A Non-Cryogenic Method for the Preparation of 2-(Indolyl) Borates, Silanes and Silanols.

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Supporting Information. Reactions were carried out under an atmosphere of dry nitrogen. Reagents and solvents were used as received from commercial sources. LDA was obtained from commercial sources as a 2.0 M solution in n-heptane/ethylbenzene/THF. Triisopropylborate was reagent grade. THF contained < 200 •g/mL water as determined by Karl-Fischer titration. All reactions were monitored by HPLC analysis using a Zorbax SB-C18, 4.6 x 250 mm column. Eluent: CH_3CN and a 0.1 % H_3PO_4/20mM $NaClO_4$ buffer. Initial conditions 70% CH_3CN, with a gradient to 90 % CH_3CN over 7 min. Flow rate: 1.5 mL/min, UV detection at 220nm.

General procedure for the preparation of N-Boc indoles. To a solution of 5-cyano indole (5.00g; 35.2mmol) and DMAP (0.086g; 0.704mmol) in CH_2Cl_2 (25ml) was added Boc anhydride (8.45g; 38.7mmol). Stirred at room temperature. After 45 min the reaction was quenched with 1N HCl (25ml). The organic layer was separated and dried over $MgSO_4$. Filtered and concentrated to yield a solid. The solid was dissolved in hot

methanol (60°C) then cooled down to room temperature. Water (100ml) was added dropwise to crystallized product. Filtered and dried to give **1g** (8.25gm, 96.7% yield).

General procedure for the preparation of 2-indolylborates. To a solution of *N*-Boc-4-chloroindole **1a** (2.00 g; 7.95 mmol) in THF (10 mL) was added triisopropylborate (2.8 mL; 12.1 mmol). The solution was cooled to 0 – 5 °C in an ice bath and LDA (2.0 M, 10 mmol) was added over 1 hr. After 30 min. the reaction was quenched by the addition of 2N HCl. The organic layer was separated, dried over $MgSO_4$ and concentrated to a solid which was recrystallized from acetonitrile/water to give **2a** (2.34 g, 99% yield); m.p. 97.8-99.0 °C; ^{1}H NMR (DMSO-d^6, 400 MHz) δ 8.40 (2H, br.s), 8.06 – 8.01 (1H, m), 7.29 – 7.24 (2H, m), 6.63 (1H, s), 1.59 (9H, s); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 150.0, 140.6 (br.) 137.4, 129.3, 125.5, 125.0, 122.6, 114.0, 109.7, 85.2, 28.0; Anal. Calcd for $C_{13}H_{15}BClNO_4$: C, 52.83; H, 5.12; N, 4.74; Cl,12.0. Found: C, 52.85; H, 4.99; N, 4.66; Cl, 11.86.

2b 2.22g (94% yield); m.p. 98.2-99.9°C; ^{1}H NMR (DMSO-d^6, 400 MHz) δ 8.27 (2H, s), 8.09 (1H, d, *J* = 8.8 Hz), 7.64 (1H, d, *J* = 1.7 Hz), 7.30 (1H, d, *J* = 8.8, 1.9 Hz), 6.63 (1H, s), 1.61 (9H, s); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 150.1, 140.8, 135.1, 132.6, 127.4, 124.2, 120.4, 116.3, 111.7, 85.0, 28.0; Anal. Calcd for $C_{13}H_{15}BClNO_4$: C, 52.83; H, 5.12; N, 4.74; Cl,12.00. Found: C, 52.84; H, 4.65; N, 4.74; Cl, 11.95.

2c 2.31g (96%yield); m.p. 104-106 °C; ^{1}H NMR (DMSO-d^6, 400 MHz) δ 8.19 (2H, s), 8.10 (1H, d, *J* = 8.24 Hz), 7.57 (1H, d, *J* = 7.60 Hz), 7.28 (1H, ddd, *J* = 8.1, 7.2, 1.0 Hz), 7.20 (1H, t, *J* = 7.3 Hz), 6.63 (1H, s), 1.61 (9H, s); ^{13}C NMR (DMSO-d^6, 100 MHz) δ

150.4, 138.5, 136.6, 131.1, 124.4, 123.0, 121.1, 115.0, 112.6, 84.4, 28.1; Anal. Calcd for $C_{13}H_{16}BNO_4$: C, 59.80; H, 6.18; N, 5.36. Found: C, 59.84; H, 6.26; N, 5.29.

2d 2.12g (92% yield); m.p. 97.7-99.3°C. ^{1}H NMR (DMSO-d^6, 400 MHz) δ 8.26 (2H, s), 8.02 (1H, d, *J* = 8.8 Hz), 7.77 (1H, s), 7.41 (1H, d, *J* = 8.8 Hz), 6.62 (1H, s), 1.60 (9H, s); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 150.1, 140.6, 135.5, 133.2, 128.7, 126.8, 123.5, 116.7, 115.5, 111.6, 85.0, 28.0; Anal. Calcd for $C_{13}H_{15}BBrNO_4$: C, 45.93; H, 4.45; N, 4.12; Br, 23.50. Found: C, 45.99; H, 4.38; N, 3.91; Br, 23.37

2e 2.11g (89% yield); m.p. 110-112 °C. ^{1}H NMR (DMSO-d^6, 400 MHz) δ 8.17 (2H, s), 7.97 (1H, d, *J* = 8.9 Hz), 7.09 (1H, s), 6.89 (1H, d, *J* = 8.9 Hz), 6.57 (1H, s), 3.78 (3H, s), 1.60 (9H, s); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 155.9, 150.4, 139.7, 132.1, 131.3, 115.6, 113.0, 112.6, 103.6, 84.2, 55.8, 28.1; Anal. Calcd for $C_{14}H_{18}BNO_5$: C, 57.76; H, 6.23; N, 4.81. Found: C, 58.03; H, 6.24; N, 4.66.

2f 2.03g (85% yield); m.p. 110-112 °C; ^{1}H NMR (DMSO-d^6, 400 MHz) δ 8.16 (2H, s), 7.97 (1H, d, *J* = 8.1 Hz), 7.35(1H, s), 7.09 (1H, d, *J* = 8.2 Hz), 6.56 (1H, s), 2.38 (3H, s), 1.61 (9H, s); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 150.4, 139.0, 135.0, 131.8, 131.4, 125.7, 120.9, 114.7, 112.5, 84.2, 28.1, 21.4; Anal. Calcd for $C_{13}H_{18}BNO_4$: C, 61.12; H, 6.59; N, 5.09. Found: C, 61.27; H, 6.72; N, 4.76.

2g 1.91g (81% yield); m.p. 245-248 °C; ^{1}H NMR (DMSO-d^6, 400 MHz) δ 8.29 (2H, s), 8.18 (1H, d, *J* = 8.6 Hz), 8.08 (1H, d, *J* = 1.1 Hz), 7.64 (1H, dd, *J* = 8.7, 1.4 Hz), 6.70 (1H, s), 1.57 (9H,s); ^{13}C NMR (DMSO-d^6, 100 MHz) δ 149.9, 141.9, 138.5, 131.3, 127.5, 126.1, 120.2, 115.9, 112.0, 105.4, 85.7, 28.0; Anal. Calcd for $C_{14}H_{15}BN_2O_4$: C, 58.77; H, 5.28; N, 9.79. Found: C, 58.72; H, 5.25; N, 9.74.

2h 1.74g (73% yield); m.p. 231-234 °C; ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 8.20 (2H, s), 8.11 (1H, dd, *J* = 4.7, 4.3 Hz), 7.32 (1H, dd, *J* = 6.8, 2.3Hz), 7.08 (1H, ddd, *J* = 9.2, 9.2, 2.4Hz), 6.63 (1H, s), 1.61 (9H, s); ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 158.4 (d, *J* = 236.3 Hz), 149.6, 140.6, 132.6, 131.6 (d, *J* = 9.9 Hz), 115.5 (d, *J* = 9.4 Hz), 111.6 (d, *J* = 3.6 Hz), 111.3 (d, *J* = 25.1 Hz), 105.8 (d, *J* = 23.4 Hz), 84.2, 27.5; ^{19}F NMR (DMSO-d^{6}, 376 MHz) δ -121.6; Anal. Calcd for $C_{13}H_{15}BFNO_4$: C, 55.95; H, 5.42; N, 5.02; F, 6.81. Found: C, 56.23; H, 5.42; N, 4.72; F, 5.62.

General Procedure for silanes or siloxanes. To a solution of *N*-Boc-5-chloroindole **1b** (2.00 g, 7.95 mmol) in THF (10 mL) was added chlorotrimethylsilane (1.5 mL, 11.8mmol). The solution was cooled to 0°C in an ice bath. LDA (2.0 M in THF, 10 mmol) was added over 1 hr. After the addition was complete the reaction was aged for 30 minutes and quenched with water (10mL). The organic layer was separated and dried over $MgSO_4$. The organics are filtered and concentrated. Flash chromatography on silica gel (5% EtOAc /hexane) gave **3a** as a colorless solid (2.15 g, 84% yield); m.p. 95.2-96.3°C; ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 7.86 (1H, d, *J* = 9 Hz), 7.62 (1H, d, *J* = 2 Hz), 7.28 (1H, dd, *J* = 9, 2 Hz), 6.84 (1H, s), 1.62 (9H, s), 0.26 (9H, s); ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 150.9, 143.5, 136.1, 132.4, 127.5, 124.9, 120.6, 119.1, 117.0, 85.3, 28.1, 0.4; Anal. Calcd for $C_{16}H_{22}ClNO_2Si$: C, 59.33, H, 6.85, N, 4.32, Cl,10.95, Si, 8.67. Found: C, 59.79, H, 6.82, N, 4.12, Si, 8.69.

3b 1.95g (78% yield); ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 7.86 (1H, d, *J* = 8.5 Hz), 7.37 (1H, s), 7.14 (1H, d, *J* = 8.6 Hz), 6.88 (1H, s), 4.53 (1H, m, *J* = 3.4 Hz), 2.37 (3H, s), 1.65 (9H, s), 0.35 (6H, d, *J* = 3.4 Hz); ^{13}C NMR (DMSO-d^{6}, 100 MHz) δ 151.3, 138.7, 136.1,

132.1, 131.2, 126.8, 121.1, 120.6, 115.3, 85.0, 28.2, 21.3, -2.3; Anal. Calcd for $C_{16}H_{23}NO_2Si$: C, 66.39, H, 8.01, N, 4.84, Si, 9.70. Found: C, 66.31, H, 8.18, N, 4.52, Si, 9.61.

3c The reaction was quenched with a saturated aqueous solution of sodium bicarbonate (10mL) and stirred for one hour. The organic layer was dried over magnesium sulfate and concentrated to a semi-solid. 6.0g (91% yield); ^{1}H NMR (DMSO-d^{6}, 400 MHz) δ 7.81 (1H, d, J = 8.5 Hz), 7.38 (1H, s), 7.11 (1H, d, J = 8.4 Hz), 6.94 (1H, s), 5.67 (1H, s), 2.37 (3H, s), 1.65 (9H, s), 0.32 (6H, s); ^{13}C NMR (DMSO-d^{6}, 125 MHz) δ 150.8, 141.7, 135.2, 131.3, 130.8, 125.9, 120.6, 119.3, 114.8,84.1, 27.6, 20.7, 1.4; ^{29}Si NMR (DMSO-d^{6}, 99.3 MHz) δ -5.9; Anal. Calcd for $C_{16}H_{23}NO_3Si$: C,62.92, H, 7.59, N, 4.59, Si, 9.19. Found: C, 62.46, H, 7.66, N, 4.33, Si, 9.01.