Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Brϕnsted Acidic Ionic Liquids-Catalyzed Dehydrative Formation of Isosorbide from Sorbitol: Introduce a Continuous Process

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Supporting Information

Contents

1. General Information.

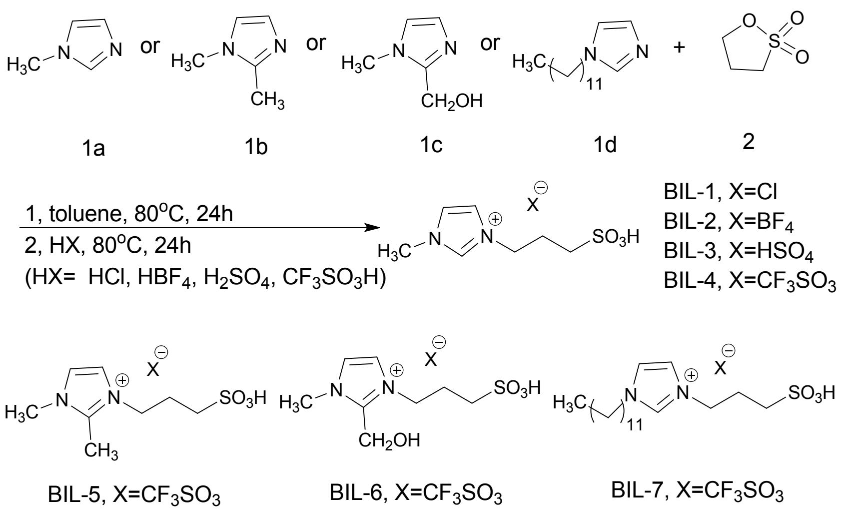
All reagents were used as received from Acros or Alfa Aesar. Solvents (AR grade) were commercially available unless otherwise stated. Water content was measured by Karl Fisher Titrator (ZKF-1). NMR spectra were recorded on a Bruker ASCEND spectrometer (^{1}H, 600 MHz; ^{13}C{^{1}H}, 150 MHz; ^{11}B{^{1}H}, 192 MHz; ^{19}F{^{1}H}, 564 MHz; ^{31}P{^{1}H}, 243 MHz). ^{1}H NMR and ^{13}C{^{1}H} NMR, chemical shift δ is referenced to the solvent signal. HPLC analysis was performed using a Phenomenex Rezex RCM-monosaccharide column (8 %; Ca^{2+}, 300 × 7.80 mm) at 80 ^{o}C, with degassed demi water as eluent, using a differential refractive index as detector. ESI-MS analysis were performed on a Bruker time of flight mass spectrometer microTOF-Q II using an electrospray ionization (ESI) souce.

X-ray Crystal Structure Analyses. Data collection was controlled by CrysAlis^{Pro} (Rigaku, 2016). Computations were performed using the SHELXTL NT ver. 5.10 program package (Bruker, 1997) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1989). Crystal drawings were produced with XP (Bruker, 1997). Bruker. (1997) SHELXTL. Structure Determination Programs, Version 5.10, Bruker AXS Inc.,6300 Enterprise Lane, Madison, WI 53719-1173, USA. *International Tables for X-ray Crystallography*: (1989) Vol. C (Kluwer Academic Publishers, Dordrecht) Tables 4.2.6.8 and 6.1.1.4. Rigaku. (2016) CrysAlis^{Pro}, Data Collection and Process Software for Rigaku Oxford Diffraction X-ray Diffractometer, Version 5.4, February, 2016. Rigaku Corporation, 9009, New Trails Drive, The Woodlands, TX77381, USA.

2. Preparation and Characterization of BILs

2.1 Preparations of BILs

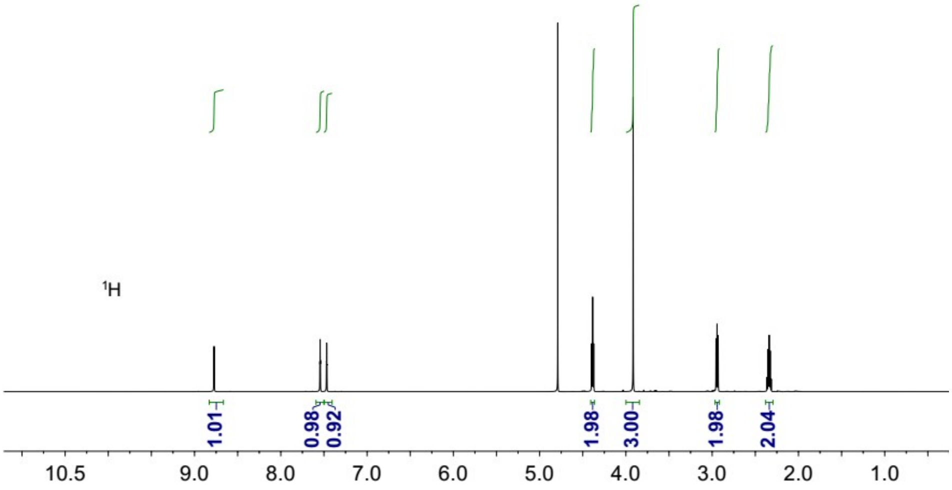
Scheme S1. The preparation pathway to BIL-1~7.



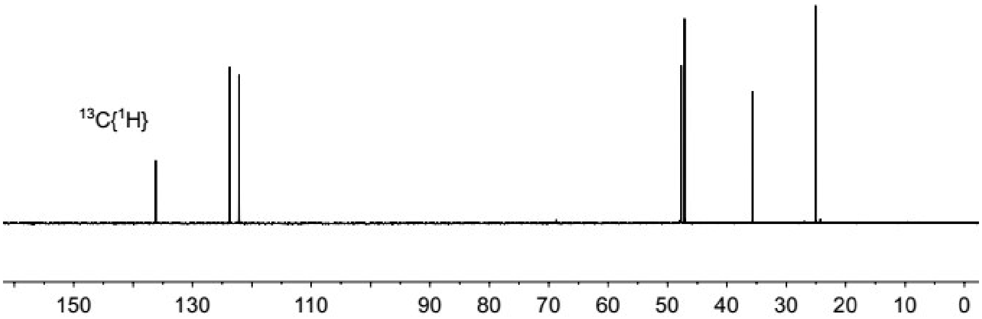
Preparation of zwitterionic precursor of BIL-1~4: In order to form the desired zwitterion, [(a) *J. Am. Chem. Soc*. 2002, **124**, 5962-5963; (b) *Catalysis Communications*, 2008, **9**: 1307-1311] methylimidazole (10.0 g, 0.12 mol) was combined with 50 mL toluene, firstly. The solution was stirred at 0 ^oC. 1, 3-propane sulfonate (14.9 g, 0.12 mol) was dropwise added to the stirring solution. After 30 min, the reaction vessel was then equipped with a reflux condenser and stirred at 80 ^oC for 24 h. The reaction was allowed to cool, and then filtered. The retained solids were washed with diethyl ether (3 × 80 mL). The solid was placed in a vacuum oven at 80 ^oC for 48 h. The white zwitterionic precursor of BIL-1~4 (21.4 g, 0.11 mol) was obtained in a yield of 80 %.

Preparation of BIL-1: A stoichiometric amount of hydrochloric acid (1.0 g, 10×10^{-3} mol, 36 wt %) was added dropwise to zwitterion precursor (2.0 g, 10×10^{-3} mol) and then stirred at 80 ^oC for 24 h. The resulting liquid was reduced via rotary evaporation to obtain the crude BIL-1. After washed with diethyl ether (3 × 50 mL) and ethyl acetate (3 × 50 mL), the product was dried in a high vacuum at 80 ^oC for 24 h to collect BIL-1 (2.1 g) in a yield of 90 %. The product (0.5 g) was dissolved in 2 mL of methanol. The mixed solution was placed in dry air at 25 ^oC overnight. Single crystal the zwitterionic precursor of BIL-1 was obtained (CCDC: 1523384).

^{1}H NMR (600 MHz, D_2O-*d₂*, 298 K): δ(ppm) 8.77 (s, 1H), 7.54 (t, *J* = 1.8 Hz, 1H), 7.47 (t, *J* = 1.8 Hz, 1H), 4.39 (t, *J* = 7.2 Hz, 2H), 3.92 (s, 3H), 2.96 (t, *J* = 1.8 Hz, 2H), 2.34 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, D_2O-*d₂*, 298 K): δ(ppm) 136.2, 123.7, 122.2, 47.7, 47.2, 35.7, 25.1, 24.3; MS: calc. for $C_7H_{13}N_2O_3S$ [*M* - Cl^-]: 205.0641, found: 205.6400.



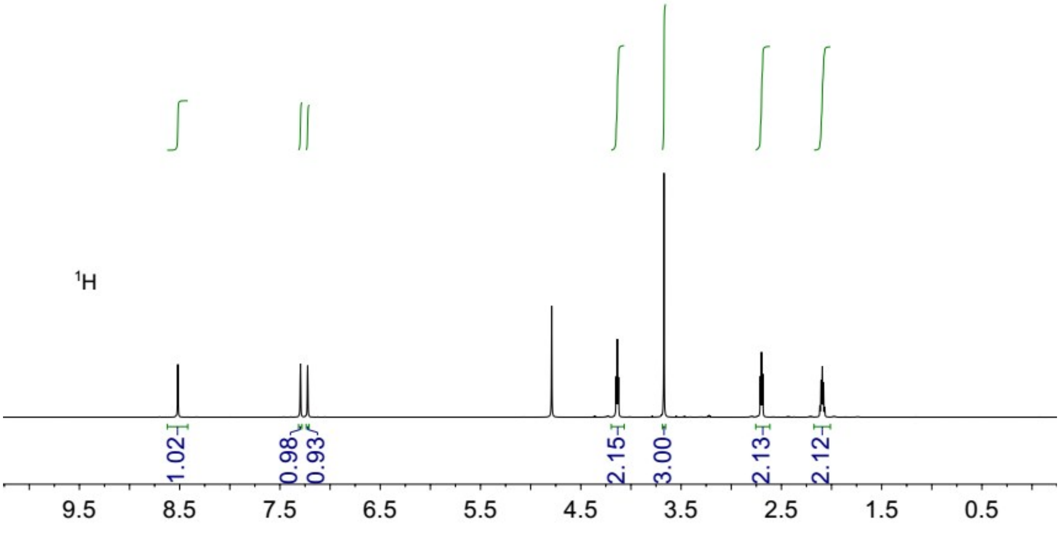
^{1}H NMR (600 MHz, D_2O, 298 K) of BIL-1



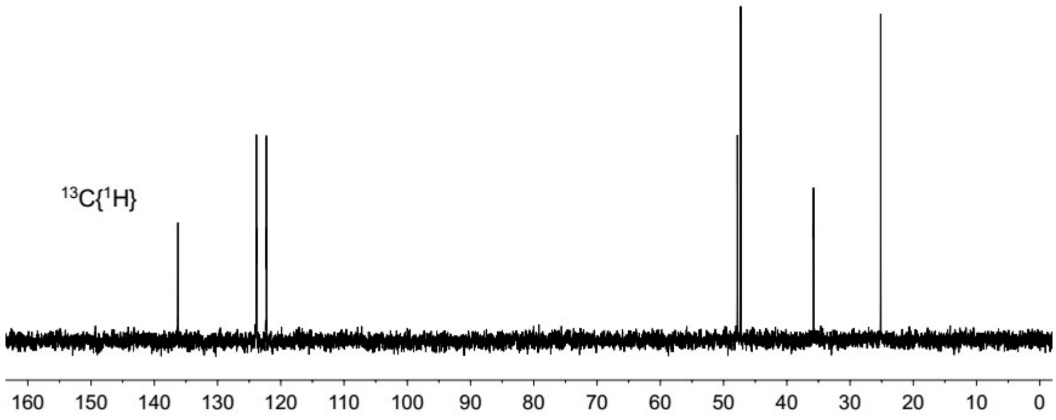
$^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) of BIL-1

Preparation of BIL-2: A stoichiometric amount of tetrafluoroboric acid (1.5 g, 10 × 10^{-3} mol, 60 wt %) was added dropwise to zwitterion precursor (2.0 g, 10 × 10^{-3} mol) and then stirred at 25 °C for 30 days. The resulting liquid was reduced via rotary evaporation to obtain the crude BIL-2. After washed with diethyl ether (3 × 50 mL) and ethyl acetate (3 × 50 mL), the product was dried in a high vacuum at 40 °C for over 48 h to collect BIL-2 (2.5 g) in a yield of 87 %. The residual water content was determined to be about 118 ppm.

^1H NMR (600 MHz, D_2O-*d₂*, 298 K): δ(ppm) 8.52 (s, 1H), 7.30 (s, 1H), 7.22 (s, 1H), 4.14 (t, *J* = 7.2 Hz, 2H), 3.67 (s, 3H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.09 (p, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, D_2O-*d₂*, 298K): δ(ppm) 136.3, 123.9, 122.3, 47.8, 47.3, 35.8, 25.2; MS: calc. for $C_7H_{13}N_2O_3S$ [M - BF_4^-]: 205.0641, found: 205.6400.



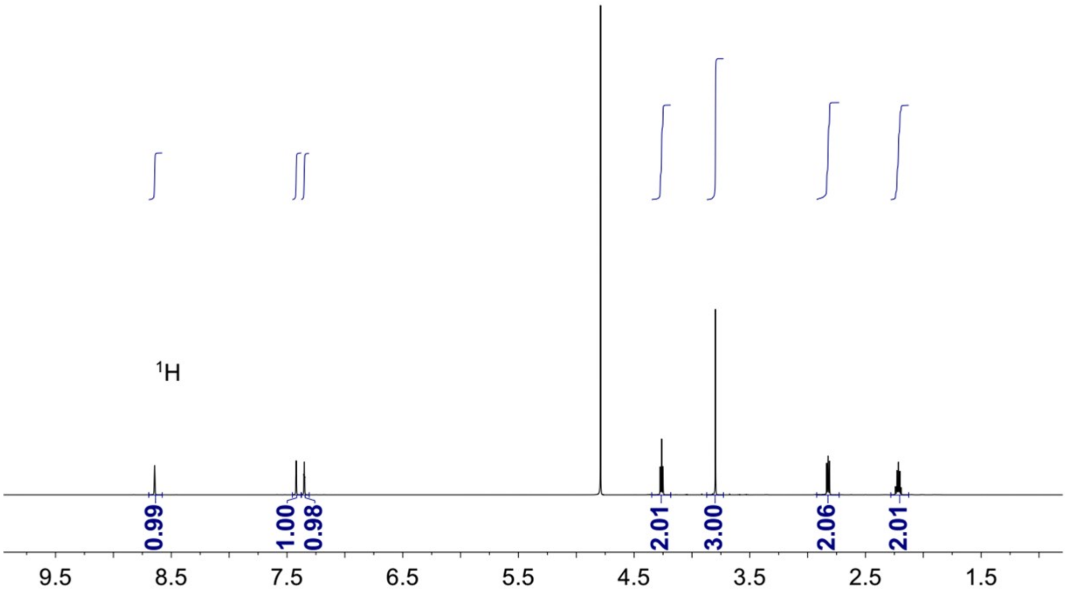
^1H NMR (600 MHz, D_2O, 298 K) of BIL-2



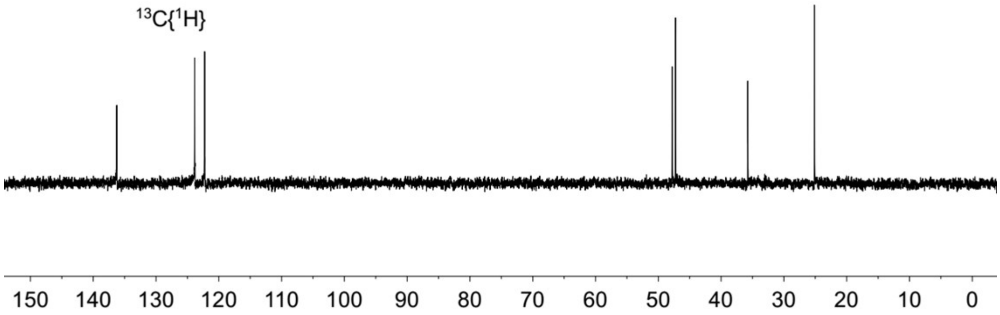
$^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) of BIL-2

Preparation of BIL-3: A stoichiometric amount of sulphuric acid (4.9 g, 0.048 mol, 98 wt %) was added dropwise to zwitterion precursor (4.0 g, 0.048 mol) and then stirred at 80 ^{o}C for 24 h. After washed with diethyl ether (3 × 50 mL) and ethyl acetate (3 × 50 mL), the resulting liquid was dried in a high vacuum at 80 ^{o}C for 48 h to collect BIL-3 (8.2 g) in a yield of 92 %. The residual water content was determined to be about 86 ppm.

^1H NMR (600 MHz, D_2O-d_2, 298K): δ(ppm) 8.64 (s, 1H), 7.42 (t, J = 1.2 Hz, 1H), 7.35 (t, J = 1.2 Hz, 1H), 4.2 (t , J = 7.2 Hz, 2H), 3.80 (s, 3H), 2.82 (t, J = 7.2 Hz, 2H), 2.22 (t, J = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, D_2O-d_2, 298 K): δ(ppm) 136.3, 123.8, 122.3, 47.8, 47.3, 35.8, 25.2.



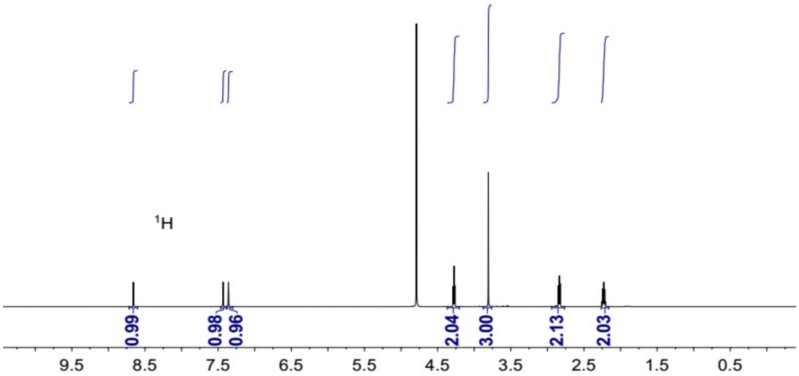
^1H NMR (600 MHz, D_2O, 298 K) of BIL-3



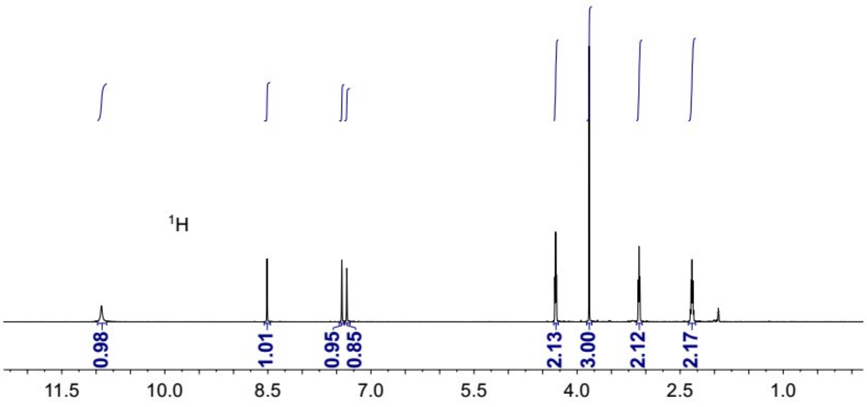
$^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) of BIL-3

Preparation of BIL-4: A stoichiometric amount of trifluoromethanesulfonic acid (7.5 g, 0.048 mol, 98 wt %) was added dropwise to zwitterion precursor (4.0 g, 0.048 mol) and then stirred at 80 ^oC for 24 h. The resulting liquid was dissolved in 20 mL acetonitrile. Activated carbon (5 g) was added to the solution. Before filtrated to obtain the product solution, the mixture was stirred for 30 min. The filtratewas reduced via rotary evaporation. After washed with diethyl ether (3 × 50 mL) and ethyl acetate (3 × 50 mL), the resulting liquid was dried in a high vacuum at 80 ^oC for 24 h to collect BIL-4 (7.7 g) in a yield of 67 %. The residual water content was determined to be about 53 ppm. The product (0.5 g) was dissolved in 2 mL of acetonitrile. Isovolumetric DMSO was added in that acetonitrile solution. The mixed solution was placed in dry air at 50 ^oC overnight. Single crystal the zwitterionic precursor of BIL-4 was obtained (CCDC: 1523385).

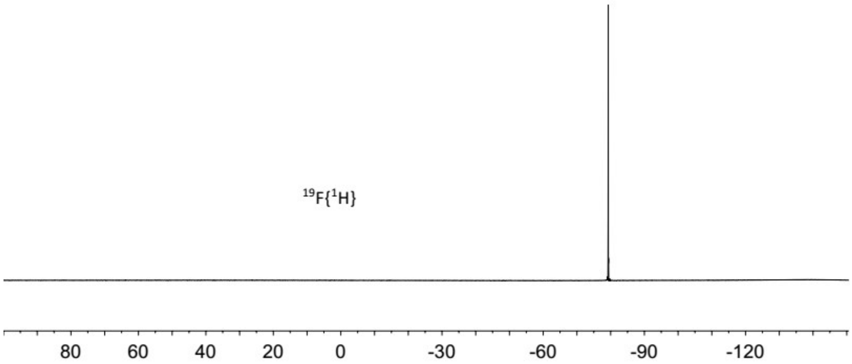
^1H NMR (600 MHz, D_2O-*d_2*, 298K): δ (ppm) 8.66 (s, 1H), 7.43 (s, 1H), 7.36 (s, 1H), 4.28 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.23 (p, *J* = 7.2 Hz, 2H); ^1H NMR (600 MHz, CD_3CN-*d_3*, 298K): δ(ppm) 10.92 (s, 1H), 8.51 (s, 1H), 7.42 (s, 1H), 7.35 (s, 1H), 4.32 (t, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.33 (p, *J* = 7.2 Hz, 2H); $^{19}F\{^1H\}$ NMR (564 MHz, CD_3CN-*d_3*, 298K): δ(ppm) -79.27; $^{13}C\{^1H\}$ NMR (150 MHz, CD_3CN-*d_3*, 298K): δ(ppm) 136.5, 123.9, 122.4, 47,7, 47.56, 36.0, 24.9. MS: calc. for $C_7H_{13}N_2O_3S$ [M - $CF_3SO_3^-$]: 205.0615, found: 205.0645; calc. for CF_3SO_3 [M - $C_7H_{13}N_2O_3S$]:148.9526, found: 148.9552.



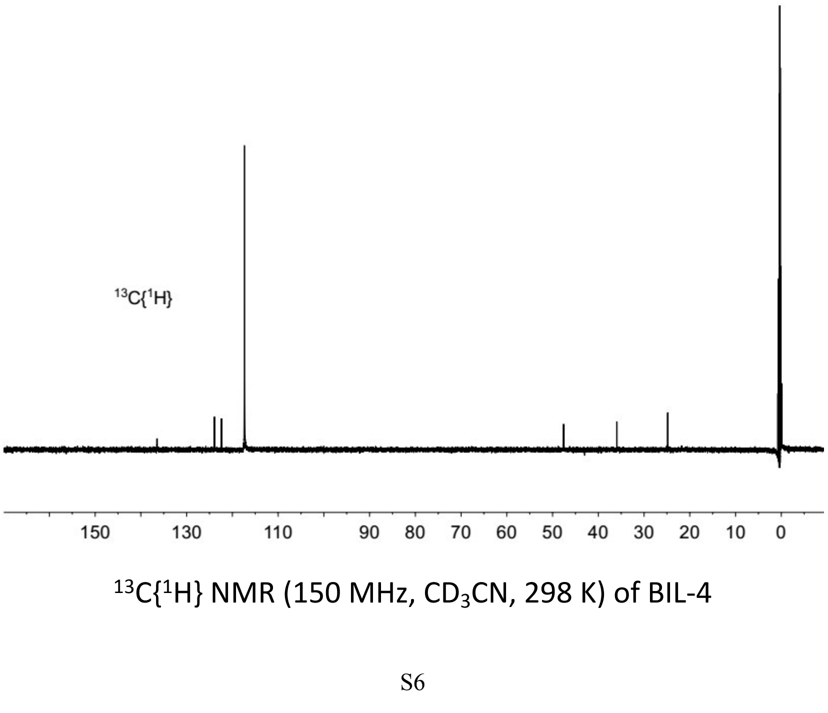
^1H NMR (600 MHz, D_2O, 298 K) of BIL-4



^1H NMR (600 MHz, CD_3CN, 298 K) of BIL-4



$^{19}F\{^1H\}$ NMR (564 MHz, CD_3CN, 298 K) of BIL-4

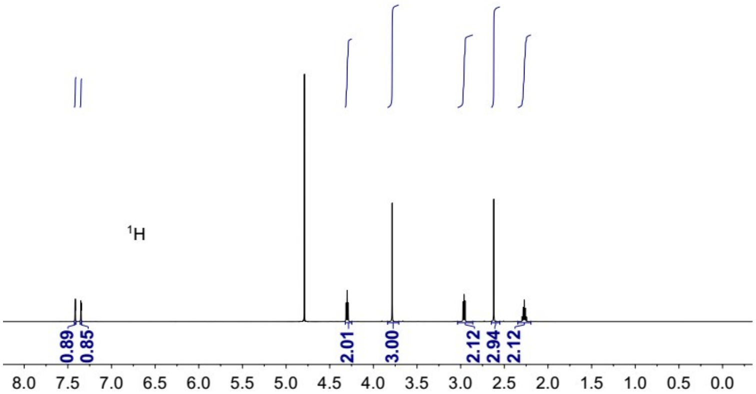


$^{13}C\{^1H\}$ NMR (150 MHz, CD_3CN, 298 K) of BIL-4

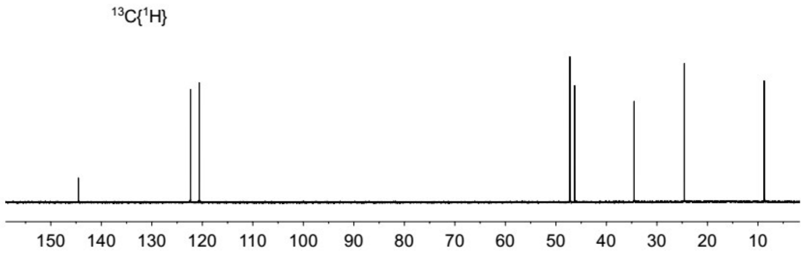
Preparation of BIL-5: In order to form the desired zwitterion precursor, 2, 3-dimethylimidazole (4.8 g, 0.05 mol) was combined with 25 mL toluene. And the solution was stirred at 0 ^{o}C. 1, 3-propane sulfonate (6.1 g, 0.05 mol) was dropwise added to the stirring solution. After 30 min, the reaction vessel was then equipped with a reflux condenser and stirred at 80 ^{o}C for 24 h. The reaction was allowed to cool, and then filtered. The retained solids were washed with diethyl ether (3 × 50 mL). The solid was placed in a vacuum oven at 80 ^{o}C for 48 h. The white zwitterionic precursor of BIL-5 (8.7 g, 0.04 mol) was obtained in a yield of 80 %.

A stoichiometric amount of trifluoromethanesulfonic acid (6.2 g, 0.04 mol, 98 wt %) was added dropwise to zwitterion precursor of BIL-5 (8.7 g, 0.04 mol) and then stirred at 80 ^{o}C for 24 h. The resulting liquid was dissolved in 20 mL acetonitrile. Activated carbon (5 g) was added to the solution. Before filtrated to obtain the product solution, the mixture was stirred for 30 min. Filtrate was reduced via rotary evaporation. After washed with diethyl ether (3 × 80 mL) and ethyl acetate (3 × 80 mL), the resulting liquid was dried in a high vacuum at 80 ^{o}C for 24 h to collect BIL-5 (5.52 g) in a yield of 75 %. The residual water content was determined to be about 48 ppm. The product (0.5 g) was dissolved in 2 mL of acetonitrile. Isovolumetric DMSO was added in that acetonitrile solution. The mixed solution was placed in dry air at 50 ^{o}C overnight. Single crystal the zwitterionic precursor of BIL-5 was obtained (CCDC: 1523386).

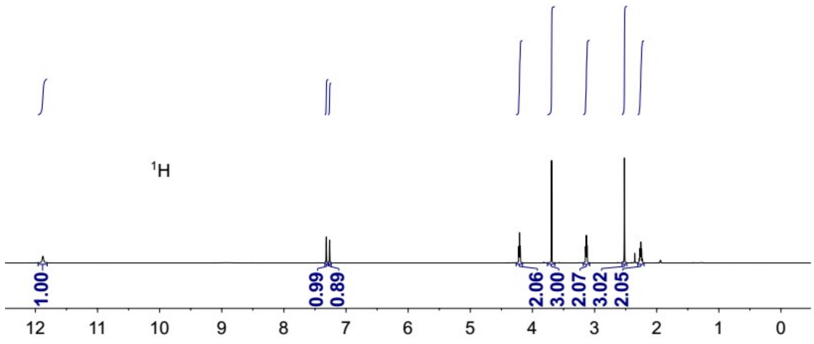
^{1}H NMR (600 MHz, D_2O-d_2, 298 K): δ(ppm) 7.42 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 1.8 Hz, 1H), 4.30 (t, J = 7.8 Hz, 2H), 3.78 (s, 3H), 2.96 (t, J = 7.8 Hz, 2H), 2.62 (s, 3H), 2.27 (p, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, D_2O-d_2, 298 K): δ(ppm) 144.5, 122.3, 120.6, 47.2, 46.3, 34.5, 24.6, 8.8; ^{19}F{^{1}H} NMR (564 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) -79.26; ^{1}H NMR (600 MHz, CD_3CN-d_3, 298 K): δ(ppm) 11.88 (s, 1H), 7.37 (s, 1H), 7.27 (s, 1H), 4.21 (t, J = 7.8 Hz, 2H), 3.69 (s, 3H), 3.13 (t, J = 7.2 Hz, 2H), 2.52 (s, 3H), 2.26 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, CD_3CN-d_3, 298 K): δ(ppm) 144.9, 122.6, 120.8, 47.7, 46.2, 34.9, 24.5, 9.2; MS: calc. for $C_8H_{15}N_2O_3S$ [M - $CF_3SO_3^-$]: 219.0798, found: 219.0796; calc. for CF_3SO_3 [M - $C_8H_{15}N_2O_3S$]:148.9526, found: 148.9556.



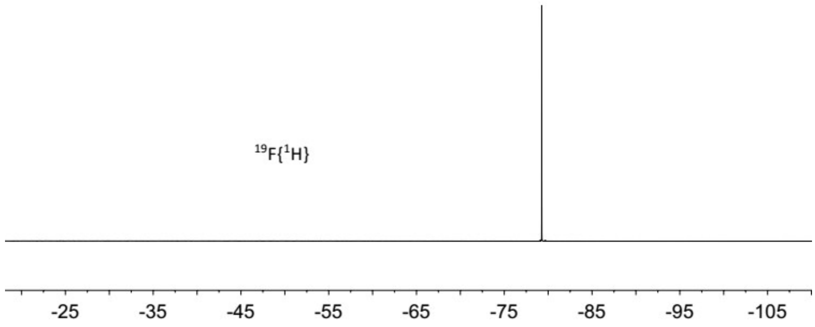
^{1}H NMR (600 MHz, D_2O, 298 K) of BIL-5



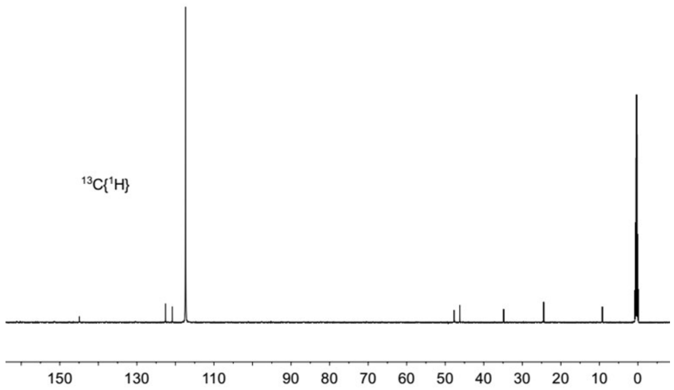
$^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) of BIL-5



^1H NMR (600 MHz, CD_3CN, 298 K) of BIL-5



$^{19}F\{^1H\}$ NMR (564 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-5



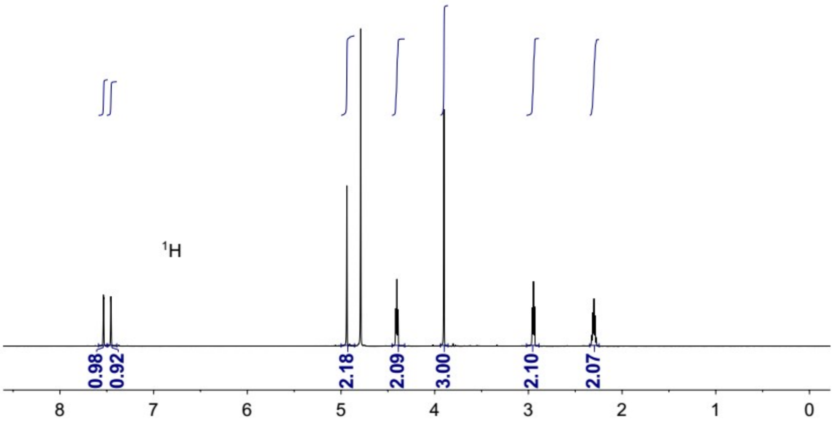
$^{13}C\{^1H\}$ NMR (150 MHz, CD_3CN, 298 K) of BIL-5

Preparation of BIL-6: In order to obtain 1-methyl-2-hydroxymethylimidazole, methylimidazole (10.0 g, 0.12 mol) and paraformaldehyde (10.0 g, 0.33 mol) were stirred at 160 ^{o}C for 1 h. By mixing with 20/5 mL methanol served as solvent doubly, the solution was recrystallized twice at -18 ^{o}C [*Journal of Coordination Chemistry*, 2014, **67**; 2393-2404]. Following above procedure, filtration of the mixture was carried out immediately. Finally, 1-methyl-2-hydroxymethylimidazole(3.4 g, 0.030 mol) was collected in a yield of 25 %.

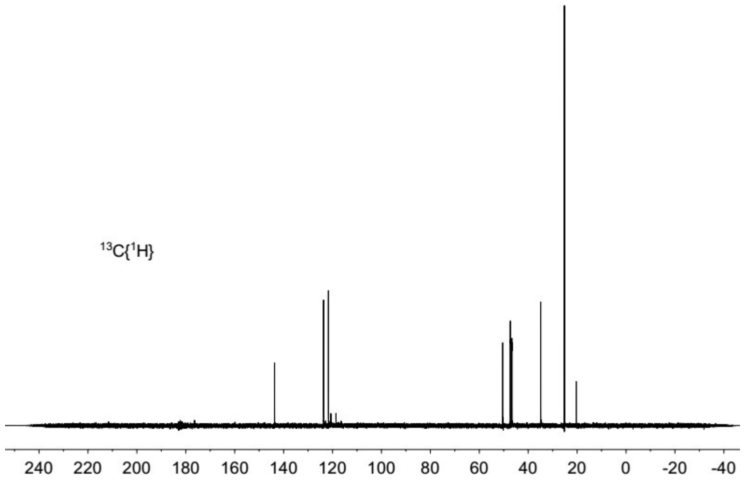
1-methyl-2-hydroxymethylimidazole (3.40 g, 0.030 mol) was combined with 10 mL toluene. And the solution was stirred at 0 ^{o}C. 1, 3-propane sulfonate (3.66 g, 0.03 mol) was dropwise added to the stirring solution. After 30 min, the reaction vessel was then equipped with a reflux condenser and stirred at 80 ^{o}C for 24 h. The reaction was allowed to cool, and then filtered. The retained solids were washed with diethyl ether (3 × 50 mL). The solid was placed in a vacuum oven at 80 ^{o}C for 48 h. The white zwitterionic precursor of BIL-6 (6.6 g, 0.028 mol) was obtained in a yield of 93 %.

A stoichiometric amount of trifluoromethanesulfonic acid (4.3 g, 0.028 mol, 98 wt %) was added dropwise to zwitterion precursor of BIL-5 (6.6 g, 0.028 mol) and then stirred at 80 ^{o}C for 24 h. The resulting liquid was dissolved in 20 mL acetonitrile. Activated carbon (5 g) was added to the solution. Before filtrated to obtain the product solution, the mixture was stirred for 30 min. Filtrate was reduced via rotary evaporation. After washed with diethyl ether (3 × 80 mL) and ethyl acetate (3 × 80 mL), the resulting liquid was dried in a high vacuum at 80 ^{o}C for 24 h to collect BIL-5 (8.2 g, 0.021 mol) in a yield of 75 %. The residual water content was determined to be about 71 ppm.

^{1}H NMR (600 MHz, D_2O-d_2, 298 K): δ(ppm) 7.53 (s, 1H), 7.46 (s, 1H), 4.94 (s, 2H), 4.40 (t, *J* = 7.8 Hz, 2H), 3.90 (s, 3H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.30 (p, 2H); ^{13}C{^{1}H} NMR (150 MHz, D_2O-d_2, 298 K): δ(ppm) 143.7, 123.7, 121.7, 50.5, 47.3, 46.7, 34.9, 25.2, 20.4; MS: calc. for $C_8H_{15}N_2O_4S$ [M - $CF_3SO_3^-$]: 235.0747, found: 235.0751; calc. for CF_3SO_3 [M - $C_8H_{15}N_2O_4S$]:148.9528, found: 148.9562.



^{1}H NMR (600 MHz, D_2O, 298 K) of BIL-6



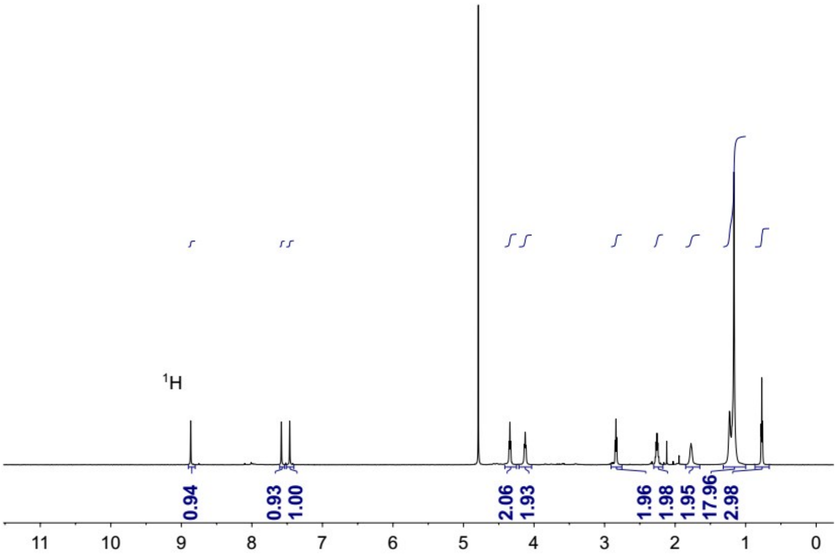
$^{13}C\{^1H\}$ NMR (150 MHz, D_2O, 298 K) of BIL-6

Preparation of BIL-7: Imidazole (15.0 g, 0.220 mol) and equimolar NaOH (9.3 g, 0.232 mol) were directly mixed to product sodium imidazolate with equal molar water. After dried in a vacuum oven at 110 °C for 4 h, the sodium imidazolate (19.8 g, 0.22 mol) and 1-bromine dodecane at 0.9 mol equiv were well mixed with 100 mL THF at room temperature. The mixture was heated at 65 °C and stirred overnight. Then, the mixture was allowed to cool and filtered. The filtrate was reduced via rotary evaporation. The crude product was purified with activated carbon (10 g) and $MgSO_4$ (5 g) in 250 mL CH_2Cl_2. The mixture was filtered and filtrate was concentrated [*Ind. Eng. Chem. Res*. 2011, **50**:13614-13619]. Finally, the pale yellow color product 1d (30.68 g, 0.130 mol) was obtained in a yield of 59 %.

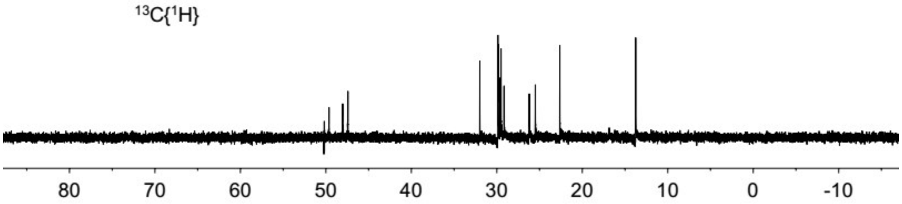
Compound 1d (7.08 g, 0.030 mol) was combined with 10 mL toluene. And the solution was stirred at 0 °C. 1, 3-propane sulfonate (3.66 g, 0.030 mol) was dropwise added to the stirring solution. After 30 min, the reaction vessel was then equipped with a reflux condenser and stirred at 80 °C for 24 h. The reaction was allowed to cool, and then filtered. The retained solids were washed with diethyl ether (3 × 50 mL). The solid was placed in a vacuum oven at 80 °C for 48 h. The white zwitterionic precursor of BIL-7 (8.95 g, 0.025 mol) was obtained in a yield of 83 %.

A stoichiometric amount of trifluoromethanesulfonic acid (3.83 g, 0.025 mol, 98 wt %) was added dropwise to zwitterion precursor of BIL-7 (8.95 g, 0.025 mol) and then stirred at 80 °C for 24 h. The resulting liquid was dissolved in 20 mL acetonitrile. Activated carbon (5 g) was added to the solution. Before filtrated to obtain the product solution, the mixture was stirred for 30 min. Filtrate was reduced via rotary evaporation. After washed with diethyl ether (3 × 80 mL) and ethyl acetate (3 × 80 mL), the resulting liquid was dried in a high vacuum at 80 °C for 24 h to collect BIL-5 (8.2 g, 0.021 mol) in a yield of 75 %.

^{1}H NMR (600 MHz, D_2O-*d$_2$*, 298 K): δ(ppm) 8.87 (s, 1H), 7.58 (s, 1H), 7.46 (s, 1H), 4.34 (t, *J* = 7.2 Hz, 2H), 4.13 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.26 (m, 2H), 1.78 (s, 2H), 1.20 (m, 18H), 0.77 (t, *J* = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, D_2O-*d$_2$*, 298 K): δ(ppm) 135.7, 122.7, 122.5, 49.6, 48.0, 47.4, 32.0, 29.9, 29.9, 29.8, 29.8, 29.6, 29.5, 29.2, 26.2, 25.5, 22.6, 16.9, 13.8; MS: calc. for $C_{18}H_{35}N_2O_3S$ [*M* - $CF_3SO_3^-$]: 359.2363, found: 359.2359; calc. for CF_3SO_3 [*M* - $C_{18}H_{35}N_2O_3S$]:148.9528, found: 148.9563.

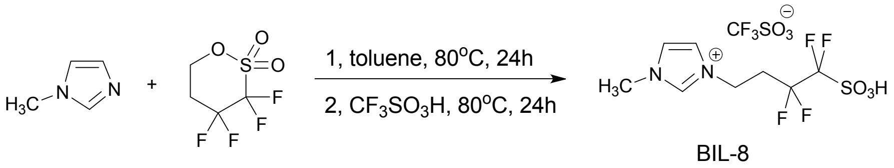


^{1}H NMR (600 MHz, D_2O, 298K) of BIL-7



^{13}C{^{1}H} NMR (150 MHz, D_2O, 298 K) of BIL-7

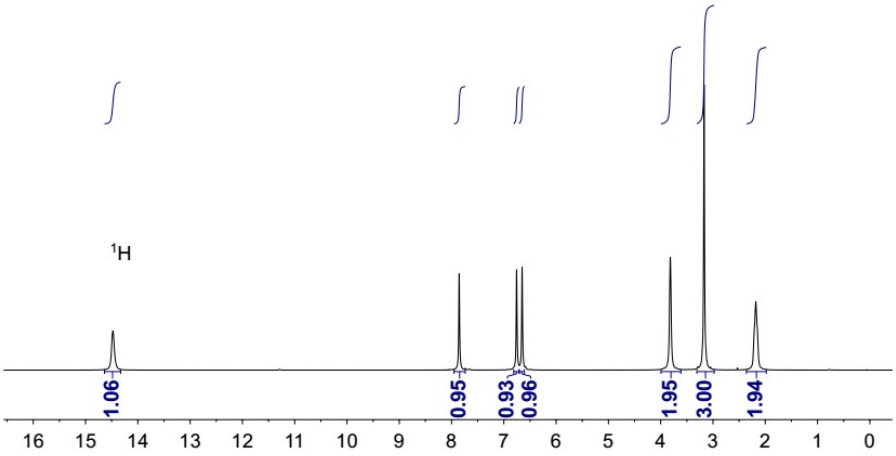
Scheme S2. The preparation pathway to BIL-8.



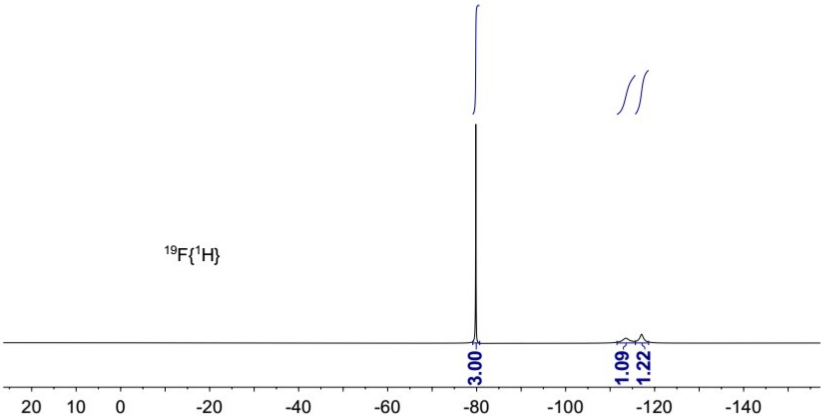
Preparation of BIL-8: methylimidazolium (2.46 g, 0.030 mol) was combined with 10 mL toluene. And the solution was stirred at 0 °C. 3, 3, 4, 4-tetrafluoro-1, 4-butane sulfonate (6.24 g, 0.030 mol) was dropwise added to the stirring solution. After 30 min, the reaction vessel was then equipped with a reflux condenser and stirred at 80 °C for 24 h. The reaction was allowed to cool, and then filtered. The retained solids were washed with diethyl ether (3 × 50 mL). The solid was placed in a vacuum oven at 80 °C for 48 h. The white zwitterionic precursor of BIL-8 (7.83 g, 0.027 mol) was obtained in a yield of 90 %.

A stoichiometric amount of trifluoromethanesulfonic acid (4.13 g, 0.027 mol, 98 wt %) was added dropwise to zwitterion precursor of BIL-8 (7.83 g, 0.027 mol) and then stirred at 80 °C for 24 h. The resulting liquid was dissolved in 20 mL acetonitrile. Activated carbon (5 g) was added to the solution. Before filtrated to obtain the product solution, the mixture was stirred for 30 min. Filtrate was reduced via rotary evaporation. After washed with diethyl ether (3 × 50 mL) and ethyl acetate (3 × 50 mL), the resulting liquid was dried in a high vacuum at 80 °C for 24 h to collect BIL-8 (9.33 g, 0.021 mol) in a yield of 78 %. The residual water content was determined to be about 85 ppm. NMR spectra was collected by measuring neat ionic liquids with d_6-dimethylsulfoxide as an external lock at 80 °C.

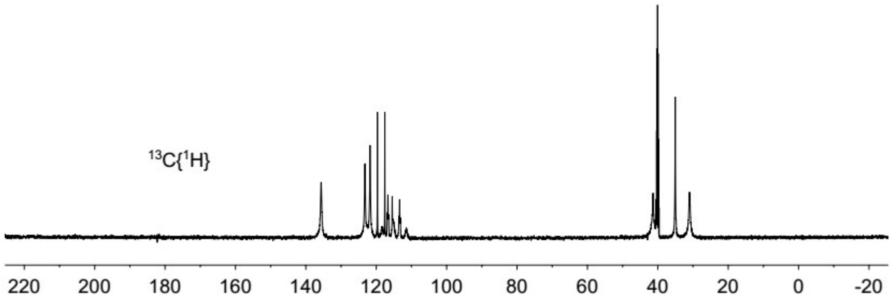
^{1}H NMR (600 MHz, DMSO-d_6, 353 K): δ(ppm) 14.48 (s, 1H), 7.85 (s, 1H), 6.76 (s, 1H), 6.65 (s, 1H), 3.82 (s, 2H), 3.17 (s, 3H), 2.18 (s, 2H); ^{19}F{^{1}H} NMR (564 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) -79.80 (s, 3F), -114.57 (s, 1F), -117.04 (s, 1F); ^{13}C{^{1}H} NMR (150 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) 135.7, 123.2, 121.8, 119.7, 117.6, 116.7 (t, J = 30 Hz, CF_2), 113.4 (t, J = 45 Hz, CF_2), 35.1, 31.0.



^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-8

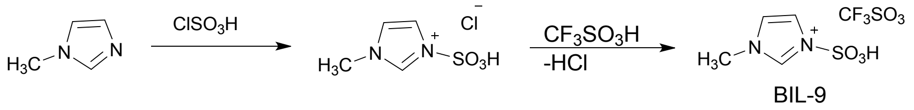


$^{19}F\{^1H\}$ NMR (564 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-8



$^{13}C\{^1H\}$ NMR (150 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-8

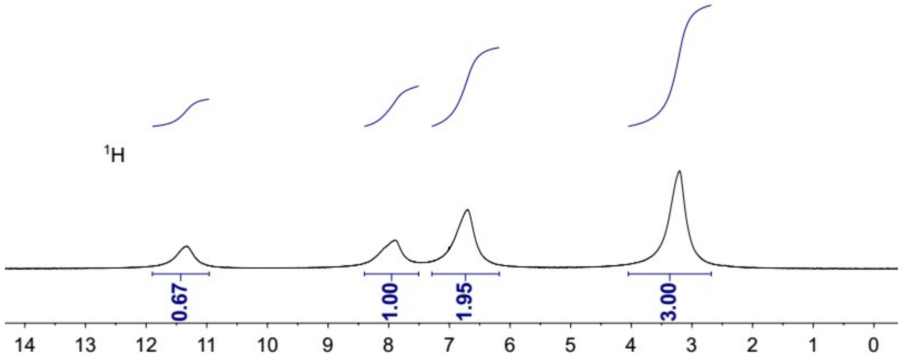
Scheme S3 The preparation pathway to BIL-9.



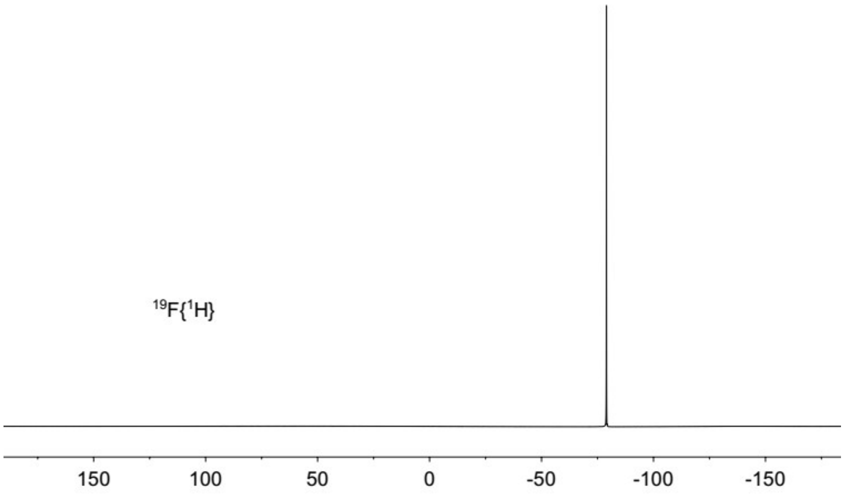
Preparation of BIL-9: 1-Methylimidazole (2.00 g, 0.024mol) in dry dichloromethane (100 mL) was added to a round-bottomed flask (200 mL), and chlorosulfonic acid (2.78 g, 0.024 mol) was then added dropwise at room temperature. The reaction mixture was then stirred for 30 min, and the dichloromethane was decanted after the reaction mixture was allowed to settle for 5 min. The residue was washed with dry dichloromethane (5 × 50 mL) to remove excess of chlorosulfonic acid and dried under vacuum [*J. org. Chem.* 2012, **77**: 3640-3645]. Then, trifluoromethanesulfonic acid (3.67 g, 0.024 mol, 98 wt %) was dropwise added to flask at room temperature under a continuous vacuum to remove the HCl gas that is produced. The resulting mixture was stirred for 10 min under vacuum to give BIL-9 (6.86 g, 0.022 mol) as a white soild in 90 % yield. The residual water content was determined to be about 44 ppm. NMR spectra was collected by measuring neat ionic liquids with d_6-dimethylsulfoxide as an external lock at 80 °C.

^1H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) 11.33 (s, 1H), 7.89 (s, 1H), 7.01 (s, 2H), 3.21 (s, 3H); $^{19}F\{^1H\}$ NMR (564 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) -79.08; $^{13}C\{^1H\}$

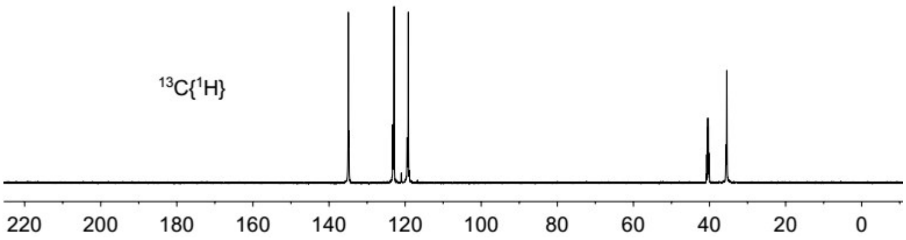
NMR (150 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) 134.9, 122.9, 119.2, 35.5; MS: calc. for $C_4H_7N_2$ [M – $SO_3HCF_3SO_3^-$]: 83.0604, found: 83.0583; calc for $C_4H_7N_2O_3S$ [M - $CF_3SO_3^-$]: 163.0138, found: 1633.0158 calc. for CF_3SO_3: 148.9526, found: 148.9555.



^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-9



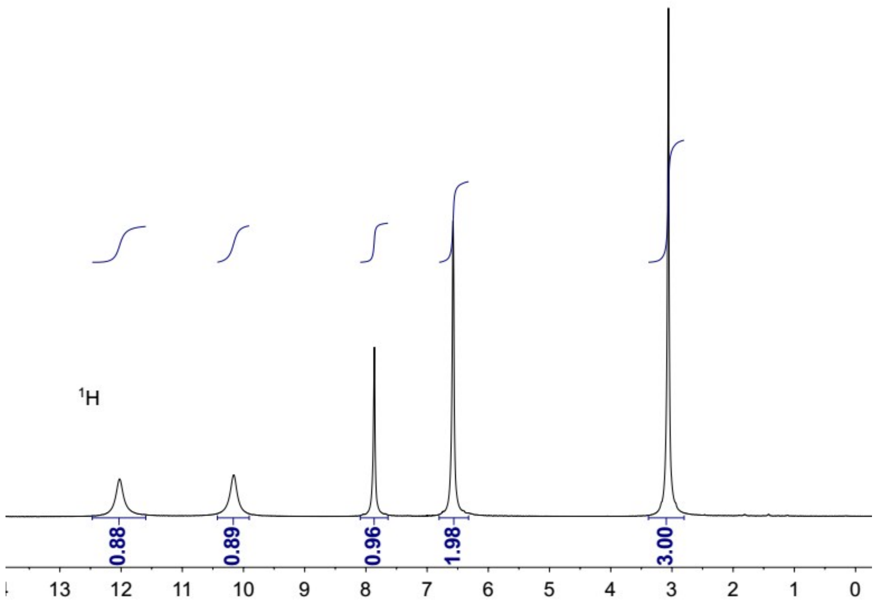
^{19}F{^{1}H} NMR (564 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-9



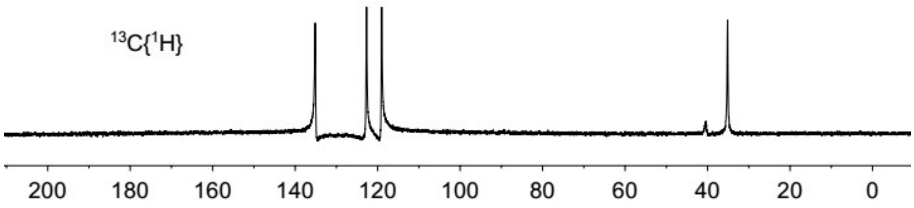
^{13}C{^{1}H} NMR (150 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-9

Preparation of [Hmim][HSO$_4$]: 1-methylimidazole (2.46 g, 0.030 mol) and equimolar sulphuric acid (3 g, 0.03 mol, 98 wt %) were mixed and stirred at 50 ^{o}C for 24 h. Then, yellow oil liquid was formed and washed repeatedly with ether (3 × 50 mL) and dried in a vacuum at 80 ^{o}C for 24 h. Finally, [Hmim][HSO$_4$](4.86 g, 0.027 mol) was obtained in a yield of 90 %. NMR spectra was collected by measuring neat ionic liquids with d_6-dimethylsulfoxide as an external lock at 80 °C.

^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) 12.02 (s, 1H), 0.16 (s, 1H), 7.86 (s, 1H), 6.57 (s, 2H), 3.06 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) 135.1, 122.7, 119.0, 35.1.



^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K) of [Hmim][HSO$_4$]



^{13}C{^{1}H} NMR (150 MHz, neat, external d_6-DMSO lock, 353 K) of [Hmim][HSO$_4$]

2.2 ^{1}H NMR Spectroscopy: In a glovebox, dry, neat ionic liquids were loaded into NMR tubes (5 mm, borosilicate glass) containing sealed capillaries with d_6-dimethylsulfoxide as an external lock. ^{1}H NMR spectra were recorded at 80 °C.

BIL-2: ^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K): δ(ppm) 10.43 (s, 1H), 7.87 (s, 1H), 6.80 (s 1H), 6.73 (s, 1H), 3.68 (t, J = 7.2 Hz, 2H), 3.20 (s, 3H), 2.43 (s, 2H), 1.68 (m, 2H);

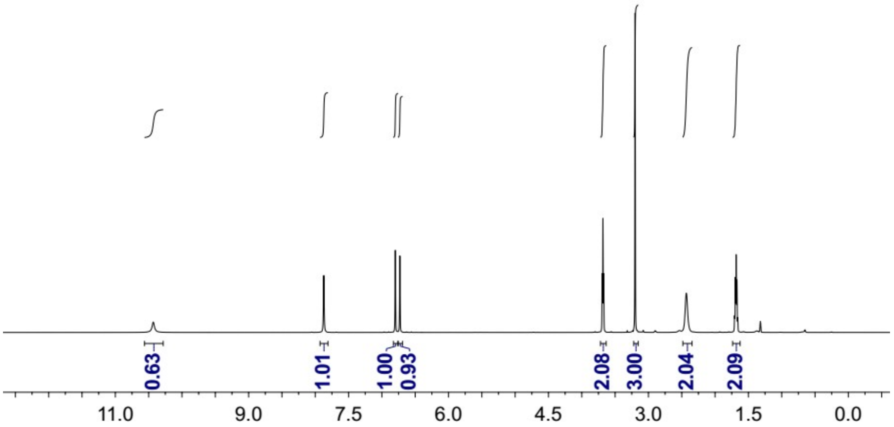
BIL-3: ^{1}H NMR (600 MHz, neat, external *d*$_6$-DMSO lock, 353 K): δ(ppm) 12.20 (s, 2H), 7.92 (s, 1H), 6.80 (s, 1H), 6.75 (s, 1H), 3.67 (s, 2H), 3.20 (s, 3H), 2.45 (s, 2H), 1.65 (s, 2H);

BIL-4: ^{1}H NMR (600 MHz, neat, external *d*$_6$-DMSO lock, 353 K): δ(ppm) 11.81 (s, 1H), 7.95 (s, 1H), 6.82 (s, 1H), 6.76 (s, 1H), 3.68 (s, 2H), 3.20 (s, 3H), 2.51 (s, 2H), 1.70 (s, 2H);

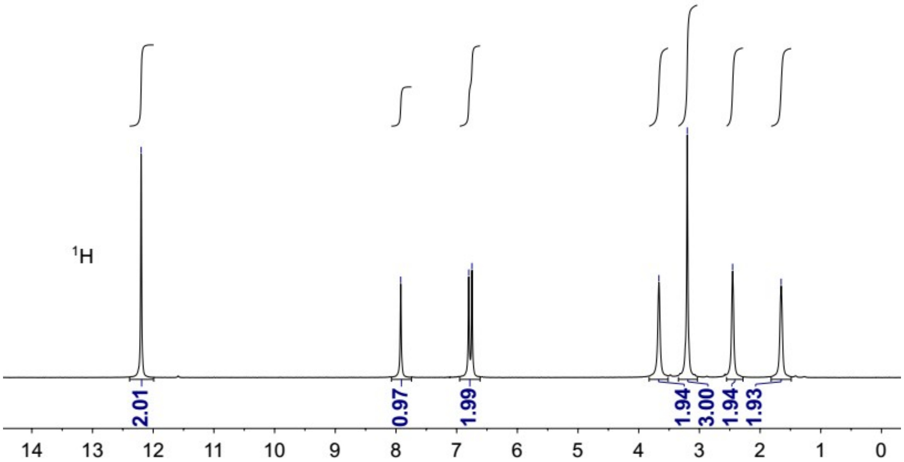
BIL-5: ^{1}H NMR (600 MHz, neat, external *d*$_6$-DMSO lock, 353 K): δ(ppm) 11.93 (s, 1H), 6.80 (d, *J* = 22.2 Hz, 2H), 3.71 (s, 2H), 3.20 (s, 3H), 2.64 (s, 2H), 2.03 (s, 3H), 1.73 (s, 2H);

BIL-6**:** ^{1}H NMR (600 MHz, neat, external *d*$_6$-DMSO lock, 353 K): δ(ppm)7.24 (s, 2H), 6.78 (s, 1H), 6.72 (s, 1H), 4.18 (s, 2H), 3.71 (t, *J* = 7.2 Hz, 2H), 3.20 (s, 3H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.69 (m, 2H);

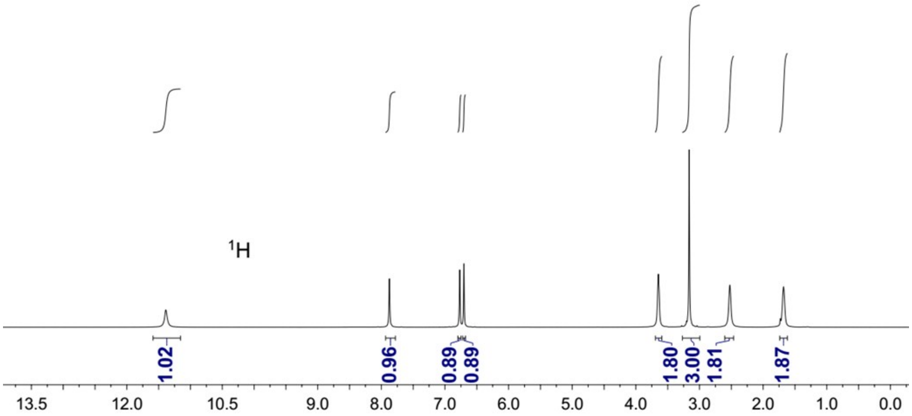
BIL-8: ^{1}H NMR (600 MHz, neat, external *d*$_6$-DMSO lock, 353 K): δ(ppm) 14.48 (s, 1H), 7.85 (s, 1H), 6.76 (s, 1H), 6.65 (s, 1H), 3.82 (s, 2H), 3.17 (s, 3H), 2.18 (s, 2H).



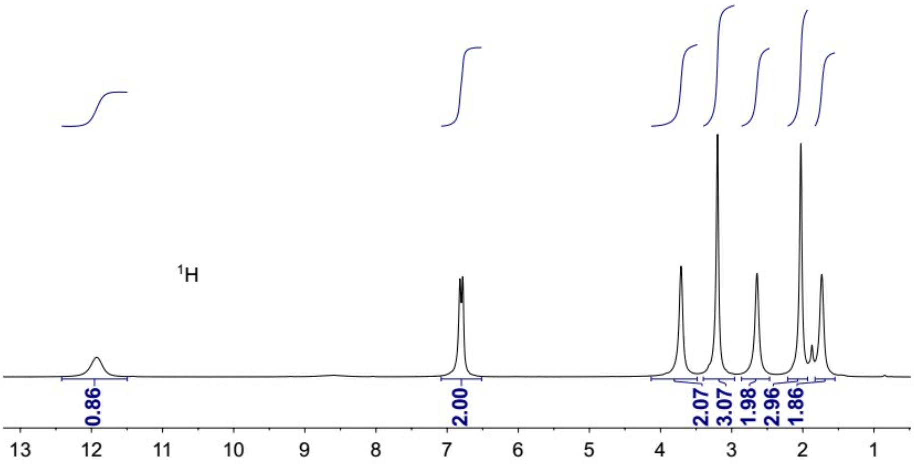
^{1}H NMR (600 MHz, neat, external *d*$_6$-DMSO lock, 353 K) of BIL-2



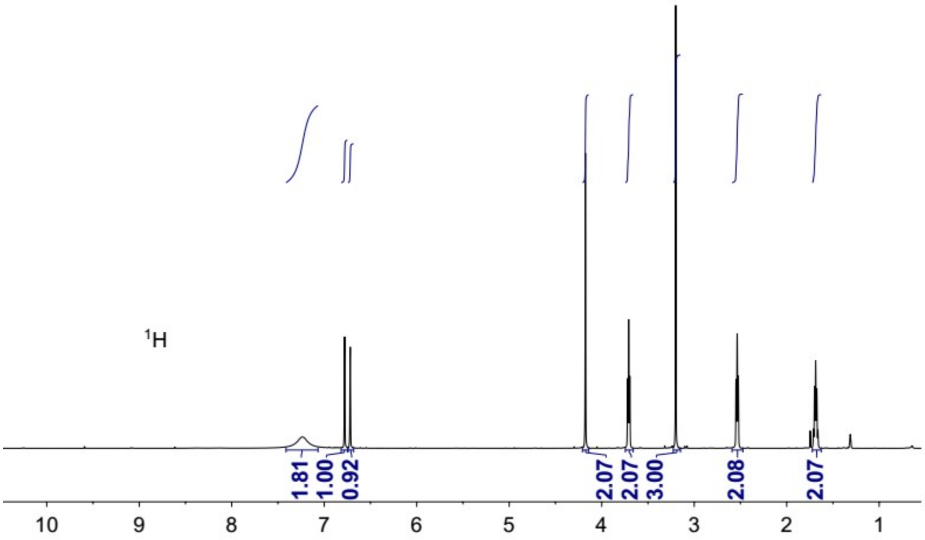
^{1}H NMR (600 MHz, neat, external *d*$_6$-DMSO lock, 353 K) of BIL-3



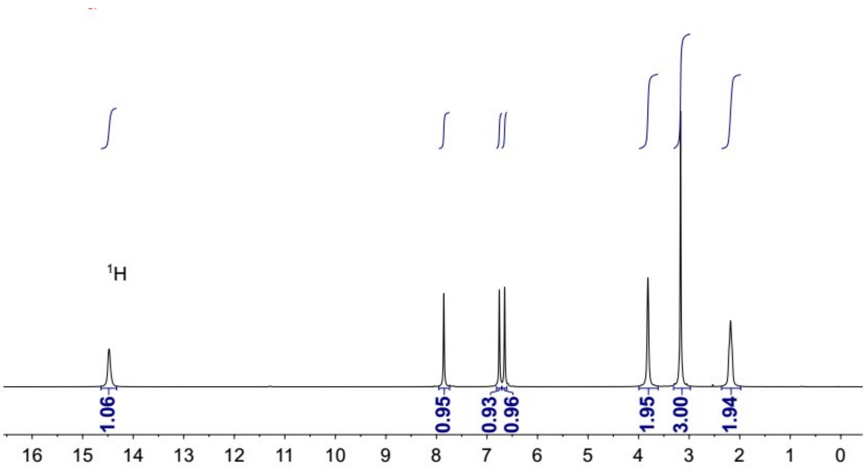
^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-4



^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-5



^{1}H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-6



^1H NMR (600 MHz, neat, external d_6-DMSO lock, 353 K) of BIL-8

2.3 Acid-Base Titration Experiments

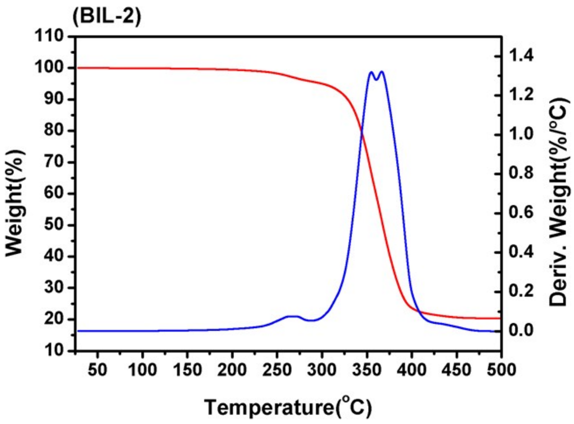
General procedures: BILs/$NaHSO_4$ solution (5 mmol/L) and sodium hydroxide titrant (0.1 mol/L) were prepared by distilled water respectively, and the latter was calibrated by potassium hydrogen phthalate that had been dried to constant weight at 105 °C before use. The acid dissociation constants [$N = (c_{NaOH} \times V_{NaOH})/(c_{BIL} \times V_{BIL})$] were determined by titrating 20.00 mL of BIL solution with standardized NaOH solution by a drop of phenothalin solution as the indicator. When the color of solution changed to pink after a drop of NaOH solution were dropped into the beaker, the volume of NaOH solution was recorded. Before the acid dissociation constant was obtained, each experiment was repeated 3 times.

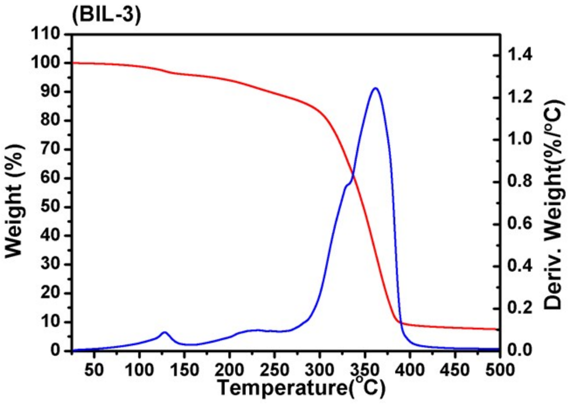
Table S1. Acid-based titration of BILs and $NaHSO_4$

Type	BIL-1	BIL-2	BIL-3	BIL-4	BIL-5	BIL-6	BIL-7	BIL-8	BIL-9	$NaHSO_4$	[Pmim][HSO_4]
N	0.4	1.96	2.02	1.05	0.90	0.99	1.05	1.0	2.20	1.07	1.19

2.4 Evaluation of Thermal Stability

Thermogravimetric Analyzer Q5000 V3.15 Build 263 was applied to investigate the thermal stability. (heating 10 °C/min to 500 °C, N_2 flow 40 mL/min, Platinum pans)





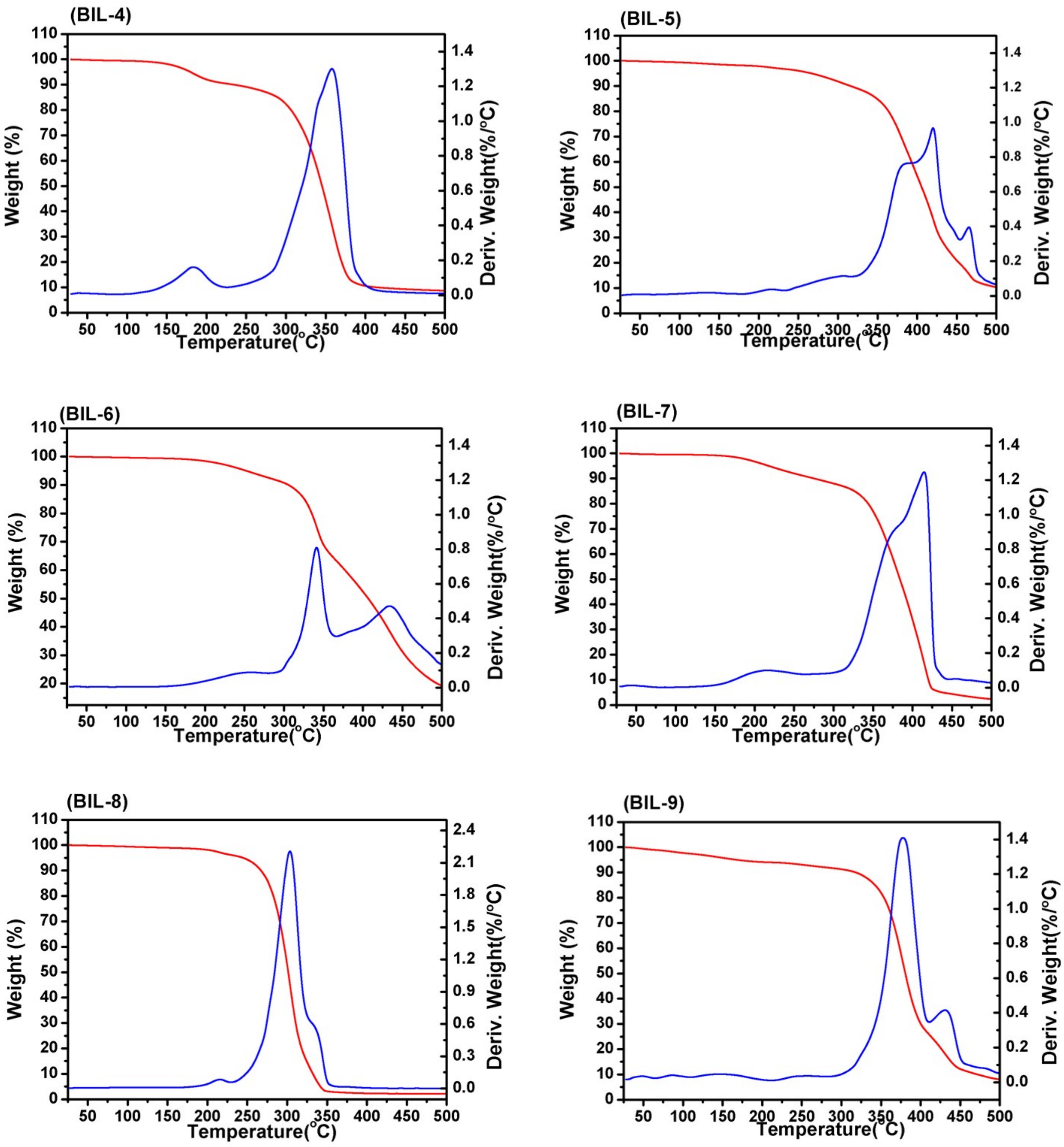


Figure S1.TG (red line) and DTG (blue line) curves of BIL-2~9

2.5 Stability Investigation of BIL-2 in the Presence of H_2O.

To investigate the stability of BIL-2 in the presence of H_2O, six BIL-2 solutions (5 mmol/L) containing with different amount of NaOH (0 eq, 0.5 eq, 1 eq, 1.5 eq, 2 eq. and 2.5 eq) were prepared by deuterium oxide as the solvent. Then the ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR were measured at 298 K.

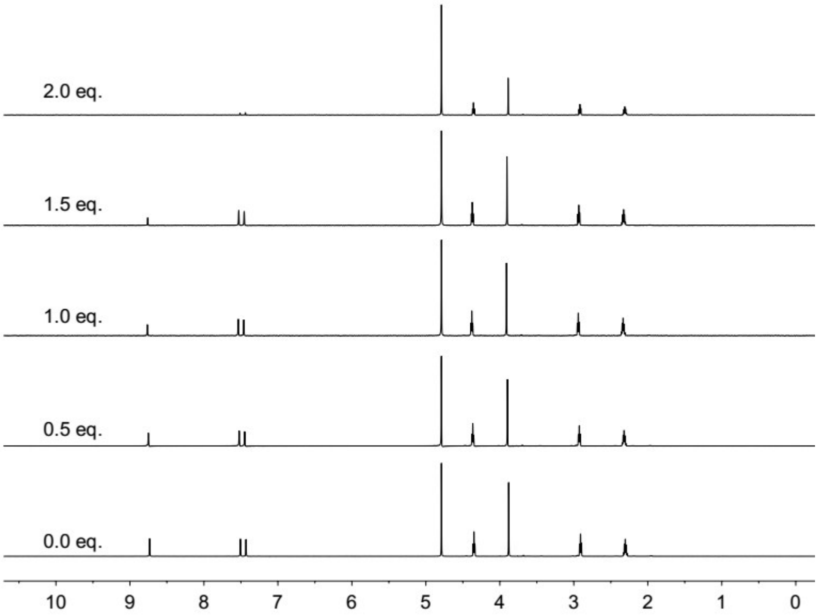


Figure S2-1. ^{1}H NMR of BIL-2 with different amount of NaOH

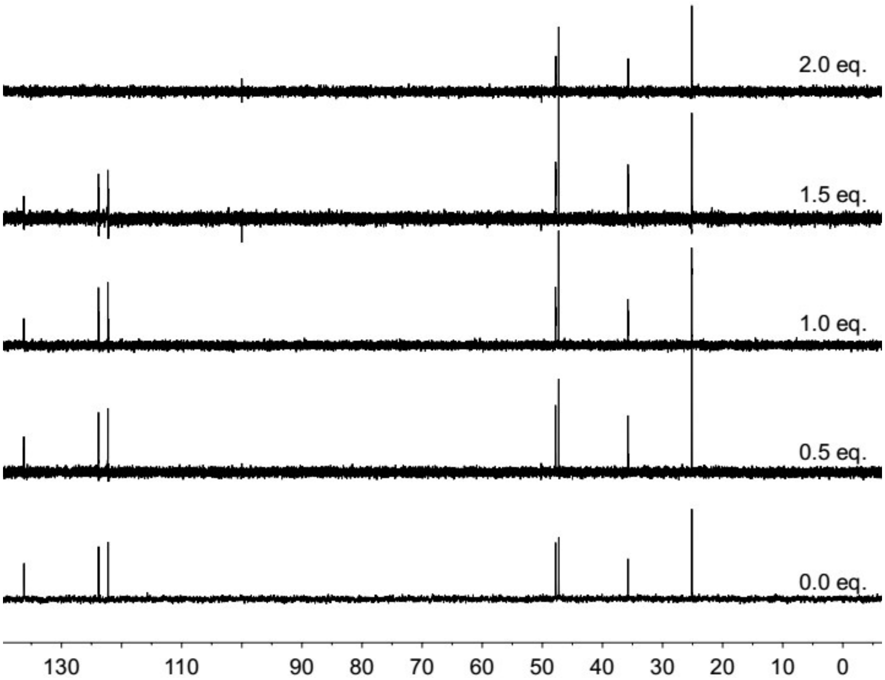


Figure S2-2. ^{13}C{^{1}H} NMR of BIL-2 with different amount of NaOH

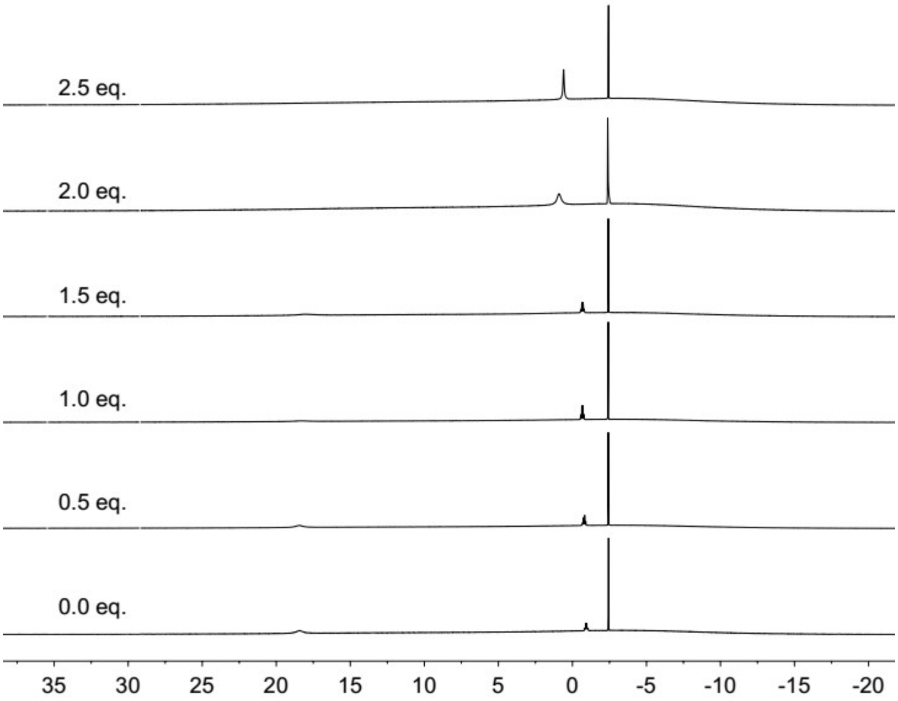


Figure S2-3. $^{11}B\{^1H\}$ NMR of BIL-2 with different amount of NaOH

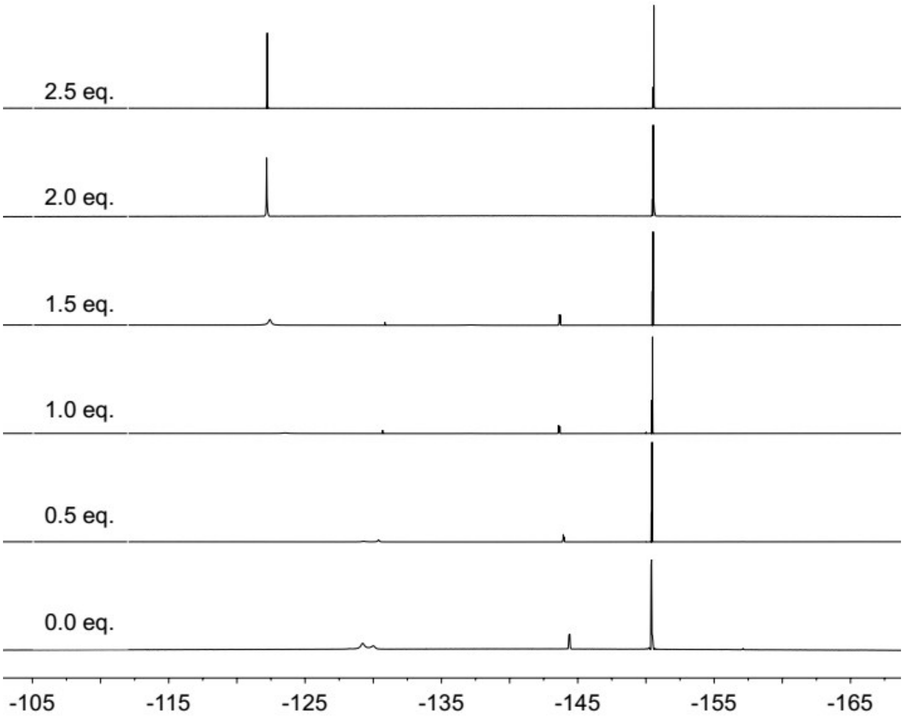
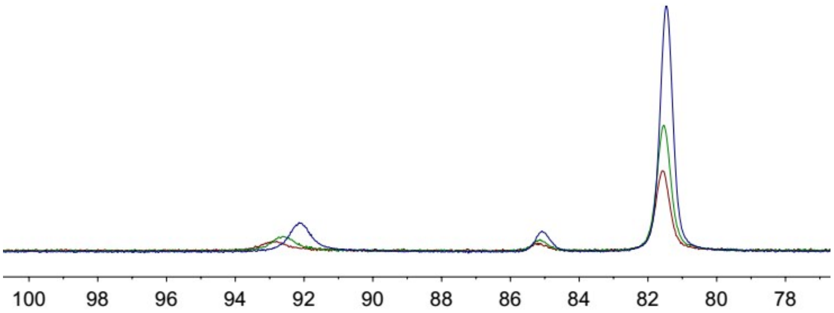
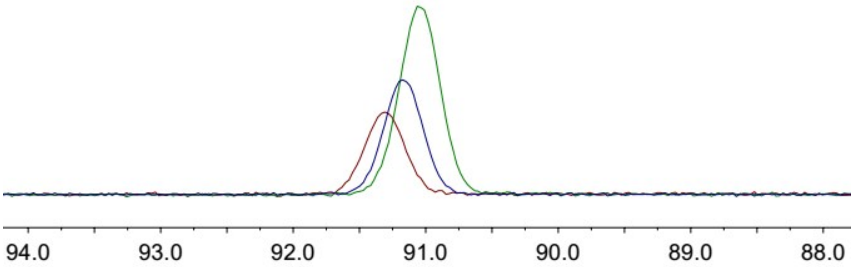


Figure S2-4. $^{19}F\{^1H\}$ NMR of BIL-2 with different amount of NaOH

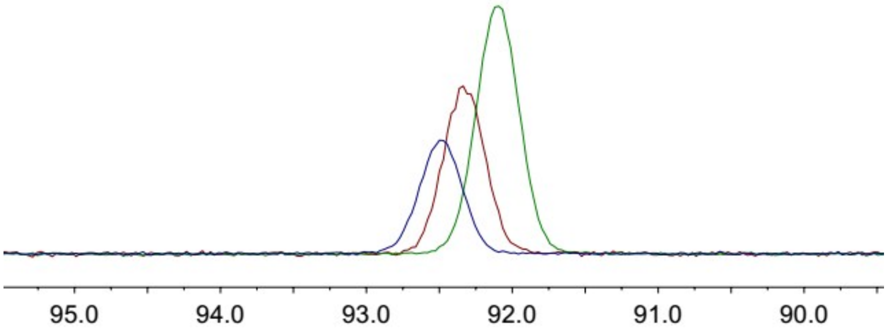
2.6 Gutmann acceptor number (AN)



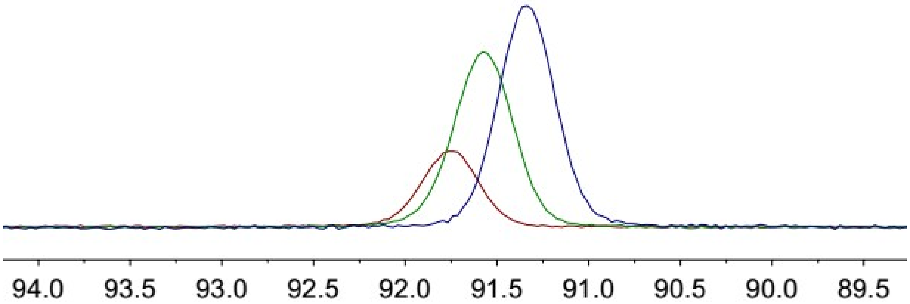
$^{31}P\{^{1}H\}$ NMR spectra (600 MHz, neat, 353 K) of TEPO for AN value of BIL-2 (δ: ppm).



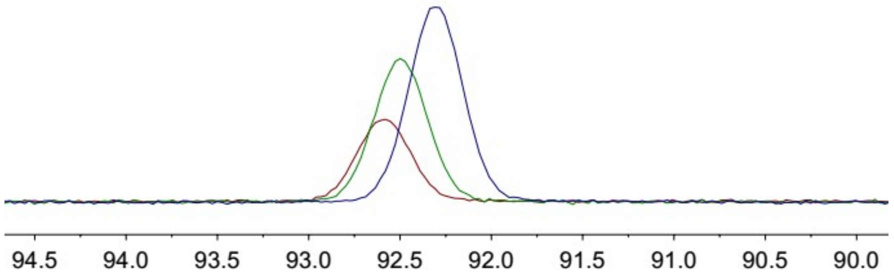
$^{31}P\{^{1}H\}$ NMR spectra (600 MHz, neat, 353 K) of TEPO for AN value of BIL-3 (δ: ppm).



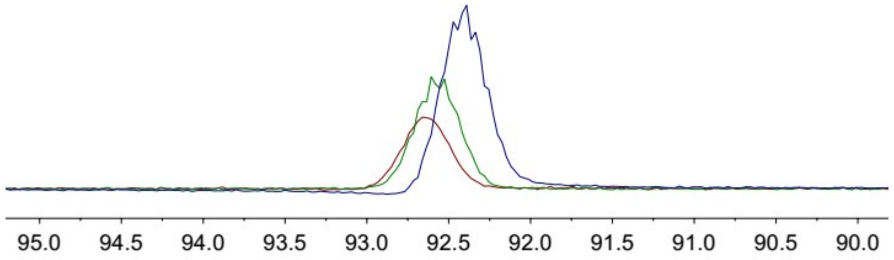
$^{31}P\{^{1}H\}$ NMR spectra (600 MHz, neat, 353 K) of TEPO for AN value of BIL-4 (δ: ppm).



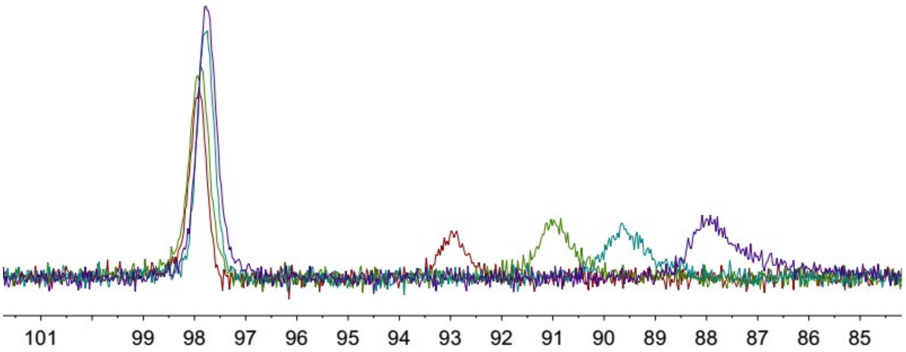
$^{31}P\{^{1}H\}$ NMR spectra (600 MHz, neat, 353 K) of TEPO for AN value of BIL-5 (δ: ppm).



$^{31}P\{^1H\}$ NMR spectra (600 MHz, neat, 353 K) of TEPO for AN value of BIL-6 (δ: ppm).



$^{31}P\{^1H\}$ NMR spectra (600 MHz, neat, 353 K) of TEPO for AN value of BIL-8 (δ: ppm).



$^{31}P\{^1H\}$ NMR spectra (600 MHz, neat, 353 K) of TEPO for AN value of BIL-9 (δ: ppm).

3 Catalytic Reactions

Table S2 Data of Catalytic experiments

		1	2	3	4	average value	error
BIL-2	$C_{sor.}$/%	91	93	90	92	91.5	±1.0
	$Y_{sorbitan}$/%	76	80	72	78	76.5	±2.5
	$Y_{isosorbide}$/%	12	10	16	9	11.8	±2.3
BIL-3	$C_{sor.}$/%	98	99	96	99	98.0	±1.0
	$Y_{sorbitan}$/%	52	56	50	55	53.3	±2.3

	$Y_{isosorbide}$/%	43	39	42	38	40.5	±2.0
BIL-4	$C_{sor.}$/%	97	98	99	99	98.3	±0.8
	$Y_{sorbitan}$/%	13	7	12	9	10.3	±2.3
	$Y_{isosorbide}$/%	75	76	74	77	75.5	±1.0
BIL-5	$C_{sor.}$/%	98	99	99	99	99.8	±0.8
	$Y_{sorbitan}$/%	5	4	5	3	4.3	±1.5
	$Y_{isosorbide}$/%	84	85	82	83	84.5	±1.0
BIL-6	$C_{sor.}$/%	98	97	98	99	98.0	±0.5
	$Y_{sorbitan}$/%	37	38	36	37	37.0	±0.5
	$Y_{isosorbide}$/%	54	56	54	56	55.0	±1.0
BIL-7	$C_{sor.}$/%	99	99	98	99	99.8	±0.8
	$Y_{sorbitan}$/%	9	7	8	9	8.3	±0.8
	$Y_{isosorbide}$/%	76	79	78	76	77.3	±1.3
BIL-8	$C_{sor.}$/%	99	98	99	99	98.8	±0.8
	$Y_{sorbitan}$/%	37	36	38	42	38.3	±1.9
	$Y_{isosorbide}$/%	64	65	63	59	62.8	±1.9
BIL-9	$C_{sor.}$/%	99	98	99	99	98.8	±0.4
	$Y_{sorbitan}$/%	67	66	68	65	66.5	±1.0
	$Y_{isosorbide}$/%	21	19	23	24	21.8	±1.8
H_2SO_4	$C_{sor.}$/%	98	97	98	98	97.5	±0.5
	$Y_{sorbitan}$/%	57	56	58	56	56.8	±0.8
	$Y_{isosorbide}$/%	33	35	34	36	34.5	±1.0
CF_3SO_3H	$C_{sor.}$/%	98	99	97	98	98.0	±0.5
	$Y_{sorbitan}$/%	78	76	79	78	77.8	±0.9
	$Y_{isosorbide}$/%	16	18	16	17	16.8	±0.8

4 Stability experiments of acid in vacuum during dehydration

The reactions were carried out in a 50 mL three flask equipped with a vacuum distillation apparatus which could be cooled by liquid nitrogen. Before catalyst BIL-4 or CF_3SO_3H (TfOH) (0.0012 mol) was added to flask, sorbitol (0.2 mol, 36.4 g) was heated to 130 ^oC until completely melted and became transparent. The reaction pressure was kept at 4 kPa, since the catalyst added. This time was assigned as t = 0. The vapour was collected as solution after condensation with liquid nitrogen by time, and its pH value was measured by pH meter, respectively.

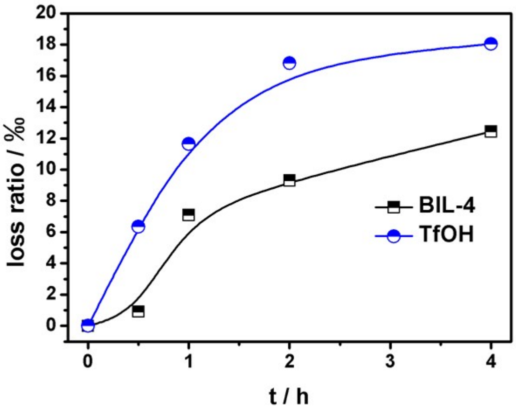


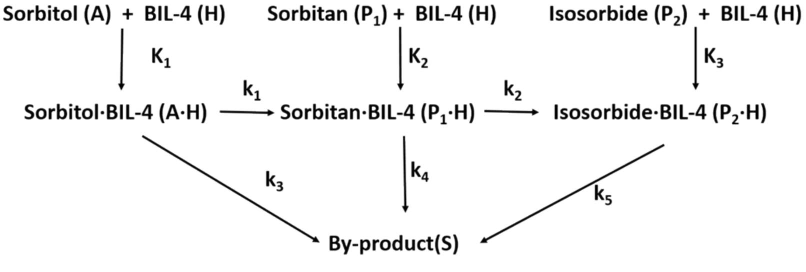
Figure S3. The catalyst loss ratio for BIL-4 and TfOH during dehydration reaction at 130 ^oC, 4 kPa.

the mole of loss catalyst = 10^{-pH} × volume of collected solution

Loss ratio = the mole of loss catalyst/the mole of catalyst

5 Dynamic experiments

Different steps are involved in the catalytic transformation such as adsorption equilibrium (Scheme S4). k_1 and k_2 are rate constants for sorbitol and 1,4-sorbitan, respectively, whereas k_3, k_4, and k_5 are rate constants for side reactions of sorbitol, 1,4-sorbitan and isosorbide. The equilibrium constants for association of sulphuric acid with sorbitol, 1,4-sorbitan, and isosorbide are denoted as K_1, K_2, and K_3, respectively. The following system of partial differential equations and equilibrium constants (1)-(7) were used to calculate kinetic parameter *via* matlab, where C_A, C_{p1}, C_{p2} and C_s are the concentrations of sorbitol, 1,4-sorbitan, isosorbide and by-product, respectively. c_{H0} is the initial concentration of ionic liquid (BIL-4) and $C_{P1.H}$, $C_{P2.H}$, and $C_{P3.H}$ are the concentrations of BIL-4 adducts with sorbitol, 1, 4-sorbitan and isosorbide.



Scheme S4 Reaction scheme of sorbitol dehydration catalysed by BILs including rate coefficients for each step. While being produced in each step, the by-product water is not shown.

$$K_1 = C_{A.H}/[C_A(C_{H0} - C_{A.H} - C_{P1.H} - C_{P2.H})] \tag{1}$$

$$K_2 = C_{P1.H}/[C_{P1}(C_{H0} - C_{A.H} - C_{P1.H} - C_{P2.H})] \tag{2}$$

$$K_3 = C_{P2.H}/[C_{P2}(C_{H0} - C_{A.H} - C_{P1.H} - C_{P2.H})] \tag{3}$$

$$-dC_A/dt = k_1C_A+k_3C_A \tag{4}$$

$$dC_{P1}/dt = k_1C_A-k_2C_{P1}-k_4C_{P1} \tag{5}$$

$$dC_{p2}/dt = k_2C_{P1}-k_5C_{P2} \tag{6}$$

$$dC_s/dt = k_3C_A+k_4C_{P1}+k_5C_{P2} \tag{7}$$

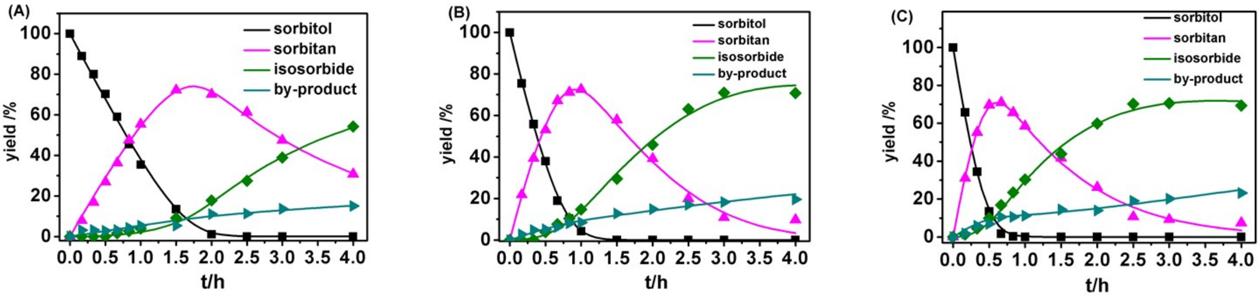


Figure S4. Time course of sorbitol dehydration by BIL-4 at (A) 130 °C, (B) 140 °C, (C) 150 °C. Data points show experimental results and lines are simulation curves based on eqs 1-7

Table S3 the absolute error of sorbitol dehydration kinetic simulation

	the absolute error /%				Average value of the absolute error /%
T/°C	sorbitol	1,4-sorbitan	isosorbide	By-product	
130	0.718403	1.030905	0.821888	0.775913	0.836777
140	0.727042	1.836823	1.785924	0.789108	1.284725
150	0.688362	2.331564	1.944828	1.214446	1.5448
Average/ %	0.711269	1.733097	1.517547	0.926489	1.222101

4 Recycling Study

Table S4. Data of Recycling Experiments

		Group1	Group2	Group3	Group4	Group5	Average
Run1	$Y_{isosorbide}$ %	70.27	72.37	69.84	73.97	71.61	71.61(±1.25)
	$C_{sorbitol}$ %	99.07	99.11	99.37	99.10	99.69	99.27(±0.21)
Run2	$Y_{isosorbide}$ %	74.30	67.73	74.46	74.92	73.22	73.33(±1.48)
	$C_{sorbitol}$ %	98.47	98.65	98.37	99.46	99.17	98.82(±0.40)
Run3	$Y_{isosorbide}$ %	75.42	72.02	74.47	73.00	74.77	74.16(±0.87)
	$C_{sorbitol}$ %	97.26	97.01	99.00	99.19	99.12	98.32(±0.94)
Run4	$Y_{isosorbide}$ %	71.23	76.75	72.56	67.13	73.13	72.16(±2.38)
	$C_{sorbitol}$ %	99.04	97.01	97.91	94.00	98.15	97.23(±1.36)
Run5	$Y_{isosorbide}$ %	68.46	73.72	70.23	72.98	70.12	71.10(±1.8)
	$C_{sorbitol}$ %	98.53	97.44	98.42	99.69	97.46	98.31(±0.68)

7 Systematic Optimization

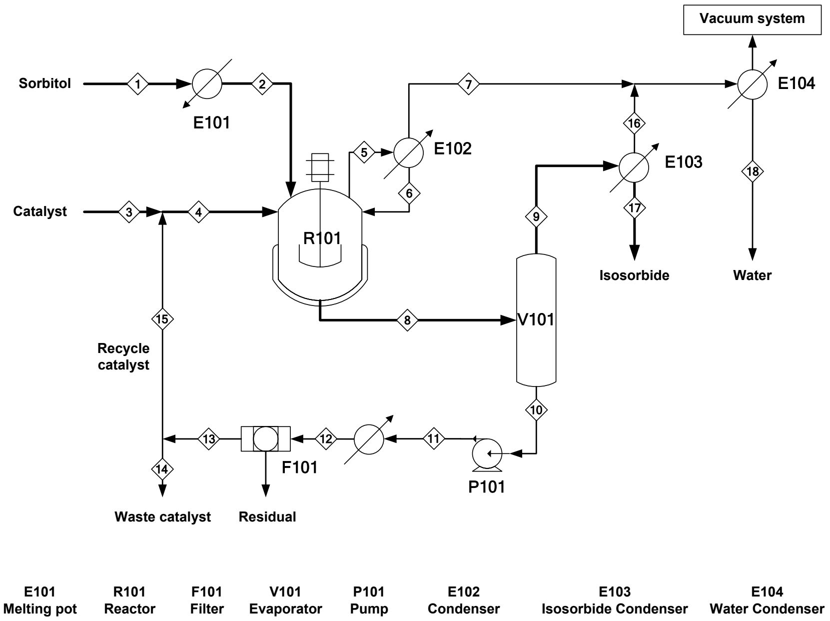


Figure S5. Process flow diagram of the dehydration process

Table S5. Key parameters for base case process modelling and streams

Item	Name	Temperature/^{o}C	Pressure/kPa	Residence time/min
R101	Reactor	160	4	90
V101	Evaporator	230	4	10
E101	Melting pot	120	101	
E102	Condenser	100	2	
E103	Isosorbide Condenser	100	2	
E104	Water Condenser	7	1	

Table S6. Materials of Process flow diagram of the dehydration process Ⅰ

STREAM ID	**C1**	**C2**	**C3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**	**C10**
Temperature/°C	25	120		129.7	160	100	100	160	230	230
Pressure/kPa	101	101		1	4	2	2	4	4	4
Vapor Frac					1	0	1	0	1	0
Mole Flow/(kmol/h)	68	68		146.296	103.425	2.877	100.548	149.18	73.023	97.87
Mass Flow/(kg/h)	12387.8	12387.8		24596.7	2245.204	402.32	1842.884	22753.72	7492.532	15261.12
Volume Flow cum/sec	0.002	0.002		0.003	25.866		43.326	0.001	21.214	0.001
Enthalpy/(Gcal/h)	-21.251	-20.682		-36.482	-6.138	-0.481	-5.77	-29.41	-8.439	-19.559
Mass Flow/(kg/h)										
SORBITOL	12387.8	12387.8		12394.26	0.001	0.001		941.778	0.008	8.074
SORBITAN				113.161	0.008	0.008		2428.456	0.094	141.447
ISOSORBI				5107.993	435.643	399.729	35.915	11000.33	7039.561	6384.993
BY-PRO				6979.451	0.028	0.028		8324.944	5.775	8724.307
WATER				1.836	1809.523	2.554	1806.969	58.211	447.094	2.295
Mass Frac										
SORBITOL	1	1		0.504				0.041		0.001
SORBITAN				0.005				0.107		0.009
ISOSORBI				0.208	0.194	0.994	0.019	0.483	0.94	0.418
BY-PRO				0.284				0.366	0.001	0.572
WATER					0.806	0.006	0.981	0.003	0.06	
Mole Flow/(kmol/h)										
SORBITOL	68	68		68.035				5.17		0.044
SORBITAN				0.689				14.793	0.001	0.862
ISOSORBI				34.953	2.981	2.735	0.246	75.273	48.17	43.691
BY-PRO				42.517				50.713	0.035	53.146
WATER				0.102	100.444	0.142	100.302	3.231	24.818	0.127
Mole Frac										
SORBITOL	1	1		0.465				0.035		

Table S6. Materials of Process flow diagram of the dehydration process Ⅰ

STREAM ID	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
SORBITAN				0.005				0.099		0.009
ISOSORBI				0.239	0.029	0.951	0.002	0.505	0.66	0.446
BY-PRO				0.291				0.34		0.543
WATER				0.001	0.971	0.049	0.998	0.022	0.34	0.001

Table S7. Materials of Process flow diagram of the dehydration process Ⅱ

STREAM ID	C11	C12	C13	C14	C15	C16	C17
Temperature/^{o}C	230.1	160	160	160	100	100	7
Pressure/kPa	200	1	1	1	2	2	1
Vapor Frac	0	0	0	0	1	0	0
Mole Flow/(kmol/h)	97.87	97.87	19.574	78.296	22.373	50.65	122.921
Mass Flow/(kg/h)	15261.12	15261.12	3052.223	12208.9	410.06	7082.473	2252.944
Volume Flow/(cum/sec)	0.001	0.001		0.001	9.641	0.001	0.001
Enthalpy/(Gcal/h)	-19.558	-19.75	-3.95	-15.8	-1.284	-8.462	-8.456
Mass Flow/(kg/h)							
SORBITOL	8.074	8.074	1.615	6.459		0.008	
SORBITAN	141.447	141.447	28.289	113.161		0.094	
ISOSORBI	6384.993	6384.993	1276.999	5107.993	7.986	7031.575	43.901
BY-PRO	8724.307	8724.307	1744.861	6979.451		5.775	
WATER	2.295	2.295	0.459	1.836	402.074	45.021	2209.043
Mass Frac							
SORBITOL	0.001	0.001	0.001	0.001			
SORBITAN	0.009	0.009	0.009	0.009			
ISOSORBI	0.418	0.418	0.418	0.418	0.019	0.993	0.019
BY-PRO	0.572	0.572	0.572	0.572		0.001	
WATER					0.981	0.006	0.981

Table S7. Materials of Process flow diagram of the dehydration process Ⅱ

STREAM ID	C11	C12	C13	C14	C15	C16	C17
Mole Flow/(kmol/h)							
SORBITOL	0.044	0.044	0.009	0.035			
SORBITAN	0.862	0.862	0.172	0.689		0.001	
ISOSORBI	43.691	43.691	8.738	34.953	0.055	48.115	0.3
BY-PRO	53.146	53.146	10.629	42.517		0.035	
WATER	0.127	0.127	0.025	0.102	22.318	2.499	122.621
Mole Frac							
SORBITOL							
SORBITAN	0.009	0.009	0.009	0.009			
ISOSORBI	0.446	0.446	0.446	0.446	0.002	0.95	0.002
BY-PRO	0.543	0.543	0.543	0.543		0.001	
WATER	0.001	0.001	0.001	0.001	0.998	0.049	0.998