# Supporting Information

## Efficient and recyclable tetraoxo-coordinated zinc catalyst for the cycloaddition of epoxides with carbon dioxide at atmospheric pressure

Ran Ma,[a,b] Liang-Nian He,[a,b]* Yue-Biao Zhou[a,b]

[a] *State Key Laboratory and Institute of Elemento-Organic Chemistry,* [b] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071 (P. R. China).*

*Email: heln@nankai.edu.cn*

*Fax: (+86)-22-2350-3878; phone: (+86)-22-2350-3878*

## Table of Contents

## I. Preparation and Characterization of $Zn(OPO)_2$

The $Zn(OPO)_2$ complex was prepared according to the published procedure: to an aqueous solution of HOPO (0.33 g , 3.0 mmol) and $Ba(OH)_2 \cdot 8H_2O$ (0.48 g, 1.5 mmol), an aqueous solution of $ZnSO_4 \cdot 7H_2O$ (0.43 g, 1.5 mmol) was added followed by stirring for 5 h at room temperature. After the filtration of $BaSO_4$ and the removal of the solvent, the residue was dissolved with a small amount of hot water and reprecipitated with methanol. The obtained white precipitate was washed with a small amount of methanol. Then, the residue was dried at 60 $^oC$ under vacuum for 24 h. Anal. Found: C, 41.78 %; N, 9.58 %; H, 2.93 %. Calcd for $C_{10}H_8N_2O_4Zn$: C, 42.06; N, 9.81; H, 2.81%. Mp 320–360 ºC (dec.). IR (KBr disk); 1625 $cm^{-1}$ for ν(C=O), $\nu$(NO)=1185 $cm^{-1}$.

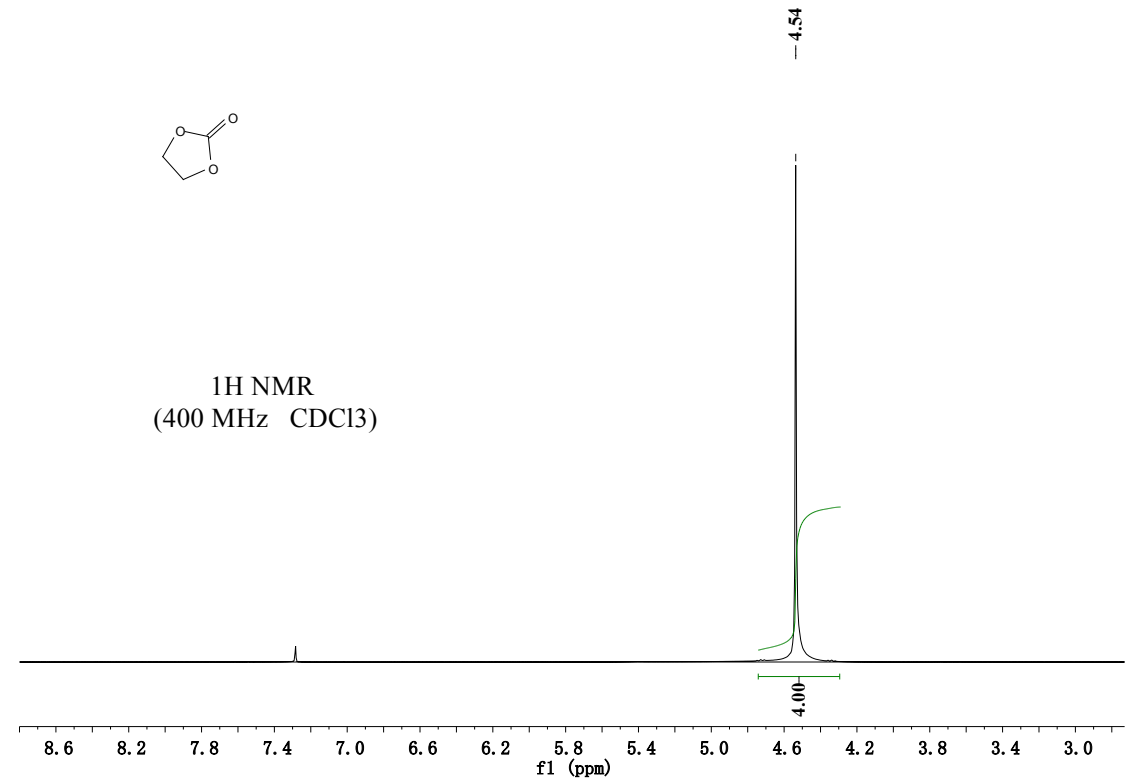
## II. Representative homogeneous and heterogeneous catalysts for the synthesis of cyclic carbonates.

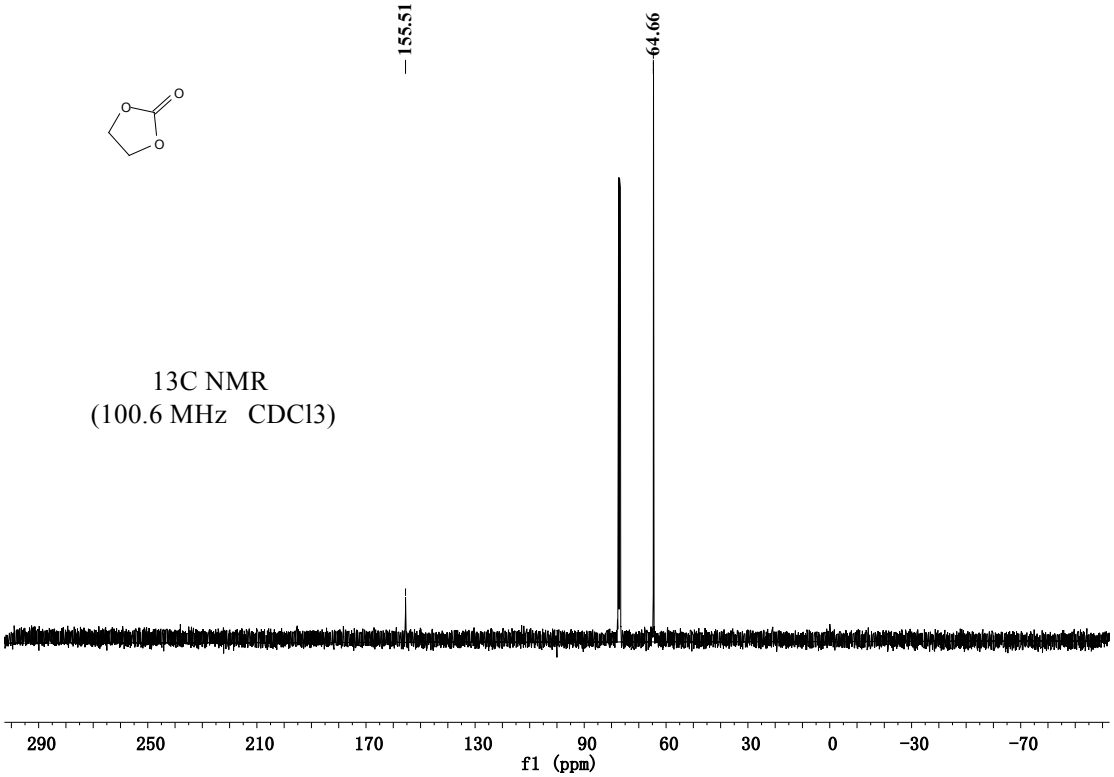
**Table S1.** Representative homogeneous and heterogeneous catalysts for the synthesis of cyclic carbonates.

| Catalyst | Co-catalyst | Reaction conditions | | | | Yields | TOF | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | Catalyst/Epoxide (Mole ratio) | $CO_2$ (MPa) | Temp. ($^oC$) | Time (h) | (%) | ($h^{-1}$)[a] | |
| $Zn(OPO)_2$ | TBAI | (PO)1:40000 | 3 | 120 | 1 | 55 | 22000 | This work |
| $Zn(OPO)_2$ | TBAB | (PO)1:40000 | 3 | 120 | 1 | 46 | 18400 | This work |
| Mg-porphyrin | - | (1,2-Epoxyhexane) 1:33333 | 1.7 | 120 | 1 | 57 | 19000 | 1 |
| $ZnBr_2$ | hexabutylguanidinium bromide. | (PO) 1:1790 | 3.0 | 140 | 1 | 81 | 8670 | 2 |
| Zn-CMP | TBAB | (PO)1:40000 | 3 | 120 | 1 | 29 | 11600 | 3 |
| Zn-porphyrin | - | (1,2-Epoxyhexane) 1:33333 | 1.7 | 160 | 1 | 79 | 40000 | 4 |
| Al-aminotriphenolate | PPN-Br | (1,2-Epoxyhexane) 1:200000 | 1 | 90 | 2 | 36 | 36000 | 5 |

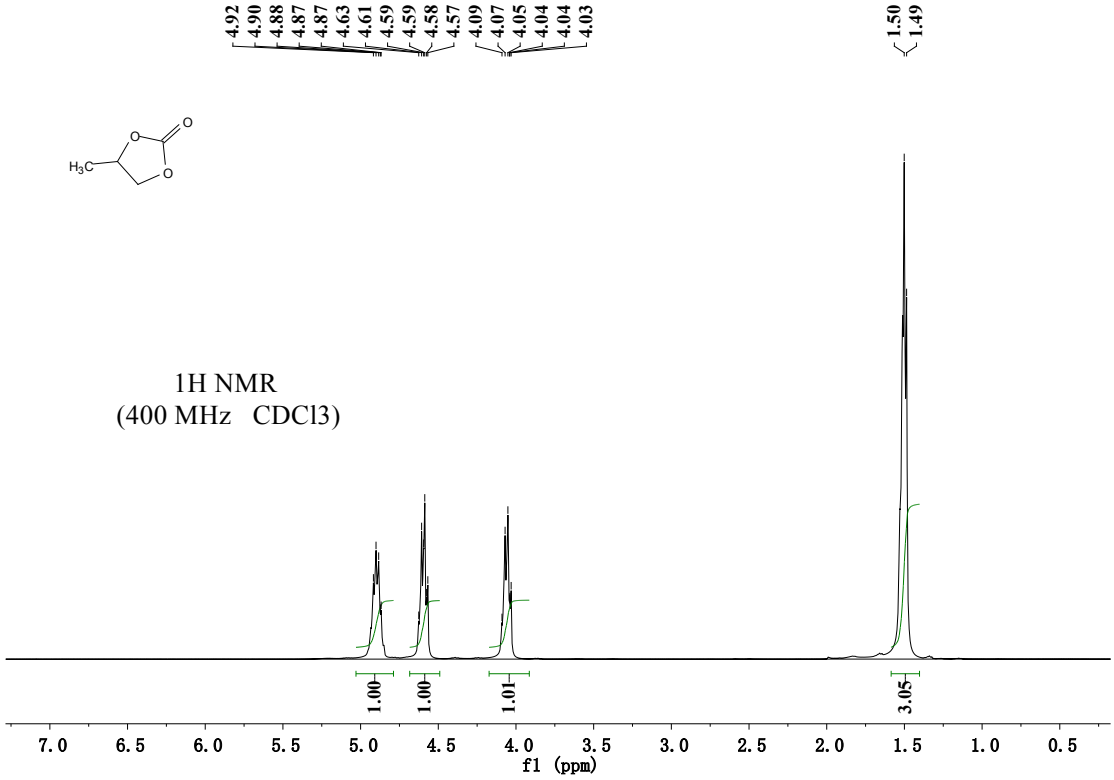
## III. Characterization data and NMR Spectra Copies

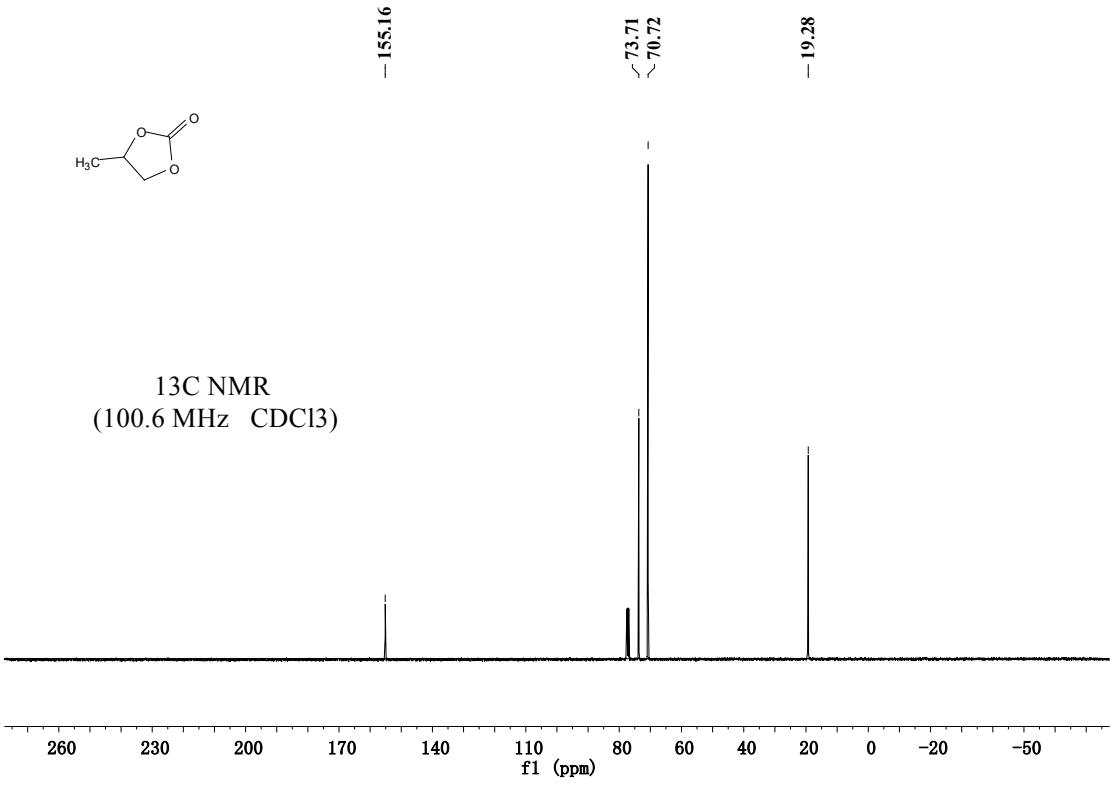
**Ethylene carbonate:** $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 4.54 (s, 4H); $^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ 155.51 (s), 64.66 (s).



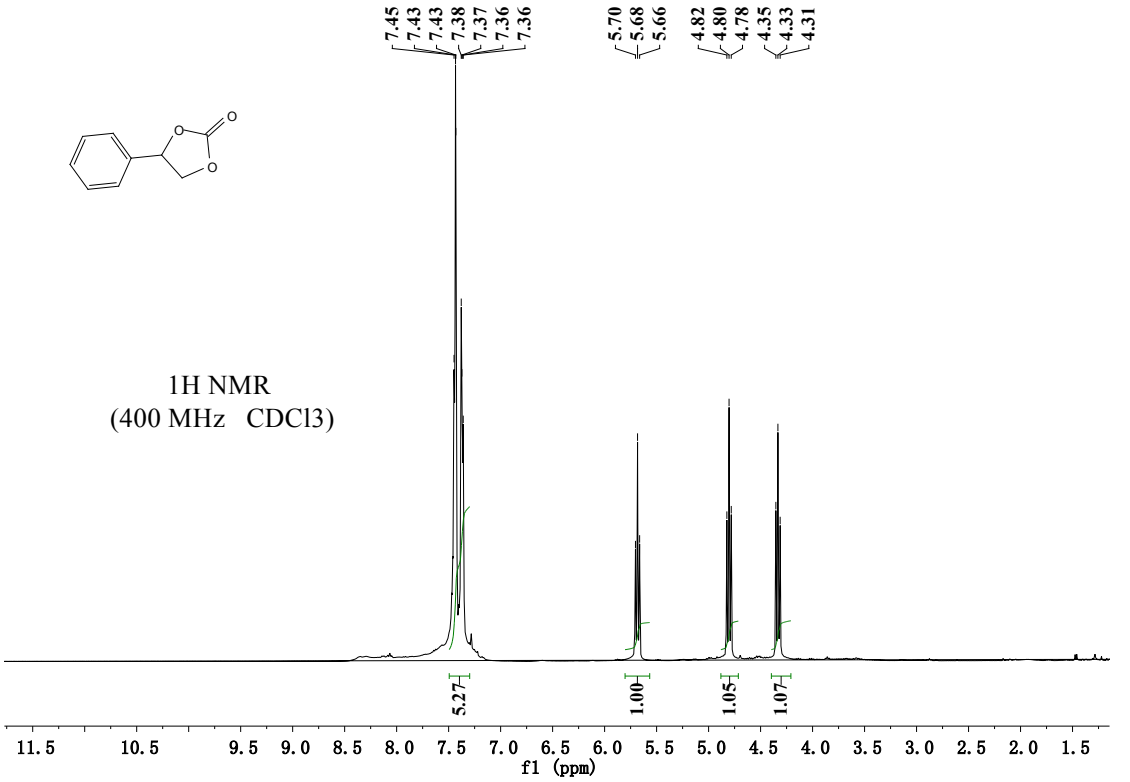
**Propylene carbonate:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.03-4.79 (m, 1H), 4.59 (dt, J = 7.9, 5.3 Hz, 1H), 4.17-3.91 (m, 1H), 1.49 (d, J = 6.2 Hz, 3H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 155.16 (s), 73.71 (s), 70.72 (s), 19.28 (s).

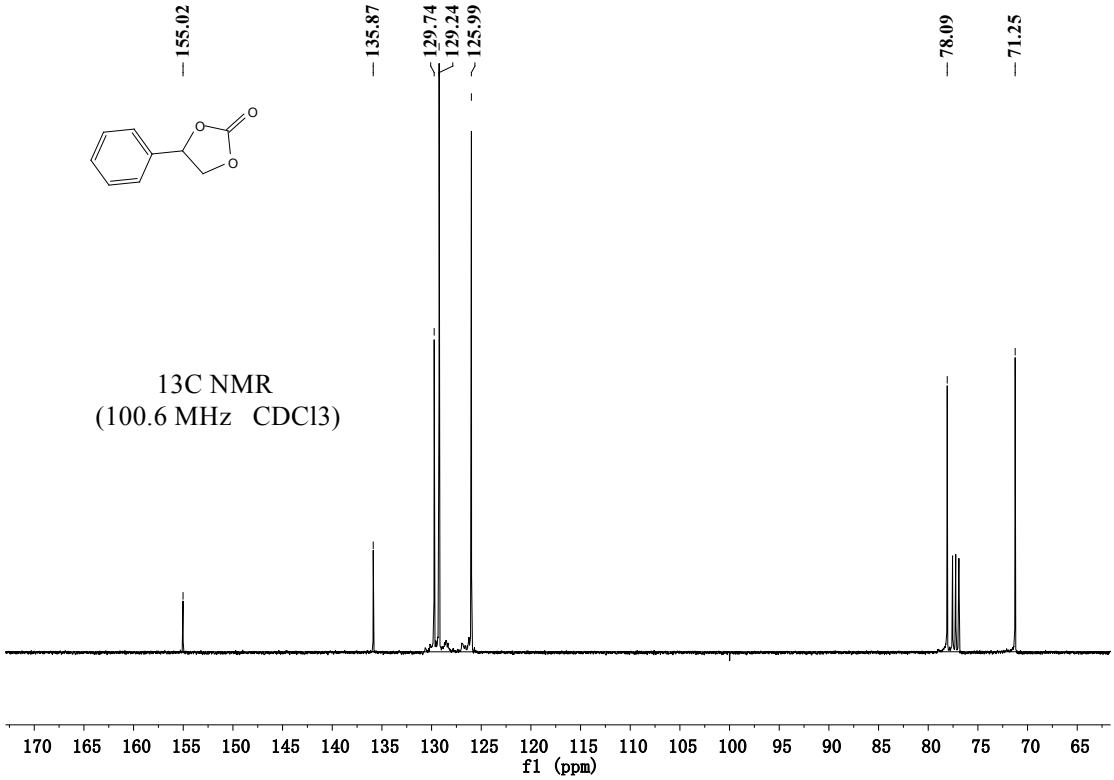


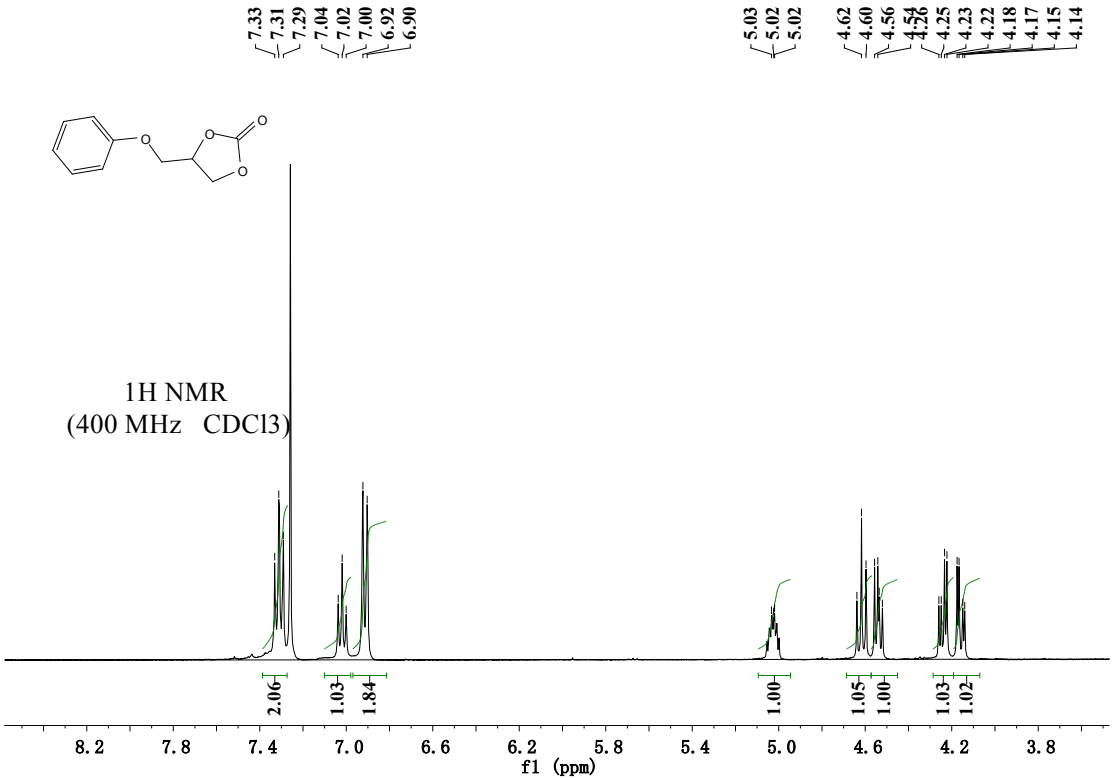

**Styrene carbonate**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.49-7.30 (m, 5H), 5.68 (t, J = 8.0 Hz, 1H), 4.80 (t, J = 8.4 Hz, 1H), 4.33 (t, J = 8.2 Hz, 1H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 155.02 (s),

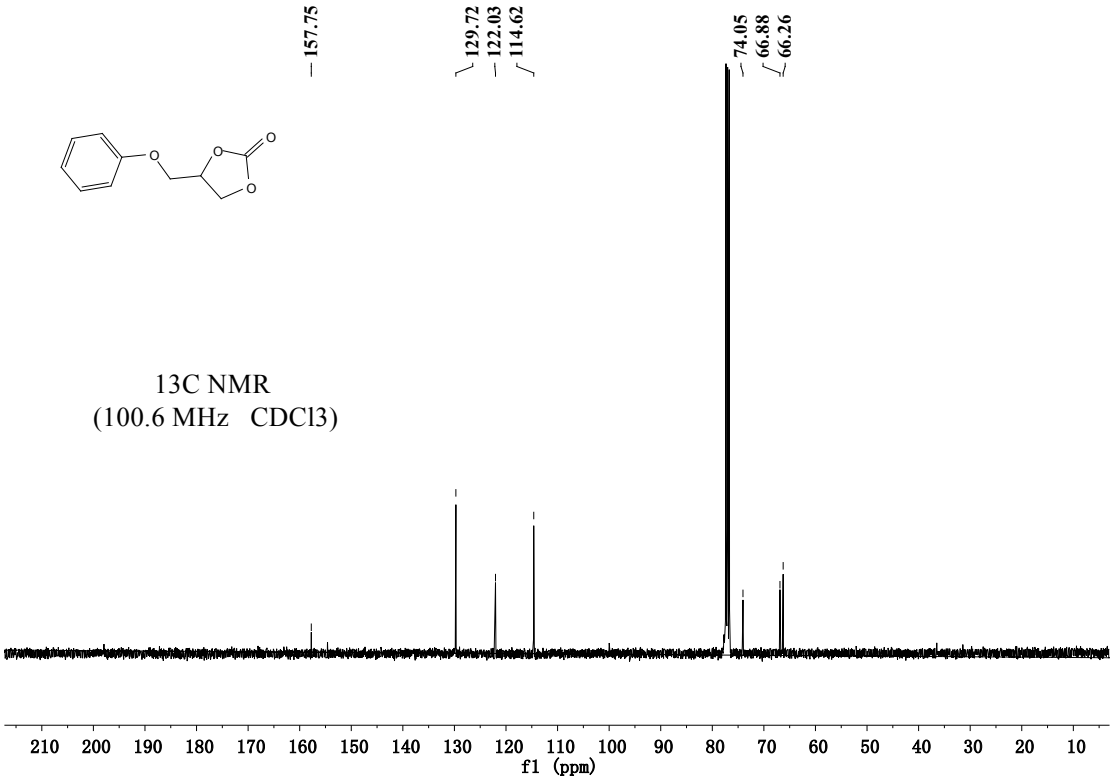
135.87 (s), 129.74 (s), 129.24 (s), 125.99 (s), 78.09 (s), 77.55 (s), 77.23 (s), 76.91 (s), 71.25 (s).



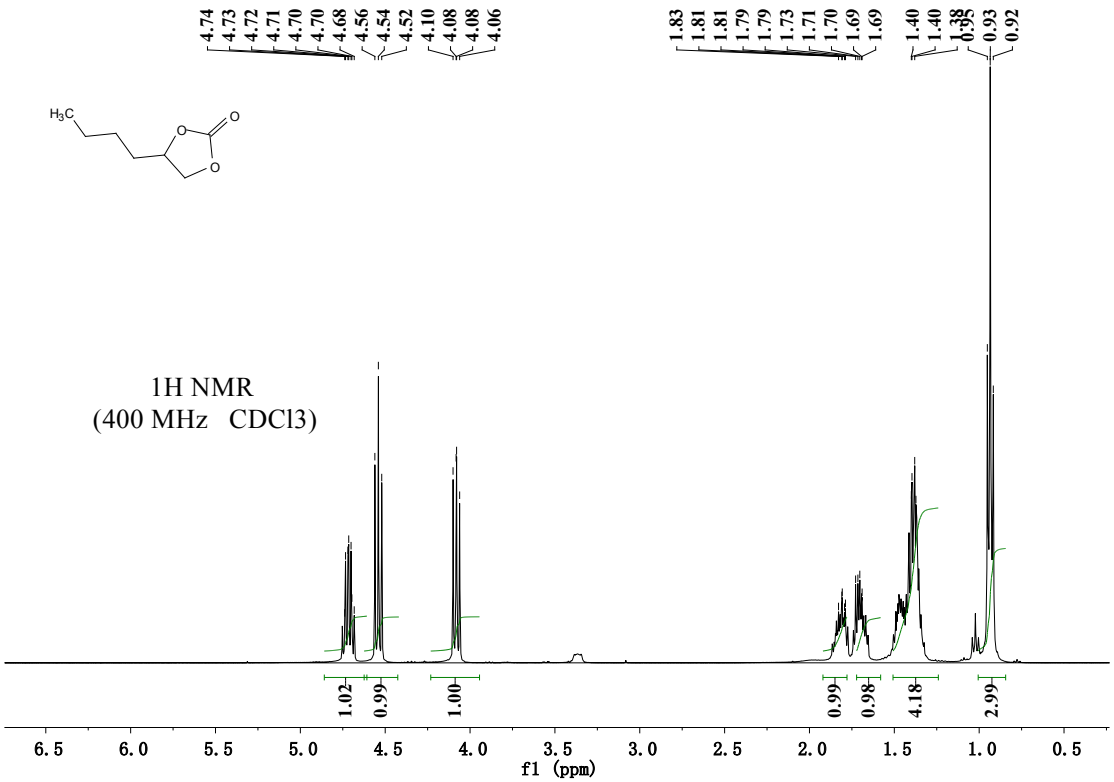



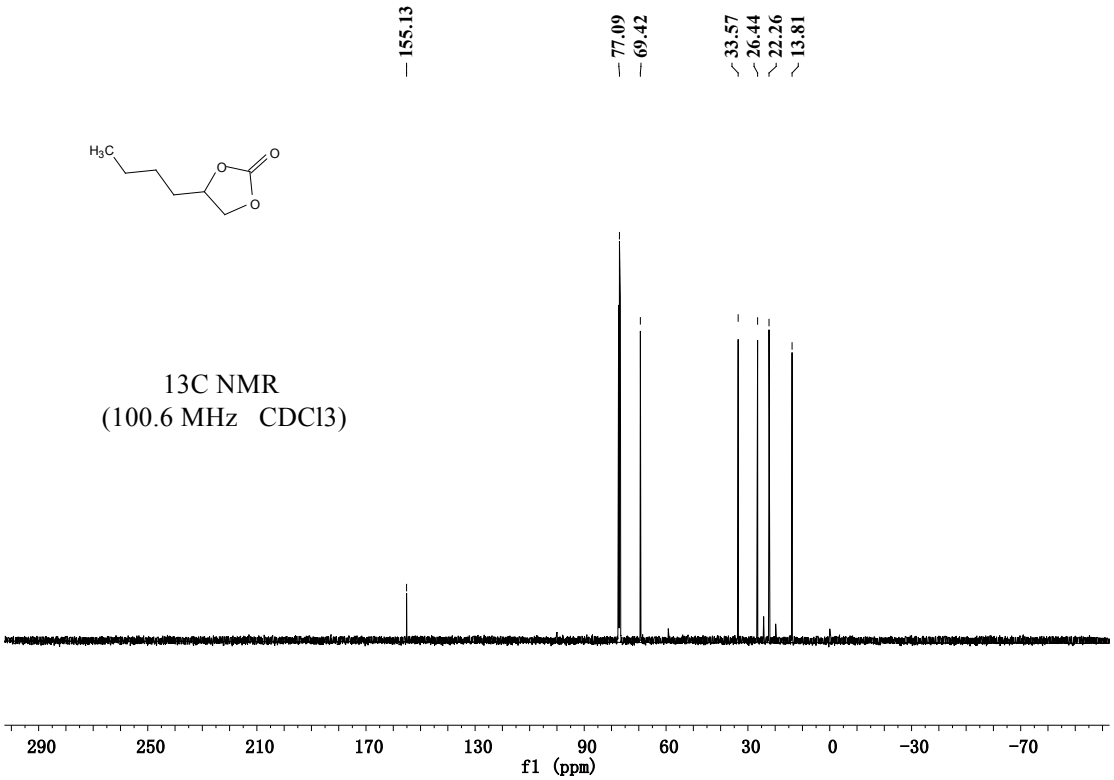

**4-Phenoxymethyl-1,3-dioxolan-2-one**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.27 (t, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 7.9 Hz, 2H), 5.09–4.95 (m, 1H), 4.62 (t, J = 8.4 Hz, 1H), 4.54 (dd, J = 8.5, 5.9 Hz, 1H), 4.24 (dd, J = 10.5, 4.4 Hz, 1H), 4.16 (dd, J = 10.5, 3.6 Hz, 1H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 129.72 (s), 122.03 (s), 114.62 (s), 74.05 (s), 66.88 (s), 66.26 (s).



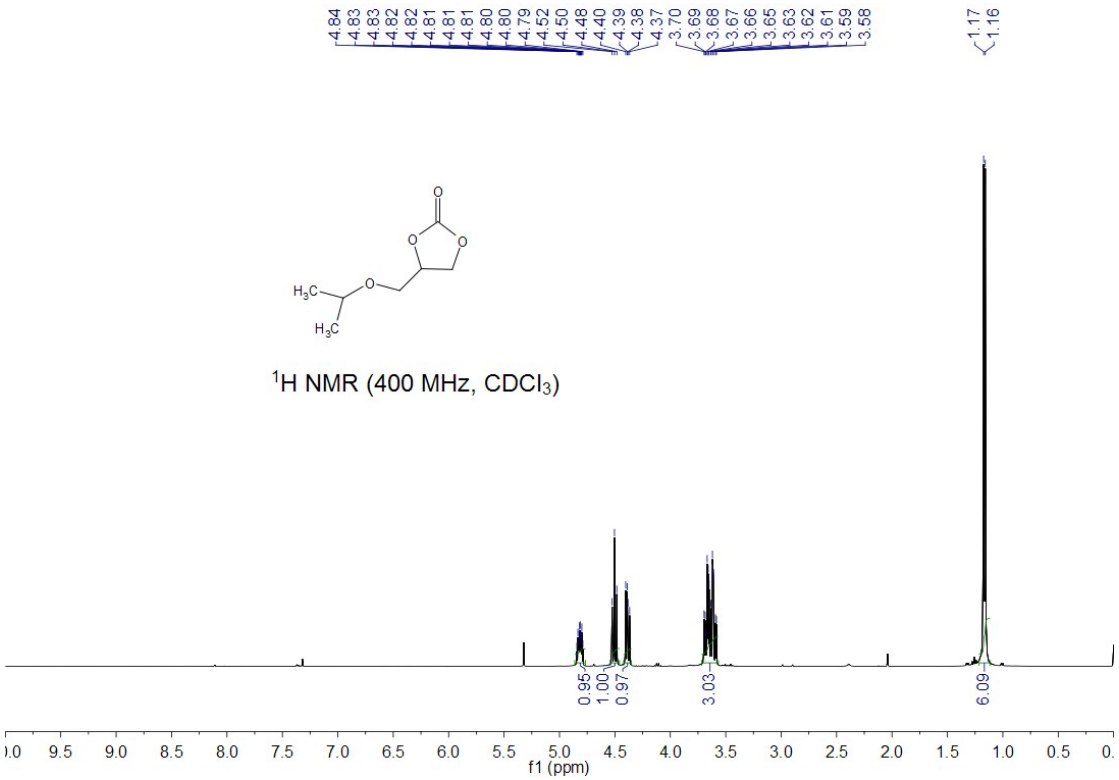



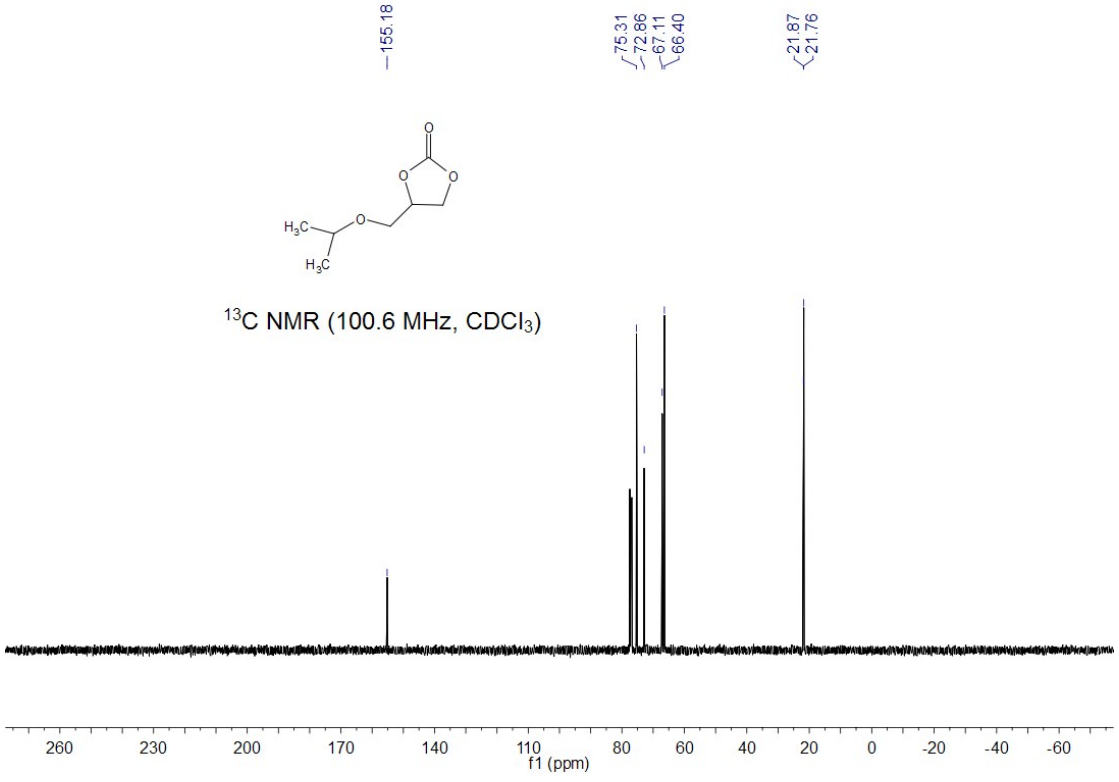

**Butylene carbonate**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.71 (tt, J = 7.5, 3.8 Hz, 1H), 4.54 (t, J = 8.1 Hz, 1H), 4.08 (dd, J = 8.4, 7.2 Hz, 1H), 1.92-1.78 (m, 1H), 1.70 (dd, J = 7.0, 2.9 Hz, 1H), 1.39 (dd, J = 8.7, 2.2 Hz, 4H), 0.93 (t, J = 7.0 Hz, 3H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 155.13 (s), 77.09 (s), 69.42 (s), 33.57 (s), 26.44 (s), 22.26 (s), 13.81 (s).



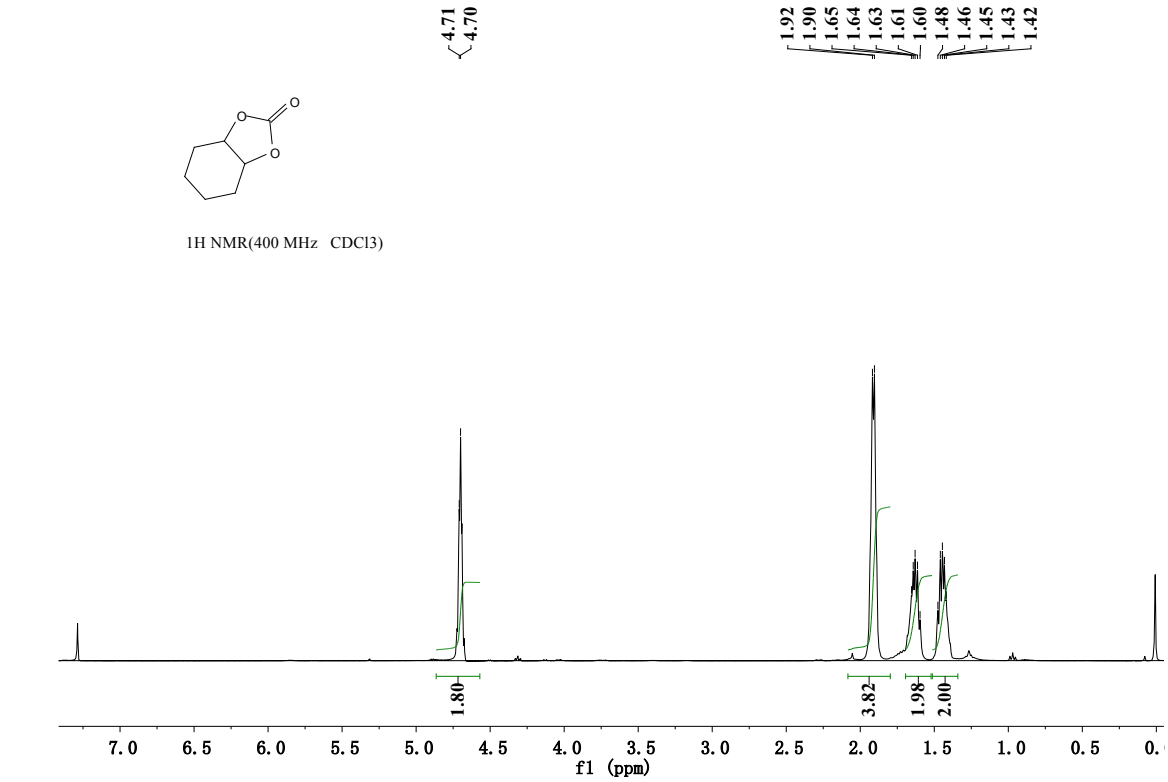

**4-*i*-Propoxy-1,3-dioxolan-2-one**

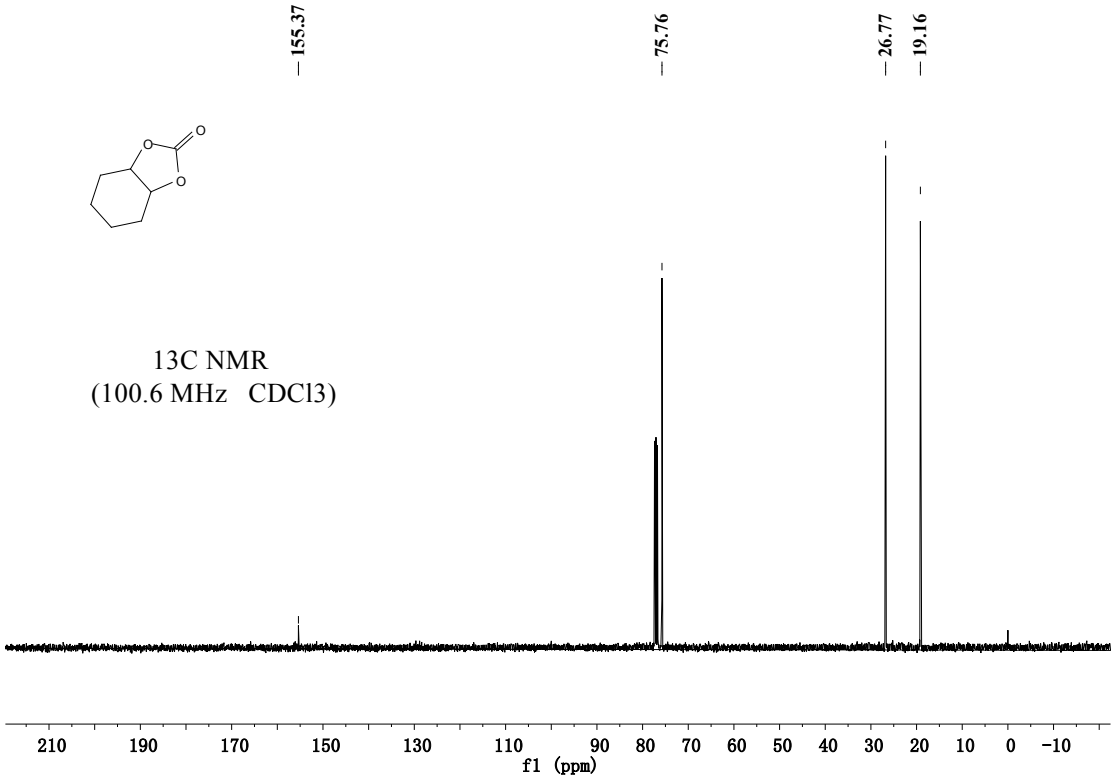



**4,4-dimethyl-1,3-dioxolan-2-one:** $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.17 (s, 2 H), 1.53 (s, 6 H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 154.65, 81.79, 75.39, 25.98.

**hexahydrobenzo[d][1,3]dioxol-2-one**: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 4.70 (s, 2H), 1.91 (d, J = 5.4 Hz, 4H), 1.69-1.52 (m, 2H), 1.51-1.34 (m, 2H); $^{13}$C NMR (100.6 MHz, $CDCl_3$) δ 155.37 (s), 75.76 (s), 26.77 (s), 19.16 (s).



## IV. Reference


(1) T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J.-y. Hasegawa, *J Am Chem Soc*, 2014, **136**, 15270.

(2) H. Xie, S. Li and S. Zhang, *J Molecul Catal A: Chem* **2006**, *250*, 30.

(3) Y. Xie, T. T. Wang, R. X. Yang, N. Y. Huang, K. Zou, W. Q. Deng, *ChemSusChem*, 2014, **7**, 2110.

(4) C. Maeda, T. Taniguchi, K. Ogawa and T. Ema, *Angew Chem Int Ed*, 2015, **54**, 134.

(5) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adan, E. Martin and A. W. Kleij, *J Am Chem Soc*, 2013, **135**, 1228.