Supplementary Information (SI) for New Journal of Chemistry.

Supplementary Materials

Fluorine-decorated ionic liquid salts used for the efficient transformation of low concentration CO_2

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Experimental Section

Materials

The commonly used solvents such as dichloromethane and toluene were distilled over CaH_2. The typical reagents and substrates including epichlorohydrin, 1,2-epoxyhexane, styrene oxide, allyl glycidyl ether, butyl glycidyl ether, phenyl ether, azobisisobutyronitrile (AIBN), carbontetrabromide, α,α'-dibromo-p-xylene, 1,4-Bis(hydroxymethyl)-2,3,5,6-tetrafluorobenzene, N-bromosuccinimide (NBS), 1-methylimidazole, tricyclohexylphosphine (TCP), tributylphosphine (TBP), and triphenylphosphine (TPP) were purchased from the Shanghai Aladdin Bio-Chem Technology Co., Ltd and other company with high purity and can be used directly without further purification.

Catalysts Preparation

Synthesis of 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene. Accordingly, 1,4-Bis(hydroxymethyl)-2,3,5,6-tetrafluorobenzene (5.71 mmol) dissolved in CH_2Cl_2 (50 mL) was cooled to about 0 °C, carbon tetrabromide (14.26 mmol) and triphenylphosphine (14.26 mmol) were added. Then the mixture were allowed to warm to room temperature and stirred for 24 h.[1] The solvent was removed and the crude mixture was purified by flash chromatography (n-hexane). The product was obtained as a white crystalline solid in 92.6% yield. ^1H NMR (400 MHz, Chloroform-*d*) δ 4.55 (s, 4H).

Synthesis of F-IL-Im. 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (1.23 g, 5 mmol) and imidazole (3.40 g, 50 mmol) dissolved in methanol (60 mL) were heated and refluxed for 24 h. Methanol was removed under vacuum and the colorless syrup left was redissolved in aqueous K_2CO_3 (6.5 g, 100 mL). Upon the resulted crystalline was filtered, washed with water (3×20 mL), and dried in vacuum for 24 h.[2] The product F-IL-Im was obtained as a white precipitate with 88.9% yield. ^1H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.86 – 7.73 (m, 2H), 5.71 (s, 2H), 3.89 (s, 3H).

Synthesis of F-IL-TPP. 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (1.23

g, 5 mmol) and triphenylphosphinc (1.049 g, 0.004 mmol) dissolved in dichloromethane. The mixture was allowed to stir at room temperature for 24 hours to obtain the phosphinium salt. Remove the solvent under pressure and collect the residue and wash with acetone to remove unreacted material. Filter the residue and dry to obtain the product. The product was obtained as a white precipitate of dicationic imidazolium salt with 86% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.86 – 7.73 (m, 2H), 5.71 (s, 2H), 3.89 (s, 3H).

Synthesis of F-IL-TBP. 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (0.671 g, 2 mmol) and tributylphosphine (0.8 g, 4 mmol) were slowly added to DMF (30 ml) and refluxed for 1h[3]. During this time a white precipitate formed. The mixture was cooled to room temperature and the precipitate was filtered and washed with petrol (40-60 °C) (3 × 100 ml) then dried for 24 h to give the title compound (0.83 g, 60%) as a white crystalline solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.86 – 7.73 (m, 2H), 5.71 (s, 2H), 3.89 (s, 3H).

Synthesis of F-IL-TCP. 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene (0.671 g, 0.002 mmol) and tricyclohexylphosphine (1.12 g, 0.004 mmol) dissolved in dichloromethane was allowed to stir at room temperature for 24 hours under N_2. The solvent was removed under vacuum, the residue was collected and washed with ether to remove unreacted material. The product was filtered, dried, and obtained with 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.86 – 7.73 (m, 2H), 5.71 (s, 2H), 3.89 (s, 3H).

Synthesis of IL-Im. Similarly, to the solution of α,α-dibromo-p-xylene (2.64 g, 10 mol) in dichloromethane, 1-methylimidazole (1.85 g, 22.5 mol) was added and the mixture was allowed to stir for 24 h at room temperature to afford the imidazolium salt. The solvent was removed and the residue collected after washed with acetone three times. The product was filtered, dried, and obtained as a white powder with 85.7% yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 4.55 (s, 4H).

Synthesis of IL-TPP. Dissolve α,α'-dibromo-p-xylene (0.528 g, 0.002 mmol) and triphenylphosphinc (1.049 g, 0.004 mmol) in distilled dichloromethane. Stir the reaction mixture for 24 hours at room temperature to obtain the quatemised salt.

Remove the solvent under pressure and collect the residue and wash with acetone to remove unreacted material. After dried under vacuum for 24 h, the was obtained as a white precipitate of dicationic imidazolium salt with 86% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.86 – 7.73 (m, 2H), 5.71 (s, 2H), 3.89 (s, 3H).

Synthesis of IL-TBP. α,α'-dibromo-p-xylene (0.528 g, 2mmol) and tributylphosphine (0.8 g, 4 mmol) were slowly added to DMF (30ml) and refluxed for 1h. During this time a white precipitate formed. The mixture was cooled to room temperature and the precipitate was filtered and washed with petrol (40-60°C)(3 × 100 ml) then dried for 24 h to give the title compound (1.02 g, 83 %) as a white crystalline solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.86 – 7.73 (m, 2H), 5.71 (s, 2H), 3.89 (s, 3H).

Synthesis of IL-TCP. α,α'-dibromo-p-xylene (0.528 g, 0.002 mmol) and tricyclohexylphosphine (1.12g, 0.004 mmol) was dissolved in distilled dichloromethane. Stir the reaction mixture for 24 hours at room temperature to obtain the quatemisedsalProtected by $N_{2.}$ Remove the solvent under pressure and collect the residue an wash with ether to remove unreacted material. The product was filtered, dried, and obtained with 72% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.31 (s, 1H), 7.86 – 7.73 (m, 2H), 5.71 (s, 2H), 3.89 (s, 3H).

Catalytic activity test

Typically, epoxide (10 mmol) and the corresponding catalyst (0.1 mol% relative to epoxide) was stirred at a preset temperature for 48 h in a 25 mL Schlenk tube equipped with CO_2 in balloon (1 atm). The conversion and selectivity were determined by ^{1}H NMR spectroscopy. For catalytic evaluation under low CO_2 concentration, 15% CO_2 mixed with 85% N_2 in volume was used and other conditions are the same with the pure CO_2 conditions.

Recyclability investigation of catalysts

Typically, epoxide (10 mmol) and the corresponding catalyst (0.1 mol% relative to epoxide) was stirred at a preset temperature for 36 h in a 25 mL Schlenk tube equipped with CO_2 in balloon (1 atm). The conversion and selectivity were determined by ^1H NMR spectroscopy. After the reaction, ethyl acetate was added into the mixture and the catalyst was precipitated and separated. After washed with ethyl acetate and dried under vacuum overnight, the catalyst was reused for the next catalytic run at the same reaction conditions.

Characterization

CO_2 sorption isotherms were collected from Micromeritics ASAP2010 at 298 K and 273 K under the pressure of 1 atm CO_2. Before the measurement, the samples were treated under vacuum at 100 °C for 12 h. The Fourier transform infrared (FTIR) spectra were measured on a Nicolet iS10 (Thermo Fisher, Waltham, USA) IR spectrometer in the range of 400-4000 cm^{-1}. Thermal gravimetric analysis (TGA) experiments were performed on a SDT Q600 V8.2 Build100 thermogravimetric analyzer under N_2 flow. ^1H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts were expressed in ppm downfield from TMS at $\delta = 0$ ppm.

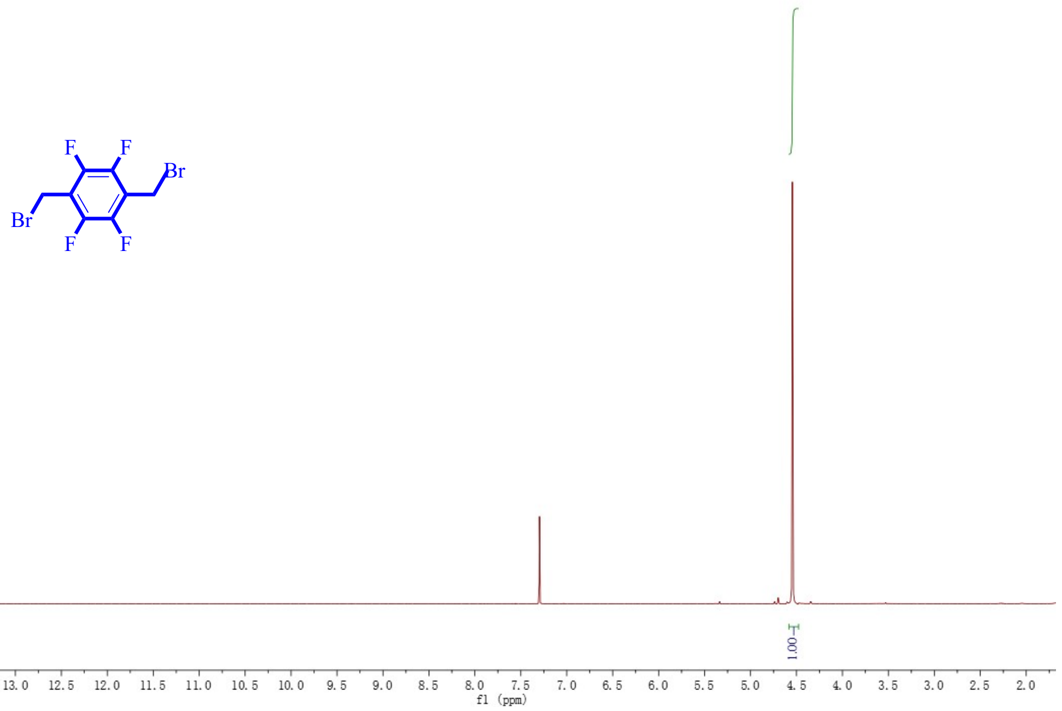


Fig. S1. ^{1}H NMR spectrum of the 1,4-bis(bromomethyl)-2,3,5,6-tetrafluorobenzene.

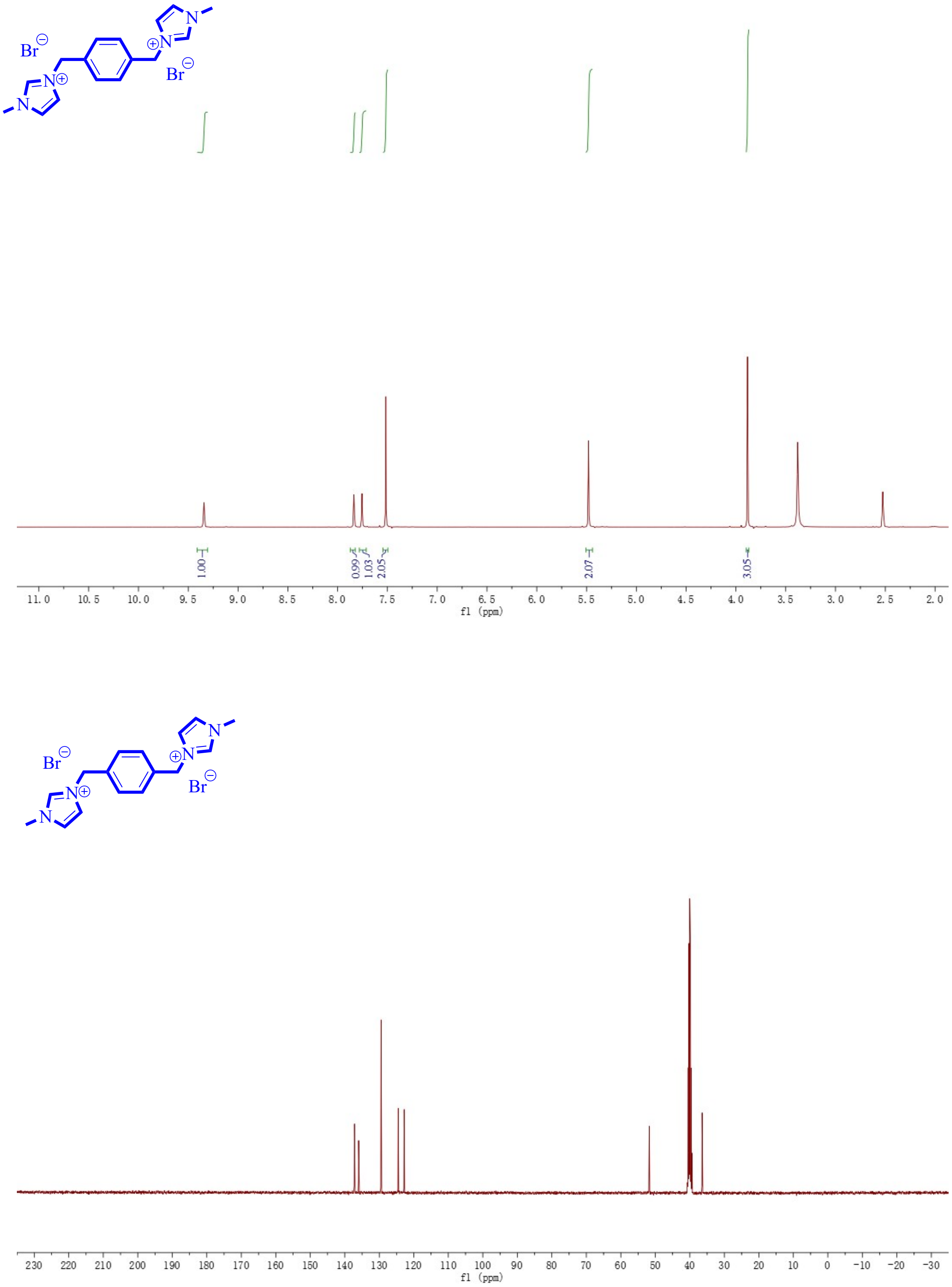


Fig. S2. ^{1}H NMR and ^{13}C NMR spectrum of the IL-Im.

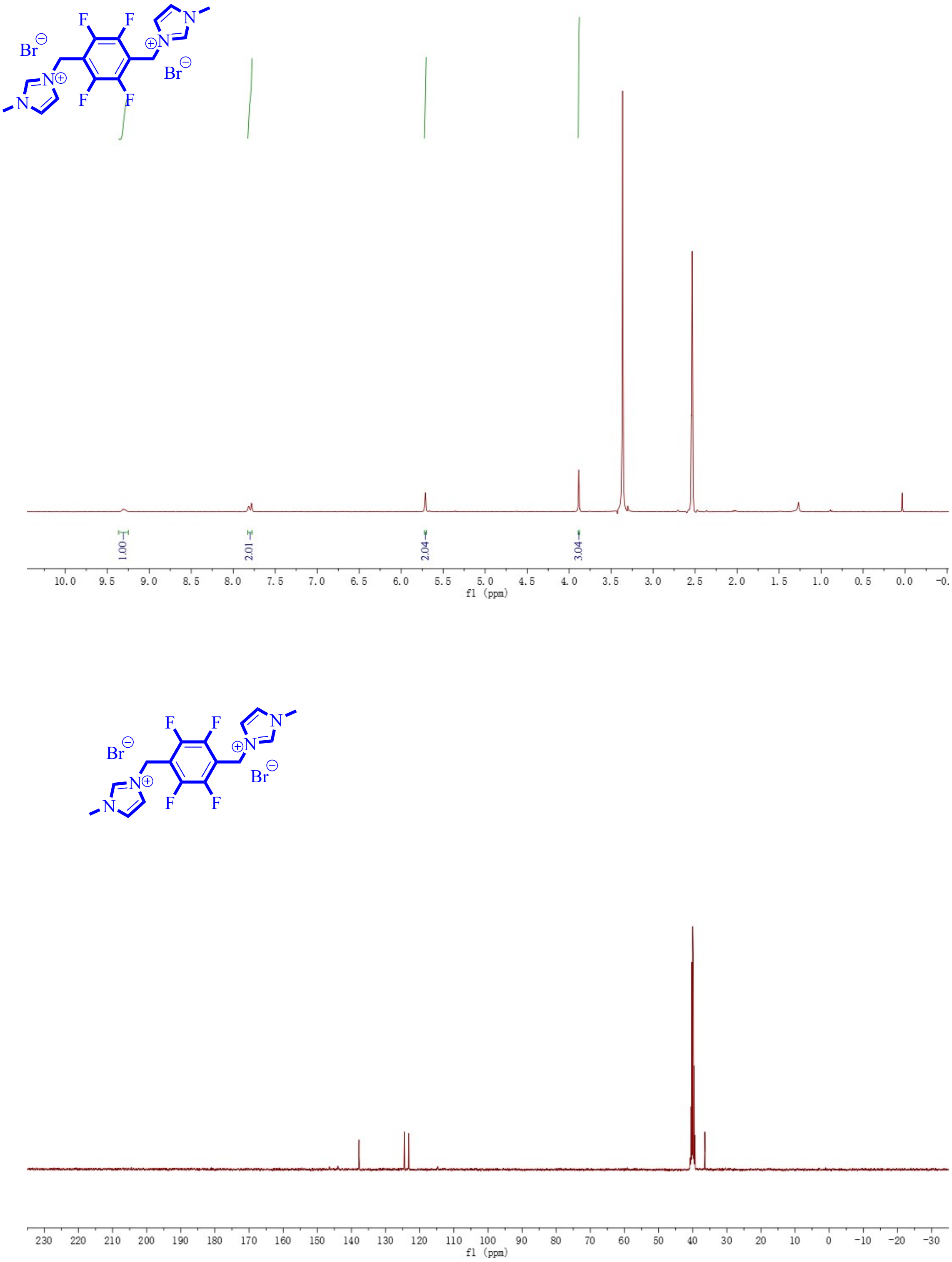


Fig. S3. ^{1}H NMR and ^{13}C NMR spectrum of the F-IL-Im.

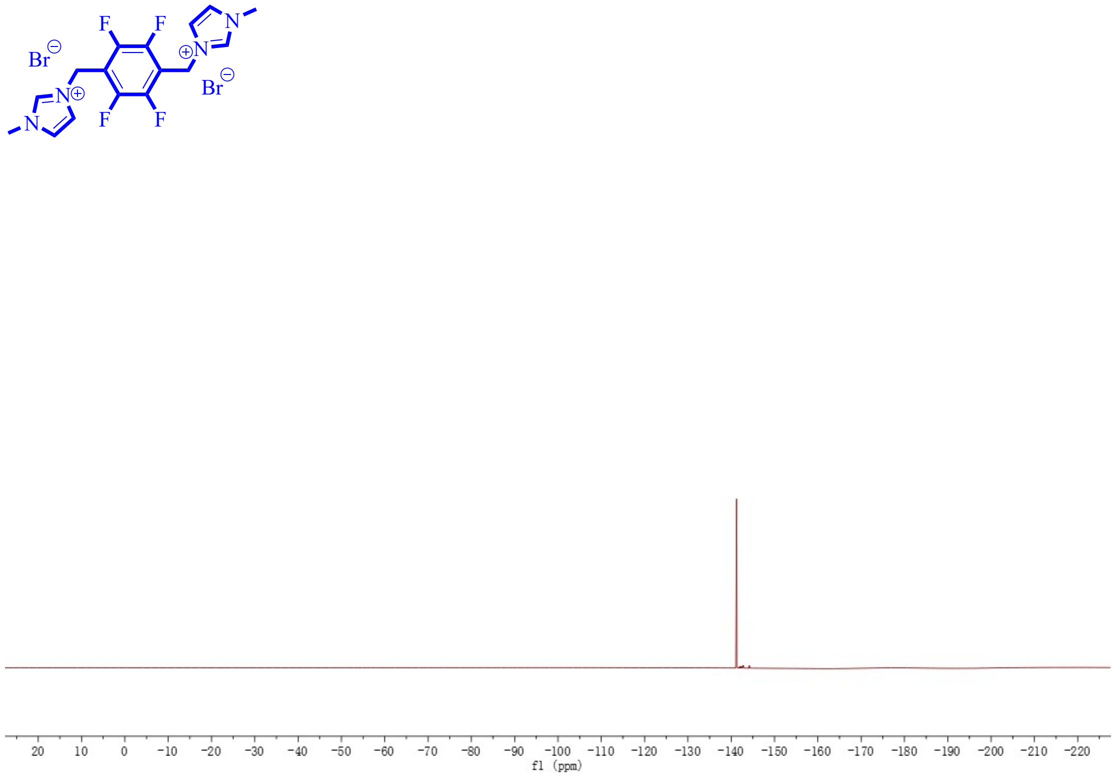


Fig. S4. ^{19}F NMR spectrum of the F-IL-1-Im.

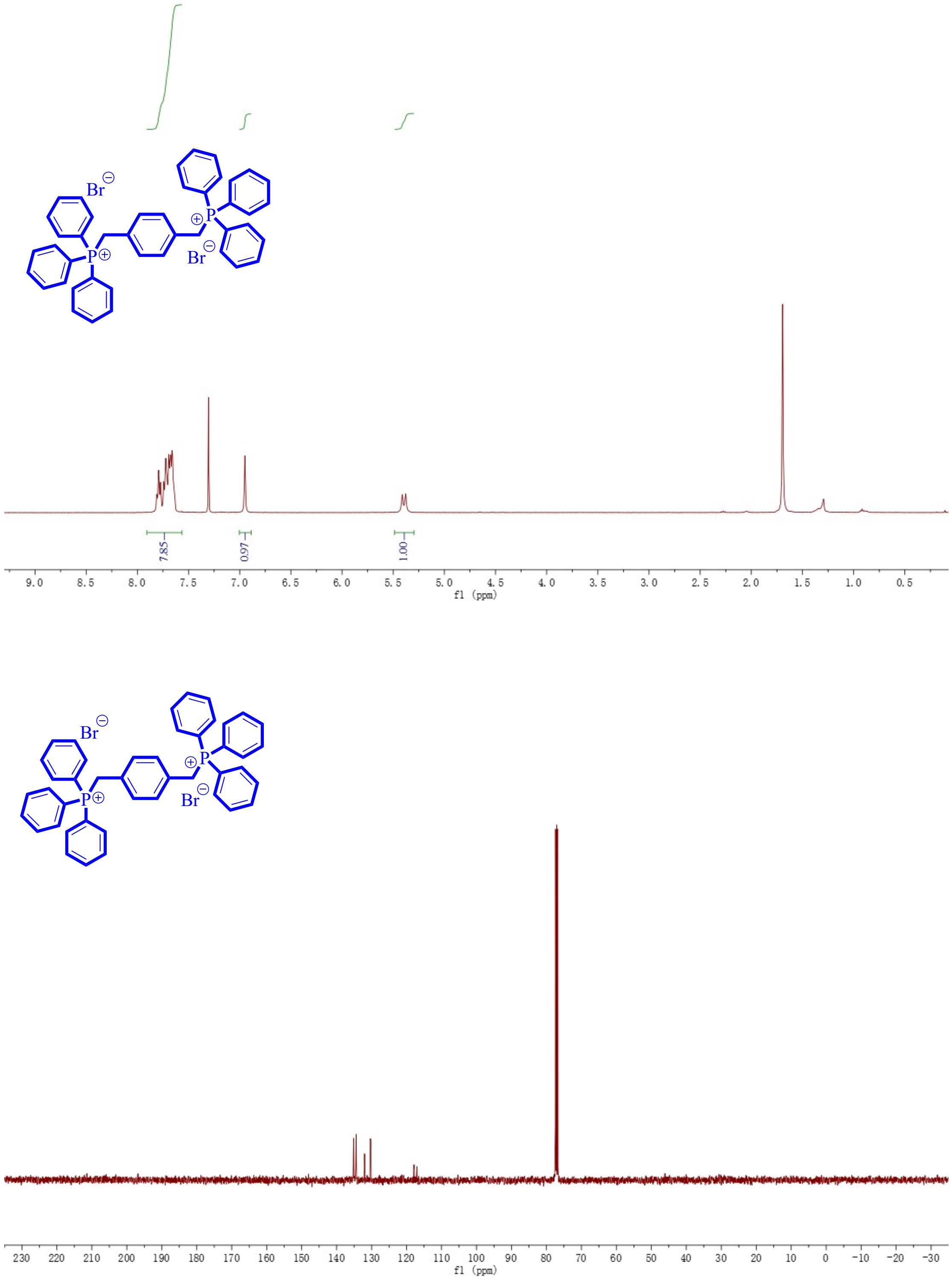


Fig. S5. ^{1}H NMR and ^{13}C NMR spectrum of the IL-TPP.

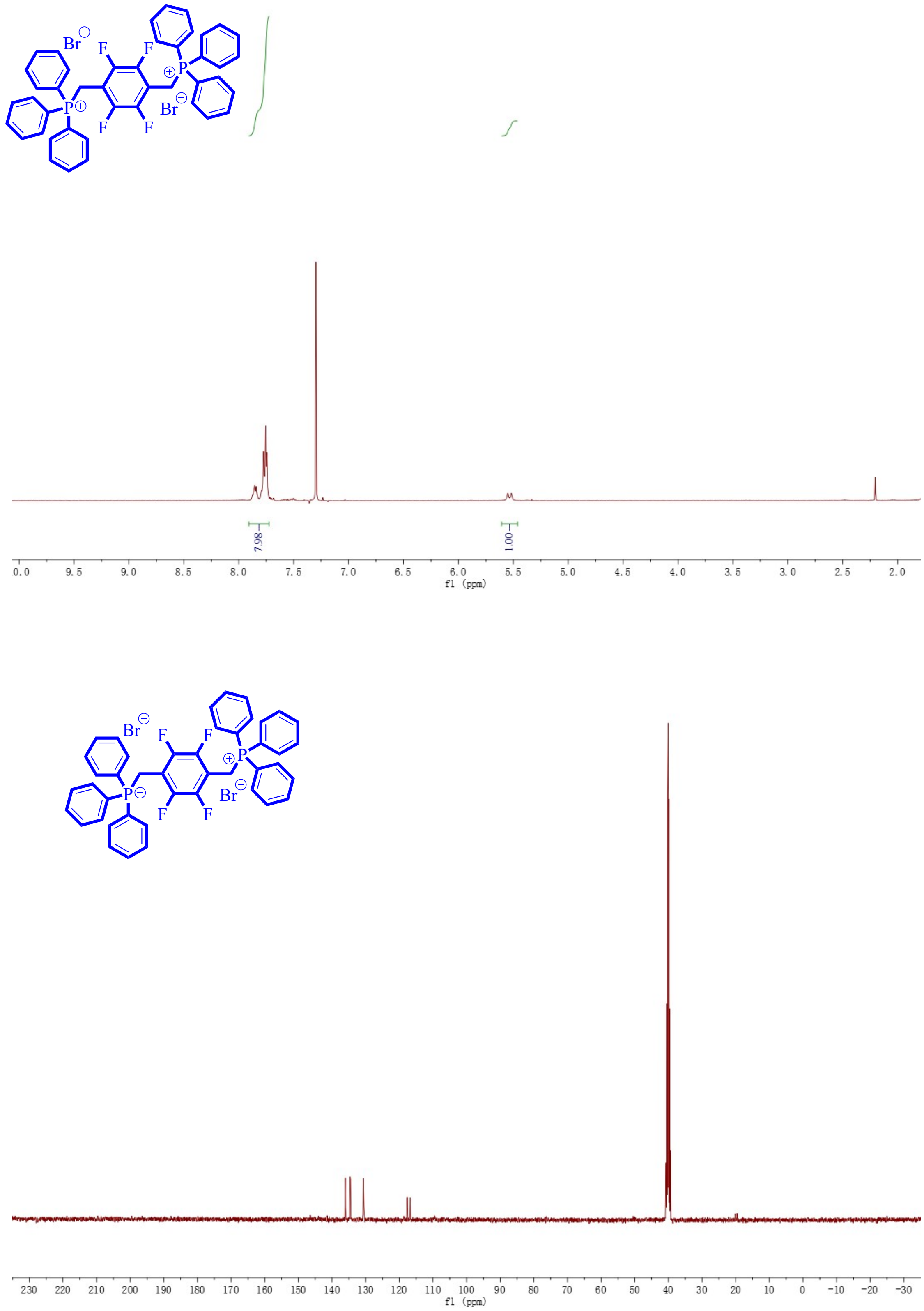


Fig. S6. ^{1}H and ^{13}C NMR spectrum of the F-IL-TPP.

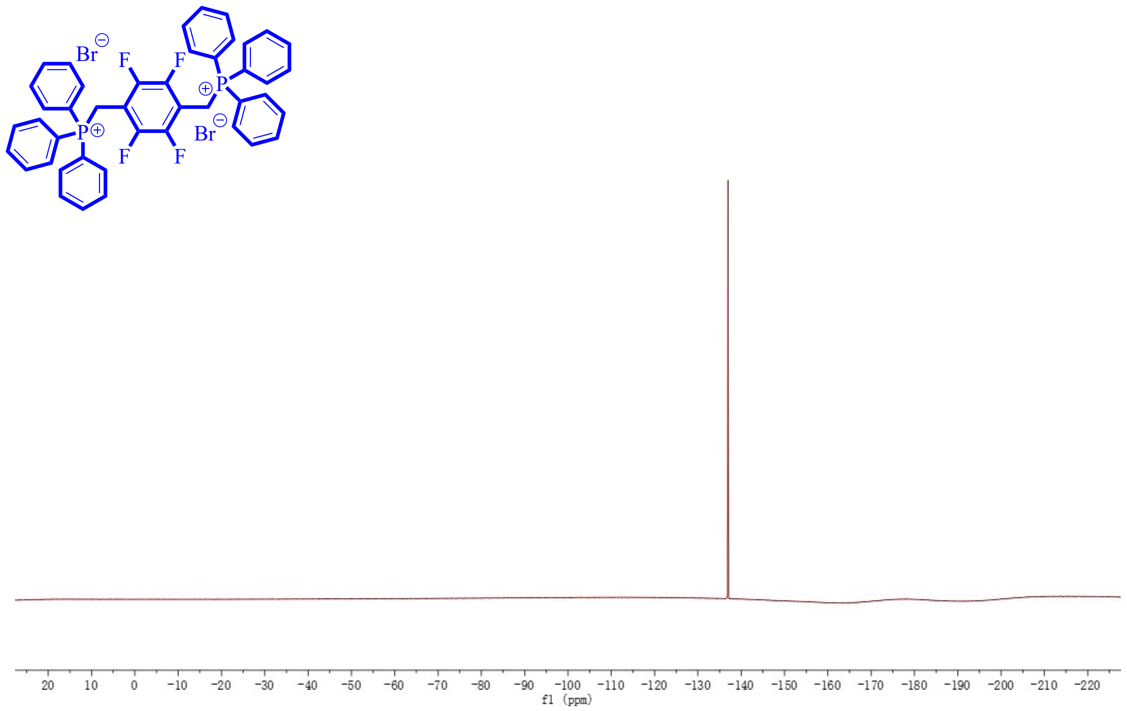


Fig. S7. ^{19}F NMR spectrum of the F-IL-TPP.

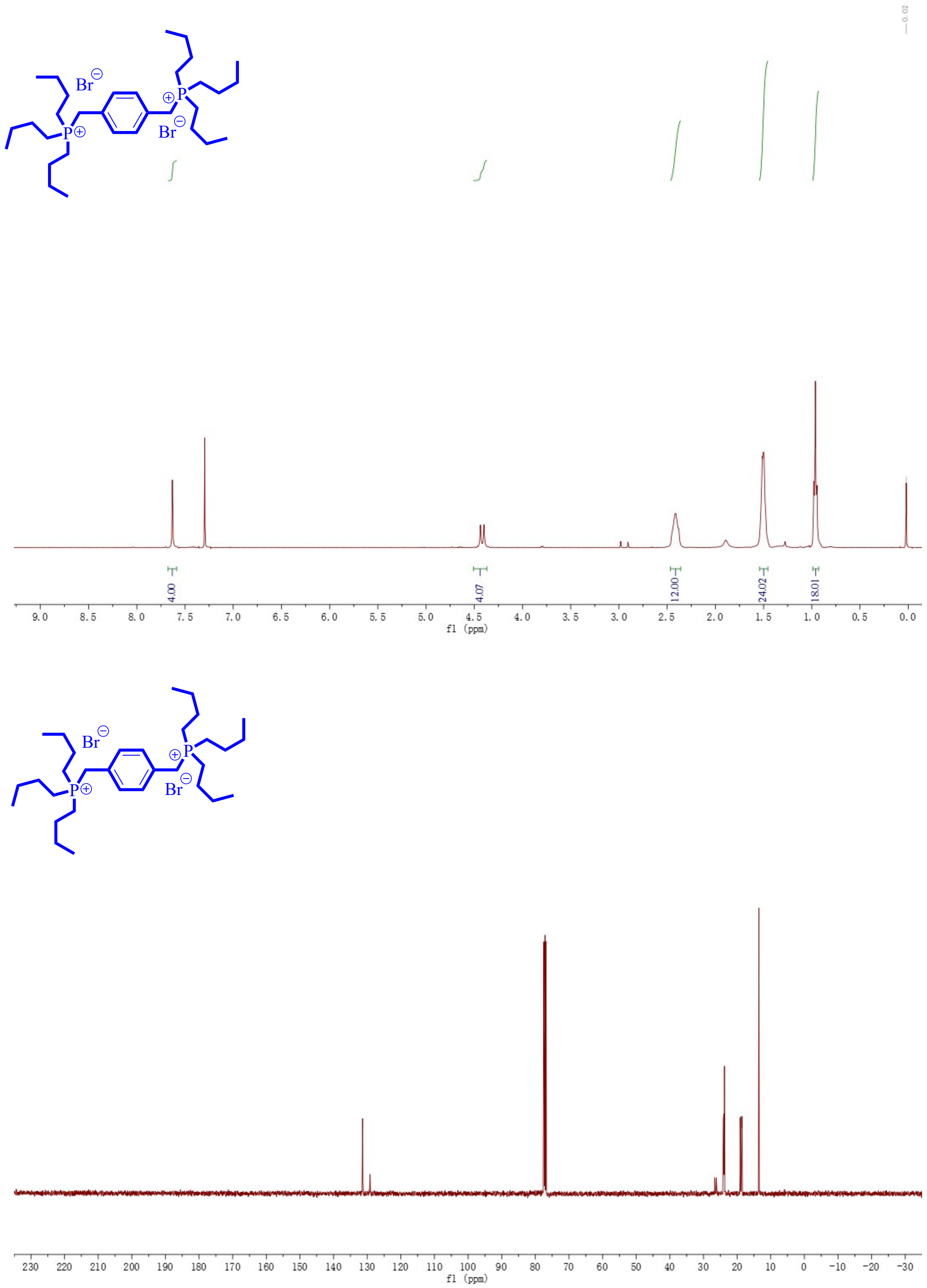


Fig. S8. ^{1}H NMR and ^{13}C NMR spectrum of the IL-TBP.

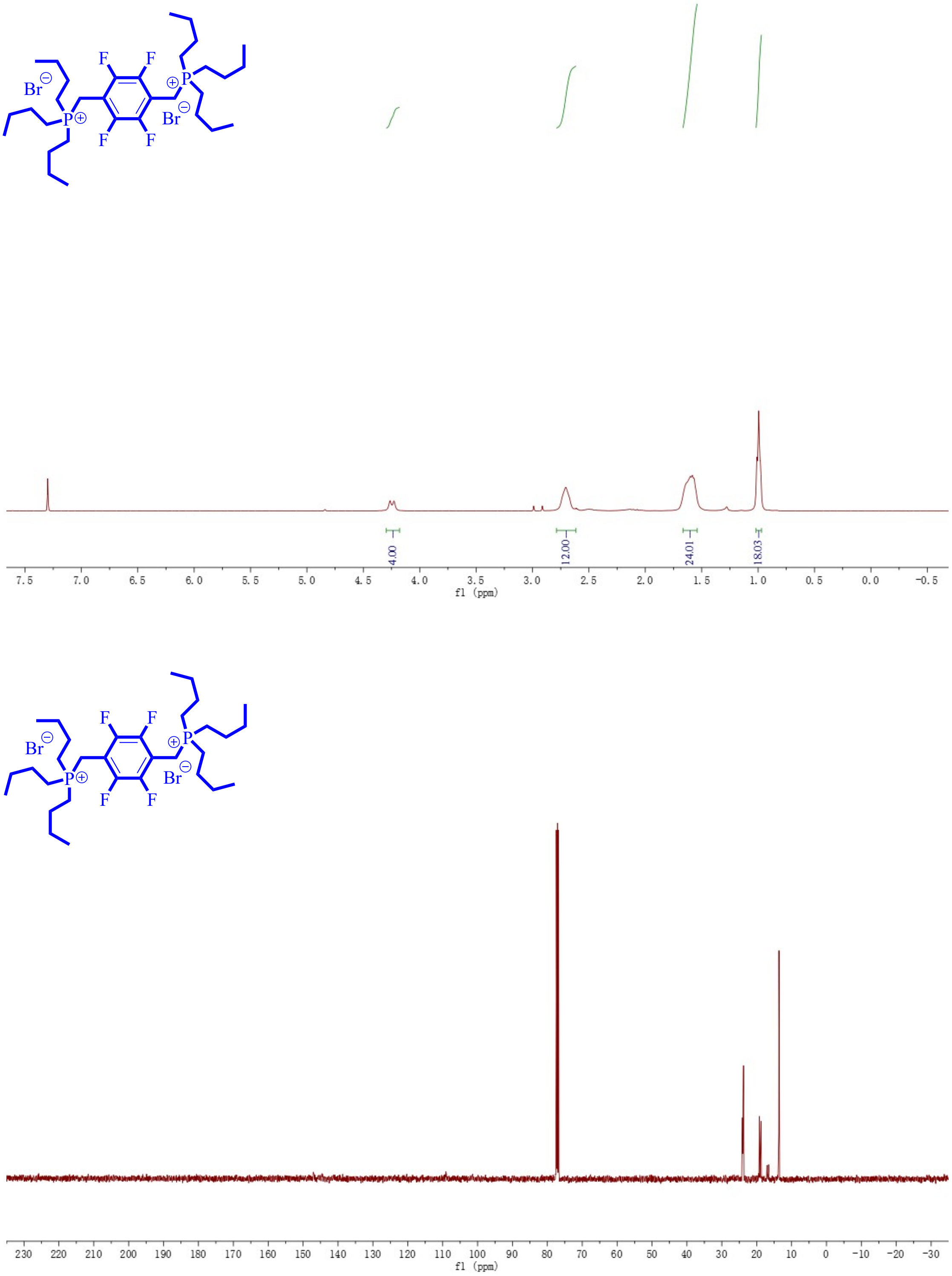


Fig. S9. ^{1}H and ^{13}C NMR spectrum of the F-IL-TBP.

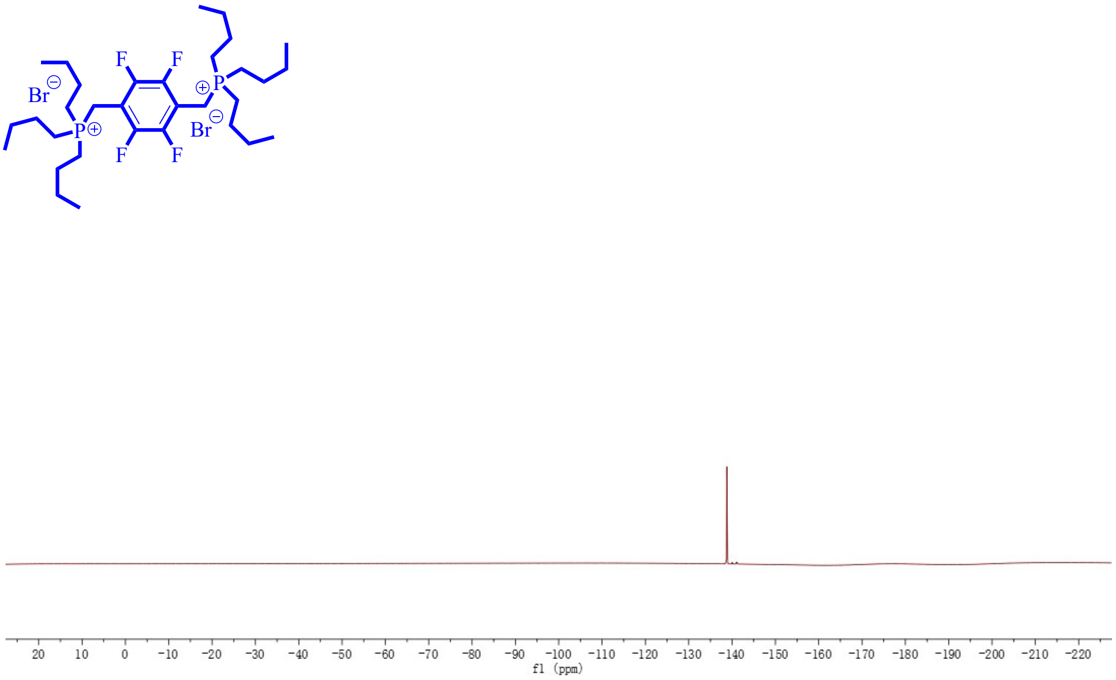


Fig. S10. ^{19}F NMR spectrum of the F-IL-TBP.

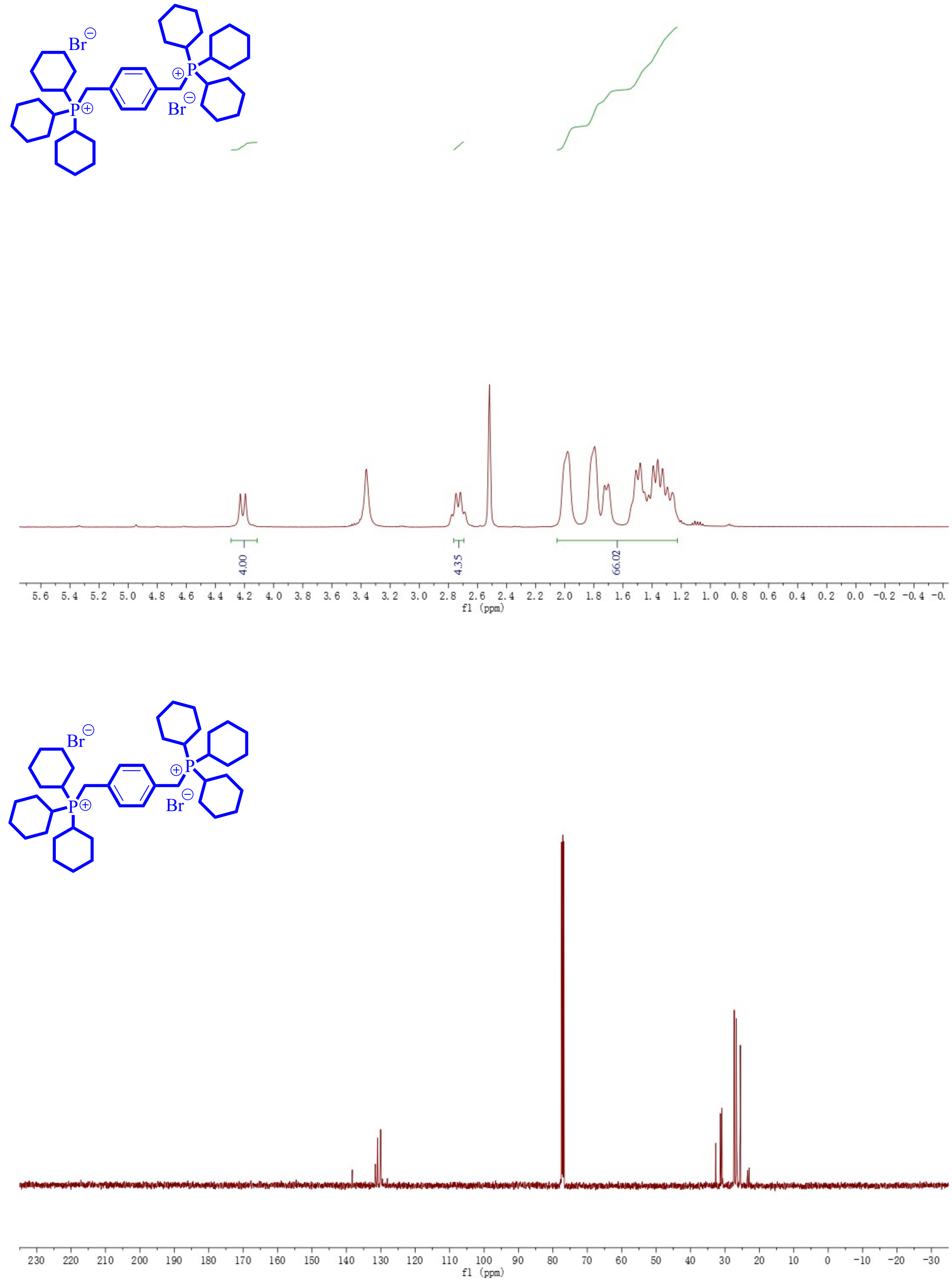


Fig. S11. ^{1}H and ^{13}C NMR spectrum of the IL-TCP.

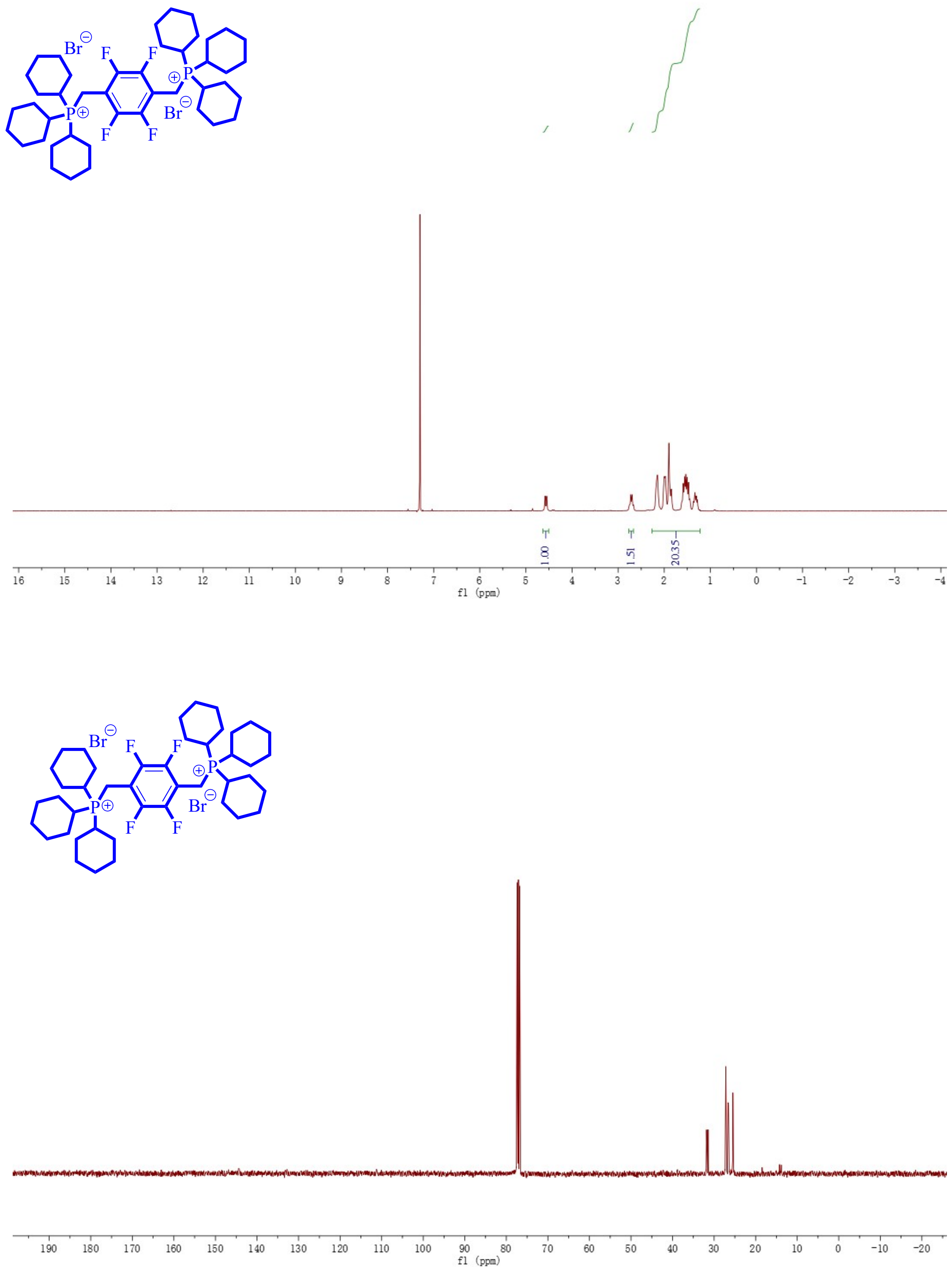


Fig. S12. ^{1}H and ^{13}C NMR spectrum of the F-IL-TCP

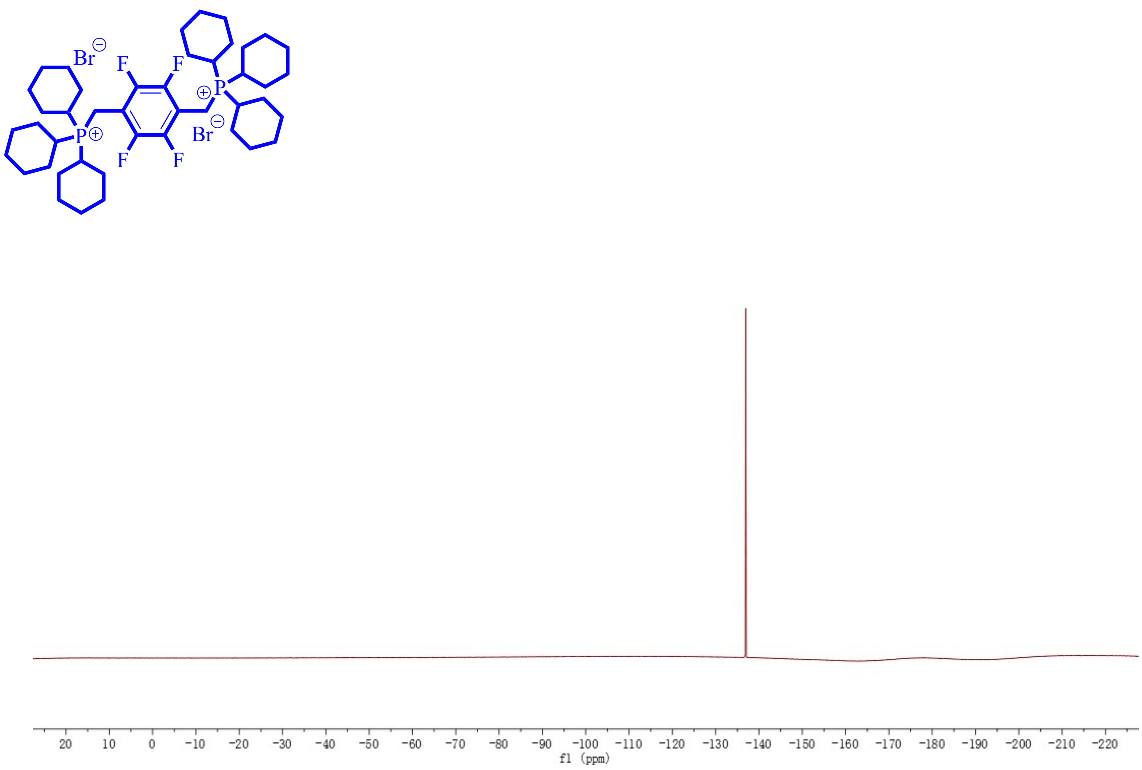


Fig. S13. ^{19}F NMR spectrum of the F-IL-TCP

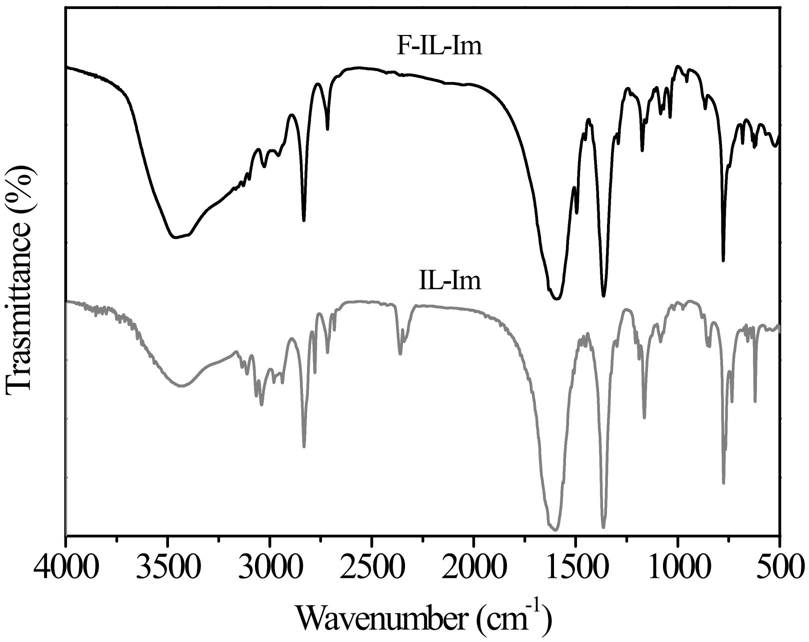


Fig. S14. FT-IR spectrum of the F-IL-Im and IL-Im.

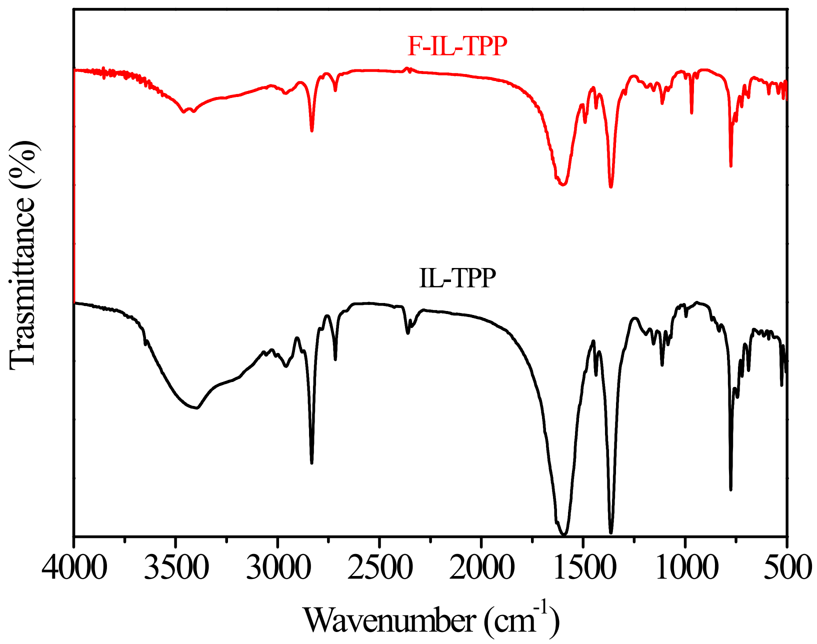


Fig. S15. FT-IR spectrum of the F-IL-TPP and IL-TPP.

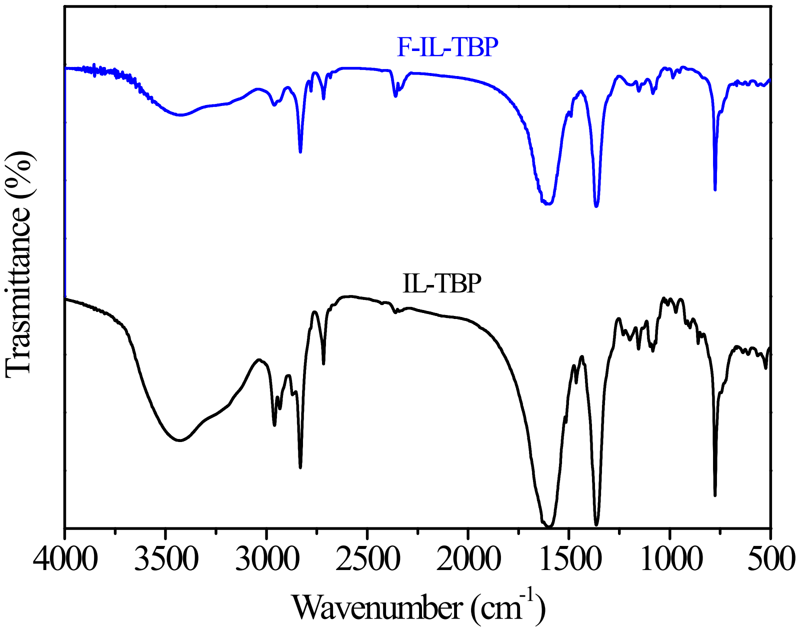


Fig. S16. FT-IR spectrum of the F-IL-TBP and IL-TBP.

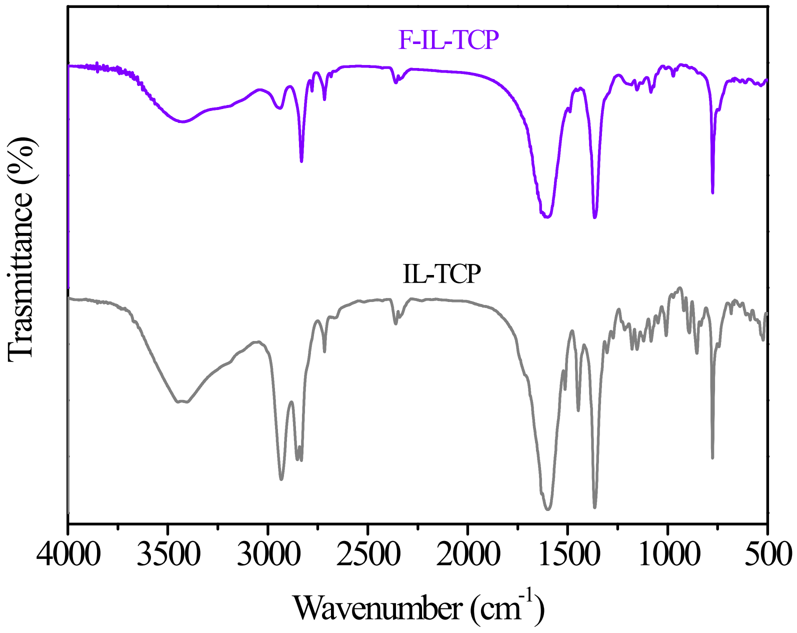


Fig. S17. FT-IR spectrum of the F-IL-TCP and IL-TCP.

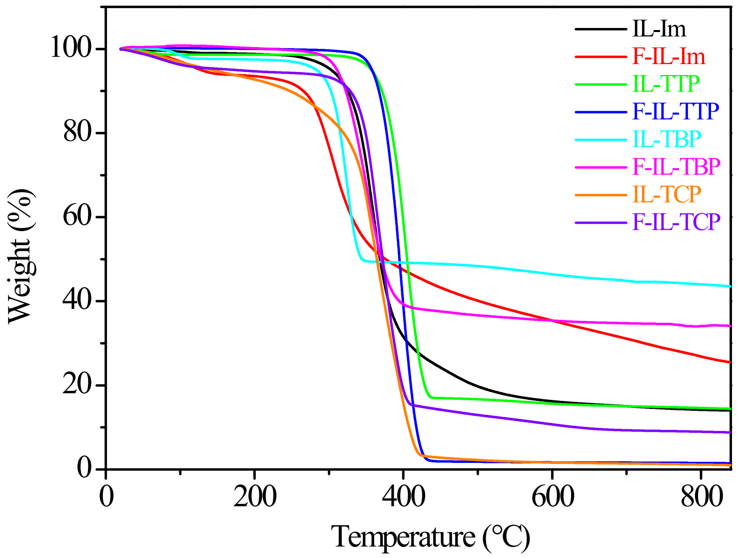


Fig. S18. TGA curves of the synthesized catalysts.

Table 1 entry 1:

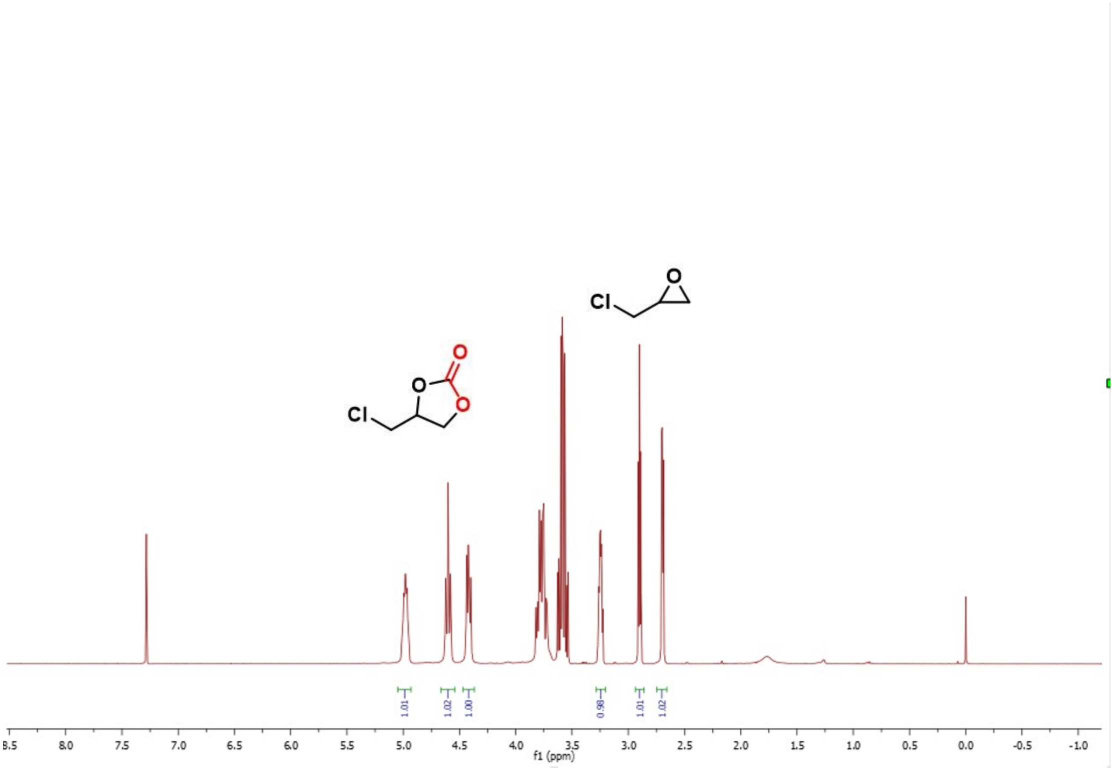


Table 1 entry 2:

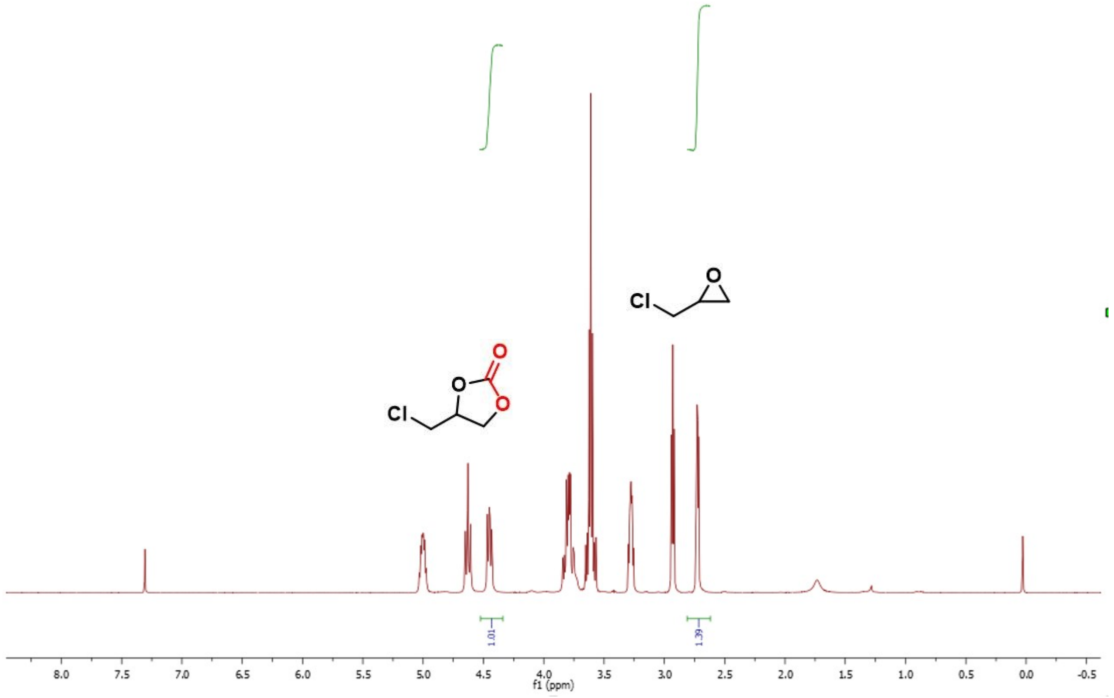
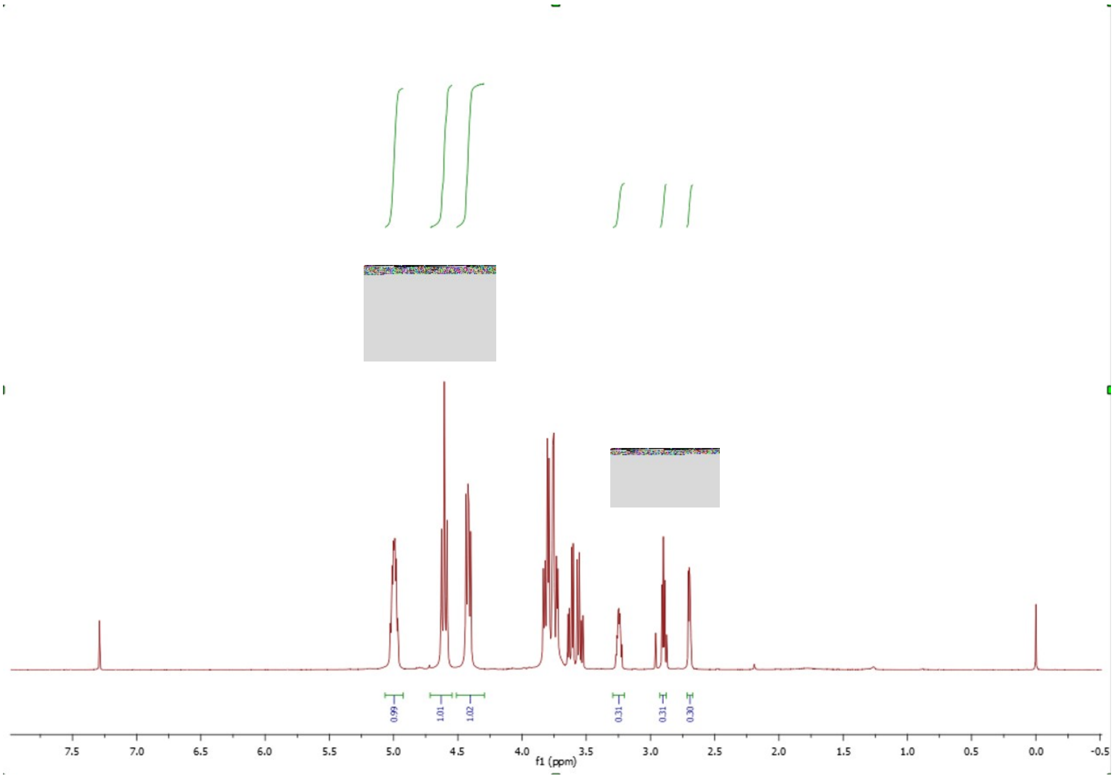


Table 1 entry 3:



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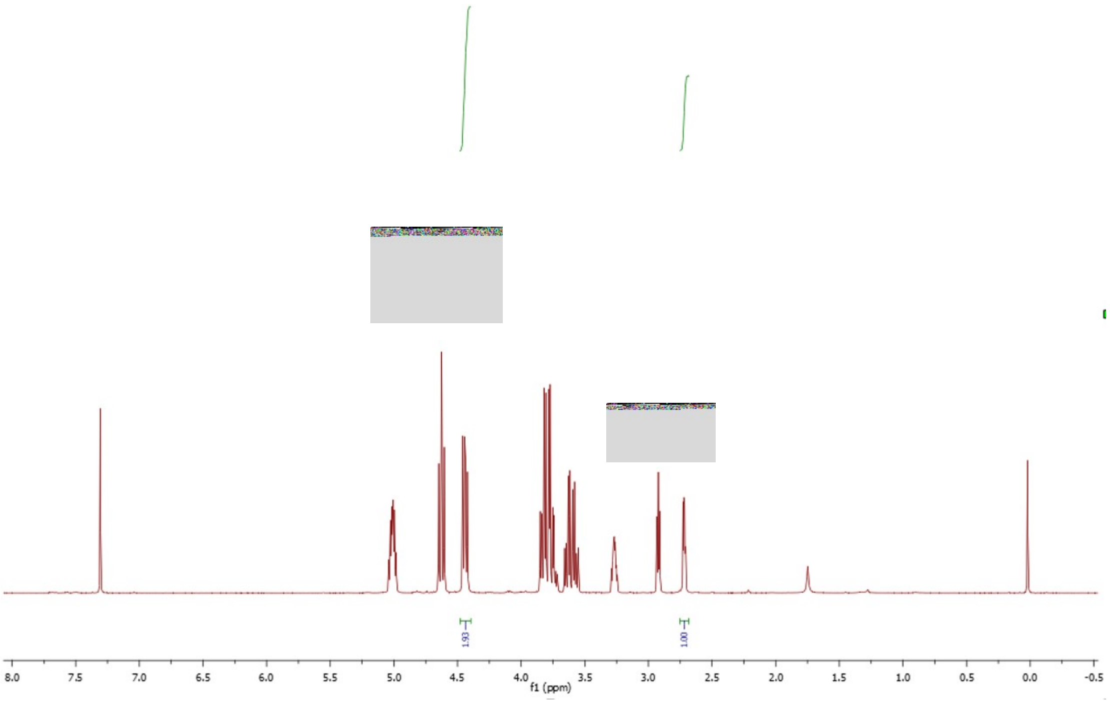

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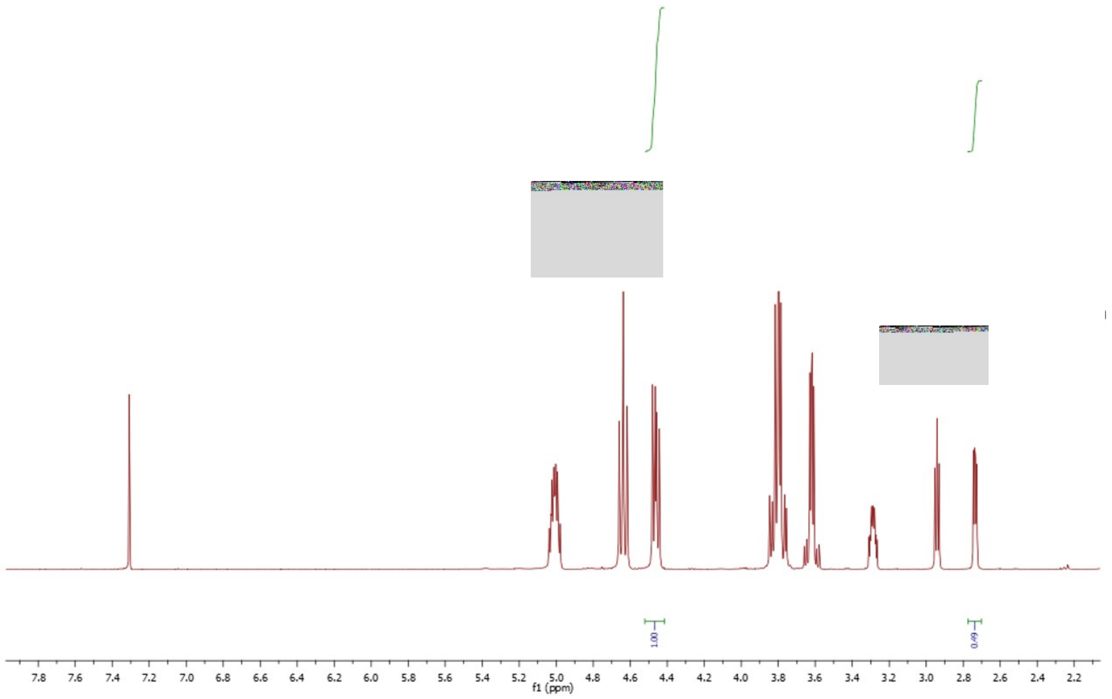

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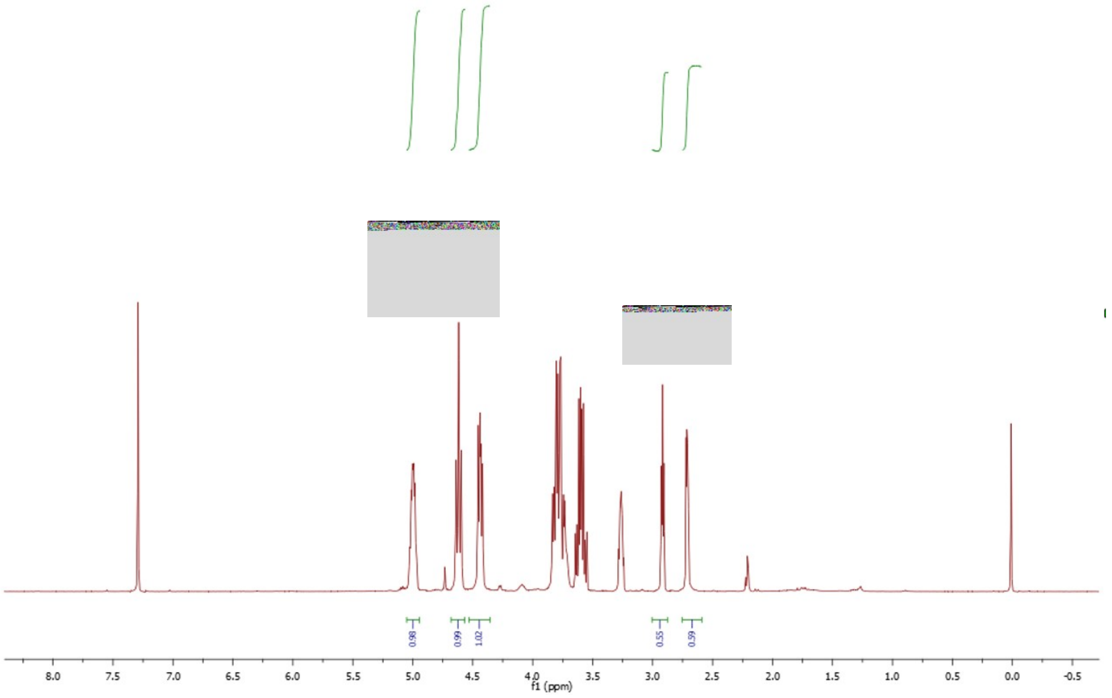

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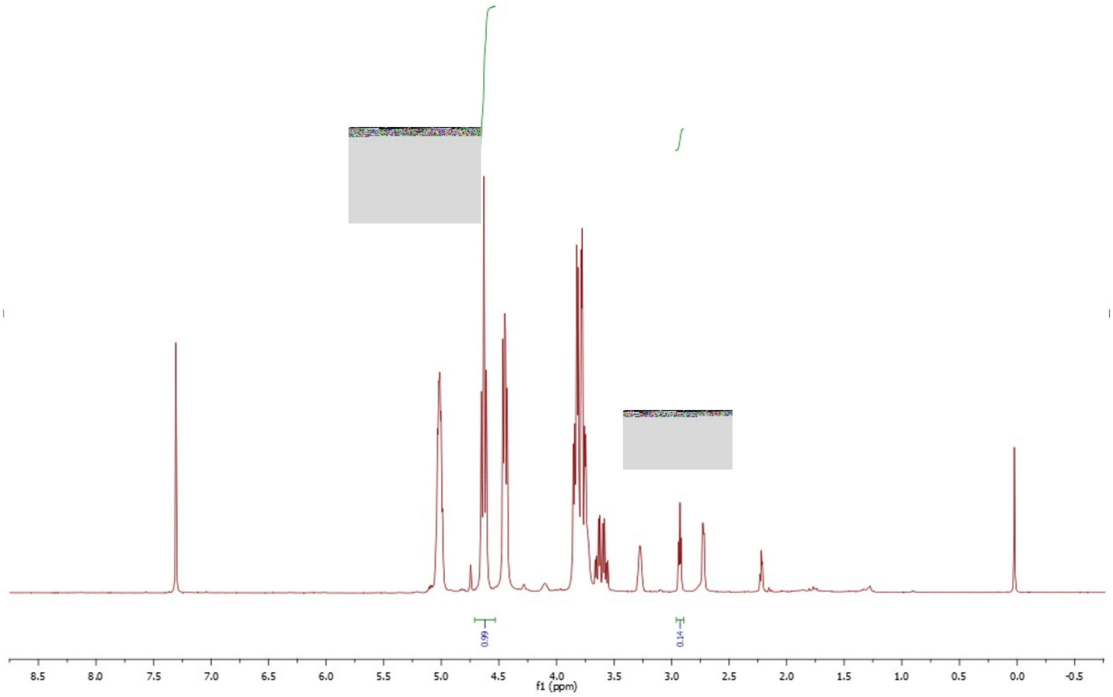

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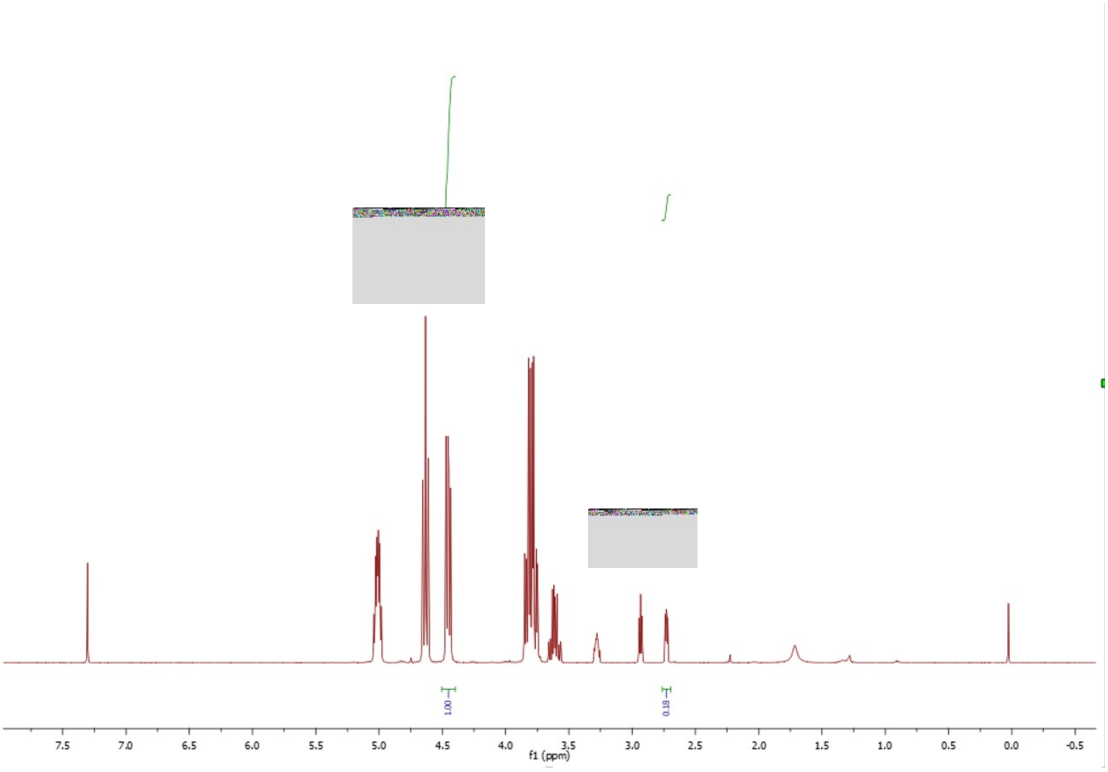


Figure S19. ^{1}H-liquid NMR of the reaction mixture in Table 1.

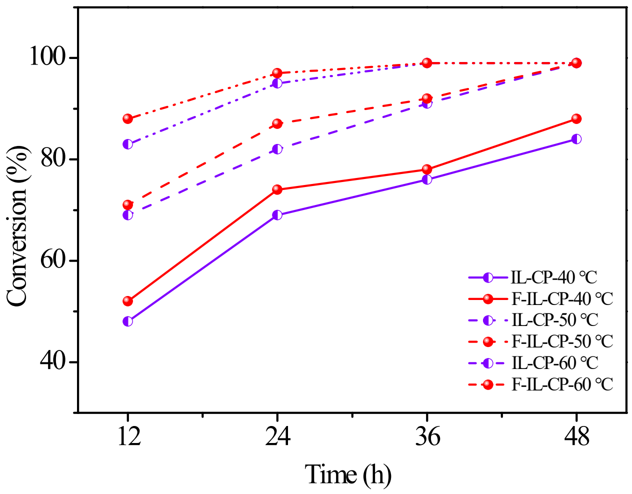
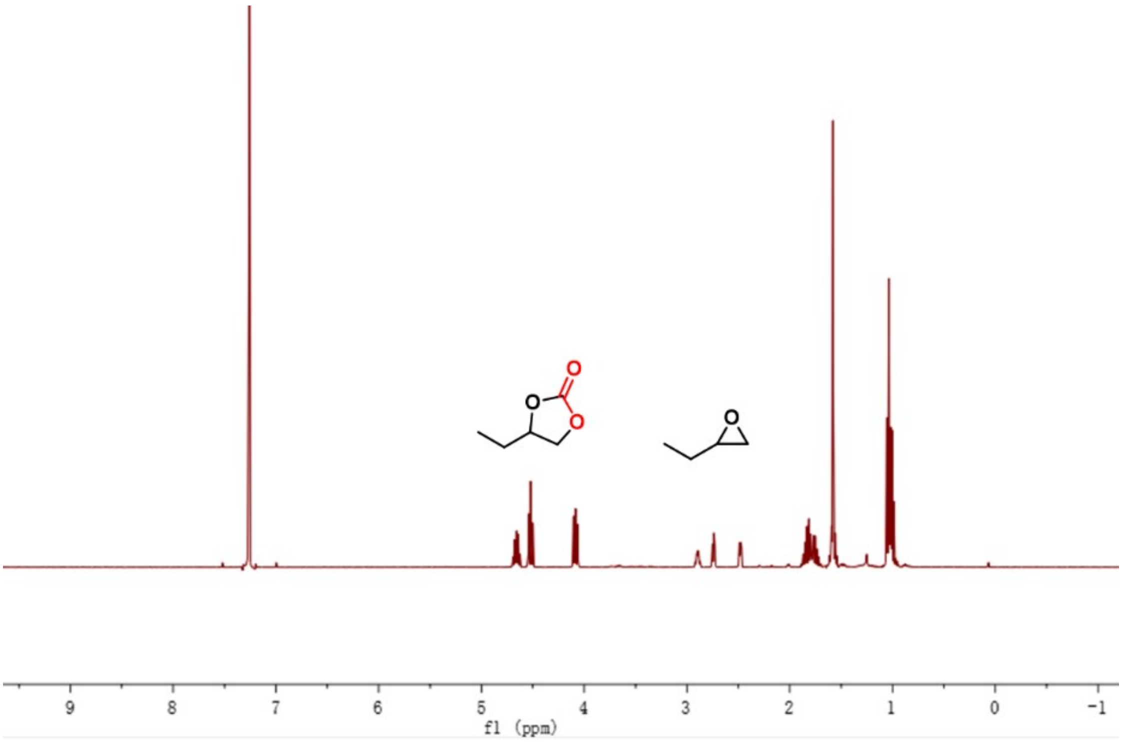


Figure S20. Effects of temperature and time on the catalytic performance of IL-CP and F-IL-CP. Conditions: epichlorohydrin (925 mg, 10 mmol), catalyst (0.11 mol%), CO_2 pressure (0.1 MPa).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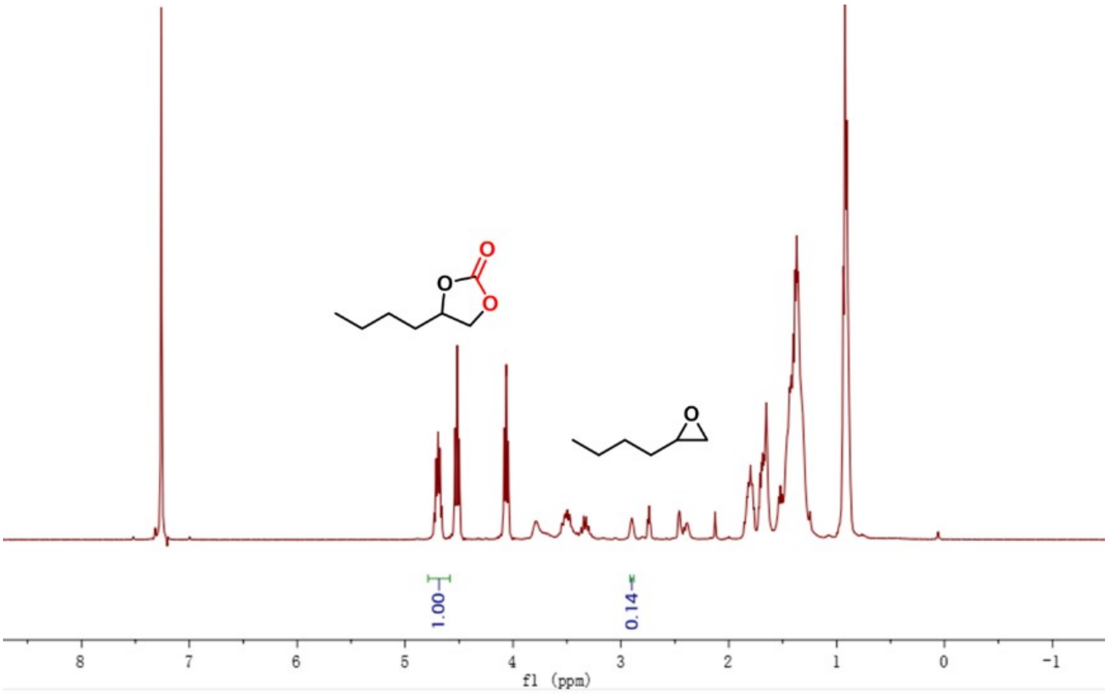
O
O
O
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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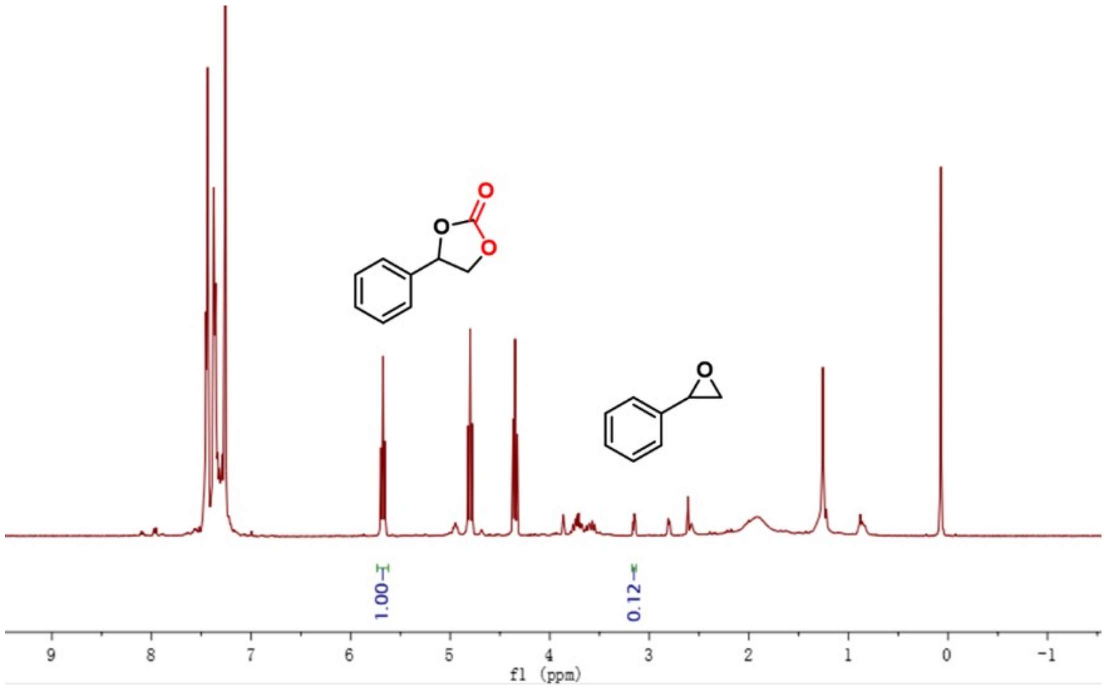
O
O
O
1.00
0.14
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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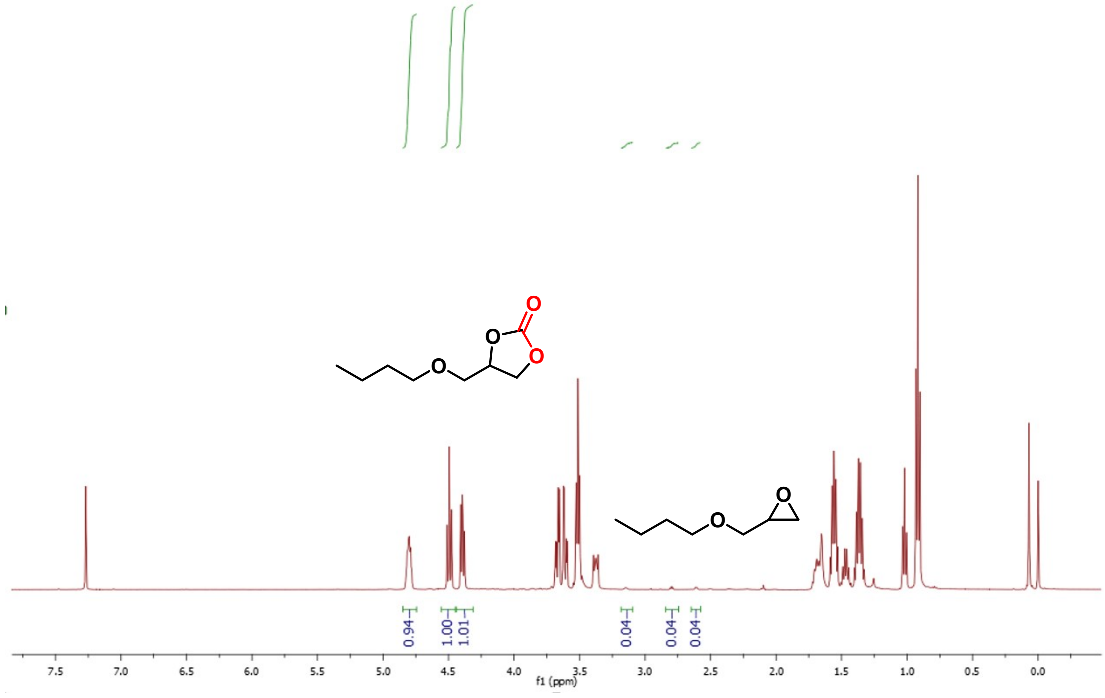
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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1.00
1.01
0.04
0.04
0.04
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

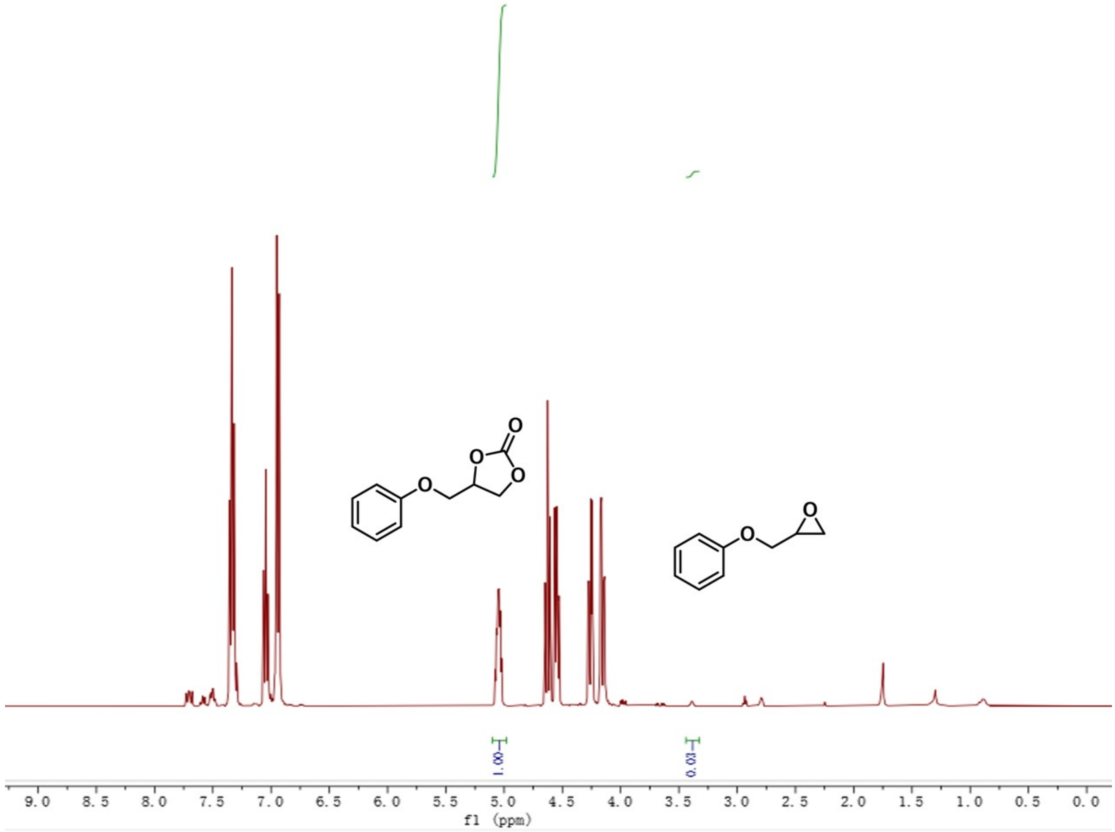
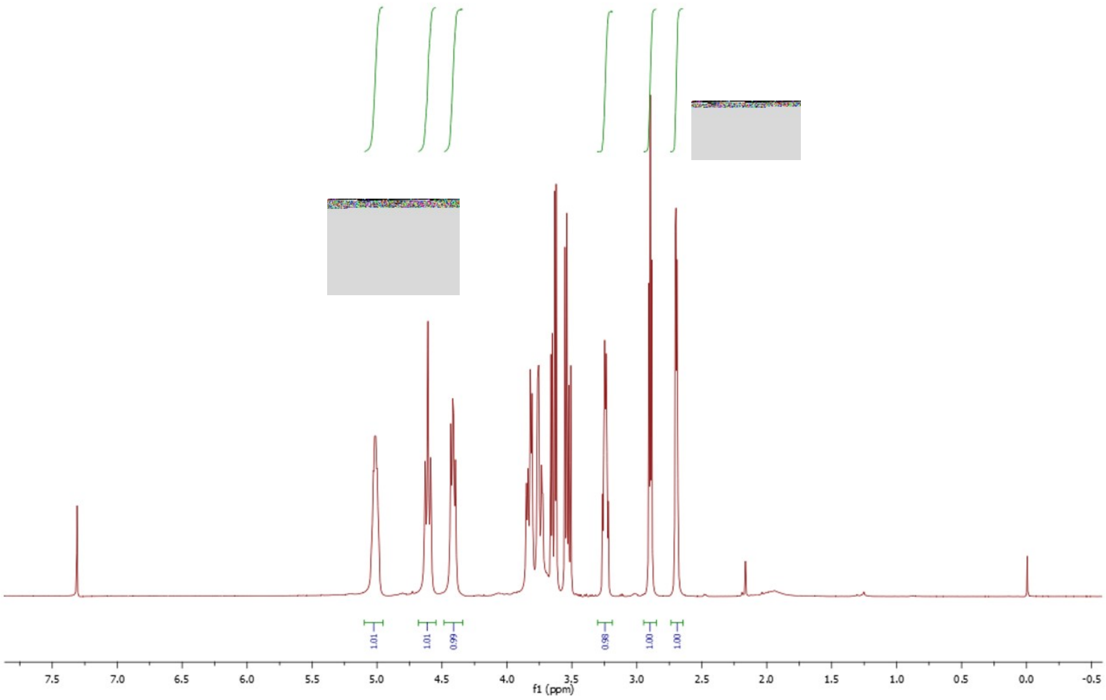
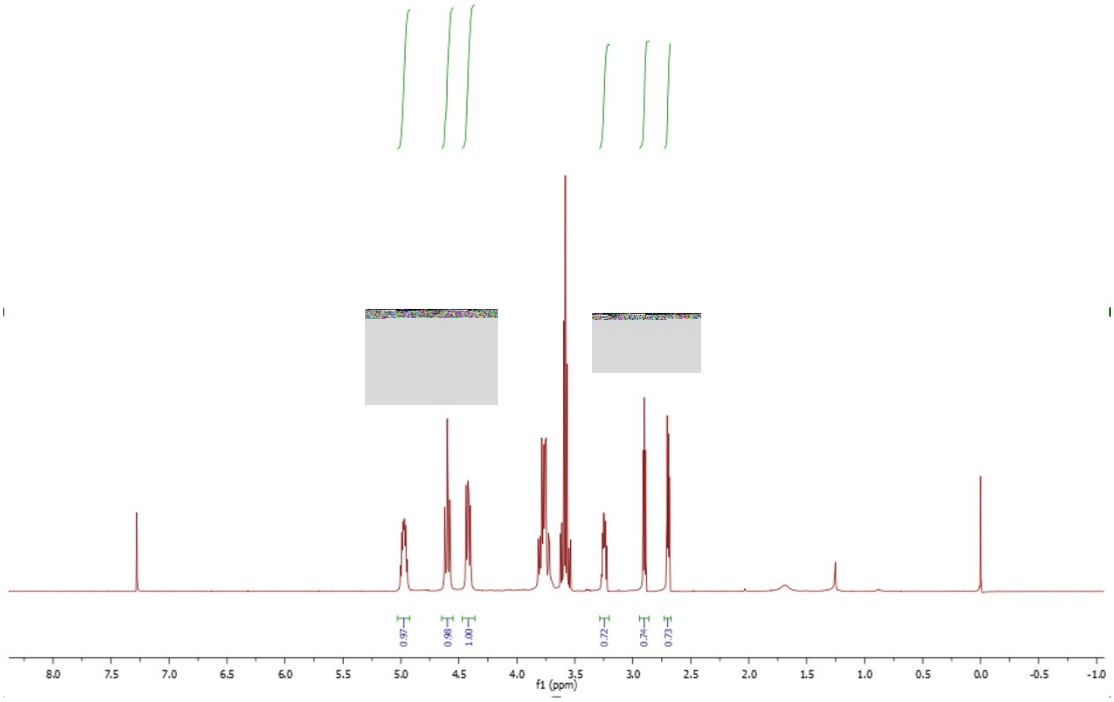


Figure S21. ^{1}H-liquid NMR of the reaction mixture of cycloaddition with various substrates listed in Table 2.

IL-Im:


1.01
1.01
0.99
0.98
1.00
1.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

F-IL-Im: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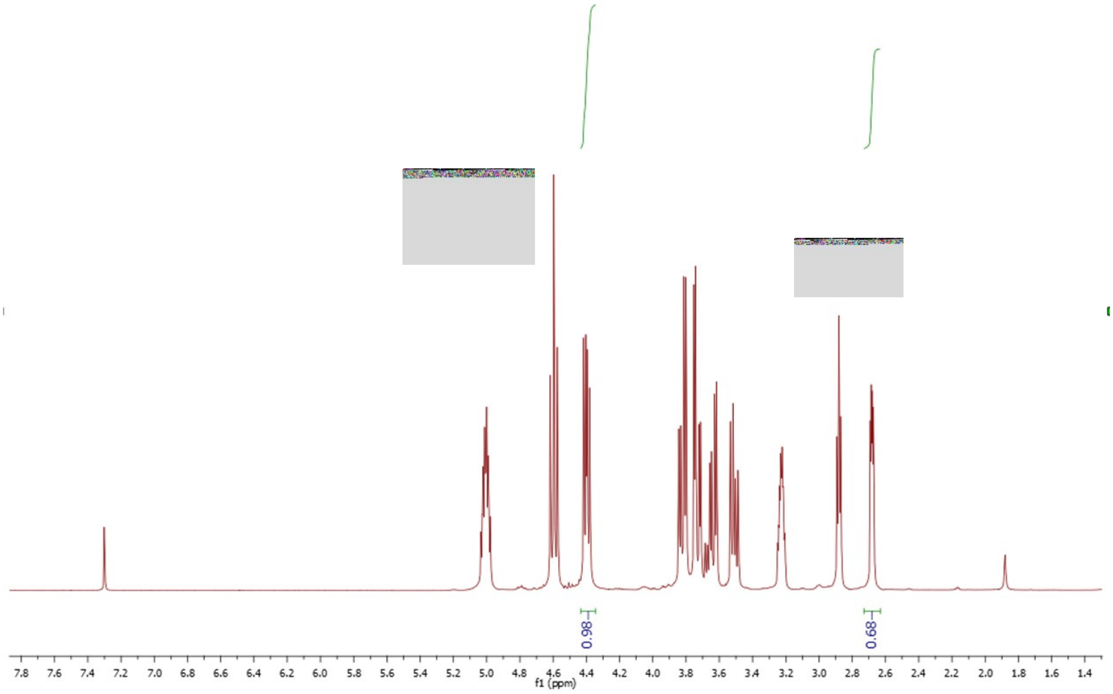
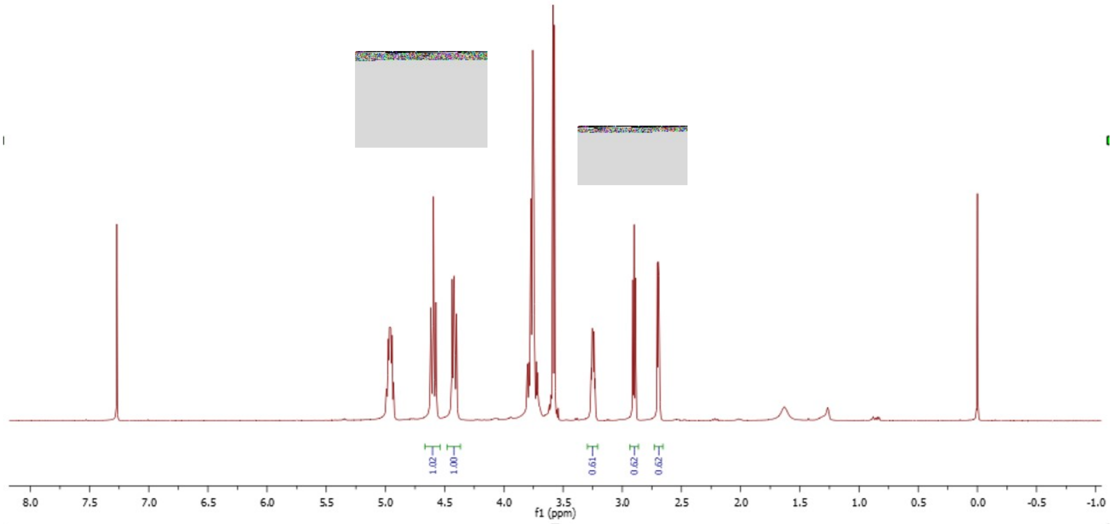
0.98
1.00
0.72
0.74
0.73
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

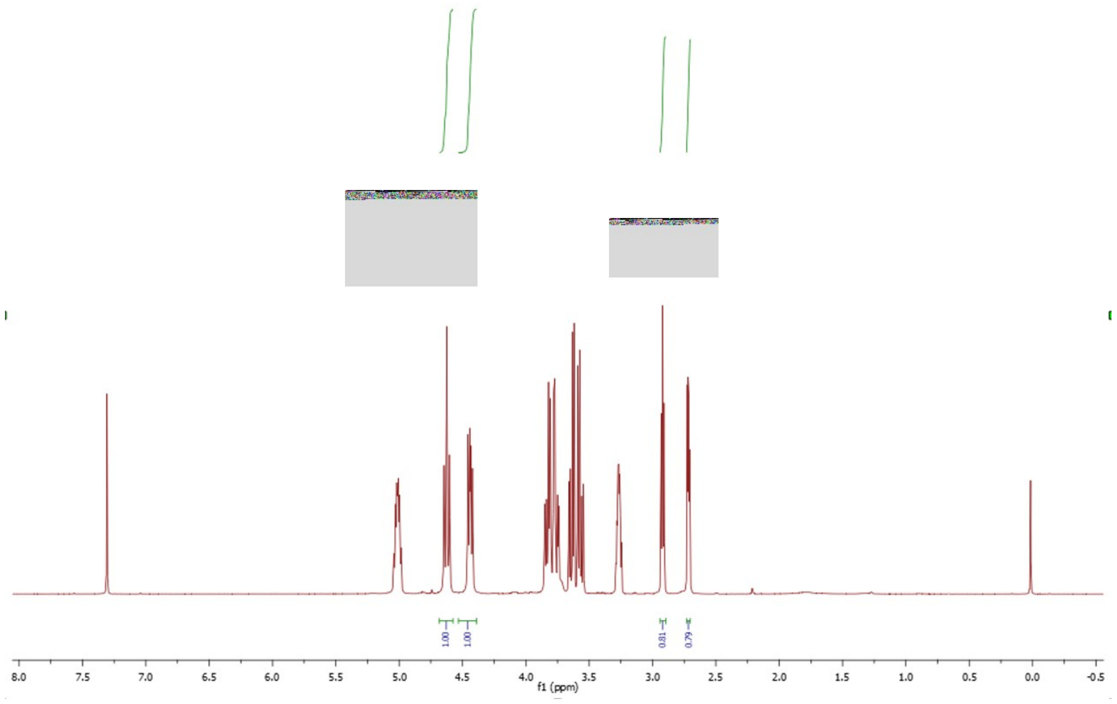
IL-TP:


0.98
0.68
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)

F-IL-TP:


1.02
1.00
0.61
0.62
0.62
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

IL-BP: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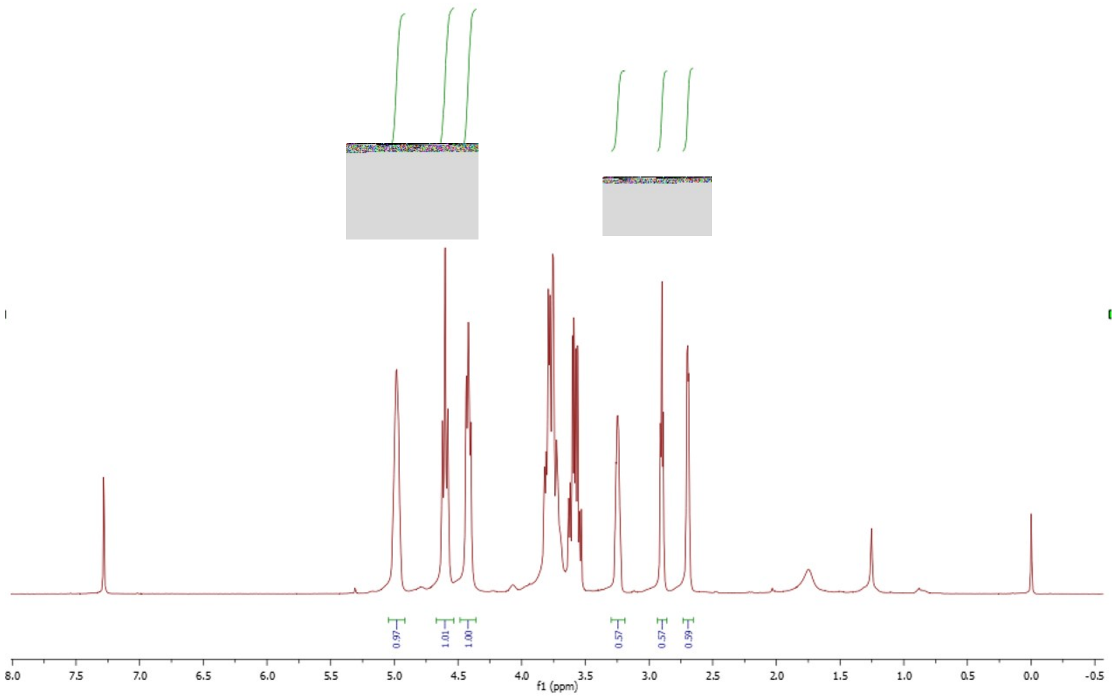
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

F-IL-BP: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1.01
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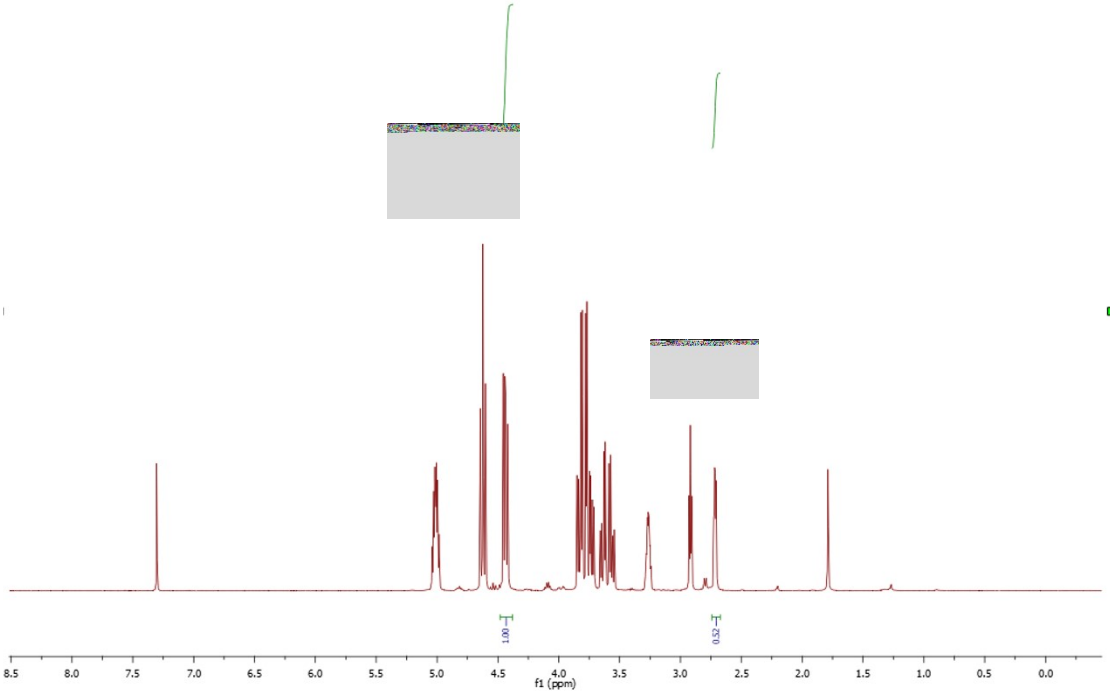
0.57
0.57
0.59
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

IL-CP:



F-IL-CP:78%

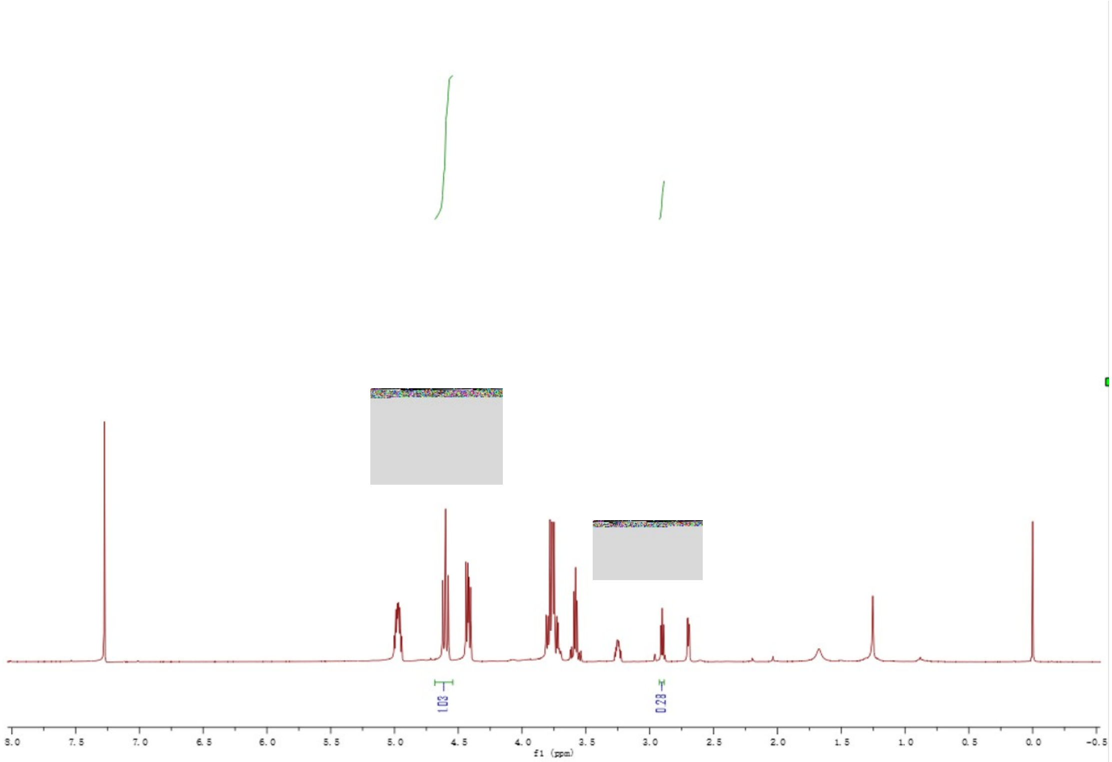
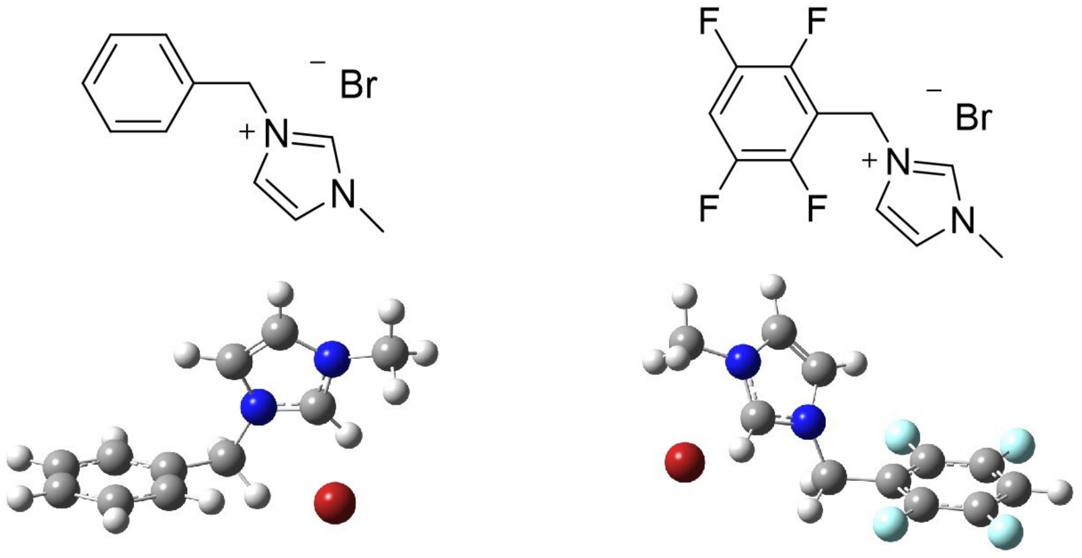


Figure S22. ^{1}H-liquid NMR of the reaction mixture in Figure 3.



BzMIMBr **F-BzMIMBr**

Figure S23. Structure of simulated ionic liquid catalysts 3-benzyl-1-methyl-1H-imidazol-3-ium bromide (BzMIMBr) and 1-methyl-3-(2,3,5,6-tetrafluorobenzyl)- 1H-imidazol-3-ium bromide (F-BzMIMBr) (white: H, gray: C, blue: N, light green: F, deep red: Br).

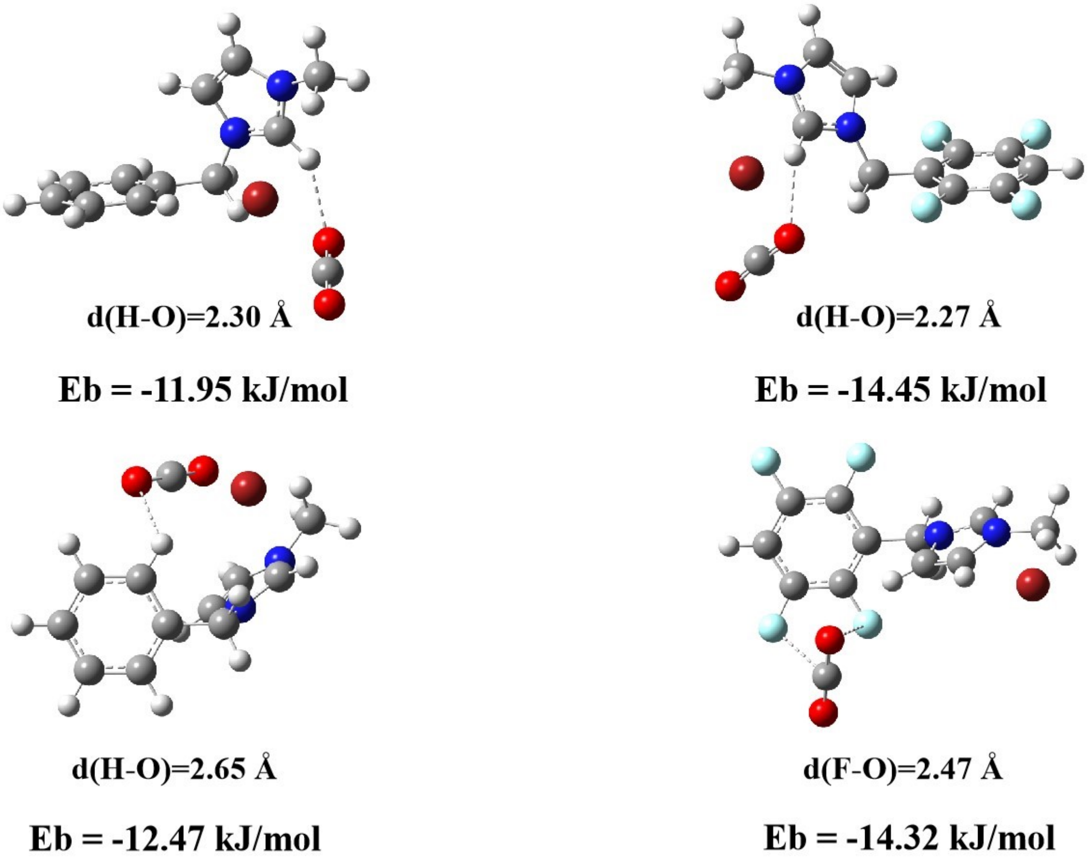


Figure S24. CO_2 binding energy of simulated ionic liquid catalysts BzMIMBr and F-BzMIMBr (white: H, gray: C, blue: N, red: O, light green: F, deep red: Br).

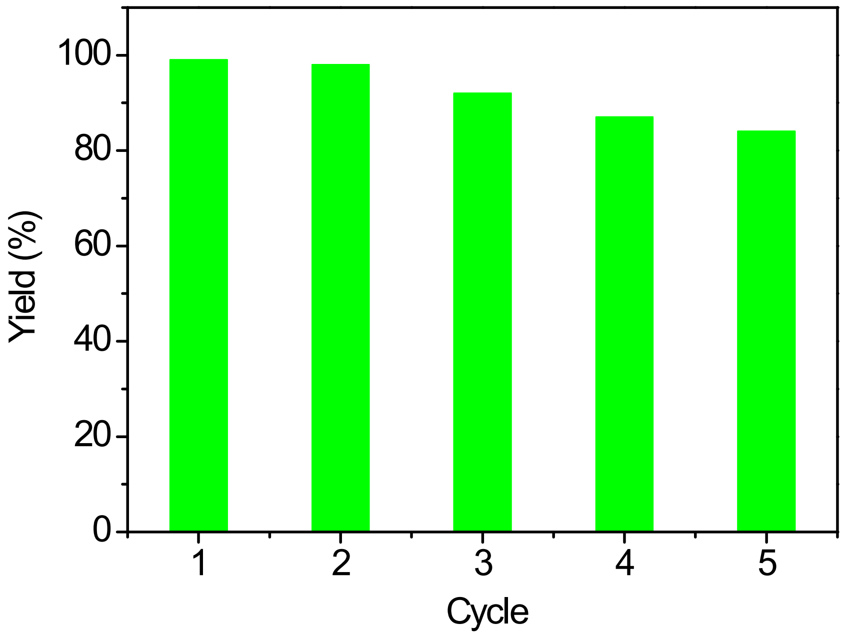


Figure S25. Recycle test of the F-IL-CP catalyst in the catalytic CO2 cycloaddition reaction with epichlorohydrin. Reaction conditions: epichlorohydrin (10 mmol), Catalyst ratio (0.11 mol%), 36 h, 1 atm of CO2, and 60 °C. The yields were determined by 1H NMR analysis.

Table S1. Catalytic performance of different catalysts in the cycloaddition of CO_2 with epichlorohydrin to form cyclic carbonate.[a]

Entry	Catalysts	Temp. (°C)	Conv. (%)[b]	Selec. (%)[b]
1	F-IL-Im	60	99	99
2	IL-Im	60	97	99
3	F-IL-TBP	60	99	99
4	IL-TBP	60	97	99
5	F-IL-TPP	60	99	99
6	IL-TPP	60	98	99
7	F-IL-TCP	60	99	99
8	IL-TCP	60	99	99

[a] Conditions: epichlorohydrin (925 mg, 10 mmol), catalyst (0.11 mol%), CO_2 pressure (0.1 MPa), reaction time (48 h). [b] Determined by liquid NMR.

Supplementary references

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