

Supporting Information

Ionic Liquids Containing Block-Copolymer Based Supramolecules

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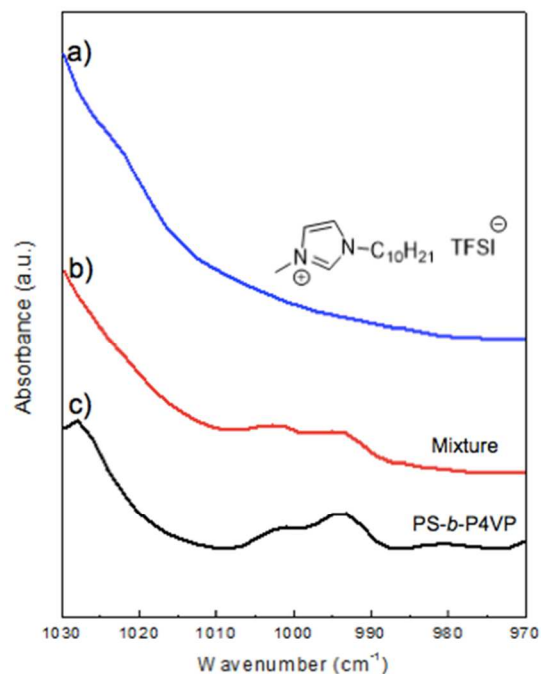


Figure S1 FTIR spectra of a) reference small molecule: 1-methyl-3-decyl imidazolium bis(trifluoromethylsulfonyl)imide, b) mixture of BCP and small molecules and c) PS-*b*-P4VP

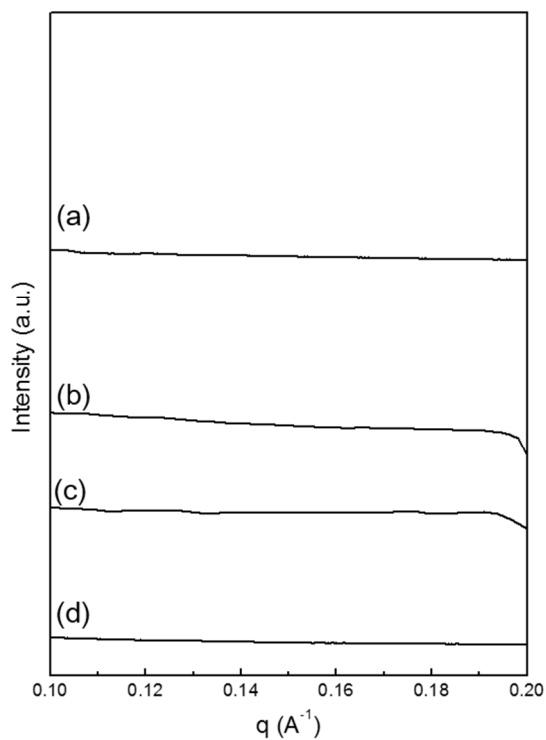


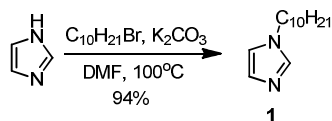
Figure S2 Small Angle X-ray Scattering (SAXS) profiles at q from 0.1 \AA^{-1} to 0.2 \AA^{-1} . (a) PS-*b*-P4VP(ILC₄I)₁ (b) PS-*b*-P4VP(ILC₄TFSl)₁ (c) PS-*b*-P4VP(ILC₁₀I)₁ (d)

PS-*b*-P4VP(ILC₁₀TFSI)

General Methods

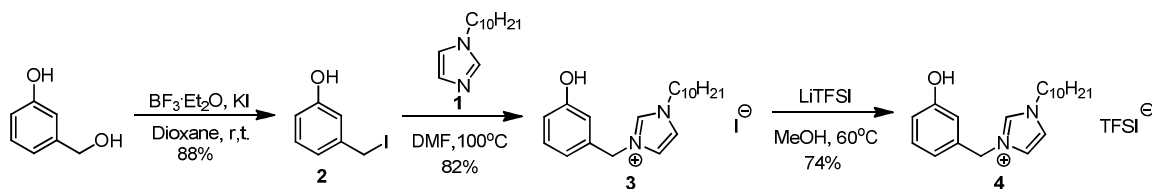
All ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on Bruker AVQ-400 MHz spectrometers and are referenced to residual solvent peaks (CDCl₃ ¹H NMR δ = 7.26 ppm, ¹³C NMR δ = 77.16 ppm; DMSO-*d*₆ ¹H NMR δ = 2.50 ppm, ¹³C NMR δ = 39.60 ppm). ESI mass spectrometry was performed on a Finnigan LTQFT (Thermo) spectrometer in positive ionization mode.

Synthesis



Scheme S1. Synthesis of **1**

1-decylimidazole (1) A 20 mL glass vial was charged with imidazole (0.75 g, 11 mmol, 1.1 equiv.) and K_2CO_3 (1.78 g, 16.5 mmol, 1.65 equiv.) in DMF (8 mL). The reaction was stirred at 100°C overnight. Then, 1-bromodecane (2.21 g, 10 mmol, 1.0 equiv.) was added and the mixture was stirred for another 24 h. The solvent was removed under vacuum. Chloroform (15 mL) was added in residue and washed by water (15 mL) for three times. The organic layer was collected and dried by anhydrous Na_2SO_4 . The solvent was removed under vacuum to yield **1** as light yellow oil (234 mg, 94%). ^1H NMR (400 MHz, CDCl_3) δ 7.42 (s, 1H), 7.01 (s, 1H), 6.87 (s, 1H), 3.88 (t, $J = 7.2$ Hz, 2H), 2.74 (m, 2H), 1.94 – 1.54 (m, 2H), 1.43 – 1.13 (m, 12H), 0.84 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.03, 129.26, 118.77, 47.05, 31.85, 31.08, 29.48, 29.43, 29.26, 29.07, 26.54, 22.67, 14.12. which were consistent with report¹.

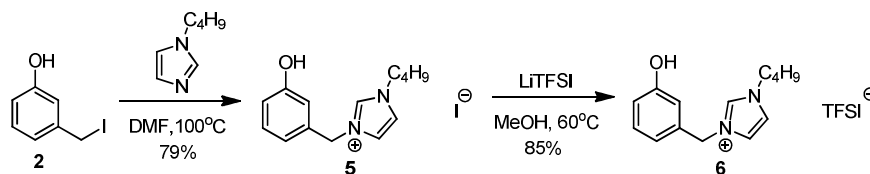


Scheme S2. Syntheses of **2-4**

3-(iodomethyl)phenol (2) A 250 mL round bottom flask was charged with 3-hydroxymethylphenol (5.01 g, 40 mmol, 1.0 equiv.) and KI (7.03 g, 42 mmol, 1.05 equiv.) in dry 1,4-dioxane (100 mL). The reaction mixture was stirred at room temperature for 30 min under nitrogen gas. Then, boron trifluoride diethyl etherate (5.3 mL, 42 mmol, 1.05 equiv.) was added into the mixture. The reaction mixture was stirred for another 5 h at room temperature. Then the solvent was removed under vacuum. The residue was dissolved in chloroform (300 mL) and wash by water (200 mL) for three times. The organic layer was collected and dried by anhydrous Na_2SO_4 and concentrated on a rotary evaporator. Column chromatography (silica gel; 10:1 hexane/ethyl acetate) yielded **2** (8.18g, 88%) as white powder. ^1H NMR (400 MHz, CDCl_3) δ 7.17 (m, 1H), 6.96 (d, $J = 7.6$ Hz, 1H), 6.86 (s, 1H), 6.73 (d, $J = 8.1$ Hz, 1H), 5.44 (s, 1H), 4.39 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 155.50, 141.00, 130.18, 121.34, 115.75, 115.21, 5.51. which were consistent with report².

1-decyl-3-(3-hydroxybenzyl) imidazolium iodide (ILC₁₀I, 3) A 20 mL glass vial was charged with 3-(iodomethyl)phenol (**2**) (0.92 g, 4 mmol, 1.0 equiv) and 1-decylimidazole (**1**) (0.83 g, 4 mmol, 1.0 equiv.) in DMF (10 mL). The reaction mixture was stirred at 100 °C overnight. The solvent was removed under vacuum. Chloroform (20 mL) was added into the residue and washed by water (20 mL) for three times. The organic layer was collected and dried by anhydrous Na₂SO₄ and concentrated on a rotary evaporator. Column chromatography (silica gel; gradient elution from 1:1 ethyl acetate/hexane to 20:1 ethyl acetate/methanol) yielded **3** (1.44g, 82%) as yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 9.77 (s, 1H), 7.37 (m, 1H), 7.33 (m, 1H), 7.24 (s, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.04 – 6.98 (m, 1H), 6.90 – 6.84 (m, 1H), 5.40 (s, 2H), 4.36 – 4.14 (m, 2H), 2.11 – 1.75 (m, 2H), 1.44 – 1.18 (m, 14H), 0.91 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.27, 135.64, 134.29, 130.44, 122.48, 120.06, 119.63, 117.24, 116.05, 52.95, 50.42, 31.85, 30.14, 29.47, 29.40, 29.26, 28.98, 26.27, 22.67, 14.15. FTMS (HR-ESI positive): [C₂₀H₃₁O₁N₂]⁺ cal. 315.2431; found, 315.2427

1-decyl-3-(3-hydroxybenzyl) imidazolium bis(trifluoromethylsulfonyl)imide (ILC₁₀TFSI, 4) A 4 mL glass vial was charged with 1-decyl-3-(3-hydroxybenzyl) imidazolium iodine (**3**) (221 mg, 0.5 mmol, 1.0 equiv) and lithium bis(trifluoromethylsulfonyl)imide (214 mg, 0.75 mmol, 1.5 equiv.) in methanol (2 mL). The reaction mixture was stirred at 60 °C overnight. The solvent was removed under vacuum. Chloroform (5 mL) was added in residue and washed by water (5 mL) for three times. The organic layer was collected and dried by anhydrous Na₂SO₄. The solvent was removed under vacuum to yield **4** as light yellow oil (218 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 1H), 7.30 – 7.15 (m, 3H), 6.93 – 6.79 (m, 3H), 5.17 (s, 2H), 4.17 – 4.05 (m, 2H), 2.02 – 1.64 (m, 2H), 1.26 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.07, 134.74, 133.58, 130.62, 122.27, 120.18, 116.79, 115.44, 99.85, 53.22, 50.15, 31.69, 29.81, 29.25, 29.13, 29.07, 28.68, 25.97, 22.51, 13.94.



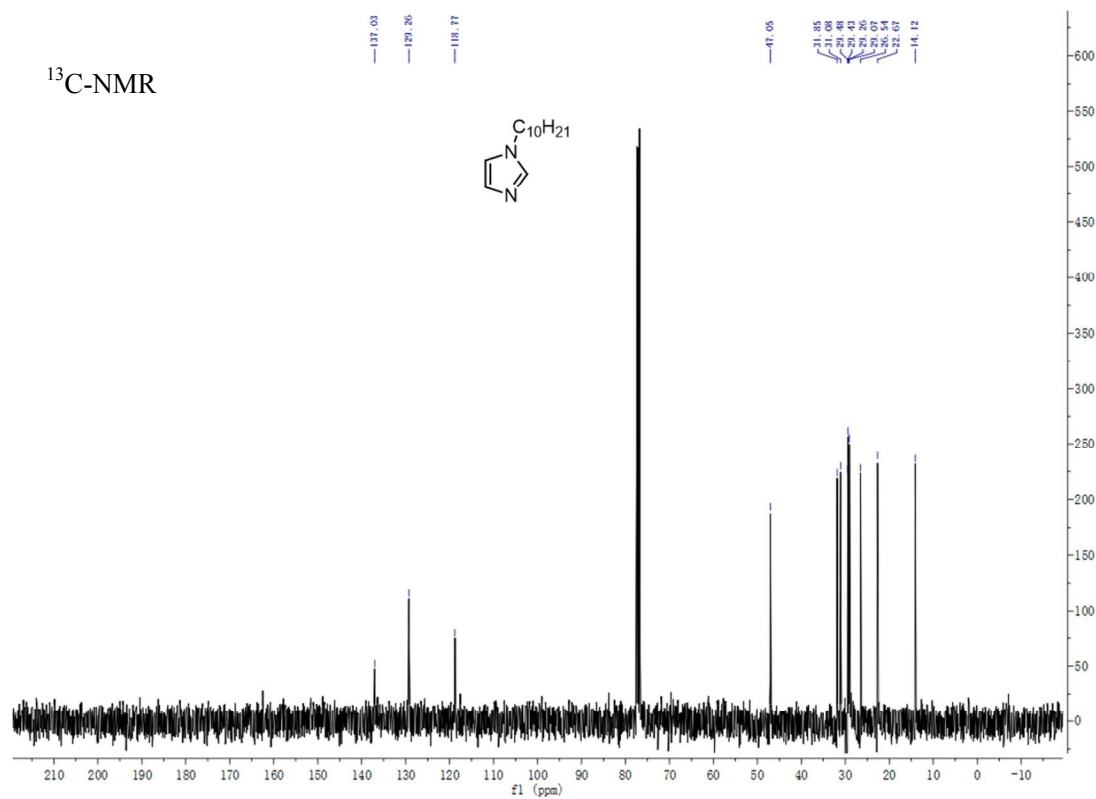
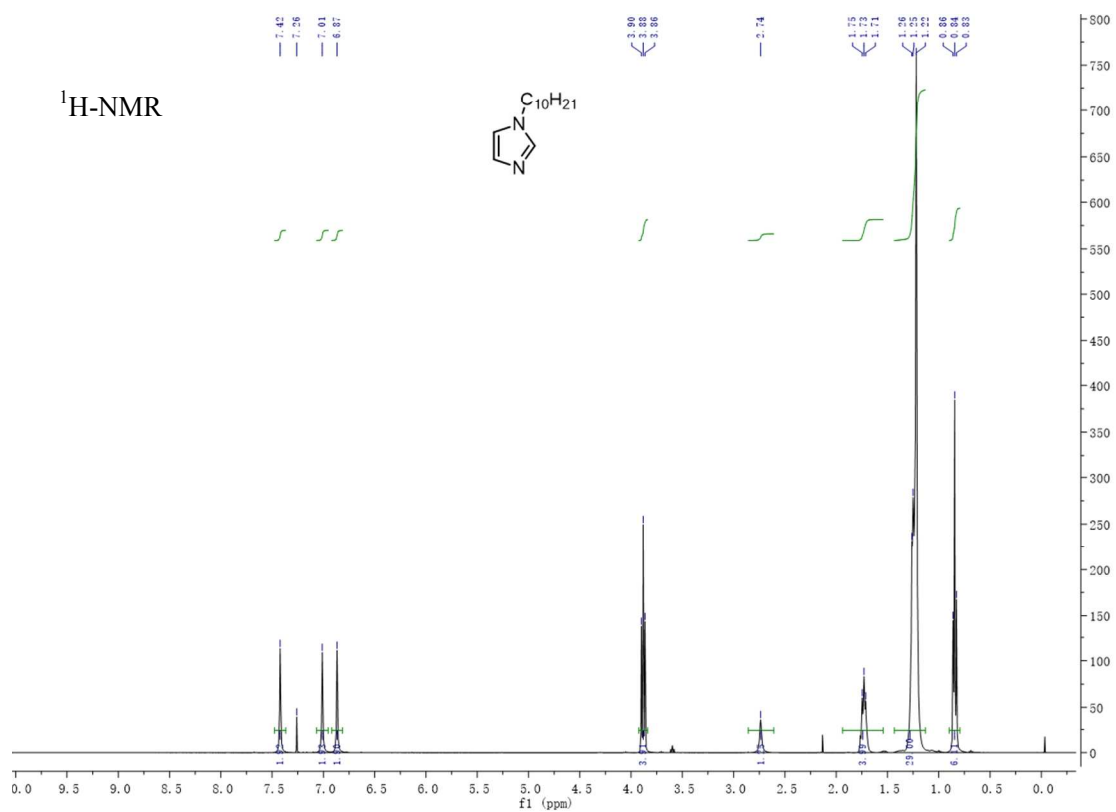
Scheme S3. Syntheses of **5** and **6**

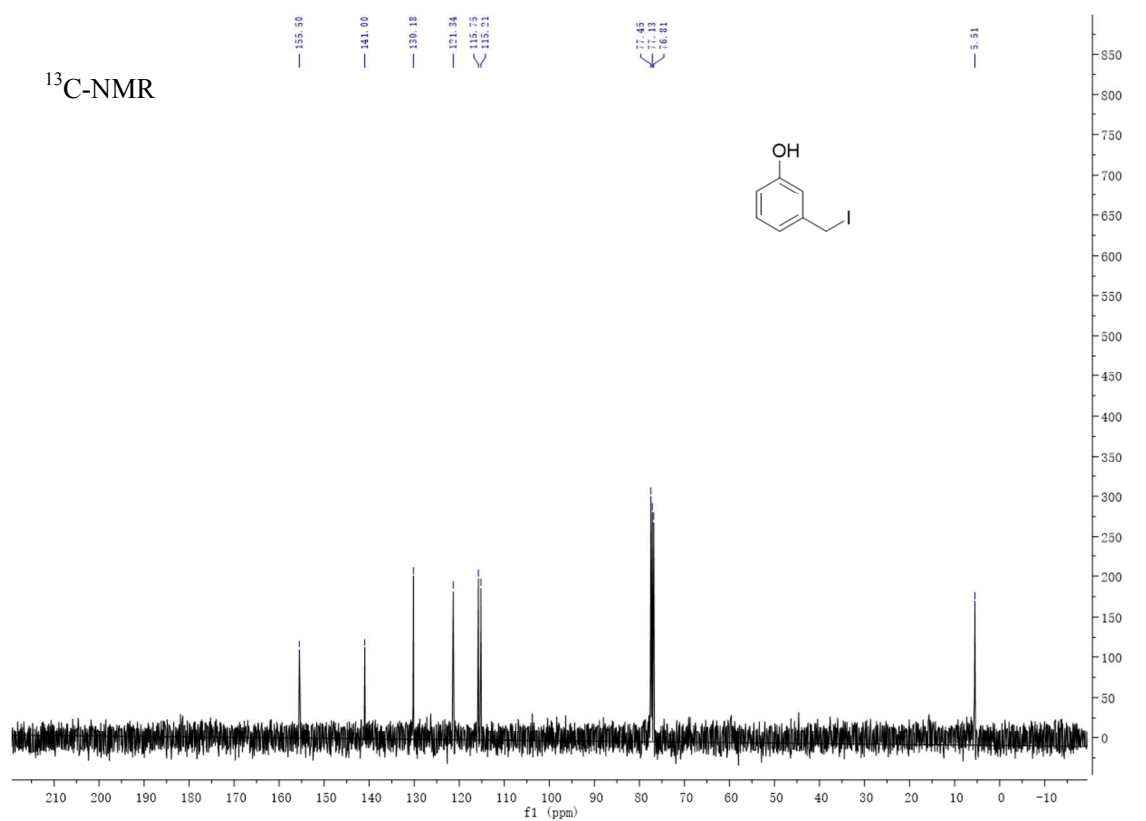
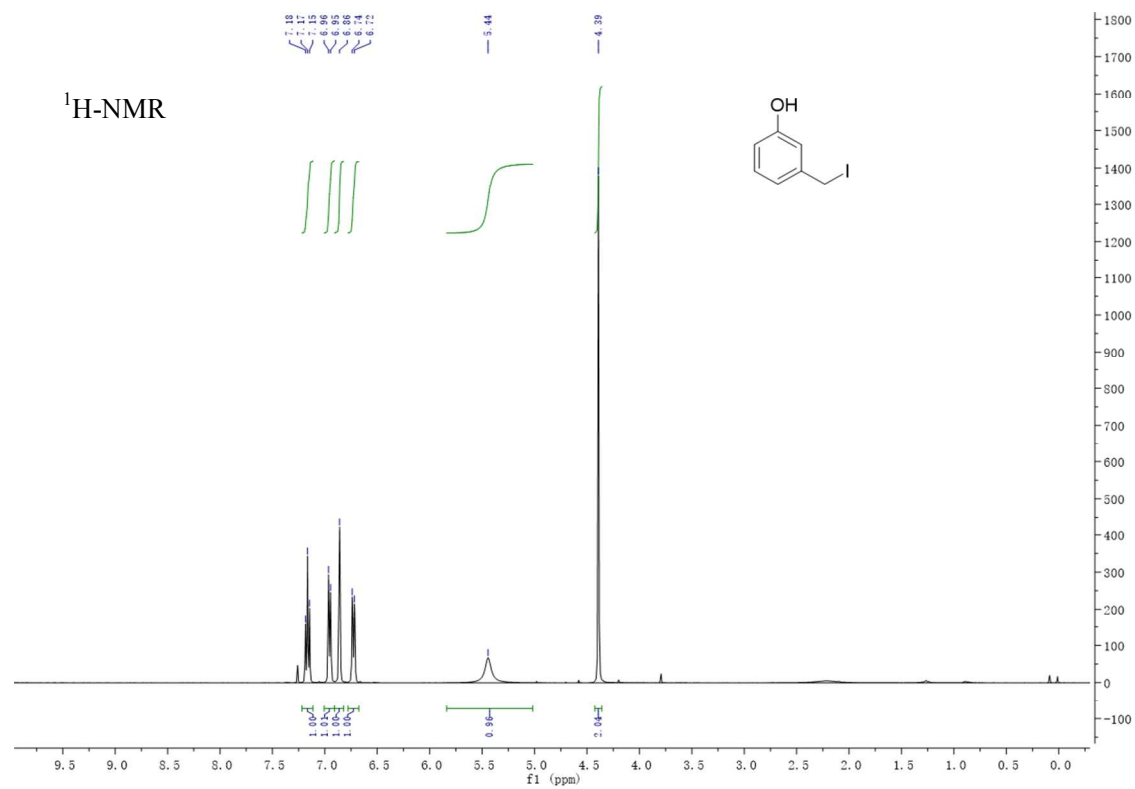
1-butyl-3-(3-hydroxybenzyl) imidazolium iodide (ILC₄I, 5) A 20 mL glass vial was charged with 3-(iodomethyl)phenol (**2**) (1.15 g, 4 mmol, 1.0 equiv) and 1-butylimidazole (0.62 g, 5 mmol, 1.0 equiv.) in DMF (10 mL). The reaction mixture was stirred at 100 °C overnight. The solvent was removed under vacuum. Chloroform (20 mL) was added into the residue and washed by water (20 mL) for three times. The opaque organic layer was collected and dried by anhydrous Na₂SO₄ and concentrated on a rotary evaporator. Column chromatography (silica gel; gradient elution from 1:1 ethyl acetate/hexane to 20:1 ethyl acetate/methanol) yielded **5** (1.40g, 79%) as

yellow oil. ^1H NMR (400 MHz, DMSO) δ 9.70 (s, 1H), 9.30 (s, 1H), 7.81 (m, 2H), 7.20 (d, J = 7.8 Hz, 1H), 6.86 – 6.69 (m, 3H), 5.34 (s, 2H), 4.19 (t, J = 7.2 Hz, 2H), 3.50 (s, 28H), 2.51 (s, 2H), 1.83 – 1.71 (m, 2H), 1.25 (dt, J = 14.8, 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 157.92, 136.30, 136.21, 130.34, 122.93, 122.82, 118.80, 115.83, 115.12, 52.13, 48.92, 31.47, 19.00, 13.49. FTMS (HR-ESI positive): $[\text{C}_{14}\text{H}_{19}\text{O}_1\text{N}_2]^+$ cal. 231.1492; found, 231.1490

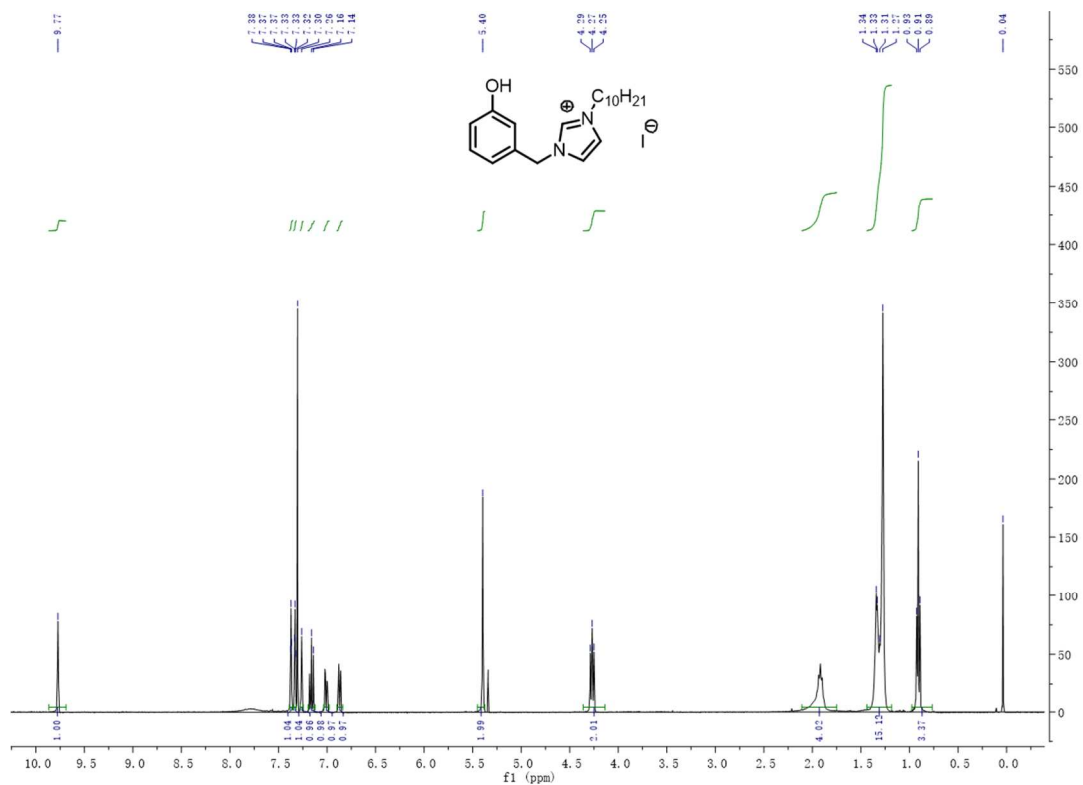
1-butyl-3-(3-hydroxybenzyl) imidazolium bis(trifluoromethylsulfonyl)imide (ILC₄TFSI, 6)

A 4mL glass vial was charged with 1-butyl-3-(3-hydroxybenzyl) imidazolium iodine (**5**) (179 mg, 0.5 mmol, 1.0 equiv) and lithium bis(trifluoromethylsulfonyl)imide (214 mg, 0.75 mmol, 1.5 equiv.) in methanol (2 mL). The reaction mixture was stirred at 60 °C overnight. The solvent was removed under vacuum. Chloroform (5 mL) was added in residue and washed by water (5 mL) for three times. The organic layer was collected and dried by anhydrous Na_2SO_4 . The solvent was removed under vacuum to yield **6** as light yellow oil (215 mg, 85%). ^1H NMR (400 MHz, DMSO) δ 9.71 (s, 1H), 9.25 (s, 1H), 7.77 (m, 2H), 7.21 (m, 1H), 6.86 – 6.70 (m, 3H), 5.31 (s, 2H), 4.17 (t, J = 7.2 Hz, 2H), 1.87 – 1.65 (m, 2H), 1.24 (dt, J = 14.8, 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 158.04, 136.31, 130.38, 122.95, 122.90, 121.34, 118.83, 118.14, 115.92, 115.20, 52.25, 49.00, 31.54, 19.05, 13.43. ^{19}F NMR (376 MHz, DMSO) δ -78.02.

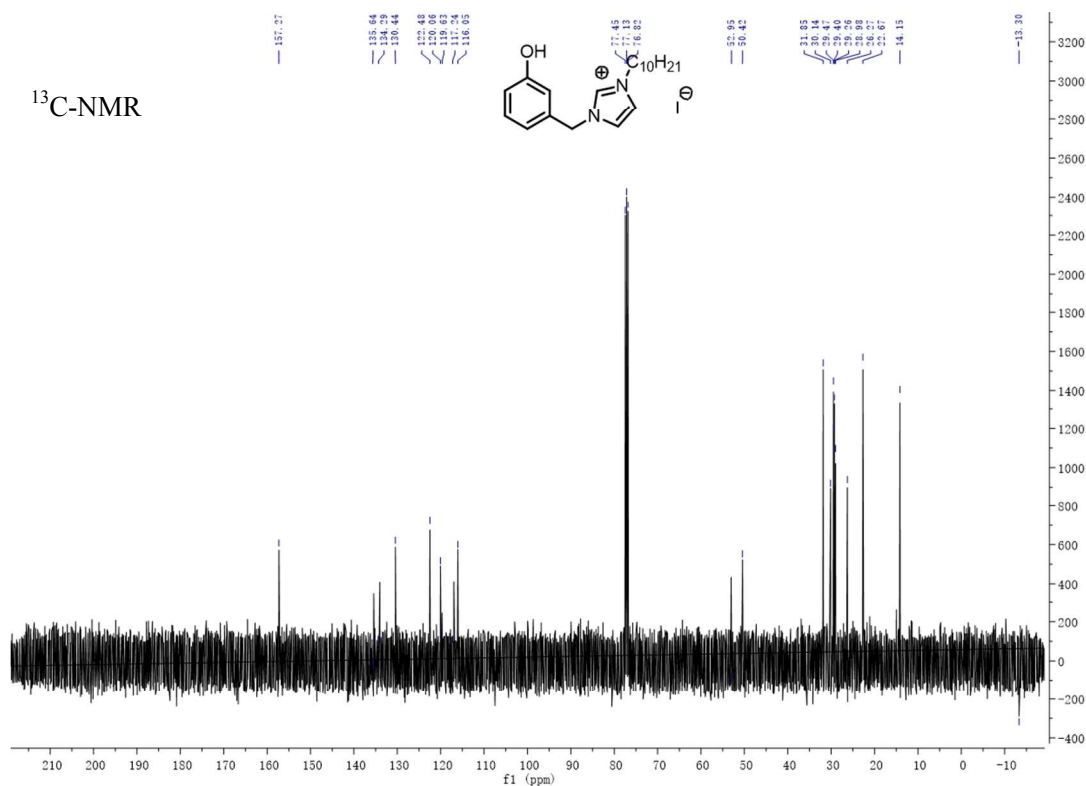




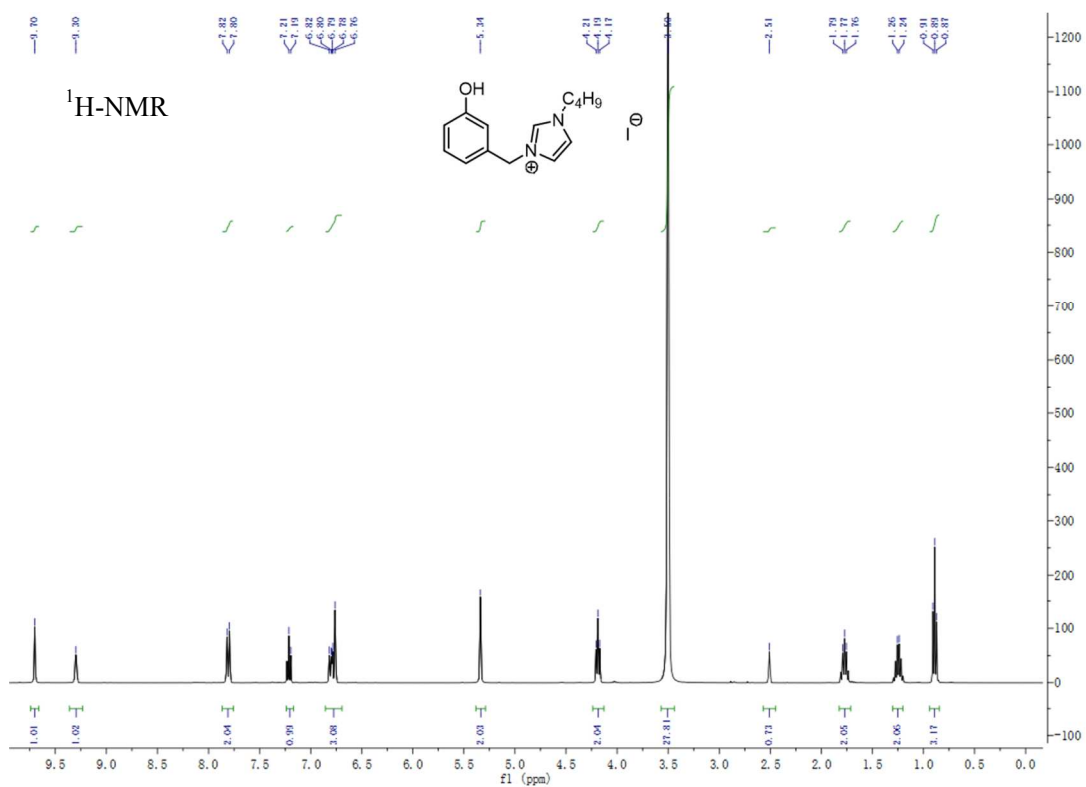
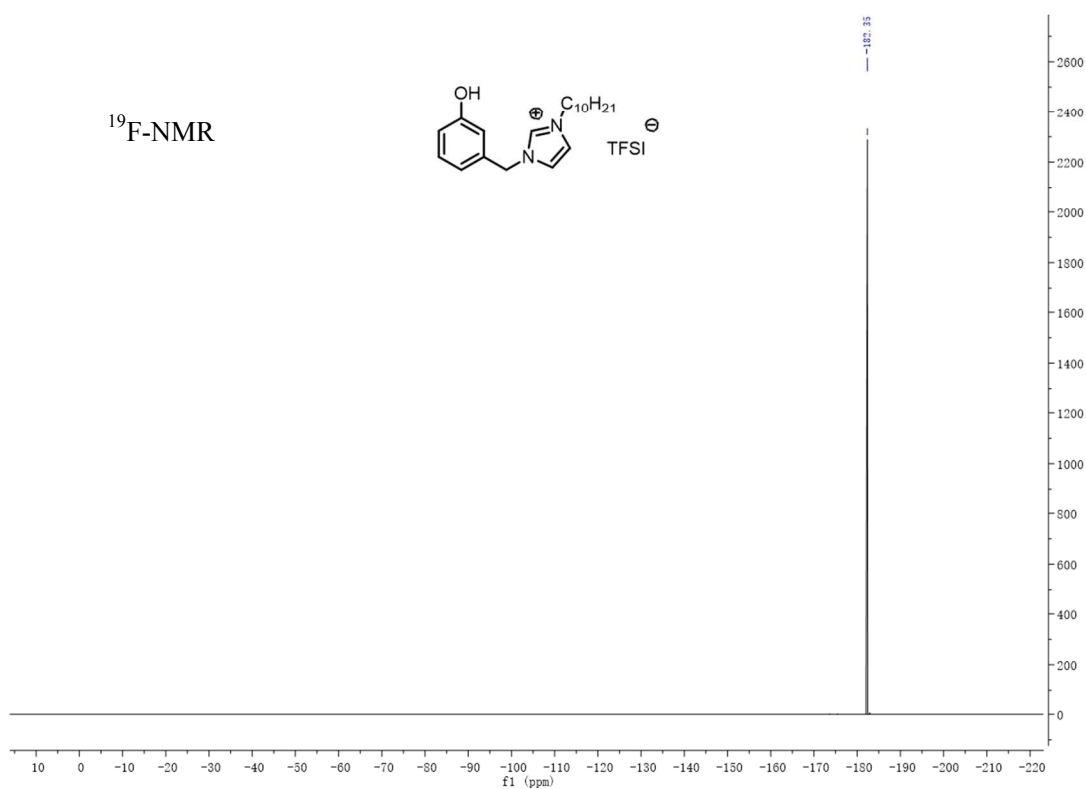
¹H-NMR

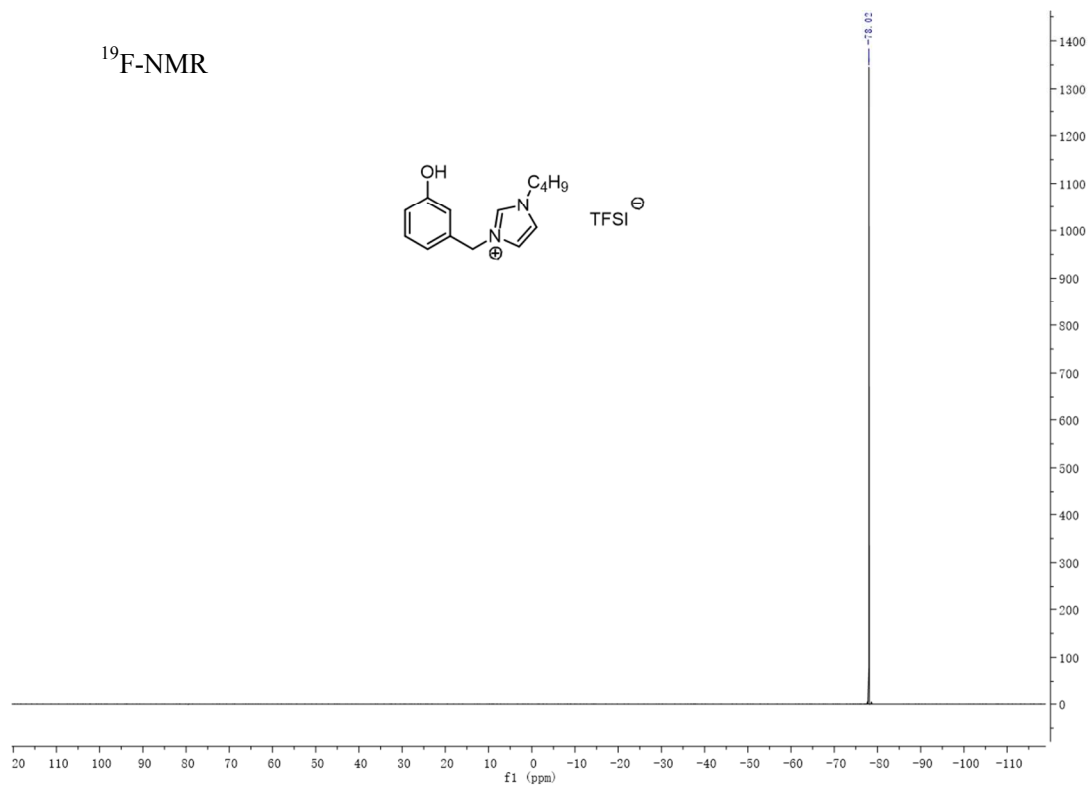
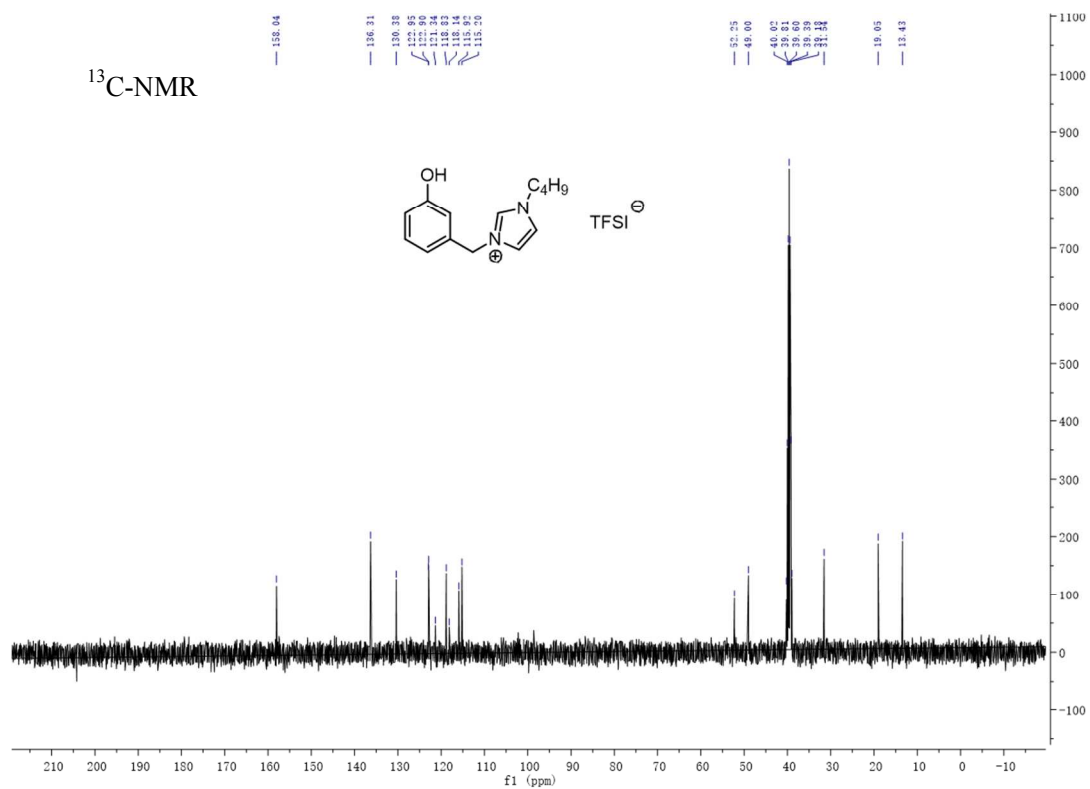


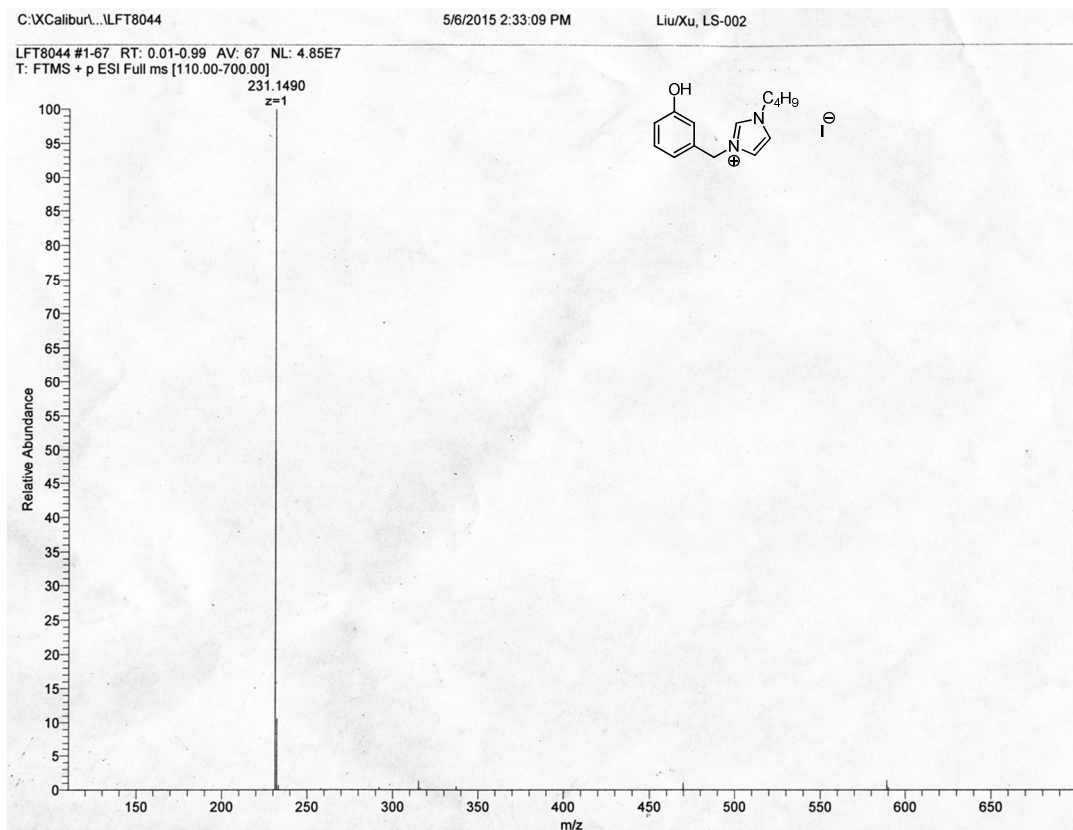
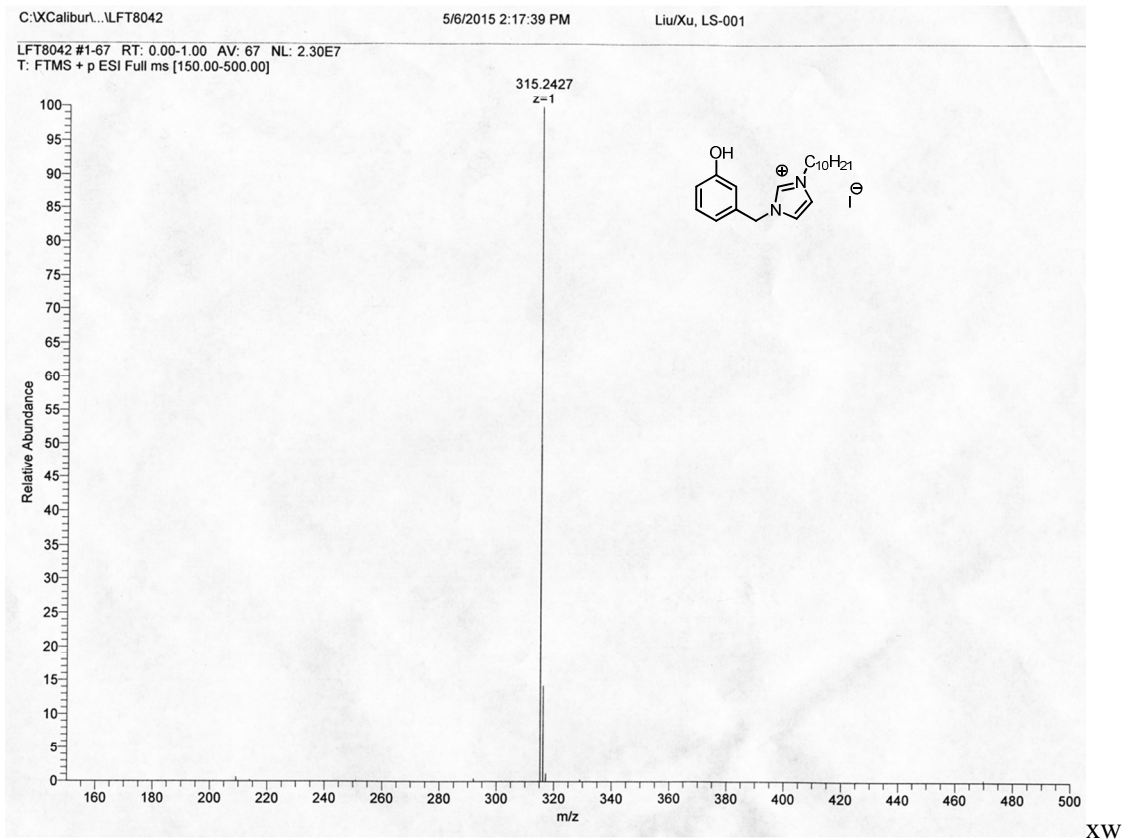
¹³C-NMR











Reference

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- (2) Tromp, R. A.; van Ameijde, S.; Pütz, C.; Sundermann, C.; Sundermann, B.; von Frijtag Drabbe Künzel, J. K.; IJzerman, A. P. *Journal of medicinal chemistry* **2004**, *47*, 5441.