Supporting Information

Efficient Iridium-catalyzed C-H Functionalization/Silylation of Heteroarenes

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I. General information 2
II. General experimental procedure 3
III. \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra 10
Experimental

General. All reactions were carried out under an argon atmosphere. Anhydrous solvents were freshly distilled from sodium benzophenone ketyl, except for CH$_2$Cl$_2$, which was distilled from CaH$_2$. Extracts were dried over anhydrous Na$_2$SO$_4$ and then filtered prior to removal of all volatiles under reduced pressure. Unless otherwise noted, commercially available materials were used without further purification. [Ir(OMe)(COD)]$_2$ was purchased from Alfa Aesar. Flash chromatography (FC) was performed using *E Merck* silica gel 60 (240–400 mesh). Thin layer chromatography was performed using precoated plates purchased from *E. Merck* (silica gel 60 PF254, 0.25 mm).

Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 300 spectrometer at operating frequencies of 300 MHz ($^1$H NMR) or 75 MHz ($^{13}$C NMR). Chemical shifts (δ) are given in ppm relative to residual solvent (usually chloroform δ 7.27 for $^1$H NMR or δ 77.23 for proton decoupled $^{13}$C NMR), and coupling constants (J) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, t for triplet, q for quadruplet, and m for multiplet, whereby the prefix app is applied in cases where the true multiplicity is unresolved, and br when the signal in question is broadened. The Michigan State University Mass Spectroscopy Facility provided high-resolution mass spectral analyses.

4-(*tert*-Butyldimethylsilyloxy)indole (5)[1]

To a solution of 4-hydroxyindole (40 mg, 0.3 mmol) in dry DMF (0.5 mL) was added imidazole (37 mg, 0.54 mmol) and TBSCl (52 mg, 0.32 mmol). The mixture was stirred at room temperature for 3 h. EtOAc (5 mL) and H$_2$O (5 mL) were added. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 3 mL). The combined organic extracts were dried with Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography using silica gel to give 78
mg (100%) of 4-(tert-butyldimethylsilyloxy)indole.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.09 (br, 1H), 7.10-7.01 (m, 3H), 6.60 (s, 1H), 6.54 (d, $J = 6.0$ Hz, 1H), 1.08 (s, 9H), 0.25 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.3, 138.0, 122.9 (2 $\times$ C), 121.9, 108.9, 104.9, 100.6, 26.0, 18.6, -4.1.

**General procedure for the 2-silylation of heteroarenes with triethylsilane.** A flamed-dried Schlenk tube was charged with heteroarene (0.2 mmol), [Ir(OMe)(COD)$_2$] (6.6 mg, 0.01 mmol) and dtpy (5.4 mg, 0.02 mmol), then evacuated and flushed with argon three times. Under a positive flow of argon, 2-norbornene (56 mg, 0.6 mmol) and dry THF (1 mL) were added. After stirring for 5 min, triethylsilane (98 $\mu$L, 0.6 mmol) was added dropwise. The reaction mixture was heated at 80°C for 24 h or indicated time. The solvent was concentrated under reduced pressure. The residue was purified by flash chromatography using silica gel to give 2-(triethylsilyl)heteroarene.

For 1-tosyl-indole, the 3-silylation product was obtained using above general procedure.

In case of furan (0.2 mmol) and thiophene (0.2 mmol), 2-norbornene (75 mg, 0.8 mmol) and triethylsilane (130 $\mu$L, 0.6 mmol) were employed.

![2-(Triethylsilyl)indole](image)

**2-(Triethylsilyl)indole (2).** 87% yield; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.10 (br, 1H), 7.66-7.64 (m, 1H), 7.41 (dd, $J = 8.1$ Hz, 0.9 Hz, 1H), 7.22-7.16 (m, 1H), 7.13-7.07 (m, 1H), 6.76-6.75 (m, 1H), 1.07-1.01 (m, 9H), 0.89-0.81 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.8, 135.8, 128.9, 122.4, 120.7, 119.8, 112.6, 111.0, 7.7, 3.8. HRMS (ESI) for C$_{14}$H$_{22}$NSi $[M+H]^+$ Calc 232.1522, Found 232.1517.
5-Methoxy-2-triethylsilyl-indole (4). 90% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.05 (br, 1H), 7.30 (d, $J = 9.0$ Hz, 1H), 7.11 (s, 1H), 6.88 (dd, $J = 8.4$ Hz, 2.1 Hz, 1H), 6.69 (s, 1H), 3.87 (s, 3H), 1.07-1.02 (m, 9H), 0.89-0.81 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 154.3, 136.7, 134.2, 129.3, 113.0, 112.2, 111.7, 101.9, 56.1, 7.7, 3.8. HRMS (ESI) for C$_{15}$H$_{24}$NOSi [MH$^+$] Calc 262.1627 Found 262.1620.

4-(tert-Butyldimethylsilyloxy)-2-(triethylsilyl)-indole (6). 82% yield; m.p 62-63 oC;
$^1$H NMR (300 MHz, CDCl$_3$) δ 8.03 (br, 1H), 7.02 (s, 1H), 7.01 (d, $J = 1.8$ Hz, 1H), 6.74 (d, $J = 2.4$ Hz, 1H), 6.48 (dd, $J = 4.8$ Hz, 3.0 Hz, 1H), 1.06 (s, 9H), 1.05-1.00 (m, 9H), 0.87-0.79 (m, 6H), 0.24 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 149.0, 140.9, 134.1, 123.1, 122.8, 110.2, 108.5, 104.6, 26.1, 18.6, 7.7, 3.8, -4.0. HRMS (ESI) for C$_{20}$H$_{36}$NOSi$_2$ [MH$^+$] Calc 362.2335 Found 362.2338.

6-Methyl-2-triethylsilylindole (8). 86% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.97 (br, 1H), 7.52 (d, $J = 7.5$Hz, 1H), 7.20 (s, 1H), 6.93 (d, $J = 8.1$ Hz, 1H), 6.70 (s, 1H), 2.47 (s, 3H), 1.06-1.00 (m, 9H), 0.88-0.80 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.4, 135.0, 132.2, 126.8, 121.6, 120.3, 112.4, 110.9, 22.0, 7.7, 3.8. HRMS (ESI) for C$_{15}$H$_{24}$NSi [MH$^+$] Calc 246.1678 Found 246.1682.
3-Methyl-2-triethylsilylindole (10). 55% yield; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.87 (br, 1H), 7.62-7.58 (m, 1H), 7.38-7.35 (m, 1H), 7.22-7.16 (m, 1H), 7.14-7.09 (m, 1H), 2.42 (s, 3H), 1.06-1.01 (m, 9H), 0.95-0.87 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 138.5, 130.9, 129.7, 122.3, 121.1, 119.1, 118.8, 110.9, 10.8, 7.7, 3.9. HRMS (ESI) for C$_{15}$H$_{23}$NSi [M$^+$] Calc 245.1600 Found 245.1606.

5-Fluoro-2-triethylsilylindole (12). 76% yield; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.11 (br, 1H), 7.34-7.26 (m, 2H), 6.99-6.92 (m, 1H), 6.72-6.71 (m, 1H), 1.08-1.02 (m, 9H), 0.90-0.82 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.1 ($J = 233.0$ Hz), 138.2, 135.5, 129.2 ($J = 9.7$ Hz), 112.5 ($J = 4.9$ Hz), 111.4 ($J = 9.7$ Hz), 110.8 ($J = 26.0$ Hz), 105.2 ($J = 22.4$ Hz), 7.7, 3.7; HRMS (ESI) for C$_{14}$H$_{21}$NFSi [MH$^+$] Calc 250.1427 Found 250.1425.

7-Chloro-2-triethylsilylindole (14). 64% yield; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.21 (br, 1H), 7.54 (dd, $J = 8.1$ Hz, 0.9 Hz, 1H), 7.18 (dd, $J = 7.8$ Hz, 0.9 Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.78 (d, $J = 2.1$ Hz, 1H), 1.08-1.02 (m, 9H), 0.91-0.83 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 137.0, 136.1, 130.4, 121.6, 120.6, 119.3, 116.5, 113.5, 7.7, 3.7; HRMS (ESI) for C$_{14}$H$_{21}$NSiCl [MH$^+$] Calc 266.1132 Found 266.1133.
6-Bromo-2-triethylsilylindole (16). 52% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.12 (br, 1H), 7.75 (s, 1H), 7.26-7.25 (m, 2H), 6.66 (s, 1H), 1.02-0.96 (m, 9H), 0.88-0.80 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 137.6, 137.4, 130.7, 125.1, 123.1, 113.0, 112.3, 112.0, 7.7, 3.7; HRMS (ESI) for C$_{14}$H$_{21}$NSiBr [MH$^+$] Calc 310.0627 Found 310.0624.

4-Nitro-2-triethylsilylindole (18). 41% yield; m.p 131-133 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.51 (br, 1H), 7.64 (dd, $J = 8.4$ Hz, 0.4 Hz, 1H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.23-7.18 (m, 1H), 6.93-6.92 (m, 1H), 1.06-1.01 (m, 9H), 0.92-0.84 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.0, 138.6, 130.1, 125.3, 121.8, 119.3, 115.8, 111.0, 102.7, 7.6, 3.6. HRMS (ESI) for C$_{15}$H$_{21}$N$_2$Si [MH$^+$] Calc 257.1474 Found 257.1470.

N-Methyl-2-triethylsilylindole (20). 49% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.62 (d, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 7.25-7.20 (m, 1H), 7.09 (t, $J = 7.2$ Hz, 1H), 6.73 (s, 1H), 3.84 (s, 3H), 1.04-0.99 (m, 9H), 0.95-0.88 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 140.4, 138.5, 128.7, 122.0, 120.7, 119.2, 113.1, 109.2, 33.2, 7.8, 4.2; HRMS (ESI) for C$_{15}$H$_{24}$NSi [MH$^+$] Calc 246.1678 Found 246.1676.
**N-Tosyl-3-triethylsilylindole (22).** 70% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.97-7.94 (m, 1H), 7.76 (d, \(J = 7.8\) Hz, 2H), 7.60-7.56 (m, 1H), 7.55 (s, 1H), 7.30-7.18 (m, 4H), 2.33 (s, 3H), 0.99-0.94 (m, 9H), 0.90-0.82 (m, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.1, 136.1, 135.5, 135.3, 132.8, 130.1, 127.0, 124.4, 123.3, 122.7, 115.4, 113.7, 21.8, 7.7, 3.9. HRMS (ESI) for C\(_{21}\)H\(_{28}\)NO\(_2\)Si [M+H\(^+\)] Calc 386.1610 Found 386.1607.

![Addtional structure image](image)

**2,5-Bis(triethylsilyl)thiophene (24).** 98% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.33 (s, 2H), 1.04-0.98 (m, 18H), 0.85-0.77 (m, 12H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 142.5, 135.6, 7.7, 4.8. HRMS (EI) for C\(_{16}\)H\(_{32}\)SSi [M+\(^+\)] Calc 312.1763 Found 312.1762.

![Additional structure image](image)

**Methyl 5-(triethylsilyl)thiophene-3-carboxylate (26).** 67% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.32 (d, \(J = 0.9\) Hz, 1H), 7.64 (d, \(J = 0.9\) Hz, 1H), 3.86 (s, 3H), 1.02-0.96 (m, 9H), 0.85-0.77 (m, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 163.8, 138.6, 138.0, 135.6, 135.0, 52.0, 7.5, 4.4. HRMS (ESI) for C\(_{12}\)H\(_{21}\)O\(_2\)SiS [M+H\(^+\)] Calc 257.1032 Found 257.1035.

![Additional structure image](image)

**Methyl 2,5-bis(triethylsilyl)thiophene-3-carboxylate** 33% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.77 (s, 1H), 3.86 (s, 3H), 1.02-0.94 (m, 24H), 0.81 (t, \(J = 7.5\) Hz, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 164.6, 152.2, 142.7, 140.0, 138.5, 51.7, 7.9, 7.6, 4.6, 4.1.
HRMS (ESI) for C_{18}H_{38}O_{2}Si_{2}S [MH^+] Calc 371.1896 Found 371.1894.

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\begin{array}{c}
\text{Cl} \quad \text{SiEt}_3 \\
\end{array}
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**5-Chloro-2-triethylsilylthiophene (28).** 91% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.00 (d, \(J = 3.6\) Hz, 1H), 6.97 (d, \(J = 3.6\) Hz, 1H), 1.02-0.96 (m, 9H), 0.81-0.73 (m, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 137.0, 134.6, 134.3, 127.6, 7.5, 4.4. HRMS (EI) for C_{10}H_{17}SSiCl [M\(^+\)] Calc 232.0509 Found 232.0508.

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\begin{array}{c}
\text{SiEt}_3 \\
\end{array}
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**2-Triethylsilyl benzothiophene (30).** 99% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.91-7.88 (m, 1H), 7.84-7.81 (m, 1H), 7.47 (s, 1H), 7.34-7.31 (m, 2H), 1.07-1.01 (m, 9H), 0.91-0.83 (m, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 143.8, 141.2, 139.2, 131.8, 124.3, 124.1, 123.6, 122.4, 7.6, 4.5. HRMS (EI) for C_{14}H_{20}SSi [M\(^+\)] Calc 248.1055 Found 248.1048.

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\begin{array}{c}
\text{SiEt}_3 \\
\end{array}
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**2-Triethylsilyl benzofuran (32).** 83% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.60-7.57 (m, 1H), 7.53-7.50 (m, 1H), 7.30-7.16 (m, 2H), 6.99 (s, 1H), 1.07-1.01 (m, 9H), 0.88-0.81 (m, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 161.6, 158.1, 128.0, 124.1, 122.2, 120.9, 117.2, 111.3, 7.3, 3.1. HRMS (EI) for C_{14}H_{20}OSi [M\(^+\)] Calc 232.1283 Found 232.1283.

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\begin{array}{c}
\text{Et}_3\text{Si} \quad \text{SiEt}_3 \\
\end{array}
\]

**2,5-Bis(triethylsilyl)furan (34).** 93% yield; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.62 (s, 2H), 1.02-0.96 (m, 18H), 0.80-0.71 (m, 12H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.8, 120.1, 7.6,
2-Dimethyl(phenyl)silyl benzothiophene (35). 92% yield; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.90-7.80 (m, 2H), 7.64-7.61 (m, 2H), 7.50 (s, 1H), 7.42-7.31 (m, 5H); 0.67 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 144.1, 141.2, 140.3, 137.4, 134.2, 132.5, 129.8, 128.2, 124.5, 124.3, 123.8, 122.4, -1.4. HRMS (EI) for C$_{16}$H$_{16}$SSi [M$^+$] Calc 268.0742 Found 268.0741.

References