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[Supporting Information]

Covalent organic frameworks: efficient, metal-free, heterogeneous organocatalysts for chemical fixation of CO_2 under mild conditions

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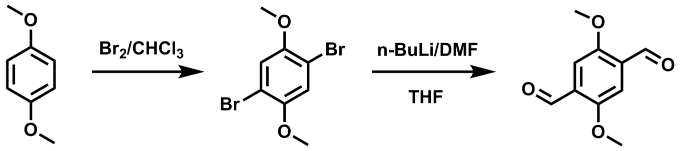
1. Materials and Synthesis

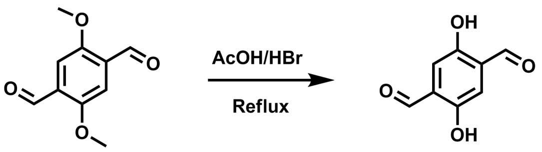
Materials. The 1,4-Dimethoxybenzene, bromine, 4-aminobenzonitrile were obtained from Sinopharm Chemical Reagent. Trifluoromethanesulfonic acid and n-Butyllithium solution in hexanes (1.6 M) were obtained from J&K Scientific. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aladdin.

Synthesis of 2,5-Dimethoxybenzene-1,4-dicarboxaldehyde[1]



To a mixture of a commercial reagent 1,4-dimethoxybenzene (5.0 g, 36.2 mmol) in $CHCl_3$ (25 mL) was added a solution of bromine (14.6 g, 91.75 mmol) in $CHCl_3$ (25 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with $CHCl_3$ and washed successively with sat. $NaHSO_3$ aq., 1 mol/L NaOH aq., and water. The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and dried under reduced pressure to give 1,4-dibromo-2,5-dimethoxybenzene (10.4 g, 35.0 mmol) in 93.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 2H, Ph-*H*), 3.84 (s, 6H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 117.2, 110.6, 57.1 ppm. Under argon, to a solution of 1,4-dibromo-2,5-dimethoxybenzene (3.0 g, 10.0 mmol) in THF (50 mL) was added n-BuLi (14 mL, 1.6 mol L^{-1}, 22.0 mmol) at -78 °C, and the resulting mixture was stirred at that temperature for 2 h. Then, anhydrous DMF (2.0 mL, 25 mmol) was added to the solution and the mixture was gradually warmed up to room temperature. After the mixture was stirred further at room temperature for 3 h, 3.0 mol/L HCl aq. (15 mL) was added to precipitate the product, which was isolated by filtration and dried under reduced pressure to give 2,5-dimethoxyterephthalaldehyde (0.56 g, 2.88 mmol) in 28.9% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.50 (s, 2H, C*H*O), 7.46 (s, 2H, Ph-*H*), 3.94 (s, 6H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 155.9, 129.3, 111.0 and 56.4 ppm.

Synthesis of 2,5-Dihydroxy-1,4-benzenedicarboxaldehyde[1]



Under argon, to a mixture of 1,4-dimethoxy-terephthaldehyde (0.20 g, 1.05 mmol) in acetic acid (10 mL) was added hydrobromic acid (8.5 mL, 73 mmol), and the resulting mixture was refluxed for 20 h. The reaction mixture was diluted with water and extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and dried under reduced pressure to give a yellow solid (0.115 g, 0.70 mmol) in 65.8% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.30 (s, 2H, O*H*), 10.29 (s, 2H, C*H*O), 7.22 (s, 2H, Ph-*H*) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.4, 154.0, 128.8, 116.3 ppm.

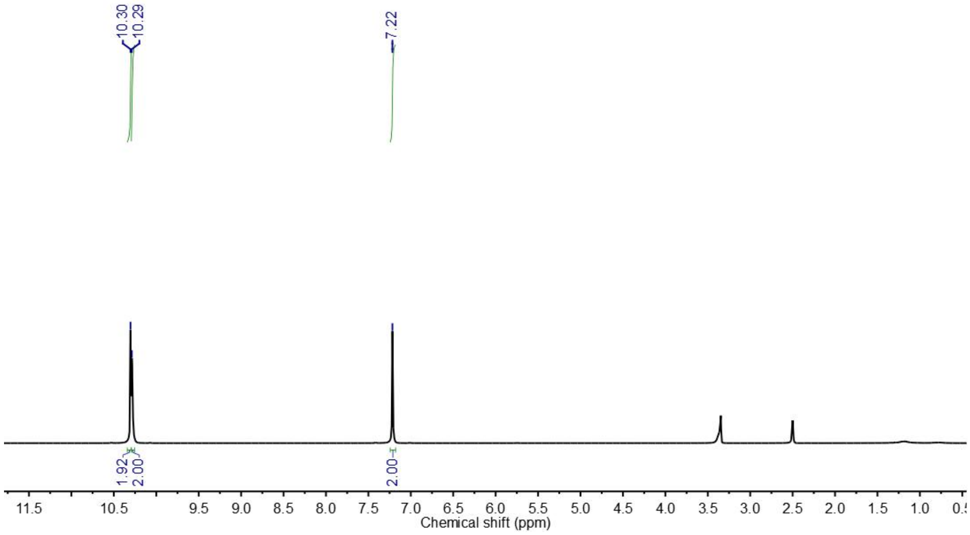


Figure: ^{1}H NMR spectrum of 2,5-Dihydroxy-1,4-benzenedicarboxaldehyde.

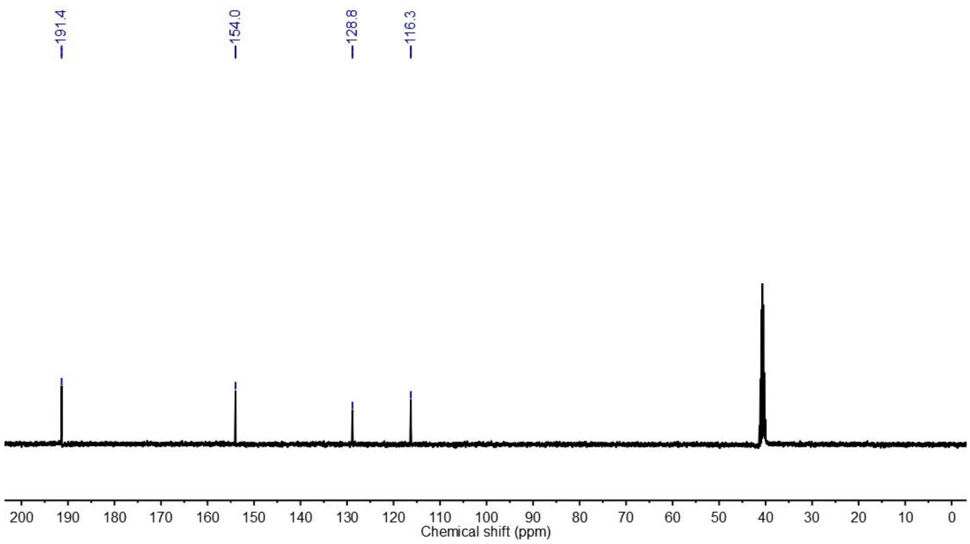
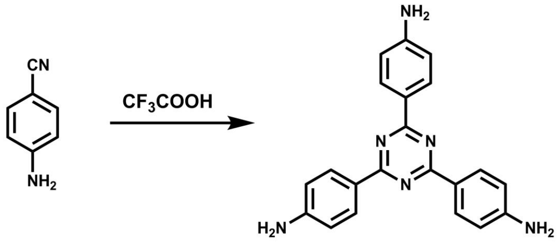


Figure: ^{13}C NMR spectrum of 2,5-Dihydroxy-1,4-benzenedicarboxaldehyde.

Synthesis of 1,3,5-tris-(4-aminophenyl)triazine



The 1,3,5-tris-(4-aminophenyl)triazine was prepared based on the reported procedure with minor modifications.[2] In a typical synthesis, 4-aminobenzonitrile (0.772 g, 6.538 mmol) was taken in a round bottom flask at 0 ºC. Then trifluoromethanesulfonic acid (2.0 mL, 22.2 mmol) was added dropwise for 20 min maintaining the temperature at 0 ºC. The resultant mixture was stirred for 24 h at room temperature in inert atmosphere. After that, distilled water (20 mL) was added to the mixture and it was neutralized by adding 2 M NaOH solution until the pH reaches to 7.0. Initially, with increase in pH, the orange precipitate dissolves to give a bright orange solution, which upon further increase in pH gives a pale yellow precipitate. The resultant pale yellow product was filtered and washed several times with distilled water. Yield: 90.6%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.34 (d, 6H, J = 8.0 Hz, Ph-H), 6.68 (d, 6H, J = 8.0 Hz, Ph-H), 5.90 (s, 6H, NH_2) ppm. ^{13}C NMR (100

MHz, DMSO-d_6): δ 170.7, 154.1, 131.3, 124.1, 114.3 ppm.

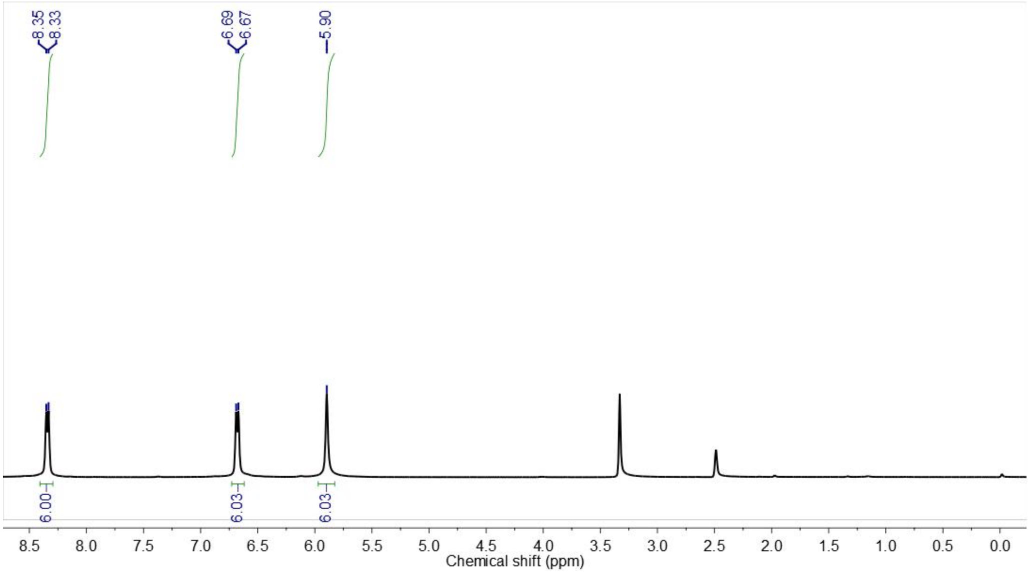


Figure: ^{1}H NMR spectrum of 1,3,5-tris-(4-aminophenyl)triazine.

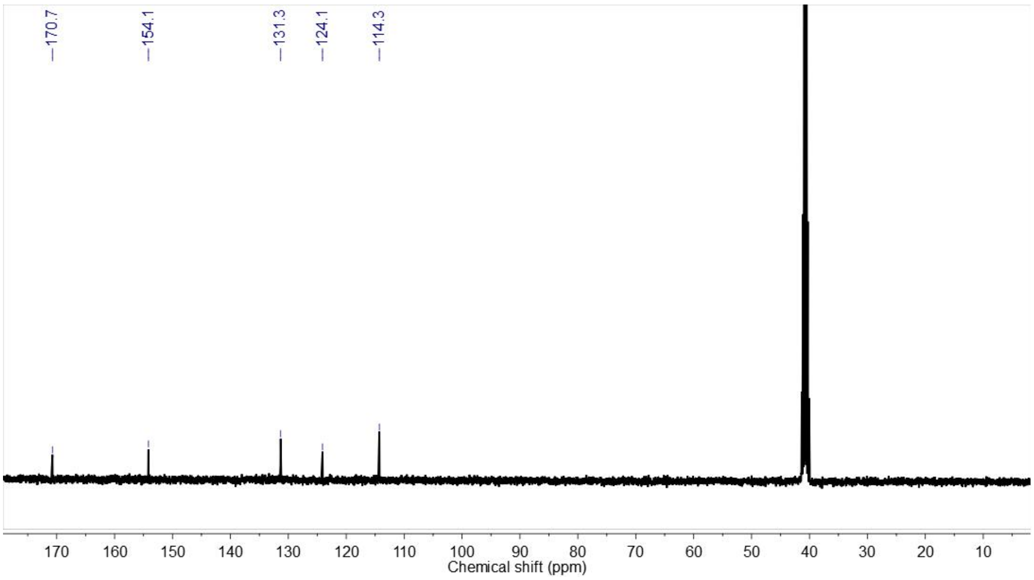
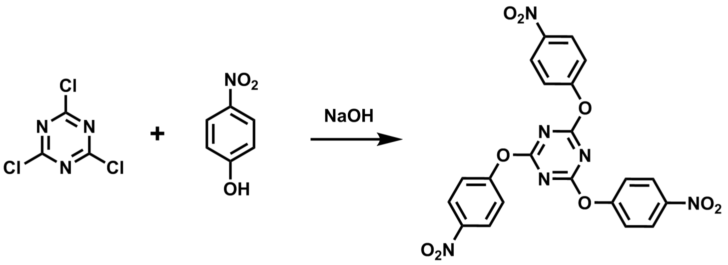


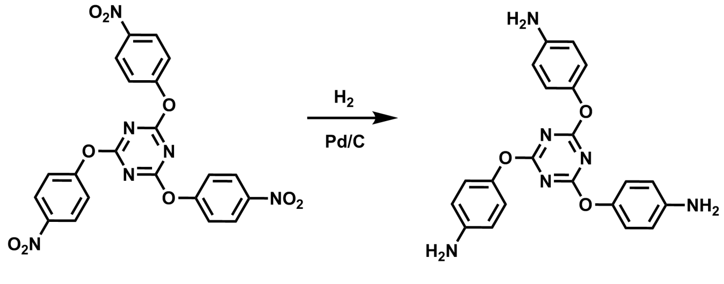
Figure: ^{13}C NMR spectrum of 1,3,5-tris-(4-aminophenyl)triazine.

Synthesis of 2,4,6-tris(4-nitrophenoxy)triazine [3]



This synthesis was adapted from a previous synthetic procedure. To a stirred solution of cyanuric chloride (1.5 g, 8.2 mmol) in acetone (100 mL) was added slowly a solution of *p*-nitrophenol (3.0 g, 25.2 mmol) and NaOH (1.0 g, 25.2 mmol) in water (100 mL) and acetone (20 mL) at 0°C. When the two solutions had been combined the mixture was heated to reflux overnight to give a white crystalline product. The product was collected by filtration and washed with water (3 × 20 mL) and MeOH (3 × 20 mL) before being dried under vacuum to give 2,4,6-tris(4-nitrophenoxy)triazine as a white solid (3.65 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (2H, d, *J* = 9 Hz, Ph-*H*), 7.33 (2H, d, *J* = 9 Hz, Ph-*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.5, 126.5, 144.5, 160.9 ppm.

Synthesis of 1,3,5-Tris(4-aminophenoxy)benzene



To a stirred solution of 2,4,6-tris(4-nitrophenoxy)triazine (1.0 g, 2.0 mmol) in 40 mL EtOAc under inert atmosphere was added slowly Pd/C 10% (0.36 g, 3.4 mmol). Once all Pd/C 10% had been added the mixture was placed under a H_2 atmosphere and stirred at room temperature overnight. The mixture was filtered to remove the Pd/C to give a clear solution. The solvent was removed under reduced pressure to give a residue which was washed with diethyl ether (3×10 mL) to give 2,4,6-tris(4-aminophenoxy)triazine as a white powder (0.51 g, 63%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.30 (2H, d, *J* = 9 Hz, Ph-*H*), 7.33 (2H, d, *J* = 9 Hz, Ph-*H*) ppm; ^{13}C NMR (100MHz, CDCl$_3$): δ 119.5, 126.5, 144.5, 160.9 ppm.

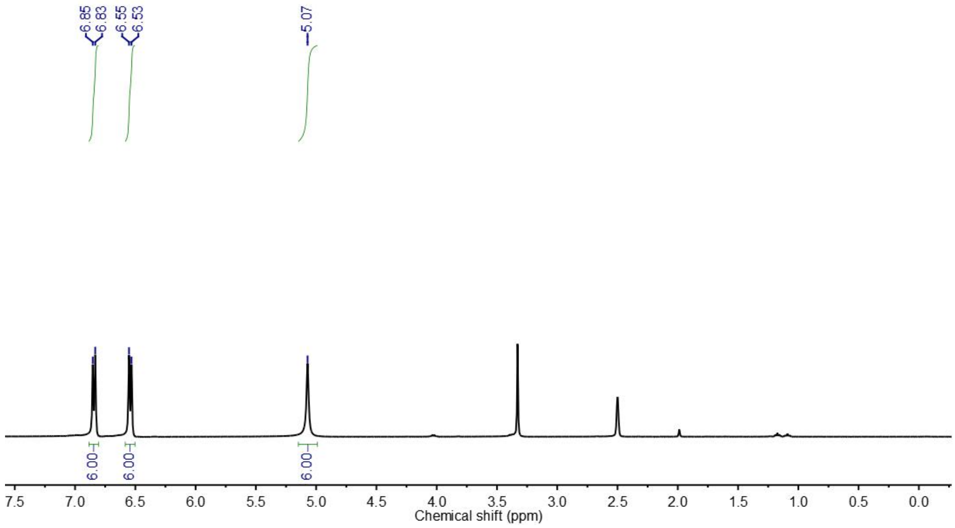


Figure: ^{1}H NMR spectrum of 1,3,5-Tris(4-aminophenoxy)benzene.

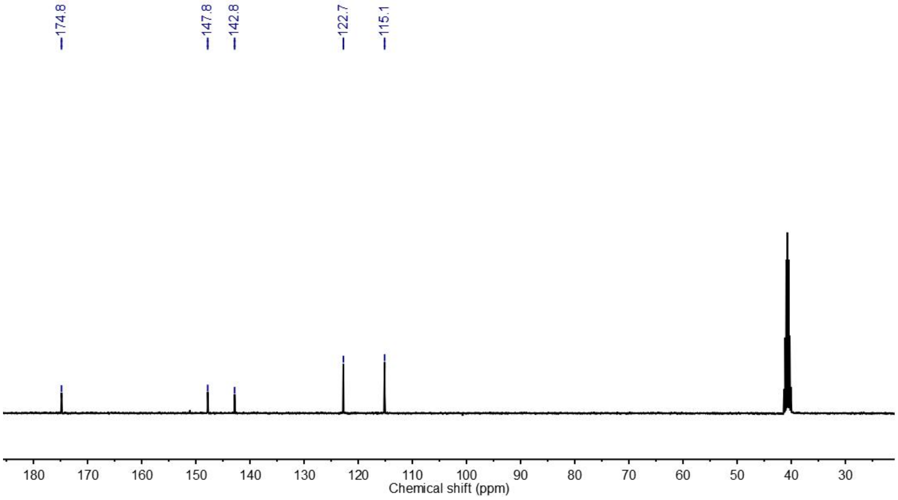
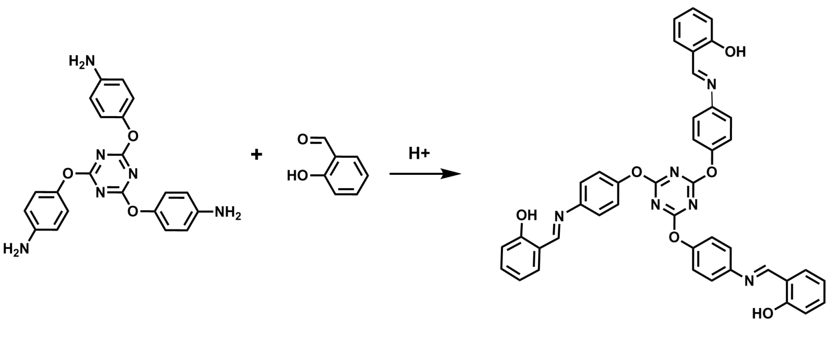


Figure: ^{13}C NMR spectrum of 1,3,5-Tris(4-aminophenoxy)benzene.

Synthesis of Model compound



This compound was synthesized by the reaction between 1,3,5-tris(4-aminophenoxy)benzene (170 mg, 0.42 mmol) and 2-hydroxybenzaldehyde (516 mg, 4.22 mmol) in 20 mL ethanol, 2 mL dioxane and 0.3 mL of aqueous acetic acid mixture under refluxing condition for one day. After that the solution was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol to remove excess 2-hydroxybenzaldehyde, and dried under vacuum to give a light yellow solid (256 mg, 85%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 13.05 (s, 3H, O*H*), 8.57 (s, 3H, C*H*O), 7.34-7.39 (m, 6H, Ph-*H*), 7.29 (d, 6H, *J* = 8 Hz, Ph-*H*), 7.22 (d, 6H, *J* = 8 Hz, Ph-*H*), 7.01 (d, 6H, *J* = 8 Hz, Ph-*H*), 6.91 (t, 6H, *J* = 8 Hz, *J* = 8 Hz, Ph-*H*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 174.0, 163.3, 161.3, 150.4, 146.8, 133.6, 132.7, 122.7, 122.4, 119.5, 119.3, 117.5 ppm

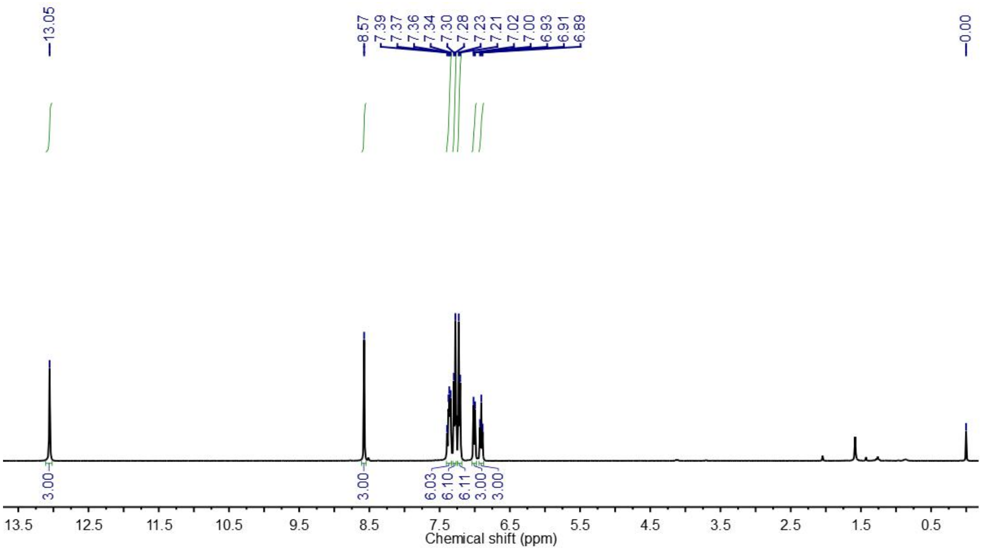


Figure: ^{1}H NMR spectrum of model compound.

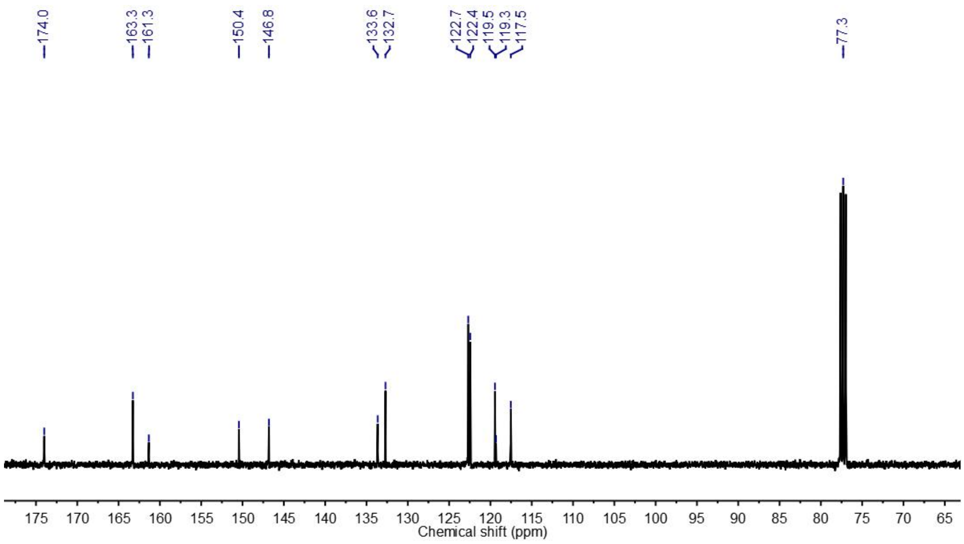


Figure: ^{13}C NMR spectrum of model compound.

2. Elemental Analysis

COFs		C%	H%	N%
COF-JLU6	Calcd.	72.12	3.85	15.29
	Found	71.56	4.02	14.82
COF-JLU7	Calcd.	66.33	3.54	14.06
	Found	65.66	3.72	13.65

Fig. S1. Elemental analysis results of COF-JLU6 and COF-JLU7.

3. Electron Micrographs

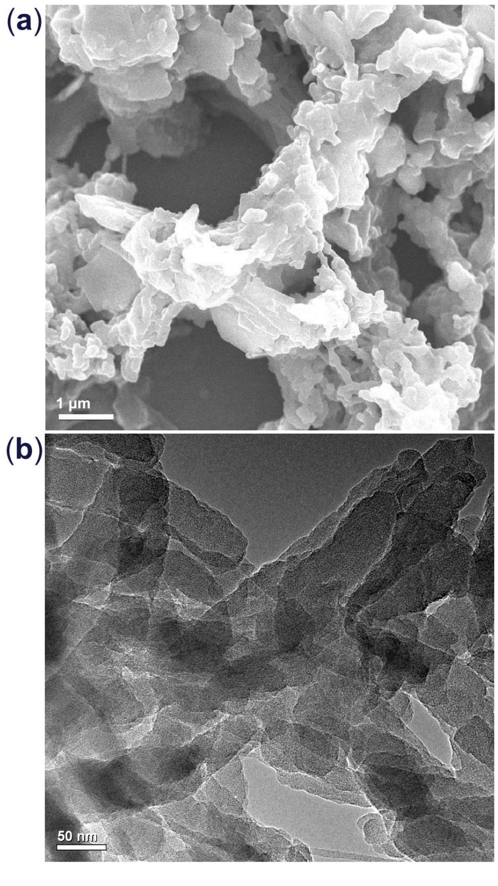


Fig. S2. (a) The FE-SEM image of COF-JLU7, (b) HR-TEM image of COF-JLU7.

4. Thermogravimetric Analysis

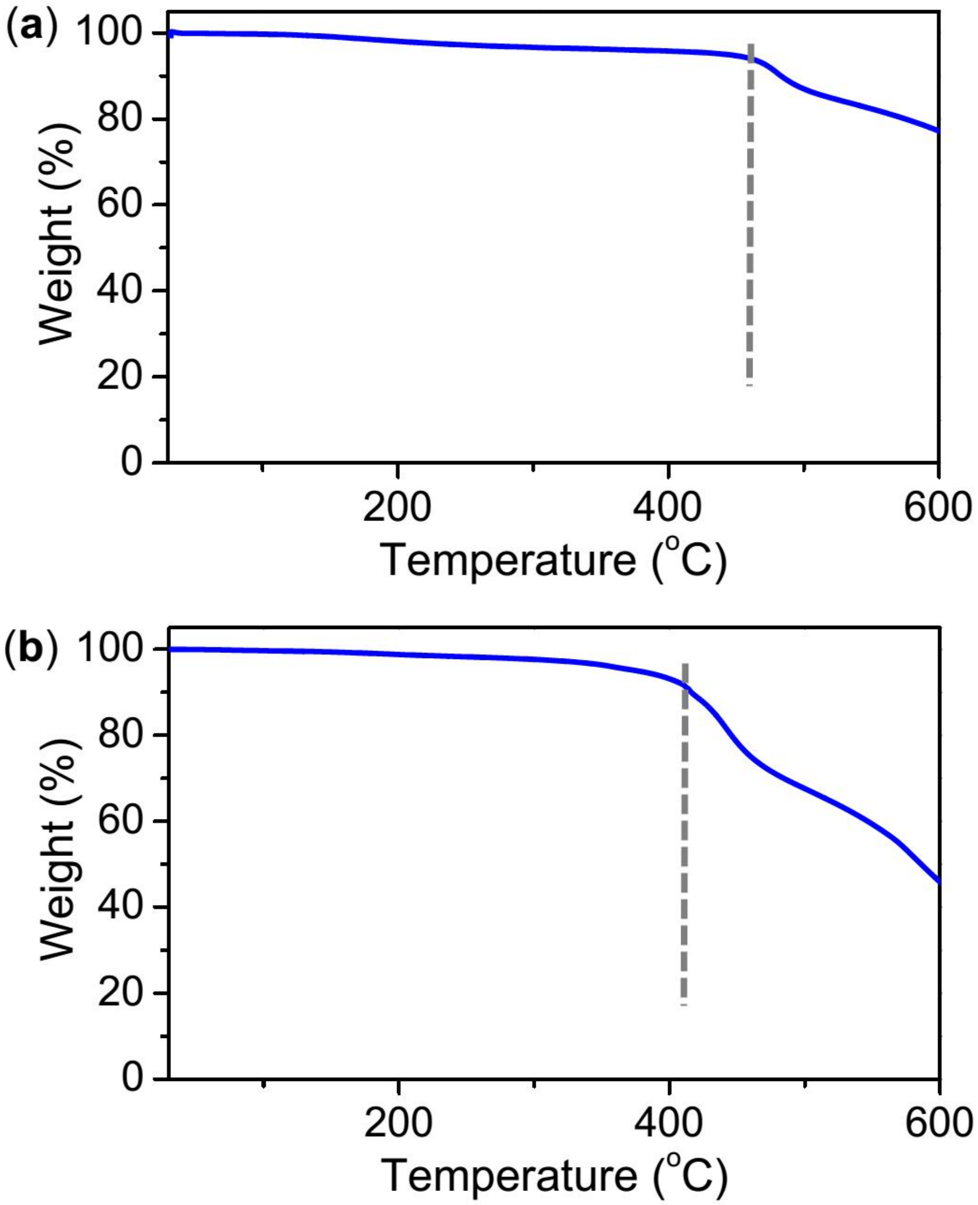


Fig. S3 TGA data of COF-JLU6 (a) and COF-JLU7 (b). TGA analysis indicates that the polymers are thermally stable up to about 460 °C for COF-JLU6 and 405 °C for COF-JLU7, respectively.

5. IR Spectra

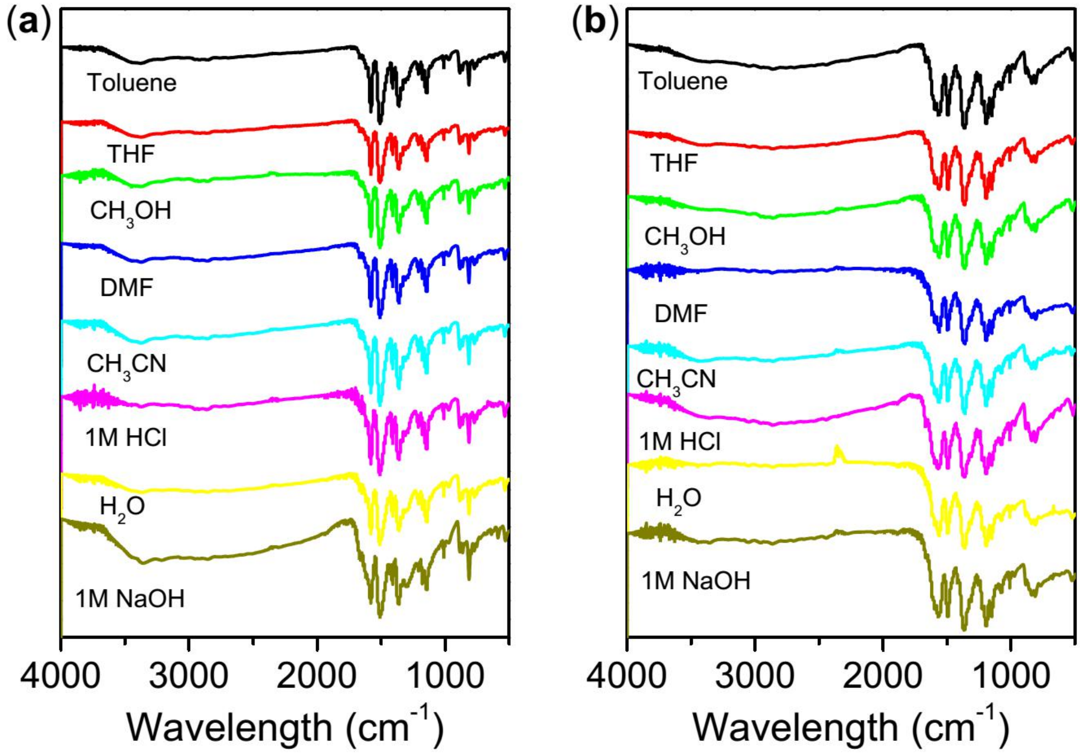


Fig. S4. IR spectra of COF-JLU6 (a) and COF-JLU7 (b) after treatment in different solvents

6. PXRD Spectra

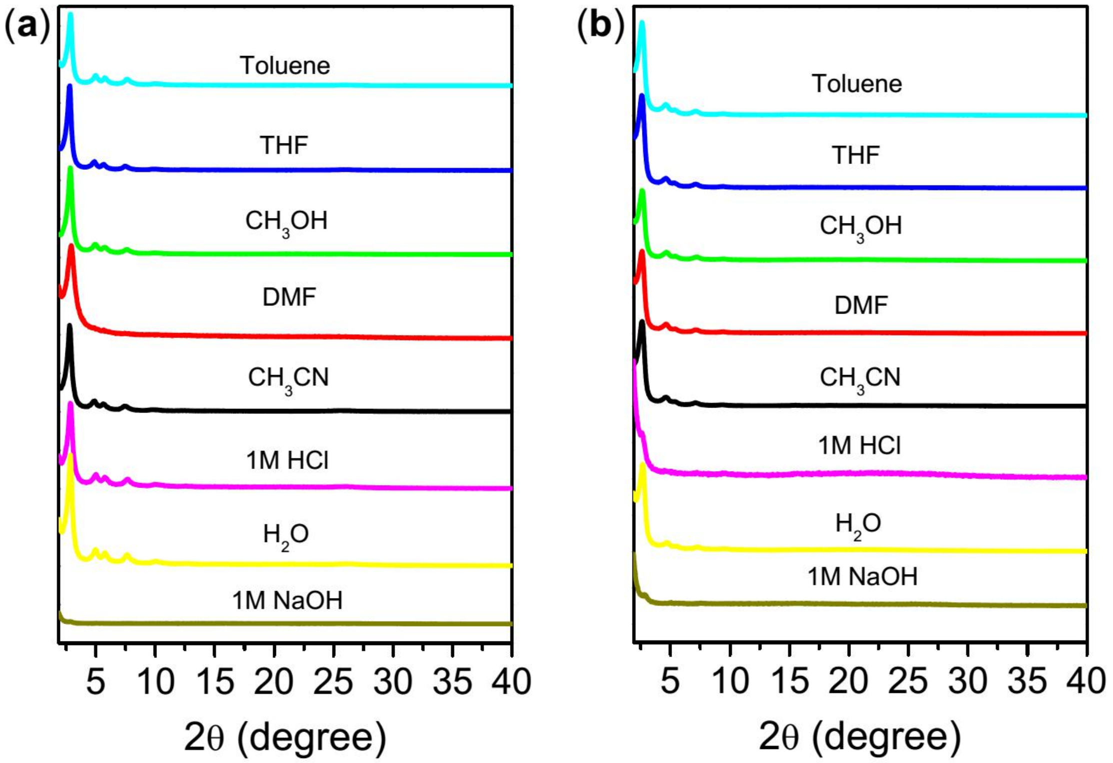


Fig. S5 PXRD curves of COF-JLU6 (a) and COF-JLU7 (b) after treatment in different solvents.

7. CO_2 Adsorption Curves and Q_{st}

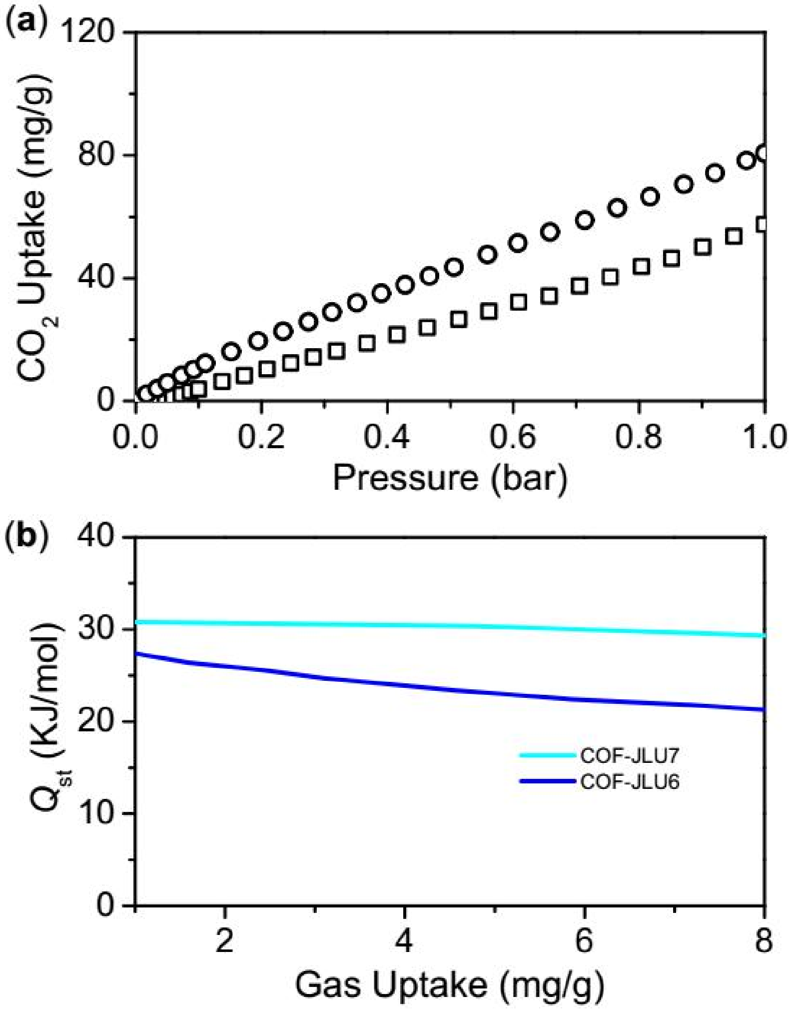
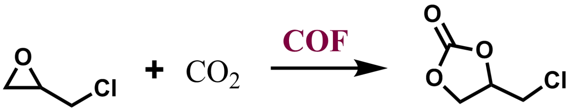


Fig. S6 CO_2 adsorption isotherms (open squares for COF-JLU6; open circles for COF-JLU7) at 298 K (a) and their adsorption heats (b).

8. Catalytic Data

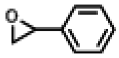
Table S1. Cycloaddition of CO_2 with Epichlorohydrin over COF-JLUs[a]



Entry	Catalyst	Co-catalyst	T (°C)	Time (h)	Conversion (%)[b]	Selectivity (%)[b]
1	COF-JLU6	TBAB	25	48	56	100
2	COF-JLU7	TBAB	25	48	67	100
3	COF-JLU6	TBAB	40	48	86	100
4	COF-JLU7	TBAB	40	48	92	100
5	COF-JLU7	TBAC	40	48	89	100
6	COF-JLU7	TBAI	40	48	93	100
7	COF-JLU7	~	40	48	0	0
8	~	TBAB	40	48	40	100

[a] Reaction conditions: Catalyst (0.051 mmole), Epichlorohydrin (10.21 mmole), Co-catalyst (0.51 mmol), CO_2 (0.1 MPa). [b] Determined by ^1H-NMR spectroscopic analysis.

Table S2. Enantiomeric excess (ee) of the cycloaddition reactions of styrene oxide catalyzed by COF-JLU7

Entry	Substrate	Peak	Reactiont time (min)	Area (μV*sec)	Area %	ee %
1		1	26.1	1539646	50.06	
		2	31.6	1535692	49.94	
2	R	1	25.9	2058369	98.49	97
		2	32	31640	1.51	
3	S	1	26.4	70527	3.5	93
		2	32	1943280	96.5	

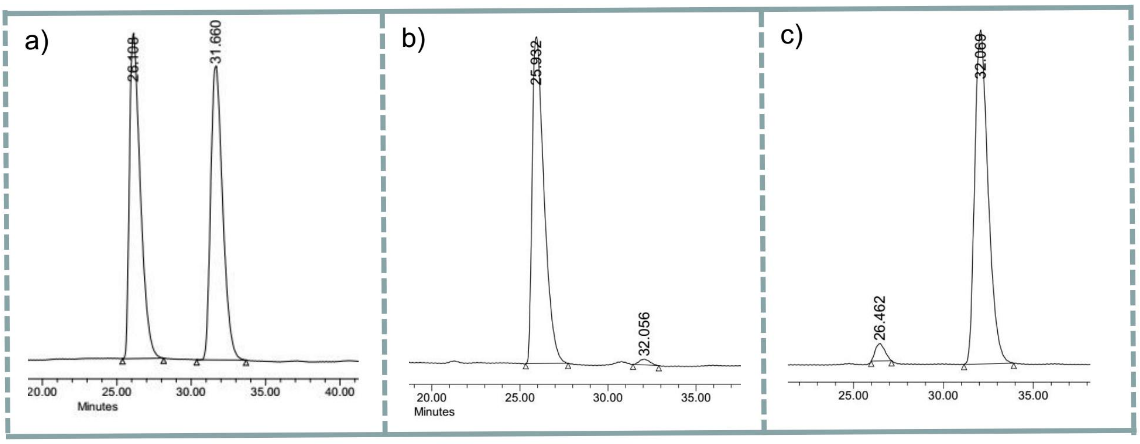
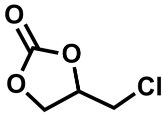


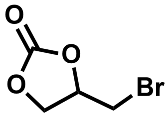
Fig. S7 HPLC spectra of racemic-phenyl(ethylene carbonate) (a), *R*-phenyl(ethylene carbonate) (b) and *S*-phenyl(ethylene carbonate) (c).

9. Characterization Data of Catalytic Products



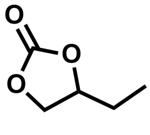
4-(chloromethyl)-1,3-dioxolan-2-one

^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.50-4.95 (1H, m, O-CH$_2$C*H*-O), 4.58 (1H, t, *J* = 8.0 Hz, O-C*H*$_2$CH-O), 4.40 (1H, dd, *J* = 8.0 and 4.0 Hz, O-C*H*$_2$CH-O), 3.81 (1H, dd, *J* = 12.0 Hz, *J* = 8.0 Hz, CHC*H*$_2$Cl), 3.75 (1H, dd, *J* = 12.0 Hz, *J* = 8.0 Hz, CHC*H*$_2$Cl) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 154.3 (C=O), 74.5, 67.3, 43.9 ppm.



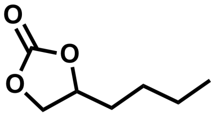
4-(Bromomethyl)-1,3-dioxolan-2-one

^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.97-4.91 (1H, m, O-CH$_2$C*H*-O), 4.60 (1H, t, *J* = 8.0 Hz, O-C*H*$_2$CH-O), 4.38-4.33 (1H, m, O-C*H*$_2$CH-O), 3.58 (2H, m, CHC*H*$_2$Cl) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 154.5 (C=O), 74.3, 68.4, 31.8 ppm.



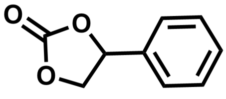
4-Ethyl-1,3-dioxolan-2-one

^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.69-4.62 (1H, m, O-CH$_2$C*H*-O), 4.51 (1H, t, *J* = 8.0 Hz, O-C*H*$_2$CH-O), 4.07 (1H, t, *J* = 8.0, O-C*H*$_2$CH-O), 1.85-1.72 (2H, m, C*H*$_2$CH$_3$), 1.01 (3H, t, *J* = 8.0 Hz, *J* = 4.0 Hz, CH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 155.5 (C=O), 78.3, 69.3, 27.2, 8.8 ppm.



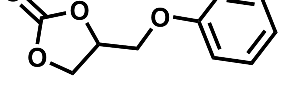
4-Butyl-1,3-dioxolan-2-one

^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 4.73-4.66 (1H, m, O-CH$_2$C*H*-O), 4.52 (1H, t, *J* = 8.0 Hz, O-C*H*$_2$CH-O), 4.06 (1H, t, *J* = 8.0, O-C*H*$_2$CH-O), 1.84-1.76 (1H, m, CHC*H*$_2$CH$_2$), 1.71-1.64 (1H, m, CHC*H*$_2$CH$_2$), 1.48-1.34 (4H, m, CH$_2$C*H*$_2$CH$_2$ and CH$_2$C*H*$_2$CH$_3$), 0.92 (3H, t, *J* = 8.0 Hz, CH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): *δ* 155.3 (C=O), 69.7, 33.9, 26.8, 22.6, 14.1 ppm.



4-phenyl-1,3-dioxolan-2-one

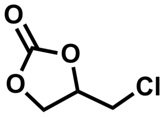
^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 7.46-7.40 (3H, m, ArH), 7.38-7.35 (2H, m, ArH), 5.67 (1H, t, *J* = 8.0 Hz, O-CH$_2$C*H*-O), 4.79 (1H, t, *J* = 8.0 Hz, O-C*H*$_2$CH-O), 4.32 (1H, t, *J* = 8.0, O-C*H*$_2$CH-O) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): *δ* 155.0 (C=O), 136.1, 129.9, 129.4, 126.1, 78.3, 71.4 ppm.

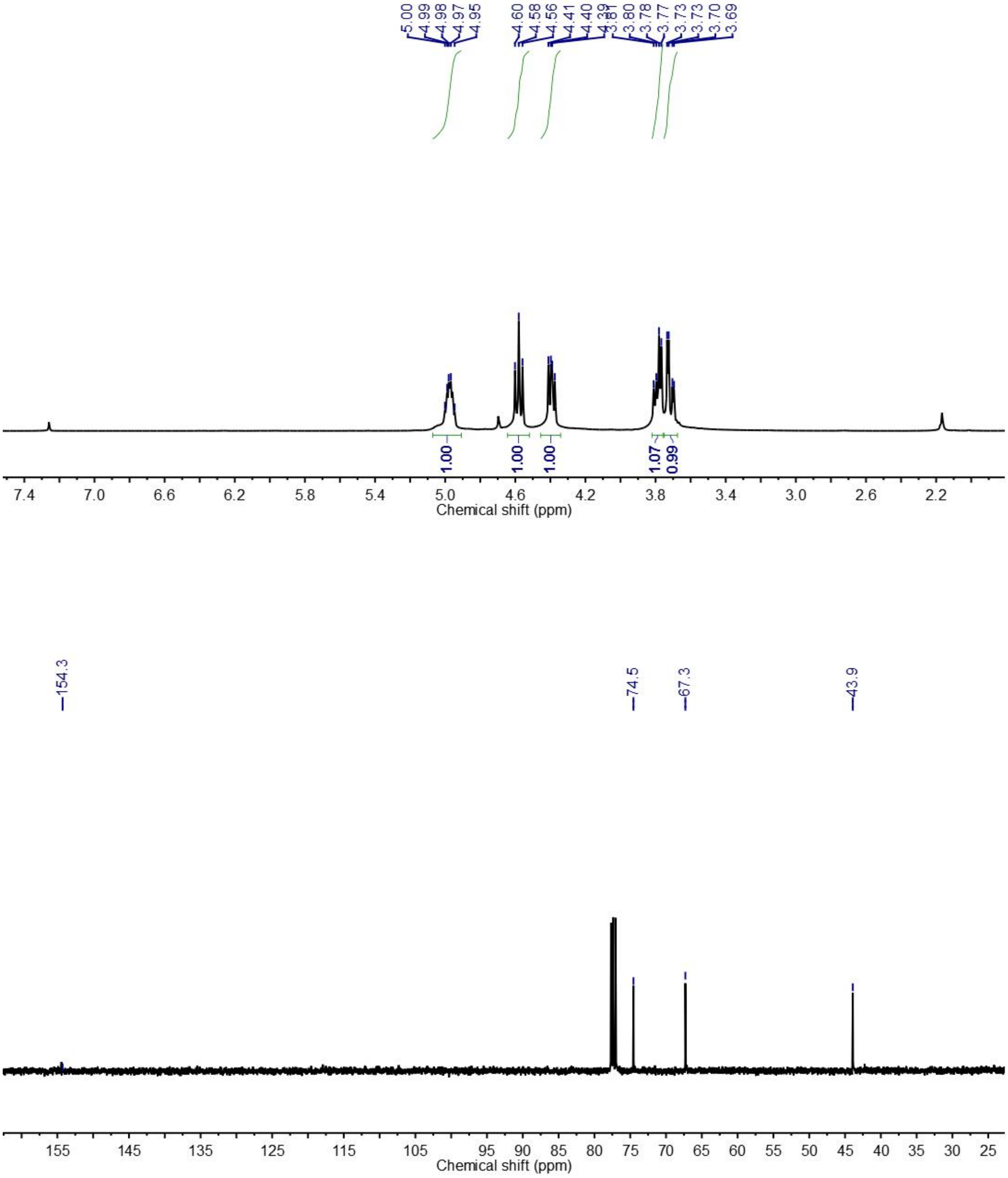


4-(phenoxymethyl)-1,3-dioxolan-2-one

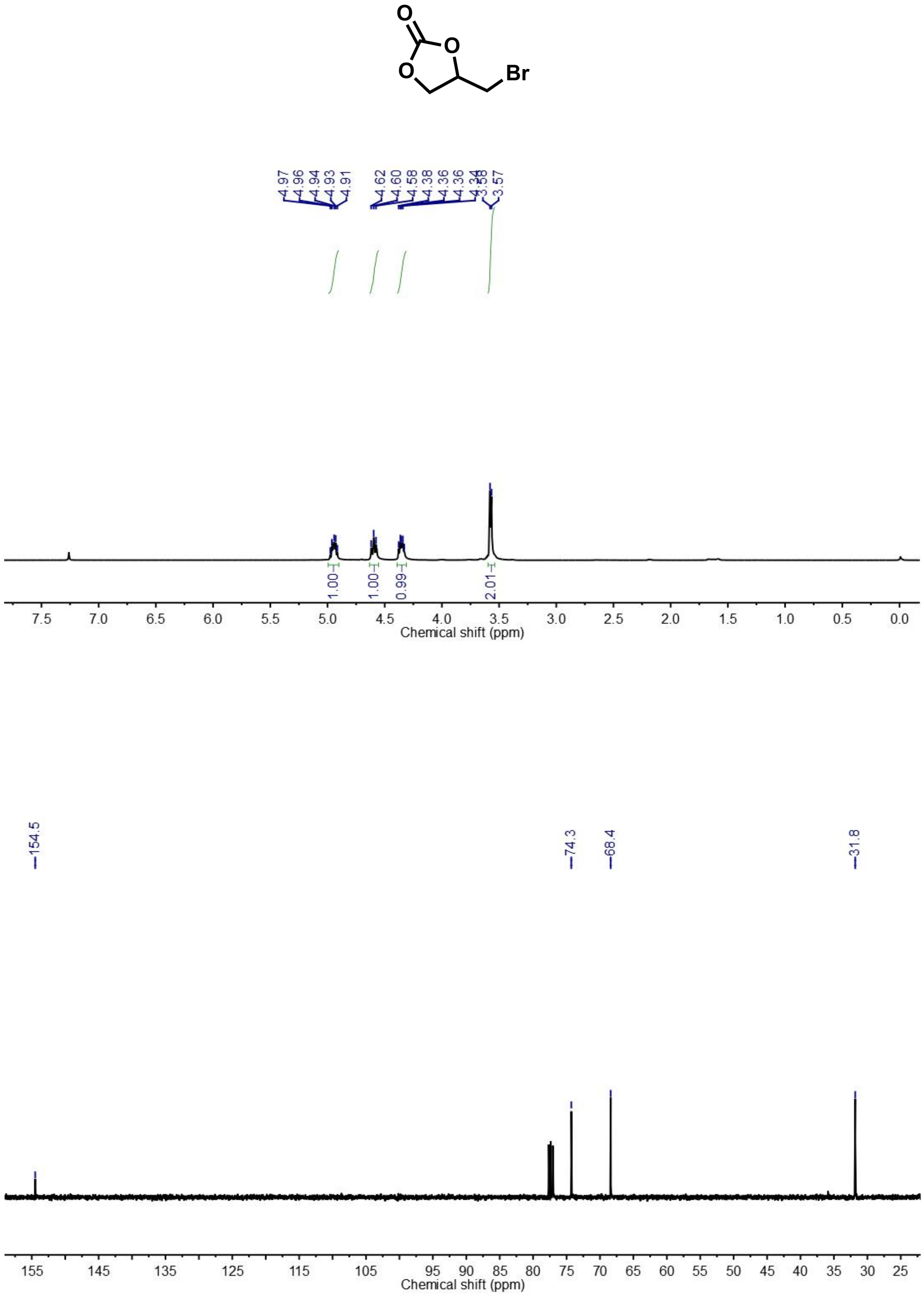
^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 7.31 (2H, t, *J* = 8.0 Hz, ArH), 7.02 (1H, t, *J* = 8.0 Hz, ArH), 6.91 (2H, d, *J* = 8.0 Hz, ArH), 5.06-5.01 (1H, m, O-CH$_2$C*H*-O), 4.62 (1H, t, *J* = 8.0 Hz, O-C*H*$_2$CH-O), 4.54 (1H, dd, *J* = 8.0 and 4.0 Hz, O-C*H*$_2$CH-O), 4.24 (1H, dd, *J* = 12.0 Hz, *J* = 8.0 Hz, CHC*H*$_2$), 4.15 (1H, dd, *J* = 12.0 Hz, *J* = 8.0 Hz, CHC*H*$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): *δ* 158.0 (C=O), 129.9, 122.2, 114.8, 74.3, 67.1, 66.5 ppm.

10. NMR Spectra of Catalytic Products

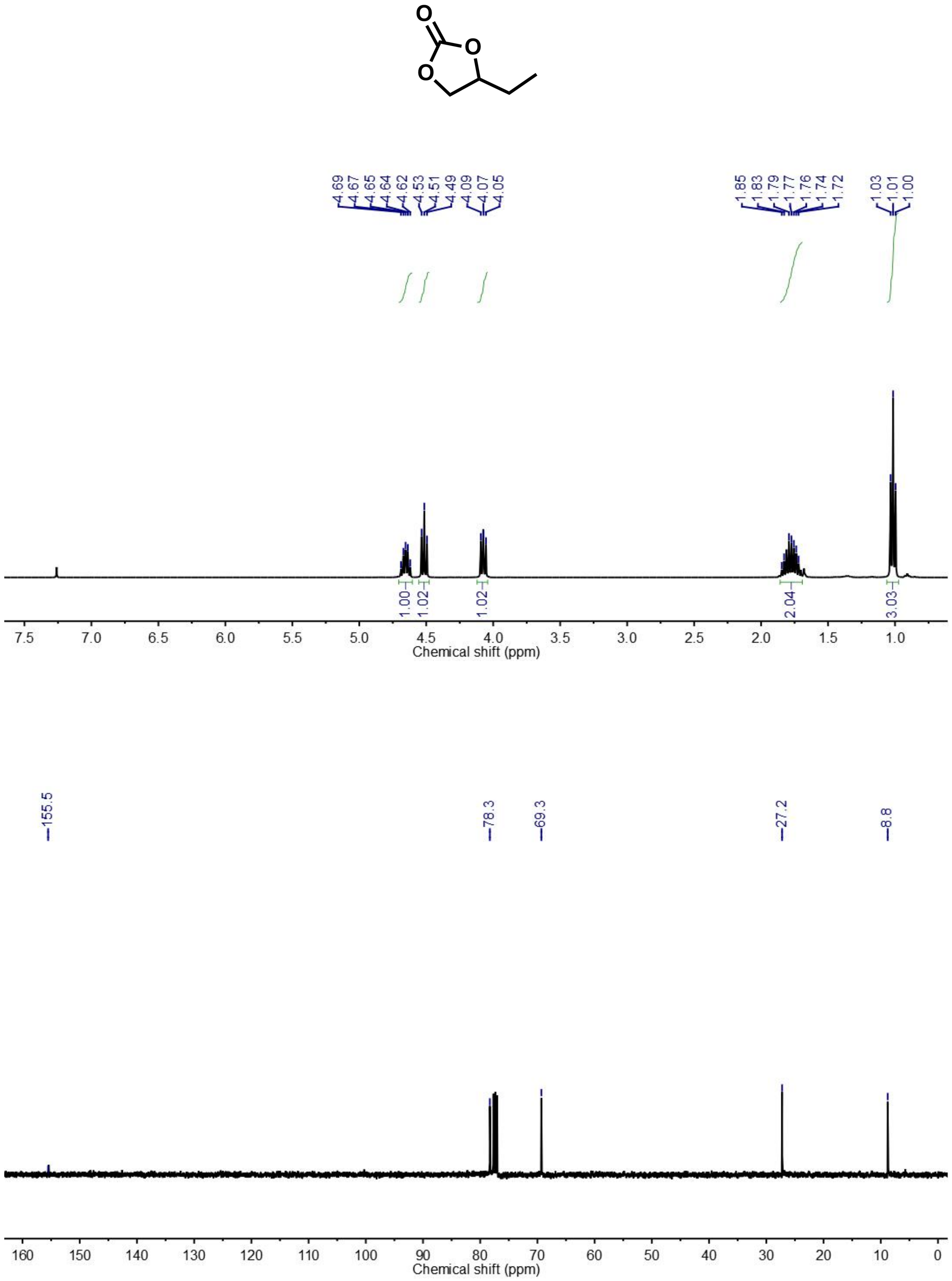




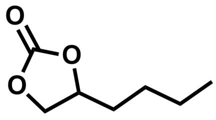
The ^{1}H-NMR and ^{13}C-NMR spectra of 4-(chloromethyl)-1,3-dioxolan-2-one.

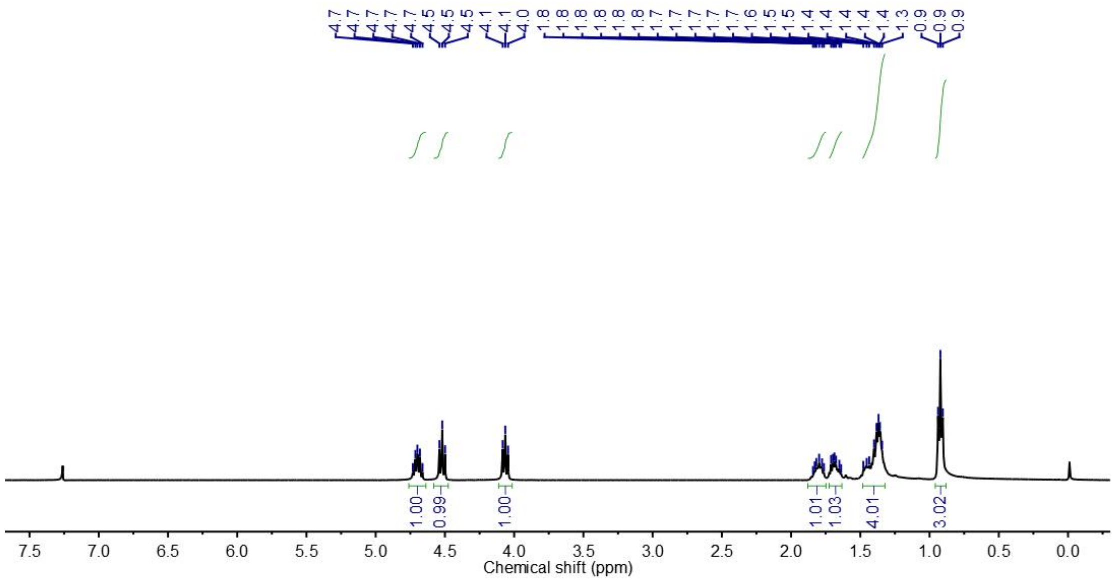


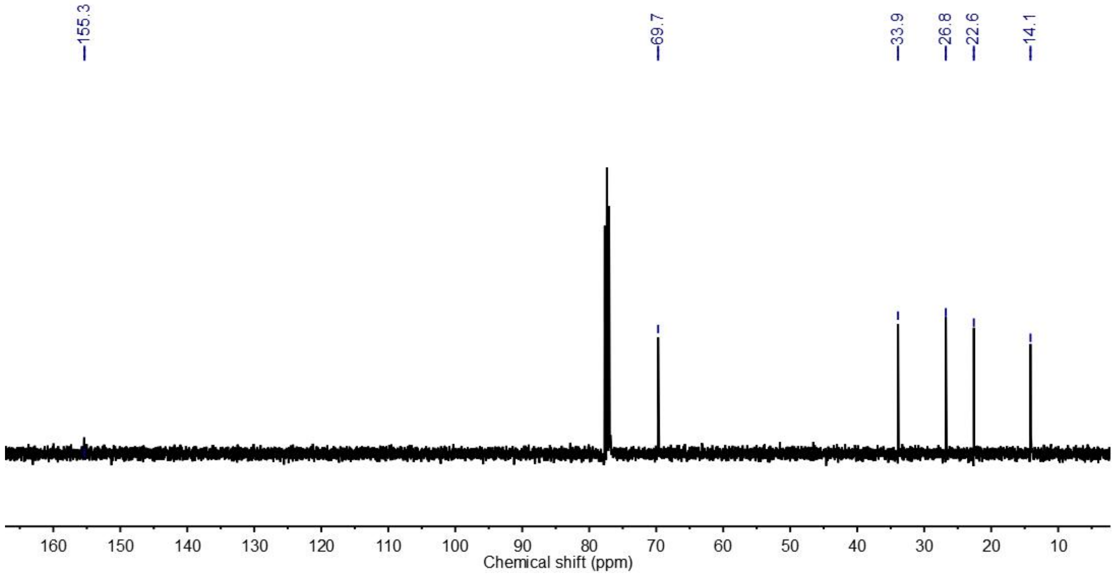
The ^{1}H-NMR and ^{13}C-NMR spectra of 4-(Bromomethyl)-1,3-dioxolan-2-one.



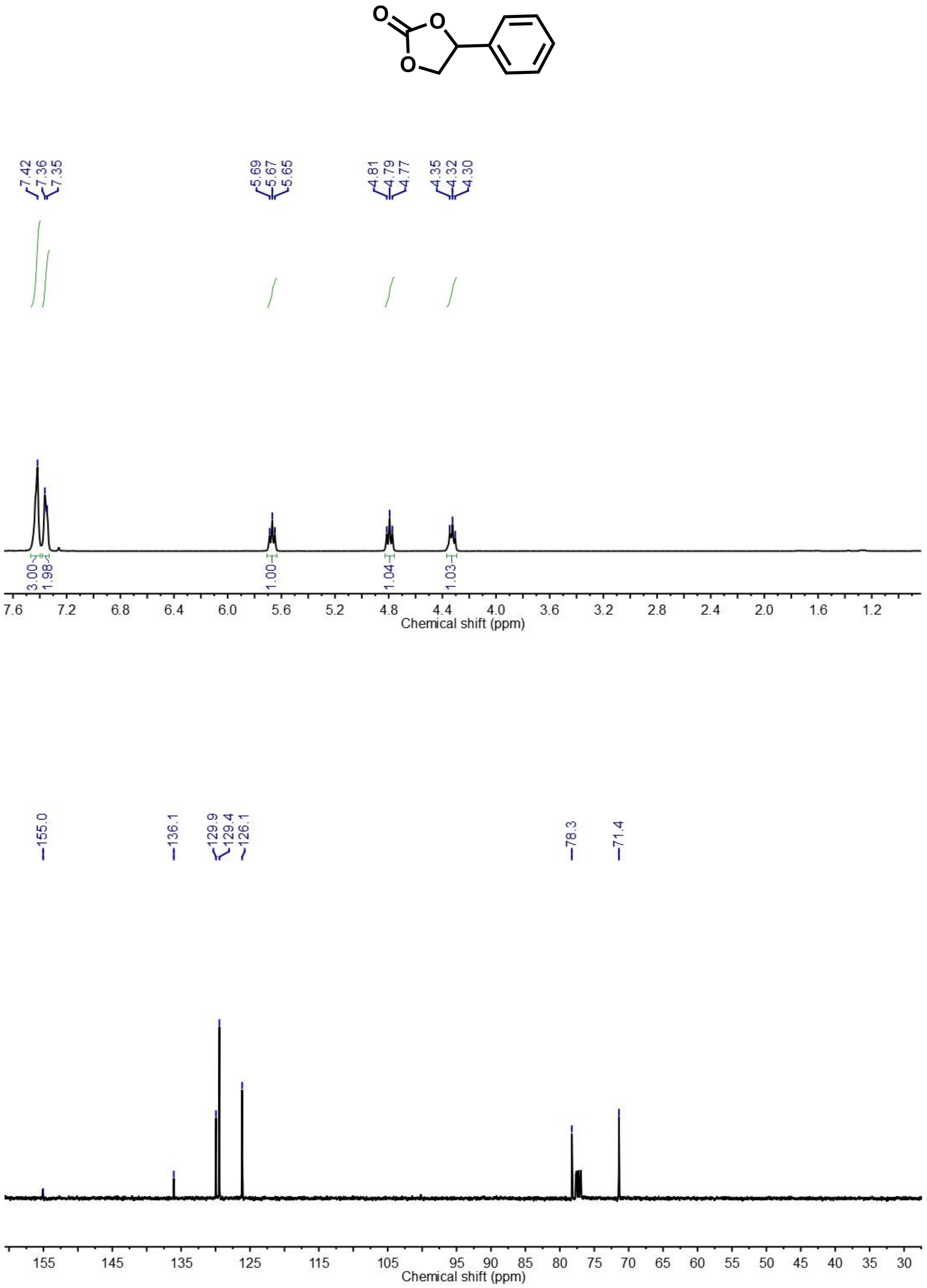
The ^{1}H-NMR and ^{13}C-NMR spectra of 4-Ethyl-1,3-dioxolan-2-one.



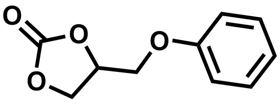


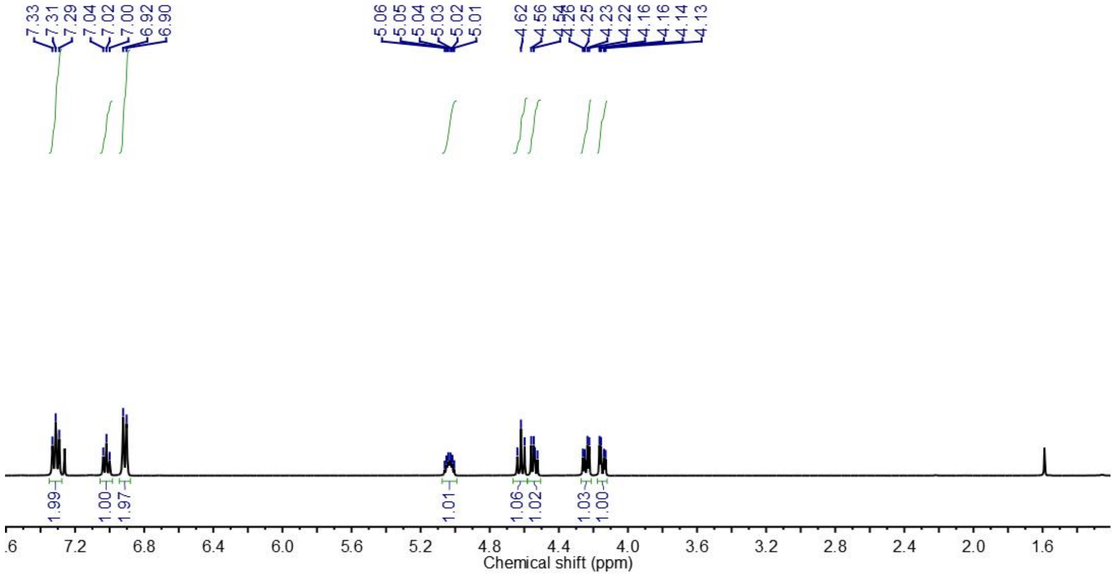


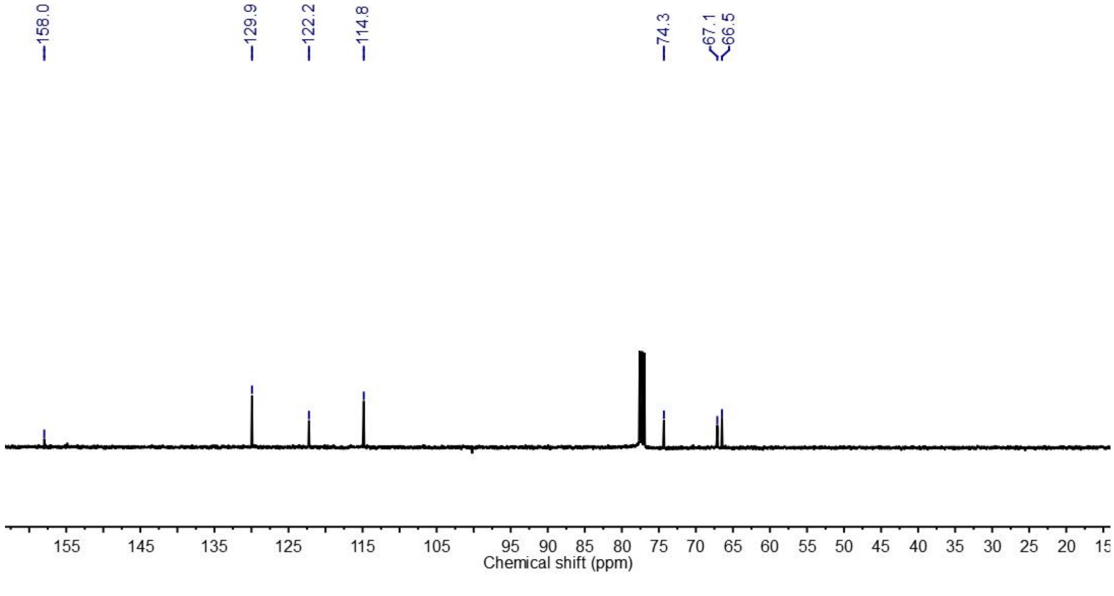
The ^{1}H-NMR and ^{13}C-NMR spectra of 4-Butyl-1,3-dioxolan-2-one.



The ^{1}H-NMR and ^{13}C-NMR spectra of 4-phenyl-1,3-dioxolan-2-one.







The ^{1}H-NMR and ^{13}C-NMR spectra of 4-(phenoxymethyl)-1,3-dioxolan-2-one.

11. References

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[2] R. Gomes, P. Bhanja, A. Bhaumik, *Chem. Commun.,* **2015**, *51*, 10050.

[3] F. C. Schaefer, J. T. Thurston, J. R. Dudley, *J. Am. Chem. Soc.,* **1951**, 73, 2990.