

Efficient Aqueous-Phase Heck and Suzuki Couplings of Aryl Bromides using Tri(4,6-dimethyl-3-sulfonatophenyl)phosphine Trisodium Salt (TXPTS)

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General. Ligand syntheses were carried out under nitrogen using a dry box and Schlenk techniques unless noted. Coupling reactions were assembled in a drybox in screw-cap vials with a silicone/Teflon® septum or a round bottom sealed with a rubber septum. Pd(OAc)₂ and TPPTS were purchased from Strem. Styrene, sodium acrylate, all boronic acids and aryl halides were purchased from Aldrich and were used without further purification. THF and diethyl ether were freshly distilled from sodium-benzophenone ketyl under nitrogen prior to use. Water (deionized) and acetonitrile were degassed by sparging with nitrogen and/or exposure to vacuum.

Tri(4,6-dimethyl-3-sulfonatophenyl)phosphine (TXPTS).¹ Fuming sulfuric acid (2.5mL, 4.75 mmol) was added to a round bottom flask under nitrogen via syringe. The round bottom was placed in a brine/ice bath. Finely ground tri(2,4-dimethylphenyl)phosphine (999.0 mg, 2.89 mmol) was added to the round bottom slowly under nitrogen. The reaction mixture was allowed to warm to room temperature and stir for 3 hours. The reaction flask was placed back in the brine/ice bath and ice (~10g) was added to the reaction flask over a 30 minute period. NaOH solution (3.85 g in 30 mL H₂O) was added to the reaction flask. A saturated NaOH solution was then added dropwise to reach a pH of 7. The resulting mixture was extracted with MeOH (100 mL) and filtered. The remaining solid was washed with a MeOH/ H₂O solution (80 ml MeOH, 4 mL H₂O). Removal of solvent from the combined MeOH filtrates under reduced pressure gave a white solid that was again extracted into MeOH (40 mL). The mixture was filtered and the solvent removed from the filtrate to give TXPTS (1.61g, 85.6%) as a colorless solid. ¹H NMR (360 MHz, CD₃OD): δ 7.32 (d, J = 4.93 Hz, 3H), 7.25 (d, J =4.93 Hz, 3H), 2.59 (s, 9H), 2.31 (s, 9H); . ¹³C NMR (90.5 MHz, CDCl₃): δ 147.5 (d, J_{C-P} =26.34 Hz), 140.5, 138.8, 135.4 (d, J_{C-P} = 4.16 Hz), 132.5, 131.5 (d, J_{C-P} =8.33 Hz), 21.4 (d, J_{C-P} =46.61 Hz), 20.6, ³¹P NMR (202.5 MHz, CD₃OD): δ -30.3.

Tri(4-methoxy-2-methylphenyl)phosphine. Magnesium turnings (1.1480 g, 47.22 mmol) were added to a round bottom equipped with a stirbar under nitrogen. THF (45mL) and 4-bromo-3-methylanisole (9.38 g, 46.64 mmol) was added to the round bottom via syringe. The reaction mixture was allowed to stir under reflux for several hours. Trichlorophosphine (1.26 ml, 14.4 mmol) was dissolved in THF (40 mL) in a second round bottom flask under N₂. The Grignard solution was cooled to -78° C, and the phosphine solution was added drop-wise via cannula. The reaction mixture was allowed to warm to room temperature and stir overnight. The solution was quenched with a saturated solution of ammonium chloride (100 mL). The product was extracted with toluene, dried with MgSO₄, and dried under vacuum (0.1 torr). The crude material was purified by flash chromatography (SiO₂) eluting with 1:1 hexane:CH₂Cl₂ to give the product as a colorless solid (4.79 g, 76%). ¹H NMR (360 MHz, CDCl₃): δ 6.77 (s, 1H), 6.3 (m, 2H), 3.79 (s, 3H), 2.36 (s, 3H). ¹³C NMR (90.5 MHz, CDCl₃): δ 160.0, 144.1 (d, J_{C-P} = 27.75 Hz), 134.4, 126.2 (d, J_{C-P} =8.33 Hz), 115.8 (d, J_{C-P} =5.54 Hz), 111.4, 55.0, 21.3 (d, J_{C-P} = 20.81 Hz). ³¹P NMR (202.5 MHz, CDCl₃): δ -34. (s).

Tri(4-methoxy-6-methyl-3-sulfonatophenyl)phosphine (TMAPTS). Fuming sulfuric acid (2.5mL, 4.75 mmol) was added to a round bottom flask under nitrogen via syringe. The round bottom was placed in a brine/ice bath. Finely ground tri(4-methoxy-2-methylphenyl)phosphine (1.26g, 3.18 mmol) was added to the round bottom slowly under nitrogen. The reaction mixture was allowed to warm to room temperature and stir for 3 hours. The reaction flask was placed back in the brine/ice bath and ice (~10 g) was added to the reaction flask over a 30 minute period. NaOH solution (3.85 g in 30 mL H₂O) was added to the reaction flask. A saturated NaOH solution was then added dropwise to reach a pH of 7. The resulting mixture was extracted with MeOH (100 mL) and filtered. The remaining solid was washed with a MeOH/ H₂O solution (80 ml MeOH, 4 mL H₂O). Removal of solvent from the combined MeOH filtrates under reduced pressure gave a white solid that was again extracted into MeOH (40 mL). The mixture was filtered and the solvent removed from the filtrate to give TMAPTS (1.08g, 54%) as a colorless solid. ¹HNMR (360MHz, CD₃OD): δ 6.82 (d, *J*=4.32 Hz, 3H), 6.39 (d, *J*=3.69 Hz, 3H), 3.31 (s, 9H), 1.75 (s, 9H). ¹³C NMR (90.5 MHz, CD₃OD): δ 158.9, 149.5 (d, *J*_{C-P}=26.36 Hz), 134.6, 131.2, 125.0 (d, *J*_{C-P}=8.32 Hz), 115.9 (d, *J*_{C-P}=4.16Hz), 57.00, 22.0 (d, *J*_{C-P}=20.81 Hz). ³¹P NMR (202.5 MHz, CD₃OD): δ -29.5 (s).

Representative procedure for the Heck coupling reactions with styrene (Table 1).

Pd(OAc)₂ (5.6 mg, 0.025 mmol), TXPTS (43.7 mg, 0.075 mmol), and Na₂CO₃ (212 mg, 2.0 mmol) were added to a 50mL round bottom flask equipped with a stir bar and rubber septum while in the dry box. Upon removing from dry box, aryl halide (1.00 mmol), styrene (156 mg, 1.50 mmol), and degassed 1:1 CH₃CN:H₂O (10 mL) were added via syringe. The round bottom was placed in an oil bath at 80 °C, and allowed to stir until complete as determined by GC (2-4 h). The reaction was poured into saturated sodium carbonate (50mL), extracted with ethyl acetate (3×30 mL), and dried with MgSO₄. Products were purified by flash chromatography (SiO₂).

E-4-Ethylstilbene (entry 1). Using the general procedure, 1-ethyl-4-iodobenzene (232 mg, 1.00 mmol) was coupled with styrene. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (70:20:10) to give *E*-4-ethylstilbene as a white solid (187.0 mg, 90% yield). mp 84-86 °C (lit.² mp 89-90 °C). ¹HNMR (360 MHz, CDCl₃): δ 7.49 (d, *J*=7.40 Hz, 2H), 7.43 (d, *J*=8.02 Hz, 2H), 7.34 (t, *J*=7.39 Hz, 2H), 7.19 (m, 3H), 7.07 (d, *J*=2.47 Hz, 2H), 2.65 (q, *J*=7.40 Hz, 2H), 1.25 (t, *J*=8.01 Hz, 3H). ¹³C NMR 90.6 MHz, CDCl₃): δ 144.3, 137.9, 135.2, 129.0, 128.6, 128.5, 128.1, 127.7, 126.9, 126.7, 29.0, 15.9.

E-4-Methylstilbene³ (entry 2). Using the general procedure, 4-bromotoluene (173.8 mg, 1.00 mmol) was coupled with styrene. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (70:20:10) to give *E*-4-methylstilbene as a white solid (176.6 mg, 90 % yield). mp 112-115 °C. ¹HNMR (360 MHz, CDCl₃): δ 7.46 (d, *J*=7.40 Hz, 2H), 7.42 (d, *J*=8.02 Hz, 2H), 7.35 (m, 2H), 7.25 (m, 1H), 7.17 (m, 2H), 7.07 (d, *J*=1.85 Hz, 2H), 2.36 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 138.1, 135.1, 130.0, 129.4, 129.1, 129.0, 128.3, 127.8, 127.0, 126.8, 21.0.

E-4-Acetylstilbene⁴ (entry 3). Using the general procedure, 4-bromoacetophenone (214.1 mg, 1.00 mmol) was coupled with styrene. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (70:20:10) to give *E*-4-acetylstilbene as a white solid (224.2 mg,

94% yield). mp 134-137 °C. ^1H NMR (360 MHz, CDCl_3): δ 7.95 (d, $J=8.02$ Hz, 2H), 7.58 (d, $J=8.02$ Hz, 2H), 7.54 (d, $J=7.4$ Hz, 2H) 7.26 (m, 5H), 2.60 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 197.8, 142.3, 137.0, 136.3, 131.8, 129.2, 129.1, 128.6, 127.8, 127.1, 126.8, 26.9.

E-4-Methoxy-2-methylstilbene (entry 4). Using the general procedure, 4-bromo-3-methylanisole (199.4 mg, 1.00 mmol) was coupled with styrene. The crude product was chromatographed eluting with hexane: CH_2Cl_2 :EtOAc (70:20:10) to give *E*-4-methoxy-2-methylstilbene as a white solid (172.5 mg, 78% yield). mp 67-70 °C. ^1H NMR (360 MHz, CDCl_3): δ 7.52 (m, 3H), 7.30 (m, 4H), 6.90 (m, 1H), 6.80 (m, 2H), 3.38 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 159.4, 138.3, 137.6, 133.1, 128.9, 128.4, 127.5, 126.9, 126.6, 126.4, 116.0, 112.0, 54.6, 20.1.

Representative procedure for the Heck coupling reactions with sodium acrylate (Table 1). $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol), TXPTS (43.7 mg, 0.075 mmol), sodium acrylate (141 mg, 1.50 mmol), and Na_2CO_3 (212 mg, 2.0 mmol) were added to a round bottom equipped with a stir bar and rubber septum while in the dry box. Upon removing from dry box, the aryl bromide (1.00 mmol) and degassed 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (10 mL) were added via syringe. The round bottom was placed in an oil bath at 80 °C and allowed to stir for several hours. The reaction mixture was added to saturated sodium carbonate (50mL). The residual aryl bromide was extracted with ethyl acetate (3×30 mL). The pH of the aqueous phase was then brought to ca. 1 using concentrated H_2SO_4 . The cinnamic acid product was extracted with CH_2Cl_2 (3×30 mL) and the combined organic extracts were dried over MgSO_4 . Removal of solvent under reduced pressure gave the crude product, which was recrystallized from $\text{H}_2\text{O}/\text{Ethanol}$.

E-4-Methylcinnamic acid (entry 5). Using the general procedure, 4-bromotoluene (173.8 mg, 1.00 mmol) was coupled with sodium acrylate. Using the general work-up procedure gave *E*-4-methylcinnamic acid as a white solid (133.9 mg, 81% yield). mp 197-199 °C (lit.⁵ mp 198-200 °C). ^1H NMR (360 MHz, CDCl_3): δ 10.13 (brs, 1H), 7.57 (m, 3H), 7.23 (d, $J=8.01$ Hz, 2H), 6.47 (d, $J=16.03$ Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 168.6, 144.8, 141.1, 132.4, 130.4, 129.1, 119.0, 21.9. NMR spectra were identical to published spectra.⁶

E-4-Methoxycinnamic acid⁷ (entry 6). Using the general procedure, 4-bromo-3-methylanisole (186.8 mg, 1.00 mmol) was coupled with sodium acrylate. Using the general work-up procedure gave *E*-4-methoxycinnamic acid as a white solid (140.6 mg, 79% yield). mp 173-174 °C (lit.⁵ mp 174 °C). ^1H NMR (360 MHz, CDCl_3): δ 10.22 (brs, 1H), 7.67 (d, $J=8.63$ Hz, 2H), 7.57 (d, $J=16.03$ Hz, 1H), 6.99 (d, $J=8.63$ Hz, 2H), 6.41 (d, $J=16.03$ Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 168.7, 161.9, 144.6, 130.8, 127.8, 117.4, 115.3, 56.2.

E-2-Methylcinnamic acid⁸ (entry 7). Using the general procedure, 2-bromotoluene (170.6 mg, 1.00 mmol) was coupled with sodium acrylate. Using the general work-up procedure gave *E*-2-methylcinnamic acid as a white solid (156.4 mg, 82% yield). mp 169-171 °C (lit. mp 175-176 °C). ^1H NMR (360 MHz, CDCl_3): δ 10.00 (brs, 1H), 7.86 (d, $J=15.42$ Hz, 1H), 7.72 (d, $J=7.4$ Hz, 1H), 7.30 (m, 3H), 6.45 (d, $J=15.41$ Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (90.6 MHz, CDCl_3): δ 168.4, 142.1, 138.1, 131.6, 130.9, 127.4, 127.3, 121.1, 20.2. One pair of carbons were coincident in the ^{13}C NMR.

Representative Procedure for the Suzuki Cross-Coupling Reactions. $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol), phosphine (0.0625 mmol), boronic acid (1.20 mmol) and Na_2CO_3 (0.21 g, 2.0 mmol) were added to a round bottom equipped with a stir bar and rubber septum while in the dry box. Upon removing from dry box the arylbromide (1.00 mmol) and degassed 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (10 mL) were added via syringe. The reaction was placed in a pre-heated oil bath and allowed to stir until determined to be complete by GC (1-4 hours). The reaction was poured into saturated sodium carbonate (50mL), extracted with ethyl acetate (3×30 mL), and dried with MgSO_4 . Products were purified by flash chromatography on silica gel.

4-Methylbiphenyl⁹ (entry 1). Using the general procedure, 4-bromotoluene (180.7 mg, 1.06 mmol) was coupled with phenylboronic acid (146 mg, 1.20 mmol) using TMAPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane: CH_2Cl_2 :EtOAc (75:20:5) to give 4-methylbiphenyl as a colorless, low-melting point solid (169.2 mg, 95% yield). ¹HNMR (360 MHz, CDCl_3): δ 7.56 (d, J =1.23 Hz, 2H), 7.46 (d, J =8.02 Hz, 2H), 7.39 (m, 1H), 7.37 (m, 2H), 7.25 (d, J =8.02, 2H), 2.36 (s, 3H).

4-Methoxybiphenyl⁹ (entry 2). Using the general procedure, 4-bromoanisole (188.2 mg, 1.01 mmol) was coupled with phenylboronic acid (146 mg, 1.20 mmol) using TXPTS/Pd(OAc)₂ at 80 °C. The crude product was chromatographed eluting with hexane: CH_2Cl_2 :EtOAc (75:20:5) to give 4-methoxybiphenyl as a white solid (183.0 mg, 99% yield). mp 84-86 °C (lit.⁵ mp 86-90 °C). ¹HNMR (360 MHz, CDCl_3): δ 7.54 (m, H), 7.44 (m, 2H), 7.29 (m, 2H), 6.97 (d, J =8.63 Hz, 2H), 3.85 (s, 3H).

4-Fluoro-4'-methylbiphenyl¹⁰ (entry 3). Using the general procedure, 4-bromotoluene (171.0mg, 1.00 mmol) was coupled with 4-fluorophenylboronic acid (169 mg, 1.20 mmol) using TXPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane: CH_2Cl_2 :EtOAc (75:20:5) to give 4-methyl-4'-fluorobiphenyl as a white solid (176.6 mg, 94% yield). mp 74-77 °C. ¹HNMR (360 MHz, CDCl_3): δ 7.52 (d, J =8.63 Hz, 2H), 7.43 (d, J =8.02 Hz, 2H), 7.23 (d, J =8.02 Hz, 2H), 7.10 (d, J =8.64 Hz, 2H), 2.39 (s, 3H).

4-Methoxy-4'-methylbiphenyl¹¹ (entry 4). Using the general procedure, 4-bromotoluene (173.8 mg, 1.00 mmol) was coupled with 4-methoxyphenylboronic acid (182 mg, 1.20 mmol) using TXPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane: CH_2Cl_2 :EtOAc (75:20:5) to give 4-methoxy-4'-methylbiphenyl as a white solid (185.5 mg, 92% yield). mp 106-108 °C. ¹HNMR (360 MHz, CDCl_3): δ 7.49 (d, J =8.63 Hz, 2H), 7.44 (d, 8.02 Hz, 2H), 7.22 (d, J =8.02 Hz, 2H), 6.96 (d, J =8.63 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H). ¹³CNMR (90.6 MHz, CDCl_3): δ 159.6, 138.0, 136.3, 129.4, 127.9, 127.7, 126.6, 114.1, 55.3, 21.2.

4-Acetyl biphenyl¹² (entry 5). Using the general procedure, 4'-bromoacetophenone (202.7 mg, 1.02 mmol) was coupled with phenylboronic acid (146 mg, 1.20 mmol) using TXPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane: CH_2Cl_2 :EtOAc (75:20:5) to give 4-acetyl biphenyl as a white solid (182.1 mg, 91% yield). mp 115-117 °C (lit mp 119-120 °C). ¹HNMR (360 MHz, CDCl_3): δ 8.03 (d, J = 8.63 Hz, 2H), 7.68 (d, J =8.63 Hz, 2H), 7.62 (d, J =7.39 Hz, 2H), 7.51 (m, 3H), 2.69 (s, 3H). ¹³CNMR (90.6 MHz, CDCl_3): δ 197.7, 145.8, 139.9, 135.8, 128.9, 128.8, 128.2, 127.3, 127.2, 26.6.

4-Acetyl-4'-methoxybiphenyl⁹ (entry 6). Using the general procedure, 4'-bromoacetophenone (210.3 mg, 1.06 mmol) was coupled with 4-methoxyphenylboronic acid using TXPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (75:20:5) to give 4-acetyl-4'-methoxybiphenyl as a white solid (222.6 mg, 93% yield). mp 149-151 °C. ¹HNMR (360 MHz, CDCl₃): δ 8.03 (d, *J*=8.63 Hz, 2H), 7.65 (d, *J*=8.63 Hz, 2H), 7.58 (d, *J*=9.25 Hz, 2H), 6.99 (d, *J*=8.63 Hz, 2H), 3.87 (s, 3H), 2.63 (s, 3H).

4-Fluoro-4'-methoxybiphenyl¹³ (entry 7). Using the general procedure, 4-bromoanisole (186.8 mg, 1.00 mmol) was coupled with 4-fluorophenylboronic acid (169 mg, 1.20 mmol) using TMAPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (75:20:5) to give 4-fluoro-4'-methoxybiphenyl as a white solid (194.7 mg, 97% yield). mp 86-88 °C. ¹HNMR (360 MHz, CDCl₃): δ 7.49 (m, 4H), 7.12 (d, *J*=8.63 Hz, 2H), 6.96 (d, *J*=6.78 Hz, 2H), 3.84 (s, 3H).

4-Methoxy-2-methylbiphenyl¹⁴ (entry 8). Using the general procedure, 4-bromo-3-methylanisole (199.4 mg, 0.99 mmol) was coupled with phenylboronic acid (146 mg, 1.20 mmol) using TXPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (75:20:5) to give 4-methoxy-2-methylbiphenyl (174.8 mg, 88% yield as a pale yellow oil). ¹HNMR (360 MHz, CDCl₃): δ 7.30 (m, 5H), 7.15 (d, 1H, *J*=8.63 Hz), 6.69 (m, 2H), 3.67 (s, 3H), 2.15 (s, 3H). ¹³CNMR (90.6 MHz, CDCl₃): δ 158.8, 141.6, 136.4, 134.5, 130.6, 129.2, 127.9, 126.3, 115.6, 111.0, 60.0, 13.9.

2,4'-Dimethylbiphenyl¹⁵ (entry 9). Using the general procedure, 4-bromotoluene (173.8 mg, 1.02 mmol) was coupled with 2-methylphenylboronic acid (163 mg, 1.20 mmol) using TMAPTS/Pd(OAc)₂ at 80 °C. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (75:20:5) to give 2,4'-dimethylbiphenyl as a pale yellow oil (146.6 mg, 86% yield). ¹HNMR (360 MHz, CDCl₃): δ 7.07 (m, 8H), 2.23 (s, 3H), 2.13 (s, 3H). ¹³C NMR (90.6 MHz, CDCl₃): δ 142.1, 139.4, 136.6, 135.6, 130.6, 130.2, 129.4, 129.1, 127.4, 126.1, 21.4, 20.8.

4-Methoxy-2,2'-dimethylbiphenyl (entry 10). Using the general procedure, 4-bromo-3-methylanisole (199.4 mg, 0.99 mmol) was coupled with 2-methylphenylboronic acid (163 mg, 1.20 mmol) using TXPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (75:20:5) to give 4-methoxy-2,2'-dimethylbiphenyl as a pale yellow oil (157.0 mg, 75% yield). ¹HNMR (360 MHz, CDCl₃): δ 7.13 (m, 3H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.63 Hz, 1H), 6.69 (m, 2H), 3.69 (s, 3H), 2.02 (s, 3H), 1.85 (s, 3H); ¹³C NMR (90.6 MHz, CDCl₃): δ 158.6, 141.2, 137.1, 136.2, 134.1, 130.2, 129.8, 129.7, 127.0, 125.4, 115.2, 110.8, 55.0, 20.0, 19.8.

2,6-Dimethylbiphenyl¹⁶ (entry 11). Using the general procedure, 2-bromo-*m*-xylene (187.5 mg, 1.01 mmol) was coupled with phenylboronic (146 mg, 1.20 mmol) acid using TXPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (75:20:5) to give 2,6-dimethylbiphenyl as a pale yellow oil (145.3 mg, 78% yield). ¹HNMR (360 MHz, CDCl₃): δ 7.71 (m, 2H), 7.62 (m, 1H), 7.43 (m, 5H), 2.36 (s, 6H).

4-Fluoro-2',6'-dimethylbiphenyl (entry 12). Using the general procedure, 2-bromo-*m*-xylene (187.5 mg, 1.01 mmol) was coupled with 4-fluorophenylboronic acid (169 mg, 1.20 mmol) using TMAPTS/Pd(OAc)₂ at 50 °C. The crude product was chromatographed eluting with hexane:CH₂Cl₂:EtOAc (75:20:5) to give 4-fluoro-2',6'-dimethylbiphenyl (175.8 mg, 87% yield as a pale yellow oil). ¹H NMR (360 MHz, CDCl₃): δ 7.12 (m, 7H), 2.05 (s, 6H). ¹³C NMR (90.6 MHz, CDCl₃): δ 161.8 (d, ¹J_{C-F}=244.14 Hz), 140.8, 136.9 (d, ¹J_{C-F}=4.16 Hz), 136.2, 130.6 (d, ¹J_{C-F}=6.93 Hz), 127.3, 127.2, 115.5 (d, ¹J_{C-F}=22.20 Hz), 20.8.

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