

Supplementary Material

The Guanidine Promoted Direct Synthesis of Open-Chain Carbonates

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Reagents and standards

All the alcohols and alkyl bromides (AR) used were purchased from Sinopharm Chemical Reagent Co., LTD (China), organic bases (AR) and n-undecane (GR, as internal standard) were purchased from Aladdin Bio-Chem Technology Co., LTD (China), chloroform-d (with 0.1% TMS) was purchased from Xuanguang Medical Technology Co., LTD (China), and carbon dioxide (99.99%) was purchased from Xiangyun Gongmao Co., LTD (China). All the reagents were used as received unless otherwise mentioned. CO₂ was made to pass through a concentrated H₂SO₄ trap and a molecular sieve trap before usage.

Instrumentation

A gas chromatograph (SP-6890, Lunan Ruihong) with a split/splitless injector system, and a flame ionization detector (FID) was used for separation and determination of reaction mixtures. Ultrapure Nitrogen (gas generator, Kelin Pufeng, CT-1) was used as the carrier gas at constant flow rate of 40 mL/min. The injection port was held at 270 °C and used in the splitless mode with splitless flow rate 50 mL/min. Separation was carried out on a DB-5, 30 m × 0.32 mm capillary column with a 0.50 μm stationary film thickness, 95% methyl-5% phenyl copolymer column (Agilent). The oven temperature was programmed as follows: initial 80 °C, from 80 °C (held 2 min) to 180 °C at the rate of 20 °C/min. The total time for one GC run was 7 min. The FID temperature was maintained at 270 °C, hydrogen gas was generated with gas generator (CT-1, Kelin Pufeng) at a flow of 20 mL/min. The flow of zero air (gas generator, Kelin Pufeng, CT-1) was 400 mL/min. The ¹H (400 MHz) and ¹³C (101 MHz) NMR spectra were obtained using a Bruker Advance 400M spectrometer (400MHz). The chemical shifts of the products were reported in ppm with reference to Me₄Si as the internal standard in CDCl₃ solution. The data were reported in the following order: chemical shift, multiplicity and integration.

Experimental Section

1. An internal standard method based on gas chromatography for quantitative detection of dibutyl ether and dibutyl carbonate

1.1 Preparation of standard samples

Considering the composition of the model reaction system mixture, the standard sample used in this study was comprised of 1-butanol (100 μL), 1-bromobutane (100 μL), dibutyl ether (DBE, 100 μL) and dibutyl carbonate (DBC, 100 μL). Here, 1-butanol, 1-bromobutane and DBE were used as purchased, DBC was isolated and purified by column chromatography on silica using chloroform as eluent, and was proved to be pure by $^1\text{H}/^{13}\text{C}$ NMR spectroscopy. N-Undecane (undc, 100 μL) was taken as the internal standard due to its polarity and boiling point. Therefore, a typical GC spectrum was given in Fig. S1.

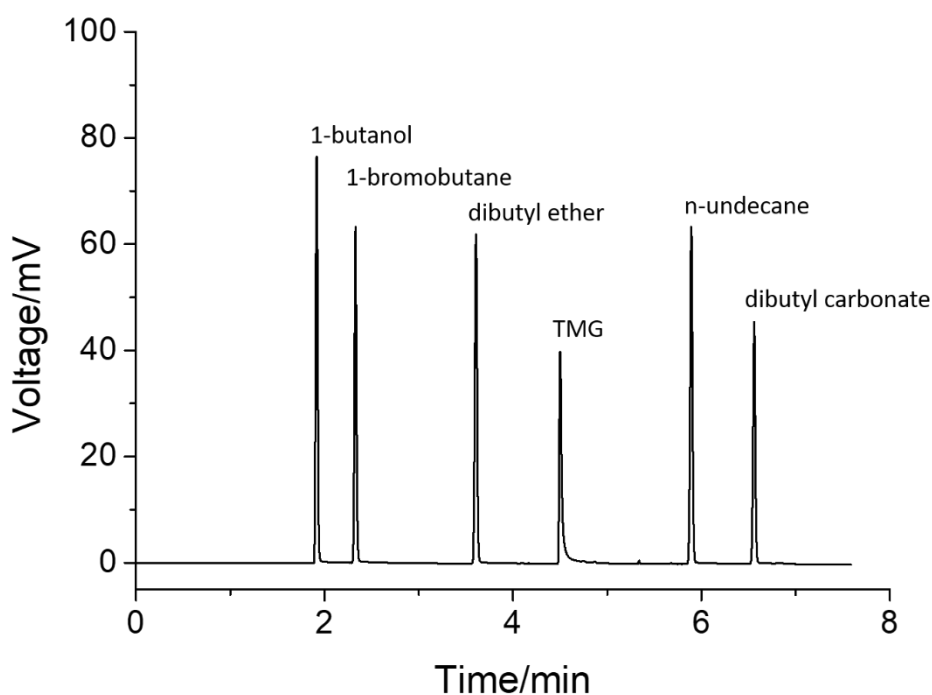


Fig. S1 The GC spectrum of standard sample.

1.2 The internal standard calibration curves

A series of samples composed with a certain amount of DBE, DBC and undc were prepared for the construction of internal standard calibration curves, and the mass ratio m_{DBE}/m_{undc} and m_{DBC}/m_{undc} were calculated. These samples were then analyzed with gas chromatography, and the peak area integral ratio of I_{DBE}/I_{undc} and I_{DBC}/I_{undc} were recorded. After that, the plots of area ratio against mass ratio were made respectively. As a result, good linear relationships were shown in both curves (Fig. S2).

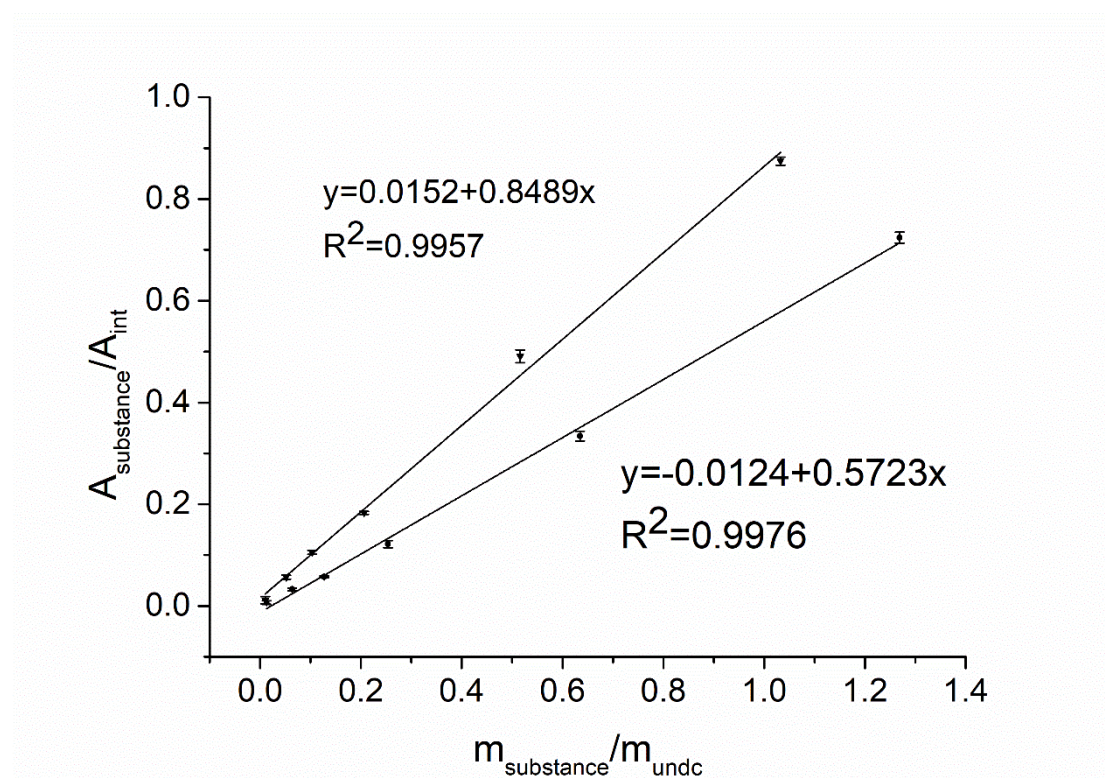


Fig. S2 The calibration curves of area ratio against mass ratio. (▼ dibutyl ether, ● dibutyl carbonate).

Thus, the mass of ether and carbonate could be calculated from the mass of n-undecane added and the peak area of DBE/DBC and n-undecane. The conversion of 1-bromobutane was calculated following equation 1, and the carbonate selectivity was calculated following equation 2. In the equation, $m_{substance}$ stand for the weight, $M_{substance}$ for the molecular weight, and $n_{substance}$ for the molar amount of the corresponding substance.

$$\text{Conversion\%}(\text{bromide}) = \frac{m_{DBE} + m_{DBC}}{M_{DBE} + M_{DBC}} \times 100\% \quad (1)$$

$$\text{Yield\%}(\text{carbonate}) = \frac{\frac{m_{\text{DBC}}}{M_{\text{DBC}}}}{\frac{m_{\text{DBE}}}{M_{\text{DBE}}} + \frac{m_{\text{DBC}}}{M_{\text{DBC}}}} \times 100\% \quad (2)$$

Then, a sample mixture (DBE 100 μL , n-undc 100 μL , DBC 100 μL , dissolved in acetonitrile 1000 μL) was analyzed using the above method for 7 times to test the repeatability, the results were listed in Table S1. As a result, the RSD% of $I_{\text{DBE}}/I_{\text{undc}}$ and $I_{\text{DBC}}/I_{\text{undc}}$ was 4.75% and 3.26% respectively. Considering that the amount of DBE was very low in the reaction system in most cases, the repeatability of this GC quantitative method was good.

Table S1 The repeatability test of the GC quantitative method.

Entry	$I_{\text{DBE}}/I_{\text{int}}$	$I_{\text{DBC}}/I_{\text{int}}$
1	0.96	0.71
2	0.88	0.72
3	0.88	0.72
4	1.00	0.66
5	0.94	0.67
6	0.96	0.69
7	0.97	0.69
average	0.94	0.70
SD	0.04	0.02
RSD%	4.75	3.26

2. General procedure for the reaction of 1-butane, 1-bromobutane, CO₂ and bases.

To a 10 mL Schlenk tube, 1-butanol (0.74 g, 10 mmol), 1-bromobutane (0.69 g, 5 mmol), base (5 mmol) and n-undecane 50 μ L were added. The mixture was mixed together with magnetic stirrer. Then, the system was purged with CO₂ (99.99%, 40 mL/min) for 15 s. After that, CO₂ was bubbled into the mixture with the flow rate of 5 mL/min. The reaction system was heated with water bath (50 °C) for 6 hours. When the reaction stopped, the resulting solution was directly used in GC determination. The carbonate conversions and selectivity given by different bases were listed in Table S2.

The products were isolated by column chromatography on silica (zcx-II, 200-300 mesh, silica: sample = 20: 1) using chloroform as eluent. The obtained dibutyl carbonate and dibutyl ether were characterized by ¹H/¹³C NMR analysis (chloroform-d), and the spectra were shown respectively.

Dibutyl ether (Fig. S5)

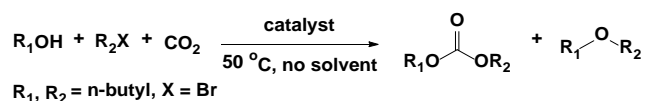
¹H NMR (400 MHz, CDCl₃) δ 3.40-3.37 (m, 2H), 1.57-1.50 (m, 2H), 1.40-1.31 (m, 2H), 0.92- 0.89 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 70.77, 32.01, 19.51, 14.06.

Dibutyl carbonate (Fig. S6)

¹H NMR (400 MHz, CDCl₃) δ 4.10-4.06 (m, 2H), 1.64-1.57 (m, 2H), 1.40-1.31 (m, 2H), 0.91-0.87 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.49, 67.71, 30.75, 18.97, 13.67.

Table S2 Activity screening of bases and co-components (additional) ^a.

Entry	Base/mmol	Co-component/mmol	Conversion/% ^b	Selectivity/%
1	Na ₂ CO ₃ /2.5	-	trace	0.0
2	NaOH/5	-	26	0
3	K ₂ CO ₃ /2.5	-	trace	0
4	KOH/5	TBAB/1	62	0
5	N-methyl morpholine/5	-	trace	0
6	N-methyl pyridine/5	-	trace	0
7	N-methyl pyrrole/5	-	trace	0
8	diethylamine/5	-	trace	0
9	triethylamine/5	-	4	41
10	Arginine/5	-	3	92
11	piperidine/5	-	trace	0
12	DBU/5	-	13 ^c	99

^a Reaction condition: 1-butanol: 1-bromobutane = 2: 1, 50 °C, 6 h, CO₂ (99.99%, bubbling, 5 mL/min).

^b Conversion and selectivity determined by GC yields.

^c Conversion and selectivity determined by isolated yield.

3. The temperature control experiment of TMG promoted linear carbonate synthesis system

To a 10 mL Schlenk tube, 1-butanol (0.74 g, 10 mmol), 1-bromobutane (0.69 g, 5 mmol), tetramethylguanidine (TMG, 5 mmol) and n-undecane 50 μ L were added. The mixture was mixed together with magnetic stirrer. Then, the system was purged with CO₂ (99.99%, 40 mL/min) for 15 s. After that, CO₂ was bubbled into the mixture with the flow rate of 5 mL/min. The system was heated with water bath to a certain temperature and held for 6 hours. When the reaction stopped, the resulting solution was directly used in GC determination.

4. The time-dependent experiment of TMG promoted linear carbonate synthesis system

To a 50 mL 2-necked flask, 1-butanol 7.41 g (100 mmol), 1-bromobutane 6.85 g (50 mmol), n-undecane 500 μ L were added and mixed with magnetic stirrer. Then, the flask was heated to 50 °C in constant temperature water bath, and the reaction system was purged with CO₂ (99.99%, 40 mL/min) for 30 s. After that, TMG 5.76 g (50 mmol) was put in to the flask. The reaction was carried out with CO₂ bubbling (5 mL/min) and reflux condensation. The sample of reaction system were taken over time (100 μ L/time), and dissolved in acetone 400 μ L for gas chromatography analysis. The results of quantitative GC analysis were listed in Table S3.

Table S3 The DBC yield and selectivity of the time-dependent experiment.

Entry	time/ h	Yield/ %	Selectivity/ %
1	0	0	0
2	0.5	0	60
3	1	1	83
4	1.5	3	91
5	2	6	95
6	2.5	8	96
7	3	11	96
8	3.5	15	97
9	4	19	97
10	4.5	22	97
11	5	26	97
12	5.5	30	98
13	6	35	98
14	6.5	38	98
15	7	42	98
16	7.5	44	98
17	8	49	98
18	9	53	99
19	10	60	99
20	11	67	99
21	12	73	99
22	13	82	99
23	14	86	99
24	15	90	99
25	16	95	99
26	17	97	99
27	18	98	99
28	19	99	99
29	20	99	99
30	22	99	99
31	24	99	99

5. The general procedure of the reaction of 1-butanol and various organobromides

To a 10 mL glass Schlenk tube, 1-butanol (0.74 g, 10 mmol), organobromide (5 mmol), tetramethylguanidine (0.58g, 5 mmol) and n-undecane 50 μ L were added. The mixture was mixed together with magnetic stirrer, and the system was purged with CO₂ (99.99%, 5 mL/min) for 15 s. After that, CO₂ was bubbled into the mixture with the flow rate of 5 mL/min. The reaction system was heated with water bath (50 °C) for 24 hours. When the reaction was stopped, the crude mixture was loaded into a chromatography column (silica, zcx-II, 200-300 mesh, silica: sample = 20: 1) to isolate the products. The bromide conversion was determined by GC, and the carbonate yield was calculated by isolated mass. The characterization of corresponding carbonate was carried out using ¹H/¹³C NMR, with chloroform-d as solvent.

5.1 The reaction of 1-butanol and bromoethane

To the reaction system, bromoethane (0.54 g, 5 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product ethyl butyl carbonate (0.66 g) was obtained as a colorless oily liquid, and the corresponding NMR spectra was shown in Fig. S7.

¹H NMR (400 MHz, CDCl₃) δ 4.20-4.10 (m, 4H), 1.66-1.60 (m, 2H), 1.42-1.36 (m, 2H), 1.31-1.28 (m, 3H), 0.94-0.90 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.42, 67.82, 63.92, 30.79, 19.04, 14.40, 13.78.

5.2 The reaction of 1-butanol and 1-bromopropane

To the reaction system, 1-bromopropane (0.61 g, 5 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product propyl butyl carbonate (0.76g) was obtained as a colorless oily liquid, and the corresponding NMR spectra was shown in Fig. S8.

¹H NMR (400 MHz, CDCl₃) δ 4.14-4.06 (m, 4H), 1.71-1.62 (m, 4H), 1.42-1.36 (m, 2H), 0.97-0.91 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 155.57, 69.55, 67.85, 30.80, 22.14, 19.04, 13.79, 10.32.

5.3 The reaction of 1-butanol and 1-bromohexane

To the reaction system, 1-bromohexane (0.83 g, 5 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with

mixed solvent (petroleum ether: ethyl acetate = 3: 2). The product butyl hexyl carbonate (0.70 g) was obtained as a pale yellow oily liquid, and the corresponding NMR spectra was shown in Fig. S9. ^1H NMR (400 MHz, CDCl_3) δ 4.13-4.08 (m, 4H), 1.67-1.60 (m, 4H), 1.41-1.26 (m, 8H), 0.94-0.85 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.56, 68.13, 67.82, 31.52, 30.79, 28.74, 25.49, 22.63, 19.03, 14.10, 13.77.

5.4 The reaction of 1-butanol and 1-bromododecane

To the reaction system, 1-bromododecane (1.25 g, 5 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with mixed solvent (petroleum ether: ethyl acetate = 3: 2). The product butyl dodecyl carbonate (0.65 g) was obtained as a colorless solid, and the corresponding NMR spectra was shown in Fig. S10.

^1H NMR (400 MHz, CDCl_3) δ 4.14-4.09 (m, 4H), 1.68-1.61 (m, 4H), 1.42-1.25 (m, 20H), 0.95-0.91 (m, 3H), 0.89-0.85 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.55, 68.13, 67.81, 31.51, 30.78, 28.74, 25.48, 22.62, 19.03, 14.09, 13.76.

5.5 The reaction of 1-butanol and benzyl bromide

To the reaction system, benzyl bromide (0.86 g, 5 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product butyl benzyl carbonate (0.46 g) was obtained as a colorless oily liquid, and the corresponding NMR spectra was shown in Fig. S11.

^1H NMR (400 MHz, CDCl_3) δ 7.40-7.33 (m, 5H), 5.17-5.15 (m, 2H), 4.17-4.14 (m, 2H), 1.67-1.62 (m, 2H), 1.42-1.37 (m, 2H), 0.95-0.91 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.40, 135.43, 128.71, 128.62, 128.47, 69.59, 68.18, 30.76, 19.03, 13.79.

5.6 The reaction of 1-butanol and bromobenzene

To the reaction system, benzyl bromide (0.79 g, 5 mmol) was added as the reactant. When the reaction was stopped, no products were detected.

6. The general procedure of the reaction of various alcohols and 1-bromobutane

To a 10 mL Schlenk tube, 1-bromobutane (0.69 g, 5 mmol), alcohol (10 mmol), TMG (0.58 g, 5 mmol) and n-undecane 50 μ L were added. The mixture was mixed together with magnetic stirrer. Then, the system was purged with CO₂ (99.99%, 5 mL/min) for 15 s. After that, CO₂ was bubbled into the mixture with the flow rate of 5 mL/min. The reaction system was heated with water bath (50 °C) for 24 hours. When the reaction was stopped, the crude mixture was loaded into a chromatography column (silica, zcx-II, 200-300 mesh, silica: sample = 20: 1) to isolate the products. The bromide conversion was determined by GC, and the carbonate yield was calculated by isolated mass. The characterization of corresponding carbonate was carried out using ¹H/¹³C NMR, with chloroform-d as solvent.

6.1 The reaction of 1-bromobutane and ethanol

To the reaction system, ethanol (0.46 g, 10 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product ethyl butyl carbonate (0.51 g) was obtained as a colorless oily liquid, and the corresponding NMR spectra was shown in Fig. S7.

6.2 The reaction of 1-bromobutane and 1-propanol

To the reaction system, 1-propanol (0.60 g, 10 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product propyl butyl carbonate (0.65 g) was obtained as a colorless oily liquid, and the corresponding NMR spectra was shown in Fig. S8.

6.3 The reaction of 1-bromobutane and 1-hexanol

To the reaction system, 1-hexanol (1.02 g, 10 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with mixed solvent (petroleum ether: ethyl acetate = 3: 2). The product butyl hexyl carbonate (0.96 g) was obtained as a pale yellow oily liquid, and the corresponding NMR spectra was shown in Fig. S9.

6.4 The reaction of 1-bromobutane and 1-dodecanol

To the reaction system, 1-dodecanol (1.86 g, 10 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with mixed solvent (petroleum ether: ethyl acetate = 3: 2). The product butyl dodecyl carbonate (0.53 g) was obtained as a colorless solid, and the corresponding NMR spectra was shown in Fig. S10.

6.5 The reaction of 1-bromobutane and phenol

To the reaction system, phenol (0.94 g, 10 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product butyl phenyl carbonate (0.88 g) was obtained as a colorless oily liquid, and the corresponding NMR spectra was shown in Fig. S12.

^1H NMR (400 MHz, CDCl_3) δ 7.2-7.24 (m, 2H), 6.93-6.87 (m, 3H), 3.96-3.93 (m, 2H), 1.79-1.72 (m, 2H), 1.51-1.45 (m, 2H), 0.98-0.94 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.24, 129.54, 120.56, 114.58, 67.66, 31.48, 19.40, 14.02.

6.6 The reaction of 1-bromobutane and benzyl alcohol

To the reaction system, benzyl alcohol (1.08 g, 10 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product butyl benzyl carbonate (0.72 g) was obtained as a colorless oily liquid, and the corresponding NMR spectra was shown in Fig. S11.

6.7 The reaction of tert-butyl bromide and benzyl alcohol

To the reaction system, benzyl alcohol (1.08 g, 10 mmol) and tert-butyl bromide (0.69 g, 5 mmol) was added as the reactant. After GC determination, the reaction mixture was loaded into a chromatography column and eluted with chloroform. The product tert-butyl benzyl carbonate (0.55 g) was obtained as a colorless oily liquid, and the corresponding NMR spectra (chloroform-d) was shown in Fig. S13.

^1H NMR (400 MHz, CDCl_3) δ 7.39-7.32 (m, 5H), 5.10 (s, 2H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.58, 135.72, 128.66, 128.46, 128.43, 82.42, 68.84, 27.90.

7. $^1\text{H}/^{13}\text{C}$ NMR spectra of relative substances

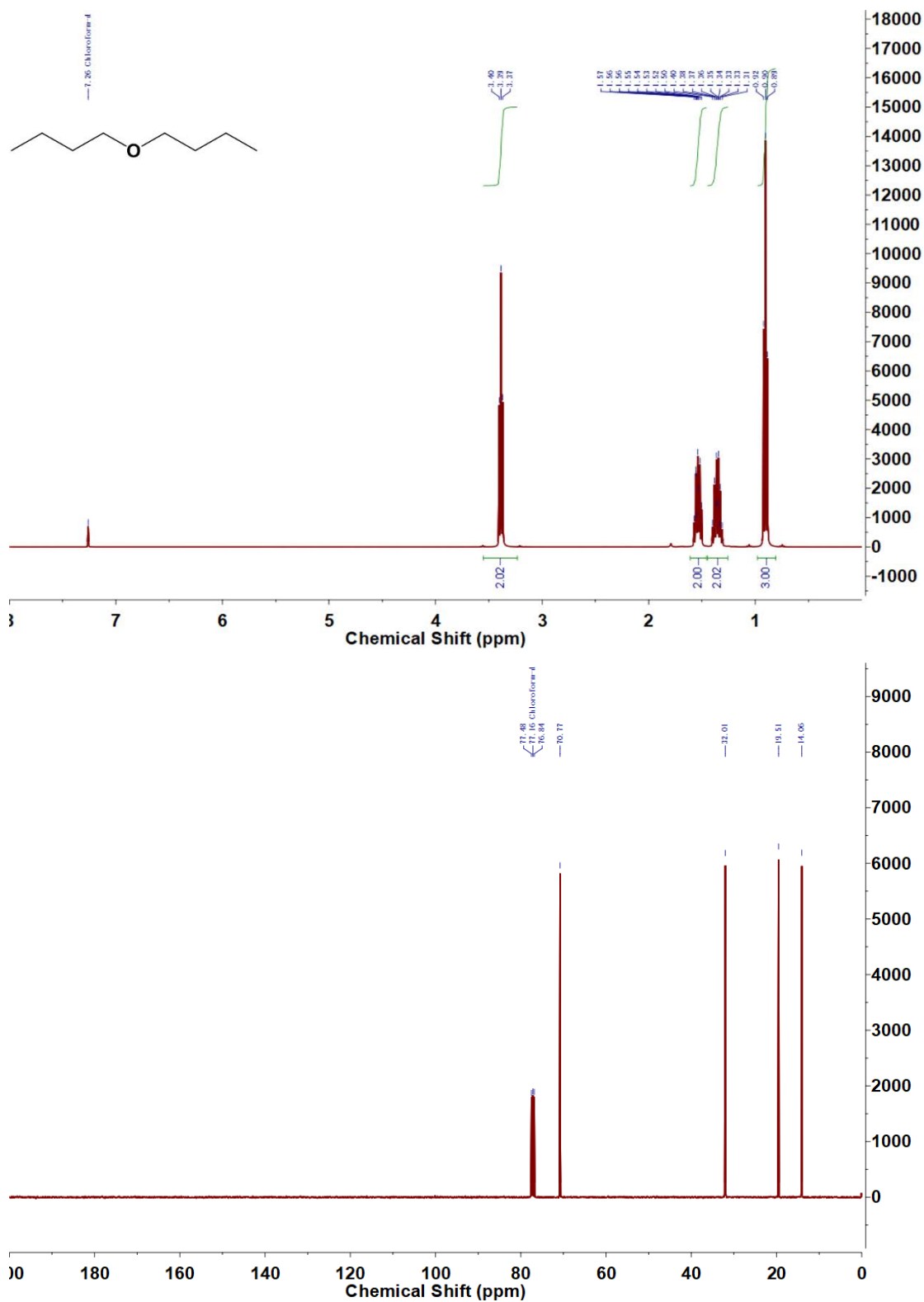


Fig. S5 The $^1\text{H}/^{13}\text{C}$ NMR spectra of dibutyl ether.

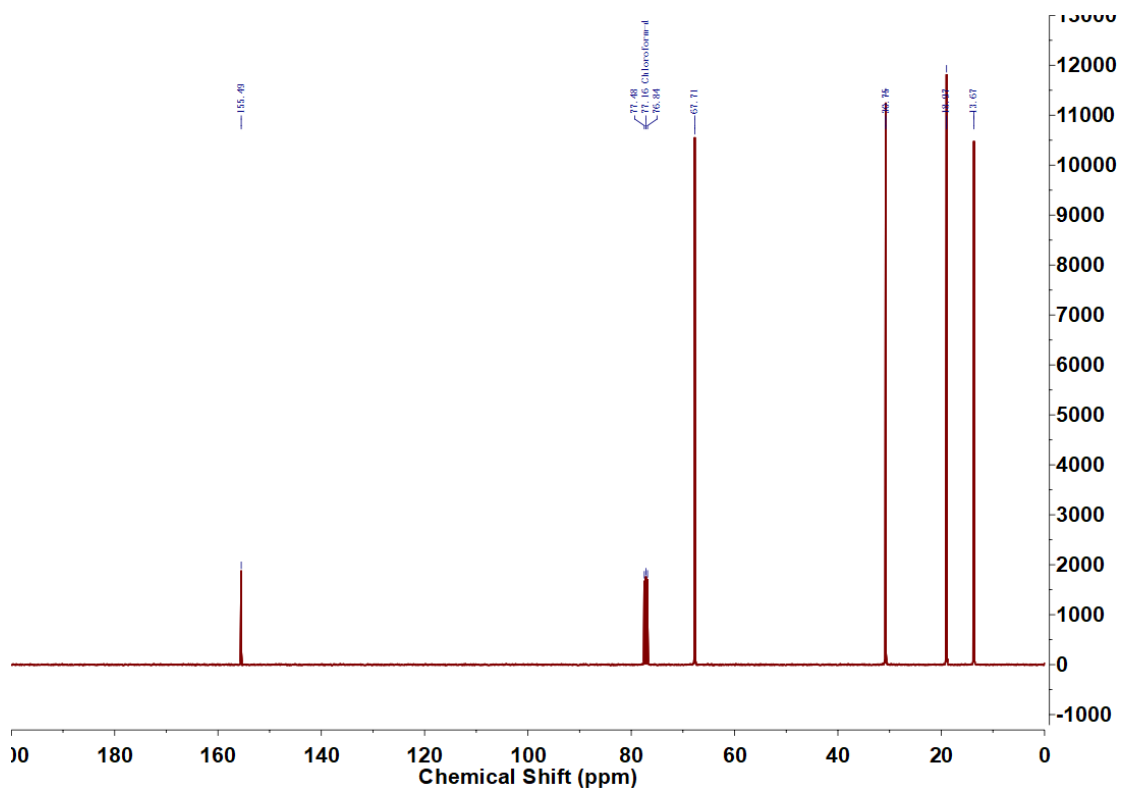
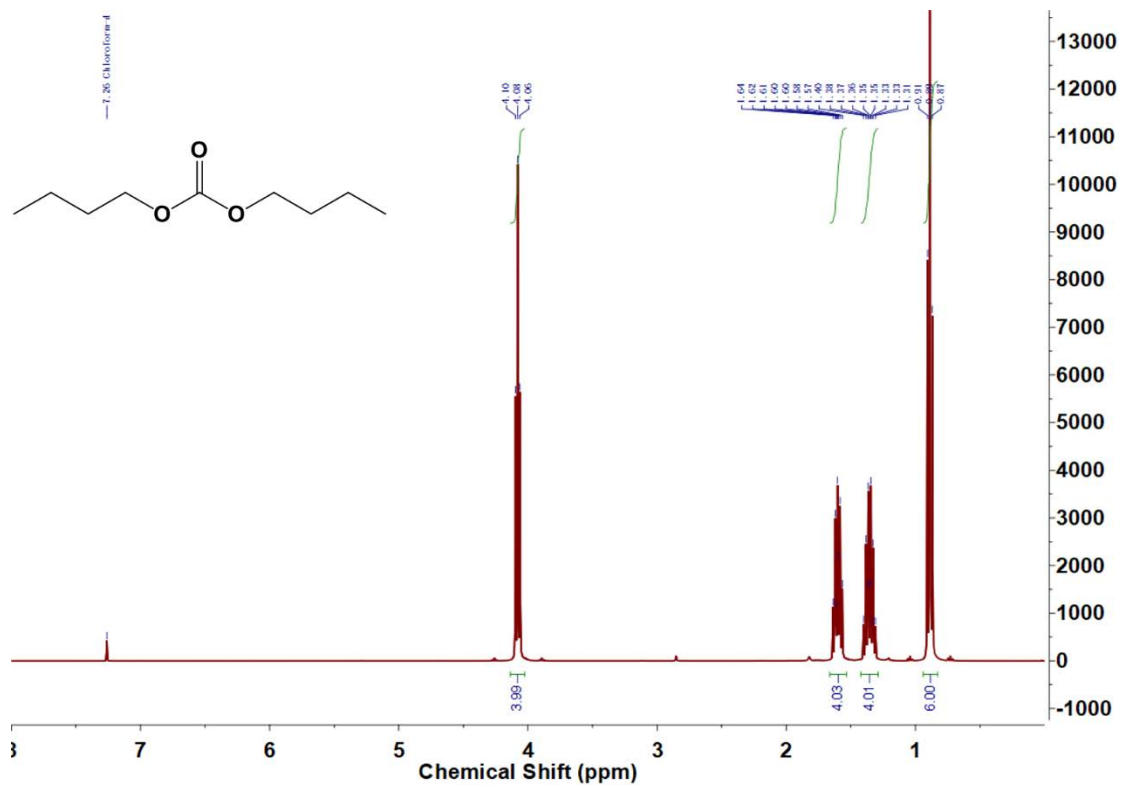


Fig. S6 The ¹H/¹³C NMR spectra of dibutyl carbonate.

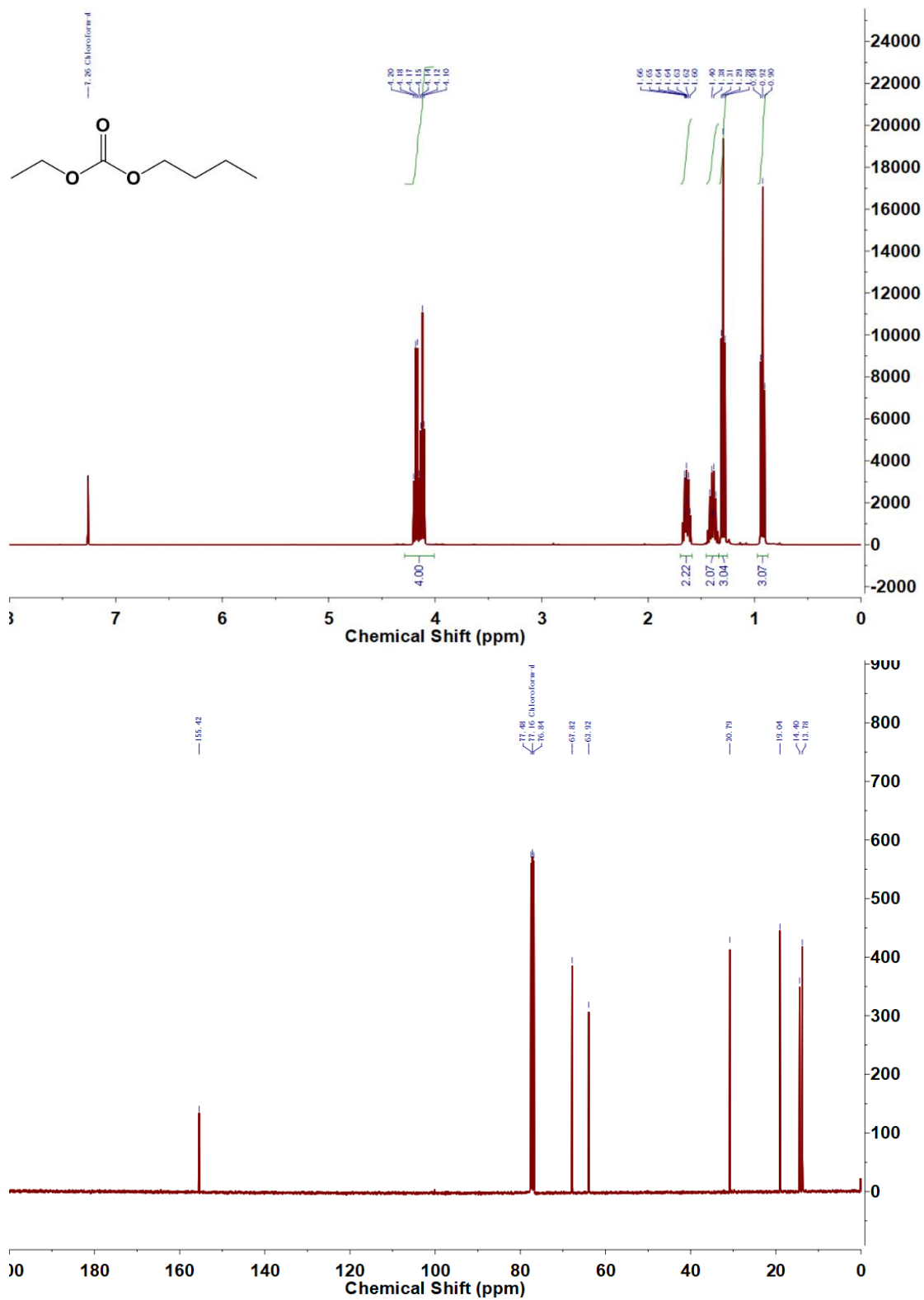


Fig. S7 The ¹H/¹³C NMR spectra of ethyl butyl carbonate.

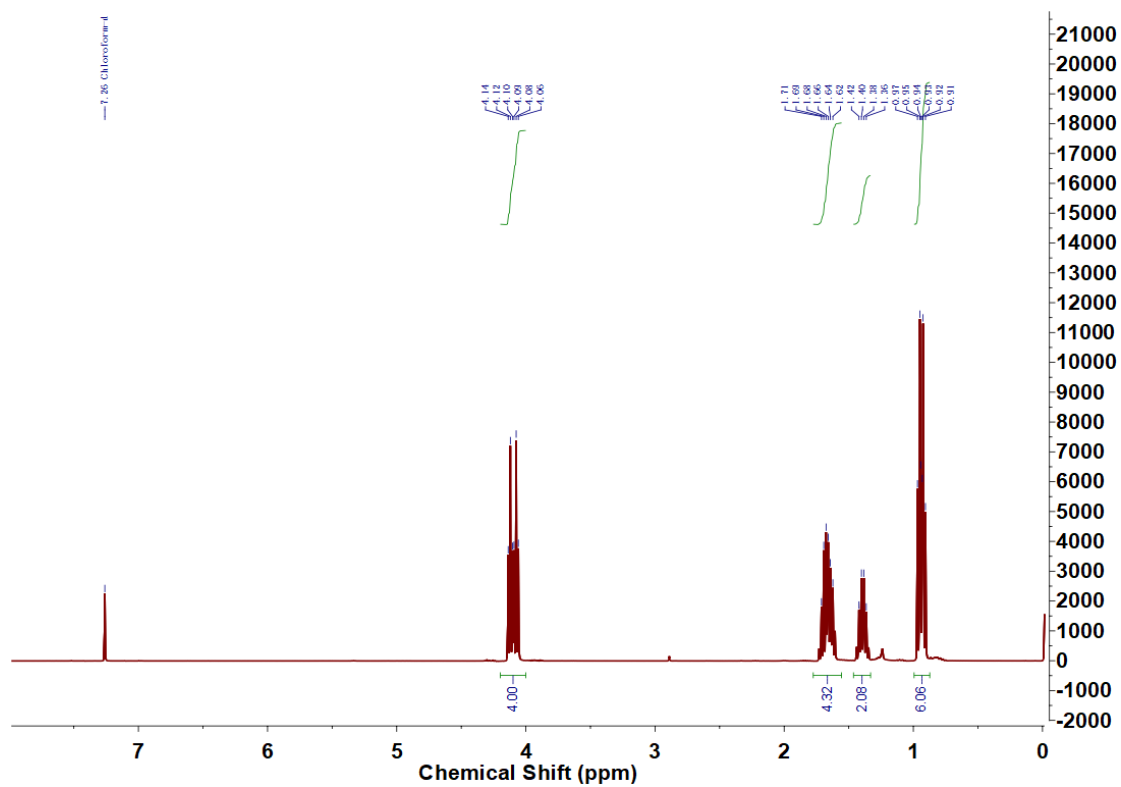
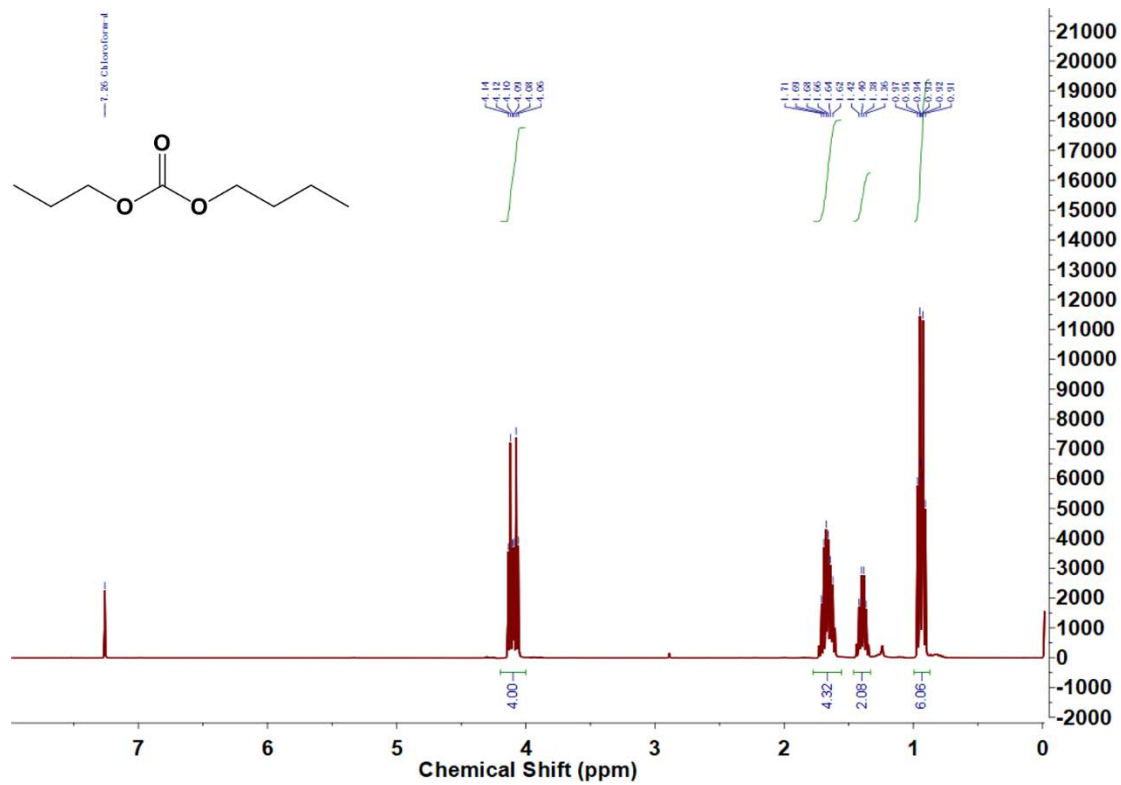


Fig. S8 The $^1\text{H}/^{13}\text{C}$ NMR spectra of propyl butyl carbonate.

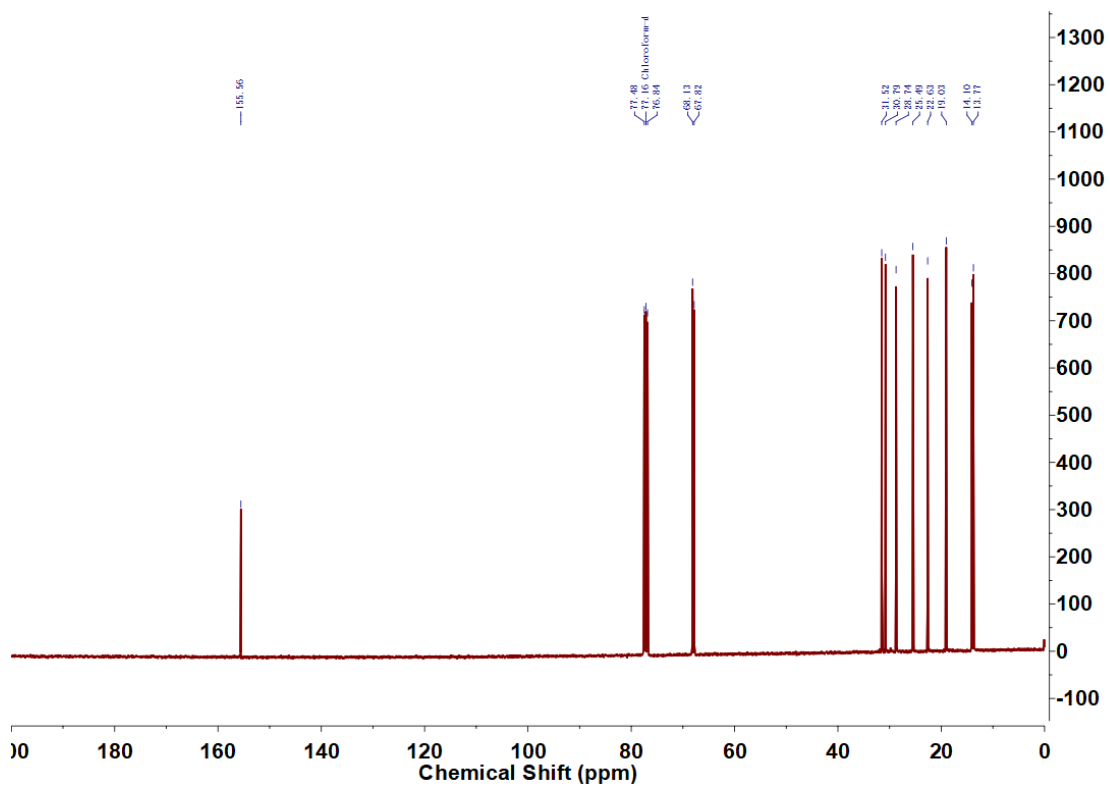
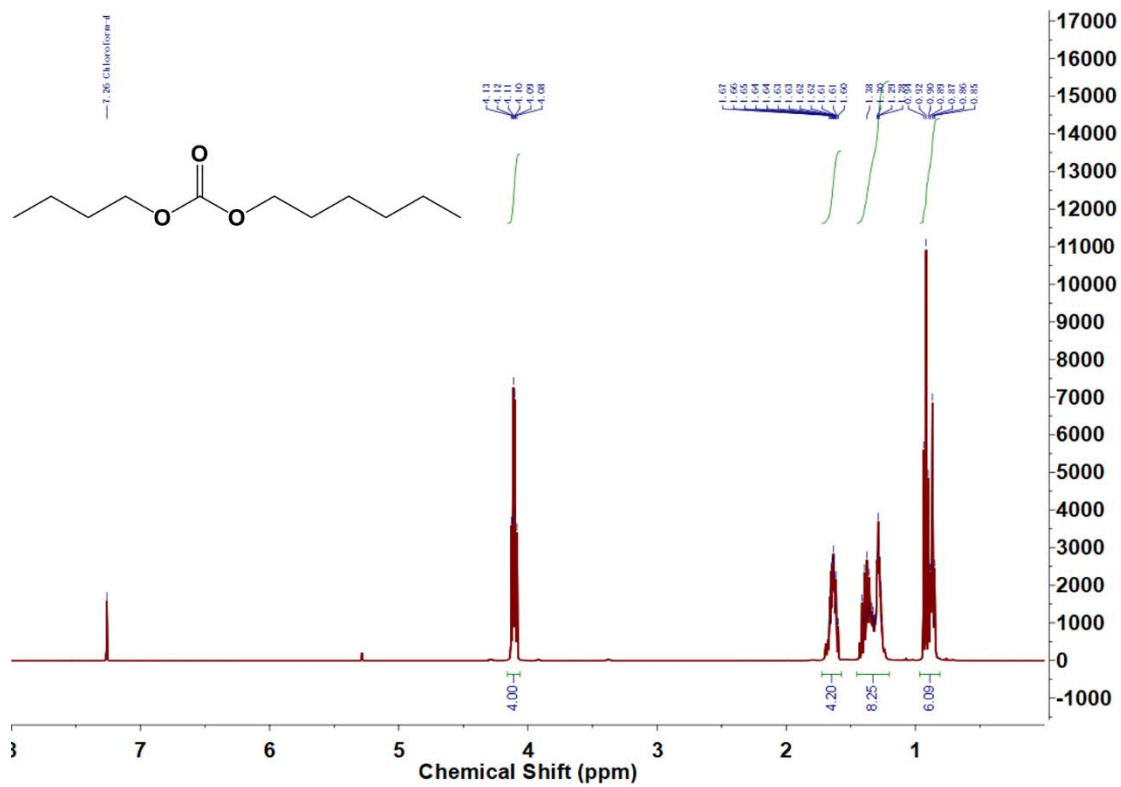


Fig. S9 The $^1\text{H}/^{13}\text{C}$ NMR spectra of butyl hexyl carbonate.

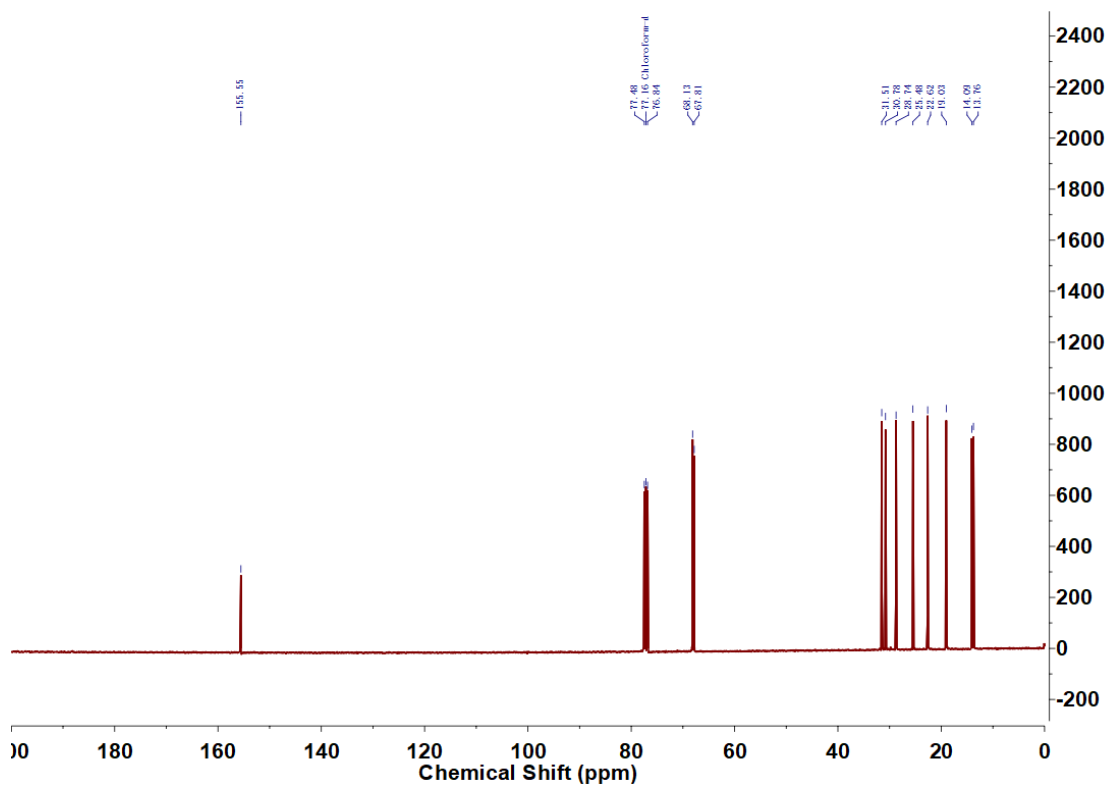
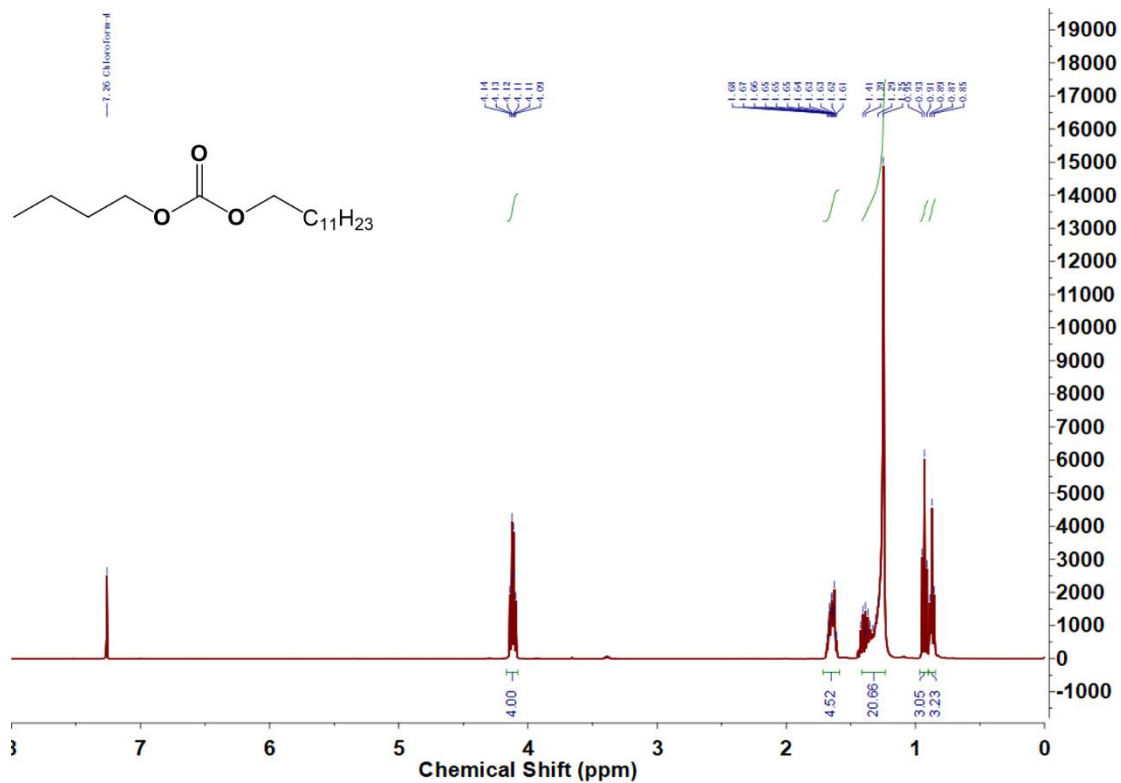


Fig. S10 The $^1\text{H}/^{13}\text{C}$ NMR spectra of butyl dodecyl carbonate.

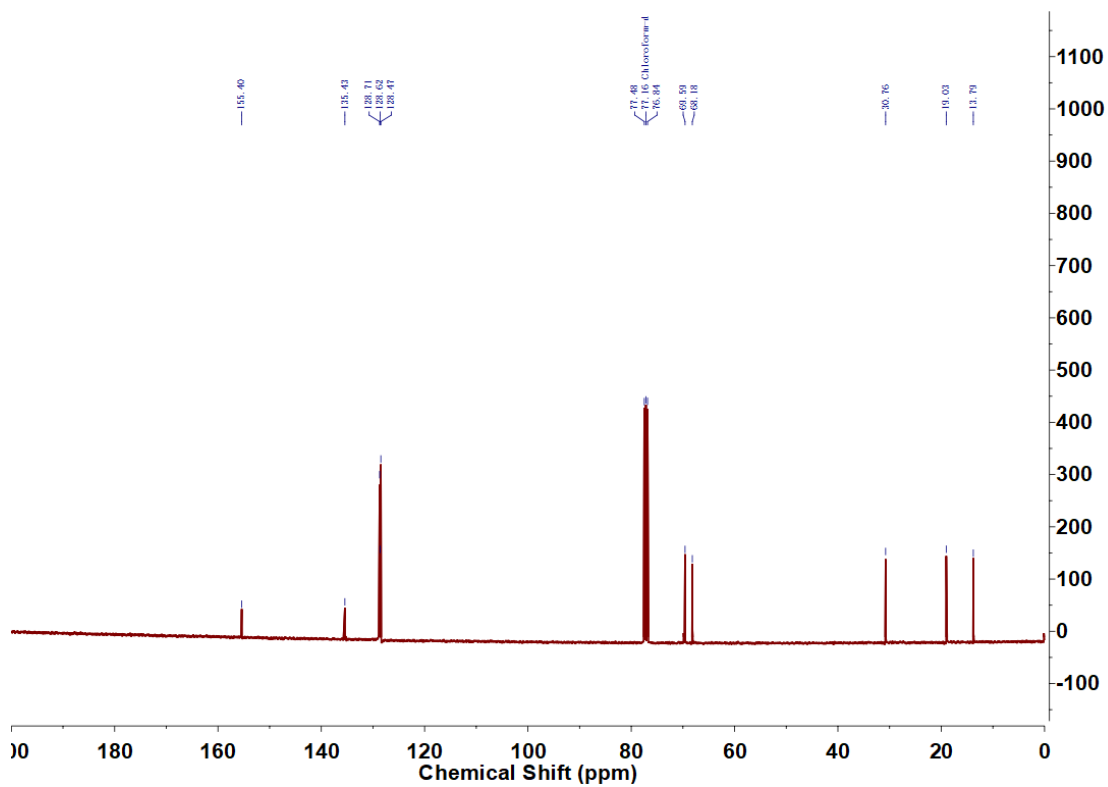
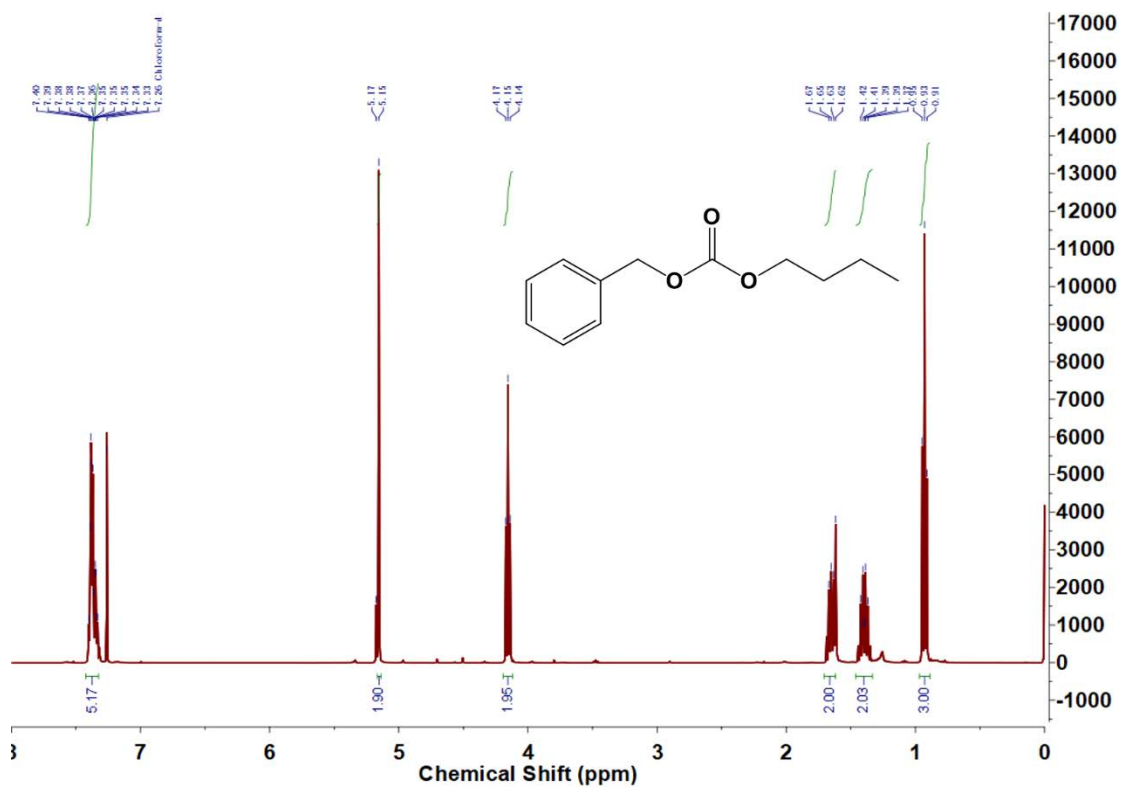


Fig. S11 The ¹H/¹³C NMR spectra of butyl benzyl carbonate.

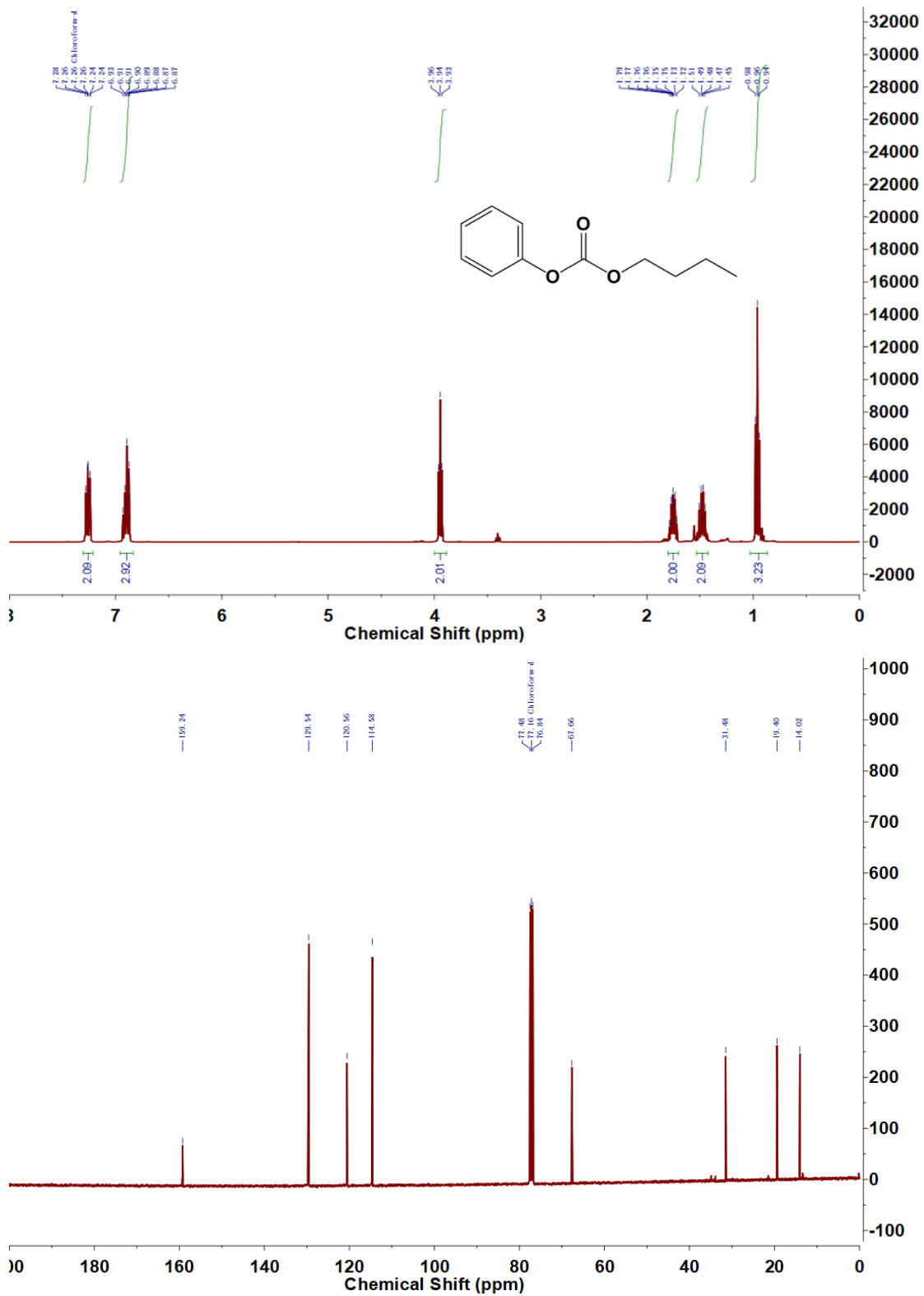


Fig. S12 The $^1\text{H}/^{13}\text{C}$ NMR spectra of butyl phenyl carbonate.

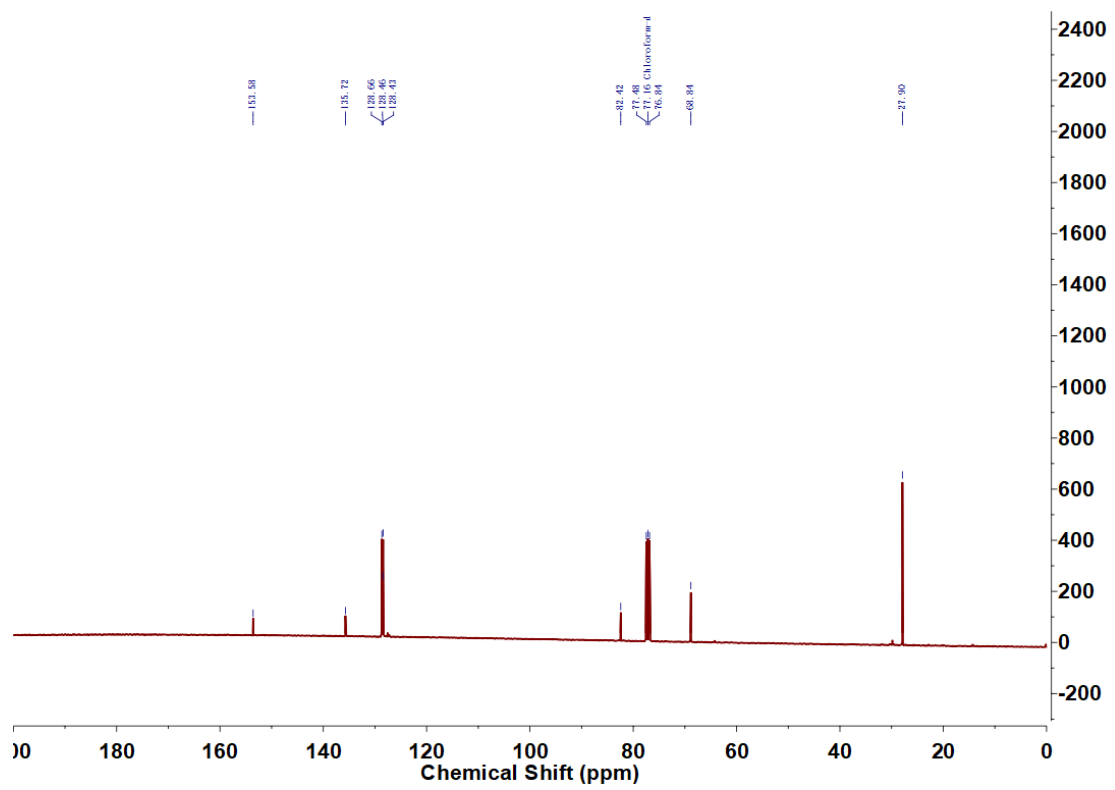
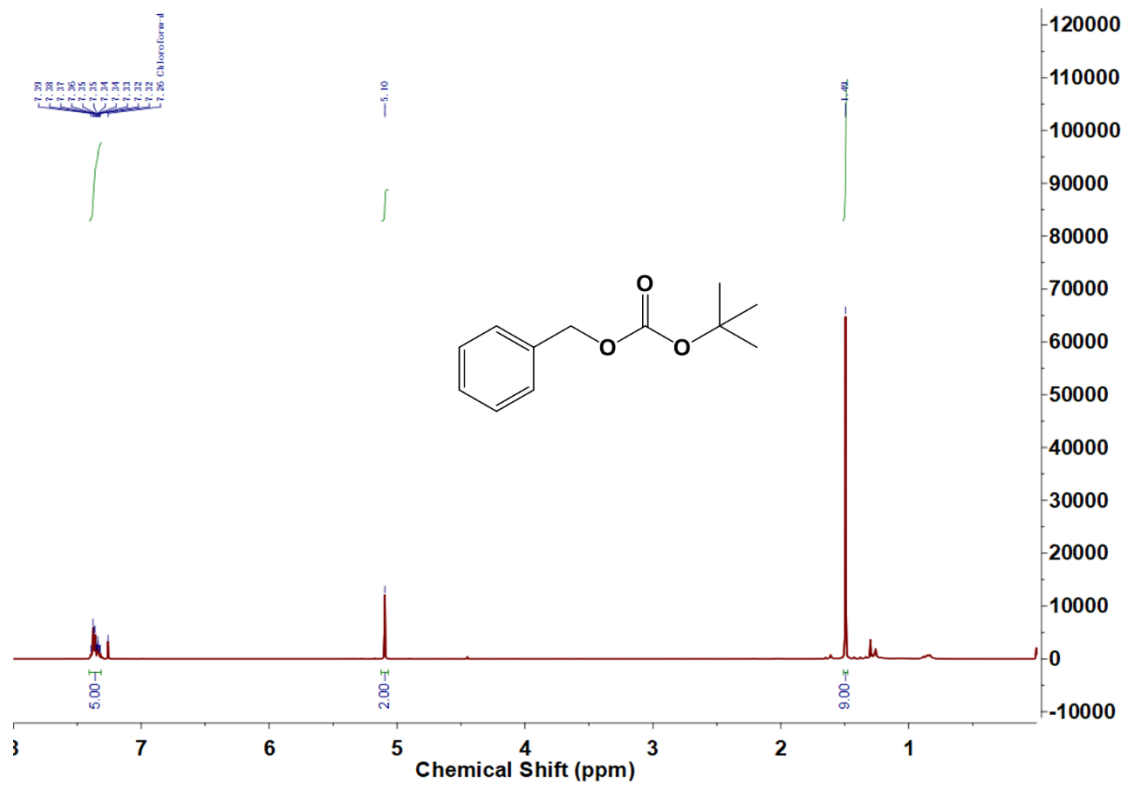


Fig. S13 The ¹H/¹³C NMR spectra of tert-butyl benzyl carbonate.