Supplementary Materials

Advancing CO_2 conversion: integrated use of dual active catalytic sites in flexible, porous polymeric porphyrin and ionic liquid composite networks

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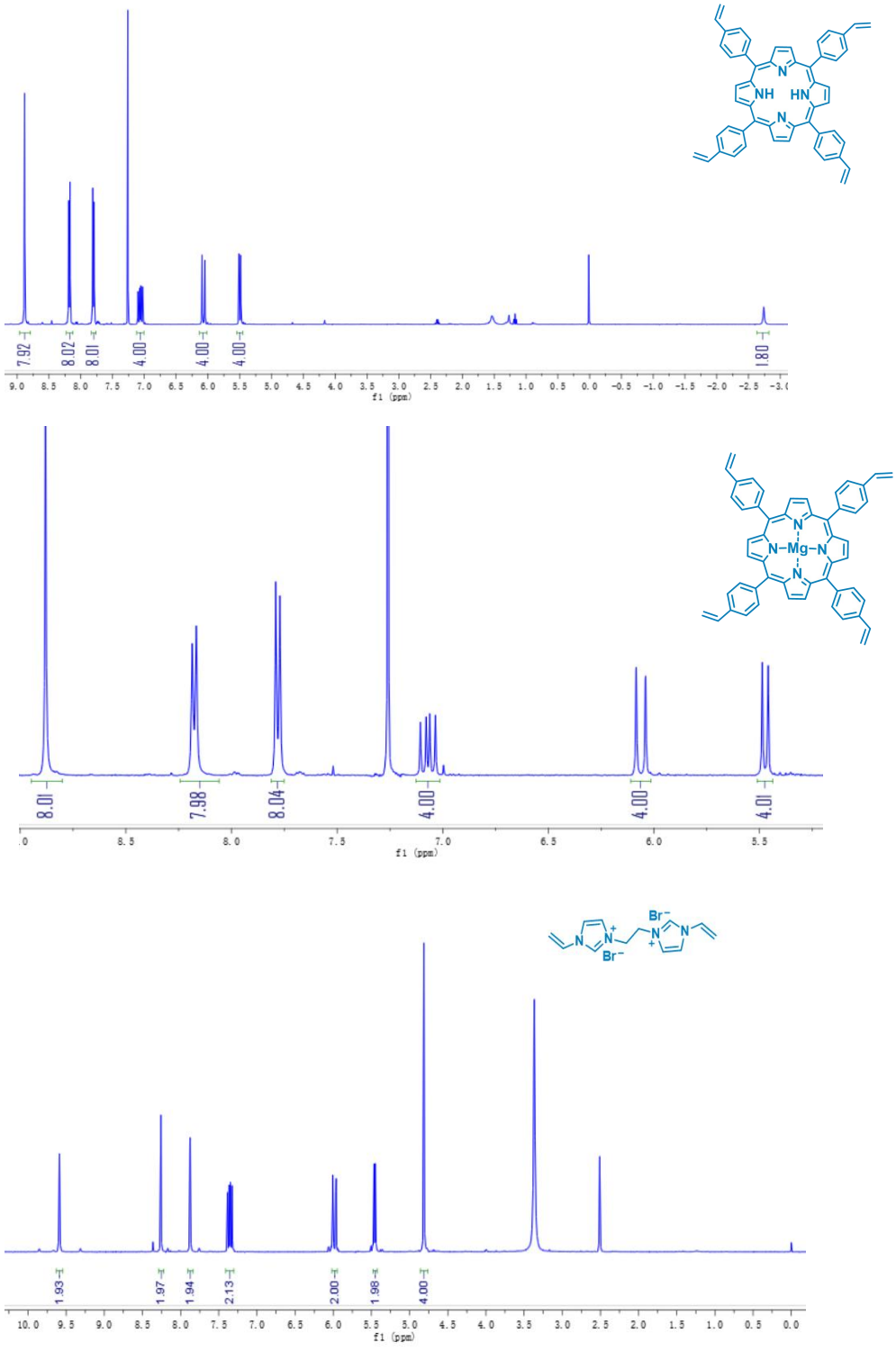
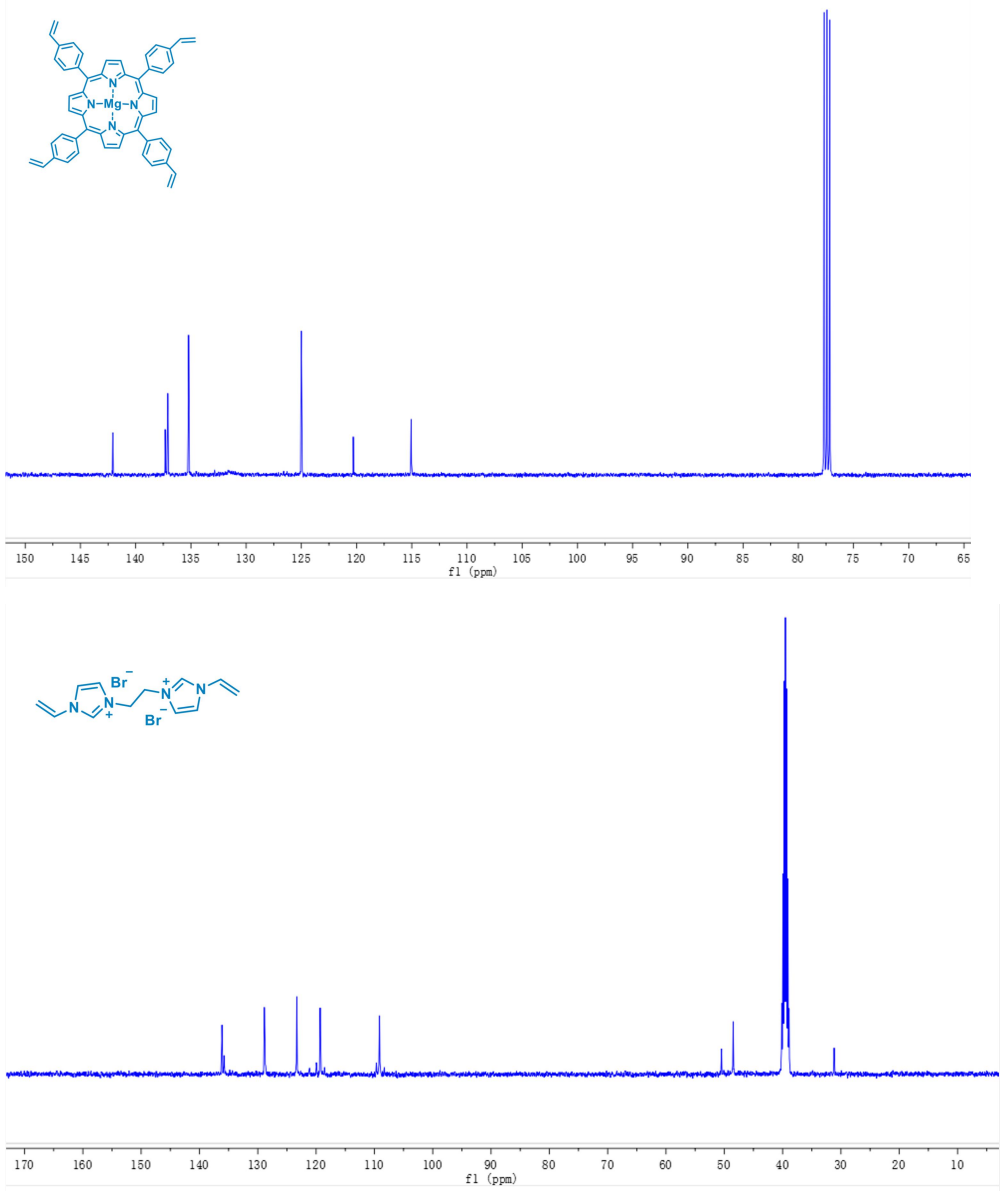
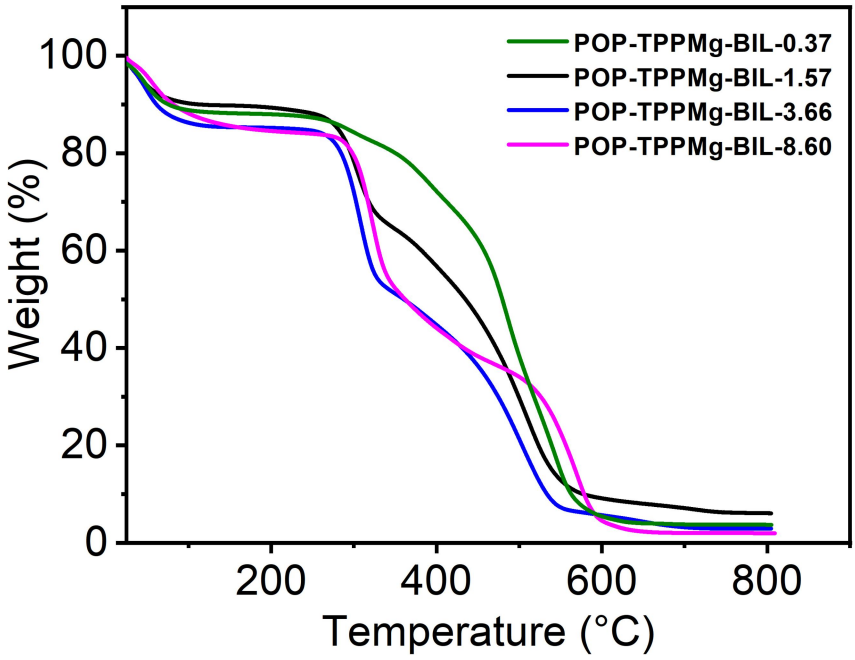


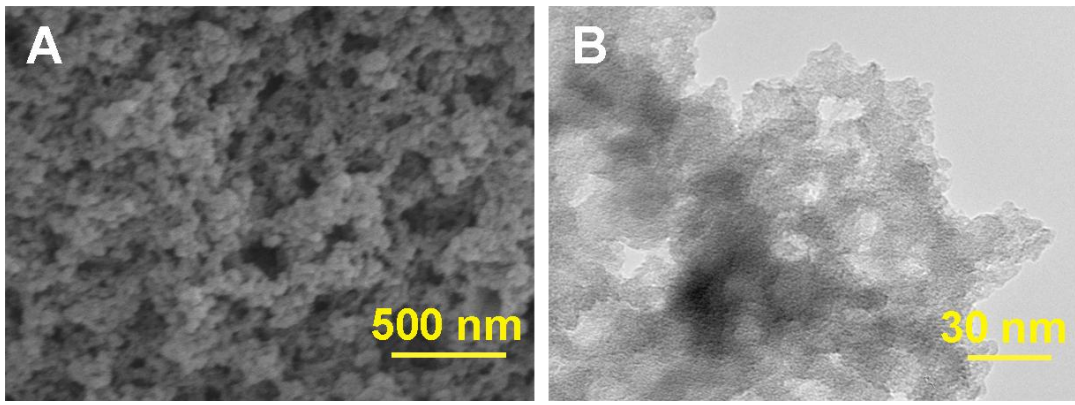
Supplementary Figure 1. ^{1}H NMR spectra of v-TPP, v-TPPMg, and BIL.



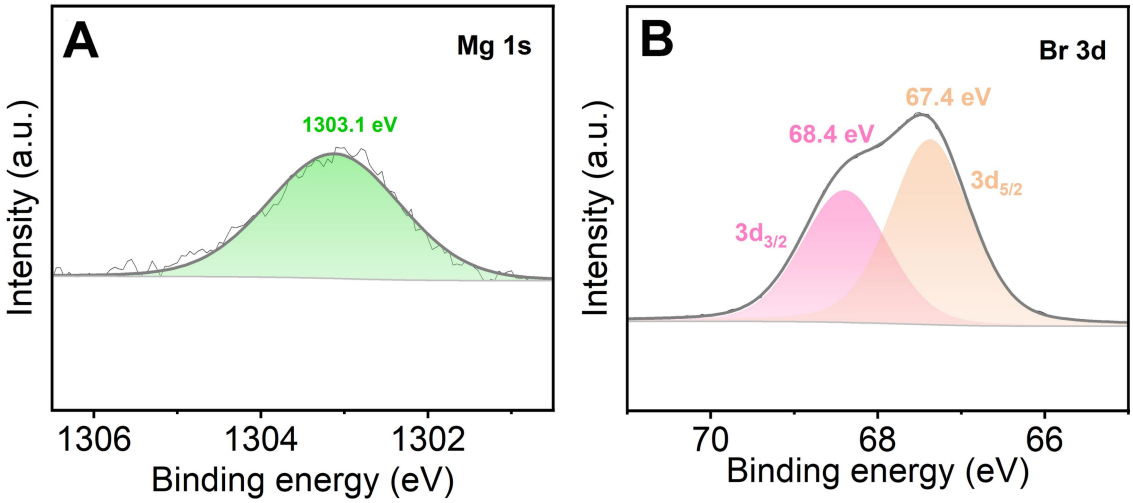
Supplementary Figure 2. ^{13}C NMR spectra of v-TPPMg and BIL.



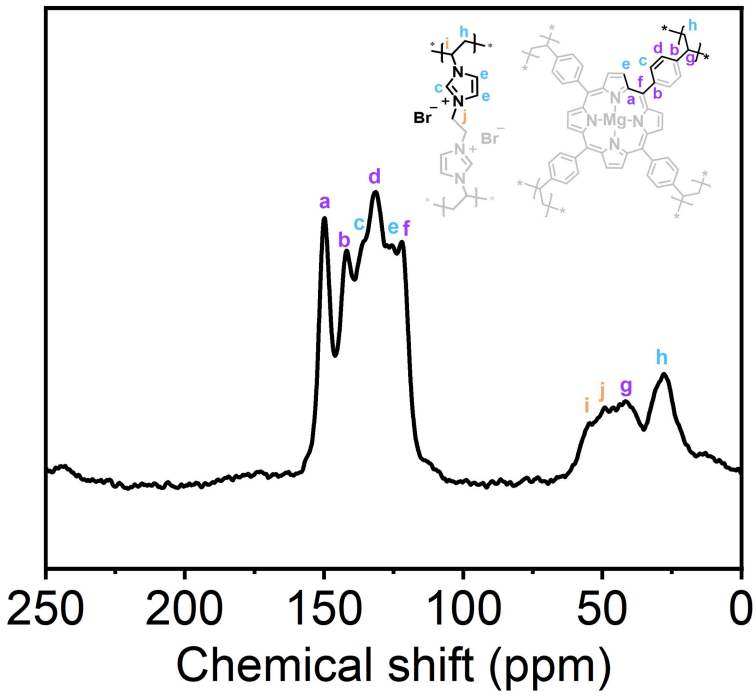
Supplementary Figure 3. TG curves of POP-TPPMg-BIL-x.



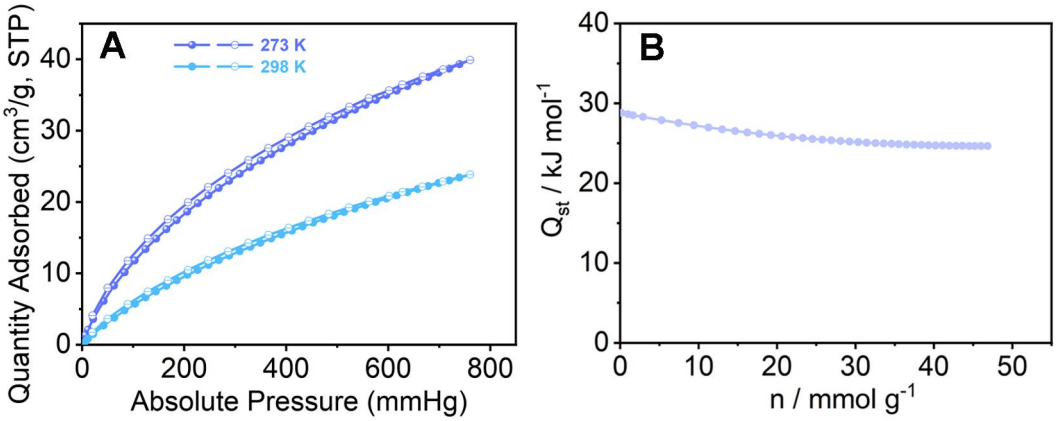
Supplementary Figure 4. (A) SEM and (B) high-resolution TEM images of POP-TPPMg.



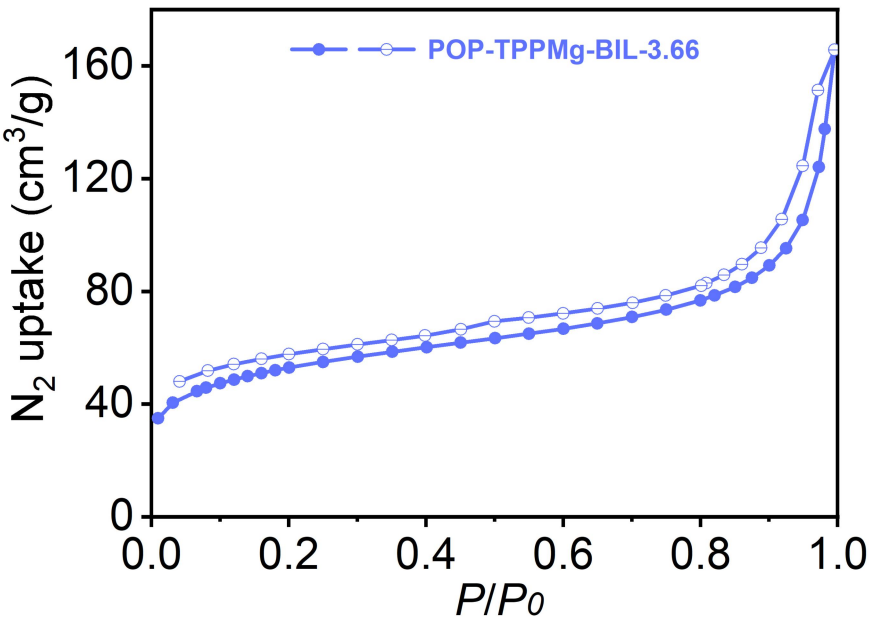
Supplementary Figure 5. (A) Mg 1s, and (B) Br 3d spectra of the as synthesized POP-TPPMg-BIL-1.57 catalyst.



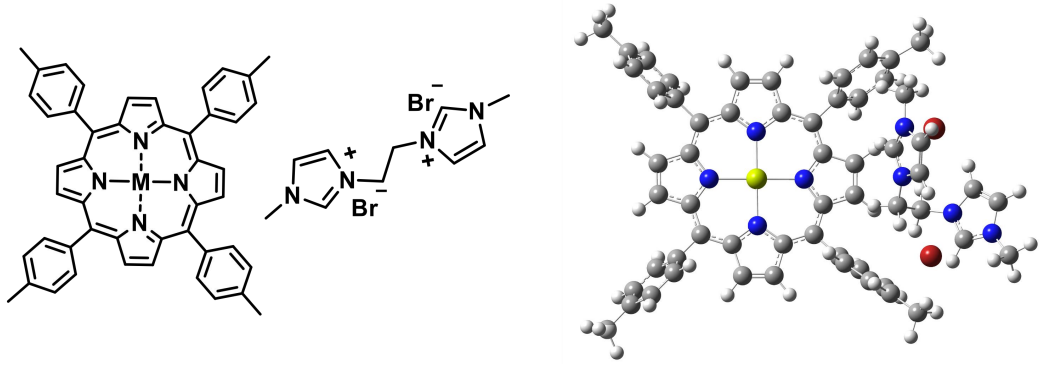
Supplementary Figure 6. ^{13}C MAS NMR spectrum of POP-TPPMg-BIL-1.57.



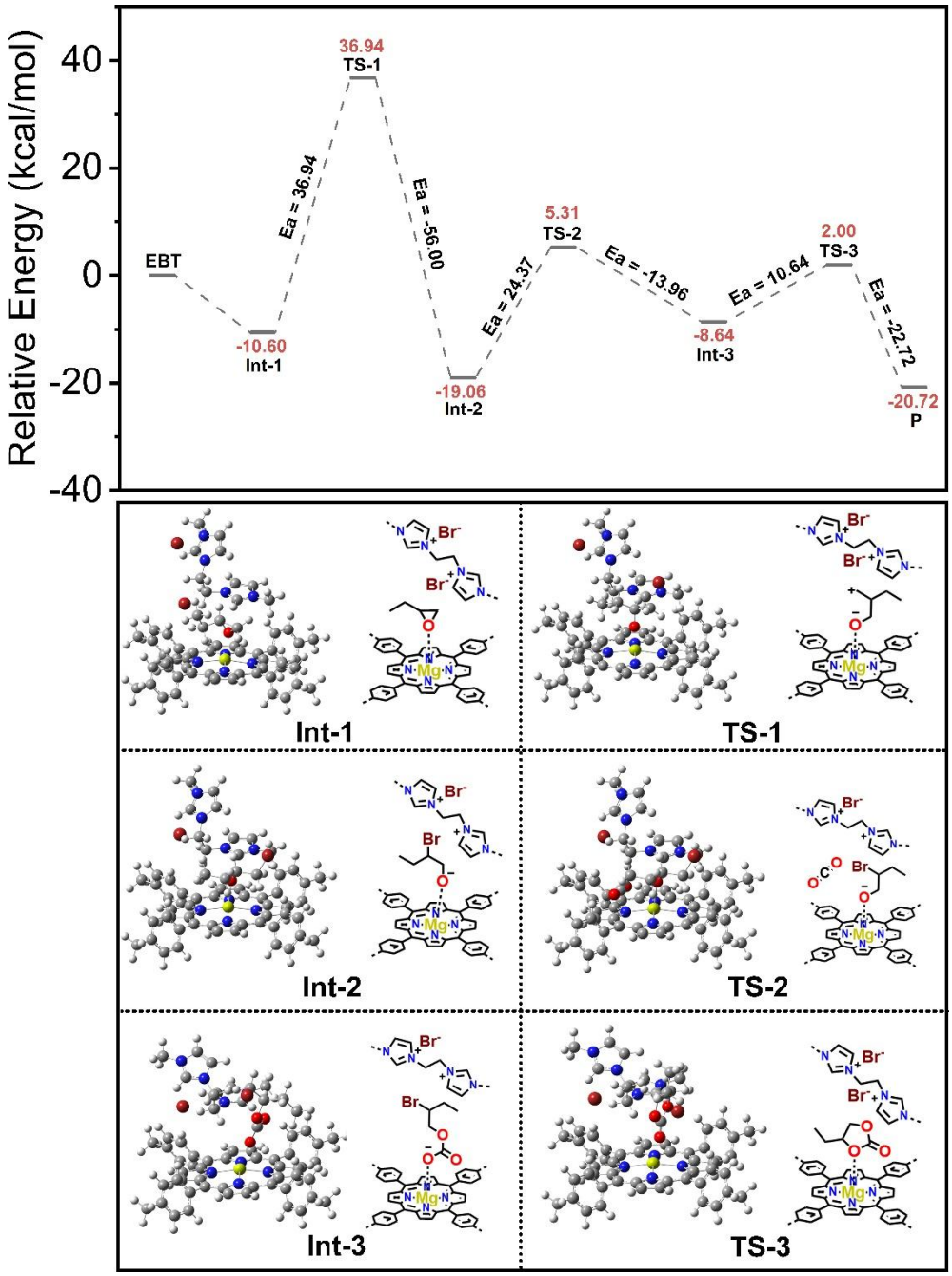
Supplementary Figure 7. (A) CO_2 sorption isotherms at different temperatures for POP-TPPMg-BIL-1.57 and (B) the calculated isosteric heat (Q_{st}) by Virial Method.



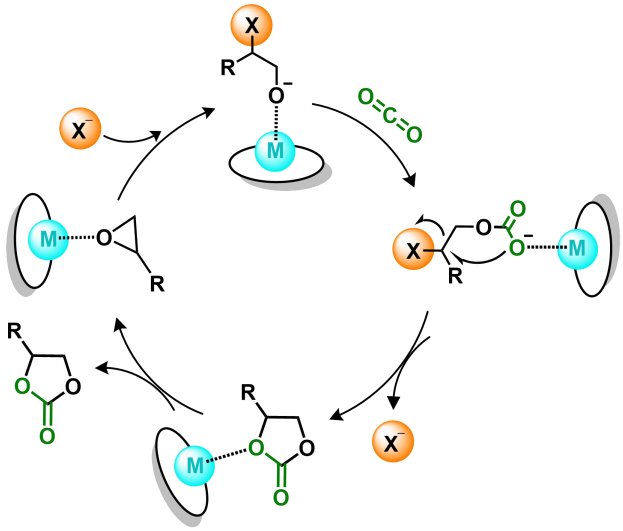
Supplementary Figure 8. N_2 sorption isotherms for POP-TPPMg-BIL-3.66. The BET surface area and pore volume were calculated to be 174 m^2/g and 0.26 cm^3/g, respectively.



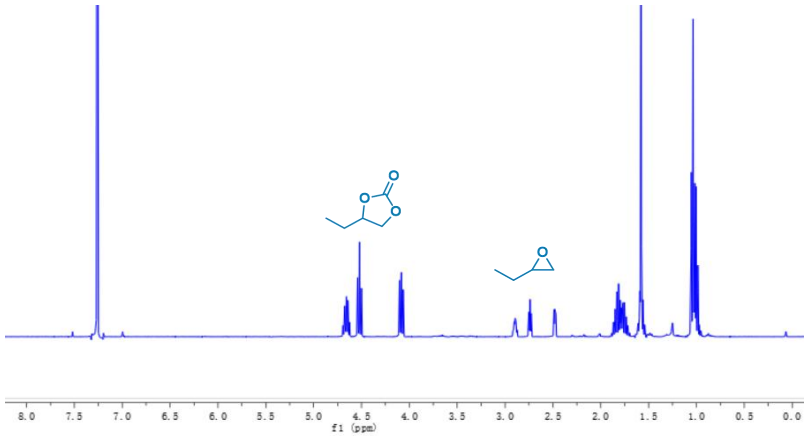
Supplementary Figure 9. For simplicity in the calculations, the structure of POP-TPPMg-BIL-1.57 is represented by the simplified structures shown (white: H, gray: C, blue: N, yellow: Mg, red: Br).



Supplementary Figure 10. DFT-calculated free energy profiles and the optimized geometries of key intermediates and transition states for the POP-TPPMg-BIL-1.57 catalyzed CO_2 cycloaddition with 1,2-epoxybutane (white: H, gray: C, blue: N, yellow: Mg, red: Br).



Supplementary Figure 11. Proposed mechanism of cycloaddition between CO_2 and epoxides over bifunctional heterogeneous catalysts.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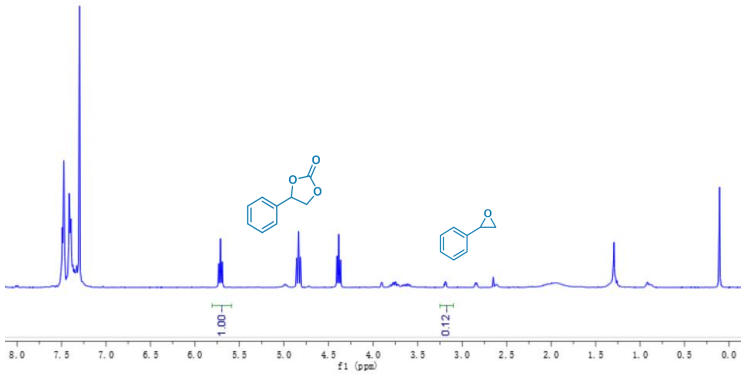
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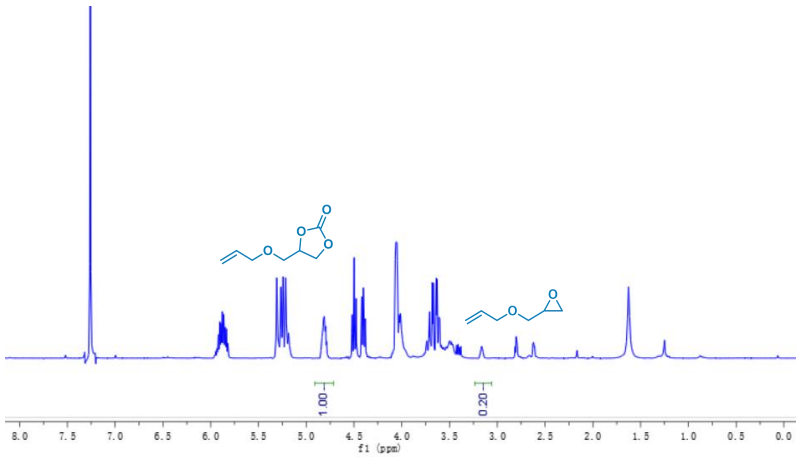
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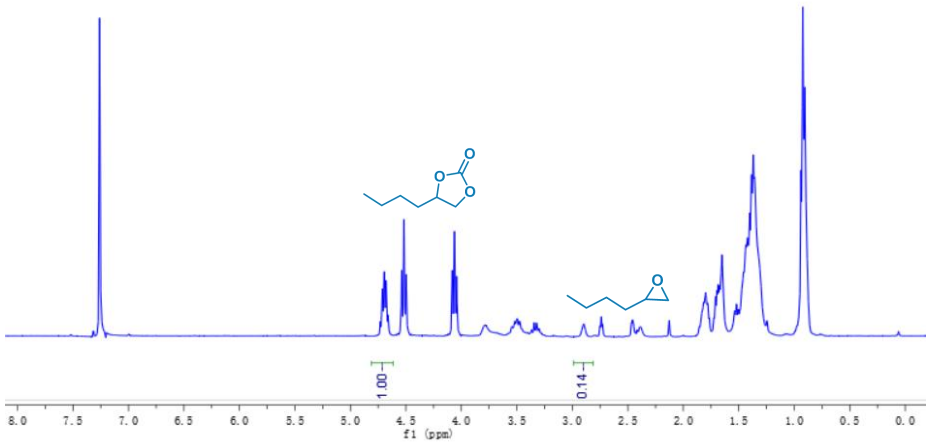
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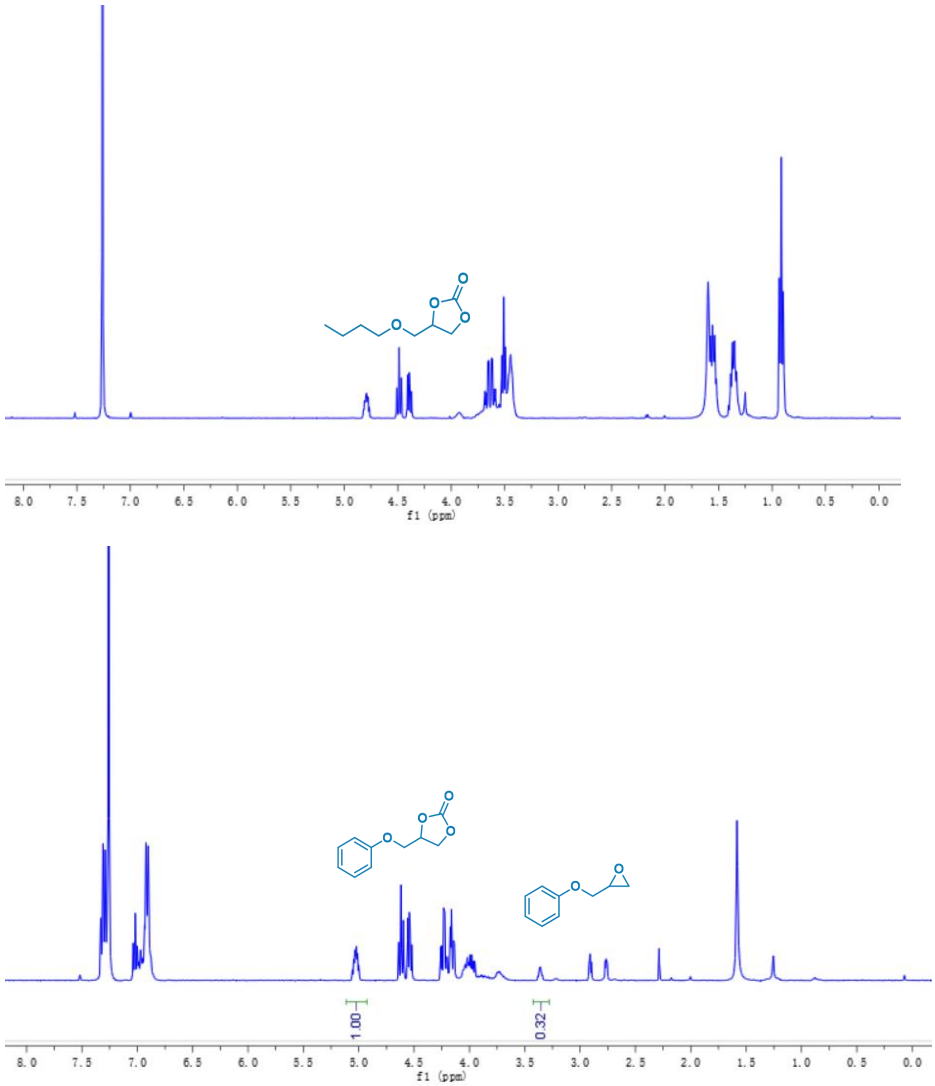
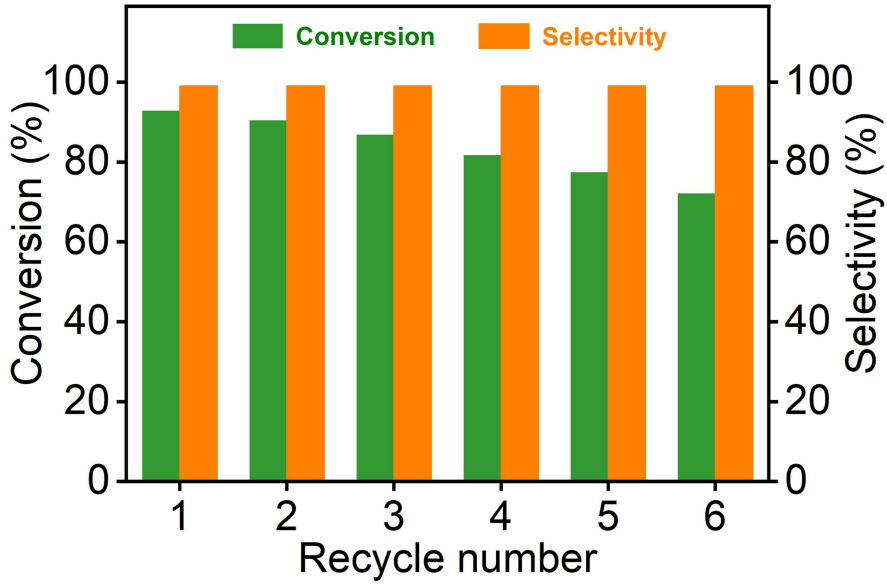
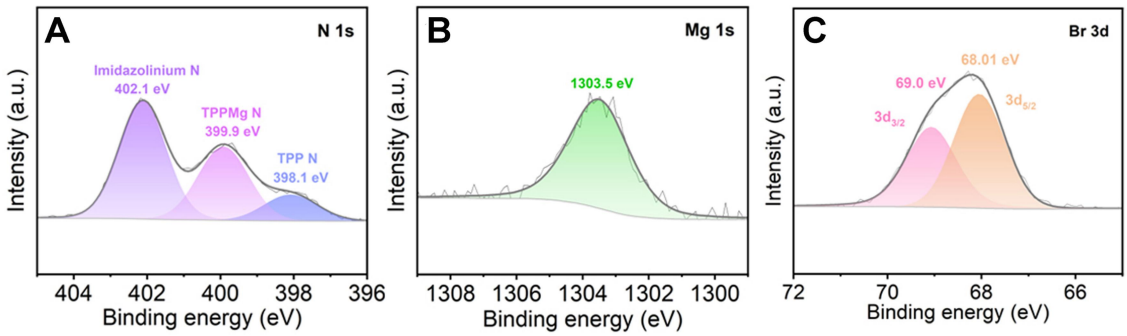


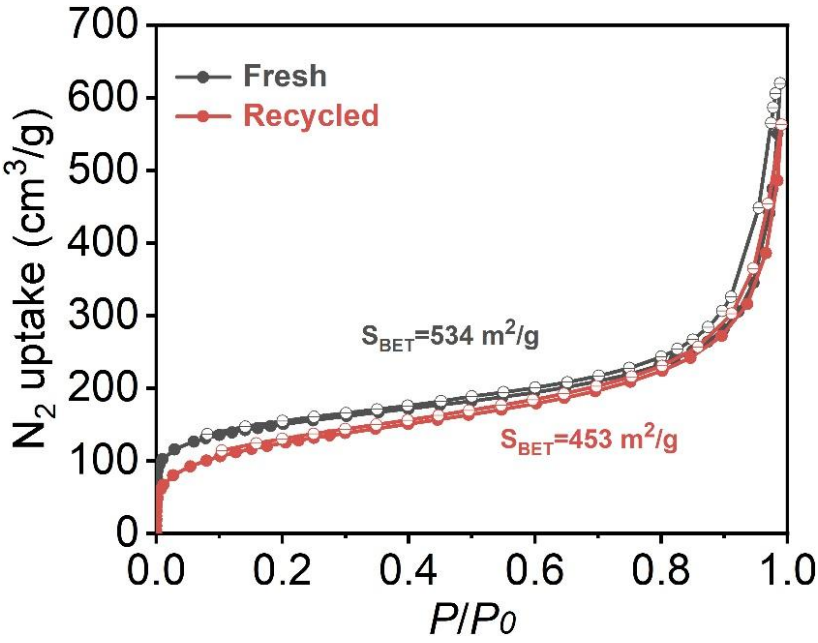
Supplementary Figure 12. ^{1}H NMR spectra of various products.



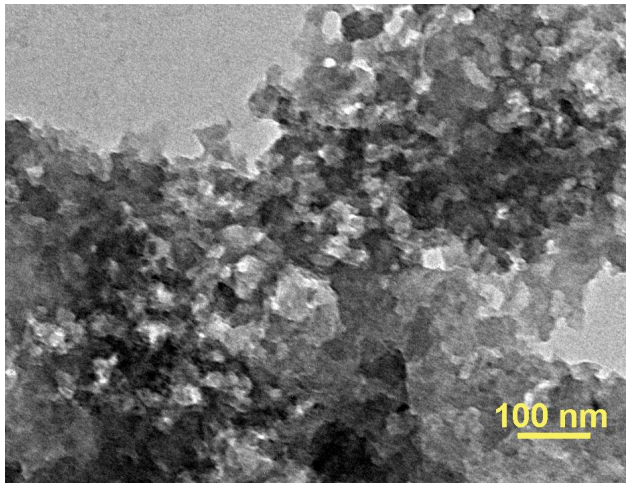
Supplementary Figure 13. Conversion and selectivity during recycling tests in the cycloaddition of 1,2-epoxybutane with CO_2 using the POP-TPPMg-BIL-1.57 catalyst. Reaction conditions: 1,2-epoxybutane (10 mmol)，POP-TPPMg-BIL-1.57 (44.4 mg)，50 °C, and 1 atm CO_2.



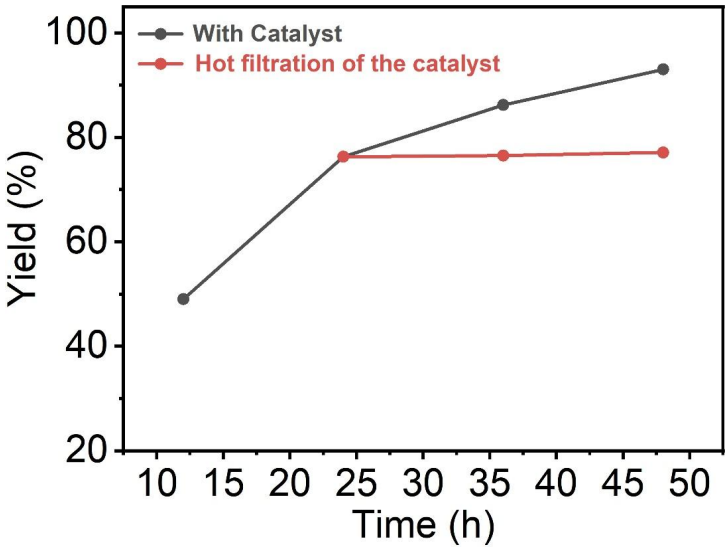
Supplementary Figure 14. (A) N 1s spectrum, (B) Mg 1s spectrum, and (C) Br 3d spectrum of the POP-TPPMg-BIL-1.57 catalyst after six recycling cycles.



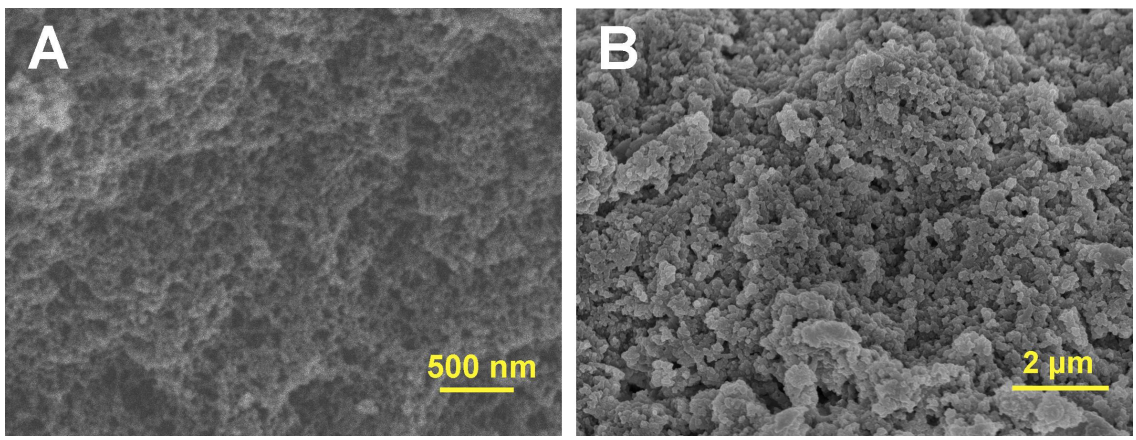
Supplementary Figure 15. N_2 sorption isotherms of POP-TPPMg-BIL-1.57 before and after the catalytic reaction. The BET surface area and pore volume were calculated to be 534 m^2/g and 0.96 cm^3/g for the as-synthesized POP-TPPMg-BIL-1.57 catalyst, and 453 m^2/g and 0.86 cm^3/g for the recycled catalyst.



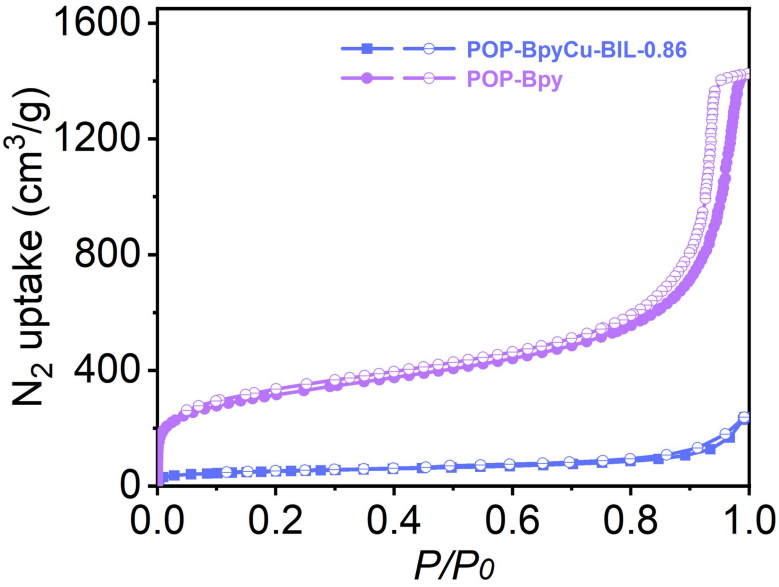
Supplementary Figure 16. TEM image of POP-TPPMg-BIL-1.57 after six recycling cycles.



Supplementary Figure 17. Yield versus reaction time for the cycloaddition reaction between 1,2-epoxybutane and CO_2. Reaction conditions: 1,2-epoxybutane (10 mmol), POP-TPPMg-BIL-1.57 catalyst (44.4 mg), and CO2 (1 atm) at 50 °C. After 24 hours of reaction, the catalyst was removed via filtration, and the reaction mixture was allowed to proceed for an additional 24 hours. Yields were determined by ^{1}H NMR spectroscopy.



Supplementary Figure 18. SEM images of (A) POP-Bpy and (B) POP-BpyCu-BIL-0.86.



Supplementary Figure 19. N_2 sorption isotherms of POP-Bpy and POP-BpyCu-BIL-0.86 collected at 77 K. The BET surface areas and pore volumes were calculated as follows: 1123 m^2/g and 2.14 cm^3/g for POP-Bpy, and 182 m^2/g and 0.36 cm^3/g for POP-BpyCu-BIL-0.86.

Supplementary Table 1. Comparison of catalytic performance between POP-TPPMg-BIL-1.57, TPPMg&BIL, and the POP-TPPMg&BIL binary system in the cycloaddition of CO_2 with 1,2-epoxybutane[a].

Entry	Catalyst	Time (h)	Conv. (%)[b]
1	POP-TPPMg-BIL-1.57	48	99
2	BIL/TPPMg	48	99
3	BIL/POP-TPPMg	48	95

[a]Reaction conditions: 1,2-epoxybutane (10 mmol), POP-TPPMg-BIL-1.57 catalyst (44.4 mg, 0.333 mol% and 1.046 mol% based on Mg and Br species, respectively), and CO_2 (1 atm). [b]Product yield determined by ^{1}H NMR spectroscopy.

Supplementary Table 2. Comparison of the catalytic performance of this study with other catalytic systems from literature in the cycloaddition of CO_2 with 1,2-epoxybutane.

Entry	Catalyst	*T* (°C)	Time (h)	Conv. (%)	Ref.
1	POP-TPPMg-BIL-1.57	50	48	89.0	This work
2	POP-PA-NH_2	60	48	69.4	Ref. S1
3	POP-PA-COOH	60	48	53.6	Ref. S1
4	POP-PA-OH	60	48	54.6	Ref. S1
5	POP-BnCl-CP	60	48	90.1	Ref. S2
6	POP-BnCl-PB	60	48	70.9	Ref. S2
7	POP-BnCl-PP	60	48	61	Ref. S2
8	POP-PBnCl-TPPMg-4	40	48	52.4	Ref. S3
9	POP-PBnCl-TPPMg-12	40	48	89.3	Ref. S3
10	PCP-Cl	100	12	98	Ref. S4
11	Al-iPOP-1	40	6	99	Ref.S5
12	POF-PNA-Br	40	48	98	Ref. S6
13	pPI-1/pPI-2	80	72	98/90	Ref. S7
14	HIP-COOH-TMG	110	8	99	Ref. S8
15	AC-IL-NTf2	120	13	83	Ref. S9
16	IP 1	70	6	99.9	Ref. S10
17	IP 2	70	6	85.4	Ref. S10
18	IP 3	70	6	74.6	Ref. S10
19	P-DBTMGH	100	4	96	Ref. S11
20	CoPor-HIP	80	6	96	Ref. S12

Supplementary Table 3. Comparison of catalytic performances across different catalytic systems in the cycloaddition of CO2 with 1,2-epoxybutane[a].

Entry	Catalyst	Time (h)	Conv. (%)[b]
1	POP-BpyCu-BIL-0.86	48	70.4
2	v-BpyCu&PBIL	48	99.0
3	v-BpyCu&v-BIL	36	99.0
4	POP-BpyCu&PBIL	48	44.8
5	POP-BpyCu-BIL-0.14	48	43.5

[a]Reaction conditions: 1,2-epoxybutane (1.08 g, 15 mmol), POP-BpyCu-BIL-0.86 catalyst (24.6 mg, corresponding to 0.067 mol% Cu and 0.115 mol% Br based on catalyst content), CO_2 (1 atm), and 50 °C. [b]Product yield determined by ^{1}H NMR.

Supplementary References

[1] Dai Z, Bao Y, Yuan J, Yao J, Xiong Y. Different functional groups modified porous organic polymers used for low concentration CO_2 fixation. *Chem Commun* 2021;57:9732.[DOI: 10.1039/d1cc03178c]

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Incorporation of phenolic skeleton into imidazolium ionic polymers as recyclable catalysts for efficient fixation of CO_2 into cyclic carbonates. *Chem Eng J* 2024;481:148359.[DOI: 10.1016/j.cej.2023.148359]
[11]Qu Q, Cheng L, Wang P, Fang C, Li H, Ding J, Wan H, Guan G. Guanidine-functionalized basic binuclear poly(ionic liquid)s for low partial pressure CO_2 fixation into cyclic carbonate. *Sep Purif Technol* 2024;339:126682.[DOI: 10.1016/j.seppur.2024.126682]
[12]Xu W, Zhang Z, Wu Y, Chen K, Luo R, Cobalt porphyrin-based hypercrosslinked ionic polymers as biomimetic nanoreactors for CO_2 conversion to cyclic carbonates. *Chem Commun* 2024;60:1599.[DOI: 10.1039/D3CC05593K]