

Supporting Information

Halogen-free Fixation of Carbon Dioxide into Cyclic Carbonates via Bifunctional Organocatalysts†

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Experimental details

1. General information

All reactions and experiments were carried out under air without using Schlenk technique, moisture-free inert conditions and dry solvents, unless stated otherwise. Acetonitrile, methanol, dichloromethane, dimethylformamide, dimethylacetamide, dimethyl sulfoxide and *n*-hexane were obtained in analytical grade from commercially available sources and were used without any further purification or drying. 1,2-Epoxybutane (99%), cyclohexane oxide (96%), propylene oxide (99.5%) and styrene oxide (97.5%) were obtained from J&K Scientific, 1-tert-butoxy-2,3-epoxypropane (96%), 1,2-butylene carbonate (98%) were obtained from TCI (Shanghai), cyclohexene oxide (98%) and phenoxypropene oxide (99%) were obtained from Beijing Innochem, dodecane (99%) was obtained from Alfa Aesar, CO₂ (99.99%) was obtained from Beijing Analytical Instrument and used as they received. Solution NMR spectra were recorded in deuterated solvents on a BRUKER AVIII HD 400 and BRUKER AVIII HD 300 spectrometer; data are given in ppm relative to 1% TMS solution in CDCl₃ or DMSO using the solvent signals as a secondary reference (¹H, ¹³C). NMR spectra were recorded at room temperature (r.t.), if not mentioned otherwise. The Bruker Topspin software package (version 3.2) was used for measuring and processing of the spectra. IR spectra were recorded at room temperature on a TENSOR-27 spectrometer. Quantitative analysis of the reaction products was performed by gas chromatography (GC) analysis with dodecane as internal standard on an Agilent 7890B using N₂ as carrier gas equipped with a capillary column from Agilent and a FID detector. The structures of reaction intermediate complexes **I** and **II** were optimized and the single point energies were calculated at M06-2X/6-31G(d) level using Gaussian 09 software package.^{1,2}

1.1. Procedure for ¹H NMR experiment of catalyst **1** with and without epoxide (1,2-Epoxybutane) at temperatures 25, 50, 75 and 100 °C (Fig. 2a):

12 mg (4 mmol) of N,N'-bis(4-carboxyphenyl)ethylenediamine (catalyst **1**) was dissolved using 0.6 ml DMF-*d*₇ as the solvent in a 5 mm NMR tube. After complete dissolution of **1**, ¹H NMR measurements were conducted on a Bruker AVIII 500WB machine at 25, 50, 75 and 100 °C by heating the sample directly in the instrument. Similarly, the same amount of catalyst **1** was dissolved using 0.6 ml DMF-*d*₇ as solvent in another 5 mm NMR tube, then 57.7 mg (80 mmol) of 1,2-Epoxybutane was added (epoxide/catalyst ratio = 20:1). After dissolving the epoxide in the mixture, the ¹H NMR analyses were conducted in the same way at 25, 50, 75 and 100 °C.

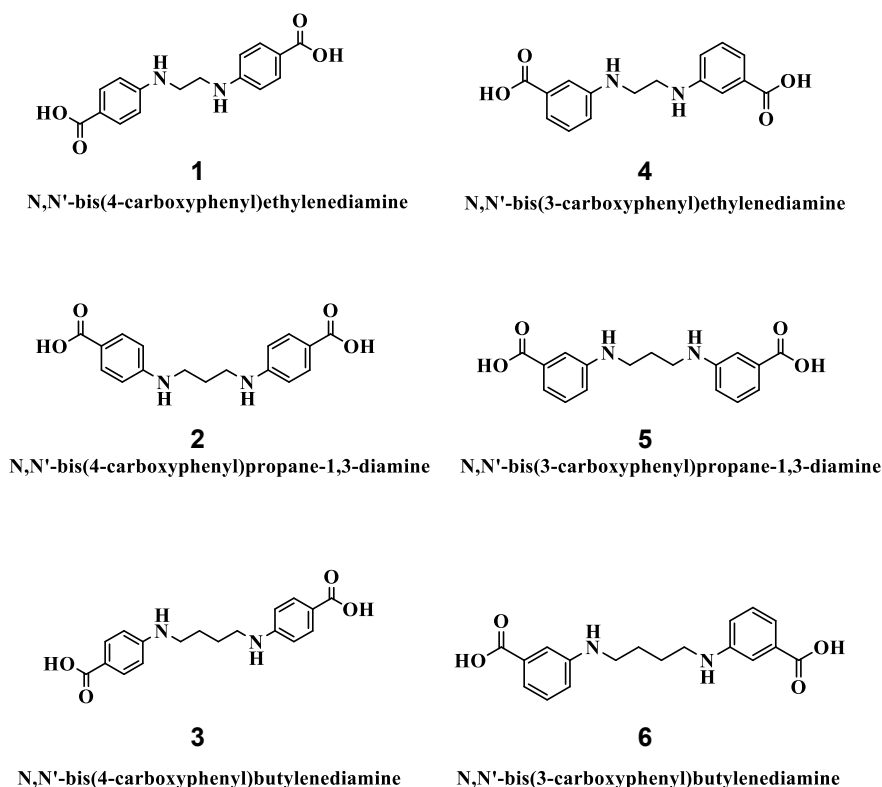
1.2. Procedure for ¹³C NMR/FT-IR experiments of catalyst **1** with and without CO₂ (Fig. 2b, Fig. S9):

To study the interactions of CO₂ and catalyst **1**, two experiments were carried out. For the first experiment, a certain amount of N,N'-bis(4-carboxyphenyl)ethylenediamine (catalyst **1**) was added into a 16 mL high pressure stainless-steel autoclave equipped with a magnetic stir bar. The reactor was then placed in a constant temperature furnace at 60 °C and stirred at this temperature for a certain time. For the second experiment, the same amount of **1** was added

into another reactor, which after removal of the air was charged with CO₂ to 1 MPa pressure and similarly placed in a constant temperature furnace at 60 °C and stirred at this temperature for the same time period. After cooling to room temperature, samples taken from both reactors were analyzed by FT-IR spectroscopy and after dissolving in DMSO-*d*₆ by ¹³C NMR spectroscopy.

2. Preparation of the catalysts

The catalytic compounds shown in Scheme S1 were prepared according to our recent publication using ethyl 4-aminobenzoate or ethyl 3-aminobenzoate as the starting material, respectively.³



Scheme S1 Diamine/carboxylic acid based catalytic compounds used in this work.

3. Catalytic reactions

In a typical procedure, a certain amount of the catalyst and substrate were loaded into the 16 mL stainless-steel autoclave equipped with a magnetic stirrer. 2 mL DMF as the solvent was added into the reactor. The air in the reactor was removed by blowing CO₂ into the reactor in three times. Afterwards, the reactor was charged with CO₂ to the desired pressure. The reactor was placed in a constant temperature furnace set and the reaction mixture was stirred during the reaction time. After reaction, the reactor was cooled down in the ice water and excess of the CO₂ was absorbed by an ethyl acetate cold trap. The liquid product was quantitatively analyzed by gas chromatography (GC) (Agilent 7890B) equipped with a capillary column using a flame ionization detector by using dodecane as the internal standard. In order to identify the reaction products, required analyses were also run on a GC-MS (Agilent-7890B-5977A).

4. ^1H and ^{13}C NMR spectra and data of the catalysts 1-7

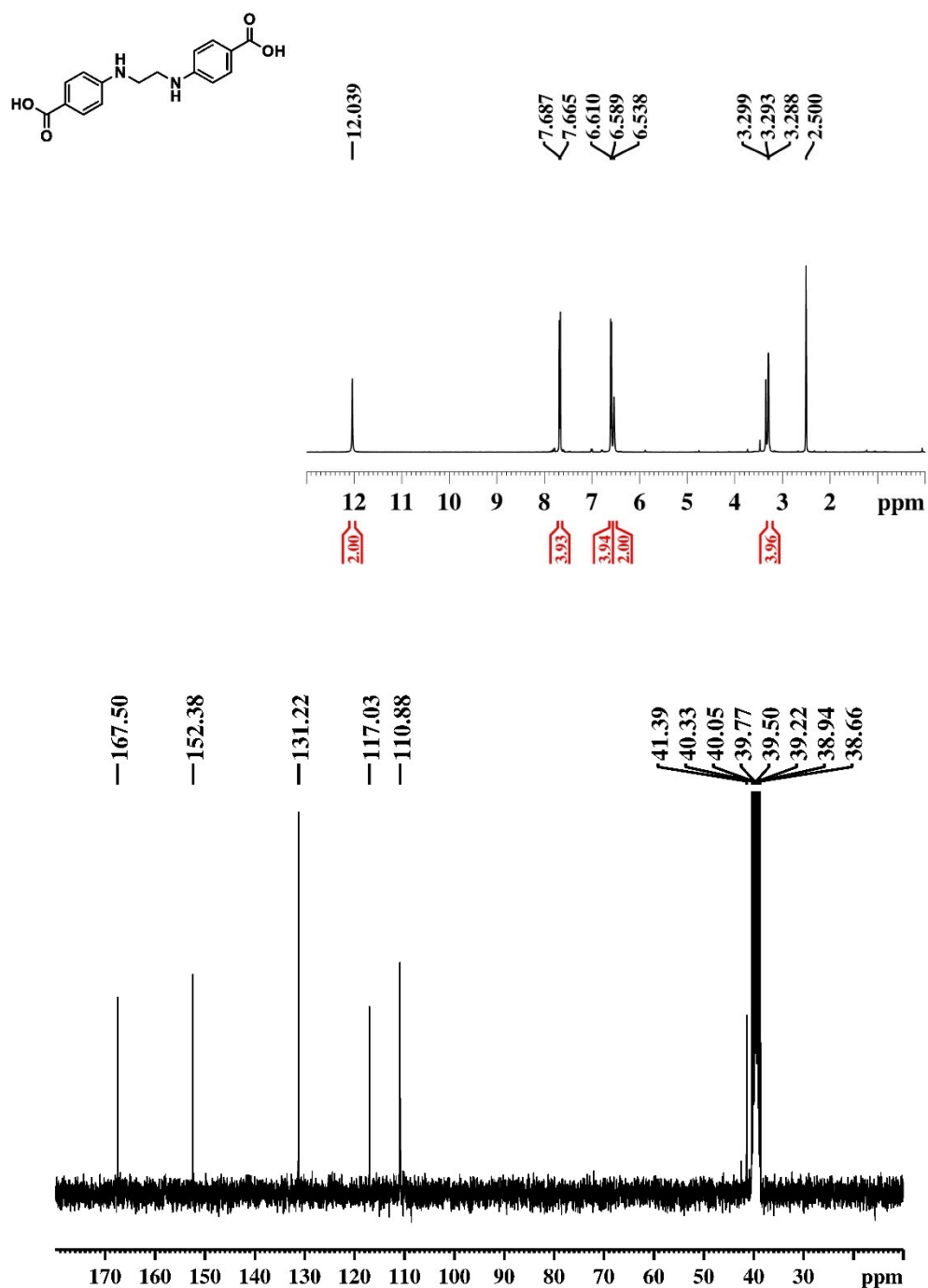


Fig. S1 ^1H (top) and ^{13}C NMR (down) spectra of **1**.

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ = 12.04 (s, 2H), 7.68 (d, J = 8.5 Hz, 4H), 6.65 – 6.56 (m, 4H), 6.53 (d, J = 5.5 Hz, 2H), 3.32 – 3.24 (m, 4H).

^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ = 167.50, 152.38, 131.22, 117.03, 110.88, 41.39.

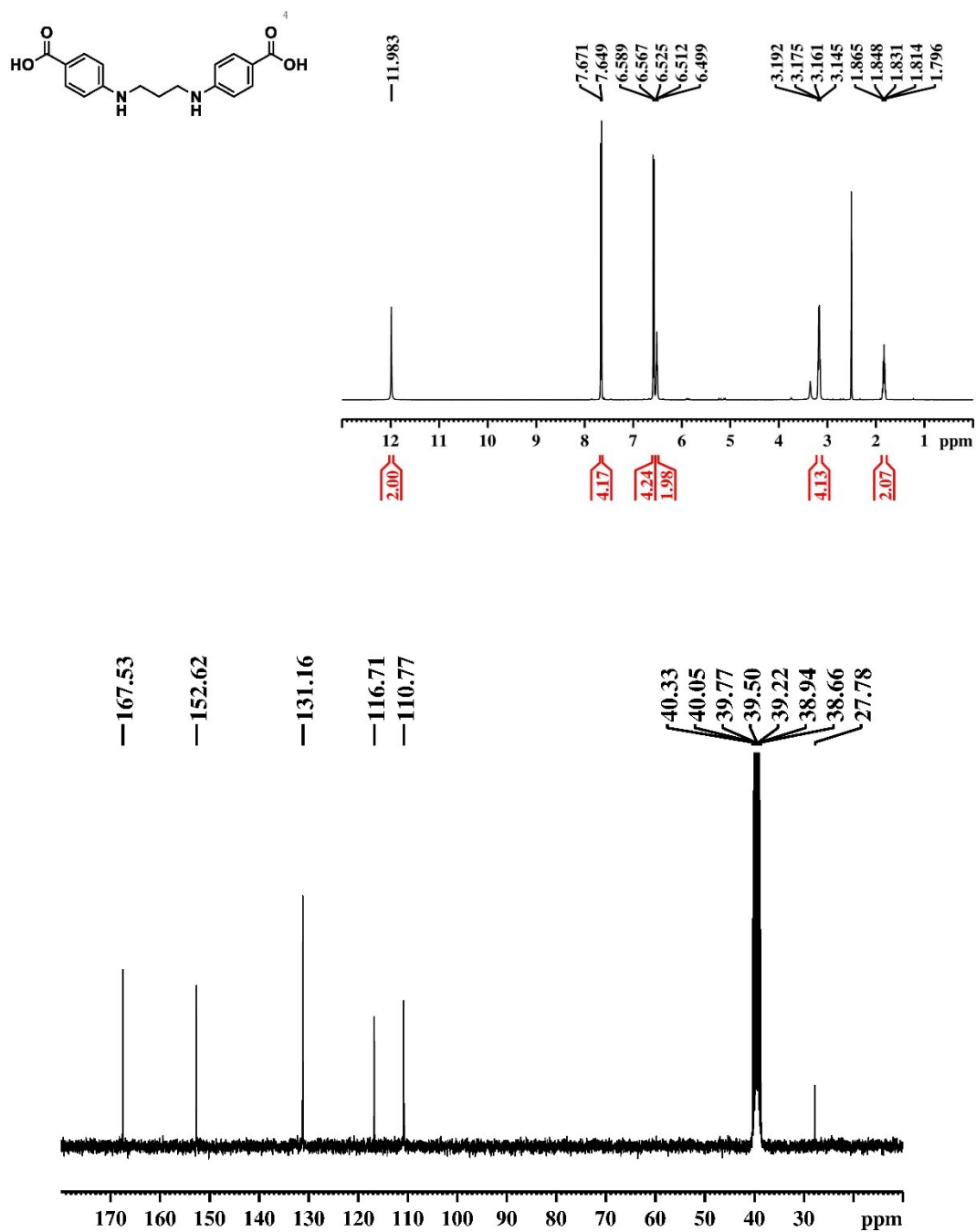


Fig. S2 ¹H (top) and ¹³C NMR (down) spectra of **2**.

¹H NMR (400 MHz, DMSO-*d*₆) δ = 11.98 (s, 2H), 7.71 – 7.62 (m, 4H), 6.62 – 6.55 (m, 4H), 6.51 (t, *J* = 5.5 Hz, 2H), 3.17 (q, *J* = 6.4 Hz, 4H), 1.83 (p, *J* = 6.9 Hz, 2H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ = 167.53, 152.62, 131.17, 116.72, 110.78, 27.78.

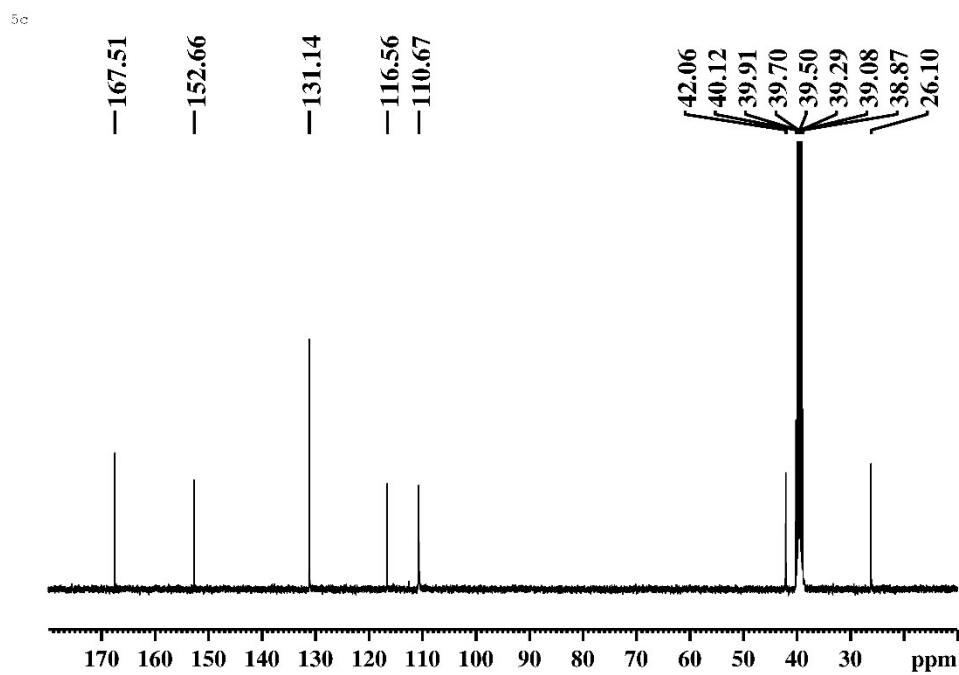
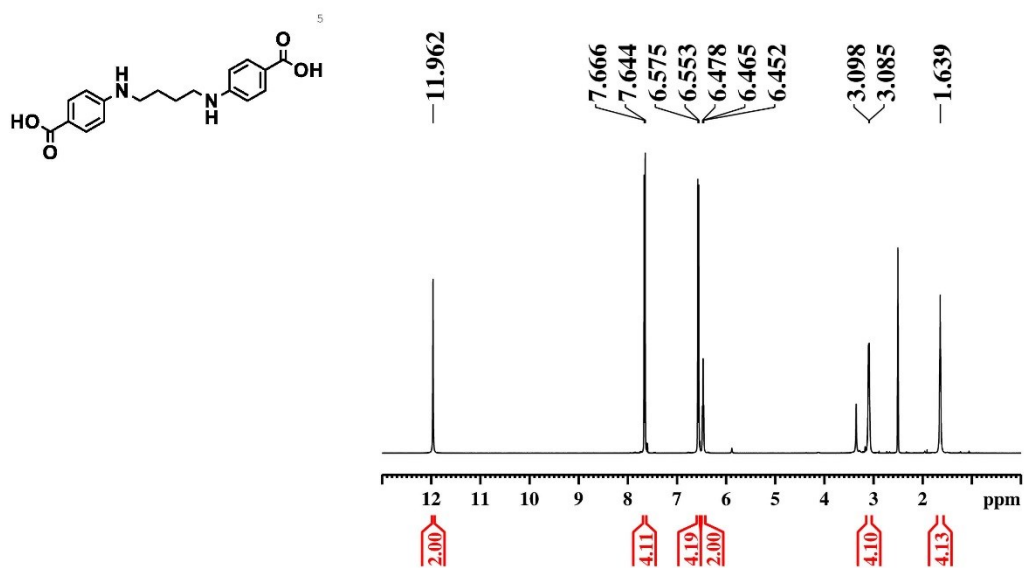


Fig. S3 ^1H (top) and ^{13}C NMR (down) spectra of **3**.

^1H NMR (400 MHz, DMSO- d_6) δ = 11.96 (s, 2H), 7.70 – 7.62 (m, 4H), 6.63 – 6.51 (m, 4H), 6.46 (t, J = 5.4 Hz, 2H), 3.09 (q, J = 6.0 Hz, 4H), 1.64 (h, J = 2.8 Hz, 4H).

^{13}C NMR (101 MHz, DMSO- d_6) δ = 167.51, 152.66, 131.14, 116.56, 110.67, 42.06, 26.10.

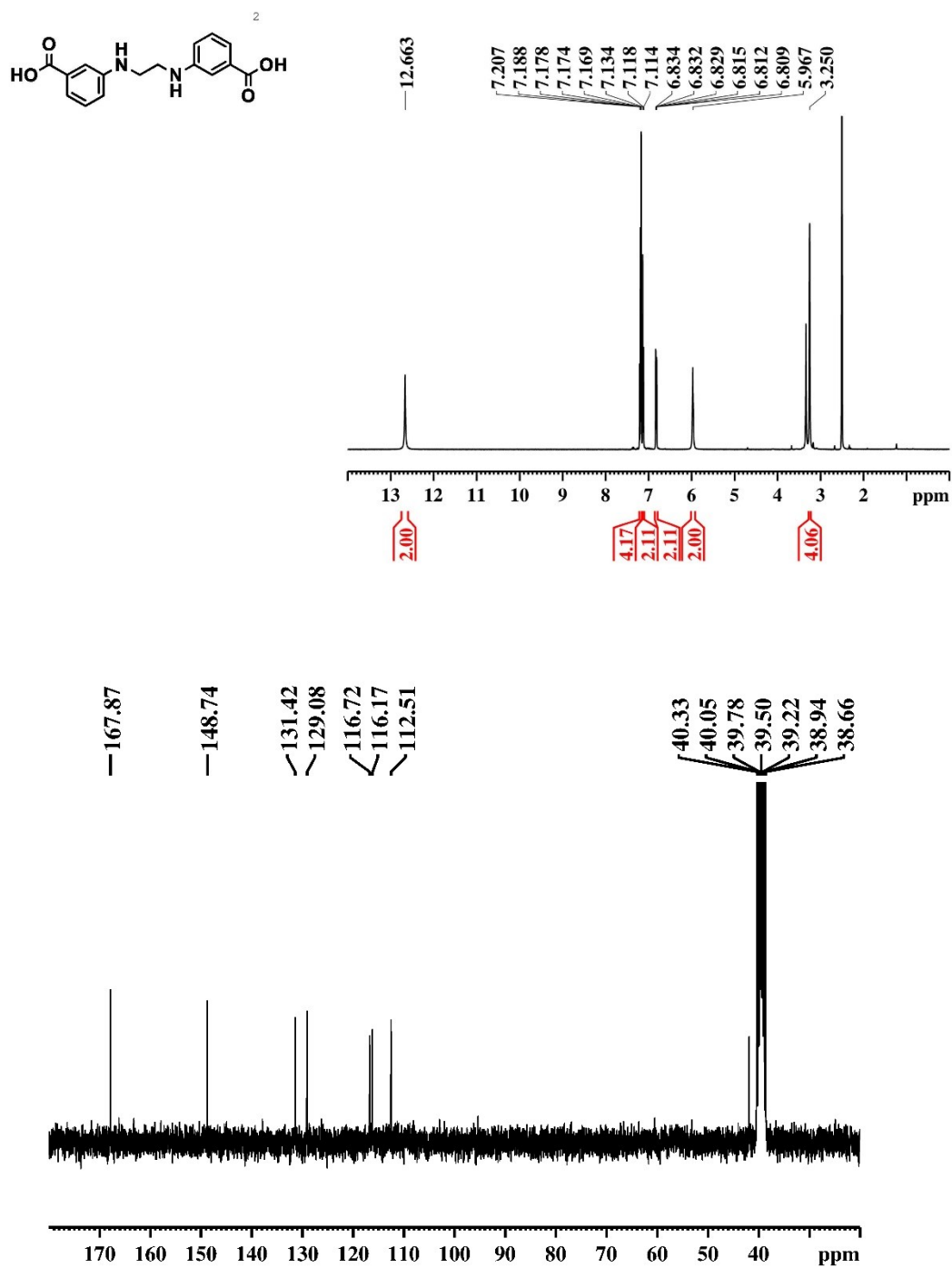


Fig. S4 ¹H (top) and ¹³C NMR (down) spectra of **4**.

¹H NMR (400 MHz, DMSO-*d*₆) δ = 12.66 (s, 2H), 7.20 – 7.15 (m, 4H), 7.12 (dt, *J* = 7.6, 1.3 Hz, 2H), 6.85 – 6.80 (m, 2H), 5.97 (d, *J* = 5.4 Hz, 2H), 3.25 (t, *J* = 2.4 Hz, 4H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ = 167.87, 148.74, 131.42, 129.08, 116.72, 116.17, 112.51, 41.85.

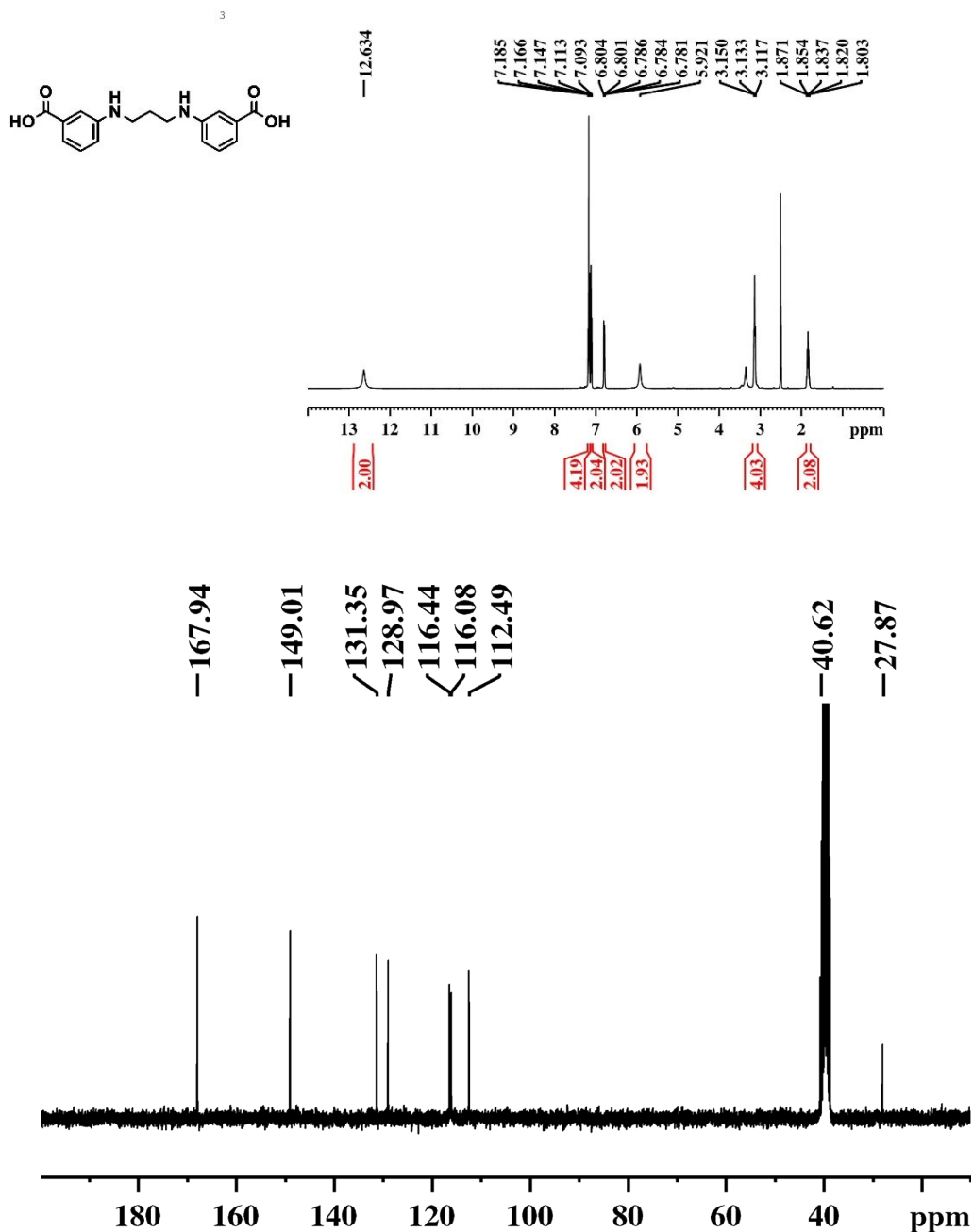


Fig. S5 ¹H (top) and ¹³C NMR (down) spectra of **5**.

¹H NMR (400 MHz, DMSO-*d*₆) δ = 12.63 (s, 2H), 7.16 (d, J = 7.6 Hz, 4H), 7.10 (dt, J = 7.6, 1.4 Hz, 2H), 6.79 (ddd, J = 8.0, 2.6, 1.2 Hz, 2H), 6.01 – 5.79 (m, 2H), 3.13 (t, J = 6.9 Hz, 4H), 1.84 (p, J = 6.9 Hz, 2H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ = 167.94, 149.01, 131.35, 128.97, 116.44, 116.08, 112.49, 40.62, 27.88.

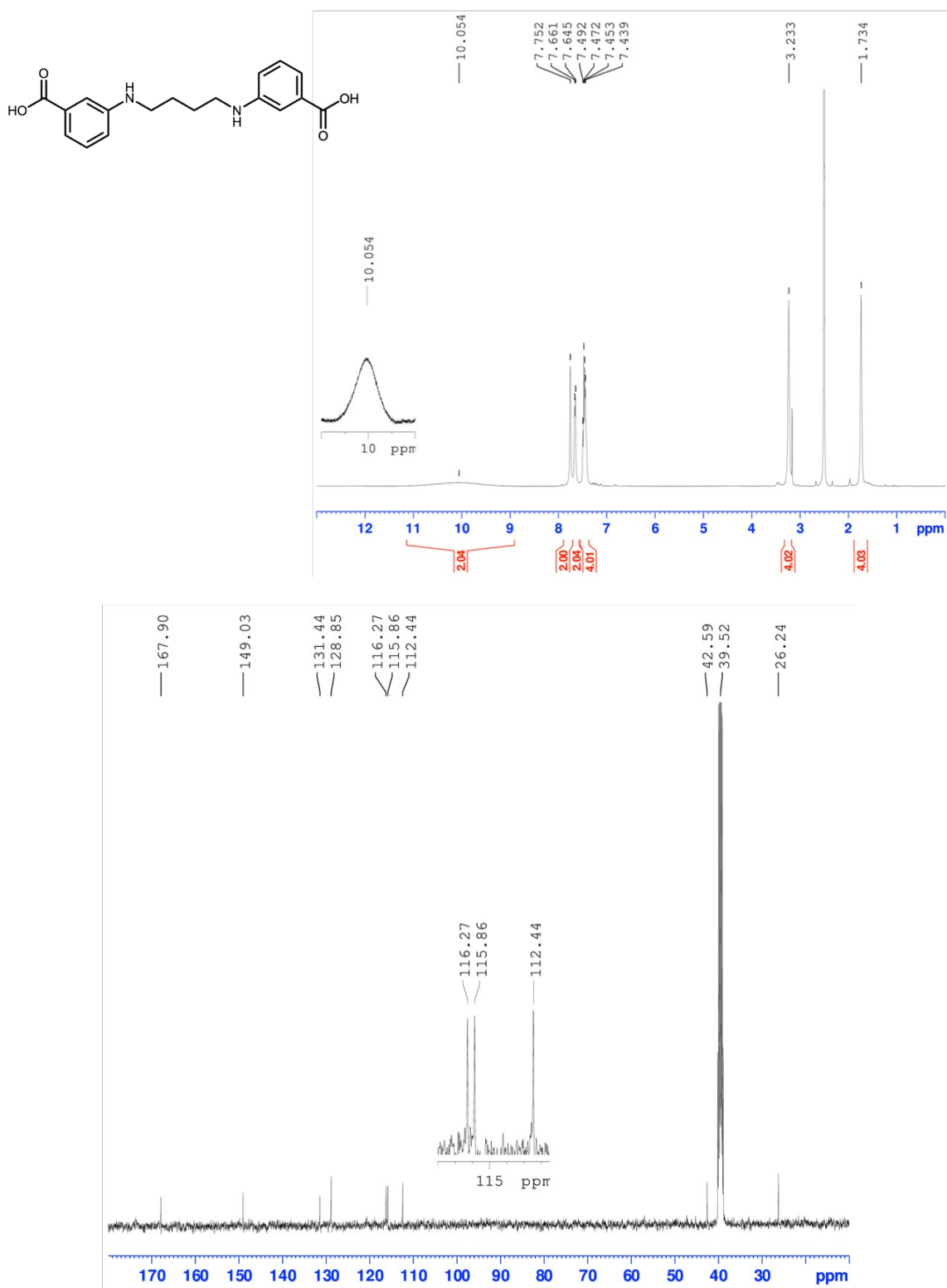


Fig. S6 ¹H (top) and ¹³C NMR (down) spectra of **6**.

¹H NMR (400 MHz, DMSO-*d*₆) δ = 10.05 (s, 2H), 7.75 (s, 2H), 7.65 (d, *J* = 6.3 Hz, 2H) 7.49 – 7.44 (m, 4H), 3.23 (m, 4H), 1.73 (m, 4H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ = 167.90, 149.03, 131.44, 128.85, 116.27, 115.86, 112.44, 42.59, 26.24.

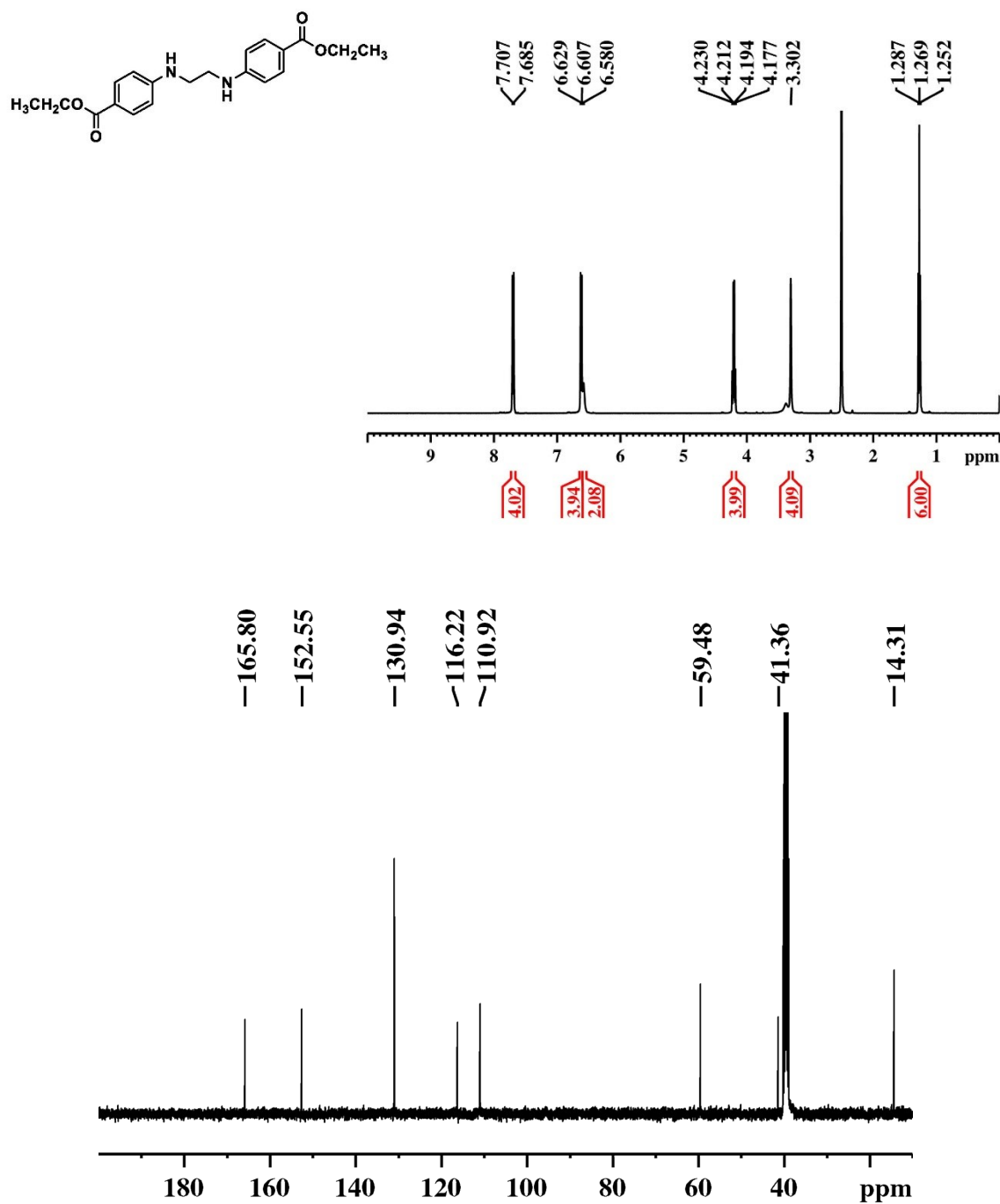


Fig. S7 ¹H (top) and ¹³C NMR (down) spectra of 7.

¹H NMR (400 MHz, DMSO-*d*₆) δ = 7.70 (d, *J* = 7.1 Hz, 4H), 6.62 (d, *J* = 7.1 Hz, 4H), 6.58 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.30 (s, 4H), 1.27 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ = 165.80, 152.55, 130.94, 116.23, 110.93, 59.49, 41.36, 14.31.

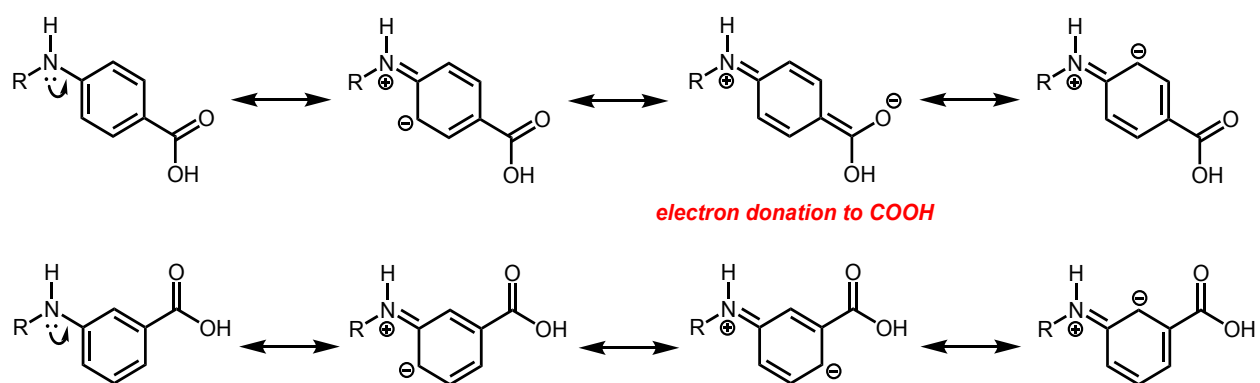


Fig. S8 Illustration of the resonance effect for *para* (top) and *meta* (down) positioned carboxylic acids.

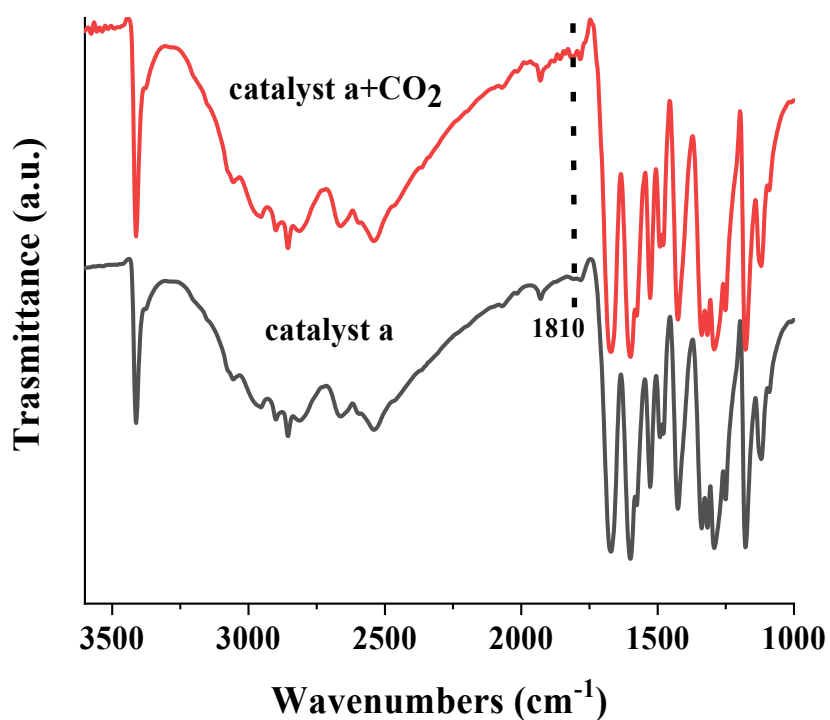


Fig. S9 FT-IR spectra of the catalyst **1** before and after interacting with CO₂.

Table S1. Effect of the functional groups and their synergy in catalytic materials on the conversion of CO₂ and 1,2-Epoxybutane into 1,2-Butylene carbonate (cf. equation in Table 1)^a

Entry	Solvent	Catalyst	Yield (%)	Sel. (%)
1	DMF	1 ^b	18	99
2	DMF	1 ^c	0	99
3	DMF	1	86	99
4	DMF	7	23	98
5	DMF	8	61	99
6	DMF	7+8 ^d	74	99

^a Reaction conditions: 1,2-Epoxybutane (10 mmol), catalyst (7 mol%), DMF (2 mL), temperature (120 °C), CO₂ (2 MPa), reaction time (24h). ^b Catalyst with pre-adsorbed CO₂ was used and reaction mixture was pressurized with 2 MPa argon during the reaction (Preparation of catalyst **1** with pre-adsorbed CO₂: Catalytic amount of **1** was added into reactor and after removal of the air was charged with CO₂ to 1 MPa pressure. The reactor was then placed in a constant temperature furnace at 60 °C and stirred at this temperature for a while. After cooling to room temperature, treated material was used for catalytic reaction). ^c Catalyst without pre-adsorbed CO₂ was used and reaction mixture was pressurized with 2 MPa argon during the reaction. ^d The total amount of catalytic material (7 mol%) consists of equal amounts of **7** and **8** (3.5 mol% each). The yields and selectivities were determined by GC using dodecane as internal standard.

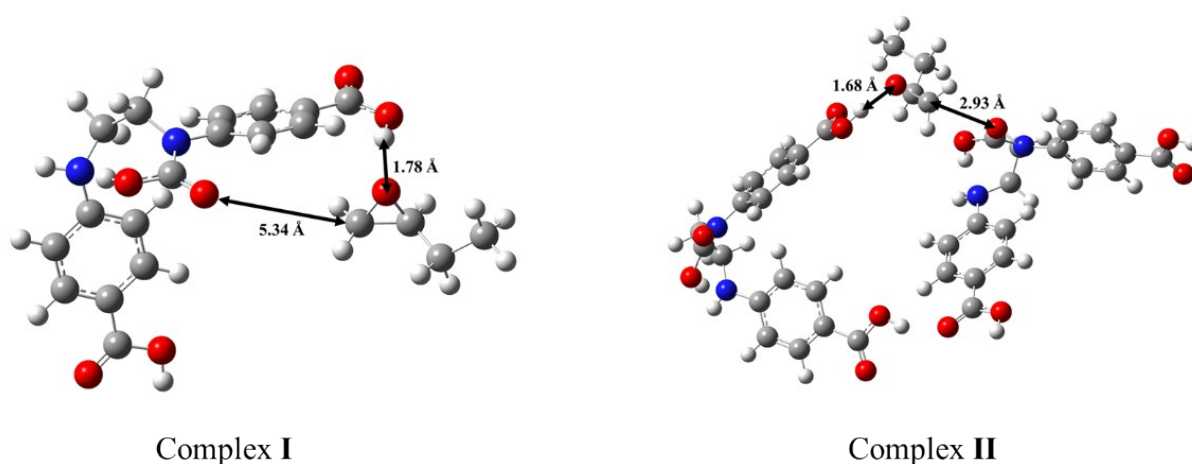


Fig. S10 Optimized DFT structures for possible reaction intermediates at M06-2X/6-31G(d) level using Gaussian 09. Complex **I** shows monomolecular ring opening with activated CO₂ and 1,2-Epoxybutane in one catalyst **1** molecule (single point energy = -8.01 kcal/mol). In contrast, complex **II** shows bimolecular ring opening with two catalyst **1** molecules, where activated CO₂ in first molecule (in carbamate form) attacks 1,2-Epoxybutane activated in the second catalyst molecule (single point energy = -23.6 kcal/mol).

References

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2. P. C. Hariharan and J. A. Pople, *Theoretica chimica acta*, 1973, **28**, 213-222.
3. S. Bulut and W. L. Queen, *The Journal of Organic Chemistry*, 2018, **83**, 3806-3818.