Room-Temperature Hiyama Cross-Couplings of Arylsilanes with Alkyl Bromides and Iodides

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Supporting Information

I. General

PdBr₂ (Aldrich and Strem), P(*t*-Bu)₂Me (Strem), Bu₄NF (1.0 M solution in THF; Aldrich), (MeO)₃SiPh (Aldrich and Alfa Aesar), 1-bromododecane (Avocado), 1-bromo-2-cyclohexylethane (Aldrich), benzyl 4-bromobutyl ether (Aldrich), 2-(2-bromoethyl)-1,3-dioxolane (Aldrich), 6-bromohexanenitrile (Alfa Aesar), 5-bromopentyl acetate (Avocado), and ethyl 6-bromohexanoate (Avocado) were used as received.

6-Bromo-1-(morpholin-4-yl)-hexan-1-one,¹ 11-iodoundec-1-yne,² the aryltrimethoxysilanes (Table 3),³ and [HP(*t*-Bu)₂Me]BF₄⁴ were prepared according to literature procedures.

THF was purified by passing through a neutral alumina column under argon.

For all new compounds, characterization data is provided in Section II.

II. Hiyama Cross-Coupling Reactions

Cross-Coupling Procedure with $P(t\text{-Bu})_2\text{Me}$. In a glove box, $P(t\text{-Bu})_2\text{Me}$ (16 mg, 0.10 mmol) was added to a suspension of PdBr_2 (10.6 mg, 0.040 mmol) in THF (2.4 mL). This mixture was stirred for 30 minutes, and to this homogeneous orange-yellow solution was added $(\text{MeO})_3\text{SiPh}$ (224 μL , 1.20 mmol), TBAF (2.4 mL, 2.4 mmol), and the alkyl halide (1.00 mmol). The resulting mixture was stirred vigorously for 14 hours at room temperature. The reaction mixture was then filtered through a short pad of silica gel (washed with ~ 100 mL of Et_2O or EtOAc), concentrated, and purified by column chromatography.

Cross-Coupling Procedure with $[\text{HP}(t\text{-Bu})_2\text{Me}]\text{BF}_4$. In the air, PdBr_2 (10.6 mg, 0.040 mmol) and $[\text{HP}(t\text{-Bu})_2\text{Me}]\text{BF}_4$ (24.8 mg, 0.10 mmol) were placed in a vial equipped with a stir bar. The vial was closed with a septum screw-cap, and then it was evacuated and refilled with argon (three times). THF (2.4 mL) and TBAF (0.10 mL, 0.10 mmol) were added, and the resulting mixture was stirred vigorously for 30 minutes at room temperature. To the resulting homogeneous orange-yellow solution was added $(\text{MeO})_3\text{SiPh}$ (224 μL , 1.20 mmol), TBAF (2.3 mL, 2.3 mmol), and the alkyl bromide (1.00 mmol). The reaction mixture was stirred vigorously for 14 hours at room temperature. The reaction mixture was then filtered through a short pad of silica gel (washed with ~ 100 mL of Et_2O or EtOAc), concentrated, and purified by column chromatography.

Table 2, entry 8. Solvent for chromatography: 25% EtOAc in hexane; colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.30-7.27 (*m*, 2H), 7.21-7.16 (*m*, 3H), 3.69-3.64 (*m*, 4H), 3.64-3.60 (*m*, 2H), 3.47-3.43 (*m*, 2H), 2.63 (*t*, $J = 7.7$ Hz, 2H), 2.29 (*t*, $J = 7.7$ Hz, 2H), 1.71-1.62 (*m*, 4H), 1.43-1.35 (*m*, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 171.9, 142.7, 128.6, 128.5, 125.9, 67.2, 66.9, 46.2, 42.0, 36.0, 33.2, 31.5, 29.6, 25.3.

IR (neat, cm^{-1}): 3422, 2927, 2855, 1652, 1431, 1272, 1231, 1116, 1032, 848.

HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 284.1621. Found: 284.1628.

Table 3, entry 2. Solvent for chromatography: 5% EtOAc in hexane; colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.15-6.94 (*m*, 4H), 4.13 (*q*, $J = 7.1$ Hz, 2H), 2.59 (*t*, $J = 7.7$ Hz, 2H), 2.30 (*t*, $J = 7.5$ Hz, 2H), 1.70-1.58 (*m*, 4H), 1.39-1.32 (*m*, 2H), 1.25 (*t*, $J = 7.1$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 174.2, 130.1, 130.0, 115.5, 115.3, 60.6, 35.3, 34.7, 31.6, 29.0, 25.2, 14.7.

IR (neat, cm^{-1}): 2981, 2935, 2860, 1735, 1601, 1510, 1221, 1033, 833.

HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{19}\text{FO}_2$ (M) $^+$: 238.1364. Found: 238.1360.

Table 3, entry 3. Solvent for chromatography: 3% EtOAc in hexane; colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.21-6.99 (*m*, 4H), 4.15 (*q*, $J = 7.2$ Hz, 2H), 2.60 (*t*, $J = 7.8$ Hz, 2H), 2.36 (*s*, 3H), 2.32 (*t*, $J = 7.6$ Hz, 2H), 1.72-1.61 (*m*, 4H), 1.43-1.36 (*m*, 2H), 1.28 (*t*, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 174.3, 142.3, 138.2, 129.6, 128.6, 126.8, 125.8, 60.6, 36.1, 34.7, 31.6, 29.2, 25.3, 21.8, 14.7.

IR (neat, cm^{-1}): 2980, 2933, 2858, 1736, 1609, 1463, 1373, 1179, 781.

HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$ (M^+): 234.1614. Found: 234.1607.

Table 3, entry 4. Solvent for chromatography: 3% EtOAc in hexane; colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.83-7.33 (*m*, 7H), 4.13 (*q*, $J = 7.2$ Hz, 2H), 2.79 (*t*, $J = 7.7$ Hz, 2H), 2.31 (*t*, $J = 7.5$ Hz, 2H), 1.78-1.66 (*m*, 4H), 1.45-1.40 (*m*, 2H), 1.25 (*t*, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 174.0, 140.2, 133.8, 132.1, 128.0, 127.8, 127.6, 127.6, 126.5, 126.1, 125.3, 60.4, 36.1, 34.5, 31.2, 29.0, 25.1, 14.5.

IR (neat, cm^{-1}): 3052, 2980, 2933, 2857, 1733, 1507, 1372, 1180, 817.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$ (M^+): 270.1614. Found: 270.1627.

Table 3, entry 6. Solvent for chromatography: hexane; colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.15-6.94 (*m*, 4H), 2.59 (*t*, J = 8.1 Hz, 2H), 1.87-1.64 (*m*, 5H), 1.51-1.45 (*m*, 2H), 1.29-1.14 (*m*, 4H), 0.98-0.89 (*m*, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 139.0, 129.8, 115.2, 115.0, 39.8, 37.4, 33.3, 32.6, 26.9, 26.5.

IR (neat, cm^{-1}): 3039, 2923, 2852, 1601, 1510, 1222, 1157, 823.

HRMS (ESI) Calcd for $\text{C}_{14}\text{H}_{19}\text{F}$ (M) $^+$: 206.1465. Found: 206.1466.

Table 3, entry 7. Solvent for chromatography: hexane; colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.20-6.99 (*m*, 4H), 2.58 (*t*, J = 8.2 Hz, 2H), 2.34 (*s*, 3H), 1.80-1.64 (*m*, 5H), 1.53-1.47 (*m*, 2H), 1.31-1.15 (*m*, 4H), 0.99-0.89 (*m*, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 143.5, 138.7, 129.4, 128.4, 126.5, 125.5, 39.7, 37.6, 33.5, 33.4, 26.9, 26.6, 21.6.

IR (neat, cm^{-1}): 3024, 2922, 2851, 1609, 1448, 780, 699.

HRMS (ESI) Calcd for $\text{C}_{15}\text{H}_{22}(\text{M})^+$: 202.1716. Found: 202.1708.

Table 3, entry 8. Solvent for chromatography: hexane; colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 7.82-7.34 (*m*, 7H), 2.79 (*t*, J = 8.1 Hz, 2H), 1.82-1.66 (*m*, 5H), 1.65-1.58 (*m*, 2H), 1.35-1.18 (*m*, 4H), 1.02-0.93 (*m*, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 141.0, 133.9, 132.1, 127.9, 127.8, 127.6, 126.4, 126.0, 125.2, 39.5, 37.5, 33.6, 33.5, 26.9, 26.6.

IR (neat, cm^{-1}): 3052, 3021, 2922, 2851, 1600, 1508, 1447, 852, 815, 743.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{22}(\text{M})^+$: 238.1716. Found: 238.1713.

Table 3, entry 9. Solvent for chromatography: 5% EtOAc in hexane; pale-yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 7.10-6.82 (*m*, 4H), 3.80 (*s*, 3H), 2.58 (*t*, $J = 7.6$ Hz, 2H), 2.34 (*t*, $J = 7.1$ Hz, 2H), 1.72-1.59 (*m*, 4H), 1.51-1.46 (*m*, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 158.0, 134.3, 129.4, 120.0, 113.9, 55.5, 34.8, 31.1, 28.4, 25.5, 17.3.

IIR (neat, cm^{-1}): 3002, 2935, 2858, 2245, 1612, 1513, 1246, 1036, 831.

HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{17}\text{NONa}(\text{M}+\text{Na})^+$: 226.1202. Found: 226.1207.

Table 3, entry 10. Solvent for chromatography: 5% EtOAc in hexane; pale-yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 7.14-6.95 (*m*, 4H), 2.61 (*t*, $J = 7.6$ Hz, 2H), 2.35 (*t*, $J = 7.1$ Hz, 2H), 1.73-1.60 (*m*, 4H), 1.53-1.47 (*m*, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 162.7, 137.7, 129.9, 119.9, 115.3, 35.0, 31.0, 28.4, 25.4, 17.3.

IR (neat, cm^{-1}): 3041, 2935, 2861, 2246, 1601, 1510, 1220, 1158, 834.

HRMS (ESI) Calcd for $\text{C}_{12}\text{H}_{14}\text{FNNa}(\text{M}+\text{Na})^+$: 214.1002. Found : 214.1006.

Table 3, entry 11. Solvent for chromatography: 5% EtOAc in hexane; pale-yellow oil.

^1H NMR (400 MHz, CDCl_3): δ 7.21-6.98 (*m*, 4H), 2.61 (*t*, $J = 7.8$ Hz, 2H), 2.34 (*t*, $J = 7.2$ Hz, 2H), 2.33 (*s*, 3H), 1.75-1.62 (*m*, 4H), 1.54-1.48 (*m*, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 142.1, 130.1, 129.4, 128.5, 126.8, 125.5, 120.0, 35.7, 30.9, 28.5, 25.5, 21.6, 17.3.

IR (neat, cm^{-1}): 3018, 2934, 2859, 2245, 1608, 1463, 784, 700.

HRMS (ESI) Calcd for $\text{C}_{13}\text{H}_{17}\text{NNa}$ ($\text{M}+\text{Na}$) $^+$: 210.1253. Found: 210.1251.

Equation 3. Solvent for chromatography: hexane; colorless oil.

^1H -NMR (400 MHz, CDCl_3): δ 7.31-7.16 (*m*, 5H), 2.61 (*t*, $J = 7.8$ Hz, 2H), 2.19 (*td*, $J = 7.1, 2.7$ Hz, 2H), 1.95 (*s*, 1H), 1.66-1.58 (*m*, 2H), 1.57-1.49 (*m*, 2H), 1.41-1.29 (*m*, 10H).

^{13}C -NMR(100 MHz, CDCl_3): δ 143.1, 128.6, 128.4, 125.8, 85.0, 68.3, 36.2, 31.7, 29.7, 29.6, 29.5, 29.3, 29.0, 28.7, 18.6.

IR (neat, cm^{-1}): 3310, 3026, 2927, 2855, 2118, 1653, 1465, 1030, 698.

HRMS (ESI) Calcd for $\text{C}_{17}\text{H}_{24}\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 251.1770. Found: 251.1775.

References

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Integral

2.1386
4.0432
2.0488
5.1803
2.0000
2.0034
2.0050

2.9477	0.9851	1.9547	1.0000
2.0441	2.0673	3.9876	2.1095

Integral