

Palladium-Catalyzed Hiyama Cross-Couplings of Aryl Arenesulfonates with Arylsilanes

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Supporting Information

1. General experimental methods (S2)
2. General experimental procedure and characterization data. (S2-S6)
3. References (S7)
4. Copies of ^1H , ^{13}C NMR spectra of products (S8-S47)

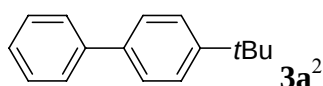
General experimental methods:

All reactions were performed in Schlenk tubes under nitrogen atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

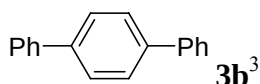
XPhos, TBAF (1.0 M in THF), triethoxy(thiophen-2-yl)silane and PhSi(OMe)₃ were purchased from Aldrich. PhSi(OEt)₃, 4-MeOC₆H₄Si(OMe)₃, 4-MeC₆H₄Si(OMe)₃, 4-CF₃C₆H₄Si(OMe)₃, 2-MeC₆H₄Si(OMe)₃ were prepared according to the reported procedure.¹

General procedure for the Hiyama couplings of aryl arenesulfonates:

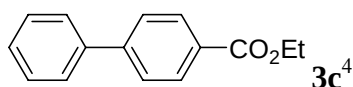
A test tube with stir bar was charged with Pd(OAc)₂ (2.2 mg, 4 mol %), Xphos (11.9 mg, 10 mol %) and arenesulfonate **1** (0.25 mmol). The tube was evacuated and back-filled with argon (this was repeated two additional times). siloxane **2** (2.0 equiv) and TBAF (0.5 mL, 1.0 M in THF) were added through syringe. The reaction mixture was allowed to stir at 80 °C. After cooling to room temperature, it was directly subjected to flash chromatography on silica gel to yield the desired products **3**.



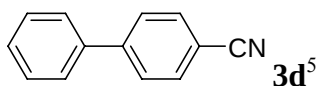
¹H NMR (CDCl₃, 400M Hz): δ (ppm) 1.39 (s, 9H), 7.34 (t, *J* = 7.3, 1H), 7.42–7.50 (m, 4H), 7.55–7.62 (m, 4H). ¹³C NMR (100M Hz): δ (ppm) 150.4, 141.2, 138.4, 128.8, 127.1(5), 127.1(0), 126.9, 125.8, 34.7, 31.5.



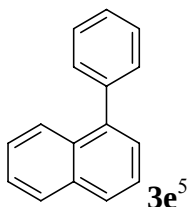
¹H NMR (CDCl₃, 400M Hz): δ (ppm) 7.37 (t, *J* = 7.3, 2H), 7.47 (t, *J* = 7.8, 4H), 7.55 (t, *J* = 8.2, 1H), 7.65–7.69 (m, 7H).



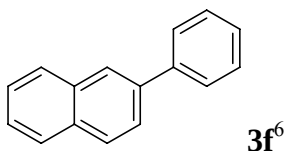
¹H NMR (400M Hz, CDCl₃): δ (ppm) 1.42 (t, *J* = 7.1, 3H), 4.38–4.44 (m, 2H), 7.39 (t, *J* = 7.3, 1H), 7.47 (t, *J* = 7.6, 2H), 7.62–7.67 (m, 4H), 8.12 (d, *J* = 8.2, 2H). ¹³C NMR (100M Hz): δ (ppm) 166.6, 145.6, 140.2, 130.2, 129.3, 129.0, 128.2, 127.4, 127.1, 61.1, 14.5.



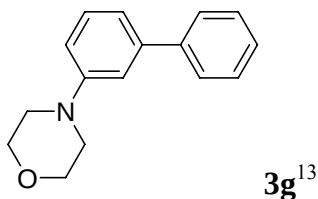
¹H NMR (400M Hz, CDCl₃): δ (ppm) 7.40-7.50 (m, 3H), 7.59 (d, *J* = 7.3, 2H), 7.66-7.73 (m, 4H). ¹³C NMR (100M Hz): δ (ppm) 145.8, 139.3, 132.7, 129.2, 128.8, 127.8, 127.3, 119.1, 111.0.



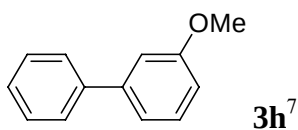
¹H NMR (400M Hz, CDCl₃): δ (ppm) 7.44-7.58 (m, 9H), 7.88-7.96 (m, 3H). ¹³C NMR (100M Hz): δ (ppm) 140.9, 140.4, 133.9, 131.8, 130.2, 128.4, 127.8, 127.4, 127.1, 126.2, 125.9, 125.5.



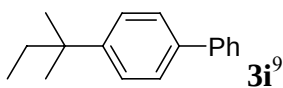
¹H NMR (400M Hz, CDCl₃): δ (ppm) 7.41 (t, *J* = 7.3, 1H), 7.50-7.55 (m, 4H), 7.75-7.79 (m, 3H), 7.88-7.95 (m, 3H), 8.07 (s, 1H). ¹³C NMR (100M Hz): δ (ppm) 141.2, 138.7, 133.8, 132.7, 129.0, 128.5, 128.3, 127.8, 127.6, 127.5, 126.4, 126.1, 125.9, 125.7.



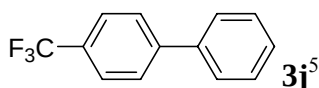
¹H NMR (400M Hz, CDCl₃): δ (ppm) 3.23 (t, *J* = 4.8, 4H), 3.90 (t, *J* = 4.8, 4H), 6.91-6.94 (m, 1H), 7.12-7.14 (m, 2H), 7.34-7.38 (m, 2H), 7.43-7.46 (m, 2H), 7.58-7.61 (m, 2H). ¹³C NMR (100M Hz): δ (ppm) 151.8, 142.5, 141.8, 129.7, 128.8, 127.4, 119.3, 114.9, 114.8, 67.1, 49.6.



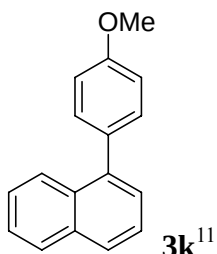
¹H NMR (400M Hz, CDCl₃): δ (ppm) 3.88 (s, 1H), 6.91-6.94 (m, 1H), 7.15-7.22 (m, 2H), 7.36-7.48 (m, 4H), 7.60-7.63 (m, 2H). ¹³C NMR (100M Hz): δ (ppm) 160.0, 142.9, 141.2, 129.9, 128.9, 127.5, 127.3, 119.8, 113.0, 112.8, 55.4.



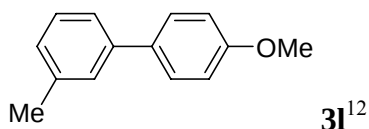
¹H NMR (400M Hz, CDCl₃): δ (ppm) 0.75 (t, *J* = 7.3, 3H), 1.35 (s, 6H), 1.68-1.74 (m, 2H), 7.34 (t, *J* = 7.3, 1H), 7.42-7.47 (m, 4H), 7.55-7.64 (m, 4H). ¹³C NMR (100M Hz): δ (ppm) 148.8, 141.2, 138.2, 128.8, 127.1(0), 127.0(6), 126.8, 126.5, 37.9, 37.0, 28.6(0), 28.5(6), 9.3.



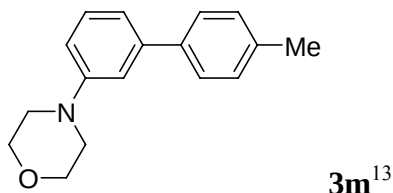
¹H NMR (400M Hz, CDCl₃): δ (ppm) 7.40-7.50 (m, 3H), 7.61 (d, *J* = 8.3, 2H), 7.70 (s, 4H). ¹³C NMR (100M Hz): δ (ppm) 144.8, 139.9, 129.4 (q, *J* = 31.5), 129.1, 128.3, 127.5, 127.4, 125.8 (q, *J* = 3.8), 125.1 (q, *J* = 399.5).



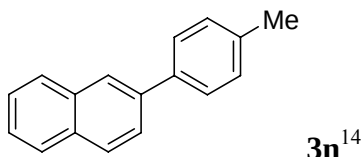
¹H NMR (400M Hz, CDCl₃): δ (ppm) 3.90 (s, 3H), 7.04 (d, *J* = 8.2, 2H), 7.41-7.53 (m, 6H), 7.84 (d, *J* = 8.2, 1H), 7.89-7.95 (m, 2H). ¹³C NMR (100M Hz): δ (ppm) 159.0, 140.0, 133.9, 133.2, 131.9, 131.2, 128.4, 127.4, 127.0, 126.2, 126.0, 125.8, 125.5, 113.8, 55.5.



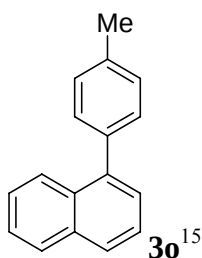
¹H NMR (400M Hz, CDCl₃): δ (ppm) 2.41 (s, 3H), 3.85 (s, 3H), 6.97 (d, *J* = 8.7, 2H), 7.13 (d, *J* = 7.4, 1H), 7.29-7.37 (m, 3H), 7.52 (d, *J* = 8.7, 2H). ¹³C NMR (100M Hz): δ (ppm) 159.2, 140.9, 138.4, 134.0, 128.7, 128.3, 127.7, 127.5, 123.9, 114.2, 55.4, 21.7.



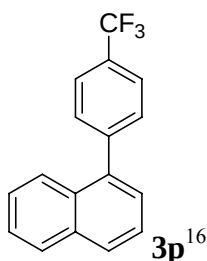
¹H NMR (400M Hz, CDCl₃): δ (ppm) 2.42 (s, 3H), 3.24 (t, *J* = 4.8, 4H), 3.90 (t, *J* = 4.8, 4H), 6.90-6.93 (m, 1H), 7.12-7.14 (m, 2H), 7.27 (d, *J* = 8.2, 2H), 7.36 (t, *J* = 7.8, 1H), 7.50 (d, *J* = 7.8, 2H). ¹³C NMR (100M Hz): δ (ppm) 151.8, 142.4, 138.9, 137.2, 129.6, 129.5, 127.2, 119.2, 114.7, 114.6, 67.1, 49.6, 21.2.



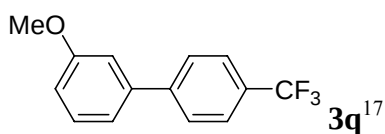
¹H NMR (CDCl₃, 400M Hz): δ (ppm) 2.44 (s, 3H), 7.31 (d, *J* = 7.8, 2H), 7.46-7.54 (m, 2H), 7.64 (d, *J* = 8.2, 2H), 7.75-7.93 (m, 4H), 8.04 (s, 1H). ¹³C NMR (100M Hz): δ (ppm) 138.6, 138.3, 137.3, 133.8, 132.6, 129.7, 128.5, 128.3, 127.7, 127.4, 126.3, 125.9, 125.7, 125.5, 21.2.



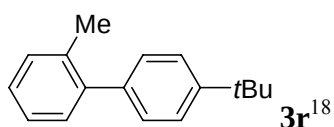
¹H NMR (CDCl₃, 400M Hz): δ (ppm) 2.48 (s, 3H), 7.32 (d, *J* = 7.8, 2H), 7.41-7.55 (m, 6H), 7.86 (d, *J* = 8.3, 1H), 7.91-7.96 (m, 2H). ¹³C NMR (100M Hz): δ (ppm) 140.4, 137.9, 137.0, 133.9, 131.8, 130.1, 129.1, 128.4, 127.5, 127.0, 126.2, 126.0, 125.8, 125.5, 21.3.



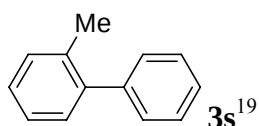
¹H NMR (CDCl₃, 400M Hz): δ (ppm) 7.41-7.57 (m, 3H), 7.62 (d, *J* = 8.3, 2H), 7.69-7.77 (m, 3H), 7.82 (d, *J* = 8.7, 1H), 7.93 (s, *J* = 9.2, 2H).



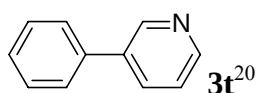
¹H NMR (CDCl₃, 400M Hz): δ (ppm) 2.48 (s, 3H), 6.94-6.97 (m, 1H), 7.12-7.19 (m, 2H), 7.39 (t, *J* = 8.0, 1H), 7.69 (s, 4H). ¹³C NMR (100M Hz): δ (ppm) 160.2, 144.7, 141.4, 130.1, 127.6, 125.8 (q, *J* = 3.8), 119.8, 113.5, 113.2, 55.4.



¹H NMR (CDCl₃, 400M Hz): δ (ppm) 1.39 (s, 9H), 2.31 (s, 3H), 7.24-7.29 (m, 6H), 7.44 (d, *J* = 8.2, 2H). ¹³C NMR (100M Hz): δ (ppm) 149.6, 141.9, 139.0, 135.6, 130.4, 130.0, 128.9, 127.1, 125.8, 125.0, 34.6, 31.5, 20.7.

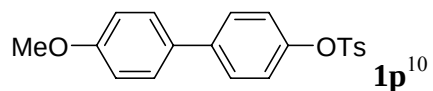


¹H NMR (CDCl₃, 400M Hz): δ (ppm) 2.28 (s, 3H), 7.23-7.27 (m, 4H), 7.31-7.36 (m, 3H), 7.39-7.45 (m, 2H).

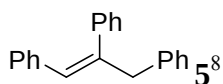


¹H NMR (CDCl₃, 400M Hz): δ (ppm) 7.34-7.43 (m, 2H), 7.46-7.50 (m, 2H), 7.57-7.59 (m, 2H),

7.87 (td, $J = 2.1$, $J = 7.4$, 1H), 8.59 (dd, $J = 1.7$, $J = 3.7$, 1H), 8.85 (d, $J = 1.4$, 1H).



^1H NMR (400M Hz, CDCl_3): δ (ppm) 2.44 (s, 3H), 3.83 (s, 3H), 6.95 (d, $J = 8.2$, 2H), 7.01 (d, $J = 8.2$, 2H), 7.31 (d, $J = 8.2$, 2H), 7.42-7.46 (m, 4H), 7.73 (d, $J = 8.2$, 2H). ^{13}C NMR (100M Hz): δ (ppm) 159.5, 148.6, 145.5, 139.9, 132.5, 132.4, 129.9, 128.7, 128.2, 127.8, 122.7, 114.4, 55.4, 21.8.



^1H NMR (400M Hz, CDCl_3): δ (ppm) 3.80 (s, 2H), 6.45 (s, 2H), 6.95-6.98 (m, 2H), 7.08-7.11 (m, 5H), 7.22-7.32 (m, 8H). ^{13}C NMR (100M Hz): δ (ppm) 142.3, 141.2, 139.3, 137.3, 129.4, 129.2, 128.8, 128.5, 128.4, 128.3, 128.0, 127.1, 126.5, 126.3, 47.1.

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