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CO_2 Promoted Synthesis of Asymmetric Organic Carbonate by Switchable Agents Based on DBU and Alcohols

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Table S1 The comparison of the catalytic performance of the reported catalytic systems and that used in this work.

Catalysts	Reaction	T /°C	t /h	Con. %	Sel. %	Recyclable
TBD[5]	Transesterificationof DMC and alcohols	80	1	96-98	83-93	No
PS-DBU[23]	N-phenoxycarbonylation of N-Heteroaromatics (HetNH) and diphenyl carbonate	120	24	73-90	99	Yes
MCM-41 -TBD[24]	Transesterificationof EMC and alcohols /amines	125	15	80-96	94-99	Yes
TiO_2 nanofibers[19]	Transesterificationof DMC and alcohols	100	8	31-70	99	Yes
DBU+CO_2 (this work)	Transesterificationof DMC and alcohols/ amines	100	8	47-92	92-99	Yes

The numbers in the square brackets refer to the reference number cited in the article.

Tables S2 The p$K_b$values of different bases used in this work.

Bases	pK_b(25 ^{o}C, in water)
TBD	-1.2 ±1.0
KOH	-0.70
DBU	0.5 ±1.5
TMG	1.0 ±1.0
Et_3N	3.25
K_2CO_3	3.75

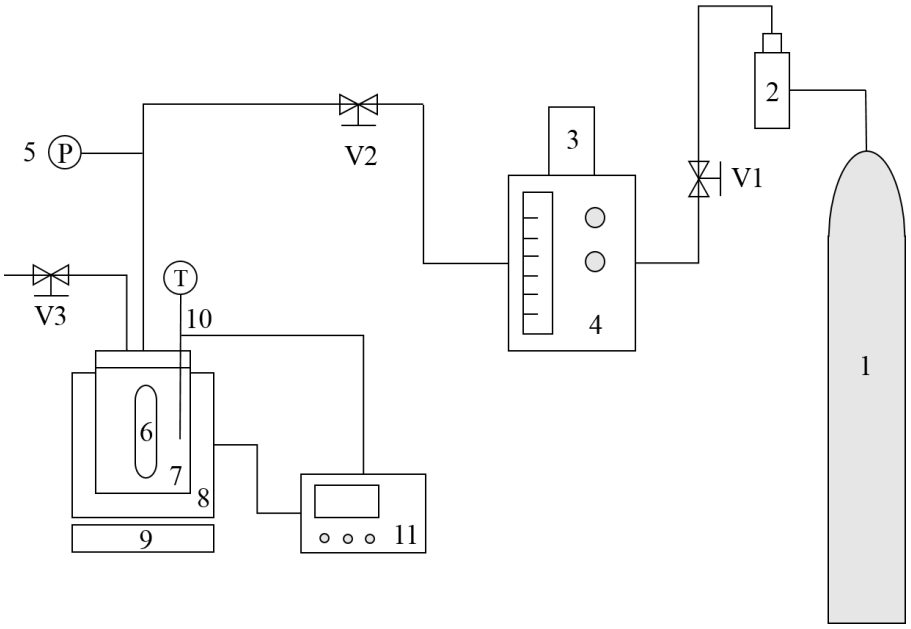


Fig. S1 Apparatus for phase behavior.1. CO_2 gas cylinder, 2. Drying tower, 3. Cold trap, 4. High-pressure metering pump, 5. Pressure sensor, 6. View window, 7. Reacting vessel, 8. Heating jacket,9. Magnetic stirrer, 10. Thermocouple, 11. Temperature sensor. V1,V2 and V3: valve.

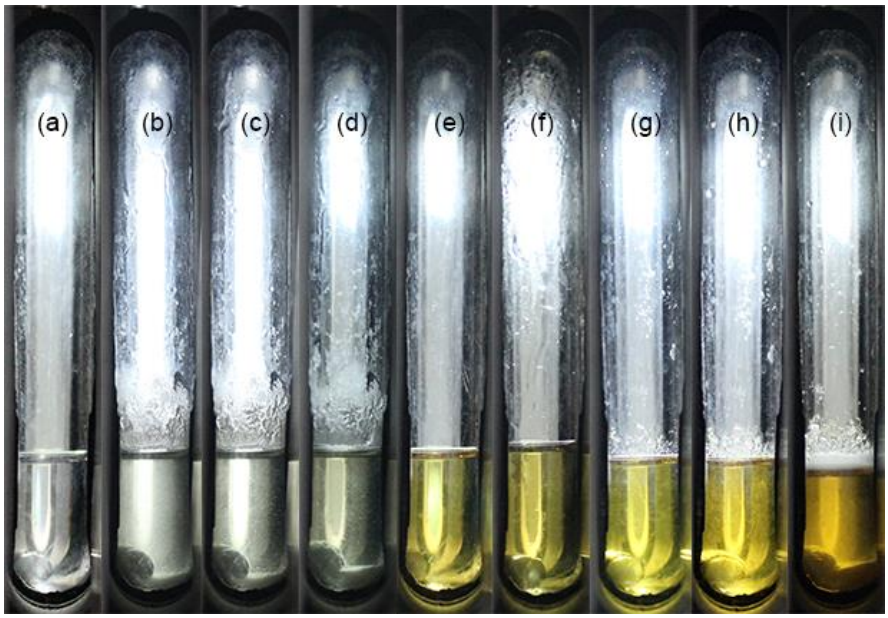


Fig. S2 Visual observations of a reaction mixture containing DBU, ethanol, DMC, toluene, and CO_2 under reaction conditions. The working volume of the viewing cell was about 60 mL. DBU 5 mmol, ethanol 5 mmol, DMC 15 mmol and toluene 3.0 ml. CO_2 was charged for b−h. (a) DBU, ethanol, DMC, toluene, 25 °C, (b) DBU, ethanol, DMC, toluene, purging three times with 0.1 MPa CO_2 and then charged with CO_2 up to 0.5 MPa at 25 °C, (c) 0.5 MPa, 50°C, (d) 0.5 MPa, 70°C, (e) 0.5 MPa, 90°C, (f) 1.0 MPa, 90°C, (g) 2.0 MPa, 90 °C, (h) 3.0 MPa, 90 °C, (i) 0.1 MPa, 25 °C, autoclave was cooled and CO_2 was released.

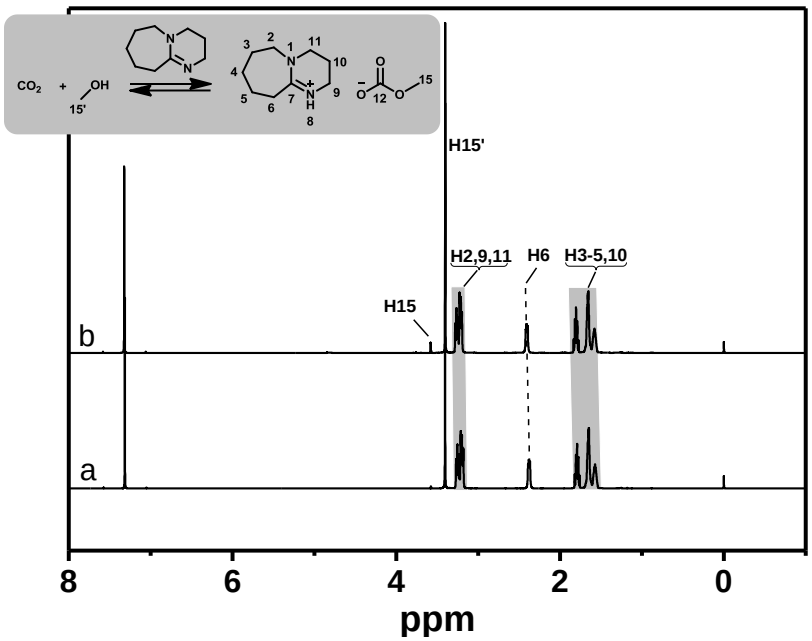


Fig. S3 ^{1}H NMR spectra of equimolar mixture of DBU/methanol, before and after bubbling CO_2. (a) DBU/methanol, (b) bubbling CO_2 to DBU/methanol for 10 min.

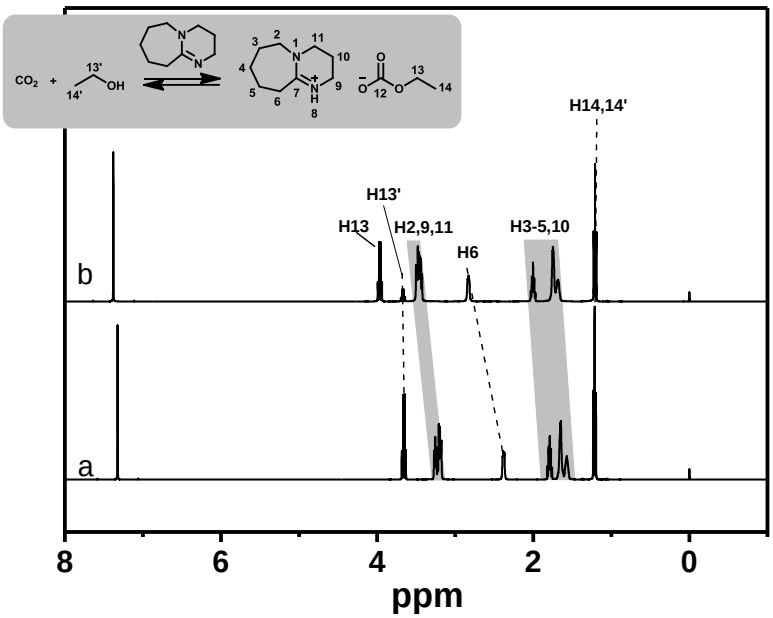


Fig. S4 ^{1}H NMR spectra of equimolar mixture of DBU/ethanol, before and after bubbling CO_2. (a) DBU/ethanol, (b) bubbling CO_2 to DBU/ethanol for 10 min.

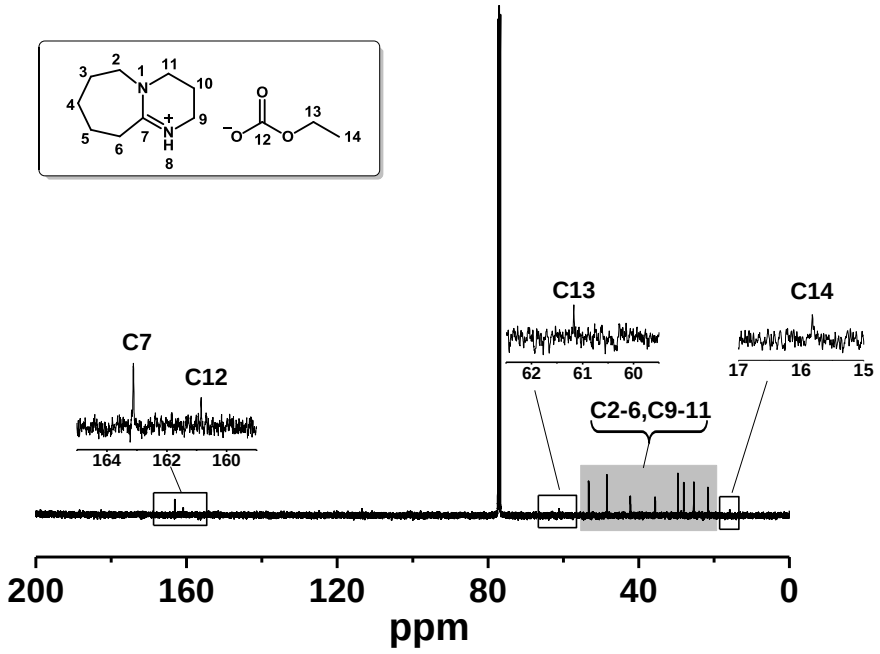


Fig. S5 ^{13}C NMR ($CDCl_3$ as a solvent) spectra of [DBUH][$O(CO)OCH_2CH_3$].

Reaction Kinetics

The reaction was periodically monitored by the GC. In a typical kinetics experiment, the concentration of DMC (3.0 M), CO_2 pressure (1.0 MPa) and alcohol (1.0 M) was constant. In order to examine the effect of DBU concentration on the rate of transesterification reaction, the concentration of DBU was varied from 0.50M to 1.25 M. The other reaction conditions have been given in the Figure captions (Fig.S6). Reaction rates (R_0) for the kinetic studies were determined from the slopes of reaction profiles ($[DBU]_0$-$[DBU]_t$ vs time) at low conversions (<15%) (Initial rate method).

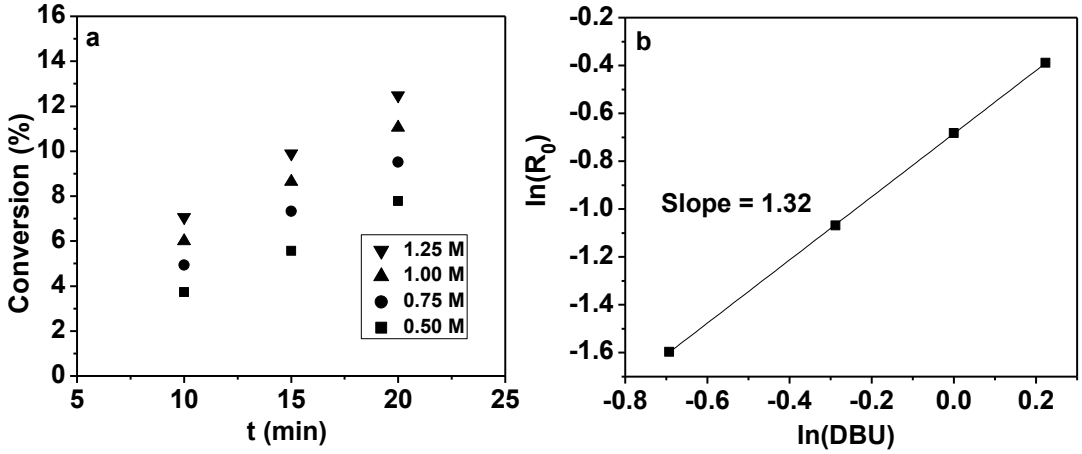


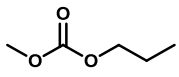
Fig. S6 The relationship between the initial reaction rate (R_0) and the initialconcentrations of DBU. Reaction conditions: DBU (0.50-1.25 M), DMC (3.0 M), ethanol (1.0 M), CO_2 pressure (1.0 MPa), 100 ^oC.

Table S3 The conductivity of DUB, ethanol and their mixture(30 °C)

Sample	Conductivity/μs·cm^{-1}
DBU	2.85
EtOH	4.14
[a]DBU/EtOH	77.9

[a]The molar ratio of DBU and EtOH was 1:3.

Propyl methyl carbonate[1]: colorless liquid, petroleum ether/ethyl acetate = 12:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, *J* = 7.4 Hz, 3H, -*CH*$_3$-) 1.69 (m, 2H, -*CH*$_2$-CH_3-), 3.78 (s, 3H, -O-*CH*$_3$-), 4.10 (m, 2H, -*CH*$_2$-O-).^{13}C NMR (100 MHz, $CDCl_3$): δ 155.90, 69.54, 54.60, 22.02, 10.18. MS (ESI): calculated $[M + H]^+$:119.1, found:119.1.FT-IR (*v*, cm^{-1}): 2966, 2878, 1753, 1544, 1448, 1274.



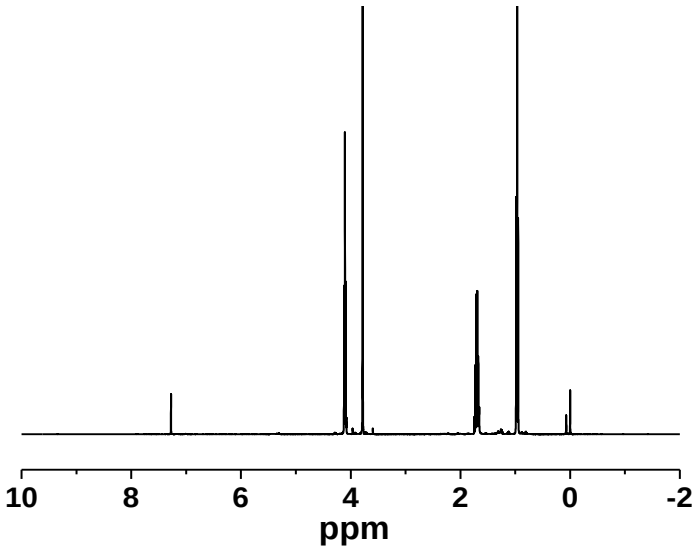


Fig. S7 ^{1}H NMR spectra of propyl methyl carbonate.

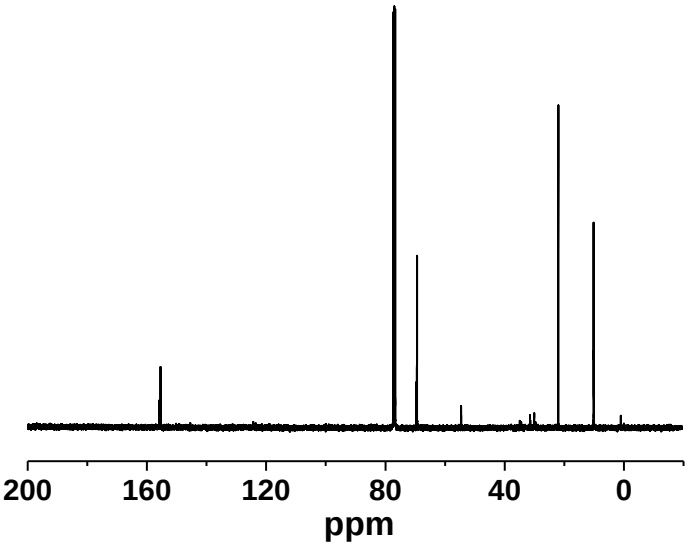
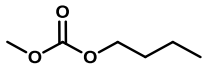


Fig. S8 ^{13}C NMR spectra of propyl methyl carbonate.

Butyl methyl carbonate[1]:colorless liquid, petroleum ether/ethyl acetate = 12:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94 (t, *J* = 7.4 Hz, 3H, -*CH*$_3$-), 1.41 (m, 2H, -CH_2-*CH*$_2$-CH_3-), 1.66 (m, 2H, -*CH*$_2$-CH_2-CH_3-), 3.78 (s, 3H, -O-*CH*$_3$-), 4.15 (t, *J* = 6.8 Hz, 3H, -*CH*$_2$-O-).^{13}C NMR (100 MHz, $CDCl_3$): δ 155.90, 67.93, 54.59, 30.65, 18.88, 13.61. MS (ESI): calculated [M]:132.1, found:132.1. FT-IR (*v*, cm^{-1}): 2961, 2875, 1750, 1541, 1444, 1274.



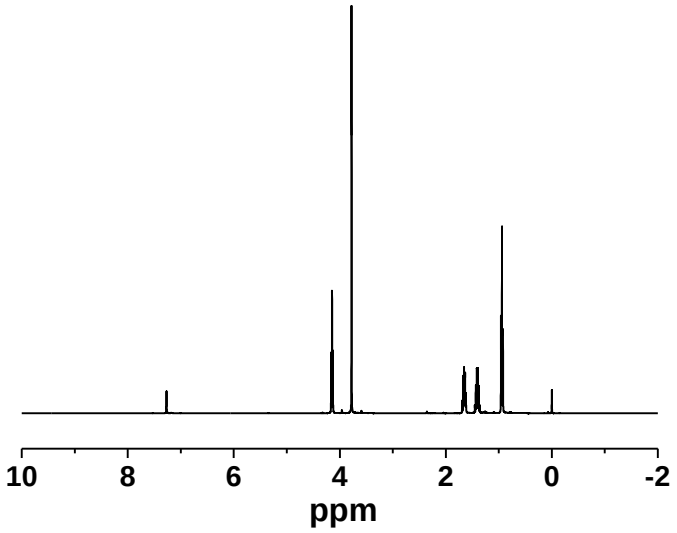


Fig. S9 ^{1}H NMR spectra of butyl methyl carbonate.

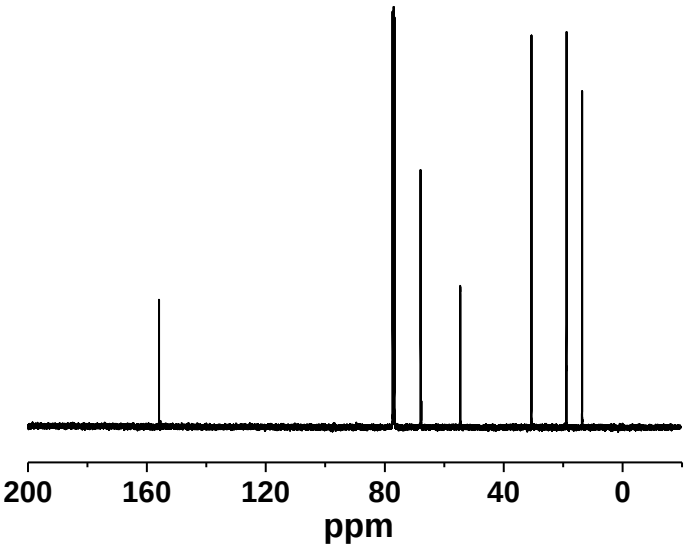
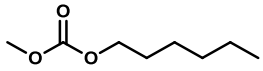


Fig. S10 ^{13}C NMR spectra of butyl methyl carbonate.

Hexyl methyl carbonate[2]: colorless liquid, petroleum ether/ethyl acetate = 12:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 6.8 Hz, 3H, -*CH*$_3$-), 1.33 (m, 6H, aliphatic -*CH*$_2$-), 1.66 (m, 2H, aliphatic -*CH*$_2$-), 3.78 (s, 3H, -O-*CH*$_3$-), 4.14 (t, *J* = 6.8 Hz, 3H, -*CH*$_2$-O-).^{13}C NMR (100 MHz, $CDCl_3$): δ 155.91, 68.28, 54.62, 31.39, 28.62, 25.35, 22.51, 13.98.MS (ESI): calculated $[M + H]^+$:161.1, found:161.0. FT-IR (*v*, cm^{-1}): 2963, 2878, 1753, 1547, 1446, 1275.



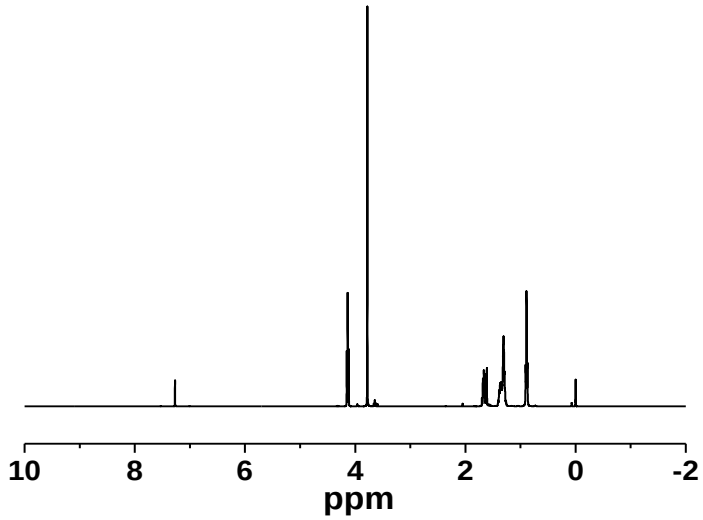


Fig. S11 ^{1}H NMR spectra of hexyl methyl carbonate.

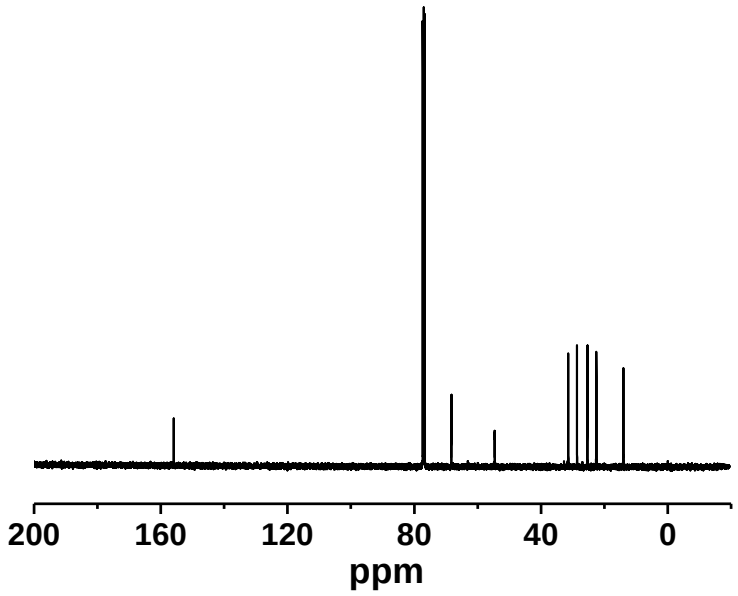
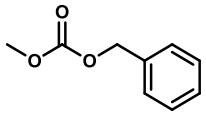


Fig. S12 ^{13}C NMR spectra of hexyl methyl carbonate.

Benzyl methyl carbonate[3]: colorless liquid, petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H, -*CH*$_3$-O-), 5.17 (m, 2H, -O-*CH*$_2$-), 7.36 (m, 10H, -*CH*-).^{13}C NMR (100 MHz, $CDCl_3$): δ 155.75, 135.25, 128.61, 128.55, 128.31, 69.66, 54.89. MS (ESI): calculated [M]:166.1, found:166.1. FT-IR (*v*, cm^{-1}): 3034, 2957, 1749, 1585, 1444, 1269.



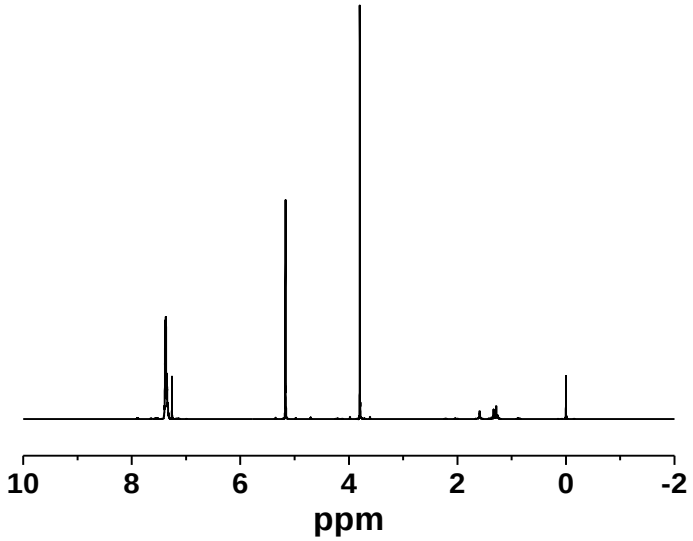


Fig. S13 ^{1}H NMR spectra of benzyl methyl carbonate.

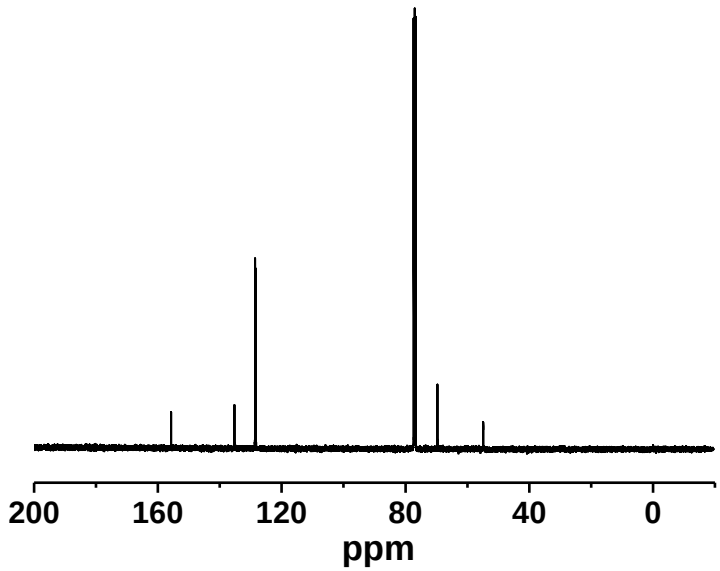
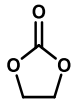


Fig. S14 ^{13}C NMR spectra of benzyl methyl carbonate.

1,3-dioxolan-2-one[4]: colorless liquid,petroleum ether/ethyl acetate = 3:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.54 (s, 4H, -(CH_2)$_2$-).^{13}C NMR (100 MHz, $CDCl_3$): δ 155.54, 64.48.MS (ESI): calculated [M]:88.0, found:88.1. FT-IR (ν, cm^{-1}): 2994, 1798, 1161, 1065.



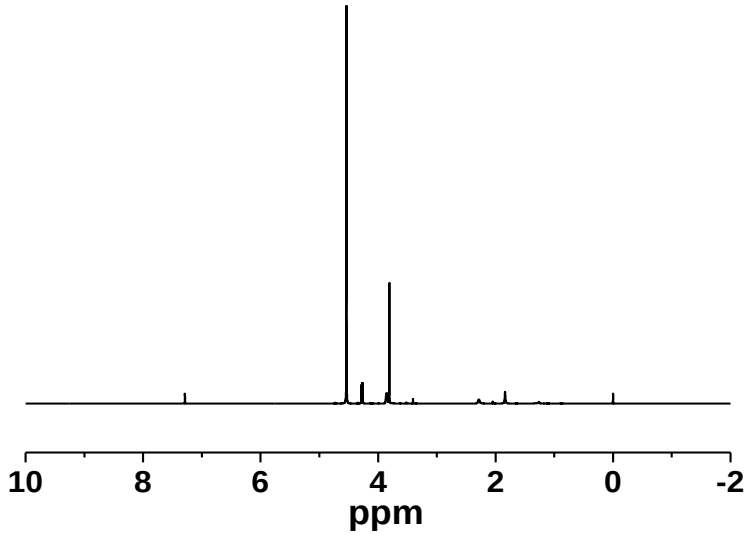


Fig. S15 ^{1}H NMR spectra of 1,3-dioxolan-2-one.

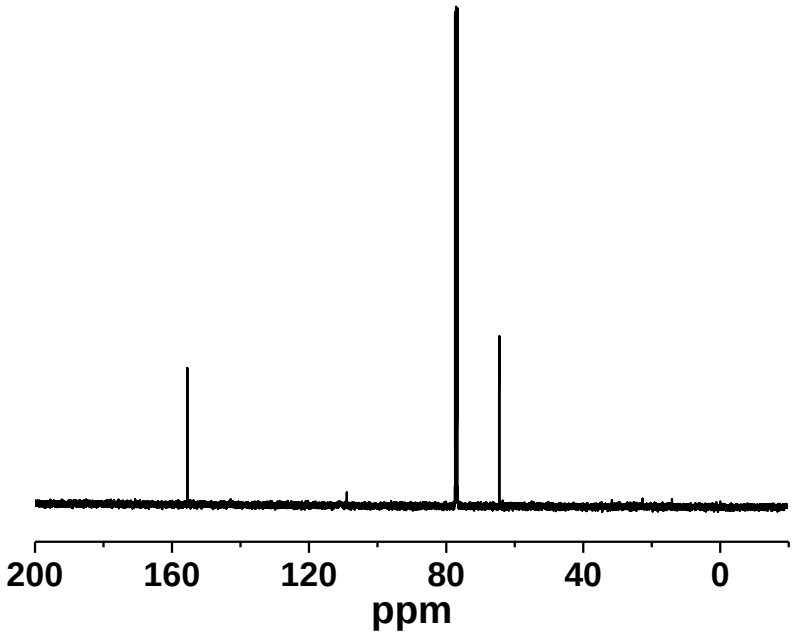
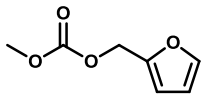


Fig. S16 ^{13}C NMR spectra of 1,3-dioxolan-2-one.

Furan-2-ylmethyl methyl carbonate: yellow liquid,petroleum ether/ethyl acetate = 12:1.^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 3H, -*CH*$_3$-O-), 5.12 (s, 2H, -C-*CH*$_2$-O-), 6.36 (dd, *J*= 2.0, 3.2 Hz, 1H, -CH-*CH*-C-), 6.46 (d, *J*= 3.2 Hz, 1H, -CH-*CH*-CH-), 7.43(dd, *J*= 0.8, 2.0 Hz, 1H, -O-*CH*-CH-).^{13}C NMR (100 MHz, $CDCl_3$): δ 155.54, 148.70, 143.54, 111.28, 110.58, 61.35, 54.93. MS (ESI): calculated [M]:156.1, found:156.0. FT-IR (*v*, cm^{-1}): 2959, 1751, 1502, 1445, 1265.



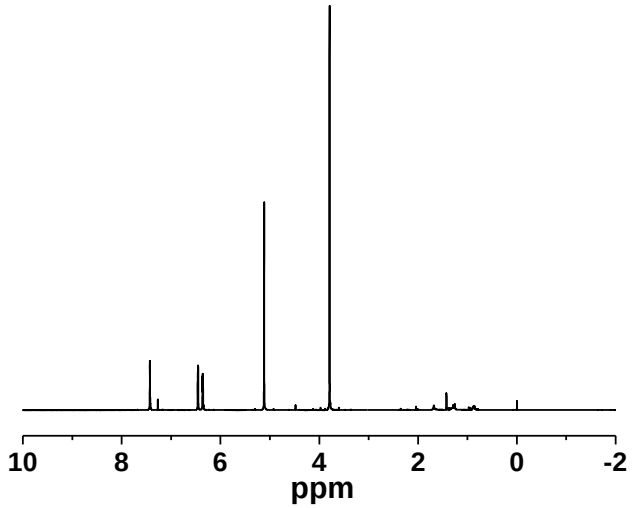


Fig. S17 ^{1}H NMR spectra of furan-2-ylmethyl methyl carbonate.

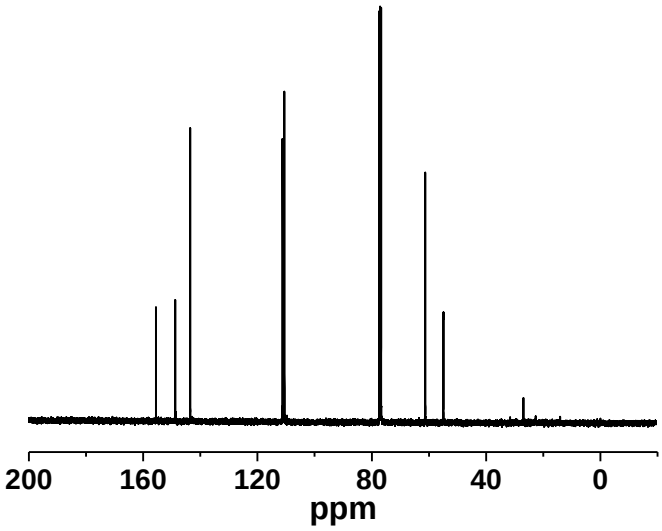
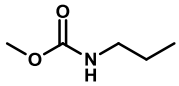


Fig. S18 ^{13}C NMR spectra of furan-2-ylmethyl methyl carbonate.

Methyl propyl carbamate[5]: colorless oil,petroleum ether/ethyl acetate = 10:1.^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (t, *J* = 9.5 Hz, 3H, -*CH*$_3$-), 1.52 (m, 2H, -*CH*$_2$-CH_3-), 3.14 (dd, *J* = 16.5, 8.0 Hz, 2H, -*CH*$_2$-NH-), 3.66 (s, 3H, -*CH*$_3$-O-), 4.77 (s, 1H, -*NH*-).^{13}C NMR (100 MHz, $CDCl_3$): δ 157.15, 51.91, 42.74, 23.17, 11.14. MS (ESI): calculated $[M + H]^+$:117.1, found:117.1. FT-IR (*v*, cm^{-1}):3336, 2965, 1705, 1543, 1462, 1269.



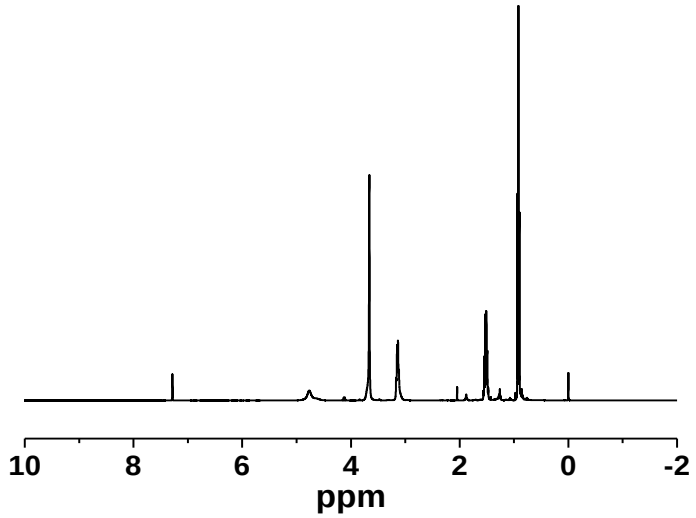


Fig. S19 ^{1}H NMR spectra of methyl propyl carbamate.

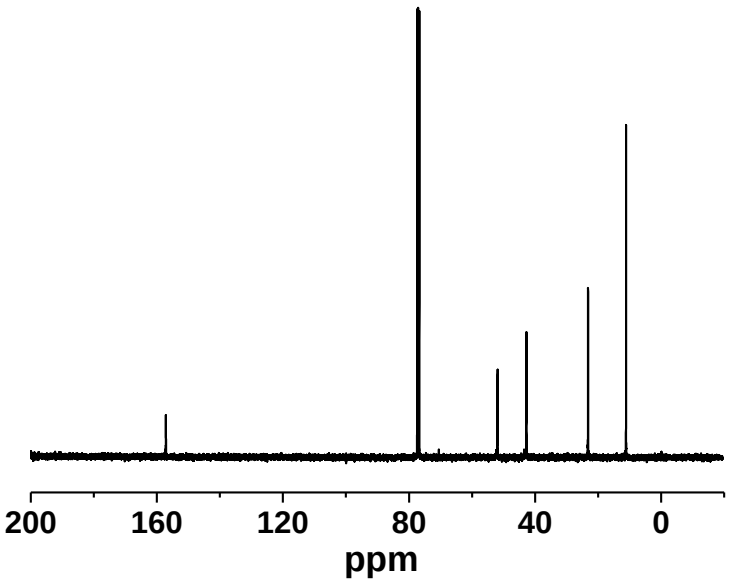
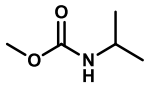


Fig. S20 ^{13}C NMR spectra of methyl propyl carbamate.

Methyl *iso*propyl carbamate[6]: colorless oil,petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (d, J = 7.4 Hz, 6H, -(CH_3)$_2$-CH-), 3.67 (s, 3H, -CH_3-O-), 3.81 (m, 1H, -*CH*-), 4.55(s, 1H, -*NH*-).^{13}C NMR (100 MHz, $CDCl_3$): δ 156.26, 51.76, 43.02, 22.99. MS (ESI): calculated $[M + 2H]^+$:118.1, found:118.1. FT-IR (v, cm^{-1}): 3326, 2974, 1697, 1535, 1460, 1257.



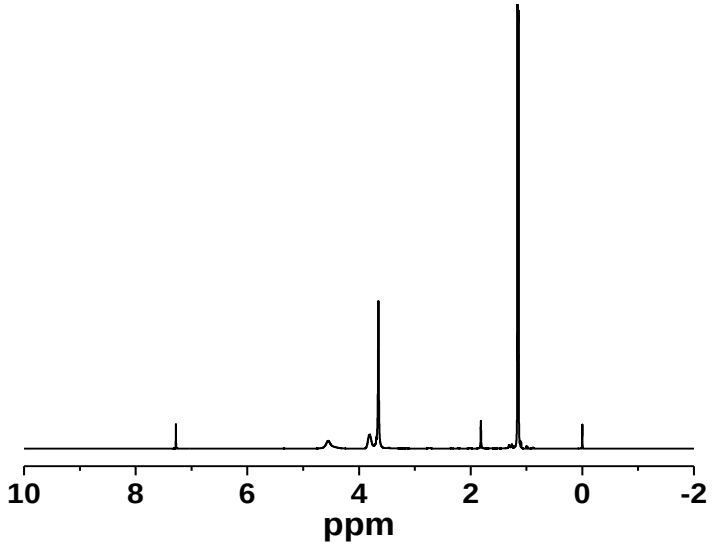


Fig.S21 ^{1}H NMR spectra of methyl *iso*propyl carbamate.

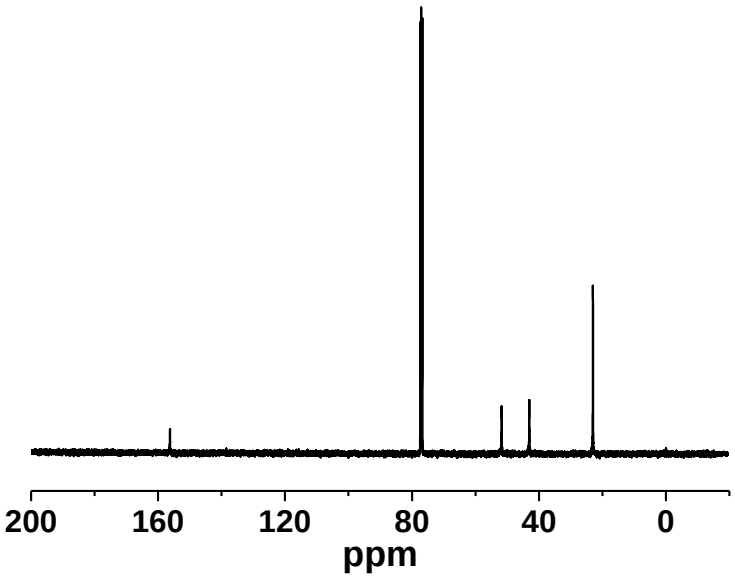
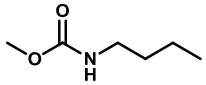


Fig. S22 ^{13}C NMR spectra of methyl *iso*propyl carbamate.

Methyl butyl carbamate[5]: colorless oil,petroleum ether/ethyl acetate = 10:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (t, *J* = 9 Hz, 3H, -*CH*$_3$-), 1.34 (m, 2H, -CH_2-*CH*$_2$-CH_3-), 1.48 (m, 2H, -*CH*$_2$-CH_2-CH_3-), 3.18 (dd, *J* = 16, 8 Hz, 2H, -*CH*$_2$-NH-), 3.66 (s, 3H, -*CH*$_3$-O-), 4.70 (s, 1H, -*NH*-).^{13}C NMR (100 MHz, $CDCl_3$): δ 157.12, 51.91, 40.74, 32.04, 19.84, 13.68.MS (ESI): calculated $[M + 2H]^+$:132.1, found:132.1. FT-IR (*v*, cm^{-1}):3336, 2959, 1708, 1538, 1464, 1269.



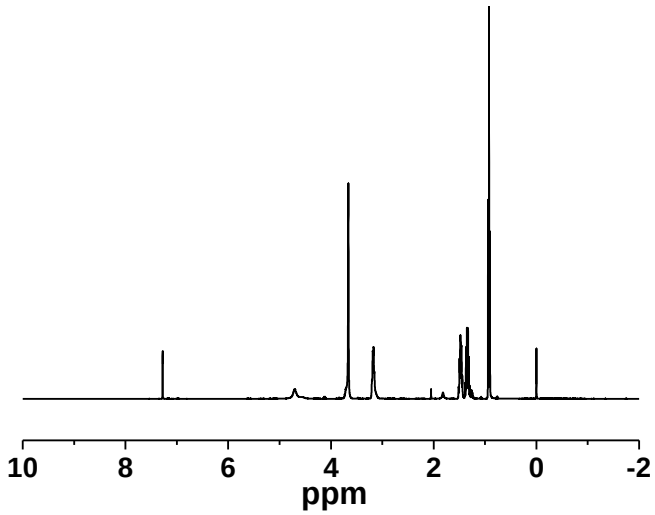


Fig. S23 ^{1}H NMR spectra of methyl butyl carbamate.

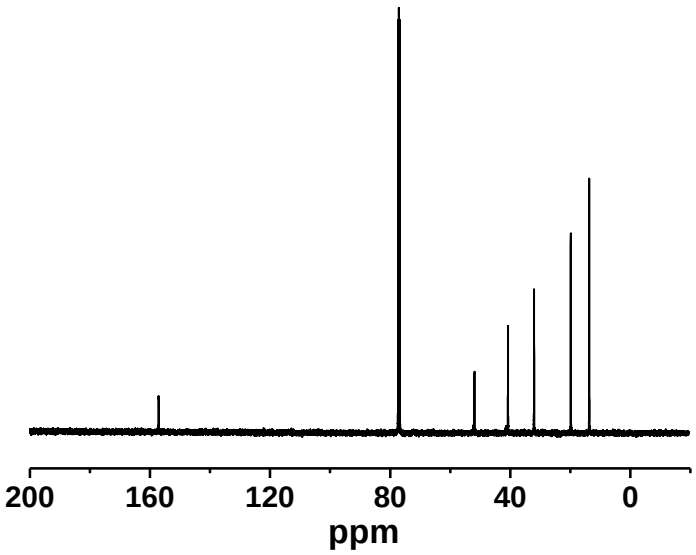


Fig. S24 ^{13}C NMR spectra of methyl butyl carbamate.

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