Supporting Information

Si–C Bond Cleavage by Hydride Complexes of Rhodium and Iridium: Comparison of Si–C(sp^2) and Si–C(sp^3) Activation

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Synthesis

Preparation of {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$SiMe$_2$ (1b)

A Schlenk tube was charged with 994 mg of {*o*-PPh$_2$(C$_6$H$_4$)}Li·Et$_2$O (2.91 mmol) and 10 mL of toluene, and the solution was cooled to −78 ºC. SiMe$_2$Cl$_2$ (152 μL, 1.26 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at 100 °C for 15 h. After the mixture was then allowed to cool to room temperature, the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (5 mL × 3) and dried under vacuum to afford **1b** (635 mg, 1.09 mmol) in 87% yield as a white powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 0.91 (s, 6H, SiC*H*$_3$), 6.97–7.14 (m, 16H, *H*$_{arom}$), 7.17–7.38 (m, 10H, *H*$_{arom}$), 7.88–7.90 (m, 2H, *H*$_{arom}$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 2.7, 128.0, 128.2, 129.0, 129.2, 133.4, 135.3, 136.5, 136.6, 138.5, 143.1. ^{29}Si{^{1}H} NMR (79 MHz, CDCl$_3$): δ −7.1 (t, J_{Si-P} = 10.7 Hz). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ −11.9 (s). Anal. Calc. for C$_{38}$H$_{34}$P$_2$Si: C, 78.59; H, 5.90. Found: C, 78.53; H, 6.04.

Preparation of {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$SiEt$_2$ (1c)

A Schlenk tube was charged with 1.27 g of {*o*-PPh$_2$(C$_6$H$_4$)}Li·Et$_2$O (3.71 mmol) and 10 mL of toluene, and the solution was cooled to −78 ºC. SiEt$_2$Cl$_2$ (263 μL, 1.76 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at 100 °C for 15 h. After the mixture was then allowed to cool to room temperature, the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (3 mL × 3) and dried under vacuum to afford **1c** (640 mg, 1.05 mmol) in 60% yield as a white powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.08 (t, J_{H-H} = 7.8 Hz, 6H, SiCH$_2$C*H*$_3$), 1.95 (q, J_{H-H} = 7.8 Hz, 4H, SiC*H*$_2$CH$_3$), 6.92–6.96 (m, 14H, *H*$_{arom}$), 7.01–7.05 (m, 2H, *H*$_{arom}$), 7.08–7.14 (m, 8H, *H*$_{arom}$), 7.33–7.36 (m, 2H, *H*$_{arom}$), 8.27–8.29 (m, 2H, *H*$_{arom}$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 6.8, 7.9, 128.0, 128.1, 128.2, 129.0, 133.4, 135.4, 137.2, 138.7, 143.3, 146.8. ^{29}Si{^{1}H} NMR (79 MHz, CDCl$_3$): δ −9.2 (t, J_{Si-P} = 9.2 Hz). ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ −13.0 (s). Anal. Calc. for C$_{40}$H$_{38}$P$_2$Si: C, 78.92; H, 6.29. Found: C, 78.53; H, 6.04.

Preparation of {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(Ph)

A Schlenk tube was charged with 681 mg of {*o*-PPh$_2$(C$_6$H$_4$)}Li·Et$_2$O (1.99 mmol) and 12 mL of toluene, and the solution was cooled to −78 ºC. SiPhHCl$_2$ (140 μL, 0.951 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at 100 °C for 15 h. After the mixture was then allowed to cool to room temperature, the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (3 mL × 2), and dried under vacuum to afford {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(Ph) (571 mg, 0.908 mmol) in 77% yield as a white powder. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.31 (m, 1H, Si*H*), 7.06–7.47 (m, 33H, *H*$_{arom}$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 127.8, 128.1, 128.2, 128.3, 129.2, 129.9, 133.5, 133.7, 134.4, 134.8, 136.3, 137.8, 142.8, 144.4. ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ −12.1 (s). Anal. Calc. for C$_{42}$H$_{34}$P$_2$Si: C, 80.23; H, 5.45. Found: C, 80.55; H, 5.78.

Preparation of {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-tolyl)

A Schlenk tube was charged with 236 mg of {*o*-PPh$_2$(C$_6$H$_4$)}Li·Et$_2$O (0.691 mmol) and 5 mL of toluene, and the solution was cooled to −78 ºC. SiHCl$_3$ (35.0 μL, 0.345 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at ambient temperature for 15 h, the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (2 mL × 2), and dried under vacuum to afford crude {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(Cl) (197 mg, 0.336 mmol) as a white powder. ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ = −13.3 ppm (the purity was estimated to ≈ 95%). After the white residue was dissolved in toluene (5 mL), the solution was cooled to −78 ºC. *p*-CH$_3$C$_6$H$_4$MgBr (400 μL, 1.0 M in THF, 0.400 mmol) was added slowly to the prepared reaction solution, and then the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 100 ºC for 15 h, the mixture was allowed to cool to room temperature. To quench an excess amount of *p*-CH$_3$C$_6$H$_4$MgBr, a 0.20 mL portion of H$_2$O was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature, and then the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (20 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et$_2$O (2 mL × 3), and dried under vacuum to afford {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-tolyl) (185 mg, 0.288 mmol) in 86% yield as a white powder. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 2.07 (s, 3H, *p*-C*H*$_3$C$_6$H$_4$), 6.80 (m, 1H, Si*H*), 6.94–7.06 (m, 19H, *H*$_{arom}$), 7.23–7.39 (m, 9H, *H*$_{arom}$), 7.54–7.56 (m, 2H, *H*$_{arom}$), 7.65–7.67 (m, 2H, *H*$_{arom}$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 21.7, 128.1, 128.2, 128.5, 129.9, 133.5, 133.6, 133.8, 134.4, 136.4, 137.7, 137.8, 139.0, 142.8, 144.4. ^{31}P{^{1}H} NMR (162 MHz, C$_6$D$_6$): δ −11.9 (s). Anal. Calc. for C$_{43}$H$_{36}$P$_2$Si: C, 80.35; H, 5.65. Found: C, 80.08; H, 5.81.

Preparation of {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-methoxyphenyl)

A Schlenk tube was charged with 150 mg of {*o*-PPh$_2$(C$_6$H$_4$)}Li·Et$_2$O (0.440 mmol) and 5 mL of toluene, and the solution was cooled to −78 ºC. SiHCl$_3$ (22.3 μL, 0.220 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at ambient temperature for 15 h, the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (2 mL × 2), and dried under vacuum to afford crude {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(Cl) (126 mg, 0.214 mmol) as a white powder. After the white residue was dissolved in THF (2.5 mL), the solution was cooled to −78 ºC. *p*-(MeO)C$_6$H$_4$MgBr (514 μL, 0.5 M in THF, 0.257 mmol) was added slowly to the prepared reaction solution, and then the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 60 °C for 20 h, the mixture was allowed to cool to room temperature. To quench an excess amount of *p*-(MeO)C$_6$H$_4$MgBr, a 0.20 mL portion of H$_2$O was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature, and then the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (15 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et$_2$O (1.5 mL × 2), and dried under vacuum to afford {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-methoxyphenyl) (116 mg, 0.176 mmol) in 82% yield as a white powder. ^{1}H NMR (400

MHz, $CDCl_3$): δ 3.78 (s, 3H, *p*-C*H*$_3$OC$_6$H$_4$), 6.25 (m, 1H, Si*H*), 6.74–6.76 (m, 2H, H_{arom}), 7.04–7.38 (m, 30H, H_{arom}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.2, 128.3, 128.4, 128.5, 130.0, 133.7, 133.8, 134.0, 134.6, 137.8, 138.0, 138.1, 142.9, 143.4, 144.5. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ −12.1 (s). Anal. Calc. for $C_{43}H_{36}OP_2Si$: C, 78.40; H, 5.51. Found: C, 77.98; H, 5.64.

Preparation of {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-dimethylaminophenyl)

A Schlenk tube was charged with 188 mg of {*o*-PPh$_2$(C$_6$H$_4$)}Li·Et$_2$O (0.549 mmol) and 5 mL of toluene, and the solution was cooled to −78 ºC. $SiHCl_3$ (27.3 μL, 0.2705 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at ambient temperature for 15 h, the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (2 mL × 2), and dried under vacuum to afford crude {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(Cl) (166 mg, 0.283 mmol) as a white powder. After the white residue was dissolved in toluene (3 mL), the solution was cooled to −78 ºC. *p*-(Me$_2$N)C$_6$H$_4$MgBr (680 μL, 0.5 M in THF, 0.340 mmol) was added slowly to the prepared reaction solution, and then the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 110 °C for 15 h, the mixture was allowed to cool to room temperature. To quench an excess amount of *p*-(Me$_2$N)C$_6$H$_4$MgBr, a 0.20 mL portion of H_2O was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature, and then the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (15 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (1.5 mL × 2), and dried under vacuum to afford {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-dimethylaminophenyl) (142 mg, 0.212 mmol) in 75% yield as a white powder. ^1H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 6H, *p*-(C*H*$_3$)$_2$NC$_6$H$_4$), 6.50–6.52 (m, 2H, H_{arom}), 6.84 (m, 1H, Si*H*), 6.99–7.08 (m, 16H, H_{arom}), 7.25–7.40 (m, 10H, H_{arom}), 7.57–7.59 (m, 2H, H_{arom}), 7.75–7.76 (m, 2H, H_{arom}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 40.4, 128.0, 128.2, 129.7, 133.5, 133.7, 133.8, 134.3, 137.5, 137.8, 138.1, 143.4, 143.9, 144.4, 151.2. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ −12.0 (s). Anal. Calc. for $C_{44}H_{39}NP_2Si$: C, 78.66; H, 5.85; N, 2.08. Found: C, 78.65; H, 6.13; N, 1.90.

Preparation of {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-fluorophenyl)

A Schlenk tube was charged with 131 mg of {*o*-PPh$_2$(C$_6$H$_4$)}Li·Et$_2$O (0.386 mmol) and 2 mL of toluene, and the solution was cooled to −78 ºC. $SiHCl_3$ (19.0 μL, 0.192 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at ambient temperature for 15 h, the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (1 mL × 2), and dried under vacuum to afford crude {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(Cl) (109 mg, 0.186 mmol) as a white powder. After the white residue was dissolved in toluene (4 mL), the solution was cooled to −78 ºC. *p*-FC$_6$H$_4$MgBr (240 μL, 0.90 M in THF, 0.223 mmol) was added slowly to the prepared reaction solution, and then the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 100 °C for 15 h, the mixture was allowed to cool to room temperature. To quench an excess amount of *p*-FC$_6$H$_4$MgBr, a 0.20 mL portion of H_2O was added to the mixture at −78 °C. After the mixture

was allowed to warm to room temperature, the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (15 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (2 mL × 3), and dried under vacuum to afford {*o*-$(Ph_2P)C_6H_4$}$_2$Si(H)(*p*-fluorophenyl) (97.6 mg, 0.151 mmol) in 81% yield as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.30 (m, 1H, Si*H*), 6.88–6.92 (m, 2H, H_{arom}), 7.07–7.41 (m, 30H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 128.2, 128.3, 128.4, 128.5, 130.1, 133.5, 133.7, 133.8, 134.5, 137.5, 137.7, 138.2, 142.3, 144.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ –110.4 (s). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ –12.1 (s). Anal. Calc. for $C_{42}H_{33}FP_2Si$: C, 78.00; H, 5.14. Found: C, 77.58; H, 5.44.

Preparation of {*o*-$(Ph_2P)C_6H_4$}$_2$Si(Me)(Ph) (4b)

A Schlenk tube was charged with 479 mg of {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (1.40 mmol) and 7.5 mL of toluene, and the solution was cooled to −78 ºC. $SiMePhCl_2$ (113 μL, 0.698 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at 100 °C for 15 h. The mixture was then allowed to cool to room temperature, and the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (2 mL × 2), and dried under vacuum to afford **4b** (282 mg, 0.439 mmol) in 63% yield as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (m, 3H, SiCH_3), 7.01–7.45 (m, 33H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 4.3, 127.7, 128.1, 128.3, 128.9, 129.5, 133.4, 135.8, 138.1, 138.3, 138.4, 138.5, 143.6, 146.0, 146.4. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ –11.3 (s). Anal. Calc. for $C_{43}H_{36}P_2Si$: C, 80.35; H, 5.65. Found: C, 80.40; H, 5.82.

Preparation of {*o*-$(Ph_2P)C_6H_4$}$_2$Si(Me)(Et) (4c)

A Schlenk tube was charged with 591 mg of {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (1.73 mmol) and 7.5 mL of toluene, and the solution was cooled to −78 ºC. $SiMeEtCl_2$ (110 μL, 0.817 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at 100 °C for 15 h. The mixture was then allowed to cool to room temperature, and the resulting solution was filtered through a Celite pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (2 mL × 2), and dried under vacuum to afford **4c** (429 mg, 0.722 mmol) in 88% yield as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ 0.92 (s, 3H, SiCH_3), 0.99 (t, $J_{H\text{-}H}$ = 7.8 Hz, 3H, $SiCH_2CH_3$), 1.57 (q, $J_{H\text{-}H}$ = 7.8 Hz, 2H, $SiCH_2CH_3$), 6.98–7.06 (m, 16H, H_{arom}), 7.11–7.18 (m, 8H, H_{arom}), 7.35–7.38 (m, 2H, H_{arom}), 7.91–7.93 (m, 2H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 0.12, 8.1, 9.4, 128.0, 128.2, 129.1, 133.3, 133.5, 135.4, 136.8, 138.6, 143.2, 147.5. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ –12.3 (s). Anal. Calc. for $C_{39}H_{36}P_2Si$: C, 78.76; H, 6.10. Found: C, 78.42; H, 6.17.

Preparation of {*o*-$(Ph_2P)C_6H_4$}$_2$Si(Me)(*p*-tolyl) (4d)

A Schlenk tube was charged with 139 mg of {*o*-$PPh_2(C_6H_4)$}Li·Et_2O (0.406 mmol) and 2 mL of toluene, and the solution was cooled to −78 ºC. $SiMeCl_3$ (24.0 μL, 0.203 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at 100 °C for 15 h. The mixture was then allowed to cool to room temperature, and the resulting solution was filtered through a Celite

pad. Removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (1 mL × 2) and dried under vacuum to afford {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) (87.7 mg, 0.146 mmol, 72%) in ≈ 99% purity (see Figure S19). ^{1}H NMR (400 MHz, C_6D_6): δ 1.41 (m, 3H, SiCH_3), 6.95–7.04 (m, 17H, H_{arom}), 7.08–7.15 (m, 7H, H_{arom}), 7.32–7.35 (m, 2H, H_{arom}), 8.25–8.27 (m, 2H, H_{arom}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.6, 128.3, 128.9, 130.4, 133.3, 135.3, 136.9, 137.4, 137.8, 142.7, 145.2. ^{31}P NMR (162 MHz, C_6D_6): δ –12.7 (s).

A Schlenk tube was filled with 87.7 mg of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) (0.146 mmol) and 4 mL of toluene, and the solution was cooled to −78 ºC. *p*-$CH_3C_6H_4MgBr$ (219 μL, 1.0 M in THF, 0.219 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 100 °C for 15 h, the mixture was then allowed to cool to room temperature. To quench an excess amount of *p*-$CH_3C_6H_4MgBr$, a 0.20 mL portion of H_2O was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature, and then the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (15 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (2 mL × 3), and dried under vacuum to afford **4d** (66.3 mg, 0.101 mmol) in 69% yield as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ 1.41 (m, 3H, SiCH_3), 2.11 (s, 3H, *p*-C$H_3C_6H_4$), 6.95–7.06 (m, 16H, H_{arom}), 7.16–7.22 (m, 7H, H_{arom}), 7.29–7.33 (m, 3H, H_{arom}), 7.45–7.48 (m, 2H, H_{arom}), 7.53–7.55 (m, 2H, H_{arom}), 7.71–7.73 (m, 2H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 4.2, 21.7, 128.0, 128.2, 128.5, 129.4, 133.3, 133.5, 134.9, 135.9, 138.0, 138.4, 138.6, 143.5, 146.1, 146.6. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ –11.2 (s). Anal. Calc. for $C_{44}H_{38}P_2Si$: C, 80.46; H, 5.83. Found: C, 80.33; H, 6.00.

Preparation of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-methoxyphenyl) (4e)

{*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) was prepared in a manner similar to that reported in the section "Preparation of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-tolyl) (**4d**)." A Schlenk tube was charged with 99.2 mg of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) (0.165 mmol) and 2 mL of THF, and the solution was cooled to −78 ºC. *p*-(MeO)C_6H_4MgBr (396 μL, 0.5 M in THF, 0.198 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 60 °C for 20 h, the mixture was then allowed to cool to room temperature. To quench an excess amount of *p*-(MeO)C_6H_4MgBr, a 0.20 mL portion of H_2O was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature, and then the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (15 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (1.5 mL × 2), and dried under vacuum to afford **4e** (85.9 mg, 0.128 mmol) in 77% yield as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ 1.42 (m, 3H, SiCH_3), 3.30 (s, 3H, *p*-CH_3OC$_6H_4$), 6.72–7.75 (m, 2H, H_{arom}), 6.99–7.07 (m, 18H, H_{arom}), 7.21–7.24 (m, 2H, H_{arom}), 7.30–7.34 (m, 4H, H_{arom}), 7.46–7.51 (m, 4H, H_{arom}), 7.71–7.73 (m, 2H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 4.29, 55.1, 128.1, 128.2, 128.3, 129.5, 133.4, 133.6, 135.9, 137.4, 138.0, 138.1, 138.5, 143.6, 146.3, 146.8. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ –11.1 (s). Anal. Calc. for $C_{44}H_{38}OP_2Si$: C, 78.55; H, 5.69. Found: C, 78.59; H, 5.66.

Preparation of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-dimethylaminophenyl) (4f)

{*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) was prepared in a manner similar to that reported in the section "Preparation of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-tolyl) (**4d**)." A Schlenk tube was charged with 90.3 mg of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) (0.150 mmol) and 2.5 mL of toluene, and the solution was cooled to −78 ºC. *p*-(Me_2N)C_6H_4MgBr (360 μL, 0.5 M in THF, 0.180 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 110 °C for 15 h, the mixture was then allowed to cool to room temperature. To quench an excess amount of *p*-(Me_2N)C_6H_4MgBr, a 0.20 mL portion of H_2O was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature, and then the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (15 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with hexane (1.5 mL × 2), and dried under vacuum to afford **4f** (78.1 mg, 0.114 mmol) in 76% yield as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ 1.46 (m, 3H, SiCH_3), 2.50 (s, 6H, *p*-(CH_3)$_2$NC_6H_4), 6.52–6.54 (m, 2H, H_{arom}), 6.98–7.55 (m, 28H, H_{arom}), 7.79–7.81 (m, 2H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 4.33, 40.4, 128.1, 128.2, 128.3, 128.5, 129.3, 133.4, 133.6, 134.9, 135.8, 137.0, 138.1, 138.8, 143.5, 147.1. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −11.1 (s). HRMS (FAB+): $[M]^+$ Calc. for $C_{45}H_{41}NP_2Si$: 685.2483; Found: 685.2471. Anal. Calc. for $C_{45}H_{41}NP_2Si$: C, 78.80; H, 6.03; N, 2.04. Found: C, 78.52; H, 6.28; N, 2.07.

Preparation of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-fluorophenyl) (4g)

{*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) was prepared in a manner similar to that reported in the section "Preparation of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-tolyl) (**4d**)." A Schlenk tube was charged with 78.2 mg of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl) (0.130 mmol) and 4 mL of toluene, and the solution was cooled to −78 ºC. *p*-FC_6H_4MgBr (173 μL, 0.9 M in THF, 0.156 mmol) was added slowly to the prepared reaction solution, and the mixture was allowed to warm to room temperature. After the reaction mixture was stirred at 100 °C for 15 h, the mixture was then allowed to cool to room temperature. To quench an excess amount of *p*-FC_6H_4MgBr, a 0.20 mL portion of H_2O was added to the mixture at −78 °C. The mixture was allowed to warm to room temperature, and then the solution was stirred at room temperature for 2 h. After removing the volatile materials under vacuum, the residue was dissolved in benzene (15 mL). The resulting solution was filtered through a Celite pad, and removal of the volatile materials in vacuo gave a white solid. The residue was washed with Et_2O (2 mL × 3), and dried under vacuum to afford **4g** in 77% yield as a white powder. ^{1}H NMR (400 MHz, C_6D_6): δ 1.36 (m, 3H, SiCH_3), 6.96–7.07 (m, 16H, H_{arom}), 7.17–7.20 (m, 7H, H_{arom}), 7.26–7.30 (m, 3H, H_{arom}), 7.34–7.38 (m, 2H, H_{arom}), 7.44–7.47 (m, 2H, H_{arom}), 7.60–7.62 (m, 2H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 4.21, 128.2, 128.3, 128.4, 129.6, 133.3, 133.5, 134.2, 135.9, 137.7, 137.9, 138.3, 143.6, 145.6, 146.0. ^{19}F{^{1}H} NMR (376 MHz, C_6D_6): δ −110.6 (s). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ −11.2 (s). Anal. Calc. for $C_{43}H_{35}FP_2Si$: C, 78.16; H, 5.34. Found: C, 77.72; H, 5.68.

Preparation of {(*o*-$Ph_2PC_6H_4$)$_2$(Me)Si}Rh(CO)(PPh_3) (3b)

A 50-mL Schlenk tube was charged with **1b** (196 mg, 0.338 mmol), RhH(CO)(PPh_3)$_3$ (**2**) (310 mg, 0.338 mmol), and toluene (10 mL), and the reaction mixture was stirred at 50 °C for 8 h. The solvent was then removed under

reduced pressure to give a pale orange solid. The residue was washed with hexane (3 mL × 3) and dried under vacuum to afford 296 mg of **3b** (0.0496 mmol) as an orange powder in 91% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 1.46 (s, 3H, SiCH_3), 6.40–6.41 (m, 4H, H_{arom}), 6.70–7.10 (m, 30H, H_{arom}), 7.18–7.30 (m, 3H, H_{arom}), 7.65–7.67 (m, 4H, H_{arom}), 7.83–7.85 (m, 2H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 4.5, 127.6, 127.8, 128.3, 128.7, 129.0, 131.0, 132.6, 133.5, 134.6, 137.4, 139.5, 140.5, 149.7, 155.1, 204.3. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 32.3 (dt, J_{P-Rh} = 95.5 Hz, J_{P-P} = 34.9 Hz, *P*Ph$_3$), 49.2 (dd, J_{P-Rh} = 145.0 Hz, J_{P-P} = 34.9 Hz, *P*Ph$_2$). IR (KBr): 1897 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{56}H_{46}OP_3RhSi$: C, 70.14; H, 4.84. Found: C, 69.96; H, 5.24.

Preparation of {(*o*-Ph$_2$PC$_6$H$_4$)$_2$(Et)Si}Rh(CO)(PPh$_3$) (3c)

A 50-mL Schlenk tube was charged with **1c** (174 mg, 0.286 mmol), RhH(CO)(PPh$_3$)$_3$ (**2**) (263 mg, 0.286 mmol), and toluene (7 mL), and the reaction mixture was stirred at 50 °C for 10 h. The solvent was then removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (3 mL × 3) and dried under vacuum to afford 258 mg of **3c** (0.265 mmol) as an orange powder in 93% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 1.53 (t, J_{H-H} = 7.8 Hz, 3H, SiCH$_2$CH_3), 2.02 (q, J_{H-H} = 7.8 Hz, 2H, SiCH_2CH$_3$), 6.58–6.59 (m, 4H, H_{arom}), 6.68–6.72 (m, 6H, H_{arom}), 6.78–7.13 (m, 25 H, H_{arom}), 7.31–7.33 (m, 2H, H_{arom}), 7.56–7.57 (m, 4H, H_{arom}), 7.93–7.65 (m, 2H, H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 10.0, 13.2, 127.6, 127.9, 128.4, 128.8, 129.0, 131.5, 132.6, 133.4, 134.6, 137.1, 139.8, 141.1, 150.1, 154.4, 203.7. ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$): δ 64.3 (m). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 31.2 (dt, J_{P-Rh} = 94.2 Hz, J_{P-P} = 34.3 Hz, *P*Ph$_3$), 49.7 (dd, J_{P-Rh} = 145.0 Hz, J_{P-P} = 34.3 Hz, *P*Ph$_2$). IR (KBr): 1923 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{57}H_{48}OP_3RhSi$: C, 70.37; H, 4.97. Found: C, 70.03; H, 5.29.

Preparation of {(*o*-Ph$_2$PC$_6$H$_4$)$_2$(*p*-tolyl)Si}Rh(CO)(PPh$_3$) (3d)

A 50-mL Schlenk tube was charged with {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-tolyl) (39.1 mg, 0.0608 mmol), RhH(CO)(PPh$_3$)$_3$ (**2**) (55.9 mg, 0.0608 mmol), and toluene (3 mL), and the reaction mixture was stirred at 80 °C for 5 h. The solvent was then removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (1.5 mL × 3) and dried under vacuum to afford 46.4 mg of **3d** (0.0448 mmol) as an orange powder in 74% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 2.21 (s, 3H, *p*-CH_3C$_6$H$_4$), 6.44–6.48 (m, 2H, H_{arom}), 6.67–7.12 (m, 38H, H_{arom}), 7.36–7.38 (m, 2H, H_{arom}), 7.64–7.65 (m, 3H, H_{arom}), 7.87–7.89 (m, 2H H_{arom}). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 22.3, 127.8, 128.2, 129.0, 129.3, 129.7, 131.5, 132.9, 133.7, 134.1, 134.7, 137.0, 137.2, 137.5, 137.9, 139.7, 140.8, 151.4, 153.7, 204.2. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 32.1 (dt, J_{P-Rh} = 94.2 Hz, J_{P-P} = 34.3 Hz, *P*Ph$_3$), 49.6 (dd, J_{P-Rh} = 145.0 Hz, J_{P-P} = 34.3 Hz, *P*Ph$_2$). IR (KBr): 1924 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{62}H_{50}OP_3RhSi$: C, 71.95; H, 4.87. Found: C, 71.64; H, 5.19.

Preparation of {(*o*-Ph$_2$PC$_6$H$_4$)$_2$(*p*-methoxyphenyl)Si}Rh(CO)(PPh$_3$) (3e)

A 50-mL Schlenk tube was charged with {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-methoxyphenyl) (44.0 mg, 0.0668 mmol), RhH(CO)(PPh$_3$)$_3$ (**2**) (61.4 mg, 0.0668 mmol), and toluene (3 mL), and the reaction mixture was stirred at 80 °C for 5 h. The solvent was then removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (1.5 mL × 3) and dried under vacuum to afford 55.1 mg of **3e** (0.0524 mmol) as an orange powder in 78% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 3.36 (s, 3H, *p*-CH_3OC$_6$H$_4$), 6.42–6.45 (m, 4H, H_{arom}), 6.67–7.07 (m, 34H,

H_{arom}), 7.36–7.38 (m, 2H, H_{arom}), 7.60–7.67 (m, 5H, H_{arom}), 7.87–7.89 (m, 2H H_{arom}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 55.4, 127.6, 128.0, 128.7, 129.1, 131.3, 132.7, 133.6, 134.6, 137.2, 138.1, 139.5, 140.6, 151.2, 153.6, 203.6. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 32.0 (dt, J_{P-Rh} = 95.5 Hz, J_{P-P} = 33.0 Hz, PPh$_3$), 49.5 (dd, J_{P-Rh} = 146.9 Hz, J_{P-P} = 33.0 Hz, PPh$_2$). IR (KBr): 1924 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{62}H_{50}O_2P_3RhSi$: C, 70.85; H, 4.80. Found: C, 70.45; H, 4.98.

Preparation of {(*o*-Ph$_2$PC$_6$H$_4$)$_2$(*p*-dimethylaminophenyl)Si}Rh(CO)(PPh$_3$) (3f)

A 50-mL Schlenk tube was charged with {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-dimethylaminophenyl) (36.1 mg, 0.0537 mmol), RhH(CO)(PPh$_3$)$_3$ (**2**) (49.3 mg, 0.0537 mmol), and toluene (3 mL), and the reaction mixture was stirred at 80 °C for 5 h. The solvent was then removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (1.5 mL × 3) and dried under vacuum to afford 50.0 mg of **3f** (0.0470 mmol) as an orange powder in 87% yield. ^1H NMR (400 MHz, C_6D_6): δ 2.55 (s, 6H, *p*-(CH_3)$_2$NC$_6$H$_4$), 6.41–6.44 (m, 4H, H_{arom}), 6.65–7.12 (m, 34H, H_{arom}), 7.36–7.38 (m, 2H, H_{arom}), 7.63–7.61 (m, 2H H_{arom}), 7.69–7.73 (m, 3H, H_{arom}), 7.94–7.96 (m, 2H H_{arom}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 40.4, 127.2, 127.5, 128.3, 128.6, 130.8, 132.3, 133.2, 134.3, 136.9, 137.4, 139.3, 140.4, 150.6, 153.6, 203.1. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 32.2 (dt, J_{P-Rh} = 94.2 Hz, J_{P-P} = 33.7 Hz, PPh$_3$), 49.8 (dd, J_{P-Rh} = 146.9 Hz, J_{P-P} = 33.7 Hz, PPh$_2$). IR (KBr): 1925 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{63}H_{53}NOP_3RhSi$: C, 71.12; H, 5.02; N, 1.32. Found: C, 71.35; H, 5.36; N, 1.11

Preparation of {(*o*-Ph$_2$PC$_6$H$_4$)$_2$(*p*-fluorophenyl)Si}Rh(CO)(PPh$_3$) (3g)

A 50-mL Schlenk tube was charged with {*o*-(Ph$_2$P)C$_6$H$_4$}$_2$Si(H)(*p*-fluorophenyl) (43.3 mg, 0.0670 mmol), RhH(CO)(PPh$_3$)$_3$ (**2**) (61.5 mg, 0.0670 mmol), and toluene (3 mL), and the reaction mixture was stirred at 80 °C. After 5 h, the solvent was removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (2 mL × 3) and dried under vacuum to afford 49.7 mg of **3g** (0.0478 mmol) as an orange powder in 71% yield. ^1H NMR (400 MHz, C_6D_6): δ 6.42–6.46 (m, 2H, H_{arom}), 6.68–7.09 (m, 39H, H_{arom}), 7.35–7.63 (m, 4H, H_{arom}), 7.75–7.77 (m, 2H, H_{arom}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 127.6, 128.1, 128.8, 129.0, 129.2, 131.4, 132.5, 132.7, 133.6, 133.9, 134.6, 137.1, 138.6, 139.3, 139.4, 140.5, 151.4, 153.4, 203.7. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ –111.9 (s). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 32.0 (dt, J_{P-Rh} = 95.5 Hz, J_{P-P} = 34.3 Hz, PPh$_3$), 49.4 (dd, J_{P-Rh} = 145.0 Hz, J_{P-P} = 34.3 Hz, PPh$_2$). IR (KBr): 1921 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{61}H_{47}FOP_3RhSi$: C, 70.52; H, 4.56. Found: C, 70.23; H, 4.75.

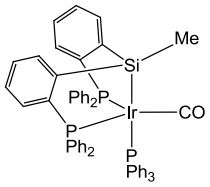
Preparation of {(*o*-Ph$_2$PC$_6$H$_4$)$_2$(Ph)Si}Ir(CO)(PPh$_3$) (6a)

A 50-mL Schlenk tube was charged with **1a** (97.6 mg, 0.138 mmol), IrH(CO)(PPh$_3$)$_3$ (**5**) (140 mg, 0.138 mmol), and toluene (6 mL), and the reaction mixture was stirred at 110 °C. After 60 h, the solvent was removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (2 mL × 3) and dried under vacuum to afford 139 mg of **6a** (0.125 mmol) as an orange powder in 91% yield. ^1H NMR (400 MHz, C_6D_6): δ 6.41–6.45 (m, 4H, H_{arom}), 6.67–7.05 (m, 30H, H_{arom}), 7.29–7.73 (m, 12H, H_{arom}), 7.90–7.92 (m, 2H, H_{arom}). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 127.3, 127.6, 128.0, 128.7, 129.1, 129.4, 131.3, 132.8, 133.7, 134.3, 134.8, 136.8, 137.6, 139.3, 140.4, 141.0, 143.0, 152.8, 190.1. $^{29}Si\{^1H\}$ NMR (79 MHz, $CDCl_3$): δ 47.5 (dt, J_{Si-P} = 97.5 Hz,

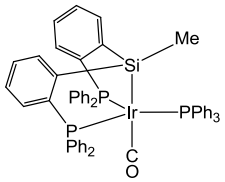
$J_{Si\text{-}P}$ = 10.5 Hz). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ 2.6 (t, J_{P-P} = 25.7 Hz, *P*Ph_3), 25.5 (d, J_{P-P} = 25.7 Hz, *P*Ph_2). IR (KBr): 1925 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{61}H_{48}IrOP_3Si$: C, 65.99; H, 4.36. Found: C, 66.32; H, 4.74.

Preparation of {(*o*-$Ph_2PC_6H_4)_2$(Me)Si}Ir(CO)(PPh_3) (6b)

A 50-mL Schlenk tube was charged with **1b** (64.7 mg, 0.111 mmol), IrH(CO)(PPh_3)$_3$ (**5**) (112 mg, 0.111 mmol), and toluene (10 mL), and the reaction mixture was stirred at 80 °C. After 14 h, the solvent was removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (2 mL × 3) and dried under vacuum to afford 94.5 mg of **6b** (0.0902 mmol) as an orange powder in 81% yield. **6b-A**: ^{1}H NMR (400 MHz, C_6D_6): δ 1.52 (s, 3H, SiC*H*$_3$), 6.32–7.71 (m, 41H, H_{arom}), 7.91–7.93 (m, 2H, H_{arom}). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 2.3, 127.5, 127.8, 128.8, 130.8, 131.5, 132.5, 133.6, 134.7, 136.9, 139.4, 140.0, 145.7, 150.6, 153.7, 191.4. $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ 3.0 (t, $J_{P\text{-}P}$ = 25.7 Hz, *P*Ph_3), 25.2 (d, $J_{P\text{-}P}$ = 25.7 Hz, *P*Ph_2). IR (KBr): 1918 cm^{-1} ($\nu_{C\equiv O}$). **6b-B**: ^{1}H NMR (400 MHz, C_6D_6): δ 0.41 (s, 3H, SiC*H*$_3$), 6.32–7.71 (m, 41H, H_{arom}), 7.97–7.99 (m, 2H, H_{arom}). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ 9.9 (t, $J_{P\text{-}P}$ = 100.3 Hz, *P*Ph_3), 36.5 (d, $J_{P\text{-}P}$ = 100.3 Hz, *P*Ph_2). IR (KBr): 1959 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{56}H_{46}IrOP_3Si$: C, 64.17; H, 4.42. Found: C, 64.43; H, 4.82.



6b-A



6b-B

Preparation of {(*o*-$Ph_2PC_6H_4)_2$(Et)Si}Ir(CO)(PPh_3) (6c)

A 50-mL Schlenk tube was charged with **1c** (177 mg, 0.291 mmol), IrH(CO)(PPh_3)$_3$ (**5**) (293 mg, 0.291 mmol), and toluene (7 mL), and the reaction mixture was stirred at 100 °C. After 36 h, the solvent was removed under reduced pressure to give a pale orange solid. The residue was washed with hexane (3 mL × 3) and dried under vacuum to afford 294 mg of **6c** (0.277 mmol) as an orange powder in 95% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 1.57 (t, $J_{H\text{-}H}$ = 7.8 Hz, 3H, $SiCH_2CH_3$), 2.11 (q, $J_{H\text{-}H}$ = 7.8 Hz, 2H, $SiCH_2CH_3$), 6.54–6.58 (m, 4H, H_{arom}), 6.65–7.10 (m, 33H, H_{arom}), 7.28–7.60 (m, 4H, H_{arom}), 8.00–8.02 (m, 2H, H_{arom}). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 10.0, 11.5, 127.5, 128.1, 128.3, 129.0, 129.3, 131.4, 132.6, 133.4, 134.8, 136.5, 139.6, 140.8, 151.3, 153.6, 191.2. $^{29}Si\{^{1}H\}$ NMR (79 MHz, $CDCl_3$): δ 50.0 (dt, J_{Si-P} = 94.6 Hz, J_{Si-P} = 9.8 Hz). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ 1.2 (t, J_{P-P} = 25.7 Hz, *P*Ph_3), 25.5 (d, J_{P-P} = 25.7 Hz, *P*Ph_2). IR (KBr): 1918 cm^{-1} ($\nu_{C\equiv O}$). Anal. Calc. for $C_{57}H_{48}IrOP_3Si$: C, 64.45; H, 4.55. Found: C, 64.61; H, 4.86.

Selectivity determined from the reactions of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(R)

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Ph)(H). An NMR tube was charged with {*o*-(Ph_2P)C_6H_4}$_2$Si(Ph)(H) (5.7 mg, 0.0091 mmol), **2** (8.4 mg, 0.0091 mmol), toluene-d_8 (0.50 mL), and trimesitylphosphine (7.1 mg) as an internal standard. Reaction was performed at 60 °C for 1 h to afford **3a** quantitatively (within the detection of ^{31}P NMR spectroscopy).

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(H) (4a). An NMR tube was charged with **4a** (5.8 mg, 0.0103 mmol), **2** (9.4 mg, 0.0103 mmol), mesitylene-d_{12} (0.50 mL), and trimesitylphosphine (8.0 mg) as an internal standard. Reaction was performed at 60 °C for 1 h to afford **3b** quantitatively (within the detection of ^{31}P NMR spectroscopy).

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Ph) (4b). An NMR tube was charged with **4b** (10.0 mg, 0.0156 mmol), **2** (14.3 mg, 0.0156 mmol), mesitylene-d_{12} (0.50 mL), and trimesitylphosphine (12 mg) as an internal standard. Reaction was performed at 60 °C for 2 h to afford a 61:39 mixture of **3b** and **3a**. The experiment was repeated three times, and it was confirmed that the error of the yields was within 1%.

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Et) (4c). An NMR tube was charged with **4c** (9.3 mg, 0.0156 mmol), **2** (14.3 mg, 0.0156 mmol), mesitylene-d_{12} (0.50 mL), and trimesitylphosphine (12 mg) as an internal standard. Reaction was performed at 60 °C for 1 h to afford a 11:89 mixture of **3b** and **3c**. The experiment was repeated three times, and it was confirmed that the error of the yields was within 1%.

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-tolyl) (4d). An NMR tube was charged with **4d** (10.2 mg, 0.0156 mmol), **2** (14.3 mg, 0.0156 mmol), mesitylene-d_{12} (0.50 mL), and trimesitylphosphine (12 mg) as an internal standard. Reaction was performed at 60 °C for 2 h to afford a 56:44 mixture of **3b** and **3d**. The experiment was repeated three times, and it was confirmed that the error of the yields was within 1%.

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-methoxyphenyl) (4e). An NMR tube was charged with **4e** (10.5 mg, 0.0156 mmol), **2** (14.3 mg, 0.0156 mmol), mesitylene-d_{12} (0.50 mL), and trimesitylphosphine (12.1 mg) as an internal standard. Reaction was performed at 60 °C for 2 h to afford a 50:50 mixture of **3b** and **3e**. The experiment was repeated three times, and it was confirmed that the error of the yields was within 1%.

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-dimethylaminophenyl) (4f). An NMR tube was charged with **4f** (10.7 mg, 0.0156 mmol), **2** (14.3 mg, 0.0156 mmol), mesitylene-d_{12} (0.50 mL), and trimesitylphosphine (12.1 mg) as an internal standard. Reaction was performed at 60 °C for 2 h to afford a 38:62 mixture of **3b** and **3f**. The experiment was repeated three times, and it was confirmed that the error of the yields was within 1%.

Reaction of 2 with {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-fluorophenyl) (4g). An NMR tube was charged with **4g** (10.3 mg, 0.0156 mmol), **2** (14.3 mg, 0.0156 mmol), mesitylene-d_{12} (0.50 mL), and trimesitylphosphine (12 mg) as an internal standard. Reaction was performed at 60 °C for 2 h to afford a 66:34 mixture of **3b** and **3g**. The experiment was repeated three times, and it was confirmed that the error of the yields was within 2%.

Selectivity data determined from the reactions of $RhH(CO)(PPh_3)_3$ (2) with 4b

A 50-mL Schlenk tube was charged with **4b** (60.0 mg, 0.0934 mmol), $RhH(CO)(PPh_3)_3$ (**2**) (85.8 mg, 0.0934 mmol), mesitylene-d_{12} (3.0 mL), and trimesitylphosphine (72.6 mg) as an internal standard. The solution was divided up evenly into six NMR sample tubes. The reactions were performed under appropriate conditions (see below). The experiment was repeated three times, and it was confirmed that the error of the yields was within 2%.

Table S1 Selectivity data determined from the reactions of **2** with **4b**

entry	conditions	Yield[a] of Si–Ph activation product	Yield[a] of Si–Me activation product
1	40 ºC, 12 h	72(2)% (**3b**)	28(2)% (**3a**)
2	60 ºC, 2 h	61(1)% (**3b**)	39(1)% (**3a**)
3	80 ºC, 30 min	54(1)% (**3b**)	46(1)% (**3a**)
4	100 ºC, 10 min	50(1)% (**3b**)	50(1)% (**3a**)
5	130 ºC, 5 min	46(2)% (**3b**)	54(2)% (**3a**)
6	160 ºC, 5 min	41(1)% (**3b**)	59(1)% (**3a**)

[a]Determined by ^{31}P NMR spectroscopy.

Selectivity data determined from the reactions of $IrH(CO)(PPh_3)_3$ (5) with 4b

A 50-mL Schlenk tube was charged with **4b** (50.0 mg, 0.0778 mmol), $IrH(CO)(PPh_3)_3$ (**5**) (78.4 mg, 0.0778 mmol), mesitylene-d_{12} (2.5 mL), and trimesitylphosphine (60.4 mg) as an internal standard. The solution was divided up evenly into five NMR sample tubes. The reactions were performed under appropriate conditions (see below). The experiment was repeated three times, and it was confirmed that the error of the yields was within 2%.

Table S2 Selectivity data determined from the reactions of **5** with **4b**

entry	conditions	Yield[a] of Si–Ph activation product	Yield[a] of Si–Me activation product
1	60 ºC, 48 h	44(1)% (**6b**)	56(1)% (**6a**)
2	80 ºC, 24 h	37(2)% (**6b**)	63(2)% (**6a**)
3	100 ºC, 6 h	32(1)% (**6b**)	68(1)% (**6a**)
4	130 ºC, 1 h	27(1)% (**6b**)	73(1)% (**6a**)
5	160 ºC, 1 h	22(1)% (**6b**)	78(1)% (**6a**)

[a]Determined by ^{31}P NMR spectroscopy.

Selectivity data determined from the reactions of $RhH(CO)(PPh_3)_3$ (2) with 4c

A 50-mL Schlenk tube was charged with **4c** (37.0 mg, 0.0622 mmol), $RhH(CO)(PPh_3)_3$ (**2**) (57.2 mg, 0.0622 mmol), mesitylene-d_{12} (2.0 mL), and trimesitylphosphine (48.4 mg) as an internal standard. The solution was divided up evenly into four NMR sample tubes. The reactions were performed under appropriate conditions (see below). The experiment was repeated three times, and it was confirmed that the error of the yields was within 1%.

Table S3 Selectivity data determined from the reactions of **2** with **4c**

entry	conditions	Yield[a] of Si–Et activation product	Yield[a] of Si–Me activation product
1	40 ºC, 10 h	11(1)% (**3b**)	89(1)% (**3c**)
2	60 ºC, 1 h	11(1)% (**3b**)	89(1)% (**3c**)
3	80 ºC, 30 min	12(1)% (**3b**)	88(1)% (**3c**)
4	160 ºC, 5 min	13(1)% (**3b**)	87(1)% (**3c**)

[a]Determined by ^{31}P NMR spectroscopy.

Eyring plot for the reaction of 2 with 1a. A Schlenk tube was charged with **2** (24.0 mg, 0.0261 mmol), **1a** (92.1 mg, 0.131 mmol), toluene-d_8(1.6 mL), and trimesitylphosphine (30.4 mg) as an internal standard. The solution was divided up evenly into four NMR sample tubes and the reactions were performed under appropriate temperature (50, 60, 70, and 80 °C). The reactions were monitored by ^{31}P NMR spectroscopy. The rate constants were calculated on the basis of the time conversion of [**2**]: $k = 1.61 \times 10^{-4}$ (50 °C); 3.76×10^{-4} (60 °C); 9.82×10^{-4} (70 °C); 1.90×10^{-3} (80 °C) (Table S4). The temperature dependence of the rate constants yielded the following activation parameters (Eyring plot was shown in Figure S1): $\Delta H^{\ddagger} = 18.3 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19.3 \pm 2.1$ cal mol^{-1}K^{-1}.

Table S4 *k* at various temperature

temp. (ºC)	k (s^{-1})
50	1.61×10^{-4}
60	3.76×10^{-4}
70	9.82×10^{-4}
80	1.90×10^{-3}

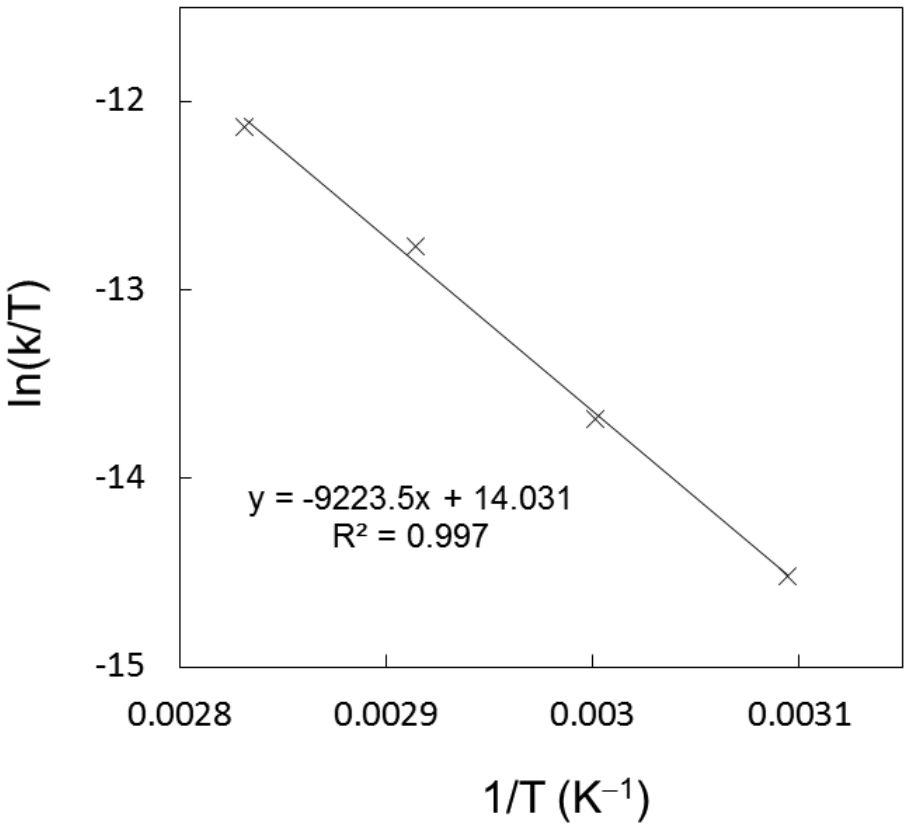


Figure S1 Eyring plot

Eyring plot for the reaction of 2 with 1b. A Schlenk tube was charged with **1b** (75.8 mg, 0.131 mmol), toluene-d_8(1.6 mL), and trimesitylphosphine (30.4 mg) as an internal standard. The solution was divided up evenly into four NMR sample tubes. After the sample was evacuated at −78 °C, **2** (6.0 mg, 0.00653 mmol) was introduced into each tube. The reactions were performed at appropriate temperature (0, 10, 20, and 30 °C). The reactions were monitored by ^{31}P NMR spectroscopy. The rate constants were calculated on the basis of the time conversion of [**2**]: $k = 7.18 \times 10^{-5}$ (0 °C); 2.30×10^{-4} (10 °C); 7.05×10^{-4} (20 °C); 2.55×10^{-3} (30 °C) (Table S5). The temperature dependence of the rate constants yielded the following activation parameters (Eyring plot was shown in Figure S2): $\Delta H^{\ddagger} = 18.8 \pm 0.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8.5 \pm 2.8$ cal mol^{-1}K^{-1}.

Table S5 *k* at various temperature

temp. (ºC)	k (s^{-1})
0	7.18×10^{-5}
10	2.30×10^{-4}
20	7.05×10^{-4}
30	2.55×10^{-3}

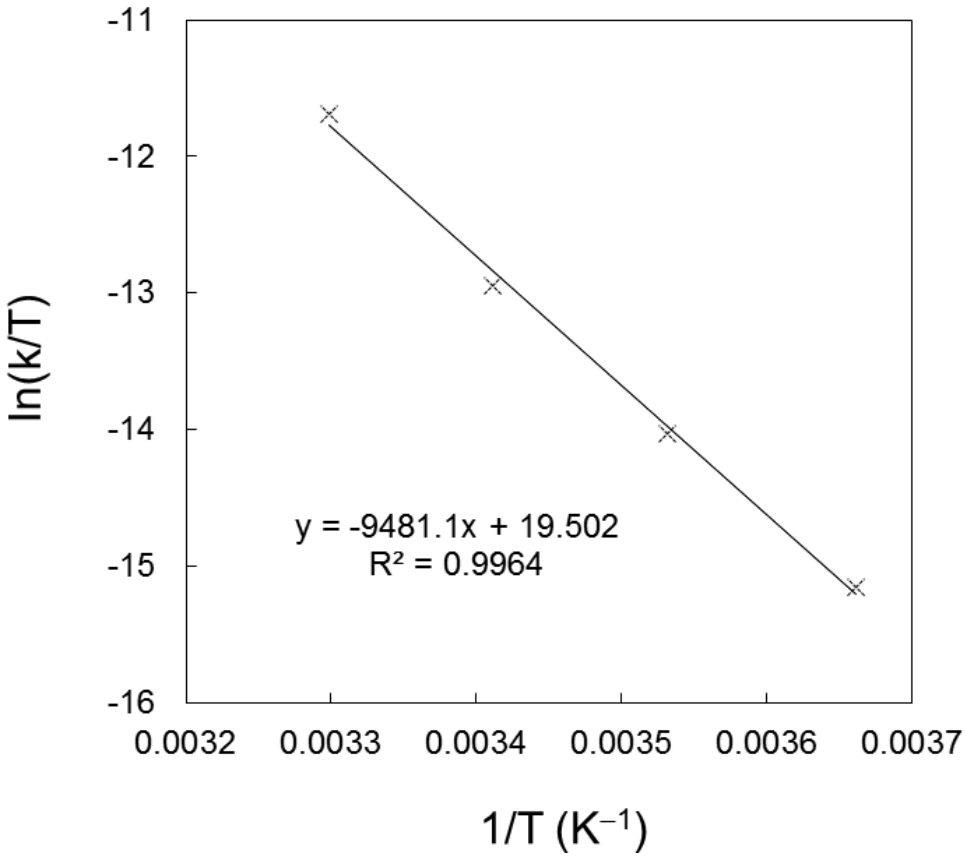
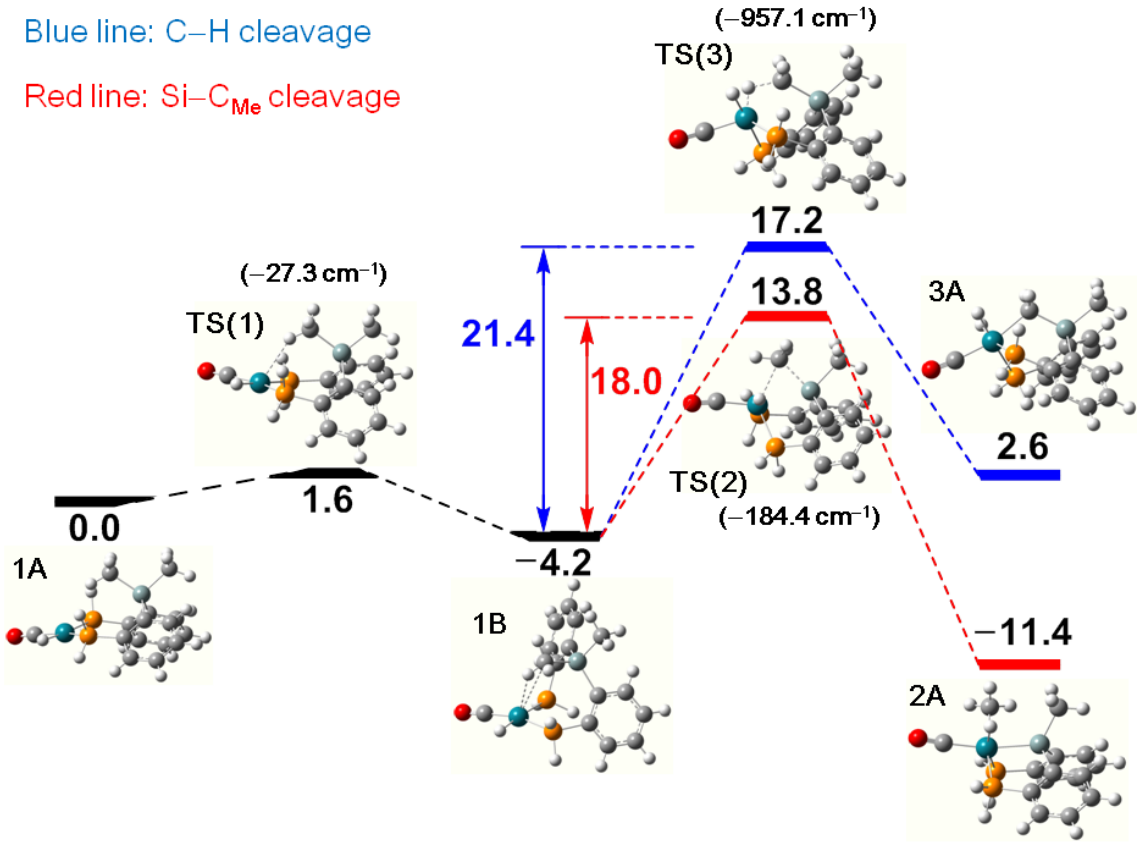


Figure S2 Eyring plot

DFT calculation for the Si–C_{Me} activation by Rh(H)(CO)(PPh_3)$_3$ (2).

To get more insight into the mechanistic information on the Si–C(sp^3) activation by Rh(H)(CO)(PPh_3)$_3$ (**2**), we performed density functional theory (DFT) calculations using model compounds {*o*-(H_2P)-(C_6H_4)}$_2$Si(Me)$_2$Rh(H)(CO) (**1A**), where the phenyl groups were replaced by hydrogens (Scheme S1). The calculations were carried out at B3PW91[1] level in conjunction with the Stuttgart/Dresden ECP[2] and associated with triple-ζ SDD basis sets for Rh. For C, H, O, P, and Si, 6-311G(d,p) basis sets were employed. All calculations were performed by utilizing the Gaussian09 program.[3] Frequency calculations at the same level were performed on optimized structures to ensure that minima exhibit only positive frequency and that transition states exhibit only one imaginary frequency. The intrinsic reaction coordinate (IRC) calculations[4] were also performed to unambiguously connect the transition states with the reactants and the products. The molecular structures were drawn by using the *GaussView version 4.1.2* program.[5] Cartesian Coordinates were shown in Table S18-S24.



Scheme S1 Computed reaction profiles for the oxidative addition of C–H (in blue) and Si–C_{Me} (in red) bonds. Relative energies (at 298.15 K) are given in kcal/mol.

Once 16 electron complex **1A** featuring a square planar geometry was formed, the kinetic barrier to the σC–H complex **1B** is highly accessible ($\Delta G^{\ddagger}_{298}$ = 1.6 kcal/mol). Not only C–H but also Si–C_{Me} activation reactions potentially occur via the σC–H complex **1B**. The transition state for Si–C_{Me} cleavage TS(**2**) is lower in energy than the corresponding one for C–H cleavage TS(**3**) by 3.4 kcal/mol, strongly supporting that the Si–C_{Me} cleavage is accessible without the C–H cleavage.

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Result of X-ray diffraction study of **3a**

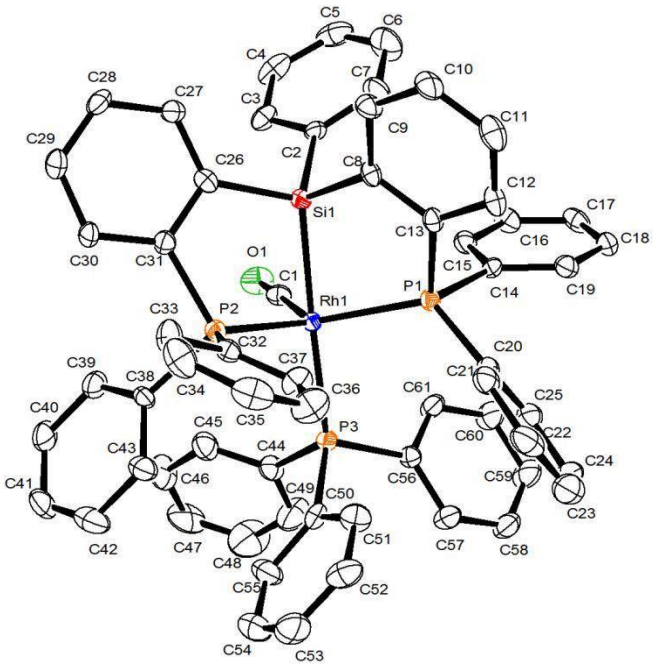


Figure S3. Molecular structure of **3a** (40% probability).

Table S6. Crystallographic data for **3a**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{61}H_{48}OP_3RhSi$	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1021.95	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Prism	Monochrometer	Graphite
Crystal color	Pale Yellow	2θ max (°)	55
Crystal size (mm)	0.25 × 0.05 × 0.03	Reflections collected	37223
Crystalizing solution	Et_2O (23 °C)	Independent reflections	11027 (R_{int} = 0.063)
Crystal system	Monoclinic	Reflections observed (> 2σ)	7400
Space group	$P2_1/c$ (#14)	Abs. correction type	Multi-scan
a (Å)	11.1258(7)	Abs. transmission	0.705 (min.), 0.985 (max.)
b (Å)	16.2240(10)	(c) Refinement (CrystalStructure 3.8)	
c (Å)	27.441(2)	R_1 ($I > 2\sigma(I)$)	0.0582
β (º)	99.718(3)	wR_2 ($I > 2\sigma(I)$)	0.1771
Volume (Å^3)	4882.2(6)	Data	11027
Z value	4	Restraints	0
D_{calc} (g/cm^3)	1.389	Parameters	652
Mesurement temp. (K)	200	Goodness of fit on F^2	1.002
μ (MoKα) (mm^{-1})	0.515	Largest diff. peak and hole	1.73 and −1.05 e.Å^{-3}

Table S7. Selected bond lengths (Å) and angles (°).

Rh1-P1	2.3780(12)	Rh1-P2	2.3594(11)	Rh1-P3	2.3945(11)	Rh1-Si1	2.3531(11)
Rh1-C1	1.879(4)	C1-O1	1.150(5)	Si1-C2	1.885(4)	Si1-C8	1.888(4)
Si1-C26	1.886(4)						

P1-Rh1-P2	117.92(4)	P1-Rh1-P3	99.00(4)	P2-Rh1-P3	102.79(4)
P1-Rh1-C1	125.41(14)	P2-Rh1-C1	111.31(14)	P3-Rh1-C1	91.60(14)
P1-Rh1-Si1	80.10(4)	P2-Rh1-Si1	80.65(4)	P3-Rh1-Si1	176.40(4)
C1-Rh1-Si1	86.13(14)	Rh1-C1-O1	177.1(3)	Rh1-Si1-C2	120.85(15)
Rh1-Si1-C8	108.67(14)	Rh1-Si1-C26	108.83(15)		

Result of X-ray diffraction study of **3b**

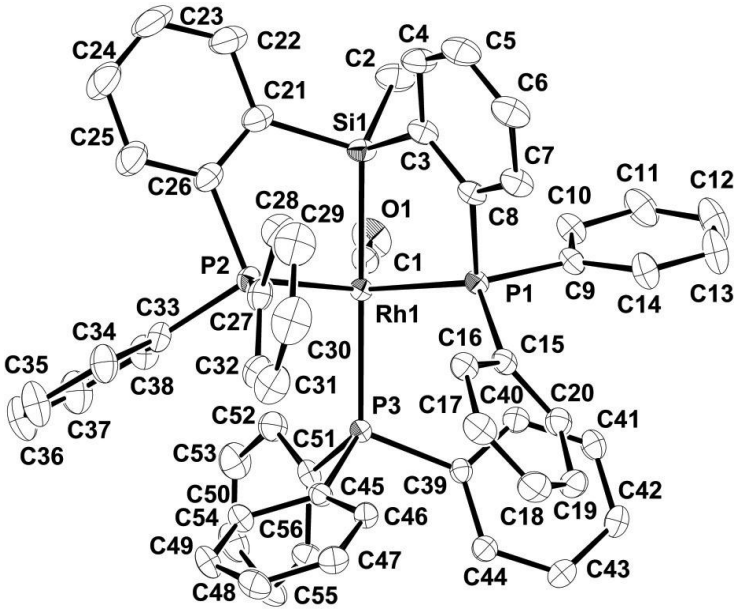


Figure S4. Molecular structure of **3b** (40% probability).

Table S8. Crystallographic data for **3b**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{56}H_{46}OP_3RhSi{\cdot}2(CH_2Cl_2)$	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1128.69	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Prism	Monochrometer	Graphite
Crystal color	Pale Yellow	2θ max (°)	55
Crystal size (mm)	0.35 × 0.25 × 0.15	Reflections collected	20790
Crystalizing solution	CH_2Cl_2, *n*-hexane (23 °C)	Independent reflections	11765 (R_{int} = 0.0277)
Crystal system	Triclinic	Reflections observed (> 2σ)	10988
Space group	*P*-1 (#2)	Abs. correction type	Multi-scan
a (Å)	12.0136(7)	Abs. transmission	0.7962 (min.), 0.9046 (max.)
b (Å)	12.8856(5)	(c) Refinement (Shelxl-97)	
c (Å)	17.6972(11)	R_1 ($I > 2\sigma(I)$)	0.0428
α (º)	94.380(3)	wR_2 ($I > 2\sigma(I)$)	0.1037
β (º)	105.563(3)	R_1 (all data)	0.0471
γ (º)	90.173(2)	wR_2 (all data)	0.1062
Volume (Å^3)	2630.6(2)	Data / Restraints / Parameters	11765 / 0 / 620
Z value	2	Goodness of fit on F^2	1.075
D_{calc} (g/cm^3)	1.425	Largest diff. peak and hole	0.893 and −0.928 e.Å^{-3}
Mesurement temp. (K)	200		
μ(MoKα) (mm^{-1})	0.682		

Table S9. Selected bond lengths (Å) and angles (°).

Rh1-P1	2.3601(6)	Rh1-P2	2.3591(6)	Rh1-P3	2.3974(6)	Rh1-Si1	2.3601(7)
Rh1-C1	1.869(3)	C1-O1	1.150(5)	Si1-C2	1.885(4)	Si1-C8	1.888(4)
Si1-C26	1.886(4)						

P1-Rh1-P2	108.65(2)	P1-Rh1-P3	98.22(2)	P2-Rh1-P3	99.53(2)
P1-Rh1-C1	119.83(8)	P2-Rh1-C1	125.71(8)	P3-Rh1-C1	96.45(8)
P1-Rh1-Si1	81.91(2)	P2-Rh1-Si1	80.86(2)	P3-Rh1-Si1	179.53(2)
C1-Rh1-Si1	83.09(8)	Rh1-C1-O1	177.1(3)	Rh1-Si1-C2	120.85(15)
Rh1-Si1-C8	108.67(14)	Rh1-Si1-C26	108.83(15)		

Result of X-ray diffraction study of **3c**

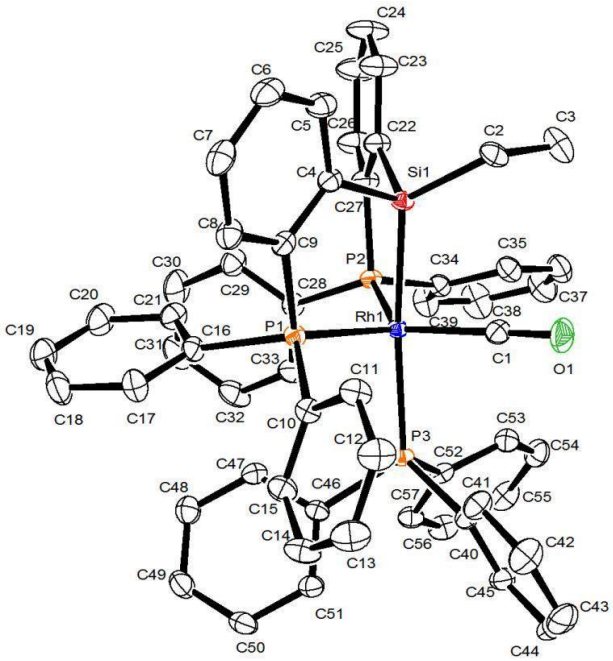


Figure S5. Molecular structure of **3c** (40% probability).

Table S10. Crystallographic data for **3c**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{57}H_{48}OP_3RhSi$	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	972.92	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Prism	Monochrometer	Graphite
Crystal color	Yellow	2θ max (°)	55
Crystal size (mm)	0.20 × 0.15 × 0.15	Reflections collected	18534
Crystalizing solution	Et_2O, *n*-pentane (23 °C)	Independent reflections	10572 (R_{int} = 0.028)
Crystal system	Triclinic	Reflections observed (> 2σ)	9576
Space group	*P*-1 (#2)	Abs. correction type	Multi-scan
a (Å)	12.272(3)	Abs. transmission	0.738 (min.), 0.924 (max.)
b (Å)	12.984(3)	(c) Refinement (CrystalStructure 3.8)	
c (Å)	16.181(4)	R_1 ($I > 2\sigma(I)$)	0.0369
α (°)	80.866(6)	wR_2 ($I > 2\sigma(I)$)	0.1118
β (°)	85.510(6)	Data	10572
γ (°)	68.890(5)	Restraints	0
Volume (Å^3)	2374.1(9)	Parameters	616
Z value	2	Goodness of fit on F^2	1.004
D_{calc} (g/cm^3)	1.361	Largest diff. peak and hole	1.10 and −0.89 e.Å^{-3}
Mesurement temp. (K)	200		
μ(MoKα) (mm^{-1})	0.525		

Table S11. Selected bond lengths (Å) and angles (°).

Rh1-P1	2.3569(5)	Rh1-P2	2.3625(5)	Rh1-P3	2.3851(5)	Rh1-Si1	2.3548(5)
Rh1-C1	1.8645(18)	C1-O1	1.155(2)	Si1-C2	1.891(2)	Si1-C4	1.892(2)
Si1-C22	1.902(2)						

P1-Rh1-P2	117.469(17)	P1-Rh1-P3	98.235(18)	P2-Rh1-P3	100.417(19)
P1-Rh1-C1	119.91(7)	P2-Rh1-C1	119.15(8)	P3-Rh1-C1	90.07(7)
P1-Rh1-Si1	83.154(19)	P2-Rh1-Si1	83.84(2)	P3-Rh1-Si1	174.163(17)
C1-Rh1-Si1	84.34(7)	Rh1-C1-O1	178.57(19)	Rh1-Si1-C2	121.59(7)
Rh1-Si1-C4	109.49(7)	Rh1-Si1-C22	108.86(7)		

Result of X-ray diffraction study of **6a**

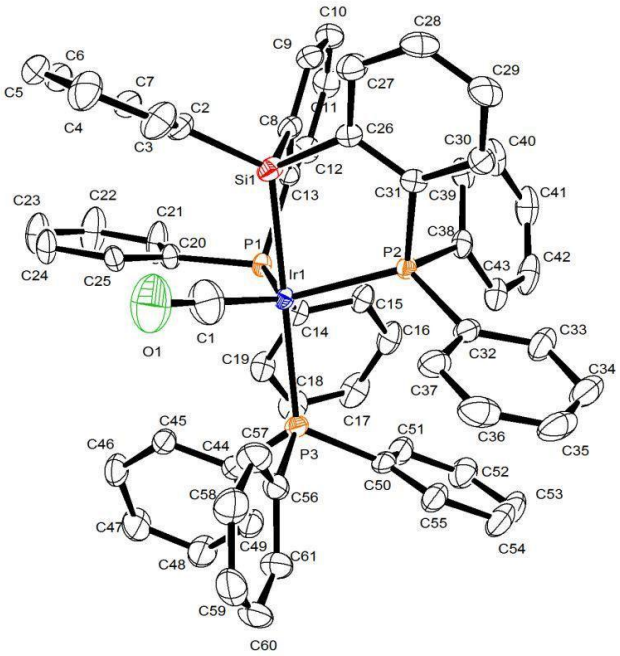


Figure S6. Molecular structure of **6a** (40% probability).

Table S12. Crystallographic data for **6a**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{61}H_{48}IrOP_3Si \cdot 1/2(Et_2O)$	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1131.80	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Prism	Monochrometer	Graphite
Crystal color	Pale Yellow	2θ max (°)	55
Crystal size (mm)	0.20 × 0.08 × 0.08	Reflections collected	40576
Crystalizing solution	Et_2O (23 °C)	Independent reflections	11649 (R_{int} = 0.049)
Crystal system	Monoclinic	Reflections observed (> 2σ)	9581
Space group	$P2_1/n$ (#14)	Abs. correction type	Multi-scan
a (Å)	12.039(2)	Abs. transmission	0.606 (min.), 0.800 (max.)
b (Å)	20.100(4)	(c) Refinement (CrystalStructure 3.8)	
c (Å)	21.779(5)	R_1 ($I > 2\sigma(I)$)	0.0417
β (º)	104.258(2)	wR_2 ($I > 2\sigma(I)$)	0.0940
Volume (Å^3)	5107.8(18)	Data	11649
Z value	4	Restraints	0
D_{calc} (g/cm^3)	1.472	Parameters	683
Mesurement temp. (K)	200	Goodness of fit on F^2	1.013
μ (MoKα) (mm^{-1})	2.782	Largest diff. peak and hole	1.96 and − 1.63 e.Å^{-3}

Table S13. Selected bond lengths (Å) and angles (°).

Ir1-P1	2.3253(9)	Ir1-P2	2.3253(11)	Ir1-P3	2.3638(12)	Ir1-Si1	2.3857(14)
Ir1-C1	1.792(7)	C1-O1	1.219(9)	Si1-C2	1.879(5)	Si1-C8	1.899(4)
Si1-C26	1.896(4)						

P1-Ir1-P2	106.84(3)	P1- Ir1-P3	102.46(4)	P2- Ir1-P3	99.28(4)
P1- Ir1-C1	117.9(2)	P2-Rh1-C1	128.3(2)	P3- Ir1-C1	95.1(2)
P1- Ir1-Si1	81.40(4)	P2- Ir1-Si1	80.48(4)	P3- Ir1-Si1	175.98(4)
C1- Ir1-Si1	82.0(2)	Ir1-C1-O1	178.6(6)	Ir1-Si1-C2	121.22(17)
Ir1-Si1-C8	106.93(16)	Ir1-Si1-C26	107.25(15)		

Result of X-ray diffraction study of **6b**

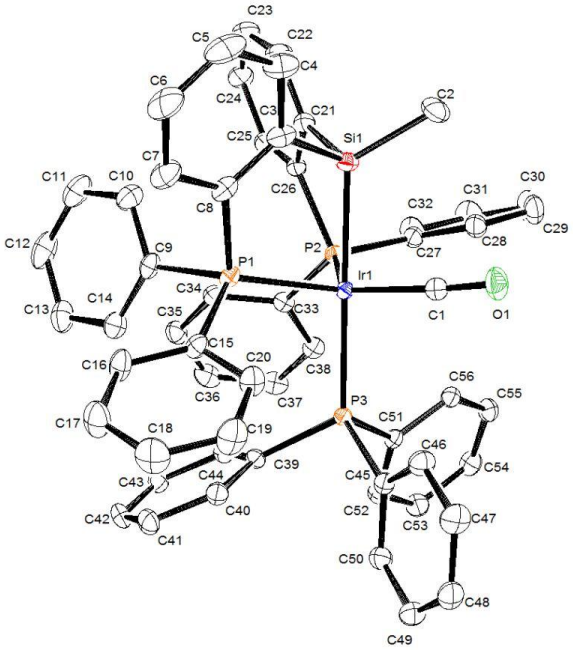


Figure S7. Molecular structure of **6b** (40% probability).

Table S14. Crystallographic data for **6b**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{56}H_{46}IrOP_3Si{\cdot}2(CH_2Cl_2)$	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1218.07	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Platelet	Monochrometer	Graphite
Crystal color	Colorless	2θ max (°)	55
Crystal size (mm)	0.35 × 0.25 × 0.20	Reflections collected	20788
Crystalizing solution	CH_2Cl_2, *n*-hexane (23 °C)	Independent reflections	11792 (R_{int} = 0.026)
Crystal system	Triclinic	Reflections observed (> 2σ)	11271
Space group	*P*-1 (#2)	Abs. correction type	Multi-scan
a (Å)	12.020(2)	Abs. transmission	0.419 (min.), 0.559 (max.)
b (Å)	12.852(3)	(c) Refinement (CrystalStructure 3.8)	
c (Å)	17.695(3)	R_1 (I > 2σ(I))	0.0315
α (°)	85.644(4)	wR_2 (I > 2σ(I))	0.0930
β (°)	74.360(4)	Data	11792
γ (°)	90.106(5)	Restraints	0
Volume (Å^3)	2623.8(9)	Parameters	663
Z value	2	Goodness of fit on F^2	1.013
D_{calc} (g/cm^3)	1.542	Largest diff. peak and hole	2.35 and − 1.24 e.Å^{-3}
Mesurement temp. (K)	200		
μ(MoKα) (mm^{-1})	2.909		

Table S15. Selected bond lengths (Å) and angles (°).

Ir1-P1	2.3382(7)	Ir1-P2	2.3370(6)	Ir1-P3	2.3811(8)	Ir1-Si1	2.3805(9)
Ir1-C1	1.857(2)	C1-O1	1.165(3)	Si1-C2	1.884(3)	Si1-C3	1.893(3)
Si1-C21	1.895(2)						

P1-Ir1-P2	108.57(2)	P1- Ir1-P3	99.35(2)	P2- Ir1-P3	98.06(2)
P1- Ir1-C1	126.19(9)	P2-Rh1-C1	120.08(9)	P3- Ir1-C1	95.45(10)
P1- Ir1-Si1	81.01(2)	P2- Ir1-Si1	81.84(2)	P3- Ir1-Si1	179.64(2)
C1- Ir1-Si1	84.31(10)	Ir1-C1-O1	175.2(2)	Ir1-Si1-C2	122.01(13)
Ir1-Si1-C3	107.97(12)	Ir1-Si1-C21	106.70(11)		

Result of X-ray diffraction study of **6c**

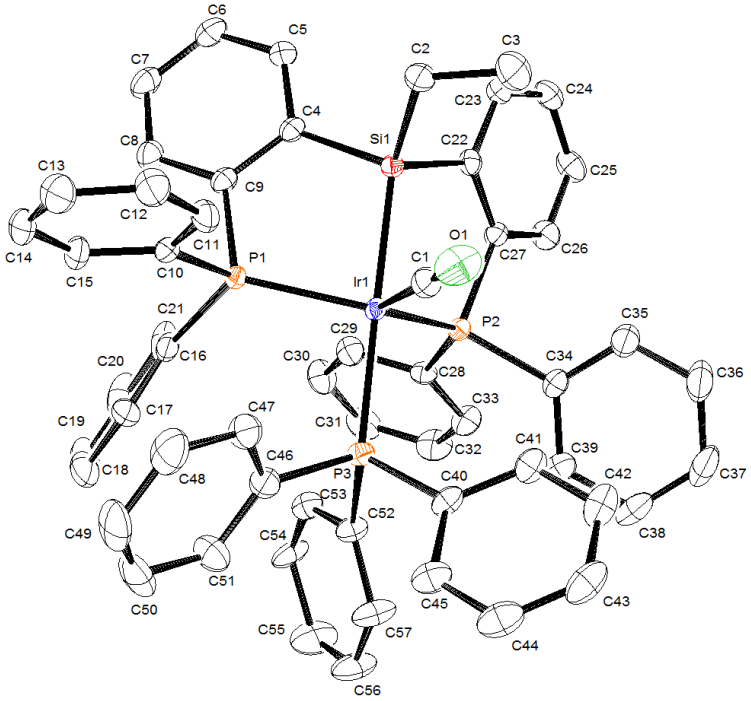


Figure S8. Molecular structure of **6c** (40% probability).

Table S16. Crystallographic data for **6c**.

(a) Crystal data		(b) Intensity measurements	
Empirical formula	$C_{57}H_{48}IrO_1P_3Si$, 0.5($C_4H_{10}O$)	Diffractometer	Rigaku/MSC Mercury CCD
Formula weight	1099.21	Radiation	MoKα (λ = 0.71069 Å)
Crystal description	Platelet	Monochrometer	Graphite
Crystal color	Colorless	2θ max (°)	55
Crystal size (mm)	0.25 × 0.12 × 0.03	Reflections collected	38992
Crystalizing solution	Et_2O, *n*-pentane (23 °C)	Independent reflections	11200 (R_{int} = 0.0492)
Crystal system	Monoclinic	Reflections observed (> 2σ)	10356
Space group	$P2_1/n$ (#14)	Abs. correction type	Multi-scan
a (Å)	12.104(3)	Abs. transmission	0.5331 (min.), 0.9186 (max.)
b (Å)	21.128(5)	(c) Refinement (Shelxl-97)	
c (Å)	19.248(5)	R_1 ($I > 2\sigma(I)$)	0.0482
β (º)	91.887(3)	wR_2 ($I > 2\sigma(I)$)	0.0904
Volume (Å^3)	4920(2)	R_1 (all data)	0.0555
Z value	4	wR_2 (all data)	0.0927
D_{calc} (g/cm^3)	1.484	Data / Restraints / Parameters	11200 / 0 / 6212
Mesurement temp. (K)	200	Goodness of fit on F^2	1.230
μ (MoKα) (mm^{-1})	2.878	Largest diff. peak and hole	1.446 and − 1.203 e.Å^{-3}

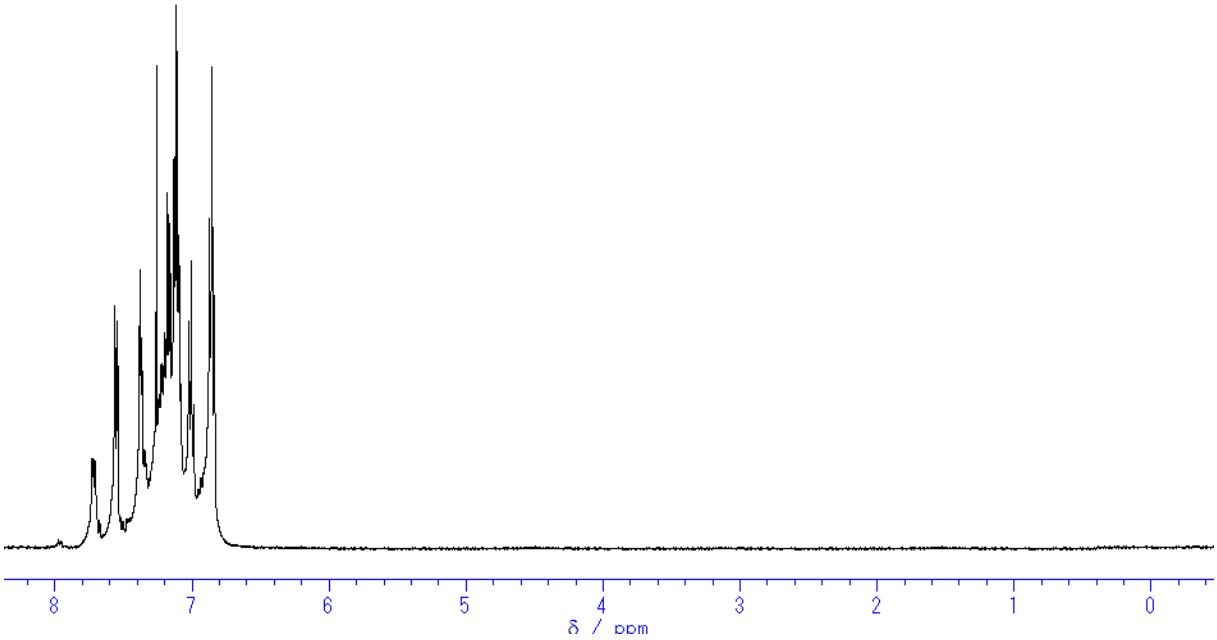
Table S17. Selected bond lengths (Å) and angles (°).

Ir1-P1	2.3327(11)	Ir1-P2	2.3273(11)	Ir1-P3	2.3793(11)	Ir1-Si1	2.3868(12)
Ir1-C1	1.871(5)	C1-O1	1.146(6)	Si1-C2	1.892(5)	Si1-C4	1.897(4)
Si1-C22	1.891(5)						

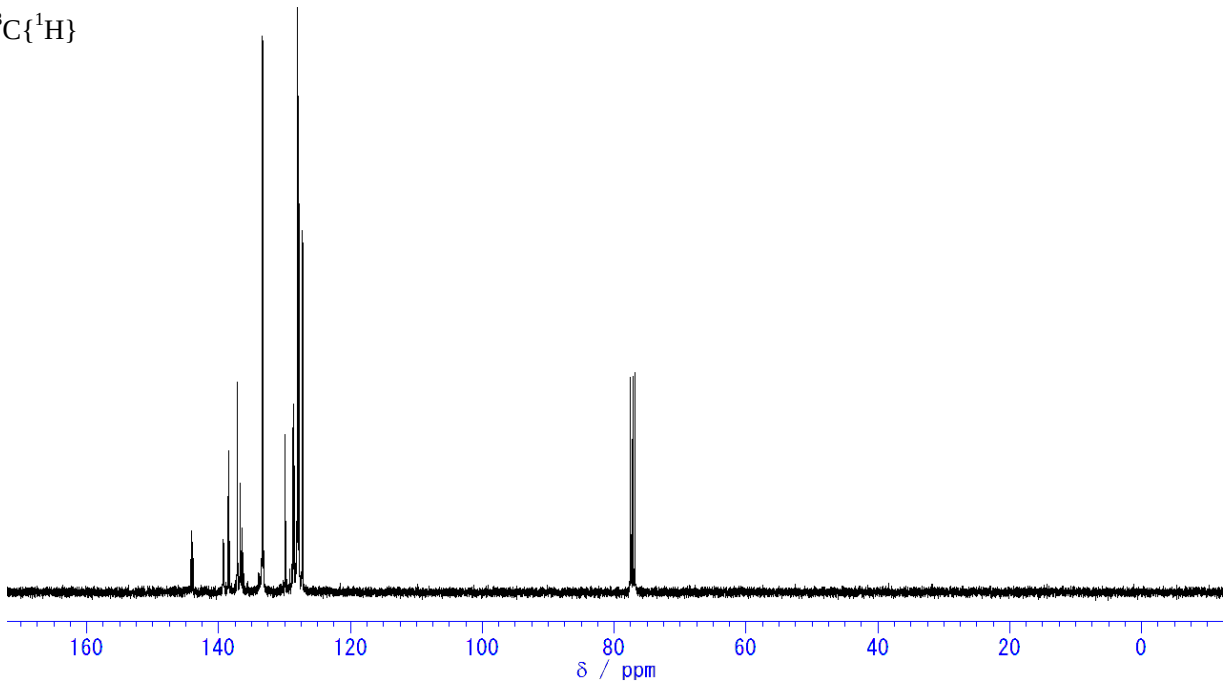
P1-Ir1-P2	119.10(4)	P1- Ir1-P3	98.99(4)	P2- Ir1-P3	98.02(4)
P1- Ir1-C1	118.93(15)	P2-Rh1-C1	118.99(16)	P3- Ir1-C1	90.19(15)
P1- Ir1-Si1	82.07(4)	P2- Ir1-Si1	83.38(4)	P3- Ir1-Si1	177.48(4)
C1- Ir1-Si1	87.30(15)	Ir1-C1-O1	178.6(5)	Ir1-Si1-C2	122.22(16)
Ir1-Si1-C4	108.49(14)	Ir1-Si1-C22	108.39(14)		

Figure S9. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$$SiPh_2$ (**1a**).

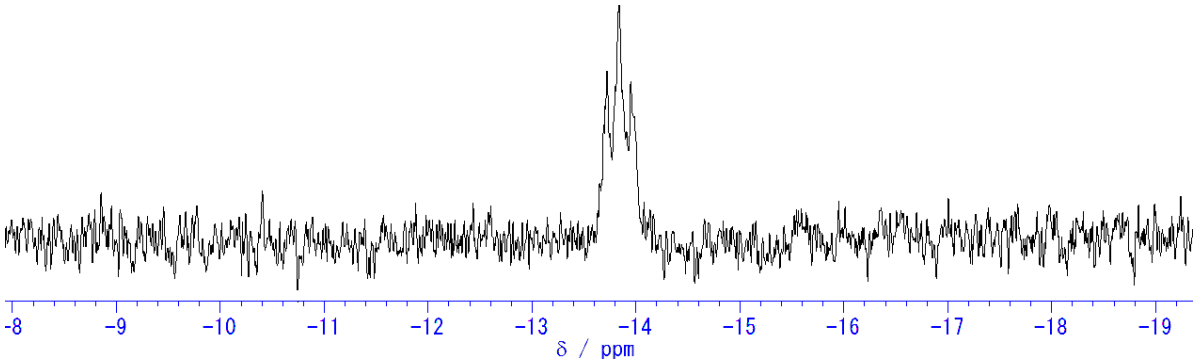
^1H



$^{13}C\{^1H\}$



$^{29}S\{^{1}H\}$



$^{31}P\{^{1}H\}$

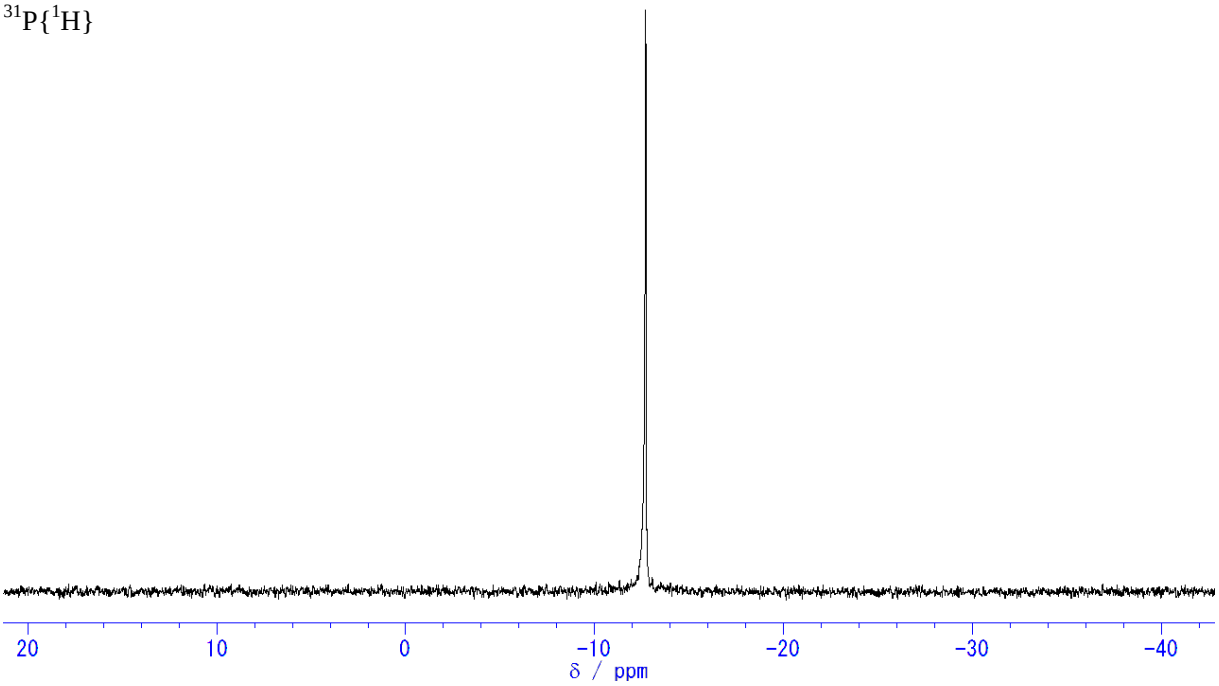
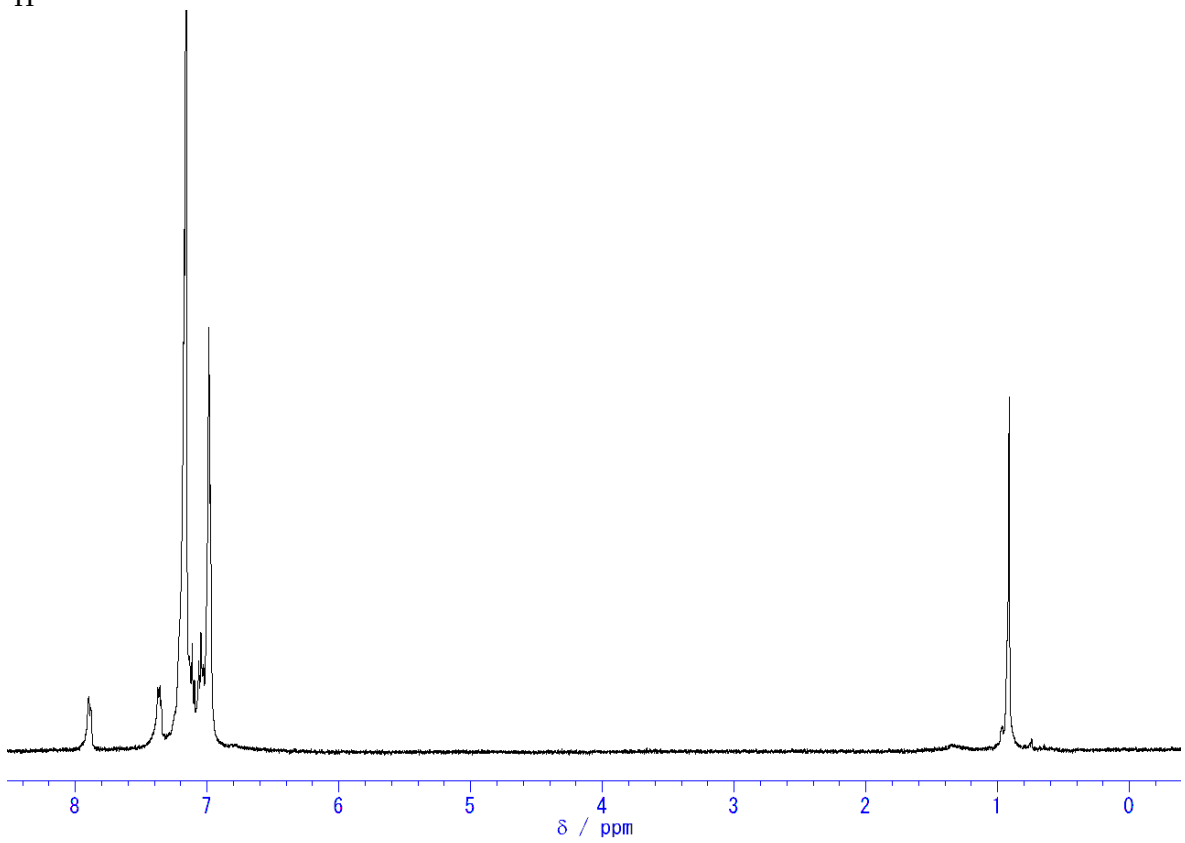
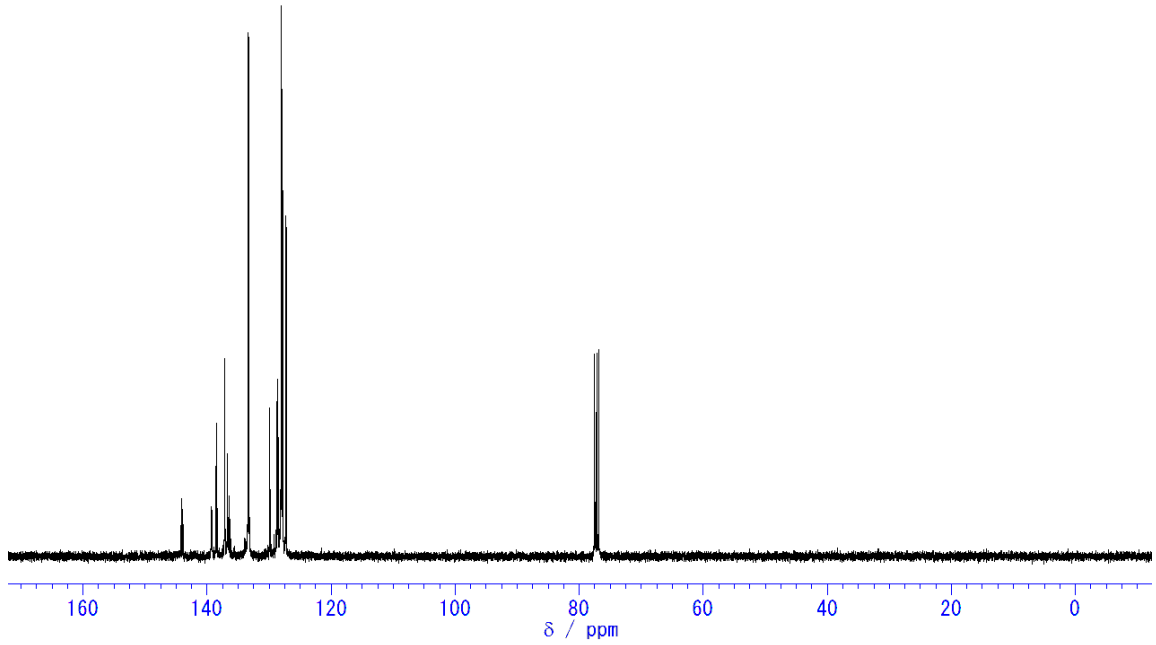


Figure S10. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$$SiMe_2$ (**1b**).

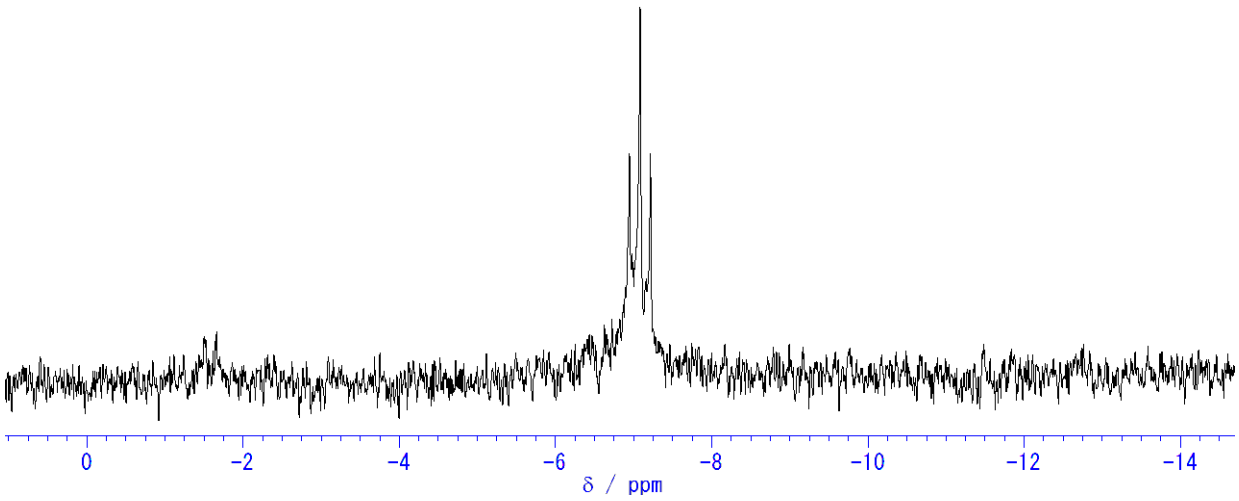
^1H



$^{13}C\{^1H\}$



$^{29}Si\{^{1}H\}$



$^{31}P\{^{1}H\}$

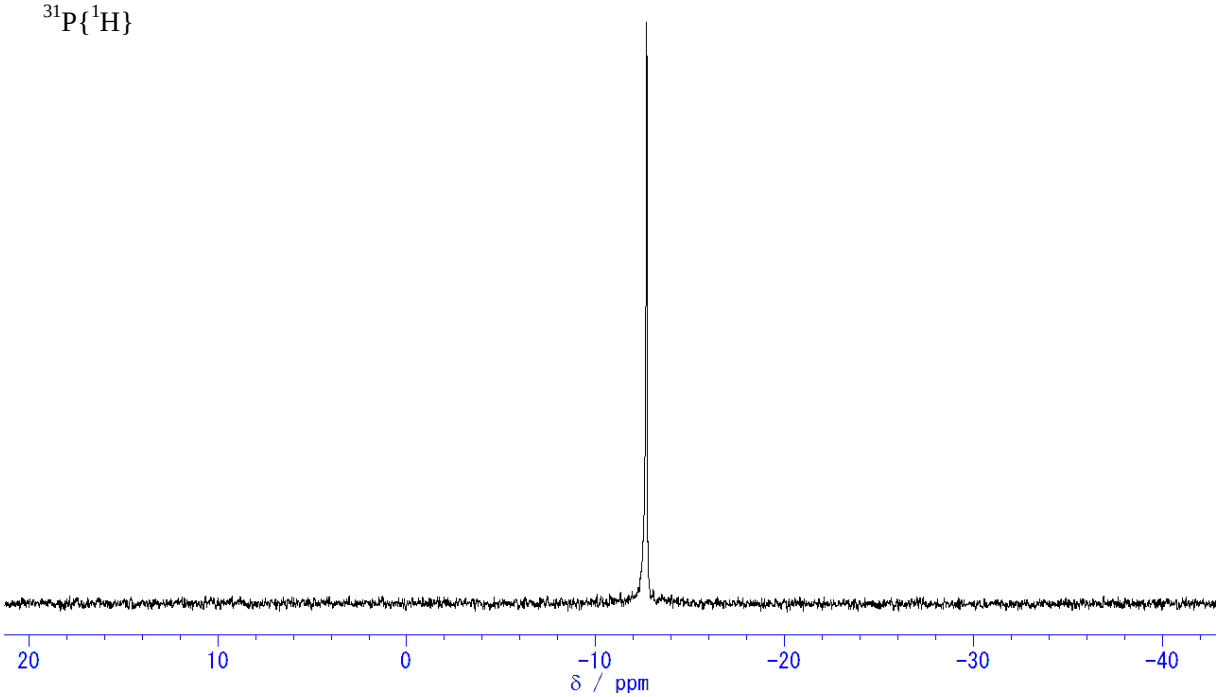
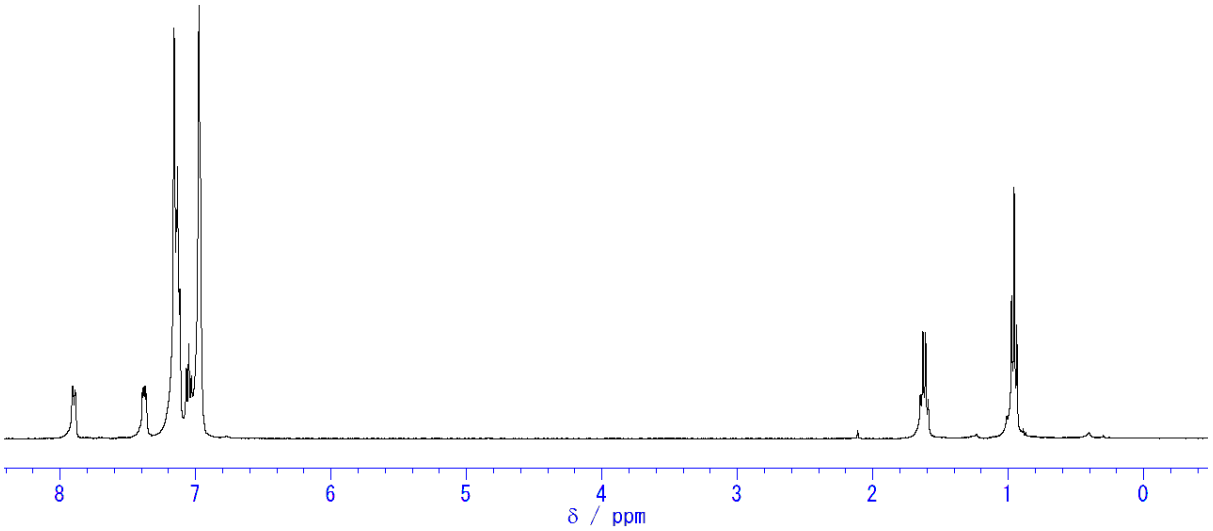
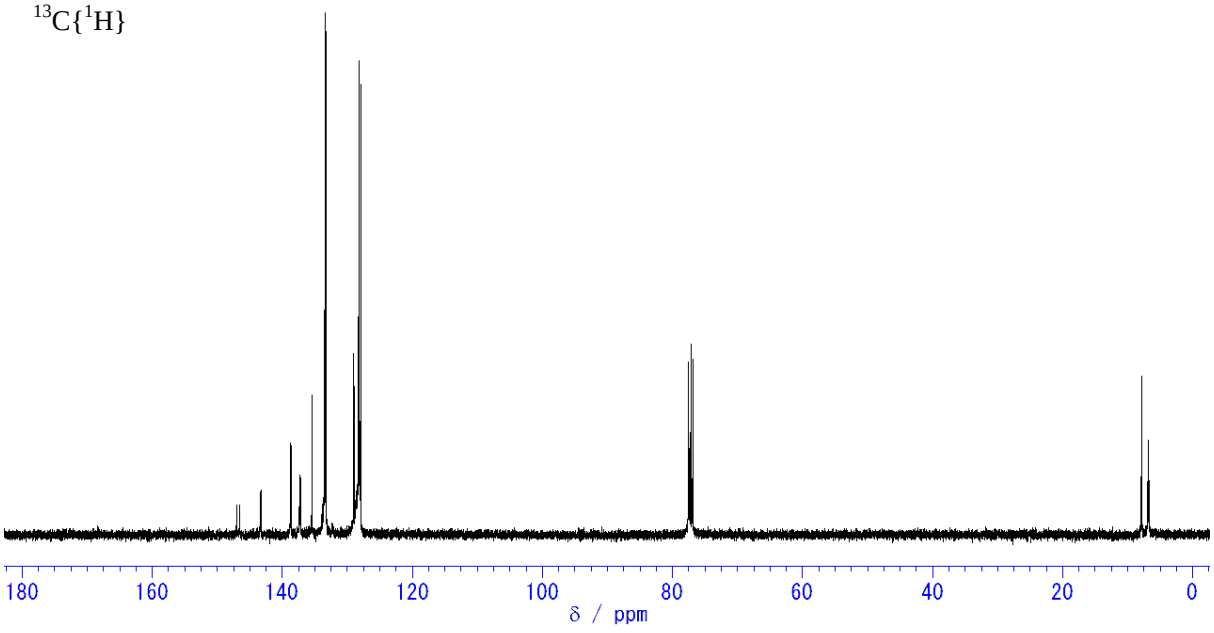


Figure S11. NMR spectra of {*o*-$(Ph_2P)C_6H_4\}_2SiEt_2$ (**1c**).

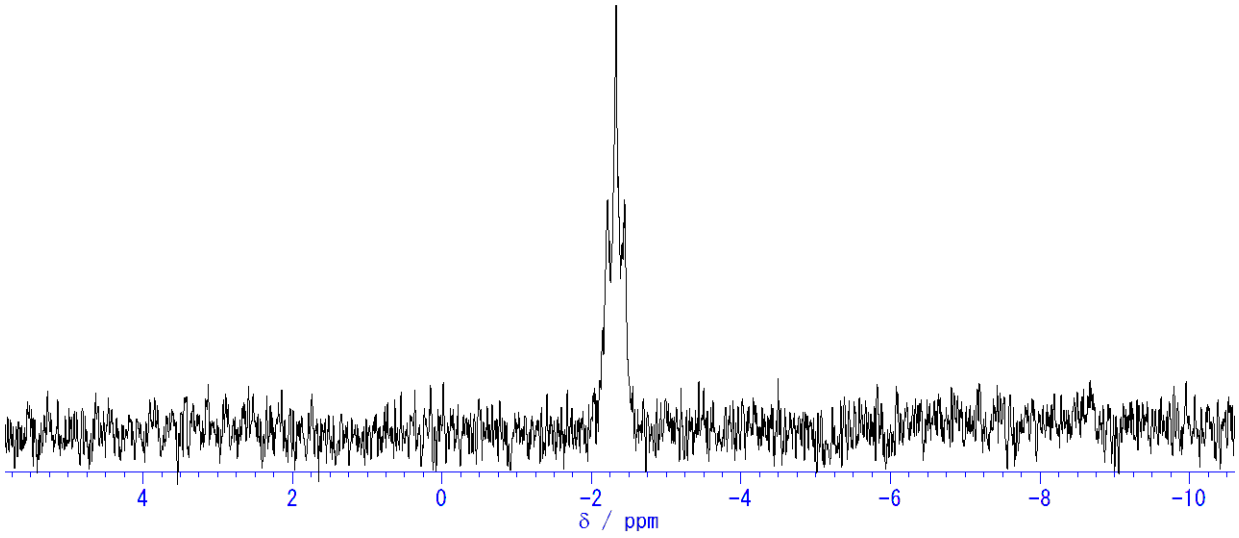
^1H



$^{13}C\{^1H\}$



$^{29}Si\{^{1}H\}$



$^{31}P\{^{1}H\}$

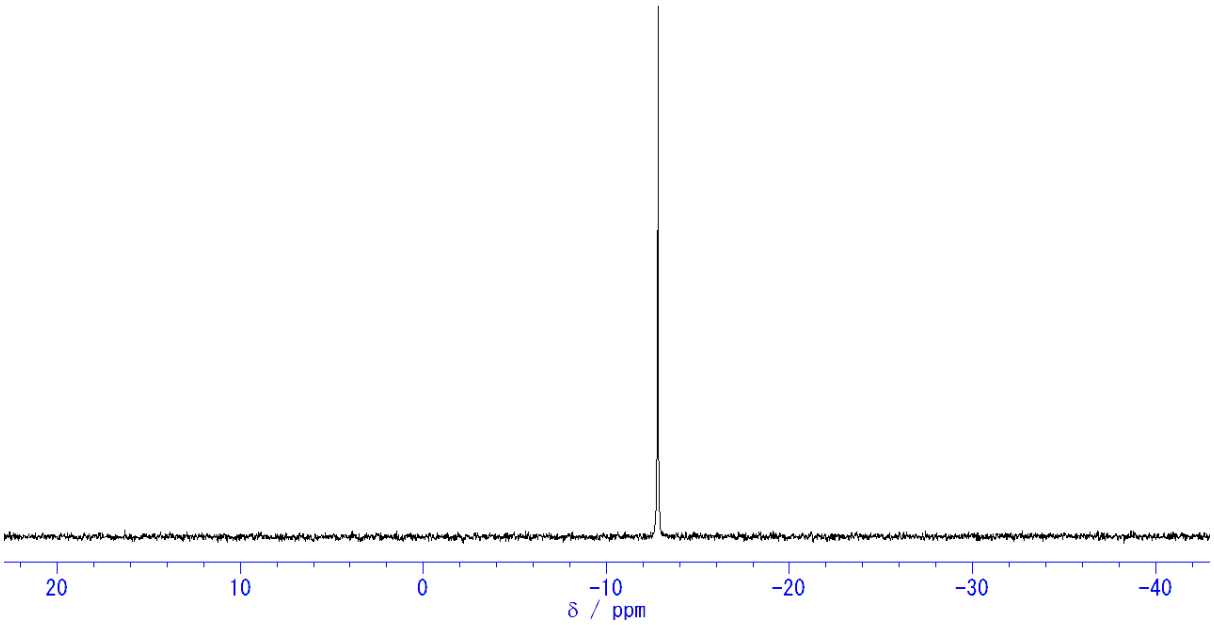
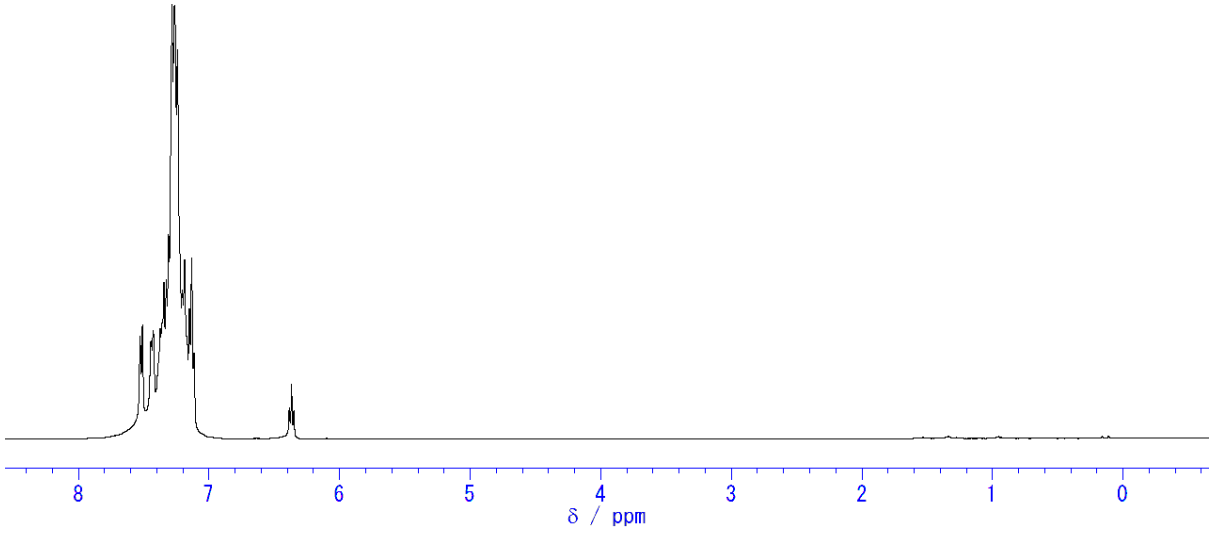
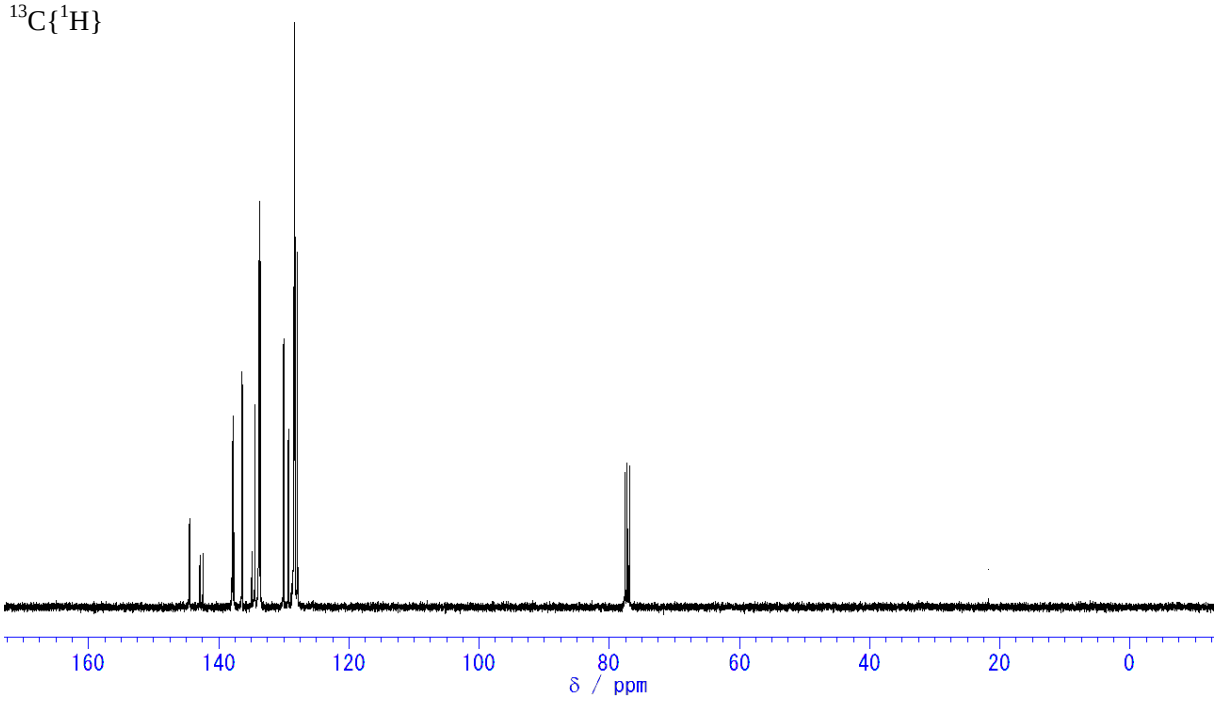


Figure S12. NMR spectra of {*o*-$(Ph_2P)C_6H_4\}_2Si(H)(Ph)$.

^{1}H



$^{13}C\{^{1}H\}$



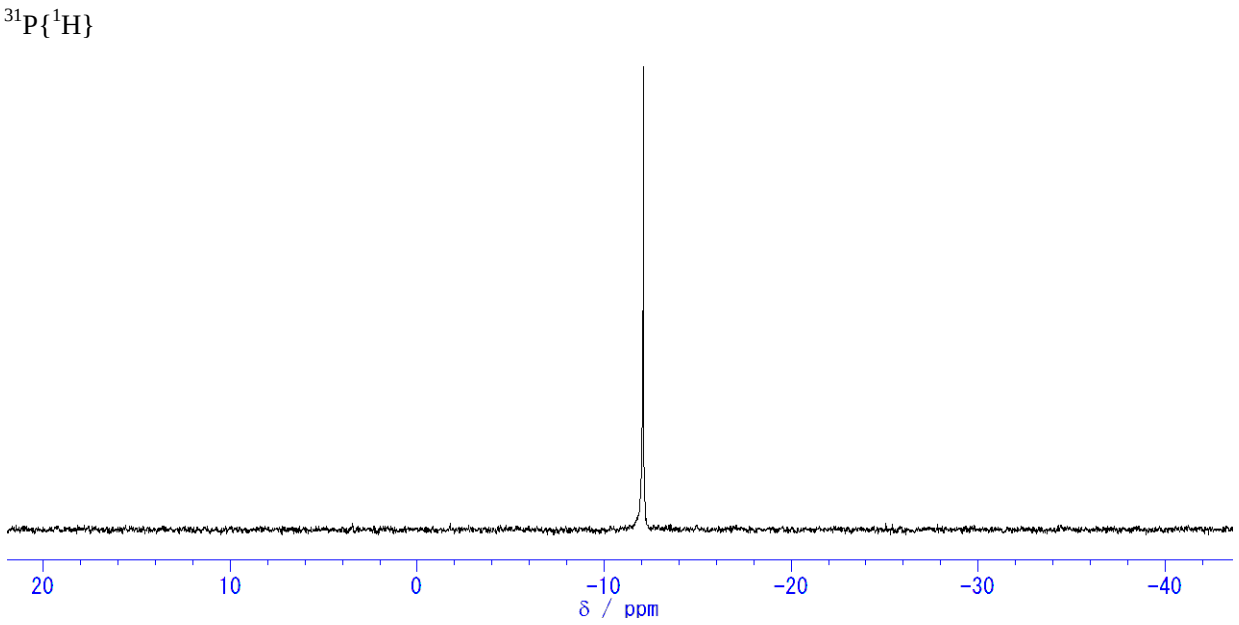
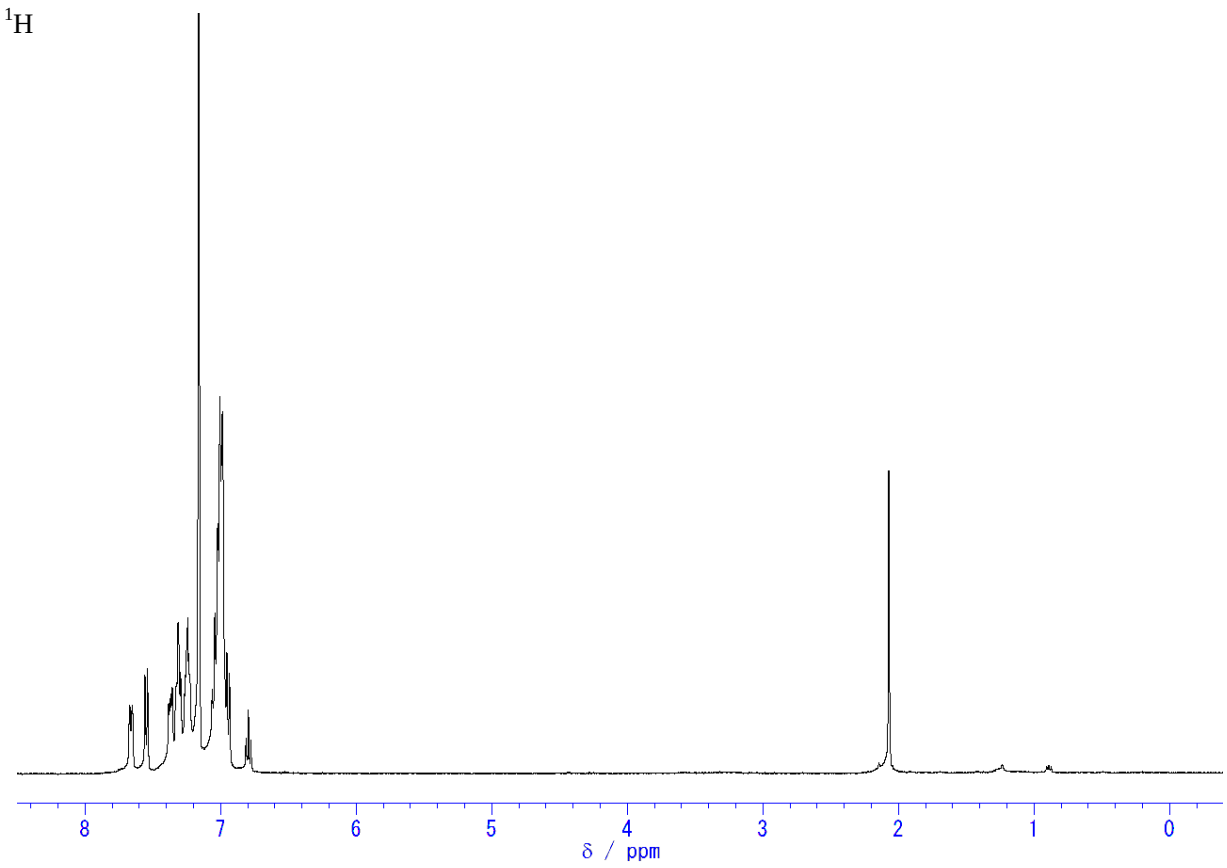
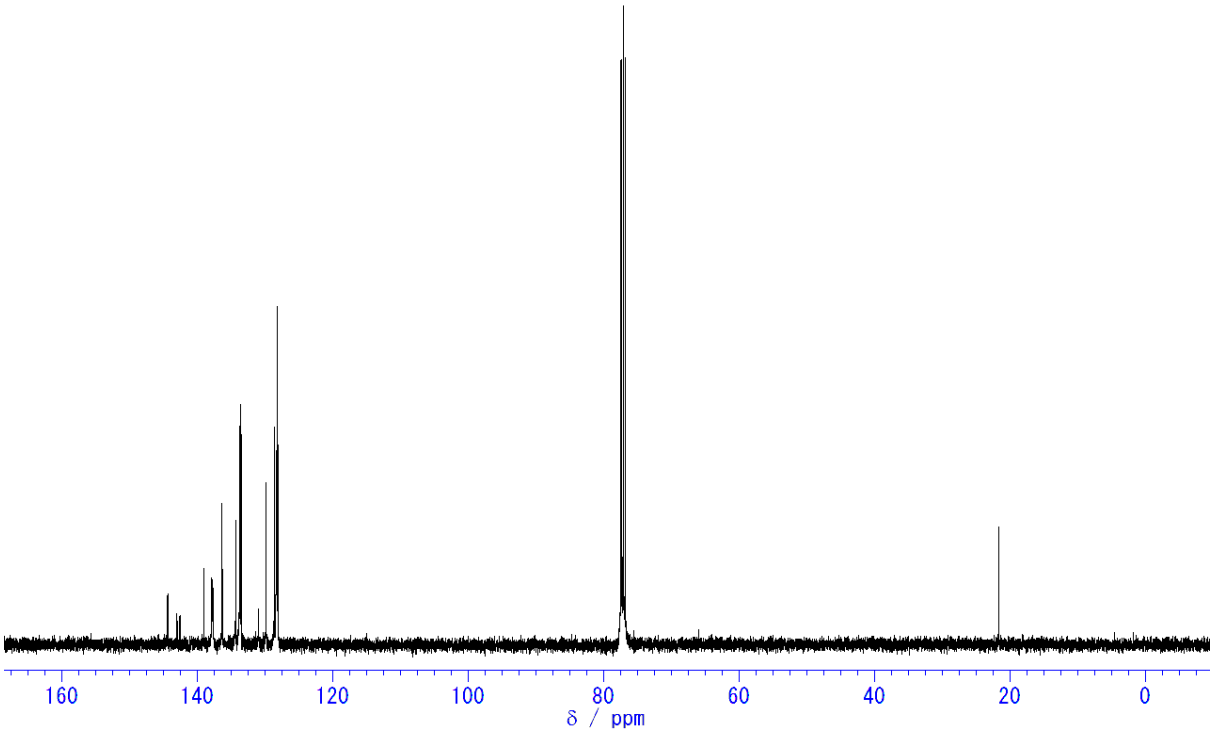


Figure S13. NMR spectra of $\{o\text{-}(Ph_2P)C_6H_4\}_2Si(H)(p\text{-tolyl})$.



$^{13}C\{^{1}H\}$



$^{31}P\{^{1}H\}$

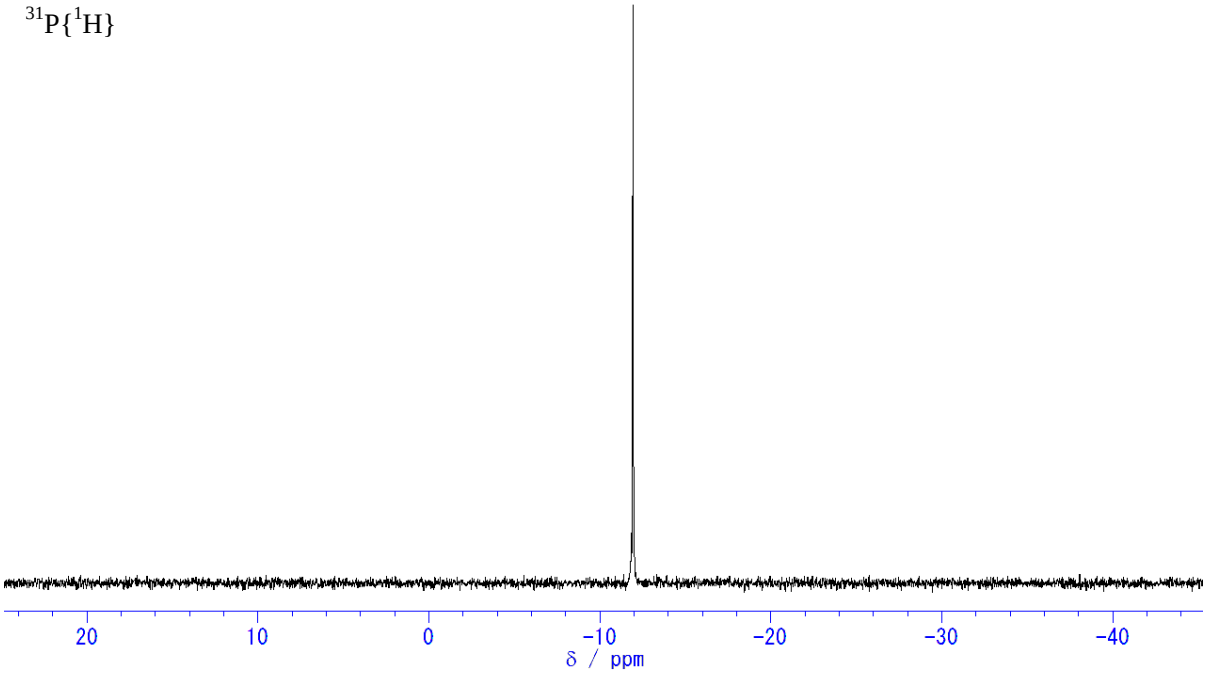
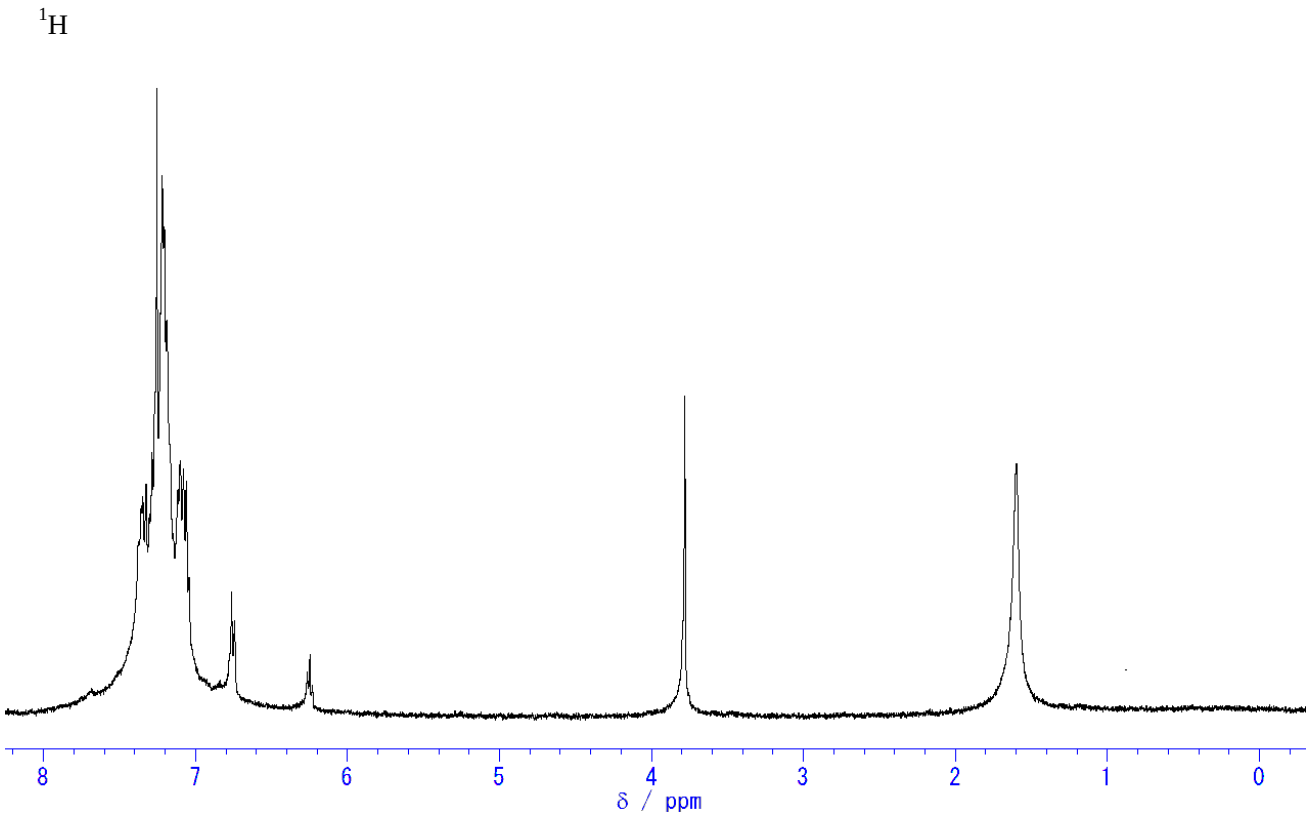
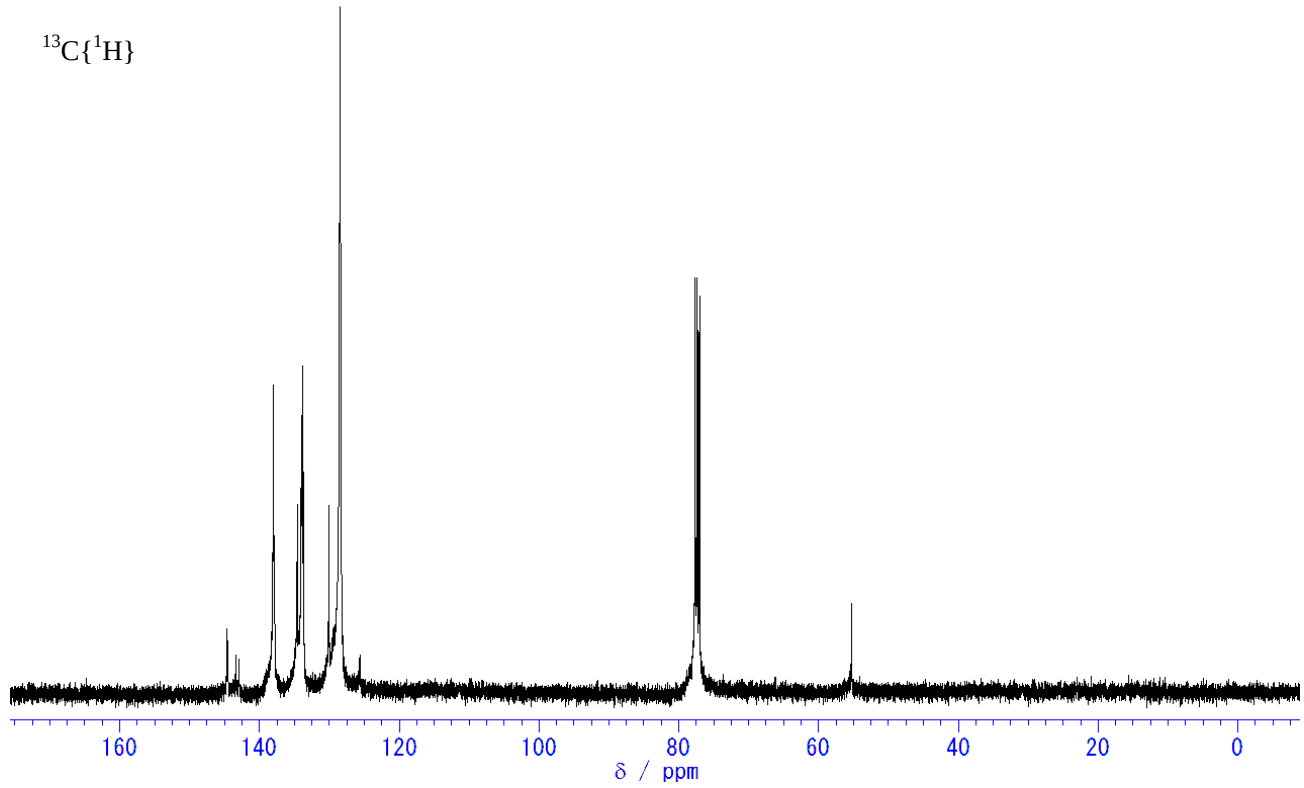
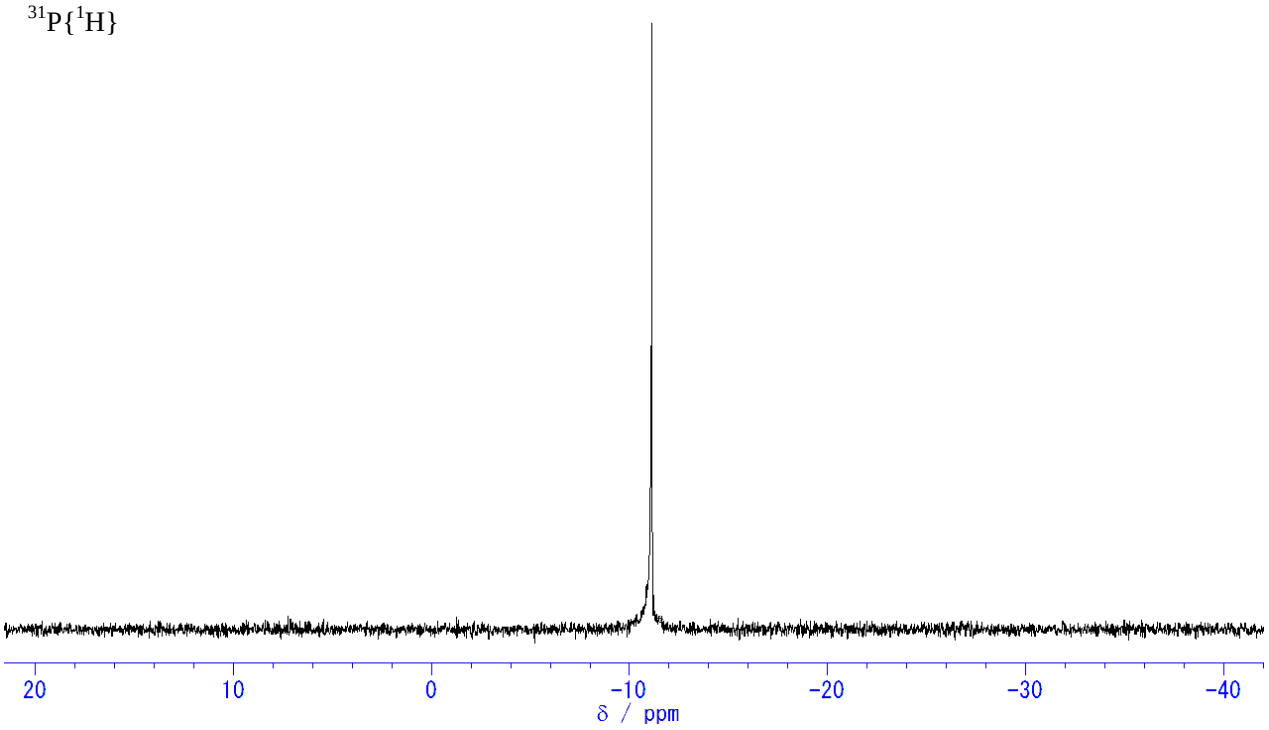


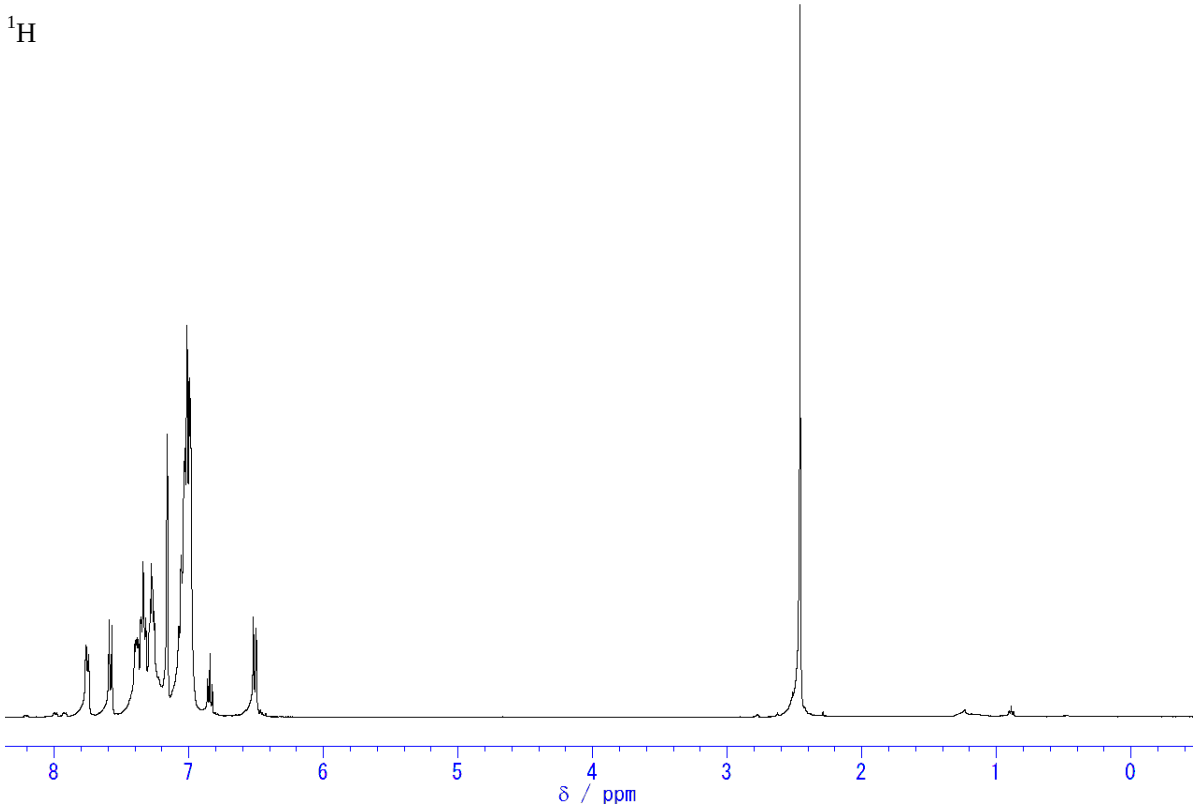
Figure S14. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(H)(*p*-methoxyphenyl).



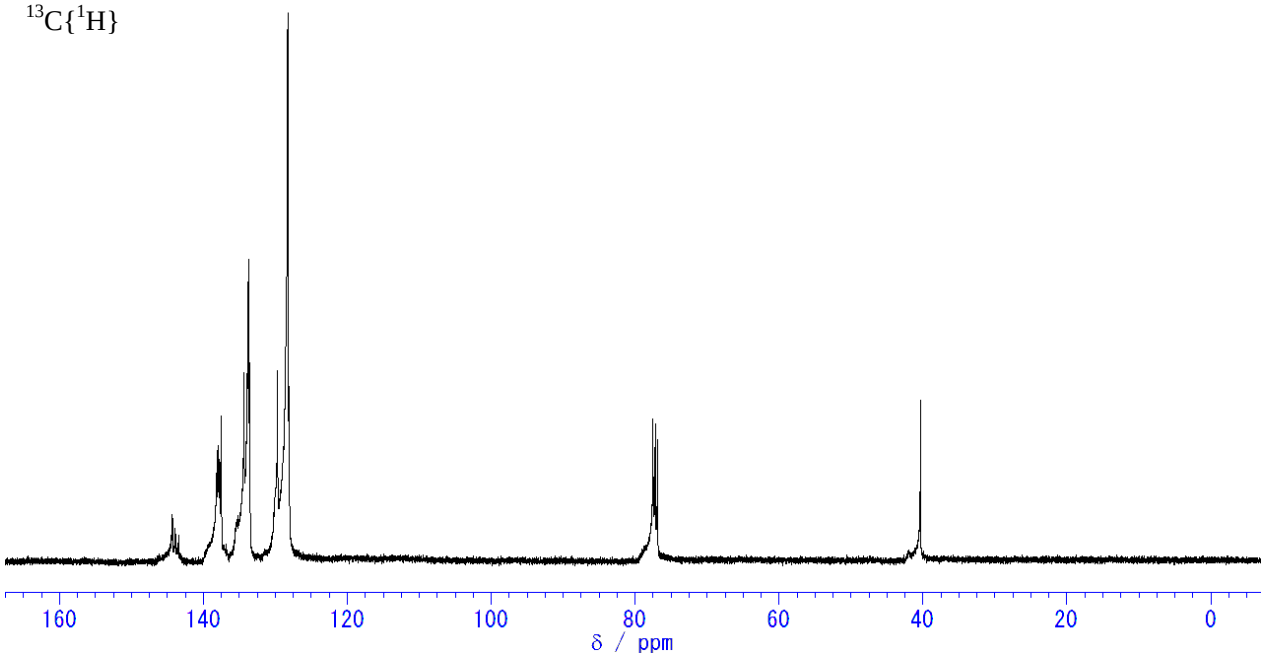




SFigure 15. NMR spectra of {*o*-$(Ph_2P)C_6H_4\}_2Si(H)$(*p*-dimethylaminophenyl).



$^{13}C\{^{1}H\}$



$^{31}P\{^{1}H\}$

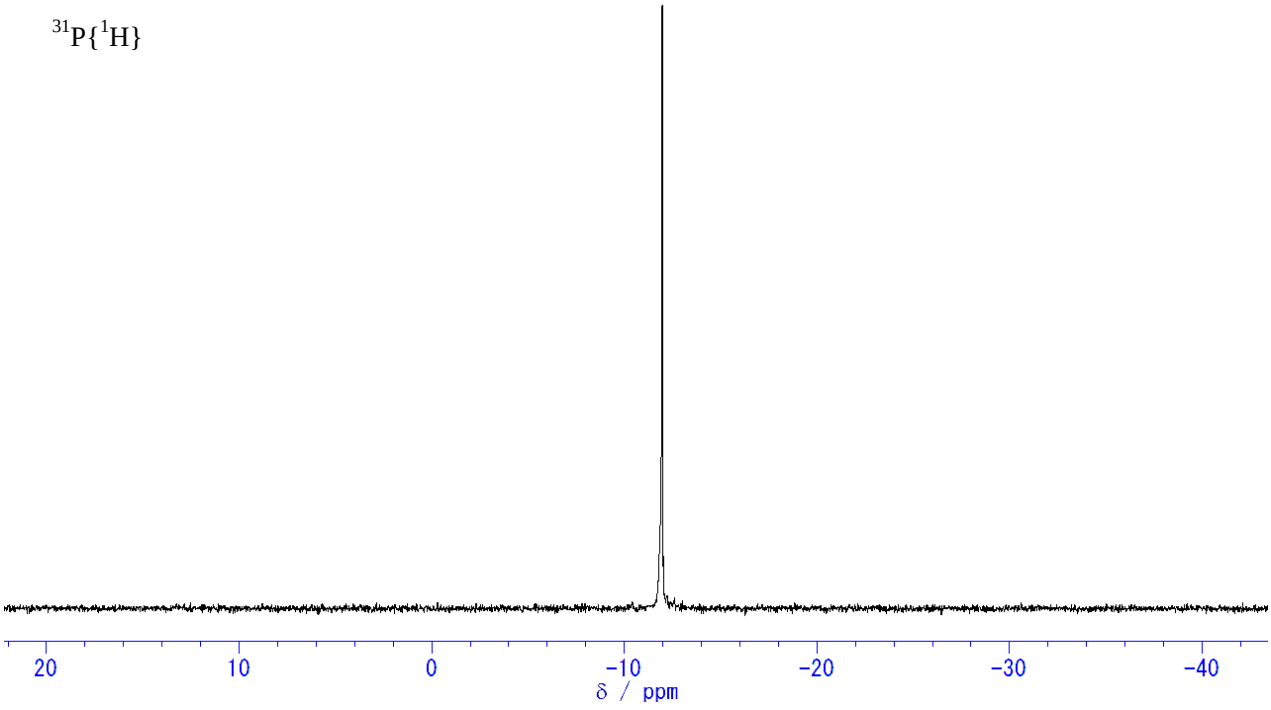
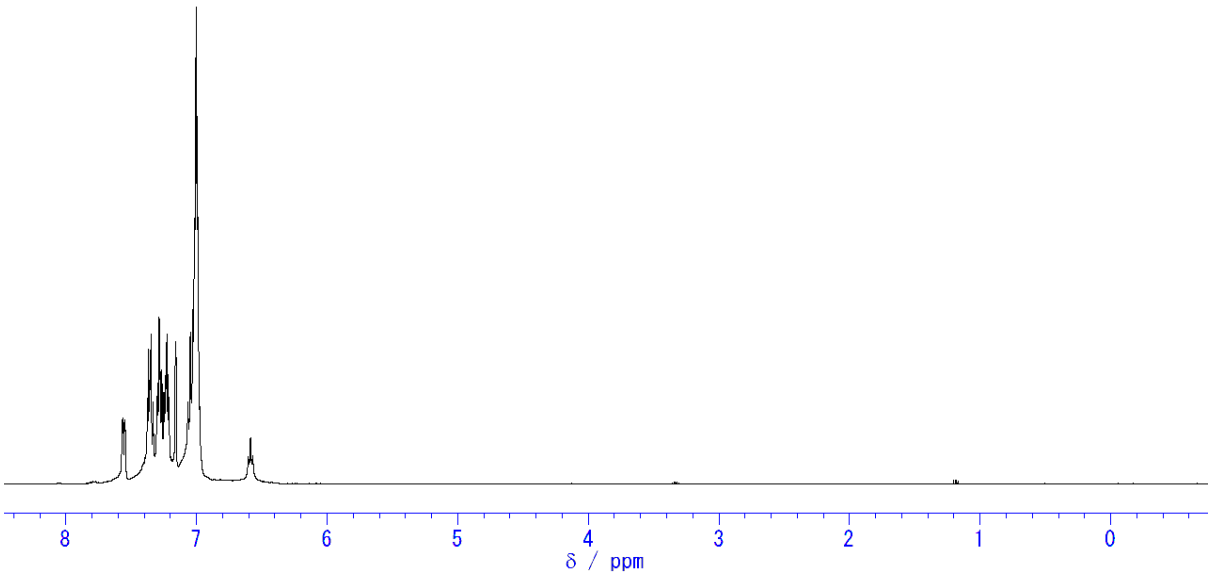
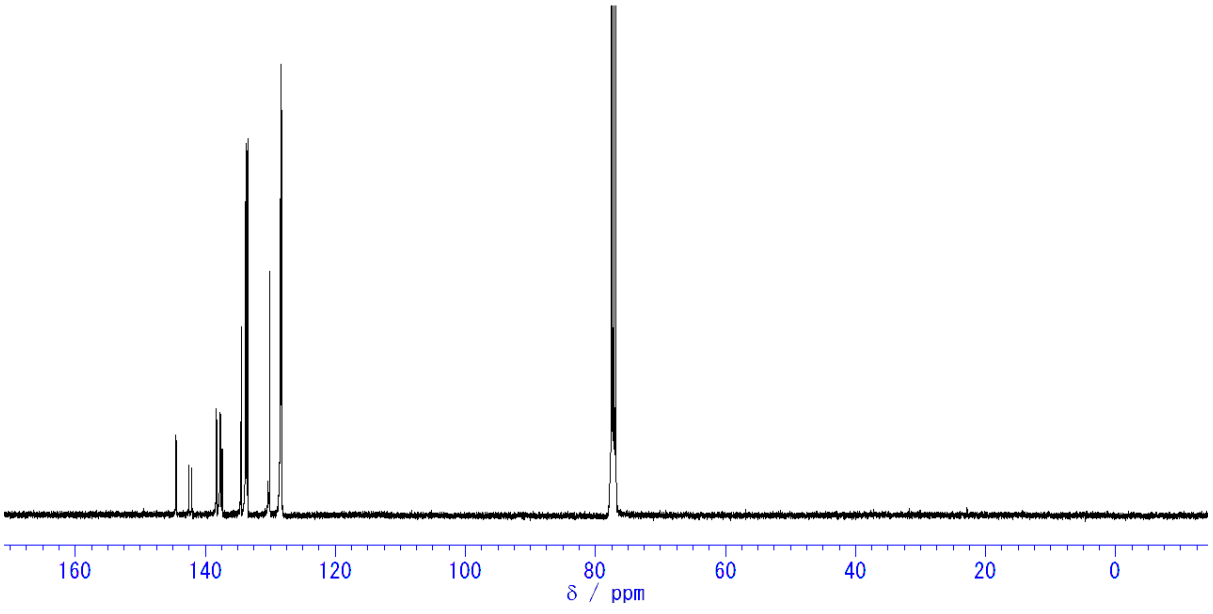


Figure S16. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(H)(*p*-fluorophenyl).

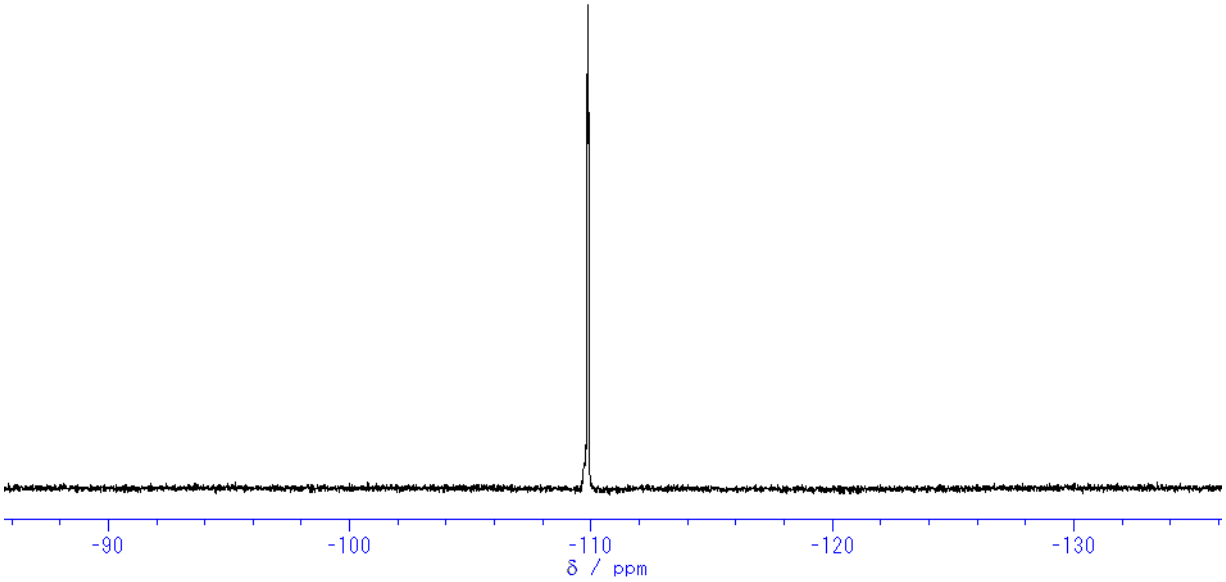
^{1}H



$^{13}C\{^{1}H\}$



$^{19}F\{^{1}H\}$



$^{31}P\{^{1}H\}$

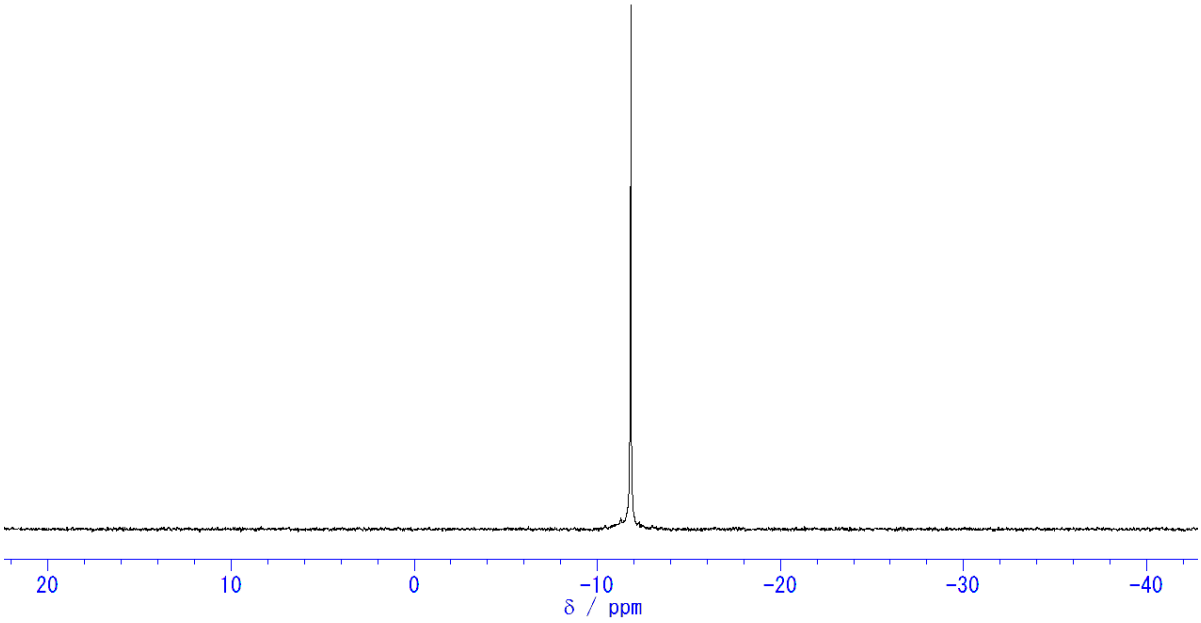
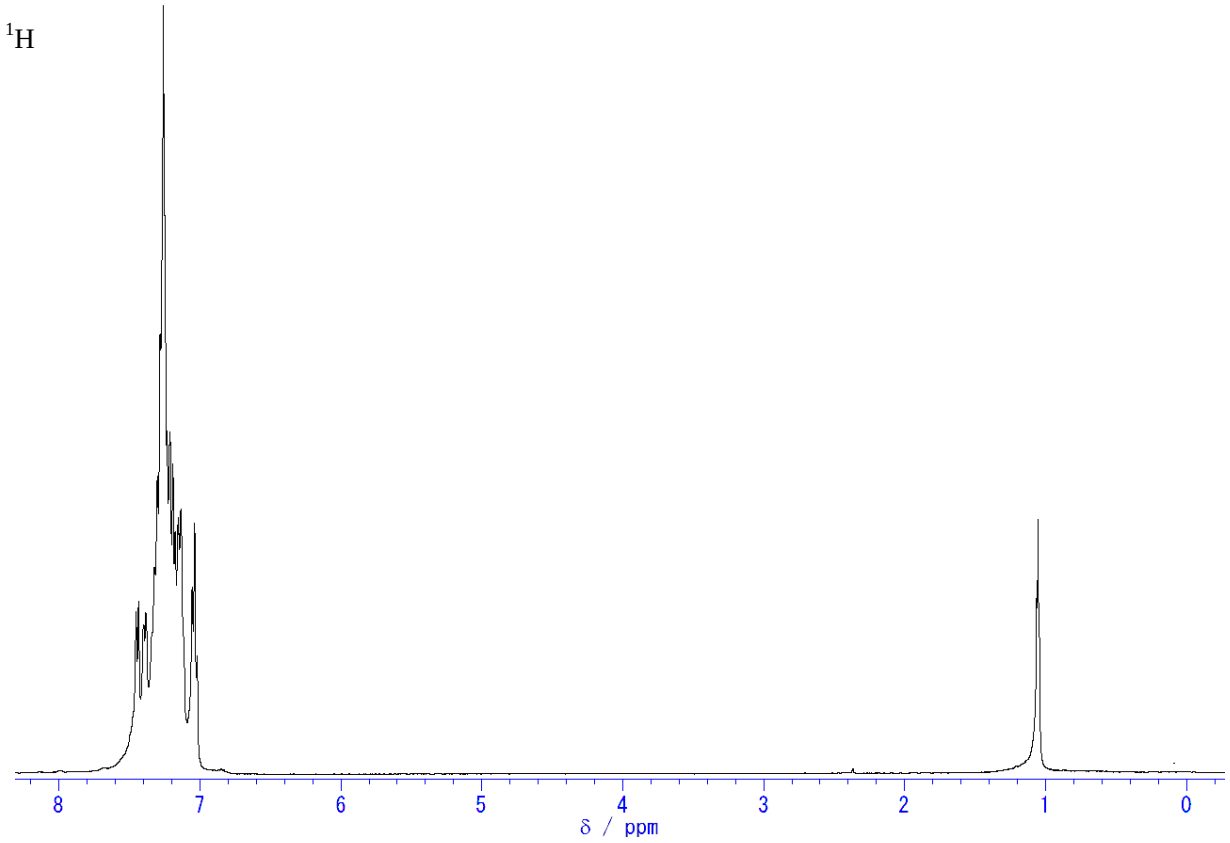
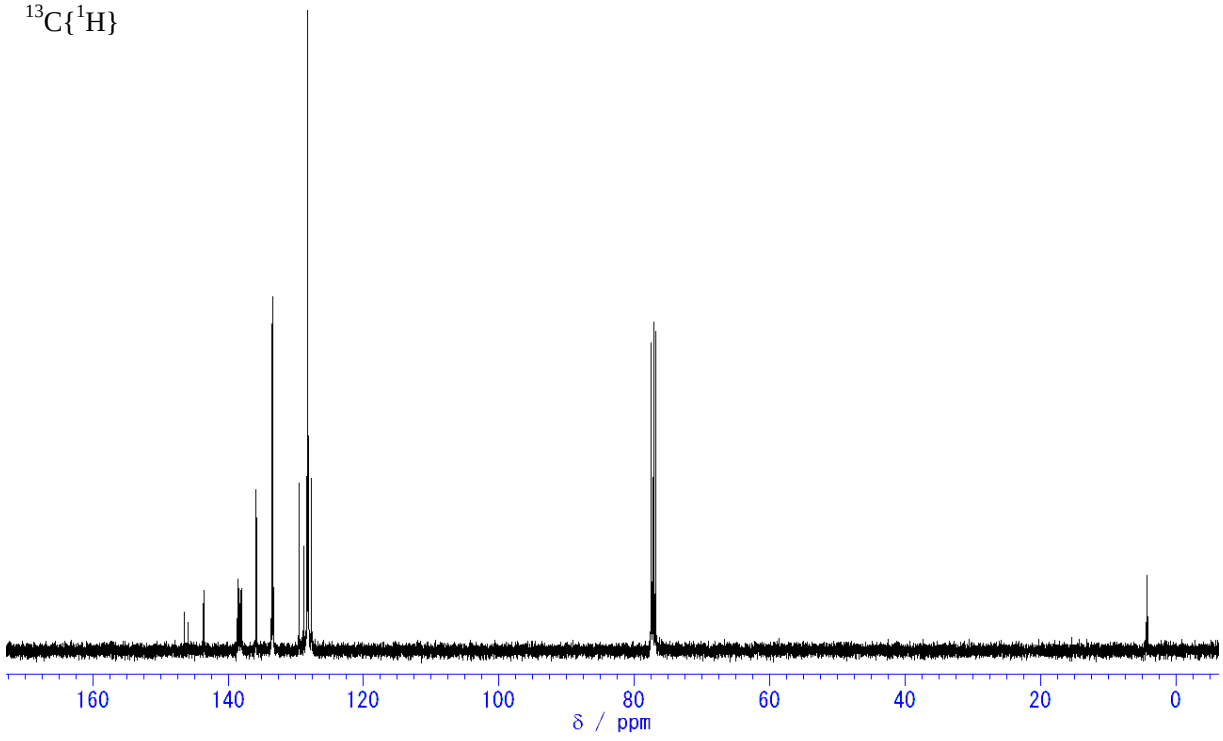


Figure S17. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Ph) (**4b**).





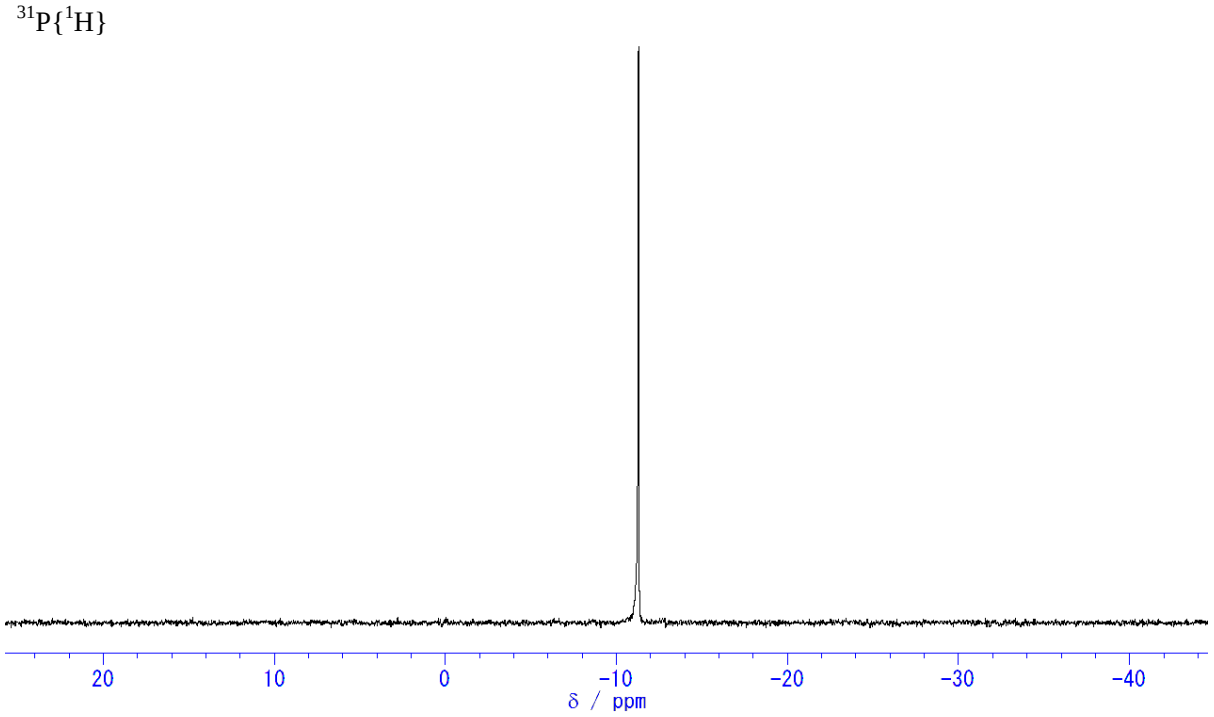
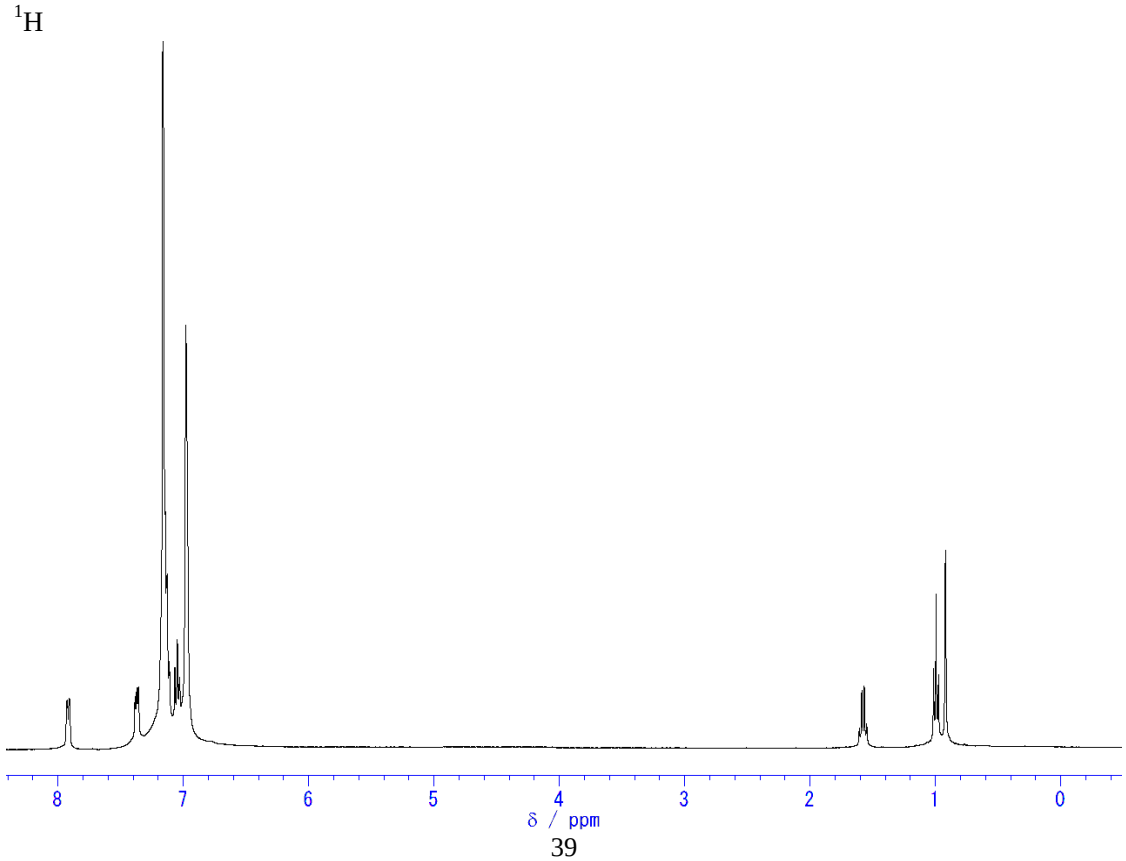
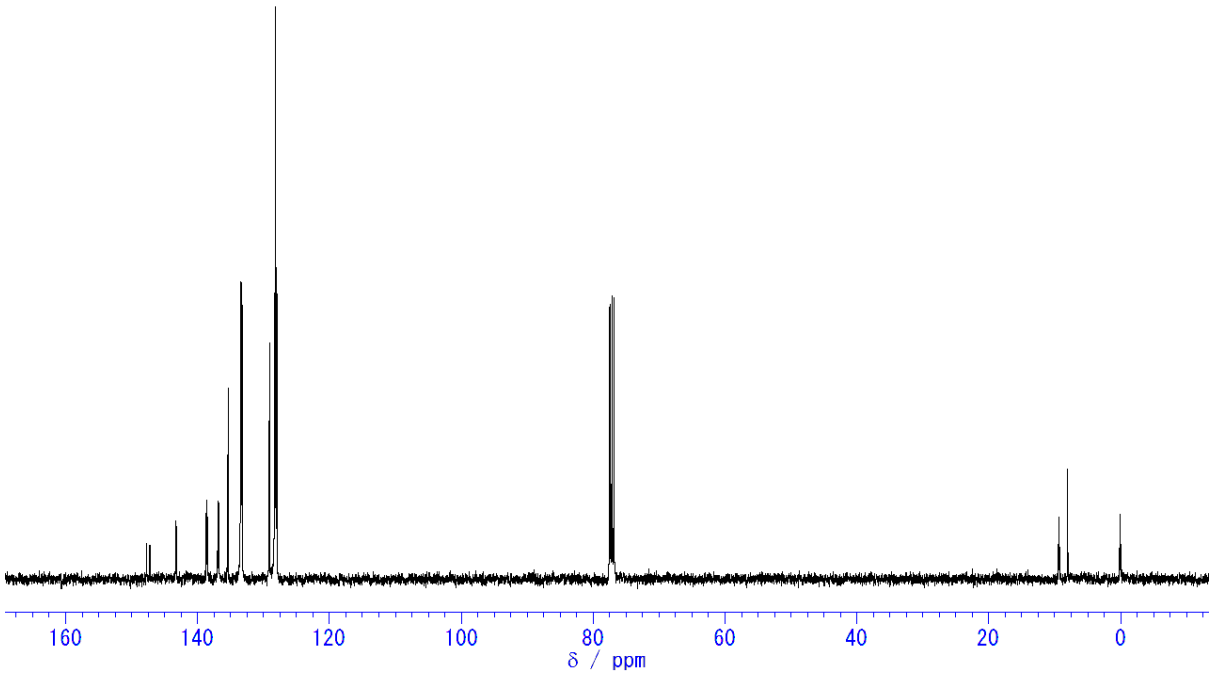


Figure S18. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Et) (**4c**).



$^{13}C\{^{1}H\}$



$^{31}P\{^{1}H\}$

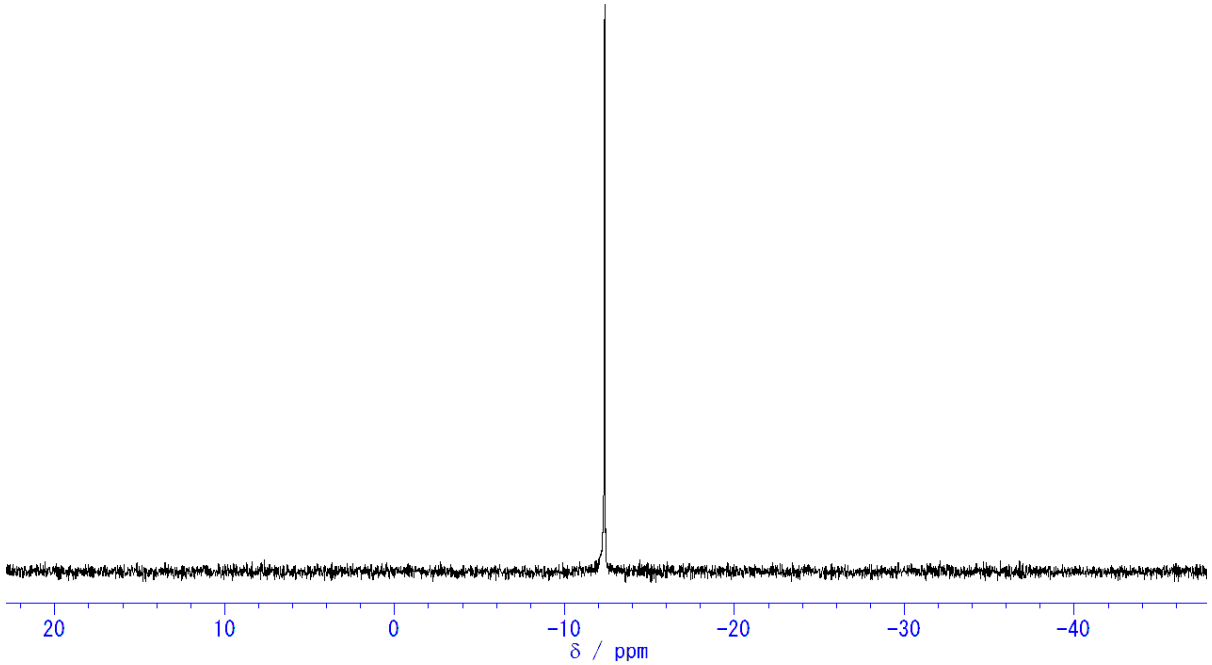
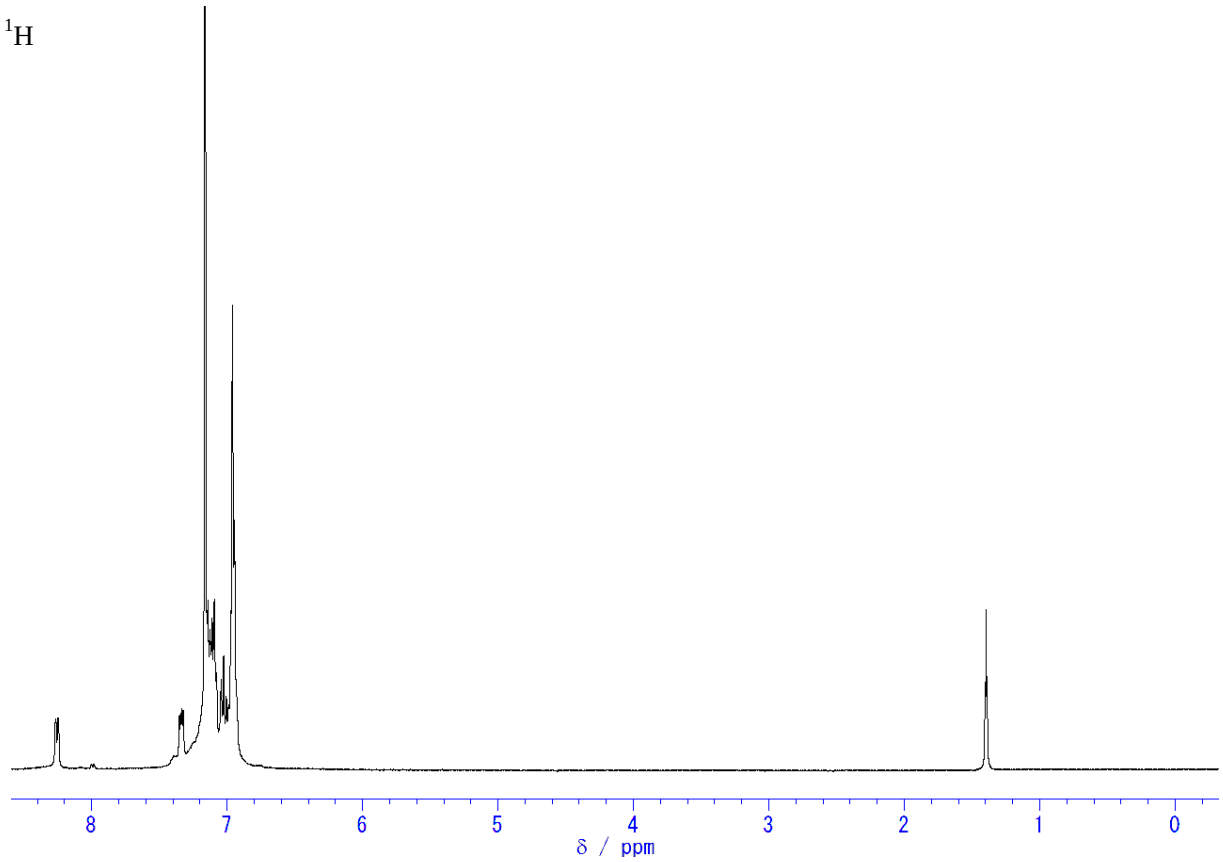
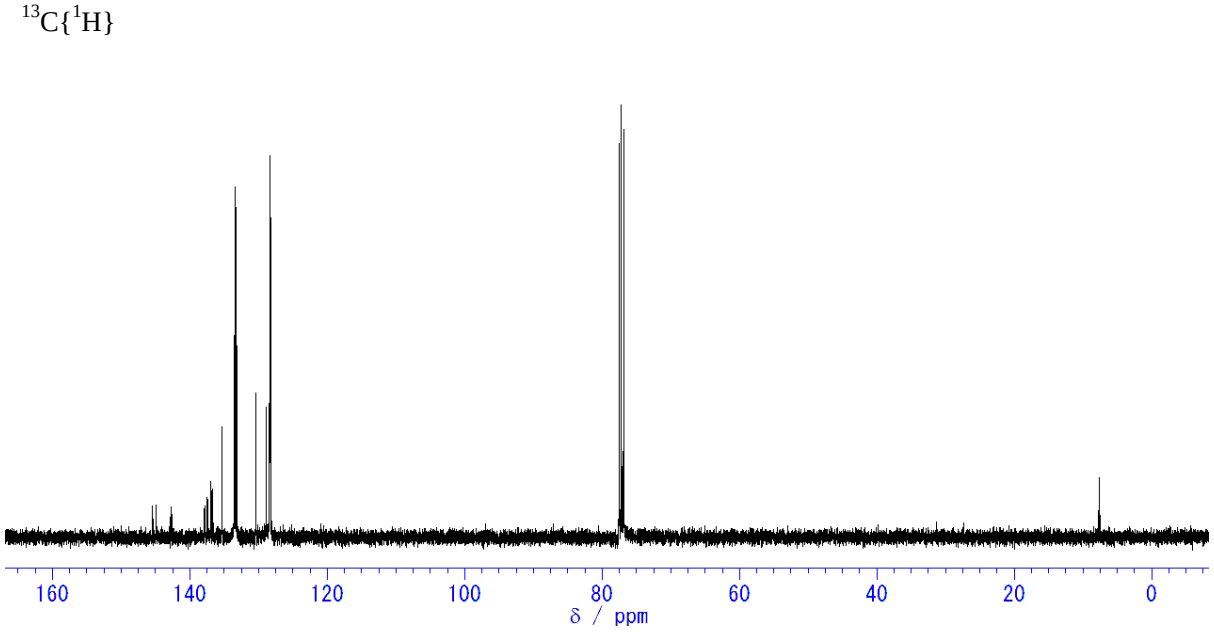


Figure S19. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(Cl).





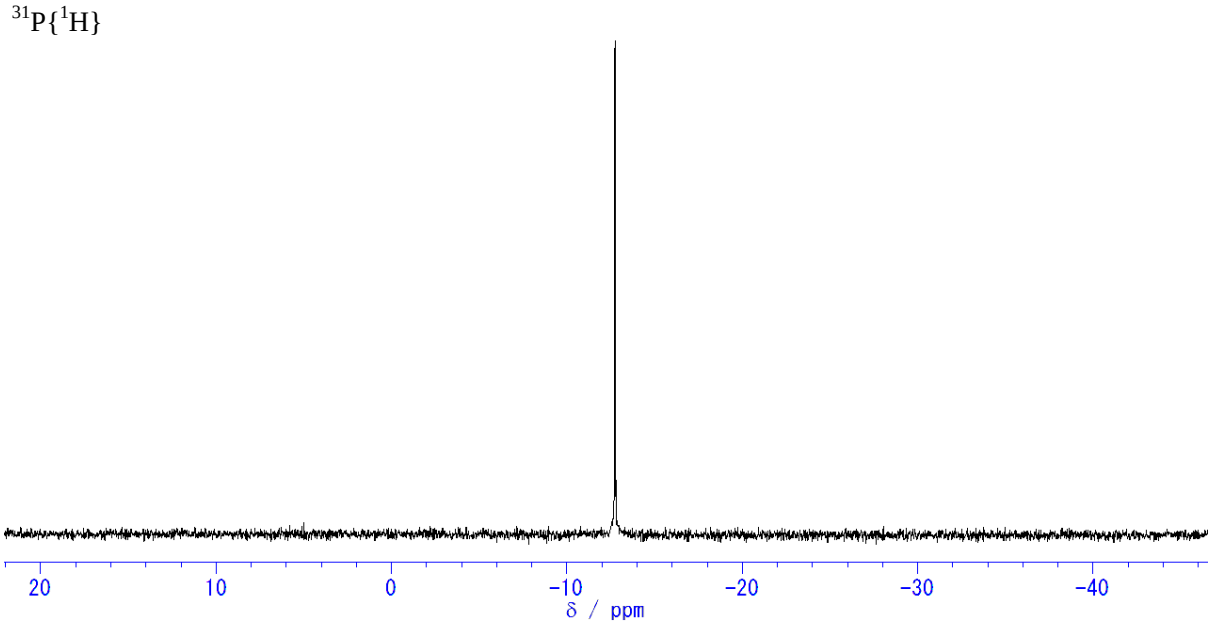
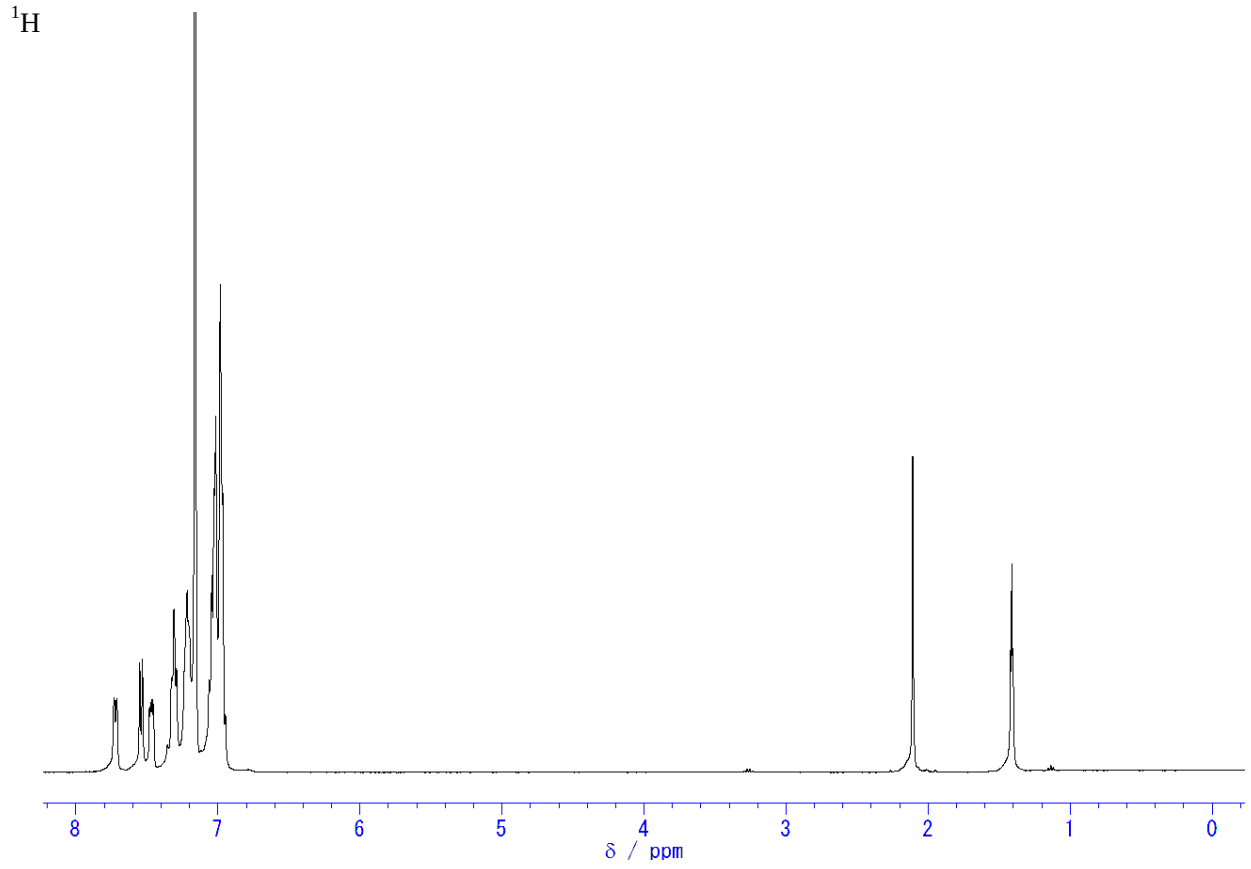
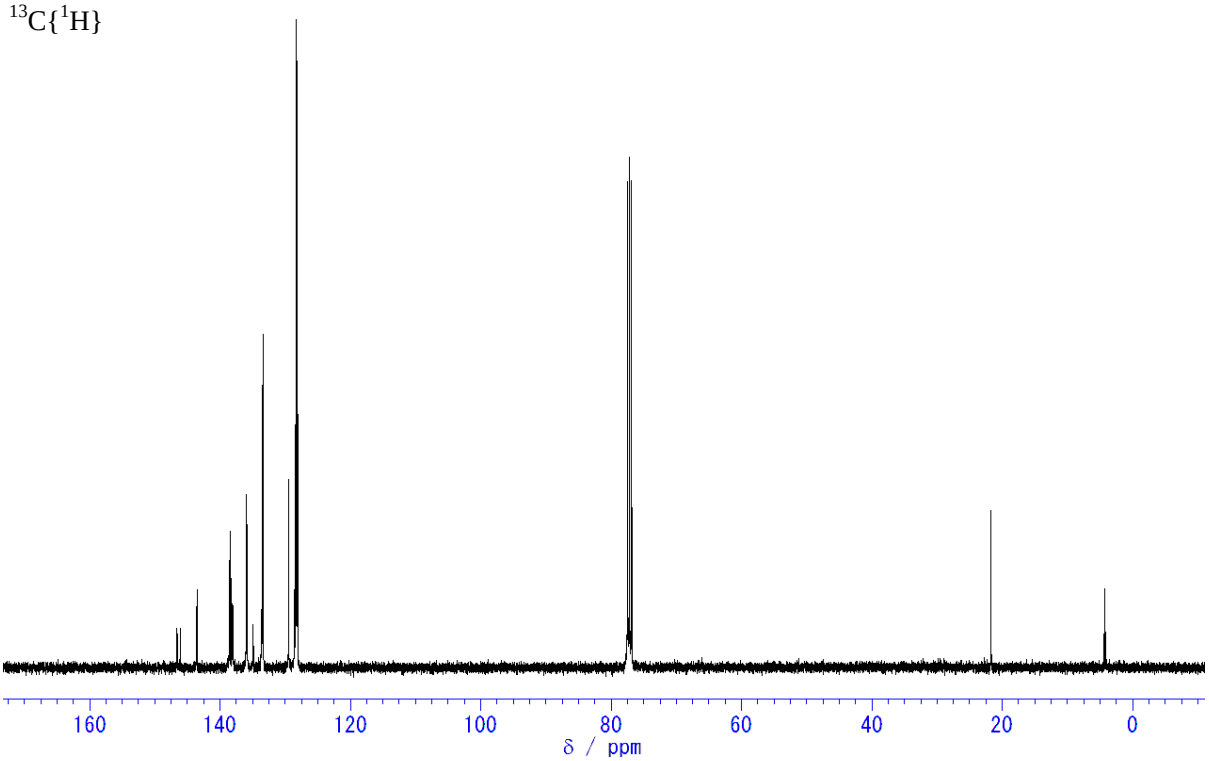


Figure S20. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-tolyl) (**4d**).



$^{13}C\{^{1}H\}$



$^{31}P\{^{1}H\}$

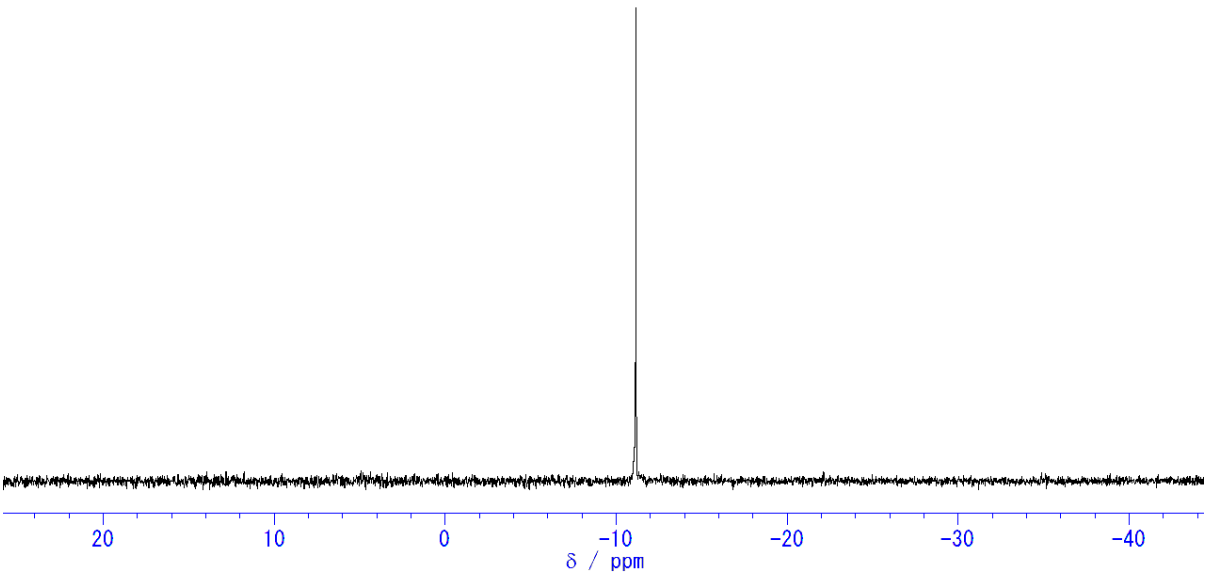
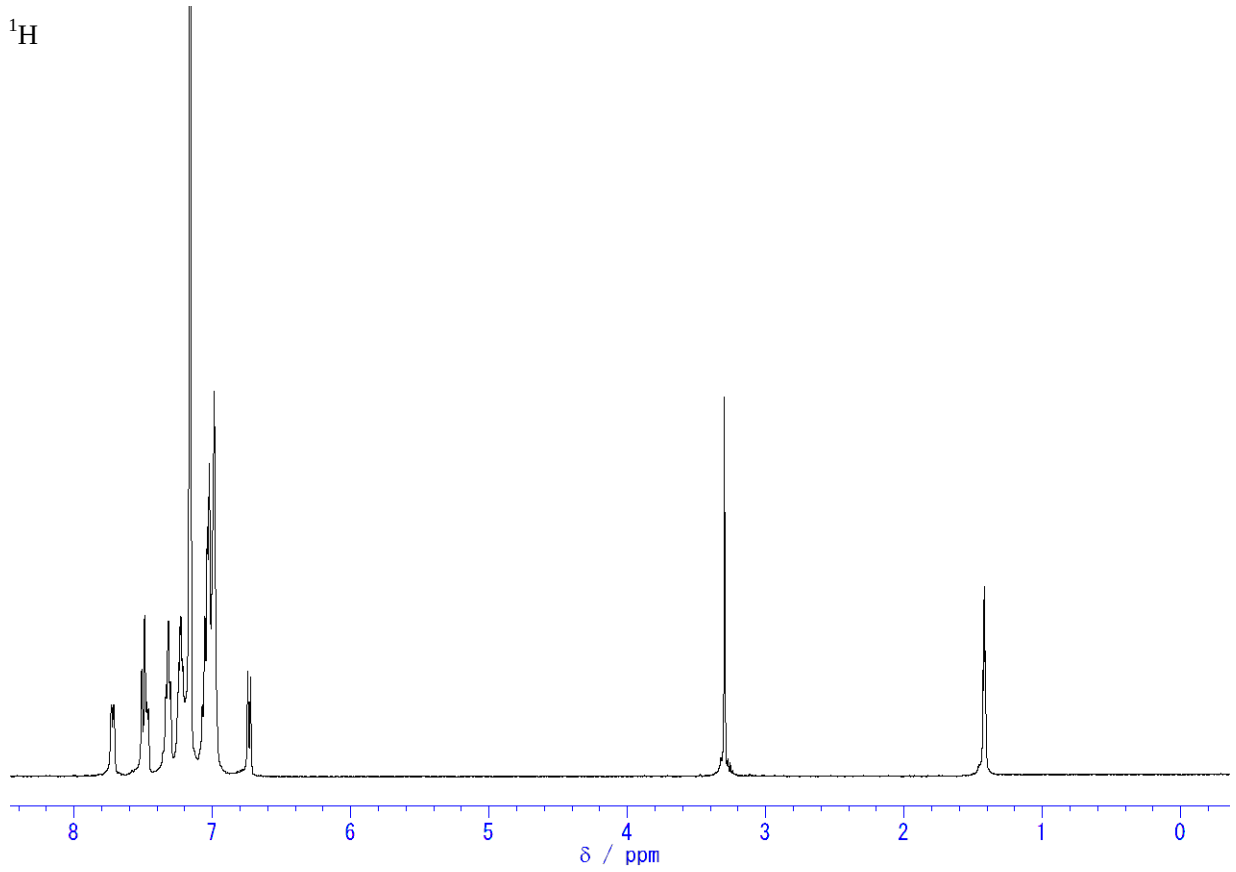
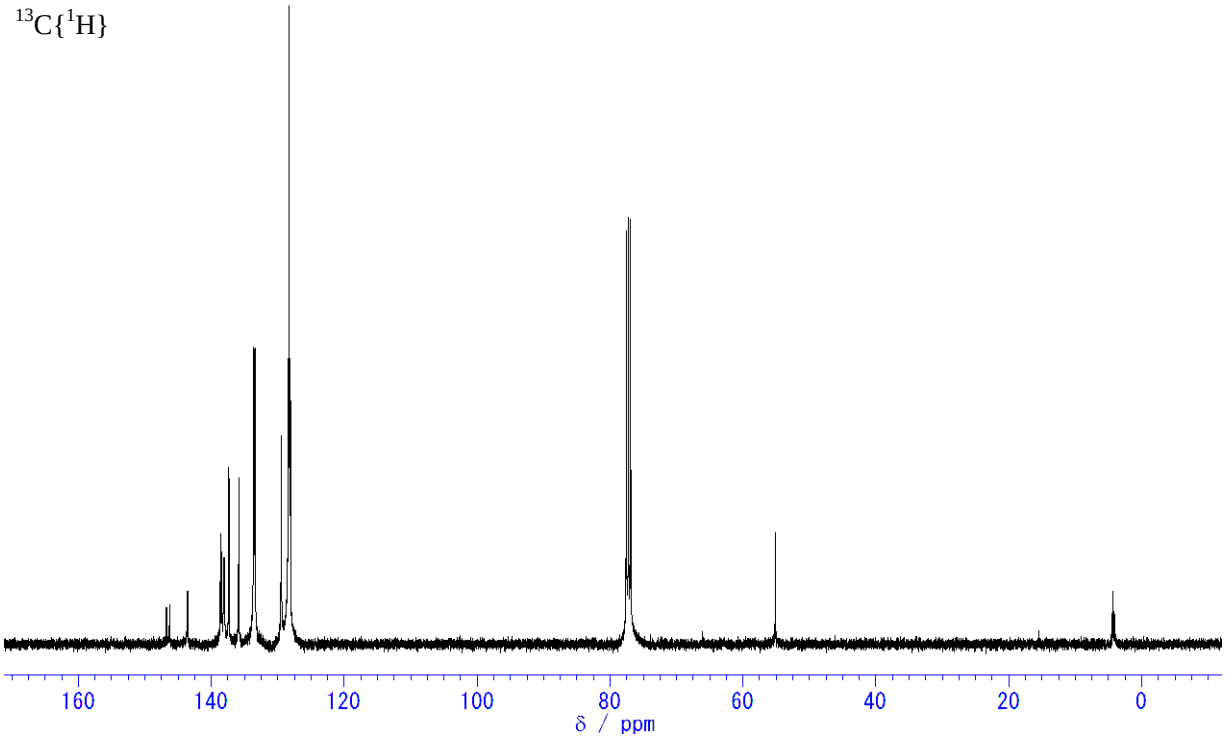


Figure S21. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-methoxyphenyl) (**4e**).





$^{31}P\{^{1}H\}$

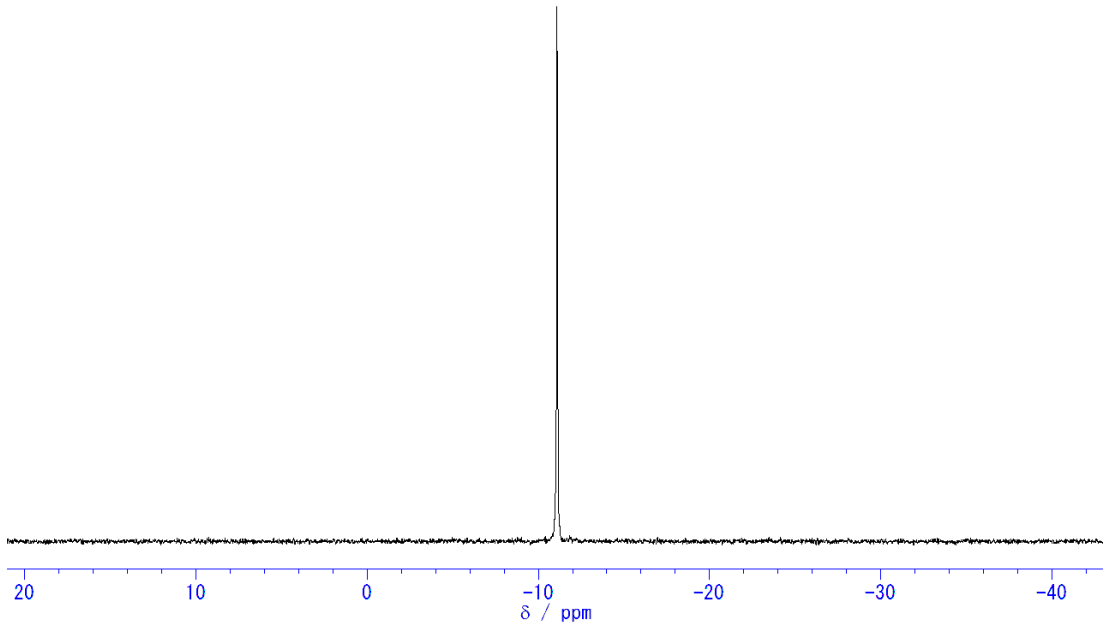
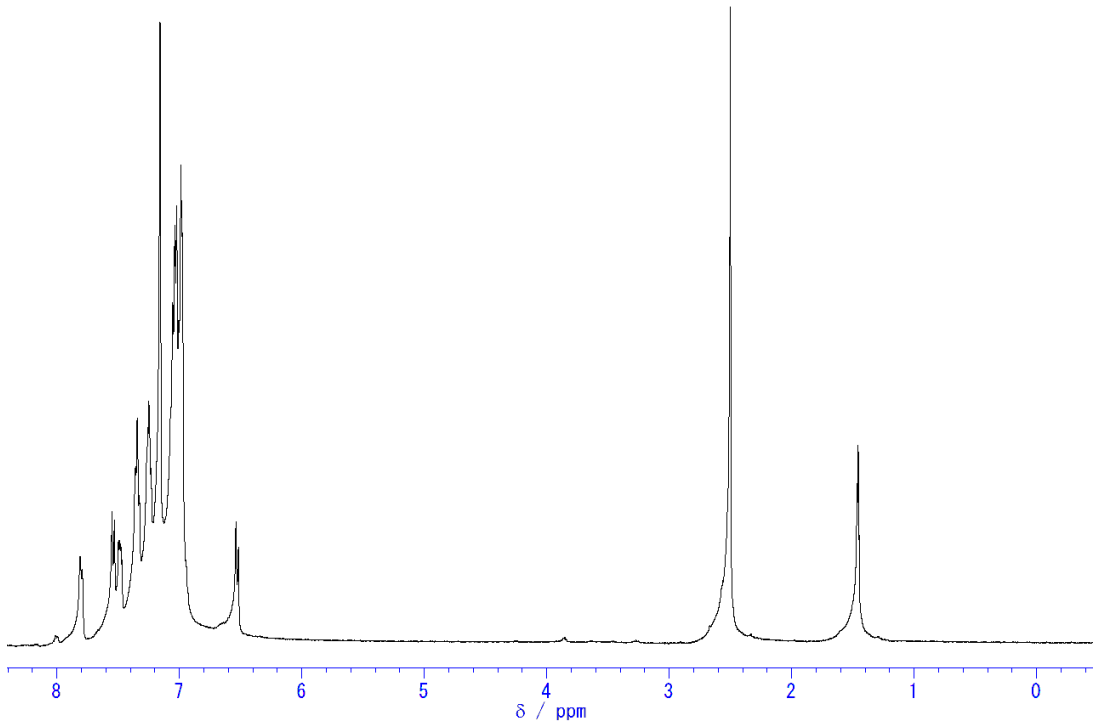
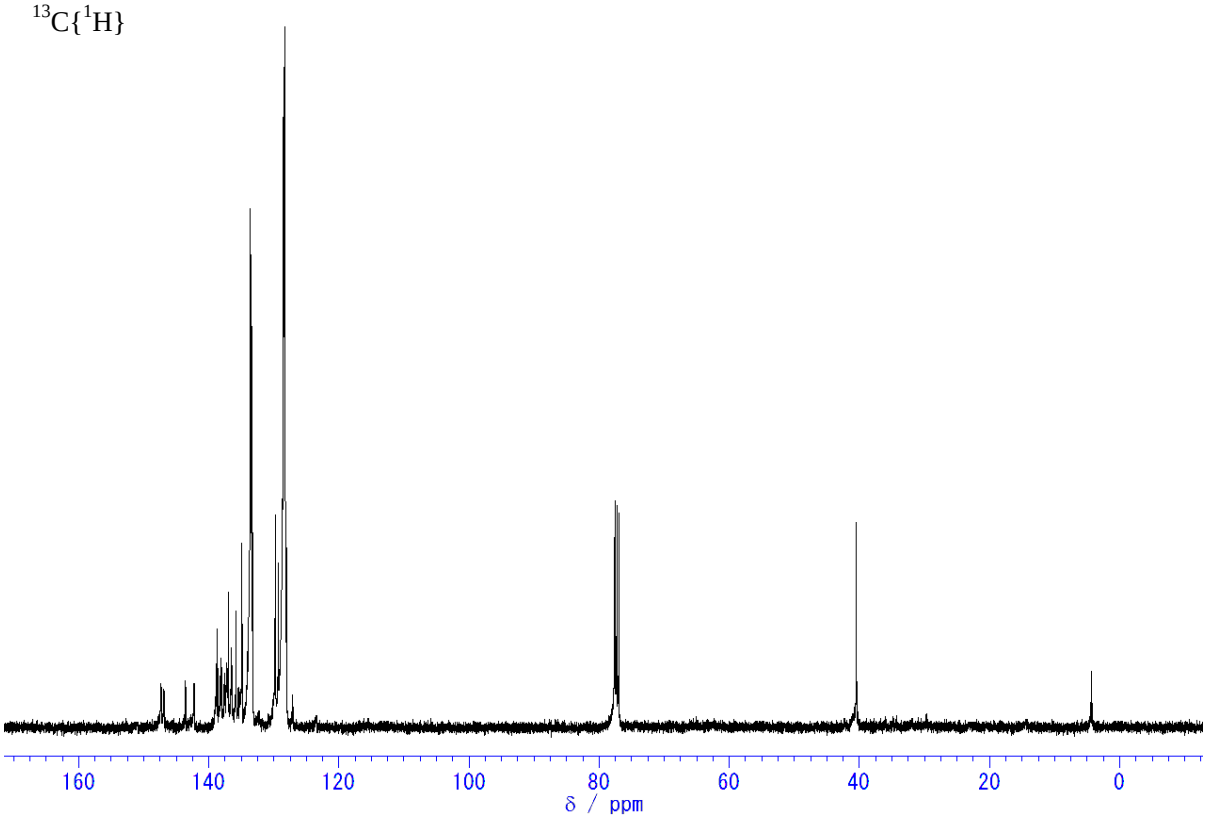


Figure S22. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-dimethylaminophenyl) (**4f**).

^{1}H



$^{13}C\{^{1}H\}$



$^{31}P\{^{1}H\}$

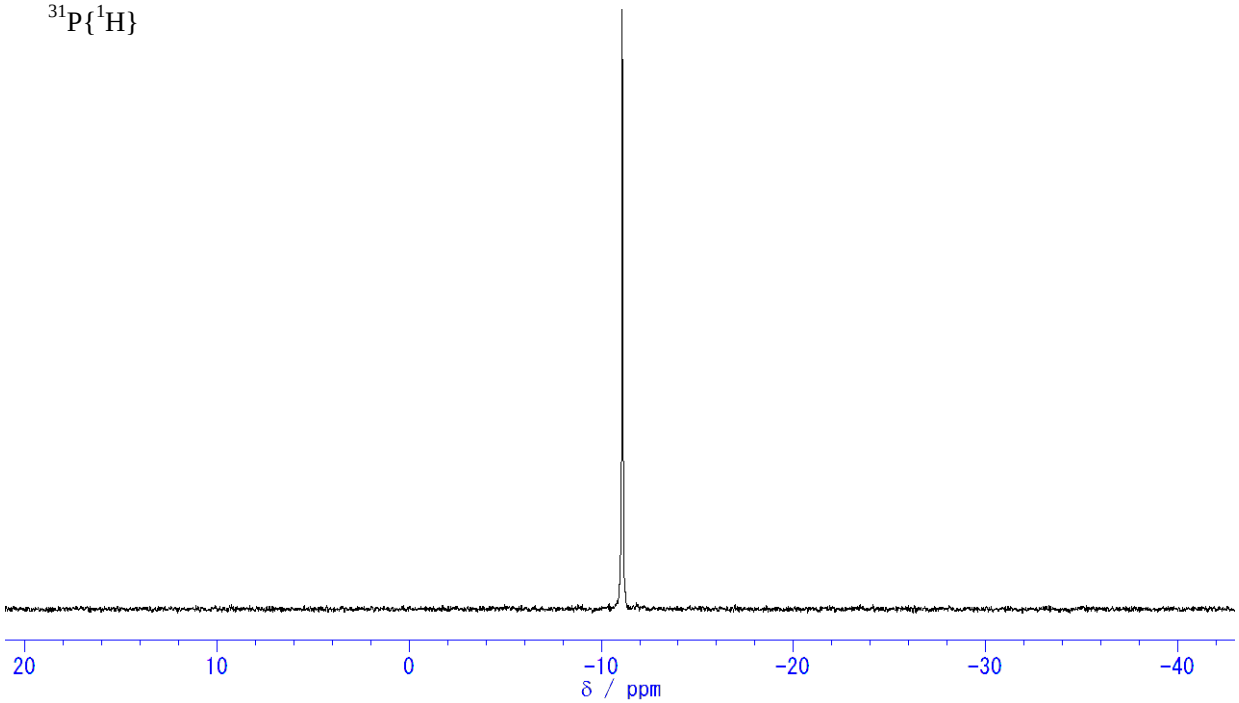
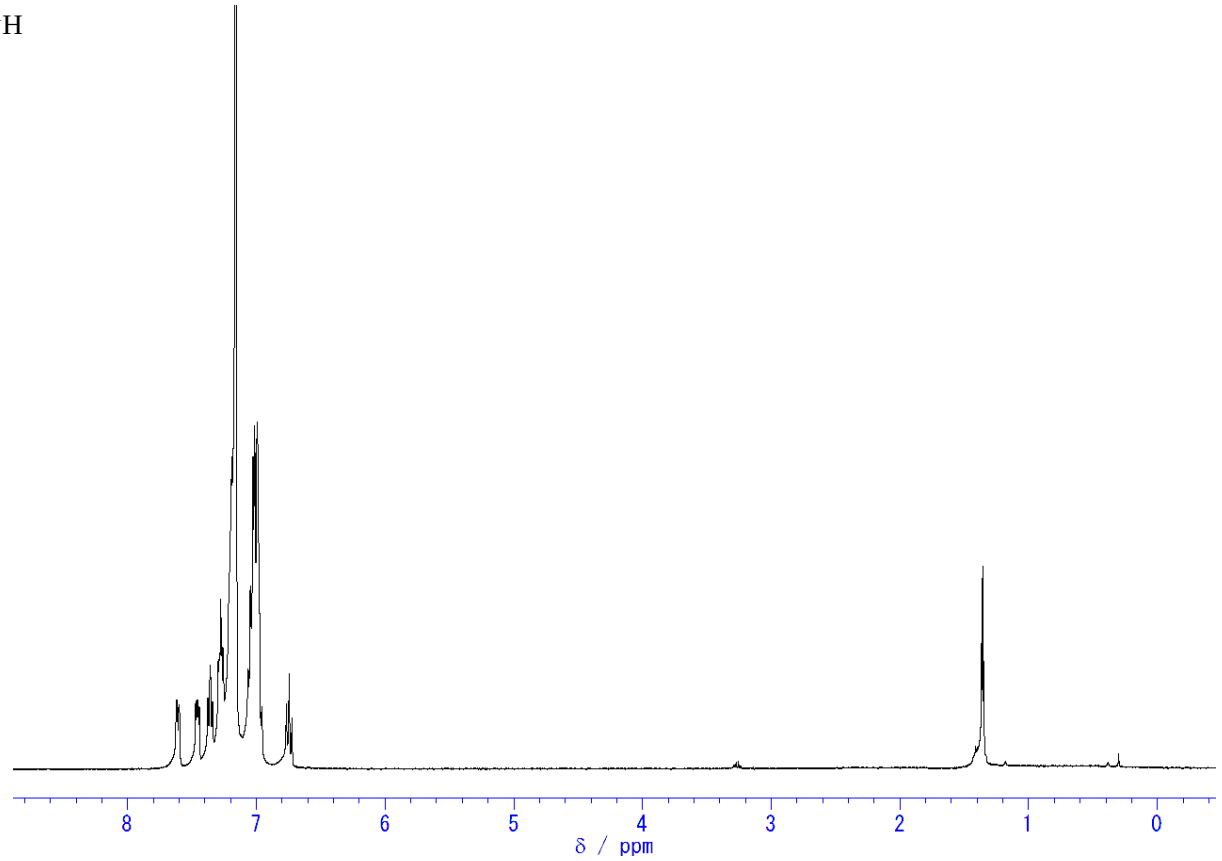
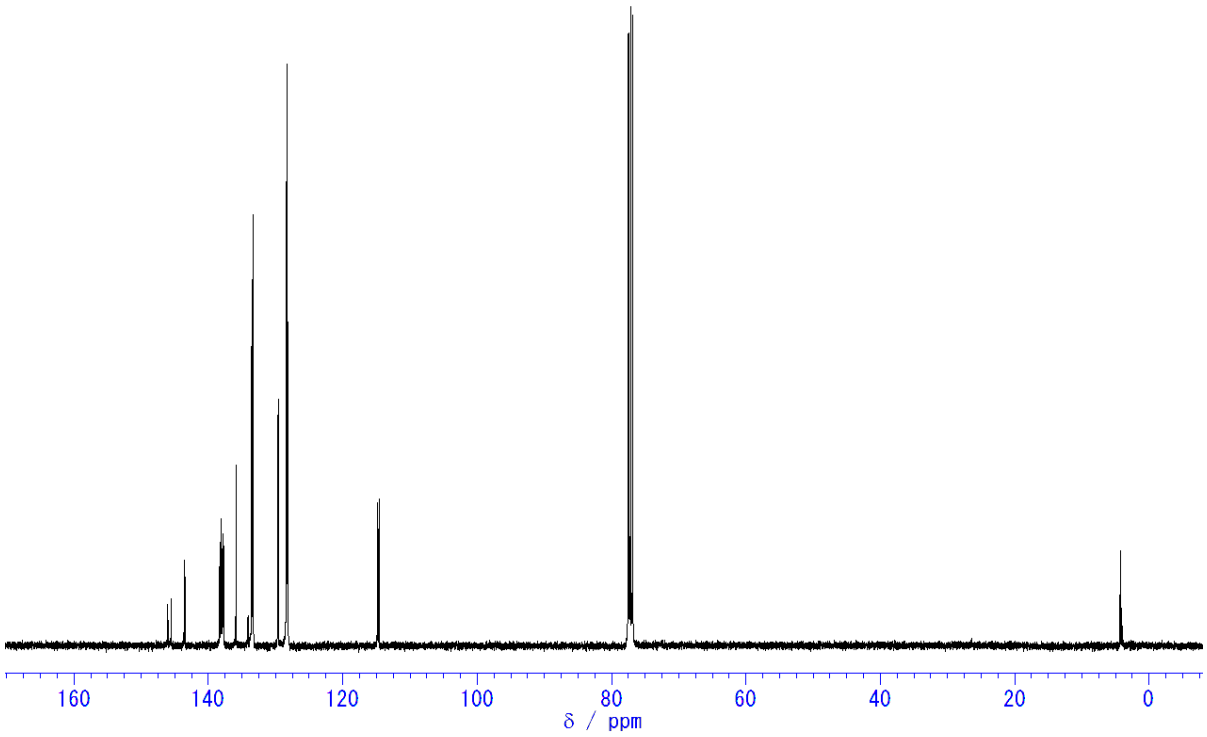


Figure S23. NMR spectra of {*o*-(Ph_2P)C_6H_4}$_2$Si(Me)(*p*-fluorophenyl) (**4g**).

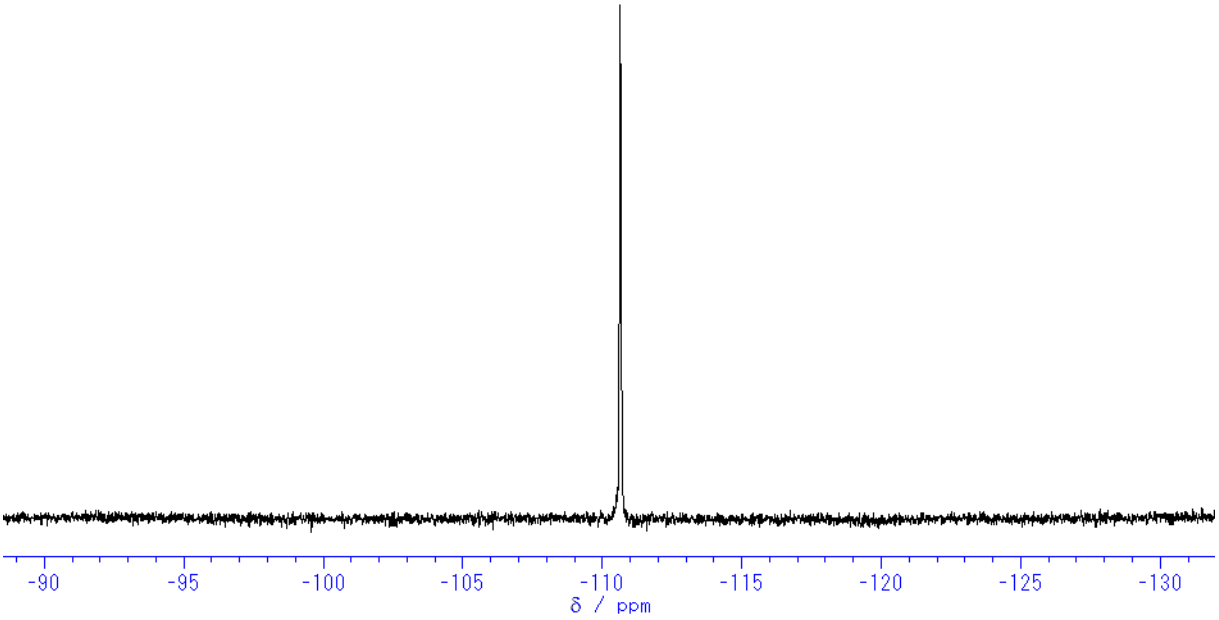
^1H



$^{13}C\{^1H\}$



$^{19}F\{^{1}H\}$



$^{31}P\{^{1}H\}$

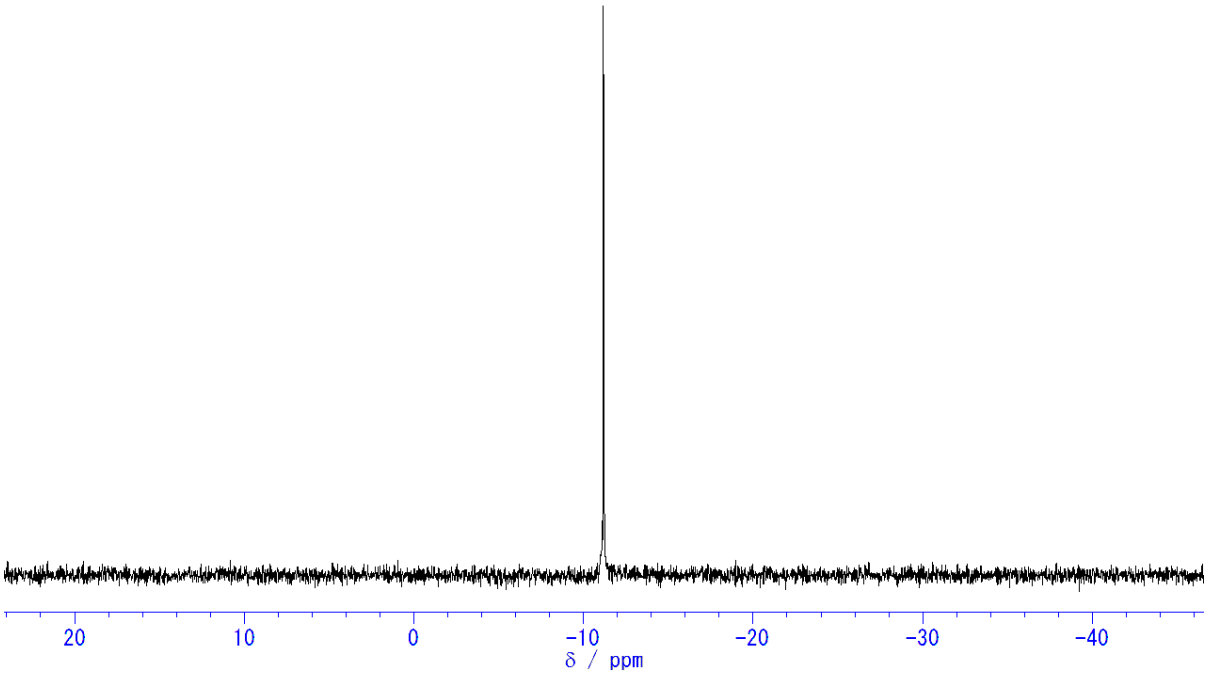
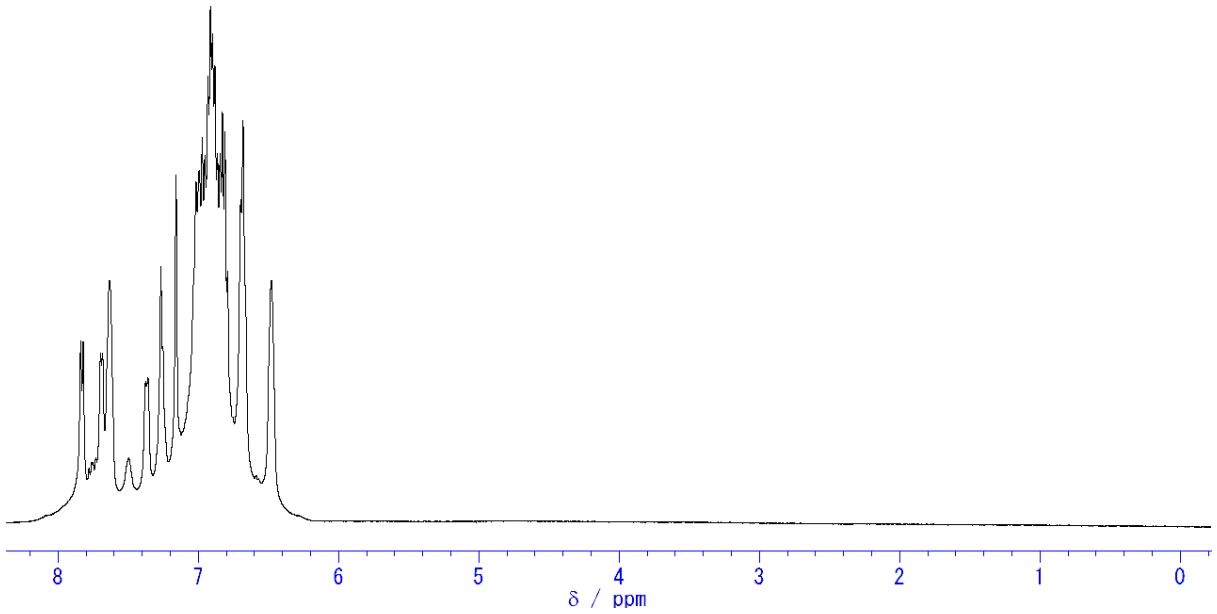
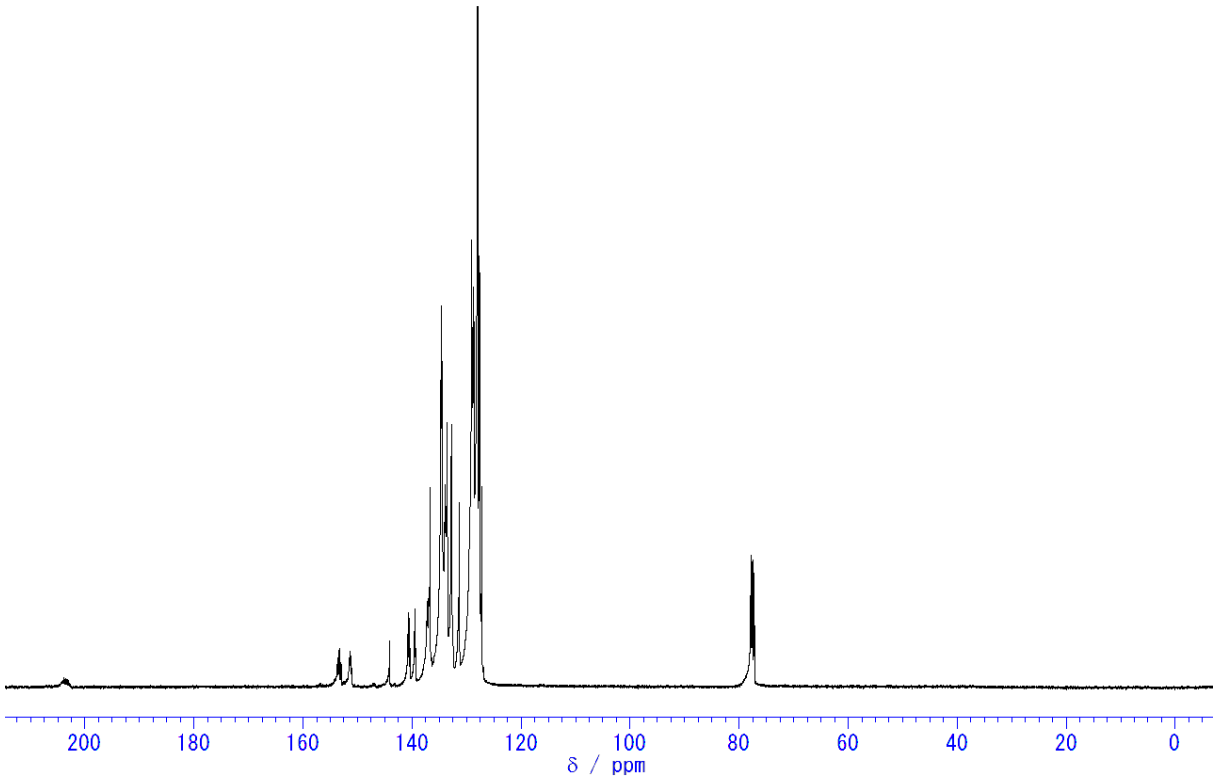


Figure S24. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(Ph)Si}Rh(CO)(PPh_3) (**3a**).

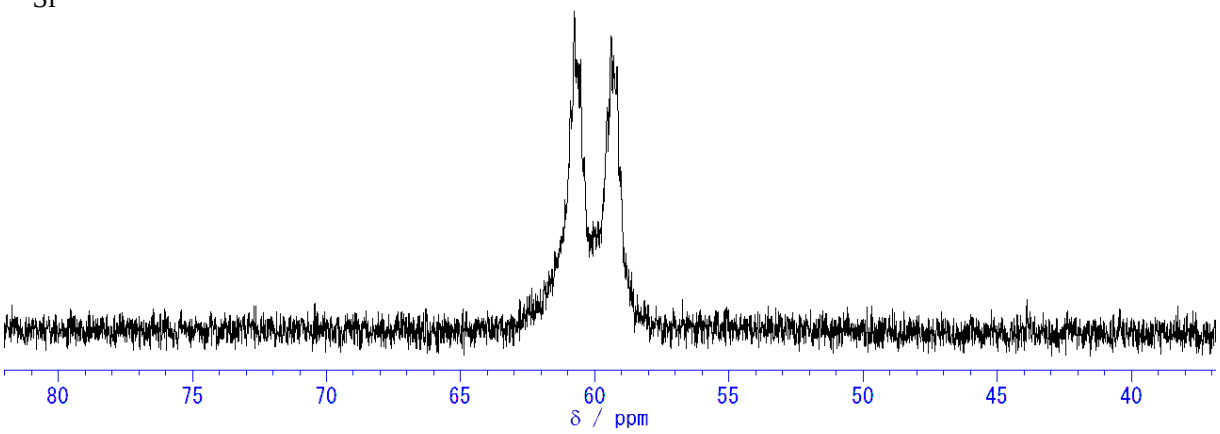
^1H



$^{13}C\{^1H\}$



^{29}Si



$^{31}P\{^{1}H\}$

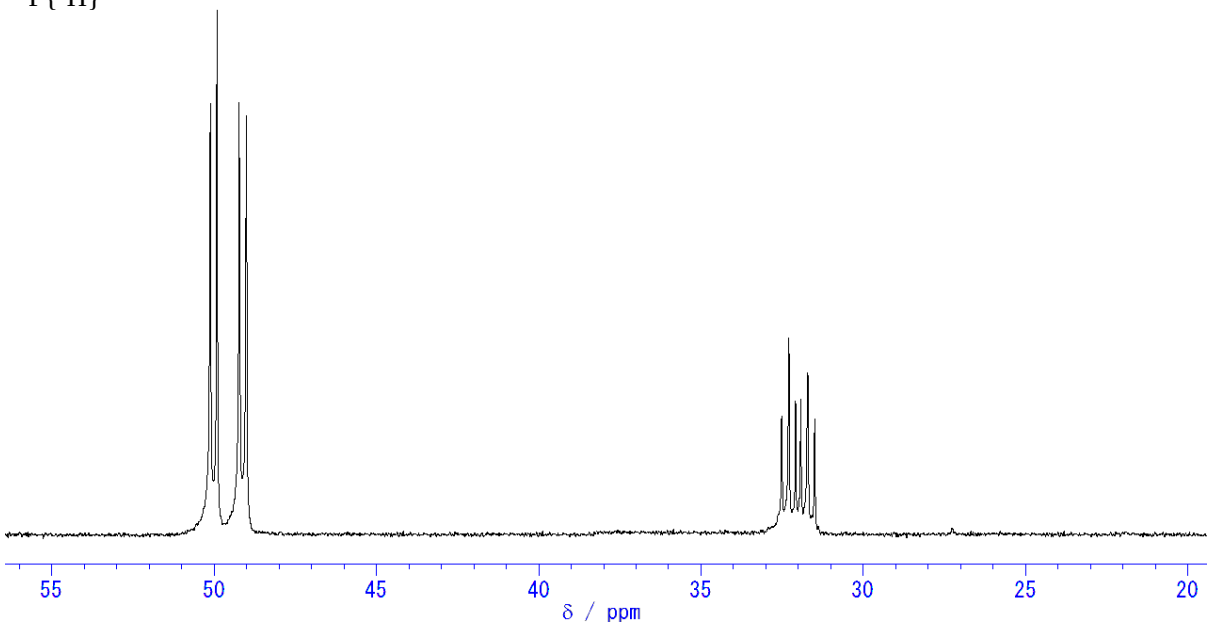
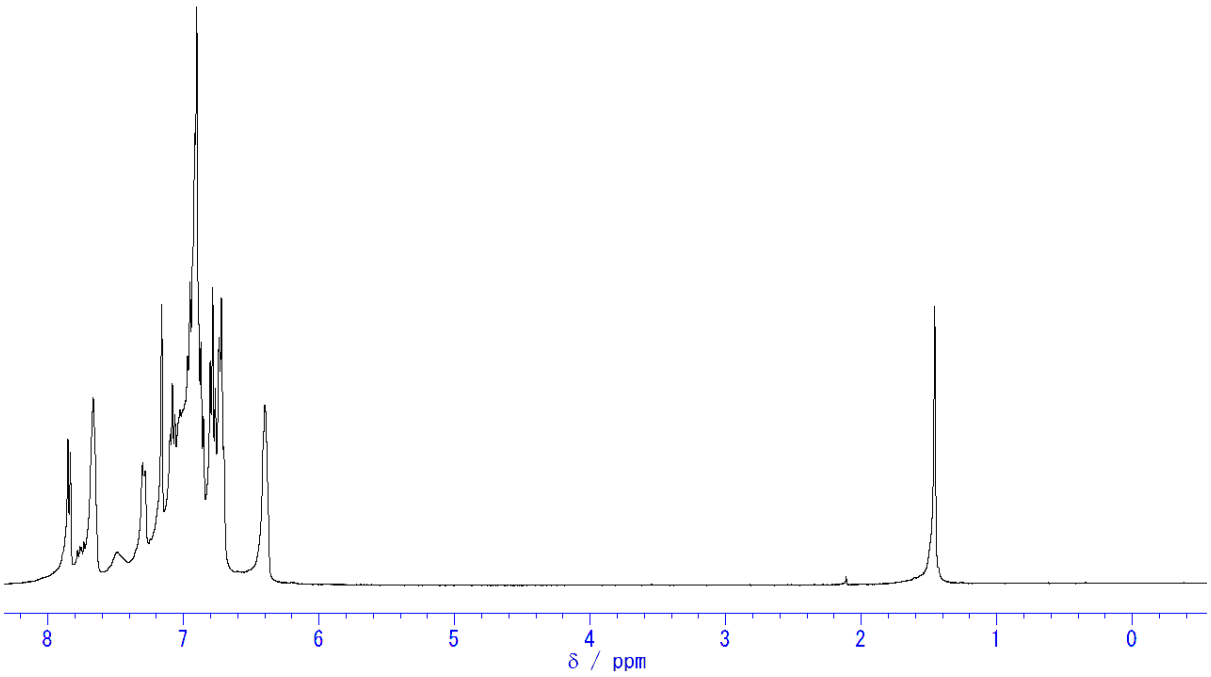
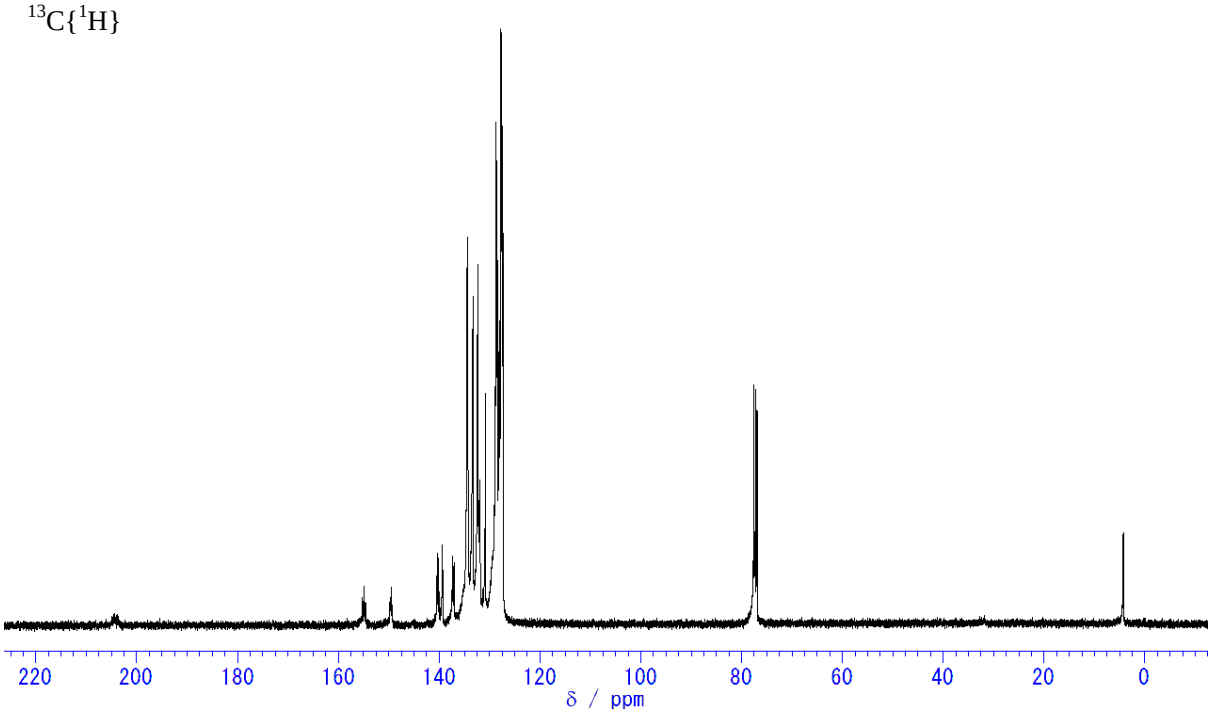


Figure S25. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(Me)Si}Rh(CO)(PPh_3) (**3b**).

^1H



$^{13}C\{^1H\}$



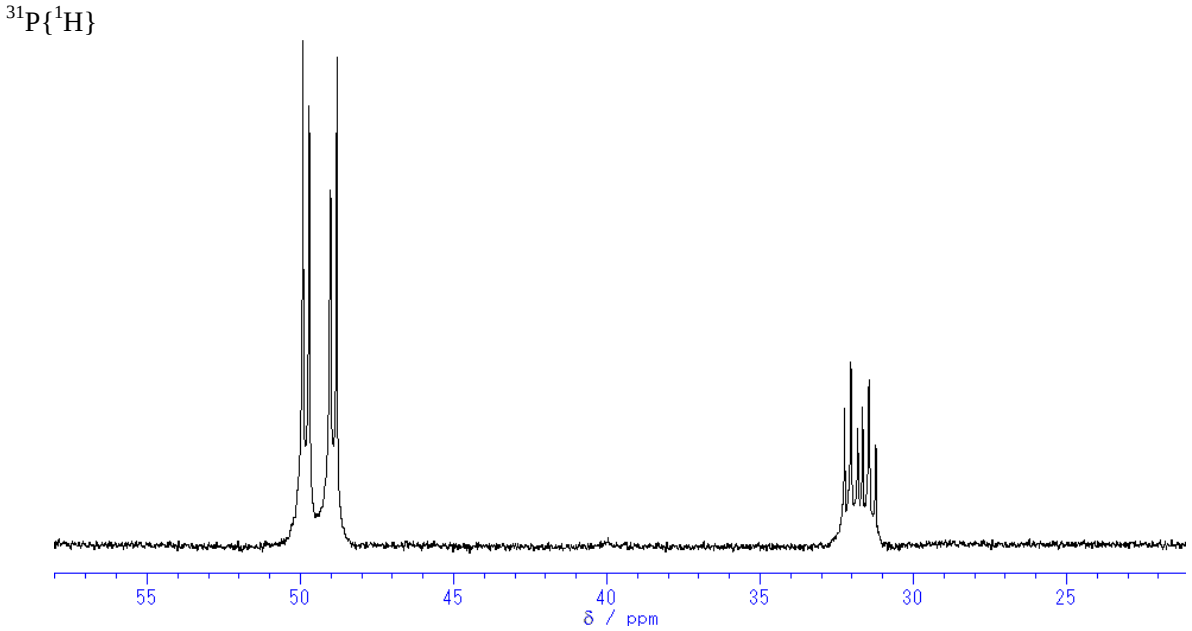
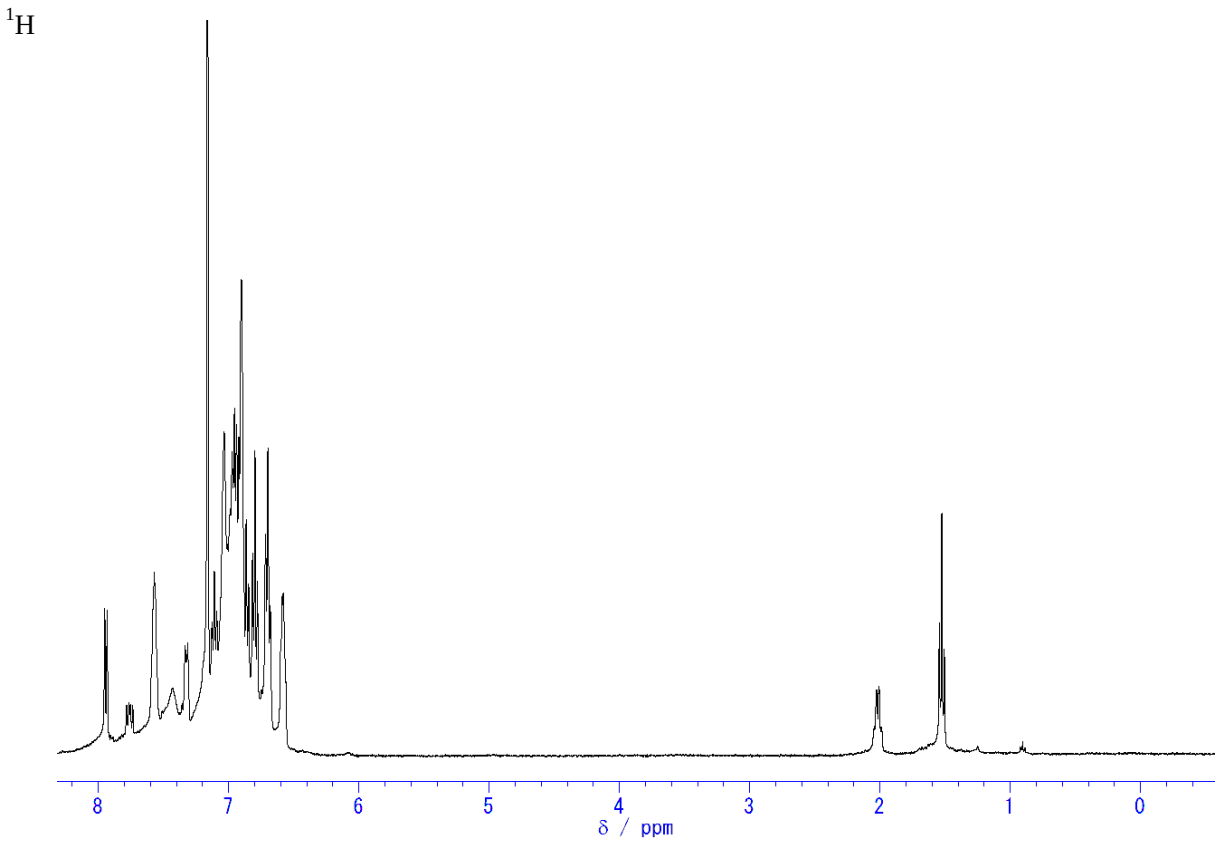
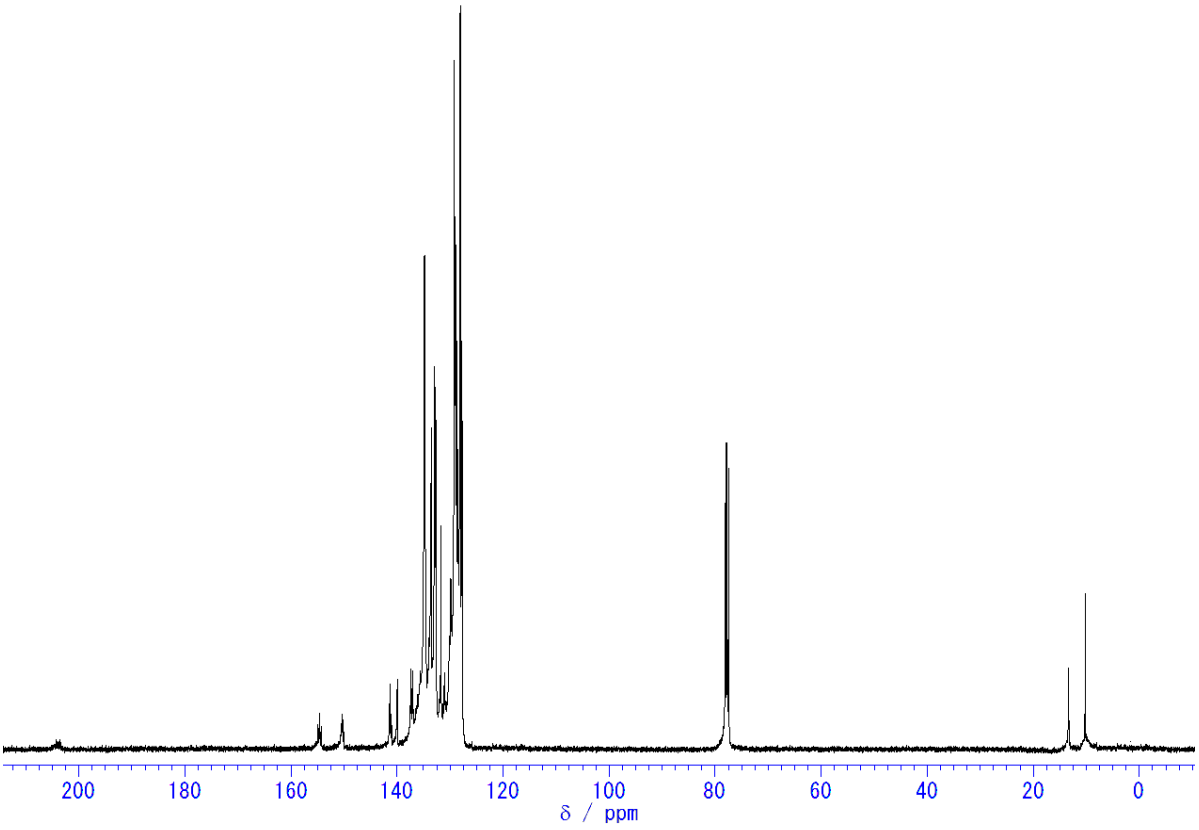


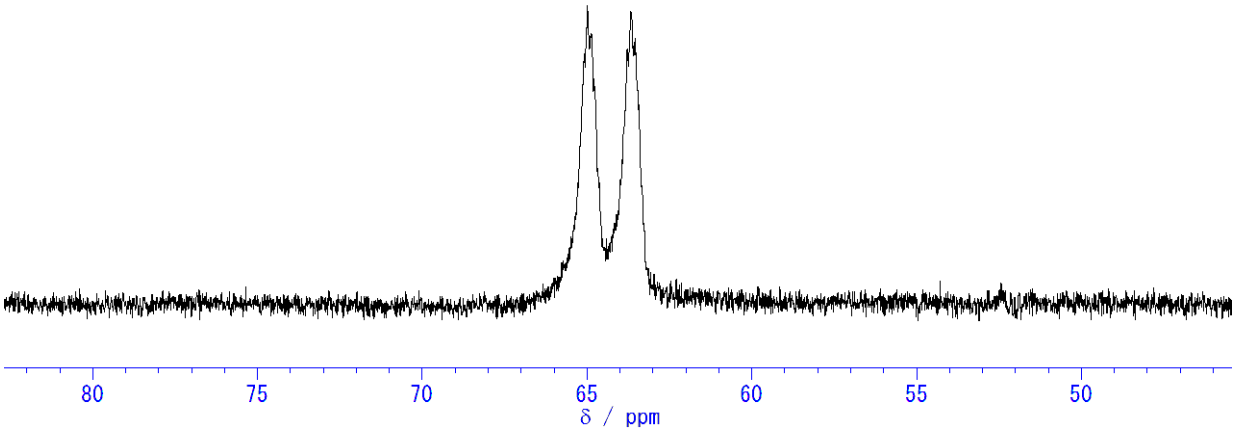
Figure S26. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(Et)Si}Rh(CO)(PPh_3) (**3c**).



$^{13}C\{^{1}H\}$



$^{29}Si\{^{1}H\}$



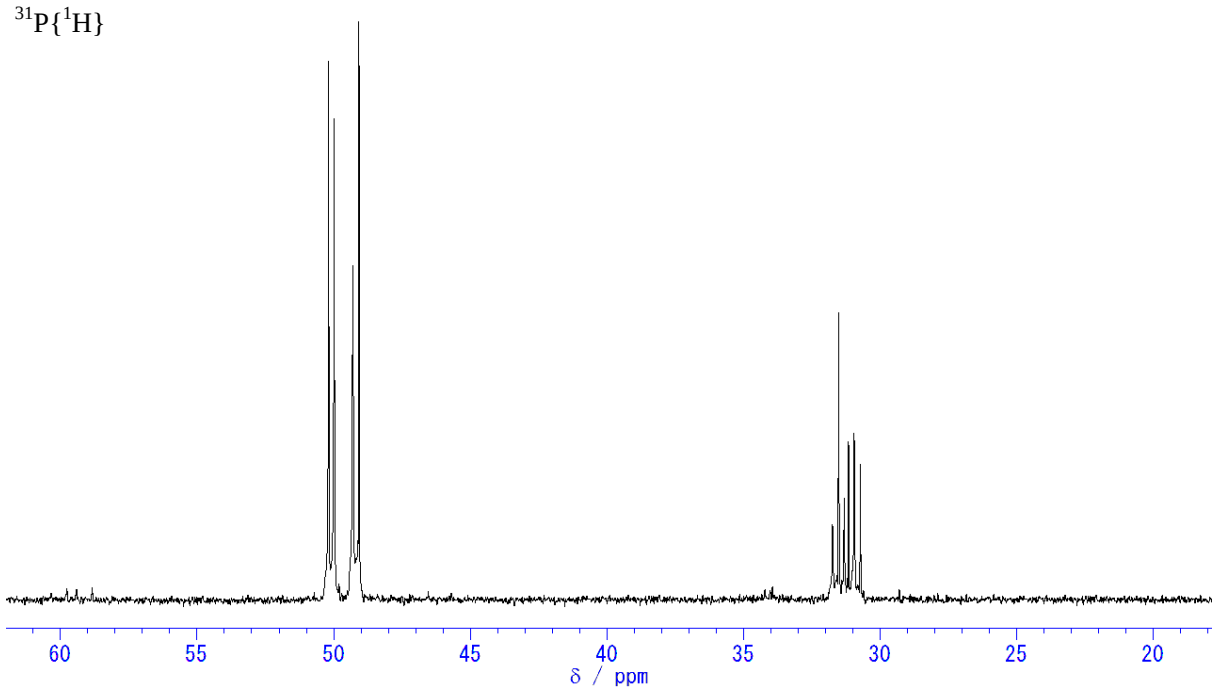
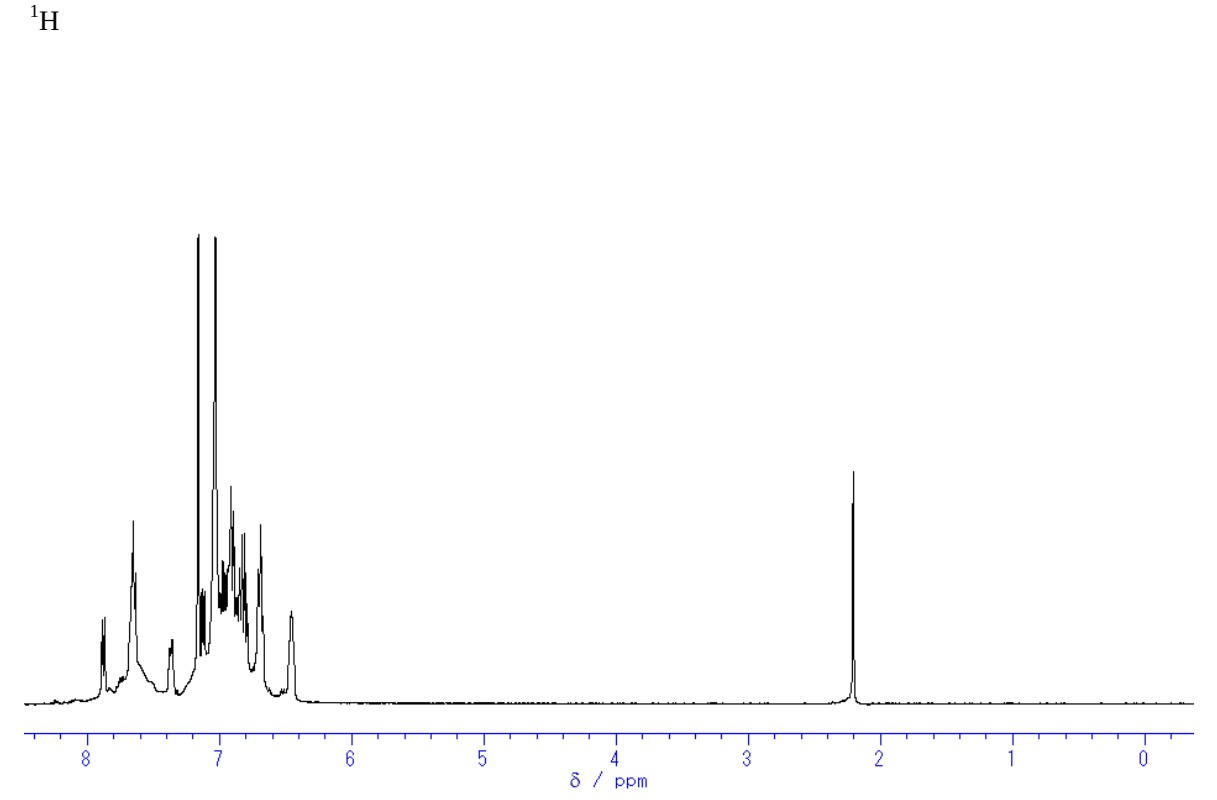
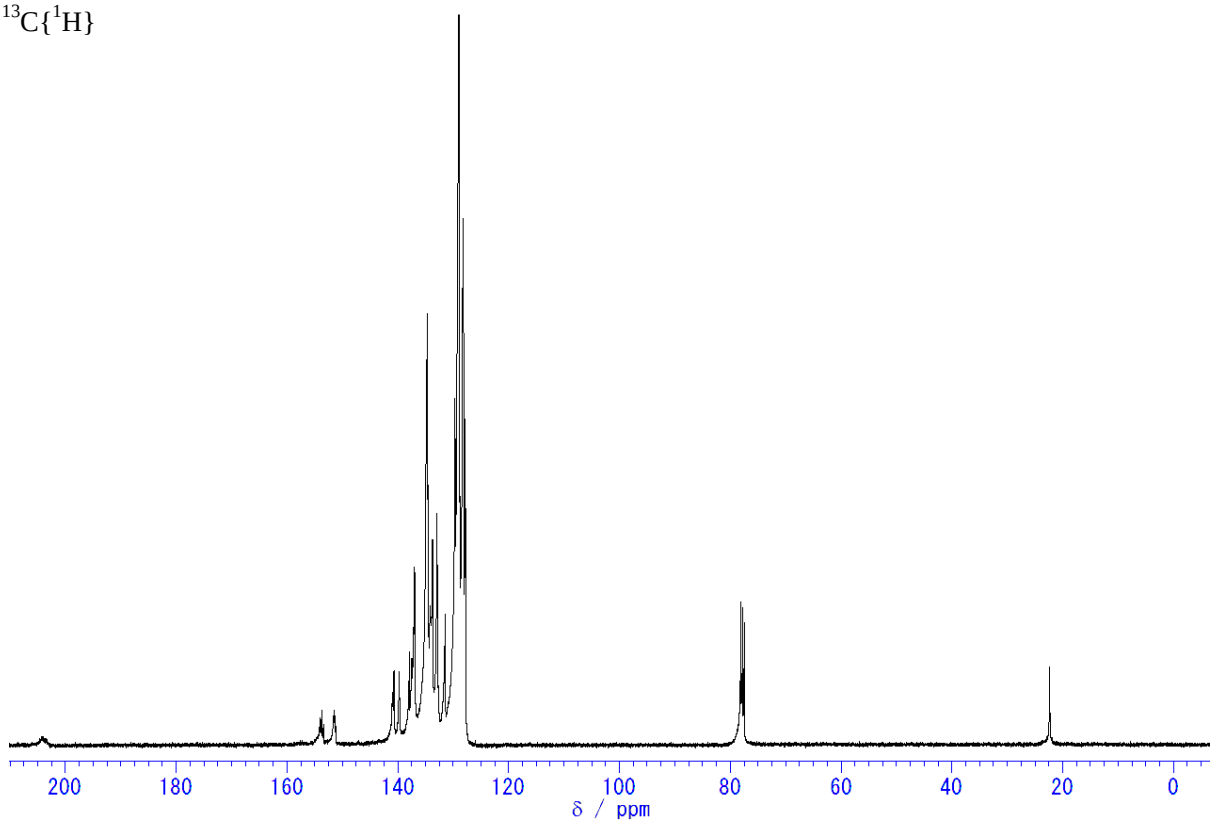


Figure S27. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(*p*-tolyl)Si}Rh(CO)(PPh_3) (**3d**).



$^{13}C\{^{1}H\}$



$^{31}P\{^{1}H\}$

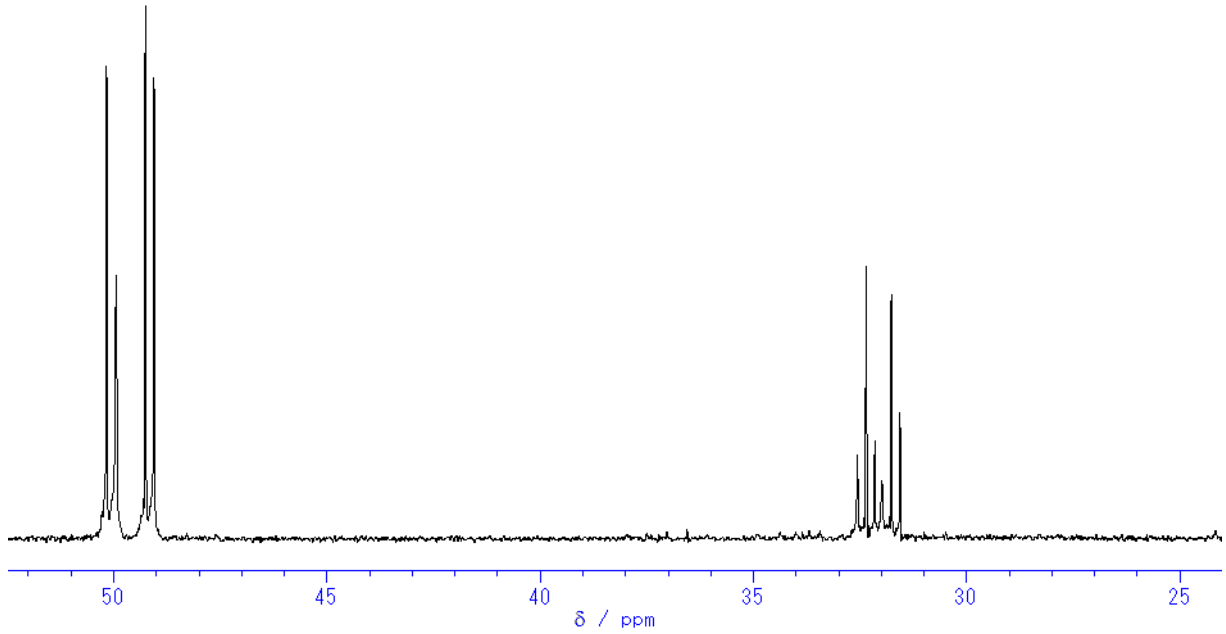
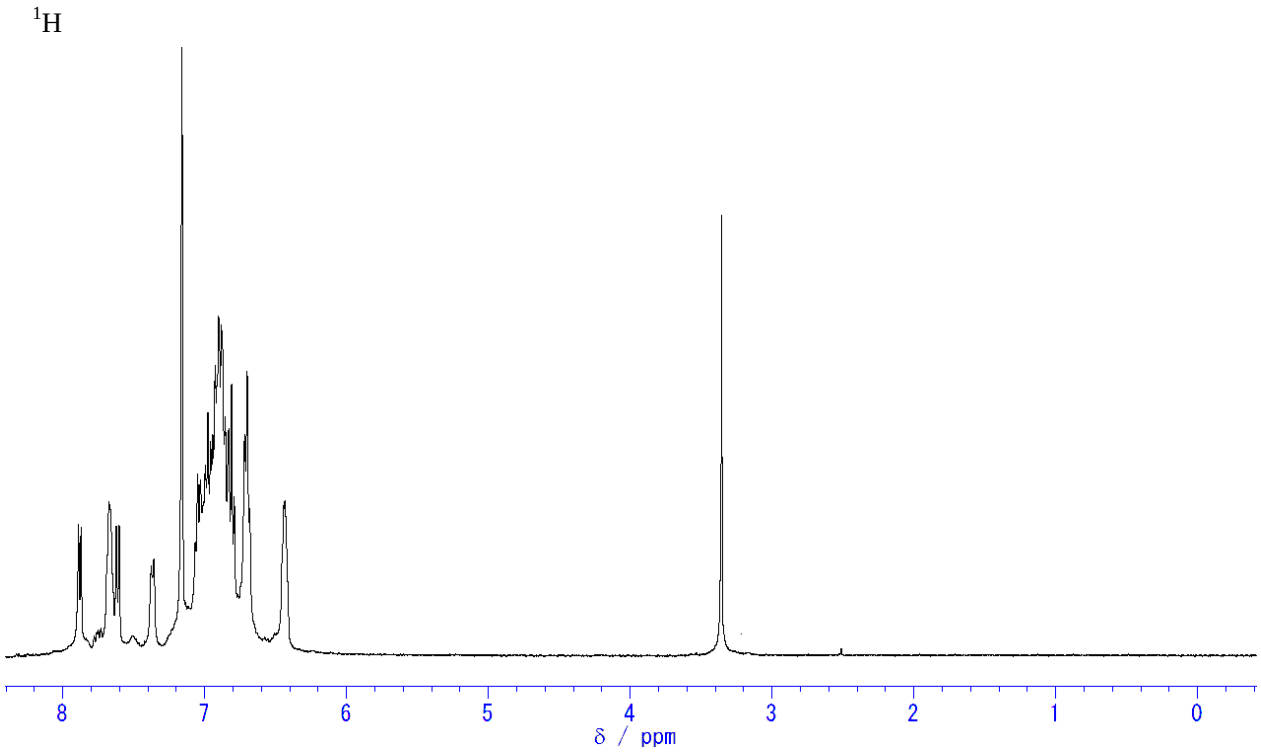
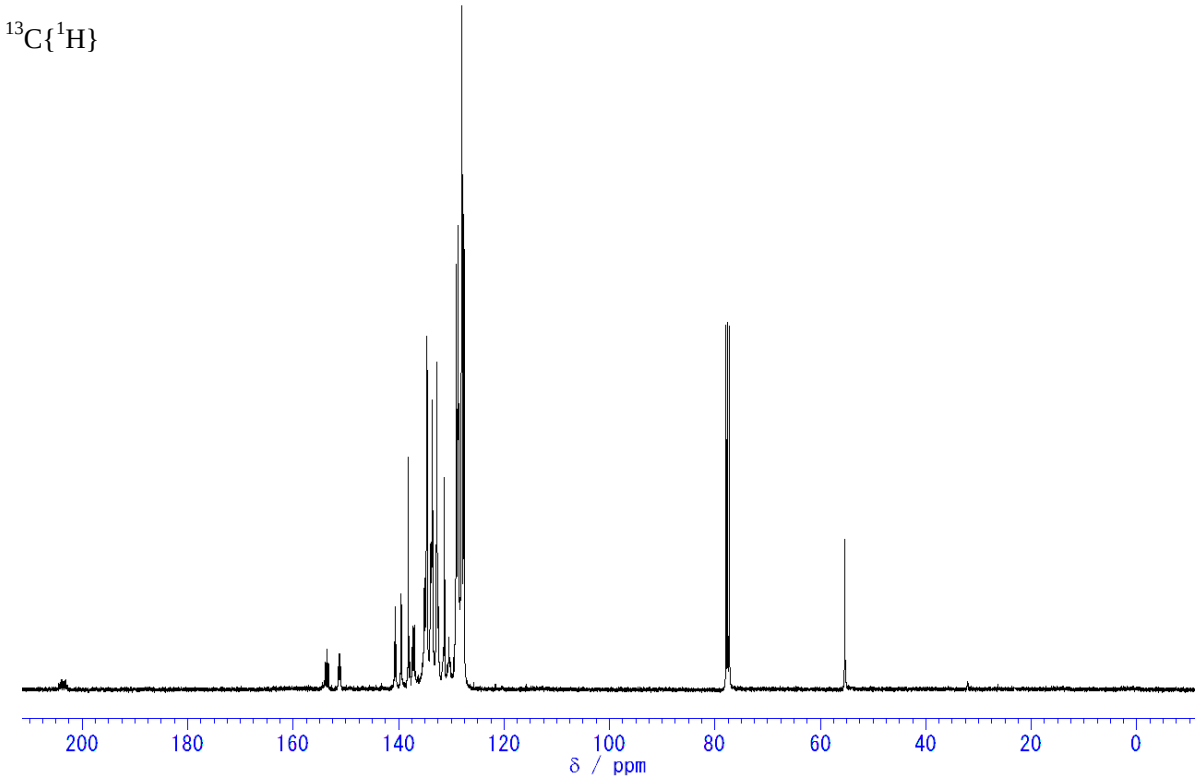


Figure S28. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(*p*-methoxyphenyl)Si}Rh(CO)(PPh_3) (**3e**).





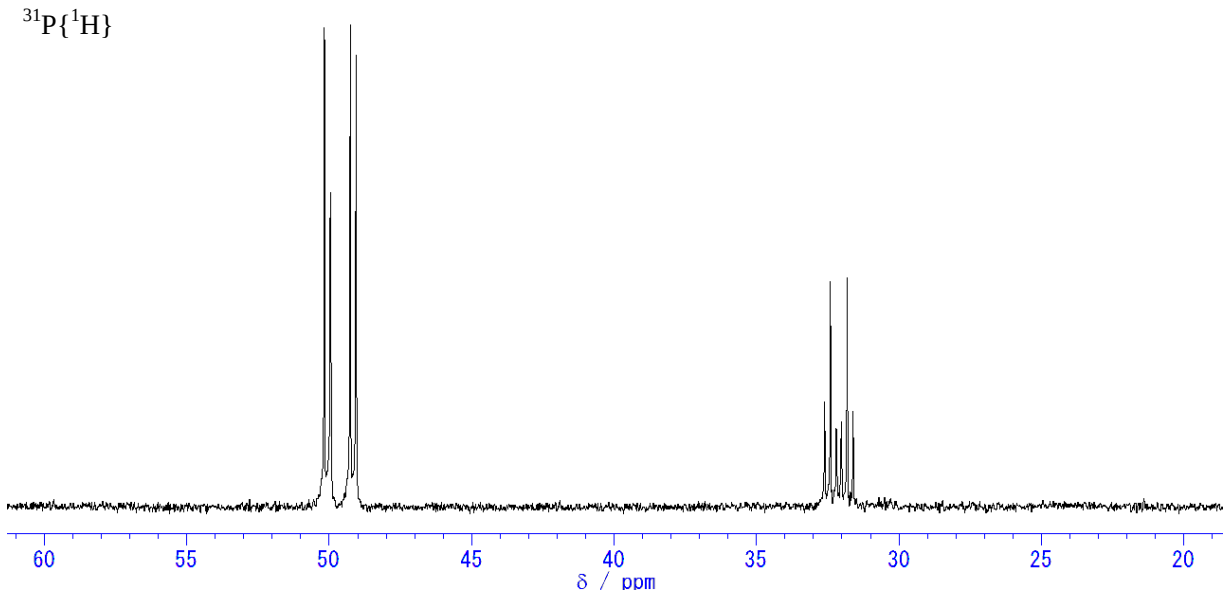
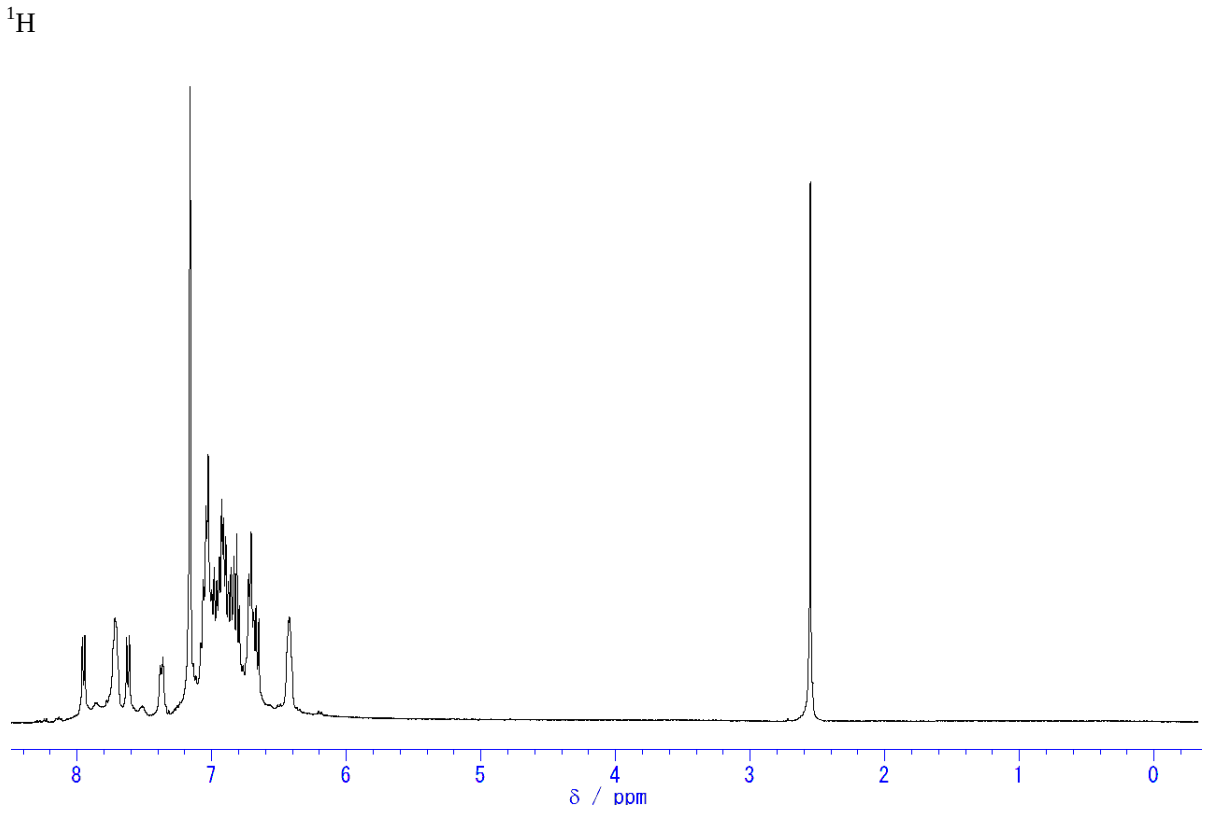
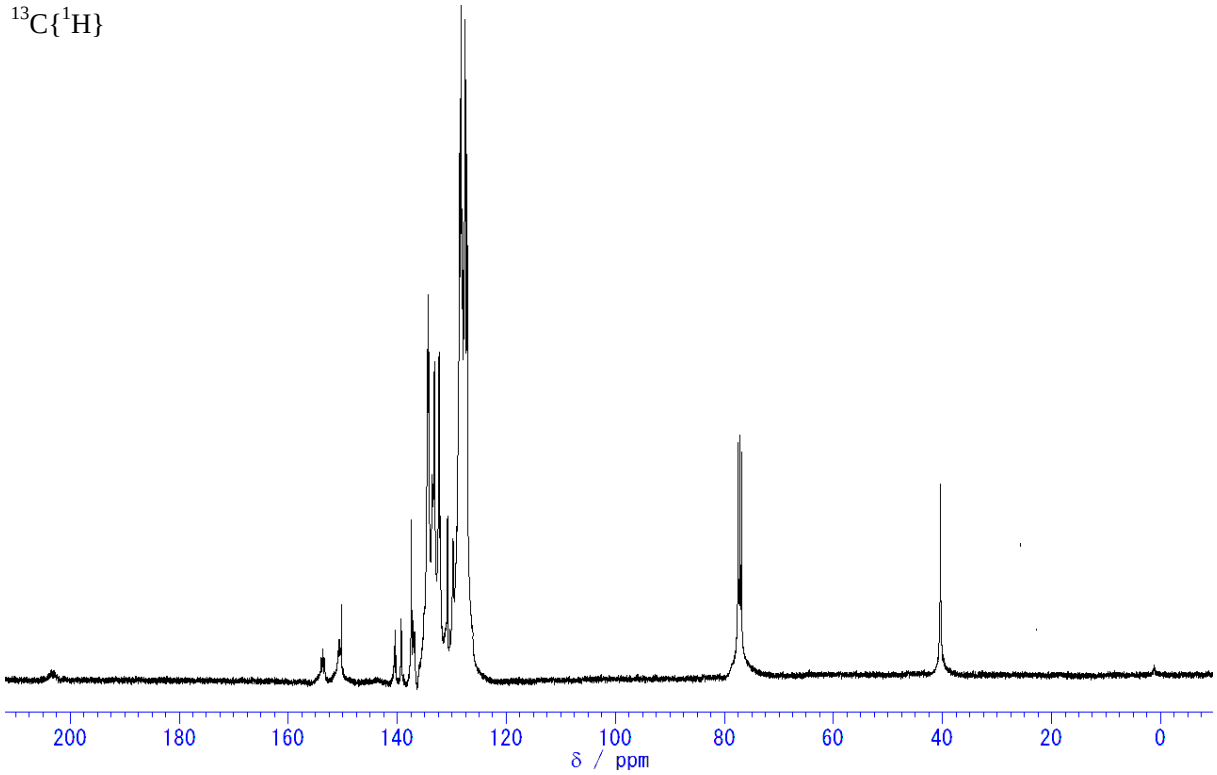


Figure S29. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(*p*-dimethylaminophenyl)Si}Rh(CO)(PPh_3) (**3f**).



$^{13}C\{^{1}H\}$



$^{31}P\{^{1}H\}$

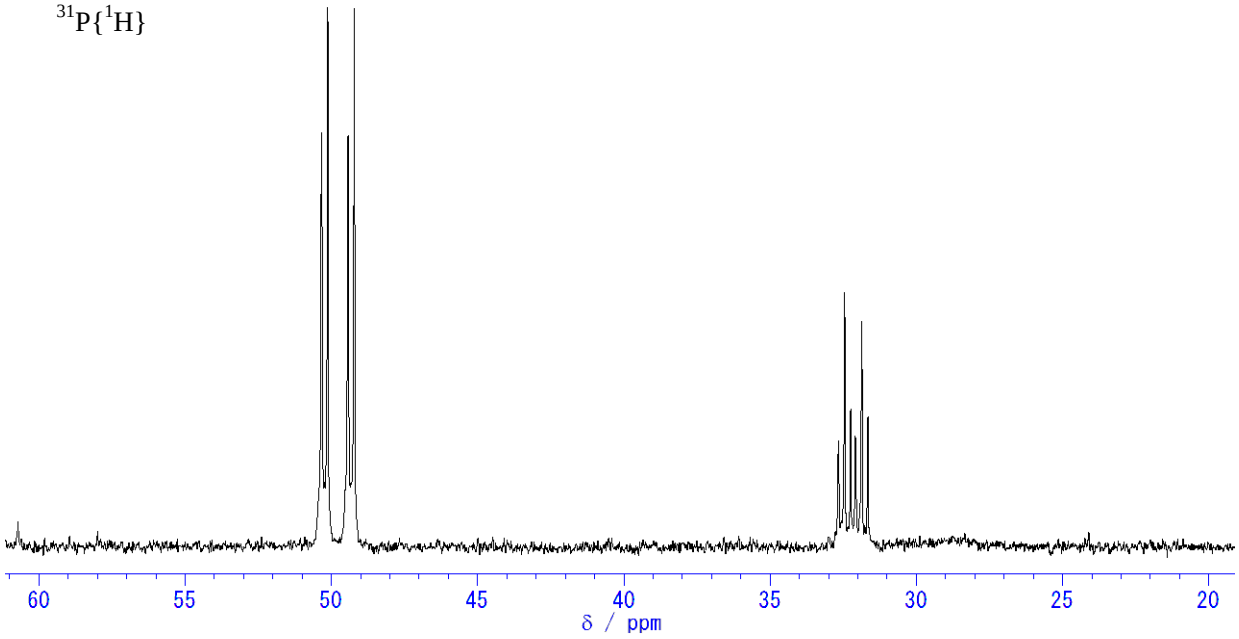
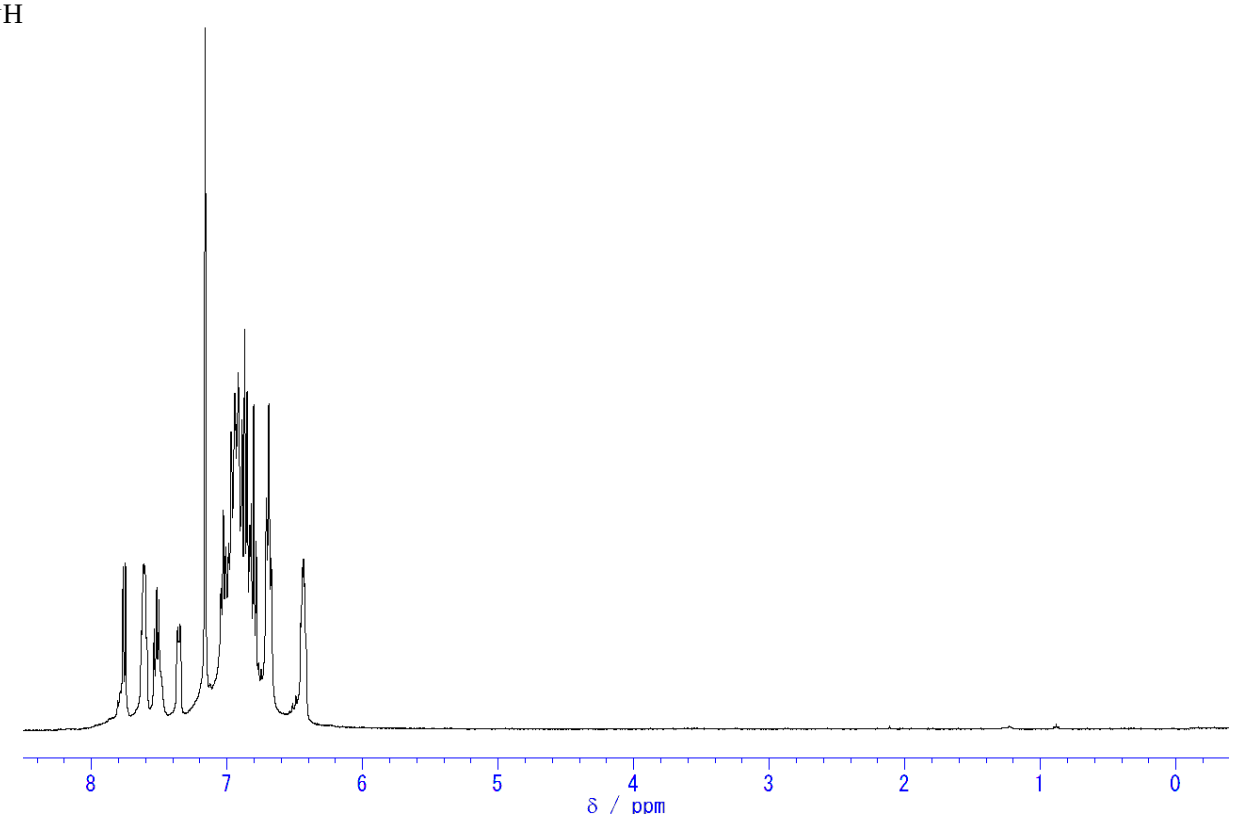
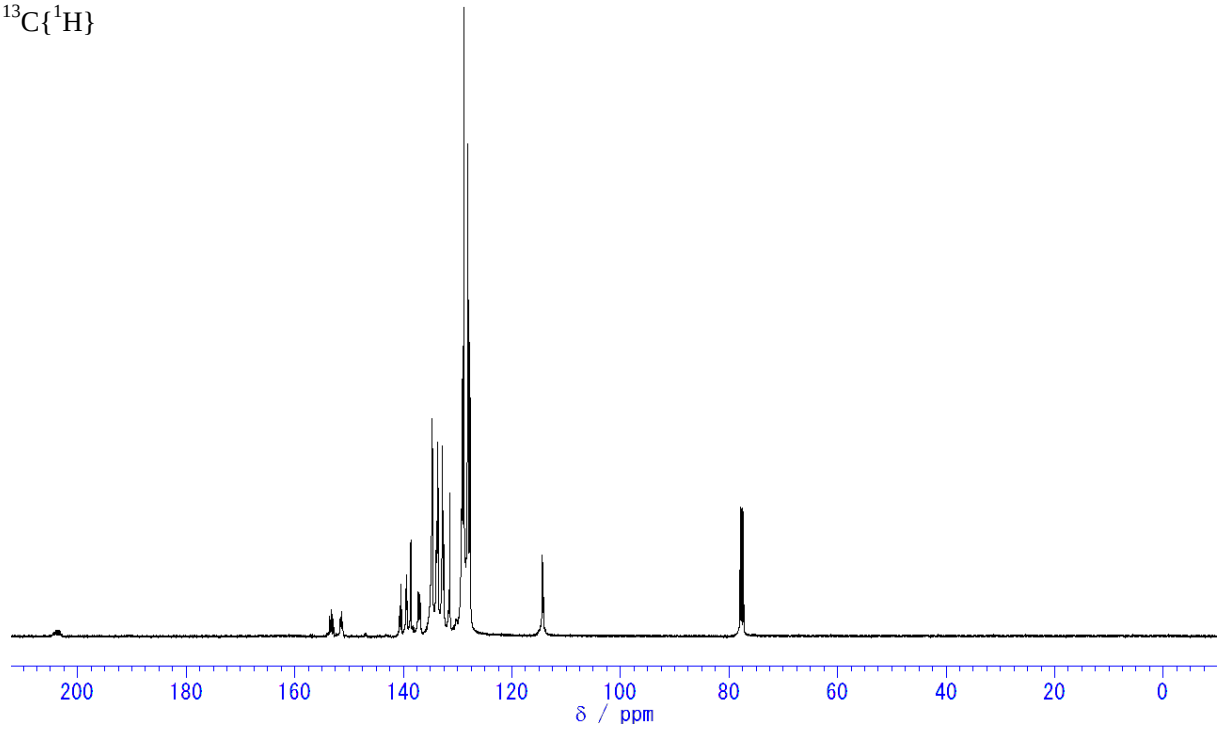


Figure S30. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(*p*-fluorophenyl)Si}Rh(CO)(PPh_3) (**3g**).

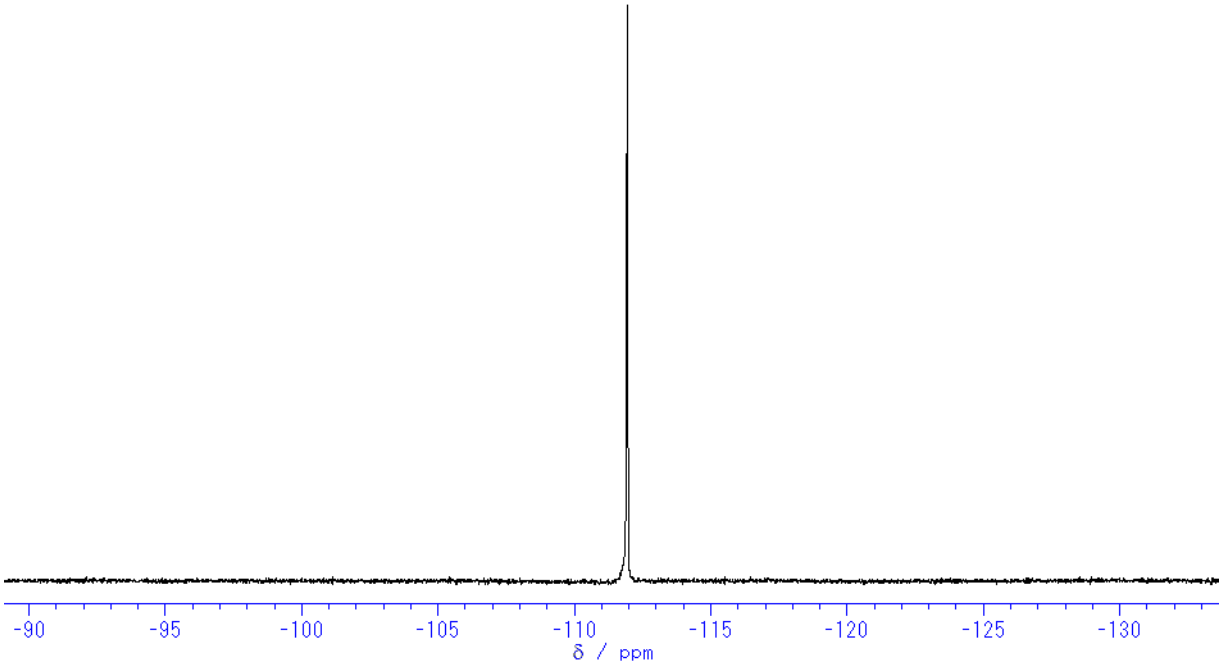
^{1}H



$^{13}C\{^{1}H\}$



$^{19}F\{^{1}H\}$



$^{31}P\{^{1}H\}$

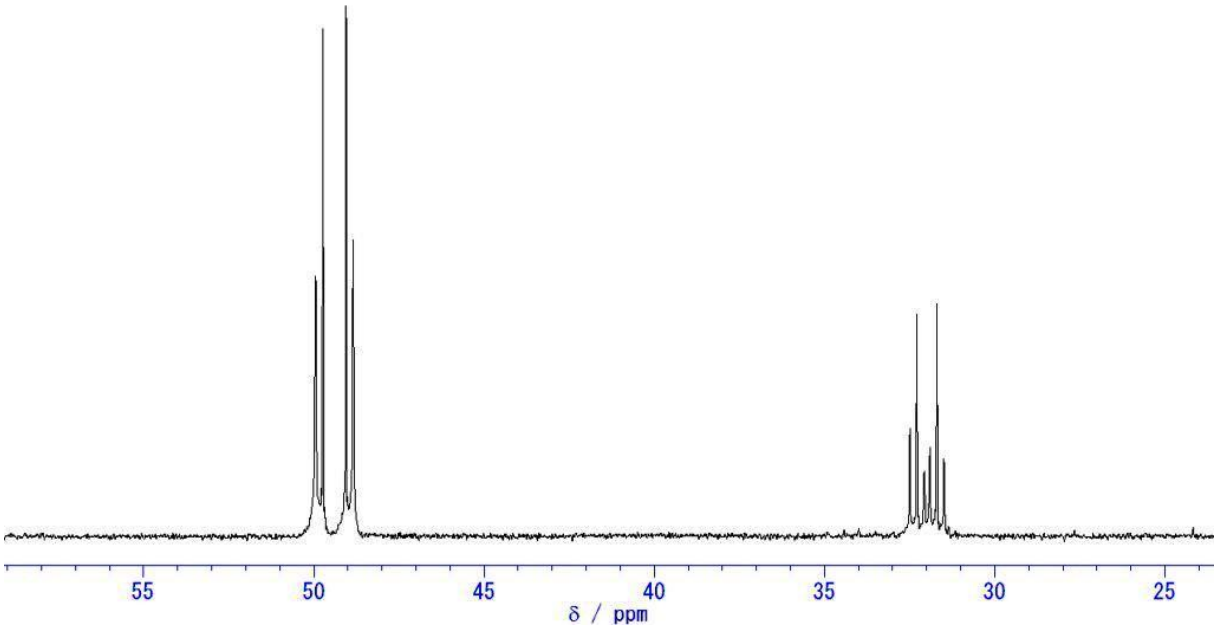
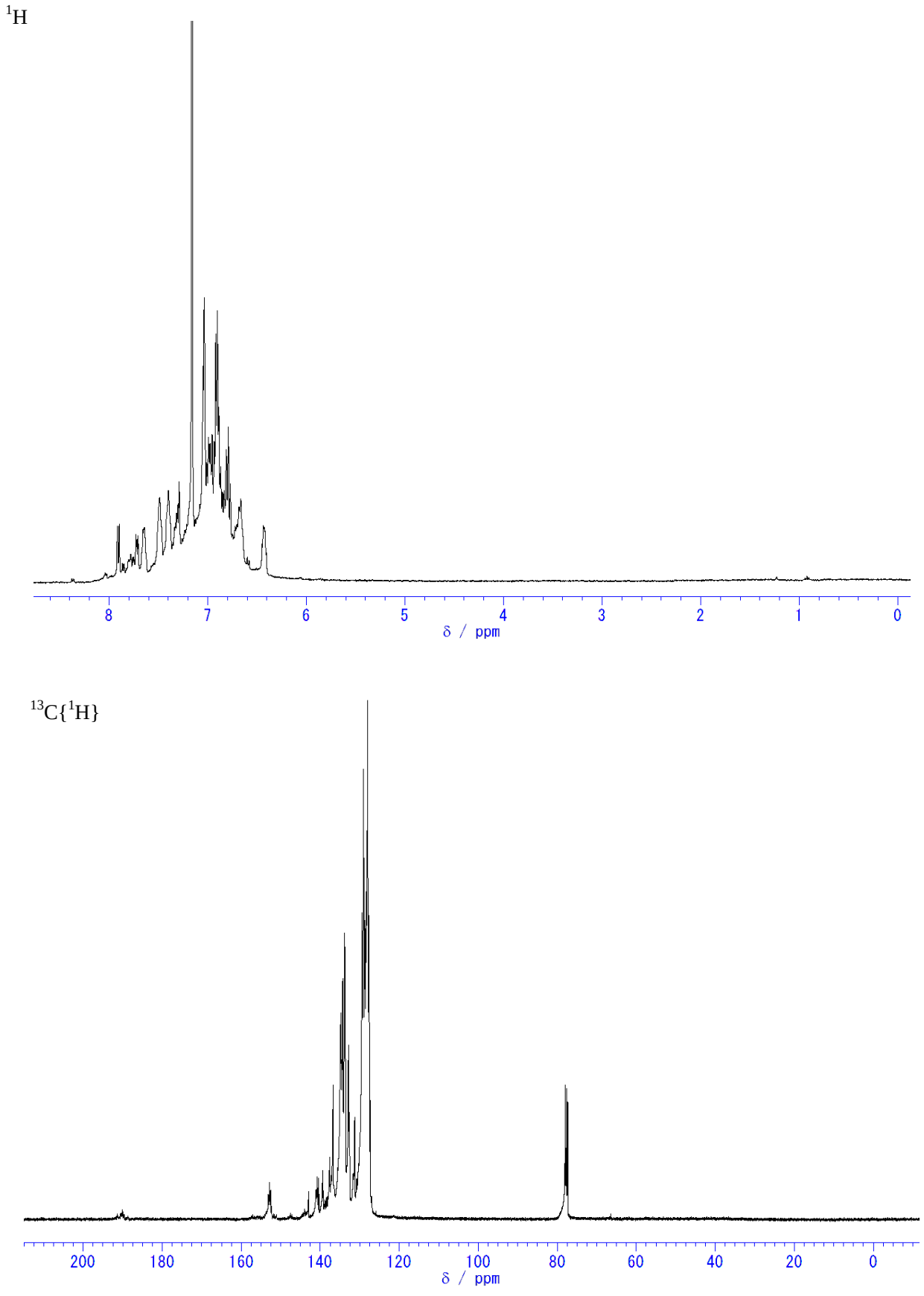
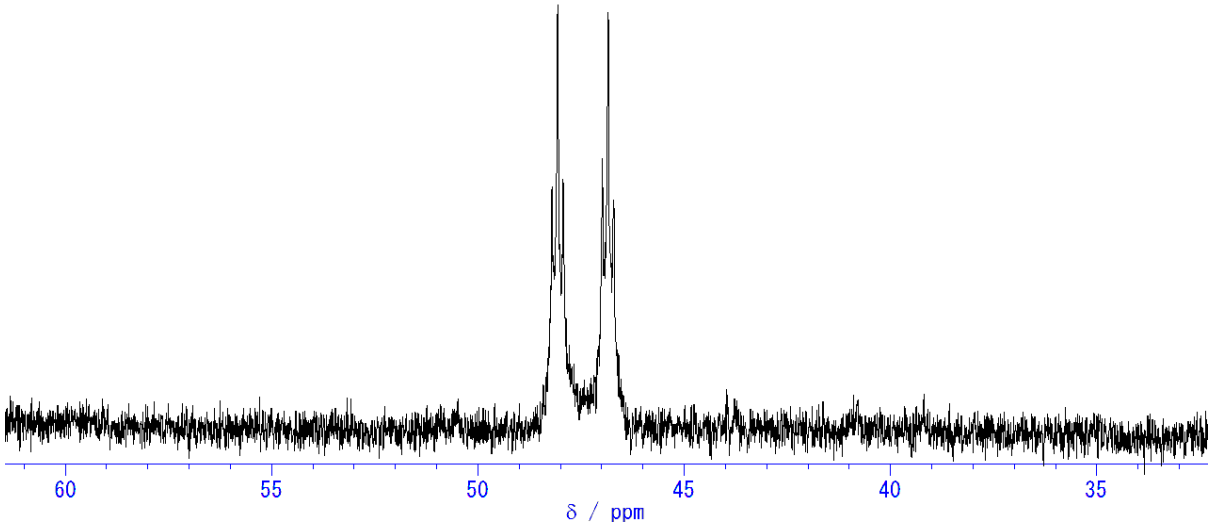


Figure S31. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(Ph)Si}Ir(CO)(PPh_3) (**6a**).



$^{29}Si\{^{1}H\}$



$^{31}P\{^{1}H\}$

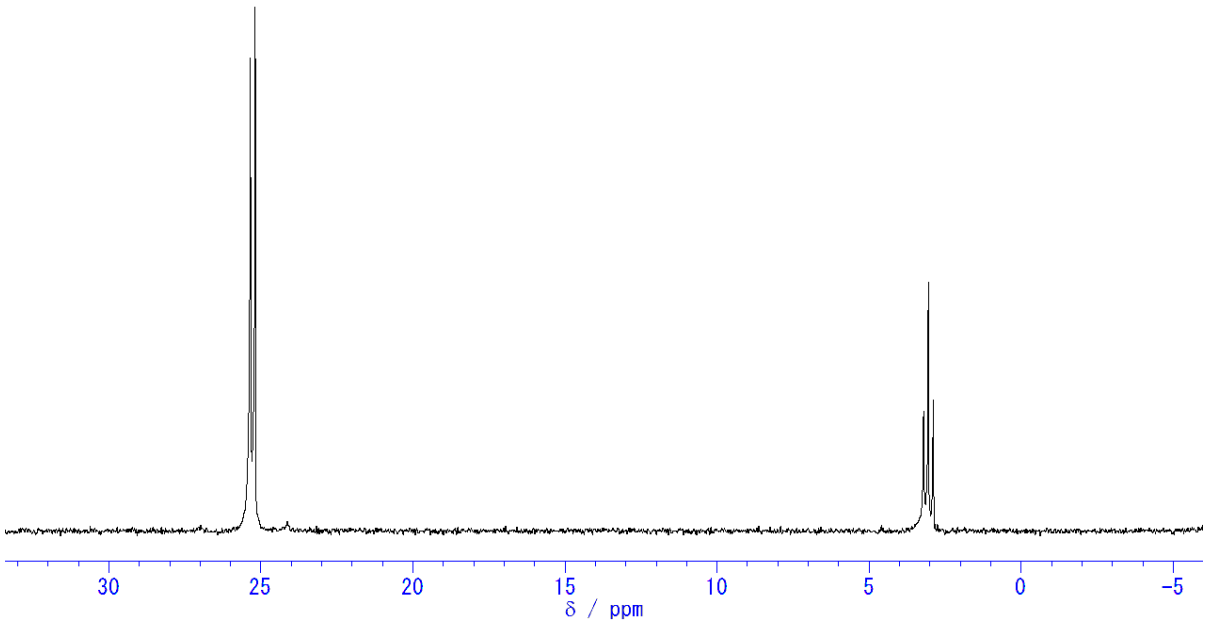
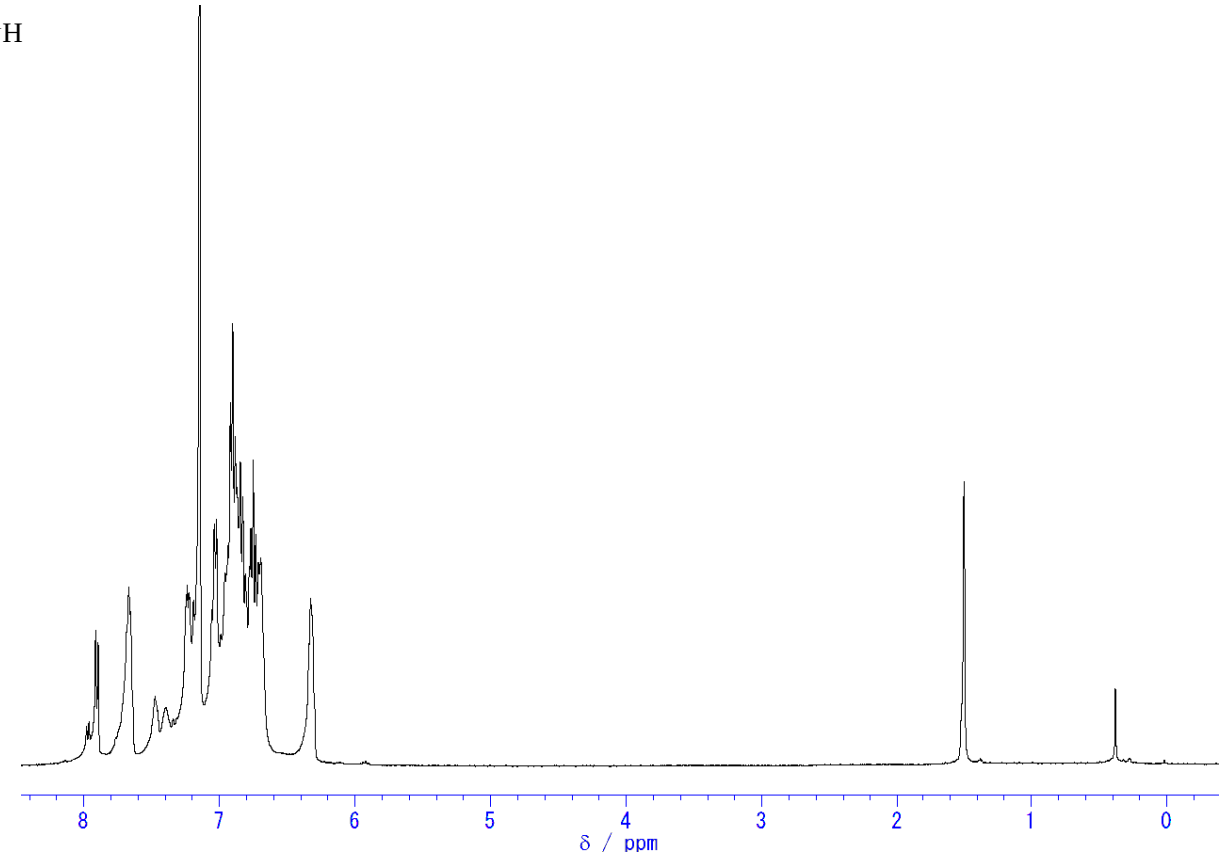
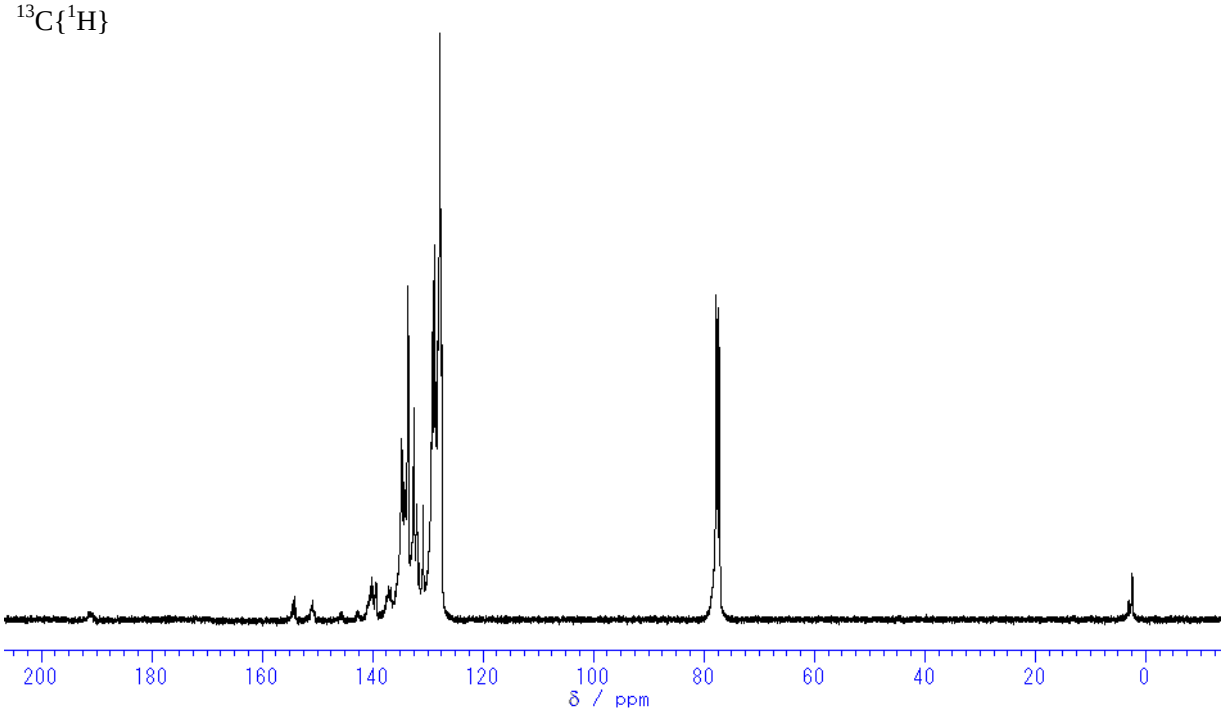


Figure S32. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(Me)Si}Ir(CO)(PPh_3) (**6b**).

^1H



$^{13}C\{^1H\}$



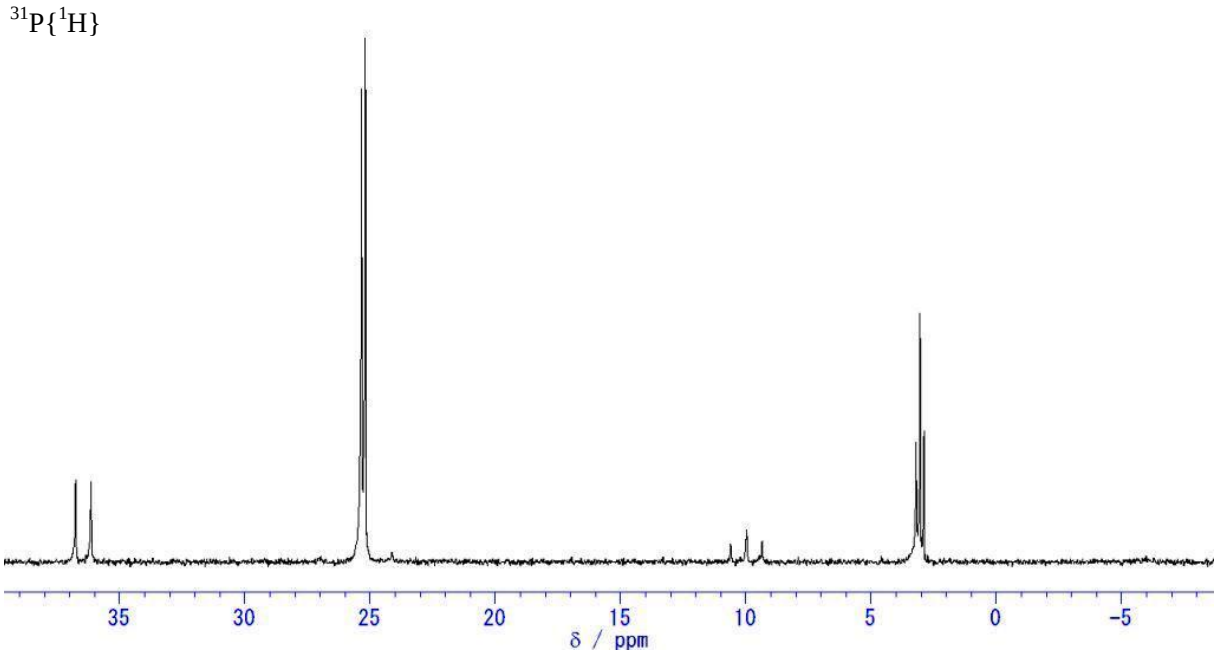
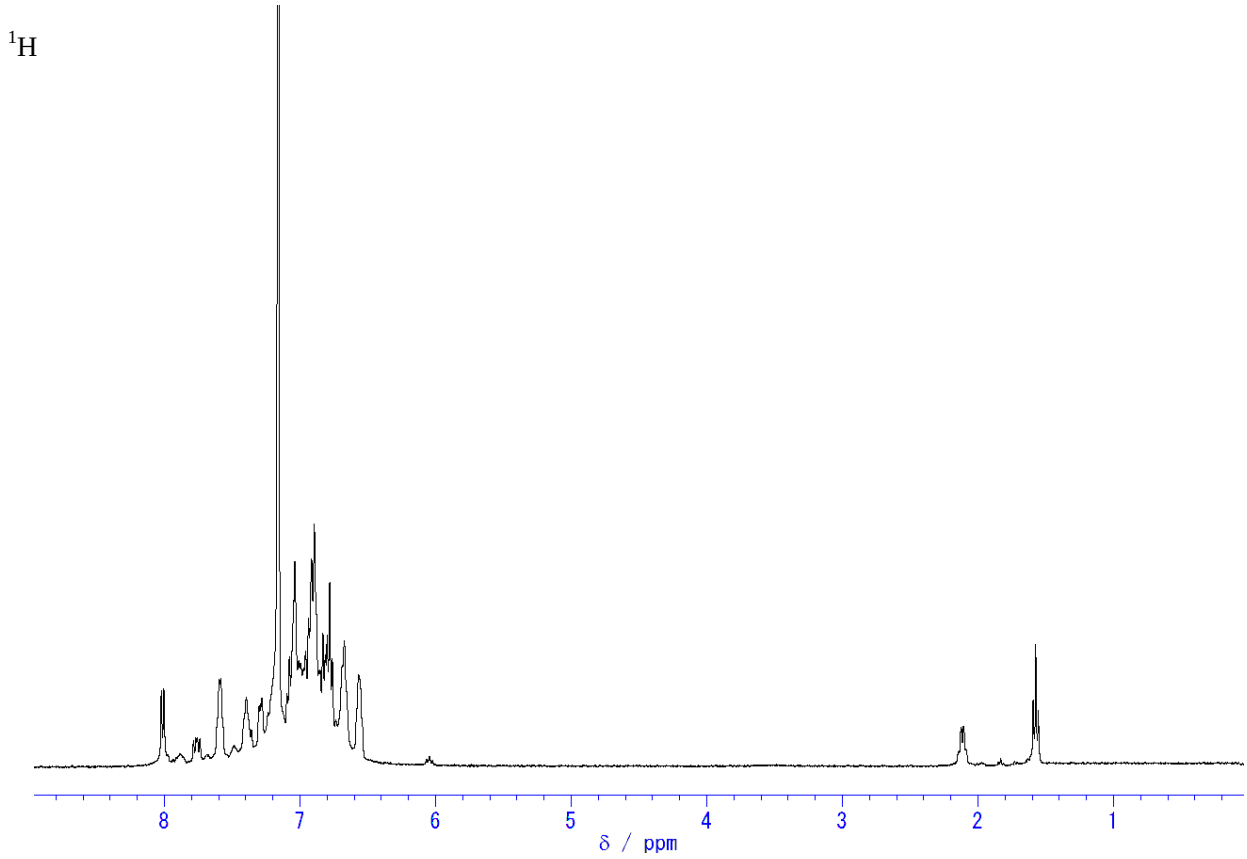
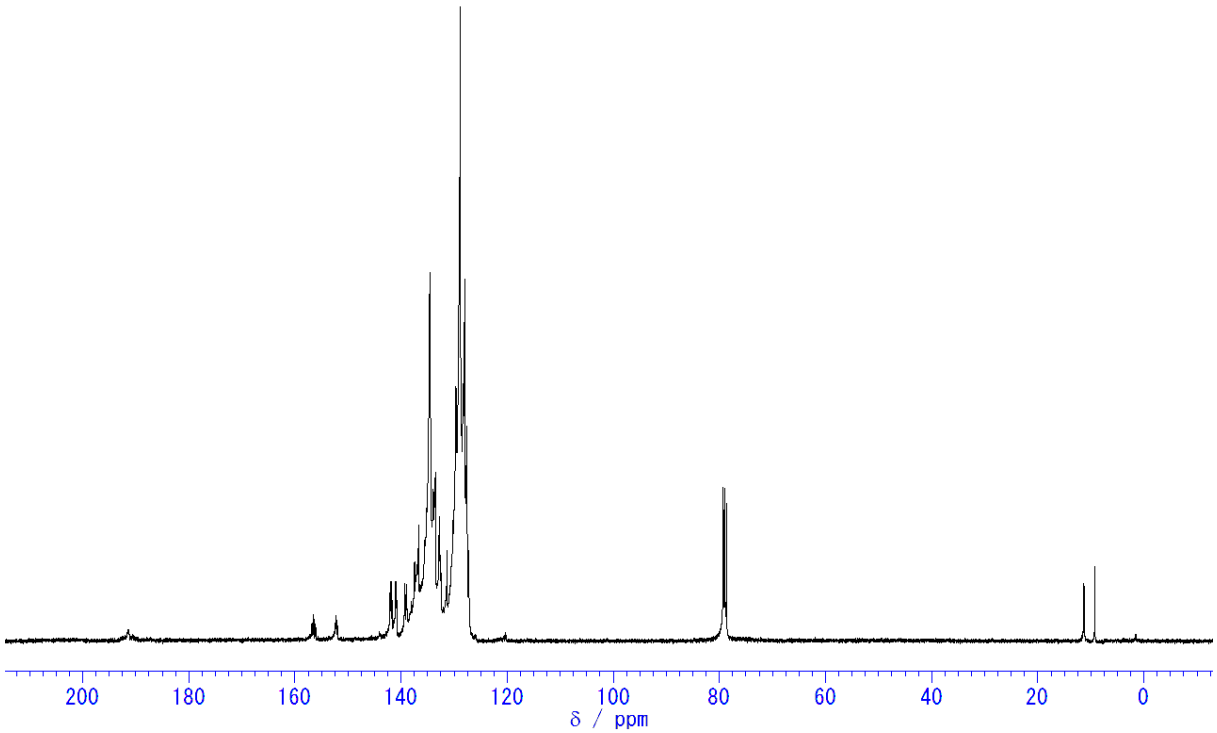


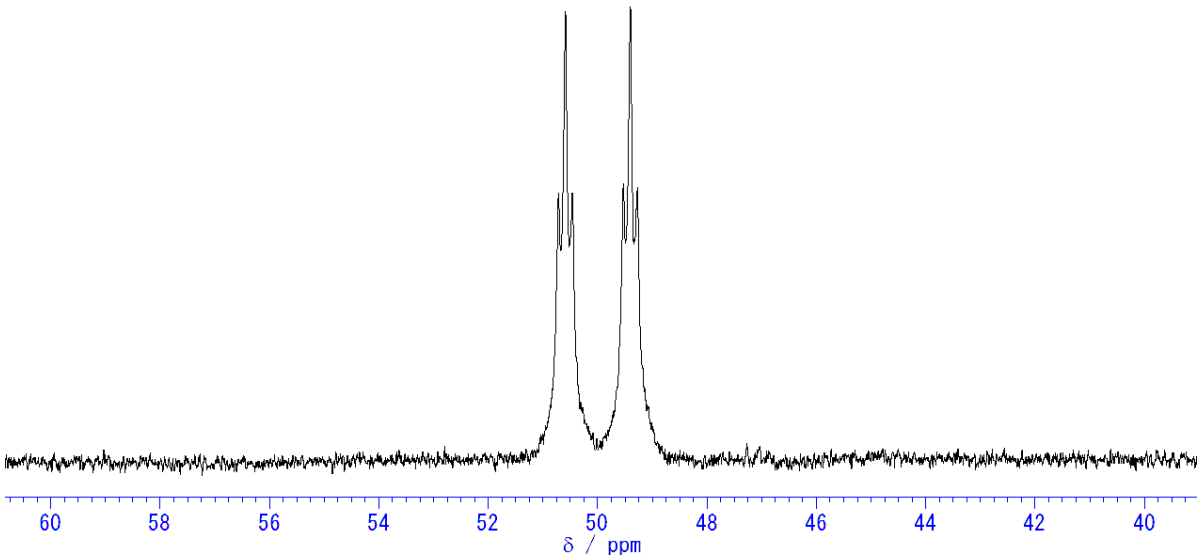
Figure S33. NMR spectra of {(*o*-$Ph_2PC_6H_4)_2$(Et)Si}Ir(CO)(PPh_3) (**6c**).



$^{13}C\{^{1}H\}$



$^{29}Si\{^{1}H\}$



$^{31}P\{^{1}H\}$

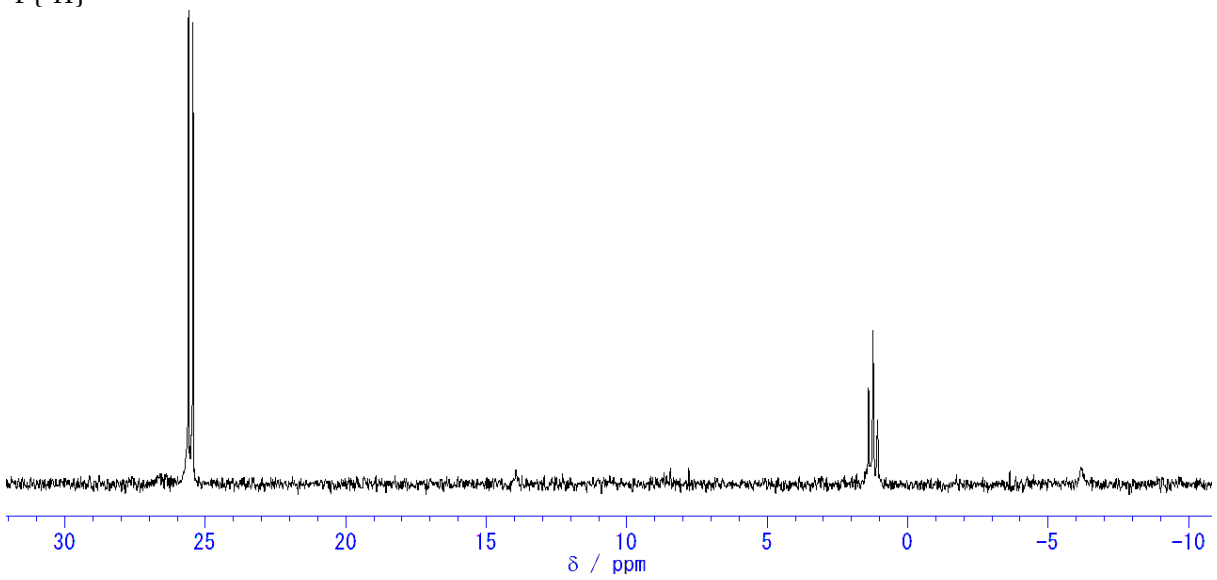


Table S18. Cartesian coordinate of **1A**.

	X	Y	Z
Si	0.389179	0.188617	0.45373
C	1.188180	1.131107	1.91232
C	2.199760	0.421375	2.57900
C	0.939763	2.449705	2.34696
C	2.946034	0.973360	3.61310
H	2.424330	-0.596905	2.27879
C	1.691527	3.002168	3.38964
C	2.692739	2.275273	4.02002
H	3.721926	0.387084	4.09442
H	1.491023	4.017743	3.71630
H	3.264825	2.725279	4.82465
C	1.646397	0.323942	-0.97472
C	2.600593	-0.705280	-1.02920
C	1.791026	1.383330	-1.89758
C	3.667204	-0.693303	-1.92011
H	2.514998	-1.548463	-0.35208
C	2.872576	1.393699	-2.78581
C	3.811995	0.370780	-2.79741
H	4.381452	-1.510245	-1.92226
H	2.981986	2.214079	-3.48837
H	4.642842	0.406024	-3.49430
C	-1.376163	0.656607	-0.00212
H	-1.705329	-0.010054	-0.80714
H	-2.033025	0.476739	0.85567
H	-1.526676	1.686622	-0.33386
C	0.248855	-1.625509	0.96060
H	-0.484193	-1.707050	1.76956
H	-0.123267	-2.217758	0.11847
H	1.170462	-2.092566	1.31294
Rh	-0.513869	4.235904	-0.64205
H	-0.773460	4.792525	-2.11885
C	-1.536321	5.728278	-0.24177
O	-2.166482	6.672944	-0.07673
P	0.581314	2.773526	-2.07840
H	1.278612	3.463224	-3.09304
H	-0.366084	2.134362	-2.91665
P	-0.332783	3.529517	1.57170
H	-1.511821	2.912073	2.06741
H	-0.292435	4.570681	2.53013

Table S19. Cartesian coordinate of **1B**.

	X	Y	Z
Si	0.456757	0.410441	0.469123
C	0.993578	1.252739	2.092083
C	1.081628	0.437436	3.229910
C	1.256491	2.630196	2.261264
C	1.387586	0.946589	4.488025
H	0.898833	-0.628405	3.138701
C	1.563144	3.137286	3.526782
C	1.624379	2.304986	4.638420
H	1.436375	0.282263	5.344686
H	1.758730	4.198109	3.648923
H	1.861192	2.720042	5.612599
C	1.659782	0.864844	-0.952868
C	2.909166	0.229413	-0.868804
C	1.436411	1.694262	-2.072905
C	3.898309	0.396378	-1.831165
H	3.124035	-0.413412	-0.020315
C	2.428950	1.851408	-3.045243
C	3.654764	1.207279	-2.930894
H	4.853639	-0.105899	-1.719441
H	2.246213	2.493245	-3.901682
H	4.413167	1.345145	-3.694489
C	-1.369738	0.739534	0.169013
H	-1.722823	0.284243	-0.761323
H	-1.923630	0.277403	0.993802
H	-1.622635	1.808176	0.155901
C	0.623273	-1.459358	0.682685
H	-0.126029	-1.836968	1.385175
H	0.440486	-1.946241	-0.280292
H	1.606481	-1.781339	1.034697
Rh	-0.711628	4.107875	-0.485197
H	-1.928364	4.373304	-1.493593
C	-1.552074	5.452897	0.495925
O	-2.101911	6.300037	1.038777
P	-0.077663	2.726732	-2.212128
H	0.181533	3.346491	-3.455953
H	-1.036730	1.790429	-2.668444
P	1.167369	3.820881	0.855491
H	1.629132	4.966299	1.548072
H	2.388834	3.516165	0.200635

Table S20. Cartesian coordinate of **2A**.

	X	Y	Z
Si	0.543521	0.717925	0.139453
C	1.312433	1.109046	1.857018
C	2.011158	0.164405	2.621930
C	1.190708	2.404677	2.382825
C	2.572227	0.495348	3.849156
H	2.117524	-0.852930	2.256164
C	1.752562	2.743807	3.617049
C	2.445269	1.789184	4.349139
H	3.107323	-0.256013	4.421550
H	1.645267	3.750393	4.011132
H	2.879146	2.050231	5.308824
C	2.013605	0.587186	-1.090416
C	2.942098	-0.463157	-1.083122
C	2.181739	1.593140	-2.053270
C	3.993663	-0.506130	-1.989831
H	2.842685	-1.265368	-0.357512
C	3.237644	1.556781	-2.968800
C	4.144046	0.506065	-2.935559
H	4.699208	-1.330783	-1.964103
H	3.351382	2.343636	-3.709036
H	4.963358	0.473217	-3.646231
C	-2.197817	1.829713	0.895515
H	-1.746729	1.349794	1.768645
H	-2.830296	2.646397	1.251859
H	-2.827489	1.098058	0.390231
C	-0.243491	-0.994803	0.243910
H	-1.094269	-0.986035	0.929853
H	-0.607533	-1.298133	-0.741648
H	0.460810	-1.757233	0.592416
Rh	-0.733563	2.612461	-0.482329
H	-1.299905	1.512542	-1.473580
C	-2.044745	3.906733	-1.111880
O	-2.871285	4.591607	-1.501277
P	0.945053	2.946219	-2.043222
H	1.777923	4.097183	-2.013947
H	0.587069	3.037991	-3.410991
P	0.243792	3.622509	1.385797
H	-0.613377	4.192189	2.360868
H	1.159870	4.706096	1.310664

Table S21. Cartesian coordinate of **3A**.

	X	Y	Z
Si	0.314405	-0.098507	0.428435
C	1.009370	0.581786	2.065376
C	1.382045	-0.292570	3.095056
C	1.112234	1.964340	2.322595
C	1.822354	0.171490	4.330423
H	1.316276	-1.364256	2.935081
C	1.544216	2.431264	3.566266
C	1.899251	1.537842	4.569725
H	2.096977	-0.534178	5.108042
H	1.606339	3.498806	3.754674
H	2.234557	1.909768	5.532351
C	1.582693	0.333049	-0.944974
C	2.859409	-0.235111	-0.819246
C	1.345188	1.132399	-2.081316
C	3.859715	-0.030430	-1.761941
H	3.083614	-0.849521	0.048653
C	2.350329	1.335641	-3.033284
C	3.603654	0.757789	-2.877382
H	4.837050	-0.481704	-1.623983
H	2.155061	1.955208	-3.903403
H	4.375134	0.927797	-3.621218
C	-1.358291	0.637958	0.143072
H	-1.886963	0.113225	-0.659893
H	-1.959648	0.500566	1.045199
H	-2.147850	2.911786	1.002724
C	0.292982	-1.985976	0.531408
H	-0.386337	-2.322125	1.321094
H	-0.080468	-2.390324	-0.414603
H	1.276085	-2.430531	0.712228
Rh	-1.291357	2.754855	-0.310802
H	-2.710595	2.411654	-0.887440
C	-1.674377	4.568937	-0.710893
O	-2.005075	5.638294	-0.944314
P	-0.260708	1.996320	-2.285992
H	0.062110	2.829567	-3.385797
H	-1.022352	1.042089	-3.004268
P	0.651836	3.154732	1.010756
H	0.637435	4.352213	1.763040
H	1.910191	3.359913	0.385228

Table S22. Cartesian coordinate of **TS(1)**.

	X	Y	Z
Si	0.377004	0.226273	0.426690
C	1.136835	1.065406	1.964960
C	1.838429	0.203131	2.825641
C	1.186865	2.444836	2.260366
C	2.579657	0.661581	3.907302
H	1.809593	-0.866054	2.646350
C	1.946209	2.900816	3.344711
C	2.646206	2.023775	4.161558
H	3.106065	-0.043741	4.542186
H	1.985948	3.963951	3.560953
H	3.230195	2.405251	4.992645
C	1.681959	0.456780	-0.954382
C	2.798376	-0.387500	-0.842128
C	1.691719	1.388311	-2.012520
C	3.877301	-0.323140	-1.715430
H	2.839295	-1.116313	-0.039339
C	2.777338	1.448896	-2.893021
C	3.868446	0.602343	-2.749270
H	4.721143	-0.992529	-1.583848
H	2.771458	2.170729	-3.703987
H	4.701977	0.668583	-3.440667
C	-1.397819	0.713263	0.039743
H	-1.749280	0.165743	-0.841527
H	-2.021022	0.400476	0.885421
H	-1.570923	1.781718	-0.131995
C	0.255914	-1.630614	0.759204
H	-0.403752	-1.814749	1.613342
H	-0.198836	-2.109072	-0.114195
H	1.201049	-2.142534	0.950808
Rh	-0.652978	4.054198	-0.786811
H	-1.298552	4.431222	-2.196715
C	-1.744769	5.467129	-0.274262
O	-2.441850	6.350284	-0.049569
P	0.325094	2.589592	-2.280318
H	0.831461	3.209289	-3.443962
H	-0.630624	1.759985	-2.917570
P	0.199204	3.740618	1.373437
H	-0.828614	3.863997	2.345403
H	0.951968	4.857507	1.813769

Table S23. Cartesian coordinate of **TS(2)**.

	X	Y	Z
Si	0.342563	0.677135	0.279277
C	1.265442	1.314832	1.853316
C	2.215614	0.487445	2.472587
C	1.041398	2.571395	2.439909
C	2.906004	0.884686	3.610768
H	2.430283	-0.489456	2.052654
C	1.718991	2.969287	3.596563
C	2.653821	2.128135	4.182621
H	3.642231	0.222047	4.054862
H	1.522039	3.943262	4.035585
H	3.185538	2.441803	5.074943
C	1.666513	0.523222	-1.147505
C	2.292391	-0.695745	-1.447656
C	2.107098	1.649950	-1.856332
C	3.303058	-0.784169	-2.400273
H	1.982889	-1.602707	-0.942646
C	3.130482	1.574396	-2.801380
C	3.730912	0.352442	-3.077165
H	3.754582	-1.747192	-2.617922
H	3.450042	2.465299	-3.334555
H	4.517847	0.286378	-3.821400
C	-1.713727	0.929896	0.468474
H	-1.742844	0.685510	1.532764
H	-2.462134	1.719024	0.326276
H	-2.053917	0.079848	-0.120706
C	0.102307	-1.182900	0.688728
H	-0.551427	-1.301072	1.556987
H	-0.370067	-1.704428	-0.151403
H	1.032925	-1.709013	0.915233
Rh	-0.752009	2.880288	-0.488656
H	-1.034028	2.224178	-1.903074
C	-2.111593	4.170410	-0.980084
O	-2.774129	5.010454	-1.393184
P	1.219052	3.204251	-1.500847
H	2.230418	4.006202	-0.902944
H	1.236546	3.839276	-2.766846
P	-0.138903	3.695365	1.607476
H	-1.103124	3.927386	2.624481
H	0.524609	4.942319	1.724047

Table S24. Cartesian coordinate of **TS(3)**.

	X	Y	Z
Si	0.462091	0.300499	0.374040
C	1.173680	0.967803	2.009719
C	1.513593	0.079835	3.039099
C	1.337993	2.345669	2.260723
C	1.979398	0.527760	4.271342
H	1.402204	-0.988642	2.883068
C	1.797311	2.795245	3.500575
C	2.117407	1.889941	4.505537
H	2.226594	-0.187177	5.049618
H	1.907827	3.859561	3.684953
H	2.473468	2.249593	5.465380
C	1.747535	0.665577	-1.000977
C	2.967957	-0.009177	-0.835011
C	1.619179	1.491185	-2.137036
C	4.017166	0.117280	-1.736969
H	3.111065	-0.646039	0.033683
C	2.674294	1.610704	-3.048170
C	3.869178	0.930506	-2.853484
H	4.947394	-0.414568	-1.565222
H	2.561840	2.250323	-3.918366
H	4.679262	1.040695	-3.566996
C	-1.252606	1.001718	0.183093
H	-1.803753	0.588989	-0.663308
H	-1.799858	0.674900	1.076724
H	-1.792558	2.362883	0.706392
C	0.364045	-1.584328	0.491495
H	-0.331377	-1.885920	1.281251
H	-0.021521	-1.980794	-0.453085
H	1.325298	-2.070485	0.680120
Rh	-0.990812	3.176688	-0.406393
H	-2.337227	2.967777	-1.193458
C	-1.597782	4.954972	-0.323027
O	-2.014842	6.024261	-0.291464
P	0.100850	2.499235	-2.382296
H	0.566809	3.343822	-3.422732
H	-0.657161	1.637897	-3.217701
P	0.917482	3.549267	0.943083
H	0.949793	4.747378	1.694782
H	2.186472	3.704599	0.323992