Electronic Supplementary Material (ESI) for Dalton Transactions.

Introduction of organogermyl functionalities to the cage silsesquioxanes

Magdalena Grzelak,[a,b]* Dawid Frąckowiak, [b] Rafał Januszewski,[a,b] Bogdan Marciniec[a,b]*

[a] Faculty of Chemistry, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 8, 61–614, Poznań, Poland

E-mail: magdalena.grzelak@amu.edu.pl, bogdan.marciniec@amu.edu.pl

[b] Center for Advanced Technology, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 10, 61–614, Poznań, Poland

Content

General Information

Chlorotriethylgermane (ABCR), chlorodimethylphenylgermane (Gelest); chlorodimethylsilane, dichlorodimethylsilane (Alfa Aesar); allylmagnesium chloride (2 M in THF), vinylmagnesium bromide (1 M in THF), tetrachlorosilane, trichlorosilane, triethylamine, Karstedt's catalyst [$Pt_2(dvs)_3$], H_2PtCl_6, $[Rh(COD)Cl]_2$, PtO_2, toluene, dichloromethane, (Sigma-Aldrich); TrisilanolIsobutyl POSS, DiSilanolIsobutyl POSS, TetraSilanolPhenyl POSS (Hybrid Plastics), $CDCl_3$ (Deutero), THF and diethyl ether (Fisher Chemical). THF and diethyl ether were distilled from sodium/benzophenone ketyl. Silsesquioxane substrates, i.e. **2** (7,17-dimethyl-7,17-dihydro-1,3,5,9,11,13,15,1-octaphenylhexacyclo[9.13.$1^{1,9}$.$1^{3,15}$.$1^{5,13}$.$1^{11,19}$]decasiloxane),[1] **3** (mono-decker silsesquioxane),[2] **4** [(hydro)heptaisobutylsilsesquioxane],[3] **5** (octahydrosilsesquioxane),[4] **6** [(dimethylsiloxy)hepta(isobutyl)octasilsesquioxane],[5] **7** [oktakis(dimethylsiloxy)silsesquioxane][6] were prepared according to literature procedures. Allyl- and vinylgermanes **1a–d** were prepared from the respective chlorogermanes and allyl- and vinylmagnesium Grignard reagents. The representative synthetic procedure is given below.

Allyltriethylgermane

A magnetic stirrer and approx. 30 mL of freshly distilled diethyl ether were placed in a 50-mL, two-necked round-bottomed flask (previously dried under reduced pressure and filled with argon, equipped with a reflux condenser and an argon plug and gas bubbler). Then, 1.5 g (1.28 mL, 7.68 mmol) of chlorotriethylgermane was added to the stirred solvent, followed by the dropwise addition of 5 mL (9.99 mmol) of 2 M allyl magnesium chloride solution. The resulting suspension was vigorously stirred for 24 h at room temperature. After this time, GC/MS analysis was performed and full conversion of chlorogermanane to allyl derivative was confirmed. The precipitate was partially filtered on a sintered funnel and washed with pentane. The resulting milky suspension was filtered on a short celite column, rinsed with small portions of pentane. The solvent was removed under reduced pressure on a rotary evaporator, and the obtained crude product was subjected to a "trap to trap" distillation. Pure allyltriethylgermane was obtained as a colorless liquid (1.36 g, 88% yield).

[1] Y. Morimoto, K. Watanabe, N. Ootake, J. Inagaki, K. Yoshida, K. Ohguma, US Patent 7449539 B2, 2008.

[2] J. D. Lichtenhan, US Patent 6660823 B1, 2003.

[3] M. Takeda, K. Kuroiwa, M. Mitsuishi, J. Matsui, Chem. Lett. 2015, 44, 1560–1562.

[4] P. A. Agaskar, Inorg. Chem. 1991, 30, 2707–2708.

[5] B. Dudziec, M. Rzonsowska, B. Marciniec, D. Brząkalski, B. Woźniak, Dalton Trans. 2014, 43, 13201–13207.

[6] N. L. Dias Filho, H. A. De Aquino, G. Pires, L. Caetano, J. Braz. Chem. Soc. 2006, 17, 533–541.

Measurements

Nuclear magnetic resonance spectroscopy (NMR)

The ^{1}H (300, 400 MHz), ^{13}C (75, 101 MHz), 135DEPT and ^{29}Si NMR (79 MHz) spectra were recorded with a Varian XL 300 MHz spectrometer and Varian VNMR-S 400 MHz spectrometer with samples in $CDCl_3$ solution. The chemical shifts are reported in ppm and were referenced to the residual solvent signals (δH = 7.26 ppm, δC = 77.36 ppm for $CDCl_3$).

***In situ* FT-IR spectroscopy**

Real-timeFT-IR measurements were performed on a Mettler Toledo ReactIR 15 equipped with a DS 6.3 mm AgXDiComp Fiber Probe with a diamond sensor, and a Mercury Cadmium Telluride detector. For all the spectra 256 scans were recorded with the resolution of 1 cm^{-1} in 1, 5 and 10 min intervals.

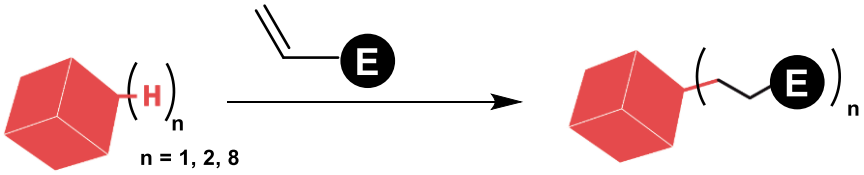
Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOFMS) and HRMS (ESI)

MALDI-TOF mass spectra were recorded on a UltrafleXtreme mass spectrometer (Bruker Daltonics), equipped with a SmartBeam II laser (355 nm) in 500-4000 m/z range. 2,5-Dihydroxybenzoic acid (DHB) served as matrix. HRMS (ESI) mass spectra were recorded on QTOF (Impact HD, Bruker).

General procedure for the synthesis of functionalized POSS derivatives.

To a 5 mL glass reactor equiped with *in situ* FT-IR probe SQ (100 mg, 1.0 eq.) of **2**, **3**, **5-7**, vinylgermane, allylgermane or vinylsilane (1.0/2.0 or 8.0 eq.) and toluene (1 mL) were added. The reaction mixture was stirred at 100°C for few minutes. After this time, the catalyst 10^{-4} mol% (per SiH group was added). After reaction, the mixture was filtered off by glass filter type G4 with silica-gel and Celite, solvent was evaporated and excess was removed under reduced pressure to give corresponding products **2-3a-f** and **5-7a-d**.

Molar ratio [**1**] : [**2**] : [Pt] – 1 : 2 : 2 x 10^{-4}, [**1**] : [**3/6**] : [Pt] – 1 : 1 : 10^{-4}, [**1**] : [**5/7**] : [Pt] – 1 : 8 : 8 x 10^{-4}



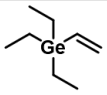
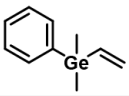
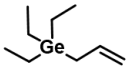
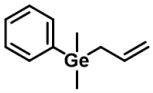
(2-7)

General scheme for functionalized POSS synthesis.

Picture of reaction system

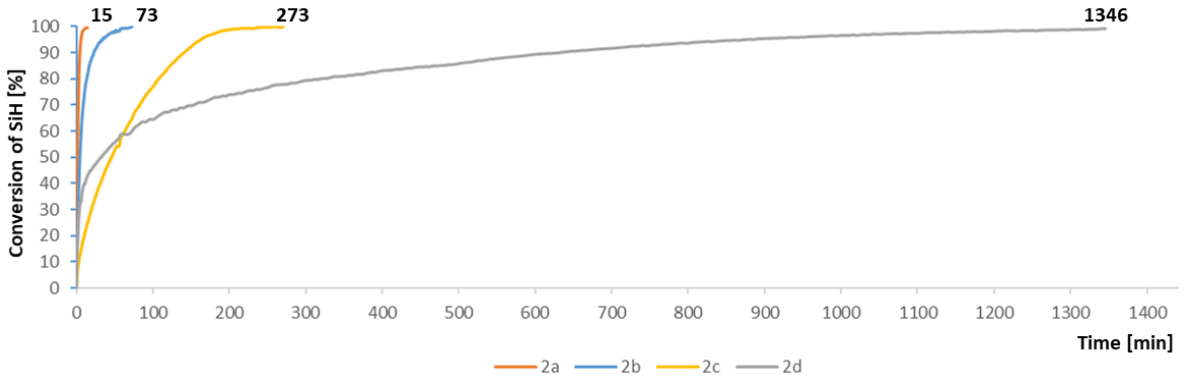
Hydrosilylation of vinyl- and allylgermanes with silsesquioxanes and spherosilicates and kinetic plots for the formation of products 2a-2d, 3a-3d, 5a-5d, 6a-6d, 7a-7d.

Hydrosilylation of vinyl- and allylgermanes (**1a**–**1d**) with double-decker silsesquioxane (**2**).

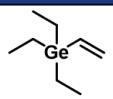
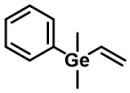
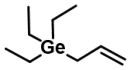
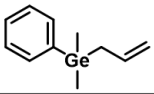
Product	Ge	Molar ratio [1]:[2]:[Pt]	Reaction time [min][a]	Yield [%][b]
2a	 **1a**	**1 : 2 : 2 x 10^{-4}**	**73**	**90**
2b	 **1b**	**1 : 2 : 2 x 10^{-4}**	**15**	**89**
2c	 **1c**	**1 : 2 : 2 x 10^{-4}**	**1346**	**93**
2d	 **1d**	**1 : 2 : 2 x 10^{-4}**	**273**	**90**

[a] Reaction monitored by FT-IR *in situ* and time measured for complete conversion of SQ. [b] Isolated yield.

Kinetic plots for the formation of **2a-2d** products.

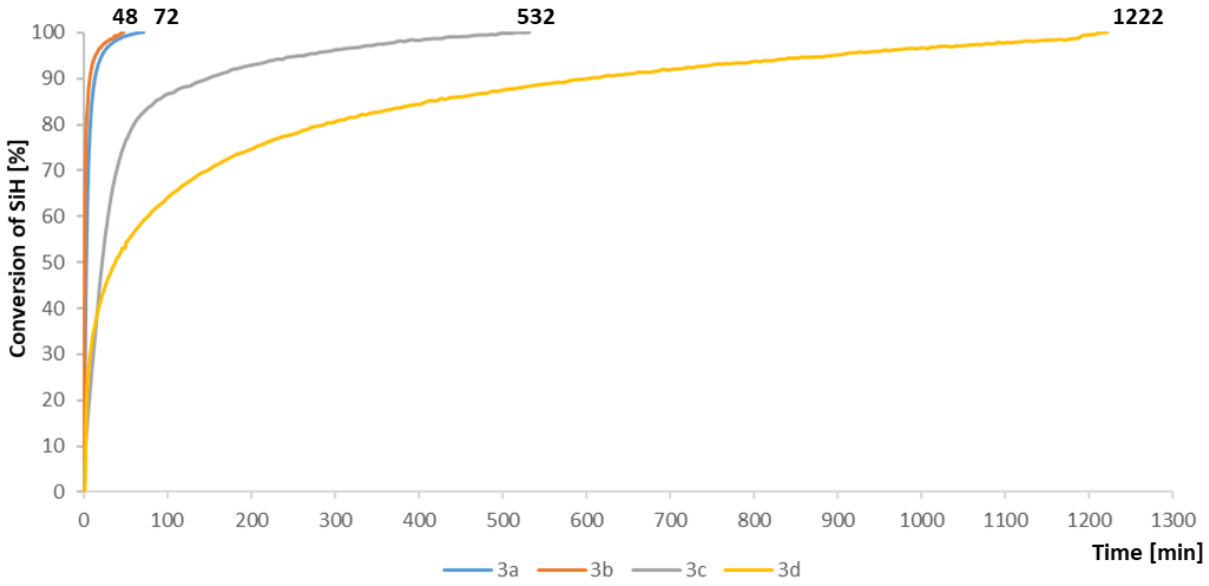


Hydrosilylation of vinyl- and allylgermanes (**1a**–**1d**) with mono-decker silsesquioxane (**3**).

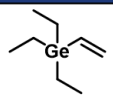
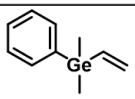
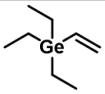
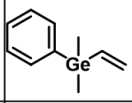
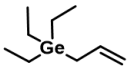
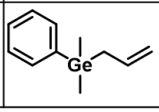
Product	Ge	Molar ratio [1]:[3]:[Pt]	Reaction time [min][a]	Yield [%][b]
3a	 **1a**	**1 : 1 : 10^{-4}**	**72**	**92**
3b	 **1b**	**1 : 1 : 10^{-4}**	**48**	**95**
3c	 **1c**	**1 : 1 : 10^{-4}**	**532**	**90**
3d	 **1d**	**1 : 1 : 10^{-4}**	**1222**	**90**

[a] Reaction monitored by FT-IR *in situ* and time measured for complete conversion of SQ. [b] Isolated yield.

Kinetic plots for the formation of **3a-3d** products.

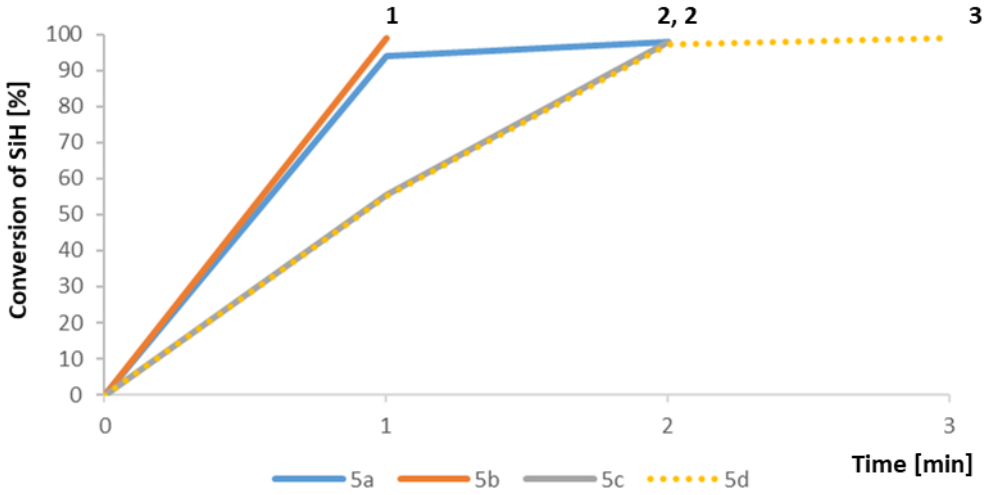


Hydrosilylation of vinyl- and allylgermanes (**1a**–**1d**) with cubic silsesquioxane (**4** and **5**).

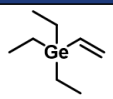
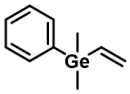
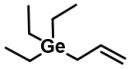
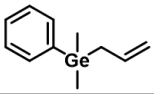
SQ	Product	Ge	Molar ratio [1]:[4/5]:[Pt]	Reaction time [a]	SiH Conversion [%][b]	Yield [%][c]
4	Not isolated	 1a	1 : 1 : 10^{-4}[d]	30 h	65	-
4	Not isolated	 1b	1 : 1 : 10^{-4}	14 h	73	-
5a	5a	 1a	1 : 8 : 8 x 10^{-4}	2 min	98	94
5b	5b	 1b	1 : 8 : 8 x 10^{-4}	1 min	99	92
5c	5c	 1c	1 : 8 : 8 x 10^{-4}	2 min	98	94
5d	5d	 1d	1 : 8 : 8 x 10^{-4}	3 min	99	91

[a] Reaction monitored by FT-IR *in situ.* [b] Confirmed by ^{1}H NMR spectroscopy. [c] Isolated yield.

Kinetic plots for the formation of **5a-5d** products.

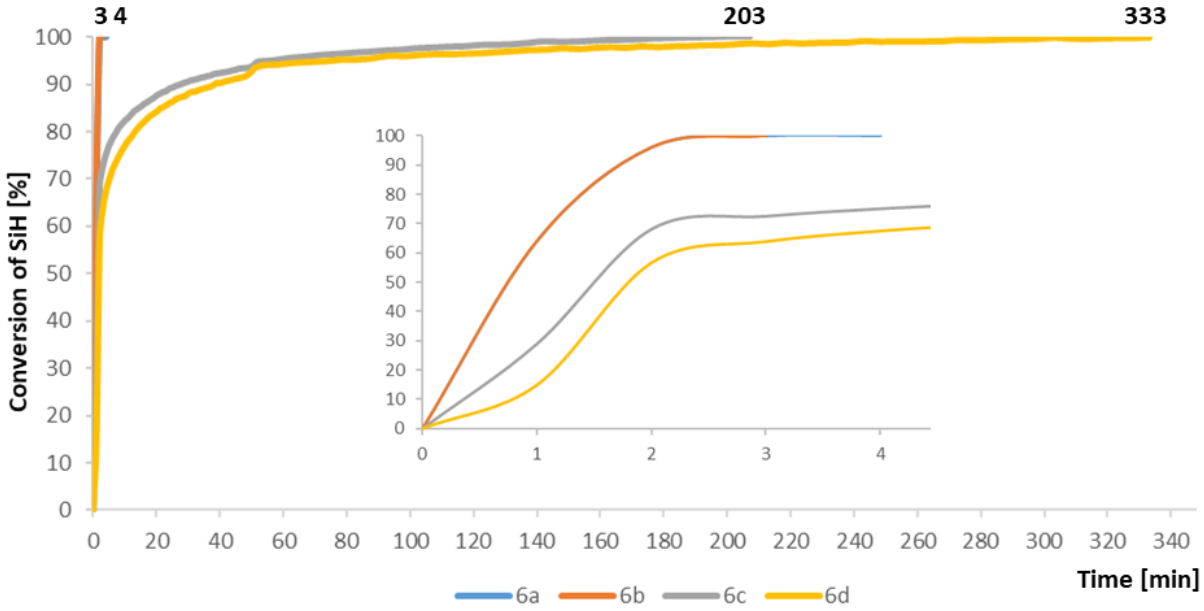


Hydrosilylation of vinyl- and allylgermanes (**1a**–**1d**) with spherosilicate (**6**).

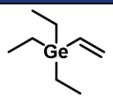
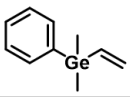
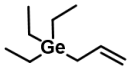
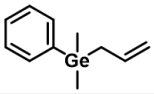
Product	Ge	Molar ratio [1]:[6]:[Pt]	Reaction time [min][a]	Yield [%][b]
6a	 **1a**	**1 : 1 : 10^{-4}**	**4**	**98**
6b	 **1b**	**1 : 1 : 10^{-4}**	**3**	**93**
6c	 **1c**	**1 : 1 : 10^{-4}**	**203**	**91**
6d	 **1d**	**1 : 1 : 10^{-4}**	**333**	**97**

[a] Reaction monitored by FT-IR *in situ* and time measured for complete conversion of SQ. [b] Isolated yield.

Kinetic plots for the formation of **6a-6d** products.

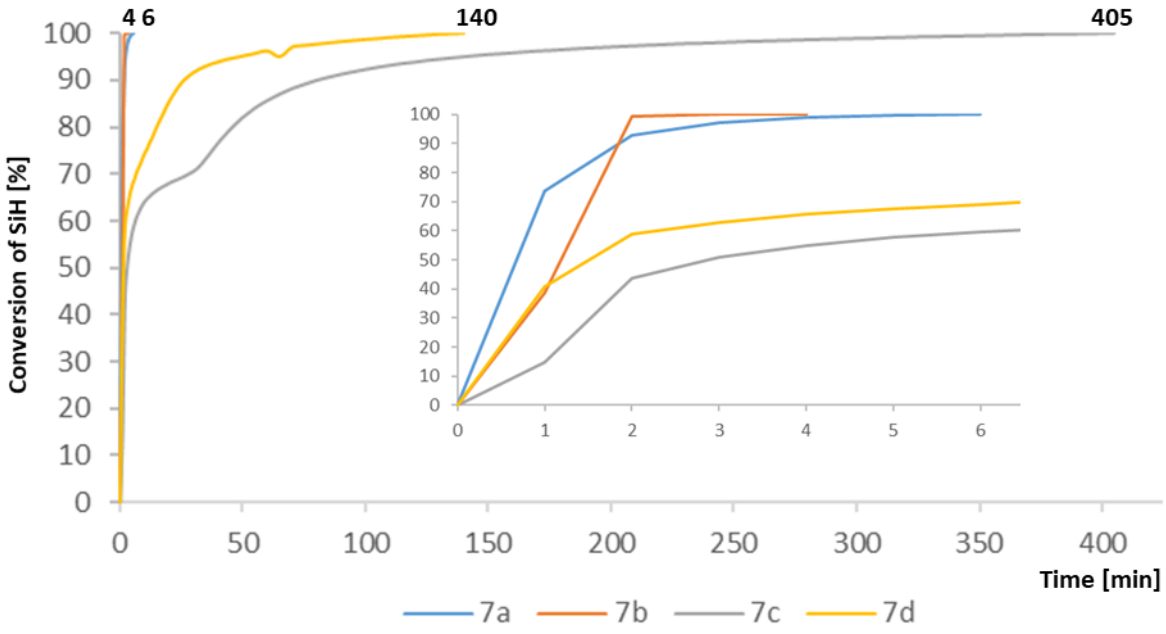


Hydrosilylation of vinyl- and allylgermanes (**1a**–**1d**) with octaspherosilicate (**7**).

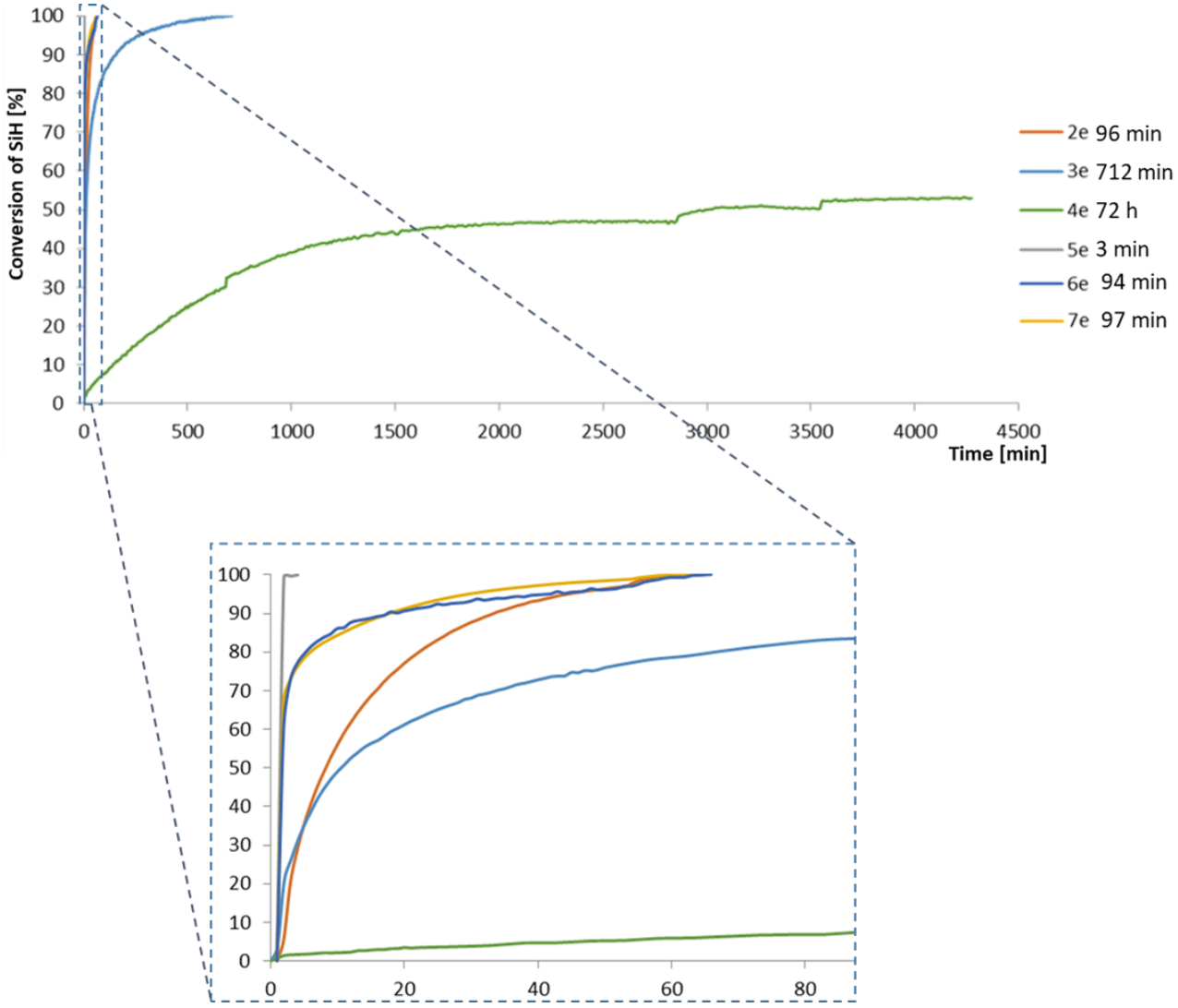
Product	Ge	Molar ratio [1]:[7]:[Pt]	Reaction time [min][a]	Yield [%][b]
7a	 **1a**	**1 : 8 : 8 x 10^{-4}**	**6**	**94**
7b	 **1b**	**1 : 8 : 8 x 10^{-4}**	**4**	**95**
7c	 **1c**	**1 : 8 : 8 x 10^{-4}**	**405**	**92**
7d	 **1d**	**1 : 8 : 8 x 10^{-4}**	**140**	**91**

[a] Reaction monitored by FT-IR *in situ* and time measured for complete conversion of SQ. [b] Isolated yield.

Kinetic plots for the formation of **7a-7d** products.

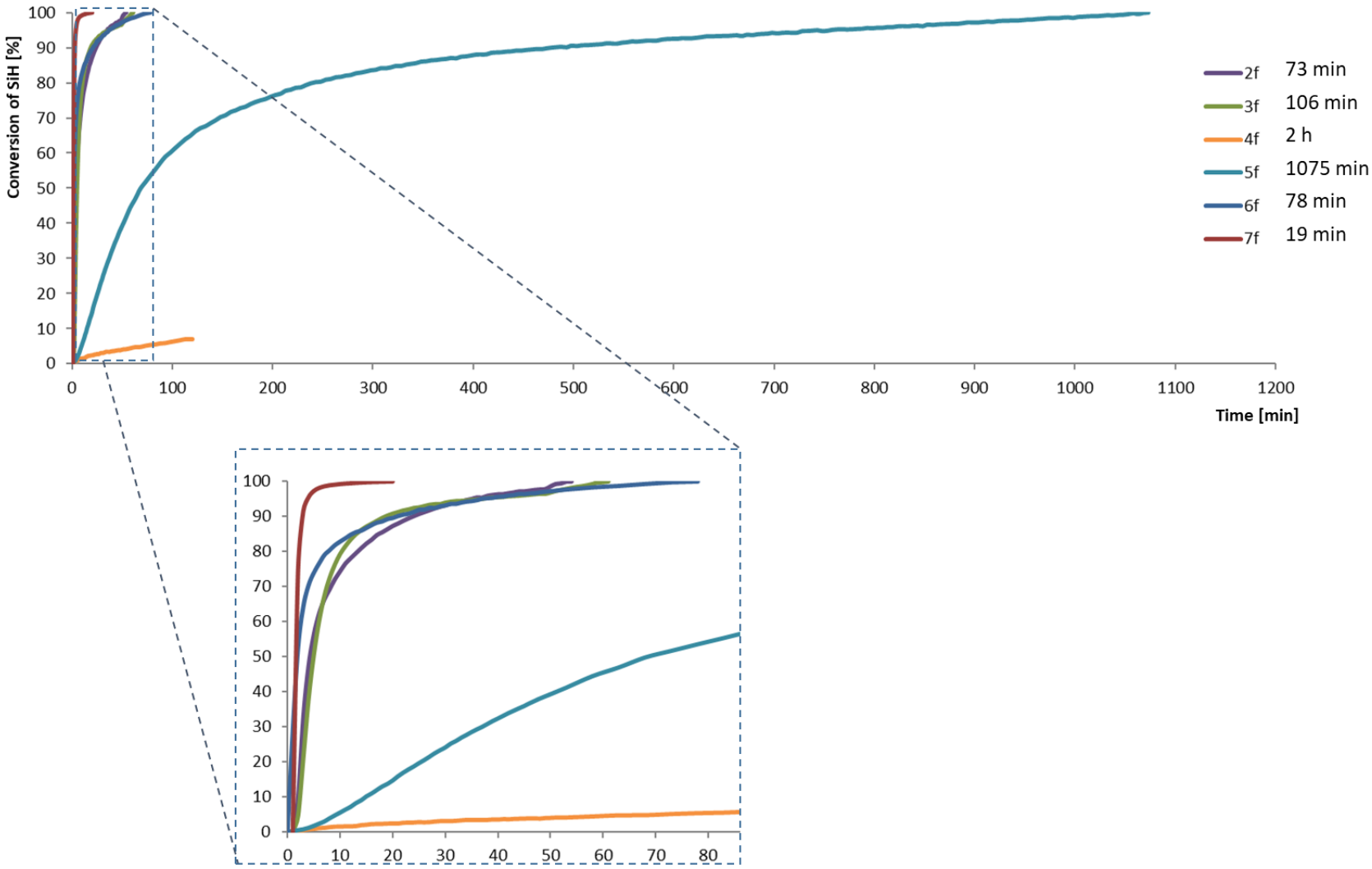


Kinetic plots for the hydrosilylation of $Et_3SiCH=CH_2$ with silsesquioxanes and spherosilicates.



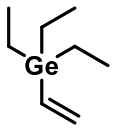
For **4e** addition of catalyst (10^{-4} mol%) after 48 h, 60 h and after 72h. After the last catalyst addition further conversion of SiH was not observed

Kinetic plots for the hydrosilylation of $PhSi(Me)_2CH=CH_2$ with silsesquioxanes and spherosilicates.



The ^{1}H NMR and ^{13}C NMR of germane substrates 1a-1d

(1a)

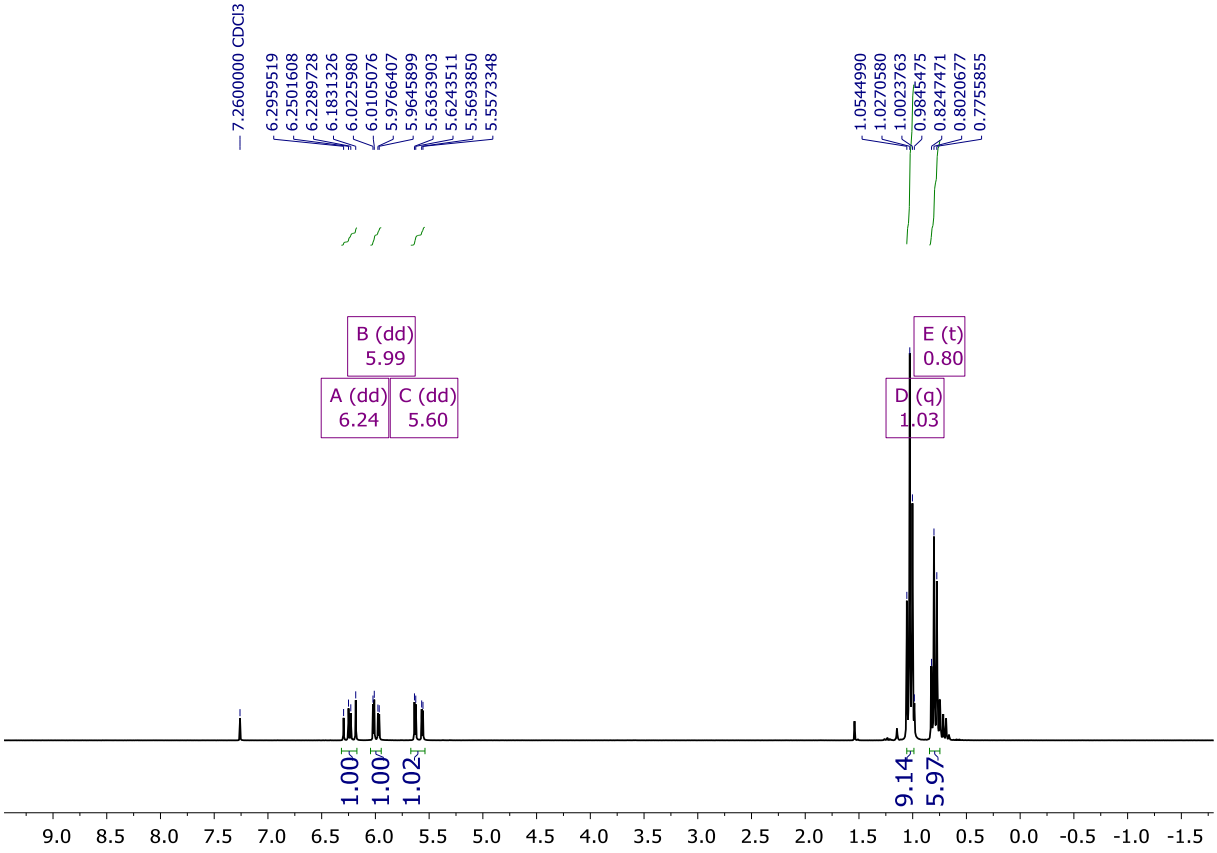


Chemical Formula: $C_8H_{18}Ge$

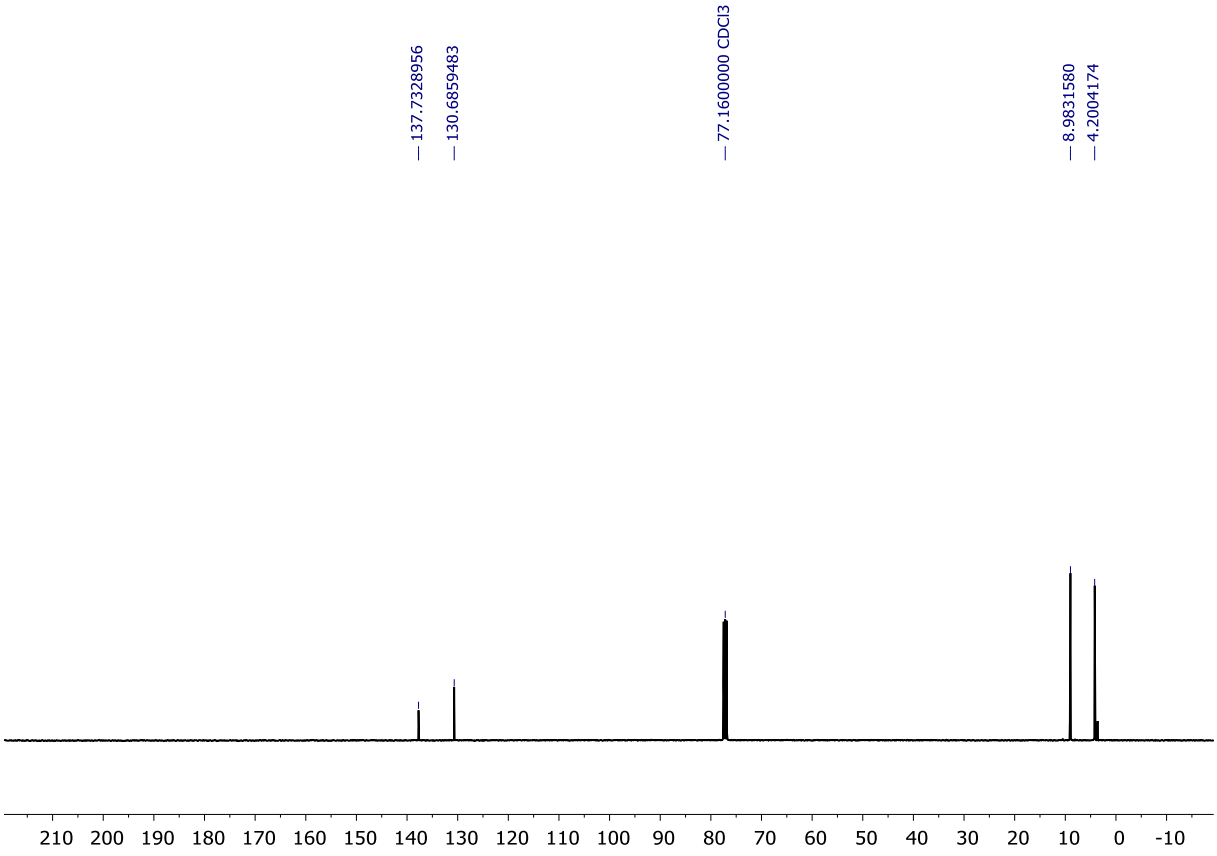
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.24 (dd, *J* = 20.1, 13.8 Hz, 1H), 5.99 (dd, *J* = 13.8, 3.6 Hz, 1H), 5.60 (dd, *J* = 20.1, 3.6 Hz, 1H), 1.03 (q, *J* = 7.8 Hz, 9H), 0.80 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.73, 130.69, 8.98, 4.20.

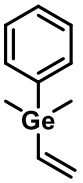
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



(1b)

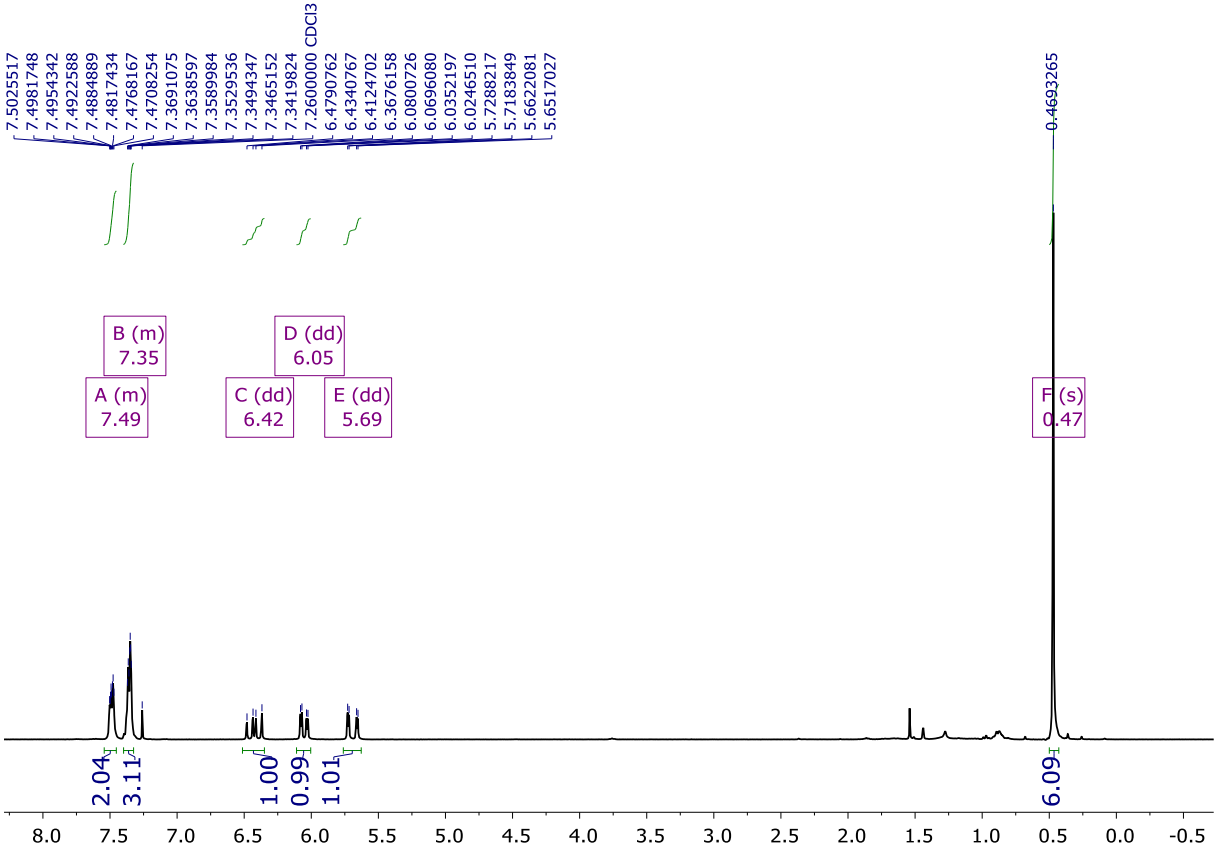


Chemical Formula: $C_{10}H_{14}Ge$

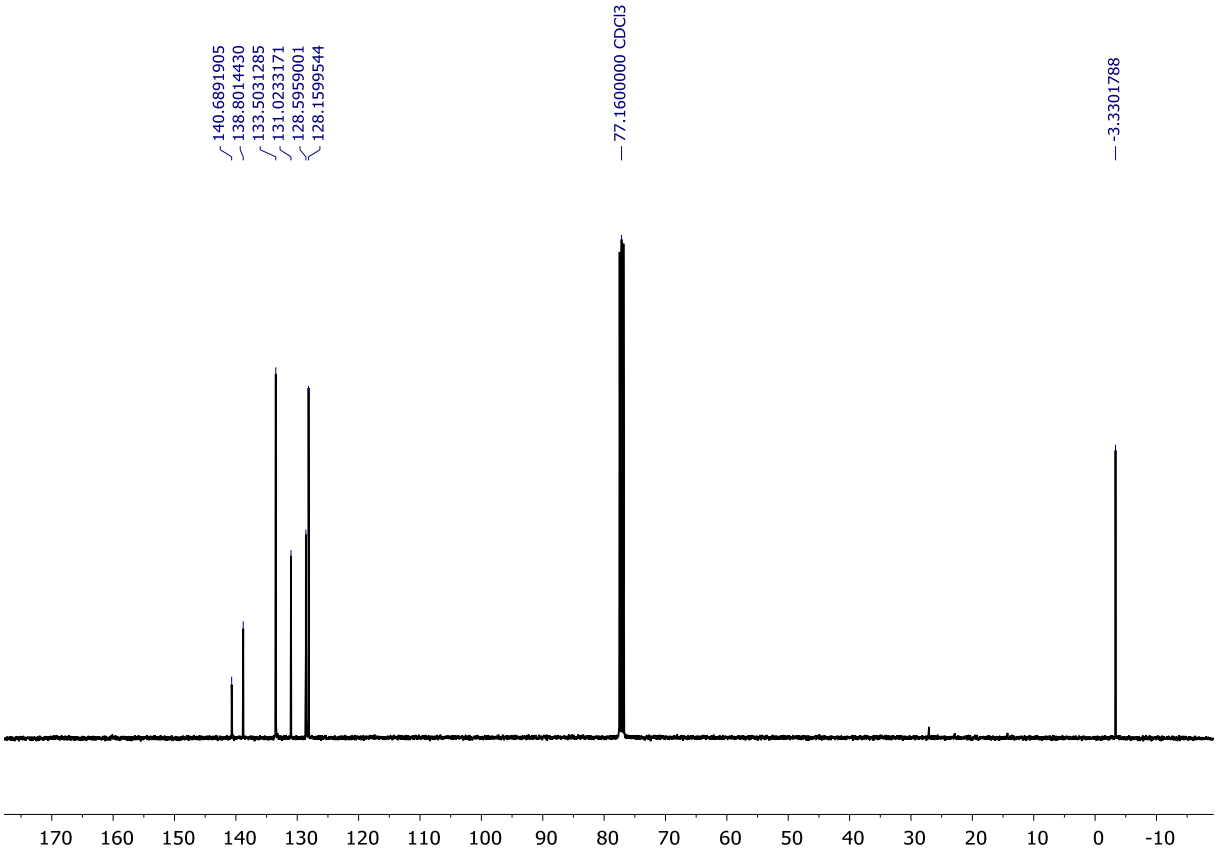
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.54 – 7.45 (m, 2H), 7.43 – 7.31 (m, 3H), 6.42 (dd, *J* = 20.0, 13.5 Hz, 1H), 6.05 (dd, *J* = 13.5, 3.2 Hz, 1H), 5.69 (dd, *J* = 20.0, 3.1 Hz, 1H), 0.47 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.69, 138.80, 133.50, 131.02, 128.60, 128.16, -3.33.

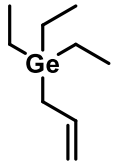
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



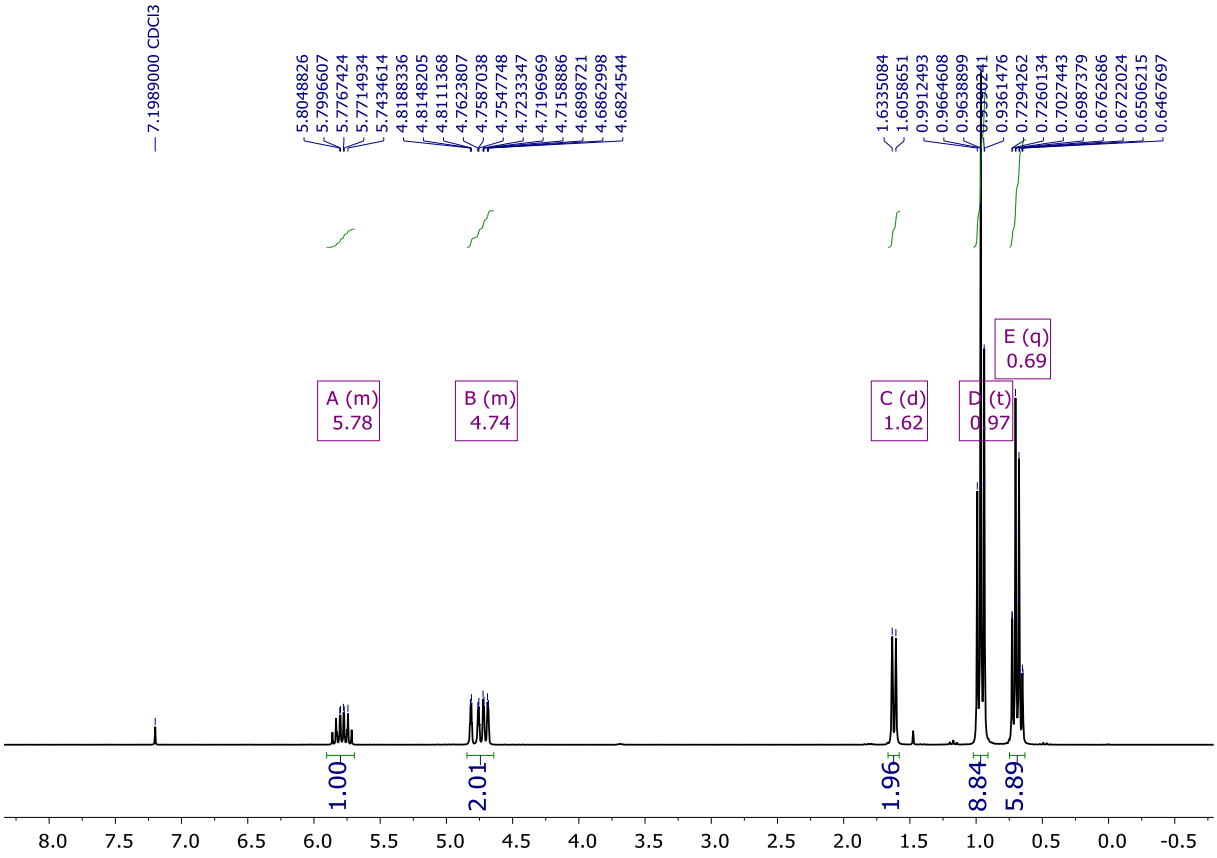
(1c)



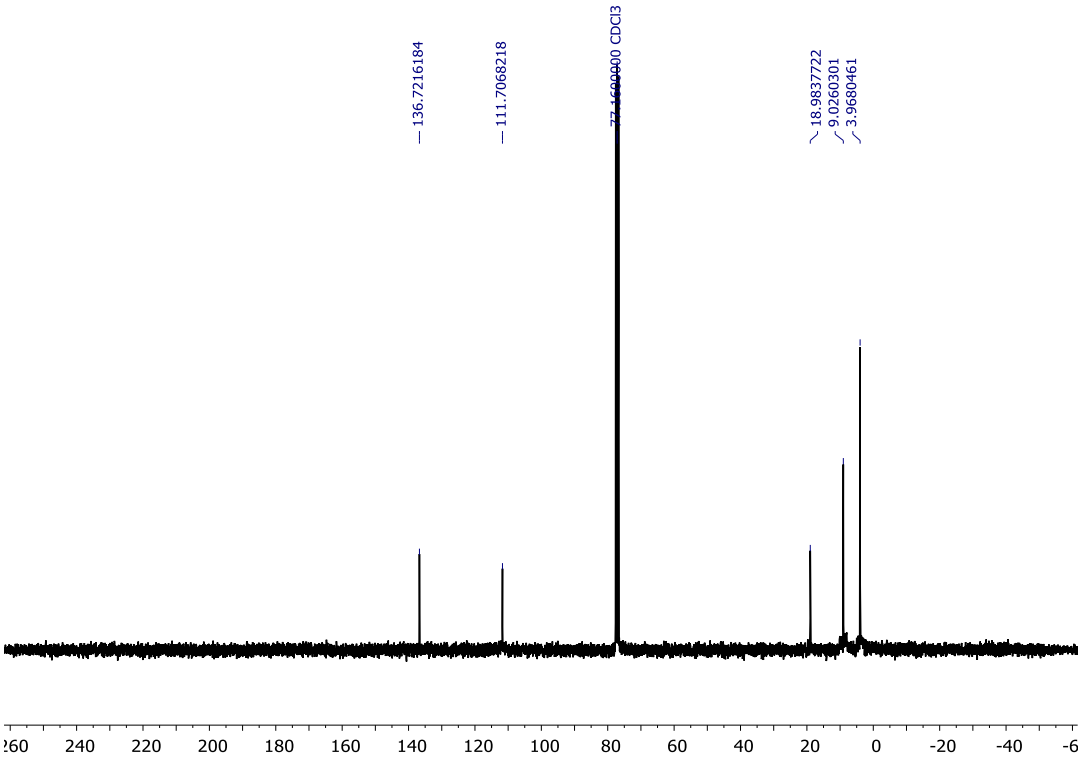
Chemical Formula: $C_9H_{20}Ge$

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.90 – 5.66 (m, 1H), 4.82 – 4.68 (m, 2H), 1.62 (d, *J* = 8.3 Hz, 2H), 0.97 (t, 9H), 0.69 (q, *J* = 7.8, 1.1 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 136.72, 111.71, 18.98, 9.03, 3.97.

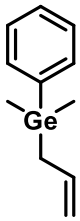
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



(1d)

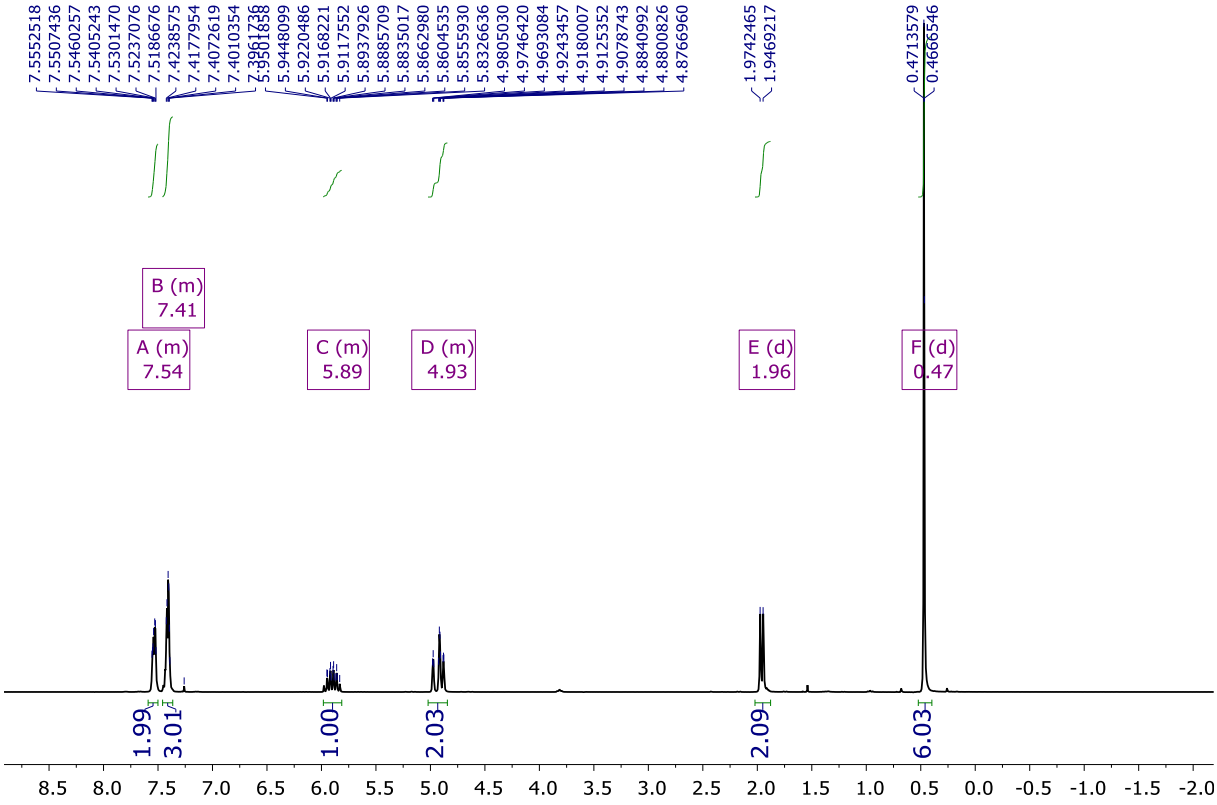


Chemical Formula: $C_9H_{20}Ge$

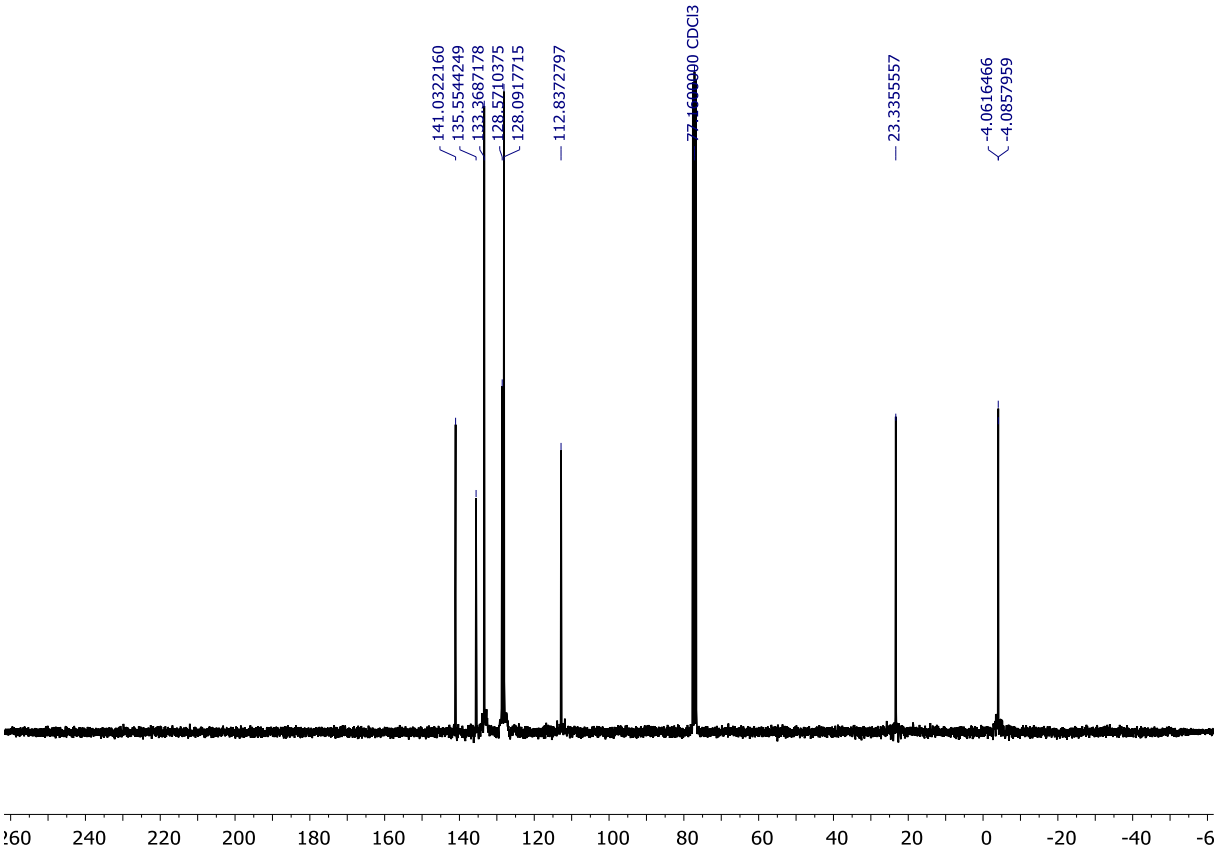
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.60 – 7.48 (m, 2H), 7.46 – 7.34 (m, 3H), 6.02 – 5.78 (m, 1H), 5.03 – 4.80 (m, 2H), 1.96 (d, *J* = 8.2 Hz, 2H), 0.47 (d, *J* = 1.4 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.03, 135.55, 133.37, 128.57, 128.09, 112.84, 23.34, -4.06, -4.09.

^{1}H NMR (300 MHz, $CDCl_3$)

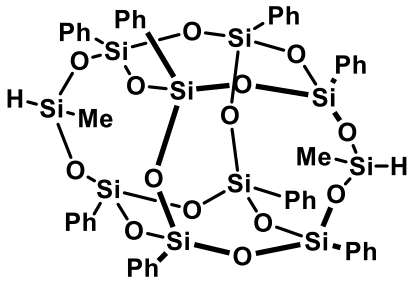


^{13}C NMR (101 MHz, $CDCl_3$)



The ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, MALDI TOF and ESI data of silsesquioxanes and spherosilicates 2-7

(2) *cis/trans*



Chemical Formula: $C_{50}H_{48}O_{14}Si_{10}$

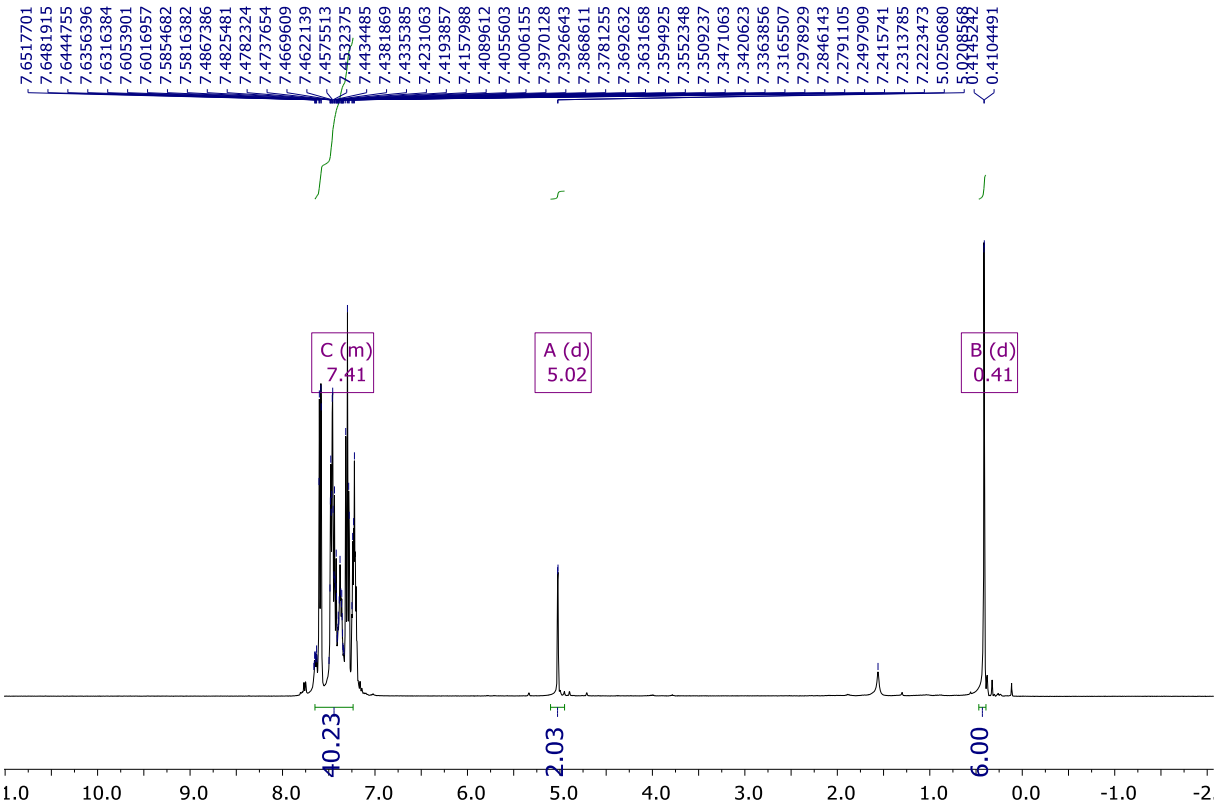
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.22 (m, 40H), 5.02 (d, 2H), 0.41 (d, *J* = 1.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.24, 134.20, 134.17, 134.07, 131.74, 130.90, 130.63, 130.55, 127.97, 127.83, 127.79, 127.75, 0.77.

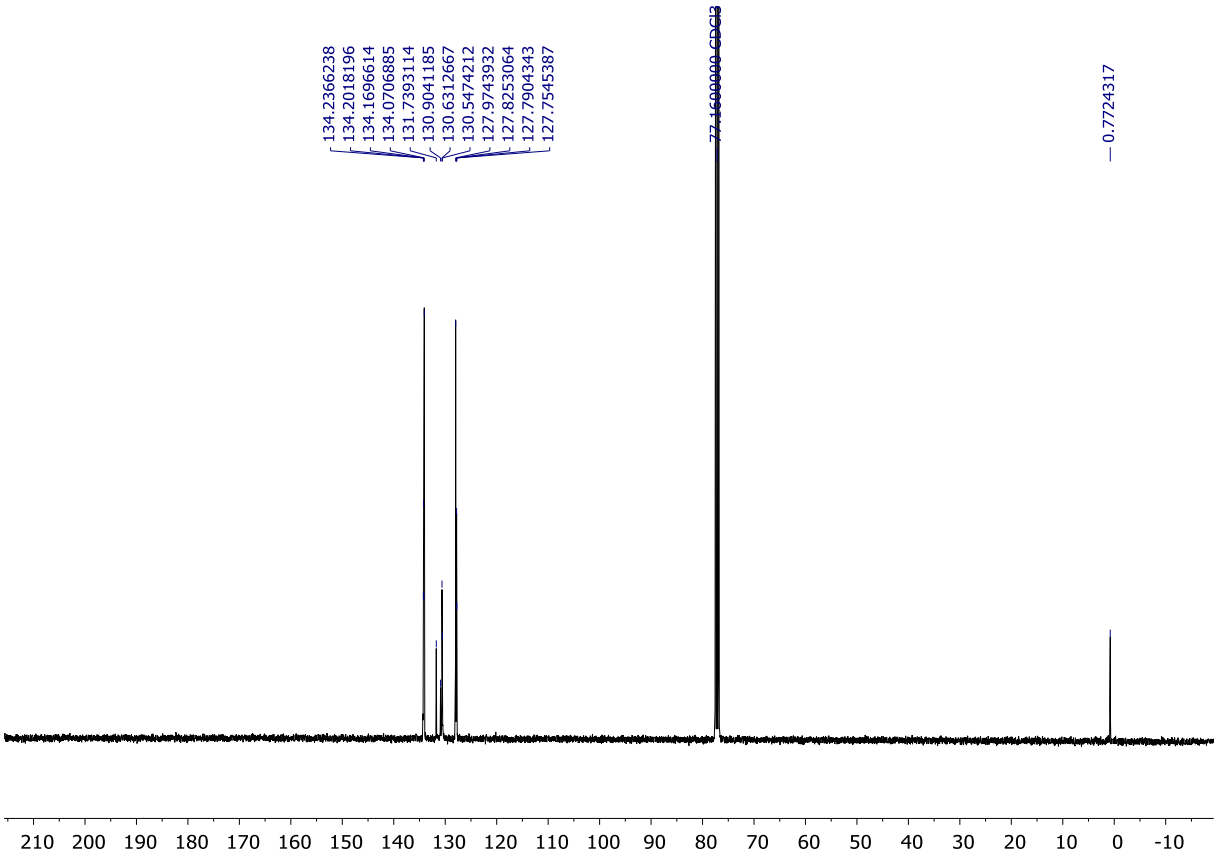
^{29}Si NMR (79 MHz, $CDCl_3$) δ -32.80, -77.83, -79.12, -79.31, -79.51.

MALDI-TOF MS (m/z): calcd. for $C_{50}H_{48}O_{14}Si_{10}Na$ 1176,76; found 1176,08.

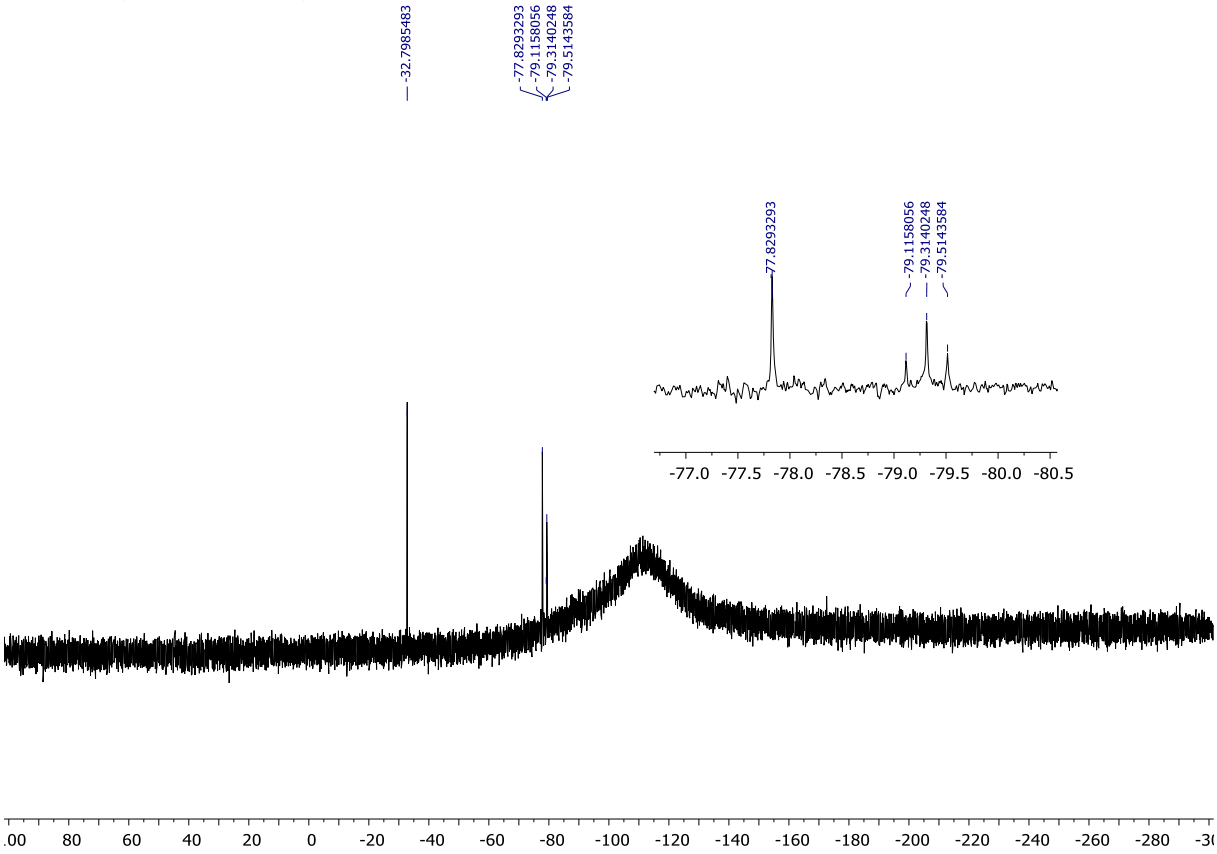
^{1}H NMR (400 MHz, $CDCl_3$)



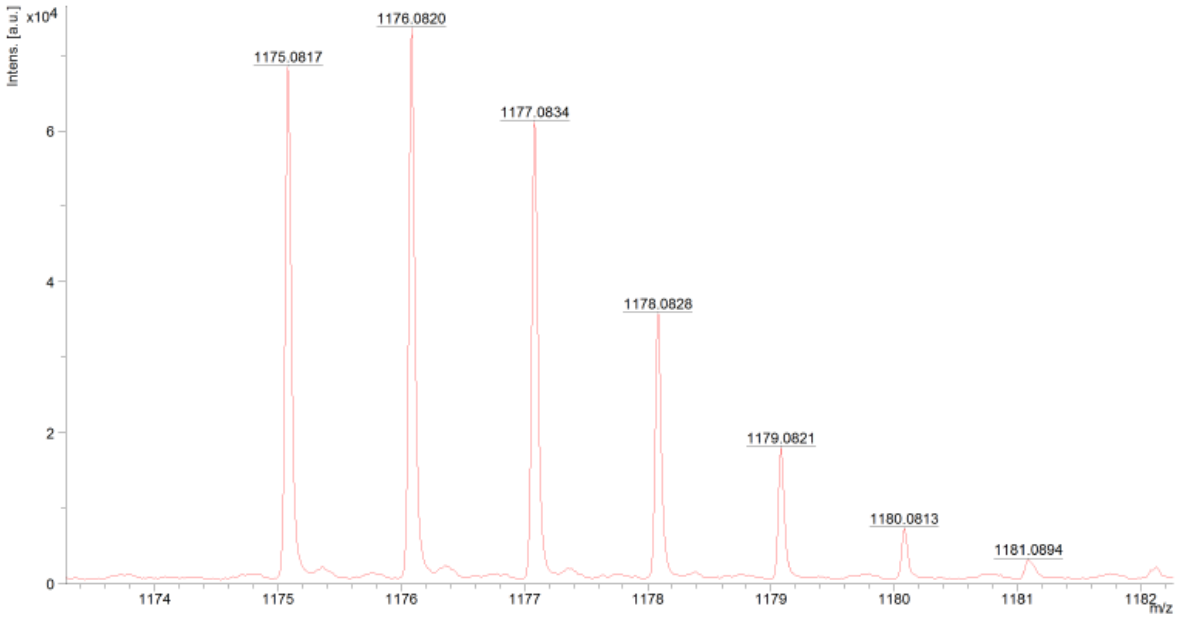
^{13}C NMR (101 MHz, $CDCl_3$)



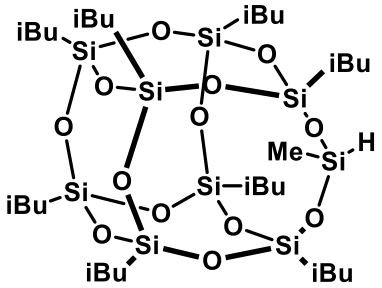
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
6
4
2
0
1175.0817
1176.0820
1177.0834
1178.0828
1179.0821
1180.0813
1181.0894
1174
1175
1176
1177
1178
1179
1180
1181
1182
m/z

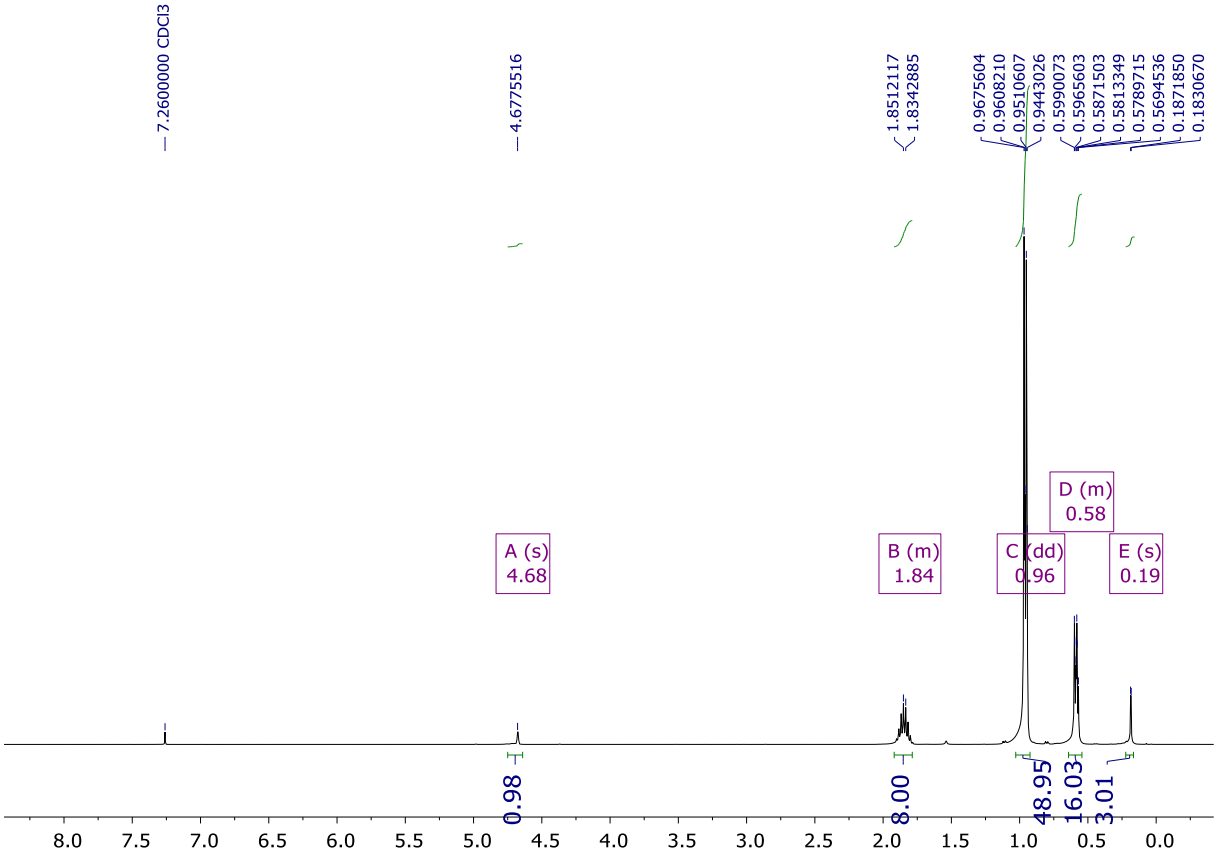
(3)



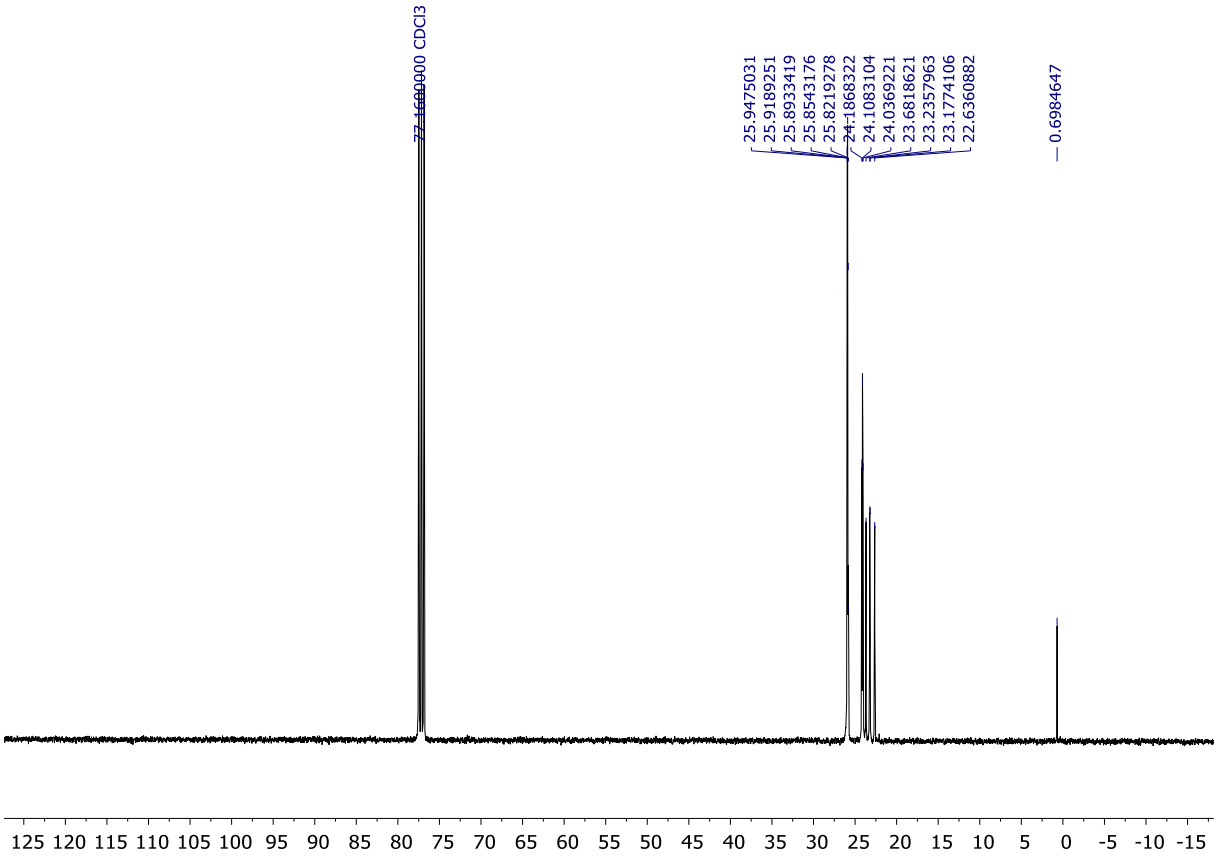
Chemical Formula: $C_{33}H_{76}O_{13}Si_9$

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (s, 1H), 2.03 – 1.71 (m, 8H), 0.98 (dd, *J* = 6.6, 2.7 Hz, 48H), 0.68 – 0.53 (m, 16H), 0.21 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 25.95, 25.92, 25.89, 25.85, 25.82, 24.19, 24.11, 24.04, 23.68, 23.24, 23.18, 22.64, 0.70.
^{29}Si NMR (79 MHz, $CDCl_3$) δ -37.01, -66.96, -68.19, -68.90, -69.13.
MALDI-TOF MS (m/z): calcd. for $C_{33}H_{76}O_{13}Si_9Na$ 955,31; found 955,33.

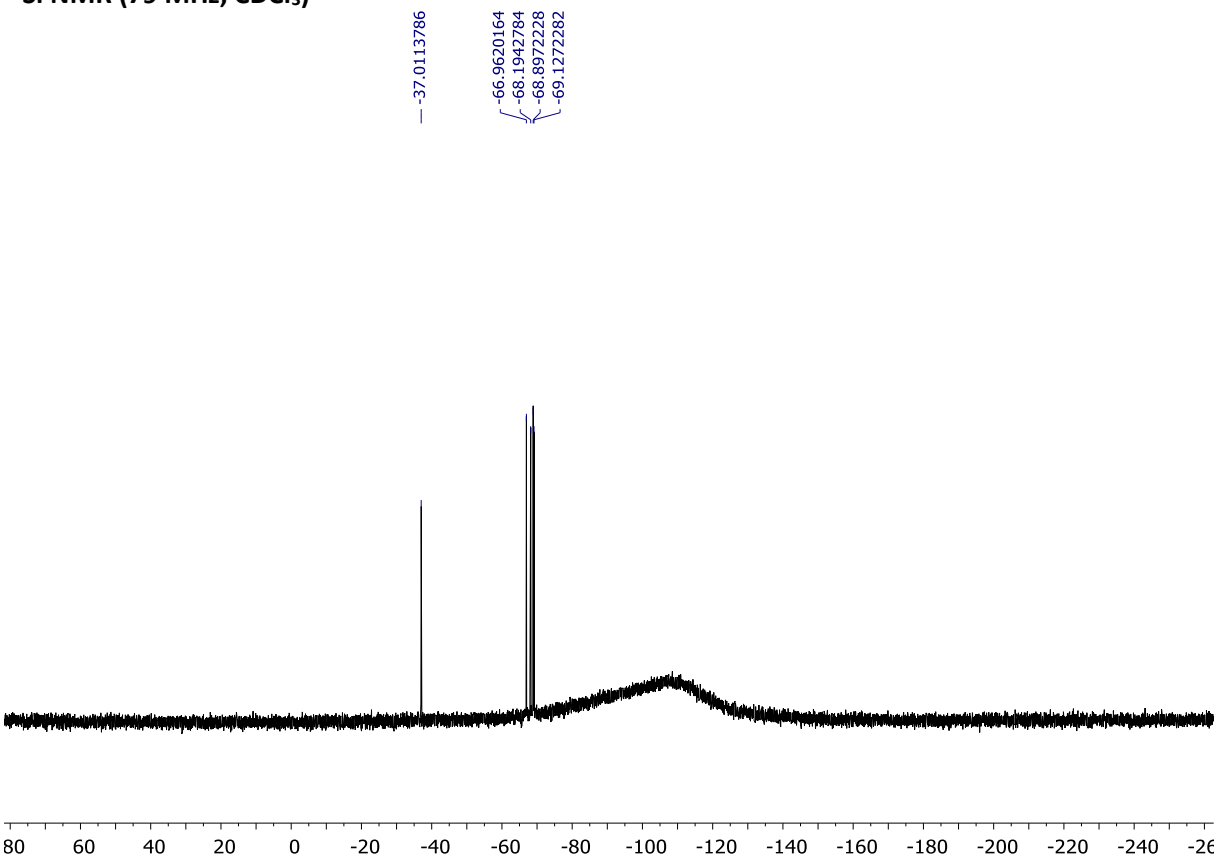
^{1}H NMR (400 MHz, $CDCl_3$)



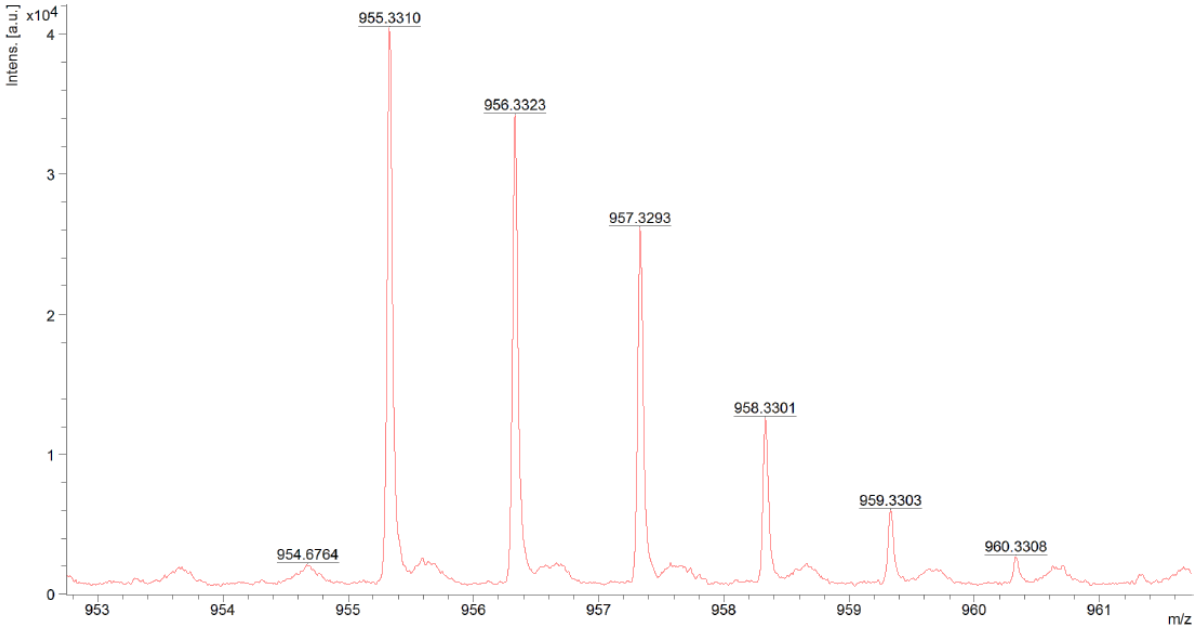
^{13}C NMR (101 MHz, $CDCl_3$)



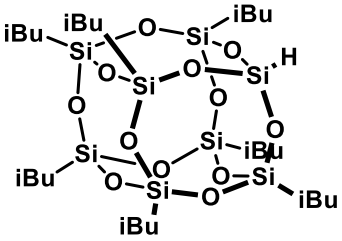
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
4
3
2
1
0
955.3310
956.3323
957.3293
958.3301
959.3303
960.3308
954.6764
953
954
955
956
957
958
959
960
961
m/z

(4)



Chemical Formula: $C_{28}H_{64}O_{12}Si_8$

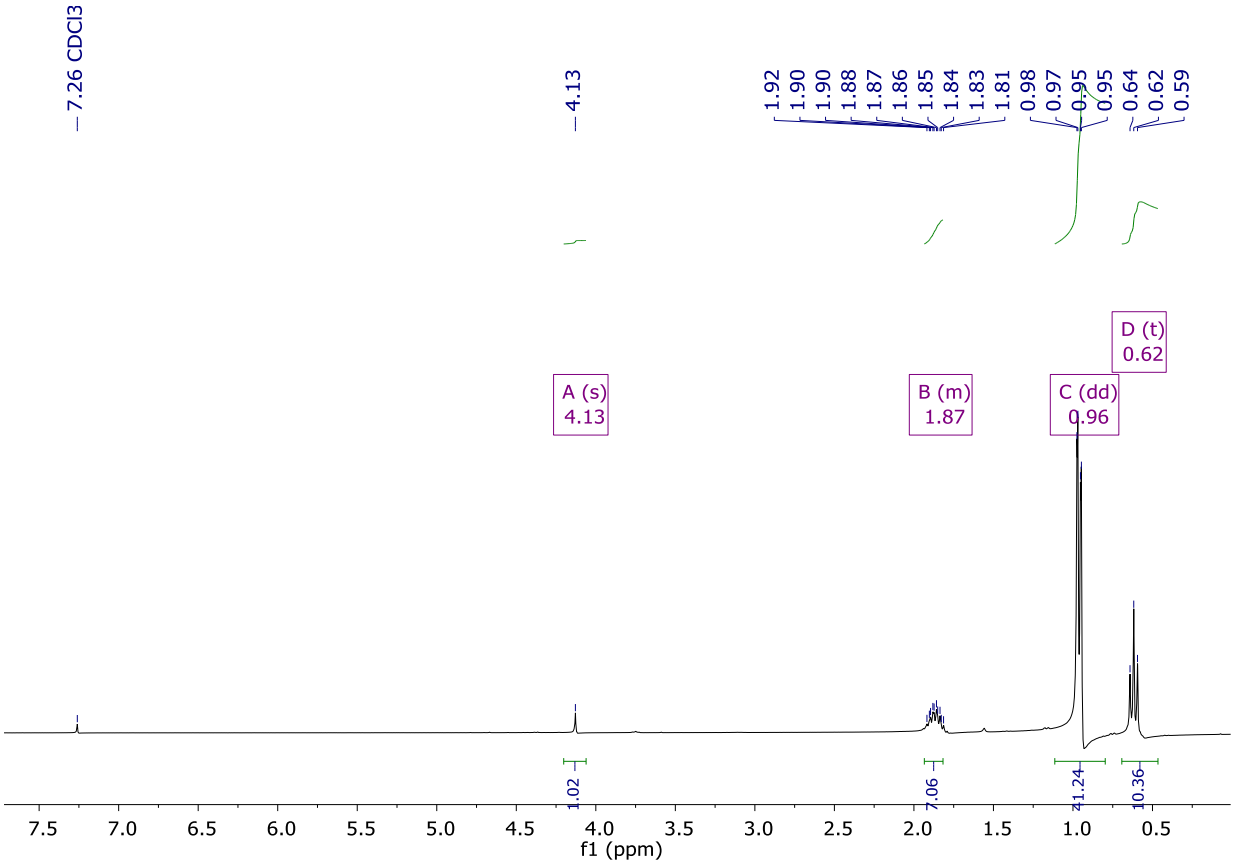
^{1}H NMR (300 MHz, Chloroform-d) δ 4.13 (s, 1H), 1.92 – 1.79 (m, 7H), 0.96 (dd, J = 6.6, 1.8 Hz, 42H), 0.62 (t, J = 7.1 Hz, 14H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 25.85, 25.81, 23.99, 22.64, 22.48.

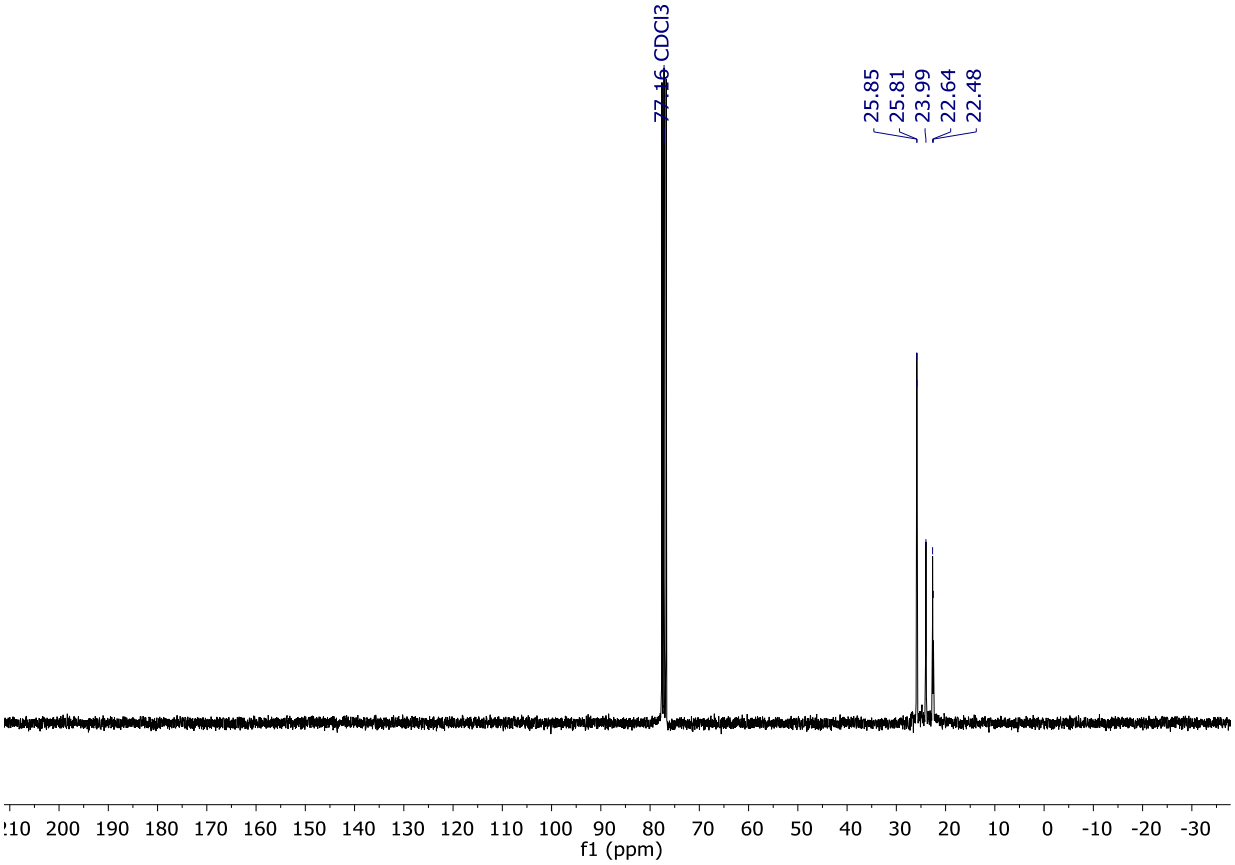
^{29}Si NMR (79 MHz, $CDCl_3$) δ -67.55, -67.88, -85.02.

MALDI-TOF MS (m/z): calcd. for $C_{28}H_{64}O_{12}Si_8$ 816,26; found 817,26.

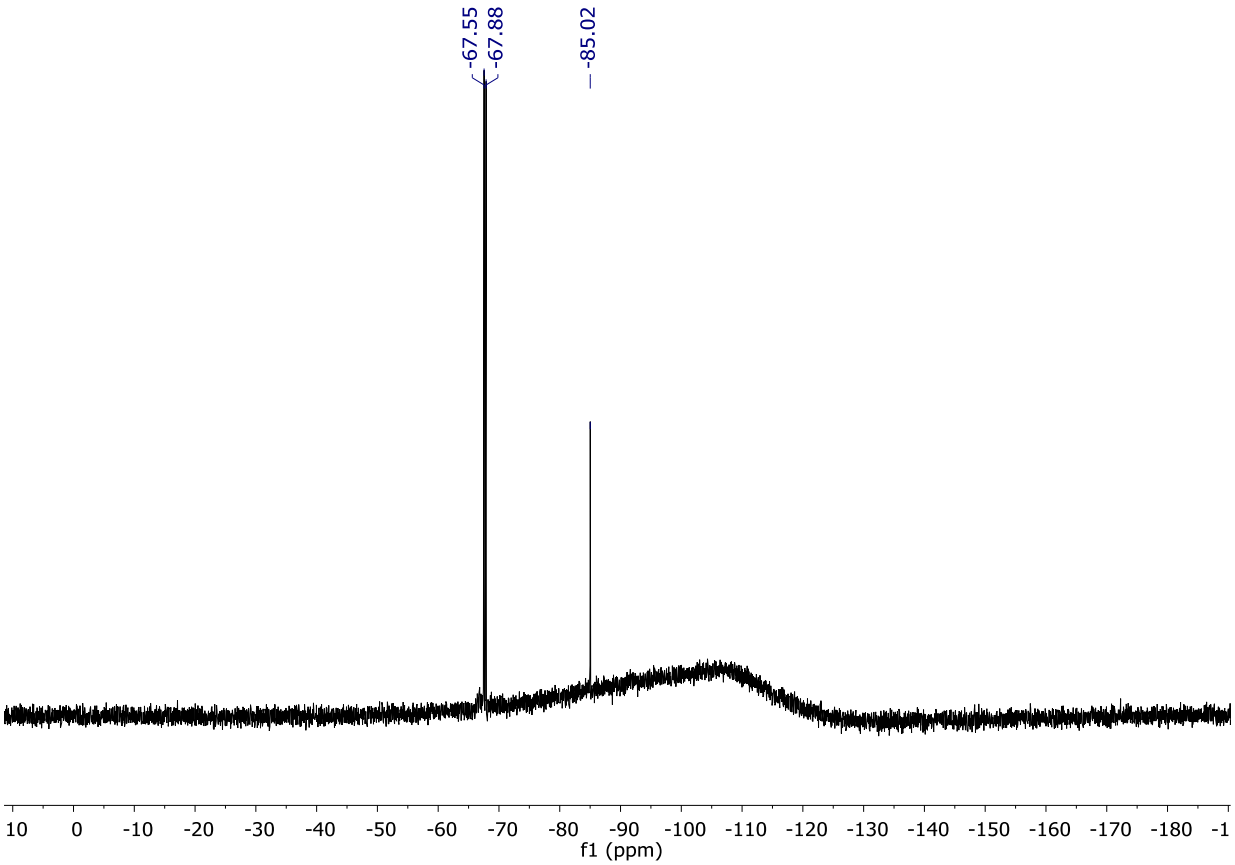
^{1}H NMR (300 MHz, $CDCl_3$)



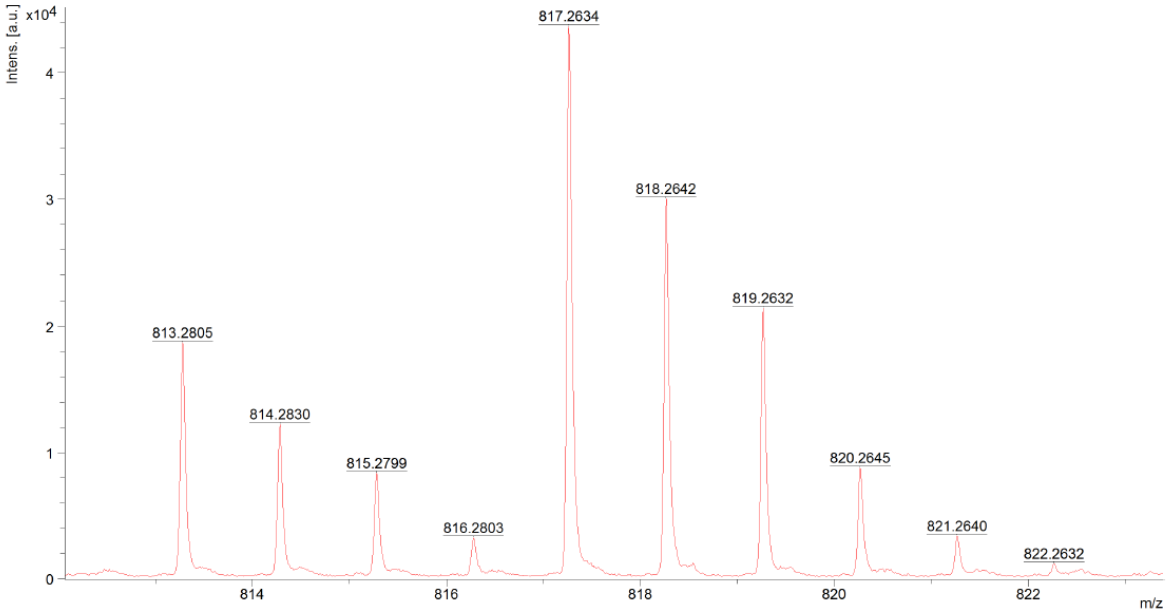
^{13}C NMR (101 MHz, $CDCl_3$)



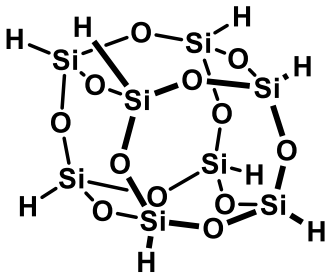
^{29}Si NMR (79MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
4
3
2
1
0
817.2634
818.2642
819.2632
813.2805
814.2830
815.2799
816.2803
820.2645
821.2640
822.2632
814
816
818
820
822
m/z

(5)



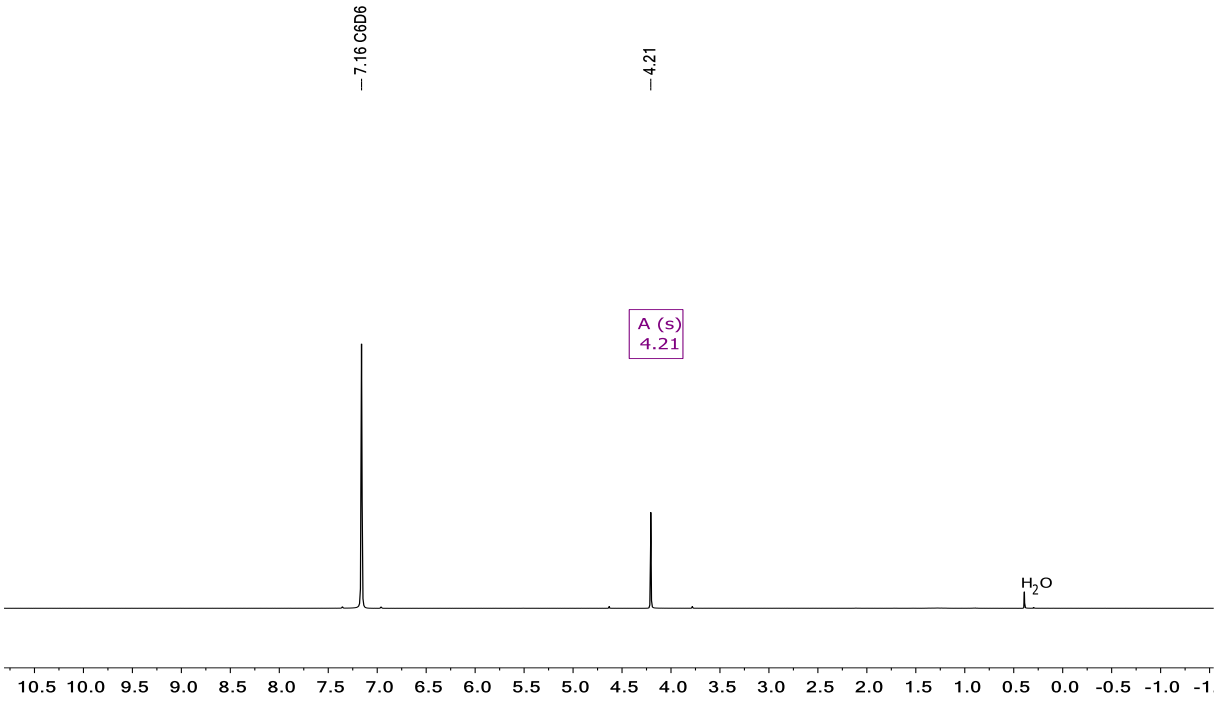
Chemical Formula: $H_8O_{12}Si_8$

^{1}H NMR (400 MHz, C_6D_6) δ 4.21 (s, 1H).

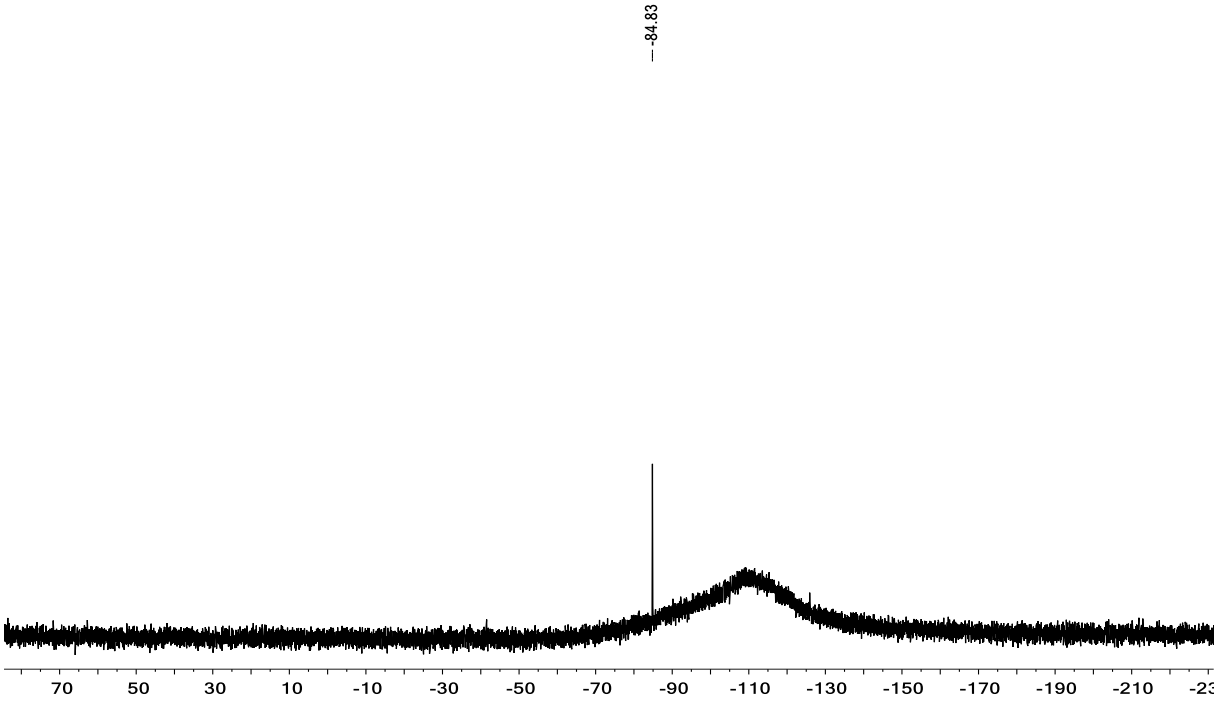
^{29}Si NMR (79 MHz, C_6D_6) δ -84.83

MALDI-TOF MS (m/z): calcd. for $H_8O_{12}Si_8$ 423,82; found 426,34.

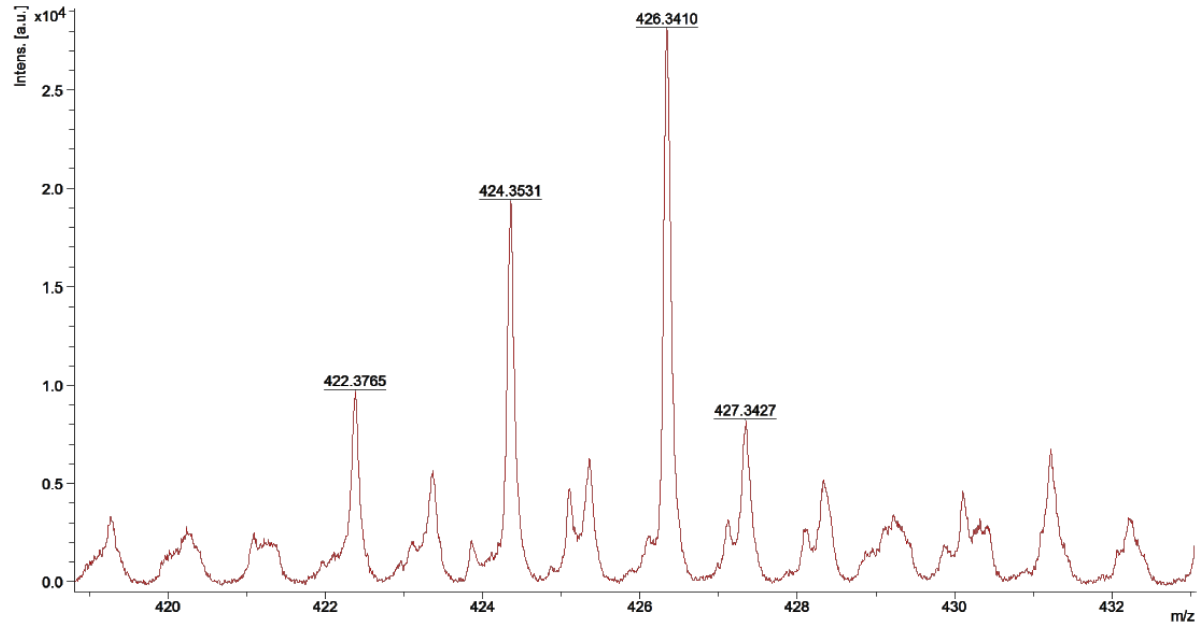
^{1}H NMR (400 MHz, C_6D_6)



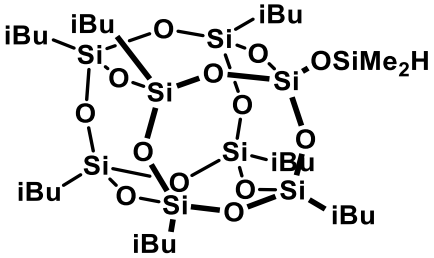
^{29}Si NMR (79 MHz, C_6D_6)



MALDI-TOF



(6)



Chemical Formula: $C_{30}H_{70}O_{13}Si_9$

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 – 4.66 (m, 1H), 1.95 – 1.78 (m, 7H), 0.96 (dd, J = 6.6, 3.3 Hz, 42H), 0.68 – 0.56 (m, 14H), 0.22 (d, J = 2.8 Hz, 6H).

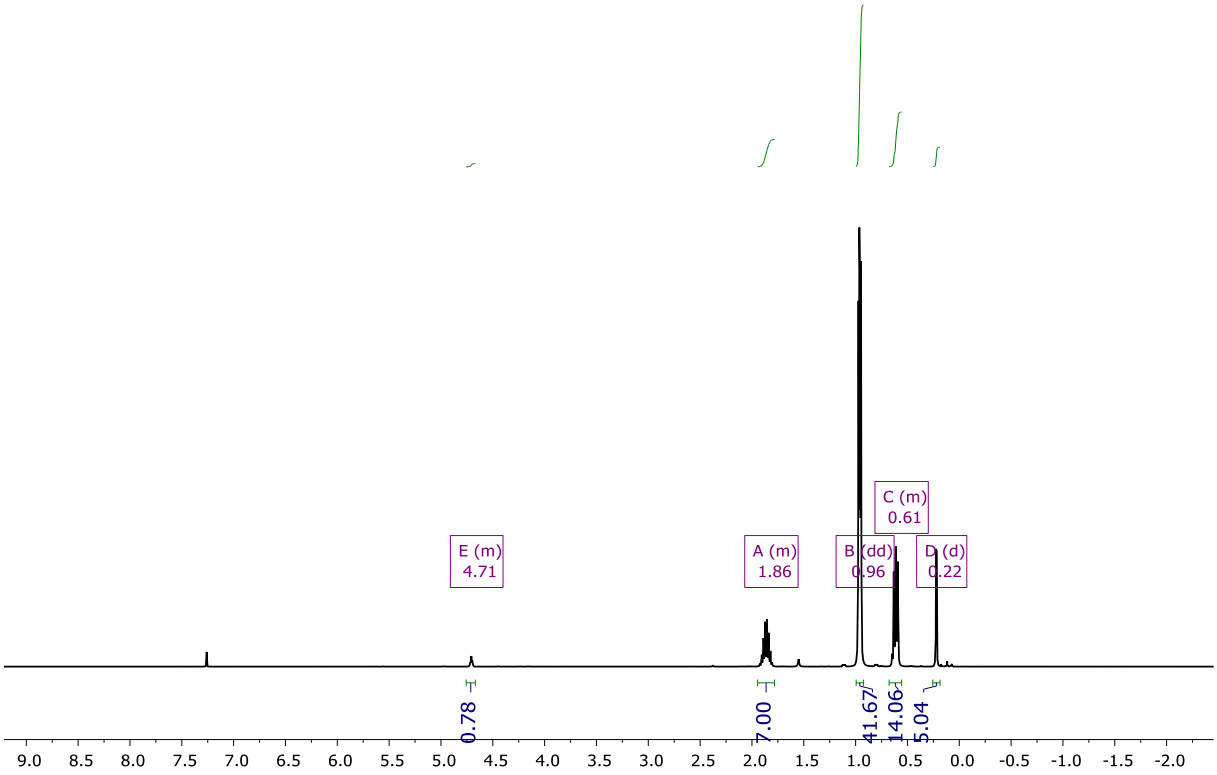
^{13}C NMR (101 MHz, $CDCl_3$) δ 25.84, 25.83, 24.01, 23.97, 22.59, 22.50, 0.33.

^{29}Si NMR (79 MHz, $CDCl_3$) δ -2.97, -66.93, -67.86, -109.05.

MALDI-TOF MS (m/z): calcd. for $C_{30}H_{70}O_{13}Si_9Na$ 913,26; found 913,26.

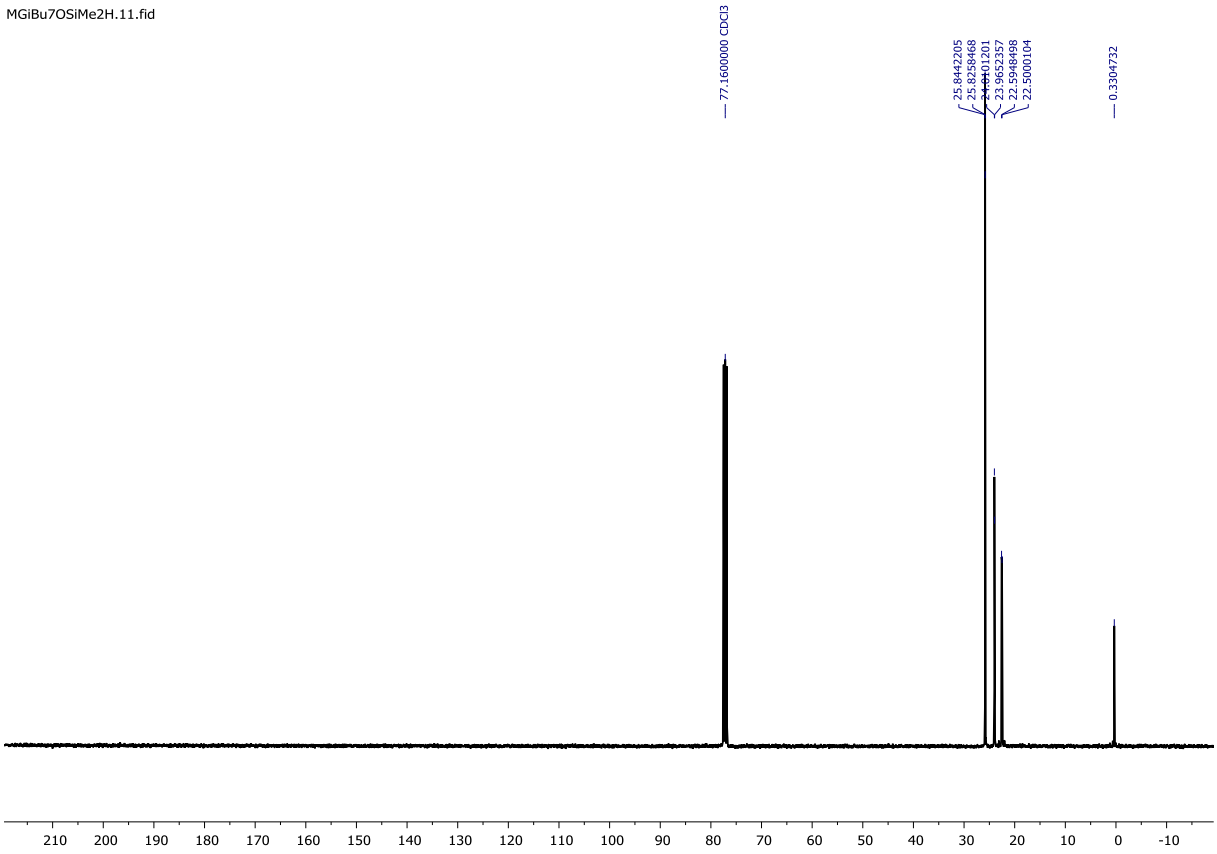
^{1}H NMR (400 MHz, $CDCl_3$)

MGiBu7OSiMe2H.10.fid



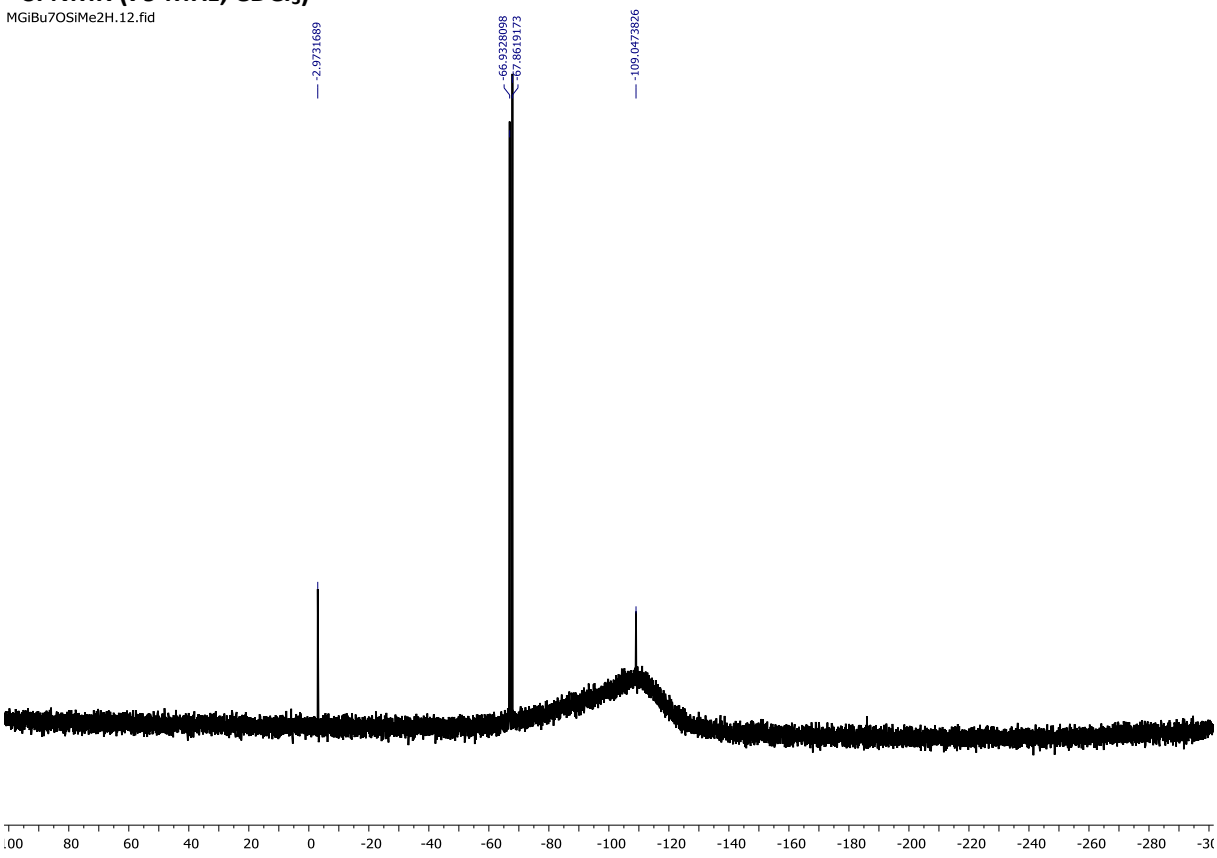
^{13}C NMR (101 MHz, $CDCl_3$)

MGiBu7OSiMe2H.11.fid

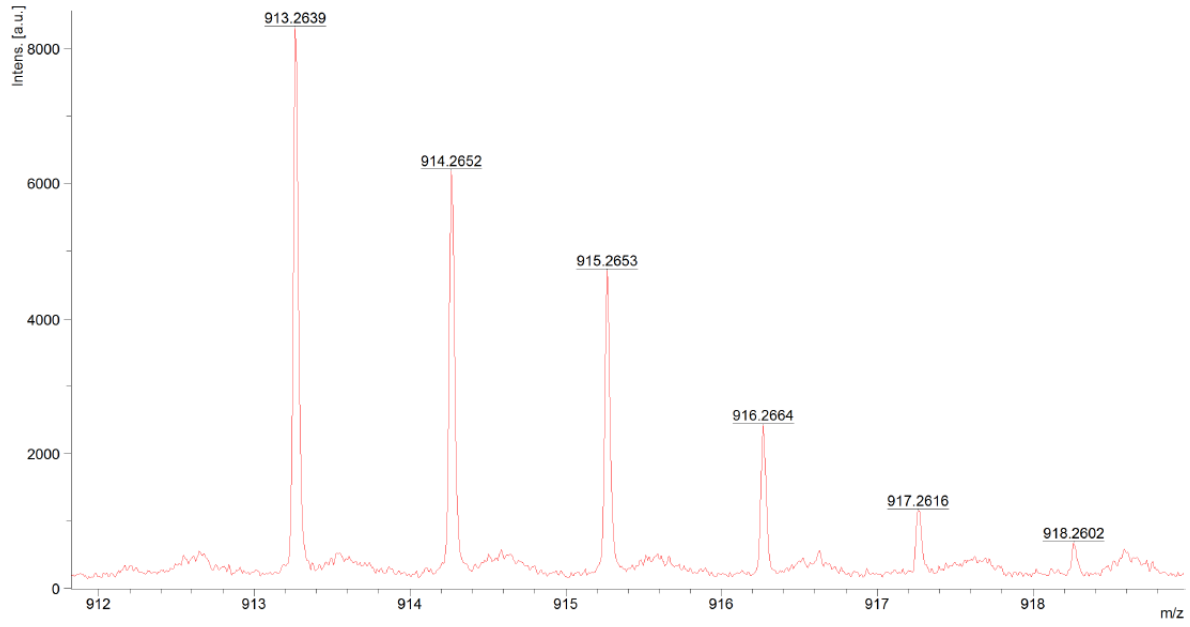


^{29}Si NMR (79 MHz, $CDCl_3$)

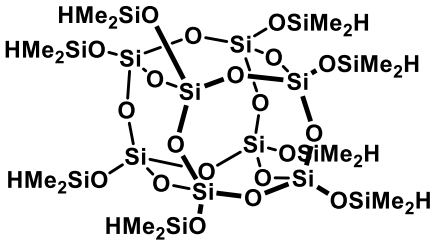
MGiBu7OSiMe2H.12.fid



MALDI-TOF


Intens. [a.u.]
8000
6000
4000
2000
0
913.2639
914.2652
915.2653
916.2664
917.2616
918.2602
912
913
914
915
916
917
918
m/z

(7)



Chemical Formula: $C_{16}H_{56}O_{20}Si_{16}$

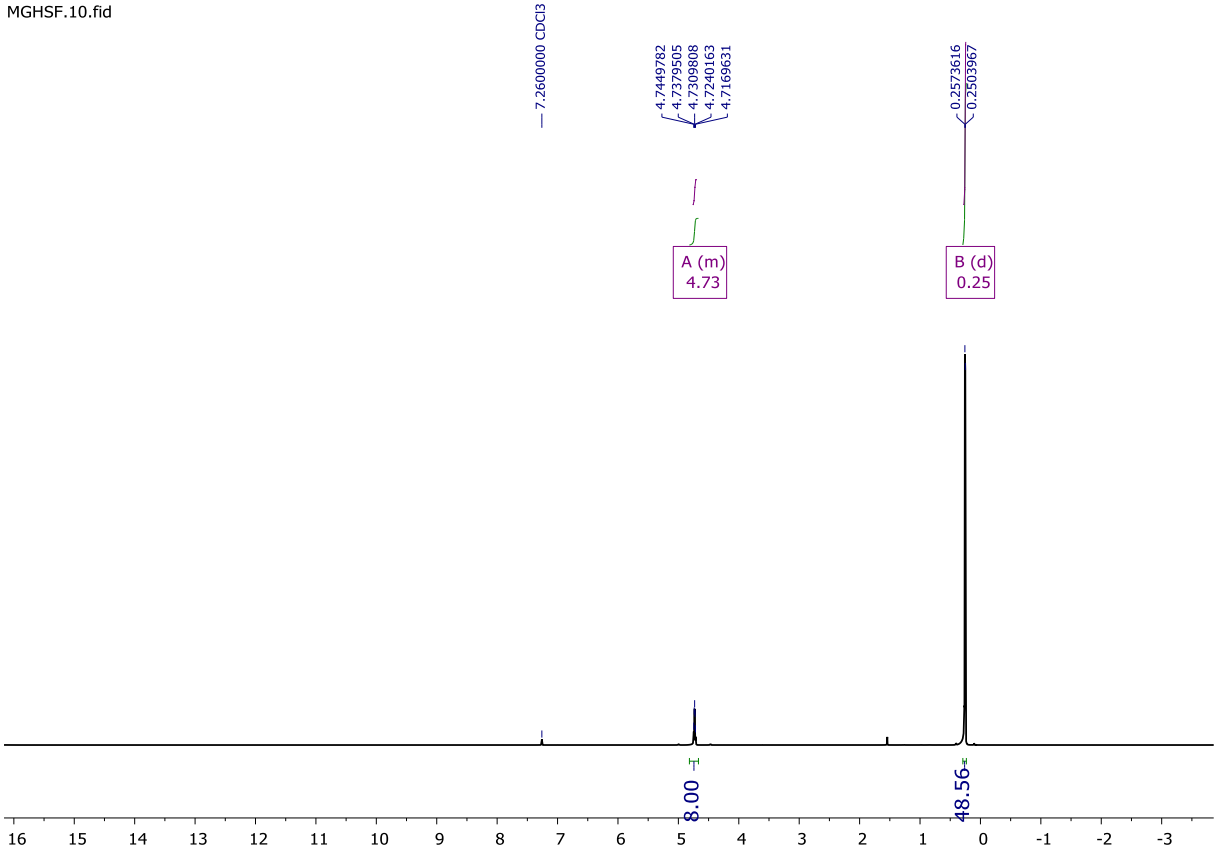
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 – 4.70 (m, 8H), 0.25 (d, J = 2.8 Hz, 48H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 0.20.

^{29}Si NMR (79 MHz, $CDCl_3$) δ -1.40, -108.67.

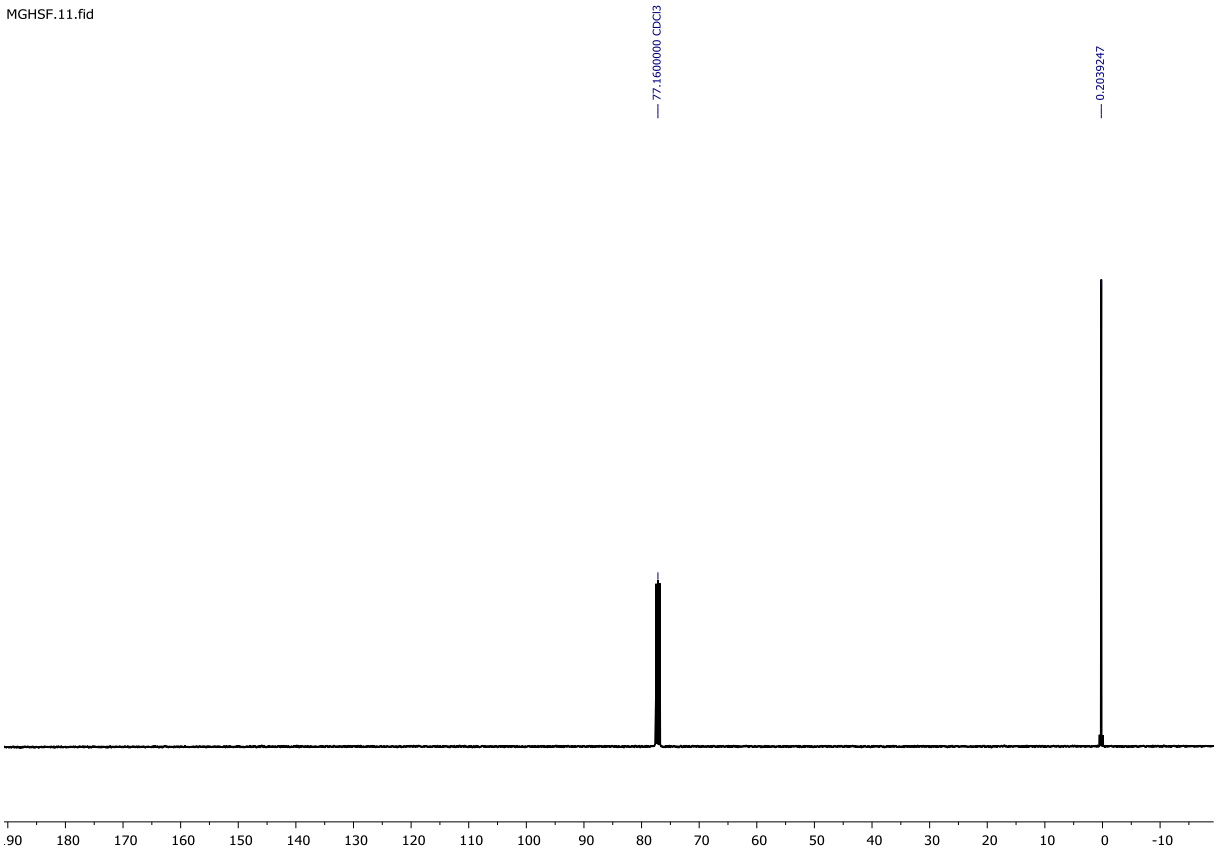
MALDI-TOF MS (m/z): calcd. for $C_{16}H_{56}O_{20}Si_{16}Na$ 1040,95; found 1040,95.

^{1}H NMR (400 MHz, $CDCl_3$)



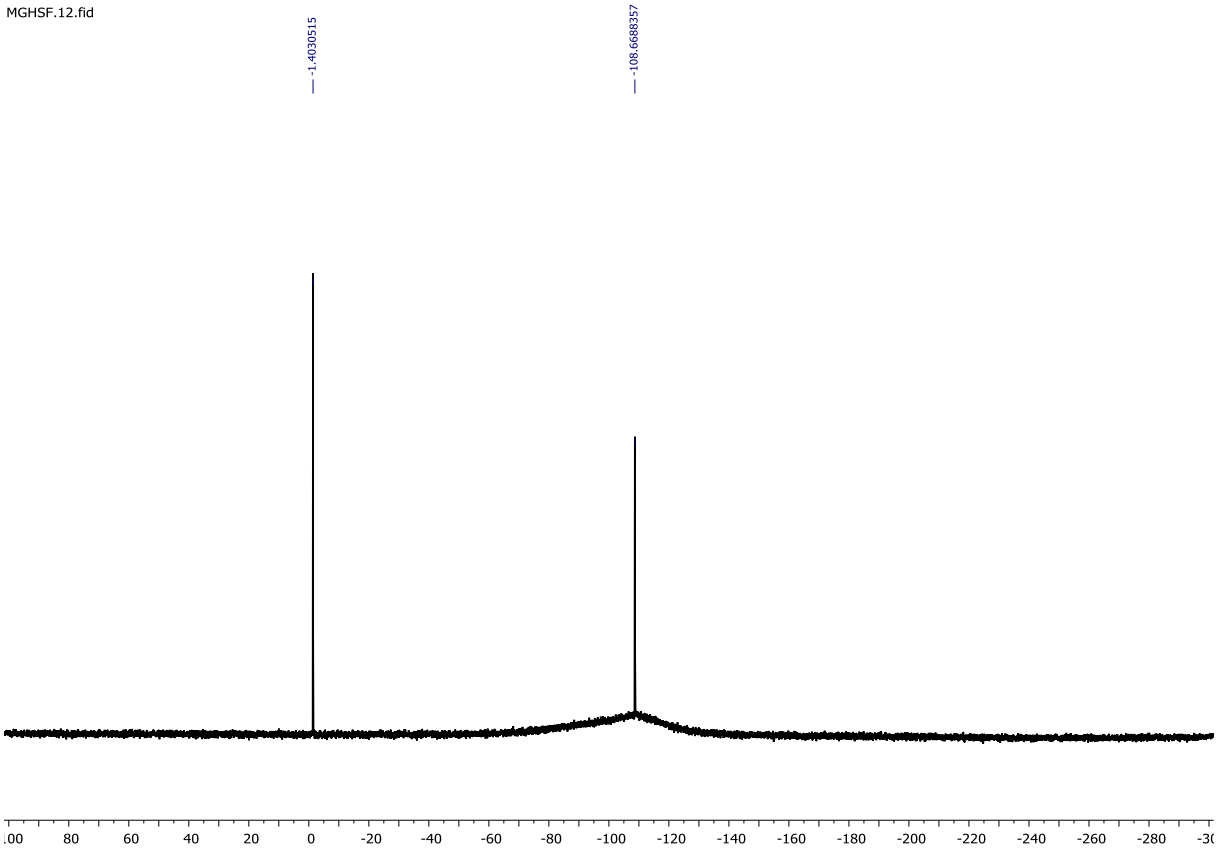
^{13}C NMR (101 MHz, $CDCl_3$)

MGHSF.11.fid

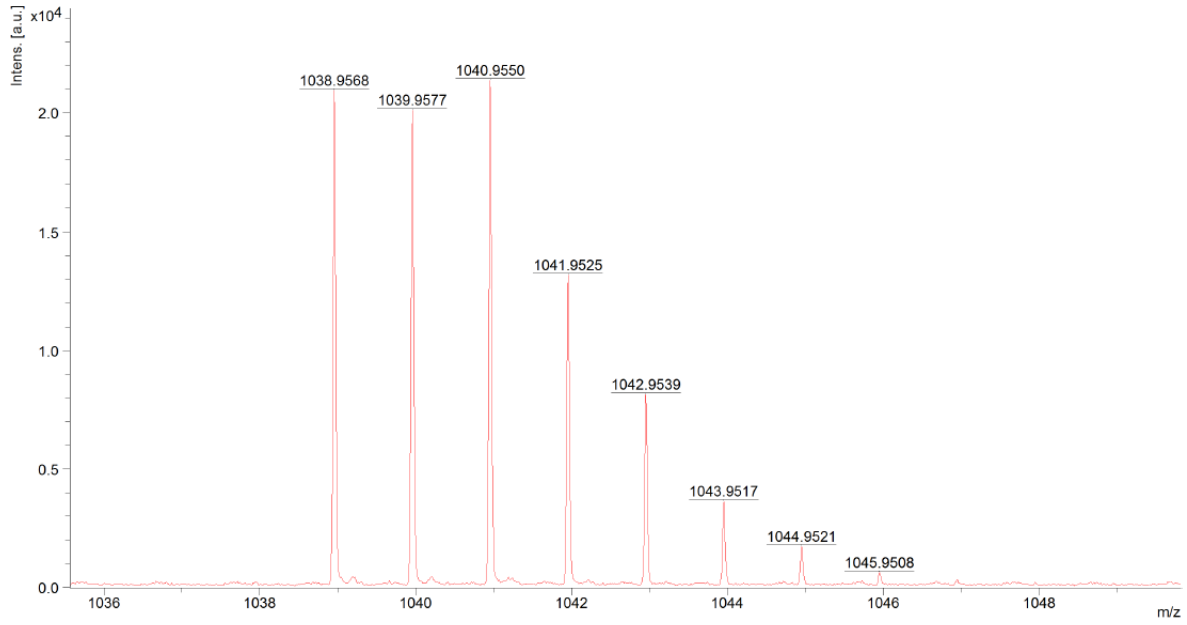


^{29}Si NMR (79 MHz, $CDCl_3$

MGHSF.12.fid



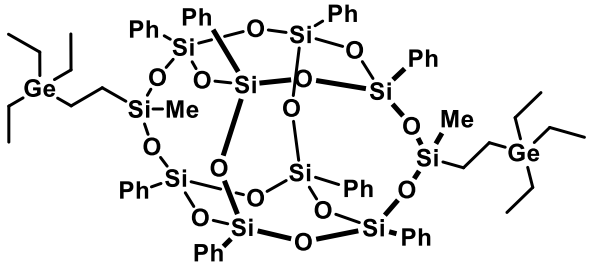
MALDI-TOF


Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
1038.9568
1039.9577
1040.9550
1041.9525
1042.9539
1043.9517
1044.9521
1045.9508
1036
1038
1040
1042
1044
1046
1048
m/z

The ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, MALDI TOF and ESI data of products with germyl moiety 2a-d, 3a-d, 5a-d, 6a-d, 7a-d.

(2a-2d)

(2a)



Chemical Formula: $C_{66}H_{84}Ge_2O_{14}Si_{10}$

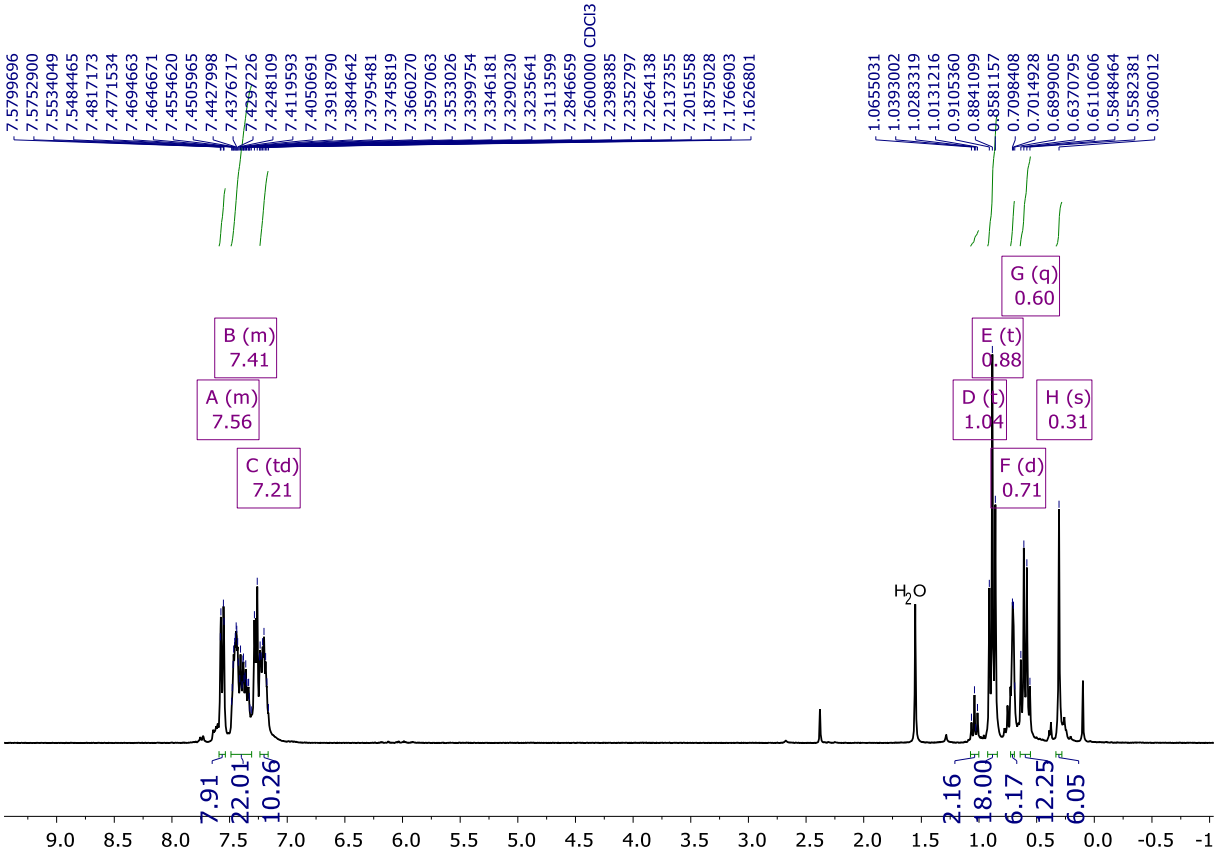
^{1}H NMR (300 MHz, Chloroform-d) δ 7.61 – 7.52 (m, 8H), 7.49 – 7.28 (m, 22H), 7.21 (td, J = 7.5, 7.0, 3.0 Hz, 10H), 1.04 (t, J = 7.9 Hz, 2H), 0.88 (t, J = 7.9 Hz, 18H), 0.71 (d, J = 2.5 Hz, 6H), 0.60 (q, J = 7.9 Hz, 12H), 0.31 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.22, 134.12, 132.40, 131.33, 130.40, 129.19, 127.87, 127.77, 127.73, 127.68, 10.66, 9.04, 3.51, 2.56, -1.51.

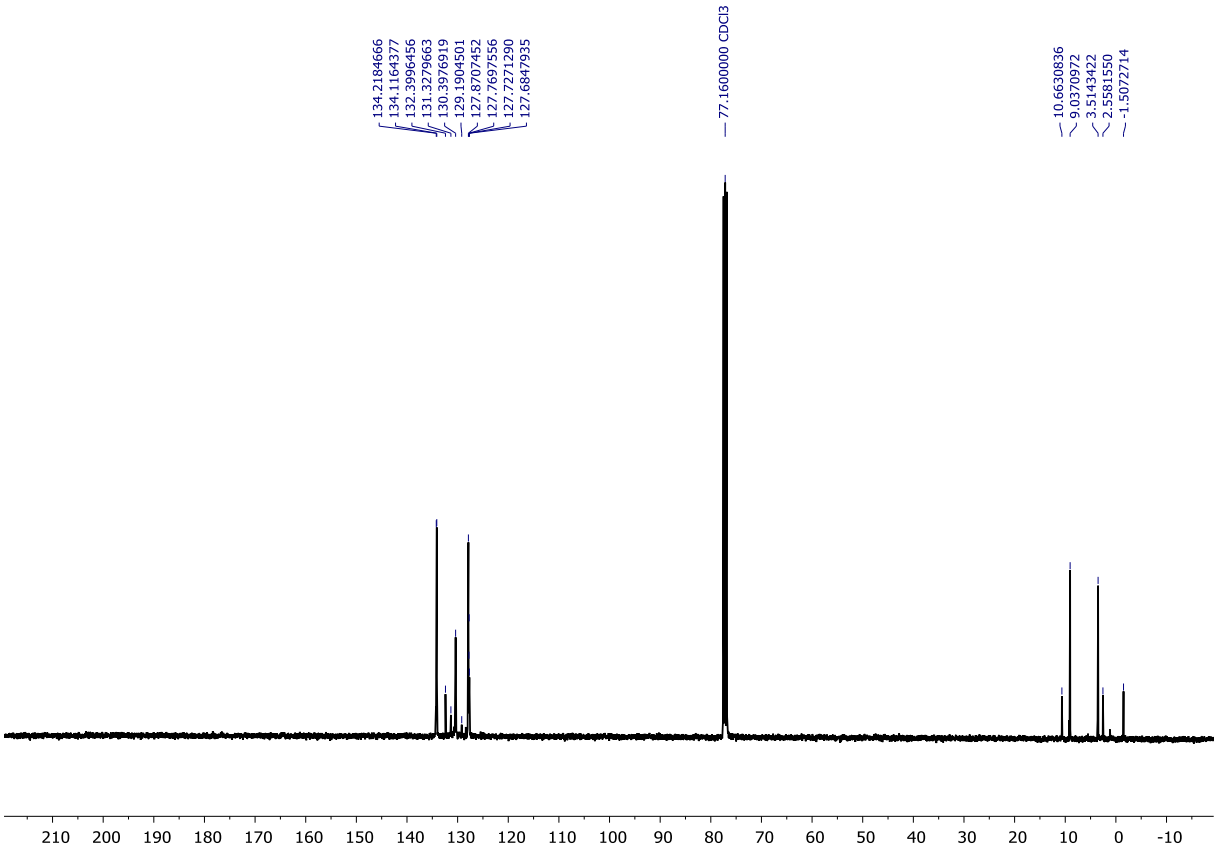
^{29}Si NMR (79 MHz, $CDCl_3$) δ -17.81, -78.70, -79.67.

MALDI-TOF MS (m/z): calcd. for $C_{66}H_{84}Ge_2O_{14}Si_{10}Na$ 1551,19; found 1551,19.

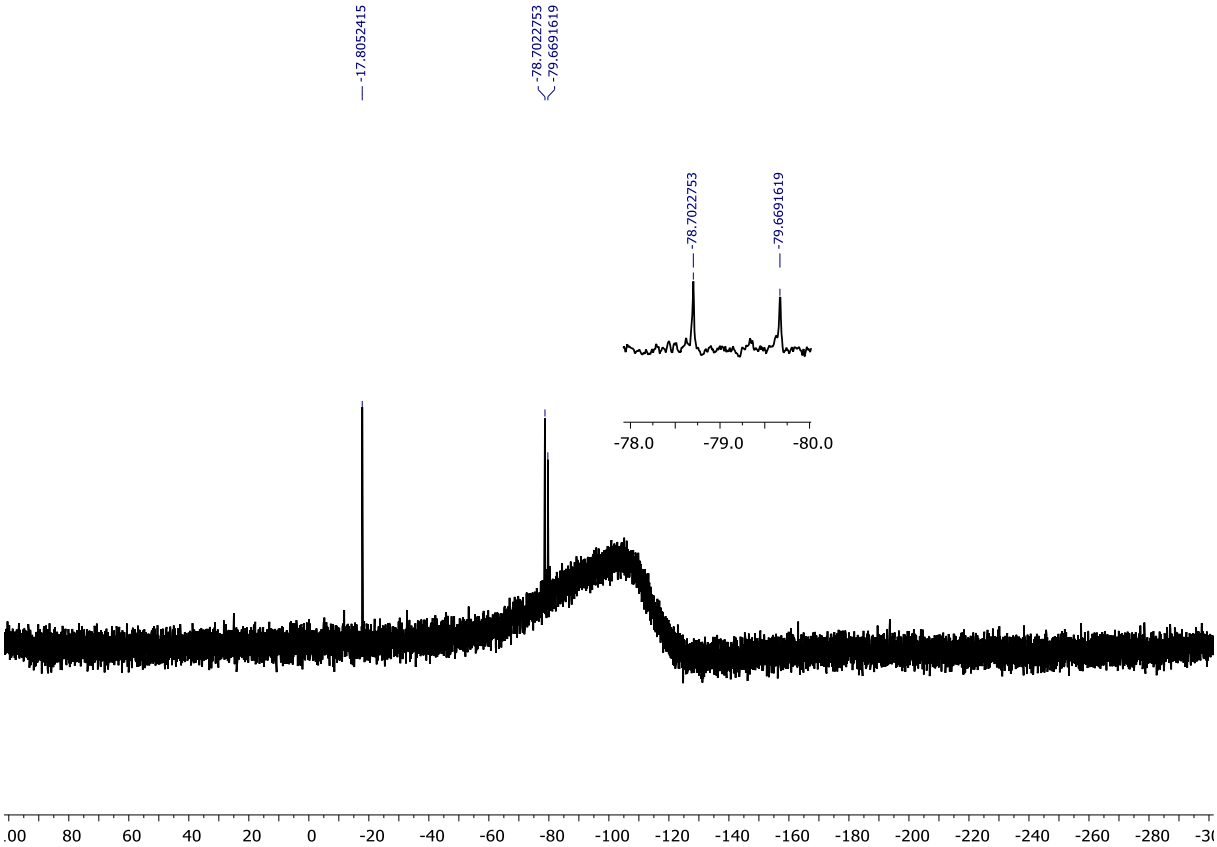
^{1}H NMR (300 MHz, $CDCl_3$)



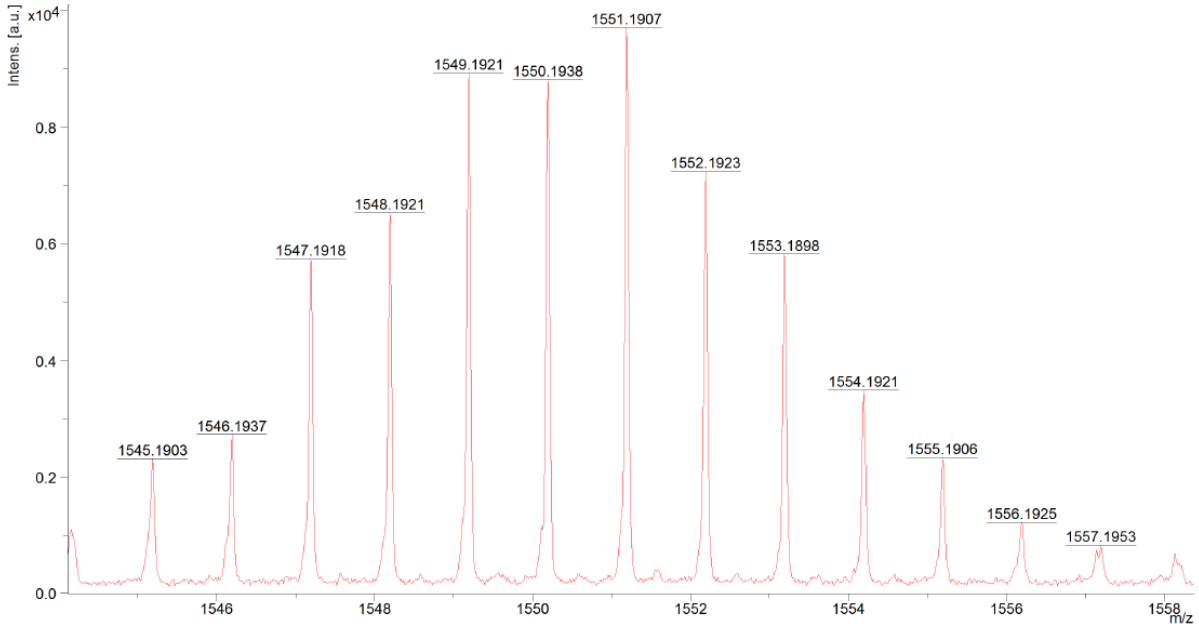
^{13}C NMR (101 MHz, $CDCl_3$)



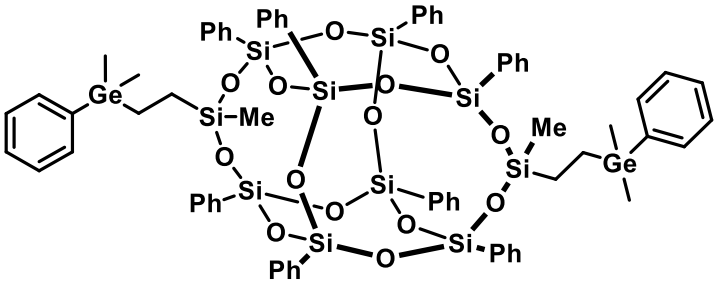
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
0.8
0.6
0.4
0.2
0.0
1545.1903
1546.1937
1547.1918
1548.1921
1549.1921
1550.1938
1551.1907
1552.1923
1553.1898
1554.1921
1555.1906
1556.1925
1557.1953
1546
1548
1550
1552
1554
1556
1558
m/z

(2b)



Chemical Formula: $C_{70}H_{76}Ge_2O_{14}Si_{10}$

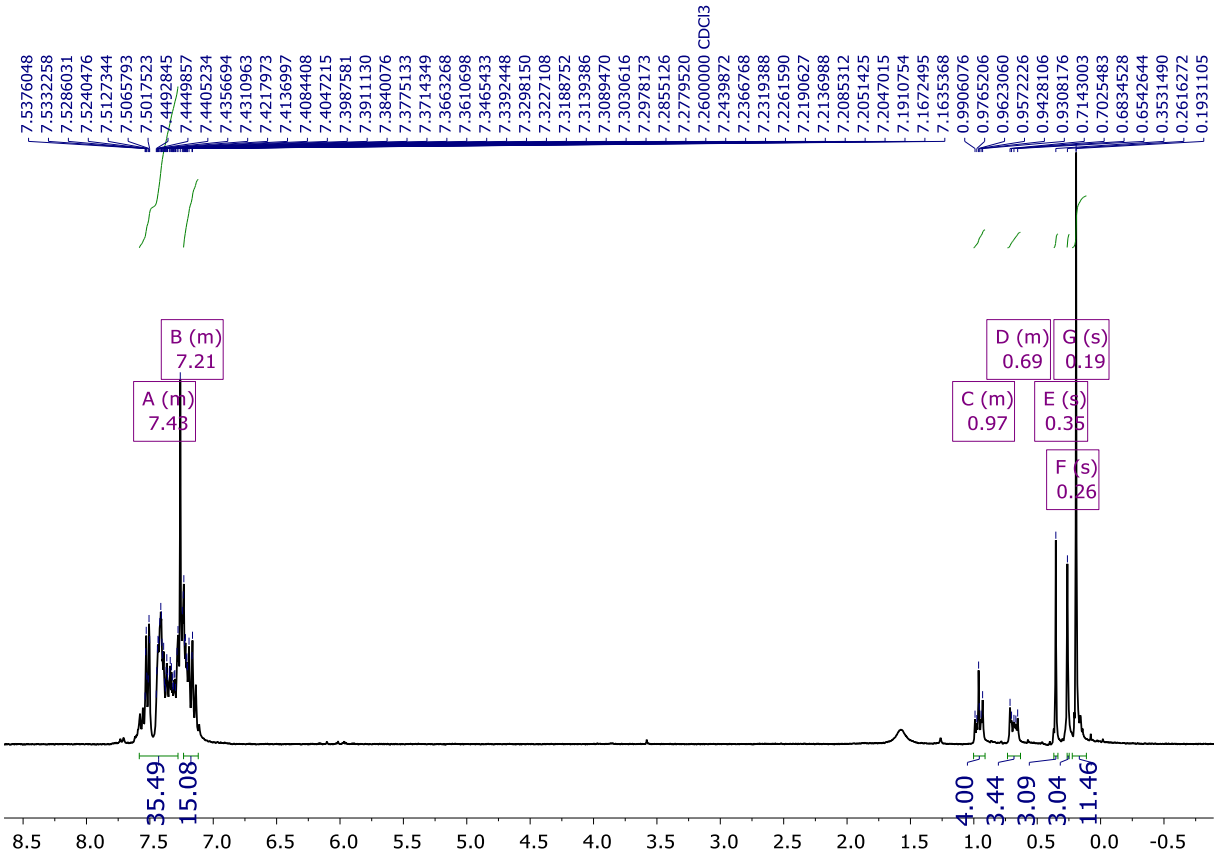
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 – 7.28 (m, 35H), 7.25 – 7.11 (m, 15H), 1.00 – 0.92 (m, 4H), 0.73 – 0.64 (m, 4H), 0.35 (s, 3H), 0.26 (s, 3H), 0.19 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.20, 134.09, 133.46, 133.39, 132.27, 130.44, 128.24, 127.98, 127.91, 127.79, 10.55, 7.17, -1.34, -4.35.

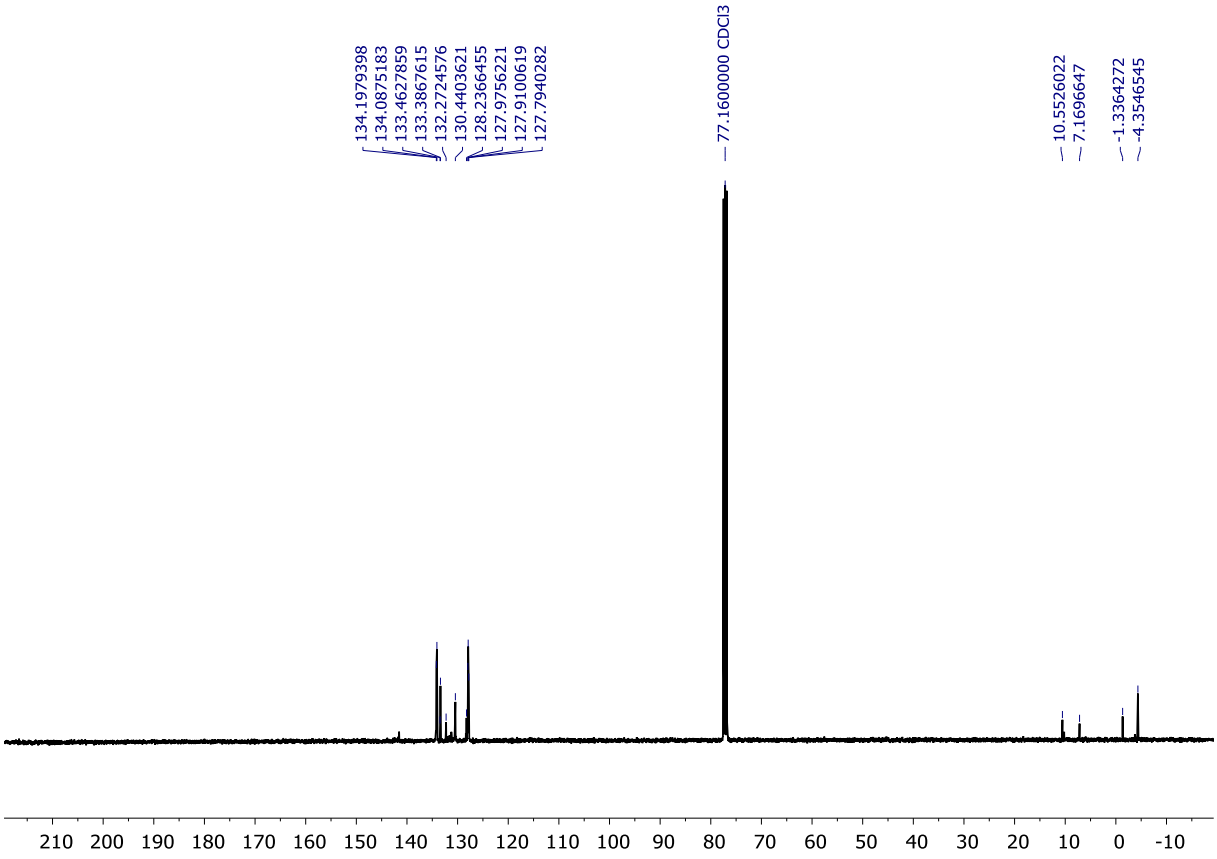
^{29}Si NMR (79 MHz, $CDCl_3$) δ -17.89, -78.68, -79.66.

MALDI-TOF MS (m/z): calcd. for $C_{70}H_{76}Ge_2O_{14}Si_{10}Na$ 1591,12; found 1591,12.

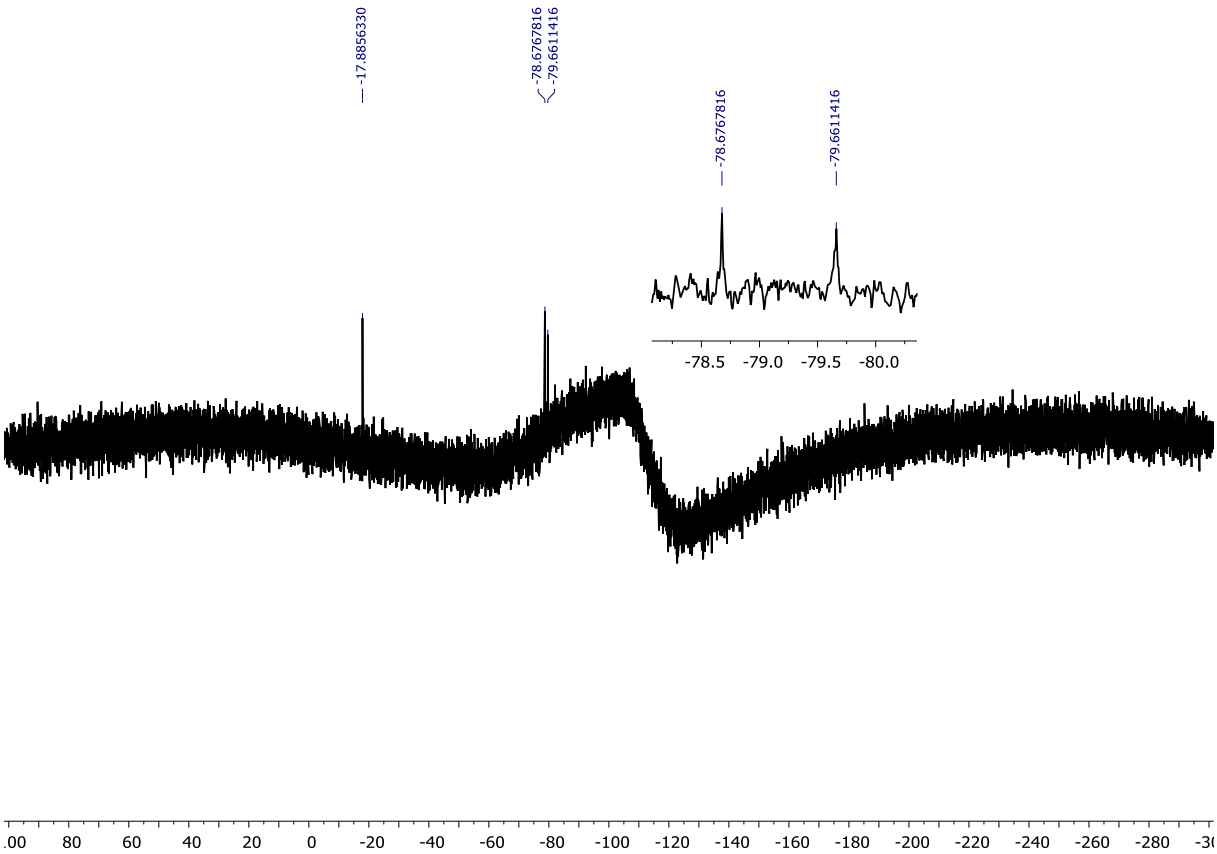
^{1}H NMR (300 MHz, $CDCl_3$)



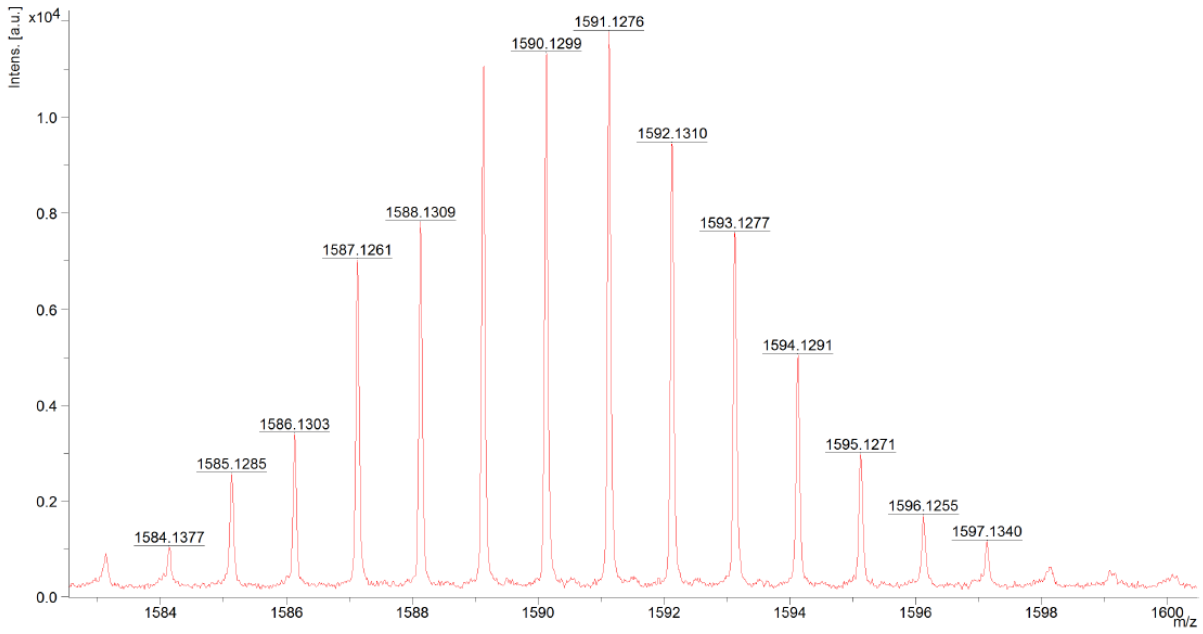
^{13}C NMR (101 MHz, $CDCl_3$)



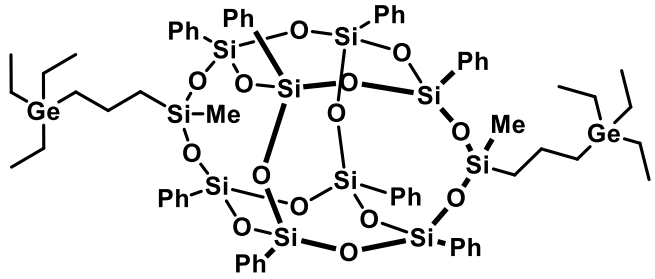
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
1584.1377
1585.1285
1586.1303
1587.1261
1588.1309
1590.1299
1591.1276
1592.1310
1593.1277
1594.1291
1595.1271
1596.1255
1597.1340
1584
1586
1588
1590
1592
1594
1596
1598
1600
m/z

(2c)



Chemical Formula: $C_{68}H_{88}Ge_2O_{14}Si_{10}$

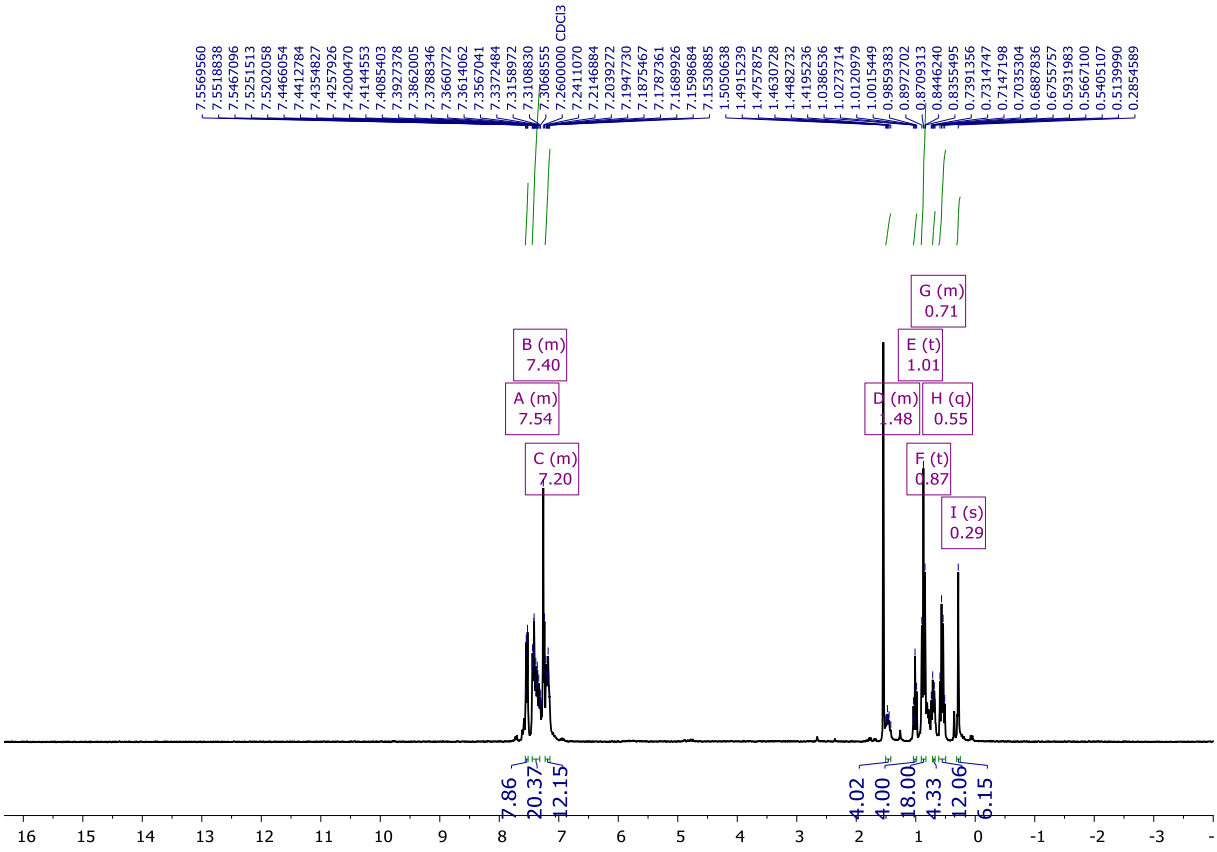
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 8H), 7.46 – 7.30 (m, 20H), 7.25 – 7.14 (m, 12H), 1.52 – 1.41 (m, 4H), 1.01 (t, *J* = 7.9 Hz, 4H), 0.87 (t, *J* = 7.9 Hz, 18H), 0.75 – 0.66 (m, 4H), 0.55 (q, *J* = 8.0 Hz, 12H), 0.29 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.21, 134.09, 132.35, 130.40, 127.88, 127.78, 127.74, 127.70, 21.53, 18.86, 15.87, 9.07, 3.96, -0.71.

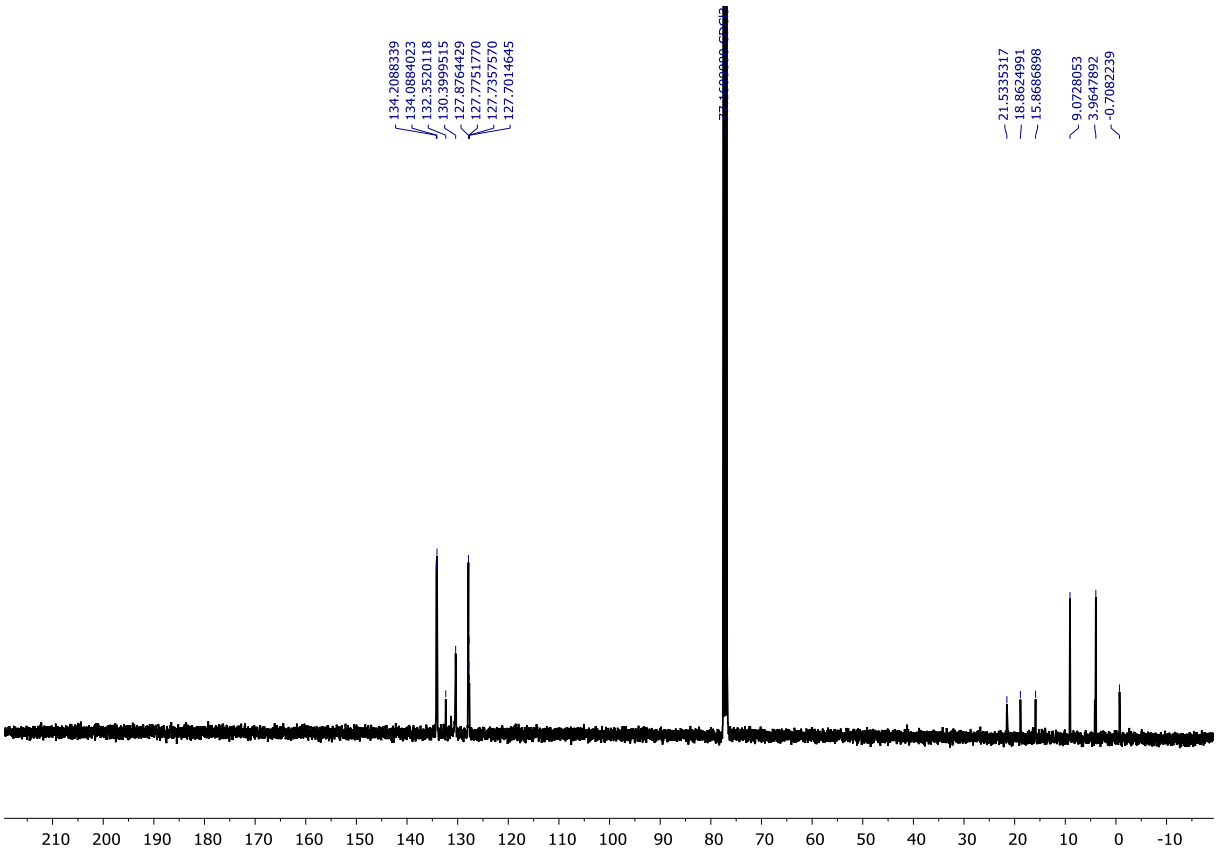
^{29}Si NMR (79 MHz, $CDCl_3$) δ -17.79, -78.73, -79.68.

MALDI-TOF MS (m/z): calcd. for $C_{68}H_{88}Ge_2O_{14}Si_{10}Na$ 1579,22; found 1579,32.

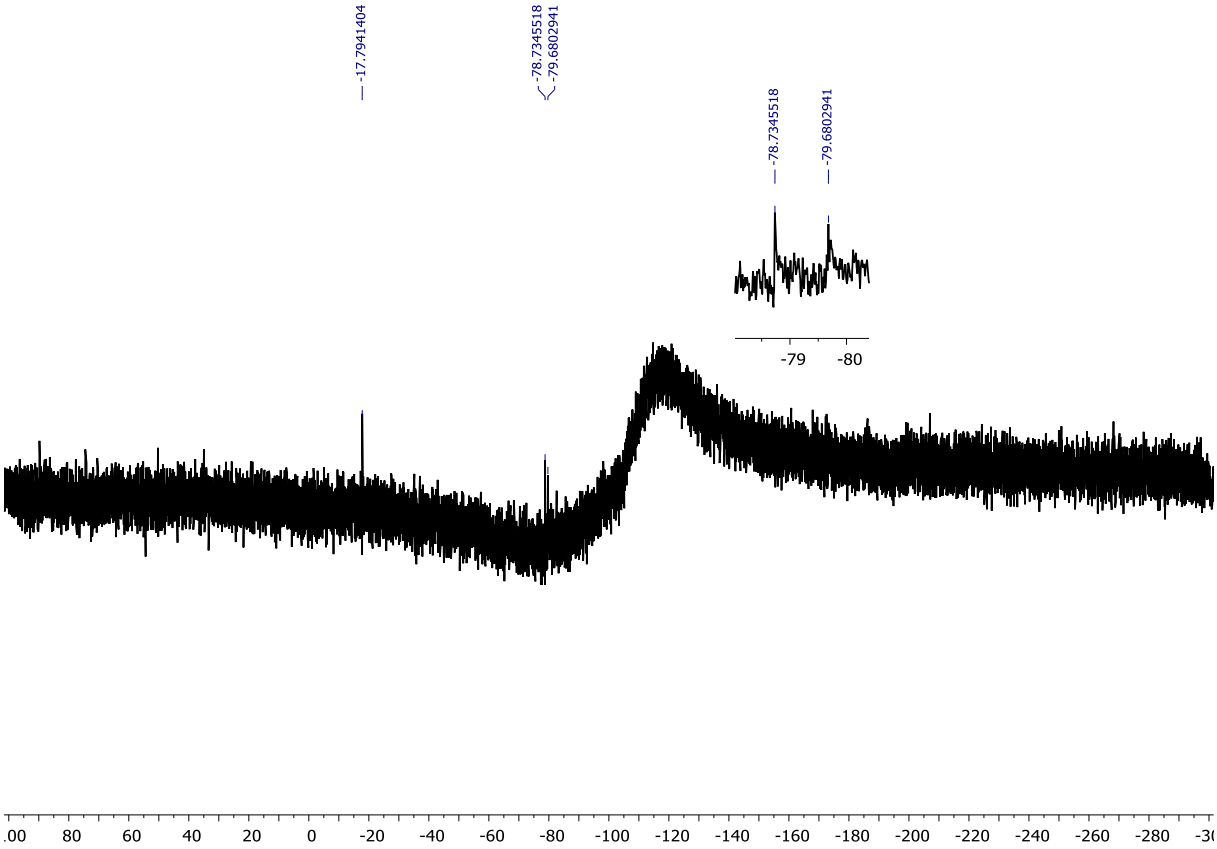
^{1}H NMR (300 MHz, $CDCl_3$)



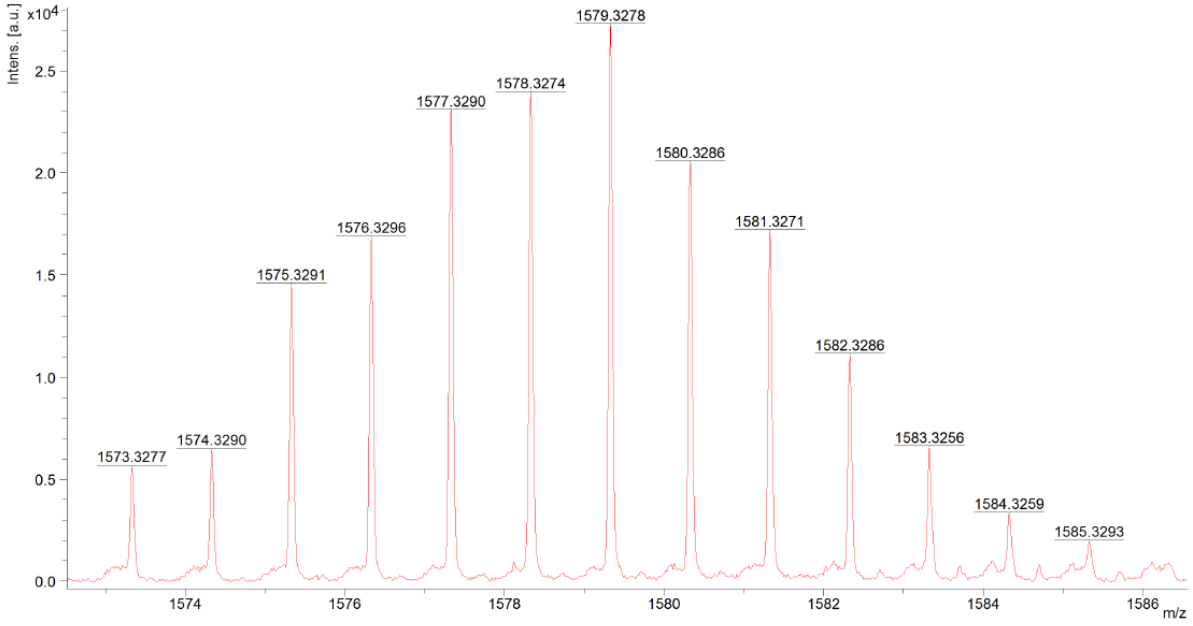
^{13}C NMR (101 MHz, $CDCl_3$)



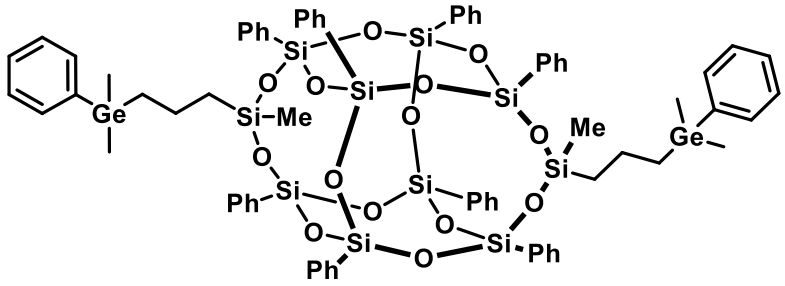
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
2.5
2.0
1.5
1.0
0.5
0.0
1573.3277
1574.3290
1575.3291
1576.3296
1577.3290
1578.3274
1579.3278
1580.3286
1581.3271
1582.3286
1583.3256
1584.3259
1585.3293
1574
1576
1578
1580
1582
1584
1586
m/z

(2d) ***cis/trans***



Chemical Formula: $C_{72}H_{80}Ge_2O_{14}Si_{10}$

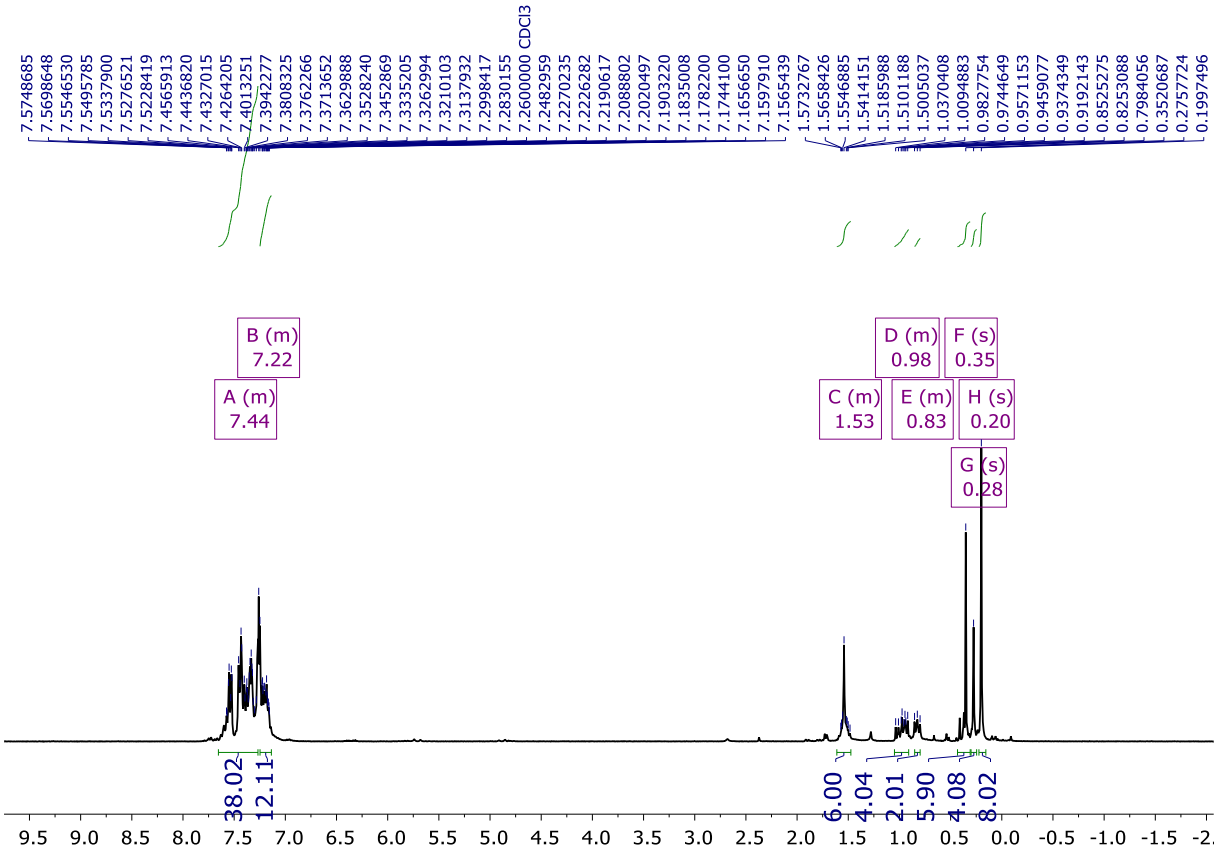
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.65 – 7.28 (m, 38H), 7.26 – 7.14 (m, 12H), 1.60 – 1.48 (m, 6H), 1.06 – 0.90 (m, 4H), 0.88 – 0.78 (m, 2H), 0.35 (s, 6H), 0.28 (s, 4H), 0.20 (s, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.03, 134.22, 134.20, 134.18, 134.16, 134.14, 134.12, 134.09, 134.07, 134.05, 133.35, 133.28, 130.55, 130.45, 128.21, 128.04, 128.01, 127.97, 127.95, 127.91, 127.88, 127.86, 127.83, 127.81, 127.78, 21.01, 19.94, 18.70, -0.72, -3.45, -3.75.

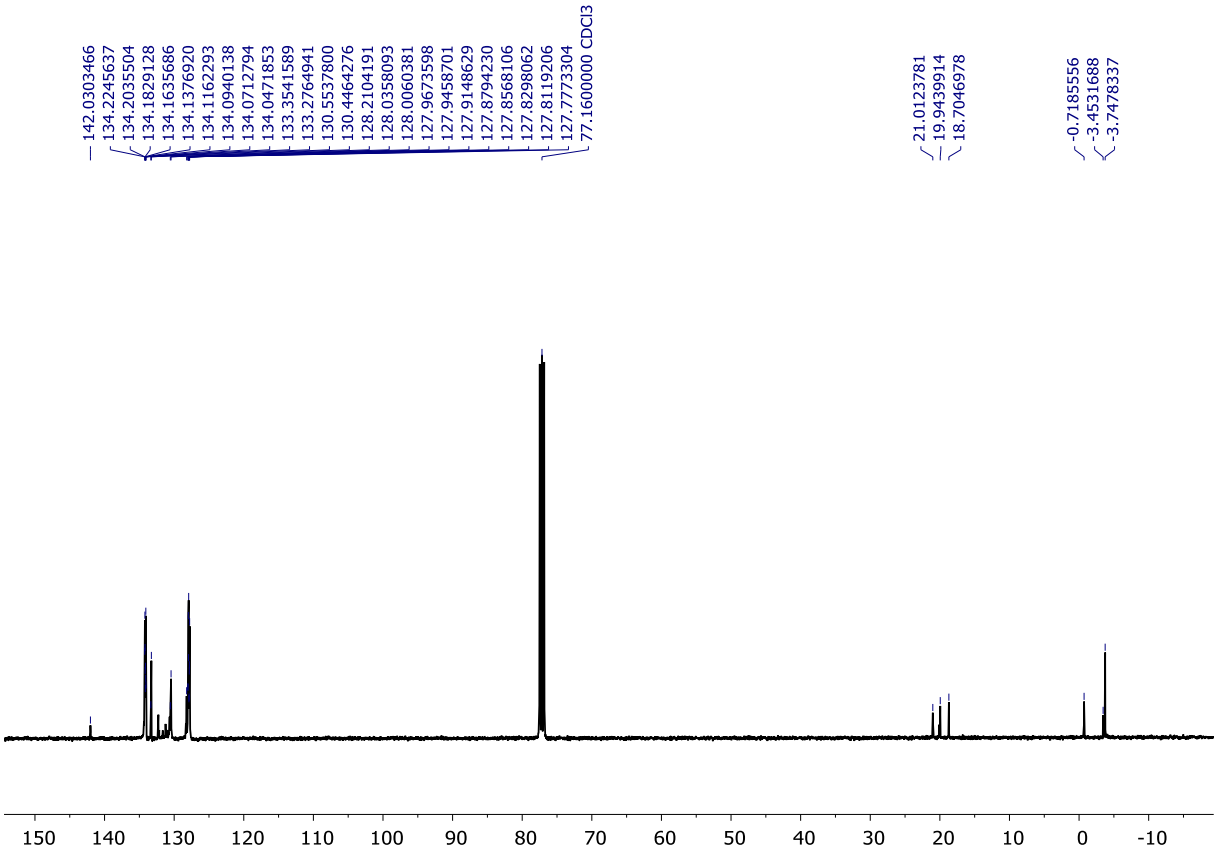
^{29}Si NMR (79 MHz, $CDCl_3$) δ -66.82, -67.04, -67.09, -67.32, -84.60, -84.66, -84.74, -84.81.

MALDI-TOF MS (m/z): calcd. for $C_{72}H_{80}Ge_2O_{14}Si_{10}Na$ 1619,16; found 1619,15.

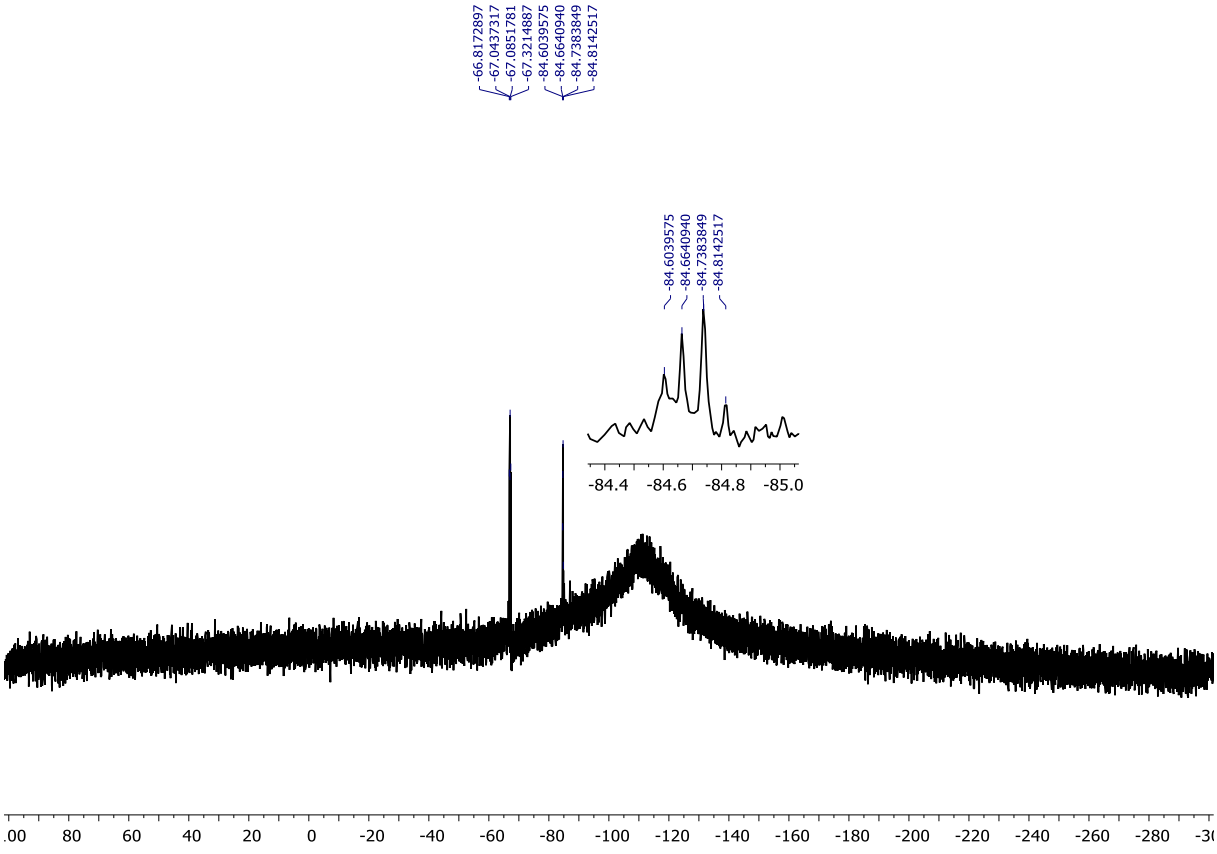
^{1}H NMR (300 MHz, $CDCl_3$)



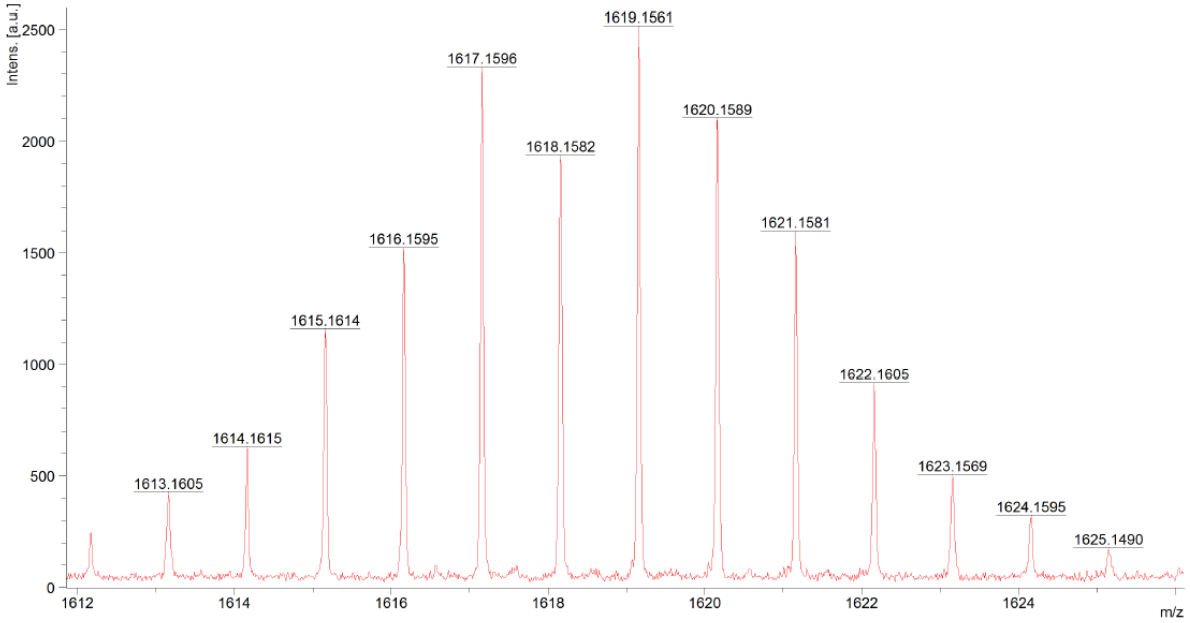
^{13}C NMR (101 MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)

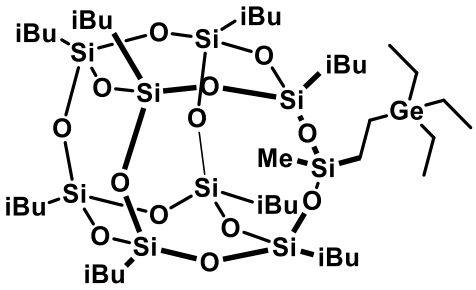


MALDI-TOF


Intens. [a.u.]
2500
2000
1500
1000
500
0
1612
1614
1616
1618
1620
1622
1624
m/z
1613.1605
1614.1615
1615.1614
1616.1595
1617.1596
1618.1582
1619.1561
1620.1589
1621.1581
1622.1605
1623.1569
1624.1595
1625.1490

(3a-d)

(3a)



Chemical Formula: $C_{41}H_{94}GeO_{13}Si_9$

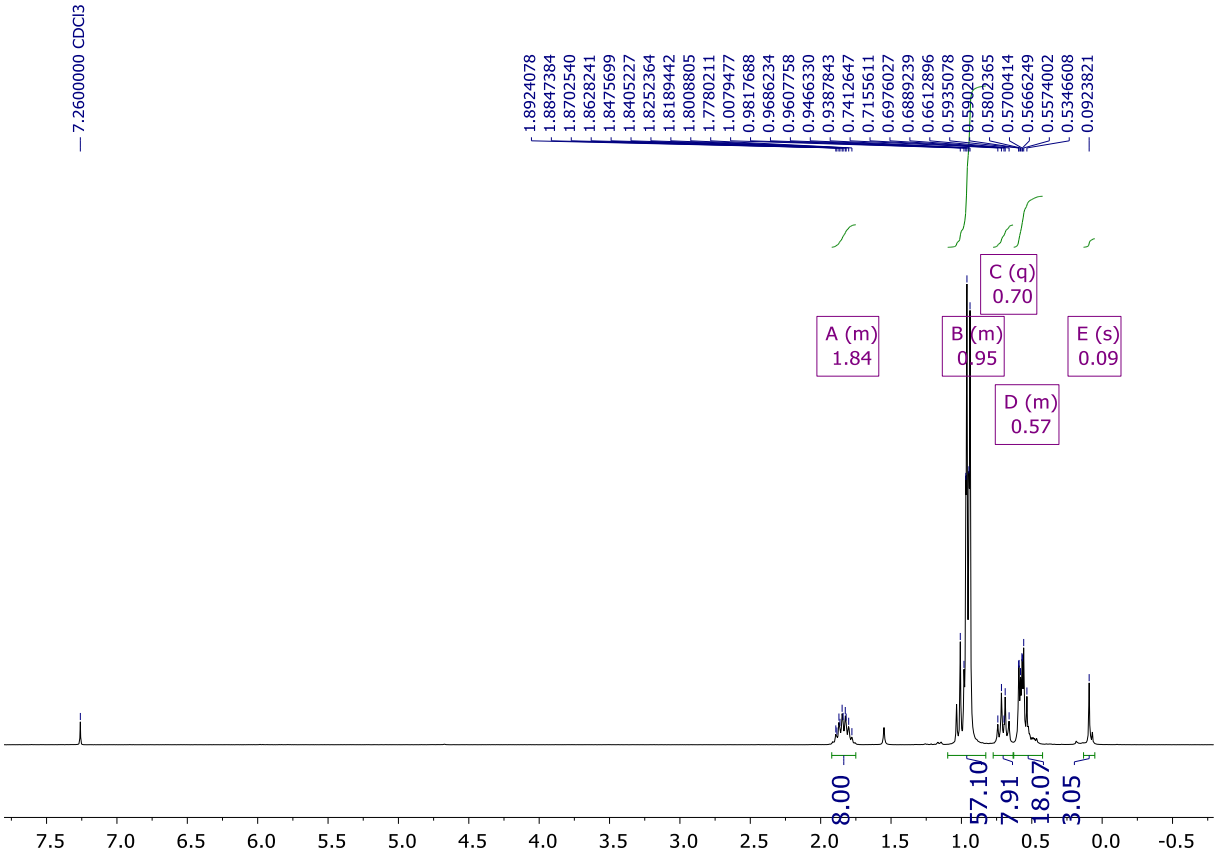
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 – 1.77 (m, 8H), 1.04 – 0.90 (m, 57H), 0.70 (q, *J* = 8.0 Hz, 8H), 0.61 – 0.50 (m, 18H), 0.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 25.96, 25.95, 25.89, 25.87, 25.82, 24.25, 24.12, 24.04, 23.91, 23.25, 22.66, 10.67, 9.14, 3.59, 2.57, -1.74.

^{29}Si NMR (79 MHz, $CDCl_3$) δ -22.07, -67.06, -69.18.

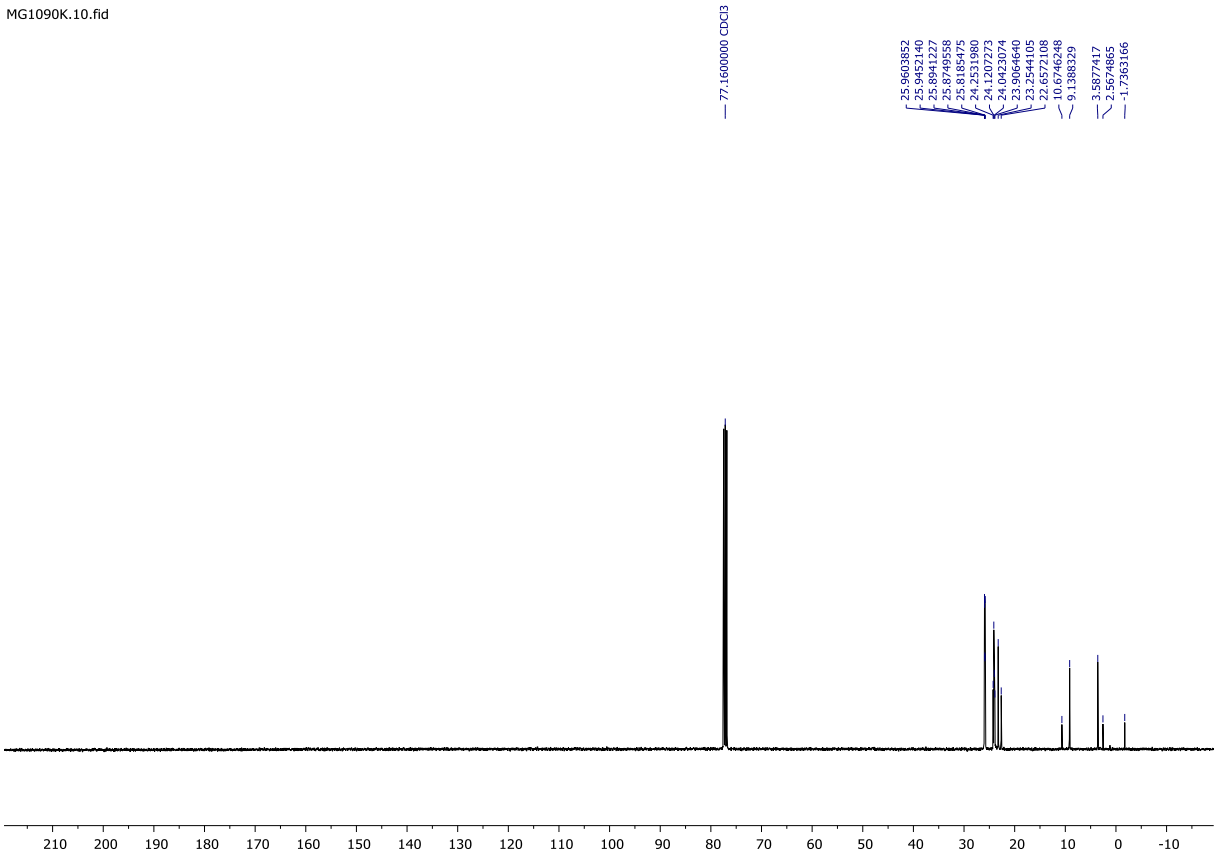
MALDI-TOF MS (m/z): calcd. for $C_{41}H_{94}GeO_{13}Si_9Na$ 1143,37; found 1143,37.

^{1}H NMR (300 MHz, $CDCl_3$)



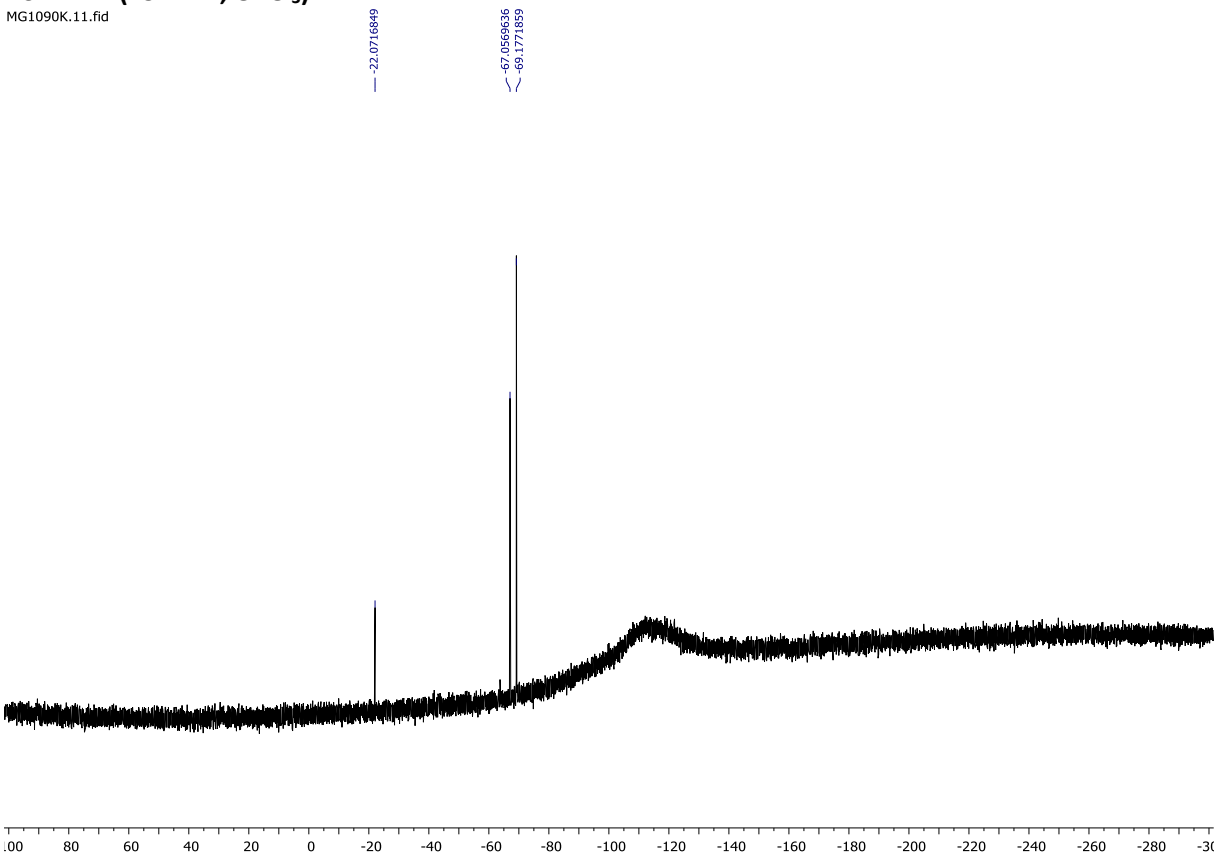
^{13}C NMR (101 MHz, $CDCl_3$)

MG1090K.10.fid

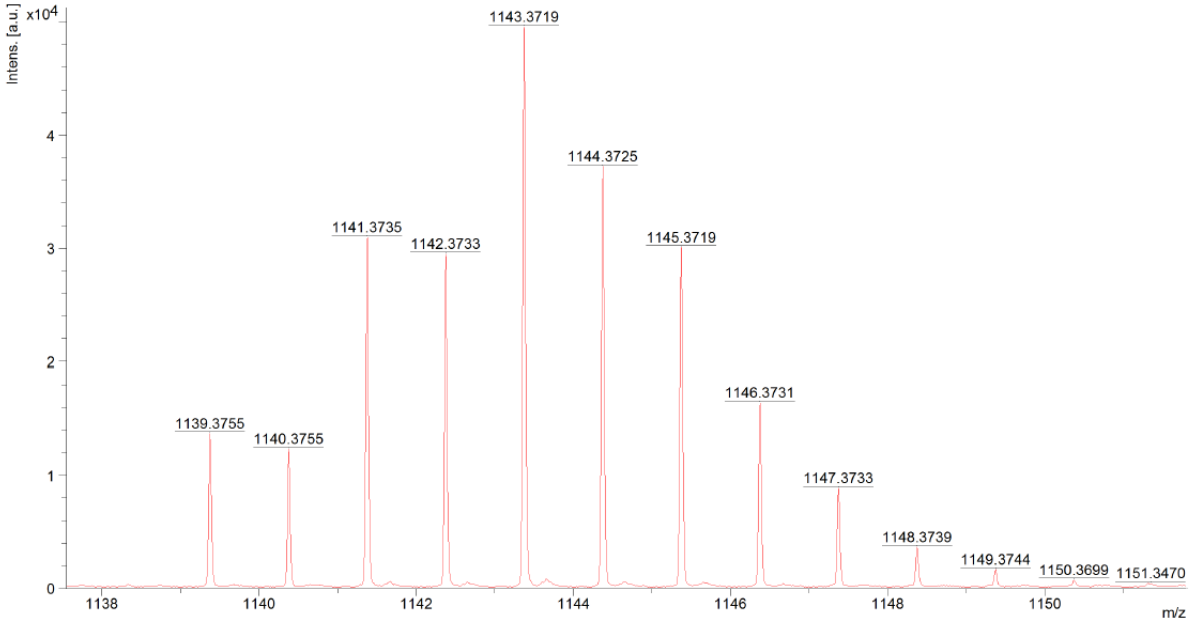


^{29}Si NMR (79 MHz, $CDCl_3$)

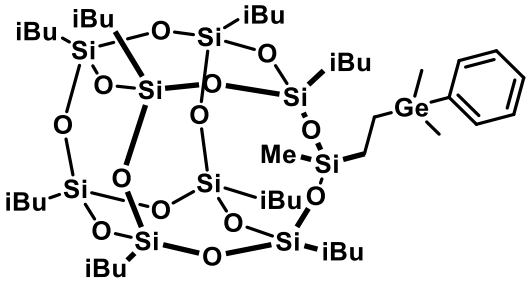
MG1090K.11.fid



MALDI-TOF


Intens. [a.u.]
x10^4
4
3
2
1
0
1143.3719
1144.3725
1141.3735
1142.3733
1145.3719
1146.3731
1139.3755
1140.3755
1147.3733
1148.3739
1149.3744
1150.3699
1151.3470
1138
1140
1142
1144
1146
1148
1150
m/z

(3b)



Chemical Formula: $C_{43}H_{90}GeO_{13}Si_9$

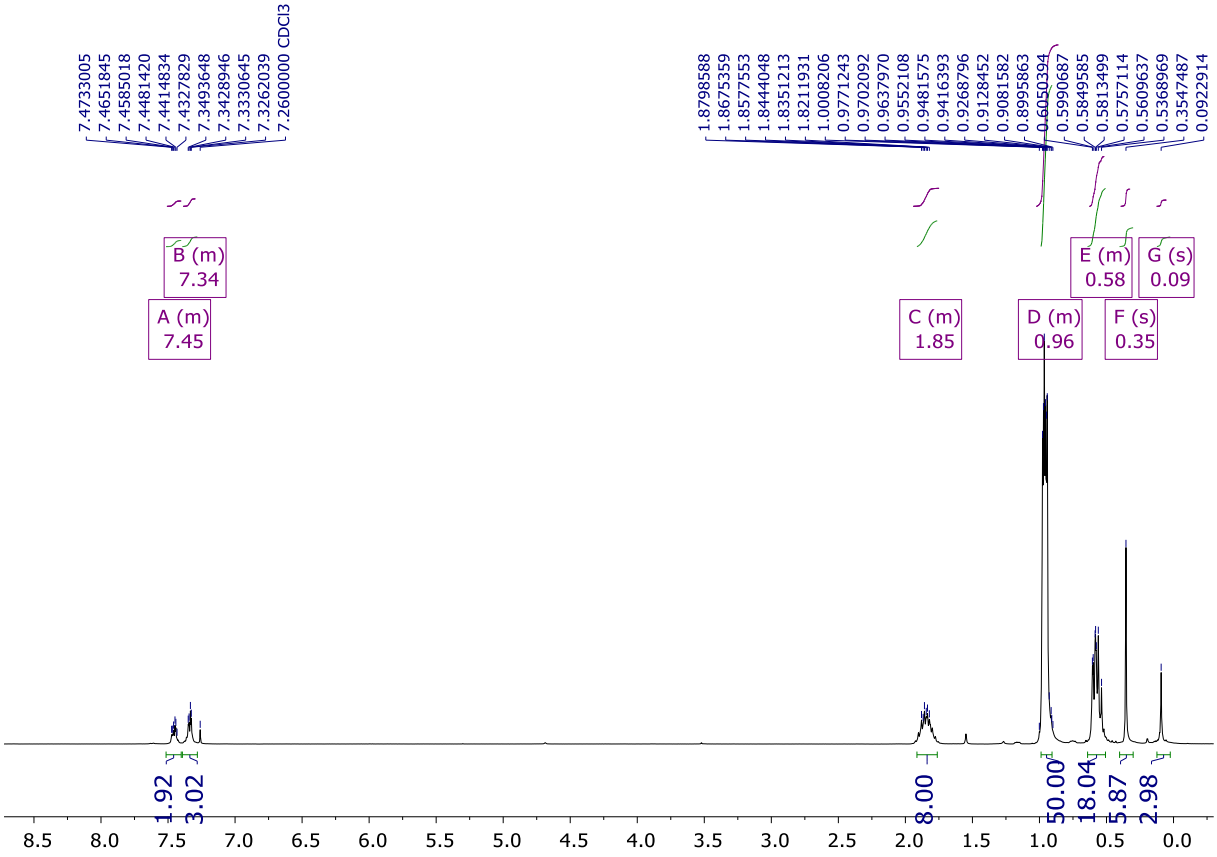
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 2H), 7.34 (m, 3H), 1.94 – 1.75 (m, 8H), 1.02 – 0.87 (m, 50H), 0.62 – 0.52 (m, 18H), 0.35 (s, 6H), 0.09 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.87, 133.44, 128.34, 128.04, 25.95, 24.11, 23.87, 23.24, 22.64, 10.57, 7.40, -1.63, -4.27.

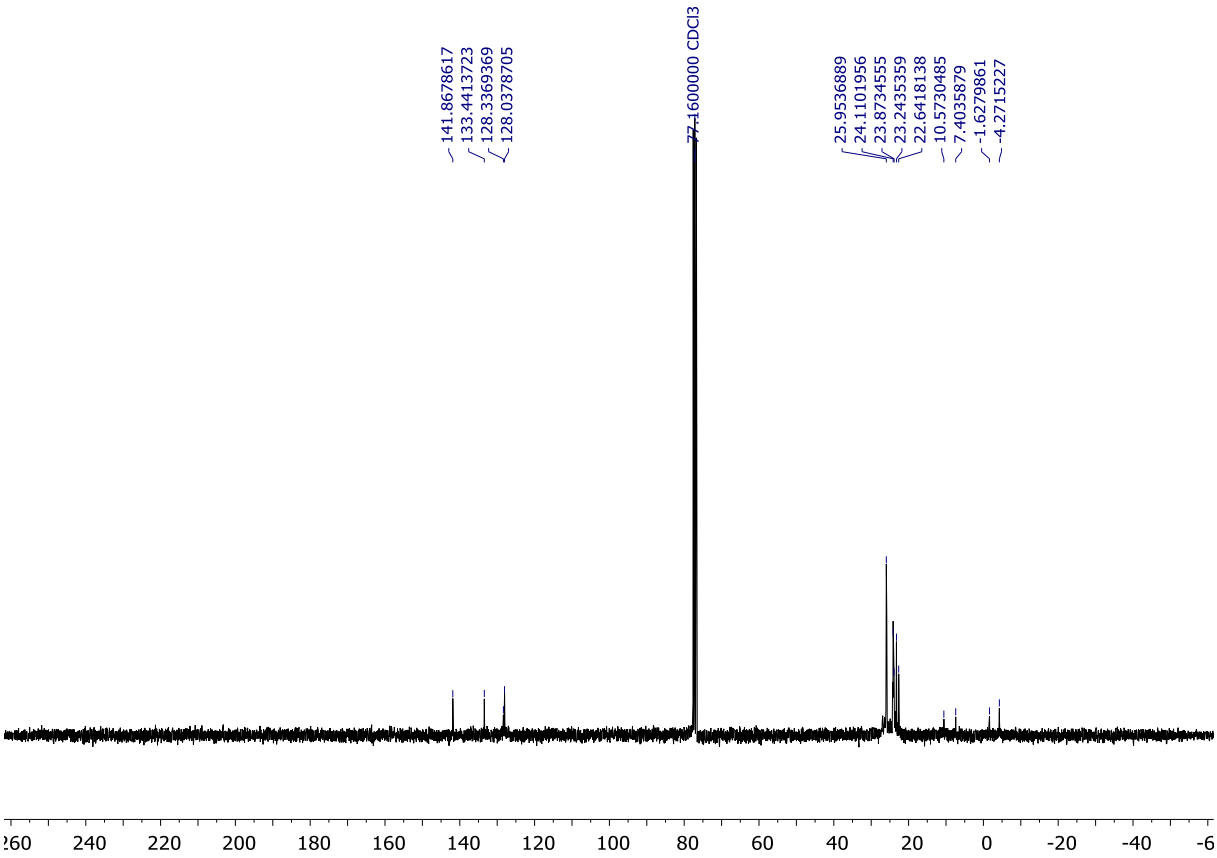
^{29}Si NMR (79 MHz, $CDCl_3$) δ -22.19, -67.04, overlapping signals from silsesquioxane core (-69.11, -69.16, -69.20).

MALDI-TOF MS (m/z): calcd. for $C_{43}H_{90}GeO_{13}Si_9Na$ 1163,34; found 1163,34.

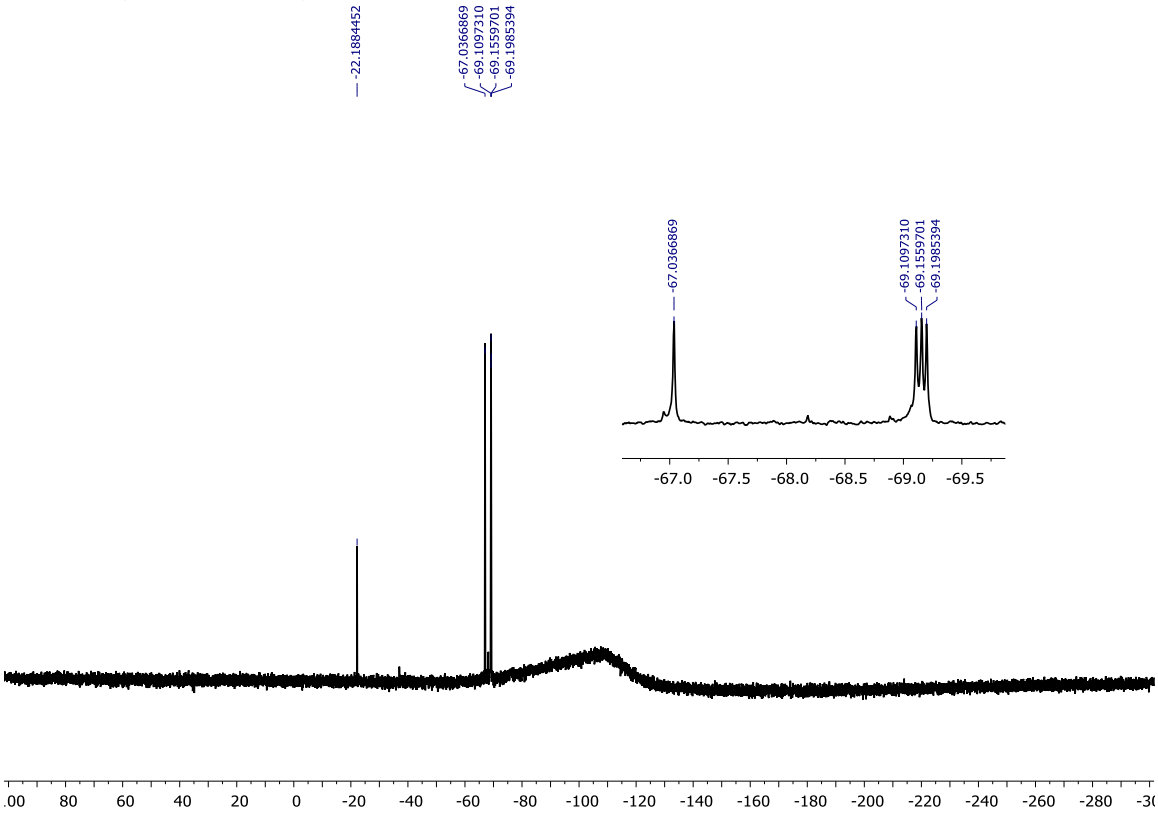
^{1}H NMR (300 MHz, $CDCl_3$)



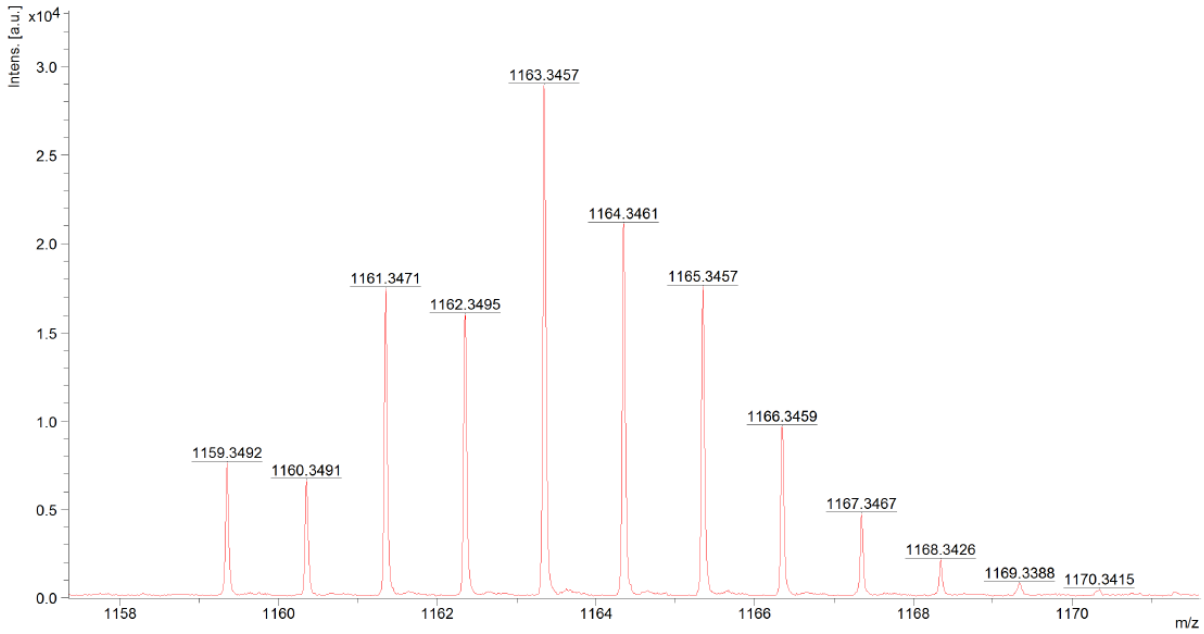
^{13}C NMR (101 MHz, $CDCl_3$)



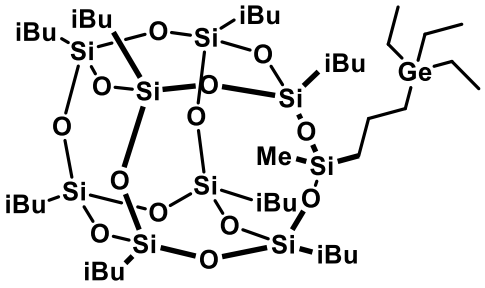
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1159.3492
1160.3491
1161.3471
1162.3495
1163.3457
1164.3461
1165.3457
1166.3459
1167.3467
1168.3426
1169.3388
1170.3415
1158
1160
1162
1164
1166
1168
1170
m/z

(3c)



Chemical Formula: $C_{42}H_{96}GeO_{13}Si_9$

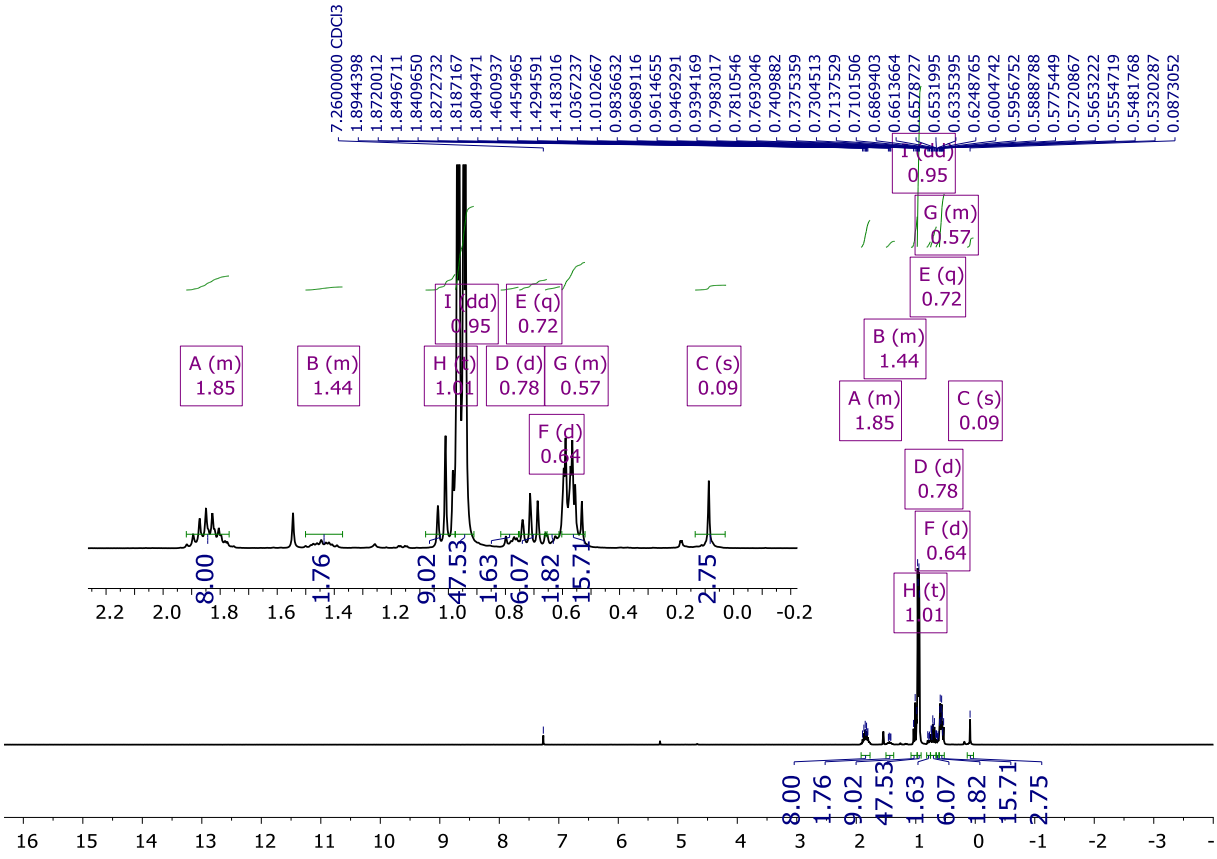
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 – 1.75 (m, 8H), 1.48 – 1.39 (m, 2H), 1.01 (t, *J* = 8.0 Hz, 9H), 0.95 (dd, *J* = 6.6, 2.2 Hz, 48H), 0.78 (d, *J* = 8.7 Hz, 2H), 0.72 (q, 6H), 0.64 (d, *J* = 8.5 Hz, 2H), 0.61 – 0.52 (m, 16H), 0.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 25.96, 25.92, 25.88, 25.82, 24.26, 24.11, 24.04, 23.92, 23.27, 22.66, 21.72, 18.94, 15.99, 9.17, 4.08, -0.92.

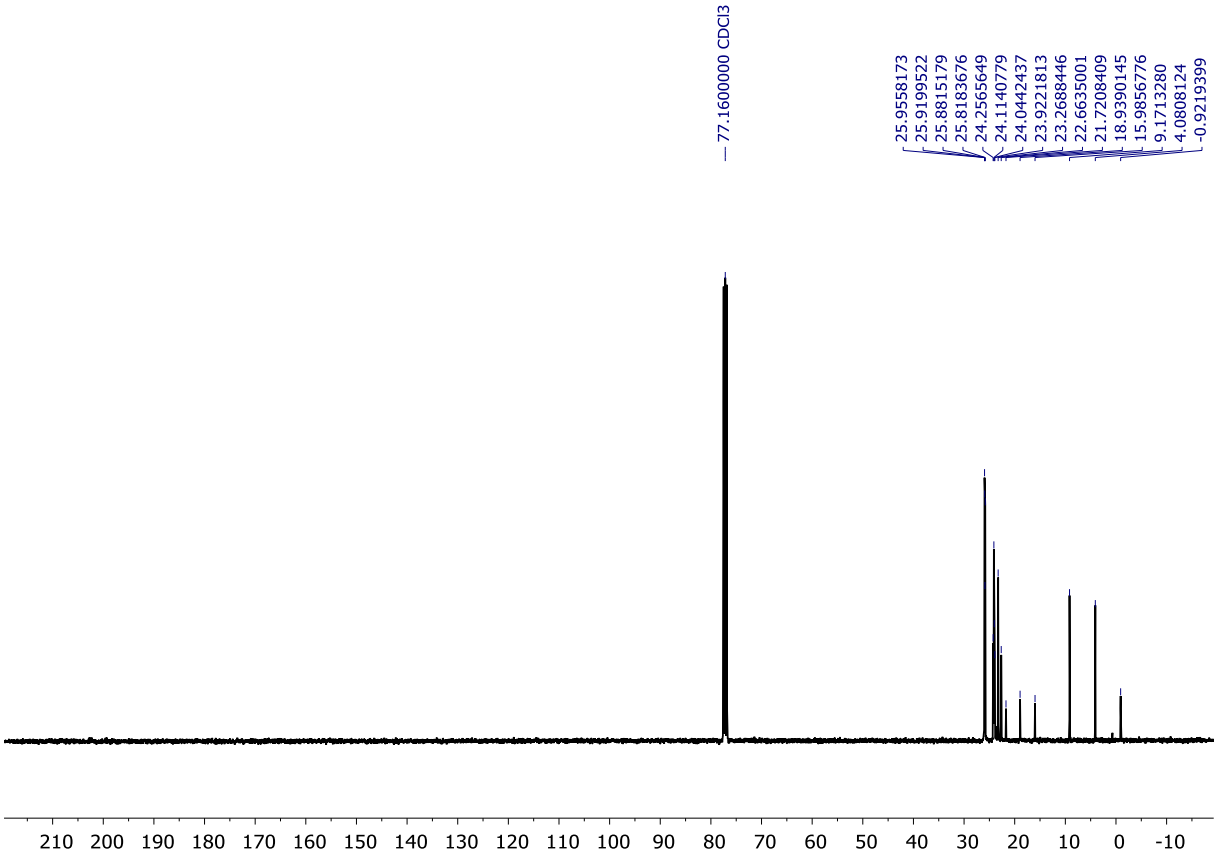
^{29}Si NMR (79 MHz, $CDCl_3$) δ -22.17, -67.06, -69.16, -69.22, -69.25.

MALDI-TOF MS (m/z): calcd. for $C_{42}H_{96}GeO_{13}Si_9Na$ 1157,39; found 1157,39.

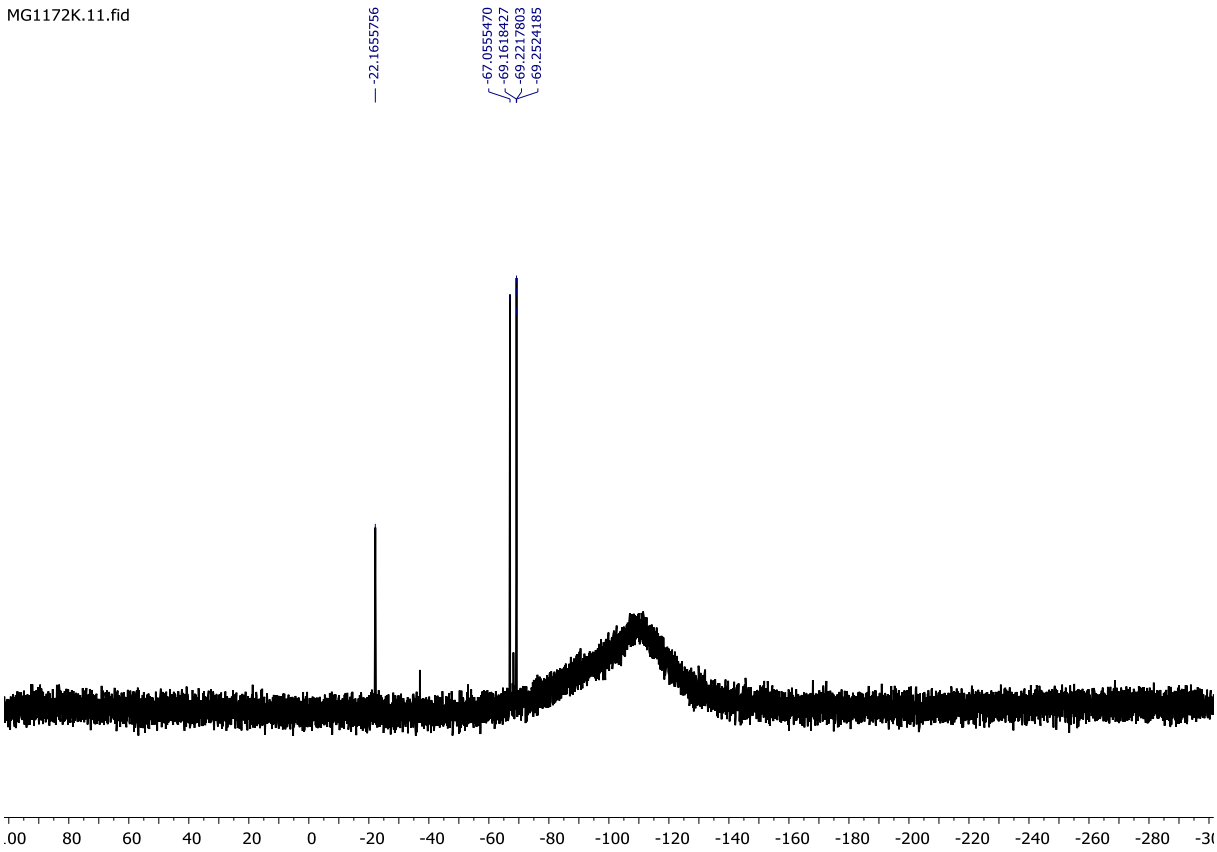
^{1}H NMR (300 MHz, $CDCl_3$)



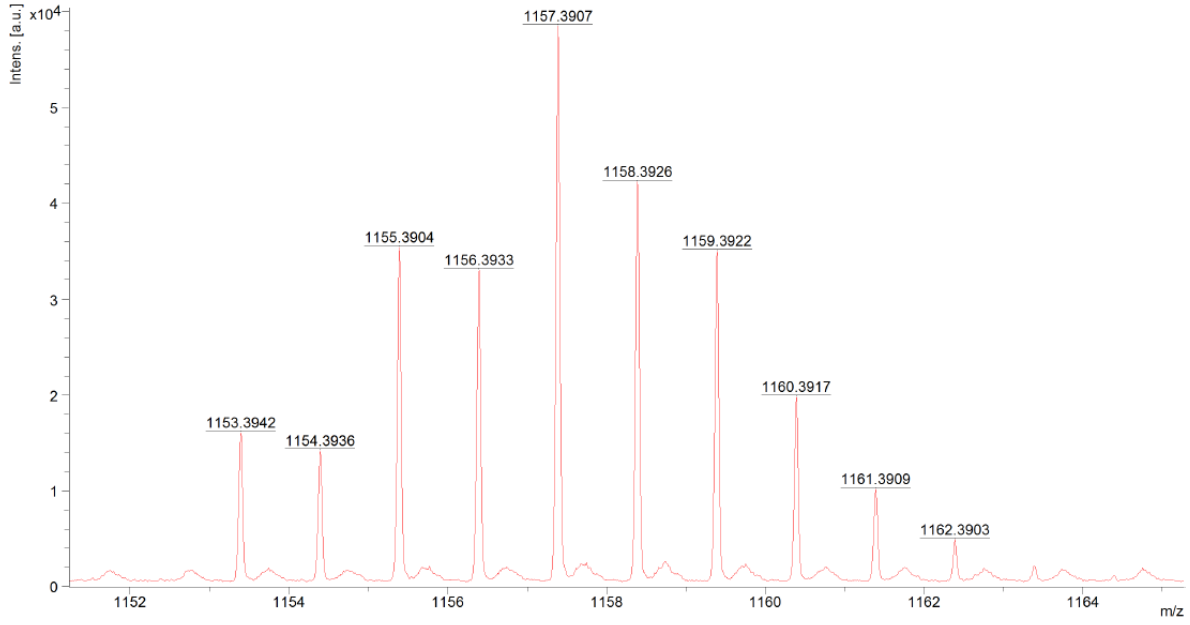
^{13}C NMR (101 MHz, $CDCl_3$)



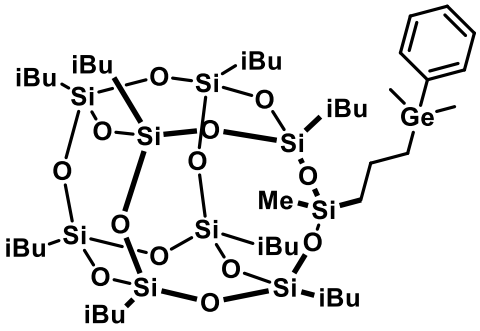
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
5
4
3
2
1
0
1157.3907
1158.3926
1155.3904
1156.3933
1159.3922
1160.3917
1153.3942
1154.3936
1161.3909
1162.3903
1152
1154
1156
1158
1160
1162
1164
m/z

(3d)



Chemical Formula: $C_{44}H_{92}GeO_{13}Si_9$

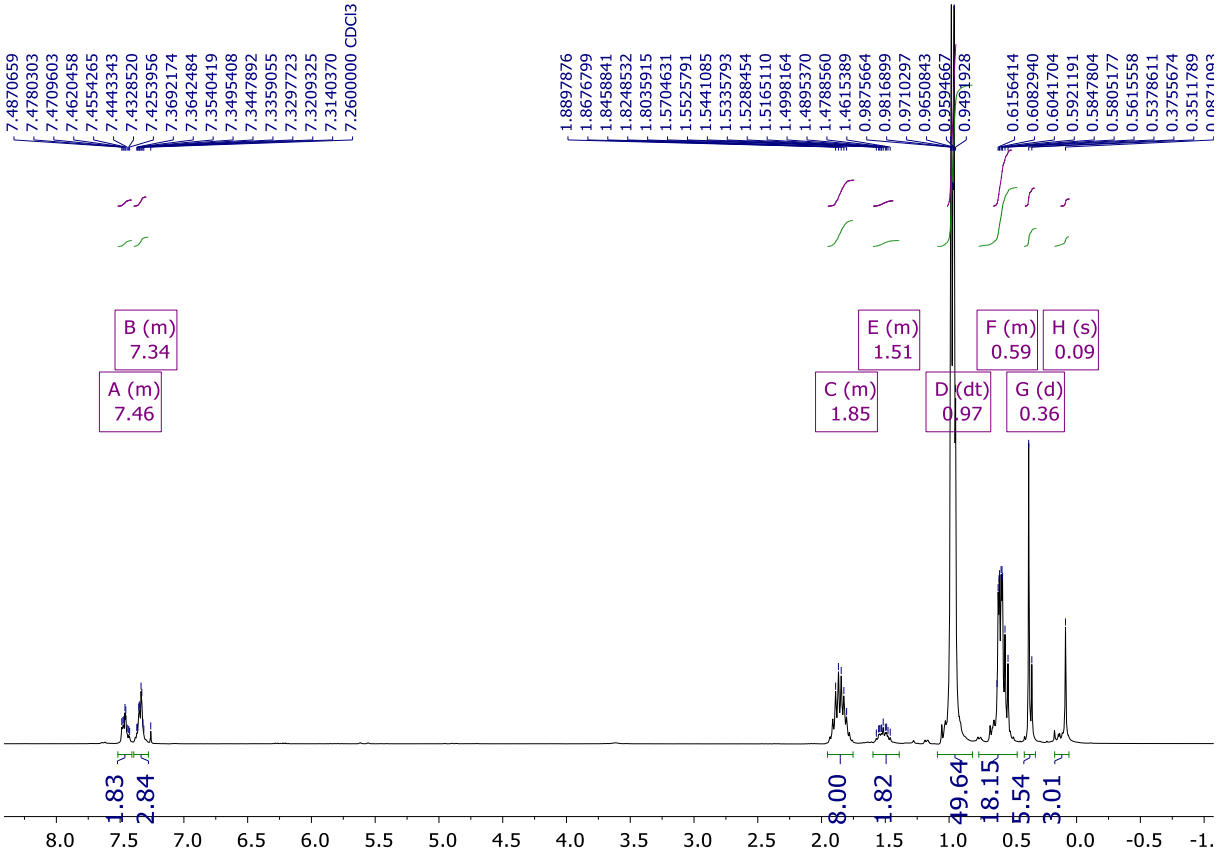
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 2H), 7.39 – 7.30 (m, 3H), 1.95 – 1.75 (m, 8H), 1.59 – 1.44 (m, 2H), 0.97 (dt, *J* = 6.6, 2.4 Hz, 50H), 0.65 – 0.51 (m, 18H), 0.36 (d, *J* = 7.3 Hz, 6H), 0.09 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.15, 133.35, 128.32, 128.05, 25.99, 25.95, 25.90, 25.85, 24.27, 24.14, 24.07, 23.90, 23.27, 21.24, 20.19, 18.82, -0.89, -3.54.

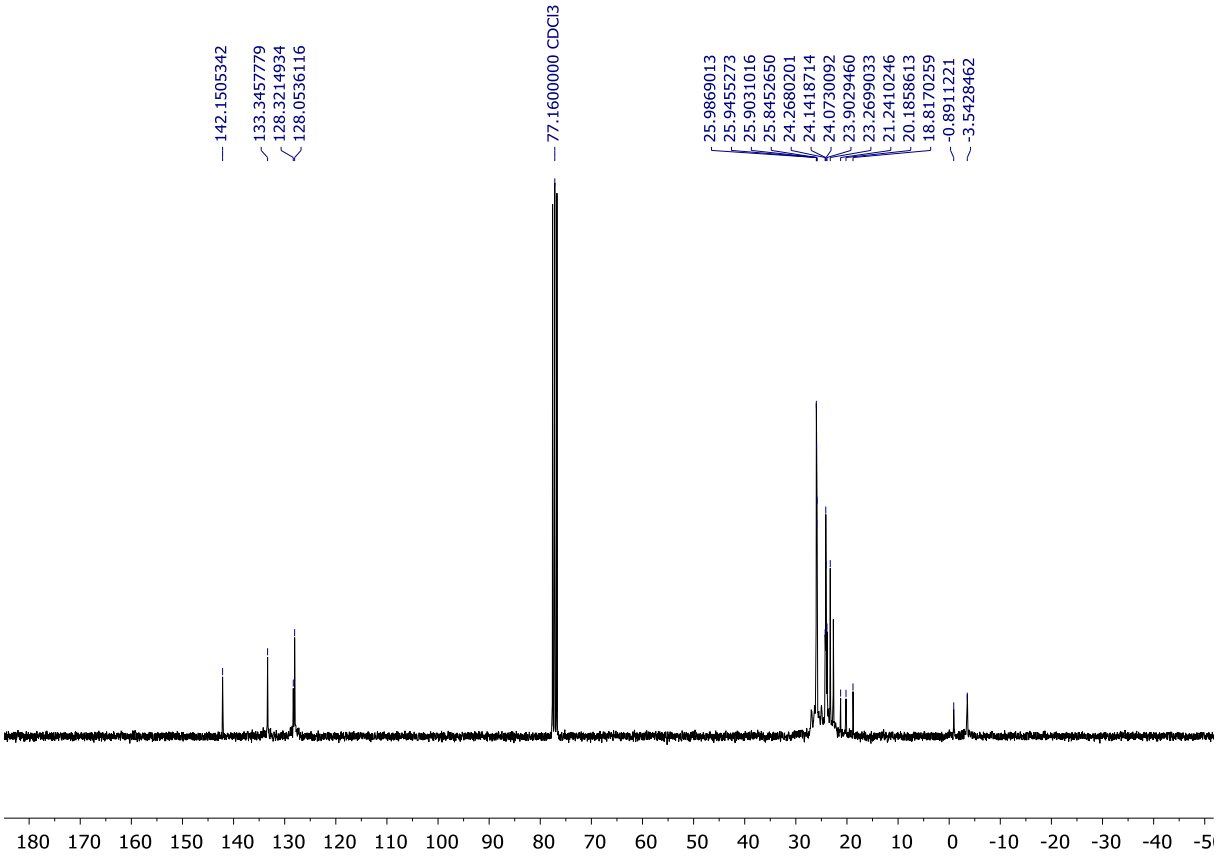
^{29}Si NMR (79 MHz, $CDCl_3$) δ -22.25, -67.03, -69.21.

MALDI-TOF MS (m/z): calcd. for $C_{44}H_{92}GeO_{13}Si_9Na$ 1177,36; found 1177,36.

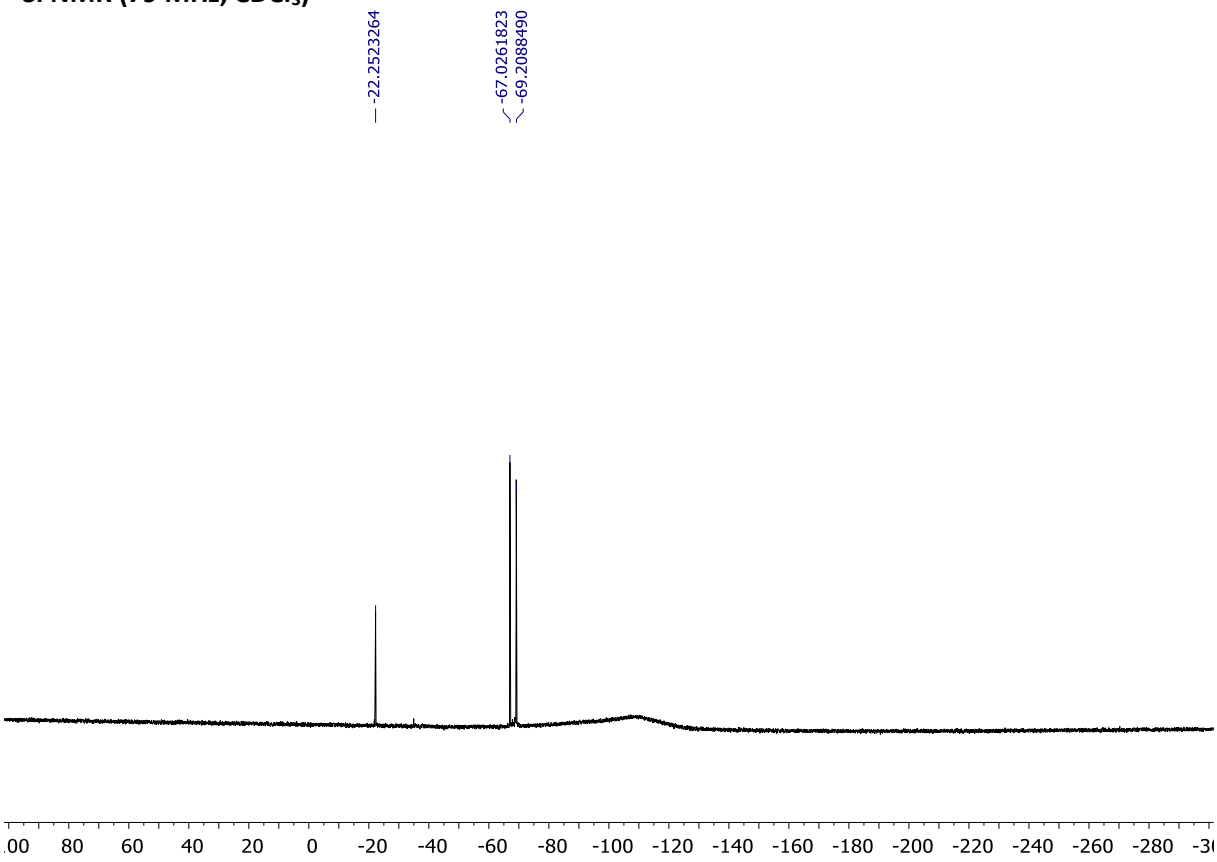
^{1}H NMR (300 MHz, $CDCl_3$)



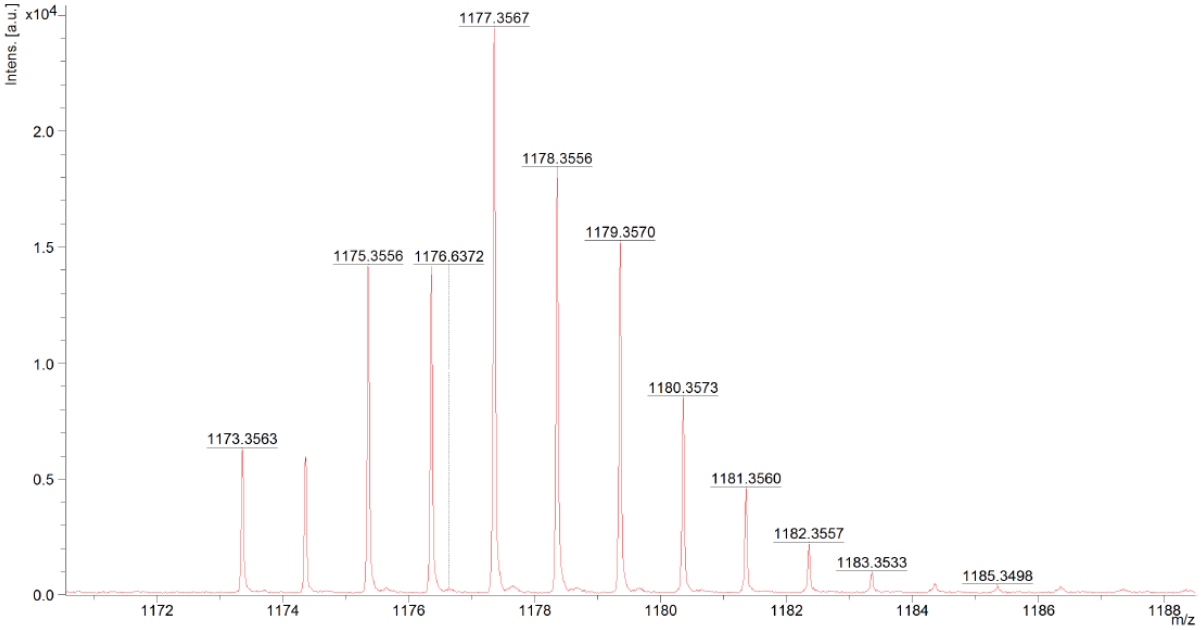
^{13}C NMR (101 MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)

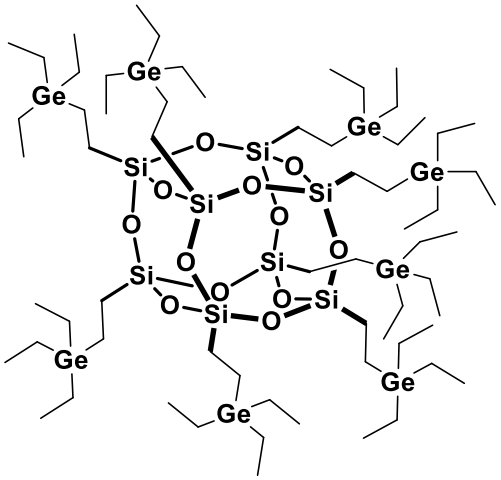


MALDI-TOF


Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
1177.3567
1178.3556
1179.3570
1175.3556
1176.6372
1180.3573
1173.3563
1181.3560
1182.3557
1183.3533
1185.3498
1172
1174
1176
1178
1180
1182
1184
1186
1188
m/z

(5a-d)

(5a)



Chemical Formula: $C_{64}H_{152}Ge_8O_{12}Si_8$

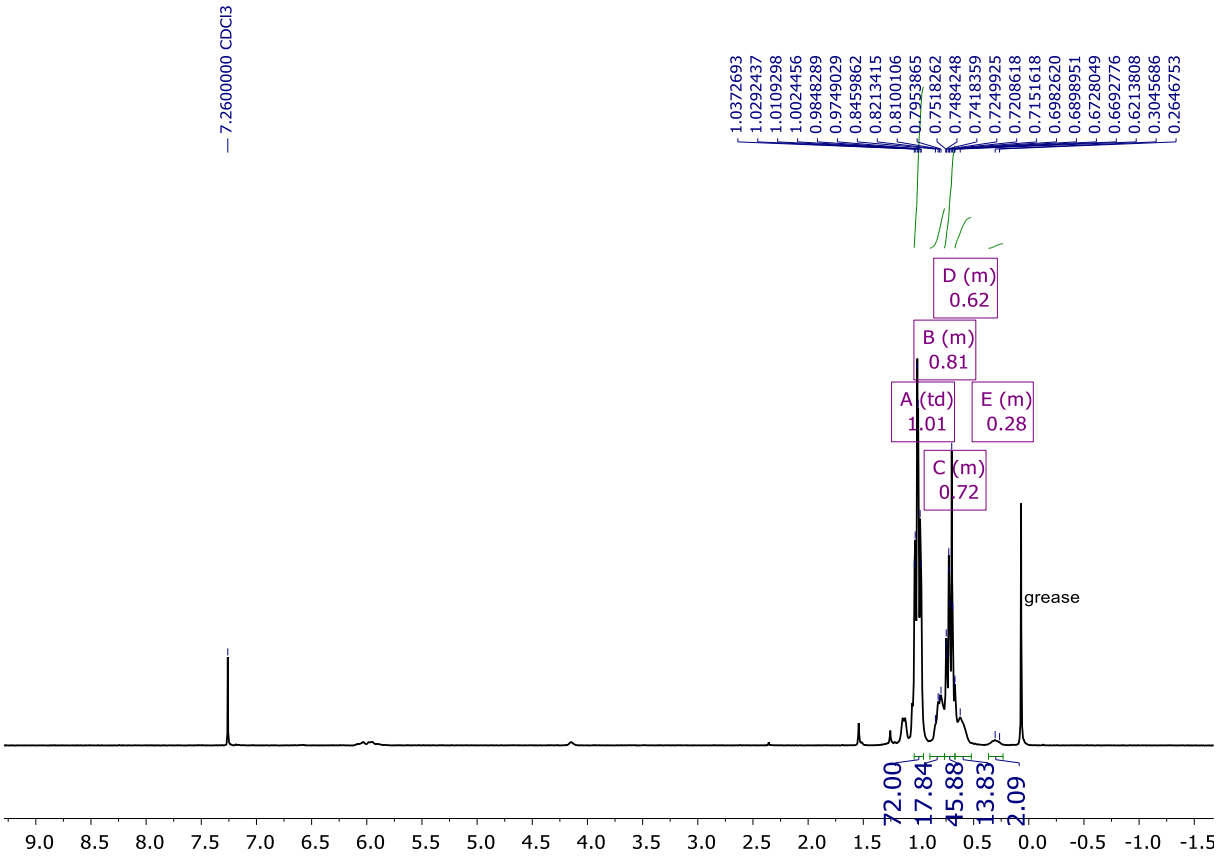
^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.01 (td, *J* = 8.1, 2.7 Hz, 72H), 0.90 – 0.76 (m, 18H), 0.76 – 0.66 (m, 48H), 0.66 – 0.52 (m, 14H), 0.42 – 0.18 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 9.19, 9.11, 5.48, 4.02, 3.59, 3.55, 1.17.

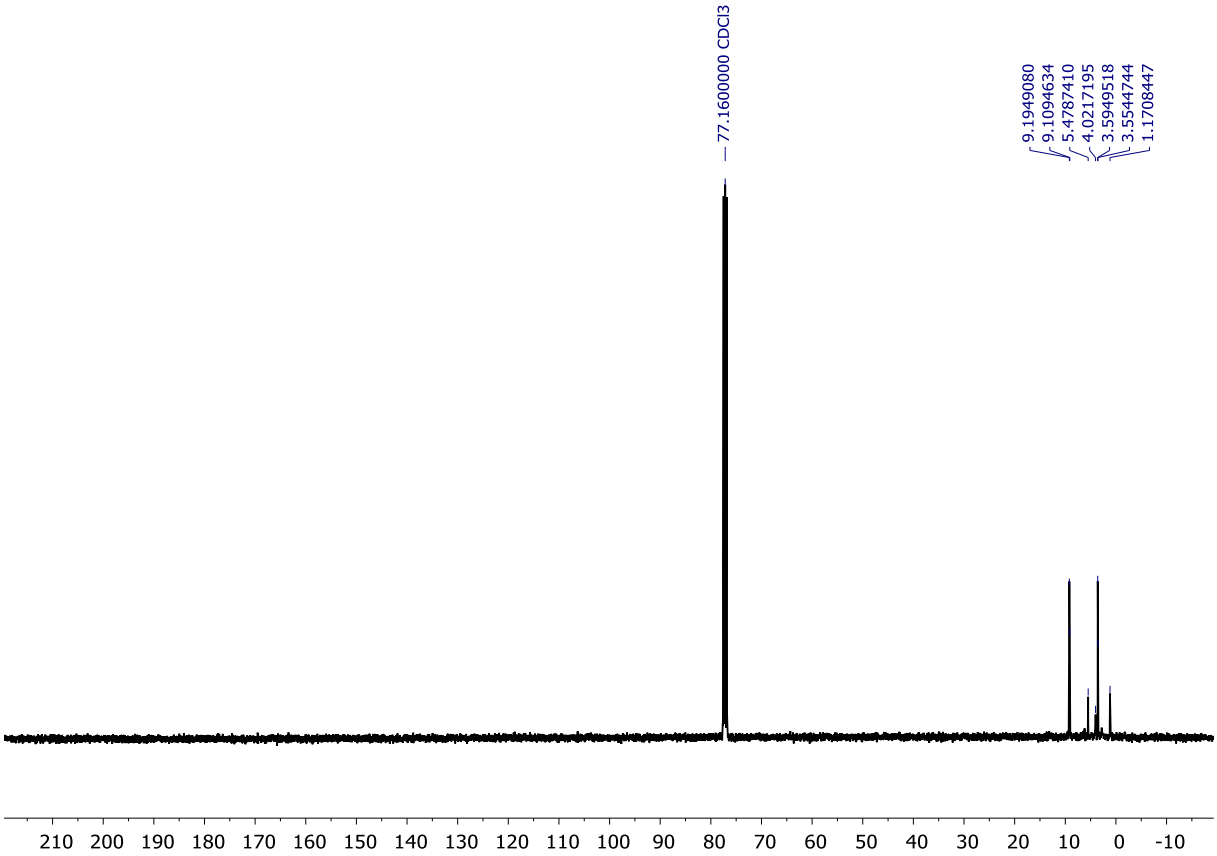
^{29}Si NMR (119 MHz, $CDCl_3$) δ -66.82.

HRMS (ESI): m/z calculated for $C_{64}H_{152}Ge_8O_{12}Si_8$ 1928,31; found 1929,09.

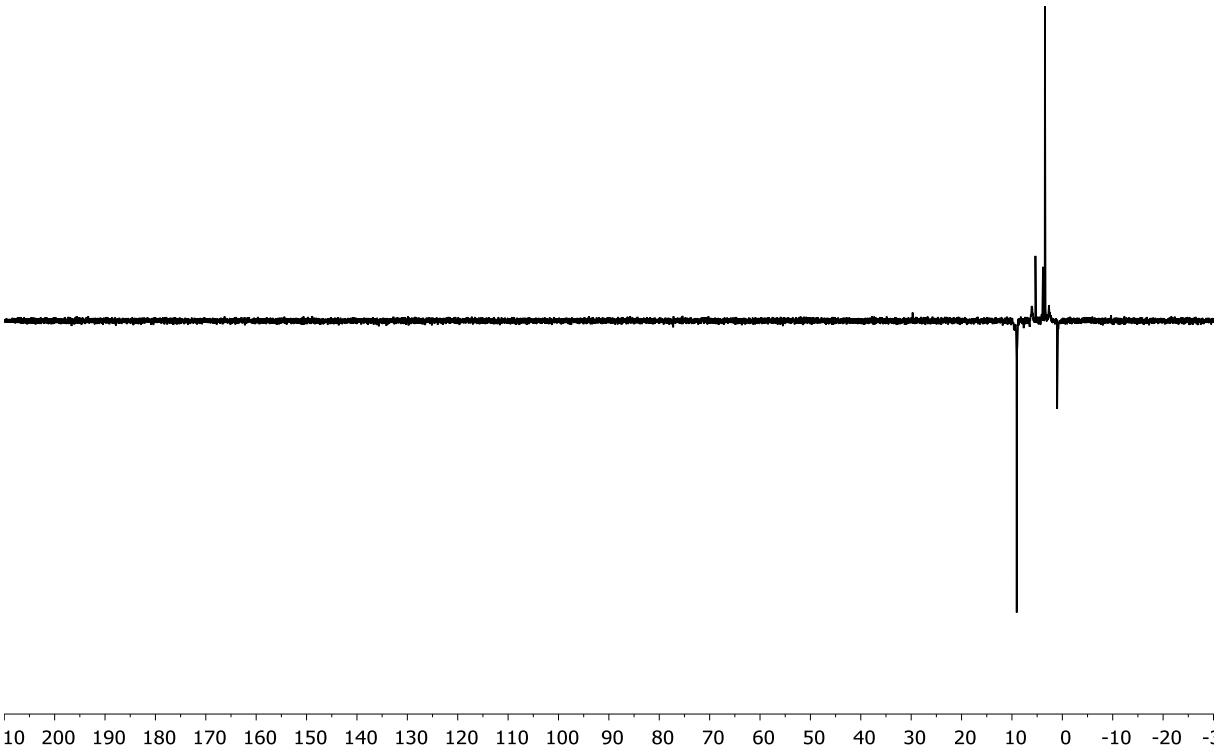
^{1}H NMR (300 MHz, $CDCl_3$)



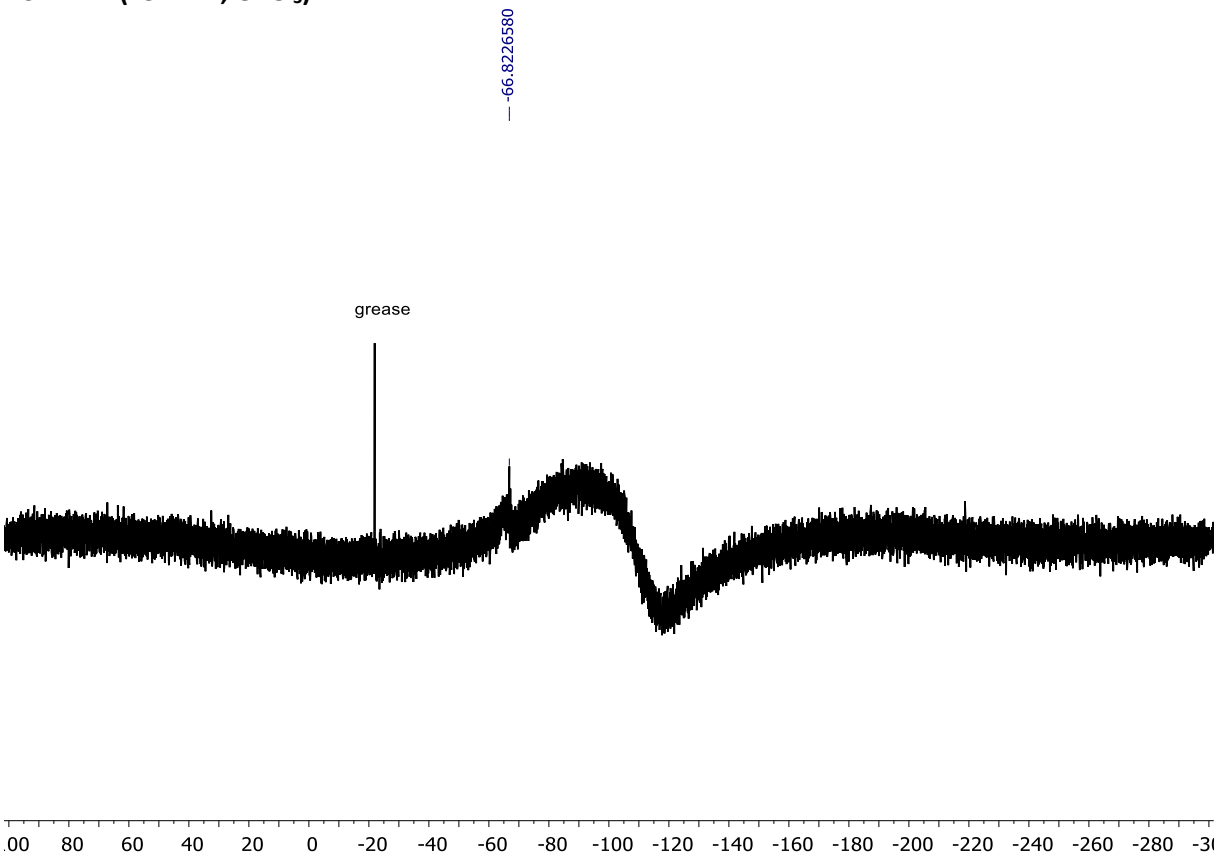
^{13}C NMR (101 MHz, $CDCl_3$)



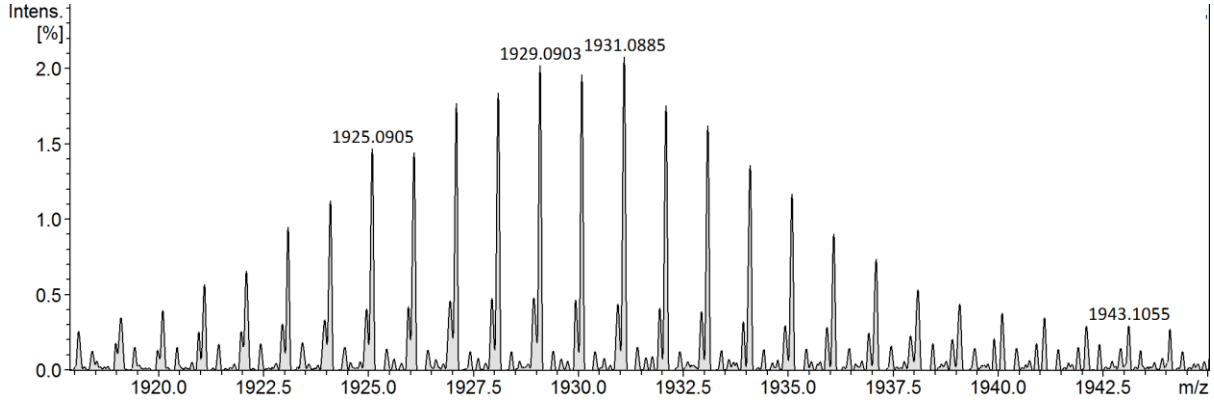
DEPT 135 NMR



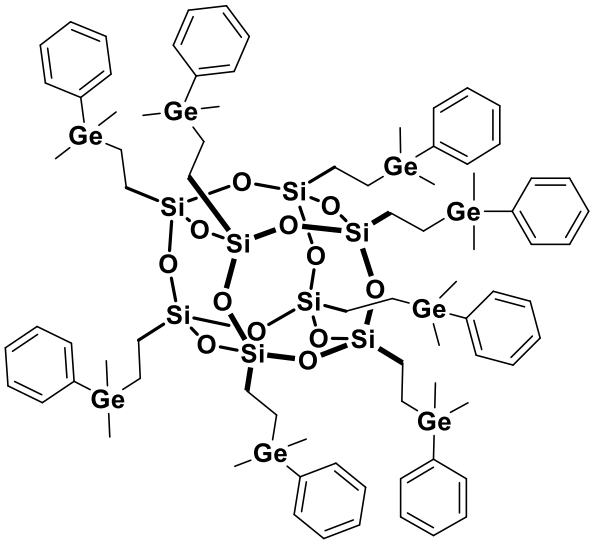
^{29}Si NMR (79 MHz, $CDCl_3$)



HRMS (ESI)



(5b)



Chemical Formula: $C_{80}H_{120}Ge_8O_{12}Si_8$

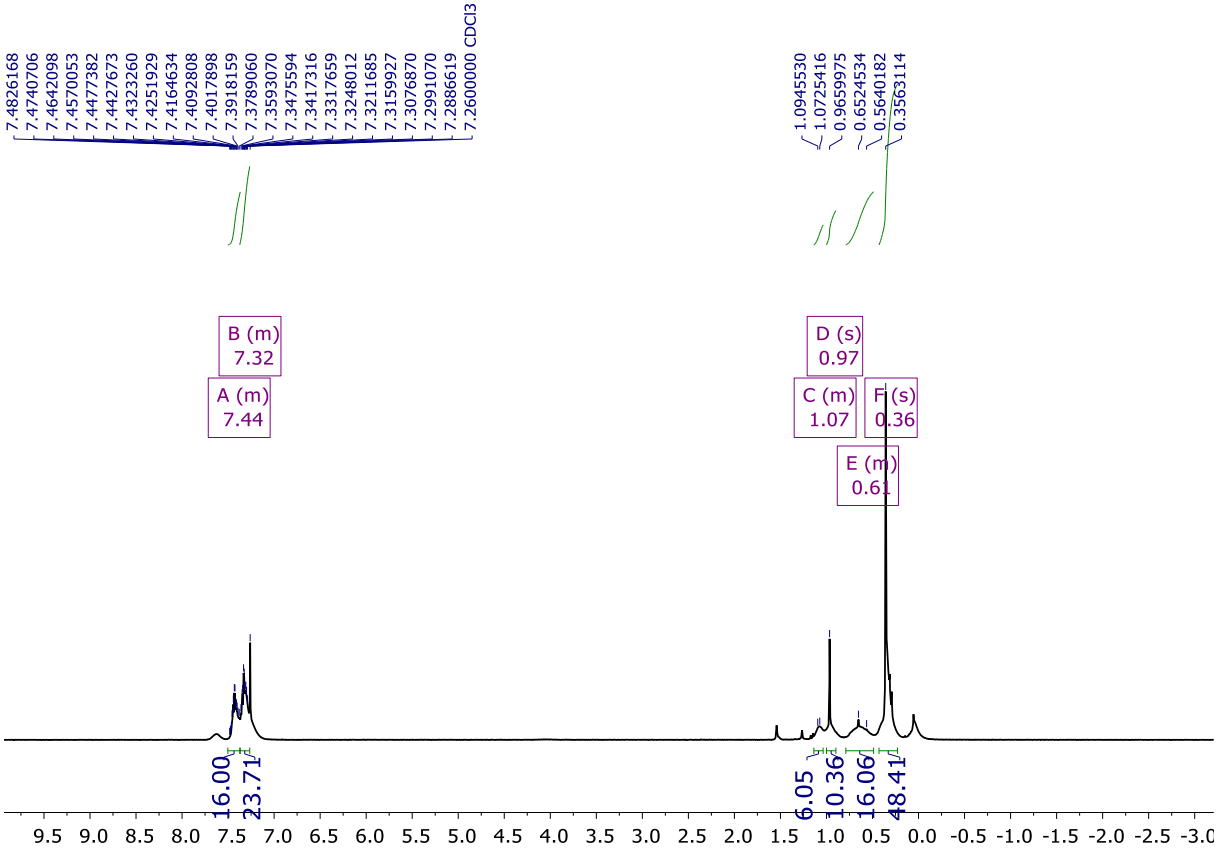
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 – 7.37 (m, 16H), 7.36 – 7.27 (m, 24H), 1.14 – 1.03 (m, 6H), 0.97 (s, 10H), 0.80 – 0.48 (m, 16H), 0.36 (s, 48H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.73, 134.27, 133.46, 133.39, 128.37, 128.05, 127.97, 10.21, -4.23.

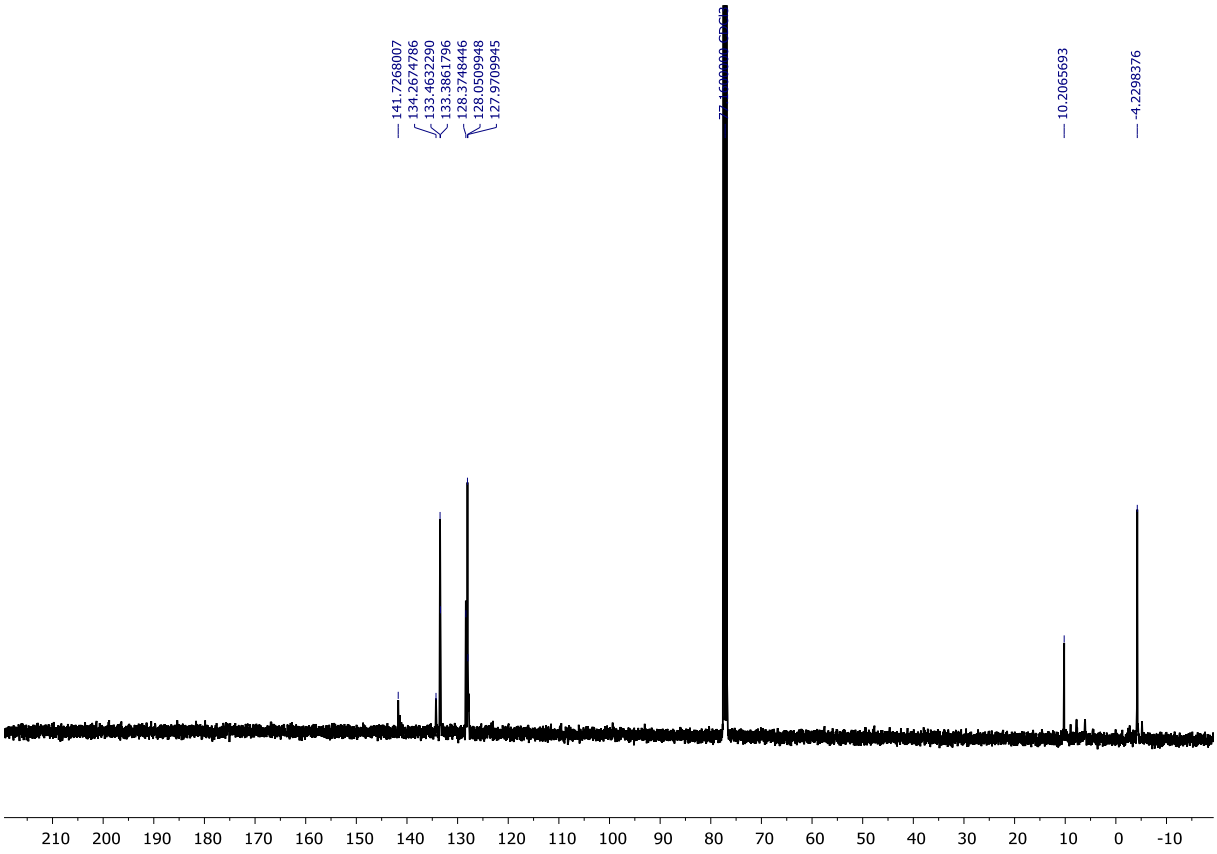
^{29}Si NMR (119 MHz, $CDCl_3$) δ -66.64.

HRMS (ESI): m/z calculated for $C_{80}H_{120}Ge_8O_{12}Si_8$ 2088,06; found 2093.

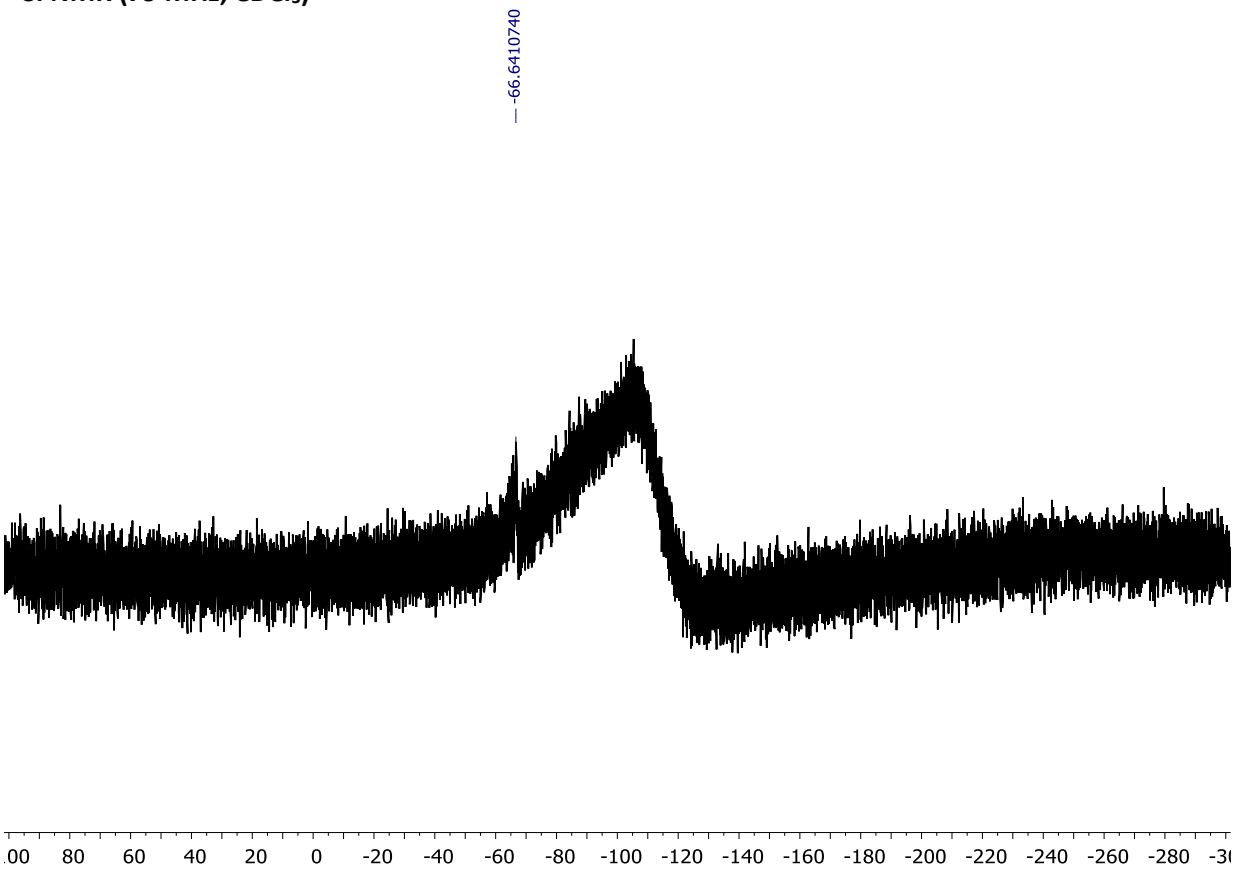
^{1}H NMR (300 MHz, $CDCl_3$)



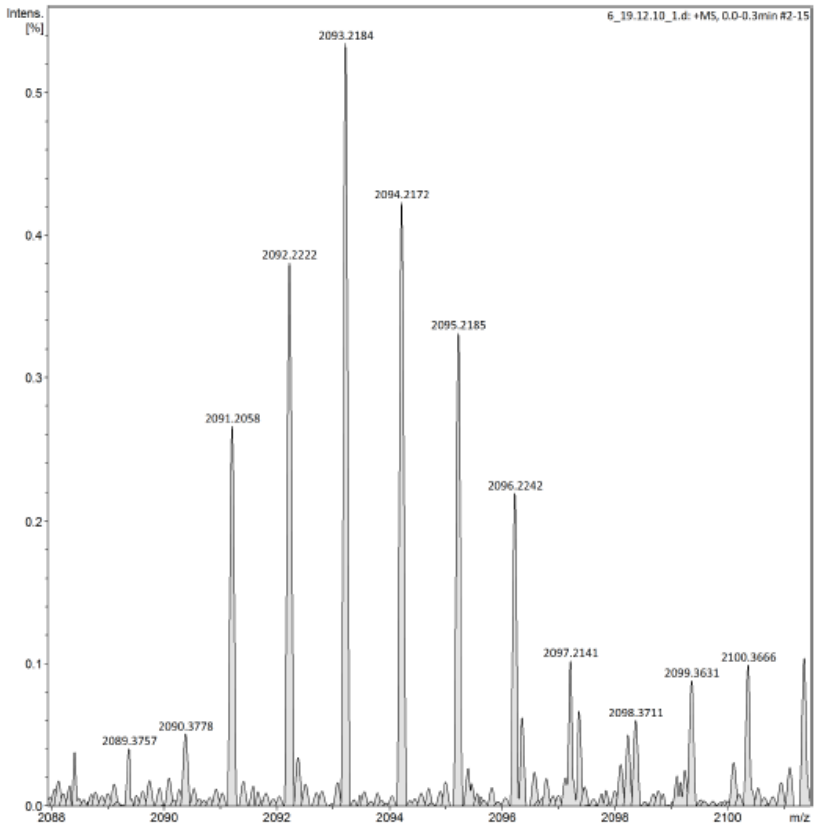
^{13}C NMR (101 MHz, $CDCl_3$)



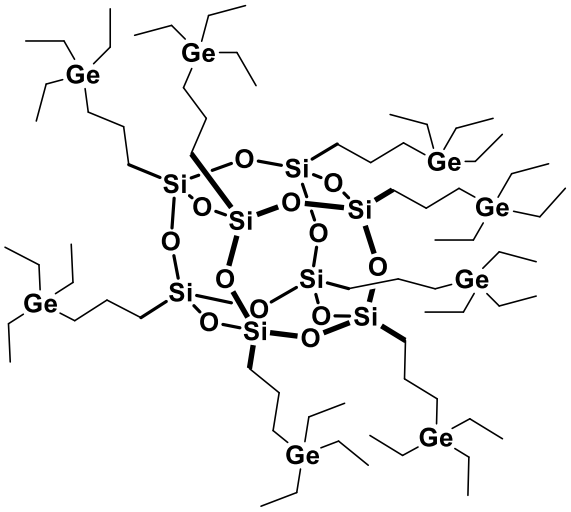
^{29}Si NMR (79 MHz, $CDCl_3$)



HRMS (ESI)


6_19.12.10_1.d: +MS, 0.0-0.3min #2-15
Intens.
[%]
0.5
0.4
0.3
0.2
0.1
0.0
2093.2184
2094.2172
2092.2222
2095.2185
2091.2058
2096.2242
2097.2141
2100.3666
2099.3631
2098.3711
2090.3778
2089.3757
2088
2090
2092
2094
2096
2098
2100
m/z

(5c)



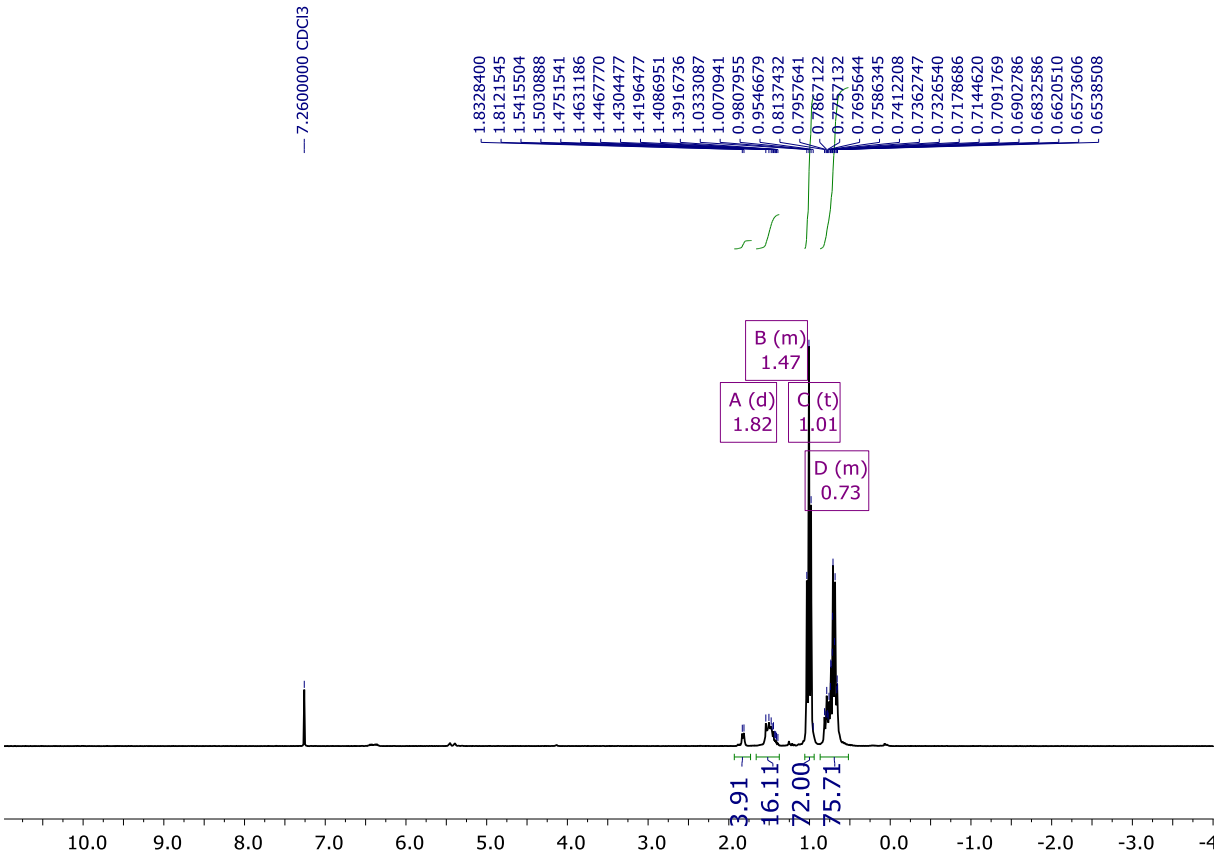
Chemical Formula: $C_{72}H_{168}Ge_8O_{12}Si_8$

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.82 (d, *J* = 6.2 Hz, 4H), 1.65 – 1.37 (m, 16H), 1.01 (t, *J* = 7.9 Hz, 72H), 0.87 – 0.59 (m, 76H).

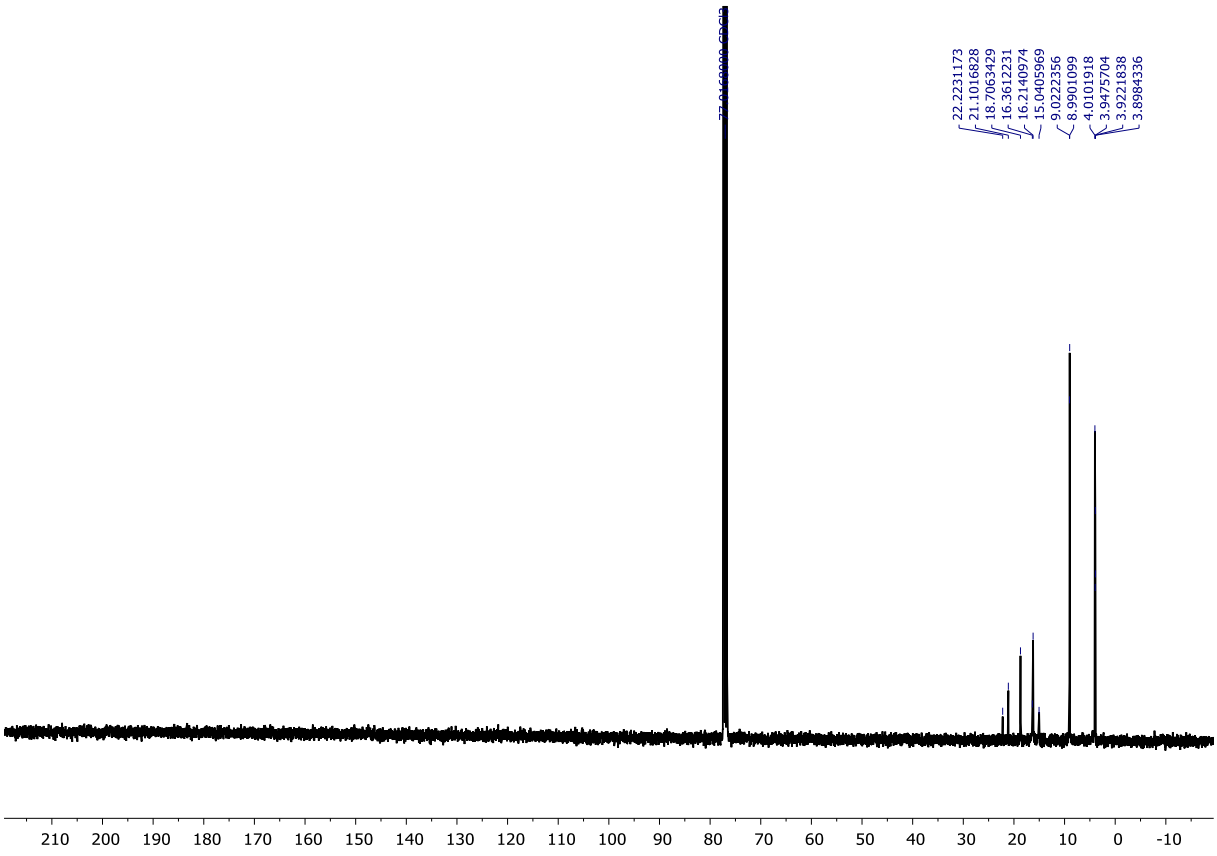
^{13}C NMR (101 MHz, $CDCl_3$) δ 22.22, 21.10, 18.71, 16.36, 16.21, 15.04, 9.02, 8.99, 4.01, 3.95, 3.92, 3.90.

^{29}Si NMR (79 MHz, $CDCl_3$) δ -67.11, -67.35.

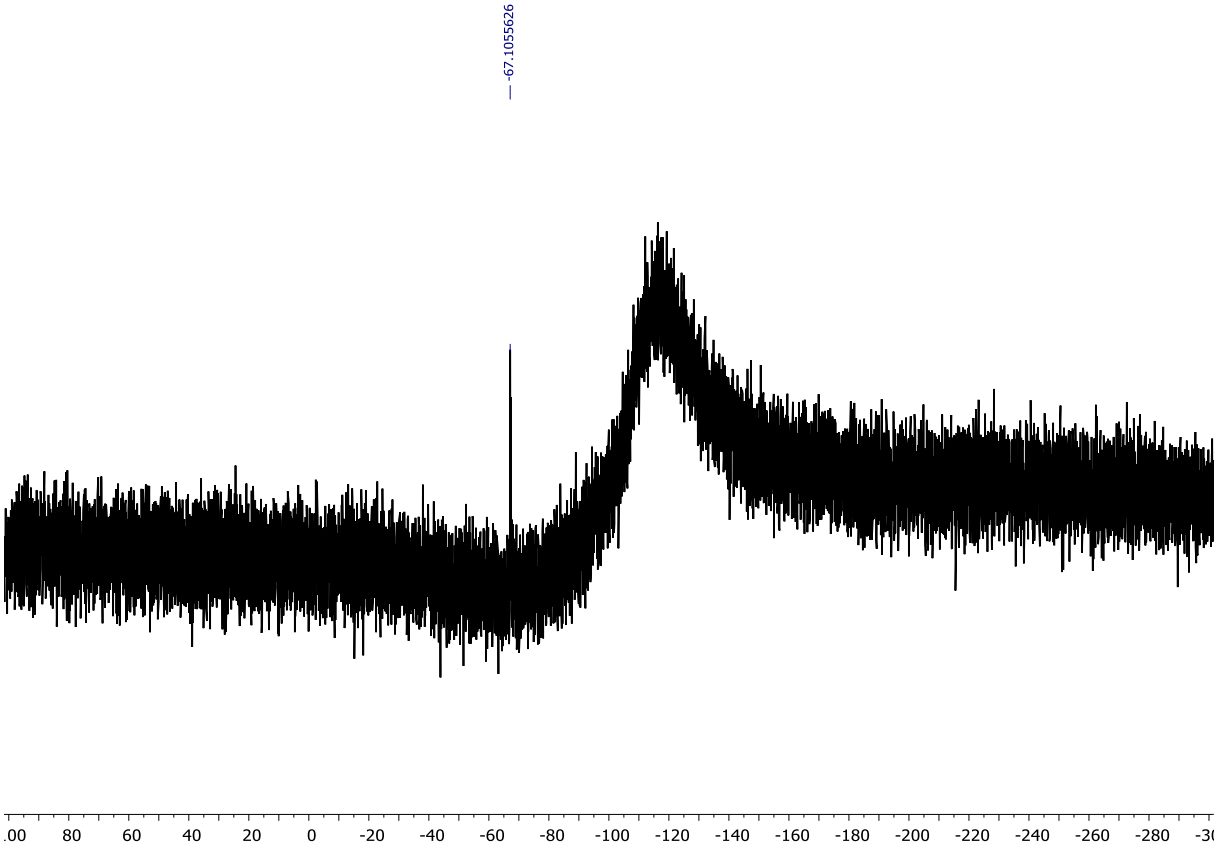
^{1}H NMR (300 MHz, $CDCl_3$)



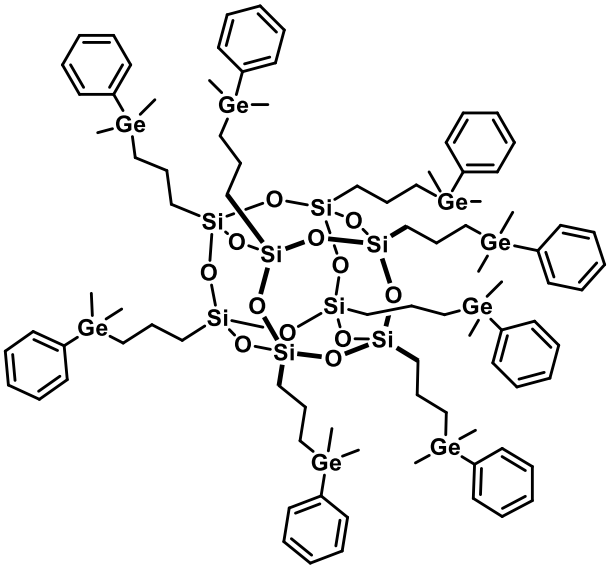
^{13}C NMR (101 MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)



(5d)



Chemical Formula: $C_{88}H_{136}Ge_8O_{12}Si_8$

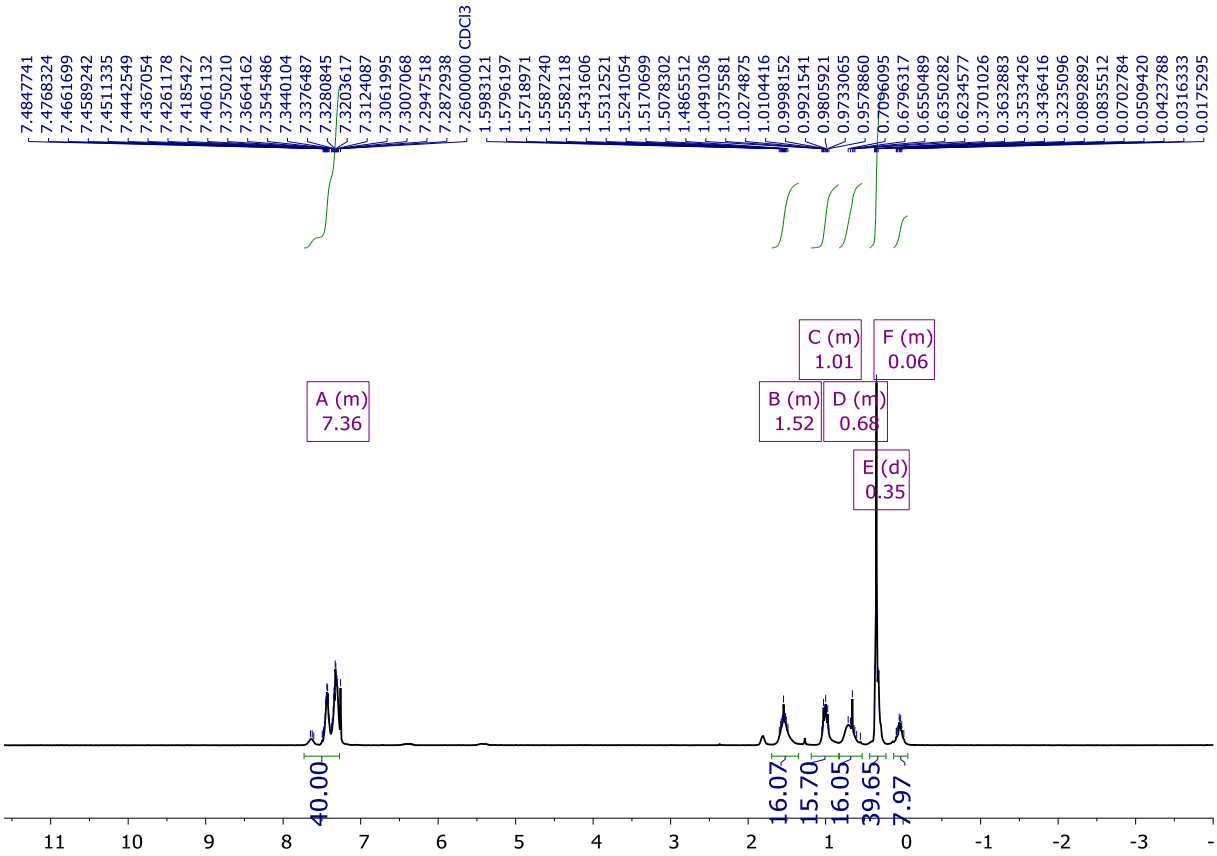
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.75 – 7.27 (m, 40H), 1.68 – 1.32 (m, 16H), 1.13 – 0.84 (m, 16H), 0.82 – 0.53 (m, 16H), 0.35 (d, *J* = 2.9 Hz, 40H), 0.15 – -0.05 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.06, 134.15, 133.78, 133.35, 133.32, 128.71, 128.31, 128.21, 128.04, 127.86, 20.91, 20.12, 19.53, 18.71, 16.08, -3.45.

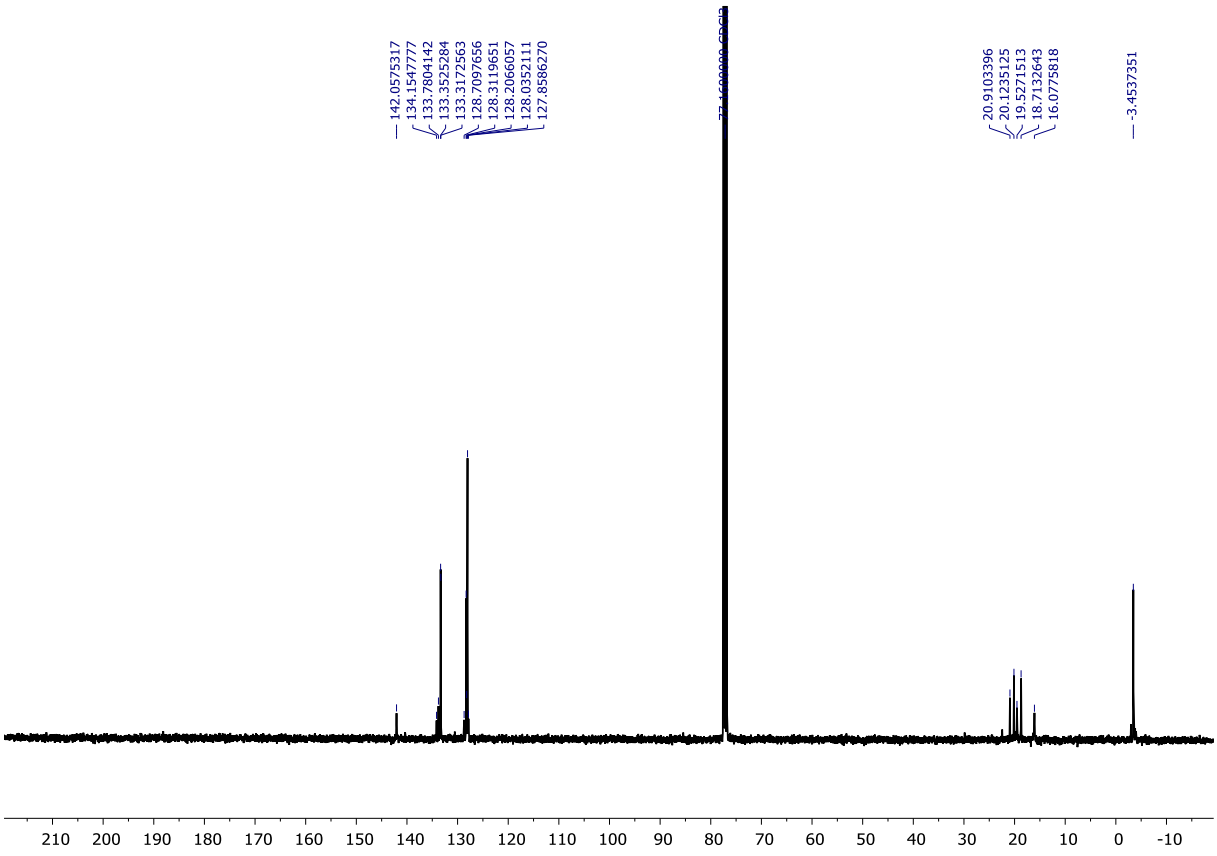
^{29}Si NMR (79 MHz, $CDCl_3$) δ -67.22.

HRMS (ESI): m/z calculated for$C_{88}H_{136}Ge_8O_{12}Si_8K$ 2239,15, found 2239,64.

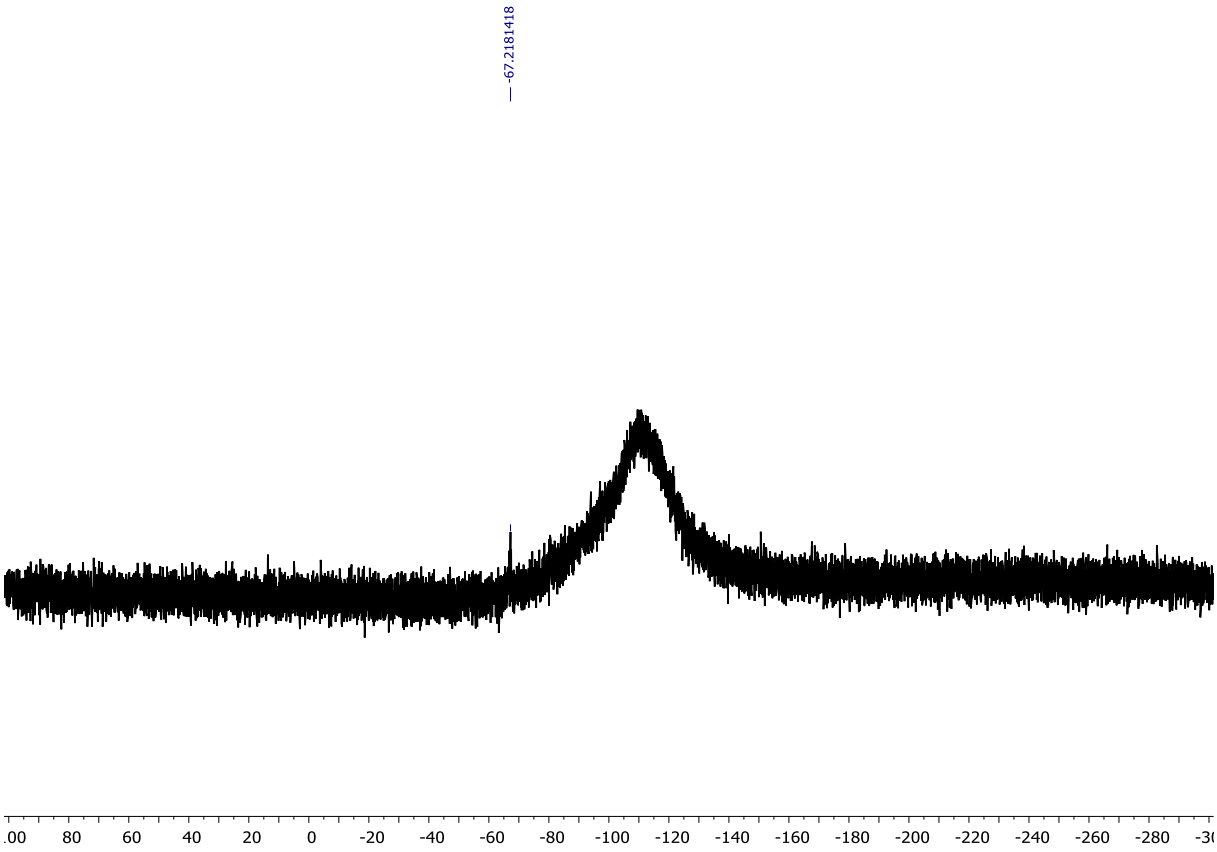
^{1}H NMR (300 MHz, $CDCl_3$)



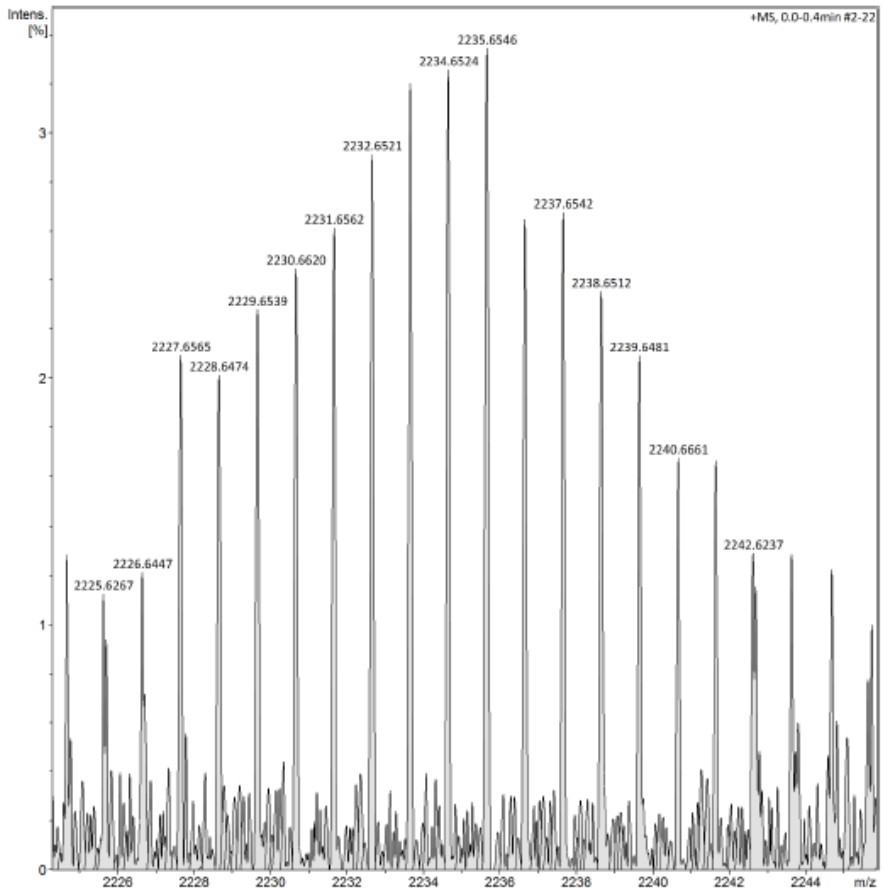
^{13}C NMR (101 MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)

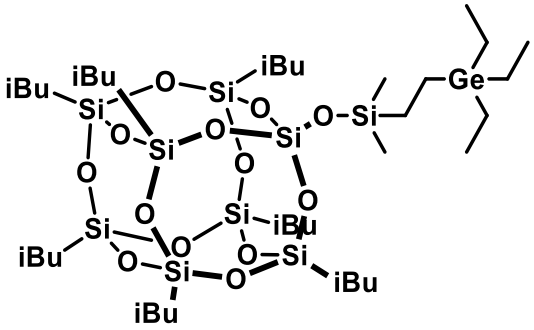


HRMS (ESI)


Intens.
[%]
+MS, 0.0-0.4min #2-22
3
2
1
0
2225.6267
2226.6447
2227.6565
2228.6474
2229.6539
2230.6620
2231.6562
2232.6521
2234.6524
2235.6546
2237.6542
2238.6512
2239.6481
2240.6661
2242.6237
2226
2228
2230
2232
2234
2236
2238
2240
2242
2244
m/z

(6a-d)

(6a)



Chemical Formula: $C_{38}H_{88}GeO_{13}Si_9$

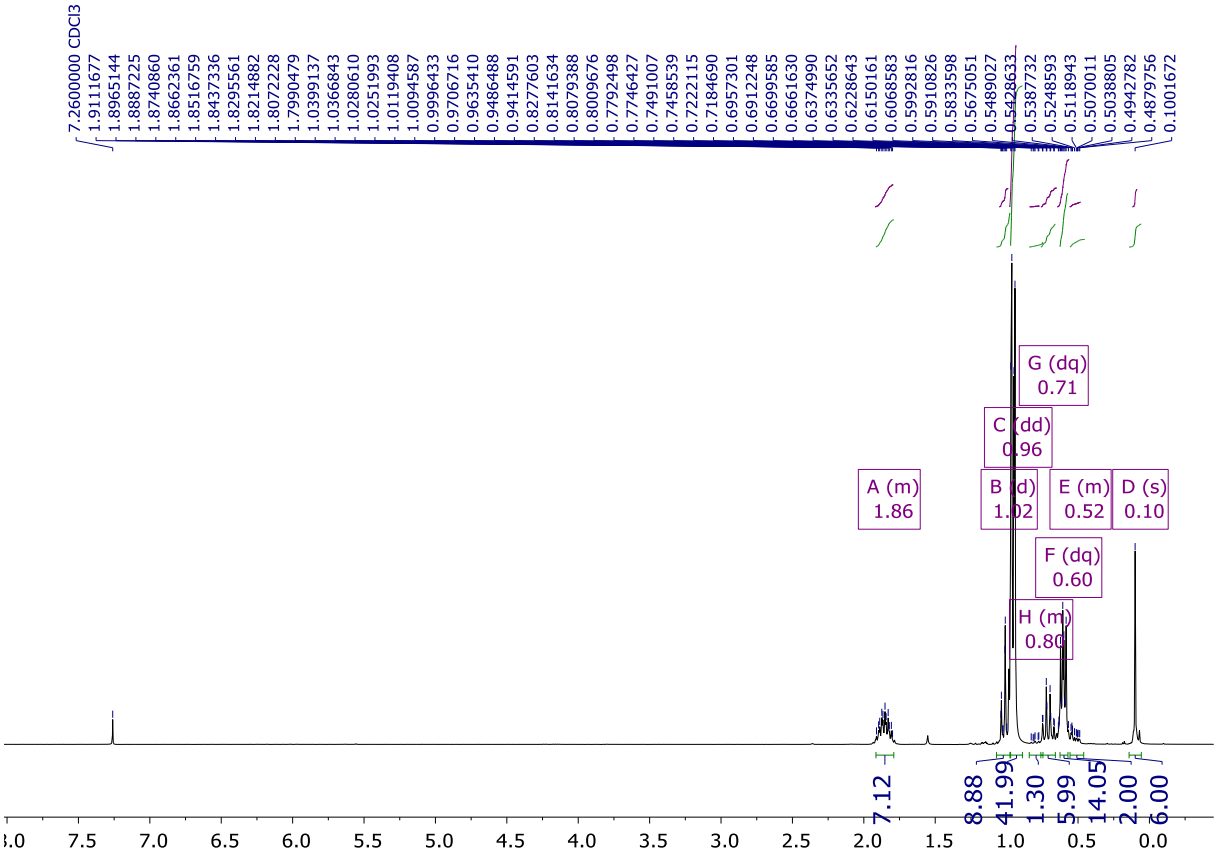
^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.92 – 1.80 (m, 7H), 1.02 (d, 9H), 0.96 (dd, *J* = 6.6, 2.1 Hz, 42H), 0.84 – 0.77 (m, 2H), 0.71 (dq, *J* = 7.8, 1.1 Hz, 6H), 0.60 (dq, *J* = 7.1, 4.8, 4.0 Hz, 14H), 0.56 – 0.48 (m, 2H), 0.10 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 25.85, 24.00, 22.58, 22.54, 11.50, 9.19, 3.56, 2.65, -0.89.

^{29}Si NMR (79 MHz, $CDCl_3$) δ 11.35, -67.09, -67.88, -109.58.

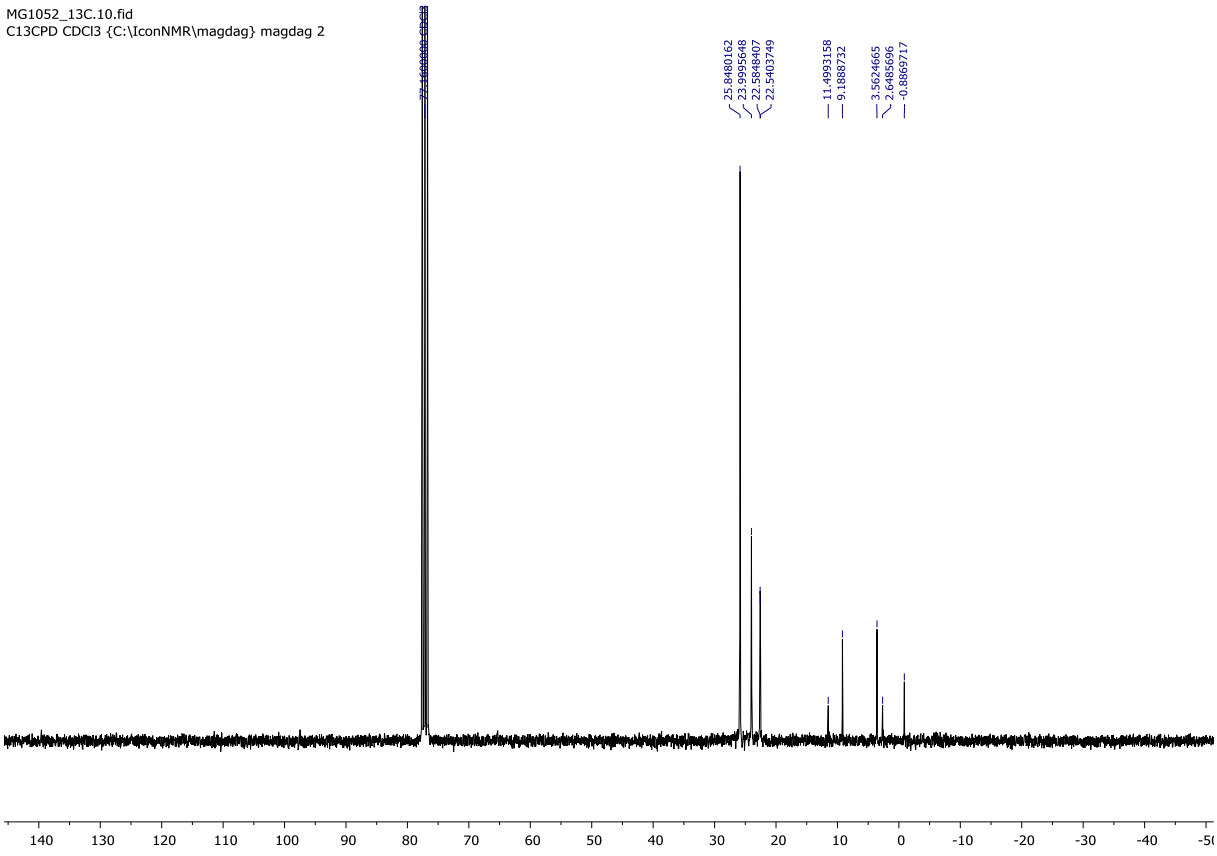
MALDI-TOF MS (m/z): calcd. for $C_{38}H_{88}GeO_{13}Si_9Na$ 1101,33; found 1101,33.

^{1}H NMR (300 MHz, $CDCl_3$)



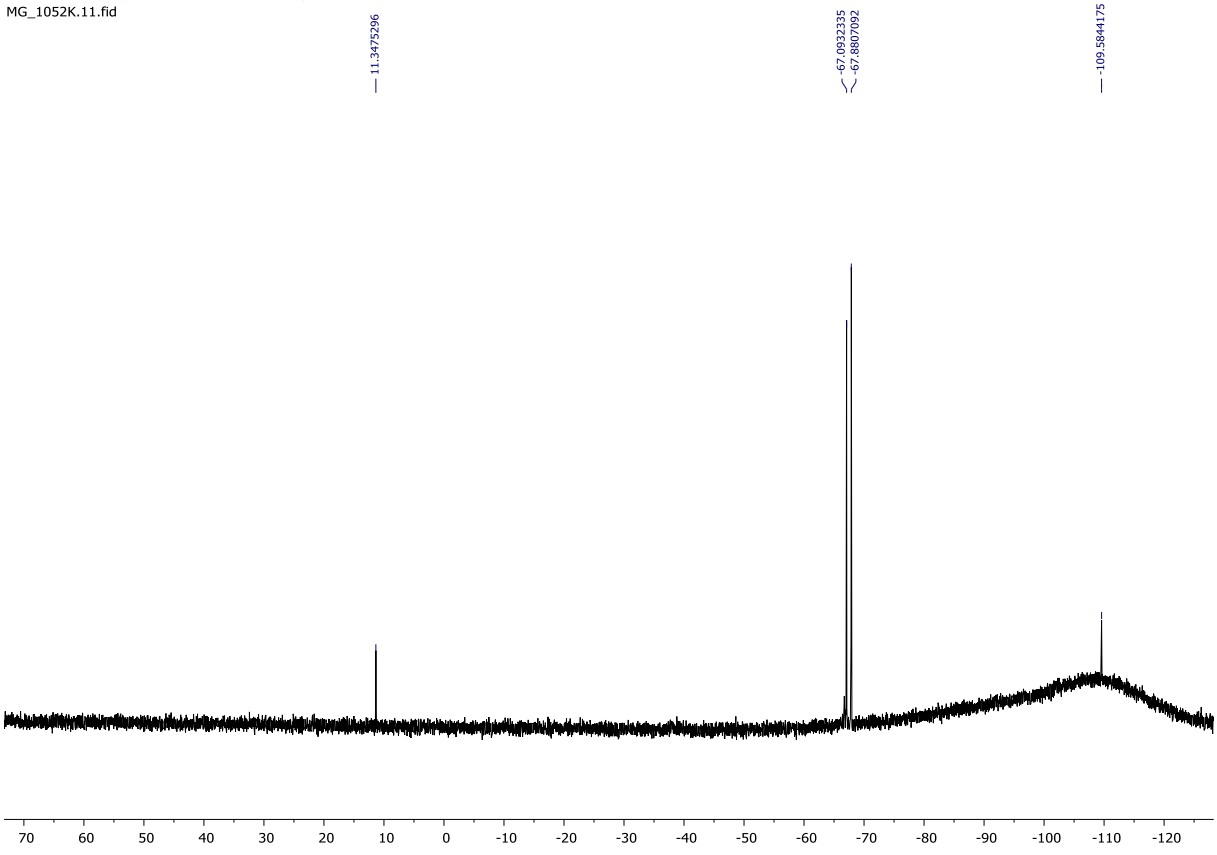
^{13}C NMR (101 MHz, $CDCl_3$)

MG1052_13C.10.fid
C13CPD CDCl3 {C:\IconNMR\magdag} magdag 2

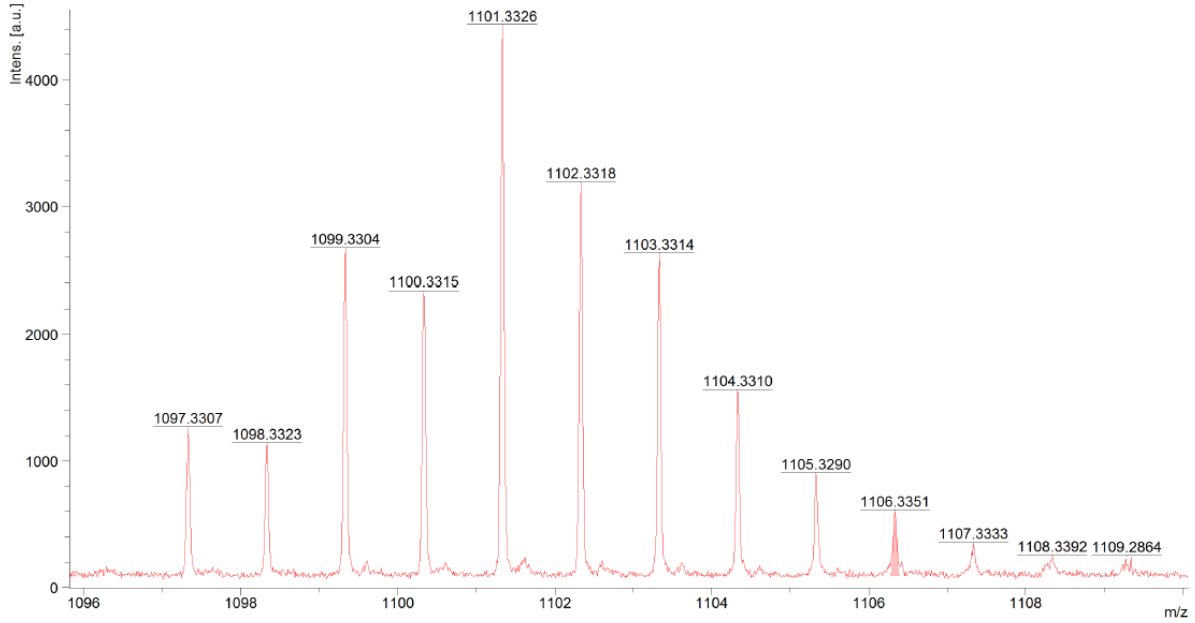


^{29}Si NMR (79 MHz, $CDCl_3$)

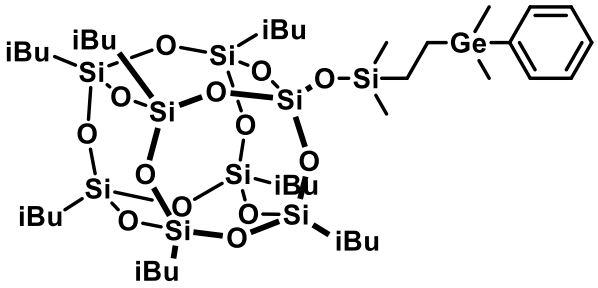
MG_1052K.11.fid



MALDI-TOF


Intens. [a.u.]
4000
3000
2000
1000
0
1101.3326
1102.3318
1099.3304
1103.3314
1100.3315
1104.3310
1097.3307
1098.3323
1105.3290
1106.3351
1107.3333
1108.3392
1109.2864
1096
1098
1100
1102
1104
1106
1108
m/z

(6b)



Chemical Formula: $C_{40}H_{84}GeO_{13}Si_9$

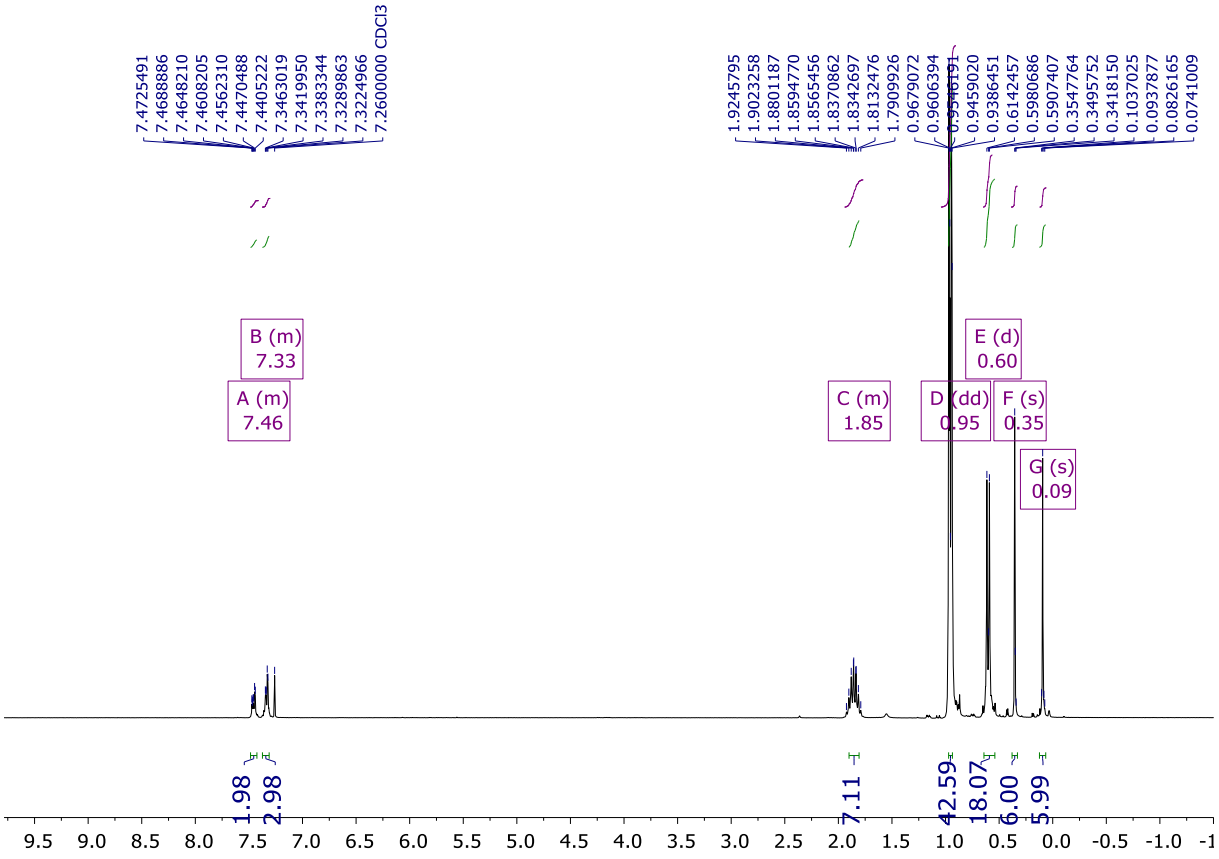
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.48 – 7.42 (m, 2H), 7.33 (m, 3H), 1.94 – 1.77 (m, 7H), 0.95 (dd, *J* = 6.6, 2.2 Hz, 42H), 0.60 (d, *J* = 7.1 Hz, 18H), 0.35 (s, 6H), 0.09 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.84, 133.45, 128.33, 128.04, 25.85, 23.99, 22.58, 11.39, 7.64, -0.82, -4.24.

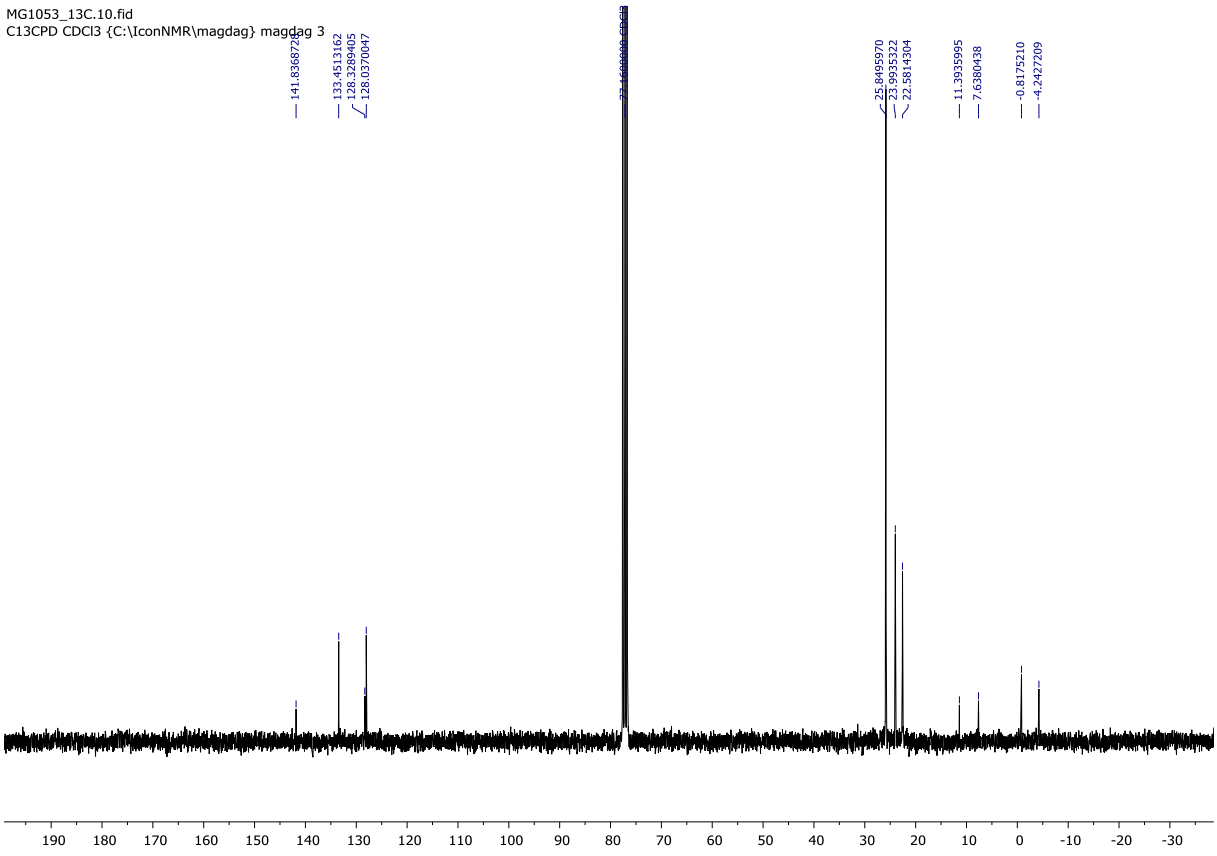
^{29}Si NMR (79 MHz, $CDCl_3$) δ 11.40, -67.07, -67.87, -109.60.

MALDI-TOF MS (m/z): calcd. for $C_{40}H_{84}GeO_{13}Si_9Na$ 1121,29; found 1121,30.

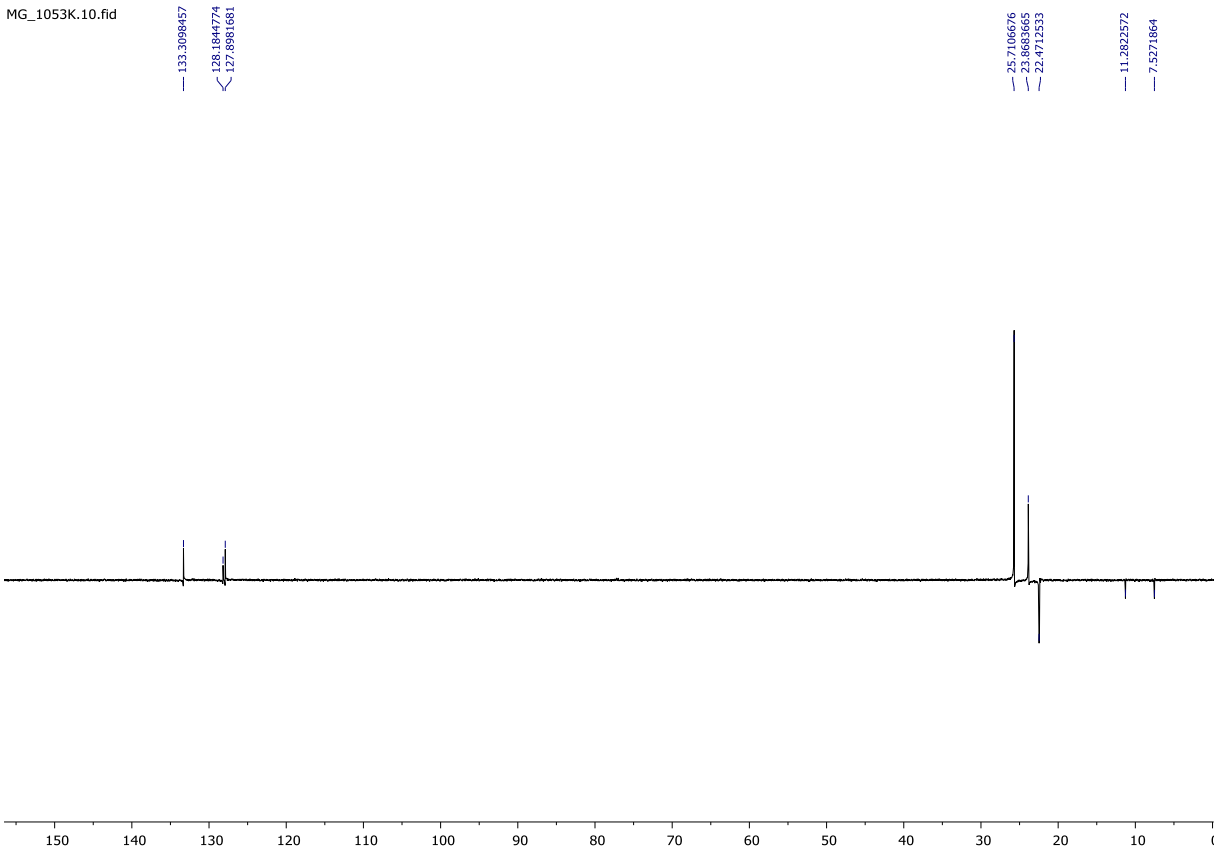
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

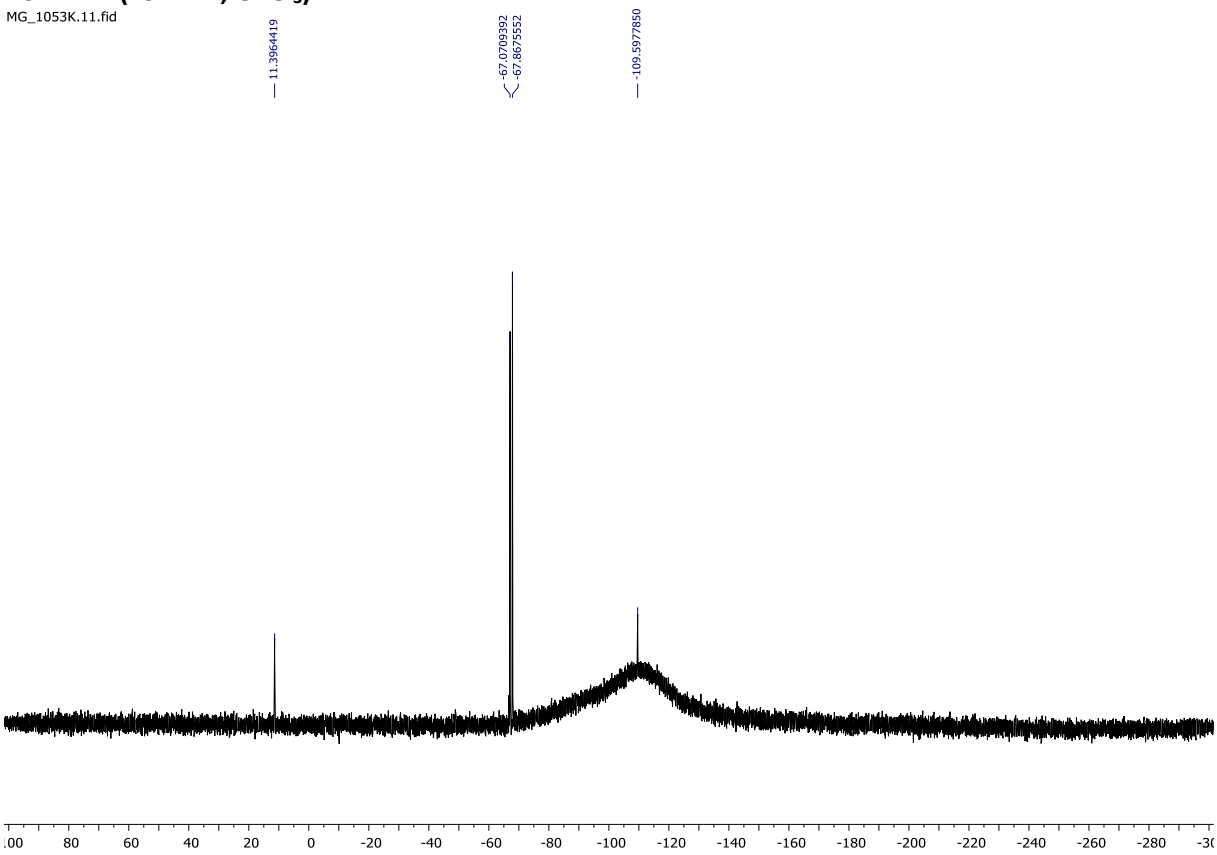


DEPT 135 NMR

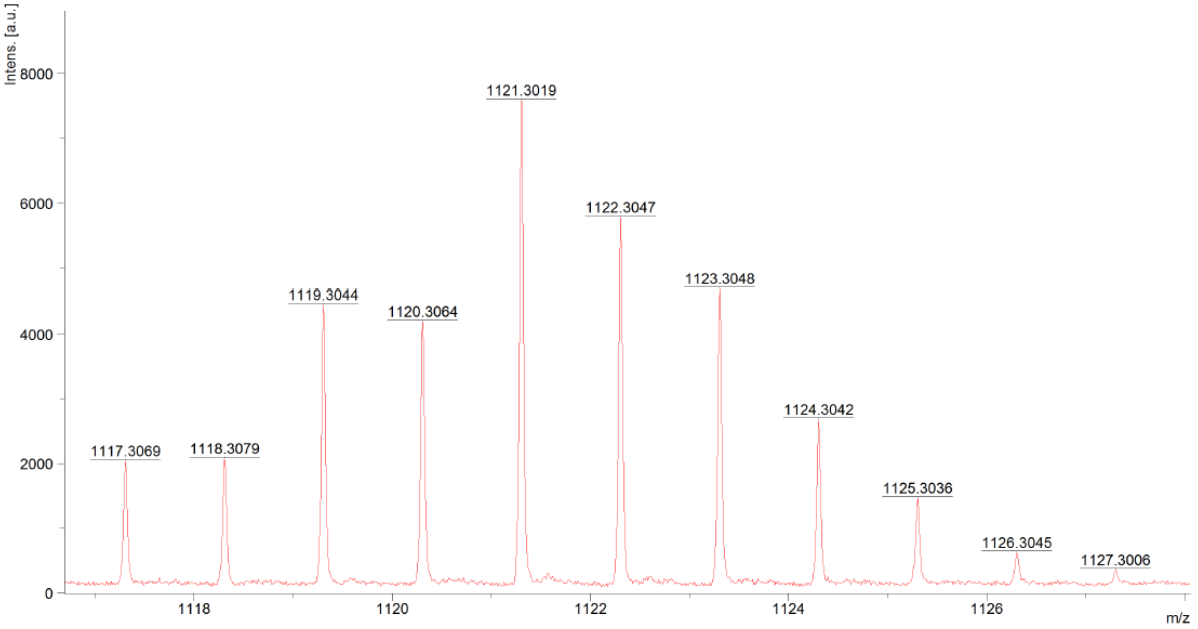


^{29}Si NMR (79 MHz, $CDCl_3$)

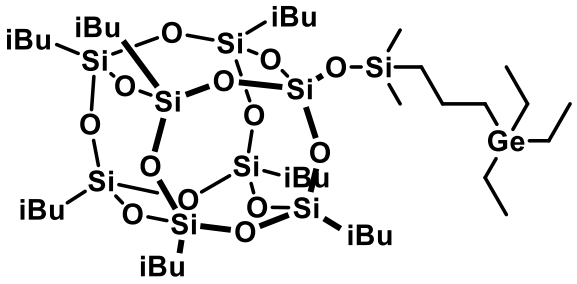
MG_1053K.11.fid



MALDI-TOF



(6c)



Chemical Formula: $C_{39}H_{90}GeO_{13}Si_9$

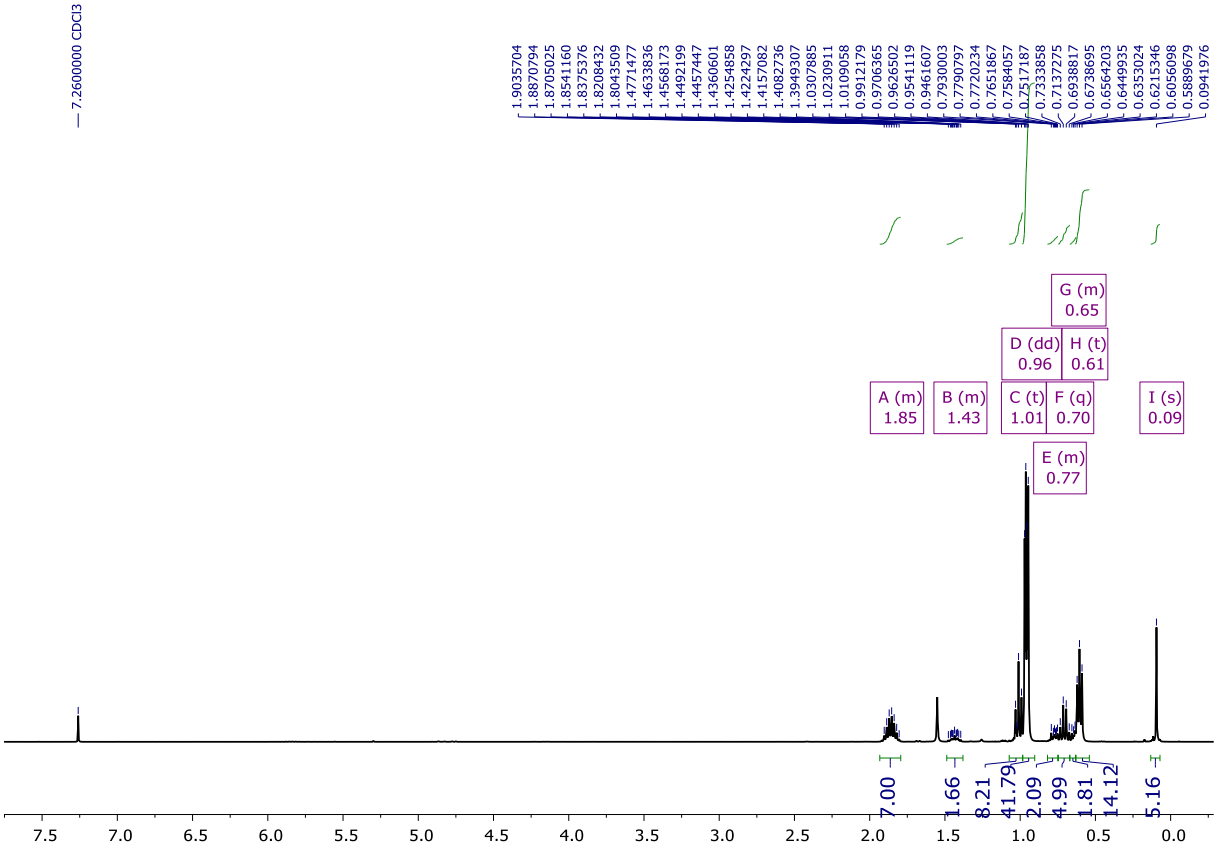
^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.93 – 1.79 (m, 7H), 1.48 – 1.39 (m, 2H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.96 (dd, *J* = 6.6, 3.2 Hz, 42H), 0.81 – 0.75 (m, 2H), 0.70 (q, *J* = 7.9 Hz, 6H), 0.66 – 0.63 (m, 2H), 0.61 (t, *J* = 6.5 Hz, 14H), 0.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 25.84, 24.01, 23.98, 22.62, 22.56, 19.00, 16.08, 9.17, 4.10, -0.04.

^{29}Si NMR (79 MHz, $CDCl_3$) δ 10.76, -67.09, -67.88, -109.69.

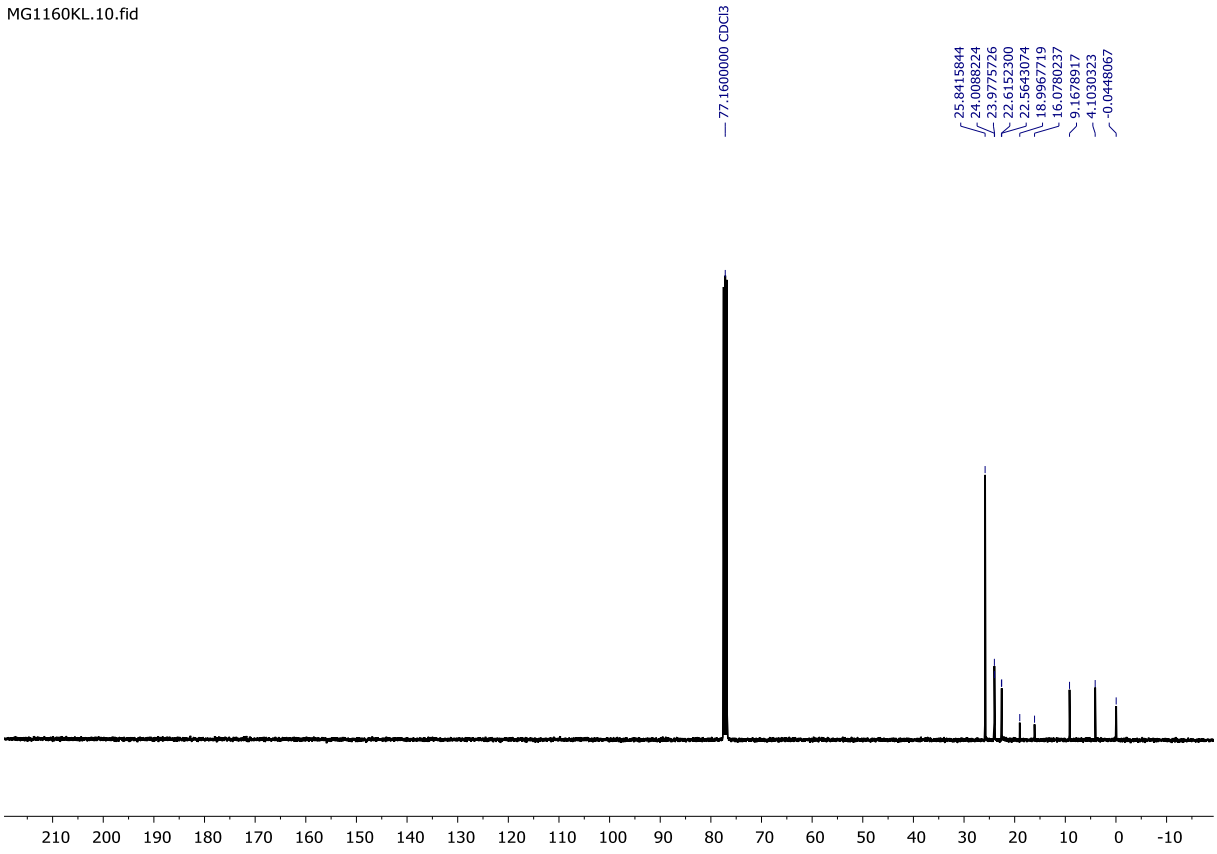
MALDI-TOF MS (m/z): calcd. $C_{39}H_{90}GeO_{13}Si_9Na$ 1115,34; found 1115,34.

^{1}H NMR (400 MHz, $CDCl_3$)



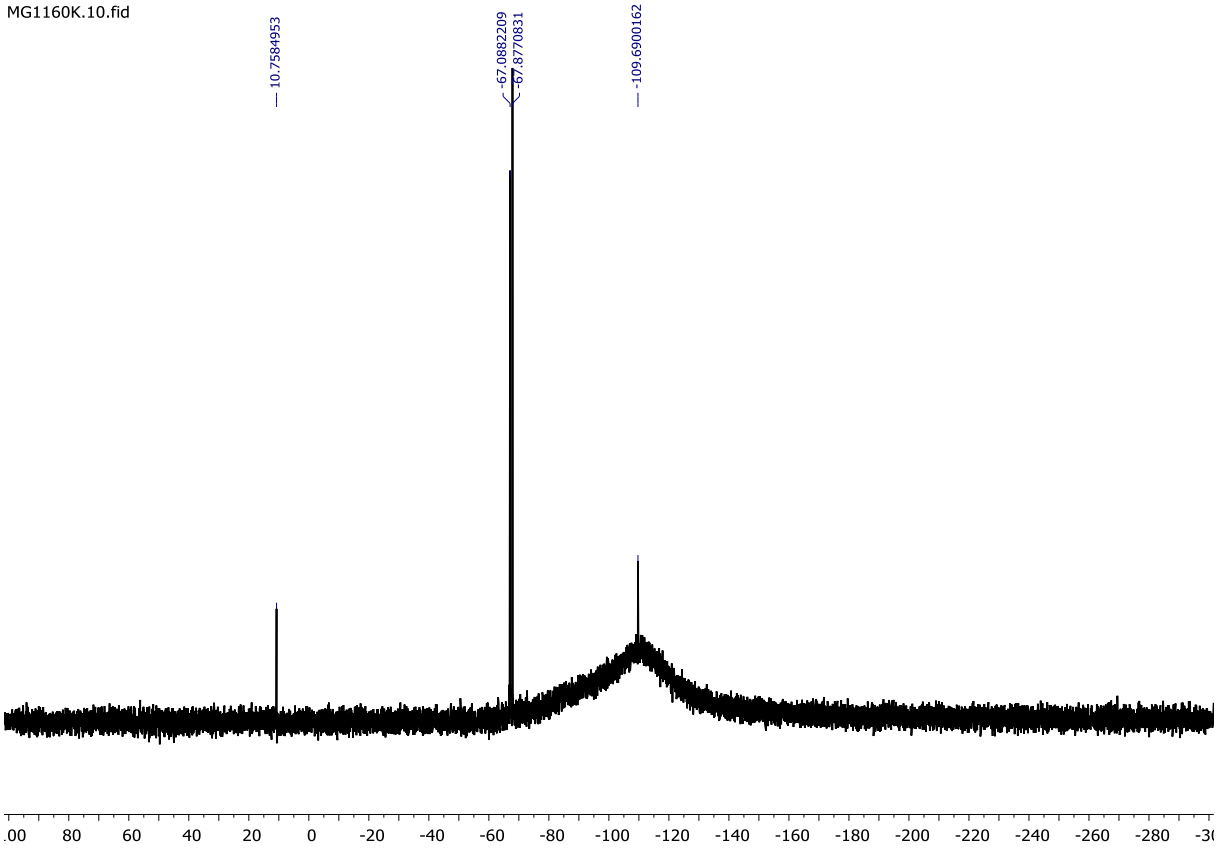
^{13}C NMR (101 MHz, $CDCl_3$)

MG1160KL.10.fid

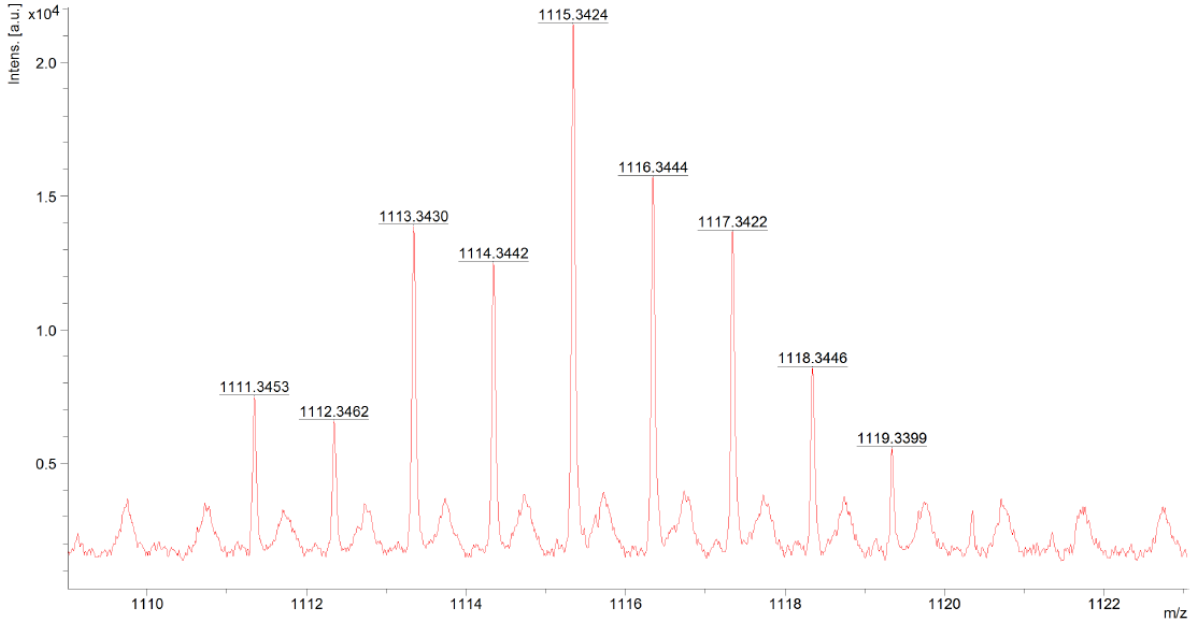


^{29}Si NMR (79 MHz, $CDCl_3$)

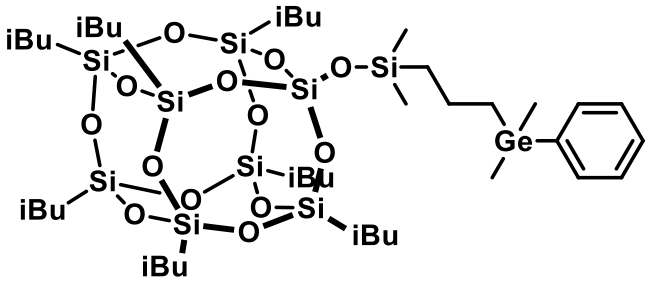
MG1160K.10.fid



MALDI-TOF


Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
1111.3453
1112.3462
1113.3430
1114.3442
1115.3424
1116.3444
1117.3422
1118.3446
1119.3399
1110
1112
1114
1116
1118
1120
1122
m/z

(6d)



Chemical Formula: $C_{41}H_{86}GeO_{13}Si_9$

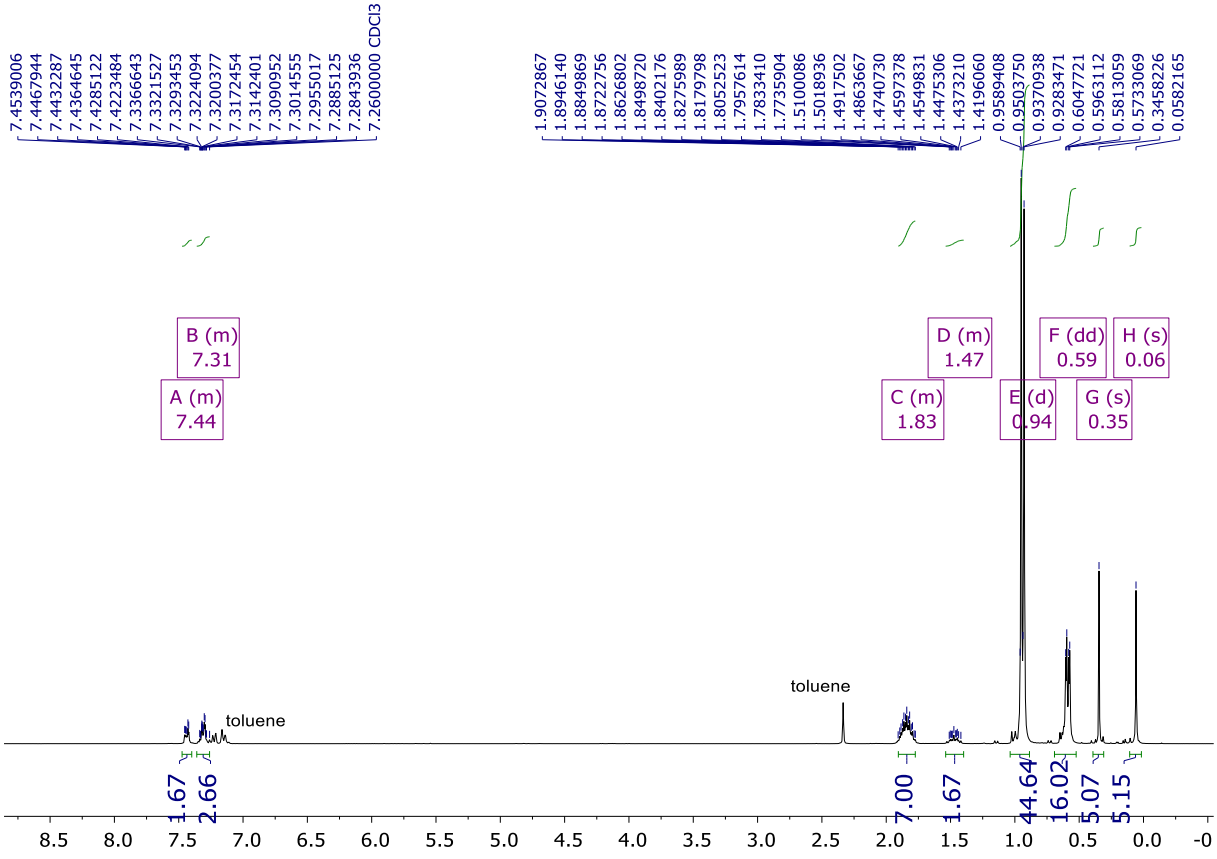
^{1}H NMR (300 MHz, Chloroform-d) δ 7.46 – 7.41 (m, 2H), 7.35 – 7.27 (m, 3H), 1.91 – 1.77 (m, 7H), 1.53 – 1.41 (m, 2H), 0.94 (d, J = 6.6 Hz, 44H), 0.59 (dd, J = 7.0, 2.5 Hz, 16H), 0.35 (s, 6H), 0.06 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.21, 138.01, 133.36, 129.20, 128.40, 128.31, 128.06, 125.47, 25.87, 24.05, 24.01, 22.67, 22.62, 22.58, 22.09, 20.30, 18.87, -0.03, -0.05, -3.42, -3.45.

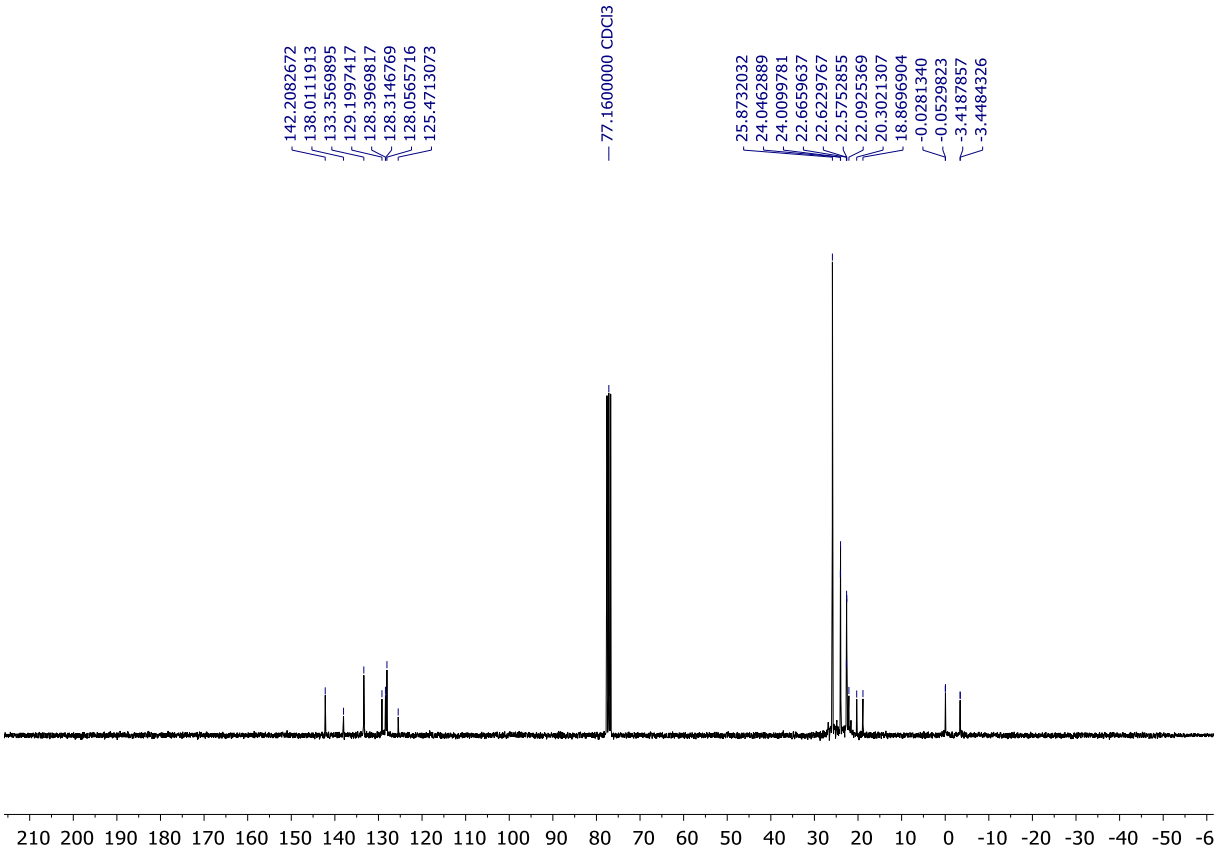
^{29}Si NMR (79 MHz, $CDCl_3$) δ 10.76, -67.05, -67.84, -109.63.

MALDI-TOF MS (m/z): calcd. for $C_{41}H_{86}GeO_{13}Si_9Na$ 1135,31; found 1135,31.

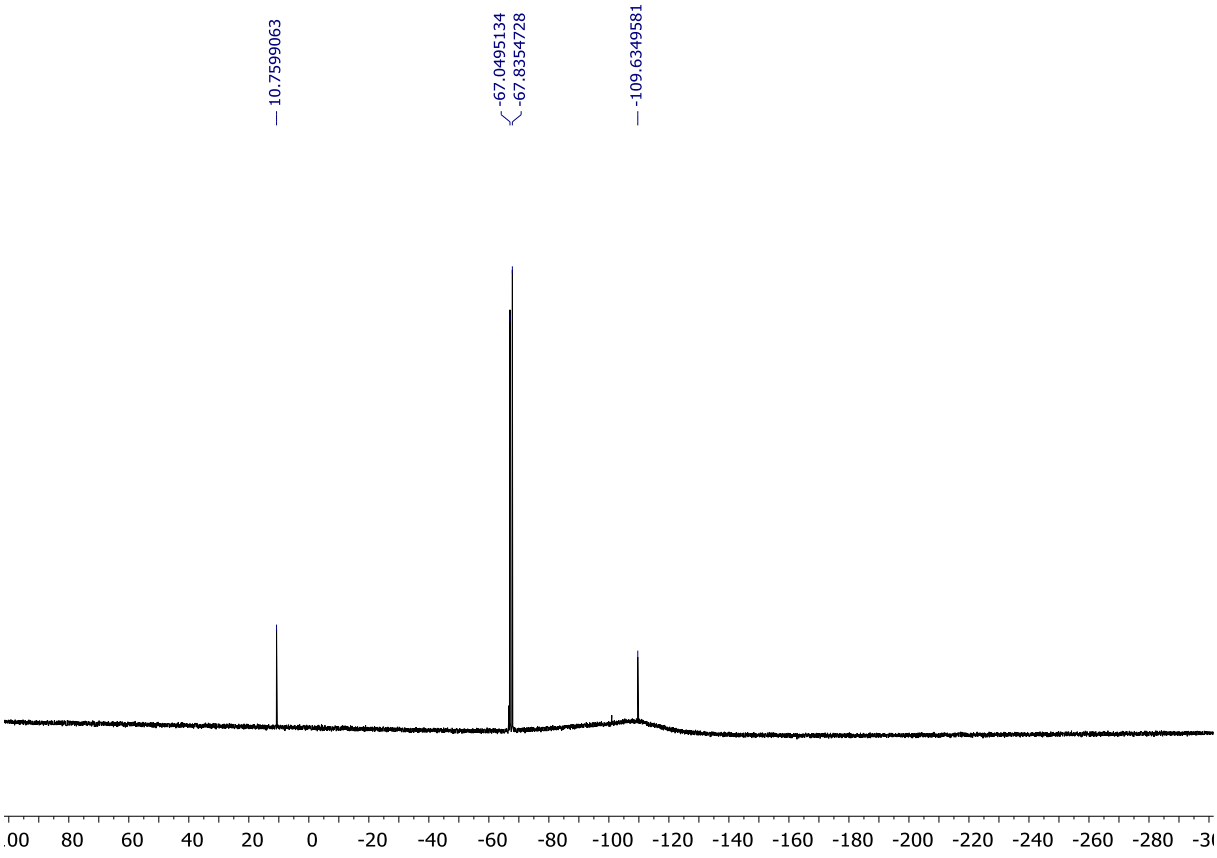
^{1}H NMR (300 MHz, $CDCl_3$)



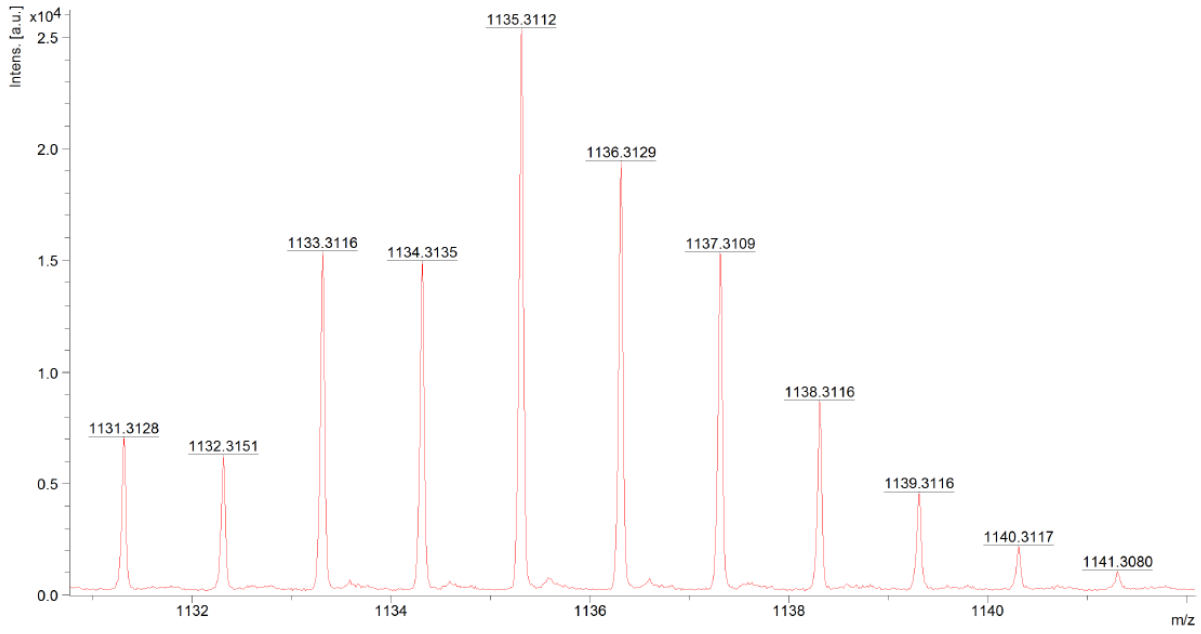
^{13}C NMR (101MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)

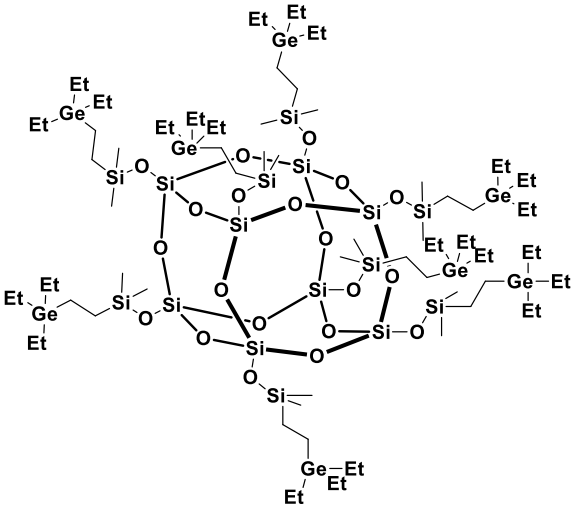


MALDI-TOF


Intens. [a.u.]
x10^4
2.5
2.0
1.5
1.0
0.5
0.0
1131.3128
1132.3151
1133.3116
1134.3135
1135.3112
1136.3129
1137.3109
1138.3116
1139.3116
1140.3117
1141.3080
1132
1134
1136
1138
1140
m/z

(7a-d)

(7a)



Chemical Formula: $C_{80}H_{200}Ge_8O_{20}Si_{16}$

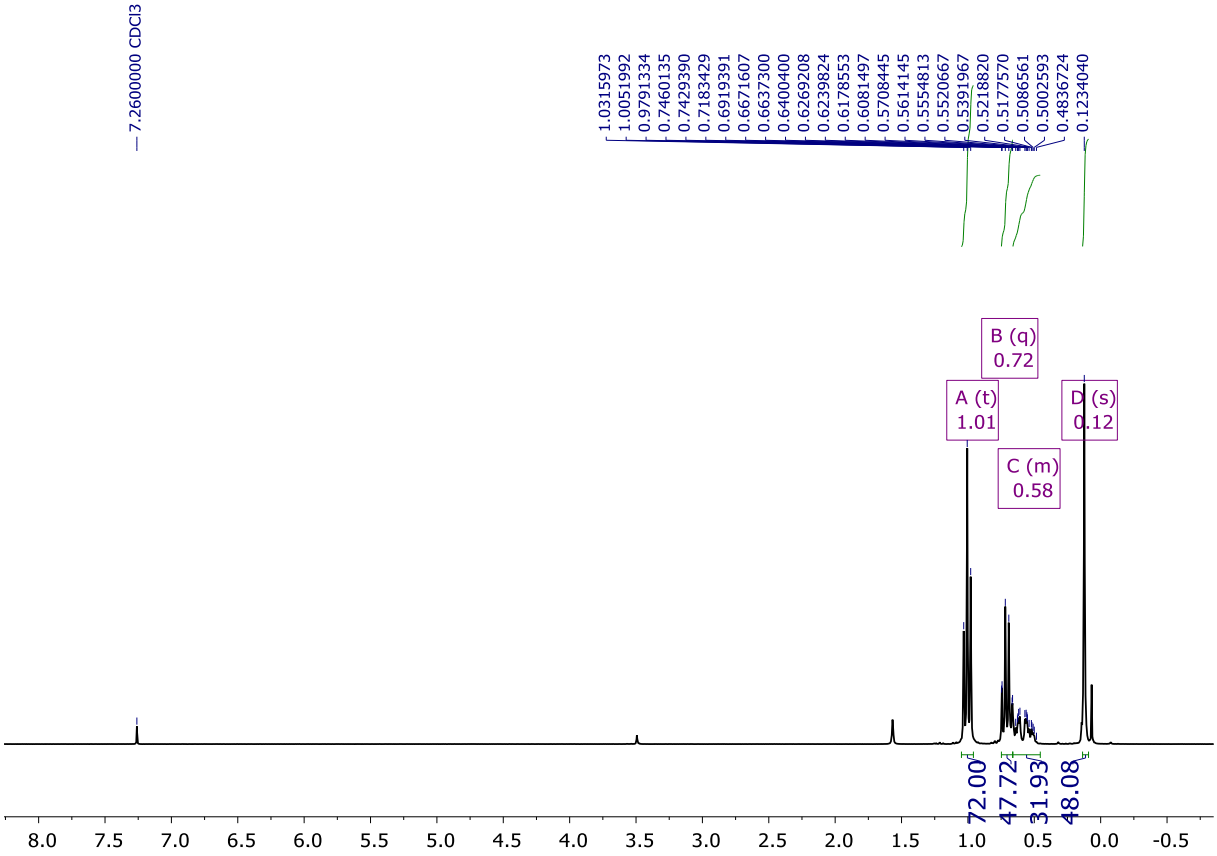
^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.01 (t, *J* = 7.9 Hz, 72H), 0.72 (q, 48H), 0.65 – 0.48 (m, 32H), 0.12 (s, 48H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 11.36, 9.16, 3.55, 2.59, -0.94.

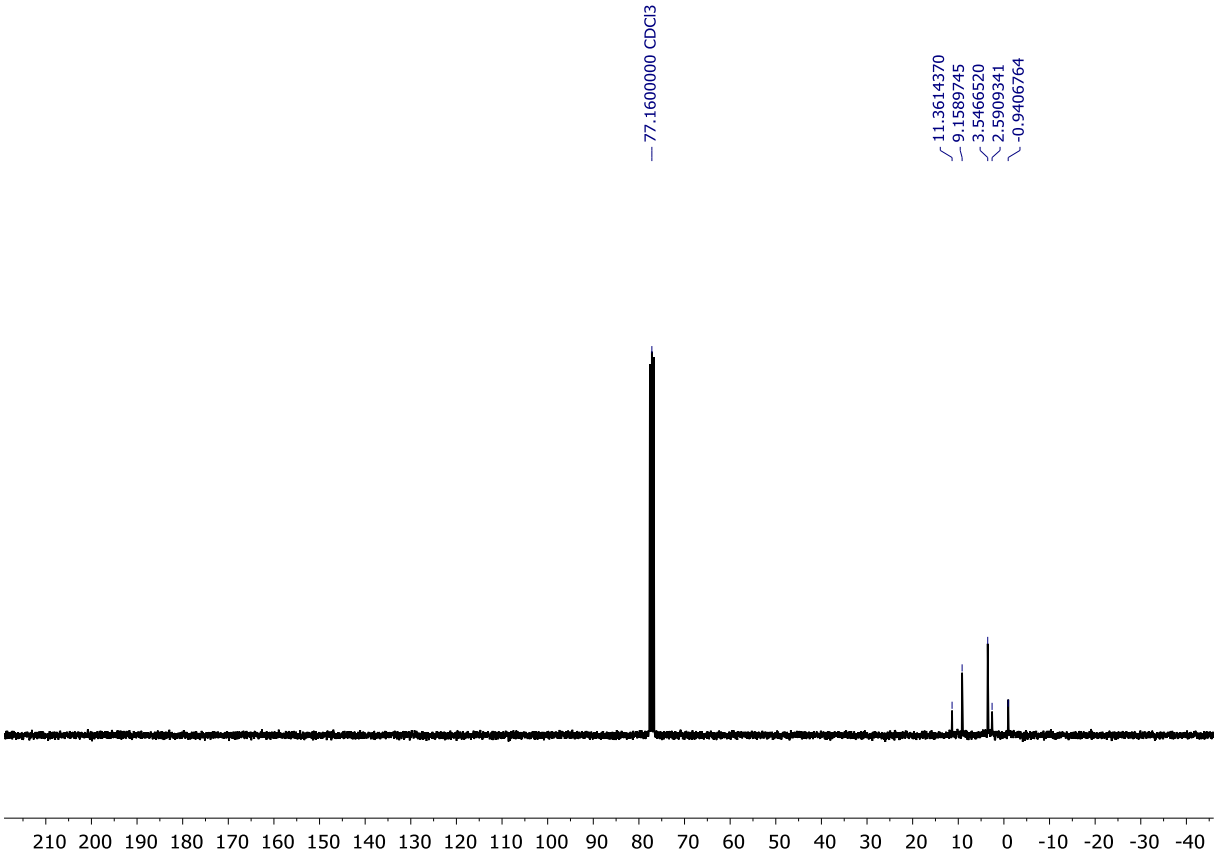
^{29}Si NMR (79 MHz, $CDCl_3$) δ 12.29, -108.81.

MALDI-TOF MS (m/z): calcd. for $C_{80}H_{200}Ge_8O_{20}Si_{16}Na$ 2535,85;found 2535,56.

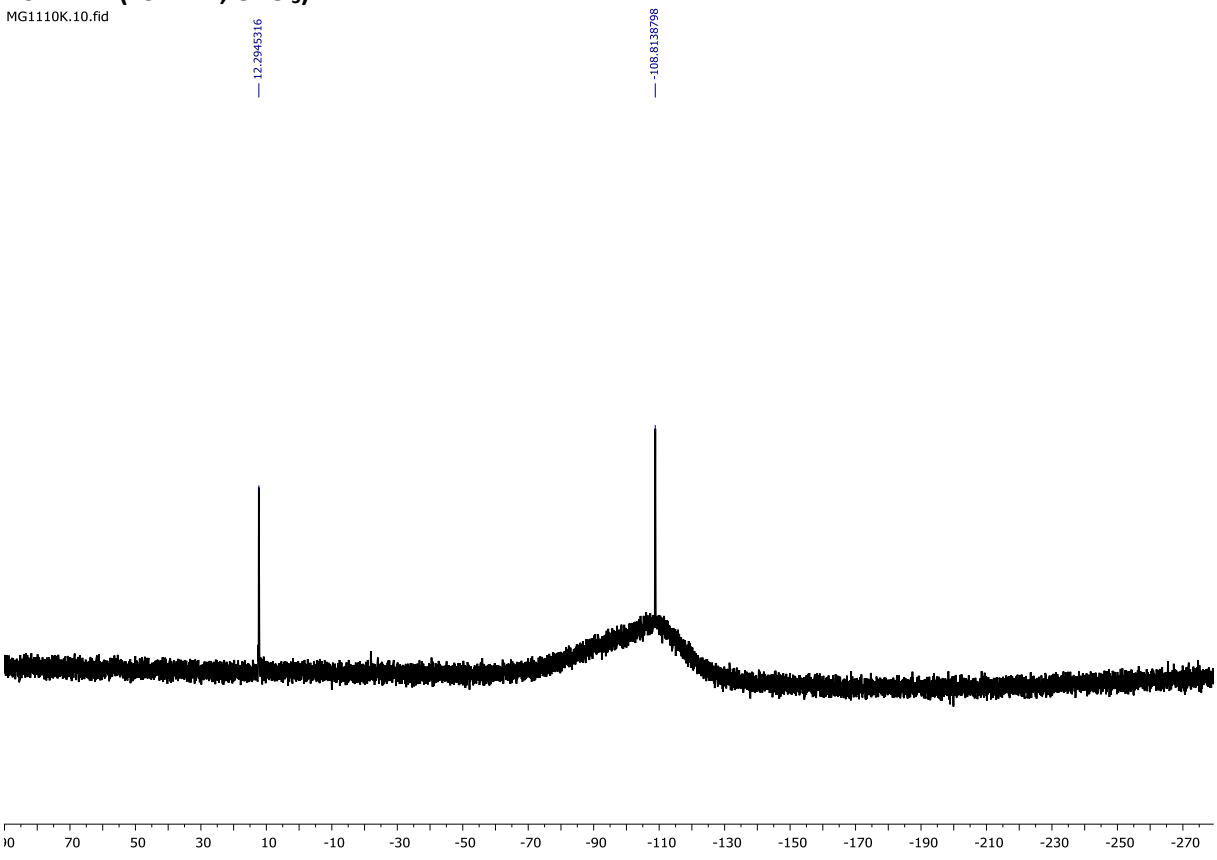
^{1}H NMR (300 MHz, $CDCl_3$)



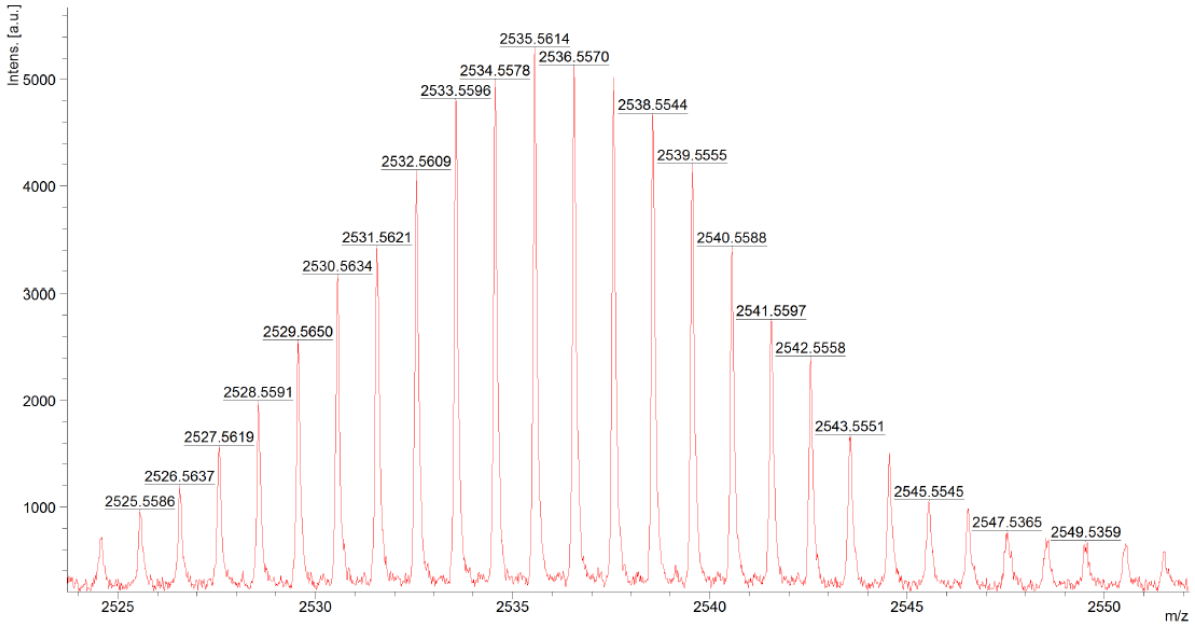
^{13}C NMR (101 MHz, $CDCl_3$)



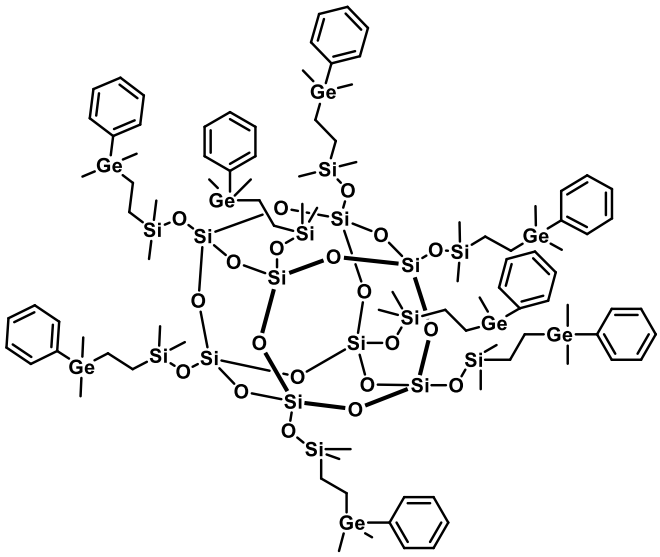
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
5000
4000
3000
2000
1000
2525.5586
2526.5637
2527.5619
2528.5591
2529.5650
2530.5634
2531.5621
2532.5609
2533.5596
2534.5578
2535.5614
2536.5570
2538.5544
2539.5555
2540.5588
2541.5597
2542.5558
2543.5551
2545.5545
2547.5365
2549.5359
2525
2530
2535
2540
2545
2550
m/z

(7b)



Chemical Formula: $C_{95}H_{168}Ge_8O_{20}Si_{16}$

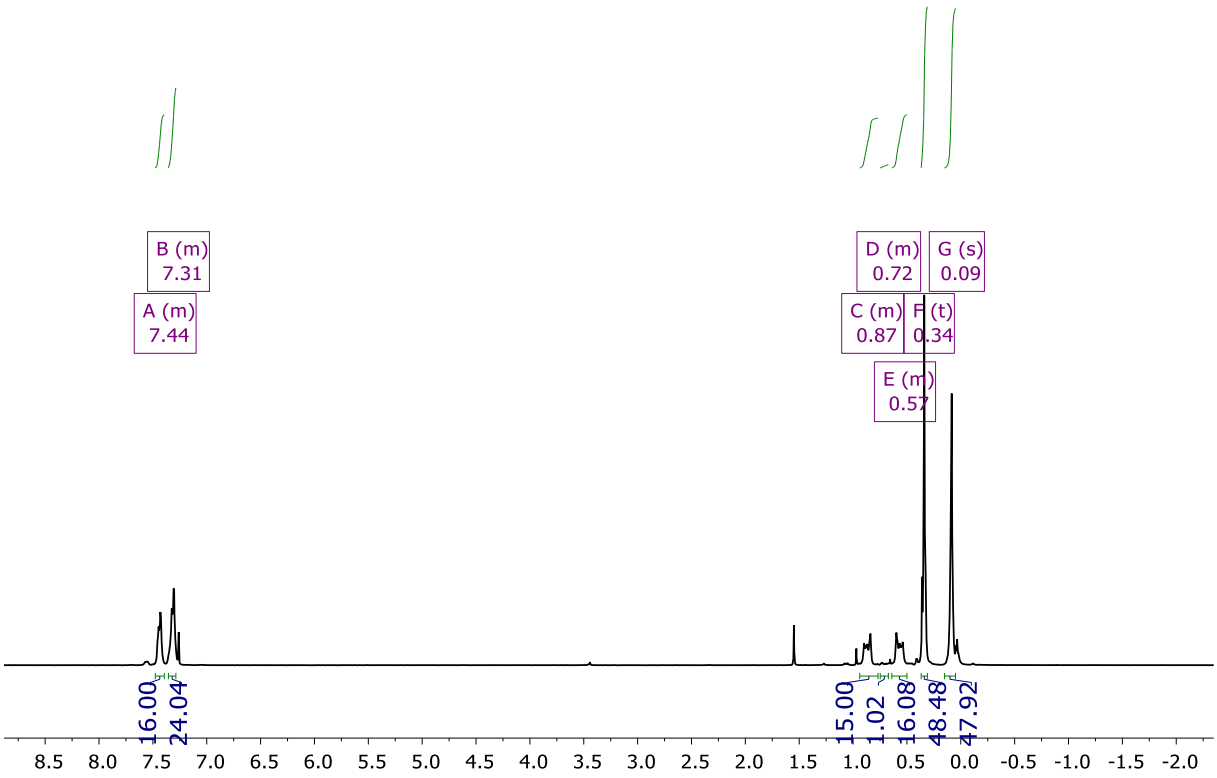
^{1}H NMR (300 MHz, Chloroform-d) δ 7.46 – 7.40 (m, 16H), 7.36 – 7.28 (m, 24H), 0.92 – 0.81 (m, 15H), 0.74 – 0.68 (m, 1H), 0.63 – 0.51 (m, 16H), 0.34 (t, 48H), 0.09 (s, 48H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.71, 133.45, 128.33, 128.04, 11.27, 7.59, -0.80, -4.22.

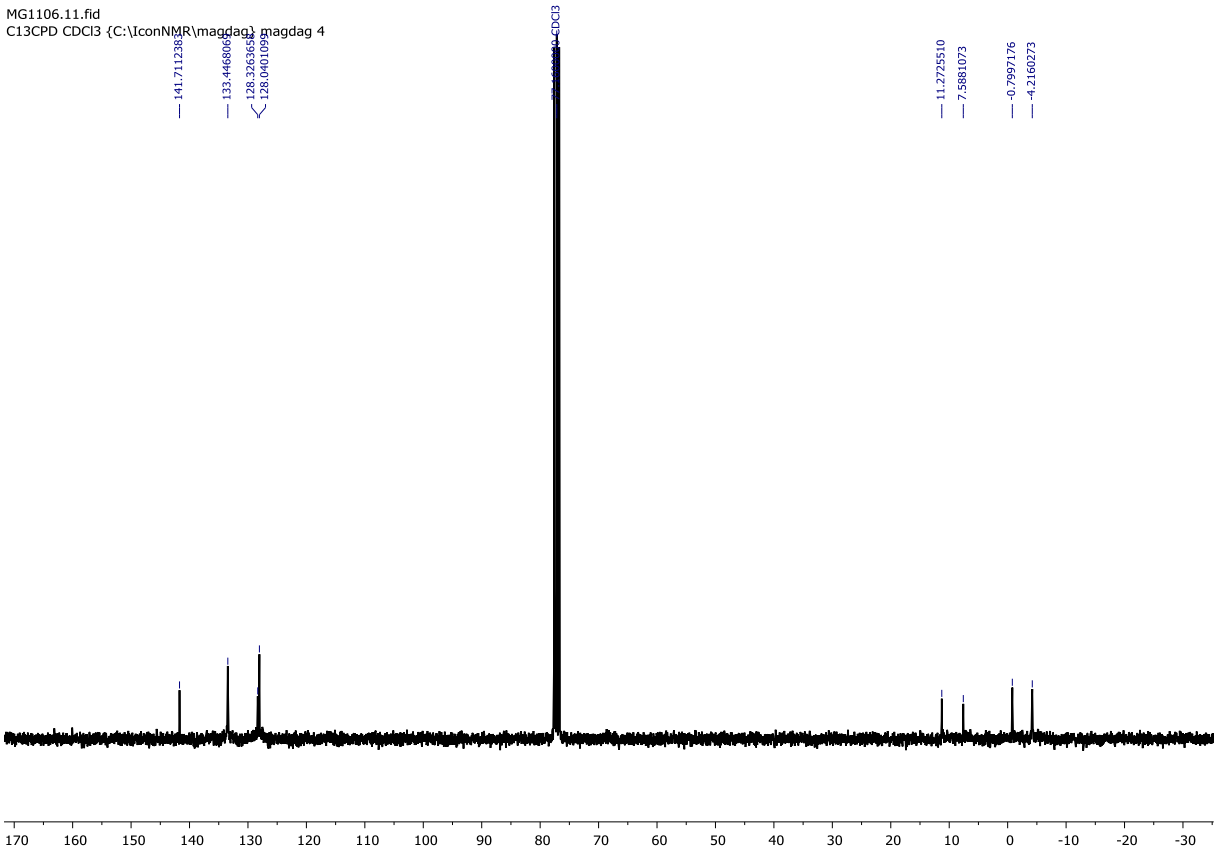
^{29}Si NMR (79 MHz, $CDCl_3$) δ 12.68, -108.77.

MALDI-TOF MS (m/z): calcd. for $C_{95}H_{166}Ge_8O_{20}Si_{16}$ 2666,20;found 2663,35.

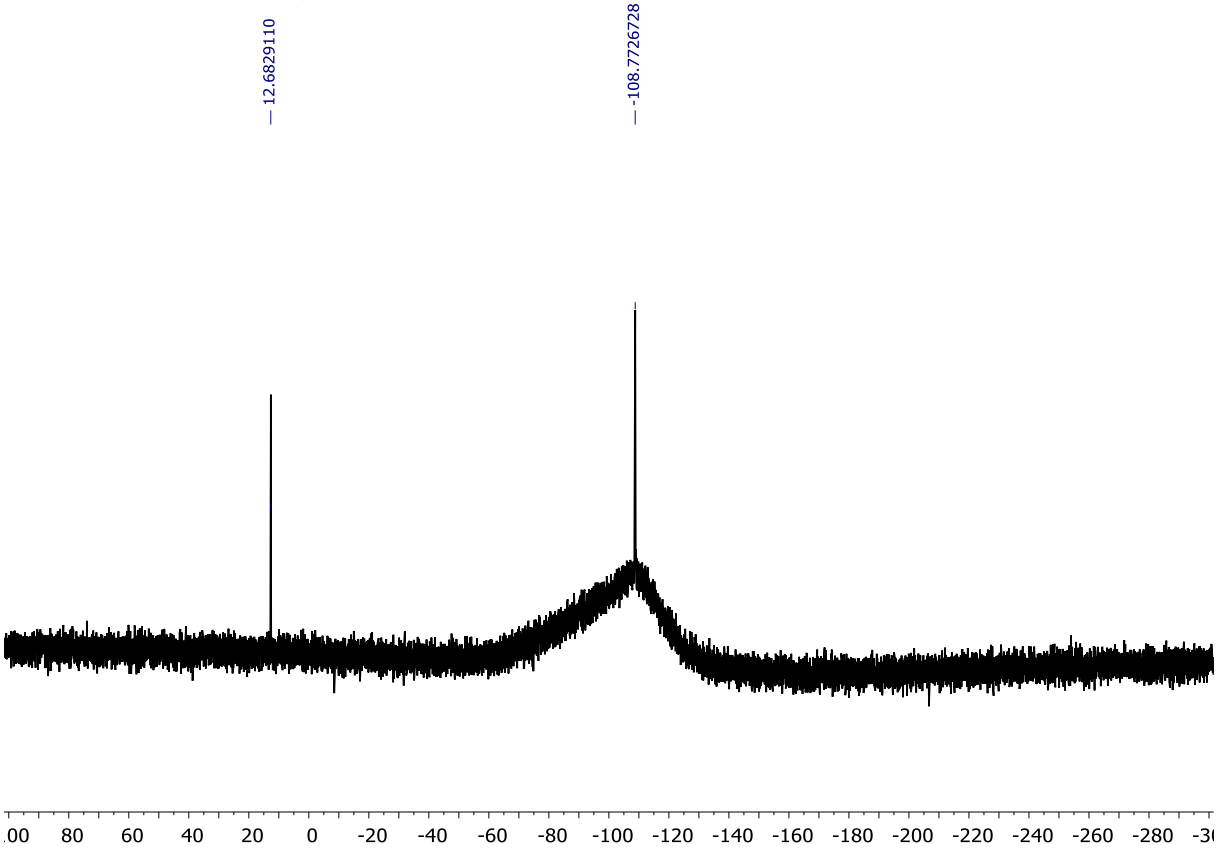
^{1}H NMR (300 MHz, $CDCl_3$)



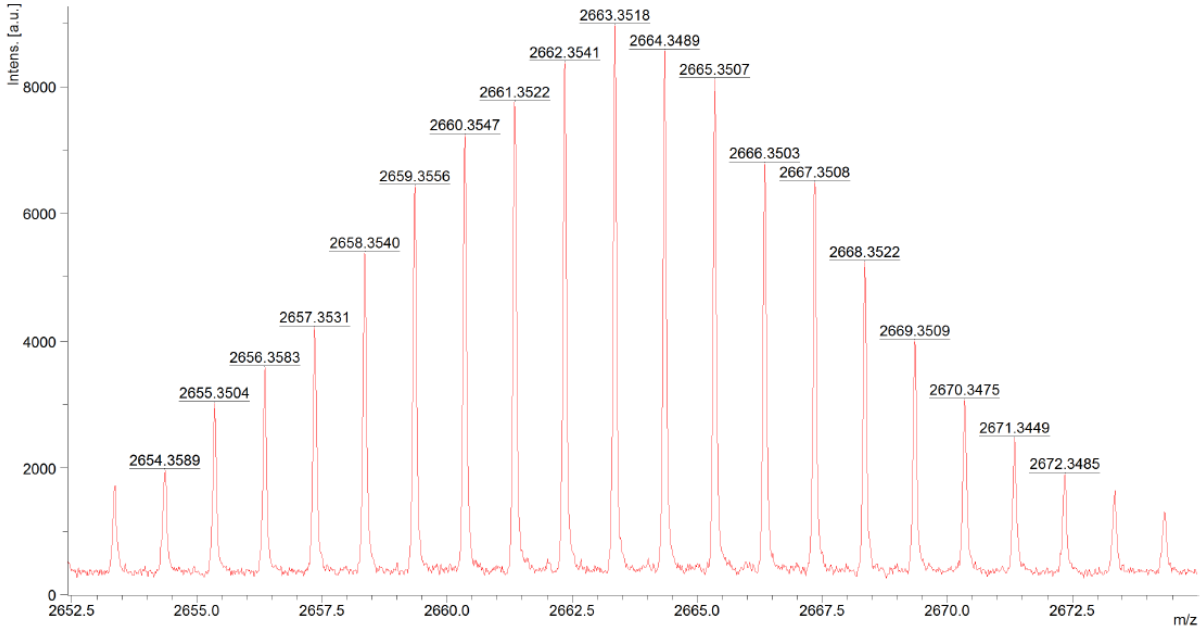
^{13}C NMR (101 MHz, $CDCl_3$)



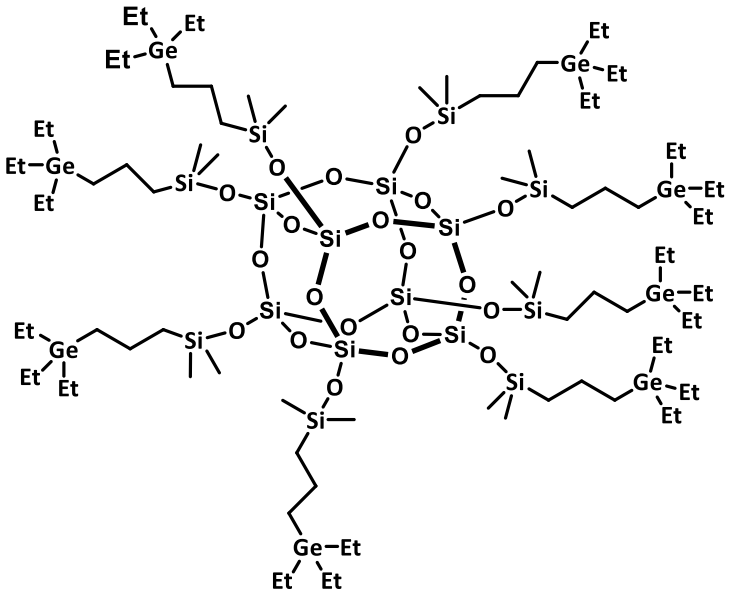
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
8000
6000
4000
2000
0
2652.5
2655.0
2657.5
2660.0
2662.5
2665.0
2667.5
2670.0
2672.5
m/z
2654.3589
2655.3504
2656.3583
2657.3531
2658.3540
2659.3556
2660.3547
2661.3522
2662.3541
2663.3518
2664.3489
2665.3507
2666.3503
2667.3508
2668.3522
2669.3509
2670.3475
2671.3449
2672.3485

(7c)



Chemical Formula: $C_{88}H_{216}Ge_8O_{20}Si_{16}$

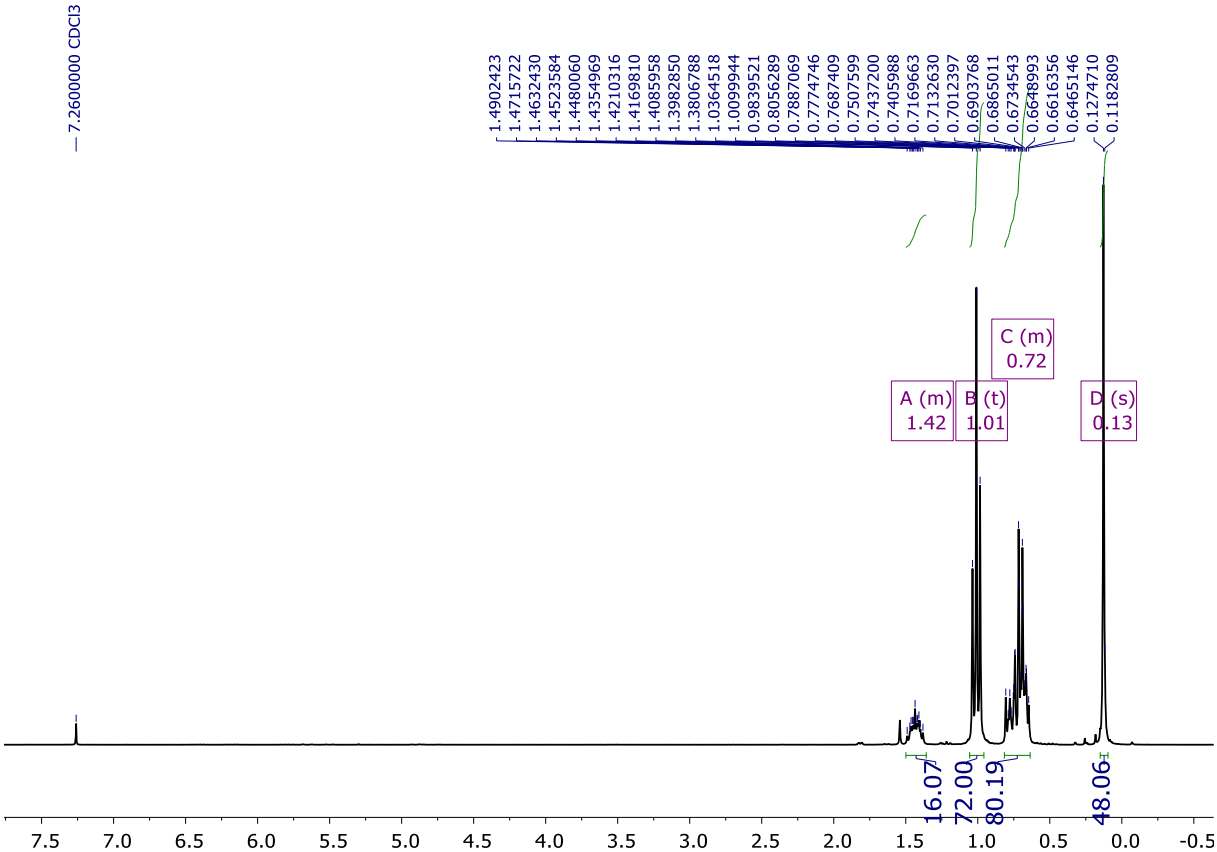
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 – 1.37 (m, 16H), 1.01 (t, *J* = 7.9 Hz, 72H), 0.81 – 0.64 (m, 80H), 0.13 (s, 48H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 22.39, 19.00, 16.08, 9.17, 4.12, -0.06.

^{29}Si NMR (79 MHz, $CDCl_3$) δ 11.90, -108.94.

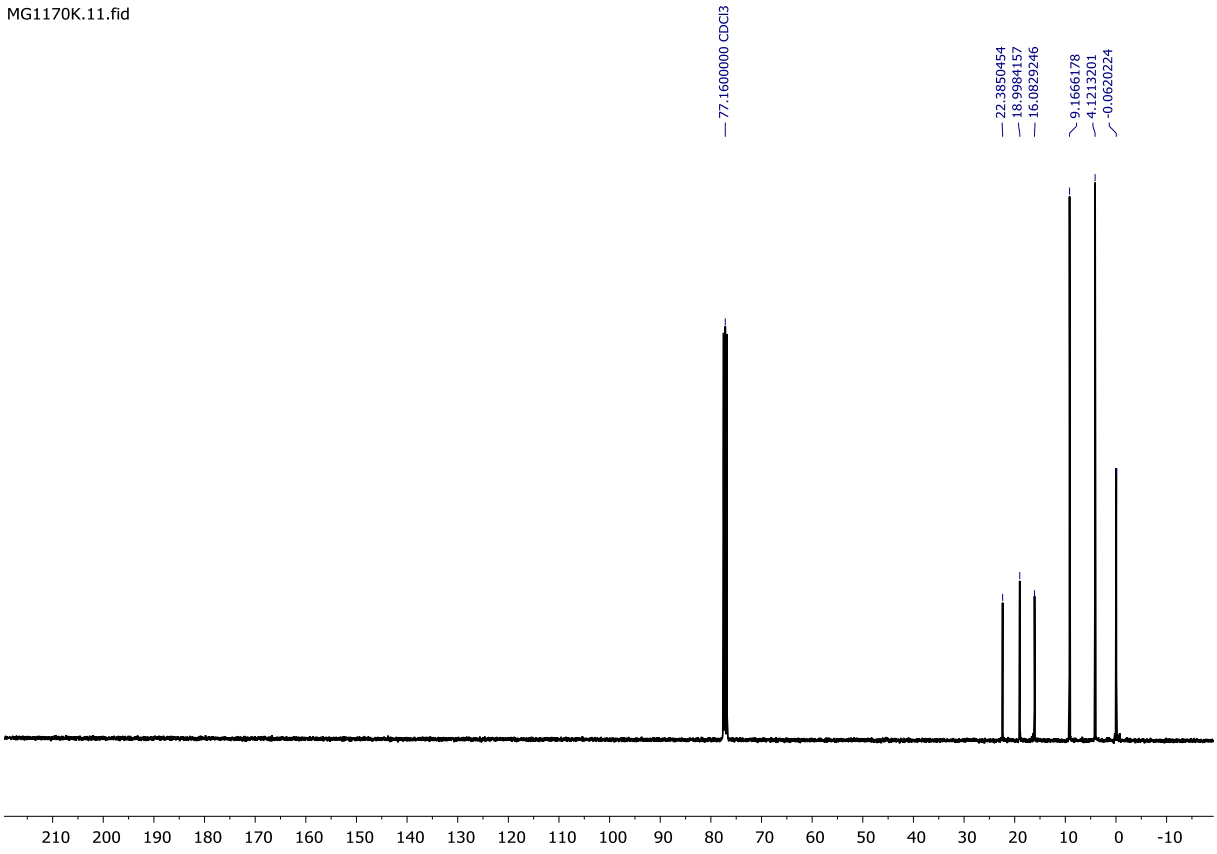
MALDI-TOF MS (m/z): calcd. for $C_{88}H_{216}Ge_8O_{20}Si_{16}Na$ 2655,58;found 2647,58.

^{1}H NMR (300 MHz, $CDCl_3$)



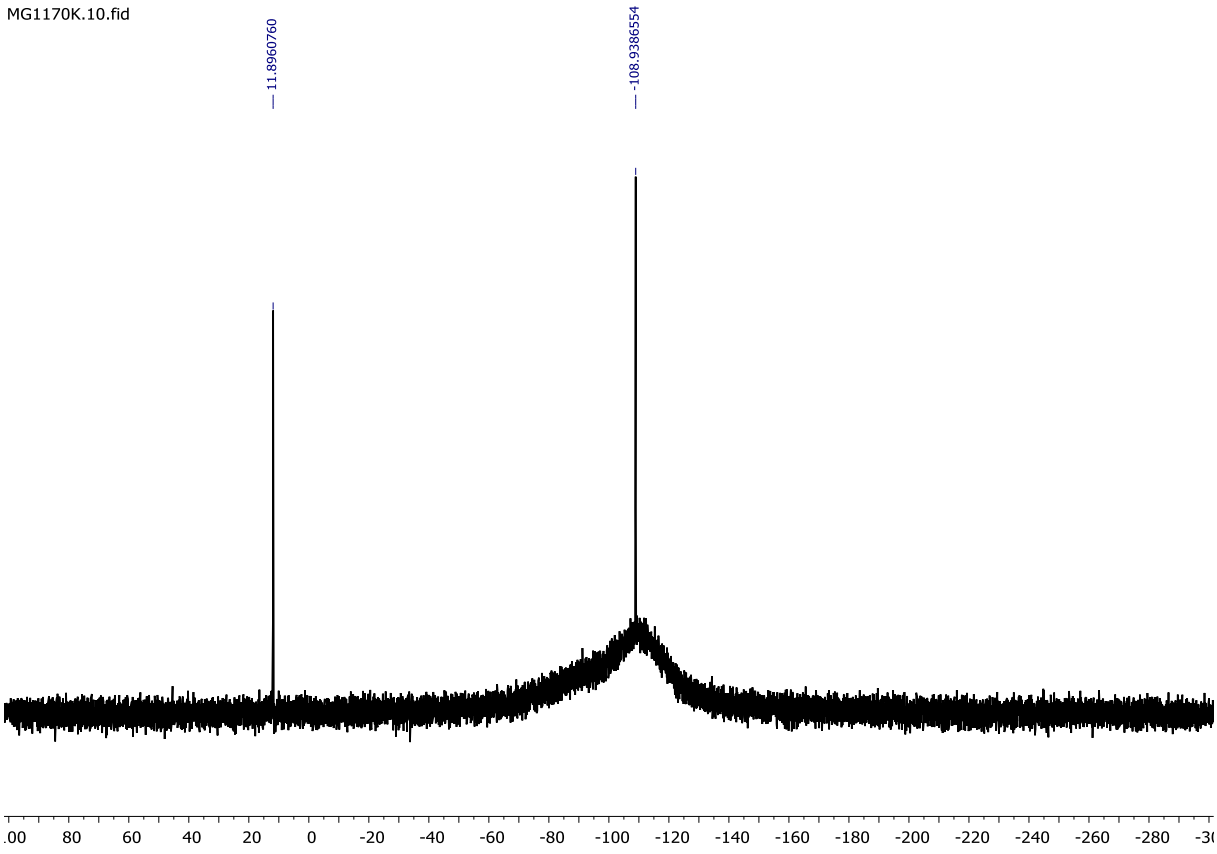
^{13}C NMR (101 MHz, $CDCl_3$)

MG1170K.11.fid

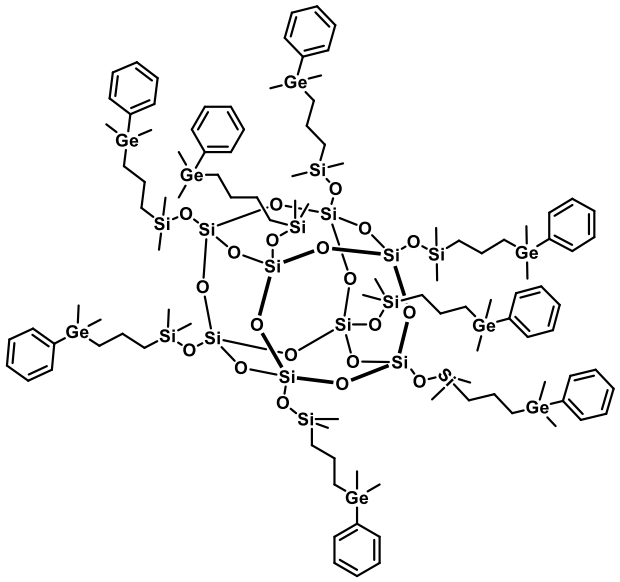


^{29}Si NMR (79 MHz, $CDCl_3$)

MG1170K.10.fid



(7d)



Chemical Formula: $C_{105}H_{186}Ge_8O_{20}Si_{16}$

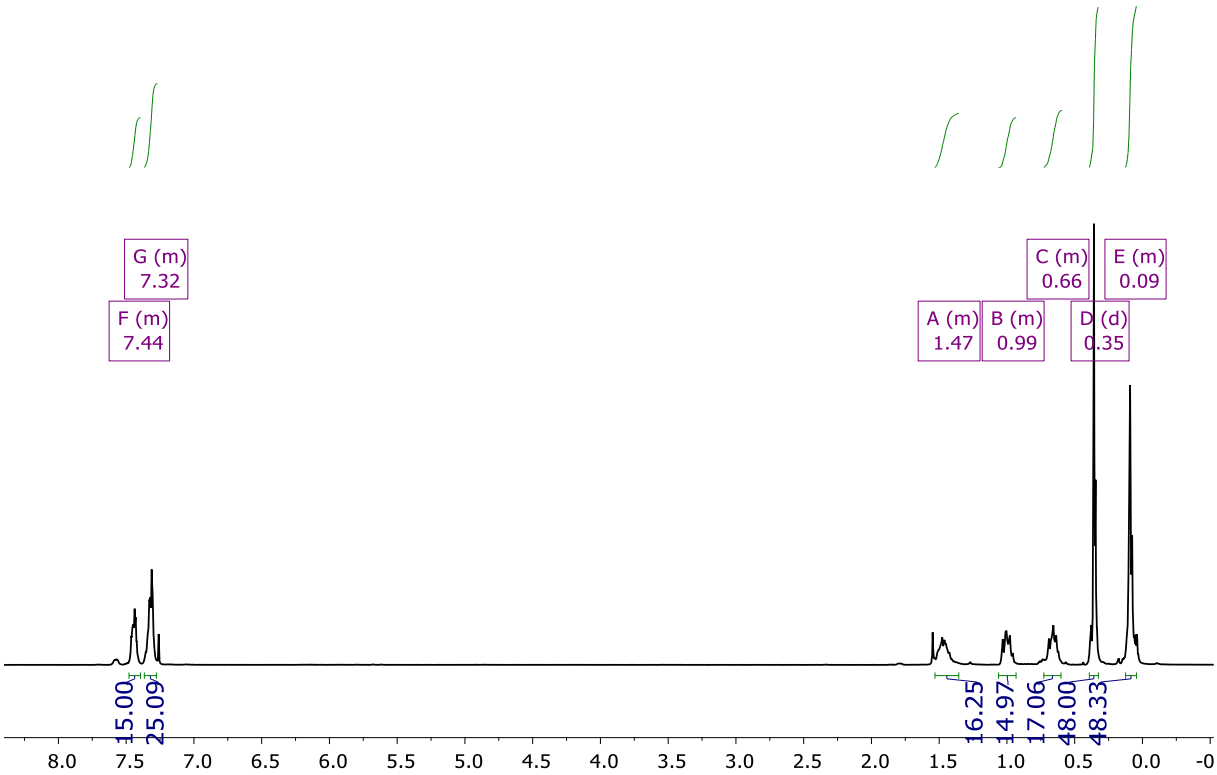
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.49 – 7.40 (m, 15H), 7.36 – 7.28 (m, 25H), 1.53 – 1.40 (m, 16H), 1.07 – 0.95 (m, 15H), 0.66 (m, 17H), 0.35 (d, *J* = 3.6 Hz, 48H), 0.15 – 0.02 (m, 48H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.11, 133.33, 128.30, 128.03, 21.90, 20.26, 18.81, -0.04, -3.43.

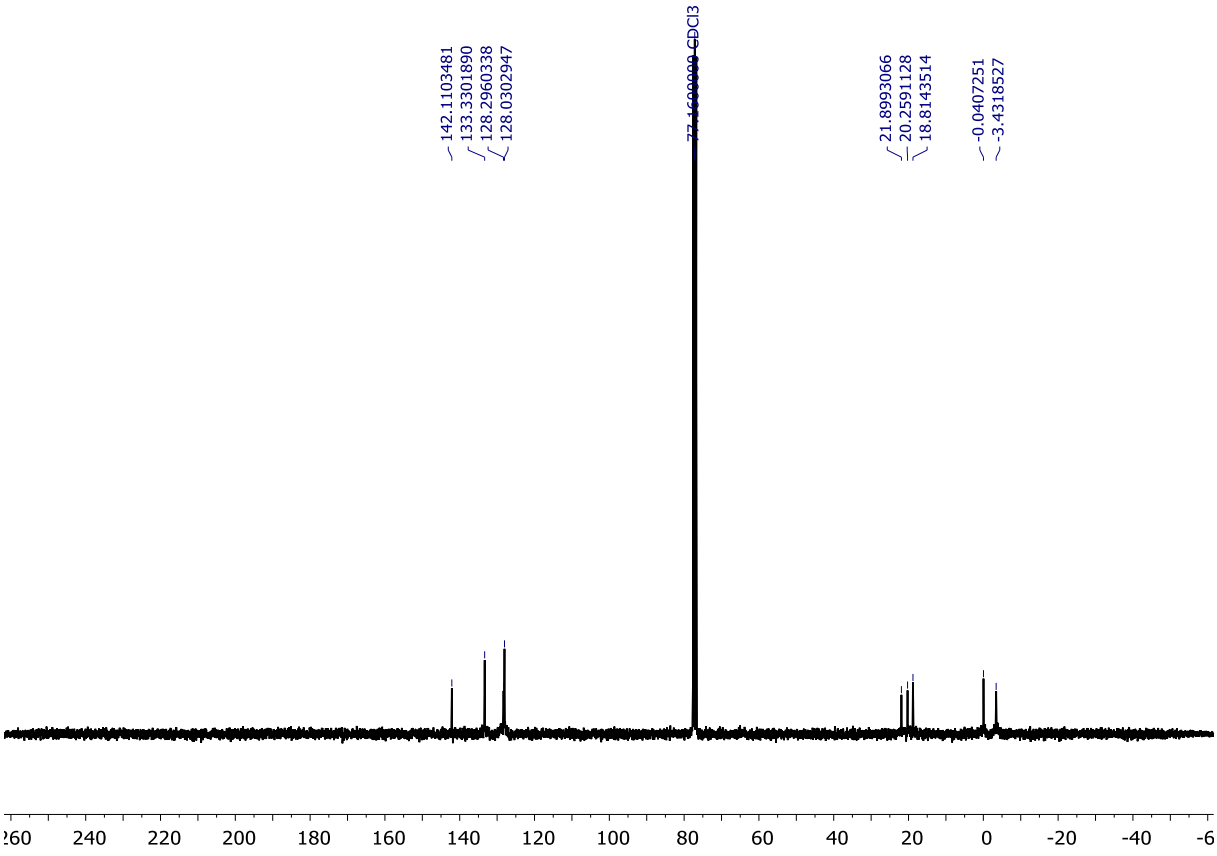
^{29}Si NMR (79 MHz, $CDCl_3$) δ 12.06, -108.88.

MALDI-TOF MS (m/z): calcd. for $C_{105}H_{186}Ge_8O_{20}Si_{16}$ 2806,35;found 2807,36.

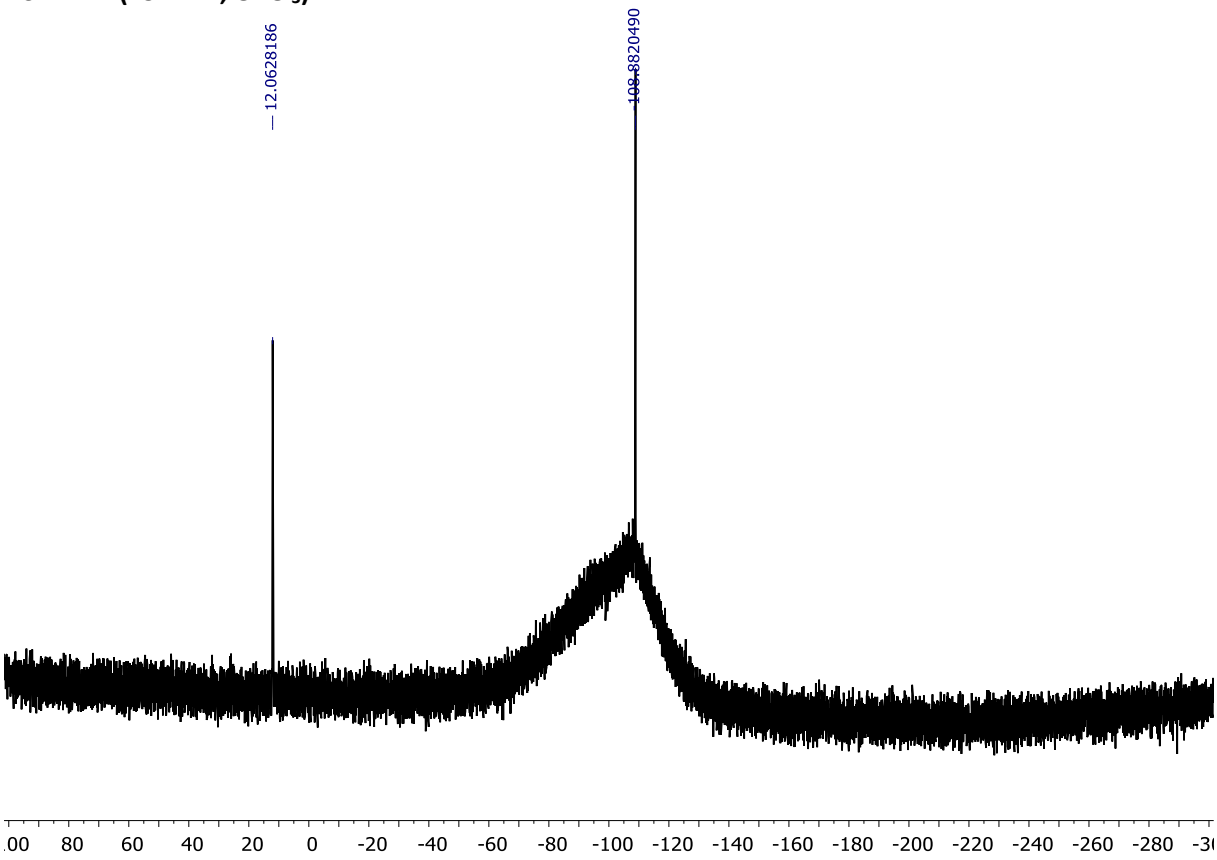
^{1}H NMR (300 MHz, $CDCl_3$)



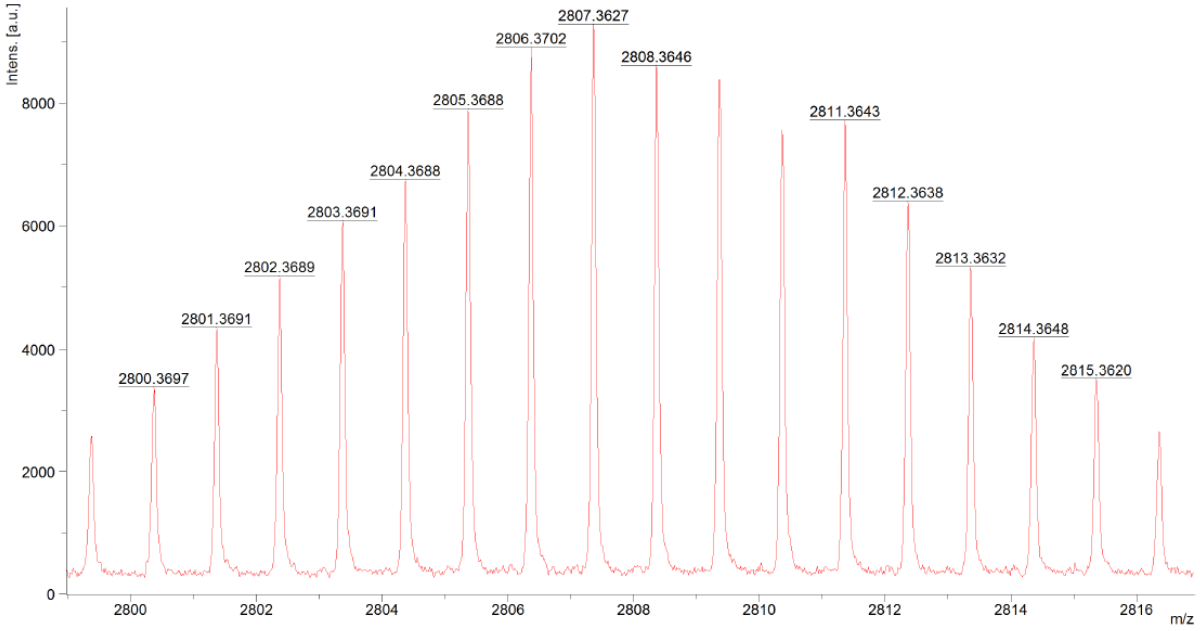
^{13}C NMR (101 MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)

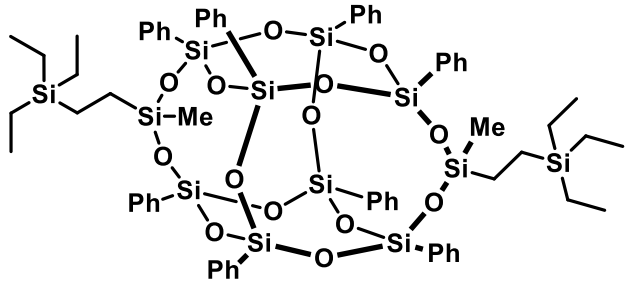


MALDI-TOF


Intens. [a.u.]
8000
6000
4000
2000
0
2800.3697
2801.3691
2802.3689
2803.3691
2804.3688
2805.3688
2806.3702
2807.3627
2808.3646
2811.3643
2812.3638
2813.3632
2814.3648
2815.3620
2800
2802
2804
2806
2808
2810
2812
2814
2816
m/z

The ^{1}H NMR and ^{13}C NMR, ^{29}Si NMR and MALDI TOF or ESI data of products with silyl moiety 2e-f, 3e-f, 5e-f, 6e-f, 7e-f.

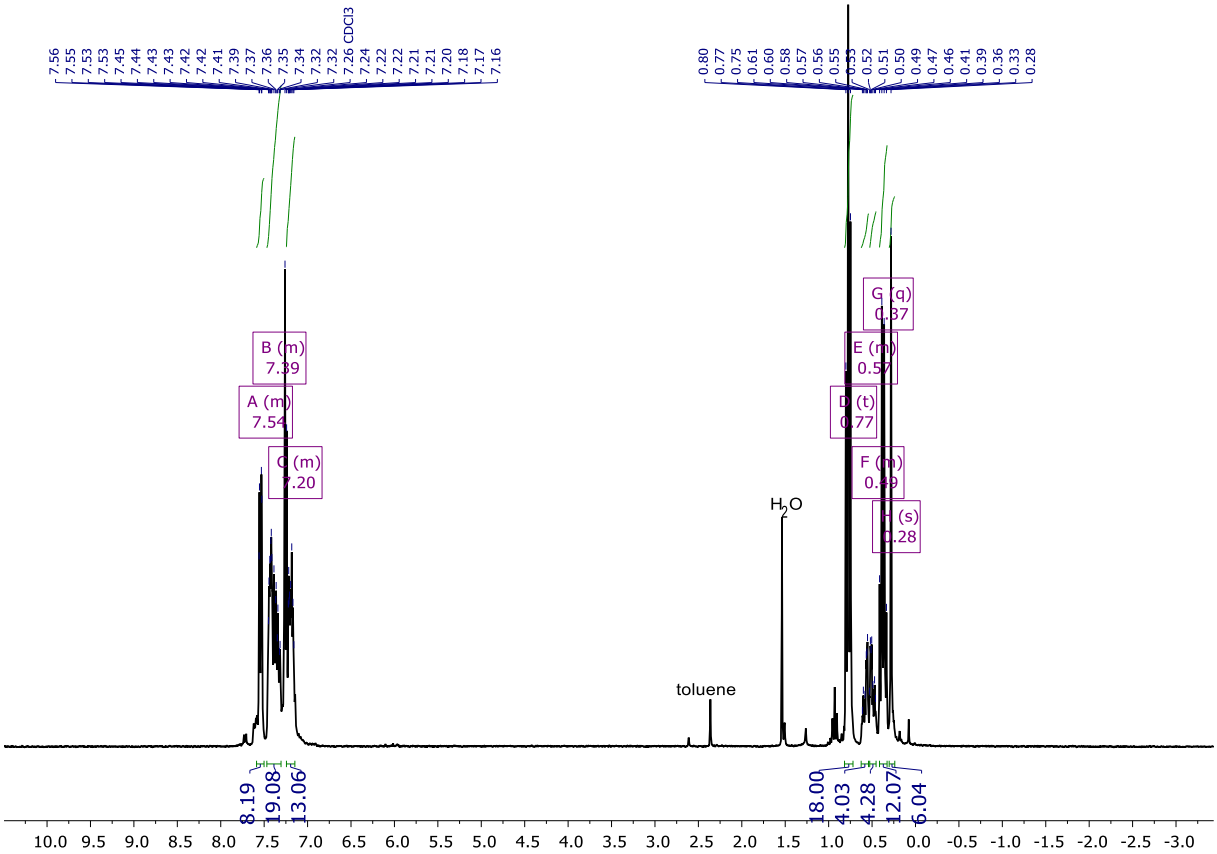
(2e)



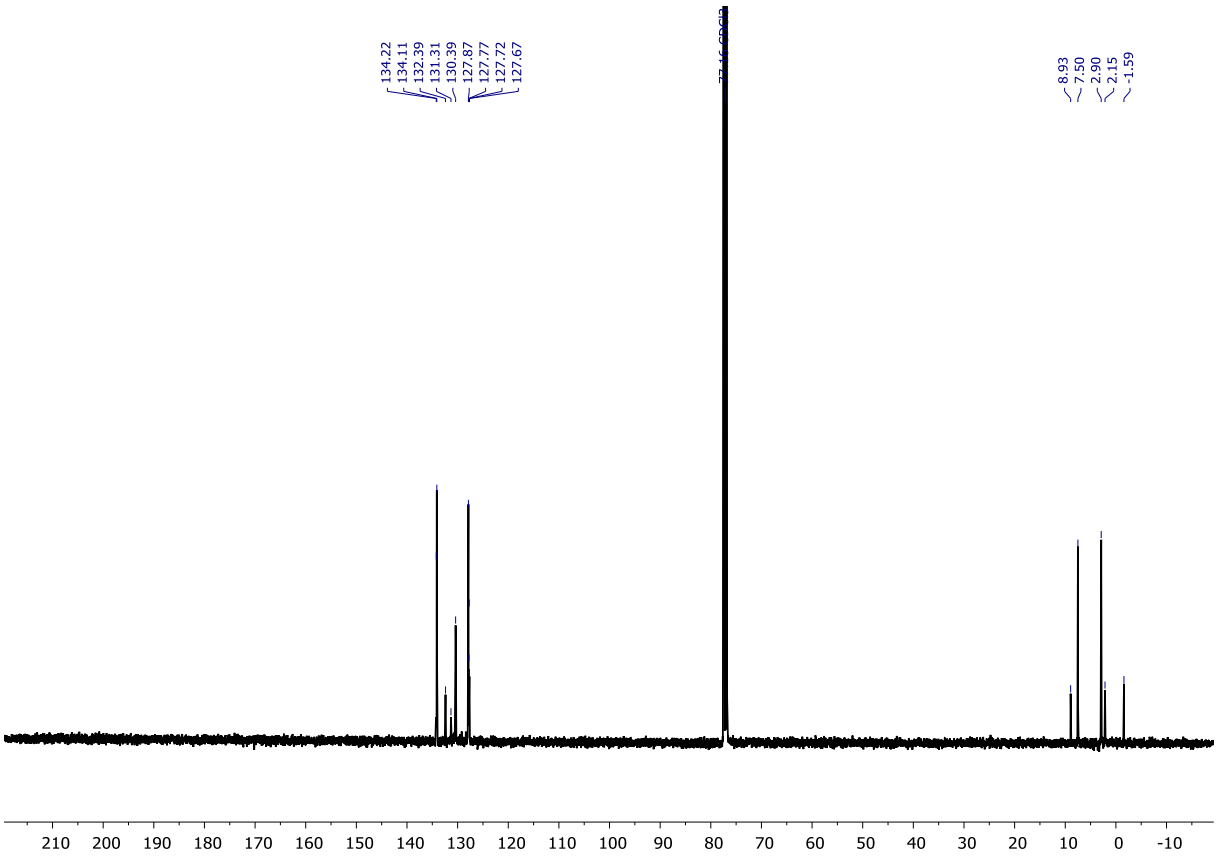
Chemical Formula: $C_{66}H_{84}O_{14}Si_{12}$

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.59 – 7.50 (m, 8H), 7.48 – 7.29 (m, 19H), 7.25 – 7.15 (m, 13H), 0.77 (t, *J* = 7.9 Hz, 18H), 0.63 – 0.55 (m, 4H), 0.53 – 0.45 (m, 4H), 0.37 (q, *J* = 7.9 Hz, 12H), 0.28 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 134.22, 134.11, 132.39, 131.31, 130.39, 127.87, 127.77, 127.72, 127.67, 8.93, 7.50, 2.90, 2.15, -1.59.
^{29}Si NMR (79 MHz, $CDCl_3$) δ 8.39, -17.29, -78.72, -79.69.
MALDI-TOF MS (m/z): calcd. for $C_{66}H_{84}O_{14}Si_{12}Na$ 1459,30; found 1460,30.

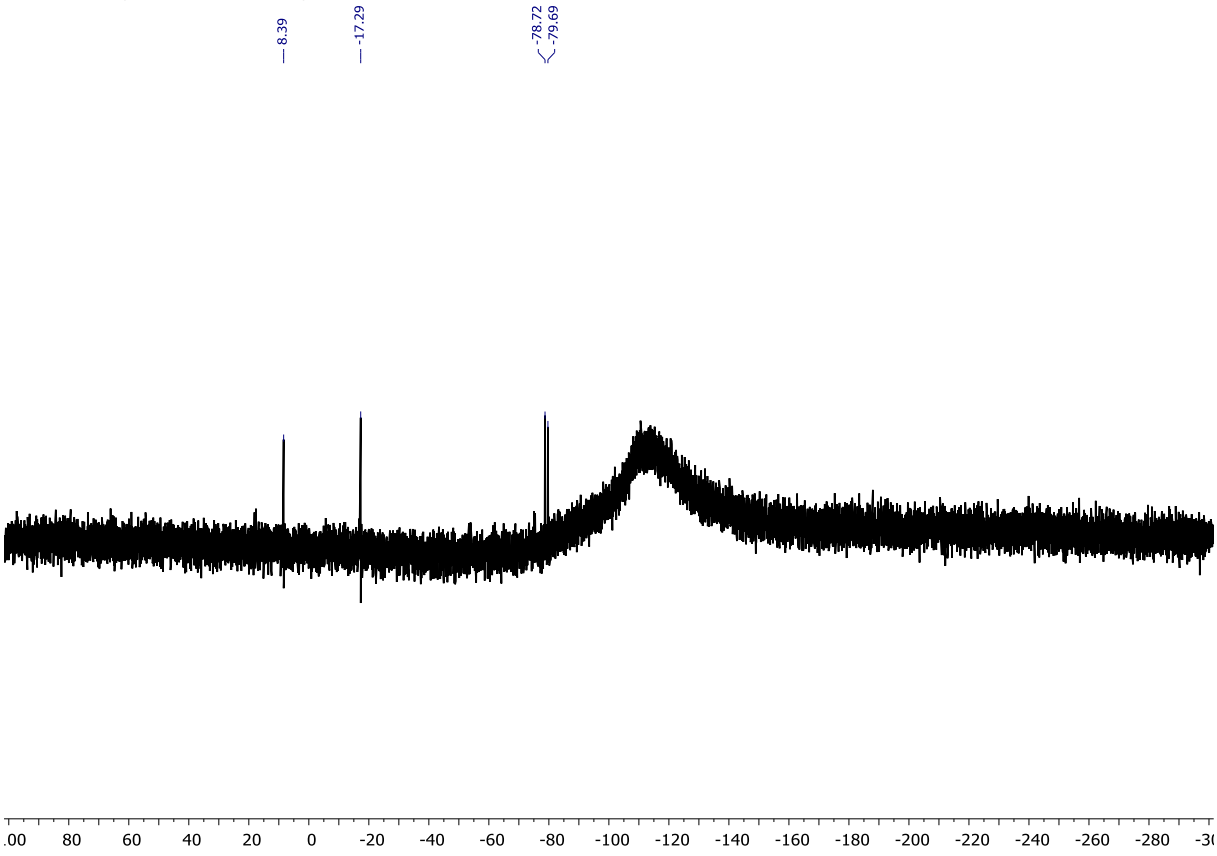
^{1}H NMR (300 MHz, $CDCl_3$)



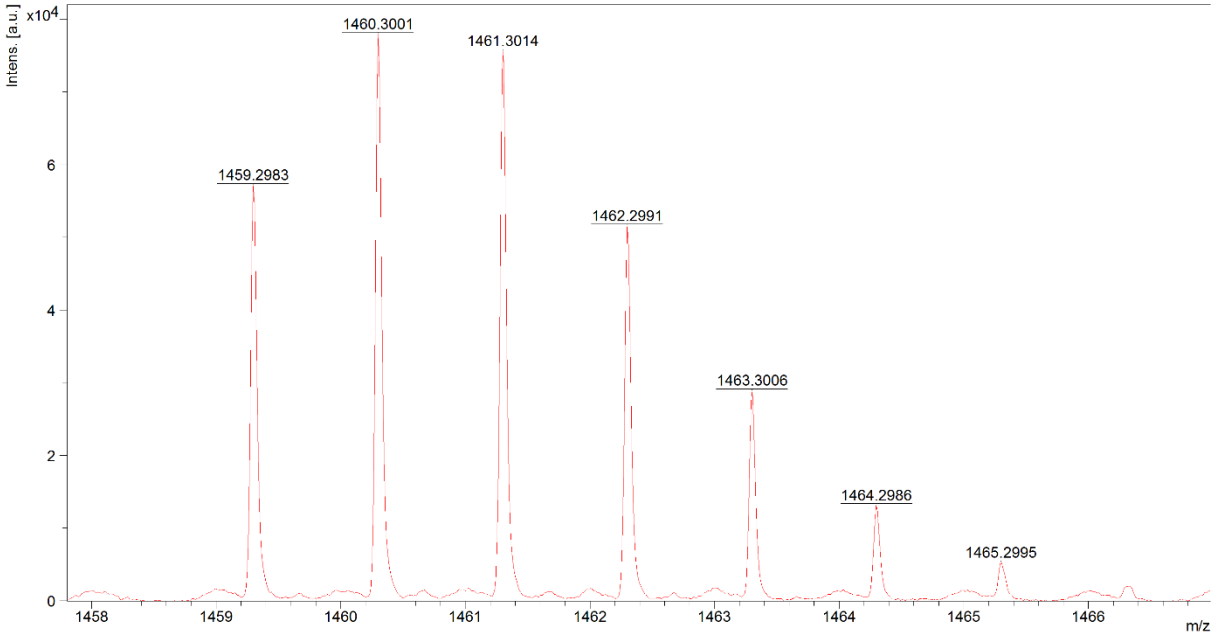
^{13}C NMR (101 MHz, $CDCl_3$)



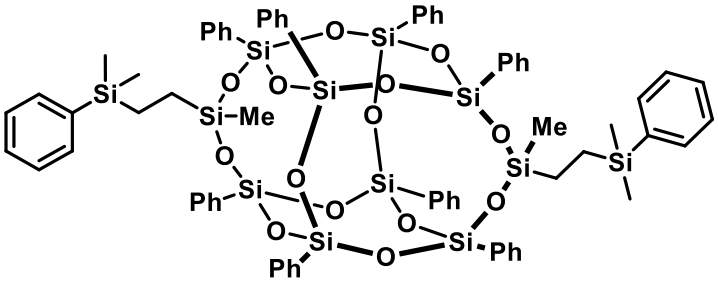
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
6
4
2
0
1459.2983
1460.3001
1461.3014
1462.2991
1463.3006
1464.2986
1465.2995
1458
1459
1460
1461
1462
1463
1464
1465
1466
m/z

(2f)



Chemical Formula: $C_{70}H_{76}O_{14}Si_{12}$

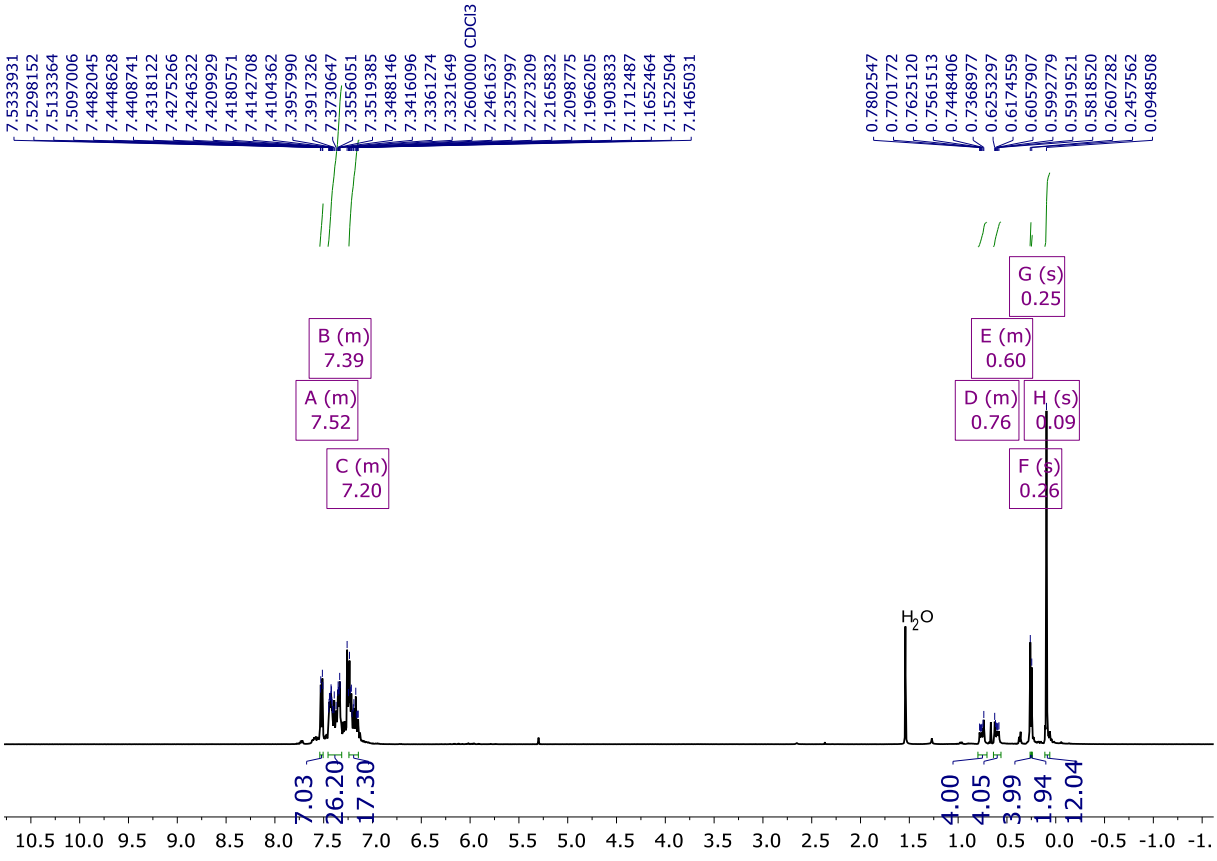
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 7H), 7.46 – 7.32 (m, 26H), 7.25 – 7.14 (m, 17H), 0.81 – 0.72 (m, 4H), 0.64 – 0.56 (m, 4H), 0.26 (s, 4H), 0.25 (s, 2H), 0.09 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.30, 134.23, 134.21, 134.19, 134.10, 133.71, 132.31, 131.27, 130.43, 128.80, 127.90, 127.78, 9.05, 6.55, -1.42, -3.58.

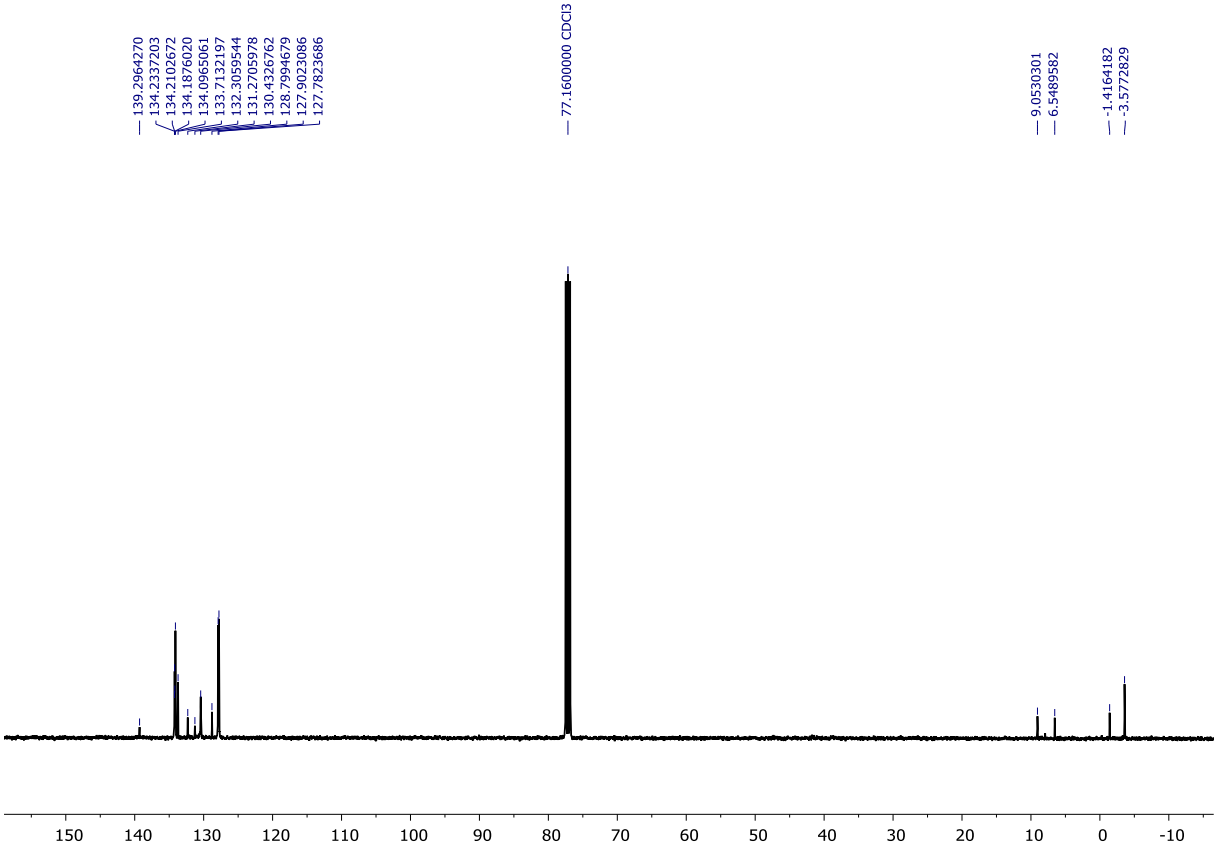
^{29}Si NMR (79 MHz, $CDCl_3$) δ -1.24, -17.41, -78.70, -79.68.

HRMS (ESI): m/z calcd. for $C_{70}H_{76}O_{14}Si_{12}$ 1476,25; found 1476,70.

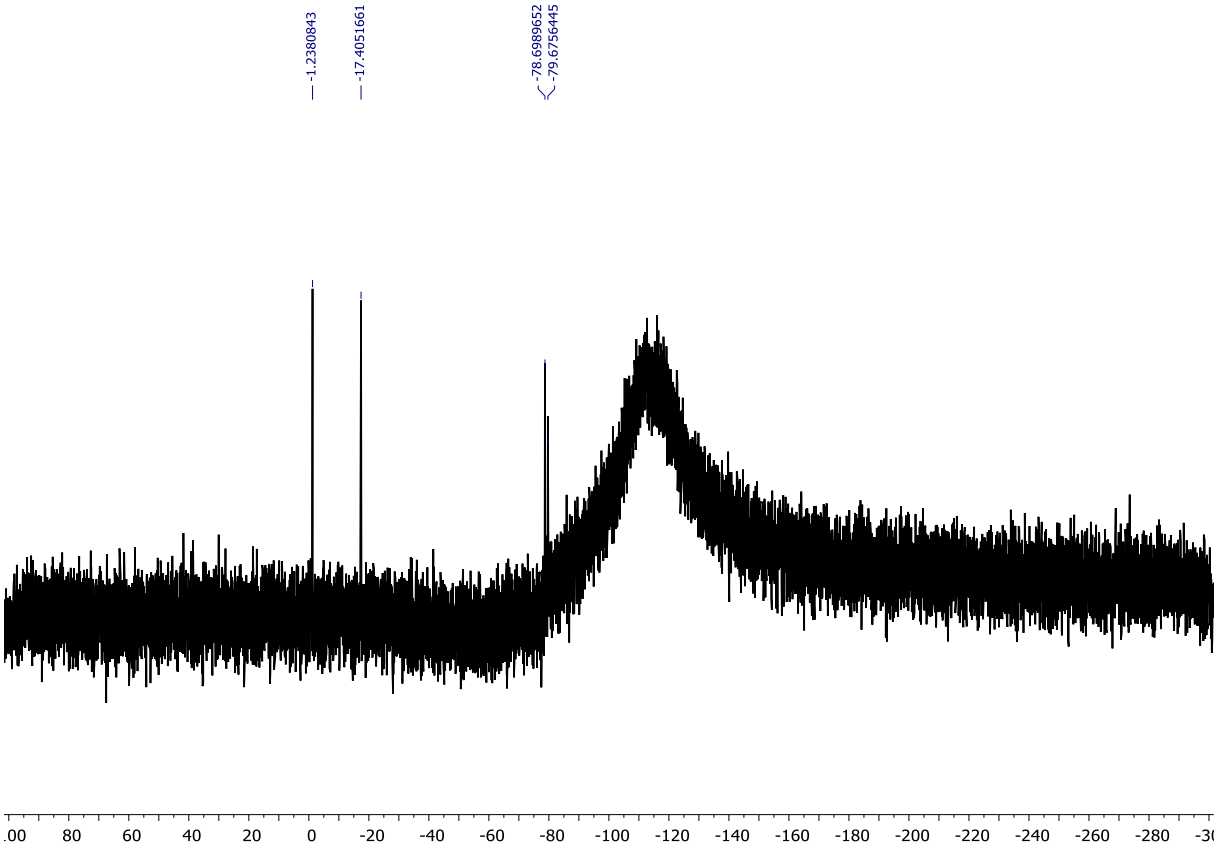
^{1}H NMR (400 MHz, $CDCl_3$)



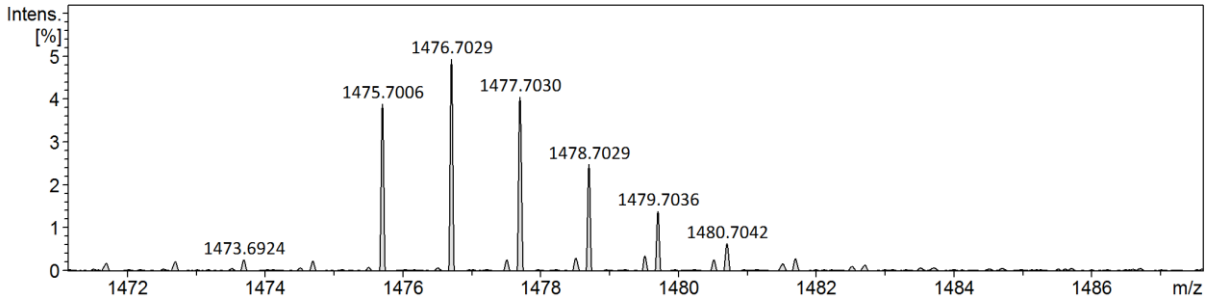
^{13}C NMR (101 MHz, $CDCl_3$)



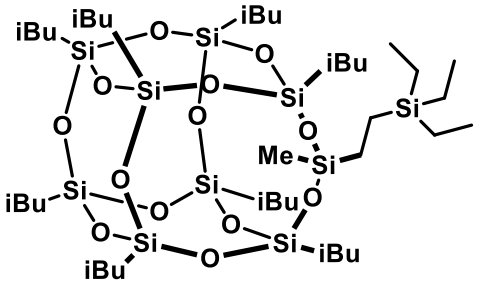
^{29}Si NMR (79 MHz, $CDCl_3$)



HRMS (ESI)


Intens.
[%]
5
4
3
2
1
0
1476.7029
1475.7006
1477.7030
1478.7029
1479.7036
1480.7042
1473.6924
1472
1474
1476
1478
1480
1482
1484
1486
m/z

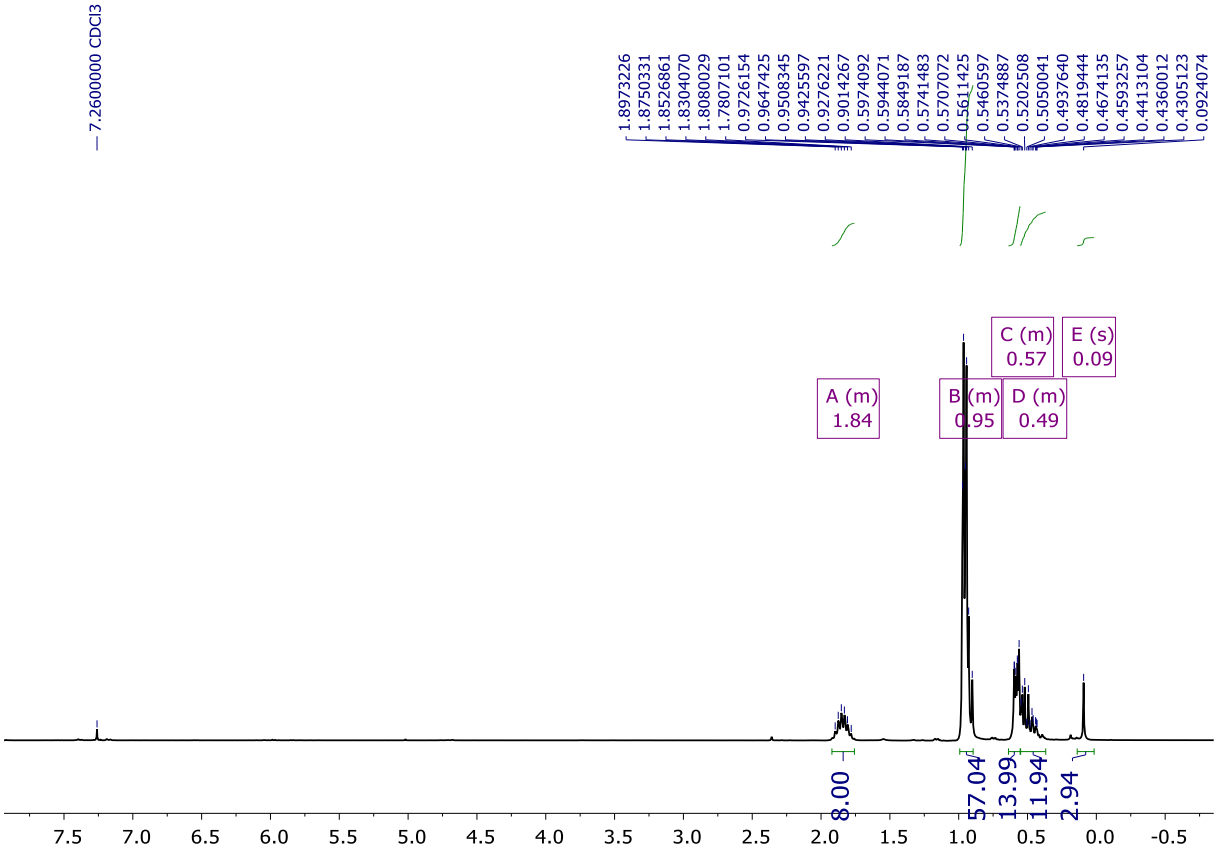
(3e)



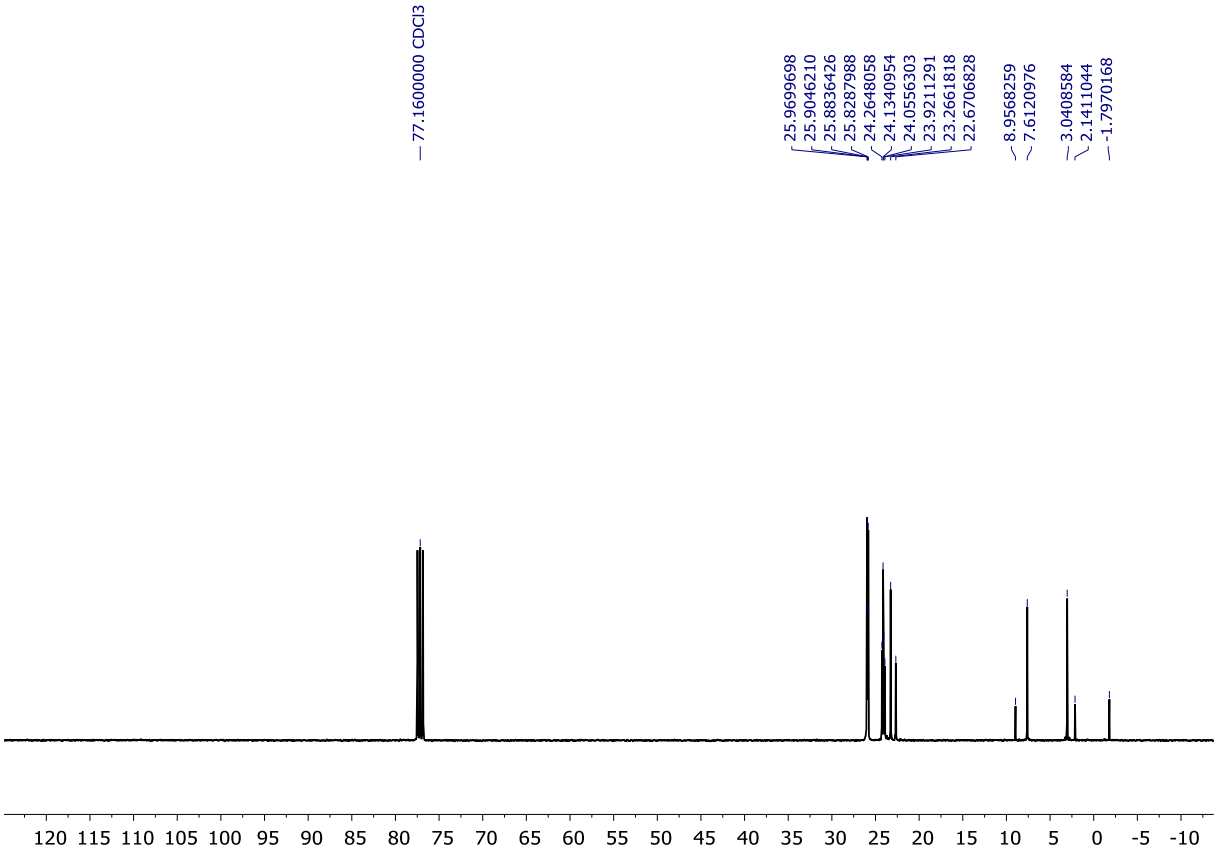
Chemical Formula: $C_{41}H_{94}O_{13}Si_{10}$

^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.93 – 1.75 (m, 8H), 1.00 – 0.89 (m, 57H), 0.63 – 0.53 (m, 14H), 0.53 – 0.38 (m, 12H), 0.09 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 25.97, 25.90, 25.88, 25.83, 24.26, 24.13, 24.06, 23.92, 23.27, 22.67, 8.96, 7.61, 3.04, 2.14, -1.80.
^{29}Si NMR (79 MHz, $CDCl_3$) δ 8.37, -21.58, -67.05, -69.18, -69.23.
MALDI-TOF MS (m/z): calcd. for $C_{41}H_{94}O_{13}Si_{10}Na$ 1097,43; found 1097,42.

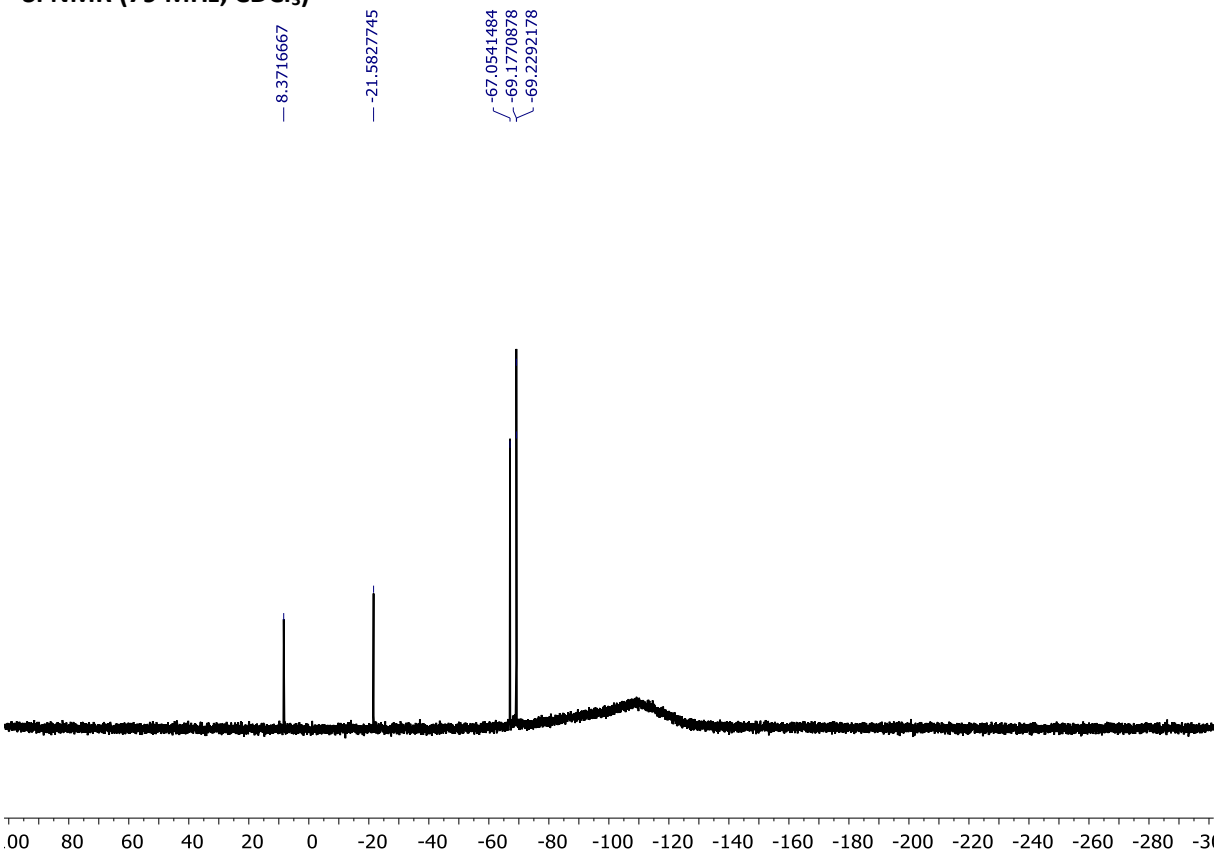
^{1}H NMR (300 MHz, $CDCl_3$)



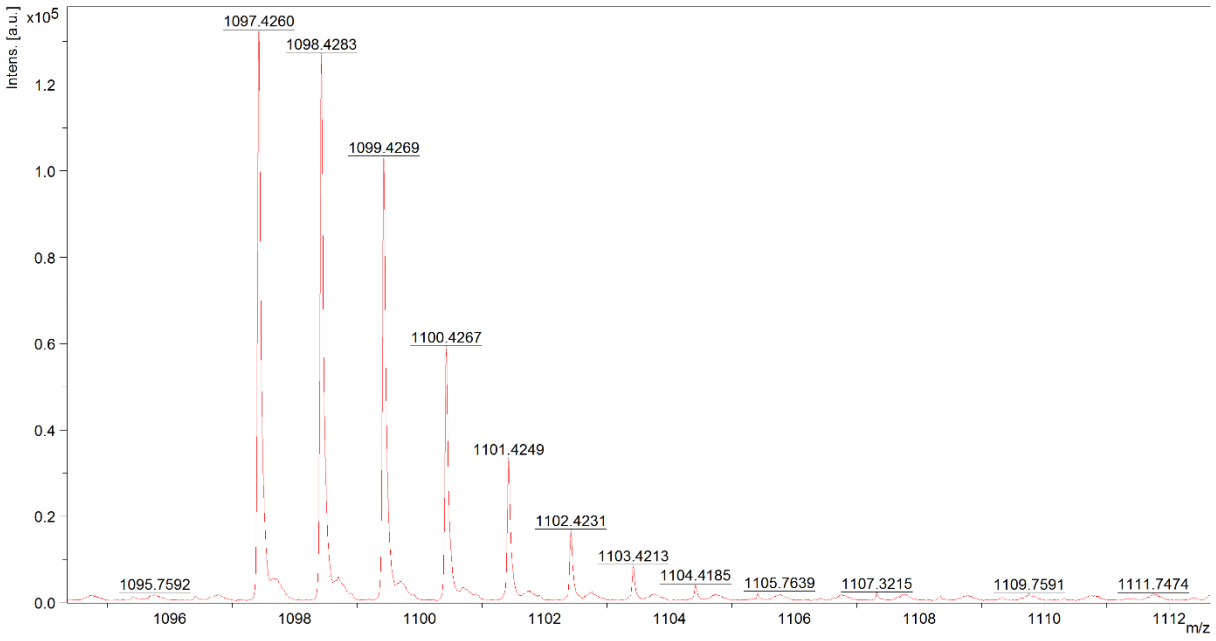
^{13}C NMR (101 MHz, $CDCl_3$)



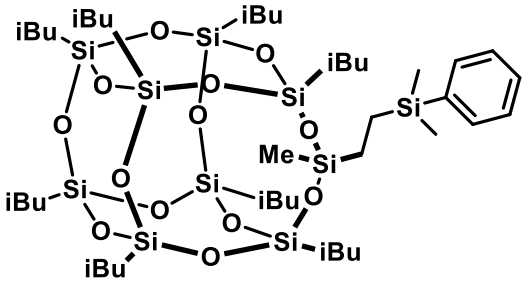
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^5
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1097.4260
1098.4283
1099.4269
1100.4267
1101.4249
1102.4231
1103.4213
1104.4185
1095.7592
1105.7639
1107.3215
1109.7591
1111.7474
1096
1098
1100
1102
1104
1106
1108
1110
1112
m/z

(3f)



Chemical Formula: $C_{43}H_{90}O_{13}Si_{10}$

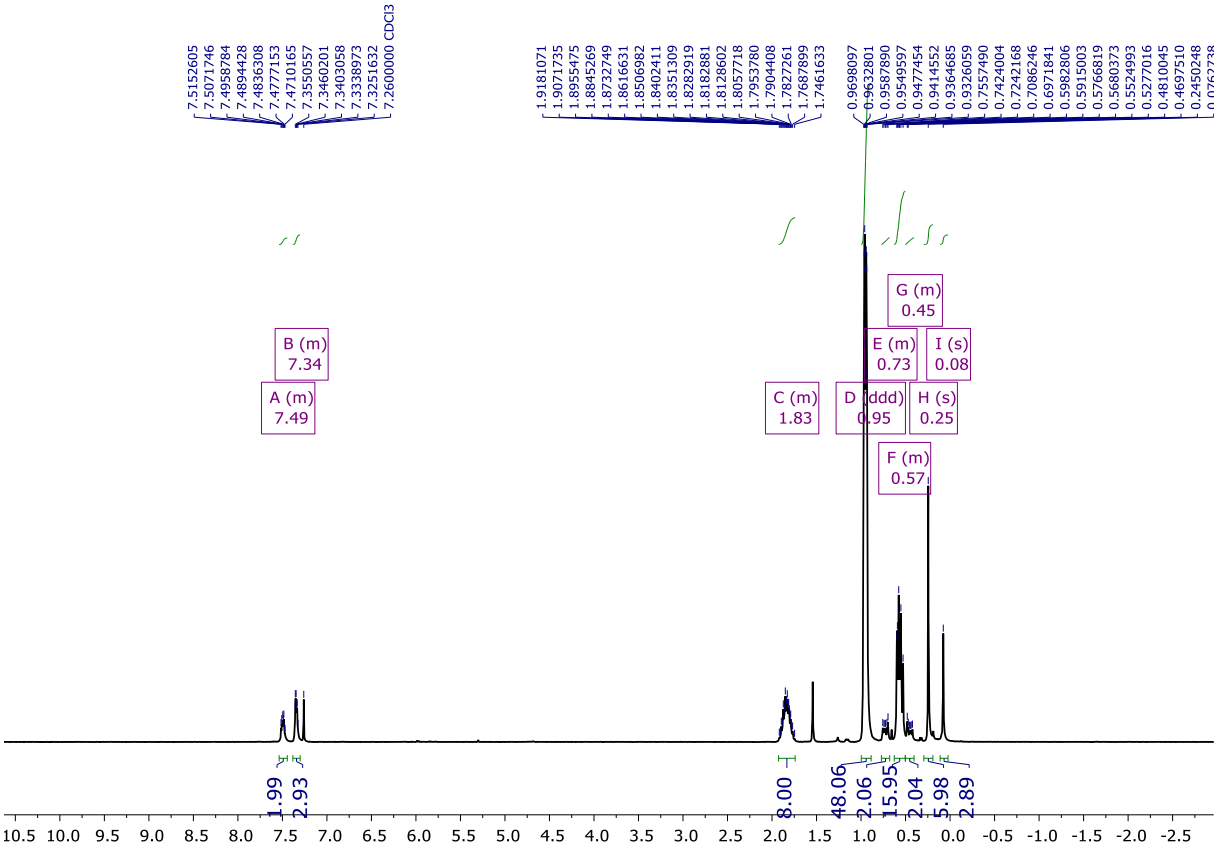
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.53 – 7.44 (m, 2H), 7.38 – 7.31 (m, 3H), 1.93 – 1.73 (m, 8H), 0.95 (ddd, *J* = 6.7, 3.0, 1.6 Hz, 48H), 0.78 – 0.68 (m, 2H), 0.63 – 0.52 (m, 16H), 0.50 – 0.40 (m, 2H), 0.25 (s, 6H), 0.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.63, 133.75, 128.89, 127.83, 25.98, 25.95, 25.88, 25.87, 25.82, 24.24, 24.11, 24.04, 23.89, 23.25, 22.66, 9.06, 6.70, -1.69, -3.44.

^{29}Si NMR (79 MHz, $CDCl_3$) δ -1.27, -21.72, -67.05, -69.14, -69.17, -69.22.

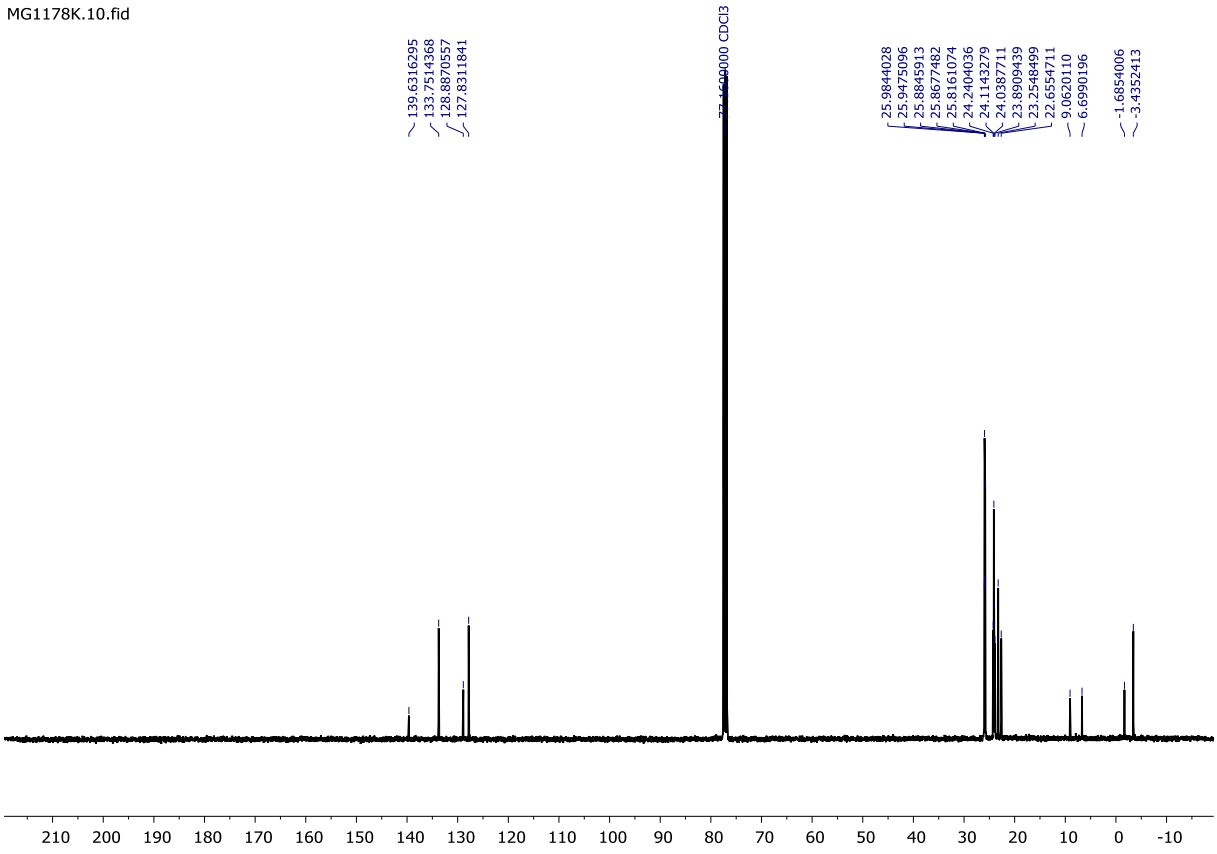
MALDI-TOF MS (m/z): calcd. for $C_{43}H_{90}O_{13}Si_{10}Na$ 1117,40; found 1117,39.

^{1}H NMR (300 MHz, $CDCl_3$)



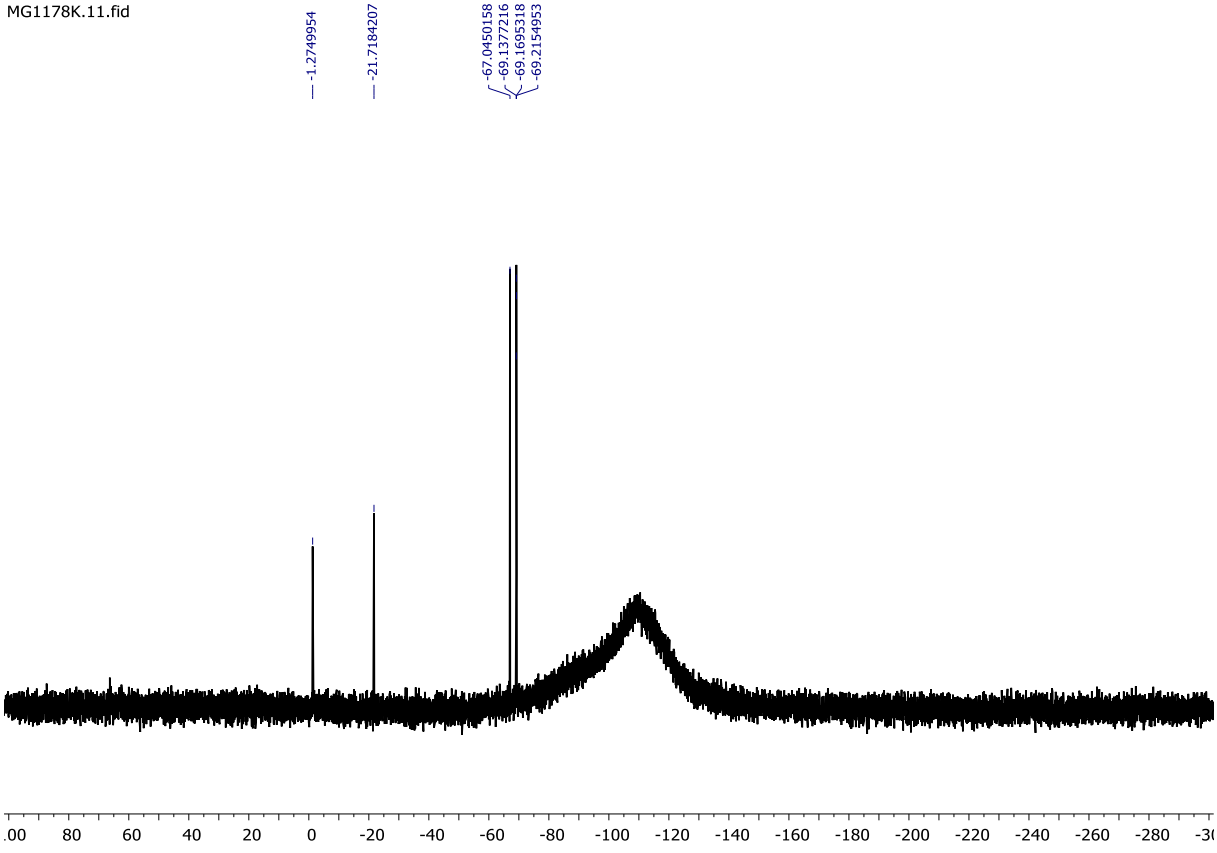
^{13}C NMR (101 MHz, $CDCl_3$)

MG1178K.10.fid

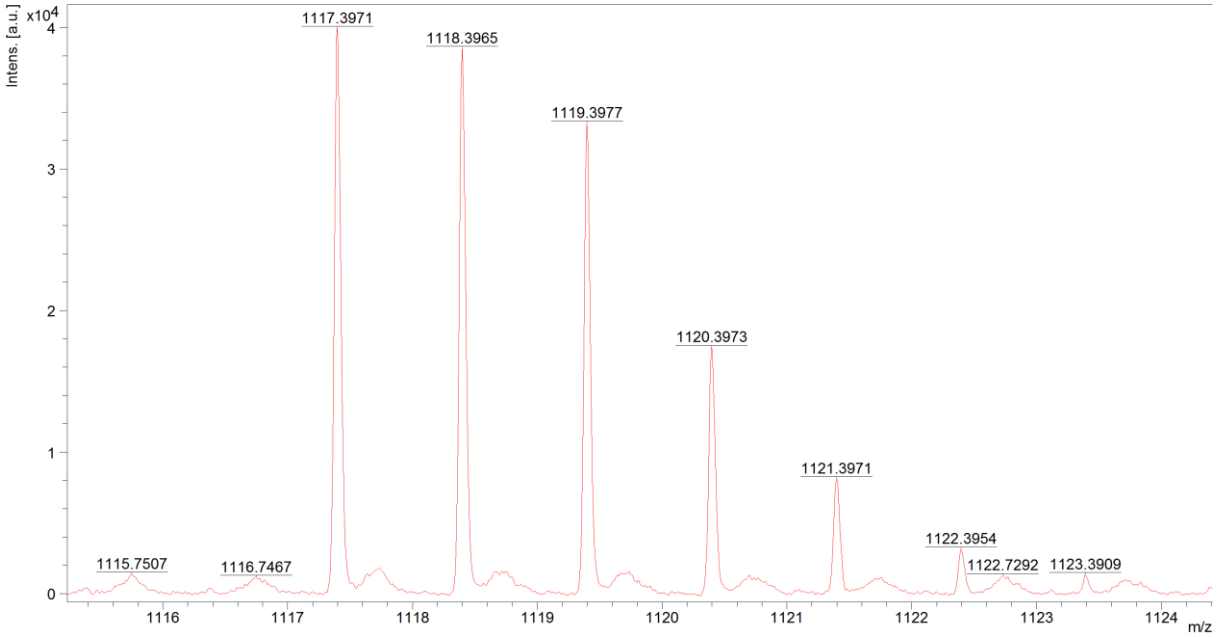


^{29}Si NMR (79 MHz, $CDCl_3$)

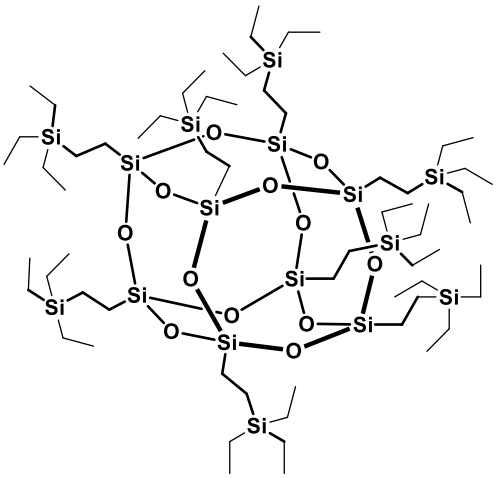
MG1178K.11.fid



MALDI-TOF


Intens. [a.u.]
x10^4
4
3
2
1
0
1117.3971
1118.3965
1119.3977
1120.3973
1121.3971
1122.3954
1122.7292
1123.3909
1115.7507
1116.7467
1116
1117
1118
1119
1120
1121
1122
1123
1124
m/z

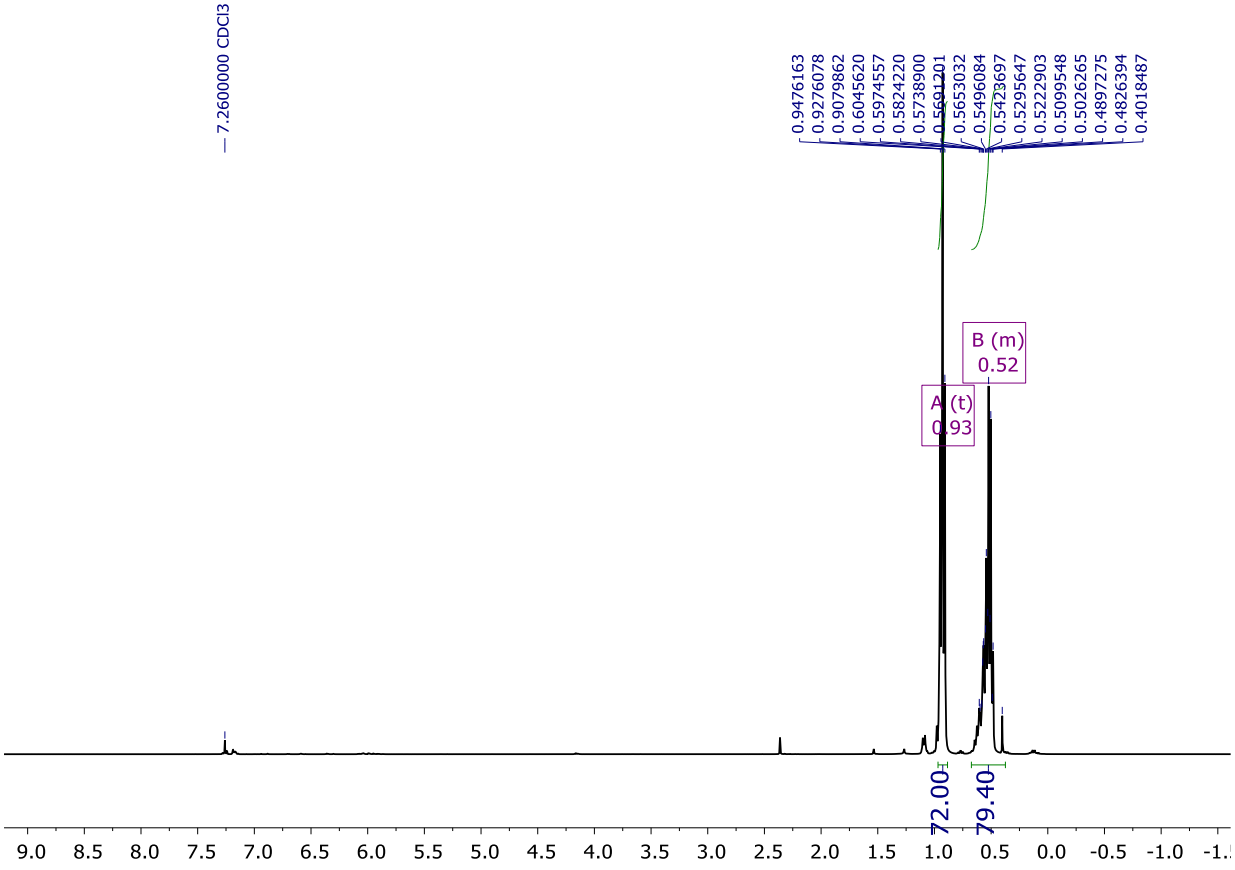
(5e)



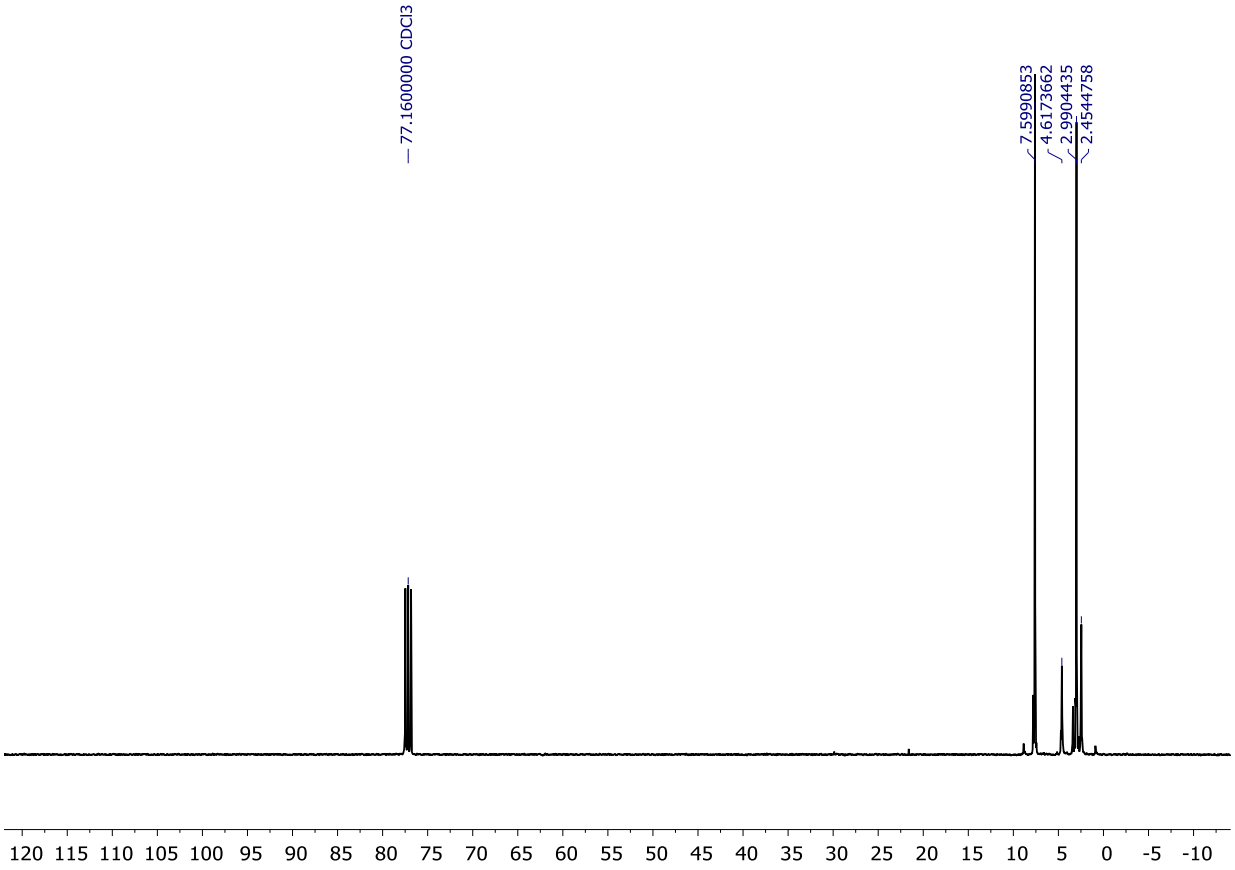
Chemical Formula: $C_{64}H_{152}O_{12}Si_{16}$

^{1}H NMR (400 MHz, Chloroform-d) δ 0.93 (t, J = 7.9 Hz, 72H), 0.65 – 0.40 (m, 80H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 7.60, 4.62, 2.99, 2.45.
^{29}Si NMR (79 MHz, $CDCl_3$) δ 8.44, -66.34.

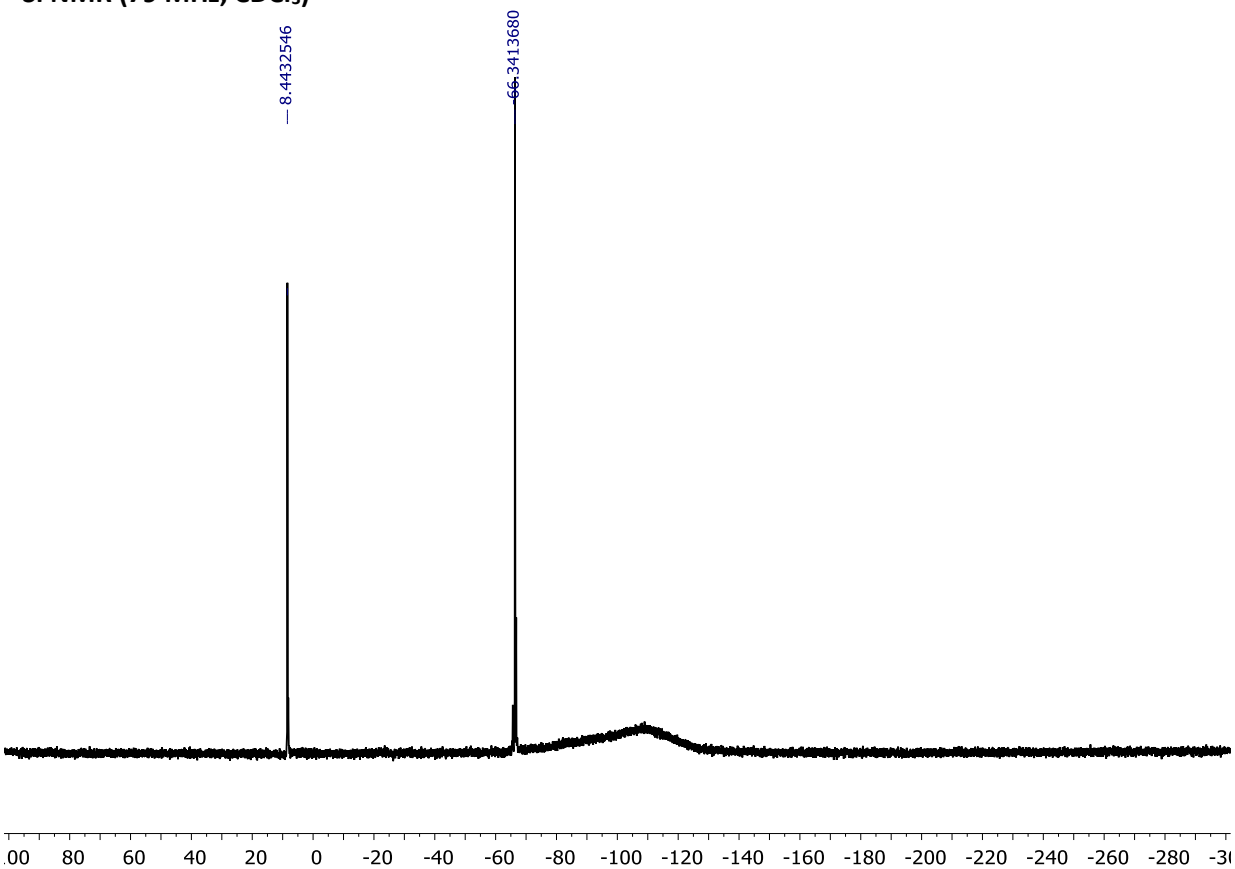
^{1}H NMR (400 MHz, $CDCl_3$)



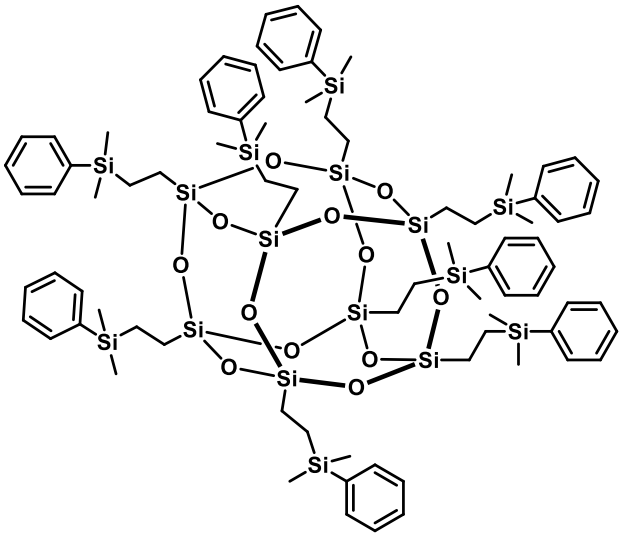
^{13}C NMR (101 MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)



(5f)



Chemical Formula: $C_{80}H_{120}O_{12}Si_{16}$

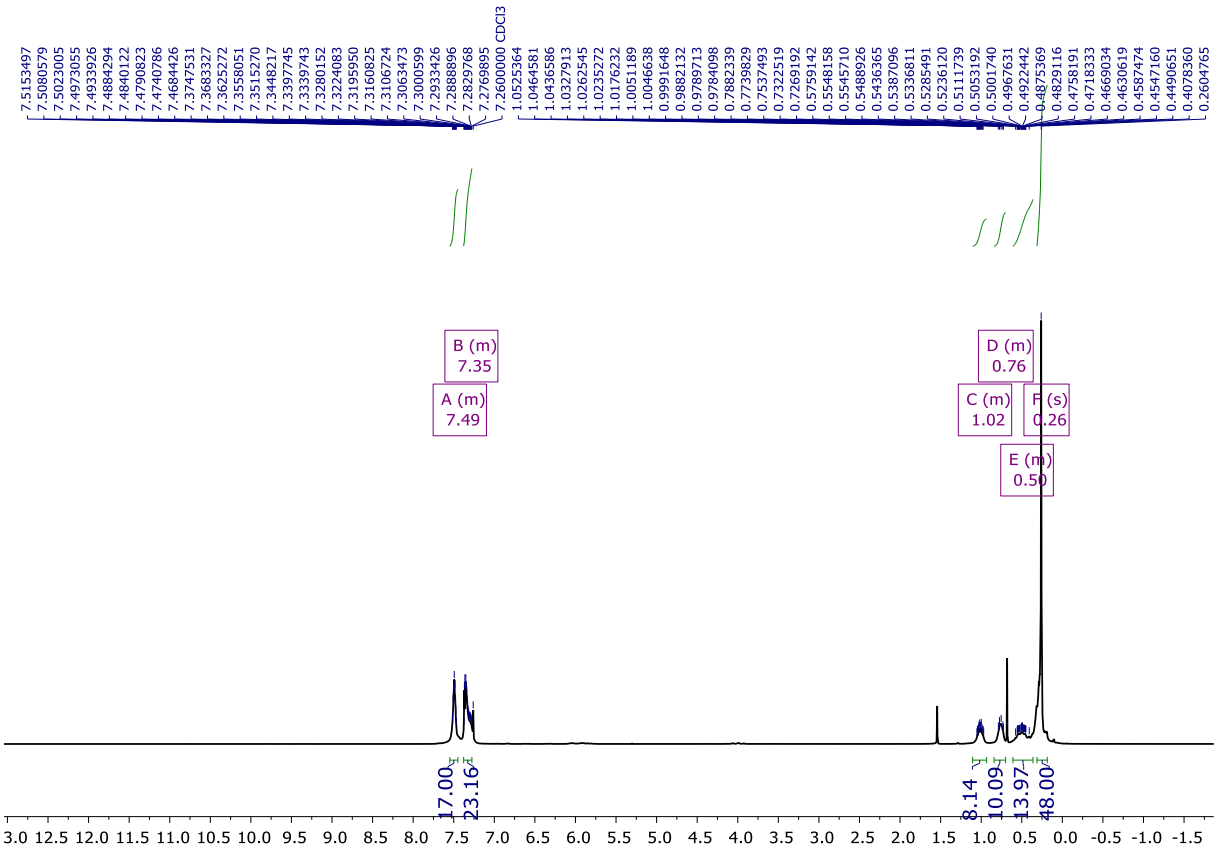
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 17H), 7.38 – 7.27 (m, 23H), 1.10 – 0.95 (m, 8H), 0.82 – 0.71 (m, 10H), 0.60 – 0.40 (m, 14H), 0.26 (s, 48H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.52, 139.24, 133.92, 133.79, 133.73, 128.98, 128.92, 127.90, 127.84, 127.73, 8.98, 8.81, 7.94, 7.22, 4.63, 3.95, -3.45

^{29}Si NMR (79 MHz, $CDCl_3$) δ -1.20, -1.37, -66.02, -66.14, -66.18, -66.23, -66.43, -66.74, -66.98, -67.02.

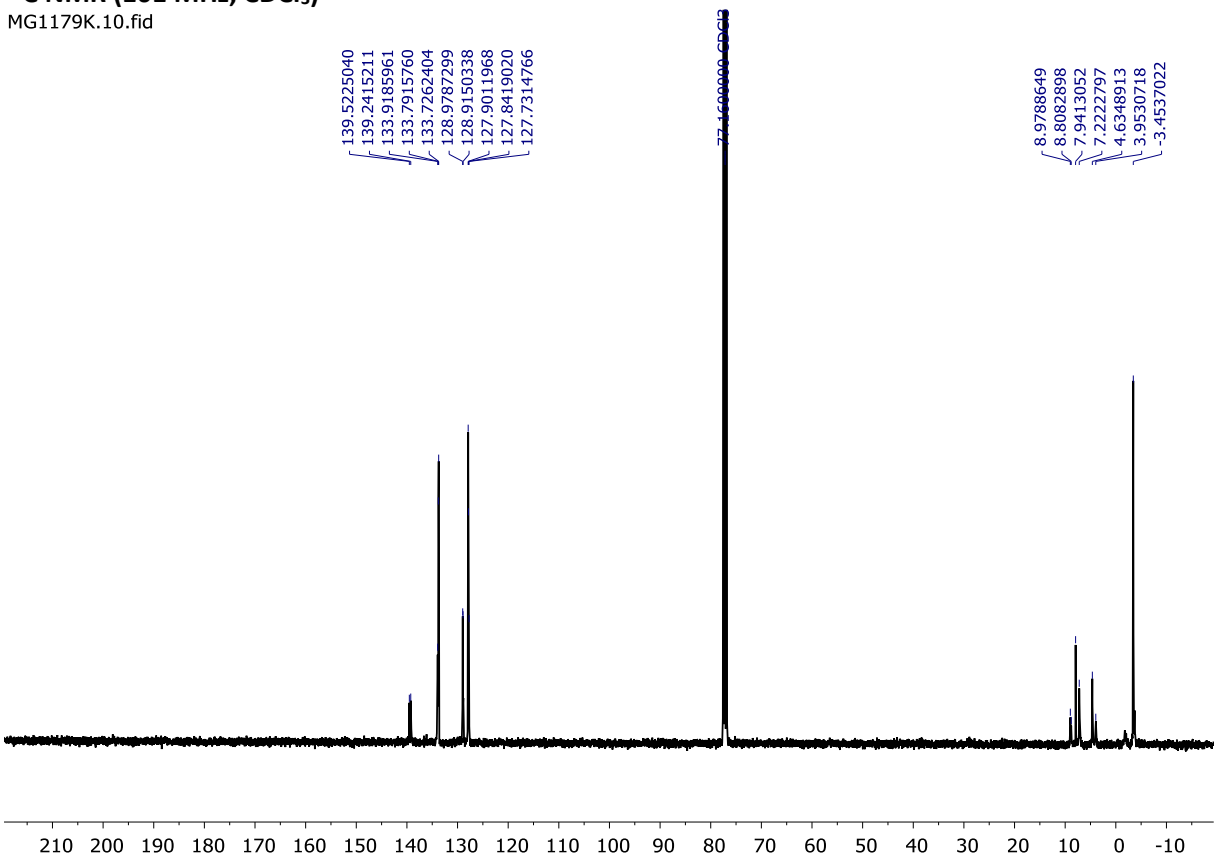
MALDI-TOF MS (m/z): calcd. for $C_{80}H_{120}O_{12}Si_{16}Na$ 1743,50; found 1745,50.

^{1}H NMR (400 MHz, $CDCl_3$)



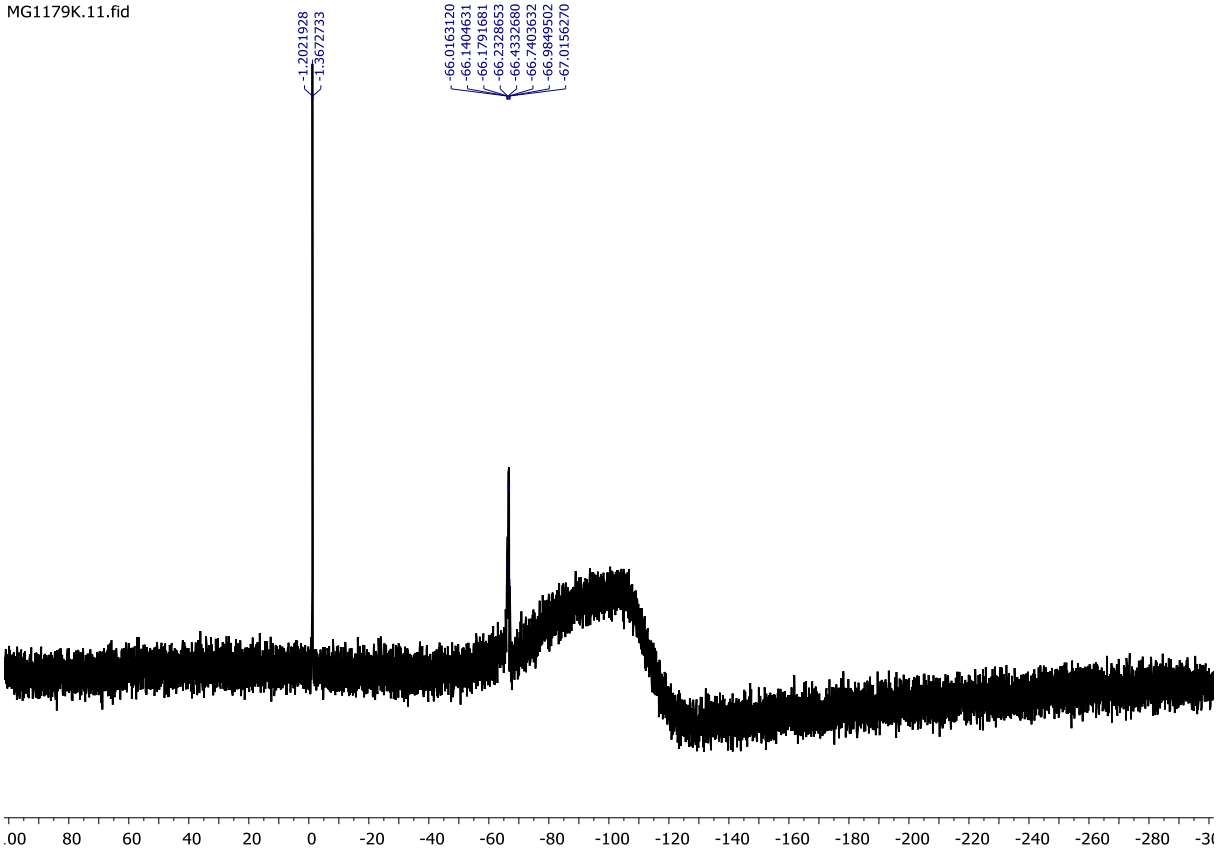
^{13}C NMR (101 MHz, $CDCl_3$)

MG1179K.10.fid

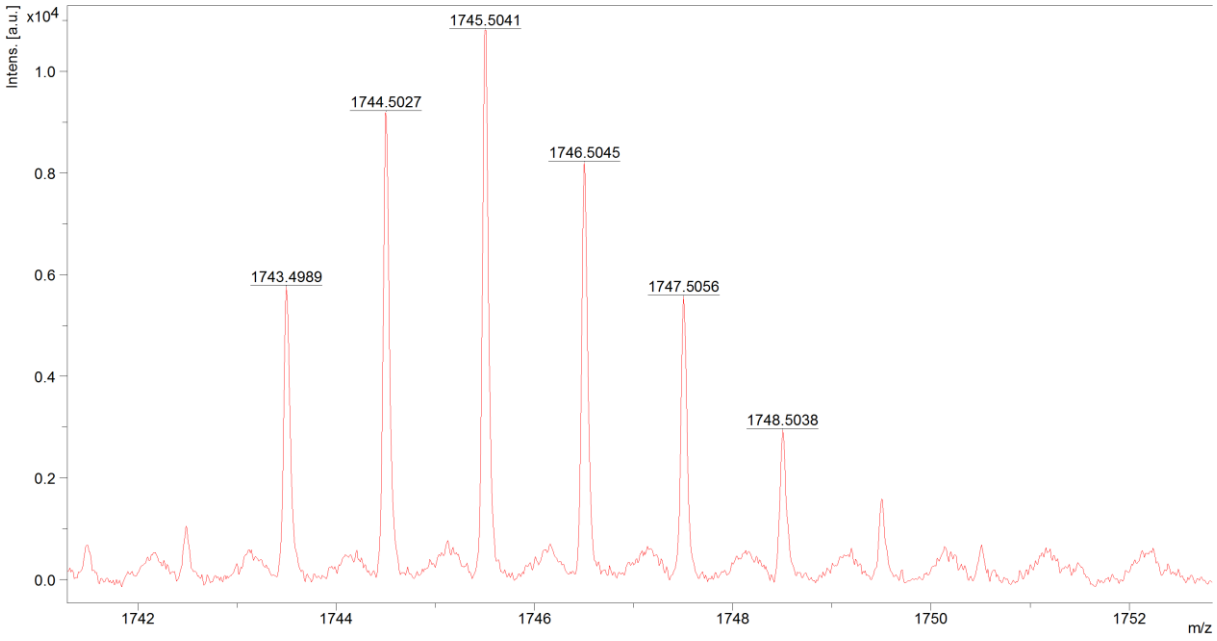


^{29}Si NMR (79 MHz, $CDCl_3$)

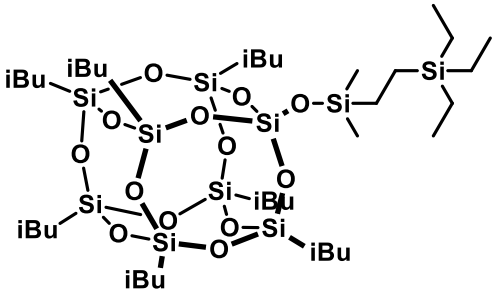
MG1179K.11.fid



MALDI-TOF


Intens. [a.u.]
x10^4
1.0
0.8
0.6
0.4
0.2
0.0
1743.4989
1744.5027
1745.5041
1746.5045
1747.5056
1748.5038
1742
1744
1746
1748
1750
1752
m/z

(6e)



Chemical Formula: $C_{38}H_{88}O_{13}Si_{10}$

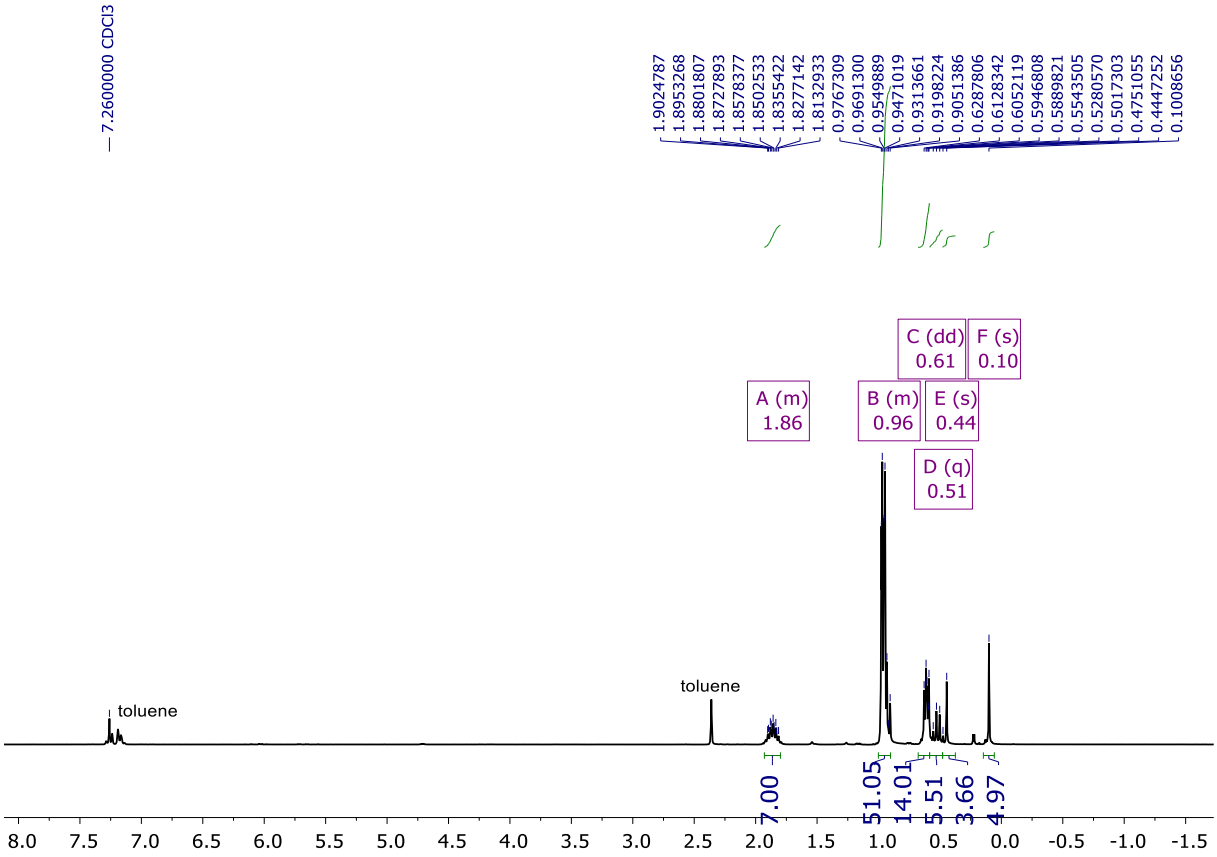
^{1}H NMR (300 MHz, Chloroform-*d*) δ 1.93 – 1.80 (m, 7H), 1.00 – 0.90 (m, 51H), 0.61 (dd, *J* = 7.1, 4.8 Hz, 14H), 0.51 (q, *J* = 7.9 Hz, 6H), 0.44 (s, 4H), 0.10 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 25.85, 24.01, 23.99, 22.66, 22.61, 22.57, 22.50, 21.61, 9.79, 7.64, 3.03, 2.24, -0.94.

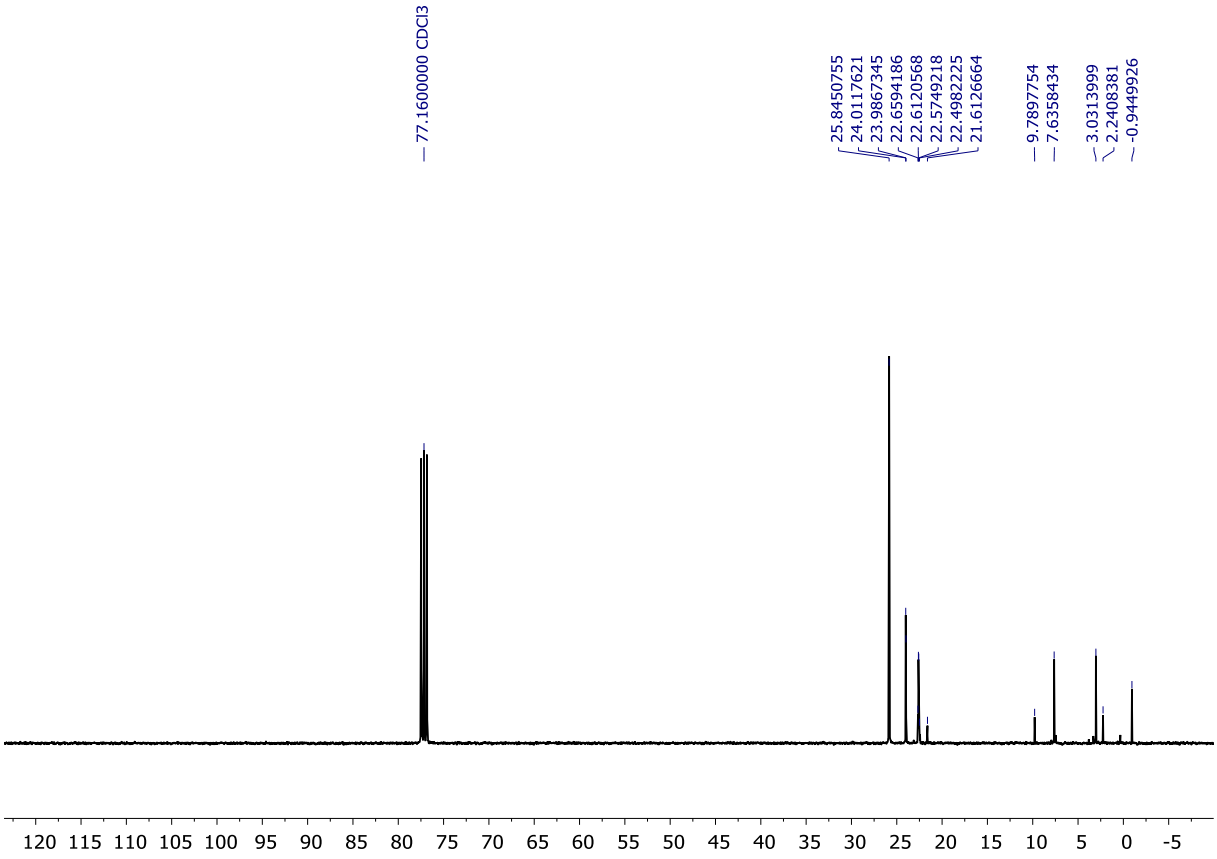
^{29}Si NMR (79 MHz, $CDCl_3$) δ 11.87, 8.42, -67.09, -67.88, -109.58.

MALDI-TOF MS (m/z): calcd. for $C_{38}H_{88}O_{13}Si_{10}Na$ 1055,38; found 1055,38.

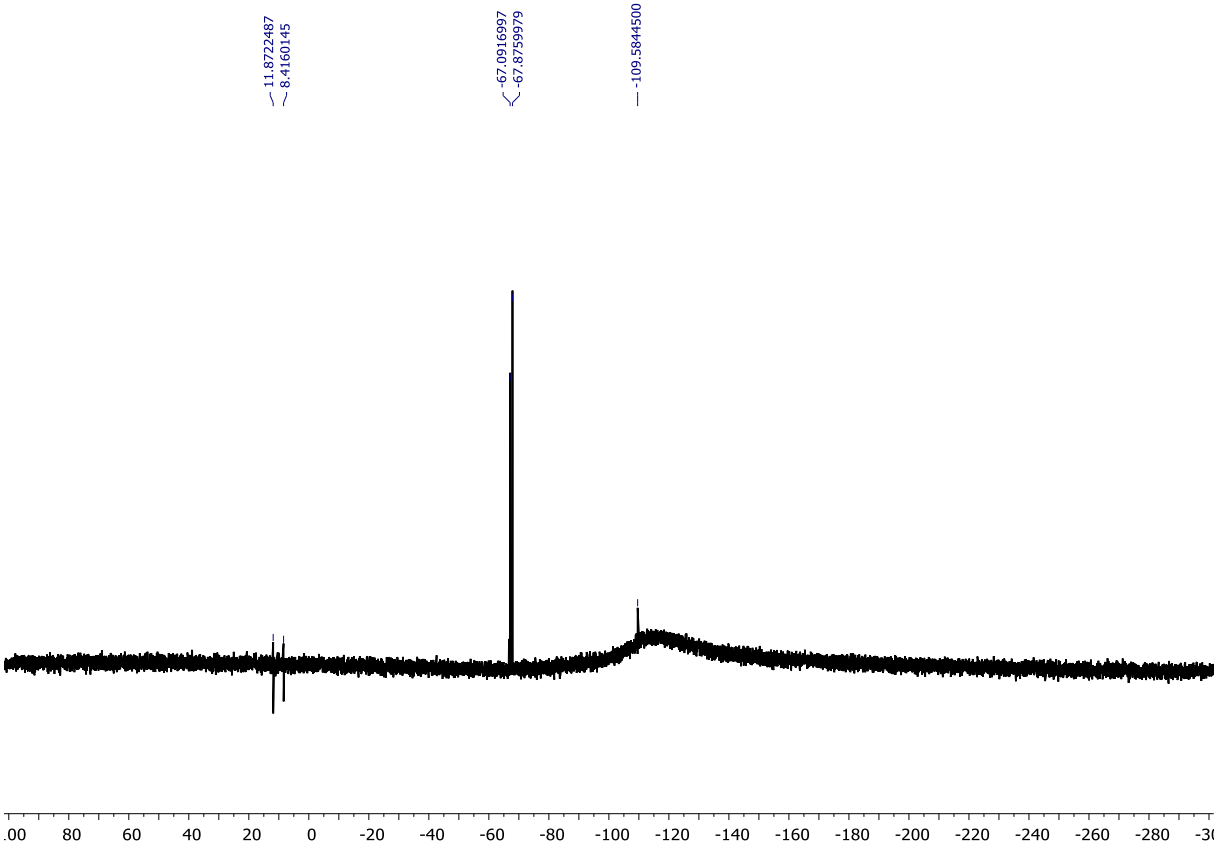
^{1}H NMR (300 MHz, $CDCl_3$)



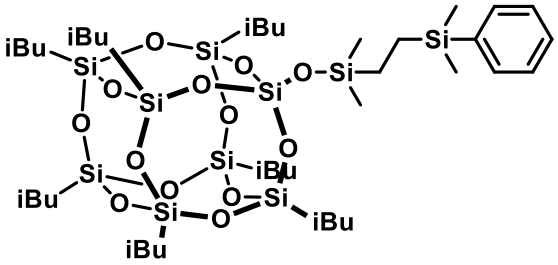
^{13}C NMR (101 MHz, $CDCl_3$)



^{29}Si NMR (79 MHz, $CDCl_3$)



(6f)



Chemical Formula: $C_{40}H_{84}O_{13}Si_{10}$

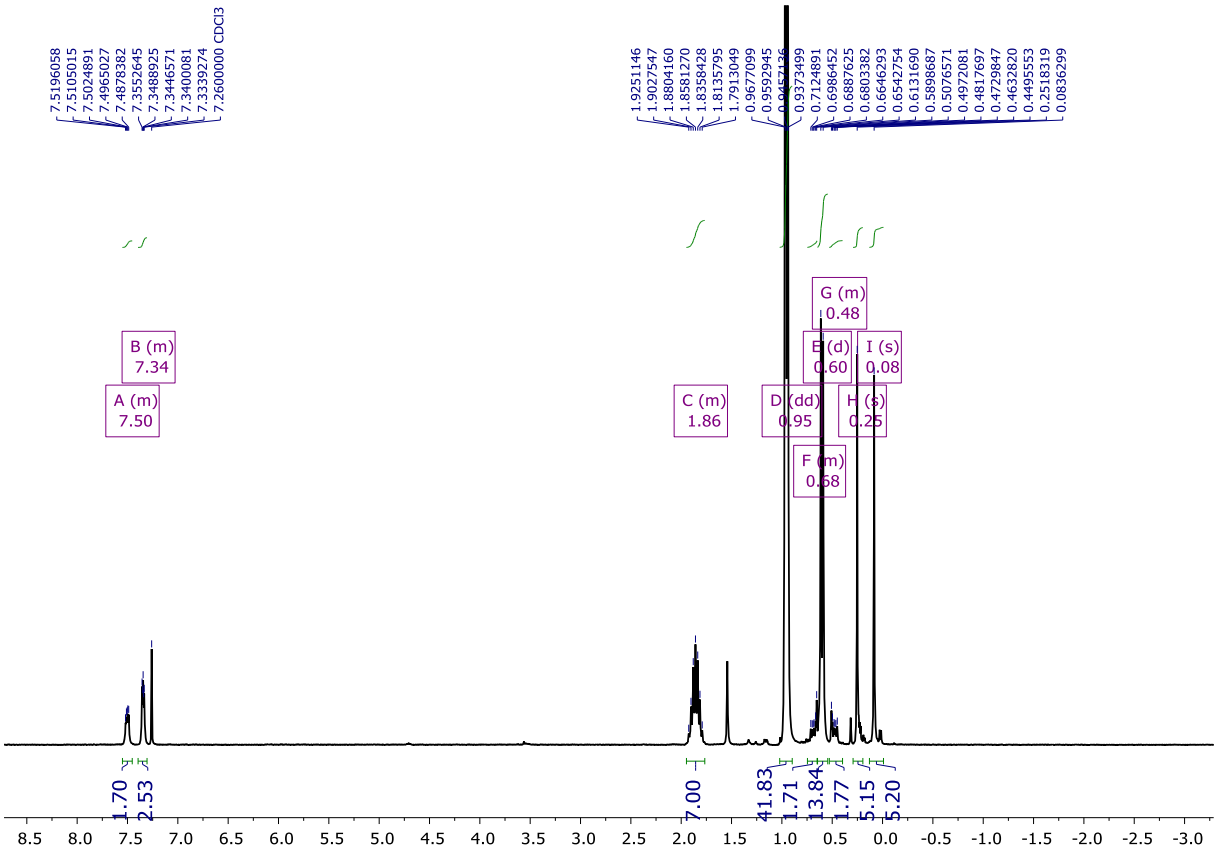
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.55 – 7.45 (m, 2H), 7.39 – 7.32 (m, 3H), 1.95 – 1.77 (m, 7H), 0.95 (dd, *J* = 6.6, 2.5 Hz, 42H), 0.74 – 0.64 (m, 2H), 0.60 (d, *J* = 7.0 Hz, 14H), 0.53 – 0.44 (m, 2H), 0.25 (s, 6H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.61, 133.78, 128.89, 127.85, 25.85, 24.01, 22.62, 9.92, 6.95, -0.88, -3.43.

^{29}Si NMR (79 MHz, $CDCl_3$) δ 11.87, -1.29, -67.08, -67.87, -109.61.

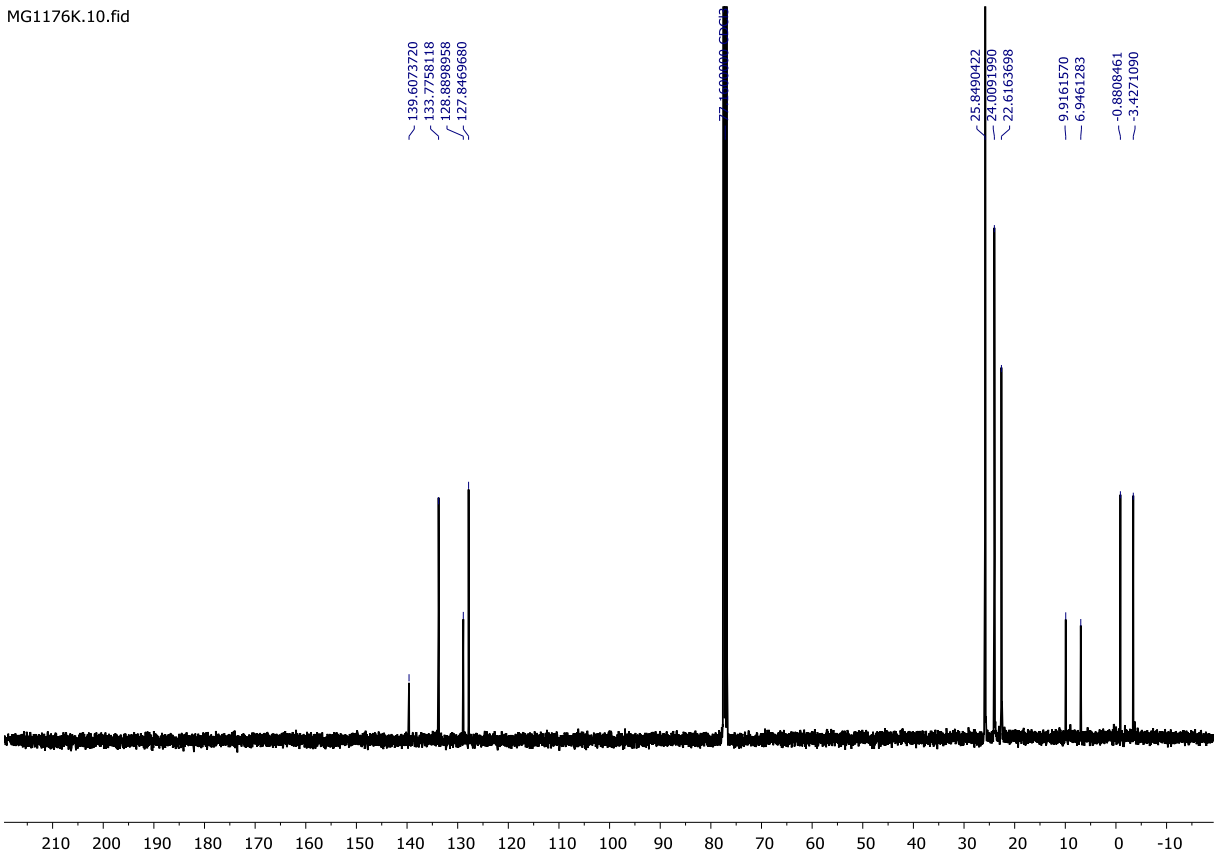
MALDI-TOF MS (m/z): calcd. for $C_{40}H_{84}O_{13}Si_{10}Na$ 1075,35; found 1075,35.

^{1}H NMR (300 MHz, $CDCl_3$)



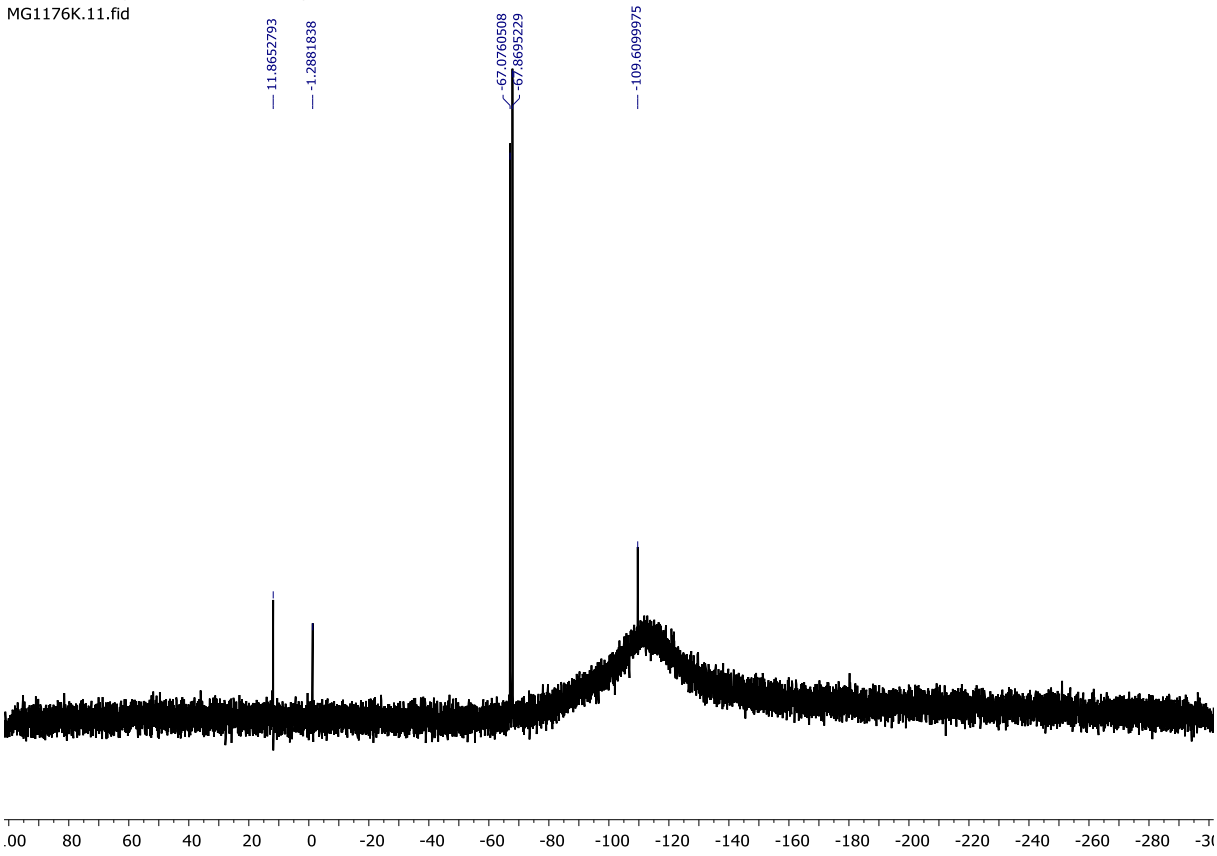
^{13}C NMR (101 MHz, $CDCl_3$)

MG1176K.10.fid

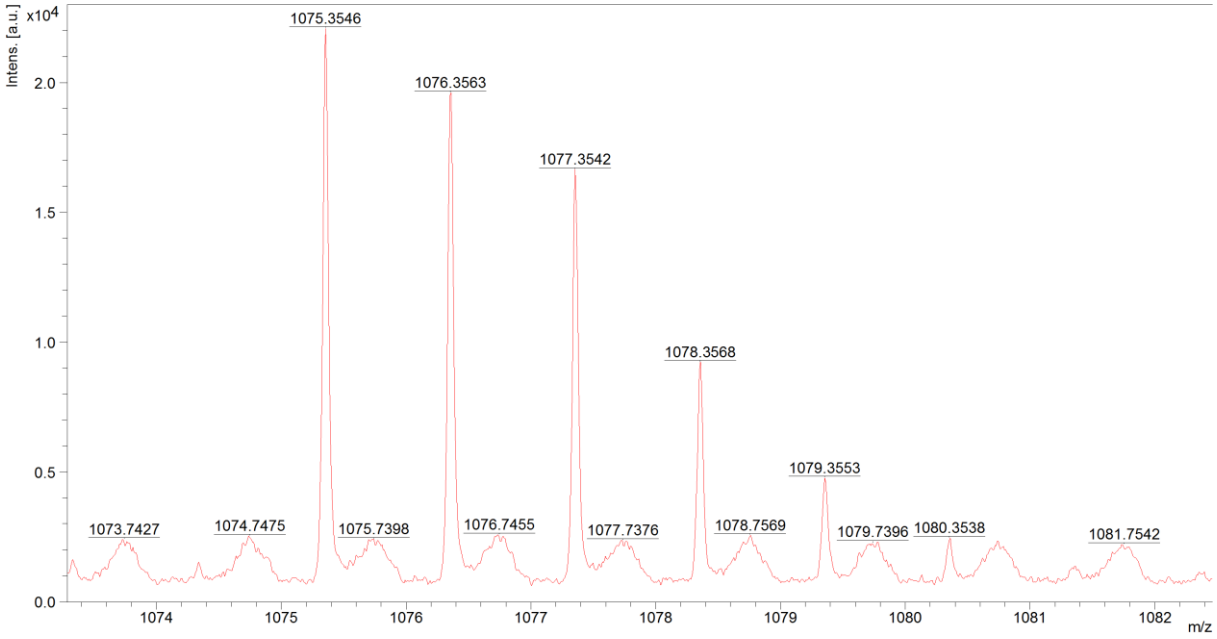


^{29}Si NMR (79 MHz, $CDCl_3$)

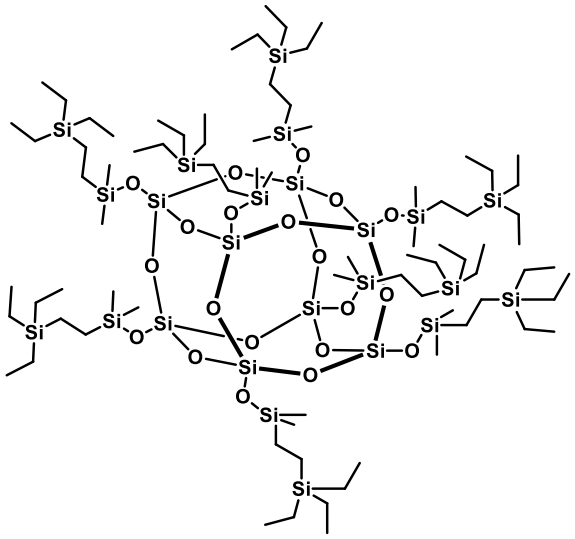
MG1176K.11.fid



MALDI-TOF


Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
1075.3546
1076.3563
1077.3542
1078.3568
1079.3553
1073.7427
1074.7475
1075.7398
1076.7455
1077.7376
1078.7569
1079.7396
1080.3538
1081.7542
1074
1075
1076
1077
1078
1079
1080
1081
1082
m/z

(7e)



Chemical Formula: $C_{80}H_{200}O_{20}Si_{24}$

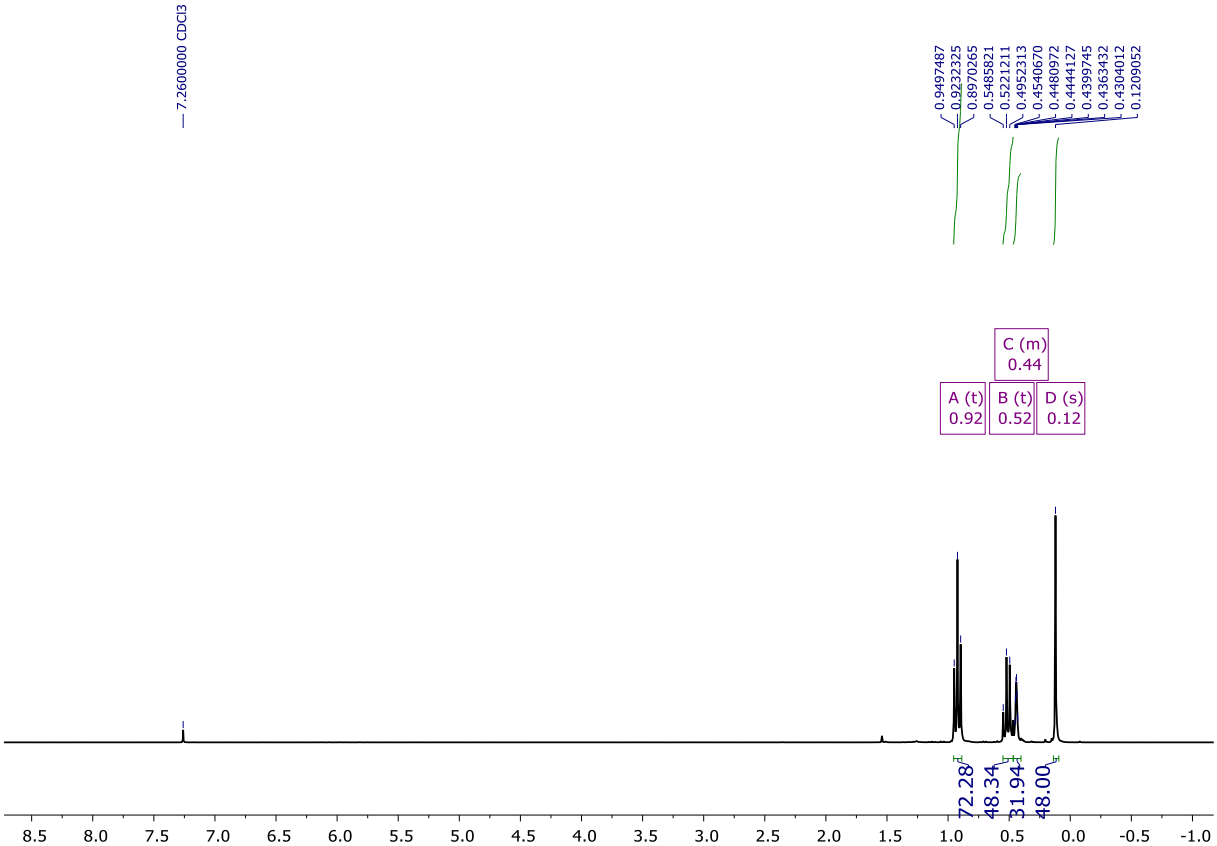
^{1}H NMR (300 MHz, Chloroform-*d*) δ 0.92 (t, *J* = 7.9 Hz, 72H), 0.52 (t, *J* = 8.0 Hz, 48H), 0.46 – 0.41 (m, 32H), 0.12 (s, 48H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 9.64, 7.62, 2.99, 2.18, -1.00.

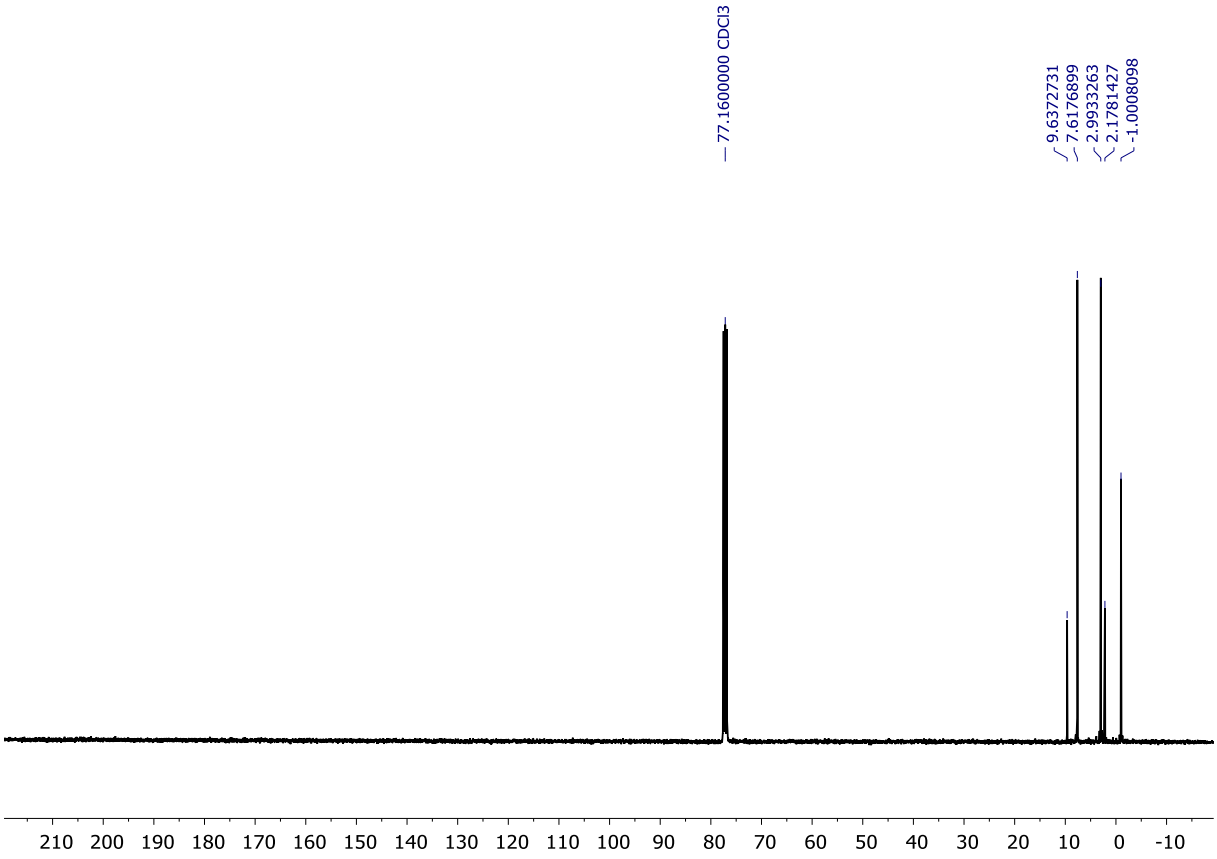
^{29}Si NMR (79 MHz, $CDCl_3$) δ 12.79, 8.44, -108.82.

MALDI-TOF MS (m/z): calcd. for $C_{80}H_{200}O_{20}Si_{24}Na$ 2175,90; found 2178,89.

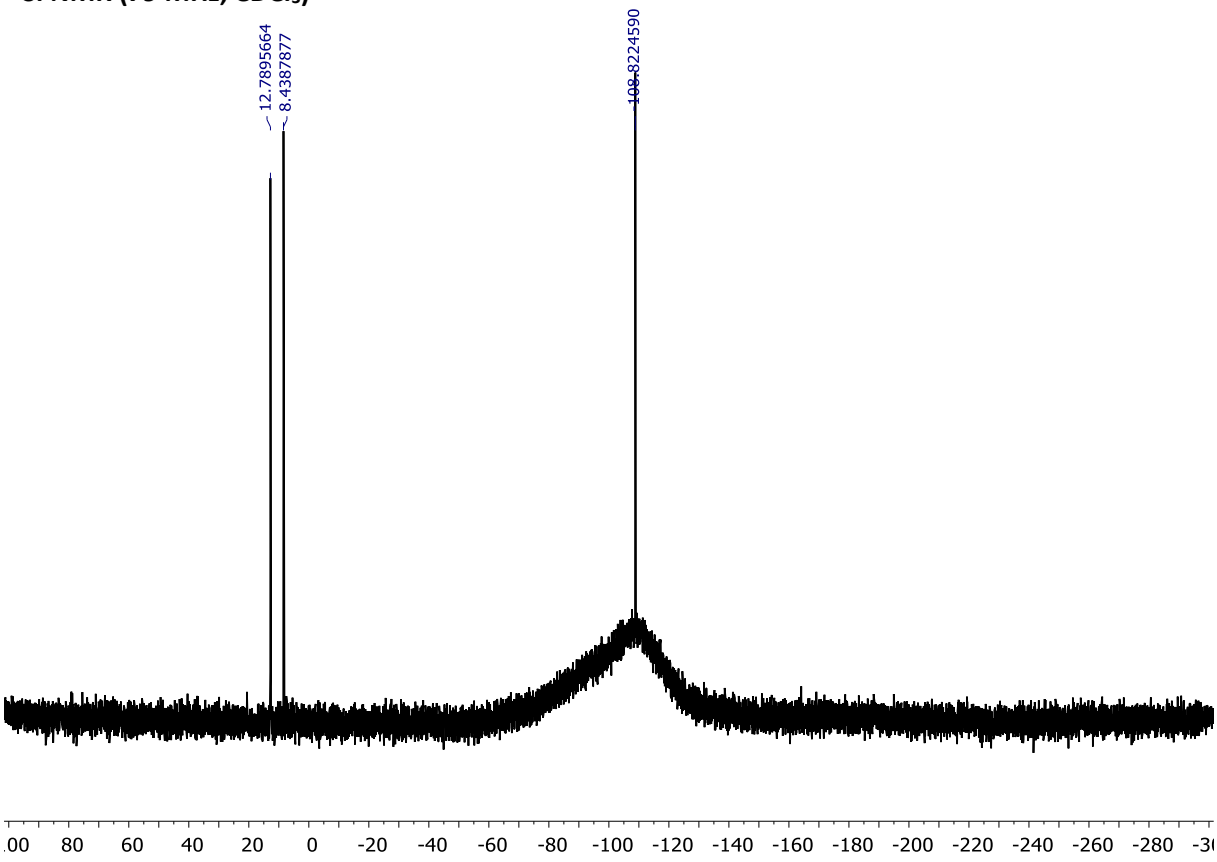
^{1}H NMR (300 MHz, $CDCl_3$)



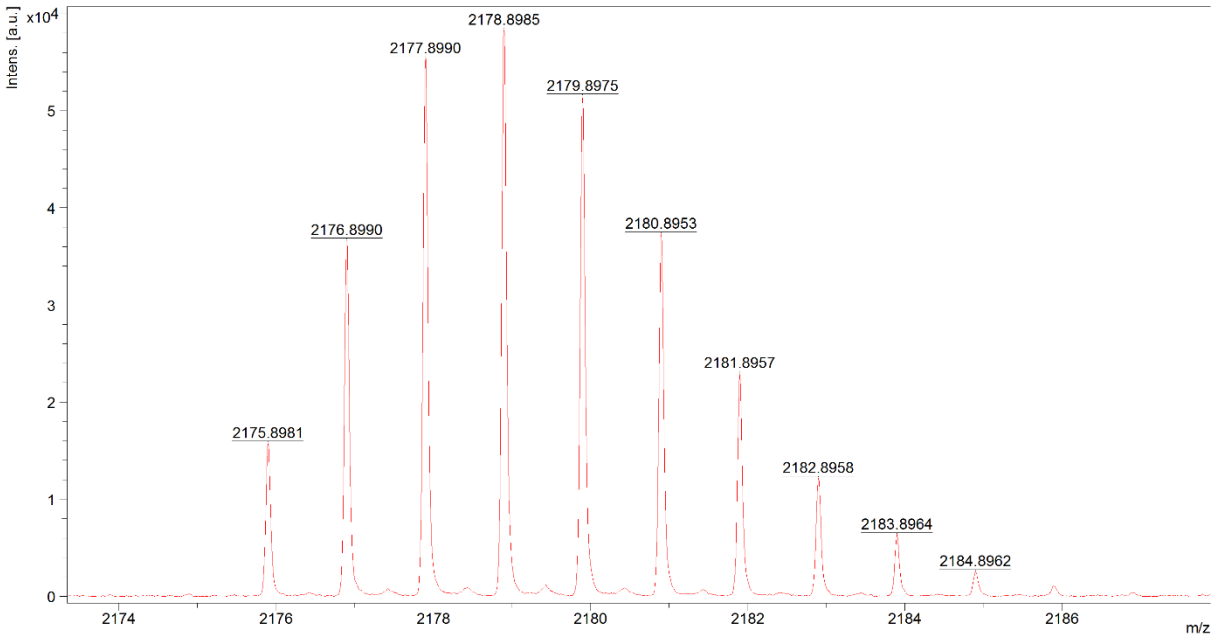
^{13}C NMR (101 MHz, $CDCl_3$)



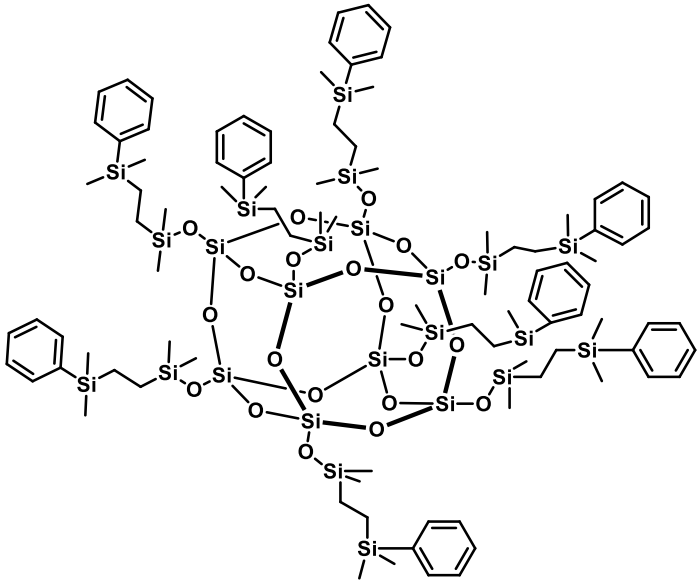
^{29}Si NMR (79 MHz, $CDCl_3$)



MALDI-TOF


Intens. [a.u.]
x10^4
5
4
3
2
1
0
2175.8981
2176.8990
2177.8990
2178.8985
2179.8975
2180.8953
2181.8957
2182.8958
2183.8964
2184.8962
2174
2176
2178
2180
2182
2184
2186
m/z

(7f)



Chemical Formula: $C_{95}H_{168}O_{20}Si_{24}$

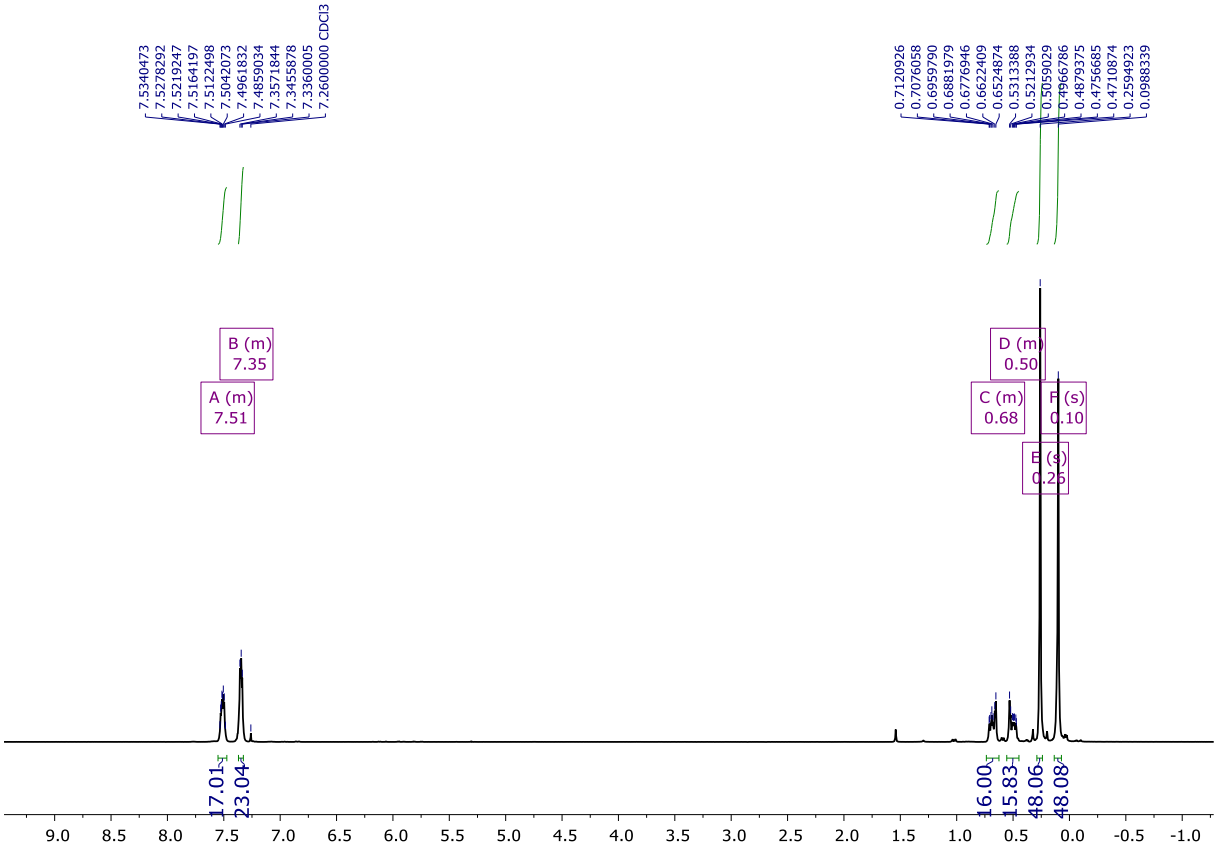
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 17H), 7.37 – 7.32 (m, 23H), 0.74 – 0.63 (m, 16H), 0.55 – 0.47 (m, 16H), 0.26 (s, 48H), 0.10 (s, 48H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.48, 133.78, 128.89, 127.85, 9.79, 6.91, -0.85, -3.38.

^{29}Si NMR (79 MHz, $CDCl_3$) δ 13.11, -1.28, -108.74.

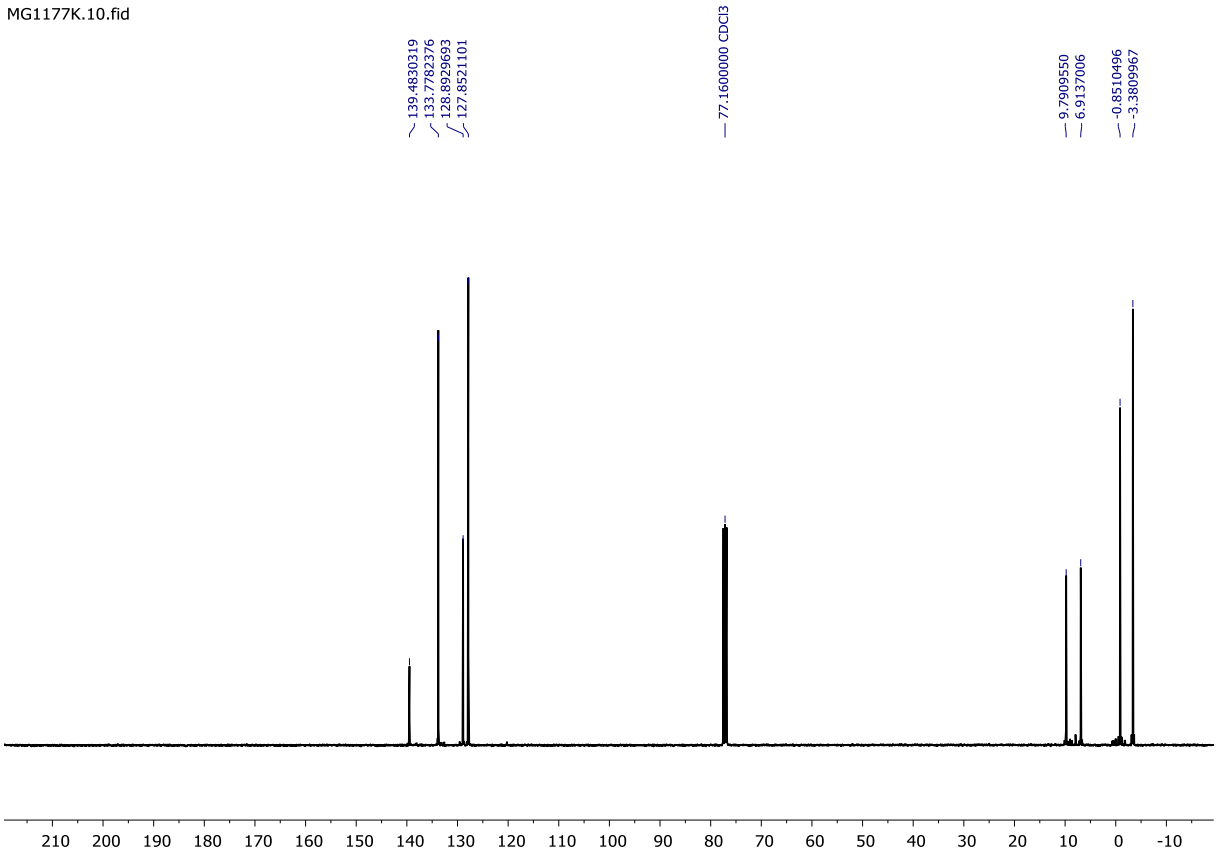
MALDI-TOF MS (m/z): calcd. for $C_{95}H_{168}O_{20}Si_{24}K$ 2339,62; found 2338,64.

^{1}H NMR (300 MHz, $CDCl_3$)



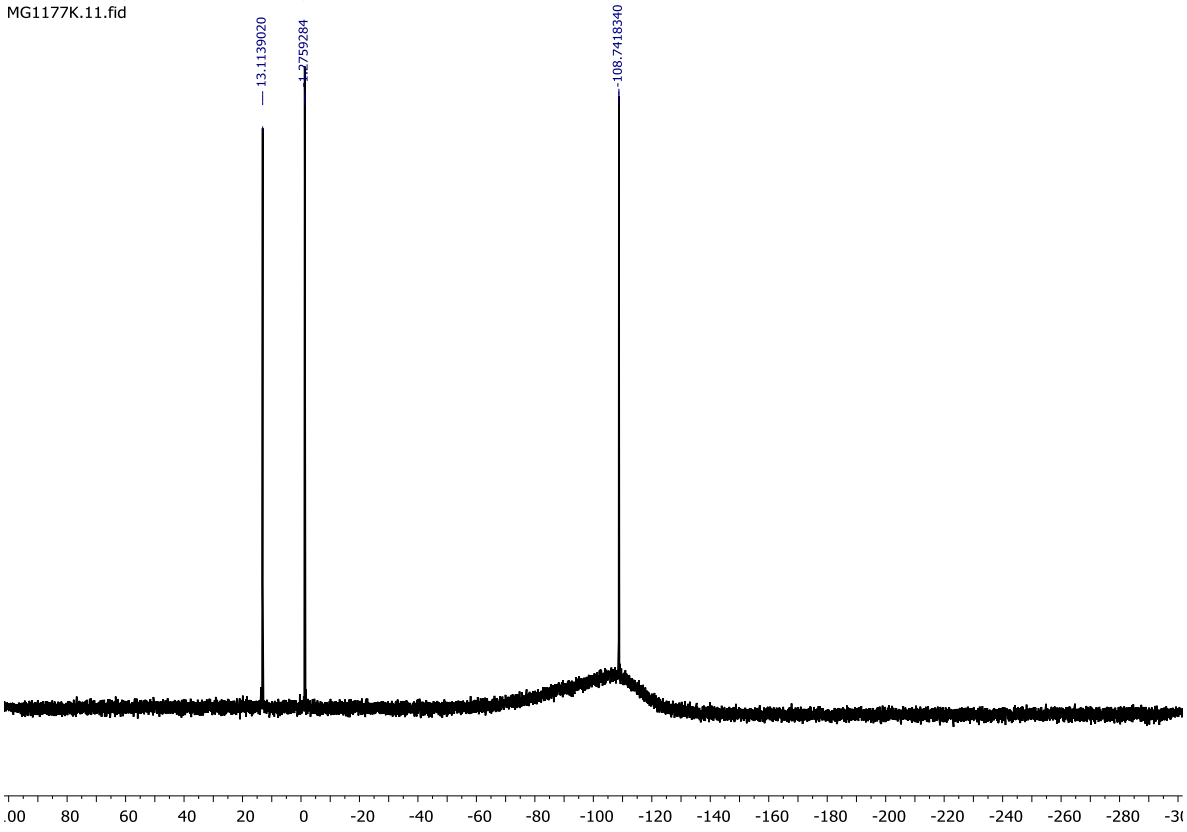
^{13}C NMR (101 MHz, $CDCl_3$)

MG1177K.10.fid

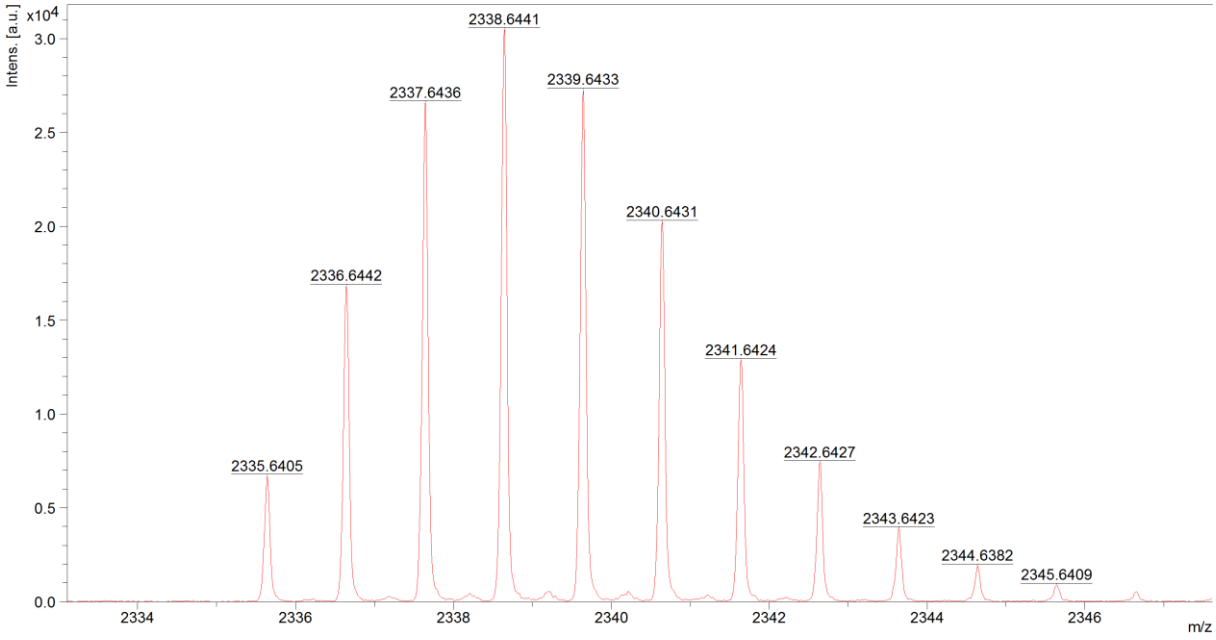


^{29}Si NMR (79 MHz, $CDCl_3$)

MG1177K.11.fid



MALDI-TOF


Intens. [a.u.]
x10^4
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2335.6405
2336.6442
2337.6436
2338.6441
2339.6433
2340.6431
2341.6424
2342.6427
2343.6423
2344.6382
2345.6409
2334
2336
2338
2340
2342
2344
2346
m/z