Supporting Information for the Paper Entitled:

# Synthetic and Mechanistic Interrogation of Pd/Isocyanide-Catalyzed Cross-Coupling: π-Acidic Ligands Enable Self-Aggregating Mono-Ligated Pd(0) Intermediates

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## S1. Synthetic Procedures and Characterization Data

**S1.1. General Considerations.** All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk and glovebox techniques. Unless otherwise stated, reagent-grade starting materials were purchased from commercial sources and either used as received or purified by standard procedures.[1] Solvents were dried and deoxygenated according to standard procedures.[2] Benzene-$d_6$ and toluene-$d_8$ (Cambridge Isotope Laboratories) were degassed and stored over 4 Å molecular sieves for 2 days prior to use. Celite 405 (Fisher Scientific) was dried under vacuum (24 h) at a temperature above 250 ˚C and stored in the glovebox prior to use. KBr (FTIR grade from Aldrich) was stirred overnight in anhydrous THF, filtered and dried under vacuum (24 h) at a temperature above 250 ˚C and stored in the glovebox prior to use. Arylboronic acids were purchased from Sigma-Aldrich and recrystallized from a 1:1 $H_2O$/EtOH solution prior to use. The compounds $CNAr^{Dipp2}$, $Pd(CNAr^{Dipp2})_2$ and *trans*-$PdBr(Mes)(CNAr^{Dipp2})_2$ were prepared by previously reported methods.[3-4] Lithium diisopropylamide (LDA) was prepared from diisopropylamine and *n*-BuLi in *n*-hexane. $[N(nBu)_4][PhBF_3]$ was prepared from $K[PhBF_3]$ and $[N(nBu)_4]Cl$ in acetone.

Solution $^1H$, $^{13}C\{^1H\}$ and $^{19}F$ NMR spectra were recorded on Varian Mercury 300 and 400 spectrometers or a Varian X-Sens 500 spectrometer. $^1H$ and $^{13}C\{^1H\}$ chemical shifts are reported in ppm relative to $SiMe_4$ ($^1H$ and $^{13}C$ $\delta$ = 0.0 ppm) with reference to residual solvent resonances of 7.26 ppm ($^1H$) and 77.16 ppm ($^{13}C$) for $CDCl_3$, 7.16 ppm ($^1H$) and 128.06 ppm ($^{13}C$) for $C_6D_6$, 5.32 ppm ($^1H$) for $CD_2Cl_2$, 2.08 ppm ($^1H$) for toluene-$d_8$. $^{19}F$ NMR spectra were referenced externally to neat trifluoroacetic acid, $F_3CC(O)OH$ ($\delta$ = –78.5 ppm vs. $CFCl_3$). FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as KBr pellets or as solutions injected into a ThermoFisher solution cell equipped with KBr windows. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. The following abbreviations were used for the intensities and characteristics of important IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak; b = broad, vb = very broad, sh = shoulder. Electrospray ionization mass spectrometry (ESI-MS) was performed at the UCSD Molecular Mass Spectrometry Facility on a Thermo LCQdeca mass spectrometer. Samples were prepared as acetone solutions and diluted to concentrations on the order of $10^{-6}$ to $10^{-5}$ M. The following settings were used during data acquisition: desolvation temp = 180 °C; infusion flow rate = 100 μL $min^{-1}$; source voltage = 4 kV.

Combustion analyses were performed by Robertson Microlit Laboratories of Madison, NJ (USA) or Midwest Microlabs of Indianapolis, IN (USA). Samples for combustion analysis were obtained from the first recrystallized batch of the reaction mixture. In a typical preparation, the crude, dry reaction mixture was dissolved in a minimum amount of solvent and stored at –40 ˚C for several days to produce crystalline material. This material was then collected, thoroughly dried under vacuum and then packaged under vacuum for shipment. In most cases, this material was also used for single-crystal X-ray structure determination.

**S1.2. Synthesis of *trans*-$PdBr(m\text{-}Xyl)(CNAr^{Dipp2})_2$ (2).** To a solution of $Pd(CNAr^{Dipp2})_2$ (0.150 g, 0.157 mmol) in $Et_2O$ (10 mL) was added 1-bromo-3,5-dimethylbenzene (23 μL, 0.17 mmol, 1.1 equiv). The reaction mixture was stirred for 24 h during which it turned a slightly darker orange color. All volatile materials were removed *in vacuo* and the resulting pale orange residue

was dissolved in $Et_2O$ (2 mL), filtered and stored at –35 ˚C overnight to produce colorless crystals, which were washed with *n*-pentane and dried *in vacuo*. Yield: 0.067 g, 0.059 mmol, 38%. $^1$H NMR (400.1 MHz, $C_6D_6$, 20 ˚C): δ = 7.33 (t, *J* = 8 Hz, 4H, *p*-Dipp), 7.18 (d, *J* = 8 Hz, 8H, *m*-Dipp), 6.85 (m, 6H, *m*-Ph and *p*-Ph), 6.41 (s, 1H, *p*-Xyl), 5.92 (s, 2H, *o*-Xyl), 2.50 (septet, *J* = 7 Hz, 8H, C*H*$(CH_3)_2$), 2.21 (s, 6H, Xyl –C*H*$_3$), 1.19 (d, *J* = 7 Hz, 24H, CH(C*H*$_3)_2$), 1.03 (d, *J* = 7 Hz, 24H, CH(C*H*$_3)_2$) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$, 20 ˚C): δ = 146.4, 139.7, 138.3, 135.6, 134.6, 133.7, 129.9, 129.7, 129.2, 126.8, 125.7, 123.5, 31.4 (*C*H$(CH_3)_2$), 24.9 (CH(*C*H$_3)_2$), 24.0 (CH(*C*H$_3)_2$), 21.7 (*m*-*C*H$_3$) ppm (extended scanning failed to conclusively locate the $C_{iso}$ $^{13}$C resonance for this complex). FTIR (KBr pellet): ($\nu_{CN}$) 2178 cm$^{-1}$ also 3059, 3020, 2960, 2925, 2866, 1591, 1582, 1460, 1363, 1113, 1056, 802, 753 cm$^{-1}$. Anal Calcd. for $C_{70}H_{83}BrN_2Pd$: C, 73.83; H, 7.35; N, 2.46. Found: C, 73.60; H, 7.61; N, 2.38.

**S1.3. Synthesis of PdCl(η$^3$-$C_3H_5$)(CNAr$^{Dipp2}$) (3).** To a solution of [Pd(μ-Cl)(η$^3$-$C_3H_5$)]$_2$ (0.086 g, 0.24 mmol) in THF (10 mL) was added CNAr$^{Dipp2}$ (0.199 g, 0.470 mmol, 2.00 equiv). The reaction mixture was stirred for 2 h during which the solution became pale yellow in color. The mixture was then concentrated *in vacuo* to 2 mL and filtered through a plug of Celite. The solution was layered with pentane (1 mL) and stored at –35 ˚C for 2 d to produce colorless crystals which were collected, washed with pentane (2 x 2 mL) and dried *in vacuo*. Yield: 0.108 g, 0.178 mmol, 38%. $^1$H NMR (300.1 MHz, $C_6D_6$, 20 ˚C): δ = 7.30 (t, *J* = 7 Hz, 2H, *p*-Dipp), 7.20 (d, *J* = 7 Hz, 4H, *m*-Dipp), 6.94 (apparent s, 3H, *m*-Ph and *p*-Ph), 4.25 (m, 1H, C*H* allyl), 3.87 (d, *J* = 7 Hz, 1H, C*H*$_2$ allyl), 3.01 (d, *J* = 6 Hz, 1H, C*H*$_2$ allyl), 2.64 (septet, *J* = 7 Hz, 4H, C*H*$(CH_3)_2$), 2.61 (d, *J* = 13 Hz, 1H, C*H*$_2$ allyl), 1.83 (d, *J* = 12 Hz, 1H, C*H*$_2$ allyl), 1.39 (d, *J* = 7 Hz, 12H, CH(C*H*$_3)_2$), 1.08 (d, *J* = 7 Hz, 12H, CH(C*H*$_3)_2$) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$, 20 ˚C): δ = 151.5 (*C*≡N), 146.7, 140.0, 134.0, 130.0, 129.9, 129.6, 127.9, 123.6, 116.4, 73.7, 56.8, 31.6, 24.6, 24.4 ppm. FTIR (KBr pellet): ($\nu_{CN}$) 2172 cm$^{-1}$ also 3061, 3018, 2963, 2926, 2867, 1595, 1578, 1458, 1382, 1363, 1056, 803, 794, 753 cm$^{-1}$. Anal Calcd. for $C_{34}H_{42}ClNPd$: C, 67.32; H, 6.98; N, 2.31. Found: C, 67.07; H, 7.00; N, 2.52.

**S1.4. Synthesis of (*μ*-$C_3H_5$)(*μ*-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ (4). Method 1.** To a suspension of PdCl(η$^3$-$C_3H_5$)(CNAr$^{Dipp2}$) (0.100 g, 0.165 mmol) in *i*PrOH (4 mL) was added a solution of NaO*t*Bu (0.017 g, 0.17 mmol, 1.1 equiv) in *i*PrOH (2 mL). The reaction mixture was stirred for 2 h and gradually became cloudy and beige in color. All volatile materials were removed *in vacuo* and the resulting residue was washed with cold (–35 ˚C) *n*-pentane (3 x 2 mL) to remove any dark brown material. The yellow solid was dissolved in THF (2 mL), filtered, and stored at –35 ˚C for one week to produce yellow crystals, which were collected and dried *in vacuo*. Yield: 0.006 g, 0.005 mmol, 6%. **Method 2.** To a 5:1 *n*-pentane/$Et_2O$ solution of (*μ*-$C_3H_5$)(*μ*-Cl)[Pd(CNAr$^{Dipp2}$)]$_2$ (0.100 g, 0.0881 mmol, 12 mL total) was added sodium isopropoxide (0.014 g, 0.18 mmol, 2.0 equiv). The reaction mixture was stirred for 30 min and gradually became cloudy and beige in color. All volatile materials were removed *in vacuo* and the resulting residue was washed with cold (–35 ˚C) pentane (3 x 2 mL) to remove any dark brown residue. The resulting yellow solid was dried *in vacuo*, dissolved in THF (4 mL), filtered, and stored at –35 ˚C overnight to produce yellow crystals. The crystals were isolated by filtration and dried *in vacuo*. Yield: 0.024 g, 0.021 mmol, 24%. $^1$H NMR (400.1 MHz, $C_6D_6$, 20 ˚C): δ = 7.31 (t, *J* = 8 Hz, 4H, *p*-Dipp), 7.16 (d, *J* = 8 Hz, 8H, *m*-Dipp), 6.93 (m, 6H, *m*-Ph and *p*-Ph), 4.27 (septet, 1H, J = 7 Hz, –OC*H*$(CH_3)_2$), 2.71 (septet, *J* = 7 Hz, 4H, C*H*$(CH_3)_2$), 2.70 (septet, *J* = 7 Hz, 4H,

C*H*($CH_3$)$_2$), 2.33 (d, 2H, *J* = 7 Hz, C*H*$_2$ allyl), 1.99 (m, 1H, allyl C*H*), 1.26 (d, *J* = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.25 (d, *J* = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 7 Hz, 30H, CH(C*H*$_3$)$_2$ and OCH(C*H*$_3$)$_2$), 0.68 (d, *J* = 12 Hz, 2H, C*H*$_2$ allyl) ppm. Due to the instability of **4** in solution, $^{13}$C{$^1$H} NMR was not obtained. FTIR (KBr pellet): ($\nu_{CN}$) 2166 and 2116 cm$^{-1}$ also 3064, 3026, 2962, 2928, 2868, 1459, 1419, 1384, 1363, 1234, 1104, 1056, 1047, 804, 792, 757 cm$^{-1}$. Anal Calcd. for $C_{68}H_{86}N_2OPd_2$: C, 70.39; H, 7.47; N, 2.41. Found: C, 71.02; H, 7.42; N, 2.21.

**S1.5. Synthesis of ($\mu$-$C_3H_5$)($\mu$-N($^i$Pr)$_2$)[Pd(CNAr$^{Dipp2}$)]$_2$ (5).** To a frozen solution of ($\mu$-$C_3H_5$)($\mu$-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ (0.150 g, 0.129 mmol) in THF (5 mL) was added a cold (*ca*. –100 ˚C) solution of lithium diisopropylamide (0.015 g, 0.14 mmol, 1.1 equiv) in THF (5 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight, during which time it turned golden brown in color. All volatiles were removed *in vacuo* and the residue was dissolved in *n*-pentane (2 mL), filtered through Celite, and stored at –35 ˚C overnight to produce yellow crystals, which were collected and dried *in vacuo*. Yield: 0.043 g, 0.036 mmol, 28%. Crystals suitable for X-ray diffraction were obtained by vapor diffusion of *n*-pentane into an $Et_2O$ solution at –35 ˚C for 3 days. $^1$H NMR (400.1 MHz, $C_6D_6$, 20 ˚C): δ = 7.32 (t, *J* = 8 Hz, 4H, *p*-Dipp), 7.17 (d, *J* = 8 Hz, 8H, *m*-Dipp), 6.95 (m, 6H, *m*-Ph and *p*-Ph), 3.27 (septet, *J* = 6 Hz, 1H, N(C*H*(CH$_3$)$_2$)$_2$), 3.18 (septet, *J* = 6 Hz, 1H, N(C*H*(CH$_3$)$_2$)$_2$), 2.75 (septet, *J* = 7 Hz, 4H, C*H*(CH$_3$)$_2$ Dipp), 2.74 (septet, *J* = 7 Hz, 4H, C*H*(CH$_3$)$_2$ Dipp), 2.46 (m, 2H, C*H*$_2$ allyl), 2.43 (m, 1H, C*H* allyl), 1.28 (d, *J* = 7 Hz, 12H, CH(C*H*$_3$)$_2$ Dipp), 1.26 (d, *J* = 7 Hz, 12H, CH(C*H*$_3$)$_2$ Dipp), 1.10 (d, *J* = 7 Hz, 24H, CH(C*H*$_3$)$_2$ Dipp), 0.94 (d, *J* = 6 Hz, 6H, NCH(C*H*$_3$)$_2$), 0.88 (d, *J* = 6 Hz, 6H, NCH(C*H*$_3$)$_2$), 0.67 (d, *J* = 12 Hz, 2H, C*H*$_2$ allyl) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$, 20 ˚C): δ = 159.5 (*C*≡N), 146.7, 146.6, 139.3, 135.3, 129.7, 129.5, 123.4, 123.3, 80.0, 55.2, 55.1, 31.5, 27.6, 27.3, 26.9, 24.6, 24.5, 24.3 ppm. FTIR (KBr pellet): ($\nu_{CN}$) 2083 and 2013 cm$^{-1}$ also 3061, 3025, 2928, 2867, 1579, 1459, 1419, 1384, 1363, 1349, 1328, 1308, 1252, 1153, 1056, 803, 791, 756 cm$^{-1}$. Anal Calcd. for $C_{71}H_{93}N_3Pd_2$: C, 70.98; H, 7.80; N, 3.50. Found: C, 70.73; H, 7.88; N, 3.39.

**S1.6. Synthesis of ($\mu$-$C_3H_5$)($\mu$-Cl)[Pd(CNAr$^{Dipp2}$)]$_2$ (6).** To a 1:1 *n*-pentane/$Et_2O$ solution of Pd(CNAr$^{Dipp2}$)$_2$ (0.300 g, 0.315 mmol, 10 mL total) was added [Pd(μ-Cl)($\eta^3$-$C_3H_5$)]$_2$ (0.058 g, 0.16 mmol, 0.50 equiv). The reaction mixture was stirred for 45 min, during which time a pale yellow precipitate formed and the solvents were removed *in vacuo*. The resulting yellow solid was dissolved in $Et_2O$ (3 mL) and *n*-pentane (2 mL), and the solution was filtered through a plug of Celite and stored at –35 ˚C overnight to produce yellow crystals. The crystals were collected, washed with *n*-pentane (2 x 2 mL) and dried *in vacuo*. Yield: 0.318 g, 0.280 mmol, 89%. Crystals suitable for X-ray analysis were obtained by slow evaporation of a dilute $Et_2O$ solution for 3 days at room temperature. $^1$H NMR (400.1 MHz, $C_6D_6$, 20 ˚C): δ = 7.26 (t, *J* = 8 Hz, 4H, *p*-Dipp), 7.15 (d, *J* = 8 Hz, 8H, *m*-Dipp), 6.94 (m, 6H, *m*-Ph and *p*-Ph), 2.76 (d, *J* = 8 Hz, 2H, C*H*$_2$ allyl), 2.69 (septet, *J* = 7 Hz, 8H, C*H*(CH$_3$)$_2$), 1.74 (m, 1H, C*H* allyl), 1.30 (d, *J* = 7 Hz, 24H, CH(C*H*$_3$)$_2$), 1.08 (d, *J* = 7 Hz, 24H, CH(C*H*$_3$)$_2$), 0.75 (d, *J* = 12 Hz, 2H, C*H*$_2$ allyl) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$, 20 ˚C): δ = 154.5 (*C*≡N), 146.7, 139.4, 134.6, 129.7, 129.6, 128.7, 123.5, 123.4, 68.8, 33.4, 31.5, 24.6, 24.3 ppm. FTIR (KBr pellet): ($\nu_{CN}$) 2121 cm$^{-1}$ also 3073, 3051, 3017, 2960, 2926, 2867, 1596, 1577, 1460, 1418, 1383, 1362, 1055, 803, 790, 755 cm$^{-1}$. Anal Calcd. for $C_{65}H_{79}ClN_2Pd_2$: C, 68.69; H, 7.01; N, 2.46. Found: C, 68.39; H, 7.19; N, 2.40.

**S1.7. Synthesis of ($\mu$-$C_3H_5$)($\mu$-O*t*Bu)[Pd(CNAr$^{Dipp2}$)]$_2$ (7).** To a solution of ($\mu$-$C_3H_5$)($\mu$-Cl)[Pd(CNAr$^{Dipp2}$)]$_2$ (0.100 g, 0.0881 mmol) in $Et_2O$ (10 mL) was added NaO*t*Bu (0.025 g, 0.26 mmol, 3.0 equiv). The reaction mixture became cloudy and bright orange in color and was stirred overnight, during which time the solution became beige in color. The solvent was then removed *in vacuo* and the resulting residue was washed with *n*-pentane (3 x 2 mL). The resulting yellow solid was dissolved in THF (4 mL), and the solution filtered through a plug of Celite, and stored at –35 ˚C overnight to produce yellow crystals which were collected, washed with *n*-pentane (3 x 2 mL), and dried *in vacuo*. Yield: 0.053 g, 0.045 mmol, 51%. Crystals of **7** • $C_6H_5F$ suitable for X-ray diffraction were obtained by vapor diffusion of $Et_2O$ into a fluorobenzene solution at –35 ˚C over 5 days. $^1$H NMR (400.1 MHz, $C_6D_6$, 20 ˚C): δ = 7.33 (t, *J* = 8 Hz, 4H, *p*-Dipp), 7.17 (d, *J* = 8 Hz, 8H, *m*-Dipp), 6.92 (apparent s, 6H, *m*-Ph and *p*-Ph), 2.72 (septet, *J* = 7 Hz, 4H, C*H*($CH_3$)$_2$), 2.70 (septet, *J* = 7 Hz, 4H, C*H*($CH_3$)$_2$), 2.25 (d, 2H, *J* = 8 Hz, C$H_2$ allyl), 2.04 (m, 1H, C*H* allyl), 1.26 (d, *J* = 7 Hz, 12H, CH(C$H_3$)$_2$), 1.23 (d, *J* = 7 Hz, 12H, CH(C$H_3$)$_2$), 1.16 (s, 9H, OC(C$H_3$)$_3$), 1.08 (d, *J* = 7 Hz, 24H, CH(C$H_3$)$_2$), 0.67 (d, *J* = 12 Hz, 2H, C$H_2$ allyl) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$, 20 ˚C): δ = 155.9 (*C*≡N), 146.7, 139.6, 135.0, 129.8, 129.6, 129.2, 123.5, 123.4, 72.1, 70.1, 37.2, 31.5, 26.7, 24.6, 24.4 ppm. FTIR (KBr pellet): ($\nu_{CN}$) 2110 and 2097 cm$^{-1}$ also 3061, 3027, 2962, 2927, 2868, 1580, 1462, 1417, 1384, 1363, 1180, 1056, 804, 792, 756 cm$^{-1}$. Anal Calcd. for $C_{69}H_{88}N_2OPd_2$: C, 70.57; H, 7.55; N, 2.39. Found: C, 70.29; H, 7.51; N, 2.32.

**S1.8. Synthesis of Pd$_3$($\eta^2$-Dipp-μ-CNAr$^{Dipp2}$)$_3$ (8).** To a THF solution of ($\mu$-$C_3H_5$)($\mu$-Cl)[Pd(CNAr$^{Dipp2}$)]$_2$ (0.153 g, 0.134 mmol, 3 mL) was added a THF solution of sodium isopropoxide (0.042 g, 0.51 mmol, 3.8 equiv). The reaction mixture was stirred for 1 h during which time it became cloudy and dark reddish brown in color. All volatile materials were removed *in vacuo*. The brown residue was extracted with 15 mL *n*-pentane, the solution was filtered through Celite and dried *in vacuo*. The resulting residue was dissolved in THF (2 mL) and stored at –35 ˚C for 7 days to produce dark red crystals which were collected and dried *in vacuo*. Yield: 0.078 g, 0.049 mmol, 48%. $^1$H NMR (400.1 MHz, $C_6D_6$, 20 ˚C): δ = 7.13 (m, 6H, *p*-Dipp), 7.01 (m, 21H, *m*-Dipp, *m*-Ph, and *p*-Ph), 2.90 (septet, *J* = 7 Hz, 12H, C*H*($CH_3$)$_2$), 1.22 (d, *J* = 7 Hz, 12H, CH(C$H_3$)$_2$), 1.10 (d, *J* = 7 Hz, 12H, CH(C$H_3$)$_2$) ppm. $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$, 20 ˚C): δ = 220.8 (*C*≡N), 141.9, 141.7, 137.8, 137.4, 135.0, 130.3, 125.6, 118.7, 31.7 (*C*H($CH_3$)$_2$), 24.6 (CH(*C*$H_3$)$_2$), 24.4 (CH(*C*$H_3$)$_2$) ppm. FTIR (KBr pellet): ($\nu_{CN}$) 1768 cm$^{-1}$ also 2963, 2931, 2868, 1458, 1383, 1363, 1177, 1047, 906, 804, 792, 758 cm$^{-1}$. ESI-MS(+) for $C_{93}H_{111}N_3Pd_3$: *m/z* = 1589.25 [M]$^+$ (calc'd, 1589.59). ]$^+$. Anal. calcd. for $C_{93}H_{111}N_3Pd_3$: C, 70.24; H, 7.04; N, 2.64. Found: C, 69.97; H, 6.90; N, 2.48.

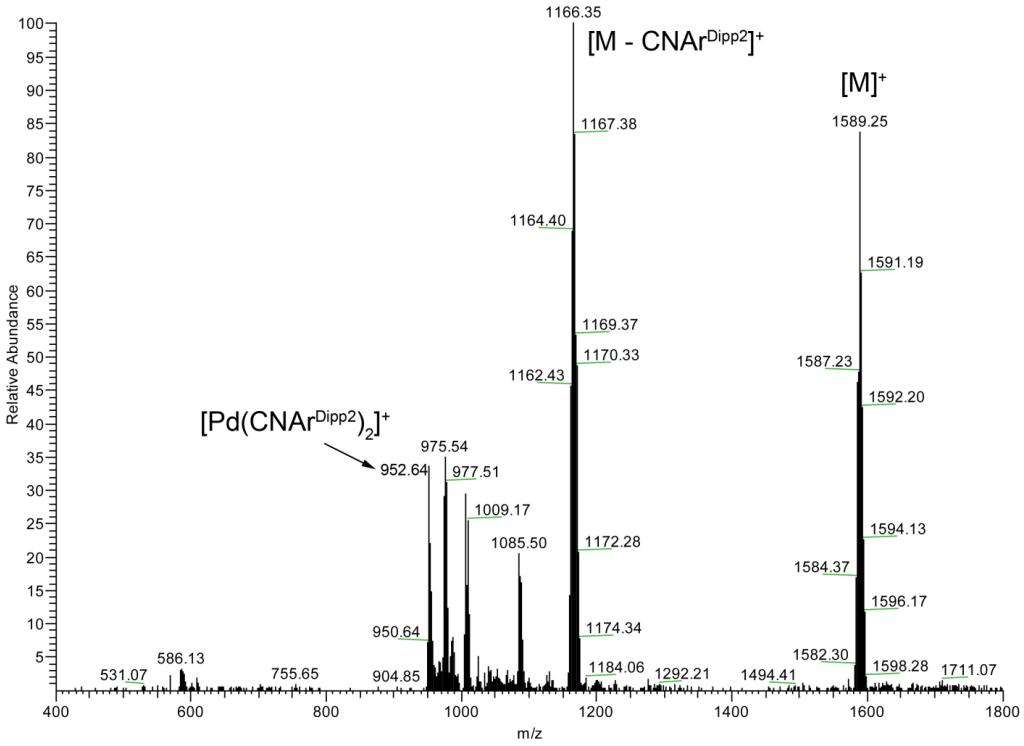


**Figure S.1.** ESI-MS(+) of $Pd_3(\eta^2$-Dipp-μ-$CNAr^{Dipp2})_3$ in acetone.

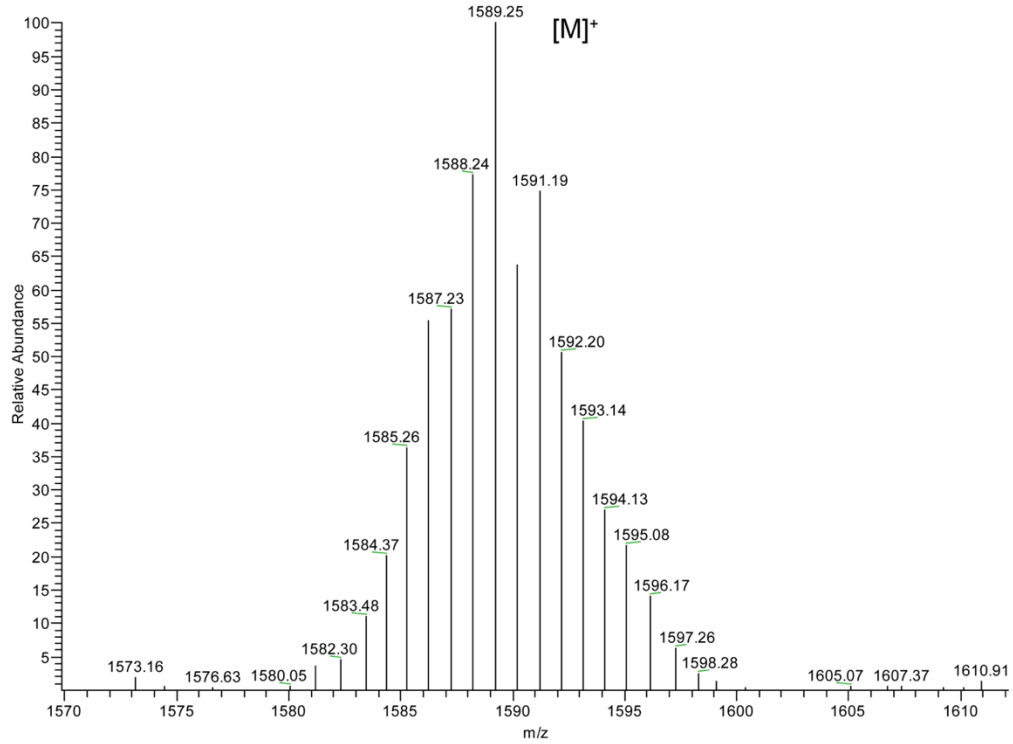


**Figure S2.** ESI-MS(+) of $Pd_3(\eta^2$-Dipp-μ-$CNAr^{Dipp2})_3$, zoom-in of the molecular ion peak.

**S1.9. Synthesis of $Pd_3(\mu\text{-}CO)_3(CNAr^{Dipp2})_3$ (9).** An $Et_2O$ solution of $Pd_3(\eta^2\text{-Dipp-}\mu\text{-}CNAr^{Dipp2})_3$ (0.080 g, 0.050 mmol, 7 mL) was loaded into a 25 mL resealable ampoule. The ampoule was connected to a Schlenk line and the solution was frozen in a liquid nitrogen bath. After the solution was degassed, 3.6 mL CO gas (0.15 mmol, 3.0 equiv) was added through the evacuated ampoule sidearm. The solution was allowed to thaw and warmed to room temperature with stirring over 1 h, during which time it changed in color from orange to yellow. All volatiles were then removed *in vacuo*. The resulting light brown residue was washed with *n*-pentane (3 x 5 mL) to afford a mustard yellow solid which is spectroscopically pure. Yield: 0.060 g, 0.036 mmol, 72%. Single crystals of **9** • $Et_2O$ suitable for X-ray diffraction were grown by storing an $Et_2O$ solution at –35 ˚C. $^1$H NMR (499.8 MHz, $C_6D_6$, 20 ˚C): δ = 7.35 (t, 6H, *J* = 8 Hz, *p*-Dipp), 7.26 (d, 12H, *J* = 8 Hz, *m*-Dipp), 6.98 (m, 9H, *m*- and *p*-Ar), 2.77 (septet, 12H, *J* = 7 Hz, C*H*$(CH_3)_2$), 1.42 (d, 36H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.17 (d, 36H, *J* = 7 Hz, CH(C*H*$_3)_2$) ppm. $^{13}$C{$^1$H} NMR (125.7, $C_6D_6$, 20 ˚C): δ = 231.8 (μ-*C*O), 161.0 (*C*NR), 146.7, 139.4, 134.9, 129.8, 129.7, 128.7, 128.3, 123.4, 31.5, 24.8, 24.2 ppm. FTIR (KBr windows, $C_6D_6$, 20 ˚C): ($\nu_{CO}$) 1871 (vs) cm$^{-1}$; ($\nu_{CN}$) 2107 (vs) cm$^{-1}$; also 3062, 3025, 2962, 2926, 2869, 1460, 1417, 1384, 1363, 1055, 805, 793, 758, 731, 695 cm$^{-1}$. Anal. calcd. for $C_{96}H_{111}N_3O_3Pd_3$: C, 68.87; H, 6.68; N, 2.51. Found: C, 68.70; H, 6.68; N, 2.62.

**S1.10. Synthesis of $Pd_3(\mu\text{-}\eta^2\text{:}\eta^1\text{-}PhNO)_3(CNAr^{Dipp2})_3$ (10) from $[Pd(\eta^2\text{-Dipp-}\mu\text{-}CNAr^{Dipp2})]_3$.** To a $Et_2O$ solution of $Pd_3(\eta^2\text{-Dipp-}\mu\text{-}CNAr^{Dipp2})]_3$ (0.060 g, 0.038 mmol, 2 mL) was added a $Et_2O$ solution of nitrosobenzene (0.012 g, 0.11 mmol, 3.0 equiv, 2 mL). After stirring for 10 min, all volatiles were removed under reduced pressure. The resulting residue was isolated and placed on a glass frit, washed with acetonitrile (3 x 10 mL), and dried *in vacuo* to afford $Pd_3(\mu\text{-}\eta^2\text{:}\eta^1\text{-PhNO})_3(CNAr^{Dipp2})_3$ as an orange powder. Yield: 0.048 g, 0.025 mmol, 66%. The spectroscopic signals of **10** obtained by this method are identical to those reported previously.[5]

## S2. Suzuki-Miyaura Cross-Coupling Procedures and Characterization Data

**S2.1. General Considerations.** GC-MS analyses were performed on a Hewlett-Packard 5890 Series II chromatograph equipped with an automatic liquid sampler and HP-5 column (30 m x 0.25 mm i.d., 0.25 $\mu$m film thickness). The following GC oven conditions were employed: inlet temp. = 220 ˚C; detector temp. = 280 ˚C; initial temp. = 60 ˚C with an initial hold time of 2 min, followed by a 30 ˚C min$^{-1}$ ramp to 260 ˚C, and then a hold at 260 ˚C for 4 min.

**S2.2. General Procedure A: Suzuki-Miyaura Cross-Coupling Reactions Using $Pd(CNAr^{Dipp2})_2$ (1).** A mixture of aryl bromide (0.52 mmol, 1.0 equiv), arylboronic acid (1.04 mmol, 2.00 equiv), $Pd(CNAr^{Dipp2})_2$ (0.005 g, 0.005 mmol, 1 mol %), NaO*t*Bu (0.150 g, 1.57 mmol, 3.00 equiv), and *i*PrOH (2.0 mL) was magnetically stirred in a sealed 25 mL resealable ampoule under argon at the indicated temperature until the aryl bromide was completely consumed as determined by GC-MS analysis. The reaction mixture was cooled to room temperature, after which the solvent was removed *in vacuo* to give a residue that was dissolved in water (6 mL) and extracted with hexanes (3 x 4 mL). The organic layers were combined and concentrated *in vacuo* to give crude biaryl product that was purified by column chromatography on silica gel, eluting with hexanes.

**S2.2.1. 4-methylbiphenyl[6] (Table 1, entry 1).** Procedure A was employed using 4-bromotoluene (64 µL, 0.52 mmol, 1.0 equiv) and phenylboronic acid (0.127 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.066 g, 0.39 mmol, 75%. MS (EI) *m*/*z*: 168 [$M^+$].

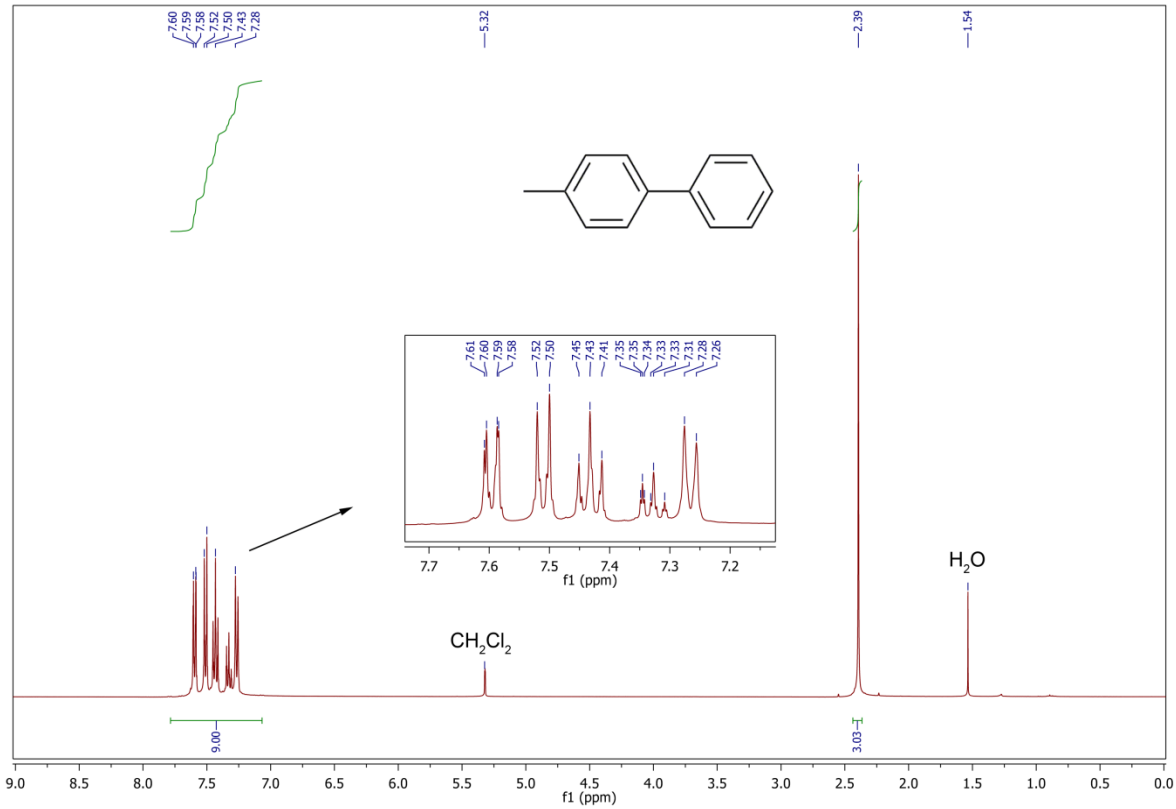


**Figure S3.** $^1$H NMR spectrum of 4-methylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.2. 2,4'-dimethylbiphenyl[7] (Table 1, entry 2 and Table 2, entry 2). Method 1.** Procedure A was employed using 4-bromotoluene (64 µL, 0.52 mmol, 1.0 equiv) and *o*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.073 g, 0.40 mmol, 77%. **Method 2.** Procedure A was employed using 2-bromotoluene (63 µL, 0.522 mmol, 1.0 equiv) and *p*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.074 g, 0.41 mmol, 78%. MS (EI) *m*/*z*: 182 [$M^+$].

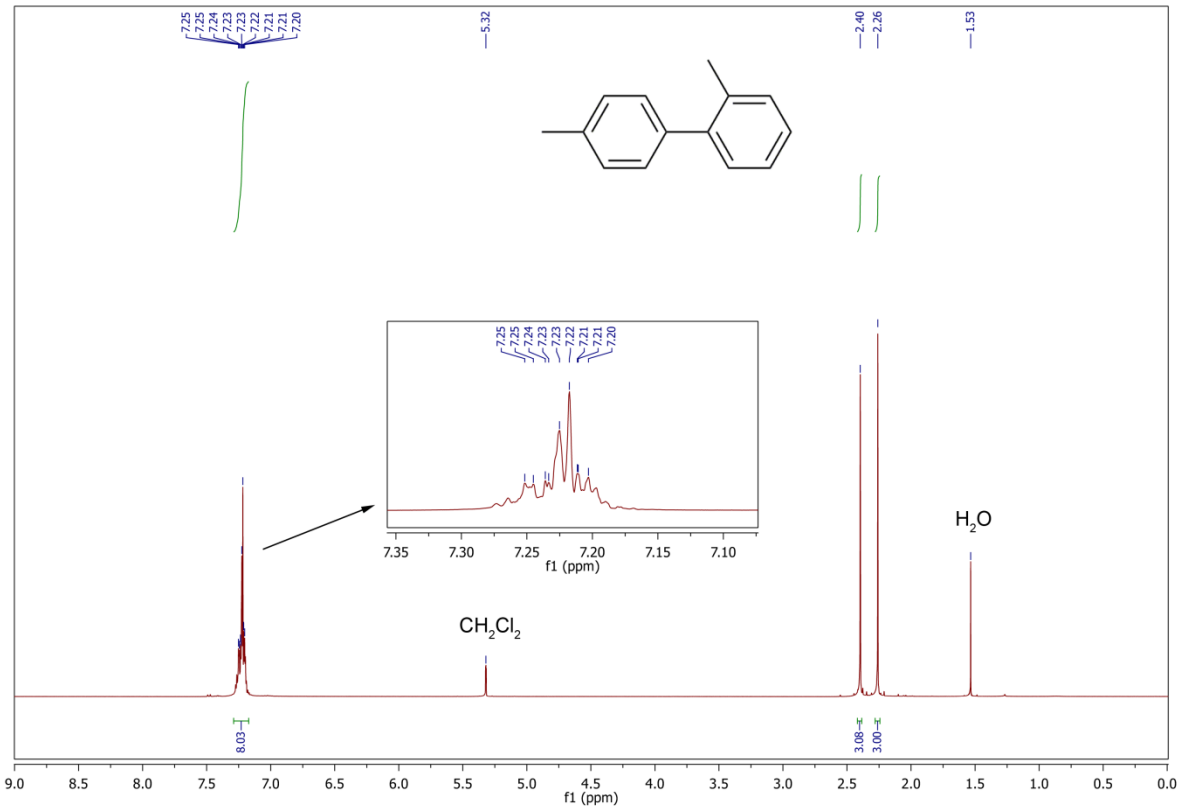


**Figure S4.** $^1$H NMR spectrum of 2,4'-dimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.3. 4-methyl-(1,1',2',1'')-terphenyl[8] (Table 1, entry 3).** Procedure A was employed using 4-bromotoluene (64 µL, 0.52 mmol, 1.0 equiv) and 2-biphenylboronic acid (0.207 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.092 g, 0.38 mmol, 73%. MS (EI) *m*/*z*: 244 [$M^+$].

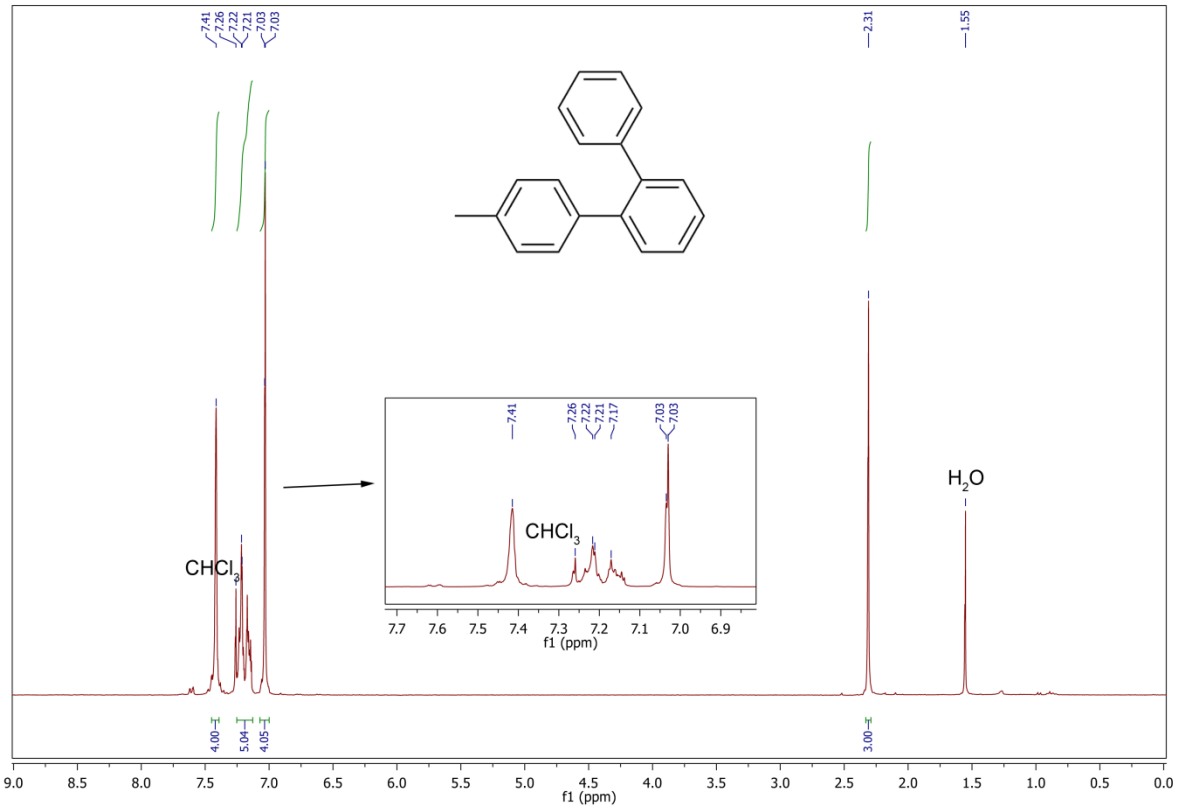


**Figure S5.** $^1$H NMR spectrum of 4-methyl-(1,1',2',1'')-terphenyl (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.4. 3-methylbiphenyl**[9] **(Table 1, entry 4).** Procedure A was employed using 3-bromotoluene (63 µL, 0.52 mmol, 1.0 equiv) and phenylboronic acid (0.127 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.065 g, 0.39 mmol, 74%. MS (EI) *m*/*z*: 168 [$M^+$].

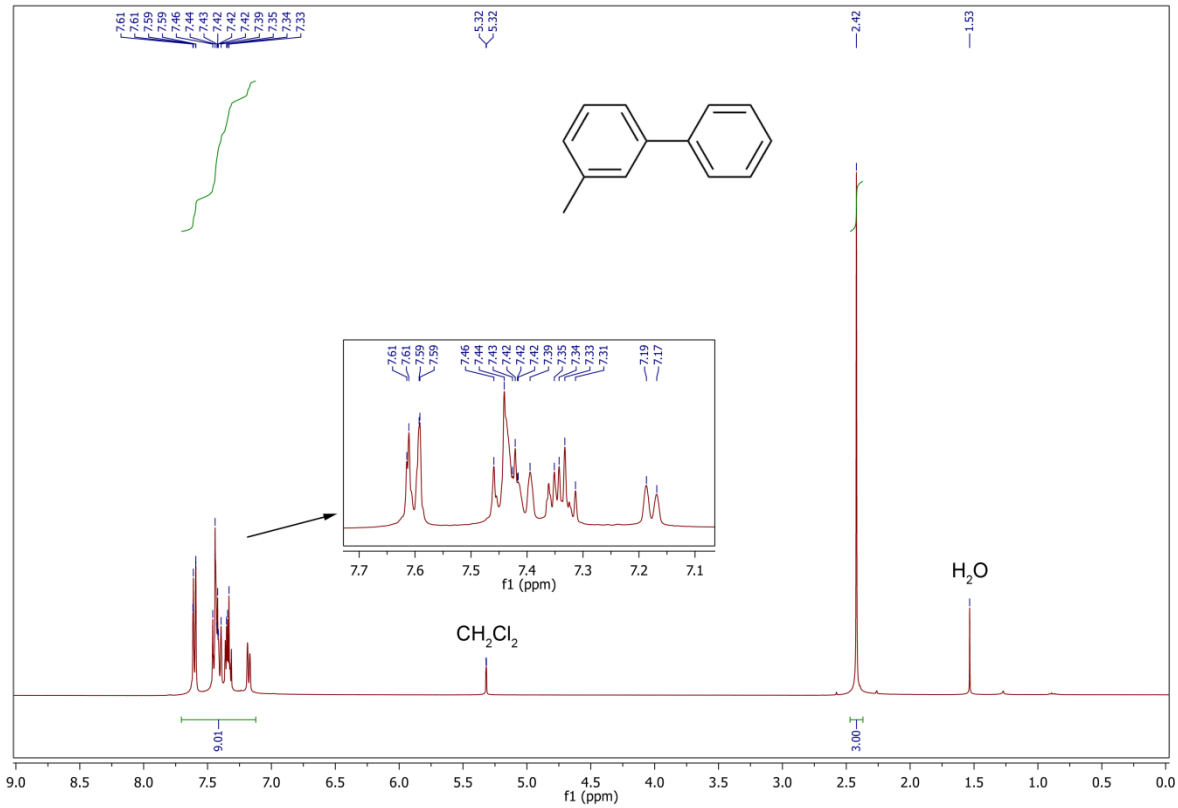


**Figure S6.** $^1$H NMR spectrum of 3-methylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.5. 3,4'-dimethylbiphenyl[10] (Table 1, entry 5).** Procedure A was employed using 3-bromotoluene (63 µL, 0.52 mmol, 1.0 equiv) and *p*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.081 g, 0.44 mmol, 85%. MS (EI) *m*/*z*: 182 [$M^+$].

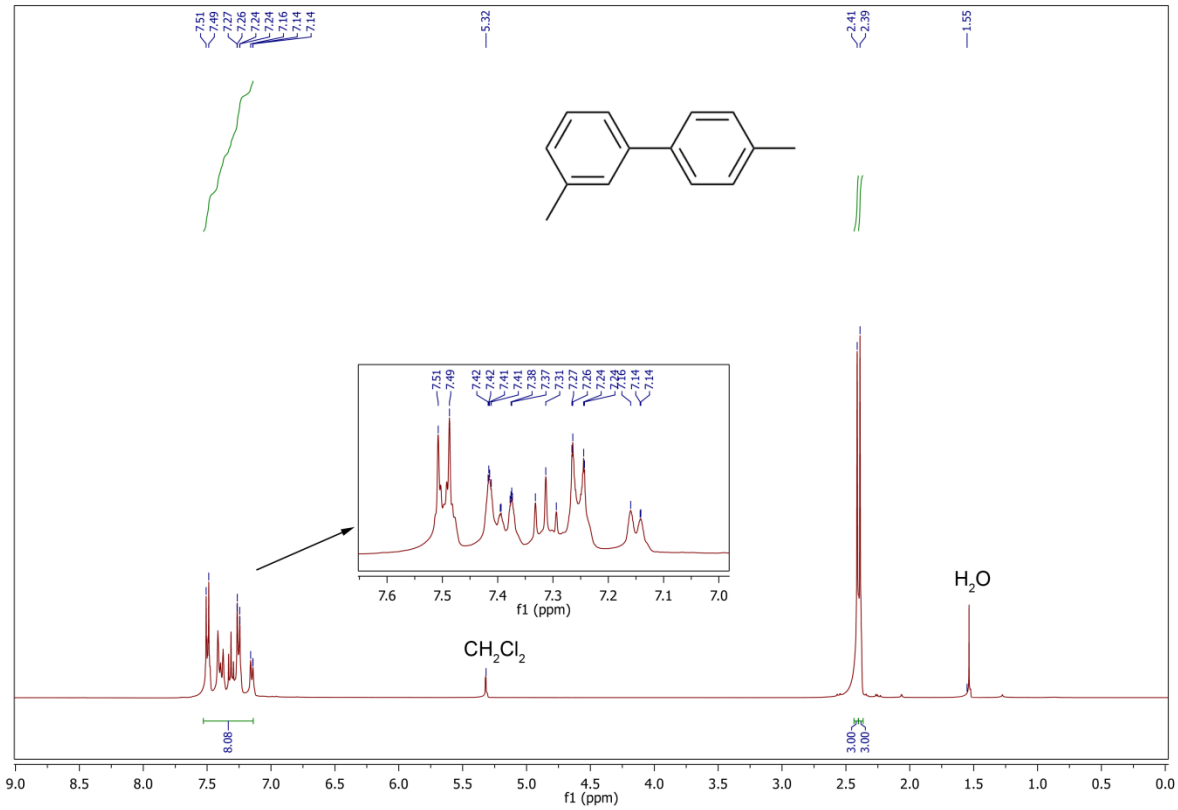


**Figure S7.** $^1$H NMR spectrum of 3,4'-dimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.6. 2,3'-dimethylbiphenyl[11] (Table 1, entry 6).** Procedure A was employed using 3-bromotoluene (63 µL, 0.52 mmol, 1.0 equiv) and *o*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.069 g, 0.38 mmol, 73%. MS (EI) *m*/*z*: 182 [$M^+$].

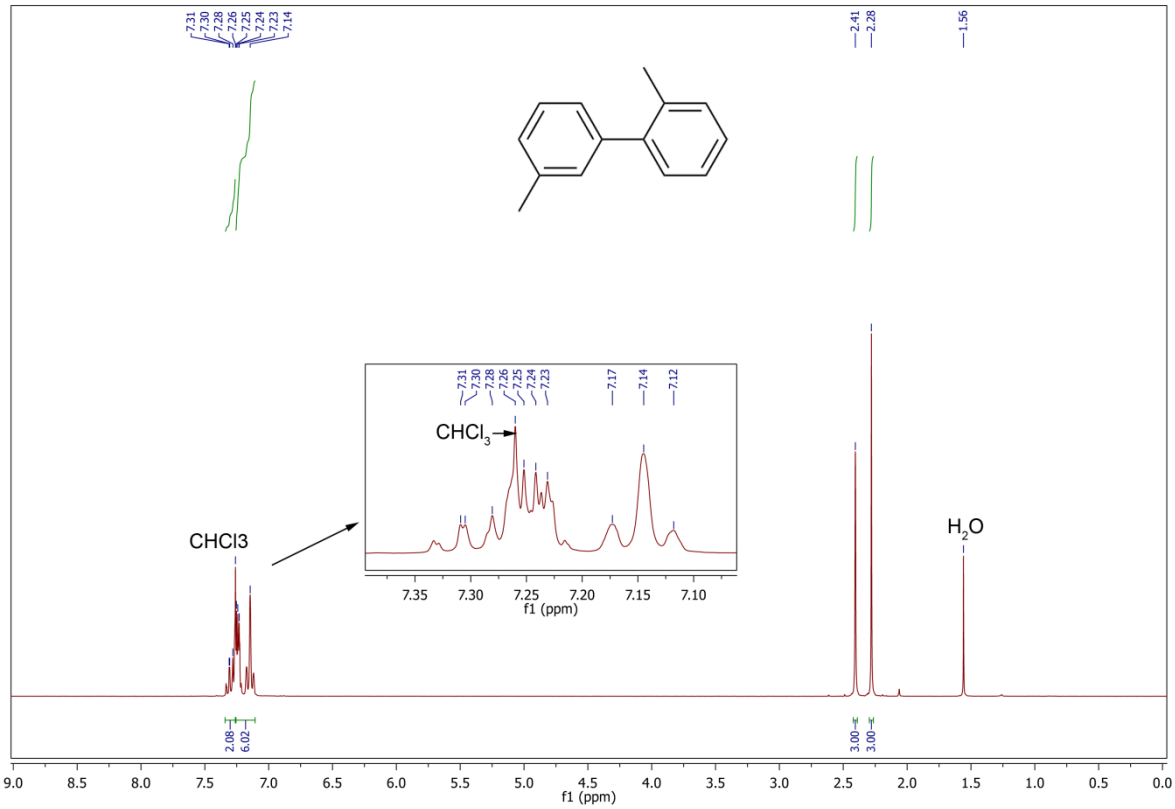


**Figure S8.** $^1$H NMR spectrum of 2,3'-dimethylbiphenyl (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.7. 3,5-dimethylbiphenyl[6] (Table 1, entry 7).** Procedure A was employed using 1-bromo-3,5-dimethylbenzene (71 µL, 0.52 mmol, 1.0 equiv) and phenylboronic acid (0.127 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.074 g, 0.40 mmol, 77%. MS (EI) *m*/*z*: 182 [$M^+$].

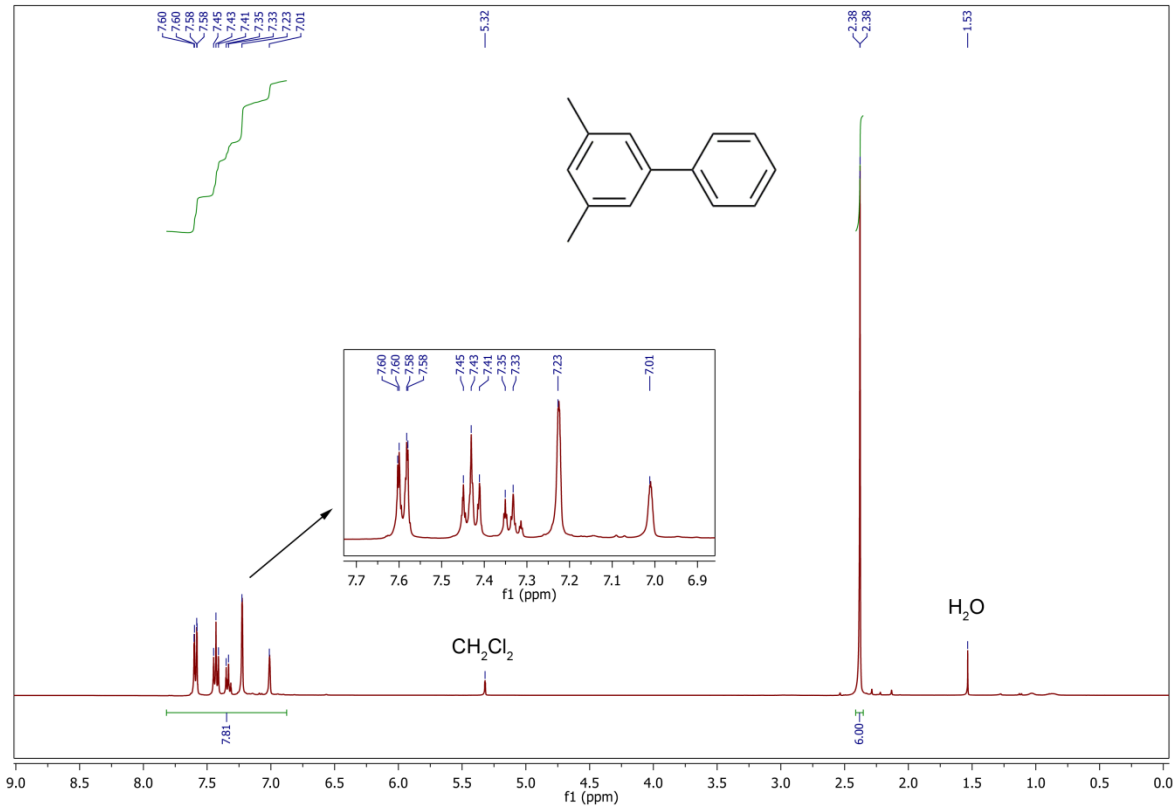


**Figure S9.** $^1$H NMR spectrum of 3,5-dimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.8. 3,4',5-trimethylbiphenyl[12] (Table 1, entry 8).** Procedure A was employed using 1-bromo,3,5-dimethylbenzene (71 µL, 0.52 mmol, 1.0 equiv) and *p*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.079 g, 0.40 mmol, 77%. MS (EI) *m*/*z*: 196 [$M^+$].

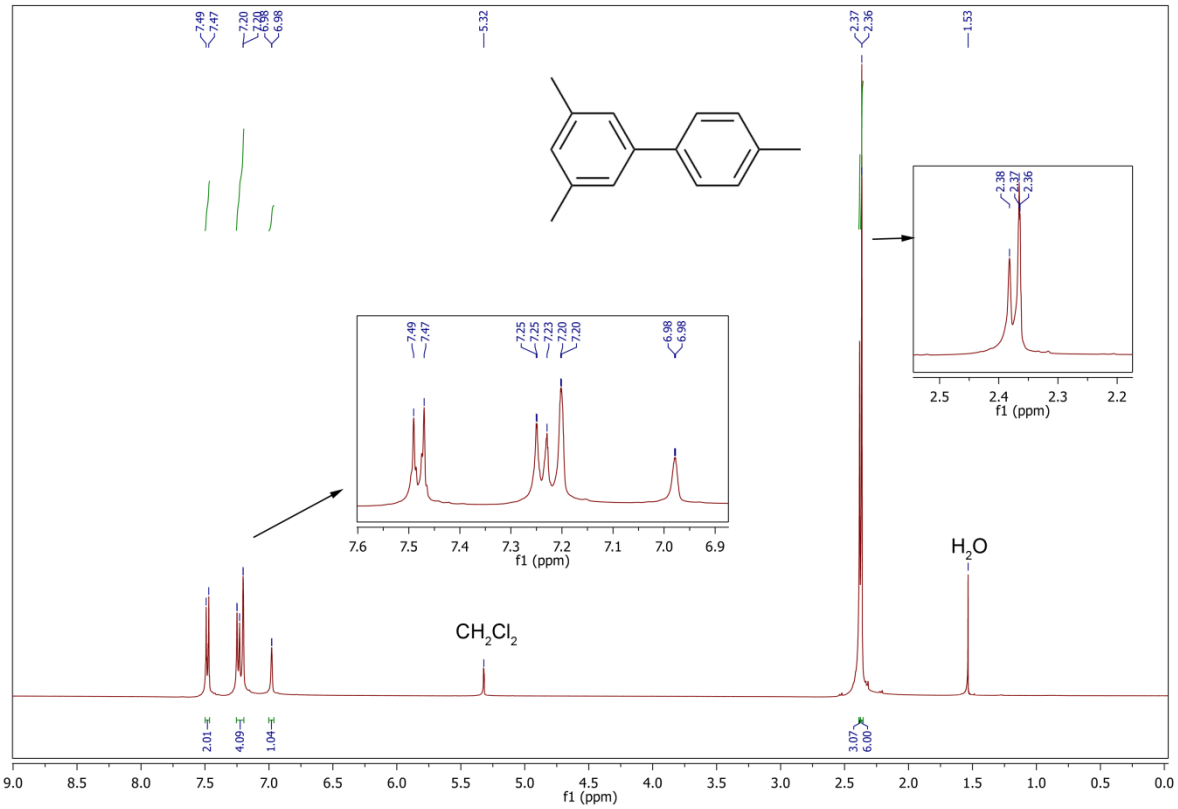


**Figure S10.** $^1$H NMR spectrum of 3,4',5-trimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.9. 2',3,5-trimethylbiphenyl[13] (Table 1, entry 9).** Procedure A was employed using 1-bromo-3,5-dimethylbenzene (71 µL, 0.52 mmol, 1.0 equiv) and *o*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.078 g, 0.40 mmol, 76%. MS (EI) *m*/*z*: 196 [$M^+$].

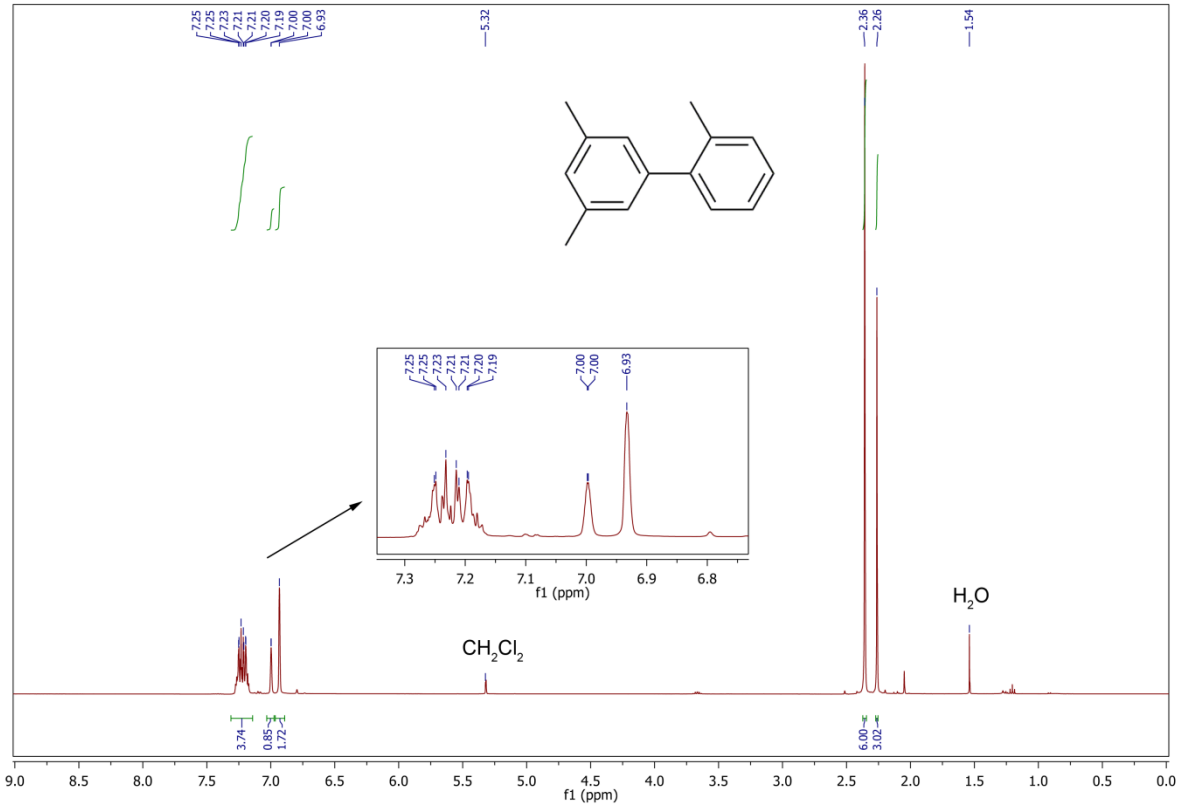


**Figure S11.** $^1$H NMR spectrum of 2',3,5-trimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.10. 3,5-dimethyl-(1,1',2',1")-terphenyl (Table 1, entry 10).** Procedure A was employed using 1-bromo-3,5-dimethylbenzene (71 μL, 0.52 mmol, 1.0 equiv) and 2-biphenylboronic acid (0.207 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. The product was isolated as a colorless oil. Isolated yield: 0.092 g, 0.36 mmol, 69%. $^{1}$H NMR (400.1 MHz, $CDCl_3$, 20 ˚C): δ = 7.47-7.35 (m, 5H), 7.23-7.13 (m, 5H), 6.83 (s, 1H), 6.75 (s, 2H), 2.19 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz, 20 ˚C) δ = 141.8, 141.5, 140.9, 140.7, 137.3, 130.6, 130.0, 128. 9, 128.2, 128.0, 127.9, 127.5, 127.4, 126.5, 21.4 ppm. HR-MS (EI) calc'd for $C_{20}H_{18}$: *m/z* = 258.1409. Found: *m/z* = 258.1402 [$M^{+}$].

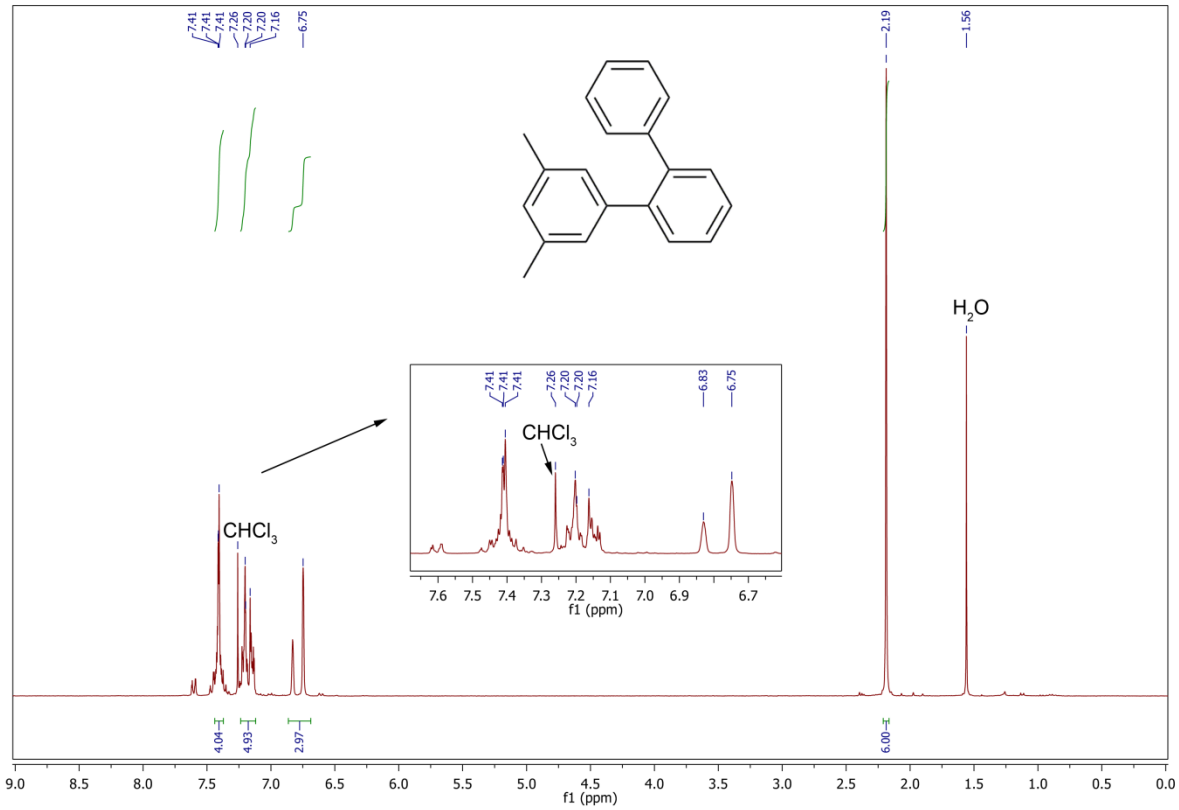


**Figure S12.** $^{1}$H NMR spectrum of 3,5-dimethyl-(1,1',2',1")-terphenyl (400.1 MHz, $CDCl_3$, 20 °C).

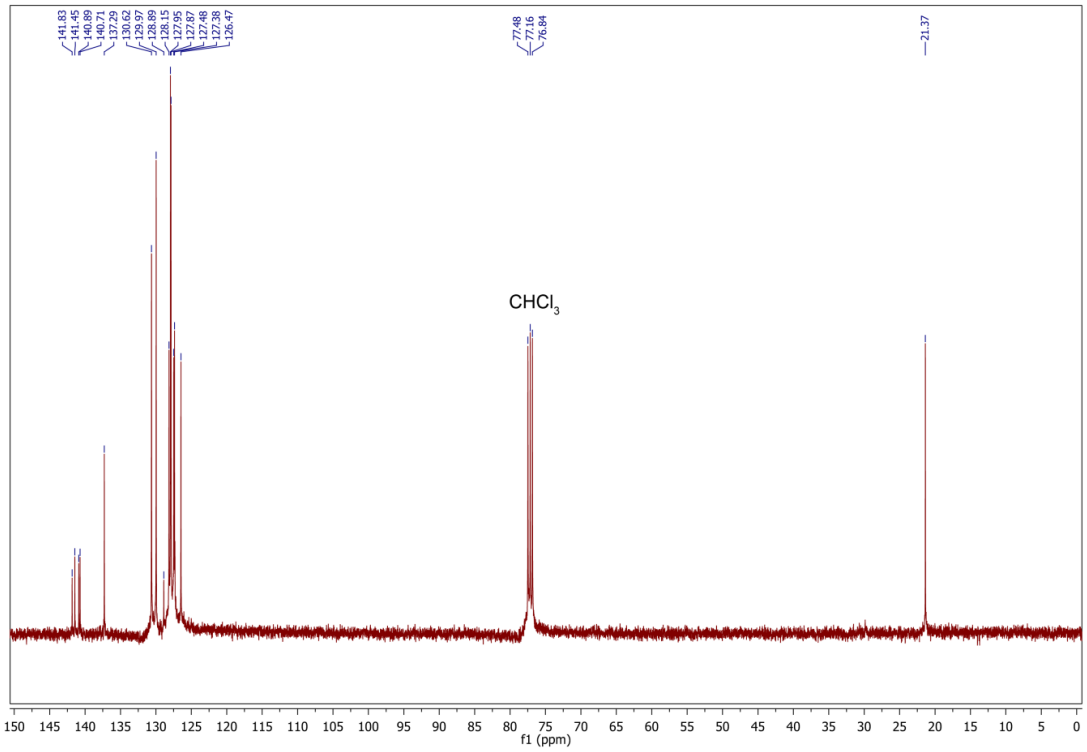


**Figure S13.** $^{13}C\{^{1}H\}$ NMR spectrum of 3,5-dimethyl-(1,1',2',1")-terphenyl (100.6 MHz, $CDCl_3$, 20 °C).

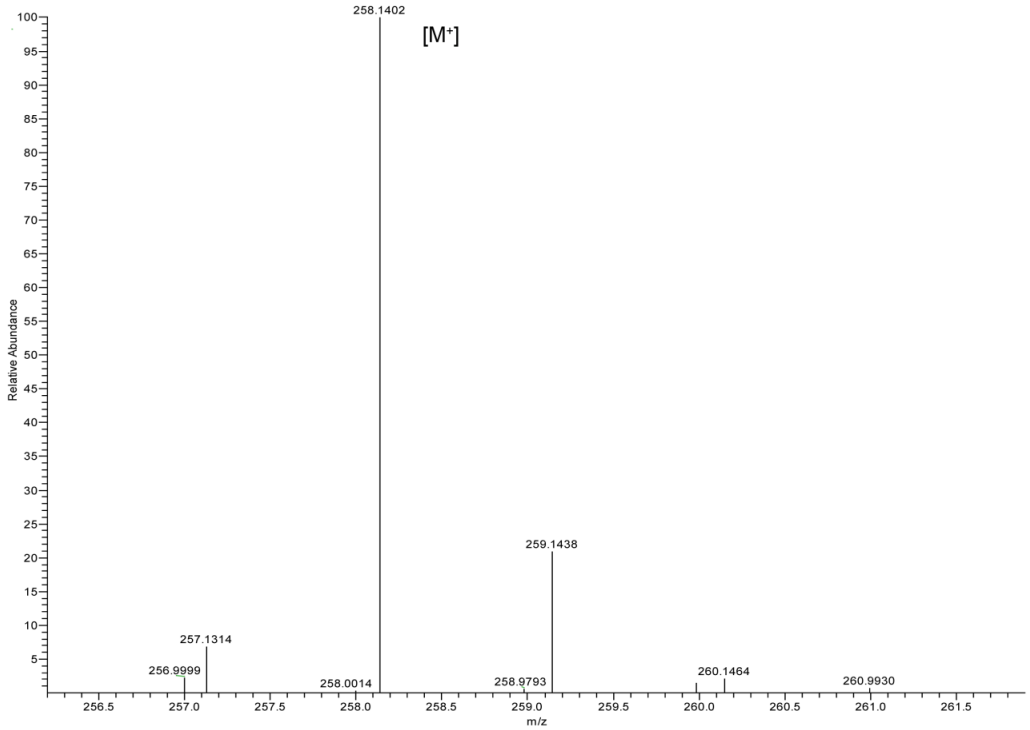


**Figure S14.** HR-MS (EI) of 3,5-dimethyl-(1,1',2',1")-terphenyl.

**S2.2.11. 1-phenylnaphthalene[9] (Table 1, entry 11).** Procedure A was employed using 1-bromonaphthalene (73 µL, 0.52 mmol, 1.0 equiv) and phenylboronic acid (0.127 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.078 g, 0.38 mmol, 74%. MS (EI) *m*/*z*: 204 [$M^+$].

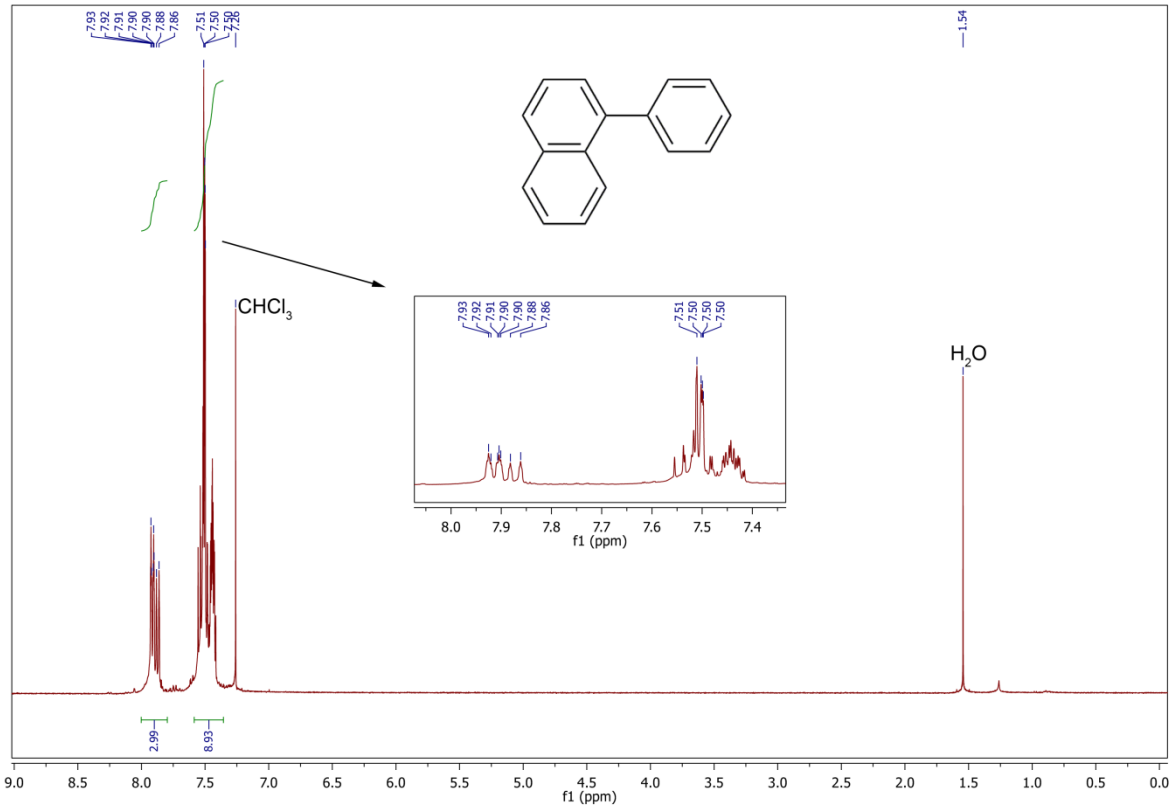


**Figure S15.** $^1$H NMR spectrum of 1-phenylnaphthalene (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.12. 1-(4-methylphenyl)-naphthalene[14] (Table 1, entry 12).** Procedure A was employed using 1-bromonaphthalene (73 µL, 0.52 mmol, 1.0 equiv) and *p*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.084 g, 0.39 mmol, 74%. MS (EI) *m*/*z*: 218 [$M^+$].

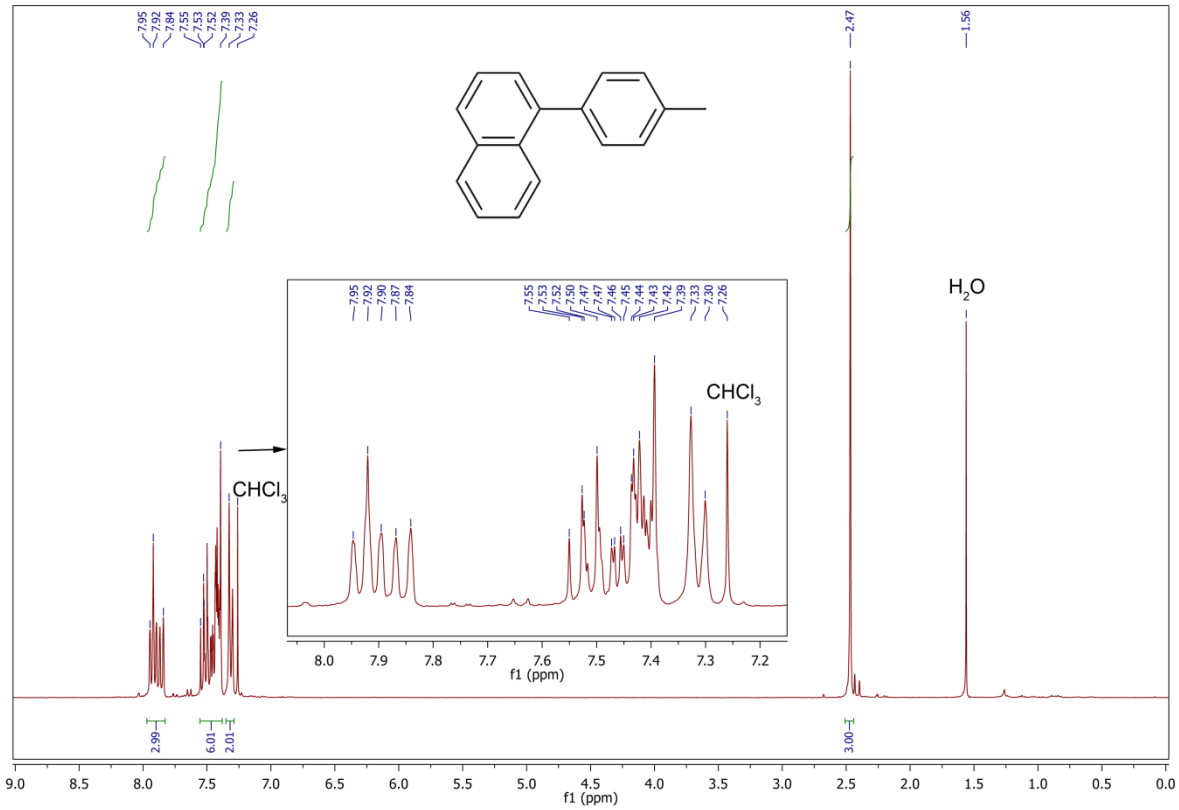


**Figure S16.** $^1$H NMR spectrum of 1-(4-methylphenyl)-naphthalene (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.13. 1-(2-methylphenyl)-naphthalene[15] (Table 1, entry 13).** Procedure A was employed using 1-bromonaphthalene (73 µL, 0.52 mmol, 1.0 equiv) and *o*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.087 g, 0.40 mmol, 74%. MS (EI) *m*/*z*: 218 [$M^+$].

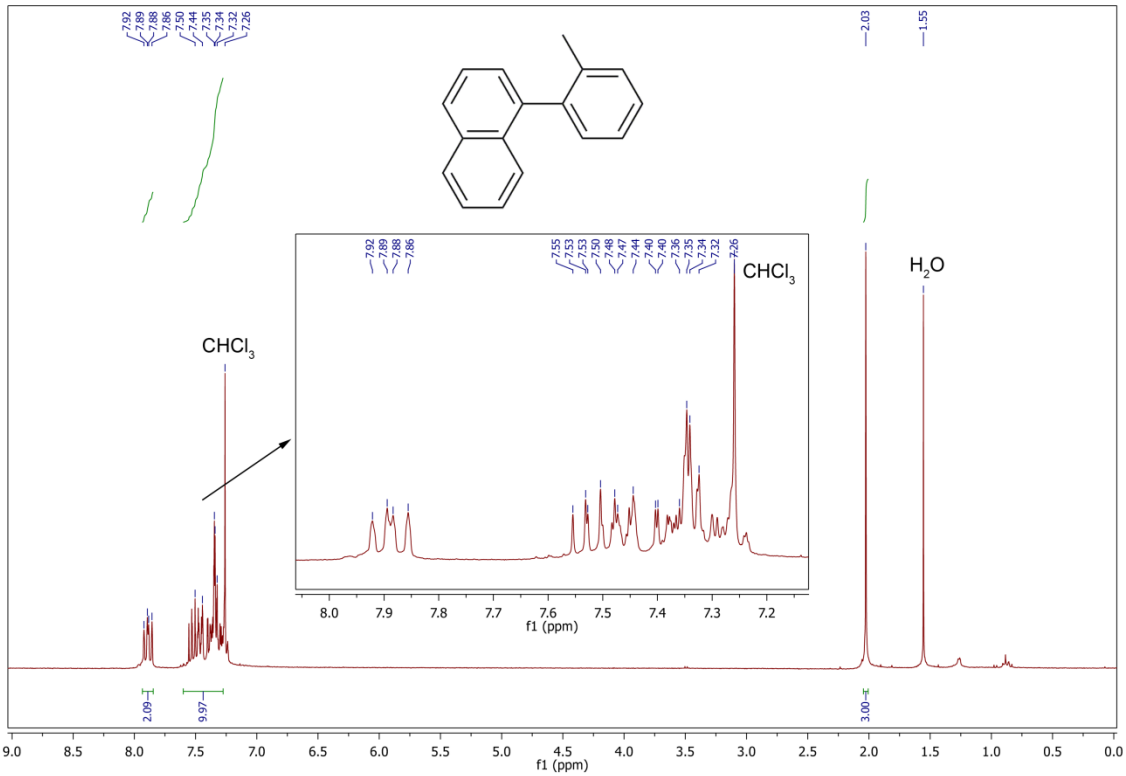


**Figure S17.** $^1$H NMR spectrum of 1-(2-methylphenyl)-naphthalene (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.14. 1,1'-biphenylnaphthalene[16] (Table 1, entry 14).** Procedure A was employed using 1-bromonaphthalene (73 μL, 0.52 mmol, 1.0 equiv) and 2-biphenylboronic acid (0.207 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at room temperature. Isolated yield: 0.104 g, 0.371 mmol, 71%. MS (EI) *m*/*z*: 280 [$M^+$].

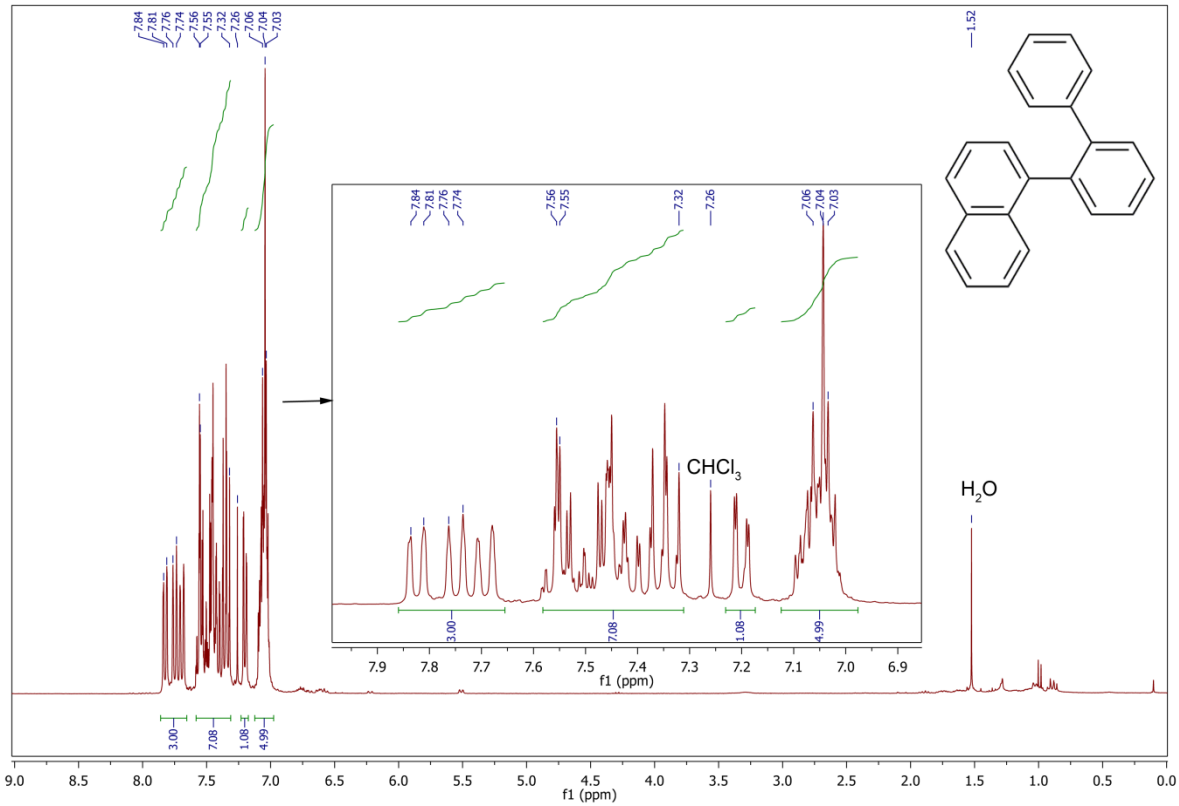


**Figure S18.** $^1$H NMR spectrum of 1,1'-biphenylnaphthalene (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.15. 2-methylbiphenyl[6] (Table 2, entry 1).** Procedure A was employed using 2-bromotoluene (63 µL, 0.52 mmol, 1.0 equiv) and phenylboronic acid (0.127 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.065 g, 0.39 mmol, 74%. MS (EI) *m*/*z*: 168 [$M^+$].

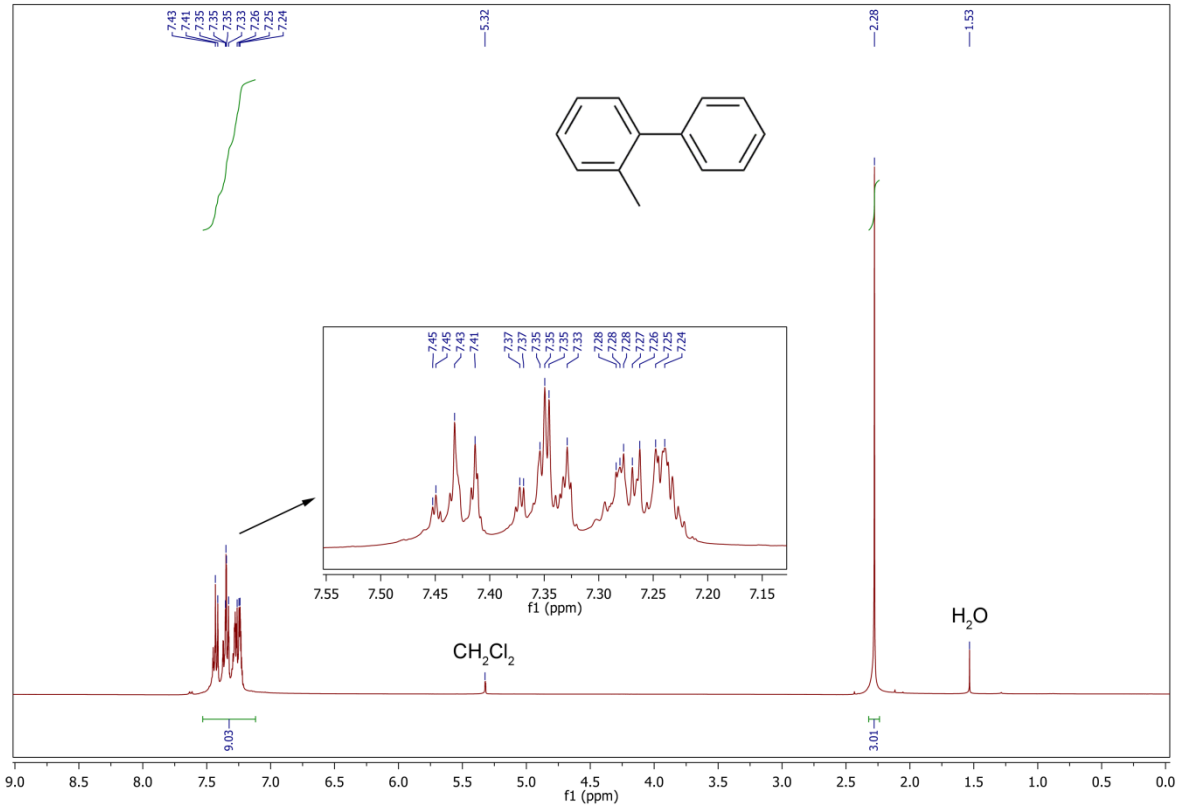


**Figure S19.** $^1$H NMR spectrum of 2-methylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.16. 2,4-dimethylbiphenyl[17] (Table 2, entry 3).** Procedure A was employed using 1-bromo-2,4-dimethylbenzene (71 µL, 0.52 mmol, 1.0 equiv) and phenylboronic acid (0.127 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.075 g, 0.41 mmol, 78%. MS (EI) *m*/*z*: 182 [$M^+$].

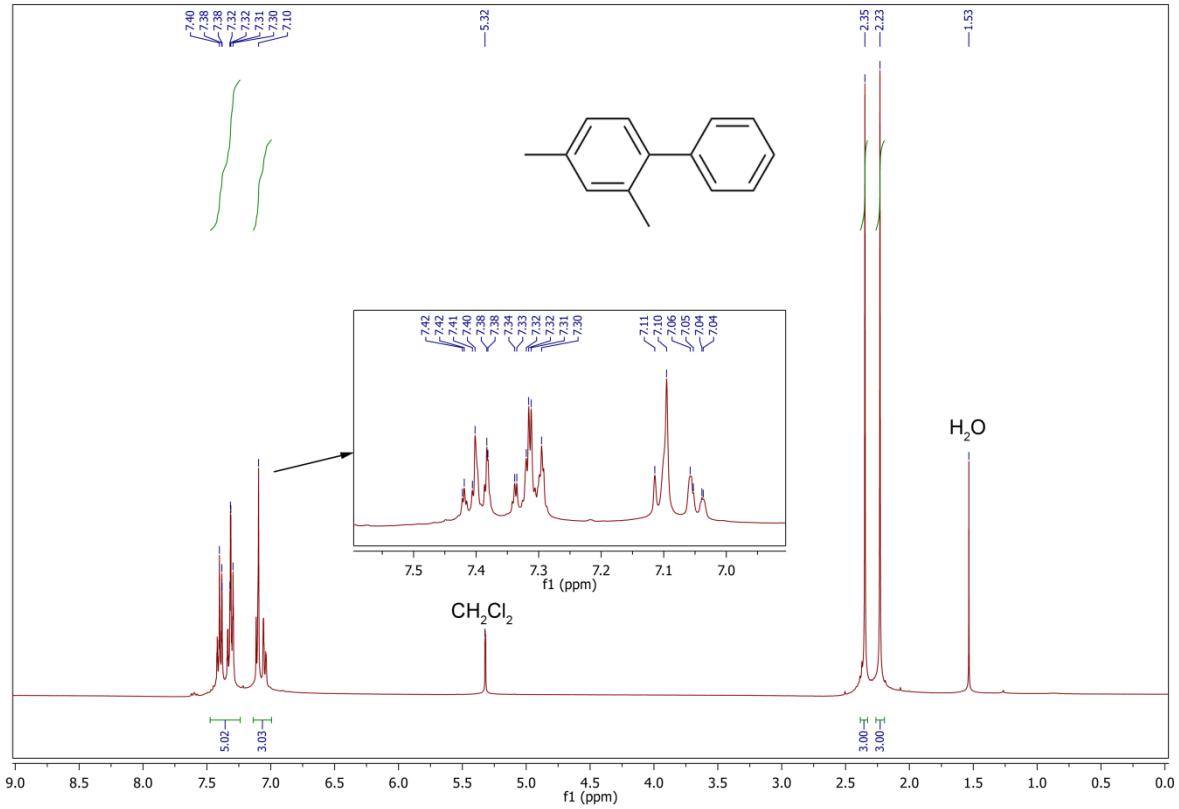


**Figure S20.** $^1$H NMR spectrum of 2,4-dimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.17. 2,4,4'-trimethylbiphenyl[18] (Table 2, entry 4).** Procedure A was employed using 1-bromo-2,4-dimethylbenzene (71 µL, 0.52 mmol, 1.0 equiv) and *p*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.078 g, 0.40 mmol, 76%. MS (EI) *m*/*z*: 196 [$M^+$].

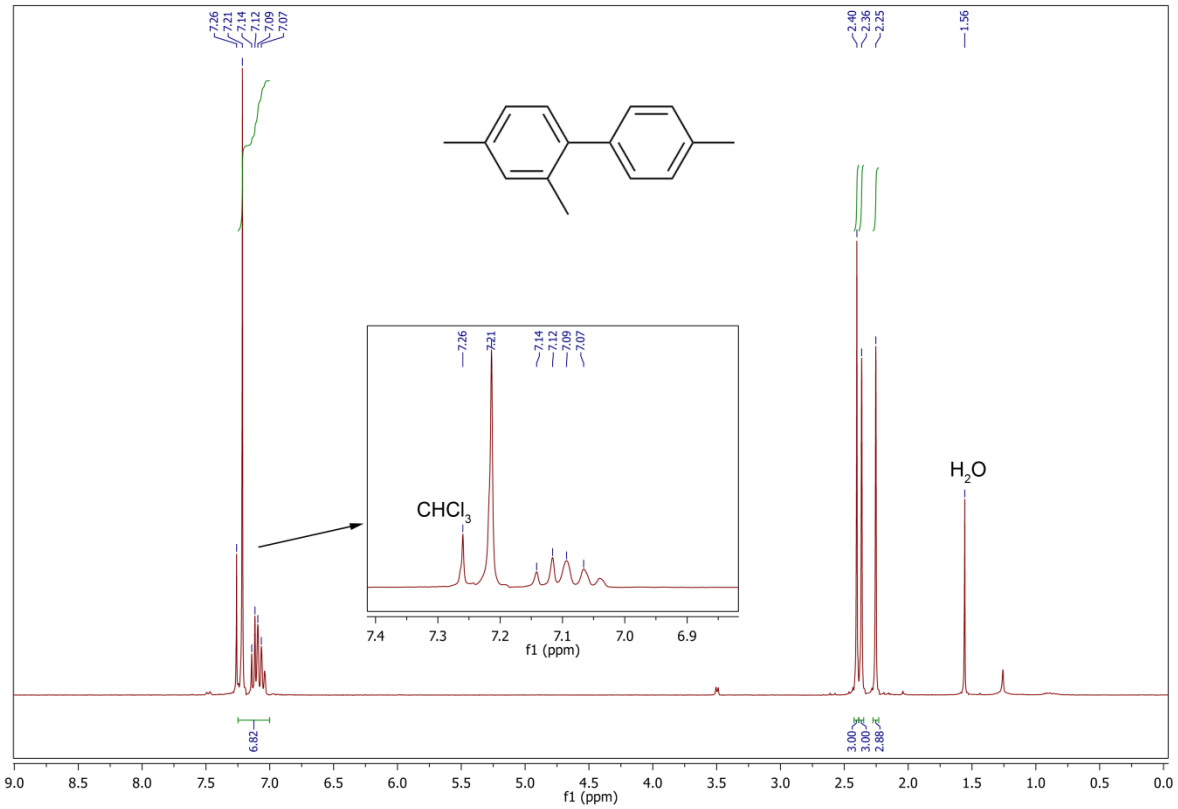


**Figure S21.** $^1$H NMR spectrum of 2,4,4'-trimethylbiphenyl (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.18. 2',2,4-trimethylbiphenyl[19] (Table 2, entry 5).** Procedure A was employed using 1-bromo-2,4-dimethylbenzene (71 µL, 0.52 mmol, 1.0 equiv) and *o*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.076 g, 0.39 mmol, 74%. MS (EI) *m*/*z*: 196 [$M^+$].

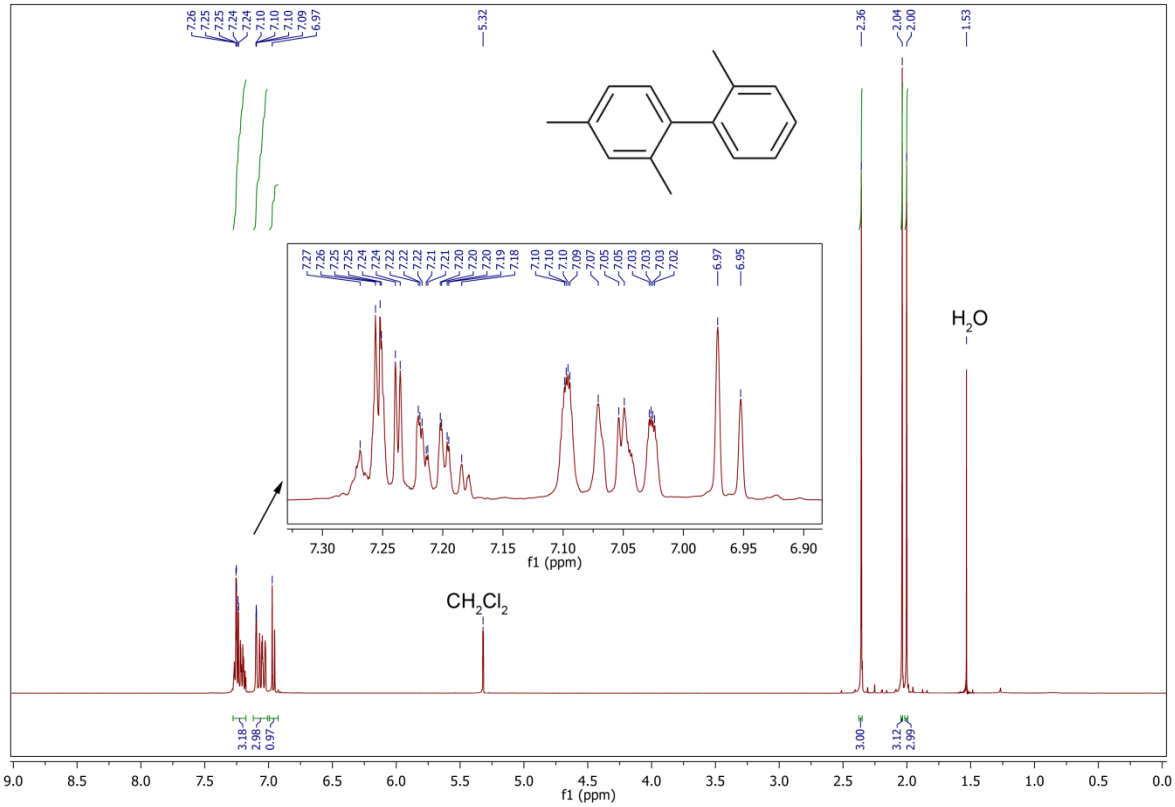


**Figure S22.** $^1$H NMR spectrum of 2',2,4-trimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.19. 2,4-dimethyl-(1,1',2',1")-terphenyl[16] (Table 2, entry 6).** Procedure A was employed using 1-bromo-2,4-dimethylbenzene (71 μL, 0.52 mmol, 1.0 equiv) and 2-biphenylboronic acid (0.207 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.102 g, 0.40 mmol, 76%. MS (EI) *m*/*z*: 258 [$M^+$].

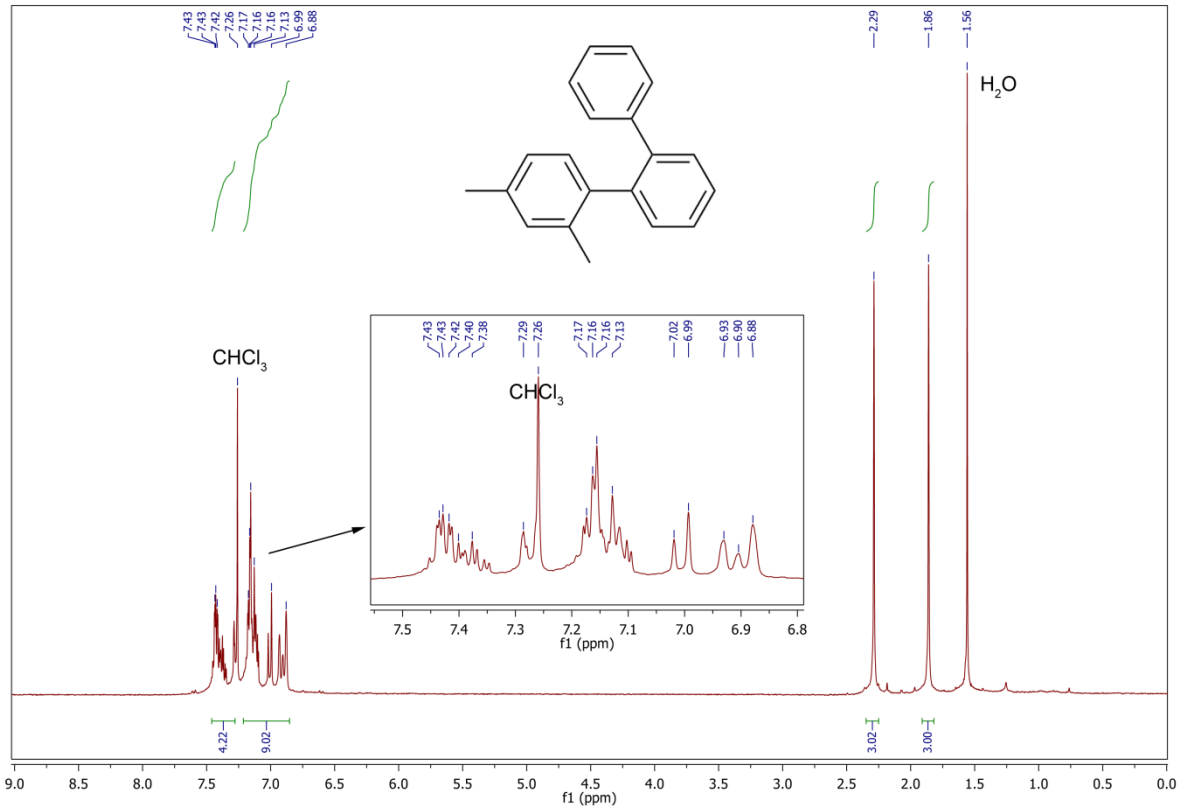


**Figure S23.** $^1$H NMR spectrum of 2,4-dimethyl-(1,1',2',1")-terphenyl (400.1 MHz, $CDCl_3$, 20 °C).

**S2.2.20. 2,6-dimethylbiphenyl[20] (Table 2, entry 7).** Procedure A was employed using 1-bromo-2,6-dimethylbenzene (70 µL, 0.52 mmol, 1.0 equiv) and phenylboronic acid (0.127 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.063 g, 0.34 mmol, 66%. MS (EI) *m*/*z*: 182 [$M^+$].

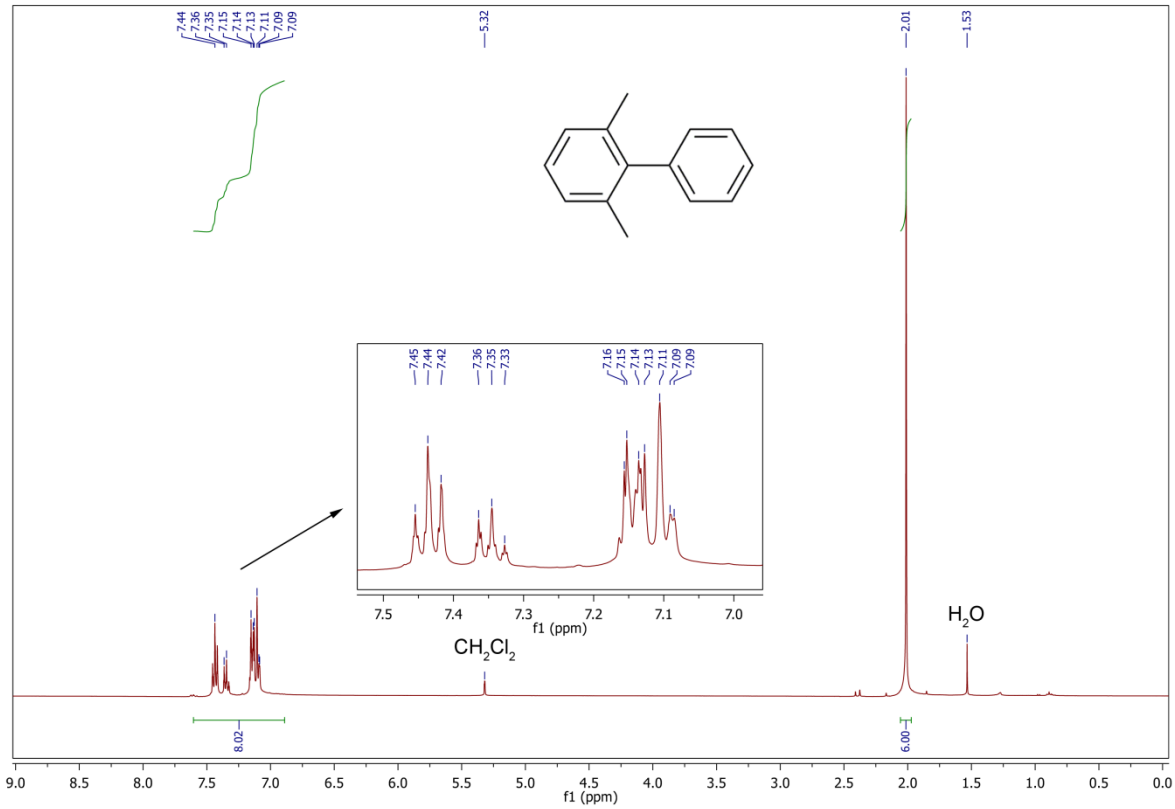


**Figure S24.** $^1$H NMR spectrum of 2,6-dimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.21. 2,4',6-trimethylbiphenyl**[21] **(Table 2, entry 8).** Procedure A was employed using 1-bromo-2,6-dimethylbenzene (70 µL, 0.52 mmol, 1.0 equiv) and *p*-tolylboronic acid (0.142 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. Isolated yield: 0.076 g, 0.39 mmol, 74%. MS (EI) *m*/*z*: 196 [$M^+$].

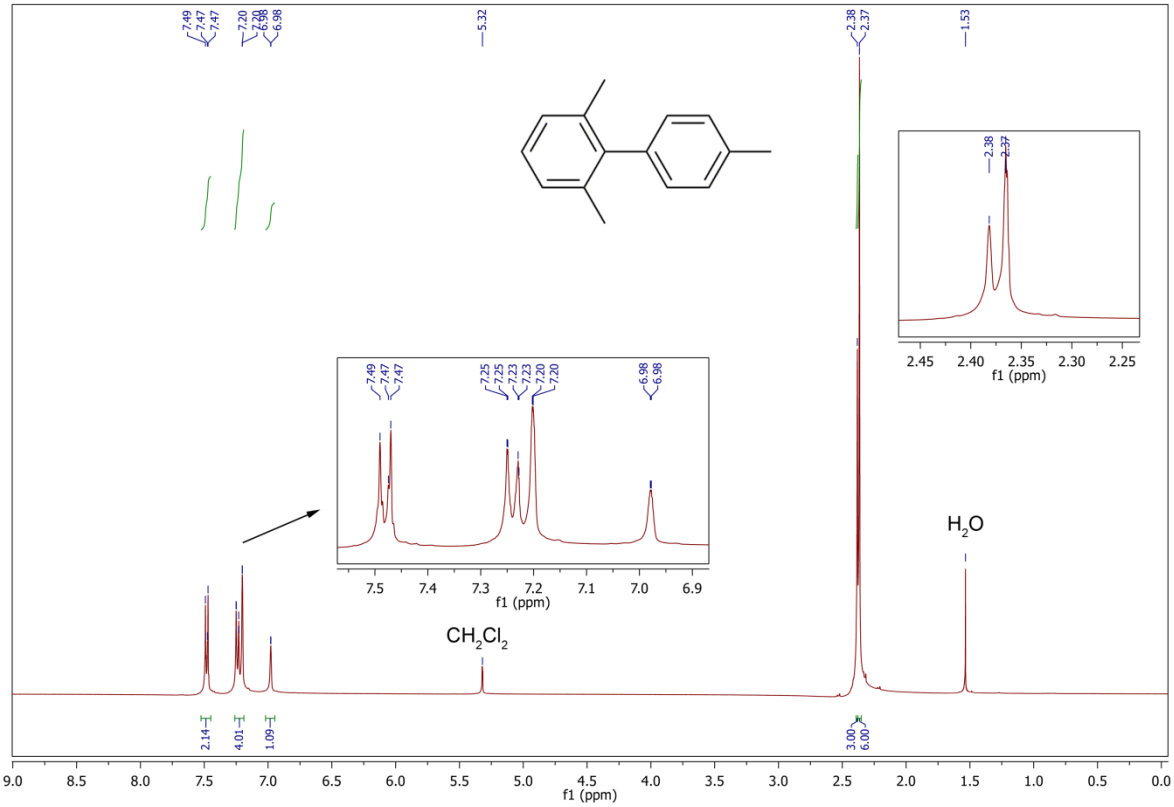


**Figure S25.** $^1$H NMR spectrum of 2,4',6-trimethylbiphenyl (400.1 MHz, $CD_2Cl_2$, 20 °C).

**S2.2.22. 2',4'-difluoro-4-methylbiphenyl (Table 2, entry 9).** Procedure A was employed using 4-bromotoluene (64 μL, 0.52 mmol, 1.0 equiv) and 2,4-difluorophenylboronic acid (0.165 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. The product was isolated as a colorless solid. Isolated yield: 0.082 g, 0.40 mmol, 77%. $^{1}$H NMR (400.1 MHz, $CDCl_3$, 20 ˚C): δ = 7.43-7.37 (m, 3H), 7.28-7.27 (m, 2H), 6.97-6.88 (m, 2H), 2.42 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 20 ˚C) δ = 163.5, 161.0, 137.7, 132.2, 131.4, 129.4, 128.9, 128.9, 111.6, 104.4, 21.3 ppm. $^{19}$F NMR (282.3 MHz, $CDCl_3$, 20 ˚C) δ = –110.6, –112.2 ppm. HR-MS (EI): Calc'd for $C_{13}H_{10}F_2$: *m/z* = 204.0750. Found: *m/z* = 204.0743.

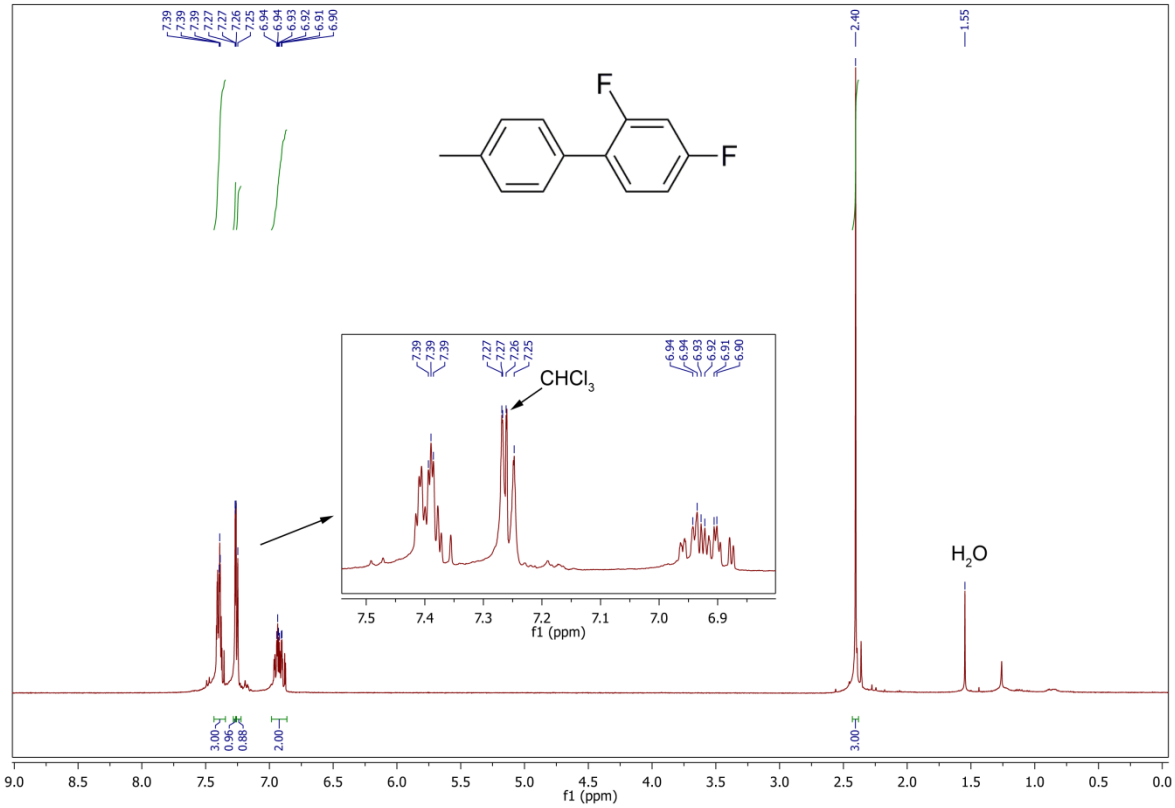


**Figure S26.** $^{1}$H NMR spectrum of 2',4'-difluoro-4-methylbiphenyl (400.1 MHz, $CDCl_3$, 20 °C).

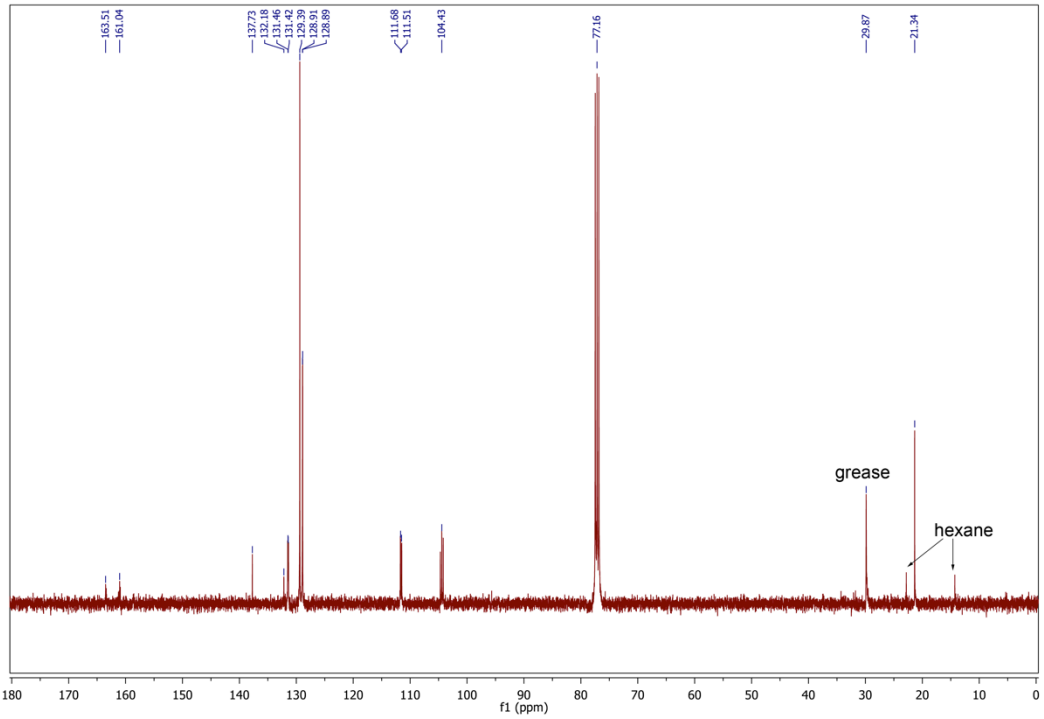


**Figure S27.** $^{13}C\{^{1}H\}$ NMR spectrum of 2',4'-difluoro-4-methylbiphenyl (100.6 MHz, $CDCl_3$, 20 °C).

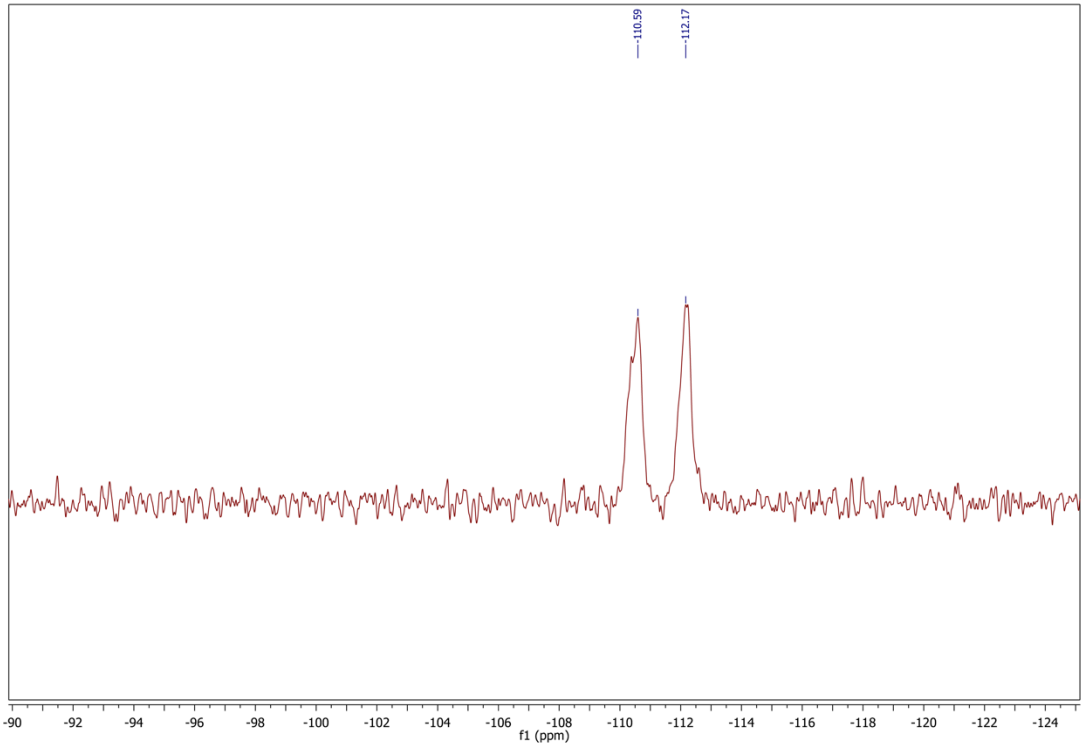


**Figure S28.** $^{19}F$ NMR spectrum of 2',4'-difluoro-4-methylbiphenyl (282.3 MHz, $CDCl_3$, 20 °C).

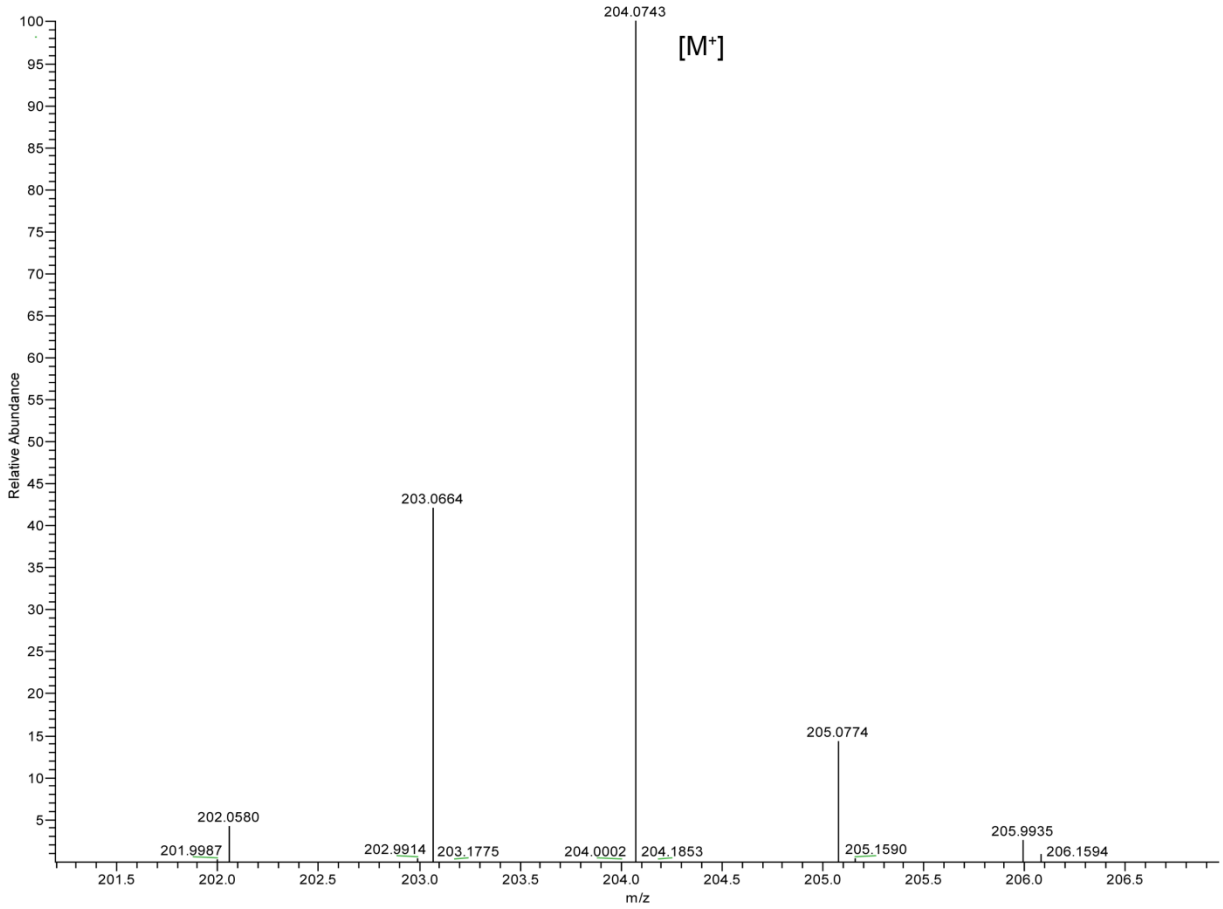


**Figure S29.** HR-MS (EI) of 2',4'-difluoro-4-methylbiphenyl.

**S2.2.23. 2',4'-difluoro-3-methylbiphenyl (Table 2, entry 10).** Procedure A was employed using 3-bromotoluene (63 µL, 0.52 mmol, 1.0 equiv) and 2,4-difluorophenylboronic acid (0.165 g, 1.04 mmol, 2.00 equiv). The reaction was conducted at 60 °C. The product was isolated as a colorless oil. Isolated yield: 0.082 g, 0.40 mmol, 77%. $^{1}$H NMR (400.1 MHz, $CDCl_3$, 20 ˚C): δ = 7.42-7.31 (m, 4H), 7.20-7.18 (m, 1H), 6.97-6.88 (m, 2H), 2.41 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$, 20 ˚C) δ = 162.3, 159.9, 138.3, 135.1, 131.6, 129.8, 129.8, 128.6, 128.5, 126.1, 111.6, 104.4, 21.6 ppm. $^{19}$F NMR (282.3 MHz, $CDCl_3$, 20 ˚C) δ = –112.5, –114.2 ppm. HR-MS (EI): Calc'd for $C_{13}H_{10}F_2$: *m/z* = 204.0750. Found: *m/z* = 204.0744.

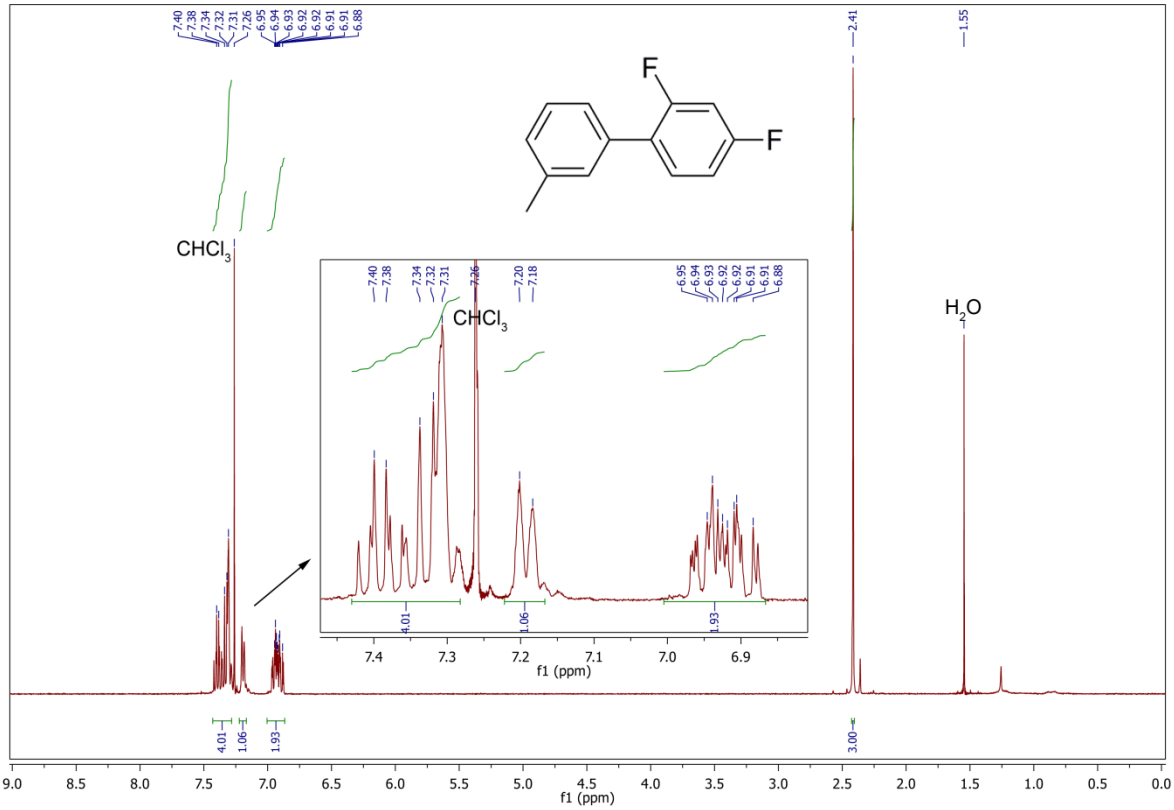


**Figure S30.** $^{1}$H NMR spectrum of 2',4'-difluoro-3-methylbiphenyl (400.1 MHz, $CDCl_3$, 20 °C).

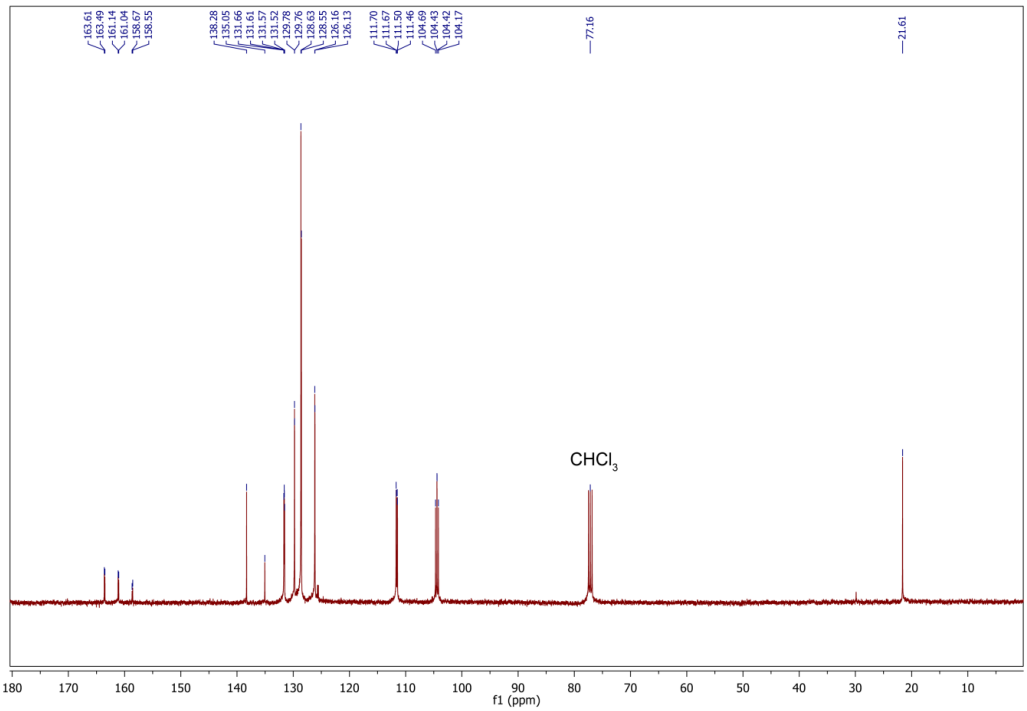


**Figure S31.** $^{13}C\{^{1}H\}$ NMR spectrum of 2',4'-difluoro-3-methylbiphenyl (100.6 MHz, $CDCl_3$, 20 °C).

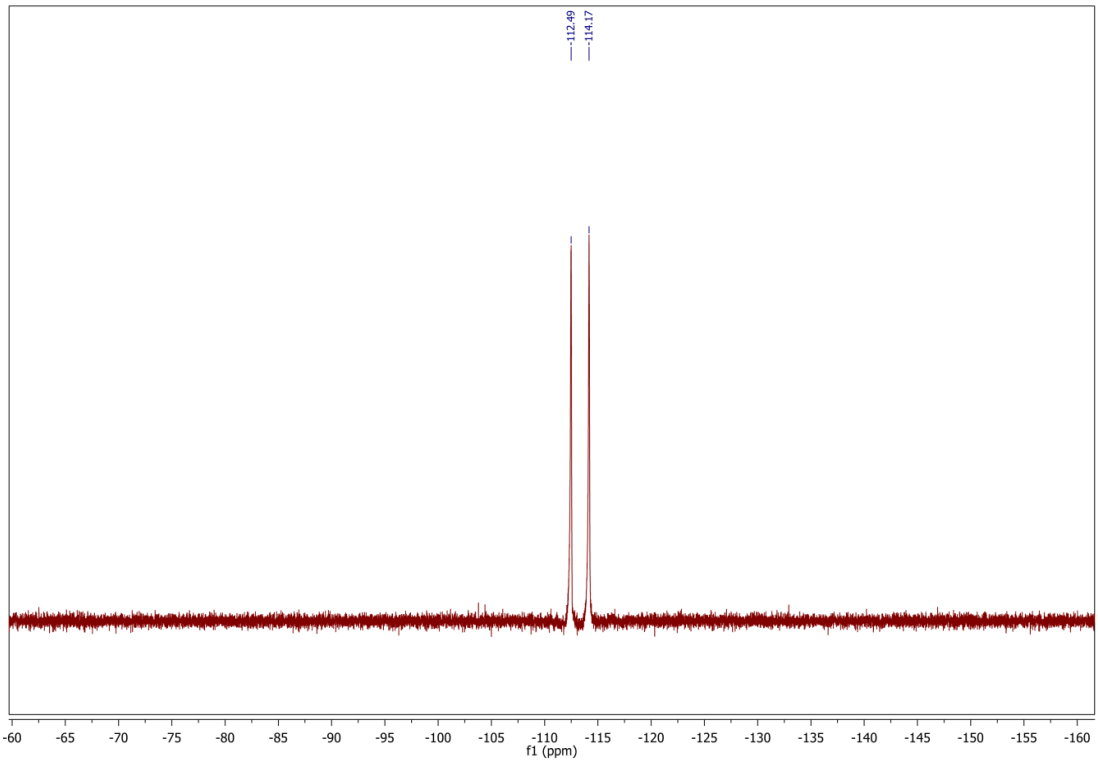


**Figure S32.** $^{19}F$ NMR spectrum of 2',4'-difluoro-3-methylbiphenyl (282.3 MHz, $CDCl_3$, 20 °C).

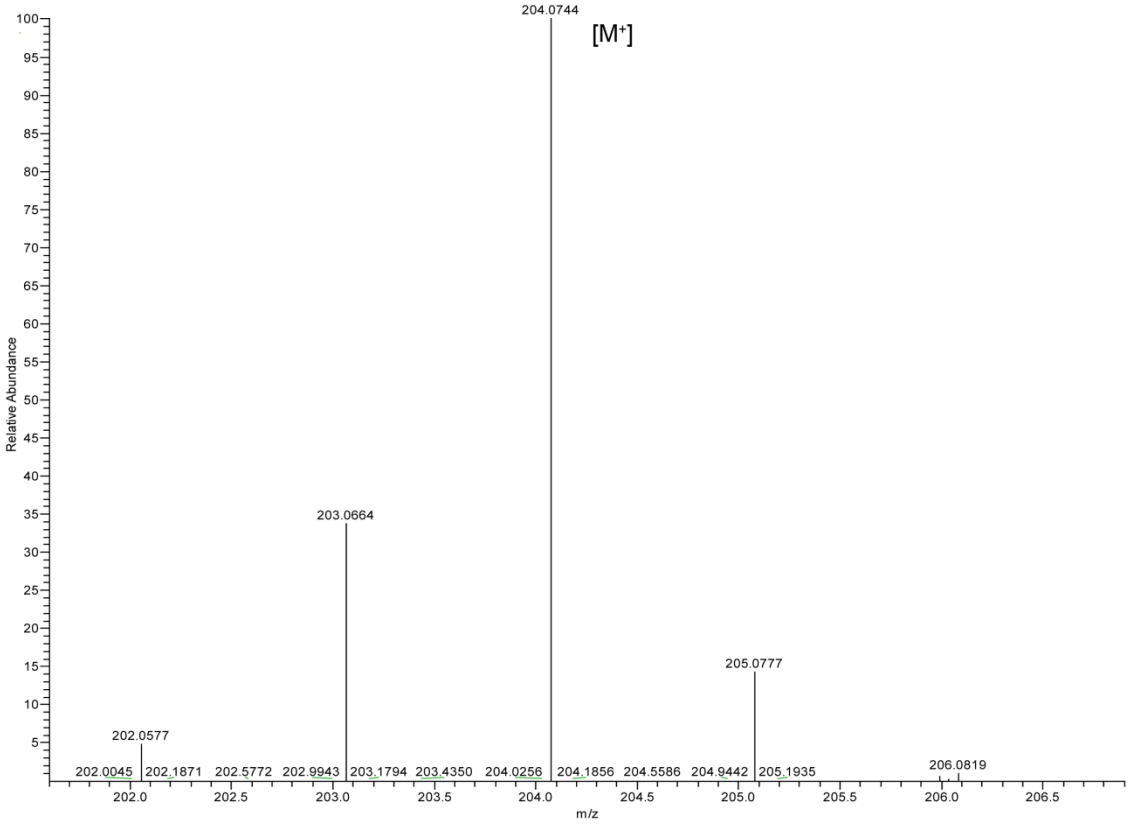


**Figure S33.** HR-MS of 2',4'-difluoro-3-methylbiphenyl.

**S2.3. General Procedure B: Suzuki-Miyaura Cross-Coupling Reactions Using Complexes with a Pd:CNAr$^{Dipp2}$ ratio of 1:1.** A solution of 1-bromo-3,5-dimethylbenzene (27 μL, 0.20 mmol, 1.0 equiv), phenylboronic acid (0.049 g, 0.40 mmol, 2.0 equiv), Pd catalyst/pre-catalyst (**1**, **3**, **4**, or **8**) and NaO*t*Bu (0.058 g, 0.60 mmol, 3.0 equiv) in *i*PrOH (1.0 mL) was magnetically stirred in a sealed 25 mL resealable ampoule under argon for 8 h. An aliquot was taken from the reaction mixture, quenched by dilution in hexane, and the yield of 3,5-dimethylbiphenyl analyzed by GC-MS. For catalyst loadings and yields, see Table 4.

## S3. Kinetics Measurements

**S3.1. General Considerations.** All measurements were obtained by $^1$H NMR on a Varian Mercury 400 MHz spectrometer. Samples were prepared in the glovebox and loaded into a J-Young tube as either $C_6D_6$, or toluene-$d_8$ solutions (0.6 mL) that contained ferrocene ($Cp_2Fe$) as an internal standard. The samples were placed in the spectrometer pre-warmed to the reaction temperature, then subjected to a 10 min equilibration period prior to initial data collection. The experiments were conducted with single pulse acquisitions. All data were processed with the MestReNova software. Plots were generated from integration of the resonance corresponding to the upfield isopropyl methyl doublet of Pd(CNAr$^{Dipp2}$)$_2$ (1.10 ppm in benzene-$d_6$) or the isopropyl methine septet of [(CNAr$^{Dipp2}$)Pd]$_2$($\mu$-$\eta^3$-$C_3H_5$)($\mu$-O$^i$Pr) (2.65 ppm in toluene-$d_8$) and include data past three half-lives.

**S3.2. General Procedure C: Kinetic analysis of the oxidative addition of MesBr to Pd(CNAr$^{Dipp2}$)$_2$.** A solution of Pd(CNAr$^{Dipp2}$)$_2$ (0.010 g, 0.010 mmol), CNAr$^{Dipp2}$ (0, 0.10, 0.25, 0.50, or 1.0 equiv) and $Cp_2Fe$ (0.002 g, 0.01 mmol) in $C_6D_6$ (0.3 mL) was frozen in a J-Young NMR tube. To the frozen solution was added a thawed solution of MesBr (16 μL, 0.10 mmol, 10 equiv) in $C_6D_6$ (0.3 mL). The entire solution was refrozen and the sealed J-Young tube was removed from the glovebox. Once the solution thawed, the sample was placed in the spectrometer.

**S3.2.1. Kinetic analysis without exogenous equivalents of CNAr$^{Dipp2}$.** Using General Procedure C, $^1$H NMR spectra were acquired every 2 min at 25 ˚C until the reaction had reached completion as indicated by the disappearance of Pd(CNAr$^{Dipp2}$)$_2$ resonances.

**S3.2.2. Kinetic analysis with 0.10 equiv. additional CNAr$^{Dipp2}$.** Using General Procedure C, $^1$H NMR spectra were acquired every 3 min at 25 ˚C until the reaction had reached completion as indicated by the disappearance of Pd(CNAr$^{Dipp2}$)$_2$ resonances.

**S3.2.3. Kinetic analysis with 0.25 equiv additional CNAr$^{Dipp2}$.** Using General Procedure C, $^1$H NMR spectra were acquired every 10 min at 25 ˚C until the reaction had reached completion as indicated by the disappearance of Pd(CNAr$^{Dipp2}$)$_2$ resonances.

**S3.2.4. Kinetic analysis with 0.5 or 1.0 equiv additional CNAr$^{Dipp2}$.** Using General Procedure C, $^1$H NMR spectra were acquired every 1 h at 25 ˚C until the reaction had reached completion as indicated by the disappearance of Pd(CNAr$^{Dipp2}$)$_2$ resonances.

**S3.3. Kinetic analysis of the oxidative addition of *m*-XylBr to Pd(CNAr$^{Dipp2}$)$_2$.** General Procedure C was employed with the following modifications: 3,5-dimethylbromobenzene (14 μL, 0.10 mmol, 10 equiv) was used instead of MesBr and $^1$H NMR spectra were acquired at 25 ˚C every 1 min until the reaction had reached completion as indicated by the disappearance of Pd(CNAr$^{Dipp2}$)$_2$ resonances.

**S3.4. Decomposition of ($\mu$-$C_3H_5$)($\mu$-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ (7 mM).** A J-Young NMR tube was charged with a solution of ($\mu$-$C_3H_5$)($\mu$-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ (0.005 g, 0.004 mmol, 7 mM) and $Cp_2Fe$ (0.002 g, 0.01 mmol, 20 mM) in toluene-$d_8$ (0.6 mL). The sample was placed in the spectrometer and $^1$H NMR spectra were acquired every 5 min at 45 ˚C until the reaction had reached completion as indicated by the disappearance of ($\mu$-$C_3H_5$)($\mu$-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ resonances.

**S3.5. Decomposition of ($\mu$-$C_3H_5$)($\mu$-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ (14 mM).** A J-Young NMR tube was charged with a solution of ($\mu$-$C_3H_5$)($\mu$-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ (0.010 g, 0.0080 mmol, 14 mM) and $Cp_2Fe$ (0.002 g, 0.01 mmol, 20 mM) in toluene-$d_8$ (0.6 mL). The sample was placed in the spectrometer and $^1$H NMR spectra were acquired every 5 min at 45 ˚C until the reaction had reached completion as indicated by the disappearance ($\mu$-$C_3H_5$)($\mu$-O$^i$Pr)[Pd(CNAr$^{Dipp2}$)]$_2$ resonances.

## S4. Details of Density Functional Theory Computational Studies

**S4.1. General details.** Density Functional Theory (DFT) calculations were carried out the mono-ligated fragment Pd(CNAr$^{Dipp2}$) using the ORCA program package.[22] Geometry optimizations and single-point calculations were performed using the BP86 pure density functional.[23-25] The all-electron Ahlrichs triple-zeta basis sets def2-TZVP (standard)[26] and def2-TZVP/J (auxiliary)[27] were used in all calculations. The resolution of identity (RI) approximation was employed.[28] Relativistic effects were included by use of the zeroth-order regular approximation (ZORA).[29-31] Optimized Cartesian coordinates are provided as a supplementary file.

## S5. Crystallographic Structure Determinations

**S5.1. General.** Single crystal X-ray structure determinations were carried out at low temperature on a Bruker P4, Platform or Kappa Diffractometer equipped with a Mo or Cu radiation source and a Bruker APEX detector. All structures were solved by direct methods with SIR 2004[32] or SHELXS[33] and refined by full-matrix least-squares procedures utilizing SHELXL.[33] Crystallographic data collection and refinement information are listed in Table S5.1.

**S5.2. Information on crystallographic disorder**. All disordered components were successfully modeled and refined anisotropically unless otherwise stated. The solid-state structure of PdCl($\eta^3$-$C_3H_5$)(CNAr$^{Dipp2}$) • 0.5 THF (**3** • 0.5 THF) contains two-site positional disorder of the allyl ligand in each of the two crystallographically independent molecules. The solid-state structure of ($\mu$-$C_3H_5$)($\mu$-N($^i$Pr)$_2$)[Pd(CNAr$^{Dipp2}$)]$_2$ (**5**) contains two-site disorder of one Dipp isopropyl group and the allyl ligand. The solid-state structure of ($\mu$-$C_3H_5$)($\mu$-Cl)[Pd(CNAr$^{Dipp2}$)]$_2$ (**6**) contains a crystallographic inversion center located between the two Pd centers, which results in two-site disorder of the allyl and chloride ligands. The solid-state structure of ($\mu$-$C_3H_5$)($\mu$-O*t*Bu)[Pd(CNAr$^{Dipp2}$)]$_2$ • $C_6H_5F$ (**7** • $C_6H_5F$) contains two-site disorder of the Pd centers, the isocyanide *C*NR carbon atoms, and the allyl and *t*-butoxide ligands. A crystallographic inversion center creates additional two-site disorder of the allyl and *t*-butoxide ligands, as well as two-site disorder of the co-crystallized molecule of fluorobenzene. In addition, the following molecules contained severely disordered solvent molecules of co-crystallization that could not be successfully modeled: *trans*-PdBr(*m*-Xyl)(CNAr$^{Dipp2}$)$_2$ • 0.5 $Et_2O$ (**2** • 0.5 $Et_2O$, 1 molecule of diethyl ether per unit cell); Pd$_3$($\eta^2$-Dipp-$\mu$-CNAr$^{Dipp2}$)$_3$ • 13 THF (**8** • 13 THF, 52 molecules of THF per unit cell). The PLATON routine SQUEEZE[34] was used to account for these disordered components as a diffuse contribution to the overall scattering without specific atom positions.

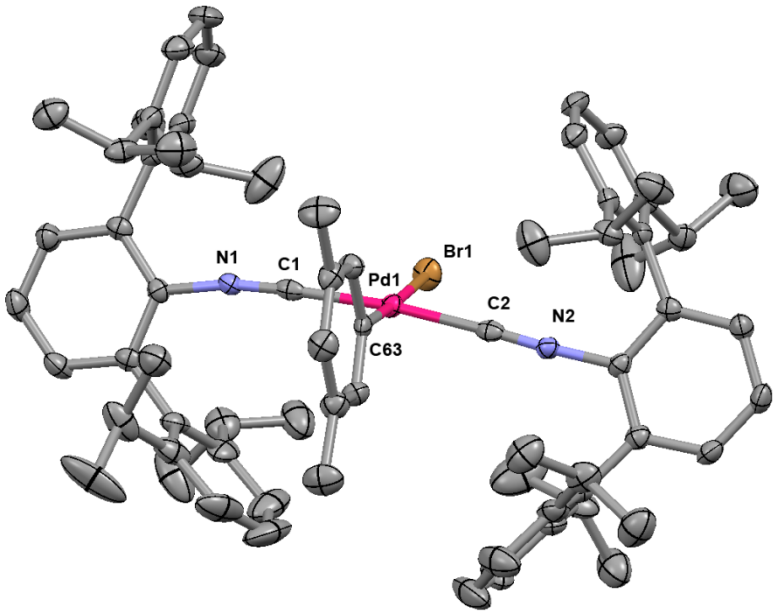


**Figure S34.** Molecular structure of *trans*-PdBr(*m*-Xyl)($CNAr^{Dipp2}$)$_2$ • 0.5 $Et_2O$ (**2** • 0.5 $Et_2O$). SQUEEZE was performed on disordered $Et_2O$ molecules of solvation. Selected bond distances (Å) and angles (°): Pd1-C1 = 1.961(4); Pd1-C2 = 1.970(5); Pd1-Br1 = 2.5019(5); Pd1-C63 = 2.027(4); C1-Pd1-C2 = 174.00(14); C1-Pd1-Br1 = 91.50(10); C2-Pd1-Br1 = 92.85(10); C1-Pd1-C63 = 88.49(14); C2-Pd1-C63 = 87.40(15); Br1-Pd1-C63 = 176.92(11).

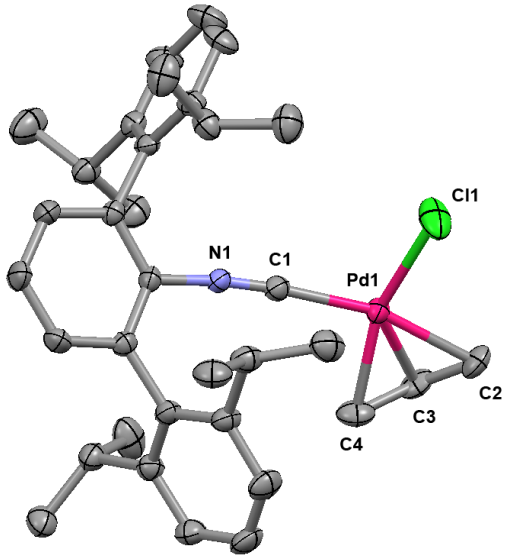


**Figure S35.** Molecular structure of PdCl($\eta^3$-$C_3H_5$)($CNAr^{Dipp2}$) • 0.5 THF (**3** • 0.5 THF). Co-crystallized molecule of THF has been omitted for clarity. There are two independent molecules of **3** in the unit cell. Stated metric parameters are reported as the mean values between these two independent molecules. Note that the allyl ligand is disordered end-over-end in both molecules. Selected bond distances (Å) and angles (°): Pd1-C1 = 1.988(2); Pd1-Cl1 = 2.3544 (8); C1-Pd1-Cl1 = 95.9(7).

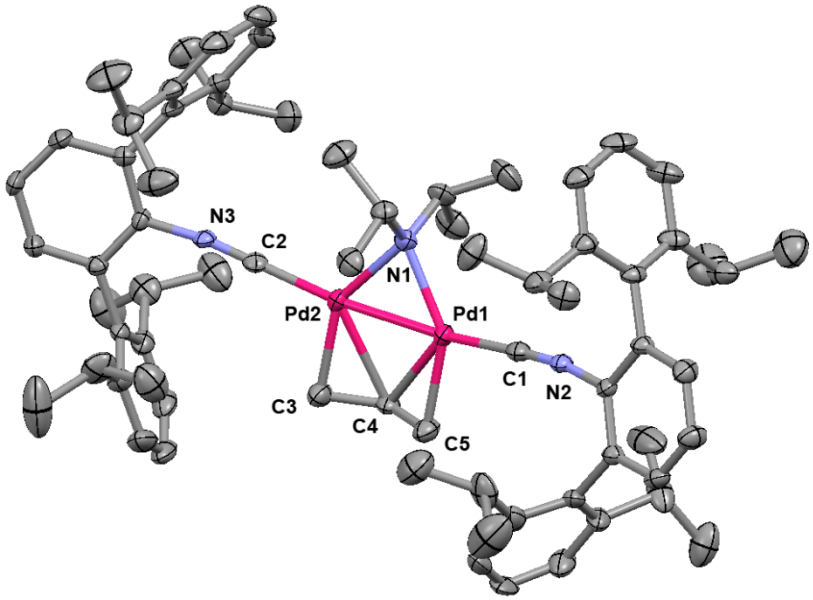


**Figure S36.** Molecular structure of ($\mu$-$C_3H_5$)($\mu$-N($^i$Pr)$_2$)[Pd(CNAr$^{Dipp2}$)]$_2$ (**5**). Selected bond distances (Å) and angles (°): Pd1-Pd2 = 2.5447(4); Pd1-C1 = 1.921(4); Pd1-C5 = 2.103(4); Pd1-N1 = 2.124(3); Pd2-C2 = 1.918(4); Pd2-C3 = 2.102(4); Pd2-N1 = 2.128(3); Pd1-N1-Pd2 = 73.51(9).

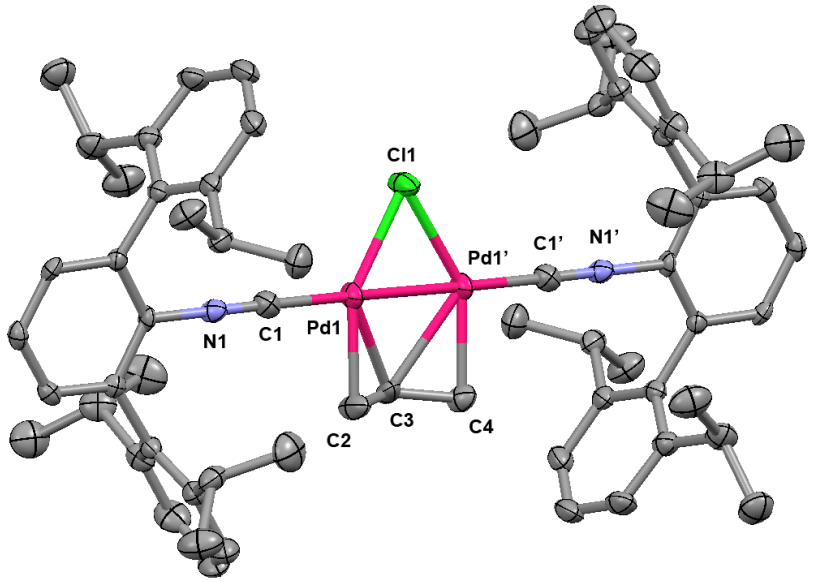


**Figure S37.** Molecular structure of ($\mu$-$C_3H_5$)($\mu$-Cl)[Pd(CNAr$^{Dipp2}$)]$_2$ (**6**). A crystallographic inversion center between the two Pd centers relates the Pd atoms and isocyanide ligands by symmetry. This also necessitates two-site, 50:50 disorder of the allyl and chloride ligands. Selected bond distance (Å): Pd1-C1 = 1.932(3).

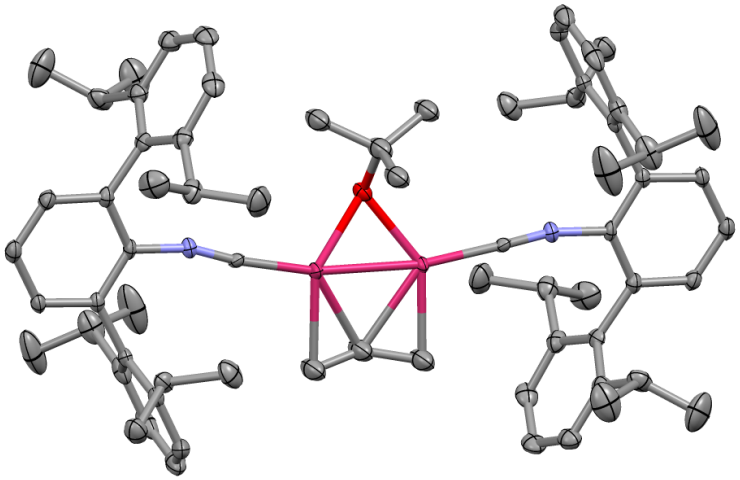

**Figure S38.** Molecular structure of ($\mu$-$C_3H_5$)($\mu$-O*t*Bu)[Pd(CNAr$^{Dipp2}$)]$_2$ • $C_6H_5F$ (**7** • $C_6H_5F$). Co-crystallized molecule of fluorobenzene has been omitted for clarity. Crystallographic disorder (see section S4.2) obviates a precise determination of relevant metrical parameters.

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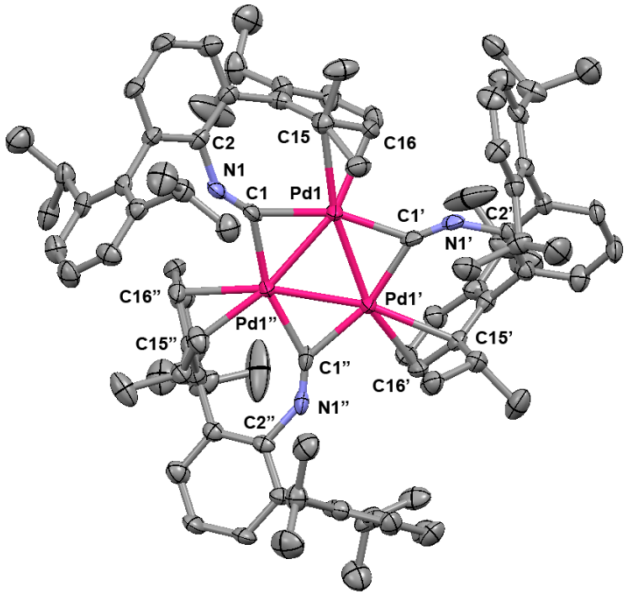


**Figure S39.** Molecular structure of Pd$_3$($\eta^2$-Dipp-$\mu$-CNAr$^{Dipp2}$)$_3$ • 13 THF (**8** • 13 THF). SQUEEZE was performed on disordered THF molecules of solvation. Note that each all Pd centers and isocyanide ligands are equivalent by crystallographic symmetry. Selected bond distances (Å): Pd-Pd = 2.6353(5); Pd-C1 = 2.102(6); Pd-C1' = 2.103(4); Pd-C15 = 2.479(4); Pd-C16 = 2.312(4); C15-C16 = 1.411(7); C16-C17 = 1.413(7); C17-C18 = 1.372(7); C18-C19 = 1.402(7); C19-C14 = 1.393(7); C14-C15 = 1.423(6).

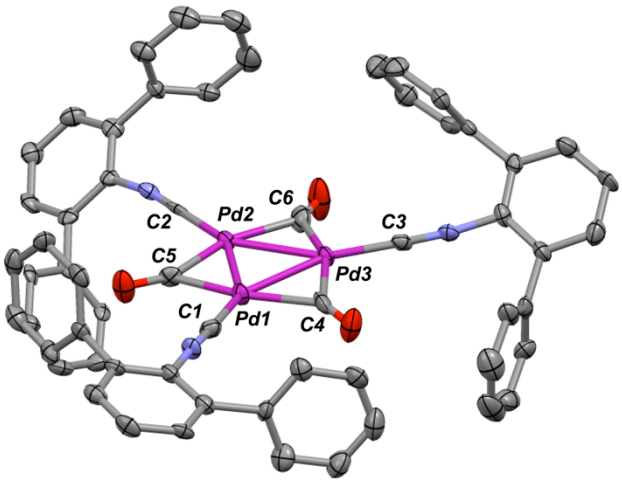


**Figure S40.** Molecular structure of $Pd_3(\mu\text{-}CO)_3(CNAr^{Dipp2})_3 \bullet Et_2O$ (**9** • $Et_2O$). Isopropyl groups and co-crystallized molecule of diethyl ether have been omitted for clarity. Selected bond distances (Å): Pd1-Pd2 = 2.6750(11); Pd2-Pd3 = 2.6851(11); Pd1-Pd3 = 2.6726(13); Pd1-C1 = 1.985(6); Pd2-C2 = 1.956(6); Pd3-C3 = 1.977(6); Pd1-C4 = 2.063(6); Pd1-C5 = 2.063(6); Pd2-C5 = 2.080(6); Pd2-C6 = 2.039(6); Pd3-C4 = 2.064(7); Pd3-C6 = 2.056(7).

**Table S1.** Crystallographic Data Collection and Refinement Information.

| Name | *trans*-PdBr(*m*-Xyl)($CNAr^{Dipp2}$)$_2$•0.5$Et_2O$ | PdCl($\eta^3$-$C_3H_5$)($CNAr^{Dipp2}$)•0.5THF | ($\mu$-$C_3H_5$)($\mu$-N($^i$Pr)$_2$)[Pd($CNAr^{Dipp2}$)]$_2$ |
|---|---|---|---|
| Formula | $C_{72}H_{88}BrN_2O_{0.5}Pd$ | $C_{36}H_{46}ClNO_{0.5}Pd$ | $C_{71}H_{93}N_3Pd_2$ |
| Crystal System | Triclinic | Monoclinic | Monoclinic |
| Space Group | *P*-1 | $P2_1/c$ | $P2_1/n$ |
| *a*, Å | 10.9266(13) | 22.184(6) | 19.5686(13) |
| *b*, Å | 14.4884(18) | 18.952(5) | 16.9767(11) |
| *c*, Å | 22.065(3) | 16.253(5) | 19.6154(13) |
| α, deg | 72.626(2) | 90 | 90 |
| β, deg | 78.681(2) | 105.030(3) | 92.8852(9) |
| γ, deg | 85.724(2) | 90 | 90 |
| V, Å$^3$ | 3268.4(7) | 6599(3) | 6508.2(7) |
| *Z* | 2 | 8 | 4 |
| Radiation (λ, Å) | Mo-Kα, 0.71073 | Mo-Kα, 0.71073 | Mo-Kα, 0.71073 |

| | | | |
|---|---|---|---|
| ρ (calcd.), g/cm$^3$ | 1.195 | 1.294 | 1.226 |
| μ (Mo Ka), mm$^{-1}$ | 0.936 | 0.669 | 0.593 |
| Temp, K | 100(2) | 100(2) | 100(2) |
| θ max, deg | 25.46 | 25.45 | 27.51 |
| data/parameters | 11642/0/685 | 12145/1/769 | 14533/0/729 |
| $R_1$ | 0.0402 | 0.0378 | 0.0472 |
| $wR_2$ | 0.0907 | 0.0834 | 0.1007 |
| GOF | 1.038 | 1.046 | 1.042 |

**Table S1.** Cont'd

| Name | ($\mu$-$C_3H_5$)($\mu$-Cl)[Pd(CNAr$^{Dipp2}$)]$_2$ | ($\mu$-$C_3H_5$)($\mu$-O*t*Bu)[Pd(CNAr$^{Dipp2}$)]$_2$•$C_6H_5F$ | Pd$_3$($\eta^2$-Dipp-$\mu$-CNAr$^{Dipp2}$)$_3$ •13 THF |
|---|---|---|---|
| Formula | $C_{65}H_{79}ClN_2Pd_2$ | $C_{75}H_{93}FN_2OPd_2$ | $C_{145}H_{215}N_3O_{13}Pd_3$ |
| Crystal System | Triclinic | Triclinic | Trigonal |
| Space Group | *P*-1 | *P*-1 | *P*-3*c*1 |
| *a*, Å | 8.534(3) | 9.3164(10) | 18.1967(5) |
| *b*, Å | 11.030(4) | 12.2291(13) | 18.1967(5) |
| *c*, Å | 16.148(5) | 16.0753(17) | 45.5371(16) |
| α, deg | 75.637(4) | 107.346(3) | 90 |
| β, deg | 84.351(5) | 92.444(3) | 90 |
| γ, deg | 85.307(4) | 105.882(3) | 120 |
| V, Å$^3$ | 1462.8(8) | 1666.0(3) | 13058.1(6) |
| *Z* | 1 | 1 | 4 |
| Radiation (λ, Å) | Mo-Kα, 0.71073 | Mo-Kα, 0.71073 | Cu-Kα, 1.54184 |
| ρ (calcd.), g/cm$^3$ | 1.290 | 1.266 | 1.286 |
| μ, mm$^{-1}$ | 0.700 | 0.586 | 3.775 |
| Temp, K | 100(2) | 100(2) | 120(2) |
| θ max, deg | 25.89 | 25.43 | 66.74 |
| data/parameters | 5535/0/342 | 6045/14/399 | 7678/0/300 |
| $R_1$ | 0.0334 | 0.0604 | 0.0574 |
| $wR_2$ | 0.0762 | 0.1886 | 0.1370 |
| GOF | 1.033 | 1.023 | 1.219 |

**Table S1.** Cont'd

| Name | $Pd_3(\mu\text{-}CO)_3(CNAr^{Dipp2})_3 \bullet Et_2O$ |
|---|---|
| Formula | $C_{100}H_{121}N_3O_4Pd_3$ |
| Crystal System | Triclinic |
| Space Group | *P*-1 |
| *a*, Å | 15.618(8) |
| *b*, Å | 16.161(8) |
| *c*, Å | 20.549(10) |
| α, deg | 80.016(7) |
| β, deg | 84.921(7) |
| γ, deg | 65.649(6) |
| V, Å$^3$ | 4653(4) |
| *Z* | 2 |
| Radiation (λ, Å) | Mo-Kα, 0.71073 |
| ρ (calcd.), g/cm$^3$ | 1.248 |
| μ, mm$^{-1}$ | 0.623 |
| Temp, K | 100 |
| θ max, deg | 48.814 |
| data/parameters | 15041 / 993 |
| $R_1$ | 0.0496 |
| $wR_2$ | 0.0700 |
| GOF | 0.754 |

## S6. References


(1) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th Ed.; Elsevier, **2003**.

(2) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, **1996**, *15*, 1518–1520.

(3) Ditri, T. B.; Fox, B. J.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *Inorg. Chem.* **2009**, *48*, 8362–8375.

(4) Labios, L. A.; Millard, M. D.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 11318–11319.
(5) Barnett, B. R.; Labios, L. A.; Moore, C. E.; England, J.; Rheingold, A. L.; Wieghardt, K.; Figueroa, J. S. *Inorg. Chem.* **2015**, *54*, 7110–7121.
(6) Shi, M.; Qian, H. X. *Tetrahedron* **2005**, *61*, 4949–4955.
(7) So, C. M.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2007**, *9*, 2795–2798.
(8) Kuriyama, M.; Shimazawa, R.; Shirai, R. *Tetrahedron* **2007**, *63*, 9393–9400.
(9) Stevens, P. D.; Fan, J. D.; Gardimalla, H. M. R.; Yen, M.; Gao, Y. *Org. Lett.* **2005**, *7*, 2085–2088.
(10) Zhou, W.-J.; Wang, K.-H.; Wang, J.-X.; Huang, D.-F. *Eur. J. Org. Chem.* **2010**, *2010*, 416–419.
(11) Rosa, G. R.; Rosa, C. H.; Rominger, F.; Dupont, J.; Monteiro, A. L. *Inorg. Chim. Acta* **2006**, *359*, 1947–1954.
(12) So, C. M.; Lee, H. W.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2009**, *11*, 317–320.
(13) So, C. M.; Lau, C. P.; Kwong, F. Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 8059–8063.
(14) Viswanathan, G. S.; Wang, M. W.; Li, C. J. *Angew. Chem. Int. Ed.* **2002**, *41*, 2138–2139.
(15) Song, C.; Ma, Y. D.; Chai, Q.; Ma, C. Q.; Jiang, W.; Andrus, M. B. *Tetrahedron* **2005**, *61*, 7438–7446.
(16) Vuoti, S.; Autio, J.; Haukka, M.; Pursiainen, J. *Inorg. Chim. Acta* **2009**, *362*, 4685–4691.
(17) Yang, H.-T.; Zhou, S.; Chang, F.-S.; Chen, C.-R.; Gau, H.-M. *Organometallics* **2009**, *28*, 5715–5721.
(18) Narender, T.; Sarkar, S.; Rajendar, K.; Tiwari, S. *Org. Lett.* **2011**, *13*, 6140–6143.
(19) Chow, W. K.; So, C. M.; Lau, C. P.; Kwong, F. Y. *J. Org. Chem.* **2010**, *75*, 5109–5112.
(20) Ackermann, L.; Potukuchi, H. K.; Althammer, A.; Born, R.; Mayer, P. *Org. Lett.* **2010**, *12*, 1004–1007.
(21) Ren, G.; Cui, X.; Wu, Y. *Eur. J. Org. Chem.* **2010**, *2010*, 2372–2378.
(22) Neese, F. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73–78.
(23) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
(24) Perdew, J. P. *Phys. Rev. B* **1986,** *33*, 8822–8824.
(25) Perdew, J. P. *Phys. Rev. B* **1986**, 34, 7406 (*Erratum*).
(26) Schaefer, A.; Horn, H.; Alchrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571–2577.
(27) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
(28) Werner, H.-J.; Manby, F. R.; Knowles, P. J. *J. Chem. Phys.* **2003**, *118*, 8149–8160.
(29) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597–4610.
(30) van Lenthe, E.; Snijders, J. G. and Baerends, E. J. *J. Chem. Phys.* **1996**, *105*, 6505–6516.
(31) Pantazis, D. A.; Chen, X. Y.; Landis, C. R.; Neese, F. *J. Chem. Theory Comput.* **2008**, *4*, 908–919
(32) Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381–388.
(33) Sheldrick, G. M. *Acta Crystallogr. A.,* **2008**, *64*, 112–122.
(34) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201.