

Supporting Information for:

## Catalytic Activation of Remote Alkenes through Silyl-Rhodium(III) Complexes

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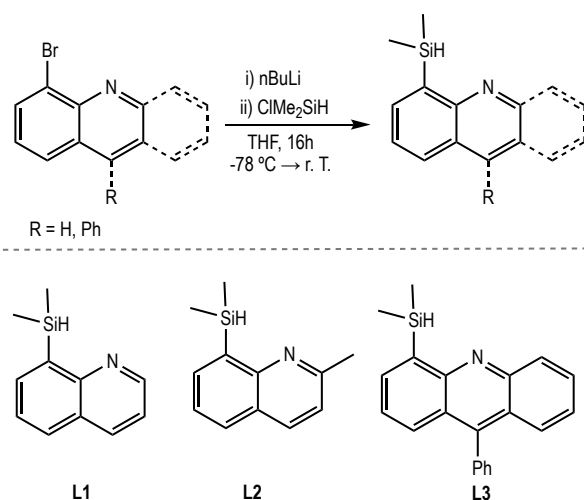
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## 1. General Procedures

All manipulations, unless otherwise stated, were performed under an atmosphere of nitrogen, using standard Schlenk techniques. Glassware was oven dried at 110°C overnight and flamed under vacuum prior to use. Dry and oxygen free solvents were employed.  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ ,<sup>1</sup>  $[\text{NaBARF}_4]$ ,<sup>2</sup> and 4-bromo-9-phenylacridine<sup>3</sup> were prepared as previously described. 8-(dimethylsilyl)quinoline,<sup>4</sup> and 8-(dimethylsilyl)-2-methylquinoline<sup>5</sup> were prepared through as previously reported including some modifications.  $\text{Et}_3\text{SiH}$  and alkenes were purchased from Aldrich. NMR spectra were recorded on Bruker Advance DPX 300 MHz and Bruker Ultra Shift 500 MHz spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to the residual solvent signals.  $^{31}\text{P}$  NMR spectra was reference against 85%  $\text{H}_3\text{PO}_4$  (external). Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS was recorded on LC/Q-TOF with Agilent Jet Stream ESI ionization source. Microanalysis was carried out with a LECO TRUSPEC microanalyzer.

## 2. Synthesis and characterization of pro-ligands L1, L2 and L3



Scheme S.1. Synthesis of L1, L2 and L3.

To a Schlenk charged with 2.4 mmol of the corresponding quinoline (8-bromoquinoline, 500 mg; 8-bromo-2-methylquinoline, 534 mg; 4-bromo-9-phenylacridine, 803 mg) in THF (10 mL) was added n-BuLi (1.5 mL of a 1.6 M solution in hexane, 2.4 mmol) at -78 °C. The reaction mixture was stirred for 1 hour and dichloromethylsilane (0.3 mL, 2.6 mmol) was added dropwise. After being stirred at room temperature overnight, the solvent was removed, quenched with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Organic layers were dried with Mg(SO<sub>4</sub>)<sub>2</sub> and solvent removed under vacuum to give L (L1= 333 mg, 74 %; L2= 334 mg, 69 %; L3= 622 mg, 82 %).

### Characterization of L1

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.9 (dd, J<sub>H-H</sub> = 2.4 Hz, J<sub>H-H</sub> = 1.8 Hz, 1H<sub>arom.</sub>), 8.15 (dd, J<sub>H-H</sub> = 6.5 Hz, J<sub>H-H</sub> = 1.8 Hz, 1H<sub>arom.</sub>), 7.9 (dd, J<sub>H-H</sub> = 5.3 Hz, J<sub>H-H</sub> = 1.6 Hz, 1H<sub>arom.</sub>), 7.8 (dd, J<sub>H-H</sub> = 6.5 Hz, J<sub>H-H</sub> = 1.55 Hz, 1H<sub>arom.</sub>), 7.5 (dd, J<sub>H-H</sub> = 6.6 Hz, J<sub>H-H</sub> = 1.5 Hz, 1H<sub>arom.</sub>), 7.4 (dd, J<sub>H-H</sub> = 4.2 Hz, J<sub>H-H</sub> = 4.0 Hz, 1H<sub>arom.</sub>), 4.8 (sept, J<sub>H-H</sub> = 3.7 Hz, Si-H), 0.5 (d, 6H, J<sub>H-H</sub> = 3.7 Hz, Si-(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):** δ 153.6 (C<sub>arom.</sub>), 150.5 (C<sub>arom.</sub>), 140.2 (C<sub>arom.</sub>), 137.6 (C<sub>arom.</sub>), 137.2 (C<sub>arom.</sub>), 130.5 (C<sub>arom.</sub>), 128.7 (C<sub>arom.</sub>), 127.1 (C<sub>arom.</sub>), 121.9 (C<sub>arom.</sub>), -2.1 (2C, Si-(CH<sub>3</sub>)<sub>2</sub>).

**<sup>29</sup>Si NMR (Chemical shift from <sup>1</sup>H-<sup>29</sup>Si HMBC) (500 MHz, CDCl<sub>3</sub>):** δ -19.2.

**Microanalysis (C<sub>11</sub>H<sub>13</sub>NSi):** Requires: C 70.53, H 7.00, N 7.48. Exp.: C 70.58, H 6.98, N 7.51.

### Characterization of L2

**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.03 (d, J<sub>H-H</sub> = 8.4 Hz, 1H<sub>arom.</sub>), 7.92 (dd, J<sub>H-H</sub> = 6.7 Hz, J<sub>H-H</sub> = 1.5 Hz, 1H<sub>arom.</sub>), 7.80 (dd, J<sub>H-H</sub> = 8.2 Hz, J<sub>H-H</sub> = 1.3 Hz, 1H<sub>arom.</sub>), 7.47 (dd, J<sub>H-H</sub> = 8.1 Hz, J<sub>H-H</sub> = 6.5 Hz, 1H<sub>arom.</sub>), 7.28 (d, J<sub>H-H</sub> = 8.4 Hz, 1H<sub>arom.</sub>), 4.75 (sept, J<sub>H-H</sub> = 3.8 Hz, Si-H), 2.75 (s, 3H, CH<sub>3</sub>), 0.55 (d, J<sub>H-H</sub> = 3.7 Hz, 6H, Si-(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):** δ 158 (C<sub>arom.</sub>), 153 (C<sub>arom.</sub>), 139 (C<sub>arom.</sub>), 137 (C<sub>arom.</sub>), 136.7 (C<sub>arom.</sub>), 129.7 (C<sub>arom.</sub>), 128 (C<sub>arom.</sub>), 125.8 (C<sub>arom.</sub>), 122 (C<sub>arom.</sub>), 26 (CH<sub>3</sub>), -2 (Si-(CH<sub>3</sub>)<sub>2</sub>).

**<sup>29</sup>Si NMR (Chemical shift from <sup>1</sup>H-<sup>29</sup>Si HMBC) (500 MHz, CDCl<sub>3</sub>):** δ -17.9.

**Microanalysis (C<sub>12</sub>H<sub>15</sub>NSi):** Requires: C 71.58, H 7.51, N 6.96. Exp.: C 71.62, H 7.55, N 6.95.

### Characterization of L3

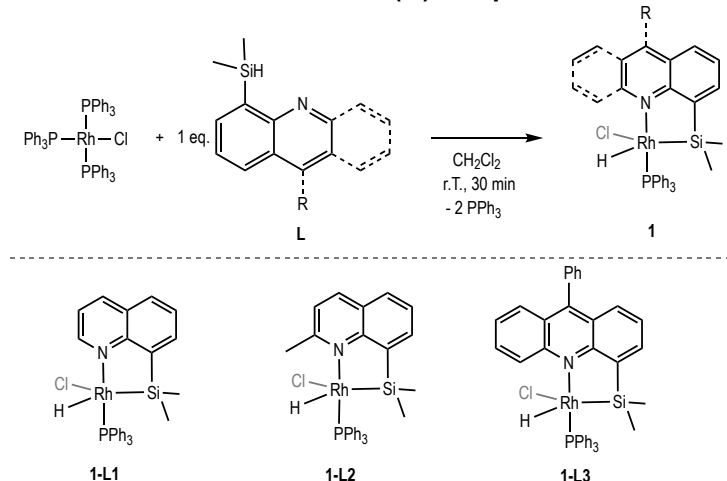
**<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** δ 8.3 (dt, J<sub>H-H</sub> = 8.9 Hz, J<sub>H-H</sub> = 0.9 Hz, 1H<sub>arom.</sub>), 8.03 (dd, J<sub>H-H</sub> = 6.3 Hz, J<sub>H-H</sub> = 1.4 Hz, 1H<sub>arom.</sub>), 7.8-7.38 (m, 9H<sub>arom.</sub>), 4.87 (sept, J<sub>H-H</sub> = 3.7 Hz, Si-H), 0.66 (d, J<sub>H-H</sub> = 3.8 Hz, Si-(CH<sub>3</sub>)<sub>2</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):** 154-124 (19C<sub>aromático</sub>), δ -2 (Si-(CH<sub>3</sub>)<sub>2</sub>).

**<sup>29</sup>Si NMR (Chemical shift from <sup>1</sup>H-<sup>29</sup>Si HMBC) (500 MHz, CDCl<sub>3</sub>):** δ -16.8

**Microanalysis (C<sub>21</sub>H<sub>19</sub>NSi):** Requires: C 80.46, H 6.11, N 4.47. Exp.: C 80.42, H 6.15, N 4.50.

### 3. Synthesis and characterization of neutral Rh(III) complexes 1-L1, 1-L2 and 1-L3



**Scheme S.2.** Synthesis of **1-L1**, **1-L2** and **1-L3**.

To a Schlenk charged with  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$  (100 mg, 0.11 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) and excess of **1.2** (0.13 mmol) of ligand **L** (**L1**, 25 mg; **L2**, 27 mg; **L3**, 41 mg) was added. The mixture was stirred for 60 minutes and concentrated under vacuum. Addition of 20 mL of pentane gave a white precipitate that was washed with pentane (2 x 3 mL) and dried under vacuum. Yield of **1** (**1-L1**= 52 mg, 80 %; **1-L2**= 55 mg, 83 %; **1-L3**= 63 mg, 81 %).

#### Characterization of 1-L1

$^1\text{H}$  RMN (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.52 (t,  $J_{\text{H-H}} = 4$  Hz,  $1\text{H}_{\text{arom.}}$ ),  $\delta$  8.28 (d,  $J_{\text{H-H}} = 8.0$  Hz,  $1\text{H}_{\text{arom.}}$ ), 7.94-7.26 (m,  $19\text{H}_{\text{arom.}}$ ), 0.64 (s, 3H, Si-CH<sub>3</sub>), -0.20 (s, 3H, Si-CH<sub>3</sub>), -17.23 (dd,  $J_{\text{Rh-H}} = 29.0$  Hz,  $J_{\text{P-H}} = 21.3$  Hz, Rh-H).

$^{13}\text{C}\{^1\text{H}\}$  RMN (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  154-121 ( $27\text{C}_{\text{arom.}}$ ), 7.7 (Si-CH<sub>3</sub>), 4.1 (Si-CH<sub>3</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  48.6 (d,  $J_{\text{P-Rh}} = 149.1$  Hz).

$^{29}\text{Si}$  NMR (Chemical shift from  $^1\text{H}$ - $^{29}\text{Si}$  HMBC) (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  41.2 ppm.

ESI-MS (MeCN): calc: 552.08; found  $m/z$  552.08. For the ion  $[\text{C}_{47}\text{H}_{43}\text{NP}_2\text{SiRh}]^+$ .

#### Characterization of 1-L2

$^1\text{H}$  RMN (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.12 (d,  $J_{\text{H-H}} = 7.9$  Hz,  $1\text{H}_{\text{arom.}}$ ), 7.9-6.86 (m,  $19\text{H}_{\text{arom.}}$ ), 3.02 (s, 3H, Si-CH<sub>3</sub>), 0.71 (s, 3H, Si-CH<sub>3</sub>), -0.17 (s, 3H, Si-CH<sub>3</sub>), -16.77 (dd,  $J_{\text{Rh-H}} = 27.7$  Hz,  $J_{\text{P-H}} = 21.8$  Hz, Rh-H).

$^{13}\text{C}\{^1\text{H}\}$  RMN (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  161-123 ( $27\text{C}_{\text{arom.}}$ ), 26.35 (1C, CH<sub>3</sub>), 7.39 (2C, Si-(CH<sub>3</sub>)<sub>2</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  48.35 (d,  $J_{\text{P-Rh}} = 147.15$  Hz).

$^{29}\text{Si}$  NMR (Chemical shift from  $^1\text{H}$ - $^{29}\text{Si}$  HMBC) (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  41.2 ppm.

ESI-MS (MeCN): calc: 566.09; found  $m/z$  566.09. For the ion  $[\text{C}_{47}\text{H}_{43}\text{NP}_2\text{SiRh}]^+$ .

#### Characterization of 1-L3

$^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.66 (d,  $J_{\text{H-H}} = 8.64$  Hz,  $1\text{H}_{\text{arom.}}$ ), 7.98-7.22 (m,  $26\text{H}_{\text{arom.}}$ ), 0.80 (s, 3H, Si-CH<sub>3</sub>), -0.11 (s, 3H, Si-CH<sub>3</sub>), -16.33 (dd,  $J_{\text{Rh-H}} = 27.3$  Hz,  $J_{\text{P-H}} = 21.4$  Hz, Rh-H).

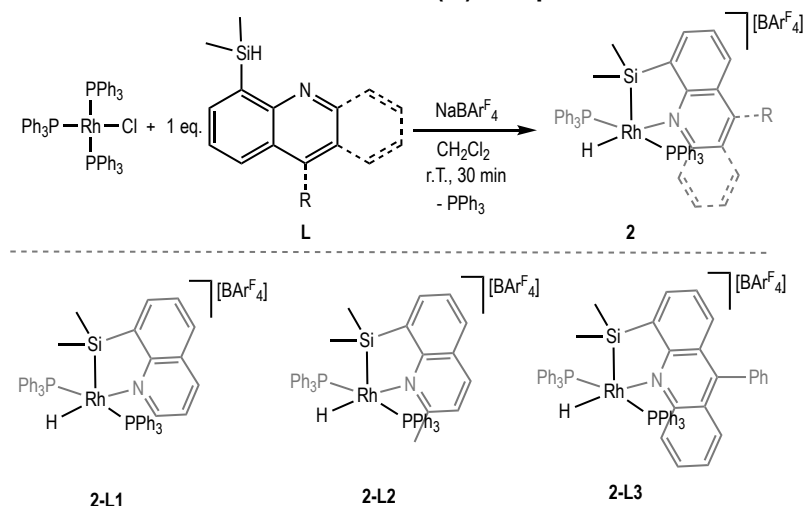
$^{13}\text{C}\{^1\text{H}\}$  RMN (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  150-110 ( $37\text{C}_{\text{arom.}}$ ), 7.63 (2C, Si-(CH<sub>3</sub>)<sub>2</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  48.45 (d,  $J_{\text{P-Rh}} = 147.82$  Hz).

$^{29}\text{Si}$  NMR (Chemical shift from  $^1\text{H}$ - $^{29}\text{Si}$  HMBC) (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  50.7 ppm.

ESI-MS (MeCN): calc: 678.13; found  $m/z$  678.12. For the ion  $[\text{C}_{47}\text{H}_{43}\text{NP}_2\text{SiRh}]^+$ .

#### 4. Synthesis and characterization of cationic Rh(III) complexes 2-L1, 2-L2 and 2-L3



**Scheme S3.** Synthesis of **2-L1**, **2-L2** and **2-L3**.

To a Schlenk charged with  $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$  (100 mg, 0.11 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 ml), the equimolar amount (0.11 mmol) of **L** (**L1**, 21 mg; **L2**, 23 mg; **L3**, 35 mg) and  $\text{NaBARF}_4$  (98 mg, 0.11 mmol) were added. The mixture was stirred for 30 minutes, filtered of via cannula and concentrated under vacuum. Addition of 20 mL of pentane gave a pale yellow precipitate that was washed with with EtOH (2 x 3mL) and pentane (2 x 3mL) and dried under vacuum. Yield of **2** (**2-L1**= 157 mg, 85 %; **2-L2**= 141 mg, 76%; **2-L3**= 123 mg, 62 %).

##### Characterization of 2-L1

$^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15-7.03 (48 $\text{H}_{\text{arom.}}$ ), 0.23 (s, 6H, Si-( $\text{CH}_3$ )<sub>2</sub>), -12.41 (dt,  $J_{\text{Rh-H}} = 17.9$  Hz,  $J_{\text{P-H}} = 13.2$  Hz, Rh-H).

$^{13}\text{C}\{^1\text{H}\}$  RMN (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  164-117 (69 $\text{C}_{\text{arom.}}$ ), 10.2 (Si-( $\text{CH}_3$ )<sub>2</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  43.8 (d,  $J_{\text{P-Rh}} = 121$  Hz).

$^{29}\text{Si}$  NMR (Chemical shift from  $^1\text{H}$ - $^{29}\text{Si}$  HMBC) (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  56.4 ppm.

ESI-MS (MeCN): calc: 814.17; found m/z 814.17. For the ion  $[\text{C}_{47}\text{H}_{43}\text{NP}_2\text{SiRh}]^+$ .

##### Characterization of 2-L2

$^1\text{H}$  RMN (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.15-7.09 (47 $\text{H}_{\text{arom.}}$ ), 1.88 (s, 3H,  $\text{CH}_3$ ) 0.18 (s, 6H, Si-( $\text{CH}_3$ )<sub>2</sub>), -12.48 (dt,  $J_{\text{Rh-H}} = 16.6$  Hz,  $J_{\text{P-H}} = 13.4$  Hz, Rh-H).

$^{13}\text{C}\{^1\text{H}\}$  RMN (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  164-117 (69 $\text{C}_{\text{arom.}}$ ), 27.1 (3C,  $\text{CH}_3$ ), 9.49 (2C, Si-( $\text{CH}_3$ )<sub>2</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  43.1 (d,  $J_{\text{P-Rh}} = 123$  Hz).

$^{29}\text{Si}$  NMR (Chemical shift from  $^1\text{H}$ - $^{29}\text{Si}$  HMBC) (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  58.6 ppm.

ESI-MS (MeCN): calc: 828.19; found m/z 828.18. For the ion  $[\text{C}_{48}\text{H}_{45}\text{NP}_2\text{SiRh}]^+$ .

##### Characterization of 2-L3

$^1\text{H}$  RMN (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.8-6.85 (54 $\text{H}_{\text{arom.}}$ ), 0.24 (s, 6H, Si-( $\text{CH}_3$ )<sub>2</sub>), -12.07 (dt,  $J_{\text{Rh-H}} = 17.5$  Hz,  $J_{\text{P-H}} = 12.6$ Hz, Rh-H).

$^{13}\text{C}\{^1\text{H}\}$  RMN (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  164-117 (69 $\text{C}_{\text{arom.}}$ ), 10.9 (Si-( $\text{CH}_3$ )<sub>2</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ ):  $\delta$  45.0 (d,  $J_{\text{P-Rh}} = 123$  Hz). ppm.

$^{29}\text{Si}$  NMR (Chemical shift from  $^1\text{H}$ - $^{29}\text{Si}$  HMBC) (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  58.4 ppm.

ESI-MS (MeCN): calc: 940.22; found m/z 940.21. For the ion  $[\text{C}_{57}\text{H}_{49}\text{NP}_2\text{SiRh}]^+$ .

## 5. Catalytic experiments

All catalytic reactions were performed under the same conditions: nitrogen atmosphere, room temperature and without solvent. The catalyst amount used was 0.5 mol%. Conversions were calculated by  $^1\text{H}$  NMR, based on the Si-H signal of the remaining silane, using 1,2-dichloroethane as internal standard (added at the end of the reaction, 0.125 mmol of dichloroethane for 0.25 mmol of silane). In the  $^1\text{H}$  NMR spectra, the signals integrate 2:1 for 1,2-dichloroethane and Si-H, respectively.

### Hydrosilylation of 1-Hexene (Table 1)

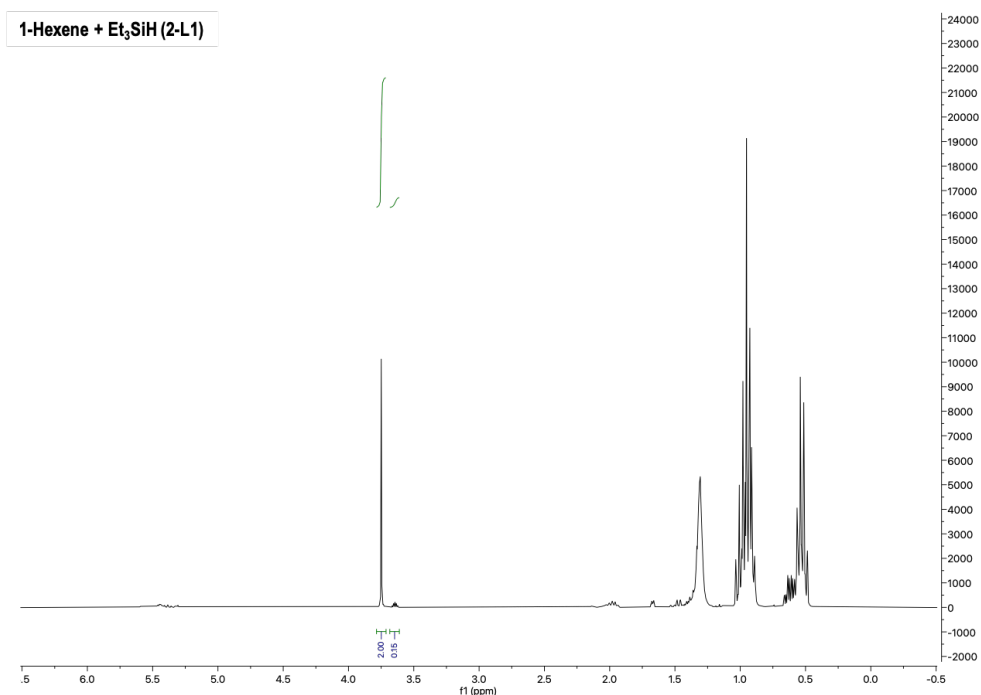


Figure S.4.  $^1\text{H}$  NMR in CDCl<sub>3</sub>.

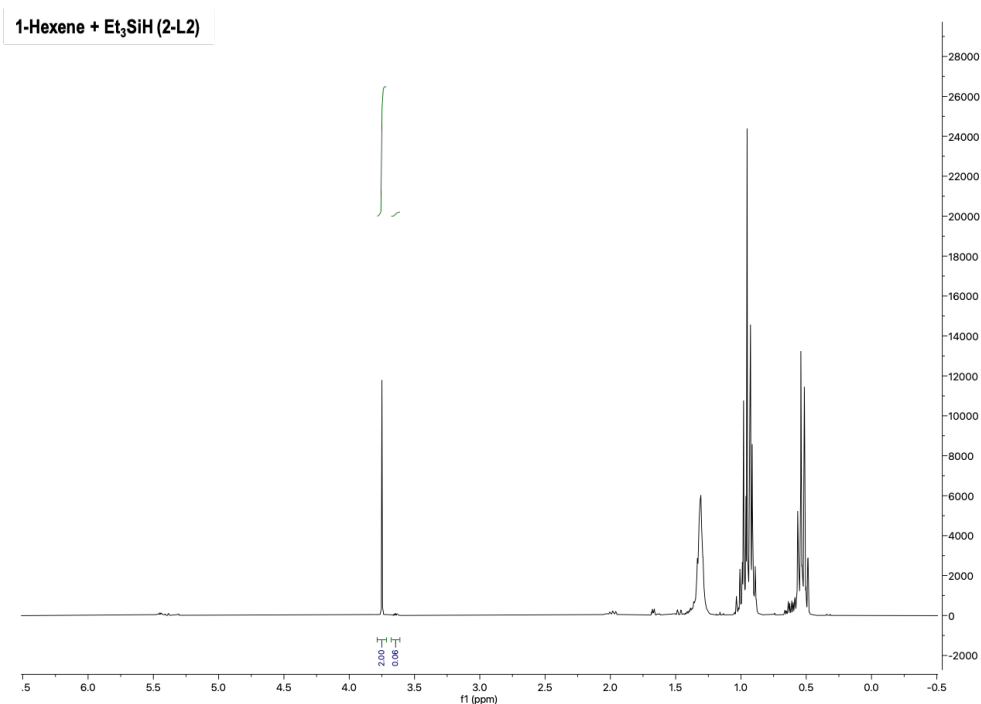


Figure S.5.  $^1\text{H}$  NMR in CDCl<sub>3</sub>.

1-Hexene + Et<sub>3</sub>SiH (2-L3)

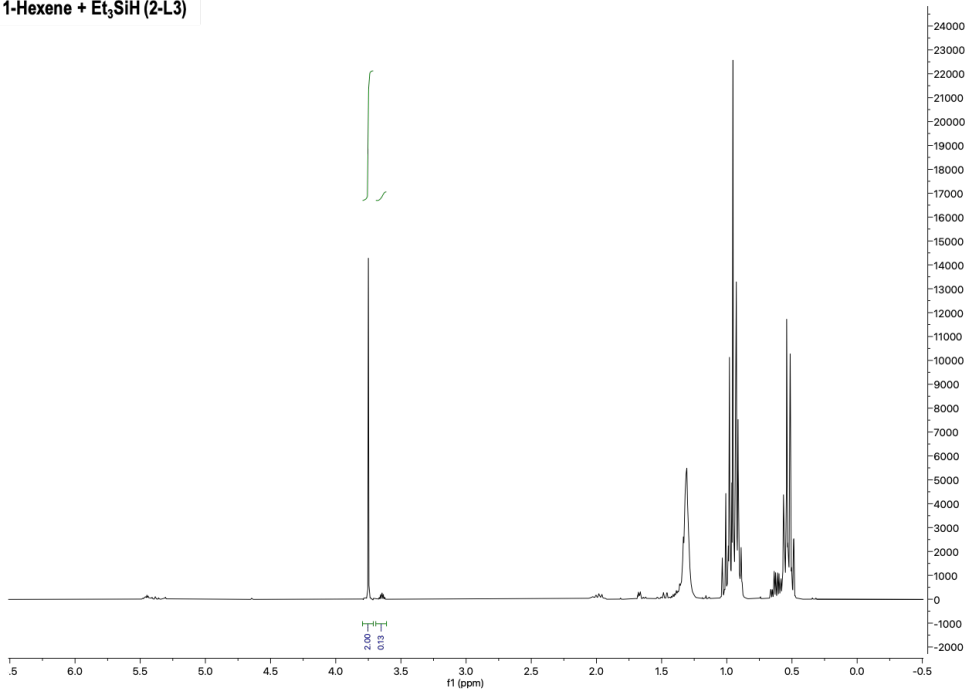


Figure S.6. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

1-Hexene + Et<sub>3</sub>SiH (2-L2) after 48h of reaction

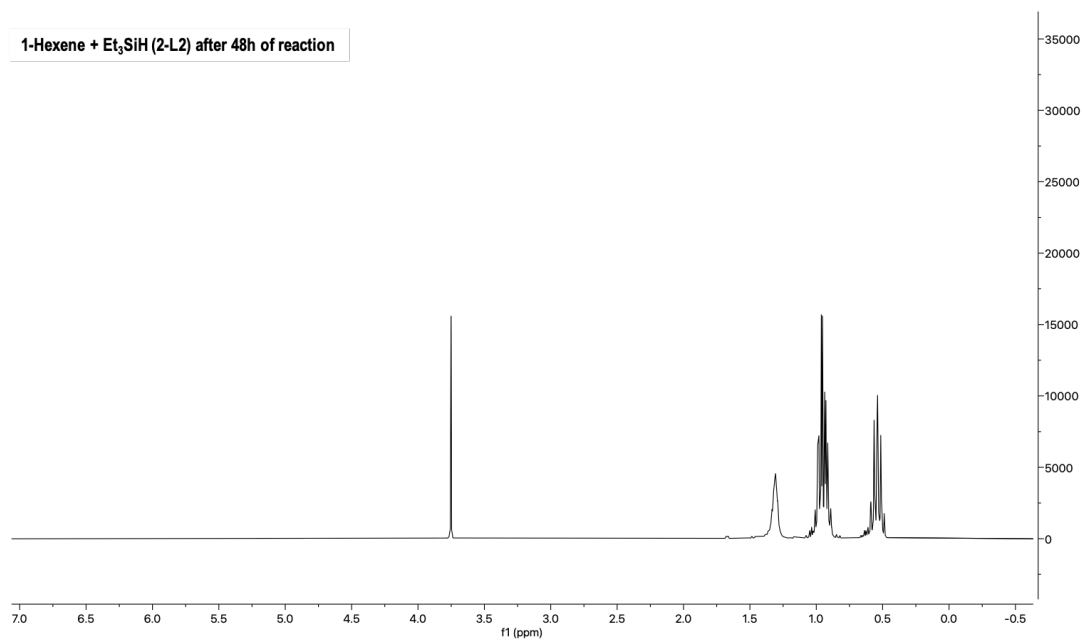


Figure S.7. <sup>1</sup>H NMR in CDCl<sub>3</sub> (48 h reaction).

## Hydrosilylation of *trans*-3-Hexene (Table 2)

*trans*-3-Hexene + Et<sub>3</sub>SiH (2-L1)

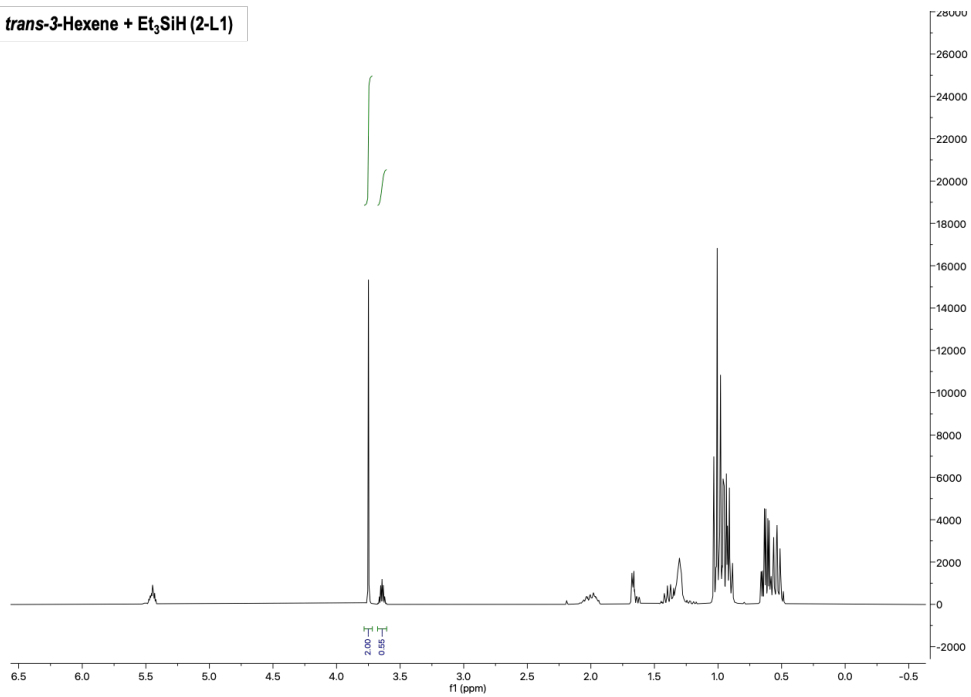


Figure S.8. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*trans*-3-Hexene + Et<sub>3</sub>SiH (2-L2)

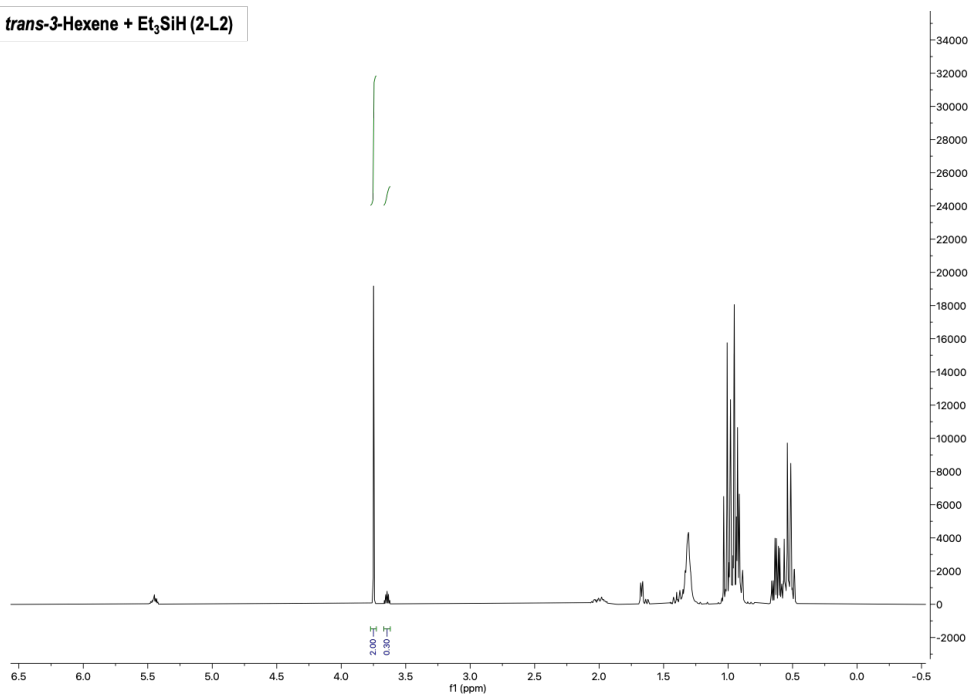
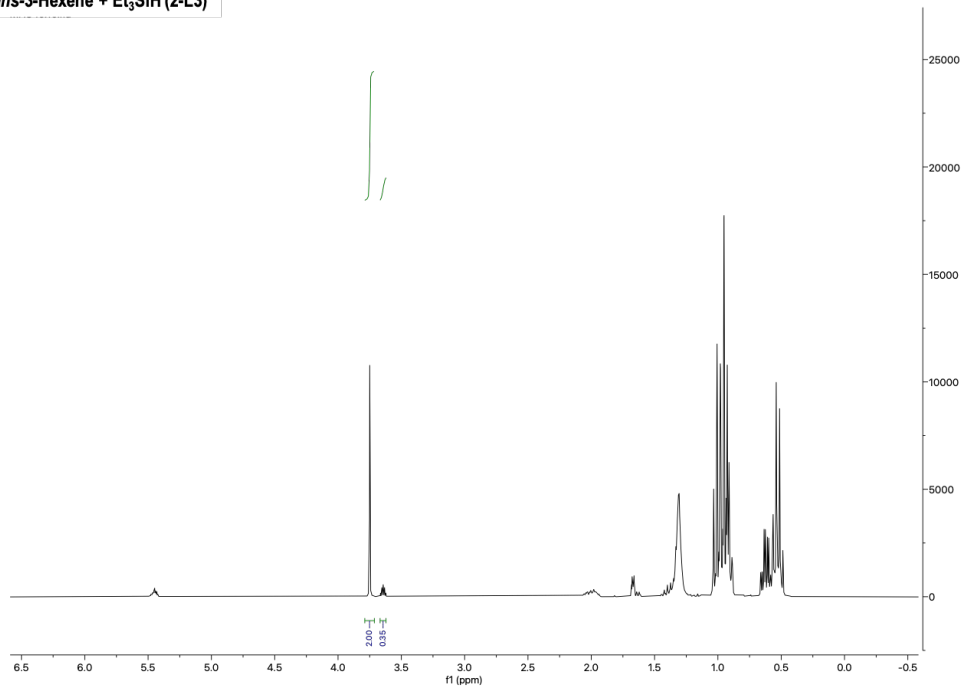


Figure S.9. <sup>1</sup>H NMR in CDCl<sub>3</sub>.



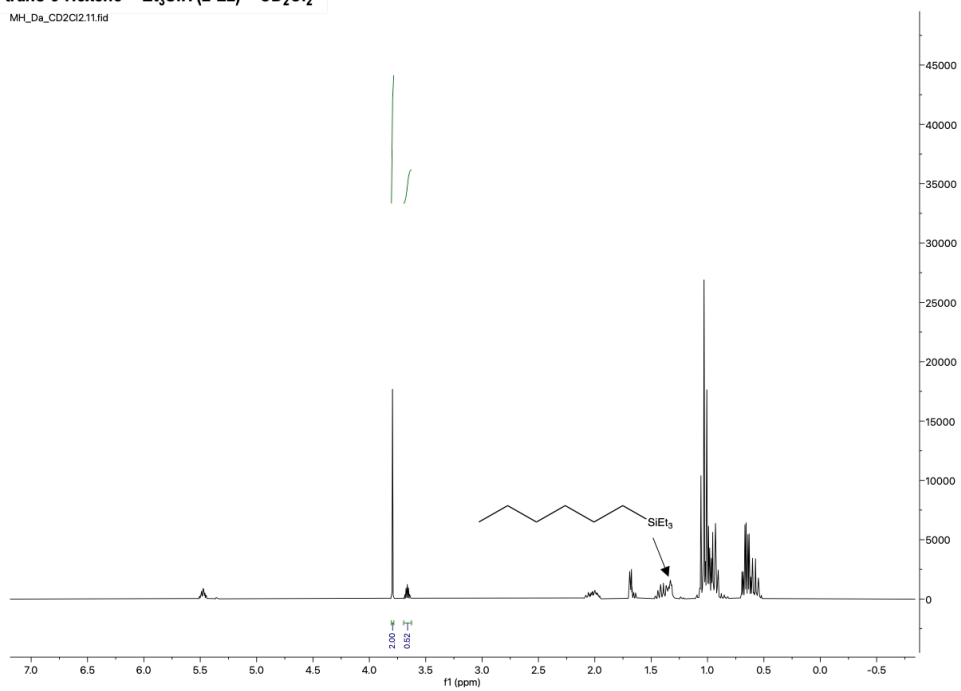
**trans-3-Hexene + Et<sub>3</sub>SiH (2-L3)**



**Figure S.10.** <sup>1</sup>H NMR in CDCl<sub>3</sub>.

**trans-3-Hexene + Et<sub>3</sub>SiH (2-L2) + CD<sub>2</sub>Cl<sub>2</sub>**

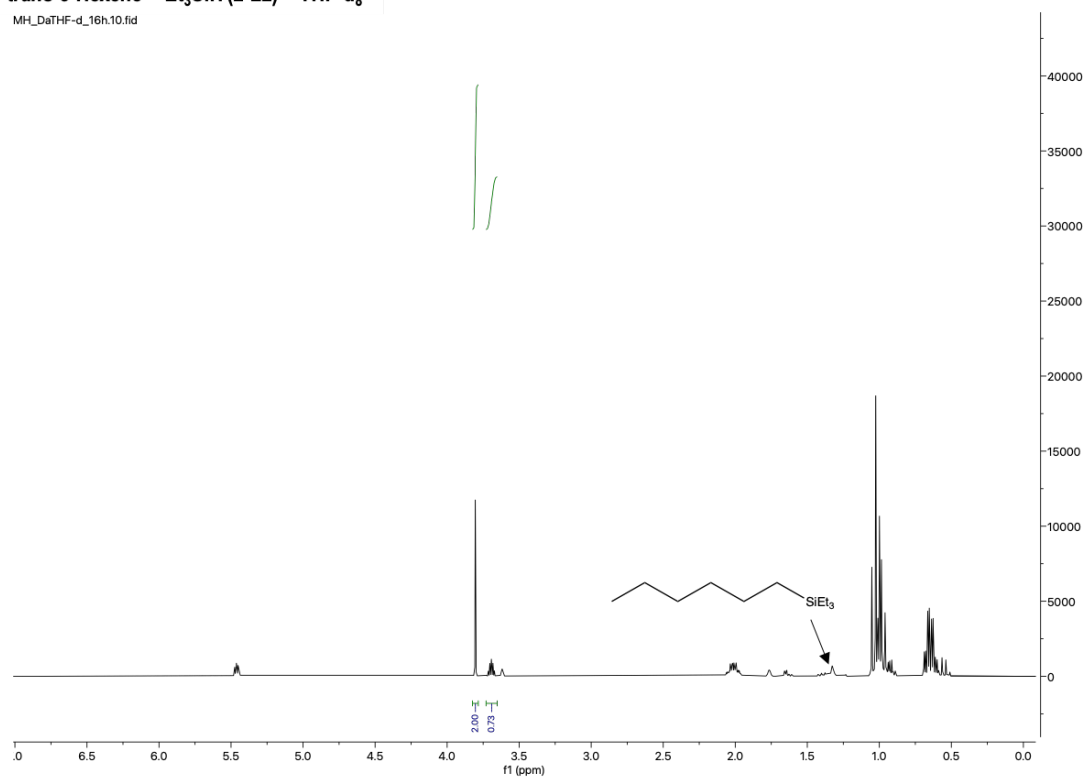
MH\_Da\_CD2Cl2.11.fid



**Figure S.11.** <sup>1</sup>H NMR in CD<sub>2</sub>Cl<sub>2</sub>.

***trans*-3-Hexene + Et<sub>3</sub>SiH (2-L2) + THF-d<sub>8</sub>**

MH\_DaTHF-d\_16h.10.fid



**Figure S.12.** <sup>1</sup>H NMR in THF-d<sub>8</sub>.

## Hydrosilylation of internal alkenes using 2-L2 (Table 3)

*trans*-2-Hexene + Et<sub>3</sub>SiH (2-L2)

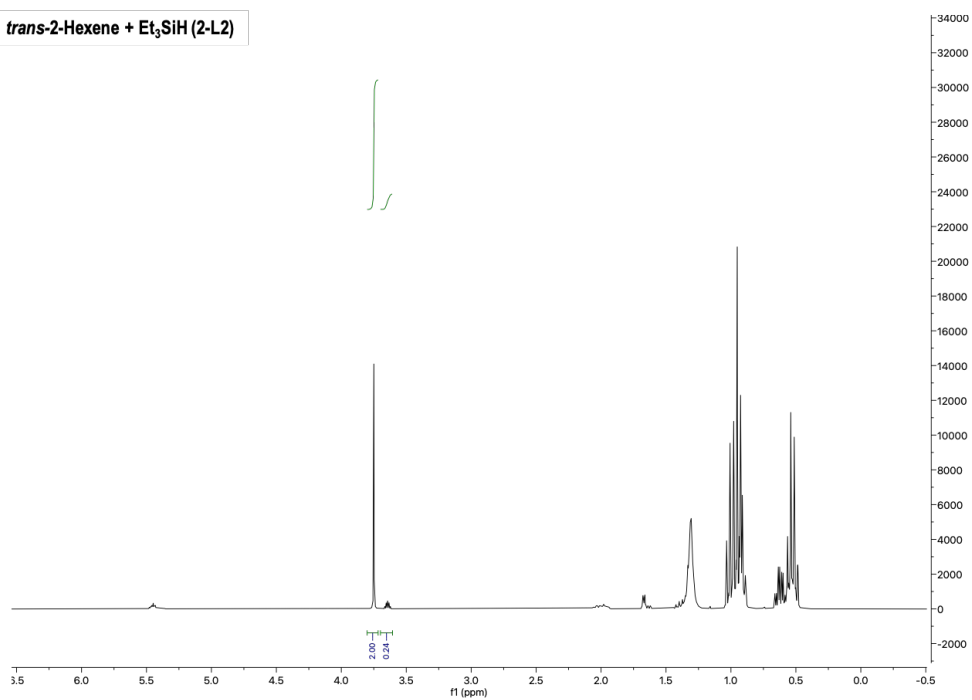


Figure S.13. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*cis*-2-Hexene + Et<sub>3</sub>SiH (2-L2)

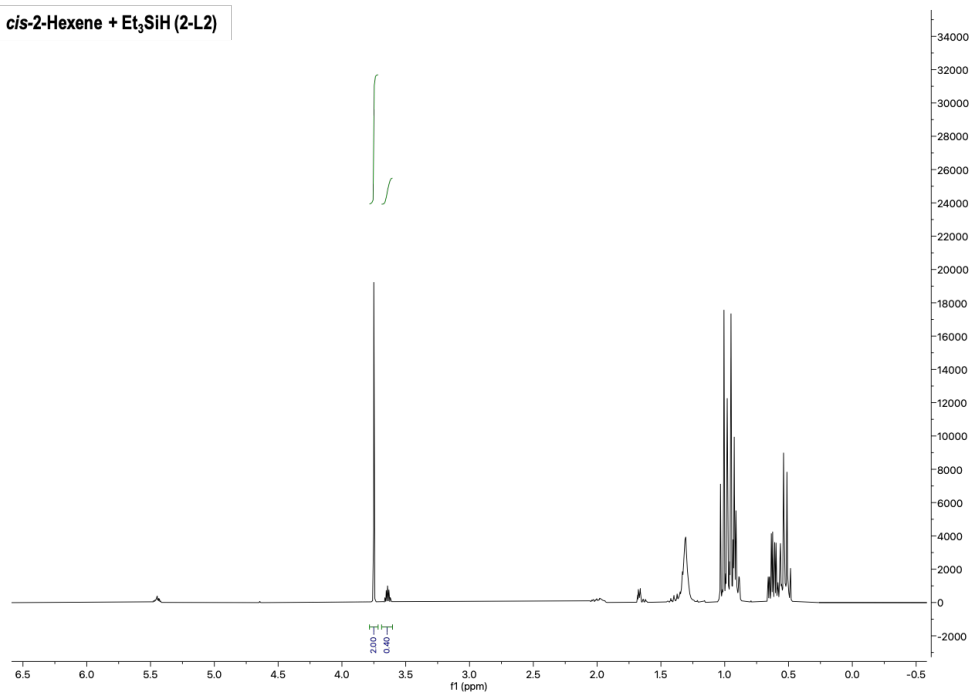


Figure S.14. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*cis*-3-Hexene + Et<sub>3</sub>SiH (2-L2)

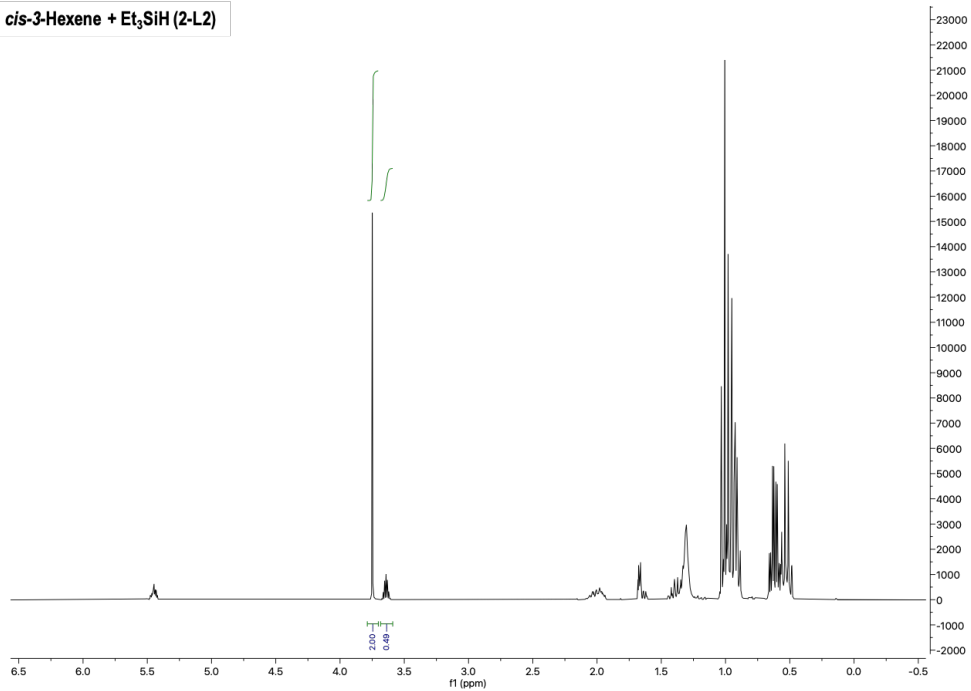


Figure S.15. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*trans*-2-Octene + Et<sub>3</sub>SiH (2-L2)

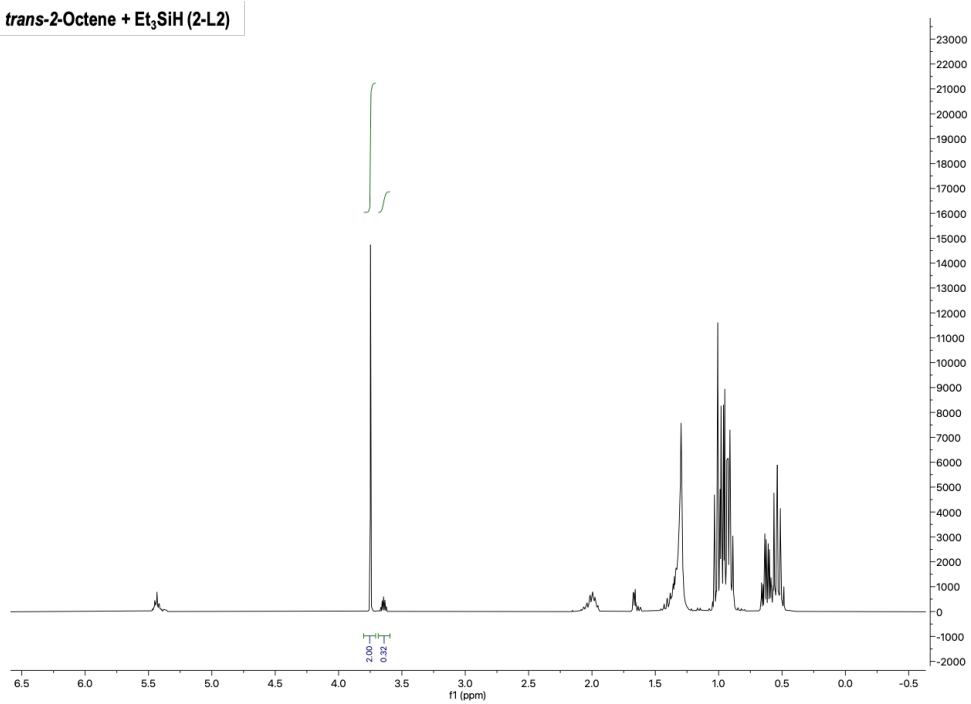


Figure S.16. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*cis*-2-Octene + Et<sub>3</sub>SiH (2-L2)

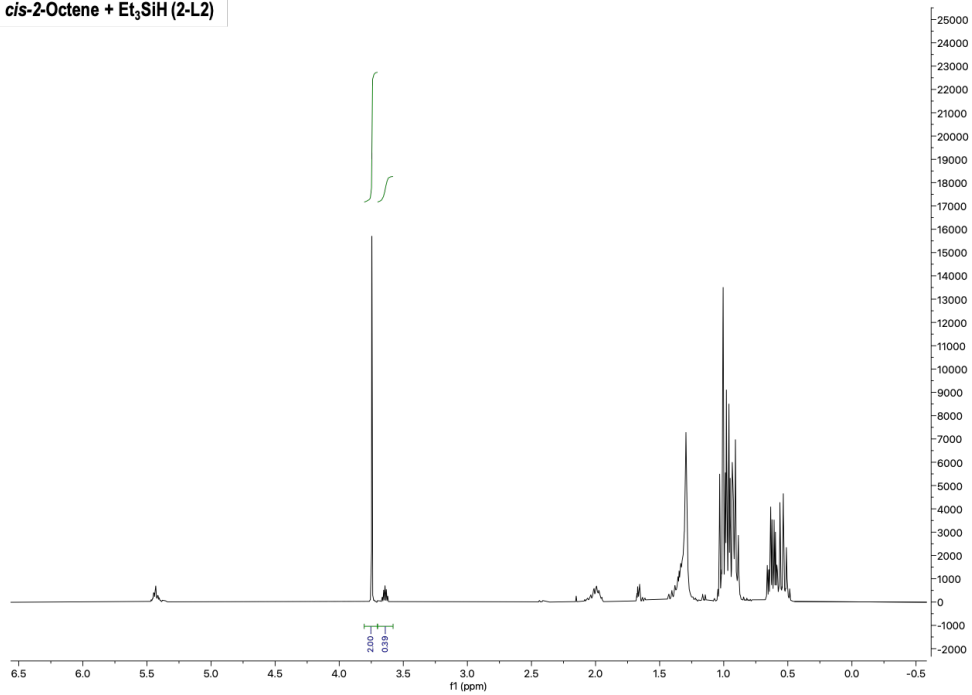


Figure S.17. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*trans*-3-Octene + Et<sub>3</sub>SiH (2-L2)

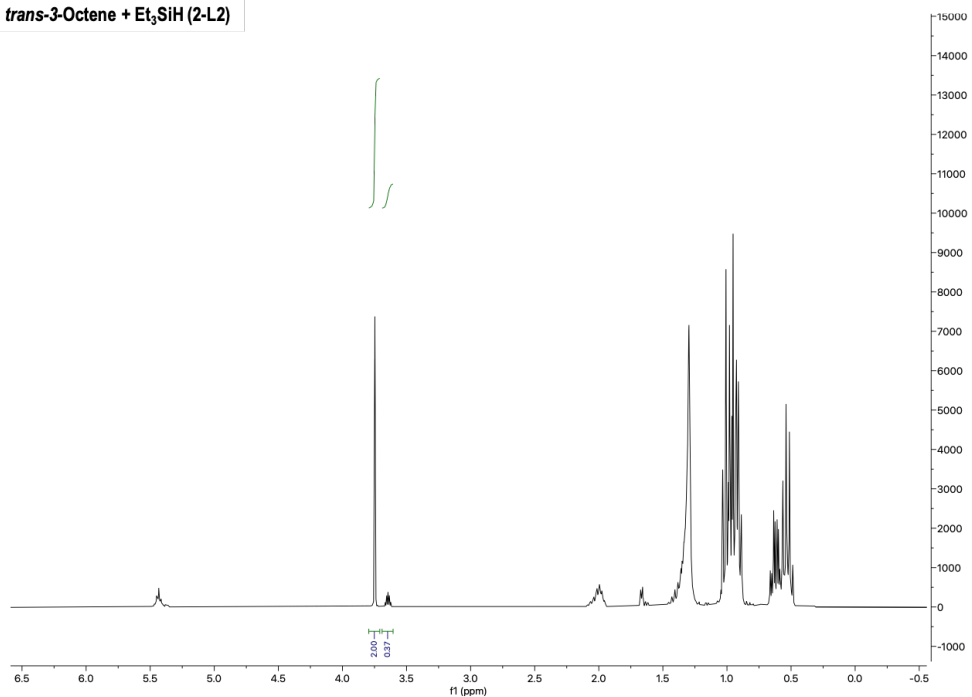


Figure S.18. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*trans*-4-Octene + Et<sub>3</sub>SiH (2-L2)

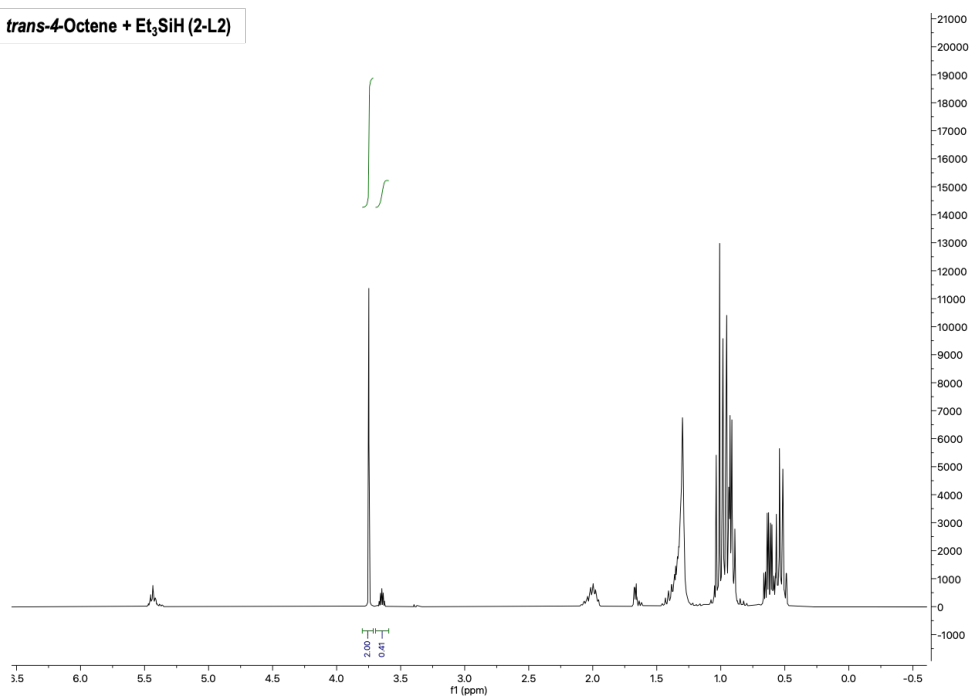


Figure S.19. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

*cis*-4-Octene + Et<sub>3</sub>SiH (2-L2)

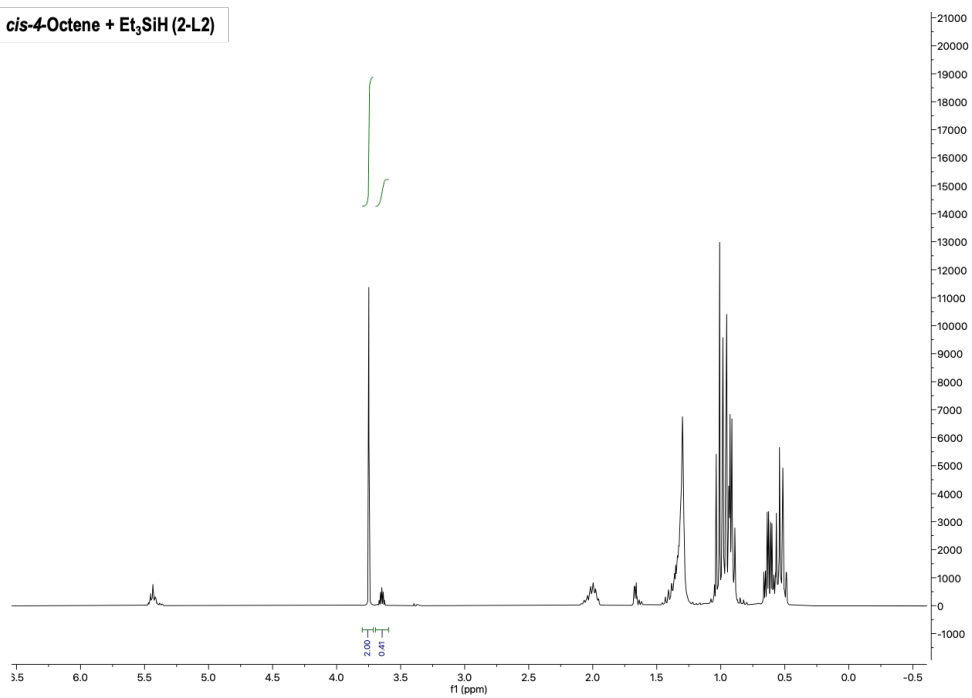


Figure S.20. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

## Hydrosilylation of other alkenes using 2-L2 (Table4)

$\alpha$ -methylstyrene + Et<sub>3</sub>SiH (2-L2)

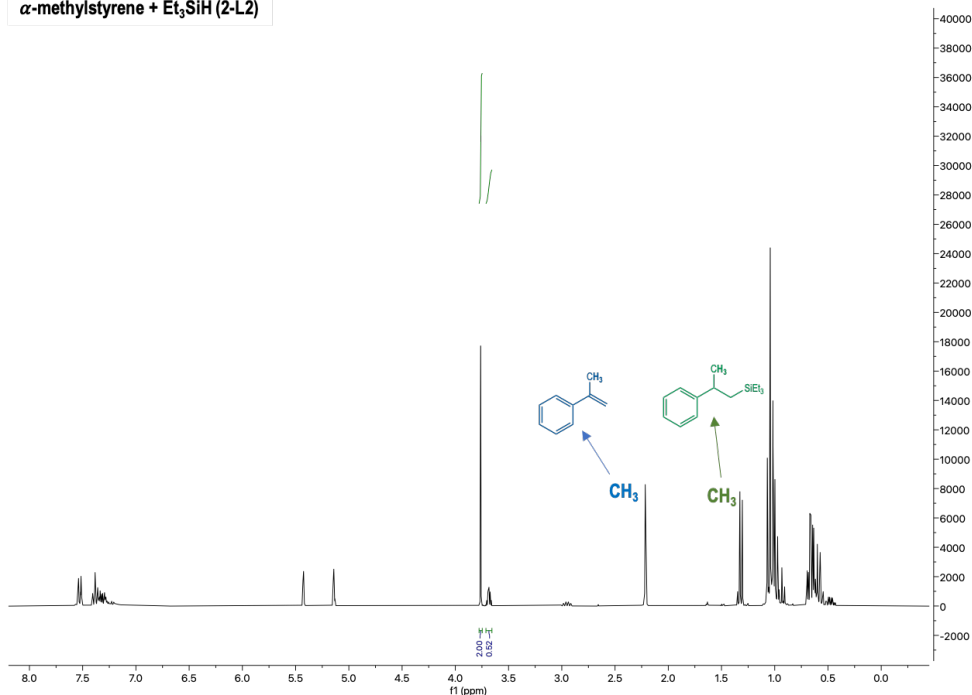


Figure S.21. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

1,1-diphenylethylene + Et<sub>3</sub>SiH (2-L2)

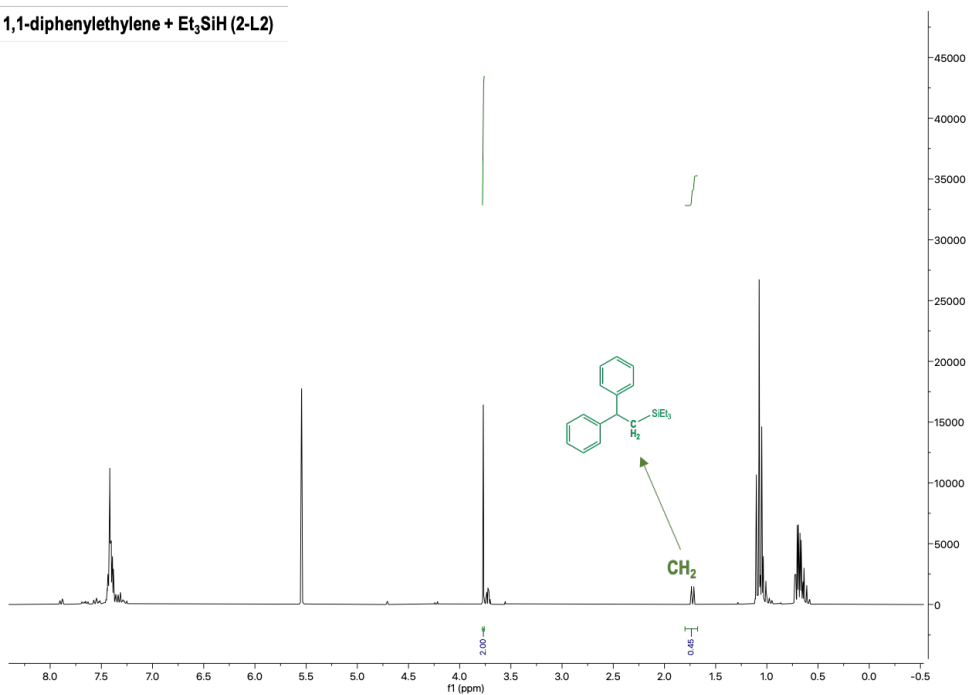


Figure S.22. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

3,3-dimethyl-1-butene + Et<sub>3</sub>SiH (2-L2)

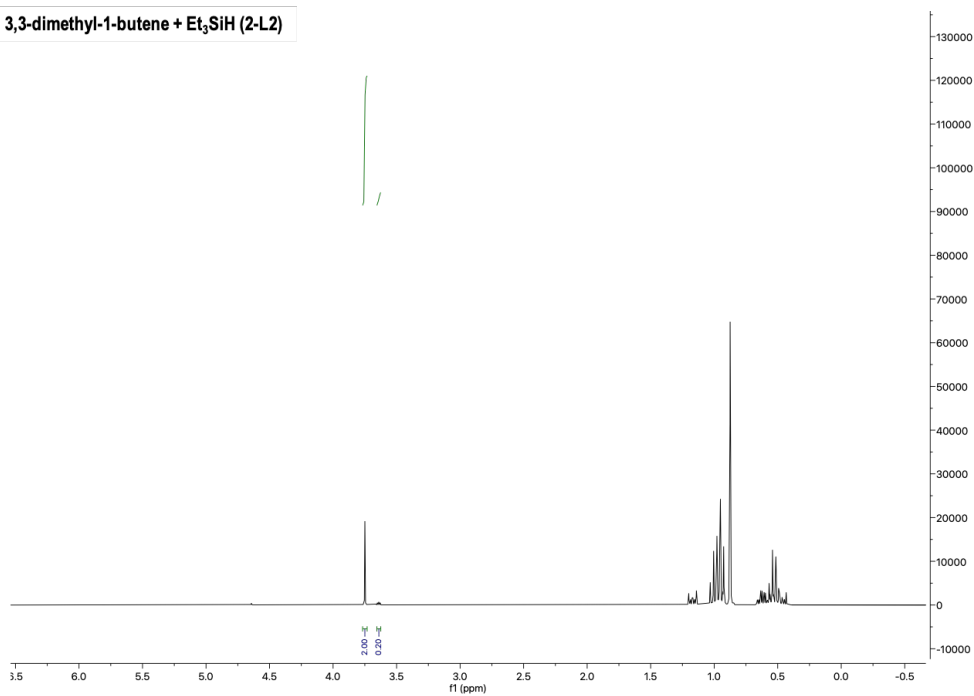


Figure S.23. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

3,3-dimethyl-1-butene + Et<sub>3</sub>SiH (2-L1)

MH\_D\_tbe\_2L1.10.fid

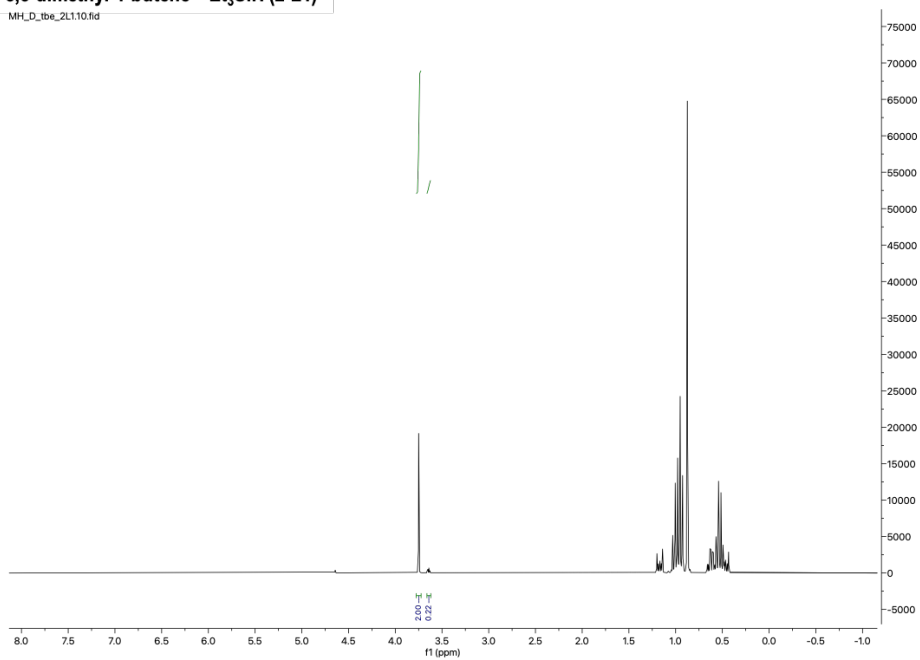


Figure S.24. <sup>1</sup>H NMR in CDCl<sub>3</sub>.



4-bromo-1-butene + Et<sub>3</sub>SiH (2-L2)

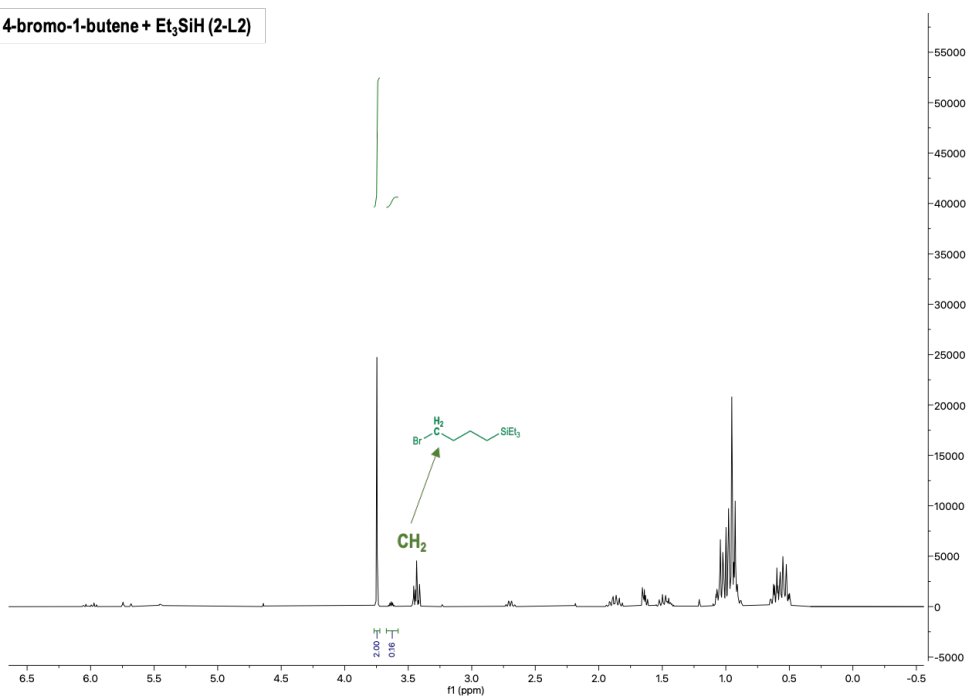


Figure S.25. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

5-hexen-2-one + Et<sub>3</sub>SiH (2-L2)

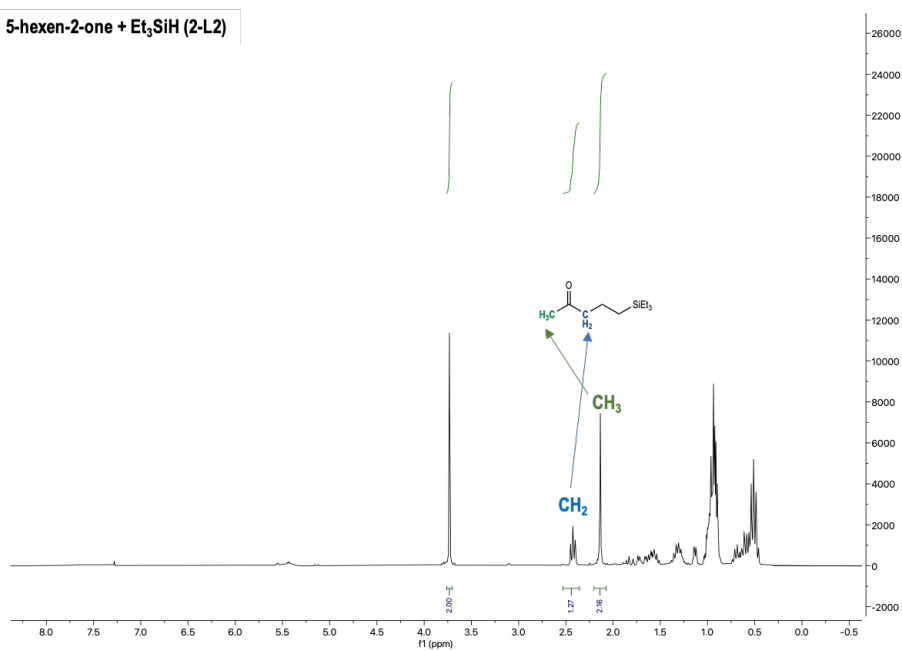


Figure S.26. <sup>1</sup>H NMR in CDCl<sub>3</sub>.

## 6. X-ray Crystallography

Crystals for **1-L2** and **2-L2** were mounted on a glass fibre and used for data collection on a Bruker D8 Venture with Photon detector equipped with graphite monochromated MoK $\alpha$  radiation ( $\lambda=0.71073$  Å). Lorentz-polarisation and empirical absorption corrections were applied. The data reduction were performed with the APEX2<sup>6</sup> software and corrected for absorption using SADABS.<sup>7</sup> Crystal structure was solved by direct methods using the SIR97 program<sup>8</sup> and refined by full-matrix least-squares on  $F^2$  including all reflections using anisotropic displacement parameters by means of the WINGX crystallographic package.<sup>9</sup> Anisotropic temperature factors were assigned to all atoms except for hydrogen atoms, which are riding their parent atoms with an isotropic temperature factor arbitrarily chosen as 1.2 times that of the respective parent. Final R(F), wR(F2) and goodness of fit agreement factors, details on the data collection and analysis can be found in Table X. CCDC 2219493 and 2219494 contains the supplementary crystallographic data for compounds **2-L2** and **1-L2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

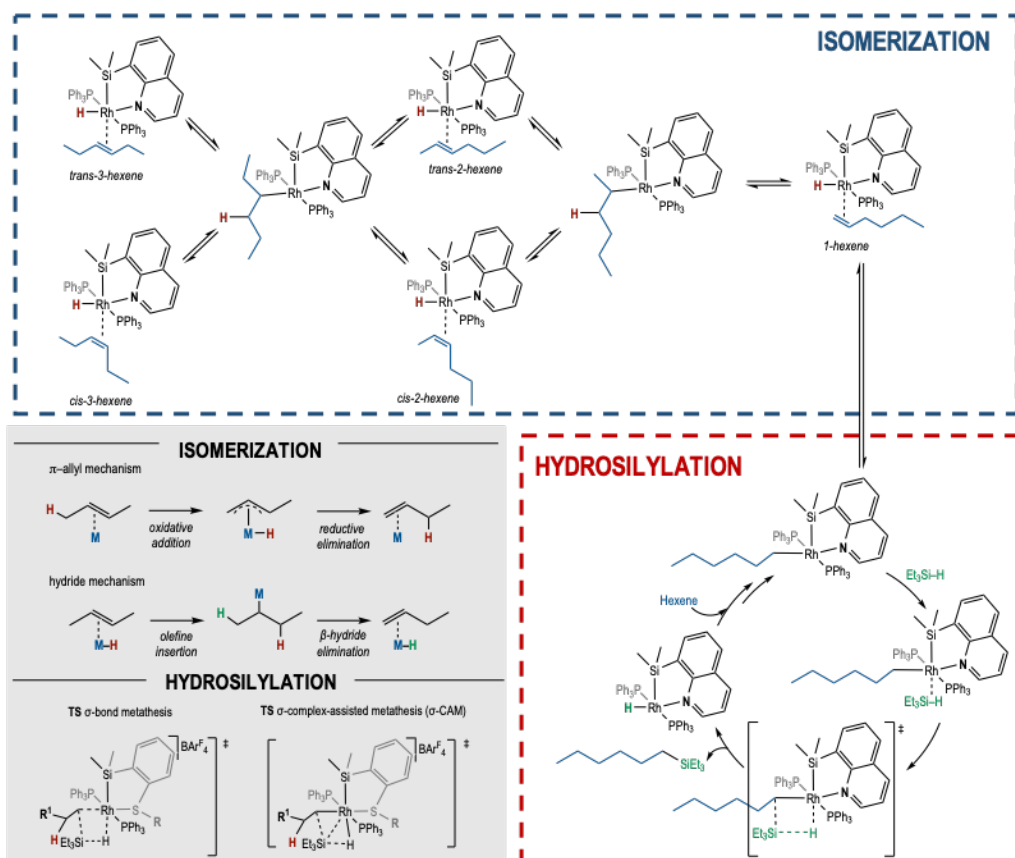
	1-L2	2-L2
CCDC number	2219494	2219493
Formula	C <sub>30</sub> H <sub>30</sub> ClNP <sub>2</sub> RhSi	C <sub>80</sub> H <sub>57</sub> BF <sub>24</sub> NP <sub>2</sub> RhSi
M	601.97	1692.01
Crystal System	Triclinic	triclinic
Space group	P-1	P - 1
T [K]	100	100
a [Å]	9.837(3)	14.6909(13)
b [Å]	9.959(2)	17.0539(14)
c [Å]	13.863(4)	17.9179(16)
$\alpha$ [deg]	87.968(3)	114.646(3)
$\beta$ [deg]	77.527(3)	100.541(3)
$\gamma$ [deg]	86.993(3)	104.702(3)
V [Å <sup>3</sup> ]	1323.97(7)	3727.6(6)
Z	2	2
Density [gcm <sup>-3</sup> ]	1.510	1.507
$\mu$ [mm <sup>-1</sup> ]	0.872	0.394
Observed reflections	6562	22659
R <sub>1</sub> [ $I > 2\sigma(I)$ ]	0.0310	0.0569
wR <sub>2</sub> [all data]	0.0723	0.1611
GoF	1.076	1.034

$$^a \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^b \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

**Table S1.** Crystallographic data and structure refinement details of all compounds.

## 7. Proposed mechanism

A mechanism for the tandem isomerization hydrosilylation reaction has been proposed based on literature precedents. For the isomerization process, two mechanisms are the most commonly accepted. Based on the characteristics of our precatalyst, we propose that a hydride-mechanism which occurs via olefin insertion and  $\beta$ -hydride elimination would result in an equilibrium between all possible alkene isomers. On the other hand, the isomerisation reaction could take place via the catalytic cycle shown in the figure below. Once the 1-hexene has coordinated to the metal centre it would undergo an insertion into the Rh-H bond. Then, by a 4 centre 4 electron transition state ( $\sigma$ -bond metathesis or  $\sigma$ -CAM), the formation of the terminal silane would take place.



## 8. References

- (1) E. W. Abel, M. A. Bennet, G. Wilkinson, *J. Chem. Soc.* 1959, 3178.
- (2) M. Brookhart, B. Grant, A. F. Volpe Jr., *A. F. Organometallics* 1992, 11, 3920.
- (3) M. Nakajima, S. Nagasawa, K. Matsumoto, T. Kuribara, A. Muranaka, M. Uvhiyama, T. Nemoto, *Angew. Chem. Int. Ed.* 2020, 59,6847.
- (4) P. I. Djurovic, A. Safir, N. Keder, R. J. Watts, *Coord. Chem. Rev.*, 1991, 111, 201.
- (5) N. Kumar, C. Laye, F. Robert, Y. Landais, *Eur. J. Org. Chem.* 2021, 3613.
- (6) Bruker Apex2, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
- (7) G.M. Sheldrick, SADABS, Program for Empirical Adsorption Correction, Institute for Inorganic Chemistry, University of Gottingen, Germany, 1996.
- (8) A. Altomare, M. C. Burla, M. Camilla, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, 32, 115.
- (9) (a) G. M. Sheldrick, SHELX-2014, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014. (b) L. J. Farrugia, *J. Appl. Cryst.*, 1999, 32, 837.

## 9. NMR Spectra

### NMR spectra of L1

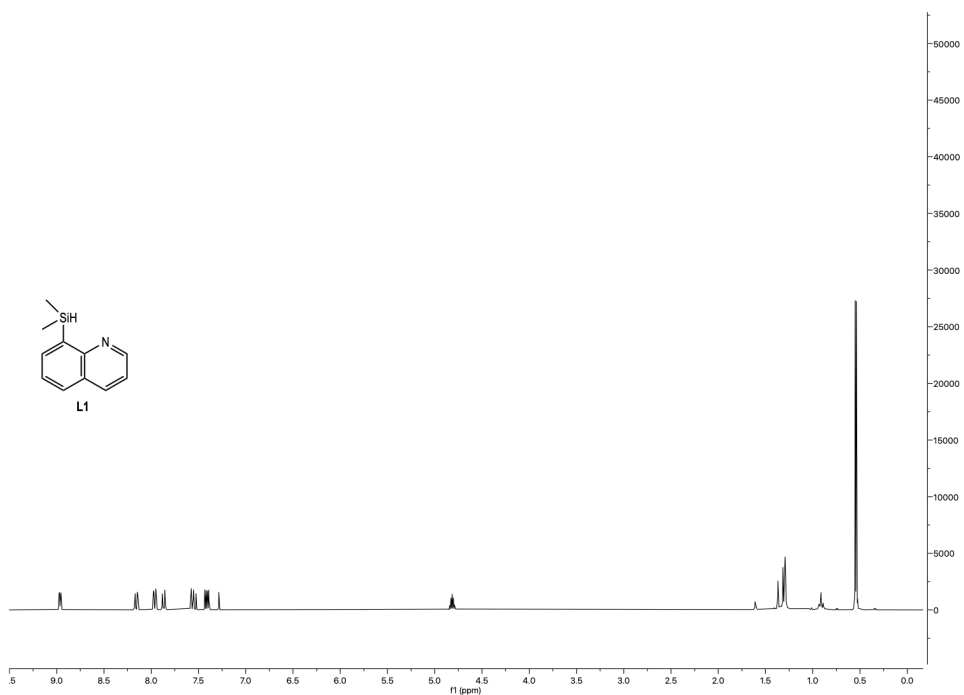


Figure S.27. <sup>1</sup>H NMR of L1.

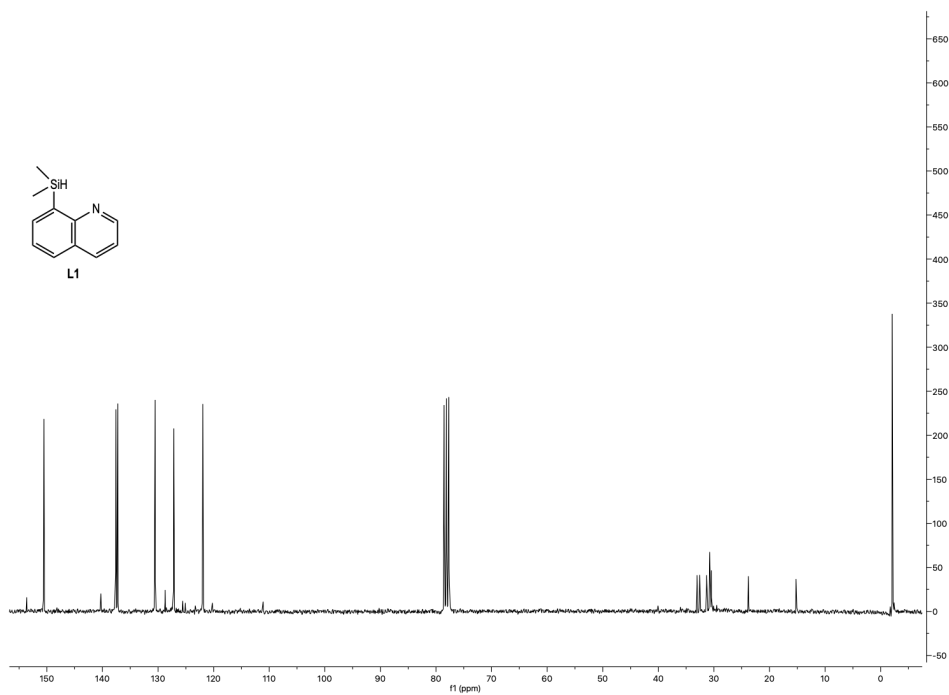
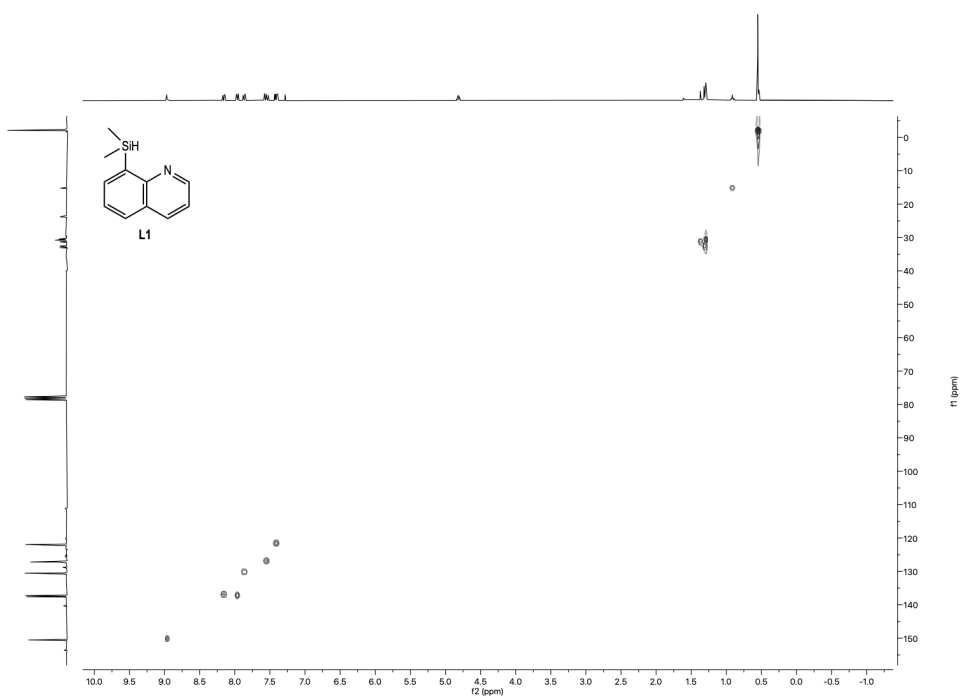
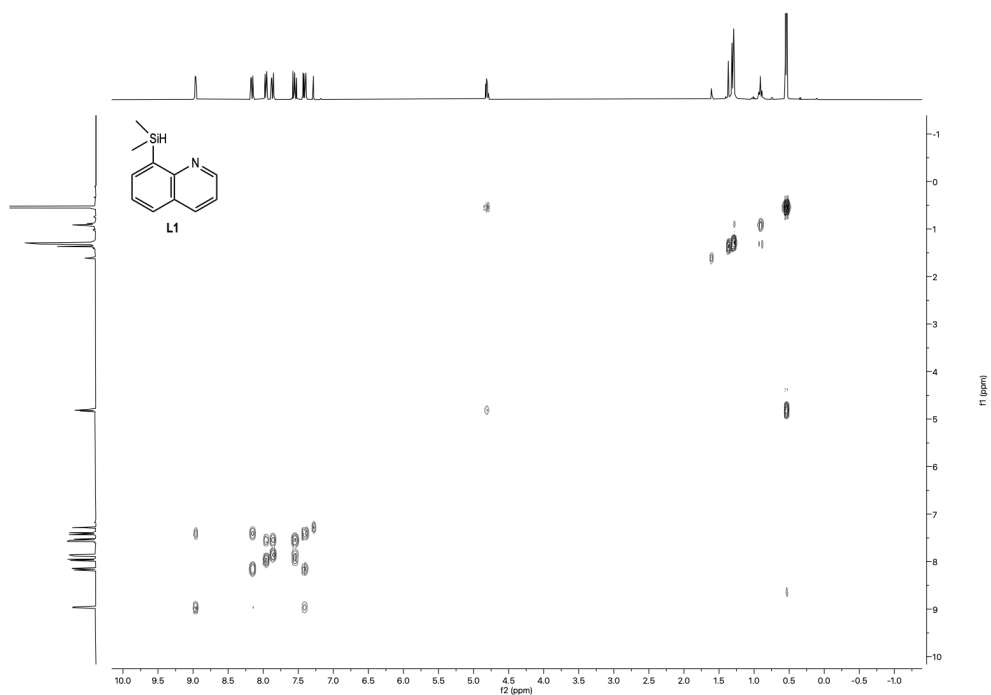
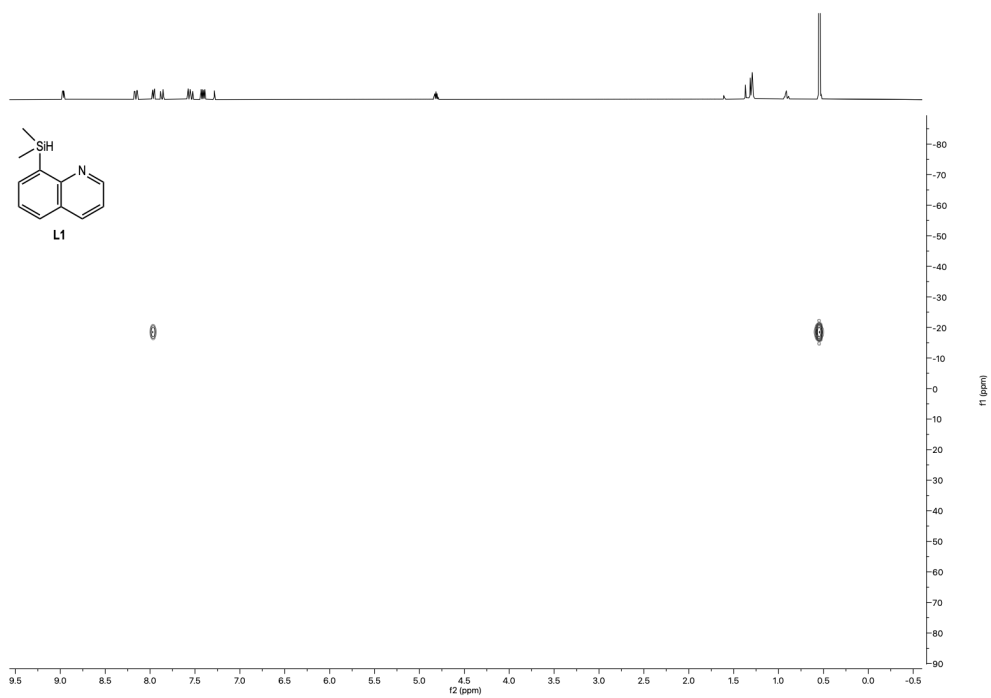


Figure S.28. <sup>13</sup>C{<sup>1</sup>H} NMR of L1.





## NMR spectra of L2

AM02.20.fid

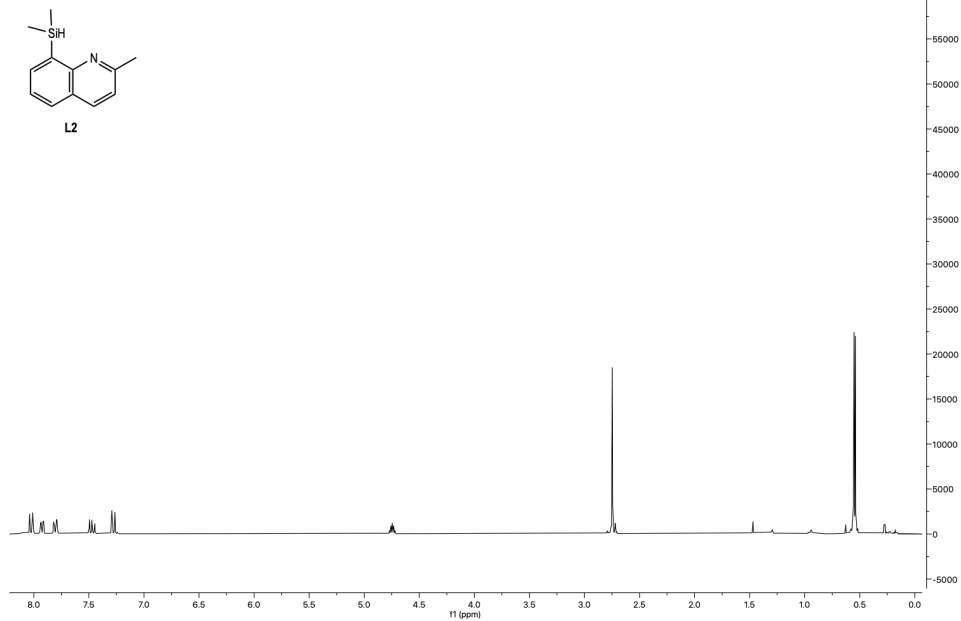


Figure S.32.  $^1\text{H}$  NMR of L2.

AM02.23.fid

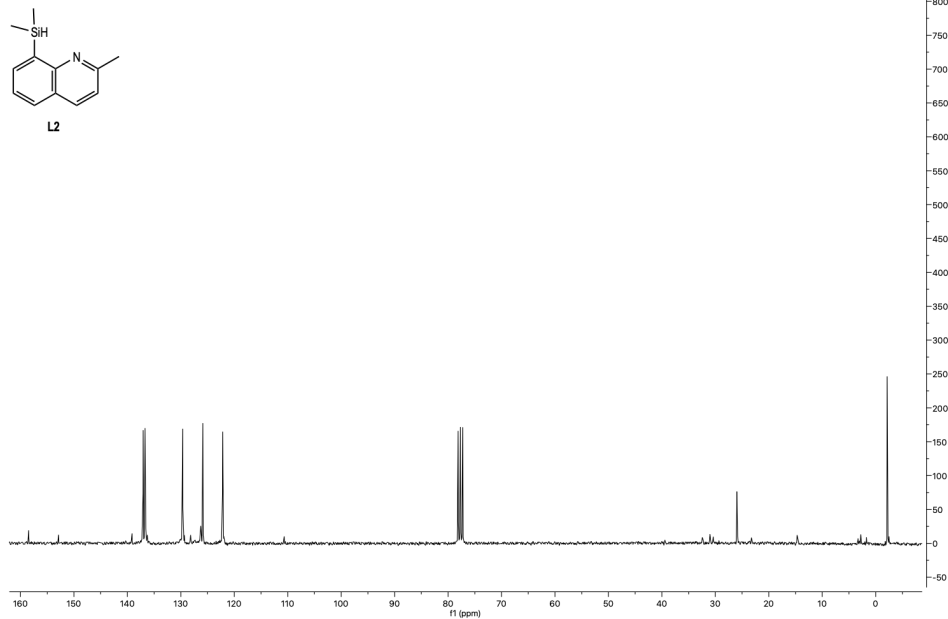


Figure S.33.  $^{13}\text{C}\{^1\text{H}\}$  NMR of L2.

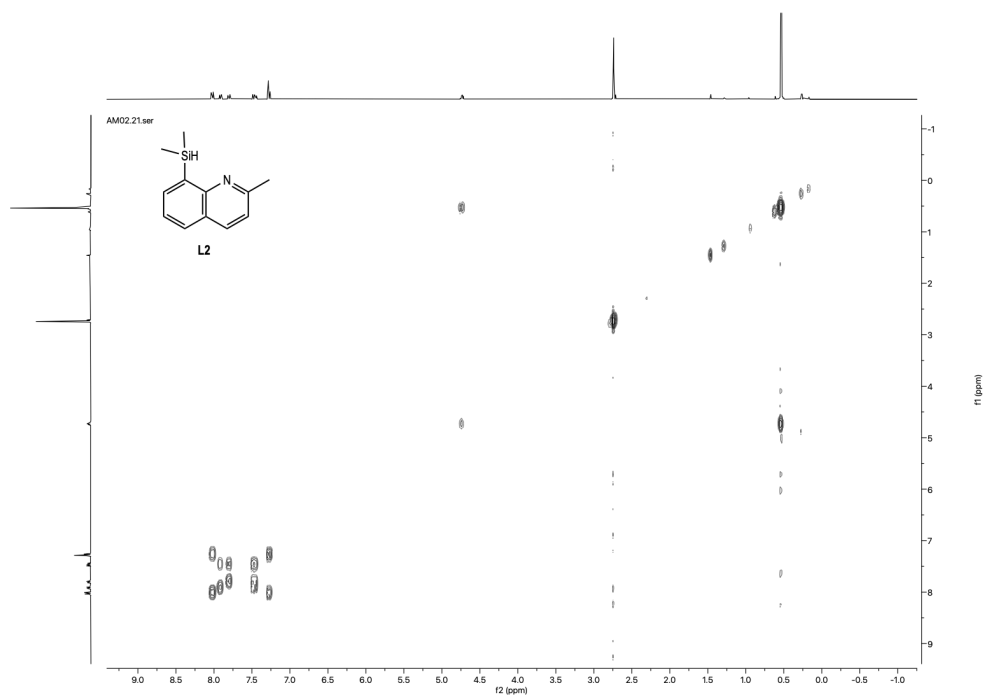


Figure S.34. COSY  $^1\text{H}$ - $^1\text{H}$  NMR of L2.

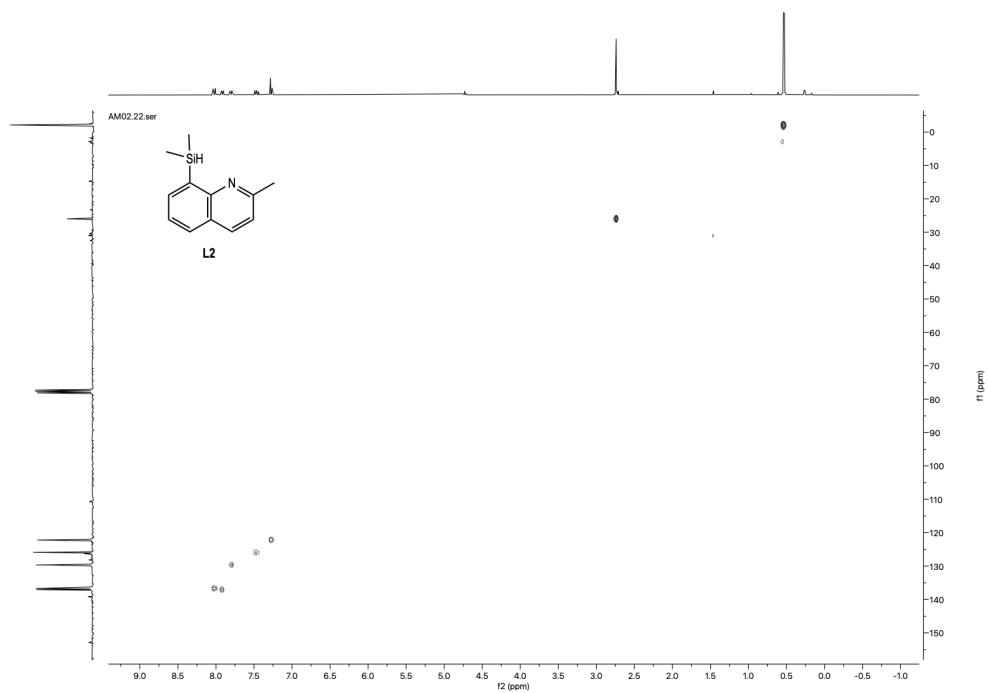
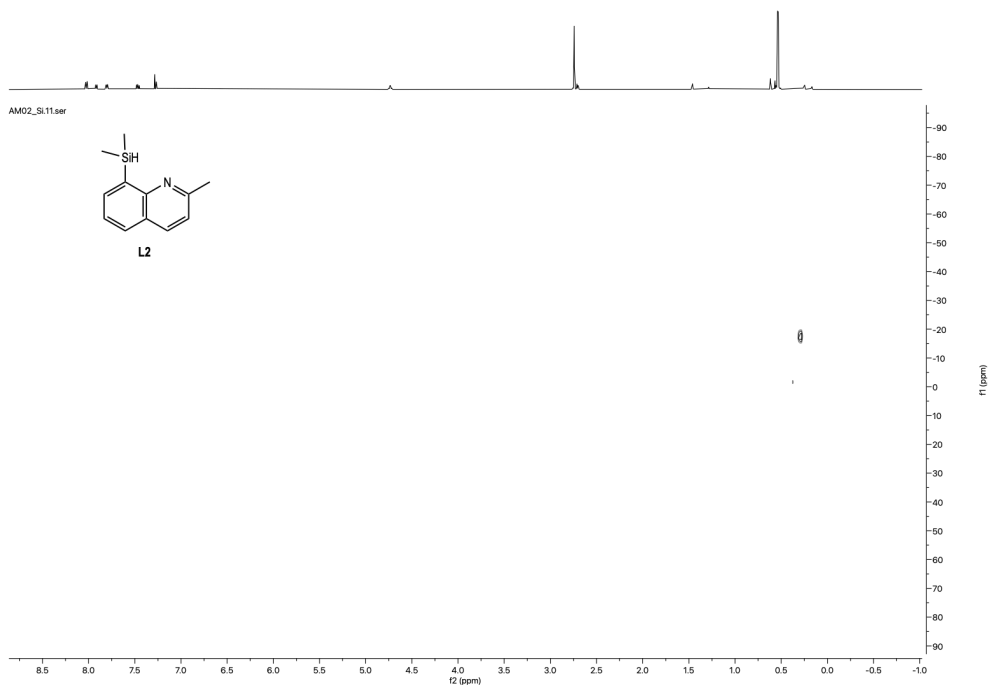


Figure S.35. HSQC  $^1\text{H}$ - $^{13}\text{C}$  NMR of L2.





**Figure S.36.** HMBC  $^1\text{H}$ - $^{29}\text{Si}$  NMR of **L2**.

## NMR spectra of L3

AM03.20.fid

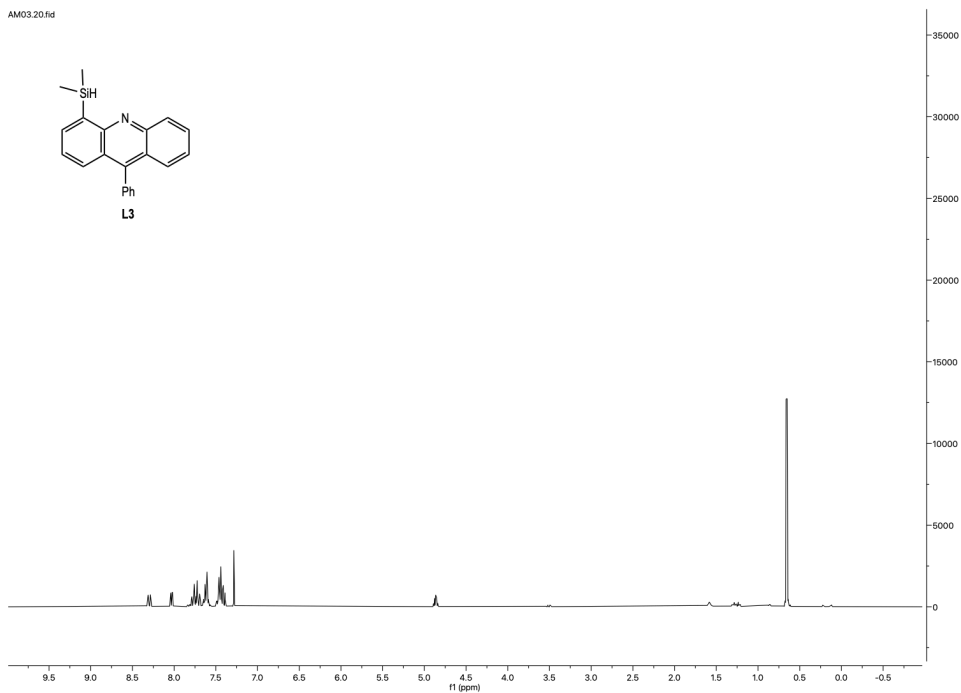


Figure S.37.  $^1\text{H}$  NMR of L3.

AM03.23.fid

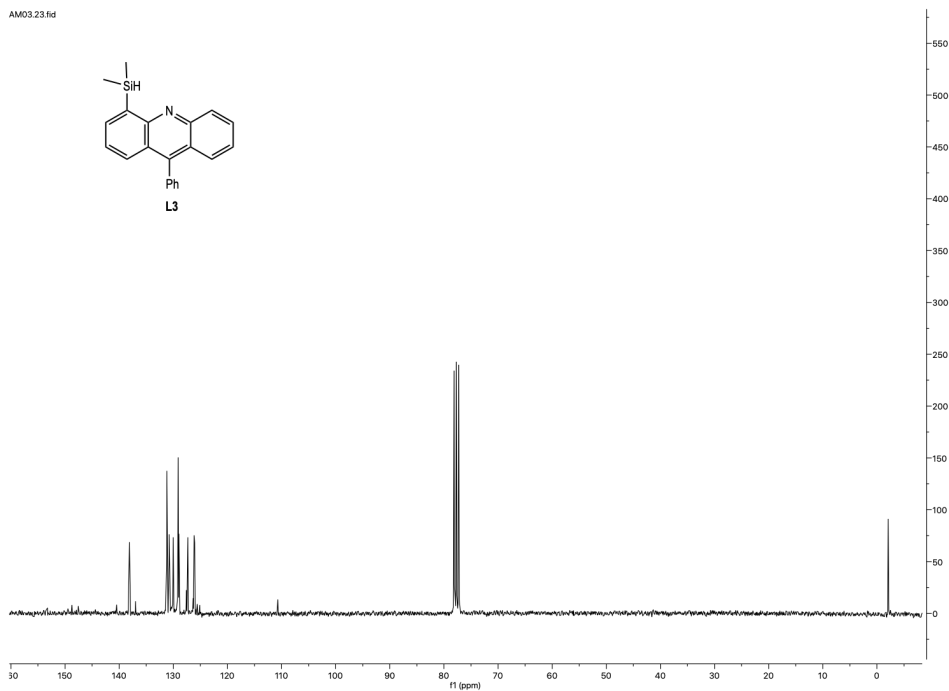
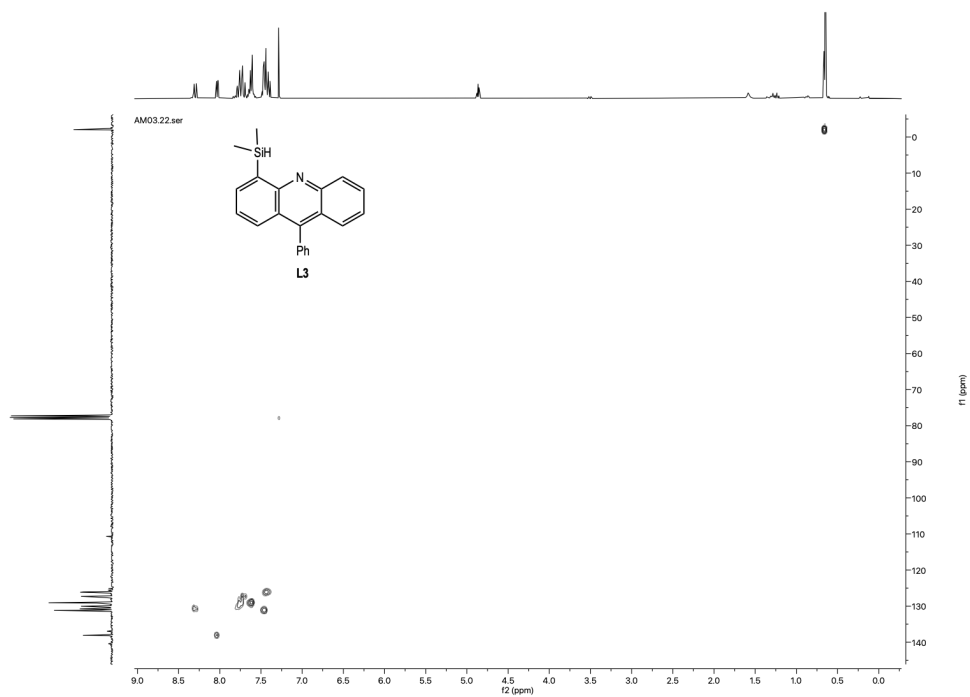
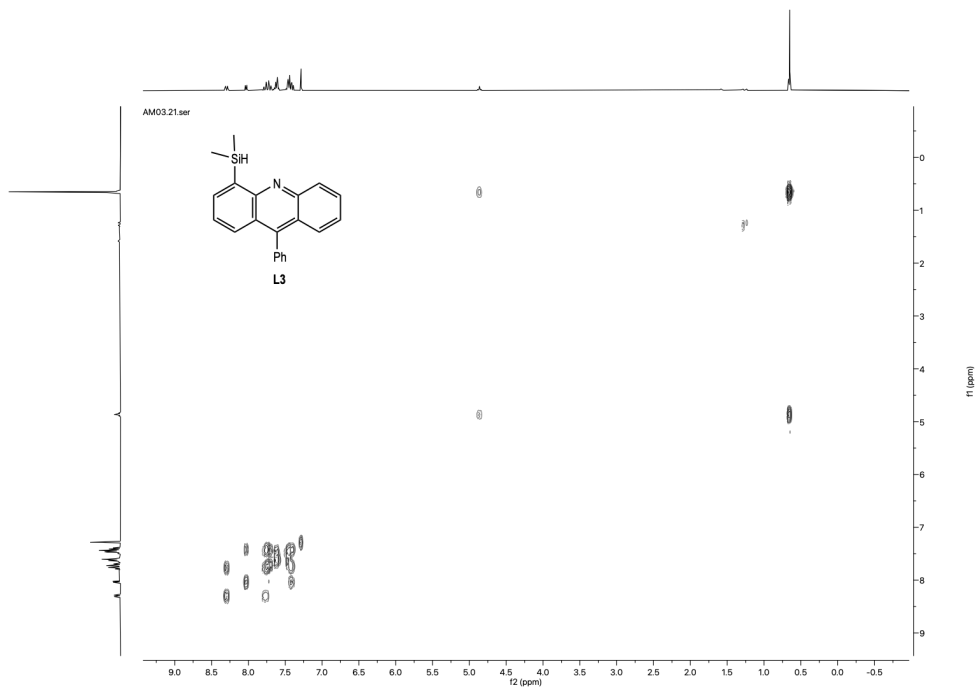


Figure S.38.  $^{13}\text{C}\{^1\text{H}\}$  NMR of L3.



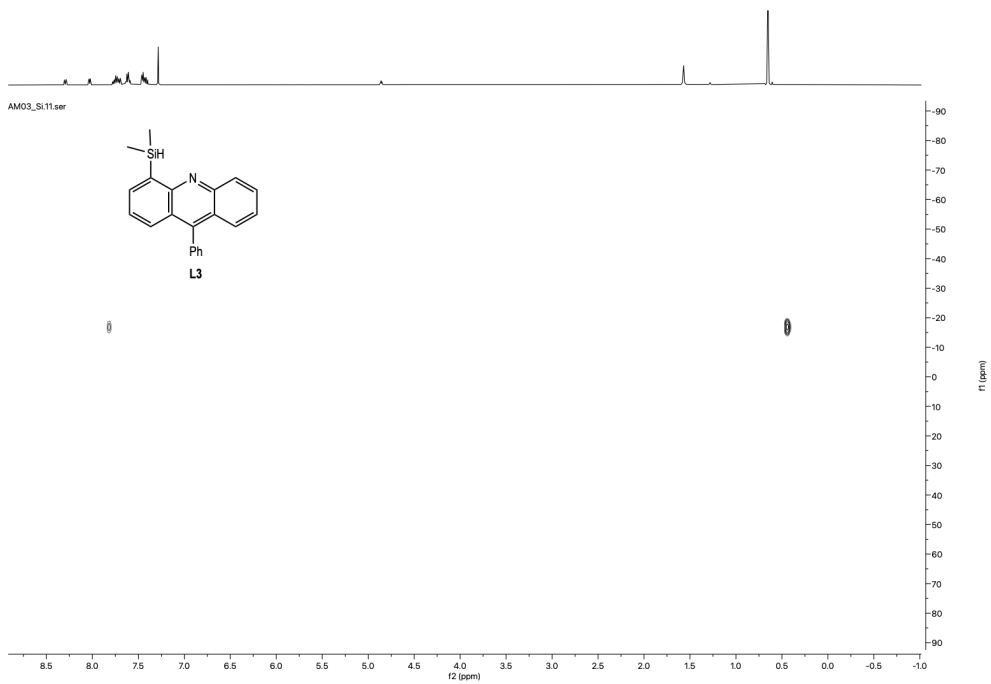


Figure S.41. HMBC  $^1\text{H}$ - $^{29}\text{Si}$  NMR of L3.

## NMR spectra of 1-L1

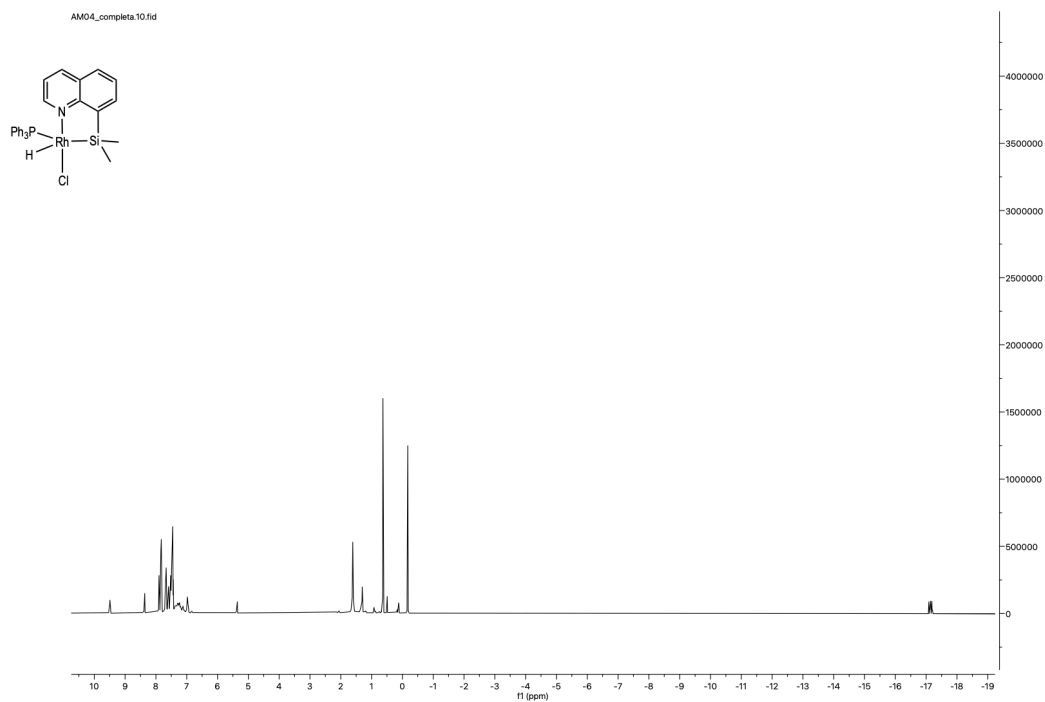


Figure S.42. <sup>1</sup>H NMR of 1-L1.

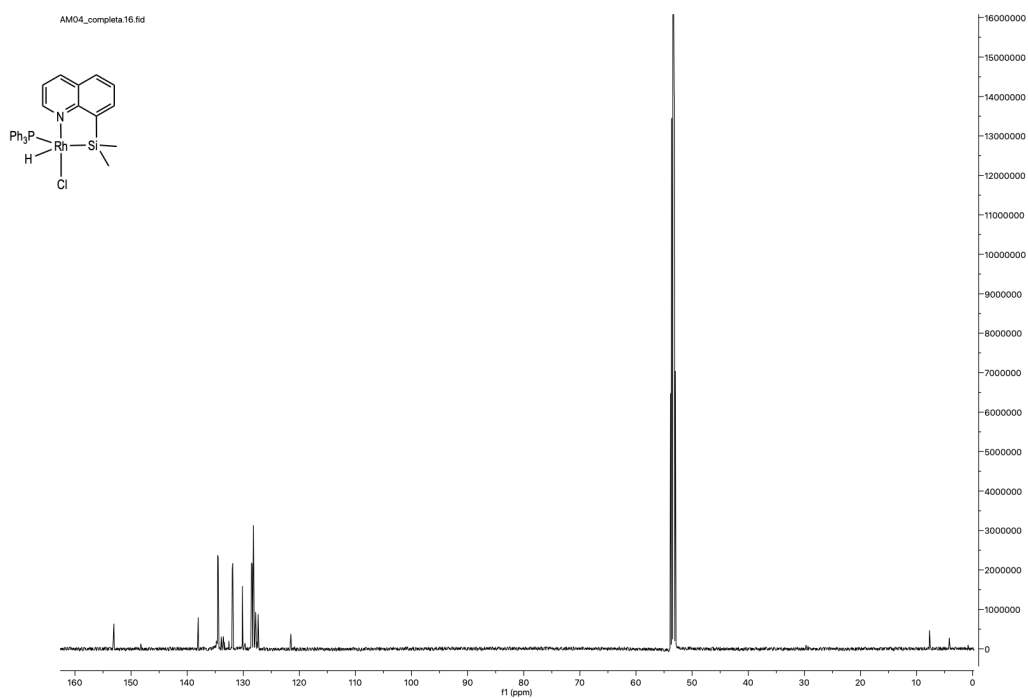
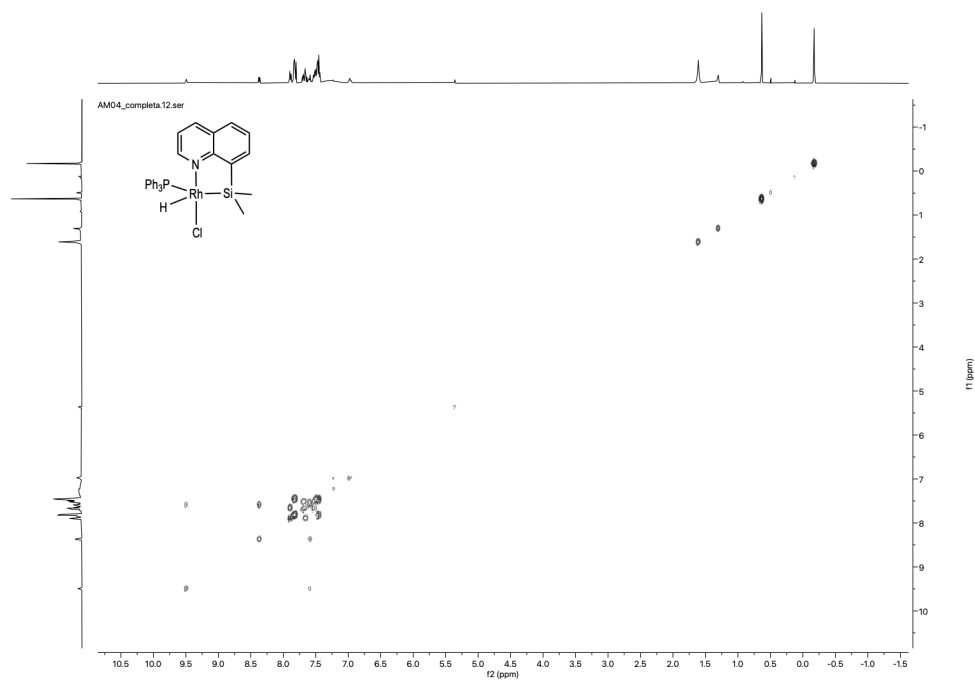
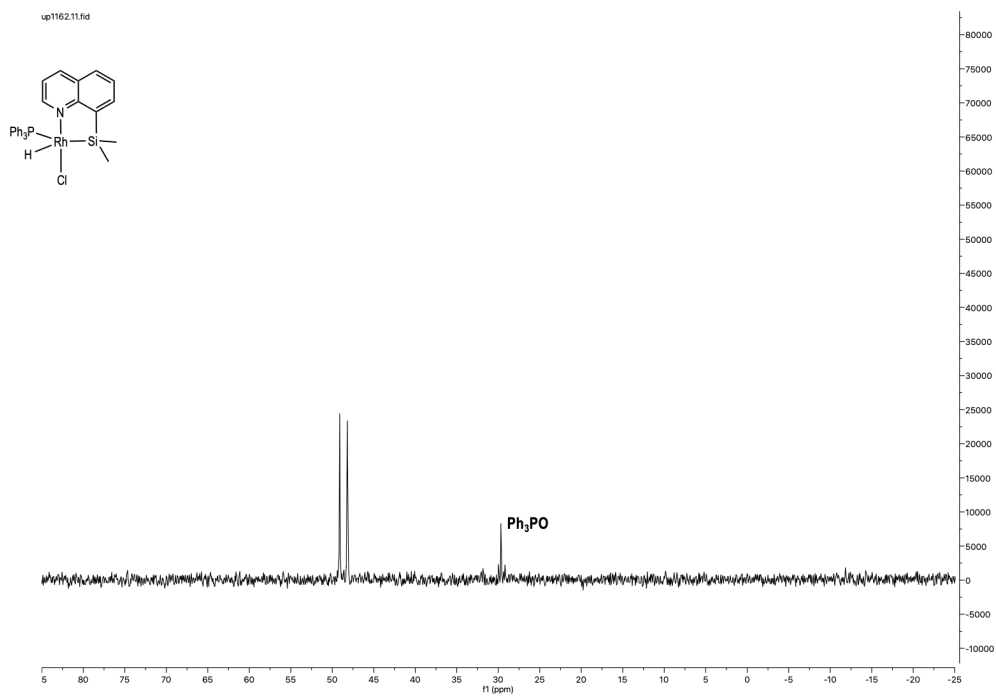
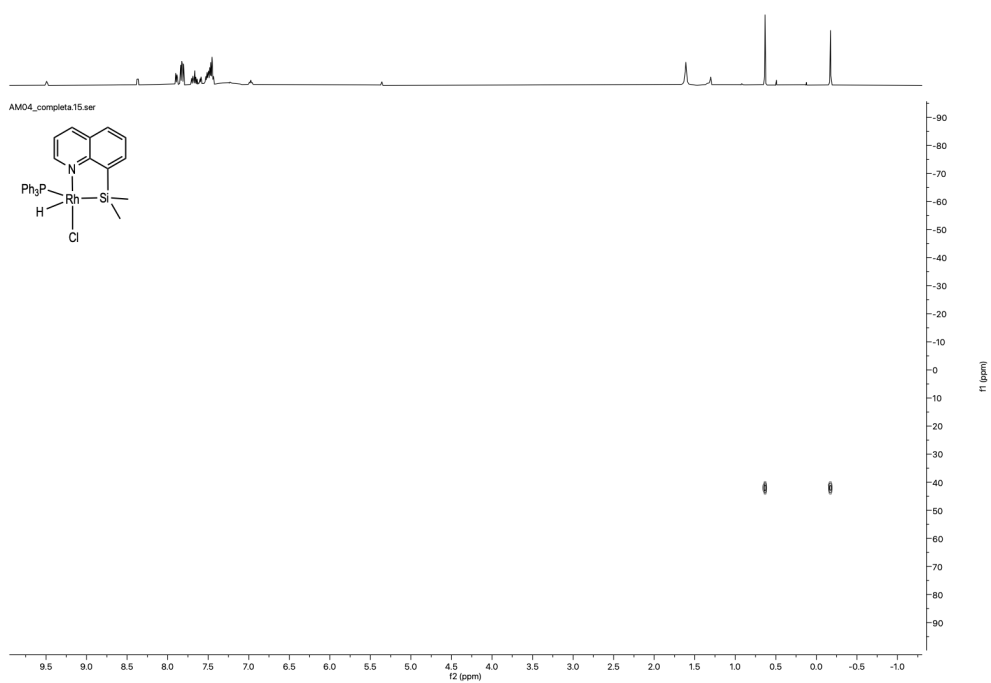
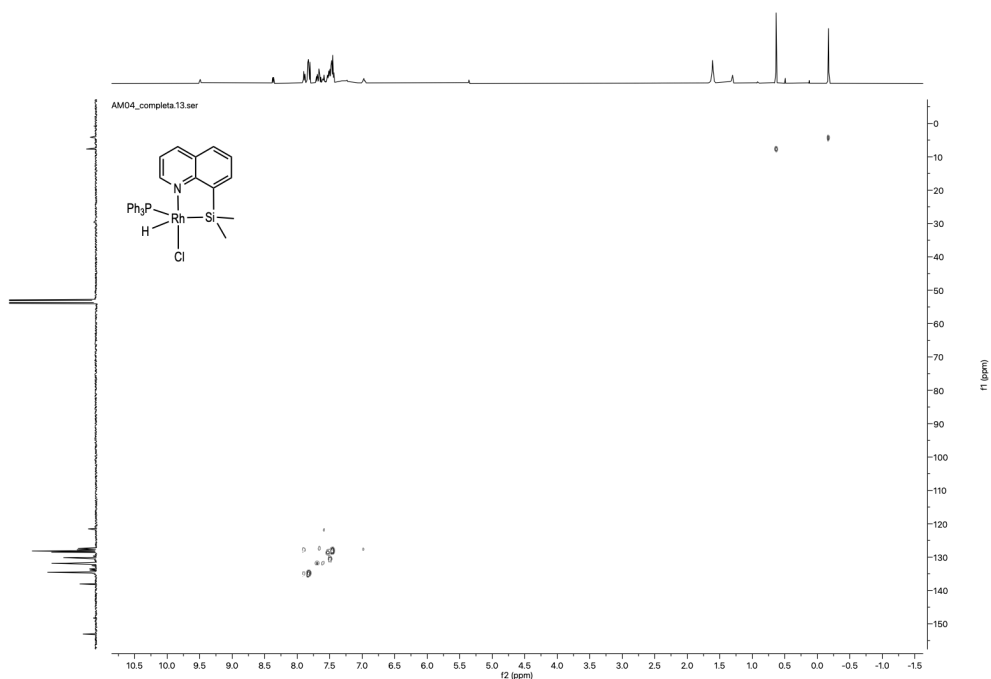


Figure S.43. <sup>13</sup>C{<sup>1</sup>H} NMR of 1-L1.





## NMR spectra of 1-L2

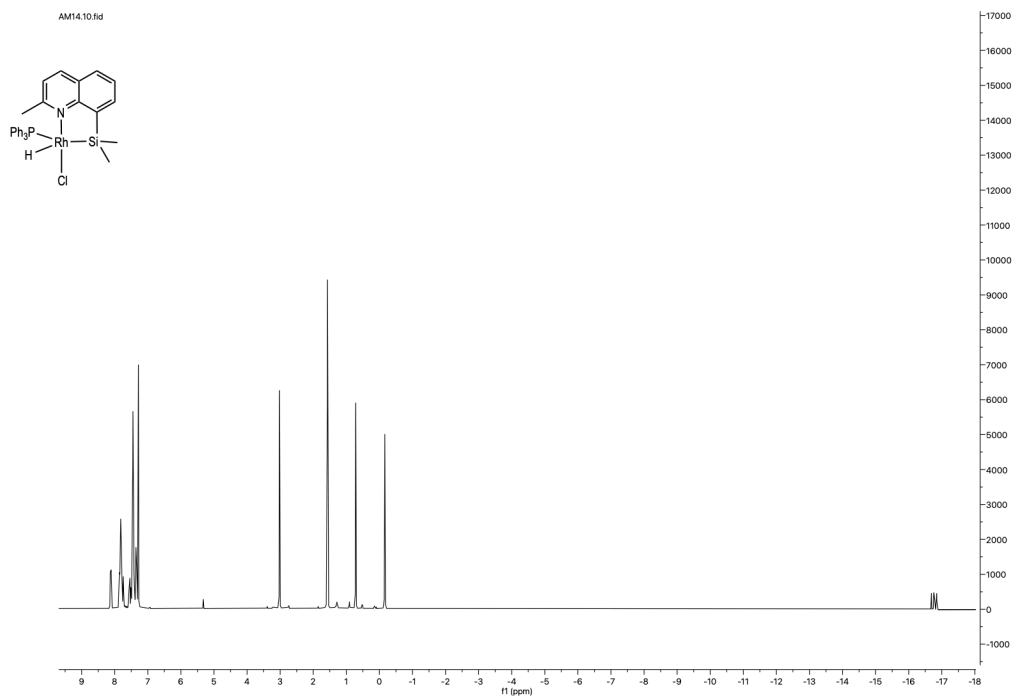


Figure S.48. <sup>1</sup>H NMR of 1-L2.

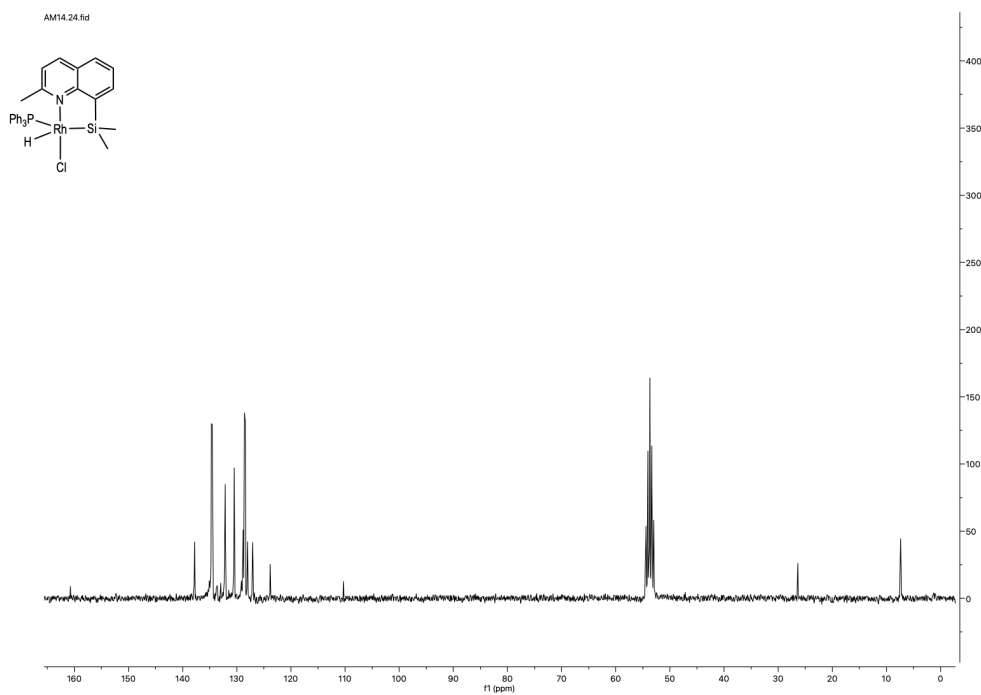


Figure S.49. <sup>13</sup>C{<sup>1</sup>H} NMR of 1-L2.



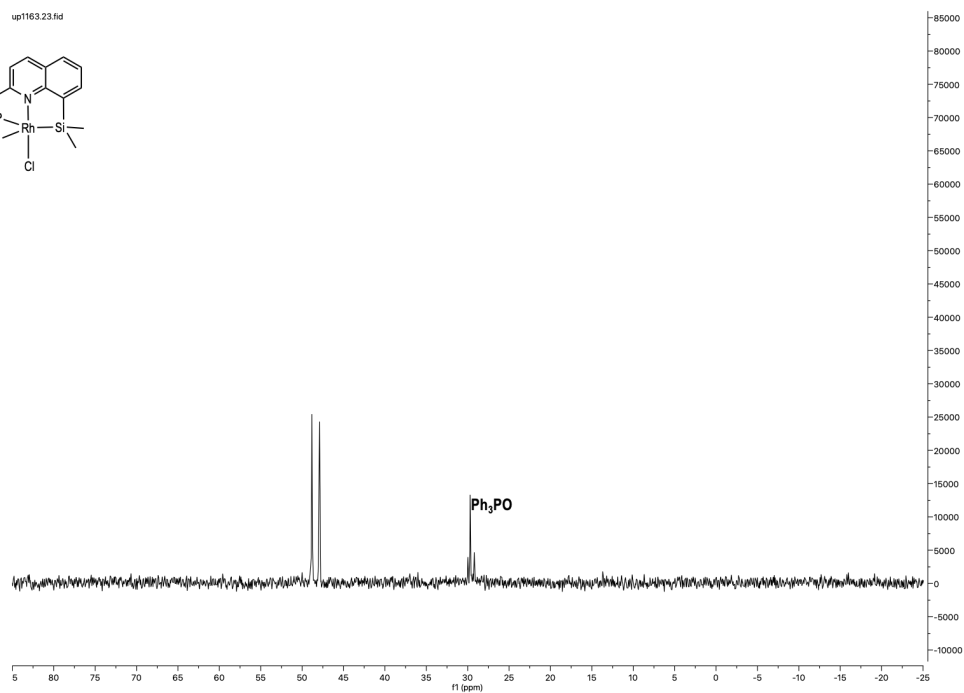
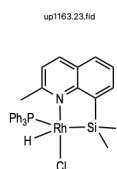


Figure S.50.  $^{31}\text{P}\{^1\text{H}\}$  NMR of 1-L2.

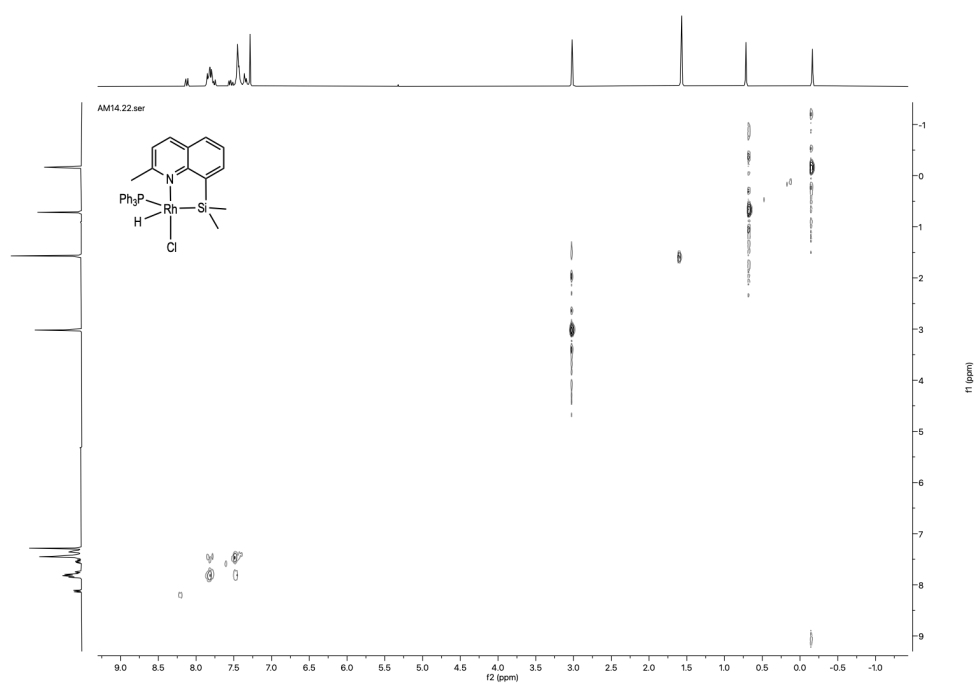
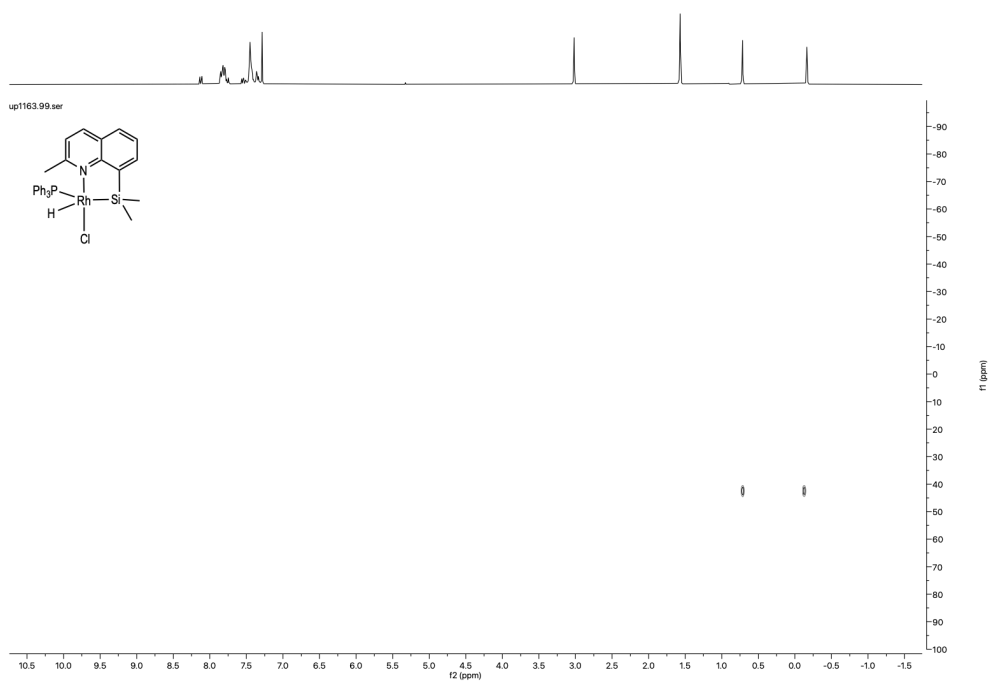
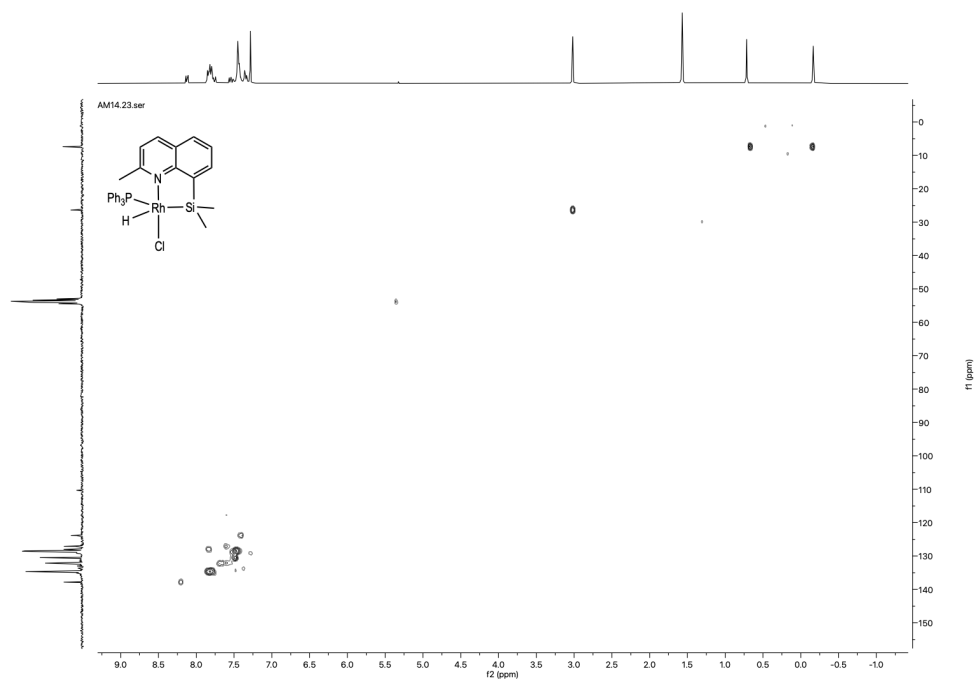


Figure S.51. COSY  $^1\text{H}$ - $^1\text{H}$  NMR of 1-L2.



## NMR spectra of 1-L3

UP1181\_completa.10.fid

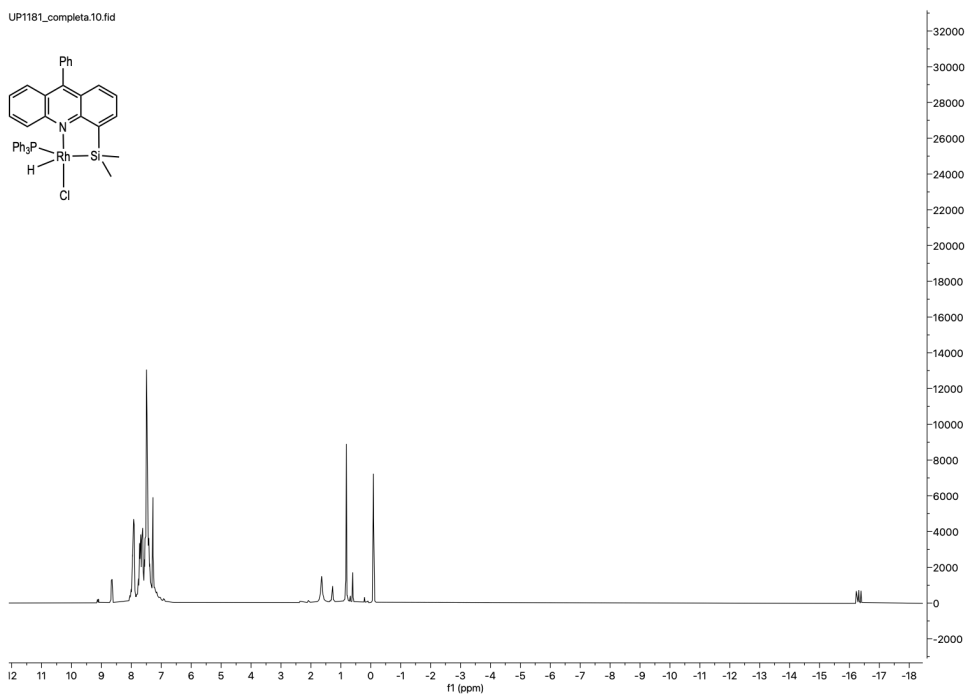
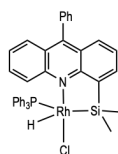


Figure S.54.  $^1\text{H}$  NMR of 1-L3.

UP1181\_completa.11.fid

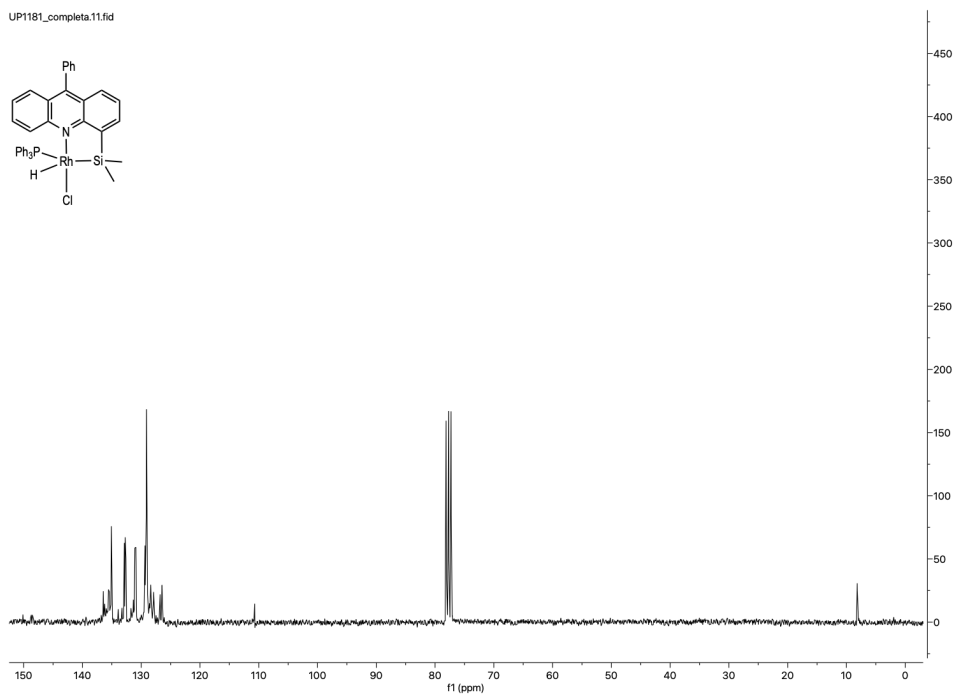
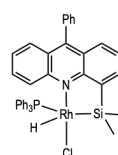


Figure S.55.  $^{13}\text{C}\{^1\text{H}\}$  NMR of 1-L3.

UP1181\_Si.12.fid

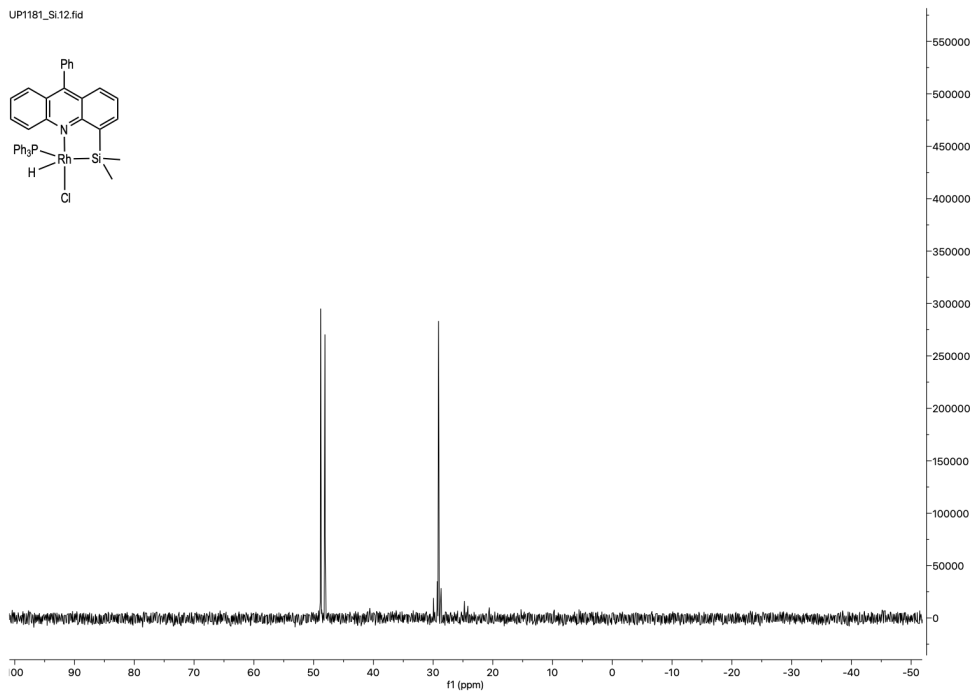
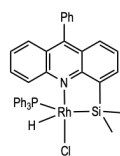


Figure S.56.  $^{31}\text{P}\{^1\text{H}\}$  NMR of 1-L3.

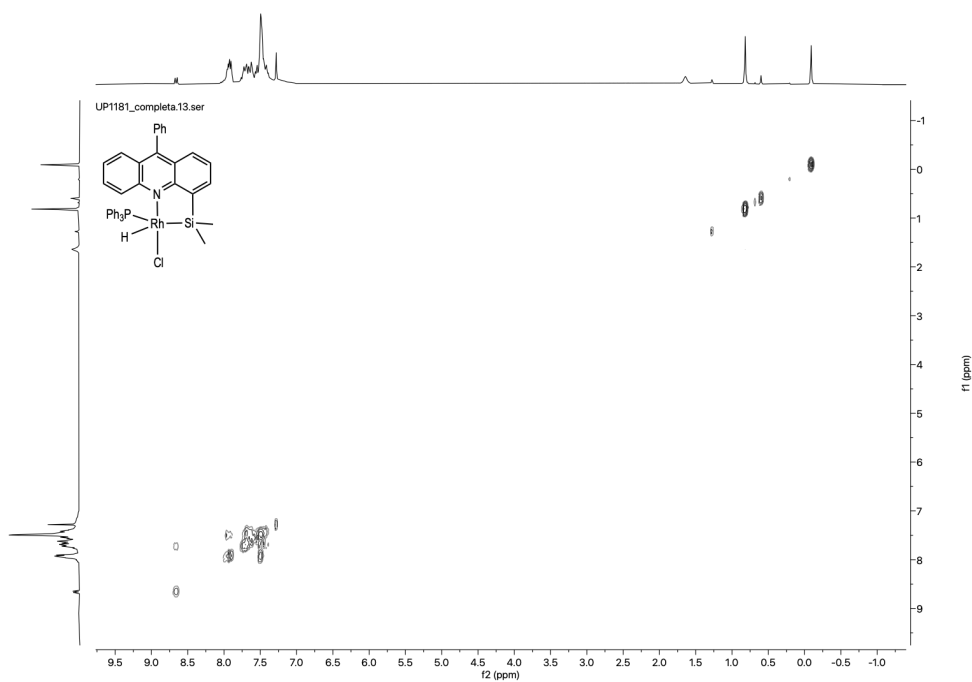


Figure S.57. COSY  $^1\text{H}$ - $^1\text{H}$  NMR of 1-L3.

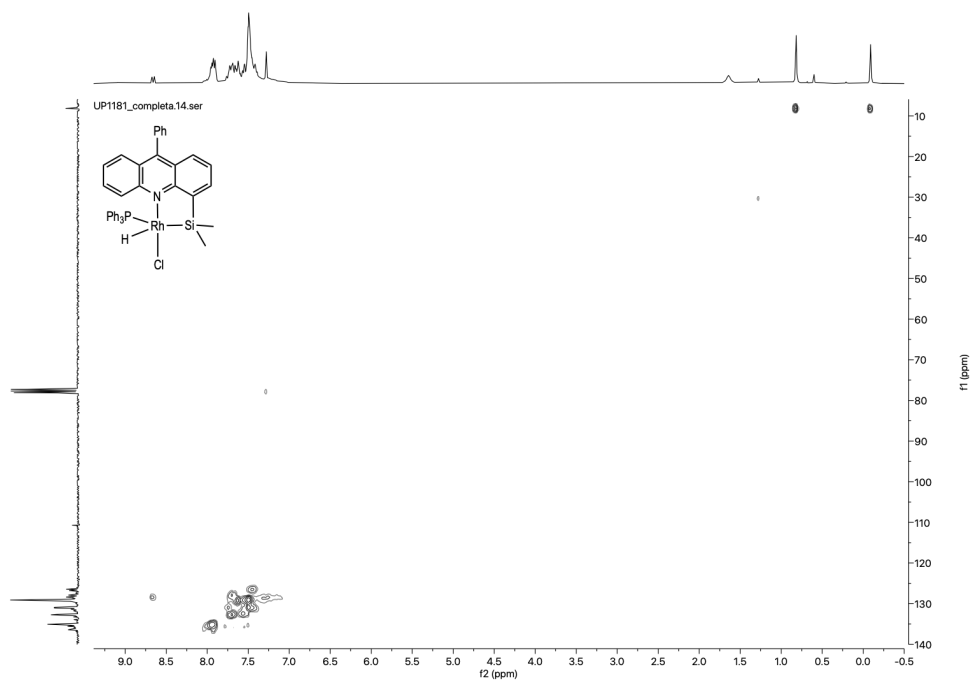


Figure S.58. HSQC  $^1\text{H}$ - $^{13}\text{C}$  NMR of 1-L3.

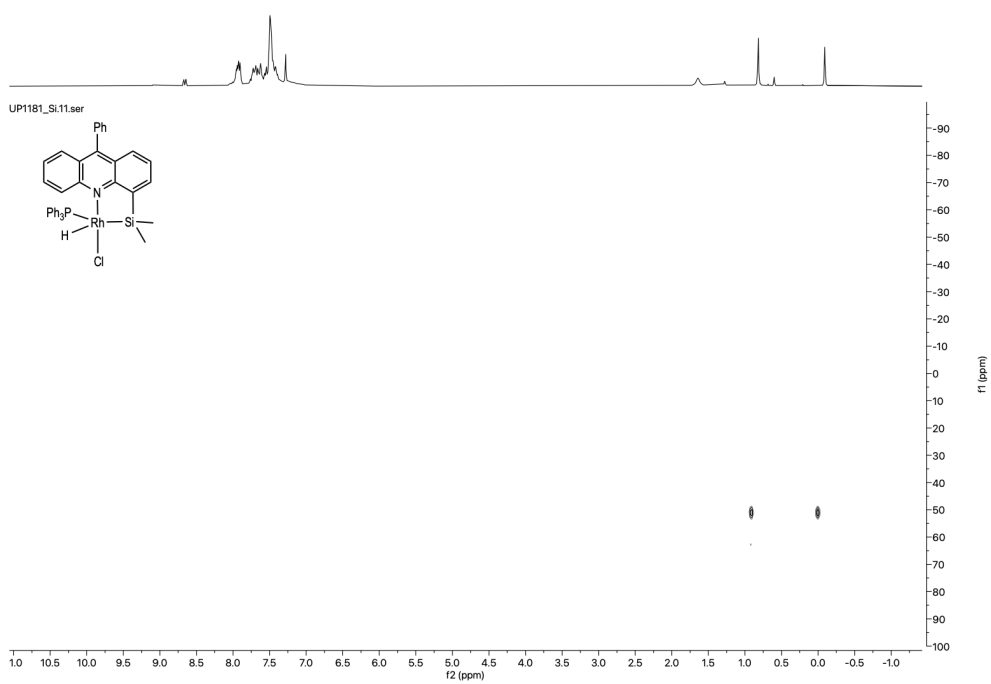


Figure S.59. HMBC  $^1\text{H}$ - $^{29}\text{Si}$  NMR of 1-L3.

## NMR spectra of 2-L1

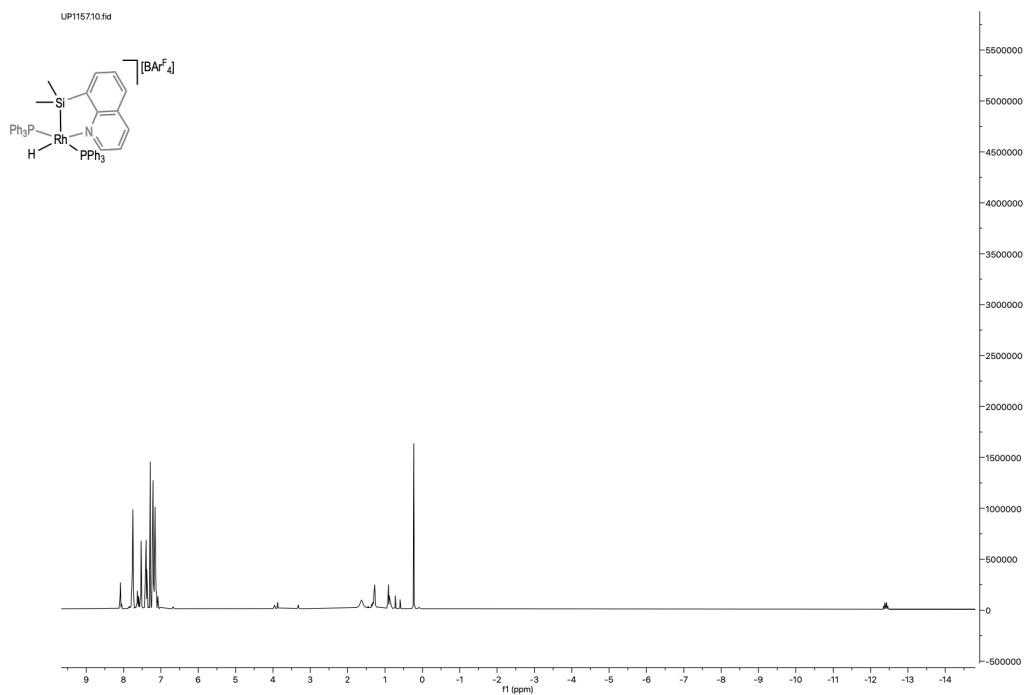


Figure S.60. <sup>1</sup>H NMR of 2-L1.

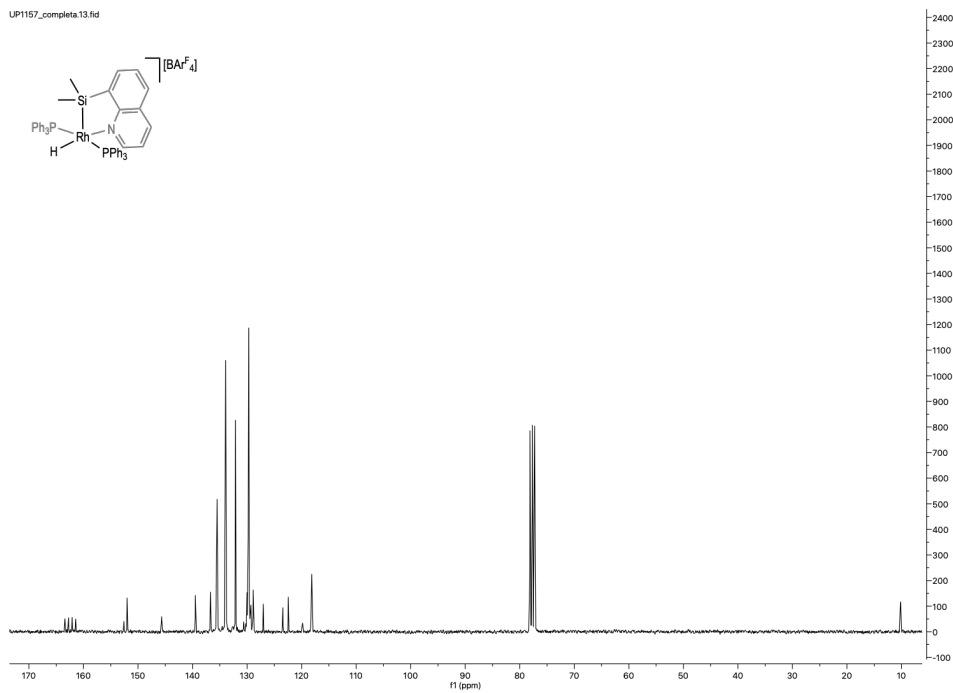
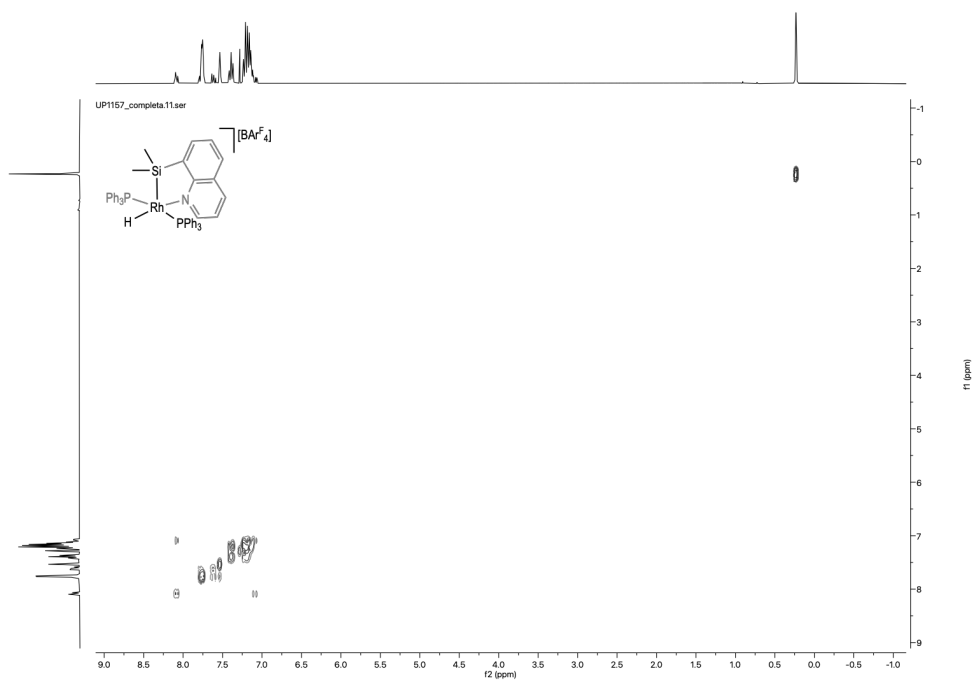
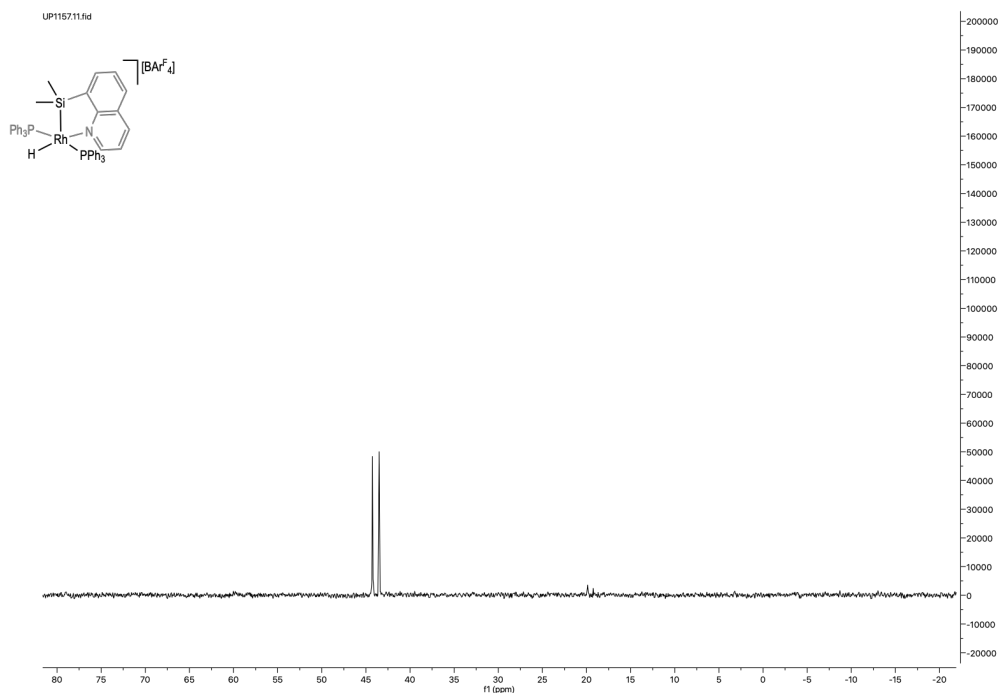
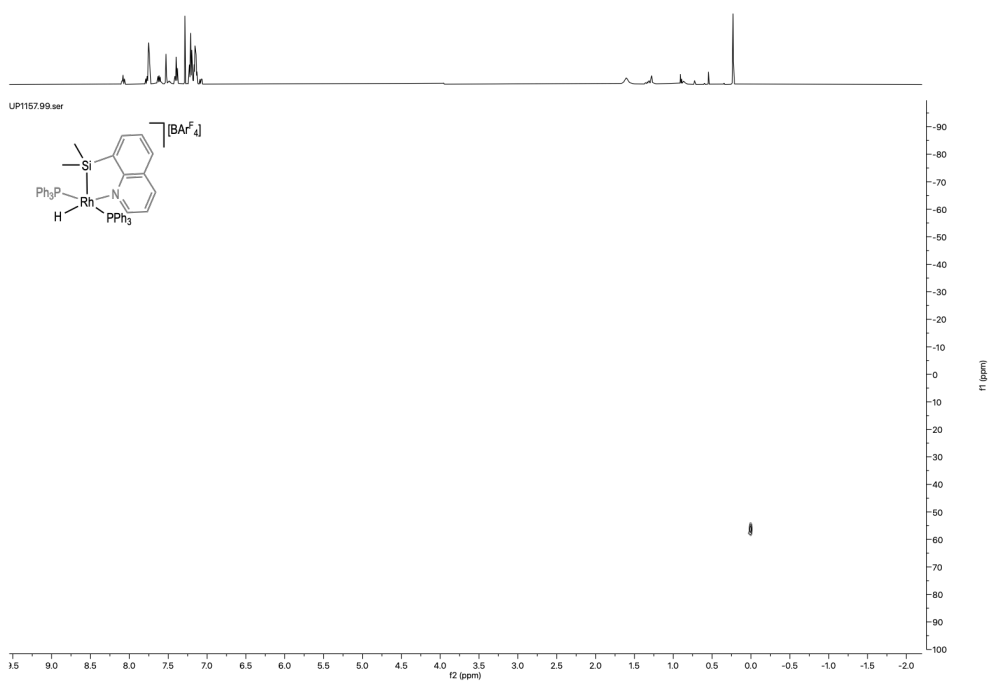
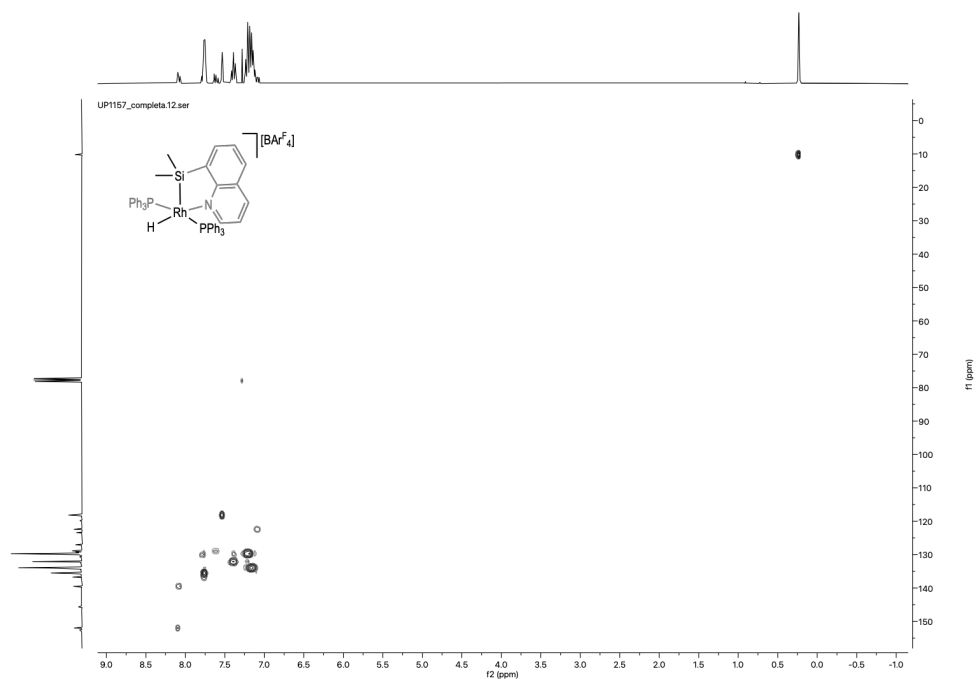


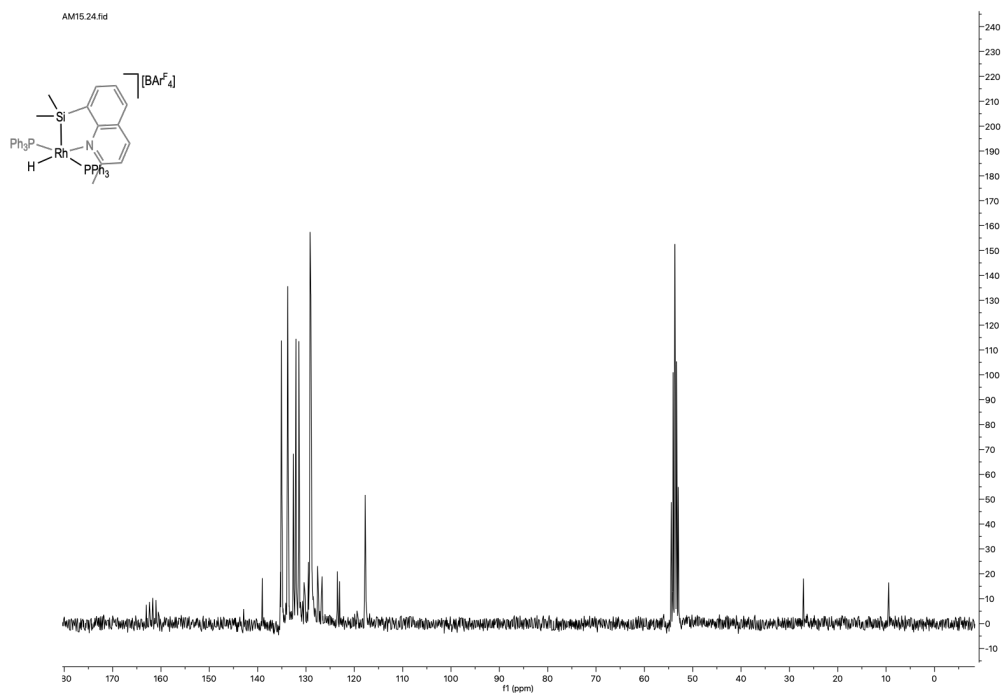
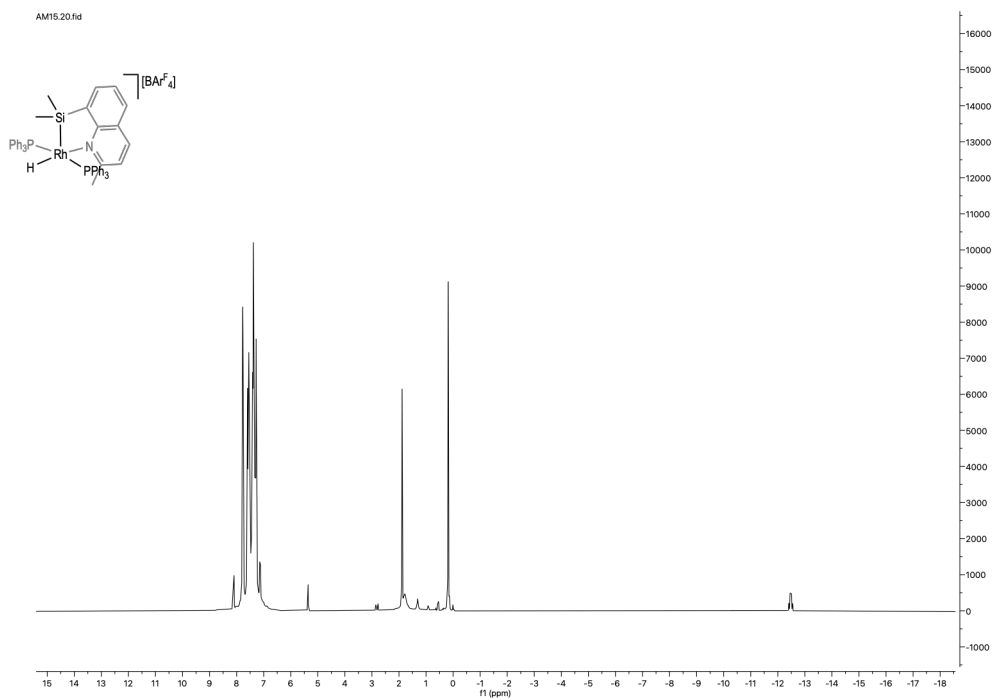
Figure S.61. <sup>13</sup>C{<sup>1</sup>H} NMR of 2-L1.







## NMR spectra of 2-L2



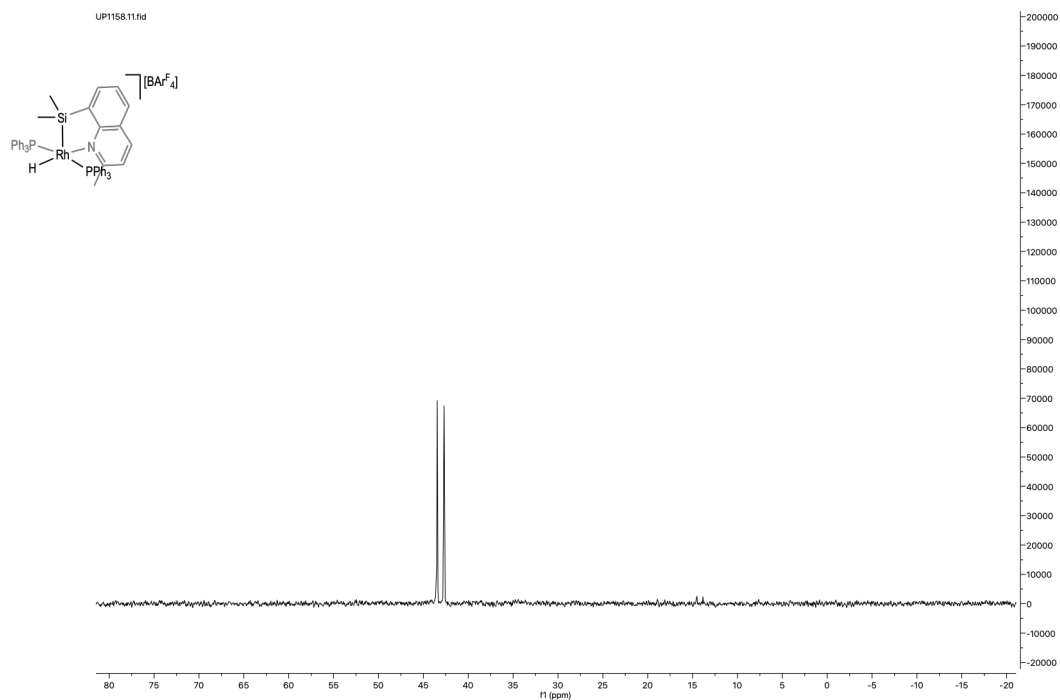


Figure S.68. <sup>31</sup>P{<sup>1</sup>H} NMR of 2-L2.

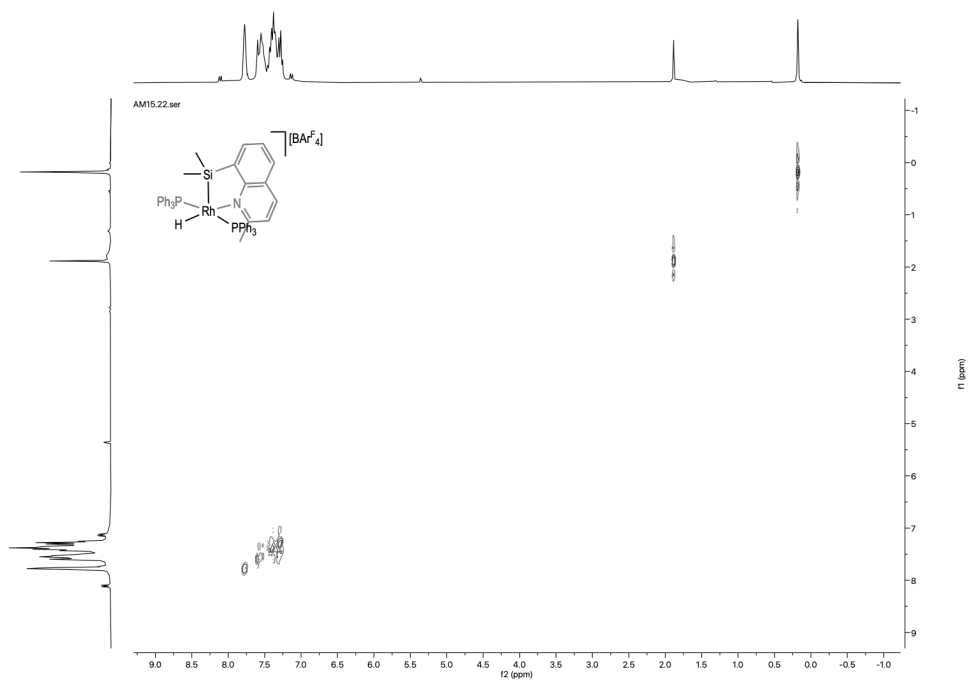
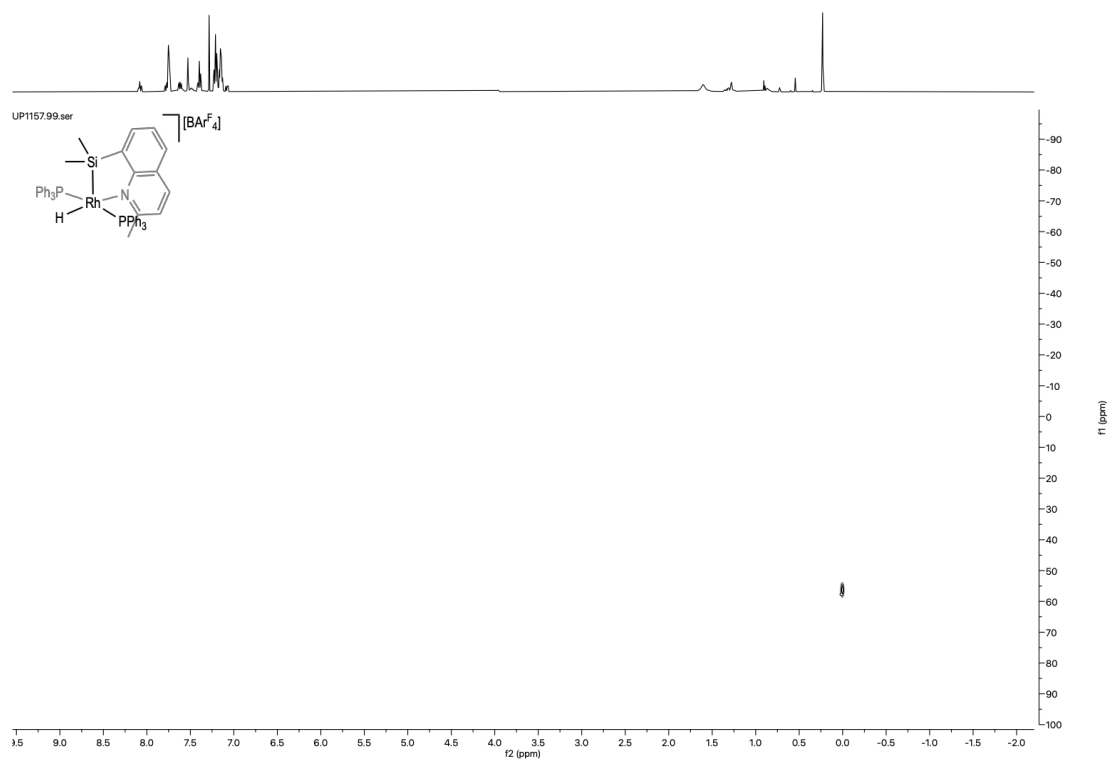
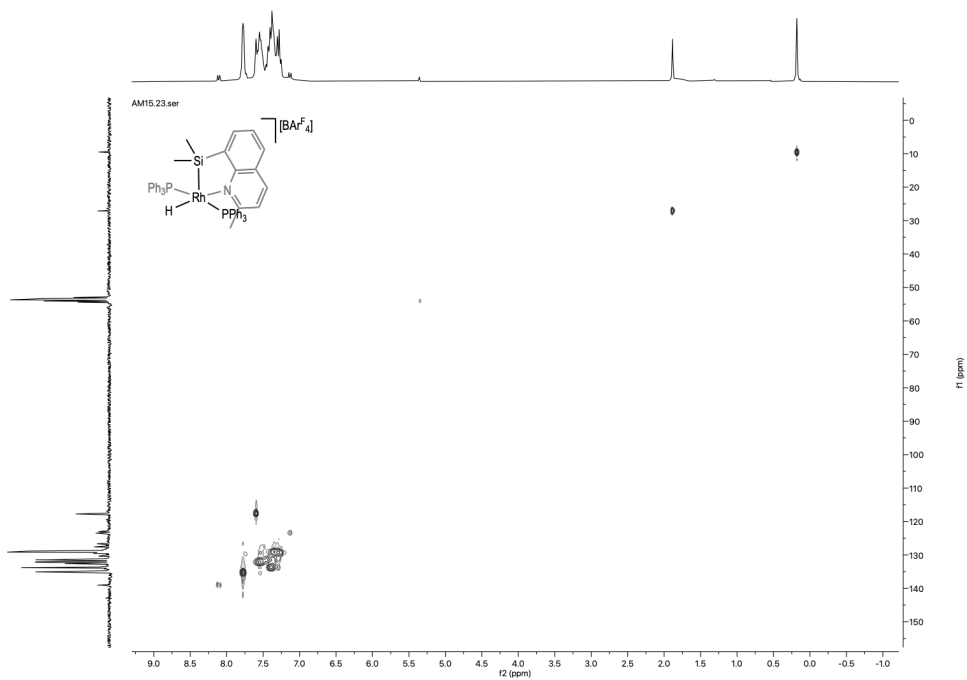
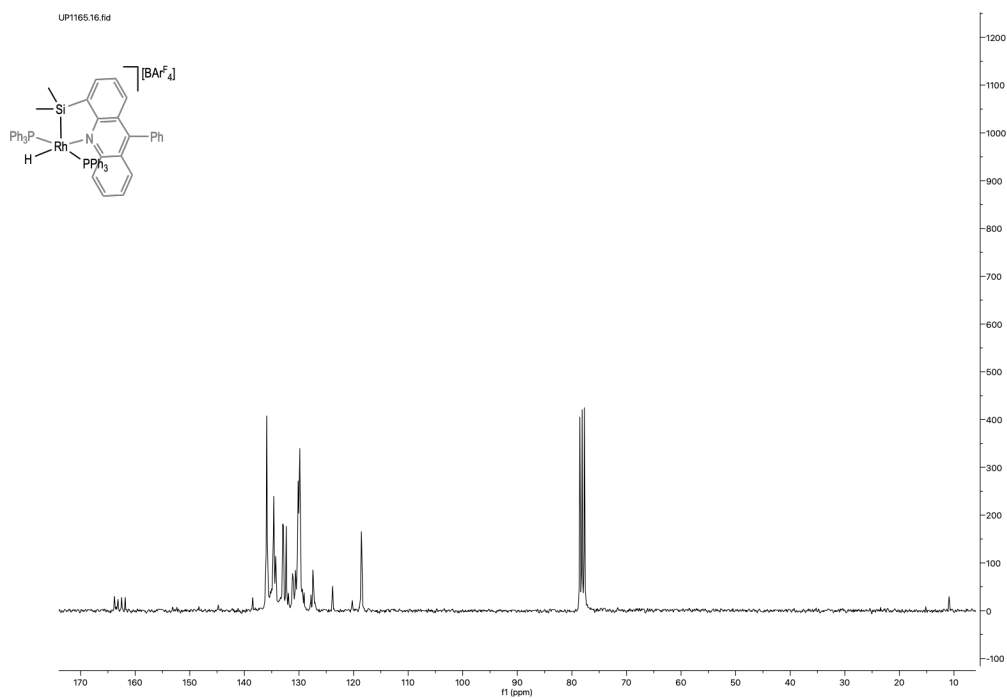
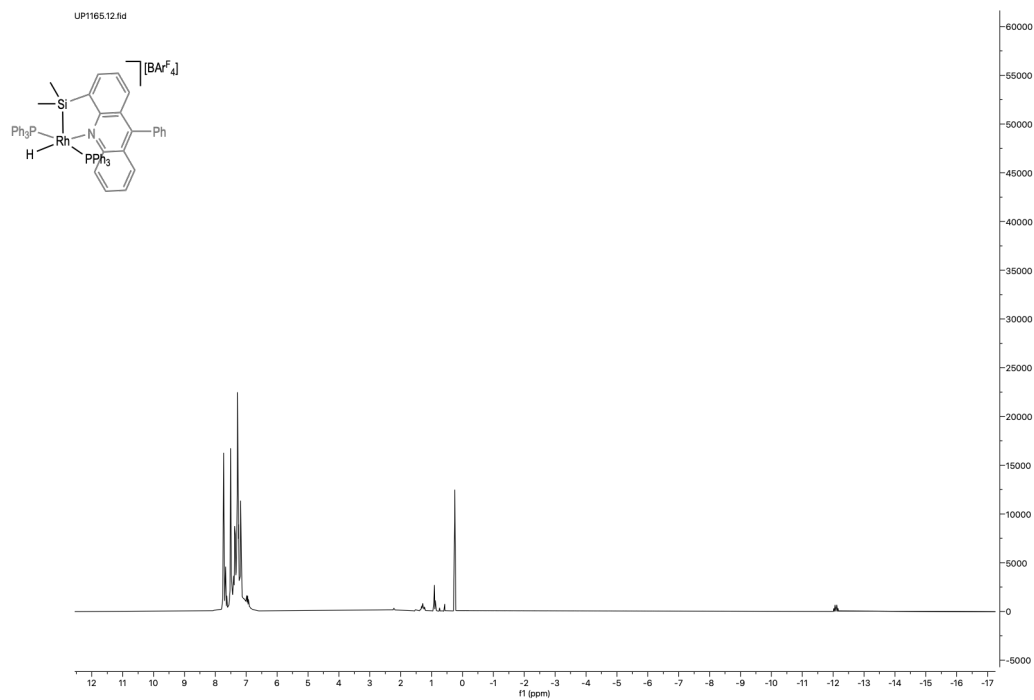


Figure S.69. COSY <sup>1</sup>H-<sup>1</sup>H NMR of 2-L2.



## NMR spectra of 2-L3



UP1165.20.fid

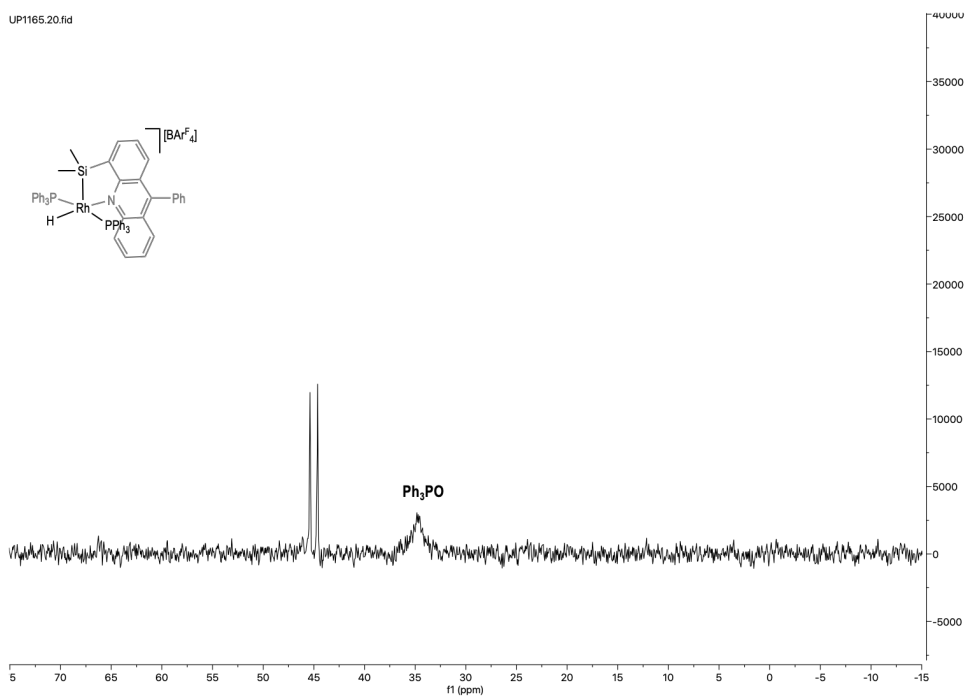


Figure S.74.  $^{31}\text{P}\{^1\text{H}\}$  NMR of 2-L3.

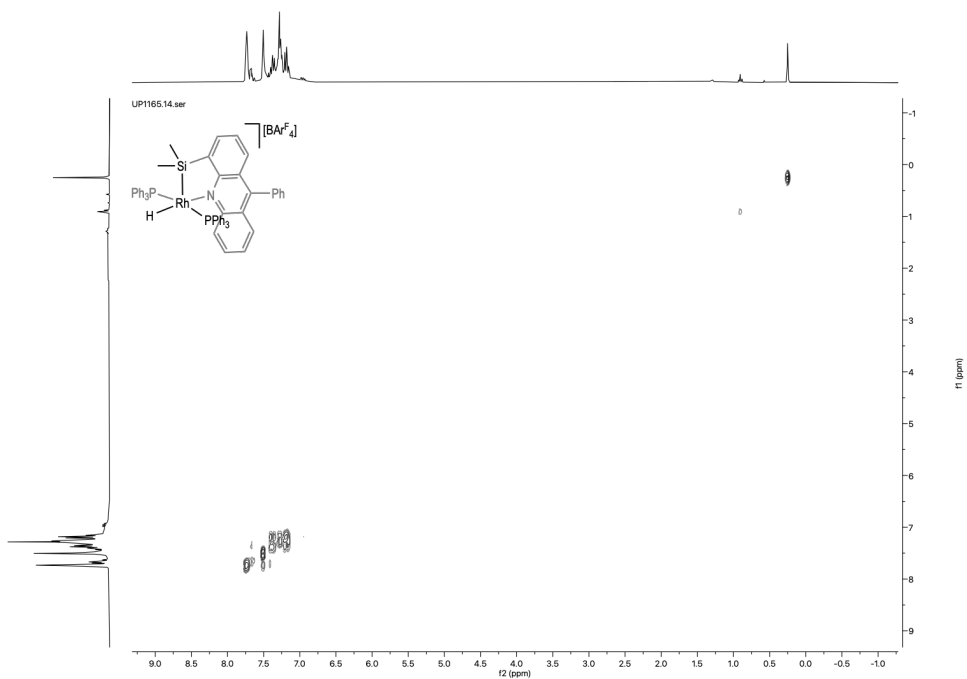
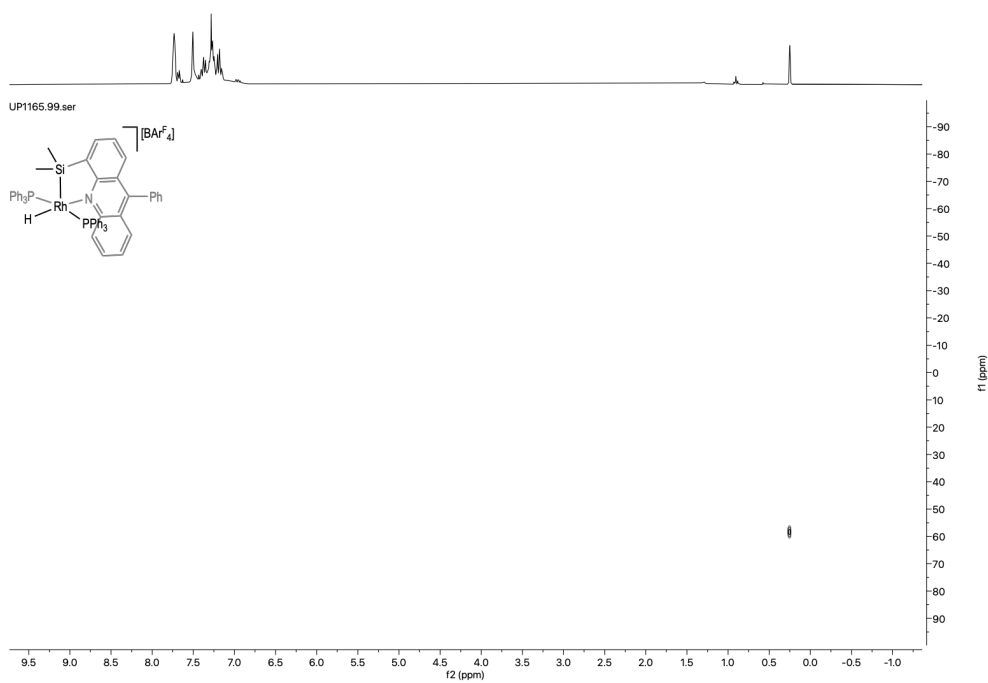
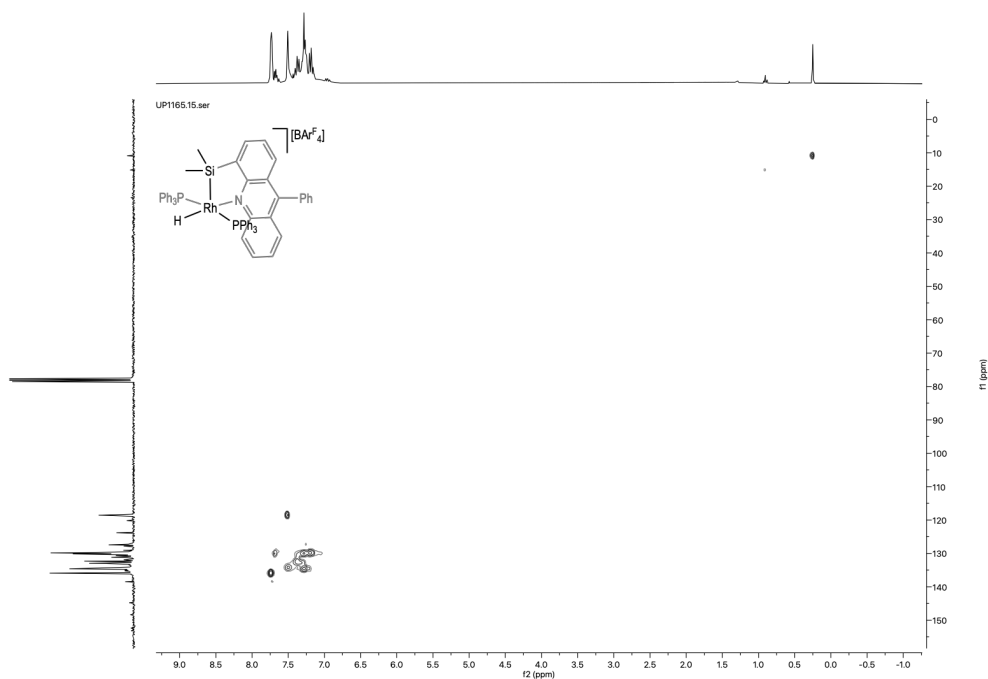


Figure S.75. COSY  $^1\text{H}$ - $^1\text{H}$  NMR of 2-L3.



## 10. MS Spectra

MS Spectrum

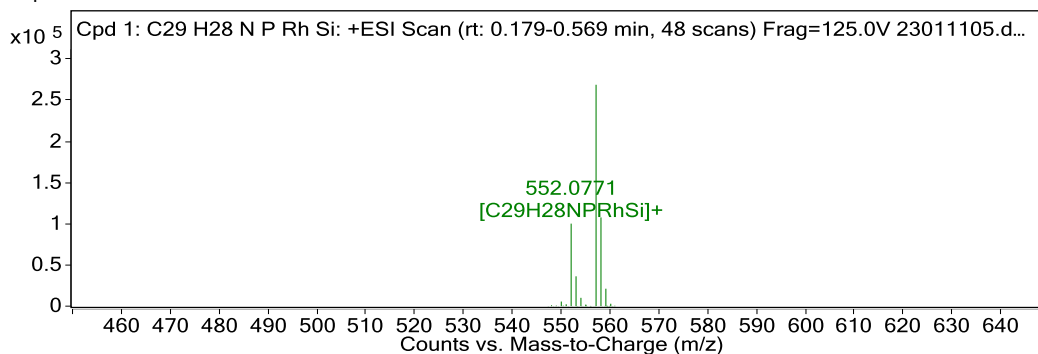


Figure S.78. MS Spectrum of 1-L1

MS Spectrum

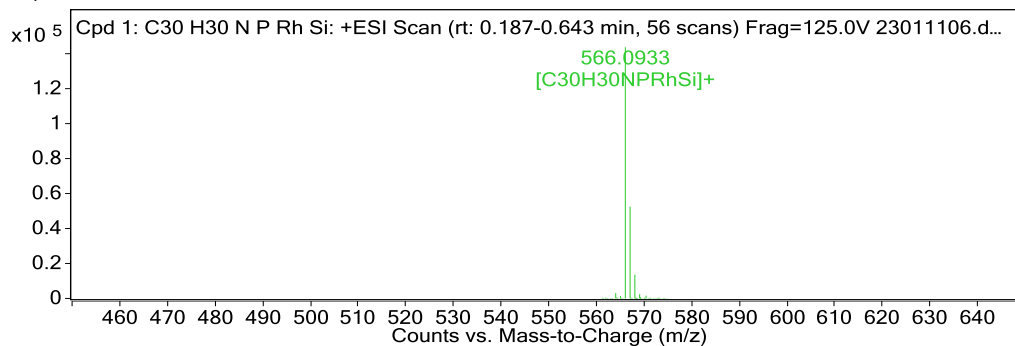


Figure S.79. MS Spectrum of 1-L2.

MS Spectrum

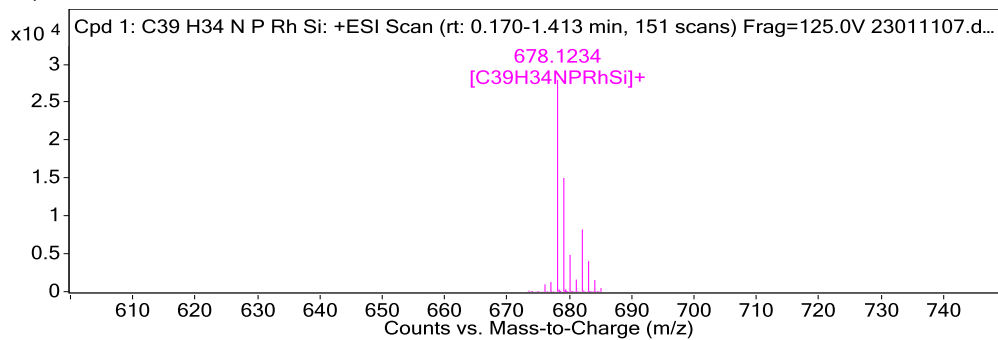


Figure S.80. MS Spectrum of 1-L3.

MS Spectrum

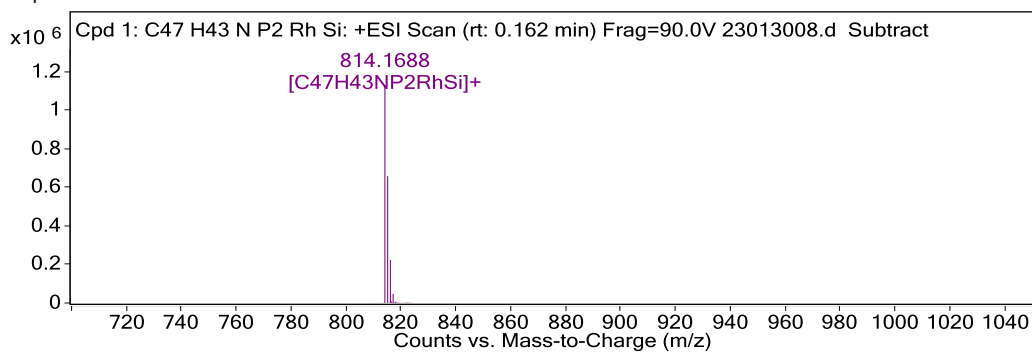


Figure S.81. MS Spectrum of 2-L1.

MS Spectrum

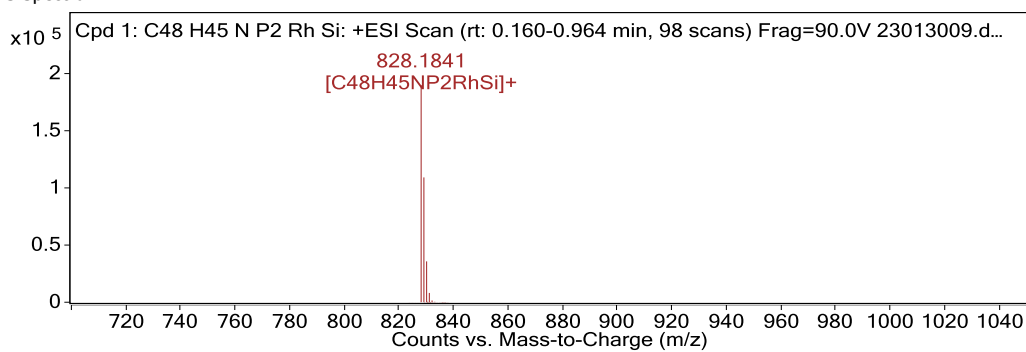


Figure S.82. MS Spectrum of 2-L2.

MS Spectrum

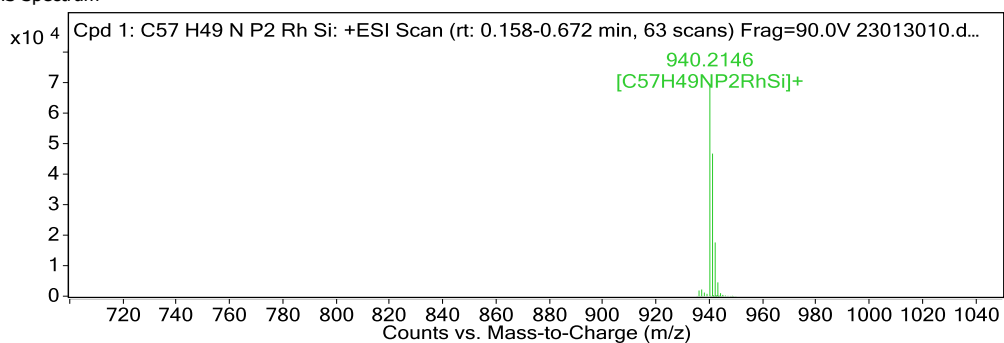


Figure S.83. MS Spectrum of 2-L3.