Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Enhancement in the active site exposure in porphyrin-based PILs /graphene composite catalyst for highly efficient conversion of CO_2

Xiao-Xuan Guo[a], Feng-Lei Zhang[b], Yaseen Muhammad[c], Dong-Liang Hu[d], Zhao-Tian Cai[a], Guo-Min Xiao*[a]

[a] *School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China*

[b] *Intelligent Transportation System Research Center, Southeast University, Nanjing 211189, China*

[c] *Institute of Chemical Sciences, University of Peshawar, 25120, KP, Pakistan*

[d] *School of Transportation, Southeast University, Nanjing 211189, China*

*Corresponding author: Guo-Min Xiao. Tel.: +86-25-52090612; fax: +86-25-52090612.

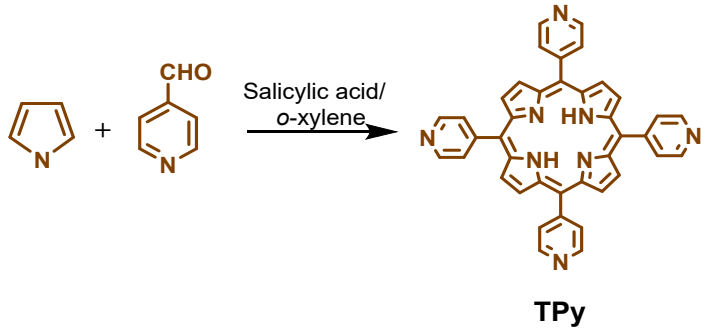
E-mail: xiaogm426@gmail.com

1. Characterization

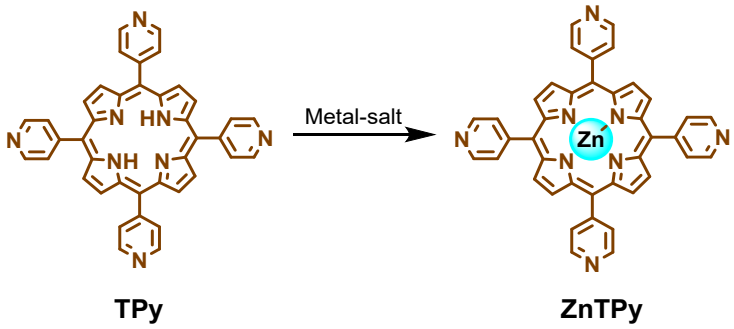
^{1}H NMR measurements were conducted on a Bruker Avance III 600 MHz spectrometer, which used $CDCl_3$ as solvent and tetramethylsilane as internal standard. Solid-State ^{13}C Nuclear Magnetic Resonance spectra were performed with a Bruker Avance III 400 MHz spectrometer. Molecular weight determination was performed by Bruker Ultraflextreme MALDI-TOF-MS. FT-IR spectra were recorded from 400 to 4000 cm-1 in a Nicolet 5700 spectrometer using potassium bromide pellets. Powder X-ray diffraction measurements were carried out on an Ultima IV diffractometer over a 2θ range from 10 to 80 ° using a step size of 0.02 $°s^{-1}$ and a dwell time of 1 s per step. The Raman spectrum data was obtained by Lab RAM HR evolution Raman spectrometer at the wavelength of 532 cm^{-1}. X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo Fisher Scientific ESCALAB 250 spectrometer with a monochromatized Al Kα X-ray source (hν = 1486.6 eV) excitation source under a base pressure of 2×10^{-9} mbar. Elemental analyses (EA) for C, H, and N were detected on a Vario EL III cube instrument. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were conducted on a SpectroBlUE ICP-OES. Samples were first digested in concentrated HNO_3 and then decomposed with a digestion instrument at 120 ℃. The suspension was filtered, and the supernatant was diluted to the desired concentrations. The NH_3-temperature-programmed desorption (NH_3-TPD) was detected through a TP-5076 catalyst analyzer (Xianquan Industrial and Trading Co., Ltd., Tianjin, China). Typically, moderate catalysts (same amount of Zn) were degassed at 150 ^{o}C under flowing helium (He) gas for 1 h, and then cooled to 30 ^{o}C. Next, the sample was exposed to NH_3 atmosphere gas for 30 min. To remove the physically adsorbed NH_3, the sample was purged with helium (He) gas for another 1 h. After that, the desorption curve of the samples at 30 ^{o}C to 450 ^{o}C with a ramp of 10 ^{o}C/min was recorded in He flow. The morphology and size of the catalyst were characterized by a scanning electron microscope (SEM, FEI Inspect F50) and

transmission electron microscope (TEM, Talos F200X). The N_2 absorption-desorption isotherms were determined at 77 K with a BeiShiDe-PS(M) Instrument. The CO_2 sorption isotherms were collected with Micromeritics ASAP 2460 3.01 analyzers at 273K and 298K, respectively. Before these tests, the samples were outgassed in a vacuum at 120 °C for more than 12 h. The reaction filtrates were analyzed by gas chromatography (GC, Shanghai Jingke GC126) equipped with an OV-1701 column and an FID detector. GC-MS (Agilent 7890B) was used to identify the substrate and products.

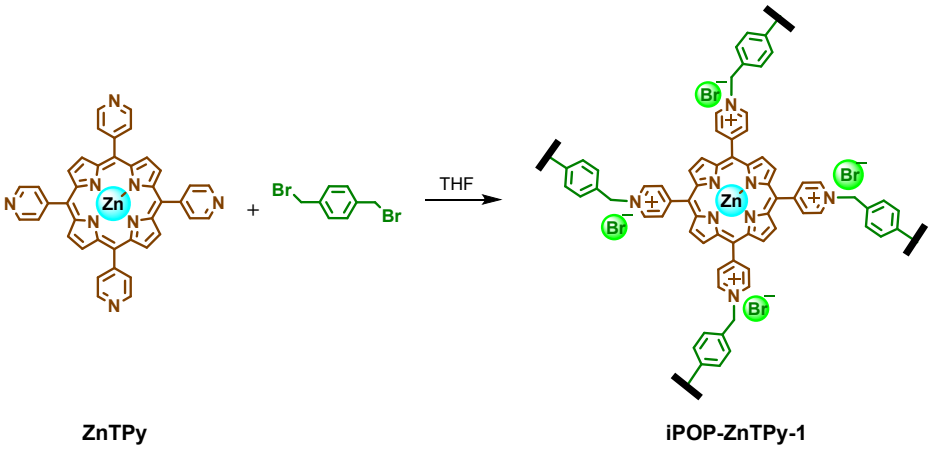
2. Synthesis of catalysts



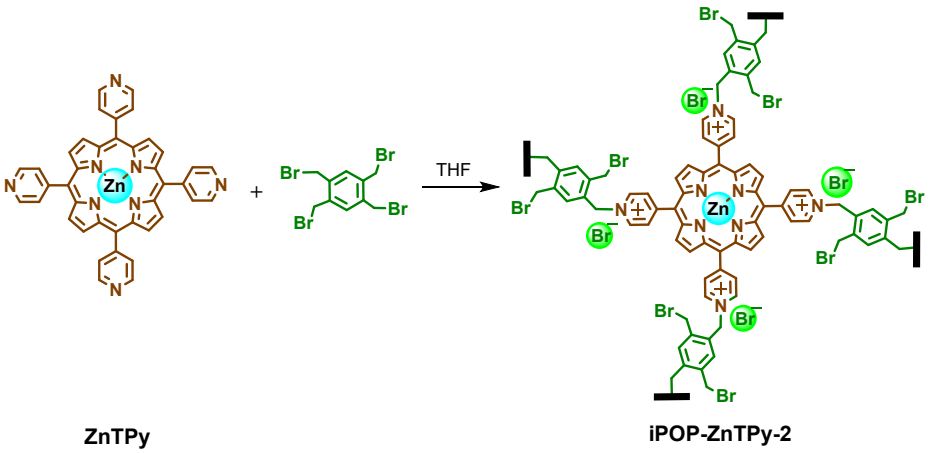
Scheme S1 Schematic illustration for the synthesis of TPy monomer.



Scheme S2 Schematic illustration for the synthesis of ZnTPy monomer.



Scheme S3 Schematic illustration for the synthesis of iPOP-ZnTPy-1.



Scheme S4 Schematic illustration for the synthesis of iPOP-ZnTPy-2.

3. Supplementary Figures

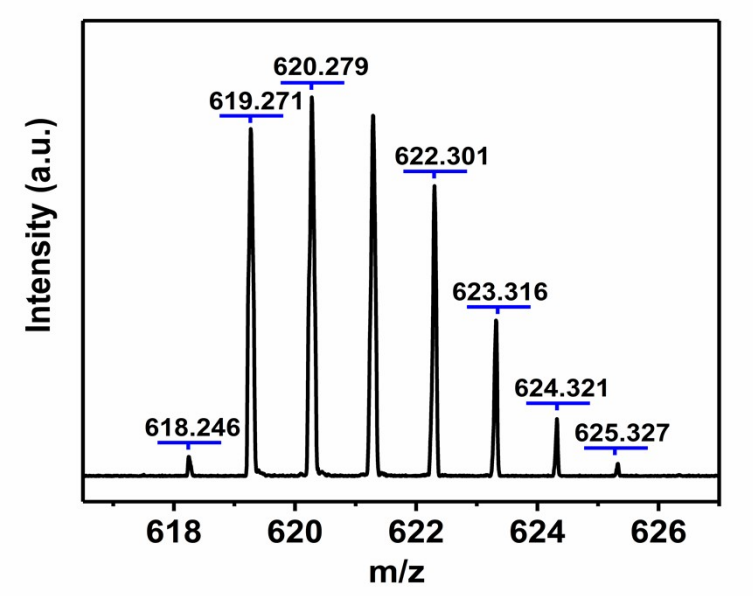


Fig. S1 MALDI-TOF-MS of TPy monomer.

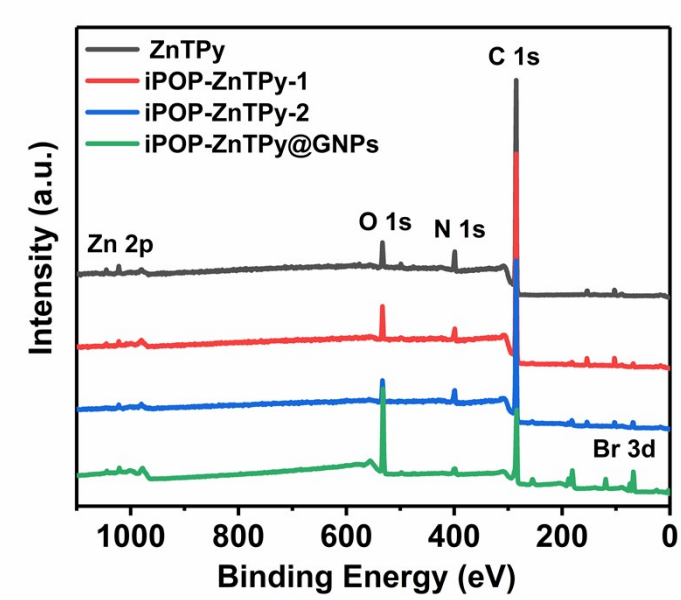


Fig. S2 X-ray photoelectron spectra (XPS) of ZnTPy, iPOP-ZnTPy-n and iPOP-ZnTPy@GNFs.

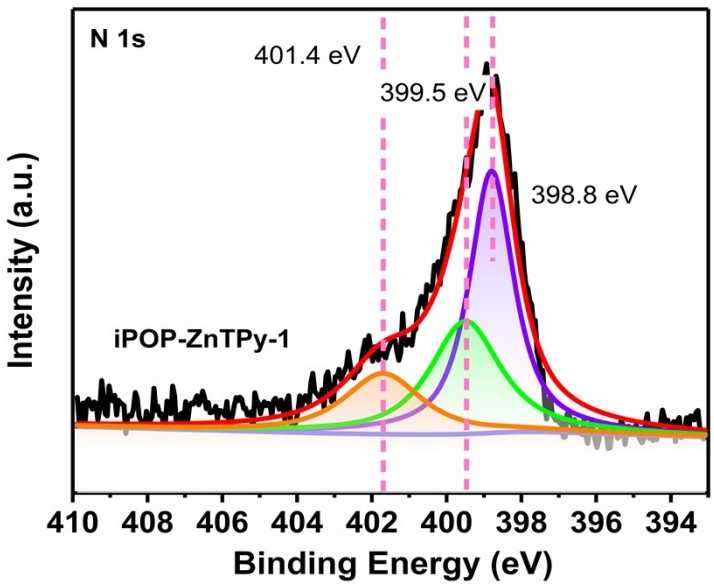


Fig. S3 N 1s XPS spectra of iPOP-ZnTPy-1.

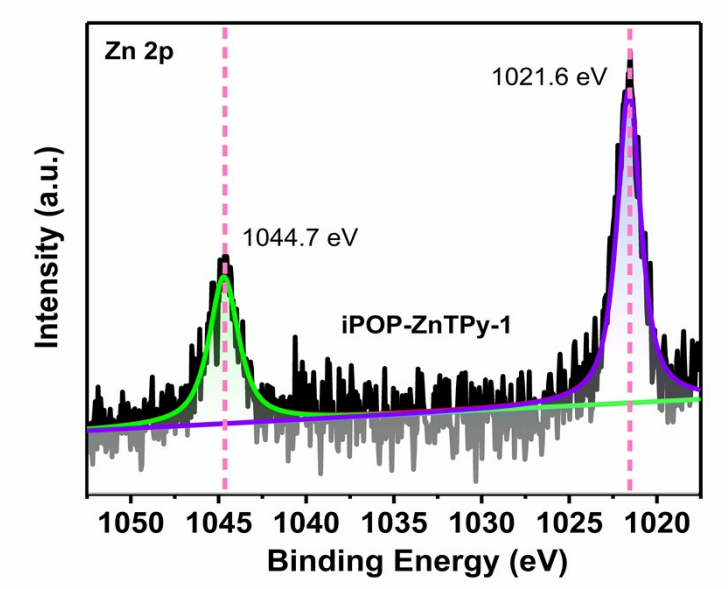


Fig. S4 Zn 2p XPS spectra of iPOP-ZnTPy-1.

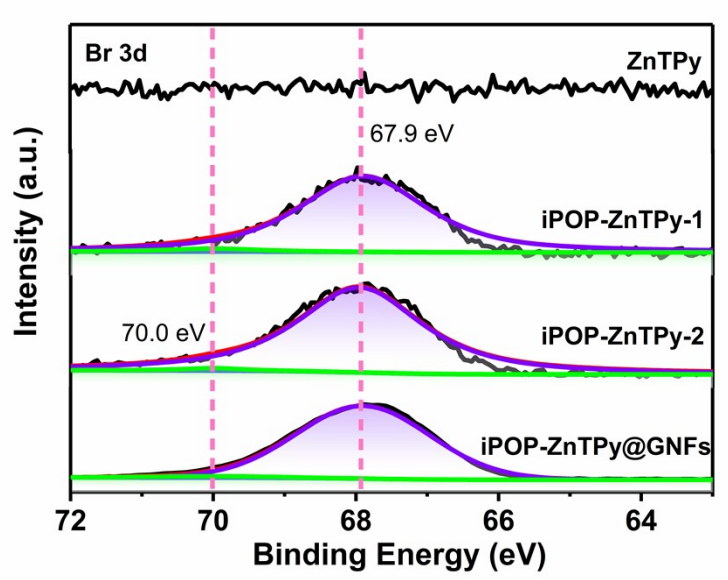


Fig. S5 Br 3d XPS spectra of ZnTPy, iPOP-ZnTPy-n and iPOP-ZnTPy@GNFs.

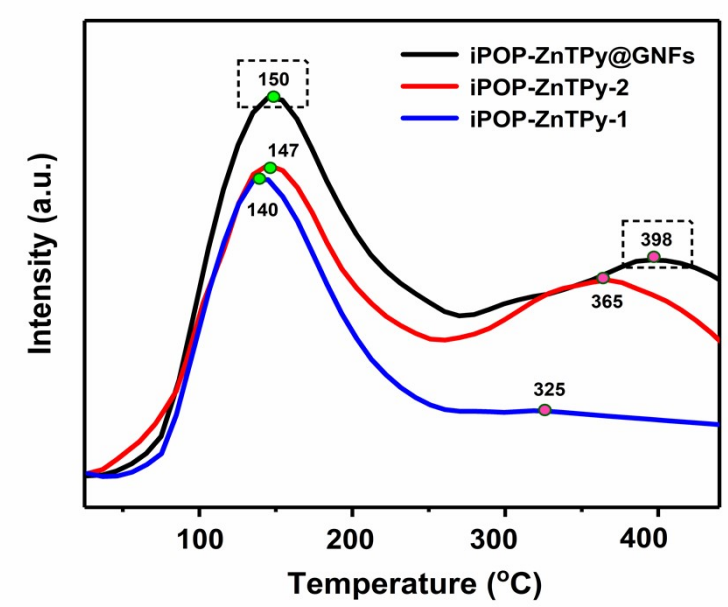


Fig. S6 NH_3-TPD curves of iPOP-ZnTPy-n and iPOP-ZnTPy@GNFs.

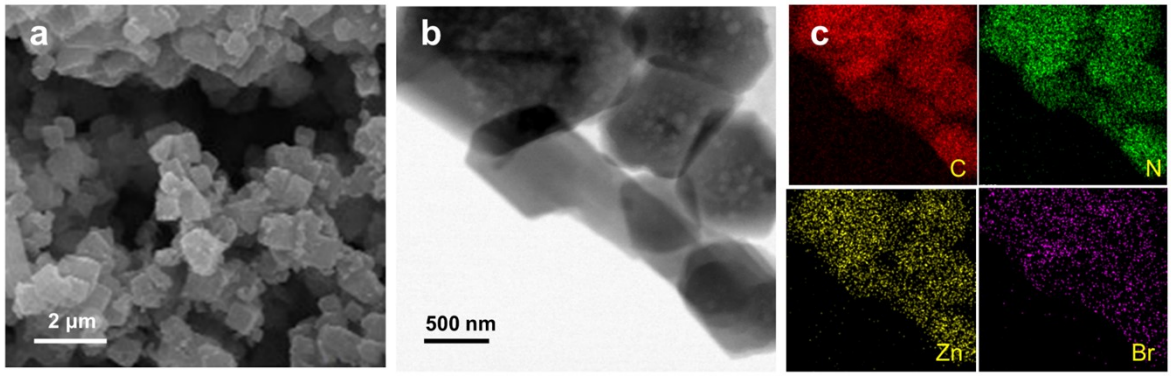


Fig. S7 (a) SEM image, (b) TEM image and (c) element mapping of iPOP-ZnTPy-1.

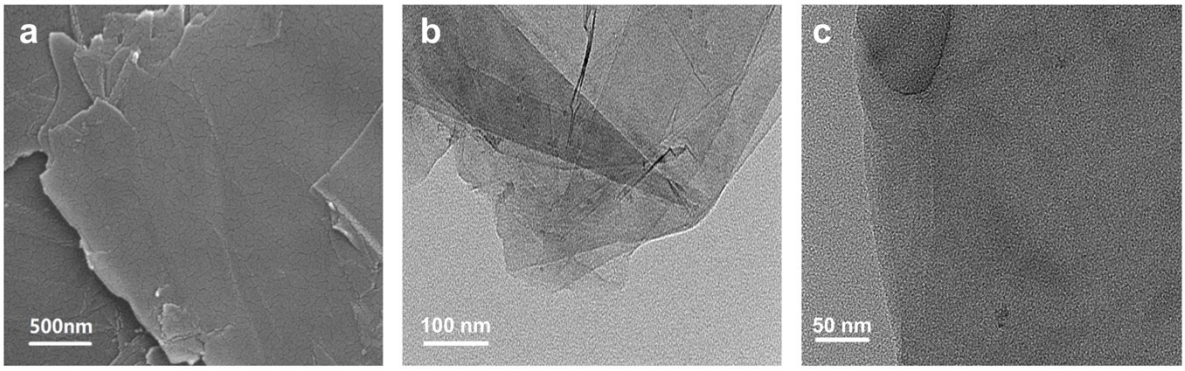


Fig. S8 SEM and TEM image of GNFs.

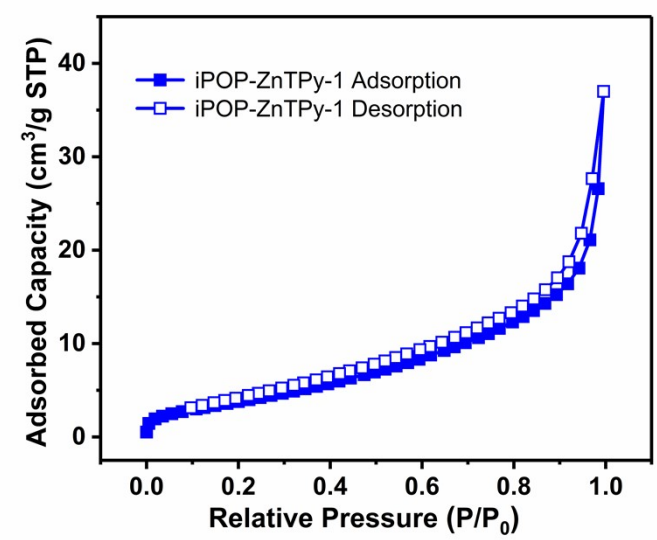


Fig. S9 N_2 adsorption-desorption isotherms at 77 K of **iPOP-ZnTPy-1**.

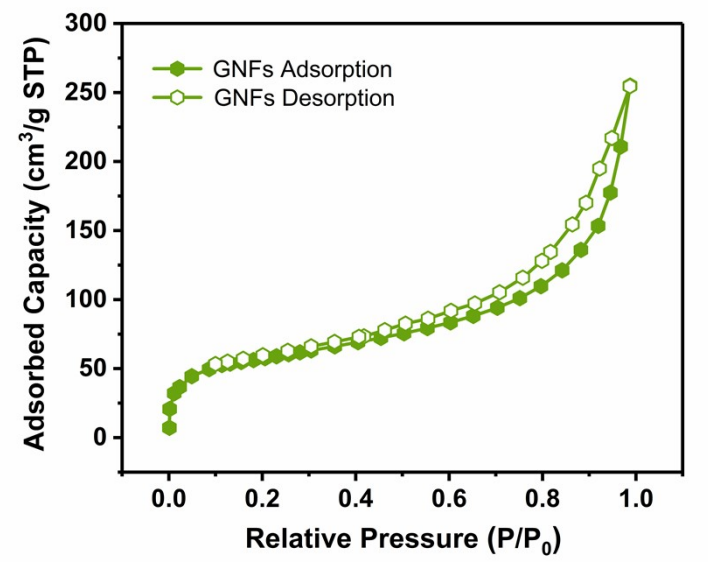


Fig. S10 N_2 adsorption-desorption isotherms at 77 K of GNFs.

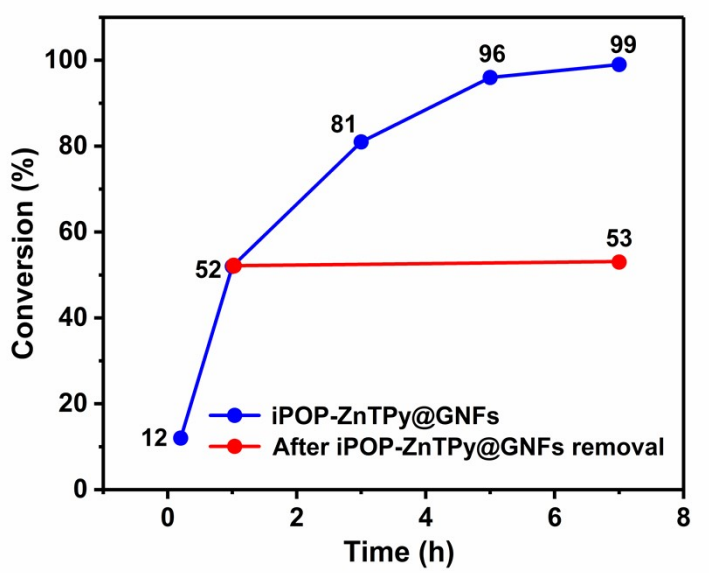


Fig. S11 The leaching test of iPOP-ZnTPy@GNFs for the cycloaddition reaction of CO_2 with PO. [Reaction conditions: PO (10.0 mmol), iPOP-ZnTPy@GNFs (S/C =1000), CO_2 1.5 MPa, 80 °C.]

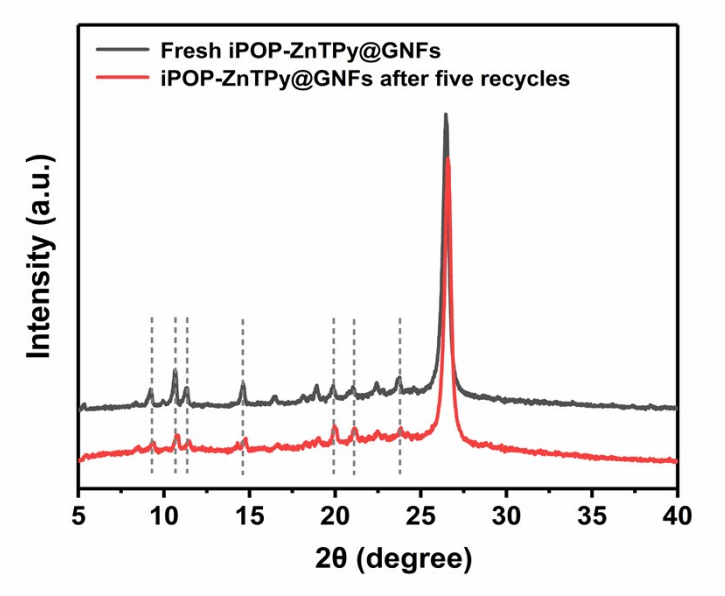


Fig. S12 XRD patterns of **iPOP-ZnTPy@GNFs** after five recycles.

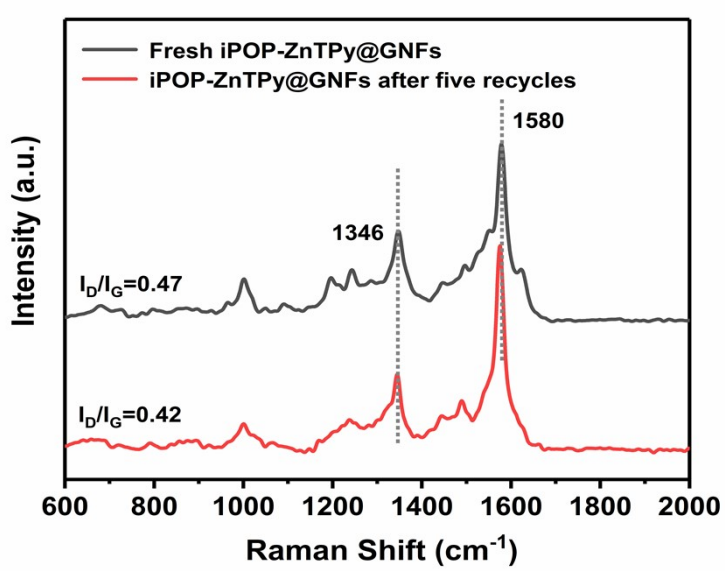


Fig. S13 Raman patterns of iPOP-ZnTPy@GNFs after five recycles.

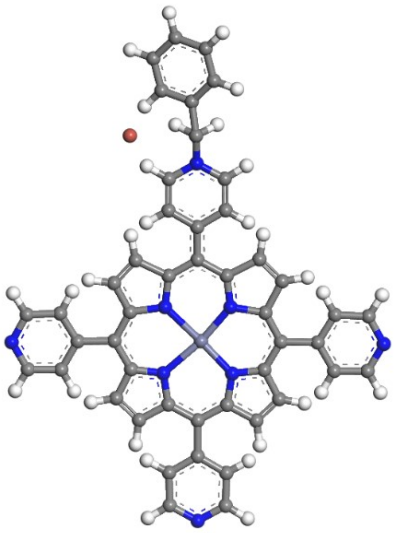


Fig. S14 The structure of model catalyst **ZnTPy-Br**. [Grey = carbon, white = hydrogen, blue = nitrogen, red = oxygen, purple = zinc, brown = bromine.]

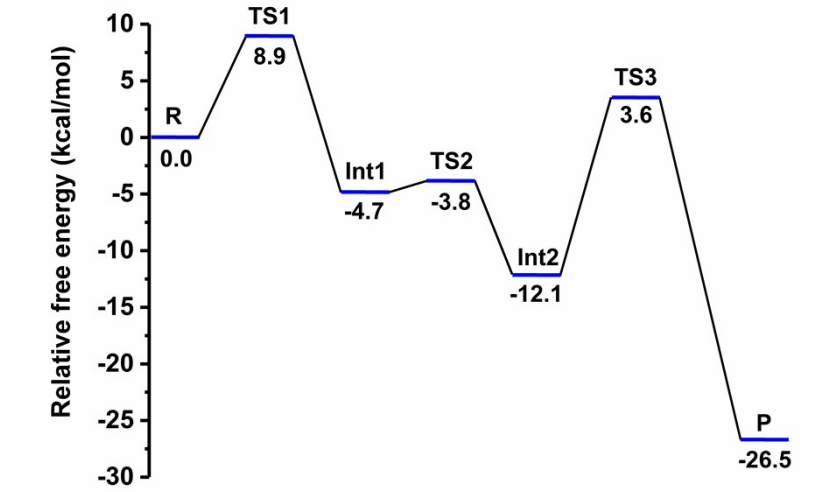


Fig. S15 B3LYP free energy spectra for the cycloaddition reaction of CO_2 with PO over **ZnTPy-Br**. [The relative energies are given in kcal mol^{-1} and relative to R1.]

4. Supplementary Tables

Table S1 The element content of **iPOP-ZnTPy-n** and **iPOP-ZnTPy@GNFs**.

Catalyst	Found (wt%)			
	C	**N**	**H**	**Zn**
ZnTPy	67.95	15.43	4.43	8.01
iPOP-ZnTPy-1	66.99	14.65	3.93	3.17
iPOP-ZnTPy-2	59.55	12.95	4.33	3.05
iPOP-ZnTPy@GNFs	-	-	-	1.06

Table S2 BET surface area, CO_2 uptakes, isosteric heat of CO_2 adsorption for various catalysts.

Catalyst	BET surface area ($m^2 \cdot g^{-1}$)	CO_2 uptakes ($mg \cdot g^{-1}$)-273 K	CO_2 uptakes ($mg \cdot g^{-1}$)-298 K	-Qst for CO_2 ($KJ \cdot mol^{-1}$)
iPOP-ZnTPy-1	14.6	-	-	-
iPOP-ZnTPy-2	18.9	33.0	17.8	24.4-23.6
iPOP-ZnTPy@GNFs	119.3	46.0	27.5	29.7-24.1
GNFs	184.2			

Table S3 Catalytic activities comparison of different one-component polymer catalysts for the cycloaddition reaction of CO_2 with PO.

Entry	Catalyst	Amount of catalyst/mol%	T/°C	P_{CO2} /Mpa	t /h	Yield/%	STY/h^{-1}	Ref.
1	PIM2	0.2	130	1	10	93	46.5	1
2	PS-HEIMBr	1.6	120	2.5	4	98	15.3	2
3	Py-Zn@MA	0.28	120	2	6	81	48.2	3
4	POM3-IM	5	120	1	8	92	2.3	4
5	Al-CPOP	1	120	0.1	24	67	2.8	5
6	Py-Im-6-Zn-5-SCD	0.01	120	0.1	4	99	2475	6
7	PSIL	0.68	110	6	7	97	20.4	7
8	SYSU-Zn@IL2	0.16	100	1	10	99	61.9	8
9	CPP-IL0.05	0.16	100	0.1	24	96	25	9
10	PP-Br-Zn-0.09	0.05	100	1.5	3	95	660	10
11	Co-HIP	0.1	80	0.1	20	96	48	11
12	POF-Zn^{2+}-I^-	0.3	60	1	8	99	41.3	12
13	DVB@ISA	0.25	60	1	24	99	16.5	13
14	**iPOP-ZnTPy@GNFs**	0.1	120	1.5	0.7	99	1507	This work
			100	1.5	3	99	330	
			80	1.5	7	99	141.4	
			60	1.5	13	99	76.2	

Table S4 Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states at B3LYP/6-31G* level of theory.

1-**R1**

N	-0.70710000	-1.68000000	-1.51920000
N	-3.07200000	-0.53270000	-0.34780000
N	0.41120000	0.93230000	-1.74310000
N	-1.88000000	2.08360000	-0.44120000
Zn	-1.16660000	0.14900000	-0.68590000
C	0.51660000	-3.45250000	-2.31430000
C	-0.76470000	-3.89340000	-2.15920000
C	0.53320000	-2.05780000	-1.91280000
C	-1.52590000	-2.79020000	-1.61240000
C	-2.85420000	-2.84830000	-1.19300000
C	-4.89200000	-1.90090000	-0.01920000
C	-5.17590000	-0.70190000	0.57120000
C	-3.56720000	-1.78730000	-0.58250000
C	-4.03080000	0.15100000	0.36140000
C	1.64550000	-1.16890000	-2.03630000
C	1.75950000	2.36240000	-2.95120000
C	2.24580000	1.10230000	-3.11160000
C	0.64430000	2.26690000	-2.03520000
C	1.42680000	0.22780000	-2.29440000
C	0.01140000	3.33890000	-1.41050000
C	-2.78640000	3.75400000	0.86330000
C	-1.69520000	4.27800000	0.22820000
C	-2.90900000	2.38320000	0.42280000
C	-1.14150000	3.22360000	-0.58940000
C	-3.92650000	1.48670000	0.79600000
C	2.98010000	-1.61070000	-1.69830000

C	4.09800000	-0.73600000	-1.72490000
C	5.29530000	-1.07990000	-1.15510000
N	5.48130000	-2.27710000	-0.54910000
C	4.44080000	-3.15920000	-0.49660000
C	3.22790000	-2.86600000	-1.05500000
C	6.48120000	-2.90890000	4.06580000
C	5.92220000	-1.69090000	4.45060000
C	5.59940000	-0.73760000	3.48220000
C	5.83610000	-0.99090000	2.13290000
C	6.40150000	-2.21360000	1.74630000
C	6.71660000	-3.17000000	2.71510000
C	6.67830000	-2.50400000	0.28640000
C	-3.55880000	-4.15610000	-1.31000000
C	-4.66490000	-4.31830000	-2.15190000
C	-5.28590000	-5.56450000	-2.21940000
N	-4.89040000	-6.63490000	-1.51850000
C	-3.83540000	-6.47080000	-0.71030000
C	-3.14330000	-5.26900000	-0.56930000
C	-4.98490000	1.98010000	1.71860000
C	-5.81720000	3.05620000	1.38770000
C	-6.78820000	3.46530000	2.30030000
N	-6.98080000	2.89020000	3.49400000
C	-6.18120000	1.86150000	3.80420000
C	-5.18290000	1.37090000	2.96470000
C	0.66410000	4.66990000	-1.52200000
C	-0.02170000	5.80140000	-1.98210000
C	0.65640000	7.01620000	-2.05260000
N	1.93810000	7.17700000	-1.69740000
C	2.58350000	6.09020000	-1.25250000

C	2.00650000	4.82480000	-1.14530000
Br	4.07750000	1.74880000	0.20930000
H	1.34430000	-3.99130000	-2.75220000
H	-1.16220000	-4.86510000	-2.41050000
H	-5.51680000	-2.77990000	-0.05950000
H	-6.08200000	-0.41810000	1.08410000
H	2.11370000	3.27200000	-3.41110000
H	3.04930000	0.78920000	-3.76060000
H	-3.43890000	4.25050000	1.56500000
H	-1.29510000	5.27610000	0.31940000
H	4.01690000	0.29000000	-2.03730000
H	6.10930000	-0.37010000	-1.09830000
H	4.62350000	-4.07320000	0.05370000
H	2.43020000	-3.58000000	-0.91380000
H	6.72980000	-3.65750000	4.81170000
H	5.73610000	-1.48620000	5.50040000
H	5.16170000	0.21390000	3.76700000
H	5.54480000	-0.23250000	1.40700000
H	7.14990000	-4.12100000	2.41500000
H	6.99830000	-3.53970000	0.14750000
H	7.46420000	-1.85790000	-0.11330000
H	-5.02730000	-3.48710000	-2.74730000
H	-6.14340000	-5.71020000	-2.87320000
H	-3.52800000	-7.34570000	-0.14070000
H	-2.30430000	-5.18520000	0.11260000
H	-5.71490000	3.55470000	0.43000000
H	-7.44750000	4.29600000	2.05670000
H	-6.34500000	1.40470000	4.77820000
H	-4.55770000	0.53900000	3.26960000

H	-1.05890000	5.72910000	-2.29210000
H	0.14450000	7.90490000	-2.41690000
H	3.62140000	6.23370000	-0.96040000
H	2.58070000	3.98380000	-0.76040000
C	1.15390000	0.33520000	1.39540000
O	-0.25580000	-0.06340000	1.20690000
C	0.07550000	1.05790000	2.07340000
C	2.02440000	-0.67410000	2.07520000
H	1.59300000	0.80670000	0.52140000
H	-0.14020000	0.85770000	3.11990000
H	-0.24440000	2.02580000	1.69930000
H	2.98500000	-0.19960000	2.28480000
H	2.21570000	-1.51580000	1.40290000
H	1.57620000	-1.05140000	2.99890000
C	-1.91650000	-1.94820000	2.32230000
O	-1.42750000	-2.84650000	1.75710000
O	-2.42250000	-1.08430000	2.92720000

2-**TS1**

N	-0.53180000	-1.64920000	-1.60350000
N	-2.96610000	-0.72510000	-0.33440000
N	0.31280000	1.05820000	-1.83830000
N	-2.02730000	1.99320000	-0.44260000
Zn	-1.10060000	0.11410000	-0.61570000
C	0.75320000	-3.27770000	-2.59210000
C	-0.47030000	-3.83140000	-2.35470000
C	0.69350000	-1.90940000	-2.11280000
C	-1.26850000	-2.81850000	-1.69700000
C	-2.56040000	-3.00150000	-1.21300000

C	-4.65410000	-2.25190000	0.00460000
C	-5.04440000	-1.08100000	0.59150000
C	-3.35000000	-2.01620000	-0.56750000
C	-3.98180000	-0.12990000	0.37320000
C	1.72930000	-0.92080000	-2.22040000
C	1.57600000	2.64290000	-2.95420000
C	2.15920000	1.43060000	-3.15670000
C	0.44690000	2.42070000	-2.07430000
C	1.38360000	0.46210000	-2.40270000
C	-0.26760000	3.41700000	-1.41780000
C	-3.10650000	3.58710000	0.83180000
C	-2.06820000	4.20600000	0.19800000
C	-3.08430000	2.20240000	0.41190000
C	-1.40810000	3.19550000	-0.59910000
C	-4.00630000	1.21510000	0.79530000
C	3.09230000	-1.22930000	-1.87910000
C	4.03040000	-0.18950000	-1.60550000
C	5.24720000	-0.44500000	-1.04230000
N	5.64200000	-1.70600000	-0.72410000
C	4.78130000	-2.73820000	-0.95840000
C	3.55370000	-2.53950000	-1.52500000
C	6.61650000	-3.03410000	3.76060000
C	5.85210000	-2.01630000	4.32950000
C	5.39310000	-0.96520000	3.53280000
C	5.69620000	-0.92450000	2.17360000
C	6.46730000	-1.94480000	1.60100000
C	6.91970000	-2.99910000	2.39860000
C	6.82830000	-1.90900000	0.13010000
C	-3.14570000	-4.36810000	-1.32340000

C	-4.25500000	-4.62970000	-2.13530000
C	-4.75430000	-5.92970000	-2.19690000
N	-4.23740000	-6.96130000	-1.51690000
C	-3.17990000	-6.70180000	-0.73760000
C	-2.60220000	-5.44000000	-0.60610000
C	-5.11110000	1.61160000	1.71070000
C	-6.05560000	2.58250000	1.35720000
C	-7.06470000	2.90390000	2.26350000
N	-7.19150000	2.33910000	3.47070000
C	-6.28340000	1.41180000	3.80200000
C	-5.23860000	1.01250000	2.97050000
C	0.28640000	4.79730000	-1.48130000
C	-0.44410000	5.87130000	-2.00260000
C	0.14160000	7.13560000	-2.02360000
N	1.37200000	7.39520000	-1.56270000
C	2.05970000	6.36260000	-1.05680000
C	1.57540000	5.05630000	-0.99290000
Br	3.64230000	2.02390000	0.88110000
H	1.57230000	-3.72200000	-3.13850000
H	-0.81110000	-4.81900000	-2.62690000
H	-5.19690000	-3.18390000	-0.03090000
H	-5.97130000	-0.87860000	1.10580000
H	1.86830000	3.59770000	-3.36410000
H	3.01360000	1.20160000	-3.77650000
H	-3.81120000	4.02460000	1.52210000
H	-1.76950000	5.24020000	0.27420000
H	3.75130000	0.85080000	-1.65530000
H	5.90710000	0.36090000	-0.75050000
H	5.11790000	-3.71500000	-0.63430000

H	2.90930000	-3.39940000	-1.62050000
H	6.97270000	-3.85780000	4.37140000
H	5.61220000	-2.04300000	5.38790000
H	4.79450000	-0.16620000	3.95820000
H	5.29960000	-0.09900000	1.58620000
H	7.51400000	-3.79490000	1.95620000
H	7.31000000	-2.84110000	-0.17530000
H	7.51900000	-1.09200000	-0.09570000
H	-4.71280000	-3.83340000	-2.71230000
H	-5.61200000	-6.15360000	-2.82800000
H	-2.77330000	-7.54680000	-0.18530000
H	-1.75420000	-5.27950000	0.05060000
H	-6.00820000	3.06740000	0.38830000
H	-7.81120000	3.65160000	2.00310000
H	-6.39480000	0.96350000	4.78720000
H	-4.52460000	0.26240000	3.29130000
H	-1.44420000	5.71830000	-2.39420000
H	-0.40510000	7.98220000	-2.43440000
H	3.05410000	6.58800000	-0.67750000
H	2.17700000	4.26400000	-0.55270000
C	1.21880000	-0.23430000	1.17520000
O	-0.18770000	0.03850000	1.19450000
C	1.17360000	1.21540000	1.24530000
C	1.73750000	-1.00860000	2.36050000
H	1.56980000	-0.64190000	0.22890000
H	1.09570000	1.69770000	2.20850000
H	1.01300000	1.79300000	0.35620000
H	2.82700000	-0.93480000	2.39430000
H	1.45240000	-2.06130000	2.28550000

H	1.32770000	-0.59980000	3.28940000
O	-1.12690000	-2.74790000	1.75130000
C	-1.73020000	-1.92940000	2.33070000
O	-2.36220000	-1.16850000	2.95240000

3-**Int1**

N	-0.76530000	-1.67530000	-1.48800000
N	-3.04560000	-0.54090000	-0.16310000
N	0.39390000	0.91780000	-1.71230000
N	-1.85930000	2.06170000	-0.32820000
Zn	-1.06400000	0.09570000	-0.38150000
C	0.40570000	-3.44700000	-2.36220000
C	-0.87320000	-3.87870000	-2.17910000
C	0.44430000	-2.06080000	-1.92370000
C	-1.60260000	-2.77660000	-1.57720000
C	-2.89860000	-2.83220000	-1.07750000
C	-4.85830000	-1.90000000	0.24440000
C	-5.09980000	-0.71310000	0.87220000
C	-3.56410000	-1.77660000	-0.39190000
C	-3.95950000	0.13630000	0.60510000
C	1.58220000	-1.19010000	-2.04330000
C	1.67600000	2.34080000	-3.00740000
C	2.17730000	1.08200000	-3.15000000
C	0.58330000	2.24820000	-2.06110000
C	1.38160000	0.21800000	-2.29620000
C	-0.08810000	3.32350000	-1.49090000
C	-2.80520000	3.79440000	0.86610000
C	-1.77550000	4.31640000	0.13520000
C	-2.86790000	2.38580000	0.54530000

C	-1.19960000	3.21890000	-0.60850000
C	-3.84610000	1.48100000	1.00310000
C	2.87630000	-1.66800000	-1.69360000
C	4.08490000	-0.91150000	-1.84650000
C	5.26330000	-1.32920000	-1.30700000
N	5.36060000	-2.47520000	-0.56810000
C	4.23220000	-3.22510000	-0.38240000
C	3.03600000	-2.87880000	-0.93620000
C	7.08980000	-1.84710000	3.95220000
C	6.33390000	-0.68280000	4.10230000
C	5.62020000	-0.17900000	3.01580000
C	5.66290000	-0.83300000	1.78550000
C	6.42530000	-1.99350000	1.62690000
C	7.13410000	-2.50040000	2.72110000
C	6.53830000	-2.69060000	0.28120000
C	-3.62720000	-4.12700000	-1.18950000
C	-4.79570000	-4.24420000	-1.95100000
C	-5.43710000	-5.47960000	-2.01920000
N	-5.00610000	-6.58110000	-1.39080000
C	-3.89120000	-6.46070000	-0.65940000
C	-3.17350000	-5.27320000	-0.52650000
C	-4.87920000	1.99180000	1.94550000
C	-5.76460000	3.01810000	1.59480000
C	-6.71120000	3.44150000	2.52600000
N	-6.83240000	2.92570000	3.75570000
C	-5.98360000	1.94310000	4.08390000
C	-5.00420000	1.44300000	3.22770000
C	0.46110000	4.68250000	-1.74560000
C	-0.30220000	5.69450000	-2.33940000

C	0.28110000	6.94290000	-2.54840000
N	1.54000000	7.24620000	-2.20570000
C	2.25980000	6.27540000	-1.62840000
C	1.77790000	4.99150000	-1.37890000
Br	3.30550000	1.75110000	0.47450000
H	1.22650000	-3.98590000	-2.81390000
H	-1.28830000	-4.84230000	-2.43320000
H	-5.48910000	-2.77520000	0.22450000
H	-5.97410000	-0.43200000	1.43930000
H	1.99440000	3.24110000	-3.51090000
H	2.95230000	0.76240000	-3.83110000
H	-3.45500000	4.31640000	1.55150000
H	-1.43200000	5.33950000	0.11680000
H	4.08000000	0.04930000	-2.33300000
H	6.17480000	-0.75170000	-1.39840000
H	4.34010000	-4.08540000	0.26620000
H	2.17270000	-3.47640000	-0.68280000
H	7.64020000	-2.25210000	4.79570000
H	6.29790000	-0.17730000	5.06200000
H	5.02170000	0.72220000	3.10190000
H	5.07830000	-0.42330000	0.97110000
H	7.72150000	-3.40890000	2.61230000
H	6.67020000	-3.76780000	0.41230000
H	7.40790000	-2.32800000	-0.27750000
H	-5.19050000	-3.38630000	-2.48470000
H	-6.34300000	-5.58990000	-2.61190000
H	-3.55410000	-7.36000000	-0.14780000
H	-2.28210000	-5.23020000	0.08950000
H	-5.72150000	3.46670000	0.60850000

H	-7.41080000	4.23400000	2.26760000
H	-6.09030000	1.53260000	5.08590000
H	-4.34020000	0.64730000	3.54720000
H	-1.32640000	5.50490000	-2.64180000
H	-0.29240000	7.73950000	-3.01820000
H	3.27770000	6.53710000	-1.34640000
H	2.39380000	4.24390000	-0.88920000
C	1.19280000	-0.09550000	1.36540000
O	-0.18470000	-0.27120000	1.31070000
C	1.48760000	1.40910000	1.25990000
C	1.77510000	-0.65240000	2.66680000
H	1.70910000	-0.58810000	0.52520000
H	1.49070000	1.92390000	2.22080000
H	0.81670000	1.89750000	0.56520000
H	2.84120000	-0.42150000	2.75570000
H	1.65830000	-1.73690000	2.70610000
H	1.24430000	-0.21450000	3.51910000
C	-0.69030000	-2.77090000	1.55510000
O	-1.73660000	-2.57570000	2.03770000
O	0.32130000	-3.15370000	1.09610000

4-**TS2**

N	-0.76320000	-1.67800000	-1.54050000
N	-3.06290000	-0.57870000	-0.20340000
N	0.40230000	0.90580000	-1.68920000
N	-1.87710000	2.02690000	-0.32050000
Zn	-1.09750000	0.07100000	-0.43310000
C	0.50190000	-3.48310000	-2.20110000
C	-0.76860000	-3.93820000	-2.02880000

C	0.48470000	-2.06310000	-1.88560000
C	-1.55720000	-2.80950000	-1.56700000
C	-2.85590000	-2.88480000	-1.07170000
C	-4.90530000	-1.93140000	0.07710000
C	-5.19460000	-0.73620000	0.66630000
C	-3.55830000	-1.82460000	-0.44270000
C	-4.03300000	0.10840000	0.48510000
C	1.60650000	-1.19150000	-2.02270000
C	1.72220000	2.35500000	-2.91040000
C	2.23820000	1.10300000	-3.05800000
C	0.60220000	2.24090000	-2.00160000
C	1.41750000	0.21430000	-2.25780000
C	-0.08320000	3.30980000	-1.42820000
C	-2.88940000	3.75730000	0.82060000
C	-1.82780000	4.28430000	0.13990000
C	-2.93240000	2.34950000	0.49860000
C	-1.21240000	3.19290000	-0.57790000
C	-3.94510000	1.45060000	0.89050000
C	2.91480000	-1.68800000	-1.66680000
C	4.15300000	-1.06710000	-1.99770000
C	5.32960000	-1.47360000	-1.42980000
N	5.37350000	-2.48010000	-0.51580000
C	4.21830000	-3.11640000	-0.17820000
C	3.01920000	-2.76650000	-0.73530000
C	7.27400000	-1.53730000	3.87000000
C	6.47780000	-0.39430000	3.97370000
C	5.69770000	0.00320000	2.88830000
C	5.71440000	-0.73600000	1.70570000
C	6.51350000	-1.87740000	1.59520000

C	7.29010000	-2.27730000	2.68790000
C	6.57890000	-2.67800000	0.30550000
C	-3.52160000	-4.21810000	-1.09410000
C	-3.89810000	-4.83760000	-2.29010000
C	-4.50250000	-6.09300000	-2.23820000
N	-4.74940000	-6.75620000	-1.10000000
C	-4.38250000	-6.15570000	0.04220000
C	-3.77340000	-4.90440000	0.10020000
C	-5.04410000	1.96830000	1.75170000
C	-5.89180000	3.00200000	1.33410000
C	-6.90700000	3.43090000	2.18660000
N	-7.13120000	2.91220000	3.40240000
C	-6.31800000	1.92120000	3.79490000
C	-5.27640000	1.41770000	3.01840000
C	0.46760000	4.67440000	-1.65420000
C	-0.27950000	5.68540000	-2.26990000
C	0.30100000	6.93990000	-2.44690000
N	1.54520000	7.24990000	-2.05470000
C	2.25110000	6.27800000	-1.45890000
C	1.76770000	4.99020000	-1.23790000
Br	3.21700000	1.70090000	0.48500000
H	1.35980000	-4.03800000	-2.55290000
H	-1.13790000	-4.94060000	-2.18370000
H	-5.54400000	-2.79730000	-0.00660000
H	-6.11600000	-0.44250000	1.14570000
H	2.05410000	3.26490000	-3.38730000
H	3.03210000	0.81400000	-3.72890000
H	-3.57660000	4.27830000	1.46940000
H	-1.49340000	5.31050000	0.13450000

H	4.20310000	-0.23460000	-2.67750000
H	6.27440000	-0.99660000	-1.65560000
H	4.29900000	-3.87310000	0.59150000
H	2.12800000	-3.24340000	-0.35340000
H	7.87740000	-1.85910000	4.71300000
H	6.46300000	0.17710000	4.89630000
H	5.06850000	0.88610000	2.94100000
H	5.08350000	-0.41010000	0.88770000
H	7.90540000	-3.17010000	2.61610000
H	6.67740000	-3.74580000	0.51220000
H	7.43800000	-2.38370000	-0.30400000
H	-3.72780000	-4.34620000	-3.24180000
H	-4.80530000	-6.58760000	-3.15880000
H	-4.58200000	-6.70520000	0.95980000
H	-3.48200000	-4.46720000	1.04910000
H	-5.76930000	3.45330000	0.35600000
H	-7.57640000	4.22910000	1.87300000
H	-6.50650000	1.50660000	4.78290000
H	-4.64820000	0.61610000	3.39010000
H	-1.28990000	5.49310000	-2.61330000
H	-0.26250000	7.73440000	-2.93140000
H	3.25670000	6.54170000	-1.13760000
H	2.37250000	4.24260000	-0.73560000
C	1.18770000	-0.17280000	1.39810000
O	-0.20220000	-0.40080000	1.31670000
C	1.42230000	1.33730000	1.27350000
C	1.77850000	-0.67620000	2.71580000
H	1.70850000	-0.66800000	0.56920000
H	1.41450000	1.85530000	2.23170000

H	0.73160000	1.80160000	0.58260000
H	2.83200000	-0.39010000	2.79280000
H	1.71320000	-1.76210000	2.78520000
H	1.23280000	-0.23450000	3.55670000
C	-0.63580000	-2.31900000	1.56480000
O	-1.72060000	-2.27870000	2.05170000
O	0.31540000	-2.91600000	1.15700000

5-**Int2**

N	0.90860000	1.88400000	-0.99150000
N	3.51170000	1.04020000	-0.05470000
N	0.08470000	-0.85650000	-1.30680000
N	2.69960000	-1.70970000	-0.32650000
Zn	1.64570000	0.09500000	-0.19620000
C	-0.62480000	3.51610000	-1.52200000
C	0.56040000	4.14700000	-1.30700000
C	-0.38910000	2.09730000	-1.31190000
C	1.51440000	3.12050000	-0.93500000
C	2.83240000	3.36380000	-0.54210000
C	5.11370000	2.66200000	0.29930000
C	5.67560000	1.46560000	0.62830000
C	3.75960000	2.38140000	-0.13150000
C	4.66340000	0.45470000	0.40290000
C	-1.37630000	1.10020000	-1.52880000
C	-1.42620000	-2.51840000	-1.85060000
C	-2.08240000	-1.32970000	-1.94010000
C	-0.07780000	-2.22090000	-1.41340000
C	-1.11570000	-0.29270000	-1.61530000
C	0.86880000	-3.18980000	-1.07640000

C	4.18590000	-3.35060000	0.33540000
C	3.07860000	-3.97960000	-0.14660000
C	3.94740000	-1.92780000	0.20540000
C	2.15610000	-2.94160000	-0.55640000
C	4.86510000	-0.92720000	0.56580000
C	-2.76010000	1.54110000	-1.46840000
C	-3.77610000	1.16180000	-2.37860000
C	-5.07780000	1.54950000	-2.17710000
N	-5.42970000	2.31020000	-1.10760000
C	-4.47470000	2.71210000	-0.21870000
C	-3.16020000	2.36750000	-0.38170000
C	-8.70220000	1.76390000	2.41390000
C	-8.20270000	0.49550000	2.71220000
C	-7.25180000	-0.09090000	1.87600000
C	-6.80660000	0.58620000	0.74270000
C	-7.30650000	1.85590000	0.43930000
C	-8.25120000	2.44570000	1.28350000
C	-6.84740000	2.58760000	-0.80480000
C	3.29260000	4.78300000	-0.52540000
C	4.27600000	5.24120000	-1.40990000
C	4.66760000	6.57770000	-1.35510000
N	4.15850000	7.47100000	-0.49690000
C	3.22050000	7.02550000	0.34880000
C	2.75840000	5.71070000	0.37630000
C	6.17360000	-1.35910000	1.13410000
C	7.09180000	-2.10620000	0.38640000
C	8.30120000	-2.47630000	0.97200000
N	8.65270000	-2.16020000	2.22490000
C	7.77120000	-1.44380000	2.93440000

C	6.53670000	-1.02220000	2.44370000
C	0.46870000	-4.62050000	-1.23230000
C	1.00760000	-5.42400000	-2.24260000
C	0.59590000	-6.75230000	-2.34310000
N	-0.29510000	-7.32250000	-1.52190000
C	-0.80210000	-6.54980000	-0.55280000
C	-0.45750000	-5.21210000	-0.36600000
Br	-4.67720000	-2.29420000	0.37270000
H	-1.55480000	3.96320000	-1.84180000
H	0.77520000	5.20080000	-1.39750000
H	5.56960000	3.63920000	0.34230000
H	6.68090000	1.28080000	0.97450000
H	-1.82890000	-3.50360000	-2.03050000
H	-3.13270000	-1.20450000	-2.14200000
H	5.07510000	-3.80320000	0.74610000
H	2.89520000	-5.04150000	-0.20750000
H	-3.53560000	0.58330000	-3.26000000
H	-5.87920000	1.27940000	-2.85310000
H	-4.83480000	3.26280000	0.64070000
H	-2.43240000	2.61430000	0.38270000
H	-9.43370000	2.22960000	3.06650000
H	-8.54730000	-0.02940000	3.59740000
H	-6.84180000	-1.07190000	2.09190000
H	-6.05110000	0.11950000	0.12050000
H	-8.63340000	3.43850000	1.06060000
H	-6.96920000	3.66830000	-0.68880000
H	-7.42290000	2.28750000	-1.68510000
H	4.72150000	4.56420000	-2.13090000
H	5.42760000	6.95010000	-2.03920000

H	2.81770000	7.75790000	1.04590000
H	2.00130000	5.40350000	1.08970000
H	6.86600000	-2.38490000	-0.63710000
H	9.02660000	-3.05380000	0.40220000
H	8.06520000	-1.19450000	3.95210000
H	5.85990000	-0.44800000	3.06690000
H	1.73160000	-5.01490000	-2.93910000
H	1.00170000	-7.38990000	-3.12610000
H	-1.52030000	-7.02490000	0.11260000
H	-0.88950000	-4.63690000	0.44580000
C	-2.55950000	-0.78580000	1.65560000
O	-1.14340000	-0.83820000	1.83650000
C	-2.91460000	-2.22000000	1.28260000
C	-3.28760000	-0.28690000	2.89570000
H	-2.78410000	-0.13280000	0.80890000
H	-3.00320000	-2.88030000	2.14460000
H	-2.21520000	-2.61360000	0.55180000
H	-4.37090000	-0.32290000	2.74430000
H	-2.98480000	0.74060000	3.09800000
H	-3.03170000	-0.91070000	3.75820000
C	-0.45330000	0.37280000	1.67800000
O	0.80310000	0.18770000	1.61450000
O	-1.09950000	1.42320000	1.62020000

6-**TS3**

N	1.10530000	2.06600000	-0.93370000
N	3.53860000	0.75800000	-0.11570000
N	-0.11450000	-0.50100000	-1.41620000
N	2.25600000	-1.81900000	-0.41450000

Zn	1.56990000	0.14210000	-0.31580000
C	-0.19250000	3.94250000	-1.22470000
C	1.08130000	4.37260000	-1.00440000
C	-0.15620000	2.49240000	-1.19090000
C	1.88940000	3.18910000	-0.79010000
C	3.25210000	3.18680000	-0.47440000
C	5.41450000	2.05930000	0.20210000
C	5.76070000	0.77510000	0.49920000
C	4.01720000	2.03900000	-0.17440000
C	4.57480000	-0.03220000	0.30880000
C	-1.25210000	1.66860000	-1.54640000
C	-1.76270000	-1.84160000	-2.32250000
C	-2.21380000	-0.56170000	-2.36690000
C	-0.47300000	-1.81340000	-1.66860000
C	-1.16890000	0.27460000	-1.80580000
C	0.22400000	-2.95120000	-1.24950000
C	3.33170000	-3.66110000	0.46840000
C	2.13790000	-4.08880000	-0.02850000
C	3.40870000	-2.23970000	0.20590000
C	1.48050000	-2.92950000	-0.59600000
C	4.50740000	-1.42310000	0.51960000
C	-2.58640000	2.23430000	-1.40630000
C	-3.63910000	2.09070000	-2.34180000
C	-4.92480000	2.44060000	-2.00950000
N	-5.21870000	2.96620000	-0.79410000
C	-4.21590000	3.21150000	0.09610000
C	-2.91670000	2.88720000	-0.19000000
C	-7.86440000	1.96150000	3.05740000
C	-7.41400000	0.64150000	3.08440000

C	-6.70680000	0.12210000	1.99790000
C	-6.45870000	0.91920000	0.88270000
C	-6.90540000	2.24580000	0.85390000
C	-7.60260000	2.76630000	1.94730000
C	-6.62360000	3.12220000	-0.34620000
C	3.94700000	4.50510000	-0.41340000
C	4.94010000	4.84530000	-1.33940000
C	5.55810000	6.09090000	-1.24370000
N	5.26130000	7.00240000	-0.30860000
C	4.31280000	6.67010000	0.57610000
C	3.63530000	5.45180000	0.56940000
C	5.70900000	-2.07980000	1.10640000
C	6.42090000	-3.06470000	0.41060000
C	7.54060000	-3.64140000	1.00730000
N	7.99090000	-3.31290000	2.22480000
C	7.30580000	-2.37110000	2.88620000
C	6.17600000	-1.73130000	2.37990000
C	-0.40790000	-4.28010000	-1.48760000
C	0.28460000	-5.29800000	-2.15930000
C	-0.33380000	-6.53070000	-2.35540000
N	-1.57380000	-6.81980000	-1.94050000
C	-2.23630000	-5.84090000	-1.31050000
C	-1.71250000	-4.57310000	-1.06160000
Br	-4.55540000	-2.01580000	0.09620000
H	-1.05870000	4.54750000	-1.45250000
H	1.44320000	5.38940000	-0.99860000
H	6.04110000	2.93710000	0.24020000
H	6.72690000	0.40690000	0.80800000
H	-2.28390000	-2.72040000	-2.66310000

H	-3.18750000	-0.26080000	-2.70970000
H	4.08120000	-4.24750000	0.97700000
H	1.73290000	-5.08800000	0.00290000
H	-3.44750000	1.69540000	-3.32930000
H	-5.75960000	2.30580000	-2.68540000
H	-4.52560000	3.60060000	1.05740000
H	-2.15740000	3.00430000	0.57150000
H	-8.40740000	2.37180000	3.90300000
H	-7.60790000	0.02070000	3.95350000
H	-6.32560000	-0.89450000	1.98780000
H	-5.89580000	0.47900000	0.06300000
H	-7.94050000	3.79950000	1.93360000
H	-6.79640000	4.17640000	-0.11220000
H	-7.25280000	2.86320000	-1.20170000
H	5.21830000	4.14900000	-2.12330000
H	6.32910000	6.37170000	-1.95860000
H	4.08350000	7.41550000	1.33520000
H	2.88220000	5.23290000	1.31860000
H	6.10840000	-3.36600000	-0.58330000
H	8.10680000	-4.40440000	0.47680000
H	7.67740000	-2.11500000	3.87640000
H	5.65710000	-0.98010000	2.96510000
H	1.28800000	-5.12370000	-2.53150000
H	0.19500000	-7.32560000	-2.87810000
H	-3.24610000	-6.07620000	-0.98120000
H	-2.33100000	-3.83280000	-0.56490000
C	-2.16390000	-1.37940000	2.29690000
O	-0.72600000	-1.24660000	2.17260000
C	-2.74600000	-0.57570000	1.14750000

C	-2.44690000	-2.86600000	2.39100000
H	-2.46670000	-0.88060000	3.22620000
H	-2.36280000	-0.69610000	0.15240000
H	-3.55020000	0.11980000	1.30870000
H	-3.51880000	-3.04700000	2.44770000
H	-1.94500000	-3.26160000	3.27840000
H	-2.05840000	-3.37830000	1.51070000
C	-0.38800000	-0.00310000	1.74160000
O	0.82700000	0.24920000	1.60790000
O	-1.37650000	0.76620000	1.49490000

7-**P1**

N	1.08160000	2.04340000	-0.81200000
N	3.56740000	0.75250000	-0.13000000
N	-0.07170000	-0.53140000	-1.39530000
N	2.33200000	-1.84370000	-0.47370000
Zn	1.62080000	0.10120000	-0.37190000
C	-0.23050000	3.90480000	-1.12660000
C	1.03950000	4.34760000	-0.90090000
C	-0.18480000	2.45760000	-1.08060000
C	1.85810000	3.17590000	-0.68150000
C	3.22840000	3.18820000	-0.39680000
C	5.41960000	2.08280000	0.20920000
C	5.79740000	0.79580000	0.45300000
C	4.01900000	2.04740000	-0.14720000
C	4.62780000	-0.02960000	0.25130000
C	-1.27080000	1.61620000	-1.43020000
C	-1.76730000	-1.88730000	-2.19100000
C	-2.24790000	-0.62180000	-2.16330000

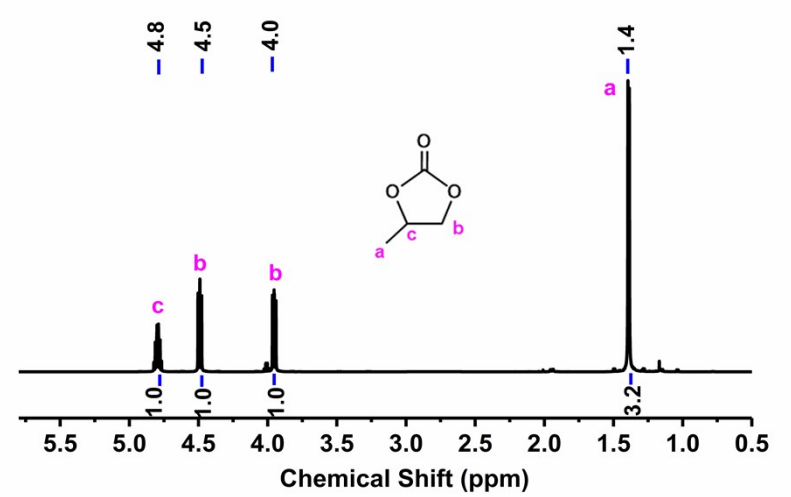
C	-0.43420000	-1.84700000	-1.63470000
C	-1.17410000	0.22670000	-1.68320000
C	0.28090000	-2.98430000	-1.24530000
C	3.45210000	-3.68120000	0.36180000
C	2.24690000	-4.11670000	-0.09950000
C	3.50680000	-2.25670000	0.11260000
C	1.56070000	-2.96040000	-0.63900000
C	4.59540000	-1.42840000	0.42060000
C	-2.61290000	2.18090000	-1.33840000
C	-3.63240000	1.99580000	-2.29990000
C	-4.92790000	2.36580000	-2.02890000
N	-5.25980000	2.95970000	-0.85710000
C	-4.29090000	3.23810000	0.05620000
C	-2.98490000	2.89020000	-0.16850000
C	-8.11270000	2.07880000	2.87850000
C	-7.67180000	0.75530000	2.94740000
C	-6.90710000	0.21880000	1.90990000
C	-6.59380000	1.00030000	0.80080000
C	-7.03300000	2.32560000	0.72990000
C	-7.78700000	2.86840000	1.77470000
C	-6.67970000	3.16740000	-0.47520000
C	3.90370000	4.51600000	-0.32840000
C	4.88610000	4.88010000	-1.25710000
C	5.48500000	6.13450000	-1.15430000
N	5.17940000	7.03330000	-0.20970000
C	4.24100000	6.67890000	0.67710000
C	3.58250000	5.45040000	0.66340000
C	5.82090000	-2.07720000	0.96590000
C	6.53420000	-3.03110000	0.22970000

C	7.67470000	-3.60540000	0.78830000
N	8.14400000	-3.30280000	2.00530000
C	7.45750000	-2.39080000	2.70560000
C	6.30780000	-1.75620000	2.23920000
C	-0.37470000	-4.31190000	-1.42770000
C	0.27450000	-5.35280000	-2.10650000
C	-0.36240000	-6.58470000	-2.23790000
N	-1.58200000	-6.85060000	-1.75370000
C	-2.20630000	-5.84850000	-1.12050000
C	-1.66000000	-4.58020000	-0.92970000
Br	-4.68170000	-1.72660000	-0.15690000
H	-1.09810000	4.50230000	-1.36760000
H	1.39250000	5.36760000	-0.90320000
H	6.02800000	2.97170000	0.27320000
H	6.77580000	0.43800000	0.73450000
H	-2.31230000	-2.76750000	-2.48500000
H	-3.27590000	-0.36010000	-2.33500000
H	4.22280000	-4.26420000	0.84210000
H	1.85320000	-5.12020000	-0.06360000
H	-3.41080000	1.54110000	-3.25470000
H	-5.74010000	2.19230000	-2.72280000
H	-4.63170000	3.68380000	0.98150000
H	-2.24590000	3.07930000	0.59870000
H	-8.70050000	2.50180000	3.68730000
H	-7.92070000	0.14800000	3.81260000
H	-6.52650000	-0.79860000	1.92110000
H	-5.97920000	0.53740000	0.03050000
H	-8.12050000	3.90230000	1.72740000
H	-6.82860000	4.23260000	-0.27710000

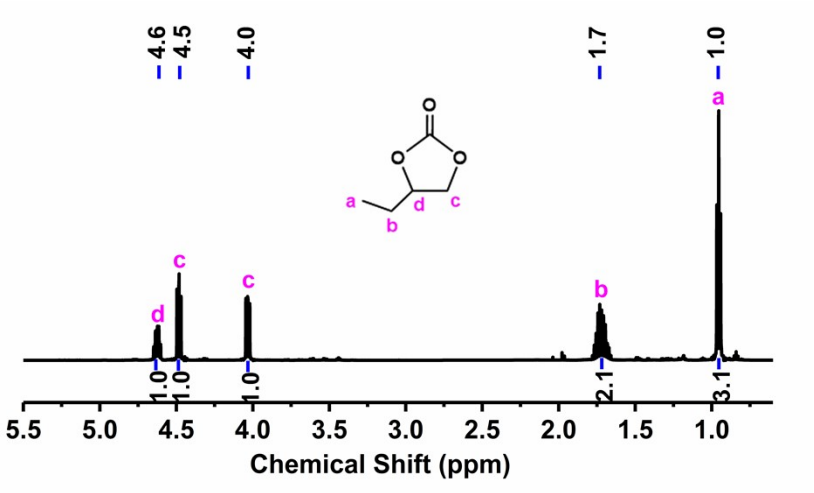
H	-7.27640000	2.90430000	-1.35240000
H	5.17060000	4.19530000	-2.04860000
H	6.24720000	6.43330000	-1.87110000
H	4.00440000	7.41420000	1.44380000
H	2.83670000	5.21440000	1.41460000
H	6.20640000	-3.31080000	-0.76560000
H	8.24210000	-4.34450000	0.22610000
H	7.84470000	-2.15570000	3.69500000
H	5.78910000	-1.02970000	2.85510000
H	1.25890000	-5.19740000	-2.53410000
H	0.13300000	-7.39820000	-2.76470000
H	-3.20250000	-6.06430000	-0.74100000
H	-2.25170000	-3.81580000	-0.43540000
C	-2.00400000	-1.24900000	2.89940000
O	-0.56010000	-0.99400000	3.02580000
C	-2.45160000	-0.08590000	2.00190000
C	-2.20850000	-2.62380000	2.29840000
H	-2.41700000	-1.17450000	3.90660000
H	-3.16290000	-0.39870000	1.22620000
H	-2.82840000	0.76950000	2.57060000
H	-3.26010000	-2.75350000	2.02520000
H	-1.88530000	-3.40350000	2.99210000
H	-1.63060000	-2.71200000	1.37480000
C	-0.17740000	-0.22620000	2.00810000
O	0.98900000	-0.04560000	1.69430000
O	-1.21000000	0.32270000	1.36590000

5. Characterization Data for Products

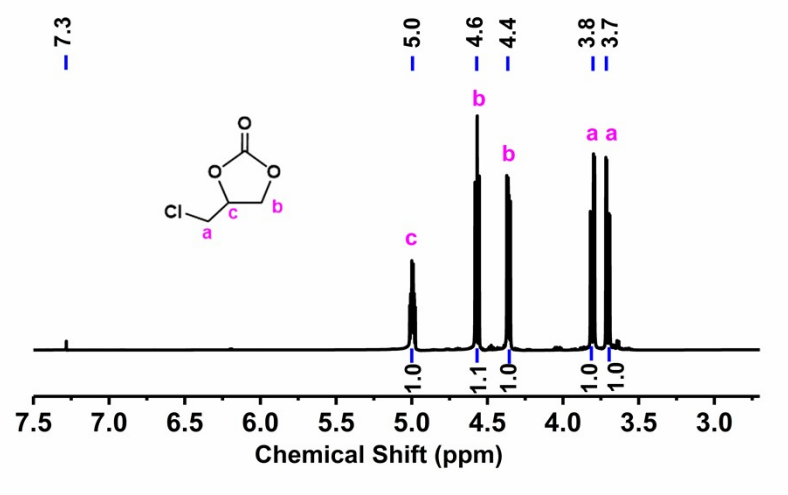
4-methyl-1,3-dioxolan-2-one (2a): ^{1}H NMR (600 MHz, $CDCl_3$, 25 ℃): δ (ppm) = 4.8 (m, 1H, ring CH-CH_3), 4.5 (t, 1H, ring CH_2), 4.0 (t, 1H, ring CH_2), 1.4 (d, 3H, CH_3).



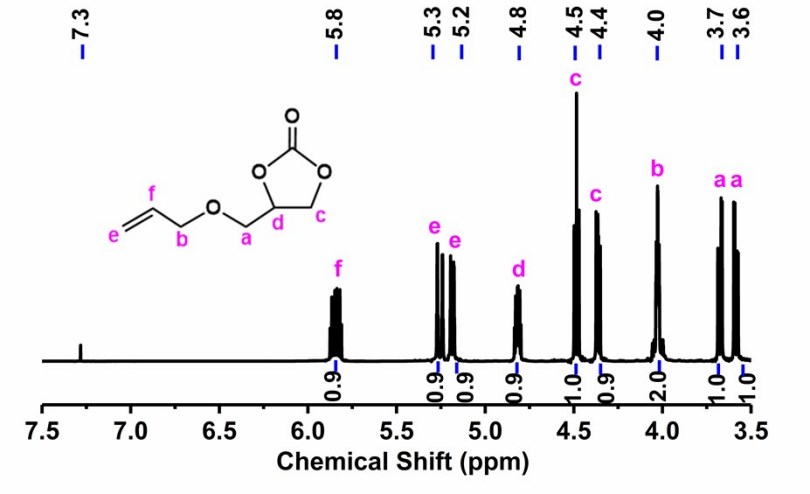
4-ethyl-1,3-dioxolan-2-one (2b): ^{1}H NMR (600 MHz, $CDCl_3$, 25 ℃): δ (ppm) = 4.6 (m, 1H), 4.5 (t, J = 10 Hz, 1H), 4.0 (t, J = 10 Hz, 1H), 1.7 (m, 2H), 1.0 (t, J = 10 Hz, 3H).



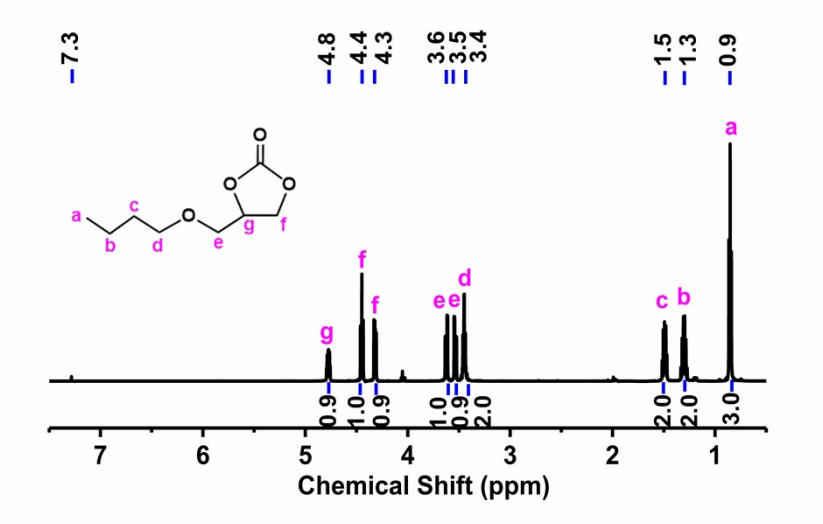
4-(chloromethyl)-1,3-dioxolan-2-one (2c): ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 5.0 (m, 1H, CH-CH_2), 4.6 (t, *J* = 8 Hz, 1H, ring CH_2), 4.4 (dd, *J* = 8 Hz, 4 Hz, 1H, ring CH_2), 3.8 (m, 1H, CH_2-Cl), 3.7 (m, 1H, CH_2-Cl).



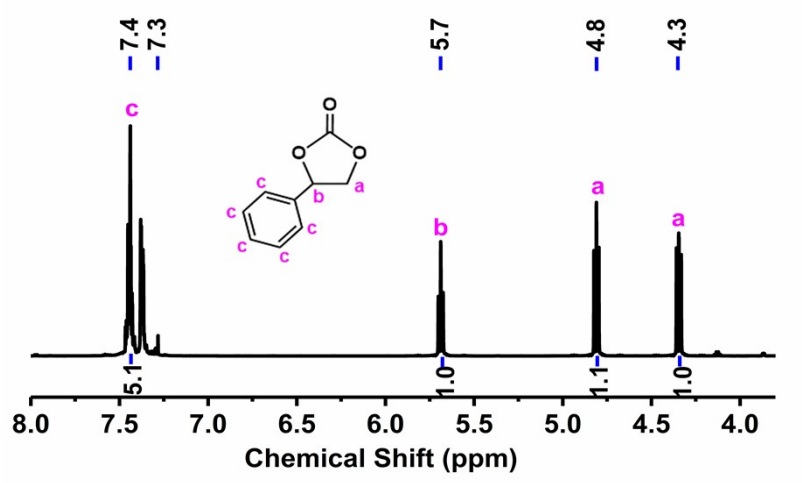
4-((allyloxy)methyl)-1,3-dioxolan-2-one (2d): ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 5.8 (m, 1H), 5.3 (d, *J* = 10 Hz, 1H), 5.2 (d, *J* = 10 Hz, 1H), 4.8 (m, 1H), 4.5 (t, *J* = 8 Hz, 1H), 4.4 (d, *J* = 8 Hz, 1H), 4.0 (m, 2H), 3.7 (m, 1H), 3.6 (m, 1H).



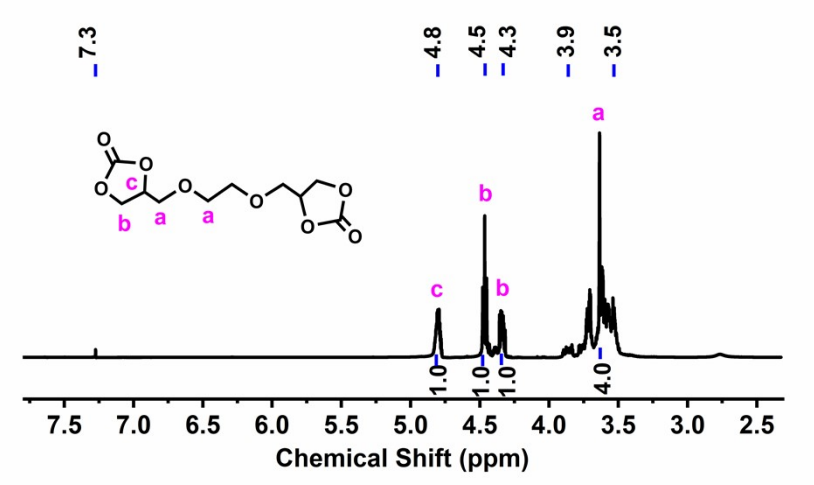
4-(butoxymethyl)-1,3-dioxolan-2-one (2e: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 4.8 (m, 1H), 4.4 (d, *J* = 10 Hz, 1H), 4.3 (d, *J* = 10 Hz, 1H), 3.6 (t, *J* = 8 Hz, 1H), 3.5 (d, *J* = 8 Hz, 1H), 3.4 (m, 2H), 1.5 (m, 2H), 1.3 (m, 2H), 0.9 (d, 3H, CH_3).



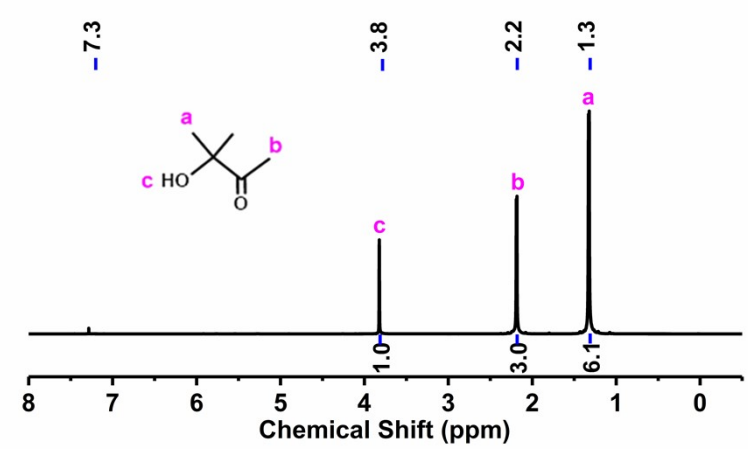
4-phenyl-1,3-dioxolan-2-one (2f): ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 7.3-7.4 (m, 5H, ring ArH), 5.7 (t, *J* = 8 Hz, 1H, PhCHO), 4.8 (t, *J* = 8 Hz, 1H, OCH_2), 4.3 (t, *J* = 8 Hz, 1H, OCH_2).



4,4'-((ethane-1,2-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one): ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 4.8 (m, 1H), 4.5-4.3 (m, 2H), 3.9-3.5 (m, 4H).



3-hydroxy-3-methyl-2-butanone: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) = 3.8 (s, 1H, OH), 2.2 (s, 3H, CH_3), 1.3 (s, 6H, 2 CH_3).



6. References

[1] W. Wang, Y. Wang, C. Li, L. Yan, M. Jiang and Y. Ding, *ACS Sustainable Chemistry & Engineering*, 2017, 5, 4523-4528.

[2] J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng and S. Zhang, *Catalysis Today*, 2009, 148, 361-367.

[3] H. Li, C. Li, J. Chen, L. Liu and Q. Yang, *Chemistry-An Asian Journal*, 2017, 12, 1095-1103.

[4] J. Wang, W. Sng, G. Yi and Y. Zhang, *Chemical Communications*, 2015, 51, 12076-12079.

[5] T.-T. Liu, J. Liang, Y.-B. Huang and R. Cao, *Chemical Communications*, 2016, 52, 13288-13291.

[6] Y. Xie, J. Liang, Y. Fu, J. Lin, H. Wang, S. Tu and J. Li, *Journal of CO_2 Utilization*, 2019, 32, 281-289.

[7] Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu and K. Ding, *Angewandte Chemie International Edition*, 2007, 46, 7255-7258.

[8] Y. Chen, R. Luo, Q. Xu, J. Jiang, X. Zhou and H. Ji, *ACS Sustainable Chemistry & Engineering*, 2018, 6, 1074-1082.

[9] C. Cui, R. Sa, Z. Hong, H. Zhong and R. Wang, *ChemSusChem*, 2020, 13, 180-187.

[10] L. Liu, S. Jayakumar, J. Chen, L. Tao, H. Li, Q. Yang and C. Li, *ACS Appl. Mater. Interfaces*, 2021, 13, 29522-29531.

[11] J. Li, Y. Han, T. Ji, N. Wu, H. Lin, J. Jiang and J. Zhu, *Industrial & Engineering Chemistry Research*, 2019, 59, 676-684.

[12] D. Ma, J. Li, K. Liu, B. Li, C. Li and Z. Shi, *Green Chemistry*, 2018, 20, 5285-5291.

[13] R. Luo, Y. Chen, Q. He, X. Lin, Q. Xu, X. He, W. Zhang, X. Zhou and H. Ji, *ChemSusChem*, 2017, 10, 1526-1533.