

## Supporting Information

### Synthesis of High Molecular Weight Isosorbide-based Polycarbonates through Efficient Activation of Endo-hydroxyl Groups by Ionic Liquid

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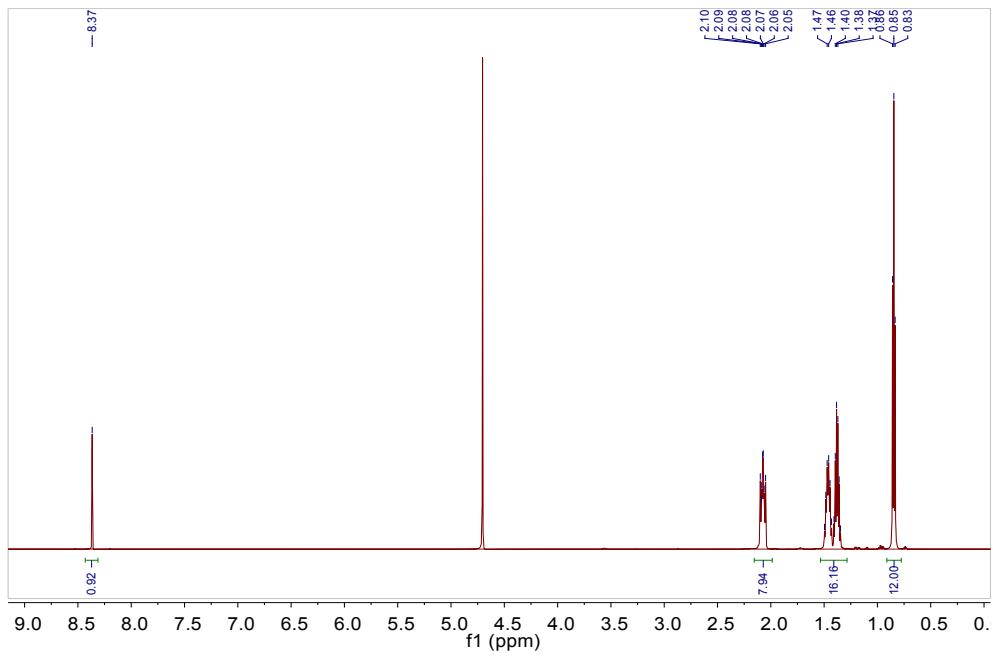


Fig. S1 The  $^1\text{H}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{HCOO}]^-$  ( $\text{D}_2\text{O}$ ).

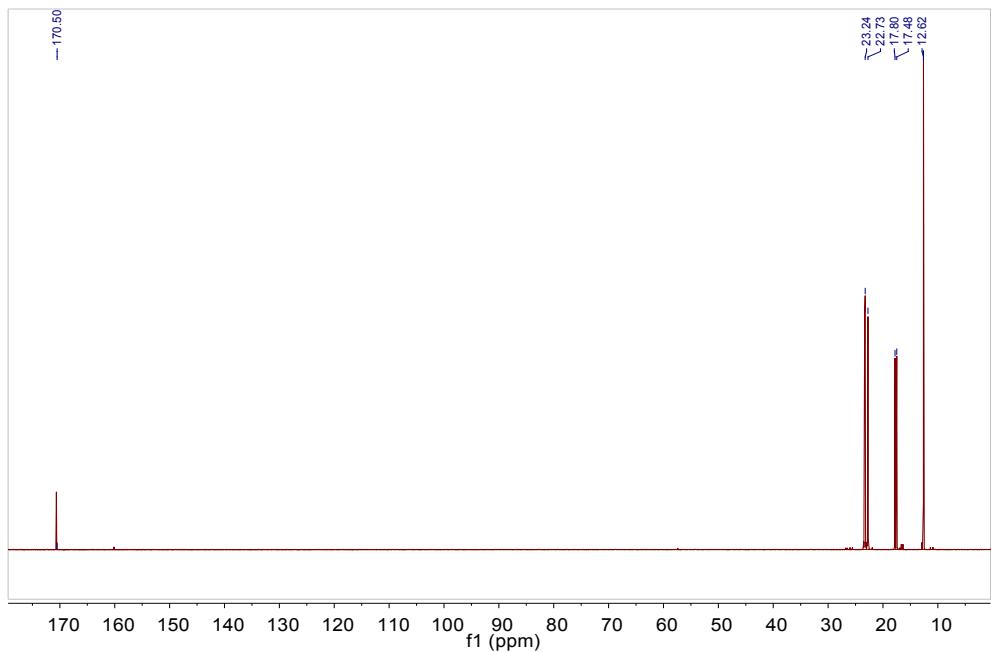


Fig. S2 The  $^{13}\text{C}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{HCOO}]^-$  ( $\text{D}_2\text{O}$ ).

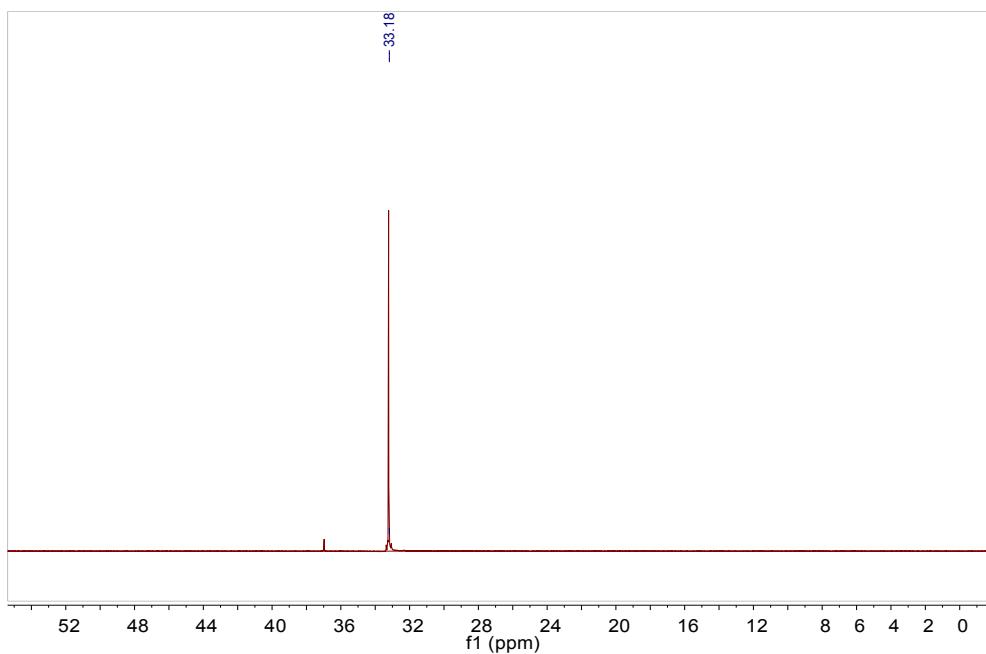


Fig. S3 The  $^{31}\text{P}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{HCOO}]^-$  ( $\text{D}_2\text{O}$ ).

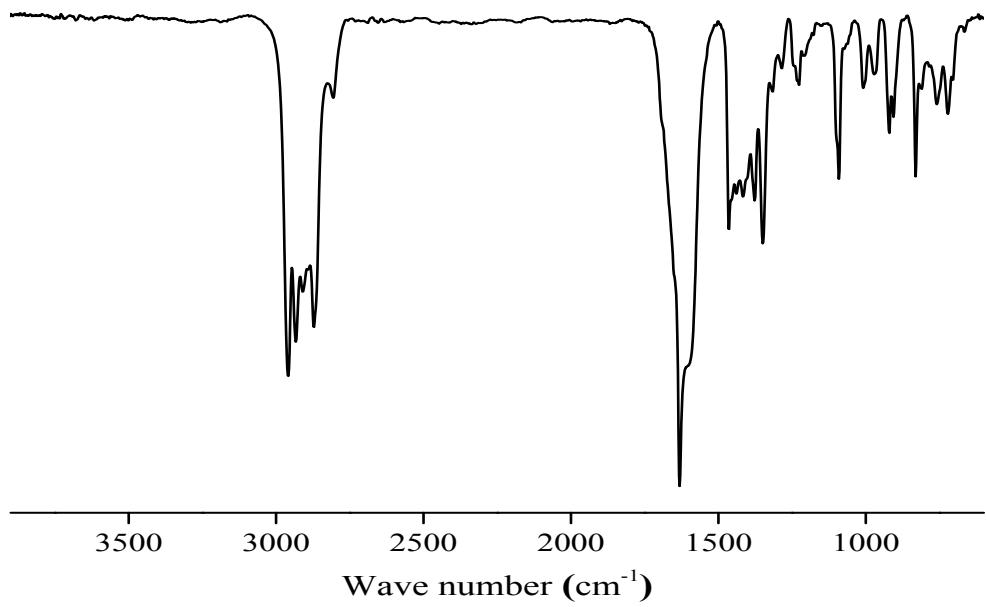


Fig. S4 FT-IR measurement of  $[\text{P}_{4444}]^+[\text{HCOO}]^-$ .

$[\text{P}_{4444}]^+[\text{HCOO}]^-$ : Yield: 85%(light yellow liquid).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.85 (12H, t), 1.41-1.57 (8H, m), 1.27-1.43 (8H, m), 2.08 (8H, m), 8.37 (1H, s).  $^{13}\text{C}$  NMR (150 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 170.6, 23.2, 22.7, 17.8, 17.5, 12.6.  $^{31}\text{P}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 33.18. FT-IR ( $\text{KBr}$ ,  $\text{cm}^{-1}$ ): 2959, 2933, 2872, 1631, 1465, 1349, 1091, 920, 830, 721.

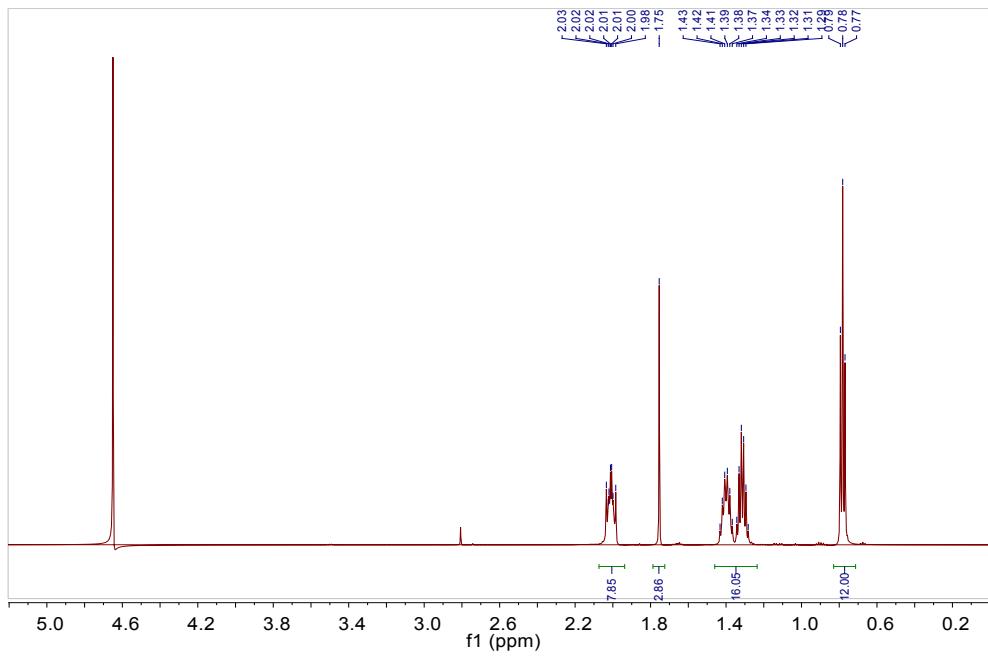


Fig. S5 The  $^1\text{H}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{COO}]^- (\text{D}_2\text{O})$ .

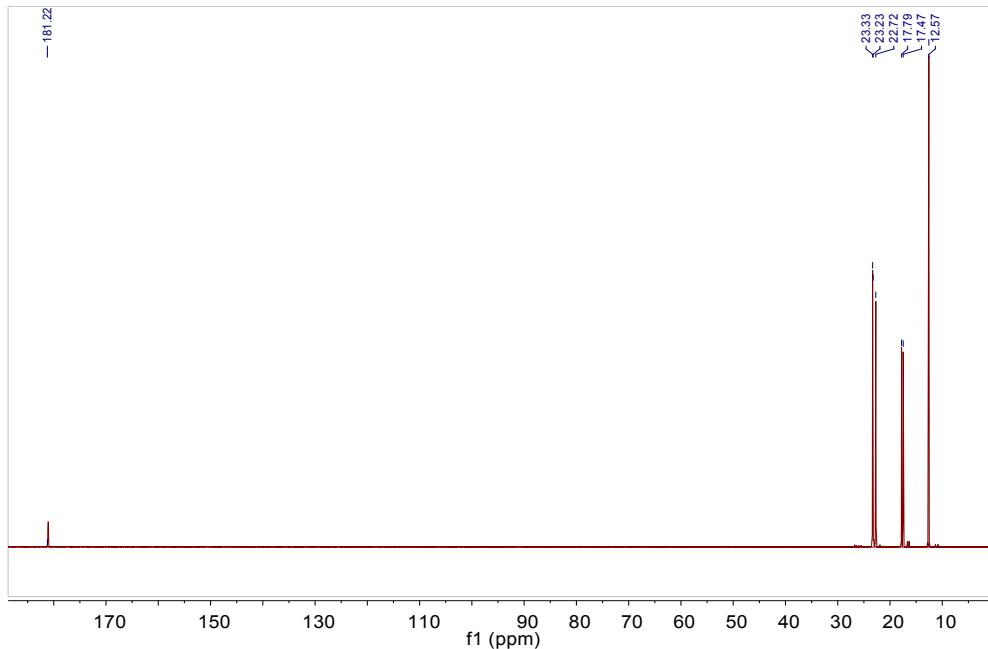


Fig. S6 The  $^{13}\text{C}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{COO}]^- (\text{D}_2\text{O})$ .

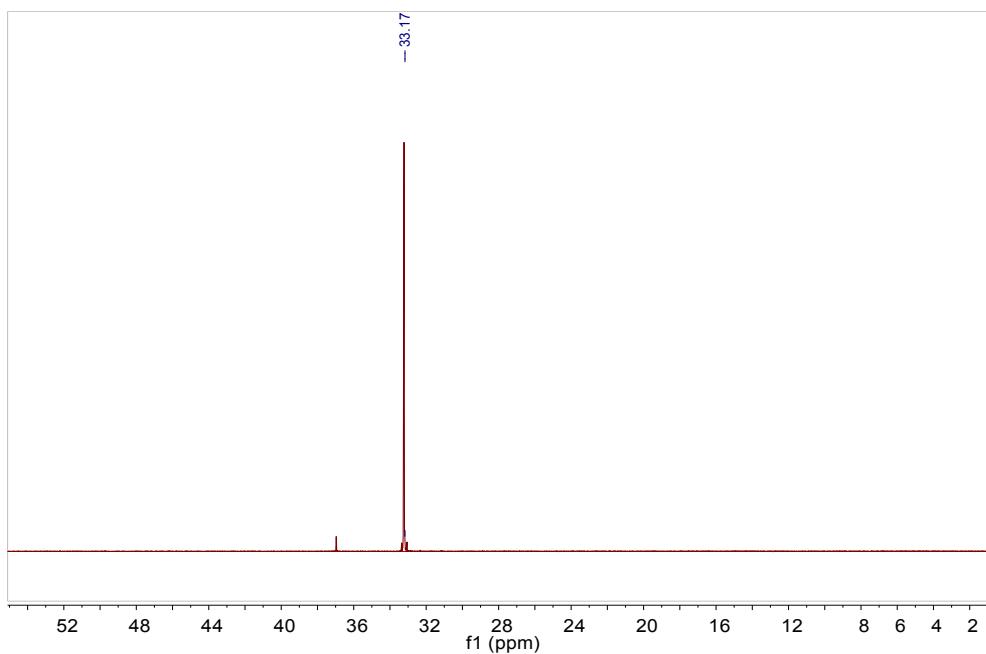


Fig. S7 The  $^{31}\text{P}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{COO}]^- (\text{D}_2\text{O})$ .

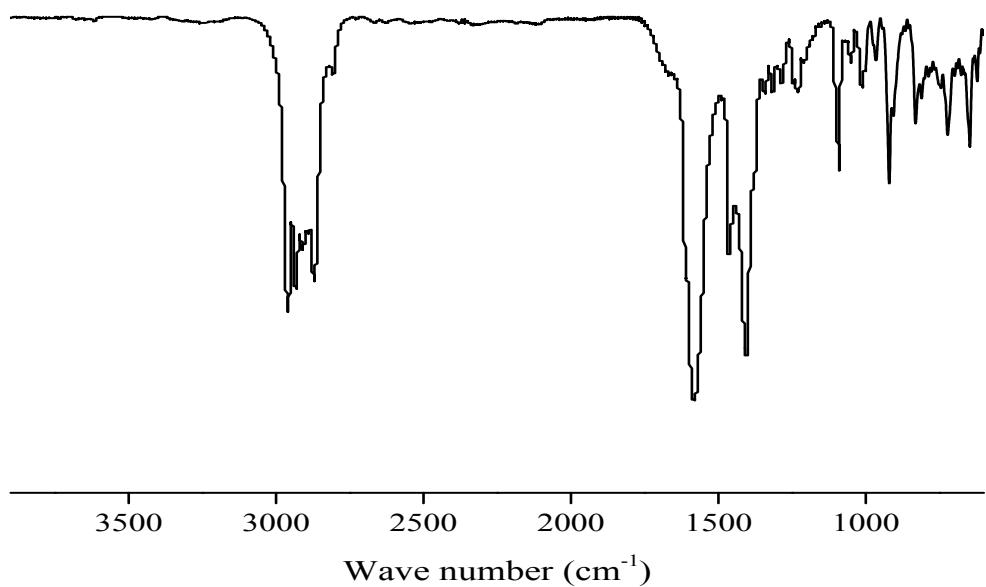


Fig. S8 The FT-IR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{COO}]^-$ .

$[\text{P}_{4444}]^+[\text{CH}_3\text{COO}]^-$ : Yield: 85% (light yellow liquid).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.78 (12H, t), 1.40 (8H, m), 1.31 (8H, m), 2.00 (8H,m), 1.75 (3H, s).  $^{13}\text{C}$  NMR (150MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 181.0, 23.7, 23.1, 22.7, 17.8, 17.5, 12.6.  $^{31}\text{P}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 33.17. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2959, 2933, 2872, 1581, 1464, 1405, 1091, 920, 831, 722.

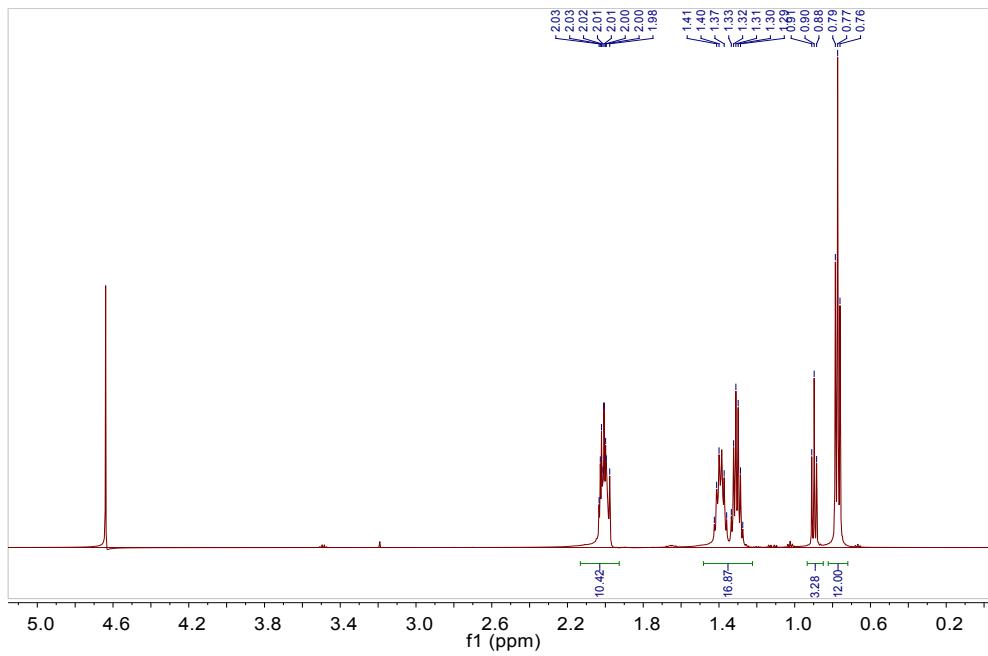


Fig. S9 The <sup>1</sup>H NMR spectrum of  $[P_{4444}]^+ [CH_3CH_2COO]^-$  ( $D_2O$ ).

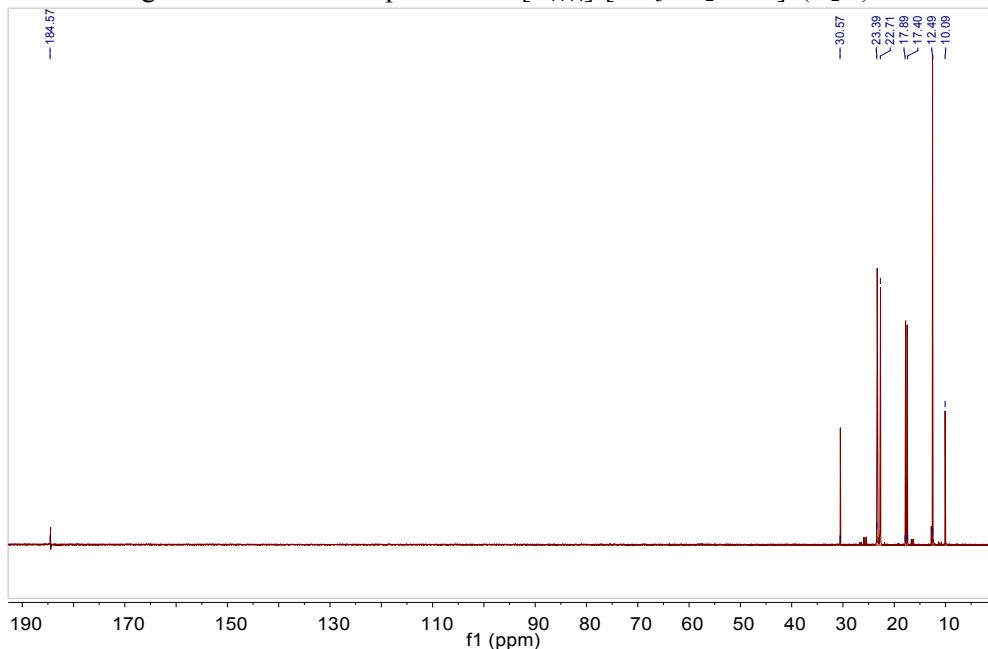


Fig. S10 The <sup>13</sup>C NMR spectrum of  $[P_{4444}]^+ [CH_3CH_2COO]^-$  ( $D_2O$ ).

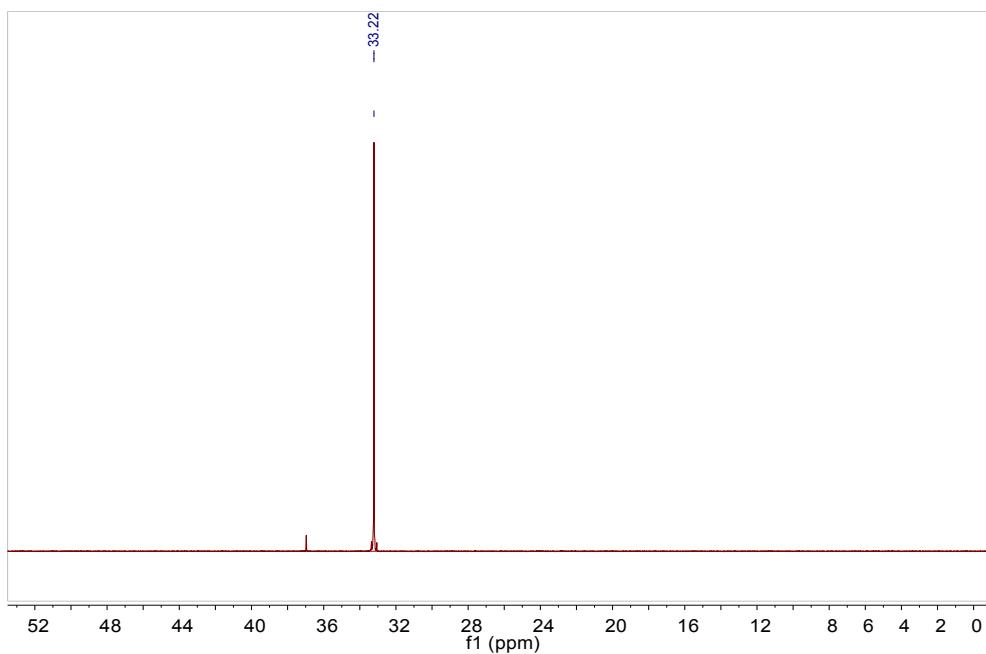


Fig. S11 The  $^{31}\text{P}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}_2\text{COO}]^- (\text{D}_2\text{O})$ .

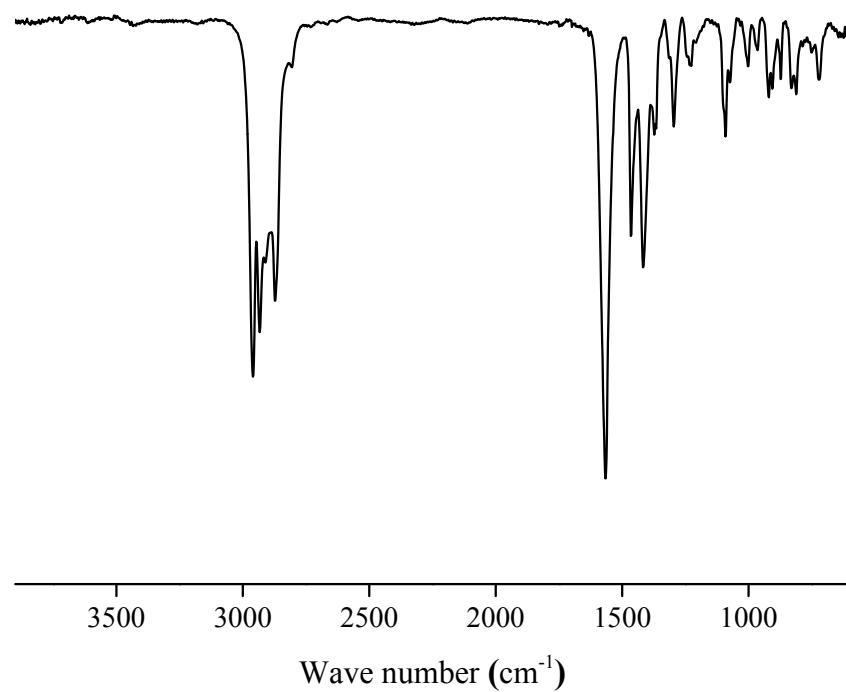


Fig.S12 The FT-IR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}_2\text{COO}]^-$ .

$[\text{P}_{4444}]^+[\text{CH}_3\text{CH}_2\text{COO}]^-$ : Yield: 87% (light yellow liquid).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.77 (12H,t), 1.20-1.35 (8H, m), 1.36-1.48 (8H,m), 1.90-2.11 (10H, m), 0.97-0.84 (3H, t).  $^{13}\text{C}$  NMR (151 MHz,  $\text{D}_2\text{O}$ )  $\delta$  184.5, 30.5, 23.4, 22.8, 17.8, 17.5, 12.5, 10.1.  $^{31}\text{P}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 33.22. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2959, 2933, 2872, 1581, 1464, 1405, 1315, 1091, 920, 831, 722.

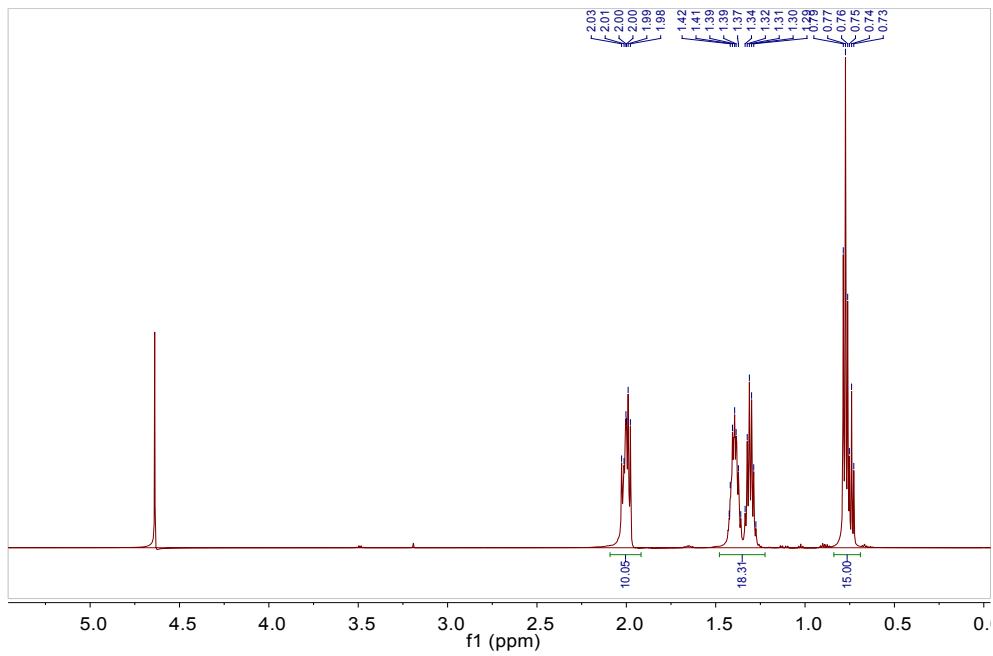


Fig. S13 The <sup>1</sup>H NMR spectrum of  $[P_{4444}]^+ [CH_3CH_2CH_2COO]^-$  ( $D_2O$ ).

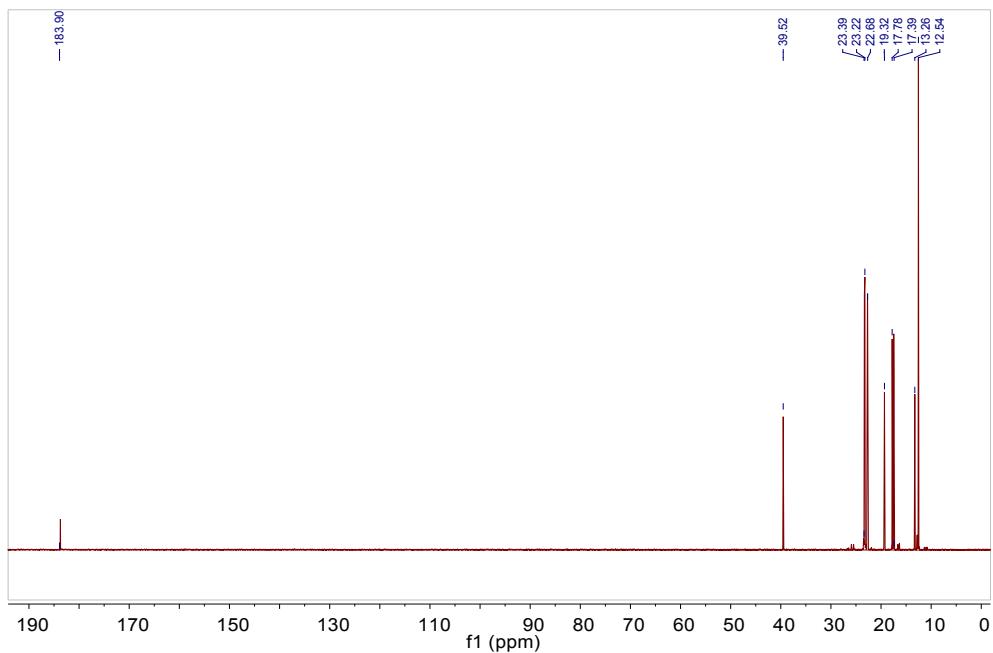


Fig. S14 The <sup>13</sup>C NMR spectrum of  $[P_{4444}]^+ [CH_3CH_2CH_2COO]^-$  ( $D_2O$ ).

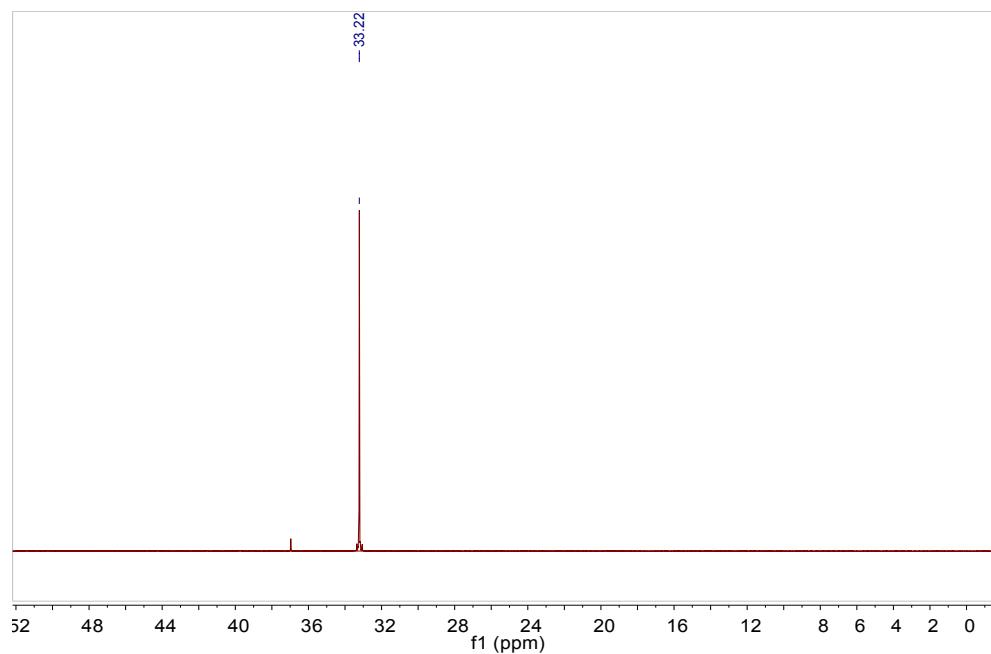


Fig. S15 The  $^{31}\text{P}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}]^-$  ( $\text{D}_2\text{O}$ ).

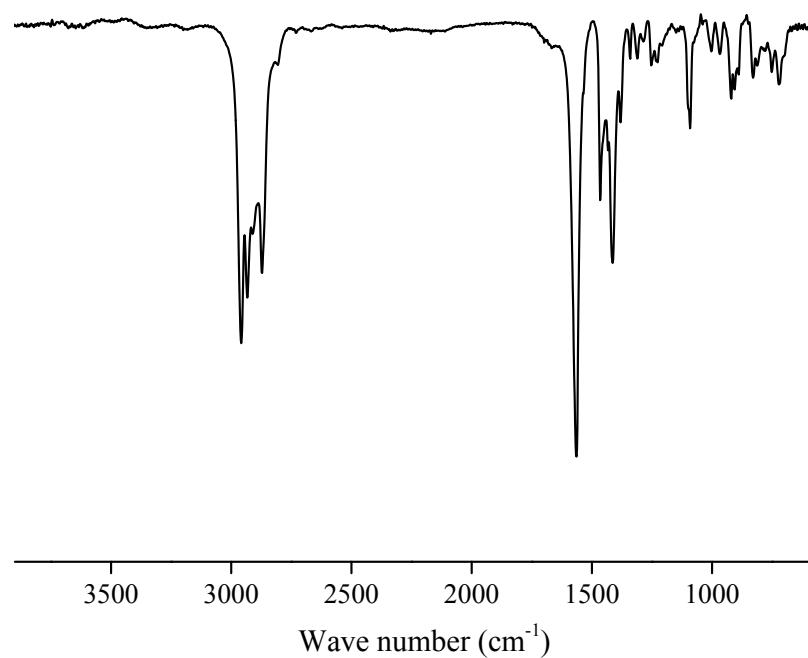


Fig. S16 The FT-IR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}]^-$

$[\text{P}_{4444}]^+[\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}]^-$ : Yield: 86% (light yellow liquid).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.77 (12H, t), 1.24-1.47 (18H, m), 2.01 (10H, m), 0.74 (3H, t).  $^{13}\text{C}$  NMR (150 MHz,  $\text{D}_2\text{O}$ )  $\delta$  183.7, 39.5, 23.3, 22.8, 19.3, 17.8, 17.5, 13.3, 12.5.  $^{31}\text{P}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 33.22. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2959, 2933, 2872, 1564, 1465, 1413, 1380, 1092, 921, 829, 722.

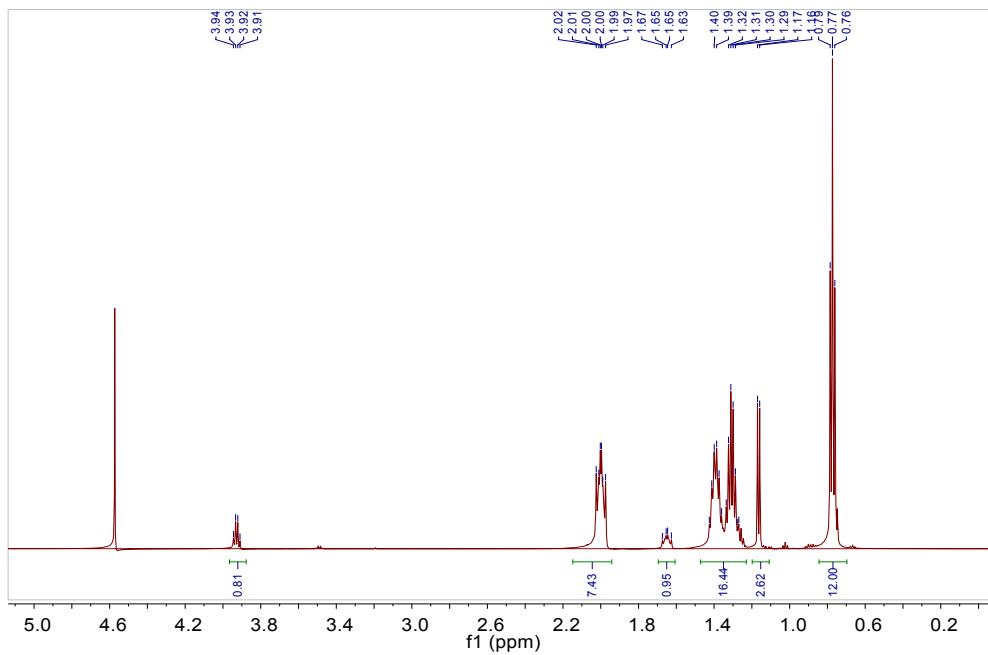


Fig. S17 The  $^1\text{H}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}(\text{OH})\text{COO}]^-$  ( $\text{D}_2\text{O}$ ).

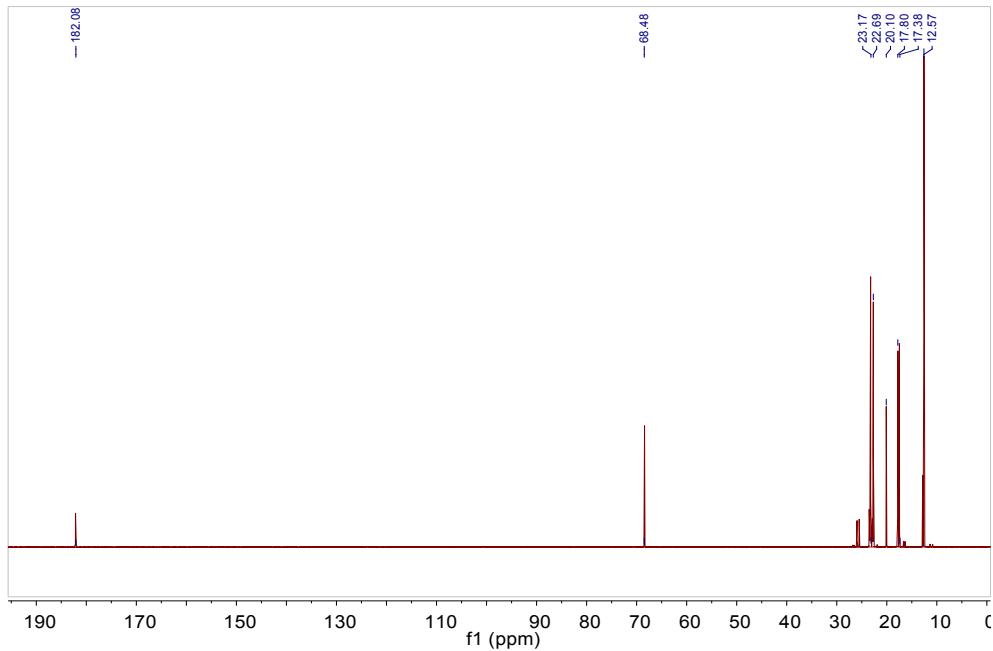


Fig. S18 The  $^{13}\text{C}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}(\text{OH})\text{COO}]^-$  ( $\text{D}_2\text{O}$ ).

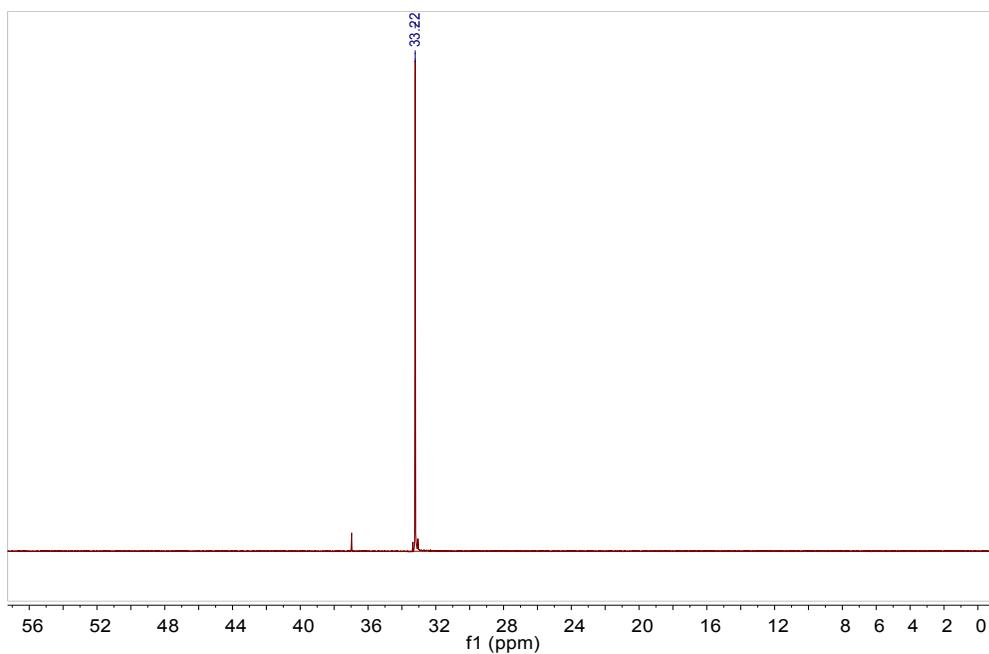


Fig. S19 The  $^{31}\text{P}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}(\text{OH})\text{COO}]^-$  ( $\text{D}_2\text{O}$ ).

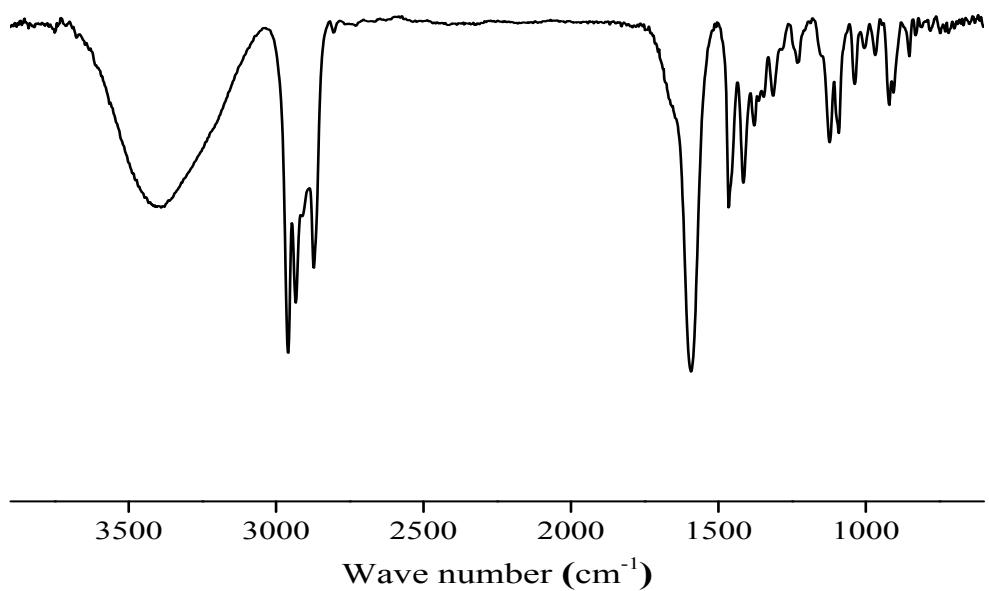


Fig.S20 The FT-IR spectrum of  $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}(\text{OH})\text{COO}]^-$   
 $[\text{P}_{4444}]^+[\text{CH}_3\text{CH}(\text{OH})\text{COO}]^-$ : Yield: 81% (light yellow liquid).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.77 (12H, t), 1.22-1.35 (8H, m), 1.39 (8H, m), 1.94-2.24 (8H, m), 3.93 (q, 1H), 1.20-1.10 (3H, d).  $^{13}\text{C}$  NMR (150 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 182.2, 68.4, 23.6, 20.1, 17.8, 17.5, 12.7.  $^{31}\text{P}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 33.22. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3378, 2959, 2933, 2873, 1594, 1465, 1415, 1379, 1222, 1095, 1040, 919, 847, 721.

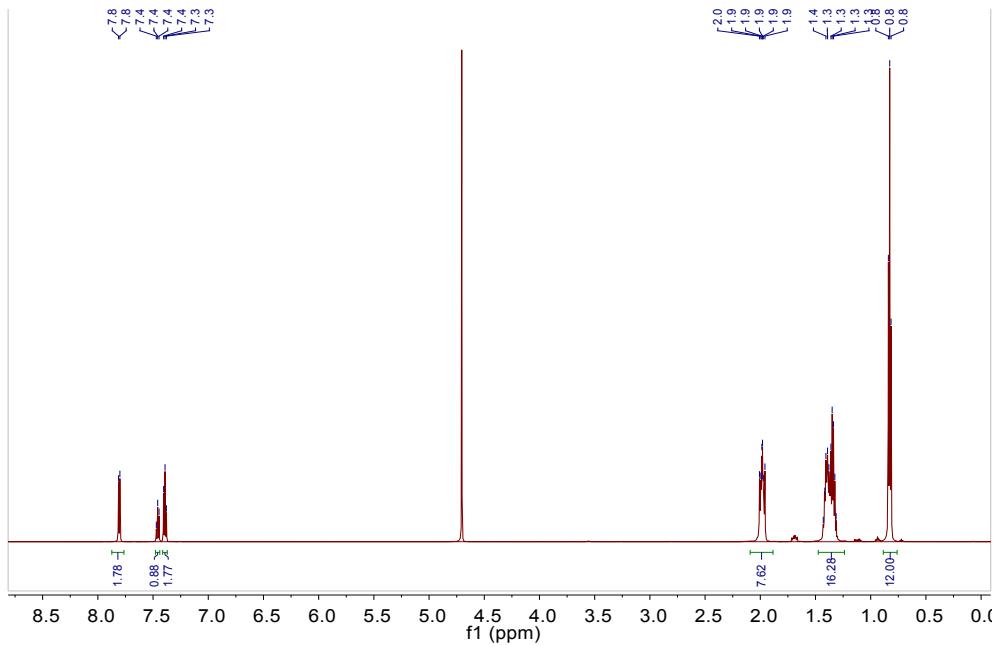


Fig. S21 The  $^1\text{H}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{C}_6\text{H}_5\text{COO}]^-$  ( $\text{D}_2\text{O}$ ).

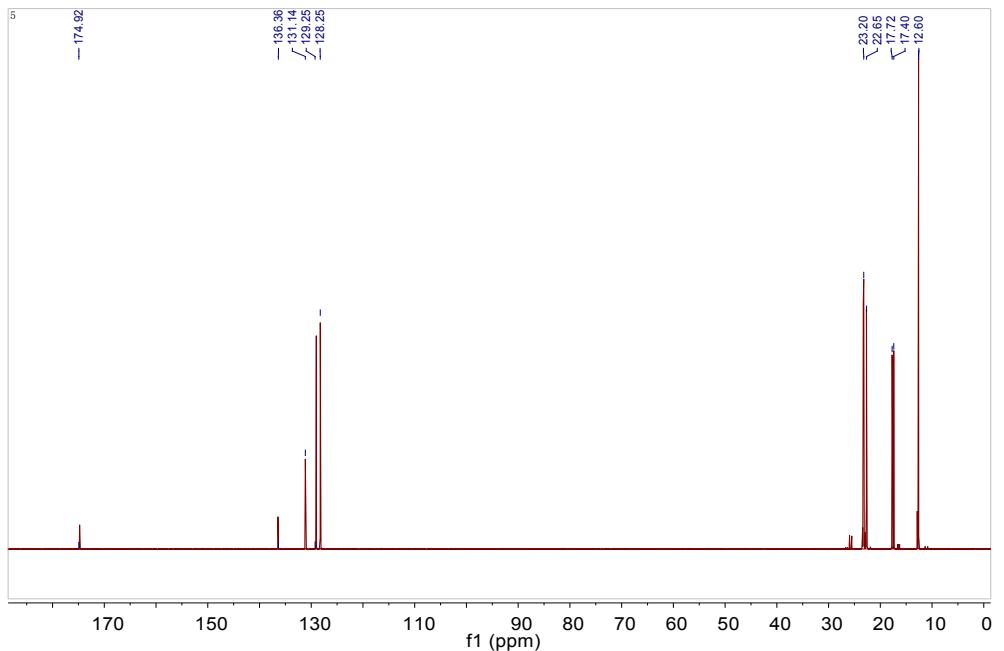


Fig. S22 The  $^{13}\text{C}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{C}_6\text{H}_5\text{COO}]^-$  ( $\text{D}_2\text{O}$ ).

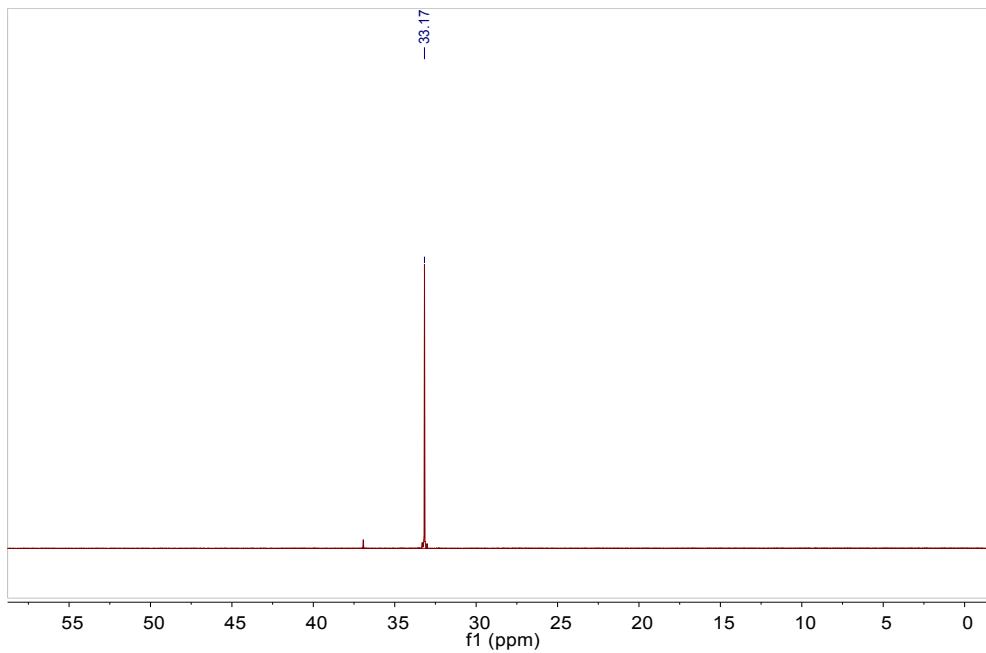


Fig. S23 The  $^{31}\text{P}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{C}_6\text{H}_5\text{COO}]^-$  ( $\text{D}_2\text{O}$ ).

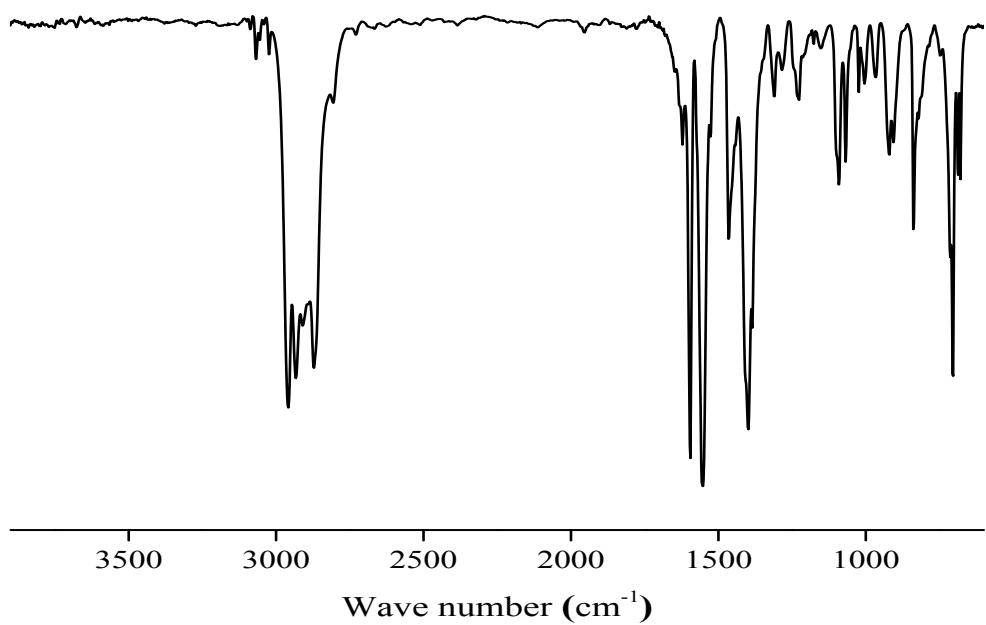


Fig.S24 The FT-IR spectrum of  $[\text{P}_{4444}]^+[\text{C}_6\text{H}_5\text{COO}]^-$ .

$[\text{P}_{4444}]^+[\text{C}_6\text{H}_5\text{COO}]^-$ : Yield: 83% (light yellow liquid).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.83 (12H, t), 1.33 (8H, m), 1.44-1.37 (8H, m), 2.16-1.84 (8H, m), 7.80 (2H, d), 7.46 (1H, t), 7.39 (2H, t).  $^{13}\text{C}$  NMR (150 MHz,  $\text{D}_2\text{O}$ )  $\delta$  174.8, 136.4, 131.1, 129.0, 128.3, 23.6, 22.7, 17.7, 17.4, 12.6.  $^{31}\text{P}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 33.17. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3068, 3023, 2959, 2933, 2872, 1595, 1552, 1464, 1398, 1091, 1068, 1023, 920, 838, 704, 678.

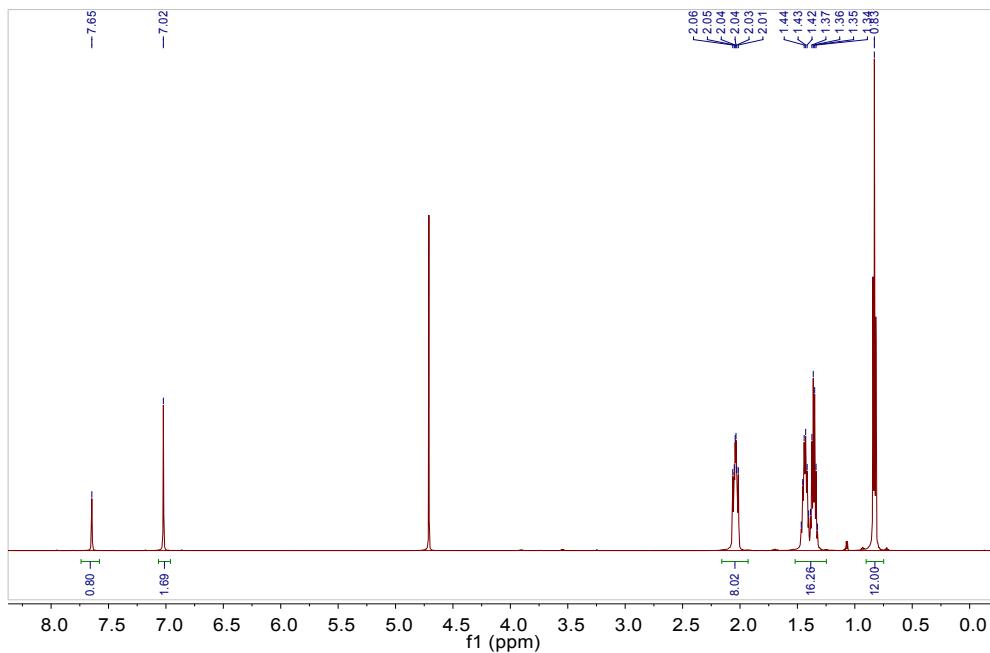


Fig. S25 The  ${}^{13}\text{C}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{Im}]^-$  ( $\text{D}_2\text{O}$ ).

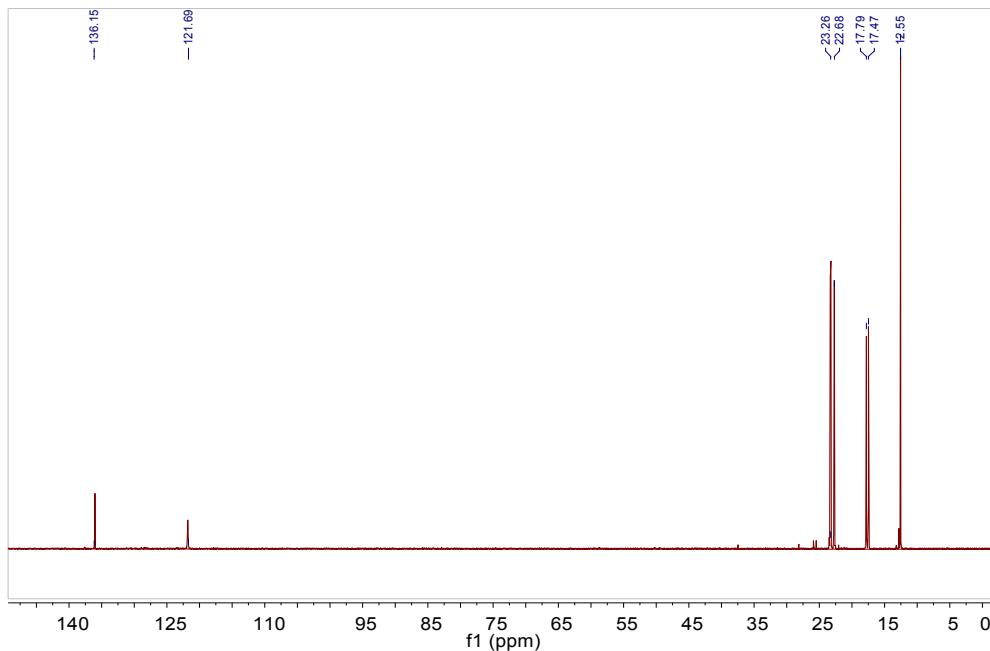


Fig. S26 The  ${}^{13}\text{C}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{Im}]^-$  ( $\text{D}_2\text{O}$ ).

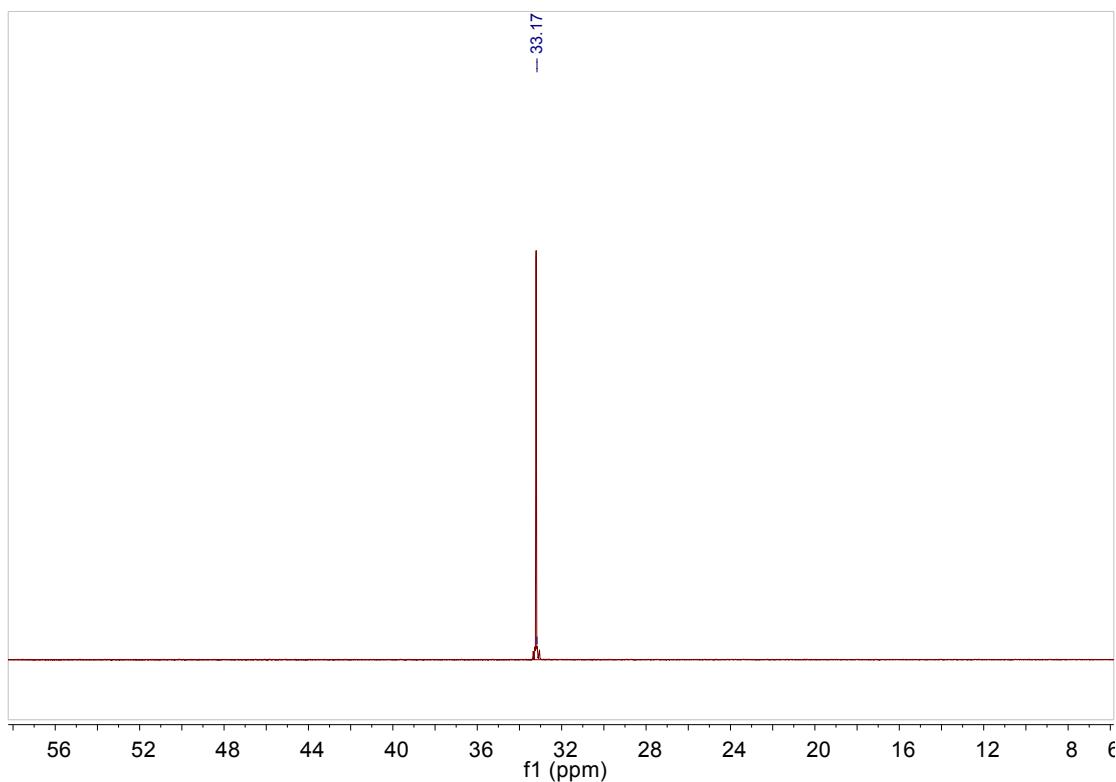


Fig. S27 The  $^{31}\text{P}$  NMR spectrum of  $[\text{P}_{4444}]^+[\text{Im}]^-$  measured by  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ).

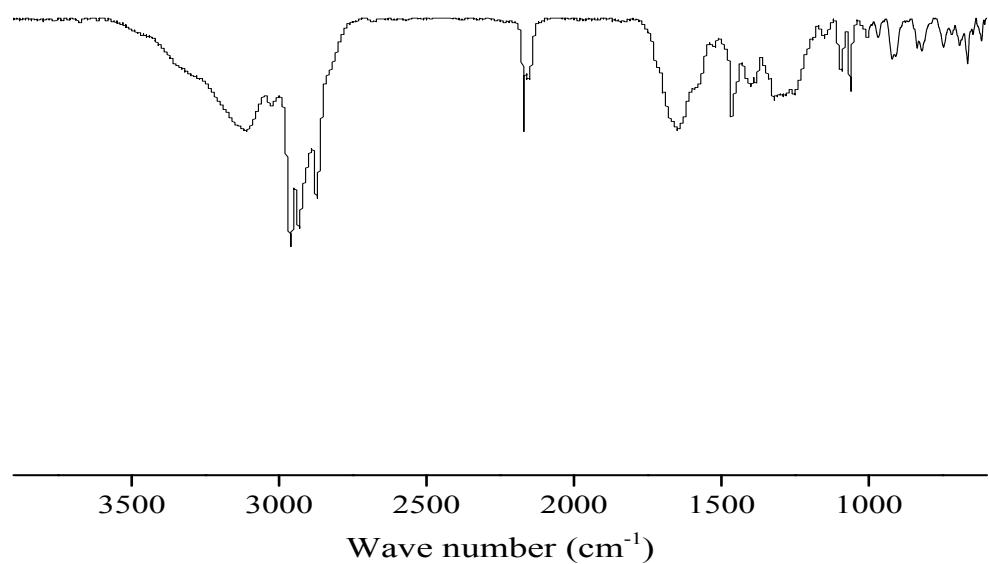


Fig.S28 The FT-IR spectrum of  $[\text{P}_{4444}]^+[\text{Im}]^-$ .

$[\text{P}_{4444}]^+[\text{Im}]^-$ : Yield: 86% (light fuchsia liquid).  $^1\text{H}$  NMR (600 MHz,  $\text{D}_2\text{O}$ ) 0.83 (12H, t), 1.29-1.50 (m, 16H), 1.99-2.09 (8H, m),  $\delta$  7.65 (1H, s), 7.02 (2H,s).  $^{13}\text{C}$  NMR (150 MHz,  $\text{D}_2\text{O}$ )  $\delta$  136.0, 121.8, 23.4, 22.7, 17.8, 17.5, 12.5.  $^{31}\text{P}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ :

33.17. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3112, 2960, 2932, 2873, 2170, 1646, 1465, 1399, 1322, 1093, 1062, 968, 919, 819, 744, 664.

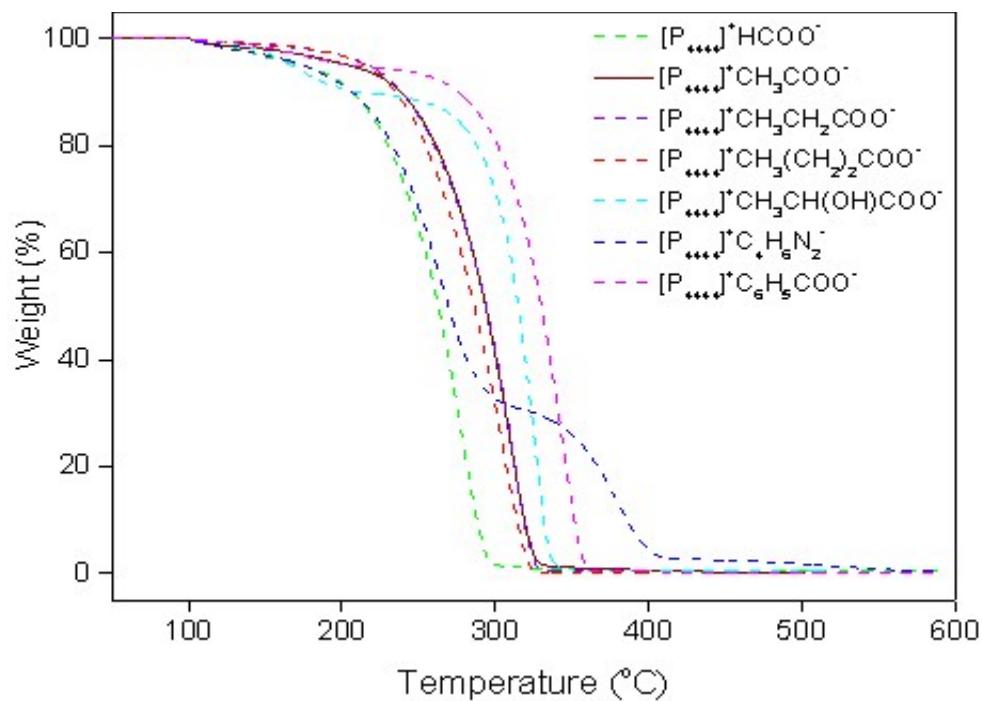


Fig. S29 TGA curves of ILs

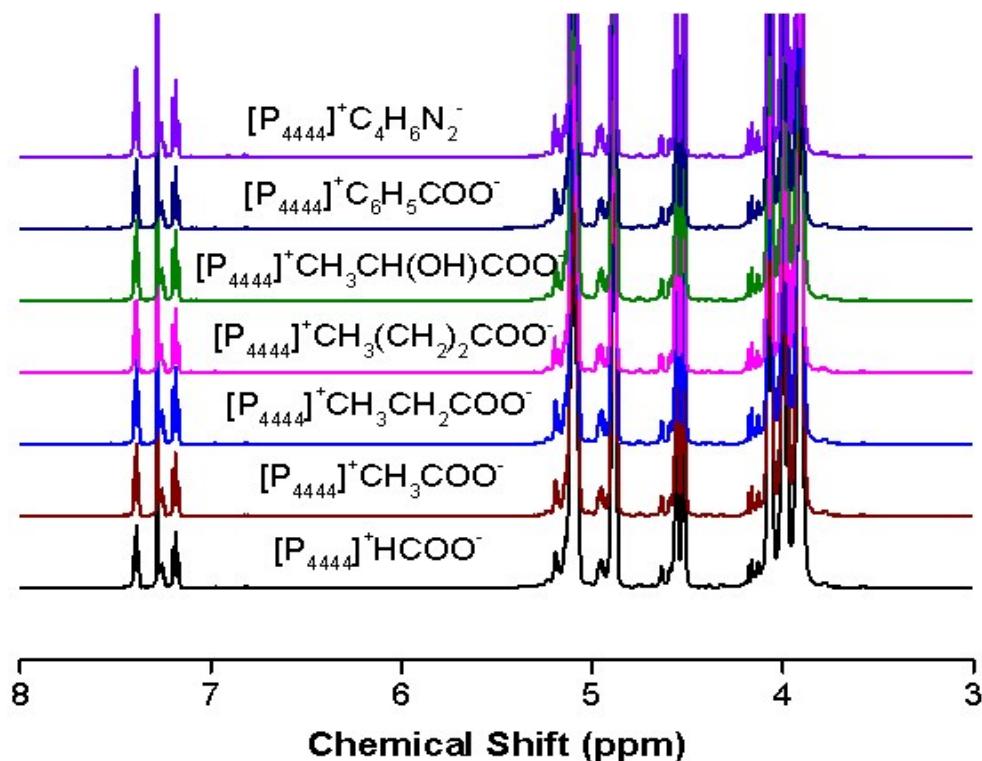


Fig. S30 Effects of different ILs on PIC terminal groups by measured by  $^1\text{H}$  NMR

Table S1 The result of effects of different catalyst on PIC terminal groups

Catalyst	exo-OH	endo-OH	endo-OH/ exo-OH	PhO-	-OH
[P <sub>4444</sub> ] <sup>+</sup> [HCOO] <sup>-</sup>	0.012	0.003	0.250	0.053	0.015
[P <sub>4444</sub> ] <sup>+</sup> [CH <sub>3</sub> COO] <sup>-</sup>	0.008	0.002	0.250	0.052	0.010
[P <sub>4444</sub> ] <sup>+</sup> [CH <sub>3</sub> CH <sub>2</sub> COO] <sup>-</sup>	0.008	0.002	0.250	0.061	0.010
[P <sub>4444</sub> ] <sup>+</sup> [CH <sub>3</sub> CH <sub>3</sub> CH <sub>2</sub> COO] <sup>-</sup>	0.008	0.002	0.250	0.054	0.010
[P <sub>4444</sub> ] <sup>+</sup> [CH <sub>3</sub> CH(OH)COO] <sup>-</sup>	0.008	0.002	0.250	0.059	0.010
[P <sub>4444</sub> ] <sup>+</sup> [C <sub>6</sub> H <sub>5</sub> COO] <sup>-</sup>	0.010	0.002	0.200	0.054	0.012
[P <sub>4444</sub> ] <sup>+</sup> [C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> ] <sup>-</sup>	0.008	0.002	0.250	0.062	0.010
[N <sub>2222</sub> ] <sup>+</sup> [CH <sub>3</sub> COO] <sup>-</sup>	0.010	0.002	0.200	0.072	0.012
[Bmim] <sup>+</sup> [CH <sub>3</sub> COO] <sup>-</sup>	0.013	0.003	0.231	0.075	0.016
[Emim] <sup>+</sup> [CH <sub>3</sub> COO] <sup>-</sup>	0.011	0.002	0.182	0.060	0.013
[Ch] <sup>+</sup> [CH <sub>3</sub> COO] <sup>-</sup>	0.009	0.002	0.222	0.076	0.011
CsCO <sub>3</sub>	0.020	0.009	0.450	0.050	0.029
LiAcac	0.017	0.011	0.647	0.008	0.028

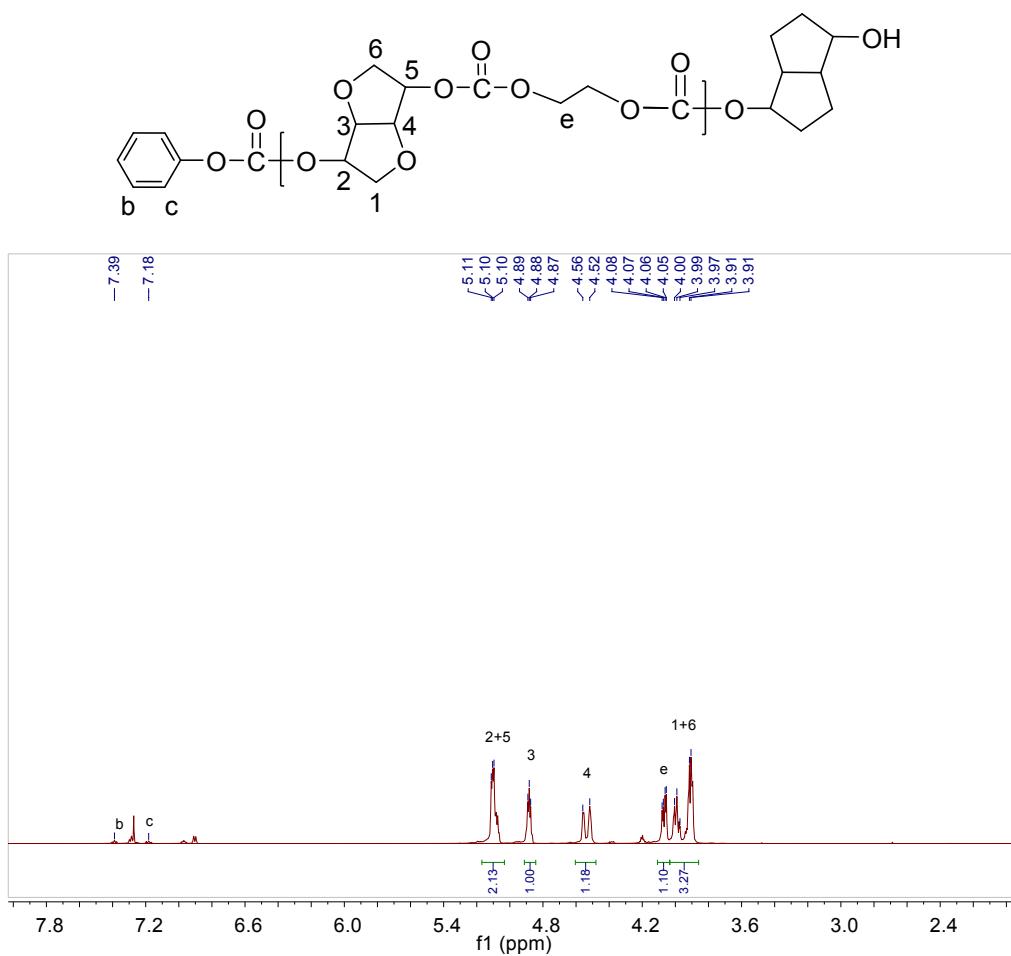


Fig. S31 The  $^1\text{H}$  NMR spectrum of PEIC ( $\text{CDCl}_3$ ).

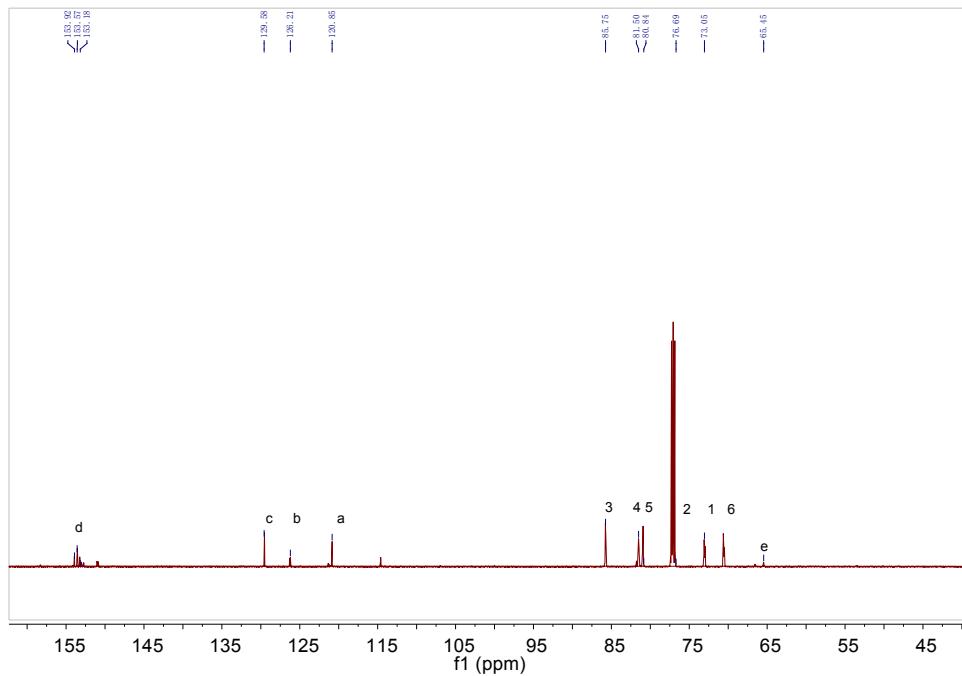
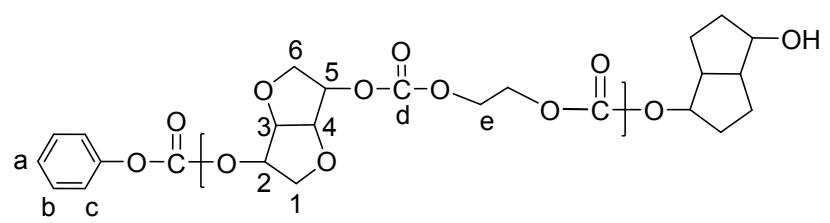


Fig. S32 The  $^{13}\text{C}$  NMR spectrum of PEIC ( $\text{CDCl}_3$ ).

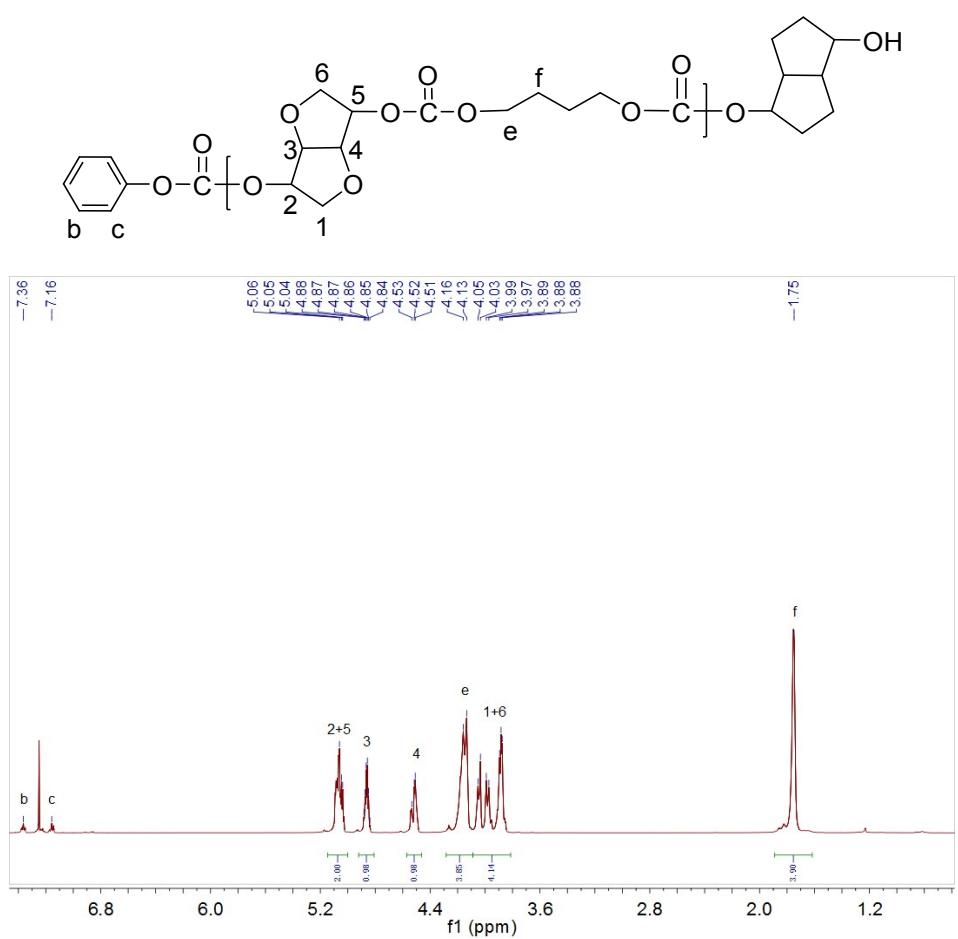
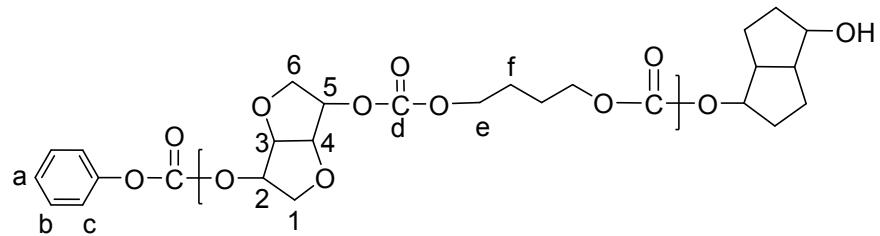


Fig. S33 The <sup>1</sup>H NMR spectrum of PBIC (CDCl<sub>3</sub>).



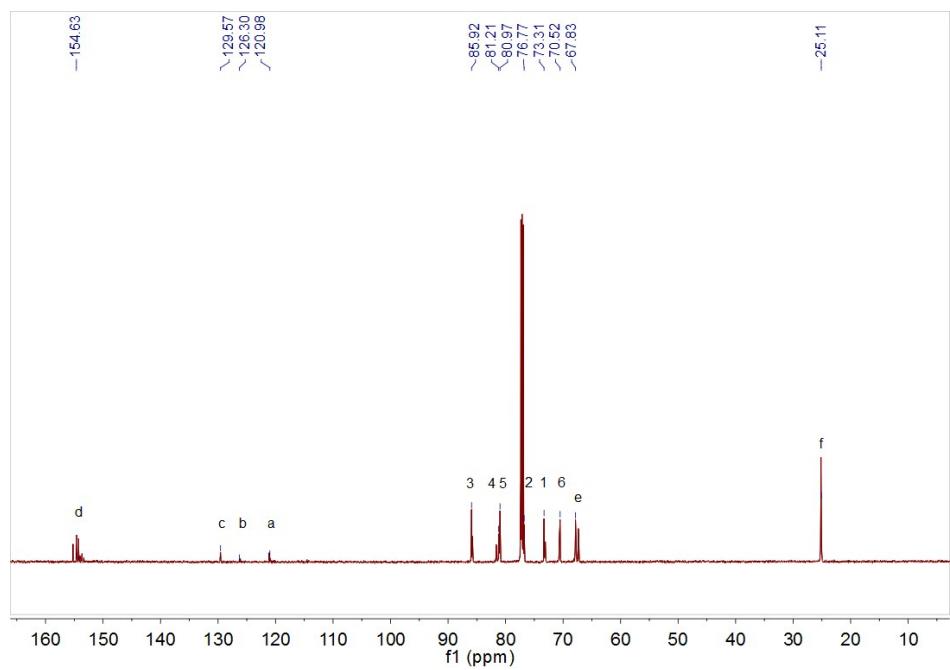


Fig. S34 The  $^{13}\text{C}$  NMR spectrum of PBIC ( $\text{CDCl}_3$ ).

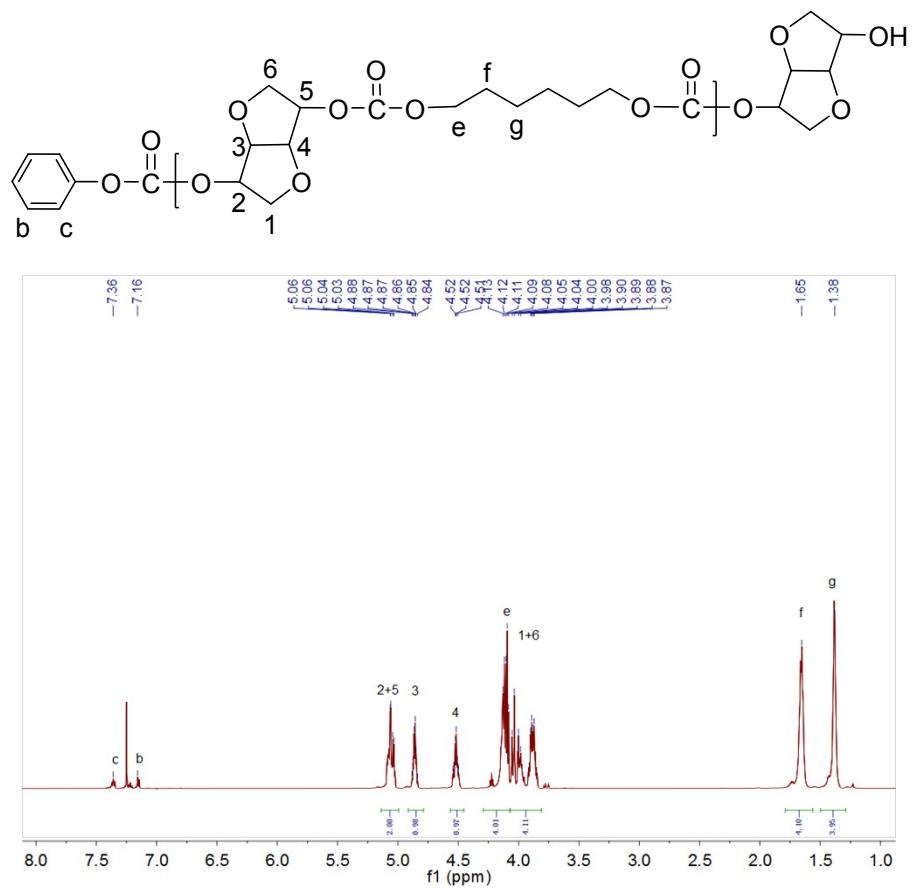


Fig. S35 The  $^1\text{H}$  NMR spectrum of PHIC ( $\text{CDCl}_3$ ).

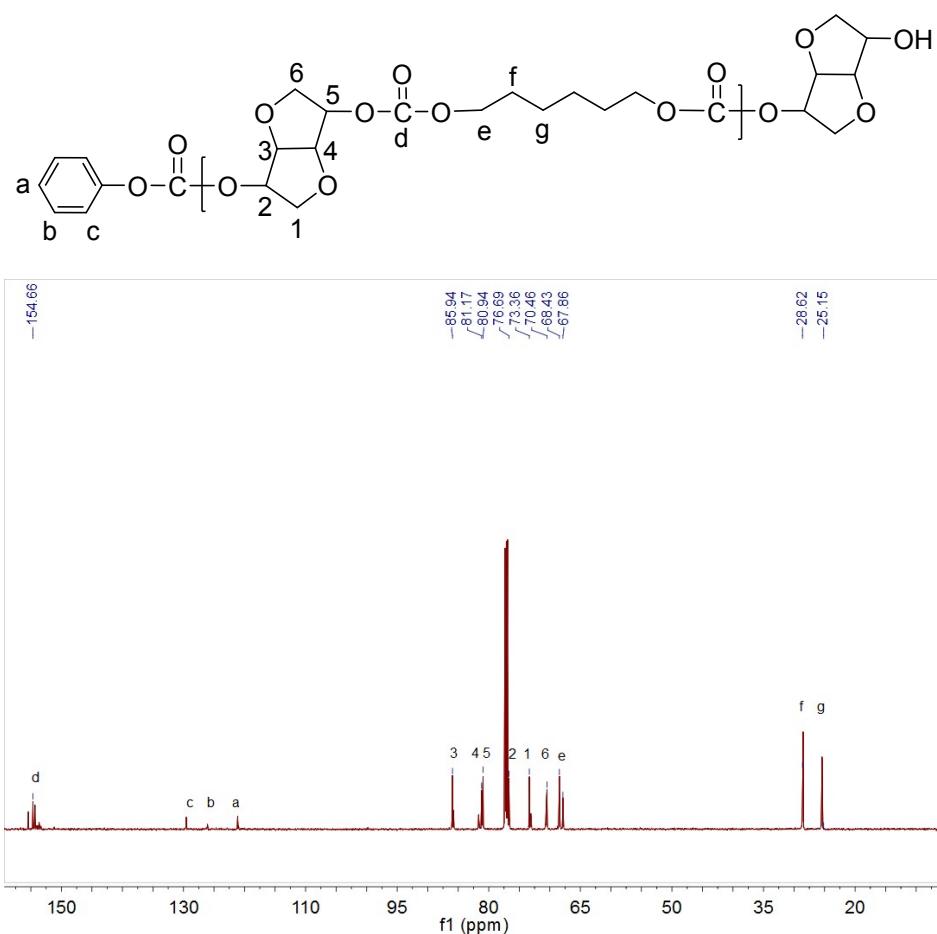
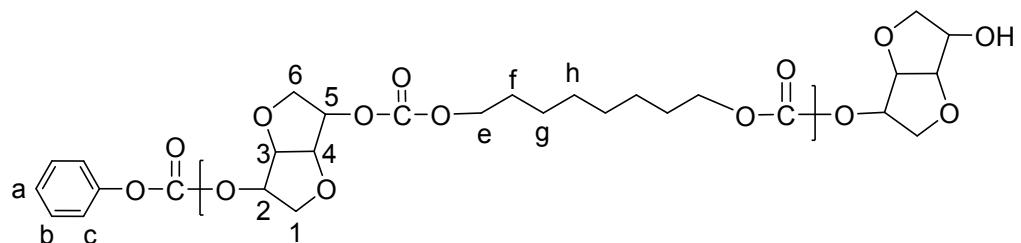


Fig. S36 The  $^{13}\text{C}$  NMR spectrum of PHIC ( $\text{CDCl}_3$ ).



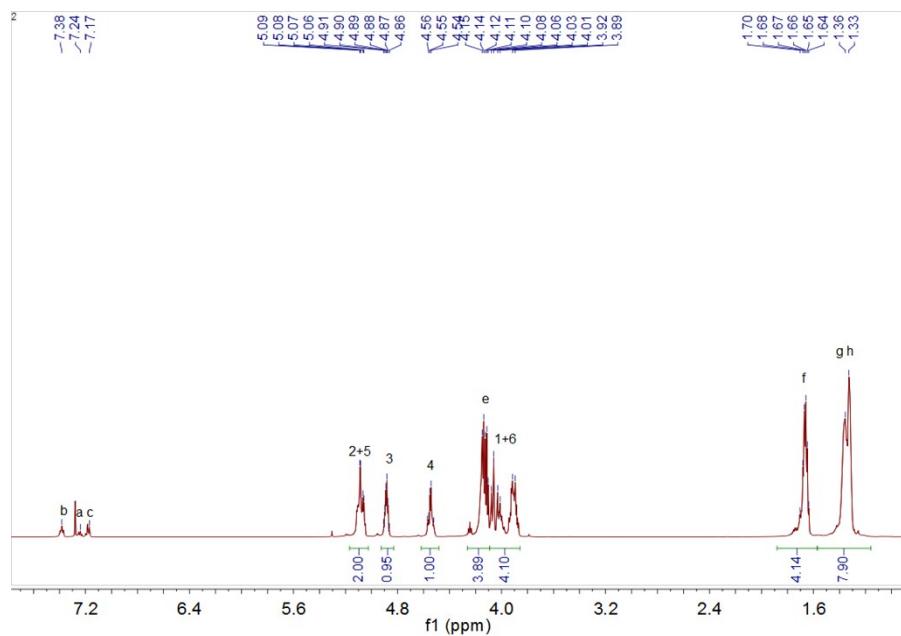


Fig. S37 The  $^1\text{H}$  NMR spectrum of POIC ( $\text{CDCl}_3$ ).

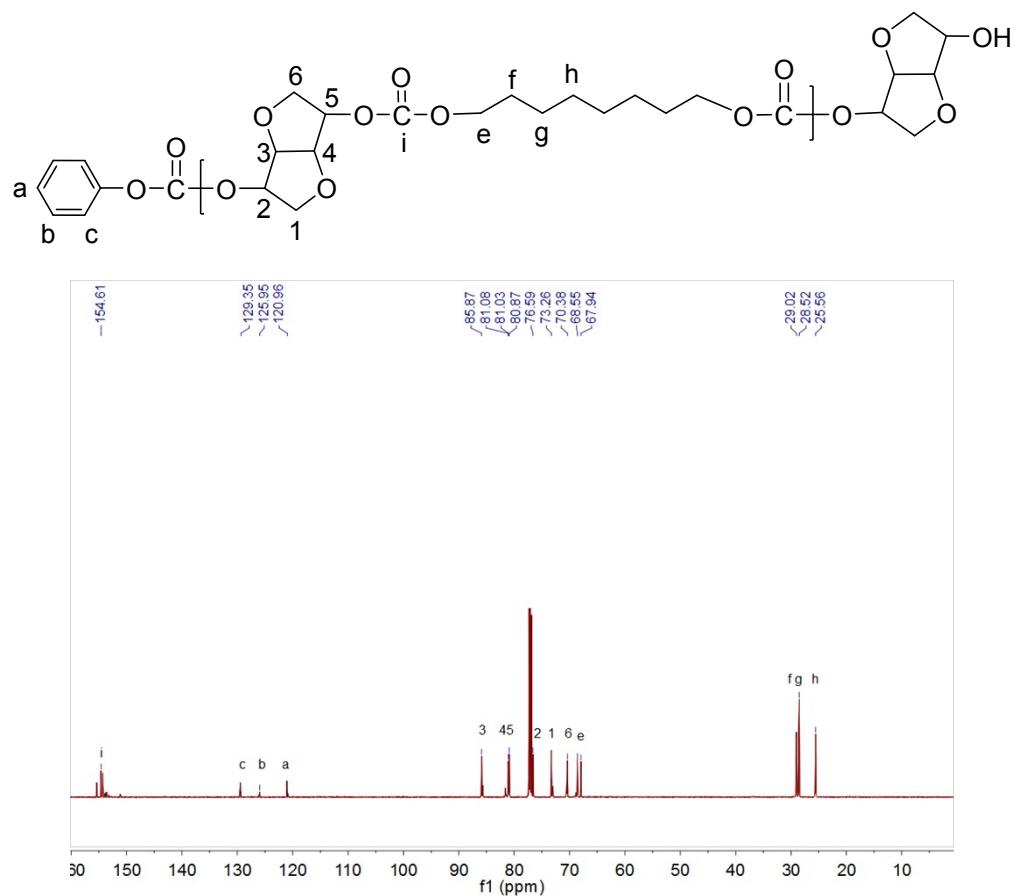


Fig. S38 The  $^{13}\text{C}$  NMR spectrum of POIC ( $\text{CDCl}_3$ ).

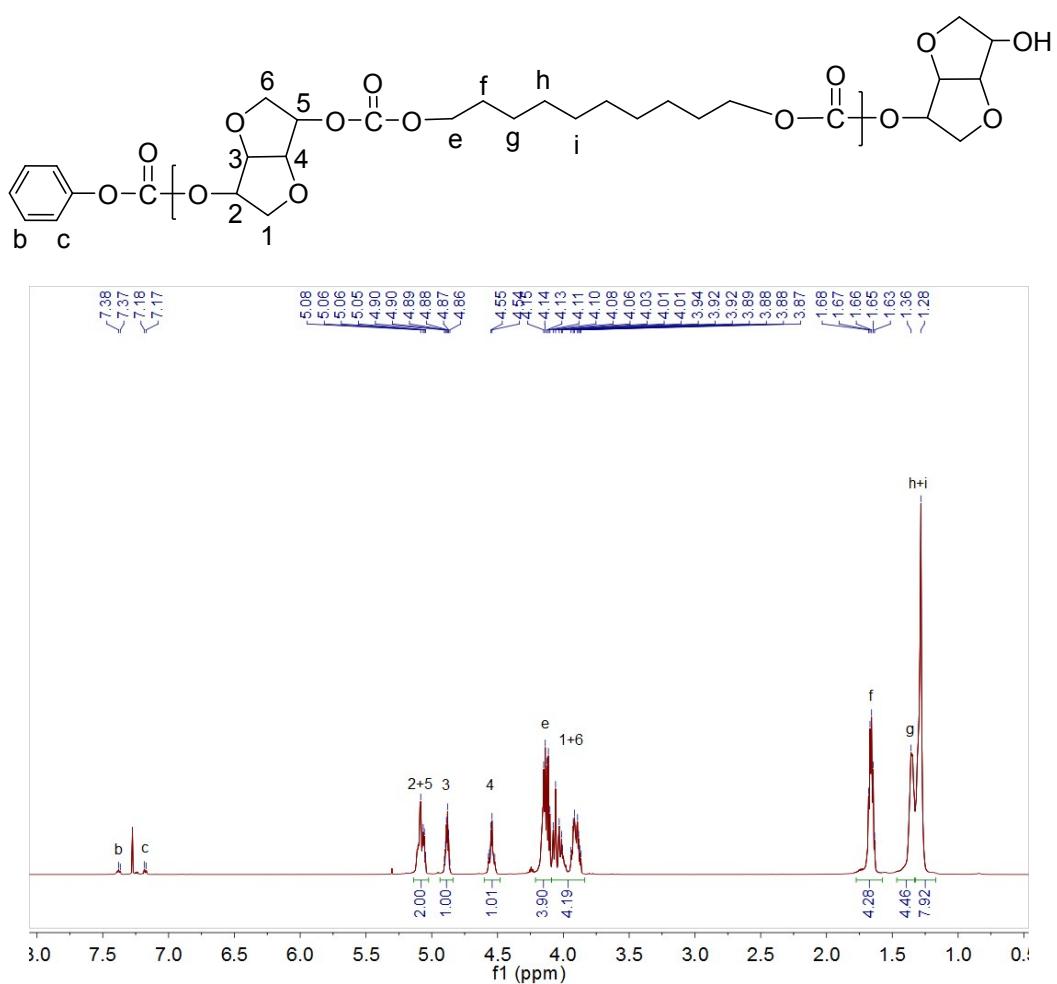


Fig. S39 The <sup>1</sup>H NMR spectrum of PAIC measured by (CDCl<sub>3</sub>).

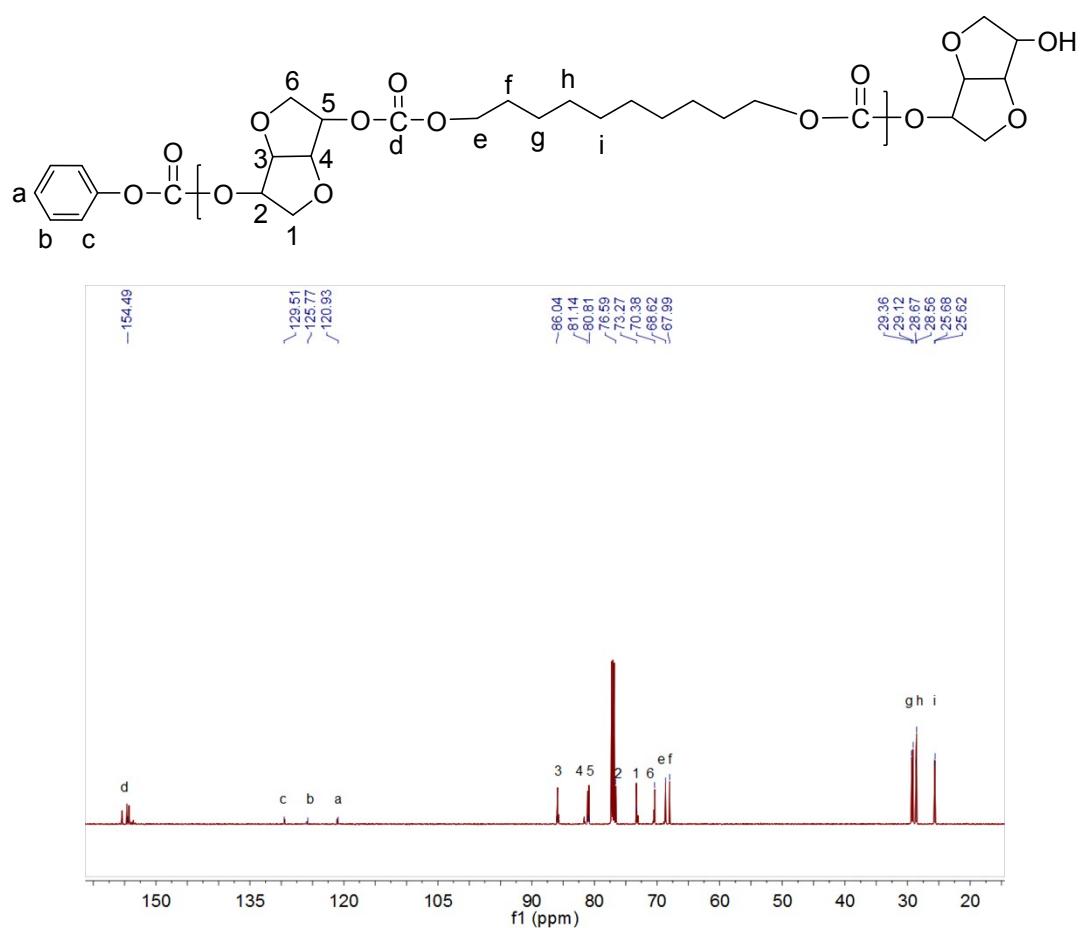


Fig. S40 The  $^{13}\text{C}$  NMR spectrum of PAIC ( $\text{CDCl}_3$ ).

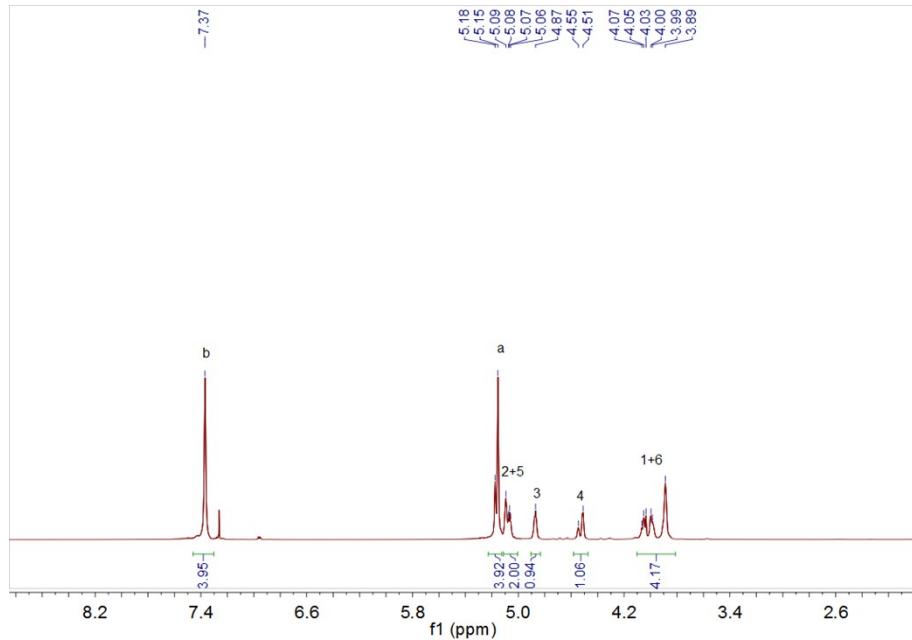
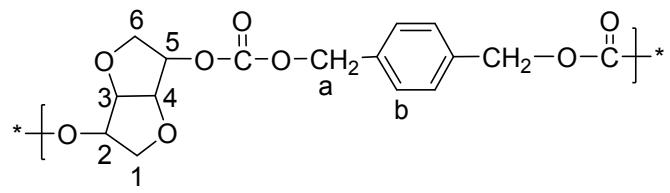


Fig. S41 The  $^1\text{H}$  NMR spectrum of PDIC ( $\text{CDCl}_3$ ).

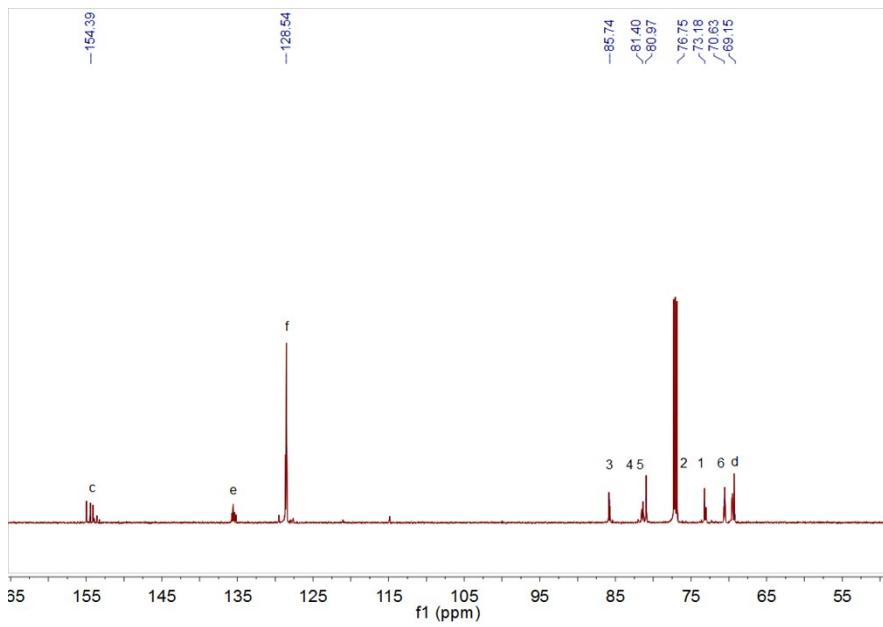


Fig. S42 The  $^{13}\text{C}$  NMR spectrum of PDIC ( $\text{CDCl}_3$ ).

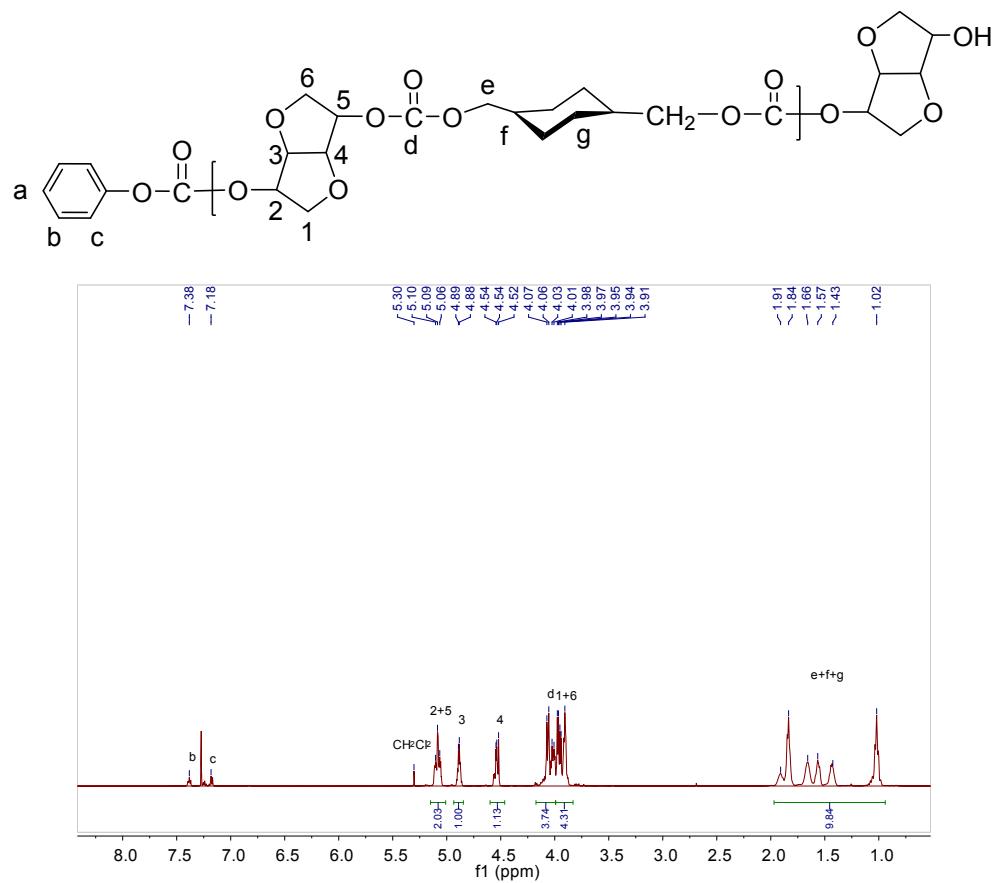


Fig. S43 The  $^1\text{H}$  NMR spectrum of PCIC ( $\text{CDCl}_3$ ).

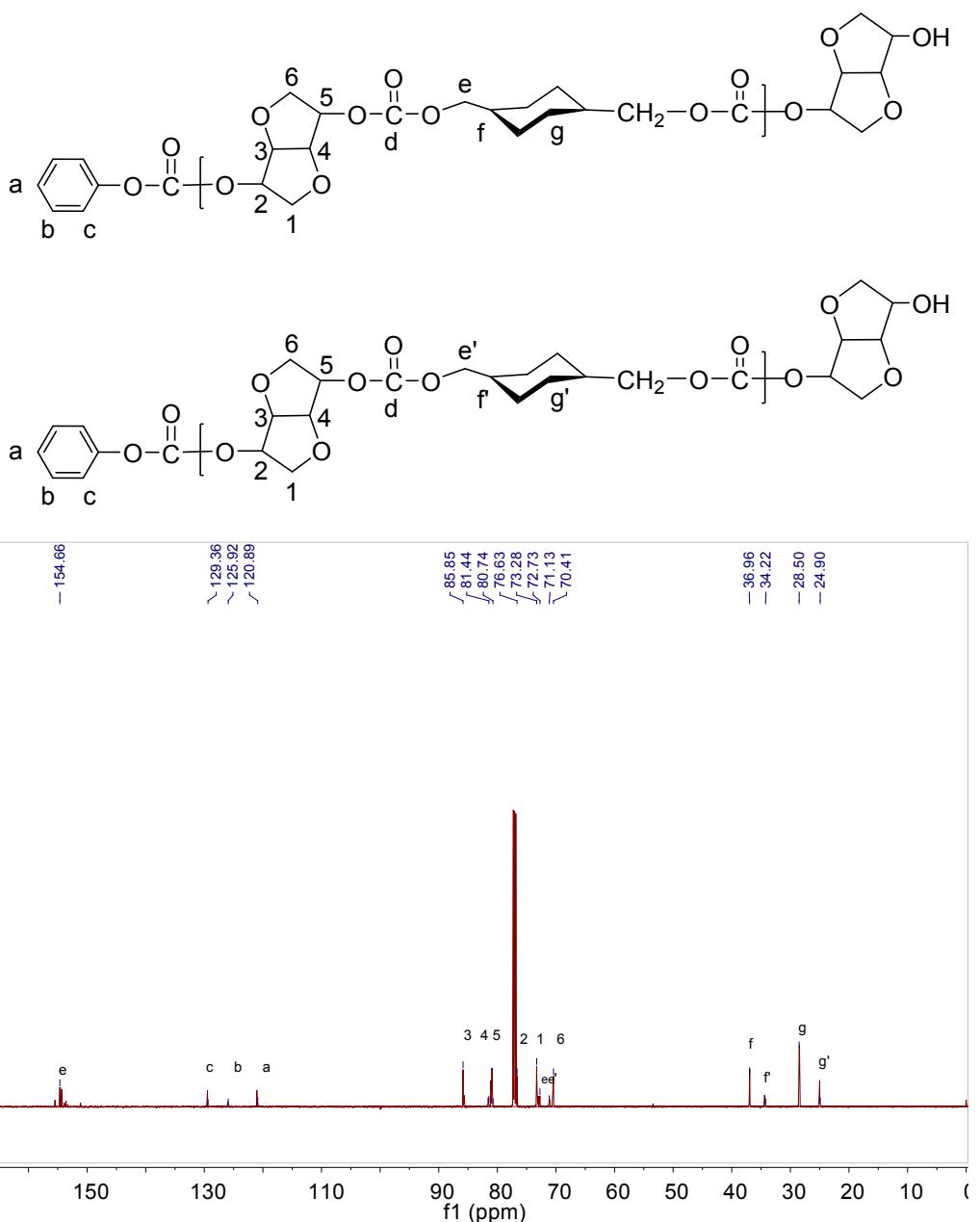


Fig. S44 The  $^{13}\text{C}$  NMR spectrum of PCIC ( $\text{CDCl}_3$ ).

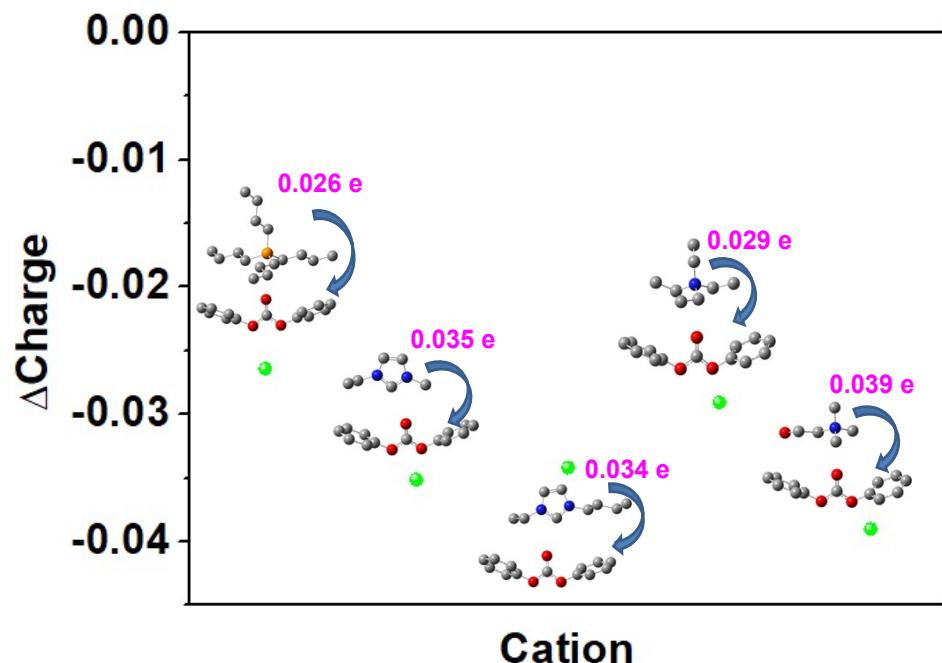


Fig. S45 Inductive effect of cations and DPC.