

# Supporting Information

## Silyl Formates for the Transfer Hydrosilylation of Ketones

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## Table of contents

1)	General considerations .....	S1
2)	Optimization of the reaction conditions .....	S2
3)	Screening of silyl formates .....	S3
4)	General procedures .....	S4
5)	Characterization of isolated and new silyl ethers (scaled up reactions) .....	S5
6)	Evidence for the crucial role of the N-H function .....	S9
7)	Study of the selectivity between aldehyde and ketone .....	S10
8)	TESOCDO synthesis .....	S11
9)	Deuterium labelling experiment .....	S14
10)	Experimental evidence of ruthenium monohydride species .....	S15
11)	Competition reactions .....	S16
12)	NMR spectra of isolated compounds .....	S17
13)	References .....	S31

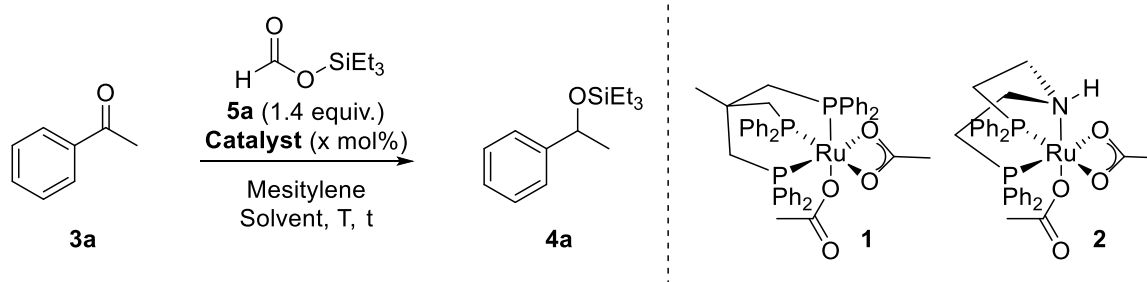
## 1. General considerations

Unless otherwise stated, all reactions were performed in a recirculating *mBraun LabMaster DP* inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware were dried overnight at 120 °C. NMR spectra were recorded in a *Bruker Avance Neo 400 MHz* spectrometer. Chemical shifts were reported as ppm downfield from residual solvent peaks. The following calibrations were used: CDCl<sub>3</sub>  $\delta$  = 7.26 and 77.16 ppm, THF-*d*<sub>8</sub>  $\delta$  = 3.58, 1.72 and 67.21, 25.31 ppm, C<sub>6</sub>D<sub>6</sub>  $\delta$  = 7.16 and 128.06 ppm, CD<sub>2</sub>Cl<sub>2</sub>  $\delta$  = 5.32 and 53.84 ppm. HRMS experiments were performed on a Bruker maXis within the service centre at Institute of Organic and Analytic Chemistry, University of Orléans. 4Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Deuterated solvents were dried and stored under molecular sieves. Toluene was dried with sodium benzophenone, distilled and stored under molecular sieves. [Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -triphos)] (**1**), *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>H</sup>P<sup>Ph</sup>)] (**2**)<sup>[1]</sup>, *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>Me</sup>P<sup>Ph</sup>)] (**2-Me**)<sup>[2]</sup>, silyl formates<sup>[3]</sup> were synthesized according to literature procedures. Ketones were purchased and used without any further purification.

## 2. Optimization of the reaction conditions

In a glovebox, a *J. Young* NMR Tube was charged with the catalyst (x mol%), C<sub>6</sub>D<sub>6</sub> (0.4 mL), acetophenone **3a** (0.1 mmol, 1.0 equiv.), mesitylene (10 μL) and the triethylsilylformate (1.4 equiv.). The tube was sealed, brought out of the glovebox and heated. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. Yields were determined by <sup>1</sup>H NMR integration versus mesitylene as an internal standard.

**Table S1.** Screening of conditions. 0.1 mmol scale

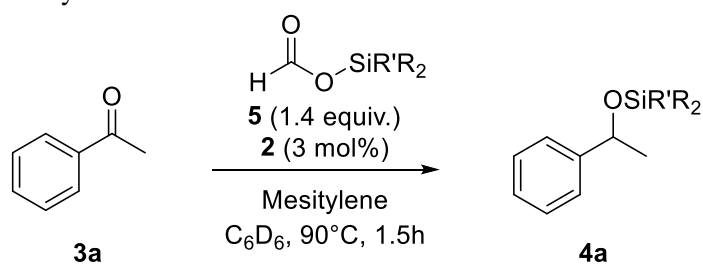


Entry	Catalyst (mol%)	Solvent	T (°C)	t (h)	Yield (%)
1	<b>1</b> (3)	CD <sub>3</sub> CN	90	24	0
2	<b>2</b> (3)	CD <sub>3</sub> CN	90	11	78
3	<b>2</b> (3)	<i>d8</i> -THF	90	2.5	99
4	<b>2</b> (3)	CD <sub>2</sub> Cl <sub>2</sub>	90	22	0
5	<b>2</b> (3)	<i>d8</i> -Toluene	90	2.5	92
6	<b>2</b> (3)	C <sub>6</sub> D <sub>6</sub>	90	1.5	99
7	<b>2</b> (3)	EtOAc	90	3	97
8	<b>2</b> (3)	Anisole	90	9	77
9	<b>2</b> (1.5)	C <sub>6</sub> D <sub>6</sub>	90	37	79
10	<b>2</b> (3)	C <sub>6</sub> D <sub>6</sub>	70	4	99
11	<b>2</b> (3)	C <sub>6</sub> D <sub>6</sub>	50	36	99

### 3. Screening of silyl formates

In a glovebox, a *J. Young* NMR Tube was charged with *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>H</sup>P<sup>Ph</sup>)] (**2**) (3 mol%), C<sub>6</sub>D<sub>6</sub> (0.4 mL), acetophenone **3a** (0.1 mmol, 1.0 equiv.), mesitylene (10  $\mu$ L) and the trialkylsilylformate (1.4 equiv.). The tube was sealed, brought out of the glovebox and heated. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. Yields were determined by <sup>1</sup>H NMR integration versus mesitylene as an internal standard.

**Table S2.** Screening of silylformates. 0.1 mmol scale



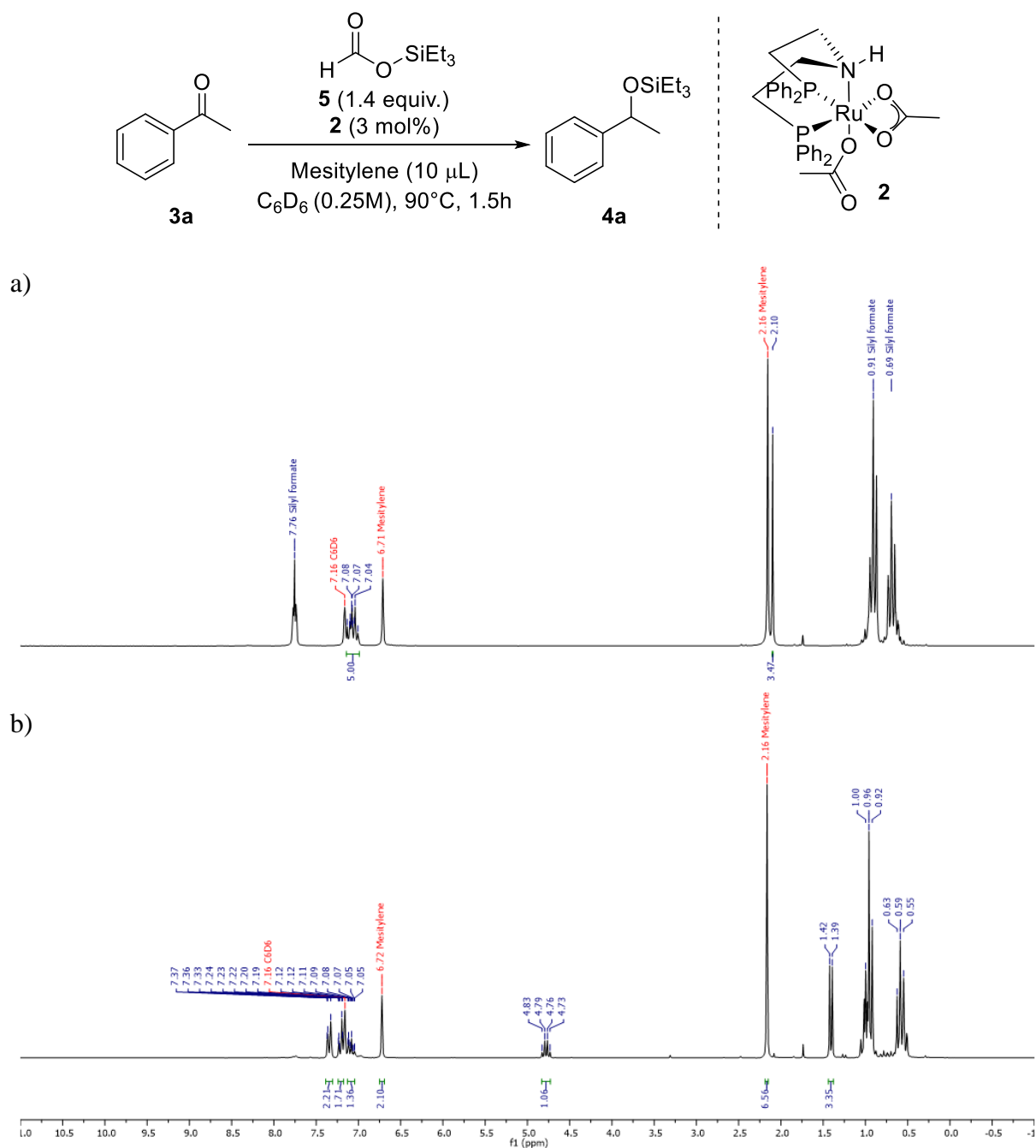
Entry	R'	R	Yield (%)
1	Et	Et	99
2	Me	Me	93
3	Ph	Me	98
4	Me	Ph	71
5	<i>t</i> Bu	Me	0
6	<i>i</i> Pr	<i>i</i> Pr	0
7	OEt	OEt	38

## 4. General procedures

### 4.1. General Procedure for NMR Scale reactions (GP1)

In a glovebox, a *J. Young* NMR Tube was charged with *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>H</sup>P<sup>Ph</sup>)] (**2**) (3 mol%), C<sub>6</sub>D<sub>6</sub> (0.4 mL), ketone (0.1 mmol, 1.0 equiv.), mesitylene (10  $\mu$ L) and the appropriate silyl formate (1.4 – 2.0 equiv.). The tube was sealed, brought out of the glovebox and heated at 90 °C. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. Yields of silylethers were determined by <sup>1</sup>H NMR integration versus mesitylene as an internal standard ( $\delta_{\text{H}} = 6.71$  and 2.15 ppm in C<sub>6</sub>D<sub>6</sub>).

Representative NMR spectra for the transfer hydrosilylation of acetophenone (**3a**) with Et<sub>3</sub>SiOCHO (**5a**) is given in Figures S1.



**Figure S1.** Representative  $^1\text{H}$  NMR spectra obtained in  $\text{C}_6\text{D}_6$  for the transfer hydrosilylation of acetophenone (**3a**) (0.1 mmol) with  $\text{Et}_3\text{SiCHO}$  (**5a**). a) Crude reaction mixture before heating;  $t = 0$ . b) Crude mixture after heating 1.5 h at  $90^\circ\text{C}$ .

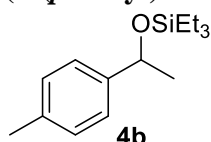
The formation of known silyl ethers **4c**,<sup>[4]</sup> **4d**,<sup>[5]</sup> **4g**,<sup>[6]</sup> **4i**,<sup>[7]</sup> **4j**,<sup>[8]</sup> **4la**,<sup>[9]</sup> **4lb**,<sup>[10]</sup> **4m**,<sup>[7]</sup> **4n**,<sup>[7]</sup> **4t**,<sup>[7]</sup> **4u**,<sup>[7]</sup> **4v**,<sup>[11]</sup> was confirmed by  $^1\text{H}$  NMR and/or  $^{13}\text{C}$  NMR analysis, with spectroscopic data in accordance with literature.

#### 4.2. General Procedure for preparative scale up reactions (GP2)

In a flamed and dried Schlenk tube, *fac*- $[\text{Ru}(\kappa^1\text{-OAc})(\kappa^2\text{-OAc})(\kappa^3\text{-PN}^{\text{H}}\text{P}^{\text{Ph}})]$  (**2**) (3 mol%), Toluene (2 mL), ketone (0.5 mmol, 1.0 equiv.) and the appropriate silyl formate (1.4 – 2.0 equiv.) were added. The Schlenk tube was sealed, and heated at  $90^\circ\text{C}$ . After reaction completion, the solvent was removed under reduced pressure. The final crude product was purified by chromatography (silica-gel, cyclohexane/ethyl acetate or petroleum ether/Ethyl acetate mixtures).

### 5. Characterization of isolated and new silyl ethers (scaled up reactions)

#### (1-(*p*-Tolyl)ethoxy)triethylsilane (**4b**)

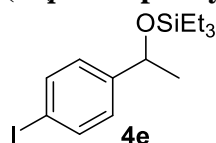


Isolated as a colorless oil in 90% yield (procedure GP2). Spectroscopic data in accordance with literature.<sup>[5]</sup>

$^1\text{H}$  NMR (200 MHz,  $d_8$ -THF):  $\delta = 7.21$  (d,  $J = 7.9$  Hz, 2H),  $7.07$  (d,  $J = 7.9$  Hz, 2H),  $4.86$  (q,  $J = 6.3$  Hz, 1H),  $2.28$  (s, 3H),  $1.36$  (d,  $J = 6.3$  Hz, 3H),  $0.91$  (t,  $J = 7.8$  Hz, 9H),  $0.63$ - $0.48$  (m, 6H).

$^{13}\text{C}$  NMR (50 MHz,  $d_8$ -THF):  $\delta = 144.8$ ,  $136.6$ ,  $129.2$ ,  $125.7$ ,  $71.2$ ,  $27.7$ ,  $21.0$ ,  $7.0$ ,  $5.4$ .

#### (1-(*p*-Iodophenyl)ethoxy)triethylsilane (**4e**)



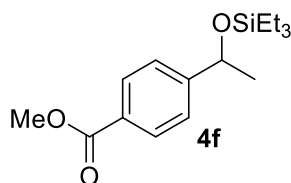
Isolated as a colorless oil in 86% yield (procedure GP2).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.63$  (d,  $J = 8.4$  Hz, 2H),  $7.09$  (d,  $J = 8.2$  Hz, 2H),  $4.80$  (q,  $J = 6.3$  Hz, 1H),  $1.38$  (d,  $J = 6.3$  Hz, 3H),  $0.91$  (t,  $J = 7.9$  Hz, 9H),  $0.61$ - $0.52$  (m, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 146.8$ ,  $137.3$ ,  $127.4$ ,  $92.1$ ,  $70.2$ ,  $27.3$ ,  $6.9$ ,  $4.9$ .

HRMS (ESI+) ( $m/z$ ):  $[\text{M} - \text{H}]^+$  calcd. for  $\text{C}_{14}\text{H}_{22}\text{IOSi}$ , 361.0479; found: 361.0481

#### Methyl 4-(1-((triethylsilyl)oxy)ethyl)benzoate (**4f**)



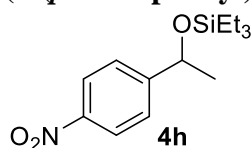
Isolated as a colorless oil in 85% yield (procedure GP2).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  = 7.99 (d,  $J$  = 8.3 Hz, 2H), 7.41 (d,  $J$  = 8.3 Hz, 2H), 4.90 (q,  $J$  = 6.4 Hz, 1H), 3.90 (s, 3H), 1.42 (d,  $J$  = 6.3 Hz, 3H), 0.91 (t,  $J$  = 8.0 Hz, 9H), 0.62-0.51 (m, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta$  = 167.3, 152.3, 129.7, 128.8, 125.3, 70.4, 52.1, 27.2, 6.9, 4.9.

**HRMS (ESI+)** ( $m/z$ ): [M + H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>27</sub>O<sub>3</sub>Si, 295.1724; found: 295.1725.

**(1-(*p*-Nitrophenyl)ethoxy)triethylsilane (4h)**

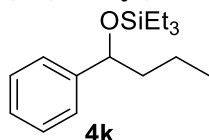


Isolated as a colorless oil in 95% yield (procedure GP2). Spectroscopic data in accordance with literature.<sup>[12]</sup>

**<sup>1</sup>H NMR (200 MHz, *d*<sub>8</sub>-THF):**  $\delta$  = 8.18 (d,  $J$  = 8.8 Hz, 2H), 7.60 (d,  $J$  = 8.8 Hz, 2H), 5.06 (q,  $J$  = 6.3 Hz, 1H), 1.42 (d,  $J$  = 6.4 Hz, 3H), 0.94 (t,  $J$  = 7.8 Hz, 9H), 0.70-0.52 (m, 6H).

**<sup>13</sup>C NMR (50 MHz, *d*<sub>8</sub>-THF):**  $\delta$  = 155.1, 147.9, 126.8, 124.0, 70.6, 27.2, 6.9, 5.2.

**(1-(Phenyl)butoxy)triethylsilane (4k)**



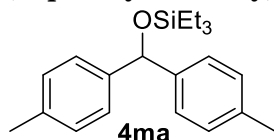
Isolated as a colorless oil in 80% yield (procedure GP2).

**<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>):**  $\delta$  = 7.36-7.28 (m, 2H), 7.24-7.06 (m, 3H), 4.63 (dd,  $J$  = 7.2, 5.1 Hz, 1H), 1.90-1.20 (m, 4H), 1.01-0.79 (m, 12H), 0.65-0.48 (m, 6H).

**<sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>):**  $\delta$  = 146.3, 128.4, 127.3, 126.3, 75.3, 43.7, 19.3, 14.3, 7.1, 5.3.

**HRMS (ESI+)** ( $m/z$ ): [M - H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>27</sub>OSi, 263.1826; found: 263.1827 (Data of the oxidized product).

**(di-*p*-Tolylmethoxy)triethylsilane (4ma)**



Isolated as a white solid in 80% yield (procedure GP2).

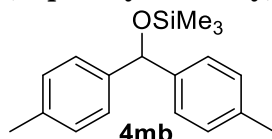
**<sup>1</sup>H NMR (200 MHz, *d*<sub>8</sub>-THF)**  $\delta$  = 7.23 (d,  $J$  = 7.6 Hz, 4H), 7.04 (d,  $J$  = 7.6 Hz, 4H), 5.75 (s, 1H), 2.26 (s, 6H), 0.89z (t,  $J$  = 7.5 Hz, 9H), 0.70 – 0.43 (m, 6H).

**<sup>13</sup>C NMR (50 MHz, *d*<sub>8</sub>-THF)**  $\delta$  = 143.5, 136.7, 129.2, 126.8, 76.9, 20.9, 7.0, 5.4.

**HRMS (ESI+)** ( $m/z$ ): [M + Na]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>30</sub>NaOSi, 349.1958; found: 349.1962.



**(di-*p*-Tolylmethoxy)triethylsilane (4mb)**



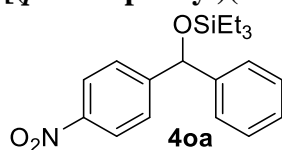
Isolated as a colorless oil in 70% yield (procedure GP2).

**<sup>1</sup>H NMR (200 MHz, CD<sub>2</sub>Cl<sub>2</sub>)**  $\delta$  = 7.20 (d, *J* = 7.7 Hz, 4H), 7.10 (d, *J* = 7.7 Hz, 4H), 5.71 (s, 1H), 2.30 (s, 6H), 0.07 (s, 9H).

**<sup>13</sup>C NMR (50 MHz, CD<sub>2</sub>Cl<sub>2</sub>)**  $\delta$  = 142.7, 137.0, 129.1, 126.6, 76.4, 21.1, 0.1.

**HRMS (ESI+)** (*m/z*): [M + Na]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>24</sub>NaOSi, 307.1489; found: 307.1491.

**[(*p*-Nitrophenyl)(Phenyl)methoxy]triethylsilane (4oa)**



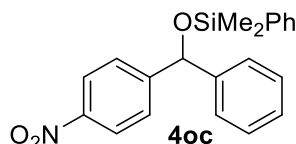
Isolated as a colorless oil in 95% yield (procedure GP2).

**<sup>1</sup>H NMR (200 MHz, *d*<sub>8</sub>-THF)**  $\delta$  = 8.15 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.47-7.36 (m, 2H), 7.34-7.17 (m, 3H), 5.96 (s, 1H), 0.89 (t, *J* = 7.7 Hz, 9H), 0.71-0.53 (m, 6H).

**<sup>13</sup>C NMR (50 MHz, *d*<sub>8</sub>-THF)**  $\delta$  = 153.4, 147.9, 144.9, 129.0, 128.1, 127.5, 127.0, 124.0, 76.4, 6.9, 5.2.

**HRMS (ESI+)** (*m/z*): [M + H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>26</sub>NO<sub>3</sub>Si, 344.1676; found: 344.1675.

**Dimethyl[(4-nitrophenyl)(phenyl)methoxy](phenyl)silane (4oc)**

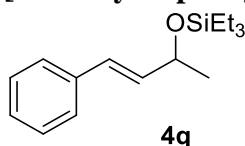


Isolated as a white solid in 63% yield (procedure GP2 with Anisole as solvent).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  = 8.16 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.48 (m, 4H), 7.47 – 7.40 (m, 1H), 7.40 – 7.24 (m, 7H), 5.80 (s, 1H), 0.35 (d, *J* = 5.0 Hz, 6H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  = 152.0, 147.0, 143.2, 136.9, 133.5, 129.9, 128.6, 127.9, 127.8, 127.0, 126.6, 123.6, 76.2, -1.1, -1.4.

**[1-Methyl-3-phenyl-(*E*)-allyloxy]triethylsilane (4q)**



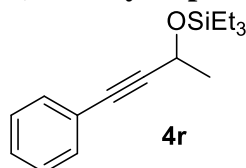
Isolated as a colorless oil in 78% yield (procedure GP2). Spectroscopic data in accordance with literature.<sup>[12]</sup>

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  = 7.39-7.35 (m, 2H), 7.28-7.34 (m, 2H), 7.25-7.17 (m, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.22 (ddd, *J* = 15.9, 5.9, 1.0 Hz, 1H), 4.47 (p, *J* = 6.3 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.67-0.60 (m, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta = 137.3, 134.6, 128.7, 128.2, 127.4, 126.5, 69.3, 24.9, 7.0, 5.0.$

**HRMS (ESI+)** (*m/z*): [M - H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>25</sub>OSi, 261.1669; found: 261.1669.

**[(1-Methyl-3-phenyl-2propynyl)oxy]triethylsilane (4r)**



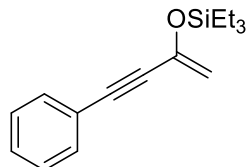
Isolated as a colorless oil in 55% yield (procedure GP2). Spectroscopic data in accordance with literature.<sup>[12]</sup>

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta = 7.43-7.39$  (m, 2H),  $7.32-7.28$  (m, 3H),  $4.74$  (q,  $J = 6.5$  Hz, 1H),  $1.52$  (d,  $J = 6.5$  Hz, 3H),  $1.01$  (t,  $J = 7.9$  Hz, 9H),  $0.73-0.65$  (m, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta = 131.7, 128.4, 128.2, 123.3, 91.9, 83.3, 59.2, 25.6, 6.9, 5.0.$

**HRMS (ESI+)** (*m/z*): [M - H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>23</sub>OSi, 259.1513; found: 259.1516.

**[(4-phenylbut-1-en-3-yn)oxy]triethylsilane**



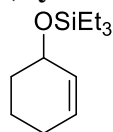
Isolated as a colorless oil in 36% yield (procedure GP2).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta = 7.47-7.44$  (m, 2H),  $7.35-7.31$  (m, 3H),  $4.78$  (d,  $J = 6.3$  Hz, 2H),  $1.04$  (t,  $J = 7.9$  Hz, 9H),  $0.72-0.74$  (m, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):**  $\delta = 139.6, 131.7, 128.7, 128.5, 122.6, 102.9, 87.2, 86.9, 6.8, 5.1.$

**HRMS (ESI+)** (*m/z*): [M - H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>21</sub>OSi, 257.1356; found: 257.1362.

**(Cyclohex-2-en-1-yloxy)triethylsilane (4s)**



**4s**

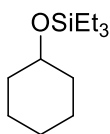
Isolated as a colorless oil in 73% yield (procedure GP2).

**<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>)**  $\delta = 5.88-5.74$  (m, 1H),  $5.73-5.52$  (m, 1H),  $4.22$  (m, 1H),  $1.89-1.57$  (m, 5H),  $1.51-1.25$  (m, 1H),  $1.03$  (t,  $J = 7.8$  Hz, 9H),  $0.75-0.51$  (m, 6H).

**<sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>)**  $\delta = 131.8, 128.8, 66.6, 33.1, 25.3, 19.9, 7.2, 5.5.$

**HRMS (ESI+)** (*m/z*): [M - H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>23</sub>OSi, 211.1513; found : 211.1510.

**(Cyclohexyloxy)triethylsilane (4w)**



**4w**

Isolated as a colorless oil in 95% yield (procedure GP2). Spectroscopic data in accordance with literature.<sup>[13]</sup>

<sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 3.74-3.49 (m, 1H), 1.89-1.58 (m, 4H), 1.53-1.30 (m, 3H), 1.29-1.10 (m, 3H), 1.04 (t,  $J$  = 7.9 Hz, 9H), 0.73-0.53 (m, 6H).

<sup>13</sup>C NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  = 70.7, 36.5, 26.0, 24.4, 7.3, 5.5.

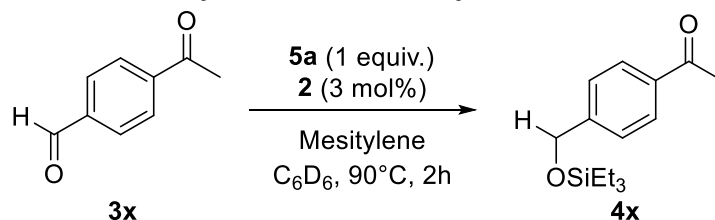
## 6. Evidence for the crucial role of the N-H function

In order to prove the importance of the role of the ligand N-H group in the hydrosilylation of ketones, the reaction was performed on aldehydes and ketones with catalysts *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>H</sup>P<sup>Ph</sup>)] (**2**) and *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>Me</sup>P<sup>Ph</sup>)] (**2-Me**) following the general procedure for NMR scale reactions (GP1).

**Table S3.** Reduction of ketones and aldehydes with catalysts **2** or **2-Me**. (0.1 mmol scale)

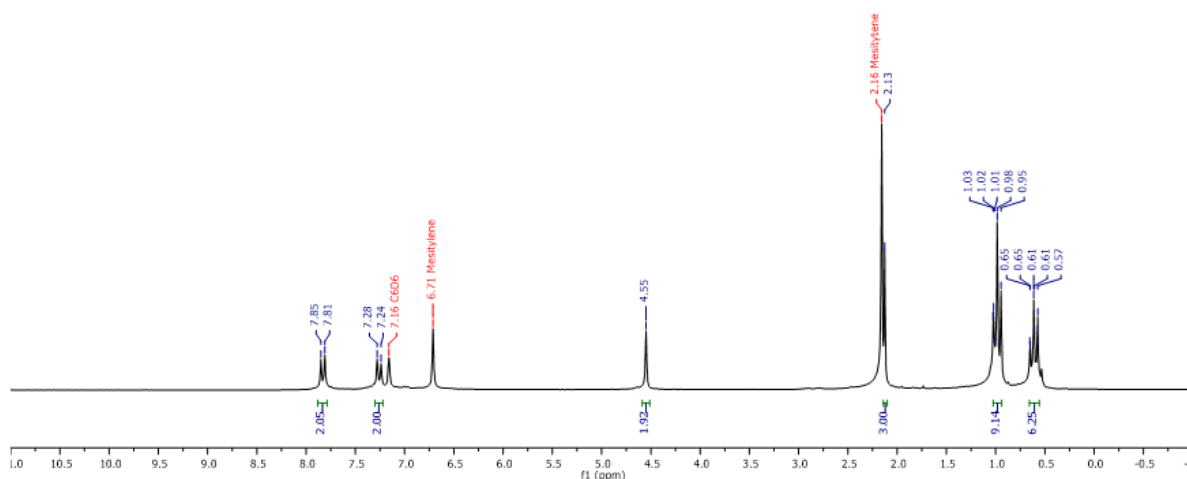
Entry	R	Cat	Yield (%)
1	Me	<b>2</b>	99
2	H	<b>2</b>	99
3	Me	<b>2-Me</b>	0
4	H	<b>2-Me</b>	99

## 7. Study of the selectivity between aldehydes and ketones



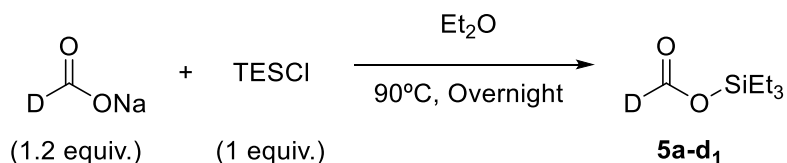
In a glovebox, a *J. Young* NMR Tube was charged with *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>H</sup>P<sup>Ph</sup>)] (**1**) (3 mol%), C<sub>6</sub>D<sub>6</sub> (0.4 mL), 4-acetylbenzaldehyde (**3x**) (0.1 mmol, 1 equiv.), mesitylene (10  $\mu$ L) and triethylsilyl formate (**5a**) (1.0 equiv.). The tube was sealed, brought out of the glovebox and heated at 90 °C. The reaction progress was monitored by <sup>1</sup>H NMR spectroscopy versus mesitylene as an internal standard. After 2 h at 90 °C, the aldehyde is fully hydro-silylated whereas the ketone remains unchanged.

NMR spectra for the transfer hydro-silylation of 4-acetylbenzaldehyde (**3x**) with Et<sub>3</sub>SiOCHO (**5a**) is given in Figure S2. Spectroscopic data is in accordance with literature.<sup>[14]</sup>



**Figure S2.** <sup>1</sup>H NMR spectra obtained in C<sub>6</sub>D<sub>6</sub> for the transfer hydro-silylation of 4-acetylbenzaldehyde (**3x**) with Et<sub>3</sub>SiOCHO (**5a**). Crude mixture after heating 2 h at 90 °C.

## 8. TESOCDO synthesis



Deuterated silylformate **5a-d<sub>1</sub>** was synthesized according to literature.<sup>[3]</sup> An oven-dried flask equipped with a *J-Young* valve was charged with deuterated sodium formate (1.2 equiv.), diethylether (11 mL) and triethylsilylchloride (10.9 mmol) under inert atmosphere. The final mixture was stirred at 90 °C overnight. Once the reaction is complete, the reaction was cold down and filtered in the glovebox through a plug of Celite. The liquid phase was collected and concentrated under vacuum at 0 °C for 2h to yield the pure product as a colourless liquid in 83% yield.

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 0.91 (t, *J* = 7.8 Hz, 9H), 0.72-0.64 (m, 6H).

<sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 160.2 (t, *J* = 33.6 Hz), 6.6, 4.8.

<sup>29</sup>Si NMR (79 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 26.5.

<sup>2</sup>H-NMR (61 MHz, Toluene): 7.76.

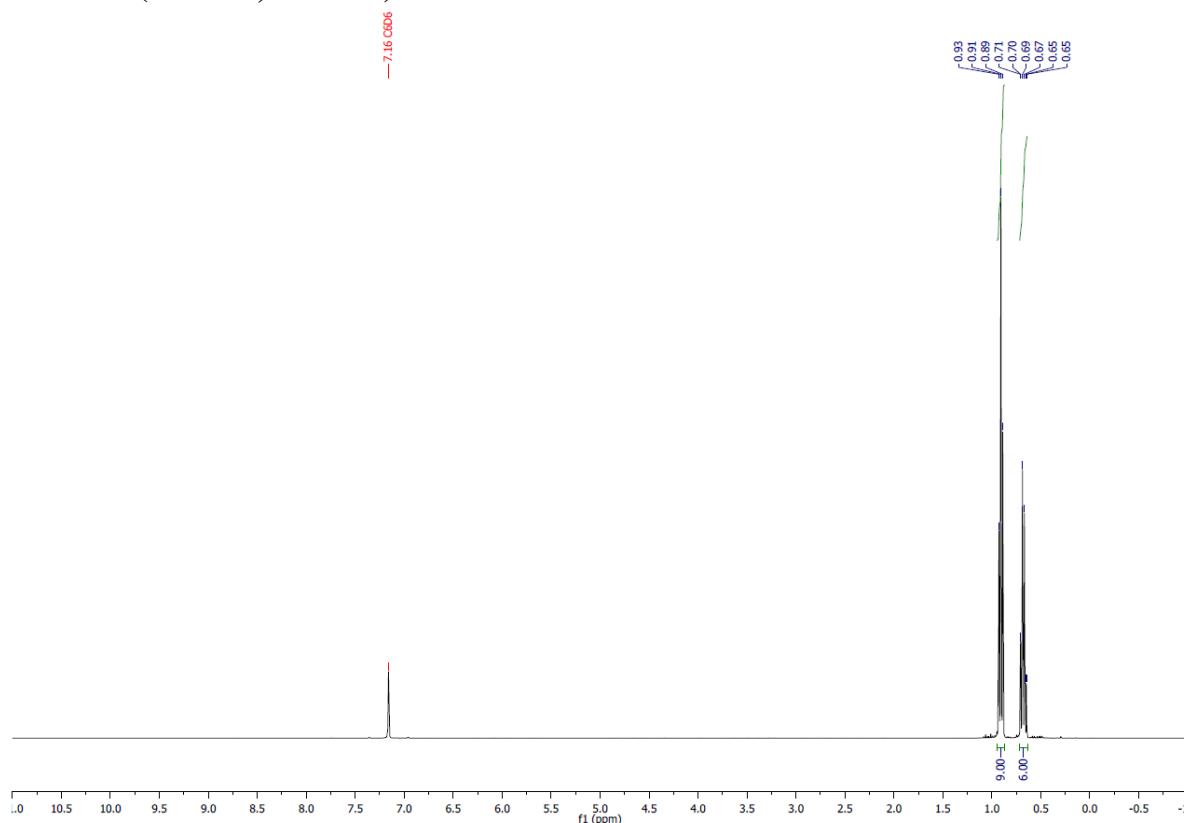


Figure S3. <sup>1</sup>H NMR of TESOCDO in C<sub>6</sub>D<sub>6</sub>.

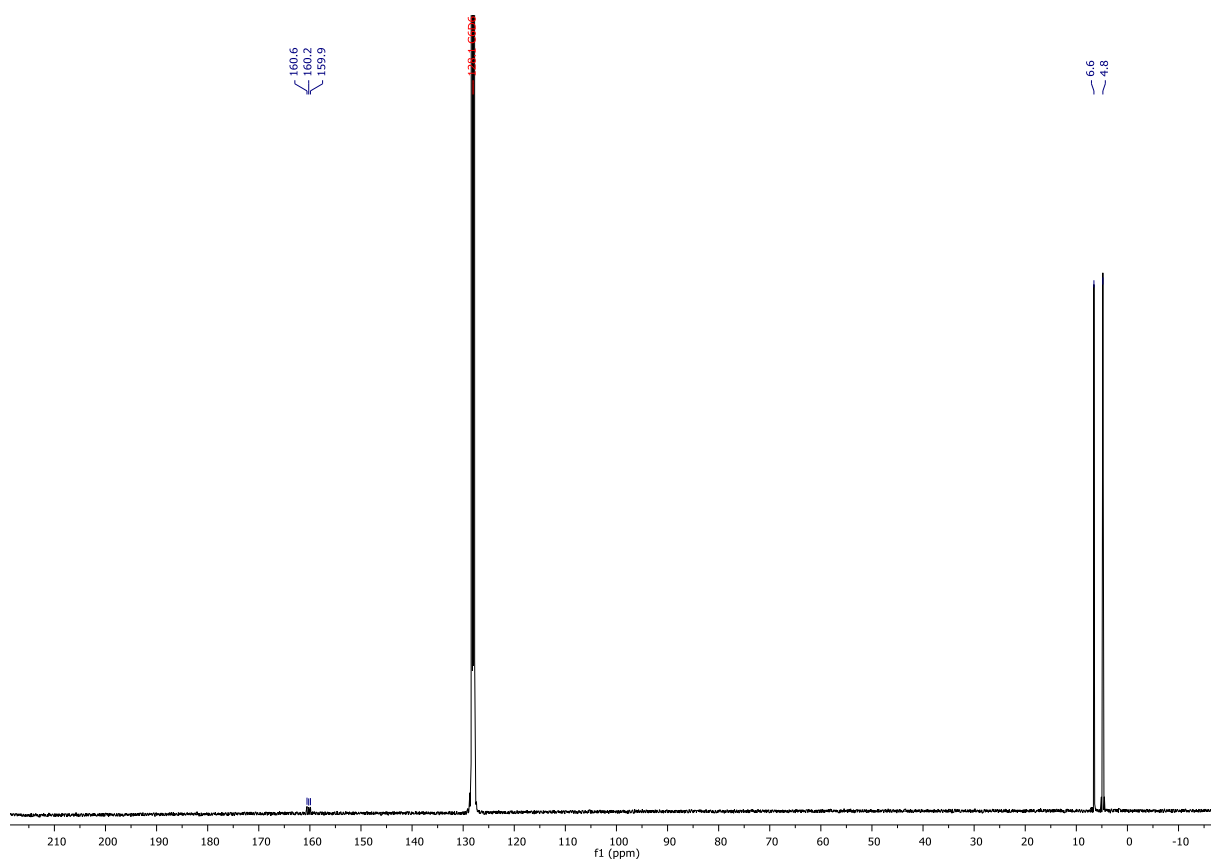


Figure S4.  $^{13}\text{C}$  NMR of TESCO in  $\text{C}_6\text{D}_6$ .

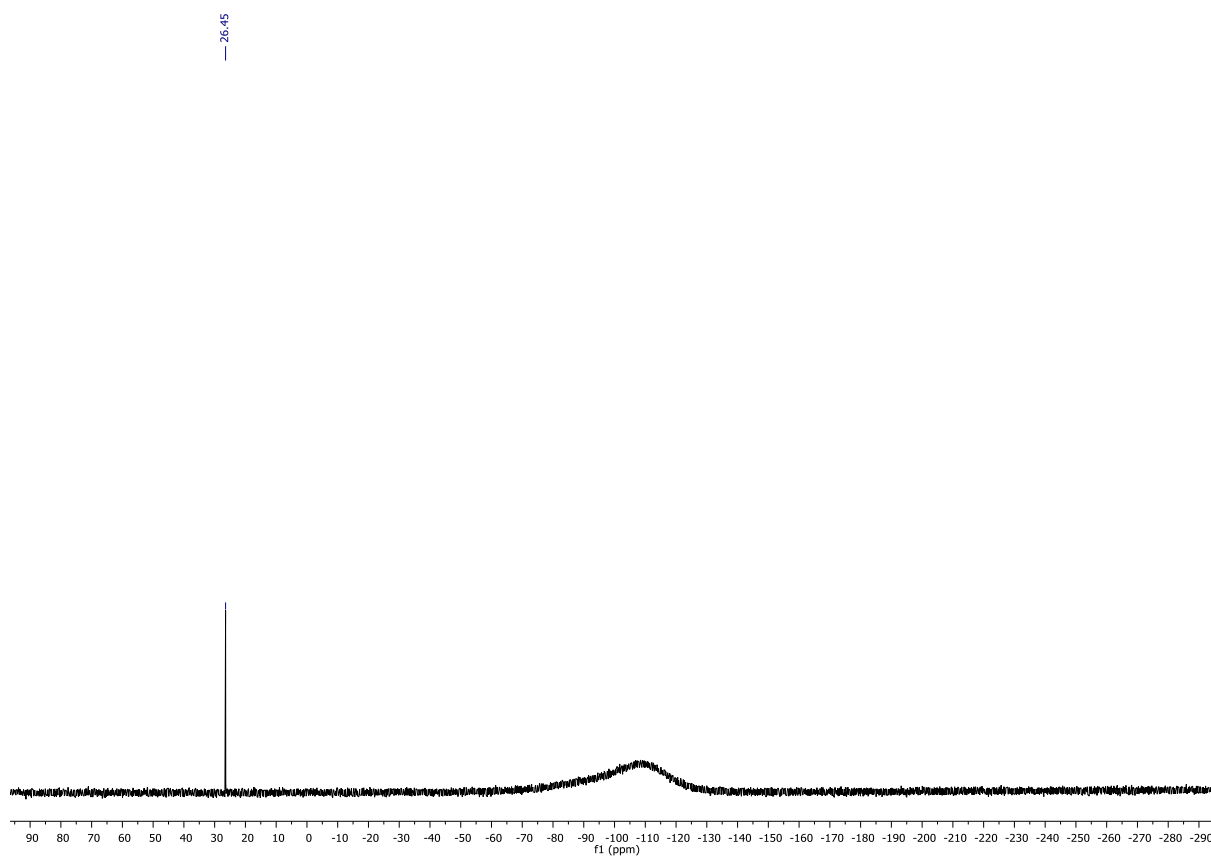
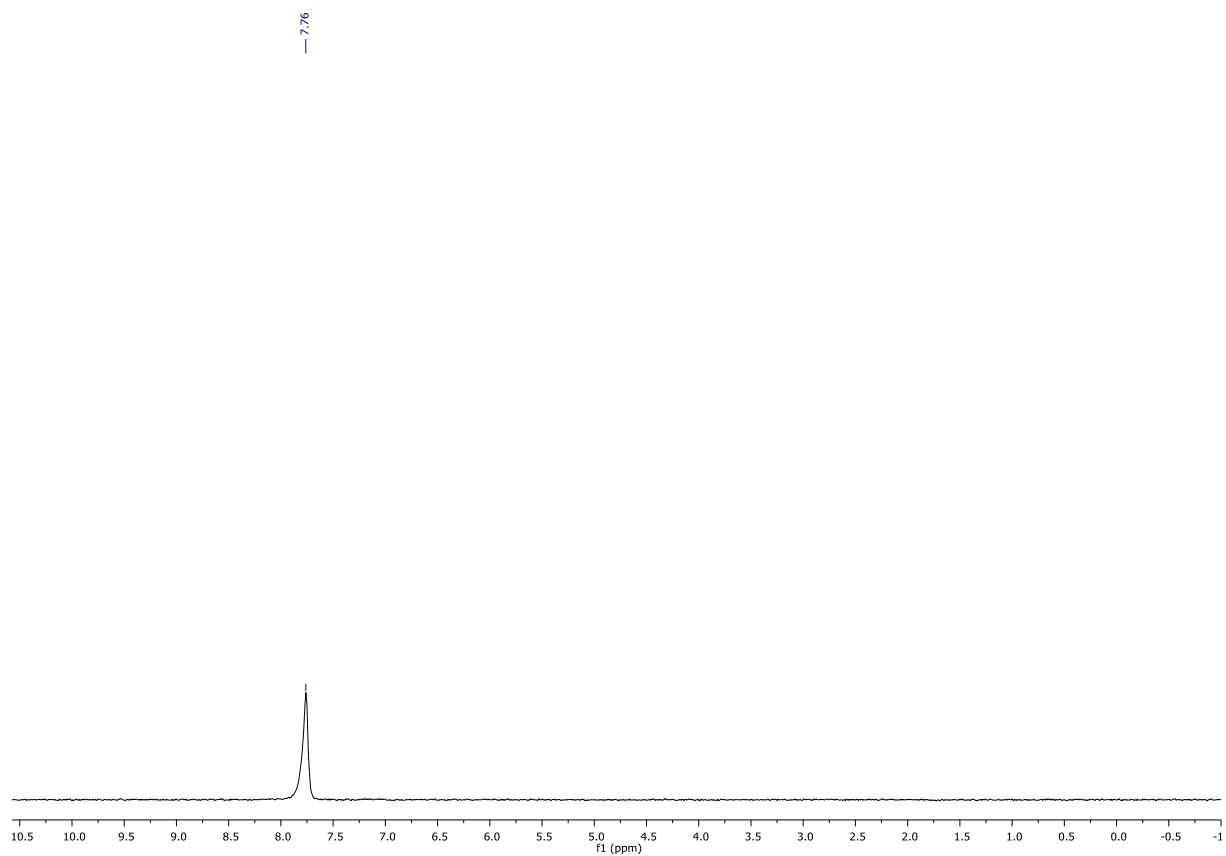
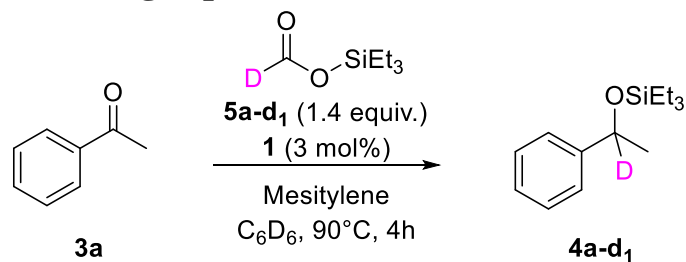


Figure S5.  $^{29}\text{Si}$  NMR of TESCO in  $\text{C}_6\text{D}_6$ .

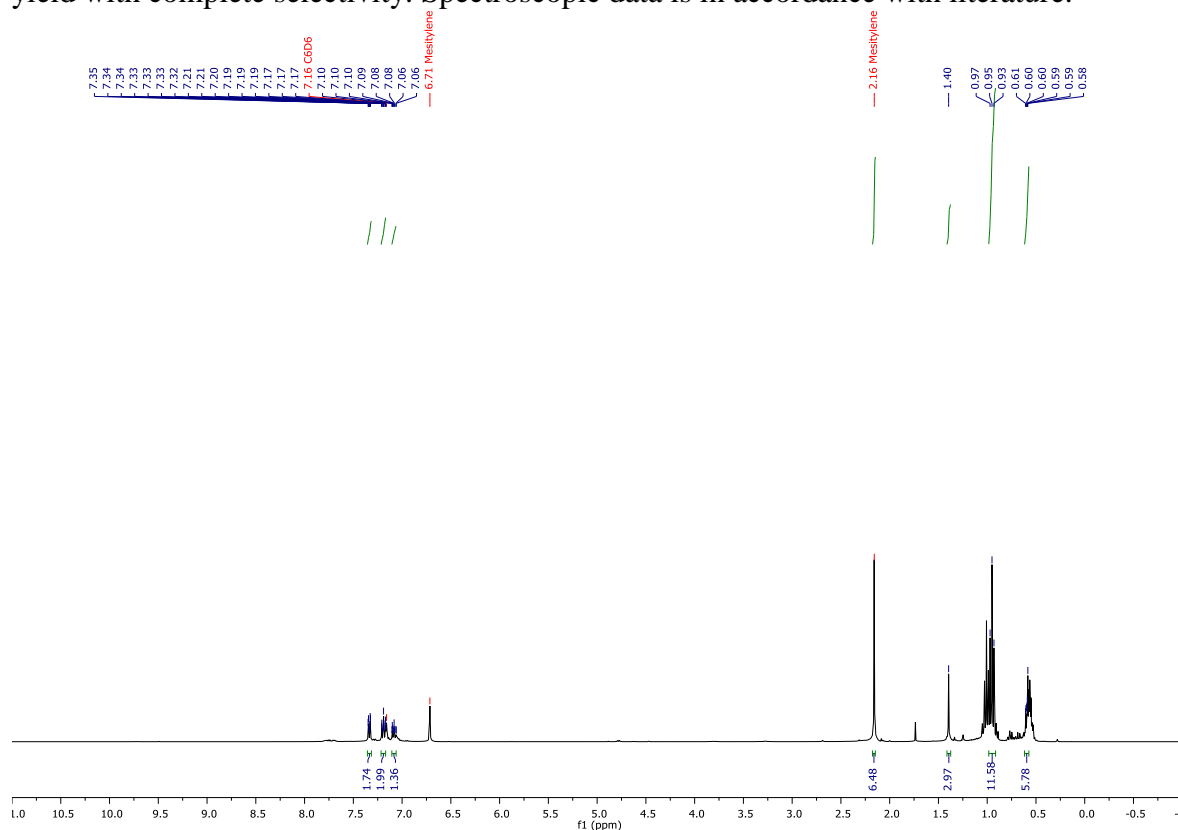


**Figure S6.**  $^2\text{H}$  NMR of TESCDO in toluene.

## 9. Deuterium labelling experiment



Acetophenone hydrosilylation was carried out according to general procedure for NMR scale reactions and **5a-d<sub>1</sub>** as silylformate source. The final product **4a-d<sub>1</sub>** was obtained in 99% NMR yield with complete selectivity. Spectroscopic data is in accordance with literature.<sup>[5]</sup>

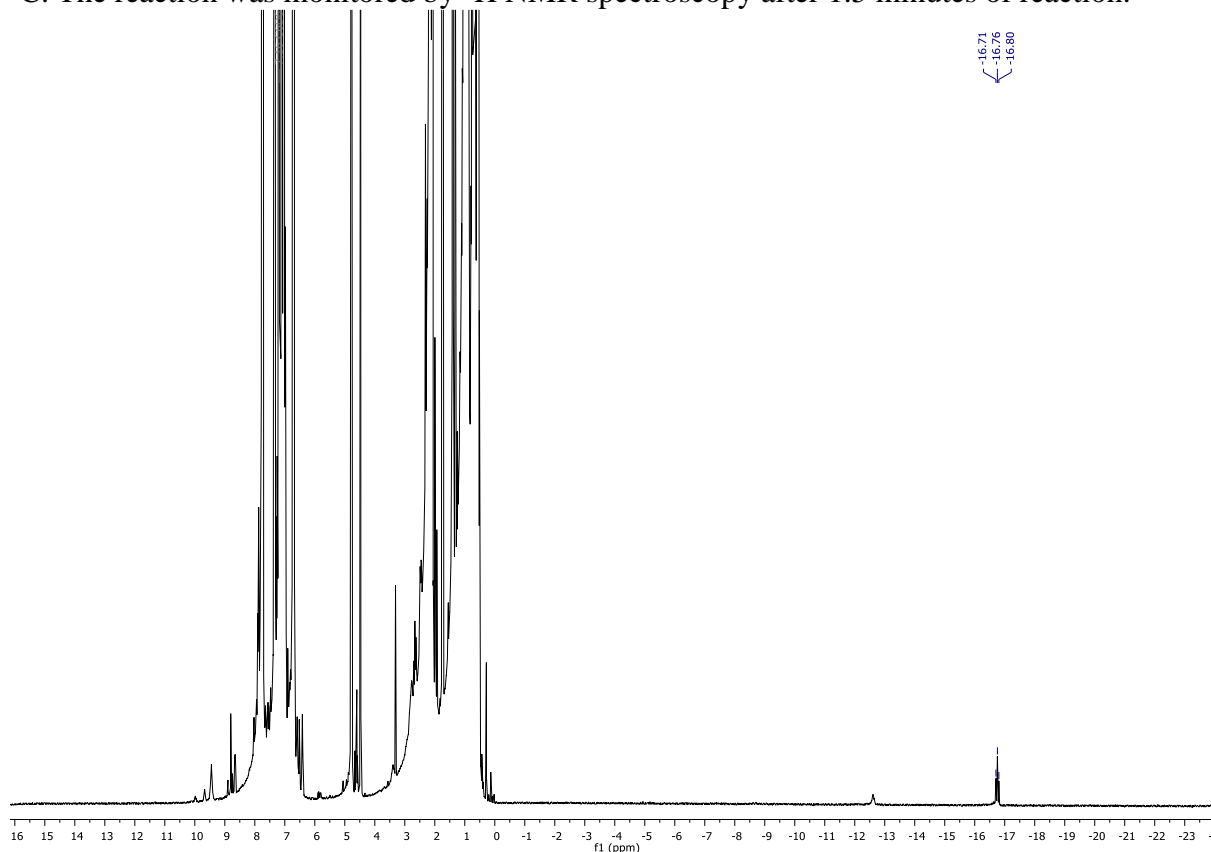


**Figure S7.**  $^1H$  NMR spectra obtained in  $C_6D_6$  for the transfer hydrosilylation of acetophenone (**3a**) with  $Et_3SiCDO$  (**5a-d<sub>1</sub>**). Crude mixture after heating 4 h at  $90^\circ C$ .

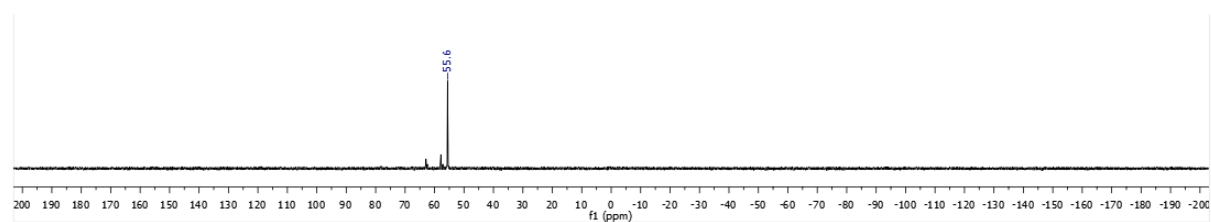


## 10. Experimental evidence of ruthenium monohydride species.

In a glovebox, a *J. Young* NMR Tube was charged with *fac*-[Ru( $\kappa^1$ -OAc)( $\kappa^2$ -OAc)( $\kappa^3$ -PN<sup>H</sup>P<sup>Ph</sup>)] (**2**) (3 mol%), C<sub>6</sub>D<sub>6</sub> (0.4 mL), ketone (0.1 mmol, 1.0 equiv.), mesitylene (10  $\mu$ L) and triethylsilyl formate (**5a**) (1.4 equiv.). The tube was sealed, brought out of the glovebox and heated at 90  $^{\circ}$ C. The reaction was monitored by <sup>1</sup>H NMR spectroscopy after 1.5 minutes of reaction.



**Figure S8.** <sup>1</sup>H NMR spectra obtained in C<sub>6</sub>D<sub>6</sub> for the transfer hydrosilylation of acetophenone (**3a**) with Et<sub>3</sub>SiCHO (**5a**). Crude mixture after heating 1.5 min at 90  $^{\circ}$ C showing the presence of a Ru-H signal



**Figure S9.** <sup>31</sup>P NMR spectra obtained in C<sub>6</sub>D<sub>6</sub> for the transfer hydrosilylation of acetophenone (**3a**) with Et<sub>3</sub>SiCHO (**5a**). Crude mixture after heating 1.5 min at 90  $^{\circ}$ C showing the presence of a Ru-H signal

## 11. Competition reactions

In order to test the compatibility of the reaction with free alcohols, amines, amides and carboxylic acids, the benchmark reaction was performed in presence of additives **8** containing these functional groups (benzamide (**8a**), benzyl alcohol (**8b**), morpholine (**8c**), and benzoic acid (**8d**), Table S4). Knowing that alcohols and carboxylic acids are silylated in presence of silyl formate **5**<sup>[15]</sup>, we envisaged that the same will occur with free amides and amines, which is why an excess of silyl formate was used in those reactions (2.4 – 3 equiv).

Compared to the benchmark reaction (Table S4, entry 1), the presence of additives slowed the reaction: 4.5 – 20 h were necessary to observe full conversion in contrast to 1.5 h in the benchmark reaction (Table S4). In presence of benzamide (**8a**), the reaction was completed within 6.5 h with a yield of 82% (entry 1). Benzyl alcohol (**8b**), morpholine (**8c**), and benzoic acid (**8d**) showed a detrimental effect on the reaction, the yield of **4a** being lowered to 24 – 58%, due to the presence of numerous side-products (entries 3-5). Silylation of alcohol **8b** and carboxylic acid **8d** was observed, whereas in the case of benzamide (**8a**) and morpholine (**8c**) derivatives, it was not possible to identify the products resulting from their reactions with silylformate **5a**.

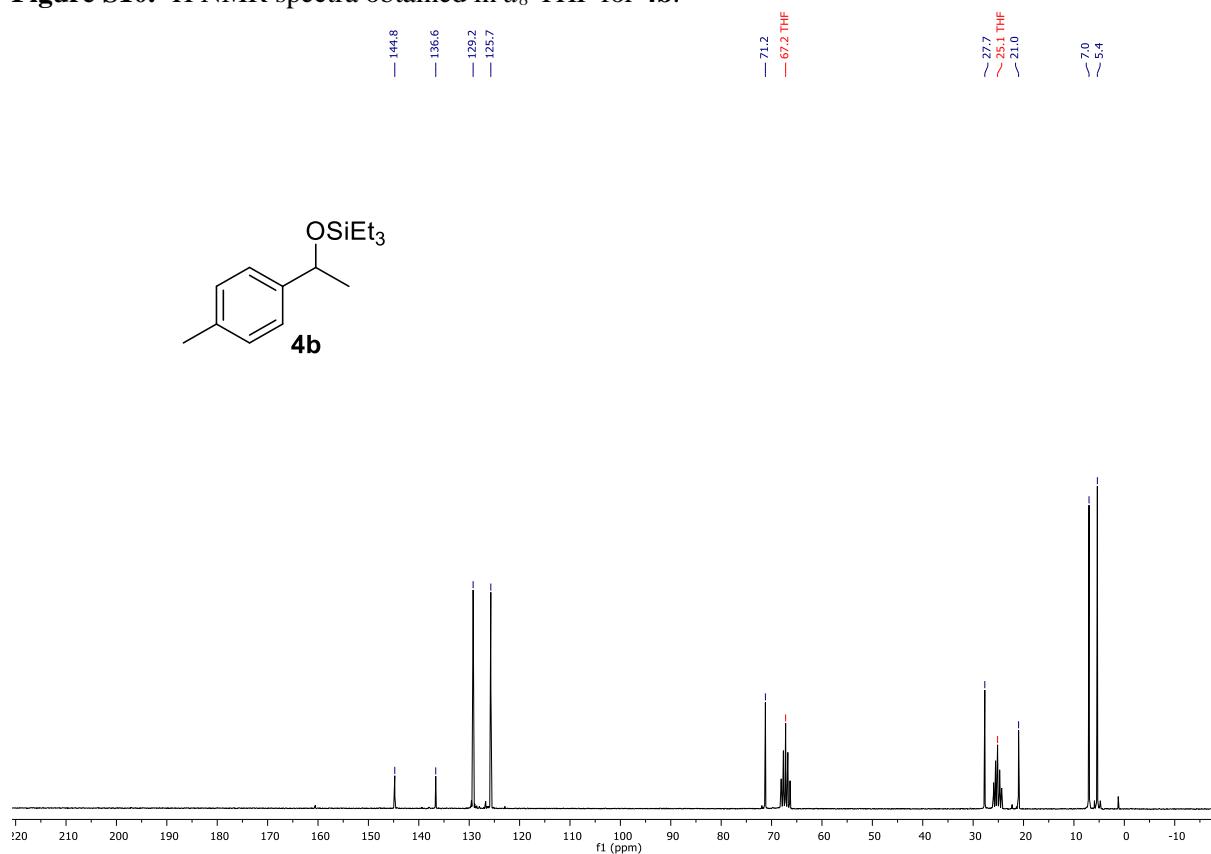
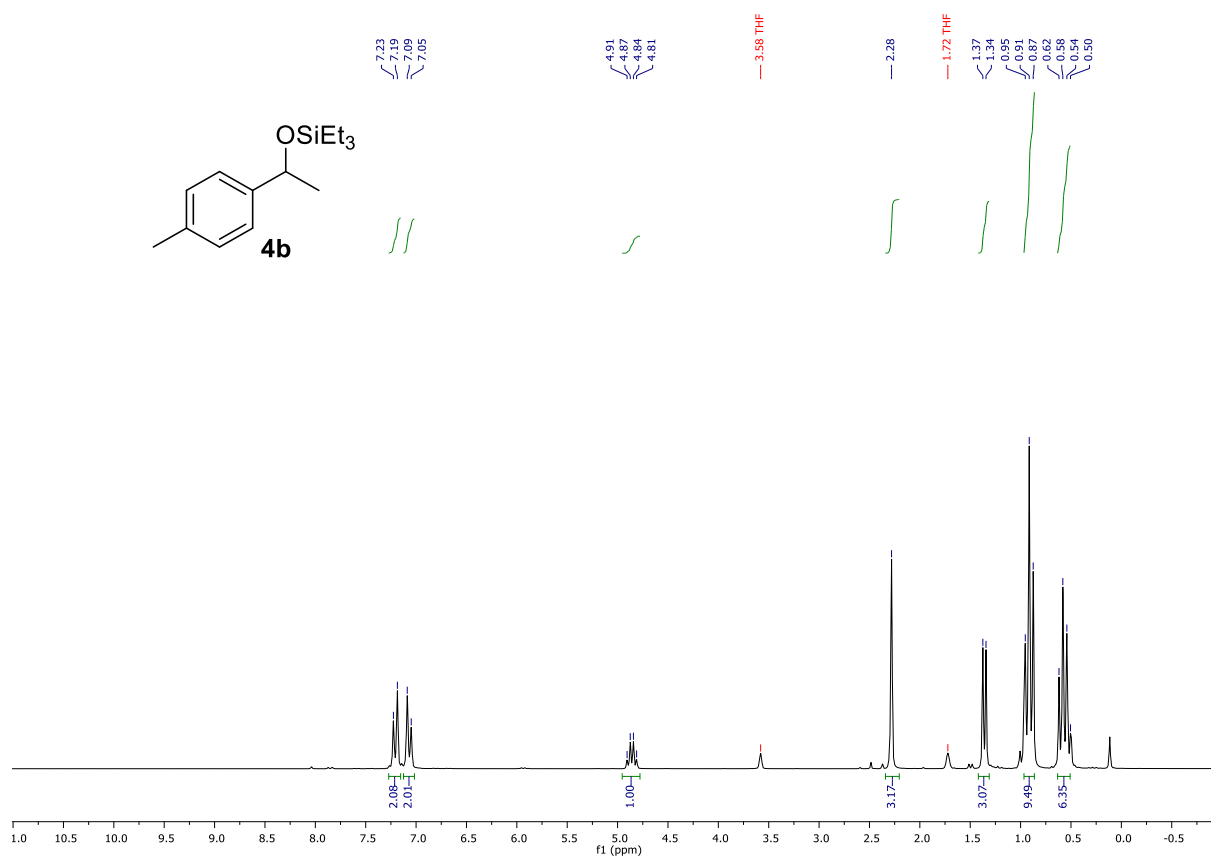
**Table S4.** Reduction of ketone **3a** in presence of additives **8** with silyl formate **5a**. (0.1 mmol scale)

Entry	Additive	5 (equiv.)	t(h)	Yield (%)
1	-	2.4	1.5	99
2	<b>8a</b>	2.4	6.5	82
3	<b>8b</b>	2.4	4.5 (20)	21 (45)
4	<b>8c</b>	2.4	4.5	24
5	<b>8d</b>	3	4.5	58

	 $P = PPh_2$
	<b>Additives</b> 

## 12. NMR spectra of isolated compounds



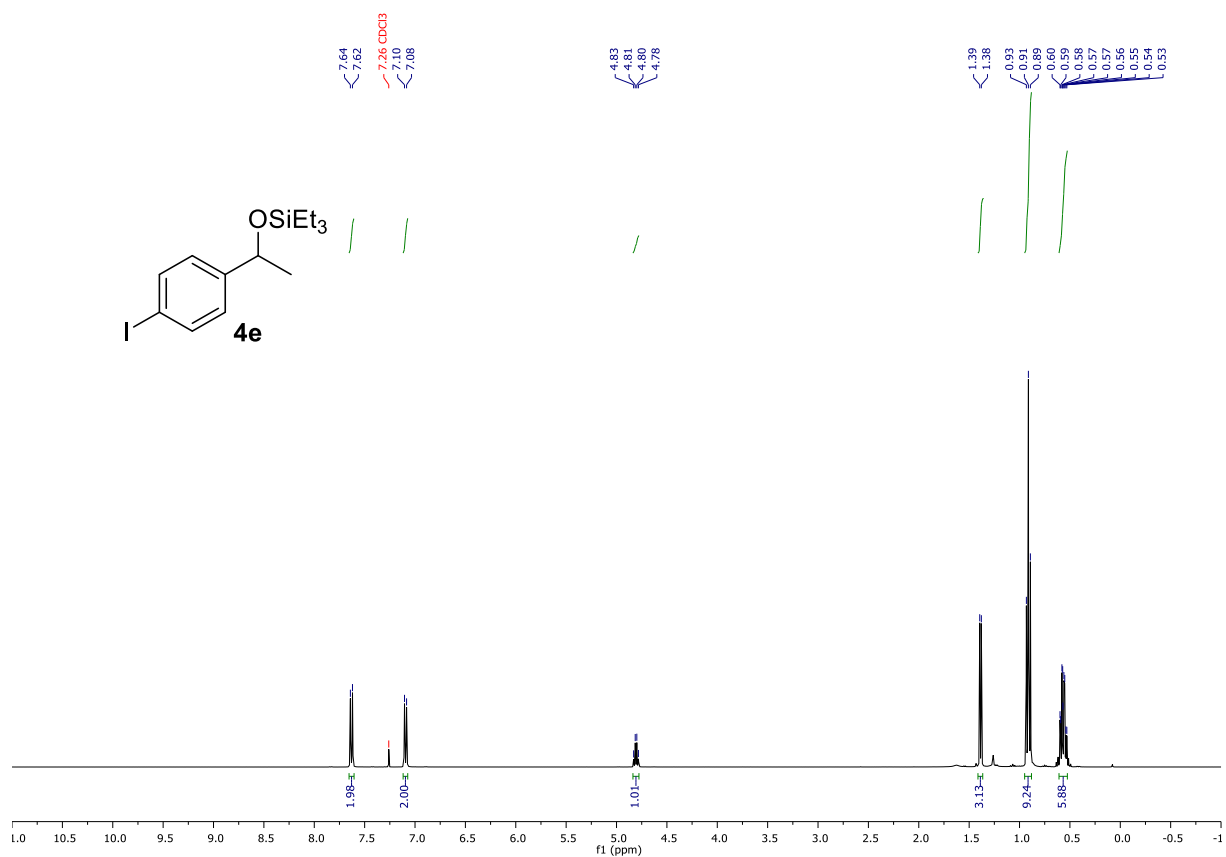


Figure S12. <sup>1</sup>H NMR spectra obtained in CDCl<sub>3</sub> for **4e**.

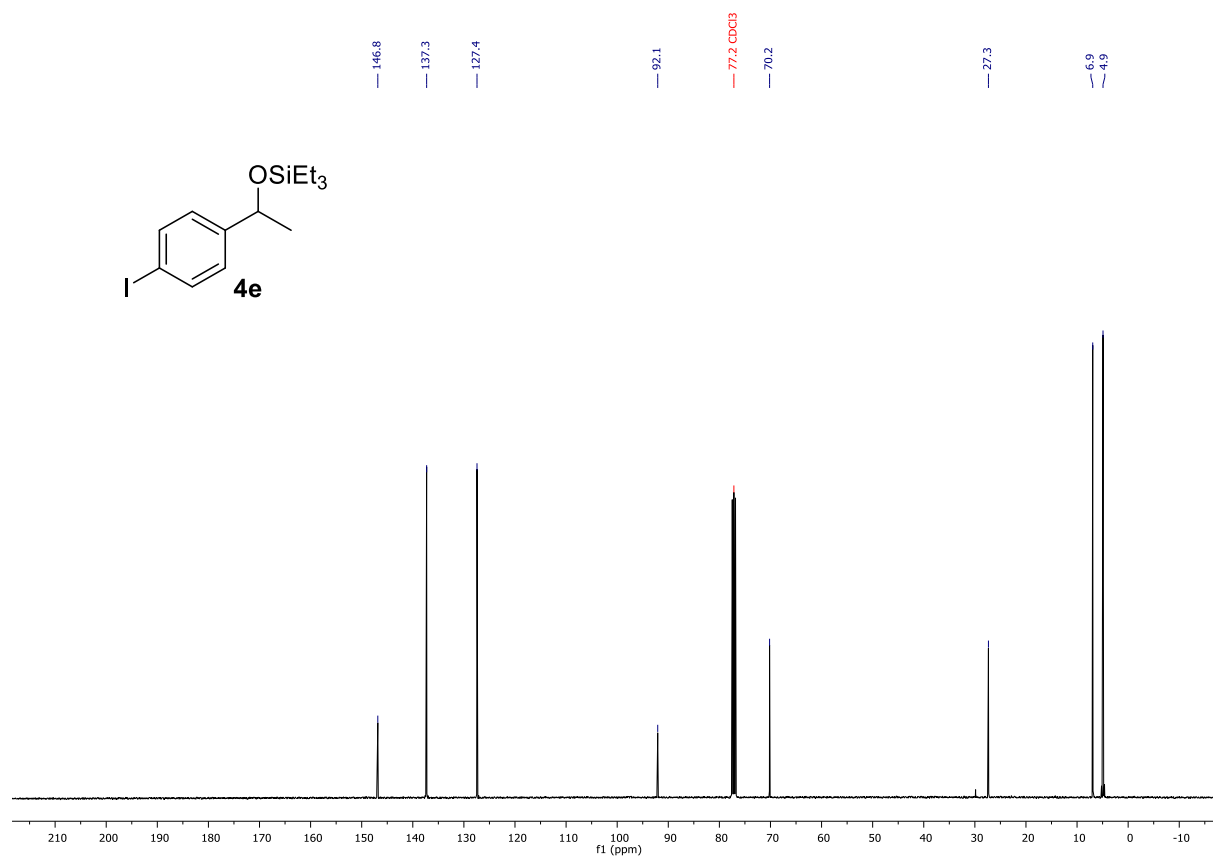


Figure S13. <sup>13</sup>C NMR spectra obtained in CDCl<sub>3</sub> for **4e**.

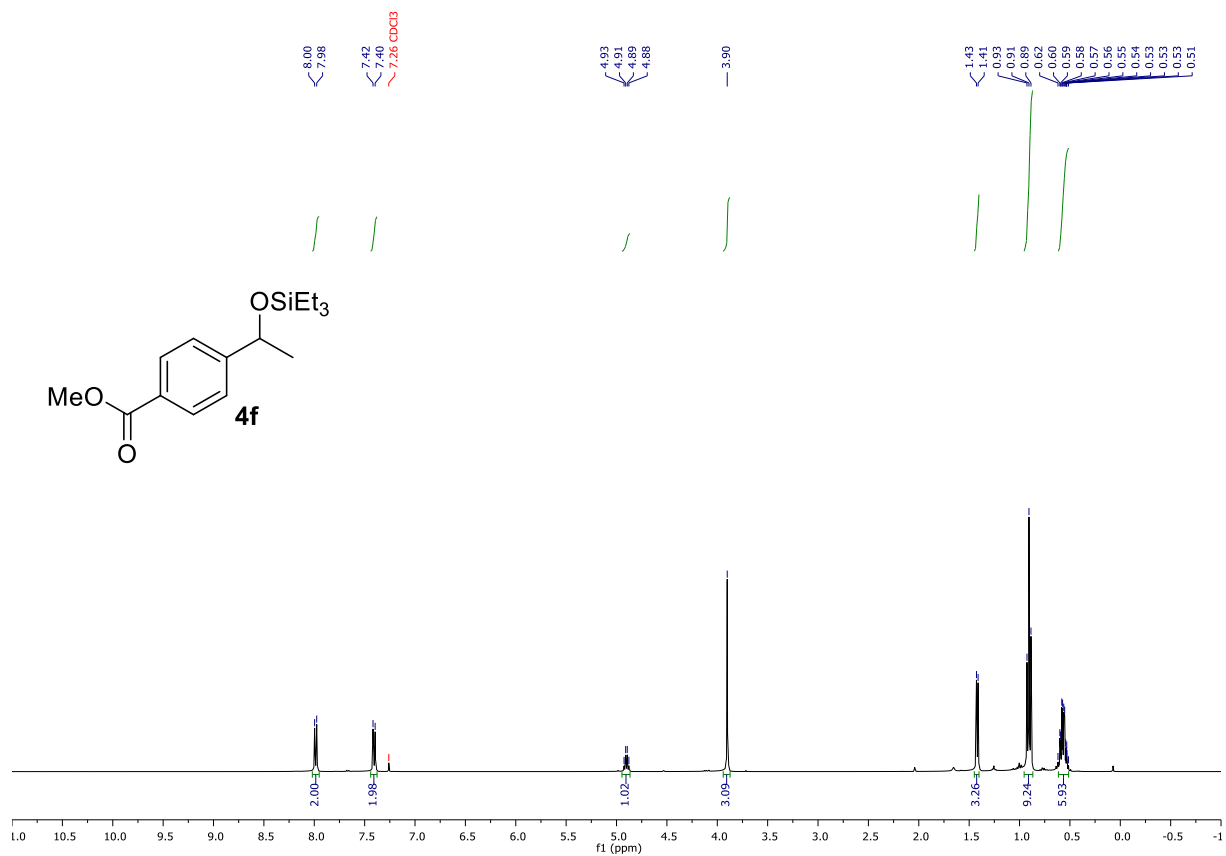


Figure S14. <sup>1</sup>H NMR spectra obtained in CDCl<sub>3</sub> for **4f**.

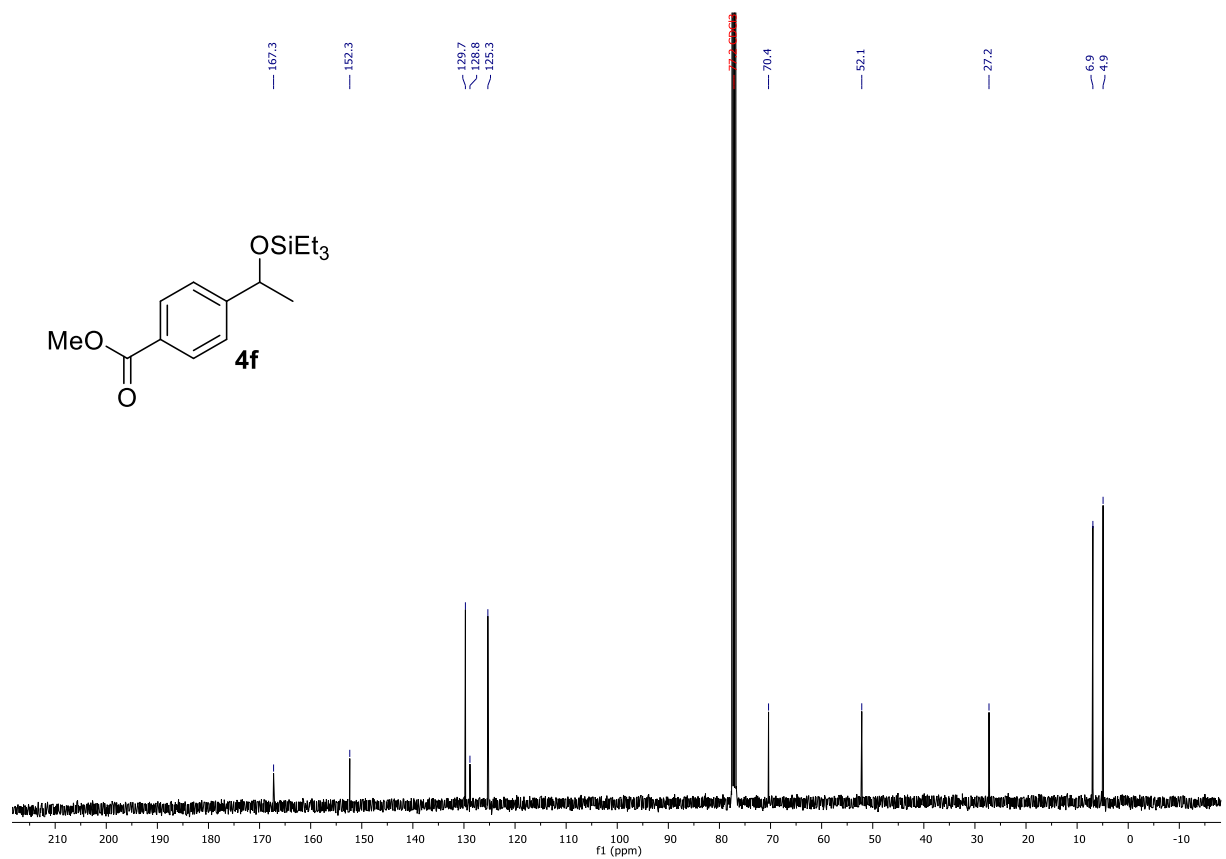


Figure S15. <sup>13</sup>C NMR spectra obtained in CDCl<sub>3</sub> for **4f**.

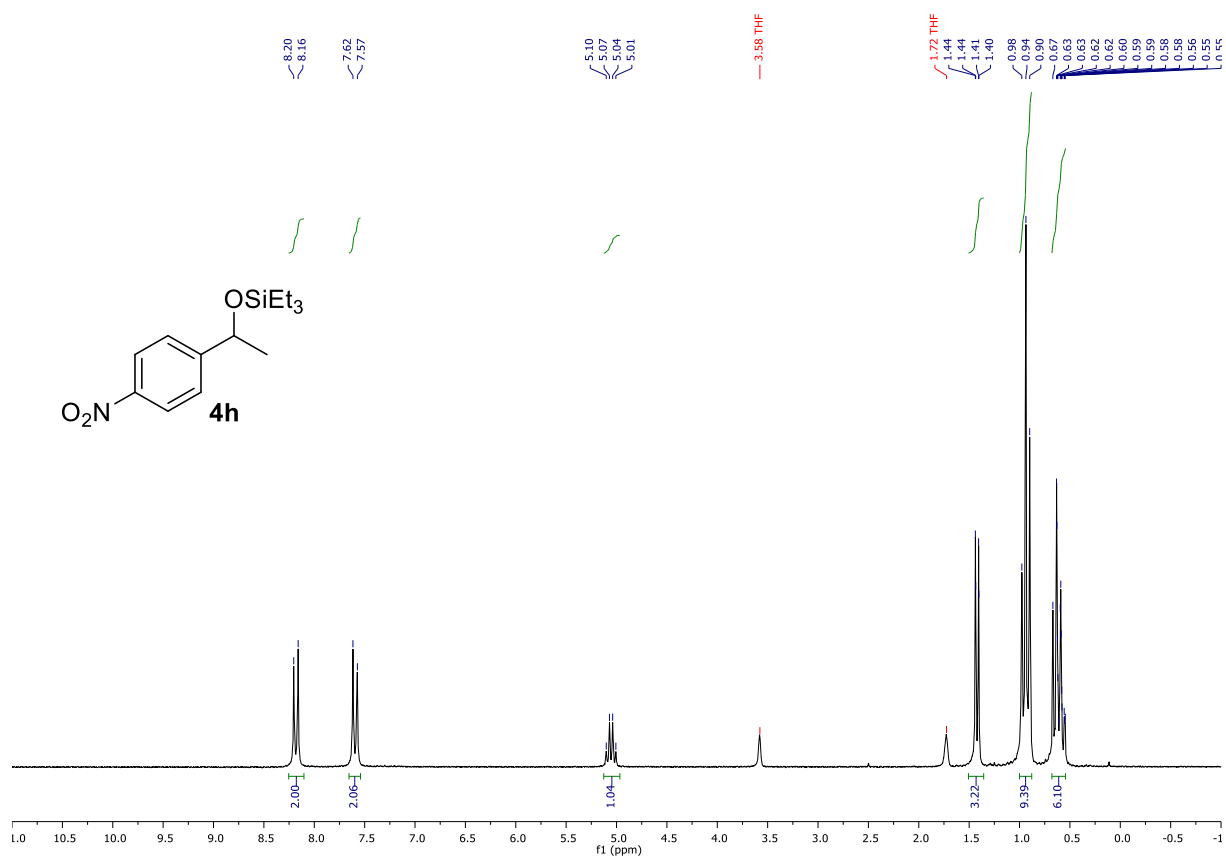


Figure S16. <sup>1</sup>H NMR spectra obtained in *d*<sub>8</sub>-THF for **4h**.

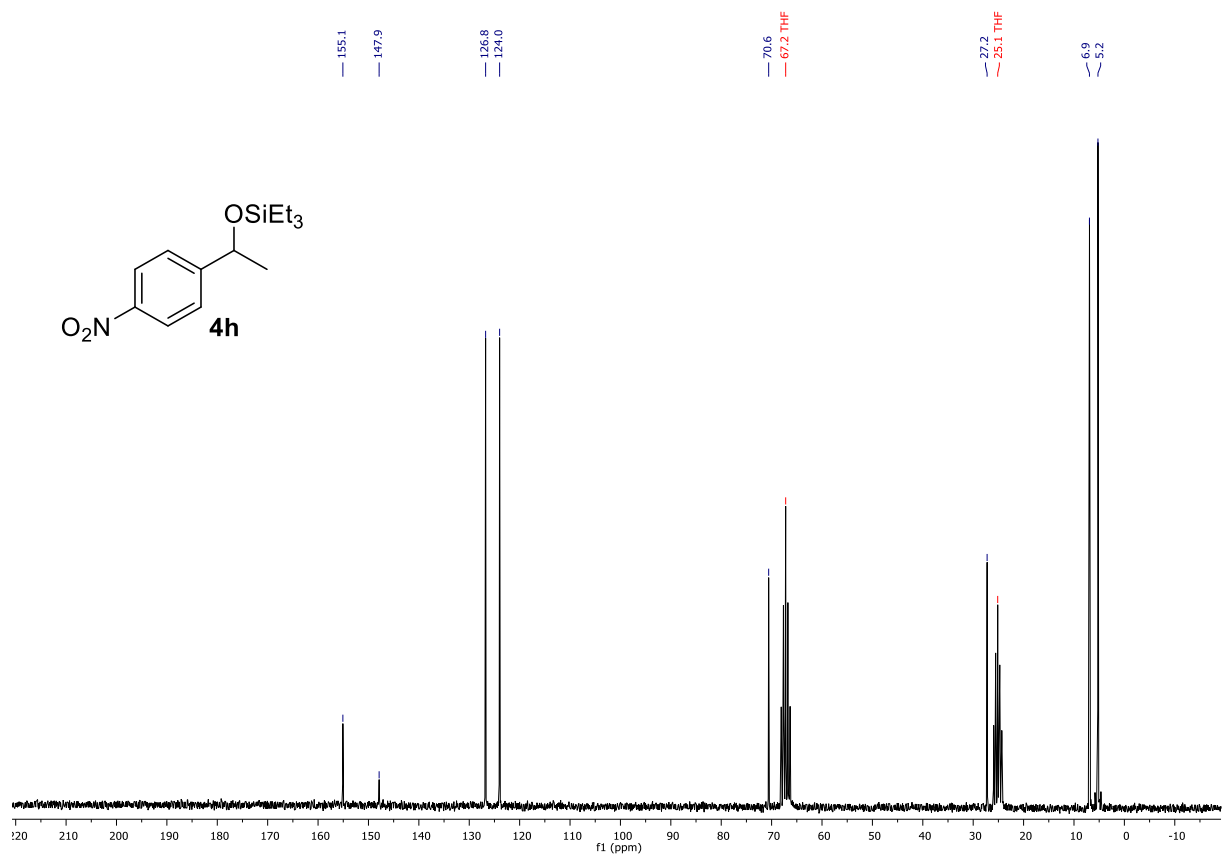


Figure S17. <sup>13</sup>C NMR spectra obtained in *d*<sub>8</sub>-THF for **4h**.

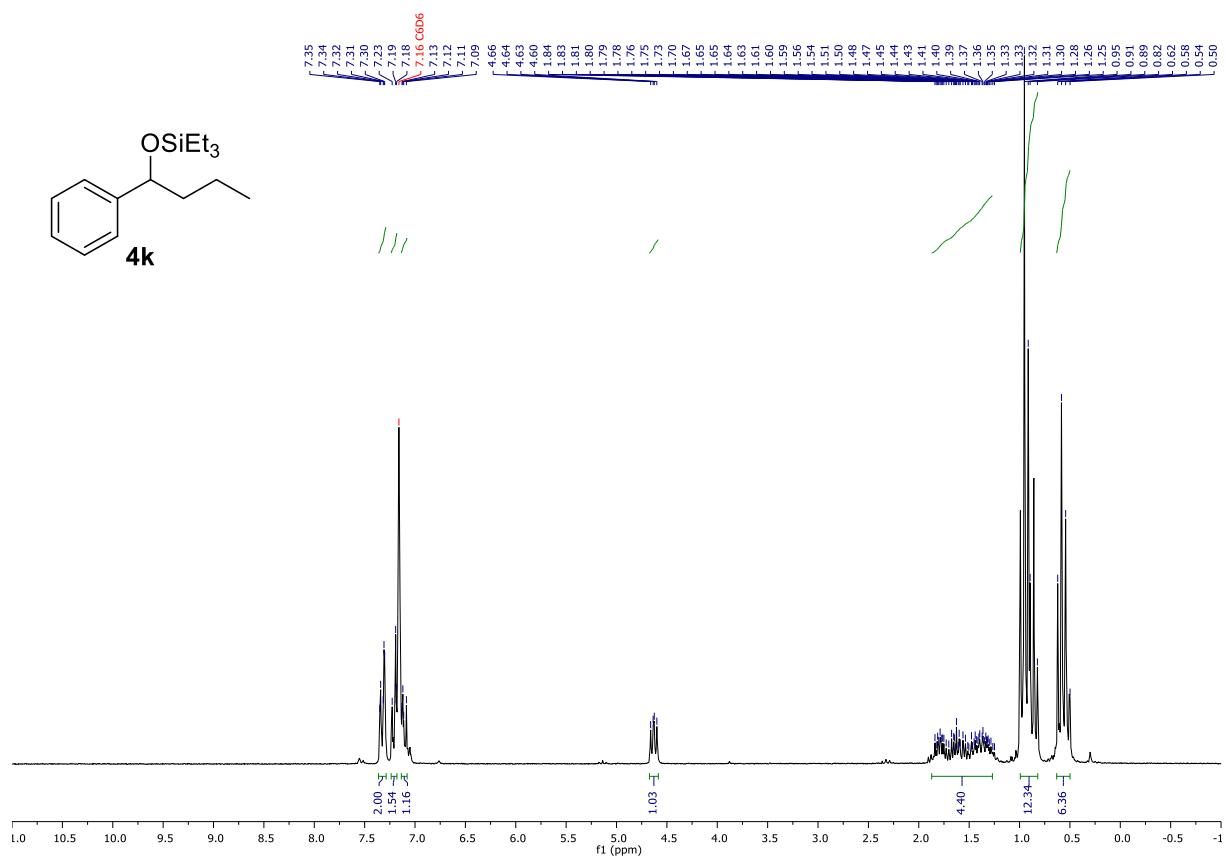


Figure S18.  $^1\text{H}$  NMR spectra obtained in  $\text{C}_6\text{D}_6$  for **4k**.

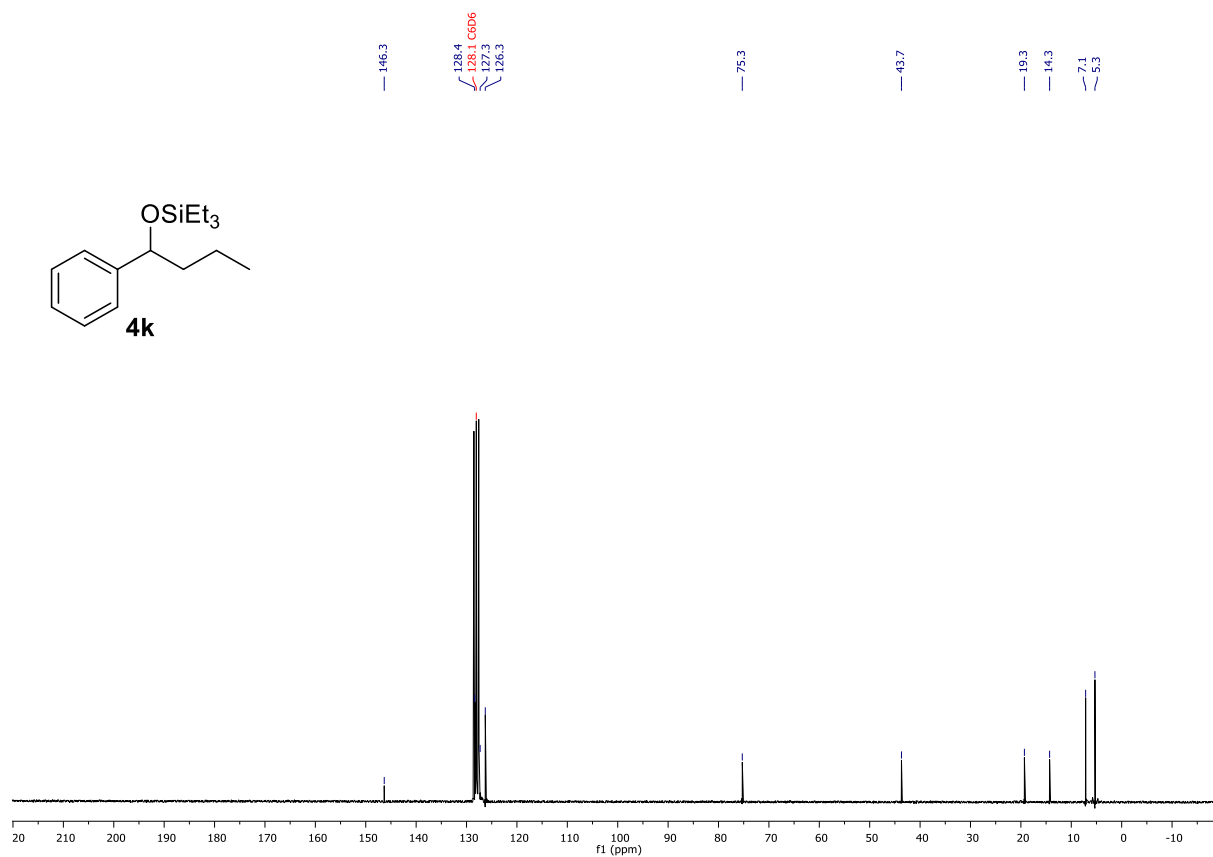
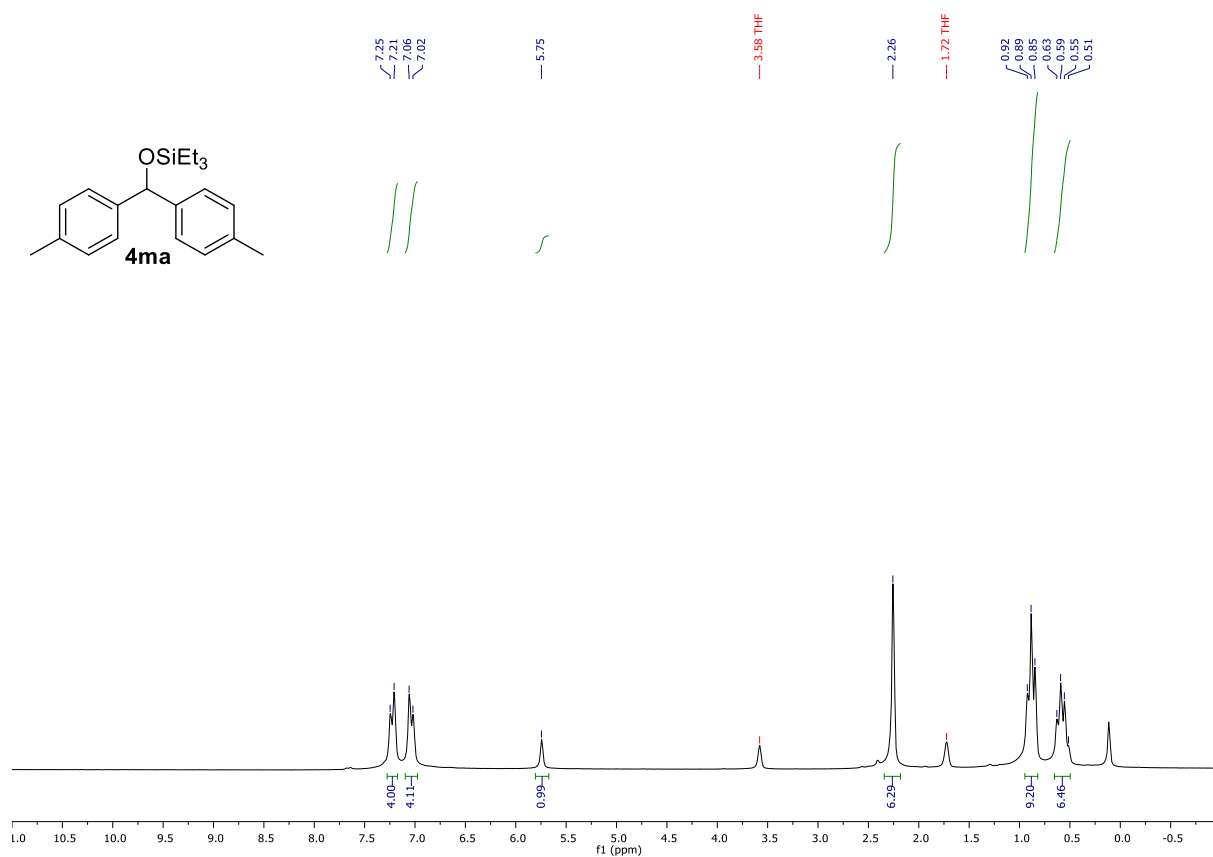
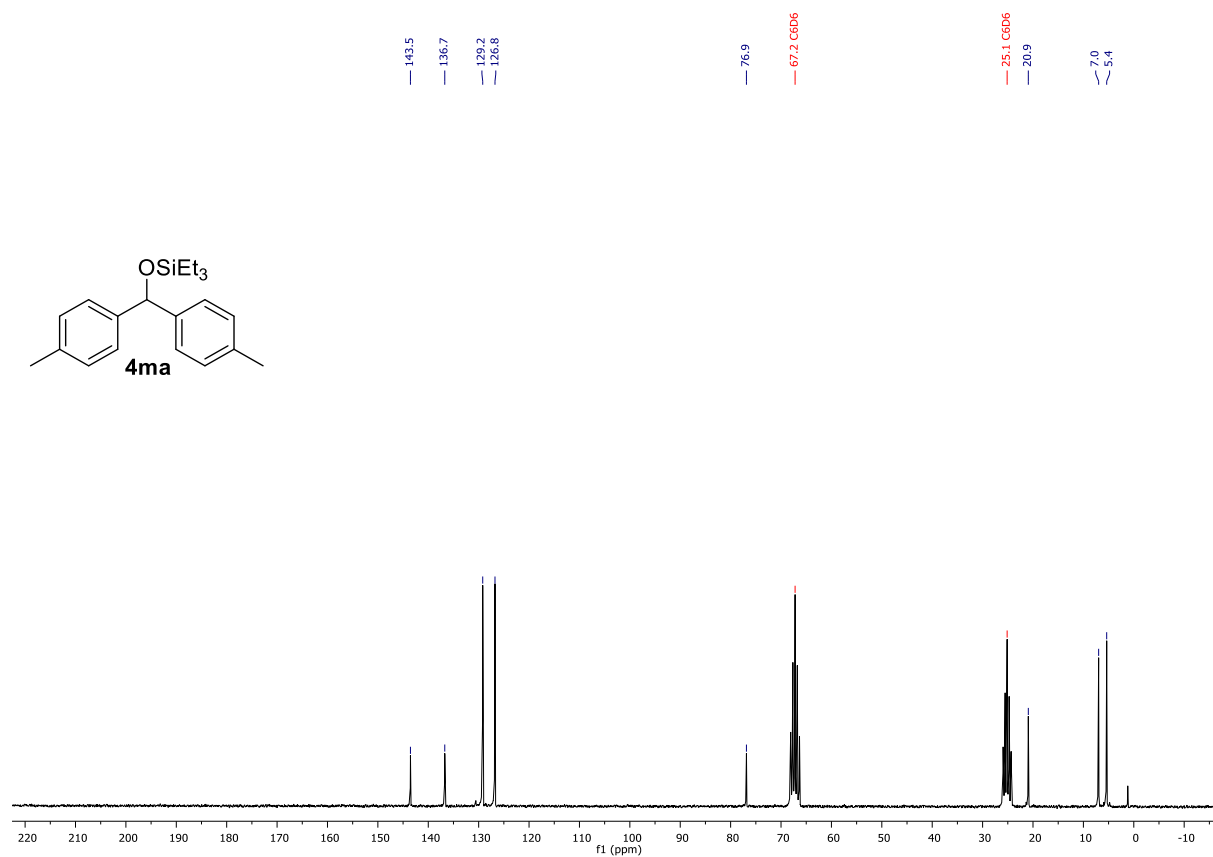


Figure S19.  $^{13}\text{C}$  NMR spectra obtained in  $\text{C}_6\text{D}_6$  for **4k**.



**Figure S20.** <sup>1</sup>H NMR spectra obtained in *d*<sub>8</sub>-THF for **4ma**.



**Figure S21.** <sup>13</sup>C NMR spectra obtained in *d*<sub>8</sub>-THF for **4ma**.



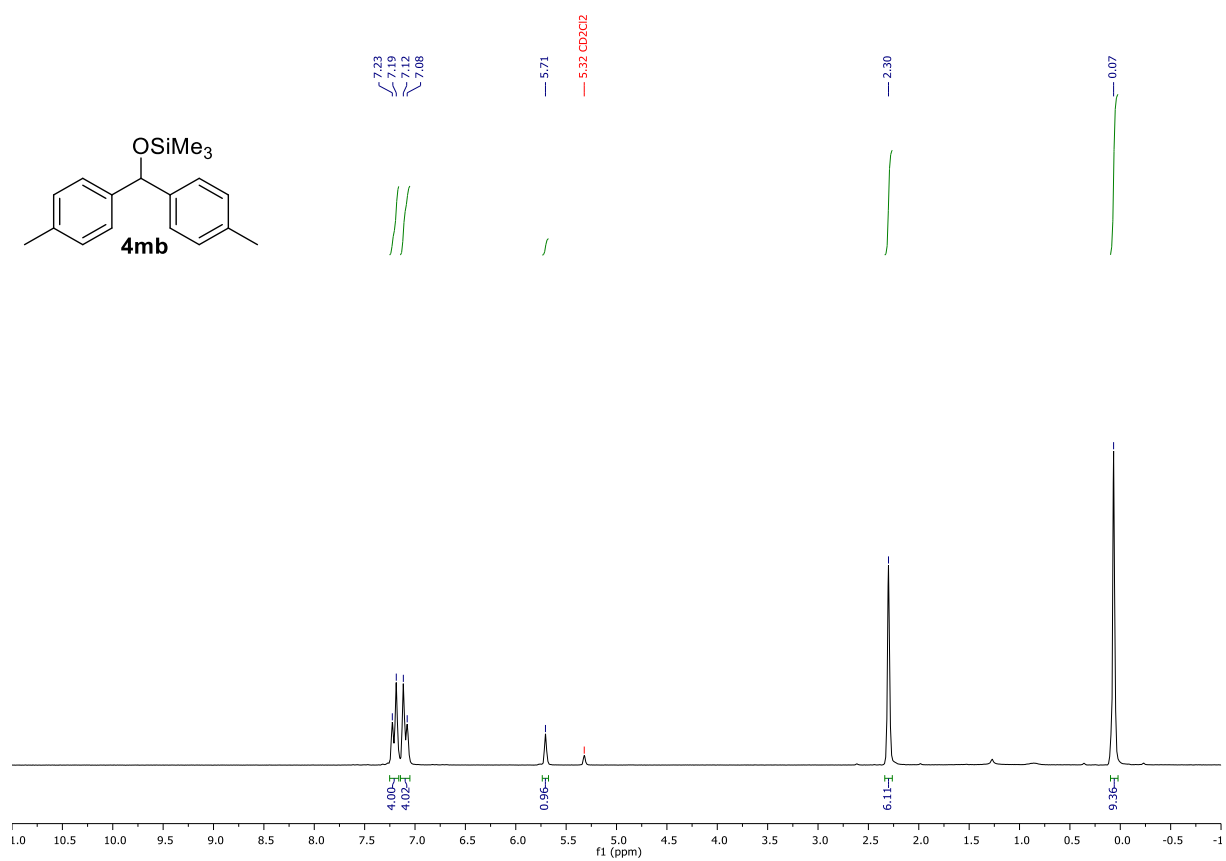


Figure S22. <sup>1</sup>H NMR spectra obtained in CD<sub>2</sub>Cl<sub>2</sub> for **4mb**.

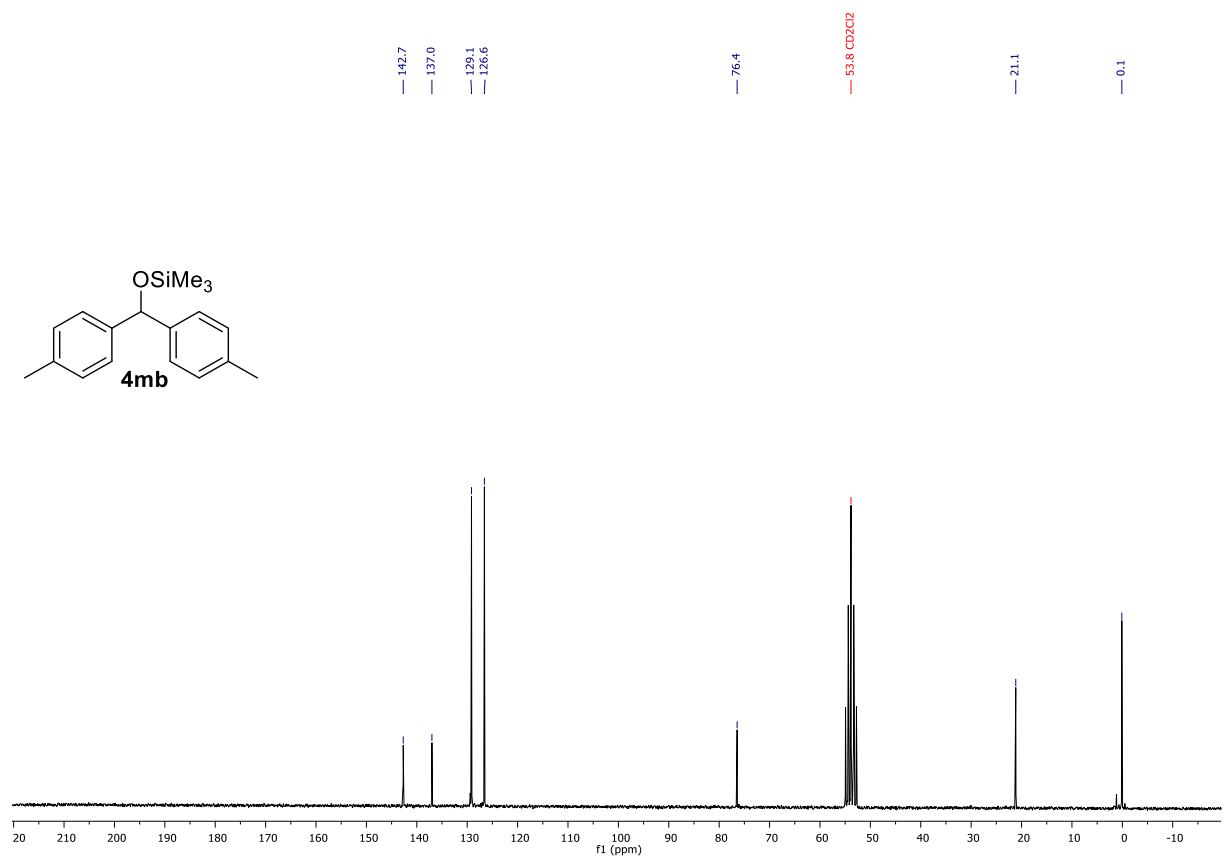


Figure S23. <sup>13</sup>C NMR spectra obtained in CD<sub>2</sub>Cl<sub>2</sub> for **4mb**.

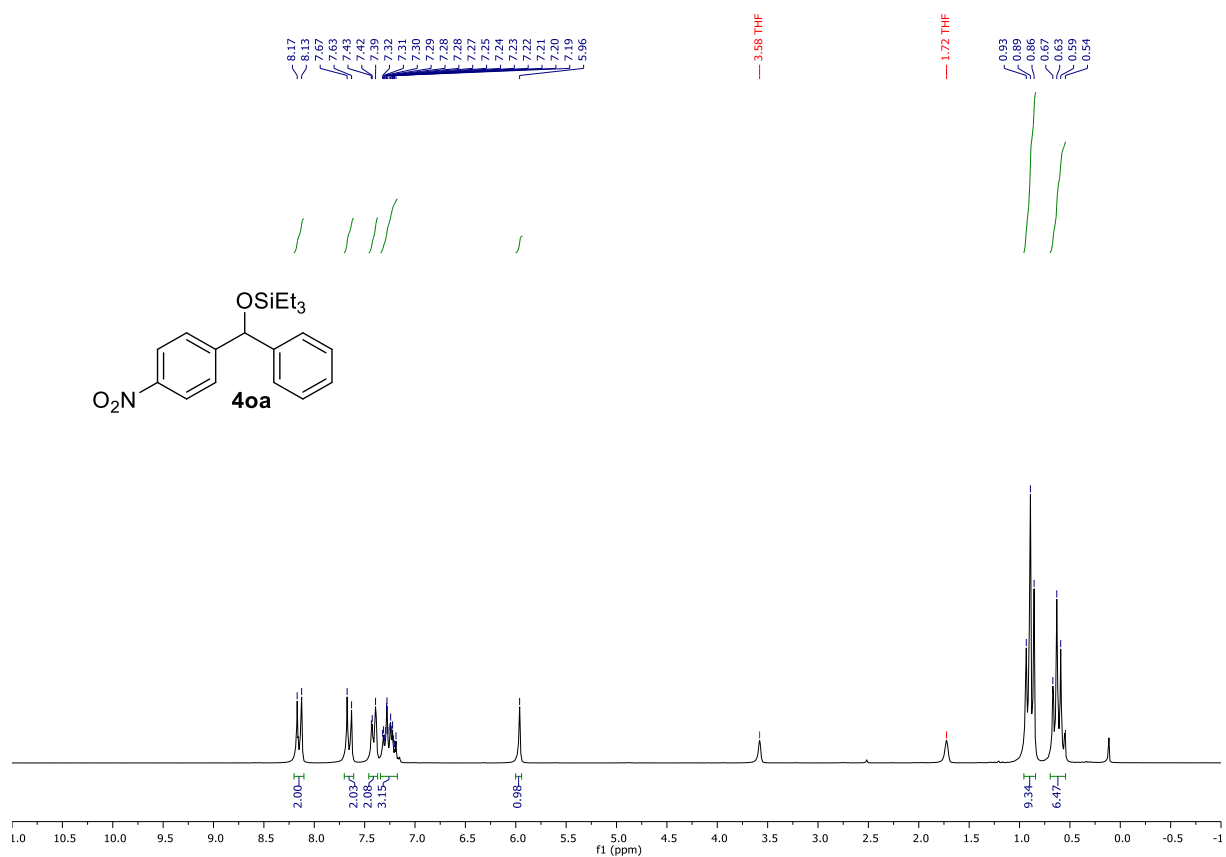


Figure S24. <sup>1</sup>H NMR spectra obtained in *d*<sub>8</sub>-THF for **4a**.

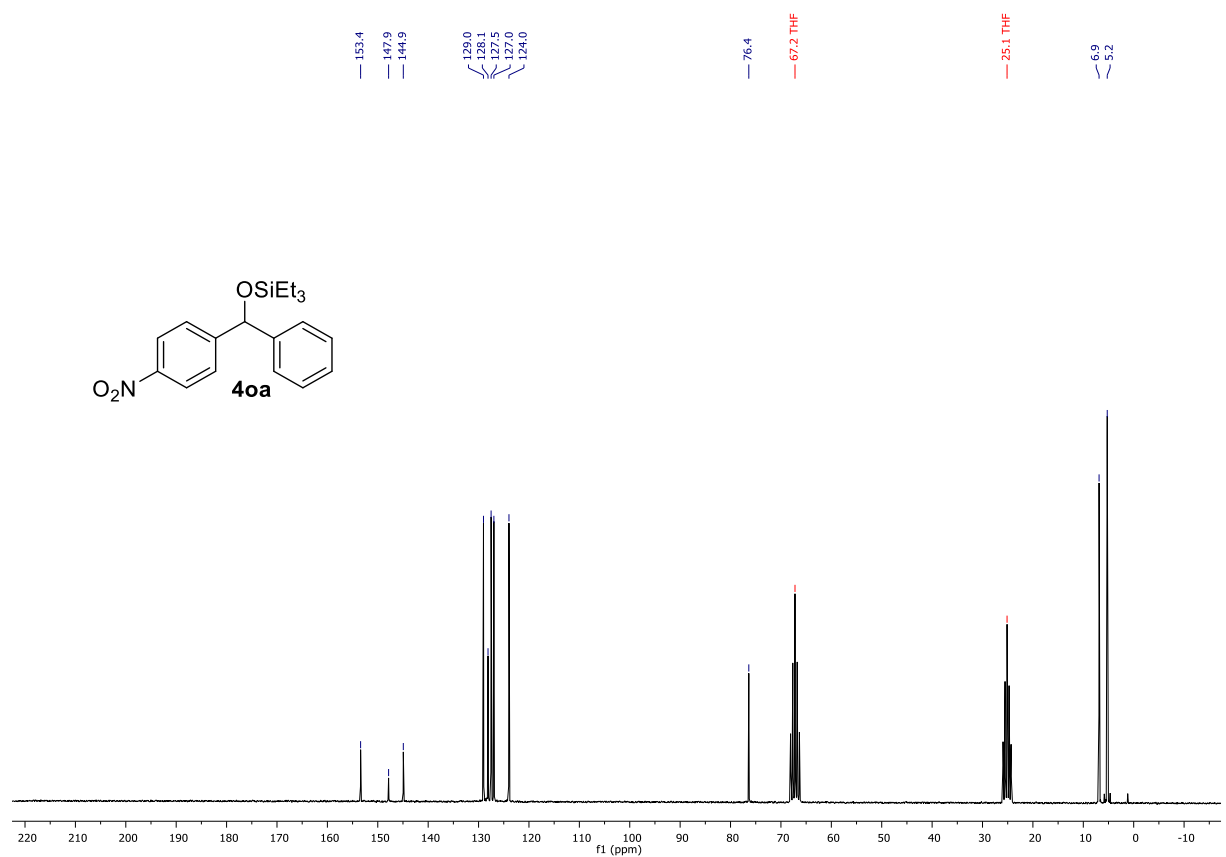


Figure S25. <sup>13</sup>C NMR spectra obtained in *d*<sub>8</sub>-THF for **4a**.

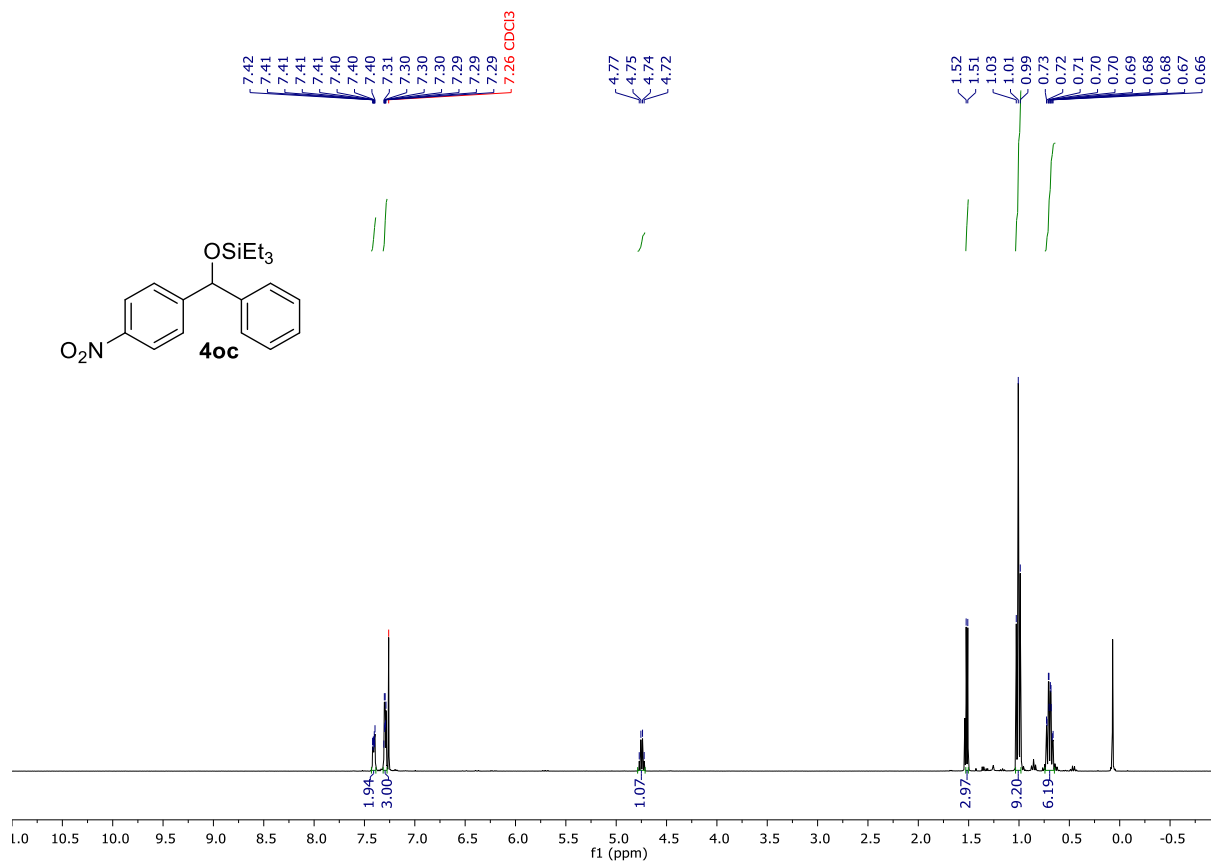


Figure S26. <sup>1</sup>H NMR spectra obtained in CDCl<sub>3</sub> for **4oc**.

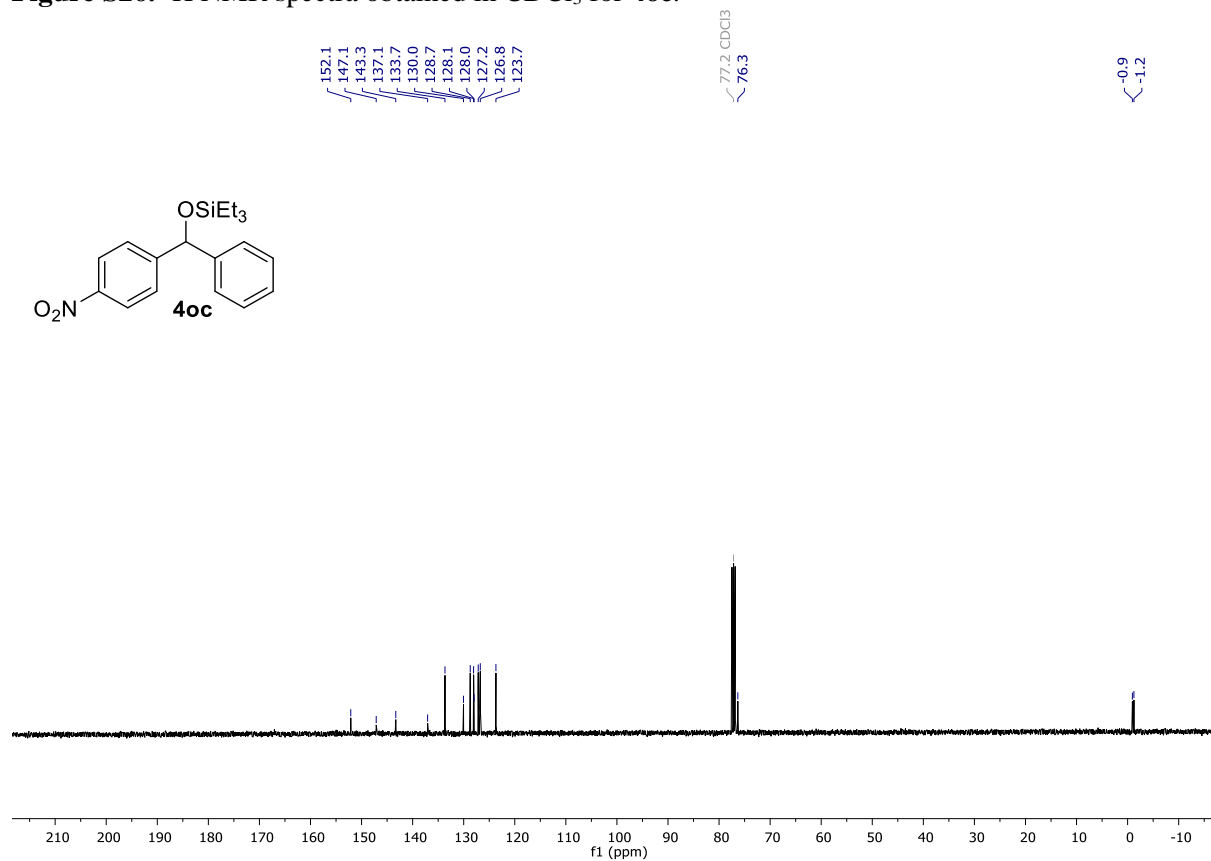


Figure S27. <sup>13</sup>C NMR spectra obtained in CDCl<sub>3</sub> for **4oc**.

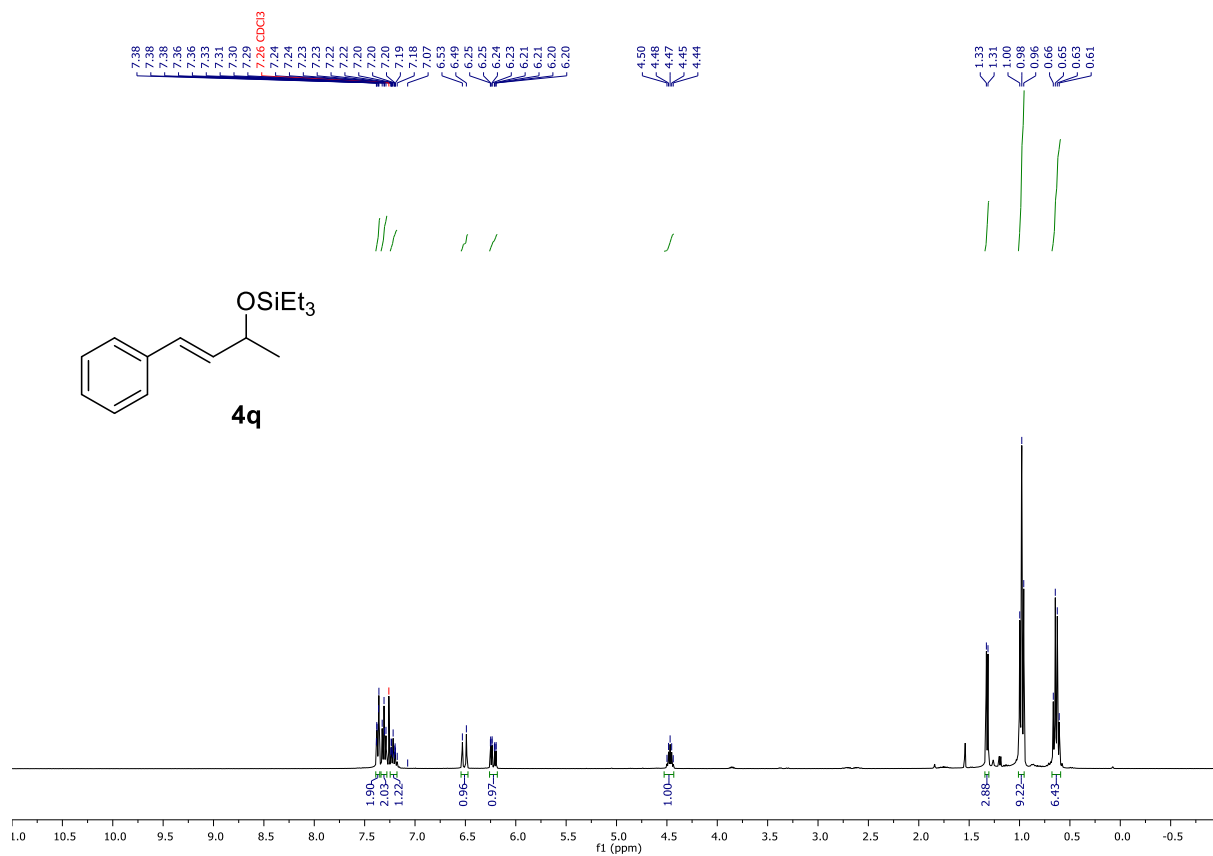


Figure S28. <sup>1</sup>H NMR spectra obtained in CDCl<sub>3</sub> for **4q**.

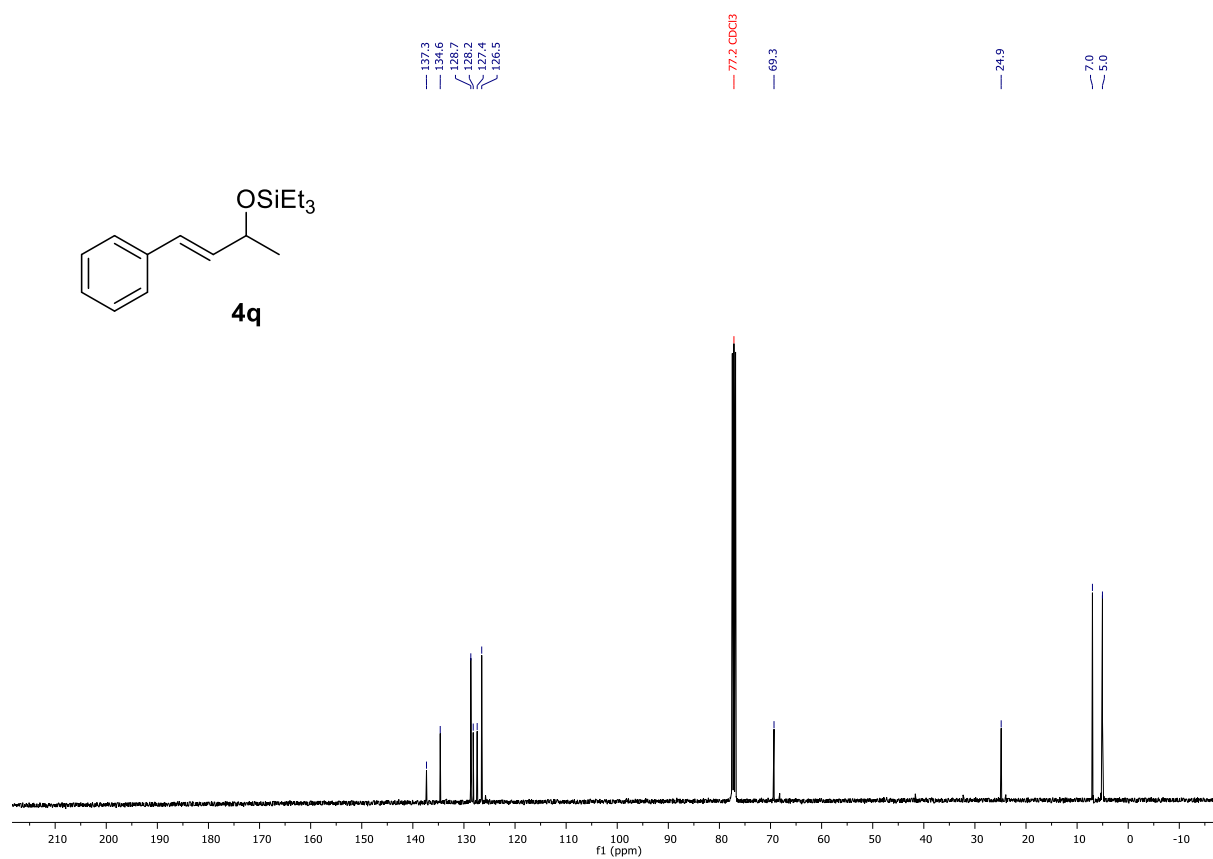
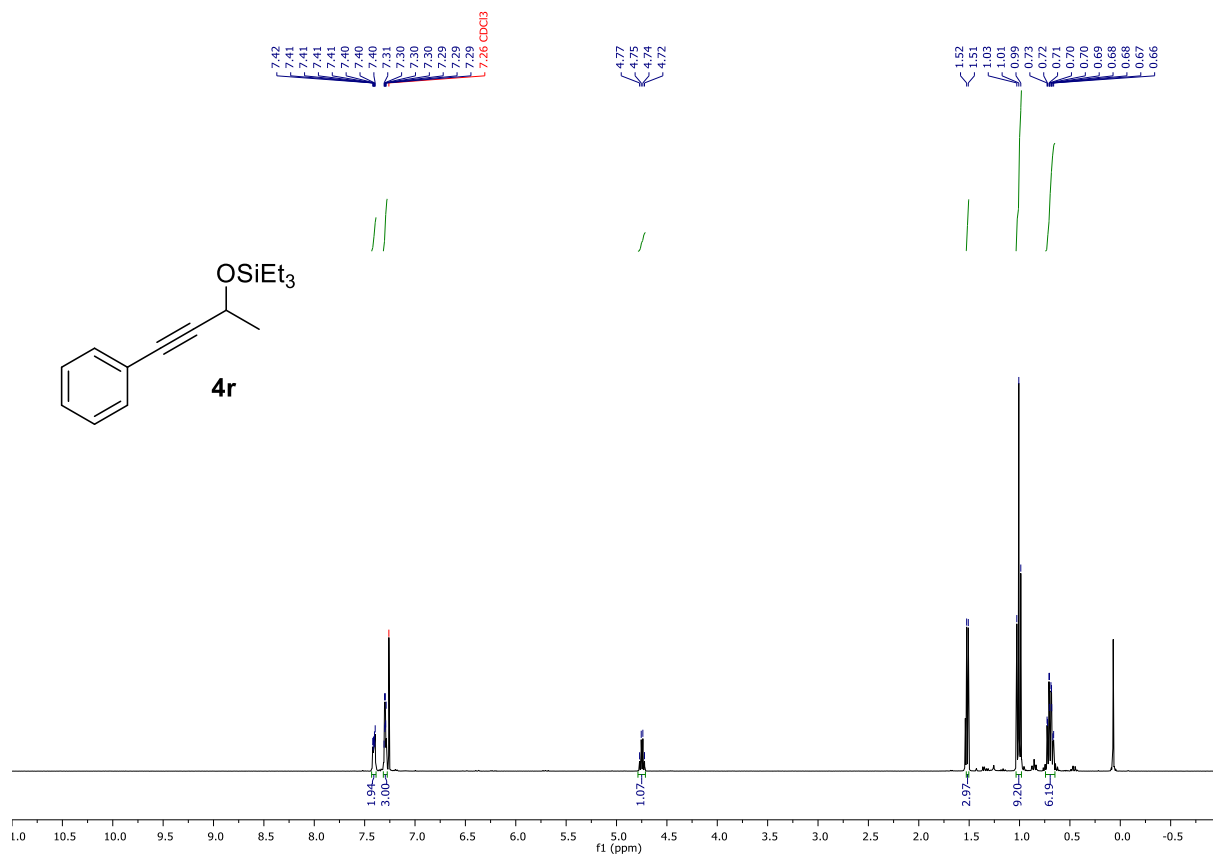
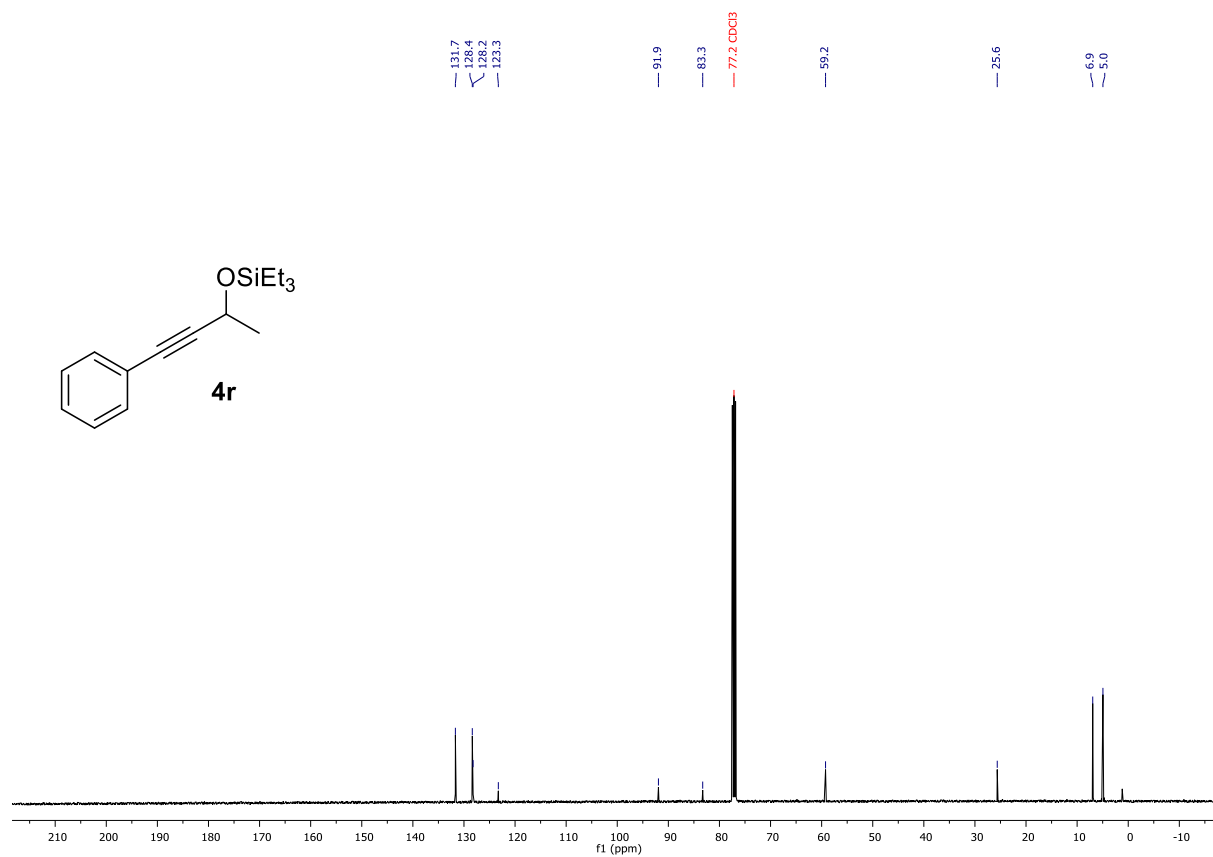


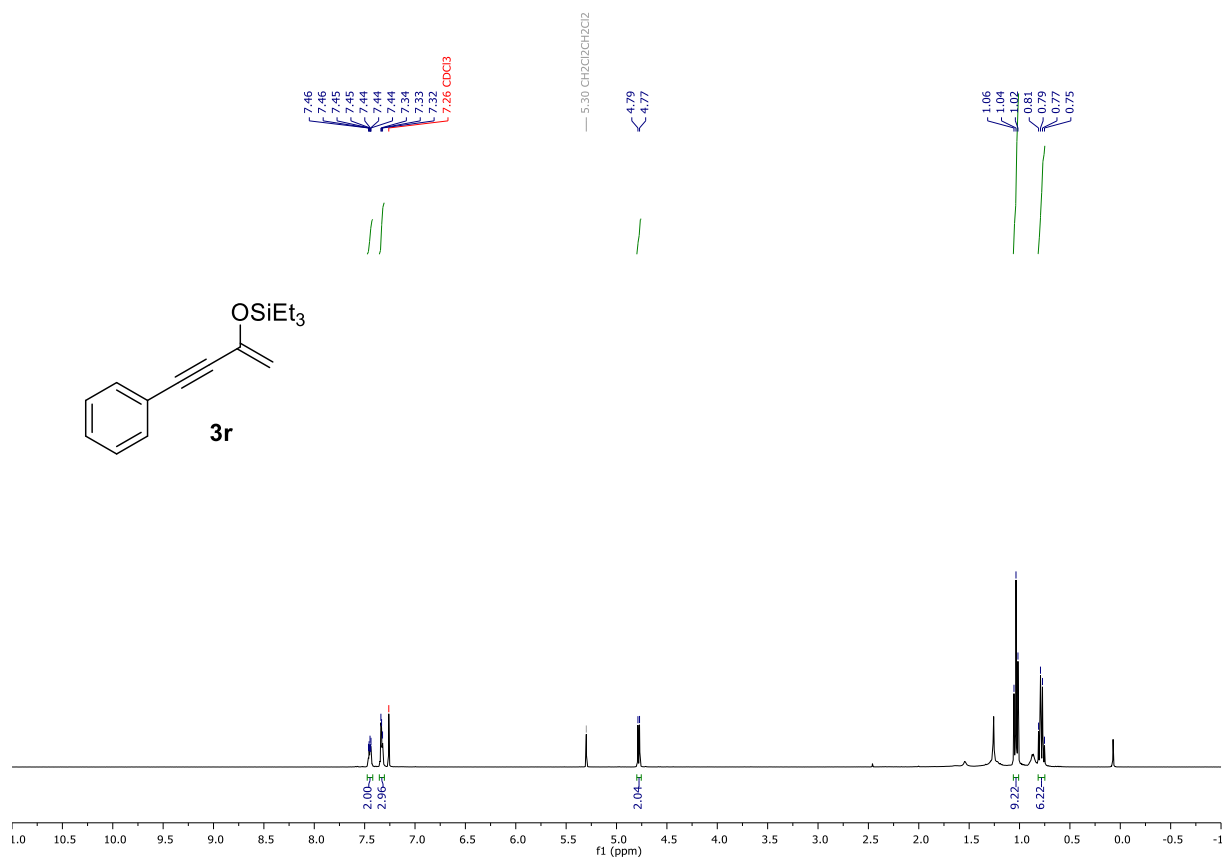
Figure S29. <sup>13</sup>C NMR spectra obtained in CDCl<sub>3</sub> for **4q**.



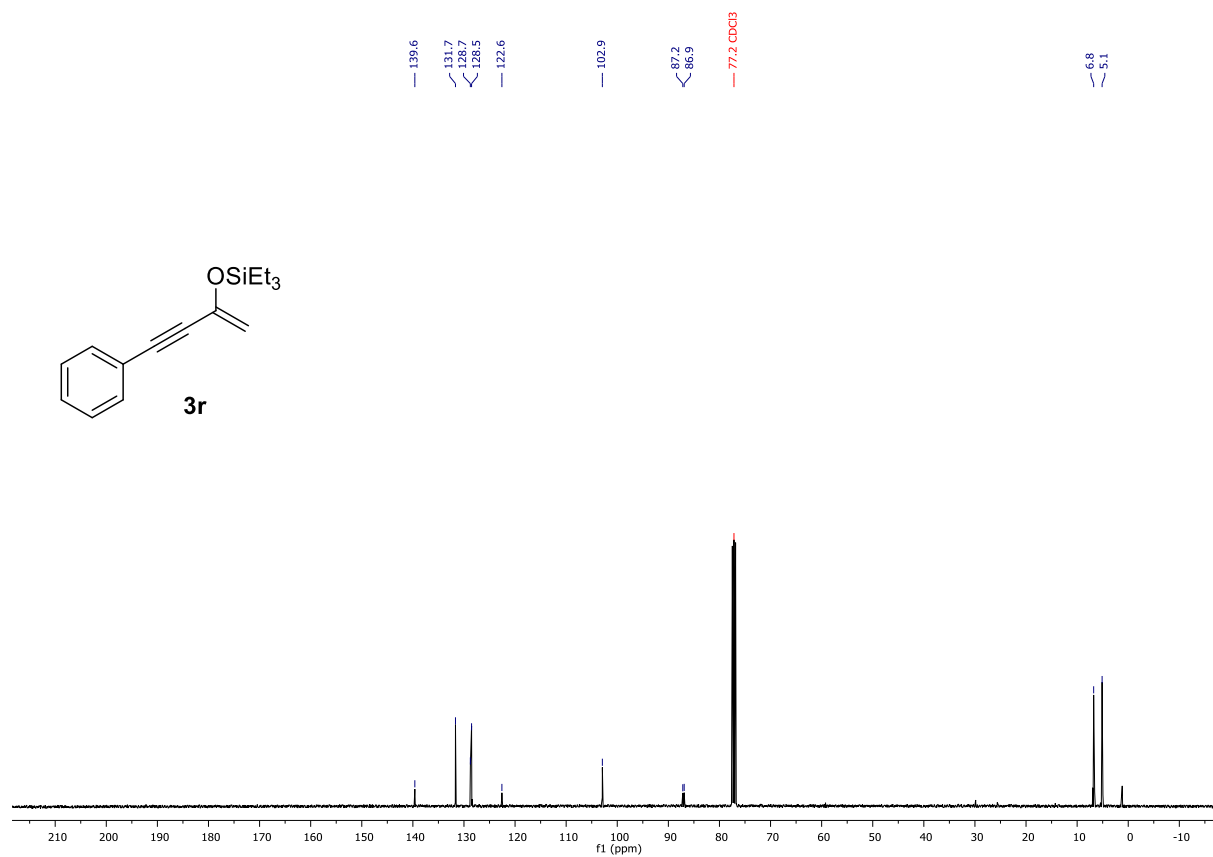
**Figure S30.** <sup>1</sup>H NMR spectra obtained in CDCl<sub>3</sub> for **4r**.



**Figure S31.** <sup>13</sup>C NMR spectra obtained in CDCl<sub>3</sub> for **4r**.



**Figure S32.**  $^1\text{H}$  NMR spectra obtained in  $\text{CDCl}_3$  for enoether byproduct from **3r**.



**Figure S33.**  $^{13}\text{C}$  NMR spectra obtained in  $\text{CDCl}_3$  for the enoether byproduct from **3r**.

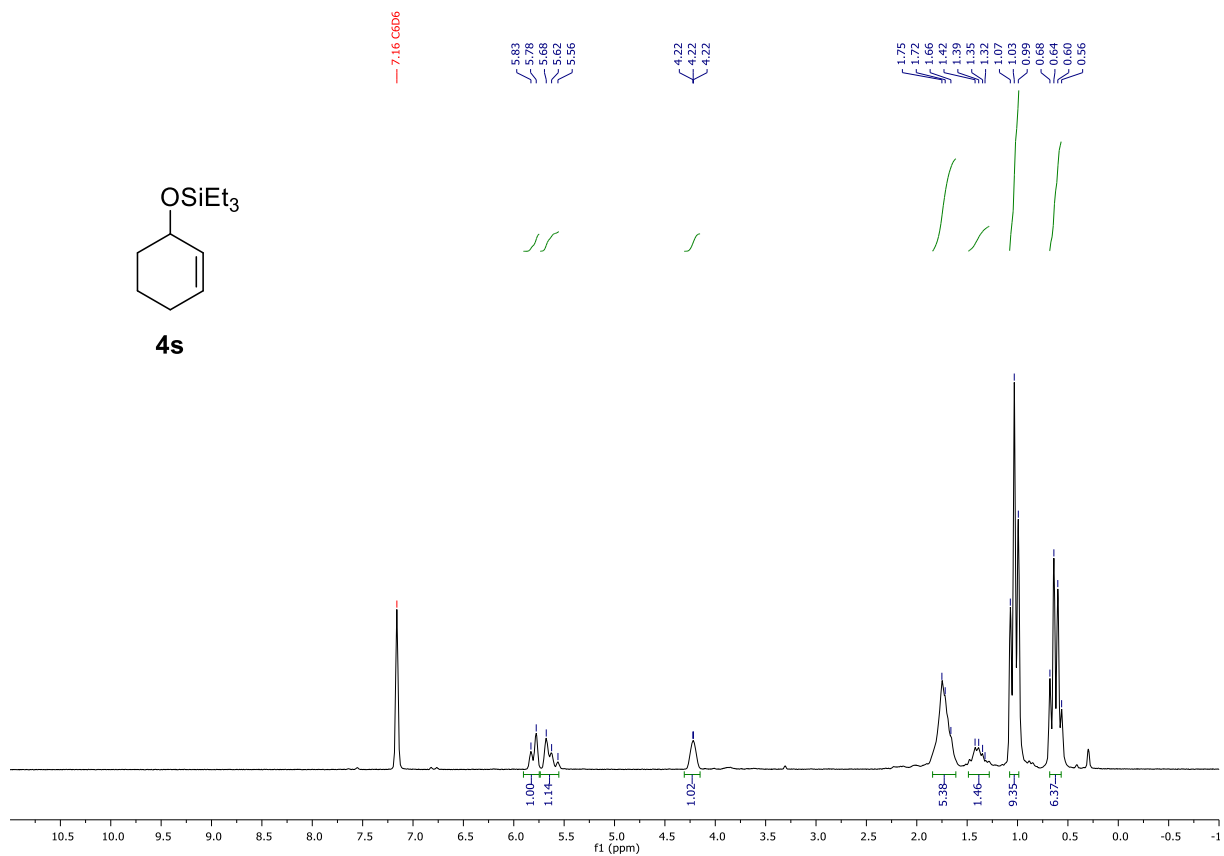


Figure S34.  $^1\text{H}$  NMR spectra obtained in  $\text{C}_6\text{D}_6$  for **4s**.

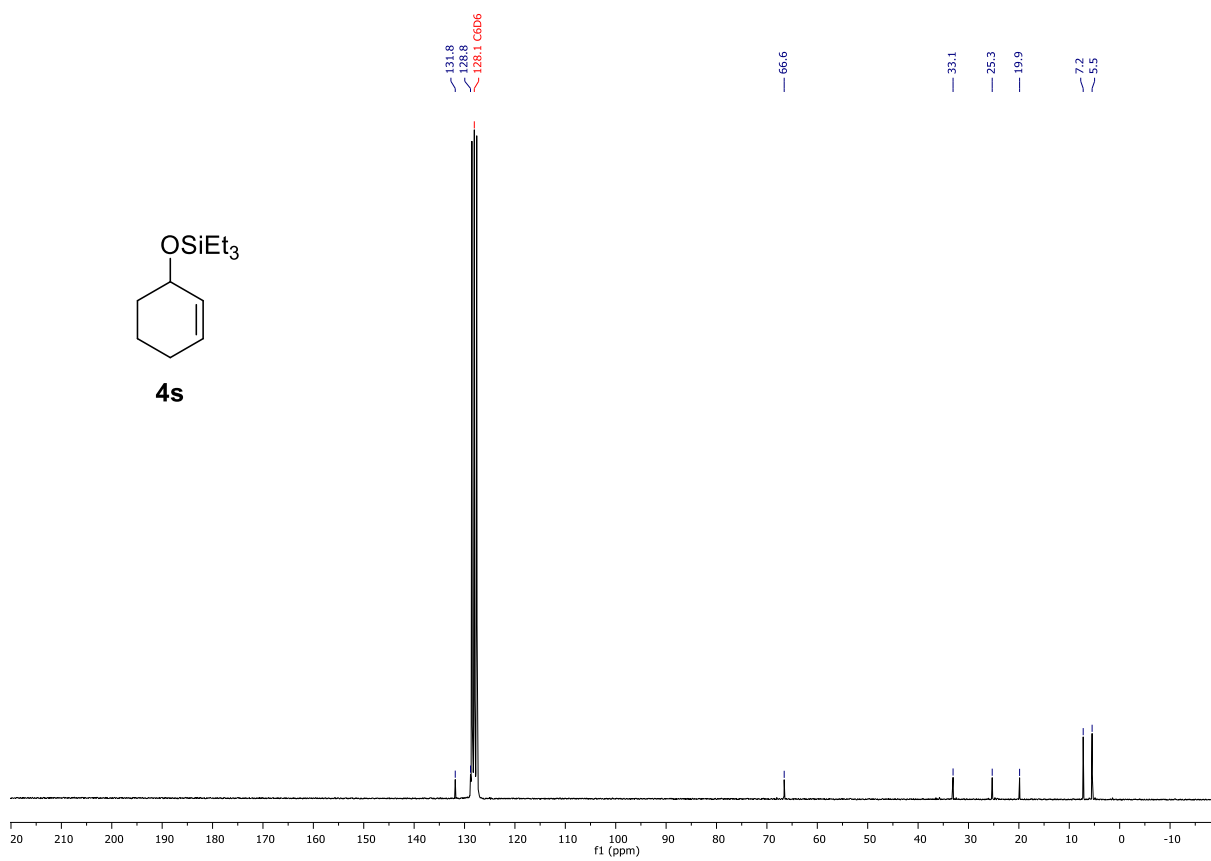


Figure S35.  $^{13}\text{C}$  NMR spectra obtained in  $\text{C}_6\text{D}_6$  for **4s**.

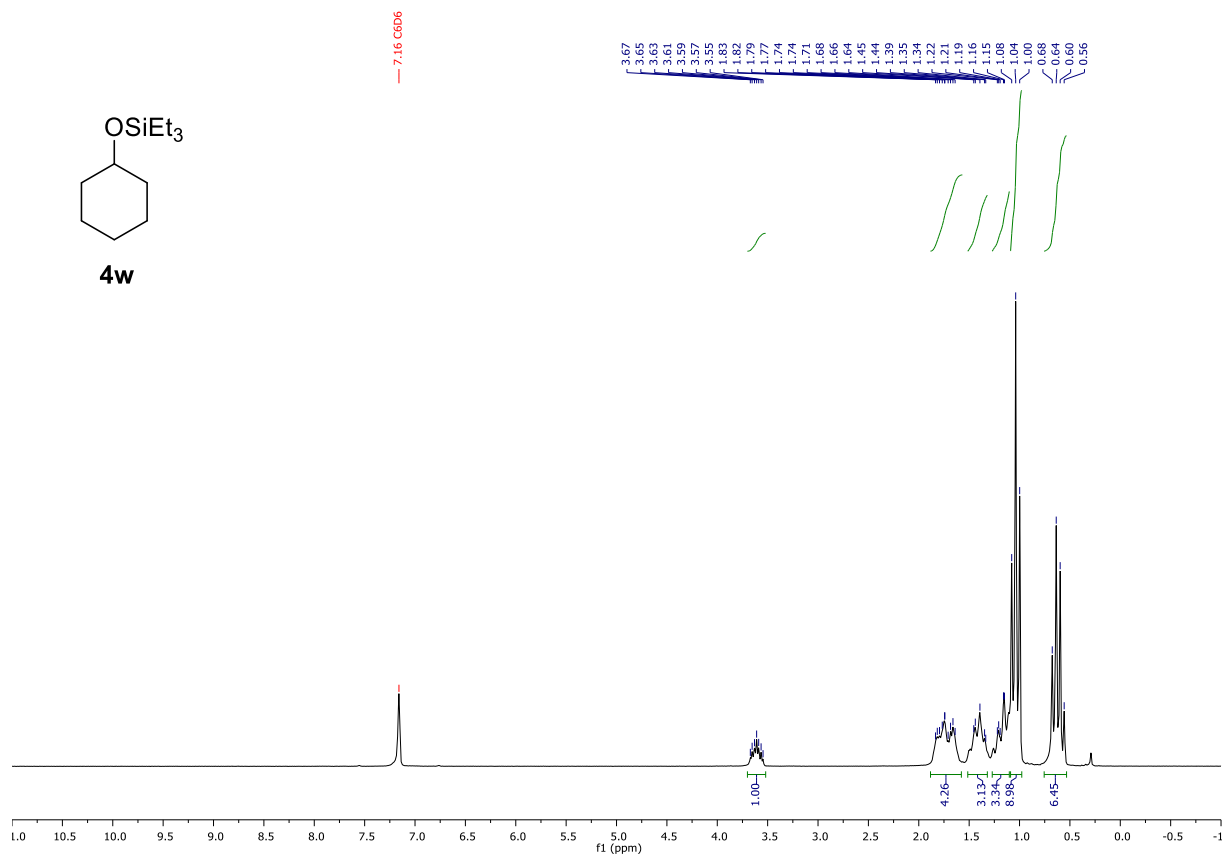


Figure S36. <sup>1</sup>H NMR spectra obtained in C<sub>6</sub>D<sub>6</sub> for **4w**.

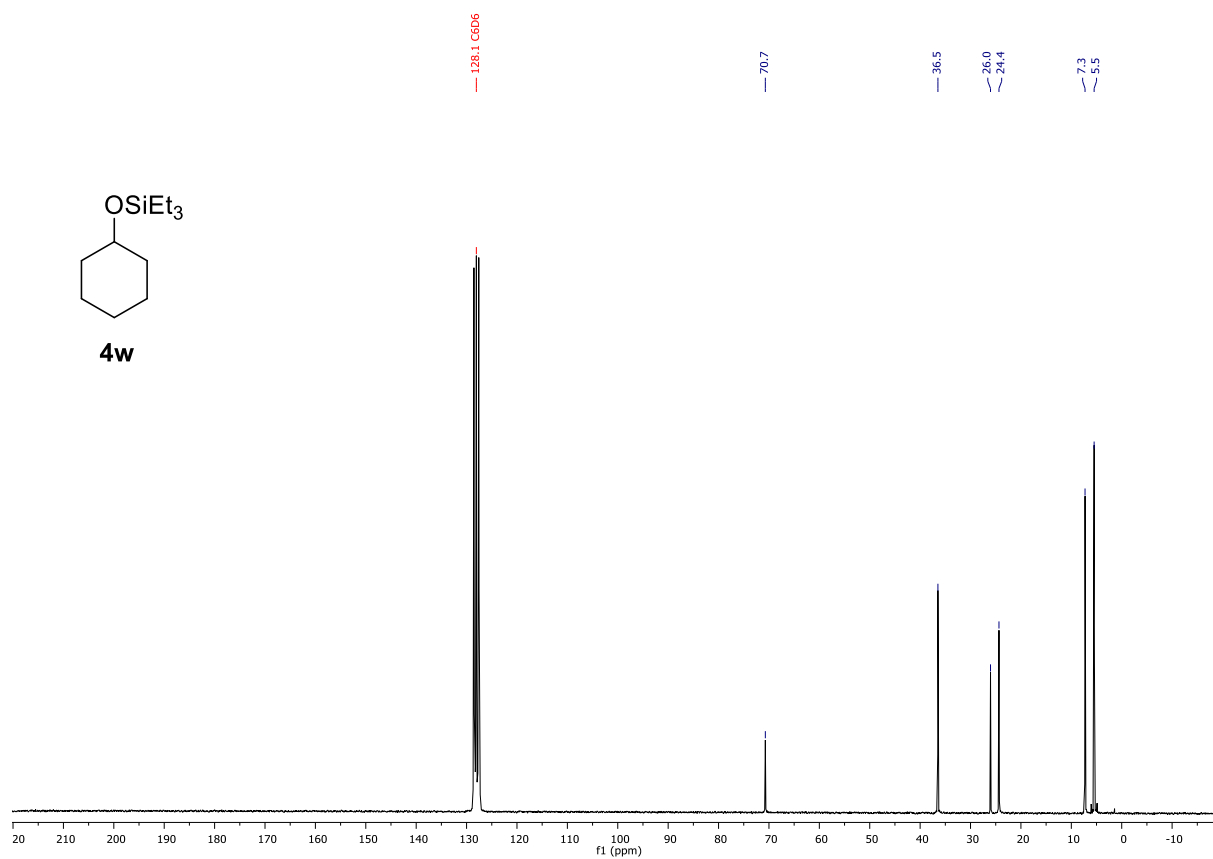


Figure S37. <sup>13</sup>C NMR spectra obtained in C<sub>6</sub>D<sub>6</sub> for **4w**.



### 13. References

- [1] Chauvier, C., Thuéry, P., Cantat, C. *Angew. Chem. Int. Ed.* **2016**, *55*, 14096-14100.
- [2] Chauvier, C., Imberdis, A., Thuéry, P., Cantat, T. *Angew. Chem. Int. Ed.* **2020**, *59*, 14019-14023.
- [3] Godou, T., Chauvier, C., Thuéry, P., Cantat, T. *Synlett* **2017** *28*, 2473-2477.
- [4] Rawat, S., Bhandari, M., Porwal, C. K., Singh, S. *Inorg. Chem.* **2020**, *59*, 7195-7203.
- [5] Rubio, M., Campos, J., Carmona, E. *Org. Lett.* **2011**, *13*, 5236-5239.
- [6] Pérez, M., Qu, Z.-W., Caputo, C. B., Podgorny, V., Hounjet, L. J., Hansen, A., Dobrovetsky, R., Grimme, S., Stephan, D. W. *Chem. Eur. J.* **2015**, *21*, 6491-6500.
- [7] Diez-González, S., Kaur, H., Zinn, F. K., Stevens, E. D., Nolan, S. P. *J. Org. Chem.* **2005**, *70*, 4784-4796.
- [8] Teci, M., Lentz, N., Brenner, E., Matt, D., Toupet, L. *Dalton Trans.* **2015**, *44*, 13991-13998.
- [9] Egbert, J. D., Nolan, S. P. *Chem. Commun.* **2012**, *48*, 2794-2796.
- [10] Kadam, S. T., Kim, S. S. *J. Organomet. Chem.* **2009**, *694*, 2562-2566.
- [11] Ison, E. A., Trivedi, E. R., Corbin, R. A., Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 15374-15375.
- [12] Du, G., Abu-Omar, M. M. *Organometallics* **2006**, *25*, 4920-4923.
- [13] Tran, B. L., Pink, M., Mindiola, D.J. *Organometallics* **2009**, *28*, 2234-2243.
- [14] Liberman-Martin, A. L., Bergman, R. G., Tilley, T. D. *J. Am. Chem. Soc.* **2015**, *137*, 5328-5331.
- [15] C. Chauvier, T. Godou and T. Cantat, *Chem. Commun.* **2017**, 11697.