Electronic Supplementary Information

Facile synthesis and bridgehead-functionalization of bicyclo[3.3.3]pentasiloxanes

Yuki Yokouchi,[a] Shintaro Ishida,[a] Tsunenobu Onodera,[b] Hidetoshi Oikawa[b] and Takeaki Iwamoto*[,a]

a. Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.

b. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Aoba-ku, Sendai 980-8577, Japan.

E-mail: iwamoto@m.tohoku.ac.jp

Contents

1. Experimental Details S2
    General Procedure S2
    Materials S2
    Synthesis of **1** S2
    Synthesis of **4** S6
    Synthesis of **5** S10
    Synthesis of **7** S14
    Synthesis of **8** S17
    Synthesis of **9** S20
2. Single crystal X-ray diffraction analyses of **1** and **9** S24
3. Thermogravimetric Analyses of **1** S27
4. Theoretical calculation S28
5. References S31

1. Experimental Details

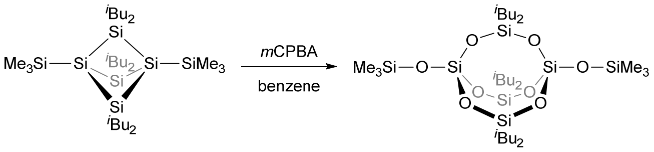
General Procedure

All reactions treating air-sensitive compounds were carried out under an inert atmosphere (N_2 or Ar) using a high-vacuum line and standard Schlenk techniques, or a glove box, as well as dry and oxygen-free solvents. NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H NMR chemical shifts were referenced to residual ^{1}H of the solvents; C_6D_6 (^{1}H δ 7.16).[S1] The ^{13}C and ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm (δ 0.00). Sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glove box. Mass spectra were recorded on a Bruker Daltonics SolariX 9.4T. UV-vis spectra were recorded on a JASCO V-660 spectrometer. Recycling preparative HPLC using ethanol (EtOH) as an eluent was performed at 5.0 mL/min rate using a Japan Analytical Industry Co., LC9201 equipped with an ODS column (FUJI SILYSIA CHEMICAL LTD., Chromatorex® C18, 20ϕ mm × 250 mm). Thermogravimetric analysis (TGA) was undertaken using a Perkin-Elmer Pyris 1 TGA apparatus under a nitrogen atmosphere (100 mL/min). Differential scanning calorimetry (DSC) was measured using Pyris Diamond DSC (PerkinElmer) under a nitrogen atmosphere (100 mL/min).

Materials

Benzene, toluene, and THF were dried with VAC-103991 type solvent purifiers. Benzene-d_6 (C_6D_6) was dried with molecular sieves (3A). Potassium *tert*-butoxide (^{t}BuOK), 18-crown-6-ether (18-c-6), *m*-chloroperoxidebenzoicacid (*m*CPBA) in 60~70% purity, iodomethane (MeI), *tert*-butylchlorodimethylsilane (^{t}BuMe$_2$SiCl), chlorodimethylvinylsilane, triethylamine (NEt_3), and standard organic solvents were commercially available and used without further purification. 1,3-bis(trimethylsilyl)hexaisobutylbicyclo[1.1.1]pentasilane (**2**) was prepared according to the published procedures.[S2]

Synthesis of 1

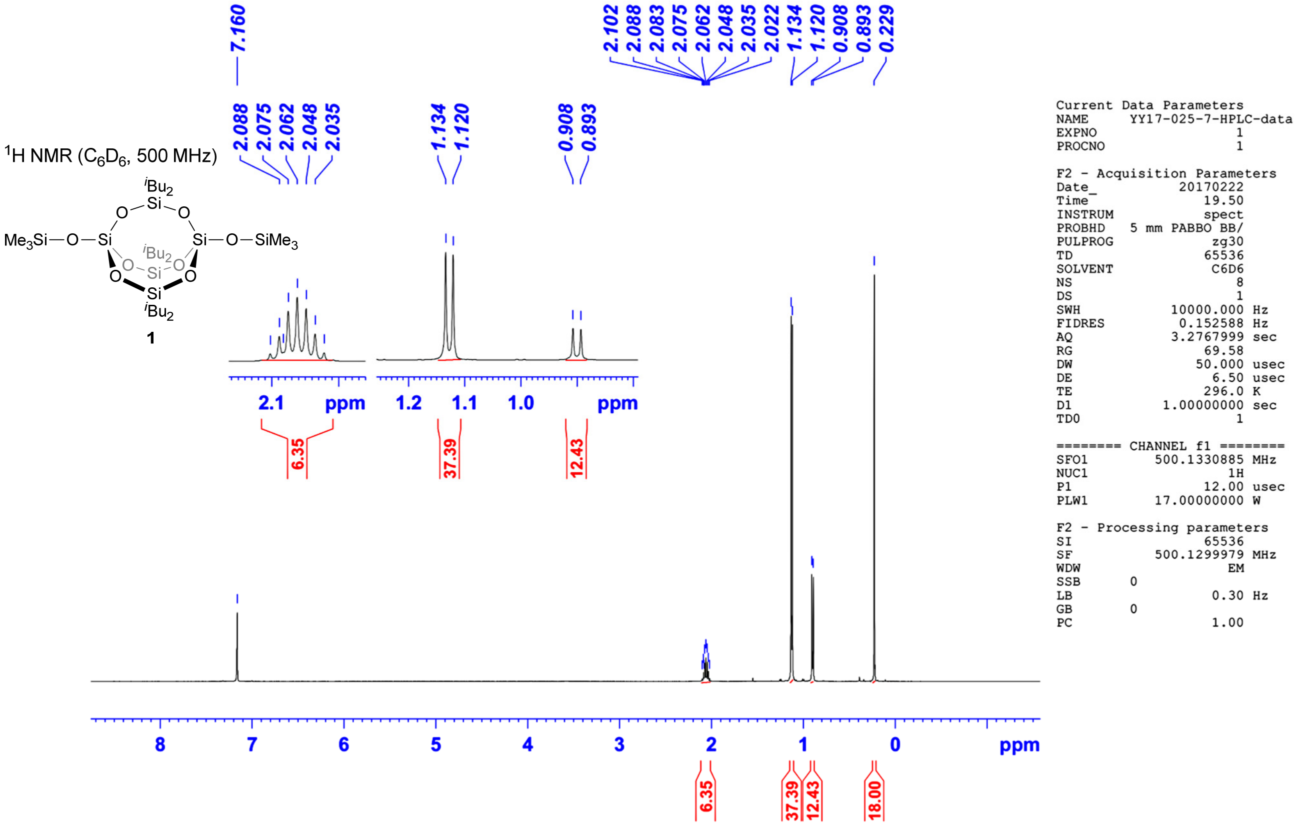


2

1, 72%

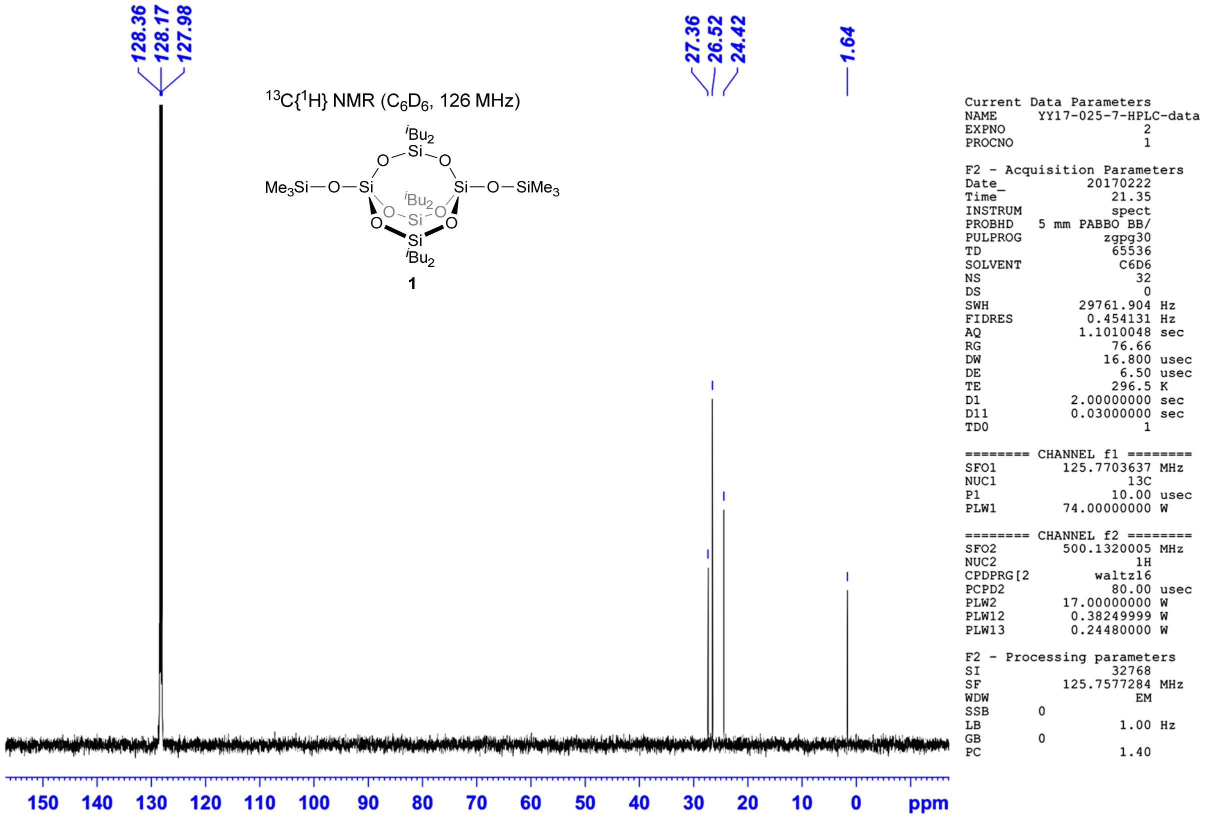
In a round-bottom flask (200 mL) equipped with a magnetic stir bar, **2** (795 mg, 1.26 mmol), *m*CPBA (3.10 g, ca. 11.5 mmol) and benzene (40 mL) were placed. The reaction mixture was stirred for 2 d at 50 °C and then the volatiles were removed under reduced pressure. The resulting residue was dissolved in hexane and then the mixture was subjected to silica-gel column chromatography to remove insoluble materials, the resulting benzoic acid, and unidentified yellow materials. Removal of the solvent in *vacuo* afforded analytically pure **1** (696 mg, 0.919 mmol, 72%) as a colorless powder.

1: a colorless powder; mp 68-69 °C; ^{1}H NMR (500 MHz, C_6D_6, 296 K) δ 0.23 (s, 18H, Si(CH_3)$_3$), 0.90 (d, J = 7.1 Hz, 12H, CH_2CH(CH$_3$)$_2$)), 1.13 (d, J = 6.6 Hz, 36H, CH$_2$CH(CH_3)$_2$)), 2.02 – 2.11 (m, 6H, CH$_2$CH(CH$_3$)$_2$)); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K) δ 1.6 (Si(CH$_3$)$_3$), 24.4 (CH$_2$$C$H(CH$_3$)$_2$), 26.5 (CH$_2$CH($CH_3$)$_2$), 27.4 ($CH_2$CH(CH$_3$)$_2$); ^{29}Si NMR (99.4 MHz, C_6D_6, 296 K) δ −101.7 (Si^{Q}), −15.2 (Si^{D}), 11.5 (Si^{M}); Elemental Anal. calcd for $C_{30}H_{72}O_6Si_7$: C, 47.57; H, 9.58%; found: C, 47.70; H, 9.66%; MS (EI, 70 eV) *m*/*z* (%) 741 (29) [M^+-CH$_3$], 699 (100) [M^+-C$_4$H$_9$].



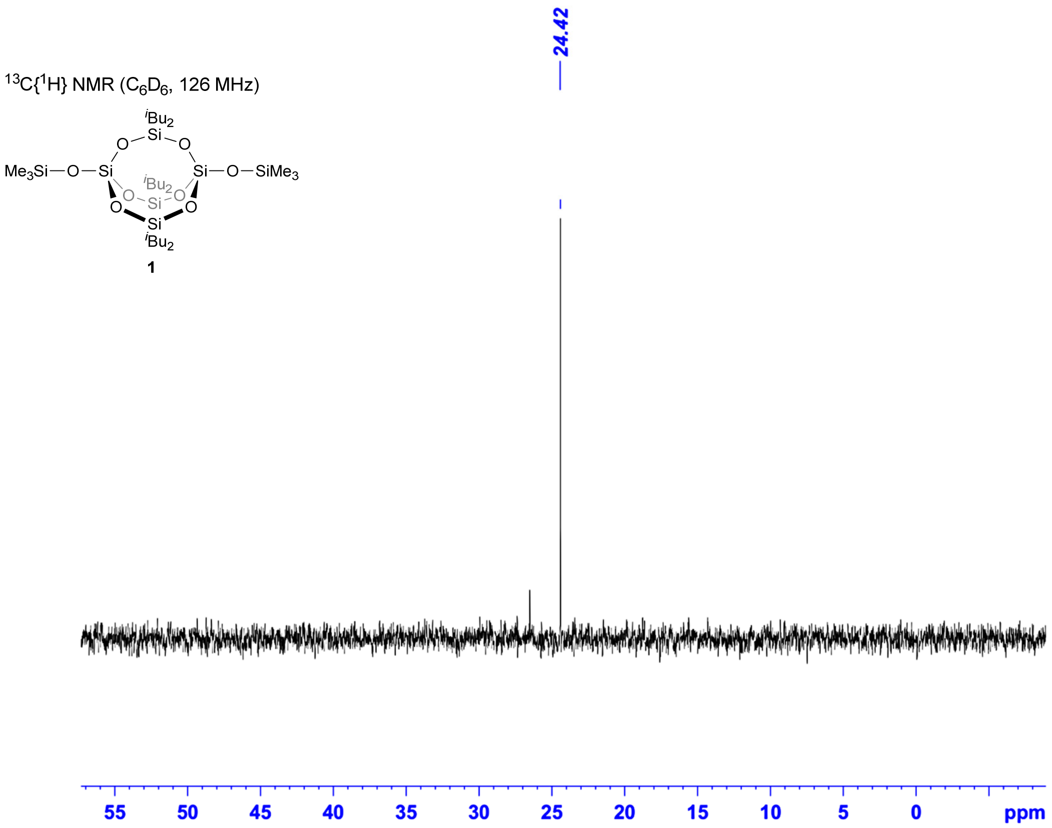
```
Current Data Parameters
NAME      YY17-025-7-HPLC-data
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170222
Time                 19.50
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT               C6D6
NS                       8
DS                       1
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2767999 sec
RG                   69.58
DW                  50.000 usec
DE                    6.50 usec
TE                   296.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           17.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1299979 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6 (126 MHz, 296 K).



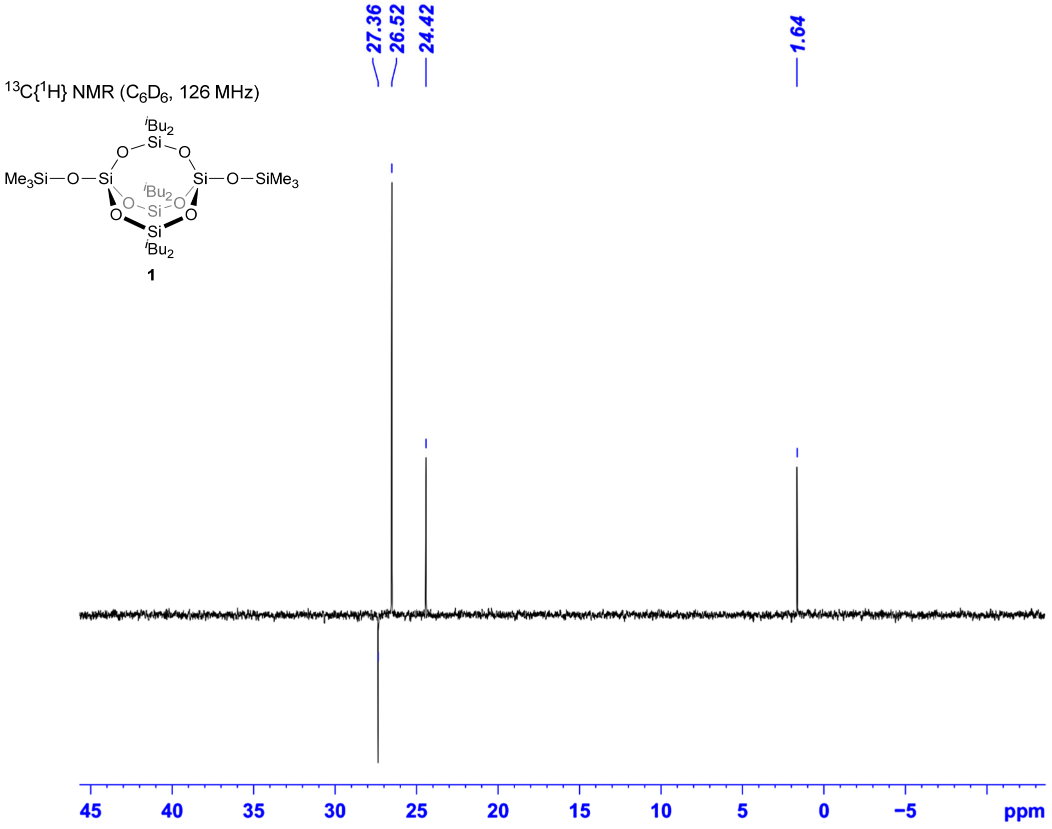
```
Current Data Parameters
NAME      YY17-025-7-HPLC-data
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170222
Time                 21.35
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT               C6D6
NS                      32
DS                       0
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                   76.66
DW                  16.800 usec
DE                    6.50 usec
TE                   296.5 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           125.7703637 MHz
NUC1                   13C
P1                   10.00 usec
PLW1           74.00000000 W

======== CHANNEL f2 ========
SFO2           500.1320005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           17.00000000 W
PLW12           0.38249999 W
PLW13           0.24480000 W

F2 - Processing parameters
SI                   32768
SF             125.7577284 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **1** in C_6D_6 (126 MHz, 297 K).



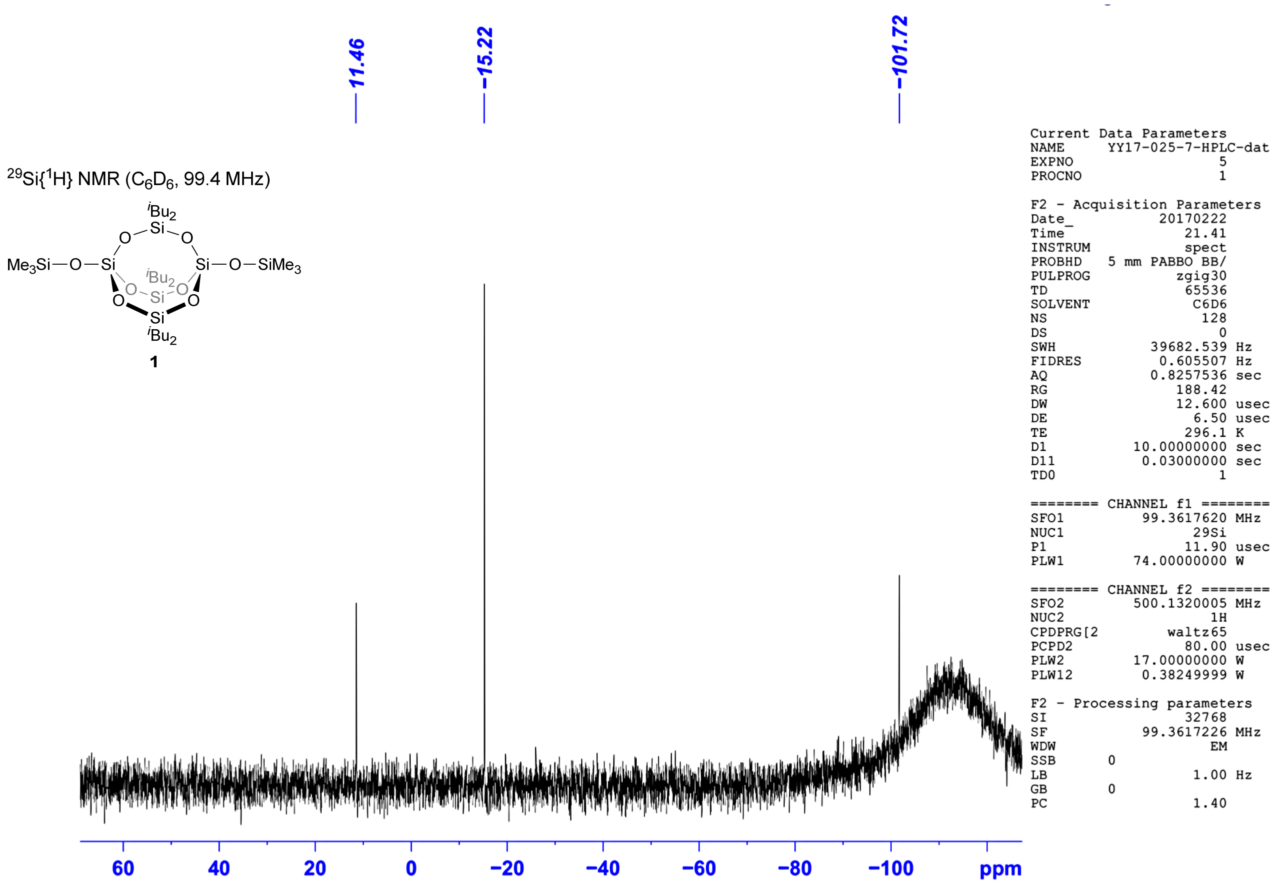
```
Current Data Parameters
NAME     YY17-025-7-HPLC-data
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_          20170222
Time              21.38
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp90
TD                65536
SOLVENT            C6D6
NS                    8
DS                    0
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG                36.97
DW               16.800 usec
DE                 6.50 usec
TE                296.4 K
CNST2       145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7703643 MHz
NUC1                13C
P1                10.00 usec
P13             2000.00 usec
PLW0      0 W
PLW1        74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5            0.500
SPOFFS5   0 Hz
SPW5        11.30599976 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2         waltz16
P3                12.00 usec
P4                24.00 usec
PCPD2             80.00 usec
PLW2        17.00000000 W
PLW12        0.38249999 W

F2 - Processing parameters
SI                32768
SF          125.7577284 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S3. $^{13}C\{^1H\}$ NMR (dept90) spectrum of **1** in C_6D_6 (126 MHz, 296 K).



```
Current Data Parameters
NAME     YY17-025-7-HPLC-data
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_          20170222
Time              21.38
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG       deptsp135
TD                65536
SOLVENT            C6D6
NS                   32
DS                    0
SWH           28846.154 Hz
FIDRES         0.440157 Hz
AQ            1.1359574 sec
RG                42.69
DW               17.333 usec
DE                 6.50 usec
TE                296.4 K
CNST2       145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7678486 MHz
NUC1                13C
P1                10.00 usec
P13             2000.00 usec
PLW0      0 W
PLW1        74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5            0.500
SPOFFS5   0 Hz
SPW5        11.30599976 W

======== CHANNEL f2 ========
SFO2        500.1315995 MHz
NUC2                 1H
CPDPRG[2         waltz16
P3                12.00 usec
P4                24.00 usec
PCPD2             80.00 usec
PLW2        17.00000000 W
PLW12        0.38249999 W

F2 - Processing parameters
SI                32768
SF          125.7577284 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

Figure S4. $^{13}C\{^1H\}$ NMR (dept135) spectrum of **1** in C_6D_6 (126 MHz, 296 K).



```
Current Data Parameters
NAME      YY17-025-7-HPLC-dat
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170222
Time                21.41
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                  65536
SOLVENT              C6D6
NS                    128
DS                      0
SWH             39682.539 Hz
FIDRES           0.605507 Hz
AQ              0.8257536 sec
RG                 188.42
DW                 12.600 usec
DE                   6.50 usec
TE                  296.1 K
D1            10.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          99.3617620 MHz
NUC1                 29Si
P1                  11.90 usec
PLW1          74.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                   1H
CPDPRG[2          waltz65
PCPD2               80.00 usec
PLW2          17.00000000 W
PLW12          0.38249999 W

F2 - Processing parameters
SI                  32768
SF             99.3617226 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

Figure S5. ^{29}Si{^{1}H} NMR spectrum of **1** in C$_6$D$_6$ (99.4 MHz, 296 K).

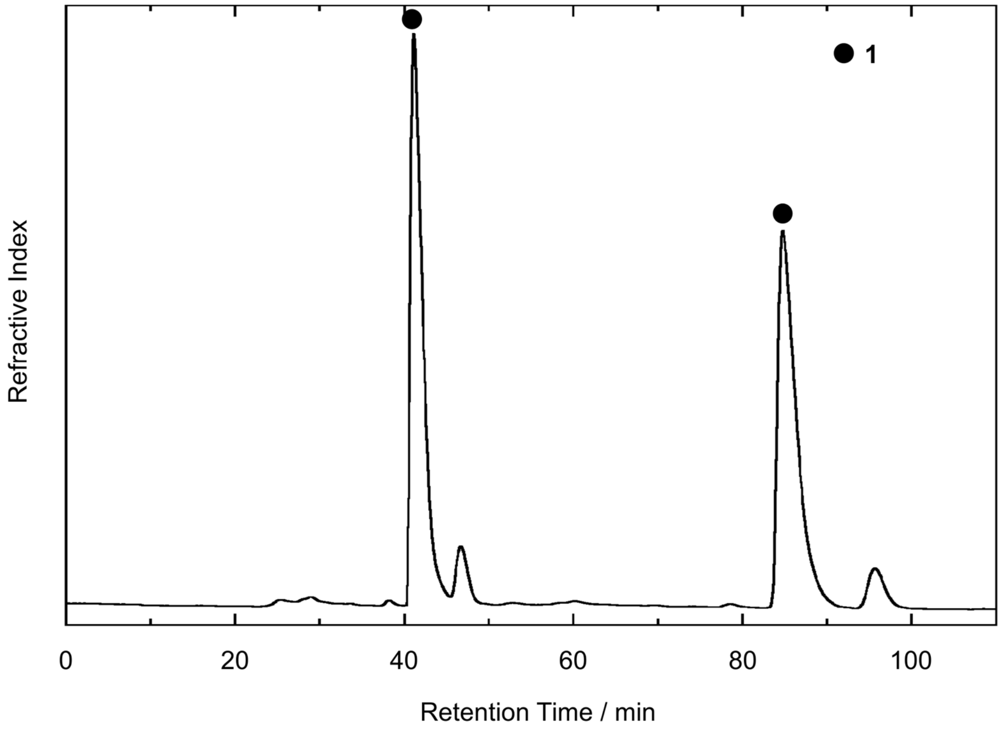
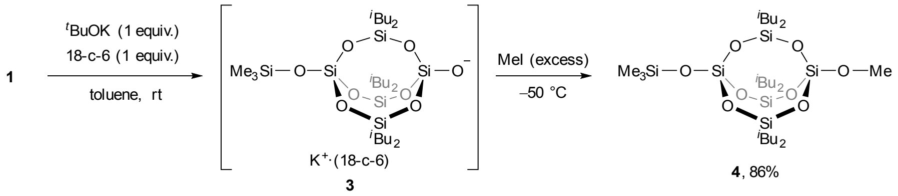


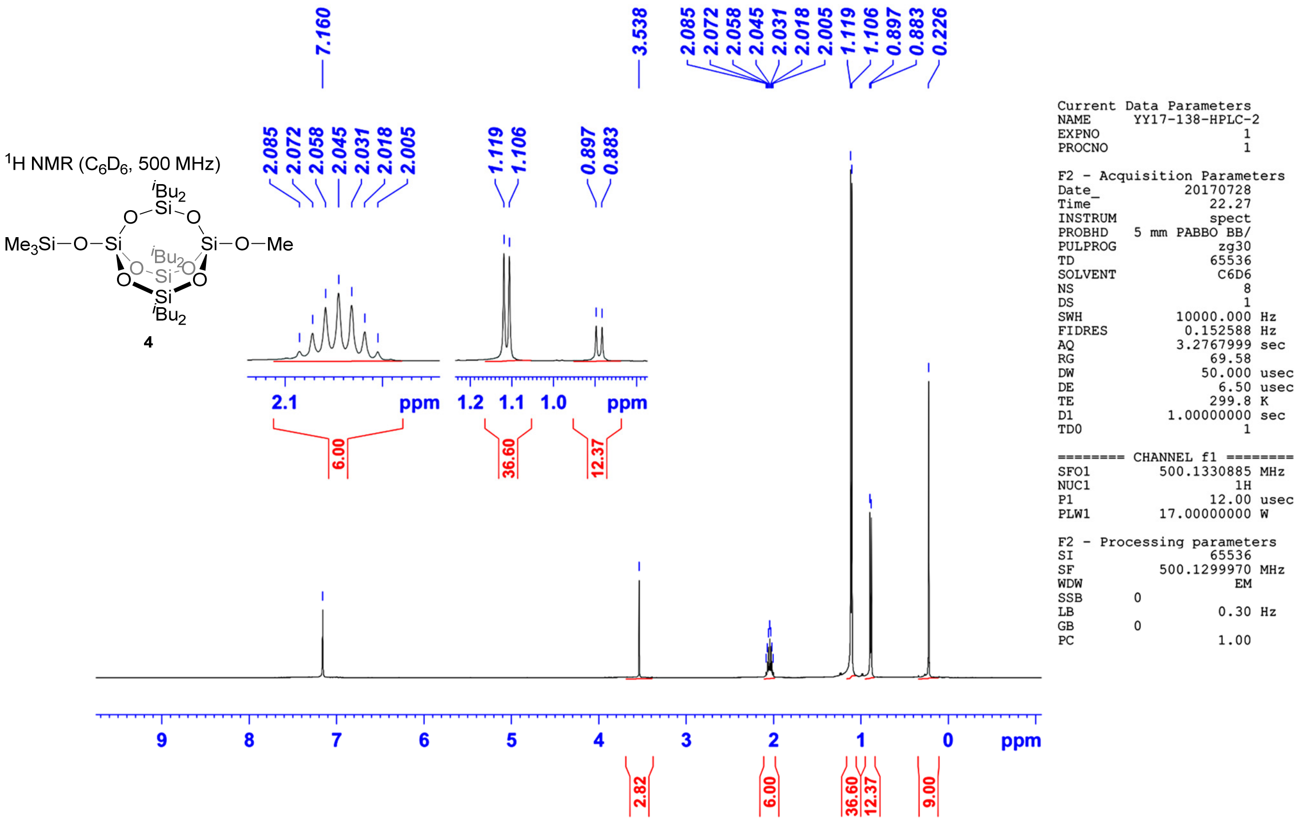
Figure S6. HPLC chart recorded during purification of **1**.

Synthesis of 4



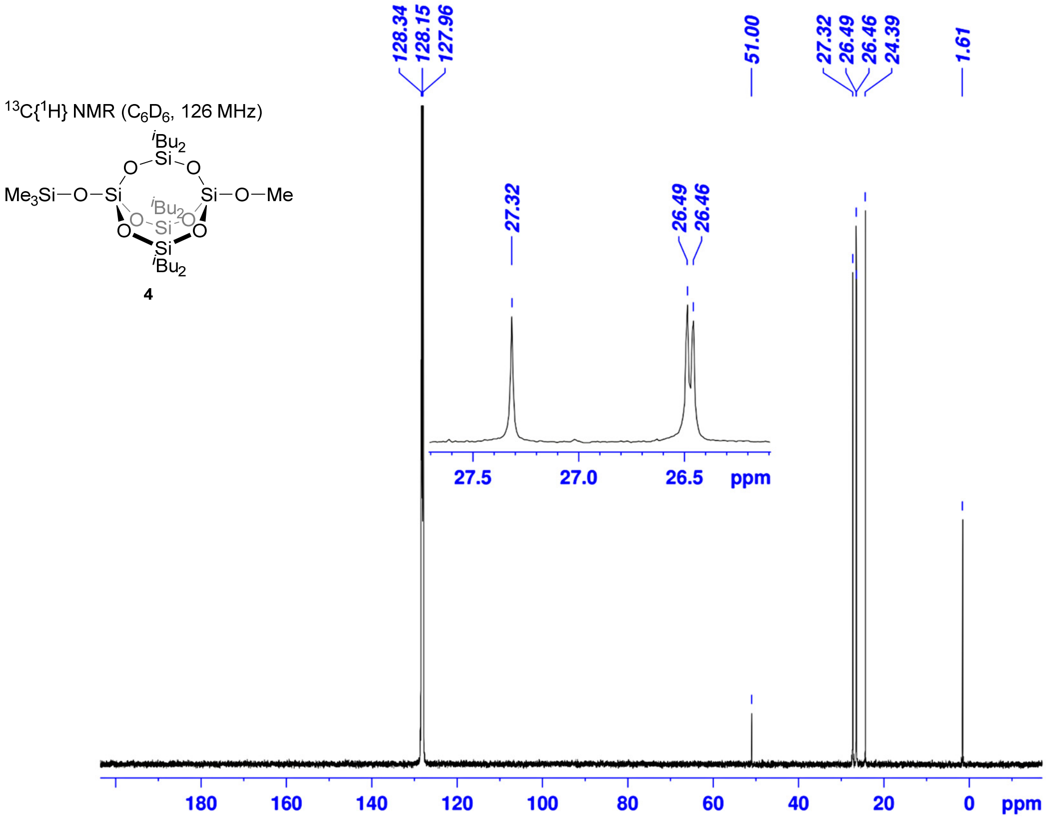
In a Schlenk tube (50 mL) equipped with a magnetic stir bar, **1** (100 mg, 0.132 mmol), 18-c-6 (35.3 mg, 0.134 mmol), ^{t}BuOK (15.4 mg, 0.137 mmol) and toluene (3 mL) were charged. The reaction mixture was stirred for 1.0 h at room temperature and then the mixture was cooled to −50 °C. To the cooled solution, MeI (316 mg, 2.11 mmol) was added with a syringe. After the reaction mixture was allowed to warm to ambient temperature, the resulting insoluble materials were filtered off through a silica gel. The resulting colorless oil was subjected to HPLC (ODS, EtOH as an eluent, room temperature) to afford **4** (79.1 mg, 0.113 mmol, 86%) as a colorless oil.

4: a colorless oil; ^{1}H NMR (500 MHz, C_6D_6, 300 K) δ 0.23 (s, 9H, Si(CH_3)$_3$), 0.89 (d, J = 7.0 Hz, 12H, CH_2CH(CH_3)$_2$), 1.13 (d, J = 6.5 Hz, 36H, $CH_2CH(CH_3)_2$), 2.00 – 2.09 (m, 6H, $CH_2CH(CH_3)_2$), 3.54 (s, 3H, OCH_3); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 300 K) δ 1.6 (Si(CH_3)$_3$), 24.4 ($CH_2CH(CH_3)_2$), 26.46 ($CH_2CH(CH_3)_2$), 26.49 ($CH_2CH(CH_3)_2$), 27.3 ($CH_2CH(CH_3)_2$), 51.0 (OCH_3); ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 300 K) δ −101.9 (Si^{Q}), −94.7 (Si^{T}), −14.6 (Si^{D}), 11.5 (Si^{M}); MS (EI, 70 eV) m/z (%) 684 (11) [M$^+$+H–CH_3], 642 (100) [M$^+$+H–(^{i}Bu)], 585 (27) [M$^+$+H–2 (i-Bu)]; Elemental analysis calcd for $C_{28}H_{66}O_8Si_6$: C, 48.09; H, 9.51; found: C, 48.03; H, 9.49.



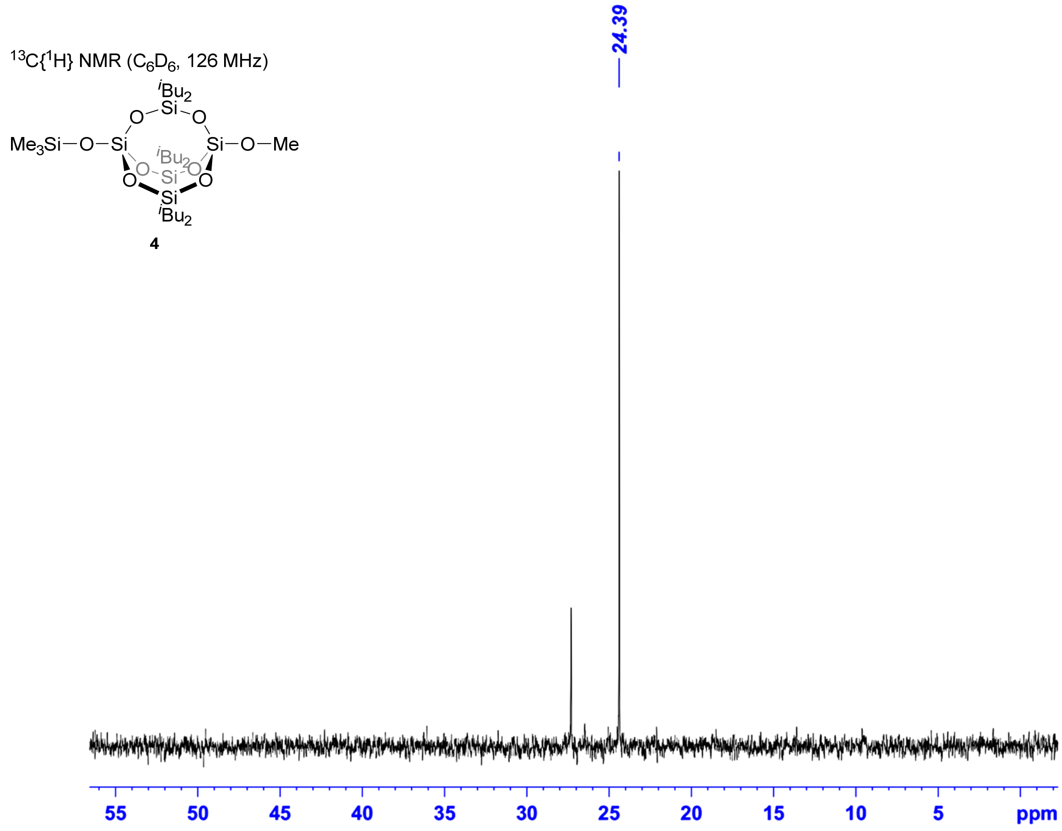
```
Current Data Parameters
NAME      YY17-138-HPLC-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170728
Time                22.27
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                      8
DS                      1
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                  69.58
DW                 50.000 usec
DE                   6.50 usec
TE                  299.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          17.00000000 W

F2 - Processing parameters
SI                  65536
SF           500.1299970 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

Figure S7. ^{1}H NMR spectrum of **4** in C_6D_6 (126 MHz, 300 K).



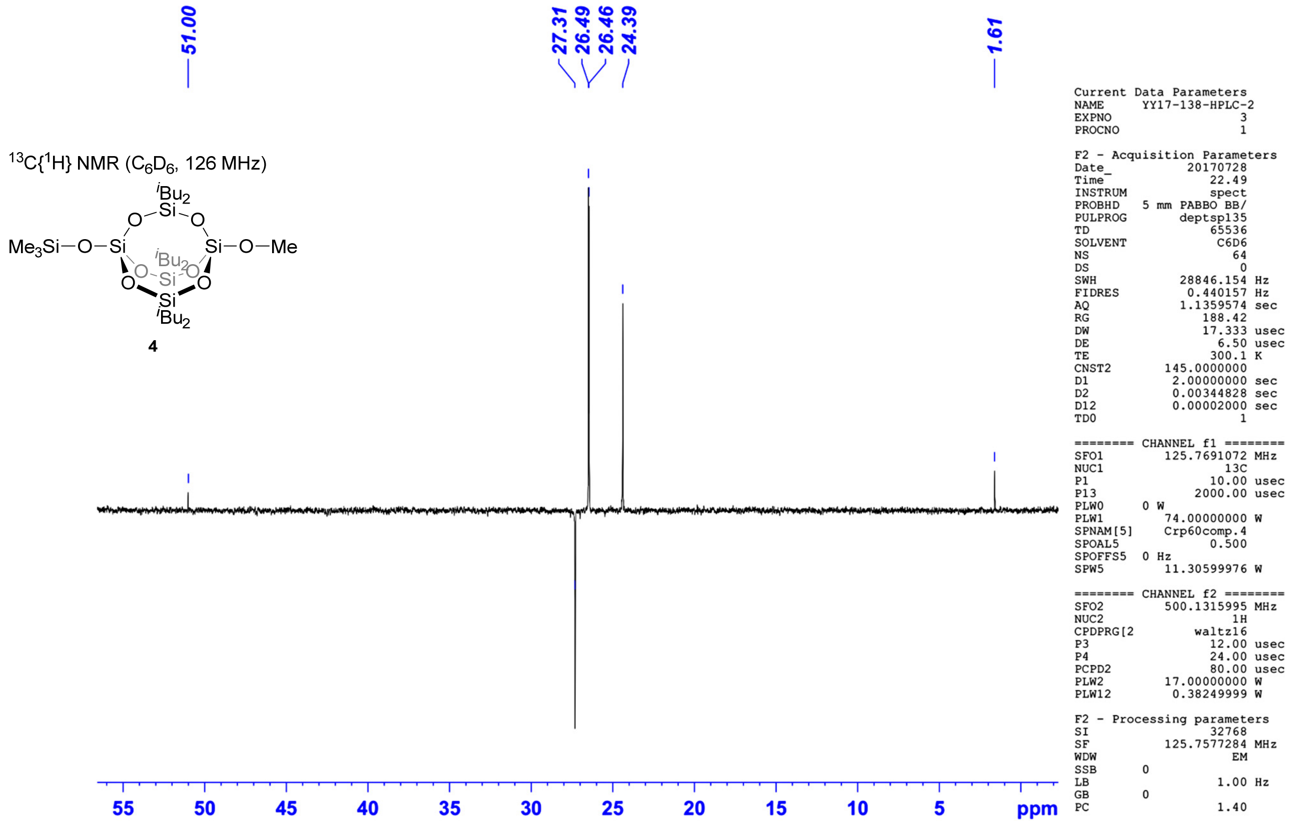
```
Current Data Parameters
NAME      YY17-138-HPLC-2
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170728
Time                22.53
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                  1024
DS                     0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                188.42
DW                16.800 usec
DE                  6.50 usec
TE                 300.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         74.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W
PLW13         0.24480000 W

F2 - Processing parameters
SI                 32768
SF           125.7577284 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **4** in C_6D_6 (126 MHz, 300 K).



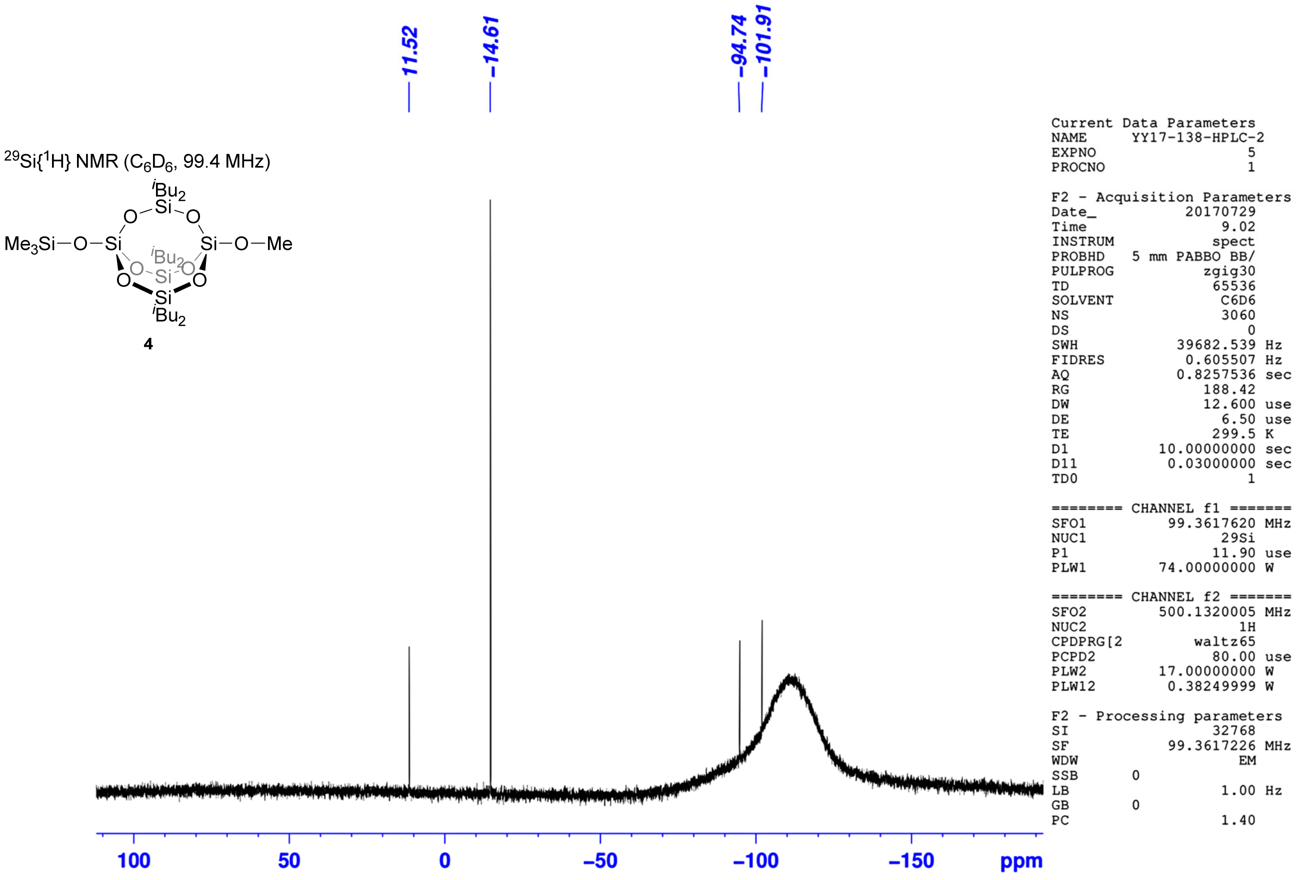
```
Current Data Parameters
NAME      YY17-138-HPLC-2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170728
Time                22.49
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG         deptsp90
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                188.42
DW                16.800 usec
DE                  6.50 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703643 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
PLW0     0 W
PLW1         74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5         11.30599976 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz16
P3                 12.00 usec
P4                 24.00 usec
PCPD2              80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF           125.7577284 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Figure S9. $^{13}C\{^1H\}$ NMR (dept90) spectrum of **4** in C_6D_6 (126 MHz, 300 K).



```
Current Data Parameters
NAME      YY17-138-HPLC-2
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_          20170728
Time              22.49
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG       deptsp135
TD                65536
SOLVENT            C6D6
NS                   64
DS                    0
SWH           28846.154 Hz
FIDRES         0.440157 Hz
AQ            1.1359574 sec
RG               188.42
DW               17.333 usec
DE                 6.50 usec
TE                300.1 K
CNST2       145.0000000
D1           2.00000000 sec
D2           0.00344828 sec
D12          0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7691072 MHz
NUC1                13C
P1                10.00 usec
P13             2000.00 usec
PLW0     0 W
PLW1        74.00000000 W
SPNAM[5]    Crp60comp.4
SPOAL5            0.500
SPOFFS5  0 Hz
SPW5        11.30599976 W

======== CHANNEL f2 ========
SFO2        500.1315995 MHz
NUC2                 1H
CPDPRG[2        waltz16
P3                12.00 usec
P4                24.00 usec
PCPD2             80.00 usec
PLW2        17.00000000 W
PLW12        0.38249999 W

F2 - Processing parameters
SI                32768
SF          125.7577284 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Figure S10. $^{13}C\{^1H\}$ NMR (dept135) spectrum of **4** in C_6D_6 (126 MHz, 300 K).



```
Current Data Parameters
NAME      YY17-138-HPLC-2
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_          20170729
Time               9.02
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgig30
TD                65536
SOLVENT            C6D6
NS                 3060
DS                    0
SWH           39682.539 Hz
FIDRES         0.605507 Hz
AQ            0.8257536 sec
RG               188.42
DW               12.600 use
DE                 6.50 use
TE                299.5 K
D1          10.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 =======
SFO1         99.3617620 MHz
NUC1               29Si
P1                11.90 use
PLW1        74.00000000 W

======== CHANNEL f2 =======
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2        waltz65
PCPD2             80.00 use
PLW2        17.00000000 W
PLW12        0.38249999 W

F2 - Processing parameters
SI                32768
SF           99.3617226 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Figure S11. $^{29}Si\{^1H\}$ NMR spectrum of **4** in C_6D_6 (99.4 MHz, 300 K).

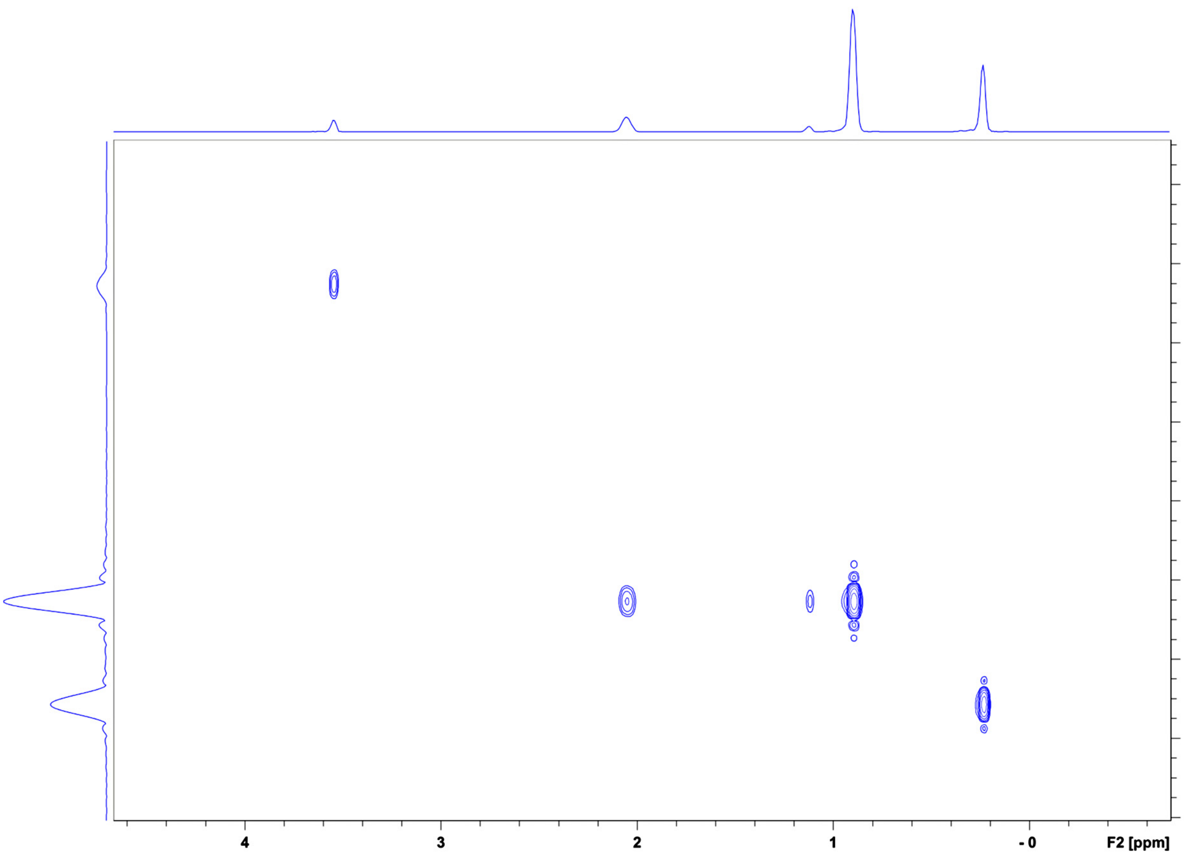


Figure S12. ^{1}H-^{29}Si HMBC 2D NMR spectrum of **4** in C_6D_6 (300 K).

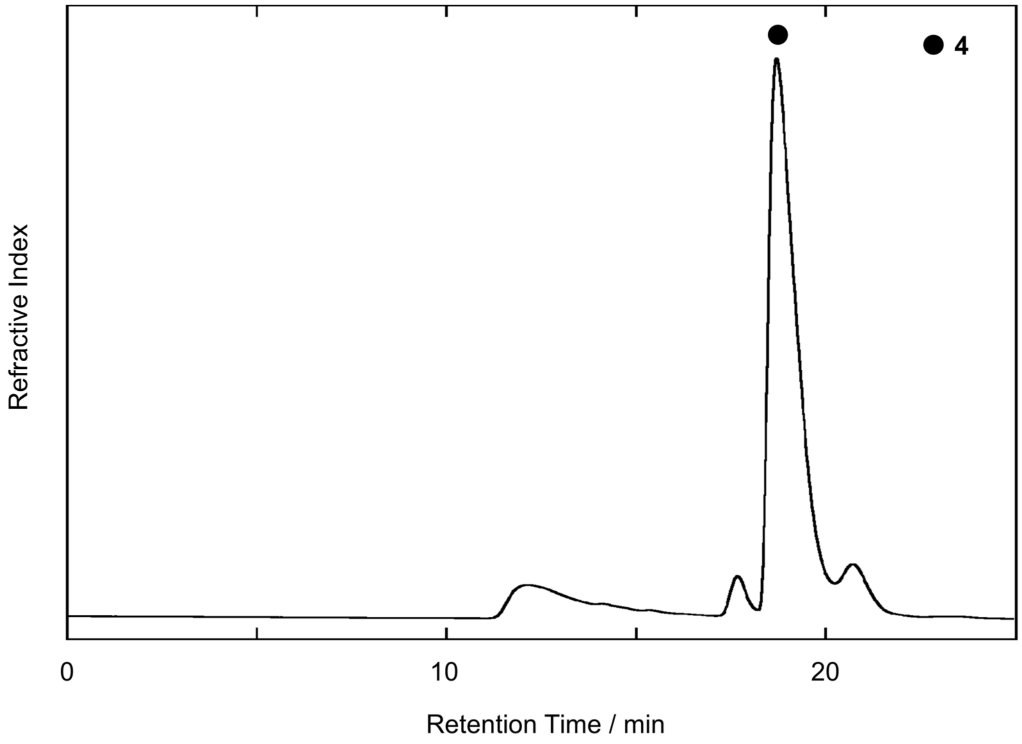
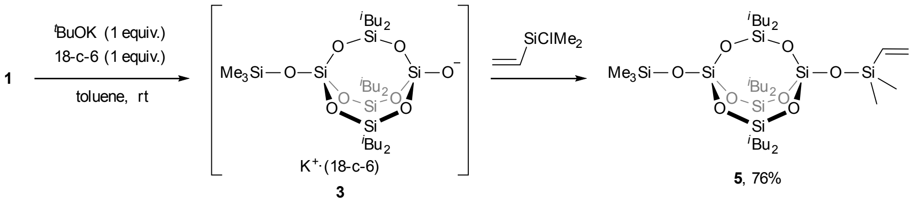


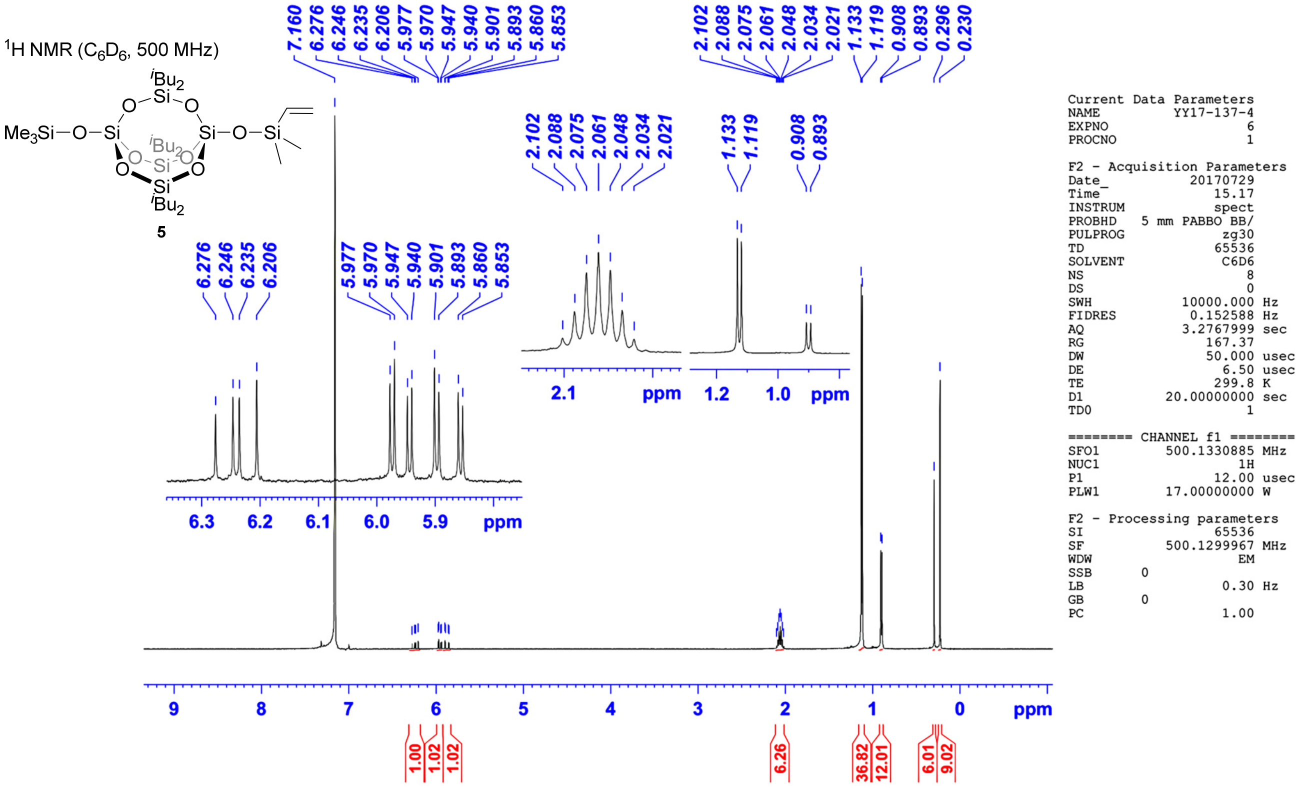
Figure S13. HPLC chart recorded during purification of **4**.

Synthesis of 5



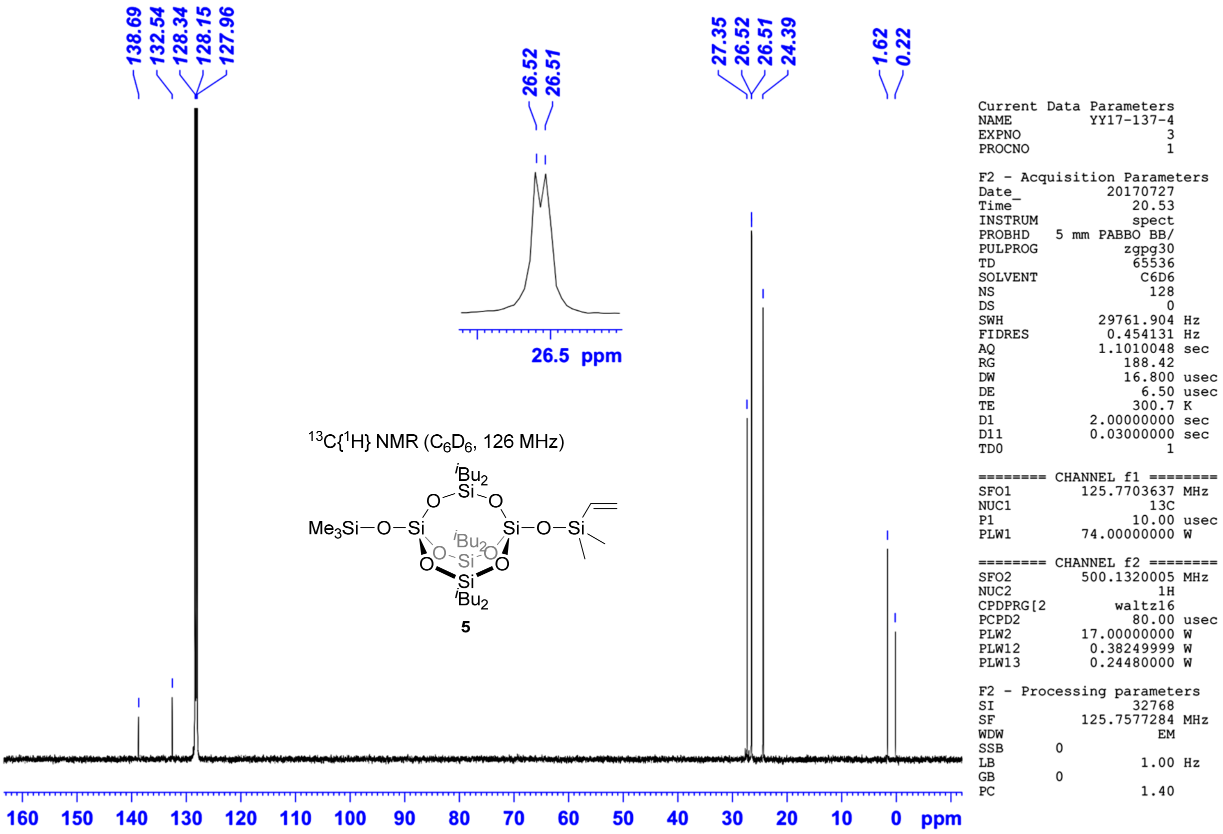
In a Schlenk tube (50 mL) equipped with a magnetic stir bar, compound **1** (100.0 mg, 0.132 mmol), 18-crown-6-ether (35.2 mg, 0.133 mmol), ^{t}BuOK (15.3 mg, 0.136 mmol) and toluene (3 mL) were charged. The reaction mixture was stirred for 1.0 h at room temperature and then chlorodimethylvinylsilane (18 mg, 0.149 mmol) was added to the mixture. The resulting insoluble materials were filtered off through a silica gel. After removal of the solvent from the filtrate in *vacuo*, the resulting oil was subjected to HPLC (ODS, EtOH as an eluent, room temperature) to afford **5** (77.0 mg, 0.100 mmol, 76%) as a colorless oil.

5: a colorless oil; ^{1}H NMR (500 MHz, C_6D_6, 300 K) δ 0.23 (s, 9H, Si(CH_3)$_3$), 0.30 (s, 6H, Si(CH_3)$_2$(CH=CH$_2$)), 0.90 (d, *J* = 7.1 Hz, 12H, CH_2CH(CH$_3$)$_2$), 1.13 (d, *J* = 6.6 Hz, 36H, CH$_2$CH(CH_3)$_2$), 2.02 – 2.10 (m, 6H, CH$_2$$CH$(CH$_3$)$_2$), 5.88 (dd, *J* = 3.8, 20.4 Hz, 1H, SiMe$_2$(CH=CH_2)), 5.96 (dd, *J* = 3.8, 14.9 Hz, 1H, SiMe$_2$(CH=CH_2)), 6.24 (dd, *J* = 14.9, 20.4 Hz, 1H, SiMe$_2$(CH=CH$_2$)); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 301 K) δ 0.2 (Si(CH_3)$_2$(CH=CH$_2$)), 1.6 (Si(CH_3)$_3$), 24.4 (CH$_2$$CH$(CH$_3$)$_2$), 26.51 (CH$_2$CH($CH_3$)$_2$), 26.52 (CH$_2$CH($CH_3$)$_2$), 27.4 ($CH_2$CH(CH$_3$)$_2$), 132.5 (SiMe$_2$(CH=$CH_2$)), 138.7 (SiMe$_2$($CH$=CH$_2$)); ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 300 K) δ −101.78 (Si^Q), −101.76 (Si^Q), −15.2 (Si^D), –0.4 (Si^M, *Si*Me$_2$(HC=CH$_2$)), 11.5 (Si^M, *Si*Me$_3$); MS (EI, 70 eV) *m*/*z* (%) 754 (11) [M$^+$+H–Me], 712 (78) [M$^+$+H–(*i*-Bu)], 655 (59) [M$^+$+H–2(*i*-Bu)], 73 (100) [SiMe$_3$$^+$]. Elemental analysis calcd for $C_{31}H_{72}O_8Si_7$: C, 48.39; H, 9.43; found: C, 48.42; H, 9.34.



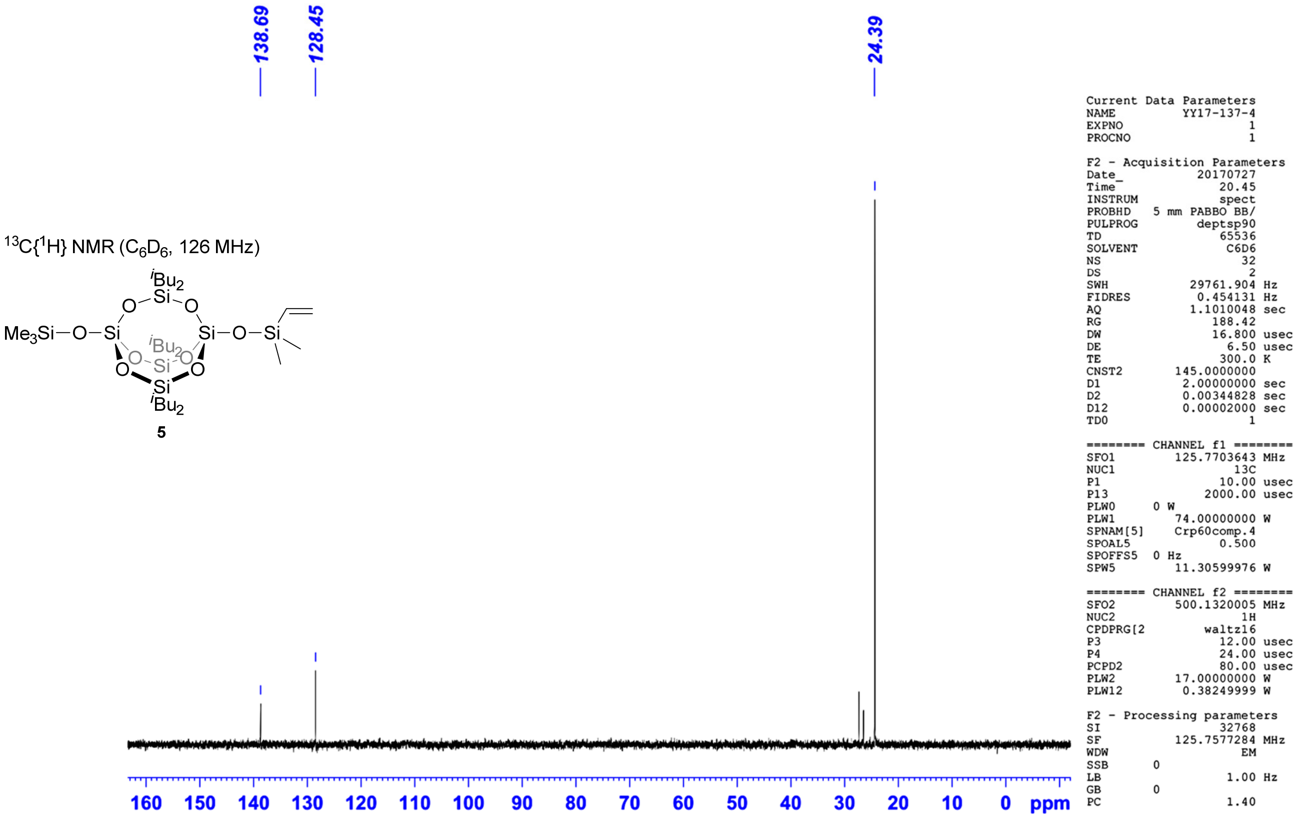
```
Current Data Parameters
NAME            YY17-137-4
EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170729
Time                 15.17
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   65536
SOLVENT               C6D6
NS                       8
DS                       0
SWH              10000.000 Hz
FIDRES            0.152588 Hz
AQ               3.2767999 sec
RG                  167.37
DW                  50.000 usec
DE                    6.50 usec
TE                   299.8 K
D1             20.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1330885 MHz
NUC1                    1H
P1                   12.00 usec
PLW1           17.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.1299967 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

Figure S14. ^{1}H NMR spectrum of **5** in C_6D_6 (126 MHz, 300 K).



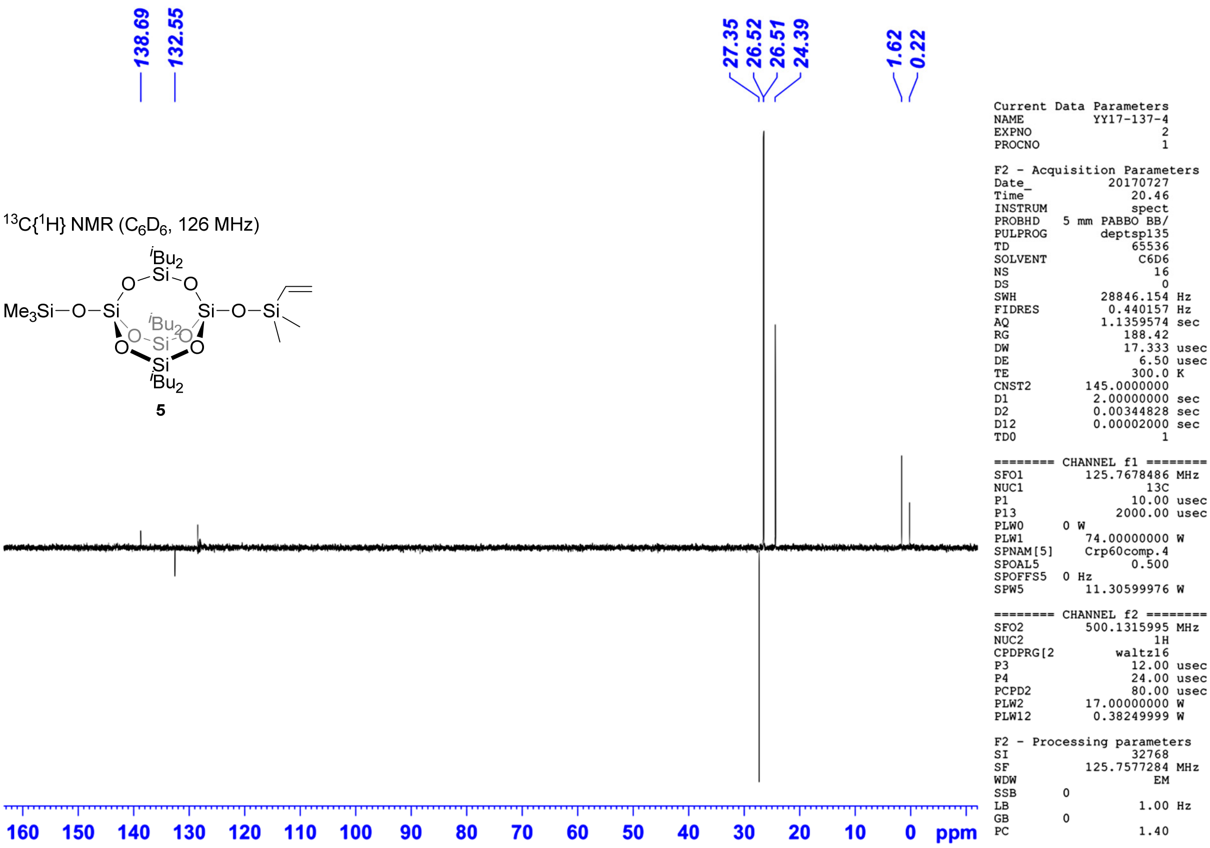
```
Current Data Parameters
NAME           YY17-137-4
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170727
Time                20.53
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT              C6D6
NS                    128
DS                      0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                 188.42
DW                 16.800 usec
DE                   6.50 usec
TE                  300.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7703637 MHz
NUC1                  13C
P1                  10.00 usec
PLW1          74.00000000 W

======== CHANNEL f2 ========
SFO2          500.1320005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          17.00000000 W
PLW12          0.38249999 W
PLW13          0.24480000 W

F2 - Processing parameters
SI                  32768
SF            125.7577284 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

Figure S15. $^{13}C\{^1H\}$ NMR spectrum of **5** in C_6D_6 (126 MHz, 301 K).



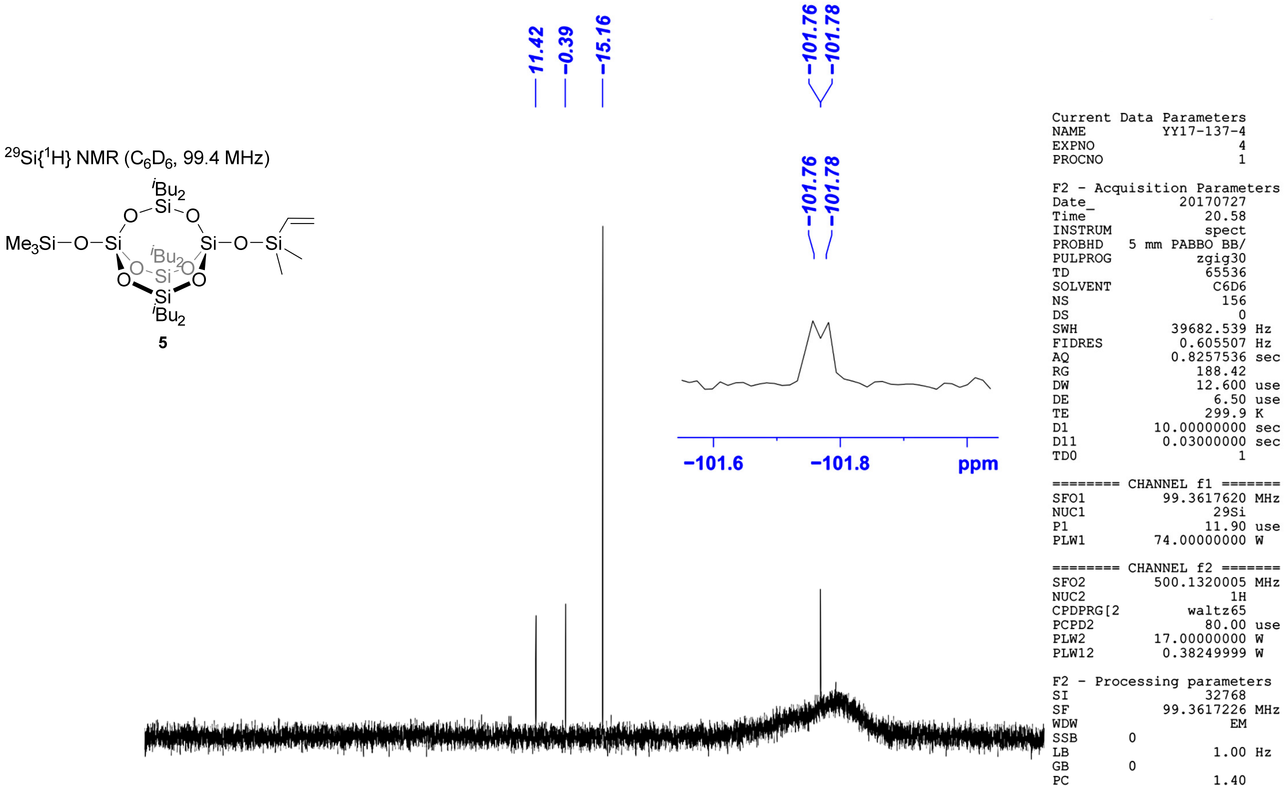
```
Current Data Parameters
NAME           YY17-137-4
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170727
Time                20.45
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          deptsp90
TD                  65536
SOLVENT              C6D6
NS                     32
DS                      2
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                 188.42
DW                 16.800 usec
DE                   6.50 usec
TE                  300.0 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.7703643 MHz
NUC1                  13C
P1                  10.00 usec
P13               2000.00 usec
PLW0     0 W
PLW1          74.00000000 W
SPNAM[5]      Crp60comp.4
SPOAL5              0.500
SPOFFS5  0 Hz
SPW5          11.30599976 W

======== CHANNEL f2 ========
SFO2          500.1320005 MHz
NUC2                   1H
CPDPRG[2          waltz16
P3                  12.00 usec
P4                  24.00 usec
PCPD2               80.00 usec
PLW2          17.00000000 W
PLW12          0.38249999 W

F2 - Processing parameters
SI                  32768
SF            125.7577284 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

Figure S16. $^{13}C\{^1H\}$ NMR (dept90) spectrum of **5** in C_6D_6 (126 MHz, 300 K).



```
Current Data Parameters
NAME          YY17-137-4
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170727
Time               20.46
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     0
SWH            28846.154 Hz
FIDRES          0.440157 Hz
AQ             1.1359574 sec
RG                188.42
DW                17.333 usec
DE                  6.50 usec
TE                 300.0 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7678486 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
PLW0     0 W
PLW1         74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5         11.30599976 W

======== CHANNEL f2 ========
SFO2         500.1315995 MHz
NUC2                  1H
CPDPRG[2         waltz16
P3                 12.00 usec
P4                 24.00 usec
PCPD2              80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF           125.7577284 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Figure S17. $^{13}C\{^1H\}$ NMR (dept135) spectrum of **5** in C_6D_6 (126 MHz, 300 K).



```
Current Data Parameters
NAME          YY17-137-4
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170727
Time               20.58
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                 65536
SOLVENT             C6D6
NS                   156
DS                     0
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8257536 sec
RG                188.42
DW                12.600 use
DE                  6.50 use
TE                 299.9 K
D1           10.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 =======
SFO1          99.3617620 MHz
NUC1                29Si
P1                 11.90 use
PLW1         74.00000000 W

======== CHANNEL f2 =======
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz65
PCPD2              80.00 use
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF            99.3617226 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Figure S18. $^{29}Si\{^1H\}$ NMR spectrum of **5** in C_6D_6 (99.4 MHz, 300 K).

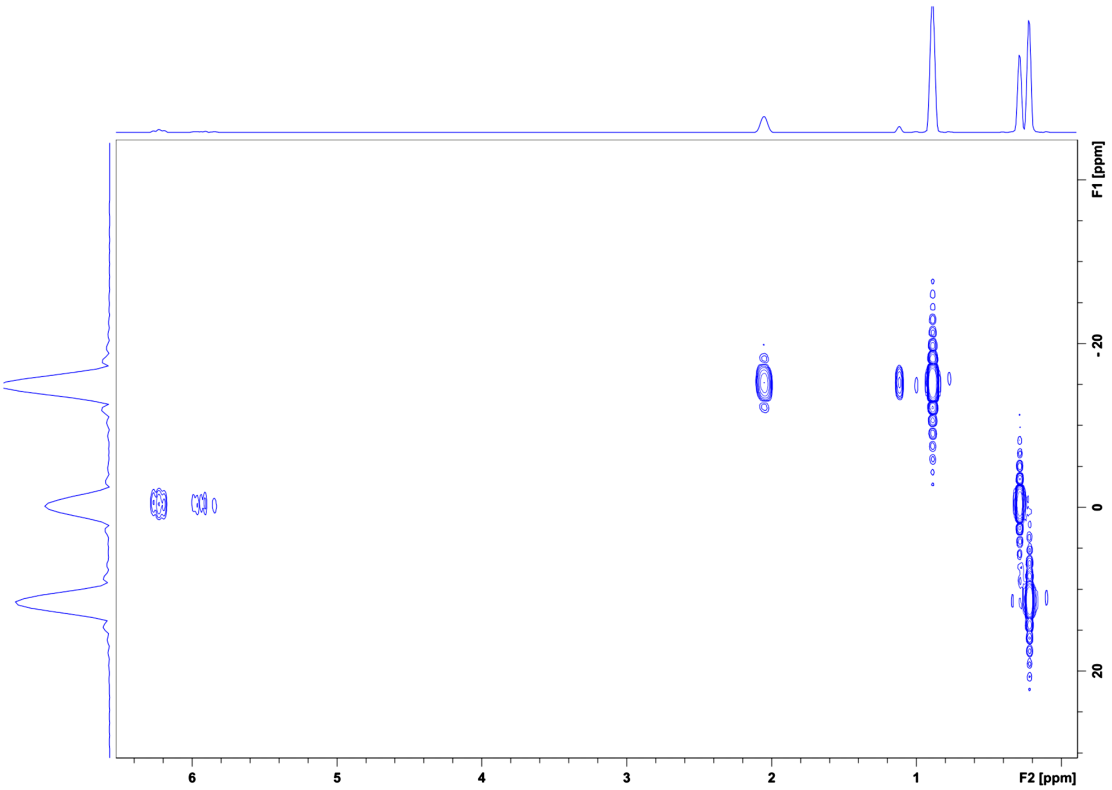


Figure S19. ^{1}H-^{29}Si HMBC 2D NMR spectrum of **5** in C_6D_6 (300 K).

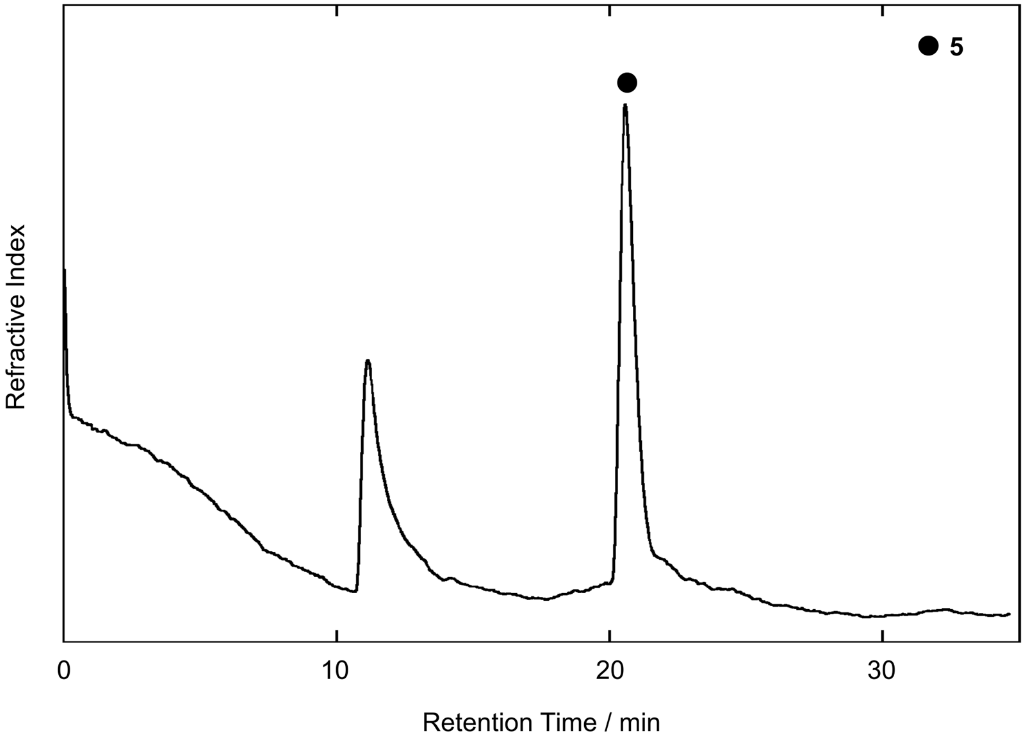
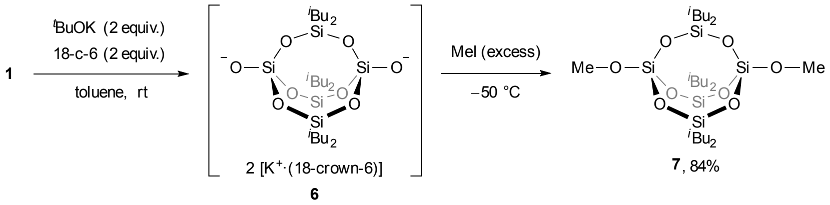


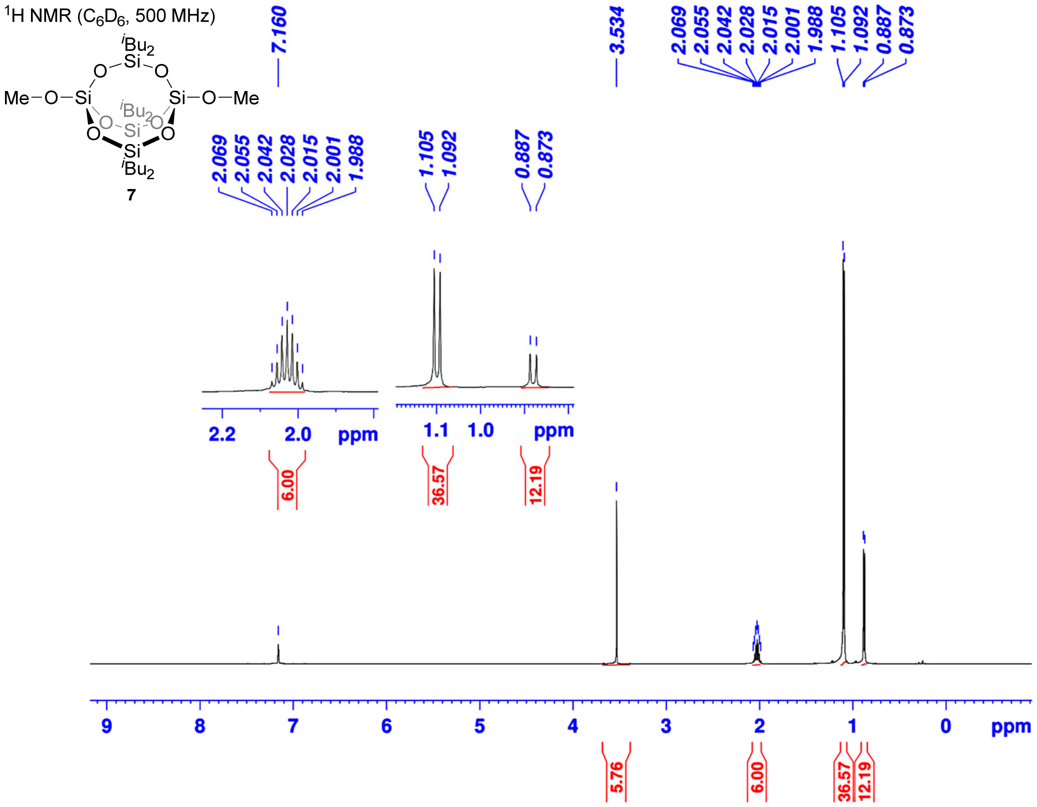
Figure S20. HPLC chart recorded during purification of **5**.

Synthesis of 7



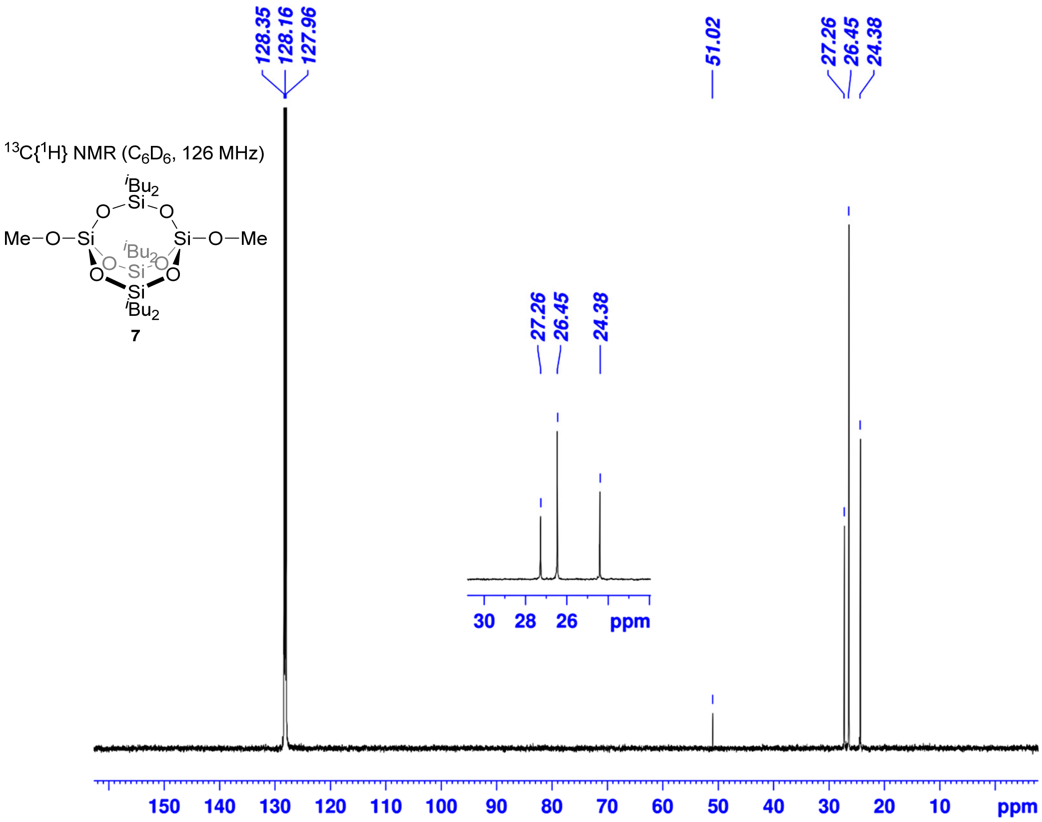
In a Schlenk tube (50 mL) equipped with a magnetic stir bar, **1** (100 mg, 0.132 mmol), 18-c-6 (73.5 mg, 0.278 mmol), ^{t}BuOK (31.6 mg, 0. 282 mmol), and toluene (6 mL) were charged. The reaction mixture was stirred for 1.0 h at room temperature and then toluene (4 mL) was added to mixture. The mixture was cooled to –50 °C before MeI (406 mg, 2.71 mmol) was added to the cooled solution through a syringe. After the resulting suspension was allowed to warm to ambient temperature, the resulting insoluble materials were filtered off through a silica gel. Removal of the volatiles under reduced pressure afforded **7** as a colorless waxy solid (70.8 mg, 0.110 mmol, 84%).

7: a colorless waxy solid; ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 0.88 (d, J = 7.0 Hz, 12H, $CH_2CH(CH_3)_2$), 1.10 (d, J = 6.5 Hz, 36H, $CH_2CH(CH_3)_2$), 1.99 – 2.07 (m, 6H, $CH_2CH(CH_3)_2$), 3.53 (s, 6H, OCH_3); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 299 K) δ 24.4 ($CH_2CH(CH_3)_2$), 26.5 ($CH_2CH(CH_3)_2$), 27.3 ($CH_2CH(CH_3)_2$), 51.0 (OCH_3); $^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 298 K) δ –94.9 (Si^T), –14.0 (Si^D); MS (EI, 70 eV) m/z (%): 583 (100) [M$^+$–(i-Bu)], 527 (65.1) [M$^+$+H–2(i-Bu)], 471 (14) [M$^+$+H–3(i-Bu)]. Elemental analysis calcd for $C_{26}H_{60}O_8Si_7$: C, 48.70; H, 9.43; found: C, 48.85; H, 9.61.



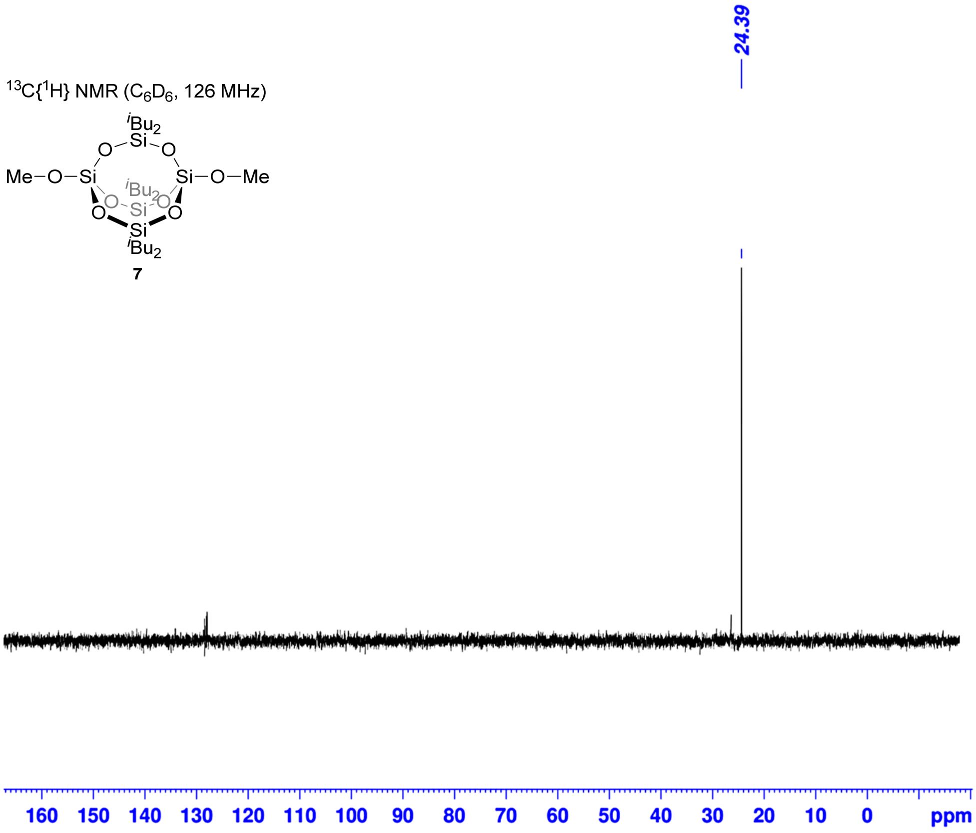
```
Current Data Parameters
NAME           YY17-085-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170512
Time                18.33
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                      8
DS                      1
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                  59.61
DW                 50.000 usec
DE                   6.50 usec
TE                  297.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          17.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1299974 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```

Figure S21. ^{1}H NMR spectrum of **7** in C_6D_6 (126 MHz, 298 K).



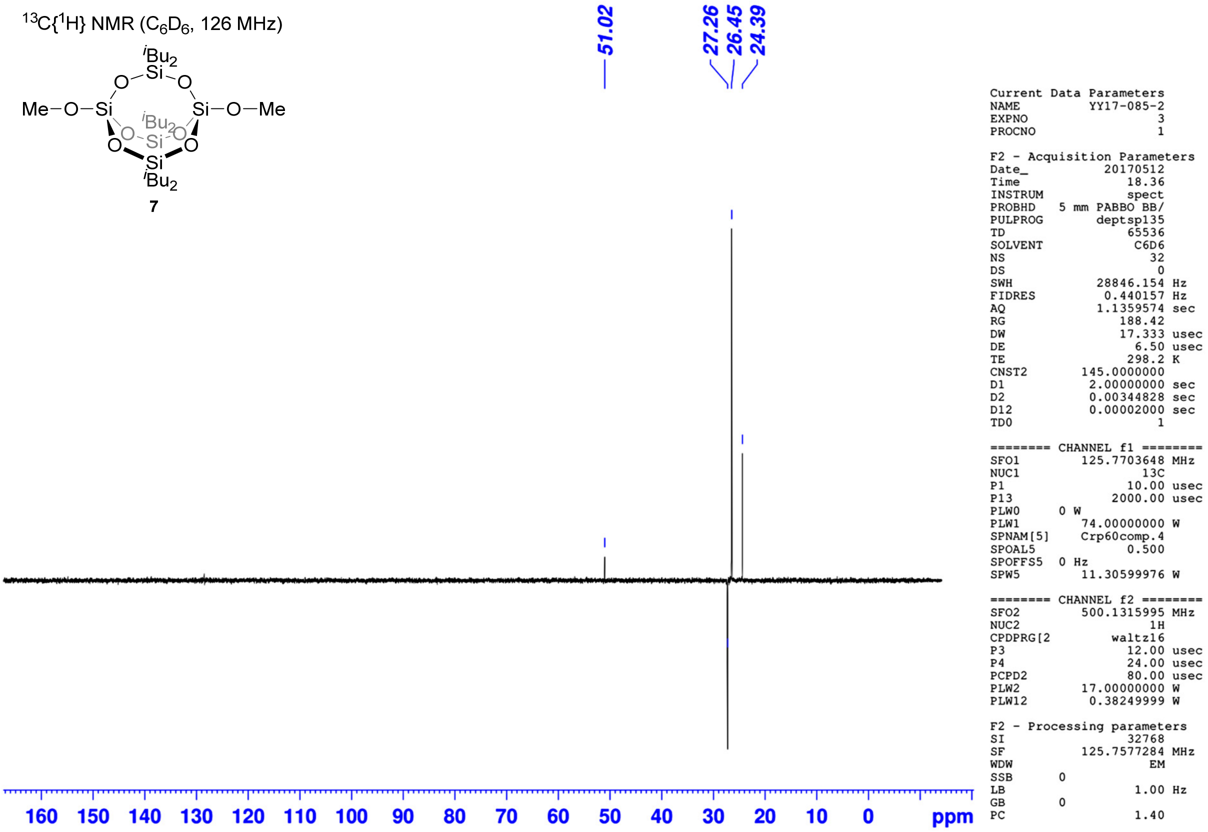
```
Current Data Parameters
NAME          YY17-085-2
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170512
Time               18.40
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                   128
DS                     0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                188.42
DW                16.800 usec
DE                  6.50 usec
TE                 298.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703637 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         74.00000000 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W
PLW13         0.24480000 W

F2 - Processing parameters
SI                 32768
SF           125.7577284 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Figure S22. $^{13}C\{^1H\}$ NMR spectrum of **7** in C_6D_6 (126 MHz, 299 K).



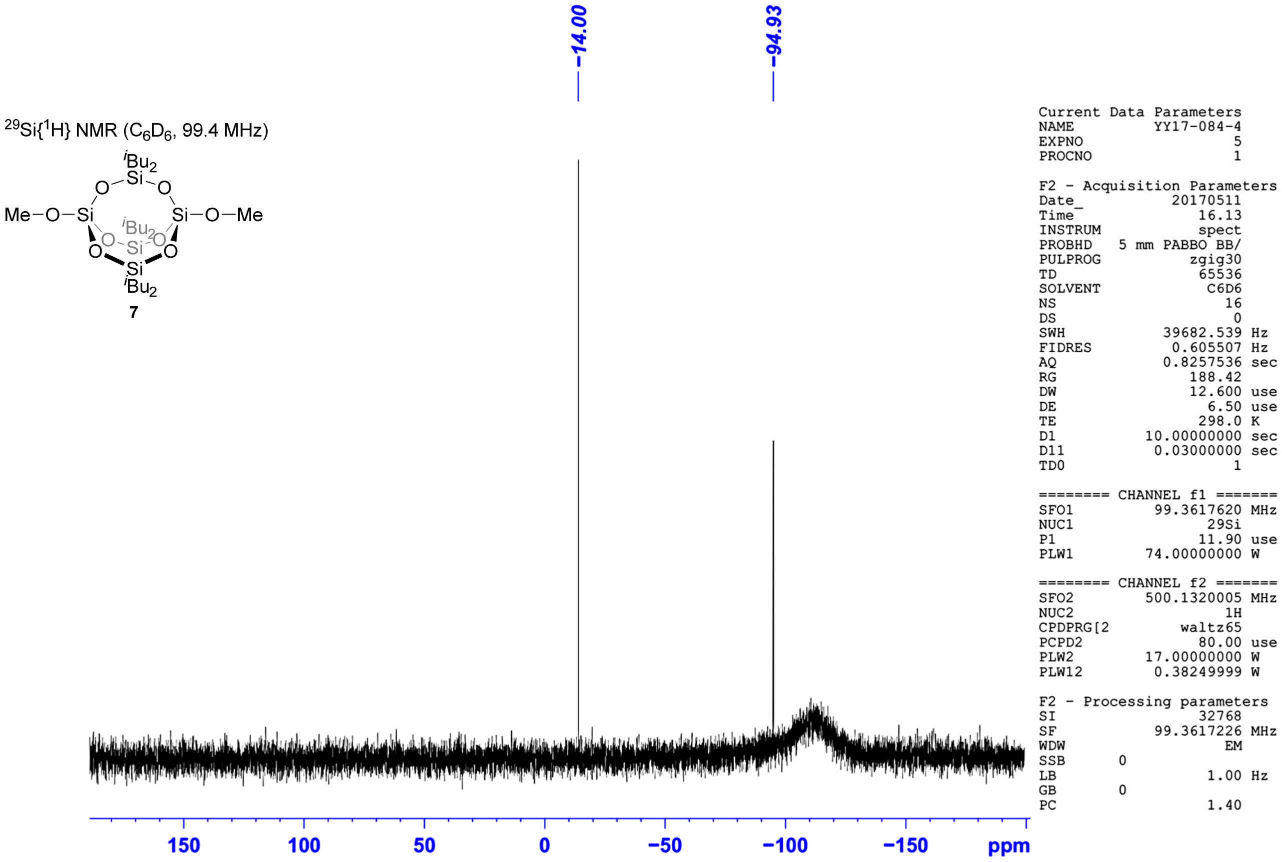
```
Current Data Parameters
NAME          YY17-085-2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170512
Time               18.35
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG         deptsp90
TD                 65536
SOLVENT             C6D6
NS                     9
DS                     0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                188.42
DW                16.800 usec
DE                  6.50 usec
TE                 298.1 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703643 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
PLW0      0 W
PLW1         74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5         11.30599976 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz16
P3                 12.00 usec
P4                 24.00 usec
PCPD2              80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF           125.7577284 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Figure S23. $^{13}C\{^1H\}$ NMR (dept90) spectrum of **7** in C_6D_6 (126 MHz, 298 K).



```
Current Data Parameters
NAME          YY17-085-2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170512
Time               18.36
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT             C6D6
NS                    32
DS                     0
SWH            28846.154 Hz
FIDRES          0.440157 Hz
AQ             1.1359574 sec
RG                188.42
DW                17.333 usec
DE                  6.50 usec
TE                 298.2 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7703648 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
PLW0     0 W
PLW1         74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5         11.30599976 W

======== CHANNEL f2 ========
SFO2         500.1315995 MHz
NUC2                  1H
CPDPRG[2         waltz16
P3                 12.00 usec
P4                 24.00 usec
PCPD2              80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF           125.7577284 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

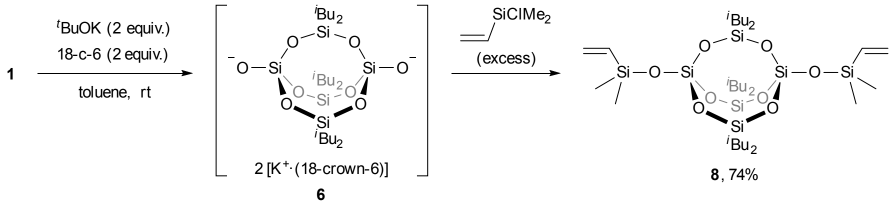
Figure S24. $^{13}C\{^1H\}$ NMR (dept135) spectrum of **7** in C_6D_6 (126 MHz, 298 K).



```
Current Data Parameters
NAME          YY17-084-4
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170511
Time               16.13
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     0
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8257536 sec
RG                188.42
DW                12.600 use
DE                  6.50 use
TE                 298.0 K
D1           10.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 =======
SFO1          99.3617620 MHz
NUC1                29Si
P1                 11.90 use
PLW1         74.00000000 W

======== CHANNEL f2 =======
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz65
PCPD2              80.00 use
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF            99.3617226 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

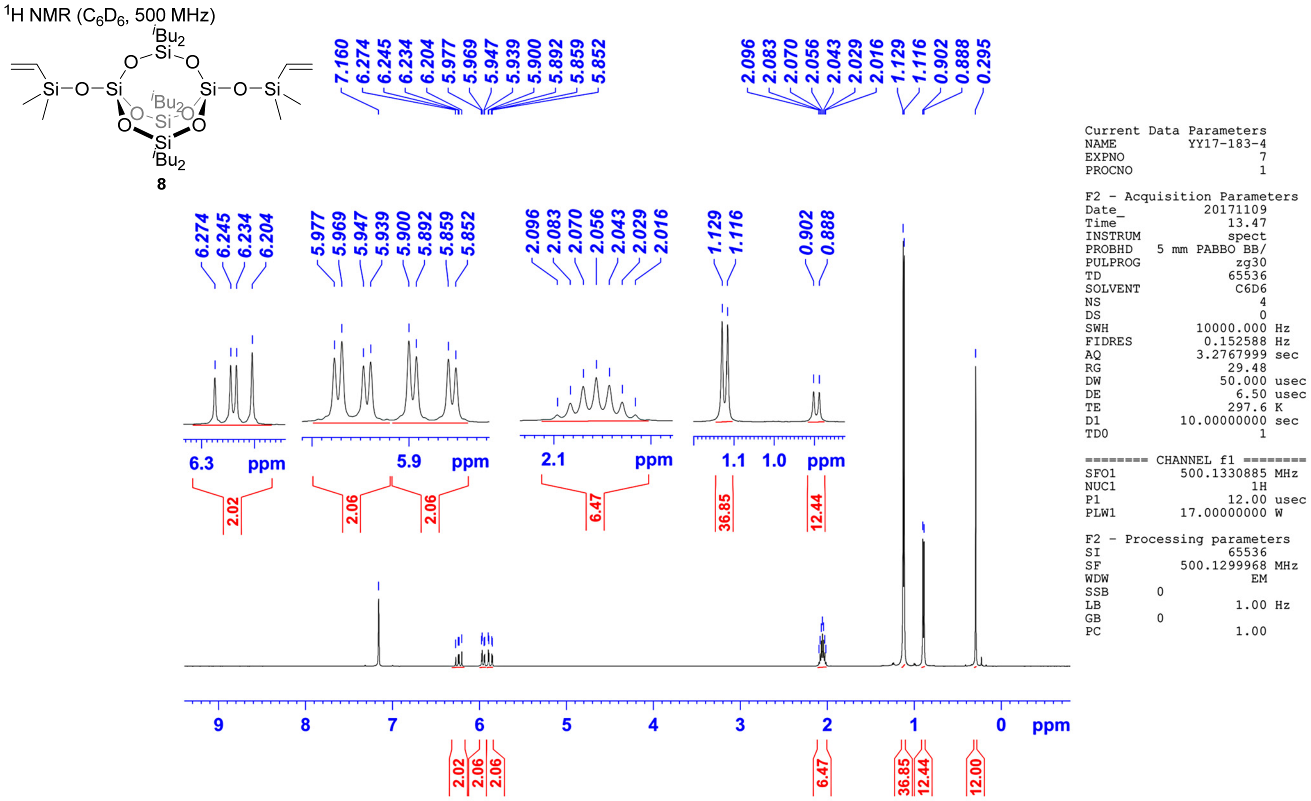
Figure S25. $^{29}Si\{^1H\}$ NMR spectrum of **7** in C_6D_6 (99.4 MHz, 298 K).

Synthesis of 8



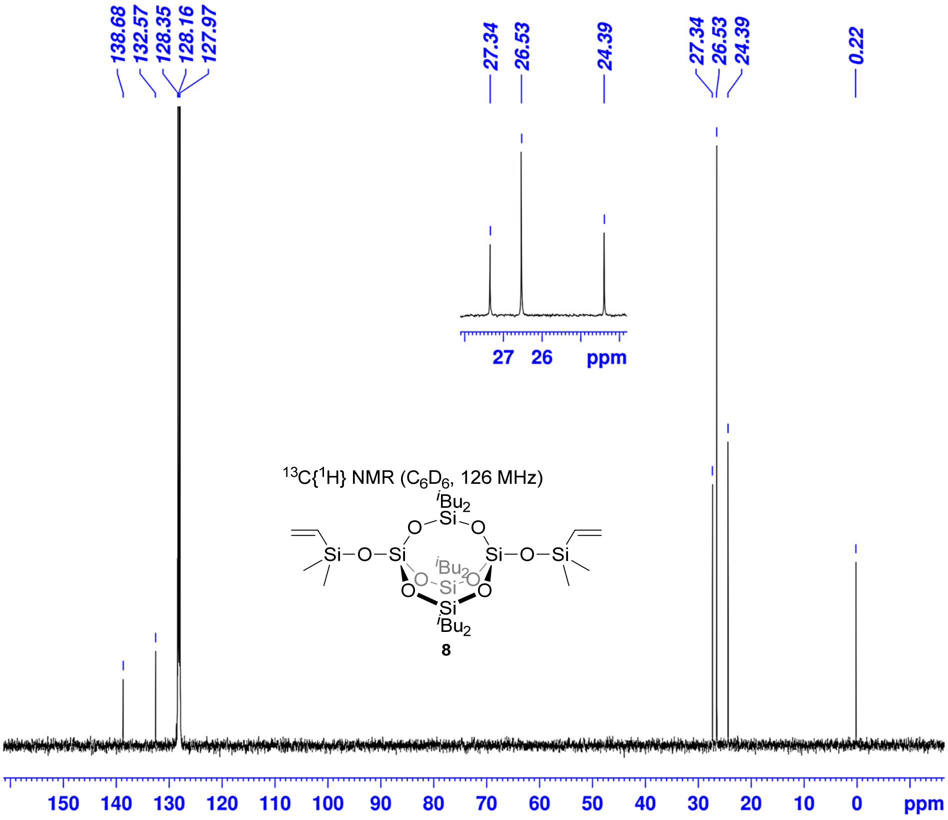
In a Schlenk tube (50 mL) equipped with a magnetic stir bar, compound **1** (50.0 mg, 0.0660 mmol), 18-crown-6-ether (38.4 mg, 0.145 mmol), ^{t}BuOK (16.3 mg, 0.145 mmol) and toluene (3 mL) were charged. The reaction mixture was stirred for 1.0 h at room temperature and then chlorodimethylvinylsilane (39.1 mg, 0.324 mmol) was added to the mixture. The resulting insoluble materials were filtered off through a silica gel. After removal of the solvent from the filtrate in *vacuo*, the resulting oil was subjected to HPLC (ODS, EtOH as an eluent, room temperature) to afford **8** (38.2 mg, 0.0489 mmol, 74%) as a colorless oil.

8: a colorless oil; ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 0.30 (s, 12H, Si(CH_3)$_2$(CH=CH$_2$)), 0.90 (d, J = 7.0 Hz, 12H, CH_2CH(CH$_3$)$_2$), 1.12 (d, J = 6.5 Hz, 36H, CH$_2$CH(CH_3)$_2$), 2.02 – 2.10 (m, 6H, CH$_2$CH(CH$_3$)$_2$), 5.88 (dd, J = 4.0, 20.5 Hz, 2H, SiMe$_2$(CH=CH_2)), 5.96 (dd, J = 4.0, 15.0 Hz, 2H, SiMe$_2$(CH=CH_2)), 6.24 (dd, J = 15.0, 20.5 Hz, 2H, SiMe$_2$(CH=CH$_2$)); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K) δ 0.2 (Si(CH$_3$)$_2$(HC=CH$_2$)), 24.4 (CH$_2$$C$H(CH$_3$)$_2$), 26.5 (CH$_2$CH($CH_3$)$_2$), 27.3 ($CH_2$CH(CH$_3$)$_2$), 132.6 (SiMe$_2$(CH=$CH_2$)), 138.7 (SiMe$_2$($C$H=CH$_2$)); ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 298 K) δ −101.8 (Si^{Q}), −15.0 (Si^{D}), −0.4 (Si^{M}); MS (EI, 70 eV) *m/z* (%): 766 (12) [M$^+$+H–Me], 724 (100) [M$^+$+H–(*i*-Bu)], 667 (67) [M$^+$+H–2(*i*-Bu)]. Elemental analysis calcd for $C_{32}H_{72}O_8Si_7$: C, 49.18; H, 9.29; found: C, 49.24; H, 9.55.



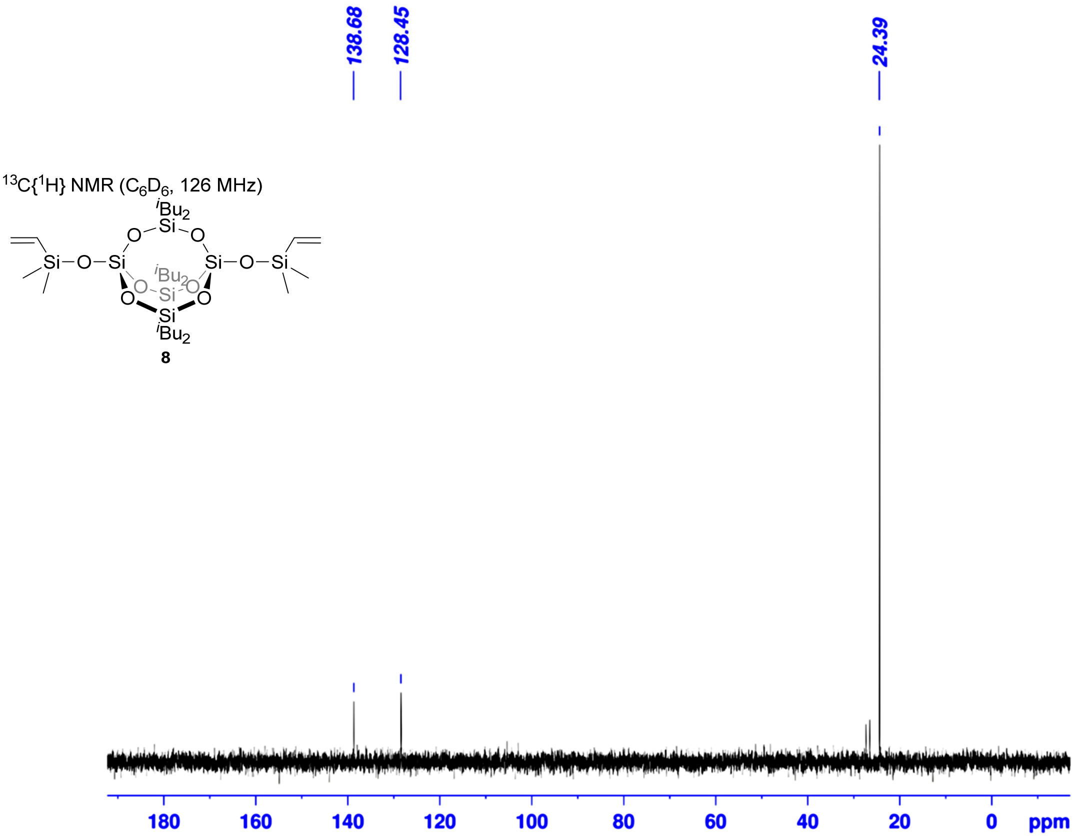
```
Current Data Parameters
NAME           YY17-183-4
EXPNO                   7
PROCNO                  1

F2 - Acquisition Parameters
Date_            20171109
Time                13.47
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                      4
DS                      0
SWH             10000.000 Hz
FIDRES           0.152588 Hz
AQ              3.2767999 sec
RG                  29.48
DW                 50.000 usec
DE                   6.50 usec
TE                  297.6 K
D1            10.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          17.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.1299968 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.00
```

Figure S26. ^{1}H NMR spectrum of **8** in C_6D_6 (126 MHz, 298 K).



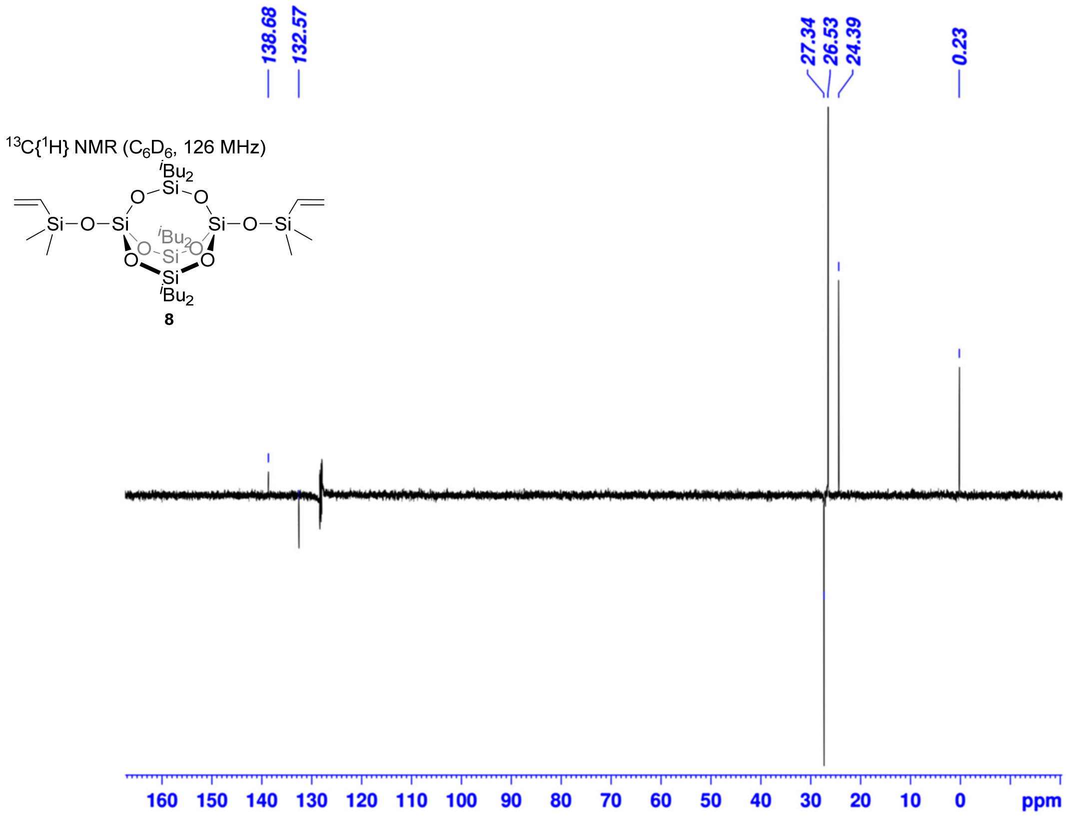
```
Current Data Parameters
NAME             YY17-183-4
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20171110
Time                  21.43
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT                C6D6
NS                      128
DS                        0
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                   188.42
DW                   16.800 usec
DE                     6.50 usec
TE                    298.2 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            125.7703637 MHz
NUC1                    13C
P1                    10.00 usec
PLW1            74.00000000 W

======== CHANNEL f2 ========
SFO2            500.1320005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2            17.00000000 W
PLW12            0.38249999 W
PLW13            0.24480000 W

F2 - Processing parameters
SI                    32768
SF              125.7577284 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

Figure S27. $^{13}C\{^1H\}$ NMR spectrum of **8** in C_6D_6 (126 MHz, 298 K).



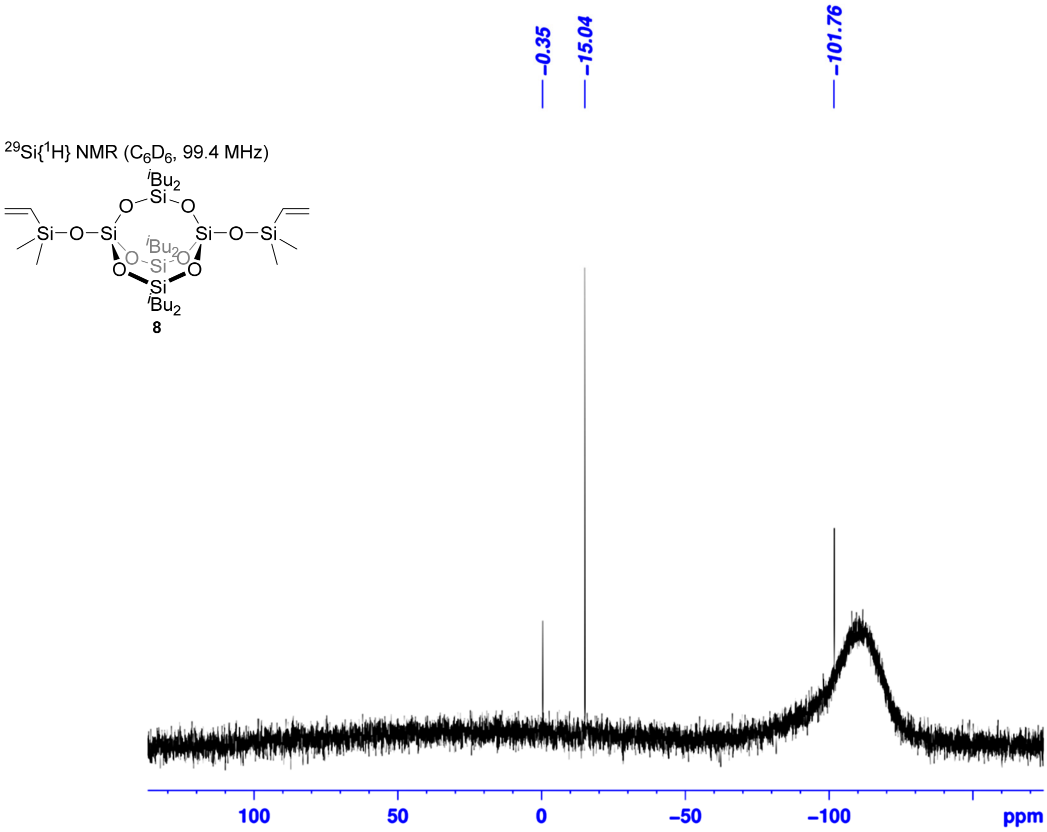
```
Current Data Parameters
NAME             YY17-183-4
EXPNO                     8
PROCNO                    1

F2 - Acquisition Parameters
Date_              20171110
Time                  21.35
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG            deptsp90
TD                    65536
SOLVENT                C6D6
NS                       32
DS                        0
SWH               29761.904 Hz
FIDRES             0.454131 Hz
AQ                1.1010048 sec
RG                   188.42
DW                   16.800 usec
DE                     6.50 usec
TE                    297.5 K
CNST2           145.0000000
D1               2.00000000 sec
D2               0.00344828 sec
D12              0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            125.7703643 MHz
NUC1                    13C
P1                    10.00 usec
P13                 2000.00 usec
PLW0     0 W
PLW1            74.00000000 W
SPNAM[5]        Crp60comp.4
SPOAL5                0.500
SPOFFS5  0 Hz
SPW5            11.30599976 W

======== CHANNEL f2 ========
SFO2            500.1320005 MHz
NUC2                     1H
CPDPRG[2            waltz16
P3                    12.00 usec
P4                    24.00 usec
PCPD2                 80.00 usec
PLW2            17.00000000 W
PLW12            0.38249999 W

F2 - Processing parameters
SI                    32768
SF              125.7577284 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```

Figure S28. $^{13}C\{^1H\}$ NMR (dept90) spectrum of **8** in C_6D_6 (126 MHz, 298 K).



```
Current Data Parameters
NAME          YY17-183-4
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171110
Time               21.40
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG        deptsp135
TD                 65536
SOLVENT             C6D6
NS                    96
DS                     0
SWH            28846.154 Hz
FIDRES          0.440157 Hz
AQ             1.1359574 sec
RG                188.42
DW                17.333 usec
DE                  6.50 usec
TE                 297.7 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         125.7691072 MHz
NUC1                 13C
P1                 10.00 usec
P13              2000.00 usec
PLW0     0 W
PLW1         74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5         11.30599976 W

======== CHANNEL f2 ========
SFO2         500.1315995 MHz
NUC2                  1H
CPDPRG[2         waltz16
P3                 12.00 usec
P4                 24.00 usec
PCPD2              80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF           125.7577284 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Figure S29. $^{13}C\{^1H\}$ NMR (dept135) spectrum of **8** in C_6D_6 (126 MHz, 298 K).



```
Current Data Parameters
NAME          YY17-183-4
EXPNO                 15
PROCNO                 1

F2 - Acquisition Parameters
Date_           20171111
Time               17.01
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgig30
TD                 65536
SOLVENT             C6D6
NS                   451
DS                     0
SWH            39682.539 Hz
FIDRES          0.605507 Hz
AQ             0.8257536 sec
RG                188.42
DW                12.600 use
DE                  6.50 use
TE                 297.5 K
D1           10.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 =======
SFO1          99.3617620 MHz
NUC1                29Si
P1                 11.90 use
PLW1         74.00000000 W

======== CHANNEL f2 =======
SFO2         500.1320005 MHz
NUC2                  1H
CPDPRG[2         waltz65
PCPD2              80.00 use
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                 32768
SF            99.3617226 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Figure S30. $^{29}Si\{^1H\}$ NMR spectrum of **8** in C_6D_6 (99.4 MHz, 298 K).

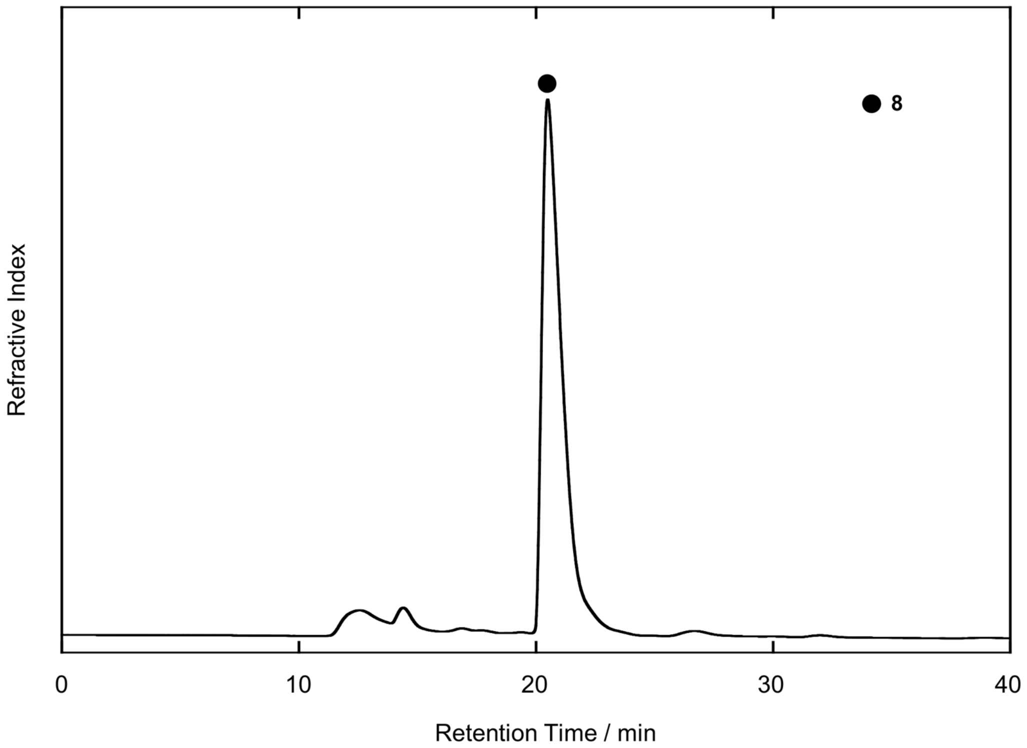
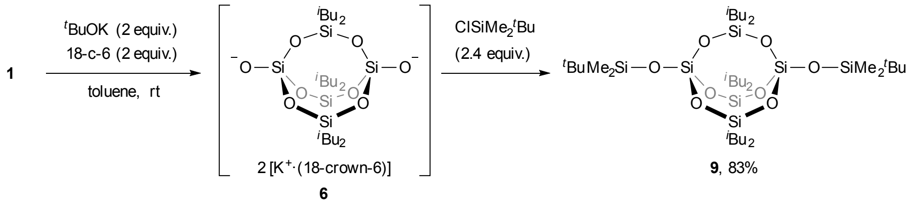


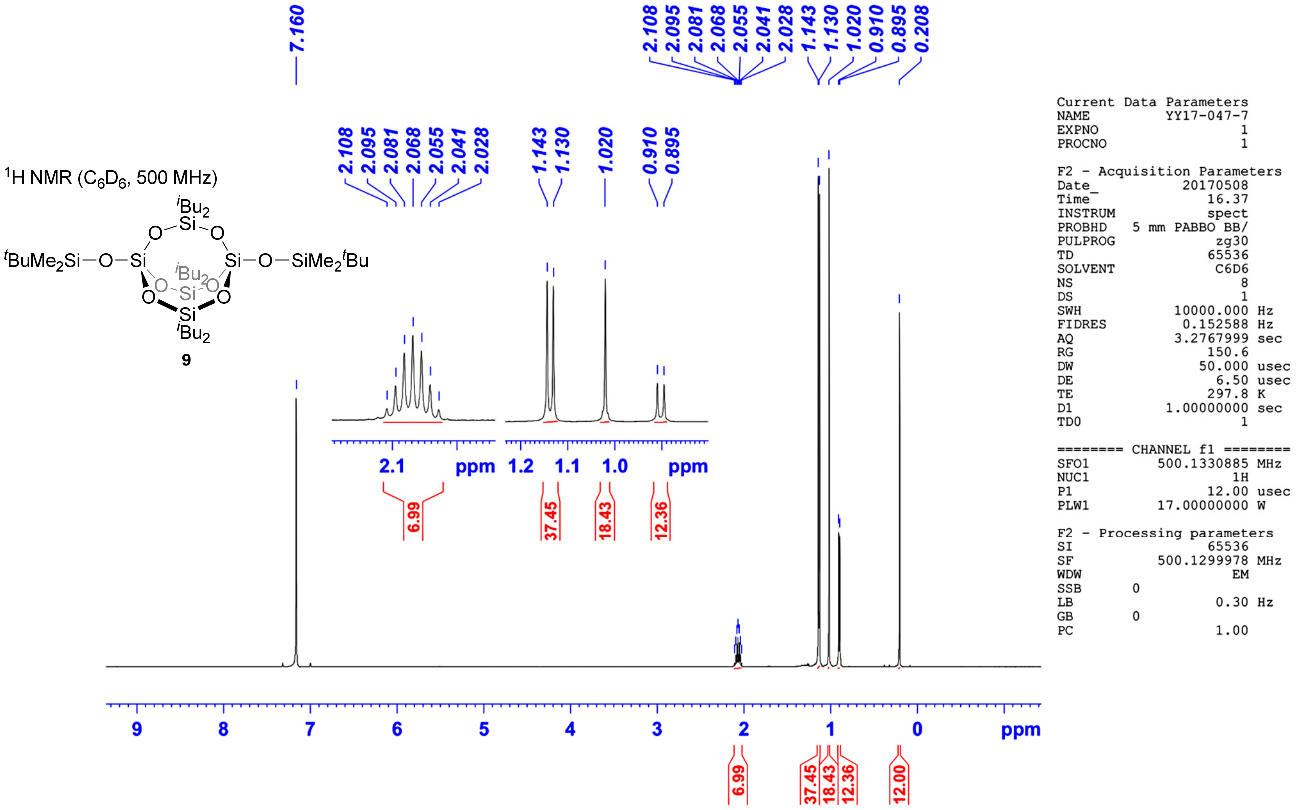
Figure S31. HPLC chart recorded during purification of **8**.

Synthesis of 9



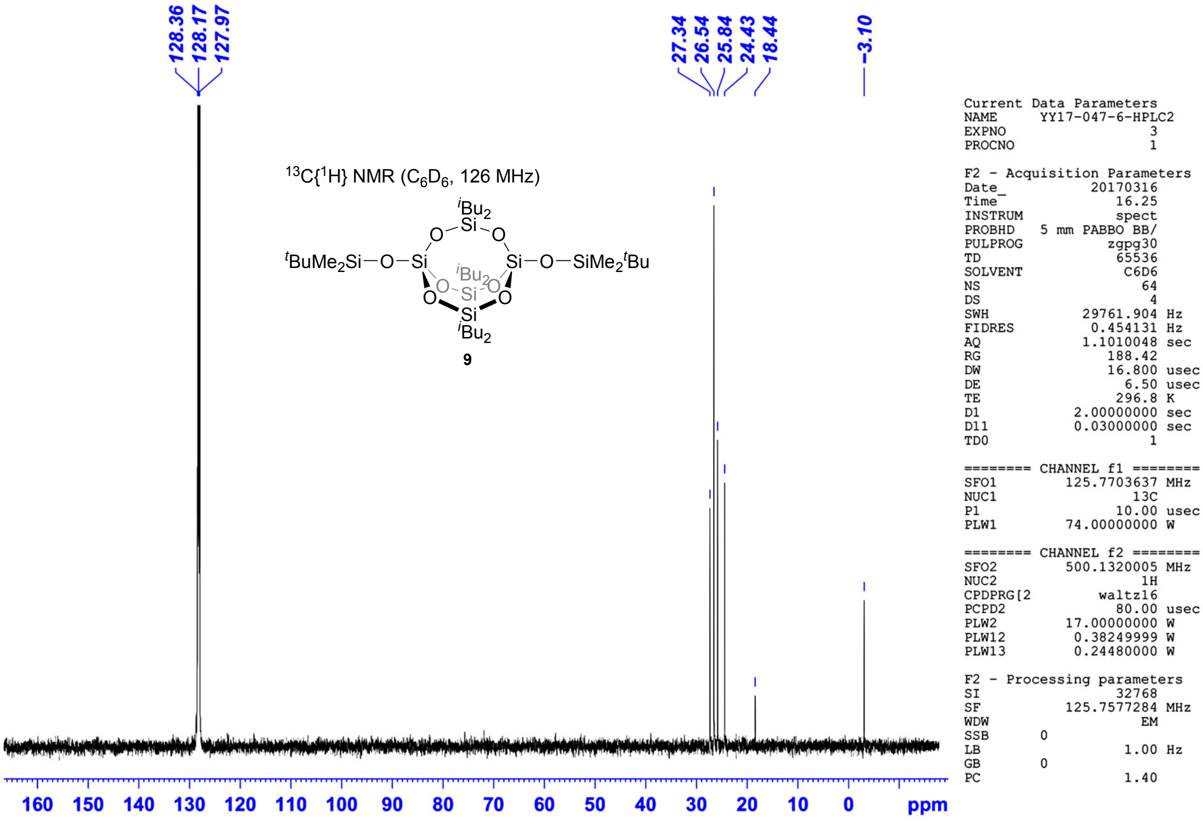
In a Schlenk tube (50 mL) equipped with a magnetic stir bar, **1** (50.0 mg, 0.0660 mmol), 18-c-6 (36.7 mg, 0.139 mmol), ^{t}BuOK (15.6 mg, 0.139 mmol), and toluene (3 mL) were charged. The reaction mixture was stirred for 1.5 h at room temperature and then *tert*-butylchlorodimethylsilane (24.1 mg, 0.161 mmol) was added to the mixture. After the volatiles were removed in *vacuo*, hexane (10 mL) was added to the resulting solid. The resulting insoluble materials were filtered off through a silica gel. The resulting colorless powder was subjected to HPLC (ODS, EtOH as an eluent, room temperature) to afford **9** (42.1 mg, 0.0500 mmol, 83%) as a white powder.

9: a white powder; mp 120-121 °C; ^{1}H NMR (500 MHz, C_6D_6, 298 K) δ 0.21 (s, 12H, Si(CH_3)$_2{}^t$Bu), 0.90 (d, J = 7.5 Hz, 12H, CH_2CH(CH$_3$)$_2$), 1.02 (s, 18H, C(CH_3)$_3$) 1.14 (d, J = 6.5 Hz, 36H, CH$_2$CH(CH_3)$_2$), 2.03 – 2.11 (m, 6H, CH$_2$CH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 297 K) δ –3.1 (Si(CH$_3$)$_2{}^t$Bu), 18.4 (C(CH$_3$)$_3$), 24.4 (CH$_2$$C$H(CH$_3$)$_2$), 25.8 (C($CH_3$)$_3$), 26.5 (CH$_2$CH($CH_3$)$_2$), 27.3 ($CH_2$CH(CH$_3$)$_2$); ^{29}Si{^{1}H} NMR (99.4 MHz, C_6D_6, 296 K) δ –102.2 (Si^{Q}), –15.3 (Si^{D}), 13.8 (Si^{M}); MS (EI, 70 eV) *m*/*z* (%) 826 (2) [M$^+$+H–CH$_3$], 784 (100) [M$^+$+H–C$_4$H$_9$]; Elemental analysis calcd for $C_{36}H_{84}O_8Si_7$: C, 51.37; H, 10.06; found: C, 51.58; H, 10.19.



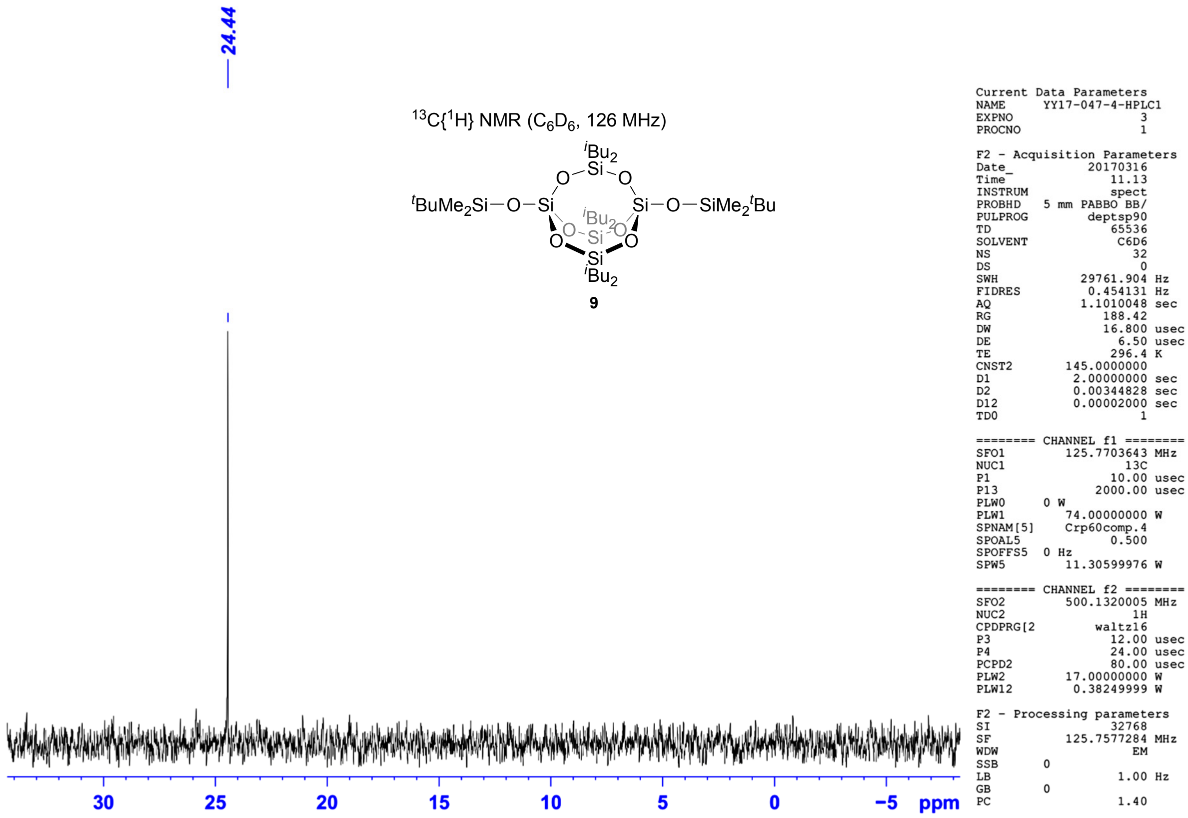
```
Current Data Parameters
NAME         YY17-047-7
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20170508
Time              16.37
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT            C6D6
NS                    8
DS                    1
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ            3.2767999 sec
RG                150.6
DW               50.000 usec
DE                 6.50 usec
TE                297.8 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                 1H
P1                12.00 usec
PLW1        17.00000000 W

F2 - Processing parameters
SI                65536
SF          500.1299978 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

Figure S32. ^{1}H NMR spectrum of **9** in C_6D_6 (126 MHz, 298 K).



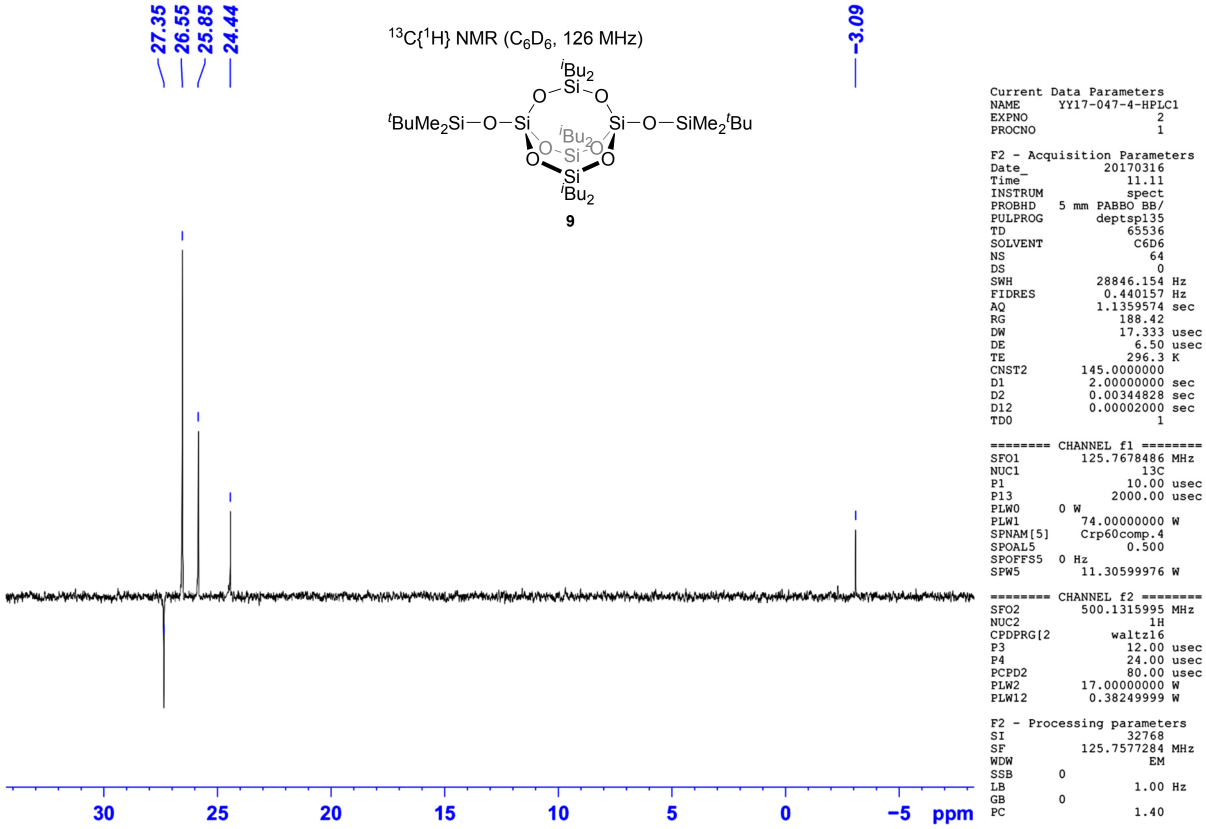
```
Current Data Parameters
NAME    YY17-047-6-HPLC2
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20170316
Time              16.25
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT            C6D6
NS                   64
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               188.42
DW               16.800 usec
DE                 6.50 usec
TE                296.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7703637 MHz
NUC1                13C
P1                10.00 usec
PLW1        74.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2        17.00000000 W
PLW12        0.38249999 W
PLW13        0.24480000 W

F2 - Processing parameters
SI                32768
SF          125.7577284 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

Figure S33. ^{13}C{^{1}H} NMR spectrum of **9** in C_6D_6 (126 MHz, 297 K).



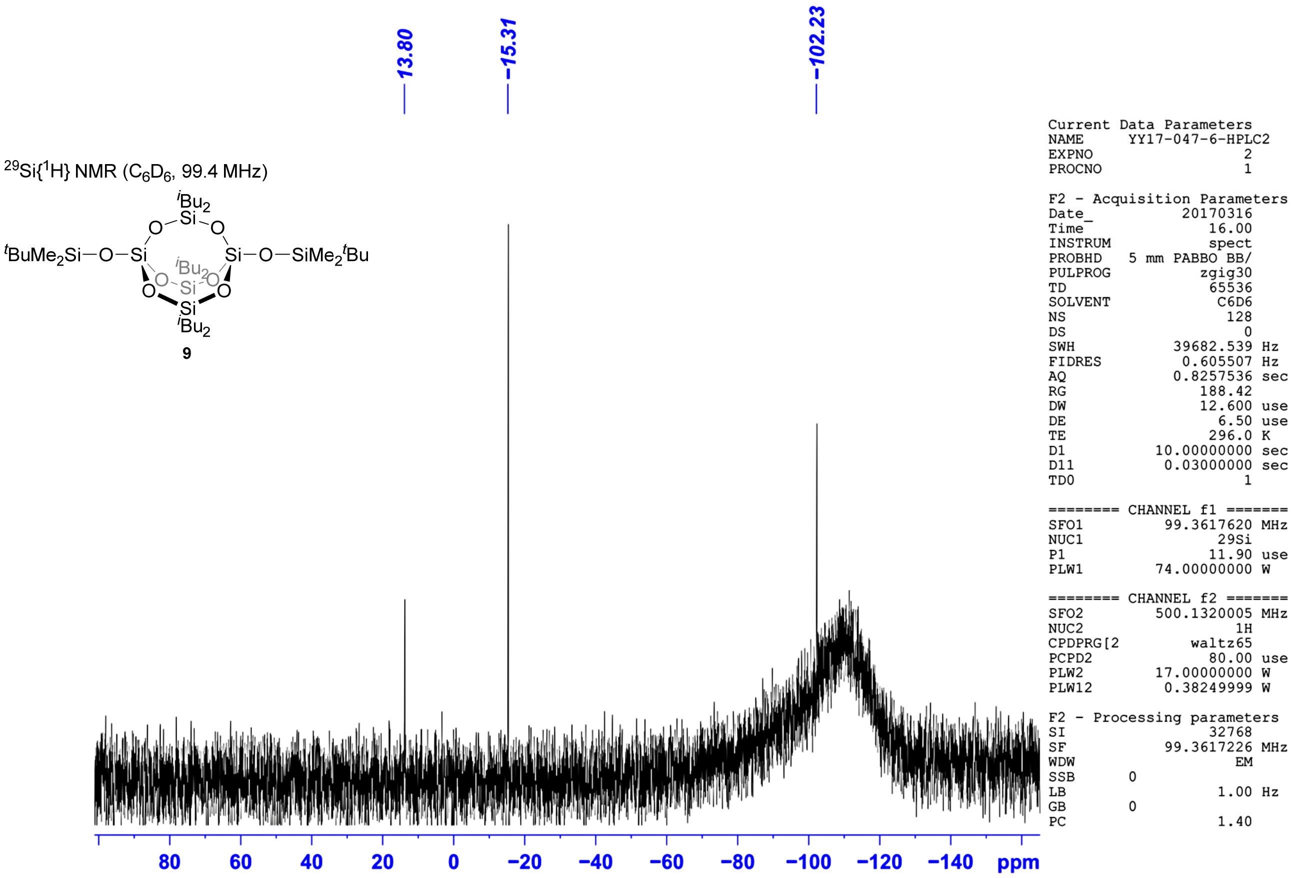
```
Current Data Parameters
NAME     YY17-047-4-HPLC1
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170316
Time                11.13
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          deptsp90
TD                  65536
SOLVENT              C6D6
NS                     32
DS                      0
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                 188.42
DW                 16.800 usec
DE                   6.50 usec
TE                  296.4 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7703643 MHz
NUC1                  13C
P1                  10.00 usec
P13               2000.00 usec
PLW0     0 W
PLW1         74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5              0.500
SPOFFS5  0 Hz
SPW5         11.30599976 W

======== CHANNEL f2 ========
SFO2         500.1320005 MHz
NUC2                   1H
CPDPRG[2          waltz16
P3                  12.00 usec
P4                  24.00 usec
PCPD2               80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                  32768
SF           125.7577284 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

Figure S34. $^{13}C\{^1H\}$ NMR (dept90) spectrum of **9** in C_6D_6 (126 MHz, 296 K).



```
Current Data Parameters
NAME     YY17-047-4-HPLC1
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170316
Time                11.11
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG         deptsp135
TD                  65536
SOLVENT              C6D6
NS                     64
DS                      0
SWH            28846.154 Hz
FIDRES          0.440157 Hz
AQ             1.1359574 sec
RG                 188.42
DW                 17.333 usec
DE                   6.50 usec
TE                  296.3 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7678486 MHz
NUC1                  13C
P1                  10.00 usec
P13               2000.00 usec
PLW0     0 W
PLW1         74.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5              0.500
SPOFFS5  0 Hz
SPW5         11.30599976 W

======== CHANNEL f2 ========
SFO2         500.1315995 MHz
NUC2                   1H
CPDPRG[2          waltz16
P3                  12.00 usec
P4                  24.00 usec
PCPD2               80.00 usec
PLW2         17.00000000 W
PLW12         0.38249999 W

F2 - Processing parameters
SI                  32768
SF           125.7577284 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```

Figure S35. $^{13}C\{^1H\}$ NMR (dept135) spectrum of **9** in C_6D_6 (126 MHz, 296 K)



```
Current Data Parameters
NAME      YY17-047-6-HPLC2
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170316
Time                 16.00
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG             zgig30
TD                   65536
SOLVENT               C6D6
NS                     128
DS                       0
SWH             39682.539 Hz
FIDRES           0.605507 Hz
AQ              0.8257536 sec
RG                  188.42
DW                  12.600 use
DE                    6.50 use
TE                   296.0 K
D1             10.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 =======
SFO1           99.3617620 MHz
NUC1                  29Si
P1                   11.90 use
PLW1           74.00000000 W

======== CHANNEL f2 =======
SFO2          500.1320005 MHz
NUC2                    1H
CPDPRG[2            waltz65
PCPD2                80.00 use
PLW2           17.00000000 W
PLW12           0.38249999 W

F2 - Processing parameters
SI                   32768
SF             99.3617226 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

Figure S36. ^{29}Si{^{1}H} NMR spectrum of **9** in C_6D_6 (99.4 MHz, 296 K).

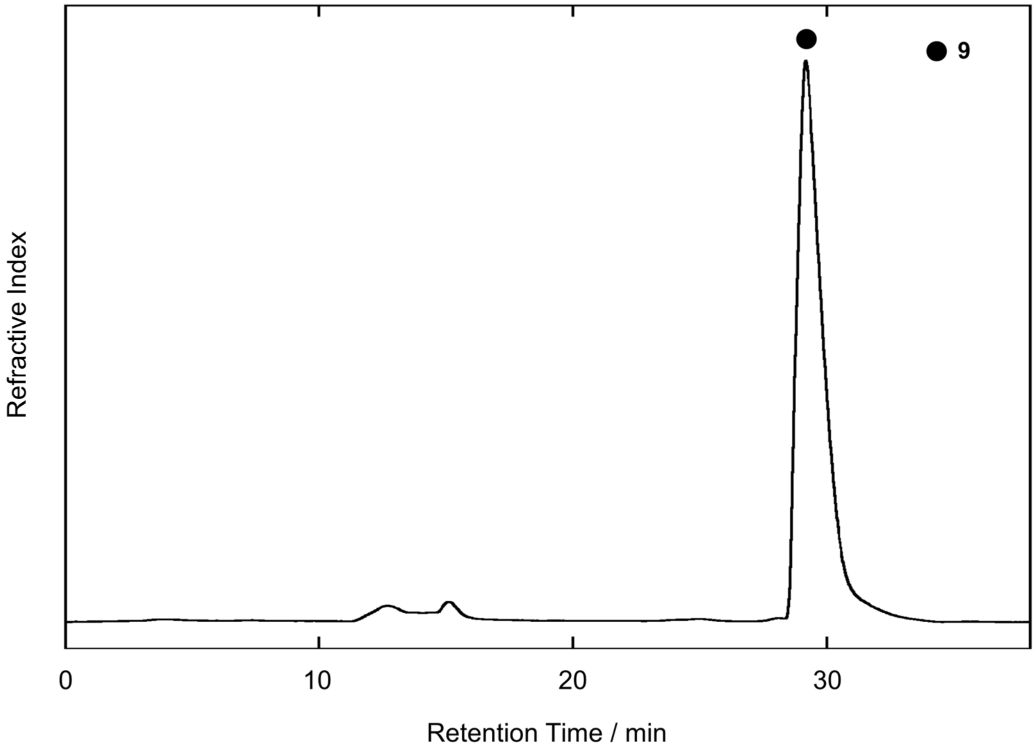


Figure S37. HPLC chart of **9**.

2. Single crystal X-ray diffraction analyses of 1 and 9

Single crystals suitable for X-ray diffraction study were obtained by recrystallization from EtOH at room temperature for **1** and **9**. The single crystals for data collection coated by Apiezon® grease was mounted on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS[S3] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELEX-2014).[S4] Molecular structures ware analyzed by Yadokari-XG[5] software.

Compound **9** was measured at different temperatures (100 K, 173 K, 223 K) using the same single crystal in the order 100 K → 223 K → 173 K.

Crystal data for **1** (CCDC-1576828) (100 K): 0.20 mm × 0.20 mm × 0.10 mm; $C_{30}H_{72}O_8Si_7$; Formula weight 757.50; tetragonal; space group $I4_1/a$; a = 29.5020(5) Å, b = 29.5020(5) Å, c = 10.4338(2) Å, V = 9081.2(4) Å^3, Z = 8, D_{calcd} = 1.108 Mg m^{-3}, 58962 reflections measured, 4457 unique (R_{int} = 0.0306), which were used in all calculations; $R1$ = 0.0810 ($I > 2\sigma(I)$), $wR2$ = 0.2110 (all data), GOF = 1.077, max/min residual electron densities 0.573/–0.308 e/Å^3.

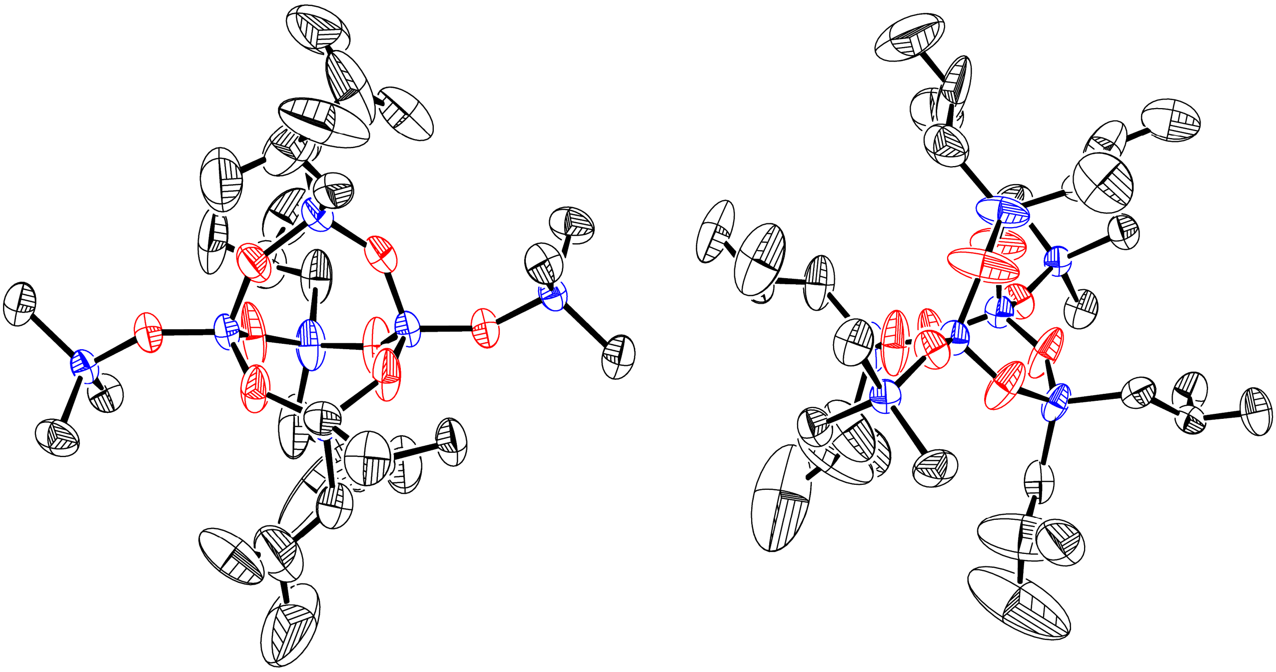


Figure S38. ORTEP drawings of **1** (atomic displacement parameters are set at the 50% possibility; hydrogen atoms are omitted for clarity).

Crystal data for **9** (CCDC-1576829) (100 K): 0.30 mm × 0.30 mm × 0.30 mm; $C_{36}H_{84}O_8Si_7$; Formula weight 841.66; monoclinic; space group $C2/c$; a = 18.2557(12) Å, b = 13.4289(9) Å, c = 21.0576(13) Å, β = 104.5550(10)°, V = 4996.7(6) Å^3, Z = 4, D_{calcd} = 1.119 Mg m^{-3}, 36402 reflections measured, 5751 unique (R_{int} = 0.0205), which were used in all calculations; $R1$ = 0.0297 ($I > 2\sigma(I)$), $wR2$ = 0.0790 (all data), GOF = 1.064, max/min residual electron densities 0.514/–0.437 e/Å^3.

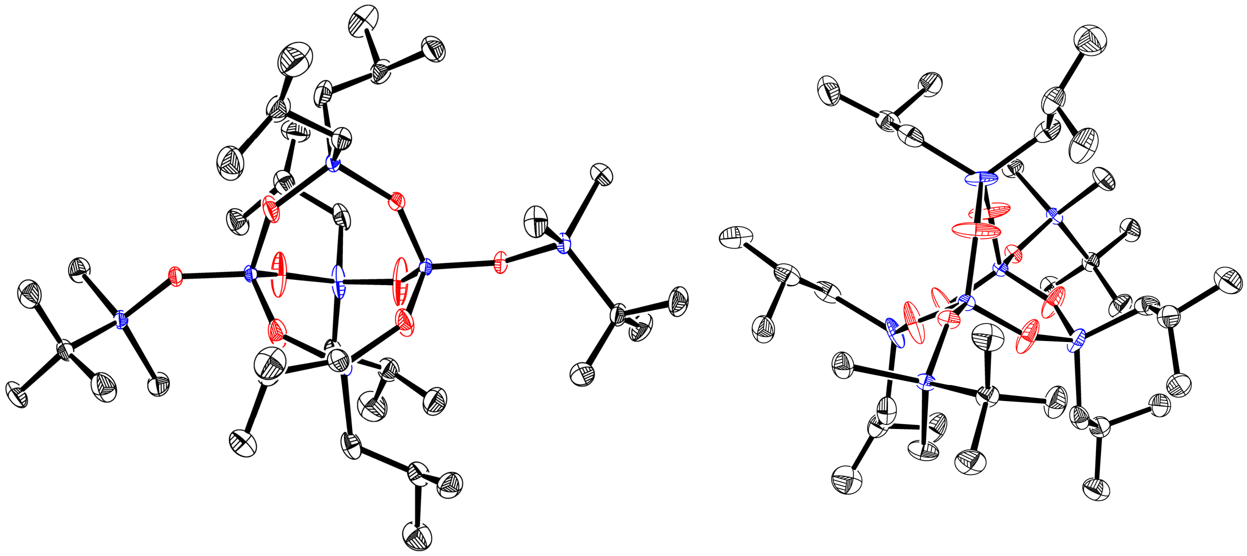


Figure S39. ORTEP drawings of **9** (atomic displacement parameters are set at the 50% possibility; hydrogen atoms are omitted for clarity). The sample was measured at 100 K.

Crystal data for **9** (CCDC: 1576899) (173 K): 0.30 mm × 0.30 mm × 0.30 mm; $C_{36}H_{84}O_8Si_7$; Formula weight 841.66; monoclinic; space group *C*2/*c*; *a* = 18.4236(4) Å, *b* = 13.5947(3) Å, *c* = 21.1068(5) Å, β = 104.2450(10)°, *V* = 5123.9(2) Å^3, *Z* = 4, D_{calcd} = 1.091 Mg m^{-3}, 30476 reflections measured, 4518 unique (R_{int} = 0.0221), which were used in all calculations; *R*1 = 0.0537 ($I > 2\sigma(I)$), *wR*2 = 0.1513 (all data), GOF = 1.039, max/min residual electron densities 1.446/– 0.516 e/Å^3. The observed large residual density (Q peak, 1.45 e/A^3) found near silicon atoms of the bridgehead siloxy group (alert B after CIFcheck) should be due to a disordered silicon atom as the similar disordered silicon atom was found at the similar positions in the same single crystal measured at 223 K. While the silicon atoms were modeled at two positions with the ratio of 92:8, the corresponding carbon atoms with a minor site occupancy factor were not able to be modeled properly.

Crystal data for **9** (CCDC-1576830) (223 K): 0.30 mm × 0.30 mm × 0.30 mm; $C_{36}H_{84}O_8Si_7$; Formula weight 841.66; monoclinic; space group *C*2/*c*; *a* = 19.0349(5) Å, *b* = 13.7423(3) Å, *c* = 21.0422(5) Å, β = 103.8890(10)°, *V* = 5343.4(2) Å^3, *Z* = 8, D_{calcd} = 1.046 Mg m^{-3}, 32950 reflections measured, 4920 unique (R_{int} = 0.0308), which were used in all calculations; *R*1 = 0.0703 ($I > 2\sigma(I)$), *wR*2 = 0.2335 (all data), GOF = 1.061, max/min residual electron densities 0.453/– 0.390 e/Å^3.

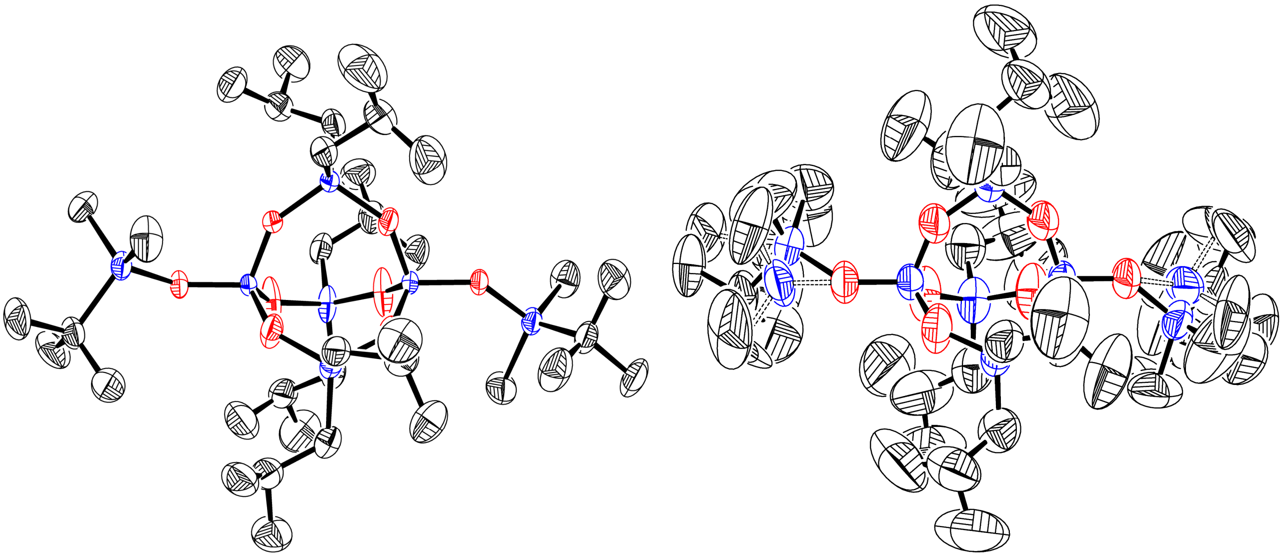


Figure S40. ORTEP drawings of **9** measured at 173 K (left) and at 223 K (right)**.** Atomic displacement parameters are set at the 50% possibility. Hydrogen atoms are omitted for clarity.

3. Thermogravimetric Analyses of 1

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of **1** were examined under dry nitrogen gas flow (100 mL min^{-1}) at the temperature range of 25–400 °C with heating rates of 0.1 K min^{-1}, 1.0 K min^{-1} or 10 K min^{-1} for **1**. The samples (2–4 mg) were loaded in an open aluminum pan for each measurement.

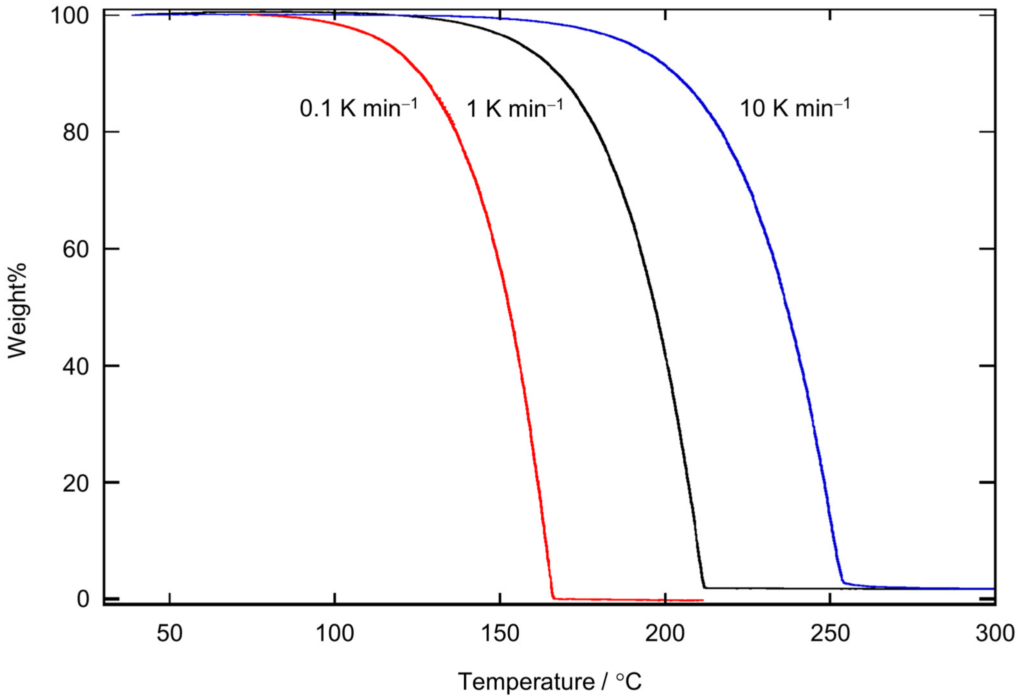


Figure S41. TGA curves of **1** with variable heating rates.

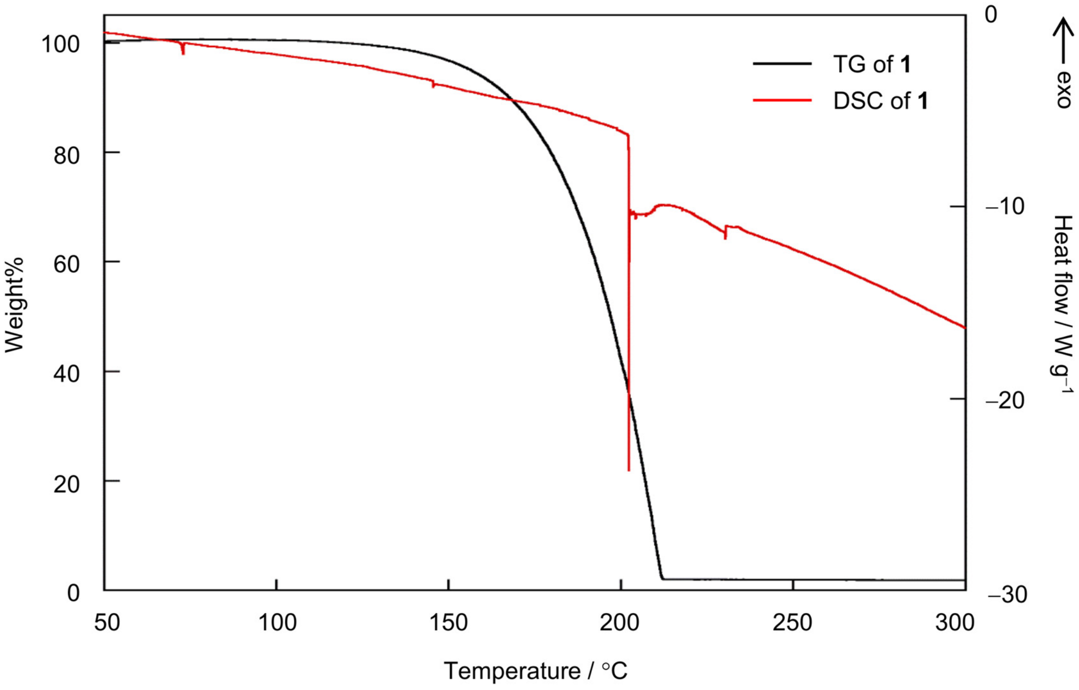
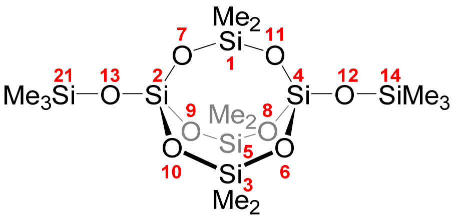


Figure S42. TGA and DSC profiles of **1** with heating rate of 1.0 K min^{-1}.

4. Theoretical calculation

All theoretical calculations were performed using Gaussian 09[S6] and NBO programs.[S7] Geometry optimization and NBO analysis of **1’** was performed at the B3PW91/6-31G(d) level of theory. Atomic coordinates and energies of **1’** were summarized in Tables S1. Natural population analysis was summarized in Table S2.



1'

TableS1. Atomic Coordinates of **1’** Optimized at the B3PW91/6-31G(d) Level of Theory

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-0.276557	-1.017511	2.123009
2	14	0	1.851598	0.216733	0.218741
3	14	0	0.000650	2.681145	0.001860
4	14	0	-1.852346	0.217655	-0.217979
5	14	0	0.276595	-1.014545	-2.123921
6	8	0	-1.340374	1.716778	0.207274
7	8	0	1.094774	-0.237053	1.602373
8	8	0	-1.096168	-0.238188	-1.601241
9	8	0	1.477391	-0.845811	-0.980881
10	8	0	1.340335	1.715730	-0.208072
11	8	0	-1.479042	-0.844045	0.982600
12	8	0	-3.449425	0.244823	-0.465009
13	8	0	3.448662	0.242954	0.465985
14	14	0	-4.966613	-0.358092	-0.108214
15	6	0	0.809480	-0.208172	-3.722365
16	6	0	-0.065274	-2.841402	-2.316039
17	6	0	0.067167	-2.844979	2.305948
18	6	0	-0.807922	-0.219171	3.725953
19	6	0	-0.195188	3.717332	-1.539596
20	6	0	0.197986	3.710466	1.547741
21	14	0	4.965932	-0.358615	0.107151
22	1	0	0.011570	-0.255122	-4.472143
23	1	0	1.059124	0.845961	-3.559944
24	1	0	1.694580	-0.702843	-4.138598
25	1	0	-0.833136	-3.018321	-3.077822
26	1	0	0.838583	-3.384819	-2.614187
27	1	0	-0.422886	-3.271278	-1.374043
28	1	0	-0.835963	-3.390690	2.602102
29	1	0	0.424438	-3.269819	1.361543
30	1	0	0.835790	-3.024957	3.066248
31	1	0	-1.693015	-0.715519	4.140187
32	1	0	-0.009539	-0.270458	4.474943
33	1	0	-1.057081	0.835940	3.569232
34	1	0	0.697986	4.325212	-1.723388
35	1	0	-0.358809	3.081440	-2.416412
36	1	0	-1.053725	4.392774	-1.451137
37	1	0	1.056992	4.385649	1.461873
38	1	0	-0.694654	4.318197	1.734592
39	1	0	0.361518	3.070577	2.421659
40	6	0	-5.404656	0.102665	1.661728
41	1	0	-4.697824	-0.343216	2.370840
42	1	0	-5.380441	1.189066	1.804862

43	1	0	-6.409811	-0.247829	1.926459
44	6	0	-4.950639	-2.227342	-0.315818
45	1	0	-4.691267	-2.510292	-1.342533
46	1	0	-4.215302	-2.688308	0.353577
47	1	0	-5.931612	-2.661526	-0.086961
48	6	0	-6.153972	0.444005	-1.322590
49	1	0	-7.183258	0.103110	-1.157451
50	1	0	-6.141499	1.535241	-1.221874
51	1	0	-5.881811	0.202039	-2.356261
52	6	0	5.402502	0.104866	-1.662445
53	1	0	4.695554	-0.340515	-2.371756
54	1	0	5.377517	1.191442	-1.804098
55	1	0	6.407720	-0.244634	-1.928254
56	6	0	6.153730	0.442398	1.321807
57	1	0	7.183062	0.102202	1.155515
58	1	0	6.140689	1.533762	1.222578
59	1	0	5.882378	0.198905	2.355332
60	6	0	4.951012	-2.228153	0.312138
61	1	0	4.692684	-2.512635	1.338694
62	1	0	4.215263	-2.688507	-0.357224
63	1	0	5.931967	-2.661592	0.081807

E(RB3PW91) = -3107.41908612
Zero-point correction= 0.492760 (Hartree/Particle)
Thermal correction to Gibbs Free Energy (298.15 K) = 0.409430

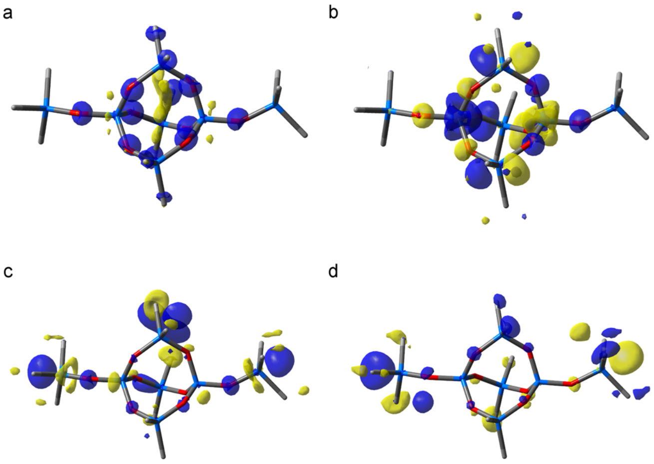


Figure S43. Frontier Kohn-Sham orbitals of **1'**; LUMO (a), LUMO+1 (b), LUMO+2 (c), LUMO+3 (d).

TableS2. Summary of Natural Population Analysis of **1'** Optimized at the B3PW91/6-31G(d) Level of Theory

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Si	1	2.20587	9.99757	1.74261	0.05395	11.79413
Si	2	2.50346	9.99657	1.43041	0.06956	11.49654
Si	3	2.20713	9.99756	1.74172	0.05359	11.79287
Si	4	2.50358	9.99657	1.43031	0.06954	11.49642
Si	5	2.20587	9.99757	1.74262	0.05395	11.79413
O	6	-1.26561	1.99982	7.25464	0.01116	9.26561
O	7	-1.26740	1.99981	7.25656	0.01103	9.26740
O	8	-1.26748	1.99981	7.25663	0.01103	9.26748
O	9	-1.26762	1.99982	7.25690	0.01090	9.26762
O	10	-1.26558	1.99982	7.25460	0.01116	9.26558
O	11	-1.26768	1.99982	7.25696	0.01090	9.26768

O	12	-1.26017	1.99981	7.25007	0.01030	9.26017
O	13	-1.26018	1.99981	7.25007	0.01030	9.26018
Si	14	2.02797	9.99776	1.93094	0.04334	11.97203
C	15	-1.26381	1.99947	5.25545	0.00890	7.26381
C	16	-1.26318	1.99947	5.25485	0.00886	7.26318
C	17	-1.26322	1.99947	5.25489	0.00887	7.26322
C	18	-1.26376	1.99947	5.25540	0.00889	7.26376
C	19	-1.26356	1.99947	5.25525	0.00884	7.26356
C	20	-1.26360	1.99947	5.25529	0.00884	7.26360
Si	21	2.02795	9.99776	1.93095	0.04334	11.97205
H	22	0.26571	0.00000	0.73372	0.00057	0.73429
H	23	0.26942	0.00000	0.72974	0.00083	0.73058
H	24	0.26243	0.00000	0.73699	0.00059	0.73757
H	25	0.26429	0.00000	0.73513	0.00058	0.73571
H	26	0.26387	0.00000	0.73554	0.00059	0.73613
H	27	0.26762	0.00000	0.73155	0.00083	0.73238
H	28	0.26388	0.00000	0.73554	0.00059	0.73612
H	29	0.26765	0.00000	0.73152	0.00083	0.73235
H	30	0.26427	0.00000	0.73515	0.00058	0.73573
H	31	0.26245	0.00000	0.73696	0.00059	0.73755
H	32	0.26570	0.00000	0.73373	0.00057	0.73430
H	33	0.26939	0.00000	0.72978	0.00083	0.73061
H	34	0.26461	0.00000	0.73481	0.00058	0.73539
H	35	0.26864	0.00000	0.73053	0.00082	0.73136
H	36	0.26462	0.00000	0.73480	0.00058	0.73538
H	37	0.26460	0.00000	0.73482	0.00058	0.73540
H	38	0.26462	0.00000	0.73480	0.00058	0.73538
H	39	0.26868	0.00000	0.73049	0.00083	0.73132
C	40	-1.24702	1.99950	5.23894	0.00859	7.24702
H	41	0.26315	0.00000	0.73598	0.00087	0.73685
H	42	0.26381	0.00000	0.73544	0.00075	0.73619
H	43	0.25848	0.00000	0.74094	0.00058	0.74152
C	44	-1.24807	1.99950	5.24000	0.00857	7.24807
H	45	0.26250	0.00000	0.73674	0.00076	0.73750
H	46	0.26532	0.00000	0.73378	0.00090	0.73468
H	47	0.25864	0.00000	0.74078	0.00057	0.74136
C	48	-1.24379	1.99949	5.23593	0.00837	7.24379
H	49	0.25783	0.00000	0.74158	0.00058	0.74217
H	50	0.26428	0.00000	0.73497	0.00076	0.73572
H	51	0.26411	0.00000	0.73515	0.00075	0.73589
C	52	-1.24702	1.99950	5.23894	0.00859	7.24702
H	53	0.26313	0.00000	0.73600	0.00087	0.73687
H	54	0.26382	0.00000	0.73542	0.00075	0.73618
H	55	0.25850	0.00000	0.74092	0.00058	0.74150
C	56	-1.24380	1.99949	5.23593	0.00837	7.24380
H	57	0.25784	0.00000	0.74157	0.00058	0.74216
H	58	0.26428	0.00000	0.73496	0.00076	0.73572
H	59	0.26412	0.00000	0.73514	0.00075	0.73588
C	60	-1.24807	1.99950	5.24000	0.00857	7.24807
H	61	0.26250	0.00000	0.73674	0.00076	0.73750
H	62	0.26534	0.00000	0.73376	0.00090	0.73466
H	63	0.25865	0.00000	0.74078	0.00057	0.74135
* Total *		0.00000	109.97365	159.42308	0.60327	270.00000

5. References

S1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

S2. T. Iwamoto, D. Tsushima, E. Kwon, S. Ishida and H. Isobe, *Angew. Chem. Int. Ed.*, 2012, **124**, 2390.

S3. G. M. Sheldrick, SADABS, Empirical Absorption Correction Program; Göttingen, Germany, 1996.

S4. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **A64**, 112.

S5. Yadokari-XG 2009, Release of Software for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.* 2009, **51**, 218.

S6. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

S7. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.