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Supporting Information

Efficient Synthesis of 3,4-Disubstituted 7-Azaindoles Employing SEM as a Dual Protecting-Activating Group

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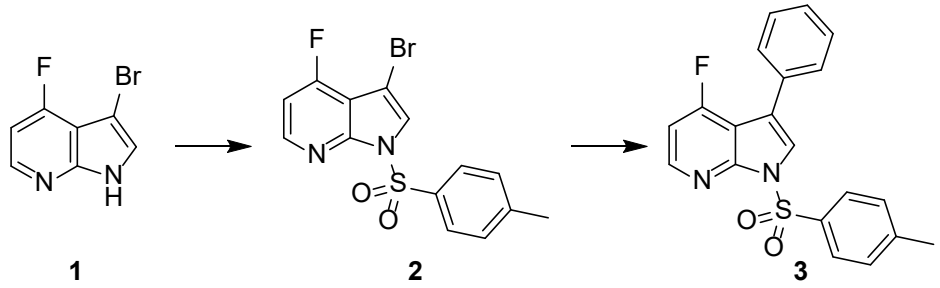
General Methods

All synthetic chemistry was performed in standard laboratory glassware unless indicated otherwise in the examples. Commercial reagents were used as received. ^{1}H NMR was performed on a Bruker Avance 300™ at 300 MHz or a Bruker Avance DRX™ 500 at 500 MHz. ^{13}C NMR was performed on a Bruker Avance 300™ at 75 MHz or a Bruker Avance DRX™ 500 at 125 MHz. For complicated splitting patterns, the apparent splitting is tabulated. High resolution ESI mass spectrometry (HRMS) was performed on an Agilent 6230C TOF LC/MS system detecting ions in positive mode. Analytical thin layer chromatography was performed on silica (Macherey-Nagel ALUGRAM Xtra SIL G, 0.2 mm, UV254 indicator or EMD TLC Silica Gel 60G, F254 indicator) and was visualized under UV light or by staining as indicated. Silica gel chromatography was performed manually, or with an Isco COMBIFLASH™ for gradient elutions. Preparative HPLC was performed using a Wufeng LC-100™ instrument equipped with a Gemini™ 5 µm NX-C18 column, 100 x 30 mm.

Synthesis and Characterization of Intermediates for Nucleophilic Aromatic Substitution

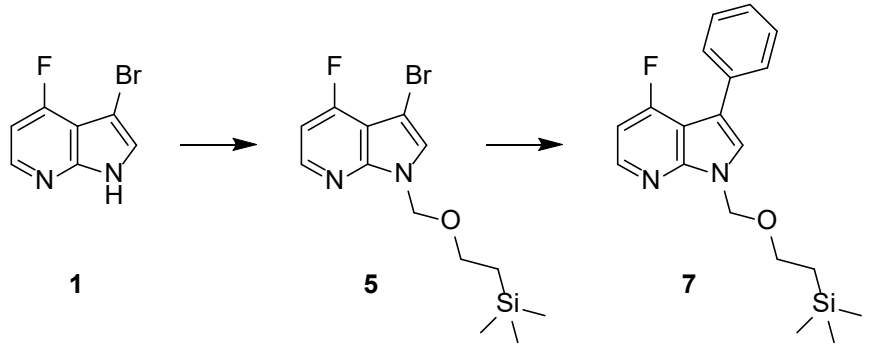


3-Bromo-4-fluoro-1-(*p*-tolylsulfonyl)pyrrolo[2,3-*b*]pyridine (2)

To a suspension of **1** (3.04 g, 14.2 mmol) in dichloromethane (150 mL) was added tetrabutylammonium hydrogen sulfate (100 mg, 0.294 mmol), aqueous sodium hydroxide (6 M, 50 mL, 300 mmol) and *p*-toluenesulfonyl chloride (3.40 g, 17.8 mmol) in portions. The reaction mixture was stirred at room temperature for 2 h. The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated to give the title compound (4.5 g, 12.2 mmol, 87%) as a pale yellow solid. R_f: 0.40 (heptanes:EtOAc, 4:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.51 – 8.40 (m, 1H), 8.23 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.26 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.58 (d, *J* = 161.9 Hz), 148.78 (d, *J* = 7.0 Hz), 148.45 (d, *J* = 8.4 Hz), 146.74, 134.30, 130.68, 128.37, 126.69, 119.90 (d, *J* = 12.0 Hz), 107.51 (d, *J* = 14.6 Hz), 90.20, 21.64. HRMS (ESI): m/z calcd for $C_{14}H_{11}BrFN_2O_2S$ $[M+H]^+$, 368.9709; found 368.9695.

4-Fluoro-3-phenyl-1-(*p*-tolylsulfonyl)pyrrolo[2,3-*b*]pyridine (3)

To a solution of **2** (300 mg, 0.813 mmol) in 1,4-dioxane (6 mL) was added phenylboronic acid (119 mg, 0.975 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (30 mg, 0.041 mmol) and aqueous potassium carbonate (2 M, 1.22 mL, 2.44 mmol). The reaction mixture was stirred at 100 °C for 16 h under argon. The reaction mixture was evaporated andthe residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 88:12) to give the title compound (260 mg, 0.709 mmol, 87%) as a colorless oil. R_f: 0.46 (hexanes:EtOAc, 4:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.48 – 8.41 (m, 1H), 8.11 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.50 – 7.43 (m, 4H), 7.43 – 7.38 (m, 1H), 7.32 – 7.24 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.29 (d, *J* = 265.3 Hz), 149.81 (d, *J* = 10.0 Hz), 147.82 (d, *J* = 7.3 Hz), 146.45, 134.61, 132.14, 130.56, 128.98, 128.92, 128.37, 128.23, 124.35, 118.63, 109.91 (d, *J* = 15.5 Hz), 107.34 (d, *J* = 16.6 Hz), 21.59. HRMS (ESI): m/z calcd for $C_{20}H_{16}FN_2O_2S$ $[M+H]^+$, 367.0917; found 367.0905.



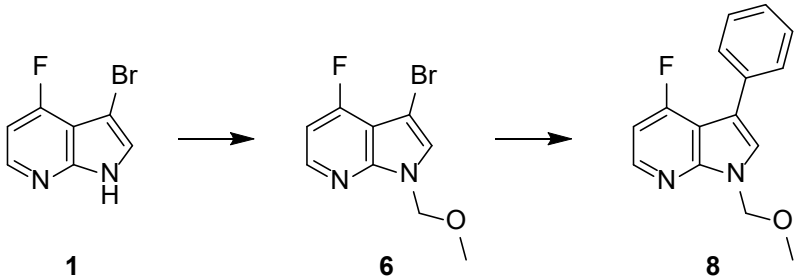
2-[(3-Bromo-4-fluoropyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (5)

To a mixture of sodium hydride (60% dispersion in mineral oil, 960 mg, 24.0 mmol) in dry *N*,*N*-dimethylformamide (20 mL) was added a solution of **1** (4.0 g, 18.6 mmol) in dry *N*,*N*-dimethylformamide (22 mL) dropwise at 10 °C. The mixture was stirred at 10 °C for 10 min. To the reaction mixture was added a solution of (2-chloromethoxyethyl)trimethylsilane (3.62 mL, 20.5 mmol) in dry *N*,*N*-dimethylformamide (5 mL) dropwise while maintaining the temperature between 5-10 °C. The reaction mixture was stirred at 5 °C for 2 h. The reaction mixture was poured into cold water (300 mL) and extracted with dichloromethane (2 x 150 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated. The residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 92:8) to give the title compound (4.89 g, 14.2 mmol, 76%) as a white solid. R_f: 0.29 (hexanes:EtOAc, 9:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.47 – 8.29 (m, 1H), 7.95 (s, 1H), 7.19 – 7.06 (m, 1H), 5.62 (s, 2H), 3.53 (t, *J* = 5.2 Hz, 2H), 0.82 (t, *J* = 5.3 Hz, 2H), -0.10 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.63 (d, *J* = 263.5 Hz), 150.30 (d, *J* = 9.7 Hz), 146.66 (d, *J* = 6.8 Hz), 129.64, 108.19 (d, *J* = 14.3 Hz), 104.32 (d, *J* = 14.7 Hz), 83.99, 73.26, 66.23, 17.56, -0.97. HRMS (ESI): m/z calcd for $C_{13}H_{19}BrFN_2OSi$ $[M+H]^+$, 345.0434; found 345.0423.

2-[(4-Fluoro-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (7)

To a solution of **5** (3.50 g, 10.1 mmol) in 1,4-dioxane (300 mL) was added phenylboronic acid (1.85 g, 15.2 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (370 mg, 0.506 mmol) and

aqueous potassium carbonate (2 M, 15 mL, 30 mmol). The reaction mixture was stirred at 100 °C for 16 h under argon and then evaporated. The residue was taken up in dichloromethane (200 mL) and the mixture was washed with water (1 x 100 mL). The organic layer was dried over sodium sulfate, filtered and evaporated. The residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 90:10) to give the title compound (1.82 g, 5.31 mmol, 53%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.40 – 8.31 (m, 1H), 7.96 (s, 1H), 7.69 – 7.57 (m, 2H), 7.50 – 7.40 (m, 2H), 7.36 – 7.28 (m, 1H), 7.17 – 7.06 (m, 1H), 5.70 (s, 2H), 3.59 (t, *J* = 8.0 Hz, 2H), 0.85 (t, *J* = 8.0 Hz, 2H), -0.09 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.29 (d, *J* = 262.0 Hz), 151.89 (d, *J* = 11.5 Hz), 145.73 (d, *J* = 7.1 Hz), 134.05, 128.98, 128.32 (d, *J* = 4.1 Hz), 127.96, 126.97, 114.43 (d, *J* = 2.8 Hz), 106.91 (d, *J* = 15.3 Hz), 104.18 (d, *J* = 17.0 Hz), 73.33, 66.19, 17.62, -0.94. HRMS (ESI): m/z calcd for $C_{19}H_{24}FN_2OSi$ $[M+H]^+$, 343.1642; found 343.1635.



1 **6** **8**

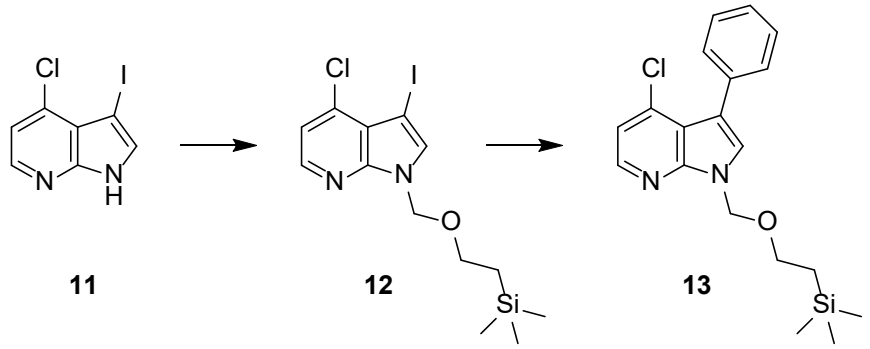
3-Bromo-4-fluoro-1-(methoxymethyl)pyrrolo[2,3-*b*]pyridine (6)

To a solution of **1** (1.0 g, 4.67 mmol) in dry *N*,*N*-dimethylformamide (50 mL) was added cesium carbonate (3.08 g, 9.45 mmol) followed by methoxymethyl chloride (530 μL, 7.00 mmol) dropwise at 0 °C over 5 min. The reaction mixture was allowed to warm to room temperature and stirred at room temperature for 2 h. The reaction mixture was evaporated. The residue was taken up in water (20 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated. The residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 25:75) to give the title compound (893 mg, 3.46 mmol, 74%) as an orange solid. R_f: 0.60 (hexanes:EtOAc, 4:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.41 – 8.31 (m, 1H), 7.97 (s, 1H), 7.19 – 7.08 (m, 1H), 5.59 (s, 2H), 3.23 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.66 (d, *J* = 263.3 Hz), 150.31 (d, *J* = 9.8 Hz), 146.75 (d, *J* = 6.7 Hz), 129.65, 108.26 (d, *J* = 14.1 Hz), 104.42 (d, *J* = 14.8 Hz), 84.13, 75.20, 56.66. HRMS (ESI): m/z calcd for $C_9H_9BrFN_2O$ $[M+H]^+$, 258.9882; found 258.9873.

4-Fluoro-1-(methoxymethyl)-3-phenylpyrrolo[2,3-*b*]pyridine (8)

Prepared by the same general method used for compound **7** starting from intermediate **6** (120 mg, 0.465 mmol) to afford the title compound (85 mg, 0.332 mmol, 72%) as a white solid. R_f: 0.21 (heptanes:EtOAc, 4:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.43 – 8.15 (m, 1H), 7.99 – 7.89 (m, 1H), 7.75 – 7.56 (m, 2H), 7.54 – 7.38 (m, 2H), 7.39 – 7.27 (m, 1H), 7.19 – 7.07 (m, 1H), 5.67 (s, 2H), 3.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.33 (d, *J* = 261.9 Hz), 151.89 (d, *J* = 11.6 Hz), 145.82 (d, *J* = 6.9 Hz), 134.00, 128.97, 128.36 (d, *J* = 4.2 Hz), 127.96, 127.00, 114.50 (d, *J* = 2.6 Hz), 106.99 (d, *J* = 15.3 Hz),

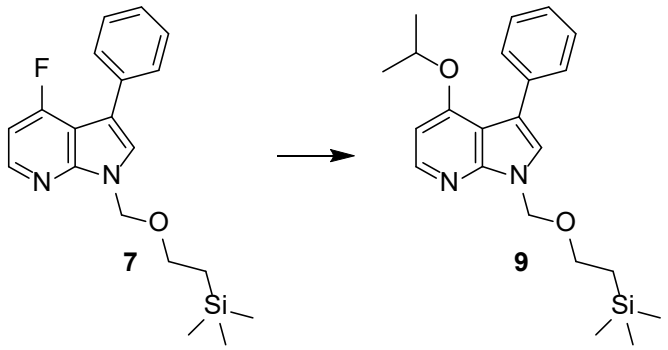
104.28 (d, *J* = 16.8 Hz), 75.30, 56.70. HRMS (ESI): m/z calcd for $C_{15}H_{14}FN_2O$ $[M+H]^+$, 257.1090; found 257.1084.



2-[(4-Chloro-3-iodopyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (12)
Prepared by the same general method used for compound **5** starting from intermediate **11** (1.0 g, 3.60 mmol) to afford the title compound (1.18 g, 2.88 mmol, 80%) as a colorless oil. R_f: 0.44 (heptanes:EtOAc, 9:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.23 (d, *J* = 5.1 Hz, 1H), 7.99 (s, 1H), 7.26 (d, *J* = 5.1 Hz, 1H), 5.57 (s, 2H), 3.48 (t, *J* = 8.0 Hz, 2H), 0.78 (t, *J* = 8.0 Hz, 2H), -0.13 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.16, 144.48, 136.39, 135.84, 118.34, 117.33, 73.16, 66.22, 51.33, 17.57, -0.94. HRMS (ESI): m/z calcd for $C_{13}H_{19}ClIN_2OSi$ $[M+H]^+$, 409.0000; found 408.9986.

2-[(4-Chloro-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (13)
Prepared by the same general method used for compound **7** starting from intermediate **12** (750 mg, 1.84 mmol) to afford the title compound (444 mg, 1.24 mmol, 67%) as an off-white solid. R_f: 0.36 (heptanes:EtOAc, 9:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28 (d, *J* = 5.1 Hz, 1H), 7.83 (s, 1H), 7.52 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.31 (m, 1H), 7.28 (d, *J* = 5.1 Hz, 1H), 5.69 (s, 2H), 3.58 (t, *J* = 8.0 Hz, 2H), 0.84 (t, *J* = 8.0 Hz, 2H), -0.09 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.11, 143.96, 135.30, 134.04, 130.64, 129.67, 128.15, 127.19, 118.14, 116.24, 116.04, 73.19, 66.16, 17.58, -0.99. HRMS (ESI): m/z calcd for $C_{19}H_{24}ClN_2OSi$ $[M+H]^+$, 359.1346; found 359.1331.

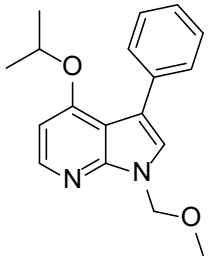
General Procedure for Nucleophilic Aromatic Substitution



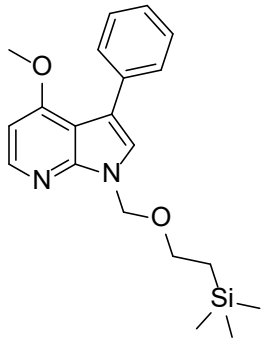
2-[(4-Isopropoxy-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (9)

To a mixture of isopropanol (300 μL, 3.94 mmol) in dry dimethyl sulfoxide (3 mL) was added sodium hydride (60% dispersion in mineral oil, 157 mg, 3.92 mmol) in small portions. The reaction mixture was stirred at room temperature for 15 min. To the reaction mixture was added a solution of intermediate **7** (150 mg, 0.438 mmol) in dry dimethyl sulfoxide (3 mL) at room temperature. The reaction mixture was stirred at room temperature for 15 min, poured into water (60 mL) and extracted with a mixture of chloroform and 2-propanol (3:1, 3 x 15 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated to give the title compound (165 mg, 0.431 mmol, 98%) as a pale yellow oil. Rf: 0.11 (hexanes:EtOAc, 9:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.17 (d, J = 5.5 Hz, 1H), 7.69 – 7.56 (m, 3H), 7.41 – 7.32 (m, 2H), 7.31 – 7.19 (m, 1H), 6.78 (d, J = 5.5 Hz, 1H), 5.63 (s, 2H), 4.91 – 4.79 (m, 1H), 3.57 (t, J = 8.1 Hz, 2H), 1.30 (d, J = 6.0 Hz, 6H), 0.85 (t, J = 8.0 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.80, 150.72, 145.46, 135.21, 129.52, 128.01, 126.30, 125.64, 116.38, 108.39, 100.83, 72.94, 70.48, 65.89, 22.04, 17.65, -0.90. HRMS (ESI): m/z calcd for $C_{22}H_{31}N_2O_2Si$ $[M+H]^+$, 383.2155; found 383.2138.

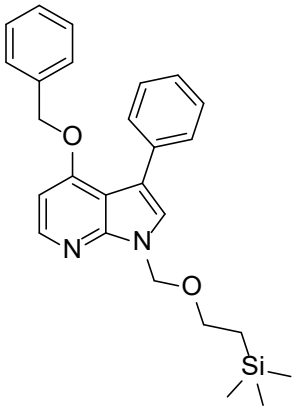
Synthesis and Characterization of Nucleophilic Aromatic Substitution Products



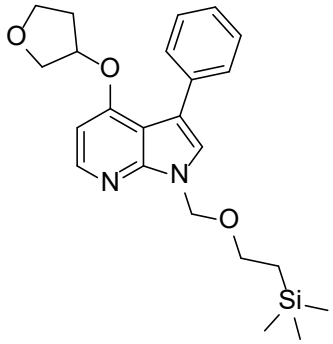
4-Isopropoxy-1-(methoxymethyl)-3-phenylpyrrolo[2,3-*b*]pyridine (10)
Prepared by the same general method as compound **9** starting from intermediate **8** (50 mg, 0.195 mmol). The crude product was purified by gradient silica gel chromatography eluting with heptanes:ethyl acetate (100:0 to 25:75) to afford the title compound (38 mg, 0.094 mmol, 48%) as a colorless oil. R_f: 0.51 (heptanes:EtOAc, 1:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.18 (d, J = 5.5 Hz, 1H), 7.68 – 7.57 (m, 3H), 7.42 – 7.33 (m, 2H), 7.30 – 7.21 (m, 1H), 6.80 (d, J = 5.5 Hz, 1H), 5.60 (s, 2H), 4.92 – 4.80 (m, 1H), 3.26 (s, 3H), 1.30 (d, J = 6.0 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.85, 150.72, 145.55, 135.15, 129.56, 128.01, 126.33, 125.68, 116.44, 108.45, 100.89, 74.93, 70.51, 56.48, 22.05. HRMS (ESI): m/z calcd for $C_{18}H_{21}N_2O_2$ [M+H]$^+$, 297.1603; found 297.1598.



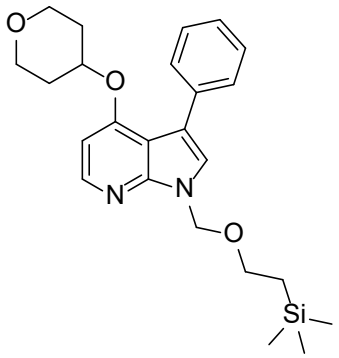
2-[(4-Methoxy-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (14a)
Prepared by the same general method as compound **9** starting from intermediate **7** (140 mg, 0.409 mmol). The crude product was purified by gradient silica gel chromatography eluting with heptanes:ethyl acetate (100:0 to 90:10) to afford the title compound (124 mg, 0.350 mmol, 86%) as a colorless oil. R_f: 0.24 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.21 (d, J = 5.5 Hz, 1H), 7.66 – 7.53 (m, 3H), 7.45 – 7.31 (m, 2H), 7.31 – 7.20 (m, 1H), 6.80 (d, J = 5.6 Hz, 1H), 5.63 (s, 2H), 3.89 (s, 3H), 3.56 (t, J = 8.0 Hz, 2H), 0.84 (t, J = 8.0 Hz, 2H), -0.09 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.71, 150.39, 145.66, 135.38, 129.21, 128.34, 126.34, 125.84, 116.24, 107.82, 99.67, 73.02, 65.94, 55.91, 17.68, -0.88. HRMS (ESI): m/z calcd for $C_{20}H_{27}N_2O_2Si$ [M+H]$^+$, 355.1842; found 355.1832.



2-[(4-Benzyloxy-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (14b)
Prepared by the same general method as compound **9** starting from intermediate **7** (140 mg, 0.409 mmol). The crude product was purified by preparative HPLC to afford the title compound (130 mg, 0.302 mmol, 74%) as a colorless oil. R_f: 0.18 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.22 (d, J = 5.5 Hz, 1H), 7.64 (s, 1H), 7.62 – 7.55 (m, 2H), 7.42 – 7.31 (m, 5H), 7.29 – 7.14 (m, 3H), 6.91 (d, J = 5.6 Hz, 1H), 5.64 (s, 2H), 5.27 (s, 2H), 3.57 (t, J = 7.9 Hz, 2H), 0.84 (t, J = 7.9 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.74, 150.53, 145.56, 136.55, 135.19, 129.45, 128.74, 128.38, 128.29, 128.19, 126.30, 125.91, 116.30, 108.07, 100.69, 73.03, 70.21, 65.96, 17.68, -0.87. HRMS (ESI): m/z calcd for $C_{26}H_{31}N_2O_2Si$ $[M+H]^+$, 431.2155; found 431.2142.

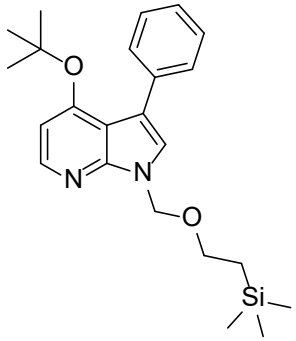


Trimethyl-[2-[(3-phenyl-4-tetrahydrofuran-3-yloxypyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyl]silane (14c)
Prepared by the same general method as compound **9** starting from intermediate **7** (180 mg, 0.526 mmol). The crude product was purified by gradient silica gel chromatography eluting with heptanes:ethyl acetate (100:0 to 80:20) to afford the title compound (155 mg, 0.378 mmol, 72%) as a colorless oil. R_f: 0.38 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, J = 5.5 Hz, 1H), 7.68 – 7.51 (m, 3H), 7.42 – 7.33 (m, 2H), 7.29 – 7.20 (m, 1H), 6.74 (d, J = 5.6 Hz, 1H), 5.63 (s, 2H), 5.34 – 5.21 (m, 1H), 3.93 (dd, J = 10.2, 4.6 Hz, 1H), 3.80 – 3.70 (m, 3H), 3.56 (t, J = 7.9 Hz, 2H), 2.34 – 2.17 (m, 1H), 2.02 – 1.88 (m, 1H), 0.84 (t, J = 7.9 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.45, 150.63, 145.43, 135.15, 129.49, 128.08, 126.43, 125.83, 116.31, 108.26, 100.98, 78.24, 73.01, 72.54, 66.94, 65.96, 32.92, 17.68, -0.88. HRMS (ESI): m/z calcd for $C_{23}H_{31}N_2O_3Si$ $[M+H]^+$, 411.2104; found 411.2110.



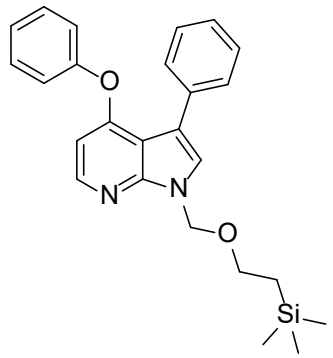
Trimethyl-[2-[(3-phenyl-4-tetrahydropyran-4-yloxypyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyl]silane (14d)

Prepared by the same general method as compound **9** starting from intermediate **7** (140 mg, 0.409 mmol). The crude product was purified by gradient silica gel chromatography eluting with heptanes:ethyl acetate (100:0 to 80:20) to afford the title compound (125 mg, 0.295 mmol, 72%) as a colorless oil. R_f: 0.38 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.17 (d, J = 5.5 Hz, 1H), 7.67 – 7.52 (m, 3H), 7.44 – 7.34 (m, 2H), 7.31 – 7.21 (m, 1H), 6.85 (d, J = 5.6 Hz, 1H), 5.62 (s, 2H), 4.92 – 4.79 (m, 1H), 3.69 – 3.60 (m, 1H), 3.63 – 3.50 (m, 4H), 3.52 – 3.40 (m, 1H), 2.06 – 1.90 (m, 2H), 1.69 – 1.49 (m, 2H), 0.84 (t, J = 8.0 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.40, 150.74, 145.47, 135.35, 129.60, 128.13, 126.43, 125.78, 116.36, 108.60, 101.01, 72.98, 71.90, 65.94, 64.46, 31.63, 17.69, -0.87. HRMS (ESI): m/z calcd for $C_{24}H_{33}N_2O_3Si$ $[M+H]^+$, 425.2260; found 425.2262.

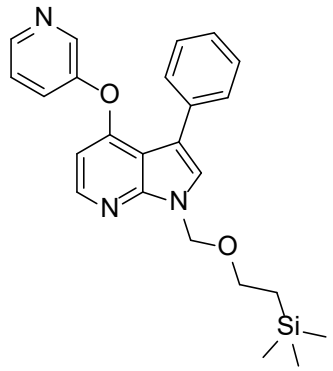


2-[(4-*tert*-Butoxy-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (14e)

Prepared by the same general method as compound **9** starting from intermediate **7** (120 mg, 0.350 mmol). The crude product was purified by preparative HPLC to afford the formate salt of the title compound (75 mg, 0.170 mmol, 48%) as a colorless oil. R_f: 0.44 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.42 (s, 1H), 8.15 (d, J = 5.7 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.43 – 7.32 (m, 2H), 7.31 – 7.19 (m, 1H), 6.97 – 6.79 (m, 1H), 5.62 (s, 2H), 3.56 (t, J = 7.9 Hz, 2H), 1.29 (s, 9H), 0.82 (t, J = 8.0 Hz, 2H), -0.06 – -0.17 (m, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.85, 157.55, 150.92, 144.77, 135.35, 129.89, 128.07, 126.36, 126.15, 116.56, 111.57, 107.37, 80.79, 72.97, 65.94, 28.69, 17.68, -0.90. HRMS (ESI): m/z calcd for $C_{23}H_{33}N_2O_2Si$ $[M+H]^+$, 397.2311; found 397.2312.

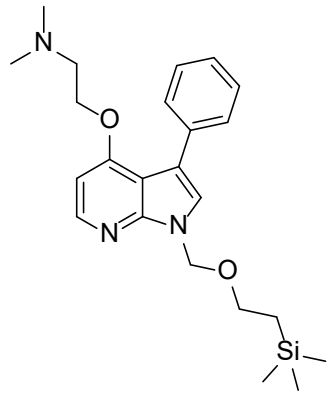


Trimethyl-[2-[(4-phenoxy-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyl]silane (14f)
Prepared by the same general method as compound **9** starting from intermediate **7** (120 mg, 0.350 mmol), with the reaction mixture heated to 80 °C for 4 h. The crude product was purified by gradient silica gel chromatography eluting with heptanes:ethyl acetate (100:0 to 90:10) to give the title compound (58 mg, 0.139 mmol, 48%) as a colorless oil. R_f: 0.29 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, *J* = 5.4 Hz, 1H), 7.78 (s, 1H), 7.70 – 7.61 (m, 2H), 7.50 – 7.41 (m, 2H), 7.40 – 7.30 (m, 2H), 7.29 – 7.20 (m, 2H), 7.21 – 7.09 (m, 2H), 6.41 (d, *J* = 5.5 Hz, 1H), 5.68 (s, 2H), 3.60 (t, *J* = 8.0 Hz, 2H), 0.87 (t, *J* = 7.9 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.82, 154.69, 145.34, 130.76, 129.20, 128.45, 127.13, 126.56, 125.50, 120.81, 115.97, 109.66, 109.00, 103.86, 100.92, 73.17, 66.10, 17.70, -0.86. HRMS (ESI): m/z calcd for $C_{25}H_{29}N_2O_2Si$ $[M+H]^+$, 417.1998; found 417.1999.



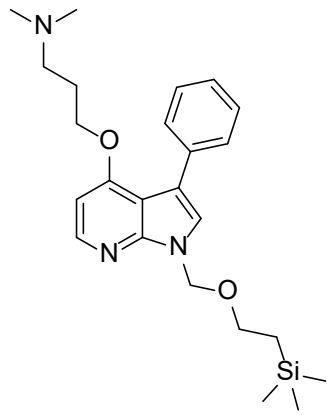
Trimethyl-[2-[[3-phenyl-4-(3-pyridyloxy)pyrrolo[2,3-*b*]pyridin-1-yl]methoxy]ethyl]silane (14g)
Prepared by the same general method as compound **9** starting from intermediate **7** (120 mg, 0.350 mmol), with the reaction mixture heated to 50 °C for 16 h. The crude product was purified by preparative HPLC to give the title compound (30 mg, 0.072 mmol, 21%) as a colorless oil. R_f: 0.30 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.47 – 8.41 (m, 2H), 8.23 (d, *J* = 5.4 Hz, 1H), 7.81 (s, 1H), 7.65 – 7.54 (m, 3H), 7.44 (dd, *J* = 8.4, 4.7 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.28 – 7.17 (m, 1H), 6.52 (d, *J* = 5.4 Hz, 1H), 5.70 (s, 2H), 3.61 (t, *J* = 8.0 Hz, 2H), 0.87 (t, *J* = 8.0 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.60, 151.68, 146.33, 145.45, 142.45, 134.79, 129.20, 128.49, 127.82, 127.47, 126.68,

125.31, 123.68, 115.84, 109.19, 104.44, 73.20, 66.15, 17.69, -0.87. HRMS (ESI): m/z calcd for $C_{24}H_{28}N_3O_2Si$ $[M+H]^+$, 418.1951; found 418.1956.



***N,N*-Dimethyl-2-[3-phenyl-1-(2-trimethylsilylethoxymethyl)pyrrolo[2,3-*b*]pyridin-4-yl]oxyethanamine (14h)**

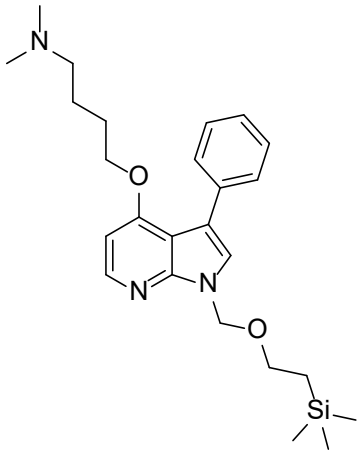
Prepared by the same general method as compound **9** starting from intermediate **7** (140 mg, 0.409 mmol). The crude product was purified by gradient silica gel chromatography eluting with chloroform:methanol (100:0 to 95:5) to give the title compound (102 mg, 0.247 mmol, 61%) as a colorless oil. R_f: 0.34 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, J = 5.5 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.63 (s, 1H), 7.41 – 7.31 (m, 2H), 7.30 – 7.21 (m, 1H), 6.80 (d, J = 5.6 Hz, 1H), 5.63 (s, 2H), 4.22 (t, J = 5.6 Hz, 2H), 3.56 (t, J = 8.0 Hz, 2H), 2.61 (t, J = 5.6 Hz, 2H), 2.13 (s, 6H), 0.84 (t, J = 7.9 Hz, 2H), -0.09 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 159.88, 150.48, 145.58, 135.22, 129.48, 128.19, 126.30, 125.72, 116.37, 115.28, 100.19, 73.00, 66.74, 65.93, 57.84, 45.90, 17.68, -0.87. HRMS (ESI): m/z calcd for $C_{23}H_{34}N_3O_2Si$ $[M+H]^+$, 412.2420; found 412.2416.



***N,N*-Dimethyl-3-[3-phenyl-1-(2-trimethylsilylethoxymethyl)pyrrolo[2,3-*b*]pyridin-4-yl]oxypropan-1-amine (14i)**

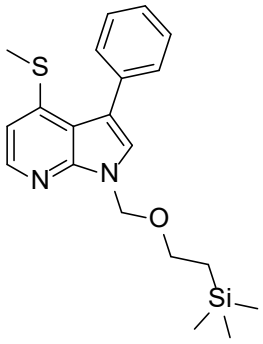
Prepared by the same general method as compound **9** starting from intermediate **7** (120 mg, 0.350 mmol). The crude product was purified by gradient silica gel chromatography eluting with chloroform:methanol (100:0 to 95:5) to give the title compound (83 mg, 0.195 mmol, 56%) as a colorless

oil. R_f: 0.22 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.17 (d, *J* = 5.5 Hz, 1H), 7.65 – 7.54 (m, 3H), 7.41 – 7.32 (m, 2H), 7.30 – 7.21 (m, 1H), 6.76 (d, *J* = 5.6 Hz, 1H), 5.63 (s, 2H), 4.15 (t, *J* = 6.0 Hz, 2H), 3.56 (t, *J* = 7.9 Hz, 2H), 2.21 (t, *J* = 7.1 Hz, 2H), 2.07 (s, 6H), 1.87 – 1.75 (m, 2H), 0.84 (t, *J* = 7.9 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.09, 150.43, 145.62, 135.35, 129.42, 128.17, 126.36, 125.65, 116.34, 107.94, 100.11, 72.99, 66.73, 65.92, 56.05, 45.56, 27.02, 17.68, -0.87. HRMS (ESI): m/z calcd for $C_{24}H_{36}N_3O_2Si$ $[M+H]^+$, 426.2577; found 426.2582.

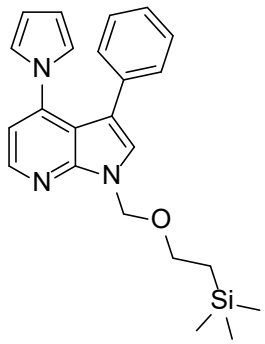


***N,N*-Dimethyl-4-[3-phenyl-1-(2-trimethylsilylethoxymethyl)pyrrolo[2,3-*b*]pyridin-4-yl]oxybutan-1-amine (14j)**

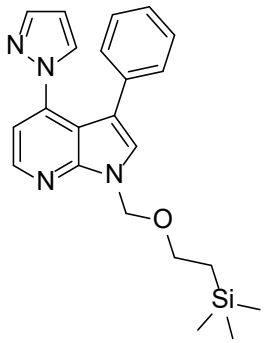
Prepared by the same general method as compound **9** starting from intermediate **7** (120 mg, 0.350 mmol). The crude product was purified by gradient silica gel chromatography eluting with chloroform:methanol (100:0 to 95:5) to give the title compound (70 mg, 0.159 mmol, 45%) as a colorless oil. R_f: 0.24 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.18 (d, *J* = 5.4 Hz, 1H), 7.66 – 7.52 (m, 3H), 7.40 – 7.31 (m, 2H), 7.30 – 7.20 (m, 1H), 6.76 (d, *J* = 5.6 Hz, 1H), 5.63 (s, 2H), 4.14 (t, *J* = 6.1 Hz, 2H), 3.56 (t, *J* = 8.0 Hz, 2H), 2.15 (t, *J* = 7.3 Hz, 2H), 2.05 (s, 6H), 1.75 – 1.61 (m, 2H), 1.48 – 1.36 (m, 2H), 0.84 (t, *J* = 8.0 Hz, 2H), -0.09 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 160.10, 150.45, 145.62, 135.29, 129.38, 128.12, 126.35, 125.65, 116.36, 107.91, 100.12, 72.98, 68.37, 65.92, 59.14, 45.60, 26.84, 24.08, 17.68, -0.87. HRMS (ESI): m/z calcd for $C_{25}H_{38}N_3O_2Si$ $[M+H]^+$, 440.2733; found 440.2719.



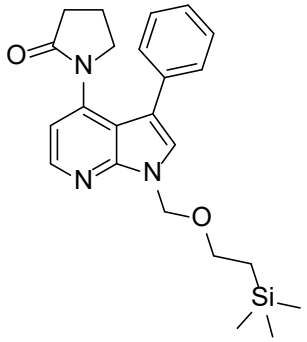
Trimethyl-[2-[(4-methylsulfanyl-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyl]silane (14k)
To a solution of intermediate **7** (300 mg, 0.876 mmol) in dry dimethyl sulfoxide (7 mL) was added sodium methanethiolate (307 mg, 4.38 mmol) and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water (70 mL) and extracted with a mixture of chloroform and 2-propanol (3:1, 2 x 20 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated. The residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 90:10) to give the title compound (286 mg, 0.772 mmol, 88%) as a colorless oil. R_f: 0.20 (hexanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.20 (d, J = 5.1 Hz, 1H), 7.58 (s, 1H), 7.48 – 7.28 (m, 5H), 6.98 (d, J = 5.3 Hz, 1H), 5.65 (s, 2H), 3.56 (t, J = 7.9 Hz, 2H), 2.44 (s, 3H), 0.84 (t, J = 7.9 Hz, 2H), -0.05 – -0.13 (m, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.05, 143.53, 143.29, 135.24, 130.76, 128.07, 127.48, 127.28, 117.06, 115.66, 111.59, 72.97, 66.01, 17.68, 14.03, -0.87. HRMS (ESI): m/z calcd for $C_{20}H_{27}N_2OSSi$ $[M+H]^+$, 371.1613; found 371.1605.



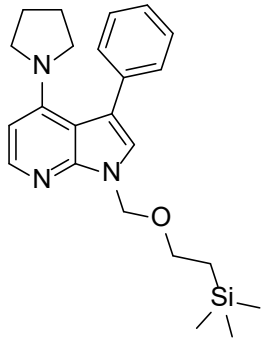
Trimethyl-[2-[(3-phenyl-4-pyrrol-1-ylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyl]silane (14l)
Prepared by the same general method as compound **9** starting from intermediate **7** (300 mg, 0.876 mmol) to give the title compound (338 mg, 0.867 mmol, 99%) as a yellow solid. R_f: 0.30 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.39 (d, J = 5.1 Hz, 1H), 7.88 (s, 1H), 7.20 (d, J = 5.1 Hz, 1H), 7.16 – 7.04 (m, 3H), 7.00 – 6.92 (m, 2H), 6.78 – 6.69 (m, 2H), 6.08 – 5.91 (m, 2H), 5.73 (s, 2H), 3.62 (t, J = 7.9 Hz, 2H), 0.86 (t, J = 8.0 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.52, 144.30, 141.52, 134.70, 129.21, 128.32, 127.96, 126.47, 122.37, 115.72, 113.24, 111.60, 110.00, 73.22, 66.23, 17.70, -0.89. HRMS (ESI): m/z calcd for $C_{23}H_{28}N_3OSi$ $[M+H]^+$, 390.2002; found 390.1996.



Trimethyl-[2-[(3-phenyl-4-pyrazol-1-ylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyl]silane (14m)
Prepared by the same general method as compound **9** starting from intermediate **7** (150 mg, 0.435 mmol) to give the title compound (97 mg, 0.248 mmol, 57%) as a white solid. R_f: 0.46 (heptanes:EtOAc, 4:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.45 (d, *J* = 5.1 Hz, 1H), 7.92 (s, 1H), 7.61 – 7.48 (m, 2H), 7.34 (d, *J* = 5.2 Hz, 1H), 7.25 – 7.07 (m, 3H), 6.98 – 6.88 (m, 2H), 6.27 – 6.15 (m, 1H), 5.75 (s, 2H), 3.63 (t, *J* = 8.0 Hz, 2H), 0.87 (t, *J* = 8.0 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.51, 144.16, 141.51, 140.83, 134.68, 132.60, 129.66, 128.35, 128.13, 126.55, 115.65, 113.20, 111.39, 107.22, 73.25, 66.26, 17.70, -0.87. HRMS (ESI): m/z calcd for $C_{22}H_{27}N_4OSi$ $[M+H]^+$, 391.1954; found 391.1946.

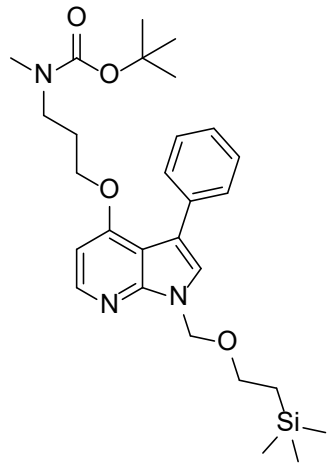


1-[3-Phenyl-1-(2-trimethylsilylethoxymethyl)pyrrolo[2,3-*b*]pyridin-4-yl]pyrrolidin-2-one (14n)
Prepared by the same general method as compound **9** starting from intermediate **7** (120 mg, 0.350 mmol) to give the title compound (136 mg, 0.333 mmol, 95%) as an off-white solid. R_f: 0.28 (heptanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.35 (d, *J* = 5.1 Hz, 1H), 7.77 (s, 1H), 7.47 – 7.38 (m, 2H), 7.37 – 7.27 (m, 3H), 7.10 (d, *J* = 5.1 Hz, 1H), 5.69 (s, 2H), 3.61 (t, *J* = 8.0 Hz, 2H), 3.50 (t, *J* = 6.9 Hz, 2H), 2.09 (t, *J* = 8.0 Hz, 2H), 1.88 – 1.65 (m, 2H), 0.86 (t, *J* = 8.0 Hz, 2H), -0.07 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 173.85, 150.15, 144.09, 140.09, 135.21, 128.70, 128.47, 128.32, 126.87, 116.28, 114.68, 114.38, 73.08, 66.20, 50.35, 30.94, 18.42, 17.72, -0.87. HRMS (ESI): m/z calcd for $C_{23}H_{30}N_3O_2Si$ $[M+H]^+$, 408.2107; found 408.2114.



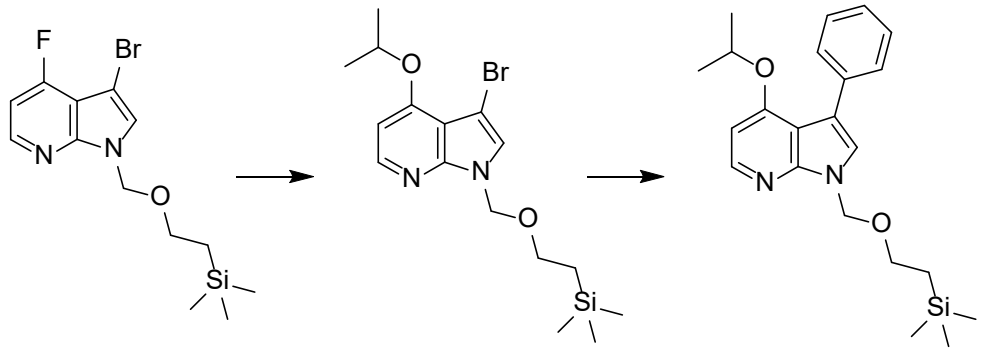
Trimethyl-[2-[(3-phenyl-4-pyrrolidin-1-ylpyrrolo[2,3-b]pyridin-1-yl)methoxy]ethyl]silane (14o)
A solution of intermediate **7** (150 mg, 0.437 mmol) in neat pyrrolidine (740 µL, 8.87 mmol) was stirred at 80 °C for 16 h. The reaction mixture was evaporated and the residue was taken up in water (15 mL). The

mixture was extracted with dichloromethane (2 x 15 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated. The residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 90:10) to give the title compound (139 mg, 0.353 mmol, 80%) as a colorless oil. R_f: 0.29 (hexanes:EtOAc, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.00 (d, *J* = 5.5 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.42 – 7.34 (m, 3H), 7.31 – 7.22 (m, 1H), 6.50 (d, *J* = 5.6 Hz, 1H), 5.60 (s, 2H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.00 – 2.83 (m, 4H), 1.67 – 1.50 (m, 4H), 0.83 (t, *J* = 8.0 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 151.09, 150.35, 144.21, 137.39, 128.65, 128.55, 126.44, 125.23, 117.12, 108.27, 102.90, 72.88, 65.86, 51.35, 24.63, 17.72, -0.87. HRMS (ESI): m/z calcd for $C_{23}H_{32}N_3OSi$ $[M+H]^+$, 394.2315; found 394.2310.



tert-Butyl _N_-methyl-_N_-[3-[3-phenyl-1-(2-trimethylsilylethoxymethyl)pyrrolo[2,3-_b_]pyridin-4-yl]oxypropyl]carbamate (16)

To a solution of *tert*-butyl *N*-(3-hydroxypropyl)-*N*-methylcarbamate (535 mg, 2.83 mmol) in dry dimethyl sulfoxide (4.0 mL) was added sodium hydride (60% dispersion in mineral oil, 119 mg, 2.97 mmol) in small portions and the mixture was stirred at room temperature for 30 min. To the mixture was added a solution of intermediate **7** (484 mg, 1.41 mmol) in dry dimethyl sulfoxide (6 mL) at room temperature. The reaction mixture was stirred at room temperature for 30 min, poured into water (100 mL) and extracted with a mixture of chloroform and isopropanol (3:1, 3 x 80 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated to give the title compound (628 mg, 1.23 mmol, 86%) as a colorless oil. R_f: 0.38 (heptanes:EtOAc, 2:1). ^{1}H NMR (300 MHz, Chloroform-d) δ 8.25 (d, J = 5.6 Hz, 1H), 7.74 – 7.56 (m, 2H), 7.43 – 7.33 (m, 2H), 7.33 – 7.16 (m, 2H), 6.58 (d, J = 5.6 Hz, 1H), 5.71 (s, 2H), 4.17 – 4.06 (m, 2H), 3.60 (t, J = 8.2 Hz, 2H), 3.23 – 3.10 (m, 2H), 2.69 (s, 3H), 2.03 – 1.90 (m, 2H), 1.39 (s, 9H), 0.95 (t, J = 8.2 Hz, 2H), -0.04 (s, 9H). ^{13}C NMR (75 MHz, Chloroform-d) δ 160.12, 155.81, 150.36, 145.35, 135.31, 129.50, 127.67, 126.23, 123.99, 117.31, 108.53, 99.15, 79.39, 77.25, 73.16, 66.24, 45.75, 34.69, 28.43, 17.83, 1.05, -1.40. HRMS (ESI): m/z calcd for $C_{28}H_{42}N_3O_4Si$ $[M+H]^+$, 512.2945; found 512.2936.



5 **17** **9**

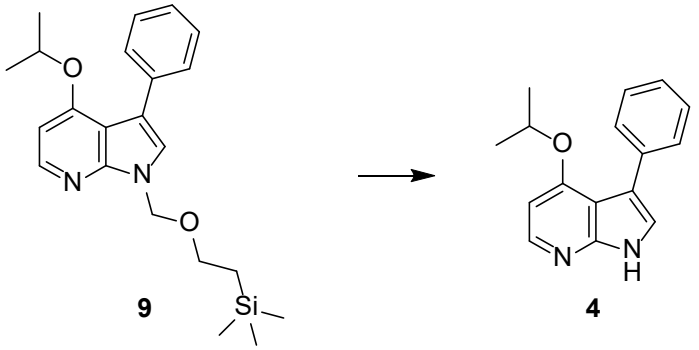
2-[(3-Bromo-4-isopropoxypyrrolo[2,3-b]pyridin-1-yl)methoxy]ethyltrimethylsilane (17)

To a mixture of isopropanol (90 μL, 1.16 mmol) in dry dimethylsulfoxide (3 mL) was added sodium hydride (60% dispersion in mineral oil, 49 mg, 1.22 mmol) in small portions and the mixture was stirred at room temperature for 15 min. To the mixture was added a solution of **5** (200 mg, 0.581 mmol) in dry dimethylsulfoxide (3 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h, poured into water (30 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over sodium sulfate, filtered and evaporated. The residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 90:10) to give the title compound (176 mg, 0.458 mmol, 79%) as an off-white crystalline solid. R_f: 0.41 (hexanes:EtOAc, 4:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (d, J = 5.6 Hz, 1H), 7.63 (s, 1H), 6.77 (d, J = 5.6 Hz, 1H), 5.54 (s, 2H), 4.92 – 4.76 (m, 1H), 3.56 – 3.41 (m, 2H), 1.36 (d, J = 6.0 Hz, 6H), 0.88 – 0.75 (m, 2H), -0.09 (s, 9H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.50, 149.07, 146.44, 126.93, 108.92, 101.15, 86.20, 72.82, 70.91, 65.95, 22.18, 17.62, -0.90. HRMS (ESI): m/z calcd for C16H26BrN2O2Si $[M+H]^+$, 385.0947; found 385.0946.

2-[(4-Isopropoxy-3-phenylpyrrolo[2,3-*b*]pyridin-1-yl)methoxy]ethyltrimethylsilane (9)

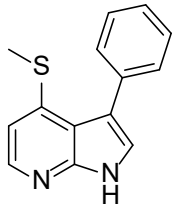
To a solution of **17** (100 mg, 0.260 mmol) in 1,4-dioxane (8.6 mL) was added phenylboronic acid (48 mg, 0.390 mmol), [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (10 mg, 0.013 mmol) and aqueous potassium carbonate (2 M, 390 μL, 0.780 mmol). The reaction mixture was stirred at 100 °C for 16 h under argon and then evaporated. The residue was purified by gradient silica gel column chromatography eluting with heptanes:ethyl acetate (100:0 to 90:10) to give the title compound (64 mg, 0.168 mmol, 65%) as a pale yellow oil.

Synthesis and Characterization of Deprotected Products



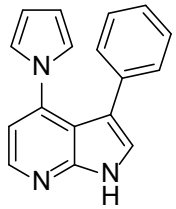
4-Isopropoxy-3-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (4)

A mixture of **9** (165 mg, 0.431 mmol) and hydrogen chloride (4.7 M in 1,4-dioxane, 4.32 mL, 20.3 mmol) was stirred at 50 °C for 3 h and then evaporated. The residue was taken up in water (5 mL) and to the mixture was added 5 M aqueous sodium hydroxide to achieve pH ≥ 11. The reaction mixture was stirred at room temperature for 25 min, then acidified to pH 4 by addition of acetic acid. The mixture was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over sodium sulfate, filtered and evaporated to give the title compound (106 mg, 0.420 mmol, 98%) as a white solid. R_f: 0.60 (chloroform:MeOH, 9:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.74 (s, 1H), 8.10 (d, J = 5.4 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.46 – 7.41 (m, 1H), 7.38 – 7.32 (m, 2H), 7.25 – 7.18 (m, 1H), 6.68 (d, J = 5.5 Hz, 1H), 5.05 – 4.67 (m, 1H), 1.30 (d, J = 5.9 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 158.57, 151.61, 145.19, 135.93, 129.50, 127.90, 125.84, 122.55, 116.06, 107.96, 99.84, 70.15, 22.10. HRMS (ESI): m/z calcd for $C_{16}H_{17}N_2O$ $[M+H]^+$, 253.1341; found 253.1338.

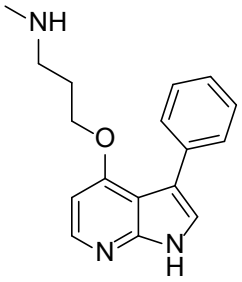


4-Methylsulfanyl-3-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (19a)

Prepared by the same general method as compound **4** starting from intermediate **14k** (200 mg, 0.540 mmol) to give the title compound (85 mg, 0.354 mmol, 66%) as a pale yellow solid. R_f: 0.50 (chloroform:MeOH, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.86 (s, 1H), 8.14 (d, J = 5.2 Hz, 1H), 7.53 – 7.23 (m, 5H), 7.44 (s, 1H), 6.90 (d, J = 5.3 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 147.85, 143.34, 142.45, 135.94, 130.82, 127.94, 126.86, 124.52, 116.80, 115.17, 110.69, 14.00. HRMS (ESI): m/z calcd for $C_{14}H_{13}N_2S$ $[M+H]^+$, 241.0799; found 241.0792.



3-Phenyl-4-pyrrol-1-yl-1*H*-pyrrolo[2,3-*b*]pyridine (19b)
Prepared by the same general method as compound **4** starting from intermediate **14l** (335 mg, 0.861 mmol). The crude product was purified by gradient silica gel chromatography eluting with heptanes:ethyl acetate (100:0 to 60:40) to give the title compound (85 mg, 0.328 mmol, 38%) as a white solid. R_f: 0.42 (chloroform:MeOH, 9:1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.23 (s, 1H), 8.32 (d, J = 5.1 Hz, 1H), 7.78 – 7.54 (m, 1H), 7.14 – 7.05 (m, 4H), 7.00 – 6.90 (m, 2H), 6.79 – 6.69 (m, 2H), 6.03 – 5.94 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 151.49, 144.01, 141.16, 135.35, 128.19, 127.99, 126.27, 126.05, 122.35, 115.44, 112.33, 111.07, 109.81. HRMS (ESI): m/z calcd for $C_{17}H_{14}N_3$ $[M+H]^+$, 260.1188; found 260.1183.



***N*-Methyl-3-[(3-phenyl-1*H*-pyrrolo[2,3-*b*]pyridin-4-yl)oxy]propan-1-amine (22)**
A mixture of intermediate **16** (484 mg, 0.946 mmol) and hydrogen chloride (4.7 M in 1,4-dioxane, 9.45 mL, 44.5 mmol) was stirred at room temperature for 2 h and then evaporated. The residue was taken up in a mixture of chloroform and methanol (1:1, 15 mL). To the mixture was added ethylenediamine (125 µL, 1.89 mmol) and the reaction mixture was stirred at 50 °C for 30 min, then evaporated. The residue was purified by preparative HPLC to give the title compound (208 mg, 0.740 mmol, 78%) as a white solid. R_f: 0.15 (chloroform:MeOH, 4:1). ^{1}H NMR (300 MHz, Methanol-d_4) δ 8.11 (d, J = 5.6 Hz, 1H), 7.69 – 7.54 (m, 2H), 7.45 – 7.33 (m, 2H), 7.33 – 7.19 (m, 2H), 6.71 (d, J = 5.7 Hz, 1H), 4.22 (t, J = 5.9 Hz, 2H), 2.58 (t, J = 7.4 Hz, 2H), 2.32 (s, 3H), 2.07 – 1.85 (m, 2H). ^{13}C NMR (75 MHz, Methanol-d_4) δ 160.48, 150.04, 144.24, 135.79, 129.25, 127.34, 125.63, 121.50, 116.76, 108.20, 98.31, 65.83, 48.48, 34.10, 27.67. HRMS (ESI): m/z calcd for $C_{17}H_{20}N_3O$ $[M+H]^+$, 282.1606; found 282.1601.