Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2022

Electronic Supplementary Information

Quaternization-induced catalyst-free synthesis of viologen-linked ionic polyacetylenes towards heterogeneous catalytic CO_2 fixation

Zixuan Xu, Ke Liu, He Huang, Yadong Zhang, Minman Tong, Zhouyang Long and Guojian Chen*

School of Chemistry and Materials Science, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, 221116, China.

*Corresponding author, E-mail: gjchen@jsnu.edu.cn

Table S1 The solubility of a series of VIPA-X-T solid materials.*

Sample	Polymer yield (%)	H_2O (RT)	H_2O (80 °C)	DMSO (RT)	DMSO (80 °C)
VIPA-Br-30	53	×	partially soluble	×	completely soluble
VIPA-Br-60	81	×	slightly soluble	×	partially soluble
VIPA-Br-80	86	×	×	×	slightly soluble
VIPA-Br-100	**91**	×	×	×	×
VIPA-Cl-30	40	×	partially soluble	×	completely soluble
VIPA-Cl-60	59	×	slightly soluble	×	partially soluble
VIPA-Cl-80	72	×	×	×	slightly soluble
VIPA-Cl-100	**87**	×	×	×	×

* The solubility tests were carried out by placing 10 mg the back polymer in 5 mL water or DMSO at room temperature (RT) or 80 ℃ with stirred for 30 min. The results for the solubility of VIPA-X-T were together determined by the color of solutions and the mass of the remaining solid polymers after centrifugation.

"×" represents insoluble.

Table S2 The elemental compositions of VIPA-Cl and VIPA-Br and the reused catalyst VIPA-Br-R detected from the XPS spectra. [a]

Samples	C (at%)	N (at%)	O (at%)	Cl (at%)	Br (at%)
VIPA-Cl	77.38	8.91	7.13	6.57	-
VIPA-Br	77.22	8.97	5.71	-	8.11
VIPA-Br-R	77.34	9.55	4.53	-	8.57

[a] All elemental compositions were presented by the atomic concentration (at%).

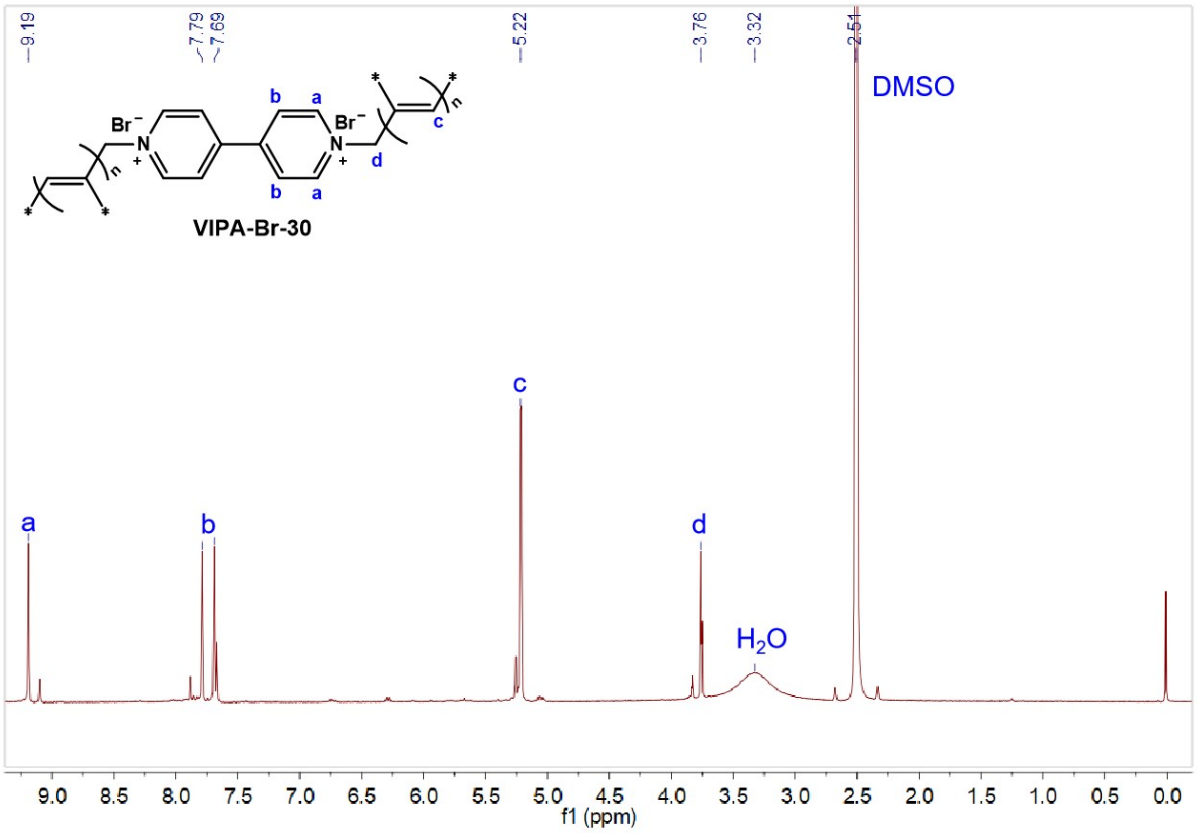


Fig. S1 [1]H NMR spectrum of VIPA-Br-30 in DMSO-d_6.

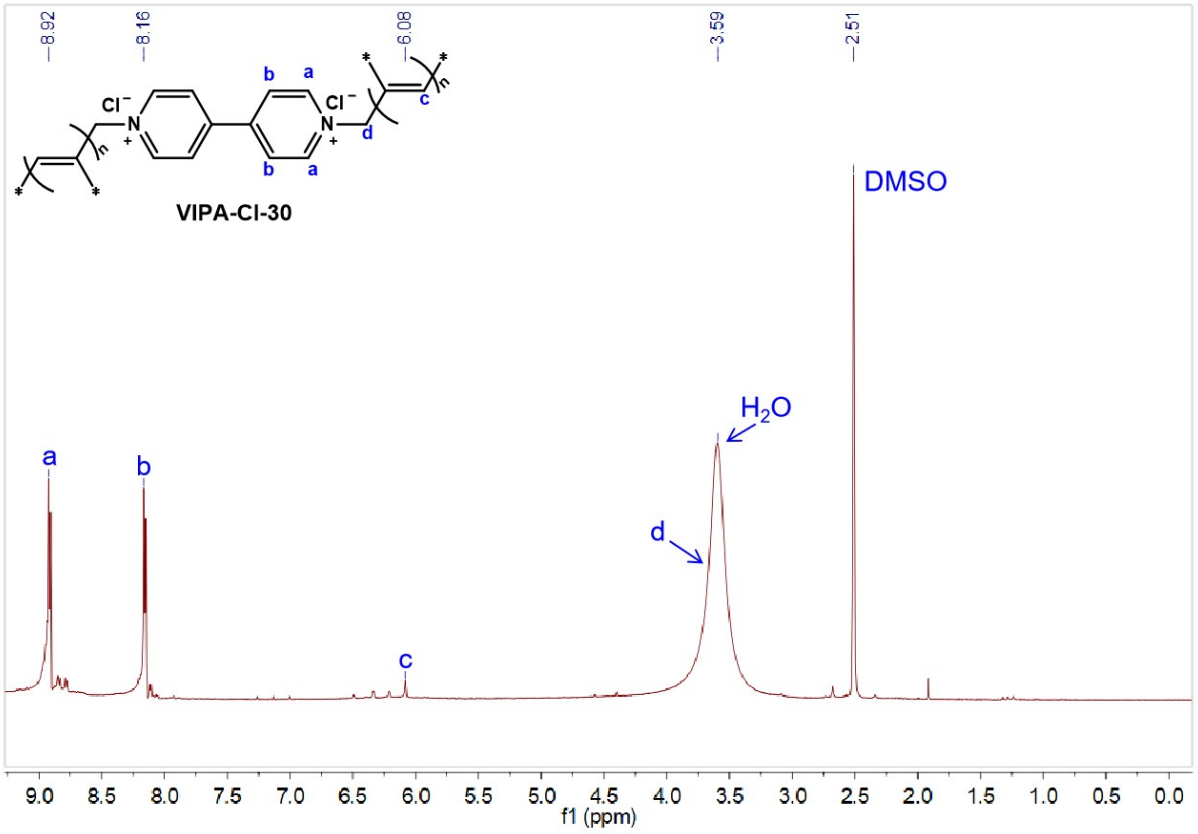


Fig. S2 [1]H NMR spectrum of VIPA-Cl-30 in DMSO-d_6.

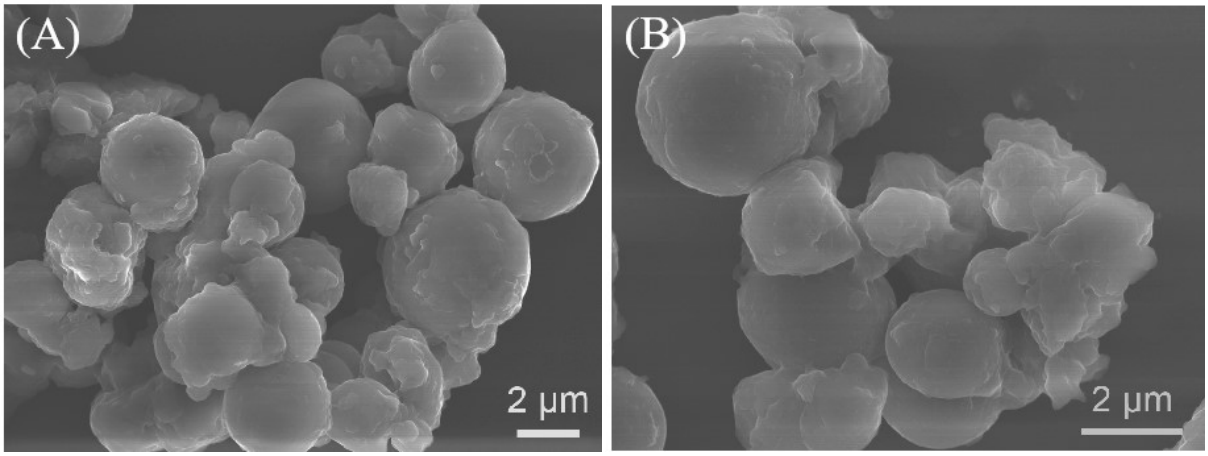


Fig. S3 SEM images of (A) VIPA-Br and (B) VIPA-Cl.

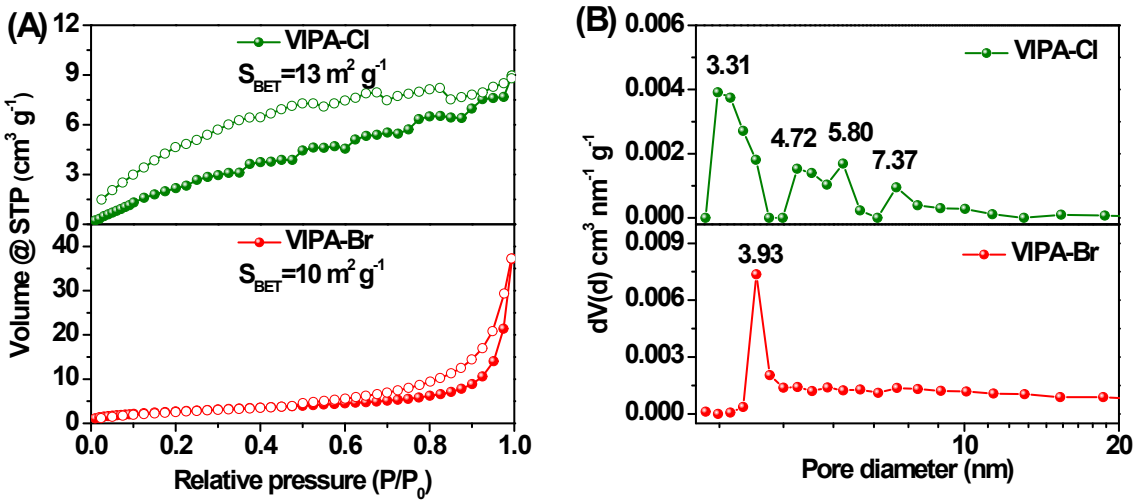


Fig. S4 (A) N_2 adsorption-desorption isotherms and (B) BJH pore size distributions of VIPA-Br and VIPA-Cl.

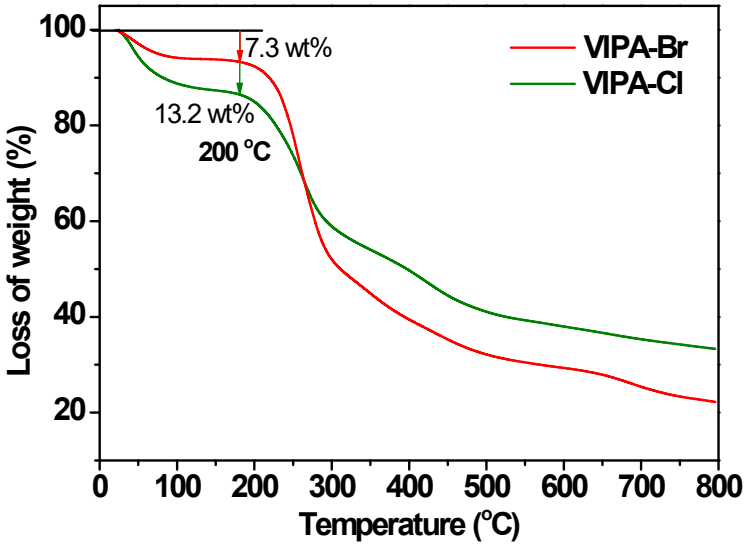


Fig. S5 Thermogravimetric analysis (TGA) curves of VIPA-Br and VIPA-Cl.

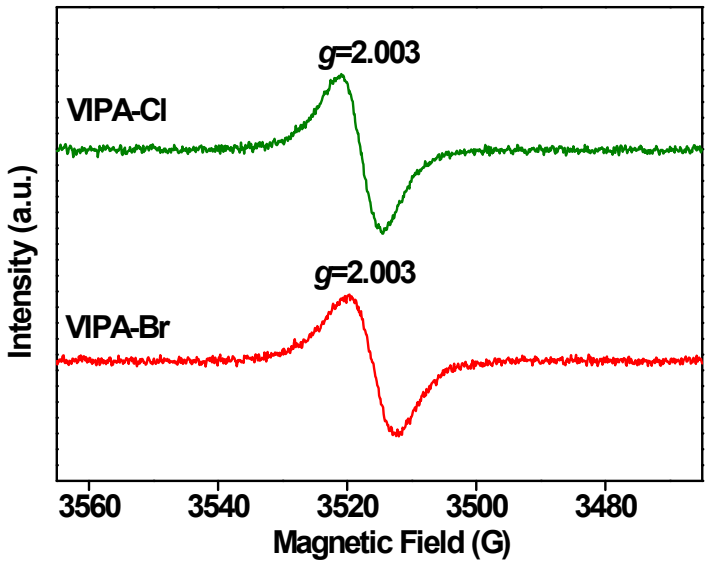
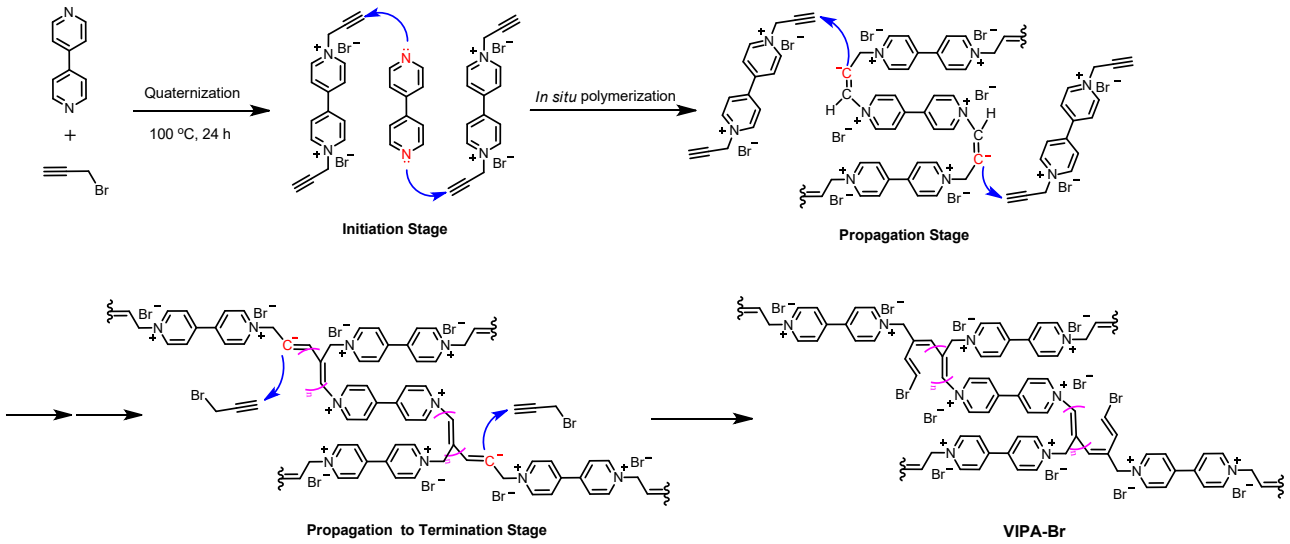


Fig. S6 Solid-state EPR spectra of VIPA-Br and VIPA-Cl at the X-band under room temperature.



Scheme S1 A proposed polymerization mechanism for the synthesis of VIPA-Br.

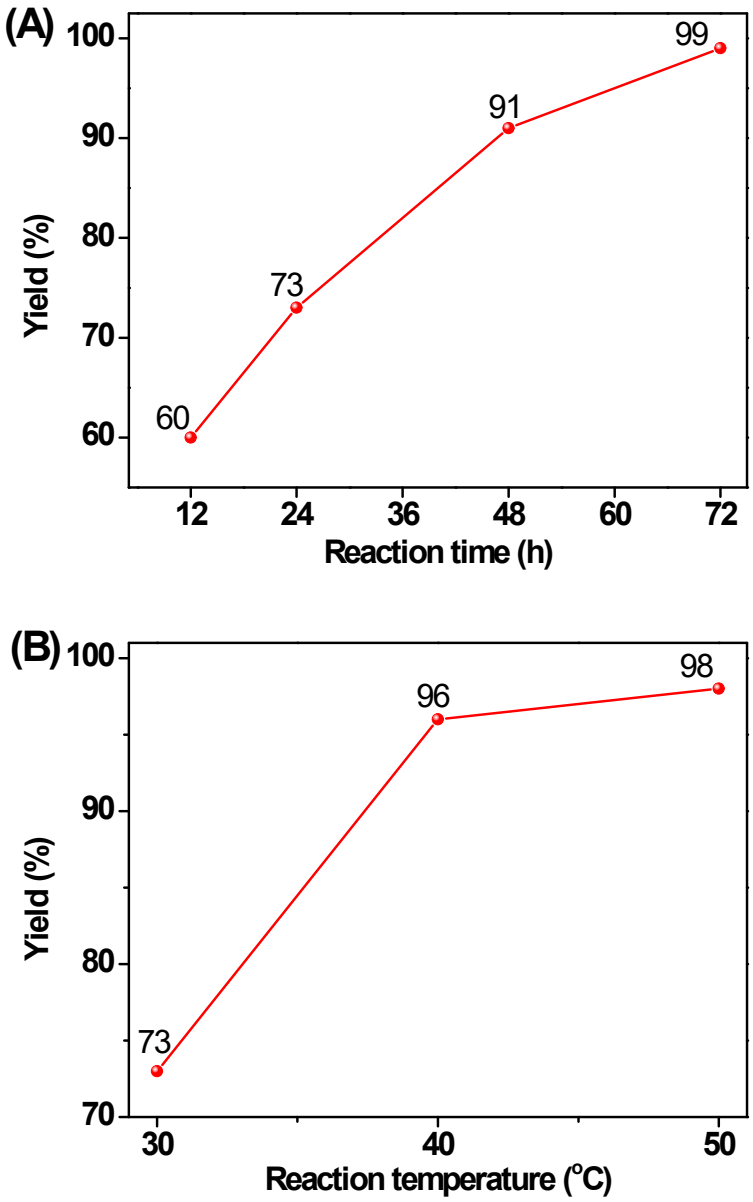


Fig. S7 (A) Kinetic curve: reaction time effect of VIPA-Br for the conversion of CO_2 with epichlorohydrin. Reaction conditions: epichlorohydrin (2 mmol), catalyst (40 mg), CO_2 balloon (0.1 MPa), 30 °C, 12-72 h. (B) Reaction temperature effect of VIPA-Br for the conversion of CO_2. Reaction conditions: epichlorohydrin (2 mmol), catalyst (40 mg), CO_2 balloon (0.1 MPa), 30-50 °C, 24 h.

Table S3 The detailed comparisons of the catalytic activity over various metal-free iPOPs and iPOPs with HBD groups or metal sites heterogeneous catalysts in the CO_2 fixation with ECH without any co-catalysts.[#]

Catalyst	CO_2 pressure (MPa)	Temperature (°C)	Time (h)	Yield (%)	Ref.
PCP-Cl	3	100	12	98	S1
cCTF-500	1	90	12	95	S2
PS-Cat 5	1	45	18	94	S3
CCTF-350	0.1	120	24	93.1	S4
PDMBr	0.1	120	12	91.3	S5
COP-222	0.1	100	24	99	S6
CPP-IL0.05	0.1	100	24	99	S7
IP3	0.1	100	24	99	S8
PDBA-Cl-SCD	0.1	90	6	99.3	S9
PVIm-6-SCD	0.1	50	24	98.2	S10
HIP-Br-2	0.1	70	96	90	S11
V-PCIF-Br	0.1	80	72	97	S12
V-iPHP-1	0.1	60	72	99	S13
Phen$^{\bullet+}$-PHP-2Br	0.1	60	72	99	S14
VIP-Br	0.1	40	72	99	S15
PIP-Bn-Cl	0.1	25	80	94.7	S16
VIPA-Br	**0.1**	**40**	**24**	**96**	**This work**
VIPA-Br	**0.1**	**30**	**72**	**99**	**This work**
PGDBr-5-2OH	0.1	70	24	91	S17
PPS-mOH-Bn	0.1	50	72	78	S18
POF-PNA-Br	0.1	40	48	94.1	S19
IMIN-Br-OH	0.1	40	72	99	S20
NHC-CAP-1(Zn^{2+})	2	100	3	97	S21
Al-iPOP-1	1	40	6	99	S22
Co-HIP	0.1	80	20	99	S23
$ZnBr_2$@Bpy-PHP-4	0.1	80	72	99	S24
iPHCP-22	0.1	60	60	99	S25
Py-Im-6-Zn-5-SCD	0.1	30	18	97	S26
CPIP-A-4	0.1	30	12	95	S27

[#] It should be pointed out that different catalysts were evaluated under different conditions. Thus, it is difficult to directly compare the activity between different catalytic systems. The represented catalytic activities using yields of the product in Table S3 should be considered in a reasonable comparison.

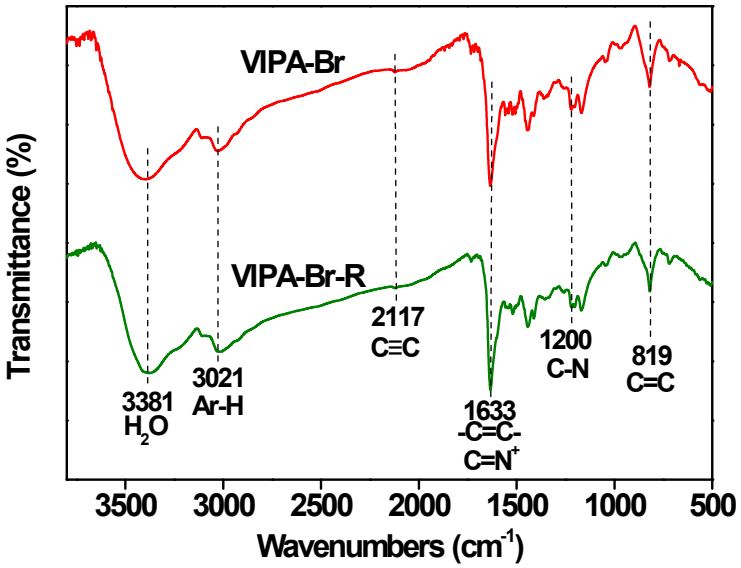


Fig. S8 FTIR of the fresh catalyst VIPA-Br and the reused catalyst VIPA-Br-R.

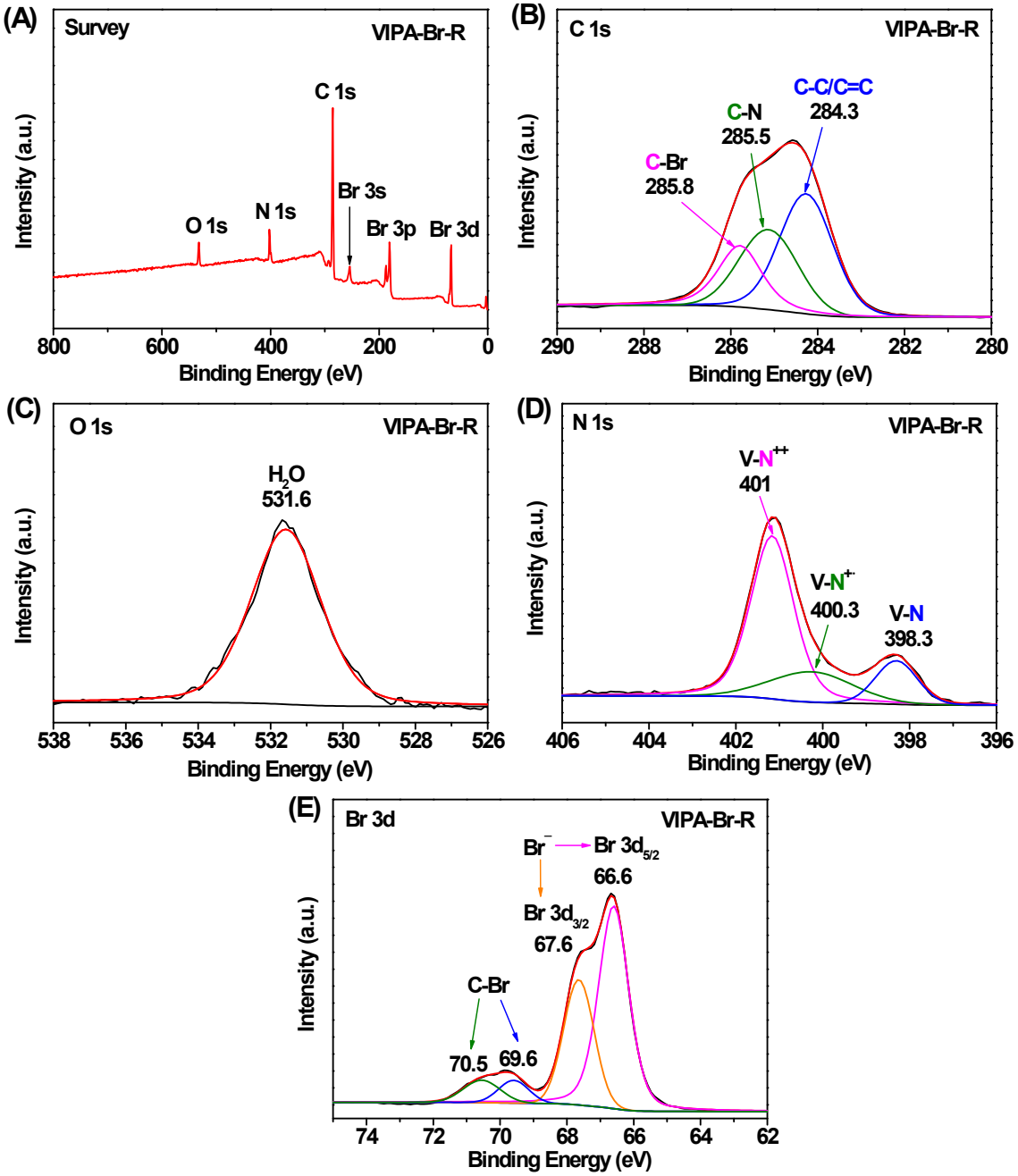


Fig. S9 XPS spectra of the reused catalyst VIPA-Br-R: (A) Survey, (B) C 1s, (C) O 1s, (D) N 1s and (E) Br 3d.

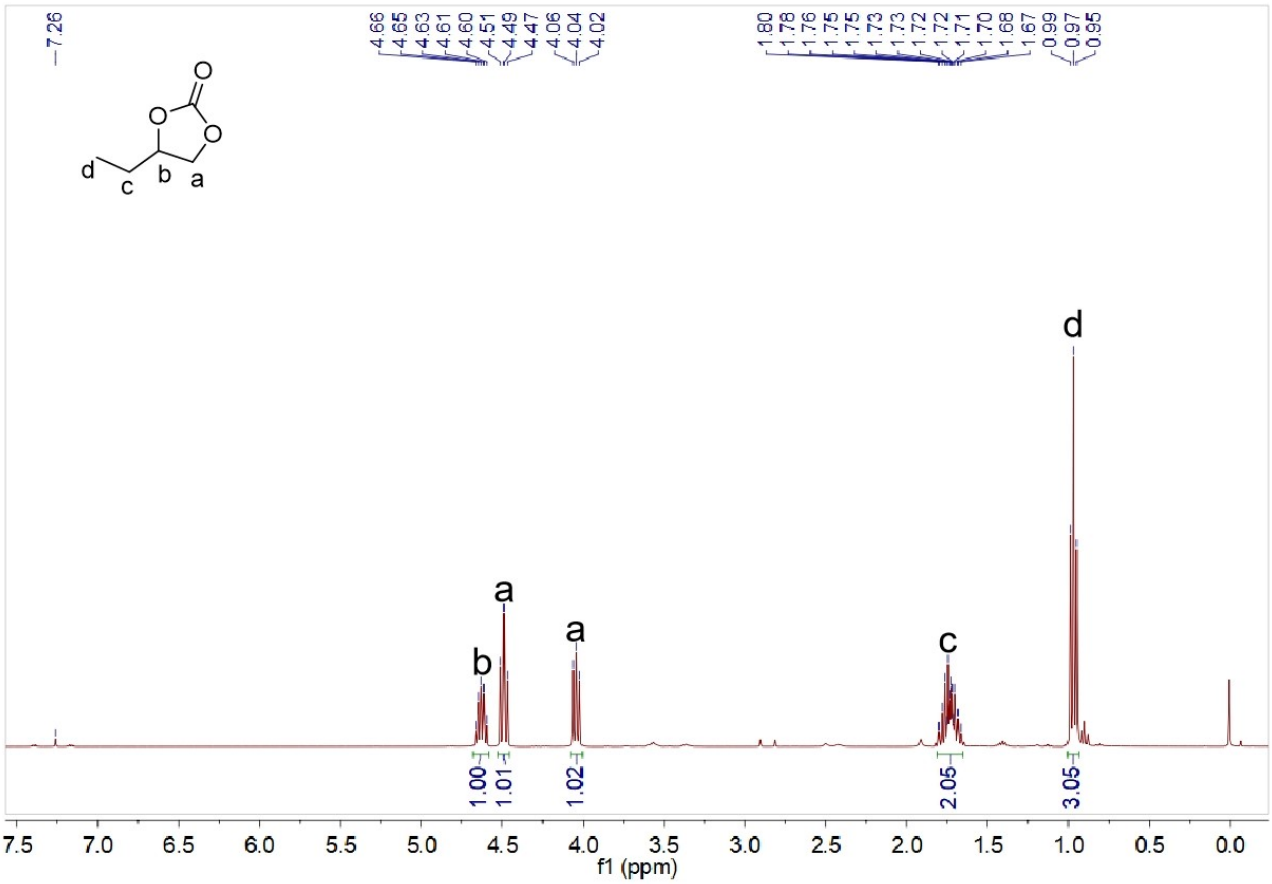


Fig. S10 ^{1}H NMR spectrum of 4-ethyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.66~4.60 (1H, CH), 4.51~4.47 (1H, CH_2), 4.06~4.02 (1H, CH_2), 1.80~1.67 (2H, CH_2), 0.99~0.95 ppm (3H, CH_3). Reaction conditions: VIPA-Br, 30 °C, 72 h, yield of 99%, selectivity of 99%.

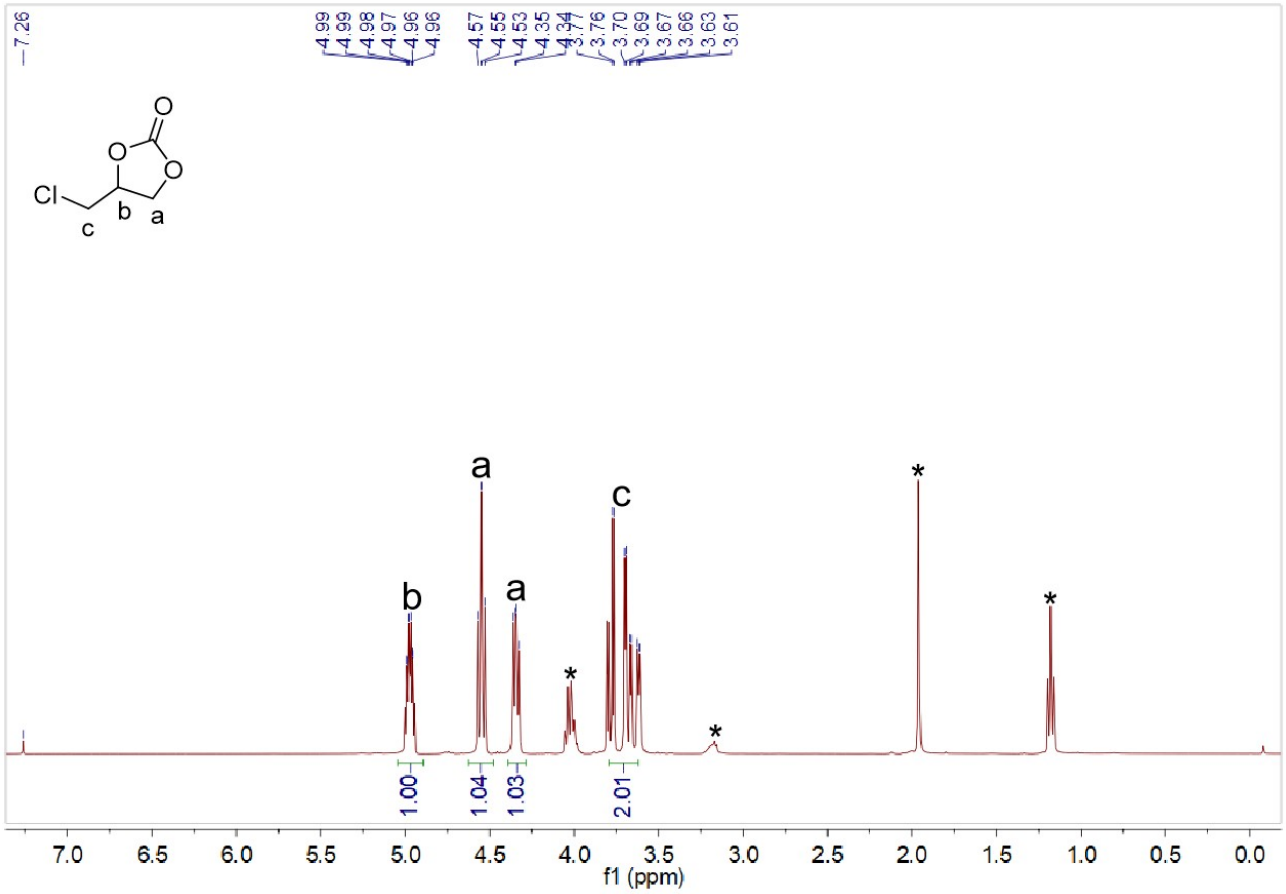


Fig. S11 ^{1}H NMR spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.99~4.96 (1H, CH), 4.57~4.53 (1H, CH_2), 4.35~4.34 (1H, CH_2), 3.77~3.61 ppm (2H, CH_2). * represents the residual solvent ethyl acetate. Reaction conditions: VIPA-Br, 30 ℃, 72 h, yield of 99%, selectivity of 99%.

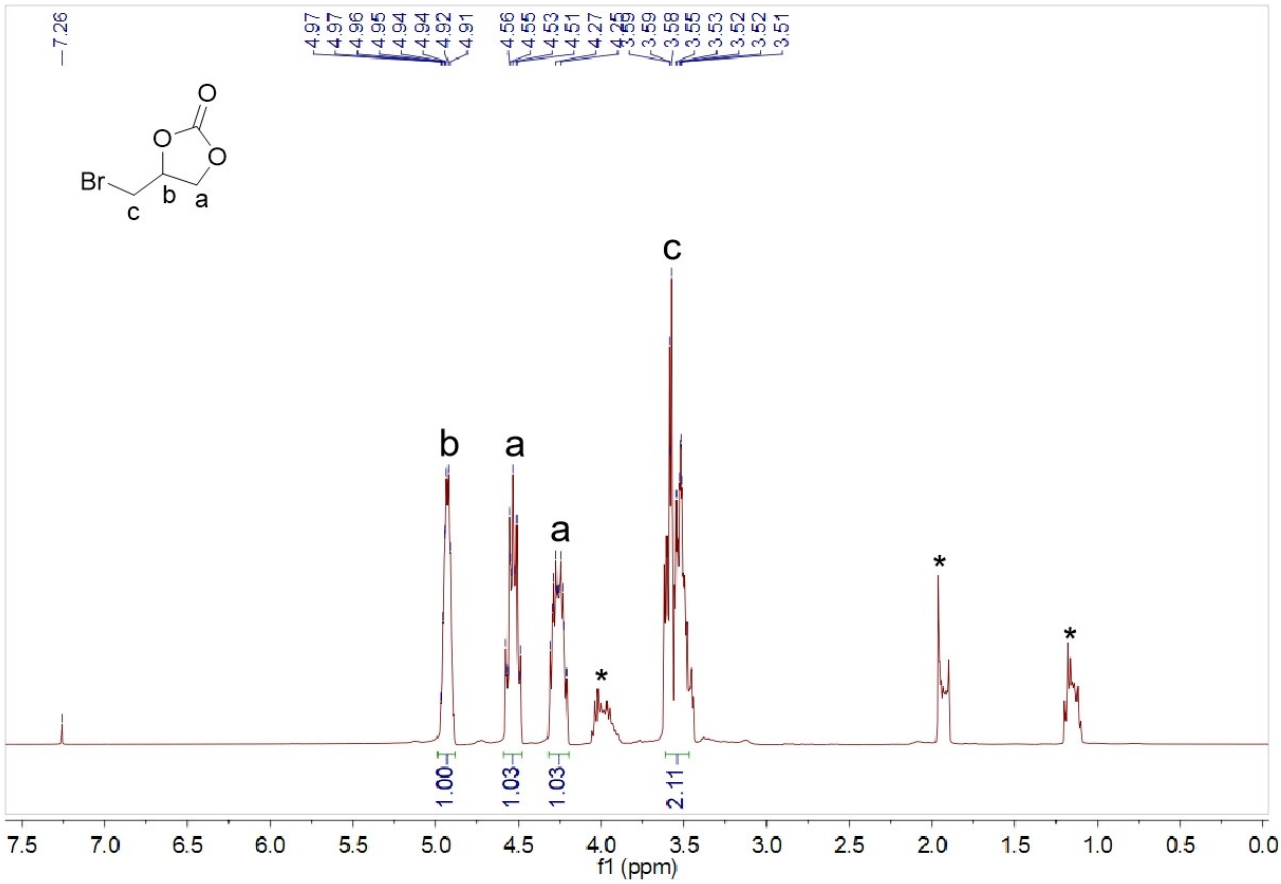


Fig. S12 ^{1}H NMR spectrum of 4-(bromomethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.97~4.91 (1H, CH), 4.56~4.51 (1H, CH_2), 4.27~4.25 (1H, CH_2), 3.59~3.51 ppm (2H, CH_2). * represents the residual solvent ethyl acetate. Reaction conditions: VIPA-Br, 40 ℃, 48 h, yield of 99%, selectivity of 99%.

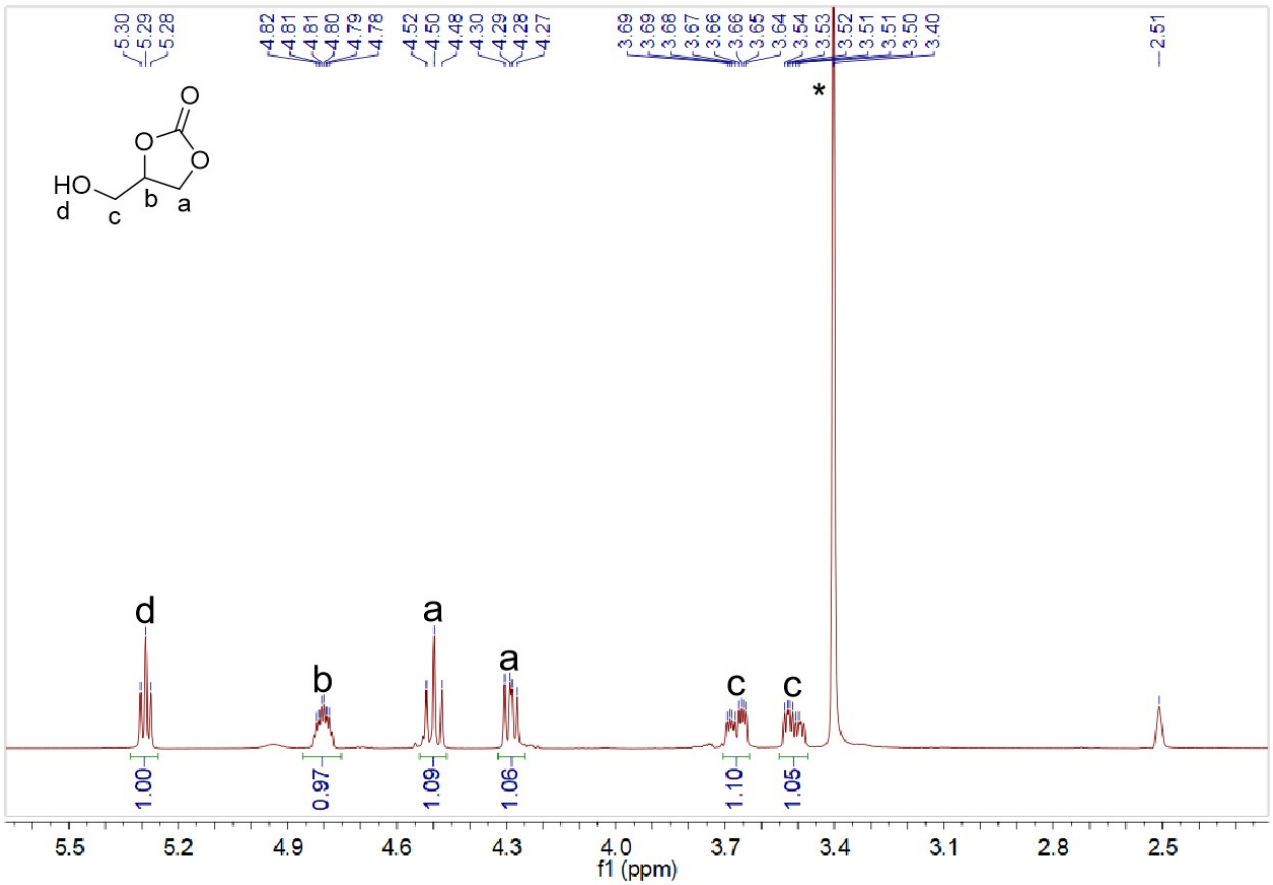


Fig. S13 ^{1}H NMR spectrum of 4-(hydroxymethyl)-1,3-dioxolan-2-one (400 MHz, d_6-DMSO): δ=5.30~5.28 (1H, OH), 4.82~4.78 (1H, OCH), 4.52~4.48 (1H, CH_2O), 4.30~4.27 (1H, CH_2O), 3.69~3.64 (1H, CH_2OH), 3.54~3.50 ppm (1H, CH_2OH). * represents the residual water. Reaction conditions: VIPA-Br, 40 ℃, 48 h, the isolated yield of 98%, selectivity of 98%.

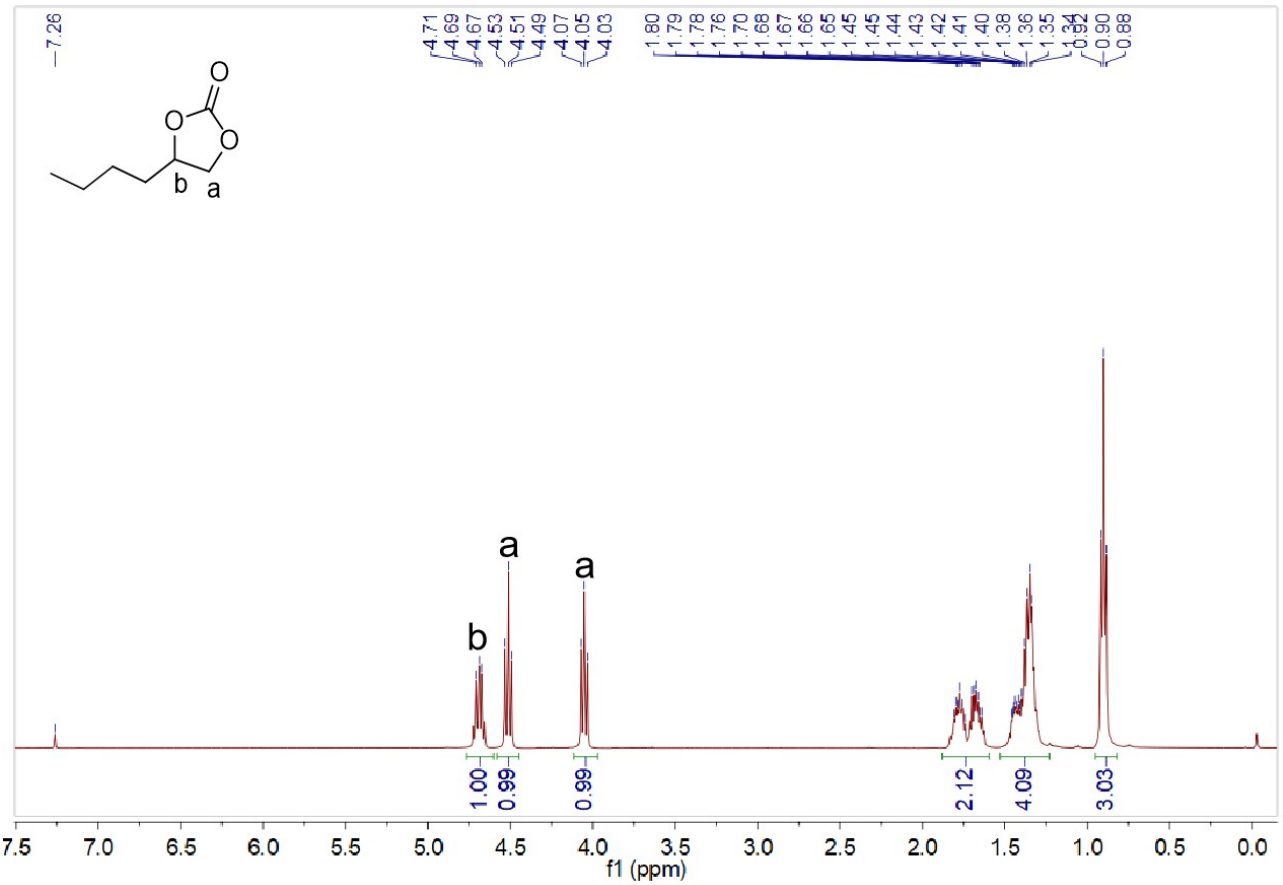


Fig. S14 ^{1}H NMR spectrum of 4-butyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=4.71~4.67 (1H, CH_2), 4.53~4.49 (1H, CH_2), 4.07~4.03 (1H, CH_2), 1.80~1.65 (2H, CH_2), 1.45~1.34 (4H, CH_2), 0.92~0.88 ppm (3H, CH_3). Reaction conditions: VIPA-Br, 80 ℃, 72 h, the isolated yield of 98%, selectivity of 98%.

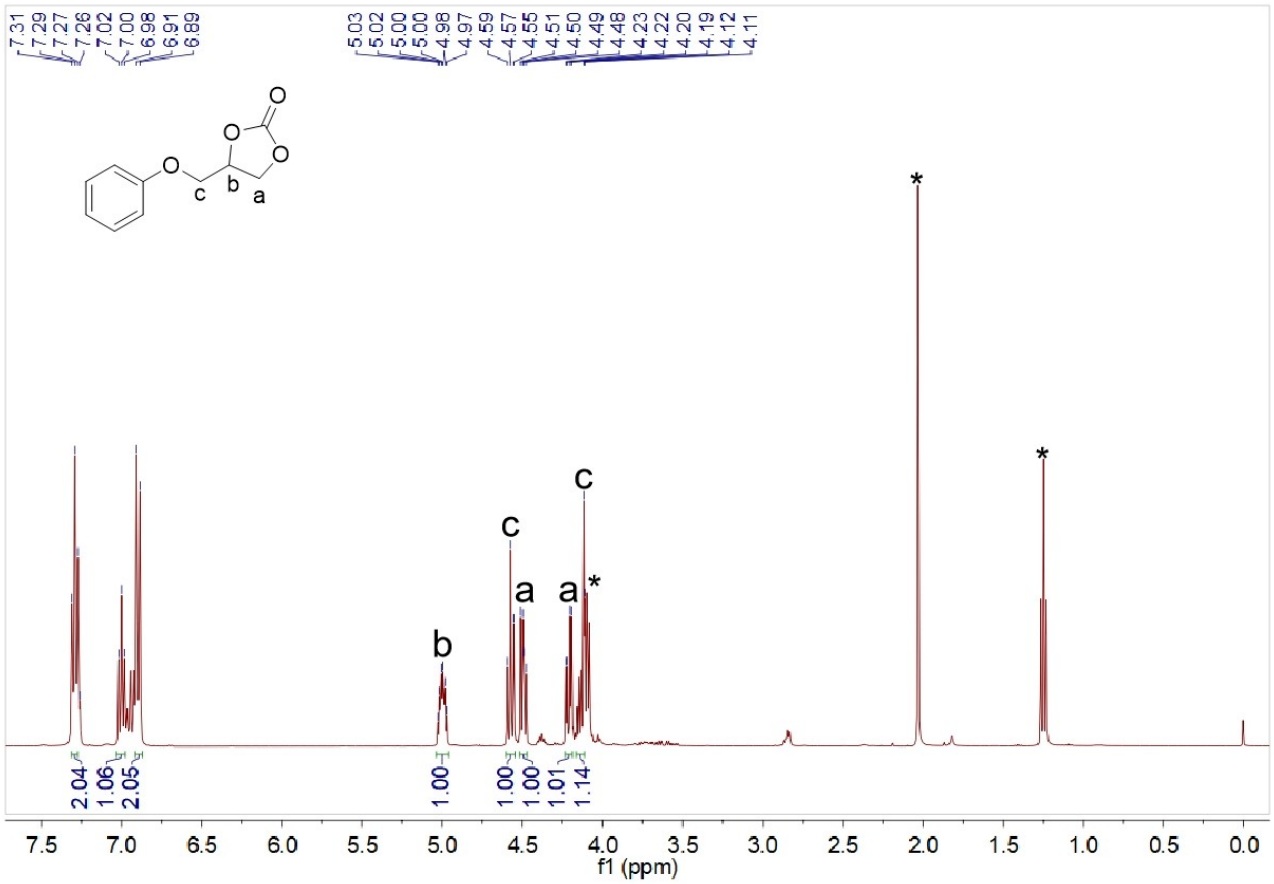


Fig. S15 ^{1}H NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=7.31~7.26 (2H, CH),7.02~6.98 (1H, CH), 6.91~6.89 (2H, CH), 5.03~4.97 (1H, CH), 4.59~4.55 (1H, CH_2), 4.51~4.48 (1H, CH_2), 4.23~4.19 (1H, CH_2), 4.12~4.11 ppm (1H, CH_2). * represents the residual solvent ethyl acetate. Reaction conditions: VIPA-Br, 80 ℃, 48 h, yield of 99%, selectivity of 99%.

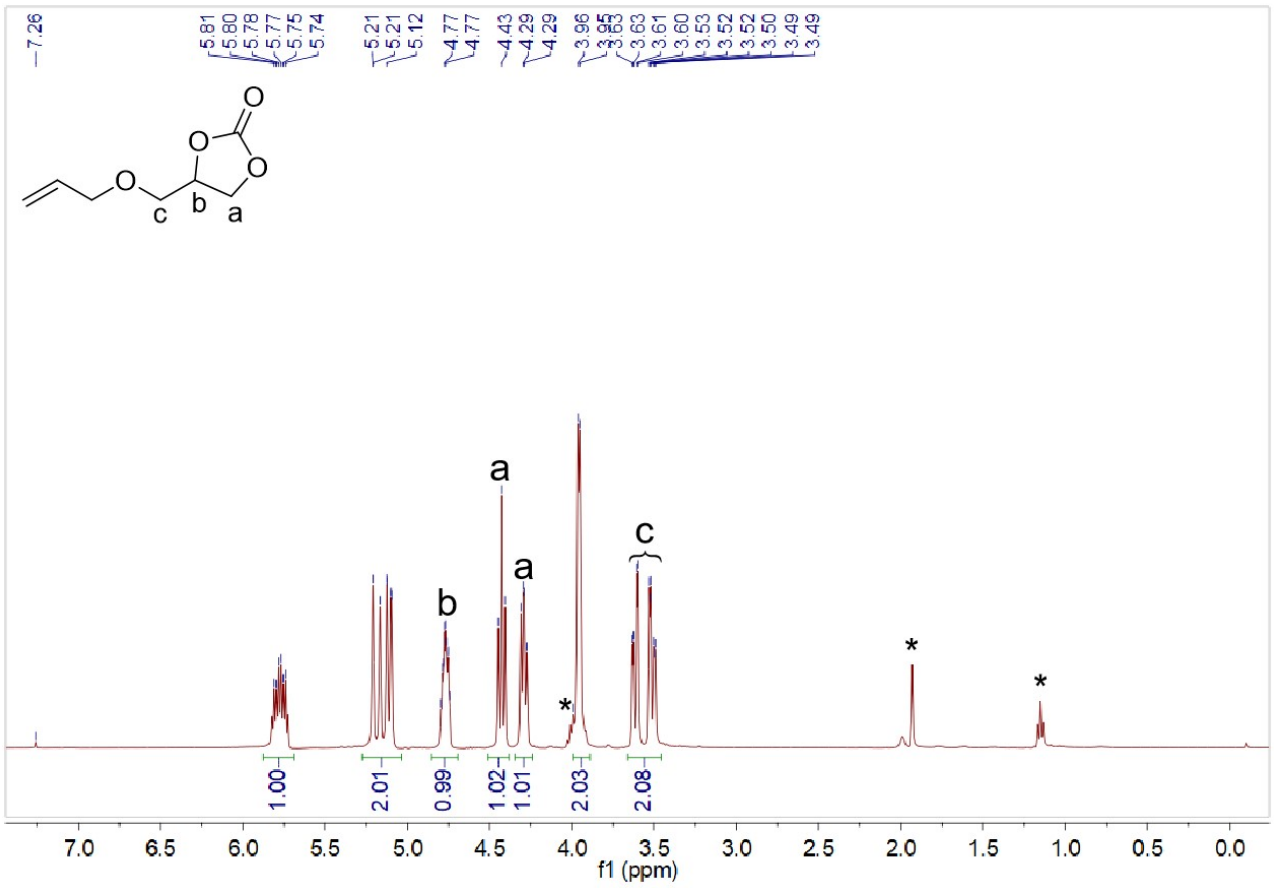


Fig. S16 ^{1}H NMR spectrum of allyloxymethyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=5.81~5.74 (1H, CH), 5.21~5.12 (2H, CH_2), 4.77 (1H, CH), 4.43~4.41 (1H, CH_2), 4.29 (1H, CH_2), 3.96~3.95 (2H, CH_2), 3.63~3.49 ppm (2H, CH_2). * represents the residual solvent ethyl acetate. Reaction conditions: VIPA-Br, 80 ℃, 48 h, the isolated yield of 98%, selectivity of 98%.

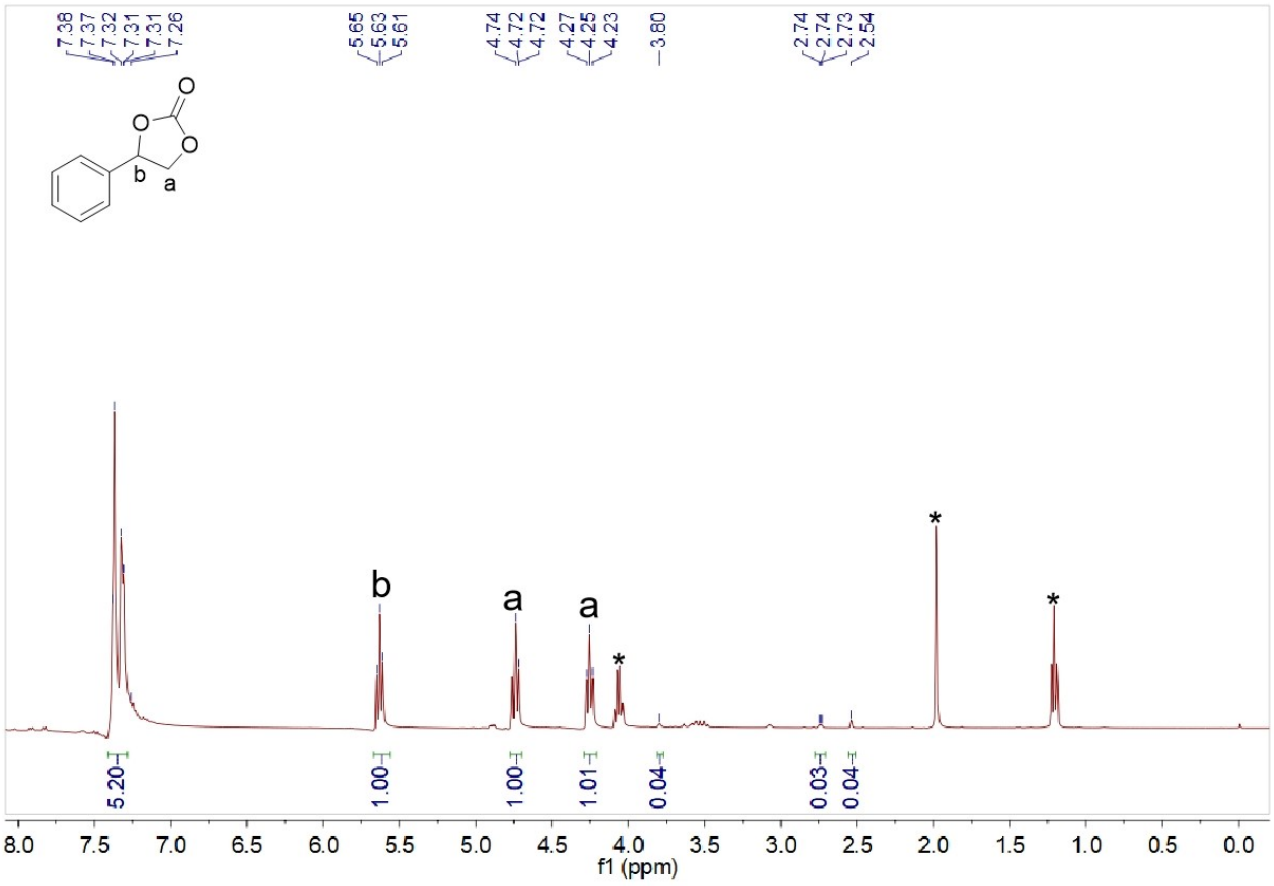


Fig. S17 ^{1}H NMR spectrum of 4-phenyl-1,3-dioxolan-2-one (400 MHz, $CDCl_3$): δ=7.38~7.26 (5H, CH), 5.65~5.61 (1H, CH), 4.74~4.72 (1H, CH_2), 4.27~4.23 ppm (1H, CH_2). * represents the residual solvent ethyl acetate. Reaction conditions: VIPA-Br, 80 ℃, 72 h, yield of 96%, selectivity of 99%.

References

S1 O. Buyukcakir, S. H. Je, D. S. Choi, S. N. Talapaneni, Y. Seo, Y. Jung, K. Polychronopoulouc and A. Coskun, *Chem. Commun*., 2016, **52**, 934–937.

S2 O. Buyukcakir, S. H. Je, S. N. Talapaneni, D. Kim and A. Coskun, *ACS Appl. Mater. Interfaces*, 2017, **9**, 7209–7216.

S3 C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij and M. A. Pericàs, *Green Chem*., 2014, **16**, 1552–1559.

S4 T.-T. Liu, R. Xu, J.-D. Yi, J. Liang, X.-S. Wang, P.-C. Shi, Y.-B. Huang and R. Cao, *ChemCatChem*, 2018, **10**, 2036–2040.

S5 X. Wang, Y. Zhou, Z. Guo, G. Chen, J. Li, Y. Shi, Y. Liu and J. Wang, *Chem. Sci*., 2015, **6**, 6916–6924.

S6 S. Subramanian, J. Oppenheim, D. Kim, T. S. Nguyen,W. M. H. Silo, B. Kim, W. A. Goddard III and C. T. Yavuz, *Chem*, 2019, **5**, 3232–3242.

S7 C. Cui, R. Sa, Z. Hong, H. Zhong and R. Wang, *ChemSusChem*, 2020, **13**, 180–187.

S8 W. Zhong, F. D. Bobbink, Z. Fei and P. J. Dyson, *ChemSusChem*, 2017, **10**, 2728–2735.

S9 Y. Xie, Q. Sun, Y. Fu, L. Song, J. Liang, X. Xu, H. Wang, J. Li, S. Tu, X. Lu and J. Li, *J. Mater. Chem. A*, 2017, **5**, 25594–25600.

S10 Y. Xie, J. Liang, Y. Fu, M. Huang, X. Xu, H. Wang, S. Tu and J. Li, *J. Mater. Chem. A*, 2018, **6**, 6660–6666.

S11 J. Li, D. Jia, Z. Guo, Y. Liu, Y. Lyu, Y. Zhou and J. Wang, *Green Chem.*, 2017, **19**, 2675–2686.

S12 G. Chen, X. Huang, Y. Zhang, M. Sun, J. Shen, R. Huang, M. Tong, Z. Long and X. Wang, *Chem. Commun.*, 2018, **54**, 12174–12177.

S13 Y. Zhang, K. Liu, L. Wu, H. Zhong, N. Luo, Y. Zhu, M. Tong, Z. Long and G. Chen, *ACS Sustainable Chem. Eng*., 2019, **7**, 16907–16916.

S14 G. Chen, Y. Zhang, K. Liu, X. Liu, L. Wu, H. Zhong, X. Dang, M. Tong and Z. Long, *J. Mater. Chem. A*, 2021, **9**, 7556–7565.

S15 Y. Zhang, K. Zhang, L. Wu, K. Liu, R. Huang, Z. Long, M. Tong and G. Chen, *RSC Adv.*, 2020, **10**, 3606–3616.

S16 Q. Sun, Y. Jin, B. Aguila, X. Meng, S. Ma and F.-S. Xiao, *ChemSusChem*, 2017, **10**, 1160–1165.

S17 Z. Guo, Q. Jiang, Y. Shi, J. Li, X. Yang, W. Hou, Y. Zhou and J. Wang, *ACS Catal.*, 2017, **7**, 6770–6780.

S18 K. Hu, Y. Tang, J. Cui, Q. Gong, C. Hu, S. Wang, K. Dong, X. Meng, Q. Sun and F.-S. Xiao, *Chem. Commun*., 2019, **55**, 9180–9183.

S19 D. Ma, K. Liu, J. Li and Z. Shi, *ACS Sustainable Chem. Eng*., 2018, **6**, 15050–15055.

S20 Y. Zhang, G. Chen, L. Wu, K. Liu, H. Zhong, Z. Long, M. Tong, Z. Yang and S. Dai, *Chem. Commun*., 2020, **56**, 3309–3312.

S21 P. Puthiaraj, S. Ravi, K. Yu and W.-S. Ahn, *Appl. Catal. B*, 2019, **251**, 195–205.

S22 Y. Chen, R. Luo, Q. Xu, J. Jiang, X. Zhou and H. Ji, *ChemSusChem*, 2017, **10**, 2534–2541.

S23 J. Li, Y. Han, T. Ji, N. Wu, H. Lin, J. Jiang and J. Zhu, *Ind. Eng. Chem. Res.*, 2019, **59**, 676–684.

S24 Y. Zhang, N. Luo, J. Xu, K. Liu, S. Zhang, Q. Xu, R. Huang, Z. Long, M. Tong and G. Chen, *Dalton Trans.*, 2020, **49**, 11300–11309.

S25 Y. Zhang, K. Liu, L. Wu, H. Huang, Z. Xu, Z. Long, M. Tong, Y. Gu, Z. Qin and G. Chen, *Dalton Trans*., 2021, **50**, 11878–11888.

S26 Y. Xie, J. Liang, Y. Fu, J. Lin, H. Wang, S. Tu and J. Li, *J. CO_2 Util.*, 2019, **32**, 281–289.

S27 J. Li, Y. Han, H. Lin, N. Wu, Q. Li, J. Jiang and J. Zhu, *ACS Appl. Mater. Interfaces*, 2020, **12**, 609–618.