Electronic Supplementary Material (ESI) for Chemical Communications


# Suzuki-Miyaura Coupling of Heteroaryl Boronic Acids and Vinyl Chlorides

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## SUPPORTING INFORMATION

**General Experimental**:

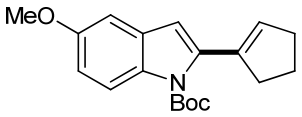
All reactions were conducted under an atmosphere of $N_2$ using standard Schlenk techniques or in a $N_2$ filled glove-box unless otherwise noted. Toluene was dried over neutral alumina under $N_2$ using a Grubbs type solvent purification system. $Pd(OAc)_2$ and SPhos was purchased from Strem and used without further purification. *N*-BOC-5-methoxy-2-indolylboronic acid (**1**), 1-chlorocyclopentene (**a**) and CsF were purchased from Sigma-Aldrich and used without further purification. Isopropanol was distilled and degassed prior to use. All the other heteroaryl boronic acids were purchased from Frontier Scientific. The heteroaryl boronic acids were stored at -40 ºC in the refrigerator within the glove box. The vinyl chlorides 1-chloro-2-methylpropene and (*Z*)-2-chloro-2-butene were purchased from TCI America. 3-Chloro-5,5-dimethyl-2-cyclohexen-1-one was bought from Alfa Aesar. 4-Chloro-1,2,5,6-tetrahydro-1-tosylpyridine[1] was prepared according to the literature procedure. All other reagents were purchased and used without further purification unless otherwise noted.

$^1H$ and $^{13}C$ Nuclear Magnetic Resonance spectra of pure compounds were acquired at 400 and 100 MHz, respectively unless otherwise noted. All spectra are referenced to a singlet at 7.27 ppm for $^1H$ and to the centerline of a triplet at 77.23 ppm for $^{13}C$. The abbreviations s, d, dd, dt, dq, t, td, tq, q, qt, quint, sept, septd, septt, m, brm, brd, brt, and brs stand for singlet, doublet, doublet of doublets, doublet of triplets, doublet of quartets, triplet, triplet of doublets, triplet of quartets, quartet, quartet of triplets, quintet, septet, septet of doublets, septet of triplets, multiplet, broad multiplet, broad doublet, broad triplet, and broad singlet, in that order. All $^{13}C$ NMR spectra were proton decoupled. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer.

**General Procedure for Suzuki-Miyaura Coupling:**

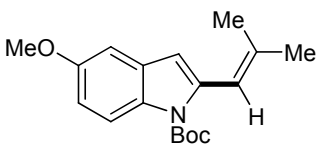
In a nitrogen-filled glove box, a screw-cap vial was charged with 1 equiv heteroaryl boronic acid, 2-4 mol% $Pd(OAc)_2$, 4-8 mol% SPhos, 1.4 equiv CsF, 1.1-1.2 equiv of vinyl chloride and isopropanol (0.2 M). The vial was brought out of the box and heated at 85 °C in an oil bath for indicated period of time. The resulting reaction mixture was filtered though a short pad of silica gel and eluted with diethyl ether. The solvent was removed *in vacuo,* and the crude product was purified by silica gel flash column chromatography.

***N*-Boc-2-(cyclopenten-1-yl)-5-methoxyindole (1a):**




The general procedure was used with 202.8 mg (0.70 mmol) of *N*-Boc-5-methoxy-2-indolylboronic acid, 3.1 mg (0.01 mmol) of $Pd(OAc)_2$, 11.5 mg (0.03 mmol ) of SPhos, 148.2 mg (0.98 mmol) of CsF and 54.2 mg of 1-chlorocyclopentene in isopropanol (3.5 ml, 0.2 M). The reaction mixture was heated at 85 °C for 3 hours. The remaining residue was purified via flash column chromatography using 5% ether in pentane ($R_f$ = 0.46) to afford the title compound **1a** and the protodeboronated indole **1a'**[2] as a colorless oil in 88% global yield (192.6 mg, 0.62 mmol; **1a:1a'** = 100:4 by $^1$H NMR) : **1a** ; $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.0 (d, *J* = 9.2 Hz, 1 H), 6.99 (d, *J* = 2.8 Hz, 1H), 6.92 (dd, *J* = 2.4 Hz, 9.2 Hz, 1H), 6.40 (s, 1H), 5.93 (m, 1H), 3.90 (s, 3H), 2.71 (m, 2H), 2.57 (m, 2H), 2.07 (quint, *J* = 6.4 Hz, 2H), 1.7 (s, 9H); $^{13}$C NMR (100 MHz , $CDCl_3$): δ (ppm) 156.0, 150.4, 139.3, 137.0, 132.0, 130.2, 129.8, 116.0, 112.6, 108.7, 102.9, 83.5, 55.7, 36.2, 33.2, 28.2, 23.8; IR ($CH_2Cl_2$, $cm^{-1}$): 2977, 2842 1731, 1615, 1474, 1126, 1034, 847, 734; HRMS (ESI) calcd for $C_{19}H_{23}NO_3Na$ $[M+Na]^+$ 336.1576, found 336.1579.

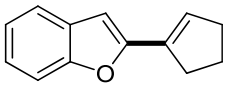
***N*-Boc-2-(2-methylpropen-1-yl)-5-methoxyindole (1b):**




The general procedure was used with 145.1 mg (0.50 mmol) of *N*-Boc-5-methoxy-2-indolylboronic acid, 2.24 mg (0.01 mmol) of $Pd(OAc)_2$, 8.20 mg (0.02 mmol) of SPhos, 106 mg of CsF (0.70 mmol) and 54.2 mg (0.60 mmol) of 1-chloro-2-methylpropene in isopropanol (2.5 ml, 0.2 M). The reaction mixture was heated at 85 °C

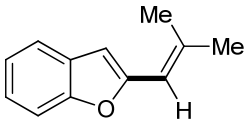
for 6 hours. The remaining residue was purified via flash column chromatography using 5% ether in pentane ($R_f$ = 0.57) to afford the title compound **1b** and the protodeboronated indole **1a'**[2] as a colorless oil in 80% global yield (121.1 mg, 0.40 mmol; **1b:1a'** = 100:5 by $^1$H NMR): **1b**; $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.04 (d, *J* = 9.2 Hz, 1H), 7.0 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 2.4 Hz, 8.0 Hz, 1H), 6.53 (s, 1H), 6.38 (brs, 1H), 3.87 (s, 3H), 1.99 (brs, 3H), 1.96 (brs, 3H), 1.69 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.0, 150.6, 138.5, 136.4, 130.7, 130.5, 118.2, 116.5, 112.4, 109.4, 102.7, 83.5, 55.7, 28.4, 26.7, 20.1; IR ($CH_2Cl_2$, $cm^{-1}$): 2978, 1729, 1615, 1477, 1365, 1315, 1165, 1123, 851, 800; HRMS (ESI) calcd for $C_{18}H_{23}NO_3Na$ $[M+Na]^+$ 324.1576, found 324.1577.

**2-(cyclopenten-1-yl)benzofuran (2a):**



The general procedure was used with 165.1 mg (1.02 mmol) of benzofuran-2-boronic acid, 4.6 mg (0.02 mmol) of $Pd(OAc)_2$, 16.7 mg (0.04 mmol) of SPhos, 217 mg of CsF (1.43 mmol) and 125.5 mg (1.22 mmol) of 1-chlorocyclopentene in isopropanol (5 ml, 0.2 M). The reaction mixture was heated at 85 °C for 6 hours. The remaining residue was purified via flash column chromatography using 2% ether in pentane ($R_f$ = 0.4) to afford the title compound **2a** as a colorless solid (mp: 68-70 °C) in 82% yield (154.6 mg, 0.84 mmol): $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54 (m, 1H), 7.46 (dd, *J* = 0.8 Hz, 8.0 Hz, 1H), 7.26 (td, *J* = 1.6 Hz, 7.2 Hz, 1H), 7.20 (td, *J* = 1.2 Hz, 7.6 Hz, 1H), 6.52 (s, 1H), 6.43 (quint, *J* = 2.0 Hz, 1H), 2.73 (m, 2H), 2.61 (m, 2H), 2.07 (quint, *J* = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz , $CDCl_3$); δ (ppm) 155.0, 154.4, 133.1, 129.3, 129.0, 124.2, 122.7, 120.9, 111.0, 102.5, 33.6, 32.5, 23.4; IR ($CH_2Cl_2$, $cm^{-1}$): 2952, 1448, 1252, 1003, 797, 746. HRMS (ESI) calcd for $C_{13}H_{13}O$ $[M+H]^+$ 185.0996, found 185.0971.

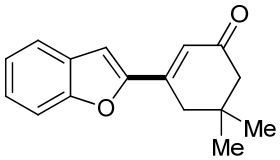
**2-(2-methylpropen-1-yl)benzofuran (2b):**




The general procedure was used with 154.2 mg (0.94 mmol) of benzofuran-2-boronic acid, 4.2 mg (0.02 mmol) of $Pd(OAc)_2$, 15.4 mg (0.04 mmol) of SPhos, 200 mg of CsF (1.32 mmol) and 102.2 mg (1.13 mmol) of 1-chloro-2-methylpropene in isopropanol (4.7 ml, 0.2 M). The reaction mixture was heated at 85 °C for 6 hours. The remaining residue was purified via

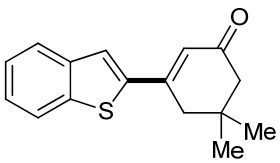
flash column chromatography using pure pentane ($R_f$ = 0.5) to afford the title compound **2b** as a colorless soild (mp: 40-42 °C) in 83% yield (133.9 mg, 0.78 mmol): $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53 (dd, *J* = 1.0 Hz, 7.5 Hz, 1H), 7.44 (m, 1H), 7.22 (m, 2H), 6.53 (s, 1H), 6.21 (brs, 1H), 2.15 (brs, 3H), 2.02 (brs, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 155.9, 154.3, 139.8, 129.3, 123.8, 122.8, 120.6, 114.7, 111.0, 103.8, 27.6, 20.7; IR ($CH_2Cl_2$, $cm^{-1}$): 2912, 1658, 1453, 1256, 1195, 1055, 846, 790; HRMS (ESI) calcd for $C_{12}H_{13}O$ $[M+H]^+$ 173.0966, found 173.0968.

**3-(Benzofuran-2-yl)-5,5-dimethylcyclohex-2-en-1-one (2c)**:




The general procedure was used with 132.1 mg (0.82 mmol) of benzofuran-2-boronic acid, 3.7 mg (0.02 mmol) of $Pd(OAc)_2$, 13.5 mg (0.03 mmol) of SPhos, 174.4 mg of CsF (1.15 mmol) and 155.3 mg (0.98 mmol) of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one in isopropanol (4.1 ml, 0.2 M). The reaction mixture was heated at 85 °C for 10 hours. The remaining residue was purified via flash column chromatography using 20% ether in pentane ($R_f$ = 0.3) to afford the title compound **2c** as a light yellow solid (mp: 114-116 °C) in 87% yield (173.1 mg, 0.72 mmol): $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.37 (m, 1H), 7.26 (m, 1H), 7.07 (s, 1H), 6.72 (brs, 1H), 2.62 (d, *J* = 1.5 Hz, 2H), 2.37 (s, 2H), 1.15 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 199.6, 155.7, 154.1, 145.1, 128.4, 126.7, 123.5, 122.5, 121.9, 111.7, 108.7, 51.5, 39.5, 33.8, 28.6; IR ($CH_2Cl_2$, $cm^{-1}$): 2958, 2872, 1660, 1608, 1382, 1300, 1113, 1014, 809, 751; HRMS (ESI) calcd for $C_{16}H_{16}O_2Na$ $[M+Na]^+$ 263.1048, found 263.1039.

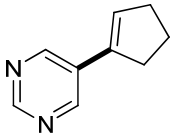
**3-(Benzothiophen-2-yl)-5,5-dimethylcyclohex-2-en-1-one (3c)**:




The general procedure was used with 179.9 mg (1.01 mmol) of benzothiophene-2-boronic acid, 9.1 mg (0.04 mmol) of $Pd(OAc)_2$, 33.2 mg (0.08 mmol) of SPhos, 214.8 mg of CsF (1.41 mmol) and 176.3 mg (1.11 mmol) of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one in isopropanol (5 ml, 0.2 M). The reaction mixture was heated at 85 °C for 10 hours. The remaining residue was purified via flash column chromatography using 20% ether in pentane ($R_f$ = 0.26) to afford the title compound **3c**

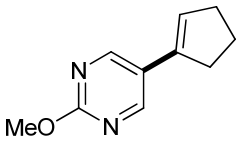
as a light yellow solid (mp: 136-138 °C) in 81% yield (209.9 mg, 0.82 mmol): $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79 (m, 2H), 7.60 (s, 1H), 7.37 (m, 2H), 6.50 (brs, 1H), 2.72 (d, *J* = 1.2 Hz, 2H), 2.36 (s, 2H), 1.16 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 199.6, 150.4, 142.9, 140.3, 139.9, 126.4, 125.0, 124.9, 124.6, 124.0, 122.5, 51.2, 41.7, 33.8, 28.6; IR ($CH_2Cl_2$, $cm^{-1}$): 2962, 1652, 1596, 1366, 829, 728; HRMS (ESI) calcd for $C_{16}H_{16}ONaS$ $[M+Na]^+$ 279.0820, found 279.0813.

**5-(cyclopenten-1-yl)pyrimidine (4a):**



The general procedure was used with 143.5 mg (1.16 mmol) of pyrimidine-5-boronic acid, 5.2 mg (0.02 mmol) of $Pd(OAc)_2$, 19.1 mg (0.05 mmol) of SPhos, 246.7 mg of CsF (1.62 mmol) and 142.53 mg (1.39 mmol) of 1-chlorocyclopentene in isopropanol (5.8 ml, 0.2 M). The reaction mixture was heated at 85 °C for 6 hours. The remaining residue was purified via flash column chromatography using 50% ether in pentane ($R_f$ = 0.21) to afford the title compound **4a** as a off-white solid (mp: 48-50 °C) in 76% yield (128.4 mg, 0.88 mmol): $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.97 (s, 1H), 8.69 (s, 2H), 6.31 (brs, 1H), 2.65 (m, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.99 (quint, *J* = 6.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.9, 153.6, 136.5, 130.5, 130.2, 33.7, 32.6, 23.2; IR ($CH_2Cl_2$, $cm^{-1}$): 2956, 2899, 2846, 1555, 1439, 1411, 1325, 1181, 725, 630, 538; HRMS (ESI) calcd for $C_9H_{11}N_2$ $[M+H]^+$ 147.0922, found 147.0935.

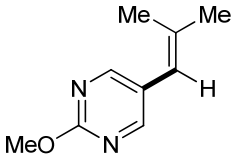
**5-(cyclopenten-1-yl)-2-methoxypyrimidine (5a):**



The general procedure was used with 138.1 mg (0.90 mmol) of 2-methoxypyrimidine-5-boronic acid, 4.0 mg (0.02 mmol) of $Pd(OAc)_2$, 14.8 mg (0.036 mmol) of SPhos, 191 mg of CsF (1.26 mmol) and 110.6 mg (1.08 mmol) of 1-chlorocyclopentene in isopropanol (4.5 ml, 0.2 M). The reaction mixture was heated at 85 °C. The reaction mixture was heated at 85 °C for 6 hours. The remaining residue was purified via flash column chromatography using 40% ether in pentane ($R_f$ = 0.35) to afford the title compound **5a** as a semi-solid in 80% yield (126.2 mg, 0.72 mmol): $^{1}$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.53 (s, 2H), 6.16 (m, 1H), 3.99 (s, 3H), 2.65 (m, 2H), 2.52 (m, 2H), 2.01 (quint, *J* = 8.0 Hz, 2H); $^{13}$C NMR

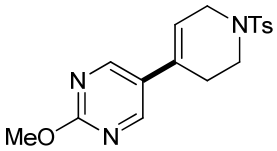
(100 MHz, $CDCl_3$): δ (ppm) 164.6, 156.1, 136.2, 127.1, 124.4, 55.0, 33.5, 32.9, 23.2; IR ($CH_2Cl_2$, $cm^{-1}$): 2957, 1607, 1592, 1556, 1479, 1031, 805; HRMS (ESI) calcd for $C_{10}H_{13}N_2O$ $[M+H]^+$ 177.1028, found 177.1034.

**5-(2-Methylpropen-1-yl)-2-methoxypyrimidine (5b):**



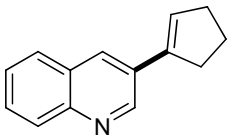

The general procedure was used with 139.1 mg (0.90 mmol) of 2-methoxypyrimidine-5-boronic acid, 4.1 mg (0.02 mmol) of $Pd(OAc)_2$, 14.9 mg (0.04 mmol) of SPhos, 192.2 mg of CsF (1.27 mmol) and 98.2 mg (1.08 mmol) of 1-chloro-2-methylpropene in isopropanol (5.8 ml, 0.2 M). The reaction mixture was heated at 85 °C for 6 hours. The remaining residue was purified via flash column chromatography using 40% ether in pentane ($R_f$ = 0.49) to afford the title compound **5b** as a colorless oil in 82% yield (121.1 mg, 0.74 mmol): $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 2H), 5.99 (brs, 1H), 3.93 (s, 3H), 1.84 (d, *J* = 0.8 Hz, 3H), 1.76 (brs, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 163.7, 158.7, 138.6, 125.9, 117.6, 54.8, 26.7, 19.4; IR ($CH_2Cl_2$, $cm^{-1}$) 2976, 1702, 1594, 1475, 1410, 1326, 1039, 804; HRMS (ESI) calcd for $C_9H_{13}N_2O$ $[M+H]^+$ 165.1028, found 165.1035.

**4-(2-Methoxypyrimidin-5-yl)-1,2,5,6-tetrahydro-1-tosylpyridine (5d):**



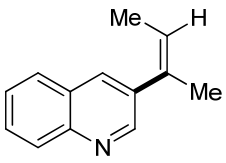

The general procedure was used with 51.3 mg (0.33 mmol) of 2-methoxypyrimidine-5-boronic acid, 1.5 mg (0.01 mmol) of $Pd(OAc)_2$, 5.5 mg (0.02 mmol) of SPhos, 69.6 mg of CsF (0.47 mmol) and 98.0 mg (0.36 mmol) of 4-chloro-1,2,5,6-tetrahydro-1-tosylpyridine in isopropanol (1.65 ml, 0.2 M) . The reaction mixture was heated at 85 °C for 6 hours. The remaining residue was purified via flash column chromatography using 50% ether in pentane ($R_f$ = 0.38) to afford the title compound **5d** as a colorless solid (178-180 °C) in 96% yield (110.7 mg, 0.32 mmol): $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 8.43 (s, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8 Hz, 2H), 5.95 (brs, 1H), 3.99 (s, 3H), 3.76 (d, *J* = 2.8 Hz, 2H), 3.33 (t, *J* = 5.6 Hz), 2.55 (brs, 2H), 2.42 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 165.2, 155.9, 144.0, 133.3, 129.9, 127.9, 127.3, 120.4, 55.2, 45.3, 42.8, 27.3, 21.7; IR ($CH_2Cl_2$, $cm^{-1}$) 2927, 1593, 1547, 1474, 1335, 1163, 726, 549; HRMS (ESI) calcd for $C_{17}H_{20}N_3O_3S$ $[M+H]^+$ 346.1225, found 346.1218.

**3-(Cyclopenten-1-yl)quinoline (6a)**:

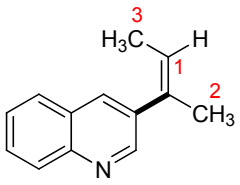


The general procedure was used with 138.4 mg (0.80 mmol) of quinoline-3-boronic acid, 3.6 mg (0.02 mmol) of $Pd(OAc)_2$, 13.1 mg (0.03 mmol) of SPhos, 170.1 mg of CsF (1.12 mmol) and 98.5 mg (0.36 mmol) of 1-chlorocyclopentene in isopropanol (4.0 ml, 0.2 M). The reaction mixture was heated at 85 °C for 10 hours. The remaining residue was purified via flash column chromatography using 25% ether in pentane ($R_f$ = 0.3) to afford the title compound **6a** as a colorless solid (mp: 52-54 °C) in 73% yield (113.6 mg, 0.582 mmol): $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.14 (d, *J* = 2.0 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.94 (brs, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.65 (m, 1H), 7.51 (m, 1H), 6.45 (t, *J* = 2.0 Hz, 1H), 2.82 (m, 2H), 2.62 (m, 2H), 2.08 (quint, *J* = 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.4, 147.1, 139.9, 131.0, 129.8, 129.3, 128.9, 128.7, 128.2, 128.0, 126.9, 33.9, 33.2, 23.2; IR ($CH_2Cl_2$, $cm^{-1}$): 2955, 2844, 1624, 1569, 1493, 786, 749, 542; HRMS (ESI) calcd for $C_{14}H_{14}N$ $[M+H]^+$ 196.1126, found 196.1128.

**3-((*Z*)-Buten-2-yl)quinoline (6e)**:

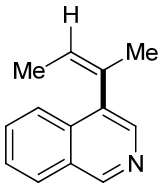


The general procedure was used with 143.3 mg (0.83 mmol) of quinoline-3-boronic acid, 3.7 mg (0.02 mmol) of $Pd(OAc)_2$, 13.6 mg (0.03 mmol) of SPhos, 176.5 mg of CsF (1.16 mmol) and 90.0 mg (0.36 mmol) of (*Z*)-2-chloro-2-butene in isopropanol (4.15 ml, 0.2 M). The reaction mixture was heated at 85 °C for 10 hours. The remaining residue was purified via flash column chromatography using 25% ether in pentane ($R_f$ = 0.35) to afford the title compound **6e** as a colorless oil in 67% yield (101.6 mg, 0.56 mmol): $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.81 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.92 (brs, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.2, 1H), 7.52 (t, *J* = 7.6, 1H), 5.75 (m, 1H), 2.12 (s, 3H), 1.65 (dd, *J* = 1.2 Hz, 6.8 Hz, 3H), $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.2, 147.0, 134.8, 134.3, 133.5, 129.3, 129.1, 128.0, 127.8, 126.8, 124.3, 25.3, 15.1; IR ($CH_2Cl_2$, $cm^{-1}$): 2970, 2916, 1567, 1490, 1450, 1126, 1035, 787, 752, 570. HRMS (ESI) calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1126, found 184.1133.



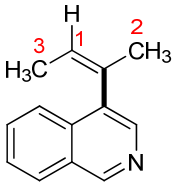

Stereochemistry was assigned on the basis of nOe of proton on C-1 with the protons on C-2 and C-3.

**3-((*Z*)-Buten-2-yl)isoquinoline (7e):**



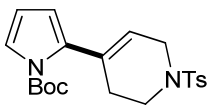

The general procedure was used with 149.6 mg (0.86 mmol) of isoquinoline-4-boronic acid, 3.9 mg (0.02 mmol) of $Pd(OAc)_2$, 14.2 mg (0.04 mmol) of SPhos, 184 mg of CsF (1.21 mmol) and 94.0 mg (1.04 mmol) of (*Z*)-2-chloro-2-butene in isopropanol (4.2 ml, 0.2 M) for 10 hours. The remaining residue was purified via flash column chromatography using 30% ether in pentane ($R_f$ = 0.3) to afford the title compound **7e** as a colorless oil in 51% yield (80.1 mg, 0.44 mmol): $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.16 (s, 1H), 8.30 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.80 (dd, *J* = 0.8 Hz, 8.4 Hz, 1H), 7.66 (m, 1H), 7.57 (m, 1H), 5.88 (m, 1H), 2.08 (quint, *J* = 1.6 Hz, 3H), 1.35 (dq, *J* = 1.2 Hz, 6.8 Hz, 3H), $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.4, 142.1, 133.9, 133.4, 132.4, 130.4, 128.6, 128.1, 127.1, 125.4, 124.6, 26.0, 15.0; IR ($CH_2Cl_2$, $cm^{-1}$): 2968, 2915, 1620, 1570, 789, 754, 606

HRMS (ESI) calcd for $C_{13}H_{14}N$ $[M+H]^+$ 184.1126, found 184.1127.




Stereochemistry was assigned on the basis of nOe of proton on C-1 with the protons on C-2 and C-3.

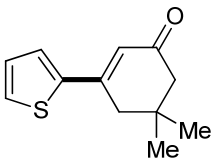
**4-(*N*-Boc-pyrrol-2-yl)-1,2,5,6-tetrahydro-1-tosylpyridine (8d):**




The general procedure was used with 47.6 mg (0.23 mmol) of *N*-Boc-2-pyrroleboronic acid, 1.0 mg (0.01 mmol) of $Pd(OAc)_2$, 3.7 mg (0.02 mmol) of SPhos, 48 mg of CsF (0.32 mmol) and 67.4 mg (0.25 mmol) of 4-chloro-1,2,5,6-tretrahydro-1-tosylpyridine in isopropanol (1.2 ml, 0.2 M). The reaction mixture was heated at 85 °C for 6 hours. The remaining residue was purified via flash column chromatography using 25% ether in pentane ($R_f$ = 0.38) to afford the title compound **8d** as a light yellow oil in 95% yield (86.7 mg, 0.215 mmol): $^1$H NMR (400

MHz, $CDCl_3$): δ (ppm) 7.70 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.16 (m, 1H), 6.08 (td, *J* = 0.8 Hz, 3.2 Hz, 1H), 5.97 (m, 1H), 5.64 (brs, 1H), 3.71 (q, *J* = 2.4 Hz, 2H), 3.29 (t, 5.6, 2H), 2.44 (brs, 5H), 1.54 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 148.9, 143.7, 135.6, 133.4, 131.2, 129.8, 127.9, 127.8, 122.19, 122.16, 113.4, 110.5, 83.9, 45.2, 43.3, 29.7, 28.1, 21.7; IR ($CH_2Cl_2$, $cm^{-1}$): 2968, 2915, 1742, 1333, 1163, 1142, 719, 549; HRMS (ESI) calcd for $C_{21}H_{26}N_2O_4NaS$ $[M+Na]^+$ 425.1511, found 425.1504.

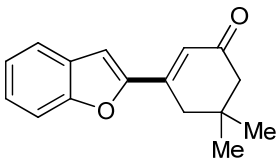
**3-(Thiophen-2-yl)-5,5-dimethyl-2-cyclohexen-1-one (9c):**




The general procedure was used with 112.8 mg (0.88 mmol) of thiophene-2-boronic acid, 7.9 mg (0.04 mmol) of $Pd(OAc)_2$, 29.0 mg (0.07 mmol) of SPhos, 187.6 mg of CsF (1.24 mmol) and 153.8 mg (0.97 mmol) of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one in isopropanol (4.4 ml, 0.2 M). The reaction mixture was heated at 85 °C for 10 hours. The remaining residue was purified via flash column chromatography using 20% ether in pentane ($R_f$ = 0.25) to afford the title compound **9c** as a yellow solid (mp: 62-64 °C) in 77% yield (139.4 mg, 0.68 mmol): $^1H$ NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41 (dd, *J* = 1.2 Hz, 2.8 Hz, 1H), 7.08 (dd, *J*= 1.2 Hz, 4.0 Hz, 1H), 6.40 (brs, 1H), 2.63 (d, *J* = 1.6 Hz, 2H), 2.30 (s, 2H), 1.11 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.6, 150.3, 143.1, 128.8, 128.4, 127.4, 121.7, 51.1, 42.1, 33.6, 28.5. IR ($CH_2Cl_2$, $cm^{-1}$): 2957, 1666, 1594, 1422, 1368, 829, 708; HRMS (ESI) calcd for $C_{12}H_{14}ONaS$ $[M+Na]^+$ 229.0663, found 229.0651.

**Gram scale reaction:**

**3-(Benzofuran-2-yl)-5,5-dimethylcyclohex-2-en-1-one (2c)**:




The general procedure was used with 1.2 g (7.41 mmol) of benzofuran-2-boronic acid, 33.2 mg (0.15 mmol) of $Pd(OAc)_2$, 122.0 mg (0.30 mmol) of SPhos, 1.58 g of CsF (10.37 mmol) and 1.41g (8.89 mmol) of 3-chloro-5,5-dimethyl-2-cyclohexen-1-one in isopropanol (37 ml, 0.2 M). The reaction mixture was heated at 85 °C for 12h. The remaining residue was purified via flash column chromatography using 20% ether in

pentane ($R_f$ = 0.3) to afford the title compound **2c** as a light yellow solid in 83% yield (1.47 g, 6.12 mmol). For spectroscopic data, see above.

**References:**

(1) R. M. Carballo, M. A. Ramírez, M. L. Rodríguez, V. S. Martín and J. I. Padrón, *Org. Lett.* 2006, **8**, 3837-3840.

(2) The spectral data for the protodeboronated indole **1a'** was consistent with the reported reference; M. Chakrabarty, T. Kundu and Y. Harigaya, *Synth. Commun.* 2006, **36**, 2069-2077.