**Preparation and Suzuki-Miyaura Coupling Reactions of Tetrahydropyridine-2-boronic Acid
Pinacol Esters**

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EXPERIMENTAL

All solvents were degassed before use. Chromatographic separations were performed under pressure on silica gel using flash-column techniques; *R_f* values refer to TLC carried out on 0.25-mm silica gel plates with the same eluant indicated for the column chromatography. ¹H NMR spectra were recorded at 200 and 400 MHz; ¹³C NMR spectra at 50.33 MHz. Mass spectra were carried out by EI at 70 eV.

General procedure for the preparation of triflates 2a-c. To a solution prepared by diluting with 25 mL of THF a 0.5 M solution of KHMDS in toluene (8.75 mL, 4.38 mmol), cooled at -78 °C and under nitrogen atmosphere, was added dropwise a solution of **1a-c** (3.50 mmol) in THF (8 mL) and the resulting mixture was stirred for 1.5 h. Afterwards a solution of PhNTf₂ (4.38 mmol) in THF (6 mL) was added dropwise, and after 1 h the reaction mixture was allowed to warm to room temperature. After 1 h, a 10% NaOH solution (50 mL) was added, the mixture was extracted with Et₂O (3 x 50 mL) and the combined organic layers were washed with brine (2 x 30 mL), and dried for 30 min over anhydrous K₂CO₃. After filtration and evaporation of the solvent the crude oil was chromatographed:

2a:^{7j} (EtOAc-petroleum ether, 1:5, 1% Et₃N, *R_f* 0.38): colorless oil (1.020 g, 80%). ¹H NMR (200 MHz, CDCl₃) δ 7.37 (m, 5 H), 5.34 (t, *J* = 3.7 Hz, 1 H), 5.20 (s, 2 H), 3.69-3.66 (m, 2 H), 2.30-2.24 (m, 2 H), 1.81-1.76 (m, 2 H).

2b:^{7j} (EtOAc-petroleum ether, 1:8, 1% Et₃N, *R_f* 0.46): colorless oil (1.044 g, 90%). ¹H NMR (200 MHz, CDCl₃) δ 5.29 (t, *J* = 3.7 Hz, 1 H), 3.62-3.57 (m, 2 H), 2.30-2.22 (m, 2 H), 1.78-1.73 (m, 2 H), 1.49 (s, 9 H).

2c:^{7d} (EtOAc-petroleum ether, 1:8, 1% Et₃N, *R_f* 0.19): white solid (0.985 g, 73%). Mp 50-51 °C; ¹H NMR (200 MHz, CDCl₃) δ 7.78 (d, *J* = 8.1 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 5.45 (t, *J* = 3.7 Hz, 1 H), 3.67-3.62 (m, 2 H), 2.45 (s, 3 H), 2.18-2.09 (m, 2 H), 1.55-1.43 (m, 2 H).

6-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (4a). **Method A.** *N*-Cbz triflate **2a** (780 mg, 2.14 mmol) was dissolved in anhydrous dioxane (14 mL) in a two-necked flask under nitrogen atmosphere. To the solution were added, in the order, bis(pinacolato)diboron **3** (816 mg, 3.21 mmol), (Ph₃P)₂PdCl₂ (46 mg, 0.066 mmol), Ph₃P (34 mg, 0.13 mmol), and anhydrous K₂CO₃ (444 mg, 3.21 mmol). The mixture was heated with an oil bath to 90 °C and left under stirring for 7 h, after which time the reaction was complete (by TLC). After cooling to room temperature the mixture was diluted with Et₂O (60 mL) and washed with water (3 x 40 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, R_f 0.20) obtaining pure **4a** (623 mg, 85%) as a white solid.

Method B. *N*-Cbz triflate **2a** (183 mg, 0.5 mmol) was dissolved in anhydrous dioxane (2.5 mL) in a Schlenk flask under nitrogen atmosphere. To the solution were added, in the order, (dppf)PdCl₂ (11 mg, 0.015 mmol), pinacolborane **6** (109 µL, 0.75 mmol), Et₃N (206 µL, 1.5 mmol). The mixture was heated with an oil bath to 50°C and left under stirring for 2 h, after which time the reaction was complete (by TLC). After cooling to room temperature the mixture was diluted with Et₂O (15 mL) and washed with water (3 x 5 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, R_f 0.20) obtaining pure **4a** (122 mg, 71%) as a white solid: mp 65-66 °C; ¹H NMR (200 MHz, CDCl₃) δ 7.35-7.20 (m, 5 H), 5.28 (br s, 1 H), 5.20 (s, 2 H), 3.59-3.50 (m, 2 H), 2.09-2.02 (m, 2 H), 1.81-1.66 (m, 2 H), 1.31 (s, 12 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 155.6 (s), 135.5 (s), 133.0 (br), 128.2 (d, 2 C), 127.9 (d, 2 C), 127.6 (d), 114.5 (d), 82.8 (s, 2 C), 68.2 (t), 41.5 (t), 24.6 (q, 4 C), 21.7 (t), 21.2 (t); MS *m/z* (%) 343 (M⁺, 0.1), 194 (20), 152 (31), 91 (100). Anal. Calcd for C₁₉H₂₆BNO₄: C, 66.49; H, 7.64; N, 4.08. Found C, 66.84; H, 7.74; N, 4.01.

6-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid tert-Butyl Ester (4b). **Method A.** Prepared as reported for **4a**, **Method A**, starting from *N*-Boc

triflate **2b** (709 mg, 2.14 mmol). The crude oil was chromatographed (EtOAc-petroleum ether, 1:5, R_f 0.28) obtaining pure **4b** (536 mg, 81%) as a colorless oil.

Method B. Prepared as reported for **4a**, **Method B**, starting from *N*-Boc triflate **2b** (166 mg, 0.5 mmol). The crude oil was chromatographed (EtOAc-petroleum ether, 1:5, R_f 0.28) obtaining pure **4b** (93 mg, 60%) as a colorless oil: ^1H NMR (200 MHz, CDCl_3) δ 5.18 (t, J = 3.7 Hz, 1 H), 3.44-3.38 (m, 2 H), 2.06-2.01 (m, 2 H), 1.99-1.68 (m, 2 H), 1.49 (s, 9 H), 1.24 (s, 12 H); ^{13}C NMR (50.33 MHz, CDCl_3) δ 156.8 (s), 111.8 (br), 83.8 (s), 81.5 (s, 2 C), 40.9 (t), 28.3 (q, 3 C), 24.9 (q, 4 C), 21.5 (t), 21.0 (t); MS m/z (%) 309 (M^+ , 6), 209 (73), 195 (100), 153 (40), 126 (37). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{BNO}_4$: C, 62.15; H, 9.13; N, 4.53. Found C, 62.17; H, 9.16; N, 4.50.

6-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydro-pyridine (4c). **Method A.** Prepared as reported for **4a**, **Method A**, starting from *N*-Ts triflate **2c** (825 mg, 2.14 mmol). The crude oil was chromatographed (EtOAc-petroleum ether, 1:7, R_f 0.19) obtaining pure **4c** (536 mg, 81%) as a colorless oil.

Method B. Prepared as reported for **4a**, **Method B**, starting from *N*-Ts triflate **2c** (193 mg, 0.5 mmol) and heating with an oil bath to 90°C. The crude oil was chromatographed (EtOAc-petroleum ether, 1:7, R_f 0.19) obtaining pure **4c** (151 mg, 83%) as a colorless oil: ^1H NMR (200 MHz, CDCl_3) δ 7.75 (d, J = 6.6 Hz, 2 H), 7.27 (d, J = 6.6 Hz, 2 H), 5.57 (t, J = 4.0 Hz, 1 H), 3.39-3.33 (m, 2 H), 2.39 (s, 3 H), 1.94-1.85 (m, 2 H), 1.37-1.28 (m, 2 H), 1.33 (s, 12 H); ^{13}C NMR (50.33 MHz, CDCl_3) δ 143.3 (s), 135.6 (s), 129.5 (d, 2 C), 127.7 (d, 2 C), 122.9 (d), 84.0 (s, 2 C), 43.8 (t), 24.6 (q, 4 C), 22.1 (t), 21.5 (q), 19.6 (t); MS m/z (%) 363 (M^+ , 20), 305 (24), 247 (23), 203 (13), 139 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{BNO}_4\text{S}$: C, 59.51; H, 7.21; N, 3.86. Found C, 59.53; H, 7.24; N, 3.84.

6-Phenyl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (12).^{7j} **Method A.** $\text{Pd}(\text{OAc})_2$ (3.4 mg, 15 μmol), Ph_3P (8 mg, 30 μmol) and boronate **4a** (52 mg, 0.15 mmol) were

dissolved in anhydrous dioxane (1.5 mL) in a Schlenk flask under nitrogen atmosphere. To the solution was added bromobenzene (24 μ L, 0.23 mmol), followed by $K_3PO_4 \cdot H_2O$ (69 mg, 0.30 mmol) and the resulting mixture was heated at 100 °C. After 1.5 h the reaction was complete (by TLC) and the mixture was diluted with Et_2O (15 mL) and washed with water (30 mL). The organic phase was dried over Na_2SO_4 , filtered and concentrated. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et_3N , R_f 0.42) obtaining pure **12** (39 mg, 88%) as a colorless oil.

Method C. To a stirred solution of **4a** (52 mg, 0.15 mmol) in THF (2 mL) were added, under nitrogen atmosphere, 2 M $Na_2CO_3(aq)$ (1.5 mL), $(Ph_3P)_2PdCl_2$ (5.3 mg, 7.5 μ mol), and phenyl trifluoromethanesulfonate (50.9 mg, 0.23 mmol). The mixture was heated to 50 °C, left under stirring 1.5 h and, after cooling, diluted with water (10 mL) and extracted with Et_2O (3 x 10 mL). The organic phase was dried 30 min over K_2CO_3 and concentrated *in vacuo*. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et_3N , R_f 0.42) obtaining pure **12** (36 mg, 82%) as a colorless oil: 1H NMR (200 MHz, $CDCl_3$) δ 7.29-7.18 (m, 8 H), 6.79 (m, 2 H), 5.42 (t, J = 4.0 Hz, 1 H), 4.93 (s, 2 H), 3.83-3.76 (m, 2 H), 2.35-2.23 (m, 2 H), 1.97-1.83 (m, 2 H).

6-Phenyl-3,4-dihydro-2H-pyridine-1-carboxylic Acid tert-Butyl Ester (13).^{7j} $Pd(OAc)_2$ (6.5 mg, 29 μ mol), Ph_3P (15.2 mg, 58 μ mol) and boronate **4b** (89 mg, 0.29 mmol) were dissolved in anhydrous dioxane (2 mL) in a Schlenk flask under nitrogen atmosphere. To the solution was added $K_3PO_4 \cdot H_2O$ (133 mg, 0.58 mmol) followed by bromobenzene (45 μ L, 0.43 mmol), and the resulting mixture was heated at 90 °C. After 6 h the reaction was complete (by TLC) and the mixture was diluted with Et_2O (15 mL) and washed with water (30 mL). The organic phase was dried over Na_2SO_4 , filtered and concentrated. The crude oil was chromatographed (CH_2Cl_2 -petroleum ether, 1:2, 1% Et_3N , R_f 0.30) obtaining pure **13** (67 mg, 90%) as a colorless oil: 1H NMR (200 MHz, $CDCl_3$) δ 7.25 (m, 5 H), 5.31 (t, J = 3.7 Hz, 1 H), 3.74-3.69 (m, 2 H), 2.29-2.23 (m, 2 H), 1.89-1.83 (m, 2 H), 1.06 (s, 9 H).

6-Phenyl-1-(toluene-4-sulfonyl)-1,2,3,4-tetrahydropyridine (14). Prepared as reported for **13**, starting from Pd(OAc)₂ (5.5 mg, 24 μmol), Ph₃P (12.8 mg, 49 μmol) and boronate **4c** (89 mg, 0.24 mmol). After 6 h the reaction was complete (by TLC) and the mixture was diluted with Et₂O (15 mL) and washed with water (30 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated. The crude oil was chromatographed (EtOAc-petroleum ether, 1:6, 1% Et₃N, R_f 0.29) obtaining pure **14** (65 mg, 85%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.56 (d, *J* = 8.4 Hz, 2 H), 7.43-7.38 (m, 2 H), 7.32-7.22 (m, 5 H), 5.48 (t, *J* = 3.7 Hz, 1 H), 3.76-3.70 (m, 2 H), 2.42 (s, 3 H), 2.10-2.01 (m, 2 H), 1.46-1.41 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 143.3 (s), 139.7 (s), 139.2 (s), 136.6 (s), 129.3 (d, 2 C), 127.6 (d, 2 C), 127.5 (d, 3 C), 126.8 (d, 2 C), 119.8 (d), 46.8 (t), 22.7 (t), 21.5 (q), 20.0 (t); MS *m/z* (%) 313 (M⁺, 23), 156 (82), 104 (100), 91 (91). Anal. Calcd for C₁₈H₁₉NO₂S: C, 68.98; H, 6.11; N, 4.47. Found C, 68.99; H, 6.31; N, 4.31.

6-*o*-Tolyl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (15). Prepared as reported for **12**, **Method A**, starting from Pd(OAc)₂ (3.4 mg, 15 μmol), Ph₃P (7.9 mg, 30 μmol), boronate **4a** (52 mg, 0.15 mmol), K₃PO₄·H₂O (69 mg, 0.30 mmol) and 2-bromotoluene (27 μL, 0.23 mmol). The reaction was stopped after 2.5 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et₃N, R_f 0.34) obtaining pure **15** (40 mg, 87%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.26-7.07 (m, 7 H), 6.84-6.82 (m, 2 H), 5.12 (t, *J* = 3.7 Hz, 1 H), 4.86 (s, 2 H), 3.83-3.77 (m, 2 H), 2.32-2.23 (m, 2 H), 2.16 (s, 3 H), 1.99-1.86 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 154.3 (s), 139.9 (s), 139.1 (s), 135.8 (s), 134.8 (s), 129.9 (d), 128.2 (d), 128.1 (d, 2 C), 127.9 (d, 2 C), 127.7 (d), 126.9 (d), 125.5 (d), 116.4 (d), 67.4 (t), 44.3 (t), 23.3 (t, 2 C), 19.4 (q); MS *m/z* (%) 307 (M⁺, 42), 262 (41), 248 (67), 91 (100). Anal. Calcd for C₂₀H₂₁NO₂: C, 78.15; H, 6.89; N, 4.56. Found C, 78.11; H, 6.65; N, 4.61.

6-Naphthalen-1-yl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (16). Method A.

Prepared as reported for **12**, **Method A**, starting from Pd(OAc)₂ (3.4 mg, 15 μmol), Ph₃P (7.9 mg, 30 μmol), boronate **4a** (52 mg, 0.15 mmol), K₃PO₄·H₂O (69 mg, 0.30 mmol) and 1-bromonaphthalene (31 μL, 0.23 mmol). The reaction was stopped after 2 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et₃N, R_f 0.27) obtaining pure **16** (47 mg, 91%) as a colorless oil.

Method C. Prepared as reported for **12**, **Method C**, starting from **4a** (52 mg, 0.15 mmol), 2 M Na₂CO₃(aq) (1.5 mL), (Ph₃P)₂PdCl₂ (5.3 mg, 7.5 μmol), and 1-naphthyl trifluoromethanesulfonate (63 mg, 0.23 mmol). The mixture was heated to 50 °C and left under stirring 2 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et₃N, R_f 0.27) obtaining pure **16** (42 mg, 81%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.98-7.93 (m, 1 H), 7.83-7.78 (m, 1 H), 7.73-7.68 (m, 1 H), 7.51-7.26 (m, 4 H), 7.15-6.98 (m, 3 H), 6.52 (br-s, 2 H), 5.34 (t, *J* = 3.7 Hz, 1 H), 4.64 (s, 2 H), 3.99-3.93 (m, 2 H), 2.39-2.31 (m, 2 H), 2.07-1.98 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 154.4 (s), 151.1 (s), 138.1 (s), 133.4 (s), 133.5 (s), 132.2 (s), 128.3(d), 128.1 (d), 127.9 (d), 127.6 (d, 2 C), 127.5 (d, 3 C), 125.9 (d), 125.4 (d), 125.2 (d), 124.9 (d), 117.4 (d), 67.3 (t), 44.6 (t), 23.6 (t), 23.4 (t); MS *m/z* (%) 343 (M⁺, 67), 298 (76), 208 (35), 91 (100). Anal. Calcd for C₂₃H₂₁NO₂: C, 80.44; H, 6.16; N, 4.08. Found C, 80.22; H, 6.02; N, 4.13.

6-(3-Methoxyphenyl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (17).

Prepared as reported for **12**, **Method A**, starting from Pd(OAc)₂ (3.4 mg, 15 μmol), Ph₃P (7.9 mg, 30 μmol), boronate **4a** (52 mg, 0.15 mmol), K₃PO₄·H₂O (69 mg, 0.30 mmol) and 3-bromoanisole (28 μL, 0.23 mmol). The reaction was stopped after 2 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et₃N, R_f 0.21) obtaining pure **17** (45 mg, 93%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.30-7.15 (m, 5 H), 6.93-6.76 (m, 4 H), 5.44 (t, *J* = 3.7 Hz, 1 H), 4.93 (s, 2 H), 3.80-3.74 (m, 2 H), 3.72 (s, 3 H), 2.32-2.24 (m, 2 H), 1.94-1.82 (m, 2 H); ¹³C NMR

(50.33 MHz, CDCl₃) δ 159.6 (s), 155.0 (s), 141.5 (s), 139.7 (s), 135.8 (s), 129.1 (d), 128.1 (d, 2 C), 127.7 (d, 3 C), 117.7 (d), 116.4 (d), 113.0 (d), 110.5 (d), 67.5 (t), 55.2 (q), 45.1 (t), 23.5 (t, 2 C); MS m/z (%) 323 (M⁺, 43), 278 (46), 250 (22), 135 (31), 91 (100). Anal. Calcd for C₂₀H₂₁NO₃: C, 74.28; H, 6.55; N, 4.33. Found C, 73.99; H, 6.43; N, 4.10.

6-(4-Methoxyphenyl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (18).

Herrmann catalyst (1.4 mg, 1.5 μ mol) and boronate **4a** (52 mg, 0.15 mmol) were dissolved in anhydrous toluene (2 mL) in a Schlenk flask under nitrogen atmosphere. To the solution was added 4-bromoanisole (28 μ L, 0.23 mmol), followed by anhydrous K₂CO₃ (41.4 mg, 0.30 mmol) and the resulting mixture was heated at 110 °C. After 8 h the reaction was complete (by TLC) and the mixture was diluted with Et₂O (15 mL), washed with water (30 mL), and dried over Na₂SO₄. Evaporation of the solvent and chromatography (EtOAc-petroleum ether, 1:8, R_f 0.36) gave pure **18** (35 mg, 73%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.22-7.18 (m, 5 H), 6.82-6.76 (m, 4 H), 5.32 (t, J = 3.7 Hz, 1 H), 4.92 (s, 2 H), 3.79 (s, 3 H), 3.78-3.73 (m, 2 H), 2.30-2.23 (m, 2 H), 1.92-1.83 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 158.8 (s), 152.8 (s), 139.3 (s), 135.8 (s), 132.1 (d), 128.0 (d, 2 C), 127.5 (d, 2 C), 126.1 (d, 2 C), 115.6 (s), 114.8 (d), 113.4 (d, 2 C), 67.4 (t), 55.2 (q), 45.2 (t), 23.6 (t), 23.5 (t); MS m/z (%) 323 (M⁺, 16), 91 (100). Anal. Calcd for C₂₀H₂₁NO₃: C, 74.28; H, 6.55; N, 4.33. Found C, 74.21; H, 6.49; N, 4.38.

6-(3-Acetylphenyl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (19).

Prepared as reported for **12**, **Method A**, starting from Pd(OAc)₂ (3.4 mg, 15 μ mol), Ph₃P (7.9 mg, 30 μ mol), boronate **4a** (52 mg, 0.15 mmol), K₃PO₄·H₂O (69 mg, 0.30 mmol) and 3'-bromoacetophenone (30 μ L, 0.23 mmol). The reaction was stopped after 2 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:5, 1% Et₃N, R_f 0.15) obtaining pure **19** (45 mg, 89%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.80-7.79 (m, 2 H), 7.49-7.26 (m, 2 H), 7.17-7.14 (m, 3 H), 6.82 (br-s, 2 H),

5.46 (t, $J = 3.7$ Hz, 1 H), 4.90 (s, 2 H), 3.82-3.77 (m, 2 H), 2.50 (s, 3 H), 2.35-2.26 (m, 2 H), 1.96-1.83 (m, 2 H); ^{13}C NMR (50.33 MHz, CDCl_3) δ 197.9 (s), 154.7 (s), 140.4 (s), 139.0 (s), 136.9 (s), 135.5 (s), 129.7 (d), 128.3(d), 128.0 (d, 2 C), 127.8 (d, 3 C), 126.9 (d), 125.1 (d), 117.2 (d), 67.5 (t), 45.1 (t), 26.7 (q), 23.6 (t), 23.4 (t); MS m/z (%) 335 (M^+ , 6), 291 (24), 91 (100). Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_3$: C, 75.20; H, 6.31; N, 4.18. Found C, 74.97; H, 6.31; N, 3.99.

6-(4-Acetylphenyl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (20). Prepared as reported for **12**, **Method A**, starting from $\text{Pd}(\text{OAc})_2$ (3.4 mg, 15 μmol), Ph_3P (7.9 mg, 30 μmol), boronate **4a** (52 mg, 0.15 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (69 mg, 0.30 mmol) and 4'-bromoacetophenone (45 mg, 0.23 mmol). The reaction was stopped after 2 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:5, 1% Et_3N , R_f 0.21) obtaining pure **20** (43 mg, 87%) as a white solid: mp 71-72 $^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3) δ 7.82 (d, $J = 8.4$ Hz, 2 H), 7.34 (d, $J = 8.4$ Hz, 2 H), 7.18-7.15 (m, 3 H), 6.84 (br-s, 2 H), 5.53 (t, $J = 3.7$ Hz, 1 H), 4.92 (s, 2 H), 3.82-3.77 (m, 2 H), 2.58 (s, 3 H), 2.36-2.27 (m, 2 H), 1.96-1.84 (m, 2 H); ^{13}C NMR (50.33 MHz, CDCl_3) δ 197.5 (s), 154.7 (s), 144.5 (s), 139.1 (s), 135.7 (s), 135.6 (s), 128.3 (d, 3 C), 128.1 (d, 2 C), 127.8 (d, 2 C), 125.2 (d, 2 C), 118.2 (d), 67.6 (t), 45.0 (t), 26.5 (q), 23.7 (t), 23.3 (t); MS m/z (%) 335 (M^+ , 6), 296 (16), 91 (100). Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_3$: C, 75.20; H, 6.31; N, 4.18. Found C, 75.01; H, 6.05; N, 4.07.

6-(4-Nitrophenyl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (21). Prepared as reported for **12**, **Method A**, starting from $\text{Pd}(\text{OAc})_2$ (3.4 mg, 15 μmol), Ph_3P (7.9 mg, 30 μmol), boronate **4a** (52 mg, 0.15 mmol), $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ (69 mg, 0.30 mmol) and 1-bromo-4-nitrobenzene (45 mg, 0.23 mmol). The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et_3N , R_f 0.21) obtaining pure **21** (42 mg, 83%) as a white solid: mp 94-95 $^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3) δ 8.00 (d, $J = 8.8$ Hz, 2 H), 7.33 (d, $J = 8.8$ Hz, 2 H), 7.24-7.15 (m, 3 H), 6.89 (br-s, 2 H), 5.53 (t, $J = 4.0$ Hz, 1 H), 4.99 (s, 2 H), 3.80-3.75 (m, 2 H), 2.36-2.27 (m, 2 H), 1.95-1.83 (m, 2 H); ^{13}C NMR

(50.33 MHz, CDCl₃) δ 154.5 (s), 146.6 (s), 146.5 (s), 138.4 (s), 135.2 (s), 128.2 (d, 2 C), 128.1 (d, 2 C), 128.0 (d), 125.7 (d, 2 C), 123.5 (d, 2C), 119.4 (d), 67.8 (t), 44.9 (t), 23.7 (t), 23.2 (t); MS m/z (%) 338 (M⁺, 5), 294 (15), 91 (100). Anal. Calcd for C₁₉H₁₈N₂O₄: C, 67.44; H, 5.36; N, 8.28. Found C, 67.40; H, 5.08; N, 8.15.

5,6-Dihydro-4*H*-[2,2']bipyridinyl-1-carboxylic Acid Benzyl Ester (22). Prepared as reported for **12**, **Method A**, starting from Pd(OAc)₂ (3.4 mg, 15 μ mol), Ph₃P (7.9 mg, 30 μ mol), boronate **4a** (52 mg, 0.15 mmol), K₃PO₄·H₂O (69 mg, 0.30 mmol) and 2-bromopyridine (21 μ L, 0.23 mmol). The reaction was stopped after 5 h. The NMR analysis of the crude reaction mixture revealed a 45% conversion into **22**. Chromatography (EtOAc-petroleum ether, 1:1, 1% Et₃N, R_f 0.30) gave pure **22** (18 mg) in 40% yield. ¹H NMR (200 MHz, CDCl₃) δ 8.47 (m, 1 H), 7.51 (t, J = 6.2 Hz, 1 H), 7.32-7.15 (m, 5 H), 7.09 (m, 1 H), 6.92 (br-s, 1 H), 5.78 (t, J = 3.7 Hz, 1 H), 4.89 (s, 2 H), 3.81-3.76 (m, 2 H), 2.36-2.23 (m, 2 H), 1.96-1.86 (m, 2 H). ¹³C NMR (50.33 MHz, CDCl₃) δ 156.8 (s), 154.7 (s), 148.6 (d), 139.3 (s), 137.4 (s), 136.0 (d), 128.1 (d, 2 C), 127.7 (d, 2 C + 1 C), 121.8 (d), 120.1 (d), 118.7 (d), 67.5 (t), 44.9 (t), 23.6 (t), 23.4 (t). MS m/z (%) 294 (M⁺, 39), 91 (100). Anal. Calcd for C₁₈H₁₈N₂O₂: C, 73.45; H, 6.16; N, 9.52. Found C, 73.38; H, 6.07; N, 9.21.

5,6-Dihydro-4*H*-[2,3']bipyridinyl-1-carboxylic Acid Benzyl Ester (23). Prepared as reported for **12**, **Method A**, starting from Pd(OAc)₂ (3.4 mg, 15 μ mol), Ph₃P (7.9 mg, 30 μ mol), boronate **4a** (52 mg, 0.15 mmol), K₃PO₄·H₂O (69 mg, 0.30 mmol) and 3-bromopyridine (22 μ L, 0.23 mmol). The reaction was stopped after 4 h. The crude oil was chromatographed (EtOAc-petroleum ether, 2:3, 1% Et₃N, R_f 0.51) obtaining pure **23** (34 mg, 77%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 8.53 (m, 1 H), 8.41 (d, J = 4.8 Hz, 1 H), 7.48 (d, J = 7.7 Hz, 1 H), 7.24-7.07 (m, 4 H), 6.87 (br-s, 2 H), 5.43 (t, J = 3.7 Hz, 1 H), 4.91 (s, 2 H), 3.80-3.75 (m, 2 H), 2.33-2.25 (m, 2 H), 1.94-1.85 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 154.6 (s), 148.1 (d), 146.6 (d), 137.0 (s),

135.5 (s), 132.4 (s + d), 128.2 (d, 2 C), 127.9 (d), 127.8 (d, 2 C), 122.8 (d), 117.8 (d), 67.6 (t), 45.0 (t), 23.6 (t), 23.3 (t); MS m/z (%) 294 (M^+ , 24), 250 (53), 159 (21), 91 (100). Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found C, 73.27; H, 6.29; N, 9.26.

6-Thiophen-2-yl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (24). Prepared as reported for **18** starting from boronate **4a** (52 mg, 0.15 mmol), Herrmann catalyst (1.4 mg, 1.5 μ mol), 2-bromothiophene (22 μ L, 0.23 mmol) and anhydrous K_2CO_3 (41.4 mg, 0.30 mmol). The reaction was stopped after 7 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et_3N , R_f 0.44) obtaining pure **24** (36 mg, 81%) as a colorless oil: 1H NMR (200 MHz, $CDCl_3$) δ 7.36-7.12 (m, 5 H), 6.96-6.91 (m, 3 H), 5.56 (t, J = 4.0 Hz, 1 H), 5.00 (s, 2 H), 3.77-3.74 (m, 2 H), 2.32-2.23 (m, 2 H), 1.91-1.80 (m, 2 H); ^{13}C NMR (50.33 MHz, $CDCl_3$) δ 155.1 (s), 143.2 (s), 135.7 (s), 134.1 (s), 128.1 (d, 2 C), 127.7 (d), 127.6 (d, 2 C), 126.7 (d), 123.8 (d), 122.5 (d), 116.3 (d), 67.6 (t), 45.3 (t), 23.4 (t, 2 C); MS m/z (%) 299 (M^+ , 64), 254 (53), 164 (55), 91 (100). Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found C, 68.22; H, 5.74; N, 4.64.

6-Thiophen-3-yl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (25). Prepared as reported for **12**, **Method A**, starting from $Pd(OAc)_2$ (3.4 mg, 15 μ mol), Ph_3P (7.9 mg, 30 μ mol), boronate **4a** (52 mg, 0.15 mmol), $K_3PO_4 \cdot H_2O$ (69 mg, 0.30 mmol) and 3-bromothiophene (21 μ L, 0.23 mmol) and anhydrous K_2CO_3 (41.4 mg, 0.30 mmol). The reaction was stopped after 2 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:11, 1% Et_3N , R_f 0.25) obtaining pure **25** (28 mg, 62%) as a colorless oil: 1H NMR (200 MHz, $CDCl_3$) δ 7.37-6.93 (m, 8 H), 5.48 (t, J = 3.7 Hz, 1 H), 4.99 (s, 2 H), 3.78-3.72 (m, 2 H), 2.30-2.24 (m, 2 H), 1.90-1.81 (m, 2 H); ^{13}C NMR (50.33 MHz, $CDCl_3$) δ 154.8 (s), 140.9 (s), 135.0 (s), 133.1 (s), 128.2 (d), 127.9 (d, 2 C), 127.3 (d, 2 C), 126.7 (d), 124.6 (d), 118.9 (d), 115.0 (d), 67.2 (t), 44.8 (t), 23.2 (t), 23.1 (t); MS m/z (%) 299

(M^+ , 4), 254 (4), 164 (3), 91 (100). Anal. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68. Found C, 68.07; H, 5.67; N, 4.73.

6-Furan-3-yl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (26). Prepared as reported for **12**, **Method C**, starting from **4a** (52 mg, 0.15 mmol), 2 M $Na_2CO_3(aq)$ (1.5 mL), $(Ph_3P)_2PdCl_2$ (5.3 mg, 7.5 μ mol), and 3-bromofuran (20 μ L, 0.23 mmol). The mixture was heated to 50 °C, left under stirring 3 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et_3N , R_f 0.34) obtaining pure **26** (30 mg, 71%) as a colorless oil: 1H NMR (200 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5 H), 7.12-7.08 (m, 2 H), 6.36 (m, 1 H), 5.43 (t, J = 3.5 Hz, 1 H), 5.06 (s, 2 H), 3.76-3.69 (m, 2 H), 2.29-2.18 (m, 2 H), 1.89-1.80 (m, 2 H); ^{13}C NMR (50.33 MHz, $CDCl_3$) attributable signals: δ 142.2 (d), 138.2 (d), 128.2 (d), 127.7 (d), 127.6 (d), 114.8 (d), 108.7 (d), 67.5 (t), 45.1 (t), 23.6 (t), 23.3 (t); MS m/z (%) 283 (M^+ , 8), 91 (100). Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found C, 72.19; H, 5.89; N, 4.88.

6-Cyclohex-1-enyl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (27). Prepared as reported for **12**, **Method C**, starting from **4a** (109 mg, 0.32 mmol), 2 M $Na_2CO_3(aq)$ (4 mL), $(Ph_3P)_2PdCl_2$ (17 mg, 23.6 μ mol), and trifluoromethanesulfonic acid cyclohex-1-enyl ester (110 mg, 0.48 mmol). The mixture was heated to 55 °C and left under stirring 1 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:12, R_f 0.38) obtaining pure **27** (64 mg, 67%) as a colorless oil: 1H NMR (200 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5 H), 5.72 (br m, 1 H), 5.22 (t, J = 4.0 Hz, 1 H), 5.12 (s, 2 H), 3.64-3.58 (m, 2 H), 2.22-2.12 (m, 2 H), 1.99 (br m, 4 H), 1.86-1.77 (m, 2 H), 1.49 (br m, 4 H); ^{13}C NMR (50.33 MHz, $CDCl_3$) δ 155.0 (s), 142.0 (s), 136.3 (s), 135.8 (s), 128.2 (d, 2 C), 127.8 (d, 2 C), 127.7 (d), 122.2 (d), 112.5 (d), 67.4 (t), 45.0 (t), 26.2 (t), 25.2 (t), 23.6 (t), 23.1 (t), 22.5 (t), 22.2 (t); MS m/z (%) 297 (M^+ , 37), 252 (23), 206 (44), 91 (100). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found C, 76.61; H, 7.99; N, 4.38.

6-Propenyl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (28). Prepared as reported for **12**, **Method C**, starting from **4a** (52 mg, 0.15 mmol), 2 M Na₂CO₃(aq) (1.5 mL), (Ph₃P)₂PdCl₂ (5.3 mg, 7.5 μmol), and *trans*-1-bromo-1-propene (19 μL, 0.23 mmol). The mixture was heated to 50 °C and left under stirring 2 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et₃N, R_f 0.40) obtaining pure **28** (30 mg, 78%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.37-7.29 (m, 5 H), 5.93 (d, *J* = 15.4 Hz, 1 H), 5.68 (dq, *J* = 15.4, 6.2 Hz, 1 H), 5.27 (t, *J* = 4.0 Hz, 1 H), 5.15 (s, 2 H), 3.64-3.58 (m, 2 H), 2.21-2.16 (m, 2 H), 1.81-1.73 (m, 2 H), 1.69 (d, *J* = 6.2 Hz, 3 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 154.6 (s), 138.1 (s), 136.2 (s), 129.1 (d), 128.2 (d, 2 C), 127.8 (d, 2 C), 127.7 (d), 123.1 (d), 113.6 (d), 67.3 (t), 44.8 (t), 23.5 (t), 23.2 (t), 17.9 (q); MS *m/z* (%) 257 (M⁺, 11), 198 (16), 91 (100). Anal. Calcd for C₁₆H₁₉NO₂: C, 74.68; H, 7.44; N, 5.44. Found C, 74.71; H, 7.54; N, 5.39.

6-Hex-1-enyl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (29).^{7j} Prepared as reported for **12**, **Method C**, starting from **4a** (52 mg, 0.15 mmol), 2 M Na₂CO₃(aq) (1.5 mL), (Ph₃P)₂PdCl₂ (5.3 mg, 7.5 μmol), and *trans*-1-iodo-1-hexene (47 mg, 0.23 mmol). The mixture was heated to 50 °C and left under stirring 5 h. The crude oil was chromatographed (EtOAc-petroleum ether, 1:8, 1% Et₃N, R_f 0.46) obtaining pure **29** (35 mg, 78%) as a colorless oil: ¹H NMR (CDCl₃) δ 7.34 (m, 5 H), 6.02-5.86 (m, 1 H), 5.72-5.41 (m, 1 H), 5.21-5.00 (m, 1 H), 5.15 (s, 2 H), 3.70 (m, 2 H), 2.02 (m, 2 H), 1.74 (m, 4 H), 1.34-1.15 (m, 6 H), 0.87 (t, *J* = 6.6 Hz, 3 H).

6-Styryl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (30). Prepared as reported for **12**, **Method C**, starting from **4a** (52 mg, 0.15 mmol), 2 M Na₂CO₃(aq) (1.5 mL), (Ph₃P)₂PdCl₂ (5.3 mg, 7.5 μmol), and *trans*-2-iodo-vinylbenzene (52 mg, 0.23 mmol). The mixture was heated to 50 °C and left under stirring 2 h. The crude oil was chromatographed (EtOAc-petroleum ether,

1:8, 1% Et₃N, R_f 0.24) obtaining pure **30** (36 mg, 75%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.39-7.13 (m, 10 H), 6.59 (m, 2 H), 5.53 (t, *J* = 4.0 Hz, 1 H), 5.15 (s, 2 H), 3.70-3.65 (m, 2 H), 2.27-2.22 (m, 2 H), 1.87-1.82 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 154.9 (s), 144.9 (s), 138.3 (s), 137.2 (s), 128.6 (d), 128.4 (d, 2 C), 128.3 (d, 2 C), 128.0 (d, 2 C), 127.9 (d), 127.8 (d), 127.1 (d), 126.4 (d, 2 C), 116.3 (d), 67.6 (t), 44.8 (t), 23.5 (t), 23.3 (t); MS *m/z* (%) 319 (M⁺, 6), 274 (6), 228 (6), 184 (6), 91 (100). Anal. Calcd for C₂₁H₂₁NO₂: C, 78.97; H, 6.63; N, 4.39. Found C, 78.90; H, 6.70; N, 4.41.

6-Benzoyl-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (31). Boronate **4a** (52 mg, 0.15 mmol) was dissolved in THF (2 mL) in a Schlenk flask under nitrogen atmosphere. To the solution were added, in the order, (Ph₃P)₂PdCl₂ (10 mg, 15 μmol), benzoyl chloride (50 μL, 0.43 mmol), 4 M Na₂CO₃(aq) (0.37 mL, 1.5 mmol). The mixture was heated with an oil bath to 55°C and left under stirring for 3 h, after which time the reaction was complete (by TLC). After cooling to room temperature the mixture was diluted with diluted with water (10 mL) and extracted with Et₂O (3 x 10 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated. The crude oil was chromatographed (EtOAc-petroleum ether, 1:5, R_f 0.24) obtaining pure **31** (25 mg, 52%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.71 (br-s, 2 H), 7.52-7.06 (m, 8 H), 5.73 (t, *J* = 3.7 Hz, 1 H), 4.91 (br-s, 2 H), 3.79-3.74 (m, 2 H), 2.33-2.25 (m, 2 H), 1.97-1.85 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 191.3 (s), 153.4 (s), 138.6 (s), 136.4 (s), 132.4 (d + s), 129.0 (d), 128.2 (d, 3 C), 128.1 (d, 2 C), 128.0 (d), 121.6 (d), 67.9 (t), 43.3 (t), 22.9 (t), 22.6 (t); MS *m/z* (%) 321 (M⁺, 11), 222 (21), 91 (100). Anal. Calcd for C₂₀H₁₉NO₃: C, 74.75; H, 5.96; N, 4.36. Found C, 74.71; H, 5.79; N, 4.42.

6-(4-Methoxy-benzoyl)-3,4-dihydro-2H-pyridine-1-carboxylic Acid Benzyl Ester (32). Boronate **4a** (26 mg, 75 μmol), was dissolved in THF (1 mL) in a Schlenk flask under nitrogen

atmosphere. To the solution were added, in the order, (Ph₃P)₂PdCl₂ (5 mg, 7.5 μmol), 4-methoxybenzoyl chloride (38 mg, 0.23 mmol), 2 M Na₂CO₃(aq) (0.37 mL, 0.75 mmol). The mixture was heated with an oil bath to 55°C and left under stirring for 2.5 h, after which time the reaction was complete (by TLC). After cooling to room temperature the mixture was diluted with diluted with water (10 mL) and extracted with Et₂O (3 x 10 mL). The organic phase was dried over Na₂SO₄, filtered and concentrated. The crude oil was chromatographed (EtOAc-petroleum ether, 1:5, R_f 0.18) obtaining pure **32** (20 mg, 76%) as a colorless oil: ¹H NMR (200 MHz, CDCl₃) δ 7.71 (br-s, 2 H), 7.24-7.06 (m, 5 H), 6.81 (d, *J* = 8.4 Hz, 2 H), 5.66 (t, *J* = 4.0 Hz, 1 H), 4.91 (br-s, 2 H), 3.82 (s, 3 H), 3.78-3.73 (m, 2 H), 2.31-2.23 (m, 2 H), 1.93-1.87 (m, 2 H); ¹³C NMR (50.33 MHz, CDCl₃) δ 189.8 (s), 162.7 (s), 153.1 (s), 138.2 (s), 132.5 (s), 131.0 (d + s), 127.9 (d), 127.7 (d, 2 C), 127.6 (d, 2 C), 120.4 (d), 113.1 (d, 2 C), 67.6 (t), 55.1 (q), 43.1 (t), 22.6 (t), 22.4 (t); MS *m/z* (%) 351 (M⁺, 15), 91 (100). Anal. Calcd for C₂₁H₂₁NO₄: C, 71.78; H, 6.02; N, 3.99. Found C, 72.00; H, 5.98; N, 4.01.