Facile Synthesis of *N*-Alkyl-*N′*-arylimidazolium Salts via Addition of Imidazoles to Arynes

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Supporting Information

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform as an eluent). Column chromatography was carried out using ICN Alumina N, Akt. I. Unless otherwise noted, commercially available reagents were used without purification. Acetonitrile was distilled from diphosphorus pentoxide. 1-(Methoxymethyl)imidazole (**1a**),[1] 1-benzylimidazole (**1b**),[1] 1-*n*-butylimidazole (**1c**),[1] 1-isopropylimidazole (**1e**),[1] 1-*tert*-butylimidazole (**1f**),[2] 1-methyl-2-phenylimidazole (**1h**),[3] 2-(trimethylsilyl)phenyl triflate (**2a**),[4] 10-(trimethylsilyl)-9-phenanthryl triflate (**2e**),[5] and 3-methoxy-2-(trimethylsilyl)phenyl triflate (**2f**)[6] were prepared according to literature procedures. 4,5-Dimethyl-2-(trimethylsilyl)phenyl triflate (**2b**) and 6-(trimethylsilyl)-5-indanyl triflate (**2c**) were synthesized from 2-iodo-4,5-dimethylphenol[7] or 6-bromo-5-indanol[8] in a similar manner as the preparation of **2a**. 3,6-Dimethoxy-2-(trimethylsilyl)phenyl triflate (**2d**) was synthesized from 2,5-dimethoxyphenol[9] in a similar manner as the preparation of **2f**.

Reaction of Arynes with Imidazoles. ***A General Procedure.*** To a solution of CsF (0.091 g, 0.60 mmol) and an imidazole (0.90 mmol) in acetonitrile (0.75 mL) was added an aryne precursor (0.30 mmol) and the mixture was stirred at 20 °C. After the time specified in Table 1 or Scheme 2, the mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Alumina column chromatography (ethyl acetate/aqueous ammonia = 95/5 then dichloromethane/methanol = 90/10 as eluents) or gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

1-Methoxymethyl-3-phenylimidazolium triflate (3a). 59% yield: Isolated by alumina column chromatography as a colorless plate: m.p. 87-88 ˚C; ^{1}H NMR ($CDCl_3$) δ 3.48 (s, 3 H), 5.71 (s, 2 H), 7.50-7.76 (m, 7 H), 9.77 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 57.9, 81.0, 120.6

(q, J = 319.8 Hz), 121.7, 122.1, 122.2, 130.6 134.3, 135.2; Anal. Calcd for $C_{12}H_{13}F_3N_2O_4S$: C, 42.60; H, 3.87; N, 8.28. Found: C, 42.61; H, 3.84; N, 8.32.

1-Benzyl-3-phenylimidazolium triflate (3b). 52% yield: Isolated by gel permeation chromatography as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 5.5 (s, 2 H), 7.28-7.78 (m, 12 H),9.67(s, 1 H); ^{13}C NMR ($CDCl_3$) δ 53.7, 120.6 (q, J = 320.2 Hz), 121.3, 121.8, 123.0, 129.2, 129.5, 129.6, 130.3, 130.5, 132.7, 134.3, 134.6; Anal. Calcd for $C_{17}H_{15}F_3N_2O_3S$: C, 53.12; H, 3.93; N, 7.29. Found: C, 53.27; H, 4.04; N, 7.50.

1-*n*-Butyl-3-phenylimidazolium triflate (3c). 45% yield: Isolated by gel permeation chromatography as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 7.2 Hz, 3 H), 1.43 (qt, J = 7.6, 7.2 Hz, 2 H), 1.94 (tt, J = 7.6, 7.2 Hz, 2 H), 4.39 (t, J = 7.2 Hz, 2 H), 7.45-7.80 (m, 7 H), 9.70 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.2, 19.3, 32.0, 50.2, 120.7 (q, J = 321.1 Hz), 121.1, 121.7, 123.3, 130.2, 130.5, 134.4, 135.1; Anal. Calcd for $C_{14}H_{17}F_3N_2O_3S$: C, 47.99; H, 4.89; N, 8.00. Found: C, 47.93; H, 4.84; N, 8.26.

1-Methyl-3-phenylimidazolium triflate (3d). 44% yield: Isolated by alumina column chromatography as a colorless needle: m.p. 91-92 ˚C; ^{1}H NMR ($CDCl_3$) δ 4.09 (s, 3 H),7.44-7.66 (m, 7 H), 9.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.8, 118.3, 120.6 (q, J = 319.8 Hz), 122.0, 123.0, 124.6, 130.4, 130.5, 134.4, 135.7; Anal. Calcd for $C_{11}H_{11}F_3N_2O_3S$: C, 42.86; H, 3.60; N, 9.09. Found: C, 42.82; H, 3.68; N, 9.06.

1-Isopropyl-3-phenylimidazolium triflate (3e). 55% yield: Isolated by alumina column chromatography as a colorless plate: m.p. 92-95 ˚C; ^{1}H NMR ($CDCl_3$) δ 1.64 (d, J = 6.9 Hz, 6 H), 5.01 (quintet, J = 6.9 Hz, 1 H), 7.45-7.76 (m, 7 H), 9.99(s, 1 H); ^{13}C NMR ($CDCl_3$) δ 22.9, 54.0, 120.6, 121.3, 122.0, 123.5 (q, J = 283.5 Hz), 130.5, 130.6, 134.2, 134.4; Anal. Calcd for $C_{13}H_{15}F_3N_2O_3S$: C, 46.42; H, 4.50; N, 8.33. Found: C, 46.70; H, 4.57; N, 8.31.

1-*tert*-Butyl-3-phenylimidazolium triflate (3f). 53% yield: Isolated by alumina column chromatography as a colorless powder: m.p. 162-165 ˚C; ^{1}H NMR (DMSO-d_6) δ 0.79 (s, 9 H), 6.65-6.85 (m, 3 H), 6.90-7.02 (m, 2 H), 7.34-7.58 (m, 2 H), 8.81 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 29.1, 60.5, 121.0 (q, J = 318.7 Hz), 121.4, 121.7, 122.4 129.9, 130.2, 133.8, 135.1; Anal. Calcd for $C_{14}H_{17}F_3N_2O_3S$: C, 47.99; H, 4.89; N, 8.00. Found: C, 48.00; H, 4.79; N, 8.05.

1,2-Dimethyl-3-phenylimidazolium triflate (3g). 56% yield: Isolated by alumina column chromatography as a colorless plate: m.p. 74-77 ˚C; ^{1}H NMR ($CDCl_3$) δ 2.63 (s, 3 H),

4.01 (s, 3 H), 7.25 (s, 1 H), 7.50-7.65 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 10.6, 35.8, 120.7 (q, J = 319.8 Hz), 121.9, 123.3, 126.0, 130.4, 130.9, 134.6, 145.1; Anal. Calcd for $C_{12}H_{13}F_3N_2O_3S$: C, 44.72; H, 4.07; N, 8.69. Found: C, 44.70; H, 4.11; N, 8.71.

1-Methyl-2,3-diphenylimidazolium triflate (3h). 33% yield: Isolated by alumina column chromatography as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 3.93 (s, 3 H), 7.27-7.86 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 36.6, 120.6 (q, J = 324.9 Hz), 121.0, 123.0, 123.1, 124.5, 126.0, 129.5, 130.0, 130.4, 130.7, 132.4, 134.9, 144.8; Anal. Calcd for $C_{17}H_{15}F_3N_2O_3S$: C, 53.12; H, 3.93; N, 7.29. Found: C, 52.92; H, 4.06; N, 7.34.

1-*tert*-Butyl-3-(3,4-dimethylphenyl)imidazolium triflate (3i). 49% yield: Isolated by alumina column chromatography as a colorless plate: m.p. 121-123 ˚C; ^{1}H NMR ($CDCl_3$) δ 1.77 (s, 9 H), 2.30 (s, 3 H), 2.35 (s, 3 H), 7.28-7.66 (m, 5 H), 9.62 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.5, 19.7, 29.8, 61.5, 119.3, 120.5 (q, J = 295.6 Hz), 120.1, 121.3, 123.2, 131.3, 132.2, 133.4, 139.6, 139.8; Anal. Calcd for $C_{16}H_{21}F_3N_2O_3S$: C, 50.78; H, 5.59; N, 7.40. Found: C, 50.60; H, 5.58; N, 7.39.

1-*tert*-Butyl-3-(5-indanyl)imidazolium triflate (3j). 63% yield: Isolated by alumina column chromatography as a colorless plate: m.p. 104-107 ˚C; ^{1}H NMR ($CDCl_3$) δ 1.79 (s, 9 H), 2.13 (tt, J = 7.6, 7.2 Hz, 2 H), 2.85-3.08 (m, 4 H), 7.28-7.64 (m, 5 H), 9.66 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.4, 29.7, 32.4, 32.6, 61.1, 118.2, 120.0, 120.3 (q, J = 304.8 Hz), 121.7, 125.7, 132.7, 132.8, 146.7, 147.0; Anal. Calcd for $C_{17}H_{21}F_3N_2O_3S$: C, 52.30; H, 5.42; N, 7.18. Found: C, 52.22; H, 5.49; N, 7.23.

1-*tert*-Butyl-3-(2,5-dimethoxylphenyl)imidazolium triflate (3k). 43% yield: Isolated by alumina column chromatography as a colorless plate: m.p. 106-109 ˚C; ^{1}H NMR ($CDCl_3$) δ 1.80 (s, 9 H), 3.85 (s, 3 H), 3.89 (s, 3 H), 7.36-7.66 (m, 5 H), 9.43 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.8, 56.4, 56.5, 61.2, 111.0, 113.6, 118.3, 119.3, 120.7 (q, J = 321.1 Hz), 123.3, 124.1, 134.7, 145.8, 154.2; Anal. Calcd for $C_{16}H_{21}F_3N_2O_5S$: C, 46.82; H, 5.16; N, 6.83. Found: C, 46.81; H, 5.11; N, 6.75.

1-*tert*-Butyl-3-(9-phenanthryl)imidazolium triflate (3l). 36% yield: Isolated by gel permeation chromatography as a pale yellow powder: m.p. 189-192 ˚C; ^{1}H NMR ($CDCl_3$) δ 1.86 (s, 9 H), 7.38-7.90 (m, 7 H), 8.12 (d, J = 6.6 Hz, 1 H), 8.42 (s, 1 H),8.67 (d, J = 7.9 Hz, 1 H), 8.78 (d, J = 8.3 Hz, 1 H), 9.23 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 29.6, 61.5, 120.7, 120.9 (q, J = 324.9 Hz), 121.5, 122.4, 123.5, 124.7, 126.1, 126.8, 127.8, 128.1, 128.9, 129.1, 129.9, 130.0, 130.6, 131.1, 135.1; Anal. Calcd for $C_{22}H_{21}F_3N_2O_3S$: C, 58.66; H, 4.70; N, 6.22. Found: C, 58.91; H, 4.86; N, 5.91.

1-Methyl-3-(3-methoxylphenyl)imidazolium triflate (3m). 56% yield: Isolated by alumina column chromatography as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3 H), 4.08 (s, 3 H), 7.00 (dd, *J* = 8.4, 1.5 Hz, 1 H), 7.11 (dd, *J* = 7.9, 1.3 Hz, 1 H), 7.17 (s, 1 H), 7.40 (t, *J* = 8.1 Hz, 1 H), 7.56 (s, 1 H), 7.64 (d, *J* = 1.7 Hz, 1 H), 9.71 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.7, 55.9, 107.3, 113.5, 116.6, 120.5 (q, *J* = 319.8 Hz), 121.0, 124.5, 131.2, 135.4, 135.7, 161.0; Anal. Calcd for $C_{12}H_{13}F_3N_2O_4S$: C, 42.60; H, 3.87; N, 8.28. Found: C, 42.61; H, 3.90; N, 8.46.

Cross-coupling reaction using 3f. ***A General Procedure.*** To a solution of an aryl chloride (0.21 mmol), phenylboronic acid (0.038 g, 0.31 mmol) and cesium carbonate (0.14 g, 0.42 mmol) in dioxane (0.60 mL) was added $Pd(dba)_2$ (3.6 mg, 6.3 μmol) and **3f** (2.2 mg, 6.3 μmol) and the mixture was stirred at 80 °C for 6 h. The mixture was diluted with ethyl acetate, filtered through a Celite plug, and concentrated. Gel permeation chromatography (chloroform as an eluent) gave the corresponding product (4-methylbiphenyl: 70% yield, 4-acetylbiphenyl: 37% yield). The cross-coupling products were found to be identical to authentic material (Aldrich) by ^{1}H NMR.

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