P,O-Ferrocenes in Suzuki-Miyaura Couplings

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General Information. All experiments were carried out under an atmosphere of argon using standard Schlenk techniques. If necessary, solvents were dried and deoxygenated by standard procedures. NMR spectra were recorded in CDCl$_3$ with a Bruker Avance III 500 spectrometer (500.3, 125.7, and 202.5 MHz for $^1$H, $^{13}$C, and $^{31}$P NMR spectra, respectively). HRMS were recorded with a Bruker Daltonik micrOTOF-QII spectrometer (ESI-TOF). Elemental analyses were measured with a Thermo FlashAE 1112, indicated values are the average of two independent measurements. The HPLC measurements were performed with a Knauer system consisting of a pump WellChrom Mini-Star K-500 and an UV detector WellChrom K-2000 operating at 245 nm.

Materials. All starting materials were obtained from commercial suppliers and used without further purification except otherwise noted. Acenaphthene was sublimed twice prior to use. 1,1$\text{ClP(2-tolyl)}_2$, 2,1$\text{ClP(2-furyl)}_2$, 1-bromo-2-methylnaphthalene, 1-bromo-2-methoxy-naphthalene, 1-bromo-2,4,6-trimethylbenzene, 2-bromo-1,5-di-tert-butyl-3-methylbenzene, 9-bromoanthracene, (2-bromophenyl)diphenylphosphine, 2-bromo-2’,6’-dimethoxybiphenyl, 2-(2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate, 2-bromo-4-tert-butylphenol, and 2-methoxyphenylboronic acid were prepared according to published procedures.

Experimental Procedures

Synthesis of 2. To a solution of 1 (3.00 g, 8.8 mmol) in anhydrous n-hexane (15 mL) n-BuLi (2.5 M in n-hexane, 3.5 mL, 8.8 mmol, 1.0 equiv.) was added dropwise over 5 min. The mixture was stirred for 12 hours at ambient temperature. After cooling to $-30^\circ$C [Zn(thf)$_2$Cl$_2$] (2.97 g, 10.6 mmol, 1.2 equiv.) in anhydrous tetrahydrofuran (40 mL) was added in a single portion, stirred for 30 min and warmed to ambient temperature. Ortho-bromoiodobenze (2.99 g, 10.6 mmol, 1.2 equiv.) and [Pd(PPh$_3$)$_4$] (0.31 g, 0.26 mmol, 3 mol-%) were added and the reaction was heated to 70$^\circ$C for 60 hours. The reaction mixture was diluted with water (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were dried over MgSO$_4$ and concentrated.
under reduced pressure. The crude material obtained was purified by column chromatography on alumina (n-hexane : diethyl ether = 95:5 (v/v)). Ferrocene 2 was isolated as red oil (2.27 g, 4.6 mmol, 52% based on 1).

$^1$H NMR (500 MHz, CDCl$_3$, 25°C, TMS): $\delta = 0.78 - 1.05$ (m, 12 H), $1.24 - 1.40$ (m, 2 H), $1.62 - 1.70$ (m, 2 H), $2.14 - 2.23$ (m, 2 H), $3.47$ (ddd, $^3$J(H,H) = 10.6, 10.6, 4.2 Hz, 1 H; OCH), $3.78 - 3.84$ (m, 2 H; H$_\beta$-C$_5$H$_4$O), $3.98 - 4.01$ (m, 1 H; H$_\alpha$-C$_5$H$_4$O), $4.04 - 4.07$ (m, 1 H; H$_\alpha$-C$_5$H$_4$O), $4.32 - 4.36$ (m, 2 H; C$_5$H$_4$C), $4.70$ (pt, $^3$J(H,H) = 4.7 Hz, 2 H; C$_5$H$_4$C), $7.05$ (ddd, $^3$J(H,H) = 8.0, 7.4 Hz, $^4$J(H,H) = 1.7 Hz, 1 H; H-4/C$_6$H$_4$Br), 7.24 – 7.28 (m, 1 H; H-5/C$_6$H$_4$Br), 7.53 (dd, $^3$J(H,H) = 8.0 Hz, $^4$J(H,H) = 1.2 Hz, 1 H; H-3/C$_6$H$_4$Br), 7.81 ppm (dd, $^3$J(H,H) = 7.8 Hz, $^4$J(H,H) = 1.7 Hz, 1 H; H-6/C$_6$H$_4$Br); $^{13}$C{$_1^H$} NMR (125.7 MHz, CDCl$_3$, 25°C, TMS): $\delta = 16.5$ (1 C; CH(CH$_3$)$_2$), 20.9 (1 C; CH(CH$_3$)$_2$), 22.2 (1 C; CH$_3$), 23.4 (1 C; C-3/C$_6$H$_9$), 25.7 (1 C; CH(CH$_3$)$_2$), 31.4 (1 C; C-5/C$_6$H$_9$), 34.4 (1 C; C-4/C$_6$H$_9$), 40.5 (1 C; C-6/C$_6$H$_9$), 48.1 (1 C; C-2/C$_6$H$_9$), 58.1 (1 C; C$_\alpha$-C$_5$H$_4$O), 58.5 (1 C; C$_\alpha$-C$_5$H$_4$O), 63.79 (1 C; C$_\beta$-C$_5$H$_4$O), 63.80 (1 C; C$_\beta$-C$_5$H$_4$O), 69.3 (1 C; C$_5$H$_4$C), 69.4 (1 C; C$_5$H$_4$C), 71.0 (1 C; C$_5$H$_4$C), 71.3 (1 C; C$_5$H$_4$C), 80.9 (1 C; C-1/C$_6$H$_9$), 86.6 (1 C; i-C$_5$H$_4$C), 122.6 (1 C; C-2/C$_6$H$_4$Br), 125.8 (1 C; i-C$_5$H$_4$O), 126.8 (1 C; C-5/C$_6$H$_4$Br), 127.2 (1 C; C-4/C$_6$H$_4$Br), 132.4 (1 C; C-6/C$_6$H$_4$Br), 133.4 (1 C; C-3/C$_6$H$_4$Br), 139.1 ppm (1 C; C-1/C$_6$H$_4$Br); HRMS: m/z: calcd for C$_{26}$H$_{31}$BrFeO: 494.0904, found 494.0903 [M]$^+$.

**Synthesis of 3a.** To a solution of 2 (0.85 g, 1.7 mmol) in anhydrous tetrahydrofuran (10 mL) n-BuLi (2.5 M in n-hexane, 0.69 mL, 1.7 mmol, 1.0 equiv.) was added dropwise over 5 min at –78°C. The mixture was stirred for 1 hour at this temperature. Thereafter neat ClP(C$_6$H$_4$-2-CH$_3$)$_2$ (0.43 g, 1.7 mmol, 1.0 equiv) was added in a single portion, stirred for 30 min at –78°C and 90 min at ambient temperature. The reaction mixture was diluted with water (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were dried over MgSO$_4$ and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on alumina (n-hexane : diethyl ether = 90:10 (v/v)). Ferrocene 3a was isolated as orange solid after
recrystallization from n-pentane at −30°C (0.41 g, 0.66 mmol, 38% based on 2).

M.p. 97 – 99°C; 1H NMR (500 MHz, CDCl3, 25°C, TMS): δ = 0.74 – 1.06 (m, 12 H), 1.24 – 1.39 (m, 2 H), 1.61 – 1.70 (m, 2 H), 2.13 – 2.23 (m, 2 H), 2.27 (s, 6 H; C6H4CH3), 3.43 (ddd, 3J(H,H) = 10.6, 10.6, 4.2 Hz, 1 H; OCH), 3.63 (ddd, 3J(H,H) = 2.5, 2.4 Hz, 4J(H,H) = 1.4 Hz, 1 H; Hβ-C5H4O), 3.66 (ddd, 3J(H,H) = 2.5, 2.4 Hz, 4J(H,H) = 1.3 Hz, 1 H; Hβ-C5H4O), 3.93 (ddd, 3J(H,H) = 2.5 Hz, 4J(H,H) = 1.4, 1.4 Hz, 1 H; Hα-C5H4O), 3.95 (ddd, 3J(H,H) = 2.4 Hz, 4J(H,H) = 1.3 Hz, 1 H; Hα-C5H4O), 4.15 – 4.21 (m, 2 H; C3H6), 4.38 (s, 2 H; C3H4), 4.75 – 4.82 (m, 3 H; H-3/C6H4P, H-3/C6H4CH3), 7.05 – 7.11 (m, 3 H; H-4/C6H4P, H-4/C6H4CH3), 7.16 – 7.20 (m, 2 H; H-6/C6H4CH3), 7.23 (ddd, J = 7.4, 7.4, 1.2 Hz, 2 H; H-5/C6H4CH3), 7.33 (ddd, 3J(H,H) = 7.6, 7.6 Hz, 4J(H,H) = 1.4 Hz, 1 H; H-5/C6H4P), 7.98 ppm (ddd, 3J(H,H) = 7.8 Hz, 4J(H,H) = 1.1 Hz, 4J(P,H) = 4.4 Hz, 1 H; H-6/C6H4P); 13C{1H} NMR (125.7 MHz, CDCl3, 25°C, TMS): δ = 16.4 (1 C; CH(CH3)2), 21.0 (1 C; CH(CH3)2), 21.19 (d, 3J(P,C) = 21.4 Hz, 1 C; C6H4CH3), 21.21 (d, 3J(P,C) = 21.4 Hz, 1 C; C6H4CH3), 22.2 (1 C; CH3), 23.3 (1 C; C-3/C6H9), 25.6 (1 C; CH(CH3)2), 31.4 (1 C; C-5/C6H9), 34.4 (1 C; C-4/C6H9), 40.5 (1 C; C-6/C6H9), 48.0 (1 C; C-2/C6H9), 57.6 (1 C; Cα-C5H4O), 58.2 (m, 1 C; Cα-C5H4O), 63.9 (1 C; Cβ-C5H4O), 64.0 (1 C; Cβ-C5H4O), 69.36 (1 C; Cβ-C5H4C), 69.44 (1 C; Cβ-C5H4C), 71.5 (d, 4J(P,C) = 8.4 Hz, 1 C; Cα-C5H4C), 71.6 (d, 4J(P,C) = 8.8 Hz, 1 C; Cα-C5H4C), 80.6 (1 C; C-1/C6H9), 87.8 (d, 3J(P,C) = 7.3 Hz, 1 C; i-C5H4C), 125.5 (1 C; i-C5H4O), 125.9 (2 C; C-4/C6H4CH3), 126.1 (1 C; C-4/C6H4P), 128.1 (1 C; C-5/C6H4P), 128.4 (2 C; C-5/C6H4P), 130.0 (d, 3J(P,C) = 4.4 Hz, 1 C; C-6/C6H4CH3), 130.01 (d, 3J(P,C) = 4.5 Hz, 1 C; C-6/C6H4CH3), 131.4 (d, 3J(P,C) = 5.6 Hz, 1 C; C-6/C6H4P), 133.4 (m, 2 C; C-3/C6H4CH3), 134.0 (1 C; C-3/C6H4P), 134.2 (d, 1J(P,C) = 14.9 Hz, 1 C; C-2/C6H4P), 136.1 (d, 1J(P,C) = 13.0 Hz, 1 C; C-2/C6H4CH3), 136.2 (d, 1J(P,C) = 12.9 Hz, 1 C; C-2/C6H4CH3), 142.3 (d, 2J(P,C) = 26.4 Hz, 2 C; C-1/C6H4CH3), 144.8 ppm (d, 2J(P,C) = 27.2 Hz, 1 C; C-1/C6H4P); 31P{1H} NMR (202.5 MHz, CDCl3, 25°C, H3PO4): δ = −27.1 ppm (s); elemental analysis calcd (%) for C40H45FeOP: C 76.43, H 7.22; found: C 75.98, H 7.46.

**Synthesis of 3b.** To a solution of 2 (1.75 g, 3.5 mmol) in anhydrous tetrahydrofuran (15 mL)
$n$-BuLi (2.5 M in $n$-hexane, 1.4 mL, 3.5 mmol, 1.0 equiv.) was added dropwise over 5 min at $-78^\circ$C. The mixture was stirred for 1 hour at this temperature. Thereafter neat ClPPh$_2$ (0.78 g, 3.5 mmol, 1.0 equiv) was added in a single portion, stirred for 30 min at $-78^\circ$C and 90 min at ambient temperature. The reaction mixture was diluted with water (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were dried over MgSO$_4$ and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on alumina ($n$-hexane : diethyl ether = 90:10 (v/v)). Ferrocene 3b was isolated as orange oil (1.02 g, 1.70 mmol, 48 % based on 2).

$^1$H NMR (500 MHz, CDCl$_3$, 25 $^\circ$C, TMS): $\delta = 0.77 – 1.07$ (m, 12 H), 1.27 – 1.40 (m, 2 H), 1.63 – 1.71 (m, 2 H), 2.16 – 2.24 (m, 2 H), 3.47 (ddd, $^3$J(H,H) = 10.6, 10.6, 4.2 Hz, 1 H; OCH), 3.71 (ddd, $^3$J(H,H) = 2.6, 2.5 Hz, $^4$J(H,H) = 1.5 Hz, 1 H; H$_\beta$-C$_5$H$_4$O), 3.73 (ddd, $^3$J(H,H) = 2.6, 2.5 Hz, $^4$J(H,H) = 1.4, 1.4 Hz, 1 H; H$_\alpha$-C$_5$H$_4$O), 3.76 (ddd, $^3$J(H,H) = 2.6, 2.5 Hz, $^4$J(H,H) = 1.4, 1.4 Hz, 1 H; H$_\alpha$-C$_5$H$_4$O), 3.77 (ddd, $^3$J(H,H) = 2.6, 2.5 Hz, $^4$J(H,H) = 1.4, 1.4 Hz, 1 H; H$_\alpha$-C$_5$H$_4$O), 4.01 (ddd, $^3$J(H,H) = 2.6 Hz, $^4$J(H,H) = 1.4, 1.4 Hz, 1 H; H$_\beta$-C$_5$H$_4$C), 4.42 – 4.44 (m, 2 H; H$_\alpha$-C$_5$H$_4$C), 6.85 (ddd, $^3$J(H,H) = 7.8 Hz, $^3$J(P,H) = 4.1 Hz, 1 H; H-3/C$_6$H$_5$P), 7.12 (ddd, $^3$J(H,H) = 7.6, 7.5 Hz, $^4$J(H,H) = 1.2 Hz, 1 H; H-4/C$_6$H$_5$P), 7.21 – 7.26 (m, 4 H; o-C$_6$H$_5$), 7.29 – 7.37 (m, 7 H; H-5/C$_6$H$_5$P, m-C$_6$H$_5$, p-C$_6$H$_5$), 8.01 ppm (ddd, $^3$J(H,H) = 7.8 Hz, $^4$J(P,H) = 4.3 Hz, $^4$J(H,H) = 1.2 Hz, 1 H; H-6/C$_6$H$_5$P); $^{13}$C{${^1}$H} NMR (125.7 MHz, CDCl$_3$, 25 $^\circ$C, TMS): $\delta = 16.4$ (1 C; CH(CH$_3$)$_2$), 20.9 (1 C; CH(CH$_3$)$_2$), 22.2 (1 C; CH$_3$), 23.3 (1 C; C-3/C$_6$H$_9$), 25.6 (1 C; CH(CH$_3$)$_2$), 31.3 (1 C; C-5/C$_6$H$_9$), 34.3 (1 C; C-4/C$_6$H$_9$), 40.5 (1 C; C-6/C$_6$H$_9$), 48.0 (1 C; C-2/C$_6$H$_9$), 57.7 (1 C; C$_\alpha$-C$_5$H$_4$O), 58.2 (1 C; C$_\alpha$-C$_5$H$_4$O), 63.72 (1 C; C$_\beta$-C$_5$H$_4$O), 63.76 (1 C; C$_\beta$-C$_5$H$_4$O), 69.1 (1 C; C$_\beta$-C$_5$H$_4$C), 69.3 (1 C; C$_\beta$-C$_5$H$_4$C), 71.7 (d, $^4$J(P,C) = 8.4 Hz, 1 C; C$_\alpha$-C$_5$H$_4$C), 71.9 (d, $^4$J(P,C) = 8.5 Hz, 1 C; C$_\alpha$-C$_5$H$_4$C), 80.6 (1 C; C-1/C$_6$H$_9$), 88.1 (d, $^3$J(P,C) = 7.4 Hz, 1 C; i-C$_5$H$_4$C), 125.5 (1 C; i-C$_5$H$_4$O), 126.1 (1 C; C-4/C$_6$H$_5$P), 128.1 (1 C; C-5/C$_6$H$_5$P), 128.2 – 128.3 (m, 6 C; m-C$_6$H$_5$, p-C$_6$H$_5$), 131.4 (d, $^4$J(P,C) = 5.0 Hz, 1 C; C-6/C$_6$H$_5$P), 133.6 – 134.0 (m, 5 C; C-3/C$_6$H$_5$P, o-C$_6$H$_5$), 135.6 (d, $^1$J(P,C) = 16.0 Hz, 1 C; C-2/C$_6$H$_5$P), 137.94 (d, $^1$J(P,C) = 12.1 Hz, 1 C; i-C$_6$H$_5$), 137.96 ($^1$J(P,C) = 12.5 Hz, 1 C; i-C$_6$H$_5$), 144.4 ppm (d, $^2$J(P,C) = 26.3 Hz, 1 C;
C-1/C_6H_4P; \textsuperscript{31}P{\textsuperscript{1}H} NMR (202.5 MHz, CDCl_3, 25 °C, H_3PO_4): \( \delta = -12.1 \) ppm (s); HRMS: \( m/z: \) calcd for C_{38}H_{41}FeOP: 600.2240, found 600.2230 \([M]^+\).

**Synthesis of 3c.** To a solution of 2 (0.60 g, 1.2 mmol) in anhydrous tetrahydrofuran (10 mL) n-BuLi (2.5 M in n-hexane, 0.48 mL, 1.2 mmol, 1.0 equiv.) was added dropwise over 5 min at \(-78 \) °C. The mixture was stirred for 1 hour at this temperature. Thereafter neat ClP(2-Furyl)_2 (0.24 g, 1.2 mmol, 1.0 equiv) was added in a single portion, stirred for 30 min at \(-78 \) °C and 90 min at ambient temperature. The reaction mixture was diluted with water (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic extracts were dried over MgSO_4 and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on alumina (n-hexane : diethyl ether = 85:15 (v/v)). Ferrocene 3c was isolated as orange oil (0.24 g, 0.41 mmol, 34 % based on 2).

\( ^1H \) NMR (500 MHz, CDCl_3, 25 °C, TMS): \( \delta = 0.76 - 1.06 \) (m, 12 H), 1.24 – 1.38 (m, 2 H), 1.62 – 1.70 (m, 2 H), 2.14 – 2.23 (m, 2 H), 3.47 (ddd, \( ^3J(H,H) = 10.6, 10.6, 4.2 \) Hz, 1 H; OCH), 3.75 (ddd, \( ^3J(H,H) = 2.6, 2.5 \) Hz, \( ^4J(H,H) = 1.5 \) Hz, 1 H; \( \text{H}_\beta\text{-C}_5\text{H}_4\text{O} \)), 3.77 (ddd, \( ^3J(H,H) = 2.6, 2.5 \) Hz, \( ^4J(H,H) = 1.5 \) Hz, 1 H; \( \text{H}_\beta\text{-C}_5\text{H}_4\text{O} \)), 3.98 (ddd, \( ^3J(H,H) = 2.6 \) Hz, \( ^4J(H,H) = 1.4 \), 1.4 Hz, 1 H; \( \text{H}_\alpha\text{-C}_5\text{H}_4\text{O} \)), 4.04 (ddd, \( ^3J(H,H) = 2.6 \) Hz, \( ^4J(H,H) = 1.4 \), 1.4 Hz, 1 H; \( \text{H}_\alpha\text{-C}_5\text{H}_4\text{O} \)), 4.23 (ddd, \( ^3J(H,H) = 2.4, 2.4 \) Hz, \( ^4J(H,H) = 1.5 \) Hz, 1 H; \( \text{H}_\beta\text{-C}_5\text{H}_4\text{C} \)), 4.25 (ddd, \( ^3J(H,H) = 2.4, 2.4 \) Hz, \( ^4J(H,H) = 1.6 \) Hz, 1 H; \( \text{H}_\beta\text{-C}_5\text{H}_4\text{C} \)), 4.39 – 4.41 (m, 2 H; \( \text{H}_\alpha\text{-C}_5\text{H}_4\text{C} \)), 6.35 – 6.38 (m, 2 H; H-4/C_4H_3O), 6.52 – 6.55 (m, 2 H; H-3/C_4H_3O), 7.15 – 7.23 (m, 2 H; H-3 and H-4/C_6H_4P), 7.31 – 7.35 (m, 1 H; H-5/C_6H_4P), 7.59 – 7.61 (m, 2 H; H-5/C_4H_3O), 7.91 ppm (ddd, \( ^3J(H,H) = 7.7 \) Hz, \( ^4J(H,H) = 1.0 \) Hz, \( ^4J(P,H) = 4.7 \) Hz, 1 H; H-6/C_6H_4P); \( ^{13}C\{^1H\} \) NMR (125.7 MHz, CDCl_3, 25 °C, TMS): \( \delta = 16.4 \) (1 C; CH(CH(CH_3)_2), 21.0 (1 C; CH(CH(CH_3)_2), 22.2 (1 C; CH_3), 23.4 (1 C; C-3/C_6H_9), 25.7 (1 C; CH(CH(CH_3)_2), 31.4 (1 C; C-5/C_6H_9), 34.4 (1 C; C-4/C_6H_9), 40.5 (1 C; C-6/C_6H_9), 48.1 (1 C; C-2/C_6H_9), 57.9 (1 C; C_\alpha\text{-C}_5\text{H}_4\text{O}), 58.3 (1 C; C_\alpha\text{-C}_5\text{H}_4\text{O}), 63.68 (1 C; C_\beta\text{-C}_5\text{H}_4\text{O}), 63.72 (1 C; C_\beta\text{-C}_5\text{H}_4\text{O}), 69.1 (1 C; C_\beta\text{-C}_5\text{H}_4\text{C}), 69.2 (1 C; C_\beta\text{-C}_5\text{H}_4\text{C}), 71.6 (d, \( ^4J(P,C) = 8.2 \) Hz, 1 C; C_\alpha\text{-C}_5\text{H}_4\text{C}), 71.8 (d, \( ^4J(P,C) = 8.3 \) Hz, 1 C; C_\alpha\text{-C}_5\text{H}_4\text{C}), 80.8 (1 C; C-1/C_6H_9), 88.7 (d, \( ^3J(P,C) = \)
7.5 Hz, 1 C; i-C₅H₄C), 110.6 (d, ³J(P,C) = 5.3 Hz, 2 C; C-4/C₄H₃O), 121.01 (d, ²J(P,C) = 22.0 Hz, 1 C; C-3/C₄H₃O), 121.02 (d, ²J(P,C) = 22.6 Hz, 1 C; C-3/C₄H₃O), 125.6 (1 C; i-C₅H₄O), 126.2 (1 C; C-4/C₄H₄P), 128.5 (1 C; C-5/C₆H₄P), 131.8 (d, ⁴J(P,C) = 7.9 Hz, 1 C; C-6/C₆H₄P), 132.9 (1 C; C-1/C₆H₄P), 147.1 (m, 2 C; C-5/C₆H₃O), 151.2 ppm (d, ¹J(P,C) = 9.9 Hz, 2 C; C-2/C₄H₃O); ³¹P{¹H} NMR (202.5 MHz, CDCl₃, 25°C, H₃PO₄): δ = –55.4 ppm (s); HRMS: m/z: calcd for C₃₄H₃₇FeO₃P: 580.1825, found 580.1825 [M]+.

**Synthesis of 2-bromo-4-tert-butyl-1-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene.** 2-(2-(2-Methoxyethoxy)ethoxy)ethyl methanesulfonate (26.0 g, 107 mmol) and 2-bromo-4-tert-butylphenol (27.0 g, 118 mmol, 1.1 equiv.) were dissolved in toluene (250 mL), K₂CO₃ (29.7 g, 215 mmol, 2.0 equiv.) was added. The suspension was heated to reflux for 12 hours. After cooling to ambient temperature the reaction mixture was washed with water (2 x 150 mL), 2 M NaOH (2 x 150 mL) and water (2 x 150 mL). The organic phase was dried over MgSO₄ and concentrated under reduced pressure to yield the title compound as light yellow oil (37.9 g, 101 mmol, 94 % based on 2-(2-(2-methoxyethoxy)ethoxy)ethyl methanesulfonate).

¹H NMR (500 MHz, CDCl₃, 25°C, TMS): δ = 1.25 (s, 9 H; C(CH₃)₃), 3.33 (s, 3 H; OCH₃), 3.49 – 3.52 (m, 2 H; CH₂OCH₃), 3.61 – 3.66 (m, 4 H; CH₂), 3.74 – 3.77 (m, 2 H; CH₂CH₂OCH₂CH₂OCH₃), 3.83 – 3.87 (m, 2 H; ArOCH₂CH₂), 4.10-4.14 (m, 2 H; ArOCH₂), 6.82 (d, ³J(H,H) = 8.6 Hz, 1 H; H-6/C₆H₃), 7.20 (dd, ³J(H,H) = 8.6 Hz, ⁴J(H,H) = 2.3 Hz, 1 H; H-5/C₆H₃), 7.50 ppm (d, ⁴J(H,H) = 2.3 Hz, 1 H; H-3/C₆H₃); ¹³C{¹H} NMR (125.7 MHz, CDCl₃, 25°C, TMS): δ = 31.2 (3 C; C(CH₃)₃), 33.9 (1 C; C(CH₃)₃), 58.8 (1 C; OCH₃), 69.0 (1 C; ArOCH₂), 69.4 (1 C; ArOCH₂CH₂), 70.3 (1 C; CH₂CH₂OCH₃), 70.5 (1 C; CH₂OCH₂CH₂OCH₃), 70.9 (1 C; CH₂CH₂OCH₂CH₂OCH₃), 71.8 (1 C; CH₂OCH₃), 111.8 (1 C; C-2/C₆H₃), 113.2 (1 C; C-6/C₆H₃), 125.0 (1 C; C-5/C₆H₃), 130.2 (1 C; C-3/C₆H₃), 145.1 (1 C; C-4/C₆H₃), 152.8 ppm (1 C; C-1/C₆H₃); elemental analysis calcd (%) for C₁₇H₂₇BrO₄: C 54.41, H 7.25; found: C 54.51, H 7.27.
**General procedure for the Suzuki-Miyaura coupling.** An oven-dried Schlenk tube was charged with \([\text{Pd}_2(\text{dba})_3]\), \(3\) (Pd:P = 1:2 (n:n)), \(13\) the boronic acid (1.5 mmol, 1.5 equiv.), powdered, anhydrous K\(_3\)PO\(_4\) (637 mg, 3.0 mmol, 3.0 equiv.), and acenaphthene\(^{14}\) (154 mg, 1.0 mmol) as internal standard. The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was repeated three times). Dry toluene (2 mL) was added through the septum via syringe and the resulting mixture was stirred at ambient temperature for 5 min. The aryl halide (1.0 mmol, 1.0 equiv.) was added via syringe (solid aryl halides were added during the initial charge, prior to securation). The reaction mixture was heated at the given temperature with vigorous stirring for 24 hours. After cooling to ambient temperature, the reaction mixture was diluted with water (25 mL) and extracted with diethyl ether (3 \(\times\) 25 mL). The combined organic extracts were dried over MgSO\(_4\) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica (diethyl ether).

**Synthesis of 2,4-dinitrobiphenyl.** The general procedure for Suzuki-Miyaura couplings was applied, using 1-chloro-2,4-dinitrobenzene (203 mg) and phenylboronic acid (183 mg). The title compound was purified by flash chromatography on silica (diethyl ether) and isolated as yellow powder (234 mg, 96 % based on aryl halide).

M.p. 107 – 109 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 7.32 – 7.37\) (m, 2 H, C\(_6\)H\(_5\)), 7.45 – 7.50 (m, 3 H, C\(_6\)H\(_5\)), 7.68 (d, \(^3\)J(H,H) = 8.5 Hz, 1 H; H-6/C\(_6\)H\(_3\)), 8.46 (dd, \(^3\)J(H,H) = 8.5 Hz, \(^4\)J(H,H) = 2.3 Hz, 1 H; H-5/C\(_6\)H\(_3\)), 8.69 ppm (d, \(^3\)J(H,H) = 2.3 Hz, 1 H; H-3/C\(_6\)H\(_3\)); \(^{13}\)C\({}^1\)H NMR (125.7 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta = 119.6\) (1 C; C-3/C\(_6\)H\(_3\)), 126.4 (1 C; C-5/C\(_6\)H\(_3\)), 127.6 (2 C; \(p\)-C\(_6\)H\(_5\)), 129.0 (2 C; \(m\)-C\(_6\)H\(_5\)), 129.5 (1 C; \(p\)-C\(_6\)H\(_5\)), 133.2 (1 C; C-6/C\(_6\)H\(_3\)), 135.1 (1 C; \(i\)-C\(_6\)H\(_5\)), 142.2 (1 C; C-1/C\(_6\)H\(_3\)), 146.8 (1 C; C-4/C\(_6\)H\(_3\)), 149.0 ppm (1 C; C-2/C\(_6\)H\(_3\)); elemental analysis calcd (%) for C\(_{12}\)H\(_8\)N\(_2\)O\(_4\): C 59.02, H 3.30, N 11.47; found: C 59.16, H 3.32, N 11.20.

**Synthesis 5-\(\text{tert}\)-butyl-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy) biphenyl.** The general
procedure for Suzuki-Miyaura couplings was applied, using 2-bromo-4-tert-butyl-1-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (375 mg) and phenylboronic acid (183 mg). The title compound was purified by flash chromatography on silica (diethyl ether) and isolated as light yellow oil (365 mg, 98% based on aryl halide).

1H NMR (500 MHz, CDCl3, 25°C, TMS): δ = 1.36 (s, 9 H; C(CH3)3), 3.38 (s, 3 H; OCH3), 3.51 – 3.56 (m, 2 H; CH2OCH3), 3.58 – 3.65 (m, 6 H; CH2), 3.75 – 3.80 (m, 2 H; ArOCH2CH2), 4.09 – 4.13 (m, 2 H; ArOCH2), 6.94 (d, 3J(H,H) = 8.5 Hz, 1 H; H-3/C6H3), 7.29 – 7.44 (m, 5 H; H-4 and H-6/C6H3, o-C6H5, p-C6H5), 7.57 – 7.61 ppm (m, 2 H; m-C6H5); 13C{1H} NMR (125.7 MHz, CDCl3, 25°C, TMS): δ = 31.5 (3 C; C(CH3)3), 34.1 (1 C; C(CH3)3), 58.9 (1 C; OCH3), 68.4 (1 C; ArOCH2), 69.6 (1 C; ArOCH2CH2), 70.5 (1 C; CH2), 70.6 (1 C; CH2), 70.8 (1 C; CH2), 71.9 (1 C; CH2OCH3), 112.6 (1 C; C-3/C6H3), 125.1 (1 C; C-6/C6H3), 126.6 (1 C; p-C6H5), 127.8 (2 C; o-C6H5), 128.0 (1 C; C-4/C6H3), 129.6 (2 C; m-C6H5), 130.4 (1 C; i-C6H5), 139.0 (1 C; C-1/C6H3), 143.8 (1 C; C-5/C6H3), 153.5 ppm (1 C; C-2/C6H3); elemental analysis calcd (%) for C23H32O4: C 74.16, H 8.66; found: C 74.15, H 9.00.

Notes and References


(13) For reactions conducted at low catalyst loadings (≤ 0.5 mol-% Pd) stoichiometric solutions of [Pd$_2$(dba)$_3$] and 3 in toluene were prepared and were added to the Schlenk tube instead of the solvent.

(14) If determination of yields was based on isolated material, addition of internal standard has been omitted.