Electronic Supplementary Information

Ionic Liquids Are not Innocent in Pd Catalysis.  C-H Arylation of Thiazolium and Imidazolium Ionic Liquids with Aryl Halides

Takahide Fukuyama,* Md. Taifur Rahman,* Hiroshi Mashima,* Hideo Takahashi* and Ilhyong Ryu*a,b,*

*Department of Chemistry, Graduate School of Science, Osaka Prefecture University
Sakai, Osaka 599-8531, Japan
bDepartment of Applied Chemistry, National Chiao Tung University
Hsinchu 30010 (Taiwan)

fukuyama@c.s.osakafu-u.ac.jp

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General information.

$^1$H NMR spectra were recorded with a JEOL JMN ECP-500 (500 MHz) spectrometer in CDCl$_3$ or CD$_3$C(O)CD$_3$ and are referenced at 0.0 ppm for TMS. $^{13}$C NMR spectra were recorded with a JEOL JMN ECP-500 (125 MHz) spectrometer and are referenced at 77.0 ppm for CDCl$_3$ or at 28.8 ppm for CD$_3$C(O)CD$_3$. $^{19}$F NMR spectra were recorded with a JEOL JMN ECP-500 (470 MHz) spectrometer. $^{31}$P NMR spectra were recorded with a JEOL JMN ECP-500 (202 MHz) spectrometer. Chemical shifts are reported in parts per million (δ). NMR yields were determined by using 1,1,2,2-tetrachloroethane as an internal standard. Infrared spectra were obtained on a Shimadzu FTIR 8400 spectrometer; absorptions are reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. The C-H arylated products 5a-5e were separated from the corresponding iodine salts by flash chromatography on silica gel (Kanto Chem. Co. Silica Gel 60N (spherical, neutral, 40-50 µm), and further purified using preparative HPLC (Japan Analytical Industry Co., Ltd., LC-908) equipped with GPC columns (JAIGEL-1H + JAIGEL-2H columns) using CHCl$_3$ as eluent. Imiazolium-based ionic liquids 1c-1e were prepared according to the reported procedures.$^1$

Synthesis of 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (1a).

To a 100 mL round bottom flask were added 4-methyl-5-thiazoleethanol (14.3 g, 100 mmol), benzyl chloride (13.1 g, 103 mmol), acetonitrile, and the mixture was stirred at 90 °C for 24 h. The resultant solid was washed with hexane, toluene, and acetonitrile. Remaining solvents were removed at 90 °C under reduced pressure to give 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride as a white solid (22.7 g, 84.1 mmol, 84%, m.p. 141-142 °C). To a 100 mL round bottom flask were added the thiazolium chloride (14.5 g, 53.7 mmol), H$_2$O (45 mL), bis(trifluoromethane)sulfonimide lithium salt (15.4 g, 53.7 mmol), and the resulting mixture was stirred at 70 °C for 10 h. The ionic liquid layer was washed with H$_2$O (10 x 50 mL). Remaining H$_2$O was removed at 90 °C under reduced pressure for 10 h to give thiazolium ionic liquid 1a as a yellow liquid (23.7 g, 46.1 mmol, 86%). Thiazolium ionic liquid (1b) was prepared with similar procedure.

Procedure for Pd-catalyzed C-H Arylation of 3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (1a).

Thiazolium based ionic liquid 1a (254.3 mg, 0.5 mmol), iodo benzene (2a, 121.0 mg, 0.6 mmol), $i$-Pr$_2$NH (200.5 mg, 1.8 mmol), PdCl$_2$(PPh$_3$)$_2$ (18.0 mg, 0.025 mmol) were placed in a screw-capped test tube. The reaction mixture was stirred at 80 °C for 3 h. NMR yield was determined using 1,1,2,2-tetrachloroethane as an internal standard. The NTf$_2$ salt was separated from the correspong iodine salt by flash chromatography on silica gel (gradient from hexane/EtOAc = 1/2 to EtOAc), which gave a mixture of NTf$_2$ salt 5a and triphenylphosphine oxide. Further purification by preparative HPLC gave pure NTf$_2$ salt 5a (117 mg 40%). The reaction of 1b with 2a was carried out in a similar manner.
Typical Procedure for Pd-catalyzed C-H Arylation of Imidazolium Ionic Liquids (Table 1, entry 6).

1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (1c, 223.3 mg, 0.5 mmol), iodobenzene (2a, 123.0 mg, 0.6 mmol), 28% NaOMe in MeOH (117.7 mg, NaOMe 0.6 mmol), PdCl$_2$(PPh$_3$)$_2$ (17.5 mg, 0.025 mmol) were placed in a screw-capped test tube. After removal of MeOH under reduced pressure, the reaction mixture was stirred at 80 °C for 3 h. NMR yield was determined by using 1,1,2,2-tetrachloroethane as an internal standard (89% yield).

Typical Procedure for Isolation of Arylated Imidazolium Ionic Liquids (Table 2, entry 1).

1-Butyl-3-methylimidazolium hexafluorophosphate (1d, 148.4 mg, 0.52 mmol), iodobenzene (2a, 127.1 mg, 0.62 mmol), 28% NaOMe in MeOH (116.2 mg, NaOMe 0.60 mmol), PdCl$_2$(PPh$_3$)$_2$ (18.6 mg, 0.026 mmol) were placed in a screw-capped test tube. After removal of MeOH under reduced pressure, the reaction mixture was stirred at 80 °C for 3 h. At this stage NMR yield was determined using 1,1,2,2-tetrachloroethane as an internal standard. The reaction mixture was poured into aqueous solution of NaPF$_6$ (840.1 mg 5.0 mmol) and stirred at room temperature for 15 min. The mixture was extracted with CHCl$_3$ (3 x 10 mL). The combined organic layers were concentrated in vacuo. The PF$_6$ salt was separated from the corresponding iodine salt by using flash chromatography on silica gel (gradient from hexane/EtOAc = 1/2 to EtOAc), which gave a mixture of PF$_6$ salt 5d and triphenylphosphine oxide. The mixture was purified by preparative HPLC to give pure PF$_6$ salt 5d (110.6 mg, 61%). 5c and 5e were obtained in 47% and 91% isolated yield respectively by using LiNTf$_2$ and LiN(CN)$_2$ in stead of NaPF$_6$.
Competition Experiment: Sonogashira reaction vs. C-H Arylation.

1-Butyl-3-methylimidazolium hexafluorophosphate (1d, 142.2 mg, 0.5 mmol), iodobenzene (2a, 102.9 mg, 0.5 mmol), 1-octyne (55.2 mg, 0.5 mmol), piperidine (147.5 mg, 1.8 mmol), PdCl2(PPh3)2 (17.6 mg, 0.025 mmol) were placed in a screw-capped test tube. After purge with Ar, the reaction mixture was stirred at 80 °C for 3 h. Yields were determined by NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard (5d: trace, 4b: 97%). The reaction using NaOMe was conducted with same procedure (5d: 30%, 4b: 50%).

3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (1a)²

\[
\text{Ph} \quad \text{+} \quad \text{S} \quad \text{NTf}_2 \quad \text{OH}
\]

\[^{1}H\text{ NMR}\text{ (500 MHz, CD}_3\text{COCD}_3\text{)} \delta 2.59\text{ (s, 3H), 3.22 (t, 2H, }J = 5.5\text{ Hz), 3.90 (q, 1H, }J = 5.3\text{ Hz), 4.44 (t, 2H, }J = 4.8\text{ Hz), 5.92 (s, 2H), 7.53-7.46 \text{ (m, 5H), 9.97 (s, 1H)}; \]

\[^{13}C\text{ NMR}\text{ (125 MHz, CD}_3\text{COCD}_3\text{)} \delta 10.91, 56.43, 59.78, 119.69\text{ (q, }J = 321.2\text{ Hz), 128.10, 155.39, 129.08, 131.89, 136.47, 142.03, 155.41; }^{19}F\text{ NMR (CD}_3\text{COCD}_3\text{)} \delta -79.62; IR\text{ (neat) 3532, 3097, 2944, 2892, 1589, 1453, 1351, 1195, 1138, 1055 cm}^{-1}; MS\text{ (FAB+) }m/\text{z (rel intensity), 234 ((M-NTf}_2\text{)+, 100), 91(33); MS (FAB-) }m/\text{z (rel intensity), 280 (NTf}_2^-\text{, 100).}

3-Ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bis(trifluoromethanesulfonyl)amide (1b)²

\[
\text{Ph} \quad \text{+} \quad \text{S} \quad \text{NTf}_2 \quad \text{OH}
\]

\[^{1}H\text{ NMR}\text{ (500 MHz, CD}_3\text{COCD}_3\text{)} \delta 1.65\text{ (t, 3H, }J = 7.3\text{ Hz), 2.61 (s, 3H), 3.18 (t, 2H, }J = 5.7\text{ Hz), 3.88 (q, 2H, }J = 5.5\text{ Hz), 4.31 (t, 1H, }J = 5.3\text{ Hz), 4.61 (q, 2H, }J = 7.2\text{ Hz), 9.87 (s, 1H)}; \]

\[^{13}C\text{ NMR}\text{ (125 MHz, CD}_3\text{COCD}_3\text{)} \delta 10.93, 13.48, 49.08, 60.33, 120.08\text{ (q, }J = 321.5\text{ Hz), 136.22, 142.23, 155.33; }^{19}F\text{ NMR (CD}_3\text{COCD}_3\text{)} \delta -79.74; IR\text{ (neat) 3536, 1589, 1455, 1352, 1193, 1138 cm}^{-1}; MS\text{ (FAB+) }m/\text{z (rel intensity), 172 ((M-NTf}_2\text{)+, 100); MS (FAB-) }m/\text{z (rel intensity), 280 (NTf}_2^-\text{, 100).}

3-Benzyl-5-(2-hydroxyethyl)-4-methyl-2-phenylthiazolium bis(trifluoromethanesulfonyl)amide (5a)

Light yellow liquid, (Rf = 0.1, CHCl₃ : MeOH = 9 : 1). \(^{1}H\text{ NMR}\text{ (500 MHz, CDCl}_3\text{)} \delta 2.37\text{ (s, 3H), 2.80 (br, 1H), 3.11 (t, 1H, }J = 5.3\text{ Hz), 3.93 (t, 2H, }J = 5.3\text{ Hz), 4.36 (q, 2H, }J = 7.3\text{ Hz), 6.94 (d, J = 6.9 Hz, 2H), 7.32-7.40 \text{ (m, 3H), 7.50-7.58 \text{ (m, 4H), 7.62-7.64 \text{ (m, 1H); }^{13}C\text{ NMR}\text{ (125 MHz, CDCl}_3\text{)} \delta 12.69, 29.85, 54.11, 60.33, 119.72\text{ (q, }J = 12.33\text{ Hz), 14.69, 14.71, 29.75, 46.39, 60.30, 119.65\text{ (q, }J = 319.5\text{ Hz), 125.07, 125.54, 125.60, 129.52, 129.72, 129.86, 132.44, 133.20, 135.00, 142.83, 169.40; }^{19}F\text{ HMR(CDCl}_3\text{)} \delta -78.49; IR\text{ (neat) 3529, 1590, 1454, 1352, 1193, 1136, 1057 cm}^{-1}; MS\text{ (FAB+) }m/\text{z (rel intensity), 310 ((M-NTf}_2\text{)+, 100); MS (FAB-) }m/\text{z (rel intensity) 280 (NTf}_2^-\text{, 100); HRMS (FAB+) m/z caled for C}_{19}\text{H}_{20}\text{N}_{1}\text{O}_{1}\text{S}_{1} ((M-NTf}_2\text{)+) 310.1260, found 310.1254; HRMS (FAB-) m/z caled for C}_{20}\text{O}_{4}\text{NF}_{6}\text{S}_{2} (NTf}_2^-\text{) 279.9173, found 279.9175.}
3-Ethyl-5-(2-hydroxyethyl)-4-methyl-2-phenylthiazolium bis(trifluoromethanesulfonyl)amide (5b)

Light Yellow liquid, (Rf = 0.09, CHCl3 : MeOH = 9 : 1). $^1$H NMR (500 MHz, CDCl3) δ 1.41 (t, J = 7.3 Hz), 2.61 (s, 3H), 3.06 (t, 1H, J = 5.3 Hz), 3.90 (t, 2H, J = 5.3 Hz), 4.36 (q, 2H, J = 7.3 Hz), 7.64-7.62 (m, 4H), 7.72-7.69 (m, 1H); $^{13}$C NMR(125 MHz, CDCl3) δ 12.33, 14.69, 14.71, 29.75, 46.39, 60.30, 119.65 (q, J = 318.8 Hz), 125.10, 129.43, 129.74, 132.88, 134.87, 141.93, 167.86; $^{19}$F NMR (CDCl3) δ -78.66; IR (neat) 3533, 1589, 1448, 1352, 1193, 1136, 1055 cm$^{-1}$; MS (FAB+) m/z (rel intensity), 248 ((M-NTf$_2$)$^+$, 100), 172 (12); MS (FAB-) m/z (rel intensity), 280 (NTf$_2^-$, 100); HRMS (FAB+) m/z calcd for C$_{14}$H$_{18}$N$_1$O$_1$S$_1$ ((M-NTf$_2$)$^+$) 248.1104, found 248.1110; HRMS (FAB-) m/z calcd for C$_2$O$_4$NF$_6$S$_2$ (NTf$_2^-$) 279.9173, found 279.9172.

1-Butyl-2-phenyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (5c)

Yellow liquid, (Rf = 0.38, hexane : EtOAc = 1 : 3). $^1$H NMR (500 MHz, CDCl3) δ 0.83 (t, J = 7.3 Hz, 3H), 1.23 (sext, J = 7.5 Hz, 2H), 1.71 (quint, J = 7.6 Hz, 2H), 3.72 (s, 3H), 3.98 (t, J = 7.3 Hz, 2H), 7.45 (d, J = 2.3 Hz, 1H), 7.47 (d, J = 2.3 Hz, 1H), 7.54-7.56 (m, 2H), 7.66-7.69 (m, 2H), 7.71-7.75 (m, 1H); $^{13}$C NMR (125 MHz, CDCl3) δ 13.08, 19.26, 31.74, 35.88, 35.91, 48.82, 118.53, 120.67, 121.09, 121.52, 121.60, 123.58, 123.65, 130.04, 132.95, 144.67; $^{19}$F NMR (470 MHz, CDCl3) δ -78.69; IR (neat) 3020, 2400, 1352, 1216,1137, 1059, 756, 669 cm$^{-1}$; MS (FAB+) m/z (rel intensity) 215 ((M-NTf$_2$)$^+$, 100), 159 (12); MS (FAB-) m/z (rel intensity) 280 (NTf$_2^-$, 100), 153 (34), 149 (34); HRMS (FAB+) m/z calcd for C$_{14}$H$_{19}$N$_2$ ((M-NTf$_2$)$^+$) 215.1548, found 215.1558; HRMS (FAB-) m/z calcd for C$_2$O$_4$NF$_6$S$_2$ (NTf$_2^-$) 279.9173, found 279.9172.

1-Butyl-2-phenyl-3-methylimidazolium hexafluorophosphate (5d)

Light brown liquid, (Rf = 0.38, hexane : EtOAc = 1 : 4). $^1$H NMR (500 MHz, CDCl3) δ 0.82 (t, J = 7.3 Hz, 3H), 1.23 (sext, J = 7.4 Hz, 2H), 1.72 (quint, J = 7.6 Hz, 2H), 3.74 (s, 3H), 3.99 (t, J = 7.3 Hz, 2H), 7.53-7.59 (m, 4H), 7.66-7.73 (m, 3H); $^{13}$C NMR (125 MHz, CDCl3) δ 13.18, 19.29, 31.83, 35.95, 48.78, 120.86, 121.67, 121.74, 123.82, 123.88, 130.01, 130.24, 132.81, 144.45; $^{31}$P NMR (202 MHz, CDCl3) δ -143.90 (sept; J = 712.1 Hz); IR (neat) 3019, 2400, 1215, 758, 669 cm$^{-1}$; MS (FAB+) m/z (rel intensity) 215 ((M-PF$_6$)$^+$, 100), 154 (65), 136 (52), 69 (39); MS (FAB-) m/z (rel intensity) 145 (PF$_6^-$, 100), 127 (14); HRMS (FAB+) m/z calcd for C$_{14}$H$_{19}$N$_2$ ((M-PF$_6$)$^+$) 215.1548, found 215.1553; HRMS (FAB-) m/z calcd for PF$_6^-$ (PF$_6^-$) 144.9642, found 144.9647.
1-Butyl-2-phenyl-3-methylimidazolium dicyanamide (5e)

Yellow liquid, (Rf = 0.35, MeOH : EtOAc = 1 : 10). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$

- 0.72 (t, $J = 7.3$ Hz, 3H), 1.51 (sext, $J = 7.4$ Hz, 2H), 1.65 (quint, $J = 7.6$ Hz, 2H), 3.70 (s, 3H), 3.95 (t, $J = 7.6$ Hz, 2H), 7.51-7.65 (m, 7H);
- $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 12.91, 19.03, 31.53, 35.97, 36.00, 48.62, 120.31, 121.49, 121.55, 123.41, 123.47, 129.76, 129.95, 132.66, 144.37; IR (neet) 3020, 2400, 1216, 757, 669 cm$^{-1}$; MS (FAB+) $m$/z (rel intensity) 215 ((M-N(CN)$_2$)$^+$, 100), 154 (75), 136 (54), 107 (18), 78 (16); MS (FAB-) $m$/z (rel intensity) 66 (N(CN)$_2^-$, 100); HRMS (FAB+) $m$/z calcd for C$_{14}$H$_{19}$N$_2$ ((M-N(CN)$_2$)$^+$) 215.1548, found 215.1547;
- HRMS (FAB-) $m$/z calcd for N(CN)$_2$ (N(CN)$_2^-$) 66.0092, found 66.0095.

1-Butyl-2-(p-methylphenyl)-3-methylimidazolium hexafluorophosphate (5f)

Light brown liquid, (Rf = 0.25, hexane : EtOAc = 1 : 2). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$

- 0.82 (t, $J = 7.3$ Hz, 3H), 1.23 (sext, $J = 7.5$ Hz, 2H), 1.71 (quint, $J = 7.6$ Hz, 2H), 2.49 (s, 3H), 3.71 (s, 3H), 3.97 (t, $J = 7.6$ Hz, 2H), 7.41-7.42 (m, 2H), 7.45-7.51 (m, 4H);
- $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.19, 19.29, 21.60, 21.64, 31.84, 35.75, 35.78, 48.70, 117.74, 121.50, 121.58, 123.61, 123.69, 129.94, 129.98, 130.69, 143.60, 144.72; $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -73.02 (d, $J = 702.5$ Hz); $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -143.90 (sept; $J = 712.1$ Hz); IR (neet) 3019, 2400, 1639, 1216, 759, 669 cm$^{-1}$; MS (FAB+) $m$/z (rel intensity) 229 ((M-PF$_6$)$^+$, 100), 154 (33), 136 (26), 69 (7); MS (FAB-) $m$/z (rel intensity) 145 (PF$_6^-$, 100); HRMS (FAB+) $m$/z calcd for C$_{15}$H$_{21}$N$_2$ ((M-PF$_6$)$^+$) 229.1705, found 229.1698; HRMS (FAB-) $m$/z calcd for PF$_6$ (PF$_6^-$) 144.9642, found 144.9642.

1-Butyl-2-(m-methylphenyl)-3-methylimidazolium hexafluorophosphate (5g)

Light brown liquid, (Rf = 0.25, hexane : EtOAc = 1 : 2). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$

- 0.82 (t, $J = 7.3$ Hz, 3H), 1.23 (sext, $J = 7.4$ Hz, 2H), 1.71 (quint, $J = 7.6$ Hz, 2H), 3.71 (s, 3H), 3.97 (t, $J = 7.6$ Hz, 2H), 7.30-7.35 (m, 2H), 7.46-7.47 (m, 1H), 7.50-7.56 (m, 3H);
- $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.20, 19.26, 21.25, 21.28, 31.80, 35.76, 35.78, 48.68, 120.75, 121.51, 121.58, 123.60, 123.67, 129.83, 129.85, 130.85, 130.46, 133.57, 140.35, 144.68; $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ -72.94 (d, $J = 714.0$ Hz); $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ -143.87 (sept; $J = 712.1$ Hz); IR (neet) 3019, 2400, 1639, 1216, 759, 669 cm$^{-1}$; MS (FAB+) $m$/z (rel intensity) 229 ((M-PF$_6$)$^+$, 100), 154 (33), 136 (26), 69 (7); MS (FAB-) $m$/z (rel intensity) 145 (PF$_6^-$, 100); HRMS (FAB+) $m$/z calcd for C$_{15}$H$_{21}$N$_2$ ((M-PF$_6$)$^+$) 229.1705, found 229.1698; HRMS (FAB-) $m$/z calcd for PF$_6$ (PF$_6^-$) 144.9642, found 144.9642.

1-Butyl-2-phenyl-3-methylimidazolium dicyanamide (5e)

1-Butyl-2-(p-methylphenyl)-3-methylimidazolium hexafluorophosphate (5f)

1-Butyl-2-(m-methylphenyl)-3-methylimidazolium hexafluorophosphate (5g)
1-Butyl-2-(m-methylphenyl)-3-methylimidazolium iodide (5g')

Yellow liquid, (Rf = 0.30, MeOH : EtOAc = 1 : 10). $^1$H NMR (500 MHz, CDCl₃) δ 0.84 (t, J = 7.3 Hz, 3H), 1.28 (sext, J = 7.5 Hz, 2H), 1.78 (quint, J = 7.4 Hz, 2H), 2.49 (s 3H), 3.88 (s, 3H), 4.10 (t, J = 7.3 Hz, 2H), 7.48-7.58 (m, 4H), 7.83 (d, J = 2.3 Hz, 1H), 7.99 (s, 1H); $^{13}$C NMR (125 MHz, CDCl₃) δ 13.18, 19.29, 21.27, 21.31, 31.92, 36.78, 48.86, 120.56, 121.86, 124.04, 129.78, 130.60, 130.66, 133.58, 140.17, 144.54; IR (neat) 3020, 2936, 2401, 1216, 757, 668 cm⁻¹; MS (FAB+) m/z (rel intensity) 229 ((M-I)+, 100), 174 (6); MS (FAB-) m/z (rel intensity) 126 (I-, 100); HRMS (FAB+) m/z calcd for C₁₅H₂₁N₂ ((M-I)+) 229.1705 found 229.1707; HRMS (FAB-) m/z calcd for I (I-) 126.9047, found 126.9045.

1-Butyl-2-(p-metoxyphenyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (5i)

Light brown liquid, (Rf = 0.40, hexane : EtOAc = 1 : 2). $^1$H NMR (500 MHz, CDCl₃) δ 0.84 (t, J = 7.3 Hz, 3H), 1.23 (sext, J = 7.5 Hz, 2H), 1.71 (quint, J = 7.6 Hz, 2H), 3.71 (s, 3H), 3.92 (s, 3H), 3.96 (t, J = 7.6 Hz, 2H), 7.14-7.47 (m, 2H), 7.41-7.47 (m, 4H); $^{13}$C NMR (125 MHz, CDCl₃) δ 13.14, 19.30, 31.76, 35.85, 48.75, 55.65, 111.97, 115.52, 115.58, 118.54, 121.09, 121.32, 121.39, 131.75, 131.79, 144.92, 162.90; 19F NMR (470 MHz, CDCl₃) δ -78.69; IR (neat) 3021, 2400, 1613, 1352, 1216, 1137, 1059, 760, 669 cm⁻¹; MS (FAB+) m/z (rel intensity) 245 ((M-NTf₂)+, 100), 244 (100), 215 (59) 188 (45) 135 (41) 74 (59); MS (FAB-) m/z (rel intensity) 280 (NTf₂-, 100), 264 (18), 211 (18), 147 (60); HRMS (FAB+) m/z calcd for C₁₅H₂₁N₂O ((M-NTf₂)+) 245.1654, found 245.1655; HRMS (FAB-) m/z calcd for C₂O₄NF₆S₂ (NTf₂-) 279.9173, found 279.9169.

1-Butyl-2-(2-pyridyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (5j)

Light brown liquid, (Rf = 0.35, hexane : EtOAc = 1 : 4). $^1$H NMR (500 MHz, CDCl₃) δ 0.83 (t, J = 7.3 Hz, 3H), 1.25 (sext, J = 7.5 Hz, 2H), 1.71-1.77 (m, 2H), 3.85 (s, 3H), 4.14 (t, J = 7.6 Hz, 2H), 7.46 (d, J = 1.8 Hz, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.62-7.64 (m, 1H), 7.95 (d, J = 7.8 Hz, 1H), 8.06-8.09 (m, 1H), 8.84 (d, J = 5.0 Hz, 1H); $^{13}$C NMR (125 MHz, CDCl₃) δ 13.02, 13.09, 19.20, 31.72, 36.28, 36.31, 49.21, 118.48, 121.03, 122.02, 123.79, 123.90, 127.21, 138.27, 140.73, 142.38, 151.04, 151.14; 19F NMR (470 MHz, CDCl₃) δ -78.76; IR (neat) 3020, 2400, 1352, 1216, 1137 1059, 760, 669 cm⁻¹; MS (FAB+) m/z (rel intensity) 216 ((M-NTf₂)+, 100), 186 (89), 160 (100), 137 (31), 73 (54); MS (FAB-) m/z (rel intensity) 280 (NTf₂-, 100), 211 (12), 143 (46); HRMS (FAB+) m/z calcd for C₁₃H₁₈N₃ ((M-NTf₂)+) 216.1501, found 216.1504; HRMS (FAB-) m/z calcd for C₂O₄NF₆S₂ (NTf₂-) 279.9173, found 279.9172.
