

Supporting Information

Sustainable Bio-based Furan Epoxy Resin with Flame

Retardancy

Jingjing Meng, Yushun Zeng, Guiqin Zhu, Jie Zhang, Pengfei Chen, Cheng Yao, Zheng Fang, and
Kai Guo*

Furan-2, 5-diyl dimethanol (**2**, FDM) synthesis

To a 250 mL Erlenmeyer flask, 5-hydroxymethylfurfural (50.4 g, 400 mmol) was added in portions to deionized water (100 mL), and then the mixture was chilled on an ice bath. Sodium borohydride (16 g, 423 mmol) was carefully added to the open flask in a well-ventilated fume hood as it was stirred magnetically. The reaction mixture was stirred on ice for 1 h then allowed to react at room temperature overnight. The reaction was added sodium chloride and extracted with ethyl acetate at 0°C several times until no product in the aqueous phase are available. The organic mixture are then dried (Na_2SO_4). The white crystalline solid (49.6g, 97%yield) was directly used in next step without further purification.

2, 5-Bis((oxiran-2-ylmethoxy)methyl)furan synthesis (**3**, BOF)

Epichlorohydrin(EPC) (25.9 g, 280 mmol), 50% w/w aqueous NaOH (9.6 g, 240 mmol), and tetrabutylammonium bromide (0.644 g, 2 mmol) were added to a three-necked round-bottomed flask (250 mL), mixed at 25°C and stirred vigorously for 30 min. Furan-2,5-diyl dimethanol(2.56 g, 20 mmol) in THF (20 mL) was added dropwise into the flask, the system was subsequently stirred at 50°C. When the FDM was complete (for 6 h), the mixture was concentrated to remove THF and recovered the remained EPC. The reaction was extracted with ethyl acetate (40 mL) three times and dried with MgSO_4 . The slightly yellow liquid was purified by silica gel column chromatography (PE/EA= 4/1~1/1) to yield the colorless liquid 3.61g in 75% yield.

ii) Synthesis of 5, 5'-(oxybis(methylene))bis(2-((oxiran-2-ylmethoxy)methyl)furan) (OmbFdE)

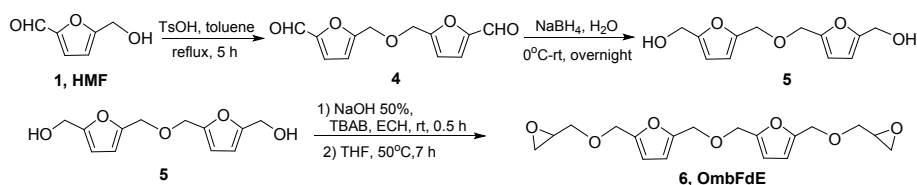


Fig. 2 Route for OmbFdE synthesis

5, 5'-(Oxybis(methylene))bis(furan-2-carbaldehyde) synthesis (**4**)

Commercial 5-hydroxymethylfurfural (50 g, 395 mmol) dissolved in 200 mL toluene was charged into a three-necked round-bottomed flask equipped with a water Dean-Stark trap. *p*-Toluenesulfonic acid monohydrate (4.5 g, 25 mmol) was also added. The mixture was then refluxed at 110°C for 5 h. Thin layer chromatography (TLC) was employed to indicate the reaction process. The reaction was extracted with DCM three times after washing with saturated bicarbonate solution. The solvent-free mixture was then isolated by column chromatography using a gradient (PE/EA=100/1~2/1). The combined, concentrated by rotary evaporation under reduced pressure, and recrystallized from 2-propanol to furnish crystalline solid 28.1 g, in 60 %.

((Oxybis(methylene))bis(furan-5,2-diyl))dimethanol (**5**) synthesis

To a 250 mL Erlenmeyer flask, **4** (14 g, 60 mmol) was added in portions to deionized water (40 mL), and then the mixture was chilled on an ice bath. Sodium borohydride (2.28 g, 60 mmol) was carefully added to the open flask in a well-ventilated fume hood as it was stirred magnetically. The reaction mixture was stirred on ice for 1 h, then it was allowed to react at room temperature overnight. The reaction was added sodium chloride and extracted with ethyl acetate at 0°C several times until no product in the aqueous phase are available. The organic mixture are then dried (Na_2SO_4). The white crystalline solid (13.7 g) in 98% yield was directly used in following step without further purification.

5, 5'-(Oxybis(methylene))bis(2-((oxiran-2-ylmethoxy)methyl)furan) (**6**, OmbFdE) synthesis

Epichlorohydrin (EPC) (26 g, 280 mmol), 50% w/w aqueous NaOH (9.6 g, 240 mmol), and tetrabutylammonium bromide (0.64 g, 2 mmol) were mixed vigorously for 30 min in a three-necked round-bottomed flask (250 mL) at 25°C. ((Oxybis(methylene))bis(furan-5,2-diyl)) dimethanol (4.76 g, 20 mmol) in THF (20 mL) was added dropwise into the flask, and the system was subsequently stirred at 50 °C for 7 h. When the

furan stock was complete, the mixture was concentrated to remove THF and remained EPC. The reaction was extracted with EA (30 mL) three times and dried with MgSO₄. The slightly yellow liquid was purified by silica gel column chromatography (PE/EA= 4/1~1/1) to yield the yellowish liquid (5.11 g) in 73% yield.

General procedure for the synthesis of cured epoxy resins

To obtain cured resin samples with optimal structure and performance, the molar ratio of epoxy group to NH was kept at the ratio of 1:1. The following processes were carried out in nitrogen atmosphere.

The epoxy-amine resins were blended with an equivalent molar ratio of functional groups at room temperature, wherein the light viscosity property allowed a mixing processes and degasification. After 30 min, the homogeneous clear liquid was then carefully poured into a polytetrafluoroethylene (PTFE) mold, and put it into vacuum oven. In order to remove any trapped air, the mixture was degassed at room temperature approximately 3*5 min. Remarkably, the epoxy-amine mixtures appear clear and homogeneous. Then the fully miscible mixture was cured at 50°C for 2 h, and post-cured at 70 °C for an additional 2 h (curing time and temperature optimization, seeing Table 1). Subsequently, the ejection of the casting from the mold after the mold was naturally cooled to room temperature to obtain cured epoxy resin. All samples were cured at the same conditions to achieve fully cured epoxy resins.

Table 1. curing time and temperature optimization ^a			A ₈₆₀ / A ₁₃₅₀					
Entry	diamine	epoxy	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Average value
1	DEGA	OmbFdE	0.118	0.099	0.083	0.082	0.073	0.091
2		BOF	0.244	0.225	0.217	0.194	0.168	0.209
3	TEGA	OmbFdE	0.083	0.082	0.0828	0.079	0.058	0.077
4		BOF	0.36	0.293	0.264	0.254	0.191	0.272
5	TGDE	OmbFdE	0.106	0.086	0.085	0.068	0.056	0.08
6		BOF	0.255	0.233	0.213	0.2	0.143	0.209

^a. Curing condition: for sample 1: 50 °C, 1 h; sample 2: 50 °C, 2 h; sample 3: 50 °C, 2 h, then 70 °C, 1 h; sample 4: 50 °C, 2 h; then 70 °C, 2 h; sample 5: 50 °C, 2 h; then 70 °C, 3 h.

Differentiation analysis of TGA curves of monomers

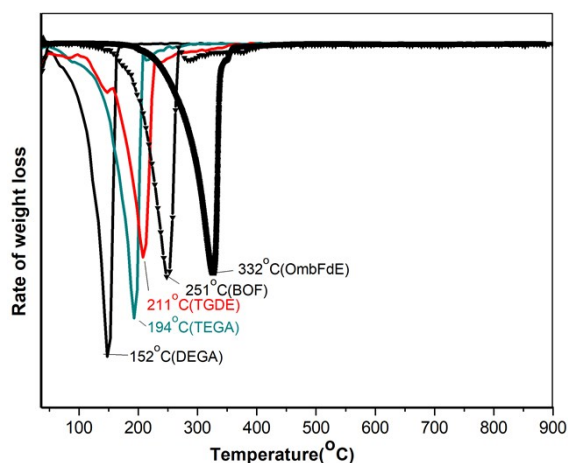


Fig. 3 DTGA curves of monomers

In order to investigate the stability of different monomers used in these new epoxy resin polymers, TGA were employed in the temperature ranging from 25°C to 900°C under N₂. Three aliphatic curing reagents, i.e. DEGA TEGA TGDE were evaluated herein. Besides, the epoxy monomer, such as BOF, OmbFdE were determined under the same conditions. The DTG curves are shown in Fig. 3.

Characterization data of products

furan-2, 5-diyl dimethanol (**2**, FDM) ¹

¹H NMR (400 MHz, DMSO-d₆) δ 6.19 (s, 2H), 4.35 (s, 4H), 3.50 (br, 2H).

2, 5-bis((oxiran-2-ylmethoxy)methyl)furan (**3**, BOF) ¹

¹H NMR (400 MHz, CDCl₃) δ 6.30 (s, 2H), 4.51 (q, *J* = 12.8 Hz, 4H), 3.77 (dd, *J* = 11.5, 3.0 Hz, 2H), 3.43 (dd, *J* = 11.5, 5.9 Hz, 2H), 3.16 (ddt, *J* = 5.9, 4.1, 2.9 Hz, 2H), 2.85-2.76 (m, 2H), 2.61 (dd, *J* = 5.0, 2.7 Hz, 2H).

5, 5'-(oxybis(methylene))bis(furan-2-carbaldehyde) (**4**) ¹

¹H NMR (400 MHz, DMSO-d₆) δ 9.51 (s, 2H), 7.44 (d, *J* = 3.5 Hz, 2H), 6.69 (d, *J* = 3.5 Hz, 2H), 4.56 (s, 4H).

¹³C NMR (100 MHz, DMSO-d₆) δ 178.88, 157.72, 152.79, 124.28, 112.80, 64.15.

((oxybis(methylene))bis(furan-5,2-diyl))dimethanol (**5**)²

¹H NMR (500 MHz, CDCl₃) δ 6.27 (d, *J* = 3.0 Hz, 1H), 6.23 (d, *J* = 3.0 Hz, 1H), 4.56 (s, 2H), 4.47 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 153.56, 150.32, 109.45, 107.37, 62.83, 56.45.

5, 5'-(oxybis(methylene))bis(2-((oxiran-2-ylmethoxy)methyl)furan) (**6**, OmbFdE)

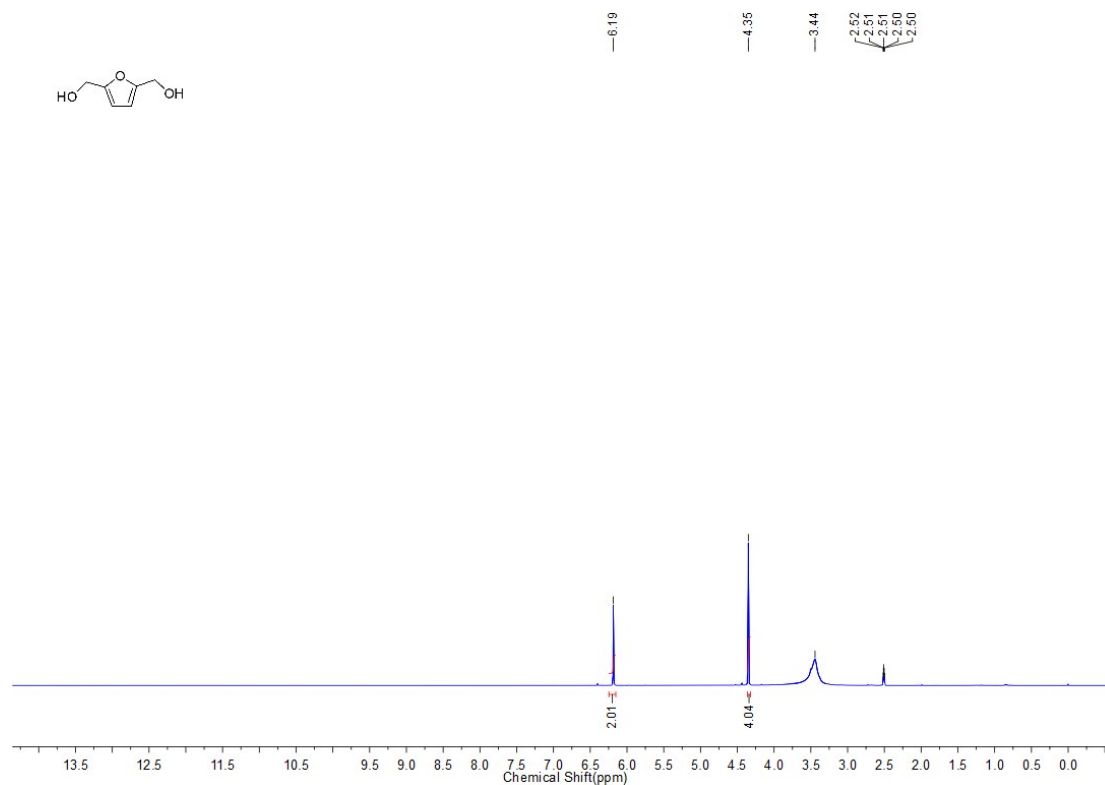
¹H NMR (400 MHz, CDCl₃) δ 6.29 (s, 4H), 4.52 (t, *J* = 11.2 Hz, 4H), 4.46 (s, 4H), 3.77 (dd, *J* = 11.5, 3.0 Hz, 2H), 3.43 (dd, *J* = 11.5, 5.9 Hz, 2H), 3.16 (ddt, *J* = 5.9, 4.1, 2.9 Hz, 2H), 2.79 (t, *J* = 4.6 Hz, 2H), 2.61 (dd, *J* = 5.0, 2.7 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 151.77, 151.75, 110.46, 110.35, 70.70, 65.16, 63.74, 50.72, 44.30.

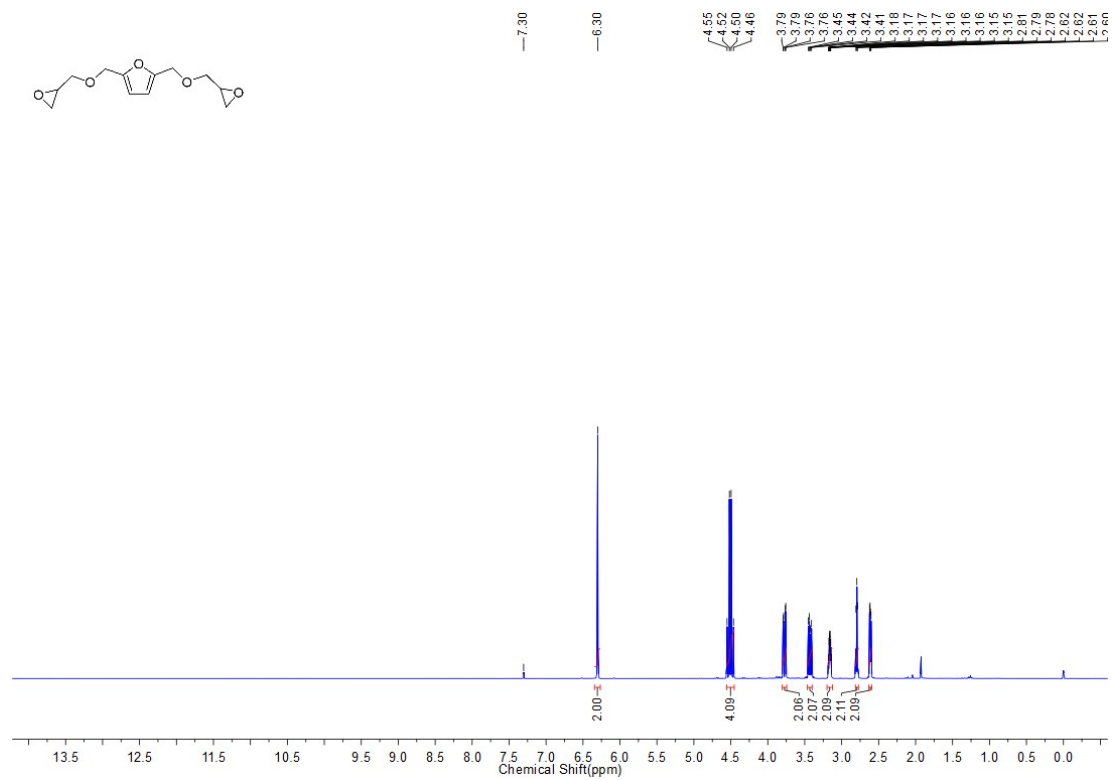
HRMS-ESI⁺ (*m/z*): C₁₈H₂₂O₇Na [M+Na]⁺ calcd for 373.1258, found 373.1254.

Copy of NMR spectra

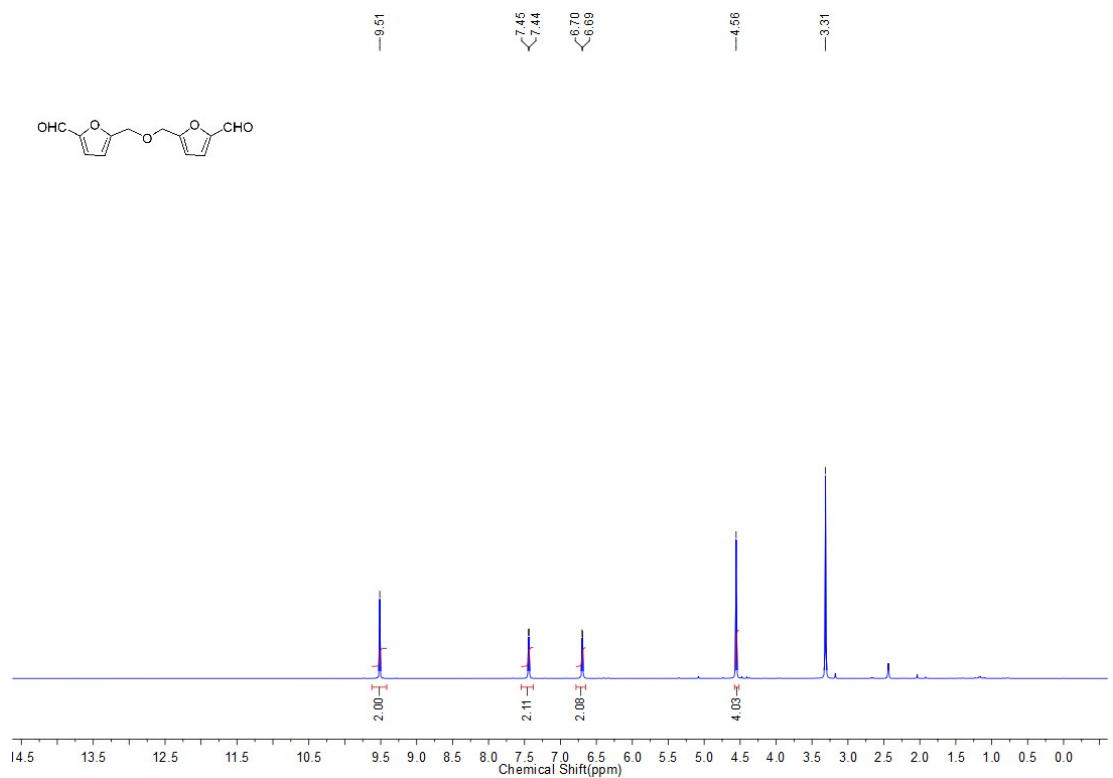
furan-2, 5-diyl dimethanol (**2**, FDM)

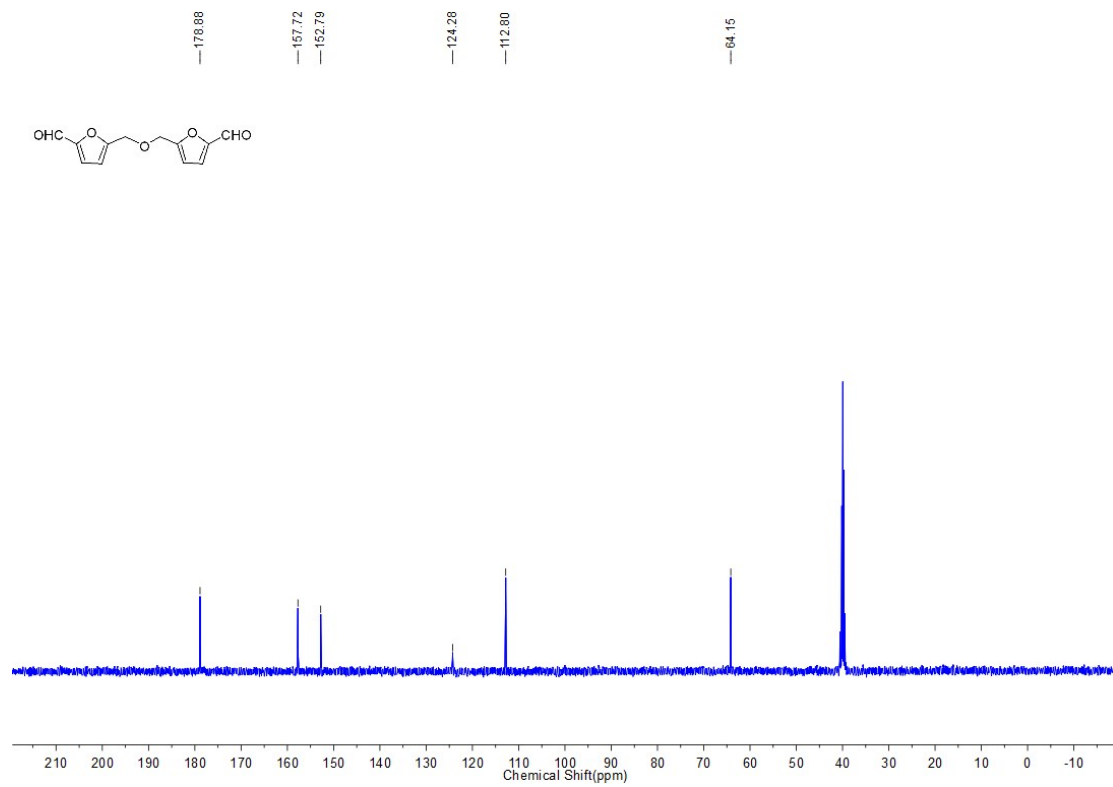


2, 5-bis((oxiran-2-ylmethoxy)methyl)furan (**3**, BOF)

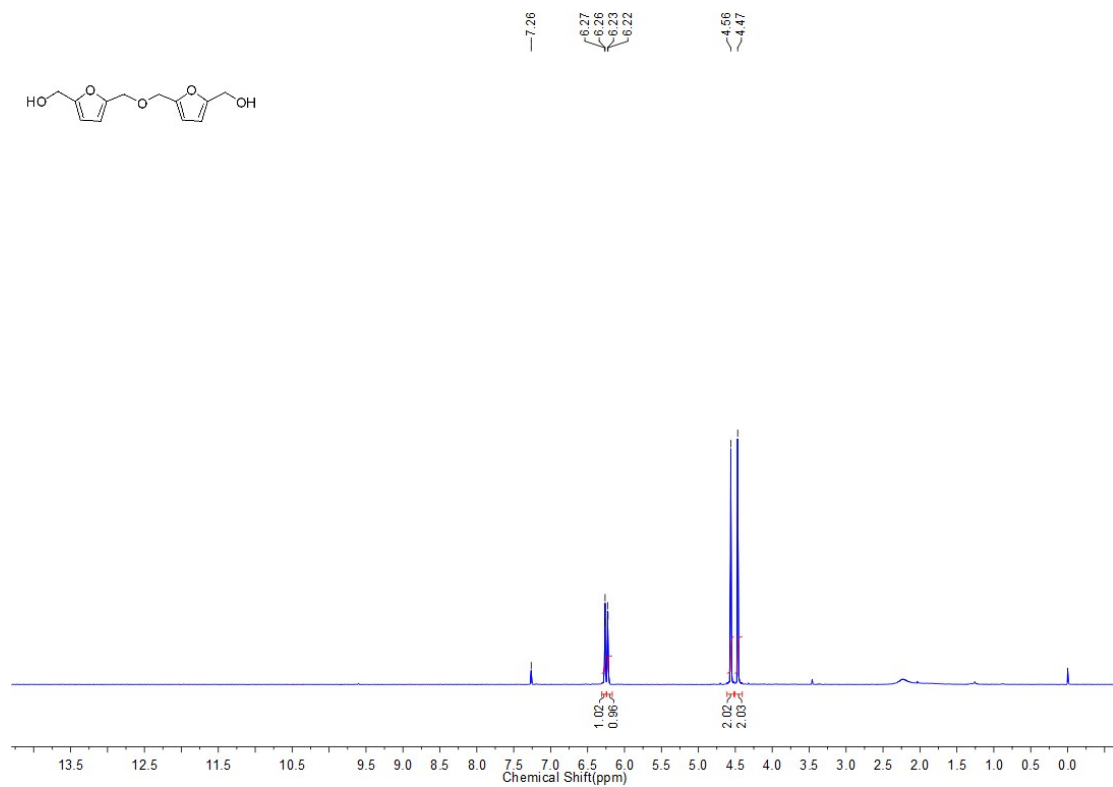


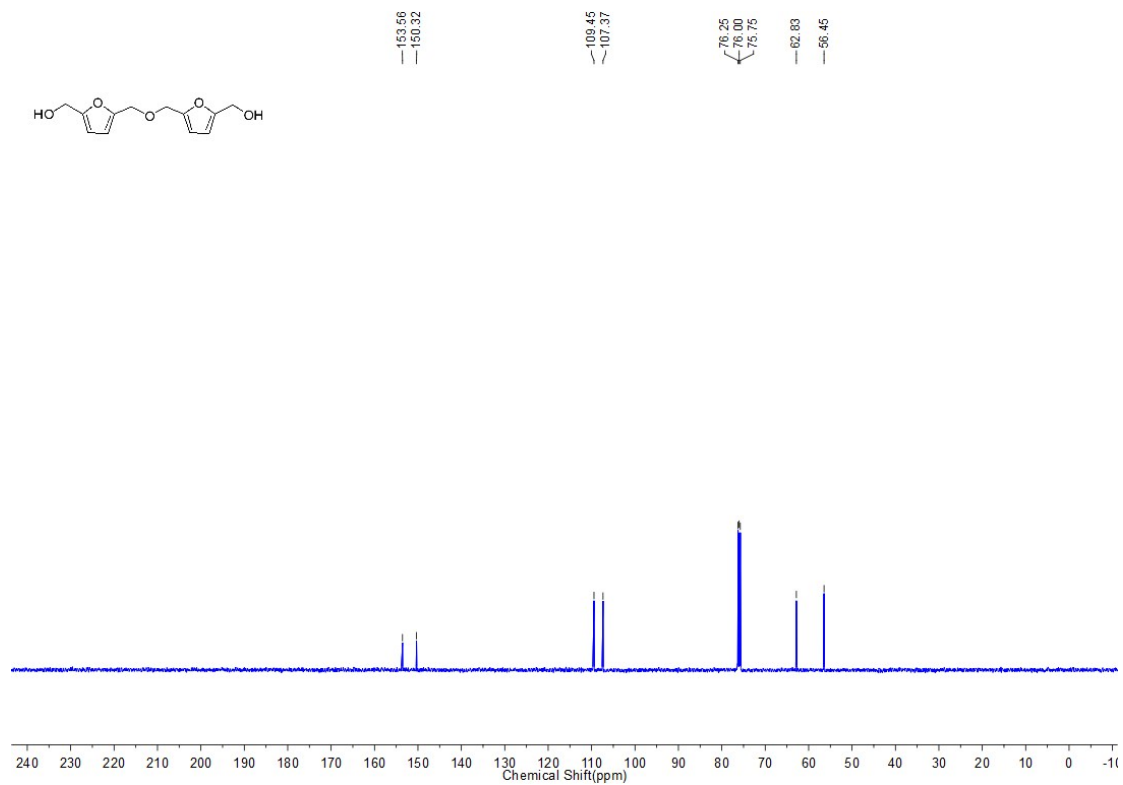
5, 5'-(oxybis(methylene))bis(furan-2-carbaldehyde) (4)



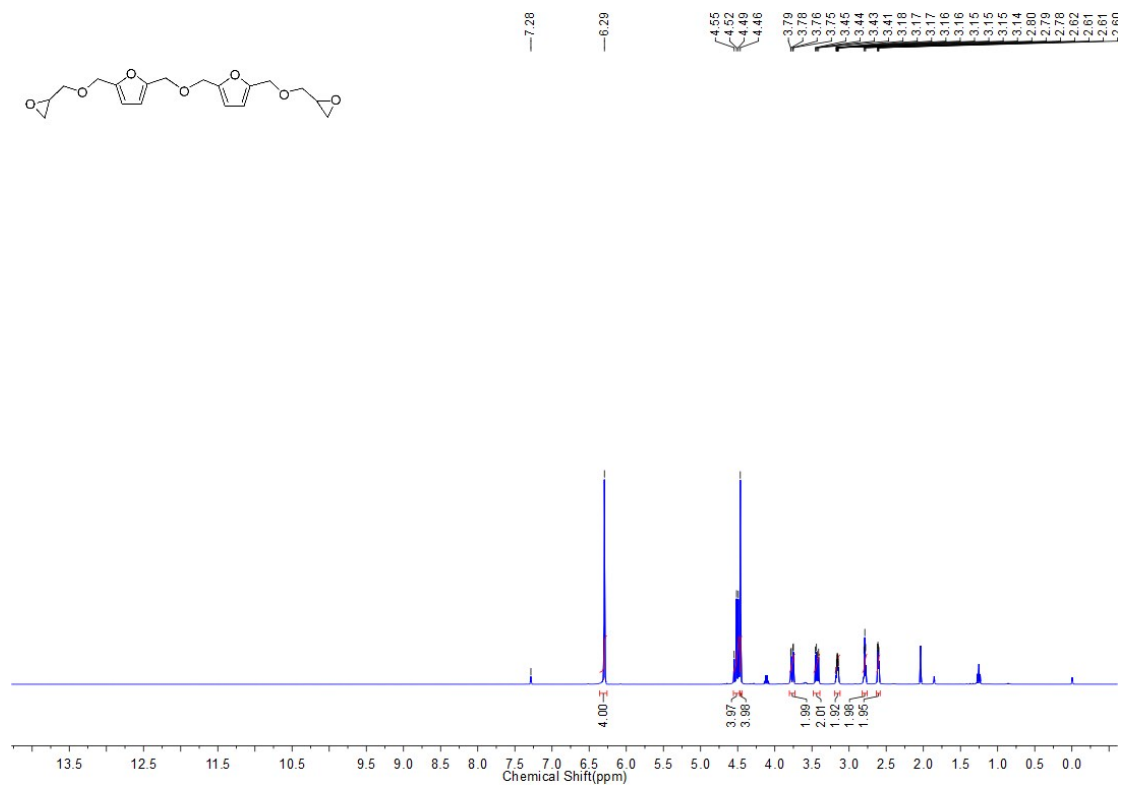


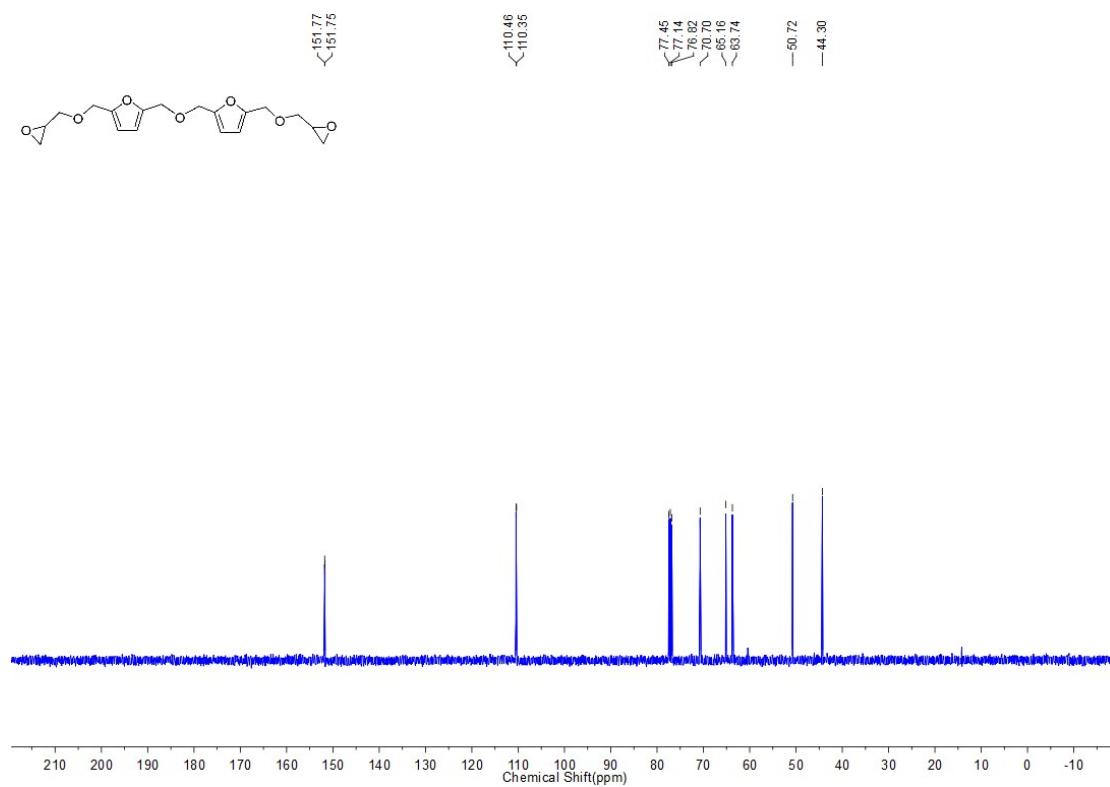
((oxymethylene)bis(furan-5,2-diyl))dimethanol (5)





5, 5'-(oxybis(methylene))bis(2-((oxiran-2-ylmethoxy)methyl)furan) (6, OmbFdE)





References:

1. S. Vijjamarri, S. Streed, E. M. Serum, M. P. Sibi and G. Du, *ACS Sustain. Chem. Eng.* 2018, **6**, 2491-2497.
2. P. Sibi, S. Sermadurai, N. Zimmermann, E. Serum, G. Ma, R. Moorthy and K. Kalliokoski, WO,2016, 2016022943.