

## Supplementary Material

### Carbon Dioxide Utilisation for the Synthesis of Unsymmetrical Dialkyl and Cyclic Carbonates

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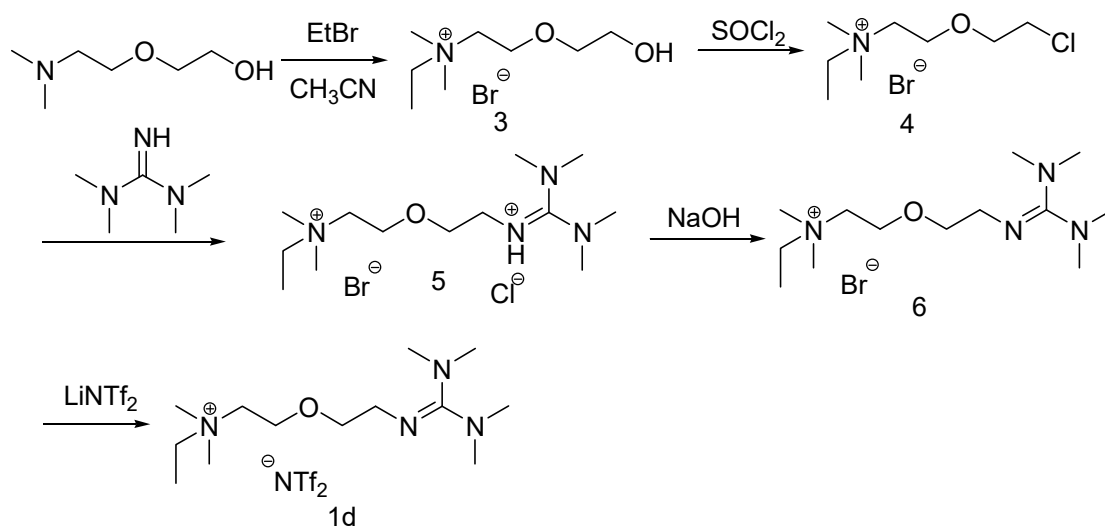
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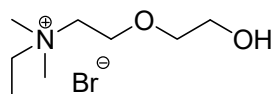
### A. Procedure for the synthesis of **1d**

(5-Diisopropylamino-3-oxapentyl)dimethylethylammonium bis{(trifluoromethyl)sulfonyl}imide [<sup>i</sup>Pr<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>N<sub>112</sub>][NTf<sub>2</sub>] (**1b**), (8-diisopropylamino-3,6-dioxaoctyl) dimethyl ethyl ammonium bis{(trifluoromethyl)sulfonyl} imide [<sup>i</sup>Pr<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N<sub>112</sub>][NTf<sub>2</sub>] (**1c**) were prepared in three steps starting with 2-dimethylaminoethanol and 2-[2-dimethylaminoethoxy] ethanol according to the previously published report.<sup>1</sup>



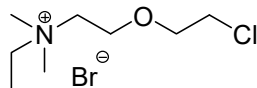
Scheme 1. Synthesis of ionic liquid **1d**

### (5-Hydroxy-3-oxapentyl)dimethylethylammonium bromide (**3**).



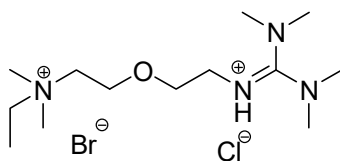
2-[2-dimethylamino ethoxy] ethanol (5.34 g, 40.0 mmol) and bromoethane (10.9 g, 100 mmol) were heated under reflux in CH<sub>3</sub>CN (20.0 mL) for 30 h. After evaporation of the solvent and excess bromoethane in *vacuo* at 60°C, a pale yellow powder was obtained (8.71 g, 90% yield). <sup>1</sup>H-NMR (CD<sub>3</sub>OD): δ = 3.99-3.88 (m, 2H), 3.74-3.66 (m, 2H), 3.64-3.57 (m, 4H), 3.53 (q, *J* = 7.3, 2H), 1.44-1.34 (m, 3H); <sup>13</sup>C-NMR (CD<sub>3</sub>OD): δ = 73.8, 65.7, 64.2, 62.3, 62.0, 51.7, 8.66. HRMS-ESI (*m/z*) calcd for C<sub>8</sub>H<sub>20</sub>NO<sub>2</sub> [M-Br]<sup>+</sup> 162.1494, 163.1526, found 162.1228, 163.1431, calcd for [Br]<sup>-</sup> 78.9183, 80.9163, found 78.9174, 80.9157.

**(5-Chloro-3-oxapentyl)dimethylethylammonium bromide (4).**



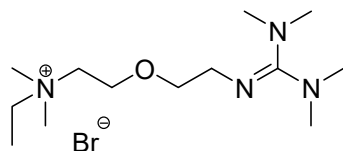
SOCl<sub>2</sub> (8.55g, 70.0 mmol) was added dropwise at 0°C to a round-bottom flask containing **3** (8.35 g, 34.4 mmol). The system was stirred for 30 min at 0°C and then kept stirring for 6 h at 80°C. After cooling to room temperature, the excess SOCl<sub>2</sub> was removed under reduced pressure. The product was dried in *vacuo* at 60 °C for 24 h, a brown red liquid was obtained (8.78 g, 98% yield). <sup>1</sup>H-NMR (CD<sub>3</sub>OD): δ = 3.99-3.88 (m, 2H), 3.74-3.66 (m, 2H), 3.64-3.57 (m, 4H), 3.53 (q, *J* = 7.3, 2H), 1.44-1.34 (m, 3H); <sup>13</sup>C-NMR (CD<sub>3</sub>OD): δ = 73.8, 65.7, 64.2, 62.3, 62.0, 51.7, 8.66. HRMS-ESI (*m/z*) calcd for C<sub>8</sub>H<sub>19</sub>ClNO [M-Br]<sup>+</sup> 80.1155, 181.1187, 182.1127, found 180.1081, 181.1138, 182.1070, calcd for [Br]<sup>-</sup> 78.9183, 80.9163, found 78.9174, 80.9157.

**{5-(1,1,3,3-tetramethylguanidyl)-3-oxapentyl} dimethylethylammonium bromide hydrochloride (5).**



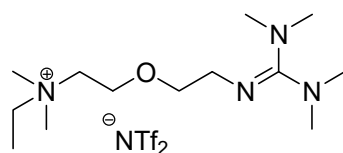
In a constant pressure dropping funnel, **4** (5.20 g, 20.0 mmol) and CH<sub>3</sub>OH (6.00 mL) were introduced. This solution was added dropwise at 0 °C to a round-bottom flask equipped with a dry nitrogen inlet containing a solution of TMG (2.30 g, 20.0 mmol) in CH<sub>3</sub>OH (6.00 mL). The system was stirred overnight at room temperature. The solvent was evaporated and the residue was further dried under vacuum (40 °C, 24 h) to yield a yellow solid (7.35 g, 98%). <sup>1</sup>H-NMR (CD<sub>3</sub>OD): δ = 3.89-3.82 (m, 2H), 3.73-3.59 (m, 4H), 3.50 (dd, *J* = 5.7, 3.6, 2H), 3.42 (q, *J* = 7.3, 2H), 3.05 (s, 6H), 2.72 (s, 12H), 1.35-1.24 (m, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 161.7, 71.1, 64.9, 62.6, 61.4, 51.3, 50.4, 43.1, 40.3, 8.58. HRMS-ESI (*m/z*) calcd for C<sub>13</sub>H<sub>32</sub>N<sub>4</sub>O [M-Br-Cl]<sup>+</sup> 260.2576, found 260.2639, calcd for [Br]<sup>-</sup> 78.9183, 80.9163, found 78.9165, 80.9143.

**{5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl} dimethylethylammonium bromide (6).**



Compound 5 (3.75g, 10.0 mmol), NaOH (0.480g, 12.0 mmol) and CH<sub>2</sub>Cl<sub>2</sub> 10.0 mL were introduced into a 25 mL round-bottom flask. The system was stirred for 24 h at room temperature. NaOH was isolated by filtration and the filtrate was evaporated on rotary evaporator. The residue was further dried under vacuum (60°C, 24 h) to yield a pale yellow liquid (3.05g, 90%).<sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 4.10-4.01 (m, 2H), 3.93 (dd,  $J$  = 5.7, 3.5 2H), 3.87-3.74 (m, 4H), 3.69 (dd,  $J$  = 5.7, 4.4, 2H), 3.41 (s, 6H), 2.75 (s, 12H), 1.44 (t,  $J$  = 7.2, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>):  $\delta$  = 167.5, 74.1, 64.8, 62.7, 61.4, 51.4, 43.2, 39.3, 8.67. HRMS-ESI ( $m/z$ ) calcd for C<sub>13</sub>H<sub>31</sub>N<sub>4</sub>O [M-Br]<sup>+</sup> 259.2498, found 259.2561, calcd for [Br]<sup>-</sup> 78.9183, 80.9163, found 78.9171, 80.9152.

**{5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl} dimethylethylammonium bis{(trifluoromethyl)sulfonyl}amide (1d).**



Lithium bis{(trifluoromethyl)sulfonyl} amide (1.58g, 5.50 mmol) in deionised water was added to a solution of **6** (1.70g, 5.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20.0 mL). The system was kept stirring for 24 h at room temperature. The CH<sub>2</sub>Cl<sub>2</sub> layer was then washed with deionised water several times to remove the salt from the organic phase. After removal of the solvent and drying overnight in high vacuum at 60°C, **1d** was obtained as a pale yellow liquid (2.43g, 90%).<sup>1</sup>H-NMR (CD<sub>3</sub>OD):  $\delta$  = 4.00-3.89 (m, 2H), 3.78 (dt,  $J$  = 5.5, 1.6, 2H), 3.75-3.68 (m 2H), 3.58 (dd,  $J$  = 5.6, 3.8, 2H), 3.50 (q,  $J$  = 7.3, 2H), 3.14 (s, 6H), 2.98 (s, 12H), 1.38 (ddd,  $J$  = 7.3, 5.3, 2.0, 3H); <sup>13</sup>C-NMR (CD<sub>3</sub>OD):  $\delta$  = 163.3, 126.0, 122.8, 119.7, 116.5, 72.4,

65.5, 64.0, 62.4, 51.7, 44.0, 39.9, 8.54. HRMS-ESI ( $m/z$ ) calcd for  $C_{13}H_{31}N_4O$   $[2M+NTf_2]^+$  798.4169, found 798.1321, calcd for  $C_2F_6NO_4S_2$   $[NTf_2]^-$  279.9173, 281.9131, found 279.8868, 281.9073.

## B. Recycling of IL

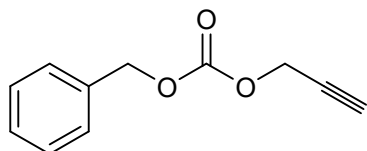
For IL recycling, ionic liquid was isolated from the reaction mixture, first, by adding diethyl ether (After the reaction, IL cannot be dissolved in  $Et_2O$ .) to remove products. Then sufficient  $Na_2CO_3$  was added into the aq. solution to liberate IL. The IL was recycled in the next run without further purification.

**Table 1** Recycle of **1c**.<sup>A</sup>

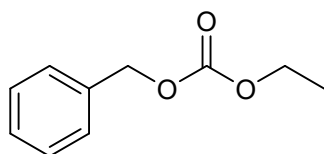
Entry	Runs	Amount of ROH, R'X, <b>1c</b>	Time / h	Yield / % <sup>B</sup>
1	Fresh	1.0, 0.5, 0.6	48	76
2	1 <sup>st</sup>	1.0, 0.5, 0.6	48	75
3	2 <sup>nd</sup>	1.0, 0.5, 0.6	48	75

<sup>A</sup> Reaction conditions:  $CO_2$  (1.0 MPa; carried out in a 16 mL stainless-steel autoclave). <sup>B</sup> Yields were determined by  $^1H$ -NMR respect to the amount of benzyl bromide used in the reaction.

## C. Characterization data of product (2a-2h)

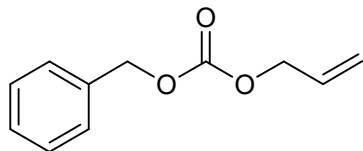


Benzyl propargyl carbonate (**2a**). Colourless liquid; Yield: 76%;  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  = 7.41-7.32 (m, 5H, ArH), 5.20 (s, 2H,  $PhCH_2O$ -), 4.74 (d,  $J$  = 2.5, 2H,  $-OCH_2-CCH$ ), 2.52 (t,  $J$  = 2.5, 1H,  $-CCH$ );  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  = 154.54 (C=O), 134.88 (Ar), 128.67 (Ar), 128.63 (Ar), 128.38 (Ar), 75.72 (CCH), 70.12 ( $PhCH_2O$ -), 55.36 ( $-OCH_2CCH$ ); HRMS-ESI ( $m/z$ ) calcd for  $C_{11}H_{10}O_3$   $[M+NH_4]^+$  208.0974, found 208.0972.

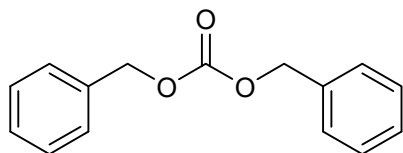


Benzyl ethyl carbonate (**2b**). Colourless liquid; Yield: 84%;  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  = 7.45-7.28 (m, 5H, ArH), 5.16 (s, 2H,  $PhCH_2O$ -), 4.21 (q,  $J$  = 7.1, 2H,  $CH_3CH_2$ -), 1.31 (t,  $J$  = 7.1, 3H,  $CH_3CH_2$ -);

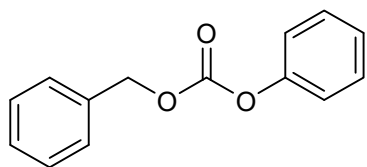
$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 155.14$  (C=O), 135.35 (Ar), 128.59 (Ar), 128.49 (Ar), 128.31 (Ar), 69.44 ( $\text{PhCH}_2\text{O}$ -), 64.14 ( $-\text{OCH}_2\text{CH}_3$ ), 14.26 ( $-\text{OCH}_2\text{CH}_3$ ); HRMS-ESI ( $m/z$ ) calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_3$  [ $\text{M}+\text{NH}_4$ ] $^+$  198.1130, found 198.1133.



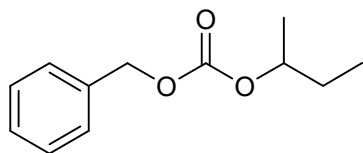
Allyl benzyl carbonate (**2c**). Colourless liquid; Yield: 81%;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 7.44$ -7.29 (m, 5H, ArH), 5.93 (ddt,  $J = 17.2, 10.4, 5.8$ , 1H,  $-\text{CH}=\text{CH}_2$ ), 5.42-5.22 (m, 2H,  $-\text{CH}=\text{CH}_2$ ), 5.17 (s, 2H,  $\text{PhCH}_2\text{O}$ -), 4.64 (dt,  $J = 5.8, 1.4$ , 2H,  $-\text{CH}_2\text{CH}=\text{CH}_2$ );  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 154.97$  (C=O), 135.35 (Ar), 131.53 ( $-\text{CH}=\text{CH}_2$ ), 128.60 (Ar), 128.54 (Ar), 128.33 (Ar), 118.95 ( $-\text{CH}=\text{CH}_2$ ), 69.66 ( $\text{PhCH}_2\text{O}$ -), 68.58 ( $-\text{OCH}_2\text{CH}=\text{CH}_2$ ); HRMS-ESI ( $m/z$ ) calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_3$  [ $\text{M}+\text{NH}_4$ ] $^+$  210.1130, found 210.1131.



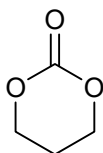
Dibenzyl carbonate (**2d**). Colourless liquid; Yield: 85%;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 7.45$ -7.28 (m, 10H, ArH), 5.17 (s, 4H,  $\text{PhCH}_2\text{O}$ -);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 155.10$  (C=O), 135.18 (Ar), 128.59 (Ar), 128.55 (Ar), 128.33 (Ar), 69.74 ( $\text{PhCH}_2\text{O}$ -); HRMS-ESI ( $m/z$ ) calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_3$  [ $\text{M}+\text{NH}_4$ ] $^+$  260.1287, found 260.1279.



Benzyl phenyl carbonate (**2e**). White solid; Yield: 83%;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 7.47$ -7.26 (m, 7H, ArH), 7.02-6.93 (m, 3H, ArH), 5.07 (s, 2H,  $\text{PhCH}_2\text{O}$ -);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta = 158.80$  (C=O), 137.09 (Ar), 129.48 (Ar), 128.58 (Ar), 127.94 (Ar), 127.48 (Ar), 114.86 (Ar), 69.93 ( $\text{PhCH}_2\text{O}$ -); HRMS-ESI ( $m/z$ ) calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_3$  [ $\text{M}+\text{H}$ ] $^+$  229.0865, found 229.0861.

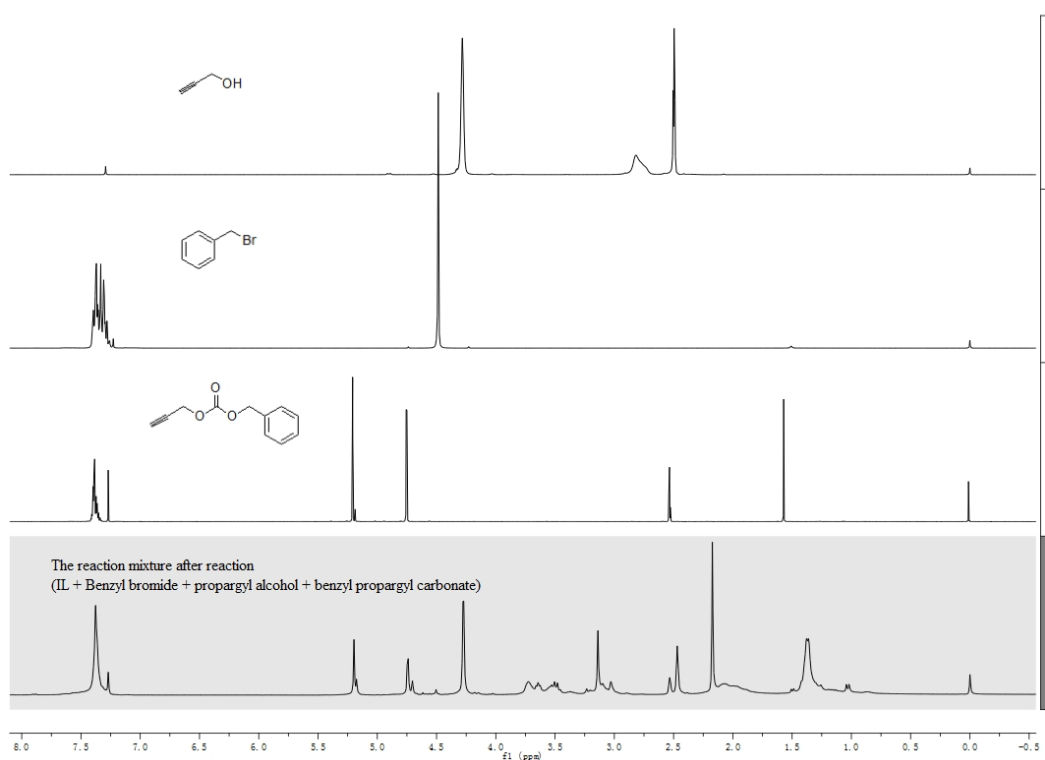


Benzyl *s*-butyl carbonate (**2f**). Colourless liquid; Yield: 67%;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.47\text{-}7.28$  (m, 5H, ArH), 5.15 (s, 2H, PhCH<sub>2</sub>O-), 4.72 (dd,  $J = 12.6, 6.3$ , 1H, -OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.73-1.52 (m, 2H, -OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.27 (d,  $J = 6.3$ , 3H, -OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 0.92 (t,  $J = 7.5$ , 3H, -OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 154.89$  (C=O), 135.48 (Ar), 128.56 (Ar), 128.42 (Ar), 128.26 (Ar), 76.80 (-OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 69.28 (PhCH<sub>2</sub>O-), 28.76 (-OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 19.36 (-OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 9.57 (-OCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>); HRMS-ESI ( $m/z$ ) calcd for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> [M+NH<sub>4</sub>]<sup>+</sup> 226.1433, found 226.1435.



1, 3-Dioxan-2-one (**2h**). White solid; Yield: 92%;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 4.46$  (t, 4H, -OCH<sub>2</sub>), 2.15 (dq,  $J = 11.5, 5.7$ , 2H, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 148.43$  (C=O), 67.90 (CH<sub>2</sub>O-), 21.77 (-OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O-).

**D. Copies of  $^1\text{H}$  NMR spectra of benzyl bromide, propargyl alcohol, benzyl propargyl carbonate and reaction mixture.**





## E. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of new products

Fig. S1: NMR spectra of (5-Hydroxy-3-oxapentyl)dimethylethylammonium bromide (**3**).

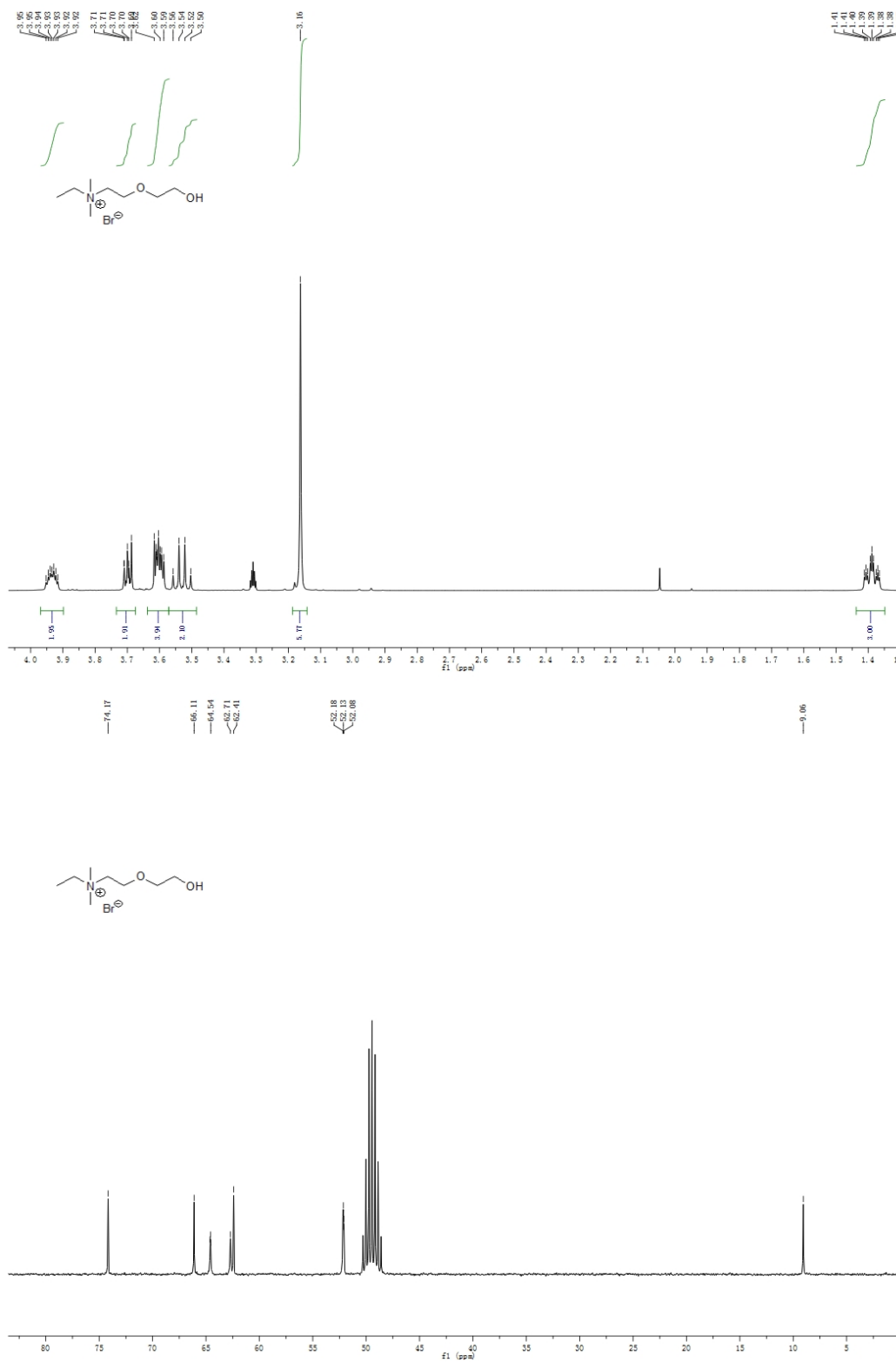


Fig. S2: NMR spectra of (5-Chloro-3-oxapentyl)dimethylethylammonium bromide (4).

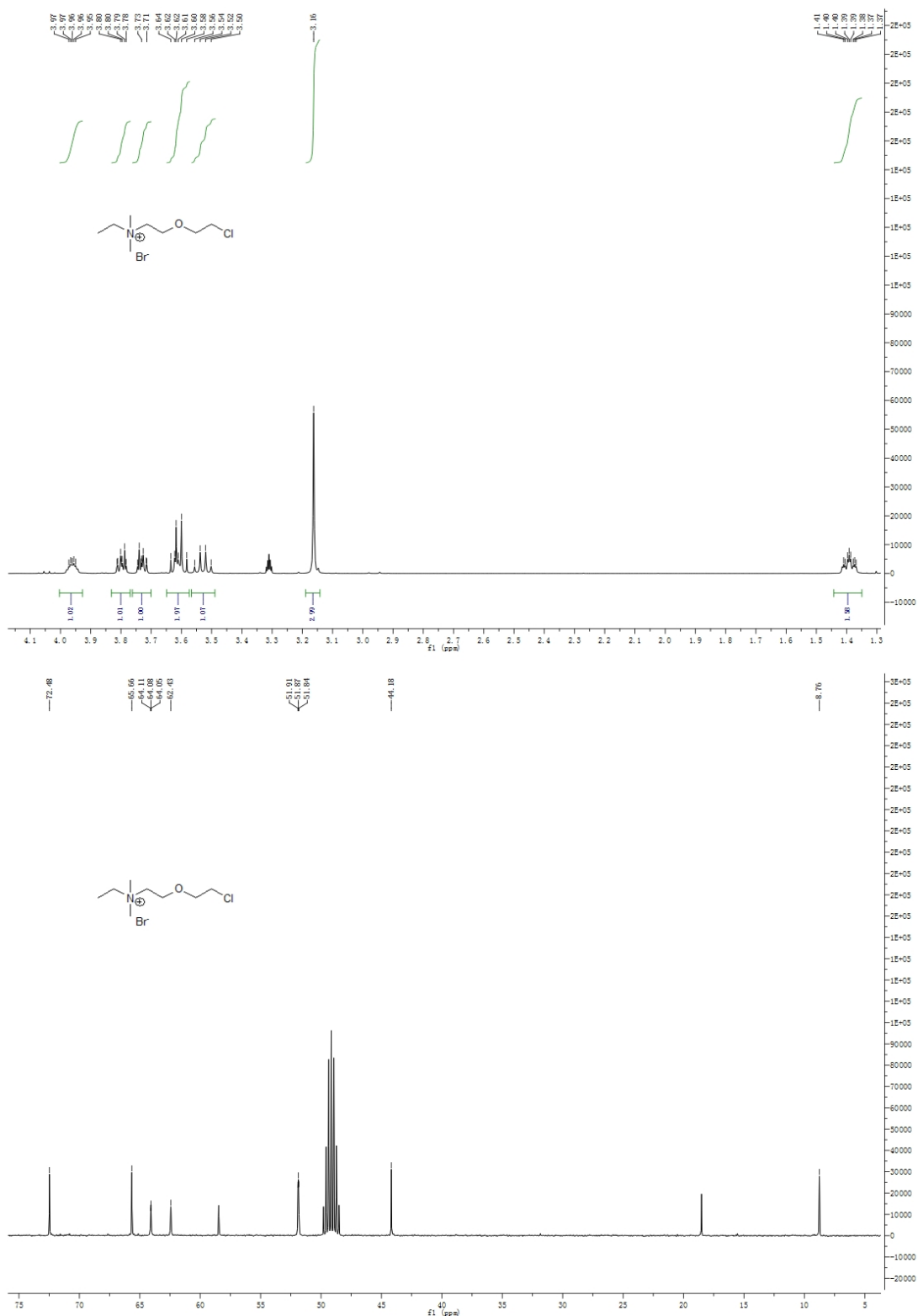


Fig. S3: NMR spectra of {5-(1,1,3,3-tetramethyl guanidyl)-3-oxapentyl} dimethylethylammonium bromide hydrochloride (5).

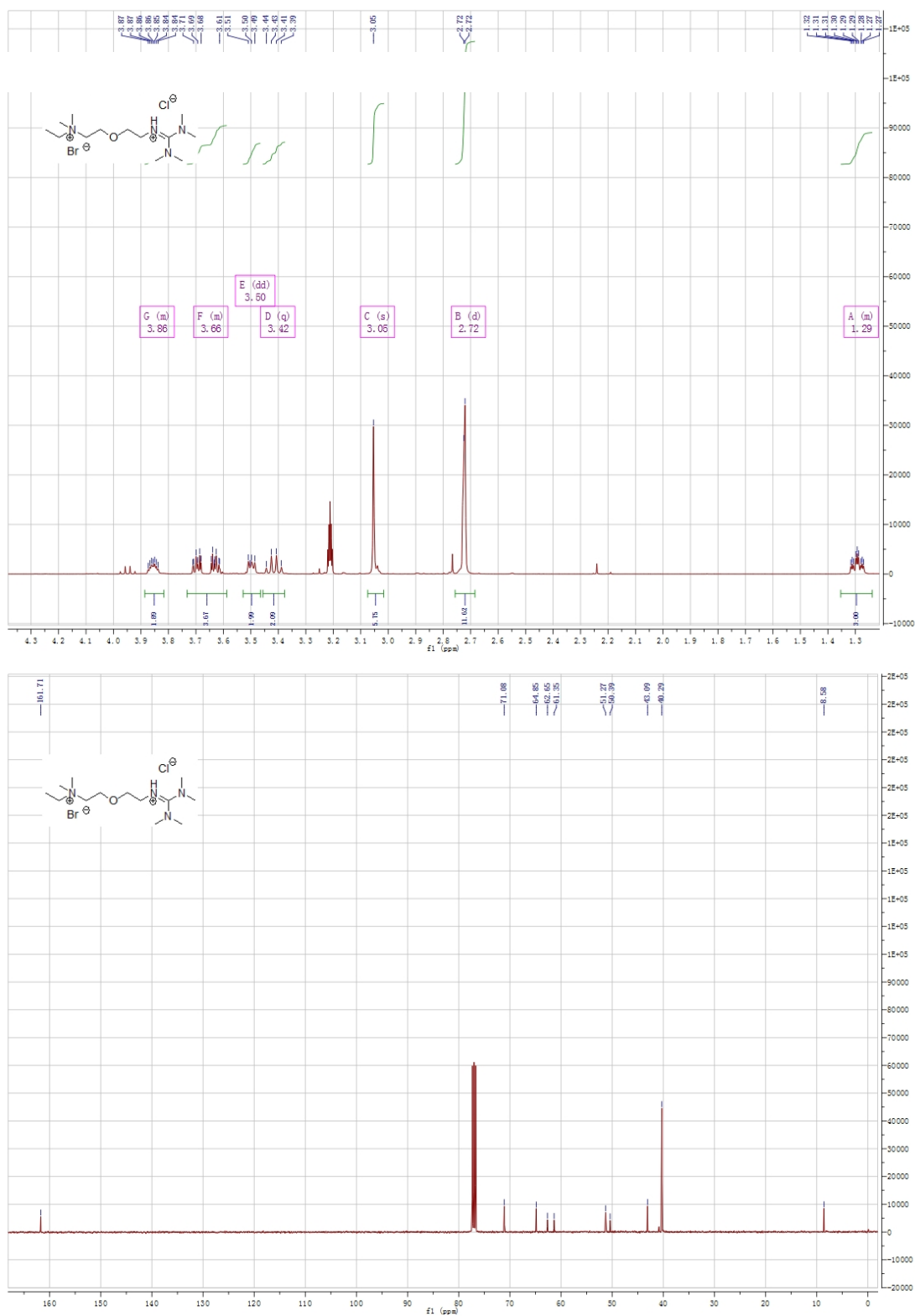


Fig. S4: NMR spectra of {5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl} dimethylethylammonium bromide (6).

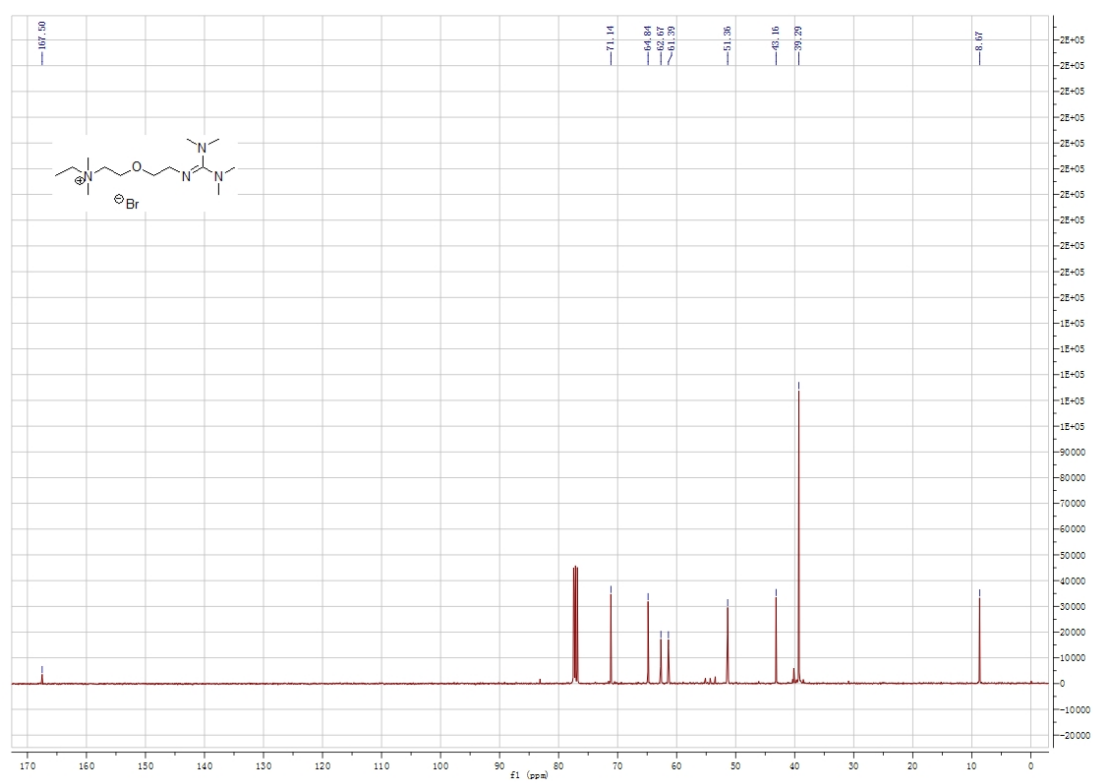
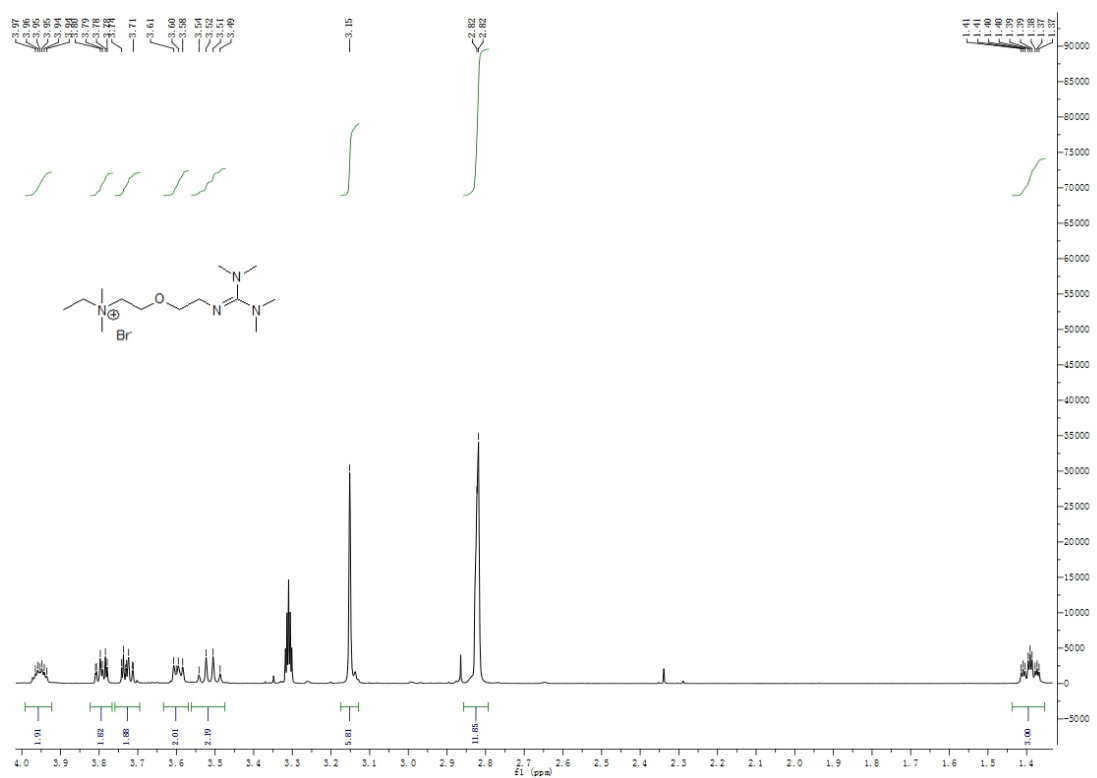


Fig. S5: NMR spectra of {5-(1,1,3,3-tetramethyl guanidyl) -3-oxapentyl} dimethylethylammonium bis{(trifluoromethyl)sulfonyl} amide (**1d**).

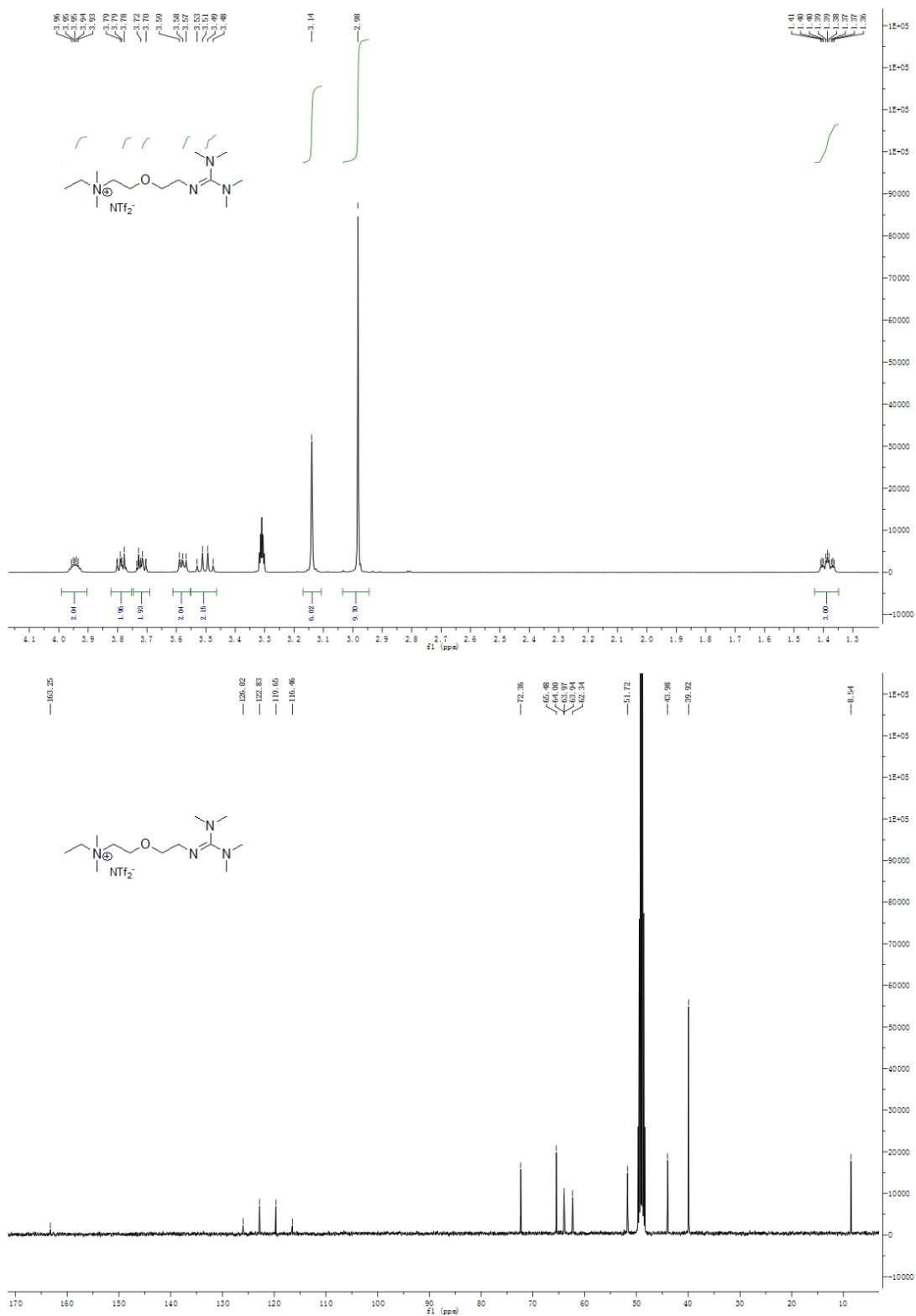
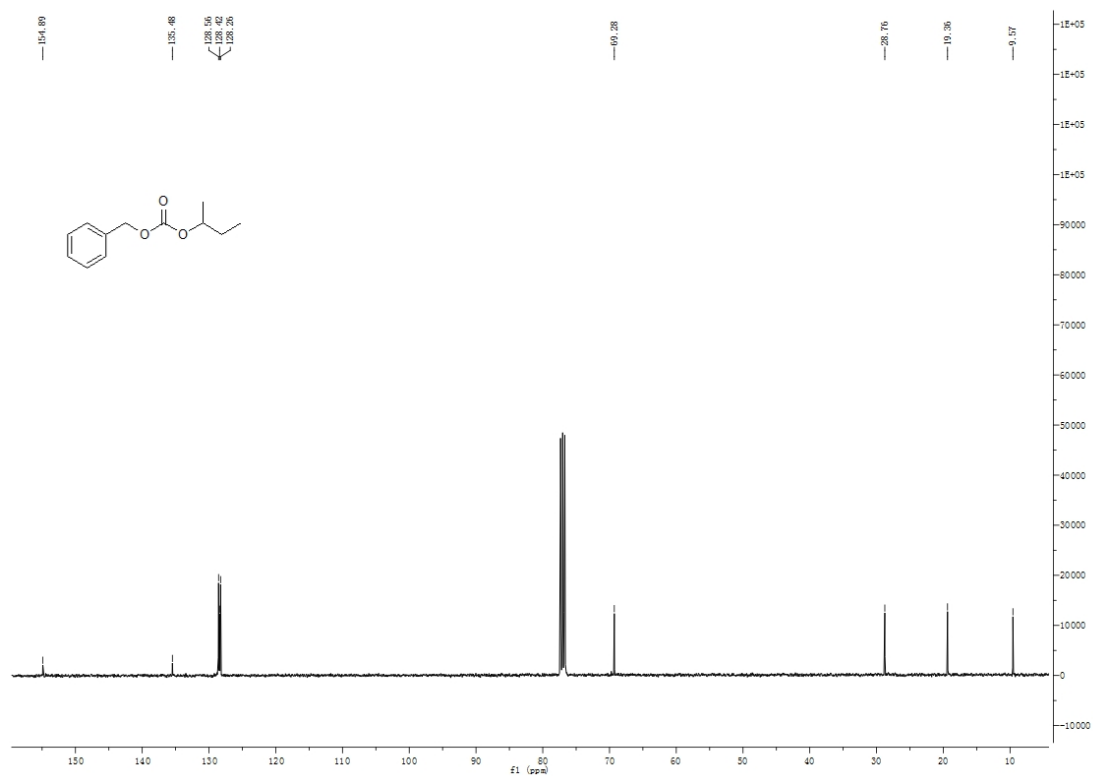
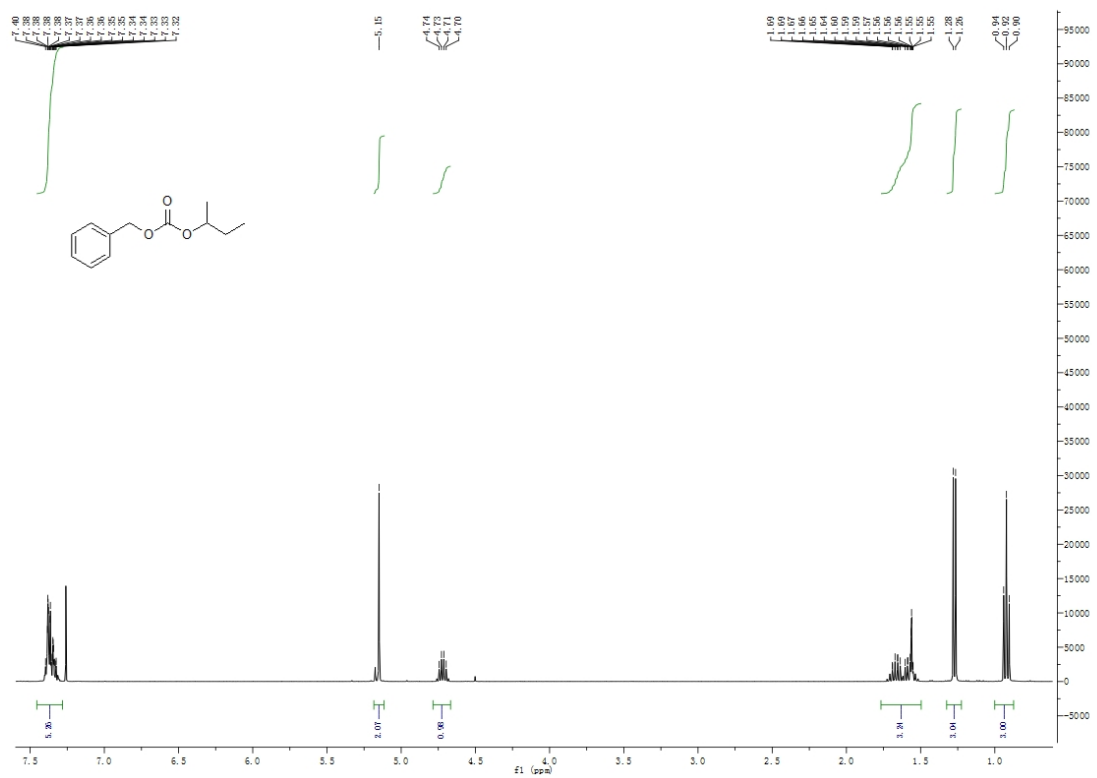


Fig. S6: NMR spectra of benzyl *s*-butyl carbonate (**2f**).



**Reference:**

1. S. A. Forsyth, U. Fröhlich, P. Goodrich, H. Q. N. Gunaratne, C. Hardacre, A. McKeown and K. R. Seddon, *New J. Chem.*, 2010, **34**, 723-731.