**Electronic Supporting Information (ESI)**

# Production of 5-(chloromethyl)furan-2-carbonyl chloride and furan-2,5-dicarbonyl chloride from biomass-derived 5-(chloromethyl)furfural (CMF)

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## Contents

## 1. Materials

Tert-butyl hypochlorite was prepared using a published procedure.[1] 5-(Chloromethyl)furfural (CMF) is most conveniently produced on a large scale from fructose using a method based on the work of Szmant and Chundury.[2] 2,5-Diformylfuran (DFF) was prepared from CMF using the method of Laugel, *et al.*[3] Nitromethane and mesitylene were purchased from Sigma-Aldrich and dried over 4 Å molecular sieves. Anhydrous ethanol, anhydrous benzene, and aluminum chloride were purchased from Sigma-Aldrich and used as received. All chromatographic separations were carried out on silica gel (40-63 μm particle size) purchased from Dynamic Adsorbents.

## 2. Experimental Procedures

### 5-(Chloromethyl)furan-2-carbonyl chloride (CMFCC) 4 and ethyl 5-(chloromethyl)furan-2-carboxylate 5

5-(Chloromethyl)furfural **3** (2.226 g, 15.40 mmol) and tert-butyl hypochlorite (10.5 mL, 10.1 g, 92.7 mmol) were introduced into a 50 mL round-bottomed flask wrapped with aluminum foil. The mixture was stirred rapidly at room temperature under air. After 24 h, a measured amount of 1,4-dioxane was added as an internal standard and the yield of CMFCC **4** was determined to be 85% by $^{1}$H NMR peak integration. The volatiles were evaporated at room temperature and the crude CMFCC **4** (2.90 g) was dissolved in anhydrous ethanol (20 mL). The clear yellow solution was stirred at 50 °C for 6 h. The solvent was evaporated and the residue was chromatographed using $CH_2Cl_2$/hexane (1:1 to 3:1 gradient) to give ethyl 5-(chloromethyl)furan-2-carboxylate **5** as a colorless oil (2.390 g, 82%). $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 3.5 Hz, 1H), 6.44 (d, *J* = 3.5 Hz, 1H), 4.55 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 158.35, 153.96, 145.02, 118.54, 111.37, 61.10, 36.68, 14.26.

### Large scale preparation of 5-(chloromethyl)furan-2-carbonyl chloride (CMFCC) 4 and ethyl 5-(chloromethyl)furan-2-carboxylate 5

5-(Chloromethyl)furfural **3** (10.47 g, 72.40 mmol) and tert-butyl hypochlorite (49.4 mL, 47.5 g, 0.436 mol) were introduced into a 500 mL round-bottomed flask wrapped with aluminum foil. The mixture was stirred rapidly at room temperature under air. After 24 h, the volatiles were evaporated at room temperature and the crude CMFCC **4** (14.10 g) was dissolved in anhydrous ethanol (90 mL). The clear yellow solution was stirred at 50 °C for 6h. The solvent was evaporated and the residue was chromatographed using $CH_2Cl_2$/hexane (1:1 to 2:1 gradient) to give ethyl 5-(chloromethyl)furan-2-carboxylate **5** as a colorless oil (10.96 g, 80.2%).

### Ethyl 5-(ethoxymethyl)furan-2-carboxylate 6

A solution of ethyl 5-(chloromethyl)furan-2-carboxylate **5** (1.486 g, 7.879 mmol) in ethanol (25 mL) was heated in a closed vessel at 150 °C for 7 h. The solvent was evaporated to give ethyl 5-(ethoxymethyl)furan-2-carboxylate **6** as a yellow oil (1.500 g, 96%). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, *J* = 3.4 Hz, 1H), 6.34 (d, *J* = 3.4 Hz, 1H), 4.40 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.47 (q, *J* = 7.0 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 158.59, 156.38, 144.36, 118.43, 110.37, 66.14, 64.55, 60.76, 14.96, 14.22. ESI-HRMS calcd. for $C_{10}H_{15}O_4$: *m/z* 199.0965 $(M+H)^+$, found: 199.0961.

### Ethyl 5-methylfuran-2-carboxylate 7

To a solution of ethyl 5-(chloromethyl)furan-2-carboxylate **5** (1.416 g, 7.508 mmol) in ethanol (50 mL) was added 10% palladium on activated carbon (145 mg) and the mixture was carefully evacuated and then backfilled with hydrogen three times. The reaction flask was pressurized to 2.5 atm hydrogen and shaken for 160 min. The mixture was filtered through a short plug of Celite, which was further rinsed with ethanol (30 mL). The solvent was evaporated to give ethyl 5-methylfuran-2-carboxylate **7** as a pale yellow oil (994 mg, 86%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.05 (d, *J* = 3.2 Hz, 1H), 6.08 (d, *J* = 3.2 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) δ158.84, 157.01, 143.22, 119.18, 108.34, 60.68, 14.36, 13.99.

### Ethyl 5-[(benzylamino)methyl]furan-2-carboxylate 8

A solution of ethyl 5-(chloromethyl)furan-2-carboxylate **5** (446 mg, 2.36 mmol) and benzylamine (1.30 mL, 1.27 g, 11.9 mmol) in ethanol (30 mL) was heated in a closed vessel at 50 °C for 24 h. The reaction was cooled to room temperature and the volatiles were evaporated under vacuum. The residue was taken up in NaOH (0.2 M, 50 mL) and the mixture was extracted with dichloromethane (3 x 50 mL). The combined organic layer was washed with water and brine and then dried over $Na_2SO_4$. The solvent was evaporated and the residue was chromatographed using DCM/EtOAc (1:0 to 0:1 gradient) to give ethyl 5-[(benzylamino)methyl]furan-2-carboxylate **8** as a yellow oil (505 mg, 82%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 4H), 7.23 (m, 1H), 7.36 – 7.18 (m, 5H), 7.10 (d, *J* = 3.5 Hz, 1H), 6.30 (d, *J* = 3.5 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 3.77 (s, 2H), 1.34 (t, *J* = 7.0 Hz, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) 158.78, 158.52, 143.94, 139.47, 128.43, 128.23, 127.13, 118.69, 109.21, 60.82, 52.82, 45.41, 14.36. ESI-HRMS calcd. for $C_{15}H_{18}NO_3$: *m/z* 260.1281 $(M+H)^+$, found: 260.1278.

### Ethyl 5-(2,4,6-trimethylbenzyl)furan-2-carboxylate 9

To a mixture of ethyl 5-(chloromethyl)furan-2-carboxylate **5** (1.05 g, 5.57 mmol), mesitylene (15 mL) and nitromethane (10 mL) was added aluminum chloride (1.41 g, 10.6 mmol) and the mixture was stirred for 24 h. The volatiles were evaporated under vacuum and the residue was chromatographed using hexane/EtOAc (10:1 to 5:1 gradient) to give ethyl 5-(2,4,6-trimethylbenzyl)furan-2-carboxylate **9** as a yellow oil (1.436 g, 95%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.01 (d, *J* = 3.3 Hz, 1H), 6.87 (s, 2H), 5.73 (d, *J* = 3.4, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 2.26 (s, 3H), 2.24 (s, 6H), 1.36 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$) δ159.20, 158.88, 143.48, 136.82, 136.37, 130.12, 129.00, 118.95, 107.97, 60.70, 28.57, 20.87, 19.85, 14.37. ESI-HRMS calcd. for $C_{17}H_{21}O_3$: *m/z* 273.1485 $(M+H)^+$, found: 273.1486.

### Furan-2,5-dicarbonyl chloride (FDCC) 11 and diethyl furan-2,5-dicarboxylate 12

2,5-Diformylfuran **10** (1.315 g, 10.60 mmol) and tert-butyl hypochlorite (14.4 mL, 13.8 g, 127 mmol) were introduced into a 50 mL round-bottomed flask wrapped with aluminum foil. The suspension was stirred rapidly at room temperature under air for 24 h, resulting in a clear yellow solution. A measured amount of 1,4-dioxane was added as an internal standard and the yield of FDCC **11** was determined to be 80% by $^1$H NMR peak integration. The volatiles were evaporated at room temperature and the crude FDCC **11** (1.840 g) was dissolved in anhydrous ethanol (20 mL). The mixture was stirred at room temperature for 5 h. The solvent was evaporated and the residue was chromatographed using $CH_2Cl_2$/hexane (1:1 to 1:0 gradient) to give diethyl furan-2,5-dicarboxylate **12** as a yellow oil (1.700 g, 76%). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.19 (s, 2H), 4.39 (q, *J* = 7.1 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 6H); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 158.06, 146.89, 118.22, 61.58, 14.24.

**Furan-2,5-diylbis(phenylmethanone) 13**

2,5-Diformylfuran **10** (650 mg, 5.24 mmol) and tert-butyl hypochlorite (7.20 mL, 6.90 g, 63.6 mmol) were introduced into a 20 mL vial wrapped with aluminum foil. The suspension was stirred rapidly at room temperature under air for 24 h. The volatiles were evaporated at room temperature and the crude FDCC **11** was dissolved in anhydrous benzene (15 mL). To this was added aluminum chloride (1.35g, 10.1 mmol) and the mixture was stirred for 20 h. The reaction was poured into aq HCl (1.0 M, 50 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organic phase was washed with brine and dried over $Na_2SO_4$. The solvent was evaporated and the residue was chromatographed using hexane/EtOAc (1:0 to 5:1 gradient) to give furan-2,5-diylbis(phenylmethanone) **13** as a pale yellow solid (950 mg, 66%). $^1$H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 4H), 7.63 (t, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 4H), 7.38 (s, 2H); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 182.38, 153.95, 136.24, 133.32, 129.66, 128.61, 120.04. ESI-HRMS calcd. for $C_{18}H_{13}O_3$: *m/z* 277.0859 $(M+H)^+$, found: 277.0861.

## 3. NMR Spectra

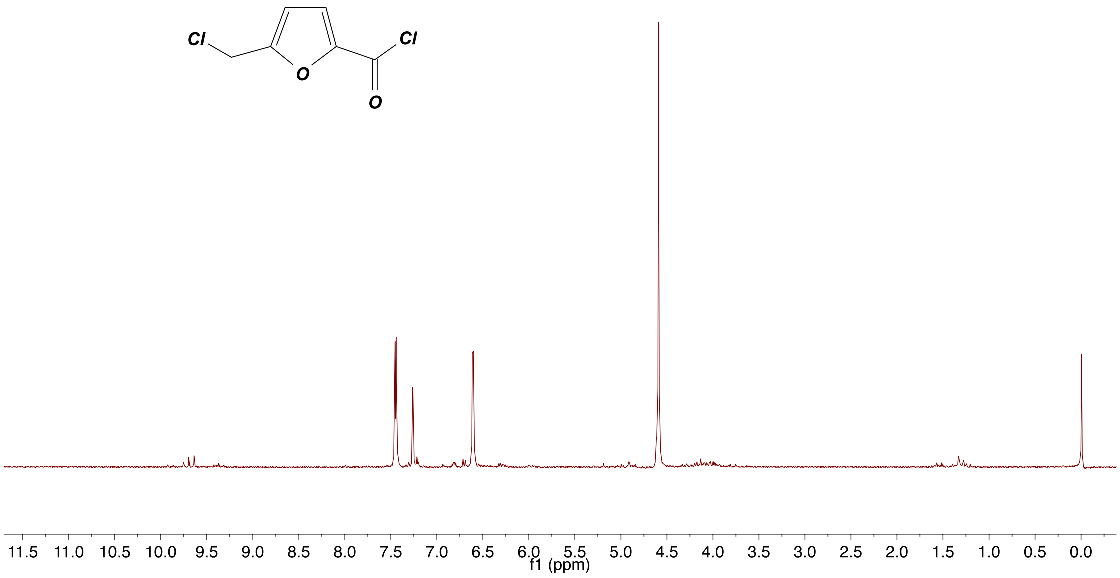

**Figure S1.** $^1$H NMR spectrum of crude CMFCC **4** in $CDCl_3$-TMS

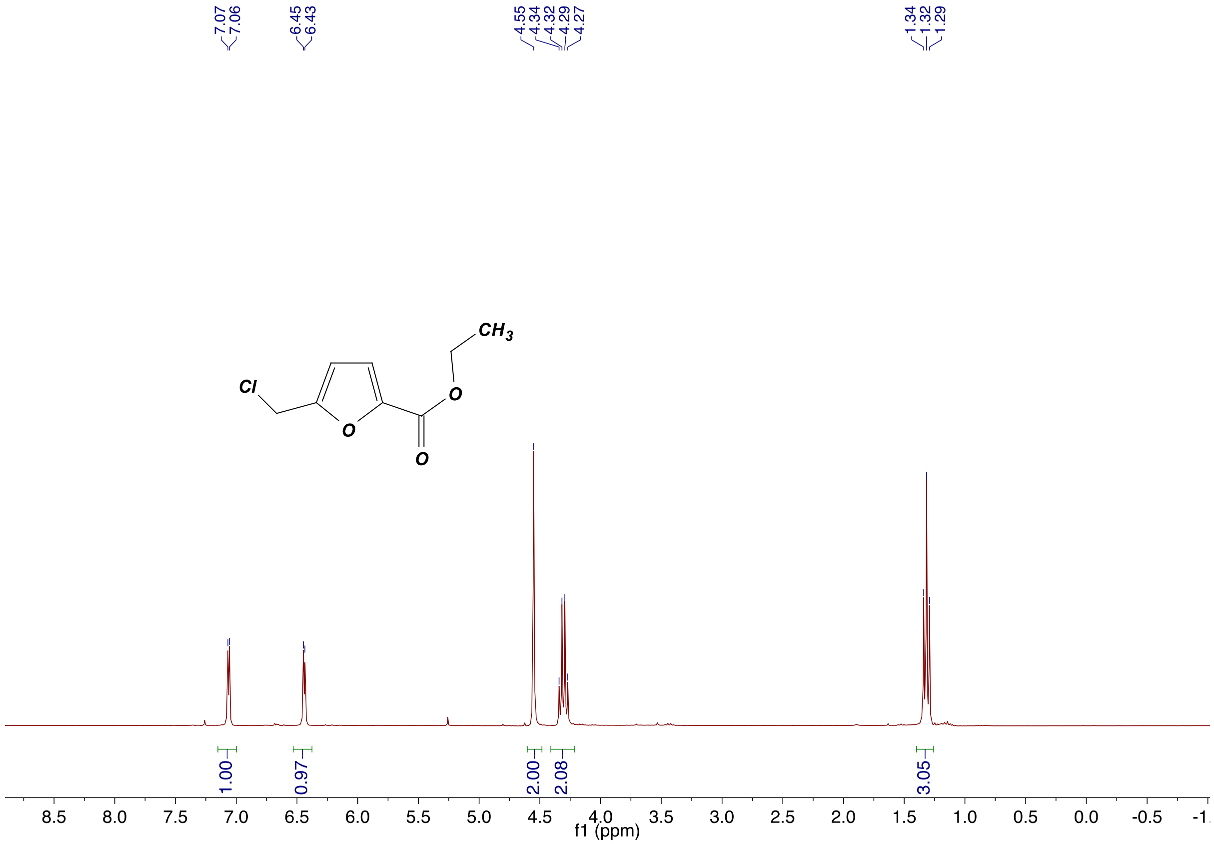

**Figure S2.** $^1$H NMR spectrum of ethyl 5-(chloromethyl)furan-2-carboxylate **5** in $CDCl_3$

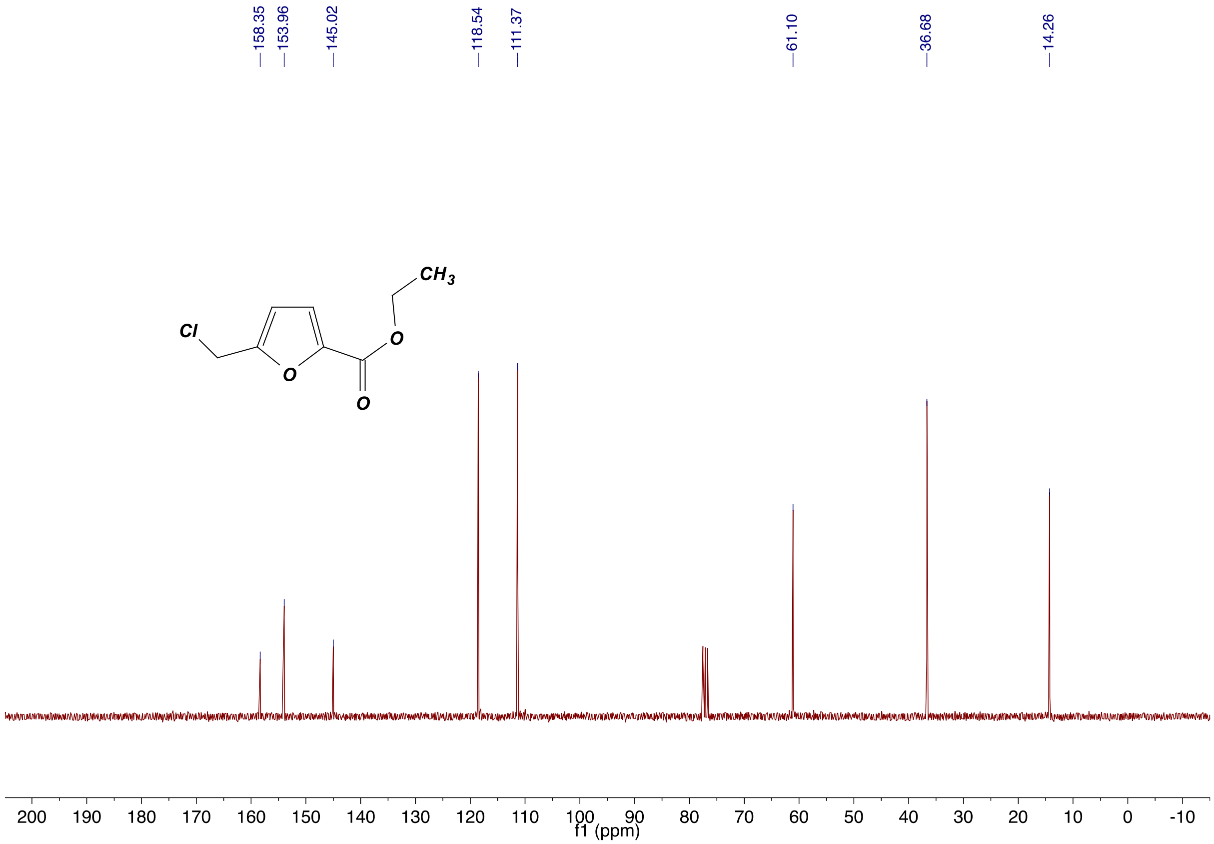

**Figure S3.** $^{13}$C NMR spectrum of ethyl 5-(chloromethyl)furan-2-carboxylate **5** in $CDCl_3$

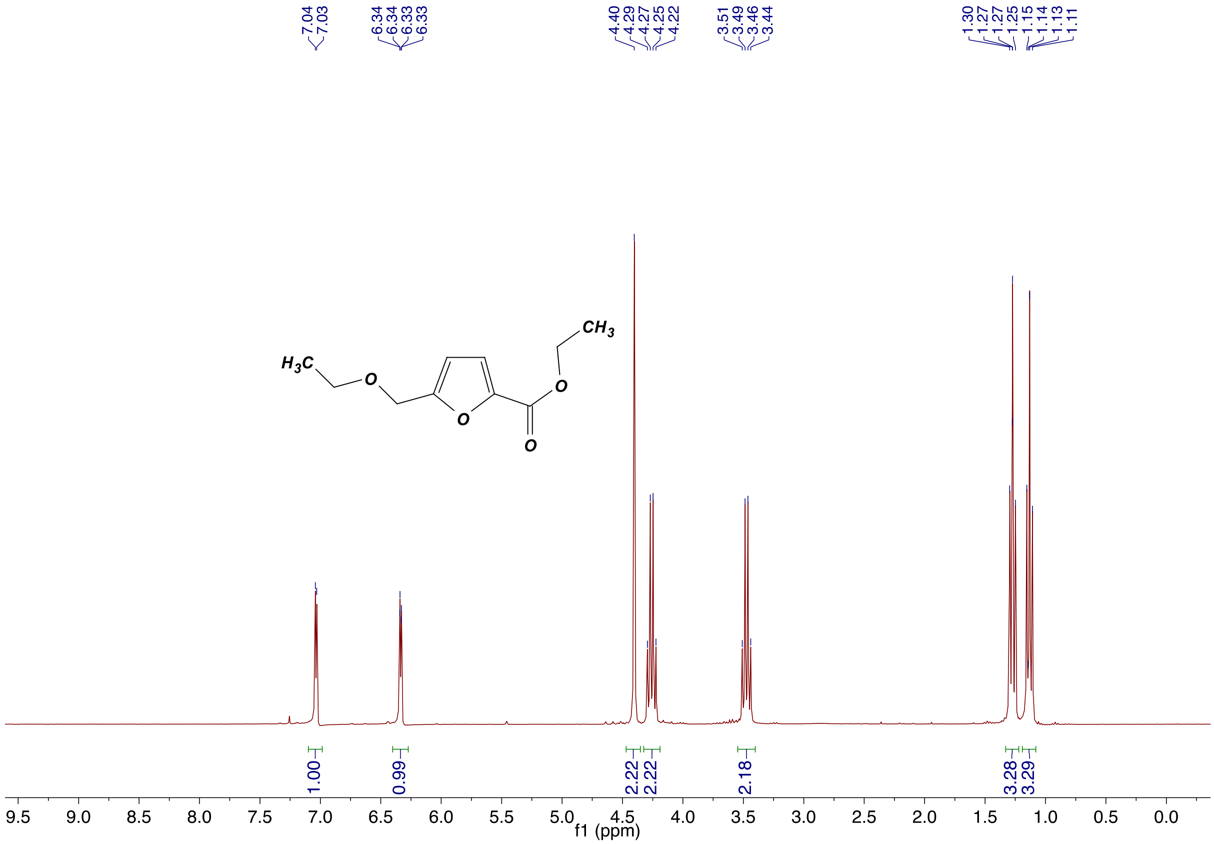

**Figure S4.** $^1H$ NMR spectrum of ethyl 5-(ethoxymethyl)furan-2-carboxylate **6** in $CDCl_3$

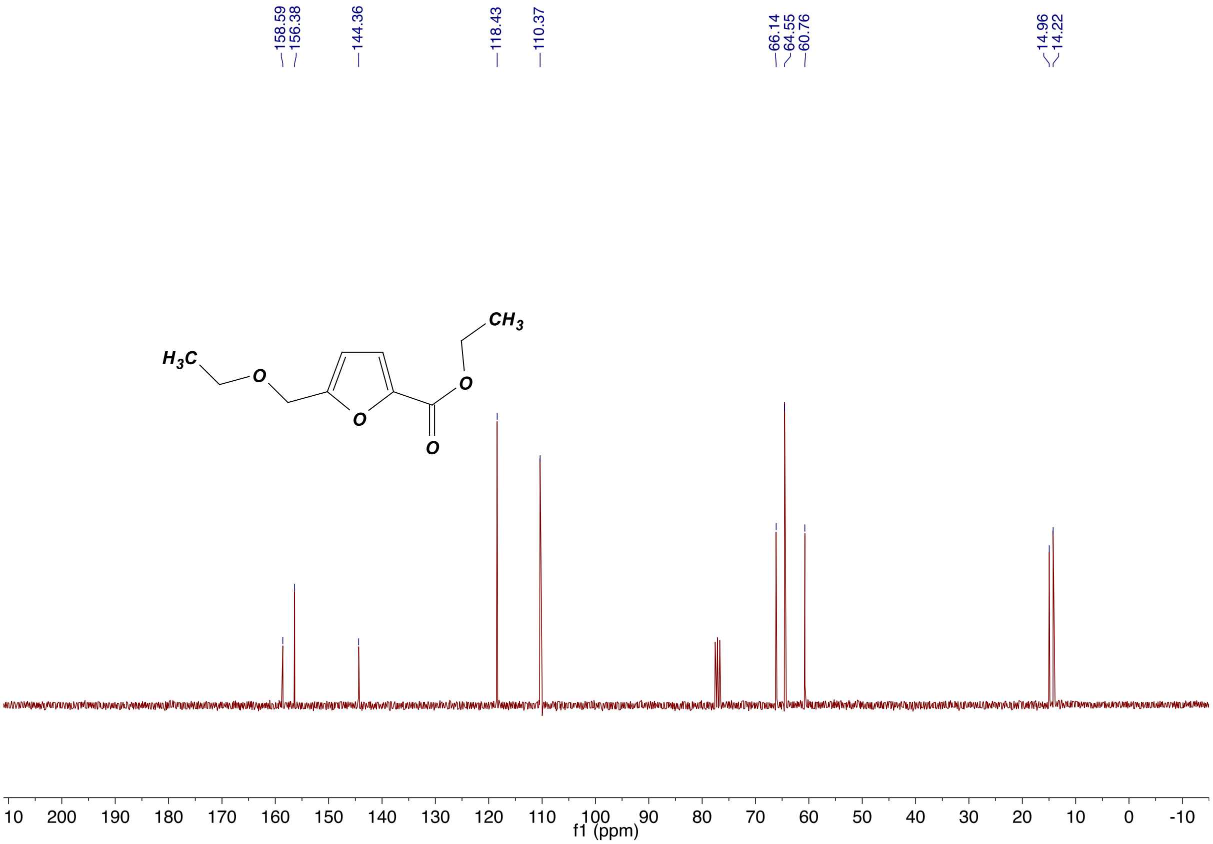

**Figure S5.** $^{13}$C NMR spectrum of ethyl 5-(ethoxymethyl)furan-2-carboxylate **6** in $CDCl_3$

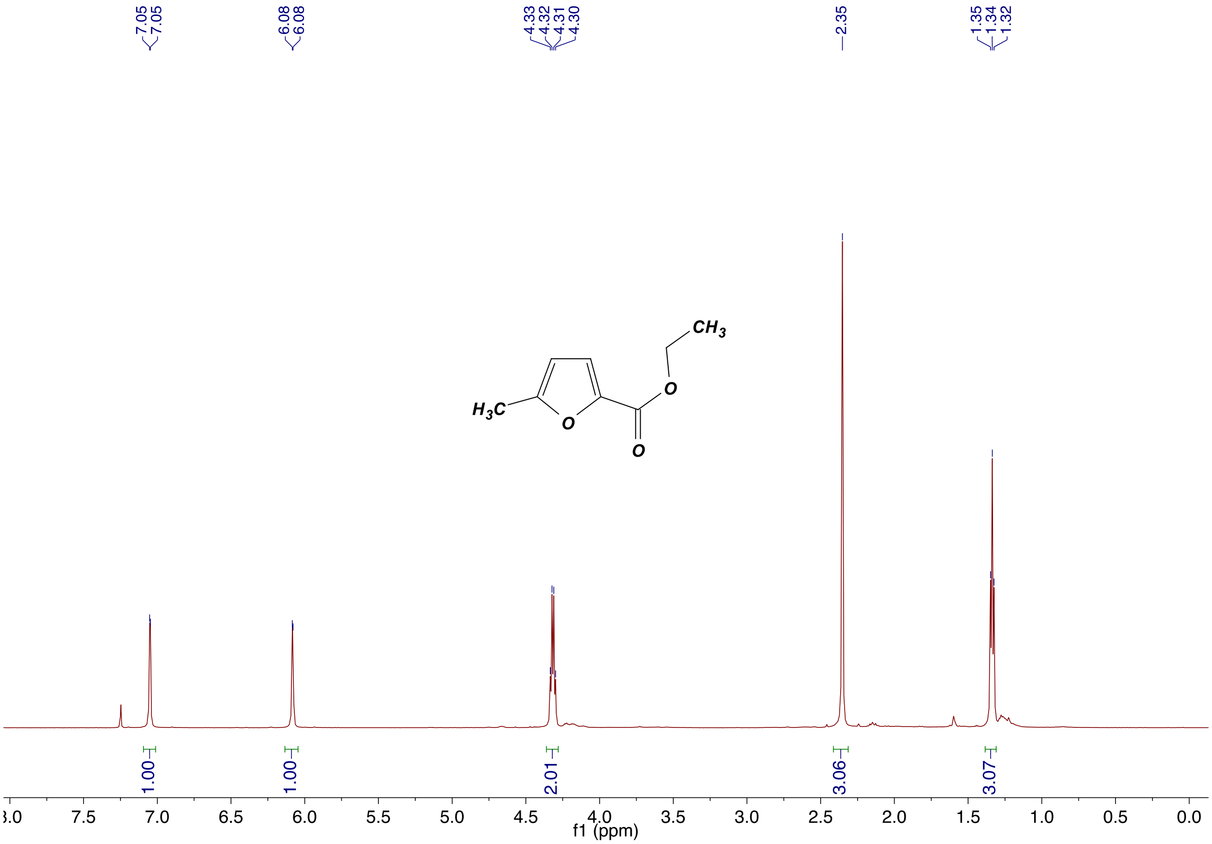

**Figure S6.** $^1$H NMR spectrum of ethyl 5-methylfuran-2-carboxylate **7** in $CDCl_3$

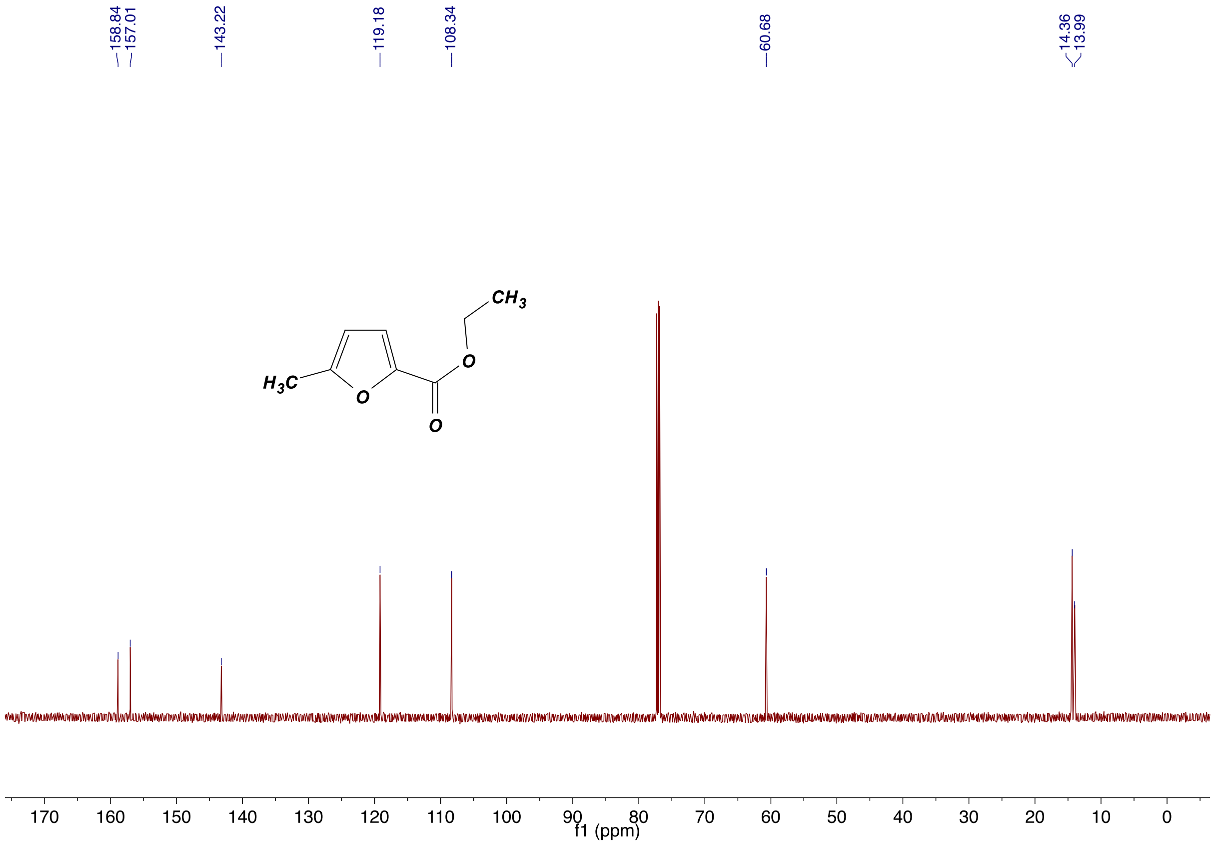

**Figure S7.** $^{13}$C NMR spectrum of ethyl 5-methylfuran-2-carboxylate **7** in $CDCl_3$

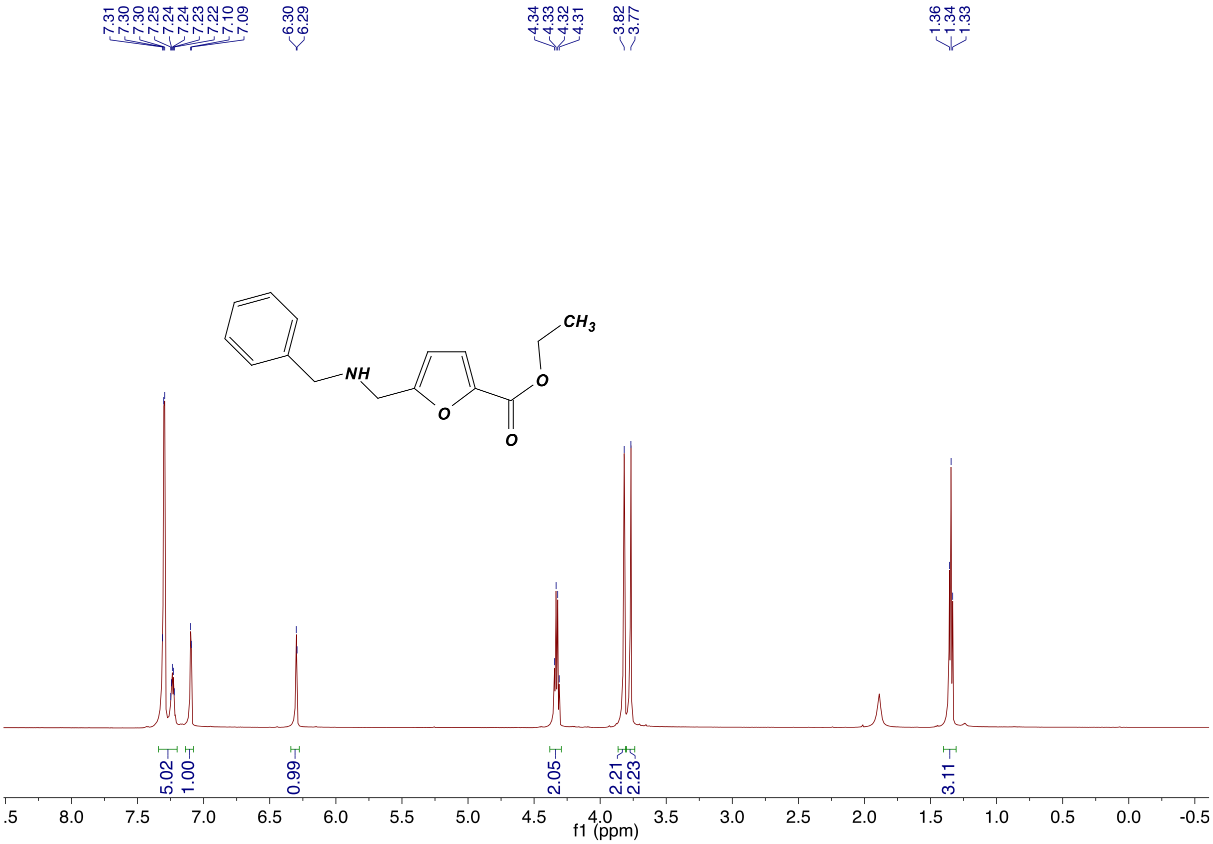

**Figure S8.** $^1$H NMR spectrum of ethyl 5-[(benzylamino)methyl]furan-2-carboxylate **8** in $CDCl_3$

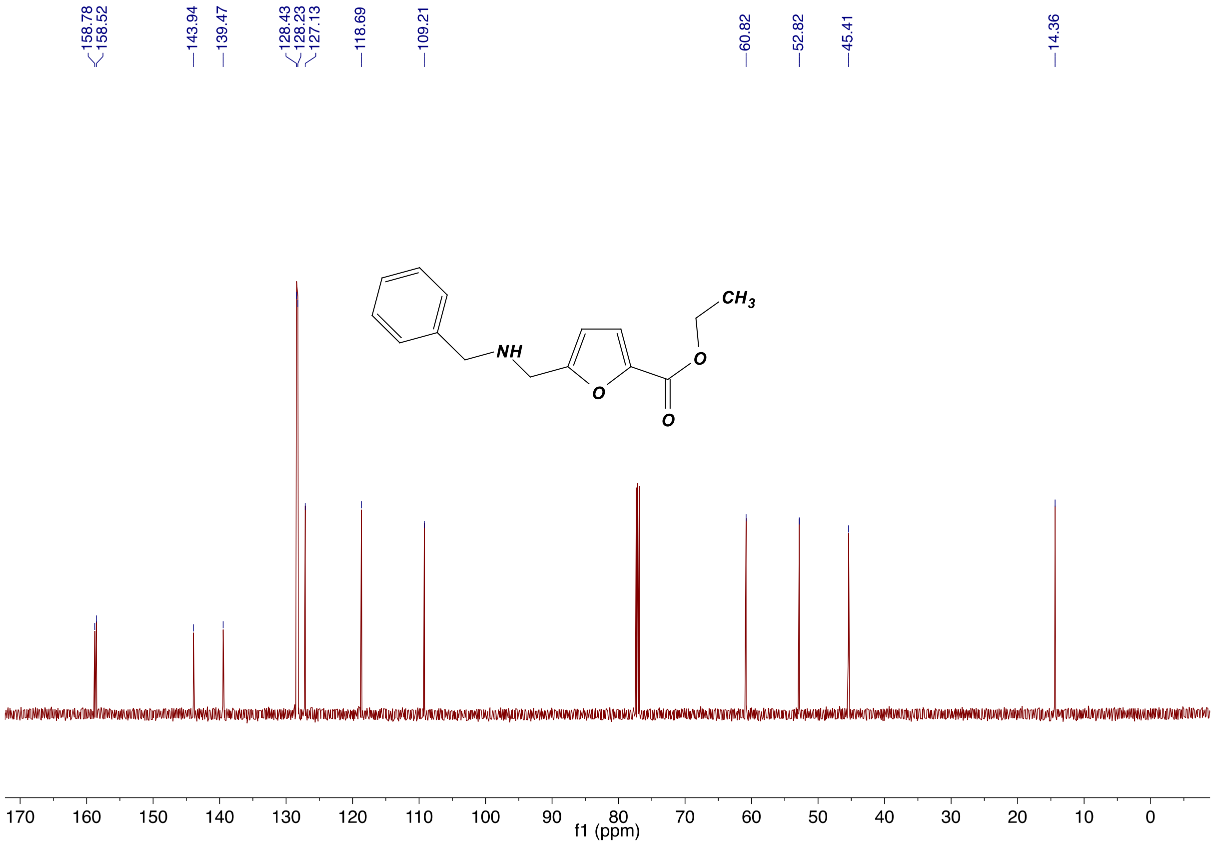

**Figure S9.** $^{13}$C NMR spectrum of ethyl 5-[(benzylamino)methyl]furan-2-carboxylate **8** in $CDCl_3$

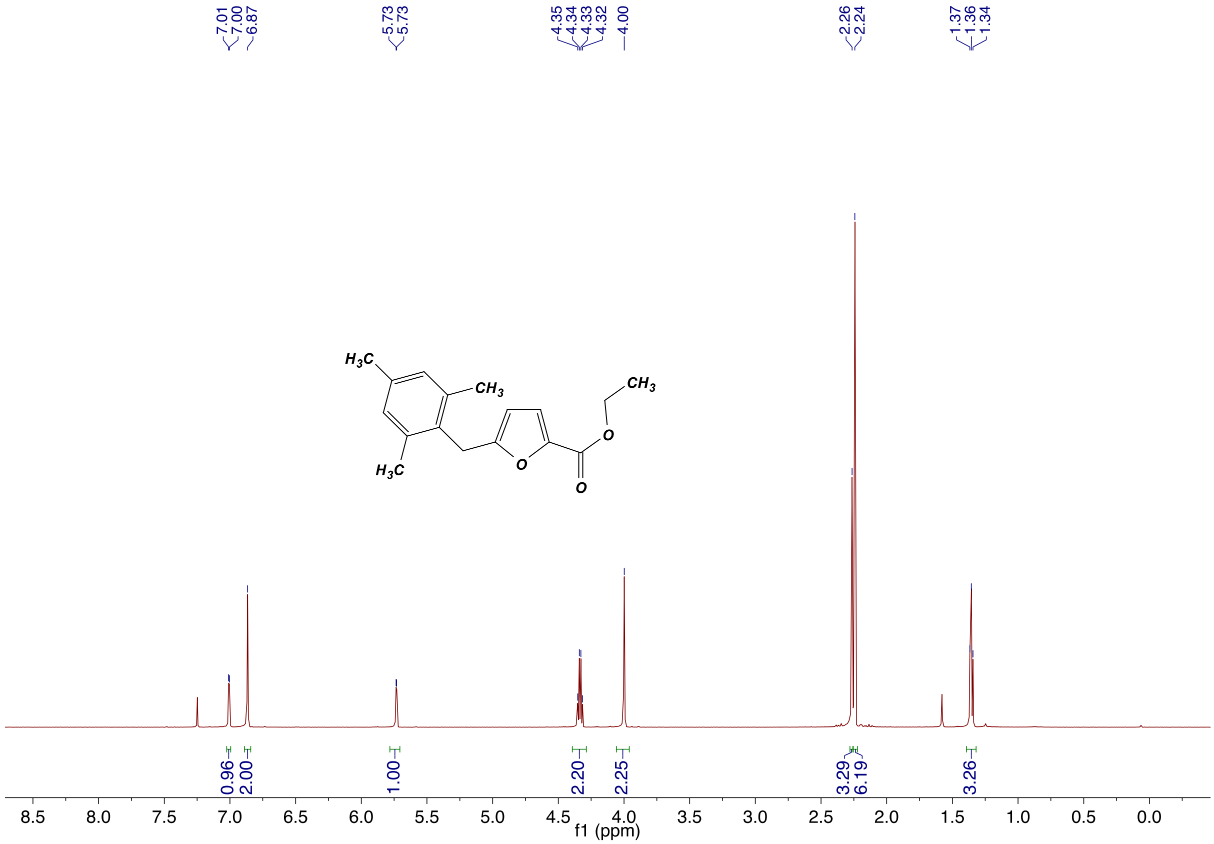

**Figure S10.** $^1$H NMR spectrum of ethyl 5-(2,4,6-trimethylbenzyl)furan-2-carboxylate **9** in $CDCl_3$

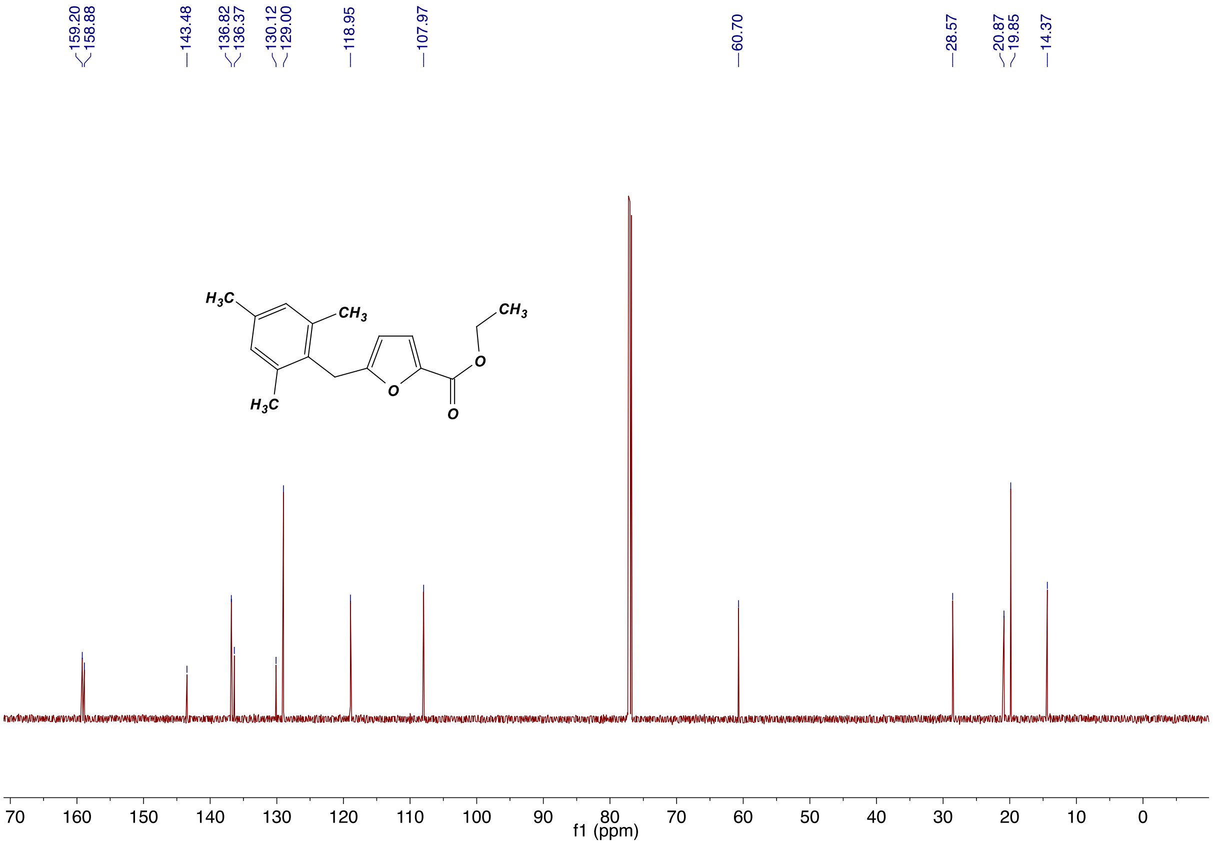

**Figure S11.** $^{13}C$ NMR spectrum of ethyl 5-(2,4,6-trimethylbenzyl)furan-2-carboxylate **9** in $CDCl_3$

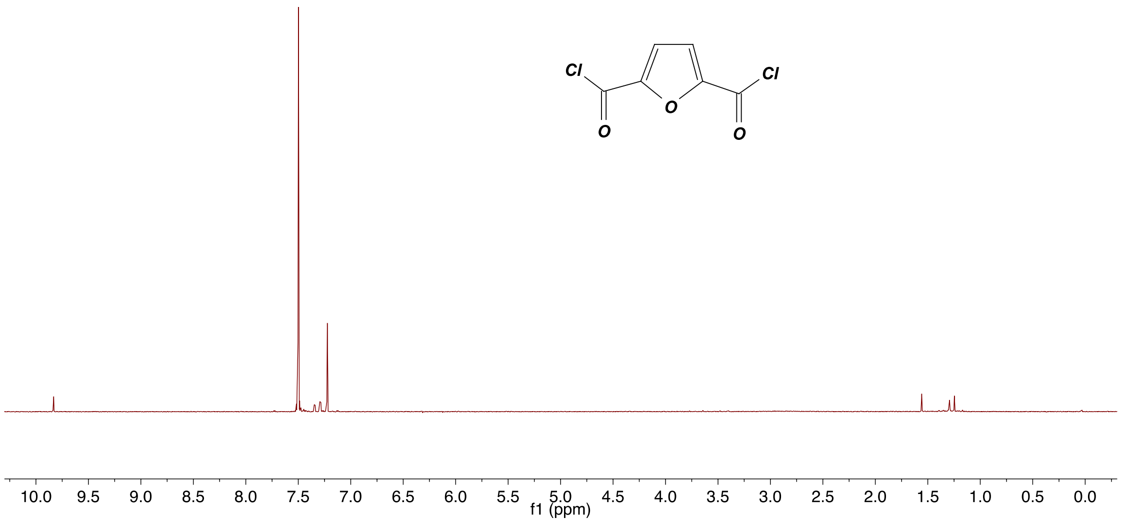

**Figure S12.** $^1$H NMR spectrum of crude FDCC **11** in $CDCl_3$

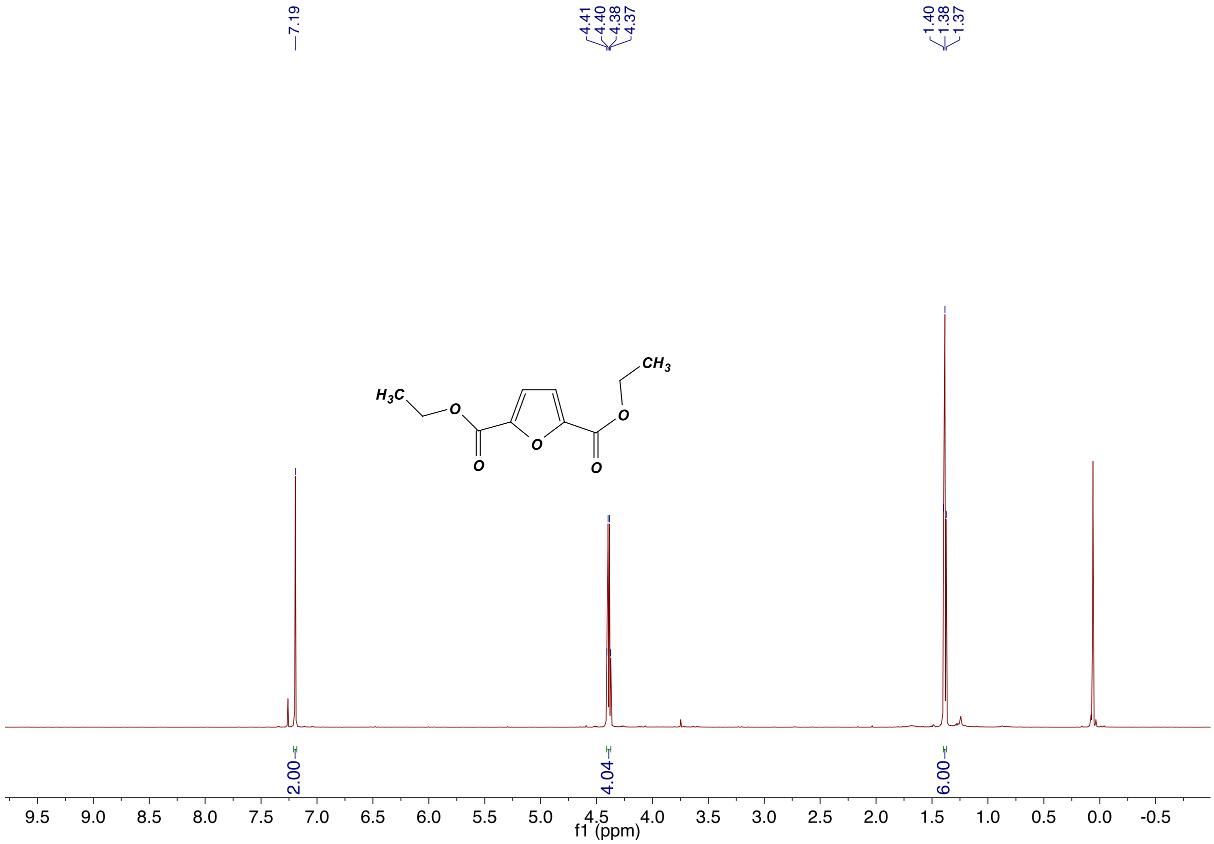

**Figure S13.** $^1$H NMR spectrum of diethyl furan-2,5-dicarboxylate **12** in $CDCl_3$-TMS

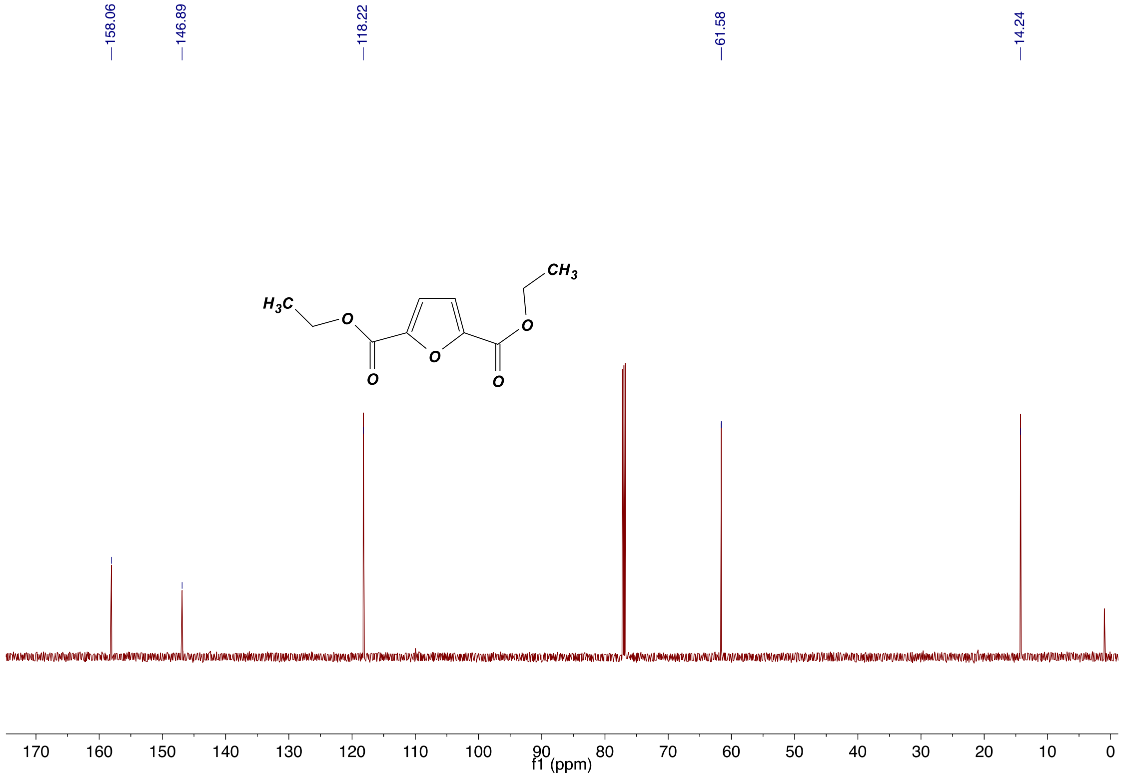

**Figure S14.** $^{13}$C NMR spectrum of diethyl furan-2,5-dicarboxylate **12** in $CDCl_3$-TMS

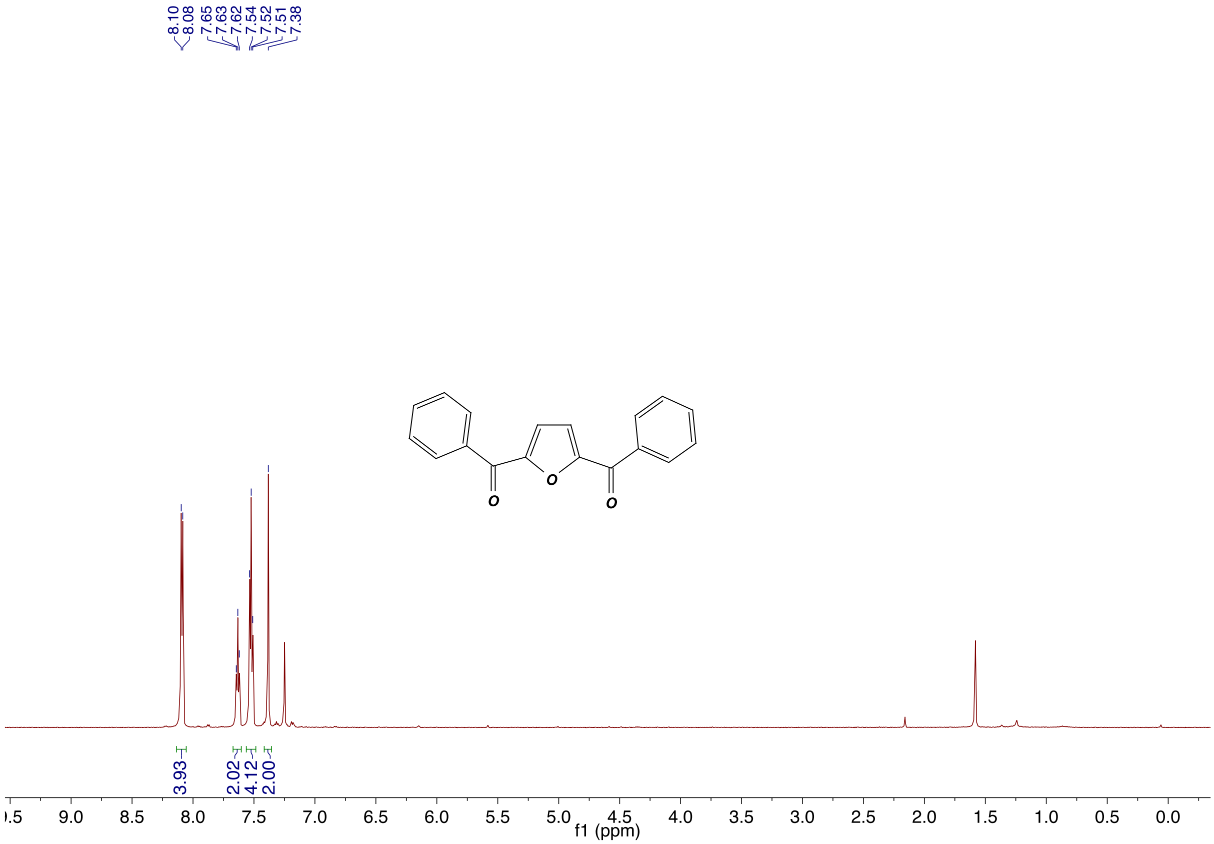

**Figure S15.** $^1$H NMR spectrum of furan-2,5-diylbis(phenylmethanone) **13** in $CDCl_3$

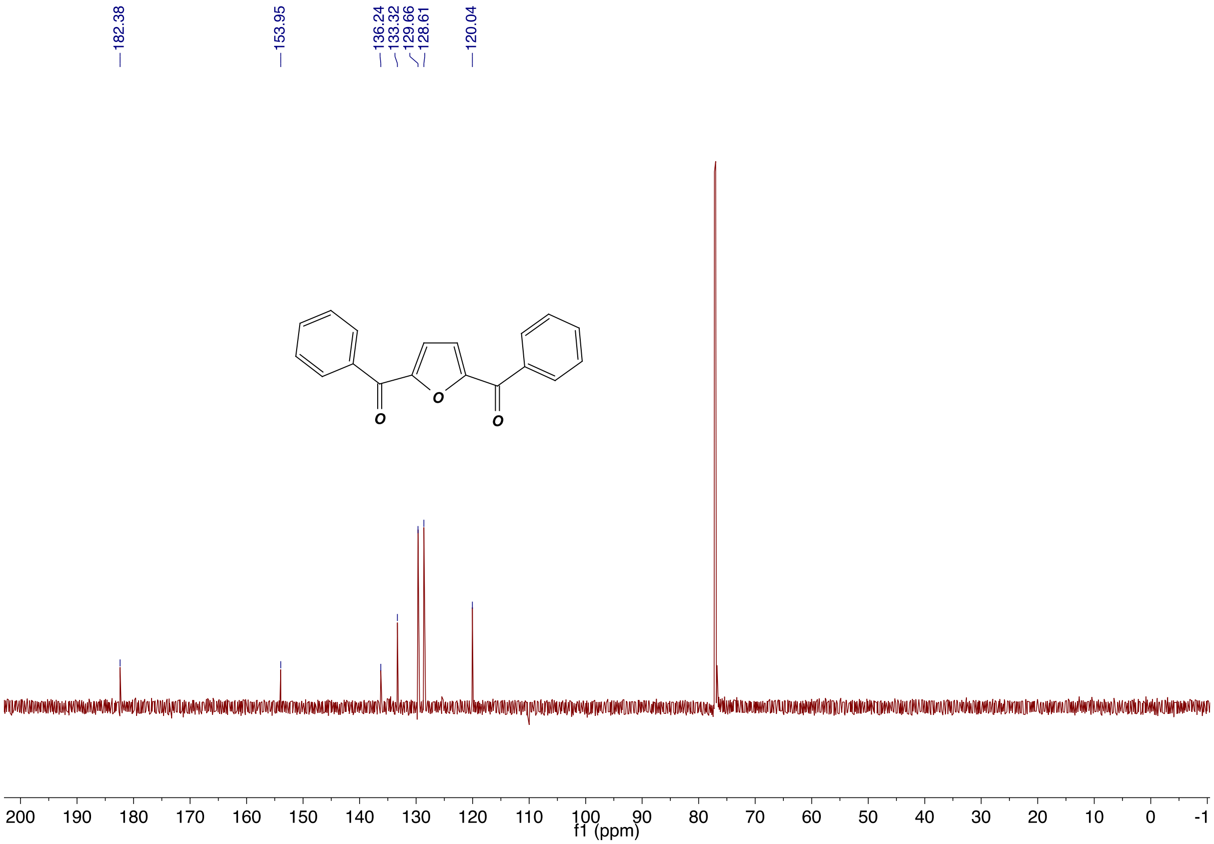

**Figure S16.** $^{13}$C NMR spectrum of furan-2,5-diylbis(phenylmethanone) **13** in $CDCl_3$

## 4. References

1. M. J. Mintz, C. Walling, *Org. Synth.* **1969**, *49*, 9.

2. H. H. Szmant, D. D. Chundury, *J. Chem. Technol. Biotechnol.* **1981**, *31*, 205.

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