

Supporting Information

Conversion of CO₂ into cyclic carbonates by a Co(II) metal-organic framework and the improvement of catalytic activity via Nanocrystallization

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Materials and Methods

Phenyl glycidyl ether and N, N-dimethylformamide (DMF) were purchased from J&K and Concord Technology, respectively. They were used without further purification. CO₂ with a purity of 99.99% was obtained from commercial source. The other epoxides and reagents were purchased from Aladdin and used as received. Power X-ray diffraction (PXRD) was tested on an Ultima IV X-ray diffractometer using Cu K α radiation in the 2θ range of 5-50°. The morphologies of the samples were measured using cold field emission scanning electron microscope (SEM, ZEISS MERLIN Compact). GC determination was performed on an Agilent Technologies 7820A GC system. The purity of cyclic carbonates was certified by a Bruker AV400 instrument and CDCl₃ as the solvent (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz).

Synthesis of 1

Cobalt(II) chloride hexahydrate CoCl₂·6H₂O (10 mmol) and H₂L (10 mmol) were dissolved in 60 mL of deionized water. The resulting solution refluxed at 80°C. After a period of time, resulting pale purple precipitate. After two hours, the solution was cooled to room temperature. The pale purple precipitate of **1** was collected, washed several times with fresh ethanol and finally dried at 80 °C, with a yield of 55%.

Synthesis of N1, N2

PVP (5.0 g) or CTAB (0.5 g) was dissolved in 60 mL of deionized water,

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.0 mmol for PVP, 0.5 mmol for CTAB) and equivalent H_2L were added to the solution. The obtained solution was stirred for two hours, then it was left overnight at room temperature. The obtained solution was precipitated with acetone to yield a pink suspension, the powder from centrifuge was washed with ethanol several times, and **N1** or **N2** was obtained. In order to prove PVP and CTAB were removed completely, **1**, **N1** and **N2** were characterized by TGA (Fig. S2) and FT-IR (Fig. S3). TGA curves of **1**, **N1** and **N2** kept unchanged. Compared with **1**, FT-IR spectra of **N1** and **N2** did not show other characteristic peaks, either. As a result, we confirmed that PVP and CTAB were removed completely.

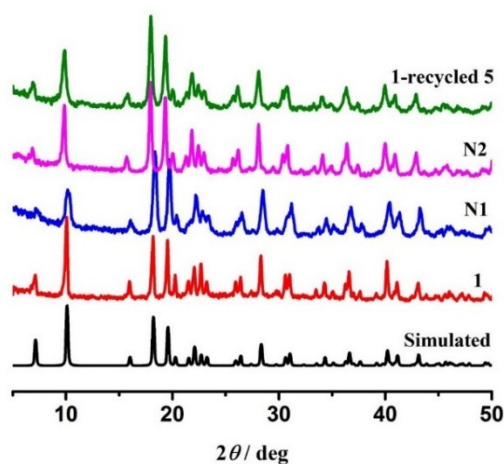


Fig. S1 Powder XRD patterns of **1**, **N1**, **N2** and **1** after cycling five times.

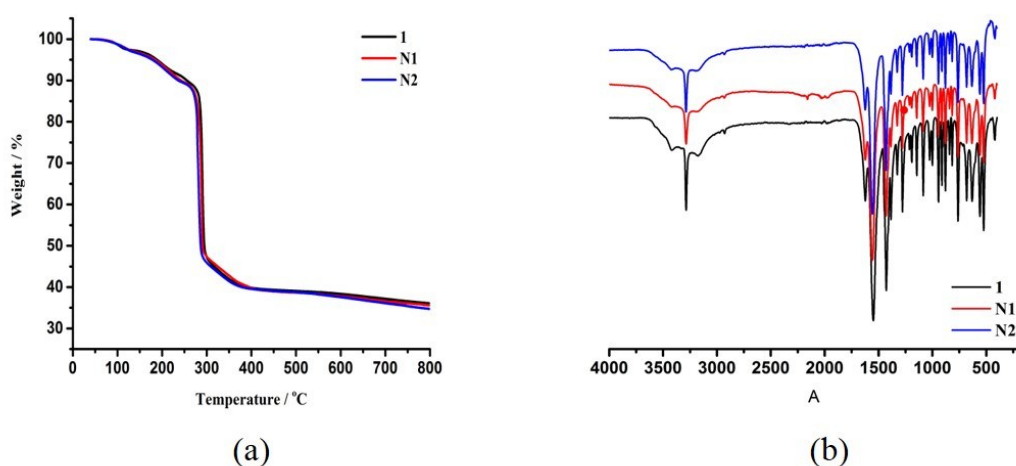


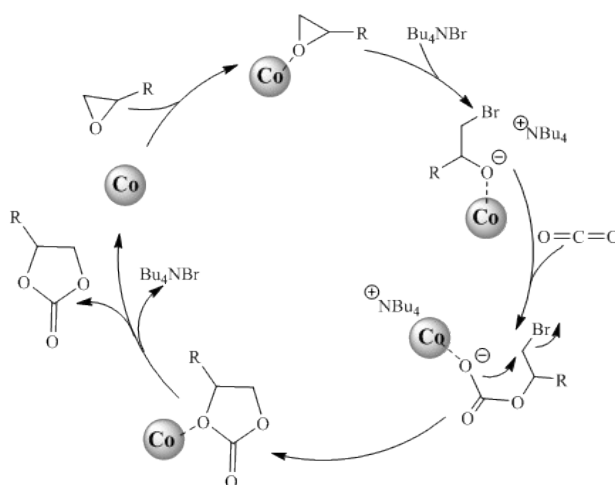
Fig. S2 TGA (a) and FT-IR spectra (b) of **1**, **N1** and **N2**.

Procedure for cycloaddition of CO_2 with epoxides

Before the catalytic reaction, a pre-activation treatment on catalyst (**1**, **N1**, **N2**) had been carried out at 100 °C under vacuum. Then in a 10 mL Schlenk tube the catalyst (50 mg, 0.19 mmol) and tetrabutylammonium bromide (TBABr) (0.5 mmol) were added. Subsequently, epoxides (5 mmol) were introduced into the reaction mixture, and added 1 mL DMF as solvent. The reaction mixture was stirred at 50 °C for 36 h under CO₂ (balloon, 1 atm). When the reaction was over, the catalyst was separated by centrifugation, the upper clear liquid was extracted by the mixture of ethyl acetate and brine. DMF existed in the water phase and the product existed the organic phase. The organic phase was extracted by column chromatography to obtain the product, ethyl acetate and petroleum ether were used as eluents.

Conceivable reaction mechanism

Based on the above experimental results and literature reports,^{1,2} the possible mechanism of the coupling of CO₂ and epoxides catalyzed by **1** and TBABr was proposed, as illustrated in Scheme S1. At first, the oxygen atom of epoxide attacked the Lewis acidic sites of Co(II), then the epoxide was activated. TBABr attacked the carbon atom of the smaller steric hindrance side, and the ring was open. The activated CO₂ interacted with the ring-opening epoxide to generate the alkyl carbonate anion intermediate. Finally, the intermediate transformed into corresponding cyclic carbonate through closing loop.



Scheme S1. The plausible reaction mechanism for the coupling of CO₂ and epoxides catalyzed by

1.

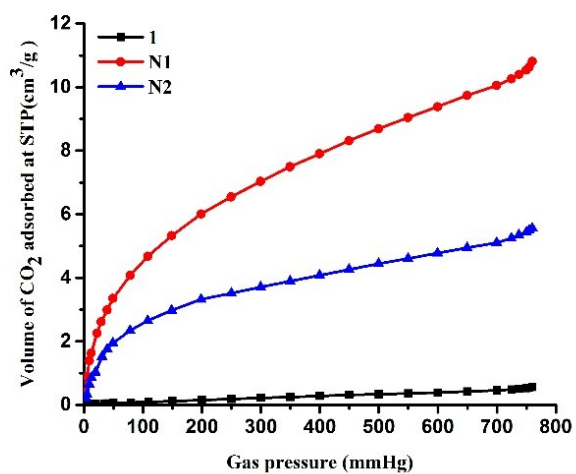


Fig. S3 CO₂ adsorption isotherm (273 K) of 1, N1 and N2.

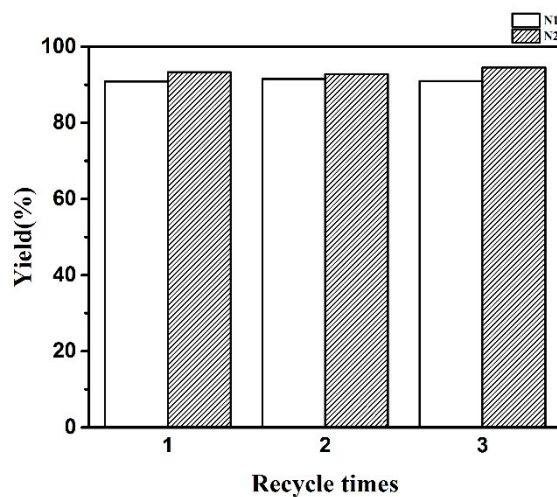


Fig. S4 The catalytic cycle of N1 and N2 for the coupling of CO₂ and propylene epoxide.

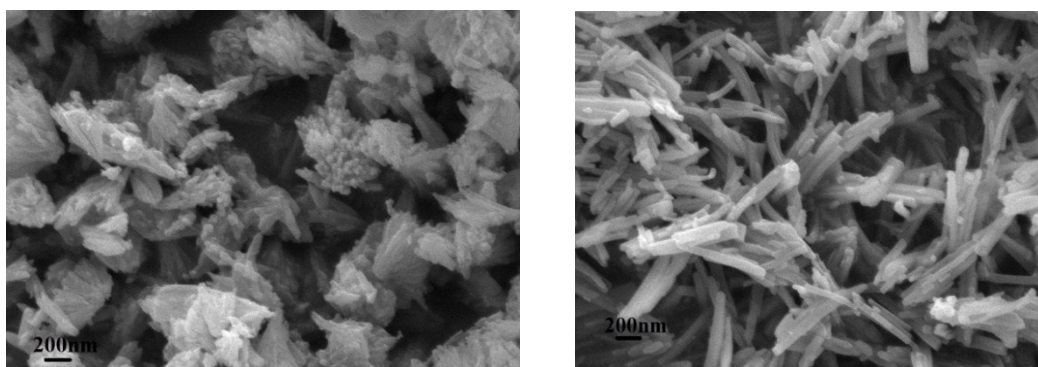
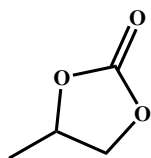
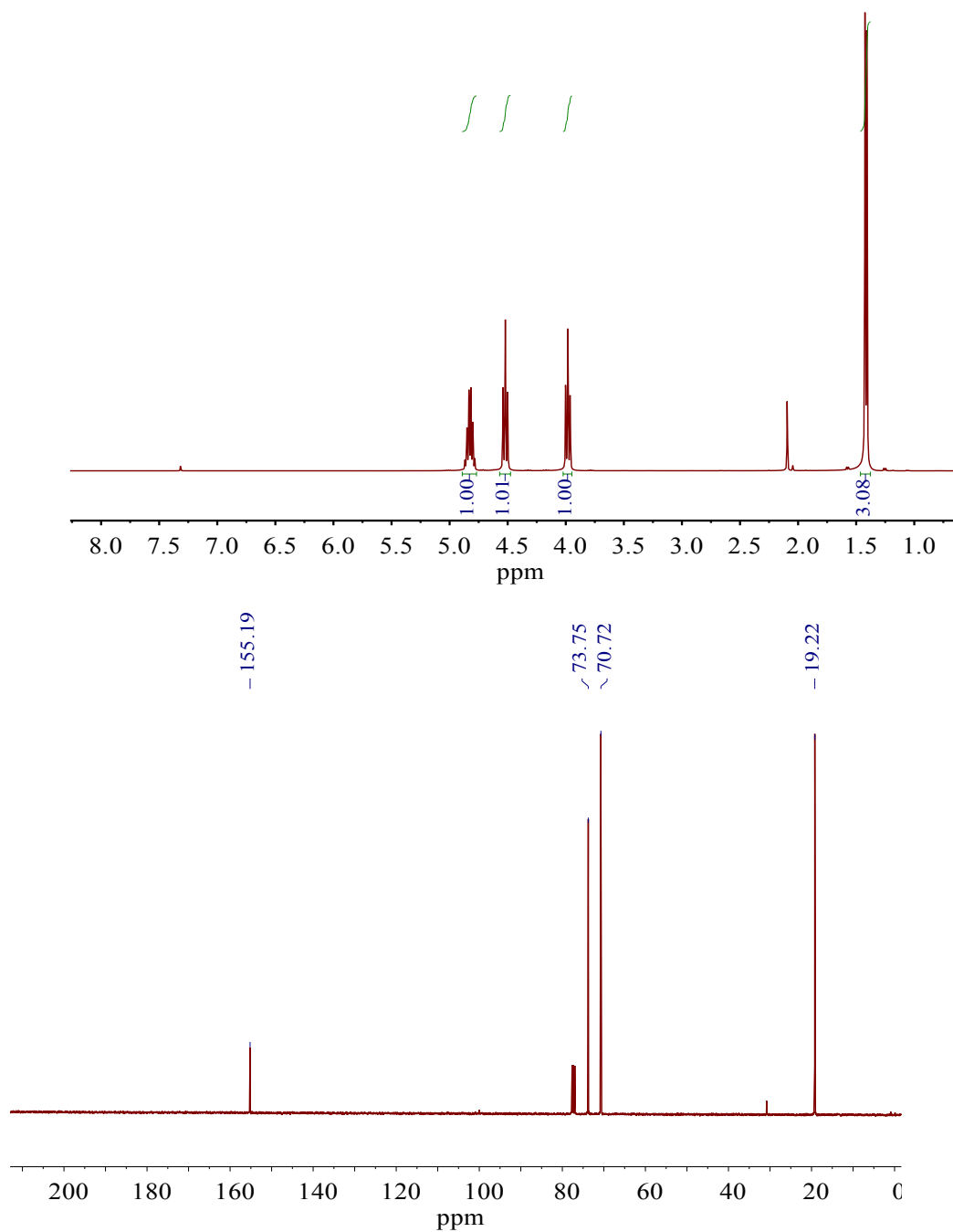


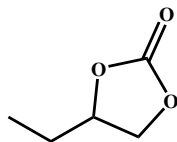
Fig. S5 After three times cycling, the SEM images of N1 (left) and N2 (right).

¹H NMR and ¹³C NMR Spectra of Products

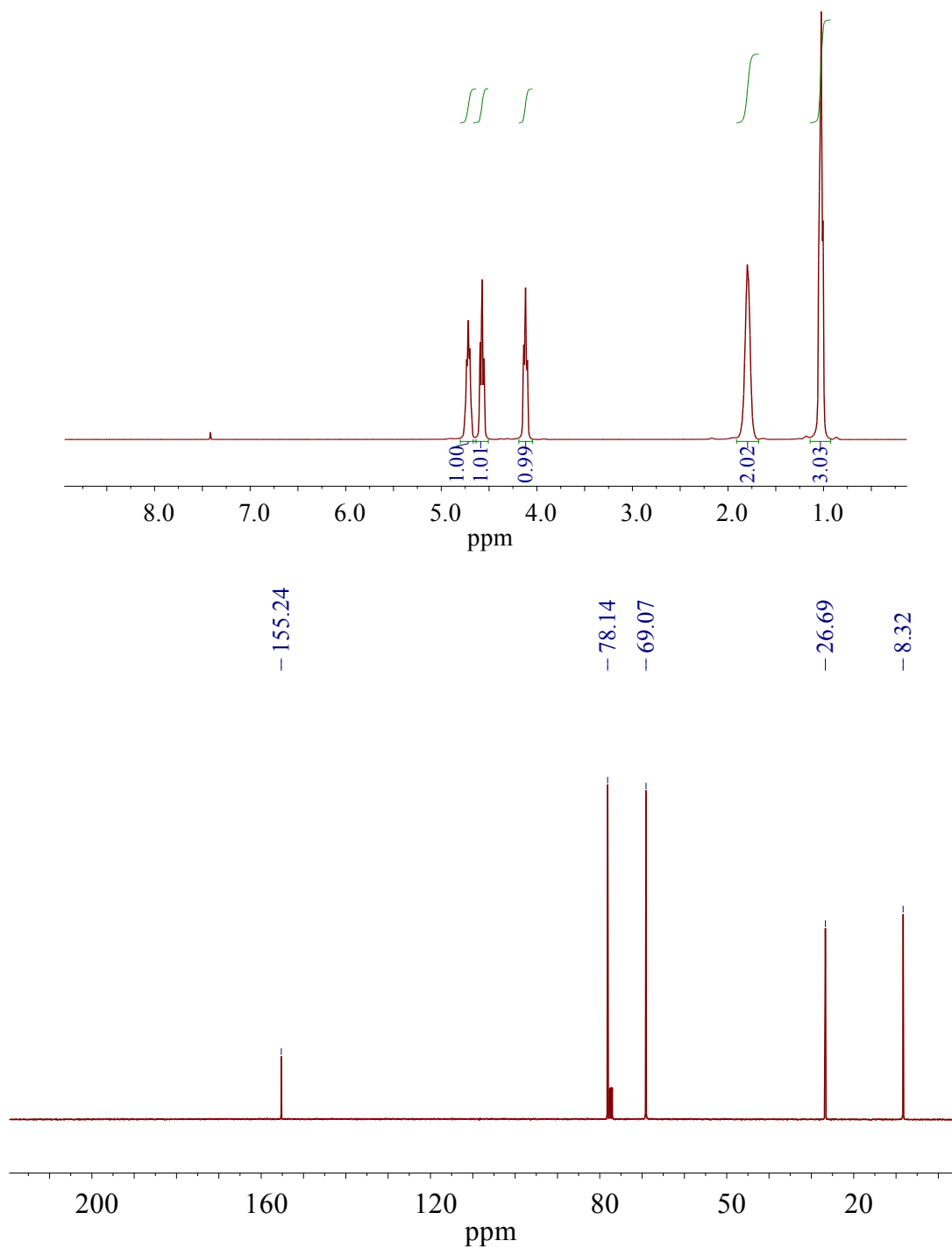


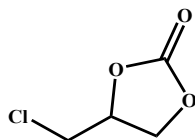
4-methyl-1,3-dioxolan-2-one Colorless liquid; ^1H NMR (400MHz, CDCl_3) δ 4.89-4.77 (m, 1H), 4.57-4.48 (m, 1H), 4.02-3.95 (m, 1H), 1.42 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 155.19, 73.75, 70.72, 19.22.



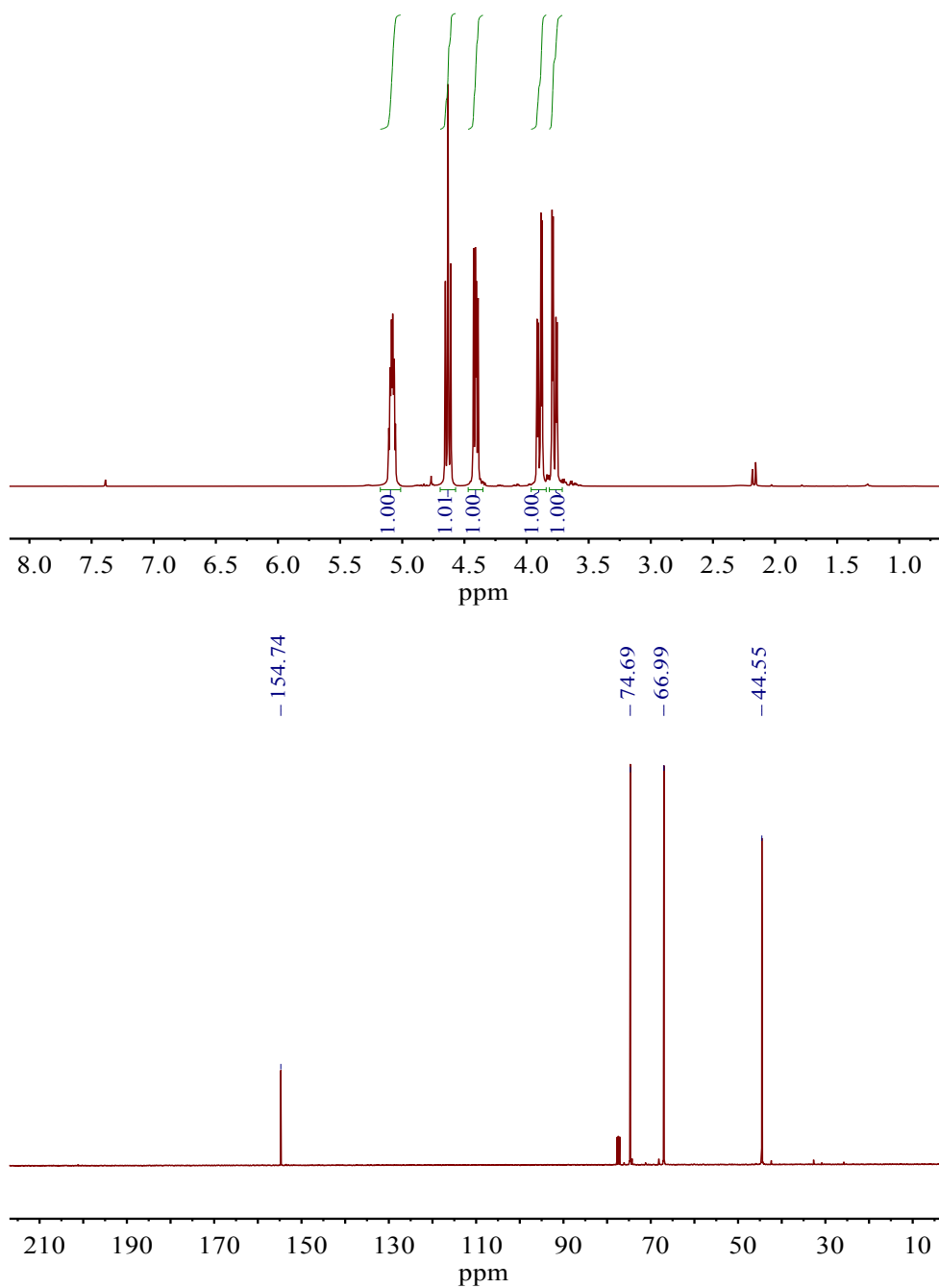


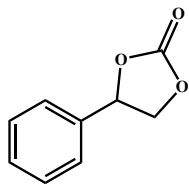
4-ethyl-1,3-dioxolan-2-one Colorless liquid; ^1H NMR (400MHz, CDCl_3) δ 4.80-4.64 (m, 1H), 4.63-4.51 (m, 1H), 4.19-4.04 (m, 1H), 1.90-1.67 (m, 2H), 1.03(dt, $J = 10.9$, 5.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 155.24, 78.14, 69.07, 26.69, 8.32.



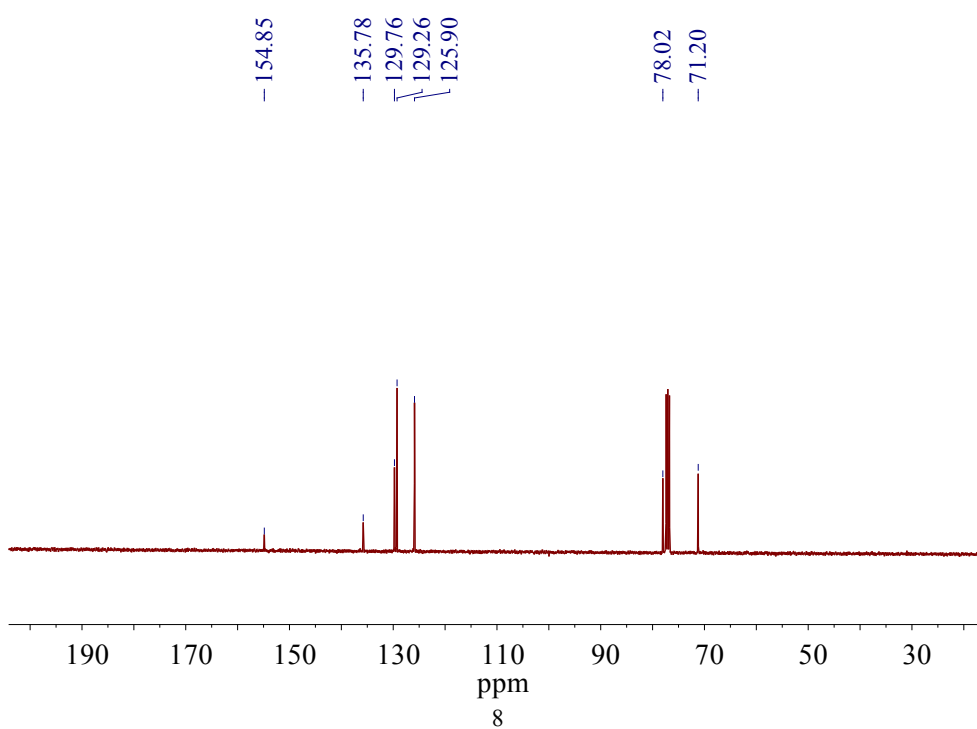
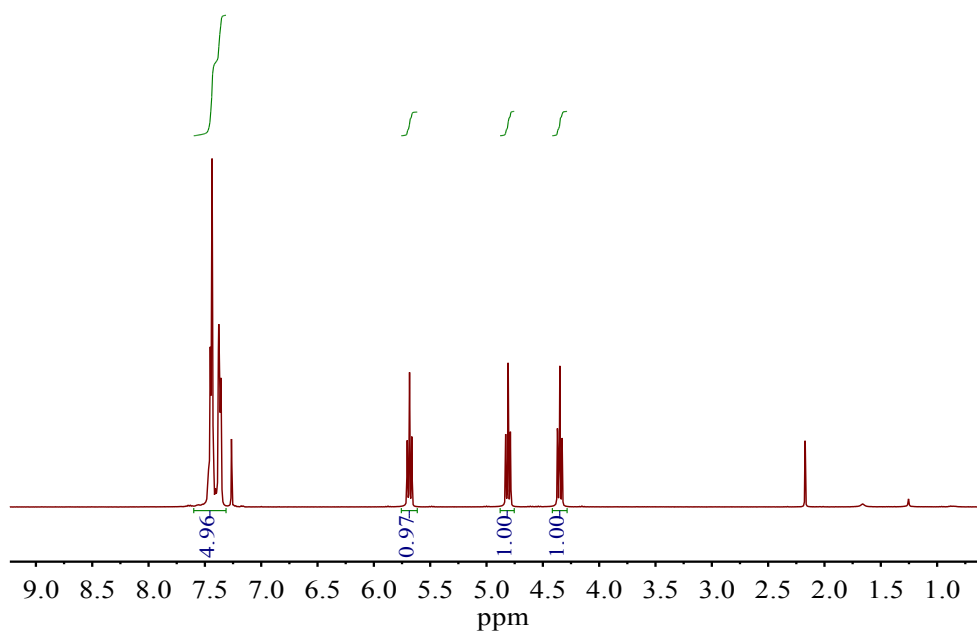


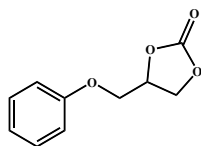
4-chloromethyl-1,3-dioxolan-2-one Colorless liquid; ^1H NMR (400MHz, CDCl_3) δ 5.08 (dq, $J = 8.9, 4.0$ Hz, 1H), 4.63 (t, $J = 8.7$ Hz, 1H), 4.41 (dd, $J = 8.9, 5.7$ Hz, 1H), 3.89 (dd, $J = 12.5, 4.0$ Hz, 1H), 3.77 (dd, $J = 12.5, 3.6$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 154.74, 74.69, 66.99, 44.55.



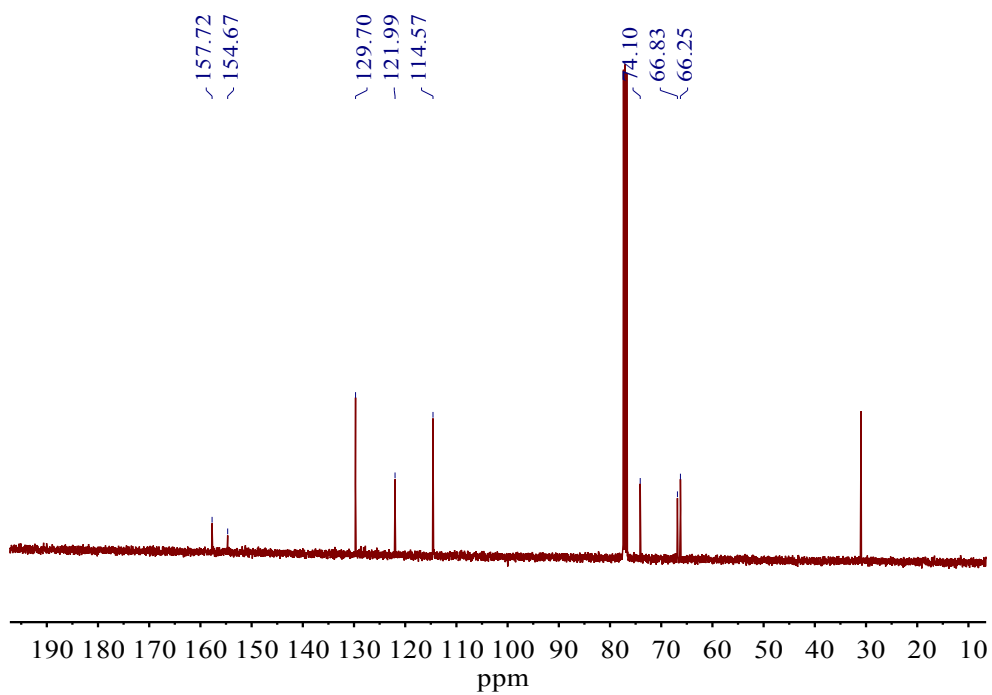
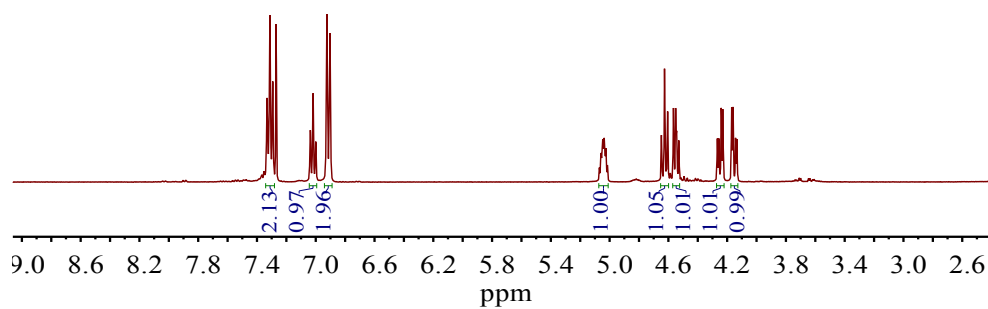


4-phenyl-1,3-dioxolan-2-one White solid; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 7.60-7.31 (m, 5H, Ar-H), 5.68 (t, $J = 8.0$ Hz, 1H), 4.81 (dd, $J = 8.4$ Hz, 1H), 4.35 (t, $J = 8.3$ Hz, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 154.85, 135.78, 129.76, 129.26, 125.90, 78.02, 71.20.





4-phenoxyethyl-1, 3-dioxolan-2-one White solid; ^1H NMR (400MHz, CDCl_3) δ 7.31 (t, $J = 8.1$ Hz, 2H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.91 (d, $J = 7.9$ Hz, 2H), 5.04 (dq, $J = 8.7, 4.2$ Hz, 1H), 4.63 (t, $J = 8.4$ Hz, 1H), 4.55 (dd, $J = 8.6, 5.8$ Hz, 1H), 4.25 (dd, $J = 10.6, 4.2$ Hz, 1H), 4.15 (dd, $J = 10.6, 3.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 157.72, 154.62, 129.70, 121.99, 114.57, 74.10, 66.83, 66.25.



References:

1. B. Ugale, S. S. Dhankhar and C. M. Nagaraja, *Cryst. Growth Des.*, 2017, **17**, 3295-3305.
2. H. H. Wang, L. Y. Z. Hou, Li, C. Y. Jiang, Y. Y. Wang and Z. Zhu, *ACS Appl. Mater. Interfaces.*, 2017, **9**, 17969-17976.