# Supporting Information

## Practical Method for Hydroxyl-group Protection Using Strontium Metal and Readily Available Silyl Chlorides

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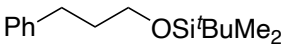
## 1. General Methods

All reagents were purchased from commercial sources (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan, Kanto Chemical Co. Inc., Tokyo, Japan, or FUJIFILM Wako Pure Chemical Co. Ltd., Osaka, Japan), and further purified by standard methods if necessary. A commercially available metallic strontium ingot (Kanto Kagaku Co., Ltd., Japan) in liquid paraffin was cut into small pieces with a small chisel in preparation for the start of each reaction. *N*, *N*-dimethylacetamide (DMA; super dehydrated grade, Kanto Kagaku Co., Ltd., Japan) was used as received. Other solvents were also super dehydrated grade and stored under inert dry gas. For apparatuses for the aluminum brock heating systems, EYELA (TOKYO RIKAKIKAI Co. Ltd., Tokyo, Japan) ChemiStation was used, and reaction temperature was measured by outside of vessel. All reactions were performed under an atmosphere of argon unless stated otherwise. For column chromatography, silica gel (Silica gel 60N, spherical neutral, particle size 63-210μn) from Kanto Kagaku Co., Ltd., was used. Also preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F (FUJIFILM Wako Pure Chemical Co. Ltd., Osaka, Japan) was used for purification. Nuclear magnetic Resonance (NMR) spectra were recorded on a JEOL JNM-ECS 400 spectrometer (JEOL Ltd., Tokyo, Japan), operating at 400 MHz for $^{1}$H-NMR, 100 MHz for $^{13}$C-NMR, and 79.5 MHz for $^{29}$Si-NMR, in $CDCl_3$ (Merck KGaA, Darmstadt, Germany) unless otherwise noted. Chloroform ($CHCl_3$) in minimum 99.8% $CDCl_3$ served as the internal standard ($\delta$ = 7.26) for $^{1}$H NMR and $CDCl_3$ was used as the internal standard ($\delta$ = 77.0) for $^{13}$C NMR. HRMS was analyzed by APCI-TOF-MS system, which atmospheric pressure chemical ionization time-of-flight (APCI-TOF) mass spectrometer XEVO Q-TOF MS system (Waters Corp.).

## 2. General procedure for silyl etherification of alcohols (Table 1, 2)

An oven-dried two-necked 10 mL glass tube containing a stirring bar was charged with some pieces of strontium metal cut into a few millimeters square (1.0 mmol, 1.0 eq). The tube was sealed and then evacuated and backfilled with an argon. DMA (4.0 mL) was injected then set to the described reaction temperature (in the case of entries 1-4 in Table 1, iodomethane (1.5 mmol) was added to the reaction vessel). Alcohol (1.0 mmol), and chlorosilane **a-e** (2.0-5.0 mmol) were added subsequently, and the reaction was quenched by adding a 10% potassium carbonate aqueous solution (10 mL) after the stated reaction time (Caution!: As described in the main text, it is possible for a reaction to appear to be complete by TLC monitoring, yet return to the starting material by quenching). The organic materials were extracted with ethyl acetate (10 mL) three times, and the combined organic layers were washed successively with brine (20 mL) and dried over anhydrous $Na_2SO_4$. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 50:1 to 9:1) to give the corresponding silyl ether product **1a-13a**, or **2b-2e**. In the case of **3a**, **4a**, and **7a** synthesis, diethyl ether and petroleum ether were used instead of ethyl acetate and hexane, and the solvent removal process should not be carried out at too low a pressure (not lower than 160 mmHg) because of the high volatility of these compounds.

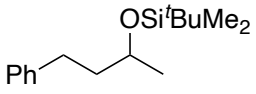
***tert*-butyldimethylsilyl 3-phenylpropyl ether (1a):[1-3]**




$^{1}$H-NMR ($CDCl_3$) δ: 7.28-7.18 (5H, m), 3.64 (2H, t, *J* = 6.4 Hz), 2.68 (2H, t, *J* = 7.8 Hz), 1.86-1.82 (2H, m), 0.91 (9H, s), 0.06 (6H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 142.2, 128.4, 128.2, 125.6, 62.4, 34.4, 32.1, 25.9, 18.3

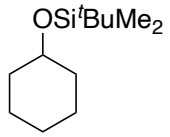
***tert*-butyldimethylsilyl 1-methyl-3-phenylpropyl ether (2a):[4]**




$^1$H-NMR ($CDCl_3$) δ: 7.26-7.19 (5H, m), 3.85 (1H, td, *J* = 12.1, 5.8 Hz), 2.72 (1H, dq, *J* = 15.1, 4.5 Hz), 2.58 (1H, dq, *J* = 15.0, 4.5 Hz), 1.78-1.69 (2H, m), 1.17 (3H, d, *J* = 6.0 Hz), 0.91 (9H, s), 0.06 (3H, s), 0.06 (3H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 142.7, 128.3, 128.3, 125.6, 68.2, 41.5, 32.2, 25.9, 23.8, 18.2

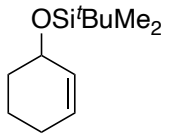
***tert*-butyldimethylsilyl cyclohexyl ether (3a):[5-7]**




$^1$H-NMR ($CDCl_3$) δ: 3.62-3.56 (1H, m), 1.73 (4H, dd, *J* = 15.8, 7.6 Hz), 1.48 (1H, dd, *J* = 10.1, 4.1 Hz), 1.33-1.15 (5H, m), 0.88 (9H, s), 0.04 (6H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 70.8, 35.9, 25.9, 25.6, 24.1, 18.2, –4.7

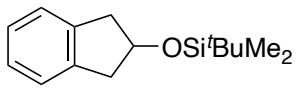
***tert*-butyldimethylsilyl 2-cyclohexenyl ether (4a):[8]**




$^1$ H-NMR ($CDCl_3$) δ: 5.77-5.72 (1H, m), 5.62 (1H, dq, *J* = 10.1, 2.1 Hz), 4.22 (1H, td, *J* = 4.5, 1.8 Hz), 2.06-1.72 (4H, m), 1.60-1.47 (2H, m), 0.90 (9H, s), 0.07 (3H, s), 0.07 (3H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 131.2, 129.1, 66.7, 32.5, 25.9, 24.9, 19.7, 18.3, –4.5, –4.6

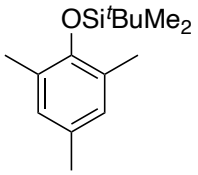
***tert*-butyldimethylsilyl 2-indanyl ether (5a):[9]**




$^1$ H-NMR ($CDCl_3$) δ: 7.19-7.13 (4H, m), 4.68 (1H, t, *J* = 6.4 Hz), 3.13 (2H, dd, *J* = 15.8, 6.6 Hz), 2.89 (2H, dd, *J* = 15.8, 5.7 Hz), 0.91 (9H, s), 0.10 (6H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 141.3, 126.4, 124.5, 73.9, 42.6, 25.9, 18.2, –4.7

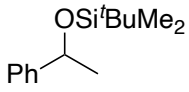
***tert*-butyldimethylsilyl 2,4,6-trimethylphenyl ether (6a):[10]**




$^1$ H-NMR ($CDCl_3$) δ: 6.79 (2H, s), 2.23 (3H, s), 2.19 (6H, s), 1.05 (9H, s), 0.19 (6H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 149.7, 130.2, 129.3, 128.2, 26.1, 20.4, 18.7, 17.7, –3.0

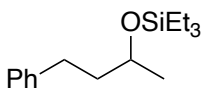
***tert*-Butyldimethylsilyl 1-phenylethyl ether (7a):[11]**




$^1$ H-NMR ($CDCl_3$) δ: 7.34-7.20 (6H, m), 4.87 (1H, q, *J* = 6.4 Hz), 1.41 (4H, d, *J* = 6.4 Hz), 0.90 (9H, s), 0.05 (3H, s), –0.03 (3H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 146.9, 128.0, 126.6, 125.1, 70.8, 27.3, 25.9, 18.3, –4.8, –4.9

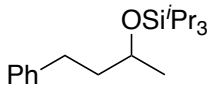
**1-methyl-3-phenylpropyl triethylsilyl ether (2b):[12]**




$^1$ H-NMR ($CDCl_3$) δ: 7.30-7.26 (2H, m), 7.19-7.16 (3H, m), 3.85 (1H, td, *J* = 12.1, 6.0 Hz), 2.72 (1H, dq, *J* = 15.1, 4.6 Hz), 2.60 (1H, dq, *J* = 15.1, 4.6 Hz), 1.83-1.67 (2H, m), 1.19 (3H, d, *J* = 6.0 Hz), 0.97 (9H, t, *J* = 7.8 Hz), 0.61 (6H, q, *J* = 8.1 Hz).

$^{13}$C-NMR ($CDCl_3$) δ: 142.6, 128.3, 128.3, 125.6, 68.0, 41.5, 32.2, 23.8, 6.9, 5.0

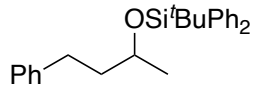
**1-methyl-3-phenylpropyl triisopropylsilyl ether (2c):[13,14]**




$^1$ H-NMR ($CDCl_3$) δ: 7.29-7.27 (2H, m), 7.21-7.16 (3H, m), 4.00 (1H, td, *J* = 11.8, 6.0 Hz), 2.71-2.64 (2H, m), 1.88-1.72 (2H, m), 1.23 (3H, d, *J* = 6.1 Hz), 1.07 (21H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 142.7, 128.3, 128.3, 125.6, 68.1, 41.7, 31.6, 23.4, 18.2, 18.1, 12.5

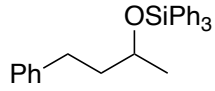
***tert*-butyldiphenylsilyl 1-methyl-3-phenylpropyl ether (2d):[13,14]**




$^1$H-NMR ($CDCl_3$) δ: 7.71-7.65 (4H, m), 7.44-7.35 (6H, m), 7.23 (2H, dt, *J* = 11.4, 2.5 Hz), 7.15 (1H, dd, *J* = 8.7, 6.4 Hz), 7.07 (2H, d, *J* = 6.9 Hz), 3.91 (1H, td, *J* = 11.9, 6.0 Hz), 2.68-2.53 (2H, m), 1.84-1.66 (2H, m), 1.12 (3H, d, *J* = 6.0 Hz), 1.07 (9H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 142.5, 135.9, 134.8, 134.4, 129.5, 129.4, 128.3, 128.2, 127.5, 127.4, 125.5, 69.2, 41.2, 31.6, 27.0, 23.2, 19.3

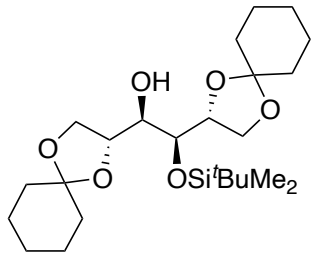
**1-methyl-3-phenylpropyl triphenylsilyl ether (2e):[15,16]**




$^1$H-NMR ($CDCl_3$) δ: 7.65-7.63 (6H, m), 7.48-7.36 (9H, m), 7.28-7.12 (4H, m), 7.04-7.02 (2H, m), 4.04 (1H, td, *J* = 12.1, 6.3 Hz), 2.71-2.64 (1H, m), 2.61-2.53 (1H, m), 1.88 (1H, tt, *J* = 11.9, 5.1 Hz), 1.74 (1H, tt, *J* = 12.1, 4.7 Hz), 1.21 (3H, d, *J* = 6.0 Hz).

$^{13}$C-NMR ($CDCl_3$) δ: 142.3, 135.5, 134.9, 129.9, 128.3, 128.2, 127.8, 125.6, 69.4, 41.1, 31.8, 23.5

**1,2:5,6-Di-O-cylcohexylidene-D-mannitol mono-*tert*-butyldimethylsilyl ether (8a):**

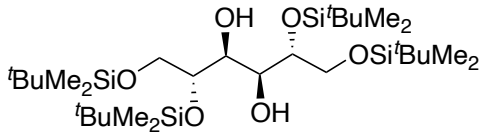



HRMS (ESI-MS) *m/z*: $[M+H]^+$ calcd. for $C_{24}H_{44}O_6Si$, 457.2986; found, 457.2978

$^1$H-NMR ($CDCl_3$) δ: 4.15-4.11 (1H, m), 4.08 (2H, dd, *J* = 12.8, 6.4 Hz), 4.02 (1H, dd, *J* = 7.8, 5.5 Hz), 3.96 (1H, dd, *J* = 8.2, 5.0 Hz), 3.90-3.85 (1H, m), 3.84-3.80 (1H, m), 3.55 (1H, t, *J* = 9.6 Hz), 2.27 (1H, d, *J* = 10.1 Hz), 1.59-1.57 (16H, br m), 1.38 (4H, br s), 0.90 (9H, s), 0.16 (6H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 109.9, 109.4, 76.2, 74.4, 72.7, 71.2, 67.7, 66.1, 36.5, 36.3, 34.9, 34.9, 26.0, 25.2, 25.1, 24.0, 24.0, 23.8, 23.8, 10.2, –4.0, –4.3.

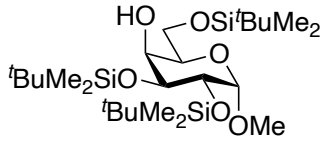
**D-mannitol 1,2,5,6-tetra-*tert*-butyldimethylsilyl ether (9a):[17,18]**




$^1$H-NMR ($CDCl_3$) δ: 3.84-3.78 (4H, m), 3.72-3.64 (4H, m), 3.35 (2H, d, *J* = 3.7 Hz), 0.88 (18H, s), 0.87 (18H, s), 0.11 (6H, s), 0.08 (6H, s), 0.05 (12H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 74.1, 70.5, 65.5, 25.9, 25.8, 18.3, 18.0, –4.4, –5.0, –5.5, –5.5.

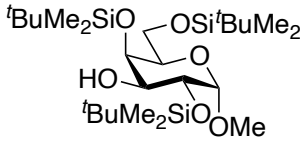
**Methyl-α-D-galactopyranoside 2,4,6-tris-*tert*-butyldimethylsilyl ether (10a):[19-21]**




$^1$H-NMR ($CDCl_3$) δ: 4.66 (1H, d, *J* = 3.7 Hz), 4.06 (1H, d, *J* = 2.7 Hz), 3.96 (1H, dd, *J* = 10.1, 3.7 Hz), 3.78 (1H, dt, *J* = 6.4, 3.4 Hz), 3.67 (3H, s), 3.38 (3H, s), 0.91 (18H, s), 0.88 (9H, s), 0.12 (3H, s), 0.10 (3H, s), 0.09 (3H, s), 0.09 (3H, s), 0.05 (6H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 100.1, 71.8, 70.8, 70.6, 70.2, 62.3, 55.1, 26.0, 25.8, 25.8, 18.5, 18.2, 18.2, –4.1, –4.5, –4.6, –4.9, –5.3, –5.4.

**Methyl-α-D-galactopyranoside 2,3,6-tris-*tert*-butyldimethylsilyl ether (11a):[19-21]**

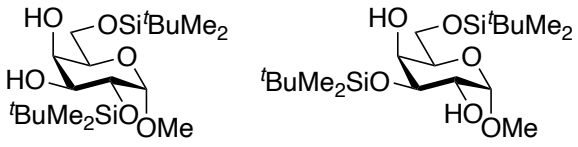



$^1$H-NMR ($CDCl_3$) δ: 4.67 (1H, s), 3.89 (2H, s), 3.86-3.85 (2H, m), 3.79-3.78 (2H, m), 3.38 (3H, s), 2.58 (1H, s), 1.58 (3H, d, *J* = 3.2 Hz), 0.91 (9H, s), 0.90 (9H, s), 0.89 (9H, s), 0.13 (3H, s), 0.11 (3H, s), 0.08 (12H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 100.4, 71.8, 70.5, 69.9, 69.8, 62.2, 55.1, 26.0, 25.9, 25.8, 18.2, 18.2, 18.0, –3.9, –4.0, –4.8, –4.8, –5.3, –5.5.

**Methyl-α-D-galactopyranoside 2,6-di-*tert*-butyldimethylsilyl ether (12a):[19-21]**

**Methyl-α-D-galactopyranoside 3,6-di-*tert*-butyldimethylsilyl ether (13a):** [19-21]



**12a**/**13a**=42/58; $^1$H-NMR ($CDCl_3$) δ: 4.76 (0.42H, d, *J* = 2.7 Hz), 4.65 (0.58H, d, *J* = 3.7 Hz), 4.06 (0.58H, d, *J* = 2.3 Hz), 3.92 (0.58H, dd, *J* = 9.4, 3.9 Hz), 3.88-3.71 (1.74H+2.94H, m), 3.39 (1.26H, s), 3.36 (1.74H, s), 2.96 (0.58H, s), 2.54 (0.42H, s), 2.41 (0.58H, d, *J* = 3.2 Hz), 1.94 (0.58H, br m), 0.89 (5.22+3.78H, s), 0.87 (5.22H, s), 0.87 (3.78H, s), 0.12 (1.26H, s), 0.09 (1.74+1.26H, s), 0.08 (1.74H, s), 0.06 (3.48H,s), 0.06 (2.52H,s).

**12a** $^{13}$C-NMR ($CDCl_3$) δ: 100.4, 72.6, 70.8, 70.1, 69.7, 62.2, 55.1, 25.8, 25.7, 18.2, 18.1, –4.5, –4.9, –5.4, –5.5.

**13a** $^{13}$C-NMR ($CDCl_3$) δ: 99.5, 70.4, 69.6, 69.6, 69.3, 62.9, 55.2, 25.8, 25.7, 18.2, 18.0, –4.6, –4.6, –5.5, –5.5.

## 3. General silyl etherification reaction by using DMAP as a catalyst (Scheme 1)[22]

An example of the silyl etherification of 3-phenylpropanol **1** catalyzed by DMAP is shown below to compare the reaction we have developed. As mentioned in the main text, the reaction was also carried out with 4-phenyl-2-butanol **2** under the same condition; however, only traces amount of the desired product was obtained.

An oven-dried two-necked 10 mL glass tube containing a stirring bar was flame-dried under vacuum and then charged with argon. To this flask, a 3-phenylpropanol **1** (136.2 mg, 1.0 mmol) with *N*, *N*-Dimethylamino-pyridine (6.9 mg, 0.05 mmol) dissolved in dry THF (2.9 mL) and then dry DMI (1.1 mL) was added successively. Triethylamine (490 μL, 3.5 mmol) and *tert*-butyldimethylsilylchloride **a** (308.2 mg, 2.0 mmol) were subsequently added to this reaction mixture, then stirred at room temperature. After 2h, the reaction was quenched by adding a saturated ammonium chloride aqueous solution (10 mL). Organic materials were extracted with ethyl acetate (10 mL) three times, and the combined organic layers were washed with brine (30 mL) then dried over anhydrous $Na_2SO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica gel (hexane / ethyl acetate = 20:1) to give the corresponding silyl ether product **1a** (248.7 mg, 99%).

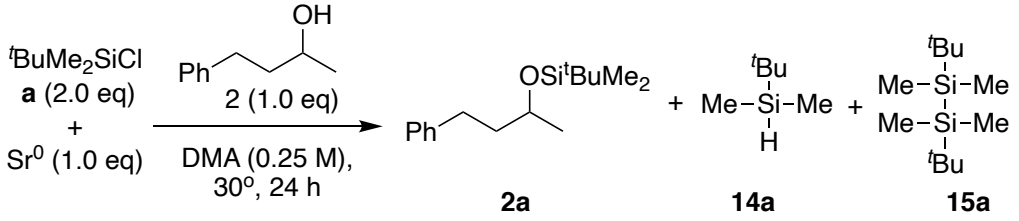
## 4. Reaction tracking experiment by $^1$H NMR analysis

The results of entry 7 in Table 1, the TLC results showed that the reaction was almost complete even at 2 hours, whereas 16% of the starting material was recovered after quenching the reaction system. And the ratio of the recovered material gradually decreases as the reaction time is extended (entries 7-10 in Table 1). In order to clarify this phenomenon, we have followed the reaction by $^1$H-NMR analysis of the crude reaction mixture.

(a) Direct observation of crude mixture by $^1$H-NMR analysis (Table 1, entry 10)

The reaction itself just followed the same procedure of "General procedure" mentioned above, however, 360 μL (20 eq) of water was added to quench the reaction. After 30 minutes of vigorous stirring, the stirring is stopped, and the mixture is allowed to stand for a further 30 minutes. The highly polar hydrous DMA is released in the lower layer and the other compounds in the upper layer. A portion of the upper layer was picked up with a Pasteur pipette, diluted with chloroform, and observed by $^1$H-NMR. As the results showed several silicon-derived compounds and the confirmed presence of 13% silane **14a** and 33% disilane **15a** compared to the silyl-protected alcohol **2a** at the end of the reaction. However, careful isolation and purification of the recovered crude product showed that only 15% of the disilane **15a** was isolated, except for the quantitative recovery of **2a** (Scheme SI-1).

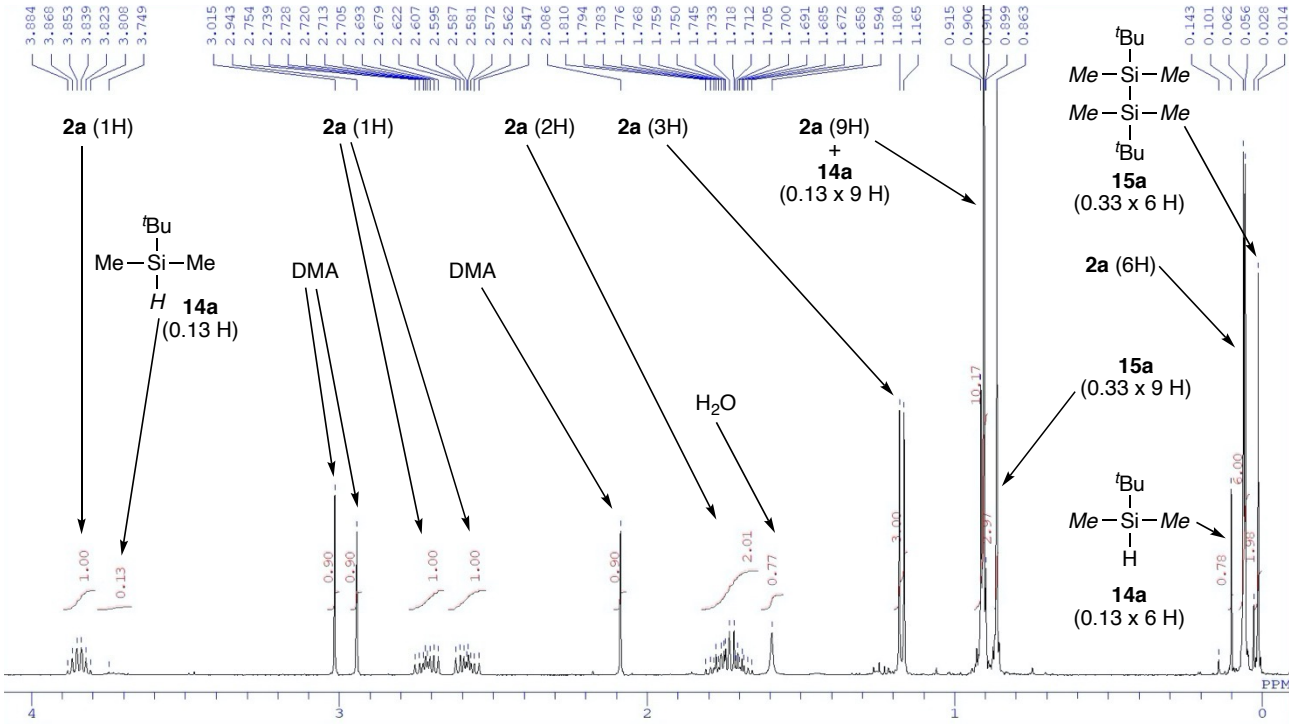
**Scheme SI-1**




**2a** **14a** **15a**

| | | | | | | |
|---|---|---|---|---|---|---|
| after quench: | 100 | : | 13 | : | 33 |
| after isolation: | quant | : | - | : | 15 |

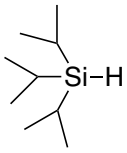
(b) $^{1}$H-NMR chart of crude mixture (Scheme SI-1: after quench)




(c) Authentic sample synthesis of possible silicon compounds as by product

Based on crude NMR analysis and $R_f$ values of TLC analysis, possible candidate compounds were pre-synthesized in order to determine the exact byproduct at the time the reaction was quenched. Triisopropylsilane **14c**[23] and hexaisopropyldisilane **15c**[24] were synthesized by the reported method described in the literature. Triisopropylsilanol **16c** and hexaisopropyldisiloxane **17c** are obtained as a mixture by hydrolysis of chlorotriisopropylsilane with aqueous 2N NaOH solution. Both compounds can be easily isolated by silica gel column chromatography.

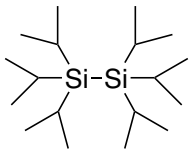
**Triisopropylsilane (14c):**[25]



$^{1}$ H-NMR ($CDCl_3$) δ: 3.30 (1H, s), 1.06 (21H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 19.4, 10.2

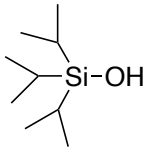
**Hexaisopropyldisilane (15c):**[24]



$^{1}$H-NMR ($CDCl_3$) δ: 1.06 (6H, s), 1.06 (36H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 18.4, 13.4

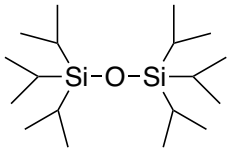
**Triisopropylsilanol (16c):**[26,27]



$^{1}$H-NMR ($CDCl_3$) δ: 1.32 (1H, d, $J$ = 3.4 Hz), 1.05 (21H, s).

$^{13}$C-NMR ($CDCl_3$) δ: 17.7, 12.2

**Hexaisopropyldisiloxane (17c):**[28]



$^{1}$H-NMR ($CDCl_3$) δ: 1.27-1.18 (6H, m), 1.10 (36H, d, $J$ = 7.1 Hz).

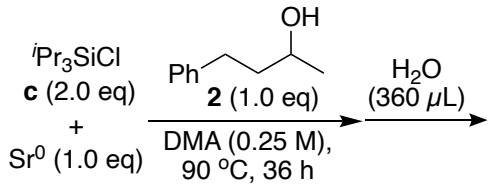
$^{13}$C-NMR ($CDCl_3$) δ: 17.7, 13.6

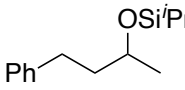
(d) Direct observation of crude mixture by $^{1}$H-NMR analysis by using triisopropyl chloride

Since the poor mass balance of silane compounds is due to the low boiling point and high volatility of **14a** and **15a**, a detailed follow-up study of the reaction system was carried out using triisopropyl chloride **c**.

The reaction was not complete under the conditions of Table 2, entry14 (2.0 eq. 2c, 90 ºC, 24 h), however, when the reaction time was extended to 36 h, it proceeded completely, and 2c was obtained quantitatively. On the other hand, when alcohol **2** was added to the reaction system together with c and strontium metal, in the beginning, the reaction was carried out at 90 ºC for 36 h. After adding water until the salt was dissolved, the reaction system was directly analyzed by 1H-NMR, and it was found that silane **14c** was present, although only 4%. In addition to **2c** (99%), **15c** (59%) and **16c** (21%) were also isolated by careful purification of the recovered compounds (Scheme SI-2). The results of these two experiments show that in both cases, it is possible to identify the compounds formed by the reaction of almost all the chlorosilane **c** initially added.

**Scheme SI-2**

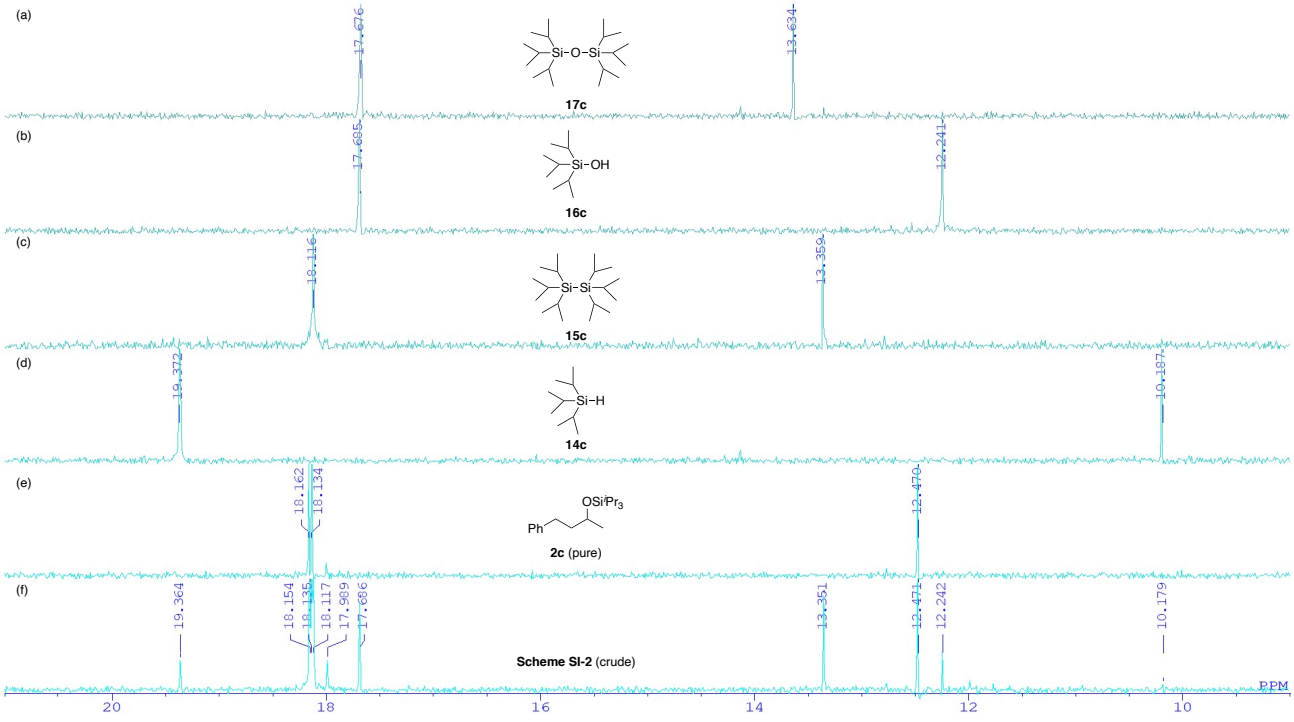



+ $^{i}Pr_3SiH$ + $^{i}Pr_3Si—Si^{i}Pr_3$ + $^{i}Pr_3SiOH$ + $^{i}Pr_3SiOSi^{i}Pr_3$

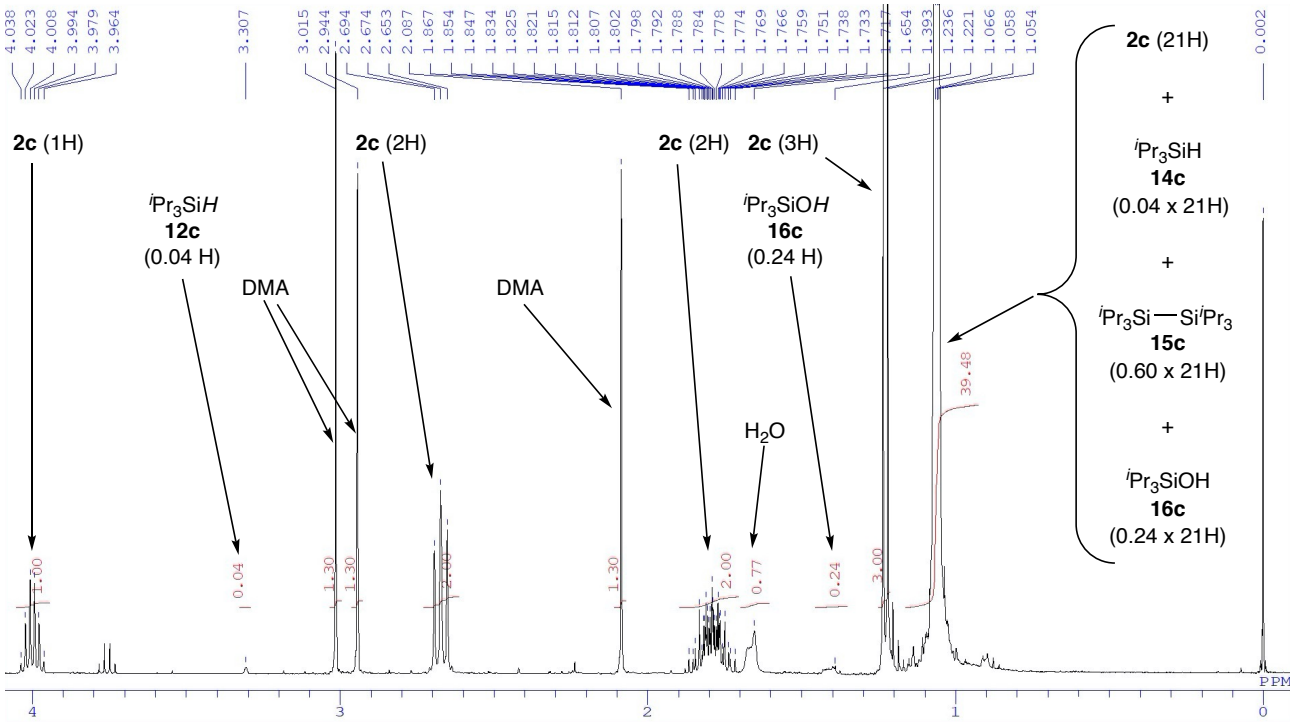
| | **2c** | | **14c** | | **15c** | | **16c** | | **17c** |
|---|---|---|---|---|---|---|---|---|---|
| after quench: | 100 | : | 4 | : | 60 | : | 24 | : | Not observed |
| after isolation: | 99 | : | Not obtained | : | 59 | : | 21 | : | Not obtained |

(e) $^{13}$C-NMR chart of crude mixture (Scheme SI-2: after quench)



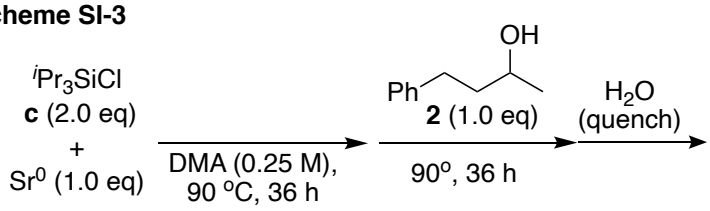

$^{13}$C-NMR chart extending from 9.0 ppm to 21.0 ppm for the (a) Isolated **17c**, (b) Isolated **16c**, (c) Isolated **15c**, (d) Isolated **14c**, (e) Isolated **2c** and (f) crude after the quenched reaction according to **Scheme SI-2**.

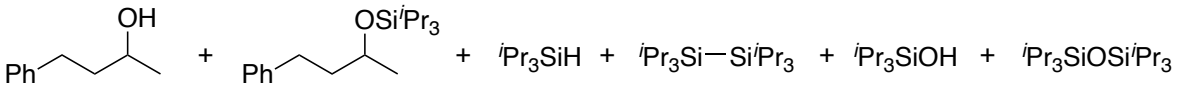
(f) $^1$H-NMR chart of crude mixture (Scheme SI-2: after quench)




(g) Elucidation of silane and disilane generation processes

**Scheme SI-3**




| **2** (recoverd) | | **2c** | | **14c** | | **15c** | | **16c** | | **17c** |
|---|---|---|---|---|---|---|---|---|---|---|
| quant | : | Not observed | : | - | : | 180 | : | 10 | : | Not observed |

The following confirmation experiments were carried out to elucidate the process of silane and disilane generation, which is not possible only by the strontium alkoxide pathway. When only strontium metal with **c** was stirred at 90 °C in DMA, the salt formation was observed gradually. After 36 hours of stirring, alcohol **2** was added to the mixture and reacted for further 36 hours; however, the silyl etherification reaction hardly proceeded, and the starting material was recovered quantitively. Moreover, two equivalents (200 mol%) of **c** to the substrate that present at the beginning of the reaction were converted most (180 mol%) of which to disilane **15c** and some (10 mol%) to silanol **16c**. In other words, the reaction proceeds only in the presence of strontium metal with **c**, becoming an inactive compound with no silyl etherification ability (Scheme SI-3).

## 5. References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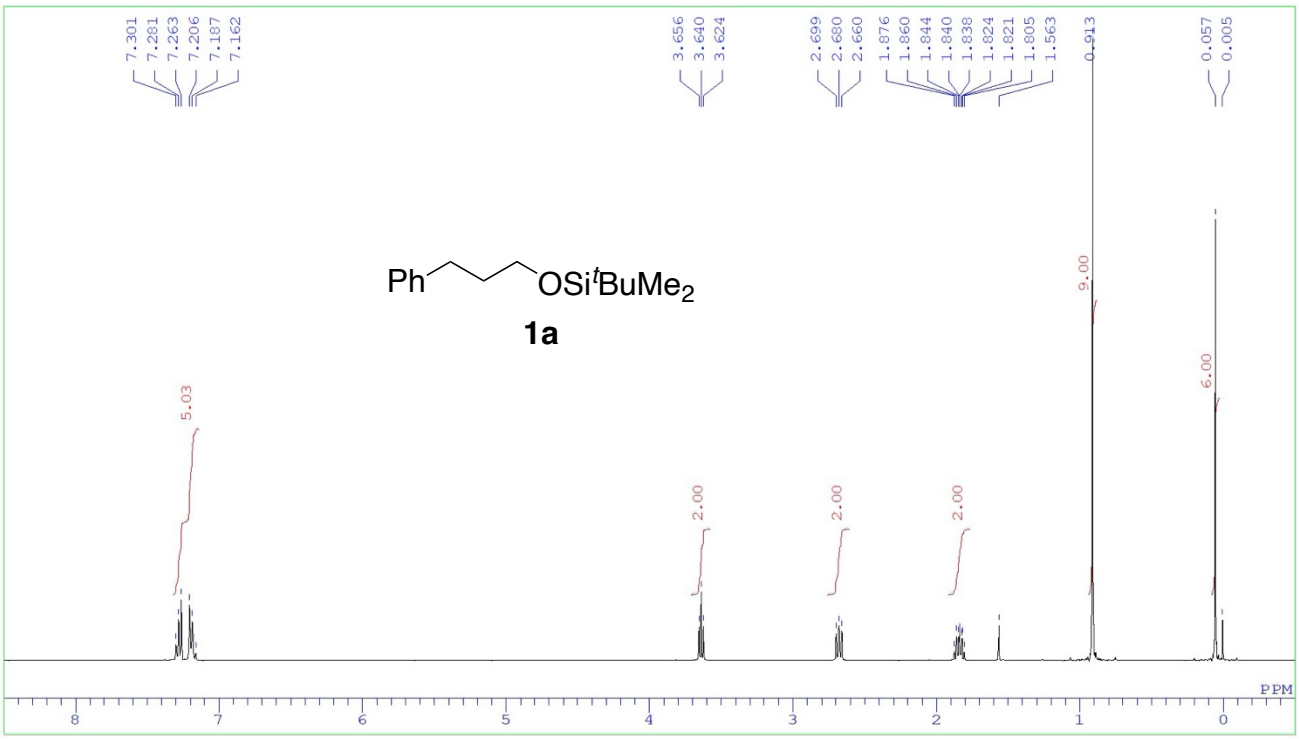
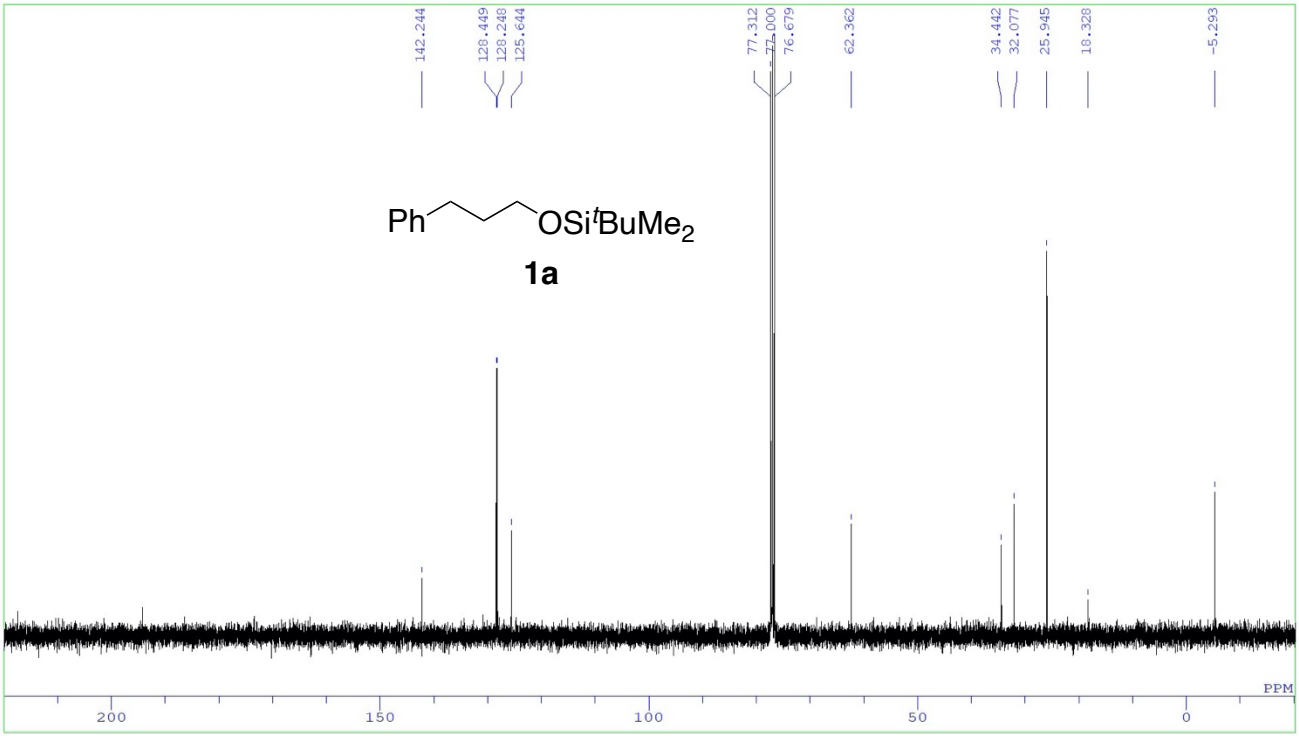
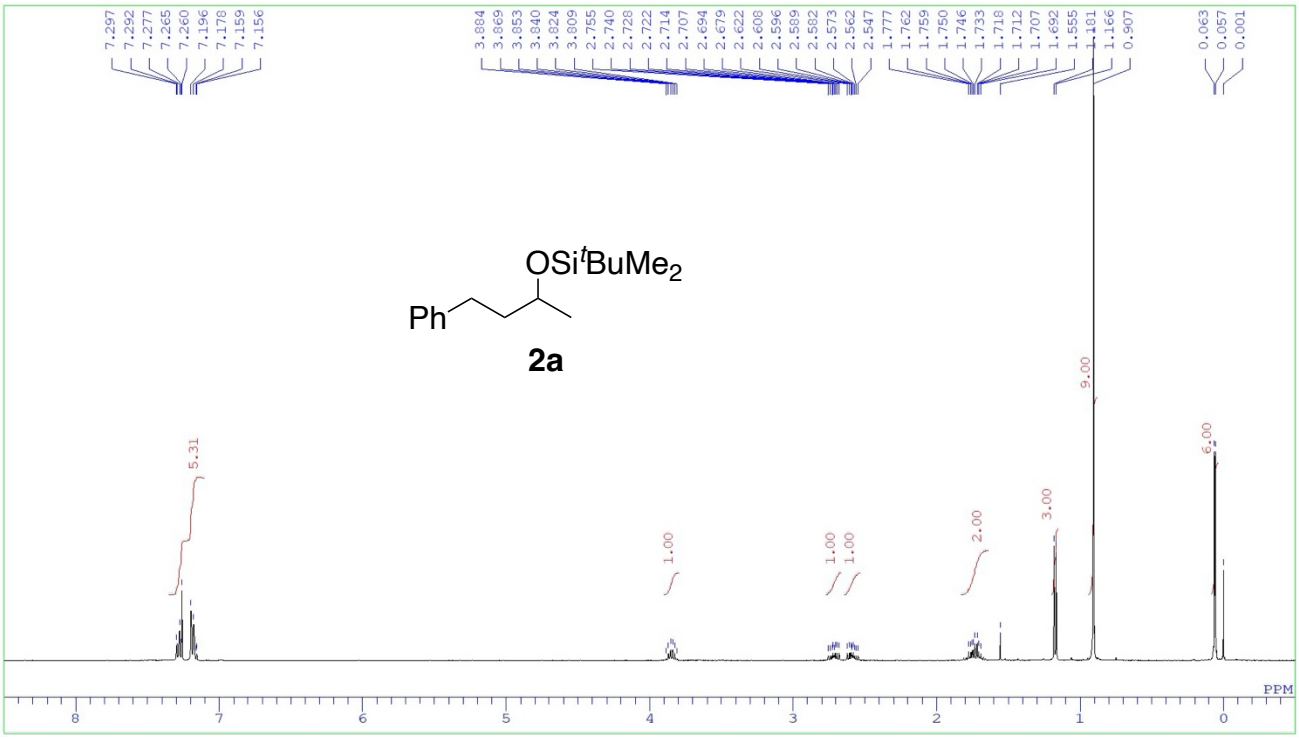
## 6. The copies of $^{1}H$ and $^{13}C$ NMR spectra

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2.728
2.722
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2.694
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2.608
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1.733
1.718
1.712
1.707
1.692
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0.063
0.057
0.001
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4
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2
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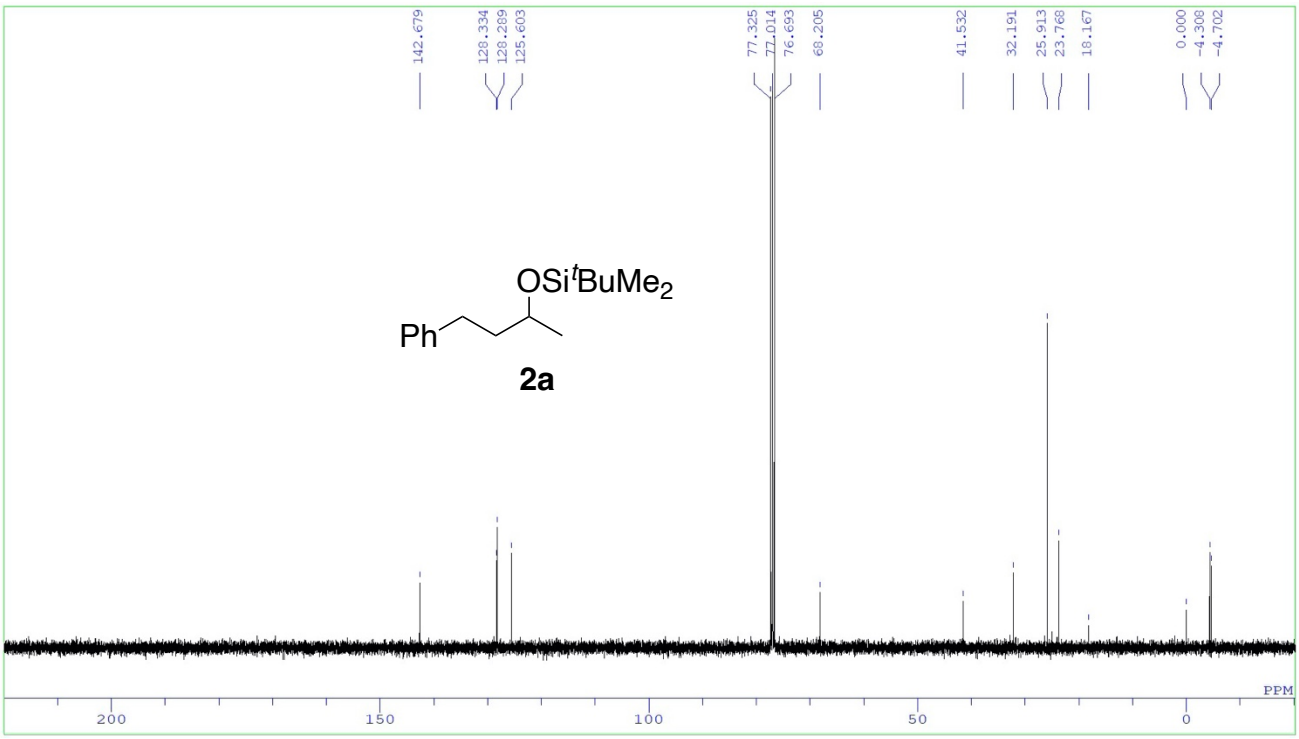
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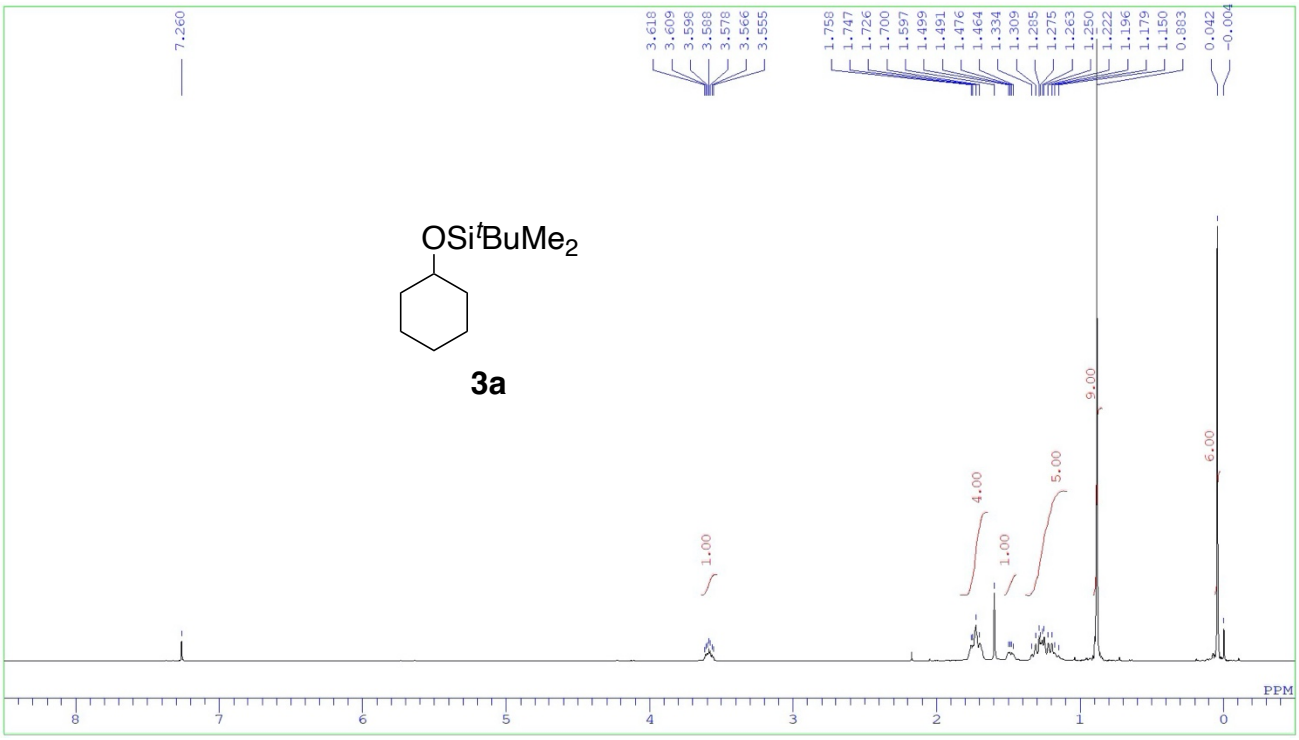
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1.597
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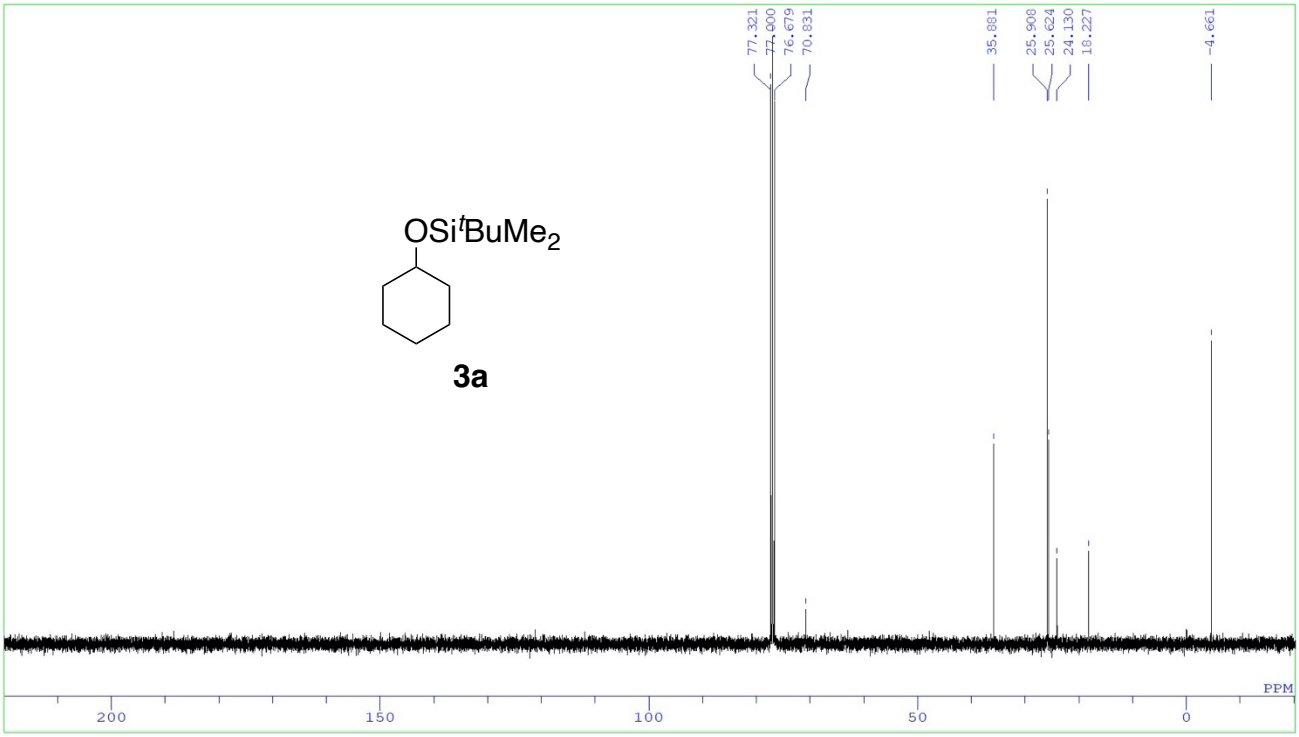
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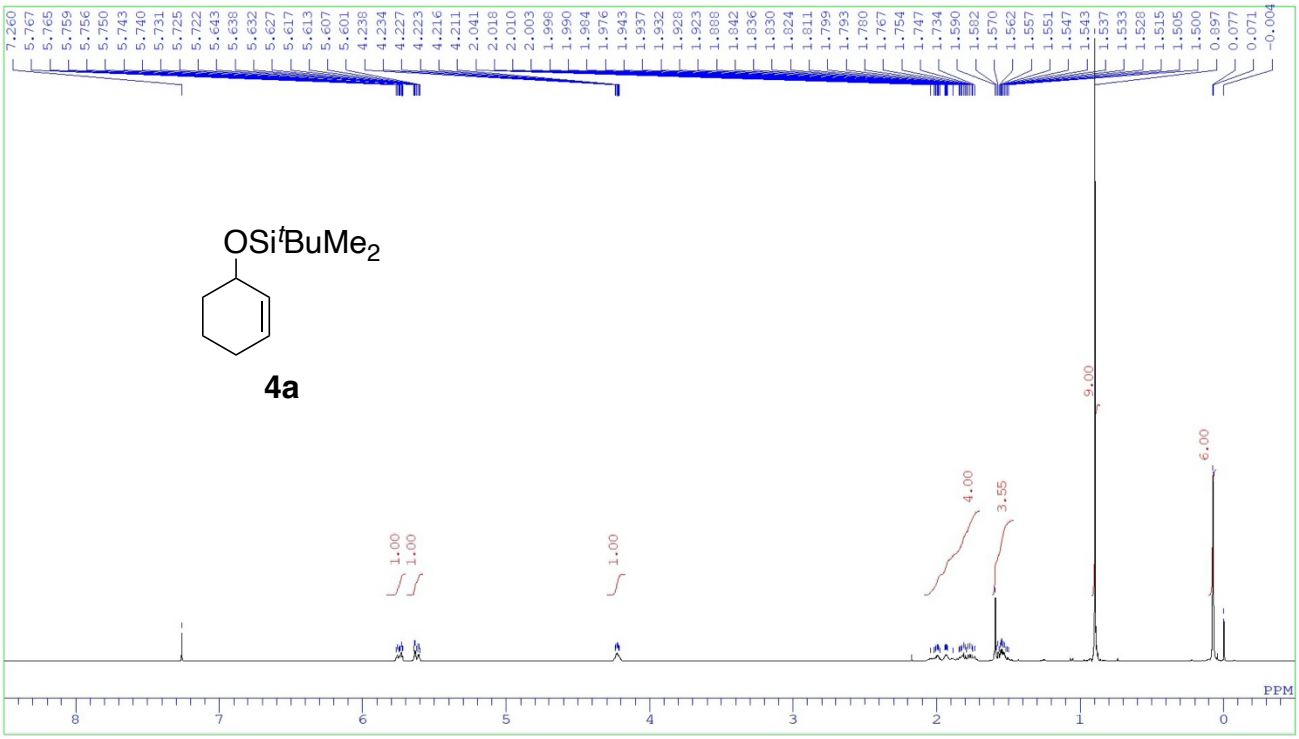
3a
PPM
200
150
100
50
0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1.00
1.00
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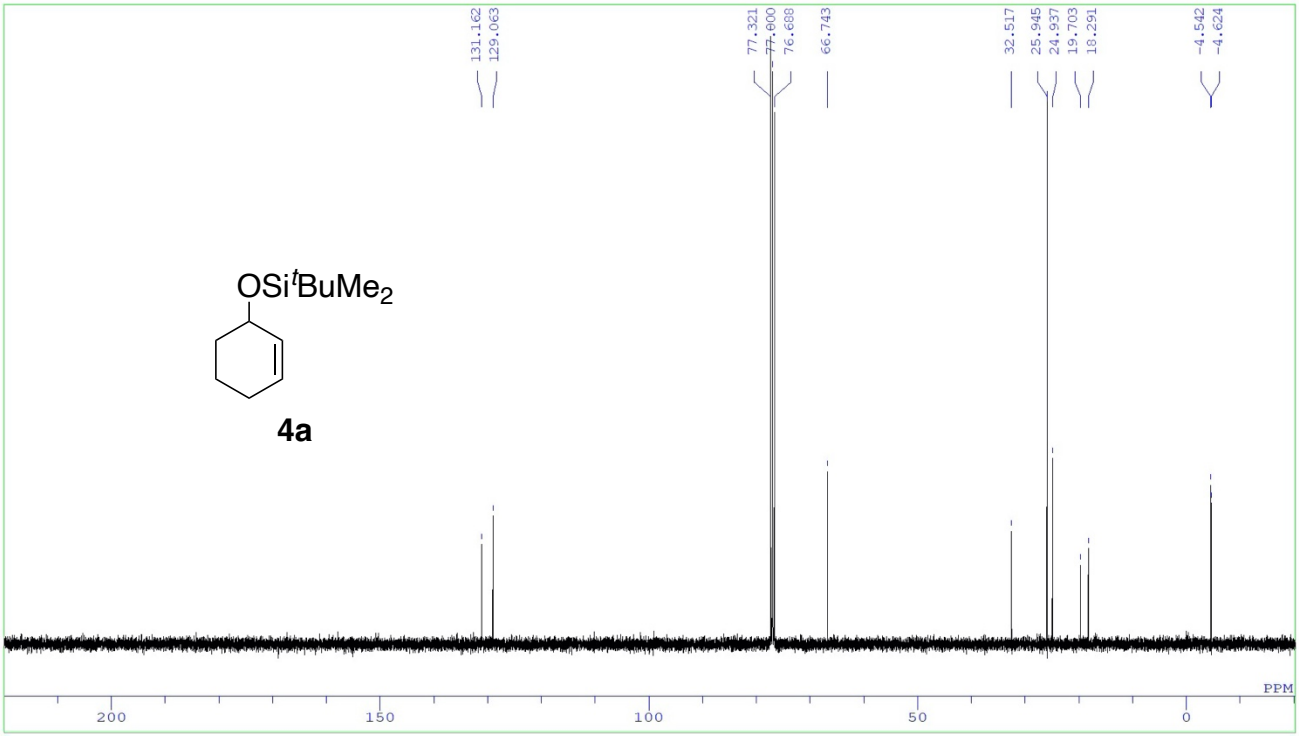
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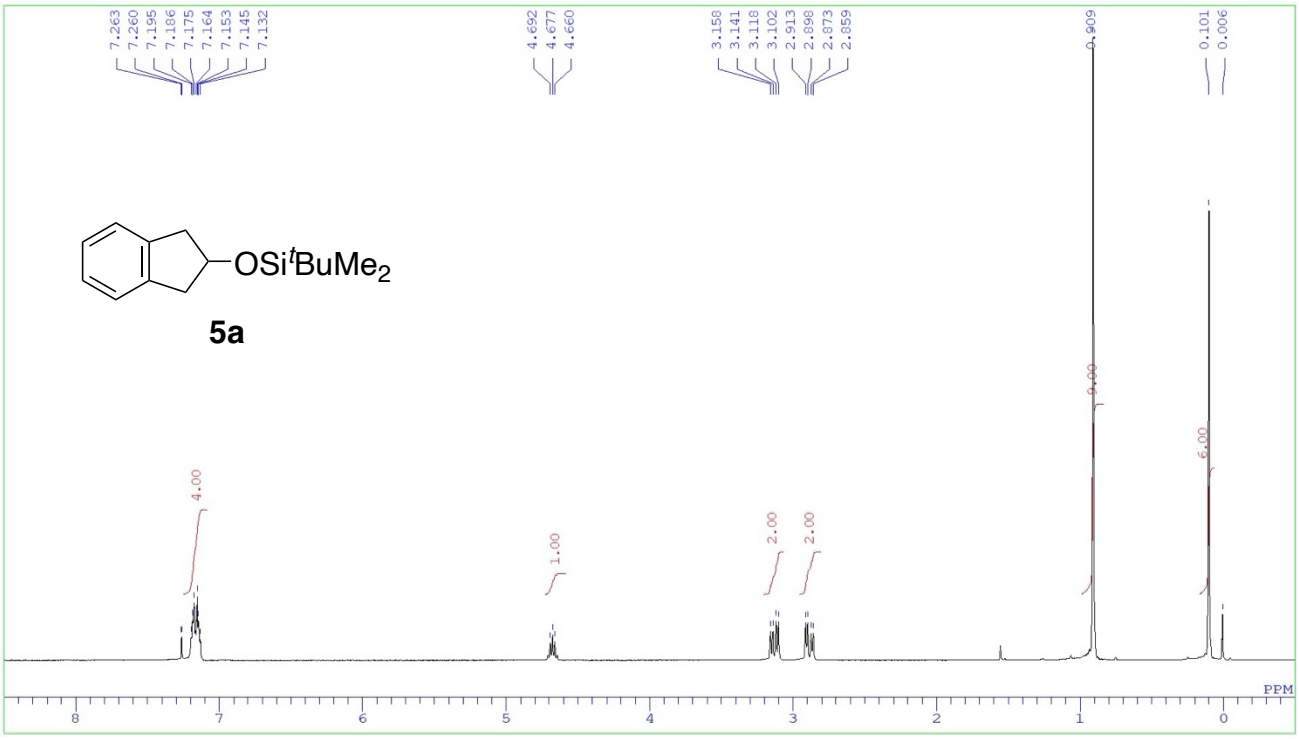
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7.145
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3.141
3.118
3.102
2.913
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PPM
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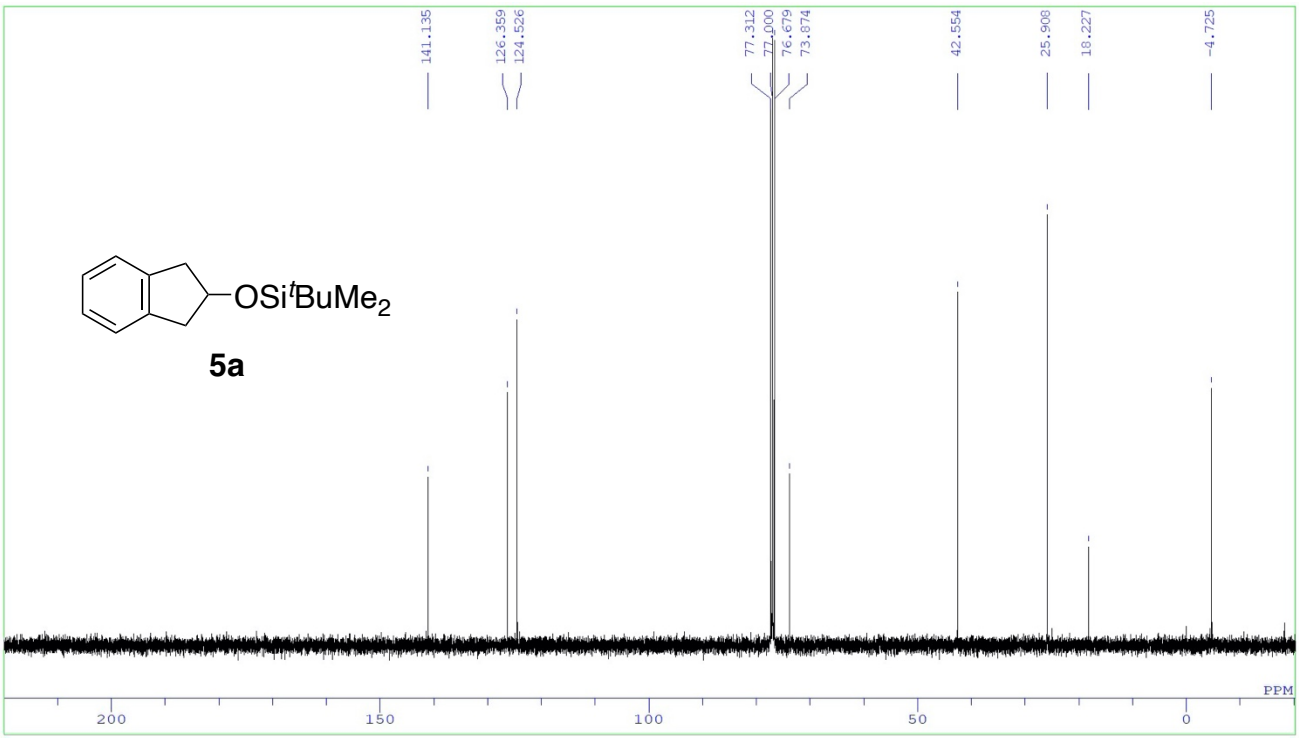
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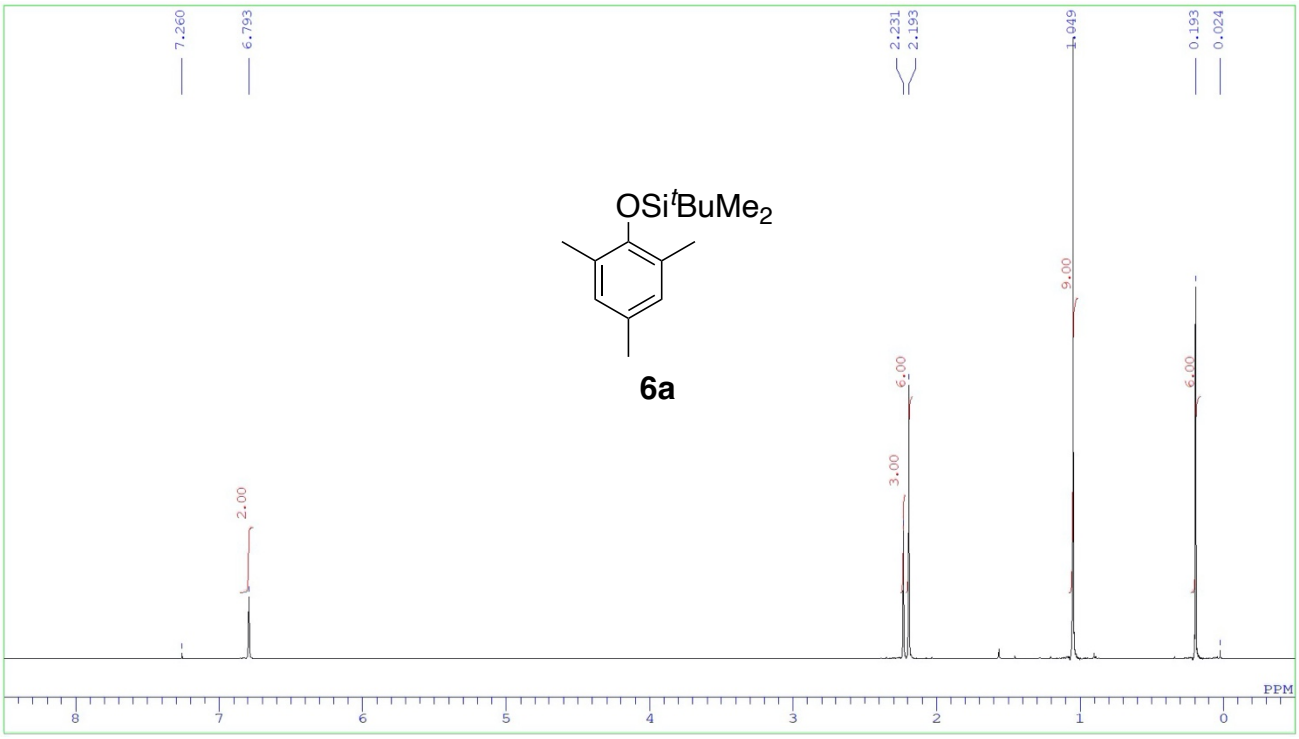
50
0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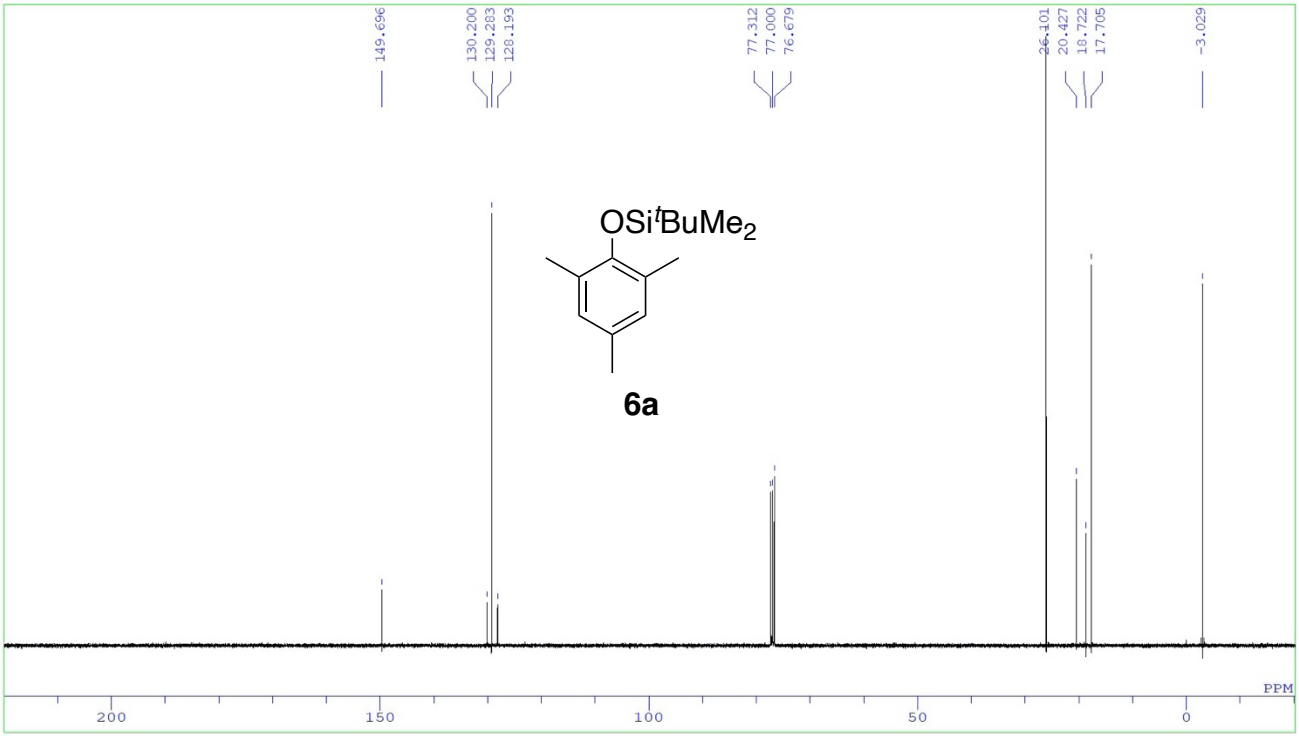
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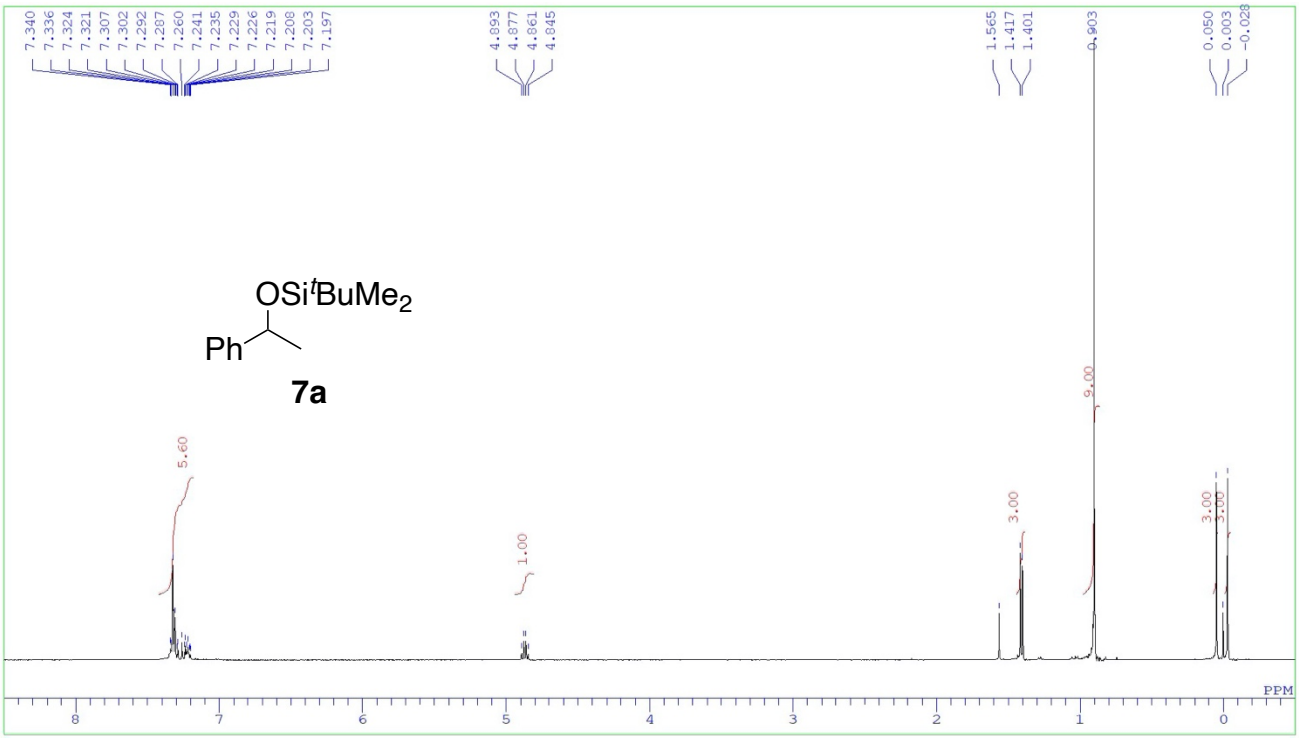
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OSi$^t$BuMe$_2$
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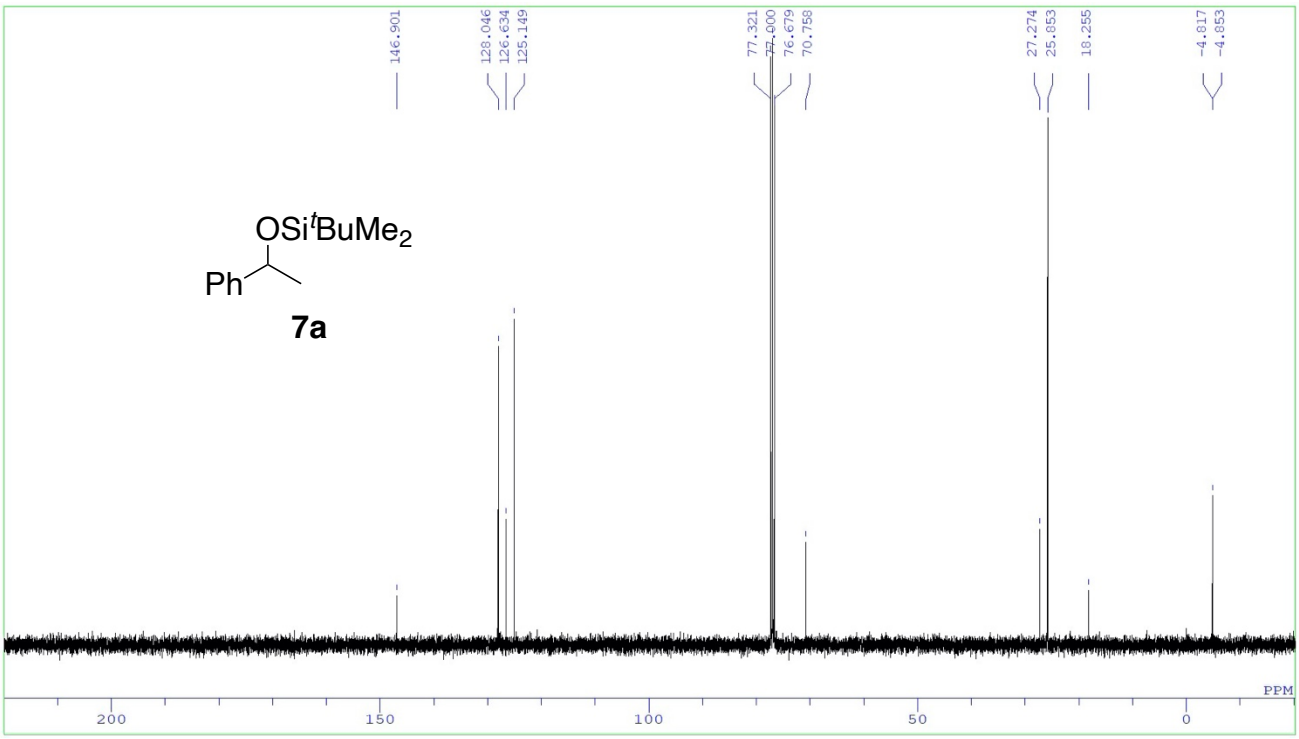
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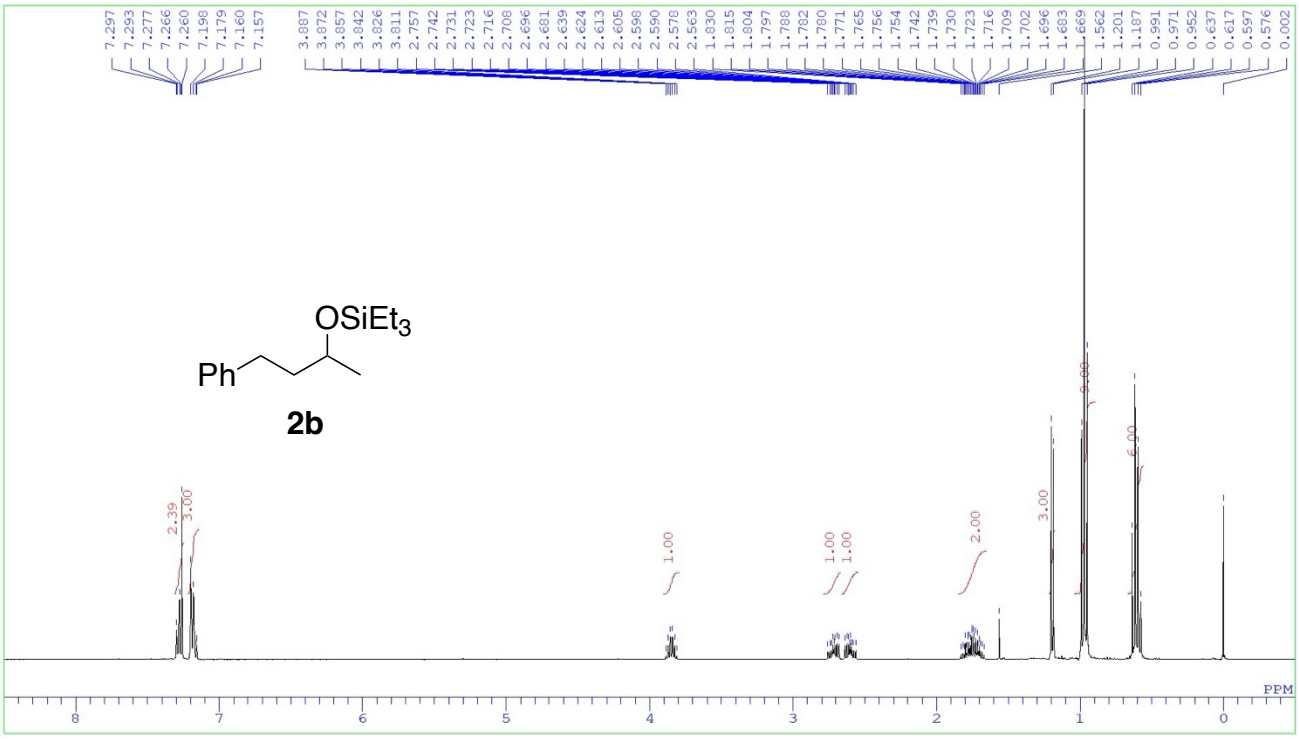
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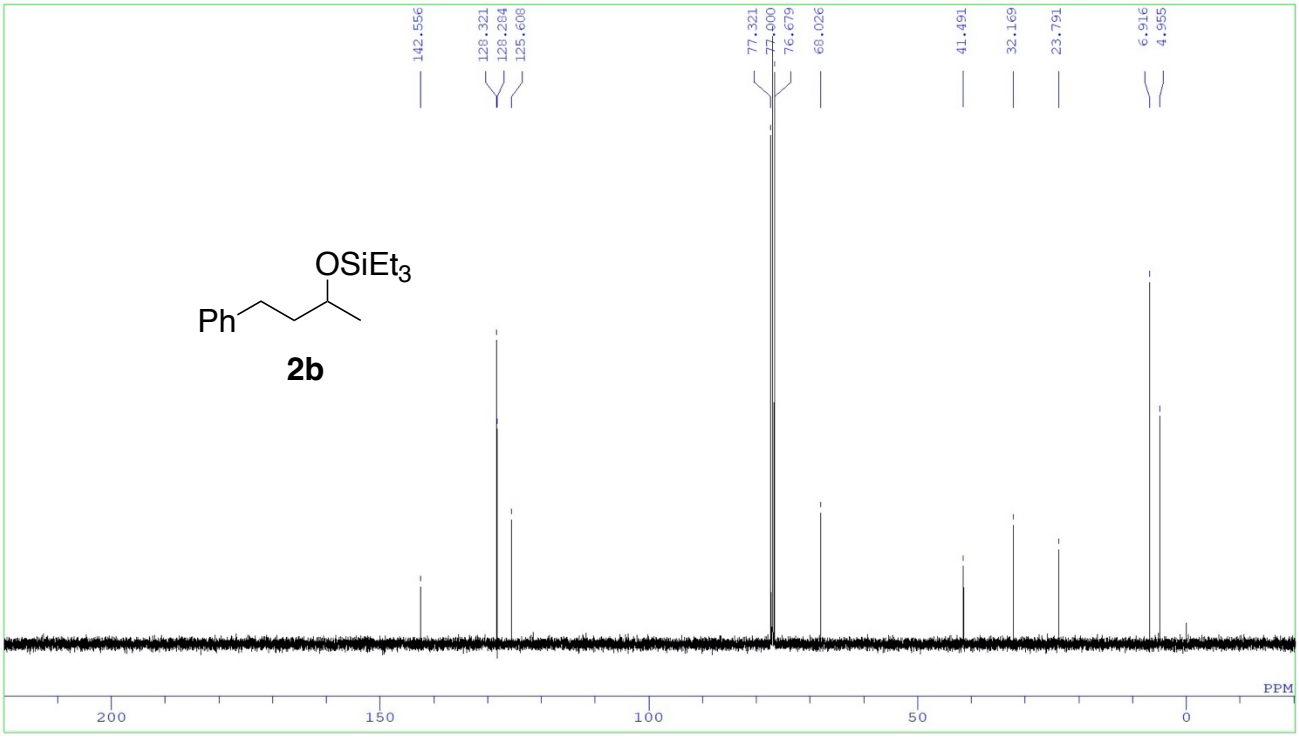
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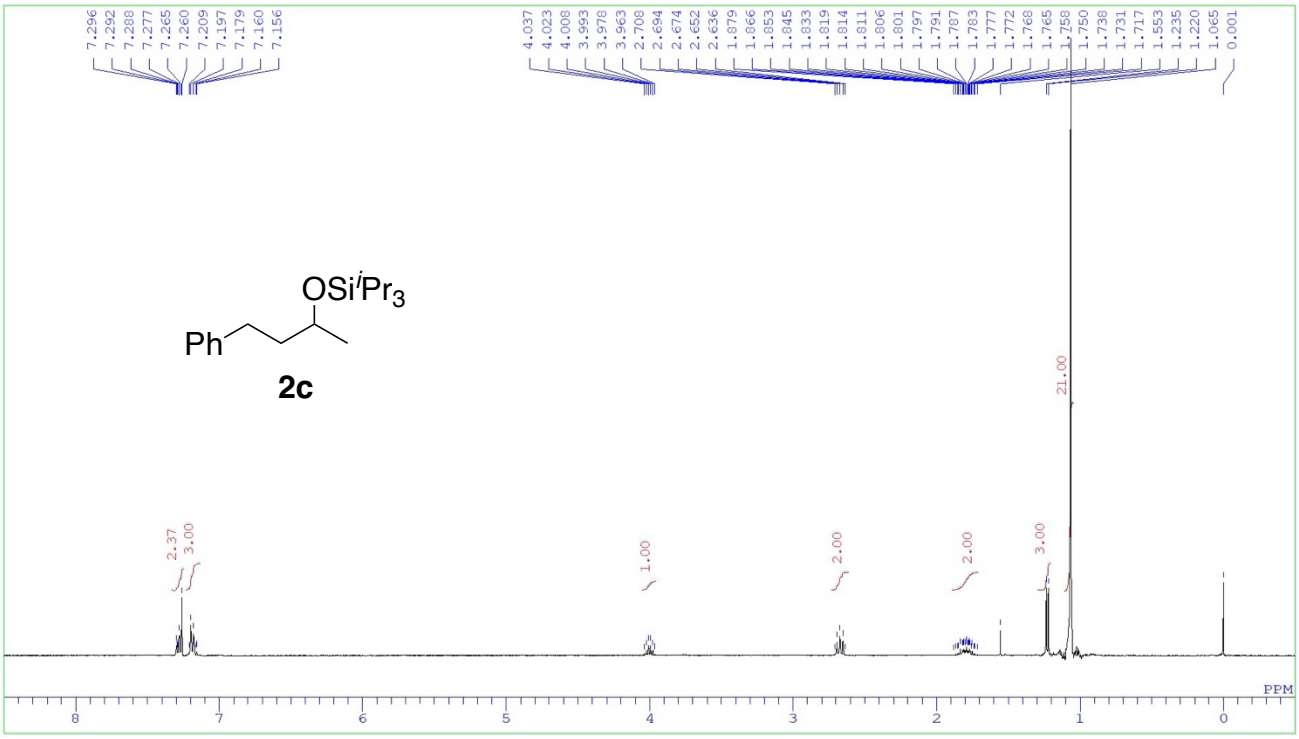
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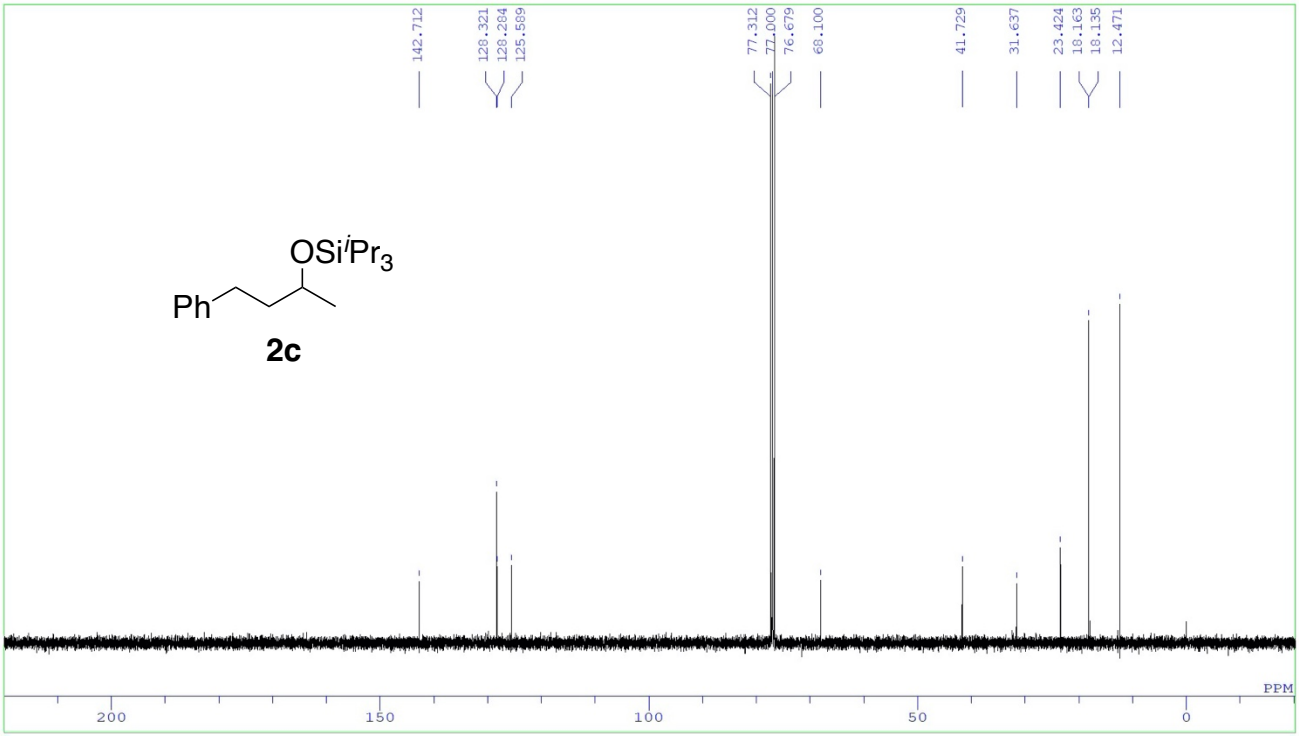
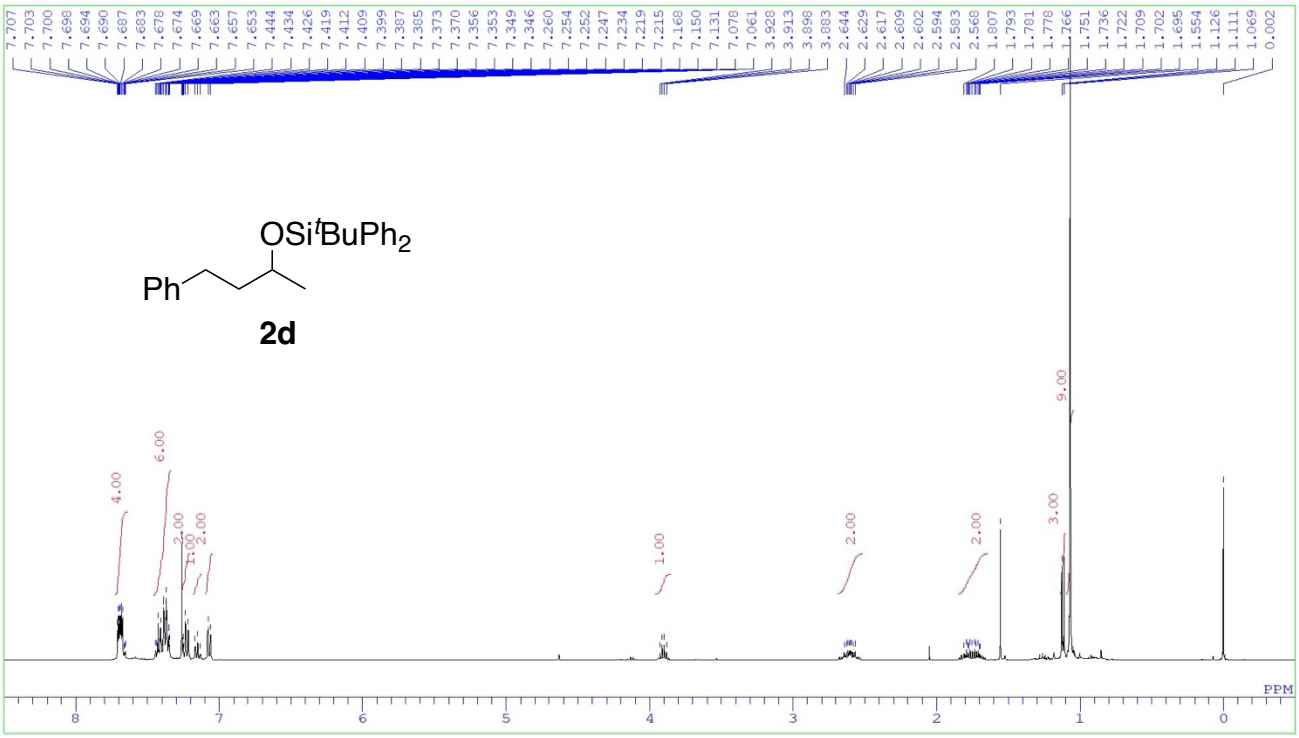
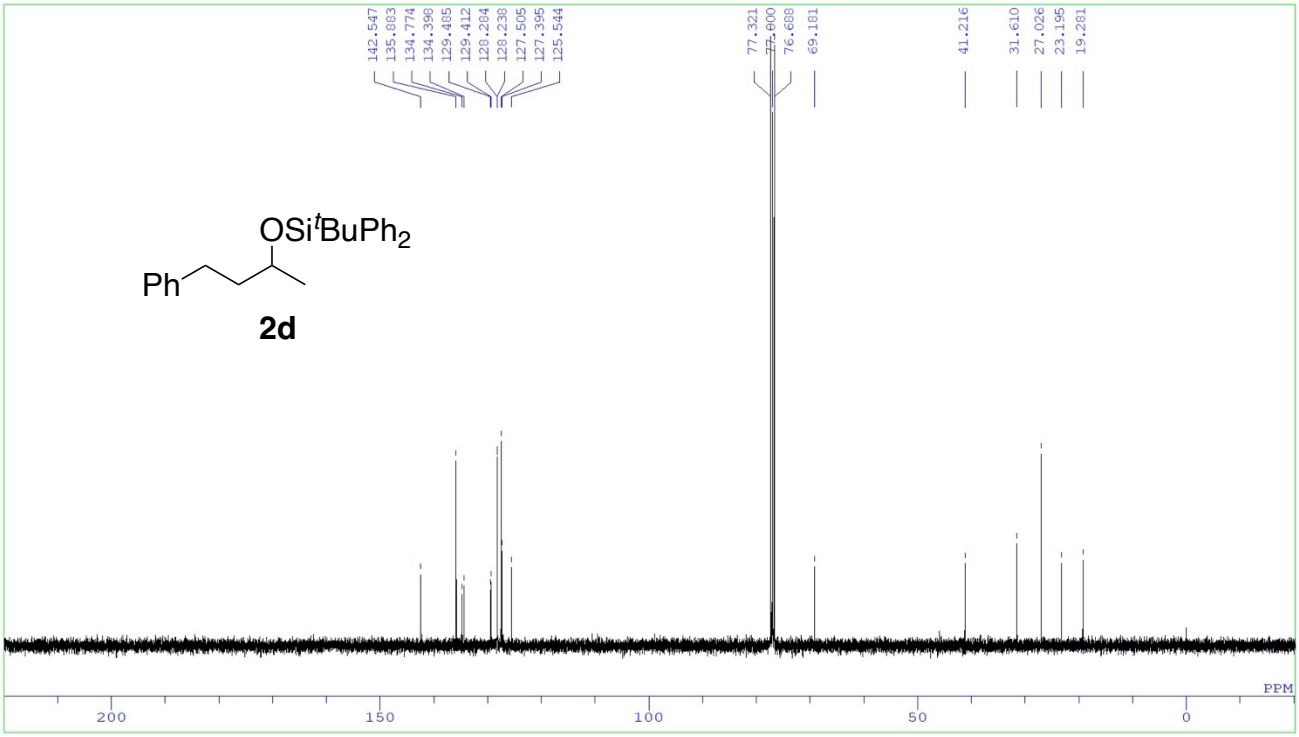
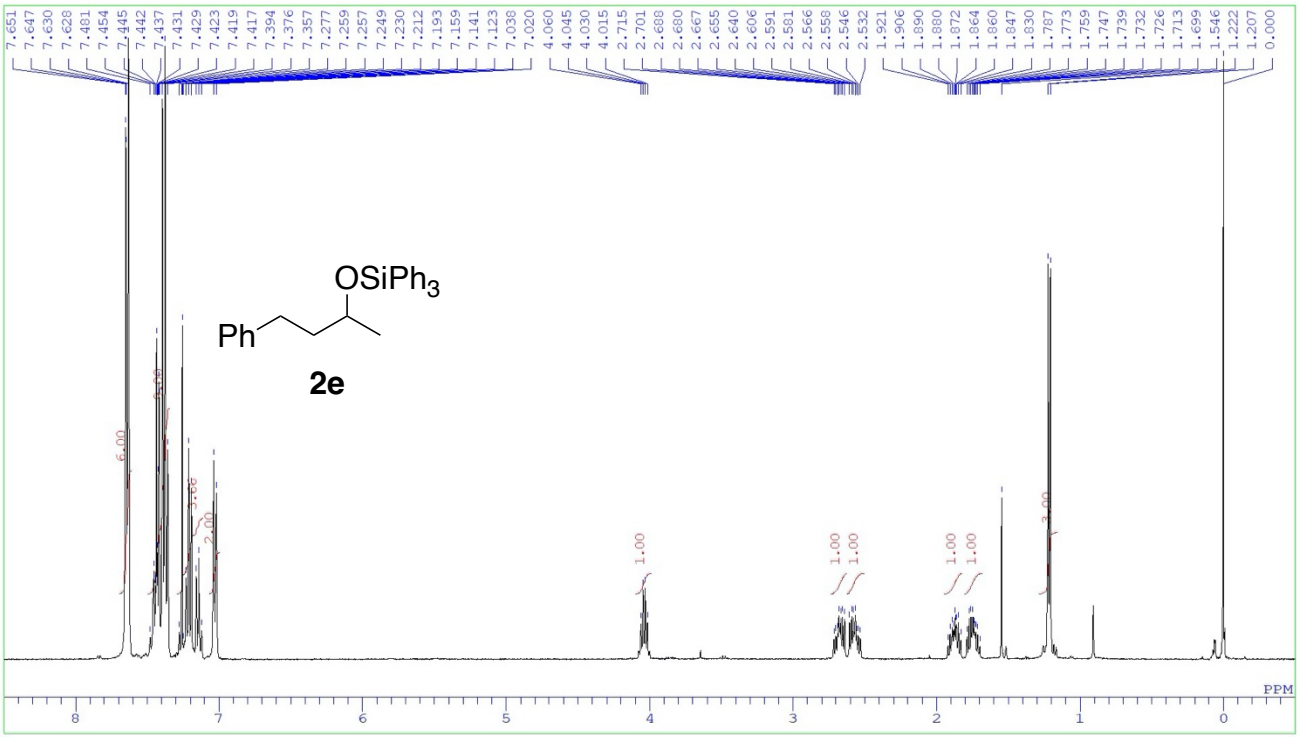
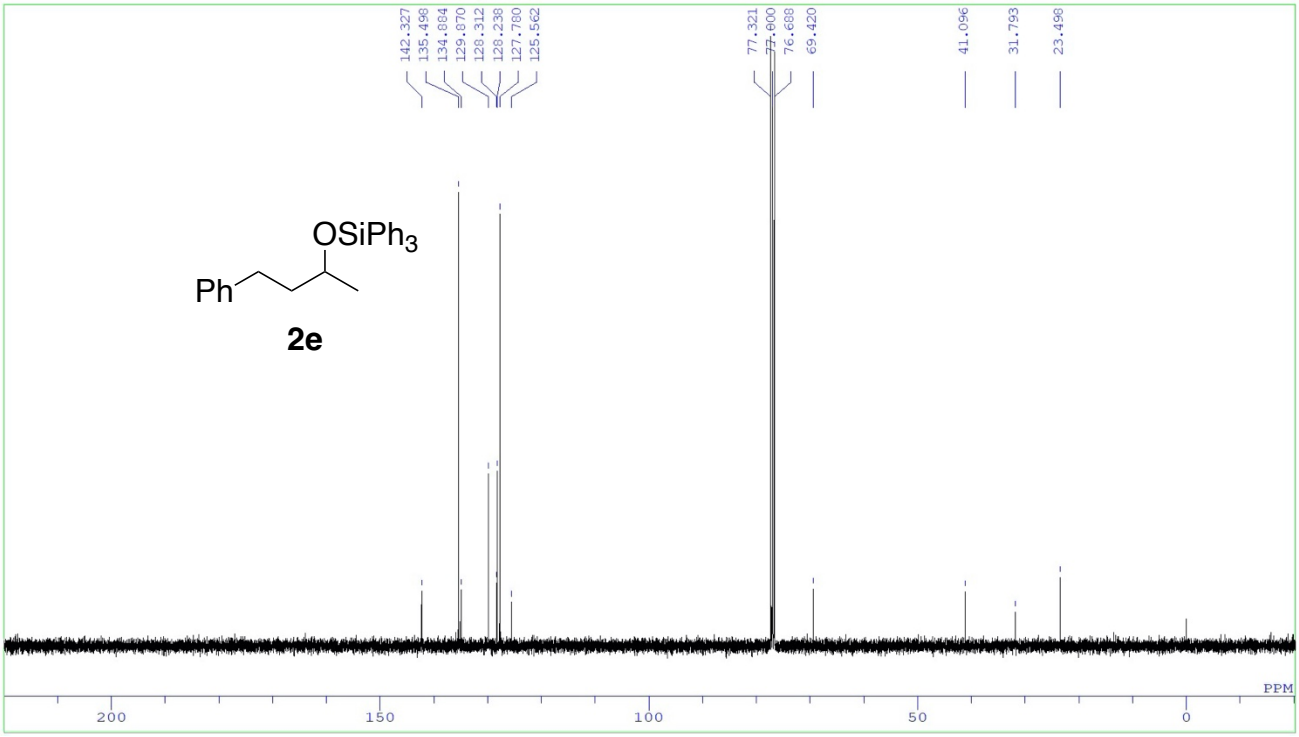
7.277
7.265
7.260
7.209
7.197
7.179
7.160
7.156
4.037
4.023
4.008
3.993
3.978
3.963
2.708
2.694
2.674
2.652
2.636
1.879
1.866
1.853
1.845
1.833
1.819
1.814
1.811
1.806
1.801
1.797
1.791
1.787
1.783
1.777
1.772
1.768
1.765
1.758
1.750
1.738
1.731
1.717
1.553
1.235
1.220
1.065
0.001
OSi$^{i}$Pr$_3$
Ph
2c
21.00
2.37
3.00
1.00
2.00
2.00
3.00
PPM
8
7
6
5
4
3
2
1
0

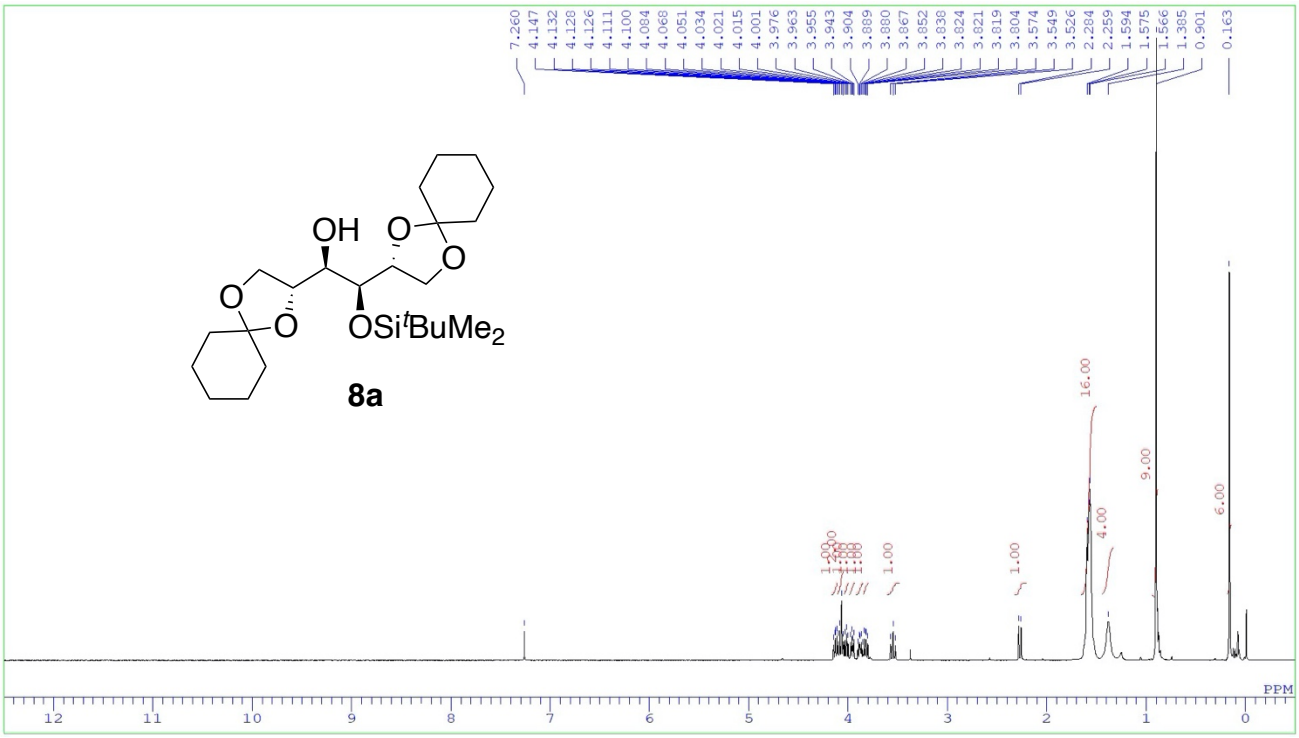

142.712
128.321
128.284
125.589
77.312
77.000
76.679
68.100
41.729
31.637
23.424
18.163
18.135
12.471
OSi$^{i}$Pr$_3$
Ph
2c
PPM
200
150
100
50
0

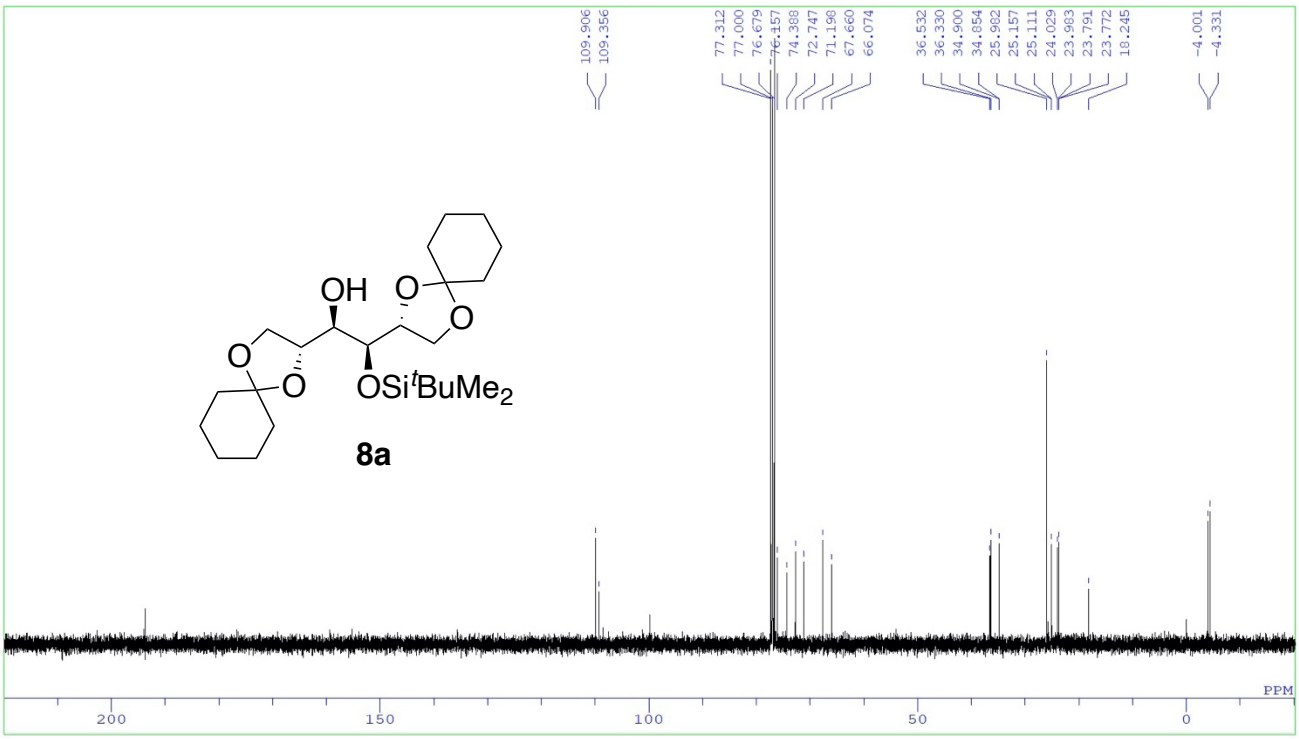

OSi$^t$BuPh$_2$
Ph
2d
PPM

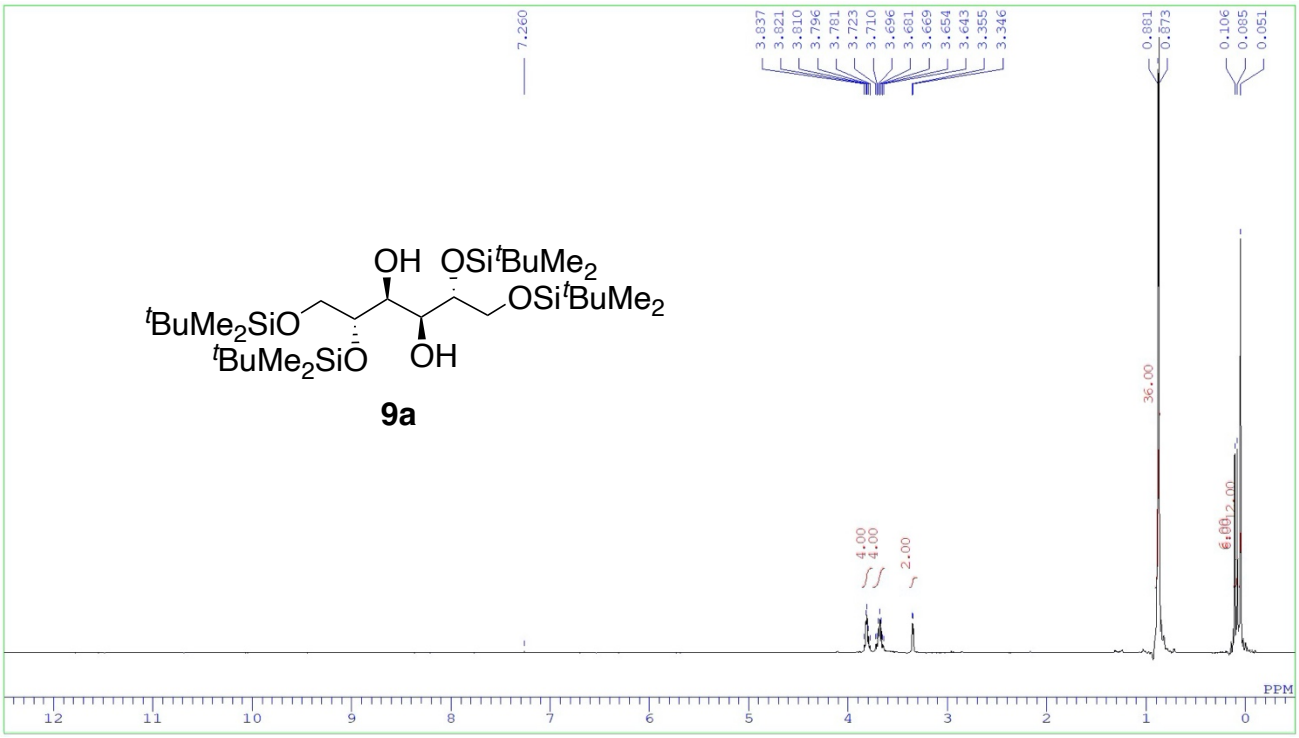

OSi$^t$BuPh$_2$
Ph
2d
PPM

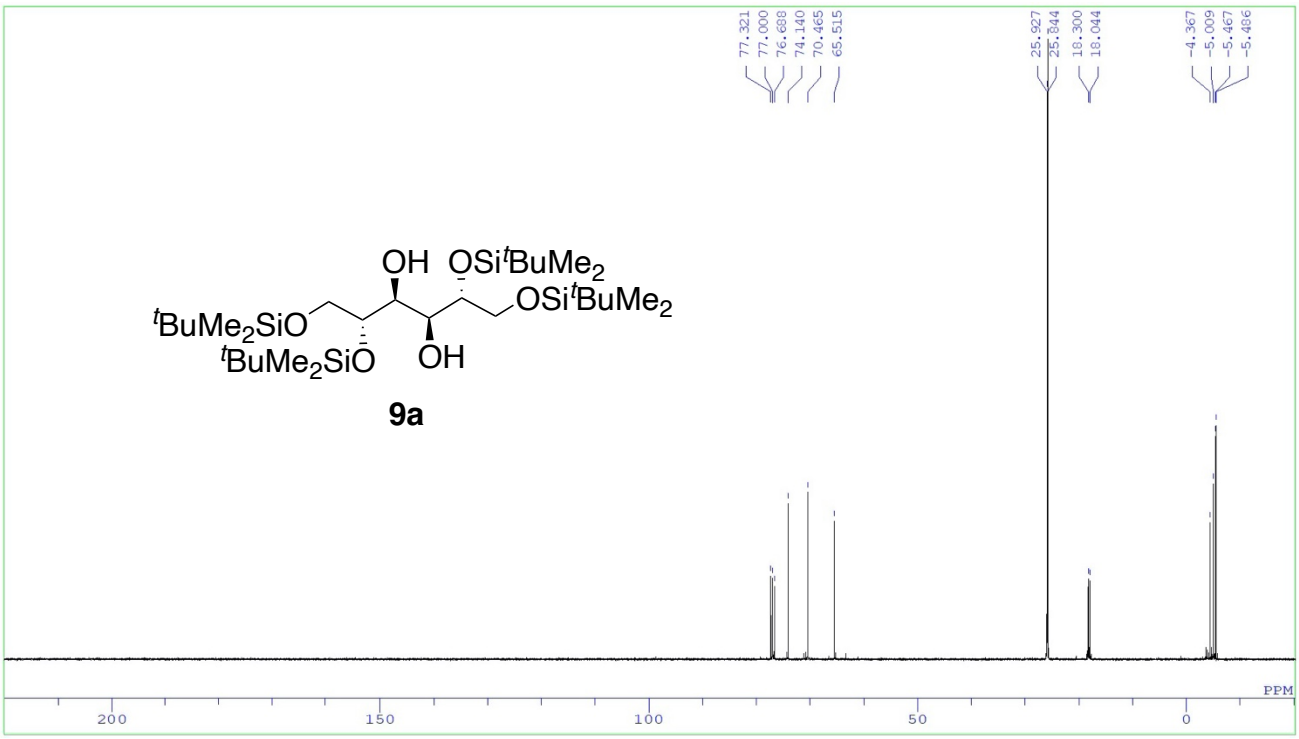

OSiPh3
Ph
2e
PPM

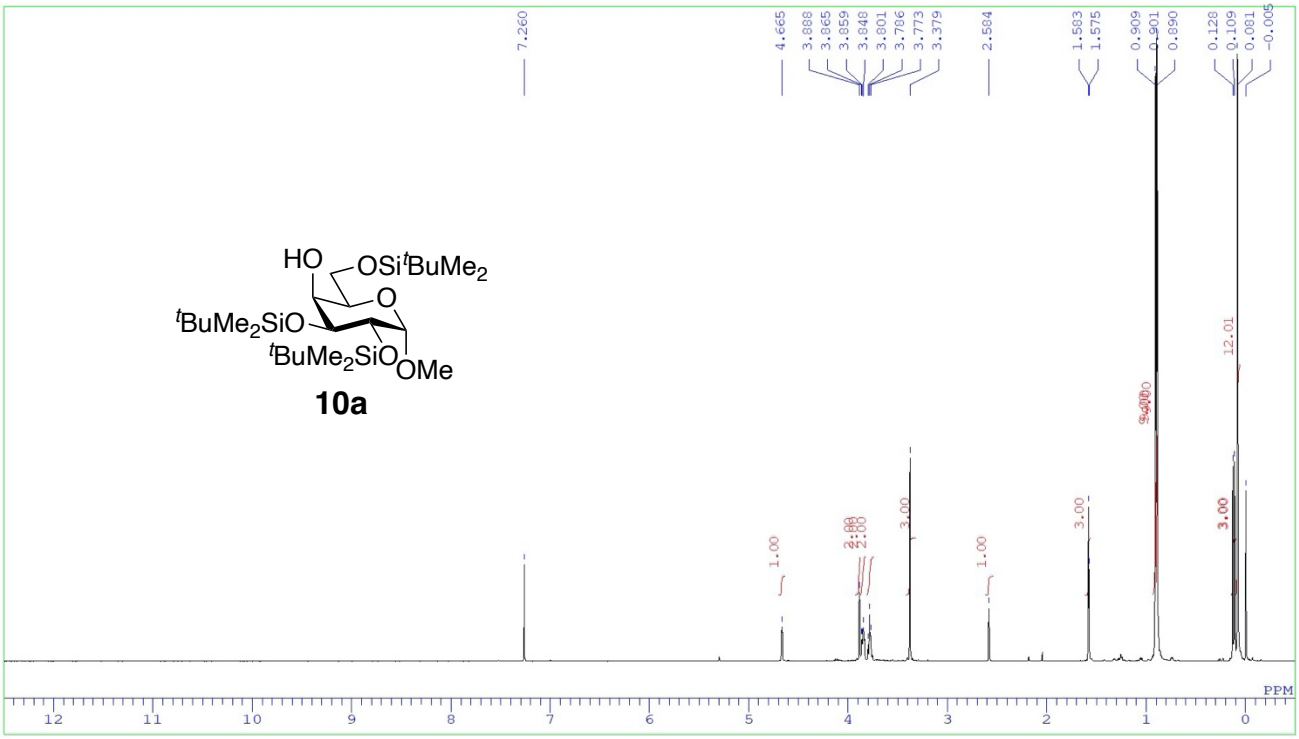

OSiPh3
Ph
2e
PPM

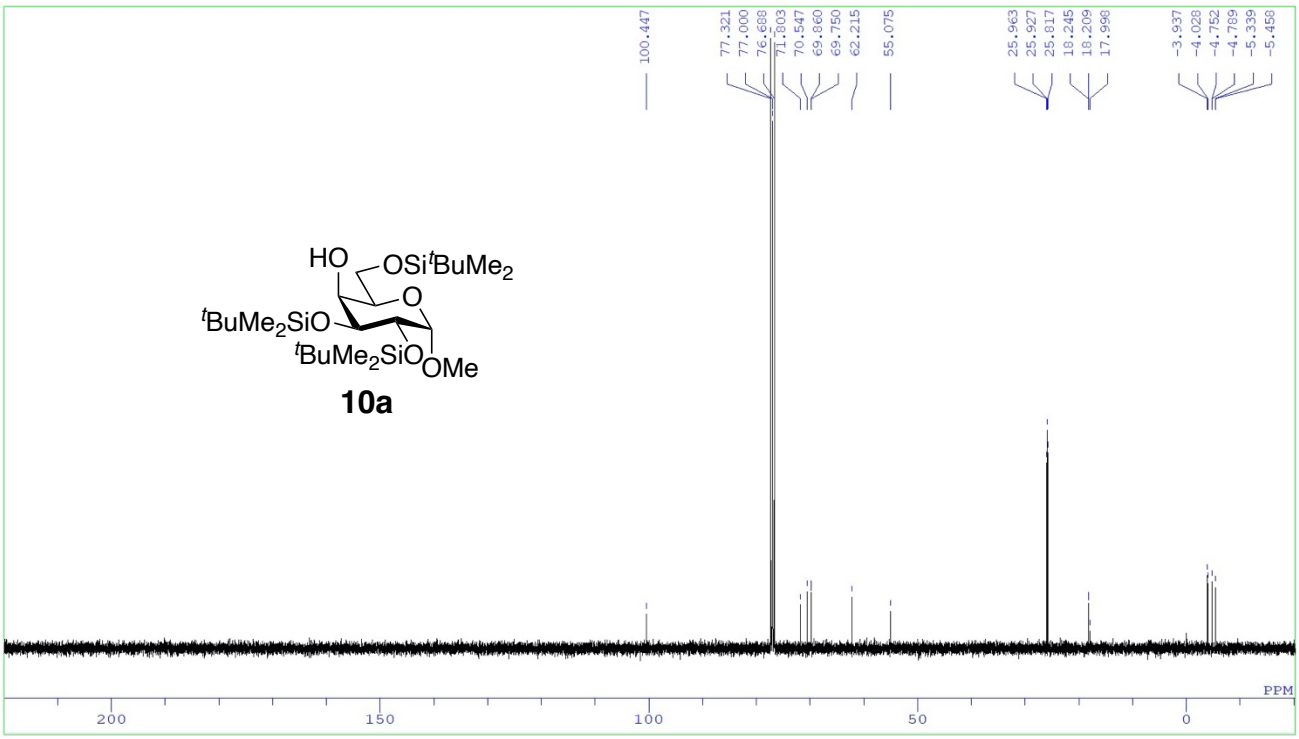

OH
O
O
O
O
OSi$^t$BuMe$_2$
8a
PPM

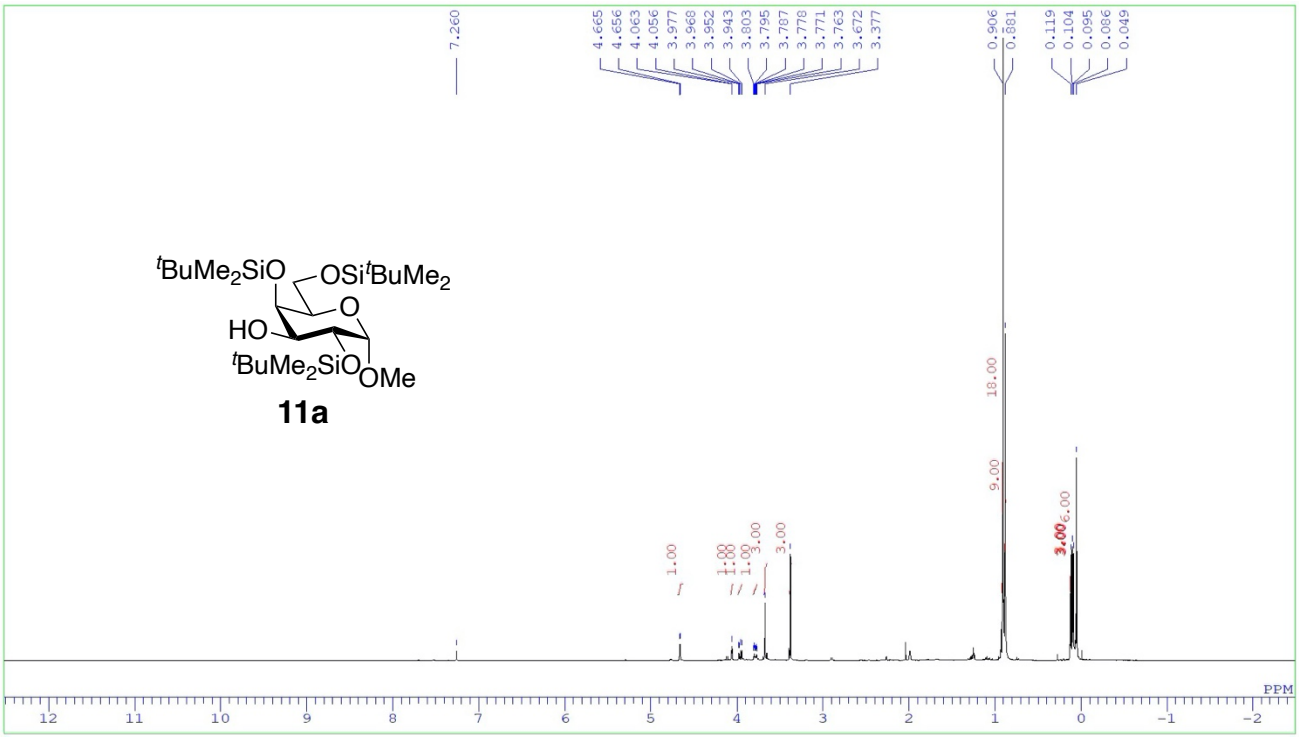

OH
O
O
O
O
OSi$^t$BuMe$_2$
8a
PPM

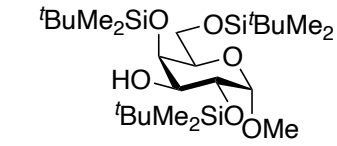

7.260
3.837
3.821
3.810
3.796
3.781
3.723
3.710
3.696
3.681
3.669
3.654
3.643
3.355
3.346
0.881
0.873
0.106
0.085
0.051
OH
OSi$^t$BuMe$_2$
OSi$^t$BuMe$_2$
$^t$BuMe$_2$SiO
$^t$BuMe$_2$SiO
OH
9a
36.00
4.00
4.00
2.00
6.00
12.00
PPM
12
11
10
9
8
7
6
5
4
3
2
1
0


77.321
77.000
76.688
74.140
70.465
65.515
25.927
25.844
18.300
18.044
-4.367
-5.009
-5.467
-5.486
OH
OSi$^t$BuMe$_2$
OSi$^t$BuMe$_2$
$^t$BuMe$_2$SiO
$^t$BuMe$_2$SiO
OH
9a
PPM
200
150
100
50
0


HO
OSi$^t$BuMe$_2$
O
$^t$BuMe$_2$SiO
$^t$BuMe$_2$SiO
OMe
10a
7.260
4.665
3.888
3.865
3.859
3.848
3.801
3.786
3.773
3.379
2.584
1.583
1.575
0.909
0.901
0.890
0.128
0.109
0.081
-0.005
PPM


HO
OSi$^t$BuMe$_2$
O
$^t$BuMe$_2$SiO
$^t$BuMe$_2$SiO
OMe
10a
100.447
77.321
77.000
76.688
71.803
70.547
69.860
69.750
62.215
55.075
25.963
25.927
25.817
18.245
18.209
17.998
-3.937
-4.028
-4.752
-4.789
-5.339
-5.458
PPM


7.260
4.665
4.656
4.063
4.056
3.977
3.968
3.952
3.943
3.803
3.795
3.787
3.778
3.771
3.763
3.672
3.377
0.906
0.881
0.119
0.104
0.095
0.086
0.049
18.00
9.00
6.00
3.00
1.00
PPM

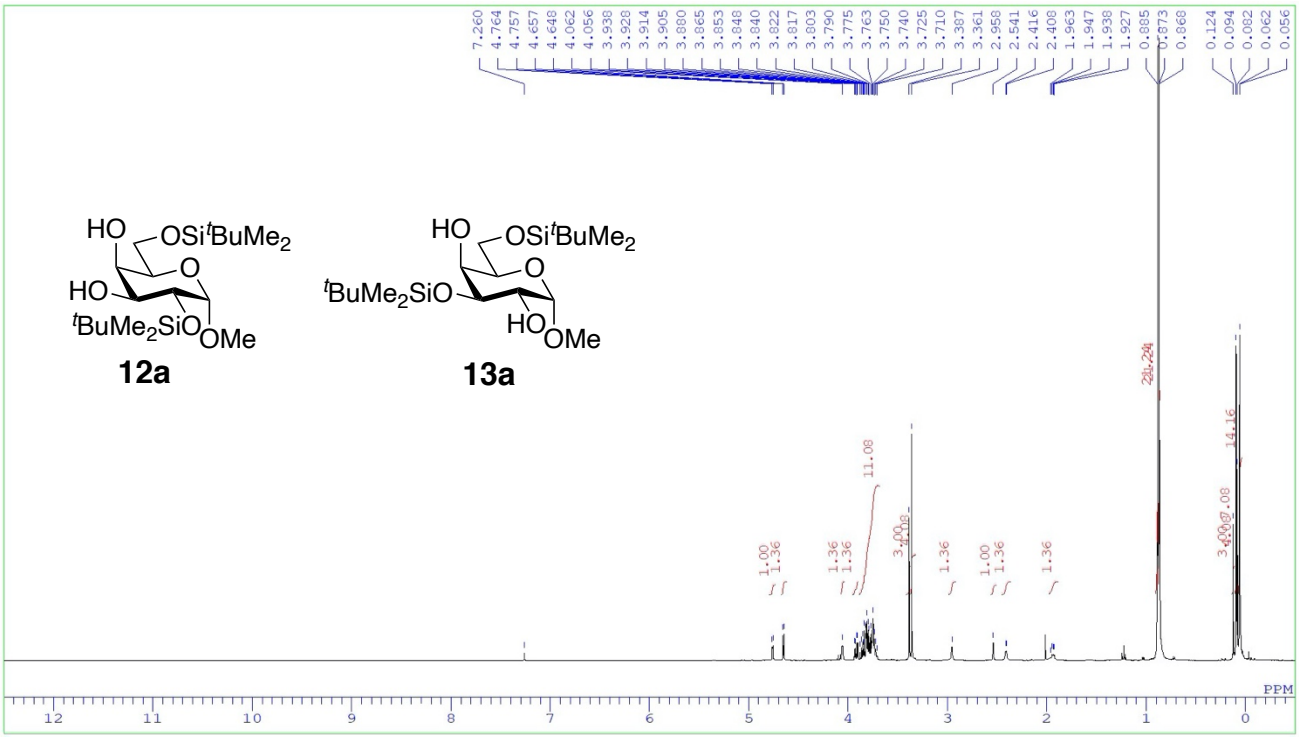

tBuMe2SiO
OSitBuMe2
O
HO
tBuMe2SiO
OMe

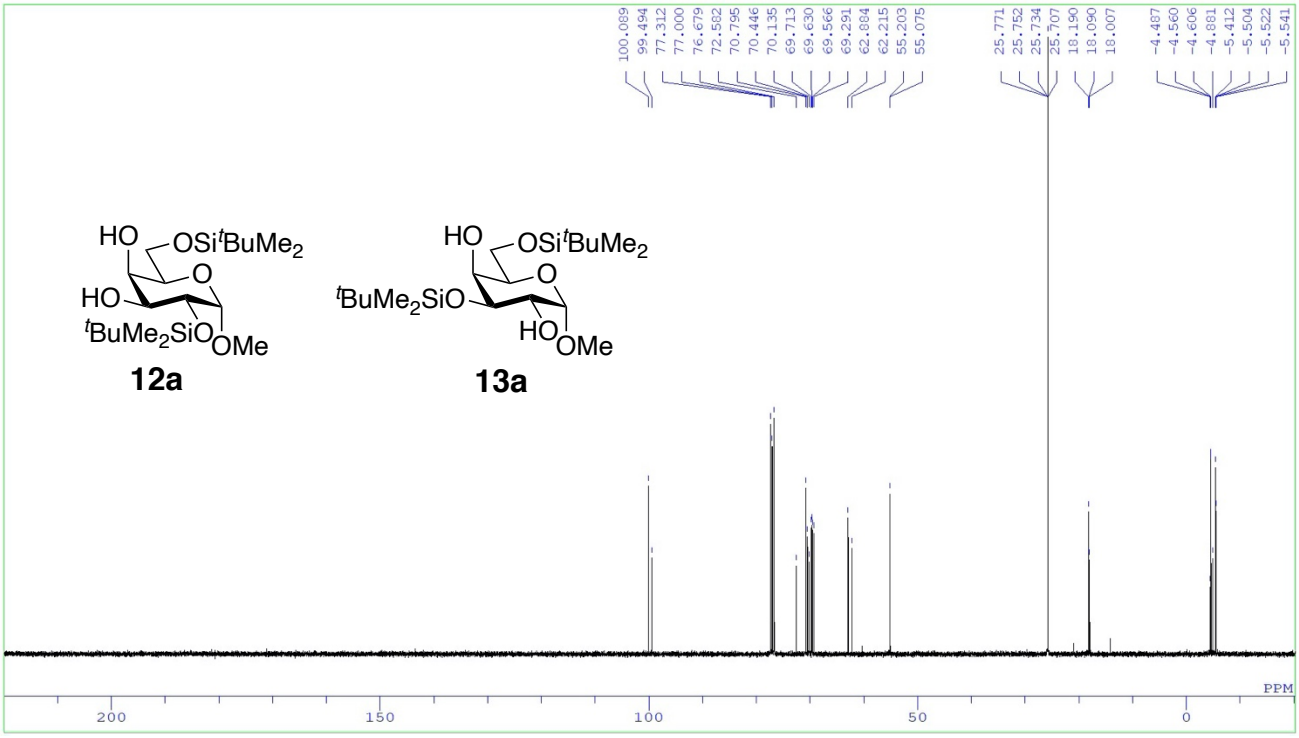
**11a**

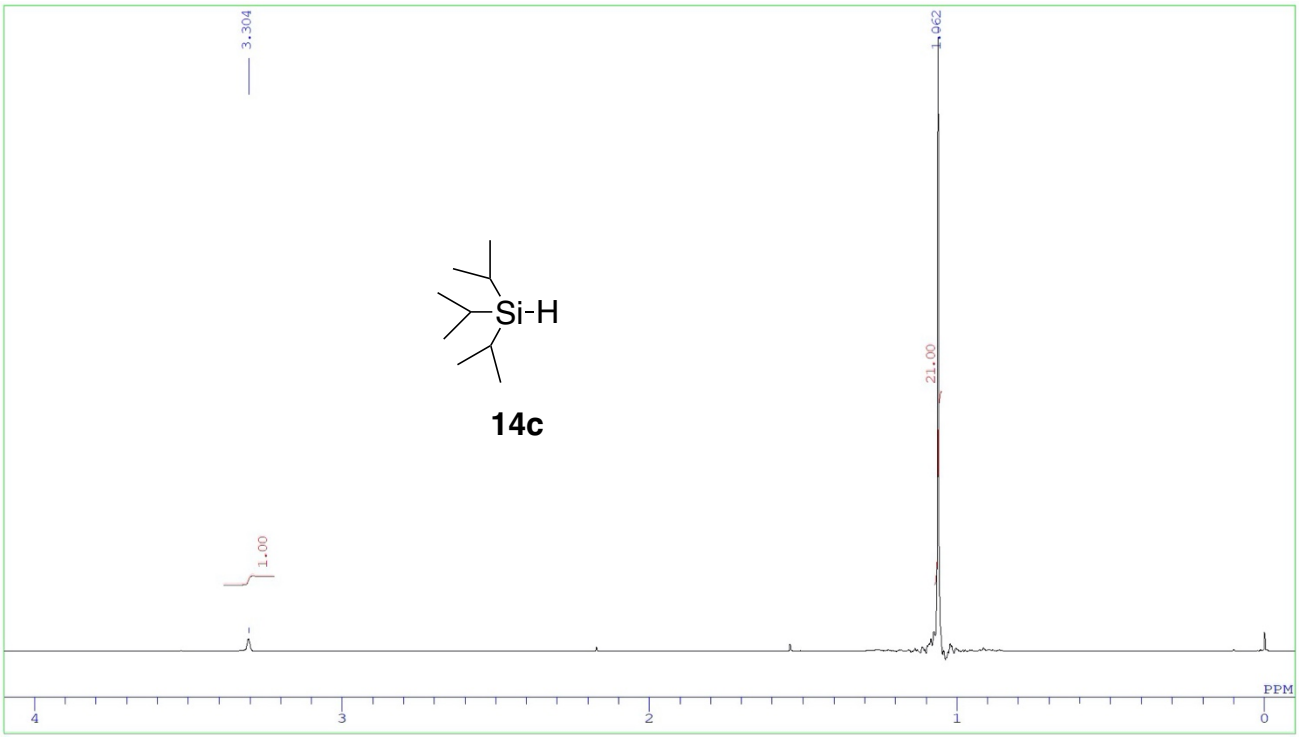

100.071
77.321
77.000
76.688
71.757
70.767
70.620
70.171
62.325
55.121
26.046
25.826
25.807
18.493
18.209
18.163
-4.129
-4.487
-4.587
-4.899
-5.312
-5.385
PPM

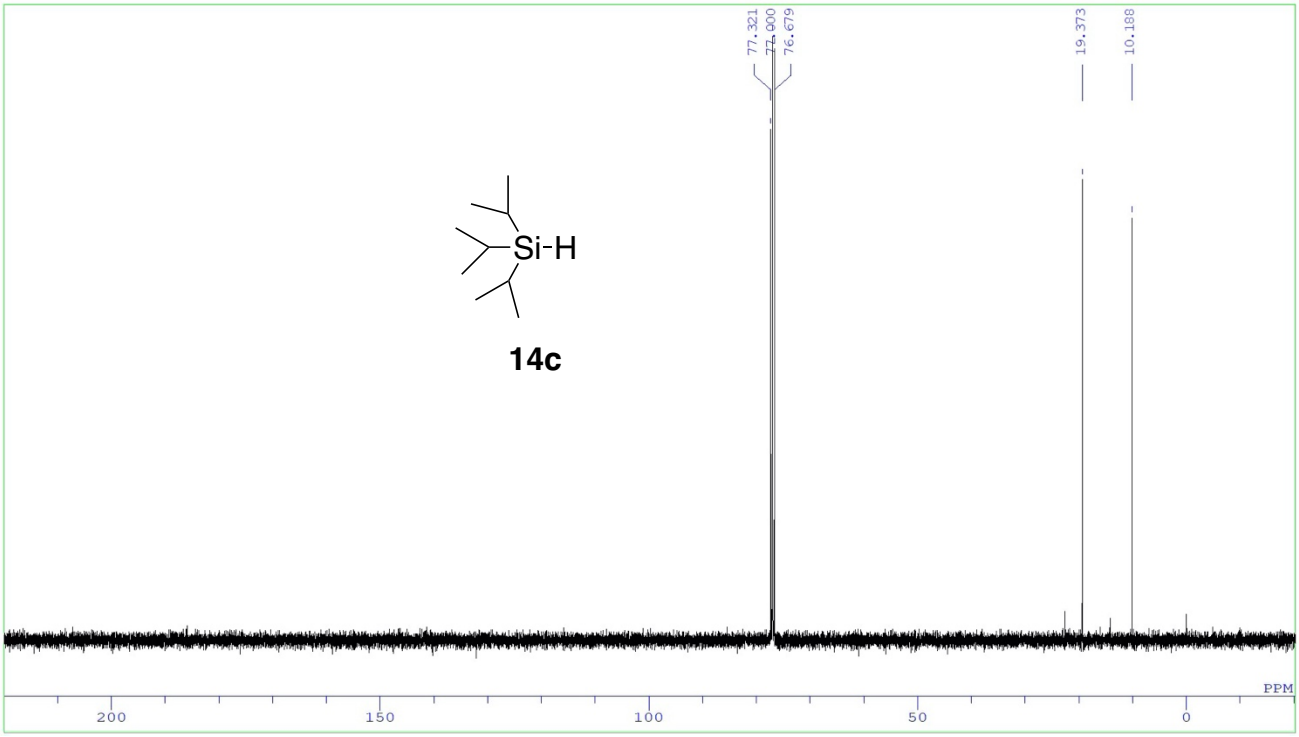

tBuMe2SiO
OSitBuMe2
O
HO
tBuMe2SiO
OMe

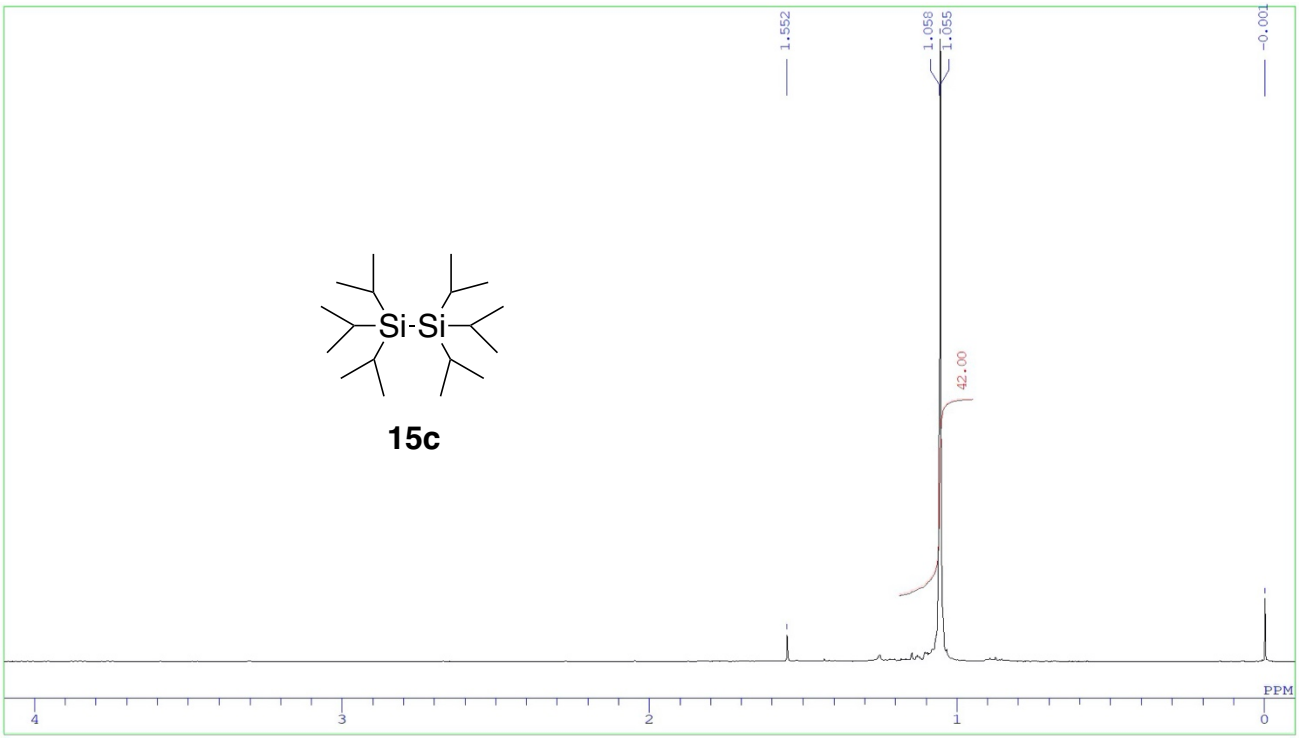
**11a**

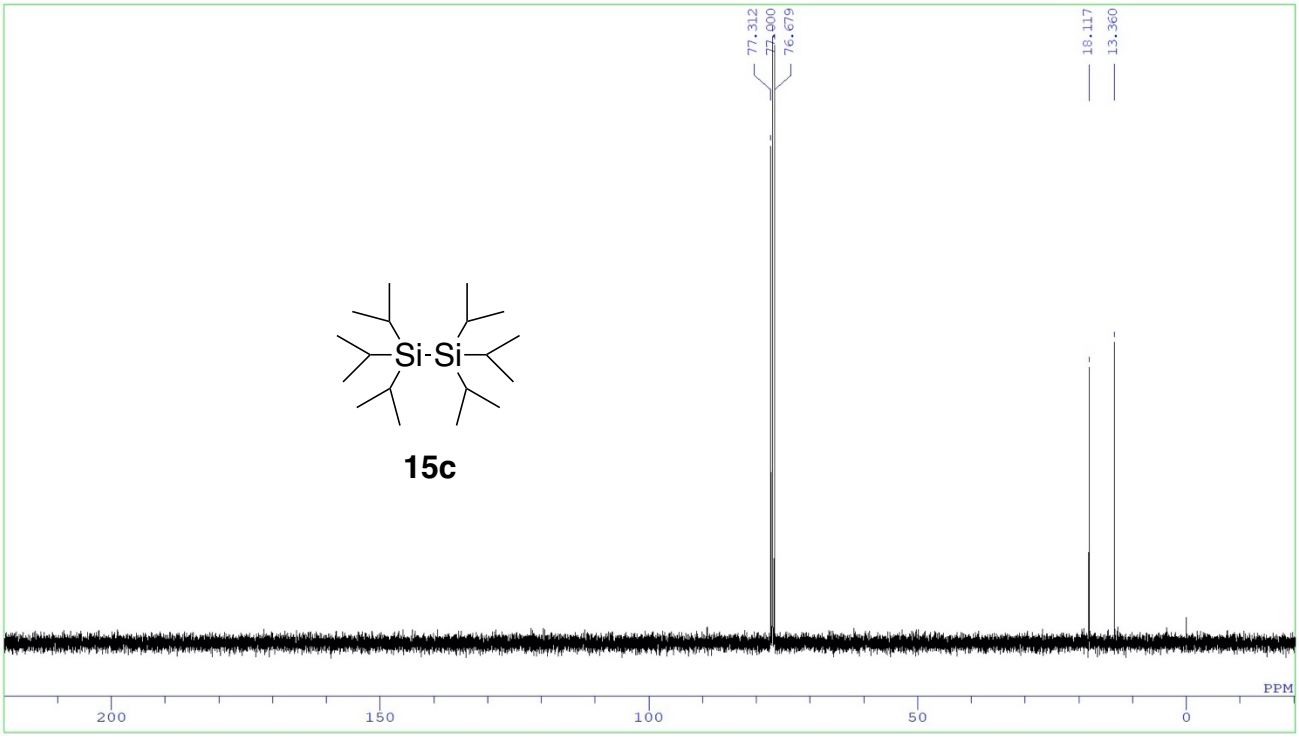

HO
OSi$^t$BuMe$_2$
O
HO
$^t$BuMe$_2$SiO
OMe
12a
HO
OSi$^t$BuMe$_2$
O
$^t$BuMe$_2$SiO
HO
OMe
13a
PPM

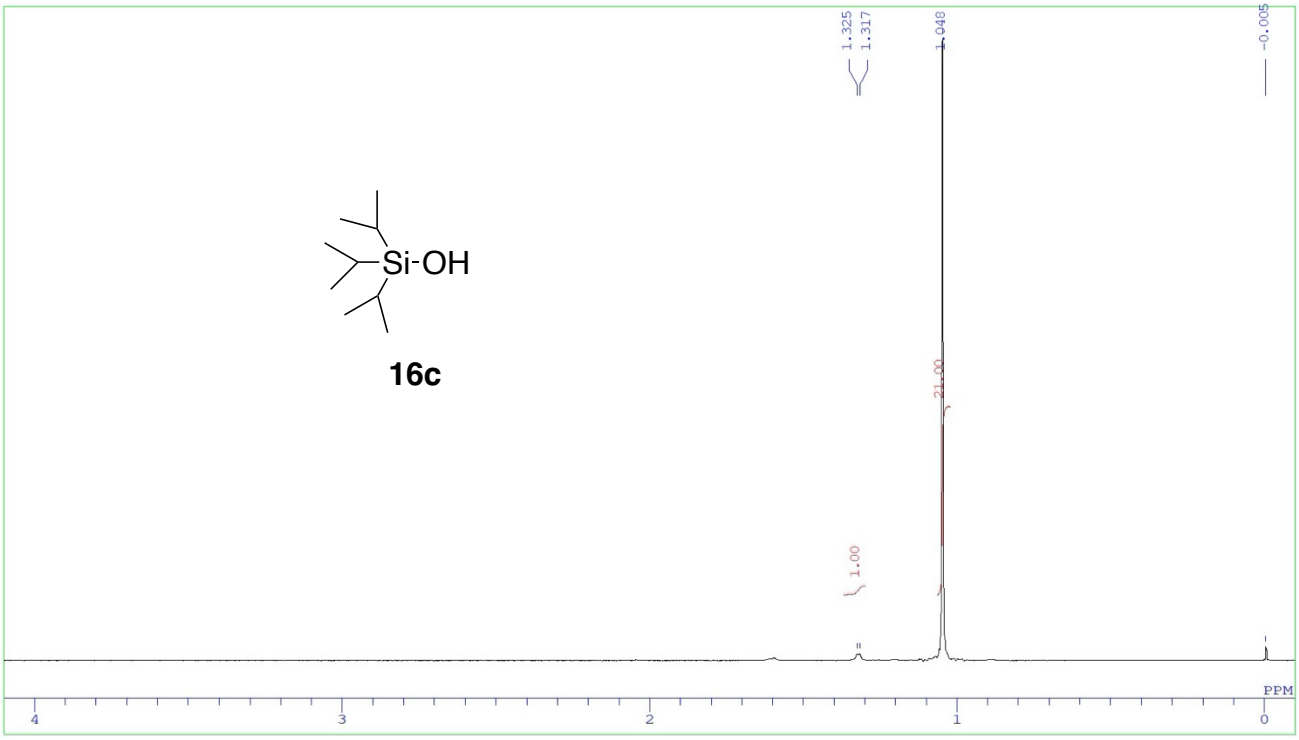

HO
OSi$^t$BuMe$_2$
O
HO
$^t$BuMe$_2$SiO
OMe
12a
HO
OSi$^t$BuMe$_2$
O
$^t$BuMe$_2$SiO
HO
OMe
13a
PPM


3.304
1.962
21.00
1.00
Si-H
14c
PPM
4
3
2
1
0

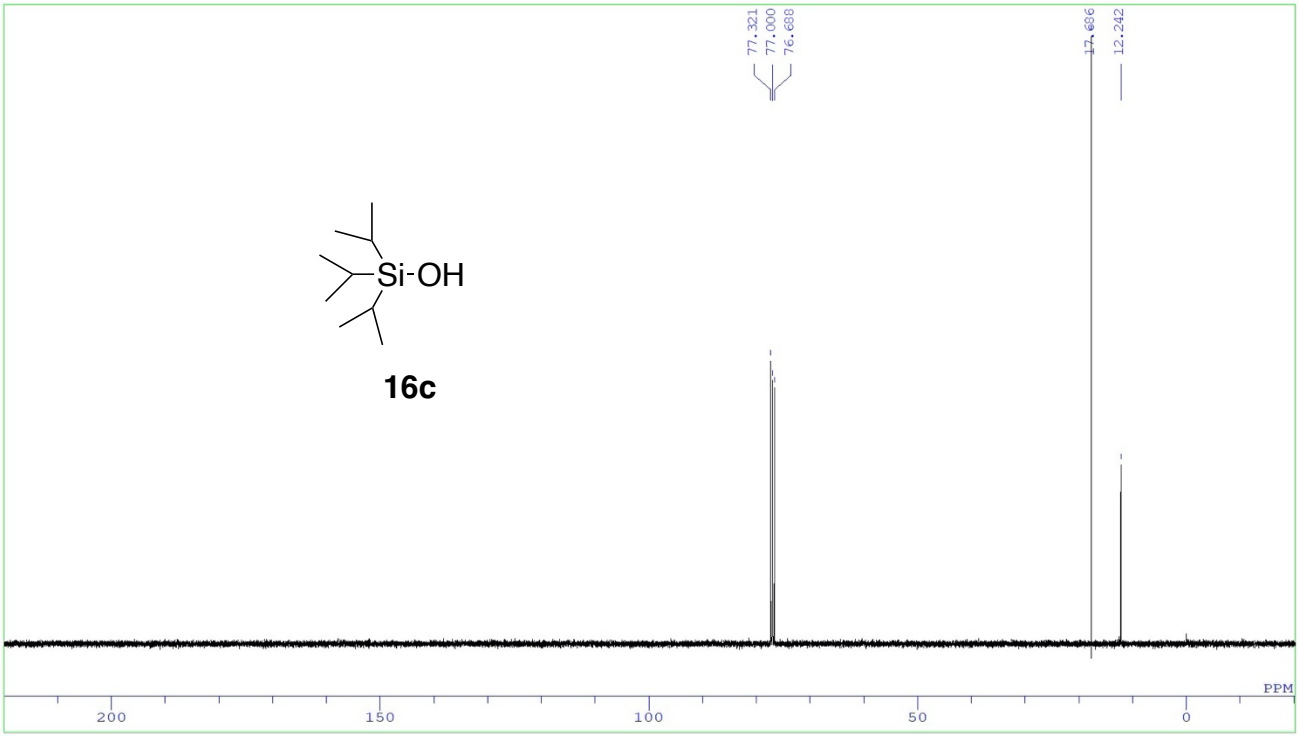

77.321
77.000
76.679
19.373
10.188
Si-H
14c
PPM
200
150
100
50
0


1.552
1.058
1.055
-0.001
42.00
Si-Si
15c
PPM
4
3
2
1
0

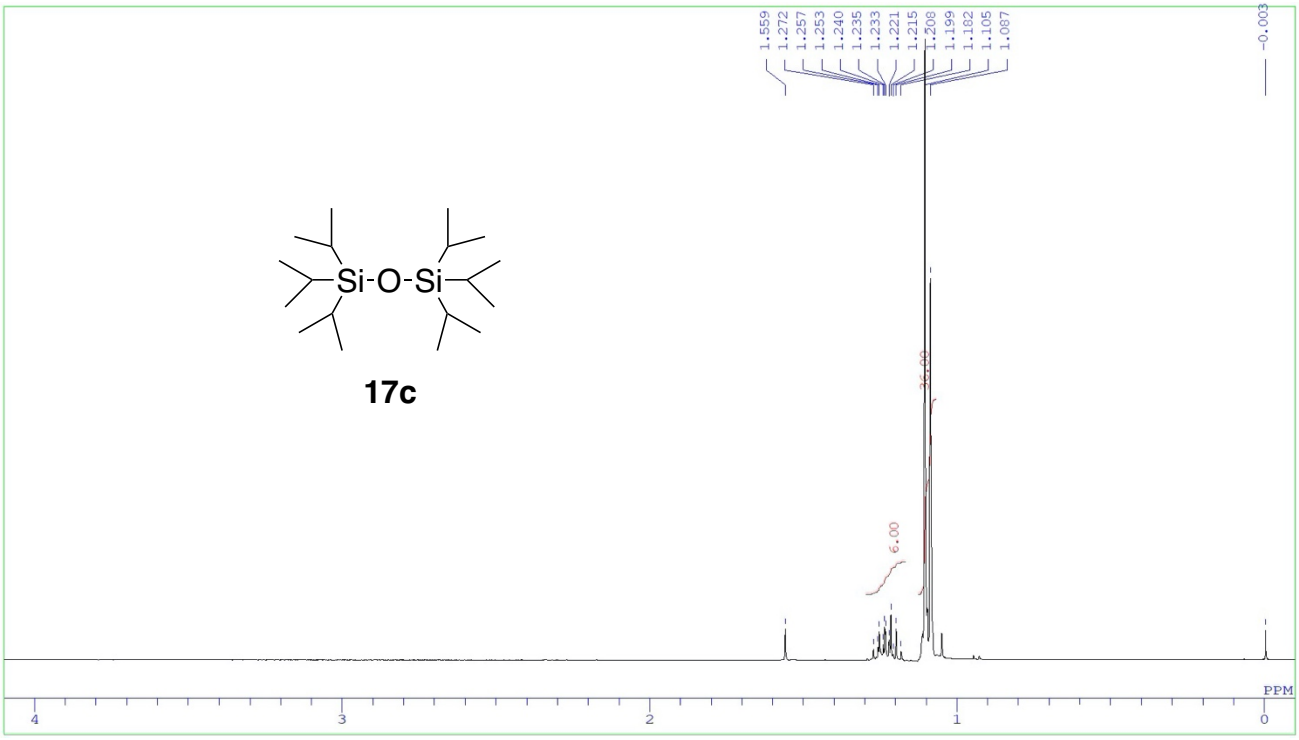

77.312
77.000
76.679
18.117
13.360
Si-Si
15c
PPM
200
150
100
50
0

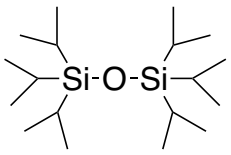

1.325
1.317
1.948
-0.005
21.00
1.00
Si-OH
PPM
4
3
2
1
0

**16c**


77.321
77.000
76.688
17.606
12.242
Si-OH
PPM
200
150
100
50
0

**16c**


1.559
1.272
1.257
1.253
1.240
1.235
1.233
1.221
1.215
1.208
1.199
1.182
1.105
1.087
-0.003
36.00
6.00
PPM
4
3
2
1
0


Si-O-Si

**17c**


77.321
77.000
76.679
17.677
13.635
PPM
200
150
100
50
0


Si-O-Si

**17c**