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Manuscript title: Pd(0)-Catalyzed Cross Coupling Reactions of Boron Derivatives with a Lactam-Derived *N*-Boc Enol Triflate

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Supporting Information

Chromatographic separations were performed under pressure on silica gel using flash-column techniques; R_f values refer to TLC carried out on 25-mm silica gel plates (Merck F254), with the same eluant indicated for the column chromatography. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50.33 MHz, respectively.

6-[(*E*)-Hex-1-enyl]-3,4-dihydro-2*H*-pyridine-1-carboxylic acid tert-butyl ester (**4a**). To a solution of **2** (93 mg, 0.28 mmol) in THF (4 mL) were added, under a nitrogen atmosphere, $(Ph_3P)_2PdCl_2$ (10 mg, 14 μmol), **3a** (85 mg, 0.42 mmol), and a 2 M aqueous Na_2CO_3 solution (1 mL) leaving the mixture under stirring for 6 h at 40 °C. Water (10 mL) was then added, the mixture extracted with diethyl ether and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded a brown oil which was purified by chromatography (CH_2Cl_2-petroleum ether 1:2, R_f 0.15) to give **4a** (61 mg, 82%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.85 (d, J = 15.6 Hz, 1 H), 5.67 (m, 1 H), 5.19 (t, J = 3.8 Hz, 1 H), 3.50 (t, J = 5.2 Hz, 2 H), 2.09 (m, 4 H), 1.75 (m, 2 H), 1.41 (s, 9 H), 1.29 (m, 4 H), 0.86 (t, J = 6.6 Hz, 3 H); ^{13}C-NMR ($CDCl_3$): δ 147.5 (s), 138.5 (s), 128.4 (d), 127.8 (d), 112.9 (d), 80.3 (s), 44.4 (t), 32.2 (t), 31.5 (t), 28.3 (q, 3 C), 23.5 (t), 23.4 (t), 22.4 (t), 14.0 (q). Anal. Calcd for $C_{16}H_{27}NO_2$: C, 72.41; H, 10.25; N, 5.28. Found: C, 72.11; H, 10.43; N, 5.01.

6-[(*E*)-Styryl]-3,4-dihydro-2*H*-pyridine-1-carboxylic acid tert-butyl ester (**4b**). To a solution of **2** (80 mg, 0.24 mmol) in THF (4 mL) were added, under a nitrogen atmosphere $(Ph_3P)_2PdCl_2$ (9 mg, 12 μmol), **3b** (80 mg, 0.36 mmol), and a 2 M aqueous Na_2CO_3 solution (1 mL) leaving the mixture under stirring for 6 h at 40 °C. Water (10 mL) was then added, the mixture extracted with diethyl ether and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded a brown oil which was purified by chromatography (CH_2Cl_2-petroleum ether 1:2, R_f 0.14) to give **4b** (52 mg, 76%) as a

colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.40-7.13 (m, 5 H), 6.55 (AB system, 2 H), 5.43 (t, *J* = 3.8 Hz, 1 H), 3.57 (m, 2 H), 2.22 (m, 2 H), 1.79 (m, 2 H), 1.37 (s, 9 H); ^{13}C-NMR ($CDCl_3$): δ 137.4 (s), 128.5 (d, 2 C), 128.2 (s), 127.9 (s), 127.7 (d), 127.1 (d), 126.3 (d), 126.2 (d, 2 C), 115.7 (d), 80.5 (s), 44.4 (t), 28.3 (q, 3 C), 23.7 (t), 23.4 (t). Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.61; H, 8.46; N, 4.77.

6-[(*E*)-(1-Ethyl-but-1-enyl)-3,4-dihydro-2*H*-pyridine-1-carboxylic acid tert-butyl ester (**4c**). To a solution of **2** (52 mg, 0.16 mmol) in THF (2 mL) were added, under a nitrogen atmosphere, $(Ph_3P)_2PdCl_2$ (11 mg, 15 μmol), **3c** (64 mg, 0.32 mmol), and a 2 M aqueous Na_2CO_3 solution (1 mL) leaving the mixture stirring for 6 h at 40 °C. Water (10 mL) was then added, the mixture extracted with diethyl ether and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded **4c** (33 mg, 77%) as an oil: ^{1}H NMR ($CDCl_3$) δ 5.37 (t, *J* = 7.0 Hz, 1 H), 5.12 (t, *J* = 3.7 Hz, 1 H), 3.51 (m, 2 H), 2.36-1.98 (m, 6 H), 1.76 (m, 2 H), 1.38 (s, 9 H), 0.96 (t, *J* = 7.7 Hz, 3 H), 0.85 (t, *J* = 7.3 Hz, 3 H); ^{13}C-NMR ($CDCl_3$) δ 141.0 (s), 126.9 (s), 126.1 (d), 113.1 (d), 112.1 (s), 80.2 (s), 44.3 (t), 28.3 (q, 3 C), 23.8 (t), 23.4 (t), 21.4 (t), 21.0 (t), 14.3 (q), 13.3 (q). Anal. Calcd for $C_{16}H_{27}NO_2$: C, 72.41; H, 10.25; N, 5.28. Found: C, 72.13; H, 10.03; N, 4.98.

5,6-Dihydro-4*H*-[2,3']bipyridinyl-1-carboxylic acid tert-butyl ester (**7**). To a solution of **2** (100 mg, 0.33 mmol) in THF (5 mL) were added, under a nitrogen atmosphere, $(Ph_3P)_2PdCl_2$ (11 mg, 15 μmol), **6a** (67 mg, 0.46 mmol), and a 2 M aqueous Na_2CO_3 solution (1.2 mL) leaving the mixture uder stirring for 2 h at 80 °C. Water (10 mL) was then added, the mixture was extracted with diethyl ether and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded **7** (78 mg, 91%) in sufficiently pure form: ^{1}H NMR ($CDCl_3$) δ 8.53 (d, *J* = 1.8 Hz, 1 H), 8.44 (dd, *J* = 4.6, 1.4 Hz, 1 H), 7.53 (d, *J* = 5.9 Hz, 1 H), 7.20 (m, 1 H), 5.34 (t, *J* = 3.7 Hz, 1 H), 3.70 (m, 2 H), 2.28 (td, *J* = 7.0, 3.7 Hz, 2 H), 1.86 (m, 2 H), 1.07 (s, 9 H); ^{13}C-NMR ($CDCl_3$): δ 147.6 (d), 146.6 (d), 137.2 (s), 132.4 (d), 131.8 (s), 128.4 (s), 122.6 (d), 116.6 (d), 80.6 (s), 44.2 (t), 27.6 (q, 3 C), 23.7 (t), 23.2 (t). Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.20; H, 7.74; N, 10.76. Found: C, 69.43; H, 7.62; N, 10.45.

6-Phenyl-3,4-dihydro-2*H*-pyridine-1-carboxylic acid tert-butyl ester (**8**). To a solution of **2** (70 mg, 0.21 mmol) in THF (3 mL) were added, under a nitrogen atmosphere, $(PPh_3)_2PdCl_2$ (8 mg, 11 μmol), **6b** (48 μL, 0.32 mmol), and 2 M aqueous

Na_2CO_3 solution (1 mL), leaving the mixture under stirring for 3 h at 40 °C. Water (10 mL) was then added, the mixture was extracted with diethyl ether and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded **8** (46 mg, 85%) in sufficiently pure form.

The same compound was obtained in 87% yield after 2 h at 40 °C starting from **2** (70 mg, 0.21 mmol) and phenylboronic acid **6c** with the same procedure as above, but adding 2 mL of the 2 M Na_2CO_3 solution to the reaction mixture. ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 5 H), 5.31 (t, J = 3.7 Hz, 1 H), 3.71 (m, 2 H), 2.26 (dt, J = 7.0, 3.7 Hz, 2 H), 1.87 (m, 2 H), 1.06 (s, 9 H); ^{13}C-NMR ($CDCl_3$): δ 140.8 (s), 131.9 (s), 128.7 (s), 127.8 (d, 2 C), 126.7 (d), 125.2 (d, 2 C), 115.0 (d), 80.3 (s), 44.4 (t), 27.7 (q, 3 C), 23.7 (t), 23.6 (t). Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 73.92; H, 8.34; N, 5.09.

4-Butyl-1,3-dioxo-2-phenyl-2,3,3a,5,7,8,9,9b-octahydro-1*H*,4*H*-pyrrolo[3,4-f]quinoline-6-carboxylic acid tert-butyl ester (**10**). *N*-phenyl-maleimide **9** (49 mg, 0.28 mmol) and **4a** (30 mg, 0.11 mmol) were left in refluxing benzene (2 mL) for 2 h under a nitrogen atmosphere. After evaporation of the solvent, the crude yellow oil was purified by chromatography (CH_2Cl_2-petroleum ether 1:2, R_f 0.06) affording pure **10** (35 mg, 74%): ^{1}H NMR ($CDCl_3$) δ 7.52-7.22 (m, 5 H), 3.93 (dt, J = 12.8, 4.0 Hz, 1 H), 3.42 (m, 1 H), 3.26 (dd, J = 8.0, 4.0 Hz, 1 H), 3.06 (m, 1 H), 2.75 (m, 1 H), 2.31 (m, 2 H), 2.07-1.11 (m, 10 H), 1.45 (s, 9 H), 0.90 (m, 3 H); ^{13}C-NMR ($CDCl_3$) δ 176.3 (s), 175.6 (s), 153.5 (s), 136.1 (s), 131.9 (s), 129.0 (d, 2 C), 128.4 (d), 126.5 (d, 2 C), 113.6 (s), 80.8 (s), 46.3 (d), 44.2 (t), 42.5 (d), 36.8 (d), 33.8 (t), 31.3 (t), 30.0 (t), 28.4 (q, 3 C), 26.3 (t), 23.5 (t), 22.8 (t), 14.1 (q); MS *m/z* 438 (M^+, 2), 382 (75), 57 (100). Anal. Calcd for $C_{26}H_{34}N_2O_4$: C, 71.20; H, 7.81; N, 6.39. Found: C, 71.51; H, 7.48; N, 6.52.

1,3-Dioxo-2,4-diphenyl-2,3,3a,5,7,8,9,9b-octahydro-1*H*,4*H*-pyrrolo[3,4-f]quinoline-6-carboxylic acid tert-butyl ester (**11**). Prepared as reported for compound **10**. Starting from **4b** (65 mg, 0.24 mmol), pure **11** (25 mg, 71%) was obtained after chromatography (EtOAc-petroleum ether, 1:3, R_f 0.29) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.55-7.20 (m, 10 H), 3.78 (dt, J = 13.2, 4.7 Hz, 1 H), 3.56 (m, 2 H), 3.42 (m, 2 H), 2.89 (m, 3 H), 2.11 (m, 1 H), 1.90 (m, 2 H), 1.47 (s, 9 H); ^{13}C-NMR ($CDCl_3$) δ 175.6 (s), 175.0 (s), 153.5 (s), 140.2 (s), 135.6 (s), 131.4 (s), 128.8 (d, 2 C), 128.3 (d, 3 C), 128.2 (d, 2 C), 127.0 (d), 126.4 (d, 2 C), 114.2 (s), 81.0 (s), 45.6 (d), 45.04 (d), 44.7 (t), 40.2 (d), 32.5 (t),

28.4 (q, 3 C), 26.7 (t), 23.4 (t); MS *m/z* 458 (M^+, 3), 402 (87), 57 (100). Anal. Calcd for $C_{28}H_{30}N_2O_4$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.49; H, 6.27; N, 6.03.