Electronic Supplementary Information for

Hollow and Microporous Catalysts Bearing Cr(III)-F Porphyrins for Room Temperature CO_2 Fixation to Cyclic Carbonates

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Fig. S1 IR spectra of tetra(4-ethynylphenyl)porphyrin and Cr(III)-Cl tetra(4-ethynylphenyl)porphyrin.

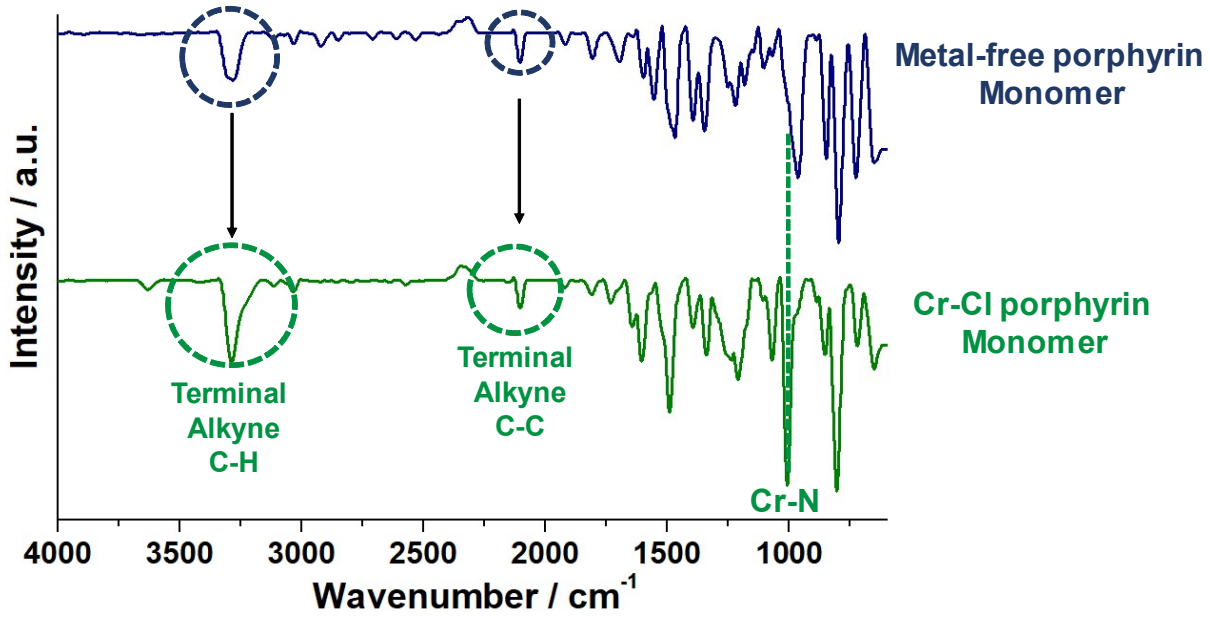
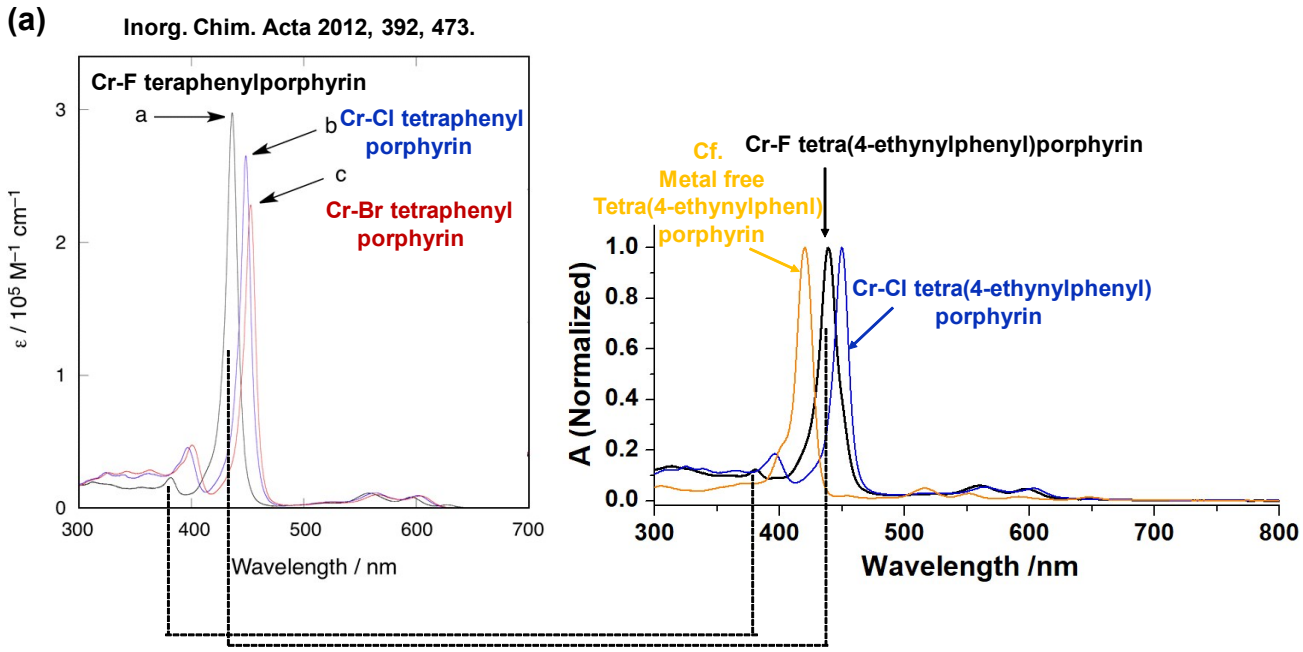
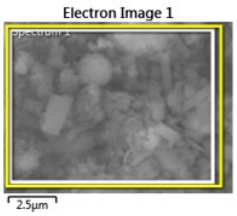


Fig. S2 (a) UV-vis absorption spectra and (b) SEM-EDS analysis of CrCl-tetra(4-ethynylphenyl)porphyrin and CrF-tetra(4-ethynylphenyl)porphyrin.



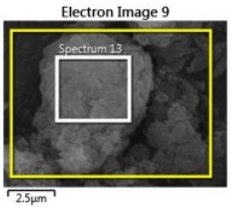
(b)

Cr-Cl porphyrin M



Element	Line Type	Apparent Concentration	k Ratio	Wt%	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
F	K series	0.03	0.00006	8.78	15.24	CaF2	Yes	
Cl	K series	0.44	0.00382	91.22	84.76	NaCl	Yes	
Total:				100.00	100.00			

Cr-F porphyrin M



Element	Line Type	Apparent Concentration	k Ratio	Wt%	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
F	K series	0.35	0.00068	72.76	83.29	CaF2	Yes	
Cl	K series	0.14	0.00126	27.24	16.71	NaCl	Yes	
Total:				100.00	100.00			

Fig. S3 PXRD pattern of H-MCrPN, H-MPN, and H-MZnPN.

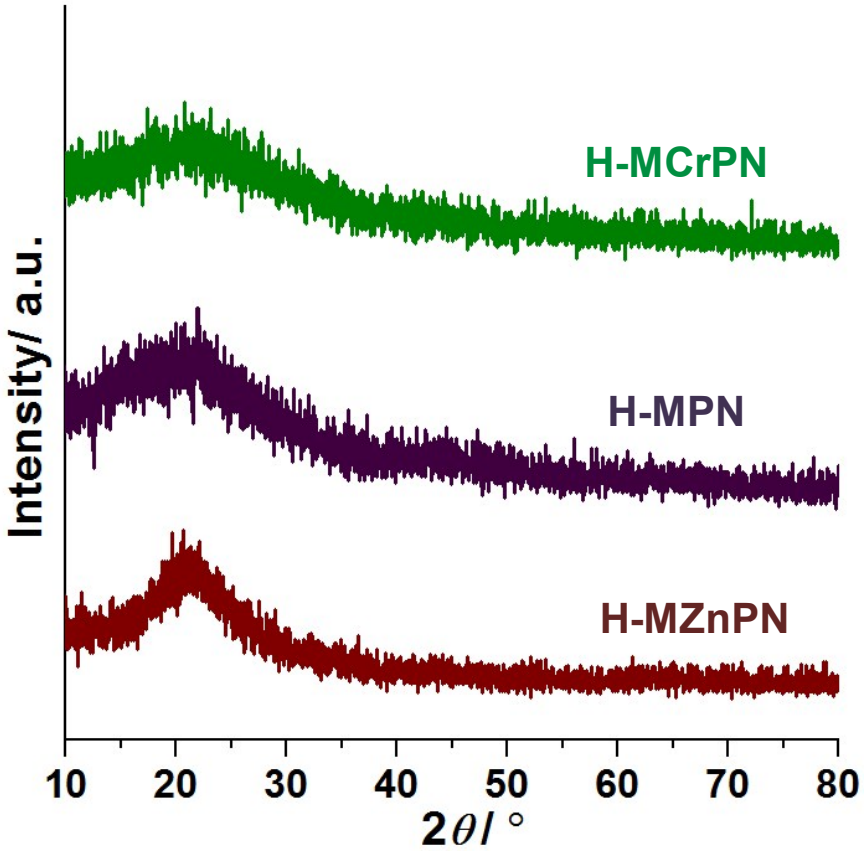
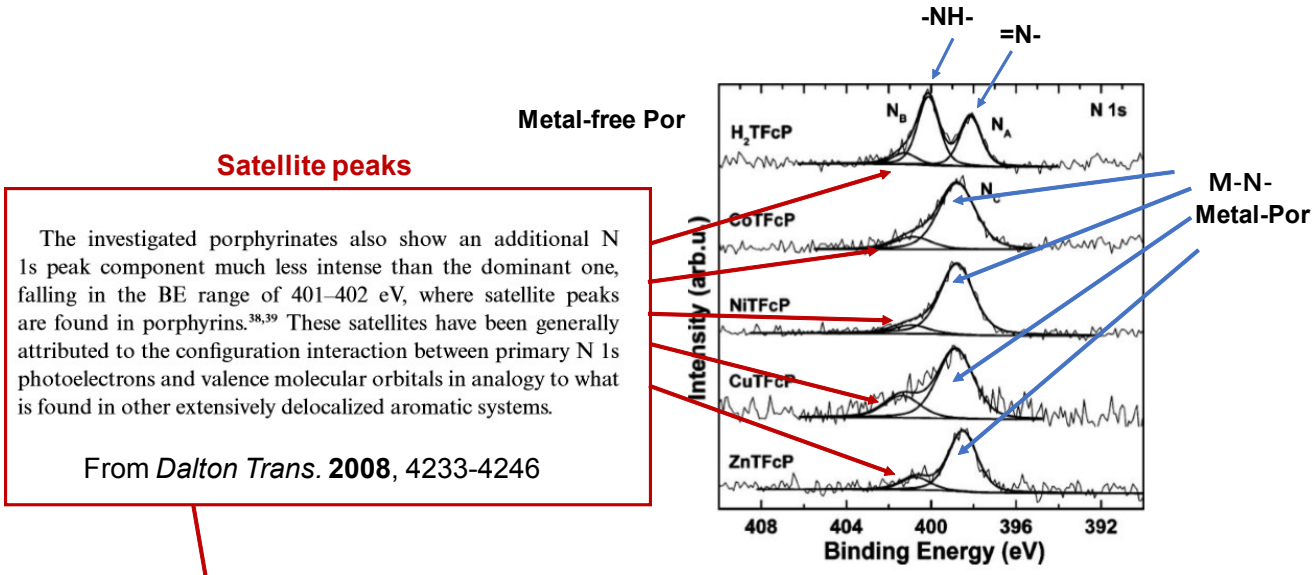


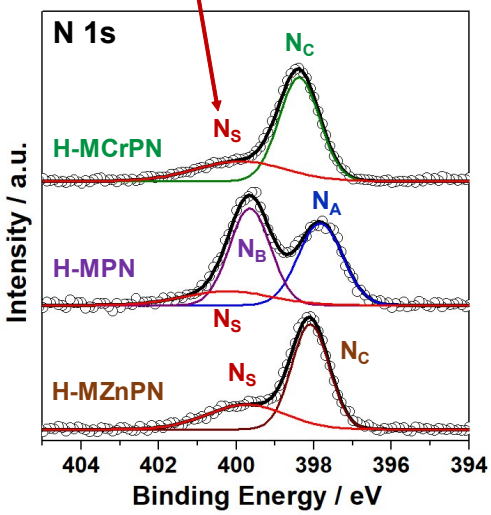
Fig. S4 XPS N 1s and C 1s orbital spectra of H-MCrPN, H-MPN, and H-MZnPN.



Satellite peaks

The investigated porphyrinates also show an additional N 1s peak component much less intense than the dominant one, falling in the BE range of 401–402 eV, where satellite peaks are found in porphyrins.[38,39] These satellites have been generally attributed to the configuration interaction between primary N 1s photoelectrons and valence molecular orbitals in analogy to what is found in other extensively delocalized aromatic systems.

From *Dalton Trans.* **2008**, 4233-4246



N_A: =N- N_C: Cr-N-, N_C: Zn-N-
N_B: -NH- N_S: Satellite peaks

sample	H-MZnPN		H-MPN			H-MCrPN	
r^2	0.99635309		0.99407862			0.99793100	
Peak	N_C	N_S	N_A	N_B	N_S	N_C	N_S
Position (eV)	398.09	399.73	397.83	399.64	400.20	398.37	399.89
FWHM	1.1286	2.3807	1.3415	1.2413	2.6407	1.2282	2.6998
Area (%)	66.93	33.07	41.09	45.16	13.75	70.53	29.47

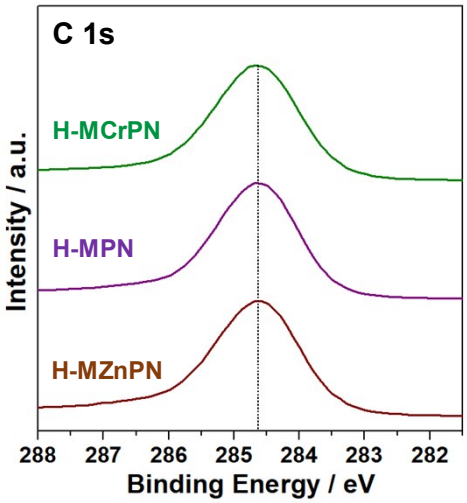


Fig. S5 (a) The catalytic activity comparison of H-MCrPN and nonhollow-MCrPN which was prepared by the same synthetic procedures of H-MCrPN without use of template. Reaction conditions: styrene oxide (12.5 mmol), no additional solvent, catalyst (0.49 mol% Cr porphyrins, 0.061 mmol, 71 mg of H-MCrPN, 73 mg of nonhollow-MCrPN), TBABr (0.90 mmol), room temperature, and CO_2 (balloon). According to elemental analysis of N (4.73wt%) in nonhollow-MCrPN, the Cr-porphyrin content in the material was calculated to 0.84 mmol/g of catalyst. (b) SEM image and (c) N_2 adsorption-desorption isotherm curves of nonhollow-MCrPN.

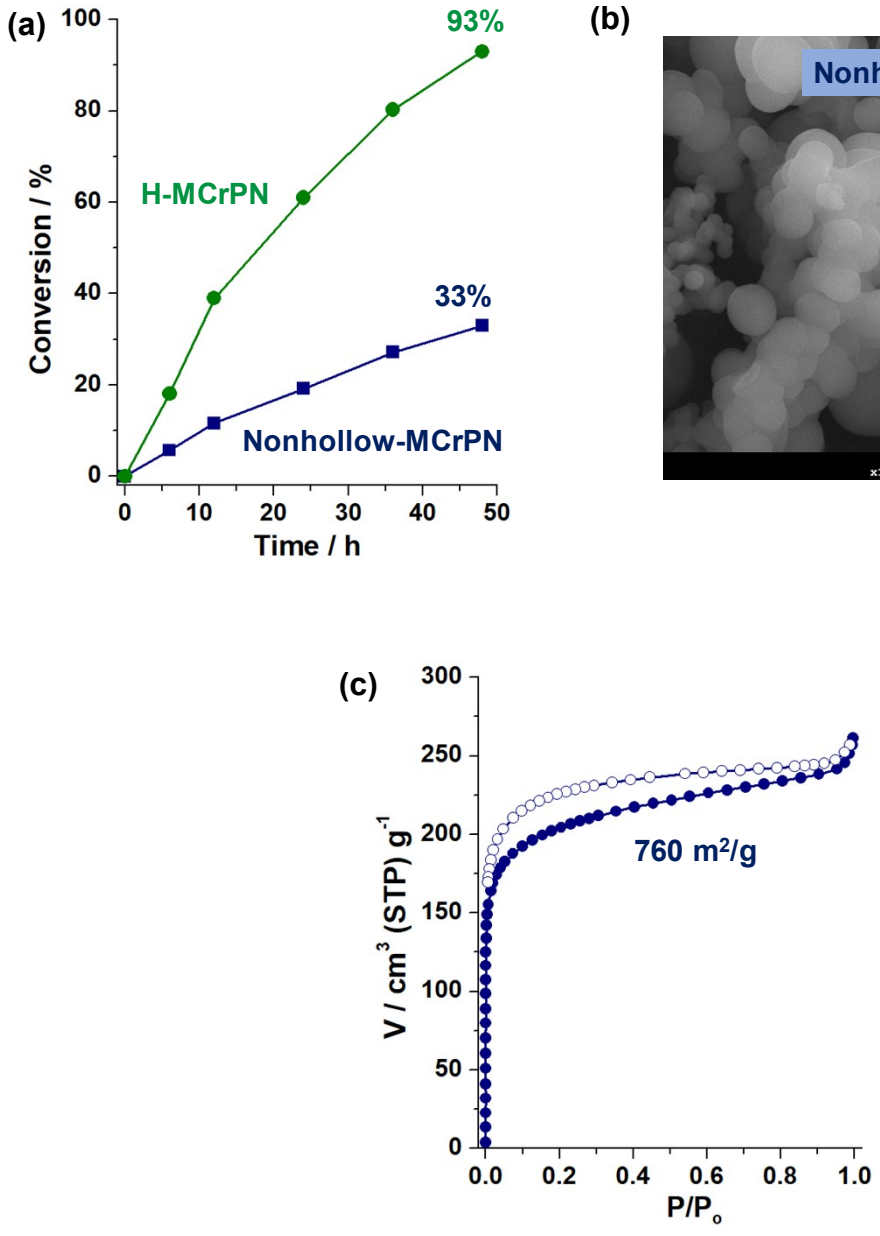


Fig. S6 The size evaluation of epoxide substrates (calculated by Gaussian09).

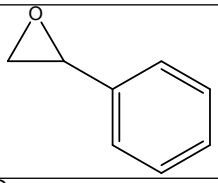
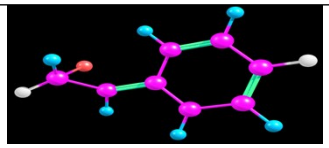
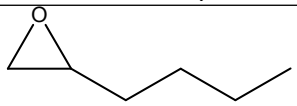
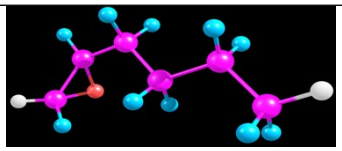
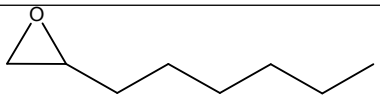
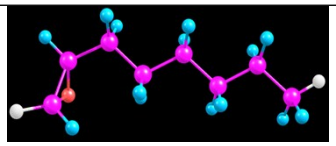
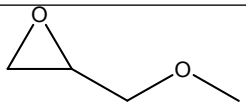
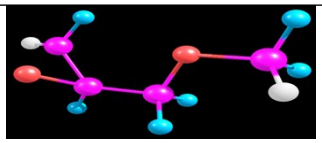
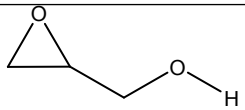
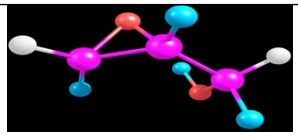
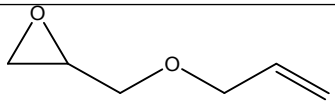
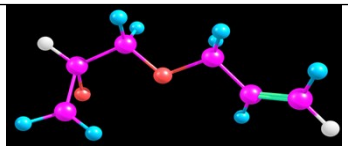
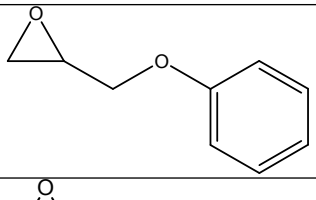
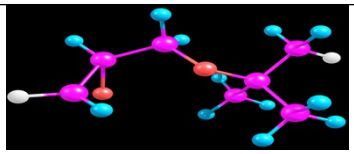
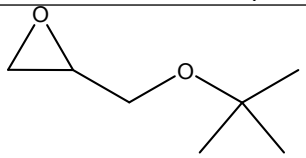
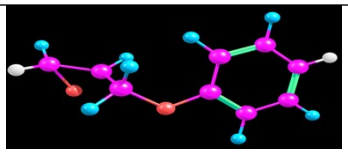
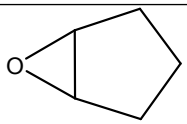
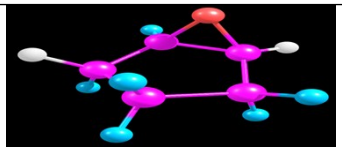
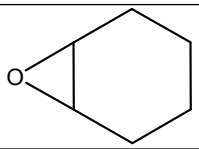
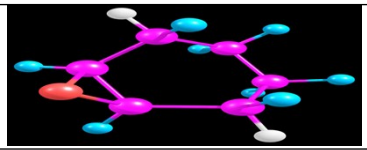
Epoxide substrate	Simulated epoxide	Distance between white balls in the left molecular figures
		7.78 Å
		8.09 Å
		10.56 Å
		6.33 Å
		4.85 Å
		8.22 Å
		9.19 Å
		7.70 Å
		4.82 Å
		5.47 Å

Fig. S7 Chemoselectivities of poor substrates (glycidol and cyclohexene oxide) for cyclic carbonate depending on co-catalysts. Reaction conditions: epoxide (12.5 mmol), no additional solvent, H-MCrPN (71 mg, 0.49 mol% metal porphyrins, 0.061 mmol), cocatalyst (0.90 mmol), room temperature, 48 h, and CO_2 (balloon).

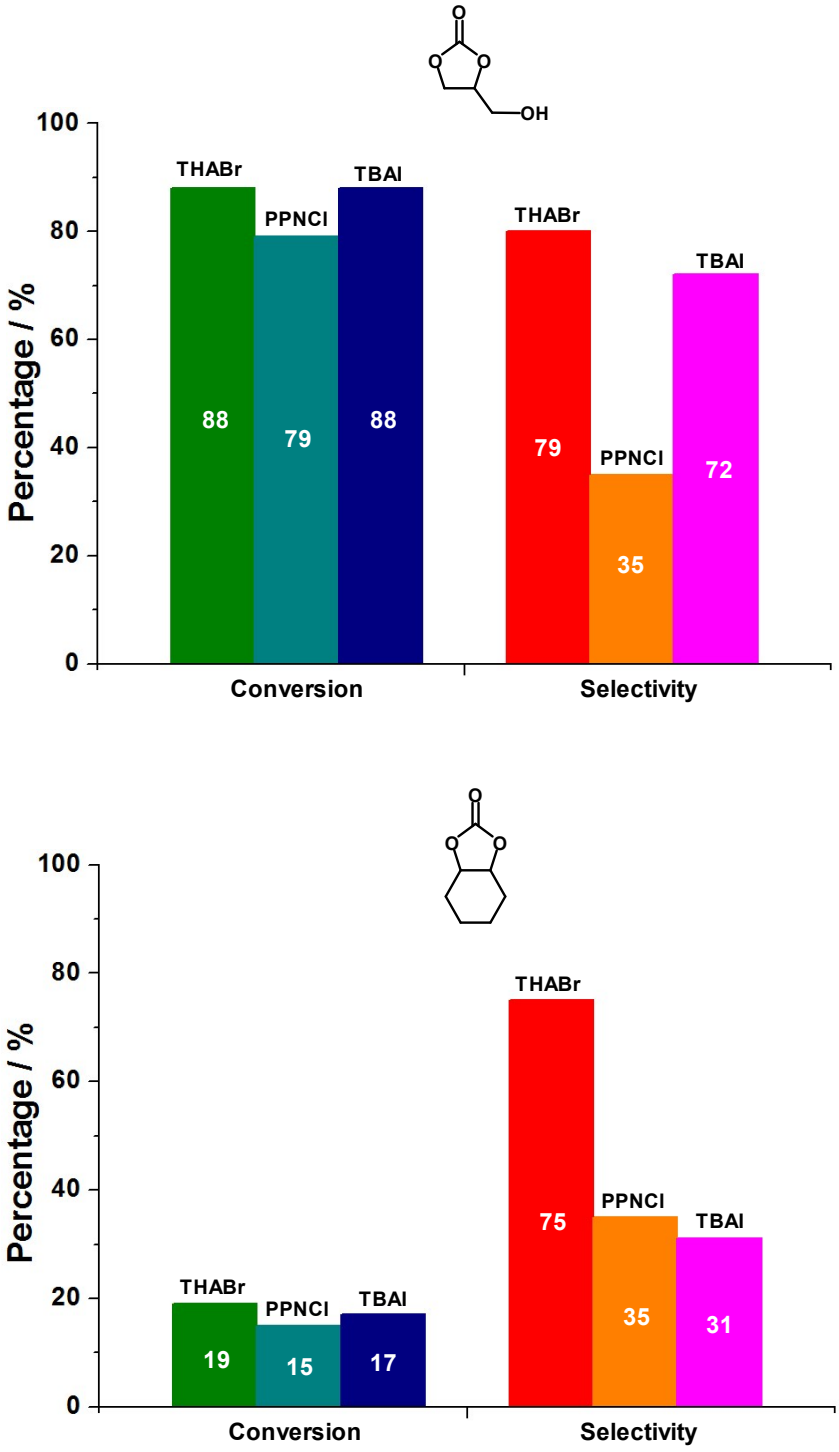


Fig. S8 IR spectra of H-MCrPN before and after reaction (after five cycles).

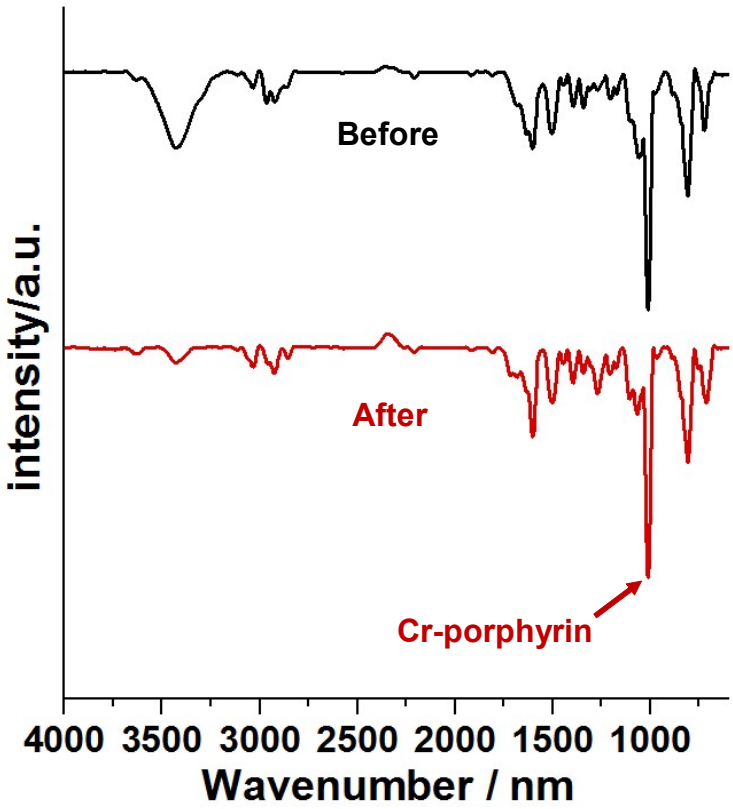
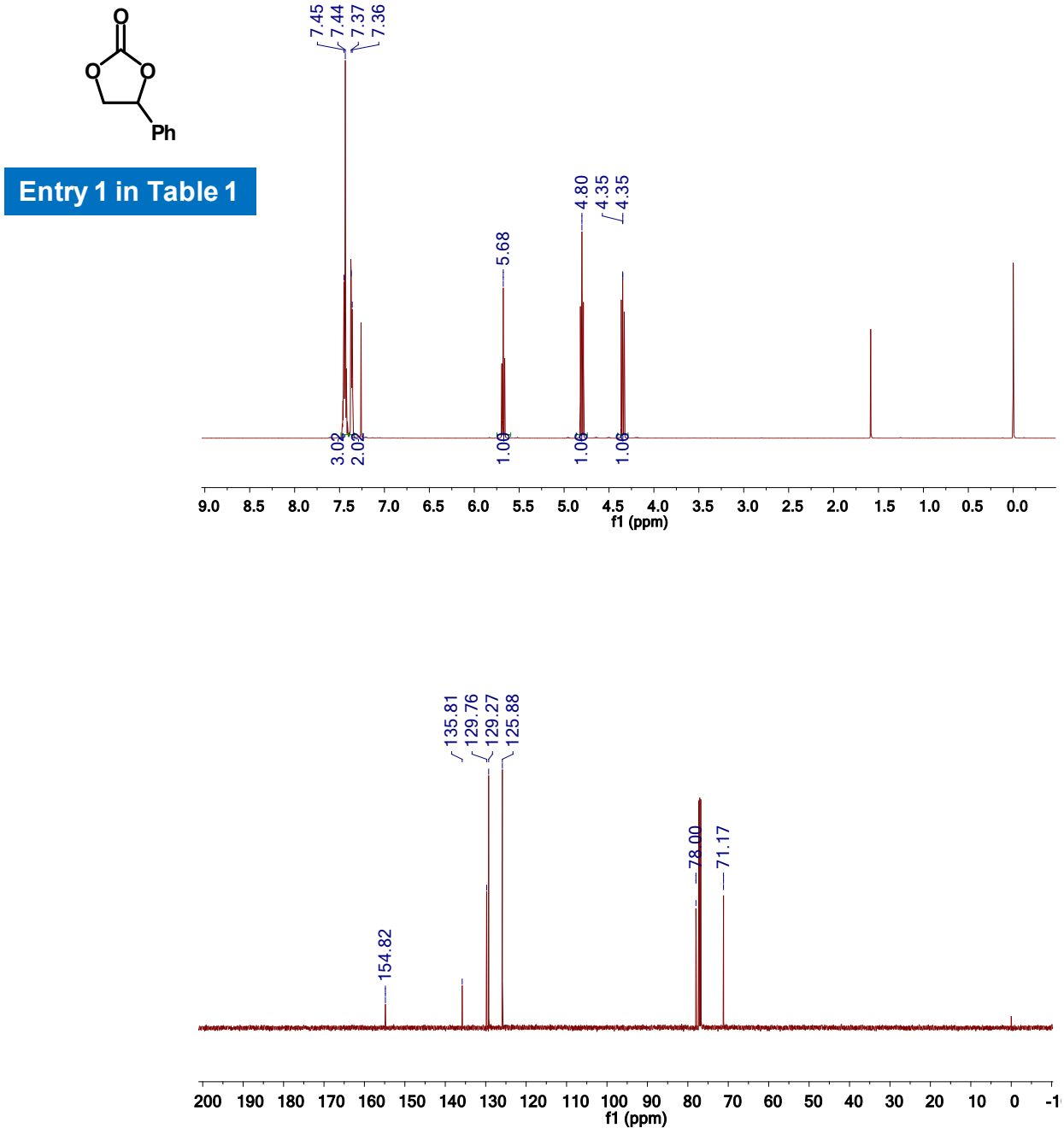
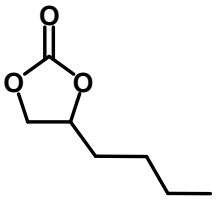


Fig. S9 ^{1}H and ^{13}C NMR spectra of products.





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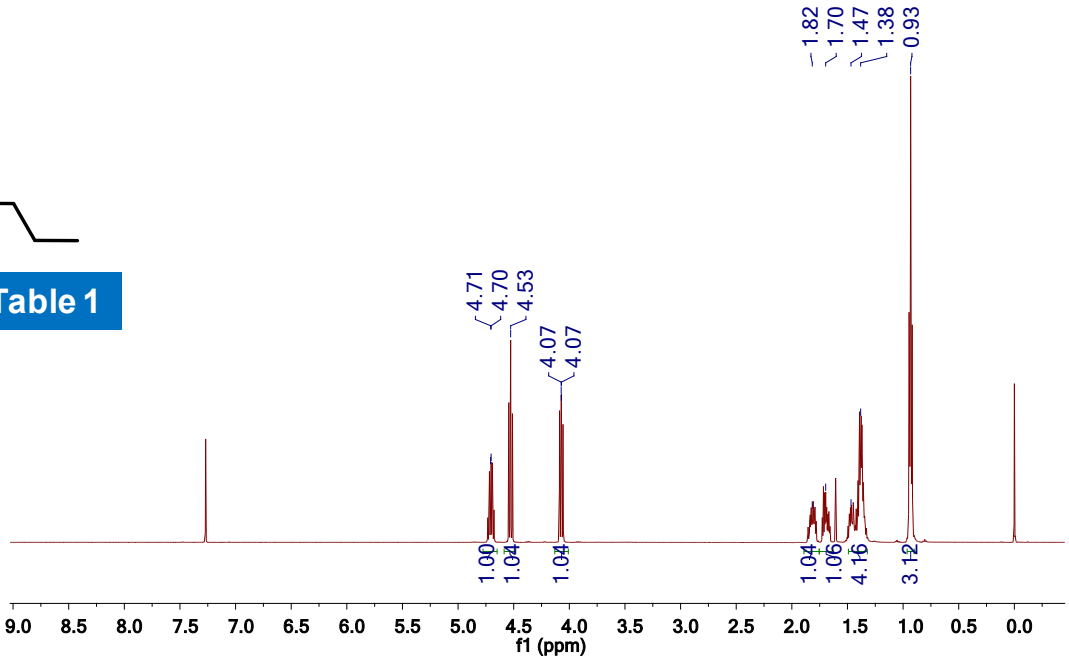

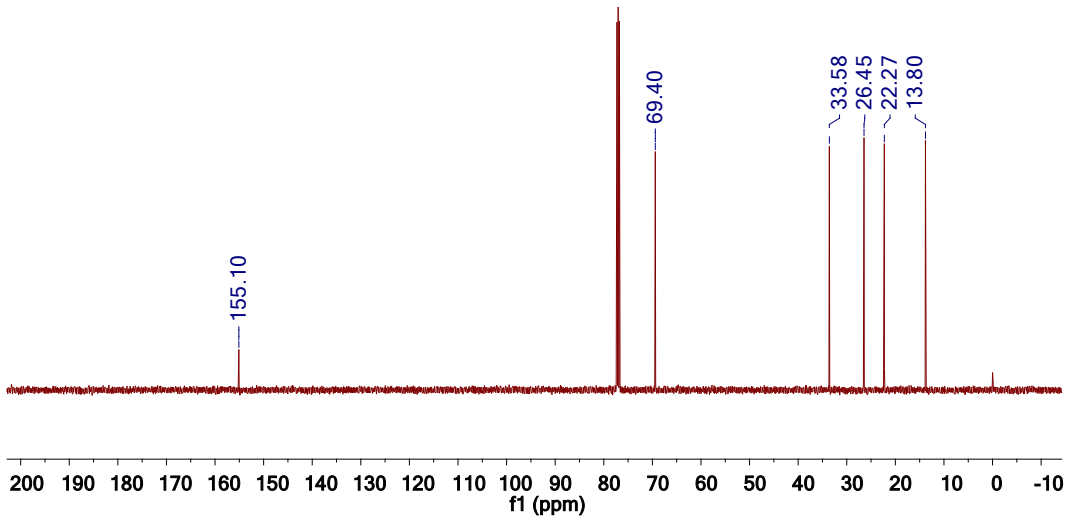

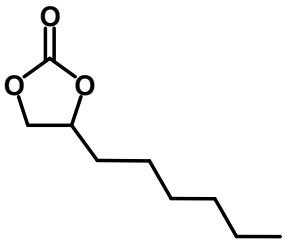

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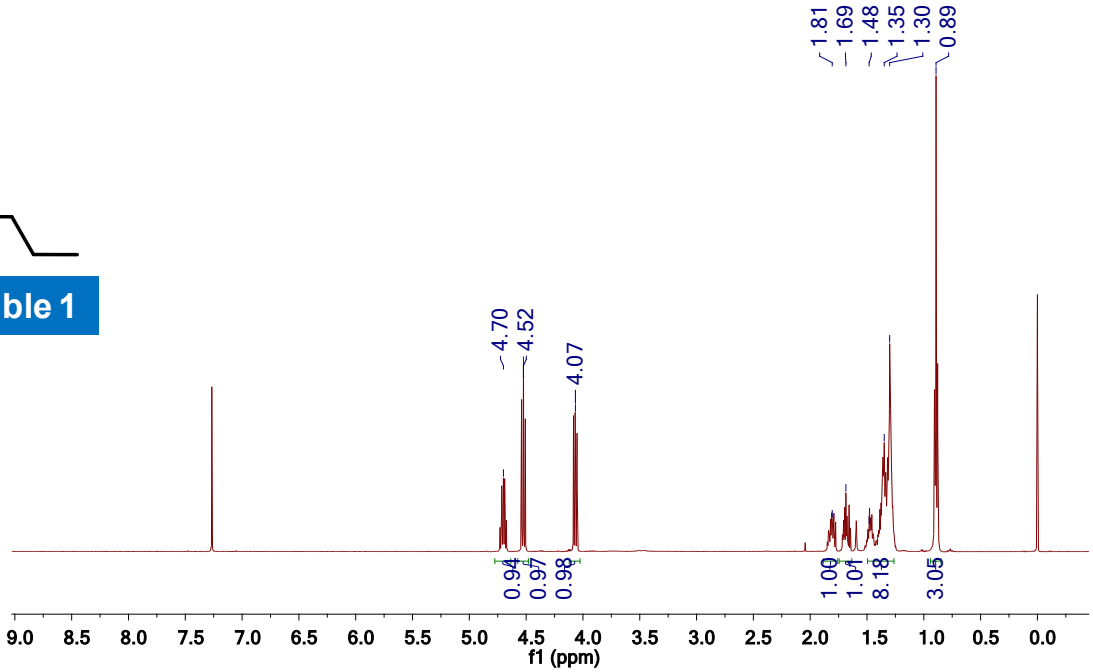

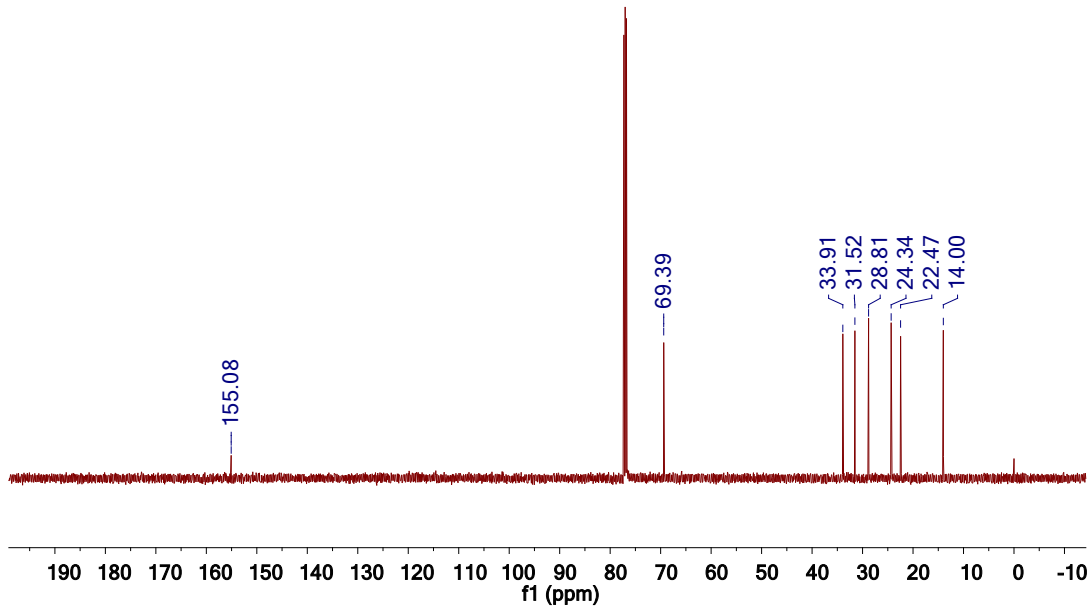

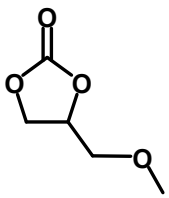

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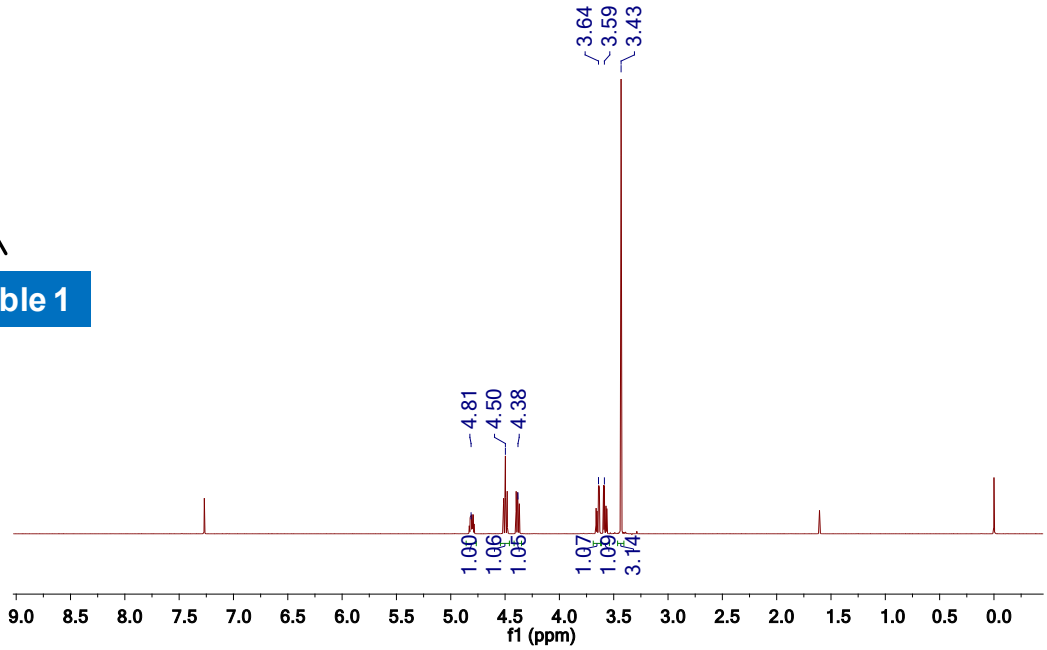

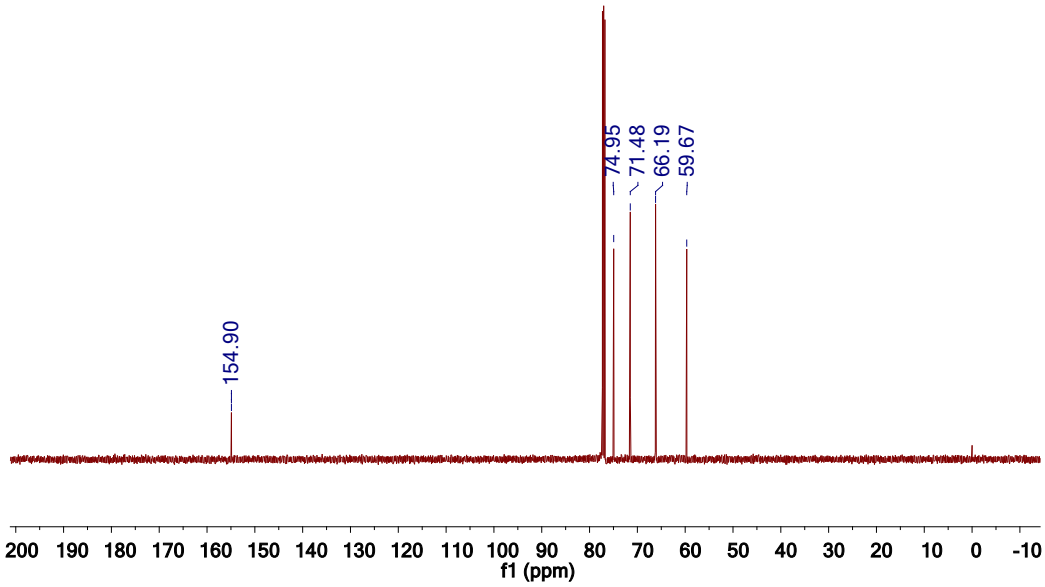

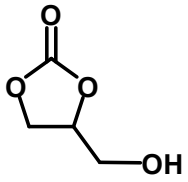

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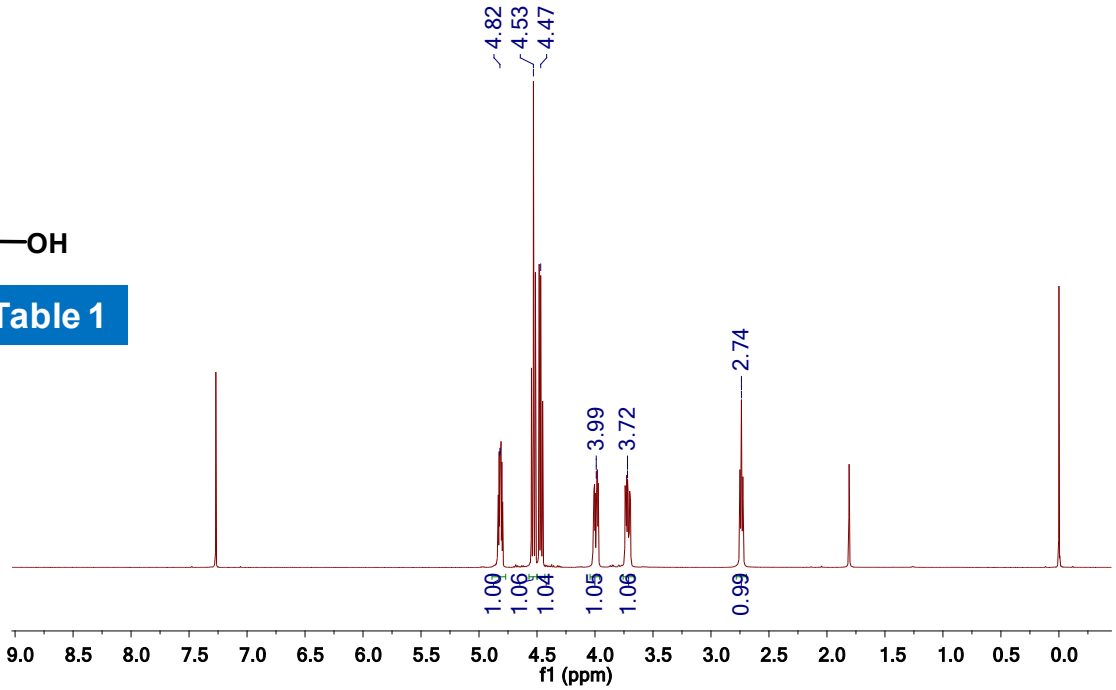

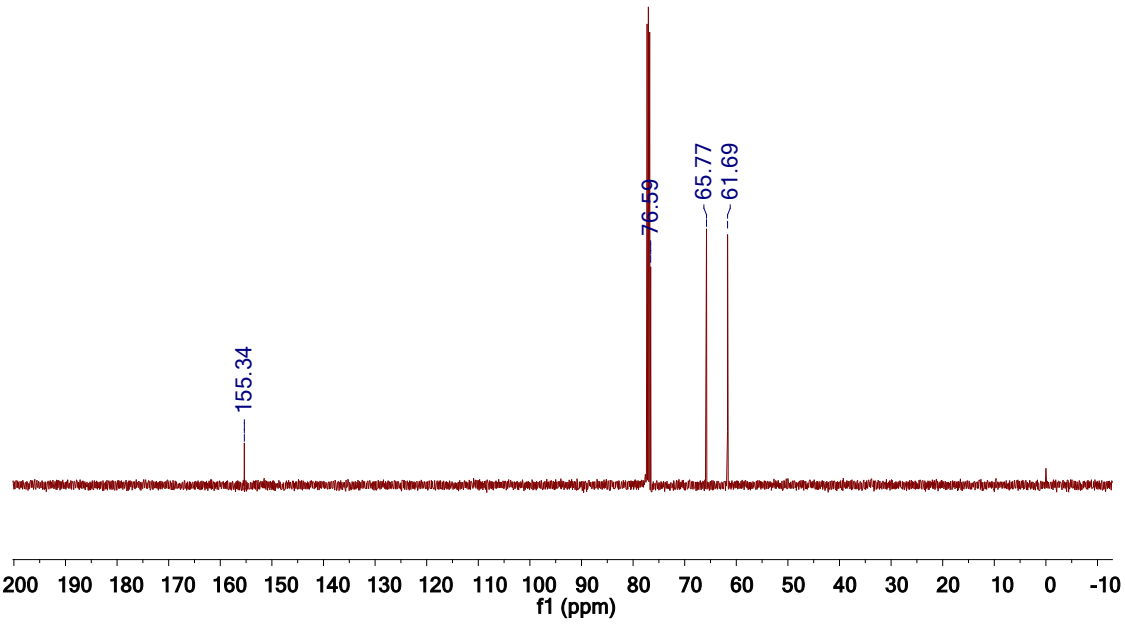

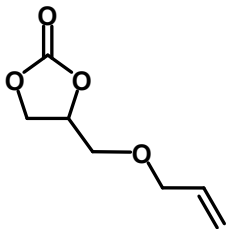

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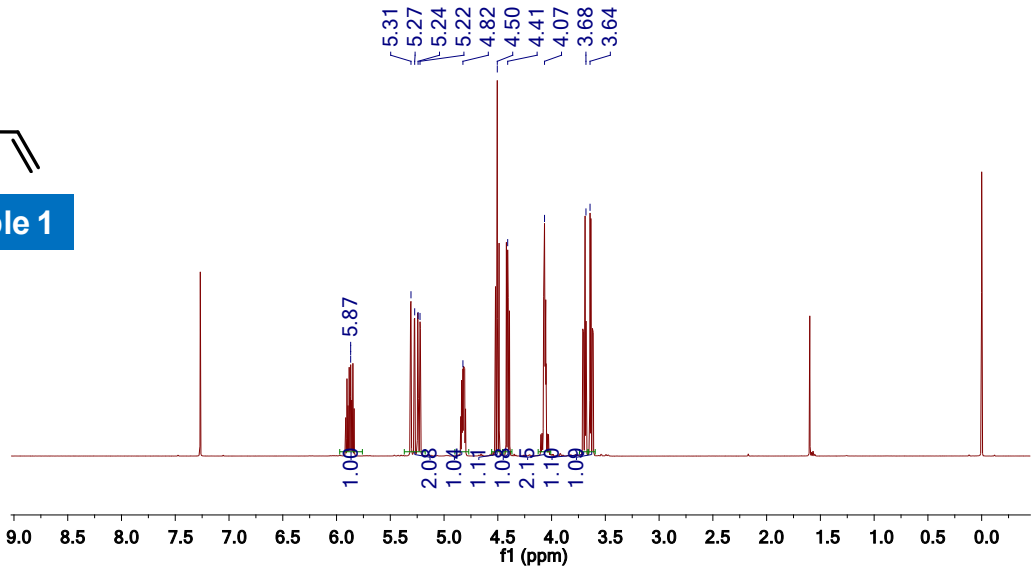

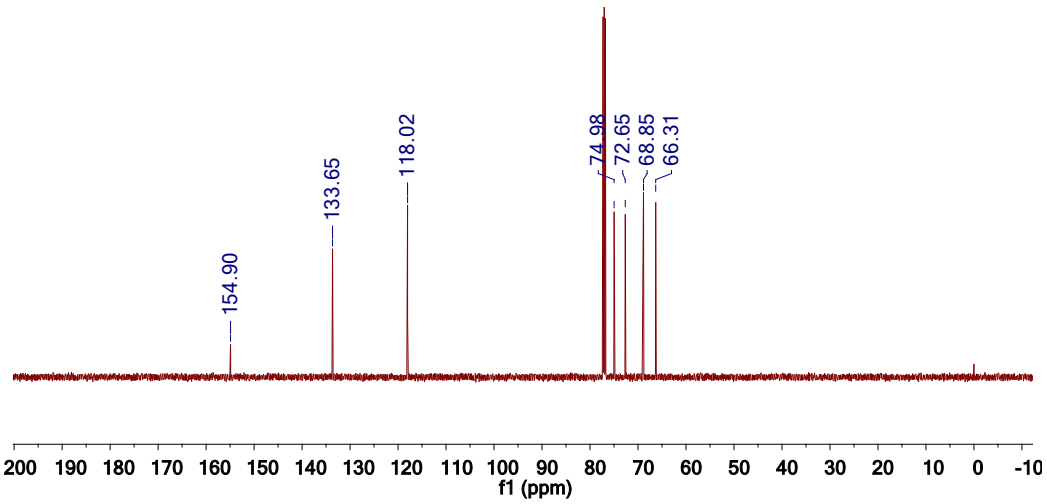

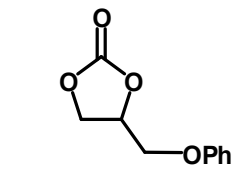

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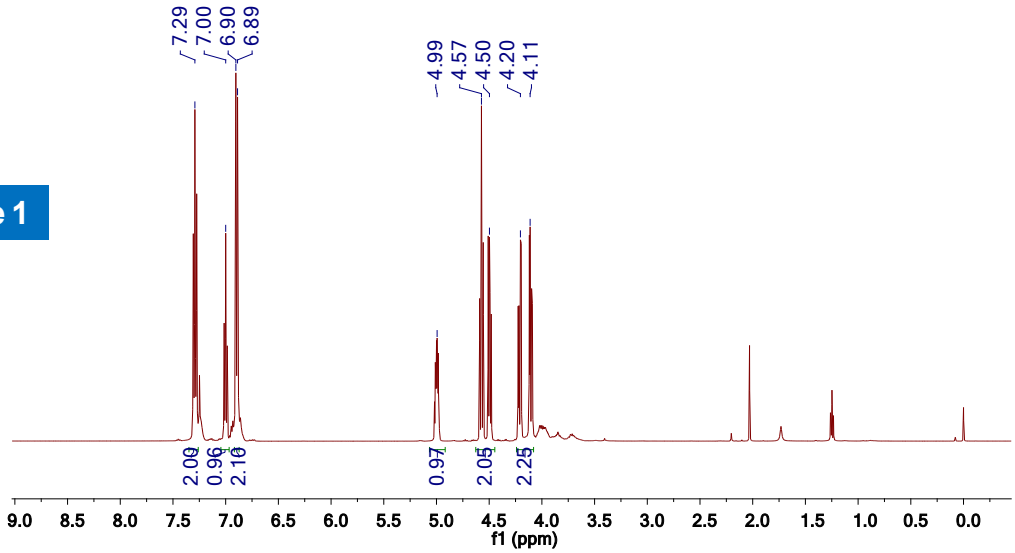

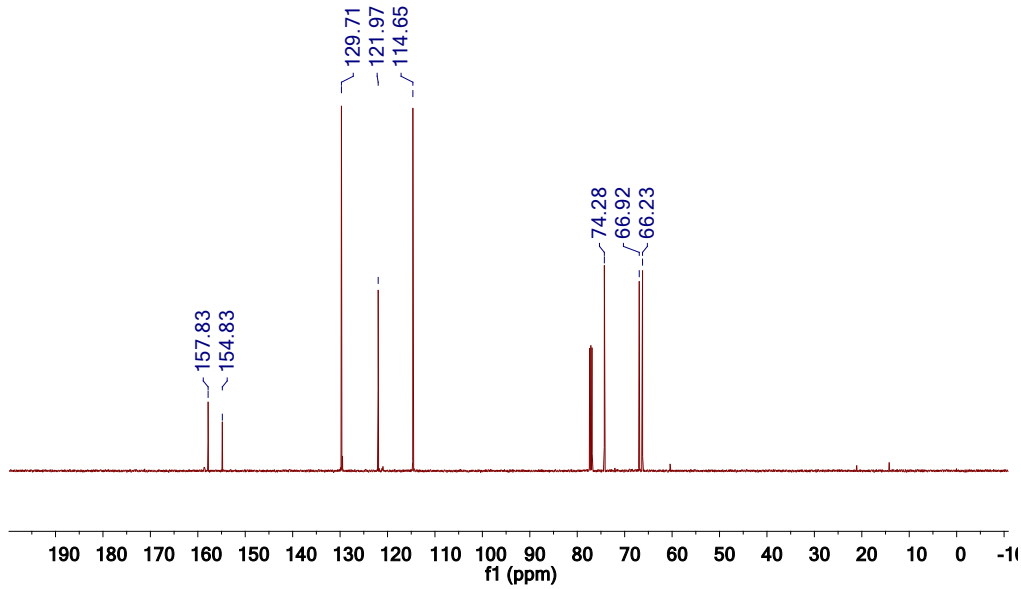

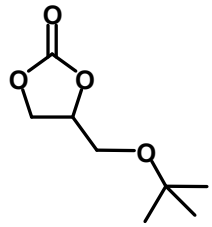

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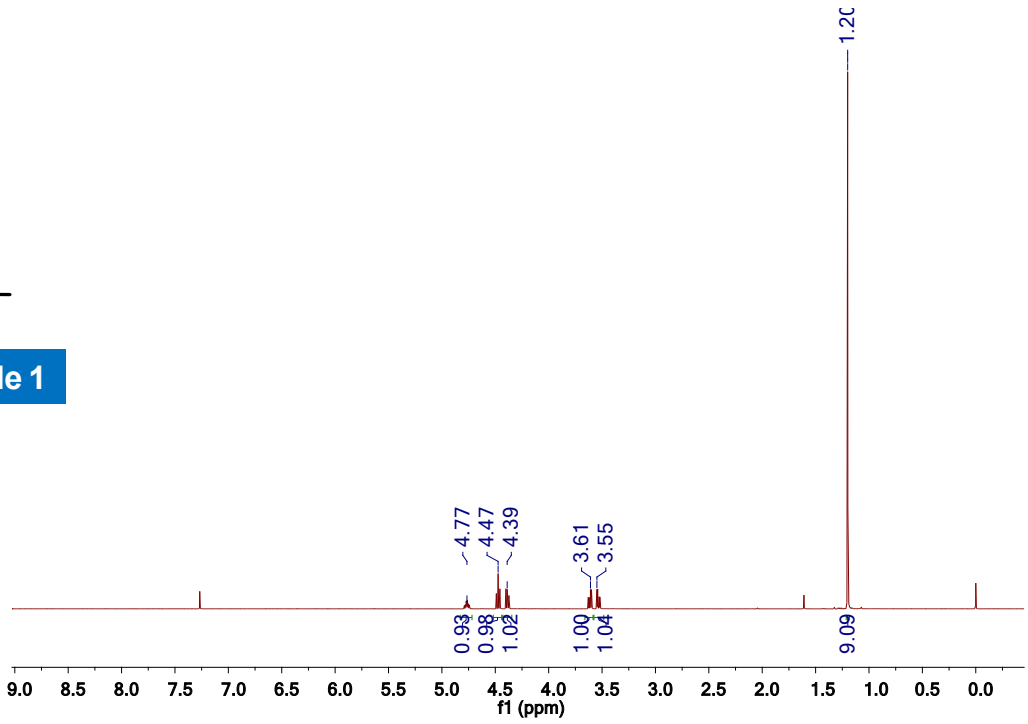

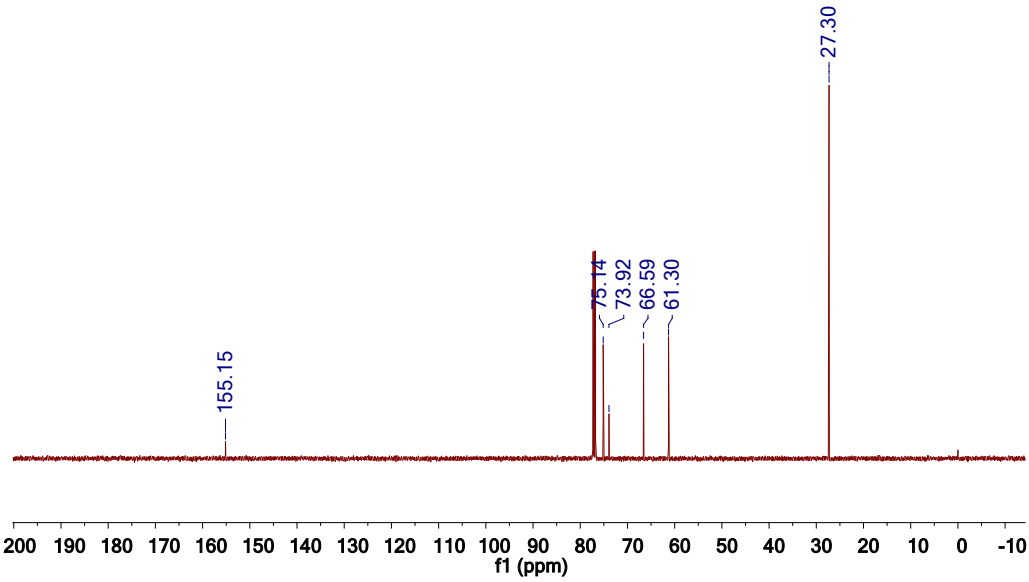

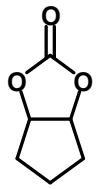

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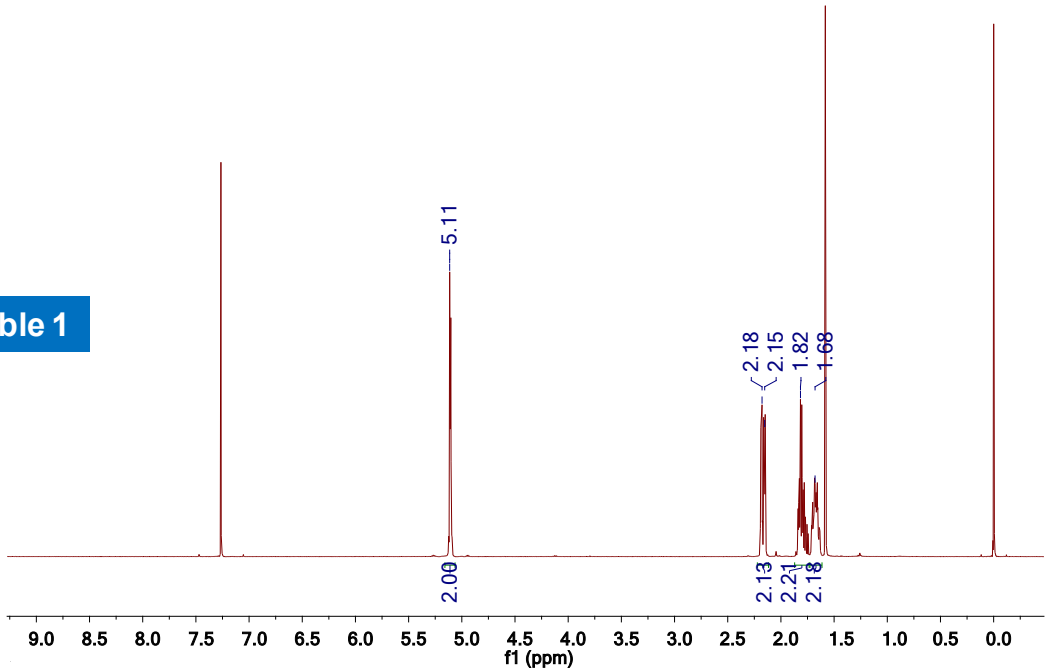

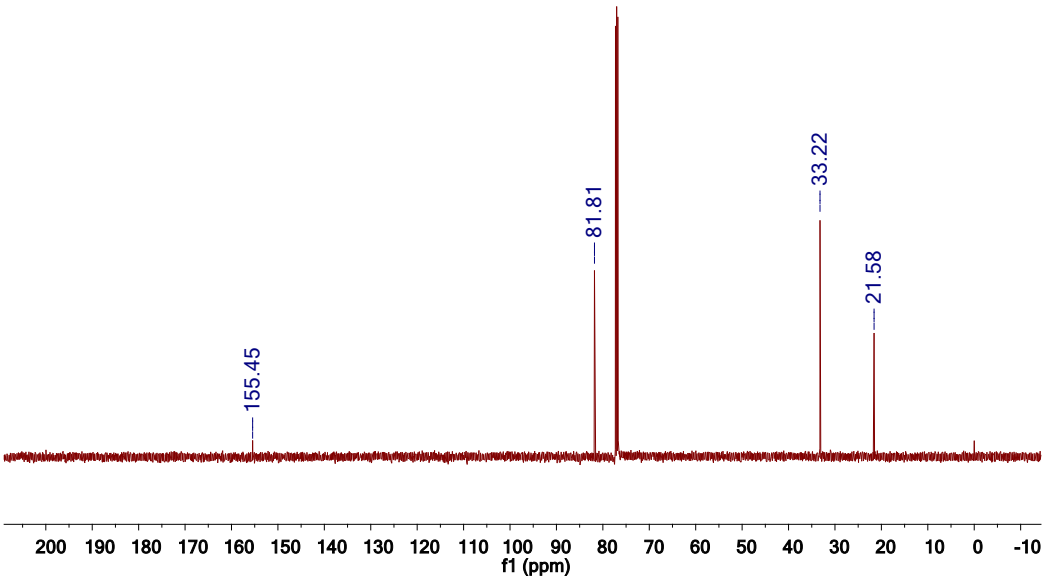

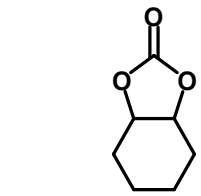

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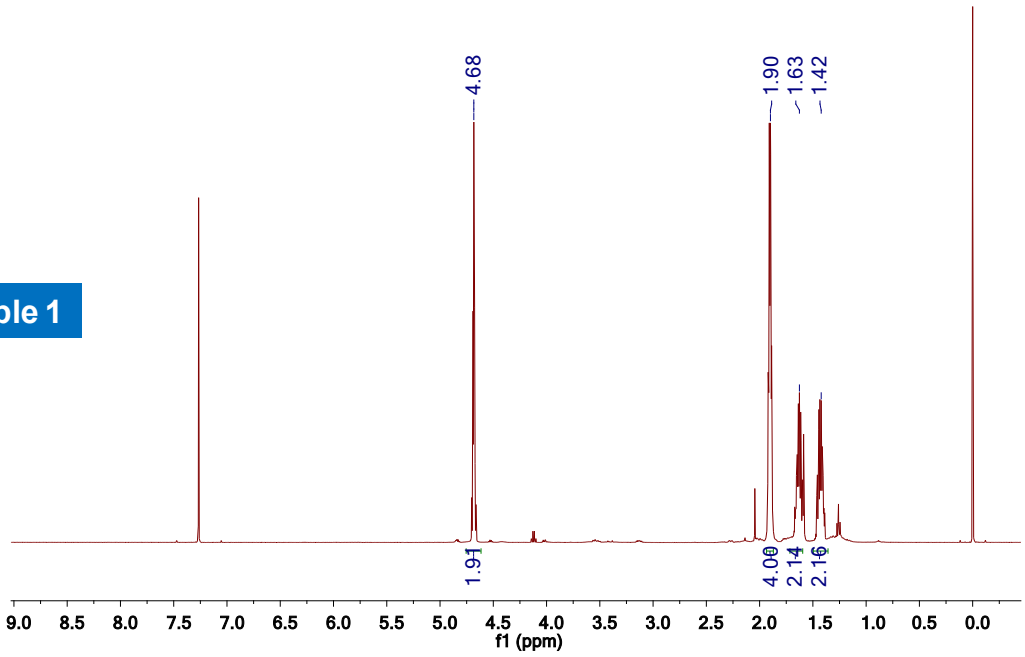

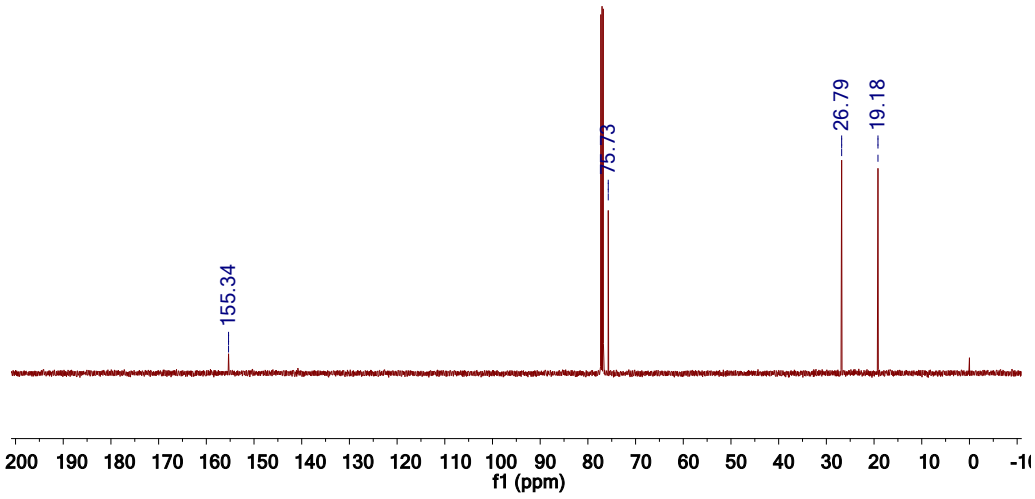

Fig. S10 (a) CO_2 sorption isotherm curves and (b) CO_2 Q_{st} behaviors of H-MCrPN.

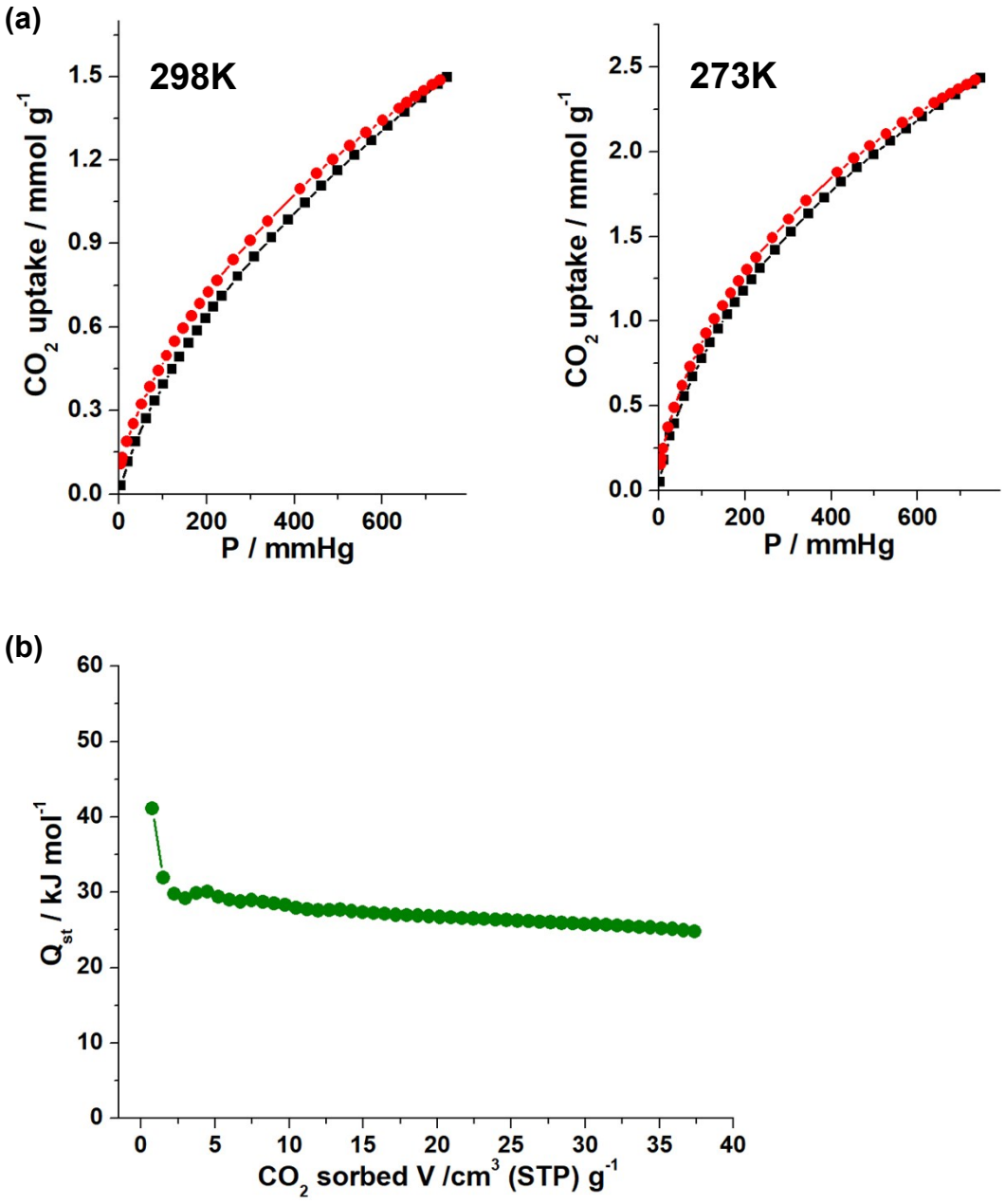

Table S1 Survey of catalytic activities of the recent heterogeneous catalytic systems for CO_2 fixation to cyclic carbonates. SO: styrene oxide, PO: propylene oxide. Reference numbers in text.

Catalyst	catalyst (mol%)	Substrate	CO pressure (atm)	Temperature (^oC)	Time (h)	Yield (%)	TON	TOF (h^{-1})	Ref
Al-salen/SiO_2	2.5	SO	1	26	24	80	32	1.3	Ref. 16
Zn cluster	2	SO	1	25	20	94	47	2.4	Ref. 17
Cr-salen/POP	0.44	SO	ambient	rt	48	51.6	117	2.4	Ref. 18
Co-salen/POP	0.488	PO*	ambient	25	48	81.5	167	3.5	Ref. 19
H-MCrPN	0.488	SO	ambient	rt	48	93	190	4	This work
Al-porphyrin/HCP	0.25	SO	9.9	40	6	91	364	61	Ref.11
Co-porphyrin/POP	0.22	SO	ambient	50	48	74.2	337	7	Ref. 20
Al-salen/ionic POP	0.25	SO	9.9	60	24	82	328	14	Ref. 10
$ZnBr_2$-NHC-polymer	1	SO	1	80	10	94	94	9	Ref. 40
Phosphonium/PIP	0.6	SO	ambient	80	72	67.4	112	1.6	Ref. 7
Phosphonium/SiO_2	1	SO	9.9	90	6	86	86	14	Ref. 37
Co-salen/POP	0.274	SO	20	100	6	97	354	59	Ref. 26
Porphyrin-catechol/COF	0.2	SO	1	110	12	98	490	41	Ref. 6
Zn-porphyrin/BIO	0.1	SO	16.8	120	4	88	880	220	Ref. 8
Zn-salen/CMP	0.1	SO	29.6	120	1	96.4	964	964	Ref. 24
PPh_3-ILBr-$ZnBr_2$/POP	0.0125	SO	29.6	120	1	20	1600	1600	Ref. 5
Amino acid/PS	0.6	SO	88.8	130	24	91	152	6.3	Ref. 41