Supporting Information

for

Phosphine-free Suzuki cross-coupling reaction using an efficient and reusable Pd catalyst in an aqueous medium under microwave irradiation.

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General experimental details.

All reagents were purchased from Sigma Aldrich and used without further purification. Ethanol were purchased from Controltec Química Fina Ltda-Brasil and Vetec Ltda-Brasil. The analyses by Gas Chromatography–Mass Spectrometry (CG-MS) were performed on a Shimadzu GCMS-QP2010S with a RTX-5MS capillary column (30 m x 0.25 mm x 0.25 µm, with the stationary phase 5% diphenyl and 95% dimethylpolysiloxane), mass detector in mode electron ionization (EI) standard (70 eV), with helium as a carrier gas. The ¹H- and ¹³C-NMR spectra were recorded on a Bruker AMX-200 spectrometer operating at 200 MHz (¹H) and 50 MHz (¹³C) in CDCl₃ with TMS as an internal standard. The ¹H- and ¹³C-NMR spectra were processed using MESTREC/NMR. Melting points were determined on a Fisatom 430 apparatus and are uncorrected.

Description of the Microwave Apparatus

Microwave reactions were conducted using a commercially available monomode microwave unit (CEM Discover). The machine consists of a continuous focused microwave power delivery system

with operator selectable power output from 0 to 300 W. Reactions were performed in a 10-mL round-bottom flask. The contents of the vessel were stirred by means of a rotating magnetic plate located below the floor of the microwave cavity and a Teflon coated magnetic stir bar in the vessel. Temperature, pressure, and power profiles were monitored using commercially available software provided by the microwave manufacturer. The temperature of the contents of the vessel was monitored using a fiber-optic probe inserted directly into the reaction mixture by means of a glass thermowell.

General Procedure for the Microwave-Assisted Suzuki Reactions

In a 10 mL glass tube were placed halide (1.0 mmol), 2-formylphenyl or 2-pyridyl MIDA boronate (1.5 mmol) or allyl MIDA boronate, K_2CO_3 (3.0 mmol), Pd EnCat30 (6 mol %) and ethanol:H₂O (4:1 v/v) or water, and a magnetic stir bar. The vessel was sealed with a septum and placed into the microwave cavity. The temperature being ramped from rt to 120 °C or 135°C. Once the reaction temperature was reached, the reaction mixture was held at this temperature for 10-18 min. After the mixture was allowed to cool to room temperature, the reaction vessel was opened and the contents were poured into a separating funnel. Water and ethyl acetate (3 x10 mL) were added. The combined organics were dried over Na₂SO₄, filtered and concentrated *in vacuo*. The organic residue was adsorbed onto silica gel, and then purified by column flash chromatography (hexane/ethyl acetate as eluent) to afford the desired product **1a-x**. The biaryls, bipyridines or allylphenols prepared are known compounds.^[23-45] The products were confirmed by comparing the ¹H NMR and mass spectral data with authentic samples reported in the literature. The spectral data of all products are given below:

4'-Acetyl-[1,1'-biphenyl]-2-carbaldehyde (1a).^[23] 4-bromoacetophenone (105 mg, 0.526 mmol), 2-formylphenylboronic acid MIDA ester (165 mg, 0.79 mmol), potassium carbonate (217 mg, 1.58 mmol), Pd EnCat30 (79 mg, 0.031 mmol), 4:1 aq. ethanol (4 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 10:1 hexane:ethyl acetate) to provide **1a** as a colorless oil (86 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 2.67 (s, 3H), 7.43-7.61 (m, 3 H), 7.63-7.72 (m, 2 H), 8.02-8.09 (m, 3 H), 9.97 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 26.9, 128.3, 128.6, 128.7, 129.7, 130.0, 130.3, 130.5, 130.8, 133.9, 136.8, 142.9, 144.7, 191.9, 197.7. Anal. Calcd for C₁₅H₁₂O₂: C, 80.34; H, 5.39%. Found: C, 80.54; H, 5.15%.

4'-Nitro-[1,1'-biphenyl]-2-carbaldehyde (1b).^[24] 4-iodonitrobenzene (91 mg, 0.365 mmol), 2-formylphenylboronic acid MIDA ester (114 mg, 0.548 mmol), potassium carbonate (117 mg, 1.095 mmol), Pd EnCat30 (56 mg, 0.022 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 8:1 hexane:ethyl acetate) to provide **1b** as a light yellow solid (70 mg, 89% yield), mp 118-120 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 7.6 Hz, 1 H), 7.57-7.67 (m, 4 H), 7.72 (t, *J* = 7.5 Hz, 1 H), 8.04 (d, *J* = 7.6 Hz, 1 H), 8.34 (d, *J* = 8.3 Hz, 1 H), 9.97 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 123.8, 129.1, 129.3, 130.8, 131.0, 133.8, 134.1, 143.2, 145.0, 147.9, 191.2. Anal. Calcd for C₁₃H₉NO₃: C, 68.72; H, 3.99; N 6.16%. Found: C, 68.55; H, 3.80; N 6.21%.

[1,1'-Biphenyl]-2,4'-dicarbaldehyde (1c).^[25] 4-bromobenzaldehyde (104 mg, 0.561 mmol), 2-formylphenylboronic acid MIDA ester (221 mg, 0.842 mmol), potassium carbonate (234 mg, 1.69 mmol), Pd EnCat30 (84.2 mg, 0.033 mmol), 4:1 aq. ethanol (4 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 7:1 hexane:ethyl acetate) to provide **1c** as a white solid (114 mg, 97% yield), mp 94-96 °C. ¹H NMR (400 MHz,

CDCl_3) δ 7.27-7.74 (m, 5 H), 7.98-8.08 (m, 3 H), 9.98 (s, 1H), 10.11 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 128.4, 128.8, 129.8, 130.7, 130.8, 133.8, 133.9, 136.0, 144.3, 144.4, 191.6, 191.8. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2$: C, 79.98; H, 4.79%. Found: C, 80.12; H, 4.64%.

4'-Methoxy-[1,1'-biphenyl]-2-carbaldehyde (1d).^[26] 4-iodoanisole (68 mg, 0.290 mmol), 2-formylphenylboronic acid MIDA ester (113 mg, 0.435 mmol), potassium carbonate (121 mg, 0.87 mmol), Pd EnCat30 (43.2 mg, 0.017 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO_2 , 15:1 hexane:ethyl acetate) to provide **1d** as a colorless oil (51 mg, 83% yield). ^1H NMR (400 MHz, CDCl_3) δ 3.88 (s, 3H), 7.01 (d, J = 8.8 Hz, 2 H), 7.31 (d, J = 8.8 Hz, 2 H), 7.42-7.46 (m, 2H), 7.62 (t, J = 7.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 10.0 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.6, 114.2, 127.6, 127.8, 130.3, 131.0, 131.5, 133.7, 134.0, 145.9, 159.9, 192.9. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$: C, 79.22; H, 5.70%. Found: C, 79.10; H, 5.59%.

4'-Methyl-[1,1'-biphenyl]-2-carbaldehyde (1e).^[27] 4-bromotoluene (90 mg, 0.53 mmol), 2-formylphenylboronic acid MIDA ester (205 mg, 0.792 mmol), potassium carbonate (219 mg, 1.59 mmol), Pd EnCat30 (79.5 mg, 0.032 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO_2 , 20:1 hexane:ethyl acetate) to provide **1e** as a light yellow oil (83 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 2.40 (s, 3H), 7.22-7.30 (m, 4H), 7.39 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.60 (td, J = 7.5, 1.2 Hz, 1H), 8.00 (dd, J = 8.2, 1.2 Hz, 1H), 9.97 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 114.4, 127.3, 127.6, 130.6, 130.9, 131.5, 133.9, 134.1, 146.0, 159.8, 192.8. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.68; H, 6.16%. Found: C, 85.73; H, 6.27%.

2-(Pyridin-4-yl)benzaldehyde (1f).^[28] 4-bromopyridine hydrochloride (72 mg, 0.392 mmol),

2-formylphenylboronic acid MIDA ester (153 mg, 0.59 mmol), potassium carbonate (162 mg, 1.17 mmol), Pd EnCat30 (59.2 mg, 0.023 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 3:2 hexane:ethyl acetate) to provide **1f** as a light orange solid (69 mg, 95% yield); mp 64-66 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.35 (m, 2 H), 7.43 (d, *J* = 7.5 Hz, 1 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.73 (dt, *J* = 7.5, 1.5 Hz, 1 H), 8.07 (d, *J* = 7.5 Hz, 1 H), 8.72 (dd, *J* = 6.2, 1.1 Hz, 2 H), 9.98 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 124.9, 128.6, 129.2, 130.5, 133.6, 134.0, 142.9, 146.1, 150.0, 191.3. Anal. Calcd for C₁₂H₉NO: C, 78.67; H, 4.95; N, 7.65%. Found: C, 78.81; H, 4.77; N, 7.60%.

2-(Pyridin-3-yl)benzaldehyde (1g).^[29] 3-bromopyridine (70 mg, 0.44 mmol), 2-formylphenylboronic acid MIDA ester (139 mg, 0.66 mmol), potassium carbonate (184 mg, 1.33 mmol), Pd EnCat30 (66 mg, 0.026 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 5:1 hexane:ethyl acetate) to provide **1g** as a colorless oil (76 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.46 (m, 2 H), 7.58 (d, *J* = 7.5 Hz, 1 H), 7.60 (t, *J* = 7.5 Hz, 1 H), 7.73 (d, *J* = 7.5 Hz, 1 H), 8.06 (d, *J* = 7.5 Hz, 1 H), 8.70 (dd, *J* = 6.4, 1.5 Hz, 2 H), 9.99 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 123.3, 128.7, 128.9, 131.2, 133.8, 133.9, 134.1, 137.4, 142.0, 149.5, 150.3, 191.5. Anal. Calcd for C₁₂H₉NO: C, 78.67; H, 4.95; N, 7.65%. Found: C, 78.90; H, 4.78; N, 7.76%.

2-(Thiophen-2-yl)benzaldehyde (1h).^[29] 2-bromothiophene (80 mg, 0.48 mmol), 2-formylphenylboronic acid MIDA ester (192 mg, 0.732 mmol), potassium carbonate (202 mg, 1.46 mmol), Pd EnCat30 (73.6 mg, 0.029 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 30:1 hexane:ethyl acetate) to provide **1h** as a light yellow oil (81 mg, 90% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.07-7.14 (m,

1 H), 7.15-7.18 (m, 1 H), 7.46-7.49 (m, 3 H), 7.60 (d, $J = 8.2$ Hz, 1 H), 8.01 (d, $J = 7.5$ Hz, 1 H), 10.20 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 127.5, 127.9, 128.0, 128.4, 129.7, 131.5, 133.7, 134.4, 138.2, 138.9, 192.2. Anal. Calcd for $\text{C}_{11}\text{H}_8\text{OS}$: C, 70.18; H, 4.28%. Found: C, 70.10; H, 4.16%.

[1,1'-Biphenyl]-2,2'-dicarbaldehyde (1i).^[30] 2-bromobenzaldehyde (90 mg, 0.486 mmol), 2-formylphenylboronic acid MIDA ester (190 mg, 0.73 mmol), potassium carbonate (201 mg, 1.46 mmol), Pd EnCat30 (72 mg, 0.03 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO_2 , 10:1 hexane:ethyl acetate) to provide **1i** as a light yellow oil (90 mg, 88% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.34 (dd, $J = 1.0, 7.8$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.66 (dt, $J = 1.2, 7.6$ Hz, 2H), 8.06 (dd, $J = 1.0, 7.8$ Hz, 2H), 9.83 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.1, 141.3, 134.7, 133.5, 131.8, 128.9, 128.7. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_2$: C, 79.98; H, 4.79%. Found: C, 80.09; H, 4.67%.

4'-Hydroxy-2'-methyl-[1,1'-biphenyl]-2-carbaldehyde (1j).^[31] 4-chloro-3-methylphenol (70 mg, 0.491 mmol), 2-formylphenylboronic acid MIDA ester (192 mg, 0.73 mmol), potassium carbonate (203 mg, 1.47 mmol), Pd EnCat30 (73 mg, 0.0294 mmol) in water (3 mL) were irradiated for 16 min. HCl aqueous solution (10%, 4 mL) was added to the reaction mixture to acidify the solution with vigorous stirring. After work-up the residue was purified by flash column chromatography (SiO_2 , 1:1 hexane:ethyl acetate) to provide **1j** as a white solid (87 mg, 84% yield); mp 148-150 °C. ^1H NMR (400 MHz, CDCl_3) δ 2.51 (s, 3H), 7.27-7.17 (m, 2H), 7.35 (d, $J = 7.4$ Hz, 1H), 7.60-7.55 (m, 2H), 7.87-7.90 (m, 2H), 9.86 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 55.5, 114.1, 121.4, 128.6, 128.7, 132.3, 133.3, 133.6, 133.7, 134.8, 135.4, 139.7, 155.6, 195.9. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}_2$: C, 79.22; H, 5.70%. Found: C, 79.33; H, 5.59%.

4-Hydroxy-[1,1'-biphenyl]-2,2'-dicarbaldehyde (1k).^[32] 2-bromo-5-hydroxybenzaldehyde (70 mg, 0.348 mmol), 2-formylphenylboronic acid MIDA ester (135 mg, 0.522 mmol), potassium carbonate (140 mg, 1.04 mmol), Pd EnCat30 (52 mg, 0.020 mmol) in water (3 mL) were irradiated for 16 min. HCl aqueous solution (10%, 4 mL) was added to the reaction mixture to acidify the solution with vigorous stirring. After work-up the residue was purified by flash column chromatography (SiO₂, 5:1 hexane:ethyl acetate) to provide **1k** as light yellow solid (59 mg, 75% yield); m.p. 131-134 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.12-7.25 (m, 2 H), 7.30 (d, *J* = 7.5 Hz, 1 H), 7.58-7.62 (m, 2 H) 7.69 (t, *J* = 7.5 Hz, 1 H), 8.02 (d, *J* = 7.6 Hz, 1 H), 9.80 (s, 1 H), 9.85 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 112.8, 122.0, 128.8, 128.9, 132.4, 133.5, 133.7, 133.8, 134.9, 135.7, 141.2, 157.0, 191.3, 192.0. Anal. Cald for C₁₄H₁₀O₃: C, 74.33; H, 4.40%. Found: C, 74.45; H, 4.28%.

2'-hydroxy-5'-nitro-[1,1'-biphenyl]-2-carbaldehyde (1l).^[33] 2-iodo-4-nitrophenol (90 mg, 0.339 mmol), 2-formylphenylboronic acid MIDA ester (132 mg, 0.509 mmol), potassium carbonate (140 mg, 1.018 mmol), Pd EnCat30 (51 mg, 0.020 mmol) in water (3 mL) were irradiated for 16 min. HCl aqueous solution (10%, 4 mL) was added to the reaction mixture to acidify the solution with vigorous stirring. After work-up the residue was purified by flash column chromatography (SiO₂, 2:1 hexane:ethyl acetate) to provide **1l** as yellow solid (59 mg, 70% yield); m.p. 134 - 136 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.55 (br.s, 1H), 7.09 (d, *J* = 9.0 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.30-7.41 (m, 3H), 8.06 (d, *J* = 2.8 Hz, 1H), 8.20 (dd, *J* = 9.0, 2.8 Hz, 1H), 9.76 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 188.6, 148.1, 141.2, 137.9, 133.1, 131.2, 130.5, 129.8, 128.3, 126.9, 126.5, 125.2, 122.7. Anal. Cald for C₁₃H₉NO₄: C, 64.20; H, 3.73; N, 5.76%. Found: C, 64.33; H, 3.79; N, 5.88%.

2-Methoxy-6-(4-nitrophenyl)pyridine (1m).^[34] 4-iodonitrobenzene (102 mg, 0.408 mmol), 6-methoxypyridylboronic acid MIDA ester (162 mg, 0.612 mmol), potassium carbonate (168 mg,

1.22 mmol), Pd EnCat30 (67 mg, 0.025 mmol), 4:1 aq. ethanol (4 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 10:1 hexane:ethyl acetate) to provide **1m** as a light yellow solid (79 mg, 84% yield); mp 104-106 °C. ¹H NMR (400 MHz, CDCl₃) δ 4.05 (s, 3H), 6.80 (d, *J* = 8.0 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.69 (t, *J* = 8.0 Hz, 1 H), 8.18-8.32 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ 53.6, 111.5, 114.0, 124.1, 127.5, 139.6, 145.2, 148.2, 152.2, 164.2. Anal. Calcd for C₁₂H₁₀N₂O₃: C, 62.60; H, 4.38; N, 12.17%. Found: C, 62.70; H, 4.24; N, 12.25%.

4-(6-Methoxypyridin-2-yl)acetophenone (1n).^[35] 4-bromoacetophenone (50 mg, 0.25 mmol), 6-methoxypyridylboronic acid MIDA ester (99 mg, 0.38 mmol), potassium carbonate (104 mg, 0.75 mmol), Pd EnCat30 (38 mg, 0.015 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 10:1 hexane:ethyl acetate) to provide **1n** as a white solid (45 mg, 81% yield); mp 73-75 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.64 (s, 3H), 4.05 (s, 3H), 6.75 (d, *J* = 8.0 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 8.01-8.16 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ 26.9, 53.5, 110.6, 113.7, 126.9, 128.9, 137.2, 139.5, 143.5, 153.4, 164.1, 198.0. Anal. Calcd for C₁₄H₁₃NO₂: C, 73.99; H, 5.77; N, 6.16%. Found: C, 74.06; H, 5.66; N, 6.09%.

4-(6-Methoxypyridin-2-yl)benzaldehyde (1o).^[36] 4-bromobenzaldehyde (60 mg, 0.32 mmol), 6-methoxypyridylboronic acid MIDA ester (128 mg, 0.48 mmol), potassium carbonate (134 mg, 0.96 mmol), Pd EnCat30 (49 mg, 0.019 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 10:1 hexane:ethyl acetate) to provide **1o** as a white solid (60 mg, 90% yield); mp 74-76 °C. ¹H NMR (400 MHz, CDCl₃) δ 4.05 (s, 3H), 6.77 (d, *J* = 7.6 Hz, 1 H), 7.42 (d, *J* = 7.6 Hz, 1 H), 7.67 (t, *J* = 7.6 Hz, 1 H),

7.96 (d, $J = 7.6$ Hz, 2 H), 8.22 (d, $J = 7.6$ Hz, 2 H), 10.07 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 53.5, 110.9, 113.9, 127.3, 130.2, 136.5, 139.5, 144.8, 153.2, 164.1, 192.1. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}_2$: C, 73.23; H, 5.20; N, 6.57%. Found: C, 73.35; H, 5.10; N, 6.50%.

2-Methoxy-6-(4-methoxyphenyl)pyridine (1p).^[37] 4-iodoanisole (50 mg, 0.21 mmol), 6-methoxypyridylboronic acid MIDA ester (84 mg, 0.32 mmol), potassium carbonate (89 mg, 0.63 mmol), Pd EnCat30 (32 mg, 0.013 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO_2 , 10:1 hexane:ethyl acetate) to provide **1p** as a colorless oil (39 mg, 87% yield). ^1H NMR (400 MHz, CDCl_3) δ 3.85 (s, 3H), 4.02 (s, 3H), 6.63 (d, $J = 7.8$ Hz, 1 H), 6.97 (d, $J = 8.0$ Hz, 1 H), 7.26 (d, $J = 8.0$ Hz, 1 H), 7.55 (t, $J = 8.0$ Hz, 1 H), 7.98-8.02 (m, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 53.3, 55.5, 108.5, 112.1, 114.2, 114.4, 127.9, 128.2, 132.0, 139.3, 154.6, 160.6, 163.9. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_2$: C, 72.54; H, 6.09; N, 6.51%. Found: C, 72.42; H, 6.18; N, 6.37%.

6-Methoxy-2,2'-bipyridine (1q).^[38] 2-bromopyridine (60 mg, 0.38 mmol), 6-methoxypyridylboronic acid MIDA ester (150 mg, 0.57 mmol), potassium carbonate (157 mg, 1.14 mmol), Pd EnCat30 (57 mg, 0.023 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO_2 , 15:1 hexane:ethyl acetate) to provide **1q** as a colorless oil (60 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3) δ 4.05 (s, 3H), 6.76 (d, $J = 8.0$ Hz, 1 H), 7.28-7.33 (m, 1 H), 7.74 (t, $J = 8.0$ Hz, 1 H), 7.80 (td, $J = 7.4$, 1.0 Hz, 1 H), 8.00 (d, $J = 7.4$ Hz, 1 H), 8.41 (d, $J = 7.5$ Hz, 1 H), 8.65 (dd, $J = 7.4$, 1.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3) δ 53.4, 111.2, 113.9, 121.2, 123.7, 136.9, 139.6, 149.3, 153.7, 156.3, 163.7. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}$: C, 70.95; H, 5.41; N, 15.04%. Found: C, 71.10; H, 5.28; N, 15.17%.

6'-Methoxy-5-nitro-2,2'-bipyridine (1r).^[39] 2-chloro-4-nitropyridine (65 mg, 0.41 mmol), 6-methoxypyridylboronic acid MIDA ester (163 mg, 0.62 mmol), potassium carbonate (170 mg, 1.23 mmol), Pd EnCat30 (62 mg, 0.025 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 10:1 hexane:ethyl acetate) to provide **1r** as a white solid (74 mg, 78% yield); mp 114-116 °C. ¹H NMR (400 MHz, CDCl₃) δ 4.06 (s, 3H), 6.88 (d, *J* = 7.8 Hz, 1 H), 7.76 (t, *J* = 7.6 Hz, 1 H), 8.13 (d, *J* = 7.4 Hz, 1 H), 8.57-8.64 (m, 2 H), 9.45 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 53.6, 113.4, 115.7, 121.0, 132.0, 139.8, 144.0, 144.9, 151.3, 161.1, 164.0. Anal. Calcd for C₁₁H₉N₃O₃: C, 57.14; H, 3.92; N, 18.17%. Found: C, 57.28; H, 3.80; N, 18.25%.

6-Methoxy-2,3'-bipyridine (1s).^[40] 3-bromopyridine (60 mg, 0.38 mmol), 6-methoxypyridylboronic acid MIDA ester (150 mg, 0.57 mmol), potassium carbonate (157 mg, 1.14 mmol), Pd EnCat30 (57 mg, 0.023 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 5:1 hexane:ethyl acetate) to provide **1s** as a colorless oil (63 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.03 (s, 3H), 6.74 (d, *J* = 8.0 Hz, 1 H), 7.35-7.41 (m, 2 H), 7.66 (t, *J* = 8.0 Hz, 1 H), 7.80 (dt, *J* = 8.0, 1.0 Hz, 1 H), 8.62 (dd, *J* = 8.0, 1.0 Hz, 1 H), 9.25 (s, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 53.5, 110.4, 114.0, 123.6, 134.1, 134.7, 139.5, 148.4, 149.8, 152.1, 164.2. Anal. Calcd for C₁₁H₁₀N₂O: C, 70.95; H, 5.41; N, 15.04 %. Found: C, 70.79; H, 5.32; N, 15.16 %.

6-Methoxy-2,4'-bipyridine (1t).^[41] 4-bromopyridine hydrochloride (80 mg, 0.41 mmol), 6-methoxypyridylboronic acid MIDA ester (163 mg, 0.61 mmol), potassium carbonate (170 mg, 1.23 mmol), Pd EnCat30 (62 mg, 0.025 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 2:1 hexane:ethyl

acetate) to provide **1t** as a colorless oil (62 mg, 81% yield). ¹H NMR (400 MHz, CDCl₃) δ 3.97 (s, 3H), 6.72 (dd, *J* = 8.3, 0.6 Hz, 1 H), 7.34 (dd, *J* = 7.4, 0.6 Hz, 1 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.81-7.87 (m, 2 H), 8.59-8.66 (m, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 53.5, 111.7, 113.6, 121.0, 139.5, 146.3, 140.4, 151.9, 164.2. Anal. Calcd for C₁₁H₁₀N₂O: C, 70.95; H, 5.41; N, 15.04 %. Found: C, 70.81; H, 5.30; N, 15.13 %.

2-(6-Methoxypyridin-2-yl)quinoline (1u).^[42] 2-bromoquinoline (70 mg, 0.33 mmol), 6-methoxypyridylboronic acid MIDA ester (133 mg, 0.50 mmol), potassium carbonate (139 mg, 1.00 mmol), Pd EnCat30 (50 mg, 0.020 mmol), 4:1 aq. ethanol (3 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 20:1 hexane:ethyl acetate) to provide **1u** as a white solid (68 mg, 84% yield); mp 79-81 °C. ¹H NMR (400 MHz, CDCl₃) δ 4.02 (s, 3H), 6.83 (d, *J* = 8.1 Hz, 1 H), 7.54 (t, *J* = 7.4 Hz, 1 H), 7.68-7.80 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1 H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.17-7.30 (m, 2H), 8.57 (d, *J* = 8.5 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 53.5, 111.5, 114.7, 119.2, 126.8, 127.7, 128.4, 129.6, 130.0, 136.7, 139.6, 148.1, 153.9, 156.3, 163.8. Anal. Calcd for C₁₅H₁₂N₂O: C, 76.25; H, 5.12; N, 11.86 %. Found: C, 76.13; H, 5.24; N, 11.69 %.

2-Methoxy-6-(thiophen-2-yl)pyridine (1v).^[43] 2-bromothiophene (100 mg, 0.61 mmol), 6-methoxypyridylboronic acid MIDA ester (240 mg, 0.92 mmol), potassium carbonate (253 mg, 1.83 mmol), Pd EnCat30 (91 mg, 0.036 mmol), 4:1 aq. ethanol (4 mL) were irradiated for 10 min. After work-up the residue was purified by flash column chromatography (SiO₂, 20:1 hexane:ethyl acetate) to provide **1v** as a light yellow oil (90 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃) δ 4.05 (s, 3H), 7.23 (dd, *J* = 3.6, 0.9 Hz, 1 H), 7.69 (dd, *J* = 5.1, 0.9 Hz, 1 H), 7.92 (dd, *J* = 5.1, 0.6 Hz, 1 H), 8.02 (dd, *J* = 8.0, 1.2 Hz, 1 H), 8.04 (t, *J* = 8.0, 1.2 Hz, 1 H), 8.49 (dd, *J* = 7.8, 1.2 Hz, 1 H). ¹³C

NMR (100 MHz, CDCl₃) δ 53.4, 108.9, 111.3, 124.3, 127.1, 127.9, 139.1, 144.9, 150.0, 163.5. Anal.

Anal. Cald for C₁₀H₉NOS: C, 62.80; H, 4.74; N, 7.32 %. Found: C, 62.67; H, 4.87; N, 7.41 %.

4-allylphenol (1w).^[44] 4-chlorophenol (100 mg, 0.77 mmol), allylboronic acid MIDA ester (230 mg, 1.16 mmol), potassium carbonate (322 mg, 2.33 mmol), Pd EnCat30 (116 mg, 0.046 mmol) in water (4 mL) were irradiated for 18 min. HCl aqueous solution (10%, 2 mL) was added to the reaction mixture to acidify the solution with vigorous stirring. After work-up the residue was purified by flash column chromatography (SiO₂, 3:1 hexane:ethyl acetate) to provide **1w** as light yellow oil; yield: 79 mg, 75%; ¹H NMR (400 MHz, CDCl₃) δ 3.35 (d, *J* = 6.5 Hz, 2 H), 5.05 - 5.11 (m, 2 H), 5.16 (s, 1 H), 5.98 - 6.08 (m, 1 H), 6.83 (dt, *J* = 8.4, 2.1 Hz, 2 H), 7.15 (dt, *J* = 8.4, 2.1 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃) δ 39.8, 115.1, 115.3, 130.0, 132.5, 137.9, 154.0. Anal. Cald for C₉H₁₀O: C, 80.56; H, 7.51 %. Found: C, 80.70; H, 7.62 %.

2-allyl-4-nitrophenol (1x).^[45] 2-iodo-4-nitrophenol (80 mg, 0.301 mmol), allylboronic acid MIDA ester (89 mg, 0.452 mmol), potassium carbonate (125 mg, 0.905 mmol), Pd EnCat30 (45 mg, 0.018 mmol) in water (3 mL) were irradiated for 10 min. HCl aqueous solution (10%, 2 mL) was added to the reaction mixture to acidify the solution with vigorous stirring. After work-up the residue was purified by flash column chromatography (SiO₂, 2:1 hexane:ethyl acetate) to provide **1x** as yellow solid; yield: 38 mg, 70%; m.p. 130- 133 °C ¹H NMR (400 MHz, CDCl₃) δ 3.30 (d, *J* = 6.4 Hz, 2 H), 5.01 - 5.09 (m, 2 H), 5.12 (br.s, 1 H), 6.01 - 6.11 (m, 1 H), 6.80 (d, *J* = 8.2 Hz, 1 H), 7.90 (s, 1 H), 7.92 (d, *J* = 8.2 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 30.1, 128.1, 128.5, 128.6, 128.8, 130.0, 136.8, 137.6, 138.5. Anal. Cald for C₉H₉NO₃: C, 60.33; H, 5.06; N, 7.82 %. Found: C, 60.45; H, 5.17; N, 7.70%.