Supplementary Information for

High-yielding and Facile Synthesis of Organosilicon Compounds containing *m*-Carboranylmethyl Group

Xiao-Jie Han, Hua-Feng Fei, Bo-Zheng Liu, Yong-Xia Tan, Xue-Zhong Zhang, Ze-Min Xie, and Zhi-Jie Zhang*

Laboratory of Advanced Polymer Materials, Institute of Chemistry Chinese Academy of Sciences Zhongguancun North First Street 2,100190 Beijing (China)

College of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, No.19A Yuquan Road, Beijing 100049 (China)

Table of contents

1. General

All moisture sensitive reactions were carried out in flame-dried glassware under nitrogen atmosphere. The solvents used were purified by distillation over the drying agents indicated and were transferred under nitrogen: Et_2O (Na), THF (Na), THP (Na), CH_2Cl_2 (CaH_2). All reactions were monitored by thin-layer chromatography (TLC) on gel F_{254} plates using UV light as visualizing agent (if applicable), and a solution of Palladium chloride (0.01 g/L) in 5% aqueous hydrochloric acid (followed by heating as developing agents).

^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ solution on a AVANCE 400 spectrometer, ^{29}Si NMR and ^{11}B NMR spectra were recorded in $CDCl_3$ solution on a Bruker AVIII 500WB respectively. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent ($CHCl_3$ (7.26 ppm), DMSO-d5 (2.50 ppm)) as internal reference for ^1H NMR and the deuterated solvent ($CDCl_3$ (77.00 ppm) or DMSO-d6 (39.51 ppm)) ^{13}C NMR, to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts and to external $Si(Me)_4$ for silicon chemical shifts. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, br = broad, m = multiplet. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the FAB technique or Waters GCT by means of the EI technique or Bruker solariX XR by means of the ESI technique. IR spectra were recorded on a Bruker TENSOR-27 FT-IR spectrometer. The X-ray single-crystal determination was performed on a Rigaku RAXIS RAPID IP X-ray single crystal diffractometer. GC was carried out on a SHIMADZU GC-2010. Melting point was afforded by EXSTAR6000 DSC6220.

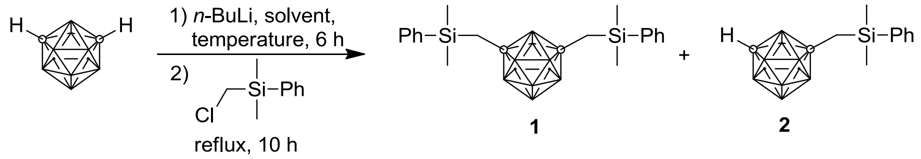
Compounds (chloromethyl)(4-methoxyphenyl)dimethylsilane[1] and (chloromethyl)dimethyl(phenyl)silane were prepared according to literature method.[2] All other chemicals were purchased from Beijing J&K Scientific.

2. Experimental section

2.1 Preparation of 1,7-bis(phenyl(dimethyl)silylmethyl)-m-carborane 1

To a solution of *n*-BuLi (2.5 M solution in *n*-hexane, 4.4 mL, 11 mmol) in dry solvent* (10 mL) was added a solution of *m*-carborane (0.72 g, 5 mmol) in solvent (10 mL). The mixture was stirred at room temperature under nitrogen for 6 h. Following (chloromethyl)dimethyl(phenyl)silane (2.03 g, 11 mmol) was added in one portion, the mixture was refluxed for 10 h. The reaction was quenched with water and the mixture was extracted with ether, the combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the yields were identified by GC.

*Solvent: THF, DE, Dioxane, DME, PhOMe, THP.



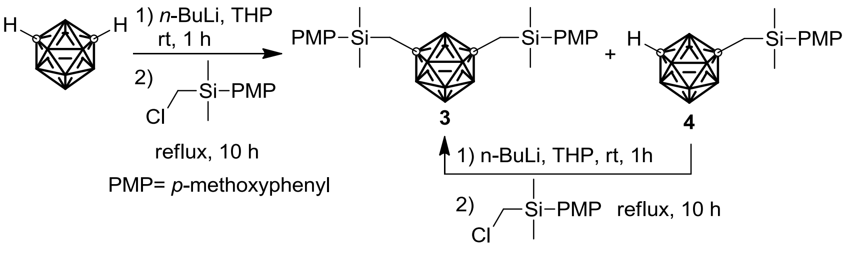
Scheme 1: Preparation of 1,7-bis(phenyl(dimethyl)silylmethyl)-*m*-carborane **1**

2.2 Preparation of 1,7-bis(4-methoxyphenyl(dimethyl)silylmethyl)-*m*-carborane 3

To a solution of *n*-BuLi (2.5 M solution in *n*-hexane, 8.8 mL, 22 mmol) in dry THP (20 mL) was added a solution of *m*-carborane (1.44 g, 10 mmol) in THP (20 mL). The mixture was vigorously stirred at room temperature under nitrogen atmosphere for 1 h (screen was listed in Table S2). Following (chloromethyl)(4-methoxyphenyl)dimethylsilane (4.40 g, 20.5 mmol) was added in one portion, the mixture was refluxed for 10 h. The reaction was quenched with water and the mixture was extracted with ether. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by recrystallization (from *n*-hexane) to afford white solid 1,7-bis(4-methoxyphenyl(dimethyl)silylmethyl)-*m*-carborane **3** (2.50 g, 50% isolated yield).

To the solution of the crude product after recrystallization dissolved in dry THP (20 mL) was added a solution of *n*-BuLi (2.5 M solution in *n*-hexane, 1 mL, 2.5 mmol). The mixture was vigorously stirred at room temperature under nitrogen atmosphere for 1 h. Following (chloromethyl)(4-methoxyphenyl)dimethylsilane (0.54 g, 2.5 mmol)was added in one portion. After refluxing for 10 h, the reaction was quenched with water and the mixture was extracted with ether. The combined extracts were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by recrystallization (from *n*-hexane) to afford **3** 2.1 g. The overall yield of **3** was 88%.

^1H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (d, J=8Hz, 2H, C6H4), 6.96-6.94 (d, J=8Hz, 2H), 3.85 (s, 6H), 3.5-1.3 (br, 10H), 1.67 (s, 4H), 0.36 ppm (s, 12H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 74.2, 25.3, -3.8 ppm. ^{29}Si NMR (500MHz, $CDCl_3$): -4.52 ppm. ^{11}B NMR (500 MHz, $CDCl_3$): δ -7.05, -10.03, -10.76 ppm. IR: ν =2608, 1595, 1502, 1278, 1250, 1112, 1029, 829, cm^{-1}. HRMS (FAB): *m/z* calcd for $C_{22}H_{40}B_{10}Si_2O_2$ $[M+1]^+$: 500.3556. Found: 500.3578. Mp 78.9 °C



Scheme 2: Preparation of 1,7-bis(4-methoxyphenyl(dimethyl)silylmethyl)-*m*-carborane **3**

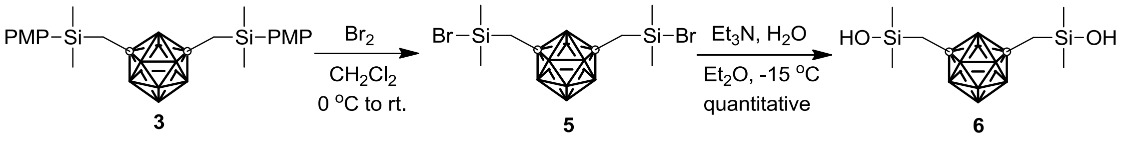
2.3 Preparation of 1,7-bis(hydroxy(dimethyl)silylmethyl)-*m*-carborane 6

To a solution of **3** (1 g, 2 mmol) in dry CH_2Cl_2 (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH_2Cl_2 (30 mL) (10 mL). The reaction mixture was stirred at 0 °C for 30 min; then warmed to room temperature for 10 h. Intermediate **5** was obtained after removing CH_2Cl_2 under reduced pressure. Subsequently, the obtained orange oily liquid **5** was dissolved in anhydrous ether (20 mL) under nitrogen atmosphere. After that, the orange solution was injected to a solution of H_2O (0.144 mL, 8 mmol) and Et_3N (2.8 mL, 20 mmol) in ether (100 mL) by nitrogen through double-tipped needle at -15 °C with vigorous stirring. At the moment, mass of white solid was precipitated immediately. Following the mixture was stirred for another 10 min and filtrated, the filtrate was condensed and recrystallized to afford the expected hydrolysed product 1,7-bis(hydroxy(dimethyl)silylmethyl)-*m*-carborane **6** (0.64g, quantitative) as white solid.

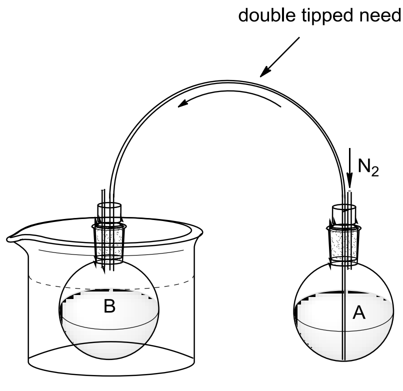
5: ^{29}Si NMR (300MHz, CH_2Cl_2): 21.36 ppm.[a]

6: ^{1}H NMR (400 MHz, D6-DMSO): δ 5.62 (s, 2H), 3.75-1.25 (br, 10H), 1.51 (s, 4H), 0.10 ppm (s, 12*H*). ^{13}C NMR (400 MHz, $CDCl_3$): δ 74.0, 28.7, -0.9 ppm. ^{29}Si NMR (500MHz, $CDCl_3$): 9.51 ppm. ^{11}B NMR (500 MHz, $CDCl_3$): δ -1.06, -2.03, -3.97, -5.00, -5.93, -6.40ppm. IR: ν =3331, 2605, 1259, 1216, 1026, 871, 837, 779 cm^{-1}.HRMS (ESI): *m/z* calcd for $C_8H_{28}B_{10}O_2Si_2$ [M+Na]+: 343.2529. Found: 343.2532. Mp 133.5 °C.

[a] **5** was very sensitive to moisture, ^{1}H and ^{13}C NMR were afforded with difficulty.



Scheme 3: Preparation of 1,7-bis(hydroxy(dimethyl)silylmethyl)-*m*-carborane **6**



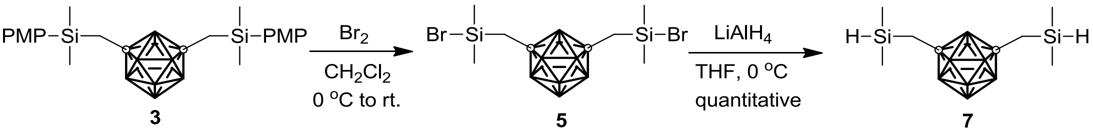
A: solution of **3** in Et_2O
B: solution of H_2O and Et_3N in Et_2O at -15 °C

Fig. 1: The sketch of hydrolysis **5**

2.4 Preparation of 1,7-bis(dimethylsilylmethyl)-*m*-carborane 7

To a solution of **3** (1 g, 2 mmol) in dry CH_2Cl_2 (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 °C for 30 min; then warmed to room temperature for 10 h. Intermediate **5** was obtained after removing CH_2Cl_2 under reduced pressure. Subsequently, the obtained orange oily liquid **5** was dissolved in THF (20 mL) under nitrogen atmosphere. The $LiAlH_4$ (2.4 M solution in THF, 2 mL, 4.8 mmol) was dropped to the orange solution at 0 °C with vigorous stirring. Following the mixture was stirred for another 10 min, the reaction was quenched by dropwise adding HCl (0.5 M, 20 mL). The mixture was extracted with Et_2O and the combined extract was condensed under reduced pressure, the orange residue was purified by filtration with column chromatography. The expected reduction product 1,7-bis(dimethylsilylmethyl)-*m*-carborane **7** (0.57 g, quantitative) was afforded as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99-3.90 (m, 2H), 3.50-1.20 (br, 10H), 1.52-1.51 (d, J=4Hz, 4H), 0.13-0.12 ppm (d, J=4Hz, 12H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 74.2, 25.4, -3.8 ppm. ^{29}Si NMR (500MHz, $CDCl_3$): -14.54 ppm. ^{11}B NMR (500 MHz, $CDCl_3$): δ -6.29, -7.26, -9.31, -9.86, -10.31, -10.77, -12.06 ppm. IR: v =2959, 2597, 2138, 1254, 1027, 884, 841, 742 cm^{-1}.HRMS (EI): *m/z* calcd for $C_8H_{28}B_{10}Si_2$ $[M-1]^+$: 287.2733. Found: 287.2653. n_D^{25}: 1.5235.

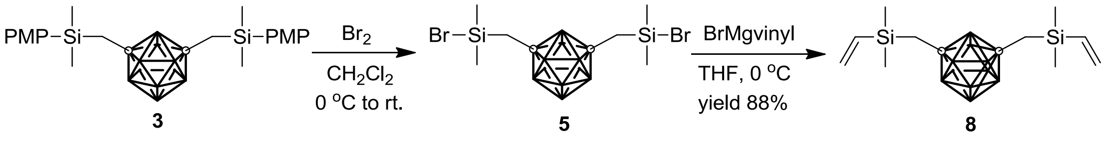


Scheme 4: Preparation of 1,7-bis(dimethylsilylmethyl)-*m*-carborane **7**

2.5 Preparation of 1,7-bis(vinyl(dimethyl)silylmethyl)-*m*-carborane 8

To a solution of **3** (1 g, 2 mmol) in dry CH_2Cl_2 (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 °C for 30 min; then warmed to room temperature for 10 h. Intermediate **5** was obtained after removing CH_2Cl_2 under reduced pressure. Subsequently, the obtained orange oily liquid **5** was dissolved in THF (20 mL) under nitrogen atmosphere. The BrMgvinyl (1 M solution in THF, 4.2 mL, 4.2 mmol) was dropped to the orange solution at 0 °C with vigorous stirring. Following the mixture was stirred for another 30 min, the reaction was quenched by water. The mixture was extracted with Et_2O and the combined extract was condensed under reduced pressure, the orange residue was purified by filtration with column chromatography. The expected reduction product 1,7-bis(vinyl(dimethyl)silylmethyl)-*m*-carborane **8** (0.59g, 88%) was afforded as colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.20-5.96 (m, 4H), 5.73-5.65 (dd, J=3Hz, 21Hz), 3.50-1.20 (br, 10H),1.54 (s, 4H), 0.16 ppm (s, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 137.6, 132.6, 74.1, 27.1, -2.6 ppm. ^{29}Si NMR (500MHz, $CDCl_3$): -6.2 ppm. ^{11}B NMR (500 MHz, $CDCl_3$): δ -6.01, -6.09, -9.12, -9.66, -10.14, -10.57, -11.72 ppm. IR: v =2955, 2597, 1405, 1254, 1028, 952, 836, 779 cm^{-1}.HRMS (EI): *m/z* calcd for $C_{12}H_{32}B_{10}Si_2$ $[M-1]^+$: 339.3046. Found: 339.2963. n_D^{25}: 1.5218.

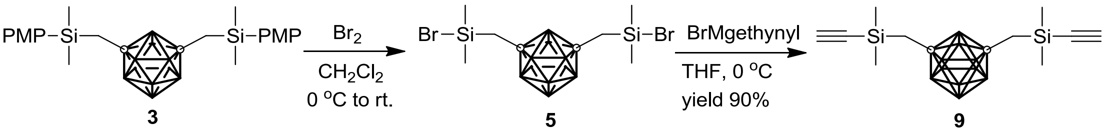


Scheme 5: Preparation of 1,7-bis(vinyl(dimethyl)silylmethyl)-*m*-carborane **8**

2.6 Preparation of 1,7-bis(ethynyl(dimethyl)silylmethyl)-*m*-carborane 9

To a solution of **3** (1 g, 2 mmol) in dry CH_2Cl_2 (30 mL) was added dropwise a solution of bromine (0.8 g, 5 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 ^{o}C for 30 min; then warmed to room temperature for 10 h. Intermediate **5** was obtained after removing CH_2Cl_2 under reduced pressure. Subsequently, the obtained orange oily liquid **5** was dissolved in THF (20 mL) under nitrogen atmosphere. The BrMgethynyl (0.5 M solution in THF, 8.4 mL, 4.2 mmol) was dropped to the orange solution at 0 ^{o}C with vigorous stirring. Following the mixture was stirred for another 30 min, the reaction was quenched by water. The mixture was extracted with Et_2O and the combined extract was condensed under reduced pressure, the orange residue was purified by filtration with column chromatography. The expected reduction product 1,7-bis(ethynyl(dimethyl)silylmethyl)-*m*-carborane **9** (0.61g, 91%) was afforded as colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ3.50-1.20 (br, 10H), 2.42 (s, 2H), 1.63 (s, 4H), 0.26 ppm (s, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 94.8, 87.8, 73.5, 26.9, -1.1 ppm. ^{29}Si NMR (500MHz, $CDCl_3$): -17.51 ppm. ^{11}B NMR (500 MHz, $CDCl_3$): δ -6.18, -7.15, -9.20, -9.81, -10.20, -10.64, -11.72 ppm. IR: ν =3287, 2600, 2037, 1257, 1028, 844, 783, 680 cm^{-1}.HRMS (EI): *m/z* calcd for $C_{12}H_{28}B_{10}Si_2$ $[M-1]^{+}$: 335.2733. Found: 335.2643. n_D^{25}: 1.5710



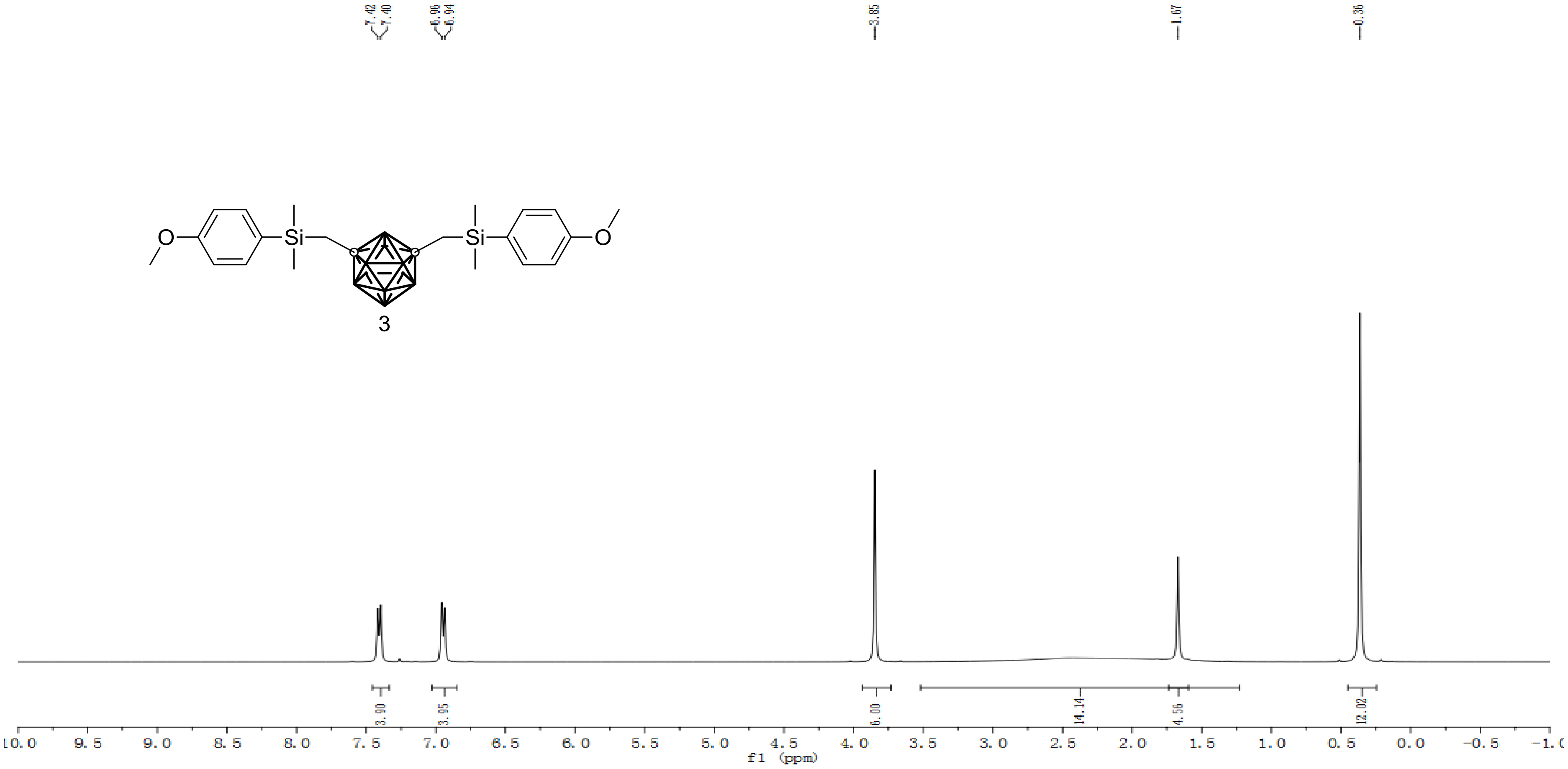
Scheme 6: Preparation of 1,7-bis(ethynyl(dimethyl)silylmethyl)-*m*-carborane **9**

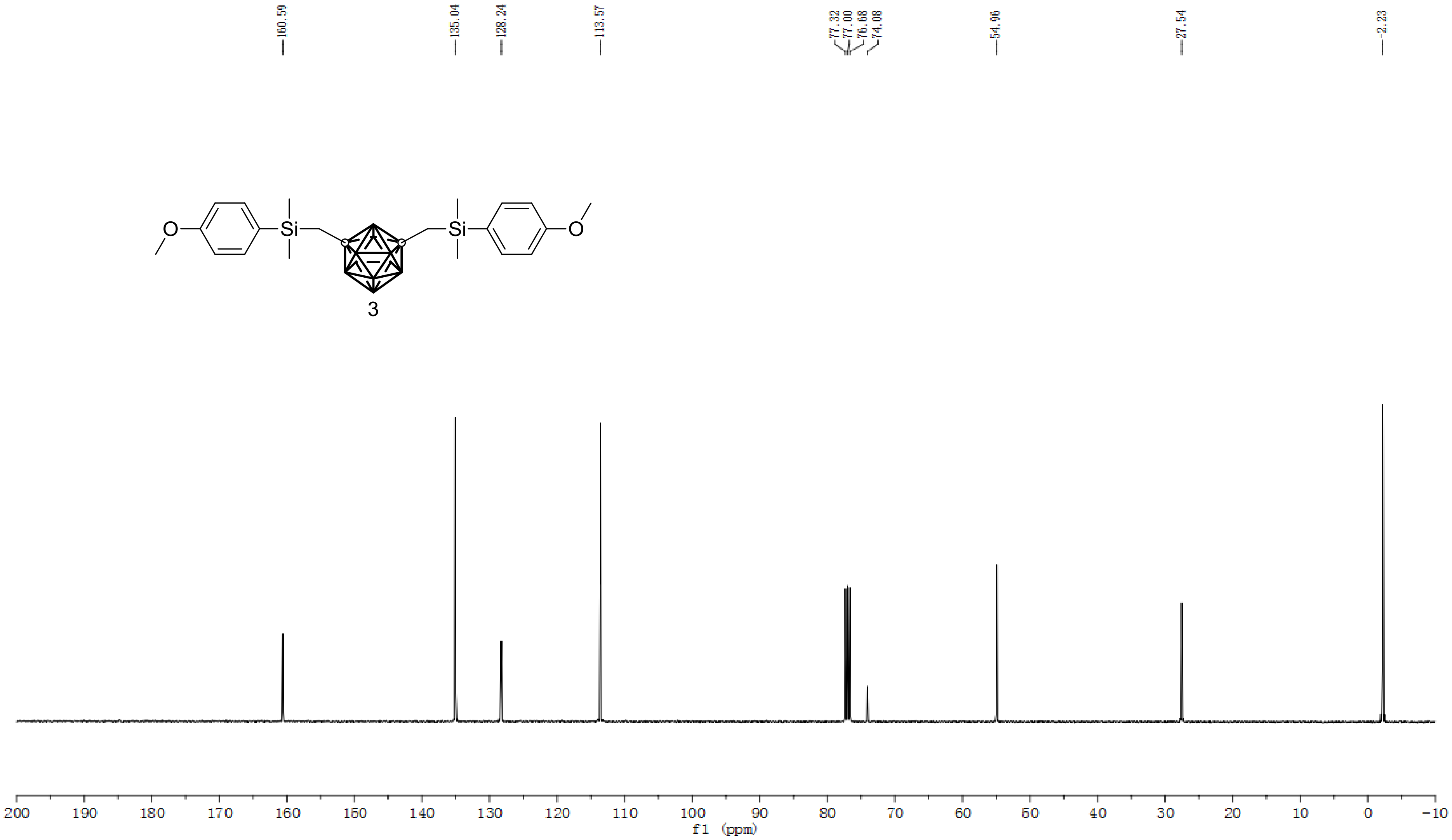
3. references

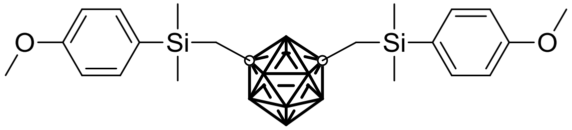
1) (a) D. M. Knauss, H. A. Al-Muallem, T. Huang and D. T. Wu, *Macromolecules*, 2000, **33**, 3557-3568; (b) K. Murakami, H. Yorimitsu and K. Oshima, *J. Org. Chem.* 2009, **74**, 1415-1417; (c) K. Murakami, H. Yorimitsu and K. Oshima, *Org. Synth*, 2010, **87,** 178-183.

2) (a) I. P. Yakovlev, Y. S. Finogenov, V. A. Gindin, V. P. Feshin, P. A. Nikitin, A. E. Shchegolev and B. A. Ivin, *Zhurnal Obshchei Khimii,* 1985, **55**, 1093-1099; (b) D. Takeda, R. Oyama, and S. Yamada, *Chem. Lett.,* 2009*,* **38**, 532-533.

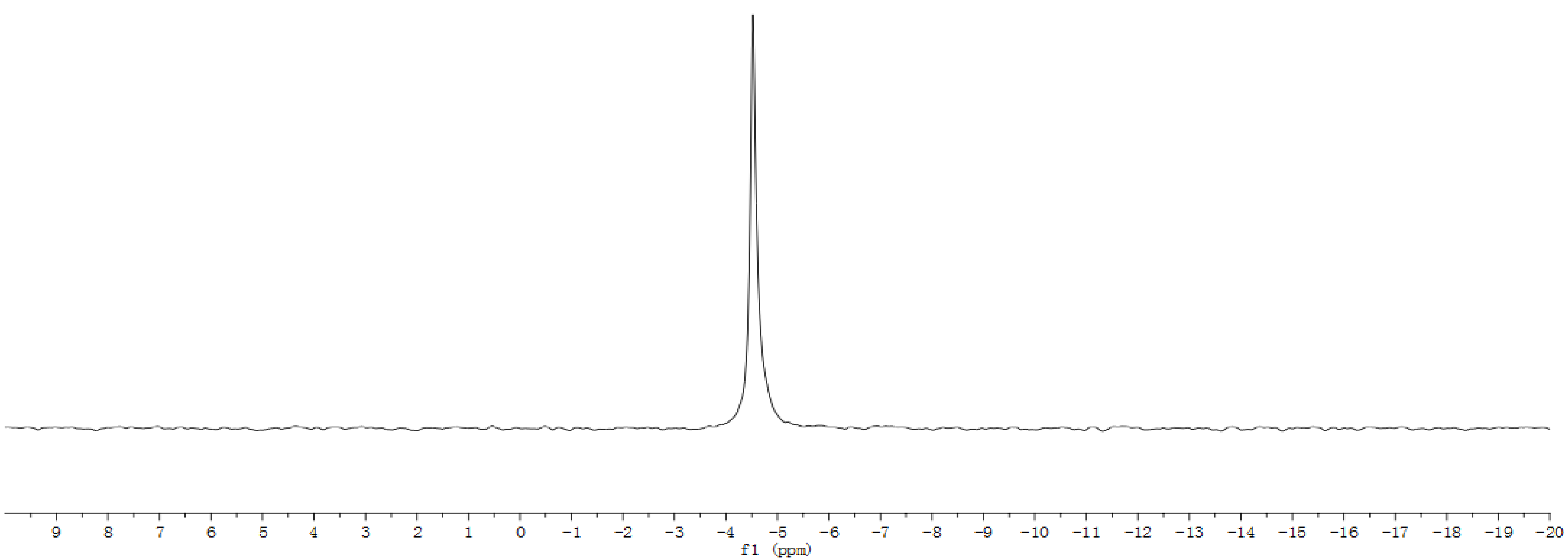
4. NMR Spectra

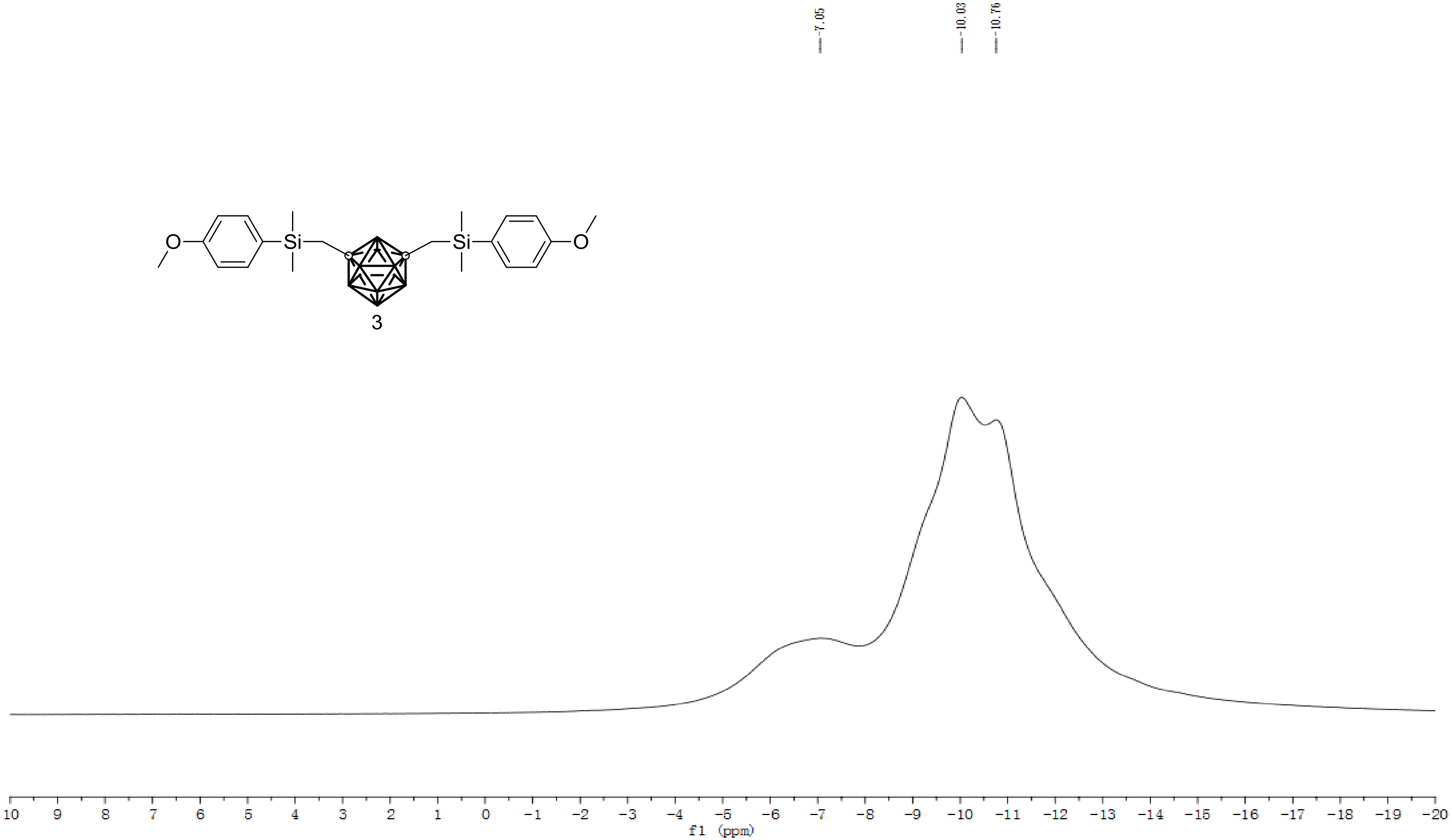


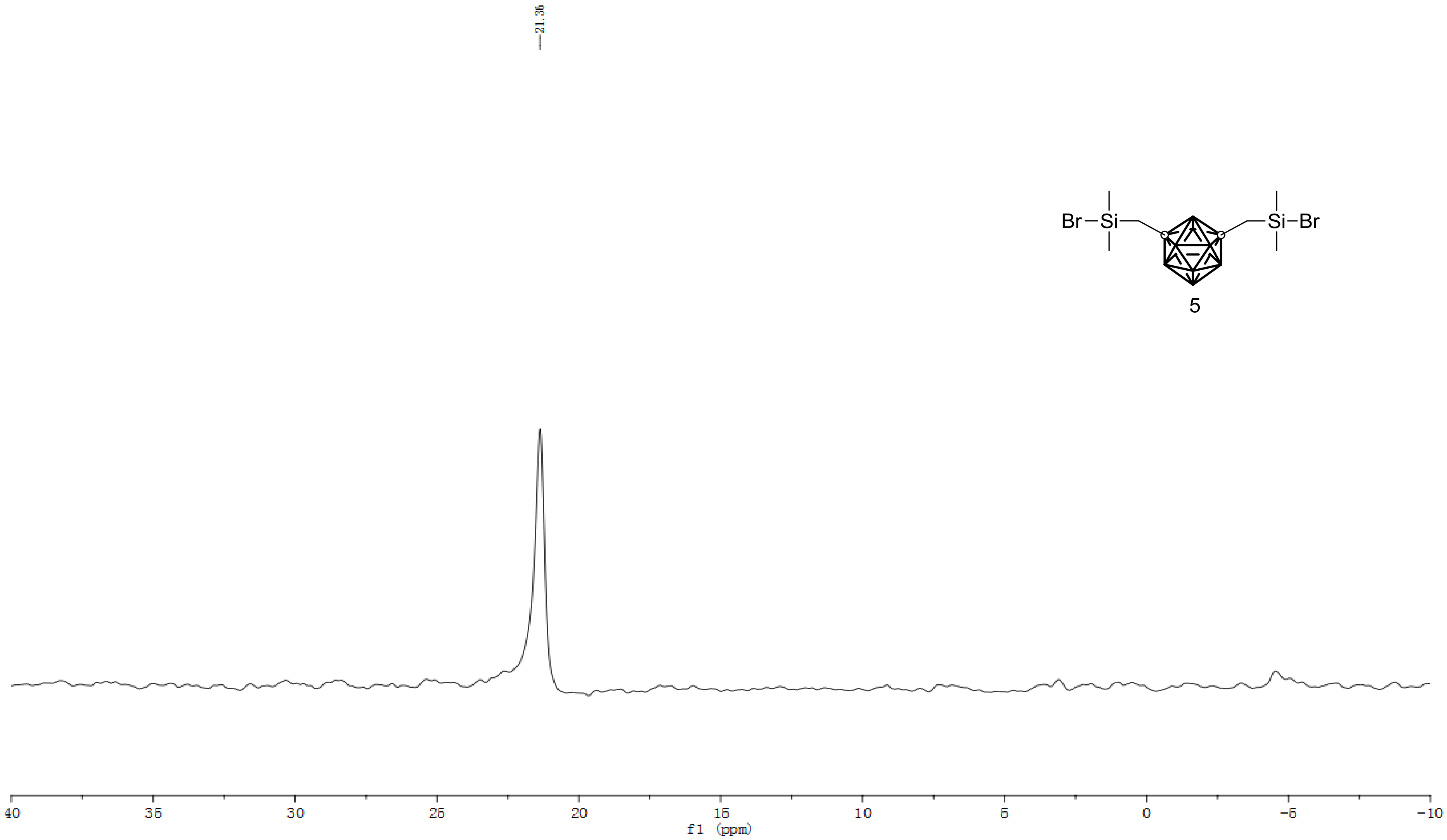

160.59
135.04
128.24
113.57
77.32
77.00
76.68
74.08
54.96
27.54
-2.23
O
Si
Si
O
3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

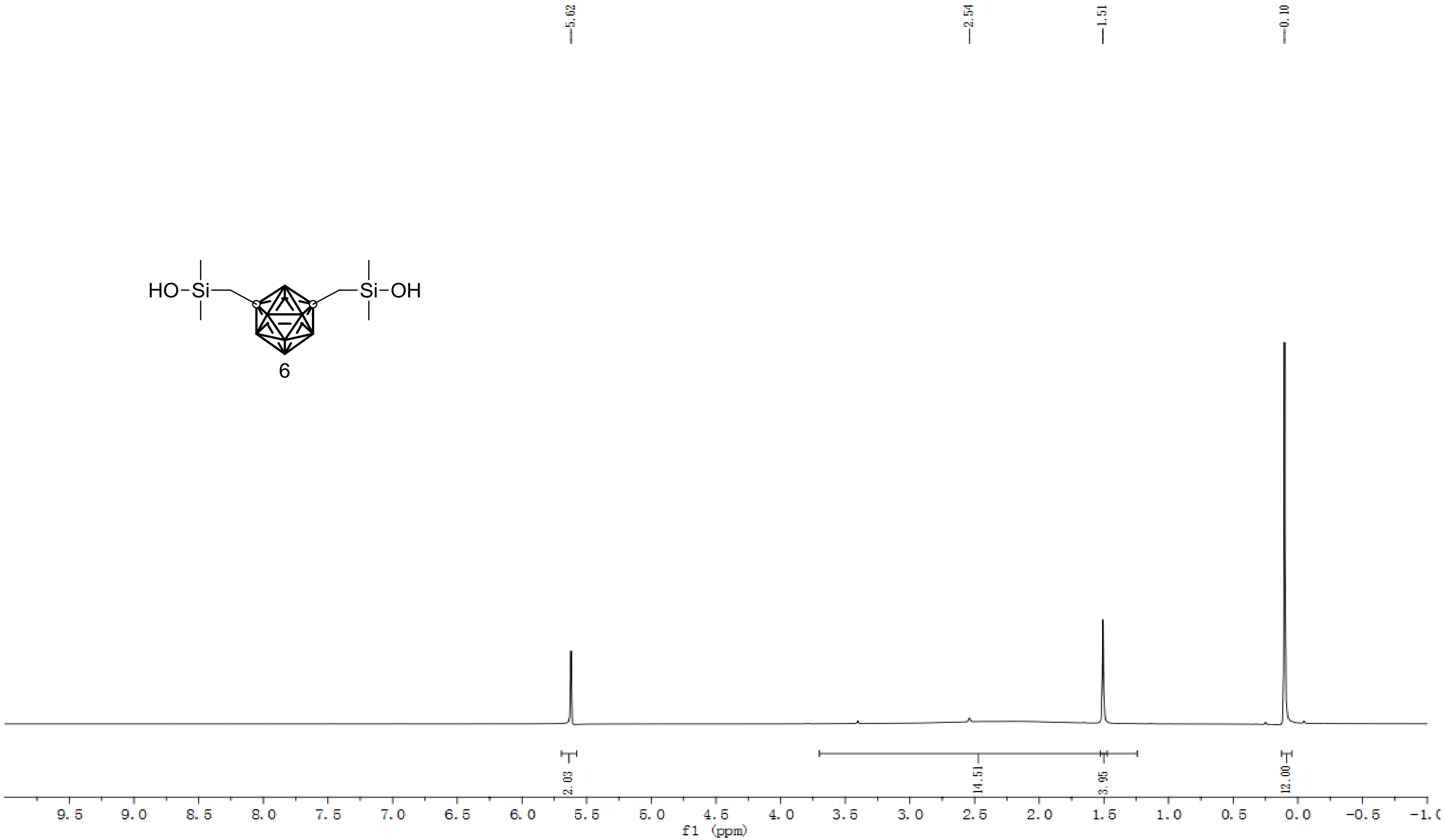

O
Si
Si
O

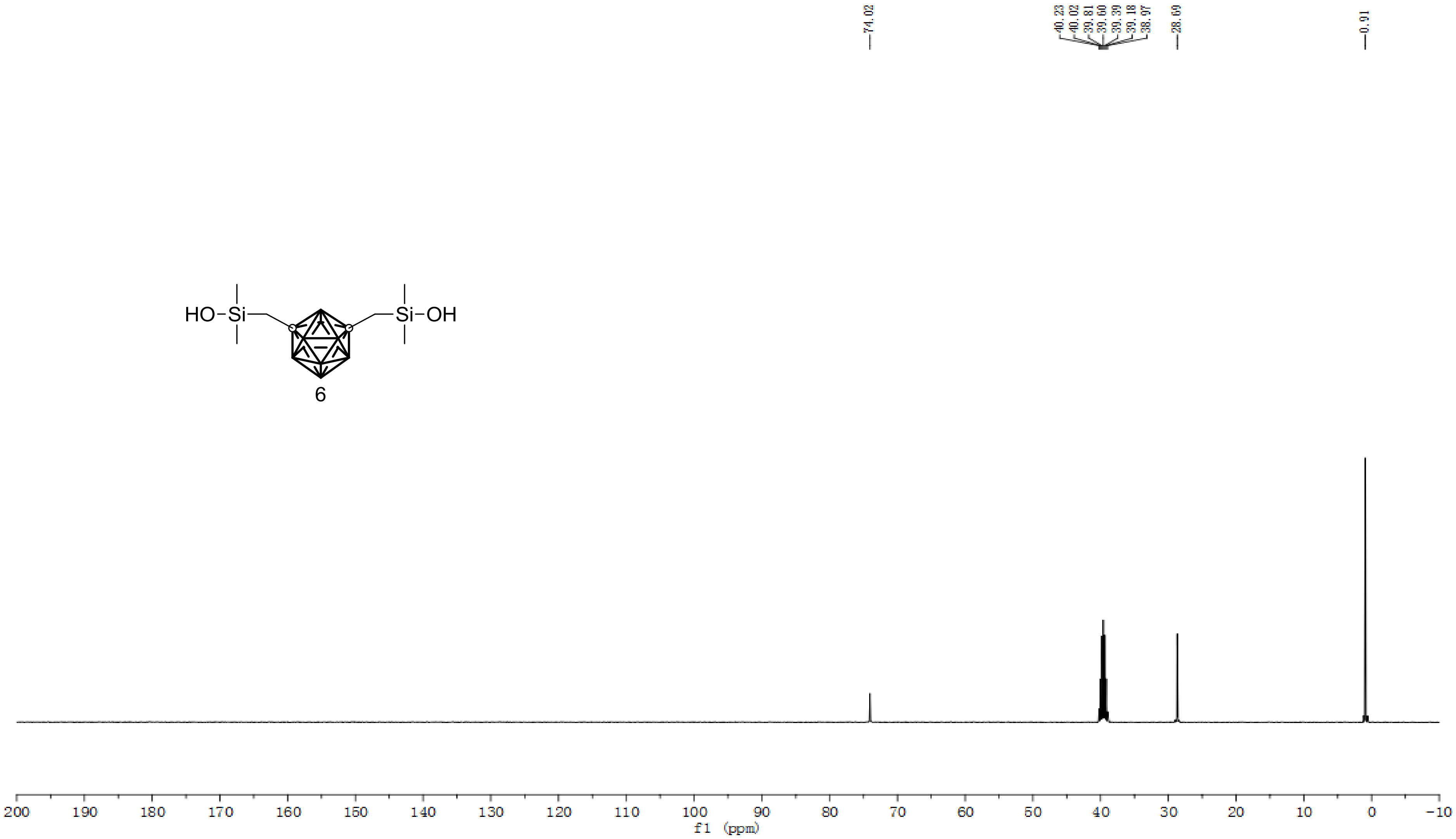
3

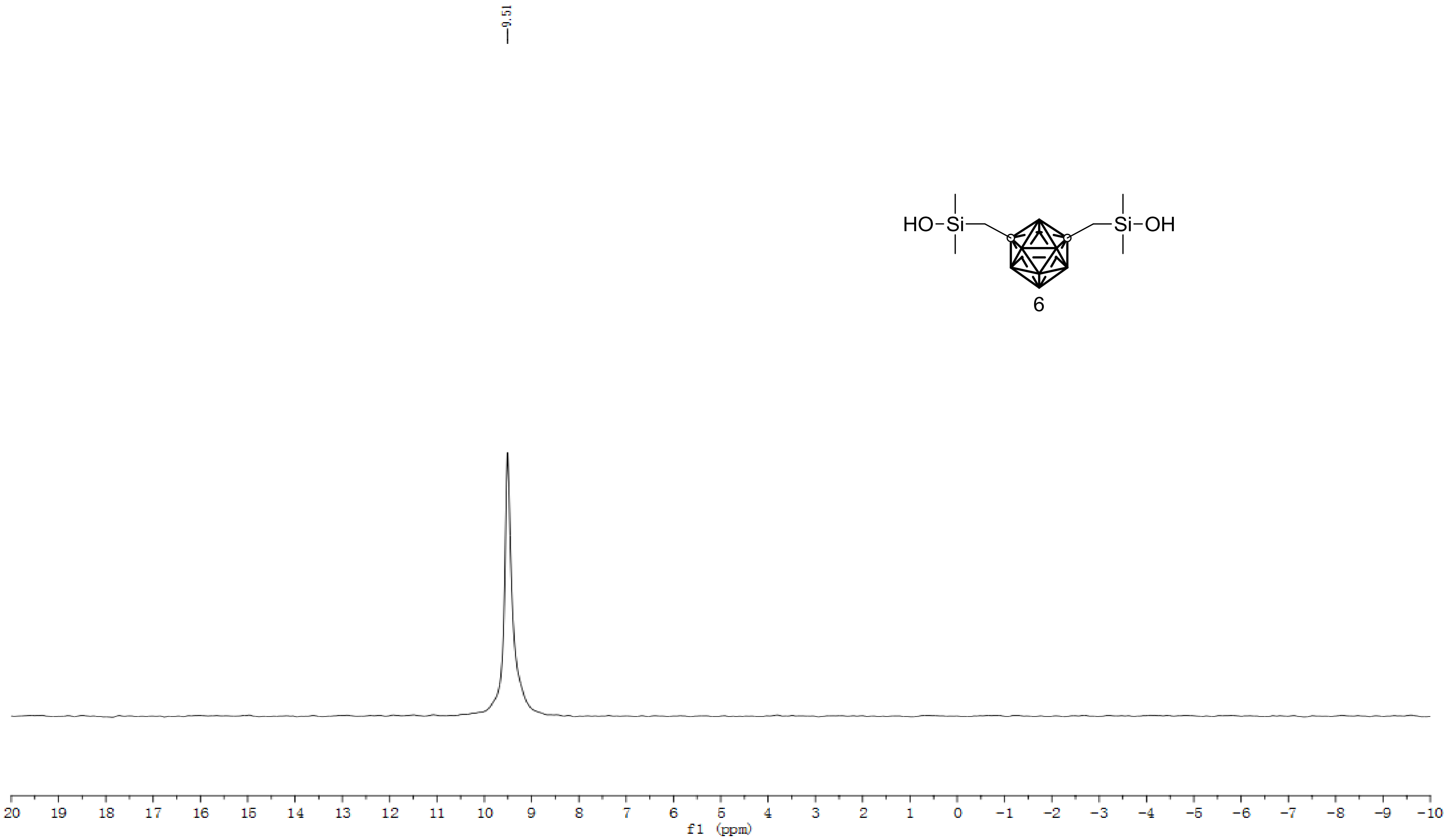

−4.52
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
−11
−12
−13
−14
−15
−16
−17
−18
−19
−20
f1 (ppm)

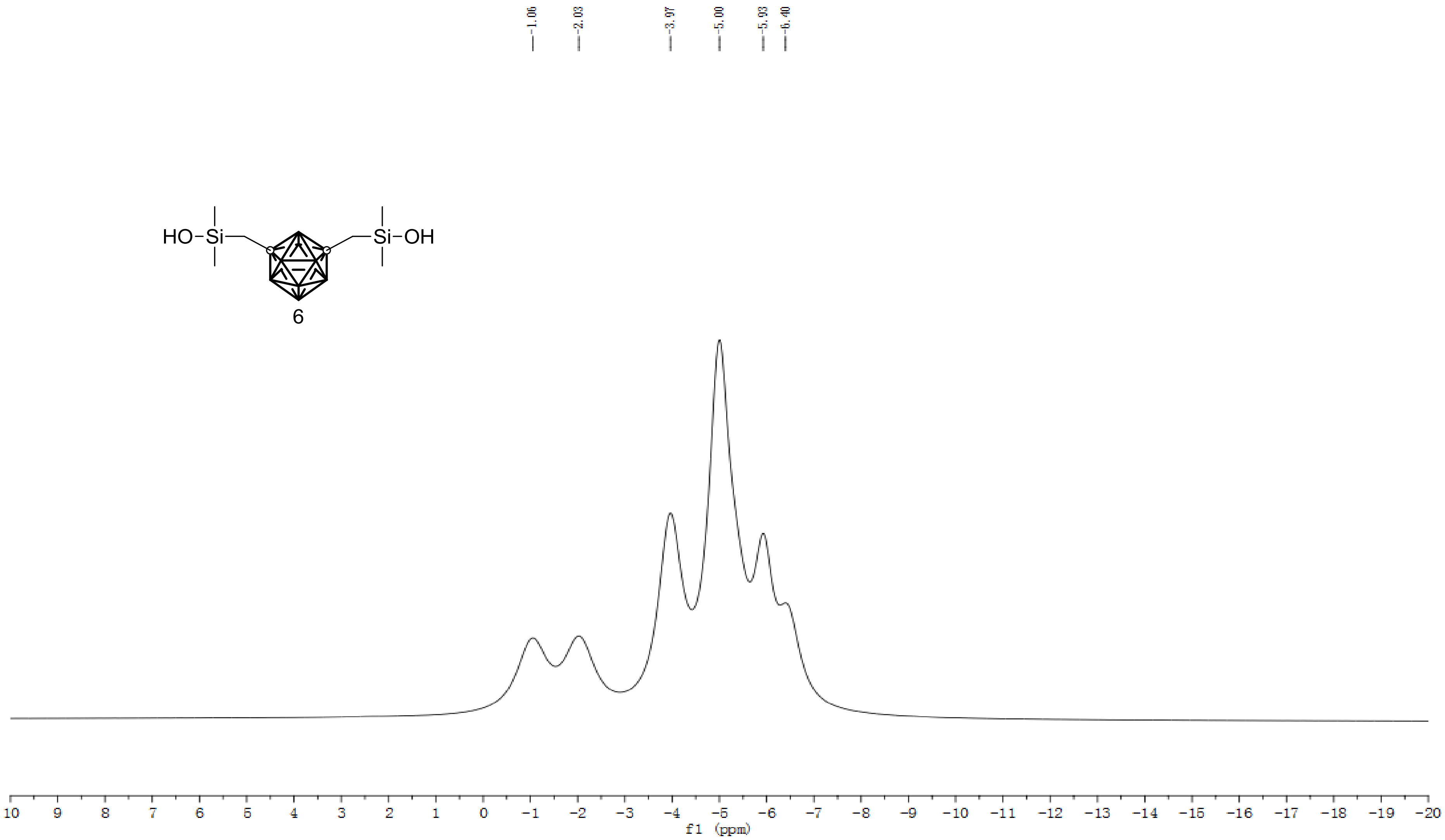

-7.05
-10.03
-10.76
O
Si
Si
O
3
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
−11
−12
−13
−14
−15
−16
−17
−18
−19
−20
f1 (ppm)

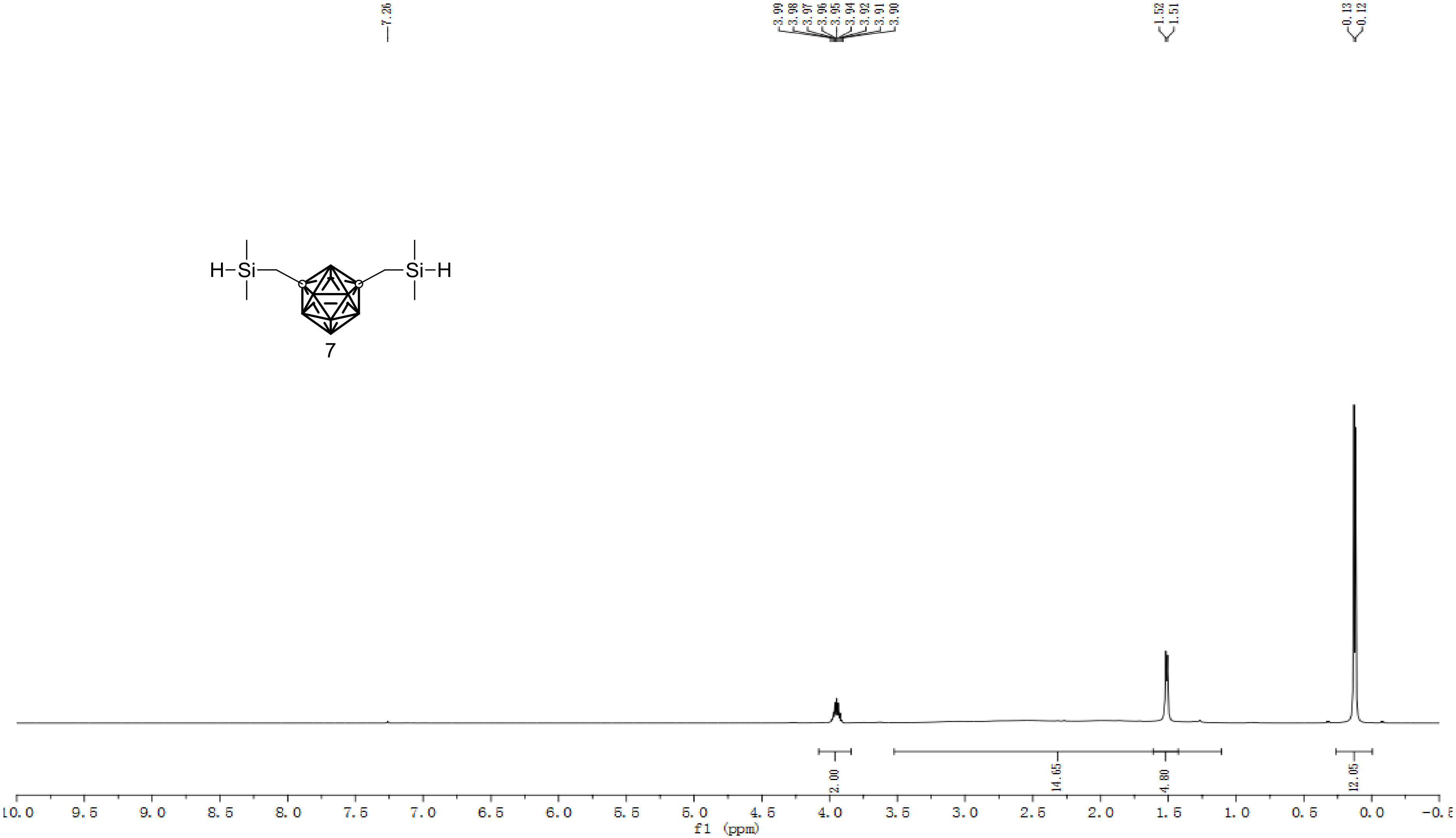

21.36
Br
Si
Br
Si
5
40
35
30
25
20
15
10
5
0
−5
−10
f1 (ppm)

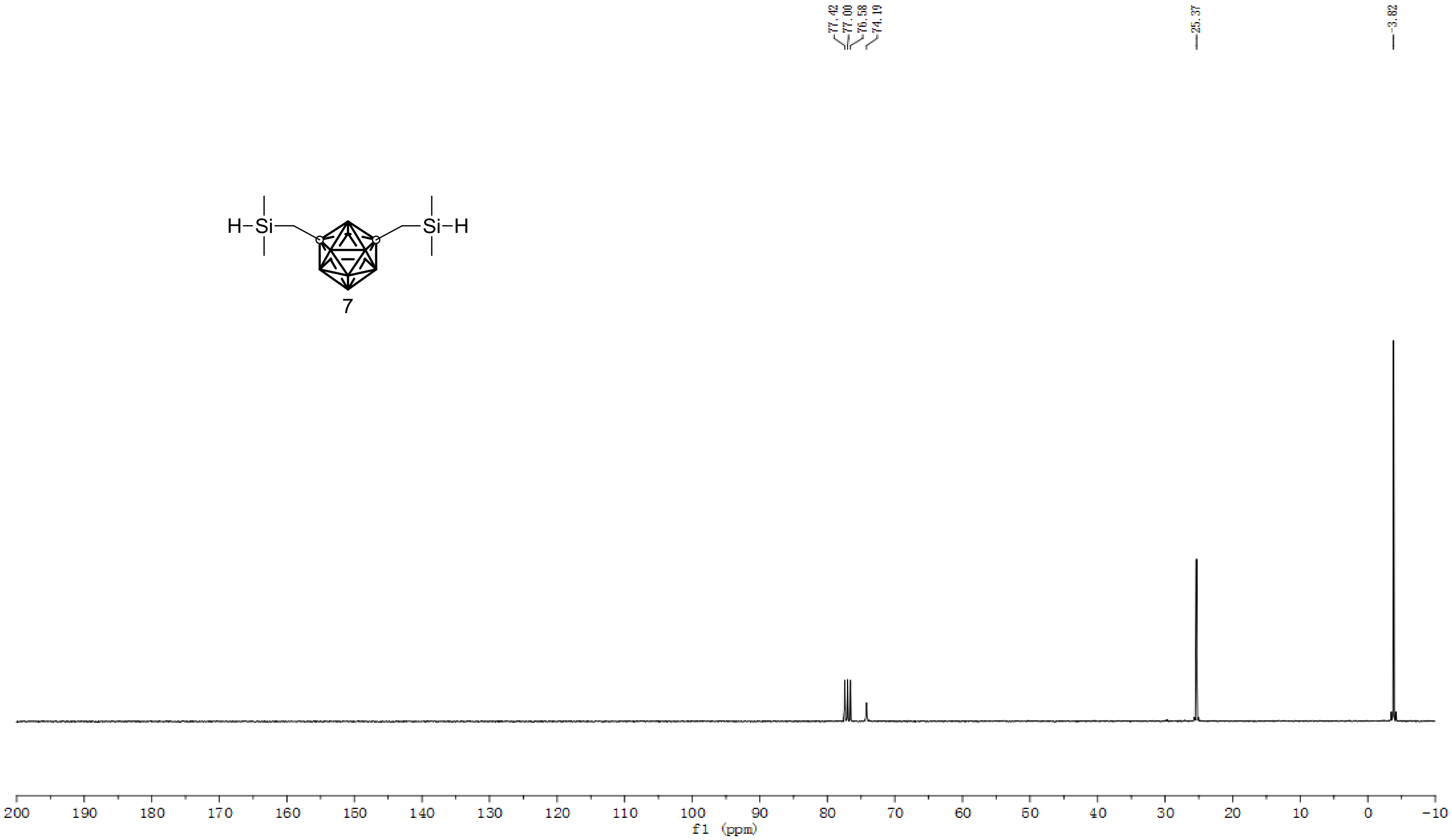

5.62
2.54
1.51
0.10
HO
Si
Si
OH
6
2.03
14.51
3.95
12.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.
f1 (ppm)

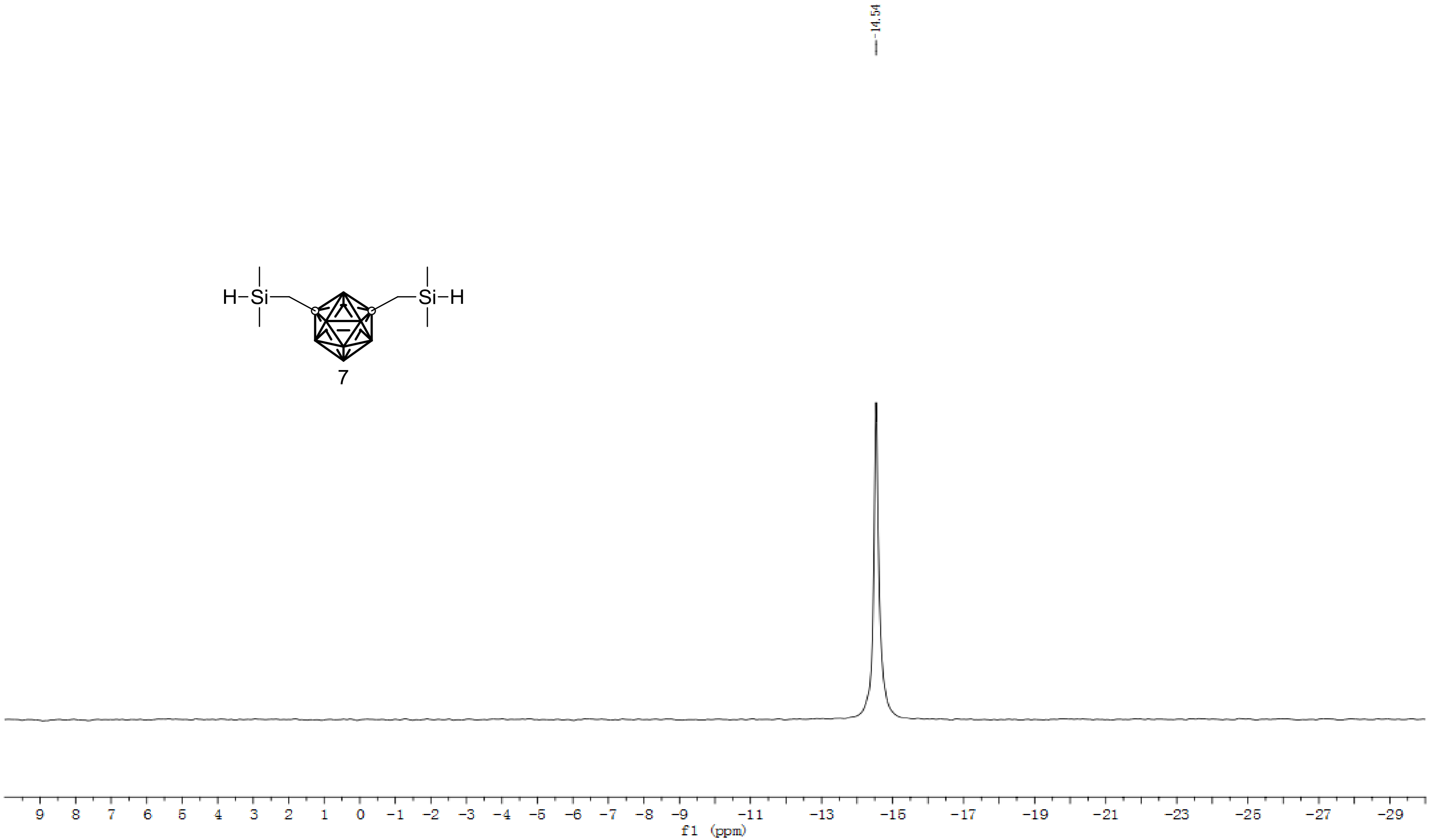

74.02
40.23
40.02
39.81
39.60
39.39
39.18
38.97
28.69
0.91
HO–Si
Si–OH
6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

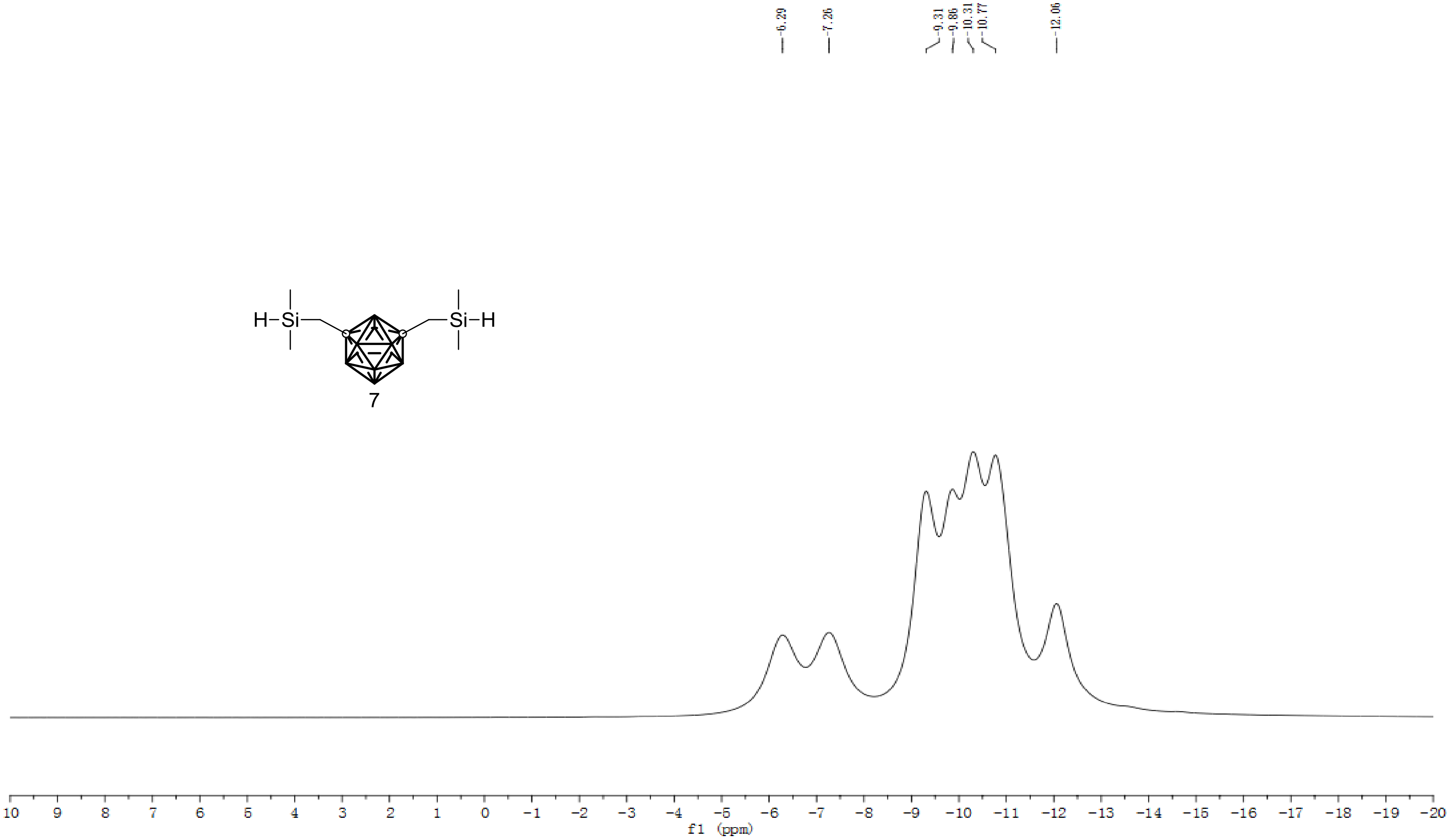

9.51
HO–Si
Si–OH
6
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
f1 (ppm)


-1.06
-2.03
-3.97
-5.00
-5.93
-6.40
HO
Si
Si
OH
6
10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4 −5 −6 −7 −8 −9 −10 −11 −12 −13 −14 −15 −16 −17 −18 −19 −20
f1 (ppm)

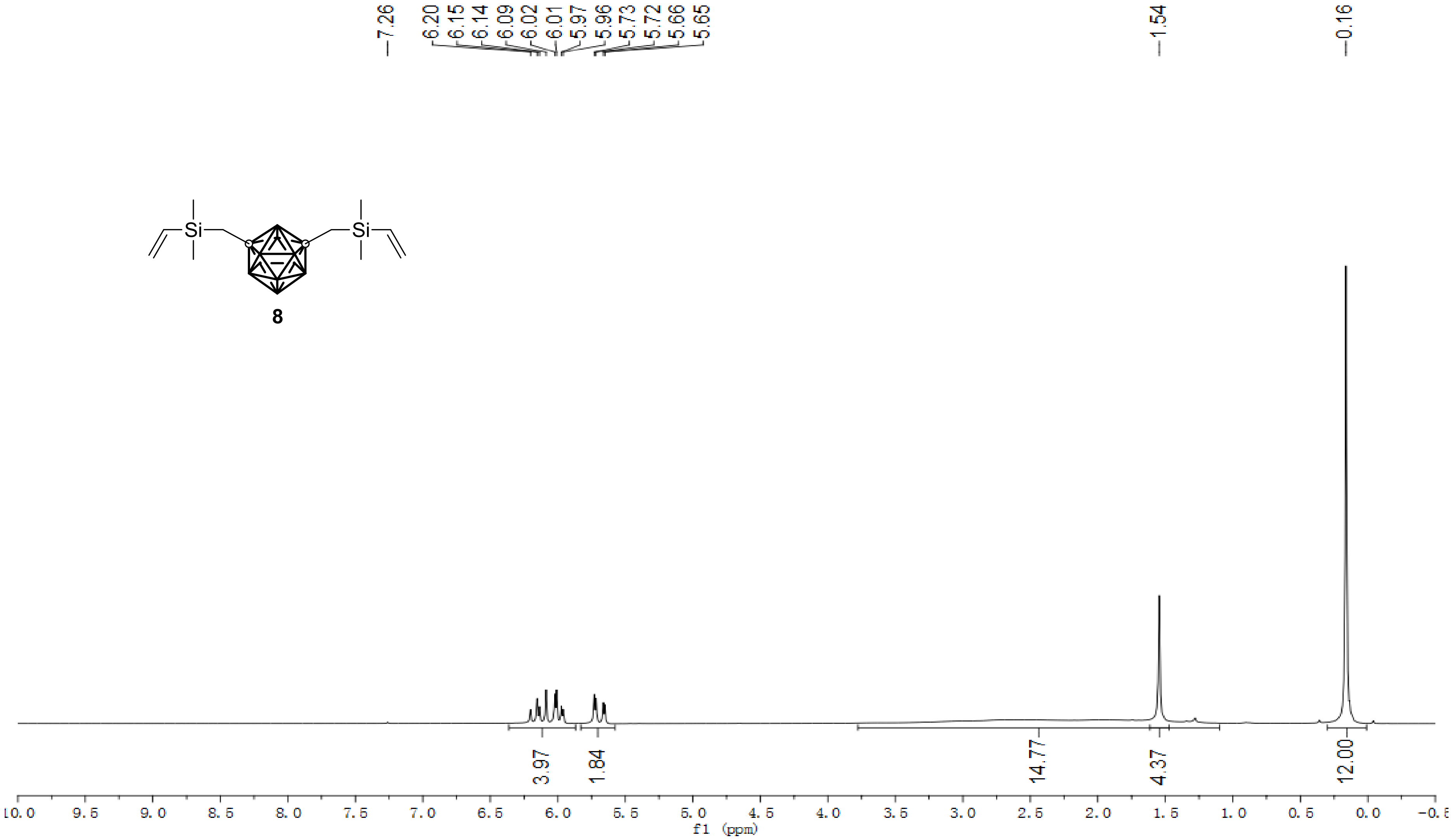

7.26
3.99
3.98
3.97
3.96
3.95
3.94
3.92
3.91
3.90
1.52
1.51
0.13
0.12
H–Si
Si–H
7
2.00
14.65
4.80
12.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

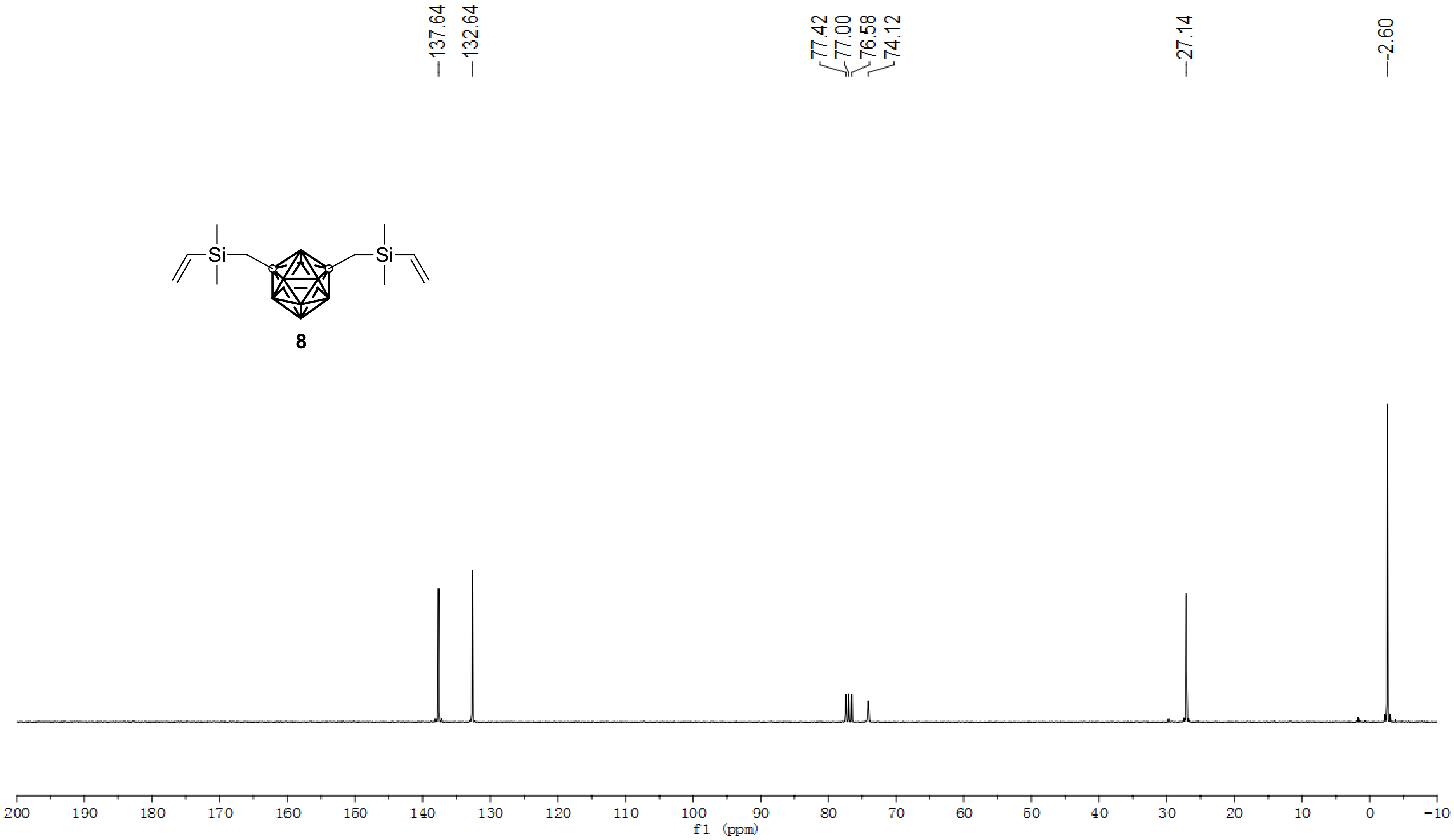

77.42
77.00
76.58
74.19
25.37
-3.82
H–Si
Si–H
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

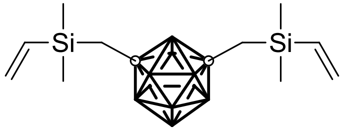

-14.54
H
Si
Si
H
7
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-11
-13
-15
-17
-19
-21
-23
-25
-27
-29
f1 (ppm)


-6.29
-7.26
-9.31
-9.86
-10.31
-10.77
-12.06
H
Si
Si
H
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−10
−11
−12
−13
−14
−15
−16
−17
−18
−19
−20
f1 (ppm)

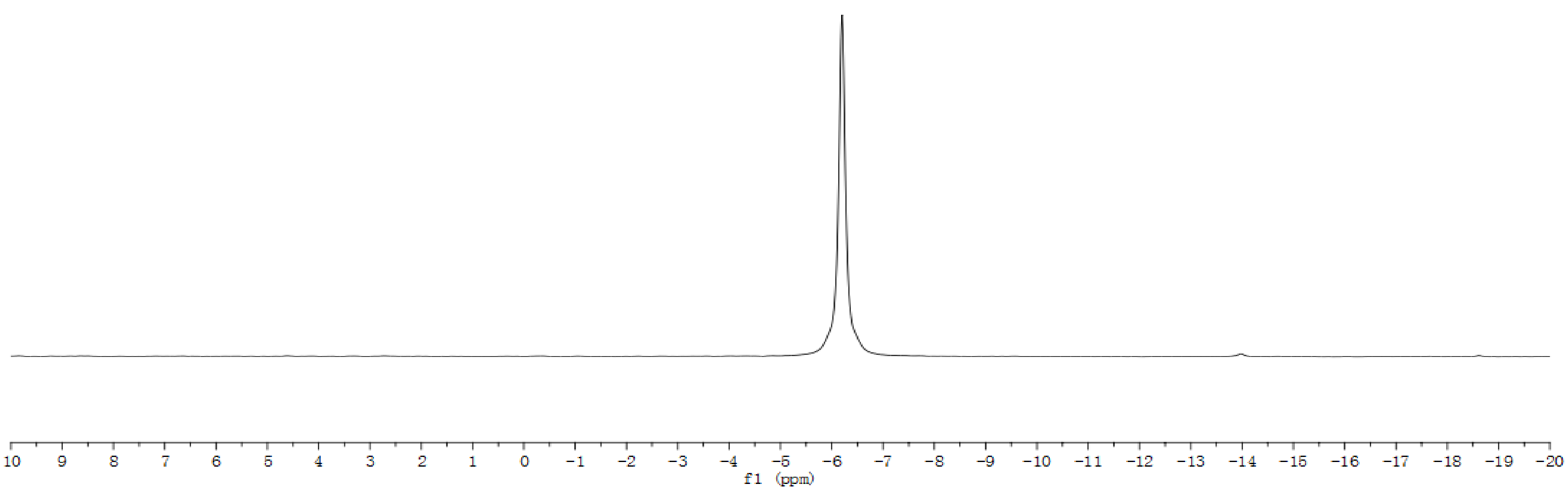
7

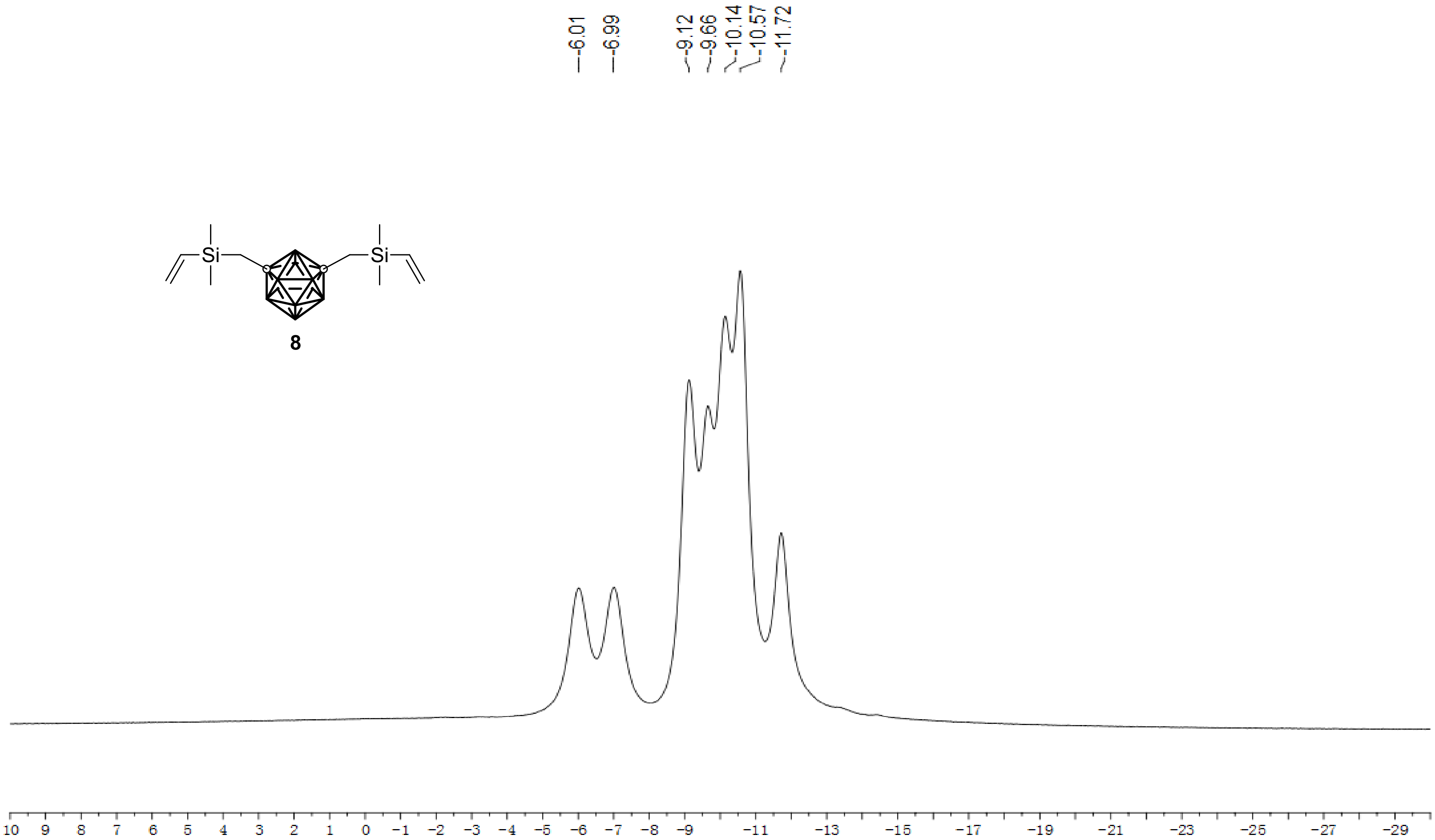

8
7.26
6.20
6.15
6.14
6.09
6.02
6.01
5.97
5.96
5.73
5.72
5.66
5.65
1.54
0.16
3.97
1.84
14.77
4.37
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

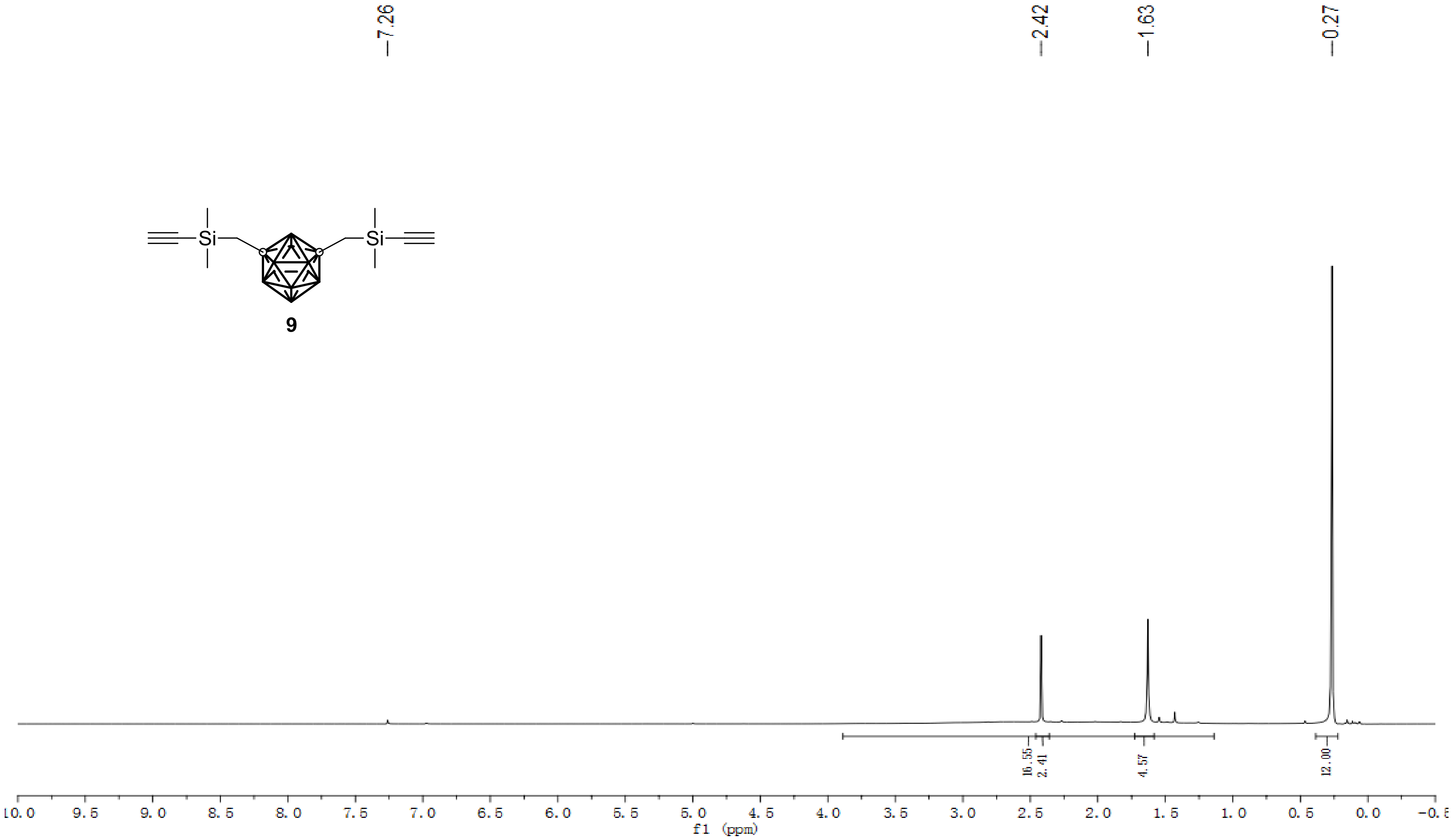

137.64
132.64
77.42
77.00
76.58
74.12
27.14
-2.60
Si
Si
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

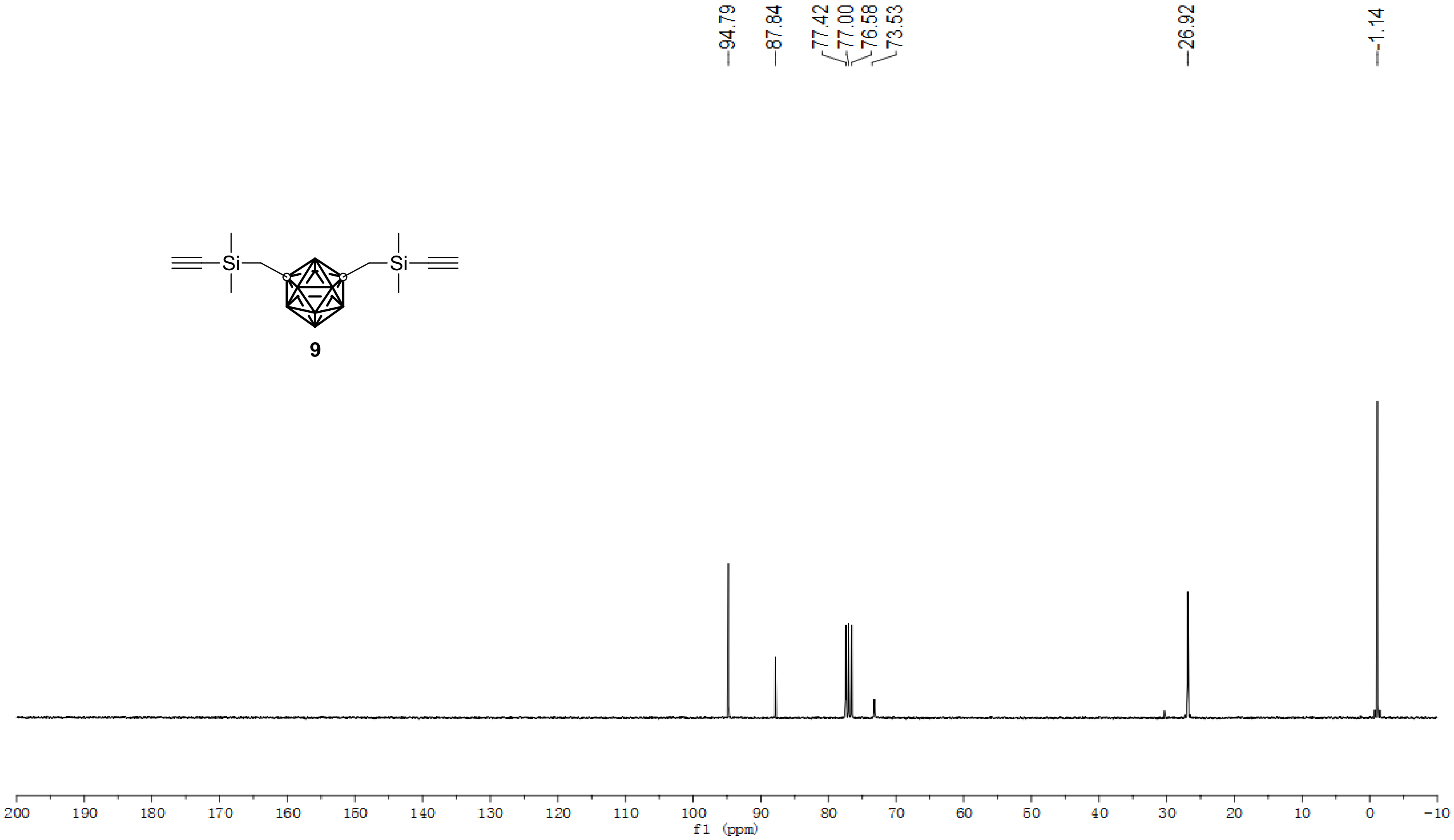


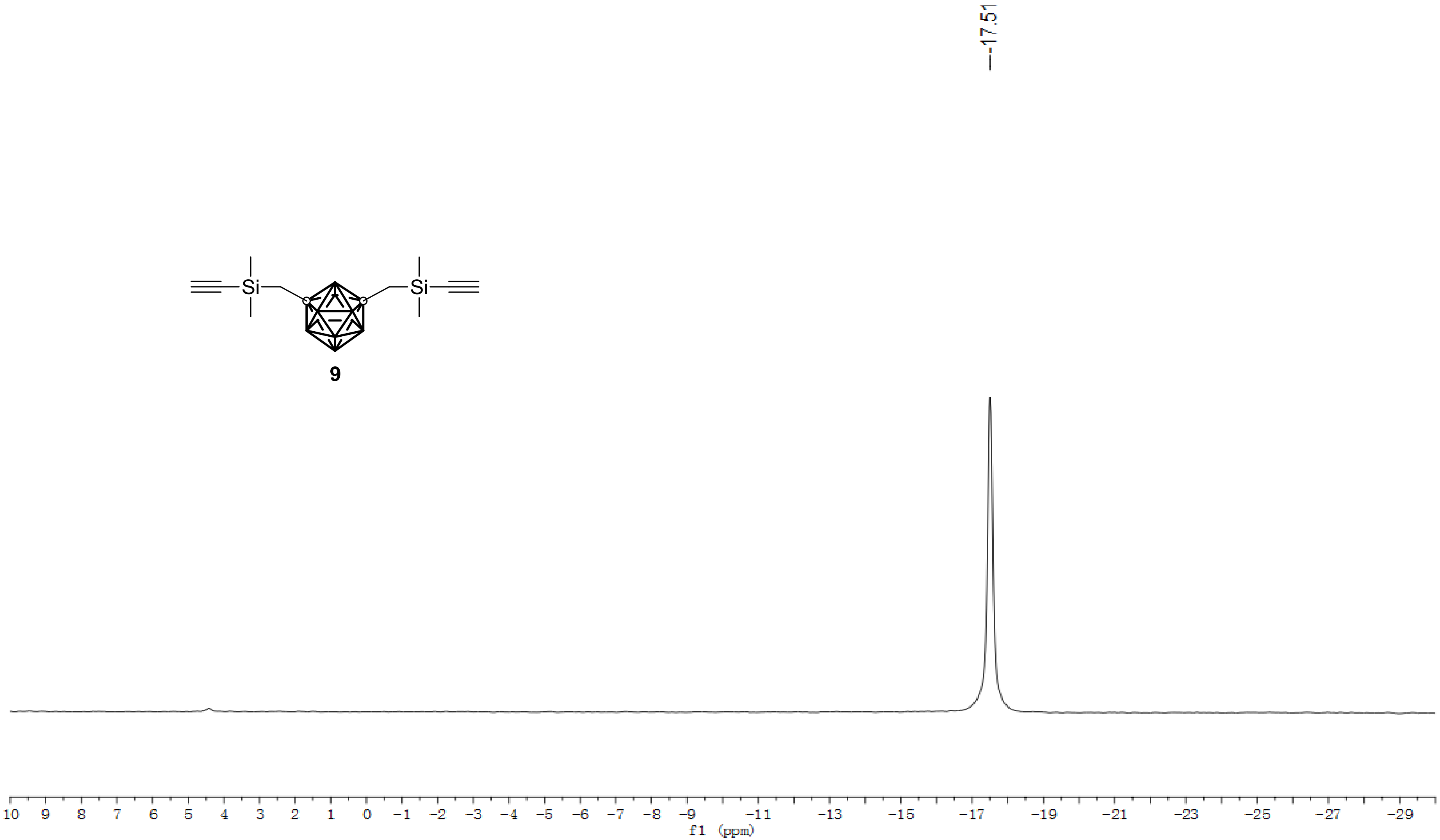
8


-6.20
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
-20
f1 (ppm)


-6.01
-6.99
-9.12
-9.66
-10.14
-10.57
-11.72
Si
Si
8
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
−5
−6
−7
−8
−9
−11
−13
−15
−17
−19
−21
−23
−25
−27
−29

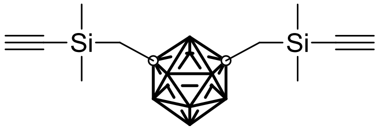

7.26
2.42
1.63
0.27
9
16.55
2.41
4.57
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


94.79
87.84
77.42
77.00
76.58
73.53
26.92
-1.14
Si
Si
9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

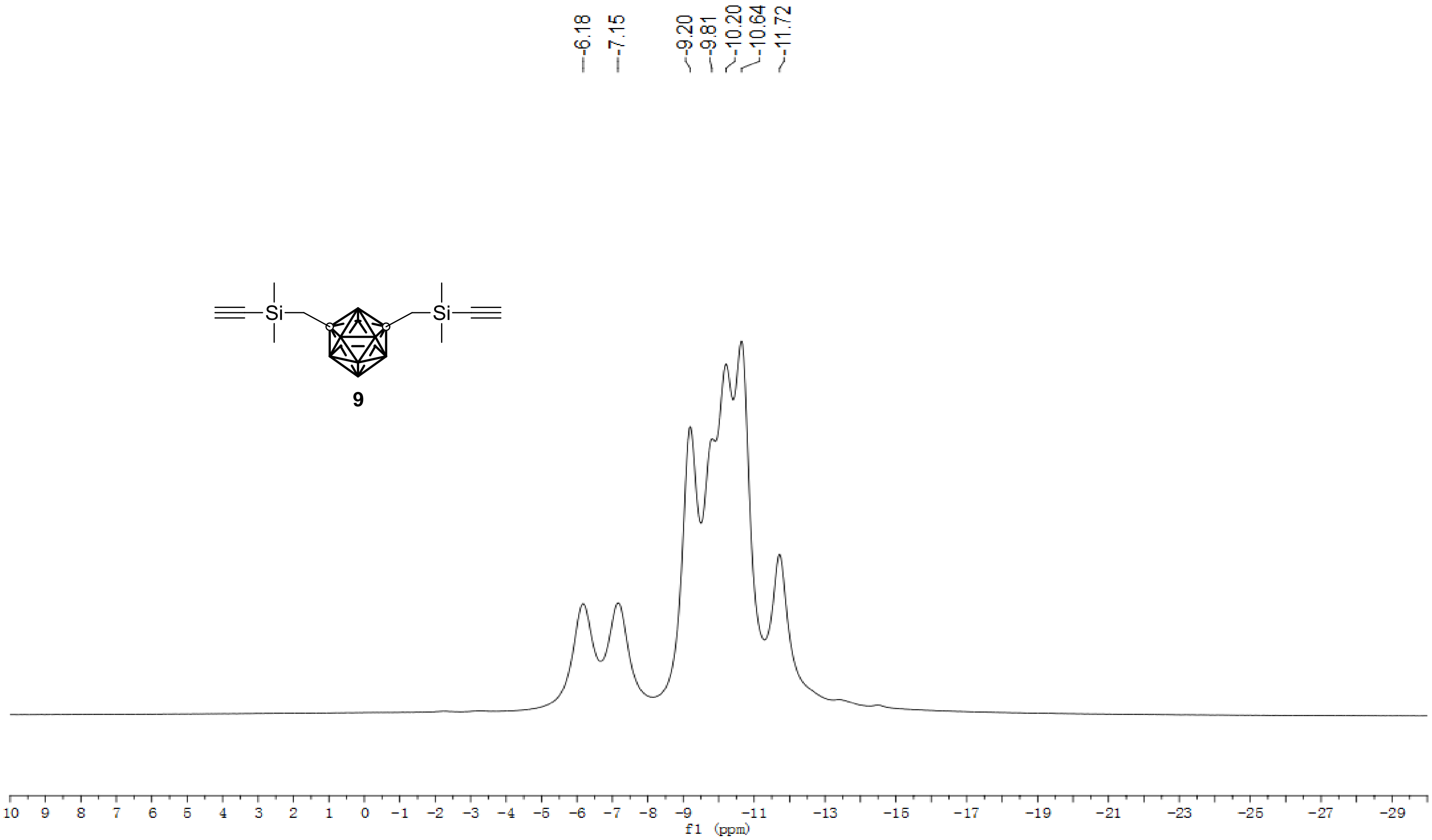


9

-17.51
Si
Si
10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4 −5 −6 −7 −8 −9 −11 −13 −15 −17 −19 −21 −23 −25 −27 −29
f1 (ppm)


Si
Si

9


-6.18
-7.15
-9.20
-9.81
-10.20
-10.64
-11.72
10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4 −5 −6 −7 −8 −9 −11 −13 −15 −17 −19 −21 −23 −25 −27 −29
f1 (ppm)