

*Supplementary Information*

**Well-defined hydrogen and organofunctional polysiloxanes with spiro-fused siloxane backbones**

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## General Information

All experimental manipulations involving air-sensitive compounds were performed in a nitrogen atmosphere of MBRAUN LABmaster Pro SP glove box.

All chemicals were reagent grade and used as received without further purification. Tris(pentafluorophenyl)borane ( $B(C_6F_5)_3$ ), tetrakis(dimethylsilyloxy)silane, phenylsilane, Karstedt's catalyst, 1-octene, allyl glycidyl ether, ethylene glycol monoallyl ether, and 4-chlorostyrene were purchased from Tokyo Chemical Industry Co., Ltd. Toluene, *n*-hexane, acetone, and  $CDCl_3$  were purchased from Fujifilm Wako Pure Chemical Corporation. *n*-Hexylsilane was purchased from Aldrich. Vinylpentamethyldisiloxane was purchased from Gelest, Inc.

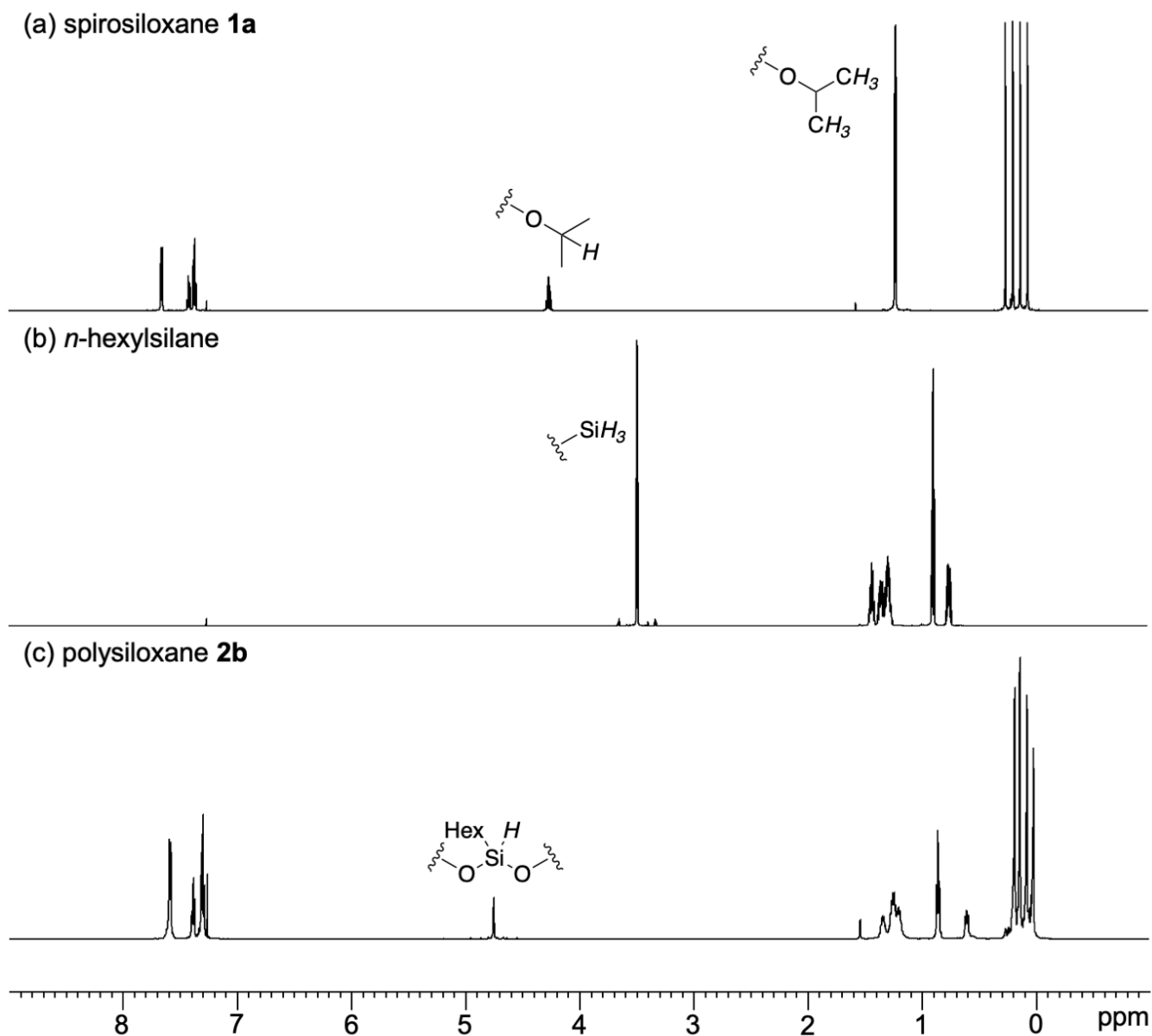
Column chromatography was performed with silica gel (Kanto Silica gel 60 N, 100-210  $\mu m$ ) or activated alumina (Fujifilm Wako Pure Chemical Corporation). Gel Permeation Chromatography (GPC) was performed with a YMC Multiple Preparative HPLC LC-Forte/R using YMC-GPC T4000-40 & YMC-GPC T2000-40 columns.

NMR spectra were recorded on Bruker AVANCE III HD ( $^1H$  NMR at 600 MHz;  $^{13}C\{^1H\}$  NMR at 150 MHz;  $^{29}Si\{^1H\}$  NMR at 119MHz) NMR spectrometer. The High-resolution ESI mass spectra were obtained on Bruker micrOTOF II. The matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectra were collected on Bruker Autoflex Speed. Differential Scanning Calorimetry (DSC) analyses were performed using HITACHI DSC7020.

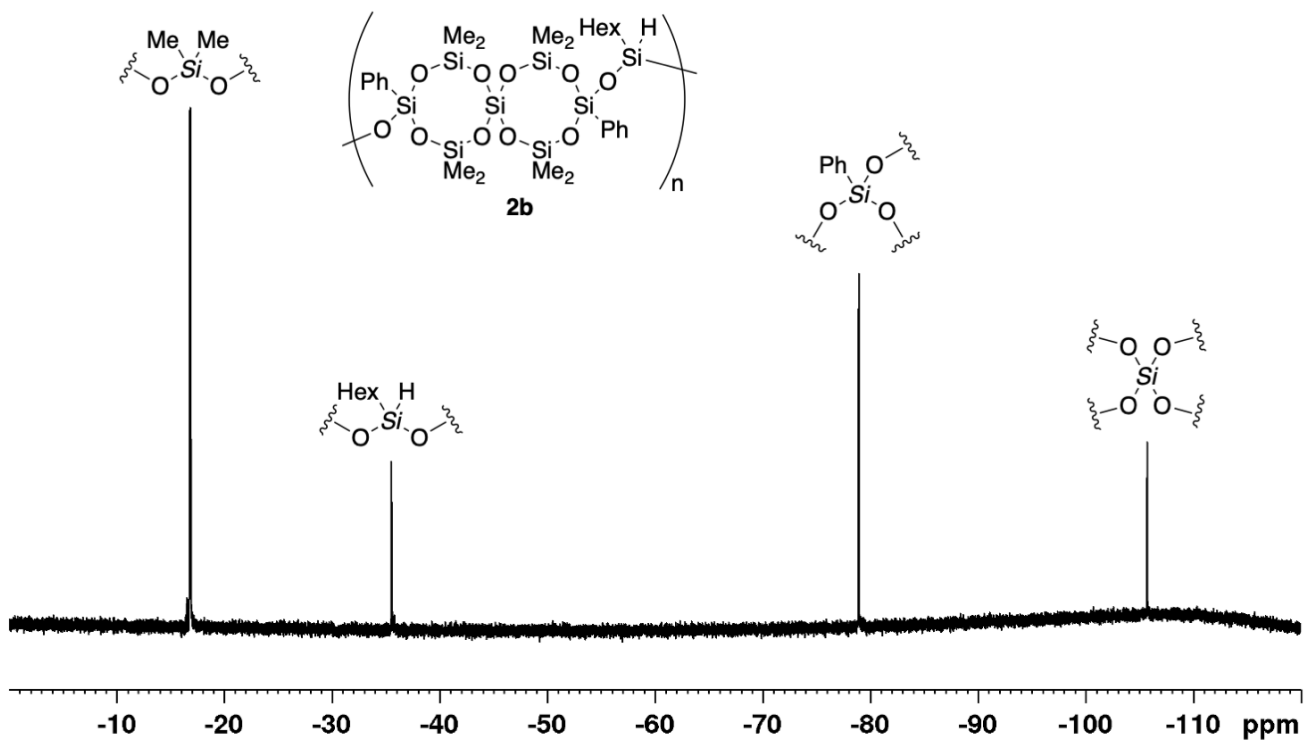
Size-exclusion chromatography (SEC) was performed at 45  $^{\circ}C$  using a Waters ACQUITY Advanced Polymer Chromatography (APC) System consisting of a p-Isocratic Solvent Manager (Model AIS), Sample Manager pFTN (Model ASM), Column Manager-S (Model AZC), PDA TS Detector (Model ADT), and Refractive Index (RI) Detector (Model URI) equipped with a Waters APC<sup>TM</sup> XT45 column (linear, 4.6 mm  $\times$  150 mm; pore size, 4.5 nm; bead size, 1.7  $\mu m$ ; exclusion limit, 5000), a Waters APC<sup>TM</sup> XT200 column (linear, 4.6 mm  $\times$  150 mm; pore size, 20.0 nm; bead size, 2.5  $\mu m$ ; exclusion limit, 70 000), and a Waters APC<sup>TM</sup> XT450 column (linear, 4.6 mm  $\times$  150 mm; pore size, 45.0 nm; bead size, 2.5  $\mu m$ ; exclusion limit, 400 000) in toluene at a flow rate of 0.70 mL  $min^{-1}$ . The number-average molecular weight ( $M_{n,SEC}$ ) and the molecular weight dispersity ( $D_M$ ) were determined based on a calibration curve prepared using polystyrene (PS) samples from a TSKgel<sup>®</sup> standard polystyrene oligomer kit (Tosoh) with weight-average molecular mass ( $M_w$ ) and ( $D_M$ ) values of  $19.0 \times 10^5$  kDa (1.04),  $9.64 \times 10^4$  g  $mol^{-1}$  (1.01),  $3.79 \times 10^4$  g  $mol^{-1}$  (1.01),  $1.74 \times 10^4$  g  $mol^{-1}$  (1.01),  $1.02 \times 10^4$  g  $mol^{-1}$  (1.02),  $5.06 \times 10^3$  g  $mol^{-1}$  (1.02),  $2.63 \times 10^3$  g  $mol^{-1}$  (1.05),  $1.01 \times 10^3$  g  $mol^{-1}$  (1.16), and  $5.9 \times 10^2$  g  $mol^{-1}$  (1.19), along with PS samples from Chemco Co. with  $M_w$  ( $D_M$ ) values of  $17.0 \times 10^5$  g  $mol^{-1}$  (<1.06),  $4.75 \times 10^4$  g  $mol^{-1}$  (1.06),  $9.00 \times 10^3$  g  $mol^{-1}$  (1.04), and  $4.00 \times 10^3$  g  $mol^{-1}$  (1.03). The values of refractive index increment,  $dn/dc$ , were found to be positive for **2a** and negative for **2b** and **2c**.

**Table S1.** Calculated molecular weights relative to poly(styrene) standards and actual molecular weights of separated peaks in approximate number distribution of polysiloxanes **2**

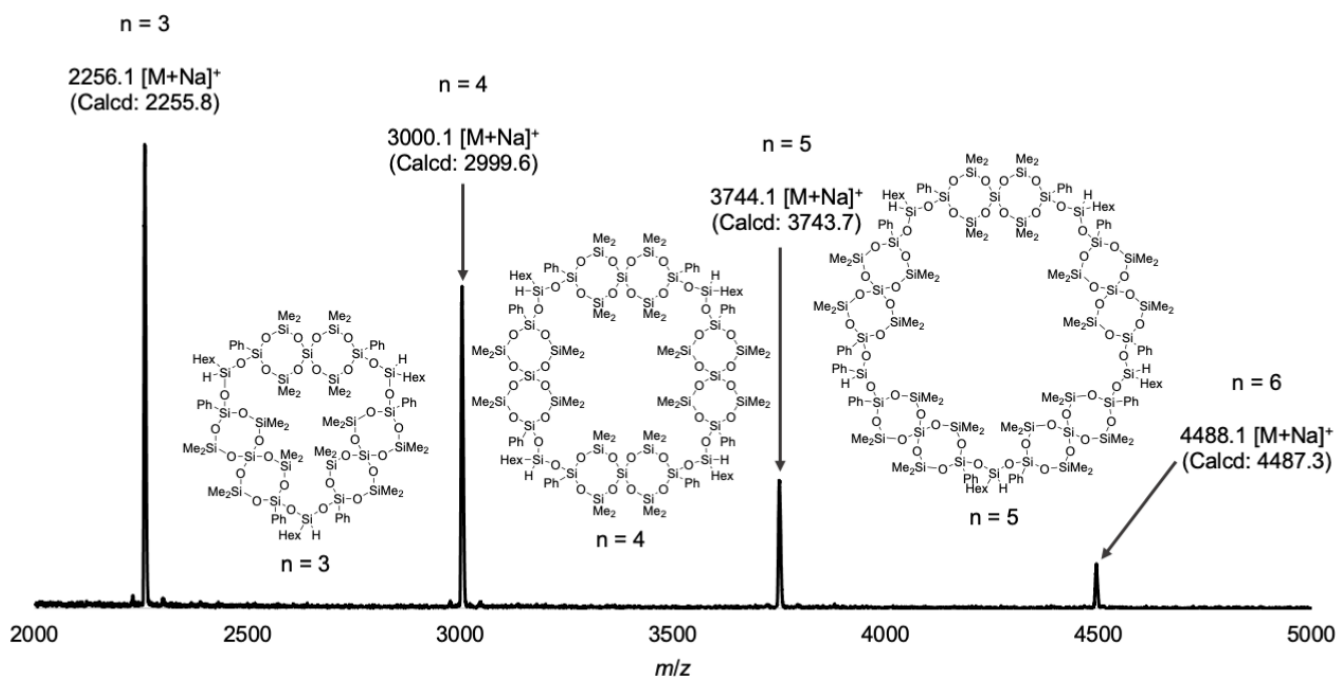
polysiloxane		M.W. of separated peak/Da			
		<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6
<b>2a</b>	PS-equivalent M.W.	1230	1630	2070	2540
	actual M.W.	2208	2944	3680	4416
<b>2b</b>	PS-equivalent M.W.	1130	1490	1890	2330
	actual M.W.	2232	2977	3721	4465
<b>2c</b>	PS-equivalent M.W.	1020	1330	1730	2160
	actual M.W.	2257	3009	3761	4513



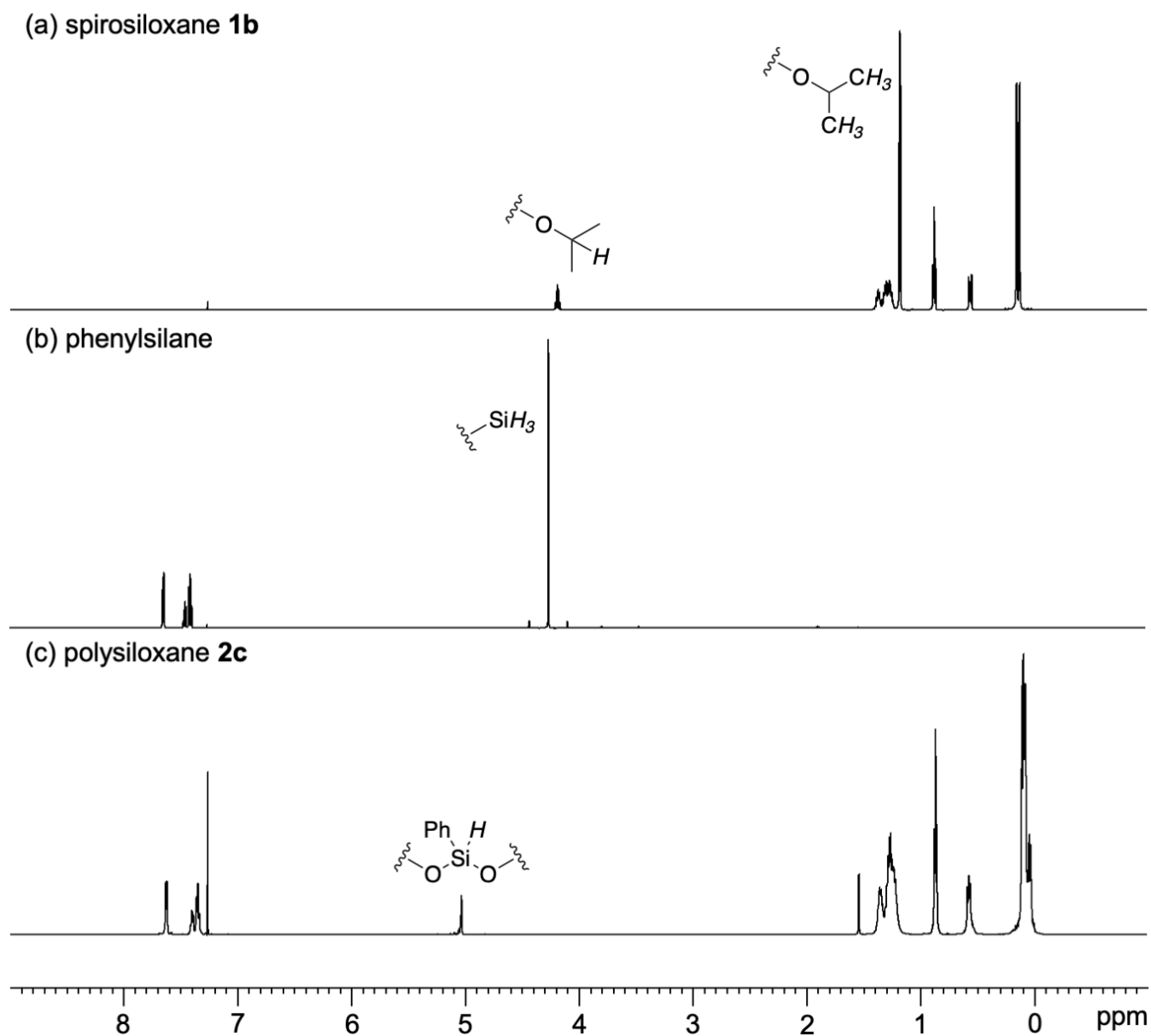
**Figure S1.** Comparing the  $^1\text{H}$  NMR spectra of spiroloxane **1a**, *n*-hexylsilane, and polysiloxane **2b**. (a) spiroloxane **1a**, (b) *n*-hexylsilane, and (c) polysiloxane **2b** ( $M_{n,\text{SEC}} = 3.86$  kDa,  $D_M = 2.96$ ), in  $\text{CDCl}_3$ .



**Figure S2.**  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of polysiloxane **2b** ( $M_{n,\text{SEC}} = 3.86$  kDa,  $D_M = 2.96$ ) in  $\text{CDCl}_3$ .



**Figure S3.** Positive-ion MALDI-TOF mass spectrum of macrocyclic polysiloxanes **2b** ( $M_{n,\text{SEC}} = 3.86$  kDa,  $D_M = 2.96$ ) acquired in reflector mode using DCTB as the matrix and sodium trifluoroacetate as the cationising agent.



**Figure S4.** Comparing the  $^1\text{H}$  NMR spectra of spiroloxane **1b**, phenylsilane, and polysiloxane **2c**. (a) spiroloxane **1b**, (b) phenylsilane, and (c) polysiloxane **2c** ( $M_{n,\text{SEC}} = 2.51$  kDa,  $D_M = 2.40$ ), in  $\text{CDCl}_3$ .

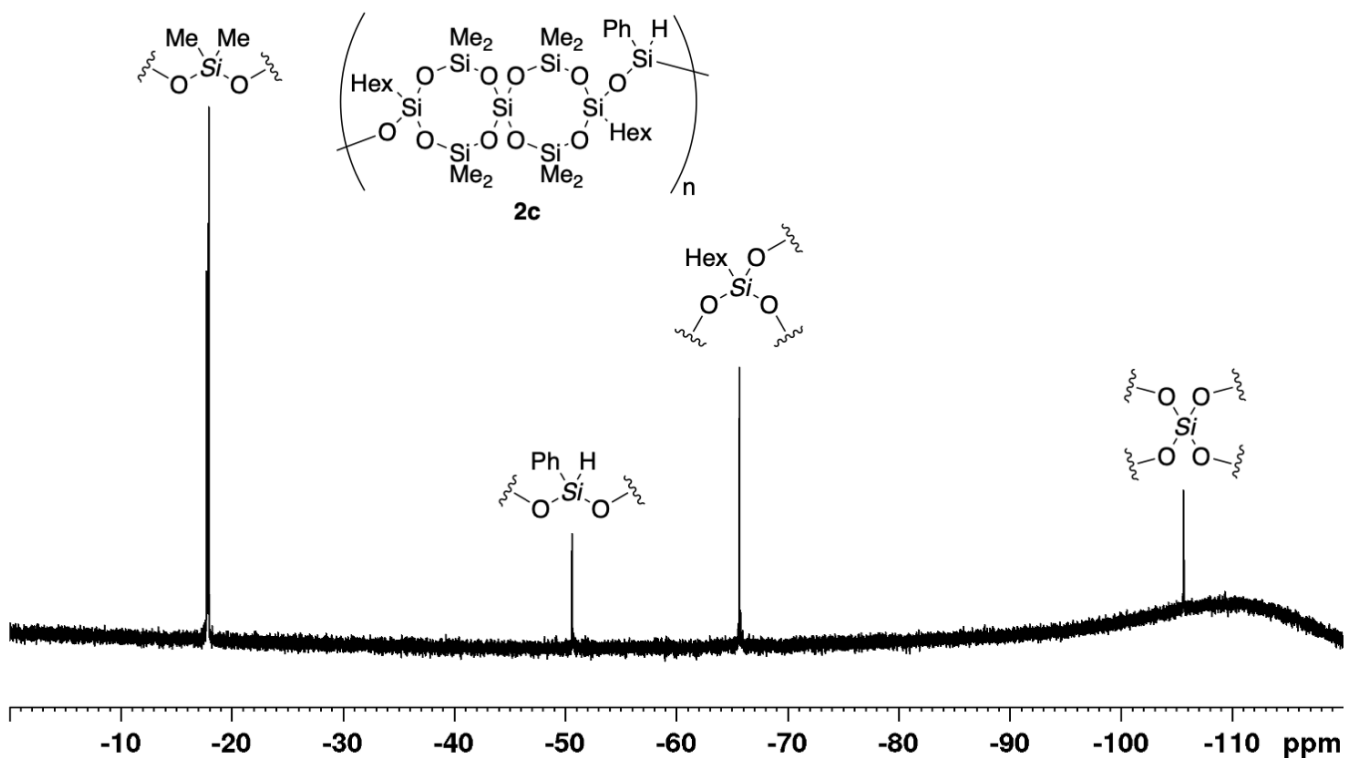


Figure S5.  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of polysiloxane **2c** ( $M_{n,\text{SEC}} = 2.51$  kDa,  $D_M = 2.40$ ) in  $\text{CDCl}_3$ .

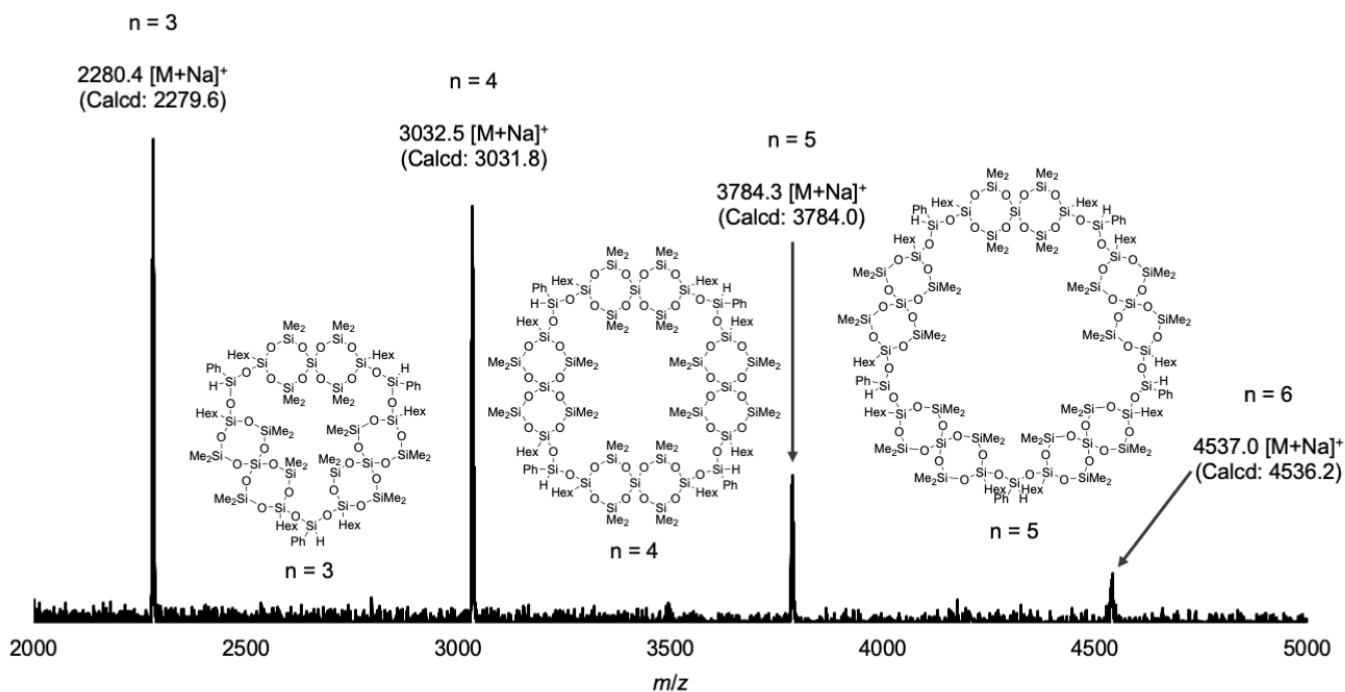
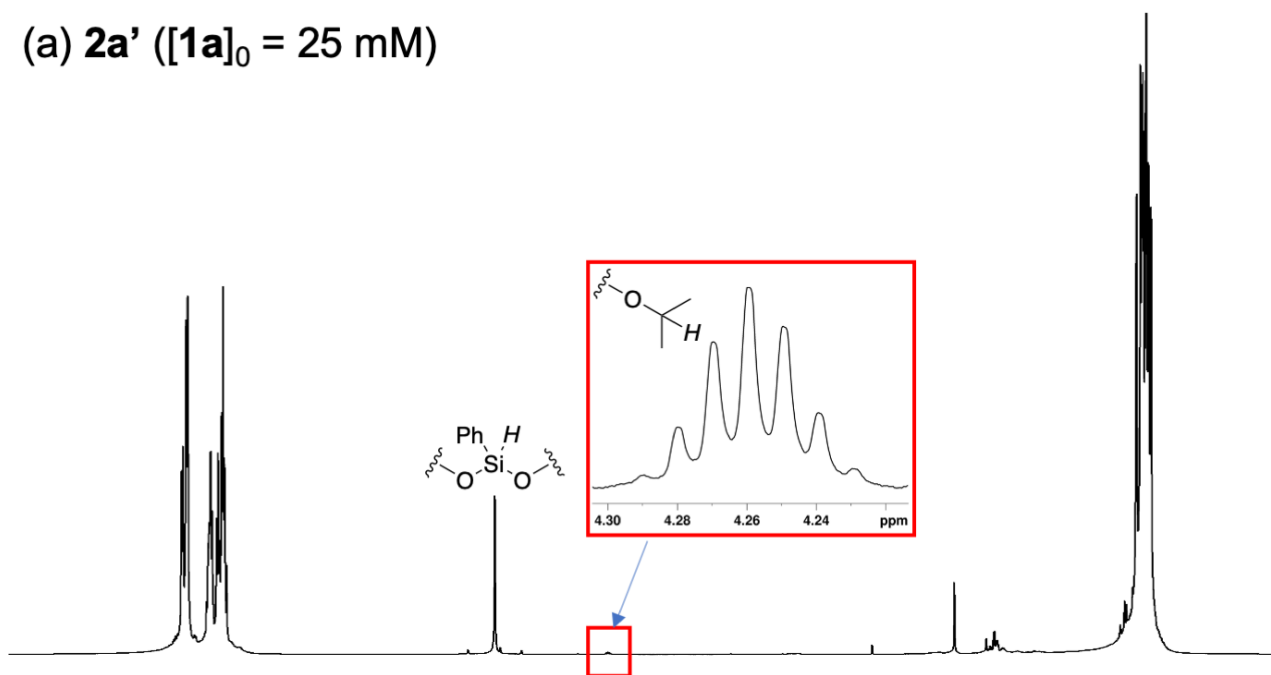


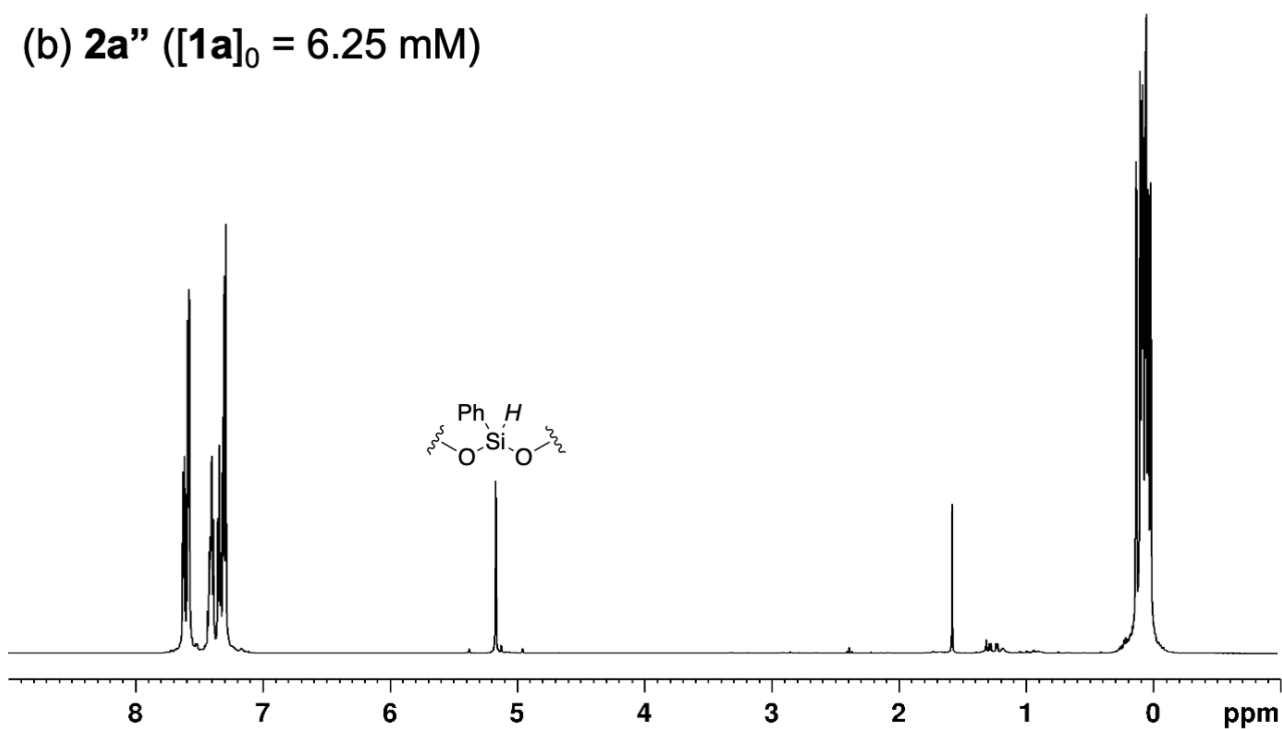
Figure S6. Positive-ion MALDI-TOF mass spectrum of macrocyclic polysiloxanes **2c** ( $M_{n,\text{SEC}} = 2.51$  kDa,  $D_M = 2.40$ ) acquired in reflector mode using DCTB as the matrix and sodium trifluoroacetate as the cationising agent.



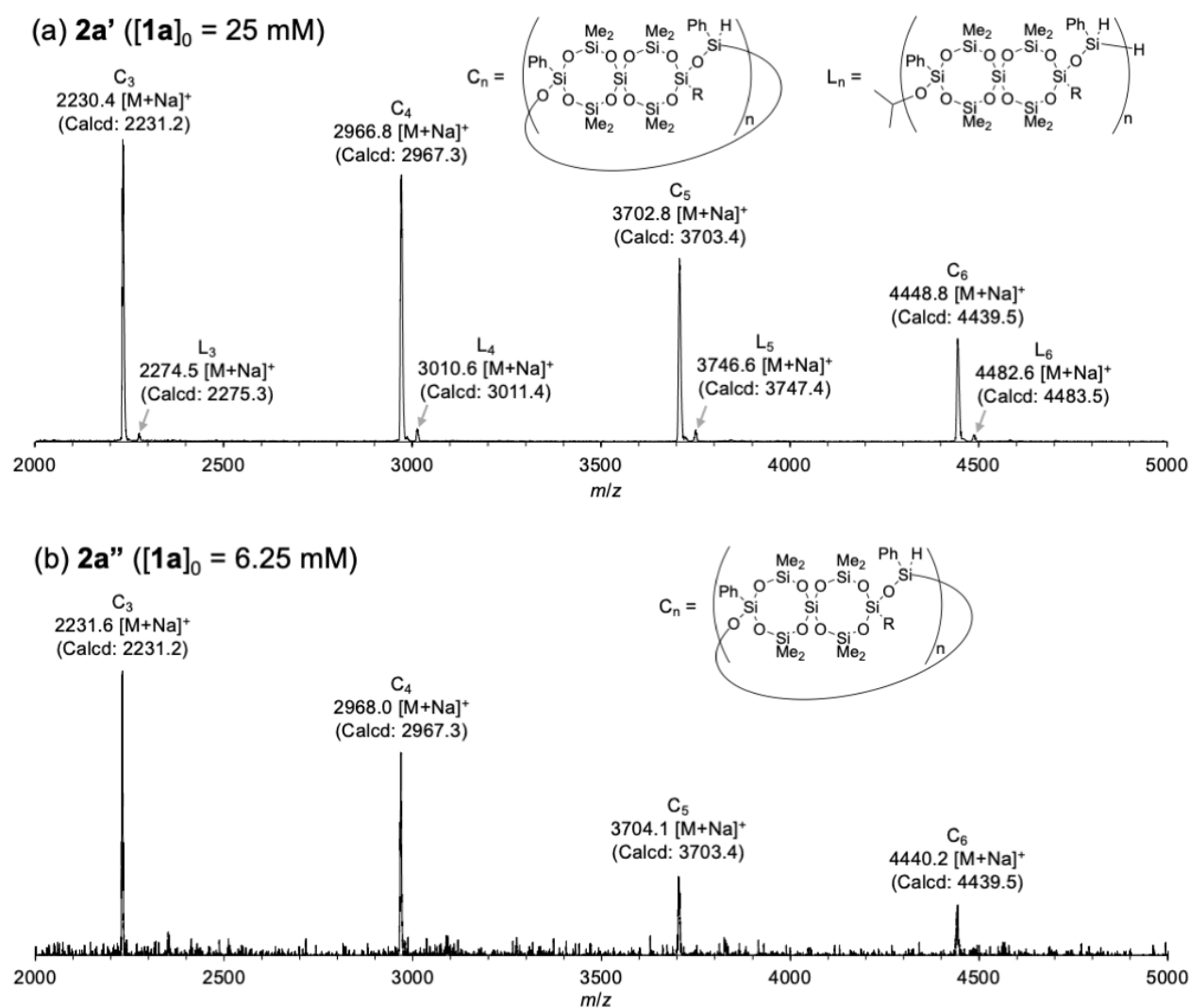
(a) **2a'** ( $[1a]_0 = 25 \text{ mM}$ )



(b) **2a''** ( $[1a]_0 = 6.25 \text{ mM}$ )

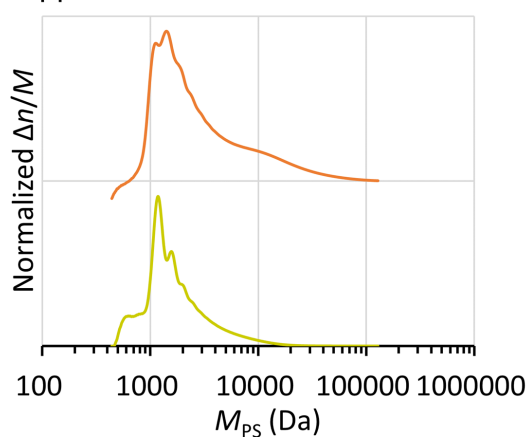


**Figure S7.**  $^1\text{H}$  NMR spectra of (a) polysiloxane **2a'** prepared under more concentrated conditions ( $[1a]_0 = 25 \text{ mM}$ ) and (b) polysiloxane **2a''** prepared under more diluted conditions ( $[1a]_0 = 6.25 \text{ mM}$ ).

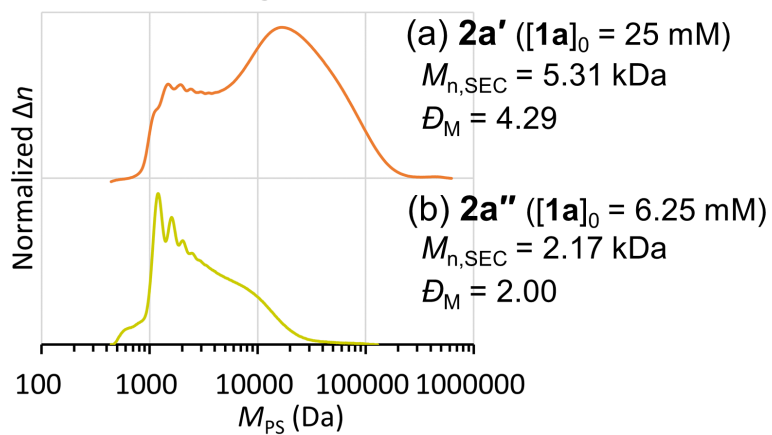


**Figure S8.** MALDI-TOF MS spectrum of (a) polysiloxane **2a'** prepared under more concentrated conditions ( $[1a]_0 = 25 \text{ mM}$ ) and (b) polysiloxane **2a''** prepared under more diluted conditions ( $[1a]_0 = 6.25 \text{ mM}$ ).

Approximate number distribution

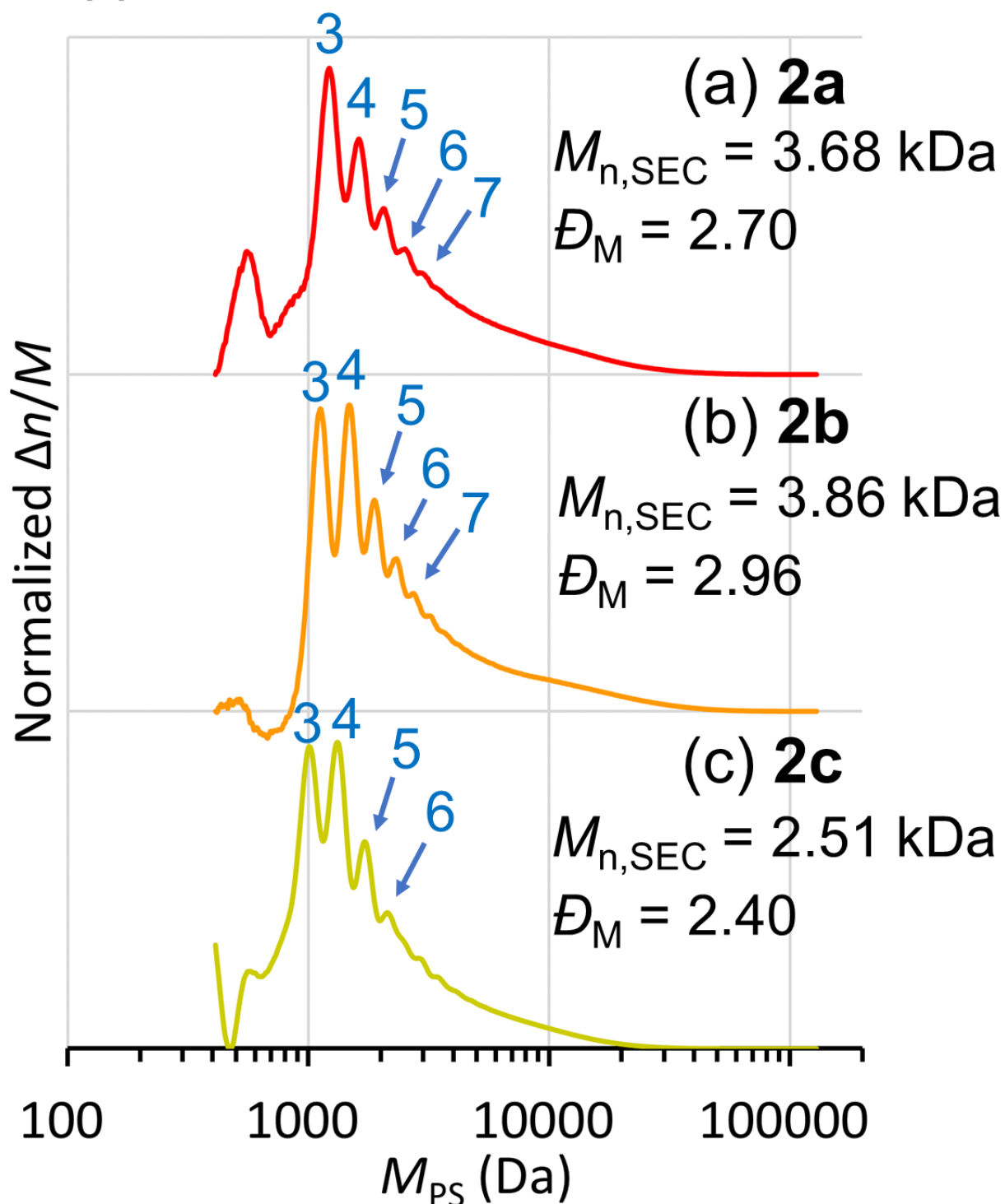


Approximate weight distribution

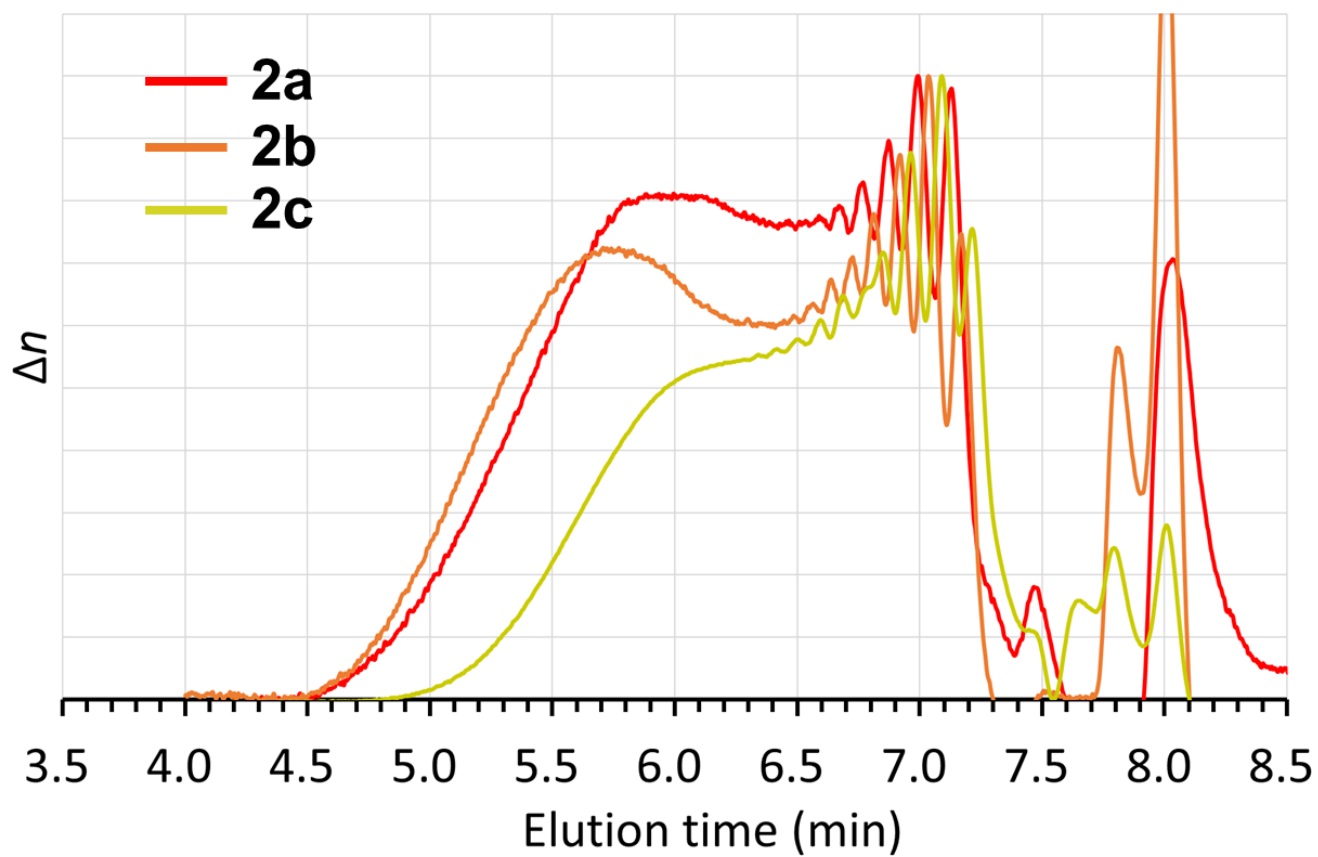


**Figure S9.** Molecular weight distributions of (a) polysiloxane **2a'** prepared under more concentrated conditions ( $[1a]_0 = 25$  mM) and (b) polysiloxane **2a''** prepared under more diluted conditions ( $[1a]_0 = 6.25$  mM), determined by SEC using toluene as the eluent, narrowly dispersed poly(styrene)s as standards, and a differential refractometer detector.

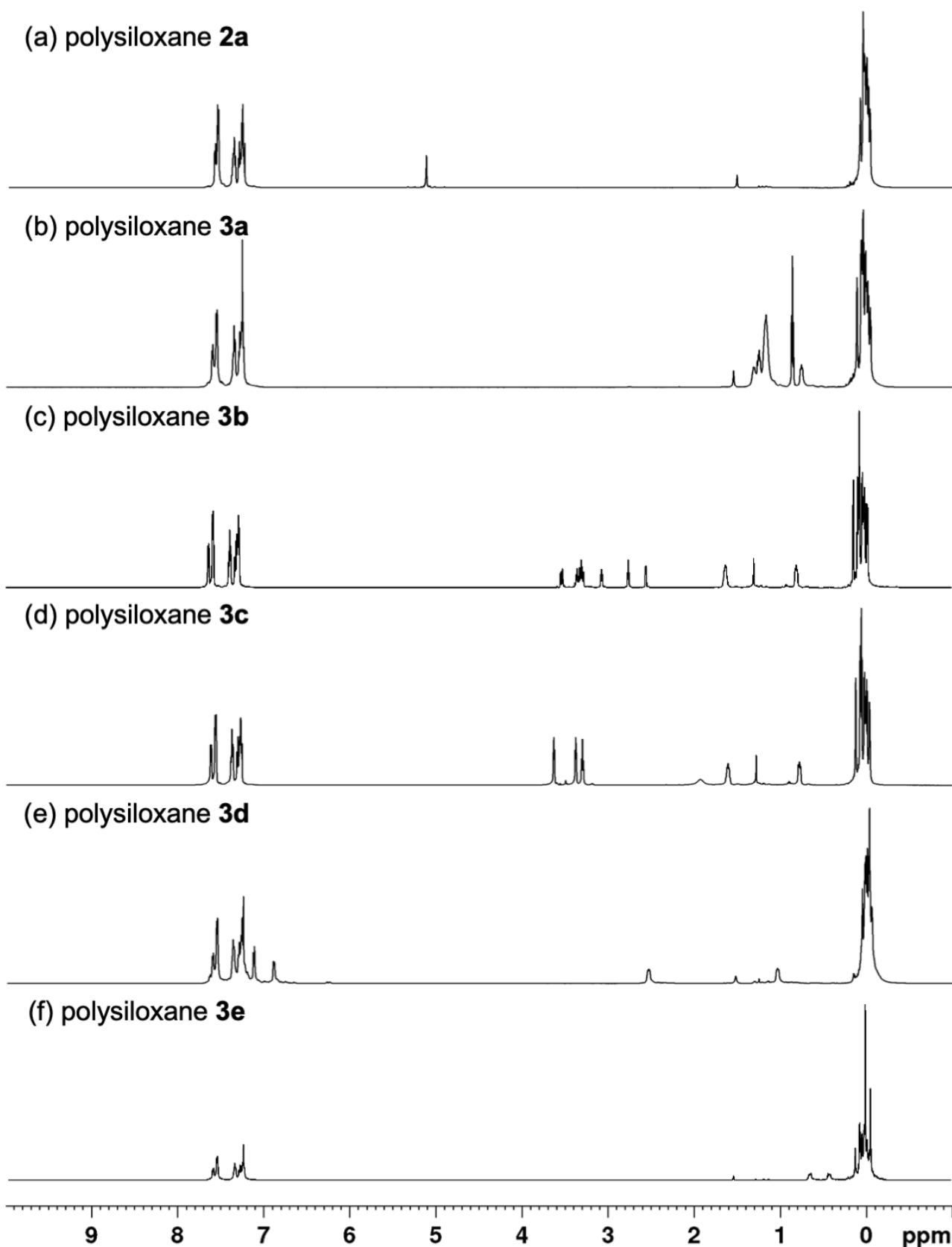
## Approximate number distribution



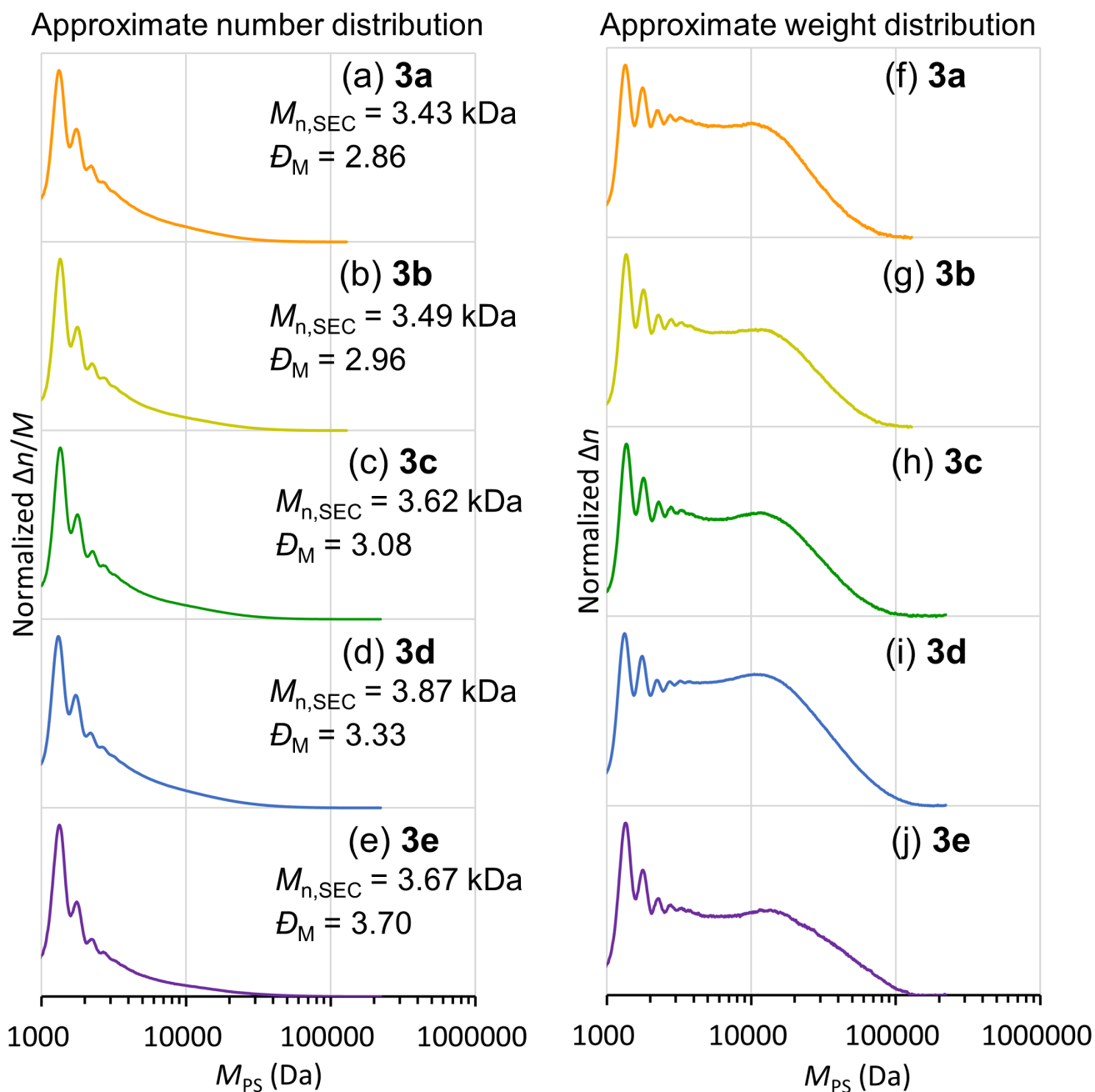
**Figure S10.** A zoomed-in version of the molecular weight distributions of polysiloxanes **2a-2c** determined by SEC



**Figure S11.** SEC curves of polysiloxanes **2a-2c** using toluene as the eluent and a differential refractometer detector.



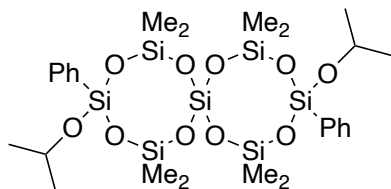
**Figure S12.** Comparing  $^1\text{H}$  NMR spectra of (a) polysiloxane **2a**, (b) polysiloxane **3a**, (c) polysiloxane **3b**, (d) polysiloxane **3c**, (e) polysiloxane **3d**, and (f) polysiloxane **3e**, in  $\text{CDCl}_3$ .



**Figure S13.** Molecular weight distributions of polysiloxanes **3a-3e** determined by SEC using toluene as the eluent, narrowly dispersed poly(styrene)s as standards, and a differential refractometer detector.

## Preparation of Spirosiloxane Monomers 1

### 4,12-diisopropoxy-2,2,6,6,10,10,14,14-octamethyl-4,12-diphenyl-1,3,5,7,9,11,13,15-octaoxa-2,4,6,8,10,12,14-heptasilaspiro[7.7]pentadecane (1a)



$B(C_6F_5)_3$  (34.2 mg, 5 mol%) and acetone (390  $\mu$ L, 5.2 mmol) were dissolved in toluene (20 mL). To the mixture was added  $Si(OSiMe_2H)_4$  (482  $\mu$ L, 1.3 mmol) with stirring at room temperature. After 30 min, phenylsilane (321  $\mu$ L, 2.6 mmol) was added. After 1 h, acetone (195  $\mu$ L, 2.6 mmol) was added. After 2 h, the reaction mixture was passed through a short silica gel pad (eluent: *n*-hexane). The crude product was purified by GPC (eluent: *n*-hexane) to give **1a** as a colourless oil (551.6 mg, 59%).

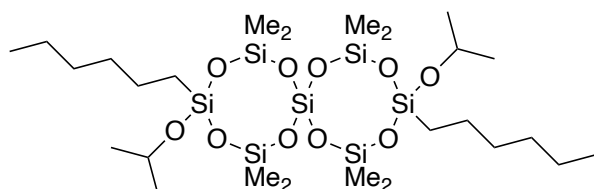
$^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  7.68-7.62 (m, 4H), 7.44-7.40 (m, 2H), 7.39-7.33 (m, 4H), 4.26 (sep,  $J$  = 6.1 Hz, 2H), 1.22 (d,  $J$  = 6.1 Hz, 12H), 0.26 (s, 6H), 0.20 (s, 6H), 0.13 (s, 6H), 0.07 ppm (s, 6H).

$^{13}C\{^1H\}$  NMR (150 MHz,  $CDCl_3$ ):  $\delta$  134.3, 133.5, 130.1, 127.8, 65.6, 25.5, 0.62, 0.54, 0.45, 0.37.

$^{29}Si\{^1H\}$  NMR (119 Hz,  $CDCl_3$ ):  $\delta$  -16.72, -16.73, -72.7, -105.6.

HRMS (ESI):  $m/z$  calculated for  $[C_{26}H_{52}NO_{10}Si_7]$  ( $M+NH_4$ ): 734.1971; found 734.1963.

### 4,12-dihexyl-4,12-diisopropoxy-2,2,6,6,10,10,14,14-octamethyl-1,3,5,7,9,11,13,15-octaoxa-2,4,6,8,10,12,14-heptasilaspiro[7.7]pentadecane (1b)



$B(C_6F_5)_3$  (76.8 mg, 5 mol%) and acetone (901  $\mu$ L, 12.0 mmol) were dissolved in toluene (45 mL). To the mixture was added  $Si(OSiMe_2H)_4$  (1116  $\mu$ L, 3.0 mmol) with stirring at room temperature. After 30 min, *n*-hexylsilane (987  $\mu$ L, 6.0 mmol) was added at 0  $^\circ$ C. After 20 h, acetone (540  $\mu$ L, 7.2 mmol) was added. After 8 h, the reaction mixture was passed through a short silica gel pad (eluent: *n*-hexane).

The crude product was purified by GPC (eluent: *n*-hexane) to give **1b** as a colourless oil (1.35 g, 61%).

$^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  4.19 (sep,  $J$  = 6.1 Hz, 2H), 1.44-1.21 (m, 16H), 1.18 (d,  $J$  = 6.1 Hz, 12H), 0.88 (t,  $J$  = 7.0 Hz, 6H), 0.60-0.52 (m, 4H), 0.16 (s, 6H), 0.15 (s, 6H), 0.131 (s, 6H), 0.126 (s, 6H).

$^{13}C\{^1H\}$  NMR (150 MHz,  $CDCl_3$ ):  $\delta$  65.0, 32.8, 31.7, 25.6, 23.1, 22.7, 14.3, 13.2, 0.52, 0.51 (two signals are missing due to overlap).

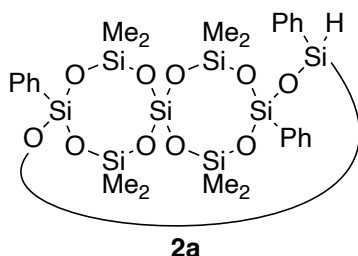
$^{29}Si\{^1H\}$  NMR (119 Hz,  $CDCl_3$ ):  $\delta$  -18.015, -18.024, -59.8, -105.5.

HRMS (ESI):  $m/z$  calculated for  $[C_{26}H_{68}NO_{10}Si_7]$  ( $M+NH_4$ ): 750.3223; found 750.3214.



## Preparation of Hydrogen Polysiloxanes 2

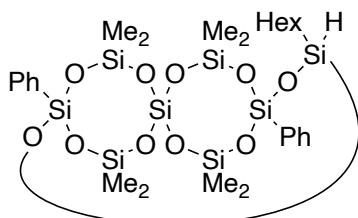
### hydrogen polysiloxane 2a



B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (10.2 mg, 1 mol%) and **1a** (1.44 g, 2.0 mmol) were dissolved in toluene (160 mL). To the mixture was added phenylsilane (247 μL, 2.0 mmol) with stirring at room temperature. After 20 h, the reaction mixture was passed through a short alumina pad (eluent: *n*-hexane), and the volatiles were removed under reduced pressure to give hydrogen polysiloxane **2a** as a colourless oil (1.46 g, >95%). The crude product was analysed by NMR, SEC, DSC, and MALDI-TOF MS without further purification and used for the next reactions.

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of the product are shown in Figure S9-S11.

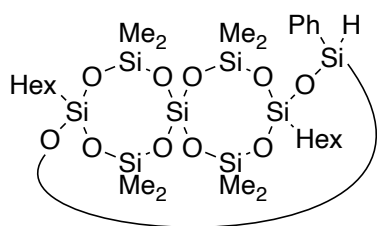
### hydrogen polysiloxane 2b



B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (2.6 mg, 1 mol%) and **1a** (358.6 mg, 0.5 mmol) were dissolved in toluene (40 mL). To the mixture was added *n*-hexylsilane (80.6 μL, 0.5 mmol) with stirring at room temperature. After 20 h, the reaction mixture was passed through a short alumina pad (eluent: *n*-hexane), and the volatiles were removed under reduced pressure to give hydrogen polysiloxane **2b** as a colourless oil (354.0 mg, 95%). The crude product was analysed by NMR, SEC, DSC, and MALDI-TOF MS without further purification.

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of the product are shown in Figure S12-S14.

### hydrogen polysiloxane **2c**



B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1.2 mg, 1 mol%) and **2a** (178.1 mg, 0.24 mmol) were dissolved in toluene (19 mL). To the mixture was added phenylsilane (29.6 μL, 0.24 mmol) with stirring at room temperature. After 20 h, the reaction mixture was passed through a short alumina pad (eluent: *n*-hexane), and the volatiles were removed under reduced pressure to give hydrogen polysiloxane **2c** as a colourless oil (173.7 mg, >95%). The crude product was analysed by NMR, SEC, DSC, and MALDI-TOF MS without further purification.

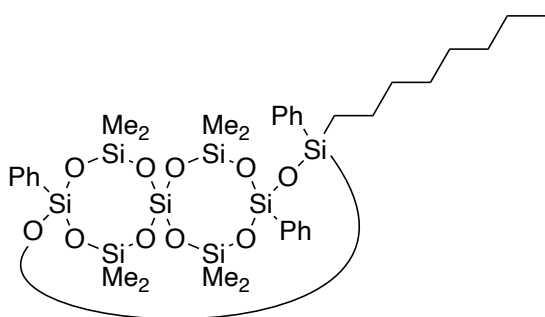
<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of the product are shown in Figure S15-S17.

## Typical Procedure for the Synthesis of Polysiloxane 3a

Karstedt's catalyst (0.1 mg, 0.1  $\mu\text{mol}$ ) and **2a** (73.7 mg, 0.10 mmol) were dissolved in toluene (0.4 mL). To the mixture was added 1-octene (16  $\mu\text{L}$ , 0.10 mmol) with stirring at room temperature. After 10 h, the reaction mixture was passed through a short silica gel pad (eluent: *n*-hexane) to give polysiloxane **3a** as a pale yellow oil (84.0 mg, >95%). The crude product was used for NMR and MALDI-TOF MS analyses without further purification.

Other polysiloxanes **3b-3e** were also synthesised in the same procedure by using different olefins.

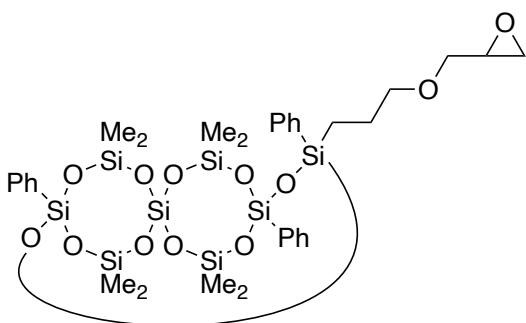
### polysiloxane 3a



pale yellow oil (84.0 mg, >95%)

$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of the product are shown in Figure S18-S20.

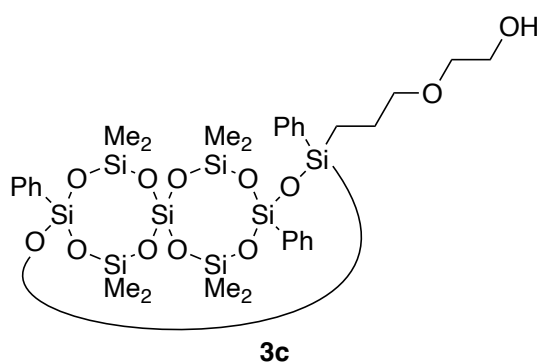
### polysiloxane 3b



pale yellow oil (80.1 mg, 94%)

$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra of the product are shown in Figure S21-S23.

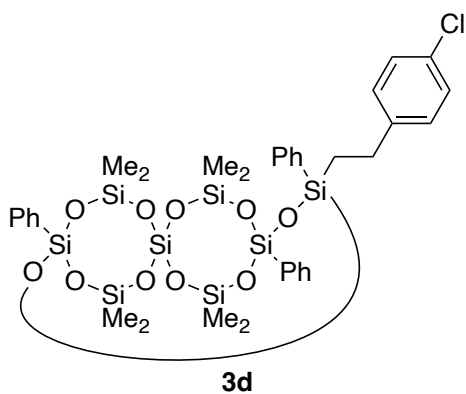
### polysiloxane 3c



pale yellow oil (78.8 mg, 94%)

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of the product are shown in Figure S24-S26.

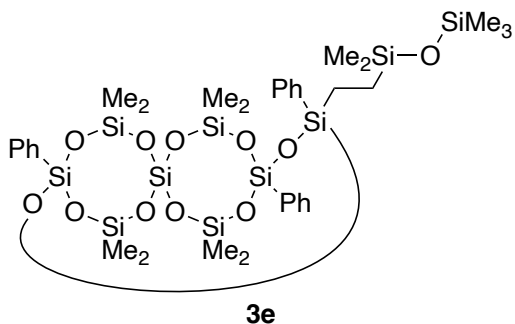
### polysiloxane 3d



yellow oil (85.8 mg, >95%)

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of the product are shown in Figure S27-S29.

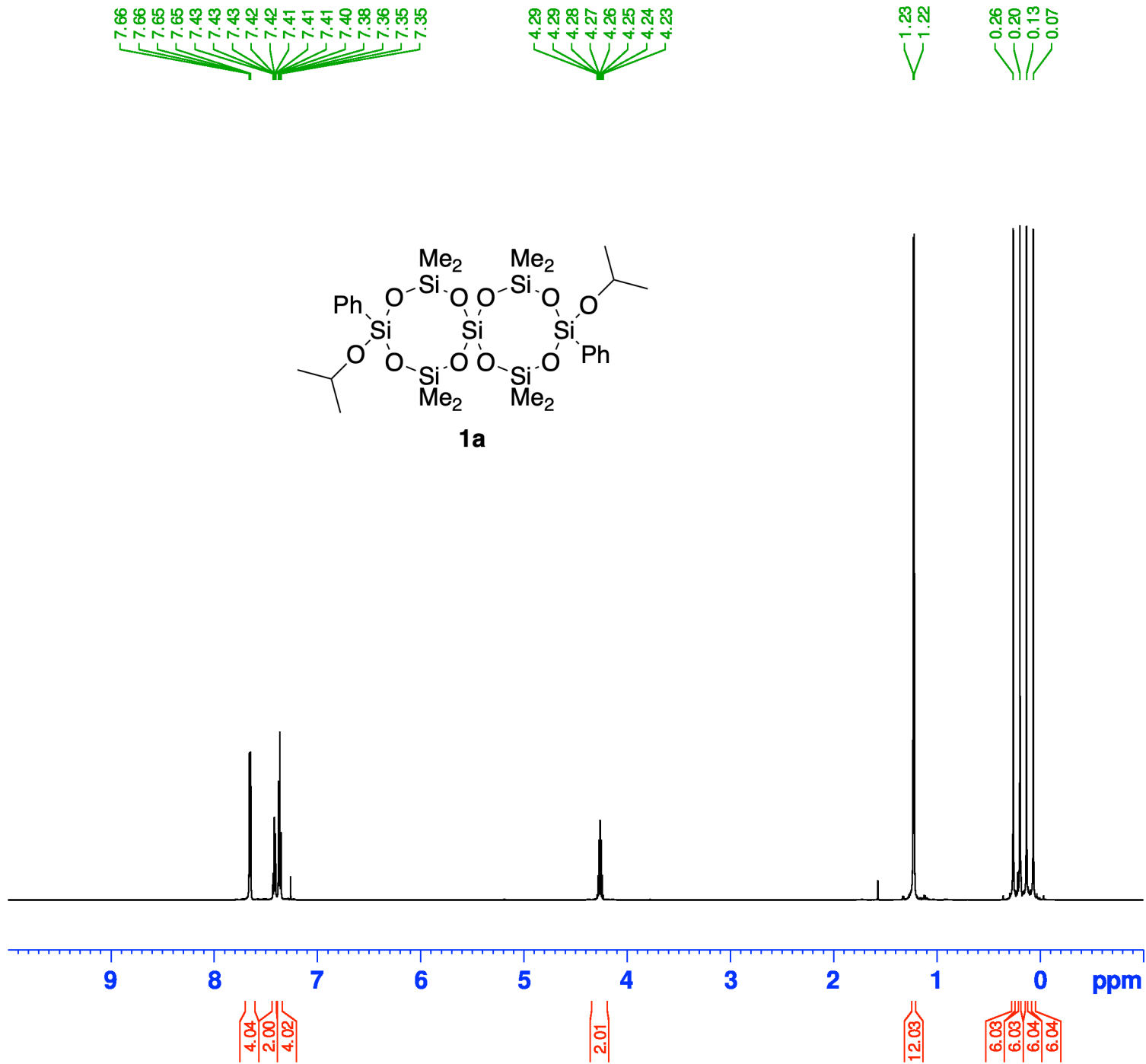
### polysiloxane 3e



pale yellow oil (90.3 mg, >95%)

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra of the product are shown in Figure S30-S32.

Figure S14. 1H NMR Spectra of Spirosiloxane 1a



```

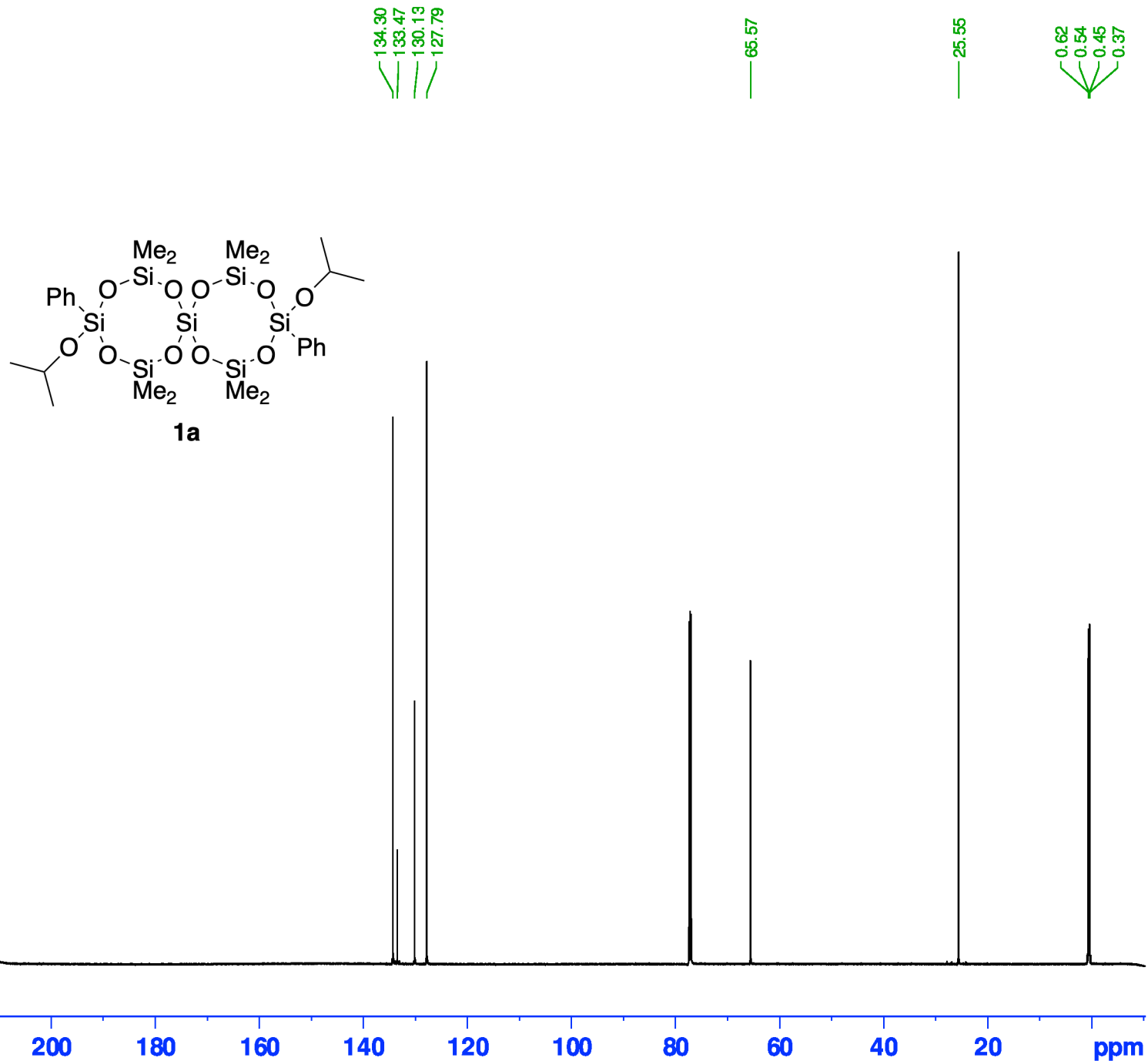
Current Data Parameters
NAME      spirosiloxanela
EXPNO     10
PROCNO    1

F2 - Acquisition Parameter
Date_     20200915
Time      13.23
INSTRUM   spect
PROBHD    5 mm CPBBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         2
SWH        12019.230 Hz
FIDRES     0.183399 Hz
AQ         2.7262976 sec
RG         11.42
DW         41.600 usec
DE         15.65 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      600.2330011 MHz
NUC1       1H
P1         12.00 usec
PLW1      19.26700020 W

F2 - Processing parameters
SI         65536
SF         600.2300149 MHz
WDW        EM
SSB        0
LB         0.20 Hz
GB         0
PC         1.00
    
```

Figure S15. <sup>13</sup>C NMR Spectra of Spirosiloxane 1a



Current Data Parameters  
 NAME spirosiloxanela  
 EXPNO 11  
 PROCNO 1

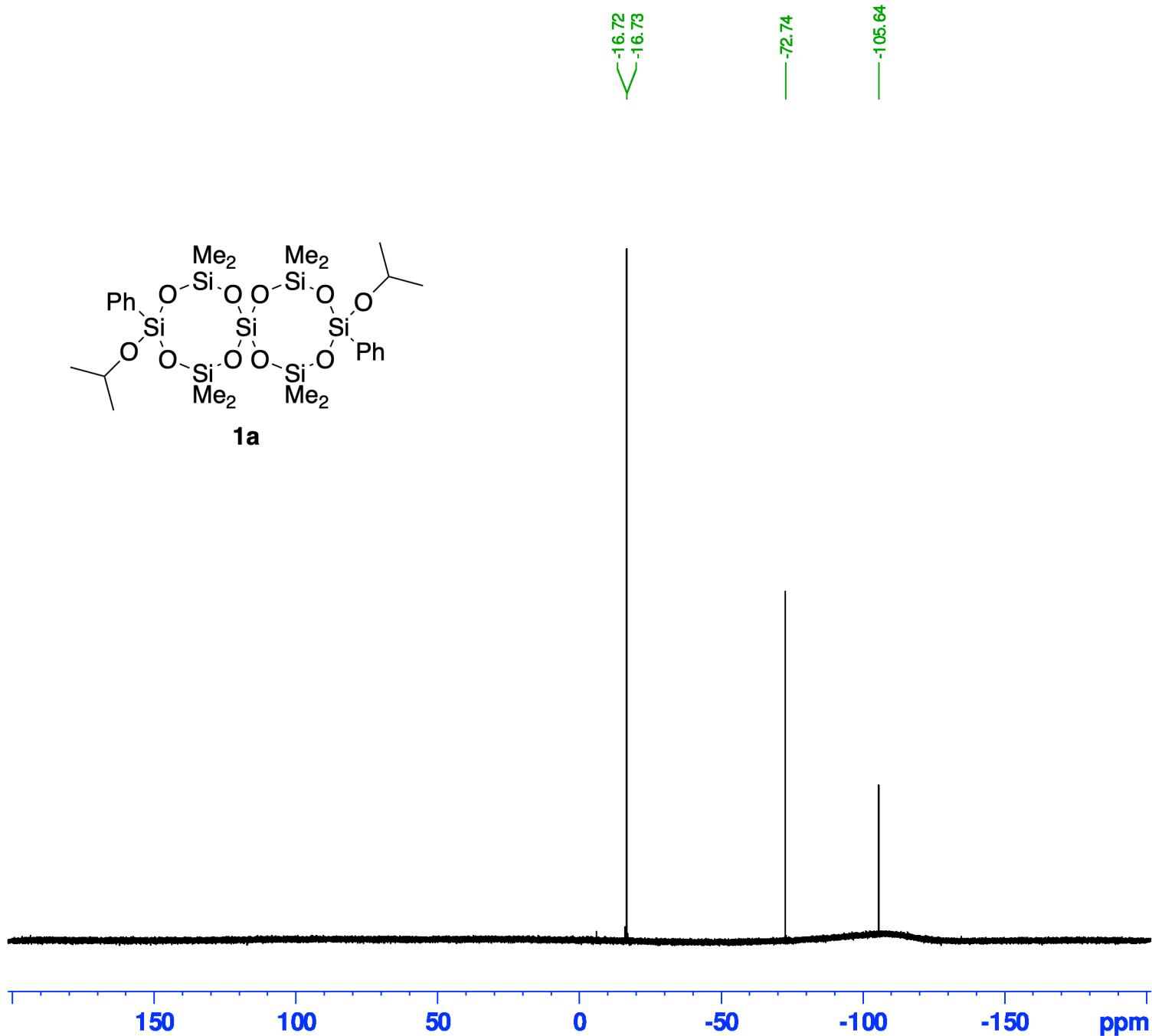
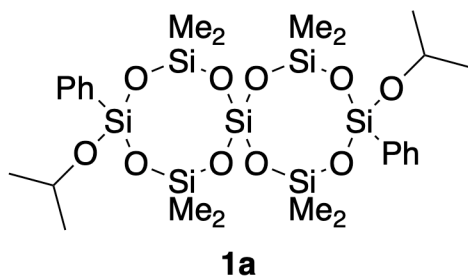
F2 - Acquisition Parameter  
 Date\_ 20200916  
 Time 7.07  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 33333.332 Hz  
 FIDRES 0.508626 Hz  
 AQ 0.9830400 sec  
 RG 193.87  
 DW 15.000 usec  
 DE 19.62 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 150.9430468 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 37.32500076 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W  
 PLW13 0.28435001 W

F2 - Processing parameters  
 SI 65536  
 SF 150.9279362 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S16. <sup>29</sup>Si NMR Spectra of Spirosiloxane 1a



Current Data Parameters  
 NAME spirosiloxanela  
 EXPNO 12  
 PROCNO 1

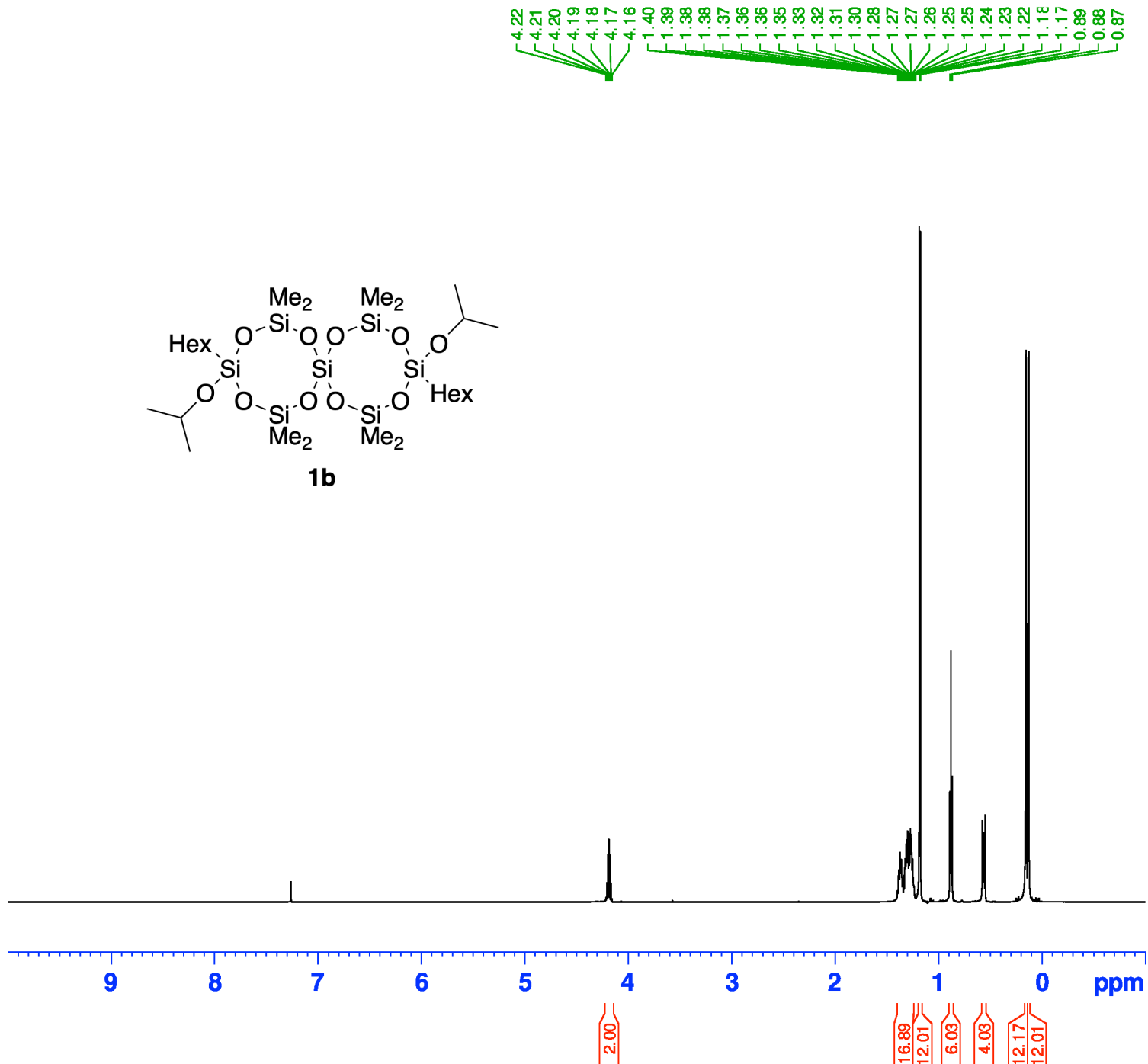
F2 - Acquisition Parameter  
 Date\_ 20200916  
 Time 7.22  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 29Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488156 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40

Figure S17. <sup>1</sup>H NMR Spectra of Spirosiloxane 1b



```

Current Data Parameters
NAME      spirosiloxane1b
EXPNO     10
PROCNO    1

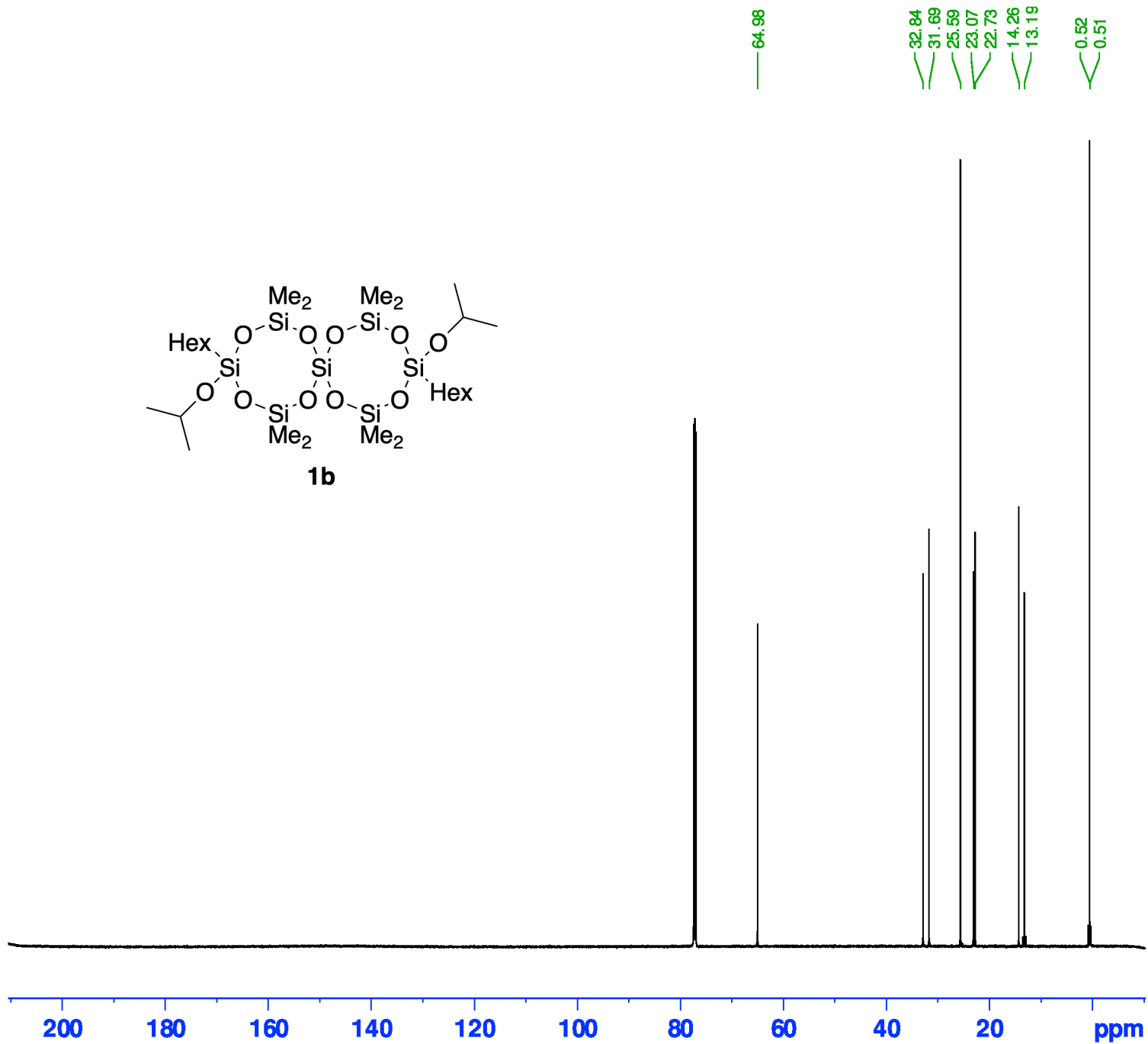
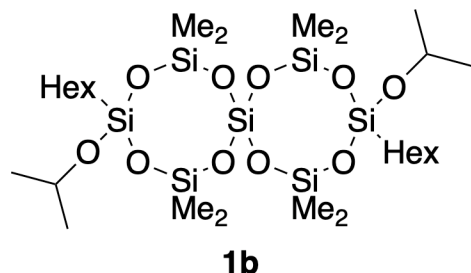
F2 - Acquisition Parameter
Date_     20200915
Time      13.27
INSTRUM   spect
PROBHD    5 mm CPBBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         8
DS         2
SWH        12019.230 Hz
FIDRES     0.183399 Hz
AQ         2.7262976 sec
RG         9.09
DW         41.600 usec
DE         15.65 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      600.2330011 MHz
NUC1      1H
P1        12.00 usec
PLW1      19.26700020 W

F2 - Processing parameters
SI        65536
SF        600.23300150 MHz
WDW       EM
SSB       0
LB        0.20 Hz
GB        0
PC        1.00
    
```



Figure S18. <sup>13</sup>C NMR Spectra of Spirosiloxane 1b



Current Data Parameters  
 NAME spirosiloxanelb  
 EXPNO 11  
 PROCNO 1

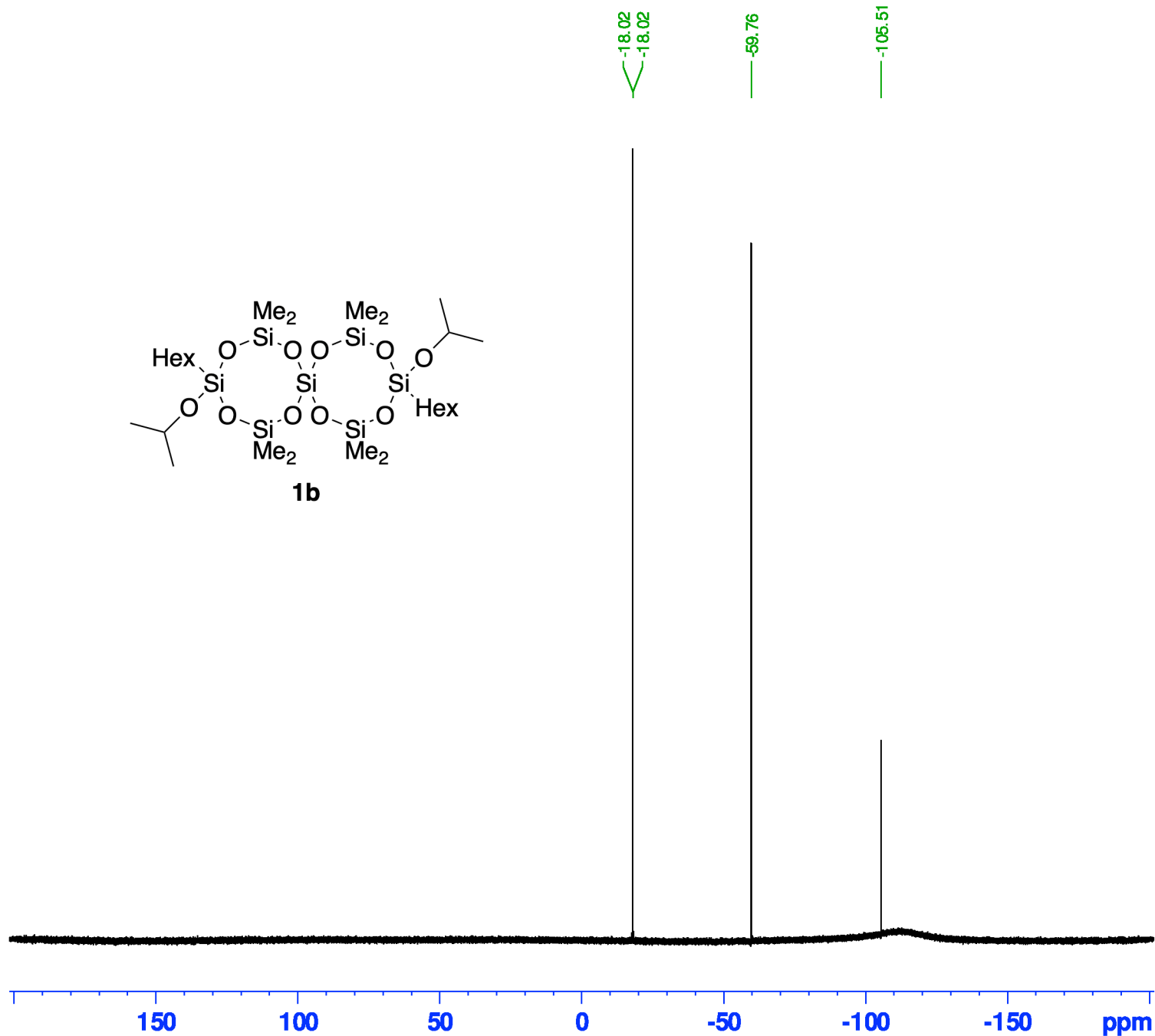
F2 - Acquisition Parameter  
 Date\_ 20200916  
 Time 7.43  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 33333.332 Hz  
 FIDRES 0.508626 Hz  
 AQ 0.9830400 sec  
 RG 193.87  
 DW 15.000 usec  
 DE 19.62 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 150.9430468 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 37.32500076 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W  
 PLW13 0.28435001 W

F2 - Processing parameters  
 SI 65536  
 SF 150.9279319 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S19. <sup>29</sup>Si NMR Spectra of Spirosiloxane 1b



Current Data Parameters  
 NAME spirosiloxanelb  
 EXPNO 12  
 PROCNO 1

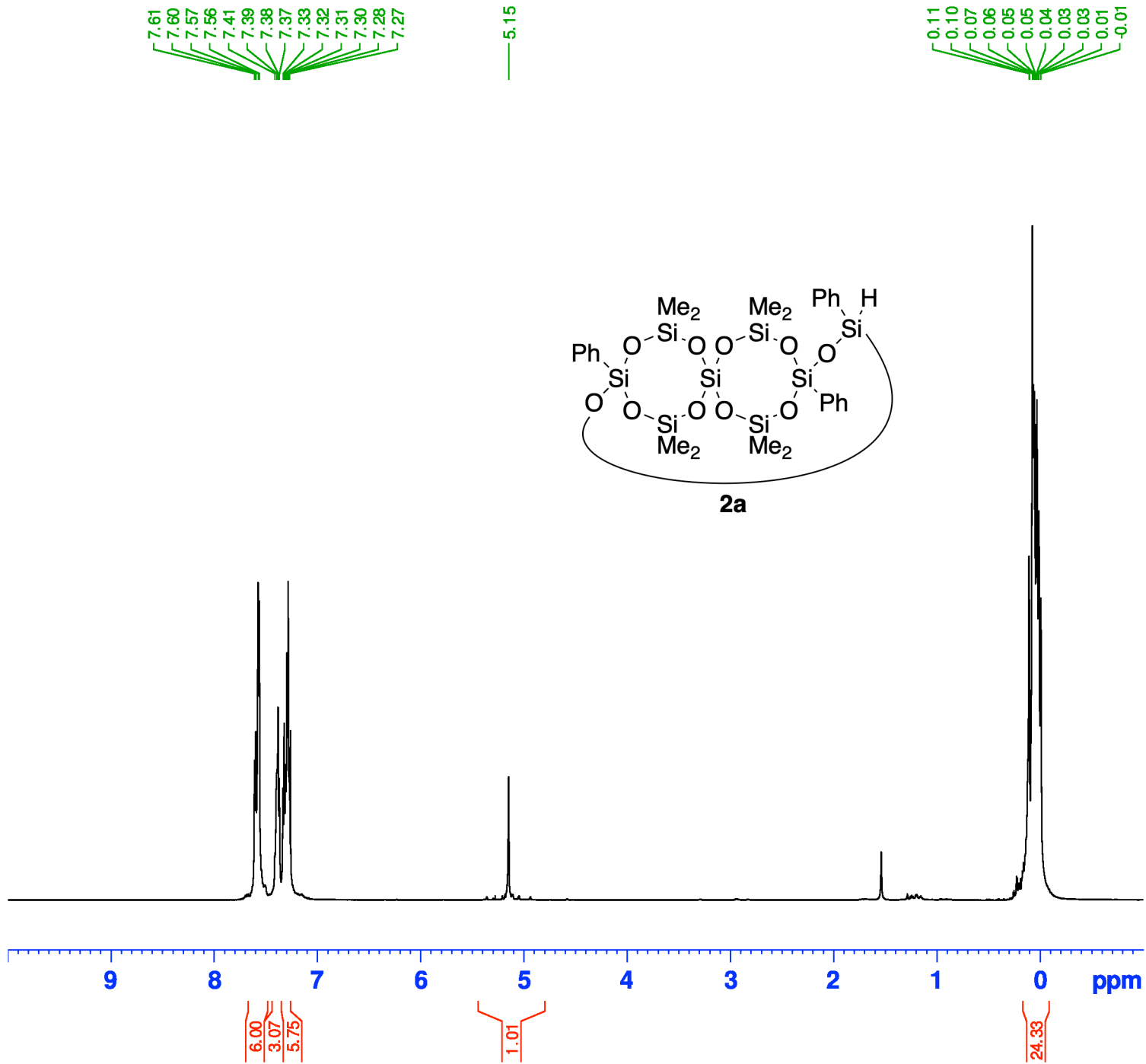
F2 - Acquisition Parameter  
 Date\_ 20200916  
 Time 7.38  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 29Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488156 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40

Figure S20. <sup>1</sup>H NMR Spectra of Polysiloxane 2a



```

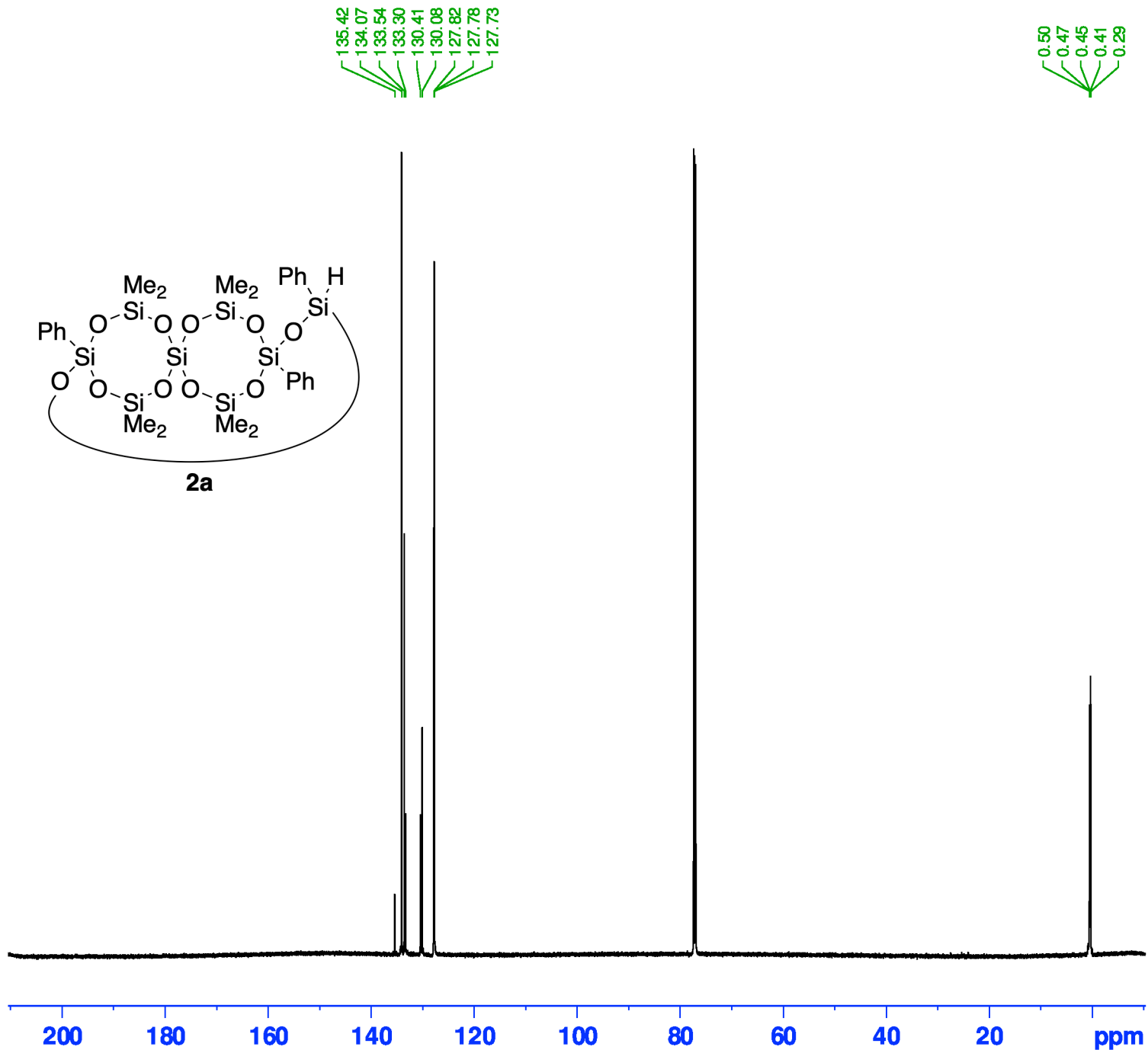
Current Data Parameters
NAME polysiloxane2a
EXPNO 10
PROCNO 1

F2 - Acquisition Parameter
Date_ 20190827
Time 12.22
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 32
DW 41.600 usec
DE 10.66 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 600.1330006 MHz
NUC1 1H
P1 11.00 usec
PLW1 25.00000000 W

F2 - Processing parameters
SI 65536
SF 600.1300142 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
    
```

Figure S21. <sup>13</sup>C NMR Spectra of Polysiloxane 2a



Current Data Parameters  
 NAME polysiloxane2a  
 EXPNO 11  
 PROCNO 1

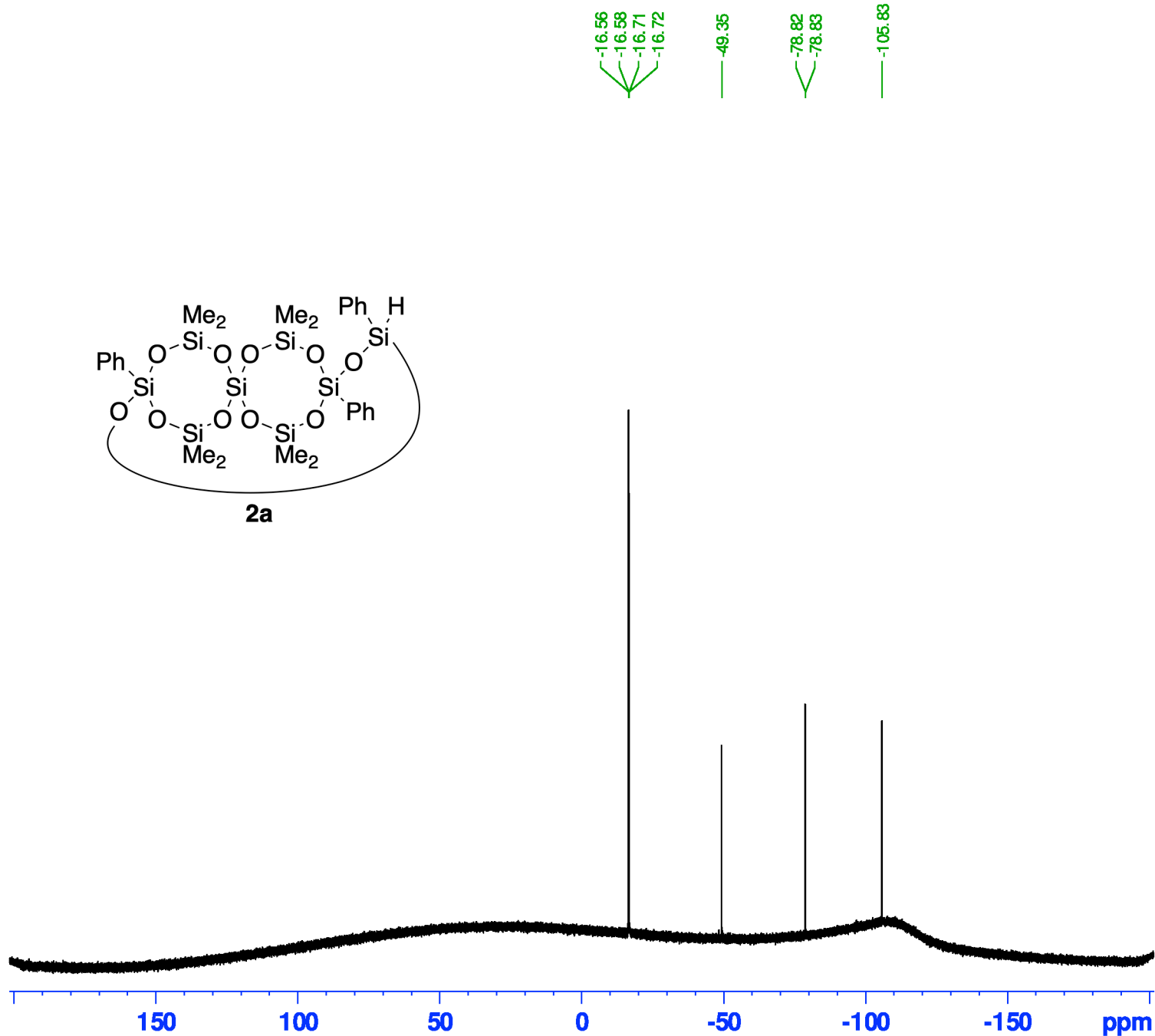
F2 - Acquisition Parameter  
 Date\_ 20190827  
 Time 16.07  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 33333.332 Hz  
 FIDRES 0.508626 Hz  
 AQ 0.9830400 sec  
 RG 193.87  
 DW 15.000 usec  
 DE 19.62 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 150.9430468 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 37.32500076 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W  
 PLW13 0.28435001 W

F2 - Processing parameters  
 SI 65536  
 SF 150.9279361 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S22.  $^{29}\text{Si}$  NMR Spectra of Polysiloxane 2a



```

Current Data Parameters
NAME polysiloxane2a
EXPNO 12
PROCNO 1

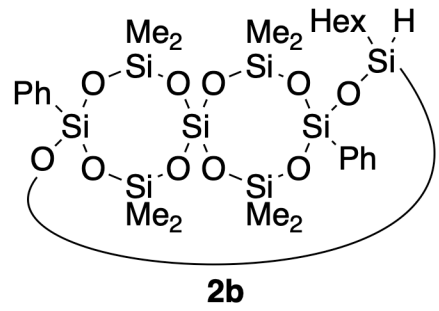
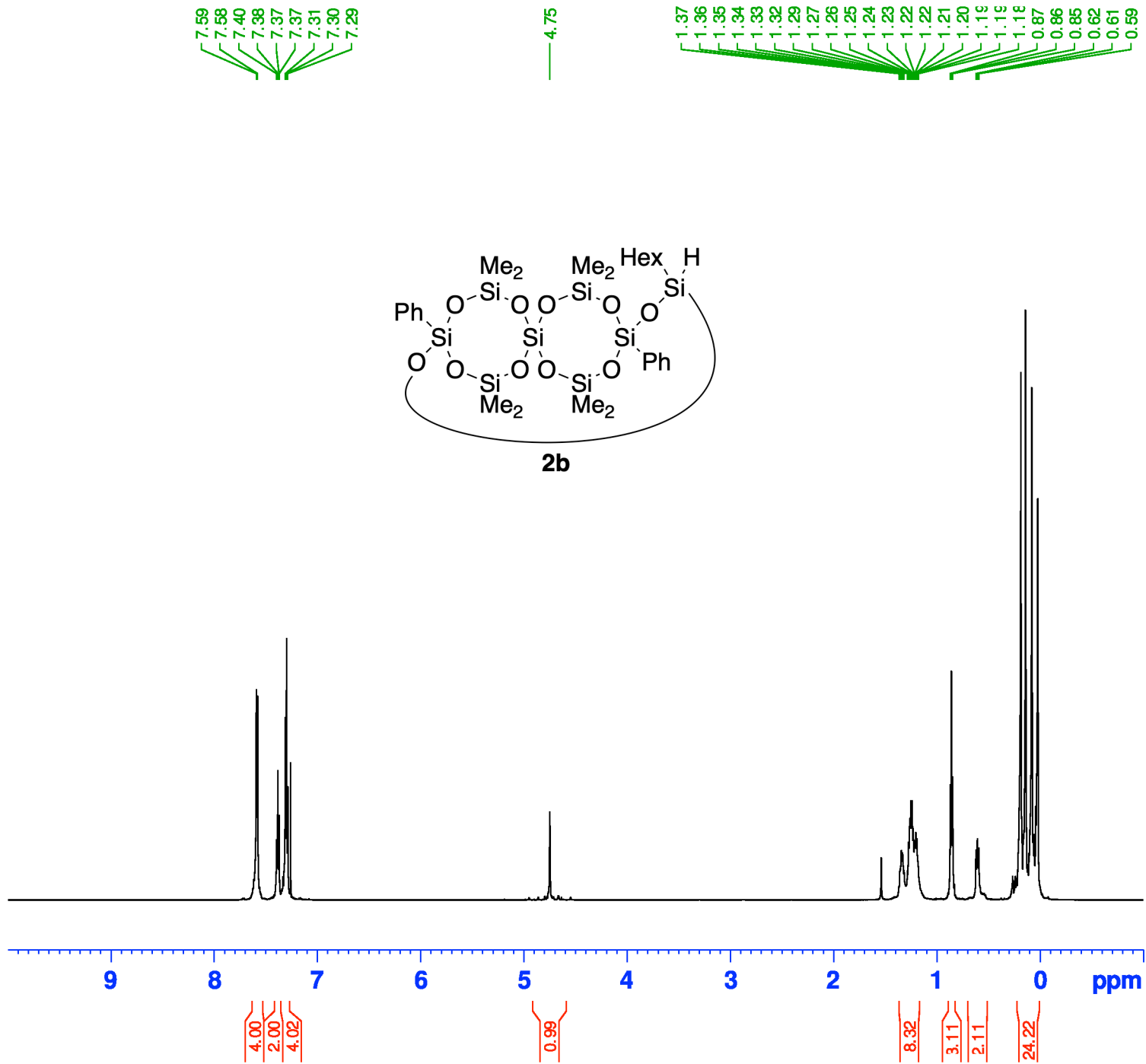
F2 - Acquisition Parameter
Date_ 20190827
Time 16.58
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgig30
TD 131072
SOLVENT CDCl3
NS 256
DS 2
SWH 48076.922 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 193.87
DW 10.400 usec
DE 18.90 usec
TE 298.0 K
D1 10.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 119.2488170 MHz
NUC1 29Si
P1 12.00 usec
PLW1 44.50000000 W

===== CHANNEL f2 =====
SFO2 600.2324009 MHz
NUC2 1H
CPDPRG[2] waltz65
PCPD2 70.00 usec
PLW2 19.26700020 W
PLW12 0.56620997 W

F2 - Processing parameters
SI 131072
SF 119.2488156 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
    
```

Figure S23. <sup>1</sup>H NMR Spectra of Polysiloxane 2b



```

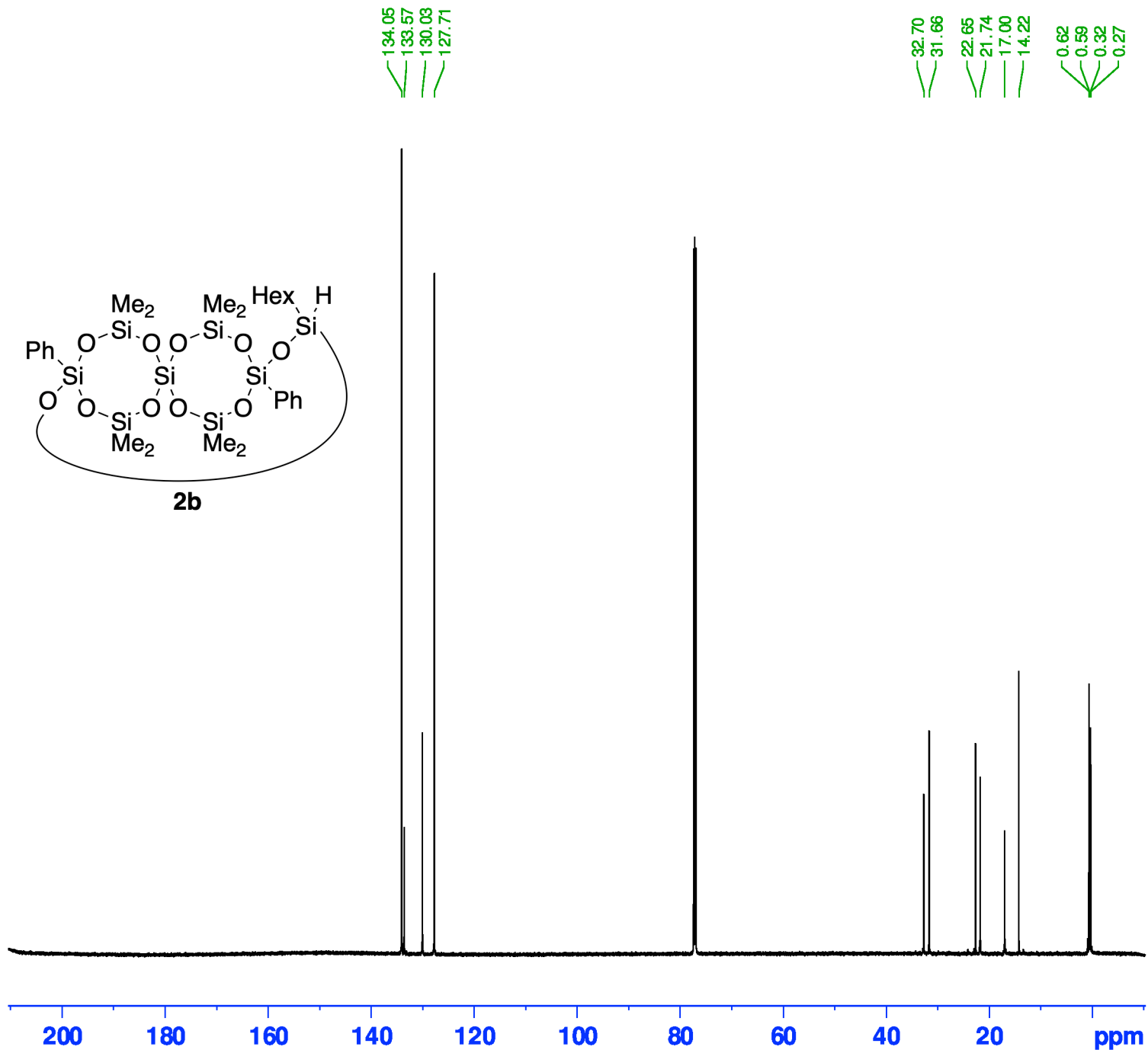
Current Data Parameters
NAME polysiloxane2b
EXPNO 10
PROCNO 1

F2 - Acquisition Parameter
Date_ 20190827
Time 14.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 28.5
DW 41.600 usec
DE 10.66 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 600.1330006 MHz
NUC1 1H
P1 11.00 usec
PLW1 25.00000000 W

F2 - Processing parameters
SI 65536
SF 600.1300141 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
    
```

Figure S24. <sup>13</sup>C NMR Spectra of Polysiloxane 2b



```

Current Data Parameters
NAME polysiloxane2b
EXPNO 11
PROCNO 1

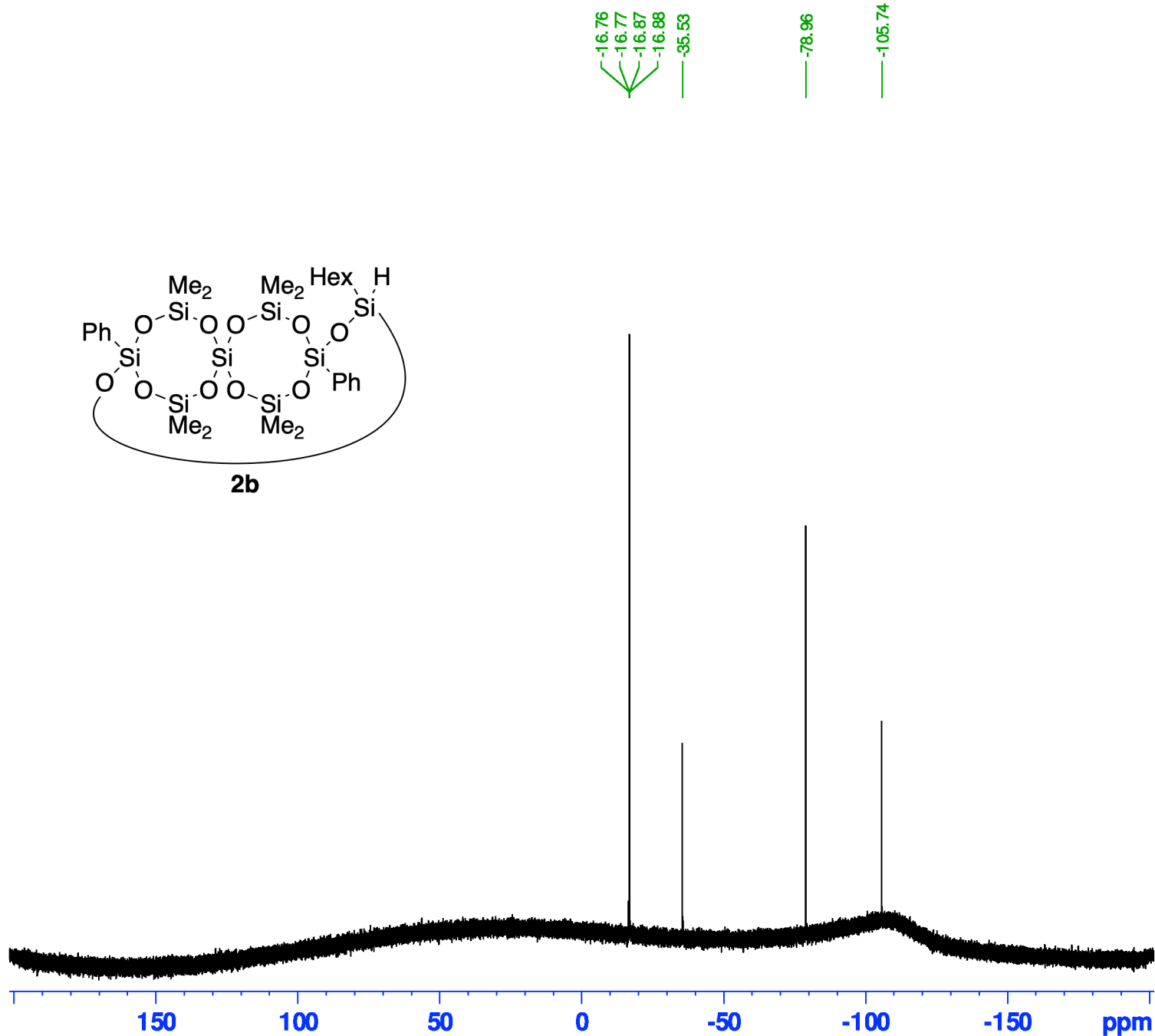
F2 - Acquisition Parameter
Date_ 20190827
Time 21.06
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 2
SWH 33333.332 Hz
FIDRES 0.508626 Hz
AQ 0.9830400 sec
RG 193.87
DW 15.000 usec
DE 19.62 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 150.9430468 MHz
NUC1 13C
P1 10.00 usec
PLW1 37.32500076 W

===== CHANNEL f2 =====
SFO2 600.2324009 MHz
NUC2 1H
CPDPRG[2] waltz65
PCPD2 70.00 usec
PLW2 19.26700020 W
PLW12 0.56620997 W
PLW13 0.28435001 W

F2 - Processing parameters
SI 65536
SF 150.9279349 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

Figure S25. <sup>29</sup>Si NMR Spectra of Polysiloxane 2b



Current Data Parameters  
 NAME polysiloxane2b  
 EXPNO 12  
 PROCNO 1

F2 - Acquisition Parameter  
 Date\_ 20190827  
 Time 21.21  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

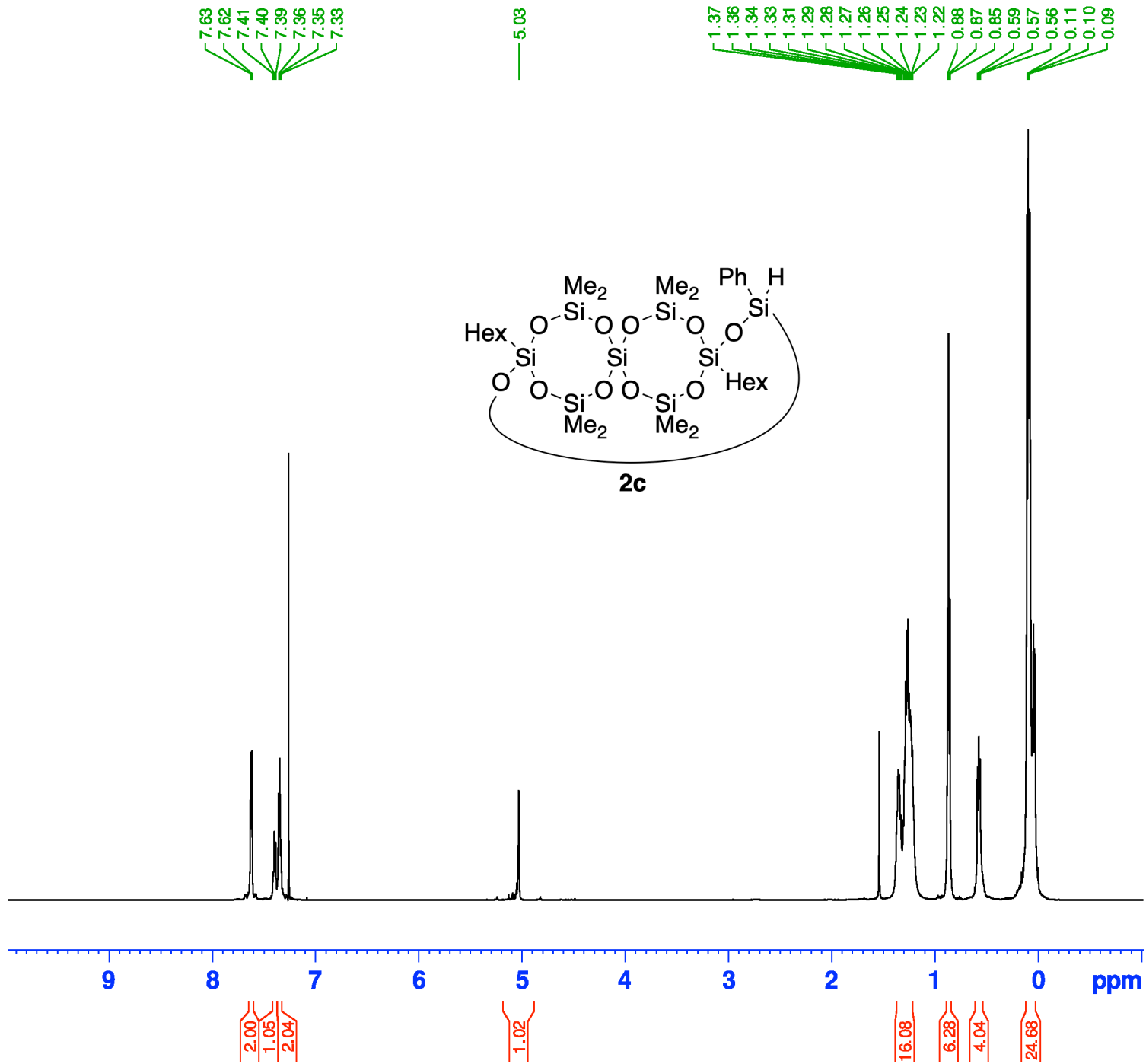
==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 29Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488156 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40



Figure S26. <sup>1</sup>H NMR Spectra of Polysiloxane 2c



```

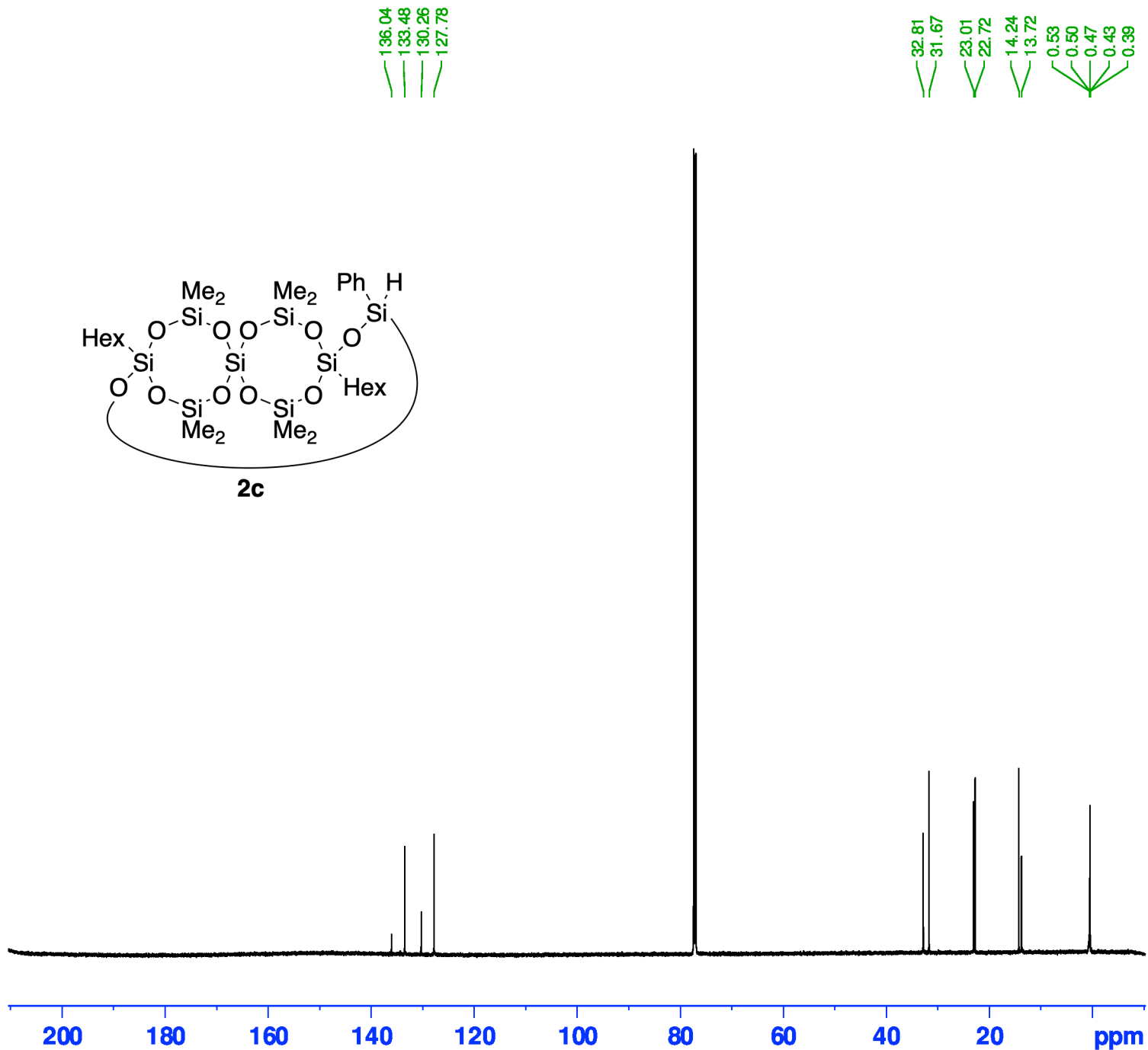
Current Data Parameters
NAME polysiloxane2c
EXPNO 10
PROCNO 1

F2 - Acquisition Parameter
Date_ 20190827
Time 14.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 50.8
DW 41.600 usec
DE 10.66 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 600.1330006 MHz
NUC1 1H
P1 11.00 usec
PLW1 25.00000000 W

F2 - Processing parameters
SI 65536
SF 600.1300142 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
    
```

Figure S27. <sup>13</sup>C NMR Spectra of Polysiloxane 2c



Current Data Parameters  
 NAME polysiloxane2c  
 EXPNO 11  
 PROCNO 1

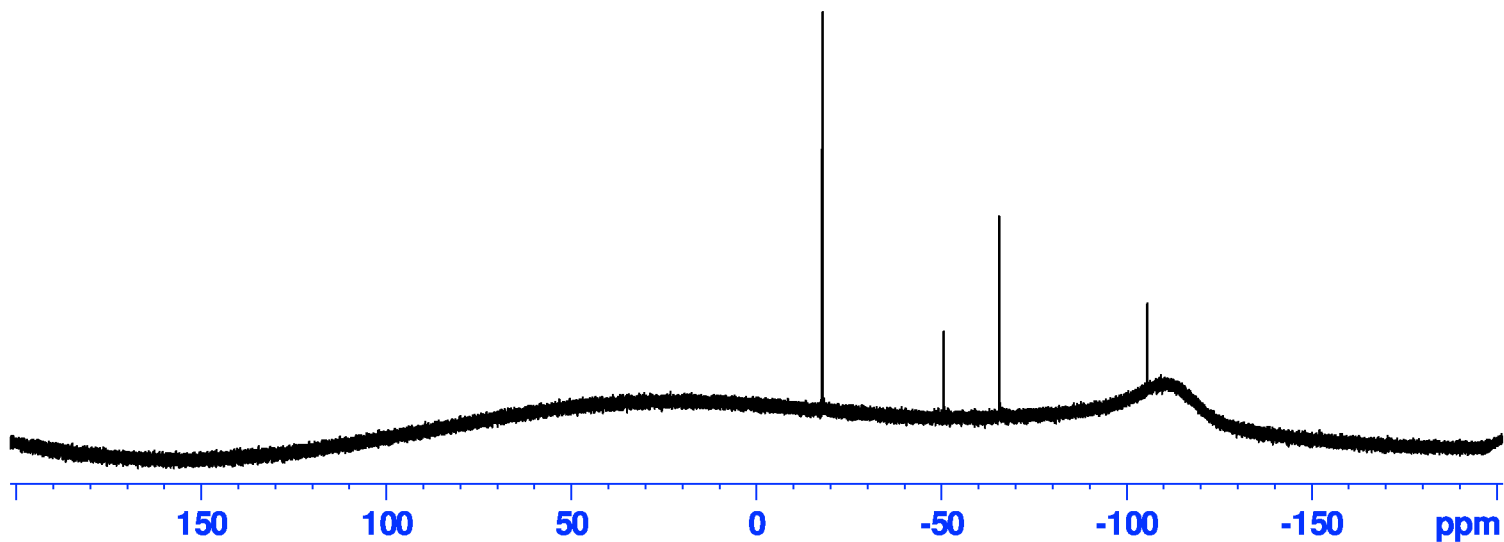
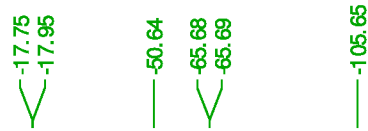
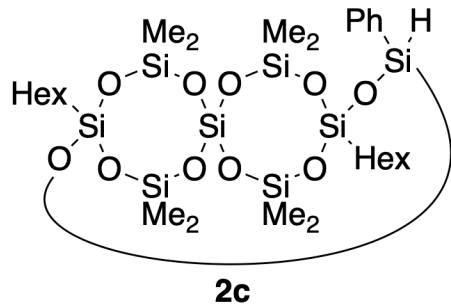
F2 - Acquisition Parameter  
 Date\_ 20190827  
 Time 18.36  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 33333.332 Hz  
 FIDRES 0.508626 Hz  
 AQ 0.9830400 sec  
 RG 193.87  
 DW 15.000 usec  
 DE 19.62 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 150.9430468 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 37.32500076 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W  
 PLW13 0.28435001 W

F2 - Processing parameters  
 SI 65536  
 SF 150.9279331 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S28. <sup>29</sup>Si NMR Spectra of Polysiloxane 2c



Current Data Parameters  
 NAME polysiloxane2c  
 EXPNO 12  
 PROCNO 1

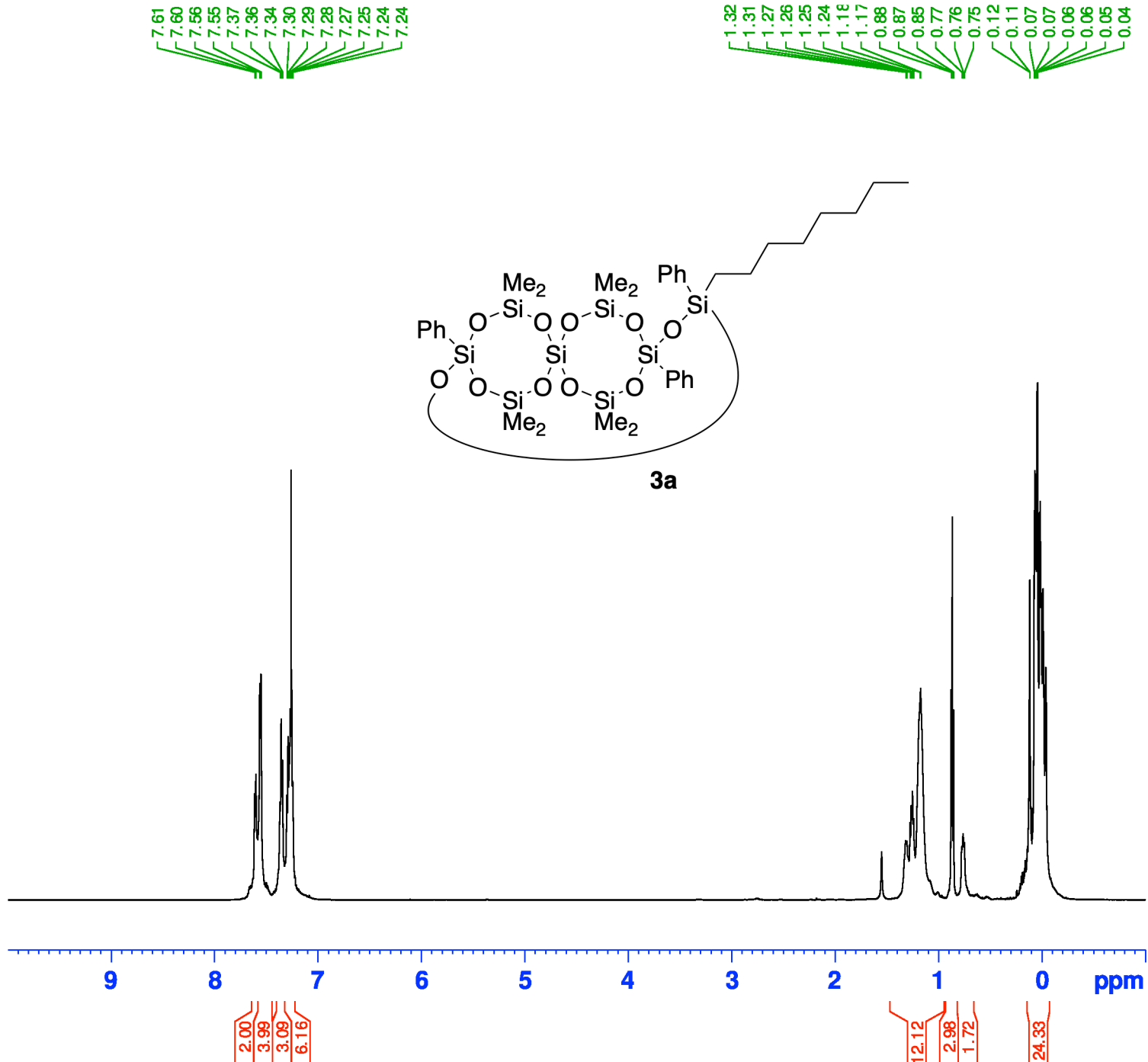
F2 - Acquisition Parameter  
 Date\_ 20190827  
 Time 19.27  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl3  
 NS 256  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 29Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488165 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40

Figure S29. <sup>1</sup>H NMR Spectra of Polysiloxane 3a



```

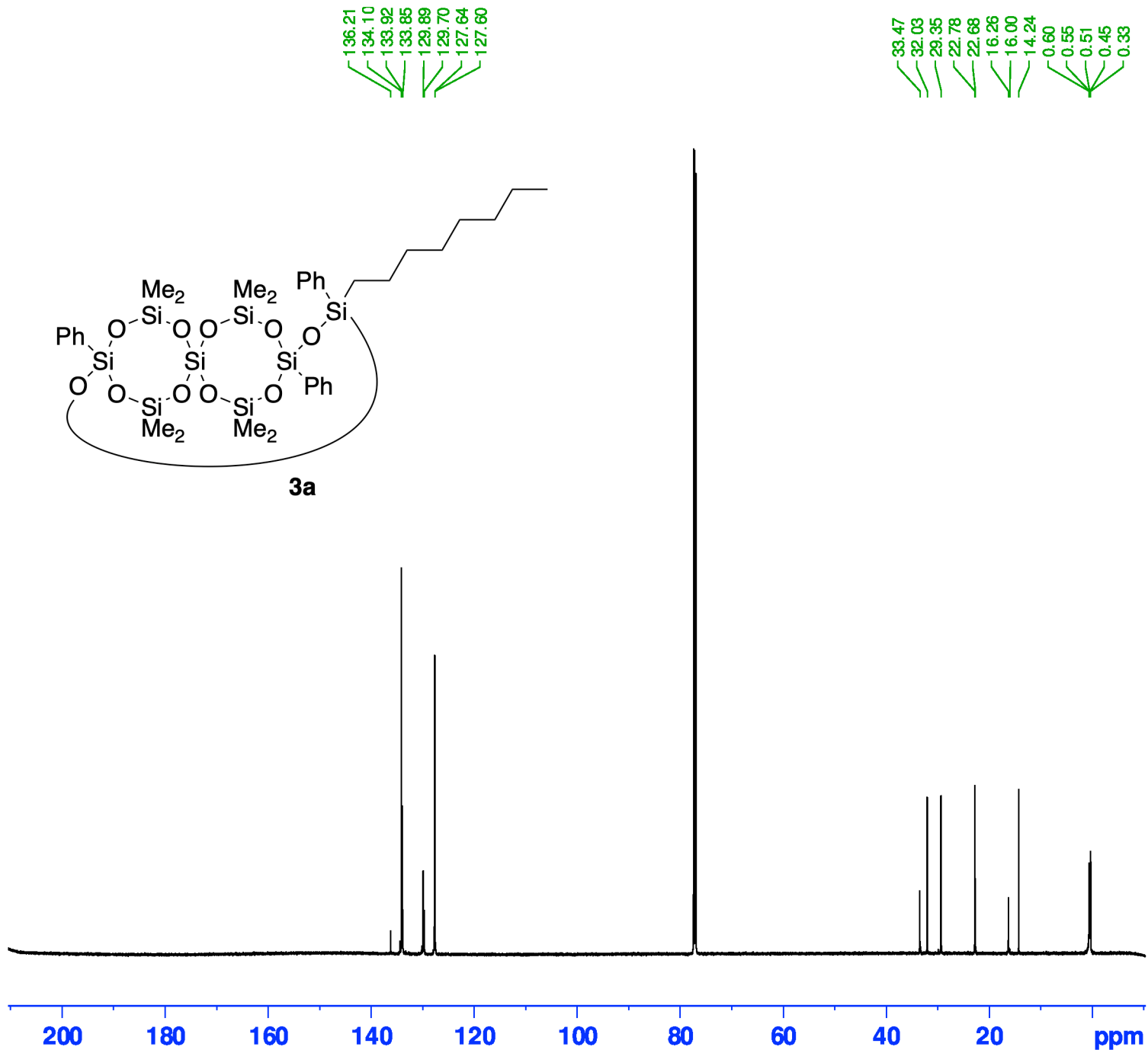
Current Data Parameters
NAME polysiloxane3a
EXPNO 10
PROCNO 1

F2 - Acquisition Parameter
Date_ 20191016
Time 11.26
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 50.8
DW 41.600 usec
DE 10.66 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 600.1330006 MHz
NUC1 1H
P1 11.00 usec
PLW1 25.00000000 W

F2 - Processing parameters
SI 65536
SF 600.1300143 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
    
```

Figure S30. <sup>13</sup>C NMR Spectra of Polysiloxane 3a



Current Data Parameters  
 NAME polysiloxane3a  
 EXPNO 11  
 PROCNO 1

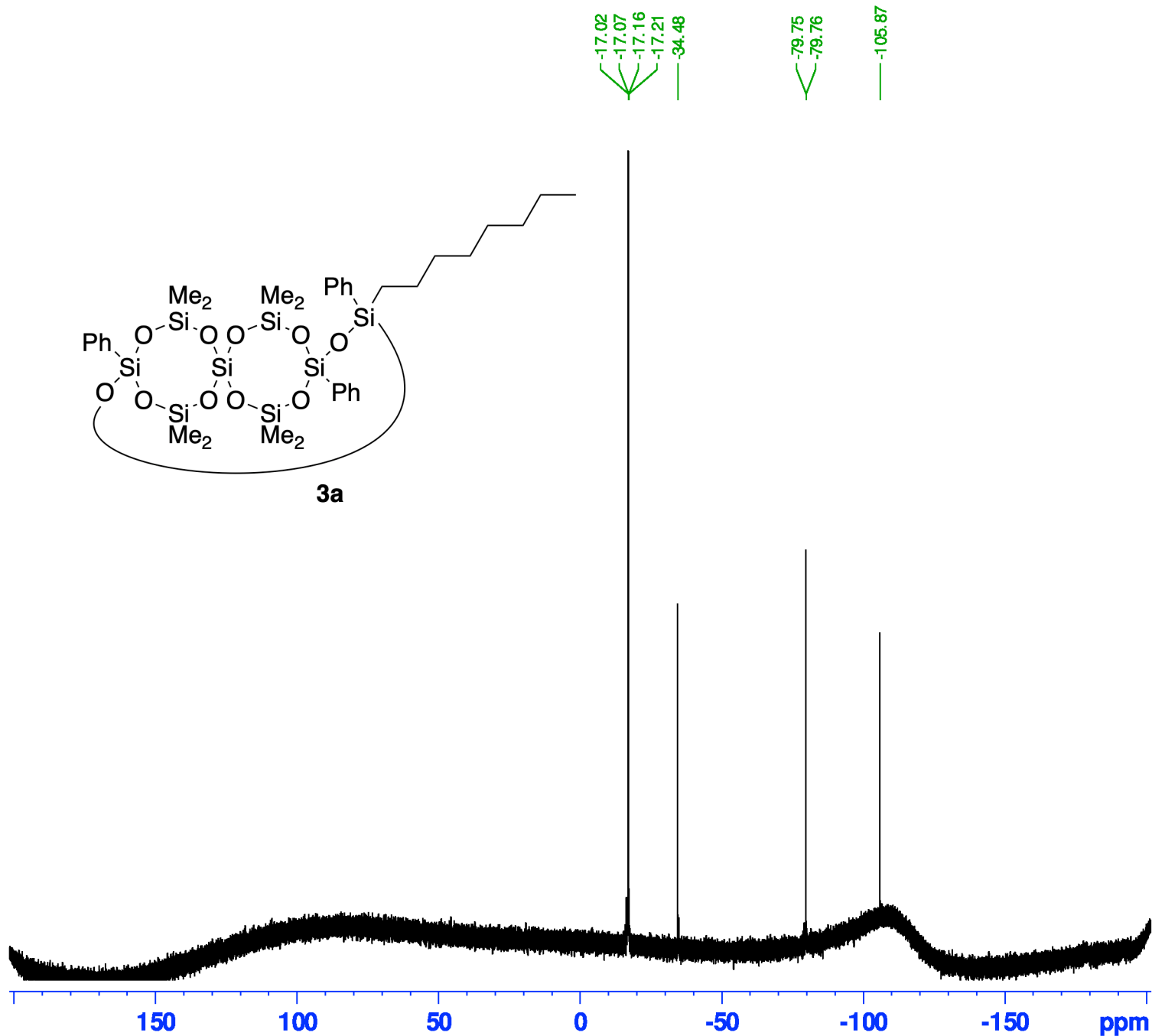
F2 - Acquisition Parameter  
 Date\_ 20191016  
 Time 21.18  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl<sub>3</sub>  
 NS 128  
 DS 2  
 SWH 33333.332 Hz  
 FIDRES 0.508626 Hz  
 AQ 0.9830400 sec  
 RG 193.87  
 DW 15.000 usec  
 DE 19.62 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 150.9430468 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 37.32500076 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W  
 PLW13 0.28435001 W

F2 - Processing parameters  
 SI 65536  
 SF 150.9279349 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S31. <sup>29</sup>Si NMR Spectra of Polysiloxane 3a



Current Data Parameters  
 NAME polysiloxane3a  
 EXPNO 12  
 PROCNO 1

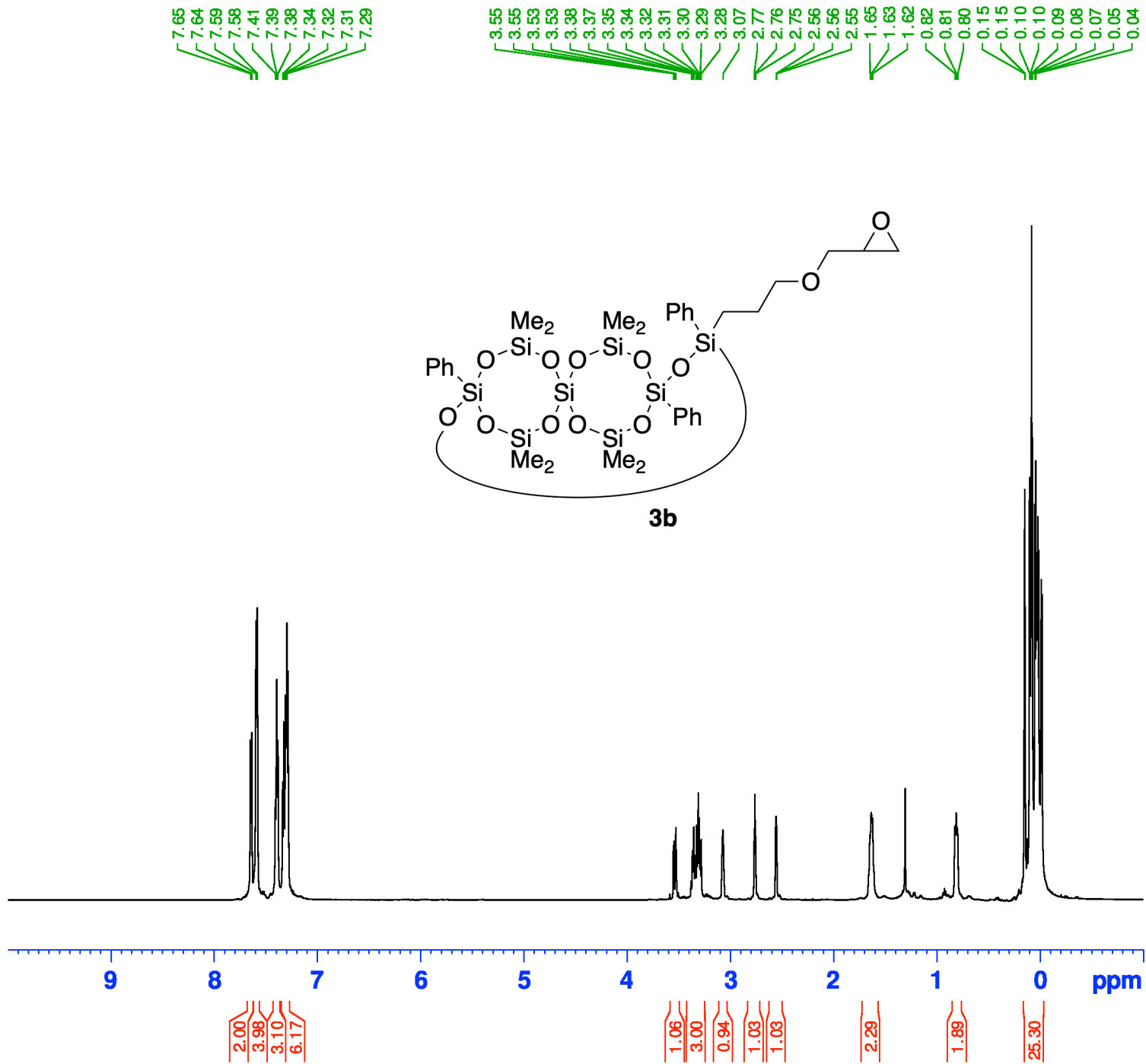
F2 - Acquisition Parameter  
 Date\_ 20191016  
 Time 22.09  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 256  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 29Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488156 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40

Figure S32. <sup>1</sup>H NMR Spectra of Polysiloxane 3b



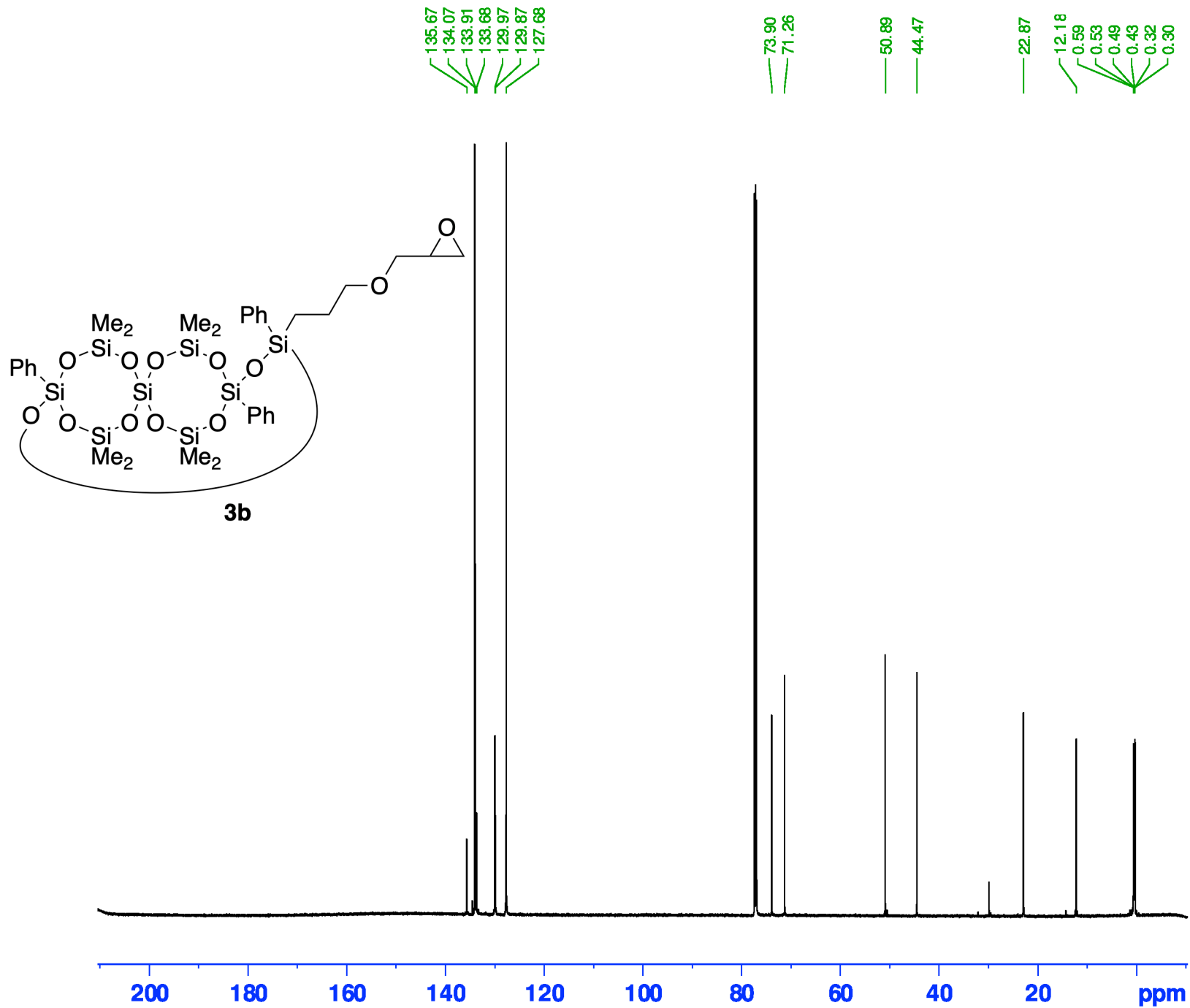
Current Data Parameters  
 NAME polysiloxane3b  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameter  
 Date\_ 20191023  
 Time 11.15  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 2  
 SWH 12019.230 Hz  
 FIDRES 0.183399 Hz  
 AQ 2.7262976 sec  
 RG 25.4  
 DW 41.600 usec  
 DE 10.66 usec  
 TE 298.0 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 SFO1 600.1330006 MHz  
 NUC1 1H  
 P1 11.00 usec  
 PLW1 25.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 600.1300000 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
 PC 1.00

Figure S33. <sup>13</sup>C NMR Spectra of Polysiloxane 3b



```

Current Data Parameters
NAME polysiloxane3b
EXPNO 11
PROCNO 1

F2 - Acquisition Parameter
Date_ 20191023
Time 12.46
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 33333.332 Hz
FIDRES 0.508626 Hz
AQ 0.9830400 sec
RG 193.87
DW 15.000 usec
DE 19.62 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

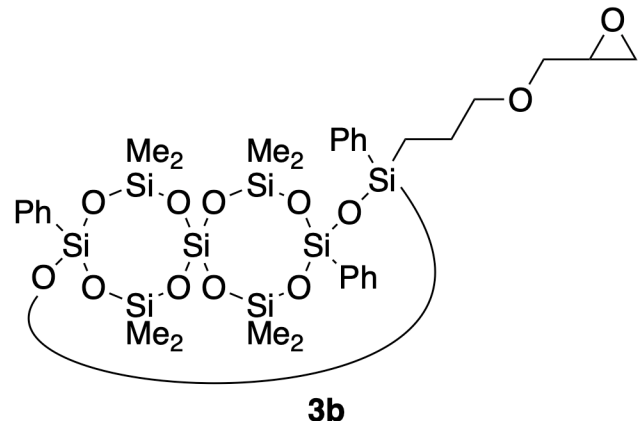
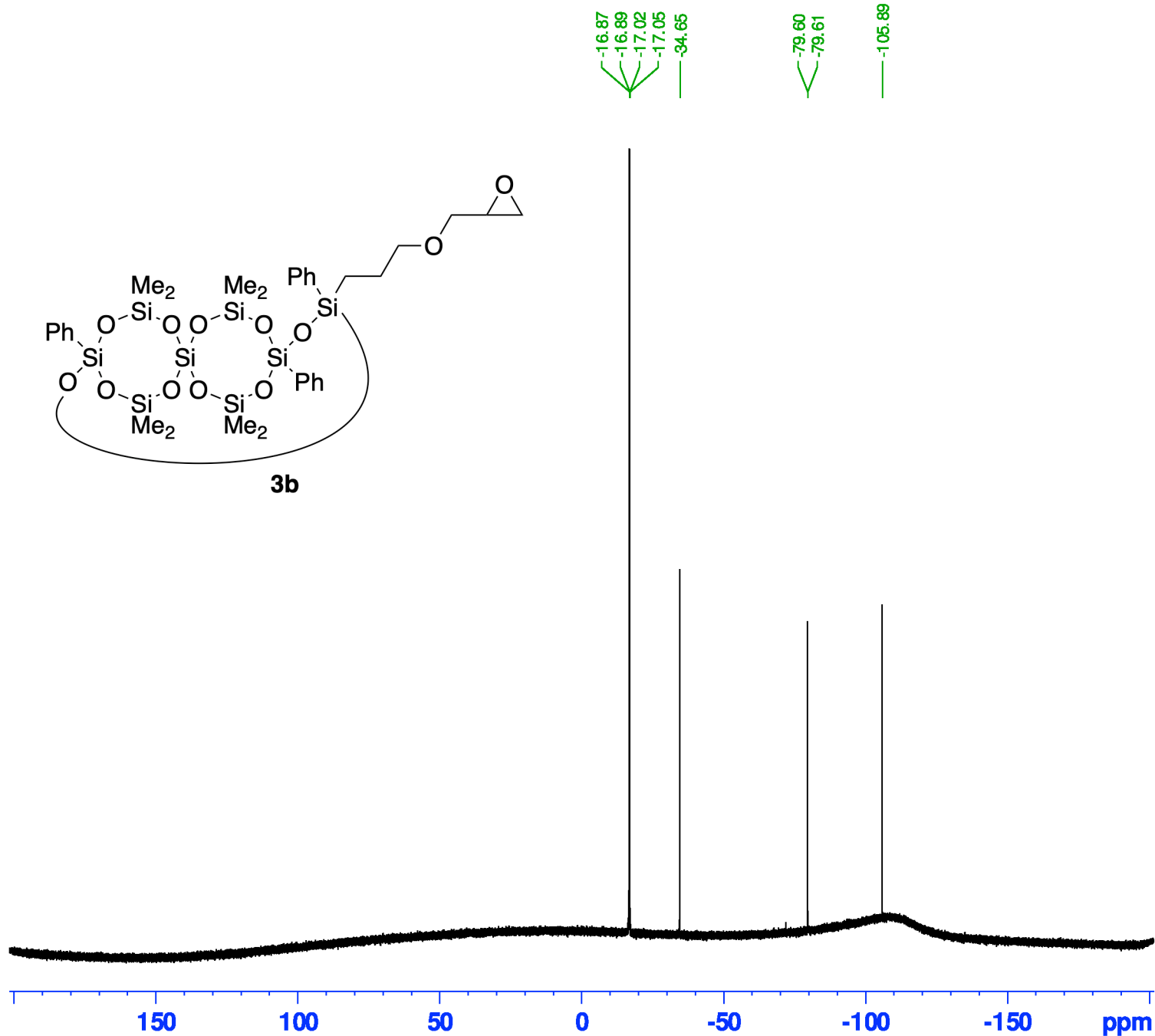
===== CHANNEL f1 =====
SFO1 150.9430468 MHz
NUC1 13C
P1 10.00 usec
PLW1 37.32500076 W

===== CHANNEL f2 =====
SFO2 600.2324009 MHz
NUC2 1H
CPDPRG[2] waltz65
PCPD2 70.00 usec
PLW2 19.26700020 W
PLW12 0.56620997 W
PLW13 0.28435001 W

F2 - Processing parameters
SI 65536
SF 150.9279385 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```



Figure S34. <sup>29</sup>Si NMR Spectra of Polysiloxane 3b



Current Data Parameters  
 NAME polysiloxane3b  
 EXPNO 12  
 PROCNO 1

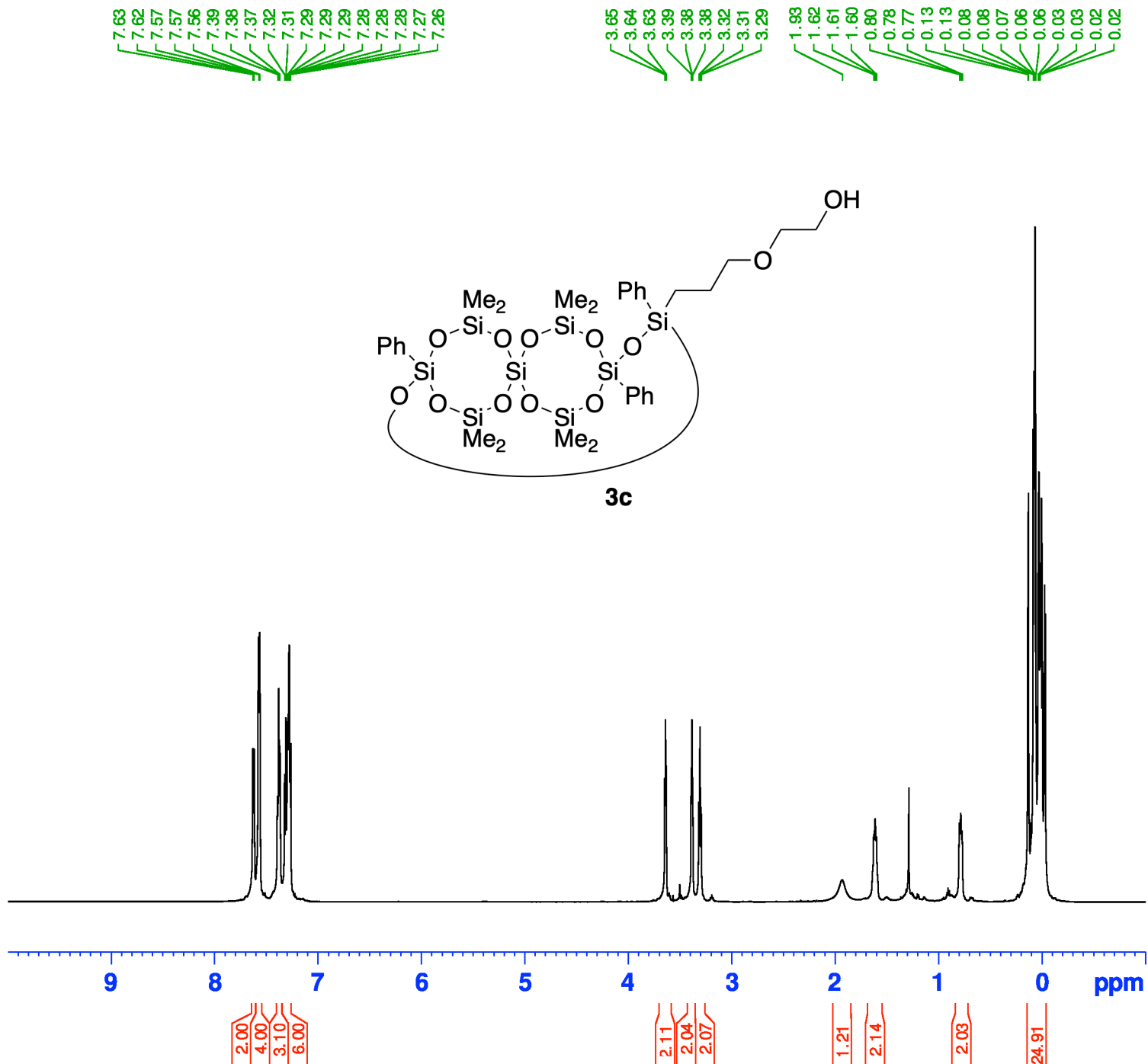
F2 - Acquisition Parameter  
 Date\_ 20191023  
 Time 13.37  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl3  
 NS 256  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 29Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488156 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40

Figure S35. <sup>1</sup>H NMR Spectra of Polysiloxane 3c



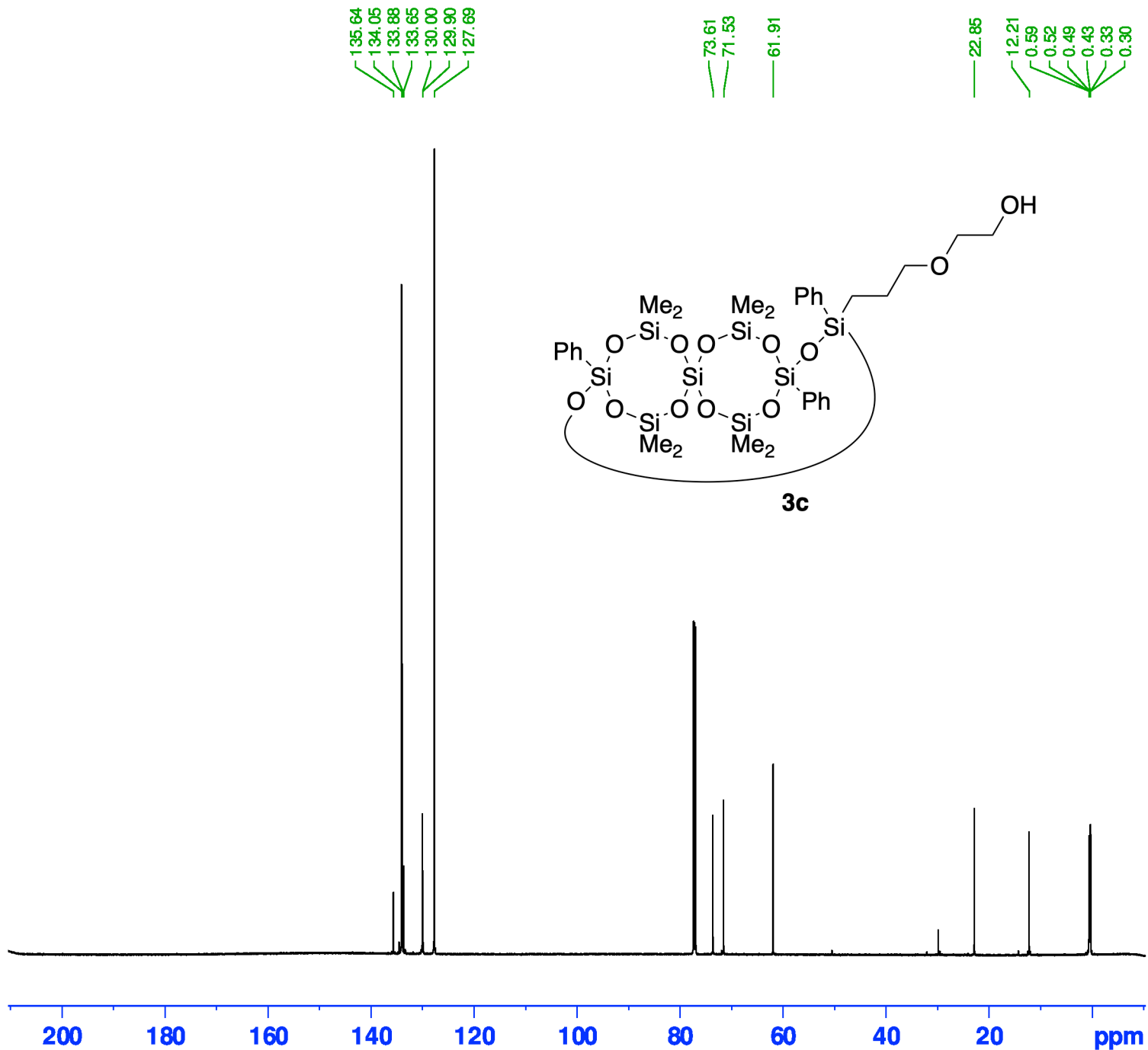
Current Data Parameters  
 NAME polysiloxane3c  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameter  
 Date\_ 20191017  
 Time 20.51  
 INSTRUM spect  
 PROBHD 5 mm PABBO BB/  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 2  
 SWH 12019.230 Hz  
 FIDRES 0.183399 Hz  
 AQ 2.7262976 sec  
 RG 22.6  
 DW 41.600 usec  
 DE 10.66 usec  
 TE 298.0 K  
 D1 1.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 SFO1 600.1330006 MHz  
 NUC1 1H  
 P1 11.00 usec  
 PLW1 25.00000000 W

F2 - Processing parameters  
 SI 65536  
 SF 600.1300141 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
 PC 1.00

Figure S36. <sup>13</sup>C NMR Spectra of Polysiloxane 3c



```

Current Data Parameters
NAME polysiloxane3c
EXPNO 11
PROCNO 1

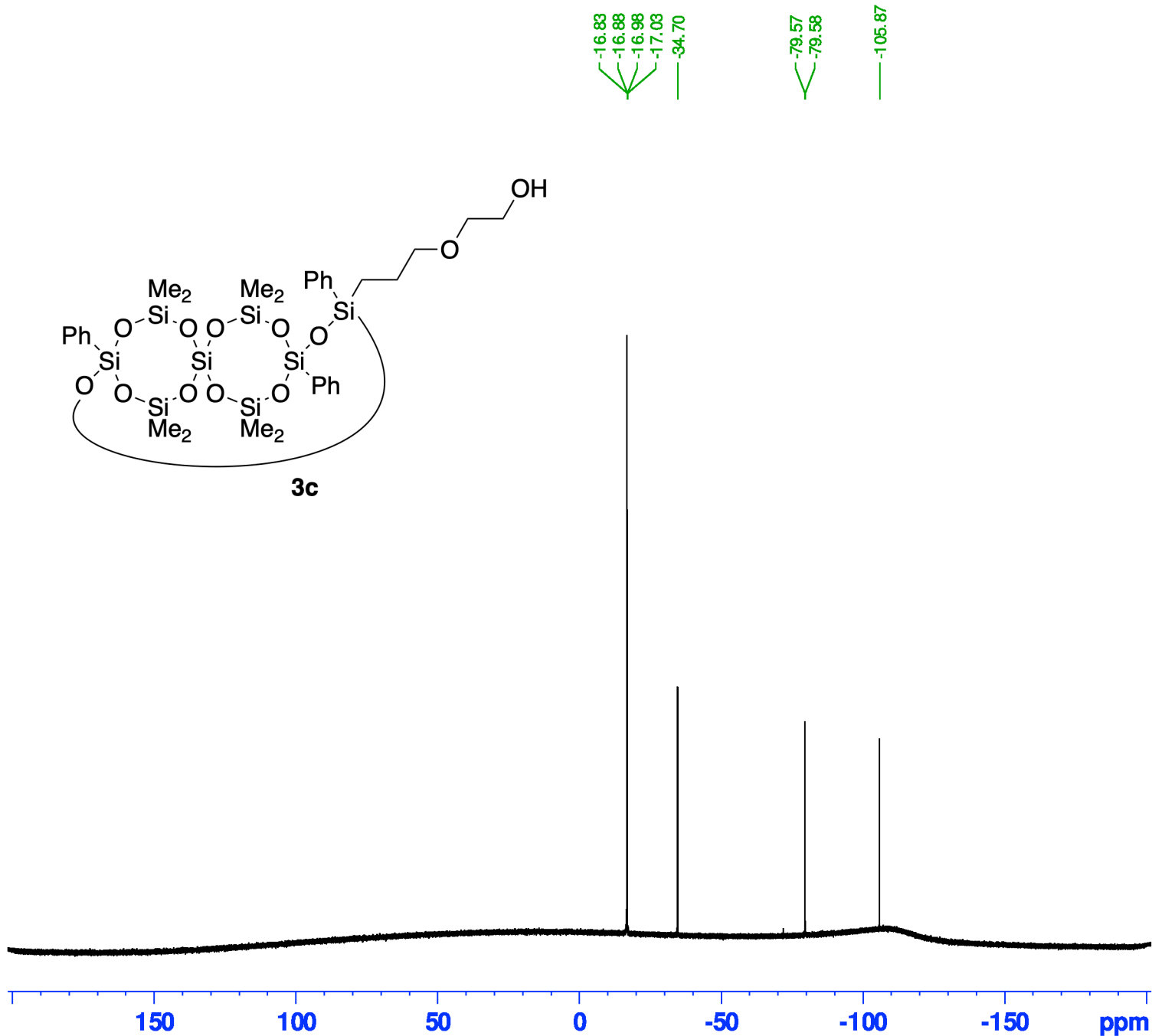
F2 - Acquisition Parameter
Date_ 20191017
Time 22.14
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 2
SWH 33333.332 Hz
FIDRES 0.508626 Hz
AQ 0.9830400 sec
RG 193.87
DW 15.000 usec
DE 19.62 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 150.9430468 MHz
NUC1 13C
P1 10.00 usec
PLW1 37.32500076 W

===== CHANNEL f2 =====
SFO2 600.2324009 MHz
NUC2 1H
CPDPRG[2] waltz65
PCPD2 70.00 usec
PLW2 19.26700020 W
PLW12 0.56620997 W
PLW13 0.28435001 W

F2 - Processing parameters
SI 65536
SF 150.9279398 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

Figure S37. <sup>29</sup>Si NMR Spectra of Polysiloxane 3c



Current Data Parameters  
 NAME polysiloxane3c  
 EXPNO 12  
 PROCNO 1

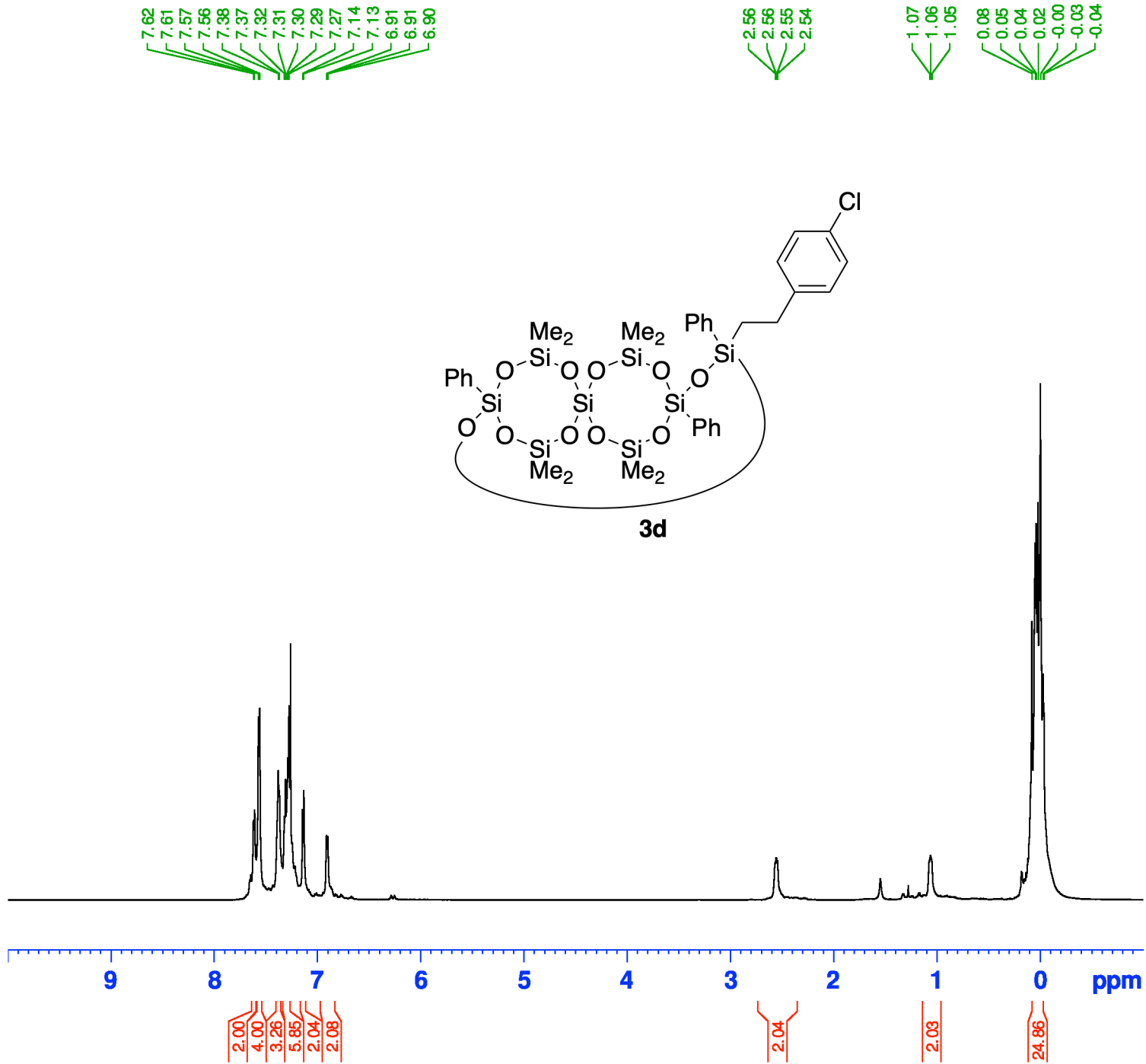
F2 - Acquisition Parameter  
 Date\_ 20191017  
 Time 23.05  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl3  
 NS 256  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 29Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488156 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40

Figure S38. <sup>1</sup>H NMR Spectra of Polysiloxane 3d



```

Current Data Parameters
NAME polysiloxane3d
EXPNO 10
PROCNO 1

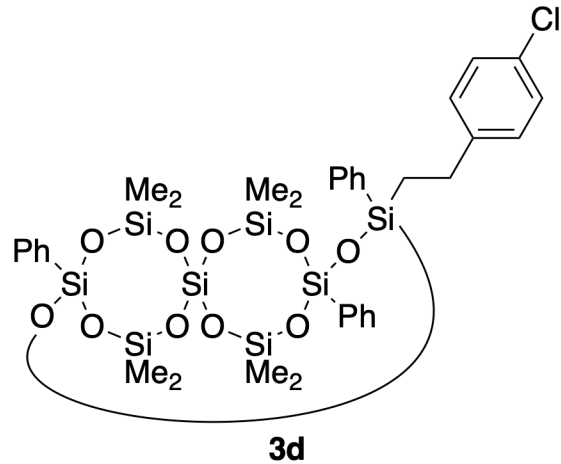
F2 - Acquisition Parameter
Date_ 20200716
Time 8.24
INSTRUM spect
PROBHD 5 mm CP2 BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 18
DW 41.600 usec
DE 15.65 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 600.1330006 MHz
NUC1 1H
P1 12.00 usec
PLW1 15.00000000 W

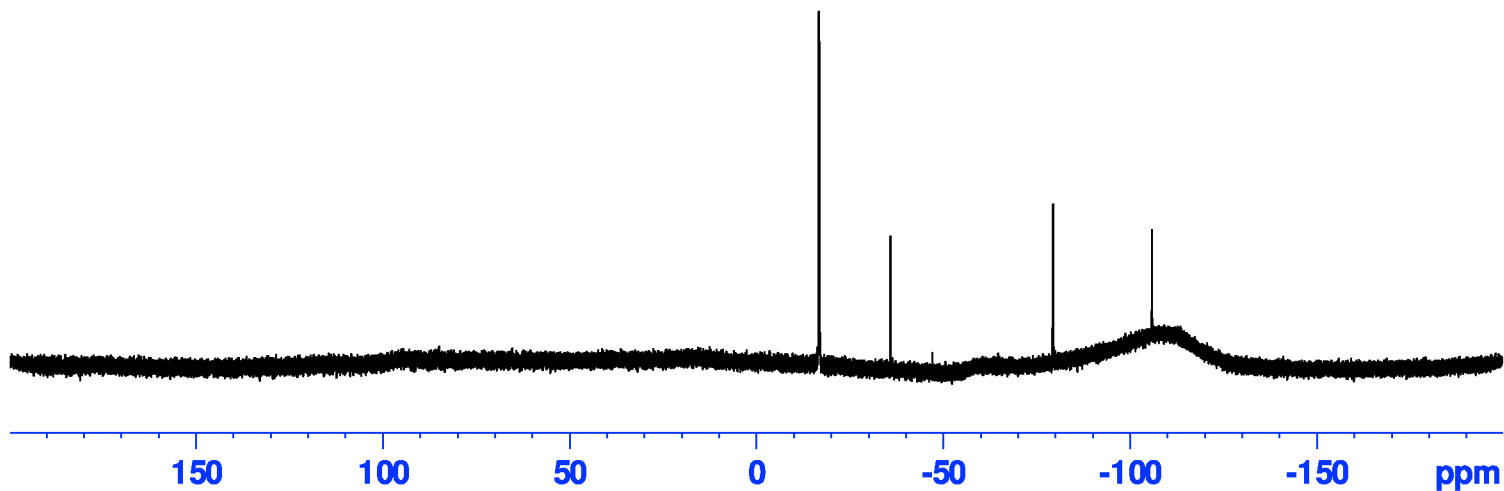
F2 - Processing parameters
SI 65536
SF 600.1300129 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
    
```



Figure S40. <sup>29</sup>Si NMR Spectra of Polysiloxane 3d



-16.75  
-16.80  
-16.92  
-16.97  
-35.94  
-79.50  
-105.92



```

Current Data Parameters
NAME polysiloxane3d
EXPNO 12
PROCNO 1

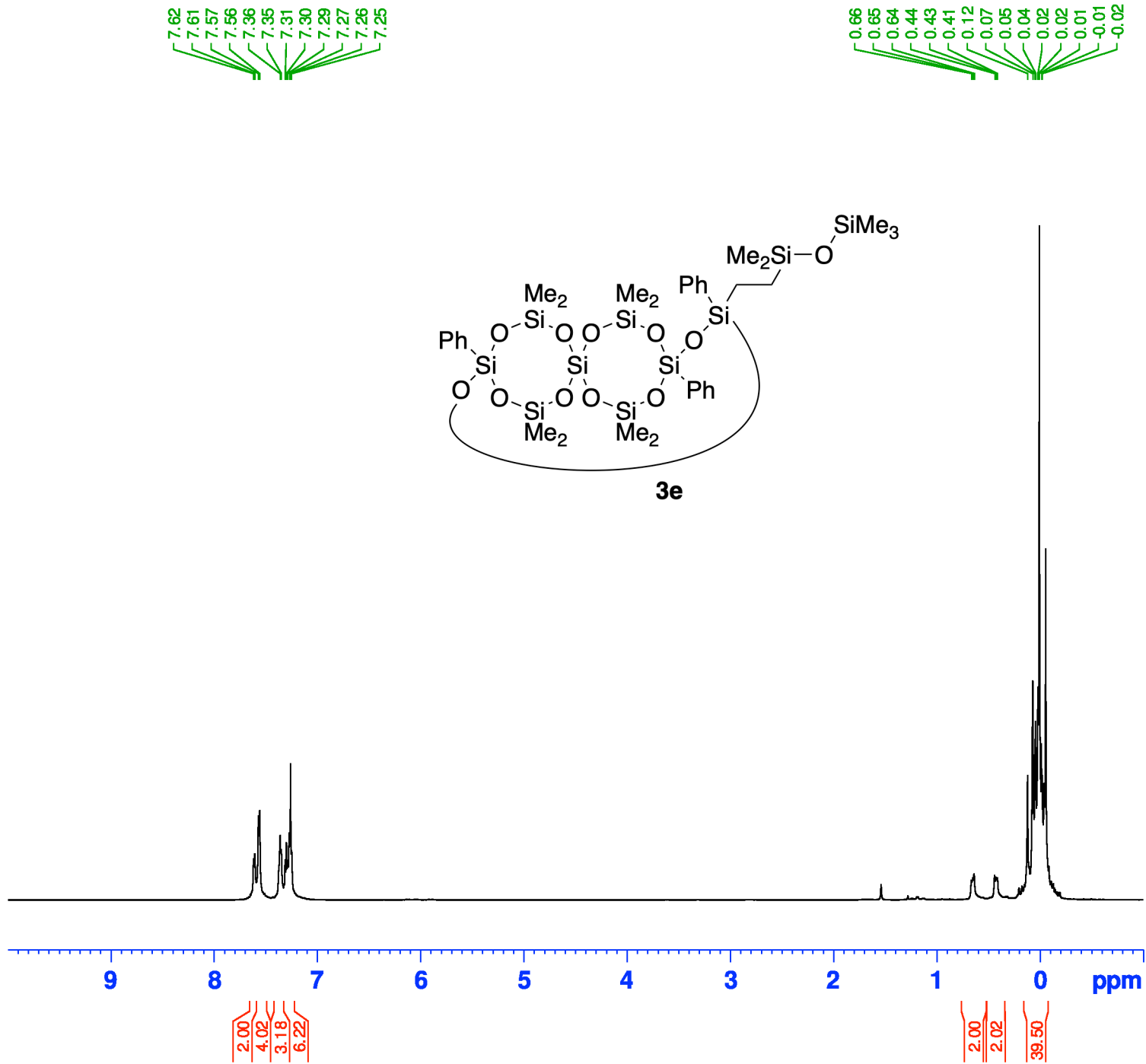
F2 - Acquisition Parameter
Date_ 20200716
Time 11.01
INSTRUM spect
PROBHD 5 mm CP2 BB-1H
PULPROG zgig30
TD 131072
SOLVENT CDCl3
NS 256
DS 2
SWH 47619.047 Hz
FIDRES 0.363304 Hz
AQ 1.3762560 sec
RG 114
DW 10.500 usec
DE 19.29 usec
TE 300.0 K
D1 10.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 119.2289493 MHz
NUC1 29Si
P1 12.00 usec
PLW1 48.00000000 W

===== CHANNEL f2 =====
SFO2 600.1324005 MHz
NUC2 1H
CPDPRG[2] waltz65
PCPD2 70.00 usec
PLW2 15.00000000 W
PLW12 0.44082001 W

F2 - Processing parameters
SI 131072
SF 119.2289480 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40
    
```

Figure S41. <sup>1</sup>H NMR Spectra of Polysiloxane 3e



7.62  
7.61  
7.57  
7.56  
7.36  
7.35  
7.31  
7.30  
7.29  
7.27  
7.26  
7.25

0.66  
0.65  
0.64  
0.44  
0.43  
0.41  
0.12  
0.07  
0.05  
0.04  
0.02  
0.02  
0.01  
-0.01  
-0.02

Current Data Parameters  
 NAME polysiloxane3e  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameter  
 Date\_ 20200716  
 Time 8.27  
 INSTRUM spect  
 PROBHD 5 mm CP2 BB-1H  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 8  
 DS 2  
 SWH 12019.230 Hz  
 FIDRES 0.183399 Hz  
 AQ 2.7262976 sec  
 RG 16  
 DW 41.600 usec  
 DE 15.65 usec  
 TE 298.0 K  
 D1 1.00000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 600.1330006 MHz  
 NUC1 1H  
 P1 12.00 usec  
 PLW1 15.00000000 W

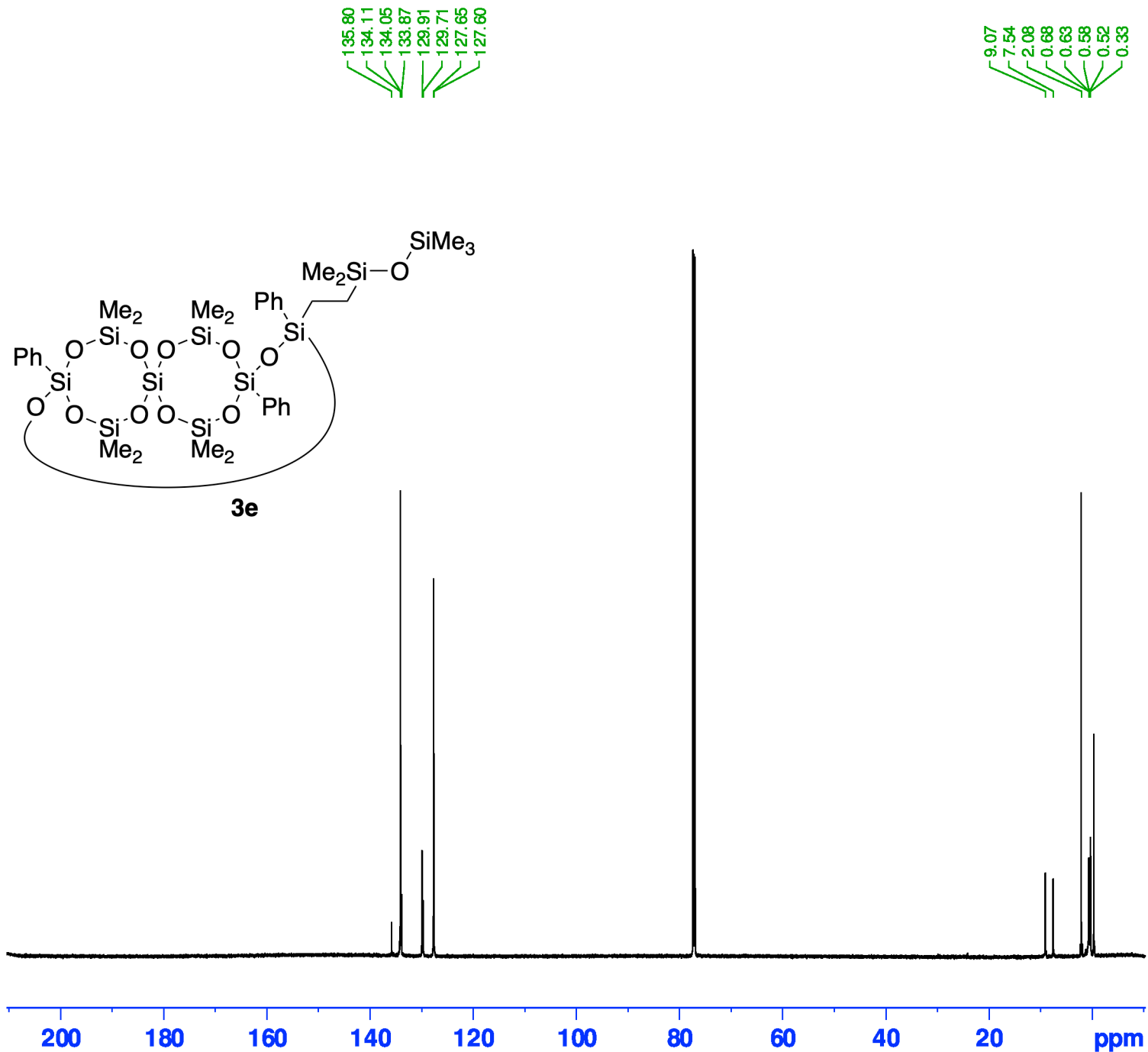
F2 - Processing parameters  
 SI 65536  
 SF 600.1300128 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
 PC 1.00

2.00  
4.02  
3.18  
6.22

2.00  
2.02  
39.50



Figure S42. <sup>13</sup>C NMR Spectra of Polysiloxane 3e



Current Data Parameters  
 NAME polysiloxane3e  
 EXPNO 11  
 PROCNO 1

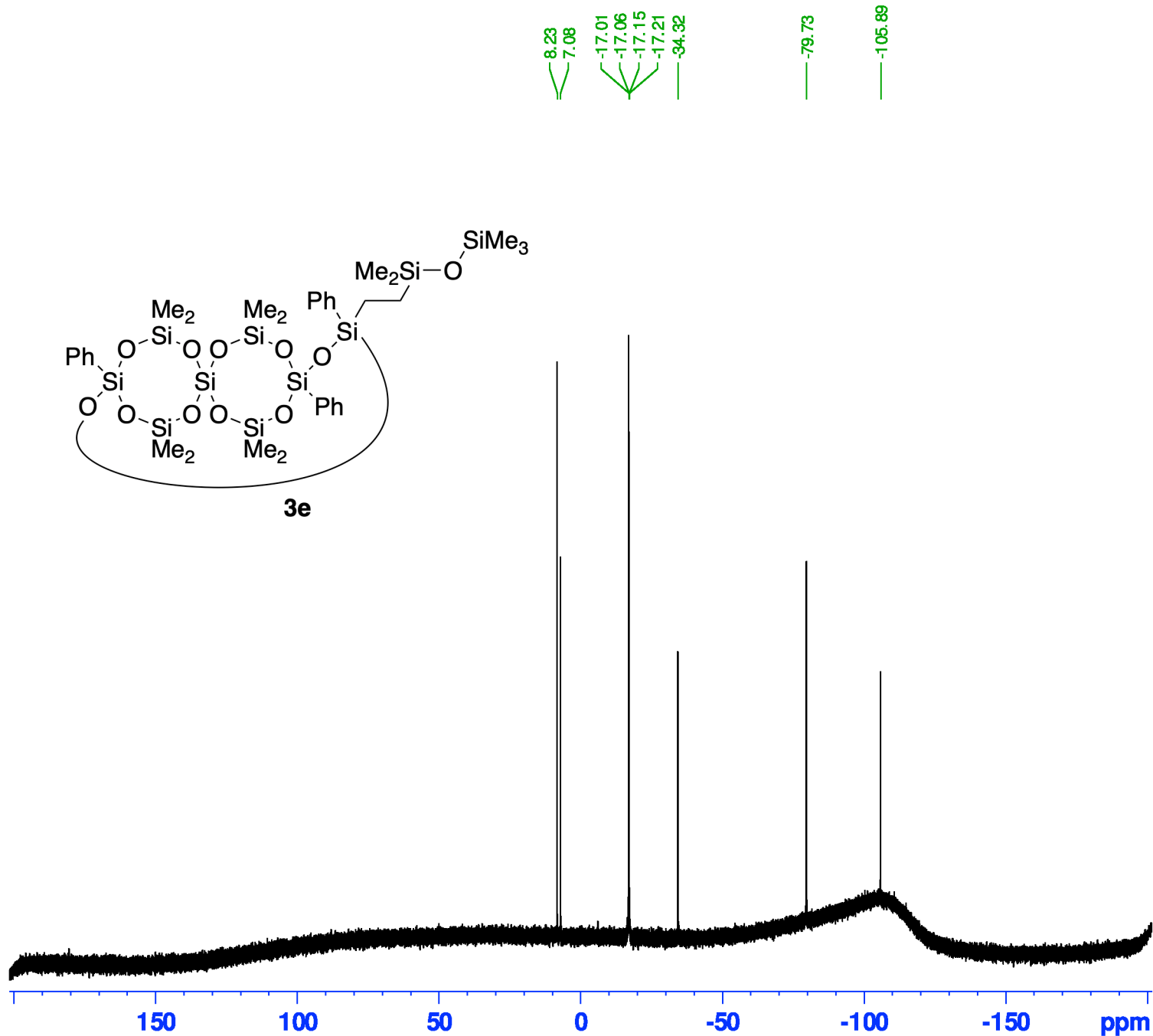
F2 - Acquisition Parameter  
 Date\_ 20200716  
 Time 10.56  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgpg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 64  
 DS 2  
 SWH 33333.332 Hz  
 FIDRES 0.508626 Hz  
 AQ 0.9830400 sec  
 RG 193.87  
 DW 15.000 usec  
 DE 19.62 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 150.9430468 MHz  
 NUC1 13C  
 P1 10.00 usec  
 PLW1 37.32500076 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 1H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W  
 PLW13 0.28435001 W

F2 - Processing parameters  
 SI 65536  
 SF 150.9279356 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

Figure S43.  $^{29}\text{Si}$  NMR Spectra of Polysiloxane 3e



Current Data Parameters  
 NAME polysiloxane3e  
 EXPNO 12  
 PROCNO 1

F2 - Acquisition Parameter  
 Date\_ 20200716  
 Time 11.48  
 INSTRUM spect  
 PROBHD 5 mm CPBBO BB-  
 PULPROG zgig30  
 TD 131072  
 SOLVENT CDCl<sub>3</sub>  
 NS 256  
 DS 2  
 SWH 48076.922 Hz  
 FIDRES 0.366798 Hz  
 AQ 1.3631488 sec  
 RG 193.87  
 DW 10.400 usec  
 DE 18.90 usec  
 TE 298.0 K  
 D1 10.00000000 sec  
 D11 0.03000000 sec  
 TD0 1

==== CHANNEL f1 =====  
 SFO1 119.2488170 MHz  
 NUC1 <sup>29</sup>Si  
 P1 12.00 usec  
 PLW1 44.50000000 W

==== CHANNEL f2 =====  
 SFO2 600.2324009 MHz  
 NUC2 <sup>1</sup>H  
 CPDPRG[2] waltz65  
 PCPD2 70.00 usec  
 PLW2 19.26700020 W  
 PLW12 0.56620997 W

F2 - Processing parameters  
 SI 131072  
 SF 119.2488156 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.40