# Si–H Activation by means of Metal Ligand Cooperation in a Methandiide Derived Carbene Complex

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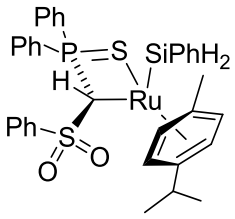
## 1. Experimental Details

### General procedures

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium or potassium (or over $P_4O_{10}$, $CH_2Cl_2$) and distilled prior to use. $H_2O$ is distilled water. $^{1}H$,$^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$ and$^{31}P\{^{1}H\}$ NMR spectra were recorded on Avance-500, Avance-400 or Avance-300 spectrometers at 22 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT and HMQC experiments. Elemental analyses were performed on an Elementarvario MICRO-cube elemental analyzer. All reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification. Carbene complex **1** was prepared according to literature procedure.[1]

### Si–H activation with complex 1

### Preparation of silyl complex 2a

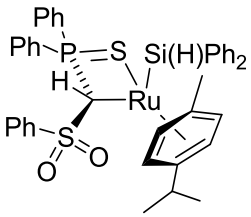



In a *J. Young*-NMR tube 30.0 mg (49.5 µmol) carbene complex **1** were dissolved in 0.7 mL dry toluene and 5.75 mg (53.1 µmol, 6.00 µL, ρ = 0.878 g·mol$^{-1}$) phenylsilane were added at room temperature. After a few seconds, the initial purple solution turned orange. $^{31}P\{^{1}H\}$ NMR spectroscopy confirmed the complete consumption of the starting carbene complex **1** and the selective formation of **2a**. The solvent was removed *in vacuo* and the residue was washed with *n*-pentane (3 x 5 mL) to remove excessive silane. The activation product **2a** was isolated as orange solid (27.8 mg, 38.9 µmol, 79%).

**$^{1}$H NMR** (300.2 MHz, $CD_2Cl_2$): δ= 1.11 (d, $^{3}J_{HH}$ = 6.87 Hz, 3 H; CH(C$H_3$)$_2$),1.18 (d, $^{3}J_{HH}$ = 6.91 Hz, 3 H; CH(C$H_3$)$_2$), 1.92 (s, 3 H; C$H_3$), 2.61-2.75 (sept., $^{3}J_{HH}$ = 6.89 Hz, 1 H; C$H$(CH$_3$)$_2$), 3.74 (d, $^{2}J_{PH}$ = 9.40, 1H; PC$H$S), 4.39 (d, $J_{AB}$ = 5.06 Hz, 1 H; Si$H$), 4.80 (d, $J_{AB}$ = 5.31 Hz, 1 H; Si$H$), 4.83 (dd, $^{3}J_{HH}$ = 5.88 Hz, $^{4}J_{HH}$ = 1.30 Hz, 1 H; C$H_{Cymene}$), 4.91 (dd, $^{3}J_{HH}$ = 5.75 Hz, $^{4}J_{HH}$ = 1.36 Hz, 1 H; C$H_{Cymene}$),5.43 (dd, $^{3}J_{HH}$ = 5.90 Hz, $^{4}J_{HH}$ = 1.33 Hz, 1 H; C$H_{Cymene}$),5.65 (dd, $^{3}J_{HH}$ = 5.77 Hz, $^{4}J_{HH}$ = 1.33 Hz, 1 H; C$H_{Cymene}$), 6.92-6.99 (m, 2 H; C$H_{PPh,ortho}$),7.13-7.42 (m, 10 H; C$H_{PPh,meta,para}$+ C$H_{SiPh,ortho,meta}$), 7.50-7.56 (m, 3 H; C$H_{SPh,meta,para}$),7.57-7.62 (m, 2 H; C$H_{SPh,ortho}$), 7.65-7.72 (m, 1 H; C$H_{SiPh,para}$), 7.96-8.05 (m, 2 H; C$H_{PPh,ortho}$). **$^{13}$C{$^{1}$H} NMR** (75.5 MHz, $CD_2Cl_2$): δ = 18.2 (C$H_3$), 21.4(CH(C$H_3$)$_2$), 23.6 (d,

$^{1}J_{PC}$ = 17.2 Hz; P*C*HS), 30.9 (CH(*C*$H_3$)$_2$), 77.9, 82.9, 89.3, 93.5 (*C*$H_{Cymene}$), 100.6 (*C*$CH_3$), 109.3 (*C*CH(CH$_3$)$_2$), 126.9 (*C*$H_{SPh,meta}$), 127.5 (*C*$H_{SiPh,meta}$), 127.7 (*C*$H_{SiPh,ortho}$), 128.4 (d, $^{3}J_{PC}$ = 12.4 Hz; *C*$H_{PPh,meta}$),128.6 (d, $^{3}J_{PC}$ = 11.6 Hz; *C*$H_{PPh,meta}$),129.1 (*C*$H_{SPh,ortho}$),129.2 (d, $^{1}J_{PC}$ = 79.8 Hz; *C*$H_{PPh,ipso}$), 130.2 (d, $^{2}J_{PC}$ = 10.9 Hz; *C*$H_{PPh,ortho}$), 132.0 (d, $^{4}J_{PC}$ = 3.17 Hz; *C*$H_{PPh,para}$), 132.3 (*C*$H_{SPh,para}$), 133.2 (d, $^{4}J_{PC}$ = 3.25 Hz; *C*$H_{PPh,para}$), 133.8 (d, $^{2}J_{PC}$ = 10.8 Hz; C*H*$_{PPh,ortho}$), 135.9 (d, $^{1}J_{PC}$ = 53.8 Hz; *C*$_{PPh,ipso}$), 136.0 (*C*$H_{SiPh,para}$), 143.7 (*C*$_{SiPh,ipso}$), 144.6 (*C*$_{SPh,ipso}$).**$^{31}$P{$^{1}$H} NMR** (162.0 MHz, $CD_2Cl_2$): δ = 65.2. **$^{29}$Si{$^{1}$H} NMR** (59.6 MHz, $CD_2Cl_2$):δ = –0.99 (d, $^{3}J_{SiP}$ = 7.68 Hz). **Anal. Calcd**. for $C_{35}H_{37}O_2PS_2RuSi$: C, 58.88; H, 5.22; S 8.98. Found: C, 58.90; H, 5.40; S 8.91.

**Preparation of silyl complex 2b**

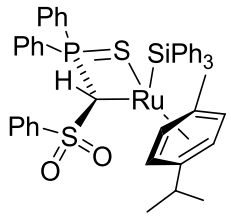



20.0 mg (33.0 µmol) carbene complex **1** were dissolved in 2 mL dry diethylether and 7.90 mg (42.9 µmol, 8.00 µL, ρ = 0.993 g·mL$^{-1}$) diphenylsilane were added. Within 10 min reaction time, the purple reaction mixture turned orange and the $^{31}$P{$^{1}$H} NMR spectrum of the mixture confirmed complete conversion to **2b**. For further purification the solvent was removed *in vacuo* and the residue washed with *n*-pentane (3 x 5 mL) to remove the excessive silane. Removal of the solvent gave **2b** as orange solid (20.1 mg, 25.5 µmol, 77%).

**$^{1}$H NMR** (300.2 MHz, $CD_2Cl_2$): δ = 1.09 (d, $^{3}J_{HH}$ = 6.90 Hz, 3 H; CH(C*H*$_3$)$_2$),1.14 (d, $^{3}J_{HH}$ = 6.84 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.78 (s, 3 H; C*H*$_3$), 2.56-2.65 (sept., $^{3}J_{HH}$ = 6.89 Hz, 1 H; C*H*(CH$_3$)$_2$), 3.86 (d, $^{2}J_{PH}$ =12.4, 1H; PC*H*S), 4.95 (d, $^{3}J_{HH}$ = 5.71 Hz, 1 H; C*H*$_{Cymene}$),5.10 (t, $^{3}J_{HH}$ = 7.16 Hz, 2 H; C*H*$_{Cymene}$), 5.34 (d, $^{3}J_{HH}$ = 5.59 Hz, 1 H; C*H*$_{Cymene}$), 5.73 (s, 1 H; Si*H*), 6.14-6.22 (m, 2 H; C*H*$_{PPh,ortho}$), 6.76-6.83 (m, 2 H; C*H*$_{SiPh,meta}$), 7.02-7.16 (m, 4 H; C*H*$_{SiPh,meta,para}$), 7.19-7.34 (m, 8 H; C*H*$_{SPh,meta}$+ C*H*$_{PPh,meta,para}$), 7.16-7.39 (m, 2 H; C*H*$_{SPh,ortho}$), 7.59-7.75 (m, 5 H; C*H*$_{SiPh,ortho}$+ C*H*$_{SPh,para}$), 8.33-8.41 (m, 2 H; C*H*$_{PPh,ortho}$). **$^{13}$C{$^{1}$H} NMR** (75.5 MHz, $CD_2Cl_2$):δ = 17.9 (*C*$H_3$),20.9 (CH(*C*$H_3$)$_2$), 24.9 (d, $^{1}J_{PC}$ = 14.4 Hz; P*C*HS), 30.7 (CH(*C*$H_3$)$_2$), 78.1, 84.9, 90.0, 94.1 (*C*$H_{Cymene}$), 98.6 (*C*$CH_3$), 109.4 (*C*CH(CH$_3$)$_2$), 126.7 (*C*$H_{SPh,meta}$),127.5 (d, $^{3}J_{PC}$ = 7.47 Hz; *C*$H_{SiPh,meta}$), 127.6 (d, $^{2}J_{PC}$ = 6.49 Hz; *C*$H_{SiPh,ortho}$), 128.4 (d, $^{3}J_{PC}$ = 8.68 Hz; *C*$H_{PPh,meta}$), 128.6 (d, $^{3}J_{PC}$ = 10.3 Hz; *C*$H_{PPh,meta}$), 128.9 (*C*$H_{SPh,ortho}$),129.6 (d, $^{1}J_{PC}$ = 79.8 Hz; *C*$H_{PPh,ipso}$), 129.8 (d, $^{2}J_{PC}$ = 11.1 Hz; *C*$H_{PPh,ortho}$), 131.4 (d, $^{4}J_{PC}$ = 2.94 Hz; *C*$H_{PPh,para}$), 132.0 (*C*$H_{SPh,para}$),133.1 (d, $^{4}J_{PC}$ = 3.02 Hz; *C*$H_{PPh,para}$), 133.7 (d, $^{2}J_{PC}$ = 10.8 Hz; C*H*$_{PPh,ortho}$), 136.3 (*C*$H_{SiPh,para}$), 137.0 (d, $^{1}J_{PC}$ = 47.1 Hz; *C*$_{PPh,ipso}$), 137.1 (*C*$H_{SiPh,para}$), 133.1 (d,

$^{4}J_{PC}$ = 3.02 Hz; *C*H$_{PPh,para}$), 133.3 (d, $^{2}J_{PC}$ = 10.8 Hz, *C*H$_{PPh,ortho}$),138.0 (*C*H$_{SiPh,ortho}$),144.1 (*C*$_{SiPh,ipso}$), 144.2 (*C*$_{SiPh,ipso}$), 146.1 (*C*$_{SPh,ipso}$). **$^{31}$P{$^{1}$H} NMR** (162.0 MHz, $CD_2Cl_2$):δ = 50.1. **$^{29}$Si{$^{1}$H} NMR** (59.6 MHz, $CD_2Cl_2$): δ = 20.1 (d, $^{3}J_{SiP}$ = 9.20 Hz). Anal. Calcd. for $C_{41}H_{41}O_2PS_2RuSi$: C, 62.33; H, 5.23; S 8.12. Found: C, 62.81; H, 5.39; S 8.12.

**Preparation of silyl complex 2c**

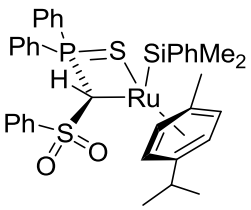



A solution of 50.1 mg (82.7 µmol) carbene complex **1** in 10 mL dry toluene was treated with 21.7 mg (82.7 mmol) triphenylsilane at room temperature. After stirring for 17 h, a color change from deep purple to yellow-orange was observed, indicating complete conversion to the activation product **2c**.The solvent was removed *in vacuo* and the residue was washed with *n*-pentane (15 mL), affording silyl complex **2c** as yellow solid (61.7 mg, 71.2 µmol, 86%). Crystals suitable for X-ray diffraction analysis could be obtained by diffusion of *n*-pentane into a solution of **2c** in toluene.

**$^{1}$H NMR** (500.1 MHz, $CD_2Cl_2$):δ = 0.97 (d, $^{3}J_{HH}$ = 6.92 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.04 (d, $^{3}J_{HH}$ = 6.89 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.81 (s, 3 H; C*H*$_3$), 2.33-2.41 (sept., $^{3}J_{HH}$ = 6.93 Hz, 1 H; C*H*(CH$_3$)$_2$), 4.06 (d, $^{2}J_{PH}$ =13.0 Hz, 1H; PC*H*S), 4.64 (d, $^{3}J_{HH}$ = 5.61 Hz, 1 H; C*H*$_{Cymene}$), 4.76 (d, $^{3}J_{HH}$ = 6.23 Hz, 1 H; C*H*$_{Cymene}$), 5.01 (d, $^{3}J_{HH}$ = 5.65 Hz, 1 H; C*H*$_{Cymene}$), 5.78 (d, $^{3}J_{HH}$ = 6.25 Hz, 1 H; C*H*$_{Cymene}$), 6.05 (q, $^{3}J_{HH}$ = 6.60 Hz, 2 H; C*H*$_{SiPh,meta}$), 6.68-6.71 (td, $^{3}J_{HH}$ = 7.81 Hz, $^{4}J_{HH}$= 2.71 Hz, 2 H; C*H*$_{SiPh,meta}$), 6.95 (t, $^{3}J_{HH}$ = 7.82 Hz, 2 H; C*H*$_{SPh,meta}$), 7.03-7.06 (td, $^{3}J_{HH}$ = 7.45 Hz, $^{4}J_{HH}$ = 0.92 Hz, 1 H; C*H*$_{SiPh,para}$), 7.13 (t, $^{3}J_{HH}$ = 7.35 Hz, 1 H; C*H*$_{SPh,para}$), 7.17 (t, $^{3}J_{HH}$ = 6.51 Hz, 1 H; C*H*$_{SiPh,para}$), 7.25 (t, $^{3}J_{HH}$ = 7.54 Hz, 1 H; C*H*$_{SiPh,para}$), 7.30-7.34 (m, 10 H; C*H*$_{SPh,ortho}$+ C*H*$_{PPh,meta,para}$+ C*H*$_{SiPh,meta}$), 7.67-7.71 (td, $^{3}J_{HH}$ = 7.61 Hz, $^{4}J_{HH}$ = 3.17 Hz, 2 H; C*H*$_{PPh,ortho}$), 7.80-7.82 (m, 6 H; C*H*$_{SiPh,ortho}$), 8.56-8.60 (m, 2 H; C*H*$_{PPh,ortho}$).**$^{13}$C{$^{1}$H} NMR** (125.8 MHz, $CD_2Cl_2$):δ =18.1 (*C*H$_3$), 22.7 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 25.1 (d, $^{1}J_{PC}$ = 16.4 Hz; P*C*HS), 31.0 (*C*H(CH$_3$)$_2$), 79.7, 90.1, 90.7, 93.5 (*C*H$_{Cymene}$), 92.6 (*C*CH$_3$), 109.9 (*C*CH(CH$_3$)$_2$), 126.7 (*C*H$_{SPh,para}$), 127.2 (*C*H$_{SiPh,meta}$), 127.3 (*C*H$_{SiPh,meta}$), 128.3 (d, $^{3}J_{PC}$ = 11.0 Hz; *C*H$_{PPh,meta}$), 128.77 (C*H*$_{SiPh,para}$), 128.79 (d, $^{3}J_{PC}$ = 13.0 Hz; *C*H$_{PPh,meta}$), 129.1 (*C*H$_{SPh,meta}$), 130.1 (d, $^{2}J_{PC}$ = 11.1 Hz; *C*H$_{PPh,ortho}$), 131.3 (d, $^{4}J_{PC}$ = 2.92 Hz; C*H*$_{PPh,\ para}$), 131.9 (*C*H$_{SPh,ortho}$), 136.5 (d, $^{1}J_{PC}$ = 103.7 Hz; *C*$_{PPh,ipso}$), 137. 8 (d, $^{1}J_{PC}$ = 138.0 Hz; *C*$_{PPh,ipso}$), 133.1 (d, $^{4}J_{PC}$ = 3.02 Hz; *C*H$_{PPh,para}$), 133.3 (d, $^{2}J_{PC}$ = 10.8 Hz, *C*H$_{PPh,ortho}$),138.0 (*C*H$_{SiPh,ortho}$), 144.1 (d, $^{3}J_{PC}$ = 1.06, *C*$_{SPh,ipso}$), 146.5 (*C*$_{SiPh,ipso}$).**$^{31}$P{$^{1}$H} NMR** (202.5 MHz, $CD_2Cl_2$): δ = 41.3. **$^{29}$Si{$^{1}$H} NMR**

(99.4 MHz, $CD_2Cl_2$): δ = 19.9 (d, $^3J_{PSi}$ = 11.3 Hz). Anal. Calcd. for $C_{47}H_{45}O_2PS_2RuSi$: C, 65.17; H, 5.24; S 7.40. Found: C, 65.22; H, 5.38; S 7.01.

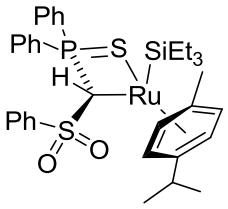
**Preparation of silyl complex 2d**




70.6 mg (0.12 mmol) carbene complex **1** were dissolved in 5 mL dry toluene and 19.1 mg (0.12 mmol, 0.02 mL, ρ = 0.889 g·mL$^{-1}$) dimethylphenylsilane were added, resulting in a color change from purple to orange within a couple of minutes. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture revealed the selective conversion to **2d**. The solvent was removed *in vacuo* and the orange oily residue was washed with *n*-pentane, affording **2d** as an orange solid (55.4 mg, 7.47 µmol, 62%).

**$^1$H NMR** (500.1 MHz, $CD_2Cl_2$): δ= 0.65 (s, 3 H; Si(C*H*$_3$)$_2$), 0.75 (s, 3 H; Si(C*H*$_3$)$_2$), 0.96 (d, $^3J_{HH}$ = 6.83 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.03 (d, $^3J_{HH}$ = 6.97 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.94 (s, 3 H; C*H*$_3$), 2.28-2.36 (sept., $^3J_{HH}$ = 6.92 Hz, 1 H; C*H*(CH$_3$)$_2$), 3.87 (d, $^2J_{PH}$ = 13.1 Hz, 1H; PC*H*S), 4.66 (dd, $^3J_{HH}$ = 5.49 Hz, $^4J_{HH}$ = 1.05 Hz, 1 H; C*H*$_{Cymene}$), 4.68 (d, $^3J_{HH}$ = 6.17 Hz, 1 H; C*H*$_{Cymene}$), 5.36 (d, $^3J_{HH}$ = 5.98 Hz, 1 H; C*H*$_{Cymene}$), 5.75 (dd, $^3J_{HH}$ = 6.17 Hz, $^4J_{HH}$ = 0.87, 1 H; C*H*$_{Cymene}$), 6.12-6.22 (m, 2 H; C*H*$_{PPh,ortho}$), 6.78-6.82 (m, 2 H; C*H*$_{PPh,meta}$), 7.03 (t, $^3J_{HH}$ = 7.41 Hz, 2 H; C*H*$_{Ph,meta}$), 7.10-7.14 (m, 1 H; C*H*$_{PPh,para}$), 7.18 (t, $^3J_{HH}$ = 7.45 Hz; C*H*$_{Ph,para}$), 7.31-7.37 (m, 3 H; C*H*$_{Ph,meta}$ + C*H*$_{Ph,para}$), 7.47 (dd, $^3J_{HH}$ = 8.45 Hz, $^4J_{HH}$ = 1.24 Hz, 2 H; C*H*$_{Ph,ortho}$), 7.64-7.68 (m, 2 H; C*H*$_{PPh,meta}$), 7.72-7.76 (m, 3 H; C*H*$_{PPh,para}$ + C*H*$_{Ph,ortho}$), 8.48-8.52 (m, 2 H; C*H*$_{PPh,ortho}$). **$^{13}C\{^1H\}$ NMR** (125.8 MHz, $CD_2Cl_2$): δ = 6.12, 6.14 (Si(*C*H$_3$)$_2$), 18.6 (*C*H$_3$), 20.6 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.6 (d, $^1J_{PC}$ = 16.9 Hz; P*C*HS), 31.0 (*C*H(CH$_3$)$_2$), 75.3 (*C*H$_{Cymene}$), 88.0 (*C*CH$_3$), 91.3, 91.6, 92.1 (*C*H$_{Cymene}$), 109.8 (*C*CH(CH$_3$)$_2$), 126.6 (*C*H$_{Ph,ortho}$), 126.9 (*C*H$_{Ph,meta/para}$), 127.2 (*C*H$_{Ph,meta/para}$), 128.4 (d, $^3J_{PC}$ = 10.9 Hz; *C*H$_{PPh,meta}$), 128.6 (d, $^3J_{PC}$ = 13.0 Hz; *C*H$_{PPh,meta}$), 128.9 (*C*H$_{Ph,meta}$), 129.9 (d, $^2J_{PC}$ = 10.9 Hz; *C*H$_{PPh,ortho}$), 130.8 (d, $^1J_{PC}$ = 84.3 Hz; *C*H$_{PPh,ipso}$), 131.3 (d, $^4J_{PC}$ = 2.95 Hz; *C*H$_{PPh,para}$), 131.9 (*C*H$_{Ph,para}$), 132.9 (d, $^4J_{PC}$ = 3.06 Hz; *C*H$_{PPh,para}$), 133.2 (d, $^2J_{PC}$ = 10.7 Hz; C*H*$_{PPh,ortho}$), 135.6 (*C*H$_{Ph,ortho}$), 137.5 (d, $^1J_{PC}$ = 43.1 Hz; *C*$_{PPh,ipso}$), 144.5 (d, $^3J_{PC}$ = 0.76 Hz; *C*$_{SPh,ipso}$), 150.4 (*C*$_{SiPh,ipso}$). **$^{31}P\{^1H\}$ NMR** (202.5 MHz, $CD_2Cl_2$): δ = 39.4. **$^{29}Si\{^1H\}$ NMR** (99.4 MHz, $CD_2Cl_2$): δ = 19.4 (d, $^3J_{SiP}$ = 10.9 Hz). **Anal. Calcd**. for $C_{37}H_{41}O_2PS_2RuSi$: C, 59.89; H, 5.57; S 8.64. Found: C, 59.40; H, 5.62; S 8.65.

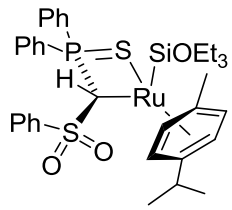
**Preparation of silyl complex 2e**



30.0 mg (49.5 µmol) carbene complex **1** were dissolved in 2 mL dry toluene and 7.91 mg (68.0 µmol, 0.01 mL, ρ = 0.73 g·mL$^{-1}$) triethylsilane were added at room temperature. After 15 min a color change from purple to orange could be observed, the $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture confirmed the formation of **2e**. The product could not be purified and isolated due to reversible reaction processes in solution. However, the reversible process could be confirmed by treatment of a solution of **2e** in $CD_2Cl_2$ with 11.1 mg (60.2 µmol, 0.01 mL, ρ = 0.993 g·mL$^{-1}$) diphenylsilane. Here, $^{31}P\{^{1}H\}$ NMR spectra revealed the selective formation of activation complex **2b** (for $^{31}P\{^{1}H\}$ NMR spectra see below).

**$^{1}$H NMR** (400.1 MHz, $CD_2Cl_2$): δ = 1.18 (d, $^{3}J_{HH}$ = 6.91 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.29 (d, $^{3}J_{HH}$ = 6.89 Hz, 3 H; CH(C*H*$_3$)$_2$), 2.27 (s, 3 H; C*H*$_3$), 2.83-2.91 (sept., $^{3}J_{HH}$ = 6.94 Hz, 1 H; C*H*(CH$_3$)$_2$), 3.10 (d, $^{2}J_{PH}$ = 1.57 Hz, 1 H; PC*H*S), 5.59 (dd, $^{3}J_{HH}$ = 5.89, 1.24 Hz, 1 H; C*H*$_{Cymene}$), 5.65 (dd, $^{3}J_{HH}$ = 5.98, 1.18 Hz, 1 H; C*H*$_{Cymene}$), 5.70(dd, $^{3}J_{HH}$ = 5.77, 1.28 Hz, 1 H; C*H*$_{Cymene}$), 5.84 (dd, $^{3}J_{HH}$ = 5.97, 1.22 Hz, 1 H; C*H*$_{Cymene}$), 6.77-6.85 (m, 2 H; C*H*$_{PPh,ortho}$), 6.97-7.30 (m, 8 H; C*H*$_{PPh,meta,para}$+ C*H*$_{SPh,meta}$), 7.31-7.51 (m, 2 H; C*H*$_{SPh,ortho}$), 7.57-7.74 (m, 1 H; C*H*$_{SPh,para}$), 8.15-8.27 (m, 2 H; C*H*$_{PPh,ortho}$). The signals of the triethylsilyl ligand could not be detected due to the excessive triethylsilane in the reaction mixture. **$^{31}P\{^{1}H\}$ NMR** (202.5 MHz, $CD_2Cl_2$): δ = 53.2. **$^{29}Si\{^{1}H\}$ NMR** (99.4 MHz, $CD_2Cl_2$, –40 °C): δ = 32.8 (d, $^{3}J_{SiP}$ = 6.28 Hz).

**Preparation of silyl complex 2f**



69.1 mg (0.11 mmol) ruthenium carbene complex **1** were dissolved in 5 mL dry toluene and 21.4 mg (0.02 mL, 0.13 mmol, ρ = 0.89 g·mL$^{-1}$) triethoxysilane were added at room temperature. Subsequently, a color change from purple to orange could be observed and the $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture revealed a complete conversion of the starting material. The solvent was evaporated *in vacuo* and the residue was kept at 1·10$^{-3}$ mbar for 10 h. After that time, complex **2f** could be obtained as an orange oil. The oil was washed with *n*-pentane (1 mL) and stored at –30 °C, giving complex **2f** as an orange solid (30.9 mg, 0.04 mmol, 36%), which melts at around –10 °C.

**$^{1}$H NMR** (500.1 MHz, $CD_2Cl_2$): δ = 1.107 (t, $^{3}J_{HH}$ = 6.99 Hz, 9 H; OCH$_2$C*H*$_3$), 1.11 (d, $^{3}J_{HH}$ = 6.86 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.15 (d, $^{3}J_{HH}$ = 6.92 Hz, 3 H; CH(C*H*$_3$)$_2$), 1.88 (s, 3 H; C*H*$_3$), 2.71-2.79 (sept., $^{3}J_{HH}$ = 6.89 Hz, 1 H; C*H*(CH$_3$)$_2$), 3.69-3.77 (m, 6 H; OC*H*$_2$CH$_3$), 4.94 (dd, $^{3}J_{HH}$ =

5.73 Hz, $^{4}J_{HH}$ = 1.40 Hz, 1 H; C*H*$_{Cymene}$), 5.09 (d, $^{2}J_{PH}$ = 12.4 Hz, 1 H; PC*H*S), 5.26 (dd, $^{3}J_{HH}$ = 6.03 Hz, $^{4}J_{HH}$ = 1.25 Hz, 1 H; C*H*$_{Cymene}$), 5.52 (dd, , $^{3}J_{HH}$ = 6.01 Hz, $^{4}J_{HH}$ = 1.33 Hz, 1 H; C*H*$_{Cymene}$), 5.65 (dd, $^{3}J_{HH}$ = 5.74 Hz, $^{4}J_{HH}$ = 1.21, 1 H; C*H*$_{Cymene}$), 7.17-7.19 (m, 4 H; C*H*$_{PPh,meta}$), 7.27 (t, $^{3}J_{HH}$ = 7.35 Hz, 2 H; C*H*$_{SPh,meta}$), 7.32-7.36 (m, 1 H; C*H*$_{SPh,para}$), 7.83-7.42 (m, 1 H; C*H*$_{PPh,para}$), 7.54 (d, $^{3}J_{HH}$ = 8.45 Hz, 2 H; C*H*$_{SPh,ortho}$), 7.68-7.72 (m, 1 H; C*H*$_{PPh,para}$), 8.17-8.22 (m, 2 H; C*H*$_{PPh,ortho}$). **$^{13}$C{$^{1}$H} NMR** (125.8 MHz, $CD_2Cl_2$): δ = 18.4 (*C*H$_3$), 18.7 (OCH$_2$*C*H$_3$), 19.5 (d, $^{1}J_{PC}$ = 16.3 Hz; P*C*HS), 21.7 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 31.0 (*C*H(CH$_3$)$_2$), 57.8 (O*C*H$_2$CH$_3$), 76.6 (*C*H$_{Cymene}$), 88.8, 89.76, 89.78 (*C*H$_{Cymene}$), 97.2 (*C*CH$_3$), 113.3 (*C*CH(CH$_3$)$_2$), 126.7 (*C*H$_{SPh}$), 128.3 (d, $^{3}J_{PC}$ = 10.8 Hz; *C*H$_{PPh,meta}$), 128.4 (d, $^{3}J_{PC}$ = 9.84 Hz; *C*H$_{PPh,meta}$), 129.0 (*C*H$_{SPh}$), 129.1 (d, $^{1}J_{PC}$ = 74.1 Hz; *C*H$_{PPh,ipso}$), 130.0 (d, $^{2}J_{PC}$ = 11.0 Hz; *C*H$_{PPh,ortho}$), 131.7 (d, $^{4}J_{PC}$ = 2.99 Hz; *C*H$_{PPh,para}$), 132.1 (*C*H$_{SPh}$), 133.0 (d, $^{4}J_{PC}$ = 3.04 Hz; *C*H$_{PPh,para}$), 134.2 (d, $^{2}J_{PC}$ = 10.6 Hz; C*H*$_{PPh,ortho}$), 137.8 (d, $^{1}J_{PC}$ = 50.9 Hz; *C*$_{PPh,ipso}$), 145.1 (d, $^{3}J_{PC}$ = 1.14 Hz; *C*$_{SPh,ipso}$). **$^{31}$P{$^{1}$H} NMR** (202.5 MHz, $CD_2Cl_2$): δ = 60.9. **$^{29}$Si{$^{1}$H} NMR** (99.4 MHz, $CD_2Cl_2$): δ = 7.44 (d, $^{3}J_{SiP}$ = 8.63 Hz).

**Hydrosilylation of norbornene**

28.0 mg (35.4 µmol) silyl complex **2b** and norbornene 11.0 mg (0.12 mmol) were dissolved in 0.5 mL $C_6D_6$ and heated to 60 °C for 20 h. After this time, the $^{31}$P{$^{1}$H} NMR of the dark brown reaction mixture showed complete consumption of the starting material. The solution was treated with $Et_2O$ (2 mL) and the yellow solution was separated from the formed precipitate (polymerized norbornene). GC-MS analysis of the filtrate revealed the presence of hydrosilylation product **4**.

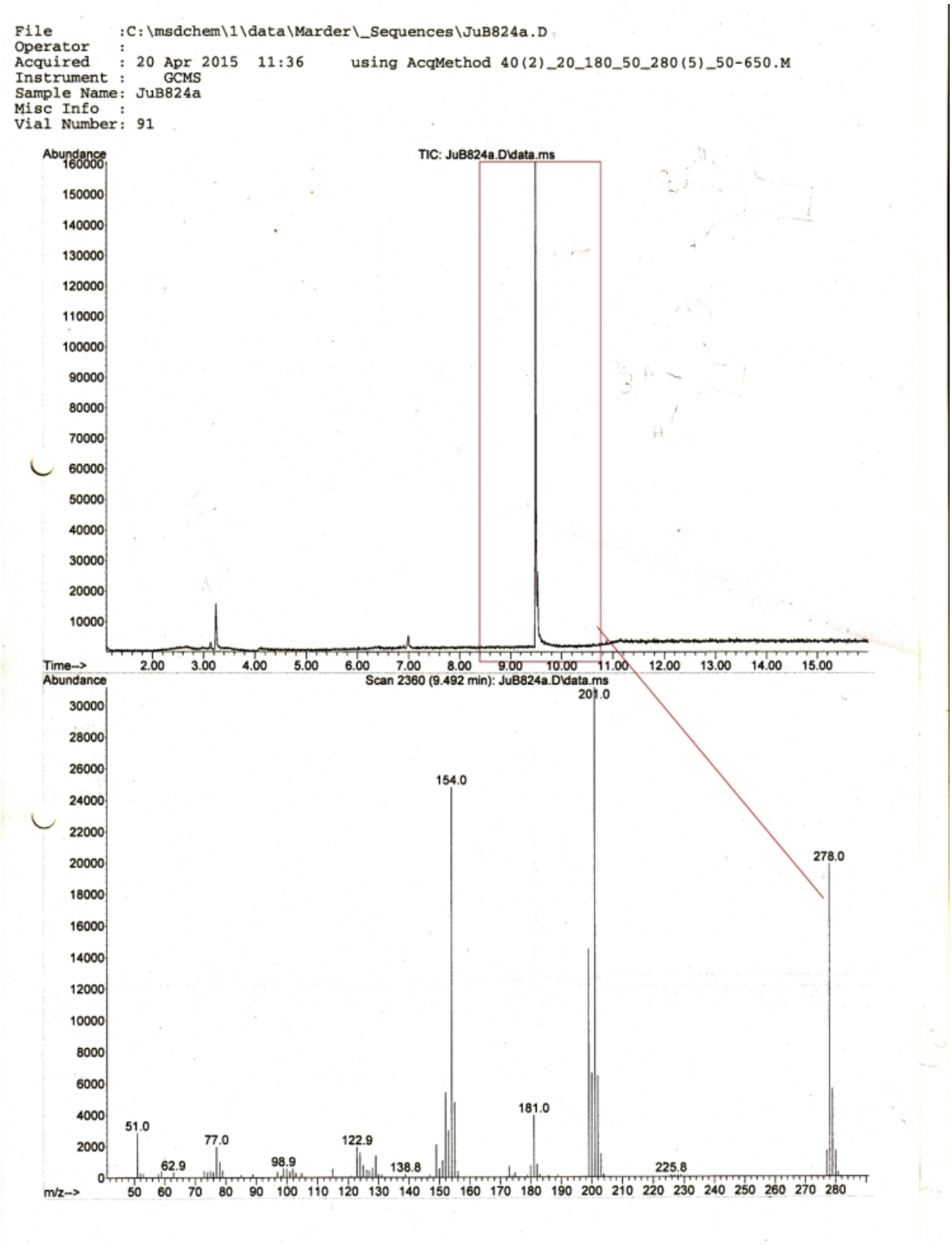



**Figure 1.** GC-MS of the product mixture from the hydrosilylation with complex **2b**.

## 2. NMR spectra of the isolated compounds

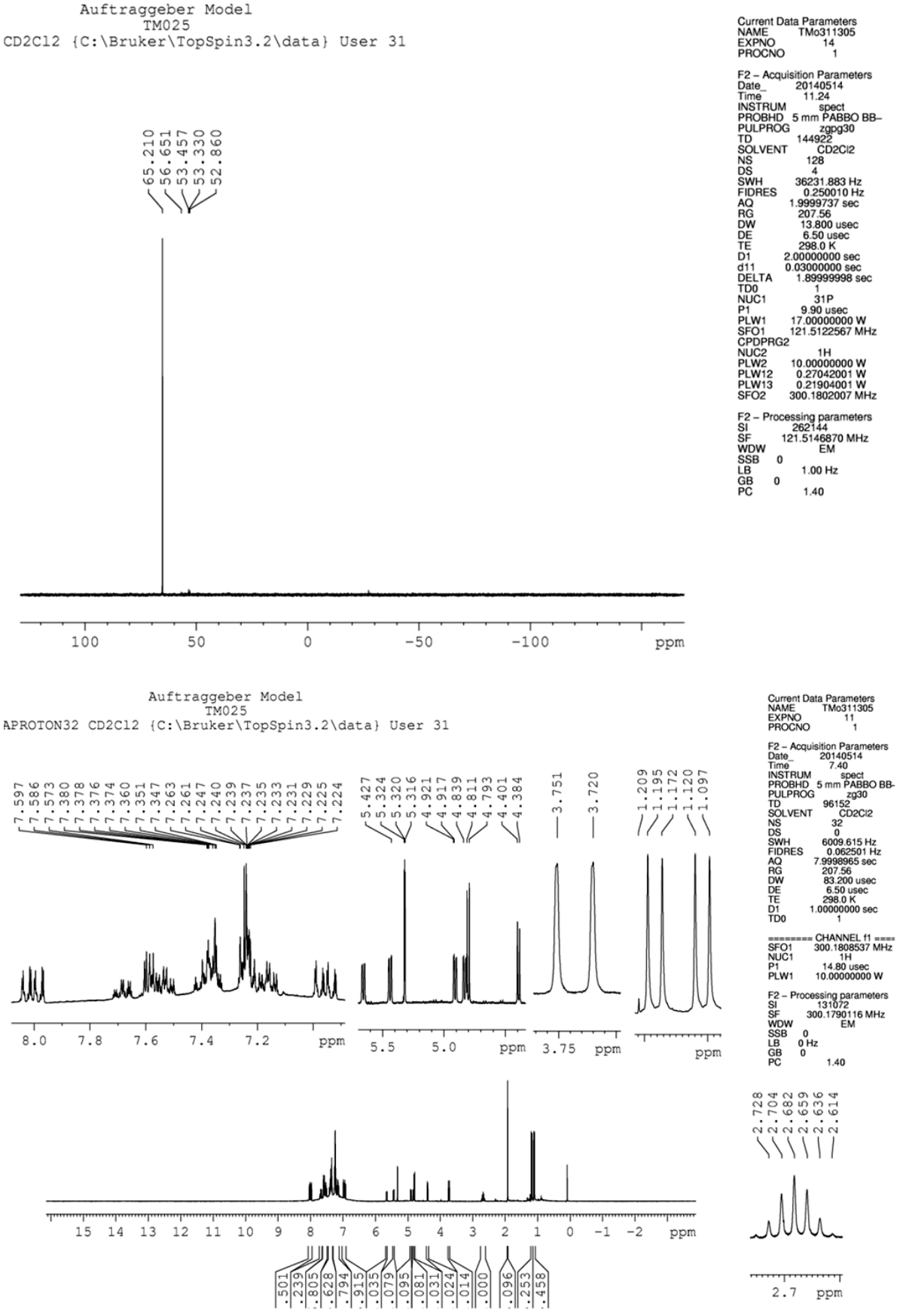



**Figure S2a**. $^{31}P\{^{1}H\}$ and $^{1}H$ NMR spectra of **2a** in $CD_2Cl_2$.

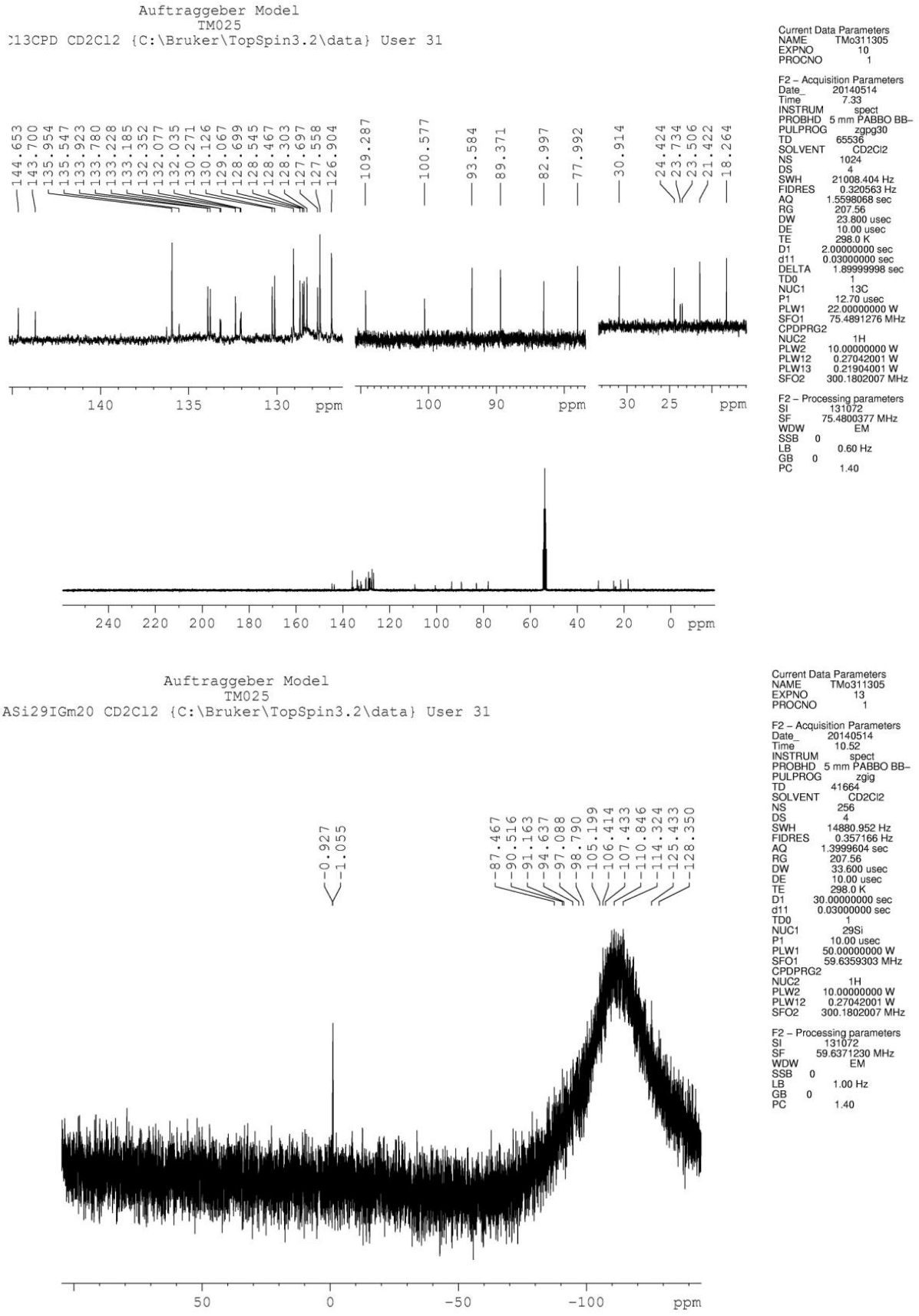



**Figure S2b.** $^{13}C\{^{1}H\}$ NMR and $^{29}Si\{^{1}H\}$ NMR spectra of **2a** in $CD_2Cl_2$

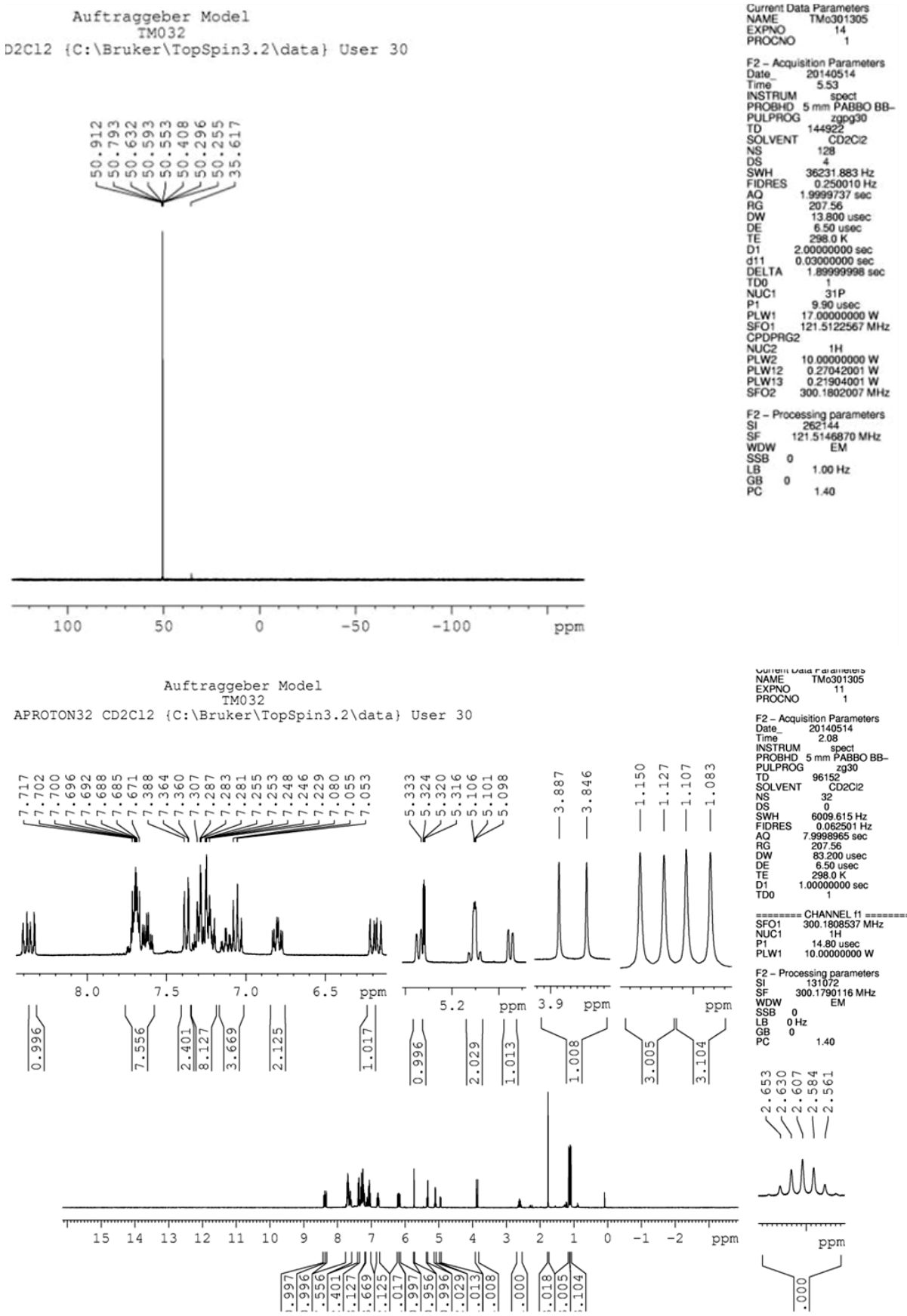



**Figure S3a**. $^{31}P\{^{1}H\}$ and $^{1}H$ NMR spectra of **2b** in $CD_2Cl_2$.

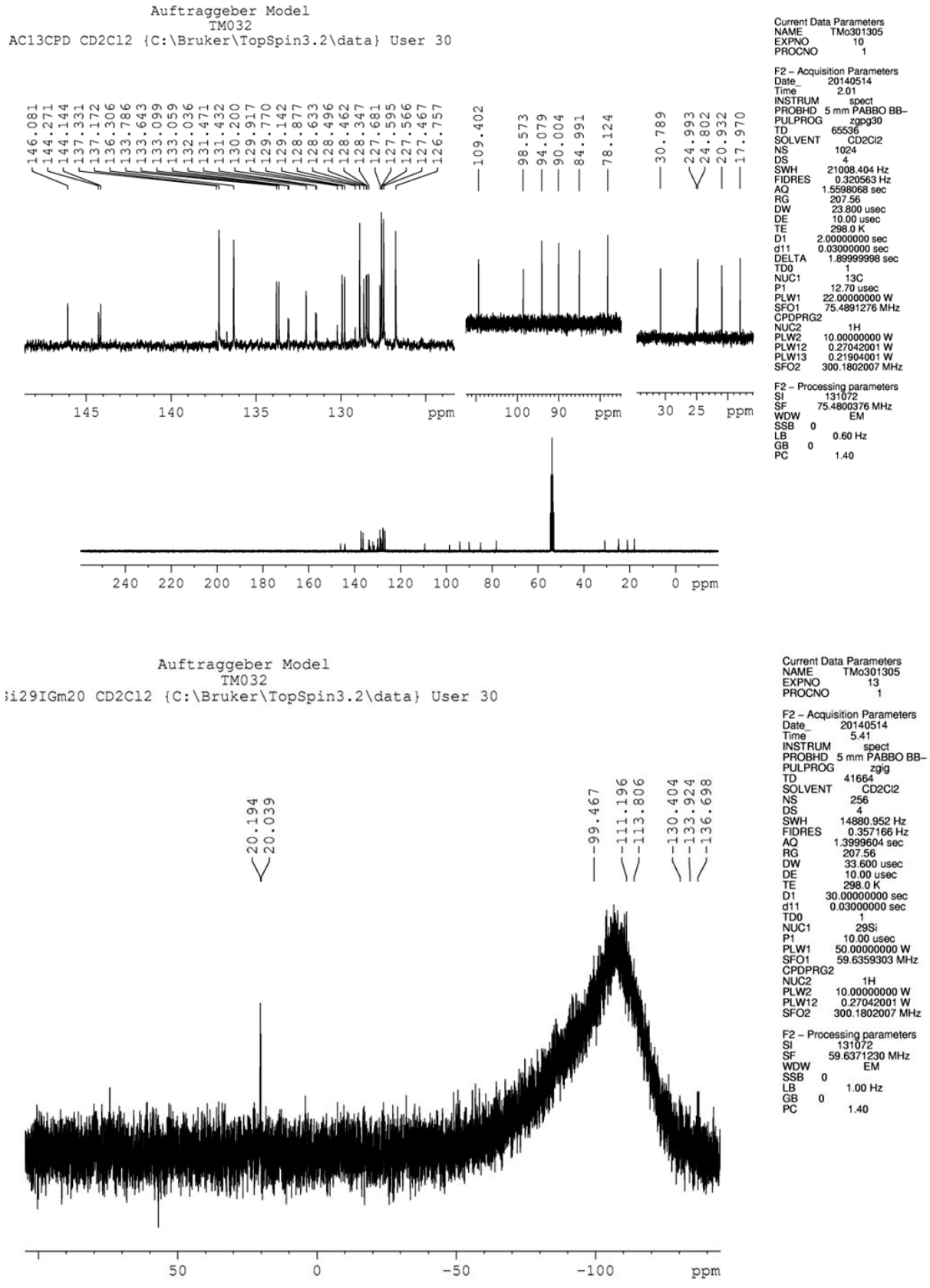



**Figure S3b.** $^{13}C\{^{1}H\}$ NMR and $^{29}Si\{^{1}H\}$ NMR spectra of **2b** in $CD_2Cl_2$.

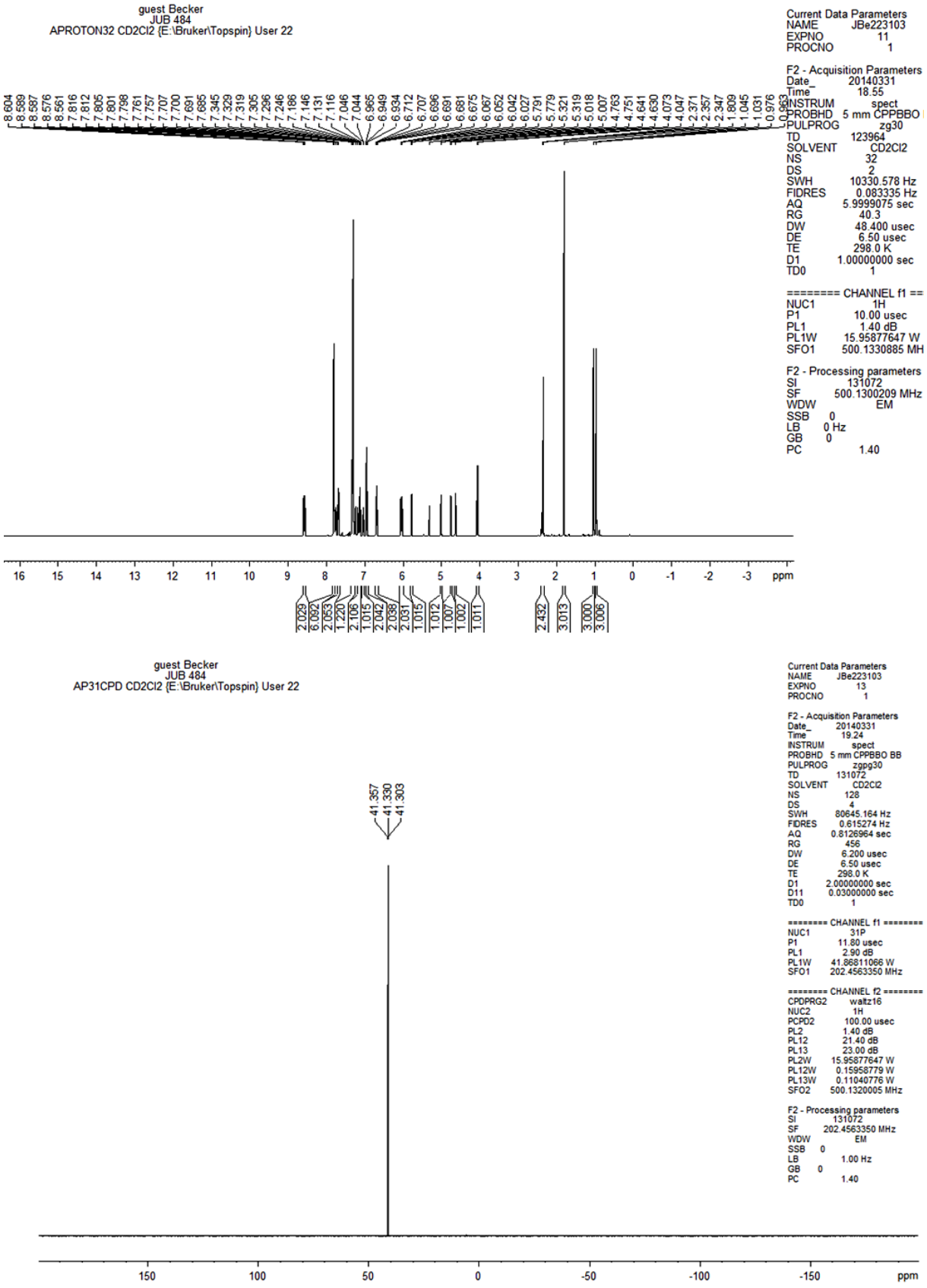



**Figure S4a**. $^{31}P\{^{1}H\}$ and $^{1}H$ NMR spectra of **2c** in $CD_2Cl_2$.

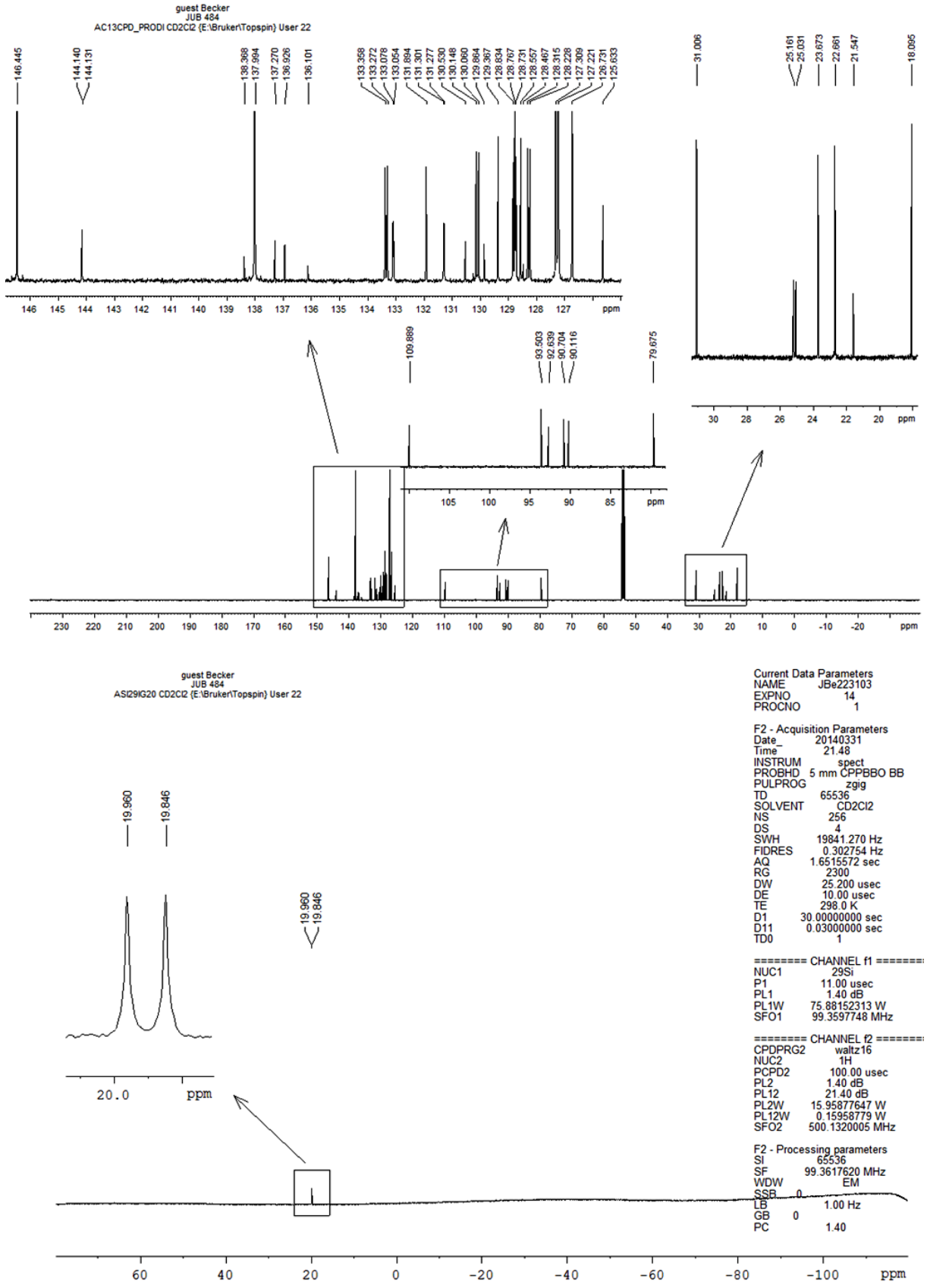



**Figure S4b.** $^{13}C\{^{1}H\}$ NMR and $^{29}Si\{^{1}H\}$ NMR spectra of **2c** in $CD_2Cl_2$.

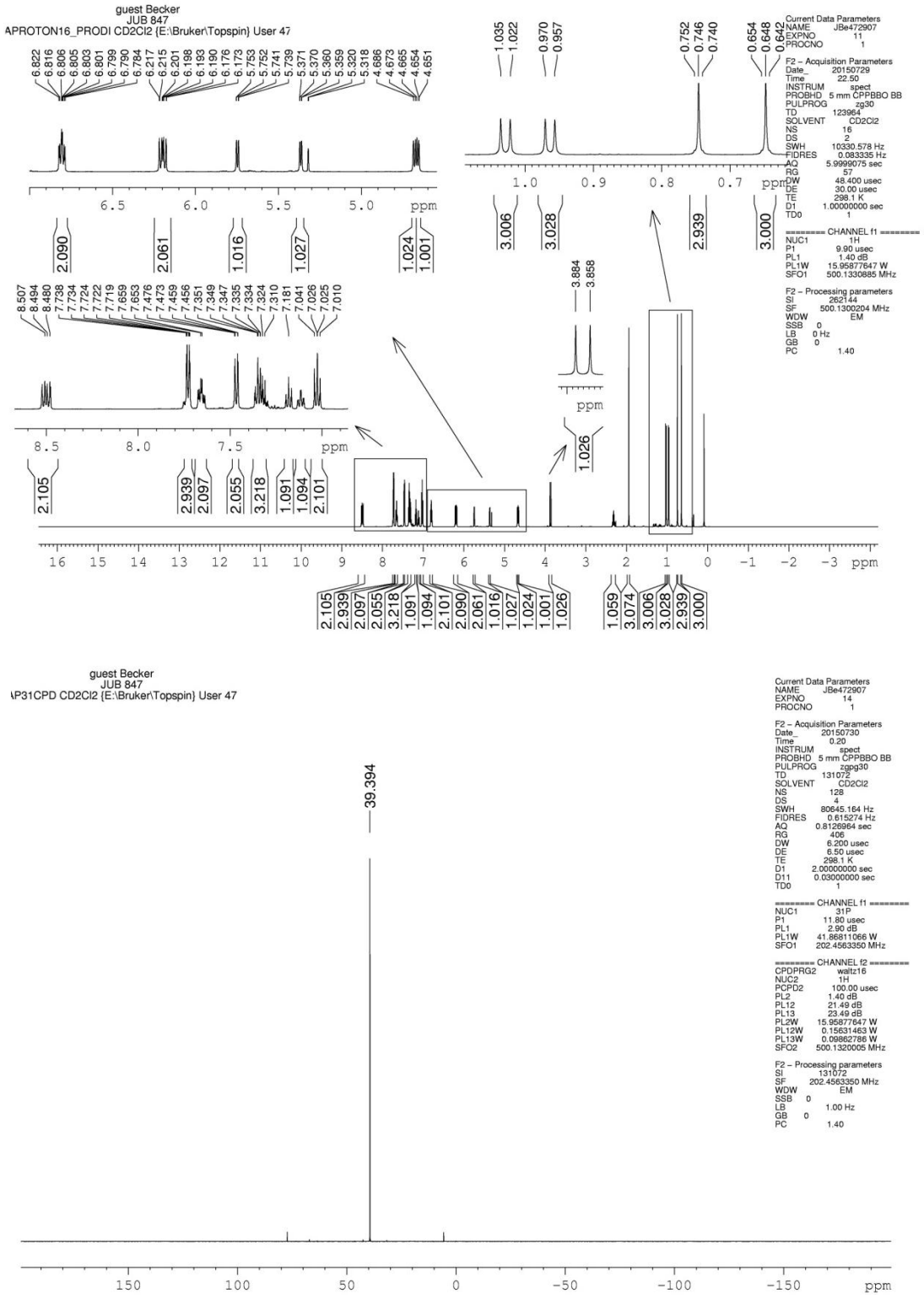



**Figure S5a**. $^{1}H$ NMR and $^{31}P\{^{1}H\}$ spectra of **2d** in $CD_2Cl_2$.

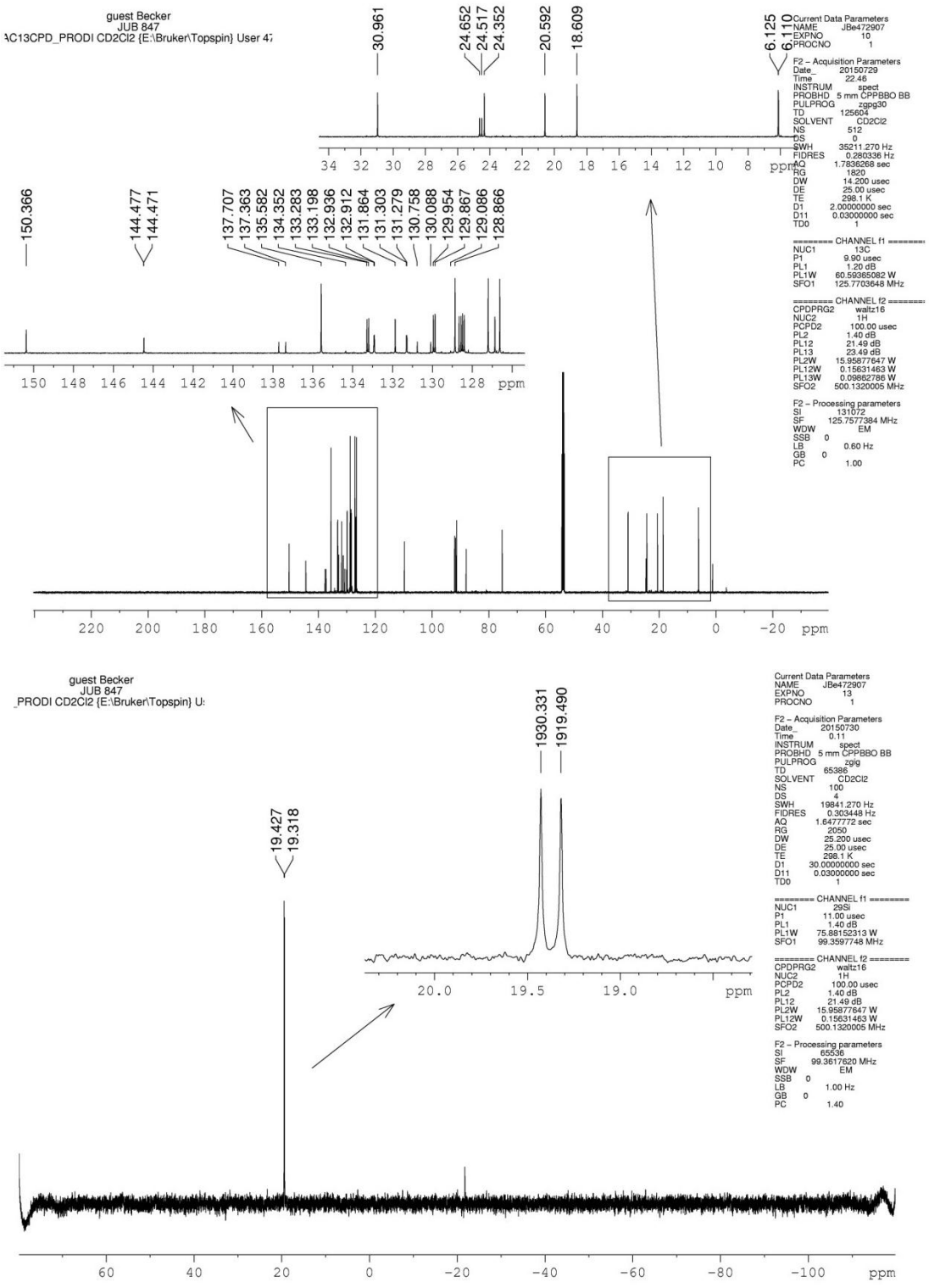



**Figure S5b.** $^{13}C\{^{1}H\}$ NMR and $^{29}Si\{^{1}H\}$ NMR spectra of **2d** in $CD_2Cl_2$.

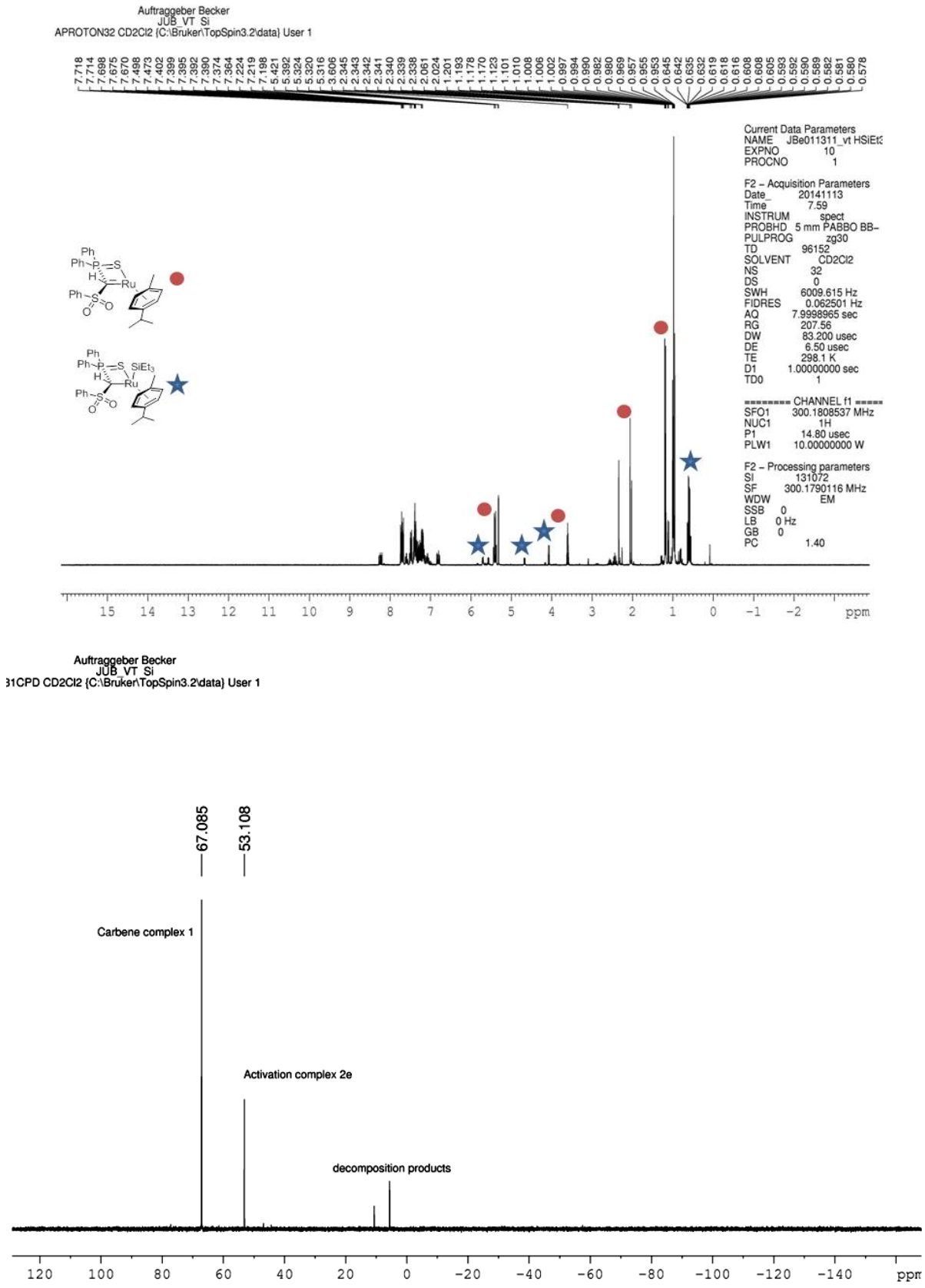



**Figure S6a.** $^{1}H$ and $^{31}P\{^{1}H\}$ NMR spectra of the reaction of **1** with $Et_3SiH$ in $CD_2Cl_2$.

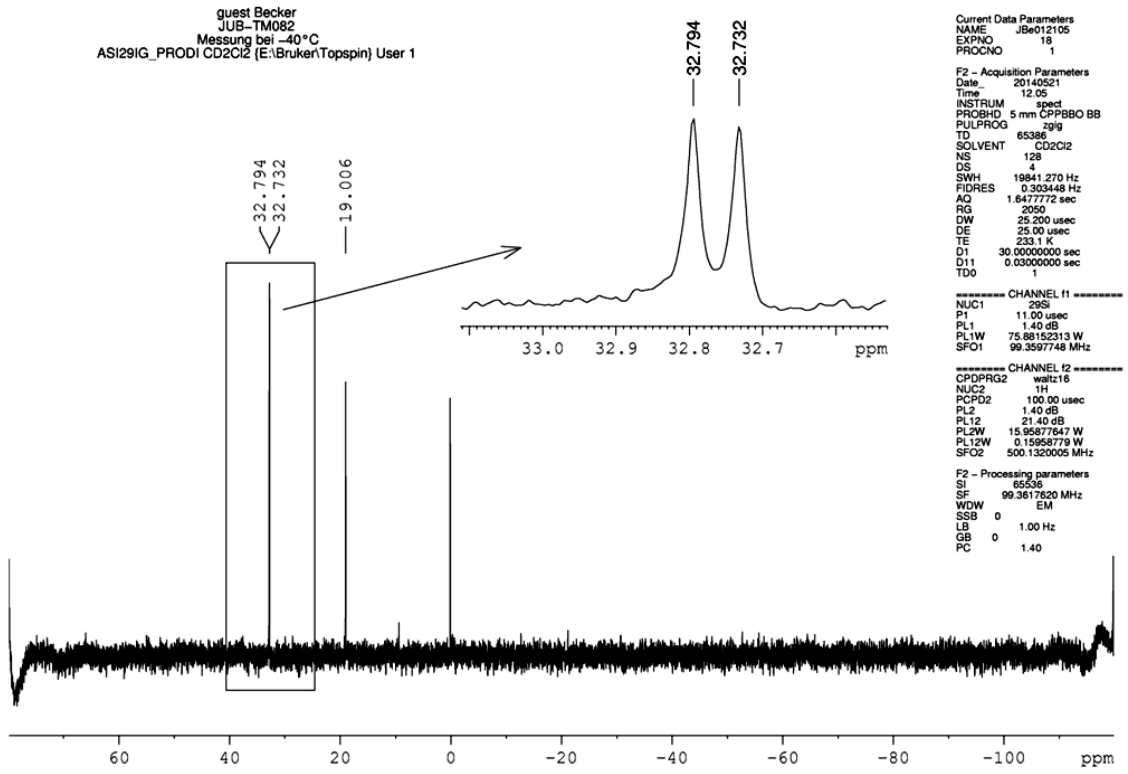



**Figure S6b.** $^{29}Si\{^{1}H\}$ NMR spectrum of the reaction of **1** with $Et_3SiH$ in $CD_2Cl_2$.

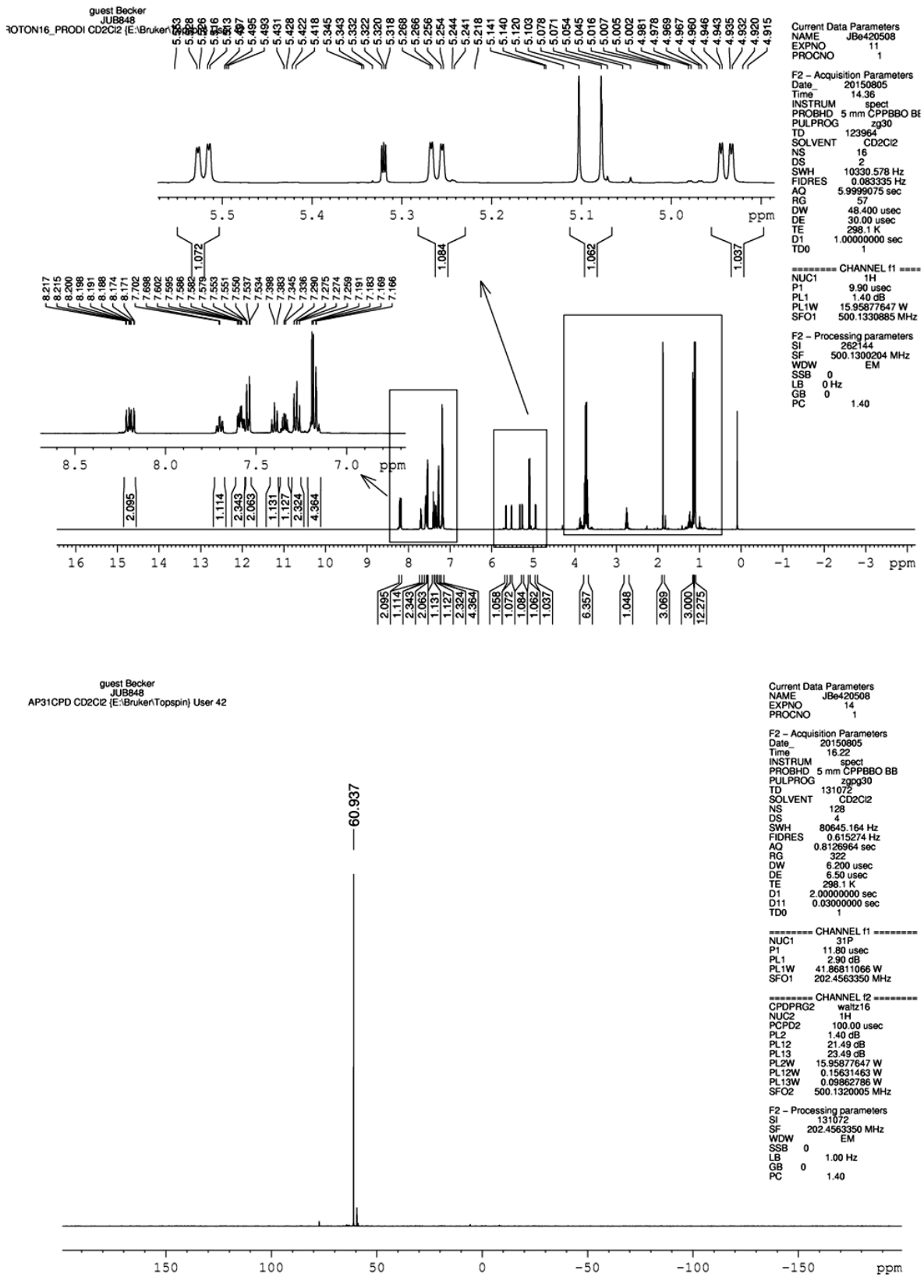



**Figure S7a**. $^{1}H$ NMR and $^{31}P\{^{1}H\}$ spectra of **2f** in $CD_2Cl_2$.

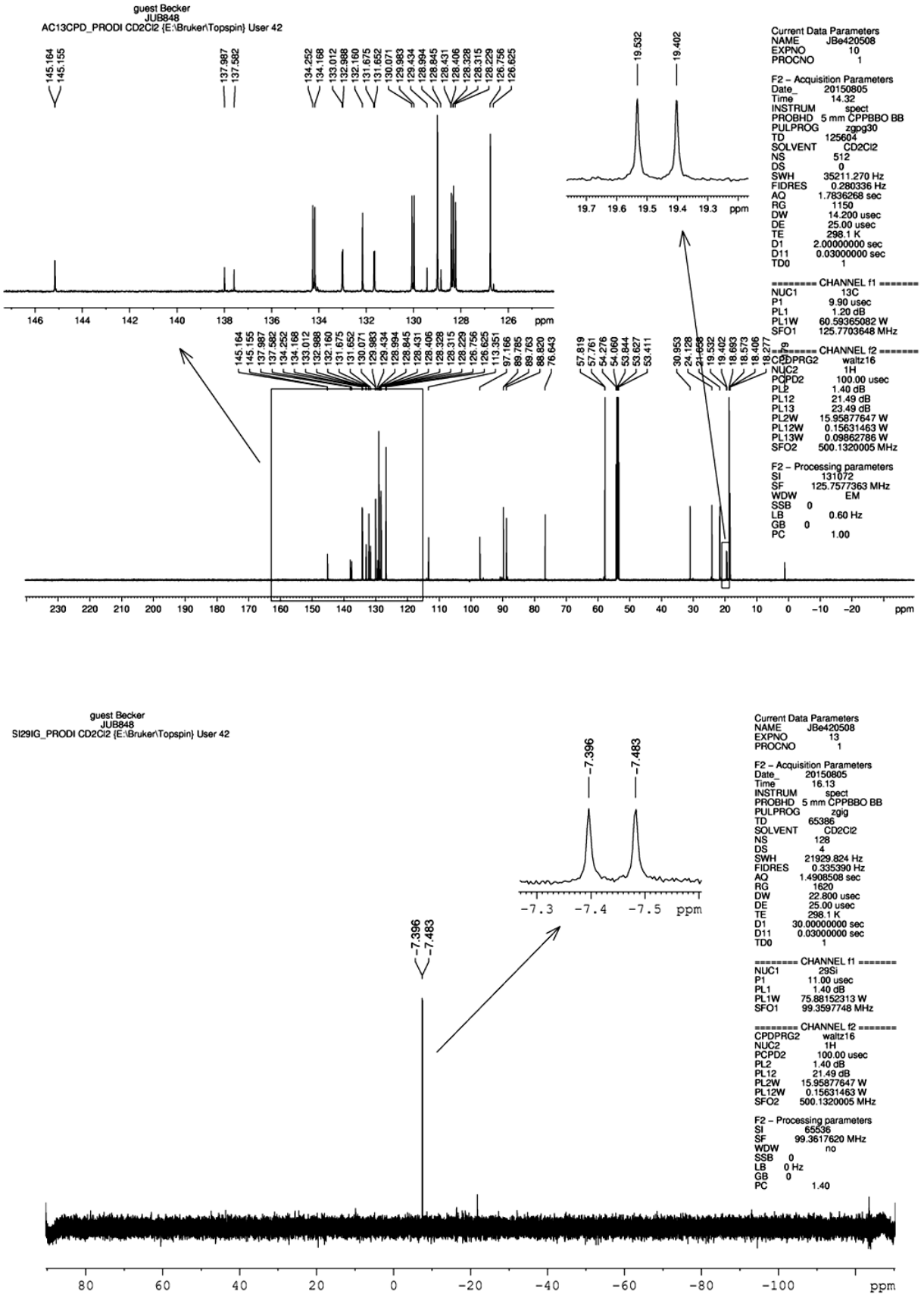



**Figure S7b.** $^{13}C\{^{1}H\}$ NMR and $^{29}Si\{^{1}H\}$ NMR spectra of **2f** in $CD_2Cl_2$.

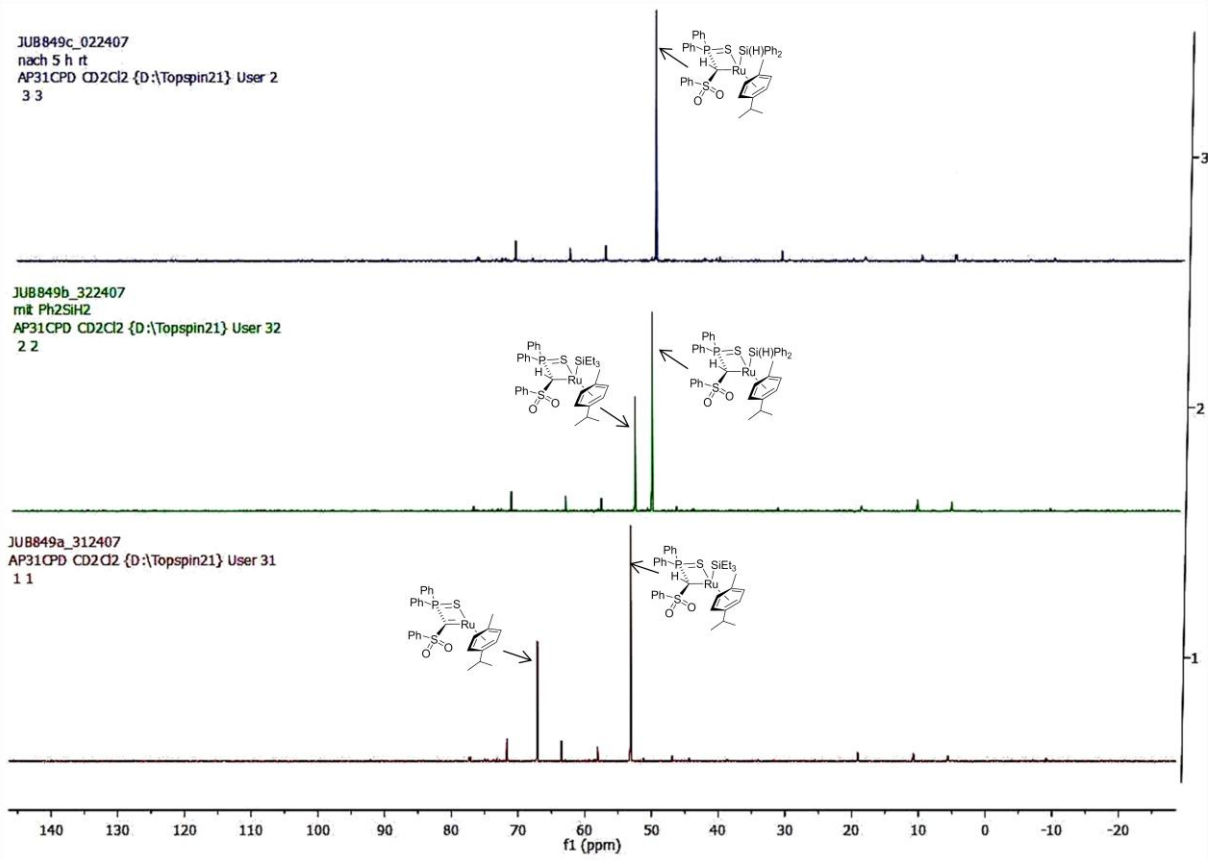



**Figure S8.** $^{31}P\{^{1}H\}$ NMR of **2e** showing the equilibrium in $CD_2Cl_2$ and trapping reaction with $Ph_2SiH_2$ to complex **2b**.

## 3. Crystal Structure Determination

Data collection of all compounds was conducted with a Bruker APEX2-CCD (D8 three-circle goniometer). The structures were solved using direct methods, refined with the Shelx software package[2] and expanded using Fourier techniques. The crystals of all compounds were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were effected at 100 K. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1063355-1063357.Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

**Table S1.** Data collection and structure refinement details for compounds **2a** and **2c**.

| Compound | **2a** | **2b** | **2c** |
|---|---|---|---|
| CCDC No. | CCDC 1063357 | CCDC 1063355 | CCDC 1063356 |
| Formula | $C_{35}H_{37}O_2PRuS_2Si$ | $C_{41}H_{41}O_2PRuS_2Si$ | $C_{47}H_{45}O_2PRuS_2Si{\cdot}½C_7H_8$ |
| Formula weight [g·mol$^{-1}$] | 713.90 | 789.99 | 912.15 |
| Temperature [K] | 100(2) | 100(2) | 100(2) |
| Wave length [Å] | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/n$ (14) | $P$-1 (2) | $P$-1 (2) |
| a [Å] | 19.0170(9) | 11.7262(4) | 9.3712(7) |
| b [Å] | 8.5520(4) | 12.1957(4) | 13.5265(9) |
| c [Å] | 20.5995(10) | 13.2281(4) | 17.6717(12) |
| α [°] | 90 | 87.9340(10) | 97.379(2) |
| β [°] | 105.150(2) | 75.0580(10) | 97.740(2) |
| γ [°] | 90 | 82.3080(10) | 101.302(2) |
| Volume [Å$^3$] | 3233.7(3) | 1811.33(10) | 2148.8(3) |
| Z | 4 | 2 | 2 |
| Calc. density [Mg·m$^{-3}$] | 1.466 | 1.448 | 1.410 |
| μ ($Mo_{K\alpha}$) [mm$^{-1}$] | 0.732 | 0.661 | 0.568 |
| F(000) | 1472 | 816 | 946 |
| Crystal dimensions [mm] | 0.14 x 0.14 x 0.04 | 0.27 x 0.23 x 0.07 | 0.30 x 0.20 x 0.20 |
| Theta range [°] | 1.30 to 26.42 | 2.31 to 25.00 | 3.11 to 25.00 |
| Index ranges | $-23 \le k \le 23$<br>$-10 \le k \le 10$<br>$-25 \le k \le 25$ | $-13 \le k \le 13$<br>$-13 \le k \le 14$<br>$-15 \le k \le 15$ | $-11 \le k \le 11$<br>$-16 \le k \le 16$<br>$-20 \le k \le 20$ |
| Reflections collected | 50602 | 21753 | 25734 |
| Independent reflections | 6636 [$R_{int}$ = 0.0264] | 6374 [$R_{int}$ = 0.0142] | 7520 [$R_{int}$ = 0.0359] |
| Data/Restraints/Parameter | 6636 / 0 / 390 | 6374 / 1 / 440 | 7520 / 0 / 558 |
| Goodness-of-fit on $F^2$ | 1.019 | 1.035 | 1.051 |
| Final R indices [I>2sigma(I)] | $R1$ = 0.0201<br>w$R2$ = 0.0504 | $R1$ = 0.0199<br>w$R2$ = 0.0507 | $R1$ = 0.0287<br>w$R2$ = 0.0756 |
| $R$ indices (all data) | $R1$ = 0.0247<br>w$R2$ = 0.0528 | $R1$ = 0.0213<br>w$R2$ = 0.0516 | $R1$ = 0.0369<br>w$R2$ = 0.0803 |
| Largest diff. peak and hole | 0.447 und –0.294 | 0.537 und –0.291 | 0.569 und –0.524 |

## 3.1 Crystal Structure Determination of **2a**

All hydrogen atoms were refined on ideal positions except for H1 at C1 and H100 and H101 at silicon, which were found in the difference Fourier map and refined independently.

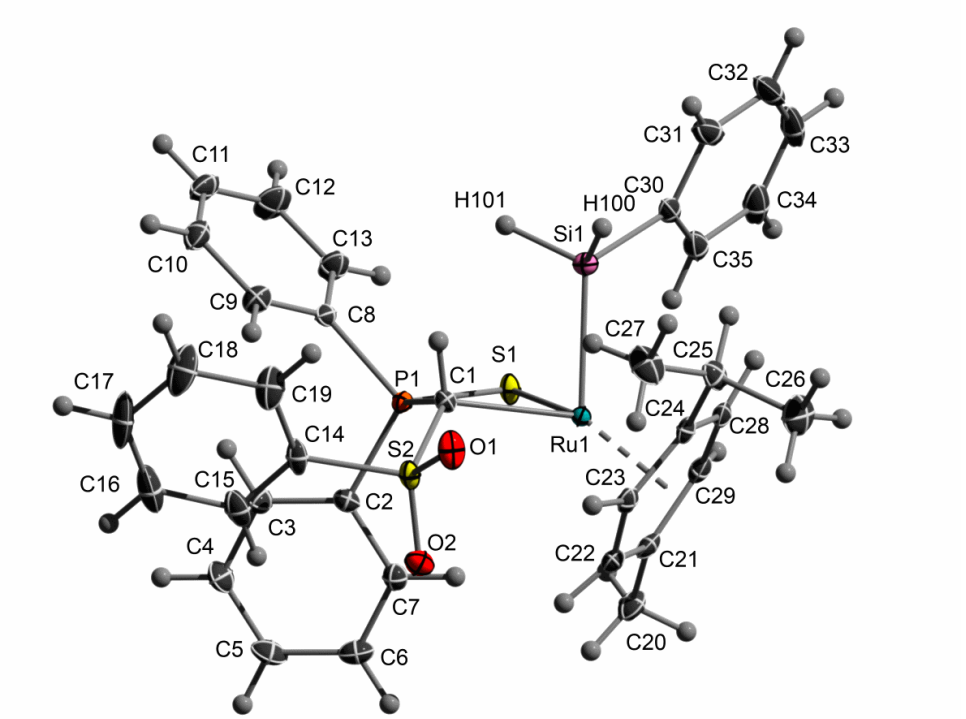



**Figure S5.** ORTEP Plot of silyl complex **2a.** Ellipsoids are drawn at the 50% probability level.

**Table S2.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) silyl complex **2a**. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ru(1) | 146(1) | 5837(1) | 2068(1) | 10(1) |
| S(1) | -778(1) | 7853(1) | 1921(1) | 15(1) |
| P(1) | -1415(1) | 6175(1) | 1392(1) | 11(1) |
| Si(1) | -184(1) | 5389(1) | 3077(1) | 15(1) |
| O(1) | -321(1) | 1849(1) | 1332(1) | 21(1) |
| C(1) | -843(1) | 4473(2) | 1599(1) | 11(1) |
| S(2) | -759(1) | 3115(1) | 980(1) | 14(1) |
| O(2) | -534(1) | 3877(1) | 445(1) | 20(1) |
| C(2) | -1670(1) | 6709(2) | 514(1) | 13(1) |
| C(3) | -2391(1) | 6736(2) | 140(1) | 18(1) |
| C(4) | -2566(1) | 7246(2) | -523(1) | 25(1) |
| C(5) | -2022(1) | 7734(2) | -808(1) | 24(1) |
| C(6) | -1301(1) | 7725(2) | -434(1) | 20(1) |
| C(7) | -1124(1) | 7219(2) | 224(1) | 16(1) |
| C(8) | -2261(1) | 5970(2) | 1629(1) | 14(1) |
| C(9) | -2704(1) | 4659(2) | 1450(1) | 19(1) |

| | | | | |
|---|---|---|---|---|
| C(10) | -3369(1) | 4577(2) | 1608(1) | 22(1) |
| C(11) | -3596(1) | 5804(2) | 1938(1) | 25(1) |
| C(12) | -3158(1) | 7101(2) | 2118(1) | 30(1) |
| C(13) | -2489(1) | 7187(2) | 1969(1) | 23(1) |
| C(14) | -1642(1) | 2338(2) | 625(1) | 18(1) |
| C(15) | -2069(1) | 2965(2) | 31(1) | 23(1) |
| C(16) | -2778(1) | 2435(3) | -212(1) | 34(1) |
| C(17) | -3048(1) | 1298(3) | 129(1) | 42(1) |
| C(18) | -2611(1) | 645(2) | 710(1) | 38(1) |
| C(19) | -1903(1) | 1168(2) | 965(1) | 27(1) |
| C(20) | 730(1) | 8597(2) | 1038(1) | 21(1) |
| C(21) | 880(1) | 7218(2) | 1504(1) | 16(1) |
| C(22) | 825(1) | 5689(2) | 1271(1) | 15(1) |
| C(23) | 944(1) | 4415(2) | 1736(1) | 14(1) |
| C(24) | 1201(1) | 4644(2) | 2438(1) | 15(1) |
| C(25) | 1457(1) | 3320(2) | 2928(1) | 18(1) |
| C(26) | 2279(1) | 3130(3) | 3029(1) | 33(1) |
| C(27) | 1066(1) | 1783(2) | 2715(1) | 30(1) |
| C(28) | 1255(1) | 6219(2) | 2673(1) | 15(1) |
| C(29) | 1062(1) | 7470(2) | 2217(1) | 16(1) |
| C(30) | 172(1) | 6881(2) | 3769(1) | 20(1) |
| C(31) | 329(1) | 6429(3) | 4445(1) | 29(1) |
| C(32) | 582(1) | 7496(3) | 4963(1) | 39(1) |
| C(33) | 679(1) | 9038(3) | 4818(1) | 37(1) |
| C(34) | 530(1) | 9526(3) | 4156(1) | 31(1) |
| C(35) | 285(1) | 8445(2) | 3639(1) | 22(1) |

**Table S3**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for silyl complex **2a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 9(1) | 10(1) | 10(1) | 0(1) | 2(1) | 0(1) |
| S(1) | 12(1) | 12(1) | 18(1) | -3(1) | 1(1) | 1(1) |
| P(1) | 10(1) | 12(1) | 11(1) | 0(1) | 2(1) | 0(1) |
| Si(1) | 15(1) | 19(1) | 13(1) | 1(1) | 5(1) | 0(1) |
| O(1) | 18(1) | 13(1) | 28(1) | -3(1) | -1(1) | 4(1) |
| C(1) | 12(1) | 11(1) | 10(1) | 0(1) | 2(1) | 0(1) |
| S(2) | 12(1) | 12(1) | 16(1) | -3(1) | 1(1) | 1(1) |
| O(2) | 21(1) | 22(1) | 17(1) | -5(1) | 7(1) | -1(1) |
| C(2) | 16(1) | 11(1) | 12(1) | 1(1) | 4(1) | 2(1) |
| C(3) | 15(1) | 23(1) | 17(1) | 4(1) | 5(1) | 1(1) |
| C(4) | 19(1) | 34(1) | 18(1) | 7(1) | -1(1) | 3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(5) | 31(1) | 25(1) | 15(1) | 7(1) | 5(1) | 4(1) |
| C(6) | 25(1) | 18(1) | 20(1) | 2(1) | 12(1) | 1(1) |
| C(7) | 15(1) | 16(1) | 17(1) | -1(1) | 4(1) | 0(1) |
| C(8) | 11(1) | 18(1) | 12(1) | 3(1) | 3(1) | 2(1) |
| C(9) | 17(1) | 19(1) | 22(1) | 1(1) | 7(1) | 0(1) |
| C(10) | 17(1) | 24(1) | 26(1) | 4(1) | 6(1) | -4(1) |
| C(11) | 15(1) | 36(1) | 26(1) | 6(1) | 10(1) | 3(1) |
| C(12) | 26(1) | 32(1) | 37(1) | -8(1) | 18(1) | 3(1) |
| C(13) | 21(1) | 24(1) | 26(1) | -6(1) | 10(1) | -2(1) |
| C(14) | 15(1) | 14(1) | 23(1) | -8(1) | -1(1) | 1(1) |
| C(15) | 23(1) | 24(1) | 20(1) | -9(1) | 0(1) | 3(1) |
| C(16) | 25(1) | 36(1) | 32(1) | -14(1) | -10(1) | 4(1) |
| C(17) | 19(1) | 33(1) | 62(2) | -17(1) | -7(1) | -8(1) |
| C(18) | 27(1) | 20(1) | 64(2) | -4(1) | 6(1) | -9(1) |
| C(19) | 22(1) | 14(1) | 40(1) | -1(1) | 1(1) | -1(1) |
| C(20) | 18(1) | 19(1) | 27(1) | 5(1) | 7(1) | -4(1) |
| C(21) | 10(1) | 18(1) | 22(1) | 3(1) | 8(1) | -2(1) |
| C(22) | 10(1) | 20(1) | 16(1) | -1(1) | 5(1) | -1(1) |
| C(23) | 9(1) | 16(1) | 17(1) | -2(1) | 5(1) | 1(1) |
| C(24) | 8(1) | 20(1) | 17(1) | 1(1) | 3(1) | 1(1) |
| C(25) | 15(1) | 21(1) | 17(1) | 1(1) | 0(1) | 5(1) |
| C(26) | 19(1) | 40(1) | 38(1) | 7(1) | 2(1) | 12(1) |
| C(27) | 37(1) | 19(1) | 27(1) | 7(1) | -2(1) | 2(1) |
| C(28) | 9(1) | 20(1) | 17(1) | -4(1) | 3(1) | -3(1) |
| C(29) | 11(1) | 16(1) | 23(1) | -5(1) | 7(1) | -4(1) |
| C(30) | 10(1) | 34(1) | 15(1) | -5(1) | 3(1) | 4(1) |
| C(31) | 21(1) | 48(1) | 17(1) | 0(1) | 6(1) | 8(1) |
| C(32) | 24(1) | 77(2) | 14(1) | -9(1) | 2(1) | 12(1) |
| C(33) | 16(1) | 65(2) | 27(1) | -28(1) | 0(1) | 6(1) |
| C(34) | 17(1) | 39(1) | 35(1) | -19(1) | 5(1) | 0(1) |
| C(35) | 14(1) | 33(1) | 19(1) | -8(1) | 2(1) | 1(1) |

## 3.2 Crystal Structure Determination of **2b**

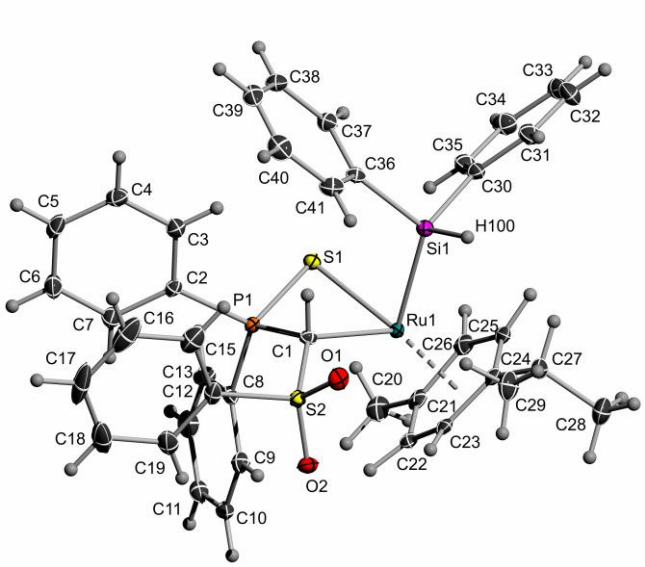



**Figure S6.** ORTEP Plot of silyl complex **2b.** Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ru(1)-C(1) 2.1861(15), Ru(1)-Si(1) 2.3855(5), Ru(1)-S(1) 2.4522(4), S(1)-P(1) 2.0148(6), S(2)-O(1) 1.4429(12), S(2)-O(2) 1.4449(12), S(2)-C(1)1.7480(16), S(2)-C(14) 1.7737(17), P(1)-C(1) P(1)-C(2), 1.8128(16), P(1)-C(8) 1.8148(17), Si(1)-C(36)1.8907(17), Si(1)-C(30)1.9004(17); C(1)-Ru(1)-Si(1)88.54(4), C(1)-Ru(1)-S(1)74.97(4), Si(1)-Ru(1)-S(1)84.240(15), S(2)-C(1)-P(1)124.10(9), S(2)-C(1)-Ru(1)123.40(8), P(1)-C(1)-Ru(1) 92.96(7).

**Table S4.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for silyl complex **2b**. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ru(1) | 7092(1) | 6489(1) | 2156(1) | 10(1) |
| S(1) | 5865(1) | 7099(1) | 943(1) | 13(1) |
| S(2) | 5093(1) | 7426(1) | 4476(1) | 12(1) |
| P(1) | 4590(1) | 7146(1) | 2299(1) | 10(1) |
| Si(1) | 7929(1) | 8166(1) | 1652(1) | 12(1) |
| O(1) | 5861(1) | 8070(1) | 4830(1) | 18(1) |
| O(2) | 5039(1) | 6305(1) | 4861(1) | 16(1) |
| C(1) | 5507(1) | 7470(1) | 3109(1) | 11(1) |
| C(2) | 3340(1) | 8205(1) | 2328(1) | 12(1) |
| C(3) | 3585(2) | 9286(1) | 2085(1) | 16(1) |
| C(4) | 2670(2) | 10130(1) | 2102(1) | 18(1) |
| C(5) | 1501(2) | 9911(2) | 2358(1) | 20(1) |
| C(6) | 1251(2) | 8847(2) | 2619(2) | 23(1) |
| C(7) | 2160(2) | 7991(2) | 2604(1) | 18(1) |
| C(8) | 3981(1) | 5840(1) | 2475(1) | 13(1) |
| C(9) | 3912(1) | 5138(1) | 3335(1) | 14(1) |
| C(10) | 3483(1) | 4128(1) | 3325(1) | 17(1) |
| C(11) | 3108(2) | 3828(1) | 2479(2) | 19(1) |
| C(12) | 3167(2) | 4531(2) | 1623(2) | 20(1) |

| | | | | |
|---|---|---|---|---|
| C(13) | 3605(2) | 5529(1) | 1617(1) | 17(1) |
| C(14) | 3628(2) | 8137(2) | 4861(1) | 16(1) |
| C(15) | 3462(2) | 9283(2) | 4765(1) | 24(1) |
| C(16) | 2314(2) | 9834(2) | 5055(2) | 37(1) |
| C(17) | 1362(2) | 9251(2) | 5433(2) | 42(1) |
| C(18) | 1535(2) | 8113(2) | 5521(2) | 37(1) |
| C(19) | 2675(2) | 7543(2) | 5233(1) | 24(1) |
| C(20) | 6527(2) | 4011(2) | 1274(2) | 23(1) |
| C(21) | 7232(2) | 4613(1) | 1818(1) | 17(1) |
| C(22) | 6923(2) | 4746(1) | 2900(1) | 16(1) |
| C(23) | 7571(2) | 5391(1) | 3380(1) | 15(1) |
| C(24) | 8611(2) | 5815(1) | 2804(1) | 16(1) |
| C(25) | 8922(2) | 5662(1) | 1694(1) | 17(1) |
| C(29) | 8810(2) | 6964(2) | 4301(2) | 26(1) |
| C(26) | 8229(2) | 5111(1) | 1214(1) | 17(1) |
| C(28) | 10370(2) | 5403(2) | 3506(2) | 28(1) |
| C(27) | 9433(2) | 6327(2) | 3306(1) | 19(1) |
| C(30) | 9036(2) | 8042(1) | 317(1) | 15(1) |
| C(31) | 10090(2) | 8523(2) | 138(2) | 21(1) |
| C(32) | 10944(2) | 8412(2) | -813(2) | 26(1) |
| C(33) | 10769(2) | 7816(2) | -1616(2) | 24(1) |
| C(34) | 9731(2) | 7337(2) | -1467(1) | 22(1) |
| C(35) | 8883(2) | 7450(1) | -514(1) | 19(1) |
| C(36) | 6908(1) | 9498(1) | 1618(1) | 14(1) |
| C(37) | 6604(2) | 9878(1) | 699(1) | 16(1) |
| C(38) | 5855(2) | 10856(1) | 675(1) | 19(1) |
| C(39) | 5385(2) | 11478(1) | 1576(2) | 21(1) |
| C(40) | 5667(2) | 11126(2) | 2501(2) | 22(1) |
| C(41) | 6424(2) | 10148(1) | 2517(1) | 18(1) |

**Table S5**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for silyl complex **2b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 9(1) | 9(1) | 11(1) | 1(1) | -2(1) | 0(1) |
| S(1) | 13(1) | 14(1) | 11(1) | 1(1) | -2(1) | 0(1) |
| S(2) | 12(1) | 13(1) | 11(1) | 0(1) | -3(1) | 0(1) |
| P(1) | 10(1) | 10(1) | 11(1) | 1(1) | -3(1) | 0(1) |
| Si(1) | 12(1) | 12(1) | 14(1) | 2(1) | -3(1) | -2(1) |
| O(1) | 18(1) | 21(1) | 16(1) | -2(1) | -7(1) | -4(1) |
| O(2) | 19(1) | 16(1) | 14(1) | 4(1) | -4(1) | -1(1) |
| C(1) | 11(1) | 11(1) | 10(1) | 1(1) | -3(1) | -2(1) |
| C(2) | 13(1) | 13(1) | 10(1) | -1(1) | -5(1) | 1(1) |
| C(3) | 15(1) | 16(1) | 16(1) | 1(1) | -4(1) | -2(1) |
| C(4) | 23(1) | 14(1) | 17(1) | 2(1) | -5(1) | -1(1) |
| C(5) | 19(1) | 19(1) | 22(1) | -1(1) | -7(1) | 6(1) |
| C(6) | 14(1) | 24(1) | 31(1) | -1(1) | -6(1) | -1(1) |
| C(7) | 16(1) | 16(1) | 23(1) | 2(1) | -6(1) | -3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(8) | 10(1) | 11(1) | 17(1) | -2(1) | -2(1) | 0(1) |
| C(9) | 12(1) | 14(1) | 16(1) | -1(1) | -3(1) | 0(1) |
| C(10) | 13(1) | 14(1) | 23(1) | 4(1) | -2(1) | 0(1) |
| C(11) | 13(1) | 12(1) | 31(1) | -4(1) | -2(1) | -2(1) |
| C(12) | 19(1) | 20(1) | 23(1) | -8(1) | -7(1) | -2(1) |
| C(13) | 19(1) | 18(1) | 16(1) | 0(1) | -5(1) | -2(1) |
| C(14) | 15(1) | 24(1) | 9(1) | -2(1) | -3(1) | 4(1) |
| C(15) | 29(1) | 24(1) | 17(1) | -5(1) | -8(1) | 7(1) |
| C(16) | 45(1) | 37(1) | 24(1) | -11(1) | -13(1) | 23(1) |
| C(17) | 24(1) | 72(2) | 20(1) | -9(1) | -6(1) | 26(1) |
| C(18) | 16(1) | 71(2) | 19(1) | 4(1) | -2(1) | 0(1) |
| C(19) | 17(1) | 39(1) | 15(1) | 4(1) | -4(1) | -2(1) |
| C(20) | 24(1) | 15(1) | 30(1) | -4(1) | -7(1) | 0(1) |
| C(21) | 18(1) | 8(1) | 24(1) | 0(1) | -6(1) | 4(1) |
| C(22) | 13(1) | 10(1) | 23(1) | 4(1) | -4(1) | 2(1) |
| C(23) | 14(1) | 12(1) | 17(1) | 4(1) | -5(1) | 3(1) |
| C(24) | 13(1) | 11(1) | 22(1) | 3(1) | -5(1) | 2(1) |
| C(25) | 11(1) | 13(1) | 22(1) | 5(1) | -1(1) | 3(1) |
| C(29) | 20(1) | 30(1) | 30(1) | -5(1) | -12(1) | -2(1) |
| C(26) | 18(1) | 13(1) | 18(1) | 0(1) | -2(1) | 6(1) |
| C(28) | 19(1) | 30(1) | 37(1) | 4(1) | -12(1) | 2(1) |
| C(27) | 13(1) | 20(1) | 25(1) | 6(1) | -7(1) | -2(1) |
| C(30) | 14(1) | 11(1) | 18(1) | 4(1) | -2(1) | 0(1) |
| C(31) | 19(1) | 19(1) | 25(1) | 1(1) | -4(1) | -5(1) |
| C(32) | 17(1) | 26(1) | 32(1) | 6(1) | -1(1) | -6(1) |
| C(33) | 20(1) | 22(1) | 21(1) | 6(1) | 4(1) | 5(1) |
| C(34) | 27(1) | 18(1) | 19(1) | 0(1) | -3(1) | 1(1) |
| C(35) | 18(1) | 17(1) | 21(1) | 3(1) | -2(1) | -5(1) |
| C(36) | 13(1) | 11(1) | 17(1) | 2(1) | -3(1) | -5(1) |
| C(37) | 18(1) | 14(1) | 15(1) | 0(1) | -2(1) | -2(1) |
| C(38) | 19(1) | 17(1) | 22(1) | 6(1) | -6(1) | -4(1) |
| C(39) | 18(1) | 10(1) | 33(1) | 1(1) | -4(1) | -1(1) |
| C(40) | 24(1) | 17(1) | 23(1) | -8(1) | -1(1) | -3(1) |
| C(41) | 21(1) | 17(1) | 16(1) | 1(1) | -5(1) | -6(1) |

## 3.3 Crystal Structure Determination of **2c**

All hydrogen atoms were refined on ideal positions except for H1 at C1, which was found in the difference Fourier map and refined independently. The asymmetric unit contains an additional toluene molecule (half a molecule). This molecule is located on the inversion centre and thus disordered over two sited.

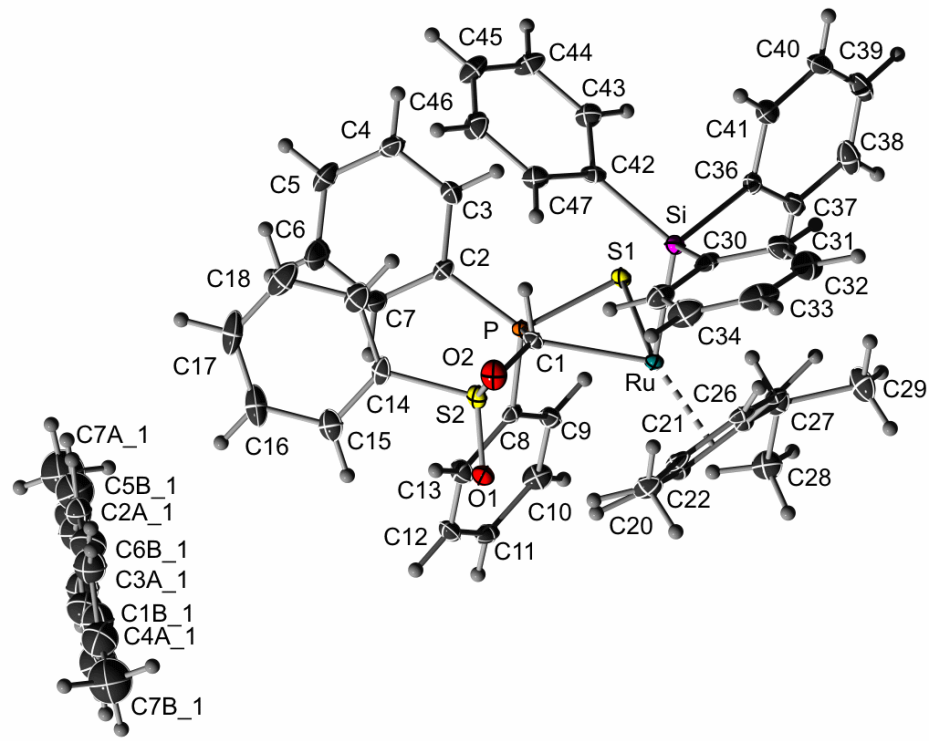



**Figure S7.** ORTEP Plot of silyl complex **2c.** Ellipsoids are drawn at the 50% probability level.

**Table S6.** Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for silyl complex **2c**. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ru(1) | 7172(1) | 6712(1) | 8560(1) | 9(1) |
| S(1) | 9382(1) | 6004(1) | 8570(1) | 12(1) |
| S(2) | 4897(1) | 5104(1) | 7004(1) | 14(1) |
| P(1) | 7835(1) | 4824(1) | 7962(1) | 10(1) |
| Si(1) | 8435(1) | 7882(1) | 7817(1) | 12(1) |
| O(1) | 3898(2) | 4710(1) | 7501(1) | 18(1) |
| O(2) | 4543(2) | 5900(1) | 6584(1) | 19(1) |
| C(1) | 6694(2) | 5567(2) | 7508(1) | 11(1) |
| C(2) | 8619(3) | 4010(2) | 7310(1) | 12(1) |
| C(3) | 9852(3) | 4438(2) | 7018(1) | 19(1) |
| C(4) | 10481(3) | 3836(2) | 6525(1) | 22(1) |
| C(5) | 9890(3) | 2808(2) | 6323(2) | 26(1) |
| C(6) | 8658(3) | 2369(2) | 6611(2) | 33(1) |
| C(7) | 8019(3) | 2964(2) | 7101(2) | 22(1) |
| C(8) | 7014(3) | 3983(2) | 8580(1) | 12(1) |
| C(9) | 7871(3) | 3924(2) | 9271(1) | 16(1) |
| C(10) | 7373(3) | 3205(2) | 9724(1) | 19(1) |

| | | | | |
|---|---|---|---|---|
| C(11) | 6012(3) | 2540(2) | 9492(1) | 17(1) |
| C(12) | 5147(3) | 2605(2) | 8809(2) | 19(1) |
| C(13) | 5632(3) | 3317(2) | 8351(1) | 17(1) |
| C(14) | 4948(3) | 4048(2) | 6301(1) | 17(1) |
| C(15) | 4075(3) | 3096(2) | 6315(2) | 22(1) |
| C(16) | 4086(3) | 2281(2) | 5757(2) | 31(1) |
| C(17) | 4963(3) | 2416(2) | 5195(2) | 34(1) |
| C(18) | 5822(3) | 3367(2) | 5175(2) | 32(1) |
| C(19) | 5814(3) | 4189(2) | 5728(1) | 24(1) |
| C(20) | 3626(3) | 7117(2) | 8178(2) | 21(1) |
| C(21) | 4967(3) | 7055(2) | 8718(1) | 15(1) |
| C(22) | 5083(2) | 6139(2) | 9026(1) | 14(1) |
| C(23) | 6246(2) | 6103(2) | 9595(1) | 13(1) |
| C(24) | 7407(2) | 6982(2) | 9878(1) | 13(1) |
| C(25) | 7302(3) | 7900(2) | 9586(1) | 14(1) |
| C(26) | 6105(3) | 7926(2) | 9010(1) | 15(1) |
| C(27) | 8693(3) | 6928(2) | 10490(1) | 16(1) |
| C(28) | 8261(3) | 6144(2) | 11015(2) | 23(1) |
| C(29) | 9408(3) | 7956(2) | 10992(2) | 29(1) |
| C(30) | 7301(3) | 8843(2) | 7537(1) | 16(1) |
| C(31) | 7706(3) | 9873(2) | 7878(2) | 23(1) |
| C(32) | 6827(3) | 10558(2) | 7721(2) | 29(1) |
| C(33) | 5536(3) | 10243(2) | 7206(2) | 31(1) |
| C(34) | 5084(3) | 9228(2) | 6860(2) | 30(1) |
| C(35) | 5952(3) | 8539(2) | 7033(2) | 22(1) |
| C(36) | 10276(3) | 8696(2) | 8369(1) | 16(1) |
| C(37) | 10831(3) | 8638(2) | 9129(2) | 17(1) |
| C(38) | 12200(3) | 9222(2) | 9514(2) | 25(1) |
| C(39) | 13059(3) | 9861(2) | 9123(2) | 28(1) |
| C(40) | 12542(3) | 9928(2) | 8362(2) | 30(1) |
| C(41) | 11173(3) | 9362(2) | 7996(2) | 23(1) |
| C(42) | 9027(3) | 7325(2) | 6887(1) | 13(1) |
| C(43) | 10460(3) | 7159(2) | 6908(1) | 19(1) |
| C(44) | 10939(3) | 6721(2) | 6258(2) | 23(1) |
| C(45) | 9996(3) | 6442(2) | 5561(2) | 25(1) |
| C(46) | 8578(3) | 6598(2) | 5516(2) | 23(1) |
| C(47) | 8096(3) | 7033(2) | 6166(1) | 17(1) |
| C11 | 1104(9) | -244(6) | 4997(4) | 37(2) |
| C21 | 666(9) | 401(5) | 4473(4) | 23(1) |
| C31 | -692(9) | 665(5) | 4477(4) | 36(2) |
| C41 | -1644(10) | 366(6) | 4949(5) | 45(2) |
| C51 | -1229(10) | -265(6) | 5479(5) | 47(2) |
| C61 | 121(11) | -570(6) | 5486(5) | 41(2) |
| C71 | 2592(9) | -532(6) | 4999(5) | 63(2) |

**Table S7**. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for silyl complex **2c**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Ru(1) | 7(1) | 11(1) | 10(1) | 1(1) | 1(1) | 3(1) |
| S(1) | 9(1) | 12(1) | 14(1) | 0(1) | 1(1) | 3(1) |
| S(2) | 11(1) | 15(1) | 14(1) | 0(1) | -2(1) | 3(1) |
| P(1) | 9(1) | 11(1) | 11(1) | 2(1) | 1(1) | 2(1) |
| Si(1) | 11(1) | 12(1) | 14(1) | 3(1) | 3(1) | 2(1) |
| O(1) | 12(1) | 20(1) | 19(1) | -2(1) | 3(1) | 1(1) |
| O(2) | 18(1) | 21(1) | 19(1) | 3(1) | -3(1) | 9(1) |
| C(1) | 9(1) | 12(1) | 13(1) | 2(1) | 1(1) | 2(1) |
| C(2) | 14(1) | 16(1) | 9(1) | 3(1) | 1(1) | 6(1) |
| C(3) | 16(1) | 18(1) | 19(1) | -2(1) | 2(1) | 0(1) |
| C(4) | 14(1) | 31(2) | 18(1) | -1(1) | 6(1) | 5(1) |
| C(5) | 29(2) | 29(2) | 22(2) | -2(1) | 10(1) | 15(1) |
| C(6) | 48(2) | 16(1) | 38(2) | -2(1) | 22(2) | 5(1) |
| C(7) | 27(2) | 16(1) | 26(2) | 2(1) | 15(1) | 2(1) |
| C(8) | 14(1) | 11(1) | 13(1) | 1(1) | 5(1) | 6(1) |
| C(9) | 12(1) | 15(1) | 19(1) | 2(1) | 3(1) | 2(1) |
| C(10) | 20(1) | 24(1) | 17(1) | 8(1) | 2(1) | 10(1) |
| C(11) | 23(1) | 13(1) | 20(1) | 5(1) | 11(1) | 5(1) |
| C(12) | 13(1) | 16(1) | 25(2) | 0(1) | 4(1) | -1(1) |
| C(13) | 16(1) | 18(1) | 16(1) | 3(1) | 0(1) | 3(1) |
| C(14) | 16(1) | 20(1) | 12(1) | -3(1) | -5(1) | 6(1) |
| C(15) | 23(1) | 22(1) | 19(1) | 2(1) | -5(1) | 5(1) |
| C(16) | 41(2) | 19(2) | 27(2) | -4(1) | -10(1) | 7(1) |
| C(17) | 47(2) | 29(2) | 21(2) | -10(1) | -9(1) | 17(2) |
| C(18) | 35(2) | 46(2) | 16(2) | 1(1) | 2(1) | 19(2) |
| C(19) | 24(2) | 31(2) | 17(1) | 1(1) | -1(1) | 8(1) |
| C(20) | 13(1) | 31(2) | 21(1) | 4(1) | 3(1) | 9(1) |
| C(21) | 10(1) | 25(1) | 13(1) | 2(1) | 4(1) | 8(1) |
| C(22) | 10(1) | 17(1) | 14(1) | -2(1) | 5(1) | 1(1) |
| C(23) | 14(1) | 16(1) | 11(1) | 2(1) | 7(1) | 5(1) |
| C(24) | 12(1) | 14(1) | 12(1) | -1(1) | 5(1) | 4(1) |
| C(25) | 12(1) | 16(1) | 14(1) | 1(1) | 7(1) | 3(1) |
| C(26) | 14(1) | 19(1) | 15(1) | 5(1) | 8(1) | 9(1) |
| C(27) | 14(1) | 22(1) | 12(1) | 0(1) | 1(1) | 8(1) |
| C(28) | 22(1) | 31(2) | 18(1) | 8(1) | -1(1) | 8(1) |
| C(29) | 27(2) | 30(2) | 21(2) | 1(1) | -10(1) | 0(1) |
| C(30) | 19(1) | 16(1) | 17(1) | 7(1) | 10(1) | 7(1) |
| C(31) | 22(1) | 17(1) | 32(2) | 7(1) | 9(1) | 5(1) |
| C(32) | 35(2) | 17(1) | 43(2) | 11(1) | 17(2) | 11(1) |
| C(33) | 37(2) | 27(2) | 45(2) | 23(2) | 24(2) | 23(1) |
| C(34) | 23(2) | 44(2) | 27(2) | 10(1) | 4(1) | 17(1) |
| C(35) | 24(2) | 23(1) | 22(1) | 4(1) | 7(1) | 10(1) |
| C(36) | 14(1) | 12(1) | 20(1) | -2(1) | 5(1) | 2(1) |
| C(37) | 14(1) | 12(1) | 25(1) | 1(1) | 4(1) | 3(1) |
| C(38) | 19(1) | 20(1) | 32(2) | -3(1) | -5(1) | 6(1) |
| C(39) | 12(1) | 19(1) | 47(2) | -7(1) | 3(1) | 0(1) |
| C(40) | 23(2) | 18(1) | 47(2) | -3(1) | 19(1) | -4(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(41) | 26(2) | 18(1) | 24(2) | 1(1) | 10(1) | 1(1) |
| C(42) | 13(1) | 12(1) | 18(1) | 7(1) | 6(1) | 4(1) |
| C(43) | 19(1) | 23(1) | 16(1) | 6(1) | 2(1) | 5(1) |
| C(44) | 21(1) | 31(2) | 22(1) | 8(1) | 9(1) | 14(1) |
| C(45) | 32(2) | 30(2) | 17(1) | 5(1) | 11(1) | 13(1) |
| C(46) | 26(2) | 28(2) | 13(1) | 2(1) | 1(1) | 6(1) |
| C(47) | 16(1) | 20(1) | 17(1) | 6(1) | 2(1) | 5(1) |
| C11 | 38(2) | 36(2) | 37(2) | 4(1) | 3(1) | 8(1) |
| C21 | 23(2) | 23(2) | 24(2) | 3(1) | 3(1) | 6(1) |
| C31 | 36(2) | 35(2) | 36(2) | 4(1) | 5(1) | 9(1) |
| C41 | 44(2) | 44(2) | 45(2) | 4(1) | 8(1) | 9(1) |
| C51 | 47(2) | 46(2) | 47(2) | 6(1) | 8(1) | 9(1) |
| C61 | 41(2) | 41(2) | 41(2) | 5(1) | 7(1) | 9(1) |
| C71 | 63(2) | 62(2) | 63(2) | 10(1) | 8(1) | 14(1) |

## 4. Computational Studies

**Methods.**

All calculations were performed without symmetry restrictions. Starting coordinates were obtained with Chem3DUltra 10.0 or directly from the crystal structure analysis. All calculations were done with the Gaussian09 (Revision B.01) program package.[3] Geometry optimizations were performed using Density-Functional Theory (DFT) with the dispersion corrected M062X functional[4]together with the 6-311+G(d,p) basis set for all non-metal atoms and the LANL2TZ(f) basis set with the corresponding effective core potential for ruthenium.Harmonic vibrational frequency analyses were performed on the same levels of theory. In previous studies by our group a comparison of experimental and calculated parameters was done on the basis of calculations using the B3LYP and the M062X functional.[1] Both functionals showed good correlation with the experimental data with the M062X functional being slightly better. Thus, this functional was chosen for the calculations. Natural bond orbital (NBO) analyses were performed with the energy-optimized structures using the NBO 5.0 program (Table 9).[5]

The vibrational frequency analyses showed no imaginary frequencies for the ground states and one imaginary frequency for the transition states. These frequencies correspond to the expected translational motion of the transition states. Intrinsic reaction coordinate (IRC) calculations[6] were carried out to ensure the connectivity of the reported minima and transition states (Figure S10 and S11).Table S8 gives the energies of all calculated compounds, Table S10-S33 the Cartesian coordinates of all optimized compounds. Figure 8 and 9show the structures of the compounds.

**Model system**.

For calculations a model system was used in which the phenyl substituents at phosphorus and sulfur were replaced by methyl groups. Additionally, the cymene ligand was replaced by a benzene ligand. As silanes $PhSiH_3$ and $Me_3SiH$ – as model system for $Et_3SiH$ – were used. For the activation of $PhSiH_3$ isomers were considered, which differ in the relative orientation of the silane to the carbene complex. A transition state for the direct Si–H addition across the M=C bond could only be located for phenylsilane directly forming the hypothetic hydrido complex. Transition states for the 1,2-addition under formation of the silyl complexes could neither be located for the $PhSiH_3$ nor for $Me_3SiH$. The 1,2-addition to the hydrido complex with $PhSiH_3$ showed a barrier comparable to that obtained for the oxidative addition. However, this barrier is highly affected by the steric demand of the silane and the ligand. For $Me_3SiH$ a transition state could only be located by freezing the H–Ru and the Si–C1 distance. The thus obtained energy ($\Delta G^{\ddagger}$ = 100 kJ/mol) revealed to be considerably higher than the energy of the transition state for the oxidative addition ($\Delta G^{\ddagger}$ = 85 kJ/mol). Optimizations without constraints resulted either in the elimination of the silane or in the oxidative addition to the metal center. Hence, it can be assumed that in the real system the concerted 1,2-addition is no feasible reaction pathway.

To computationally address the feasibility of a reversible Si-H activation the activation of $Me_3SiH$ was also studied using the phenyl-substituted carbene complex **1** with *p*-xylene instead of the cymene ligand. These calculations revealed a lower energetic preference of the Si-H activation process with the silyl complex being preferred over the carbene complex by only 32 kJ/mol. Overall, the profile shows lower activation barriers thus suggesting that indeed reversible processes – as observed in experiment – should be possible (see Figure S12, below).

**Table S8.**Calculated energies [in kJ/mol] of the optimized structures [M062x/6-311+g(d,p)/LANL2TZ(f)].

| Compound | ZPE | Enthalpy | Free energy | ΔH | ΔG |
|---|---|---|---|---|---|
| Carbene complex**1'** | -4651525.99 | -4651475.15 | -4651648.53 | - | - |
| PhSiH3 | -1372492.02 | -1372473.40 | -1372571.57 | - | - |
| **TS1** | -6023993.731 | -6023923.36 | -6024141.058 | 25.2 | 79.0 |
| **SI-H-Add (concerted)** | -6.023.994.12 | -6023923.75 | -6024146.99 | 24.8 | 73.1 |
| **TS1 (isomer1)** | -6023989.45 | -6023918.43 | -6024139.19 | 30.1 | 80.9 |
| **TS1 (isomer2)** | -6023974.53 | -6023903.87 | -6024122.97 | 44.7 | 97.1 |
| **TS (isomer3)** | -6024918.21 | -6023917.16 | -6024139.958 | 31.4 | 80.1 |
| **Int 1** | -6024023.93 | -6023951.94 | -6024171.57 | -3.4 | 48.5 |
| **Int 1 (isomer1)** | -6024013.28 | -6023940.39 | -6024167.11 | 8.2 | 53.0 |
| **Int 1 (isomer2)** | -6023970.98 | -6023897.55 | -6024126.09 | 51.0 | 94.0 |
| **Int 1 (isomer3)** | -6024002.37 | -6023930.42 | -6024149.49 | 18.1 | 70.6 |
| **TS2** | -6024023.90 | -6023952.62 | -6024169.79 | –4.1 | 50.3 |
| **SilylTransfer** | -6024009.70 | -6023941.44 | -6024152.59 | 7.1 | 67.5 |
| **Pro** | -6024163.02 | -6024091.65 | -6024313.51 | –143.1 | –93.4 |
| **Hydridocomplex** | -6024130.31 | -6024060.38 | -6024273.60 | –111.8 | –53.5 |
| **$Me_3SiH$** | -1075635.76 | -1075613.64 | -1075715.19 | - | - |
| **TS1-Me** | -5727130.97 | -5727058.14 | -5727278.65 | 30.7 | 85.1 |
| **SI-H-Add (concerted)** | -5727124.70 | -5727054.90 | -5727263.29 | 33.9 | 100.4 |
| **Int1-Me** | -5727151.55 | -5727076.14 | -5727302.62 | 12.7 | 61.1 |
| **Int1-Me (isomer1)** | -5727088.96 | -5727013.94 | -5727239.23 | 74.9 | 124.5 |
| **Int1-Me (isomer2)** | -5727150.69 | -5727076.14 | -5727298.91 | 12.7 | 64.8 |
| **TS2-Me** | -5727150.34 | -5727076.79 | -5727296.31 | 12.0 | 67.4 |
| **Silyltransfer** | -5727137.37 | -5727066.12 | -5727279.67 | 22.7 | 84.0 |
| **Pro-Me** | -5727284.87 | -5727212.39 | -5727427.09 | -123.6 | -63.4 |
| **Hydridocomplex - Me** | -5727272.65 | -5727201.16 | -5727414.46 | -112.4 | -50.7 |
| **Ph-carbene** | -6366569.55 | -6366484.90 | -6366739.69 | | |
| **Ph-TS1** | -7442080.31 | -7441975.74 | -7442264.17 | 19.0 | 86.9 |
| **Ph-Int 1 (isomer1)** | -7442098.42 | -7441992.33 | -7442282.39 | 2.4 | 68.7 |

| | | | | | |
|---|---|---|---|---|---|
| **Ph-Int 1 (isomer2)** | -7442068.00 | -7441961.33 | -7442256.34 | 33.4 | 94.8 |
| **Ph-Int 1 (isomer3)** | -7442080.80 | -7441973.27 | -7442270.67 | 21.4 | 80.4 |
| **Ph-TS2** | -7442083.76 | -7441978.43 | -7442267.66 | 16.3 | 83.4 |
| **Ph-Pro** | -7442203.73 | -7442099.50 | -7442382.77 | -104.8 | -31.7 |
| **Ph-Hydrido** | -7442186.02 | -7442082.10 | -7442366.28 | -87.4 | -15.2 |

**Table S9.** Wiberg bond indices and NBO charges of the ruthenium complex **1** during Si–H bond activation.

| | **1** | **TS1** | **Int1** | **TS2** | **Pro** |
|---|---|---|---|---|---|
| $WBI_{Ru–C}$ | 1.26 | 0.77 | 0.78 | 0.70 | 0.58 |
| $WBI_{Ru–Si}$ | – | 0.23 | 0.55 | 0.57 | 0.71 |
| $WBI_{Ru–H}$ | – | 0.34 | 0.55 | 0.44 | 0.02 |
| $WBI_{Ru–S}$ | 0.59 | 0.74 | 0.76 | 0.76 | 0.65 |
| $q_C$ | –0.93 | –1.13 | –1.08 | –1.11 | –1.00 |
| $q_{Ru}$ | –0.19 | –0.55 | –0.83 | –0.87 | –0.80 |
| $q_S$ | –0.39 | –0.33 | –0.22 | –0.24 | –0.29 |
| $q_P$ | 1.39 | 1.46 | 1.46 | 1.44 | 1.37 |
| $q_{S(Sulfonyl)}$ | 2.11 | 2.13 | 2.13 | 2.11 | 2.13 |
| $q_{Si}$ | 0.86 | 1.05 | 1.08 | 1.09 | 1.06 |
| $q_H$ | –0.15 | –0.02 | 0.22 | 0.29 | 0.27 |

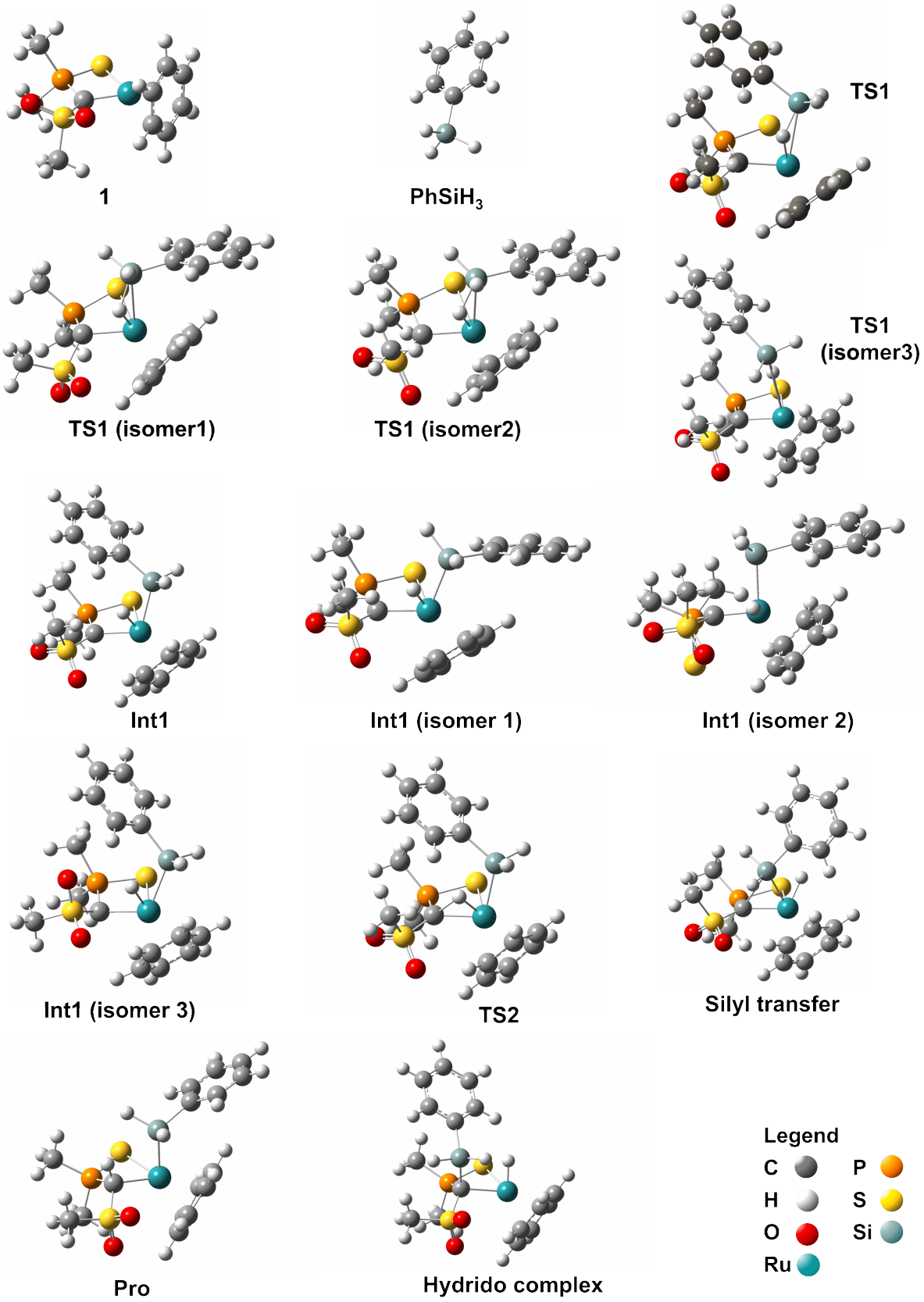



**Figure S8**. Displays of the energy-optimized structures of the activation of $PhSiH_3$.

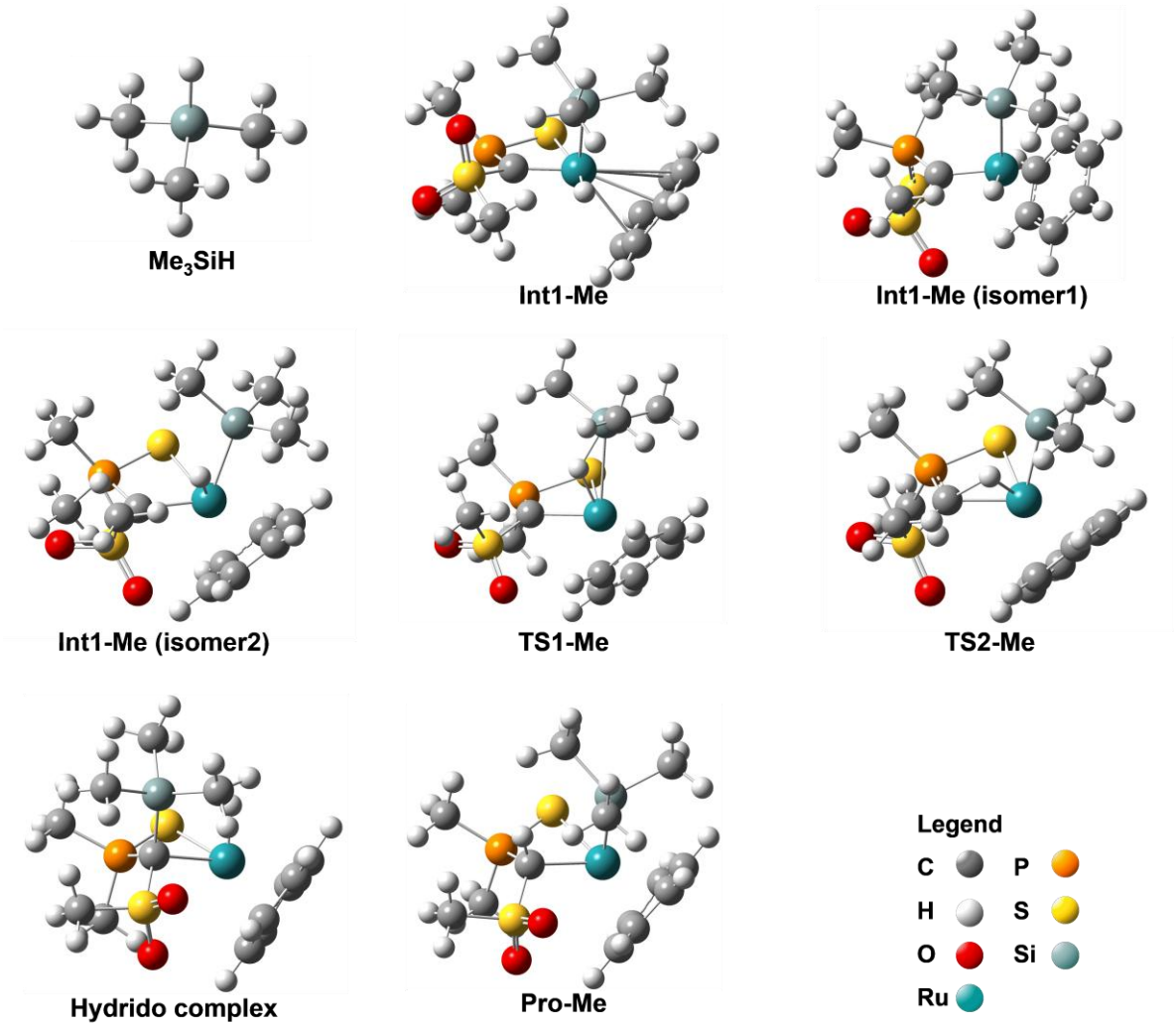



**Figure S9**. Displays of the energy-optimized structures of the activation of $Me_3SiH$.

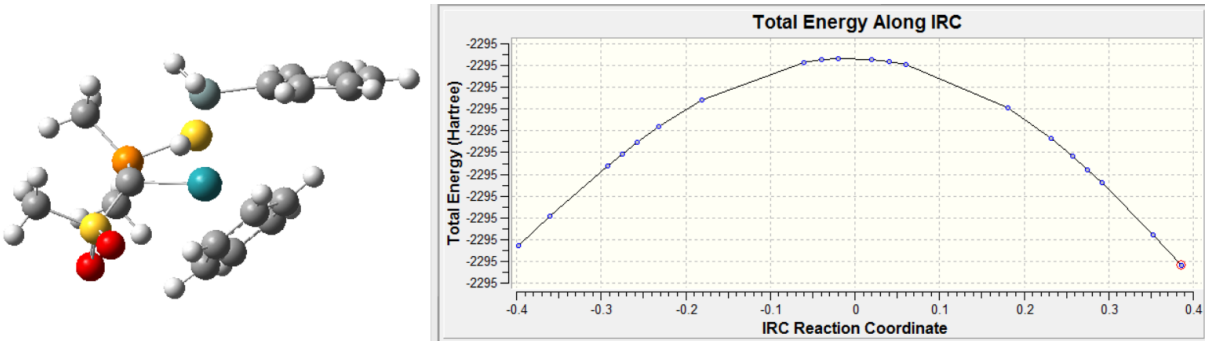



**Figure S10**. IRC calculations for the oxidative addition of $PhSiH_3$ to carbene **1** (**TS1**).

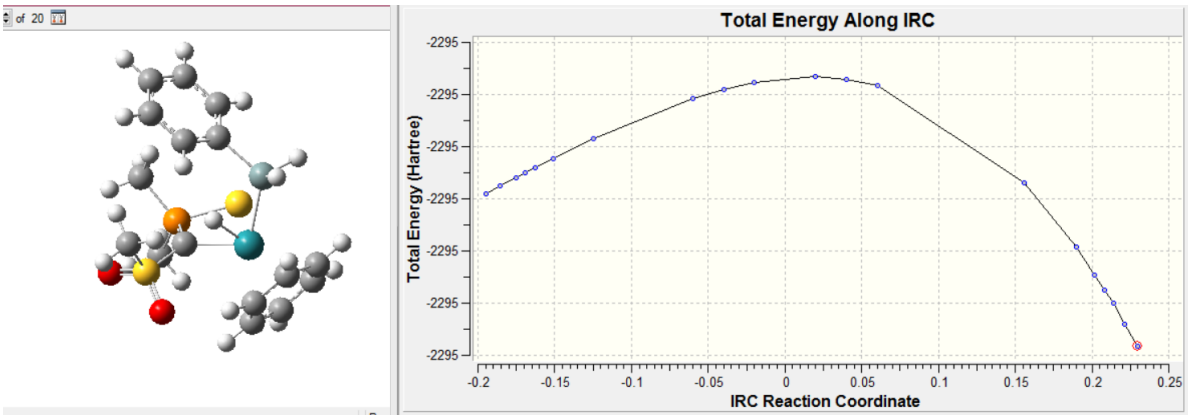



**Figure S11**. IRC calculations for the hydrogen transfer to the product **pro** (**TS2**).

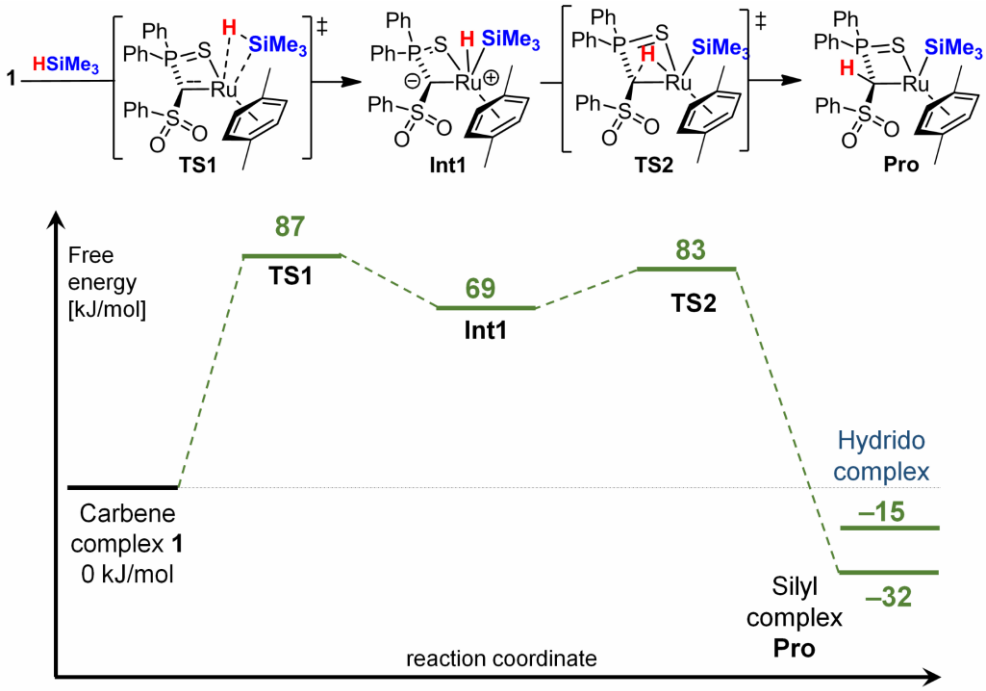



**Figure S12.** Reaction profile of the Si-H activation in $Me_3SiH$ with the phenyl substituted carbene complex.

**Table S10**. Cartesian coordinates of carbene complex **1'**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| S | 0.693012681 | -1.2260742232 | -2.2730613195 |
| P | 1.2525978004 | -0.2064725892 | -0.6043979412 |
| Ru | -1.3854009517 | -1.4149456366 | -0.7538881808 |
| C | -0.2477842269 | -0.2816458078 | 0.2694101496 |
| O | 0.8991968789 | 0.63408266 | 2.4287991998 |
| S | -0.4306701538 | 0.3995081059 | 1.8453085131 |
| O | -1.4241388847 | -0.357019665 | 2.6154041565 |
| C | -3.2682830287 | -1.2570385689 | 0.283945941 |
| C | -2.6072131163 | -2.442054477 | 0.6786303525 |

| | | | |
|---|---|---|---|
| C | -2.2253681727 | -3.3998231357 | -0.3067861023 |
| C | -2.5601546498 | -3.1984094383 | -1.665546345 |
| C | -3.1807637184 | -2.005759737 | -2.0668502196 |
| C | -3.4948228173 | -1.0140888212 | -1.1007038354 |
| H | -3.4907001801 | -0.5054157933 | 1.0293129401 |
| H | -1.6592210821 | -4.2739903932 | -0.0152604301 |
| H | -2.2227405874 | -3.9075094139 | -2.4093628042 |
| H | -3.9124986398 | -0.0691086335 | -1.4220385064 |
| H | -2.3171213819 | -2.5613517846 | 1.7139570963 |
| H | -3.3321862198 | -1.7981975474 | -3.1172563741 |
| C | -1.152483897 | 2.0212727499 | 1.5842652329 |
| H | -2.1072254051 | 1.8918069045 | 1.0777193979 |
| H | -1.2876153797 | 2.464892519 | 2.5707548122 |
| H | -0.4648111029 | 2.613325328 | 0.982611872 |
| C | 1.8237927811 | 1.4820396889 | -0.9580917432 |
| H | 2.0432944721 | 1.9822587404 | -0.0112651909 |
| H | 2.7232739804 | 1.4466397522 | -1.5752141893 |
| H | 1.0353679161 | 2.0099673708 | -1.4945267832 |
| C | 2.6403883767 | -0.9906297606 | 0.2596168472 |
| H | 3.5293146627 | -0.9634225081 | -0.3728936586 |
| H | 2.8070559308 | -0.4586619968 | 1.1980045994 |
| H | 2.3669943059 | -2.0250168083 | 0.4662514331 |

**Table S11**. Cartesian coordinates of $PhSiH_3$.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Si | -2.3417333281 | 0.0000846048 | 0.0073403973 |
| H | -2.8411812802 | -1.2128243044 | -0.6804674113 |
| H | -2.859627921 | -0.0007863811 | 1.3959335434 |
| H | -2.8410577576 | 1.2139610704 | -0.6788492543 |
| C | -0.4657342991 | -0.0000229523 | -0.0112665182 |
| C | 0.2536565454 | -1.2009393334 | -0.0115258205 |
| C | 0.2536710994 | 1.2008889794 | -0.0057985584 |
| C | 1.6447956042 | -1.2037624832 | 0.0017057562 |
| H | -0.2754519112 | -2.1488823135 | -0.0268609327 |
| C | 1.6447941483 | 1.203654092 | 0.0074339347 |
| H | -0.2754332896 | 2.148899432 | -0.0167607398 |
| C | 2.3420408165 | -0.0000788466 | 0.0121500883 |
| H | 2.1840786539 | -2.1438487261 | -0.0000188504 |
| H | 2.18407504 | 2.143738576 | 0.0101710077 |
| H | 3.425731879 | -0.0001014138 | 0.019986358 |

**Table S12**. Cartesian coordinates of **TS1**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 1.2251885911 | -0.9040012041 | -0.042554352 |
| S | -0.2142223913 | -0.8088070529 | 2.0246710451 |
| S | 0.5533108245 | 2.2585052395 | -1.1255519995 |
| P | -0.4420405466 | 1.1507710521 | 1.3980695954 |
| O | 0.0656261498 | 3.4781469004 | -0.445428129 |
| O | 1.9166848594 | 2.2758781646 | -1.696381202 |
| C | 0.2984150584 | 0.9457140534 | -0.1145674989 |
| C | 3.1877074769 | -0.7034970709 | 0.9386273495 |
| C | 2.879293968 | -2.100926132 | 0.9054648133 |

| | | | |
|---|---|---|---|
| C | 2.5987630908 | -2.7388955647 | -0.3073612472 |
| C | 2.5343531947 | -1.9521145276 | -1.4945047882 |
| C | 2.8708621503 | -0.5806556089 | -1.4872452856 |
| C | 3.2072367329 | 0.040697136 | -0.2537690389 |
| C | -2.7740799568 | -1.4245635897 | -0.4685224904 |
| C | -3.2119859146 | -0.5387433612 | -1.460319518 |
| C | -4.4101441331 | 0.1538094196 | -1.3200274949 |
| C | -5.1921360205 | -0.0391032126 | -0.1843794961 |
| C | -4.7707762993 | -0.9174653111 | 0.8095442157 |
| C | -3.5656638743 | -1.5997884247 | 0.6713116536 |
| H | -0.1888628414 | -1.1917591092 | -1.0952565525 |
| H | 2.8124573558 | -2.6515513735 | 1.834940434 |
| H | 2.3395854684 | -3.7889216758 | -0.3314506 |
| H | 2.7954139179 | 0.0295779895 | -2.3766538378 |
| H | 3.3528322295 | 1.1130230775 | -0.2438735461 |
| H | -2.6102179481 | -0.3807193857 | -2.3507861201 |
| H | -4.7326522614 | 0.8423646576 | -2.0923031866 |
| H | -6.1263937135 | 0.4985999823 | -0.072533696 |
| H | -5.3752918198 | -1.0627821155 | 1.697127268 |
| H | -3.2298933624 | -2.2594610552 | 1.4641123318 |
| H | 3.3511191594 | -0.2130745971 | 1.8886093603 |
| H | 2.2076834104 | -2.4137794125 | -2.4185387254 |
| C | 0.381945738 | 2.2642715528 | 2.5819887294 |
| H | -0.1083809219 | 2.2198505911 | 3.5566741073 |
| H | 0.3398861802 | 3.2748109757 | 2.1697789734 |
| H | 1.4218610961 | 1.951562628 | 2.6777408857 |
| C | -0.5084856894 | 2.0747576107 | -2.5663258194 |
| H | -1.5409636865 | 2.084907992 | -2.219904795 |
| H | -0.2632584 | 1.1276335238 | -3.0471655669 |
| H | -0.3067604695 | 2.9104487821 | -3.2360371231 |
| C | -2.1657573035 | 1.7248723429 | 1.4304016635 |
| H | -2.5579273666 | 1.7065062121 | 2.4491268456 |
| H | -2.7673891396 | 1.0862404776 | 0.7854232272 |
| H | -2.1671347859 | 2.7481640539 | 1.0456090153 |
| Si | -1.1603702569 | -2.3290240632 | -0.7018494984 |
| H | -1.1611572579 | -3.0592933333 | -1.9964713352 |
| H | -0.8625582217 | -3.2852411739 | 0.3769586293 |

**Table S13**. Cartesian coordinates of **TS1 (isomer 1)**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -0.0085585392 | -0.4840761862 | 0.3425566033 |
| S | 0.0557567072 | 1.8867537895 | 1.1811358263 |
| S | 3.232057393 | -0.6358378708 | -0.681086647 |
| P | 2.0536077229 | 1.7056842859 | 0.6679595201 |
| O | 4.4541707487 | 0.1440180913 | -0.3911999188 |
| O | 3.2261322328 | -2.0817980409 | -0.3809826959 |
| C | 1.9322584625 | 0.1493932775 | 0.0180667944 |
| C | 0.0936148562 | -1.5411502676 | 2.2918172753 |
| C | -1.2817264173 | -1.2298671063 | 2.0606257132 |
| C | -1.9351921905 | -1.6748690988 | 0.9066810202 |
| C | -1.1700446284 | -2.3359109622 | -0.0911898328 |
| C | 0.1849771155 | -2.6896681828 | 0.1321949633 |
| C | 0.8063389803 | -2.2991741181 | 1.343666176 |
| C | -2.8574059384 | 0.7829289132 | -1.0936379659 |
| C | -3.7511910919 | -0.1210371643 | -1.6798901327 |

| | | | |
|---|---|---|---|
| C | -5.0164940925 | -0.3326101726 | -1.1357650528 |
| C | -5.4093837888 | 0.3714422418 | -0.0031117316 |
| C | -4.5407183288 | 1.2962919634 | 0.5744549928 |
| C | -3.2763148261 | 1.5002607249 | 0.0348267149 |
| H | 0.0519811249 | 0.0037768133 | -1.3352968749 |
| H | -1.8099162683 | -0.6015657255 | 2.7669989065 |
| H | -2.9673532133 | -1.4066376498 | 0.7185366698 |
| H | 0.7766669055 | -3.1832203894 | -0.6268810882 |
| H | 1.8691171118 | -2.4744760312 | 1.453531145 |
| H | -3.4598290648 | -0.669933663 | -2.5704164803 |
| H | -5.6939656899 | -1.0403569126 | -1.5991973821 |
| H | -6.392725273 | 0.2102504746 | 0.4229206899 |
| H | -4.8511193303 | 1.8590107987 | 1.447242049 |
| H | -2.6039209288 | 2.2127606347 | 0.5003914482 |
| H | -1.6368838516 | -2.5789298432 | -1.0389866246 |
| H | 0.5954124396 | -1.1560187474 | 3.1686754939 |
| Si | -1.1279200648 | 0.915010814 | -1.8019417019 |
| H | -1.2144548105 | 0.3318611292 | -3.16611452 |
| H | -0.5761506569 | 2.2785444142 | -1.8621556016 |
| C | 3.1175917887 | 1.9092457415 | 2.1291671033 |
| H | 2.8039587808 | 1.1846985646 | 2.8802777227 |
| H | 4.1418245394 | 1.6906043632 | 1.8175265204 |
| H | 3.0407866012 | 2.9217057517 | 2.5305222533 |
| C | 2.6048845329 | 3.0516882458 | -0.4305451975 |
| H | 1.9442094705 | 3.0911310258 | -1.2963104375 |
| H | 2.5907518669 | 4.0106300969 | 0.0904730791 |
| H | 3.6233037681 | 2.8135519619 | -0.7491448441 |
| C | 3.0585502502 | -0.5812078063 | -2.4736717867 |
| H | 3.8956557784 | -1.1308399046 | -2.9033582071 |
| H | 2.113742379 | -1.0556573301 | -2.7385241275 |
| H | 3.0759454371 | 0.4626140562 | -2.7836818289 |

**Table S14**. Cartesian coordinates of **TS1**(isomer2).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -0.0871185765 | -0.471755735 | 0.1396629141 |
| S | -0.0103085418 | 1.9118459678 | 0.8970340135 |
| S | 3.0849515541 | -0.8651947967 | -0.7046855724 |
| P | 1.9489032094 | 1.669741011 | 0.3112298711 |
| O | 3.8896295161 | -0.9901751001 | 0.5345310201 |
| O | 2.6161882102 | -2.1402888221 | -1.279299966 |
| C | 1.7833484784 | 0.2190555765 | -0.5761463372 |
| C | 0.2653776272 | -1.447880443 | 2.1276902613 |
| C | -1.1144805735 | -1.0938097341 | 2.0525813214 |
| C | -1.9294482234 | -1.576630034 | 1.0205604773 |
| C | -1.321793105 | -2.3193403869 | -0.023103282 |
| C | 0.0410005886 | -2.7081608072 | 0.0422222216 |
| C | 0.823654929 | -2.2816862676 | 1.1400340332 |
| C | -3.0767010865 | 0.717673194 | -1.0592439675 |
| C | -4.0089848708 | -0.236902627 | -1.4832405831 |
| C | -5.218547028 | -0.4060935444 | -0.8124933142 |
| C | -5.5191810934 | 0.3925204314 | 0.2855428315 |
| C | -4.6143992352 | 1.3679020737 | 0.7010880686 |
| C | -3.4044248772 | 1.528101261 | 0.0356737808 |
| H | -0.2415780297 | -0.1917194532 | -1.5529508259 |
| H | -1.5254241049 | -0.4060786661 | 2.781068598 |
| H | -2.968996022 | -1.2809212578 | 0.9524532897 |
| H | 0.5162599253 | -3.2450892801 | -0.7661981452 |

| | | | |
|---|---|---|---|
| H | 1.8825164007 | -2.5109238487 | 1.1603680131 |
| H | -3.7915043989 | -0.8586792873 | -2.346814004 |
| H | -5.9257833829 | -1.1544233691 | -1.1509924064 |
| H | -6.4594988546 | 0.2650861289 | 0.8090265393 |
| H | -4.853515654 | 2.0037960337 | 1.5456596263 |
| H | -2.7030368202 | 2.2822165937 | 0.3762871732 |
| H | -1.9136949521 | -2.595334745 | -0.8881987499 |
| H | 0.8863864323 | -1.0504136672 | 2.9185529364 |
| Si | -1.4098920377 | 0.7930893353 | -1.9163051015 |
| H | -1.629805467 | 0.1847500757 | -3.2539429375 |
| H | -0.8382847762 | 2.1416867907 | -2.0532380814 |
| C | 3.0395281405 | 1.6859718809 | 1.7753312758 |
| H | 2.76286518 | 0.8506277632 | 2.4171286599 |
| H | 4.0740850547 | 1.5372752681 | 1.459956782 |
| H | 2.9262156282 | 2.6323438984 | 2.3076152759 |
| C | 2.4974798572 | 3.1385994905 | -0.6209232581 |
| H | 1.8777624815 | 3.2289443355 | -1.5123877422 |
| H | 2.3926846277 | 4.0321681765 | -0.0020157011 |
| H | 3.5437496271 | 3.0220781147 | -0.9135209466 |
| C | 4.2098814381 | -0.1584694807 | -1.9122636317 |
| H | 5.0458375792 | -0.8523401497 | -1.9975515863 |
| H | 3.679014596 | -0.057392934 | -2.8555452872 |
| H | 4.55774203 | 0.8071055059 | -1.5459361064 |

**Table S15**. Cartesian coordinates of **TS1**(isomer3).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 0.0948242485 | 0.7865810366 | 0.354825702 |
| S | 1.3548811264 | 1.8285342006 | -1.5804085902 |
| S | 2.1972839034 | -1.8481831746 | 0.8195303548 |
| P | 2.6308416254 | 0.2504405801 | -1.1936249462 |
| O | 3.5663407475 | -2.1715449411 | 0.3645190156 |
| O | 1.948627256 | -1.7464099919 | 2.2723900441 |
| C | 1.6656744724 | -0.4969178292 | -0.016868942 |
| C | 0.6162342079 | 2.2112546839 | 1.9286154626 |
| C | -0.5802884682 | 2.7065143458 | 1.3177097457 |
| C | -1.7181620348 | 1.8981745554 | 1.2381129469 |
| C | -1.6476669103 | 0.5535214078 | 1.7116460621 |
| C | -0.4940038409 | 0.0679749012 | 2.3609464214 |
| C | 0.6466691216 | 0.9123831615 | 2.468401191 |
| H | -0.5284051075 | -0.3741036867 | -0.9330780539 |
| H | -0.576925011 | 3.6866761075 | 0.8585774743 |
| H | -2.6124322295 | 2.2470272206 | 0.7380823345 |
| H | -0.4179824606 | -0.9577617303 | 2.695108261 |
| H | 1.563644579 | 0.4878101342 | 2.8555449023 |
| H | -2.4905877865 | -0.1075018985 | 1.5429669794 |
| H | 1.5122458866 | 2.8170169897 | 1.9235385635 |
| Si | -1.5754429794 | 0.1990769198 | -1.8976547107 |
| H | -1.1795534936 | -0.5087697214 | -3.135450286 |
| C | 4.2628234344 | 0.8591438107 | -0.668182875 |
| H | 4.1207938216 | 1.5019345518 | 0.2005162359 |
| H | 4.8657114301 | -0.0070928228 | -0.3872000737 |
| H | 4.7392179636 | 1.4225197917 | -1.4731513421 |
| C | 3.00676544 | -0.7061939323 | -2.6968064604 |
| H | 2.068172665 | -1.0238289495 | -3.150681008 |
| H | 3.5787895635 | -0.1072325745 | -3.4075718828 |
| H | 3.5873045971 | -1.5798253794 | -2.3893992111 |
| C | 1.1878797687 | -3.2526817281 | 0.3204876302 |

| | | | |
|---|---|---|---|
| H | 1.5135803361 | -4.1165908441 | 0.8993577385 |
| H | 0.1476244486 | -3.012106107 | 0.5402706595 |
| H | 1.3374252729 | -3.4145267754 | -0.7456733219 |
| C | -3.1953179359 | -0.4246859269 | -1.1861279701 |
| C | -3.3180357686 | -1.7475940218 | -0.740108337 |
| C | -4.2806339748 | 0.4386520536 | -1.0018386878 |
| C | -4.4847174891 | -2.1924721182 | -0.128904175 |
| H | -2.4896260919 | -2.439622955 | -0.8646699431 |
| C | -5.4513644372 | -0.0005643509 | -0.3874668148 |
| H | -4.2148846879 | 1.4683417369 | -1.3417469705 |
| C | -5.5523459509 | -1.31591235 | 0.0519339501 |
| H | -4.5624494115 | -3.2191640694 | 0.2092451372 |
| H | -6.2821597531 | 0.6822227322 | -0.2526980804 |
| H | -6.4608550412 | -1.6596640285 | 0.5321983985 |
| H | -1.6917970516 | 1.6484289861 | -2.132057529 |

**Table S16**. Cartesian coordinates of **Int1**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 1.2822199628 | -1.0034194619 | 0.2964604901 |
| S | 0.5072655282 | -0.6097356575 | 2.6041014844 |
| S | 0.1934863756 | 1.9229227692 | -1.0251283792 |
| P | -0.0999186928 | 1.2136730417 | 1.8189543629 |
| O | -0.1736311272 | 3.2291106995 | -0.4397320448 |
| O | 1.313062104 | 1.8649511744 | -1.9849086467 |
| C | 0.4176994546 | 0.855290617 | 0.2458626615 |
| C | 3.714766898 | -0.5483353221 | 0.5896852697 |
| C | 3.4725746026 | -1.9229424054 | 0.862502695 |
| C | 2.8842035776 | -2.7460118408 | -0.0993824452 |
| C | 2.404821058 | -2.1698781852 | -1.3028014417 |
| C | 2.6159863814 | -0.7990665129 | -1.5666886058 |
| C | 3.3180807093 | -0.0033338718 | -0.6285204917 |
| C | -2.1809416273 | -1.9370448784 | 0.8677889823 |
| C | -2.8734602305 | -1.3440149343 | -0.1939148115 |
| C | -4.154837271 | -0.8289659455 | -0.0224073399 |
| C | -4.7714625872 | -0.907461654 | 1.2236175975 |
| C | -4.1029051463 | -1.5027496911 | 2.2892111889 |
| C | -2.8176405149 | -2.007974556 | 2.1116437374 |
| H | -0.0615623591 | -1.0603332368 | -0.4795365663 |
| H | 3.7562189053 | -2.3352968055 | 1.8225814589 |
| H | 2.7232598327 | -3.797729067 | 0.1016920634 |
| H | 2.2458069309 | -0.3337274241 | -2.4699563816 |
| H | 3.4261419395 | 1.0539885895 | -0.8364214276 |
| H | -2.4066107705 | -1.2780663038 | -1.1731002695 |
| H | -4.671677064 | -0.3687724216 | -0.8570106733 |
| H | -5.7688593322 | -0.5068163836 | 1.3623835175 |
| H | -4.5795755356 | -1.5662106095 | 3.2606696994 |
| H | -2.2969145929 | -2.4496684514 | 2.9548406411 |
| H | 4.1749541757 | 0.0747558038 | 1.3448120393 |
| H | 1.8855231147 | -2.7874766782 | -2.0243510404 |
| C | 0.7333900195 | 2.5916084283 | 2.6621692163 |
| H | 0.4034955029 | 2.6693216765 | 3.6999613169 |
| H | 0.4894881524 | 3.5012453577 | 2.1086568874 |
| H | 1.8081401644 | 2.417345505 | 2.621127816 |
| C | -1.2338321912 | 1.4288635577 | -2.0043656099 |
| H | -2.1072919837 | 1.4280254206 | -1.353276931 |
| H | -1.0413290112 | 0.4345481017 | -2.407059262 |
| H | -1.3411727505 | 2.1526316107 | -2.8119254102 |

| | | | |
|---|---|---|---|
| C | -1.8654243368 | 1.5484102243 | 2.0970044558 |
| H | -2.0796994901 | 1.6275666349 | 3.1647263839 |
| H | -2.4540689406 | 0.7428278432 | 1.6580189961 |
| H | -2.0962840088 | 2.4941565796 | 1.5988056683 |
| Si | -0.4354233475 | -2.5960936604 | 0.6168869793 |
| H | -0.4789038588 | -3.4964480811 | -0.5757155982 |
| H | -0.0984408496 | -3.4582135952 | 1.7811907571 |

**Table S17**. Cartesian coordinates of **Int1** (isomer1).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 0.9900456814 | -0.6768081915 | 0.4590643449 |
| S | -0.2309683038 | -0.2155193907 | 2.5523148592 |
| S | 0.2931279624 | 2.2299626044 | -1.113682264 |
| P | -0.5764115837 | 1.6089923309 | 1.6400839497 |
| O | -0.1386925826 | 3.5711271903 | -0.6717797032 |
| O | 1.5403725776 | 2.0975168268 | -1.8879840723 |
| C | 0.323893266 | 1.246706812 | 0.2476698901 |
| C | 3.3705115269 | -0.2057198238 | 1.1777895185 |
| C | 3.1013124888 | -1.5551543678 | 1.5079140222 |
| C | 2.6748169514 | -2.452430494 | 0.5293627143 |
| C | 2.421828426 | -1.9812841758 | -0.7842441961 |
| C | 2.6995777946 | -0.6387716515 | -1.1224256609 |
| C | 3.2025005216 | 0.2365271893 | -0.1358765153 |
| C | -0.3089310441 | -3.7583371737 | 1.2285779446 |
| C | -0.1970723824 | -3.7410475137 | 2.6258593239 |
| C | 0.2379928539 | -4.8621825971 | 3.3245451088 |
| C | 0.5767617765 | -6.027245354 | 2.6401345239 |
| C | 0.4641849388 | -6.0683879545 | 1.2550232695 |
| C | 0.0228086932 | -4.9441207823 | 0.5598931852 |
| H | -0.1809185958 | -0.5979720377 | -0.55112691 |
| H | 3.2134257142 | -1.8928158333 | 2.5307705782 |
| H | 2.4602740191 | -3.4819114369 | 0.7888299464 |
| H | 2.5169315891 | -0.2554682643 | -2.1174098542 |
| H | 3.3427010578 | 1.2772952138 | -0.400260997 |
| H | -0.4543752434 | -2.8431986179 | 3.1776916534 |
| H | 0.3122014704 | -4.8282697722 | 4.4055465847 |
| H | 0.9195506451 | -6.898987036 | 3.1852174183 |
| H | 0.715489881 | -6.9744940564 | 0.7155132533 |
| H | -0.0640404727 | -4.993200175 | -0.5215645351 |
| H | 3.6790898281 | 0.4872054464 | 1.9490573057 |
| H | 2.04658353 | -2.6638597354 | -1.5368374316 |
| C | 0.0169530781 | 3.0040108203 | 2.6379333531 |
| H | -0.5661949032 | 3.1060142748 | 3.5549382438 |
| H | -0.0742947021 | 3.8999027572 | 2.0188931709 |
| H | 1.0661993176 | 2.8312209374 | 2.8743263906 |
| C | -0.9830555712 | 1.6780707165 | -2.2599450451 |
| H | -1.9467766952 | 1.7460029329 | -1.757285258 |
| H | -0.7629199596 | 0.6530656685 | -2.5567675244 |
| H | -0.948023151 | 2.3396543533 | -3.1250763846 |
| C | -2.3592715855 | 1.9368029636 | 1.4559177499 |
| H | -2.8291807234 | 2.0765437604 | 2.4312157885 |
| H | -2.8155354334 | 1.0870155778 | 0.9475891295 |
| H | -2.4724353882 | 2.8424229948 | 0.8537842783 |
| Si | -0.7656628339 | -2.2366074893 | 0.2010420791 |
| H | -2.1137533412 | -1.7287474193 | 0.5444402964 |
| H | -0.8396515933 | -2.7825194873 | -1.1865843329 |

**Table S18**. Cartesian coordinates of **Int1** (isomer2).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -0.7380376659 | -0.567506045 | 0.9598607633 |
| S | -1.6947136948 | 0.6316069417 | -2.9343752652 |
| S | -3.5254042981 | 0.9823722846 | 0.7574567925 |
| P | -1.268240677 | 1.6305296927 | -1.2895896764 |
| O | -4.1115364646 | 2.0238453133 | -0.0846072513 |
| O | -4.1627312409 | -0.3265396157 | 0.8124392417 |
| C | -1.7717079144 | 0.7425125371 | 0.2709583491 |
| C | 0.4634532517 | -1.7366597192 | -1.1842245987 |
| C | 1.4579755175 | -1.8449534454 | -0.2138557156 |
| C | 1.1838587516 | -2.4927820697 | 1.004538416 |
| C | -0.0770279609 | -3.0373039189 | 1.2414334719 |
| C | -1.0919010405 | -2.9193024651 | 0.2698565133 |
| C | -0.8182041214 | -2.2636134659 | -0.9358737171 |
| C | 1.4615656167 | -0.3053987479 | 3.4454305266 |
| C | 2.8083038693 | -0.1779079977 | 3.0835275967 |
| C | 3.7642806185 | -1.0875986446 | 3.528896525 |
| C | 3.3876299339 | -2.1460413267 | 4.3510445972 |
| C | 2.0553298374 | -2.2809866949 | 4.7359872542 |
| C | 1.1057276746 | -1.3687506357 | 4.2858104332 |
| H | -1.7527786489 | -0.6497336283 | 2.1006678051 |
| H | 2.4433531993 | -1.4295599813 | -0.3887454509 |
| H | 1.9485333212 | -2.5530350466 | 1.7709346408 |
| H | -2.0807545315 | -3.3155481107 | 0.4597031186 |
| H | -1.6004636943 | -2.1173731734 | -1.6711755799 |
| H | 3.1154894938 | 0.6407376416 | 2.438939101 |
| H | 4.8021065134 | -0.9703632478 | 3.2380857464 |
| H | 4.1288175729 | -2.8565059762 | 4.69780429 |
| H | 1.7598068619 | -3.0956605285 | 5.3874671154 |
| H | 0.0684668815 | -1.4923845834 | 4.585624545 |
| H | 0.6426016009 | -1.2235445937 | -2.1216066738 |
| H | -0.285153991 | -3.5251589371 | 2.185413555 |
| C | -1.8873348891 | 3.343236337 | -1.2773820863 |
| H | -1.2766679938 | 3.894255046 | -1.9957772914 |
| H | -1.7810689877 | 3.7852439396 | -0.283929008 |
| H | -2.9317297894 | 3.3526791944 | -1.573516811 |
| C | -3.4700844247 | 1.6433641254 | 2.4198280063 |
| H | -2.8481894322 | 2.5378712508 | 2.421200864 |
| H | -3.088076579 | 0.888540157 | 3.1005313213 |
| H | -4.5054272601 | 1.8976515075 | 2.6487456251 |
| C | 0.5225755431 | 1.9000735912 | -1.0552742926 |
| H | 0.8804524112 | 2.4226674407 | -1.9444689239 |
| H | 1.0503073294 | 0.9528724032 | -0.9611140354 |
| H | 0.70298548 | 2.5037772904 | -0.1641001805 |
| Si | 0.140224192 | 0.7966698191 | 2.6611847106 |
| H | 0.8519184914 | 2.0205157016 | 2.1909905018 |
| H | -0.7878360729 | 1.2375639843 | 3.7351697808 |

**Table S19**. Cartesian coordinates of **Int1** (isomer3).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 1.2813875646 | -0.7319216437 | 0.1724402277 |
| S | 0.0157756528 | -0.9242375134 | 2.2716566934 |
| S | 0.1497671094 | 2.1204616135 | -0.8948697022 |
| P | -0.4827099197 | 1.0222209064 | 1.8065864369 |
| O | 1.2653182257 | 2.0937571755 | -1.8601735108 |
| O | -1.1811181148 | 1.7991647792 | -1.4473492461 |
| C | 0.6023423908 | 1.2170855605 | 0.4870870544 |

| | | | |
|---|---|---|---|
| C | 3.6441814786 | -0.2800684306 | 0.8255601048 |
| C | 3.4556204454 | -1.6678972149 | 0.9579965281 |
| C | 2.9743436028 | -2.4245002283 | -0.119051921 |
| C | 2.648961907 | -1.7762840442 | -1.335842513 |
| C | 2.8721117543 | -0.3900222626 | -1.4905756953 |
| C | 3.3594198799 | 0.3491102393 | -0.3995912938 |
| C | -2.2223033326 | -1.753999265 | -0.3074424298 |
| C | -2.7158754355 | -0.9254621473 | -1.3222631947 |
| C | -4.03565281 | -0.4847504836 | -1.3044089935 |
| C | -4.8841691403 | -0.871878665 | -0.2712595106 |
| C | -4.4102594256 | -1.6994446814 | 0.743544292 |
| C | -3.0882092492 | -2.1331212648 | 0.7251668703 |
| H | 0.0656202622 | -0.5285743616 | -0.780043098 |
| H | 3.6490843839 | -2.1497692876 | 1.9082212882 |
| H | 2.8109987332 | -3.4891009717 | -0.0108419259 |
| H | 2.6044816716 | 0.1252511247 | -2.4026897025 |
| H | 3.4238497944 | 1.4252343939 | -0.4949922966 |
| H | -2.0594047865 | -0.5773753354 | -2.1132766871 |
| H | -4.3926281444 | 0.1731661345 | -2.0878393804 |
| H | -5.9116254741 | -0.526448064 | -0.2543067382 |
| H | -5.0685795989 | -2.0011621326 | 1.5503917692 |
| H | -2.7206802139 | -2.7620483239 | 1.52967734 |
| H | 3.9675195474 | 0.3077490312 | 1.6736918606 |
| H | 2.2439320488 | -2.3505096075 | -2.1590637855 |
| C | -0.1231602113 | 2.0898775121 | 3.2373045809 |
| H | -0.7516243597 | 1.8083948387 | 4.084954849 |
| H | -0.3170181738 | 3.1313472728 | 2.9684877927 |
| H | 0.9283849459 | 1.9714826831 | 3.4952011012 |
| C | 0.0240726477 | 3.8141820149 | -0.3097991038 |
| H | 0.9833967966 | 4.1124755026 | 0.1057372263 |
| H | -0.7726996136 | 3.876272455 | 0.431734331 |
| H | -0.2338461275 | 4.414599077 | -1.1818327507 |
| C | -2.274665514 | 1.2451025449 | 1.559177075 |
| H | -2.8131337876 | 0.8292613242 | 2.4131930781 |
| H | -2.5772325129 | 0.7473045832 | 0.6390843781 |
| H | -2.4930211092 | 2.3125067293 | 1.4692031147 |
| Si | -0.4305029607 | -2.3098608242 | -0.337497365 |
| H | -0.1643827553 | -2.8481538799 | -1.7035350186 |
| H | -0.282337862 | -3.4500879332 | 0.6074001504 |

**Table S20**. Cartesian coordinates of **TS2**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 0.8738211908 | -1.0033125083 | 0.0188858734 |
| S | 0.0098707564 | -0.2794536231 | 2.211944229 |
| S | 0.61804987 | 2.0179480963 | -1.5543330507 |
| P | -0.1101331909 | 1.5614262549 | 1.2723256679 |
| O | 0.5128021971 | 3.3935918782 | -1.0284283828 |
| O | 1.8304033229 | 1.6392335928 | -2.3031940928 |
| C | 0.3114126891 | 0.9753074022 | -0.2711333987 |
| C | 3.3081697108 | -1.1937996811 | 0.5144749331 |
| C | 2.6503982474 | -2.4279808601 | 0.7953374734 |
| C | 1.9458831408 | -3.1032273174 | -0.2032039065 |
| C | 1.7586669525 | -2.4776743124 | -1.4636395936 |
| C | 2.3524104342 | -1.2263147754 | -1.7217161453 |
| C | 3.1792589621 | -0.6145994764 | -0.7402737891 |
| C | -2.7478923339 | -1.0229155988 | 0.2109869954 |
| C | -3.1457004539 | -0.2965887256 | -0.9176348128 |

| | | | |
|---|---|---|---|
| C | -4.2738525414 | 0.517480154 | -0.8933766186 |
| C | -5.0331722145 | 0.6140760006 | 0.2700105336 |
| C | -4.6579823672 | -0.104785939 | 1.4010646576 |
| C | -3.5226551818 | -0.9108736802 | 1.370623676 |
| H | -0.3729558689 | -0.5063427316 | -0.7855736804 |
| H | 2.7181632132 | -2.8557308253 | 1.7874402505 |
| H | 1.4800896356 | -4.0584760869 | 0.0044772863 |
| H | 2.2004050713 | -0.7161672253 | -2.6627286671 |
| H | 3.6041165063 | 0.3562395558 | -0.9625891505 |
| H | -2.5651265103 | -0.3638297455 | -1.8341667087 |
| H | -4.5621664879 | 1.0736413218 | -1.7783312654 |
| H | -5.9129177885 | 1.2465958773 | 0.2938516297 |
| H | -5.2457318659 | -0.0323121778 | 2.3089962565 |
| H | -3.2282950672 | -1.4508379612 | 2.2646082803 |
| H | 3.8691533698 | -0.6976972555 | 1.2952706365 |
| H | 1.1568062612 | -2.9625394605 | -2.2211157425 |
| C | 1.0409445961 | 2.7384723992 | 2.0445920996 |
| H | 0.7426719454 | 2.9354889514 | 3.0762763599 |
| H | 1.0297369756 | 3.6550447087 | 1.4521814215 |
| H | 2.0386855135 | 2.3004332084 | 2.0228001916 |
| C | -0.7029420295 | 1.8658383493 | -2.764253177 |
| H | -1.6399689832 | 2.1246682104 | -2.2732790077 |
| H | -0.7167958334 | 0.8373139409 | -3.1254093233 |
| H | -0.4777280763 | 2.5523070979 | -3.5800034197 |
| C | -1.733769204 | 2.3529889898 | 1.4532460907 |
| H | -1.9370859861 | 2.5758294304 | 2.5026229206 |
| H | -2.4992892862 | 1.685919785 | 1.0567803613 |
| H | -1.7085551777 | 3.2794447082 | 0.873133103 |
| Si | -1.2016062623 | -2.1012234232 | 0.1597279554 |
| H | -1.3466432468 | -2.9911712871 | -1.0331414217 |
| H | -1.2382546041 | -2.9851012356 | 1.3560784722 |

**Table S21**. Cartesian coordinates of **TS2'** (silyl transfer).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 0.0300143460 | 0.9558610014 | -0.2934605861 |
| S | 0.7325727922 | 0.1591292572 | -2.4879229129 |
| S | 2.0898795567 | -1.1827409879 | 1.5555672740 |
| P | 2.0579861608 | -0.9533327986 | -1.3716083332 |
| O | 3.4729376897 | -1.5534142937 | 1.1868973414 |
| O | 1.8878586376 | -0.2744237858 | 2.6963764423 |
| C | 1.3500018374 | -0.5893550001 | 0.1483749355 |
| C | 1.4234976931 | 3.1593243497 | -0.0369319324 |
| C | 0.1578742607 | 3.4652007874 | -0.6026075200 |
| C | -1.0162138835 | 3.1263056213 | 0.0688356305 |
| C | -0.9503803291 | 2.3665980380 | 1.2632916598 |
| C | 0.3013481293 | 1.9938811348 | 1.7812933881 |
| C | 1.4915877436 | 2.4410401587 | 1.1474361040 |
| C | -3.0404199310 | -0.8864200419 | 0.1393106420 |
| C | -3.8444621169 | 0.2517034462 | 0.2711691703 |
| C | -5.2250045309 | 0.1958785004 | 0.1053095878 |
| C | -5.8384509544 | -1.0122158450 | -0.2095442215 |
| C | -5.0616560855 | -2.1554841656 | -0.3608555484 |
| C | -3.6820818264 | -2.0878892081 | -0.1882647889 |
| H | -1.2820477411 | 0.4915602047 | -0.9774111560 |
| H | 0.1020627197 | 3.9910322062 | -1.5471971032 |
| H | -1.9769060830 | 3.3970836906 | -0.3508307083 |
| H | 0.3829638156 | 1.3807342963 | 2.6681560734 |

| | | | |
|---|---|---|---|
| H | 2.4419337447 | 2.1352371933 | 1.5674475237 |
| H | -3.3887543151 | 1.2137718754 | 0.4831513771 |
| H | -5.8217024714 | 1.0945441702 | 0.2147144544 |
| H | -6.9129532200 | -1.0602112953 | -0.3422000211 |
| H | -5.5293255875 | -3.0996759325 | -0.6158759675 |
| H | -3.0934613531 | -2.9920193461 | -0.3135312019 |
| H | 2.3253077267 | 3.4546845307 | -0.5572674684 |
| H | -1.8550315661 | 2.0823365031 | 1.7856612336 |
| C | 3.7622974235 | -0.3830402297 | -1.6542353040 |
| H | 4.0764197042 | -0.6430826419 | -2.6670423082 |
| H | 4.4053119181 | -0.8522445311 | -0.9091812244 |
| H | 3.7821129808 | 0.6996632112 | -1.5298089663 |
| C | 1.3831599270 | -2.7554313159 | 2.0792705431 |
| H | 1.4720239751 | -3.4554022023 | 1.2497515402 |
| H | 0.3465422703 | -2.6187716542 | 2.3727038771 |
| H | 1.9863936044 | -3.0818886393 | 2.9260441888 |
| C | 2.0940170512 | -2.7026214017 | -1.8705122621 |
| H | 2.4128040715 | -2.7929452804 | -2.9107152945 |
| H | 1.0929564031 | -3.1174222956 | -1.7540317422 |
| H | 2.7989280998 | -3.2281818928 | -1.2209988181 |
| Si | -1.1452911735 | -0.9321175291 | 0.4017352117 |
| H | -0.8097764089 | -2.2353589776 | -0.2240895358 |
| H | -0.9884148093 | -1.0360698414 | 1.8780936069 |

**Table S22**. Cartesian coordinates of **Pro**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -1.5446546493 | -0.9863722005 | -0.2029295953 |
| S | -0.9261949431 | 0.173782827 | 1.944795766 |
| S | 1.4853491268 | -0.9496763652 | -1.8088196707 |
| P | 0.8657414838 | 0.2698234785 | 0.987693653 |
| O | 1.9853160505 | -2.152638521 | -1.1151252679 |
| O | 0.8209140099 | -1.1061350138 | -3.110731936 |
| C | 0.3871423733 | -0.0280401784 | -0.7306102169 |
| C | -1.6647693442 | -3.2567284039 | 0.5774067155 |
| C | -2.8902339014 | -2.537297513 | 0.7581511669 |
| C | -3.5663183858 | -1.9687617851 | -0.3386169855 |
| C | -2.9375001335 | -1.9831935232 | -1.6207087512 |
| C | -1.6692912826 | -2.5852536438 | -1.7732166872 |
| C | -1.0572171742 | -3.2729617115 | -0.6752071742 |
| C | -4.1660429678 | 1.5743491201 | -0.2353992229 |
| C | -5.2894581866 | 1.596331913 | -1.0786349857 |
| C | -6.5624797656 | 1.8968078466 | -0.5906117647 |
| C | -6.7406772672 | 2.1882084284 | 0.7599677125 |
| C | -5.6387660416 | 2.1774765694 | 1.6162021664 |
| C | -4.3718498534 | 1.870638312 | 1.1237291193 |
| H | 0.2396214582 | 0.9275714216 | -1.2376421603 |
| H | -3.3241462585 | -2.4615872622 | 1.7472509472 |
| H | -4.5159717641 | -1.4709080145 | -0.1971127001 |
| H | -1.1597715906 | -2.5352941434 | -2.7254125029 |
| H | -0.0885641072 | -3.735375121 | -0.8129549628 |
| H | -5.1687409211 | 1.3882126733 | -2.1376813462 |
| H | -7.4117780158 | 1.9094126486 | -1.2659533632 |
| H | -7.7274428092 | 2.4258896354 | 1.1423976439 |
| H | -5.7680960777 | 2.4095449181 | 2.6683716935 |
| H | -3.5286830858 | 1.8658670359 | 1.8073317617 |
| H | -3.4148482888 | -1.510907904 | -2.4691293733 |
| H | -1.1830874124 | -3.7199637137 | 1.4290623643 |

| | | | |
|---|---|---|---|
| Si | -2.4452152796 | 1.1279578699 | -0.918467476 |
| H | -2.6220779121 | 1.2066061331 | -2.4075330583 |
| H | -1.5450332839 | 2.2856040238 | -0.5890304868 |
| C | 2.9277878948 | 0.1090579493 | -2.1243876507 |
| H | 3.5479236421 | -0.4401394611 | -2.8329624793 |
| H | 2.5883628953 | 1.0451095219 | -2.5657519908 |
| H | 3.4755849718 | 0.2760828342 | -1.1977908733 |
| C | 1.6866410877 | 1.8908284025 | 1.2324990248 |
| H | 2.6561426588 | 1.9165066533 | 0.7288467665 |
| H | 1.0421757515 | 2.6743304547 | 0.8324341579 |
| H | 1.8294815144 | 2.0629659827 | 2.3017235672 |
| C | 2.0459825813 | -0.9600294667 | 1.6390852978 |
| H | 1.6602606363 | -1.9603942658 | 1.4567856238 |
| H | 3.0221114436 | -0.8697217434 | 1.1603795865 |
| H | 2.1362595831 | -0.7817973081 | 2.7127023073 |

**Table S23**. Cartesian coordinates of the hydrido complex.

| Atomic symobl | x | y | z |
|---|---|---|---|
| Ru | 1.1669195895 | -1.0401616613 | -0.112487652 |
| O | 2.1612380809 | 2.3834783653 | 0.1036096995 |
| C | -0.0315147175 | 0.8748696591 | -0.2307831066 |
| S | -0.3232327497 | -1.2239331681 | 1.9272822667 |
| P | -0.4398124508 | 0.745000159 | 1.5061461183 |
| S | 0.9583074927 | 2.2442901679 | -0.7241037849 |
| O | 1.1346752779 | 2.1307033041 | -2.1752654104 |
| C | 3.305195794 | -1.4340756269 | 0.8964107501 |
| C | 3.4567729085 | -0.3341866561 | 0.0717083162 |
| C | 2.9404347655 | -0.3880312126 | -1.2660147781 |
| C | 2.445225854 | -1.5906616651 | -1.8048376735 |
| C | 2.3080483177 | -2.7257618489 | -0.9508197683 |
| C | 2.6705606593 | -2.6217444577 | 0.4021575991 |
| H | -0.0801407409 | -1.5873823545 | -0.8554499491 |
| H | 3.8569026718 | 0.5988014339 | 0.4435099627 |
| H | 2.9620190559 | 0.5010701894 | -1.8830217816 |
| H | 1.863891659 | -3.6385481494 | -1.3235987254 |
| H | 2.4938142536 | -3.4534844396 | 1.0707988239 |
| H | 2.1111789287 | -1.6289926485 | -2.8323779954 |
| H | 3.5979293534 | -1.3835000597 | 1.9377362571 |
| Si | -1.3513777427 | 0.5812341139 | -1.5647131364 |
| H | -1.8637421962 | 1.904556423 | -2.0210938479 |
| H | -0.7873674076 | -0.1209792524 | -2.7295696884 |
| C | -2.8994875355 | -0.2573813555 | -0.8909903971 |
| C | -4.0894051259 | 0.4862132645 | -0.8998617606 |
| C | -2.9505272559 | -1.5624336493 | -0.3828215635 |
| C | -5.2796163592 | -0.0407770017 | -0.4071135282 |
| H | -4.0876812106 | 1.4970530666 | -1.2958956256 |
| C | -4.1374188904 | -2.0931718974 | 0.1120345728 |
| H | -2.0517251713 | -2.1655727462 | -0.3515146408 |
| C | -5.3030261779 | -1.33333003 | 0.105698548 |
| H | -6.1845435602 | 0.5556593371 | -0.4247740897 |
| H | -4.1496166879 | -3.101444661 | 0.5093330138 |
| H | -6.2257361442 | -1.7483018506 | 0.4947388533 |
| C | 0.7411939424 | 1.660181547 | 2.5457208379 |
| H | 1.749328095 | 1.3147322663 | 2.3267591055 |
| H | 0.6935732476 | 2.7365449649 | 2.378169146 |
| H | 0.4759947559 | 1.4278949496 | 3.5785927463 |
| C | -2.0544641847 | 1.4510831539 | 1.9729478833 |

| | | | |
|---|---|---|---|
| H | -2.1250330652 | 2.4856036934 | 1.6265667389 |
| H | -2.853241497 | 0.859405511 | 1.5274462727 |
| H | -2.1434209762 | 1.421444521 | 3.0609132096 |
| C | 0.0089242313 | 3.7445029298 | -0.4532378074 |
| H | -0.1668980737 | 3.8721699115 | 0.6138451408 |
| H | 0.6293096084 | 4.5562198257 | -0.8323998453 |
| H | -0.9225326217 | 3.6781996345 | -1.0112093063 |

**Table S24**. Cartesian coordinates of $Me_3SiH$.

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | -0.9418210821 | -0.2545140044 | -0.0000752414 |
| H | -1.2907690893 | -0.7950867702 | -0.8829848563 |
| H | 0.15110592 | -0.2839155291 | -0.0002405522 |
| H | -1.290585909 | -0.7950134768 | 0.8829368107 |
| C | -0.9418126854 | 2.4098816789 | 1.5384502266 |
| H | 0.1511105848 | 2.4244665758 | 1.5638945173 |
| H | -1.2906581473 | 3.4448202015 | 1.5650954874 |
| H | -1.2907666898 | 1.9155347095 | 2.4480361494 |
| C | -0.9417616467 | 2.4098539154 | -1.5383494947 |
| H | -1.2904629144 | 1.9151292359 | -2.4478243283 |
| H | -1.2908531533 | 3.4446973389 | -1.5652726925 |
| H | 0.1511580313 | 2.4247374809 | -1.5637327758 |
| Si | -1.5554986077 | 1.5218147773 | 0.0000492011 |
| H | -3.0426926211 | 1.5218673863 | 0.0000176248 |

**Table S25**. Cartesian coordinates of **TS1-Me**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 0.6906094375 | -0.5943134336 | -0.309734513 |
| S | 0.227413436 | 1.3129188283 | -1.892382809 |
| S | -2.3592098952 | -0.5416721447 | 1.2275014494 |
| P | -1.6439347185 | 1.1750625453 | -1.0259089555 |
| O | -3.6640895512 | 0.0673461648 | 0.8861391818 |
| O | -2.2887634992 | -2.0160378107 | 1.3149499457 |
| C | -1.1942927261 | 0.1117952014 | 0.2150044323 |
| C | 0.5158653084 | -2.2276101791 | -1.829419722 |
| C | 1.8952909336 | -1.8450733977 | -1.7752456576 |
| C | 2.5945374489 | -1.8901093994 | -0.5665717782 |
| C | 1.888210572 | -2.2250261359 | 0.6268713472 |
| C | 0.537226196 | -2.6213385023 | 0.5865250661 |
| C | -0.1456759327 | -2.6325881187 | -0.6633904942 |
| H | 0.9439153676 | 0.4975417925 | 0.9859330176 |
| H | 2.3844559798 | -1.4872535053 | -2.6721823774 |
| H | 3.6349508017 | -1.5972605847 | -0.5203409254 |
| H | -0.017335509 | -2.8508100351 | 1.4857611103 |
| H | -1.2073039551 | -2.8434573607 | -0.6623044309 |
| H | 2.3968193319 | -2.1662107136 | 1.5813342782 |
| H | -0.0254512894 | -2.1451287431 | -2.7621321594 |
| Si | 2.132554827 | 1.5150687136 | 0.9269728019 |
| C | -2.8509284321 | 0.5793103297 | -2.2551291473 |
| H | -2.4944499646 | -0.3732290291 | -2.6478096795 |
| H | -3.8026109371 | 0.4296220248 | -1.7406312672 |
| H | -2.9578066154 | 1.2975211539 | -3.070593877 |
| C | -2.325514049 | 2.7925266085 | -0.5456062464 |

| | | | |
|---|---|---|---|
| H | -1.62667617 | 3.284997101 | 0.1292857995 |
| H | -2.5008403062 | 3.415855232 | -1.4243375304 |
| H | -3.2674134344 | 2.5998744839 | -0.0258272455 |
| C | -2.0030344776 | -0.0042767833 | 2.9068274096 |
| H | -2.7281590089 | -0.4777680947 | 3.5681454941 |
| H | -0.9905765635 | -0.3242464541 | 3.1535684989 |
| H | -2.0900491578 | 1.0802975348 | 2.9374564213 |
| C | 1.182275296 | 3.097714335 | 1.2182415674 |
| H | 0.7930073877 | 3.4763602176 | 0.2715598975 |
| H | 0.3428162281 | 2.9264513708 | 1.8965645668 |
| H | 1.8326083217 | 3.858932788 | 1.6580466101 |
| C | 3.3849776689 | 1.7032412212 | -0.4521038359 |
| H | 3.9734872184 | 0.7961568045 | -0.5974054687 |
| H | 2.9104118648 | 1.9739462961 | -1.3950084558 |
| H | 4.0746421178 | 2.5066704553 | -0.1707346303 |
| C | 3.0383486 | 0.9619262002 | 2.4797044663 |
| H | 2.3496955017 | 0.8033472738 | 3.3127804121 |
| H | 3.5853273233 | 0.0307375609 | 2.308435365 |
| H | 3.7671400244 | 1.7184861879 | 2.7842350676 |

**Table S26**. Cartesian coordinates of **Si-H addition** (Concerted).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 0.5567787148 | 1.0972700037 | -0.118753192 |
| S | 1.0101254479 | 0.348906716 | -2.4905188525 |
| S | 1.8691152216 | -1.5864639579 | 1.4742591123 |
| P | 1.9678528217 | -1.08599913 | -1.3867530106 |
| O | 3.2819208951 | -1.9327141668 | 1.2119858404 |
| O | 1.6014292033 | -0.7847801893 | 2.6851080778 |
| C | 1.0839836665 | -0.9108886629 | 0.0994239606 |
| C | 2.1244931549 | 2.558261504 | 0.1751798471 |
| C | 1.0566185697 | 3.2483642698 | -0.4749018714 |
| C | -0.2324024895 | 3.2305408563 | 0.0686058409 |
| C | -0.46573001 | 2.4781499274 | 1.2563982413 |
| C | 0.5889937961 | 1.850041537 | 1.9535443842 |
| C | 1.8941620693 | 1.8811931756 | 1.3945568775 |
| H | -1.2256399376 | 0.3108270146 | -0.6364493029 |
| H | 1.2303577698 | 3.7035421168 | -1.4411697354 |
| H | -1.057707797 | 3.6889235293 | -0.4584520442 |
| H | 0.4046636558 | 1.2445930386 | 2.8292605123 |
| H | 2.6797346731 | 1.3048336295 | 1.8657762455 |
| H | -1.4804405772 | 2.3625113682 | 1.6180188825 |
| H | 3.0992018442 | 2.5214564615 | -0.2920837031 |
| Si | -1.7503221096 | -0.9308391367 | 0.047880123 |
| C | 3.7485505169 | -0.6752411084 | -1.386854882 |
| H | 3.8887964275 | 0.2660592361 | -0.8565929791 |
| H | 4.3080569874 | -1.4549626371 | -0.8731149428 |
| H | 4.0712762068 | -0.5624875389 | -2.4237556779 |
| C | 1.9756220759 | -2.733965071 | -2.1659146054 |
| H | 0.9592715621 | -3.0856810805 | -2.3271627145 |
| H | 2.5048528615 | -2.6810482931 | -3.1194727076 |
| H | 2.5068492348 | -3.4192529869 | -1.4993257042 |
| C | 1.0867141961 | -3.17636568 | 1.7710575966 |
| H | 1.5785036776 | -3.5981777442 | 2.6474720759 |
| H | 0.0240346016 | -3.0284298868 | 1.9502775055 |
| H | 1.2553383493 | -3.8064276625 | 0.8983725749 |
| C | -1.3842054822 | -2.4941673691 | -0.9154543901 |
| H | -1.0575043741 | -2.2010567037 | -1.9175749975 |

| | | | |
|---|---|---|---|
| H | -0.6130092857 | -3.1146135732 | -0.4657251152 |
| H | -2.3059270439 | -3.073636115 | -1.0197131219 |
| C | -1.6634364774 | -0.9360315781 | 1.9225272568 |
| H | -0.667845606 | -0.8810040734 | 2.3586509191 |
| H | -2.2513037938 | -0.0887282801 | 2.2906486544 |
| H | -2.1639212878 | -1.8375398482 | 2.2929860913 |
| C | -3.5920200745 | -0.5936137999 | -0.2938063462 |
| H | -3.9095271247 | 0.3688919235 | 0.1178694482 |
| H | -3.8026128955 | -0.5827032192 | -1.3667104435 |
| H | -4.2190581847 | -1.368333735 | 0.159265502 |

**Table S27**. Cartesian coordinates of **Int1-Me**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -0.7214227034 | -0.0105197748 | -0.1804651452 |
| S | -0.3243893716 | -1.1427642491 | 2.3393915791 |
| S | 2.2754951157 | 1.4128418289 | -0.5460828737 |
| P | 1.4474047856 | -0.4315274791 | 1.7239645756 |
| O | 2.1621531624 | 2.7637227199 | 0.0060085172 |
| O | 3.5469913478 | 0.7012725869 | -0.3698175437 |
| C | 1.0039352734 | 0.3931423996 | 0.1779064652 |
| C | -2.1848958022 | -3.3415949632 | 0.4786335607 |
| C | -3.2439967395 | -2.4916231083 | 0.7721853981 |
| C | -3.5485279012 | -1.4319673014 | -0.0814945103 |
| C | -2.8070476508 | -1.2361438103 | -1.2479103713 |
| C | -1.7260054334 | -2.0828049039 | -1.5331906656 |
| C | -1.4179505397 | -3.1300459206 | -0.6635852127 |
| H | -0.6586886161 | 0.6614836434 | -1.5816586608 |
| H | -3.8252399811 | -2.641031156 | 1.673887928 |
| H | -4.3767158078 | -0.7715029577 | 0.1449459257 |
| H | -1.1612710148 | -1.9467683756 | -2.4470814481 |
| H | -0.5808303469 | -3.7819488576 | -0.8831163658 |
| H | -1.9348163656 | -4.1493397467 | 1.1548838707 |
| H | -3.0771285669 | -0.4520191391 | -1.9448858507 |
| C | 2.6785417693 | -1.732711912 | 1.429230155 |
| H | 2.8488667121 | -2.2632564568 | 2.3679454831 |
| H | 3.5986757343 | -1.2832179376 | 1.054663997 |
| H | 2.27146188 | -2.4261019024 | 0.6931382309 |
| C | 1.9445367715 | 1.4925080825 | -2.2961658481 |
| H | 1.001928474 | 2.0094720203 | -2.4556326204 |
| H | 1.9157902687 | 0.4771846763 | -2.6851068912 |
| H | 2.7830454035 | 2.0517129721 | -2.7119414293 |
| C | 2.2451246288 | 0.7417502843 | 2.8565268406 |
| H | 2.4643964923 | 0.2232862133 | 3.7919350536 |
| H | 1.5602904999 | 1.5674440963 | 3.0461897937 |
| H | 3.165158007 | 1.1160762672 | 2.4019909643 |
| Si | -1.2966286213 | 2.2285200107 | 0.1659822144 |
| C | -0.9238771674 | 3.5256259546 | -1.1467324146 |
| H | -1.2417242609 | 3.2063050317 | -2.1422397607 |
| H | -1.4614531962 | 4.4469154414 | -0.8993029365 |
| H | 0.1416031724 | 3.7659443777 | -1.163389138 |
| C | -0.7097607129 | 2.9032288822 | 1.8209417283 |
| H | -0.8578187488 | 2.1663276517 | 2.6149254136 |
| H | 0.3522215011 | 3.1532923057 | 1.7504965473 |
| H | -1.2578552968 | 3.8133929492 | 2.0848288816 |
| C | -3.1875089067 | 2.0271837923 | 0.2616391472 |
| H | -3.4832420003 | 1.363207443 | 1.0774591375 |
| H | -3.6182470484 | 3.0137400299 | 0.4664772953 |

| | | | |
|---|---|---|---|
| H | -3.6254266092 | 1.6625016411 | -0.6707260474 |

**Table S28**. Cartesian coordinates of **Int1-Me** (isomer1).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -0.0661439674 | 0.3862583484 | 0.2740513246 |
| S | 3.9203435344 | 1.4535910303 | -0.4485893358 |
| S | 2.037350847 | -1.8027861428 | 1.2166392713 |
| P | 2.7687669061 | 0.0258361101 | -1.1754773374 |
| O | 3.3937623247 | -2.2215125868 | 0.863176411 |
| O | 1.7910137525 | -1.2708723575 | 2.5519941089 |
| C | 1.453118819 | -0.5614460862 | 0.0000268548 |
| C | 0.6368577785 | 2.9184359191 | -0.0309340512 |
| C | -0.6561971905 | 2.8853273321 | -0.5437633689 |
| C | -1.7190332408 | 2.4168640632 | 0.259337837 |
| C | -1.4868434961 | 2.0076670571 | 1.5717979328 |
| C | -0.1740216092 | 2.0168494775 | 2.0904358005 |
| C | 0.8800934561 | 2.4569852864 | 1.2816355757 |
| H | -0.5272526478 | -0.8125009812 | 1.1111232456 |
| H | -0.8529543315 | 3.2092551482 | -1.5587394354 |
| H | -2.721985894 | 2.3741567266 | -0.1480027153 |
| H | 0.0223236676 | 1.6589946416 | 3.0921679134 |
| H | 1.9015465243 | 2.4119251391 | 1.6409494706 |
| H | 1.4756509307 | 3.248304953 | -0.6316598344 |
| H | -2.3042493331 | 1.6461257542 | 2.1822400099 |
| C | 3.6839037759 | -1.3933217132 | -1.8595451431 |
| H | 4.1593271464 | -1.042652975 | -2.7778718274 |
| H | 3.0020154756 | -2.2168554237 | -2.0862688923 |
| H | 4.4290710483 | -1.7221706429 | -1.1416542655 |
| C | 0.9946411251 | -3.240973523 | 0.9984792074 |
| H | 1.1430319864 | -3.6226466894 | -0.0097741685 |
| H | -0.0416292372 | -2.9725517396 | 1.1862089477 |
| H | 1.3567314562 | -3.9564913769 | 1.7375297207 |
| C | 1.8087360609 | 0.5656969341 | -2.631726701 |
| H | 2.527222391 | 0.9032208706 | -3.3810572246 |
| H | 1.1480870159 | 1.3905537633 | -2.3702128271 |
| H | 1.2174051511 | -0.2639923886 | -3.0255839969 |
| Si | -1.4890656979 | -0.834331576 | -1.2071101743 |
| C | -0.8454714254 | -2.4740461439 | -1.8940828923 |
| H | -0.8703568596 | -3.2564518567 | -1.1332714478 |
| H | -1.4809274799 | -2.8012789 | -2.7229563258 |
| H | 0.1802643307 | -2.3903034776 | -2.262736883 |
| C | -1.923023469 | 0.2493917819 | -2.7077013682 |
| H | -2.4543539252 | 1.154736755 | -2.4002931573 |
| H | -1.0431070987 | 0.5556256149 | -3.2776984866 |
| H | -2.5835705282 | -0.3040493143 | -3.3837463271 |
| C | -3.1418484354 | -1.2063911279 | -0.3622149644 |
| H | -3.6112061473 | -0.2960272929 | 0.021938457 |
| H | -3.8397677442 | -1.6678225146 | -1.0682934289 |
| H | -3.0085017161 | -1.888731876 | 0.4809015517 |

**Table S29**. Cartesian coordinates of **Int1-Me** (isomer2).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 1.1005457692 | -0.7295943804 | 0.0067160033 |
| S | -0.2375860891 | -0.7371100359 | 2.0879242497 |
| S | 0.368100754 | 2.4529209885 | -0.9346556058 |
| P | -0.5688282234 | 1.2391441393 | 1.5712896449 |
| O | -0.1747253801 | 3.6209924962 | -0.2084538432 |
| O | 1.7134911007 | 2.5634485693 | -1.5315229568 |
| C | 0.2301606221 | 1.1286819084 | 0.0824256798 |
| C | 3.3439489961 | -0.4884924782 | 1.076606623 |
| C | 3.0580302412 | -1.8738388067 | 0.9050033385 |
| C | 2.8019637467 | -2.3910175738 | -0.364874436 |
| C | 2.6810055984 | -1.5039459167 | -1.46373231 |
| C | 2.9109881786 | -0.1253210453 | -1.2893160368 |
| C | 3.2995680829 | 0.3676698754 | -0.0163781699 |
| H | -0.0047225916 | -0.5965429162 | -1.069370918 |
| H | 3.0621234814 | -2.5314215475 | 1.765164453 |
| H | 2.6222143821 | -3.450316507 | -0.500010401 |
| H | 2.8036551619 | 0.5740719711 | -2.1068971865 |
| H | 3.4439946753 | 1.4352469625 | 0.094886475 |
| H | 3.556375666 | -0.105894068 | 2.0660745232 |
| H | 2.4184830995 | -1.888544728 | -2.4406651253 |
| C | 0.1310475081 | 2.3669604829 | 2.8158172742 |
| H | -0.3929297735 | 2.2687954982 | 3.7685007164 |
| H | 0.0372032527 | 3.3822133934 | 2.424056493 |
| H | 1.1850987834 | 2.1207798193 | 2.9428957691 |
| C | -0.712404387 | 2.2229924891 | -2.3548248439 |
| H | -1.7375909687 | 2.1691454387 | -1.9923467848 |
| H | -0.422664135 | 1.2990279587 | -2.8551547826 |
| H | -0.5731698145 | 3.0766620124 | -3.0174831156 |
| C | -2.3362356837 | 1.6741996313 | 1.5623173481 |
| H | -2.7566330544 | 1.6118257873 | 2.5678590533 |
| H | -2.8605866015 | 0.9899998232 | 0.8956711231 |
| H | -2.4173467279 | 2.6966602132 | 1.1843726802 |
| Si | -0.589129675 | -2.3361952674 | -0.5644995253 |
| C | -2.3594773321 | -1.6957609179 | -0.586053008 |
| H | -3.032712895 | -2.471000195 | -0.9643920713 |
| H | -2.6779734248 | -1.427262359 | 0.4226691944 |
| H | -2.4597739803 | -0.814687892 | -1.2259220028 |
| C | -0.4912231807 | -3.7906208212 | 0.6386467646 |
| H | -0.766766971 | -3.4971073762 | 1.6526252527 |
| H | -1.1850607343 | -4.5713462136 | 0.3089139992 |
| H | 0.5098946682 | -4.2286374145 | 0.6675877332 |
| C | -0.2368128628 | -3.0726677638 | -2.2752563136 |
| H | 0.7127437221 | -3.6155697957 | -2.3017467504 |
| H | -1.0238366262 | -3.7886618168 | -2.5322471247 |
| H | -0.2137251481 | -2.3087823313 | -3.0571554697 |

**Table S30**. Cartesian coordinates of **TS2-Me**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 1.1184950304 | -0.72657195 | 0.014290385 |
| S | -0.1811761358 | -0.7803328467 | 2.1170672438 |
| S | 0.2872673715 | 2.4580993404 | -0.8970204783 |
| P | -0.5849908815 | 1.1744751104 | 1.5948367639 |
| O | -0.3329222709 | 3.5711037345 | -0.148505645 |
| O | 1.6818001145 | 2.6245353222 | -1.3481556809 |
| C | 0.0393302006 | 1.0594055106 | 0.0113202706 |
| C | 3.3917943423 | -0.5315889411 | 1.0133505809 |

| | | | |
|---|---|---|---|
| C | 3.0566413727 | -1.9020434676 | 0.7891675119 |
| C | 2.7599559313 | -2.3571416702 | -0.4969615918 |
| C | 2.6362504642 | -1.420217234 | -1.5547609783 |
| C | 2.8756736795 | -0.0560175721 | -1.3133718037 |
| C | 3.3226198339 | 0.3751770956 | -0.0318903649 |
| H | -0.1125226448 | -0.3697413615 | -0.8806533866 |
| H | 3.0677768388 | -2.598284711 | 1.617952536 |
| H | 2.5571536806 | -3.4060143922 | -0.6735006287 |
| H | 2.7529119935 | 0.6813263647 | -2.0940643697 |
| H | 3.4982819809 | 1.4327562182 | 0.1203051575 |
| H | 3.6514230798 | -0.2037380431 | 2.0113780207 |
| H | 2.3476393151 | -1.754503396 | -2.5423164441 |
| C | 0.2530260435 | 2.318484934 | 2.7366333632 |
| H | -0.138600418 | 2.1968516117 | 3.7484356506 |
| H | 0.0926933963 | 3.3358353211 | 2.3752959057 |
| H | 1.3184978775 | 2.0875059413 | 2.7234272899 |
| C | -0.6471848998 | 2.296114038 | -2.4219729692 |
| H | -1.7016493708 | 2.2203046203 | -2.1643402246 |
| H | -0.3019566004 | 1.3991622855 | -2.9367480745 |
| H | -0.4479601379 | 3.1823697693 | -3.0235860297 |
| C | -2.3400125024 | 1.6137865513 | 1.7558314429 |
| H | -2.6552507701 | 1.5705540899 | 2.8000207153 |
| H | -2.9288407933 | 0.9194650622 | 1.1572194262 |
| H | -2.4558472587 | 2.6290277007 | 1.3684316983 |
| Si | -0.5651792128 | -2.2992816009 | -0.6074678877 |
| C | -2.3426969869 | -1.6690891015 | -0.5686009502 |
| H | -3.0147701529 | -2.4324772365 | -0.9724631914 |
| H | -2.6462295413 | -1.4540124039 | 0.4576874397 |
| H | -2.4655057518 | -0.7576836412 | -1.1603237297 |
| C | -0.4675254249 | -3.8222121998 | 0.5078562528 |
| H | -1.187226021 | -4.570852394 | 0.1600049953 |
| H | 0.5237525043 | -4.2828489743 | 0.4894061702 |
| H | -0.7098917308 | -3.5742027109 | 1.5426734102 |
| C | -0.2519935928 | -2.9236221674 | -2.3705903365 |
| H | 0.686862547 | -3.4788632923 | -2.454204764 |
| H | -1.0568335586 | -3.6054547891 | -2.6630824364 |
| H | -0.2293767501 | -2.1059389546 | -3.0964111547 |

**Table S31**. Cartesian coordinates of **TS2'-Me** (Silyl transfer).

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 0.5759300981 | -0.354424002 | -0.1721461693 |
| S | 0.1021066413 | 1.603203813 | -1.6197353841 |
| S | -2.5472479408 | -1.2062924184 | 0.5224798023 |
| P | -1.8059796266 | 1.1799426939 | -1.0049597406 |
| O | -3.0340468625 | -1.8021240992 | -0.7429156698 |
| O | -1.9983586891 | -2.175591908 | 1.4863967912 |
| C | -1.4678957895 | 0.1066535763 | 0.313293974 |
| C | 0.7886473961 | -1.9752944138 | -1.8621432489 |
| C | 2.0367672377 | -1.3036624493 | -1.6521207512 |
| C | 2.6587111443 | -1.3256213909 | -0.3996149368 |
| C | 1.9610115293 | -1.8983305632 | 0.6981469917 |
| C | 0.7091931041 | -2.5165374005 | 0.5099760298 |
| C | 0.1466601212 | -2.5962221051 | -0.7963373562 |
| H | 2.502355371 | -0.7786394734 | -2.4761702525 |
| H | 3.6107966831 | -0.8348645381 | -0.2480165003 |
| H | 0.1488870144 | -2.9106397315 | 1.3454144623 |
| H | -0.8334725988 | -3.0400286051 | -0.9275229743 |

| | | | |
|---|---|---|---|
| H | 0.3245860723 | -1.9493755182 | -2.8392351155 |
| H | 2.3887421775 | -1.8535576582 | 1.6914318898 |
| C | -2.7681729299 | 0.5449434013 | -2.4206461434 |
| H | -2.7488092559 | 1.3026523188 | -3.2067468559 |
| H | -3.7939738276 | 0.3244838937 | -2.1212647057 |
| H | -2.3120367178 | -0.3809991024 | -2.7655002562 |
| C | -4.012508082 | -0.5086999268 | 1.2923574625 |
| H | -4.4481637351 | 0.2272525301 | 0.6165205931 |
| H | -3.7238748396 | -0.052169637 | 2.2369370666 |
| H | -4.7055633284 | -1.3355232146 | 1.4457720273 |
| C | -2.7006221602 | 2.717138085 | -0.5983566163 |
| H | -2.7580618231 | 3.3481391323 | -1.4878361029 |
| H | -2.1737480594 | 3.2455894106 | 0.1932678143 |
| H | -3.7117186536 | 2.4731307474 | -0.2628852754 |
| Si | 0.3553196865 | 0.7526470974 | 2.1700160778 |
| C | -0.4115881461 | -0.4624476765 | 3.3708817841 |
| H | 0.0090426184 | -1.4655083581 | 3.2817204916 |
| H | -0.1855394916 | -0.0865134518 | 4.3749729439 |
| H | -1.487874428 | -0.5565128322 | 3.2508002339 |
| C | -0.4573791974 | 2.4423731286 | 2.2492195977 |
| H | -0.1148802919 | 2.9695855778 | 3.1446633492 |
| H | -0.1819930761 | 3.0433493242 | 1.3782755779 |
| H | -1.5429056492 | 2.3484563898 | 2.2845151181 |
| C | 2.114501793 | 1.0186944522 | 2.857792357 |
| H | 2.053530036 | 1.3532427147 | 3.8985011516 |
| H | 2.7175561968 | 0.1067440026 | 2.8462025376 |
| H | 2.6563800578 | 1.7823835583 | 2.2931218444 |
| H | 1.1066623815 | 0.9156019963 | 0.6180273153 |

**Table S32**. Cartesian coordinates of **Pro-Me**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -0.0593024678 | -0.2771522466 | 0.4511434684 |
| S | 0.2921864258 | 2.1243093445 | 1.27374905 |
| S | 2.8112220818 | -0.8229959614 | -1.1876781409 |
| P | 2.044248958 | 1.7036812476 | 0.3807769298 |
| O | 3.4050772757 | -1.3675704732 | 0.0368668812 |
| O | 2.2051093827 | -1.7472275905 | -2.1416172582 |
| C | 1.6171646109 | 0.4121292503 | -0.7890669932 |
| C | 0.2782896075 | -1.4817443079 | 2.5598275495 |
| C | -1.0674446669 | -1.032812774 | 2.3529826416 |
| C | -1.8066043594 | -1.4579595939 | 1.2426561356 |
| C | -1.1367672526 | -2.1662241632 | 0.2013157986 |
| C | 0.2357662464 | -2.469712835 | 0.3347065172 |
| C | 0.9181670946 | -2.198631461 | 1.5661367024 |
| H | 1.3301200232 | 0.8497647298 | -1.7470944833 |
| H | -1.5387466753 | -0.4033106576 | 3.0967135232 |
| H | -2.8448751296 | -1.1764540481 | 1.1369822157 |
| H | 0.7607091398 | -2.9562702715 | -0.4773488595 |
| H | 1.9590727723 | -2.4783173047 | 1.6616648098 |
| H | -1.6724322507 | -2.4598545204 | -0.6920094808 |
| H | 0.8041895763 | -1.1971181184 | 3.4622805604 |
| Si | -1.294233292 | 0.4705640757 | -1.4029373851 |
| C | 4.1377416491 | 0.0035615732 | -2.0708761779 |
| H | 4.8228560742 | -0.781408715 | -2.3900916283 |
| H | 3.7170441607 | 0.5168121502 | -2.9342570039 |
| H | 4.6432515062 | 0.6934671337 | -1.3961695836 |
| C | 2.7761324937 | 3.1742615658 | -0.4102398384 |

| | | | |
|---|---|---|---|
| H | 3.7254559403 | 2.9256137542 | -0.8892402452 |
| H | 2.0743573912 | 3.5565529494 | -1.1519759834 |
| H | 2.9386015472 | 3.9410067705 | 0.3497878336 |
| C | 3.2998470651 | 1.1444209874 | 1.5662755726 |
| H | 2.9573538182 | 0.2232798619 | 2.0344882885 |
| H | 4.2546434631 | 0.9515431733 | 1.075463651 |
| H | 3.4039958886 | 1.9336172894 | 2.3127834663 |
| C | -1.0521282154 | 2.2906809706 | -1.8954516075 |
| H | -0.0102682866 | 2.564072878 | -2.0861493079 |
| H | -1.6138787633 | 2.4833449245 | -2.8156745614 |
| H | -1.4235279201 | 2.9592402879 | -1.1165708712 |
| C | -0.9127293904 | -0.537257598 | -2.9655278808 |
| H | -1.4817342577 | -0.142243678 | -3.8139471932 |
| H | 0.1482866732 | -0.5302851246 | -3.2262329282 |
| H | -1.190569184 | -1.5879515591 | -2.8424817489 |
| C | -3.1747177101 | 0.3169444425 | -1.1639449489 |
| H | -3.5127754125 | 0.8538564604 | -0.2731810281 |
| H | -3.6881862618 | 0.749158235 | -2.0290038213 |
| H | -3.5018579396 | -0.7238423137 | -1.0815316162 |

**Table S33**. Cartesian coordinates of the hydrido complex with $Me_3SiH$.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 1.1957168532 | -0.9716192144 | -0.1262728916 |
| O | 2.1619163291 | 2.388023715 | 0.3152670931 |
| C | -0.0328347472 | 0.9437066965 | -0.1990522586 |
| S | -0.4263951031 | -1.2933286928 | 1.8006863517 |
| P | -0.4699604997 | 0.7020989289 | 1.5154228764 |
| S | 0.963861359 | 2.3584926689 | -0.5325547913 |
| O | 1.1601363726 | 2.4332068341 | -1.9839238204 |
| C | 3.3038419351 | -1.3989256448 | 0.952149412 |
| C | 3.4769435474 | -0.2543798401 | 0.1966040303 |
| C | 3.0069130353 | -0.2353678853 | -1.159459862 |
| C | 2.5532379209 | -1.4122284182 | -1.786112149 |
| C | 2.3944774903 | -2.5939368243 | -1.0023675288 |
| C | 2.6965204537 | -2.5607601389 | 0.3691652796 |
| H | -0.0038939259 | -1.5147264136 | -0.9341779355 |
| H | 3.8558665715 | 0.6585091895 | 0.6338136544 |
| H | 3.0419869695 | 0.6893714441 | -1.722063439 |
| H | 1.9777437614 | -3.4891100142 | -1.4433647483 |
| H | 2.5009984596 | -3.4297507296 | 0.9829286335 |
| H | 2.2637787259 | -1.3977186088 | -2.8278557931 |
| H | 3.5614782321 | -1.406244788 | 2.0040295242 |
| Si | -1.3547772563 | 0.6624857444 | -1.5602059632 |
| C | 0.6985758631 | 1.4927403573 | 2.6682238987 |
| H | 1.7010251236 | 1.1235643966 | 2.4623570623 |
| H | 0.7011668737 | 2.5794040343 | 2.5873260854 |
| H | 0.3816855786 | 1.1893715627 | 3.6677283795 |
| C | -2.0736824648 | 1.4365070308 | 1.9857539461 |
| H | -2.0538010246 | 2.5164561318 | 1.8200374376 |
| H | -2.866014597 | 0.9895054233 | 1.3878783824 |
| H | -2.2625113455 | 1.2308586379 | 3.041304884 |
| C | 0.0541364734 | 3.8413928138 | -0.0795446903 |
| H | -0.1183931942 | 3.8463907043 | 0.995239238 |
| H | 0.7089166013 | 4.6683513189 | -0.3543054706 |
| H | -0.8775378738 | 3.8861797659 | -0.6353098614 |
| C | -0.5881900717 | 0.0796953903 | -3.1706952659 |
| H | 0.3487942861 | 0.6070126184 | -3.3559071932 |

| | | | |
|---|---|---|---|
| H | -0.400811527 | -0.9949473737 | -3.1553069699 |
| H | -1.2750201016 | 0.2997143924 | -3.9941164609 |
| C | -2.301358615 | 2.2522426843 | -1.9540724905 |
| H | -3.1175332539 | 1.9969537306 | -2.637387172 |
| H | -2.7543480685 | 2.7088518206 | -1.0686420217 |
| H | -1.6717568496 | 2.9885490261 | -2.4597211081 |
| C | -2.666177047 | -0.5684999558 | -0.9979736919 |
| H | -2.2606726287 | -1.4099142665 | -0.4365167902 |
| H | -3.4537067057 | -0.0995922427 | -0.4031604076 |
| H | -3.1449756257 | -0.9585691199 | -1.9023603741 |

**Table S34**. Cartesian coordinates of phenyl-substituted carbene complex **Ph-1**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| C | -5.2976783063 | -1.664897816 | -0.0081686901 |
| C | -4.1821224383 | -1.0310542354 | 0.5299475807 |
| C | -5.1955340785 | -2.3364357535 | -1.2280067838 |
| S | -0.7589998396 | -1.3357363887 | 2.1751015841 |
| C | -2.9608812068 | -1.072671615 | -0.1511788728 |
| C | -3.9790798779 | -2.3761598128 | -1.9062622579 |
| C | -1.5860014971 | 1.9557176327 | 2.2496745775 |
| C | -1.9059580917 | 3.27937102 | 2.5480211257 |
| P | -1.4977459811 | -0.2918619735 | 0.5838265897 |
| C | -2.0471477044 | 1.3781895867 | 1.0625069337 |
| C | -2.6842083603 | 4.0260007404 | 1.663482954 |
| C | -2.8568938826 | -1.7471095195 | -1.3687298918 |
| C | -2.8343742302 | 2.1255836094 | 0.1769591909 |
| C | -3.1487161887 | 3.4482943642 | 0.4814441773 |
| Ru | 1.2697210001 | -1.1924855795 | 0.6209889803 |
| C | -0.0827057041 | -0.3227726781 | -0.4179604017 |
| O | -1.2688260622 | 1.0655265732 | -2.2791025782 |
| S | 0.0371978222 | 0.4860879474 | -1.9329462948 |
| C | 3.2168034251 | 3.0077095316 | -2.172123569 |
| O | 0.7098332785 | -0.368456999 | -2.9237596023 |
| C | 1.1781465616 | 1.8515807005 | -1.6401402544 |
| C | 2.9569022395 | 3.920593718 | -1.1520157879 |
| C | 0.8986703401 | 2.7671375819 | -0.6266025818 |
| C | 1.7947076913 | 3.8036743545 | -0.3840793757 |
| C | 2.3222874291 | 1.9642918223 | -2.4219641994 |
| H | -6.2458618546 | -1.6330251025 | 0.5199444145 |
| H | -4.259340704 | -0.5031307675 | 1.4781837731 |
| H | -6.0681250147 | -2.8260160005 | -1.6505557994 |
| H | -3.9017778553 | -2.8915799484 | -2.8586541028 |
| H | -0.98051006 | 1.3640640045 | 2.9312206388 |
| H | -1.5512395432 | 3.7251095149 | 3.4726809002 |
| H | -2.9318758904 | 5.0576653884 | 1.8964061458 |
| H | -1.9079855101 | -1.7702947751 | -1.8983347239 |
| H | -3.1720811852 | 1.6840540022 | -0.7561912783 |
| H | -3.7518623416 | 4.0289421768 | -0.2097749707 |
| H | 4.113679212 | 3.1054089671 | -2.7765590882 |
| H | 3.6549252656 | 4.7295926638 | -0.9576074415 |
| H | -0.0060353227 | 2.6651407232 | -0.0322176117 |
| H | 1.5860662437 | 4.5212228448 | 0.4039289842 |
| H | 2.4977462647 | 1.2426550405 | -3.2145877699 |
| C | 2.9573882029 | -1.092362067 | -0.7259733898 |
| C | 2.5885202621 | -2.4537205531 | -0.5314126539 |
| C | 2.6107867524 | -2.9813058583 | 0.798558712 |
| C | 2.9441886233 | -2.1647375089 | 1.8981599789 |
| C | 3.1773288241 | -0.7810190986 | 1.7280073978 |
| C | 3.1866653014 | -0.2552080697 | 0.3953394193 |
| H | 2.9062635489 | -0.6699858753 | -1.7240527641 |
| H | 2.2916877435 | -4.0048706177 | 0.9652942015 |
| H | 2.859111725 | -2.5660436509 | 2.9030483833 |

| | | | |
|---|---|---|---|
| H | 3.3218980813 | 0.8135239443 | 0.2438432219 |
| C | 2.170135536 | -3.297924345 | -1.7027483142 |
| H | 1.6771912232 | -2.6751196353 | -2.4545034473 |
| H | 3.0465045355 | -3.7766362948 | -2.1547834501 |
| H | 1.4763909441 | -4.0808947493 | -1.3846295821 |
| C | 3.3758663615 | 0.1323574565 | 2.9058726929 |
| H | 4.441630115 | 0.2284952778 | 3.1425057665 |
| H | 2.9830190794 | 1.1298520151 | 2.6886297454 |
| H | 2.8602660983 | -0.2534779137 | 3.7890754595 |

**Table S35**. Cartesian coordinates of **Ph-TS1**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | 1.5898350991 | -0.8585202851 | -0.0756983696 |
| S | 0.0607430661 | -0.9386778935 | -2.0891213202 |
| S | -0.6639629556 | 0.589439322 | 2.0149954377 |
| P | -1.3389086305 | -0.6580634667 | -0.6029276288 |
| O | -2.1117797473 | 0.4531762565 | 2.2770963341 |
| O | 0.2827875374 | 0.3212519223 | 3.1153002126 |
| C | -0.2642641175 | -0.3134143138 | 0.6656958885 |
| C | 1.8101603847 | -3.0752348191 | 0.1854790968 |
| C | 2.9234663158 | -2.6655657066 | -0.6197095708 |
| C | 3.8180414848 | -1.6865819895 | -0.1775209896 |
| C | 3.4950367172 | -1.0201330096 | 1.0519750302 |
| C | 2.441076146 | -1.4533755481 | 1.8837606803 |
| C | 1.5992793693 | -2.530797169 | 1.4654160003 |
| H | 1.6113799363 | 0.8697008027 | -0.148655617 |
| H | 3.0555472771 | -3.1091967778 | -1.6023654404 |
| H | 2.2045598804 | -0.9235106961 | 2.8007297713 |
| H | 1.1078925404 | -3.8045405408 | -0.2064272206 |
| H | 4.1002566173 | -0.1739335105 | 1.3673844961 |
| Si | 2.2966396687 | 1.60661119 | -1.3498983506 |
| C | 0.9672903838 | 2.8578761424 | -1.7754151077 |
| H | 1.3788088084 | 3.8736168523 | -1.7502767363 |
| H | 0.5712140962 | 2.6727800194 | -2.7793544146 |
| H | 0.1345155129 | 2.8218790841 | -1.0650813273 |
| C | 2.9212323825 | 0.7798444219 | -2.9143909832 |
| H | 2.0852789108 | 0.4114656645 | -3.5149100848 |
| H | 3.4608519594 | 1.5332633603 | -3.5042701249 |
| H | 3.6023745685 | -0.0529186385 | -2.7273059254 |
| C | 3.739167739 | 2.4254088695 | -0.4600806081 |
| H | 4.529485805 | 1.7161792758 | -0.1925158222 |
| H | 4.1888833367 | 3.1883214931 | -1.1073096712 |
| H | 3.4040172786 | 2.9197075178 | 0.4570750187 |
| C | 5.0598102149 | -1.3285376912 | -0.9450653999 |
| H | 5.2079038438 | -0.2458922546 | -0.9981991022 |
| H | 5.9365833438 | -1.7580633536 | -0.4473071279 |
| H | 5.0245375453 | -1.7235718445 | -1.963678127 |
| C | 0.4737814258 | -2.9942043492 | 2.3400896615 |
| H | 0.8548975349 | -3.7431822524 | 3.0448255578 |
| H | 0.0636758568 | -2.1538583817 | 2.9060557721 |
| H | -0.3235044427 | -3.447151892 | 1.7453955444 |
| C | -0.4307272426 | 2.3427806693 | 1.6571286328 |
| C | 0.8204518429 | 2.9245741182 | 1.8552806533 |
| C | -1.488228574 | 3.0829015917 | 1.128556763 |
| C | 1.0165564212 | 4.262261748 | 1.5115652913 |
| H | 1.6147335311 | 2.3325350131 | 2.303078724 |
| C | -1.2836031552 | 4.418868132 | 0.7881186756 |
| H | -2.4601729747 | 2.6145094666 | 1.0018360341 |
| C | -0.0330104899 | 5.0093855653 | 0.9763123122 |
| H | 1.9855496265 | 4.7270758174 | 1.6747219647 |
| H | -2.1060922278 | 4.998932639 | 0.3791772526 |
| H | 0.1214268835 | 6.0519797028 | 0.7136575944 |
| C | -2.5971741563 | 0.5892213784 | -1.047742961 |

| | | | |
|---|---|---|---|
| C | -3.7968441068 | 0.6645633752 | -0.3287484856 |
| C | -2.3126763676 | 1.5449961867 | -2.0262261891 |
| C | -4.6893535958 | 1.7047509096 | -0.5768898015 |
| H | -4.0202737578 | -0.0678187352 | 0.4408852127 |
| C | -3.209497817 | 2.5828913296 | -2.2732342056 |
| H | -1.3888620631 | 1.4698716898 | -2.5915520185 |
| C | -4.3944399051 | 2.6676087122 | -1.5434691166 |
| H | -5.6131890377 | 1.7662588748 | -0.0095412995 |
| H | -2.9808027088 | 3.3243108448 | -3.0334365318 |
| H | -5.0923832093 | 3.4784824053 | -1.7318554814 |
| C | -2.3213809218 | -2.1860482248 | -0.38001733 |
| C | -2.6213174675 | -3.014888963 | -1.4641630199 |
| C | -2.7891688637 | -2.5060025414 | 0.8989882087 |
| C | -3.3864903872 | -4.1637353322 | -1.27040375 |
| H | -2.2433299287 | -2.7685481088 | -2.4536550812 |
| C | -3.5601099704 | -3.6530543742 | 1.0858806804 |
| H | -2.548780837 | -1.8525424444 | 1.7364883814 |
| C | -3.85631449 | -4.4824402673 | 0.0041477434 |
| H | -3.6130117904 | -4.8113340842 | -2.1124331705 |
| H | -3.9267098751 | -3.8991025743 | 2.0783152118 |
| H | -4.4516790785 | -5.3785683306 | 0.1541526737 |

**Table S36**. Cartesian coordinates of **Ph-Int1**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -1.5894215119 | -0.6008196803 | 0.0981954394 |
| S | -0.074230861 | -0.7886212311 | 2.0533314828 |
| S | 0.6814805332 | 0.6877262188 | -2.0392445924 |
| P | 1.3446868326 | -0.6107002273 | 0.5646055892 |
| O | 2.1176108505 | 0.4739934155 | -2.306880563 |
| O | -0.2869113058 | 0.4627068439 | -3.1282804369 |
| C | 0.2610254458 | -0.2220999345 | -0.6897662768 |
| C | -1.8516360704 | -3.0353670388 | -0.2960526546 |
| C | -2.9146295184 | -2.6128815025 | 0.5551456746 |
| C | -3.8301858144 | -1.6340446726 | 0.1526143871 |
| C | -3.5322980345 | -0.929639956 | -1.0504084967 |
| C | -2.4681677841 | -1.3294790073 | -1.8890307975 |
| C | -1.6669448466 | -2.4612672943 | -1.5555240642 |
| H | -1.5286113808 | 0.9137372914 | -0.2913869617 |
| H | -3.0375485938 | -3.0922837526 | 1.5222629837 |
| H | -2.2495439147 | -0.7796487378 | -2.7993154982 |
| H | -1.1734843864 | -3.811300171 | 0.0469825207 |
| H | -4.1636444905 | -0.0989891252 | -1.3531359847 |
| Si | -2.3077100454 | 1.3015710291 | 1.3971069652 |
| C | -0.9834802845 | 2.5852769941 | 1.7929898707 |
| H | -1.4246585894 | 3.5895907703 | 1.8135174326 |
| H | -0.5422920808 | 2.3874015942 | 2.775755569 |
| H | -0.176404526 | 2.5937940577 | 1.0520477548 |
| C | -2.9908611792 | 0.6721202496 | 3.0481918933 |
| H | -2.1852703749 | 0.2734824217 | 3.6732268042 |
| H | -3.4492395441 | 1.5128803844 | 3.586168097 |
| H | -3.7512659329 | -0.1065674894 | 2.9395560671 |
| C | -3.7161385757 | 2.238409396 | 0.5360088564 |
| H | -4.5755419743 | 1.6149501449 | 0.267983326 |
| H | -4.0835207011 | 3.0299125874 | 1.2018851413 |
| H | -3.3543028059 | 2.7194128966 | -0.380365394 |
| C | -5.073046321 | -1.3340049107 | 0.943076464 |
| H | -5.2230221053 | -0.2592868361 | 1.0753721528 |
| H | -5.9465754271 | -1.7297847619 | 0.4129022195 |
| H | -5.0361503784 | -1.8025139026 | 1.9296139036 |
| C | -0.5961352565 | -2.92096746 | -2.4966277174 |
| H | -1.0490743079 | -3.4936128057 | -3.3146679457 |
| H | -0.0835655038 | -2.0550277504 | -2.9266634927 |
| H | 0.133178086 | -3.5549498835 | -1.9864178413 |

| | | | |
|---|---|---|---|
| C | 0.5131121169 | 2.4353864472 | -1.6423423544 |
| C | -0.7179887065 | 3.0620481369 | -1.8289536168 |
| C | 1.5837059857 | 3.1129029384 | -1.0599328223 |
| C | -0.8862129731 | 4.3793159294 | -1.4035967123 |
| H | -1.5209357273 | 2.5190601419 | -2.3201926515 |
| C | 1.4074133394 | 4.4304750182 | -0.6420548294 |
| H | 2.5407022525 | 2.6112756858 | -0.9446791719 |
| C | 0.1733458774 | 5.061761363 | -0.8059598681 |
| H | -1.842939315 | 4.874856413 | -1.5444507849 |
| H | 2.2377667993 | 4.9632157152 | -0.1873503247 |
| H | 0.0398210463 | 6.087361983 | -0.4743794337 |
| C | 2.6790088461 | 0.5572544803 | 0.9901256005 |
| C | 3.871193434 | 0.5507044245 | 0.2543908271 |
| C | 2.4645960954 | 1.5380654038 | 1.9621034699 |
| C | 4.830297681 | 1.5340135556 | 0.4819713865 |
| H | 4.037125535 | -0.1998214907 | -0.5124712683 |
| C | 3.4310376843 | 2.5160793355 | 2.1907556152 |
| H | 1.5410789702 | 1.5354362053 | 2.5325433386 |
| C | 4.6095396619 | 2.5192062296 | 1.4461260379 |
| H | 5.7478915507 | 1.5341457006 | -0.0984985376 |
| H | 3.259190823 | 3.2769363349 | 2.9464201095 |
| H | 5.3597725161 | 3.285487406 | 1.619246954 |
| C | 2.2198006526 | -2.197992487 | 0.3320871158 |
| C | 2.5088968371 | -3.0261743175 | 1.4200302474 |
| C | 2.6159802769 | -2.5667624447 | -0.9573866276 |
| C | 3.1903600677 | -4.224883399 | 1.218489333 |
| H | 2.1883200002 | -2.7403312253 | 2.4191831344 |
| C | 3.3046088198 | -3.7639404971 | -1.1520975353 |
| H | 2.3875059415 | -1.9113280294 | -1.7963838495 |
| C | 3.5884304628 | -4.5934234441 | -0.0672797569 |
| H | 3.4083526239 | -4.8720205557 | 2.0630160712 |
| H | 3.6174429885 | -4.0482191718 | -2.152689351 |
| H | 4.1194715152 | -5.5280769498 | -0.2231156222 |

**Table S37**. Cartesian coordinates of **Ph-TS2**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -1.6055138873 | -0.7723936446 | 0.2205143846 |
| S | -0.0097376151 | -0.814936354 | 2.1505433506 |
| S | 0.6869342445 | 0.7593666274 | -2.0172807774 |
| P | 1.3466437151 | -0.5615091252 | 0.6308750853 |
| O | 2.1140500521 | 0.4936081667 | -2.2738802589 |
| O | -0.296558518 | 0.4992583707 | -3.07860907 |
| C | 0.255787893 | -0.0572028399 | -0.5980561384 |
| C | -1.8002420658 | -3.136436157 | -0.1579851688 |
| C | -2.8497384715 | -2.6637777686 | 0.696994931 |
| C | -3.771921049 | -1.6958044537 | 0.2664573235 |
| C | -3.4878797527 | -1.0322253078 | -0.9666224268 |
| C | -2.3955390071 | -1.432118627 | -1.7646380465 |
| C | -1.5959015123 | -2.5718592749 | -1.4124500824 |
| H | -0.913833798 | 0.8204501119 | -0.0840446413 |
| H | -2.9691905468 | -3.1083849778 | 1.6804948542 |
| H | -2.1552527077 | -0.8844563282 | -2.6712586803 |
| H | -1.1305053743 | -3.9116744606 | 0.2028605846 |
| H | -4.1194366954 | -0.213138201 | -1.2957643254 |
| Si | -2.3397035994 | 1.2220088416 | 1.3591051358 |
| C | -1.0626367657 | 2.5704264093 | 1.7597152394 |
| H | -1.5806823307 | 3.5288705645 | 1.8945184116 |
| H | -0.5560415156 | 2.3302255645 | 2.7006802358 |
| H | -0.2950917949 | 2.7180037057 | 0.990651043 |
| C | -3.0510534695 | 0.75353294 | 3.0516939937 |
| H | -2.256427332 | 0.3588343147 | 3.6944254243 |

| | | | |
|---|---|---|---|
| H | -3.4554047352 | 1.6531346448 | 3.5349024157 |
| H | -3.8505803298 | 0.0093989404 | 3.0090183895 |
| C | -3.6934448381 | 2.1172224816 | 0.3721083727 |
| H | -4.5845207071 | 1.5136734249 | 0.1716618983 |
| H | -4.0200737623 | 3.0048642265 | 0.9292327982 |
| H | -3.2989105044 | 2.4592009171 | -0.5921538599 |
| C | -5.0152285499 | -1.3861725091 | 1.0516095022 |
| H | -5.208143427 | -0.3120634962 | 1.1078255808 |
| H | -5.8756705136 | -1.8559702501 | 0.5615753133 |
| H | -4.9486357204 | -1.7813971711 | 2.0681138656 |
| C | -0.4905594449 | -3.0088017542 | -2.324533175 |
| H | -0.9075269433 | -3.4468172653 | -3.2382815714 |
| H | 0.1119276406 | -2.1408114957 | -2.6146900505 |
| H | 0.1567635955 | -3.7451129535 | -1.8410171217 |
| C | 0.5587241954 | 2.5185477428 | -1.6762370709 |
| C | -0.652545347 | 3.1657612045 | -1.9083565116 |
| C | 1.6287837617 | 3.1758206875 | -1.0709059053 |
| C | -0.8025073128 | 4.4922957394 | -1.5050050696 |
| H | -1.4546560677 | 2.6299522413 | -2.4079824642 |
| C | 1.4701499892 | 4.5026085015 | -0.6774199018 |
| H | 2.5674131595 | 2.6505977804 | -0.9131244731 |
| C | 0.2553804471 | 5.1583363608 | -0.8868752093 |
| H | -1.7443077113 | 5.0054864366 | -1.6769806183 |
| H | 2.2974688973 | 5.0230289062 | -0.2036073985 |
| H | 0.1353959204 | 6.190511535 | -0.5713394373 |
| C | 2.6998368499 | 0.5860329792 | 1.0458858797 |
| C | 3.9062558569 | 0.5559652908 | 0.3365099528 |
| C | 2.4664283365 | 1.5979495424 | 1.9822671392 |
| C | 4.8644764443 | 1.5426985281 | 0.557631971 |
| H | 4.0903066721 | -0.2180692077 | -0.4017088982 |
| C | 3.4303840853 | 2.5788842062 | 2.2041375587 |
| H | 1.5289122965 | 1.6159930486 | 2.5292907273 |
| C | 4.6262595379 | 2.5557835788 | 1.4871082571 |
| H | 5.7950051469 | 1.5226117914 | -0.0014421653 |
| H | 3.2435983186 | 3.3626095665 | 2.9322530604 |
| H | 5.3757266143 | 3.3239066647 | 1.6551085168 |
| C | 2.1613028536 | -2.1568366238 | 0.2517360749 |
| C | 2.2672258692 | -3.140260468 | 1.2396463734 |
| C | 2.668566992 | -2.3974501001 | -1.0311695505 |
| C | 2.8785231541 | -4.3590207193 | 0.9477369716 |
| H | 1.8561766267 | -2.9578150753 | 2.2290192032 |
| C | 3.2837033412 | -3.6157755413 | -1.314197267 |
| H | 2.574330671 | -1.6351616982 | -1.8019442955 |
| C | 3.3870324497 | -4.5975163012 | -0.3285456083 |
| H | 2.9537580771 | -5.1222727483 | 1.7167164974 |
| H | 3.676032662 | -3.7990270194 | -2.310316819 |
| H | 3.8611916567 | -5.548036957 | -0.5556107784 |

**Table S38**. Cartesian coordinates of **Ph-Pro**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -1.9577055235 | -0.016849552 | -0.1279395447 |
| S | -0.720607832 | -0.1649799251 | -2.3732228198 |
| S | 0.6846680153 | -0.395269997 | 2.0048855326 |
| P | 0.756238092 | 0.3031757097 | -1.074685814 |
| O | 0.6270667278 | 0.9916407521 | 2.4823563899 |
| O | 0.012545647 | -1.4378019022 | 2.7785362976 |
| C | 0.0875850236 | -0.5415357507 | 0.3592084643 |
| C | 2.3811531953 | -0.366798741 | -1.5874710204 |
| C | 3.5940228073 | 0.2580903327 | -1.2788259972 |
| C | 4.7998646562 | -0.365171739 | -1.5937626097 |
| C | 4.8046620338 | -1.6095165201 | -2.2208628996 |
| C | 3.5981426666 | -2.231892278 | -2.5388926217 |
| C | 2.3902754444 | -1.6139995851 | -2.2242278244 |
| C | 0.9782136877 | 2.1004398513 | -0.8757310288 |

| | | | |
|---|---|---|---|
| C | 1.7602416426 | 2.6364608076 | 0.1537357138 |
| C | 1.9787777167 | 4.0108376438 | 0.2204216513 |
| C | 1.417350594 | 4.856869602 | -0.7347371326 |
| C | 0.6294834413 | 4.3267814973 | -1.75606717 |
| C | 0.409820737 | 2.9525309137 | -1.8281688419 |
| C | 2.4301079067 | -0.8179510957 | 1.9153507198 |
| C | 3.3734949435 | 0.0839798638 | 2.3963974669 |
| C | 4.7287726241 | -0.2374776453 | 2.3044538961 |
| C | 5.1217131415 | -1.4449488902 | 1.7321480112 |
| C | 4.1640721509 | -2.3457706442 | 1.2605916087 |
| C | 2.8112143561 | -2.0384071306 | 1.3564074666 |
| C | -2.7961014253 | 2.288868265 | -0.3071713749 |
| C | -3.7357790672 | 1.2961995516 | -0.7421080022 |
| C | -4.2177575 | 0.3079714797 | 0.1333923426 |
| C | -3.5452002479 | 0.166252833 | 1.3893580771 |
| C | -2.5012954667 | 1.0502410904 | 1.7402076009 |
| C | -2.211472974 | 2.2187800709 | 0.9473091003 |
| H | 0.2603991091 | -1.5946977008 | 0.1330077566 |
| H | 3.6100202485 | 1.2306745493 | -0.7978839156 |
| H | 5.7363903295 | 0.1253461381 | -1.3449195094 |
| H | 5.7468565449 | -2.0911809378 | -2.4661051704 |
| H | 3.5946844719 | -3.1964354256 | -3.0376696374 |
| H | 1.449307077 | -2.0907794789 | -2.4864710004 |
| H | 2.1825884497 | 1.9918683062 | 0.916560969 |
| H | 2.5805125421 | 4.4189209824 | 1.0269252567 |
| H | 1.5885606439 | 5.9279426677 | -0.6797087305 |
| H | 0.1857949018 | 4.982288945 | -2.4995433528 |
| H | -0.2051780546 | 2.5323739616 | -2.6197839585 |
| H | 3.0403511601 | 1.0139667852 | 2.8481619043 |
| H | 5.4740735547 | 0.4556909673 | 2.6829319052 |
| H | 6.1770610246 | -1.6895640511 | 1.6537951657 |
| H | 4.4717620484 | -3.2863965843 | 0.8141915686 |
| H | 2.0606349494 | -2.7406569828 | 1.0018339888 |
| H | -4.1545913185 | 1.3645266318 | -1.7416612736 |
| H | -1.9779224096 | 0.9091402585 | 2.6814256023 |
| H | -3.826704242 | -0.6280255341 | 2.071751278 |
| H | -2.5203360472 | 3.0922073974 | -0.9857217921 |
| Si | -2.3119767179 | -2.3413819596 | -0.2508794165 |
| C | -3.1934318403 | -3.1033222584 | 1.2561334716 |
| H | -4.2183948674 | -2.7604129128 | 1.4302001941 |
| H | -3.235177597 | -4.1936172233 | 1.1331350906 |
| H | -2.6076651361 | -2.8934698479 | 2.1600321838 |
| C | -0.8071037707 | -3.5095464991 | -0.3881809537 |
| H | -0.2578441245 | -3.5866229585 | 0.5592579545 |
| H | -1.1861557457 | -4.5128186987 | -0.6228026899 |
| H | -0.1094114308 | -3.2338373123 | -1.1883546358 |
| C | -1.3044160318 | 3.2949537875 | 1.4693174147 |
| H | -1.8551959033 | 3.9216507353 | 2.1817881274 |
| H | -0.4480906205 | 2.8605984231 | 1.989137566 |
| H | -0.9471382074 | 3.9358255784 | 0.65749842 |
| C | -5.415690894 | -0.5292286587 | -0.2197365122 |
| H | -6.2895257364 | -0.1557277573 | 0.3265840426 |
| H | -5.6343209371 | -0.46802305 | -1.2889685783 |
| H | -5.2787694932 | -1.5800148599 | 0.0440500897 |
| C | -3.2961048428 | -2.7819514213 | -1.8220280422 |
| H | -2.6345364832 | -2.6879186721 | -2.6920614699 |
| H | -3.6481412951 | -3.821503251 | -1.7808488224 |
| H | -4.1626634336 | -2.1391773015 | -2.0018973302 |

**Table S38**. Cartesian coordinates of **Ph-Hydrido complex**.

| Atomic symbol | x | y | z |
|---|---|---|---|
| Ru | -2.2461121976 | -0.224481016 | -0.26324335 |
| O | -0.2132127606 | 2.0874799294 | 1.2675066416 |
| C | -0.0693571022 | -0.4717108285 | 0.5181236438 |
| S | -1.0090623263 | -0.7784924299 | -2.3652427822 |
| P | 0.54586355 | -0.3067401825 | -1.1598221353 |
| S | 0.2830653243 | 0.7808023562 | 1.7134182051 |
| O | -0.1931733943 | 0.2518158594 | 2.9989758412 |
| C | 3.0495079202 | -1.391994547 | -0.5523172228 |
| C | 4.1442643895 | -2.2259036137 | -0.7653578063 |
| C | 4.1856768031 | -3.0478307145 | -1.892486776 |
| C | 3.1340352312 | -3.0311733239 | -2.8076556204 |
| C | 2.0341934964 | -2.2005107411 | -2.5949919734 |
| C | 1.1416434572 | 1.3655336629 | -1.5951742761 |
| C | 2.4521005697 | 1.5761394262 | -2.0355417544 |
| C | 2.8743687381 | 2.8577408966 | -2.3892314648 |
| C | 1.9936232986 | 3.9326656359 | -2.3026049593 |
| C | 0.6771247768 | 3.7209704965 | -1.8873247816 |
| C | 0.2475649172 | 2.442893505 | -1.5492496828 |
| C | 2.0547342638 | 1.041368774 | 1.9081075339 |
| C | 2.6825726393 | 2.0272382033 | 1.1487118729 |
| C | 4.0612258849 | 2.1961836164 | 1.2637768253 |
| C | 4.7934084349 | 1.4047379719 | 2.1487551673 |
| C | 4.1429725189 | 0.4653401779 | 2.9503619552 |
| C | 2.76550673 | 0.2869106206 | 2.8382542594 |
| C | -3.7000925749 | 1.6237517999 | -1.0159666443 |
| C | -3.1933385529 | 2.0803843006 | 0.1881451433 |
| C | -3.1433338173 | 1.1289444842 | 1.2755117119 |
| C | -3.8530675594 | -0.0888053353 | 1.228023544 |
| C | -4.4082405039 | -0.5317025939 | -0.0136658817 |
| C | -4.2278299497 | 0.2947007057 | -1.1445581231 |
| C | 1.9900533934 | -1.3813611655 | -1.4661697178 |
| H | -2.191113687 | -1.7552128401 | -0.1012915442 |
| H | 3.0236665202 | -0.7502455232 | 0.3258665325 |
| H | 4.9603962586 | -2.2343434501 | -0.0486822552 |
| H | 5.0363598006 | -3.7031180231 | -2.0549386423 |
| H | 3.1629934993 | -3.6733608242 | -3.6826690253 |
| H | 1.1988101505 | -2.20399945 | -3.2902657381 |
| H | 3.1546889057 | 0.7515125884 | -2.0939918021 |
| H | 3.8947339878 | 3.0111443379 | -2.7278508028 |
| H | 2.3261273695 | 4.9323163445 | -2.5668894432 |
| H | -0.0163812943 | 4.5543096372 | -1.8248819996 |
| H | -0.7754872163 | 2.2802035198 | -1.2259059674 |
| H | 2.094352861 | 2.6620026093 | 0.4942520401 |
| H | 4.5583252987 | 2.9550430195 | 0.6666687562 |
| H | 5.8677709181 | 1.5390105746 | 2.2344860389 |
| H | 4.7045807206 | -0.1212201668 | 3.6711976577 |
| H | 2.2380872408 | -0.4135228941 | 3.473544997 |
| H | -2.6342607698 | 1.4087398768 | 2.1938846087 |
| H | -4.5649512806 | -0.0545889961 | -2.1152855132 |
| H | -3.9023442285 | -0.7265791278 | 2.1041631069 |
| H | -3.6644223929 | 2.2629305783 | -1.8948643185 |
| Si | -0.0748877592 | -2.2418282477 | 1.2850142165 |
| C | 1.4210530123 | -2.6637797188 | 2.3661612403 |
| H | 2.3908768916 | -2.3576545144 | 1.963558803 |
| H | 1.3057608576 | -2.2578589277 | 3.3759994871 |
| H | 1.4374445625 | -3.7583776176 | 2.4563137366 |
| C | -1.5450111378 | -2.548286939 | 2.4226973091 |
| H | -2.4465563386 | -2.8280481823 | 1.8700302454 |
| H | -1.2928846889 | -3.3698594857 | 3.1059098325 |
| H | -1.7530426613 | -1.6593417987 | 3.0254142887 |
| C | -0.0487508932 | -3.5452429861 | -0.0806879227 |
| H | -0.6436709666 | -3.2881828305 | -0.9614606109 |
| H | 0.9756107242 | -3.7609982011 | -0.4046977347 |
| H | -0.4592728048 | -4.4692222185 | 0.3479602081 |
| C | -2.723585487 | 3.4957734507 | 0.3702151214 |
| H | -3.4570527369 | 4.0550067969 | 0.9633172194 |
| H | -1.7657455419 | 3.5275628158 | 0.8926667978 |

| | | | |
|---|---|---|---|
| H | -2.6259682042 | 3.9998010076 | -0.5969670811 |
| C | -5.1305824837 | -1.8471414593 | -0.1138210763 |
| H | -6.1981297533 | -1.7062926429 | 0.0896177332 |
| H | -5.0232100542 | -2.2727366175 | -1.1149465136 |
| H | -4.7357981272 | -2.5658034692 | 0.609003771 |

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