Supporting Information

Di-ionic multifunctional porous organic frameworks for efficient CO_2 fixation under mild and co-catalyst free conditions

Dingxuan Ma,[a] Jixin Li,[b] Kang Liu,[*a] Baiyan Li,[b] Chunguang Li[b] and Zhan Shi[*b]

[a] Laboratory of Eco-chemical Engineering, Ministry of Education, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, People's Republic of China.

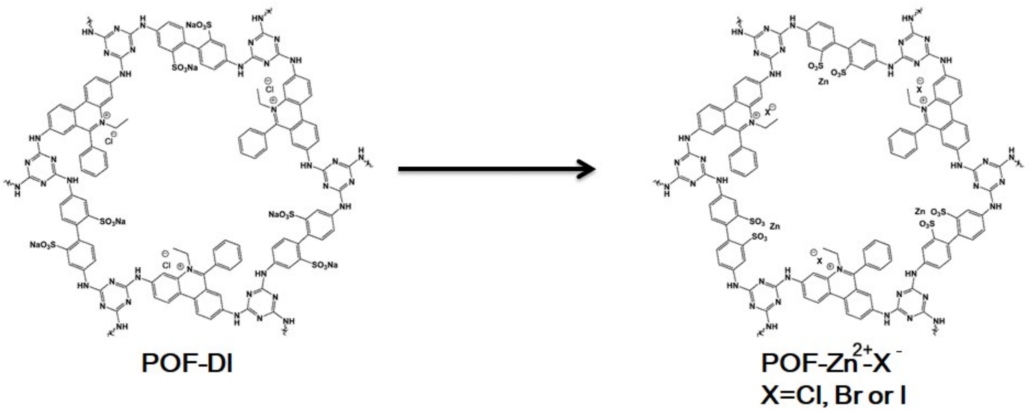
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, People's Republic of China

E-mail: liukang82@126.com; zshi@mail.jlu.edu.cn

Editorial note: This supplementary information file associated with the manuscriptDOI doi.org/10.1039/C8GC01867G replaces the version published on 18th September 2018. The previous version of this supplementary information contained incorrect SEM images for Figure S8. This revised supplementary information contains the correct SEM images in Figure S8.

I Synthesis

POF-Zn-X$^-$



Scheme S1 Ion exchange for the preparation of POF-Zn^{2+}-X^-.

Activated POF-DI (0.5 g) was dispersed in 20 mL of 0.2 M methanol solution of corresponding halide salts. After the mixture was stirred for 12 h, the residue was filtered. Repeated the above step three times, the precipitate was washed with anhydrous methanol (20 ml) five times and dried at 100 °C under vacuum to afford the goal product.

POF-DI& $ZnCl_2$

Activated POF-DI (150 mg) and $ZnCl_2$ (20 mg) were mixed uniformity, and then used as the catalyst.

II Characterization Details

Table S1 Elemental Analysis

POF	C%	H%	N%	S%	Na%	Zn%	S/Zn mole ratio
POF-DI	52.72	4.872	16.90	5.709	5.74	0	/
POF-Zn^{2+}-Cl^-	47.44	4.392	14.55	4.923	0.106	4.48	2.245
POF-Zn^{2+}-Br^-	46.74	4.302	14.38	4.607	0.143	4.23	2.226

POF-Zn^{2+}-I^-	46.33	4.221	14.22	4.564	0.117	4.04	2.309

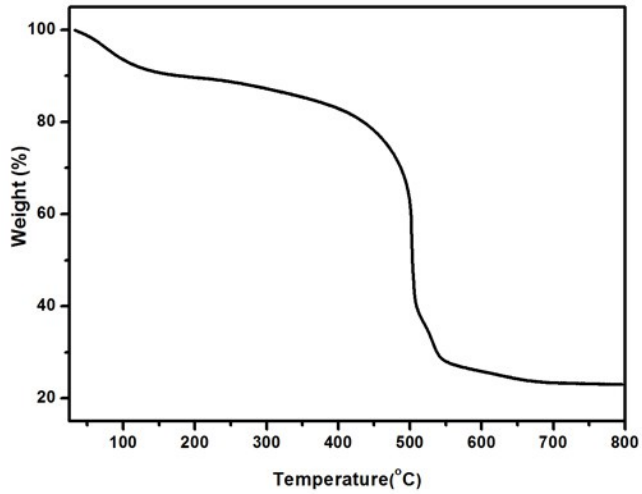


Fig. S1 TGA data of POF-DI.

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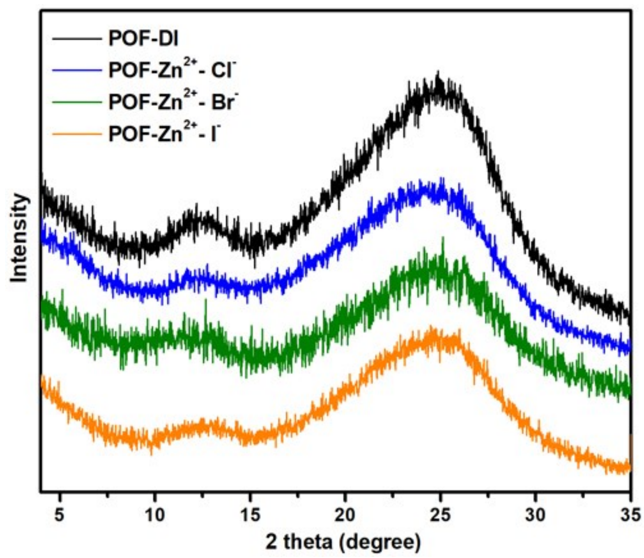


Fig. S2 PXRD patterns of POF-DI, POF-Zn^{2+}-Cl^-, POF-Zn^{2+}-Br^- and POF-Zn^{2+}-I^-.

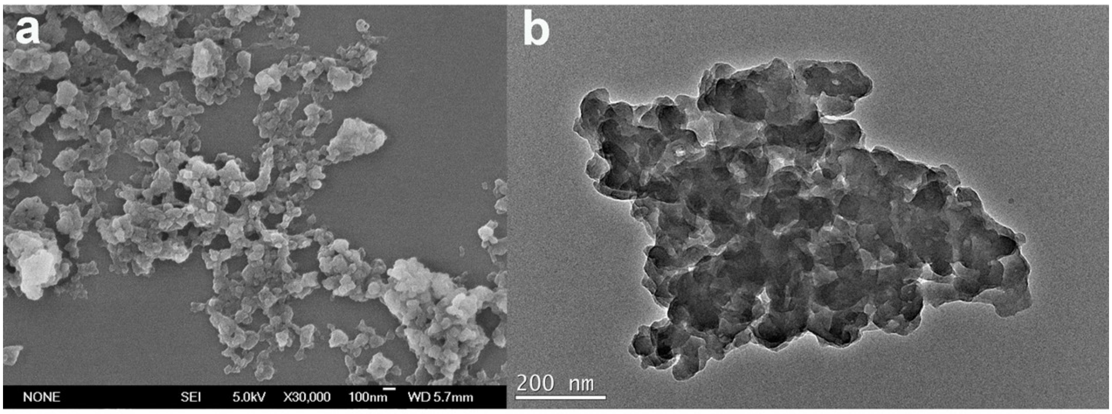


Fig. S3 SEM and TEM images of POF-DI.

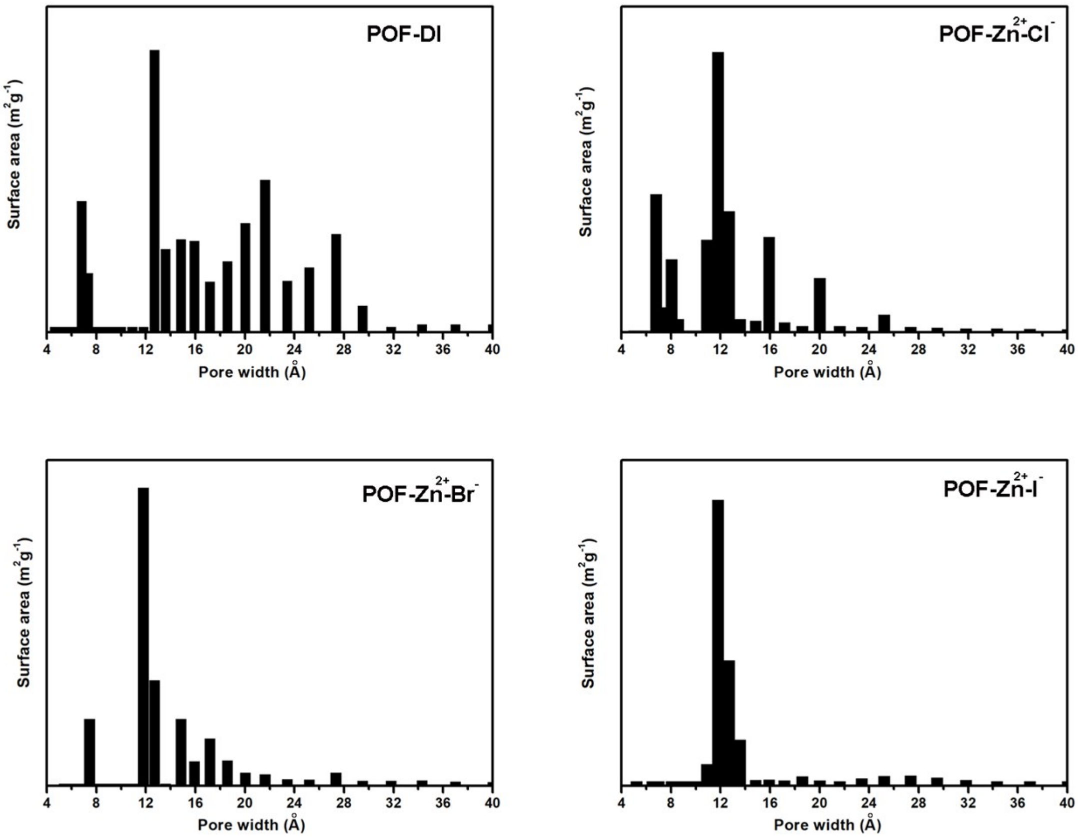


Fig. S4 Pore-size distribution profiles of POF-DI, POF-Zn^{2+}-Cl^-, POF-Zn^{2+}-Br^- and POF-Zn^{2+}-I^-.

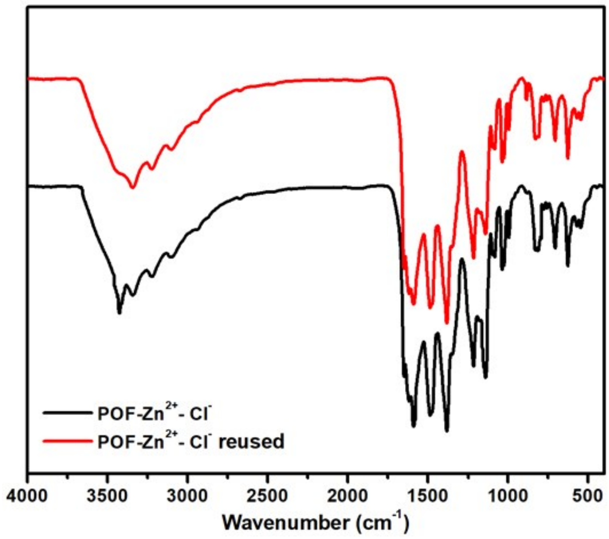


Fig. S5 Comparison of IR spectra of the as-made POF-Zn^{2+}-Cl^{-} sample and the POF-Zn^{2+}-Cl^{-} after catalysis cycles.

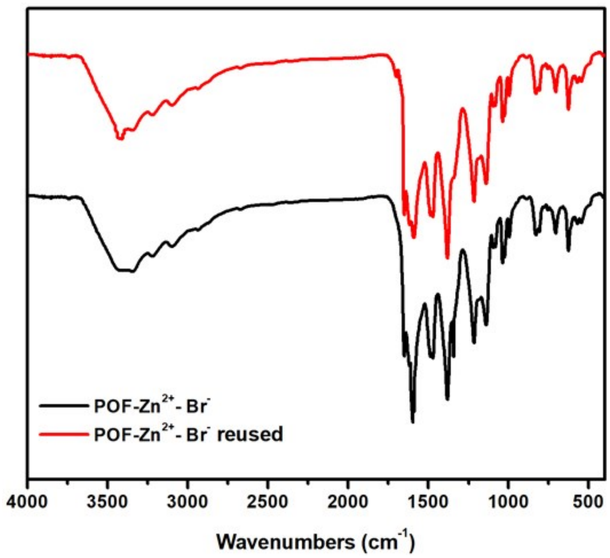


Fig. S6 Comparison of IR spectra of the as-made POF-Zn^{2+}-Br^{-} sample and the POF-Zn^{2+}-Br^{-} after catalysis cycles.

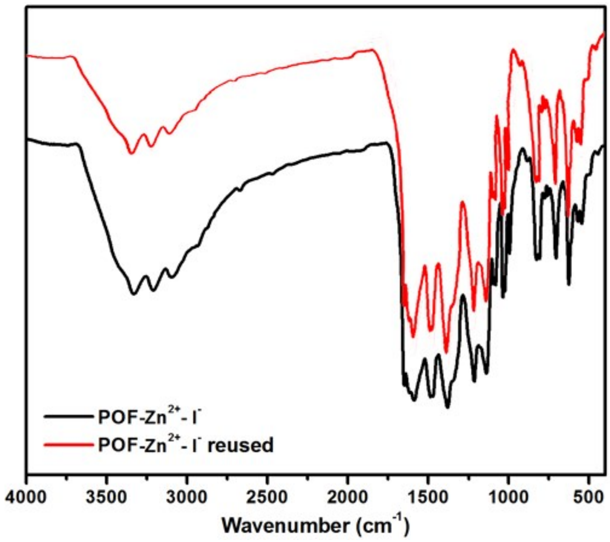


Fig. S7 Comparison of IR spectra of the as-made POF-Zn^{2+}-I^- sample and the POF-Zn^{2+}-I^- after catalysis cycles.

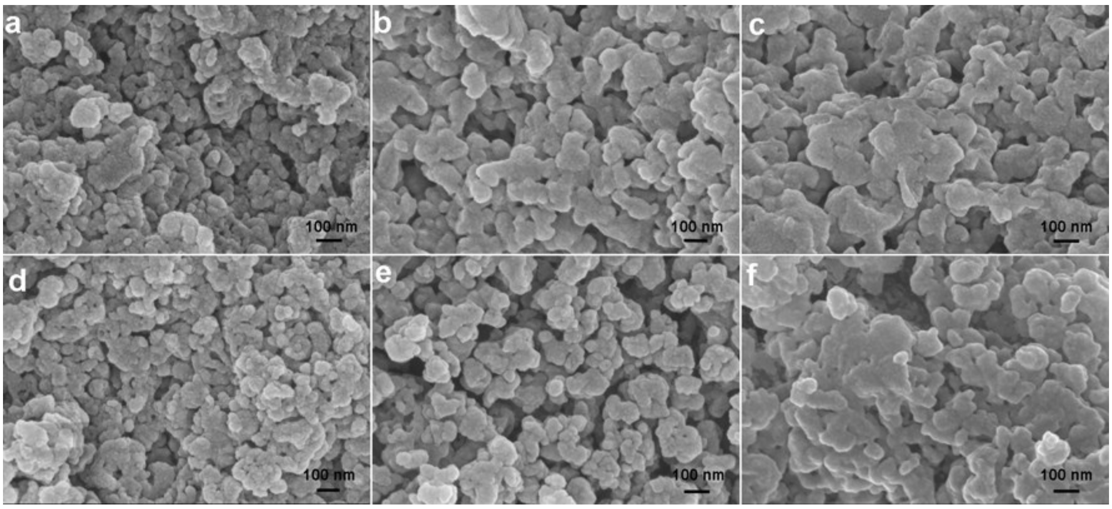


Fig. S8 Comparison of SEM of the as-made POF-Zn^{2+}-Cl^-, POF-Zn^{2+}-Br^-, POF-Zn^{2+}-I^- (a-c) and the POF-Zn^{2+}-Cl^-, POF-Zn^{2+}-Br^-, POF-Zn^{2+}-I^- after catalysis cycles (d-f).

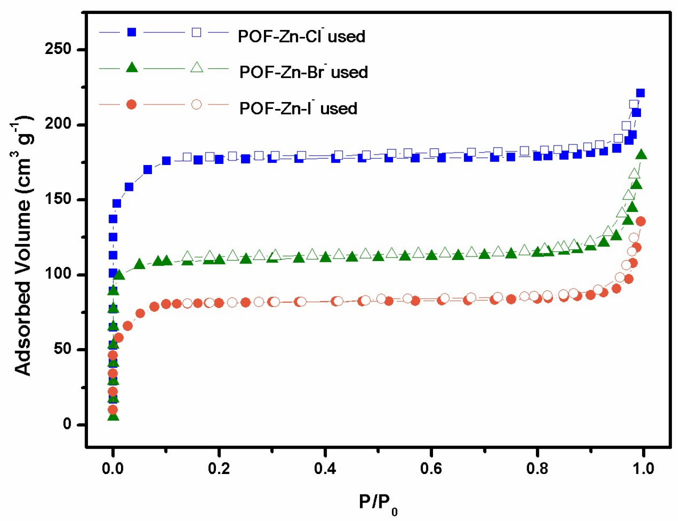


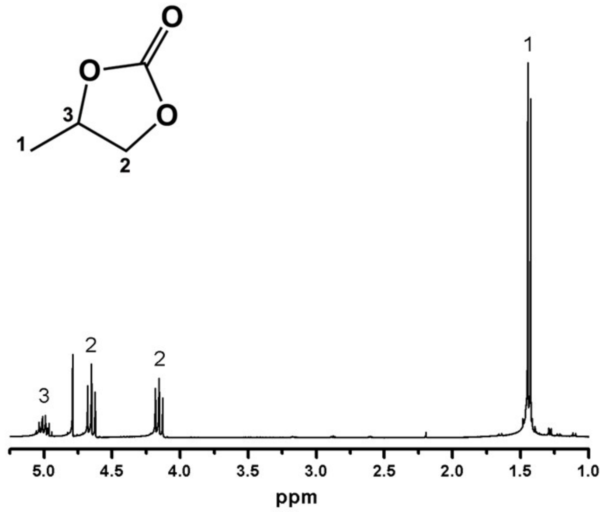
Fig. S9 N_2 adsorption/desorption isotherms of POF-DI, POF-Zn^{2+}-Cl^-, POF-Zn^{2+}-Br^- and POF-Zn^{2+}-I^- after catalysis cycles. BET surface areas of POF-Zn^{2+}-Cl^-, POF-Zn^{2+}-Br^- and POF-Zn^{2+}-I^- are 494 m^2g^{-1}, 312 m^2g^{-1} and 286 m^2g^{-1}.

Table S2 A comparison table for the present POF-Zn catalysts

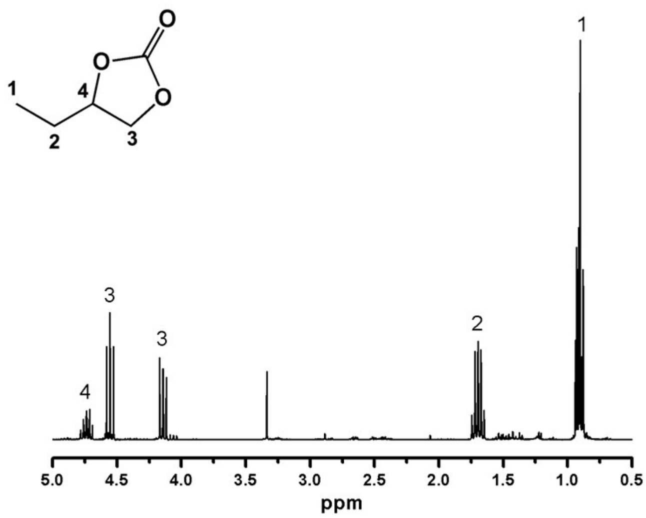
Entry	**Catalyst**	**Co-catalyst**	**Temperature (°C)**	**Pressure(MPa)**	**Yield (%)**	**Reference**
1	POF-Zn^{2+}-I^-	None	60	1	99	This work
2	Zn/HAzo-POP-1	TBAB	100	3	98	1
3	Bp-Zn@MA	TBAB	100	1	99	2
4	P-POF-Zn	TBAB	100	1.5	99	3
5	Zn@ah-PMF	TBAB	100	2	99	4
6	PAF-$ZnBr_2$	TBAB	90	1	95	5

III Characterization Data of Catalytic Products

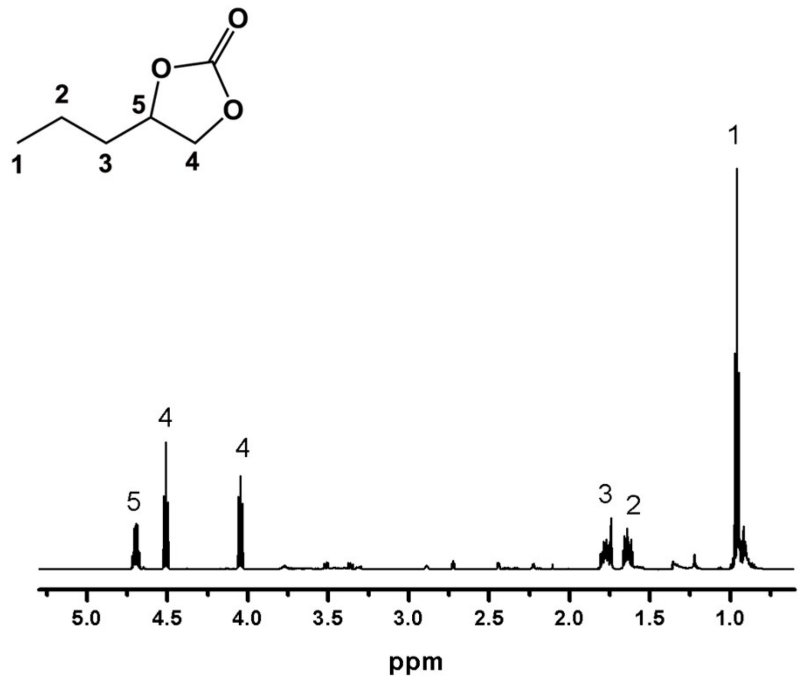
[1]H NMR Spectra of Catalytic Products



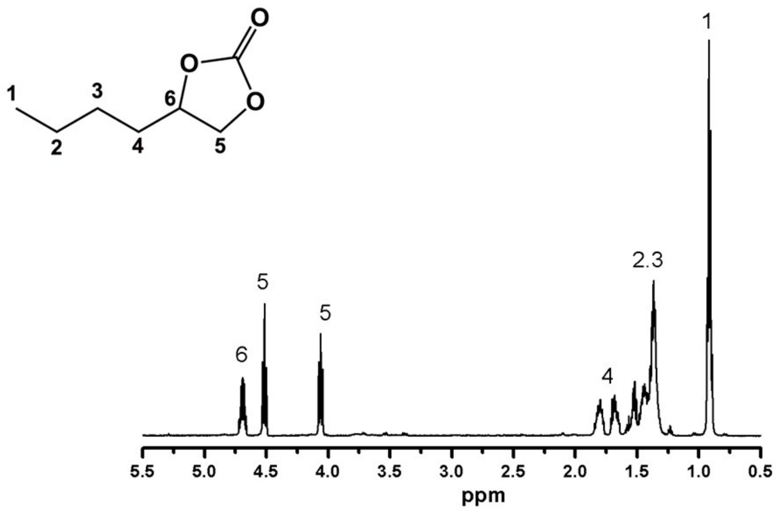
propylene carbonate (CD_4O, 400 MHz)



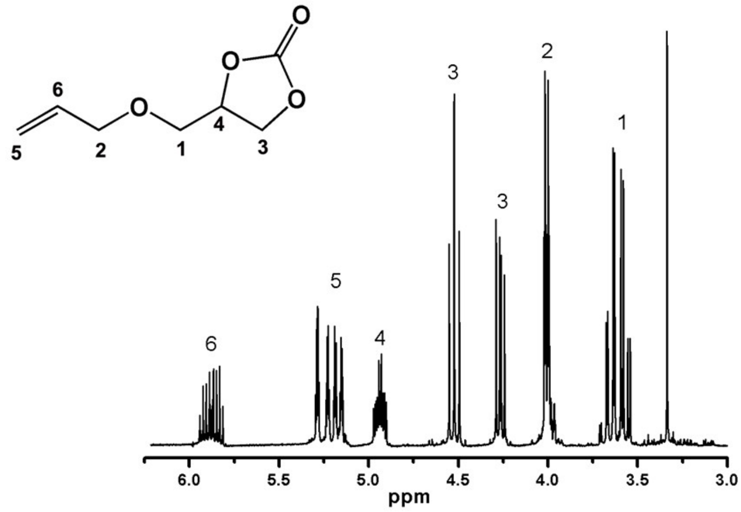
4-Ethyl-1,3-dioxolan-2-one (CD_4O, 400 MHz)



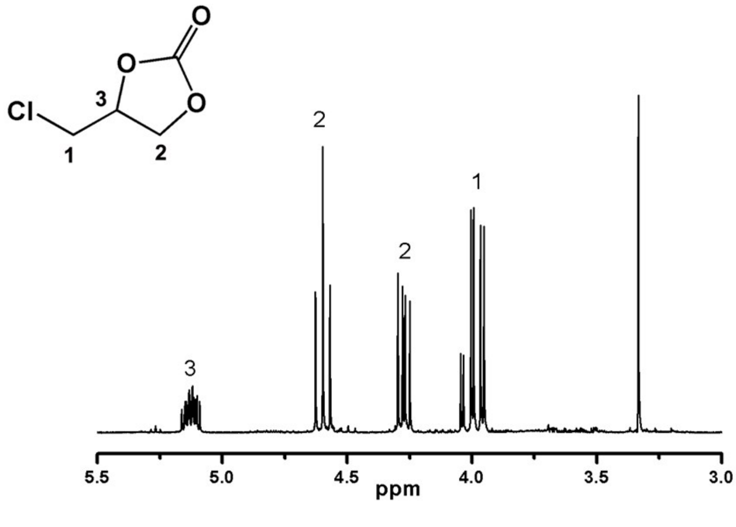
4-Propyl-1,3-dioxolan-2-one ($CDCl_3$, 400 MHz)



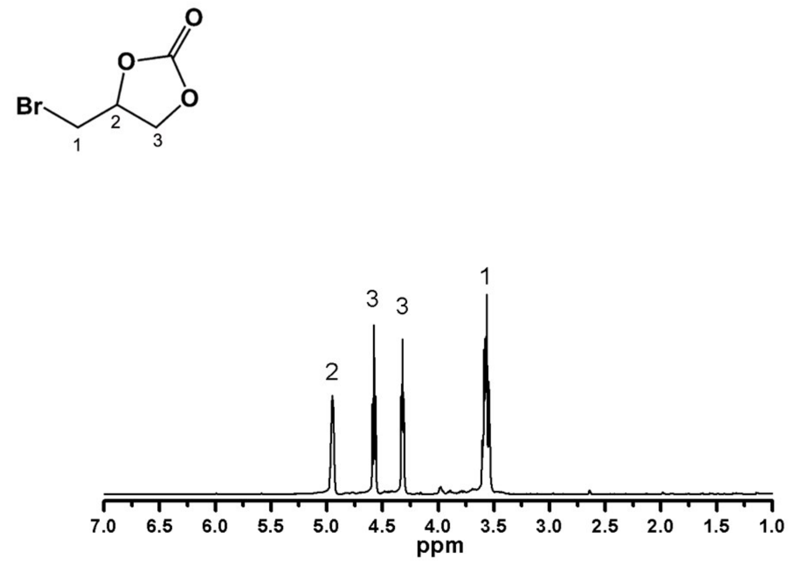
4-Butyl-1,3-dioxolan-2-one ($CDCl_3$, 400 MHz)



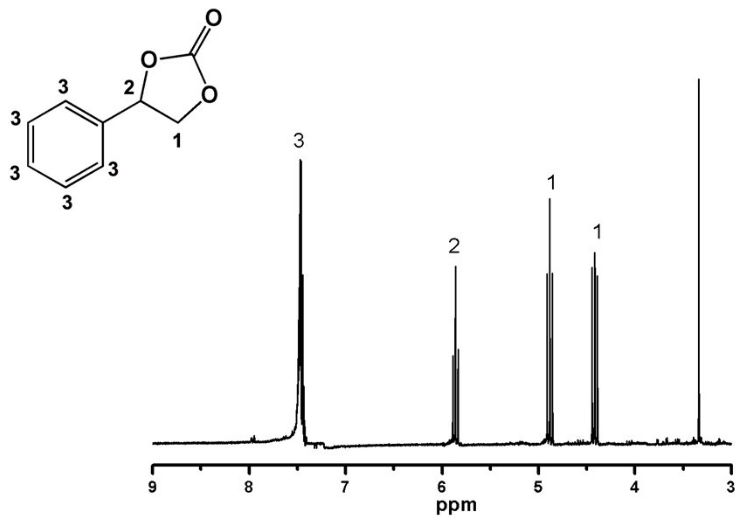
1,3-Dioxolan-2-one (CD_4O, 400 MHz)



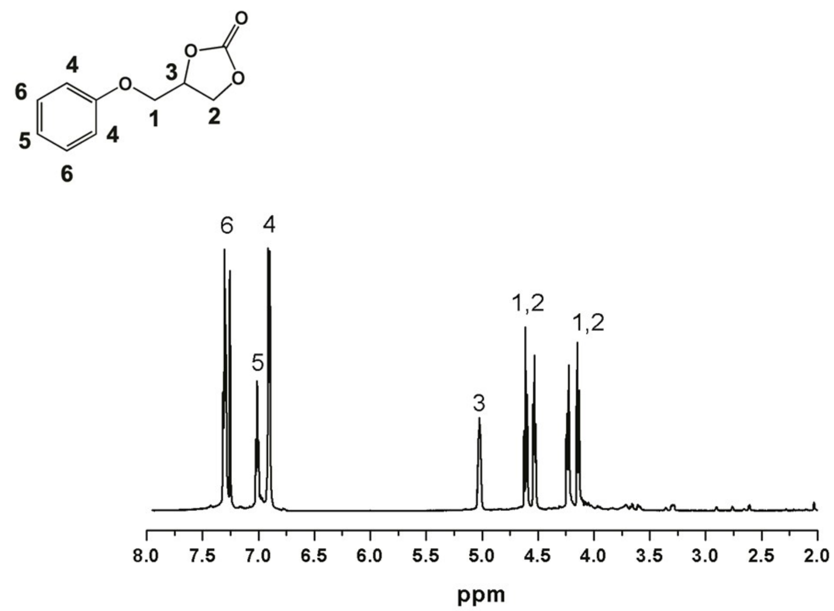
4-(chloromethyl)-1,3-dioxolan-2-one (CD_4O, 400 MHz)



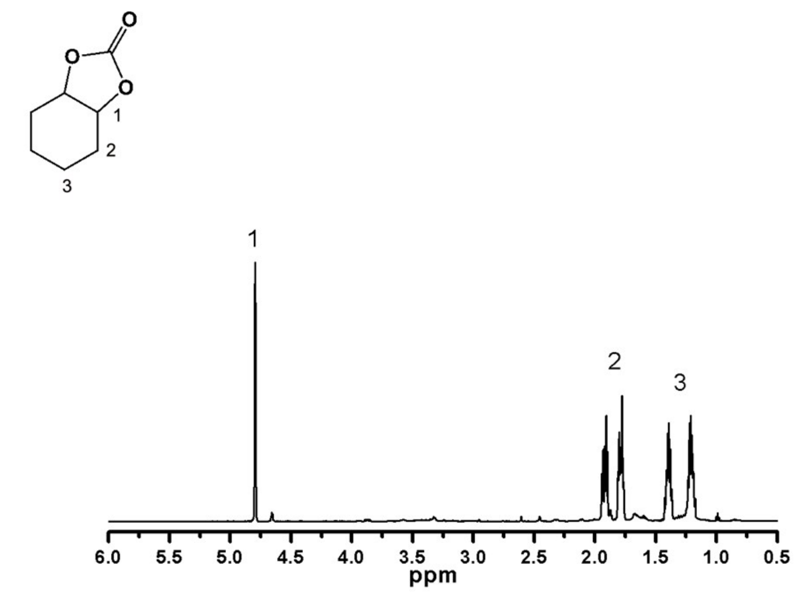
4-(Bromomethyl)-1,3-dioxolan-2-one ($CDCl_3$, 400 MHz)



4-phenyl-1, 3-dioxolan-2-one (CD_4O, 400 MHz)

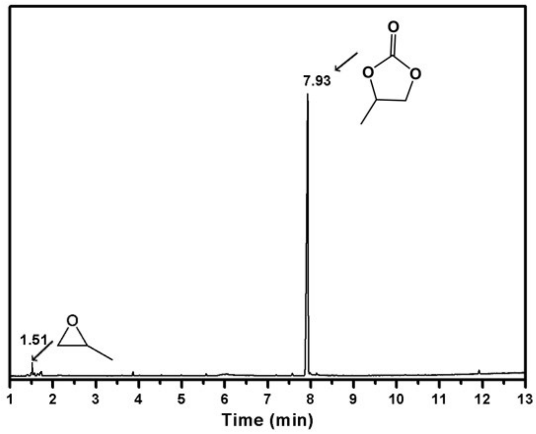


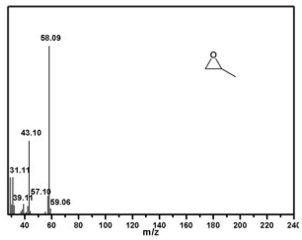
4-(phenoxymethyl)-1, 3-dioxolan-2-one ($CDCl_3$, 400 MHz)

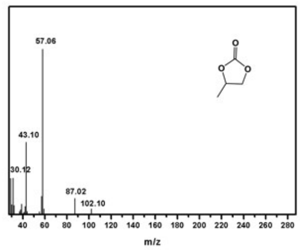


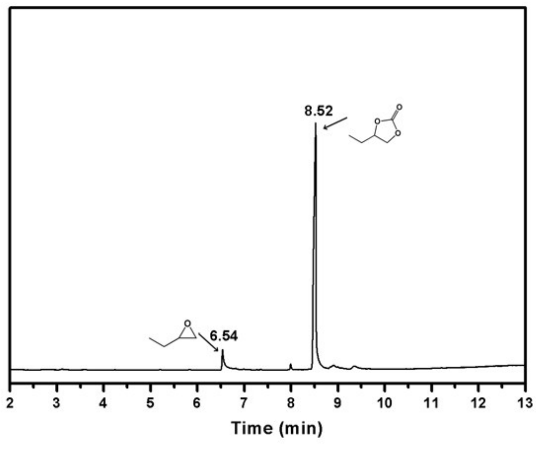
1, 3-Benzodioxol-2-one ($CDCl_3$, 400 MHz)

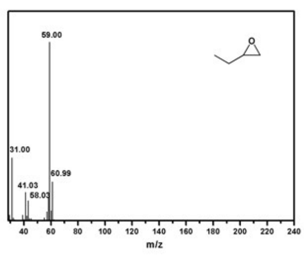
GC-MS Analysis of Catalytic Products

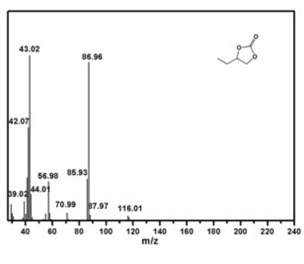


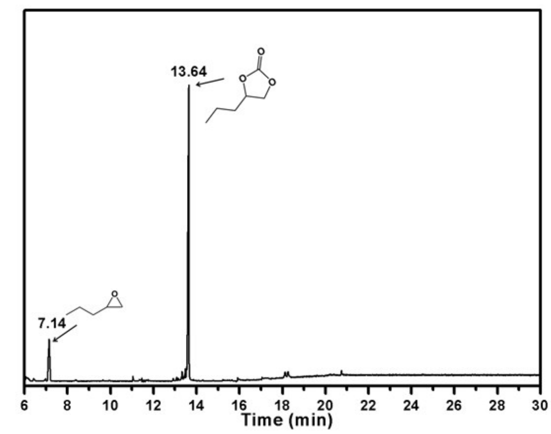








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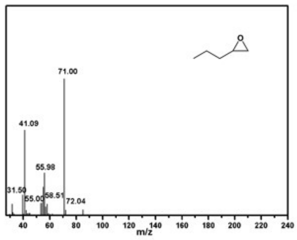
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55.98
31.50
55.00
58.51
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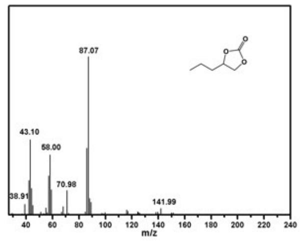
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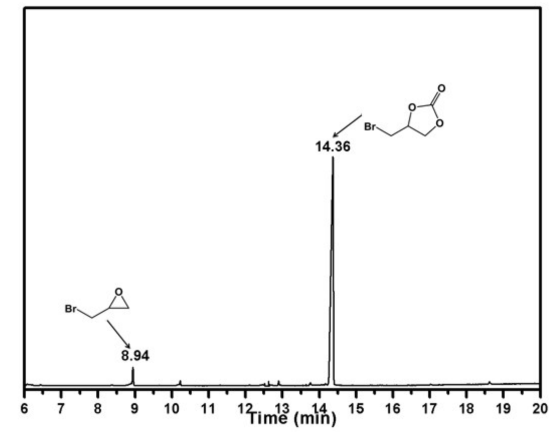
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14.36
Br
8.94
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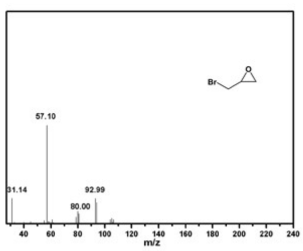
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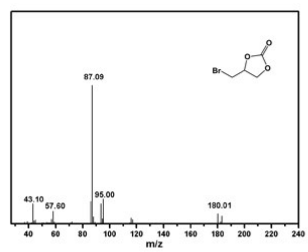
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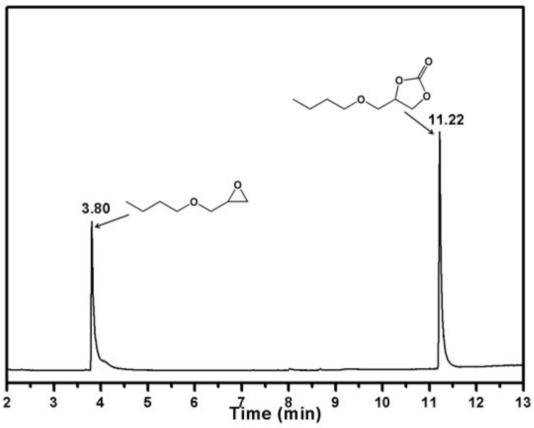
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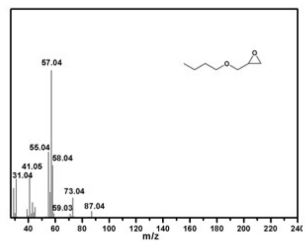
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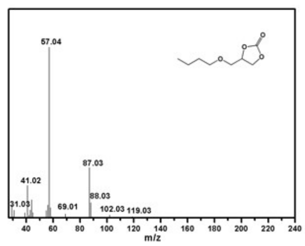
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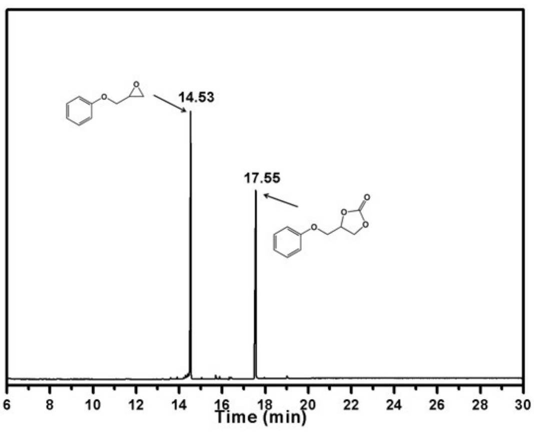
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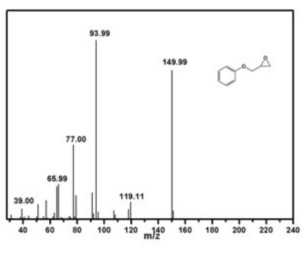
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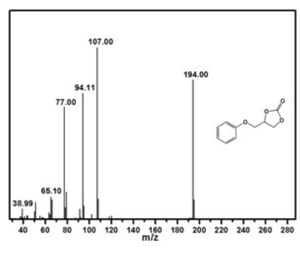
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m/z

References

1. G. Ji, Z. Yang, H. Zhang, Y. Zhao, B. Yu, Z. Ma and Z. Liu, *Angew. Chem. Int. Ed.,* 2016, **55**, 9685-9689.
2. J. Chen, H. Li, M. Zhong and Q. Yang, *Green Chem.,* 2016, **18**, 6493-6500.
3. J. Chen, M. Zhong, L. Tao, L. Liu, S. Jayakumar, C. Li, H. Li and Q. Yang, *Green Chem.,* 2018, **20**, 903-911.
4. J. Yin, T. Zhang, E. Schulman, D. Liu and J. Meng, *J. Mater. Chem. A,* 2018, **6**, 8441-8448.
5. J. Wang and Y. Zhang, *Green Chem.,* 2016, **18**, 5248-5253.