2. Experimental

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### 2.1 Materials

Furoic acid and *N, N*-dimethylcarbonyl chloride was purchased from Alfa Aesar; sodium azide from EMU; ammonium hydroxide and silica gel from Fisher Scientific; ammonium chloride from Mallinckrdt Chemicals, and 2,5-bis(hydroxymethyl)furan from Penn A Kem, LLC. The following were purchased from Sigma-Aldrich: thoinyl chloride, anhydrous dimethylformamide (DMF), anhydrous diethyl ether, dimethoxyethane, concentrated sulfuric acid, furan, furfuryl alcohol, trifluoroacetic acid, 1.6-M solution of BuLi in hexane, dichloromethane, sodium bicarbonate, pyridinium chlorochromate, potassium permanganate, sodium hydroxide, concentrated hydrochloric acid, ethanol, 7-M ammonia in methanol solution, and methanol. All chemicals and reagents were used as received.

## 2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker 600-MHz spectrometer at 25 °C. Spectra for the furanic compounds were obtained in a 0.1%–0.5% deuterated solvent solutions.

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## 3. Synthesis

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### 3.1 General

The following monomers and compounds were produced in this work: furan-2-carbonyl azide; 2-furanamine; 2,2'-Methylenedifuran; di(2-furyl)methanone; 2,5-furan dicarboxylic acid; 2,5-furan dicarboxylic acid chloride; and 2,5-furan diamide. All except di(2-furyl)methanone are relevant compounds for the production of high-performance polyamides, such as Kevlar, Nomex,<sup>\*</sup> and nylon. 2-furanamine and 2,2'-Methylenedifuran are relevant to the production of furan-based epoxies. 2,2'-Methylenedifuran is relevant to the production of furan-based polyimides. Also, di(2-furyl)methanone is relevant to production of an analog to polyether ether ketone.

### 3.2 Synthesis of Furan-2-Carbonyl Azide

Furan-2-carbonyl azide was synthesized via the chlorination of furoic acid by thionyl chloride according to the literature (9–13) using furoic acid (8.46 g) and thionyl chloride (9 mL) (figure 1). The reagents were added to a 100-mL two-neck round-bottom flask equipped with a condenser and a trap filled with methanol. The solution was stirred at reflux (78–80 °C) for 3–5 h. After that time, anhydrous DMF (0.1 mL) was added to the solution as a catalyst and allowed to continue stirring for 2 h. The thionyl chloride was further distilled and the product precipitated from solution. The white solid product was produced in a quantitative yield of greater than 90%. Characterization by  $^1\text{H}$  NMR ( $\text{CDCl}_3$  600 MHz)  $\delta$  8.05 ppm, 7.78 ppm, 6.94 ppm: (dd, 1H, Ar-H) (figure 2). The product was used without further purification.

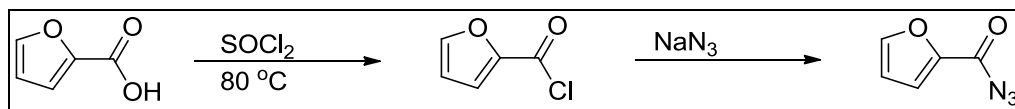


Figure 1. Synthesis of furan-2-carbonyl azide.

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<sup>\*</sup> Nomex is a registered trademark of E. I. du Pont de Nemours and Company.

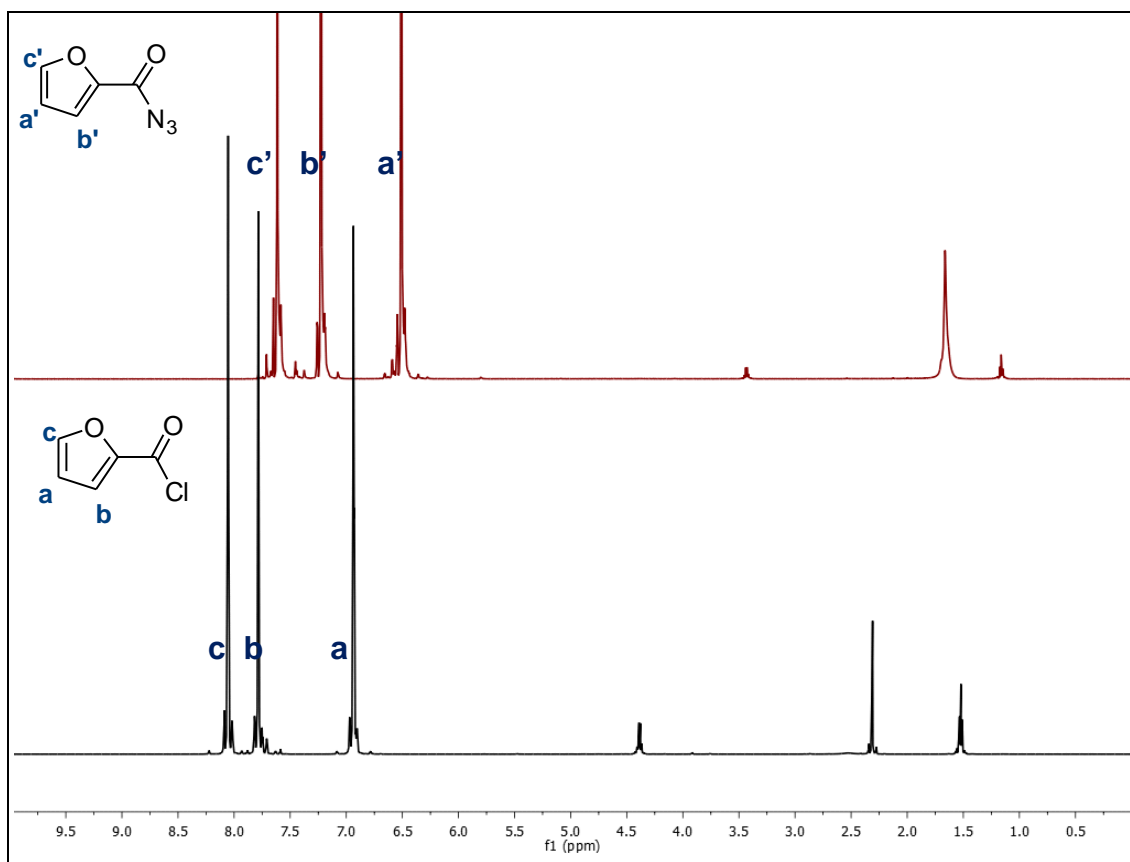


Figure 2. Characterization of furan carboxylic acid chloride and furan-2-carbonyl azide.

The last synthetic route to prepare the furan-2-carbonyl azide was done according to the literature (12–14). To the furoic acid chloride (7.48 g), 22.5 mL of anhydrous diethyl ether was added at 0 °C. A solution containing 4.53 g of sodium azide in 20 mL of water was added dropwise. The mixture was stirred at 0 °C for 15 min, then warmed to room temperature (RT) and stirred for another 2 h. After removal of the ether under reduced pressure by a rotoevaporator, the resulting off-white solid was filtered and washed with cold water. The resulting white solid that formed was dried under vacuum. The white solid product was produced in 55% yield. Characterization by  $^1\text{H}$  NMR ( $\text{CDCl}_3$  600 MHz)  $\delta$  7.61 ppm, 7.22 ppm, 6.51 ppm: (dd, 1H, Ar-H) (figure 2).

### 3.3 Synthesis of 2-Furanamine

2-Furanamine was synthesized according to a method in the literature (15) with changes to accommodate the different starting material, furoic acid (figure 3). The reaction was conducted in a 100-mL round-bottom flask equipped with an overhead stirrer. Furoic acid (1.10 g) and 5.5 mL of dimethoxyethane was added to the round-bottom flask and stirred for 10 to 15 min at RT. Concentrated sulfuric acid (4.5 mL) was added slowly and dropwise to the solution. The solution showed increased viscosity and became opaque in color. Sodium azide ( $\text{NaN}_3$ ) (1.90 g) was added slowly to the mixture and stirred for 3 to 4 h. Then ammonium hydroxide (10–15 mL)

and an additional 10–15 mL of dimethoxyethane was added to the mixture to adjust the pH to 9. The mixture separated into two phases. An extraction funnel was used to separate the solutions by using diethyl ether solvent. The organic solvent was removed under reduced pressure to produce an off-white product with a yield of 23%. Characterization by  $^1\text{H}$  NMR ( $\text{CDCl}_3$  600 MHz)  $\delta$  7.29 ppm, 6.73 ppm, 6.23 ppm: (dd, 1H, Ar-H) (figure 4).

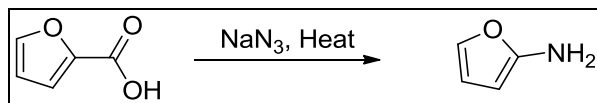


Figure 3. Synthesis of 2-Furanamine.

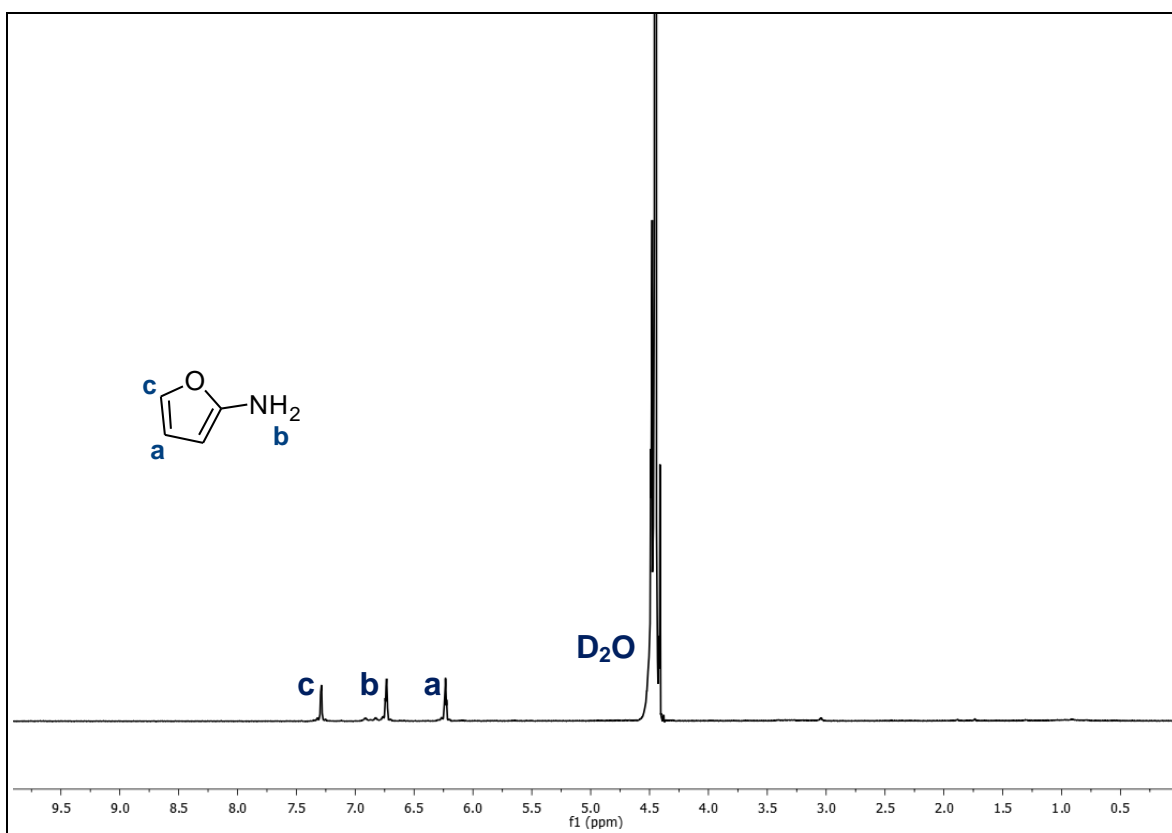


Figure 4.  $^1\text{H}$  NMR of 2-Furanamine in  $\text{D}_2\text{O}$  solvent.

Table 1. Solubility of 2-Furanamine.

Solvent	2-Furanamine
Acetone	—
Chloroform	—
Dimethylacetamide (DMAc)	—
Dimethylsulfoxide (DMSO)	+
Methanol	±
Tetrahydrofuran (THF)	—
Water	+

Note: + = soluble at RT; ± = partially soluble; — = insoluble at RT.

### 3.4 Synthesis of 2,2'-Methylenedifuran

The 2,2'-Methylenedifuran compound was synthesized according to a method in the literature (16) as per figure 5. The reaction was conducted in a 250-mL round-bottom flask equipped with a stirring bar. Furfuryl alcohol (7.71 g, 0.05 mol) was added to the round-bottom flask with furan (63.65 g, 0.94 mol) and stirred in an ice bath. After stirring for 5 to 10 min, 3.2 mL of trifluoroacetic acid (CF<sub>3</sub>COOH) was added dropwise. After stirring in the ice bath for 2 h, the solution was a bluish-green color. The solution was allowed to stir overnight. At the end of the reaction period, the solution was a dark blue color. The solution was washed with concentrated aqueous sodium bicarbonate solution (200 mL, three times) and then with water (200 mL, three times). The solution changed to a dark brown color. The mixture separated into two phases. An extraction funnel was used to separate the solutions. The organic solvent was removed under reduced pressure to produce a brown oil as product with a yield of 40%. Characterization by <sup>1</sup>H NMR (CDCl<sub>3</sub> 600 MHz) δ 7.35 ppm, 6.33 ppm, 6.11 ppm: (dd, 2H, Ar-H), 4.02 ppm: (s, H, CH<sub>2</sub>) (figure 6), and <sup>13</sup>C NMR (CDCl<sub>3</sub> 600 MHz) δ 151.49 ppm, 141.47 ppm, 110.28 ppm: (dd, 1C, Ar-H), 106.34 ppm: (dd, 1C, Ar-C), 27.30 ppm: (s, 1C, CH<sub>2</sub>) (figure 7).

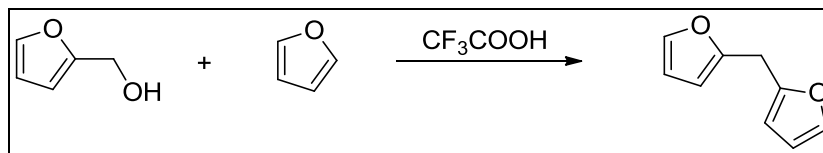


Figure 5. Synthesis of 2,2'-Methylenedifuran.

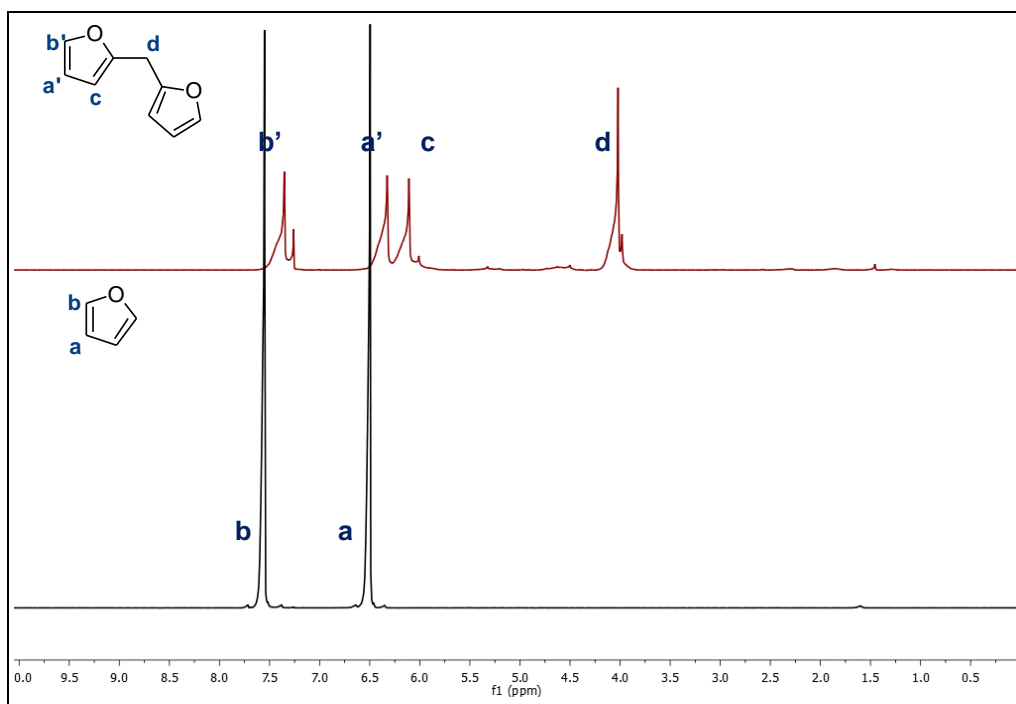


Figure 6.  $^1\text{H}$  NMR of furan to 2,2'-Methylenedifuran.

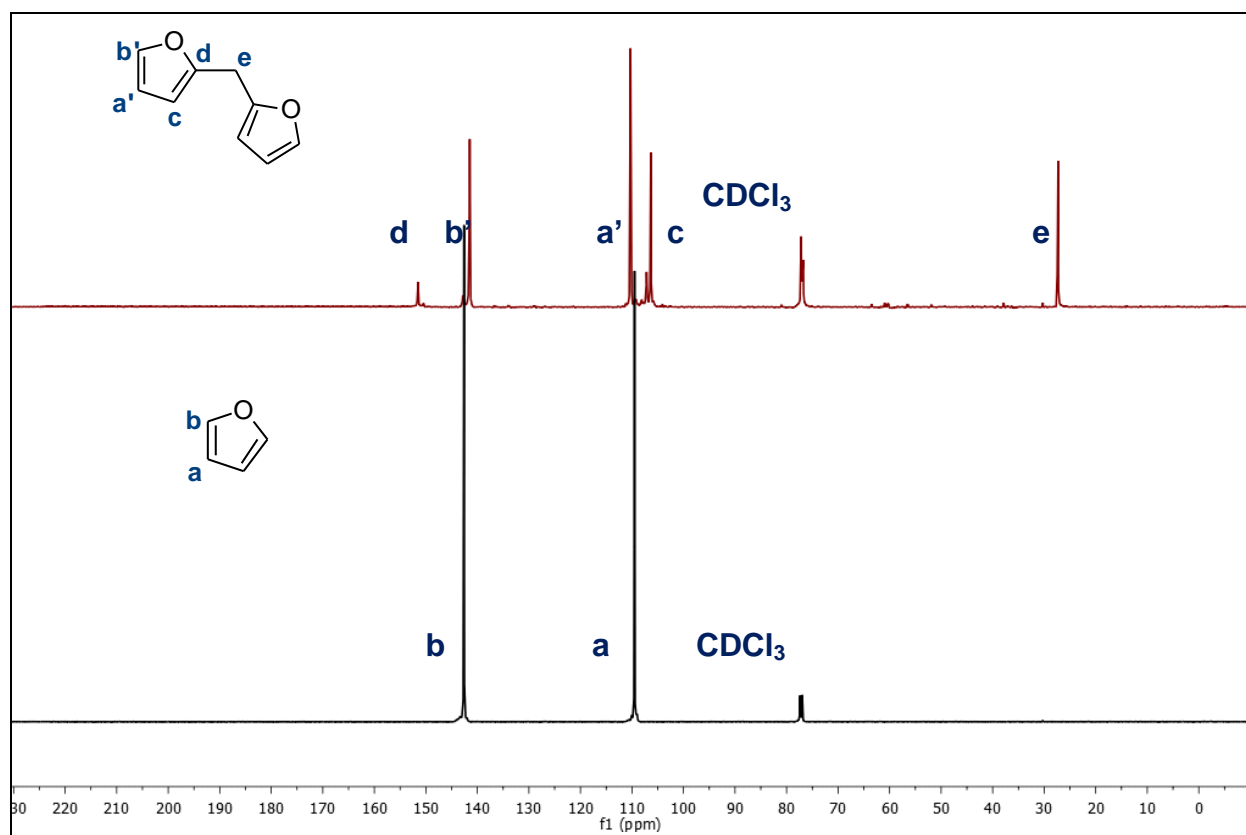


Figure 7.  $^{13}\text{C}$  NMR of furan to 2,2'-Methylenedifuran.

### 3.5 Synthesis of Di(2-furyl)methanone

The furanic compound, di(2-furyl)methanone, was prepared in accordance with the literature (17, 18) (figure 8). The reaction was conducted in a 100-mL round-bottom flask equipped with a stirring bar. To a solution of furan (0.6 mL) in anhydrous diethyl ether (11 mL) was added dropwise a 1.6-M solution of BuLi in hexane (6 mL). Upon addition of the BuLi in hexane solution, the solution color changed to reddish orange from a slightly yellow tint. The mixture was cooled to  $-50\text{ }^{\circ}\text{C}$ , and within 3 h of stirring the color changed to dark brown. *N,N*-dimethylcarbonyl chloride (DMC) (0.6 mL) was added dropwise, and the solution was allowed to warm to  $0\text{ }^{\circ}\text{C}$  and stirred for 2–3 h. Then the reaction was quenched with a saturated aqueous solution of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) (8 mL) and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL, twice) through a separatory funnel. The organic phase was dried ( $\text{MgSO}_4$ ) and rotoevaporated to remove organic solvent, producing a yellow oil product with a yield of greater than 1.0% (figure 8). The  $^1\text{H}$  NMR in figure 9 clearly shows unsuccessful formation of the furanic compound.

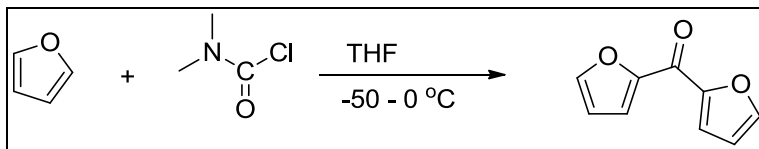


Figure 8. Synthesis of Di(2-furyl)methanone.

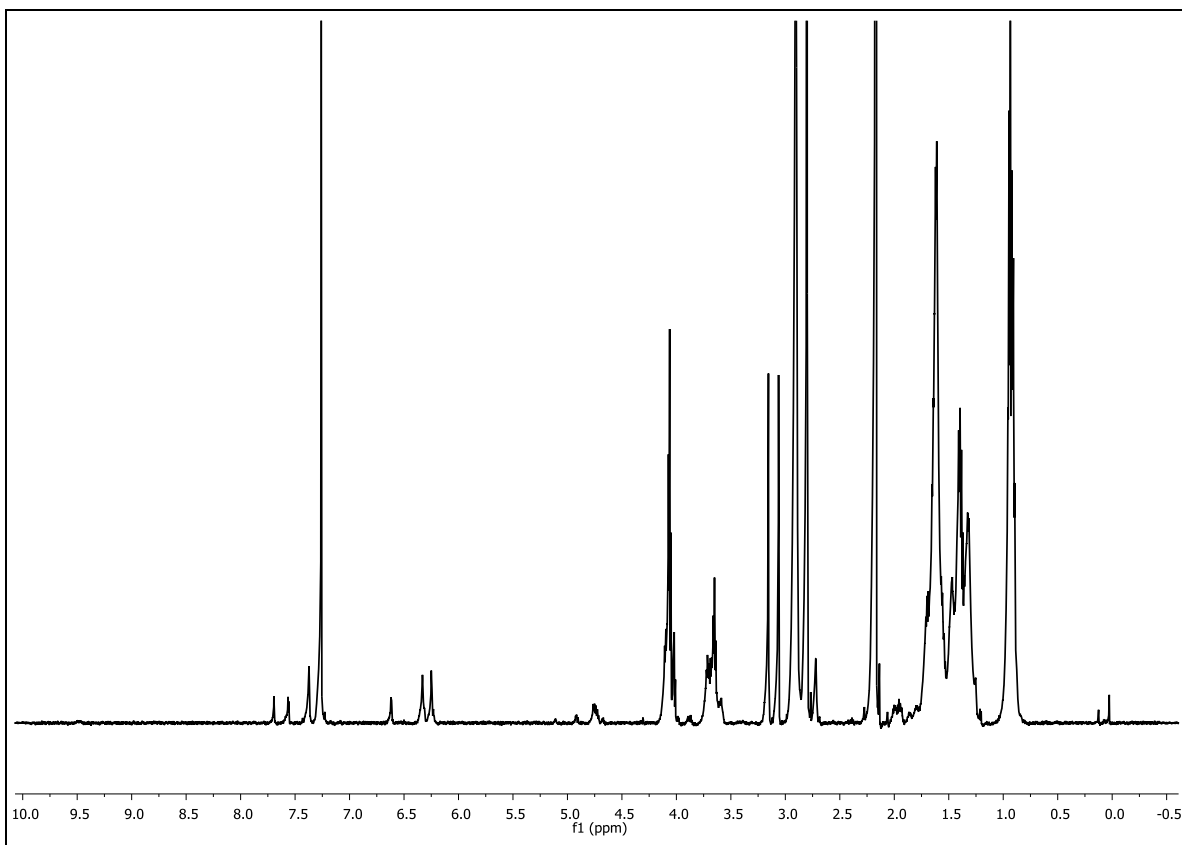


Figure 9.  $^1\text{H}$  NMR of the unsuccessful formation of Di(2-furyl)methanone.

### 3.6 Synthesis of 2,5-Furan Dicarboxylic Acid

The furan compound 2,5-furan dicarboxylic acid was prepared via the oxidation of 2,5-bis(hydroxymethyl)furan through a 2,5-diformylfuran intermediate with pyridinium chlorochromate (PCC) (figure 10). PCC is an oxidant that offers a selective oxidation of primary and secondary alcohols to aldehydes and ketones (19, 20). The oxidation reaction took place in a 500-mL round-bottom flask equipped with a stirring bar. The 2,5-bis(hydroxymethyl)furan (10.01 g, 78.12 mmol) and dichloromethane (250 mL) solution was added to a round-bottom flask and stirred at RT. PCC (37.01 g, 171.87 mmol) was added slowly to the stirring solution over 10 min. The reaction color changed from red-orange to brown. The reaction was allowed to stir for 3 h. At the end of the reaction period, the solution was passed through a fritted filter packed with silica gel to remove the chromate solids. A light yellow solution was collected in a 100-mL round-bottom flask. Flash chromatography (silica gel, EtOAc /hexane 1:1) afforded a quantitative yield greater than 95%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.82 ppm: (dd, 2H, Ar-H), 7.33 ppm: (s, 2H, O=C-H).



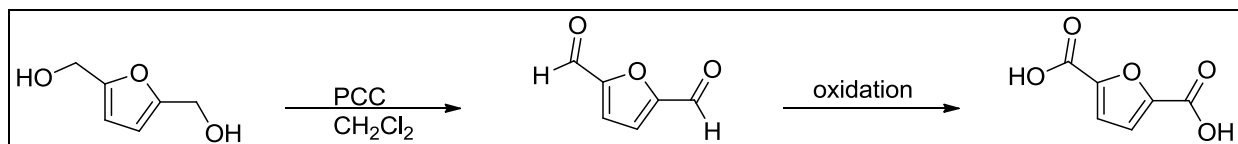


Figure 10. Synthesis of 2,5-furan dicarboxylic acid.

The purified intermediate, 2,5-diformylfuran (2.29 g, 18.47 mmol), was oxidized in a 100-mL round-bottom flask with potassium permanganate (4.47 g, 153.1 mmol) in a NaOH solution. The solution stirred overnight. The manganese oxide was filtered from the solution to obtain a light yellow solution with a pH of 13–14. The solution was acidified with concentrated HCl. At pH of 1, the white solid product precipitated from solution. The material was filtered and dried under reduced pressure. The reaction afforded a quantitative yield of greater than 95%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.31 ppm: (dd, 1H, Ar-H) (figure 11).

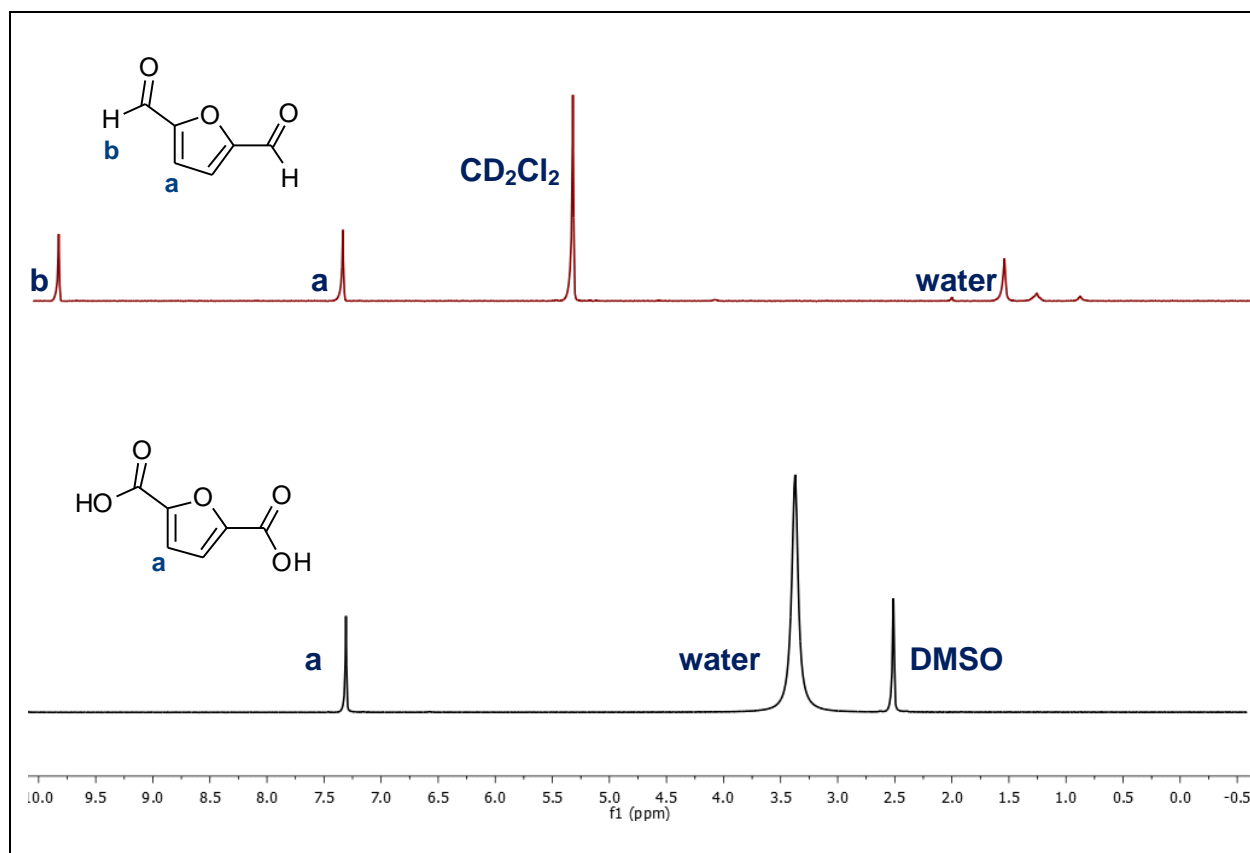


Figure 11.  $^1\text{H}$  NMR of 2,5-diformylfuran.

### 3.7 Synthesis of 2,5-Furan Dicarboxylic Acid Chloride

The diacid chloride was synthesized from 2,5-furan dicarboxylic acid (2.0 g, 12.8 mmol) and thionyl chloride (18 mL, 247.8 mmol) (figure 12). The reagents were added to a 100-mL two-neck round-bottom flask equipped with a condenser and a trap filled with methanol. The solution was stirred at reflux (78–80 °C) for 3–5 h. Then anhydrous DMF (0.1 mL) was added to the solution as a catalyst, and stirring continued for 2 h. The thionyl chloride was further distilled and the product precipitated from solution. The product was used without further purification. The white solid product was produced in a quantitative yield of greater than 95%. Characterization by  $^{13}\text{C}$  NMR (DMSO- $d_6$  600 MHz)  $\delta$  157 ppm: (s, O=C), 149 ppm: (s, Ar-C), 120.9, 121 ppm: (s, Ar-C) (figure 13).

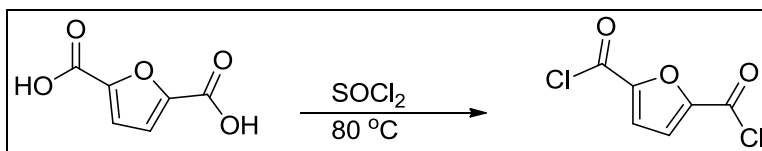


Figure 12. Acid chloride reaction toward 2,5-furan dicarboxylic acid chloride.

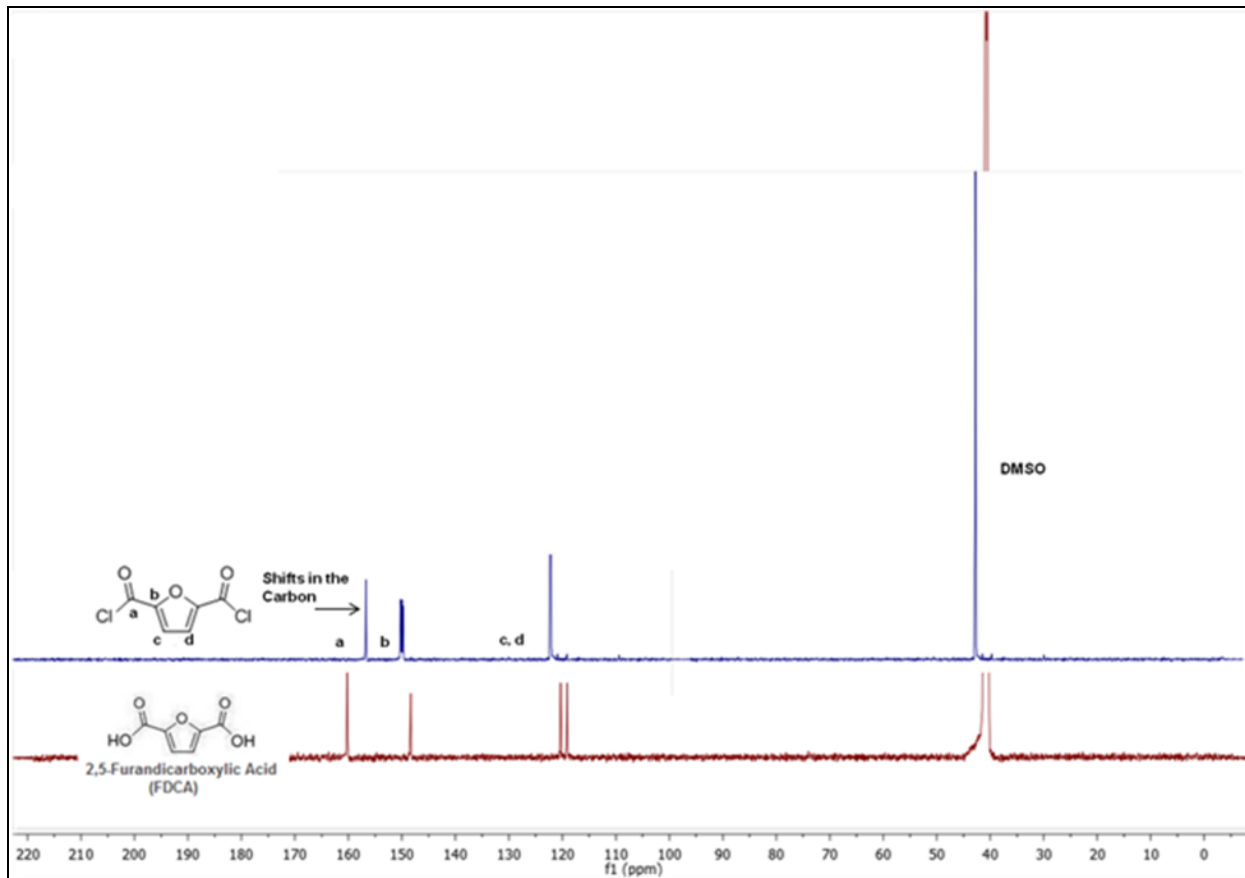


Figure 13.  $^{13}\text{C}$  NMR of 2,5-furan dicarboxylic acid chloride.

### 3.8 Synthesis of 2,5-Furan Diamide

The 2,5-furan diamide compound was synthesized from 2,5-furan dicarboxylic acid via a 2,5-diethylfurandicarboxylate, according to literature references regarding the synthesis of *p*-phenylenediamine (21, 22) (figure 14). In a 250-mL round-bottom flask equipped with a condenser and a stirring bar, 2,5-furan dicarboxylic acid (1.01 g, 6.47 mmol) was added with 90 mL of ethanol at reflux (80 °C). After complete dissolution of the acid in ethanol, 1.8 mL of concentrated HCl was added to the flask. The solution was stirred overnight. The solvent was removed under reduced pressure to obtain a light-yellow viscous liquid at RT. The reaction produced material in a quantitative yield of greater than 95%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.18 ppm: (dd, 2H, Ar-H), 4.37 ppm: (m, 4H, CH<sub>2</sub>), 1.37 ppm: (m, 6H, CH<sub>3</sub>).

The 2,5-diethylfurandicarboxylate product was used to synthesize the 2,5-furan diamide (figure 15). To the 250-mL round-bottom flask containing the furan compound, sodium chloride (NH<sub>4</sub>Cl) (1.52 g, mol) was added with 10 mL of 7-M ammonia in MeOH solution and 12 mL of MeOH and stirred at reflux overnight. The white solid product was obtained by removal of the solvent under reduced pressure. The reaction produced material in quantitative yield greater than 95%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.38 ppm: (dd, 2H, Ar-H), 3.32 ppm: (m, 4H, NH<sub>2</sub>) (figure15).

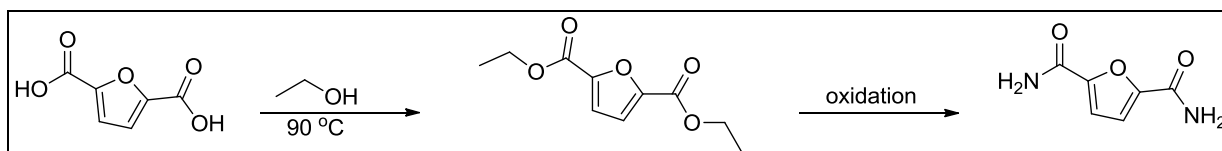


Figure 14. Synthesis of 2,5-furan diamide via 2,5-diethylfurandicarboxylate.

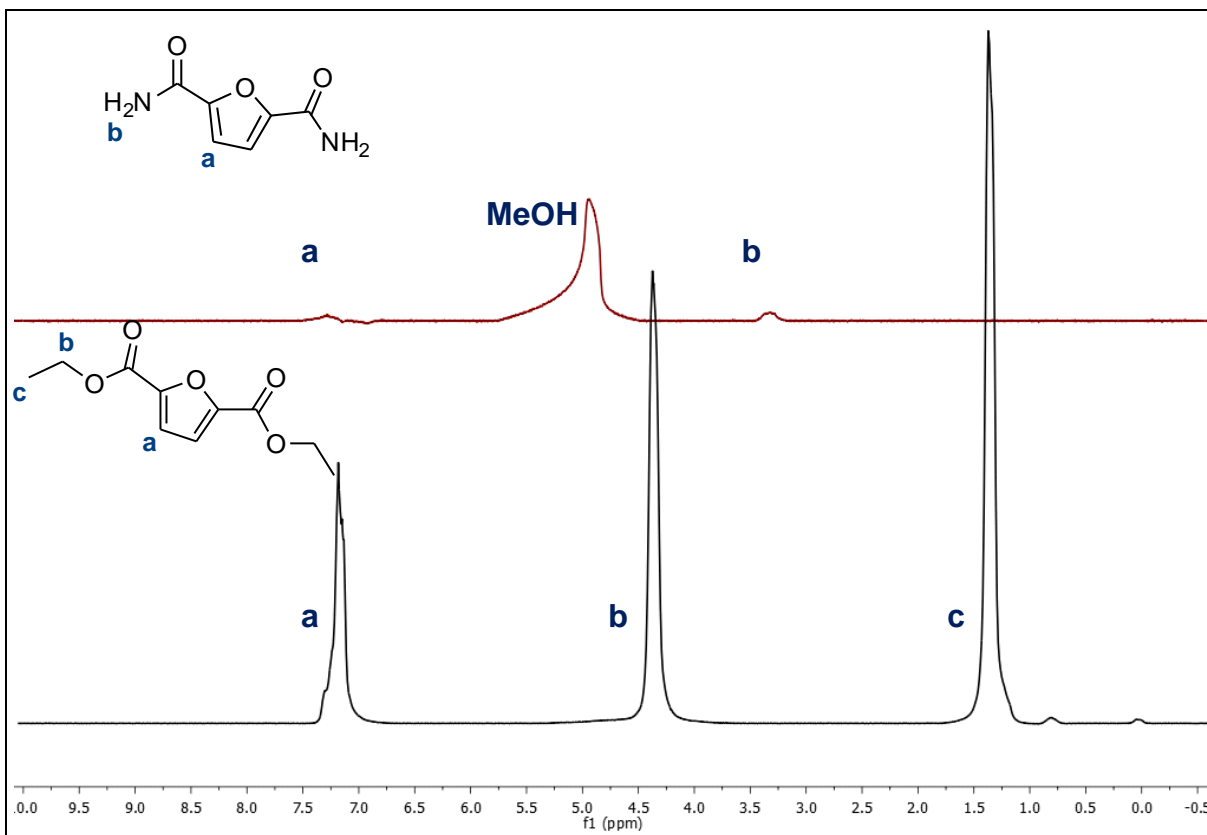


Figure 15.  $^1\text{H}$  NMR of 2,5-diethylfuran-2,5-dicarboxylate.

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## 4. Conclusions

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Furanic monomers and compounds have been synthesized to be used in polymers that could have a combination of high thermal properties and high strength. These monomers were produced at high purities in good yields using conventional synthetic organic chemistry techniques, although significant differences exist relative to producing analogous benzene-based products. These compounds are a class of furanic materials that have not been fully utilized in this capacity; however, their functionality should allow them to be competing analogs to petroleum-derived compounds that are currently investigated in high-performance applications.

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