

**Regioselective aromatic C-H silylation of five-membered heteroarenes with  
fluorodisilanes catalyzed by iridium(I) complexes**

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**Electronic Supplementary Information (ESI)**

**General Methods.** All the experiments were carried out under a nitrogen atmosphere.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  solutions using a JEOL JNM-A400II spectrometer (400 or 100 MHz) and  $\text{Me}_4\text{Si}$  or residual protiated solvent as an internal standard. High-resolution mass spectra were obtained on a JEOL JMS-DX303. GC analyses were performed on a Hitachi G-3500 instrument equipped with a glass column (OV-101 on Uniport B, 2 m). 1,2-Di-*tert*-butyl-1,1,2,2-tetrafluorodisilane,<sup>1</sup> methyl 3-thiophenecarboxylate,<sup>2</sup> 1-triisopropylsilylpyrrole,<sup>3</sup> 1-triisopropylsilylindole,<sup>4</sup>  $[\text{Ir}(\text{OMe})(\text{COD})]_2$ ,<sup>5</sup> 2,9-dibutyl-1,10-phenanthroline,<sup>6</sup> 2,9-di-*tert*-butyl-1,10-phenanthroline,<sup>6</sup> and 2-*tert*-butyl-1,10-phenanthroline<sup>7</sup> were synthesized by the reported procedures. 2,9-Diisopropyl-1,10-phenanthroline and 2-isopropyl-1,10-phenanthroline were prepared by the methods similar to those for 2,9-di-*sec*-butyl-1,10-phenanthroline<sup>8</sup> and 2-*sec*-butyl-1,10-phenanthroline,<sup>9</sup> respectively. Octane and hetroarenes were purified by distillation from appropriate drying agents. All of other compounds were used as received.

**2,9-Diisopropyl-1,10-phenanthroline.** The purity determined by NMR analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  1.47 (d, 12 H,  $J = 7.1$  Hz), 3.50-3.61 (m, 2 H), 7.54 (d, 2 H,  $J = 8.3$  Hz), 7.68 (s, 2 H), 8.14 (d, 2 H,  $J = 8.3$  Hz);  $^{13}\text{C}$  NMR  $\delta$  22.89, 37.29, 120.07, 125.43, 127.25, 136.37, 145.24, 167.84; exact mass calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_2$  264.1626, found 264.1640.

**2-Isopropyl-1,10-phenanthroline.** The purity determined by NMR analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  1.46 (d, 6 H,  $J = 7.1$  Hz), 3.63-3.73 (m, 1 H), 7.59 (d, 1 H,  $J = 4.4$  Hz),

7.61 (d, 1 H,  $J = 4.6$  Hz), 7.72 (d, 1 H,  $J = 8.8$  Hz), 7.76 (d, 1 H,  $J = 8.8$  Hz), 8.20 (d, 1 H,  $J = 8.3$  Hz), 8.23 (dd, 1 H,  $J = 8.1$  and 1.7 Hz), 9.23 (dd, 1 H,  $J = 4.3$  and 1.8 Hz);  $^{13}\text{C}$  NMR  $\delta$  23.10, 37.63, 119.96, 122.54, 125.45, 126.36, 127.05, 128.72, 135.96, 136.53, 145.21, 146.07, 150.20, 168.50; exact mass calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2$  222.1157, found 222.1155.

**General Procedure for C-H Silylation with 1,2-Di-*tert*-butyl-1,1,2,2-tetrafluorodisilane.** A resealable Schlenk tube containing  $[\text{Ir}(\text{OMe})(\text{COD})]_2$  (0.015 mmol) and 2-*tert*-butyl-1,10-phenanthroline (0.03 mmol) was flushed with nitrogen, and then charged with octane (6 mL), 1,2-di-*tert*-butyl-1,1,2,2-tetrafluorodisilane (1.0 mmol), and a heteroarene (10 mmol). The tube was sealed with a Teflon screwcap, and the mixture was stirred at 120 °C for 16-48 h. The product was isolated by Kugelrohr distillation to give an analytically pure sample.

**(*tert*-Butyldifluorosilyl)-3-methylthiophene (Table 1 and Entry 1 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  (5-silyl isomer) 1.08 (s, 9 H), 2.31 (s, 3 H), 7.30 (s, 1 H), 7.34 (s, 1 H), (4-silyl isomer) 1.05 (s, 9 H), 2.38 (s, 3 H), 7.01 (m, 1 H), 7.72 (d, 1 H,  $J = 2.7$  Hz), (2-silyl isomer) 1.08 (s, 9 H), 2.42 (s, 3 H), 7.03 (d, 1 H,  $J = 4.4$  Hz), 7.59 (d, 1 H,  $J = 4.4$  Hz);  $^{13}\text{C}$  NMR  $\delta$  (5-silyl isomer) 14.87, 17.61 (t,  $J = 15.3$  Hz), 24.60, 124.59 (t,  $J = 21.1$  Hz), 129.13, 139.27, 140.49, (4-silyl and 2-silyl isomers) not assigned; exact mass calcd for  $\text{C}_9\text{H}_{14}\text{F}_2\text{SiS}$  220.0553, found 220.0559.

**(*tert*-Butyldifluorosilyl)-3-methoxythiophene (Entry 2 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  (5-silyl isomer) 1.10 (s, 9 H), 3.84 (s, 3 H), 6.69 (d, 1 H,  $J = 1.0$  Hz), 7.17 (d, 1 H,  $J = 1.2$  Hz), (4-silyl isomer) 1.06 (s, 9 H), 3.83 (s, 3 H), 6.30 (m, 1 H), 7.65 (d, 1 H,  $J = 2.9$  Hz), (2-silyl isomer) 1.09 (s, 9 H), 3.88 (s, 3 H), 6.96 (d, 1 H,  $J = 4.9$  Hz), 7.60 (d, 1 H,  $J = 4.9$  Hz);  $^{13}\text{C}$  NMR  $\delta$  (5-silyl isomer) 17.59 (t,  $J = 15.3$  Hz), 24.52, 57.86, 105.38, 124.13 (t,  $J = 22.3$  Hz), 129.33, 160.26, (4-silyl and 2-silyl isomers) not assigned; exact mass calcd for  $\text{C}_9\text{H}_{14}\text{OF}_2\text{SiS}$  236.0503, found 236.0505.

**(*tert*-Butyldifluorosilyl)-3-chlorothiophene (Entry 3 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  (5-silyl isomer) 1.11 (s, 9 H), 7.39 (d, 1 H,  $J = 0.5$  Hz), 7.52 (d, 1 H,  $J = 0.5$  Hz), (2-silyl isomer, aromatic region) 7.12 (d, 1 H,  $J = 4.9$  Hz), 7.68 (d, 1 H,  $J = 4.9$  Hz);  $^{13}\text{C}$  NMR  $\delta$  (5-silyl isomer) 17.59 (t,

$J = 14.9$  Hz), 24.45, 126.26 (t,  $J = 21.9$  Hz), 127.39, 127.90, 137.96, (2-silyl isomer) not assigned; exact mass calcd for  $C_8H_{11}ClF_2SiS$  240.0007, found 240.0015.

**Methyl (*tert*-butyldifluorosilyl)-3-thiophenecarboxylate (Entry 4 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1H$  NMR  $\delta$  (5-silyl isomer) 1.11 (t, 9 H,  $J = 1.0$  Hz), 3.90 (s, 3 H), 7.98 (d, 1 H,  $J = 1.0$  Hz), 8.46 (s, 1 H), (2-silyl isomer, aromatic region) 7.10 (d, 1 H,  $J = 5.4$  Hz), 7.47 (d, 1 H,  $J = 5.1$  Hz);  $^{13}C$  NMR  $\delta$  (5-silyl isomer) 17.53 (t,  $J = 14.9$  Hz), 24.42, 51.97, 126.43 (t,  $J = 21.5$  Hz), 135.29, 139.04, 139.87, 162.69, (2-silyl isomer) not assigned; exact mass calcd for  $C_{10}H_{14}O_2F_2SiS$  264.0452, found 264.0447.

**(*tert*-Butyldifluorosilyl)-2-methylthiophene (Entry 5 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1H$  NMR  $\delta$  (5-silyl isomer) 1.07 (t, 9 H,  $J = 1.0$  Hz), 2.55 (s, 3 H), 6.90-6.91 (m, 1 H), 7.37 (d, 1 H,  $J = 3.4$  Hz), (4-silyl isomer) 1.05 (t, 9 H,  $J = 1.0$  Hz), 2.51 (d, 3 H,  $J = 1.0$  Hz), 6.90-6.91 (m, 1 H), 7.57 (d, 1 H,  $J = 1.2$  Hz);  $^{13}C$  NMR  $\delta$  (5-silyl isomer) 14.98, 17.60 (t,  $J = 15.7$  Hz), 24.61, 122.45 (t,  $J = 21.5$  Hz), 127.12, 138.79 (t,  $J = 1.7$  Hz), 148.71, (4-silyl isomer) not assigned; exact mass calcd for  $C_9H_{14}F_2SiS$  220.0553, found 220.0558.

**(*tert*-Butyldifluorosilyl)-2-chlorothiophene (Entry 6 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1H$  NMR  $\delta$  (5-silyl isomer) 1.10 (s, 9 H), 7.07 (d, 1 H,  $J = 3.7$  Hz), 7.35 (d, 1 H,  $J = 3.7$  Hz), (4-silyl isomer) 1.07 (s, 9 H), 7.07 (m, 1 H), 7.59 (d, 1 H,  $J = 1.2$  Hz);  $^{13}C$  NMR  $\delta$  (5-silyl isomer) 17.56 (t,  $J = 15.3$  Hz), 24.44, 124.59 (t,  $J = 21.9$  Hz), 127.79, 138.00, 138.29, (4-silyl isomer) not assigned; exact mass calcd for  $C_8H_{11}ClF_2SiS$  240.0007, found 240.0003.

**2-(*tert*-Butyldifluorosilyl)benzo[*b*]thiophene (Entry 7 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1H$  NMR  $\delta$  1.15 (s, 9 H), 7.39-7.45 (m, 2 H), 7.83 (s, 1 H), 7.91-7.95 (m, 2 H);  $^{13}C$  NMR  $\delta$  17.67 (t,  $J = 14.9$  Hz), 24.54, 122.28, 124.45, 124.59, 125.81, 126.26 (t,  $J = 20.7$  Hz), 135.72, 139.91, 143.85; exact mass calcd for  $C_{12}H_{14}F_2SiS$  256.0554, found 256.0565.

**(*tert*-Butyldifluorosilyl)thiophene (Entry 8 in Table 2).** The purity determined by NMR and GC analyses: > 95%;  $^1H$  NMR  $\delta$  (2-silyl isomer) 1.09 (s, 9 H), 7.27 (t, 1 H,  $J = 4.0$  Hz), 7.59 (d, 1 H,  $J = 3.4$  Hz), 7.76 (d, 1 H,  $J = 4.6$  Hz), (3-silyl isomer) 1.06 (s, 9 H), 7.30 (d, 1 H,  $J = 4.9$  Hz), 7.47 (m, 1 H), 7.83 (d, 1 H,  $J = 1.7$  Hz);  $^{13}C$  NMR  $\delta$  (2-silyl isomer) 17.62 (t,  $J = 15.3$  Hz), 24.57, 124.57 (t,  $J = 21.1$  Hz), 128.38, 133.40, 138.33, (3-silyl isomer) not assigned; exact mass calcd for  $C_8H_{12}F_2SiS$  206.0397, found 206.0396.

**(*tert*-Butyldifluorosilyl)-3-methylfuran (Scheme 2).** The purity determined by NMR and GC analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  (5-silyl isomer) 1.10 (t, 9 H,  $J = 1.0$  Hz), 2.06 (s, 3 H), 6.90 (s, 1 H), 7.48 (d, 1 H,  $J = 0.7$  Hz), (4-silyl isomer) 1.07 (t, 9 H,  $J = 1.0$  Hz), 2.11 (s, 3 H), 7.30 (s, 1 H), 7.58 (s, 1 H), (2-silyl isomer) 1.10 (t, 9 H,  $J = 1.0$  Hz), 2.20 (s, 3 H), 6.31 (d, 1 H,  $J = 1.7$  Hz), 7.60 (d, 1 H,  $J = 1.7$  Hz);  $^{13}\text{C}$  NMR  $\delta$  (5-silyl isomer) 9.12, 17.29 (t,  $J = 15.3$  Hz), 24.39, 119.98, 127.66 (t,  $J = 1.7$  Hz), 145.62 (t,  $J = 1.7$  Hz), 148.05 (t,  $J = 26.5$  Hz), (4-silyl isomer) 10.24, 17.69 (t,  $J = 15.7$  Hz), 24.57, 109.70 (t,  $J = 20.7$  Hz), 123.29, 140.42 (t,  $J = 2.5$  Hz), 151.31 (t,  $J = 4.5$  Hz); exact mass calcd for  $\text{C}_9\text{H}_{14}\text{OF}_2\text{Si}$  204.0782, found 204.0783.

**(*tert*-Butyldifluorosilyl)benzo[*b*]furan (Scheme 2).** The purity determined by NMR and GC analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  (2-silyl isomer) 1.16 (t, 9 H,  $J = 1.0$  Hz), 7.28 (t, 1 H,  $J = 7.8$  Hz), 7.39 (t, 1 H,  $J = 8.3$  Hz), 7.41 (s, 1 H), 7.57 (d, 1 H,  $J = 8.3$  Hz), 7.67 (d, 1 H,  $J = 7.8$  Hz), (3-silyl isomer) 1.12 (t, 9 H,  $J = 0.9$  Hz), 7.30 (t, 1 H,  $J = 7.3$  Hz), 7.36 (t, 1 H,  $J = 7.8$  Hz), 7.57 (d, 1 H,  $J = 8.1$  Hz), 7.71 (d, 1 H,  $J = 7.6$  Hz), 7.85 (s, 1 H);  $^{13}\text{C}$  NMR  $\delta$  (2-silyl isomer) 17.34 (t,  $J = 14.5$  Hz), 24.32, 111.86, 121.49, 121.99, 123.13, 126.22, 126.49, 150.16 (t,  $J = 26.5$  Hz), 158.22, (3-silyl isomer) 17.69 (t,  $J = 15.3$  Hz), 24.45, 104.68 (t,  $J = 21.9$  Hz), 111.51, 122.45, 123.52, 125.04, 129.47, 153.08 (t,  $J = 4.1$  Hz), 155.36; exact mass calcd for  $\text{C}_{12}\text{H}_{14}\text{OF}_2\text{Si}$  240.0782, found 240.0787.

**3-(*tert*-Butyldifluorosilyl)-1-triisopropylsilylpyrrole (Scheme 3).** The purity determined by NMR and GC analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  1.05 (t, 9 H,  $J = 0.5$  Hz), 1.09 (d, 18 H,  $J = 7.6$  Hz), 1.41-1.53 (m, 3 H), 6.49-6.50 (m, 1 H), 6.89 (s, 1 H), 7.10 (s, 1 H);  $^{13}\text{C}$  NMR  $\delta$  11.66, 17.71, 17.71 (t,  $J = 16.5$  Hz), 24.80, 106.67 (t,  $J = 21.1$  Hz), 115.22 (t,  $J = 2.1$  Hz), 125.53, 133.20 (t,  $J = 2.9$  Hz); exact mass calcd for  $\text{C}_{17}\text{H}_{33}\text{NF}_2\text{Si}_2$  345.2120, found 345.2126.

**3-(*tert*-Butyldifluorosilyl)-1-triisopropylsilylindole (Scheme 3).** The purity determined by NMR and GC analyses: > 95%;  $^1\text{H}$  NMR  $\delta$  1.09 (t, 9 H,  $J = 0.7$  Hz), 1.15 (d, 18 H,  $J = 7.6$  Hz), 1.67-1.79 (m, 3 H), 7.16-7.22 (m, 2 H), 7.55 (s, 1 H), 7.56 (d, 1 H,  $J = 6.8$  Hz), 7.76 (d, 1 H,  $J = 7.6$  Hz);  $^{13}\text{C}$  NMR  $\delta$  12.68, 18.00, 18.03 (t,  $J = 16.5$  Hz), 24.84, 101.34 (t,  $J = 21.5$  Hz), 114.01, 120.82, 121.96, 122.18, 134.67, 140.93 (t,  $J = 4.1$  Hz), 141.79; exact mass calcd for  $\text{C}_{21}\text{H}_{35}\text{NF}_2\text{Si}_2$  395.2276, found 395.2277.

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