Supporting Information for Heteroaromatic Thioether-Organostannane Cross-coupling

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General Experimental.

^1H and ^{13}C NMR spectra were recorded on a Varian Inova 400 spectrometer or a Mercury 300 spectrometer with chloroform (7.26 ppm ^1H , 77.0 ppm ^{13}C) as an internal reference. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel plates with F-254 indicator. Visualization was accomplished by UV light or *p*-anisaldehyde solution. 2-(Methylthio)benzothiazole, 2-chlorobenzothiazole, 2-chloroquinoline, 2-chloropyrazine, 2-chloropyrimidine, sodium thiophenoxide, 2-(tri-*n*-butylstannyl)furan, and 2-(tri-*n*-butylstannyl)thiophene were purchased from Aldrich. Solvents were purged with nitrogen for several hours, then dried and stored over 4Å sieves. All reactions were carried out under argon. Copper(I) 3-methylsalicylate (CuMeSal)¹ and 2-methyl-1-tri-*n*-butylstannylpropene² were prepared by known procedures.

2-(Phenylthio)benzothiazole

A suspension of 2-chlorobenzothiazole (0.235 mL, 1.81 mmol, 1.0 equiv) and sodium thiophenoxide (522 mg, 3.95 mmol, 2.2 equiv) in EtOH (3 mL) was stirred at reflux for 5 h. After cooling, the reaction mixture was evaporated, the residue was dissolved with H_2O , and the mixture was extracted with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 , filtered, and evaporated. Purification by SiO_2 column chromatography with 40/1 hexanes/EtOAc gave 2-(phenylthio)benzothiazole (440 mg, 100%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.3 Hz, 1H), 7.76–7.72 (m, 2H), 7.65 (d, J = 7.9 Hz, 1H), 7.55–7.45 (m, 3H), 7.43–7.38 (m, 1H), 7.29–7.24 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 169.4, 153.7, 135.3, 135.1, 130.3, 129.7 (x2), 126.0, 124.1, 121.7, 120.6.

IR (neat, cm^{-1}) 3061, 1459, 1424.

HRMS (EI) Calcd for $\text{C}_{13}\text{H}_9\text{NS}_2$: 243.0176. Found 243.0161 [M^+].

2-(Phenylthio)quinoline

A suspension of 2-chloroquinoline (446 mg, 2.73 mmol, 1.0 equiv) and sodium thiophenoxide (540 mg,

4.09 mmol, 1.5 equiv) in EtOH (4.5 mL) was stirred at reflux overnight. After cooling, the reaction mixture was evaporated, the residue was diluted with H₂O, and the mixture was extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtered, and evaporated. Purification by SiO₂ column chromatography with 3/2 hexanes/CH₂Cl₂ gave 2-(phenylthio)quinoline (574 mg, 89%) as white crystals.

M.p. 46 °C (EtOH) [lit.³ 48–49 °C (EtOH)].

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.69–7.64 (m, 3H), 7.48–7.42 (m, 4H), 6.98 (d, *J* = 8.4 Hz, 1H).

¹³C NMR (75.5 MHz, CDCl₃) δ 161.3, 147.8, 136.2, 134.9, 130.6, 129.8, 129.4, 129.0, 128.1, 127.4, 125.6 (x2), 119.3.

IR (neat, cm⁻¹) 3057, 1613, 1586, 1494.

2-(Phenylthio)pyrazine

A suspension of 2-chloropyrazine (0.250 mL, 2.80 mmol, 1.0 equiv) and sodium thiophenoxide (540 mg, 4.09 mmol, 1.5 equiv) in EtOH (4.5 mL) was stirred at reflux for 4 h. After cooling, the reaction mixture was evaporated, the residue was diluted with H₂O, and the mixture was extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtered, and evaporated. Purification by SiO₂ column chromatography with 10/1 hexanes/EtOAc gave 2-(phenylthio)pyrazine (483 mg, 92%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.35–8.32 (m, 1H), 8.23 (d, *J* = 2.5 Hz, 1H), 8.20 (d, *J* = 1.6 Hz, 1H), 7.64–7.58 (m, 2H), 7.47–7.42 (m, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 143.9, 142.6, 140.0, 135.0, 129.8, 129.6, 128.9.

IR (neat, cm⁻¹) 3057, 1509, 1454, 1382.

Anal. Calcd for C₁₀H₈N₂S: C, 63.80; H, 4.28; N, 14.88; S, 17.03. Found: C, 63.80; H, 4.31; N, 14.86; S, 16.78.

2-(Phenylthio)pyrimidine

A suspension of 2-chloropyrimidine (558 mg, 4.87 mmol, 1.0 equiv) and sodium thiophenoxide (869 mg, 6.57 mmol, 1.3 equiv) in EtOH (7.0 mL) was stirred at reflux for 4 h. After cooling, the reaction mixture was evaporated, the residue was diluted with H₂O, and the mixture was extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, filtered, and evaporated. Purification by SiO₂ column chromatography with 6/1 hexanes/EtOAc gave 2-(phenylthio)pyrimidine

(129 mg, 14%) as colorless needles.

M.p. 47–49 °C (petroleum ether) [lit.⁴ 46 °C (petroleum ether)].

¹H NMR (400 MHz, CDCl₃) δ 8.48 (d, *J* = 4.8 Hz, 2H), 7.66–7.62 (m, 2H), 7.46–7.42 (m, 3H), 6.96 (t, *J* = 4.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 172.3, 157.2, 134.9, 129.0, 128.9, 128.8, 116.7.

IR (neat, cm⁻¹) 3034, 1548, 1475, 1378.

Scheme 1, Catalyst Survey. Representative Example: 2-(4-Methylphenyl)benzothiazole

CuMeSal¹ (113 mg, 0.526 mmol, 2.2 equiv) and PdCl(PPh₃)₂CH₂Ph (9.1 mg, 0.012 mmol, 0.05 equiv) were added to a solution of 2-(4-methylphenylthio)benzothiazole (61.7 mg, 0.240 mmol, 1.0 equiv) and *p*-tolyltri-*n*-butylstannane (101 mg, 0.265 mmol, 1.1 equiv) in THF (3.0 mL). The reaction mixture was stirred at 50 °C for 14 h, then evaporated, 10% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 50/1 hexanes/Et₂O gave 2-(4-methylphenyl)-benzothiazole (49.0 mg, 91%) as off white crystals.

M.p. 83–85 °C (EtOH) [lit.⁵ 85–86 °C (EtOH)].

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H).

¹³C NMR (75.5 MHz, CDCl₃) δ 168.4, 154.3, 141.6, 135.1, 131.1, 129.9, 127.7, 126.4, 125.2, 123.2, 121.7, 21.7.

IR (neat, cm⁻¹) 3026, 2922, 1610, 1482, 1436, 1312, 1181.

Anal. Calcd for C₁₄H₁₁NS: C, 74.63; H, 4.92; N, 6.22; S, 14.23. Found: C, 74.67; H, 5.09; N, 6.12; S, 14.15.

Table 1, Entry 1. 2-(4-Chlorophenyl)benzothiazole

CuMeSal (142 mg, 0.661 mmol, 2.2 equiv) and PdCl(PPh₃)₂CH₂Ph (11.4 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 2-(methylthio)benzothiazole (54.4 mg, 0.300 mmol, 1.0 equiv) and (4-chlorophenyl)-tri-*n*-butylstannane (133 mg, 0.331 mmol, 1.1 equiv) in THF (3.6 mL). The reaction mixture was stirred at 50 °C for 20 h, 10% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was

extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 40/1 hexanes/EtOAc gave 2-(4-chlorophenyl)benzothiazole (65.6 mg, 89%) as a white solid.

M.p. 114–116 °C (EtOH) [lit.⁶ 116.5 °C (EtOH)].

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 166.5, 154.0, 136.9, 135.0, 132.0, 129.2, 128.6, 126.4, 125.3, 123.2, 121.6.

IR (neat, cm⁻¹) 3057, 2926, 1590, 1509, 1475.

Table 1, Entry 2. 2-(2-Methylprop-1-enyl)benzothiazole

CuMeSal (142 mg, 0.661 mmol, 2.2 equiv) and PdCl(PPh₃)₂CH₂Ph (11.4 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 2-(methylthio)benzothiazole (54.4 mg, 0.300 mmol, 1.0 equiv) and (2-methyl-1-propenyl)-tri-*n*-butylstannane² (114 mg, 0.330 mmol, 1.1 equiv) in THF (3.6 mL). The reaction mixture was stirred at 50 °C for 20 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 40/1 hexanes/EtOAc gave 2-(2-methylprop-1-enyl)benzothiazole (46.0 mg, 81%) as yellow crystals.

M.p. 78–79 °C (petroleum ether) [lit.⁷ 81–82 °C (petroleum ether)].

¹H NMR (300 MHz, CDCl₃) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.44 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.32 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 6.62–6.59 (m, 1H), 2.26 (s, 3H), 2.03 (s, 3H).

¹³C NMR (75.5 MHz, CDCl₃) δ 165.5, 153.2, 146.0, 134.6, 125.9, 124.5, 122.6, 121.1, 119.5, 27.7, 20.9.

IR (neat, cm⁻¹) 3053, 2097, 1652, 1440.

Table 1, Entry 4. 2-(Furan-2-yl)benzothiazole

CuMeSal (142 mg, 0.661 mmol, 2.2 equiv) and Pd(PPh₃)₄ (17.3 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 2-(phenylthio)benzothiazole (73.3 mg, 0.301 mmol, 1.0 equiv) and 2-(tri-*n*-butylstannyl)furan (118 mg, 0.330 mmol, 1.1 equiv) in THF (3.6 mL). The reaction mixture was stirred at 50 °C for 14 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an

additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ chromatography plate with 20/1 hexanes/EtOAc gave 2-(furan-2-yl)benzothiazole (58.0 mg, 96%) as white crystals.

M.p. 103–104 °C [lit.⁸ 103–104.5 °C].

¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.60 (s, 1H), 7.50–7.46 (m, 1H), 7.39–7.34 (m, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 6.60–6.57 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 157.3, 153.5, 148.5, 144.4, 134.0, 126.2, 124.9, 122.9, 121.3, 112.3, 111.2.

IR (neat, cm⁻¹) 3217, 3061, 1602, 1583, 1505.

Table 1, Entry 6. 2-(4-Chlorophenyl)pyrazine

CuMeSal (94.5 mg, 0.440 mmol, 2.2 equiv) and Pd(PPh₃)₄ (11.6 mg, 0.010 mmol, 0.05 equiv) were added to a solution of 2-(phenylthio)pyrazine (37.2 mg, 0.198 mmol, 1.0 equiv) and (4-chlorophenyl)-tri-*n*-butylstannane (88.4 mg, 0.220 mmol, 1.1 equiv) in THF (2.4 mL). The reaction mixture was stirred at 50 °C for 21 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 6/1 hexanes/EtOAc gave 2-(4-trifluoromethylphenyl)quinoline (35.0 mg, 93%) as white crystals.

M.p. 73–74 °C (petroleum ether)

¹H NMR (400 MHz, CDCl₃) δ 8.98 (s, 1H), 8.59 (s, 1H), 8.49 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 151.5, 144.1, 143.1, 141.8, 136.1, 134.6, 129.2, 128.1.

IR (neat, cm⁻¹) 3057, 2922, 1598, 1471, 1413.

FABMS: *m/z*. calcd 191.0376, found 191.0375 [M+H]⁺.

Table 1, Entry 7. 2-(Thiophen-2-yl)pyrazine

CuMeSal (142 mg, 0.661 mmol, 2.2 equiv) and Pd(PPh₃)₄ (17.3 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 2-(phenylthio)pyrazine (56.5 mg, 0.300 mmol, 1.0 equiv) and

2-(tri-*n*-butylstannyl)thiophene (123 mg, 0.330 mmol, 1.1 equiv) in THF (3.6 mL). The reaction mixture was stirred at 50 °C for 42 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ chromatography plate with 10/1 hexanes/acetone gave 2-(thiophen-2-yl)pyrazine (24.5 mg, 50%) as light yellow crystals.

M.p. 96–97 °C [lit.⁹ 97 °C].

¹H NMR (300 MHz, CDCl₃) δ 8.96 (d, *J* = 1.4 Hz, 1H), 8.52–8.50 (m, 1H), 8.41 (d, *J* = 2.9 Hz, 1H), 7.70 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.49 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.17 (dd, *J* = 5.0, 3.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 148.4, 143.9, 142.3, 141.2, 140.5, 128.9, 128.3, 125.7.

IR (neat, cm⁻¹) 3073, 1575, 1532, 1513.

Table 1, Entry 8. 2-(Furan-2-yl)pyrimidine

CuMeSal (100 mg, 0.466 mmol, 2.2 equiv) and Pd(PPh₃)₄ (12.3 mg, 0.011 mmol, 0.05 equiv) were added to a solution of 2-(phenylthio)-pyrimidine (40.0 mg, 0.212 mmol, 1.0 equiv) and 2-(tri-*n*-butylstannyl)furan (83.5 mg, 0.234 mmol, 1.1 equiv) in THF (2.6 mL). The reaction mixture was stirred at 50 °C for 18 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with CH₂Cl₂ gave 2-(furan-2-yl)pyrimidine (24.6 mg, 79%) as white crystals.

M.p. 62–64 °C [lit.¹⁰ 55–66 °C].

¹H NMR (300 MHz, CDCl₃) δ 8.75 (d, *J* = 5.3 Hz, 2H), 7.63 (d, *J* = 1.4 Hz, 1H), 7.33 (d, *J* = 3.4 Hz, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.58 (dd, *J* = 3.4, 1.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 157.6, 157.1, 151.8, 144.9, 118.5, 113.3, 112.1.

IR (neat, cm⁻¹) 3115, 1586, 1563, 1490.

Table 1, Entry 9. 2-(2-Methylprop-1-enyl)-3-nitro-pyridine

CuMeSal (141 mg, 0.657 mmol, 2.2 equiv) and PdCl(PPh₃)₂CH₂Ph (11.5 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 3-nitro-2-(*p*-tolylthio)pyridine (72.5 mg, 0.294 mmol, 1.0 equiv) and (2-methyl-1-propenyl)-tri-*n*-butylstannane (110 mg, 0.319 mmol, 1.1 equiv) in THF (3.6 mL). The

reaction mixture was stirred at 50 °C for 24 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 1/1 hexanes/CH₂Cl₂ gave 2-(2-methylprop-1-enyl)-3-nitro-pyridine (35.8 mg, 68%) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.78 (d, *J* = 4.1 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.29 (dd, *J* = 8.3, 4.8 Hz, 1H), 6.62 (s, 1H), 2.00 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 152.1, 151.2, 145.8, 132.1, 121.0, 119.5, 27.4, 20.1.

IR (neat, cm⁻¹) 2914, 1648, 1590, 1556, 1451.

HRMS (EI) Calcd for C₉H₁₀N₂O₂: 178.0742. Found 178.0744 [M⁺].

Table 1, Entry 10. 2-(Thiophen-2-yl)quinoline

CuMeSal (143 mg, 0.666 mmol, 2.2 equiv) and Pd(PPh₃)₄ (17.5 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 2-(phenylthio)quinoline (71.4 mg, 0.303 mmol, 1.0 equiv) and 2-(tri-*n*-butylstannyl)-thiophene (125 mg, 0.335 mmol, 1.1 equiv) in THF (3.6 mL). The reaction mixture was stirred at 50 °C for 14 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 3/1 hexanes/CH₂Cl₂ gave 2-(thiophen-2-yl)quinoline (63.4 mg, 99%) as off white crystals.

M.p. 130 °C (petroleum ether) [lit.¹¹ 132–133 °C (petroleum ether)].

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.9 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.74 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.70 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.49 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.47 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.16 (dd, *J* = 5.1, 3.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 152.2, 148.0, 145.3, 136.5, 129.7, 129.1, 128.5, 128.0, 127.4, 127.1, 126.0, 125.8, 117.5.

IR (neat, cm⁻¹) 3013, 2926, 1594, 1556, 1502.

Table 1, Entry 11. 2-(4-Methylphenyl)quinoline

CuMeSal (142 mg, 0.661 mmol, 2.2 equiv) and Pd(PPh₃)₄ (17.3 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 2-(phenylthio)-quinoline (70.3 mg, 0.299 mmol, 1.0 equiv) and

p-tolyl-tri-*n*-butylstannane (126 mg, 0.331 mmol, 1.1 equiv) in THF (3.6 mL). The reaction mixture was stirred at 50 °C for 7 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 2/1 hexanes/CH₂Cl₂ gave 2-(4-methylphenyl)quinoline (65.5 mg, 100%) as a white solid.

M.p. 81–82 °C (petroleum ether) [lit.¹² 81–82 °C (petroleum ether)].

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.6 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 2.44 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 157.3, 148.2, 139.3, 136.8, 136.6, 129.6, 129.5, 127.4, 127.0, 126.0, 118.8, 21.3.

IR (neat, cm⁻¹) 3034, 2918, 1598, 1556, 1498.

Anal. Calcd for C₁₆H₁₃N: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.23; H, 5.94; N, 6.32.

Table 1, Entry 12. 2-(4-Trifluoromethylphenyl)quinoline

CuMeSal (142 mg, 0.661 mmol, 2.2 equiv) and Pd(PPh₃)₄ (17.3 mg, 0.015 mmol, 0.05 equiv) were added to a solution of 2-(phenylthio)quinoline (70.2 mg, 0.298 mmol, 1.0 equiv) and (4-trifluoromethylphenyl)-tri-*n*-butylstannane (144 mg, 0.331 mmol, 1.1 equiv) in THF (3.6 mL). The reaction mixture was stirred at 50 °C for 24 h, 5% aq NH₄OH (10 mL) was added, and the mixture was stirred for an additional 10 min. The reaction mixture was filtered through a plug of Celite, and the filtrate was extracted with Et₂O. The organic layer was washed with brine (5 mL), dried over MgSO₄, and evaporated. Purification by SiO₂ column chromatography with 6/1 hexanes/CH₂Cl₂ gave 2-(4-trifluoromethylphenyl)quinoline (76.8 mg, 94%) as white crystals.

M.p. 124–125 °C (petroleum ether)

¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 8.3 Hz, 2H), 8.23 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.87–7.73 (m, 5H), 7.56 (t, *J* = 7.5 Hz, 1H).

IR (neat, cm⁻¹) 3069, 1594, 1432, 1339, 1123.

FABMS: *m/z*. calcd 274.0844, found 274.0831 [M+H]⁺.

¹ See Supporting Information for Savarin, C; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2001**, 3 (1), 91 - 93.

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