Supporting Information

Trop-Based Homobimetallic Rh Complexes: Influence of Ligands on the Structure and the Intramolecular Reactivity of Rh–H Intermediates

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General Remarks

All experiments were performed under Ar atmosphere using standard Schlenk and vacuum-line techniques or in an MBraun glove box. Glassware was flame dried on a Schlenk line or kept at 120 °C overnight prior to use. Solvents were dried and stored over 4 Å molecular sieves under Ar. Deuterated solvents were purchased from Eurisotop, degassed and distilled from the proper drying agent, and stored over 4 Å molecular sieves under Ar. The argon was provided by PANGAS and further purified with an MBraun >99 HP gas purification system. Degassed chloroform and *n*-pentane were used without purification. Air sensitive compounds were handled in a glovebox (MBraun lab master 130 or 150B-G). Small scale reactions were performed inside a glovebox. Chemicals were received from ABCR, Acros, Aldrich, Fluka, Lancaster or STREM. The following organic compounds and metal precursors were prepared by literature methods: ^{Br2}Tropketone[1], $[RhCl(C_2H_4)_2]_2$.[S2] IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500 - 4000 cm^{-1}). For solid compounds the ATR technique was used. The absorption bands are described as follows: very strong (vs), strong (s), middle (m), weak (w), or broad (br). Melting points were determined with a Büchi melting point apparatus and are not corrected. Samples were prepared in open glass capillaries. NMR measurements were carried out on Bruker Avance 200, 250, 300, 400, 500 MHz and 500 MHz cryoprobe spectrometers at room temperature (unless indicated otherwise). Chemical shifts δ are given as dimensionless numbers and the absolute values of the coupling constants are given in Hertz (Hz), the first atom mentioned in the subscript always refers to the atom that was used to observe the coupling. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), virtual triplet (vt), virtual doublet of doublets (vdd) and broad (br). NMR spectra were referenced to TMS (^{1}H, ^{13}C and ^{29}Si), $CFCl_3$ (^{19}F), H_3PO_4 (^{31}P) and $Rh(acac)_3$ (^{103}Rh). Quaternary carbons are indicated as C_{quat}, aromatic carbon and hydrogens as C_{ar} and CH_{ar}, benzylic carbons and hydrogens as C_{benz} and CH_{benz}, olefinic carbons and hydrogens as $C_{olefinic}$ and $CH_{olefinic}$. If several double bonds are present in the system, the carbons of the trop double bond are indicated as $C_{olefinetrop}$, unless noted otherwise. X-ray single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of a Bruker X8 APEX2 or D8-Venture diffractometer or on an Oxford Excalibur equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Preliminary data was collected to determine the crystal system. The space group was identified, and the data was processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXT) on OLEX2 completed by Fourier transformation and refined by full-matrix least-squares procedures.

Hydride Characterization by NMR: Complex **7** (15.0 mg, 13.9 µmol) and dppm (5.4 mg, 14 µmol) or **8** (20.0 mg, 13.7 µmol) were mixed in 0.6 mL CD_3CN in a J. Young tube. The resulting solution was freeze-pump-thawed 3 times, pressurized with 2 bar hydrogen and analyzed.

PHIP Experiments: Complex **7** (10.0 mg, 9.27 µmol) and (optionally) one equivalent of ligand (tricyclohexylphosphine, triazabycyclodecene (TBD), diphenylphosphine oxide or bis(diphenylphosphino)methane (dppm)) were dissolved in CD_3CN or THF-d_8. The solutions were transferred to medium-walled 5 mm NMR tubes (Wilmad glass P/N 503-PS-9) tightly connected with ¼ inch outer diameter PTFE tubes. Hydrogen gas enriched with parahydrogen up to 91 % using a Bruker parahydrogen generator BPHG 90 was bubbled through the solution located in an NMR tube inside a 300 MHz Bruker AV 300 NMR spectrometer using setup presented in Figure S7. H_2 gas flow rate (7 standard cm^3 per minute) was regulated with a mass flow controller (SmartTrak 50, Sierra Instruments, Monterey, CA). Hydrogen pressure was either 1 or 2 atm (in the former case safety valve was excluded from the setup presented in Figure S7), reaction temperature was 25 °C (unless otherwise specified). The effluent gas was dumped into a fume hood. ^{1}H NMR spectra were acquired using a π/4 radiofrequency (rf) pulse, which maximizes the PHIP signal in case of hyperpolarization in high magnetic field (PASADENA experiment).[S3] ^{1}H{^{31}P}PHIP experiments were performed with WALTZ-16 decoupling sequence applied on ^{31}P rf channel during signal acquisition on ^{1}H rf channel.

^{1}H PHIP NMR spectra simulations were based on the conventional spin density matrix calculations using a π/4 radiofrequency pulse as in the experiments. The spin system used for simulations consisted of three ^{1}H nuclei (two hydrides and one in a methylene group), three ^{31}P nuclei and two ^{103}Rh nuclei. J_{HP} and J_{HRh} couplings and the NMR line width were adjusted to get the best fit of experimental data.

Catalytic Hydrogenation: The catalyst, phenylacetylene and mesitylene standard were dissolved in CD_3CN (0.5 mL), for exact amounts see Table S2. The solution was transferred to a J. Young tube and the headspace was pressurized with 4.5 bar of hydrogen at ambient temperature and the reaction progress analyzed.

Synthesis and Characterisation

10,11-Dibromo-5H-dibenzo[a,d]cyclohepten-5-ol (2): A solution of sodium borohydride (0.99 g, 26.3 mmol) and potassium hydroxide (0.38 g, 6.7 mmol) in water (20 mL) was added dropwise to a suspension of **1** (10.00 g, 27.5 mmol) in methanol (200 mL). The resulting mixture was stirred for two hours at ambient temperature. The mixture was concentrated to 30 mL, diluted with water (>99 mL) and extracted with dichloromethane (3 × 75 mL). The combined organic phase was dried over magnesium sulfate and the solvent was evaporated. The resulting yellow solid was recrystallized from n-hexane to obtain pure **2** as microcrystalline solid (9.00 g, 89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.54 (d, J = 3.4Hz, 1H, OH), 5.57 (d, J = 3.4 Hz, 1H, CH_{benzyl}), 7.20 – 7.30 (m, 2H, CH_{ar}), 7.36 – 7.45 (m, 2H, CH_{ar}), 7.62 – 7.69 (m, 2H, CH_{ar}), 7.73 – 7.80 (m, 2H, CH_{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 69.9 (s, 1C, CH_{benzyl}), 120.4 (s, 2C, CH_{ar}), 125.6 (s, 2C, C_{alkene}), 126.5 (s, 2C, CH_{ar}), 130.0 (s, 2C, CH_{ar}), 130.3 (s, 2C, CH_{ar}), 132.5 (s, 2C, C_{quat}), 143.4 (s, 2C, C_{quat}). Mp: 166-169 °C. Anal. Calcd for $C_{15}H_{10}Br_2O$: C, 91.15; H, 4.94. Found: C, 90.73; H, 5.07.

10,11-Di-(trimethylsilyl)acetylene-5H-dibenzo[a,d]cyclohepten-5-ol (3): (Trimethylsilyl)acetylene (7.2 g, 10.4 mL, 73.3 mmol) was added via a syringe under argon to a solution of 10,11-dibromo-5H-dibenzo[a,d]cyclohepten-5-ol (**2**) (9 g, 24.5 mmol), $Pd(PPh_3)_4$ (1.4 g, 1.21 mmol) and CuI (0.24 g, 1.26 mmol) in a mixture of toluene (90 mL) and NEt_3 (90mL). The reaction mixture was stirred at 70°C for 12 hours and then filtered through Celite. Removing the solvent under reduced pressure left the crude product that was purified by column chromatography (Silica, n-hexane/CH_2Cl_2/Ethyl acetate: 6/1.8/0.6, R_f = 0.47). The product was obtained as a white powder by precipitation in *n*-pentane (25 mL) followed by filtration and drying under vacuum. Yield: 7.5 g (76 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.48 (s, 18 H, $Si(CH_3)_3$), 3.02 (d, $^3J_{HH}$ = 3.3 Hz, 1H, OH), 5.23 (d, $^3J_{HH}$ = 3.5 Hz, 1H, H_{benz}), 7.31 – 7.35 (m, 2H, H_{ar}), 7.35 – 7.47 (m, 2H, H_{ar}), 7.75 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}), 7.89 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 0.2 [s, 6C, $Si(CH_3)_3$], 69.8 (s, 1C, CH_{benz}), 103.8 (s, 2C, C≡*C*TMS, C_{quat}), 105.7 (s, 2C, *C*≡CTMS, C_{quat}), 120.9 (s, 2C, CH_{ar}), 126.4 (s, 2C, CH_{ar}), 128.4 (s, 2C, CH_{ar}), 129.2 (s, 2C, C_{quat}), 129.6 (s, 2C, CH_{ar}), 131.7 (s, 2C; C_{quat}), 142.9 (s, 2C, C_{quat}). ^{29}Si NMR (59.1 MHz, $CDCl_3$): δ (ppm) –17.6 [s, $Si(CH_3)_3$]. IR(ATR): 3352 (s, ν_{OH}), 3067 (w, ν_{CH}), 2957 (w, ν_{CH}), 2897 (w, ν_{CH}), 2132 (w, $\nu_{C\equiv C}$), 1244 (s), 1053 (m), 994(m), 838 (vs), 758 (s), 714 (m), 644 (w). M.p.: 167 °C. Anal. Calcd for $C_{25}H_{28}OSi_2$: C, 74.94; H, 7.04. Found: C, 74.91; H, 7.09.

10,11-Di-(trimethylsilyl)acetylene-5H-dibenzo[a,d]cyclohepten-5-Cl (4): A solution of **3** (1.66 g, 4.06 mmol) in 80 mL of CH_2Cl_2 was cooled to 0 °C. To this solution was added dropwise a solution of $SOCl_2$ (0.53 g, 0.32 mL, 4.5 mmol) and pyridine (0.35 g, 0.36 mL, 4.5 mmol) in 20 mL of CH_2Cl_2. After addition, the reaction solution was stirred for one hour at 0 °C and one hour at room temperature and the solvent was evaporated. The residue was suspended in toluene (100 mL). The resulting mixture was filtered over Celite and the toluene removed. Trituration with hexane (2 x 10 mL) gave the desired product as a slightly off-white powder Yield: 1.4 g (80 %). Endo and exo conformers are present in solution. NMR data of the major conformer: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.40 (s, 18H, $Si(CH_3)_3$), 6.10 (s, 1H, H_{benz}), 7.30 – 7.48 (m, 4H, H_{ar}), 7.75 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{ar}), 7.89 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H_{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 0.2 [s, 6C, $Si(CH_3)_3$], 60.0 (s, 1C, CH_{benz}), 104.1 (s, 2C, C≡*C*TMS), 105.8 (s, 2C, *C*≡CTMS), 127.1 (s, 2C, CH_{ar}), 128.4 (s, 2C, CH_{ar}), 129.3 (s, 2C, C_{ar}), 129.4 (s, 2C, CH_{ar}), 131.0 (s, 2C, CH_{ar}), 134.0 (s, 2C, C_{ar}), 139.2 (s, 2C, C_{ar}). NMR data of the minor conformer: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.39 (s, 18H, $Si(CH_3)_3$), 5.68 (s, 1H, H_{benz}), 7.30 – 7.48 (m, 4H, H_{ar}), 7.75 (d, $^3J_{HH}$ = 7.8 Hz, 2H, H_{ar}), 7.89 (d, $^3J_{HH}$ = 7.7 Hz, 2H, H_{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 0.1 (s, 6C, $Si(CH_3)_3$), 65.1 (s, 1C, CH_{benz}), 104.4 (s, 2C, C≡*C*TMS, C_{quat}), 105.1 (s, 2C, *C*≡CTMS, C_{quat}), 122.9 (s,

2C, CH_{ar}), 127.0 (s, 2C, CH_{ar}), 128.3 (s, 2C, CH_{ar}), 129.6 (s, 2C, C_{quat}), 129.7 (s, 2C, CH_{ar}), 132.3 (s, 2C, C_{quat}), 139.7 (s, 2C, C_{quat}). ^{29}Si NMR (59.1 MHz, $CDCl_3$): δ (ppm) −17.8 (br, $Si(CH_3)_3$). IR(ATR): 3066 (w, ν_{CH}), 2958 (w, n_{CH}), 2898 (w, ν_{CH}), 2134 (w, $\nu_{C\equiv C}$), 1247 (s), 1053 (m), 994 (m), 838 (vs), 757 (s), 696 (m), 63 1(w). M.p.: 68-72°C (Starting decomposition). Anal. Calcd for $C_{25}H_{27}ClSi_2$: C, 71.64; H, 6.49. Found: C, 74.76; H, 6.67. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{27}ClSi_2$: 418.1339; Found: 418.1334.

10,11-Di-(trimethylsilyl)acetylene-5H-dibenzo[a,d]cyclohepten-5-diphosphine (5): To a solution of diphenylphosphine (0.45 g, 0.42 mL, 2.4 mmol) in 3 mL of THF was added *n*-butyllitium (1.6 M solution in hexane, 1.02 g, 1.5 mL, 2.4 mmol) via syringe, giving a deep red solution. This solution was stirred at 65 °C for 30 minutes and then cooled to room temperature followed by addition of **4** (1 g, 2.39 mmol) in toluene (40 mL). The resulting orange reaction mixture was then stirred for 2 hours at room temperature before filtration through Celite. All volatiles were removed under reduced pressure and the resulting orange oil dissolved in Et_2O. The Et_2O was subsequently removed under vacuum to leave the fine yellow powder that was dissolved in MeOH (10 mL) and stirred vigorously until a white powder began to precipitate. The mixture was kept overnight in a fridge. The desired product was filtered and dried under vacuum. Yield: 0.85 g (63 %). Colorless single crystals were obtained from a hexane solution at low temperature. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.40 (s, 18 H, $Si(CH_3)_3$), 4.49 (d, $^2J_{PH}$ = 5.1 Hz, 1H, H_{benz}), 6.99 (d, $^3J_{HH}$ = 7.1 Hz, 2 H, H_{ar}), 7.10 – 7.40 (m, 14 H, H_{ar}), 7.85 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H_{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (ppm) 0.2 (s, $Si(CH_3)_3$), 56.3 (d, $^1J_{CP}$ = 21.6 Hz, 1C, CH_{benz}), 103.3 (s, 2C, C≡*C*TMS, C_{quat}), 106.4 (s, 2C, *C*≡CTMS, C_{quat}), 126.3 (d, $^4J_{CP}$ = 1.1 Hz, 2C, CH_{ar}), 127.9 (d, $^3J_{CP}$ = 6.4 Hz, 2C, CH_{ar}), 128.3 (s, 2C, CH_{ar}), 129.0 (d, $^3J_{CP}$ = 2.9 Hz, 2C, CH_{ar}), 129.2 (s, 2C, CH_{ar}), 130.3 (d, $^4J_{CP}$ = 1.2 Hz, 2C, CH_{ar}), 130.6 (d, J_{CP} = 6.2 Hz, 2C, C_{quat}), 133.6 (d, $^2J_{CP}$ = 19.6 Hz, 2C, CH_{ar}), 134.6 (d, J_{CP} = 4.3 Hz, 2C, C_{quat}), 138.2 (d, $^1J_{CP}$ = 20.1 Hz, 2C, C_{quat}), 141.2 (d, J_{CP} = 8.8 Hz, 2C, C_{quat}). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ (ppm) −13.2 (s, 1 P, PPh_2). ^{29}Si NMR (59.1 MHz, $CDCl_3$): δ (ppm) −17.6 (s, $Si(CH_3)_3$). IR(ATR): 3053 (w, ν_{CH}), 2958 (w, ν_{CH}), 2898 (w, ν_{CH}), 2132 (w, $\nu_{C\equiv C}$), 1247 (s), 1053 (m), 994 (m), 835 (vs), 757 (s), 703 (m). M.p.: 60-65 °C (decomp.). Anal. Calcd for $C_{37}H_{37}PSi_2$: C, 78.12; H, 6.56. Found: C, 77.91; H, 6.59.

[($^{\{(TMS)C\equiv C\}}_2$TropPPh$_2$)$_2$Rh$_4$(μ-Cl)$_4$] (6): [$Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$] (248 mg, 0.64 mmol), and **5** (400 mg, 0.70 mmol) were combined in a flask with 4 ml of benzene. After 15 minutes a precipitate started to appear. The reaction mixture was stirred for one hour and then kept in a fridge overnight. The orange precipitate was filtered, washed with n-hexane (20 mL) and dried under reduced pressure. Yield: 450 mg (83 %). Orange brown crystals were obtained by slow diffusion of pentane into solution of **6** in dichloromethane. ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 0.34 (s, 18H, $Si(CH_3)_3$), 4.79 (dd, $^2J_{PH}$ = 14.3 Hz, $^2J_{RhH}$ = 2.5 Hz, 1H, H_{benz}), 6.94 (d, $^3J_{HH}$ = 7.5 Hz, 2H, CH_{ar}), 7.09 – 7.54 (m, 14H, CH_{ar}), 7.92 (d, $^3J_{HH}$ = 7.6 Hz, 2H, CH_{ar}). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ (ppm) 0.8 (s, 6C, $Si(CH_3)_3$), 37.9 (d, *J* = 14.7 Hz, 2C, $C_{olefintrop}$), 50.5 (d, $^1J_{CP}$ = 26.3 Hz, 1C, CH_{benz}), 74.0 (d, *J* = 13.6 Hz,, 2C, C≡*C*TMS), 99.4 (d, *J* = 8.4 Hz, 2C, *C*≡CTMS), 126.2 (s, 2C, CH_{ar}), 127.3 (d, J_{CP} = 8.1 Hz, 4C, CH_{ar}), 127.7 (s, 4C, CH_{ar}), 128.6 (d, J_{CP} = 6.2 Hz, 2C, CH_{ar}), 129.9 (d, J_{CP} = 2.7 Hz, 2C, CH_{ar}), 130.4 (d, *J* = 43.3 Hz, 2C, C_{ar}), 133.7 (d, J_{CP} = 9.0 Hz, 4C, CH_{ar}), 135.5 (dd, *J* = 3.8 Hz, *J* = 1.7 Hz, 2C, C_{ar}), 135.7 (d, *J* = 8.1 Hz, 2C, C_{ar}). ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ (ppm) 99.3 (d, $^1J_{PRh}$ = 203.8 Hz, 1P, tropP). ^{103}Rh NMR (15.8 MHz, $CDCl_3$): δ (ppm) −6608 (d, $^1J_{RhP}$ = 204 Hz). ^{29}Si NMR (59.1 MHz, CD_2Cl_2): δ (ppm) −9.4 (s). IR(ATR): 3055 (w, ν_{CH}), 2955 (w, ν_{CH}), 2893 (w, ν_{CH}), 2360 (m, $\nu_{C\equiv C}$), 2340 (m, $\nu_{C\equiv C}$), 1942 (m, $\nu_{C\equiv C}$), 1483 (m), 1435 (m), 1245 (m), 1097 (m), 836 (vs), 756 (s), 741 (s), 691 (s). M.p.: decomposition > 220°C. Anal. Calcd for $C_{74}H_{74}Cl_4P_2Rh_4Si_4$: C, 52.56; H, 4.41. Found: C, 52.76; H, 4.52.

[($^{\{(TMS)C\equiv C\}}_2$TropPPh$_2$)Rh$_2$(OTf)$_2$] (7): Complex **6** (99 mg, 0.06 mmol) and AgOTf (61 mg, 0.24 mmol) were combined in a flask with 5 ml of dichloromethane. The reaction mixture was stirred overnight. The precipitate of silver(I) chloride was removed by filtration over Celite and washed with dichloromethane. After evaporation of the orange solvent under reduced pressure, the solid product is obtained without further purification. Yield: 105 mg (82 %). ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) 0.57 (s, 18 H, $Si(CH_3)_3$), 5.35 (dd, $^2J_{PH}$ = 15.5 Hz, $^2J_{RhH}$ = 2.7 Hz, 1H, H_{benz}), 7.18 (d, $^3J_{HH}$ = 6.4 Hz, 2H, CH_{ar}), 7.31 – 7.44 (m, 12H, CH_{ar}), 7.57 – 7.59 (m, 4H, CH_{ar}), 7.75 (d, $^3J_{HH}$ = 7.5 Hz, 2H, CH_{ar}). (500 MHz, CD_3CN): δ (ppm)

0.55 (s, 18H, $Si(CH_3)_3$), 5.15 (dd, $^2J_{PH}$ = 14.9 Hz, $^2J_{RhH}$ = 2.3 Hz, 1H, H_{benz}), 7.21 – 7.28 (m, 4H, CH_{ar}), 7.34 – 7.45 (m, 10H, CH_{ar}), 7.48-7.53 (m, 2H, CH_{ar}), 7.84 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH_{ar}).^{13}C NMR (75.5 MHz, CD_2Cl_2): *δ* (ppm) −0.6 (s, 6 C, $Si(CH_3)_3$), 37.0 (d, *J* = 16.9 Hz, 2C, $C_{olefintrop}$), 49.4 (d, $^1J_{CP}$ = 27.0 Hz, 1C, CH_{benz}), 65.3 (d, *J* = 16.8 Hz, 2C, C≡*C*TMS), 86.6 (d, *J* = 10.2 Hz, 2C, *C*≡CTMS), 126.8 (s, 2C, CH_{ar}), 128.1 (d, J_{CP} = 17.8 Hz, 4C, CH_{ar}), 128.4 (s, 4C, CH_{ar}), 128.4 – 128.6 (m, *J* = 2.6 Hz, 2C, C_{ar}), 129.8 (d, J_{CP} = 6.1 Hz, 2C, CH_{ar}), 131.3 (d, J_{CP} = 2.6 Hz, 2C, CH_{ar}), 133.2 (d, J_{CP} = 10.5 Hz, 4C, CH_{ar}), 133.2 (m, 2C, C_{ar}), 135.4 (dd, *J* = 3.8 Hz, *J* = 1.8 Hz, 2C, C_{ar}). (126 MHz, CD_3CN): *δ* (ppm) 0.5 (s, 6 C, $Si(CH_3)_3$), 38.1 (d, J_{CRh} = 14.9 Hz, 2C, $C_{olefintrop}$), 48.4 (d, $^1J_{CP}$ = 27.8 Hz, 1C, CH_{benz}), 75.4 (d, J_{CRh} = 11.9 Hz, 2C, C≡*C*TMS), 97.0 (dd, J_{CRh} = 7.7, 0.9 Hz, 2C, *C*≡CTMS), 127.8 (s, 2C, CH_{ar}), 129.0 (s, 2C, CH_{ar}), 129.4 (d, J_{CP} = 10.6 Hz, 4C, CH_{ar}), 129.5 (s, 2C, CH_{ar}), 129.5 (d, $^1J_{CP}$ = 46.8 Hz, C-P), 130.2 (d, J_{CP} = 6.8 Hz, 2C, CH_{ar}), 132.7 (d, J_{CP} = 2.8 Hz, 2C, CH_{ar}), 134.0 (d, J_{CP} = 9.1 Hz, 4C, CH_{ar}), 134.3 (d, J_{CP} = 7.7 Hz, 2C, C_{ar}), 136.4 (dd, *J* = 2.8 Hz, *J* = 1.3 Hz, 2C, C_{ar}).^{31}P NMR (121.5 MHz, CD_2Cl_2): *δ* (ppm) 95.9 (dd, $^1J_{PRh}$ = 211.1 Hz, $^2J_{PRh}$ = 2.3 Hz, 1P, tropP). (202.5 MHz, CD_3CN): *δ* (ppm) 104.6 (dd, $^1J_{PRh}$ = 185.6 Hz, $^2J_{PRh}$ = 4.6 Hz, 1P, tropP). ^{103}Rh NMR (15.8 MHz, $CDCl_3$): *δ* (ppm) −6513 (d, $^1J_{RhP}$ = 211 Hz). (15.8 MHz, CD_3CN): *δ* (ppm) −6852 (d, $^1J_{RhP}$ = 186 Hz). ^{19}F NMR (188.3 MHz, CD_2Cl_2): *δ* (ppm) −78.2 (s, OTf). ^{29}Si NMR (59.1 MHz, CD_2Cl_2): *δ* (ppm) −7.3 (s). IR(ATR): 3061 (w, ν_{CH}), 2956 (w, ν_{CH}), 2360 (m, $\nu_{C\equiv C}$), 2338 (m, $\nu_{C\equiv C}$), 1944 (m, $\nu_{C\equiv C}$), 1486 (m), 1436 (m), 1186 (vs), 992 (vs), 836 (vs), 759 (s), 744 (s), 689 (s). M.p.: decomposition > 220°C. Anal. Calcd for $C_{39}H_{37}F_6O_6PRh_2S_2Si_2$: C, 52.56; H, 4.41. Found: C, 52.76; H, 4.52.

[($^{\{(TMS)C\equiv C\}}_2$TropPPh$_2$)Rh$_2$(OTf)DPPM]OTf (8): Complex **7** (150 mg, 140 µmol) and bis(diphenylphosphino)methane (53.4 mg, 140 µmol) were dissolved in 4 mL of dichloromethane. The solution was left at room temperature for three hours and then layered with hexane (15 mL). The resulting needles were filtered, washed with hexane (3 x 5 mL) and dried under reduced pressure. Yield: 163 mg (80 %) ^{1}H NMR (500 MHz, CD_2Cl_2): *δ* (ppm) 0.15 (s, 9 H, $Si(CH_3)_3$), 0.48 [s, 9 H, $Si(CH_3)_3$]. 2.88 (q, *J* = 12.8 Hz, 1H, PCH_2P), 3.23 (q, *J* = 11.5 Hz, 1H, PCH_2P), 5.15 (dd, $^2J_{HP}$ = 14.5 Hz, $^3J_{HRh}$ = 2.1 Hz), 6.31 – 6.39 (m, 2H, CH_{ar}), 6.53 – 6.68 (m, 4H, CH_{ar}), 6.72 – 7.38 (m, 21H, CH_{ar}), 7.62 – 7.77 (m, 6H, CH_{ar}), 7.80 – 7.90 (m, 2H, CH_{ar}), 8.08 – 8.18 (m, 3H, CH_{ar}).^{1}H NMR (500 MHz, CD_3CN, 233 K): *δ* (ppm) 0.03 (s, 9H, $Si(CH_3)_3$), 0.48 (s, 9H, $Si(CH_3)_3$), 3.08 (m, PCH_2P), 3.18 (m, 1H, PCH_2P), 5.20 (d, 1H, $^2J_{HP}$ = 14.8 Hz), 6.26 (s br, 2H CH_{ar}), 6.53 – 7.75 (m, 34H, CH_{ar}), 8.05 (dd, *J* = 34.7, 7.9 Hz, 2H, CH_{ar}). ^{13}C NMR (128.8 MHz, CD_2Cl_2): *δ* (ppm) 0.7 (s, 6 C, $Si(CH_3)_3$), 29.0 (dd, $^1J_{CP}$ 27.2, 12.6 Hz, 1C, PCH_2P), 48.5 (d, J_{CRh} = 6.9 Hz, 1C, $C_{Olefinic}$) 48.7 (d, J_{CRh} = 7.2 Hz, 1C, $C_{Olefinic}$), 53.5 (1C, C_{benz}), 77.0 (dd, J_{CRh} = 14.2 Hz, J_{CP} = 4.7 Hz, 1C, C≡*C*TMS trans to DPPM), 90.4 (d, J_{CRh} = 17.6 Hz, 1C, C≡*C*TMS *cis* to DPPM), 91.2 (d, J_{CRh} = 9.5 Hz, 1C, *C*≡CTMS *cis* to DPPM), 109.1 (t, *J* = 8.2 Hz, 1C, *C*≡CTMS trans to DPPM), 125.0 (dd, *J* = 41.8, 2.1 Hz, 1C, C_{ar}), 127.3 – 136.4 (m, 46C, C_{ar}, CH_{ar}) 137.9 (s, 1C, C_{ar}). ^{13}C NMR (128.8 MHz, CD_3CN, 233 K): *δ* (ppm) 0.02 (s, 3C, $Si(CH_3)_3$), 0.4 (s, 3C, $Si(CH_3)_3$), 28.7 (s br, 1C, PCH_2P), 41.1 (s br, 1C, $C_{Olefinic}$), 42.1 (s br, 1C, $C_{Olefinic}$), 49.5 (d, $^1J_{CP}$ = 25.8 Hz, 1C, C_{benz}), 76.3 (s br, 1C, C≡*C*TMS trans to DPPM), 88.3 (d, J_{CRh} = 18.5 Hz, 1C, C≡*C*TMS *cis* to DPPM), 101.9 (s br, 1C, *C*≡CTMS *cis* to DPPM), 106.6 (s br, 1C, *C*≡CTMS trans to DPPM), 127.5 – 134.8 (broad m, 46C, C_{ar}, CH_{ar}) 136.2 (s, 1C, C_{ar}), 137.3 (s, 1C, C_{ar}). ^{31}P NMR (202.5 MHz, CD_2Cl_2): *δ* (ppm) 25.9 (ddd, $^1J_{PRh}$ = 142.9 Hz, $^3J_{PP}$ = 65.4 Hz, $^3J_{PP}$ = 3.4 Hz, 1P, tropP-Rh-Rh-P_{DPPM}), 32.6 (ddd, $^1J_{PRh}$ = 164.4 Hz, $^3J_{PP}$ = 65.4 Hz, $^2J_{PP}$ = 30.0 Hz, 1P, tropP-Rh-*cisP*$_{DPPM}$), 90.8 (dddd, $^1J_{PRh}$ = 183.1 Hz, $^2J_{PP}$ = 29.8 Hz, $^2J_{PRh}$ = 7.6 Hz, $^3J_{PP}$ = 3.2 Hz, 1P, tropP). ^{31}P NMR (202.5 MHz, CD_3CN, 233 K): *δ* (ppm) 19.0 (s br, 1P, tropP-Rh-Rh-P_{DPPM}), 28.8 (s br, 1P, tropP-Rh-*cisP*$_{DPPM}$), 91.8 (dm, $^1J_{PRh}$ = 163.0 Hz, 1P, tropP). ^{103}Rh NMR (15.8 Hz, CD_2Cl_2): *δ* (ppm) –7009 (dd, $^1J_{RhP}$ = 164, 181 Hz, 1Rh, tropP-Rh), –6683 (dd, $^1J_{RhP}$ = 164 Hz, $^2J_{RhP}$ = 10 Hz, 1Rh, tropP-Rh-*Rh*). ^{103}Rh NMR (15.8 Hz, CD_3CN): *δ* (ppm) –7225 (m, 1Rh, tropP-Rh) ^{19}F{^{1}H} NMR (282.4 MHz, CD_2Cl_2): *δ* (ppm) –78.8 (s, 3F, CF_3), -76.9 (s, 3F, CF_3), ^{19}F NMR (282.4 MHz, CD_3CN, 233 K): *δ* (ppm) –79.5 (s, 6F, CF_3). ^{29}Si NMR (59.6 MHz, CD_2Cl_2): *δ* (ppm) –9.1 (s, 1 Si, $SiMe_3$), –5.2 (s, 1Si, $SiMe_3$). ^{29}Si NMR (59.6 MHz, CD_3CN, 233 K): *δ* (ppm) –8.7, (s, 1Si, $SiMe_3$), –0.1 (s, 1Si, $SiMe_3$). IR(ATR): 3059 (w, ν_{CH}), 2955 (w, ν_{CH}), 2027 (w, $\nu_{C\equiv C}$), 1912 (w, $\nu_{C\equiv C}$), 1573 (w), 1484 (m), 1435 (m), 1314 (m), 1253 (s), 1148 (m), 1096 (s), 1000 (s), 843 (s), 740 (s), 690 (s), 631 (vs), 570 (m), 510 (s), 477 (m). HRMS (MALDI-TOF) m/z: $[M - 2\ OTf]^+$ Calcd for $C_{62}H_{59}P_3Rh_2Si_2$ 1158.1478; Found 1158.1470. Anal. Calcd for $C_{64}H_{59}F_6O_6P_3Rh_2S_2Si_2$: C, 52.75; H, 4.08. Found: C, 52.73; H, 4.08.

[($^{\{(TMS)C\equiv C(TMS)CH2C\}}$TropPPh$_2$)Rh$_2(OTf)_2$] (9): Complex **7** (10.0 mg, 9.27 µmol) was dissolved in dry CD_3CN and transferred to a J. Young tube. The tube was freed from Argon by three freeze pump thaw cycles and pressurized with 1 bar of hydrogen. After 15 minutes, the tube was freed from hydrogen by three freeze pump thaw cycles and filled with argon and NMR spectra recorded. ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 0.40 (s, 9 H, $CH_2Si(CH_3)_3$), 0.42 (s, 9 H, $C\equiv CSi(CH_3)_3$), 2.38 (d, $^2J_{HH}$ = 12.1 Hz, 1H, CH_2), 3.18 (d, $^2J_{HH}$ = 12.1 Hz, 1H, CH_2TMS), 5.47 (d, $^2J_{PH}$ = 16.7 Hz, 1H, CH_{benz}), 6.99 (d, J = 7.7 Hz, 1H, CH_{ar}), 7.11 (m, 1H, CH_{ar}), 7.18 – 7.31 (m, 5H, CH_{ar}), 7.38-7.59 (m, 9H, CH_{ar}), 7.75 (d, J = 7.6 Hz, 1H, CH_{ar}), 7.86 (d, J = 7.7 Hz, 1H, CH_{ar}). ^{13}C NMR (125 MHz, CD_3CN): δ (ppm) 0.5 (s, 3 C, $C\equiv CSi(CH_3)_3$), 1.1 (s, 3 C, $CH_2Si(CH_3)_3$), 35.5 (s, 1C, CH_2), 43.3 (d, $^1J_{CRh}$ = 11.0 Hz, 1C, C=*C*-C≡CTMS), 48.3 (d, J_{CRh} = 24.6 Hz, 1C CH_{benz}), 76.9 (d, J_{CRh} = 11.6 Hz, 1C, C≡*C*TMS), 98.8 (d, J_{CRh} = 7.6 Hz, 1C *C*=C-C≡C), 101.7 (d, J_{CRh} = 8.1 Hz, 1C,*C*≡CTMS), 120.8 (s, 1 C, C_{ar}), 123.4 (s, 1C, C_{ar}), 127.7 (d, J_{CP} = 45.9 Hz, 1C, C_{ar}), 127.8 (d, J_{CP} = 1.8 Hz, 1C, CH_{ar}), 129.4 (d, J_{CP} = 10.4 Hz, 2C, CH_{ar}), 129.7 (d, J_{CP} = 1.0 Hz, 1C, CH_{ar}). 129.8 (d, J_{CP} = 6.4 Hz, 1C, CH_{ar}), 129.9 (s, 2C, CH_{ar}), 130.0 (s, 1C, C_{ar}), 130.4, (d, J_{CP} = 1.2 Hz, 1C, CH_{ar}), 130.5 (s, 1C, CH_{ar}), 130.8 (d, J_{CP} = 36.8 Hz, 1C C_{ar}), 131.1 (s, 1C, CH_{ar}), 131.2 (d, J_{CP} = 6.5 Hz, 1C, CH_{ar}), 132.3 (d, J_{CP} = 2.9 Hz, 1C, C_{ar}), 132.7 (d, J_{CP} = 8.3 Hz, 2C, CH_{ar}), 132.7 (d, J_{CP} = 2.7 Hz, 2C, CH_{ar}), 134.8 (d, J_{CP} = 9.8, 2C, CH_{ar}), 137.0 (d, J_{CP} = 2.9 Hz, 1C, C_{ar}), 141.6 (s, 1C, C_{ar}), 171.1 (dd, J_{CRh} = 33.9, 11.1 Hz, 1C. $C_{Carbene}$). ^{31}P NMR (202.4 MHz): δ (ppm) 59.7 (dd, $^1J_{PRh}$ = 127.2 Hz, $^2J_{PRh}$ = 18.4 Hz). ^{103}Rh NMR (15.8 Hz, CD_3CN): δ (ppm) –7184 (d, $^1J_{RhP}$ = 126 Hz, 1Rh, tropP-Rh), –6733 (s, 1Rh, tropP-Rh-*Rh*) ^{19}F NMR (188.3 MHz, CD_3CN): δ (ppm) –79.2 (s, OTf).

[($^{\{(TMS)C=C,(TMS)CH2C\}}$TropPPh$_2$)Rh$_2(OTf)_2$] (10): Complex **7** (20 mg, 18.5 µmol) was dissolved in 0.5 mL CD_3CN in a J. Young tube. The tube was freed from argon by three freeze pump thaw cycles and pressurized with 2 bar of hydrogen. The tube was constantly shaken for 20 h. The tube was then freed from hydrogen by three freeze pump thaw cycles and filled with argon. NMR was recorded. ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) 0.01 (s, 9H, $=CHSiCH_3)_3$), 0.40 (s, 9H, $CH_2Si(CH_3)_3$), 1.99 (d, $^2J_{HH}$ = 13.1 Hz, 1H, C*H*$_2$TMS), 2.58 (d, $^3J_{HH}$ = 11.3 Hz, 1H, CH=C*H*TMS), 3.03 (d, $^2J_{HH}$ = 13.1 Hz, 1H, C*H*$_2$TMS), 5.07 (dt, $^3J_{HH}$ = 11.3 Hz, J = 2.9 Hz, 1H, C*H*=CHTMS), 5.42 (d, $^2J_{HP}$ = 15.4 Hz, 1H, CH_{benz}), 6.92 (d, J = 7.7 Hz, 1H, CH_{ar}), 7.01 (td, J = 7.6, 1.1 Hz, 1H, CH_{ar}), 7.12-7.54 (m, 14 H, CH_{ar}), 7.68 (d, J = 7.5, 1H, CH_{ar}), 7.80 (d, J = 7.8 Hz,1H, CH_{ar})). ^{13}C NMR (125 MHz, CD_3CN): δ (ppm) 1.4 (s, 3 C, $CH_2Si(CH_3)_3$), 1.7 [s, 3C, $=CHSi(CH_3)_3$], 36.7 (s, 1C, CH_2), 48.3 (d, $^1J_{CP}$ = 25.0 Hz, 1C, CH_{bnez}), 57.3 (d, J_{CRh} = 15.6 Hz, 1C, =CHTMS), 62.9 (d, J_{CRh} = 10.8 Hz, 1C, C=*C*-CH=), 81.5 (dd, J_{CRh} = 12.4, 2.7 Hz, 1C, *C*H=CHTMS), 100.0 (d, J_{CRh} = 7.1 Hz, 1C, *C*=C-CH=), 127.0 (s, 1C, CH_{ar}), 128.6 (d, $^1J_{CP}$ = 42.0 Hz, 1C, C_{ar}), 129.1 (s, 1C, CH_{ar}) 129.2 (d, J_{CP} = 10.2 Hz, 1C, CH_{ar}), 129.5 (d, J_{CP} = 5.9 Hz, 1C, CH_{ar}), 129.6 (s, 2C, CH_{ar}), 129.8 (d, J_{CP} = 26.8 Hz, 1C, CH_{ar}) 131.0 (d, J_{CP} = 5.8 Hz, 1C, CH_{ar}), 131.3 (s, 1C, CH_{ar}), 131.8 (s, 1C, CH_{ar}), 132.2 (s, 1C, C_{ar}), 132.4 (s, 1C, CH_{ar}), 132.7 (d, J_{CP} = 8.6 Hz, 4C, CH_{ar}), 132.9 (s, 1C, CH_{ar}), 134.9 (d, J_{CP} = 10.0 Hz, 4C, CH_{ar}), 136.9 (d, J_{CP} = 11.0 Hz, 1C, C_{ar}), 138.8 (d, J_{CP} = 1.8 Hz, 1C, C_{ar}), 141.7 (s, 1C, C_{ar}), 166.3 (dd, J_{CRh} = 35.7, 11.2 Hz, 1C, $C_{Carbene}$). ^{31}P{^{1}H} NMR (202.4 MHz, CD_3CN): δ (ppm) 67.0 (dd, $^1J_{PRh}$ = 136.0 Hz, $^2J_{PRh}$ = 7.1 Hz). ^{29}Si NMR: (59.1 MHz, , CD_3CN): δ (ppm) 1.2 (s, 1 Si, $=CHSiCH_3$), 1.4 (s, 1 Si, CH_2SiCH_3) ^{103}Rh NMR (15.8 Hz, CD_2Cl_2): δ (ppm) –7163 (d, $^1J_{RhP}$ = 136 Hz, 1Rh, tropP-Rh), –7066 (s, 1 Rh, tropP-Rh-*Rh*) ^{19}F NMR (188.3 MHz, CD_3CN): δ (ppm) –78.2 (s, OTf).

[($^{\{(TMS)C\equiv C\}}$$_2$TropPPh$_2$)Rh$_2H_2$DPPM]OTf$_2$ (11): Complex **8** (20.3 mg, 13.9 µmol) was dissolved in 0.5 mL CD_3CN and pressurized in a J-young NMR tube with 4.6 bar hydrogen gas. The resulting equilibrium between **8** and **10** contained the two substances in a 1:1 ratio. NMR data of **10**: ^{1}H NMR (500 MHz, CD_3CN, 233 K): δ (ppm) -20.18 (m br, 1H, H_b), -16.40 (m br, 1H, H_a), 0.41 (s, 9H, $Si(CH_3)_3$), 0.4 (s, 9H, $Si(CH_3)_3$), 2.67 (q, J = 12.8 Hz, 1H, PCH_2P), 3.04 (m, 1H, PCH_2P), 5.26 (d, $^2J_{PH}$ = 14.5 Hz, 1H CH_{benz}), 5.9) (m, 2H, CH_{ar}), 6.27 (s br, 2H, CH_{ar}), 6.80 – 7.77 (m, 30H, CH_{ar}), 8.04 (d, J = 8.2 Hz, 2H, CH_{ar}), 8.30 (d, J = 8.1 Hz, 2H, CH_{ar}). ^{13}C NMR (125 MHz, CD_3CN, 233 K): δ (ppm) –0.7 (s, 3C, $Si(CH_3)_3$), 0.7, (s, 3C, $Si(CH_3)_3$), 26.3 (s, 1C, PCH_2P), 53.4 (d, $^1J_{CP}$ = 24.7 Hz, 1C, CH_{benz}), 62.7 (s br, 1C, C_{olefin} 80.6 (s br, 1C TMS*C*≡C), 76.9 (d, J_{CRh} = 11.6 Hz, 1C, TMS*C*≡C), 89.8 (d, J_{CRh} = 7.6 Hz, 1C, *C*≡CTMS), 101.7 (d, J_{CRh} = 8.1 Hz, 1C, *C*≡CTMS). Note that the aromatic region appears as a multiplet due to many overlapping signals and no assignment could be made. ^{31}P NMR (202.4 MHz, CD_3CN, 233 K): 101 (d, $^1J_{PRh}$ = 195 Hz, 1 P, TropPPh$_2$), 53 ppm (m, 1 P, TropP-Rh-P_{DPPM}) 36 ppm (d, $^1J_{PRh}$ = 140 Hz, 1 P, TropP-Rh-Rh-P_{DPPM}). ^{103}Rh NMR (15.8 Hz, CD_3CN, 233 K) δ (ppm): –7630 (d, $^1J_{RhP}$ = 125 Hz, TropP-

Rh-*Rh*), –7758 (dd, $^{1}J_{RhP}$ = 192, 144 Hz, TropP-Rh)^{19}F NMR (188.3 MHz, CD_3CN, 233 K): *δ* (ppm) –79.5 (s, OTf).

[{(TMS)C≡C}$_2$TropPPh$_2$RhPPh$_3$]OTf (12): [$Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4$] (17.1 mg, 0.044 mmol), **5** (50 mg, 0.088 mmol) and triphenlyphosphine (23 mg, 0.088 mmol) were combined in a flask and flushed with dichloromethane (10 mL). The orange brown solution was stirred for 15 minutes. The silver(I) trifluoromethanesulfonate (22.6 mg, 0.088 mmol) was added to the solution and the mixture is stirred for 1 hour. The precipitate of silver(I) chloride was removed by filtration over celite and washed dichloromethane. The orange brown filtrate was removed under reduced pressure. Then the product was washed with *n*-hexane (10 mL) and dried under vacuum. Yield: 90 mg (94%). Orange crystals were obtained by slow diffusion of hexane into solution of **12** in THF.
^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 0.18 (s, 18H, $Si(CH_3)_3$), 4.91 (d, $^{2}J_{PH}$ = 12.6 Hz, 1H, CH_{benz}), 6.99 – 7.37 (m, 31H, CH_{ar}), 7.98 (d, $^{3}J_{HH}$ = 7.1 Hz, 2H, CH_{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): *δ* (ppm) 0.2 (s, 6C, $Si(CH_3)_3$), 55.0 (d, $^{1}J_{CP}$ = 26.5 Hz, 1C, CH_{benz}), 78.6 [d, $^{1}J_{CRh}$ = 6.1 Hz, 1C, $CH(CH_3)_2$], 78.7 (d, $^{1}J_{CRh}$ = 5.9 Hz, 1C, $C_{olefintrop}$), 82.6 (d, $^{1}J_{CRh}$ = 6.4 Hz, 1C, $C_{olefintrop}$), 100.6 (vt, *J* ≈ 1.3 Hz, 2C, *C*≡CTMS, C_{quat}), 117.3 (dd, *J* = 7.6 Hz, *J* = 0.8 Hz, 2C, C≡*C*TMS, C_{quat}), 126.6 (ddd, *J* = 1.5 Hz, *J* = 2.3 Hz, *J* = 49.8 Hz, 2C, C_{quat}), 128.4 (d, J_{CP} = 10.7 Hz, 4C, CH_{ar}), 128.5 (m, 4C, CH_{ar}), 128.7 (d, J_{CP} = 10.8 Hz, 6C, CH_{ar}), 129.0 (d, J_{CP} = 6.9 Hz, 2C, CH_{ar}), 130.0 (s, 2C, CH_{ar}), 130.3 (vdd, *J* ≈ 1.1 Hz, *J* ≈ 3.35 Hz, 2C, C_{quat}), 131.0 (dd, *J* = 1.1 Hz, *J* = 46.4 Hz, 3C, C_{quat}), 131.4 (d, J_{CP} = 2.6 Hz, 3C, CH_{ar}), 131.8 (d, J_{CP} = 2.7 Hz, 2C, CH_{ar}), 133.5 (d, J_{CP} = 10.2 Hz, 4C, CH_{ar}), 134.3 (d, J_{CP} = 13.1 Hz, 6C, CH_{ar}), 138.9 (vdd, *J* ≈ 1.1 Hz, *J* ≈ 3.35 Hz, 2C, C_{quat}). ^{31}P NMR (121.5 MHz, $CDCl_3$): *δ* (ppm) 30.7 (dd, 1 P, $^{1}J_{RhP}$ = 183.2 Hz, $^{2}J_{PP}$ = 34.0 Hz, PPh_3), 107.7 (dd, $^{1}J_{RhP}$ = 227.5 Hz, $^{2}J_{PP}$ = 34.0 Hz, 1P, PPh_2). ^{103}Rh NMR (15.8 MHz, $CDCl_3$): *δ* (ppm) –8116 (dd, $^{1}J_{RhP}$ = 183 Hz, 228 Hz). ^{29}Si NMR (59.1 MHz, $CDCl_3$): *δ* (ppm) –12.3 (s). ^{19}F NMR (188.3 MHz, $CDCl_3$): *δ* (ppm) –78.4 (s). IR(ATR): 3056(w, n_{CH}), 2957(w, v_{CH}), 2899(w, v_{CH}), 2360(w, $v_{C\equiv C}$), 2338(w, $v_{C\equiv C}$), 2122(w, $v_{C\equiv C}$), 1435 (s), 1254(s), 1145(m), 1028(m), 839(vs), 742(s), 690(m), 633 (s). M.p.: 205°C (Starting decomposition). Anal. Calcd for $C_{56}H_{52}F_3O_3P_2RhSSi_2$: C, 62.10; H, 4.84. Found: C, 61.96; H, 476.

Relevant Orbitals for the Intermetallic Bond in **8**

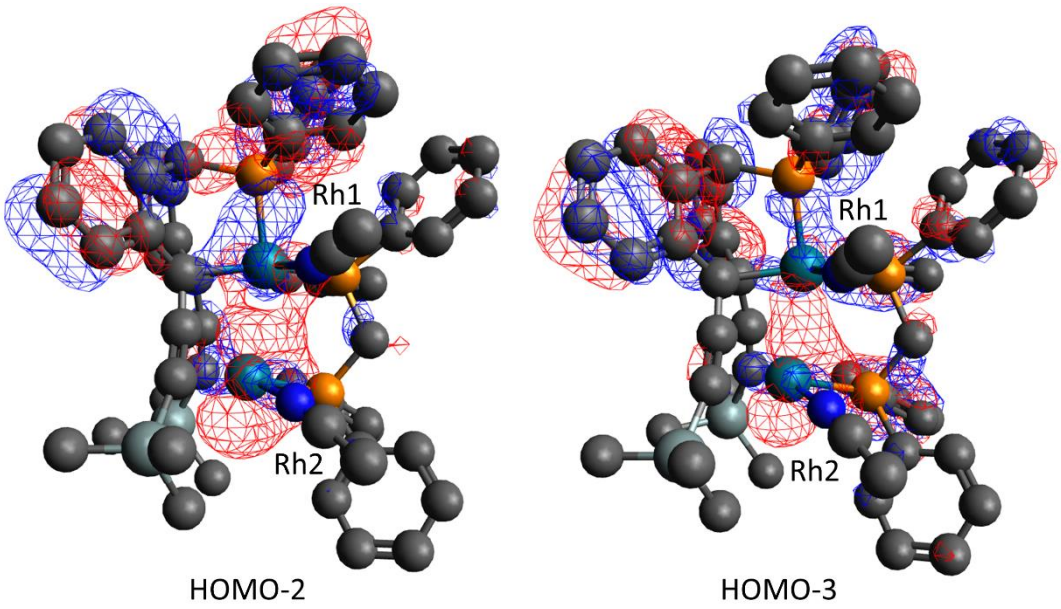


Figure S1. Calculated Orbitals for **8** relevant for the description of the intermetallic bond. Although delocalized over large parts of the ligands, the two orbitals still show an overlap between two metal orbitals. The larger contribution of Rh2 to the orbital indicates a dative bond from Rh2 to Rh1.

2D NMR data for species **9** and **10**

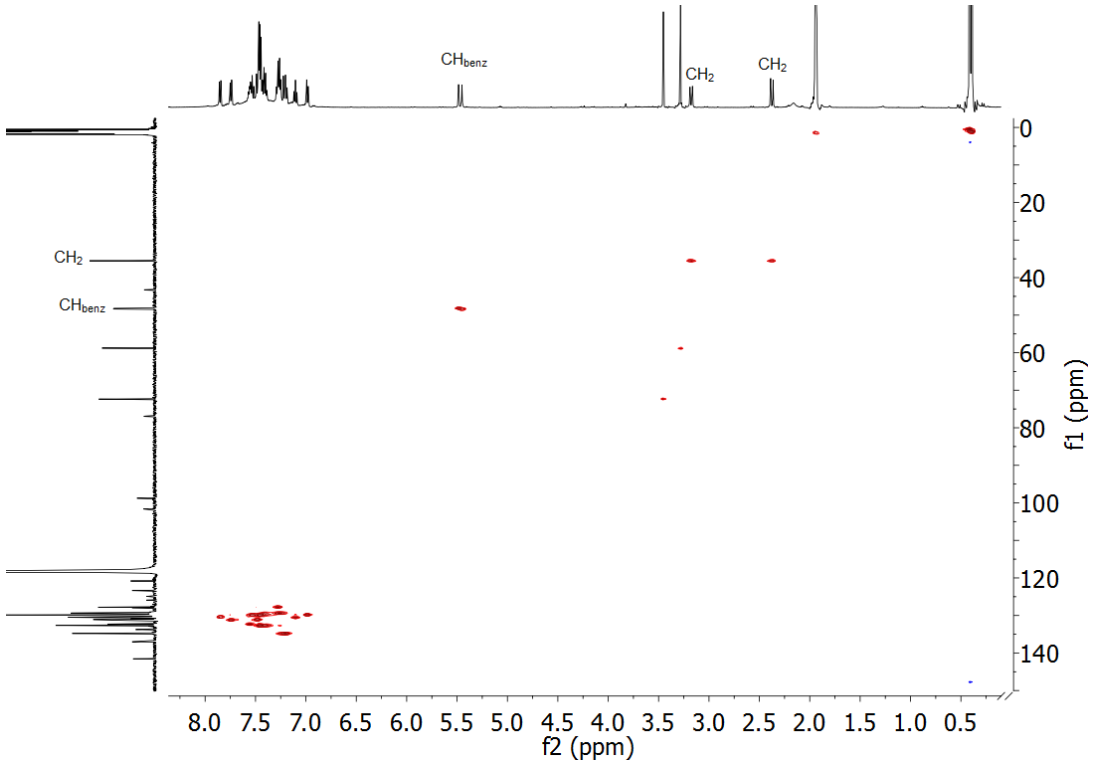


Figure S2. ^{1}H-^{13}C HSQC spectrum of **9** in CD_3CN.

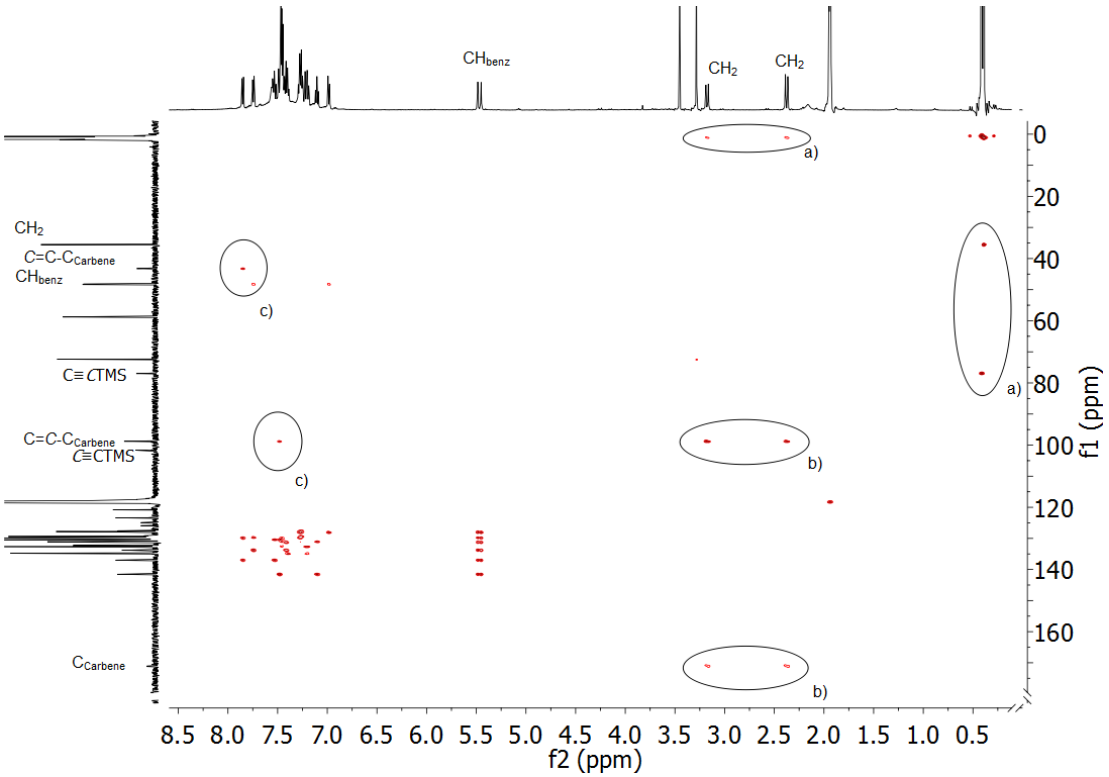


Figure S3. ^{1}H-^{13}C HMBC spectrum of **9** in CD_3CN. Cross peaks relevant for the assignment of a) the TMS region, b) coupling of the methylene group to the carbene and C=*C*-$C_{Carbene}$, and c) C=C signals coupling to the aromatic protons.

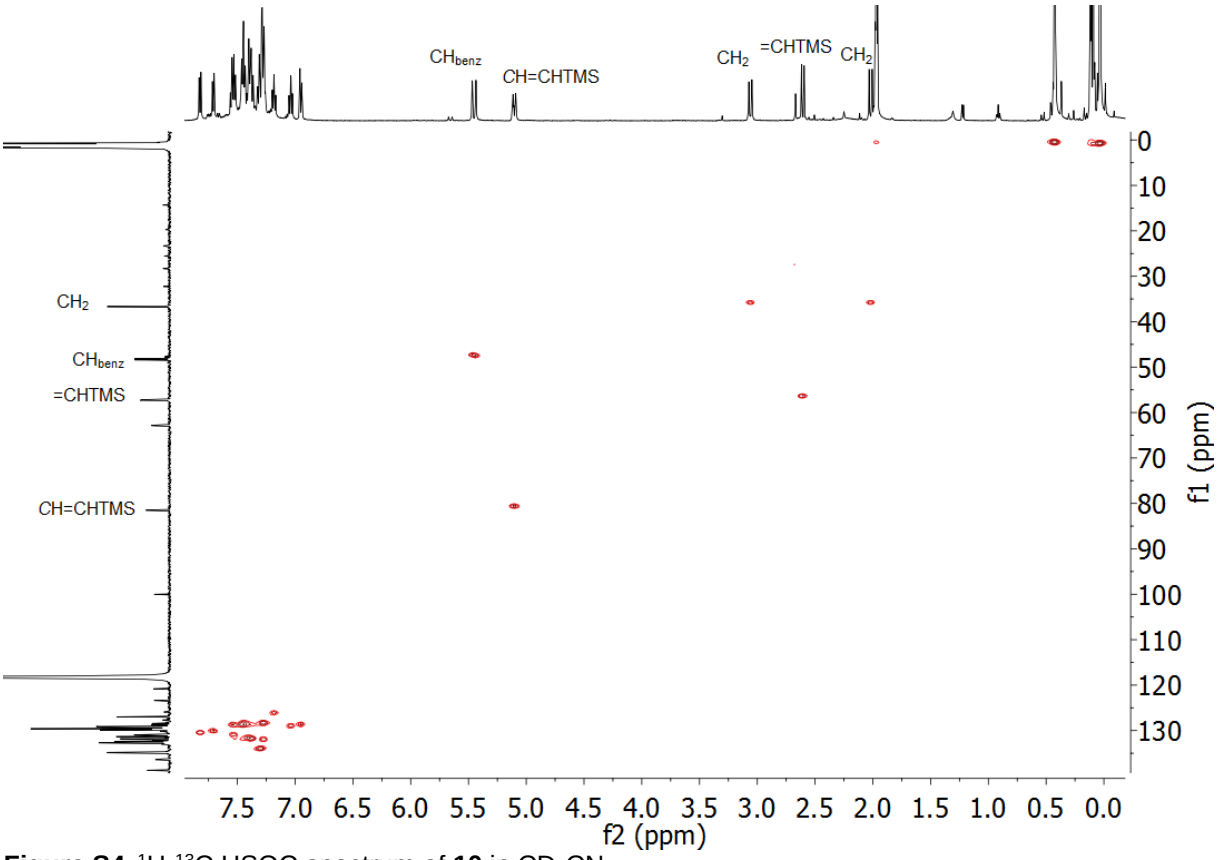


Figure S4. ^{1}H-^{13}C HSQC spectrum of **10** in CD_3CN.

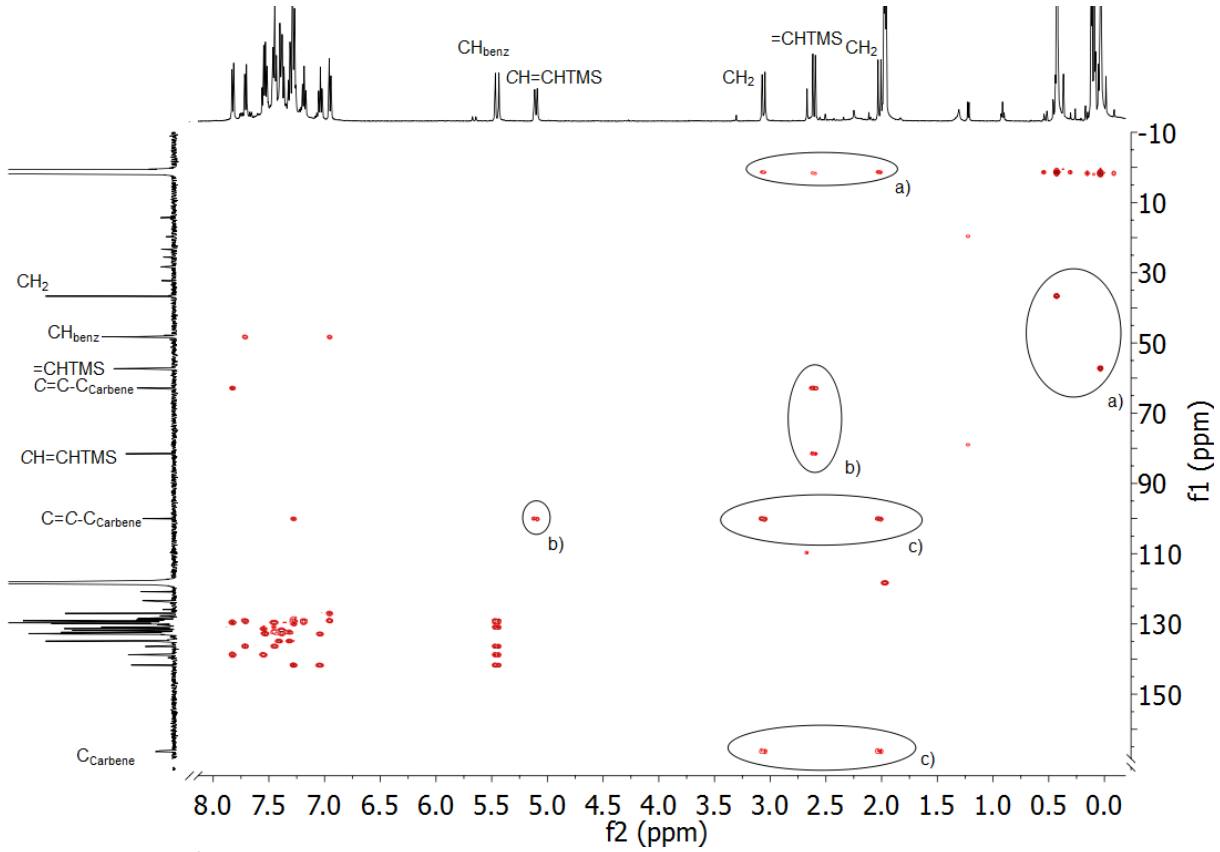


Figure S5. ^{1}H-^{13}C HMBC spectrum of **10** in CD_3CN. Cross peaks relevant for the assignment of a) signals coupled with the TMS region, b) signals coupling to the newly formed alkene CH's: cross peaks to trop-C=C carbons, c) coupling of the methylene group with carbene and C=*C*-$C_{Carbene}$ carbons.

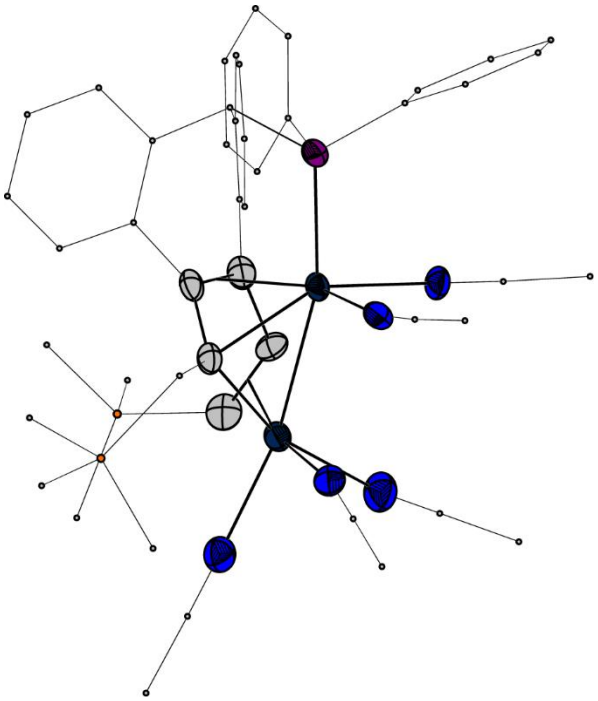


Figure S6. Crystal structure of **10**, triflate anions and solvent molecules are omitted for clarity. The structure is of poor quality, bond length and angles are therefore not discussed.

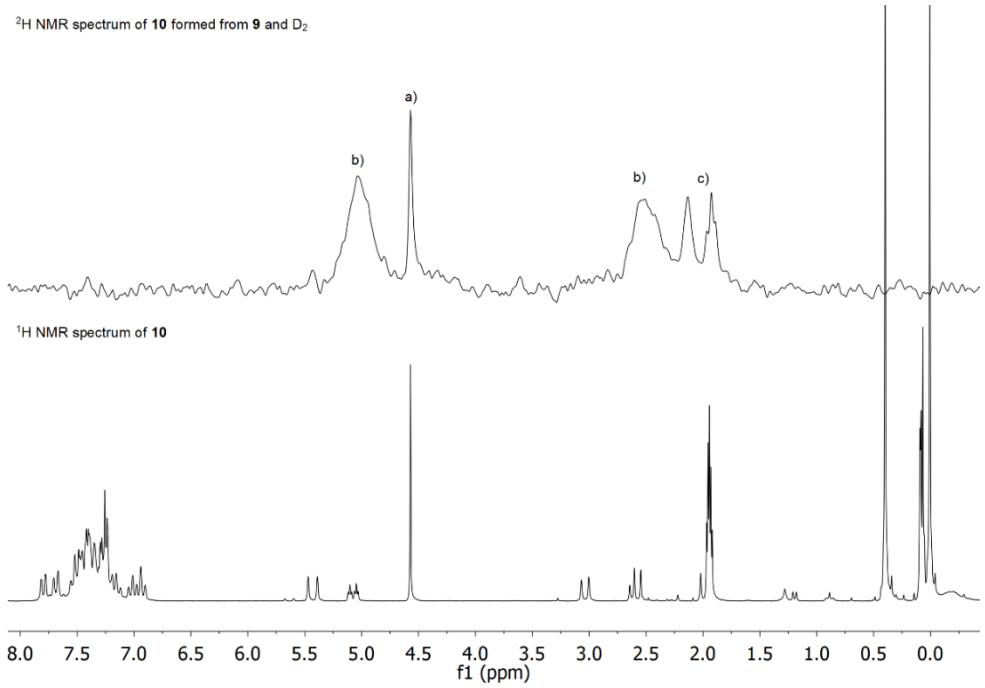


Figure S7. Top: ^{2}H NMR spectrum of **10** formed from **9** (20.0 mg, 18.5 µmol) in 0.5 mL acetonitrile in a J. Young NMR tube pressurized with 3 bar D_2 after 24 h, a) D_2, b) signals corresponding to the formed alkene C-D bonds, c) residual water (left) and solvent (acetonitrile, right). No deuterium label was detected on the methylene group.

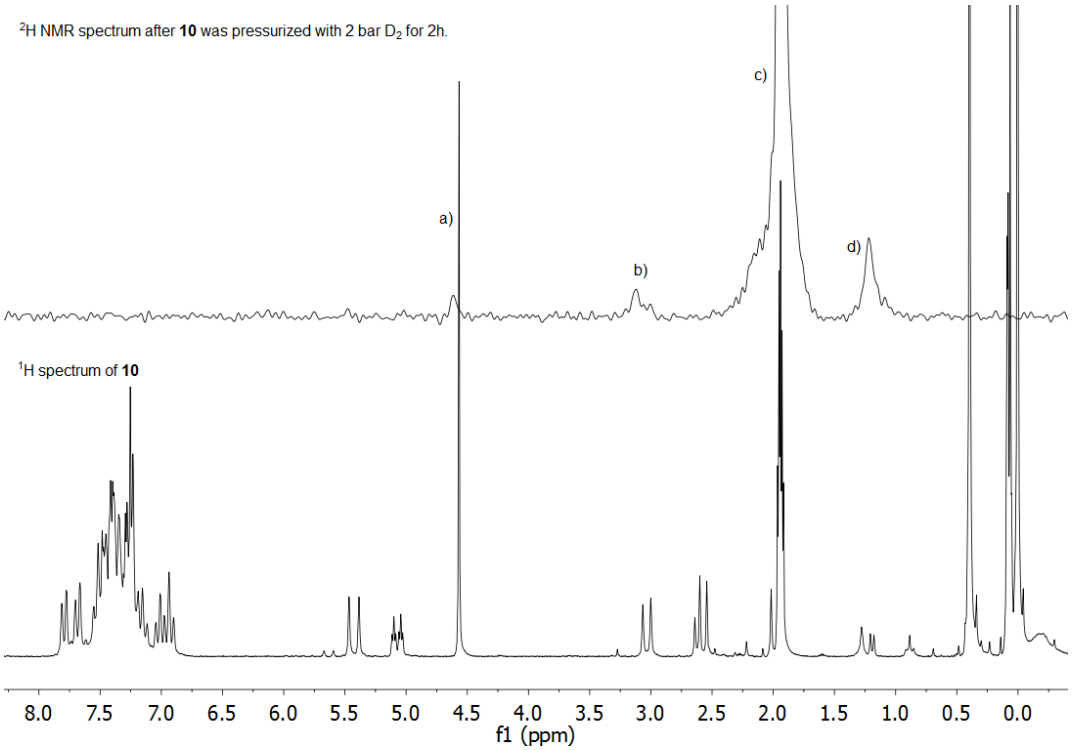


Figure S8. Top: ^{2}H NMR spectrum after **10** was exposed to 2 bar D_2 for 2 h in 0.5 mL acetonitrile in a J. Young NMR tube, a) D_2, b) signal could occur from minor H/D scrambling or unknown impurity, c) solvent (acetonitrile), d) water. Bottom: ^{1}H NMR spectrum of **10**. No deuterium label on the olefinic positions was detected.

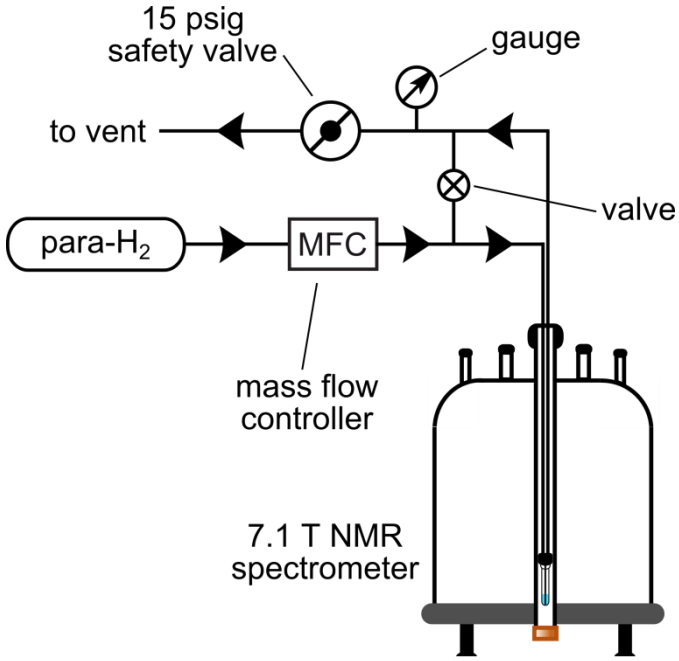


Figure S9. Scheme of the setup used for PHIP experiments**.**

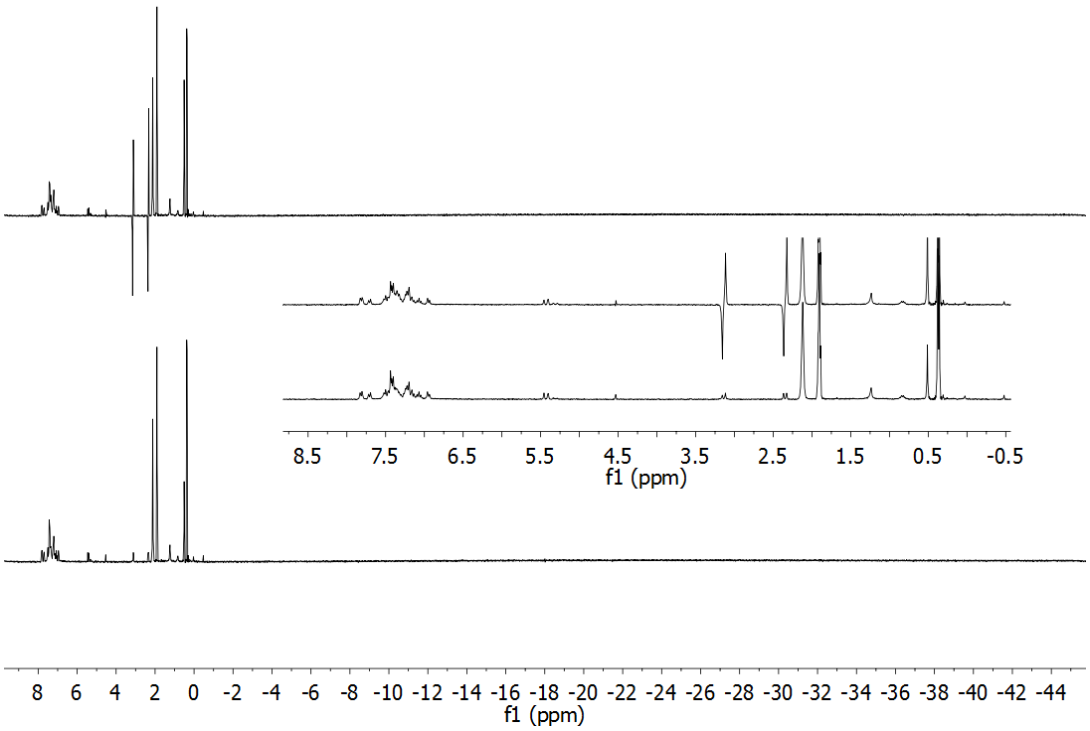


Figure S10. ^{1}H PHIP spectrum acquired after bubbling of parahydrogen at 1 atm through the solution of **7** for 10 seconds in CD_3CN without any ligand (top) and corresponding thermal spectrum after relaxation of hyperpolarization (bottom). The observed PHIP signals (2.38 ppm (J_{HH} = 12.1 Hz), 3.18 (J_{HH} = 12.1 Hz)) are assigned to species **9**. The absence of signals of hyperpolarized product **10** is due to its slow formation rates compared to the PHIP experiment time.

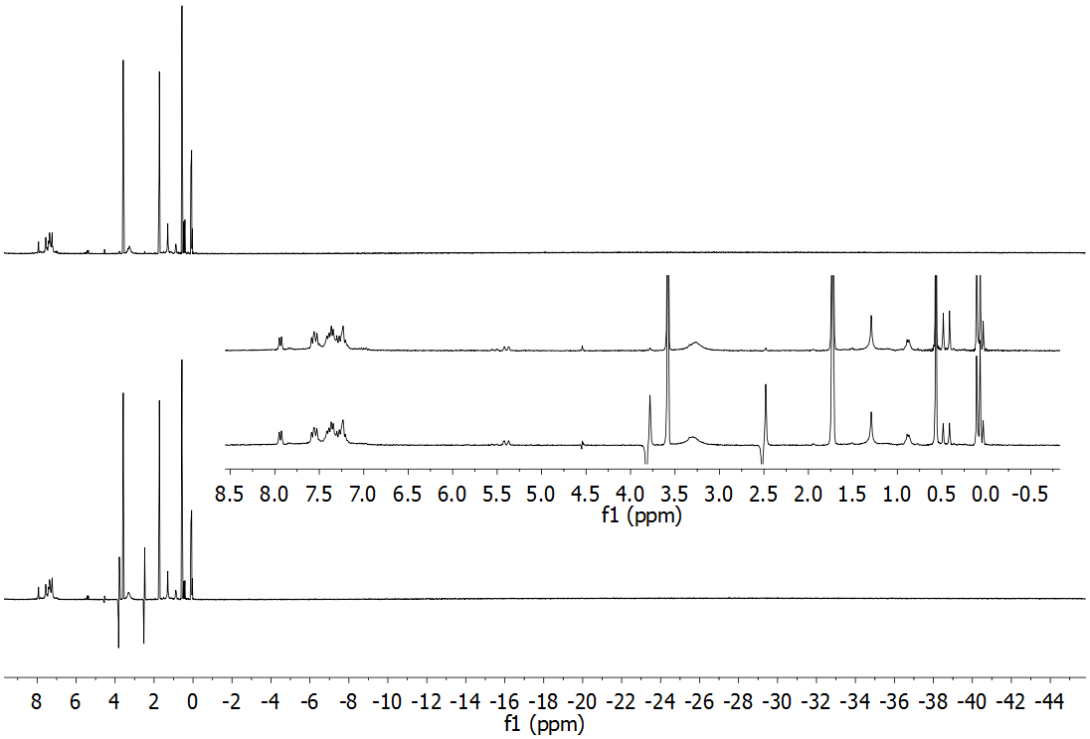


Figure S11. ^{1}H PHIP spectrum acquired after bubbling of parahydrogen at 1 atm through the solution of **7** in THF-d_8 without any ligand (bottom) and corresponding thermal spectrum after relaxation of hyperpolarization (top). The observed PHIP signals (2.49 ppm (J_{HH} = 12.3 Hz), 3.78 (J_{HH} = 12.3 Hz)) are assigned to species **9**. A small orthohydrogen signal at 4.52 ppm with a PNL (partially negative lineshape) indicates reversible H_2 activation.[S1]

NMR Characterisation of **11**

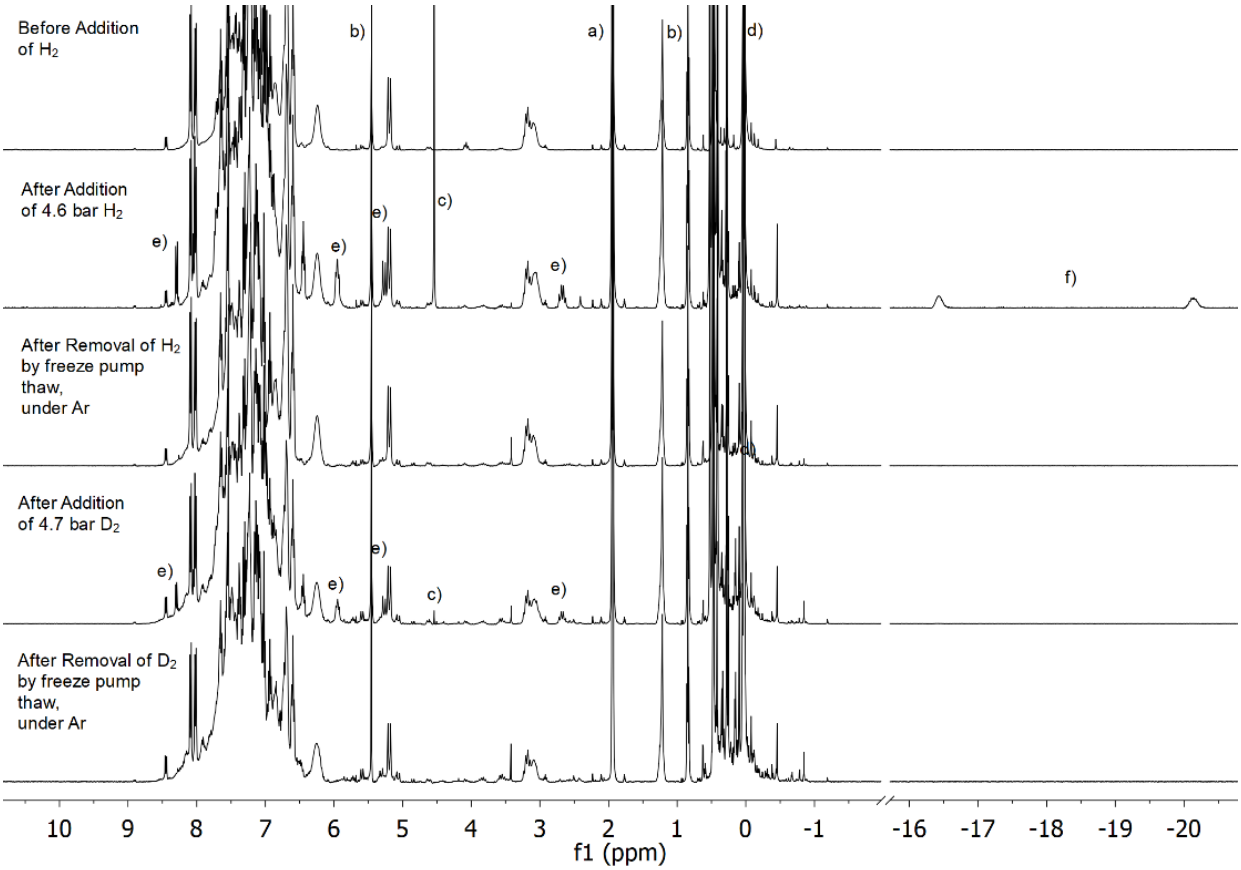


Figure S12. ^{1}H NMR spectra (from top to bottom) of 1) **8** in CD_3CN, 2) same after addition of 4.6 bar H_2, 3) after three freeze pump thaw cycles, under argon, 4) after addition of 4.7 bar D_2, 5) after three freeze pump thaw cycles, under argon; a) solvent residual signal, b) inert solvents: dichloromethane and hexane, c) H_2, d) TMS region, see Figure S10 for the details, e) characteristic signals of **11**, f) characteristic hydride signals.

The experiment shows that the formation of the hydride **11** is fully reversible.

Experimental details: **8** (20.8 mg, 14.4 µmol) was dissolved in 0.5 mL CD_3CN and added to a J-young NMR tube. Gasses were pressurized at room temperature and were removed by three freeze pump thaw cycles and the tubes were filled with argon to the atmospheric pressure.

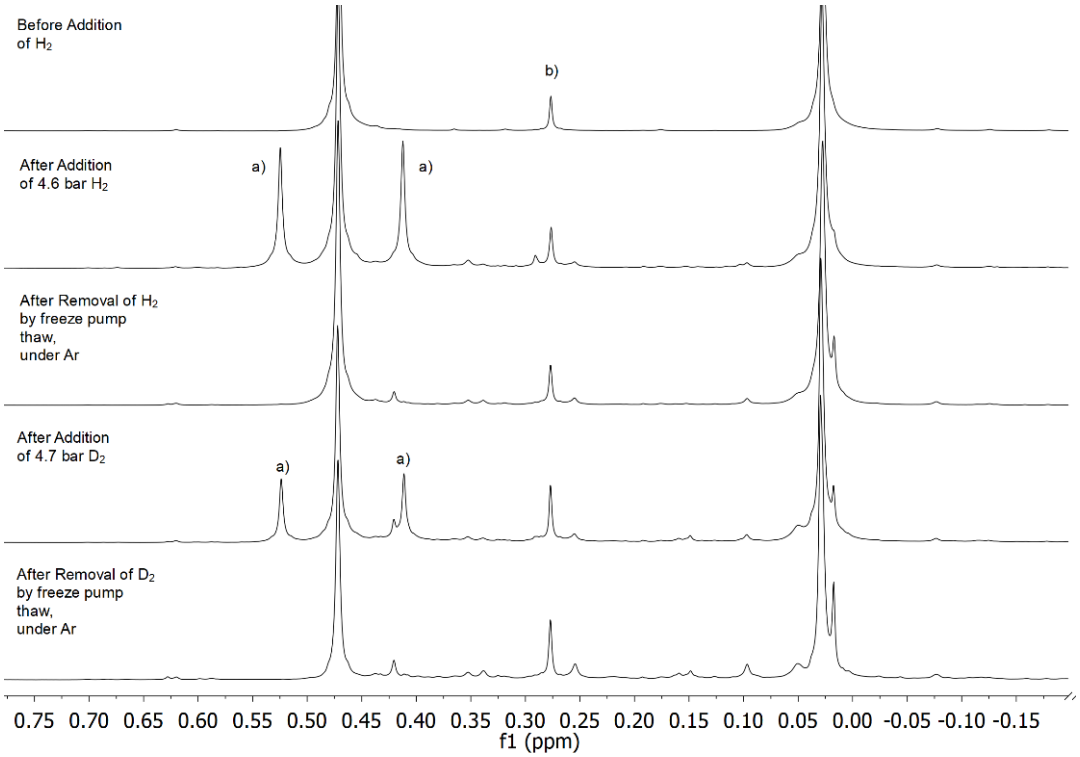


Figure S13. Magnification of the TMS region of Figure S9, a) characteristic signals of **11**, b) an unidentified side product.

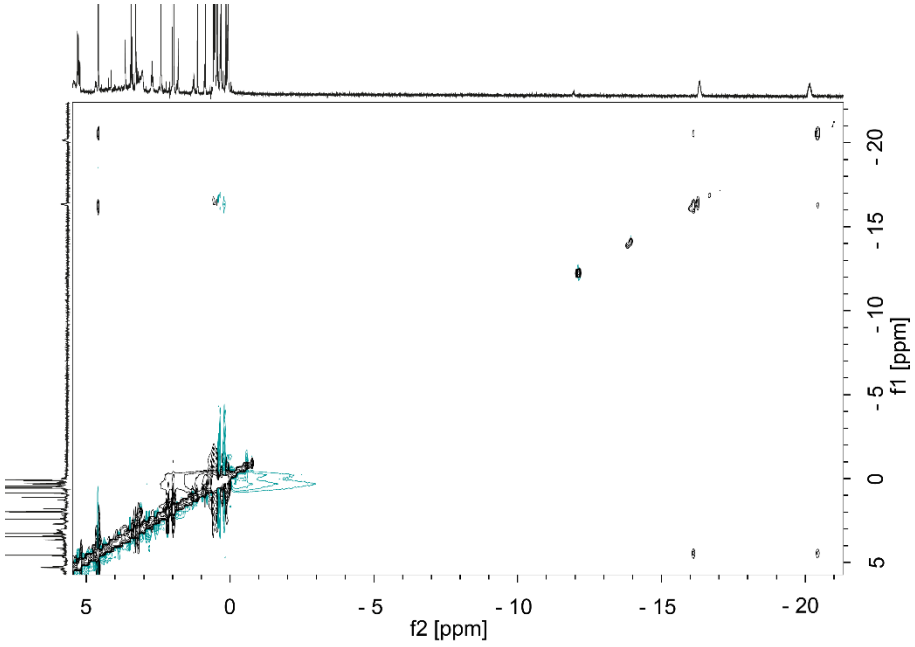


Figure S14. EXSY spectrum of the in situ formed **11** under hydrogen at 238 K shows cross peaks between the hydrides and hydrogen due to the reversible hydrogen activation. From the chemical shift difference of the hydrogen signal and the hydride, and assuming a pseudo first order reaction with constant hydrogen concentration, the reaction rates k could be estimated as ca. 10^5 s^{-1} at 238 K. Note that at higher temperatures broadening was observed in variable temperature NMR experiments (Figure S14)."

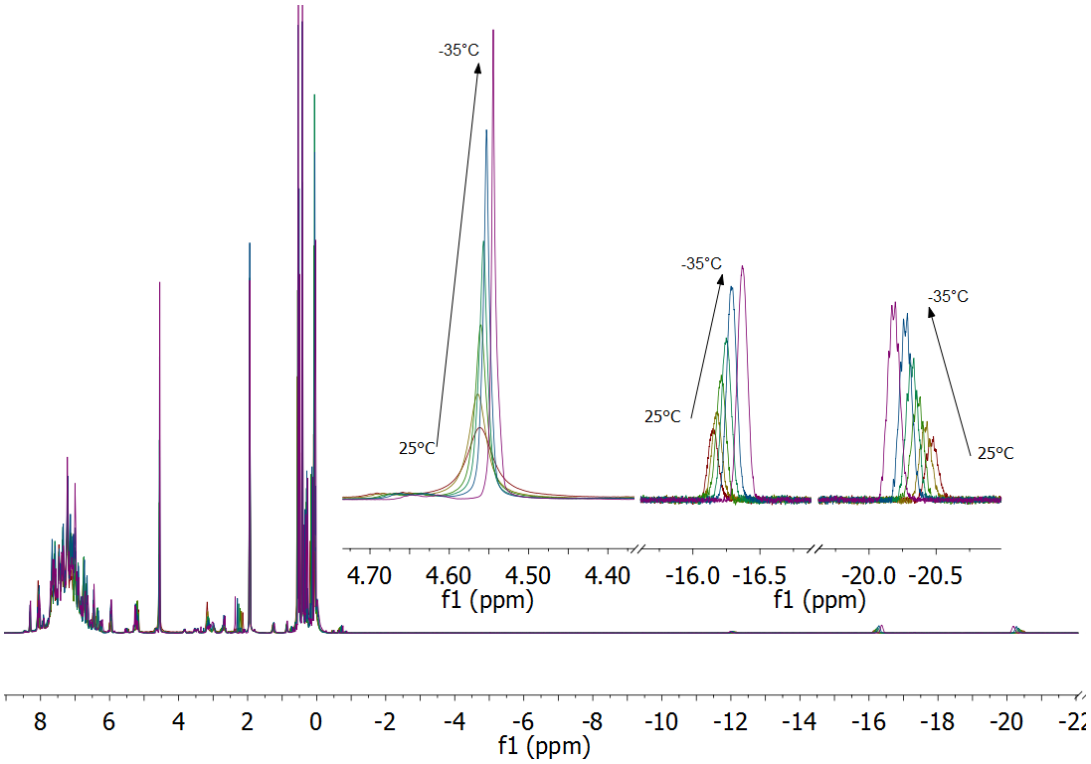


Figure S15. Variable temperature ^{1}H NMR spectra of the in situ formed **11** under hydrogen atmosphere measured at 25, 15, 5, -5, -15, -35 °C.

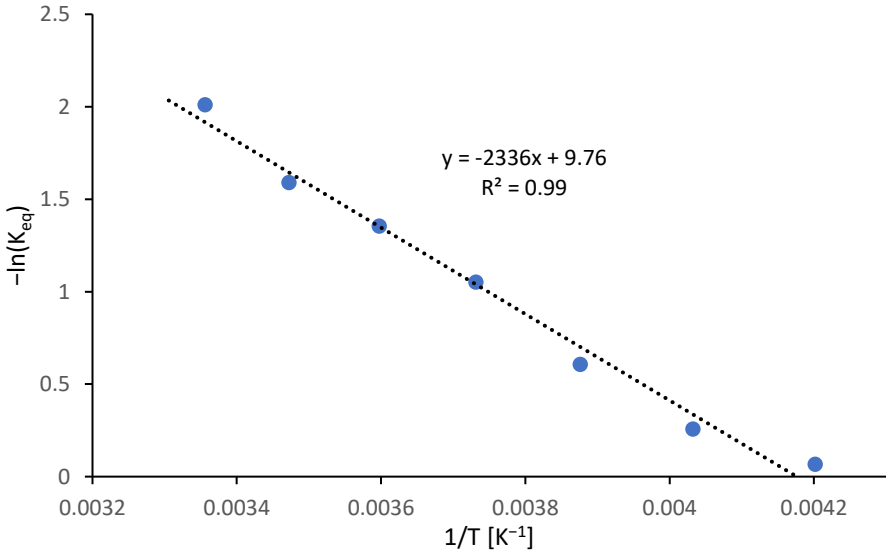


Figure S16. Van't Hoff plot obtained from the integration of the variable temperature NMR data.

From the slope and the intercept shown in Figure S15, the reaction enthalpy $\Delta_r H^0$ and the entropy $\Delta_r S^0$ can be obtained according to the following equiations (R being the universal gas constant:

$$\Delta_r H^0 = 2336\ K \cdot R = 4.64\ kcal \cdot mol^{-1} \qquad (1)$$

$$\Delta_r S^0 = 9.76 \cdot R = 19.4\ cal \cdot mol^{-1} \cdot K^{-1} \qquad (2)$$

And the Gibbs free energy $\Delta_r G^0$ according to the following equation:

$$\Delta_r G^0 = \Delta_r H^0 - 298\ K \cdot \Delta_r S^0 = 1.1\ kcal \cdot mol^{-1} \qquad (3)$$

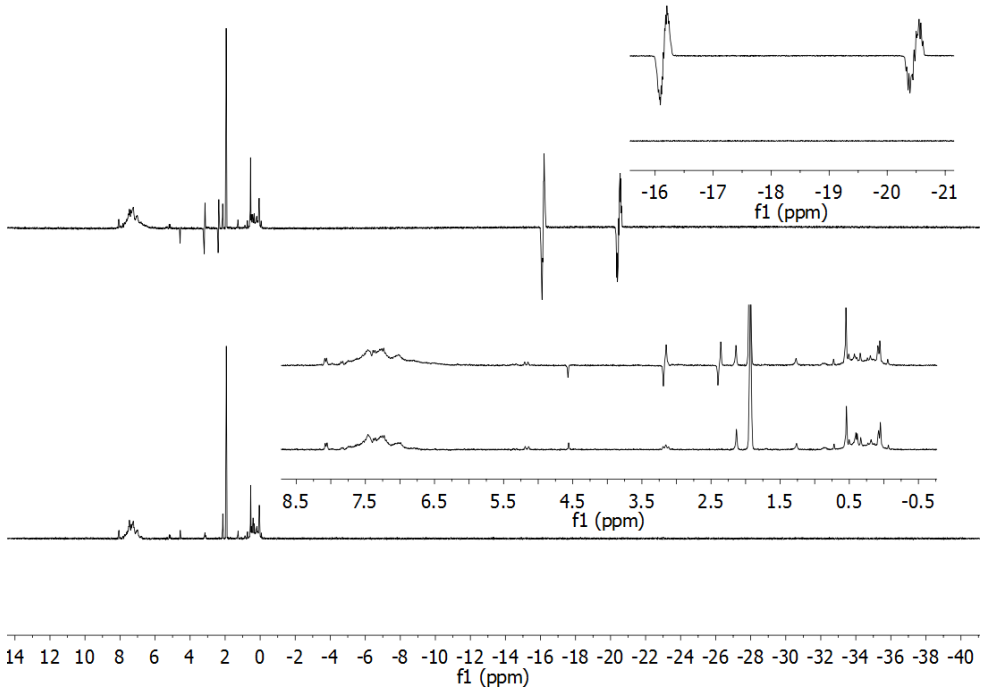


Figure S17. ^{1}H PHIP spectrum acquired after bubbling of parahydrogen at 1 atm through the solution of **7** and dppm, resulting in the formation of **8**, in CD_3CN (top) and corresponding thermal spectrum after relaxation of hyperpolarization (bottom). Observed PHIP signals (2.38 ppm (J_{HH} = 12.0 Hz), 3.17 (J_{HH} = 11.9 Hz)) are assigned to species **11** due to similar chemical shifts and couplings to those of **9**. A small orthohydrogen signal at 4.52 ppm with a PNL indicates reversible H_2 activation.[S4] Two hydride signals of species **11** were observed at -20.47 ppm and -16.15 ppm.

PHIP experiments with 8 at lower temperatures

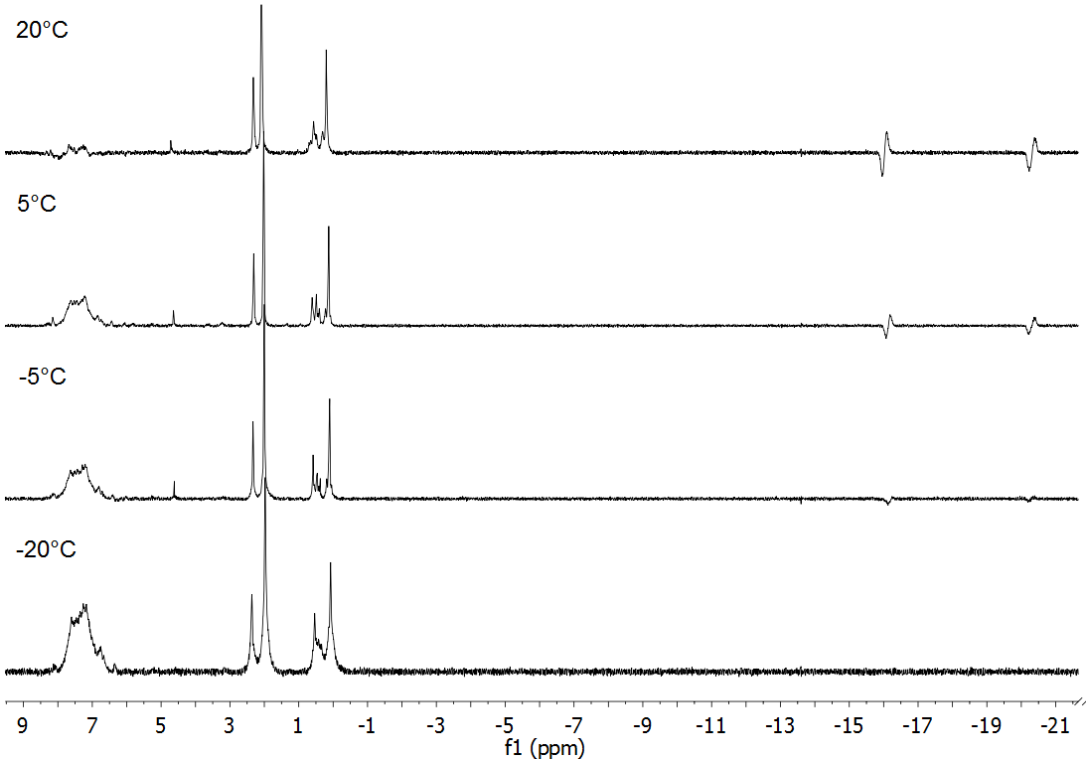


Figure S18. ^{1}H PHIP spectra acquired after bubbling of parahydrogen at 2 atm through the solution of **7** and dppm (resulting in formation of **8**) in CD_3CN. The hydride signal of **11** is lost at lower temperature.

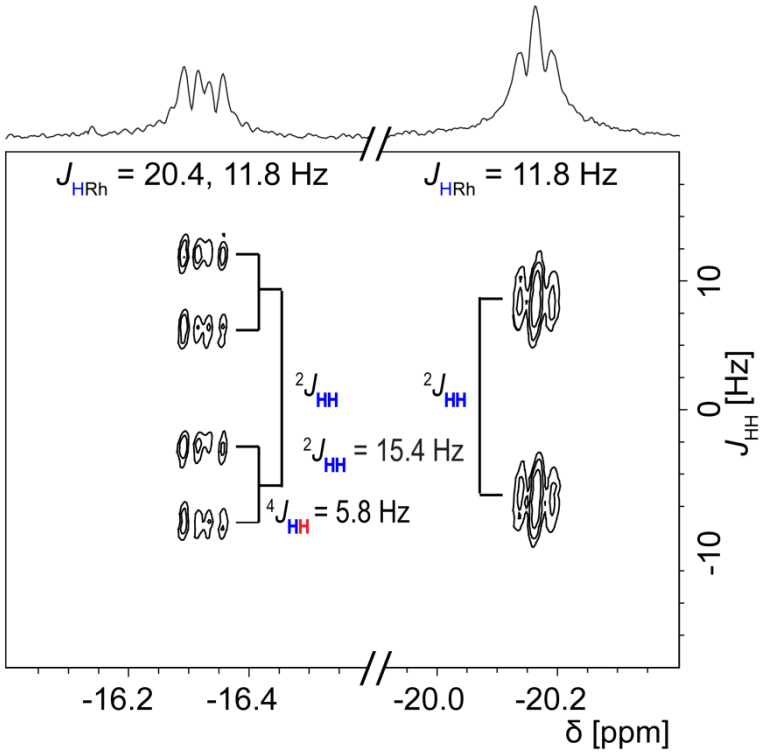


Figure S19. J-resolved $^1H\{^{31}P\}$ spectra of in situ formed **11** under hydrogen.

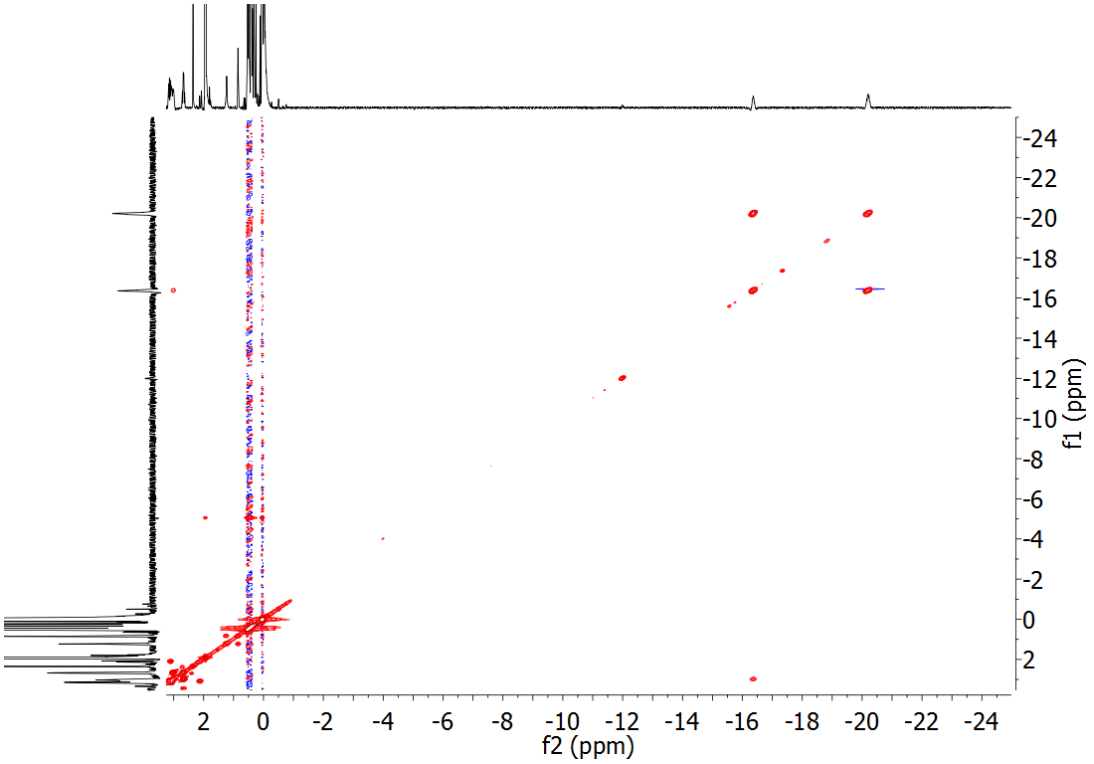


Figure S20. COSY spectrum of the in situ formed **11** under hydrogen at 238 K showing coupling of two hydrides signals, consistent with the PHIP data. The hydride signal at -16.2 ppm is coupled with the $C_{Carbene}$-C*H*$_2$ fragment.

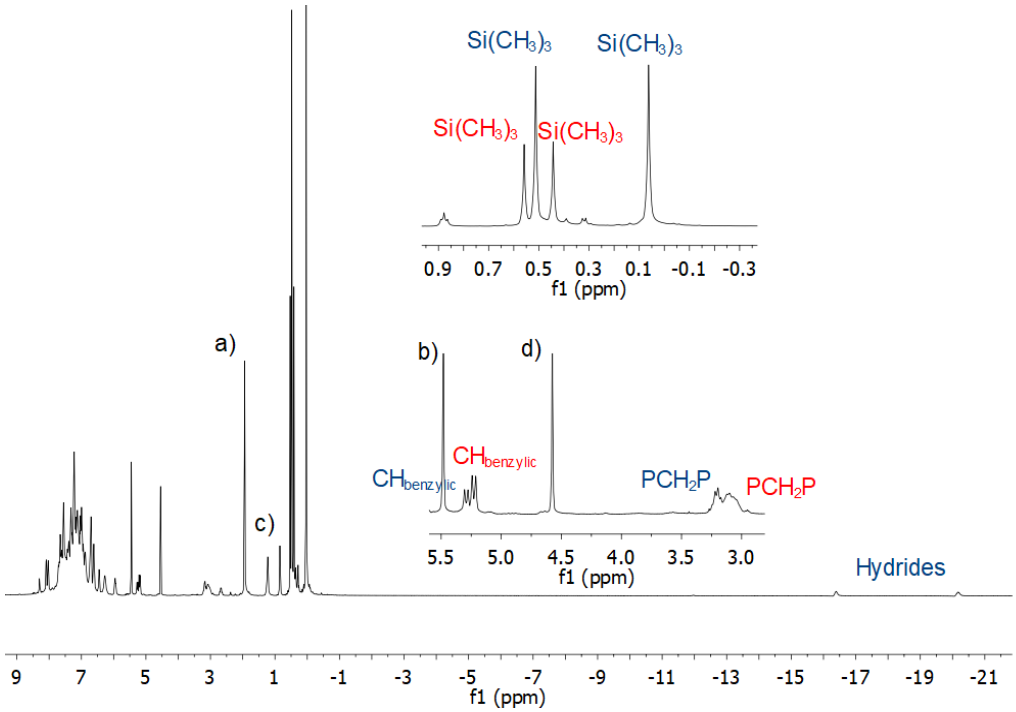


Figure S21. ^{1}H NMR of the mixture of **8** (characteristic signals labelled in red) and **11** (characteristic signals labelled in blue) at 233K in CD_3CN; a) solvent signal, b) inert solvent: dichloromethane), c) inert solvent: hexane, d) hydrogen.

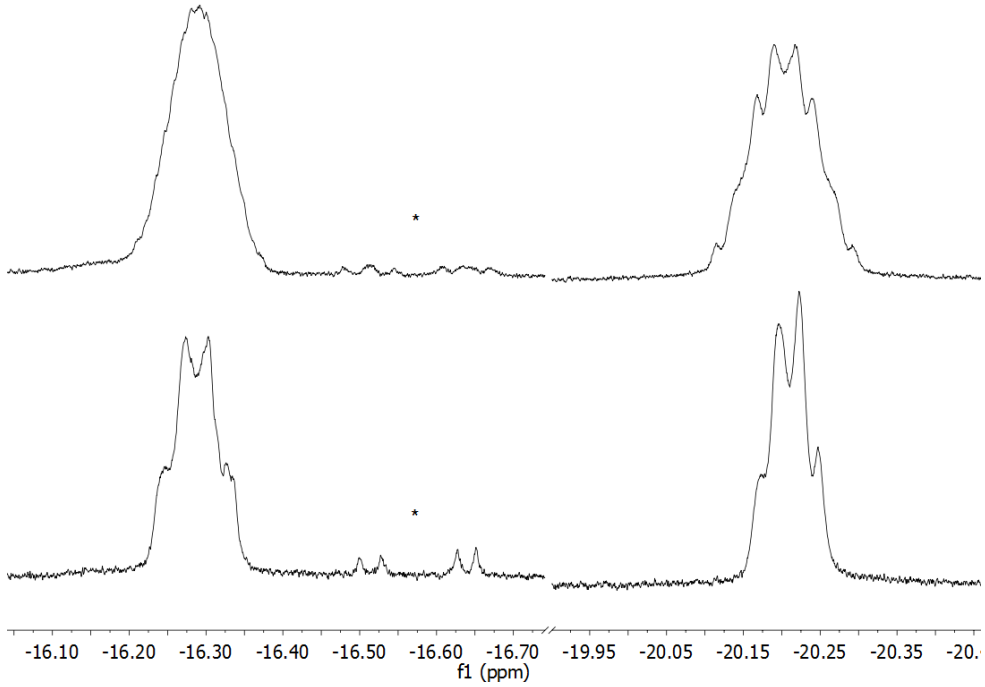


Figure S22. ^{1}H (top) and $^{1}H\{^{31}P\}$ (bottom) spectra of the hydride region of the in situ formed **11** under hydrogen at 248 K.$^{1}H\{^{31}P\}$ shows a pseudo-quartet structure for both hydride signals. * decomposition product showing that the compound decomposes slowly under hydrogen.

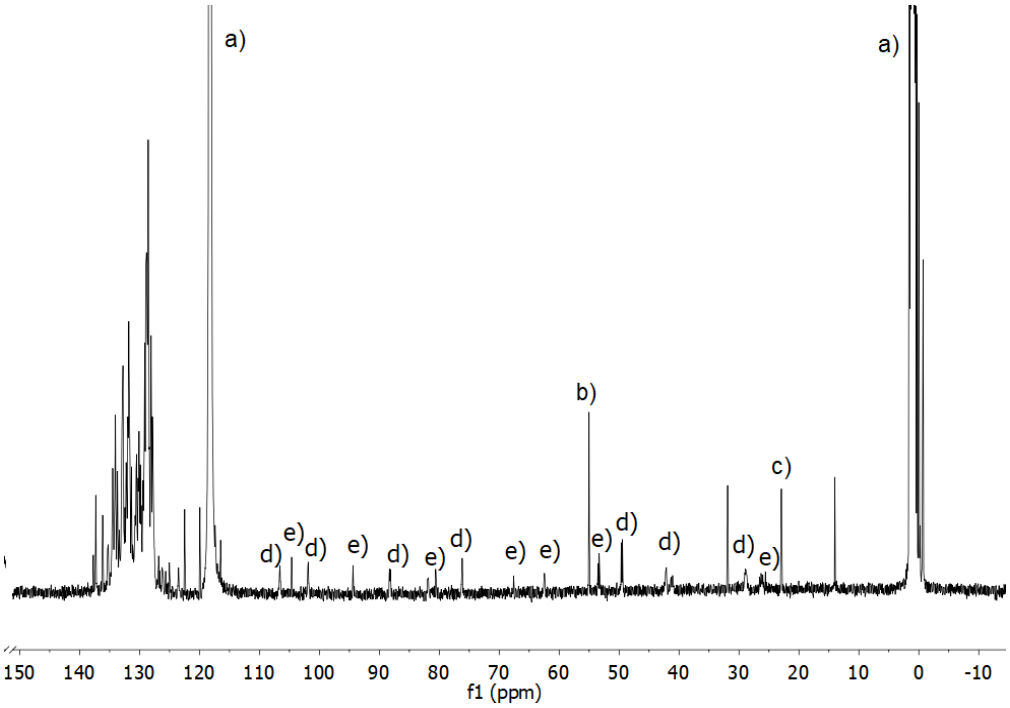


Figure S23. $^{13}C\{^{1}H\}$ NMR of the mixture of **8** and **11** at 233 K in CD_3CN; a) solvent signal, b) inert solvent: dichloromethane, c) inert solvent: hexane, d) characteristic signals of **8**, e) characteristic signals of **11**.

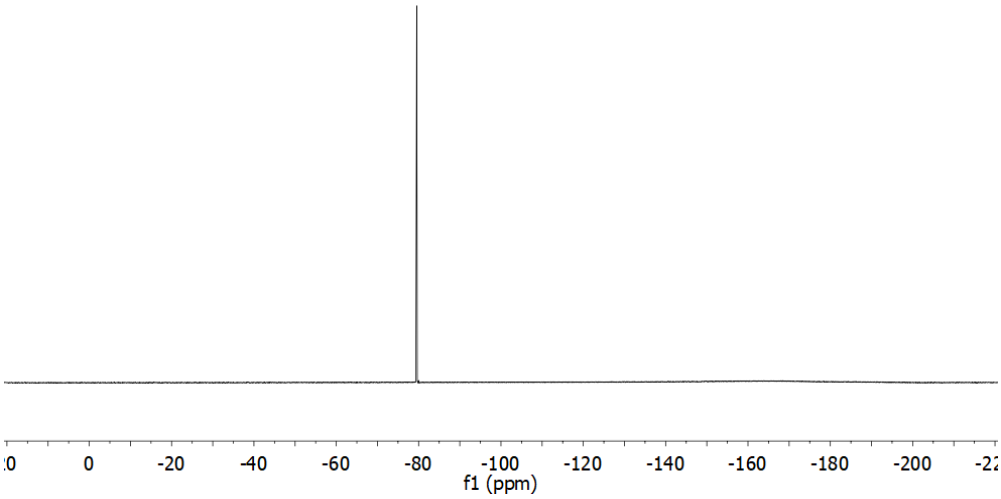


Figure S24. $^{19}F\{^{1}H\}$ NMR of the mixture of **8** and **11** at 233 K in CD_3CN. Only one signal is observed, indicating that the $^{-}$OTf is fully dissociated from the complexes.

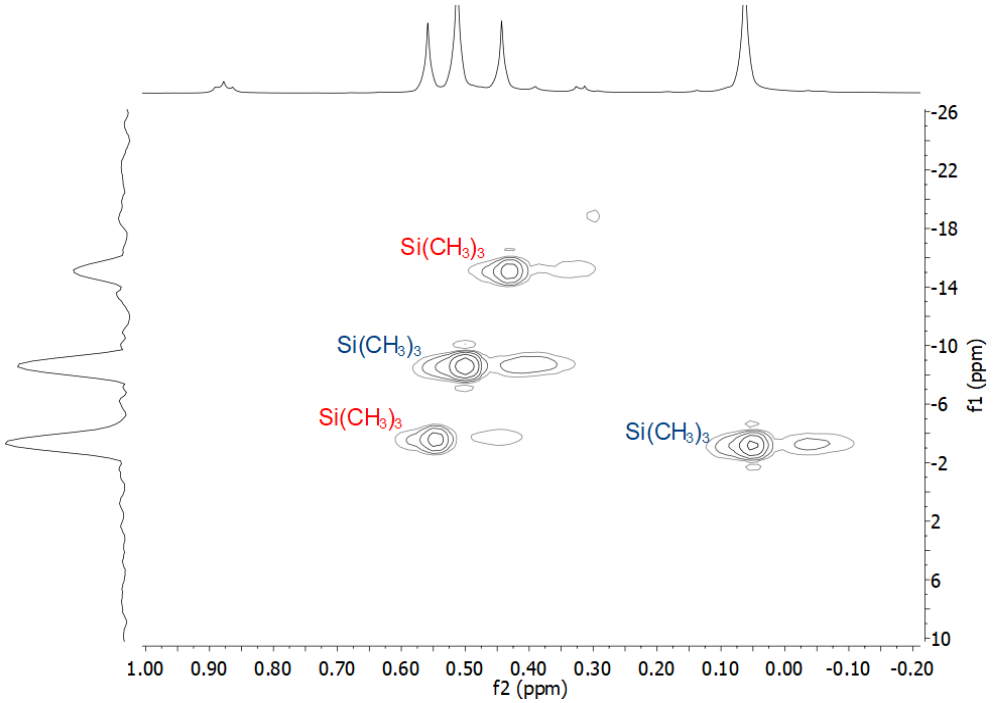


Figure S25. ^{1}H ^{29}Si HMQC of the mixture of **8** (signals labelled in blue) and **11** (signals labelled in red) at 233K in CD_3CN.

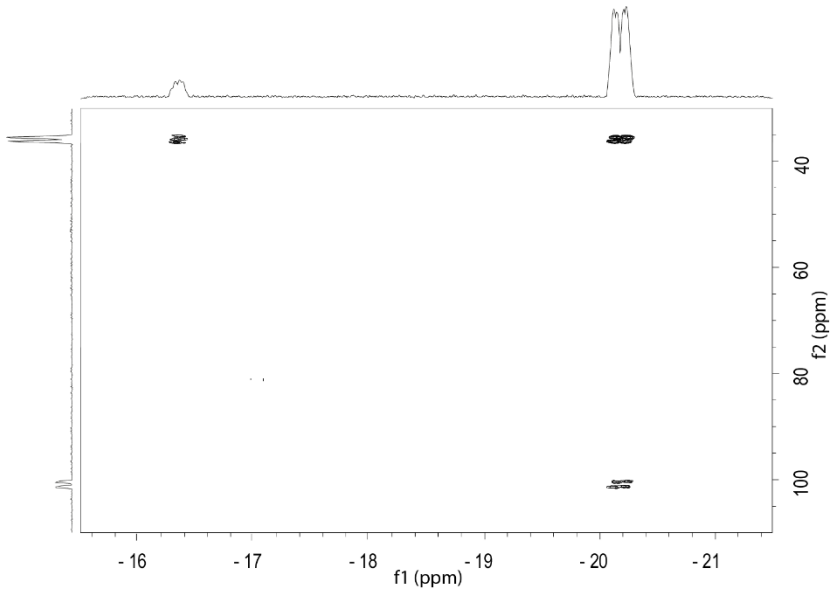


Figure S26. ^{1}H-^{31}P HMQC spectrum of the in situ formed **11** under hydrogen atmosphere at 238 K. Observed signals: δ (ppm) 101 (Trop*P*Ph$_2$, $^{1}J_{PRh}$ = 195 Hz), 36 ppm (dppm, $^{1}J_{PRh}$ = 140 Hz).

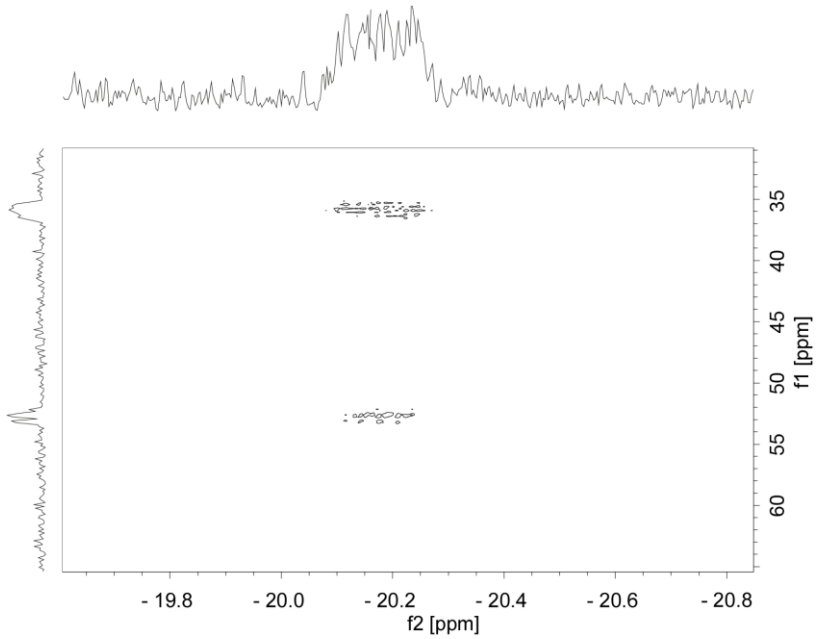


Figure S27. ^{1}H-^{31}P HMQC spectrum of the in situ formed **11** under hydrogen atmosphere at 238 K (dppm region). Observed signals: δ (ppm) 36 (m, dppm), 53 (m, dppm).

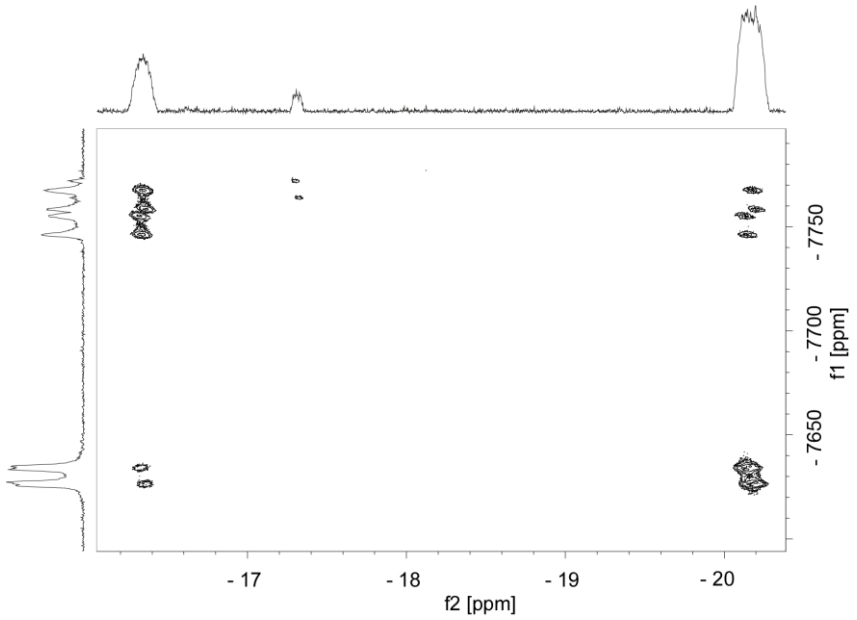


Figure S28. ^{1}H-^{103}Rh HMQC spectrum of the in situ formed **11** under hydrogen atmosphere at 238 K. δ (ppm) = –7630 (d, $^{1}J_{RhP}$ = 125 Hz, TropP-Rh-*Rh*), –7758 (dd, $^{1}J_{RhP}$ = 192, 144 Hz, TropP-Rh).

^{31}P decoupled PHIP spectra

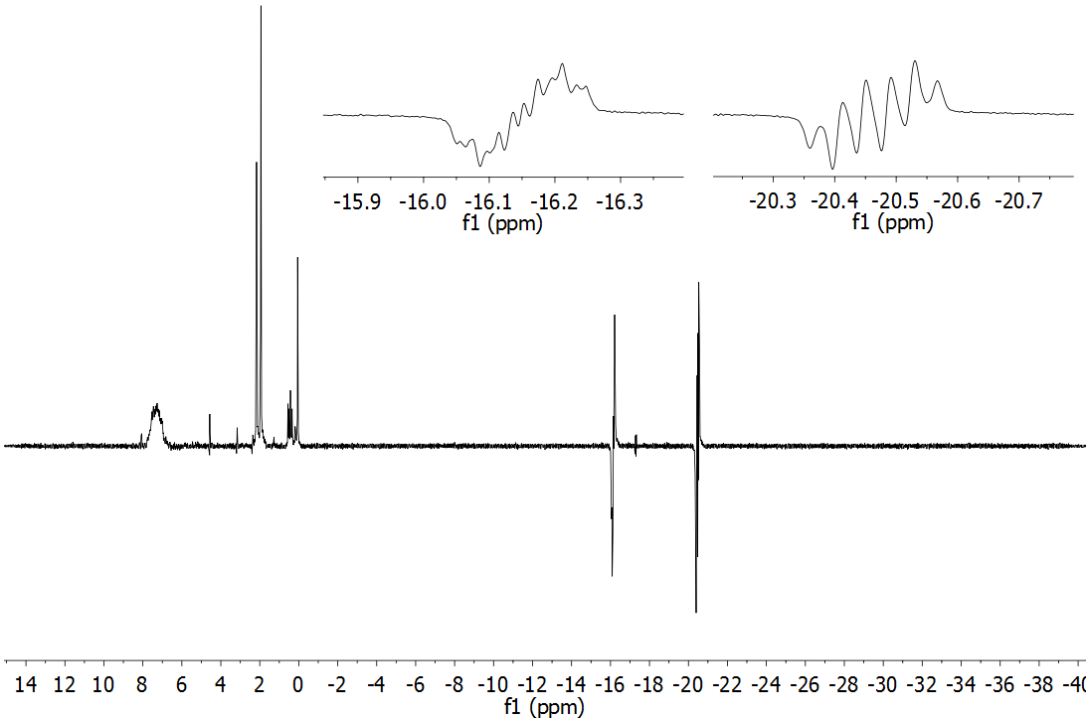


Figure S29. $^{1}H\{^{31}P\}$ decoupled PHIP spectrum acquired after bubbling of parahydrogen at 2 atm through the solution of **7** and dppm (resulting in formation of **8**) in CD_3CN. Note that only couplings arising from dppm ^{31}P nuclei were decoupled.

PHIP spectra simulations of 11

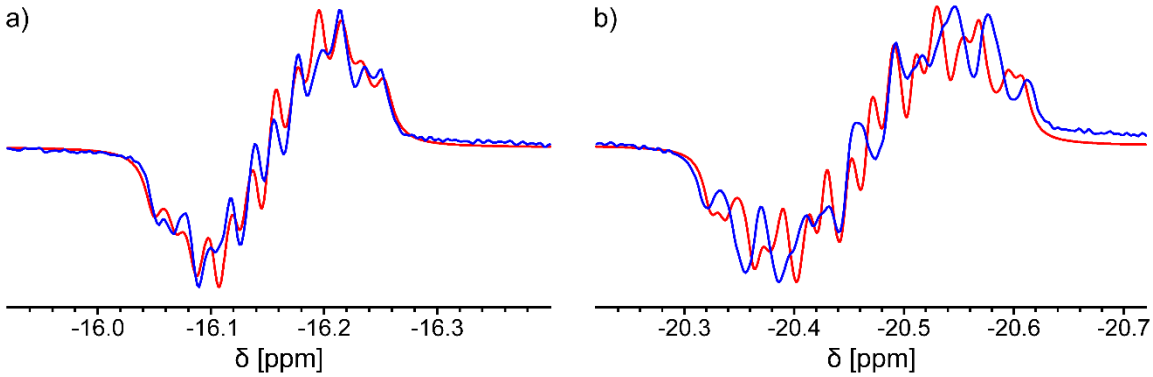
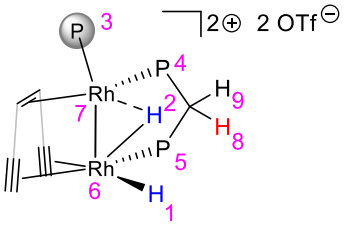


Figure S30. a) PHIP $^{1}H\{^{31}P\}$ spectrum (blue) with simulation (red) of hydride H_a (group number 1 in Table S1), b) PHIP ^{1}H spectrum (blue) with simulation (red), of hydride H_b (group number 2 in Table S1).

Table S1. J-values used for simulation. Note that only couplings to the hydride protons are listed. The structure of **11** with group numbers shown near the corresponding atoms is presented below the table.

Group #	Nucleus type	δ, ppm	J coupling, Hz								
			#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**
1	^{1}H	–16.15	X	–15.6	11	6	13	17	11.8	5.8	0
2	^{1}H	–20.47		X	24	18	4	11.8	11.8	0	0
3	^{31}P				X						
4	^{31}P					X					
5	^{31}P						X				
6	^{103}Rh							X			
7	^{103}Rh								X		
8	^{1}H									X	
9	^{1}H										X



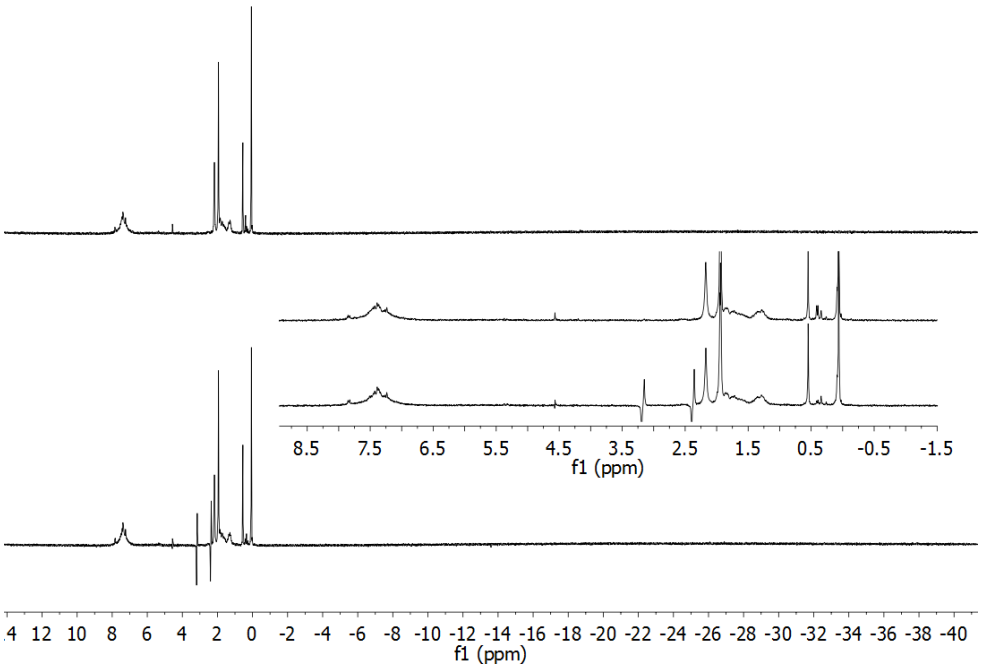


Figure S31. ^{1}H PHIP spectrum acquired after bubbling of parahydrogen at 1 atm through the solution of **7** and tricyclohexyl phosphine in CD_3CN (bottom) and corresponding thermal spectrum after relaxation of hyperpolarization (top). The observed PHIP signals (2.38 ppm (J_{HH} = 12.2 Hz), 3.17 (J_{HH} = 12.2 Hz)) can be assigned to compound **9-PCy$_3$** due to similar chemical shifts and couplings to those of **9**. A small orthohydrogen signal at 4.52 ppm with a PNL indicates reversible H_2 activation.[S1]

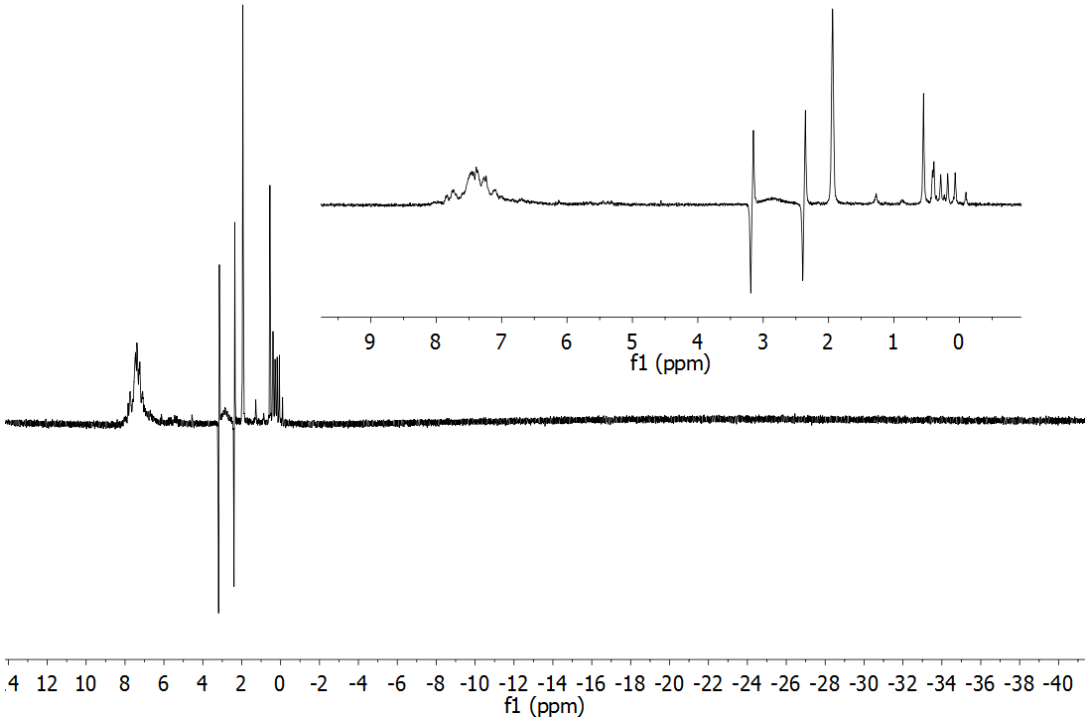


Figure S32. ^{1}H PHIP spectrum acquired after bubbling of parahydrogen at 1 atm through the solution of **7** and diphenylphosphine oxide in CD_3CN. The observed PHIP signals (2.38 ppm (J_{HH} = 12.1 Hz), 3.17 (J_{HH} = 12.2 Hz)) can be assigned to compound **9-PPh$_2$OH** due to similar chemical shifts and couplings to those of **9**. A small orthohydrogen signal at 4.52 ppm with a PNL (partially negative lineshape) indicates reversible H_2 activation.[S4]

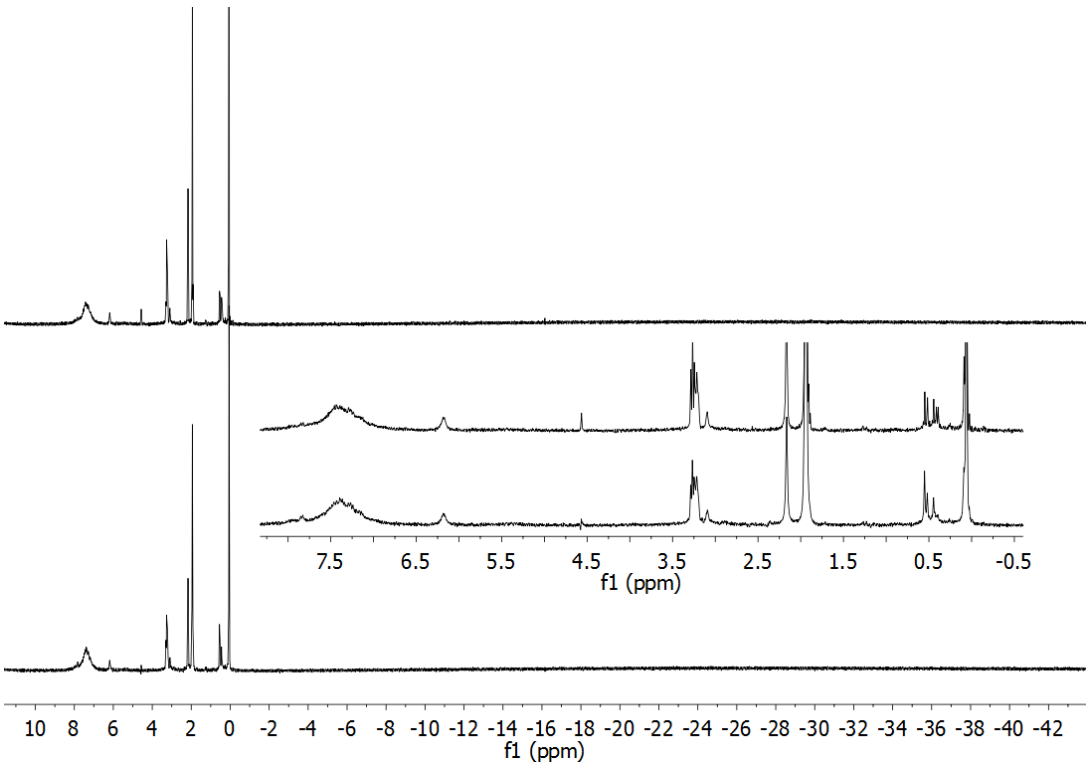


Figure S33. ^{1}H PHIP spectrum acquired after bubbling of parahydrogen at 1 atm through the solution of **7** and triazabicyclodecene in CD_3CN (bottom) and corresponding thermal spectrum after relaxation of hyperpolarization (top). Although no PHIP ligand signals were observed, PNL orthohydrogen signal indicates reversible hydrogen activation.[S4]

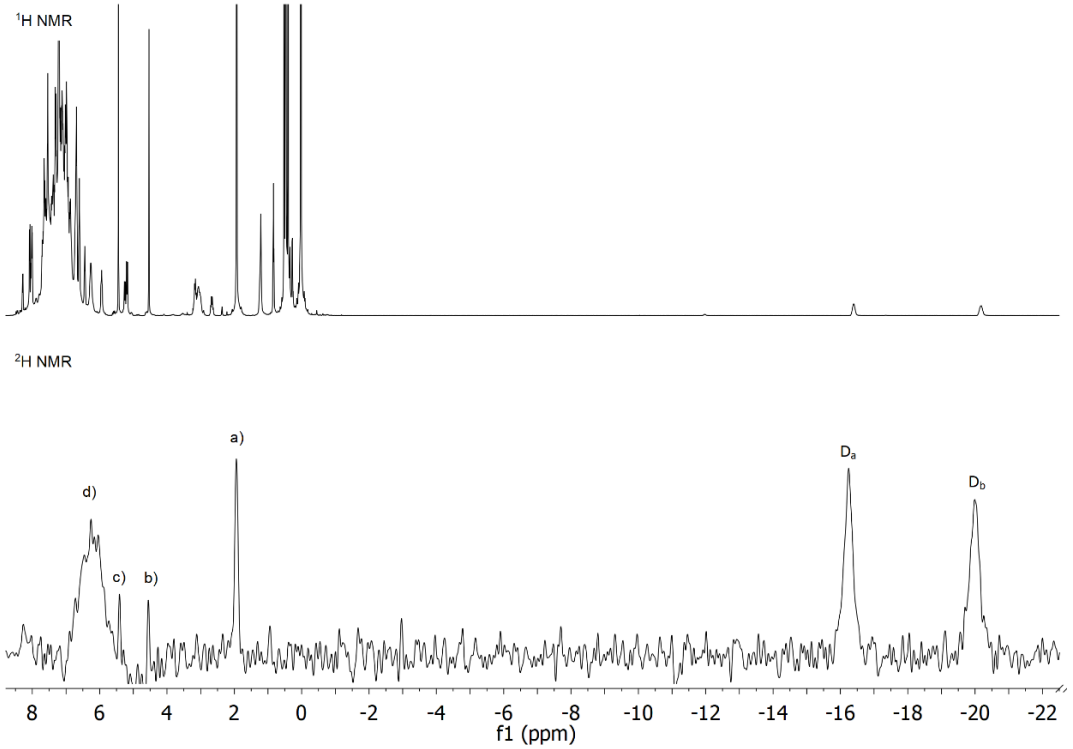


Figure S34. Top: ^{1}H NMR of a mixture of **8** and **11** after pressurizing a J. Young NMR tube containing **8** (20.3 mg, 14.1 µmol) in 0.5 mL CD_3CN with 4.6 bar H_2. Bottom: ^{2}H NMR after pressurizing **8** (23.0 mg, 16.0 µmol) in 0.5 mL acetonitrile with 4.6 bar D_2, D_a and D_b: corresponding deuteride signals, a) CD_3CN, b) D_2, c) impurity of CD_2Cl_2, d) ^{2}H signals of aromatic C-D indicate an exchange of ^{1}H to ^{2}H at the aromatic rings.

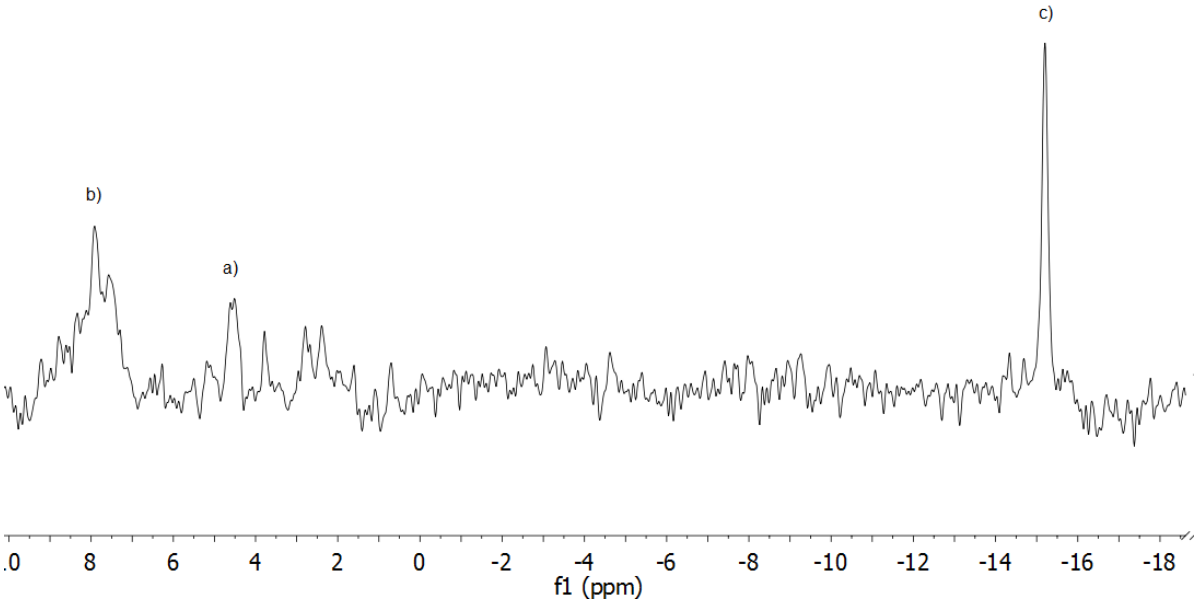


Figure S35. ^{2}H NMR spectrum of **12** (17.6 mg, 16.2 µmol) under 4.5 bar D_2 after 17 h, a) D_2, b) aromatic C-D signals indicating exchange of ^{1}H to ^{2}H in the aromatic systems, c) excitation signal.

When **8** is exposed to 4.6 bar of D_2, and the resulting mixture of **8** and **11-*d*²** rests overnight at 25°C, then ^{1}H/^{2}H scrambling on the aromatic rings is observed, indicating that the forming reaction mixture is capable of aromatic CH activation, a process that was not observed for **9**. The bridging dppm ligand therefore helps to stabilize the highly reactive hydride **11** and enables the CH activation. In order to

probe if the bimetallic Rh-Rh core is a necessary requirement for this C-H reactivity, a monometallic T-shaped complex [$^{\{(TMS)C\equiv C\}}{}_2$TropPPh$_2$RhPPh$_3$]OTf was synthesized (**12**, for crystal structure see Figure). Under the D_2 atmosphere, **12** shows ^{1}H/^{2}H scrambling in the aromatic region as well.

Crystal Structure of **12**

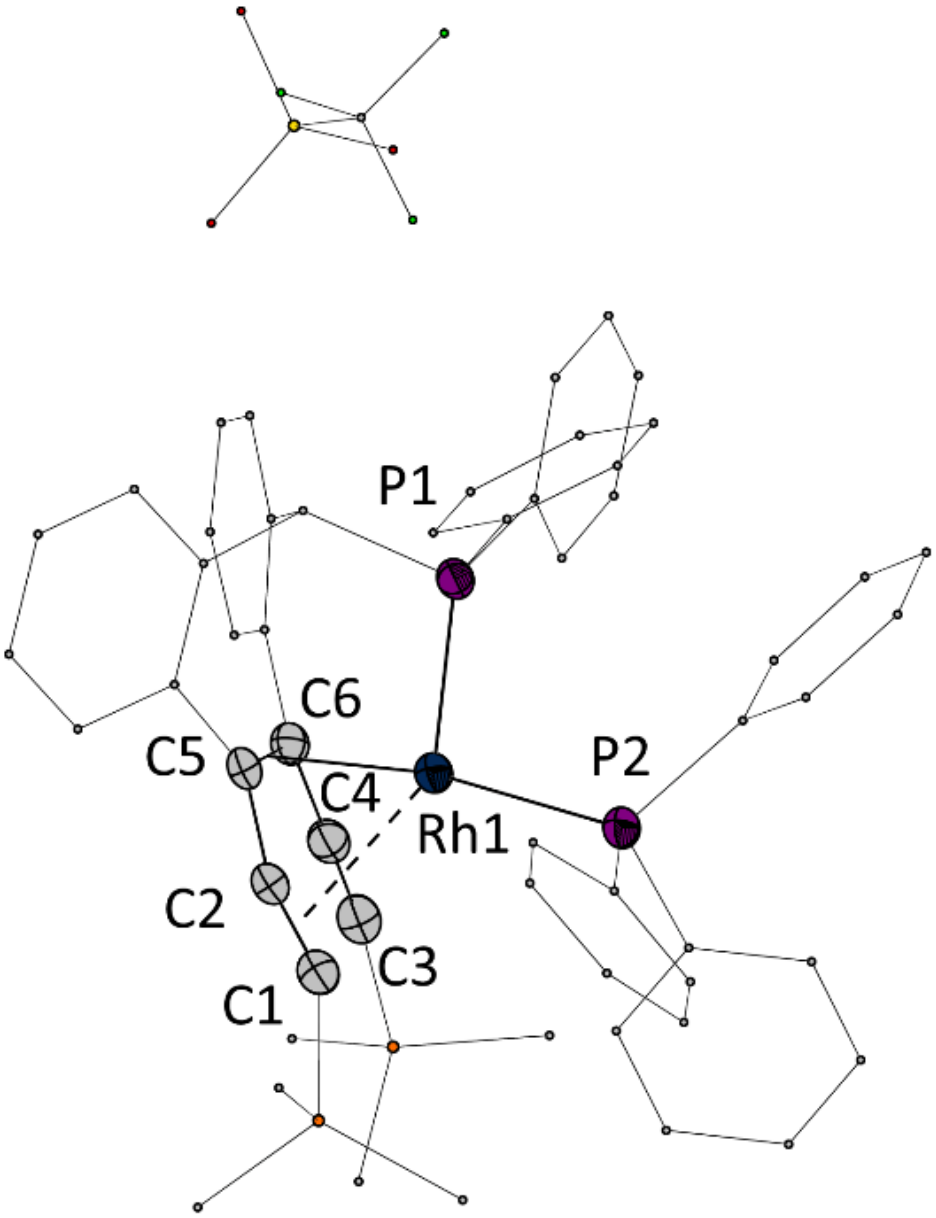


Figure S36. Crystal structure of **12**, three molecules of THF are omitted for clarity. Selected bond length (Å), and angles (°), ct, center of coordinated double bond: Rh1-P1 2.1929(8), Rh1-P2 2.3184(8), C1-C2 1.218(4), C3-C4 1.197(4), C5-C6 1.435(4),ct(C1-C2)-Rh1 2.393(3), ct(C5-C6)-Rh1 2.062(3), P1-Rh1-P2 98.54(3), P1-Rh1-ct(C5-C6) 88.55(3), P2-Rh1-ct(C5-C6) 168.65(3), C1-C2-C5 165.1(3), C3-C4-C6 176.2(3).

Semihydrogenation of Phenylacetylene

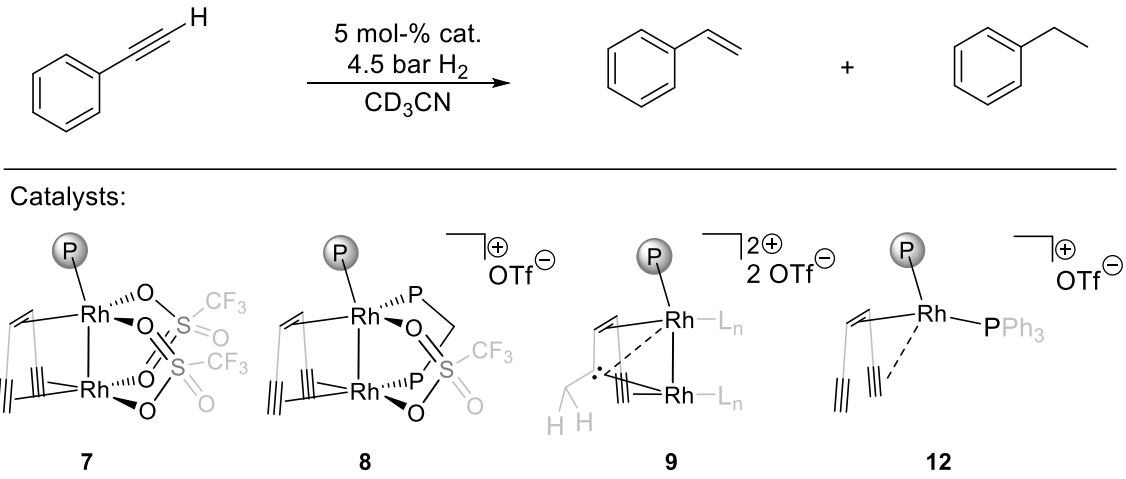


Figure S37. NMR-scale catalytic semihydrogenation of phenylacetylene.

Experimental Details: To a solution of **7**, **8, 9** and **12** in 0.5 mL CD_3CN was added mesitylene and phenylacetylene (for concentrations see table S2) in a J. Young NMR tube. The tube was pressurized with 4.5 bar hydrogen at ambient temperature. The reaction was followed by 400 MHz ^1H NMR spectroscopy.

8 was freshly prepared by dissolving **7** in 0.5 mL CD_3CN in a J. Young NMR tube. Argon was removed by three freeze pump thaw cycles and the headspace was filled with 2 bar hydrogen. The tube was shaken for 12 min, the hydrogen was removed by three freeze pump thaw cycles and the tube was filled with argon to ambient pressure at ambient temperature. Purity of **8** was verified by ^1H and ^{31}P NMR.

Table S2. Concentrations of catalyst, substrate and standard for semihydrogenation experiments, PA = phenylacetylene, Mes = mesitylene.

Entry	Catalyst	Conc. Cat. (mM)	Conc. Mes (mM)	Conc. PA (mM)
1	**7**	18.5	140	401
2	**8**	18.5	110	382
3	**9**	18.6	140	386
4	**12**	18.6	150	356

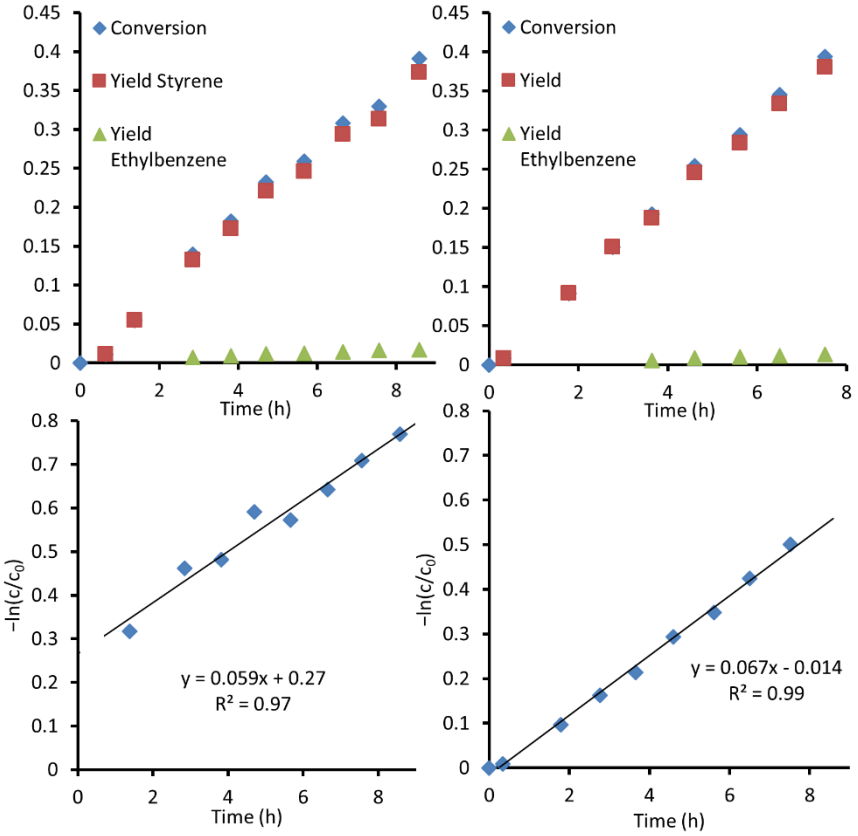


Figure S38. Top: conversion of phenylacetylene and yield of styrene and ethylbenzene with catalysts **7** (left) and **9** (right). Bottom: logarithmic plots with k_{obs} = $5.9 \cdot 10^{-2}$ h^{-1} and $6.7 \cdot 10^{-2}$ h^{-1}, respectively.

The similar rates indicate formation of the same active species with complexes **7** and **9**.

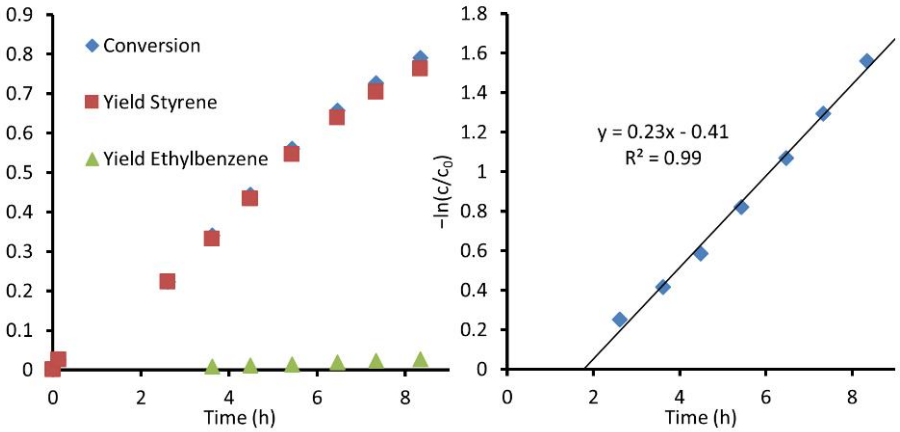


Figure S39. Left: conversion of phenylacetylene and yield of styrene and ethylbenzene with catalyst **8**. Right: logarithmic plot with k_{obs} = $2.3 \cdot 10^{-1}$ h^{-1}.

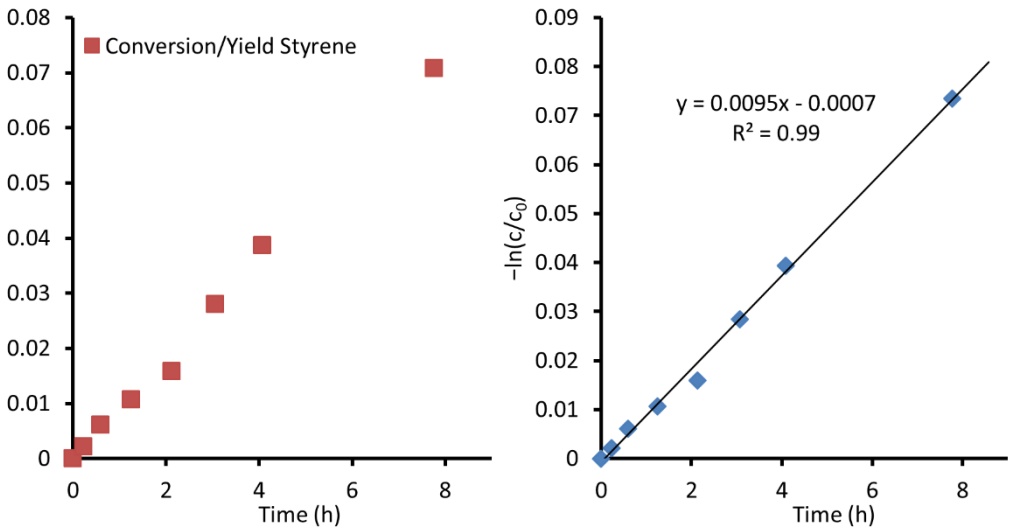


Figure S40. Left: conversion of phenylacetylene and yield of styrene with catalyst **12**. Note that no ethylbenzene or other side products are observed at low conversion. Right: logarithmic plot with k_{obs} = $9.5 \cdot 10^{-3}$ h^{-1}.

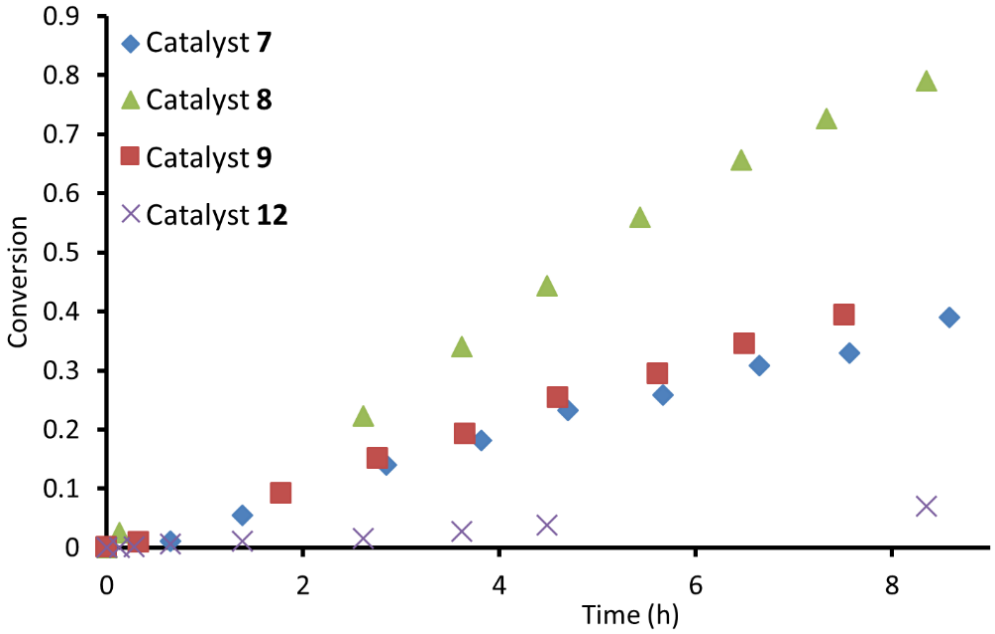


Figure S41. Conversion vs time plots for catalysts **7**-**9** and **12**.

The similar rates observed with **7** and **9** indicate that **7** is hydrogenated to **9** *in situ* in the presence of phenylacetylene.

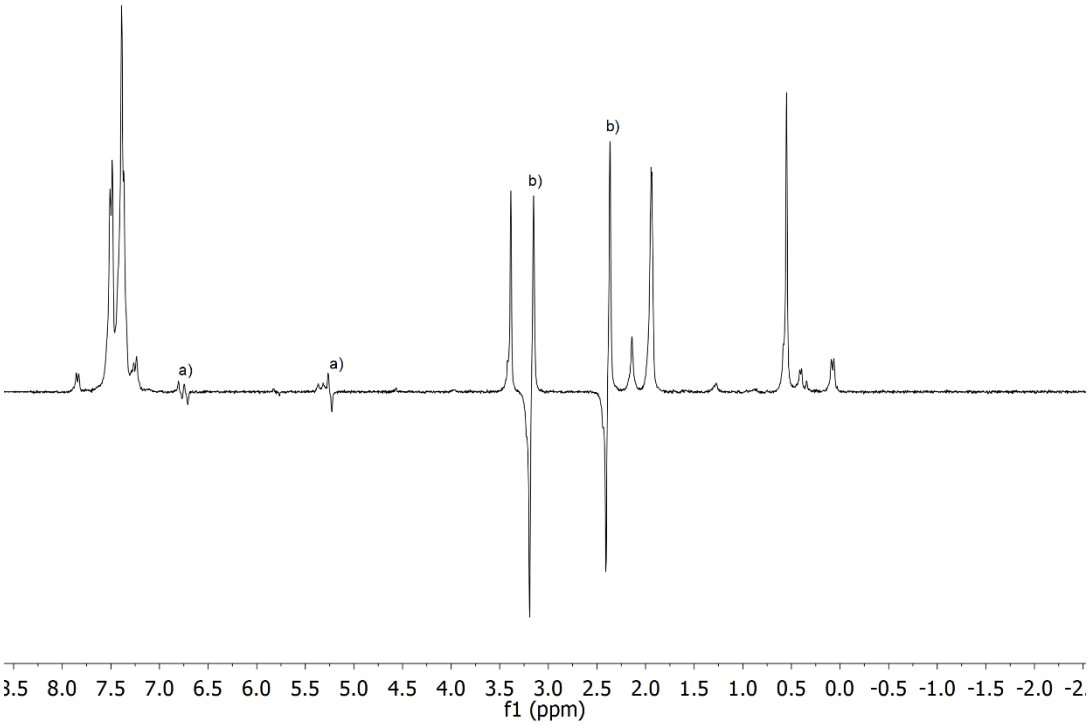


Figure S42. Catalytic hydrogenation of phenylacetylene with **7** under parahydrogen, a) hyperpolarized styrene, b) hyperpolarized signals of **9** indicates formation of **9** from **7** under the catalytic conditions.

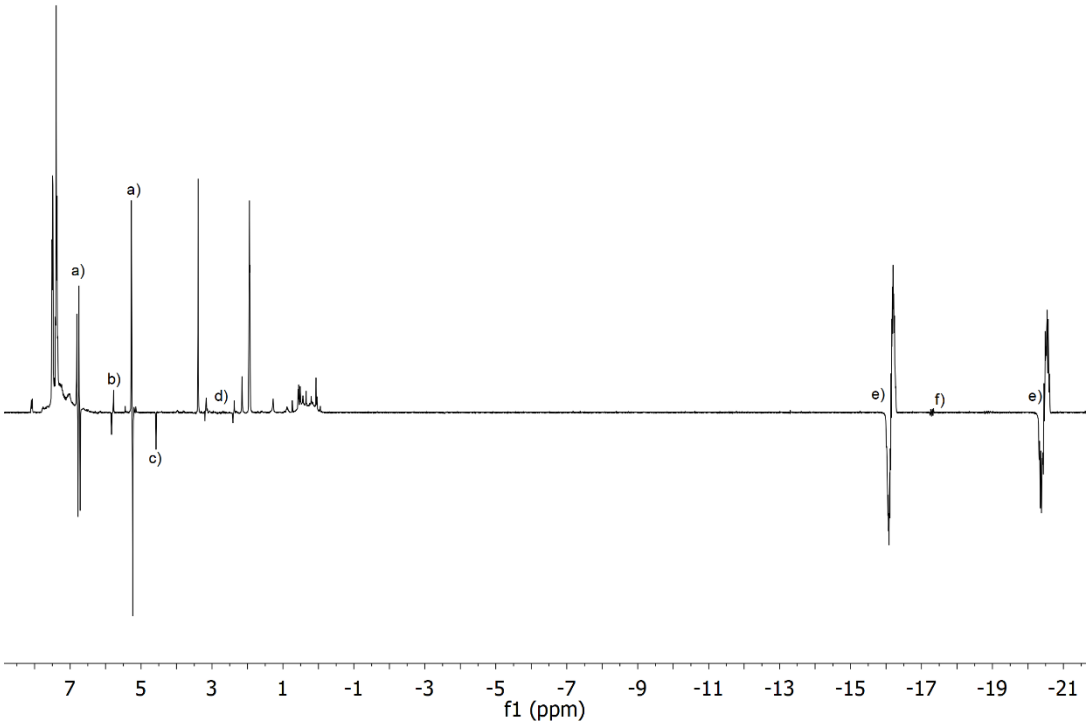


Figure S43. Catalytic hydrogenation of phenylacetylene with **8** under parahydrogen, a) hyperpolarized styrene, syn addition b) hyperpolarized styrene, anti addition, c) partially negative line shape of ortho-H_2 signal indicates a reversible hydrogen activation, d) hyperpolarized **9** from minor amounts of **7** present in the sample of **8**, e) hyperpolarized hydride signals of **11**, f) unknown species.

NMR Spectra of Compounds **2-9, 12**

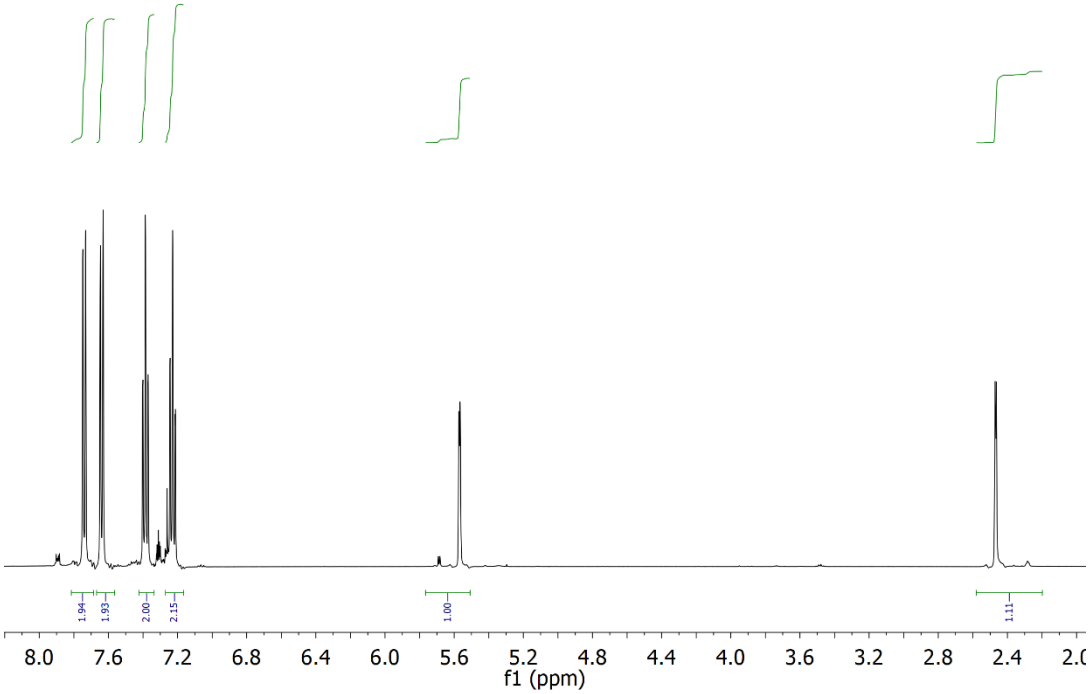


Figure S44. ^{1}H NMR of **2** in $CDCl_3$.

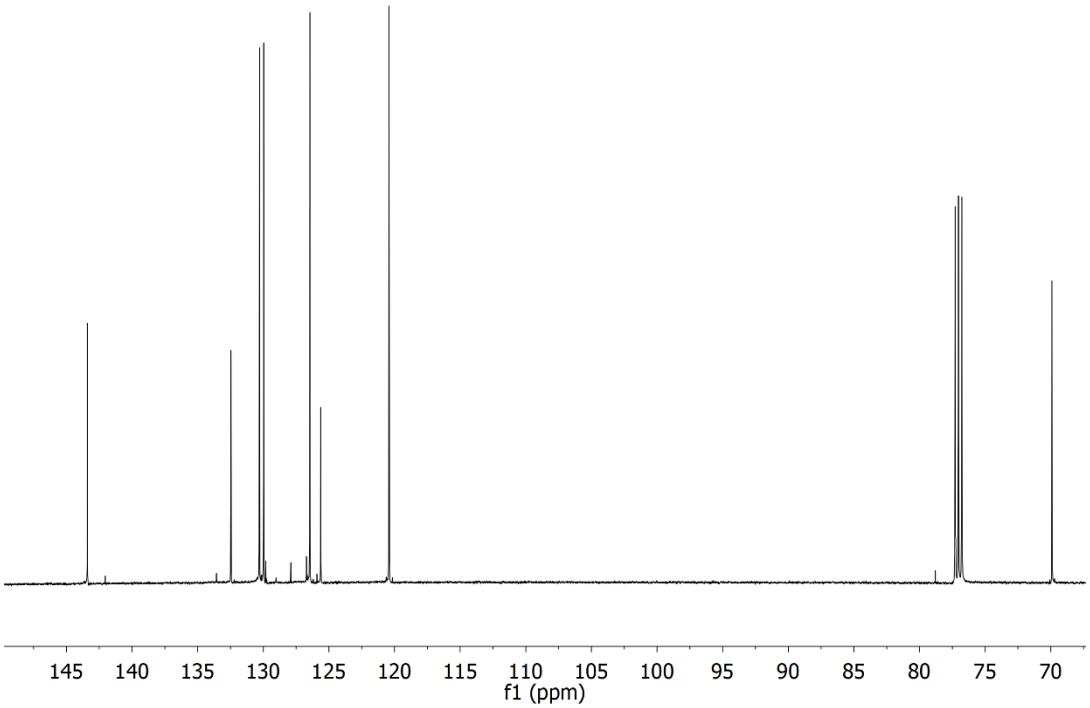


Figure S45. $^{13}C\{^{1}H\}$ NMR of **2** in $CDCl_3$.

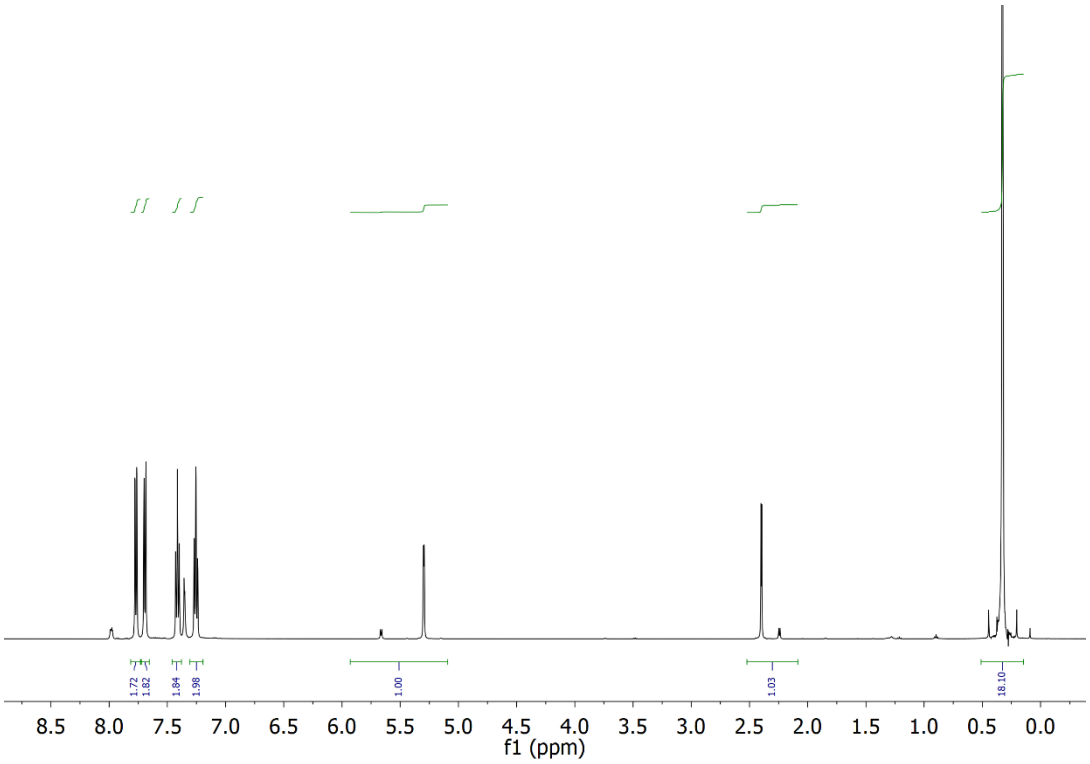


Figure S46. ^{1}H NMR of **3** in $CDCl_3$.

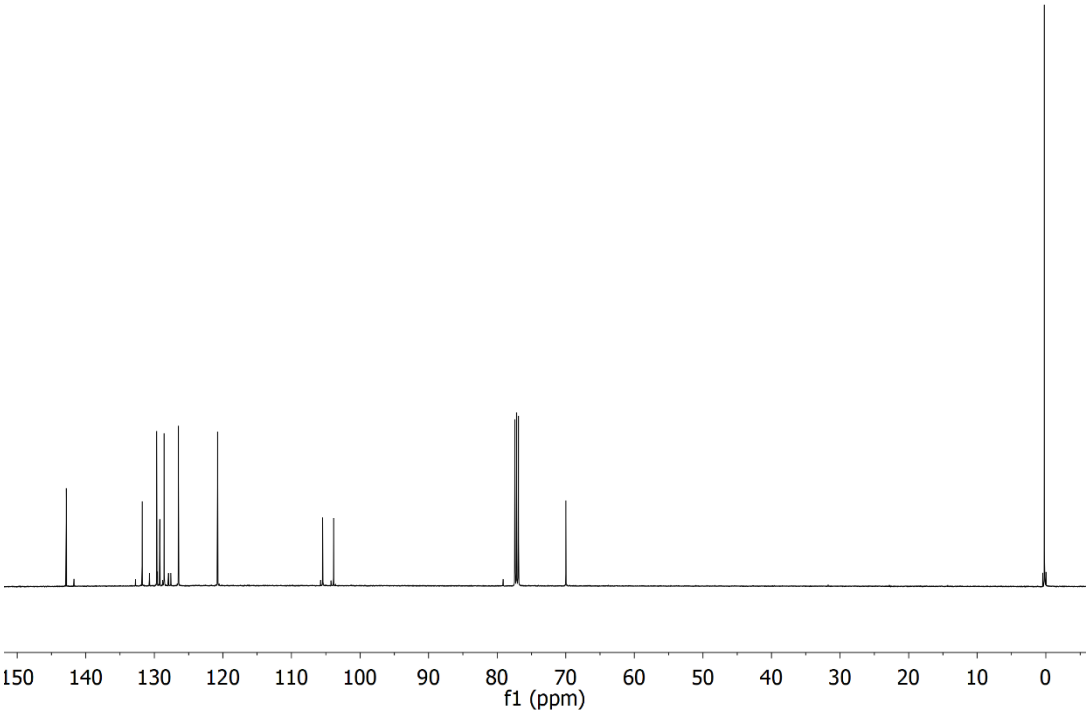


Figure S47. $^{13}C\{^{1}H\}$ NMR of **3** in $CDCl_3$.

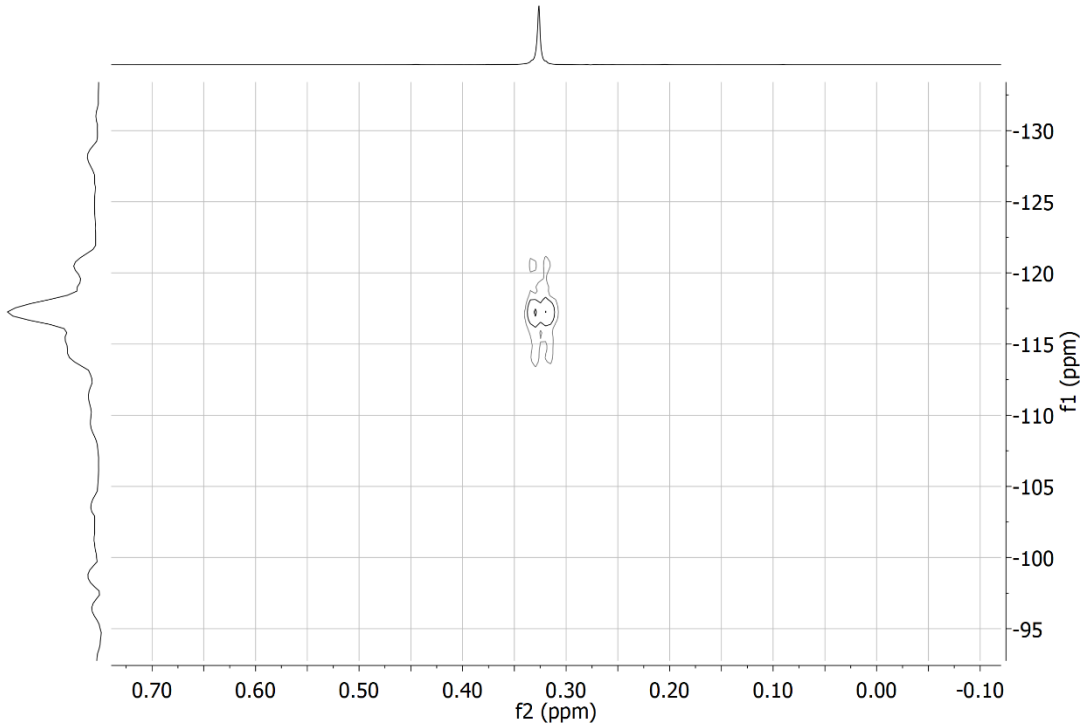


Figure S48. ^{1}H ^{29}Si HMQC of **3**.

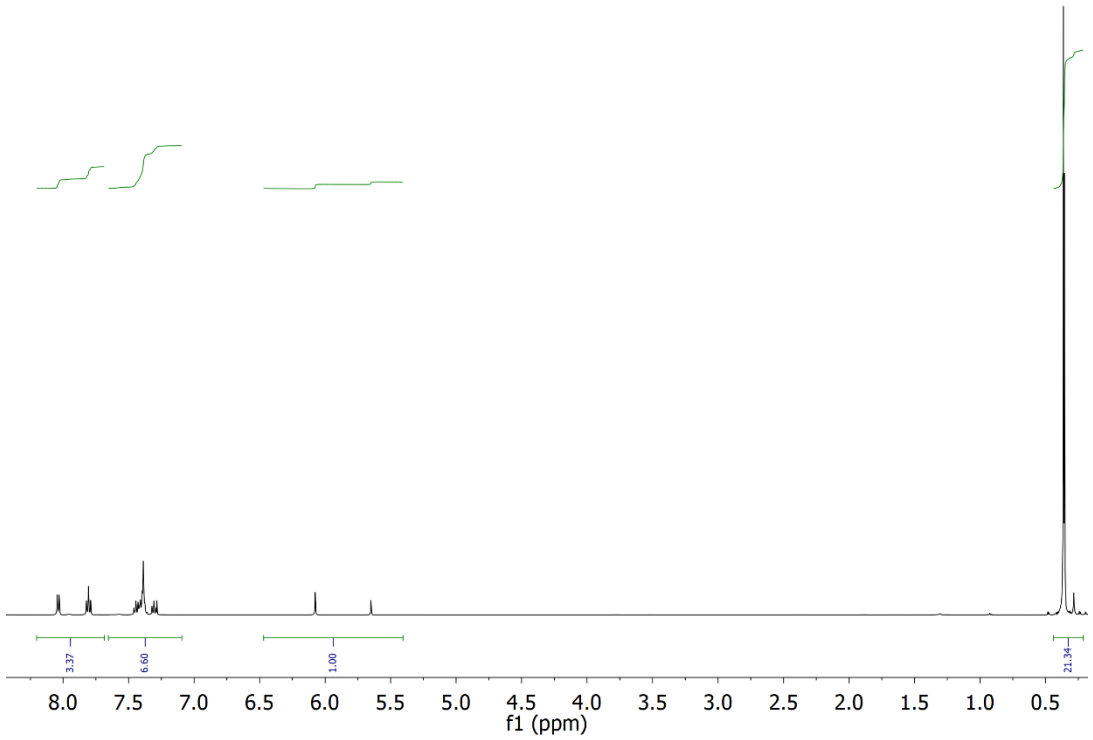
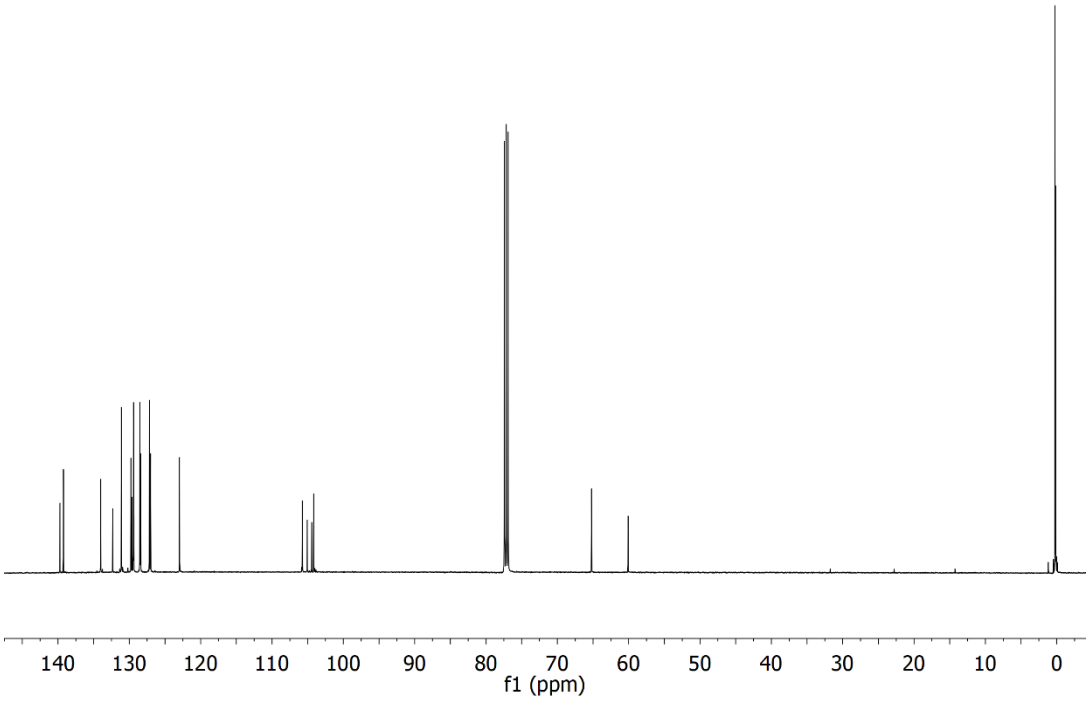


Figure S49. ^{1}H NMR of **4**. Endo and exo conformer are present in solution.



Fiugre S50. $^{13}C\{^{1}H\}$ NMR of **4** in $CDCl_3$. Endo and exo conformer are present in solution.

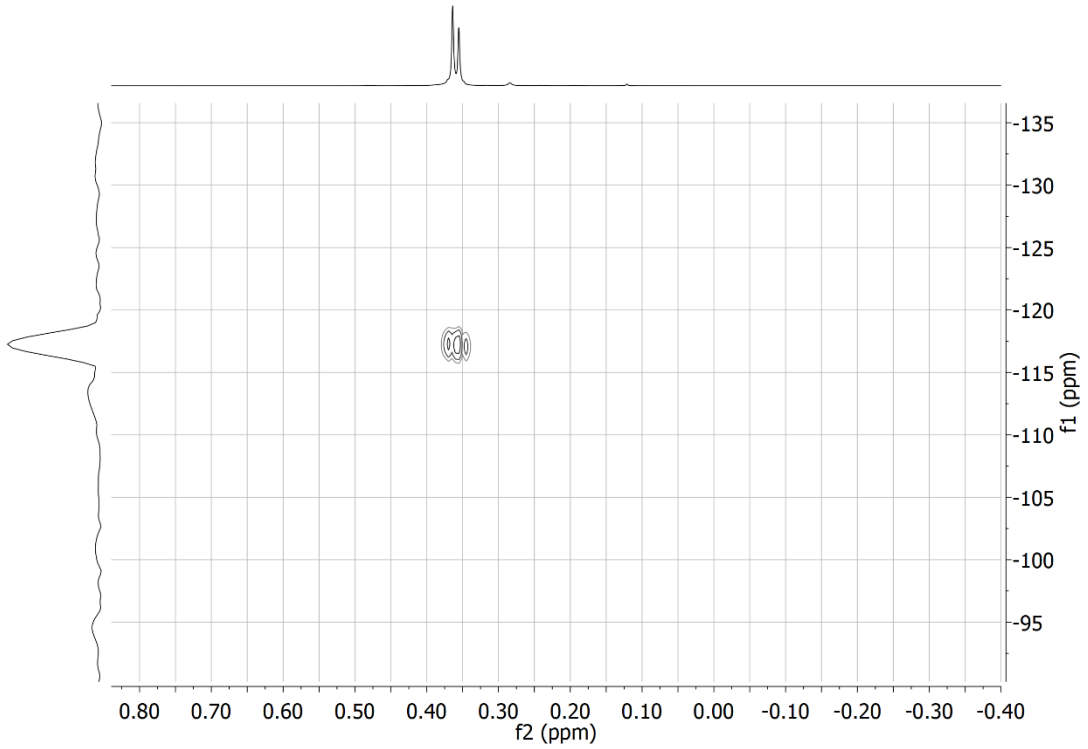


Figure S51. ^{1}H ^{29}Si HMQC of **4** in $CDCl_3$.

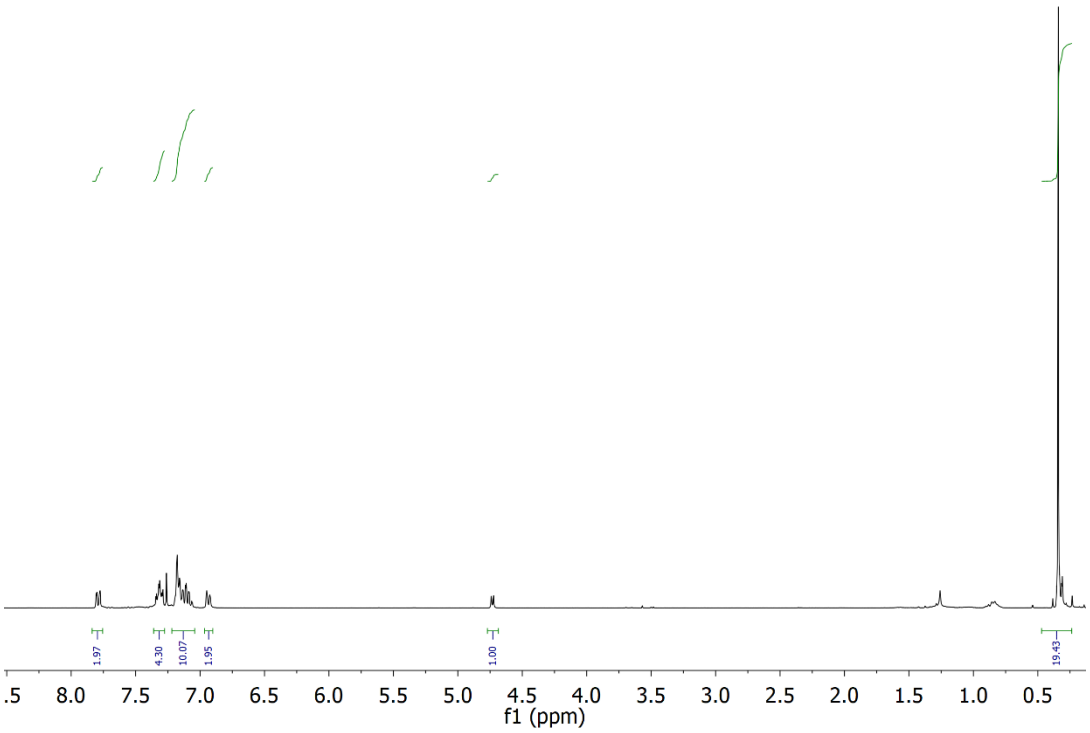


Figure S52. ^{1}H NMR of **5** in $CDCl_3$.

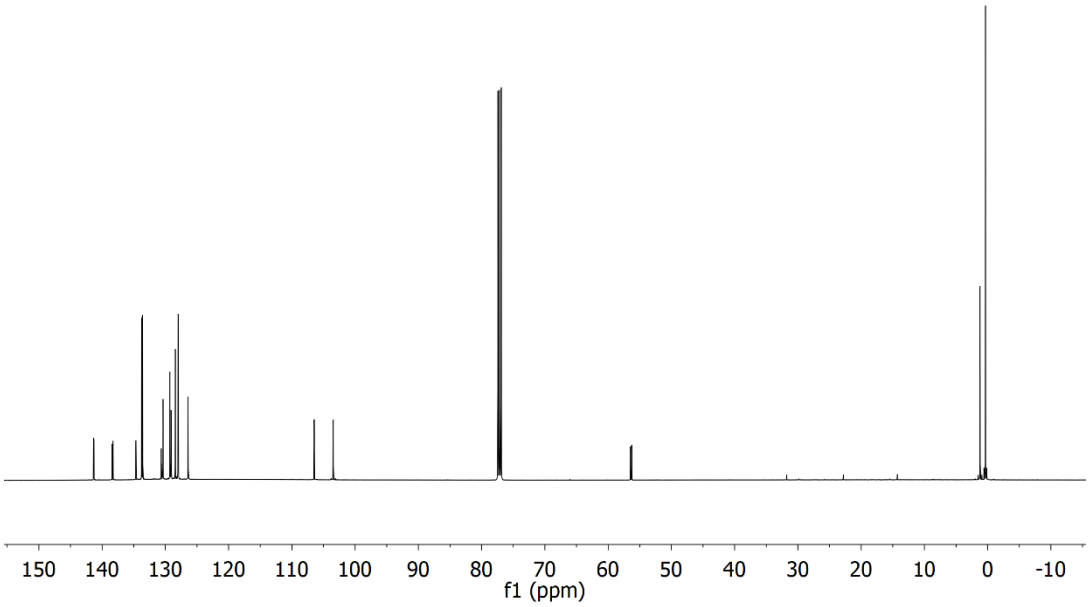


Figure S53. $^{13}C\{^{1}H\}$ NMR of **5** in $CDCl_3$.

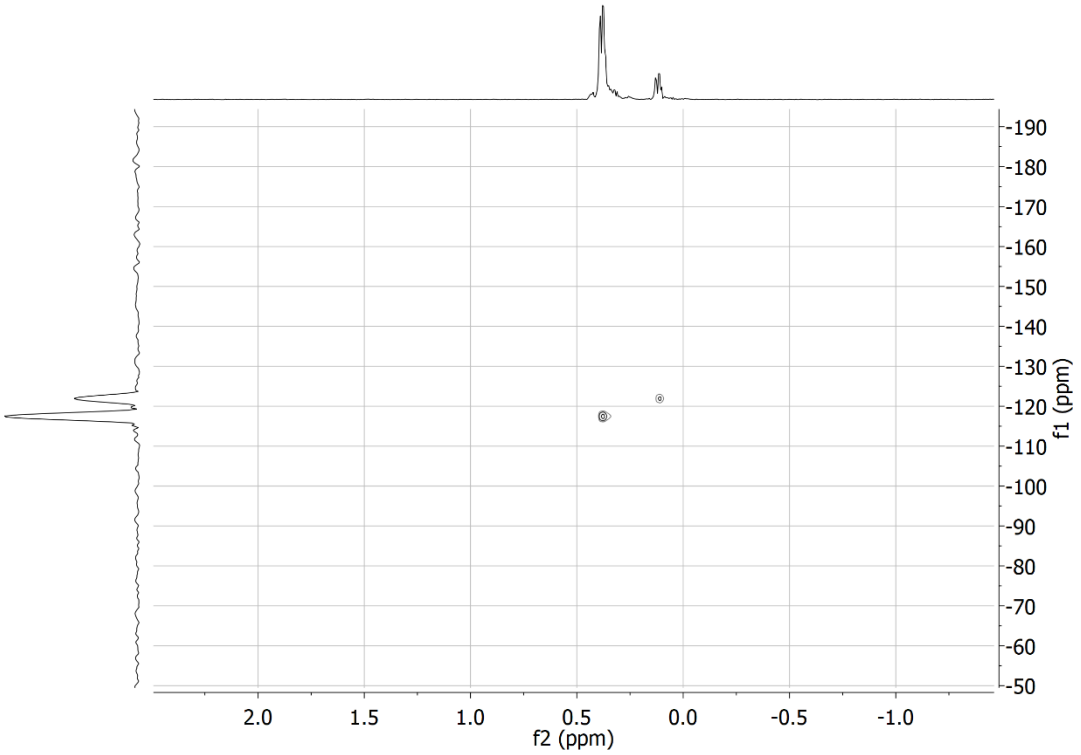


Figure S54. ^{1}H ^{29}Si HMQC NMR of **5** in $CDCl_3$.

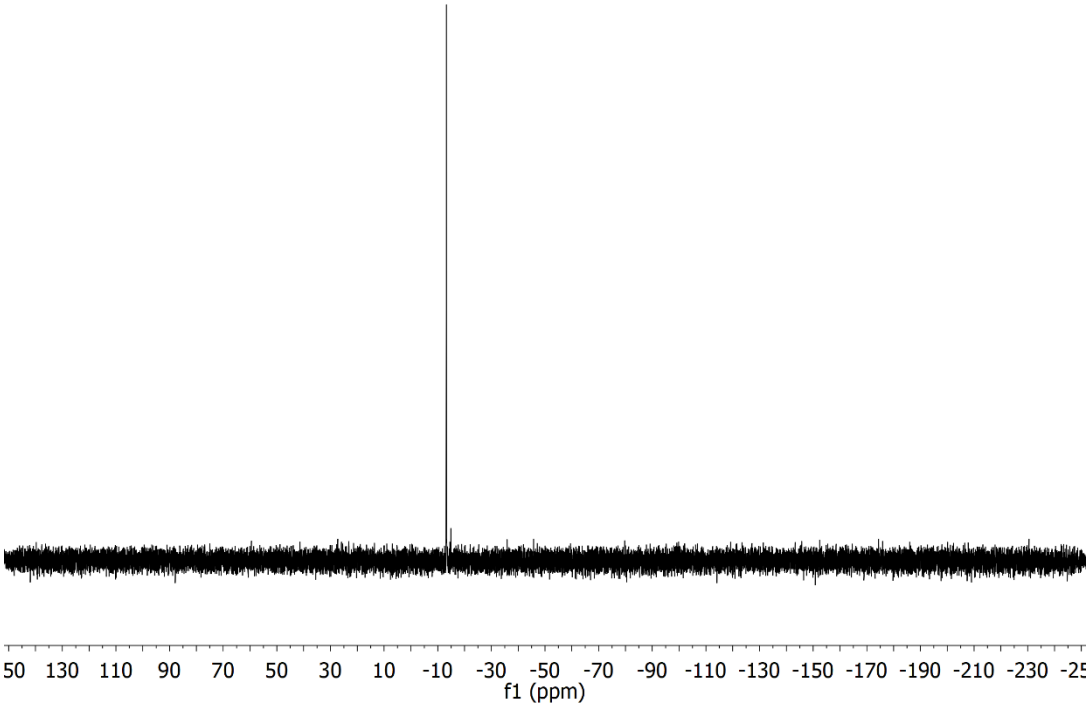


Figure S55. $^{31}P\{^{1}H\}$ NMR of **5** in $CDCl_3$.

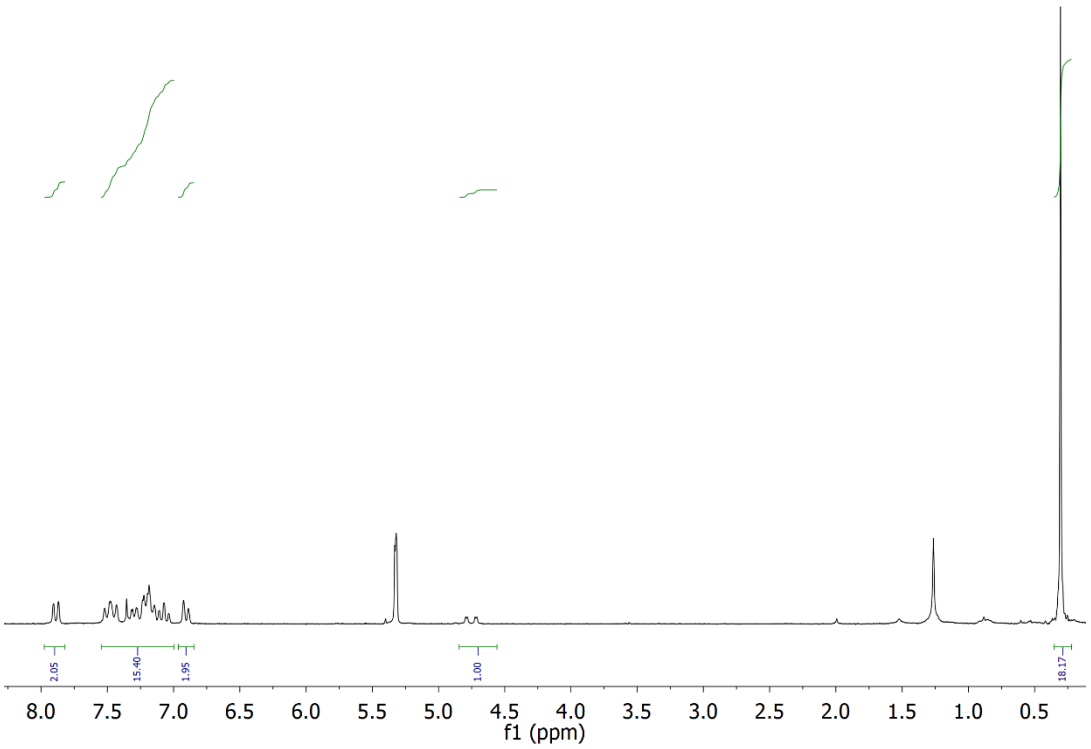


Figure S56. ^{1}H NMR of **6** in CD_2Cl_2.

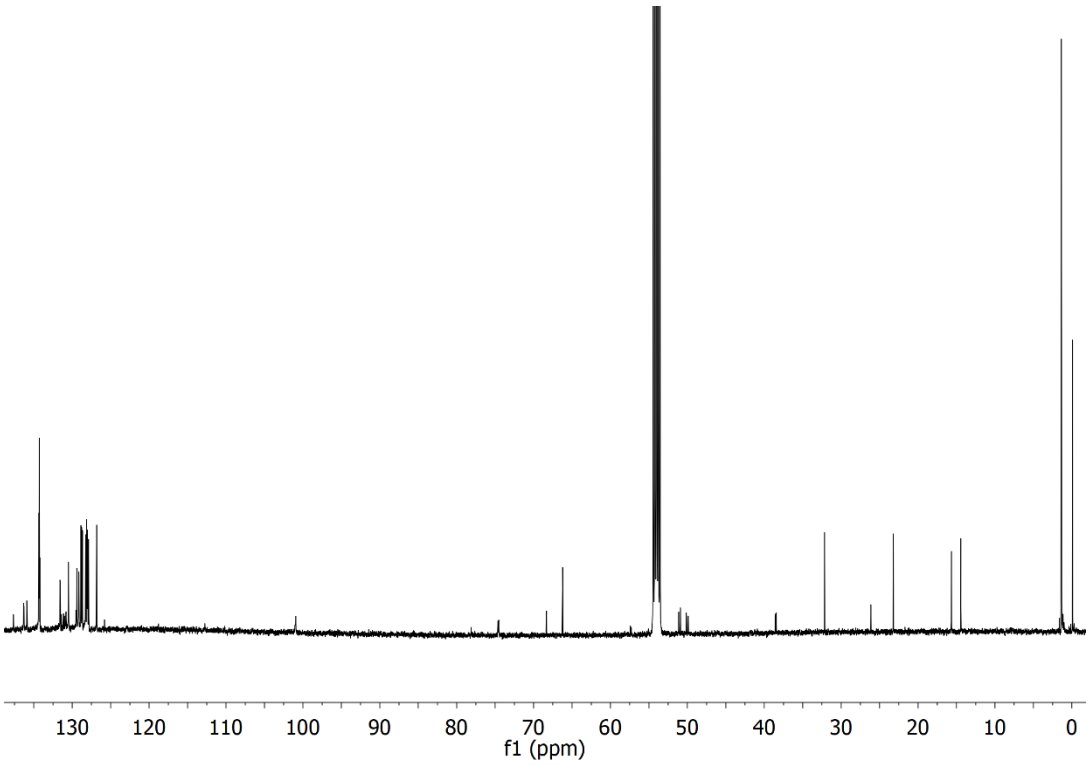


Figure S57. $^{13}C\{^{1}H\}$ NMR of **6** in CD_2Cl_2.

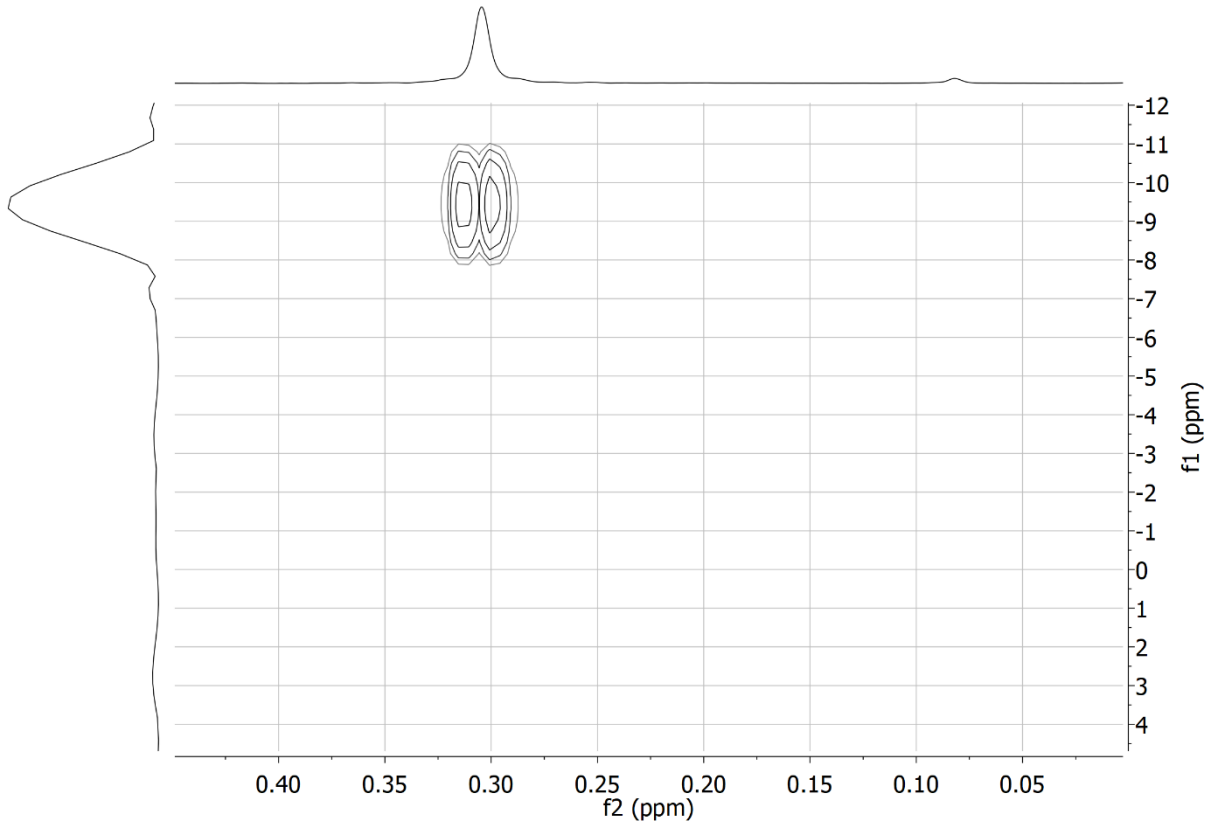


Figure S58. ^{1}H ^{29}Si HMQC of **6** in CD_2Cl_2.

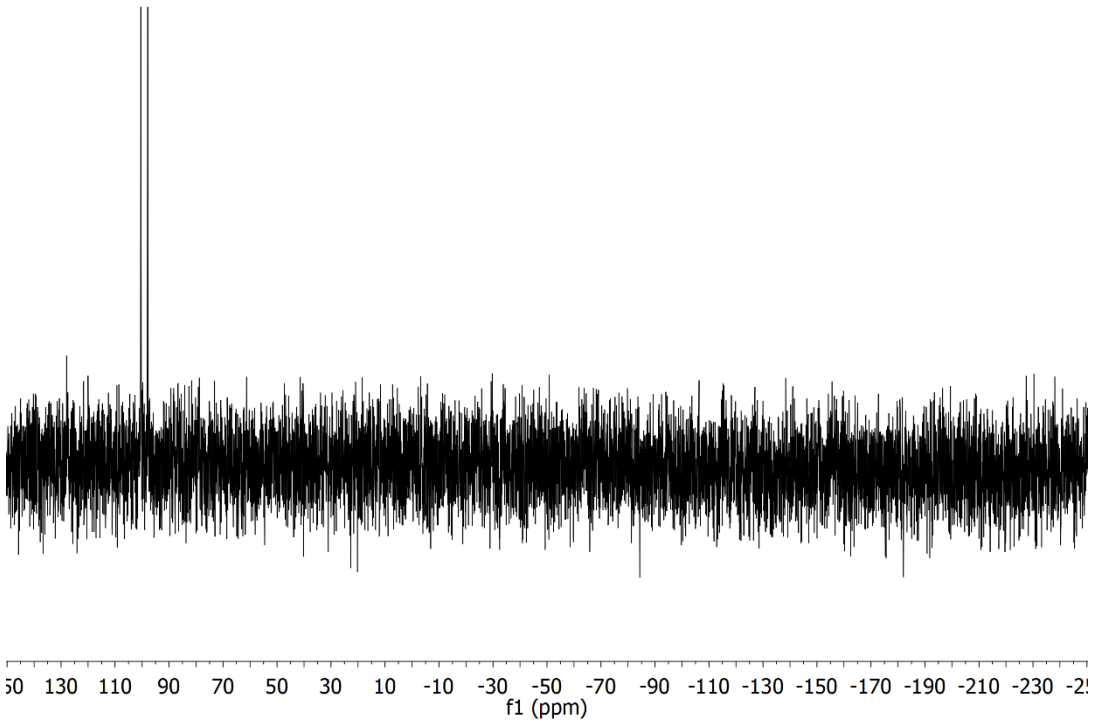


Figure S59. $^{31}P\{^{1}H\}$ NMR of **6** in $CDCl_3$.

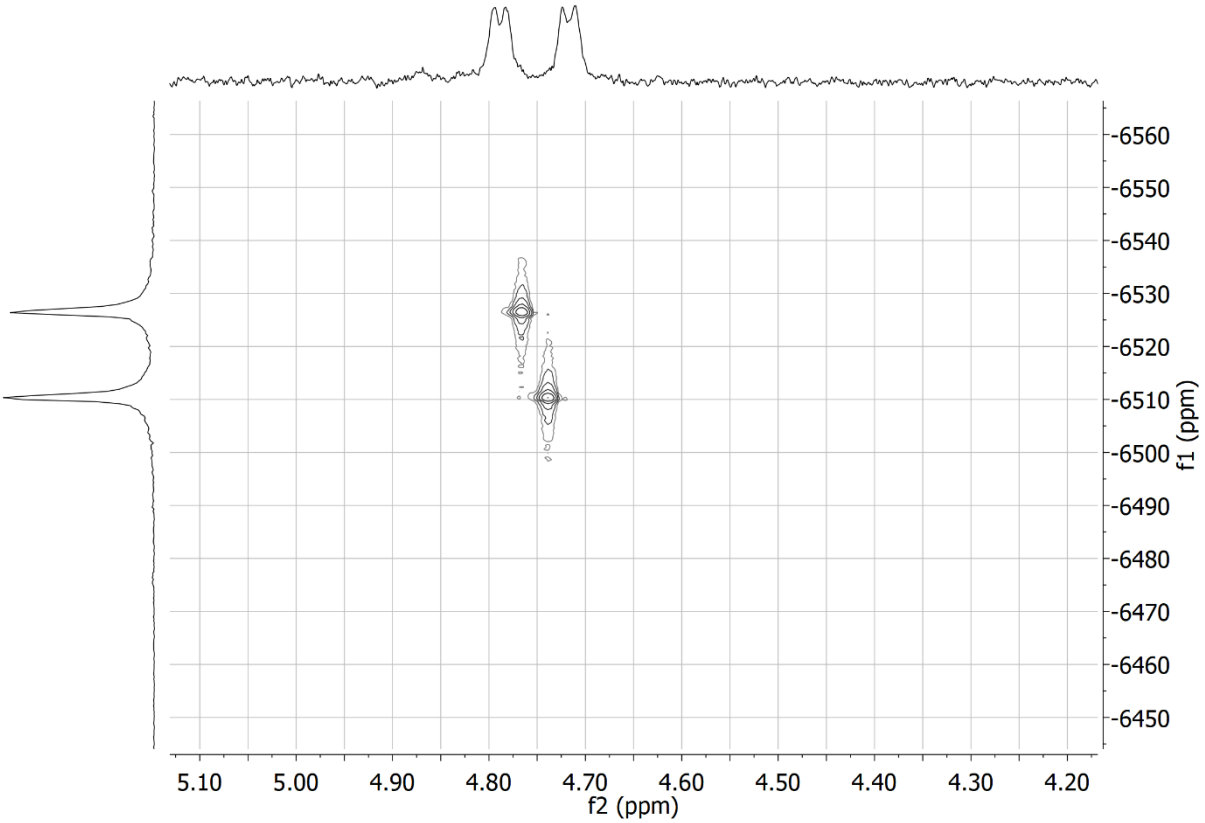


Figure S60. ^{1}H ^{103}Rh HMQC of **6** in CD_2Cl_2.

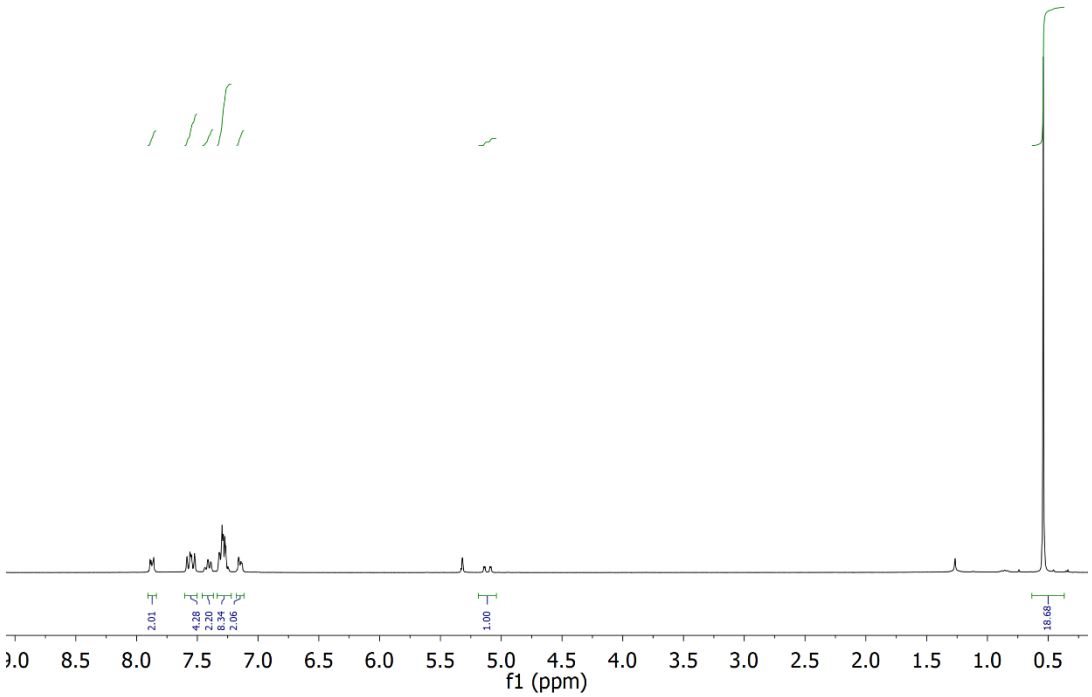


Figure S61. ^{1}H NMR of **7** in CD_2Cl_2.

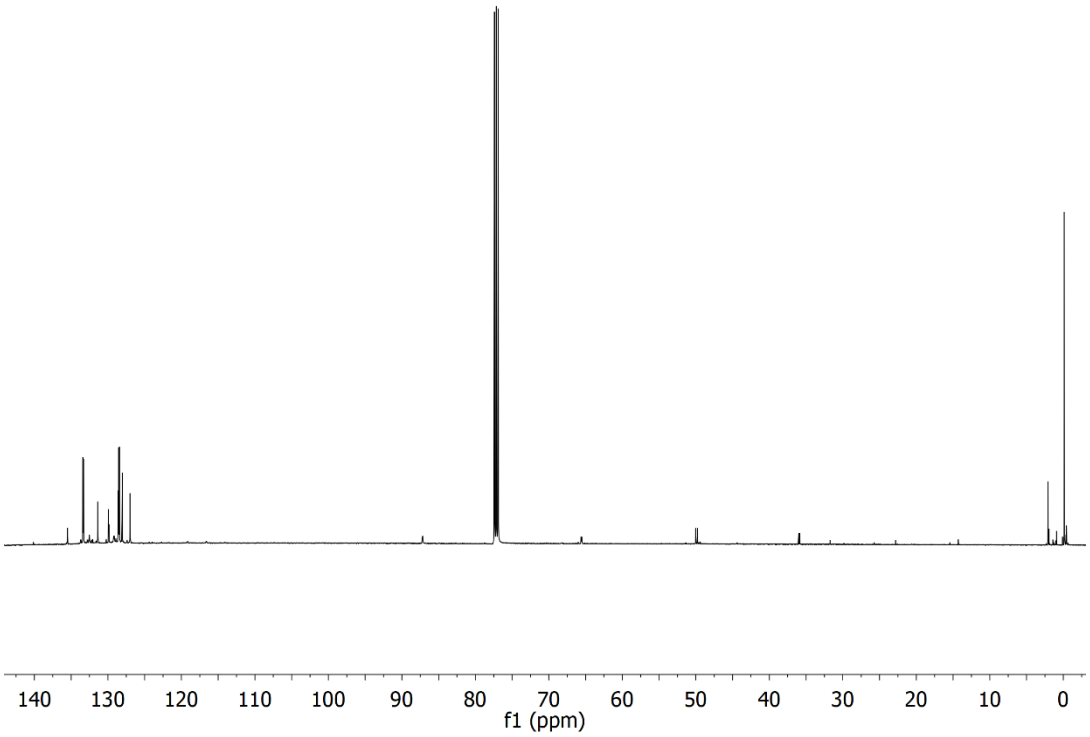


Figure S62. $^{13}C\{^{1}H\}$ NMR of **7** in $CDCl_3$.

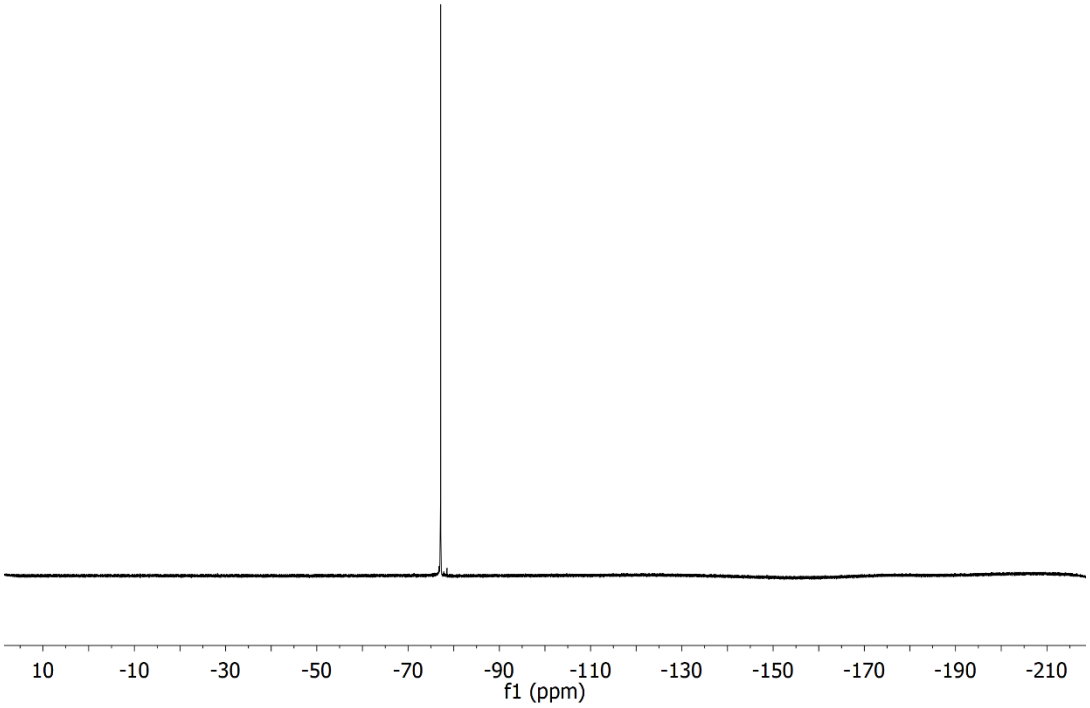


Figure S63. $^{19}F\{^{1}H\}$ NMR of **7** in CD_2Cl_2.

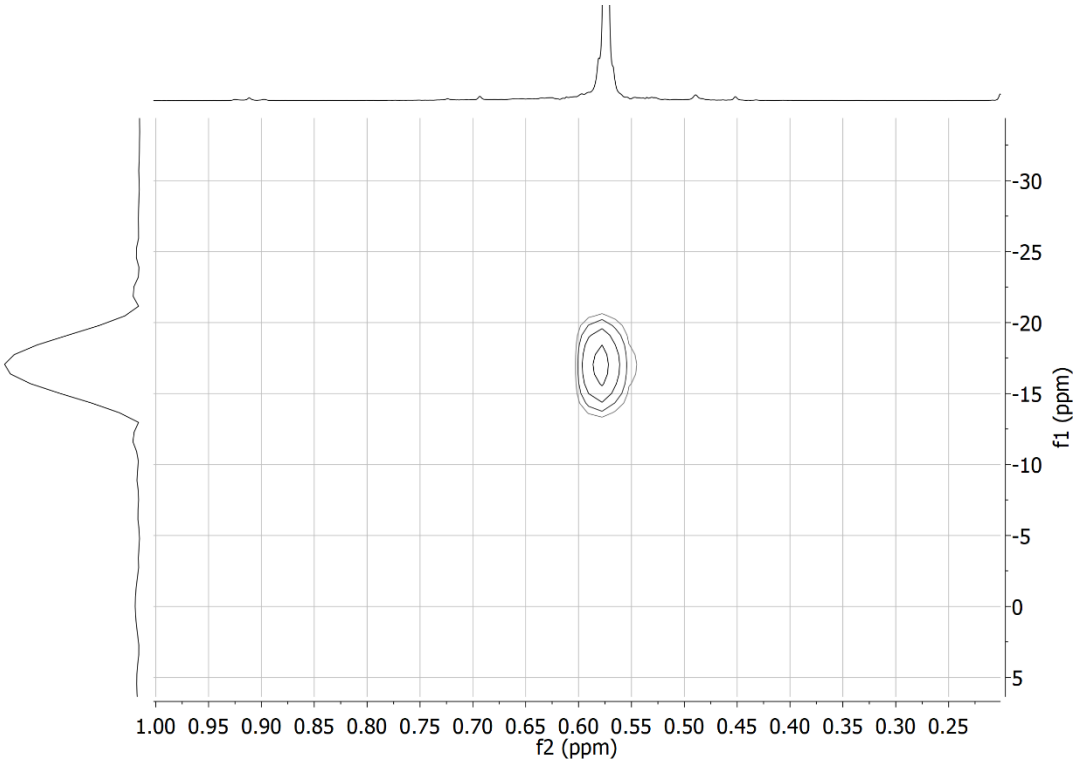


Figure S64. ^{1}H ^{29}Si HMQC of **7** in CD_2Cl_2.

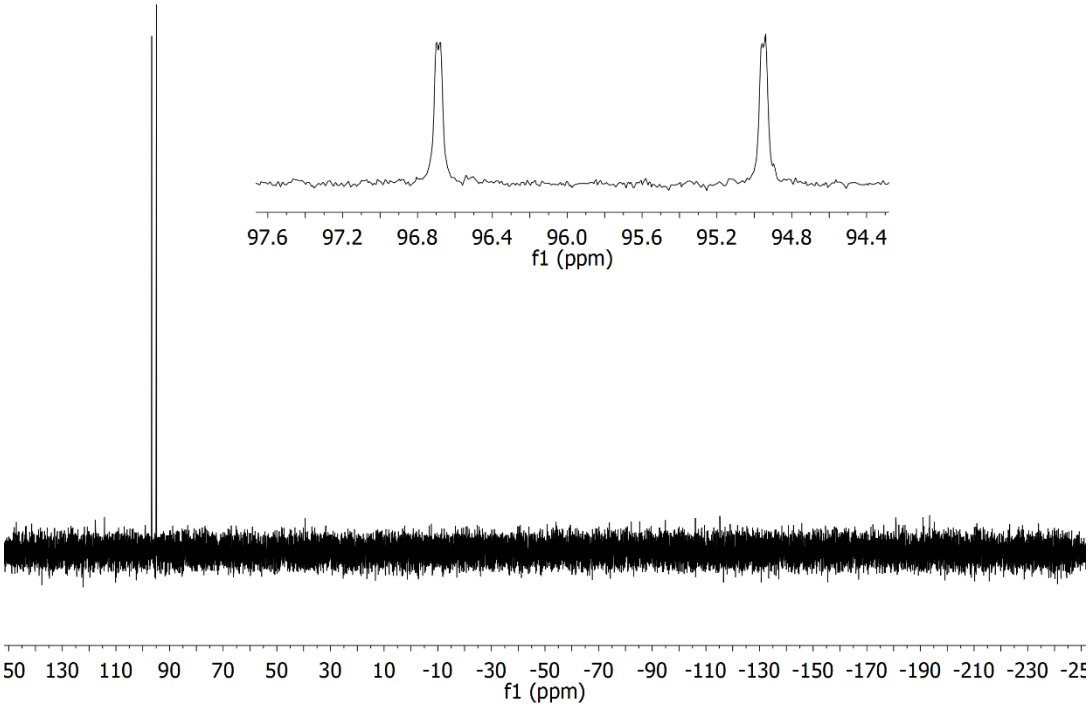


Figure S65. $^{31}P\{^{1}H\}$ NMR of **7** in CD_2Cl_2.

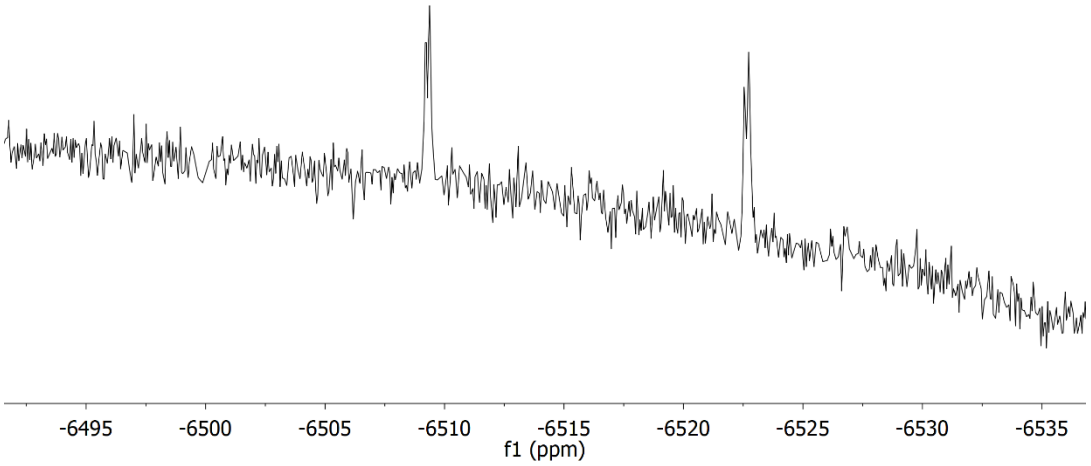


Figure S66. ^{103}Rh NMR of **7** in $CDCl_3$.

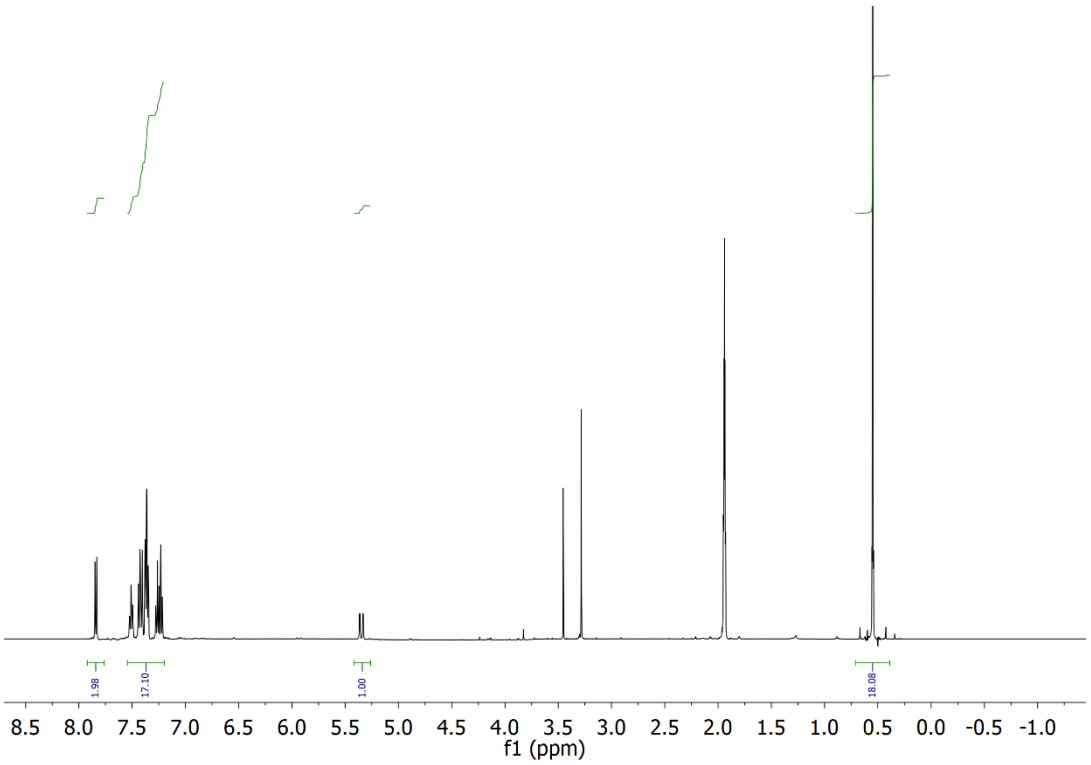


Figure S67. ^{1}H NMR of **7** in CD_3CN.

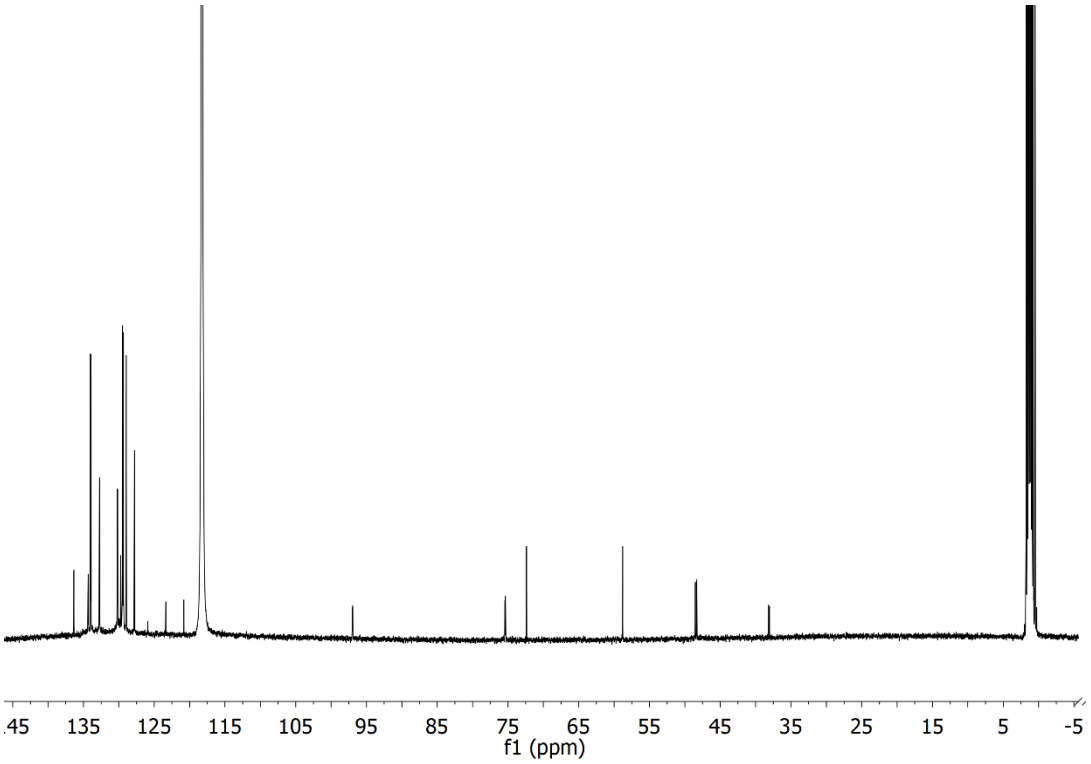


Figure S68. $^{13}C\{^{1}H\}$ NMR of **7** in CD_3CN.

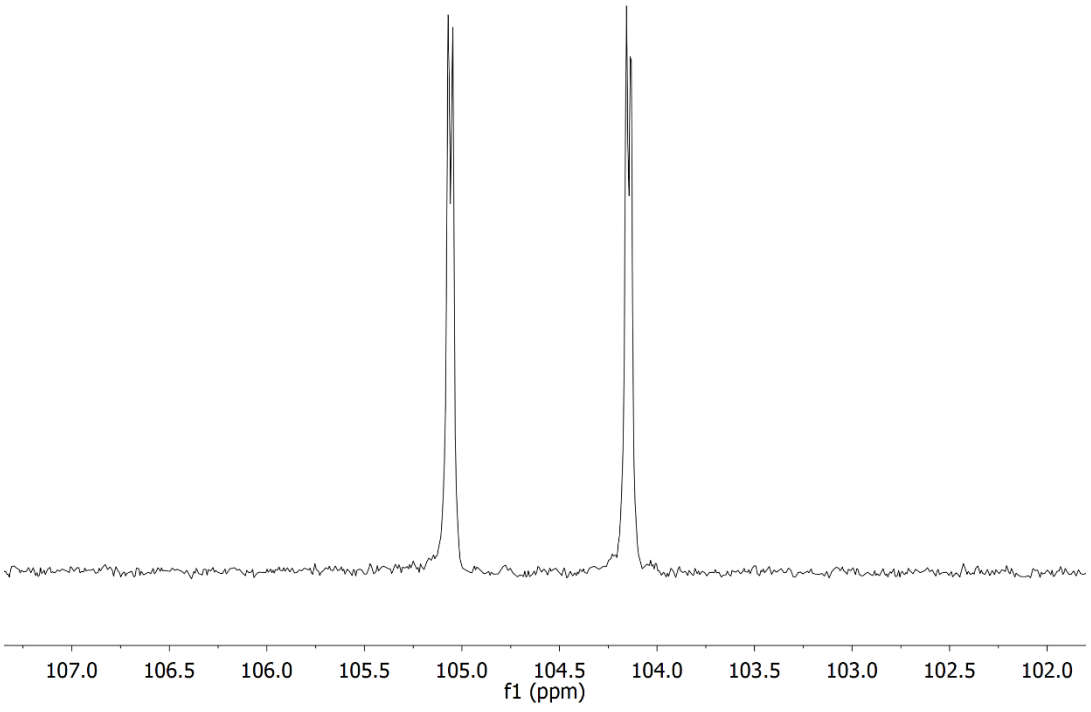


Figure S69. $^{31}P\{^{1}H\}$ NMR of **7** in CD_3CN.

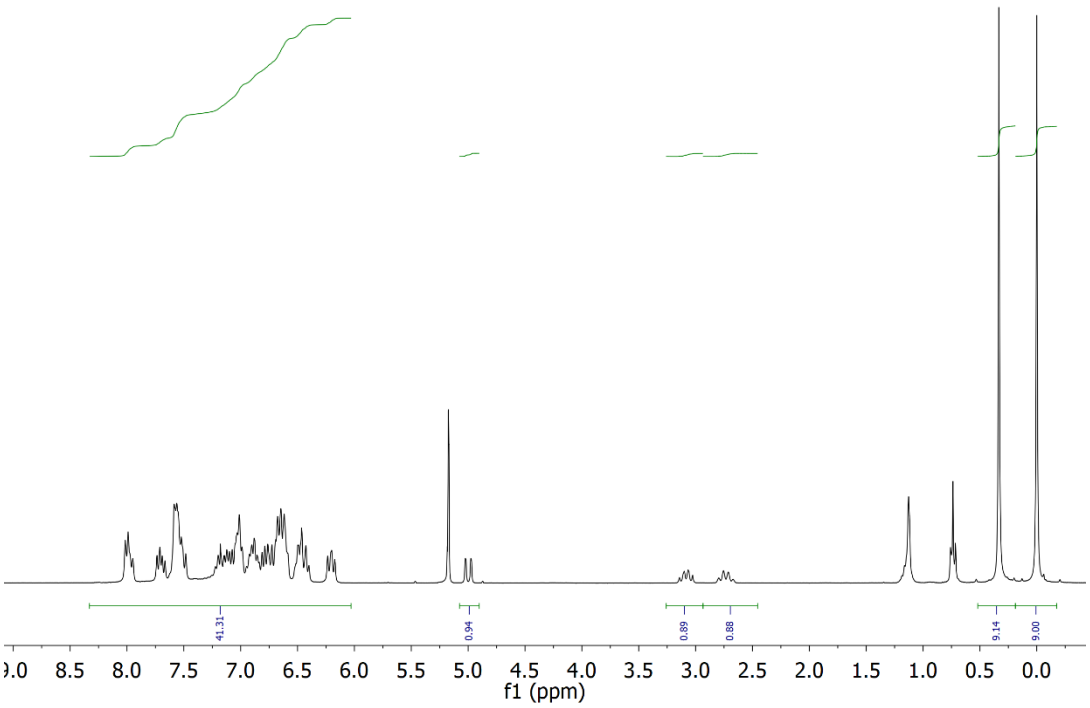


Figure S70. ^{1}H NMR of **8** in CD_2Cl_2.

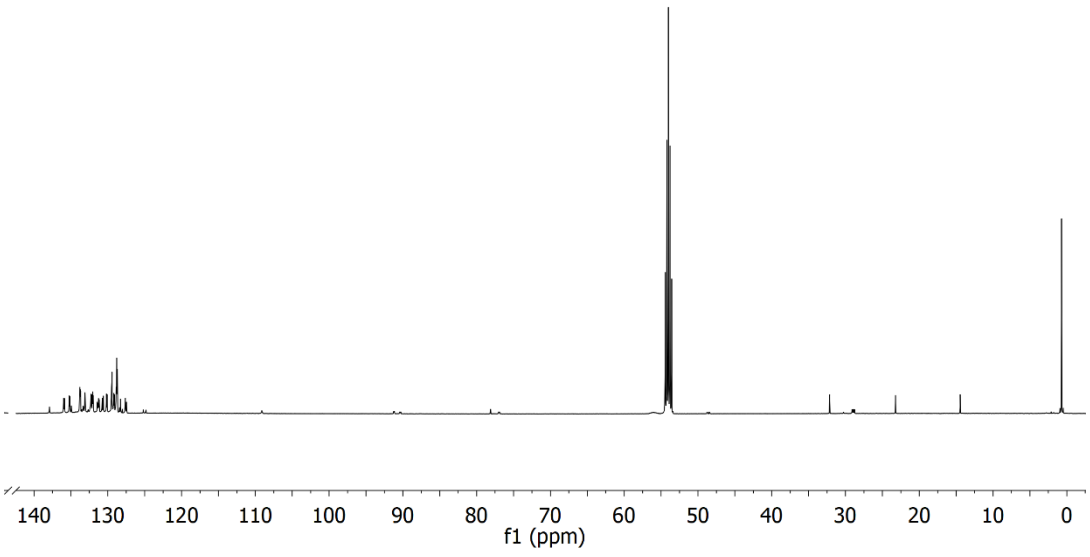


Figure S71. $^{13}C\{^{1}H\}$ NMR of **8** in CD_2Cl_2.

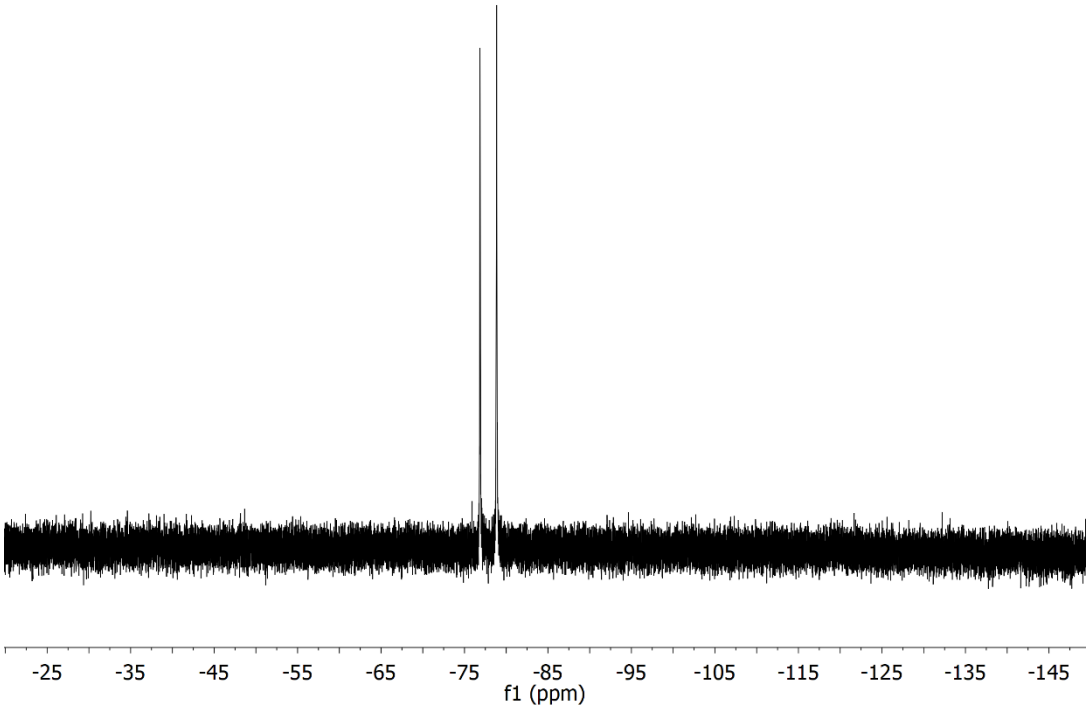


Figure S72. $^{19}F\{^{1}H\}$ NMR of **8** in CD_2Cl_2.

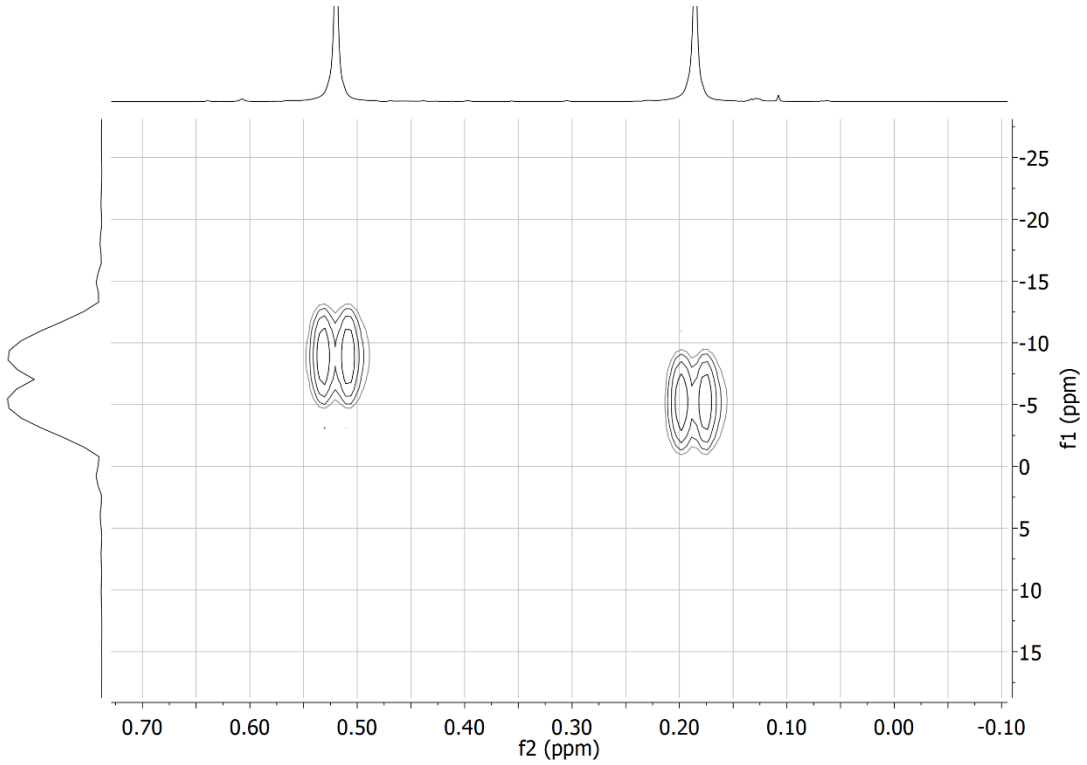


Figure S73. ^{1}H ^{29}Si HMQC of **8** in CD_2Cl_2.

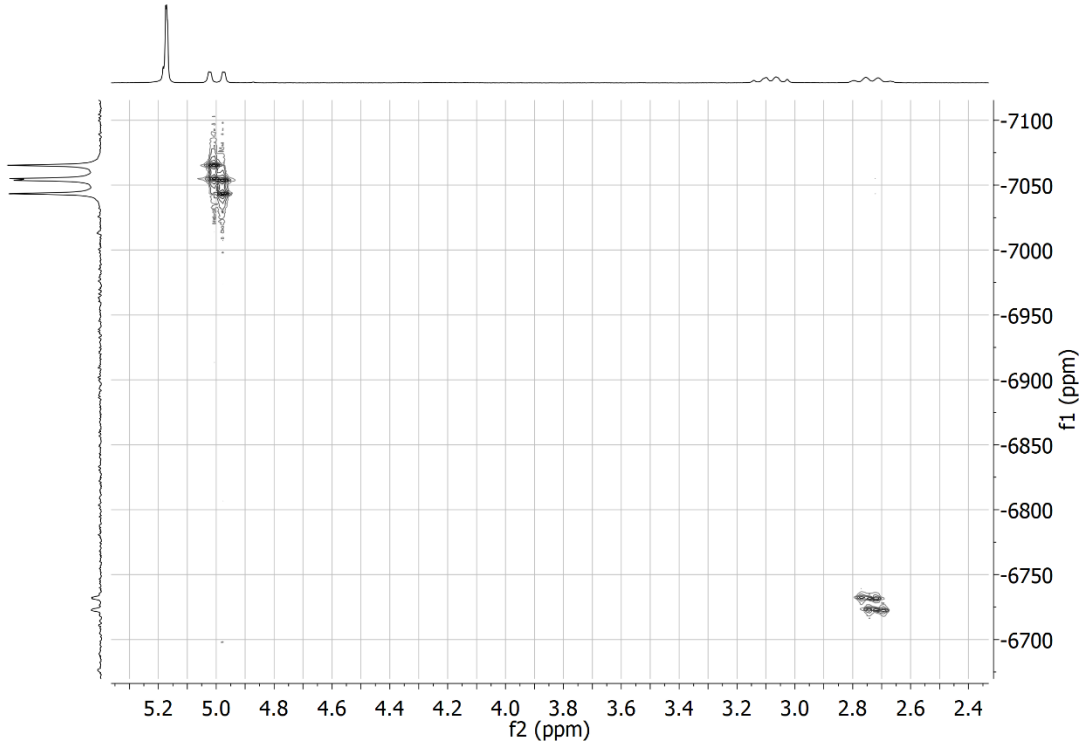


Figure S74. ^{1}H ^{103}Rh HMQC of **8** in CD_2Cl_2.

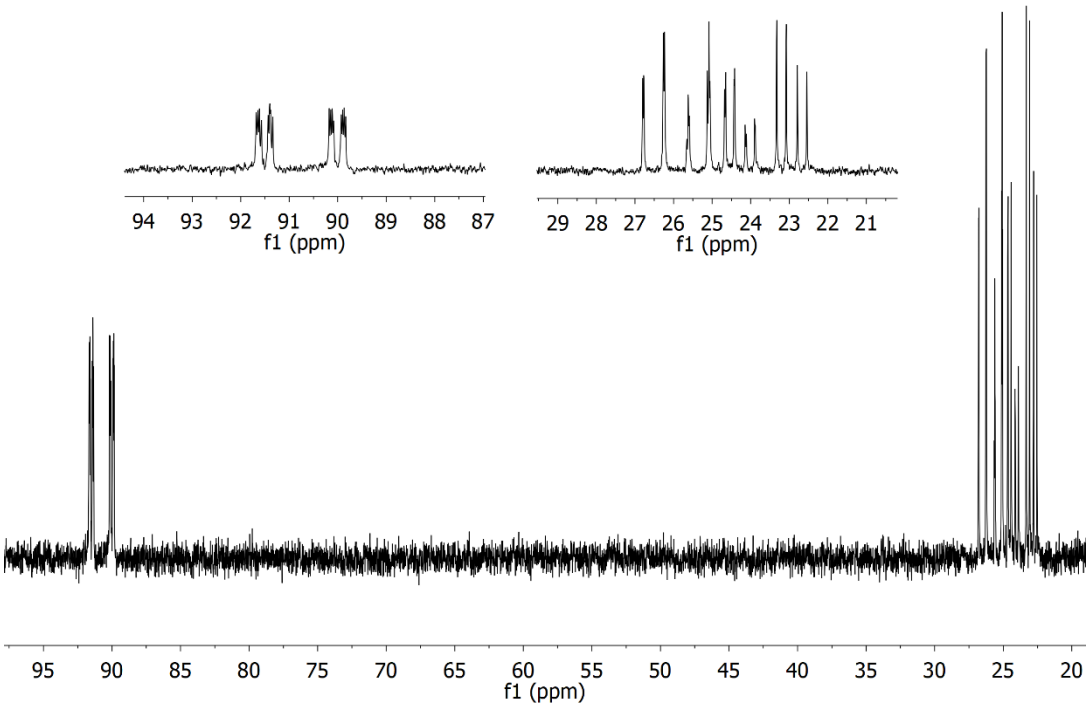


Figure S75. $^{31}P\{^{1}H\}$ NMR of **8** in CD_2Cl_2.

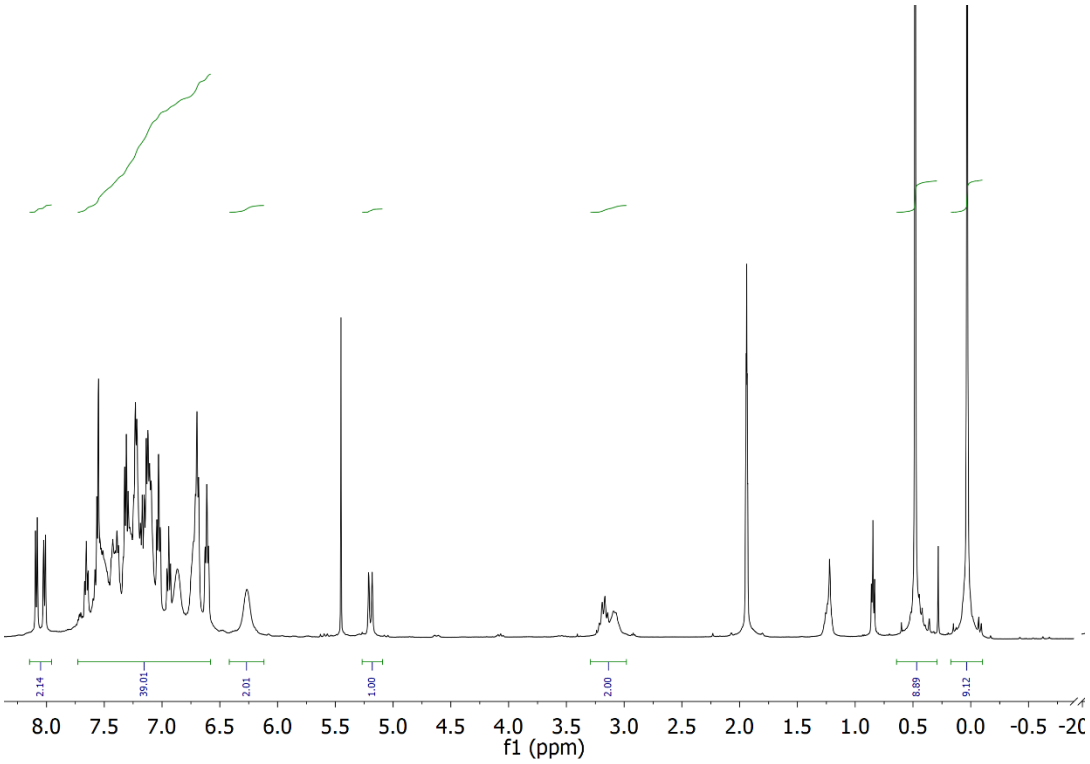


Figure S76. ^{1}H NMR spectrum of **8** in CD_3CN at 233 K.

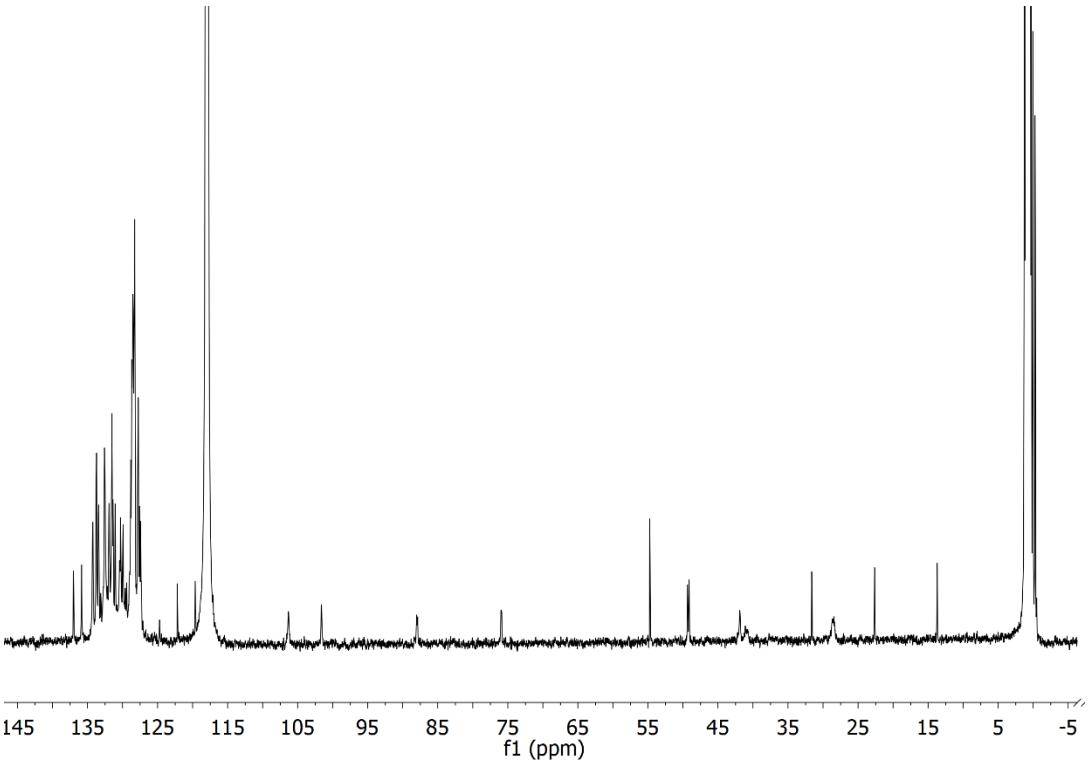


Figure S77. $^{13}C\{^{1}H\}$ NMR of **8** in CD_3CN at 233 K.

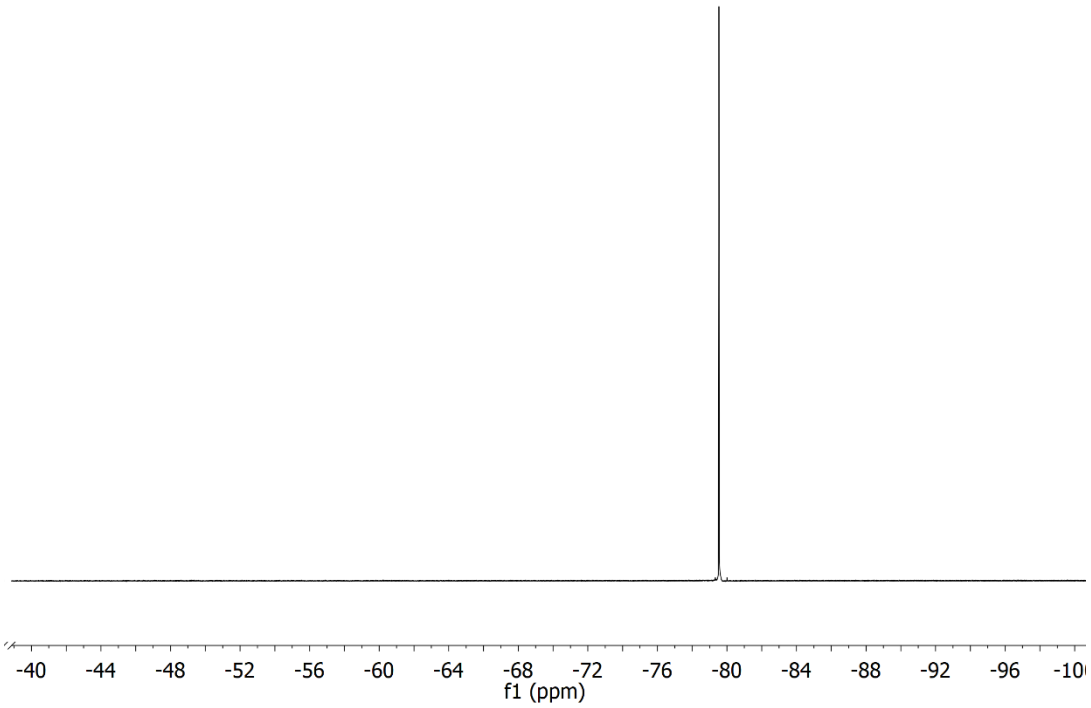


Figure S78. $^{19}F\{^{1}H\}$ NMR of **8** in CD_3CN at 233 K.

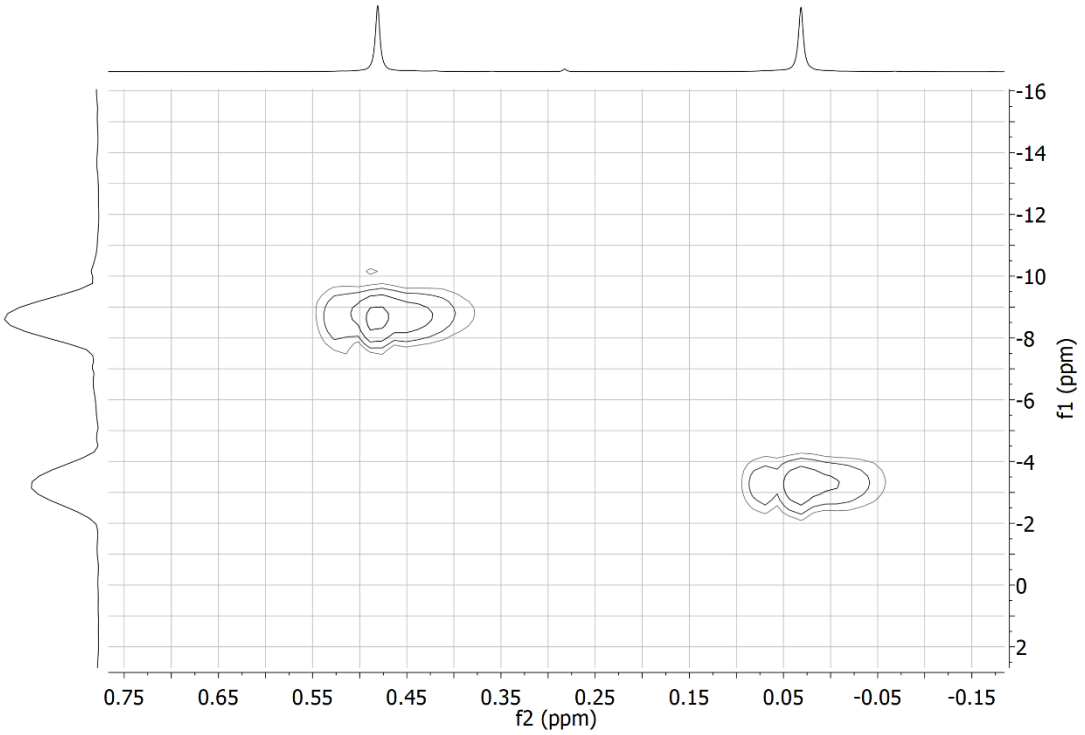


Figure S79. ^{1}H ^{29}Si HMQC NMR of **8** in CD_3CN at 233 K.

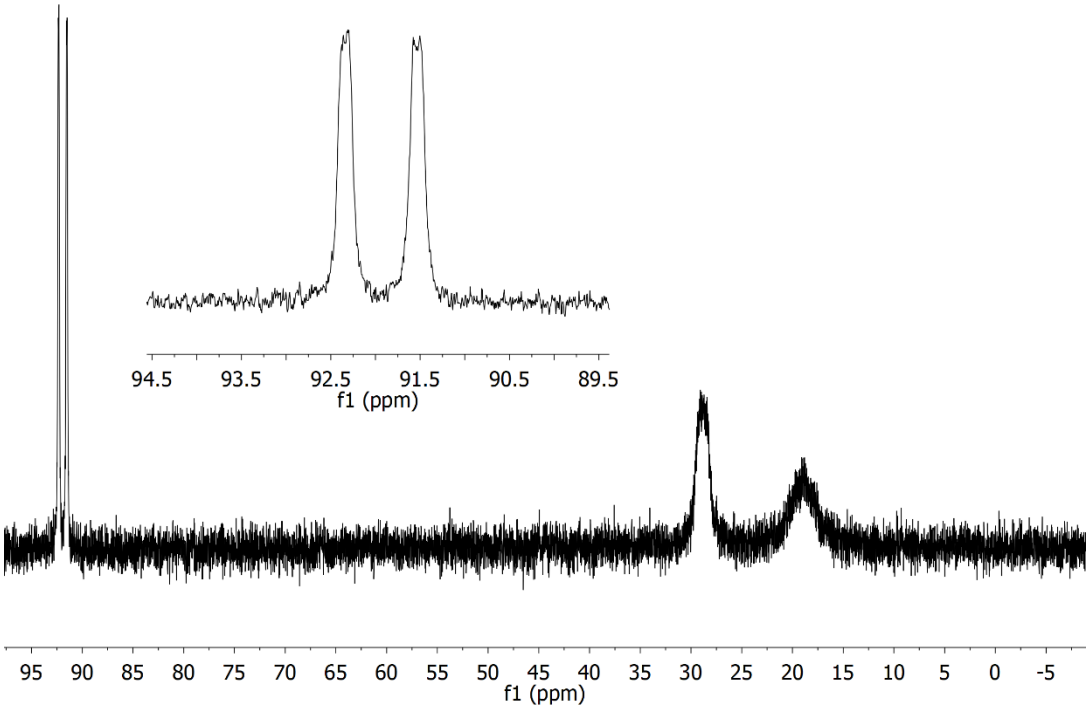


Figure S80. $^{31}P\{^{1}H\}$ NMR of **8** in CD_3CN at 233 K.

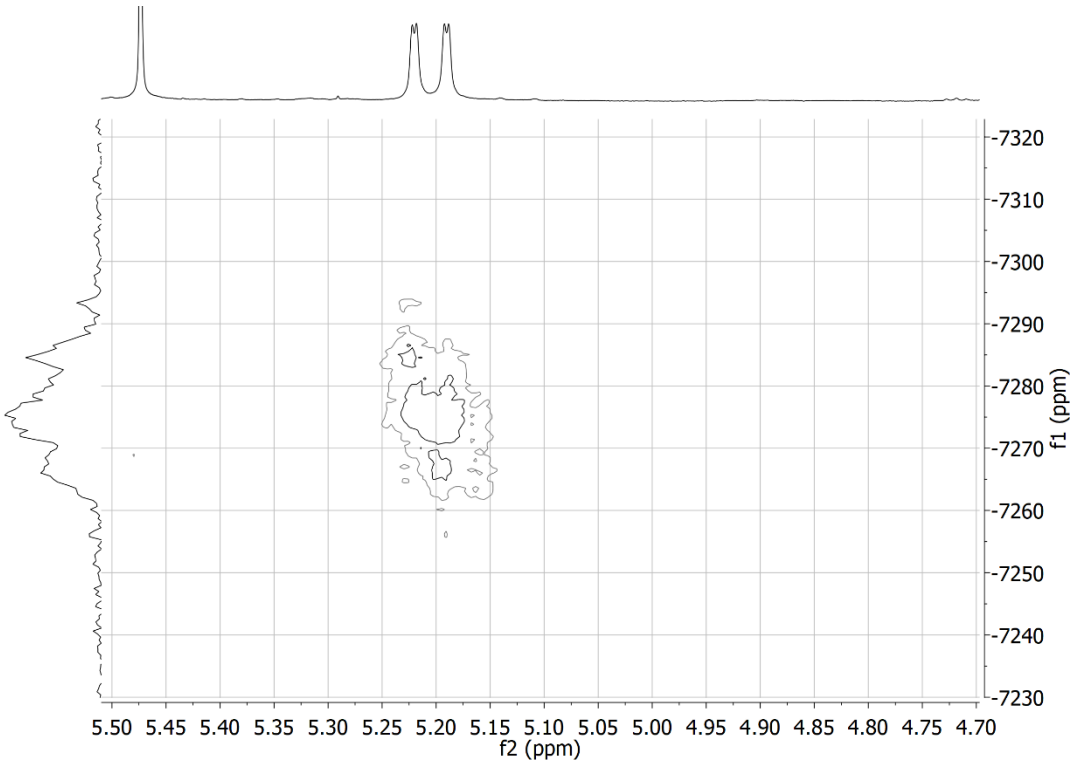


Figure S81. ^{1}H ^{103}Rh HMQC of **8** in CD_3CN at 233 K.

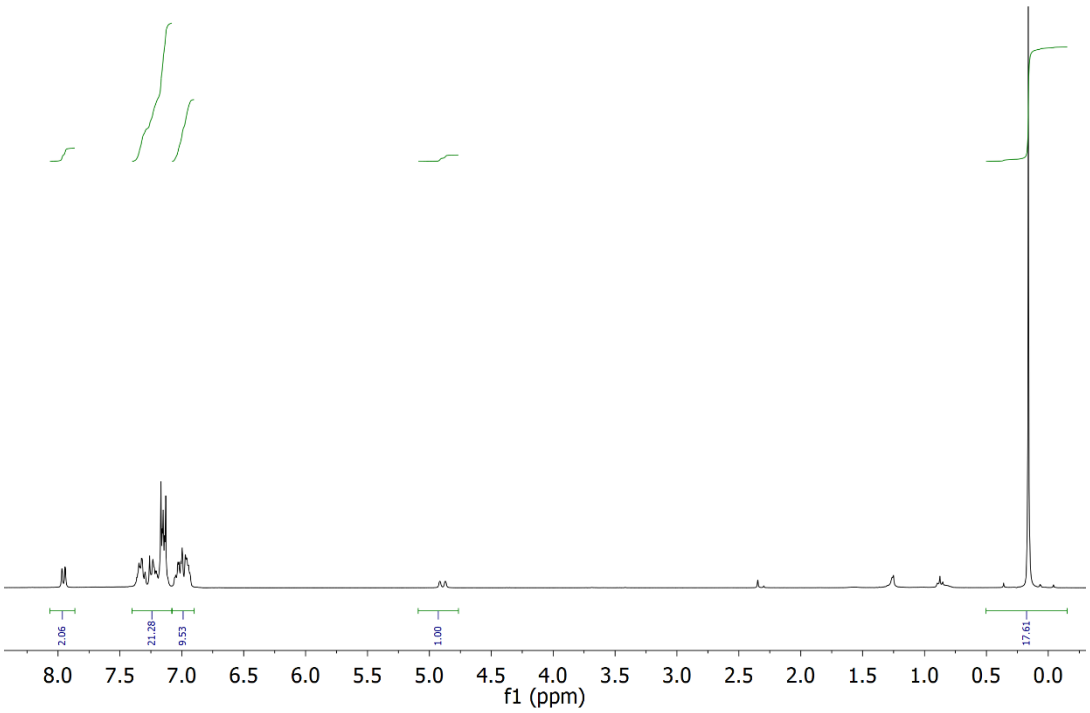


Figure S82. ^{1}H NMR of **12** in $CDCl_3$.

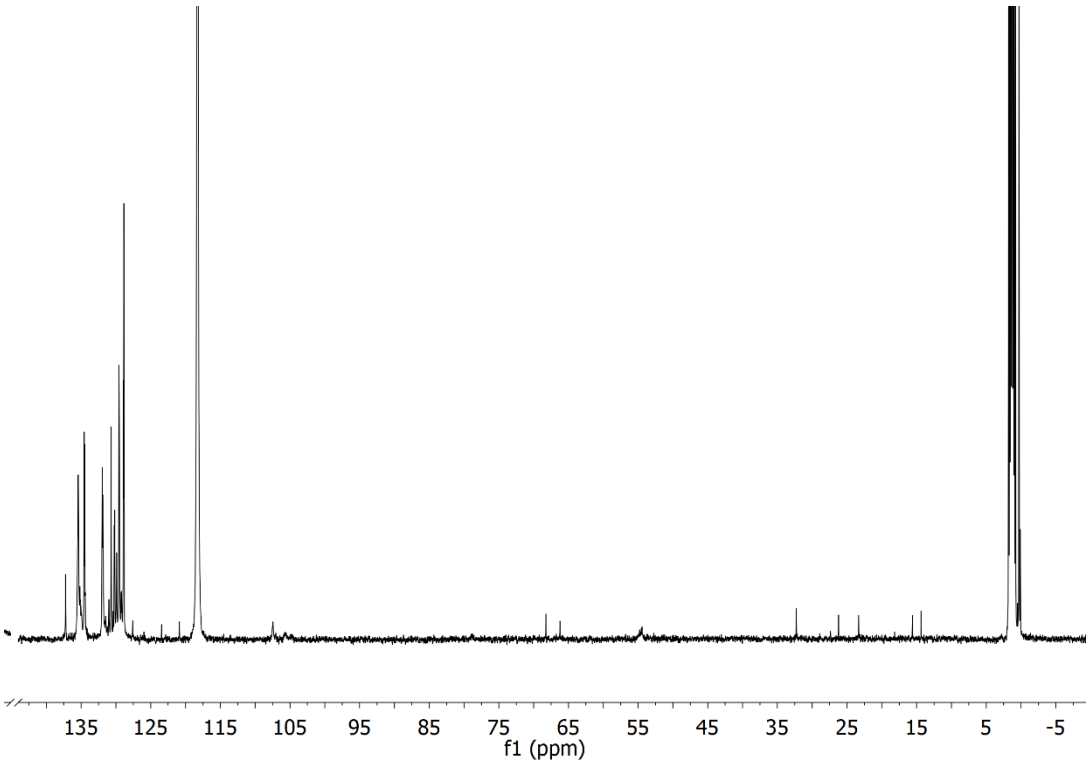


Figure S83. $^{13}C\{^{1}H\}$ NMR of **12** in CD_3CN.

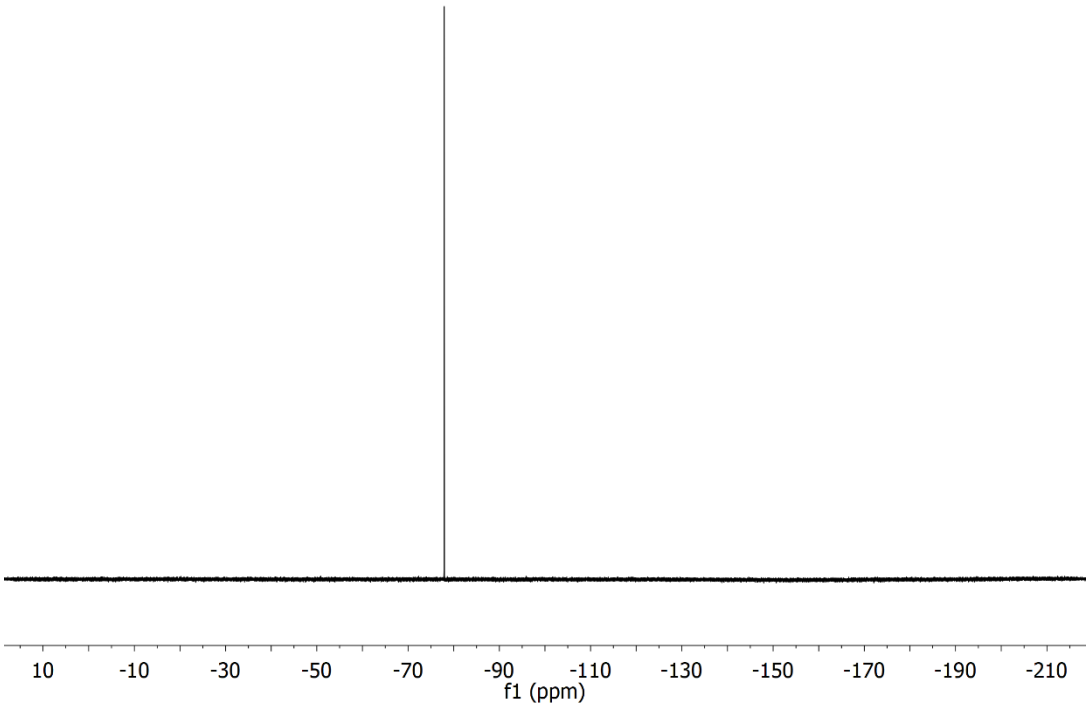


Figure S84. $^{19}F\{^{1}H\}$ NMR of **12** in $CDCl_3$.

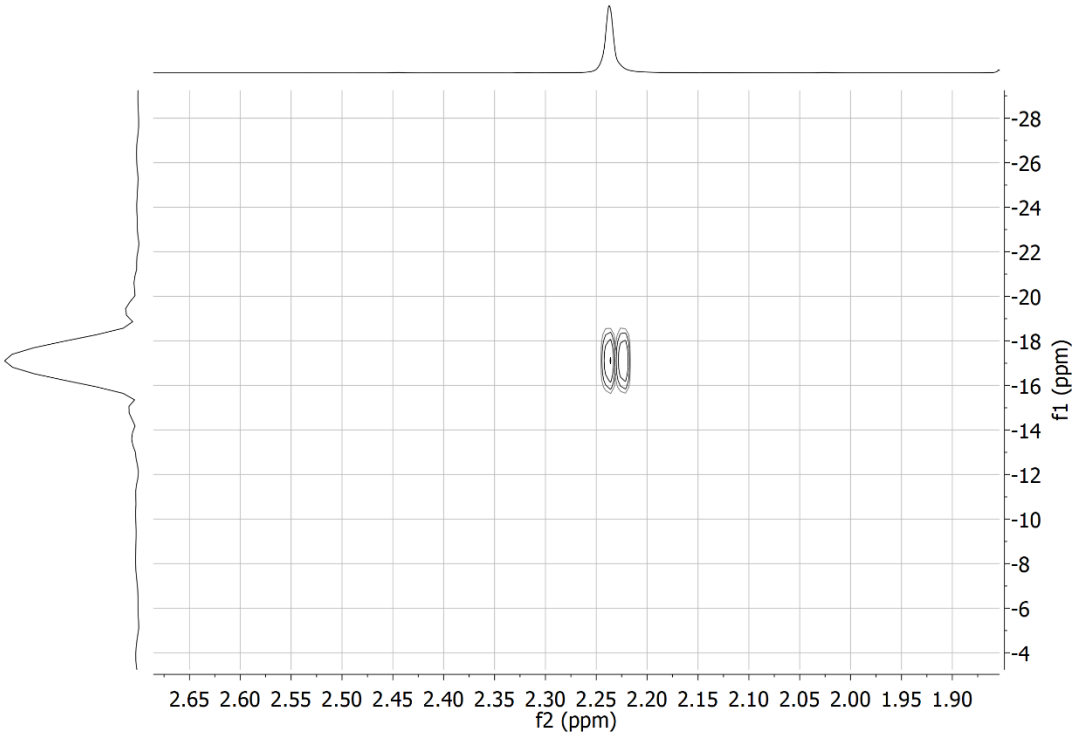


Figure S85. ^{1}H ^{29}Si HMQC NMR of **12** in CD_3CN.

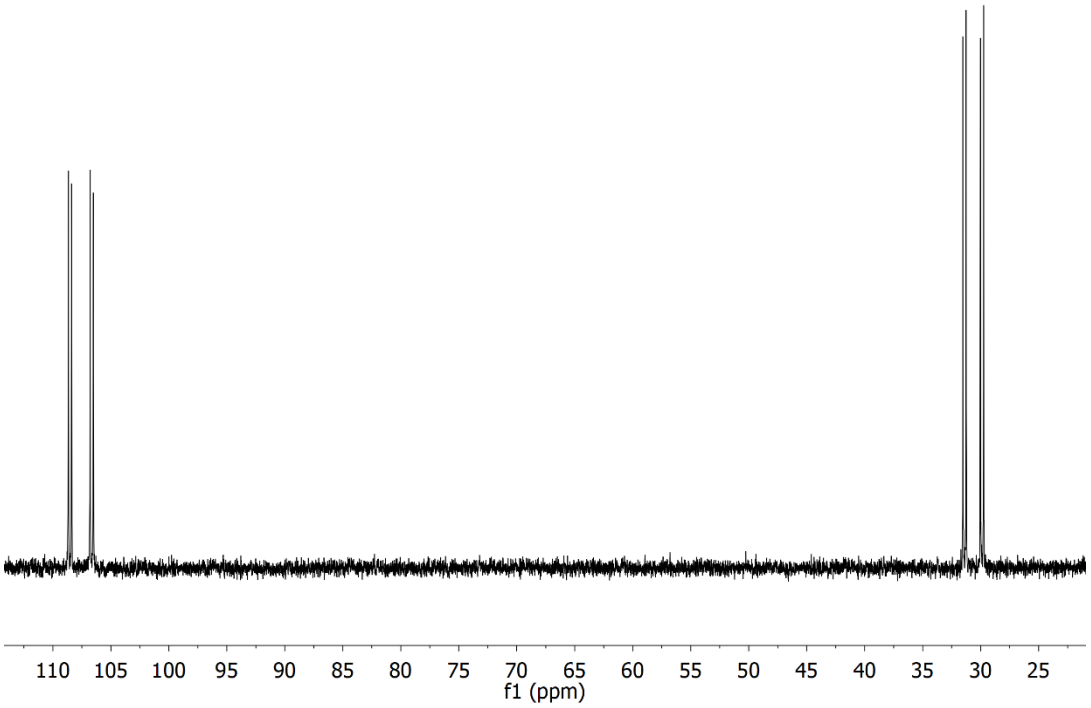


Figure S86. $^{31}P\{^{1}H\}$ NMR of **12** in $CDCl_3$.

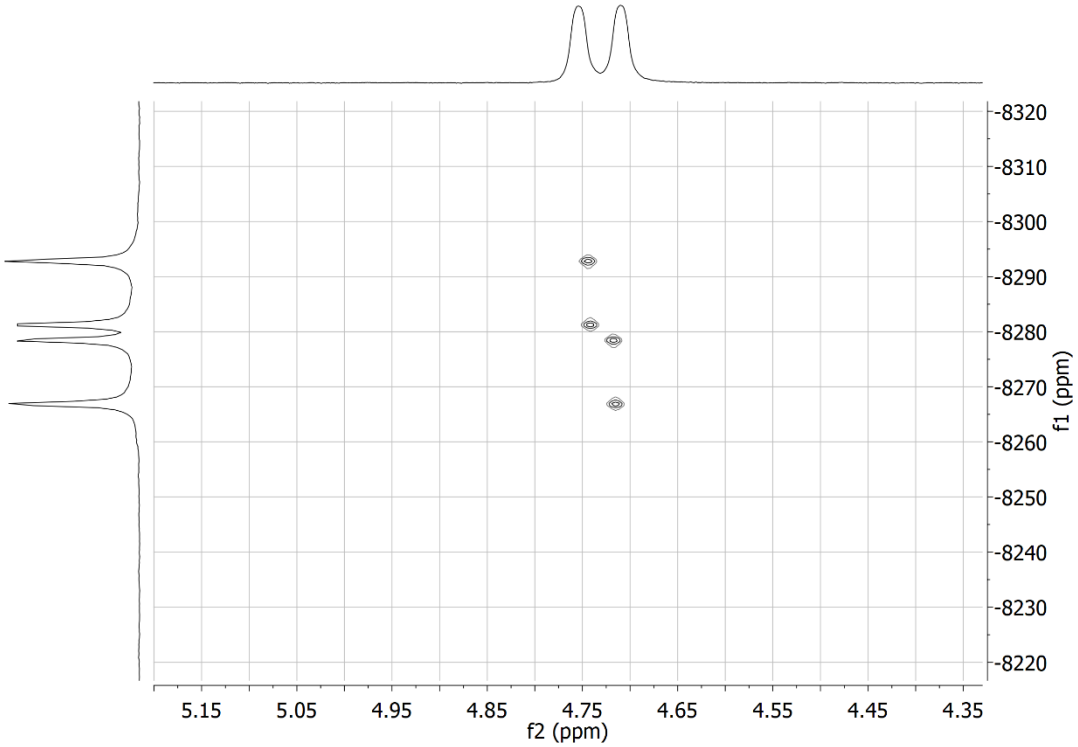


Figure S87. ^{1}H ^{103}Rh HMQC of **12** in $CDCl_3$.

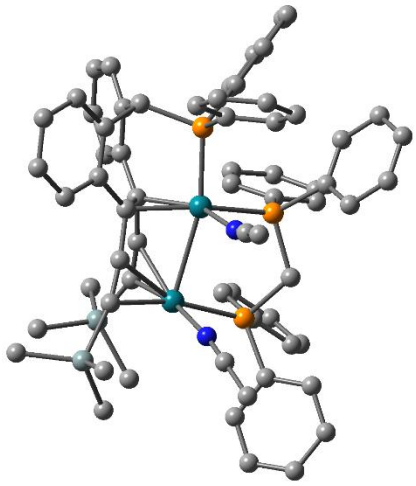
Computational Details

Density functional calculations were performed using Gaussian09[S5], revision D.01. Geometry optimizations were performed using the ωB97X-D[S6] functional in combination with the def2-SVP basis

set.[S7] The nature of each stationary point was confirmed by frequency calculations (no imaginary frequencies for minima and one for transition states). Intrinsic reaction coordinate (IRC) calculations were performed to obtain additional proof for the position of the transition state geometries. Cartesian coordinates are given in angstroms and energies in Hartree.

Optimized Structures

8-SM



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- Thermochemistry -

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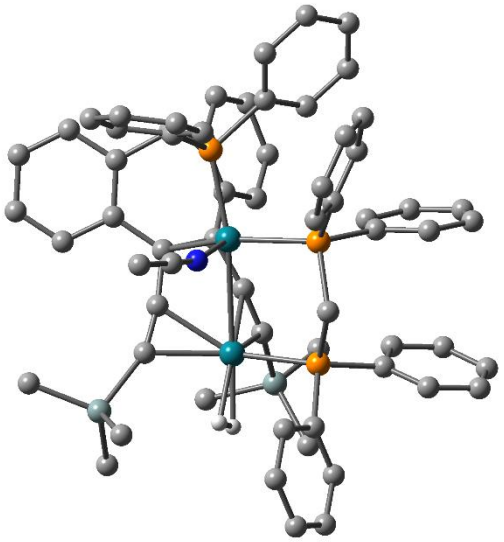
8a-H_2



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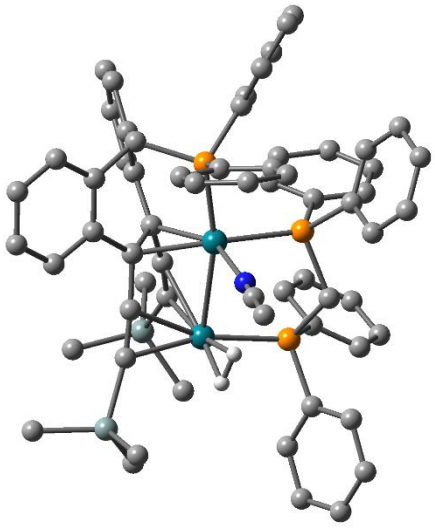
C	-4.954257000	-4.016397000	0.758592000
H	-6.568225000	-3.284519000	-0.476230000
H	-3.222824000	-4.444518000	1.984981000
H	-5.402043000	-5.002539000	0.896979000
C	-3.962121000	0.983778000	-1.117330000
C	-4.508365000	2.265811000	-0.995289000
C	-4.045792000	0.316845000	-2.351139000
C	-5.147737000	2.861251000	-2.084592000
H	-4.445968000	2.813355000	-0.055950000
C	-4.686121000	0.913419000	-3.431734000
H	-3.617098000	-0.679982000	-2.470721000
C	-5.242666000	2.188024000	-3.300073000
H	-5.586176000	3.854623000	-1.971129000
H	-4.760904000	0.373292000	-4.377958000
H	-5.756980000	2.651658000	-4.144604000
C	-1.429820000	-2.277798000	-2.448197000
C	-2.429460000	-3.215623000	-2.156062000
C	-1.390416000	-1.702447000	-3.726494000
C	-3.374979000	-3.560042000	-3.120068000
H	-2.479625000	-3.682355000	-1.170653000
C	-2.331571000	-2.056835000	-4.690463000
H	-0.627156000	-0.967658000	-3.987532000
C	-3.330649000	-2.981636000	-4.387616000
H	-4.147709000	-4.290836000	-2.875046000
H	-2.279951000	-1.612581000	-5.686568000
H	-4.067373000	-3.260483000	-5.143300000
C	0.044128000	-3.180589000	-0.116365000
C	0.339553000	-4.413614000	-0.713072000
C	0.029113000	-3.081010000	1.276803000
C	0.595781000	-5.529068000	0.079073000
H	0.354750000	-4.513003000	-1.801692000
C	0.267117000	-4.200809000	2.069896000
H	-0.168570000	-2.119422000	1.750173000
C	0.547172000	-5.426556000	1.470827000
H	0.822245000	-6.487348000	-0.391746000
H	0.234807000	-4.109738000	3.157718000
H	0.733681000	-6.308495000	2.087058000
C	3.915385000	-0.241136000	-2.217993000
C	5.280608000	-0.384878000	-1.934796000
C	3.521480000	0.512973000	-3.330903000
C	6.232804000	0.201422000	-2.764621000
H	5.607168000	-0.959670000	-1.065139000
C	4.478352000	1.097172000	-4.159309000
H	2.464773000	0.664621000	-3.561922000
C	5.834540000	0.942037000	-3.877999000
H	7.293990000	0.074581000	-2.542878000
H	4.162155000	1.674439000	-5.030185000
H	6.583683000	1.396263000	-4.529166000
C	3.364139000	-2.392136000	-0.360988000
C	4.002245000	-3.267989000	-1.254516000
C	3.206813000	-2.772325000	0.973099000
C	4.495591000	-4.488834000	-0.805877000
H	4.132436000	-2.995658000	-2.304786000
C	3.703557000	-3.994960000	1.418849000
H	2.674719000	-2.122378000	1.665196000
C	4.353401000	-4.851067000	0.534064000
H	4.999546000	-5.158325000	-1.505223000
H	3.574459000	-4.281094000	2.464303000
H	4.748873000	-5.805636000	0.886606000
H	3.754552000	1.599384000	-0.095371000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.095787 (Hartree/Particle)
Thermal correction to Energy= 1.169382
Thermal correction to Enthalpy= 1.170326
Thermal correction to Gibbs Free Energy= 0.986303
Sum of electronic and zero-point Energies= -4351.822336
Sum of electronic and thermal Energies= -4351.748742
Sum of electronic and thermal Enthalpies= -4351.747798
Sum of electronic and thermal Free Energies= -4351.93182

8-H_2



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Rh	-1.953147000	0.953859000	0.220901000
P	3.053382000	0.363138000	-0.165948000
P	0.455111000	-1.857814000	0.816550000
P	-2.568862000	-1.179152000	0.988432000
Si	-3.759297000	0.649283000	-2.926533000
Si	-3.062878000	4.317199000	0.673289000
C	-2.144983000	0.505241000	-1.949288000
C	-0.917842000	0.679982000	-1.834338000
C	0.476059000	1.033404000	-1.728796000
C	1.344810000	0.711176000	-2.897533000
C	0.779242000	0.158386000	-4.054628000
C	1.569916000	-0.212943000	-5.137549000
C	2.949106000	-0.028063000	-5.083462000

C	3.522175000	0.528306000	-3.944282000
C	2.740486000	0.898429000	-2.848488000
C	3.409397000	1.481530000	-1.622519000
C	3.015233000	2.922276000	-1.424137000
C	3.969477000	3.922780000	-1.635590000
C	3.652687000	5.265823000	-1.465716000
C	2.358941000	5.619535000	-1.086827000
C	1.398255000	4.633793000	-0.895199000
C	1.702656000	3.274614000	-1.065831000
C	0.649547000	2.241156000	-0.863265000
C	-0.610601000	2.719646000	-0.350171000
C	-1.686205000	3.201967000	0.040805000
C	-1.098924000	-1.902773000	1.827274000
H	4.411232000	6.032730000	-1.631274000
H	4.983438000	3.639506000	-1.928980000
H	2.093828000	6.669507000	-0.951153000
H	0.383967000	4.927448000	-0.620832000
H	4.604462000	0.667821000	-3.896916000
H	3.579583000	-0.315975000	-5.926339000
H	1.105898000	-0.640041000	-6.028372000
H	-0.301788000	0.015033000	-4.111345000
H	4.498791000	1.422833000	-1.758727000
H	-1.318536000	-2.923795000	2.176161000
H	-0.902980000	-1.264841000	2.701390000
H	-2.241316000	1.495998000	1.820049000
H	-1.486366000	1.098106000	1.851996000
C	-2.994254000	5.883284000	-0.340517000
H	-3.776387000	6.584122000	-0.008304000
H	-2.023393000	6.390024000	-0.230871000
H	-3.155334000	5.677862000	-1.409393000
C	-2.701822000	4.616233000	2.487753000
H	-2.740660000	3.683784000	3.072715000
H	-1.710513000	5.073746000	2.626630000
H	-3.451371000	5.302398000	2.912955000
C	-4.681374000	3.394872000	0.465856000
H	-4.904636000	3.198527000	-0.593237000
H	-4.676655000	2.435414000	1.008844000
H	-5.508236000	3.998282000	0.872580000
C	-3.807696000	2.445670000	-3.449597000
H	-3.729619000	3.117440000	-2.581485000
H	-2.974231000	2.678435000	-4.129443000
H	-4.749063000	2.671315000	-3.974979000
C	-5.210737000	0.211096000	-1.834529000
H	-5.148978000	-0.818214000	-1.452142000
H	-5.289246000	0.908187000	-0.986713000
H	-6.142766000	0.297445000	-2.415112000
C	-3.599711000	-0.499640000	-4.394270000
H	-3.507104000	-1.551866000	-4.089423000
H	-4.497745000	-0.414107000	-5.026647000
H	-2.731023000	-0.235566000	-5.016851000
N	1.021606000	0.993679000	2.339056000
C	1.344837000	1.436398000	3.353789000
C	1.793471000	1.998675000	4.615335000
H	2.225143000	1.204415000	5.239246000
H	2.568314000	2.751106000	4.412306000
H	0.952363000	2.468693000	5.142619000
C	3.866743000	-1.183480000	-0.699053000
C	5.142730000	-1.555065000	-0.252998000
C	3.226375000	-1.977110000	-1.657488000
C	5.736137000	-2.723555000	-0.727210000
H	5.686142000	-0.942164000	0.466867000
C	3.819267000	-3.143216000	-2.129644000
H	2.257185000	-1.682846000	-2.048696000
C	5.073642000	-3.525398000	-1.656008000
H	6.728014000	-3.005151000	-0.368559000
H	3.294897000	-3.751994000	-2.868708000
H	5.543078000	-4.440794000	-2.021670000
C	3.988925000	0.915494000	1.296812000
C	4.441866000	2.228397000	1.469244000
C	4.174448000	-0.015815000	2.331632000
C	5.097326000	2.592940000	2.647235000
H	4.295305000	2.978106000	0.692359000
C	4.826464000	0.353226000	3.503216000
H	3.818961000	-1.041404000	2.221018000
C	5.295761000	1.658893000	3.661913000
H	5.465580000	3.614298000	2.762282000
H	4.979434000	-0.389729000	4.288934000
H	5.822326000	1.945336000	4.574829000
C	1.658913000	-2.636202000	1.955451000
C	2.667268000	-3.472475000	1.458533000
C	1.656516000	-2.311904000	3.320054000
C	3.654648000	-3.966239000	2.309570000
H	2.691529000	-3.741425000	0.400975000
C	2.638303000	-2.816080000	4.169678000
H	0.889557000	-1.656689000	3.737242000
C	3.643587000	-3.640857000	3.664916000
H	4.433336000	-4.616717000	1.907228000
H	2.614684000	-2.570270000	5.233370000
H	4.412095000	-4.037873000	4.330963000
C	0.139208000	-3.111251000	-0.472955000
C	-0.080221000	-4.453889000	-0.135227000
C	0.081910000	-2.728176000	-1.814786000
C	-0.332330000	-5.393655000	-1.130270000
H	-0.038025000	-4.776844000	0.908427000
C	-0.151410000	-3.670804000	-2.813024000
H	0.218120000	-1.681416000	-2.084626000
C	-0.356633000	-5.005467000	-2.471329000
H	-0.500557000	-6.437763000	-0.860524000
H	-0.177323000	-3.357138000	-3.858826000
H	-0.539818000	-5.749383000	-3.249354000
C	-3.773420000	-0.888911000	2.332665000
C	-5.007319000	-0.331718000	1.964924000
C	-3.520328000	-1.161858000	3.680842000
C	-5.966992000	-0.045241000	2.930664000
H	-5.226719000	-0.135169000	0.913108000
C	-4.485507000	-0.872780000	4.646722000
H	-2.580837000	-1.616798000	3.999355000
C	-5.705273000	-0.311854000	4.275239000
H	-6.925147000	0.383995000	2.632081000
H	-4.283807000	-1.095792000	5.696123000
H	-6.458082000	-0.089290000	5.033647000
C	-3.300818000	-2.546610000	0.035865000
C	-4.047707000	-3.520271000	0.715911000
C	-3.091592000	-2.674763000	-1.339396000
C	-4.572388000	-4.607126000	0.023276000
H	-4.233892000	-3.427992000	1.788437000
C	-3.620433000	-3.763483000	-2.028296000
H	-2.504210000	-1.928830000	-1.873024000
C	-4.360096000	-4.729744000	-1.349941000
H	-5.156116000	-5.358570000	0.557985000
H	-3.448340000	-3.861503000	-3.101942000
H	-4.777153000	-5.580690000	-1.891836000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.097440 (Hartree/Particle)

Thermal correction to Energy= 1.170674

Thermal correction to Enthalpy= 1.171618

Thermal correction to Gibbs Free Energy= 0.988676

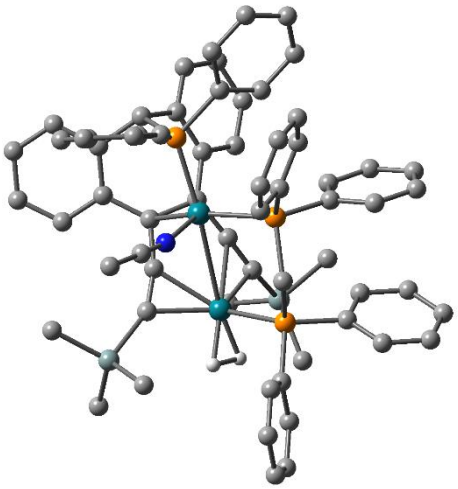
Sum of electronic and zero-point Energies= -4351.832865

Sum of electronic and thermal Energies= -4351.759632

Sum of electronic and thermal Enthalpies= -4351.758687

Sum of electronic and thermal Free Energies= -4351.941629

[TS1]‡



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Rh	1.987178000	1.145603000	0.785503000
P	-3.039793000	-0.176028000	0.062162000
P	0.049651000	-1.253068000	-1.462146000
P	2.882692000	-0.037110000	-0.959636000
Si	3.332718000	-0.747911000	3.662218000
Si	1.352634000	4.638249000	0.087878000
C	1.914814000	-0.392862000	2.460518000
C	0.698902000	-0.237734000	2.224307000
C	-0.718802000	-0.019705000	2.106554000
C	-1.626149000	-0.932229000	2.860389000
C	-1.080956000	-1.911384000	3.701385000
C	-1.893528000	-2.814544000	4.378819000
C	-3.276459000	-2.748266000	4.229723000
C	-3.831481000	-1.777387000	3.401983000
C	-3.026454000	-0.868978000	2.712708000
C	-3.674839000	0.148930000	1.797231000
C	-3.482974000	1.554891000	2.314634000
C	-4.579686000	2.268472000	2.808384000
C	-4.429562000	3.561489000	3.300775000
C	-3.168944000	4.157775000	3.310157000
C	-2.068561000	3.452635000	2.836009000
C	-2.210106000	2.150228000	2.341407000
C	-1.029369000	1.415756000	1.845017000
C	0.102240000	2.093217000	1.301430000
C	0.907200000	2.938655000	0.767747000
C	1.557496000	-0.439806000	-2.172133000
H	-5.297347000	4.101571000	3.683255000
H	-5.568713000	1.803778000	2.800920000
H	-3.041591000	5.167867000	3.703504000
H	-1.075953000	3.907483000	2.866005000
H	-4.915532000	-1.729637000	3.276755000
H	-3.923970000	-3.450330000	4.757479000
H	-1.445601000	-3.565482000	5.032081000
H	0.001541000	-1.964741000	3.830089000
H	-4.751858000	-0.066045000	1.742455000
H	1.993339000	-1.014691000	-3.005678000
H	1.201813000	0.528413000	-2.554169000
H	3.128188000	2.158449000	0.351571000
C	-0.259483000	5.590178000	-0.002888000
H	-0.106281000	6.574582000	-0.472599000
H	-1.015245000	5.043047000	-0.587487000
H	-0.679396000	5.759966000	1.000125000
C	2.086433000	4.348698000	-1.613509000
H	3.060764000	3.840558000	-1.544517000
H	1.429111000	3.720054000	-2.234641000
H	2.244114000	5.305875000	-2.135027000
C	2.588923000	5.414995000	1.251941000
H	2.168771000	5.536448000	2.261724000
H	3.502464000	4.805820000	1.330094000
H	2.881395000	6.412103000	0.886696000
C	2.999933000	0.363358000	5.129076000
H	3.016588000	1.424087000	4.834910000
H	2.019568000	0.148239000	5.580314000
H	3.770110000	0.216061000	5.902864000
C	4.983001000	-0.349744000	2.875195000
H	5.140529000	-0.885688000	1.928173000
H	5.086946000	0.732028000	2.696426000
H	5.790989000	-0.643227000	3.564131000
C	3.179542000	-2.560081000	4.116133000
H	3.250295000	-3.219757000	3.239176000
H	3.983569000	-2.842455000	4.813811000
H	2.221366000	-2.760031000	4.620138000
N	-1.043575000	1.776644000	-1.631143000
C	-1.330040000	2.605391000	-2.379304000
C	-1.721679000	3.648743000	-3.311003000
H	-0.931283000	4.408550000	-3.381075000
H	-1.902142000	3.210149000	-4.301813000
H	-2.650933000	4.113897000	-2.953840000
C	-3.594354000	-1.889237000	-0.222436000
C	-4.798722000	-2.176617000	-0.878604000
C	-2.835813000	-2.941072000	0.303247000
C	-5.208393000	-3.499249000	-1.037158000
H	-5.425051000	-1.375980000	-1.275027000
C	-3.247977000	-4.260181000	0.146903000
H	-1.913967000	-2.732507000	0.839917000
C	-4.432326000	-4.542460000	-0.533307000
H	-6.145493000	-3.713400000	-1.554417000
H	-2.638091000	-5.067371000	0.556987000
H	-4.757746000	-5.576643000	-0.662334000
C	-3.954950000	0.841918000	-1.136208000
C	-4.561435000	2.055294000	-0.790345000
C	-3.945127000	0.436730000	-2.480312000
C	-5.173576000	2.835480000	-1.772587000
H	-4.566739000	2.405108000	0.241730000
C	-4.553384000	1.220292000	-3.455322000
H	-3.467252000	-0.500114000	-2.771453000
C	-5.175042000	2.419948000	-3.103042000
H	-5.662925000	3.769308000	-1.488808000
H	-4.551226000	0.882223000	-4.493692000
H	-5.668107000	3.026779000	-3.865547000
C	-0.937840000	-1.592764000	-2.964773000
C	-1.788903000	-2.706233000	-2.990876000
C	-0.950789000	-0.702044000	-4.046965000
C	-2.644447000	-2.914210000	-4.070472000
H	-1.791601000	-3.420053000	-2.165500000
C	-1.799747000	-0.919556000	-5.130655000
H	-0.298728000	0.173022000	-4.058620000
C	-2.653966000	-2.021696000	-5.141853000
H	-3.302983000	-3.784713000	-4.074054000
H	-1.789952000	-0.226073000	-5.974051000
H	-3.319014000	-2.191594000	-5.990781000
C	0.604759000	-2.895206000	-0.899792000
C	1.144465000	-3.819899000	-1.804491000
C	0.486937000	-3.243664000	0.447907000
C	1.544498000	-5.076985000	-1.362295000
H	1.240227000	-3.568086000	-2.863947000
C	0.873517000	-4.507792000	0.888141000
H	0.099567000	-2.520250000	1.165112000
C	1.399309000	-5.425748000	-0.017845000
H	1.961892000	-5.793739000	-2.071805000
H	0.763201000	-4.770660000	1.942235000
H	1.701136000	-6.418753000	0.321764000
C	4.042708000	1.014381000	-1.901972000
C	5.269133000	1.323400000	-1.294001000
C	3.762199000	1.519638000	-3.174003000
C	6.191831000	2.133345000	-1.944331000
H	5.512935000	0.920350000	-0.306589000
C	4.691222000	2.334359000	-3.824282000
H	2.823748000	1.290734000	-3.680235000
C	5.901430000	2.644709000	-3.211687000
H	7.144899000	2.363183000	-1.464723000

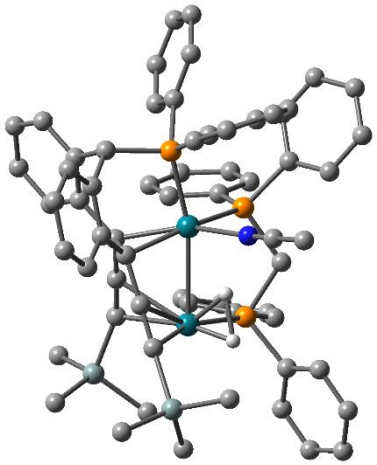
H	4.465144000	2.725291000	-4.817931000
H	6.625586000	3.281420000	-3.723232000
C	3.805616000	-1.594782000	-0.755951000
C	4.672933000	-1.998183000	-1.783325000
C	3.622014000	-2.422042000	0.352906000
C	5.345486000	-3.212949000	-1.690819000
H	4.839326000	-1.361503000	-2.655306000
C	4.302552000	-3.633126000	0.444423000
H	2.930558000	-2.125383000	1.139821000
C	5.165036000	-4.029691000	-0.574752000
H	6.023757000	-3.517594000	-2.489809000
H	4.155099000	-4.273624000	1.315892000
H	5.700963000	-4.977761000	-0.499469000
H	3.536367000	1.346734000	1.057596000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.093551 (Hartree/Particle)
Thermal correction to Energy= 1.166817
Thermal correction to Enthalpy= 1.167762
Thermal correction to Gibbs Free Energy= 0.983422
Sum of electronic and zero-point Energies= -4351.818225
Sum of electronic and thermal Energies= -4351.744959
Sum of electronic and thermal Enthalpies= -4351.744014
Sum of electronic and thermal Free Energies= -4351.928354

[TS2]‡



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P	3.061058000	0.317312000	-0.188512000
P	0.404678000	-1.772932000	0.996233000
P	-2.620456000	-1.096642000	1.019307000
Si	-3.836711000	0.587031000	-2.967229000
Si	-2.924360000	4.262414000	0.628651000
C	-2.114595000	0.397429000	-2.218480000
C	-0.895313000	0.523210000	-2.060300000
C	0.501650000	0.842612000	-1.866977000
C	1.416335000	0.409086000	-2.969461000
C	0.887498000	-0.259122000	-4.083562000
C	1.708409000	-0.732457000	-5.101800000
C	3.085328000	-0.539923000	-5.028542000
C	3.624012000	0.127931000	-3.934075000
C	2.810352000	0.603145000	-2.903755000
C	3.449718000	1.302996000	-1.725655000
C	3.047546000	2.754274000	-1.676843000
C	4.005254000	3.733328000	-1.961484000
C	3.679675000	5.084767000	-1.943750000
C	2.373485000	5.468942000	-1.645856000
C	1.410371000	4.503132000	-1.379931000
C	1.724200000	3.135418000	-1.395269000
C	0.666286000	2.124626000	-1.114815000
C	-0.583501000	2.651612000	-0.619964000
C	-1.621874000	3.164808000	-0.171313000
C	-1.178273000	-1.733196000	1.977723000
H	4.440720000	5.834334000	-2.166754000
H	5.028280000	3.427031000	-2.193908000
H	2.100344000	6.525598000	-1.633638000
H	0.386585000	4.818478000	-1.172572000
H	4.704274000	0.275236000	-3.868563000
H	3.740047000	-0.907389000	-5.820367000
H	1.268282000	-1.244896000	-5.959104000
H	-0.190820000	-0.411606000	-4.158477000
H	4.542205000	1.236171000	-1.830301000
H	-1.406731000	-2.723805000	2.398943000
H	-1.012834000	-1.033658000	2.809223000
H	-2.126563000	1.413982000	1.533275000
H	-0.962869000	0.878078000	1.247195000
C	-2.908168000	5.880754000	-0.302390000
H	-3.661628000	6.567942000	0.113908000
H	-1.927681000	6.375541000	-0.229648000
H	-3.139418000	5.731306000	-1.367800000
C	-2.397325000	4.444144000	2.418709000
H	-2.388273000	3.467498000	2.928081000
H	-1.394043000	4.890557000	2.493835000
H	-3.099623000	5.096761000	2.960740000
C	-4.573137000	3.379108000	0.513314000
H	-4.871298000	3.196123000	-0.530001000
H	-4.557762000	2.416752000	1.051906000
H	-5.357899000	3.998800000	0.975350000
C	-3.908640000	2.378297000	-3.501005000
H	-3.709901000	3.055412000	-2.656010000
H	-3.157968000	2.584795000	-4.278673000
H	-4.900983000	2.621146000	-3.912273000
C	-5.108010000	0.208012000	-1.642362000
H	-5.144505000	-0.868858000	-1.422209000
H	-4.922259000	0.749794000	-0.700840000
H	-6.105926000	0.511870000	-1.996458000
C	-3.953373000	-0.606306000	-4.399519000
H	-3.860121000	-1.650319000	-4.065686000
H	-4.931929000	-0.499888000	-4.894093000
H	-3.175311000	-0.406996000	-5.151835000
N	1.078097000	1.261219000	2.210212000
C	1.349817000	1.852865000	3.161571000
C	1.730463000	2.603512000	4.345326000
H	2.180080000	1.924227000	5.082148000
H	2.473036000	3.362125000	4.062163000
H	0.850188000	3.094002000	4.782155000
C	3.867025000	-1.278973000	-0.557259000
C	5.135631000	-1.601479000	-0.055300000
C	3.237722000	-2.170352000	-1.433780000
C	5.733163000	-2.814819000	-0.390197000
H	5.669390000	-0.915151000	0.602806000
C	3.835688000	-3.381245000	-1.767370000
H	2.273796000	-1.921314000	-1.867274000
C	5.081884000	-3.711596000	-1.236283000
H	6.718425000	-3.056814000	0.012590000
H	3.320868000	-4.065756000	-2.444214000
H	5.553540000	-4.662507000	-1.491876000
C	3.975886000	0.992943000	1.233671000
C	4.436179000	2.313278000	1.288156000
C	4.132688000	0.163876000	2.356084000
C	5.066454000	2.786226000	2.440694000
H	4.312298000	2.985849000	0.440065000
C	4.759357000	0.640685000	3.502181000
H	3.770089000	-0.865015000	2.336748000
C	5.232536000	1.953864000	3.545826000
H	5.440517000	3.811706000	2.465290000

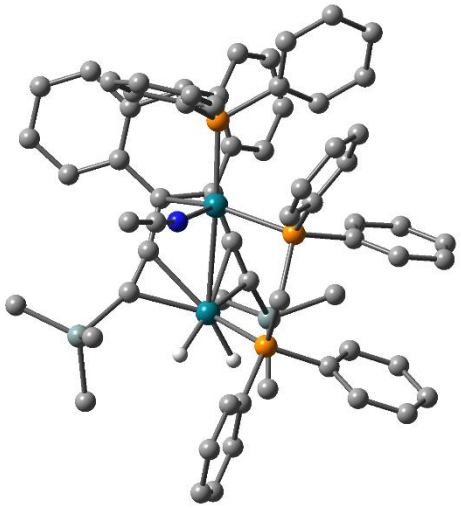
H	4.887652000	-0.023726000	4.359260000
H	5.737900000	2.325690000	4.439703000
C	1.589894000	-2.451695000	2.213178000
C	2.596103000	-3.336072000	1.802600000
C	1.581075000	-2.000031000	3.540884000
C	3.573505000	-3.756422000	2.702962000
H	2.628038000	-3.700077000	0.773938000
C	2.552729000	-2.431891000	4.440744000
H	0.818340000	-1.301082000	3.889558000
C	3.554615000	-3.307794000	4.022610000
H	4.350381000	-4.445662000	2.367297000
H	2.524580000	-2.086111000	5.476103000
H	4.314545000	-3.647828000	4.728739000
C	0.103804000	-3.125623000	-0.192461000
C	-0.123615000	-4.437035000	0.247048000
C	0.067378000	-2.849555000	-1.560746000
C	-0.360324000	-5.451968000	-0.675294000
H	-0.100056000	-4.675709000	1.313627000
C	-0.149471000	-3.867704000	-2.485539000
H	0.210454000	-1.827906000	-1.910352000
C	-0.361034000	-5.171026000	-2.042902000
H	-0.534281000	-6.471236000	-0.325749000
H	-0.157130000	-3.637695000	-3.553045000
H	-0.532266000	-5.973436000	-2.763400000
C	-3.902786000	-0.665223000	2.251083000
C	-5.255865000	-0.837649000	1.932609000
C	-3.558982000	-0.031272000	3.453132000
C	-6.244762000	-0.394187000	2.809632000
H	-5.547472000	-1.326835000	1.001388000
C	-4.548892000	0.403592000	4.329171000
H	-2.512281000	0.137007000	3.718688000
C	-5.894796000	0.223978000	4.007914000
H	-7.296029000	-0.539674000	2.554876000
H	-4.270195000	0.884197000	5.268733000
H	-6.670716000	0.564813000	4.695810000
C	-3.261865000	-2.565469000	0.159074000
C	-3.845227000	-3.591724000	0.919062000
C	-3.132047000	-2.720512000	-1.222309000
C	-4.305015000	-4.746802000	0.295881000
H	-3.958765000	-3.486227000	2.001010000
C	-3.594399000	-3.879581000	-1.842358000
H	-2.650020000	-1.943218000	-1.814829000
C	-4.183750000	-4.889967000	-1.087132000
H	-4.764860000	-5.537606000	0.891297000
H	-3.484095000	-3.996976000	-2.922065000
H	-4.550290000	-5.795101000	-1.575122000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.096001 (Hartree/Particle)
Thermal correction to Energy= 1.168711
Thermal correction to Enthalpy= 1.169655
Thermal correction to Gibbs Free Energy= 0.987555
Sum of electronic and zero-point Energies= -4351.826785
Sum of electronic and thermal Energies= -4351.754075
Sum of electronic and thermal Enthalpies= -4351.753131
Sum of electronic and thermal Free Energies= -4351.935231

8a-HH$_{ox}$



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Rh	2.023025000	0.971973000	0.852085000
P	-3.057930000	-0.070833000	0.026055000
P	0.023075000	-1.201867000	-1.495337000
P	2.867277000	-0.018212000	-0.989608000
Si	3.097317000	-1.173465000	3.781667000
Si	1.774000000	4.554510000	0.352441000
C	1.776180000	-0.582670000	2.560124000
C	0.601380000	-0.284980000	2.281768000
C	-0.794852000	0.015109000	2.107644000
C	-1.761626000	-0.842873000	2.856750000
C	-1.287333000	-1.837773000	3.722490000
C	-2.160023000	-2.688008000	4.393280000
C	-3.534199000	-2.554575000	4.212576000
C	-4.019660000	-1.569114000	3.359457000
C	-3.153171000	-0.712332000	2.678592000
C	-3.725773000	0.320258000	1.731806000
C	-3.478945000	1.724016000	2.230169000
C	-4.555851000	2.496815000	2.675865000
C	-4.361208000	3.788140000	3.156382000
C	-3.073917000	4.321714000	3.202235000
C	-1.993357000	3.557791000	2.775263000
C	-2.179056000	2.256774000	2.291582000
C	-1.020593000	1.460819000	1.830630000
C	0.180838000	2.113791000	1.400746000
C	1.054883000	2.913093000	0.951089000
C	1.523459000	-0.362269000	-2.199148000
H	-5.214373000	4.375771000	3.499743000
H	-5.565082000	2.079181000	2.639425000
H	-2.910010000	5.330454000	3.585373000
H	-0.983706000	3.969749000	2.831210000
H	-5.096614000	-1.466922000	3.208549000
H	-4.227706000	-3.215966000	4.734350000
H	-1.765066000	-3.451425000	5.065946000
H	-0.213590000	-1.948747000	3.878235000
H	-4.810005000	0.156354000	1.648213000
H	1.949008000	-0.915745000	-3.051994000
H	1.167590000	0.616983000	-2.551180000
H	3.460786000	0.474790000	1.146420000
H	2.800781000	2.051931000	0.093841000
C	0.772687000	5.882123000	1.207094000
H	1.091340000	6.878936000	0.863320000
H	-0.301679000	5.775928000	0.992185000
H	0.913811000	5.847001000	2.298344000
C	1.527380000	4.567949000	-1.507781000
H	1.954159000	3.664531000	-1.971241000
H	0.457039000	4.631328000	-1.752951000
H	2.029864000	5.443036000	-1.948963000
C	3.588877000	4.616558000	0.788537000
H	3.754495000	4.413577000	1.857559000

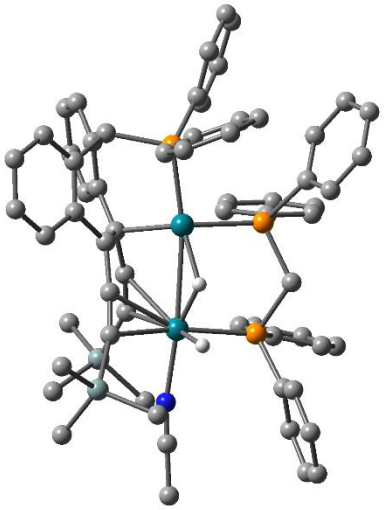
H	4.171465000	3.888044000	0.202445000
H	3.992974000	5.617669000	0.569808000
C	2.655341000	-0.332438000	5.391963000
H	2.733787000	0.761522000	5.300044000
H	1.629487000	-0.576860000	5.706563000
H	3.342397000	-0.654670000	6.190405000
C	4.802689000	-0.676212000	3.198295000
H	5.070819000	-1.127815000	2.231758000
H	4.890773000	0.418184000	3.113811000
H	5.547658000	-1.009527000	3.938372000
C	2.894226000	-3.033654000	3.897445000
H	3.030023000	-3.531971000	2.926651000
H	3.638484000	-3.446871000	4.596508000
H	1.897291000	-3.300580000	4.280995000
N	-1.000851000	1.807298000	-1.635126000
C	-1.276444000	2.542266000	-2.479135000
C	-1.647442000	3.452968000	-3.547730000
H	-2.123774000	2.882898000	-4.357366000
H	-2.367002000	4.190048000	-3.165673000
H	-0.756892000	3.970591000	-3.929474000
C	-3.629217000	-1.783326000	-0.217813000
C	-4.864139000	-2.064175000	-0.817656000
C	-2.862192000	-2.835364000	0.293382000
C	-5.297400000	-3.383351000	-0.935760000
H	-5.495228000	-1.260732000	-1.201376000
C	-3.298197000	-4.151173000	0.178272000
H	-1.916810000	-2.627540000	0.787973000
C	-4.514120000	-4.428083000	-0.446038000
H	-6.257353000	-3.593724000	-1.410874000
H	-2.682899000	-4.959962000	0.576899000
H	-4.858779000	-5.459570000	-0.542907000
C	-3.933781000	0.922220000	-1.220844000
C	-4.474860000	2.180351000	-0.928532000
C	-3.968683000	0.447731000	-2.541278000
C	-5.070285000	2.936048000	-1.939131000
H	-4.440241000	2.583585000	0.083676000
C	-4.562328000	1.207022000	-3.544779000
H	-3.542614000	-0.525266000	-2.791174000
C	-5.120560000	2.450884000	-3.245102000
H	-5.509742000	3.905803000	-1.697531000
H	-4.599378000	0.814032000	-4.562971000
H	-5.602118000	3.039025000	-4.029297000
C	-0.964651000	-1.541307000	-2.997116000
C	-1.829298000	-2.644848000	-3.009303000
C	-0.963571000	-0.666487000	-4.091815000
C	-2.684695000	-2.857882000	-4.087922000
H	-1.841962000	-3.347130000	-2.173887000
C	-1.813657000	-0.888426000	-5.174072000
H	-0.294860000	0.195768000	-4.116557000
C	-2.681222000	-1.979958000	-5.171692000
H	-3.353537000	-3.720473000	-4.081529000
H	-1.792392000	-0.208463000	-6.028328000
H	-3.345894000	-2.154179000	-6.020055000
C	0.602641000	-2.843816000	-0.955920000
C	1.151883000	-3.748796000	-1.875187000
C	0.496063000	-3.211091000	0.387819000
C	1.575242000	-5.004096000	-1.451113000
H	1.238107000	-3.482042000	-2.931817000
C	0.906754000	-4.474410000	0.809570000
H	0.099446000	-2.503614000	1.115908000
C	1.444194000	-5.371486000	-0.110015000
H	2.000701000	-5.704994000	-2.171567000
H	0.805172000	-4.753719000	1.860127000
H	1.764933000	-6.363153000	0.215850000
C	4.024423000	1.082566000	-1.878044000
C	5.233168000	1.385736000	-1.234353000
C	3.752723000	1.639824000	-3.130218000
C	6.151897000	2.239032000	-1.833424000
H	5.460084000	0.952314000	-0.256378000
C	4.676440000	2.502087000	-3.725629000
H	2.828871000	1.411958000	-3.664244000
C	5.871822000	2.803601000	-3.079957000
H	7.092206000	2.464978000	-1.327475000
H	4.459799000	2.934088000	-4.704324000
H	6.592036000	3.476394000	-3.549157000
C	3.786560000	-1.586303000	-0.885759000
C	4.564332000	-1.972628000	-1.987306000
C	3.702468000	-2.421261000	0.227748000
C	5.250323000	-3.182709000	-1.964063000
H	4.655340000	-1.322522000	-2.861180000
C	4.396602000	-3.628524000	0.250142000
H	3.075613000	-2.134904000	1.070902000
C	5.171251000	-4.009487000	-0.842938000
H	5.861171000	-3.475531000	-2.819953000
H	4.330494000	-4.277375000	1.125623000
H	5.718971000	-4.953592000	-0.821924000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.096336 (Hartree/Particle)
Thermal correction to Energy= 1.169574
Thermal correction to Enthalpy= 1.170518
Thermal correction to Gibbs Free Energy= 0.986717
Sum of electronic and zero-point Energies= -4351.823896
Sum of electronic and thermal Energies= -4351.750659
Sum of electronic and thermal Enthalpies= -4351.749715
Sum of electronic and thermal Free Energies= -4351.933516

11-HH$_{ox}$



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Rh	0.805415000	0.417420000	0.152363000
Rh	-2.067059000	0.864991000	0.003921000
P	3.050728000	0.323961000	-0.127907000
P	0.404248000	-1.836297000	0.904186000
P	-2.642127000	-1.189258000	0.938957000
Si	-3.797289000	0.867548000	-2.858060000
Si	-2.788948000	4.391407000	0.676663000
C	-2.032037000	0.430927000	-2.407213000
C	-0.830751000	0.536783000	-2.159027000
C	0.546947000	0.869818000	-1.882167000
C	1.521681000	0.492735000	-2.955388000
C	1.059139000	-0.155949000	-4.110022000
C	1.934047000	-0.578532000	-5.105305000
C	3.301125000	-0.353176000	-4.969133000
C	3.774957000	0.295852000	-3.834295000
C	2.906238000	0.719297000	-2.826760000
C	3.476927000	1.389432000	-1.598620000

C	3.033496000	2.826835000	-1.508959000
C	3.979223000	3.837644000	-1.711750000
C	3.621773000	5.180168000	-1.660141000
C	2.294061000	5.523515000	-1.412614000
C	1.343570000	4.526933000	-1.227931000
C	1.689576000	3.167421000	-1.274902000
C	0.640087000	2.126223000	-1.080887000
C	-0.637360000	2.624093000	-0.619230000
C	-1.678689000	3.130572000	-0.171113000
C	-1.185533000	-1.827078000	1.871139000
H	4.375047000	5.953788000	-1.818352000
H	5.018871000	3.563482000	-1.907277000
H	1.993941000	6.572357000	-1.376664000
H	0.303938000	4.810823000	-1.060999000
H	4.847252000	0.467550000	-3.717592000
H	3.997835000	-0.681340000	-5.742115000
H	1.543084000	-1.077442000	-5.993820000
H	-0.010381000	-0.332422000	-4.235643000
H	4.574289000	1.355851000	-1.659068000
H	-1.406702000	-2.825848000	2.276529000
H	-1.030089000	-1.138994000	2.714002000
H	-2.389335000	1.306115000	1.427282000
H	-0.889080000	0.675526000	0.979073000
C	-2.253920000	6.054762000	0.009689000
H	-2.857550000	6.855695000	0.465202000
H	-1.197889000	6.260312000	0.242528000
H	-2.387181000	6.114010000	-1.081259000
C	-2.431194000	4.218331000	2.510108000
H	-2.722280000	3.222809000	2.880516000
H	-1.359951000	4.371447000	2.712699000
H	-2.997143000	4.969091000	3.083848000
C	-4.585766000	4.031772000	0.304348000
H	-4.769637000	3.922312000	-0.775127000
H	-4.937350000	3.123527000	0.816959000
H	-5.204064000	4.869937000	0.662690000
C	-3.724079000	2.617413000	-3.505026000
H	-3.209559000	3.273970000	-2.786532000
H	-3.176186000	2.664162000	-4.458204000
H	-4.738011000	3.011760000	-3.677648000
C	-4.697141000	0.804985000	-1.199665000
H	-4.947790000	-0.225278000	-0.911603000
H	-4.164747000	1.286035000	-0.341723000
H	-5.634665000	1.380537000	-1.254654000
C	-4.519427000	-0.352990000	-4.064851000
H	-4.573760000	-1.365950000	-3.640280000
H	-5.543104000	-0.046955000	-4.333273000
H	-3.930269000	-0.391006000	-4.993668000
N	0.983475000	1.179720000	2.227965000
C	1.196058000	1.751179000	3.205893000
C	1.498719000	2.478680000	4.426289000
H	2.034336000	1.819700000	5.122839000
H	2.143090000	3.334542000	4.182517000
H	0.571858000	2.838318000	4.893070000
C	3.899185000	0.948910000	1.356691000
C	4.291334000	2.285409000	1.495712000
C	4.062673000	0.068955000	2.437979000
C	4.861764000	2.725754000	2.690962000
H	4.158496000	2.996055000	0.680451000
C	4.629089000	0.514036000	3.627912000
H	3.756661000	-0.974616000	2.352560000
C	5.034262000	1.843798000	3.756335000
H	5.182585000	3.765433000	2.781969000
H	4.764486000	-0.188875000	4.452543000
H	5.493591000	2.190531000	4.684517000
C	3.892164000	-1.240931000	-0.544960000
C	5.162501000	-1.550568000	-0.039686000
C	3.294600000	-2.112887000	-1.462336000
C	5.794140000	-2.735168000	-0.412613000
H	5.670544000	-0.875832000	0.650278000
C	3.927359000	-3.294513000	-1.834519000
H	2.329800000	-1.870936000	-1.898843000
C	5.175304000	-3.614080000	-1.300724000
H	6.780350000	-2.968309000	-0.006967000
H	3.439208000	-3.964944000	-2.544408000
H	5.673490000	-4.542400000	-1.587260000
C	1.572635000	-2.552302000	2.115882000
C	2.588867000	-3.418755000	1.692047000
C	1.537591000	-2.149973000	3.458904000
C	3.551711000	-3.868185000	2.594011000
H	2.639557000	-3.746797000	0.652338000
C	2.493638000	-2.612321000	4.360287000
H	0.766434000	-1.466192000	3.818587000
C	3.506661000	-3.468608000	3.928827000
H	4.337130000	-4.542462000	2.247907000
H	2.444453000	-2.305803000	5.407120000
H	4.255145000	-3.831571000	4.635823000
C	0.120205000	-3.148424000	-0.332152000
C	-0.116702000	-4.472103000	0.063519000
C	0.100635000	-2.829062000	-1.691534000
C	-0.349252000	-5.456433000	-0.892244000
H	-0.105514000	-4.744083000	1.122372000
C	-0.114601000	-3.816738000	-2.649235000
H	0.255851000	-1.798481000	-2.008199000
C	-0.337658000	-5.132161000	-2.250179000
H	-0.530883000	-6.485576000	-0.577218000
H	-0.111160000	-3.553789000	-3.709053000
H	-0.507229000	-5.910426000	-2.997056000
C	-3.240110000	-2.624101000	-0.005957000
C	-3.745990000	-3.734965000	0.688476000
C	-3.160808000	-2.661120000	-1.399036000
C	-4.180058000	-4.855850000	-0.010159000
H	-3.819979000	-3.723099000	1.779009000
C	-3.597456000	-3.787159000	-2.095461000
H	-2.729598000	-1.820150000	-1.942591000
C	-4.110748000	-4.880969000	-1.404358000
H	-4.579672000	-5.713222000	0.534369000
H	-3.525198000	-3.811279000	-3.184578000
H	-4.456327000	-5.760630000	-1.950812000
C	-3.927002000	-0.886785000	2.207245000
C	-5.270263000	-1.176141000	1.938918000
C	-3.593474000	-0.243661000	3.407675000
C	-6.259125000	-0.839412000	2.862908000
H	-5.555702000	-1.677751000	1.012039000
C	-4.581514000	0.082231000	4.331358000
H	-2.556205000	0.018371000	3.631922000
C	-5.917884000	-0.213728000	4.059386000
H	-7.302962000	-1.072767000	2.645355000
H	-4.309526000	0.571405000	5.268488000
H	-6.692838000	0.043954000	4.783525000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.097400 (Hartree/Particle)

Thermal correction to Energy= 1.170241

Thermal correction to Enthalpy= 1.171185

Thermal correction to Gibbs Free Energy= 0.989040

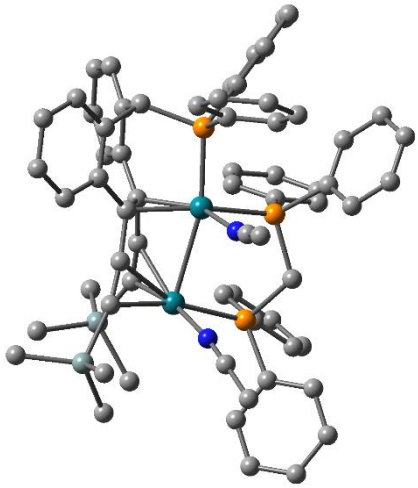
Sum of electronic and zero-point Energies= -4351.826207

Sum of electronic and thermal Energies= -4351.753366

Sum of electronic and thermal Enthalpies= -4351.752422

Sum of electronic and thermal Free Energies= -4351.934567

8-MeCN



E = -4484.39984826

Rh	0.876948000	0.430218000	0.172502000
Rh	-1.915135000	0.850843000	-0.001487000
P	3.117533000	0.416345000	-0.145081000
P	0.565912000	-1.828038000	0.895406000
P	-2.487111000	-1.297758000	0.820165000
Si	-3.607569000	0.277831000	-3.175693000
Si	-3.148936000	4.267515000	-0.016156000
C	-2.051642000	0.286539000	-2.112678000
C	-0.834600000	0.481953000	-1.914570000
C	0.555642000	0.867563000	-1.818096000
C	1.458158000	0.489392000	-2.942038000
C	0.934034000	-0.159299000	-4.068365000
C	1.758719000	-0.584395000	-5.105120000
C	3.131315000	-0.359413000	-5.035147000
C	3.663740000	0.292100000	-3.927040000
C	2.847304000	0.718338000	-2.877580000
C	3.473064000	1.414411000	-1.687684000
C	3.029976000	2.853350000	-1.614838000
C	3.952154000	3.865192000	-1.901937000
C	3.588865000	5.205995000	-1.847162000
C	2.280312000	5.545235000	-1.507570000
C	1.351097000	4.546208000	-1.244083000
C	1.702029000	3.188465000	-1.301019000
C	0.678972000	2.139502000	-1.039430000
C	-0.613074000	2.609495000	-0.606671000
C	-1.724985000	3.088609000	-0.330669000
C	-1.046437000	-1.891919000	1.802894000
H	4.322766000	5.981713000	-2.071782000
H	4.977866000	3.593544000	-2.164442000
H	1.978621000	6.593184000	-1.460893000
H	0.323977000	4.824489000	-1.003719000
H	4.740781000	0.463596000	-3.866835000
H	3.788484000	-0.689238000	-5.841447000
H	1.325814000	-1.084300000	-5.973555000
H	-0.141169000	-0.336108000	-4.134020000
H	4.566275000	1.380266000	-1.799710000
H	-1.232995000	-2.901783000	2.199776000
H	-0.950293000	-1.185207000	2.640424000
C	-3.192236000	5.463762000	-1.451809000
H	-3.995335000	6.203533000	-1.305857000
H	-2.242254000	6.013080000	-1.537584000
H	-3.372712000	4.951468000	-2.408206000
C	-2.775682000	5.166402000	1.588279000
H	-2.707507000	4.477773000	2.443169000
H	-1.820479000	5.708552000	1.515727000
H	-3.564030000	5.903803000	1.807298000
C	-4.726460000	3.259578000	0.108478000
H	-4.927259000	2.726295000	-0.833014000
H	-4.684532000	2.517096000	0.920043000
H	-5.583518000	3.924012000	0.300560000
C	-3.778157000	2.044654000	-3.770883000
H	-3.839640000	2.740784000	-2.921574000
H	-2.913022000	2.338381000	-4.384413000
H	-4.687778000	2.166194000	-4.379623000
C	-5.086766000	-0.230878000	-2.150565000
H	-4.955762000	-1.216825000	-1.681041000
H	-5.295547000	0.514953000	-1.368336000
H	-5.977325000	-0.282478000	-2.796639000
C	-3.290185000	-0.896089000	-4.599172000
H	-3.146220000	-1.931575000	-4.259321000
H	-4.151704000	-0.887586000	-5.285669000
H	-2.405404000	-0.588992000	-5.177917000
N	0.977158000	1.179613000	2.229246000
C	1.288161000	1.783379000	3.160590000
C	1.737005000	2.555435000	4.306584000
H	1.939539000	1.886931000	5.154058000
H	2.668113000	3.073095000	4.034456000
H	0.978737000	3.296885000	4.591141000
C	4.032622000	-1.129014000	-0.500053000
C	5.275333000	-1.411369000	0.083702000
C	3.508330000	-2.023888000	-1.440224000
C	5.949804000	-2.587707000	-0.236783000
H	5.729320000	-0.721638000	0.795170000
C	4.181491000	-3.199288000	-1.757871000
H	2.567775000	-1.803756000	-1.935869000
C	5.401029000	-3.489493000	-1.147322000
H	6.914759000	-2.796600000	0.228916000
H	3.747429000	-3.888163000	-2.485170000
H	5.930982000	-4.412463000	-1.391063000
C	4.007329000	1.140065000	1.275387000
C	4.544249000	2.431158000	1.284731000
C	4.114717000	0.346148000	2.429781000
C	5.200693000	2.908982000	2.421983000
H	4.463991000	3.077572000	0.411986000
C	4.771221000	0.824359000	3.557935000
H	3.696986000	-0.661918000	2.445266000
C	5.322437000	2.108229000	3.554996000
H	5.631976000	3.911798000	2.409673000
H	4.863313000	0.184349000	4.438019000
H	5.851488000	2.480811000	4.434695000
C	1.732253000	-2.459095000	2.158150000
C	2.810238000	-3.273131000	1.786806000
C	1.633010000	-2.029459000	3.489733000
C	3.769280000	-3.644097000	2.727914000
H	2.913031000	-3.620352000	0.756889000
C	2.587126000	-2.411344000	4.429845000
H	0.813229000	-1.382093000	3.807110000
C	3.661539000	-3.215954000	4.049745000
H	4.603731000	-4.277388000	2.421254000
H	2.489541000	-2.082579000	5.466602000
H	4.409000000	-3.516675000	4.786286000
C	0.405138000	-3.179716000	-0.321014000
C	0.227599000	-4.508538000	0.087967000
C	0.427585000	-2.884771000	-1.685192000
C	0.097041000	-5.520026000	-0.859011000
H	0.206151000	-4.762525000	1.151140000
C	0.320272000	-3.898085000	-2.634143000
H	0.529018000	-1.850527000	-2.011951000
C	0.156793000	-5.217929000	-2.220950000
H	-0.041149000	-6.552636000	-0.533489000
H	0.359335000	-3.650905000	-3.697231000
H	0.070331000	-6.017057000	-2.959984000
C	-3.809929000	-1.115596000	2.079007000
C	-4.998532000	-0.488981000	1.680753000
C	-3.687052000	-1.565862000	3.397904000
C	-6.041765000	-0.310256000	2.585189000
H	-5.112658000	-0.139369000	0.652504000
C	-4.736748000	-1.391682000	4.302805000
H	-2.781966000	-2.071585000	3.738490000
C	-5.912697000	-0.761434000	3.899950000
H	-6.963793000	0.175051000	2.259524000

H	-4.636005000	-1.763824000	5.324587000
H	-6.733871000	-0.631662000	4.607707000
C	-3.041748000	-2.758594000	-0.126077000
C	-3.748071000	-3.774774000	0.535605000
C	-2.739344000	-2.908524000	-1.481823000
C	-4.138377000	-4.919999000	-0.151559000
H	-4.008421000	-3.674106000	1.591193000
C	-3.135024000	-4.054947000	-2.166719000
H	-2.182862000	-2.132241000	-2.003972000
C	-3.833980000	-5.061435000	-1.505191000
H	-4.689927000	-5.703168000	0.371838000
H	-2.889815000	-4.165779000	-3.224848000
H	-4.145733000	-5.957979000	-2.044461000
N	-2.231708000	1.434150000	1.928574000
C	-2.600779000	1.738916000	2.975975000
C	-3.132124000	2.084958000	4.281283000
H	-3.623728000	1.197196000	4.705771000
H	-2.327549000	2.418372000	4.949931000
H	-3.871743000	2.890779000	4.175032000

- Thermochemistry -

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Zero-point correction= 1.128790 (Hartree/Particle)
Thermal correction to Energy= 1.205799
Thermal correction to Enthalpy= 1.206743
Thermal correction to Gibbs Free Energy= 1.016028
Sum of electronic and zero-point Energies= -4483.271058
Sum of electronic and thermal Energies= -4483.194049
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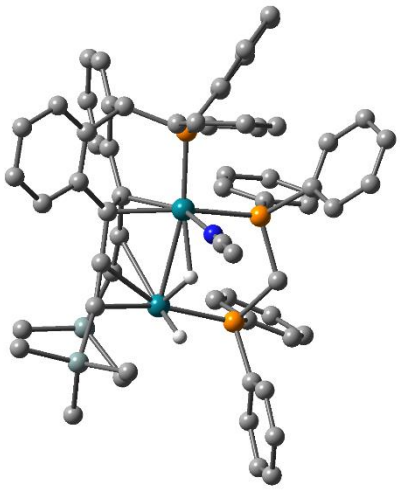
Sum of electronic and thermal Free Energies= -4483.383820

11-MeCN



E = -4485.58067119

Rh	0.941023000	0.431428000	0.248693000
Rh	-2.005077000	0.673944000	0.306268000
P	3.164924000	0.528331000	-0.260614000
P	0.804970000	-1.880801000	0.915088000
P	-2.287530000	-1.497954000	1.057202000
Si	-3.504501000	0.943407000	-3.363158000
Si	-2.888384000	4.163505000	1.219994000
C	-2.124098000	0.433500000	-2.192922000
C	-0.931517000	0.580966000	-1.907942000
C	0.446708000	0.965572000	-1.715591000
C	1.336185000	0.683874000	-2.890912000
C	0.811399000	0.014434000	-4.006788000
C	1.605462000	-0.319396000	-5.098359000
C	2.956308000	0.015789000	-5.102115000
C	3.493664000	0.679030000	-4.004837000
C	2.706174000	1.013301000	-2.901130000
C	3.359025000	1.681295000	-1.714249000
C	2.827022000	3.074661000	-1.500025000
C	3.673372000	4.160118000	-1.752865000
C	3.243037000	5.469548000	-1.574341000
C	1.939355000	5.703446000	-1.142472000
C	1.083747000	4.633408000	-0.911625000
C	1.501486000	3.304879000	-1.091289000
C	0.539497000	2.187476000	-0.860085000
C	-0.725647000	2.586609000	-0.278101000
C	-1.757767000	3.016274000	0.258200000
C	-0.755547000	-2.049869000	1.922092000
H	3.920834000	6.301056000	-1.774547000
H	4.695757000	3.969020000	-2.088679000
H	1.580605000	6.724062000	-0.997402000
H	0.059847000	4.836319000	-0.597819000
H	4.556698000	0.930355000	-3.993282000
H	3.591190000	-0.241754000	-5.951469000
H	1.162802000	-0.837614000	-5.950968000
H	-0.244880000	-0.253241000	-4.023353000
H	4.441926000	1.737657000	-1.895293000
H	-0.866834000	-3.069659000	2.318201000
H	-0.657562000	-1.365010000	2.777466000
H	-2.117536000	0.949039000	1.798924000
H	-0.633990000	0.452870000	1.066166000
C	-1.891095000	5.727906000	1.477868000
H	-2.449461000	6.430119000	2.116995000
H	-0.925284000	5.519774000	1.962520000
H	-1.694980000	6.236624000	0.521318000
C	-3.280544000	3.326650000	2.854284000
H	-3.843390000	2.391259000	2.711781000
H	-2.354491000	3.085019000	3.399419000
H	-3.882427000	3.994784000	3.490319000
C	-4.453471000	4.541298000	0.264618000
H	-4.229543000	4.996431000	-0.711531000
H	-5.069571000	3.648004000	0.089772000
H	-5.059864000	5.260536000	0.838236000
C	-3.853801000	2.732477000	-2.946296000
H	-4.241111000	2.829478000	-1.922781000
H	-2.933767000	3.332241000	-3.016809000
H	-4.597714000	3.155532000	-3.639442000
C	-5.056283000	-0.099322000	-3.207178000
H	-4.891969000	-1.130148000	-3.553017000
H	-5.460374000	-0.139319000	-2.185945000
H	-5.831746000	0.337834000	-3.856499000
C	-2.787909000	0.741941000	-5.080738000
H	-2.546309000	-0.311132000	-5.293812000
H	-3.518853000	1.074622000	-5.834798000
H	-1.873581000	1.340736000	-5.208564000
N	1.311827000	1.063297000	2.326432000
C	1.669976000	1.518551000	3.322323000
C	2.167611000	2.093961000	4.559768000
H	2.626908000	1.306256000	5.172146000
H	2.931630000	2.845874000	4.318140000
H	1.348098000	2.566584000	5.117370000
C	4.174658000	1.141018000	1.129492000
C	4.555168000	2.482258000	1.252420000
C	4.508522000	0.239933000	2.153034000
C	5.282054000	2.906049000	2.366760000
H	4.291991000	3.210891000	0.486754000
C	5.233815000	0.666590000	3.260601000
H	4.212541000	-0.807240000	2.083996000
C	5.628277000	2.001590000	3.368194000
H	5.586979000	3.951703000	2.442003000
H	5.500899000	-0.053902000	4.036422000
H	6.209968000	2.334615000	4.230457000
C	4.010273000	-0.975344000	-0.854663000
C	5.347470000	-1.257683000	-0.547152000
C	3.305462000	-1.841339000	-1.699175000

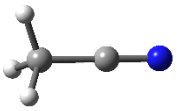
C	5.948336000	-2.412263000	-1.046108000
H	5.928169000	-0.586431000	0.087624000
C	3.906053000	-2.993733000	-2.195005000
H	2.277866000	-1.617239000	-1.976489000
C	5.227953000	-3.286326000	-1.860444000
H	6.990065000	-2.626581000	-0.799780000
H	3.333167000	-3.661654000	-2.841213000
H	5.703515000	-4.190753000	-2.245070000
C	2.092327000	-2.477748000	2.070525000
C	3.223152000	-3.149727000	1.582879000
C	2.033157000	-2.154755000	3.433469000
C	4.263750000	-3.495459000	2.442914000
H	3.305061000	-3.403231000	0.524641000
C	3.074739000	-2.504135000	4.290662000
H	1.171330000	-1.627350000	3.846273000
C	4.193630000	-3.174610000	3.797779000
H	5.135246000	-4.018395000	2.045055000
H	3.005890000	-2.261743000	5.353149000
H	5.005814000	-3.454789000	4.471386000
C	0.607390000	-3.202736000	-0.330014000
C	0.847639000	-4.550178000	-0.034659000
C	0.131852000	-2.853617000	-1.598169000
C	0.642642000	-5.526372000	-1.006797000
H	1.206057000	-4.846893000	0.953631000
C	-0.084689000	-3.831278000	-2.564760000
H	-0.072204000	-1.808008000	-1.834780000
C	0.179101000	-5.168718000	-2.272773000
H	0.844606000	-6.573700000	-0.773927000
H	-0.456998000	-3.544881000	-3.550072000
H	0.020407000	-5.936552000	-3.032742000
C	-2.758811000	-2.832262000	-0.081834000
C	-2.538126000	-4.175986000	0.250333000
C	-3.426404000	-2.517111000	-1.267001000
C	-2.960794000	-5.184706000	-0.608338000
H	-2.035337000	-4.451922000	1.178523000
C	-3.855281000	-3.530810000	-2.121346000
H	-3.604440000	-1.474745000	-1.523205000
C	-3.617813000	-4.863888000	-1.796686000
H	-2.777172000	-6.228556000	-0.348234000
H	-4.376427000	-3.280458000	-3.047232000
H	-3.949349000	-5.657767000	-2.468723000
C	-3.589386000	-1.533814000	2.346160000
C	-4.778874000	-2.243790000	2.146321000
C	-3.437151000	-0.768388000	3.511216000
C	-5.797482000	-2.187801000	3.099700000
H	-4.917381000	-2.850011000	1.249120000
C	-4.450030000	-0.722619000	4.463703000
H	-2.524691000	-0.190578000	3.681627000
C	-5.636102000	-1.430175000	4.257505000
H	-6.718478000	-2.751744000	2.938183000
H	-4.315701000	-0.132103000	5.371864000
H	-6.430086000	-1.395909000	5.005988000
N	-4.093556000	0.896632000	0.174000000
C	-5.227125000	0.878275000	0.376573000
C	-6.650597000	0.838734000	0.657319000
H	-6.813150000	0.262355000	1.579587000
H	-7.035311000	1.859505000	0.788434000
H	-7.181048000	0.355477000	-0.174723000

- Thermochemistry -

 Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

 Zero-point correction= 1.145188
(Hartree/Particle)
 Thermal correction to Energy= 1.222901
 Thermal correction to Enthalpy= 1.223845
 Thermal correction to Gibbs Free Energy= 1.030932
 Sum of electronic and zero-point
Energies= -4484.435483
 Sum of electronic and thermal
Energies= -4484.357770
 Sum of electronic and thermal
Enthalpies= -4484.356826
 Sum of electronic and thermal Free
Energies= -4484.549739

MeCN



E = -132.605188178

N	1.435873000	-0.000084000	0.000185000
C	0.280771000	0.000247000	-0.000508000
C	-1.178108000	0.000044000	0.000064000
H	-1.556566000	1.010688000	-0.204707000
H	-1.556009000	-0.683653000	-0.772305000
H	-1.554513000	-0.328188000	0.978380000

- Thermochemistry -

 Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

 Zero-point correction= 0.045556
(Hartree/Particle)
 Thermal correction to Energy= 0.049165
 Thermal correction to Enthalpy= 0.050109
 Thermal correction to Gibbs Free Energy= 0.021533
 Sum of electronic and zero-point
Energies= -132.559632
 Sum of electronic and thermal
Energies= -132.556024
 Sum of electronic and thermal
Enthalpies= -132.555079
 Sum of electronic and thermal Free
Energies= -132.583655

H_2

E = -1.17173797444

H	0.000000000	0.000000000	0.378875000
H	0.000000000	0.000000000	-0.37887500

- Thermochemistry -

 Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
 Zero-point correction= 0.010046
(Hartree/Particle)
 Thermal correction to Energy= 0.012407
 Thermal correction to Enthalpy= 0.013351
 Thermal correction to Gibbs Free Energy= -0.001479
 Sum of electronic and zero-point
Energies= -1.161692
 Sum of electronic and thermal
Energies= -1.159331
 Sum of electronic and thermal
Enthalpies= -1.158387
 Sum of electronic and thermal Free
Energies= -1.173217

References

[S1] *US Pat.,* 20080275131, 2008.

[S2] R. Cramer, J. A. McCleverty, J. Bray, *Inorg. Synth.*, **1974**, *15*, 14–18.

[S3] C. R. Bowers, D. P. Weitekamp, *J. Am. Chem. Soc*., **1987**, *109*, 5541-5542.

[S4] A. S. Kiryutin, G. Sauer, A. V. Yurkovskaya, H.-H. Limbach, K. L. Ivanov and G. Buntkowsky, J. Phys. Chem. C*, 2017, **121**,* 9879-9888*.*

[S5] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[S6] J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

[S7] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; b) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

Author Contribution

P.J., S.G., A.F., and T.G. designed the experiments. P.J., A.F., and T.G. wrote the manuscript with contributions from all authors. P.J. and S.G. performed the synthesis and analysis of the reported compounds. O.S., P.J. and N.C. performed the PHIP experiments and O.S. fitted the PHIP data. K.K. and I.K. supervised the PHIP experiments. P.J. performed the reactions with hydrogen, deuterium and the catalytic studies. P.J., M.B., G.L. and R.V. performed all other NMR experiments besides PHIP. O.F. and D.F. measured the XRD structure of complex **8** and P.J. measured all other XRD structures. J.B. performed DFT calculations. T.G., A.F., and H.G. supervised the project.