SUPPORTING INFORMATION

for

# Sodium triethylborohydride as a catalyst for dehydrogenative silylation of terminal alkynes with hydrosilanes

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**Contents**:



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## Experimental procedures

### **1.1** General remarks

All reactions were performed in oven-dried glassware under argon atmosphere. Toluene was purified by MBraun SPS-8400 system and degassed after collection. Other solvents were dried by distillation over calcium hydride.

Gas chromatography was performed on a Bruker Scion 436-GC with a 30 m Agilent VF5-ms 0.53 mm Megabore column and a TCD detector. The temperature program was as follows: 60 °C (3 min), 20 °C/min, 280 °C (20 min). Decane was used as a reference. GC-MS analyses were performed on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector. The temperature program was as follows: 60 °C (3 min), 10 °C/min, 250 °C (15 min). NMR analyses were performed on a Bruker Fourier 300 spectrometer.

### **1.2** General procedure of dehydrogenative silylation catalyzed by $NaHBEt_3$

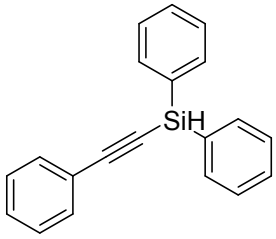
0.5 mmol of silane, 1 mL of toluene, 0.5 mmol of alkyne, and 0.1 mL of decane were placed in previously evacuated Schlenk bomb flask fitted with a plug valve. A reference sample was taken. Next, 0.05 mL of 1M solution of $NaHBEt_3$ (0.05 mmol) in toluene was added, reaction vessel was closed and heated at 100 °C with stirring.

After specified time, reaction mixture was cooled down to the room temperature and analyzed using GC and GC-MS.

Products of dehydrogenative silylation were isolated by first evaporating toluene on a rotary evaporator, then extraction with 1 mL of hexane followed by column chromatography of concentrated extract ($SiO_2$, hexane as eluent).

**Analytical data of isolated products**

*2.1. Diphenyl(phenylethynyl)silane* **1**; colorless oil, yield: 87 mg (31%)



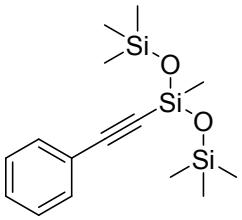

$^{1}$H NMR (300MHz, $CDCl_3$): δ7.78-7.66 (m, 4H), 7.60-7.51 (m, 2H), 7.48-7.28 (m, 9H), 5.3 (s, 1H)

$^{13}$C NMR (75 MHz, $CDCl_3$): δ135.24, 132.24, 132.18, 130.16, 129.17, 128.33, 128.17, 122.52, 109.56, 87.15

*MS (70 eV): m/z (%):* 206 (100), 284 (82), 129 (66), 205 (56), 207 (54), 105 (53), 181 (46), 178 (27), 180 (26), 204 (26), 283 (23), 285 (22), 103 (21), 130 (16), 53 (16), 179 (14), 208 (13), 182 (12), 106 (11), 155 (11).

Conforms to the literature analytical data.[1]

***1.2.*** 1,1,1,3,5,5,5-heptamethyl-3-(phenylethynyl)trisiloxane **2**; colorless oil, yield: 103 mg (32%)



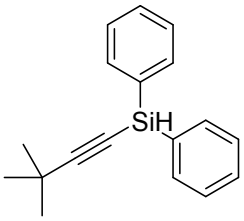

$^{1}$H NMR (300MHz, $CDCl_3$): 7.34-7.25 (m, 2H), 7.17-7.06 (m,3H), 0.07 (s,3H), 0.00 (s,18H)

*$^{13}$C NMR (75 MHz, $CDCl_3$):* 130.25, 127.02, 126.52, 121.07, 99.97, 90.75, 0.06, 0.00

*MS (70 eV): m/z (%): 307 (100), 159 (47), 308 (34),73 (25),309 (14),146 (12).*

*HRMS (ESI TOF) calcd for $C_{15}H_{26}O_2Si_3Na$: 345,1138, found: 345,1132*

***1.3.*** (3,3-dimethylbut-1-yn-1-yl)diphenylsilane **3**; colorless oil, yield: 53 mg (20%)



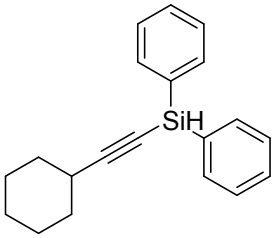

$^{1}$H NMR (300MHz, $CDCl_3$): δ7.70-7.61 (m, 4H), 7.43-7.32 (m, 6H), 5.12 (s, 1H), 1.31 (s, 9H)

*$^{13}$C NMR (75 MHz, $CDCl_3$):* δ135.09, 133.06, 129.84, 128.00, 121.08, 75.16, 30.79, 28.54

*MS (70 eV): m/z (%): 207 (100), 186 (99), 171 (52), 105 (49), 129 (45), 208 (31), 181 (23), 187 (22), 145 (21), 53 (20), 130 (20), 143 (18), 264 (17), 172 (15), 221 (13), 121 (12), 51 (11), 84 (11), 183 (11), 188 (11), 67 (10).*

Conforms to the literature analytical data.[2]

***1.4.*** *(cyclohexylethynyl)diphenylsilane* **4**; colorless oil, yield: 87 mg (30%)



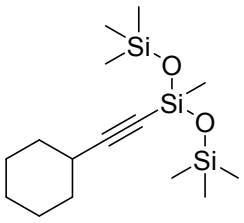

$^{1}$H NMR (300MHz, $CDCl_3$):7.72-7.59 (m, 4H), 7.45-7.30 (m, 6H), 5.25-5.03 (s, 1H), 2.61-2.44 (m, 1H), 1.92-1.68 (m, 4H), 1.62-1.25 (m, 6H)

*$^{13}$C NMR (75 MHz, $CDCl_3$):*135.10, 133.01, 129.88, 128.02, 116.96, 76.94, 32.38, 30.26, 25.83, 24.76

*MS (70 eV): m/z (%): 212 (100), 105 (95), 183 (56), 181 (54), 207 (53),208 (44), 106 (34), 53 (33), 131 (30), 209 (30), 189 (27), 129 (26), 133 (24), 107 (24), 134 (24), 130 (23), 144 (21), 213 (20), 79 (19), 169 (18), 182 (18), 190 (17), 155 (16), 121 (15), 157 (13), 171 (12), 132 (12), 103 (11), 222 (11), 158 (10), 55 (10).*

Conforms to the literature analytical data.[3]

***1.5.*** *3-(cyclohexylethynyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane* **5**; colorless oil, yield: 118 mg (36%)



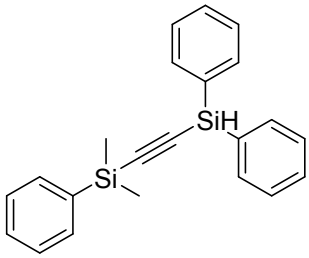
$^{1}$H NMR (300MHz, $CDCl_3$): 2.44-2.32 (m, 1H), 1.87-1.63 )m, 4H), 1.54-1.22(m, 6H), 0.20-0.08 (m, 21H)

*$^{13}$C NMR (75 MHz, $CDCl_3$): 106.85, 81.10, 30.57, 27.96, 24.12, 23.05, 0.21, 0.00*

*MS (70 eV): m/z (%): 313 (100), 73 (92), 207 (75), 231 (41), 314 (34), 208 (18), 315 (17), 133 (15), 83 (13), 189 (11), 59 (11), 191 (11), 232 (11), 74 (10), 209 (10).*

*HRMS (ESI TOF) calcd for $C_{15}H_{32}O_2Si_3Na$: 351,1608, found: 351,1598*

***1.6.*** *((Diphenylsilyl)ethynyl)dimethyl(phenyl)silane* **6**; colorless oil, yield: 68 mg (20%)

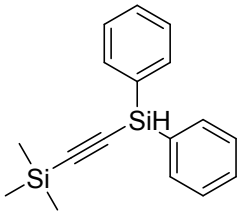


$^{1}$H NMR (300MHz, $CDCl_3$): 7.74-7.64 (m, 6H), 7.46-7.35 (m, 9H), 5.21 (s, 1H), 0.51 (s, 6H)

*$^{13}$C NMR (75 MHz, $CDCl_3$):*137.27, 136.21, 135.87, 135.33, 134.77, 132.85, 131.15, 130.59, 129.13, 128.95, 118.52, 109.18, 0.00

*MS (70 eV): m/z (%): 105 (100), 197 (87), 327 (77), 135 (63), 264 (48), 86 (42), 78 (36), 57 (35), 209 (33), 106 (33), 77 (31), 342 (31), 23 (30), 206 (30), 249 (29), 119 (29), 283 (26), 59 (24), 266 (23), 107 (22), 198 (22), 51 (22), 73 (22), 158 (20), 147 (20), 181 (20), 328 (20), 195 (18), 165 (17), 132 (17), 259 (17), 159 (16), 109 (16), 91 (16), 146 (15), 152 (15), 180 (15), 87 (14), 211 (14), 97 (13), 186 (13), 343 (13), 341 (12), 50 (12), 171 (12), 60 (12), 129 (12),163 (12), 81 (12), 149 (11), 288 (10), 136 (10).*

***1.7.*** *((diphenylsilyl)ethynyl)trimethylsilane,* **7**; colorless oil, yield: 118 mg (42%)




$^{1}$H NMR (300MHz, $CDCl_3$): 7.75-7.65 (m, 4H), 7.48-7.39 (m, 6H), 5.19 (s, 1H), 0.28 (s, 9H)

*$^{13}$C NMR (75 MHz, $CDCl_3$):* 135.42, 132.25, 130.33, 128.34, 120.11, 106.22, 0.00

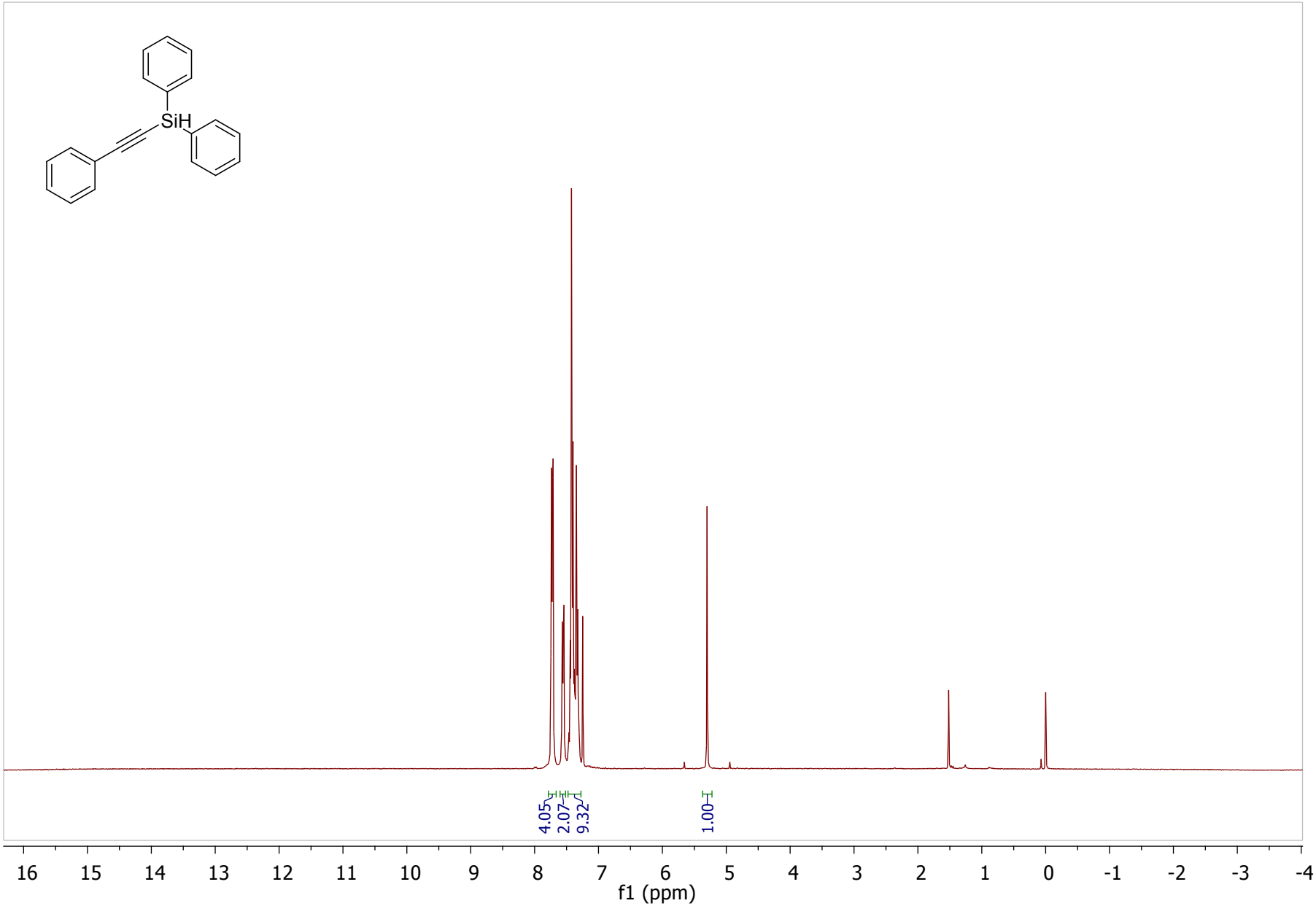
*MS (70 eV): m/z (%): 135 (100), 265 (85), 202 (74), 187 (73), 105 (56), 197 (29), 73 (27), 280 (27),245 (26), 266 (23), 181 (22), 207 (20), 53 (19), 203 (19), 129 (17), 188 (16), 107 (14), 159 (12),143 (12), 221 (11), 131 (11), 51 (10), 182 (10), 195 (10), 136 (10).*

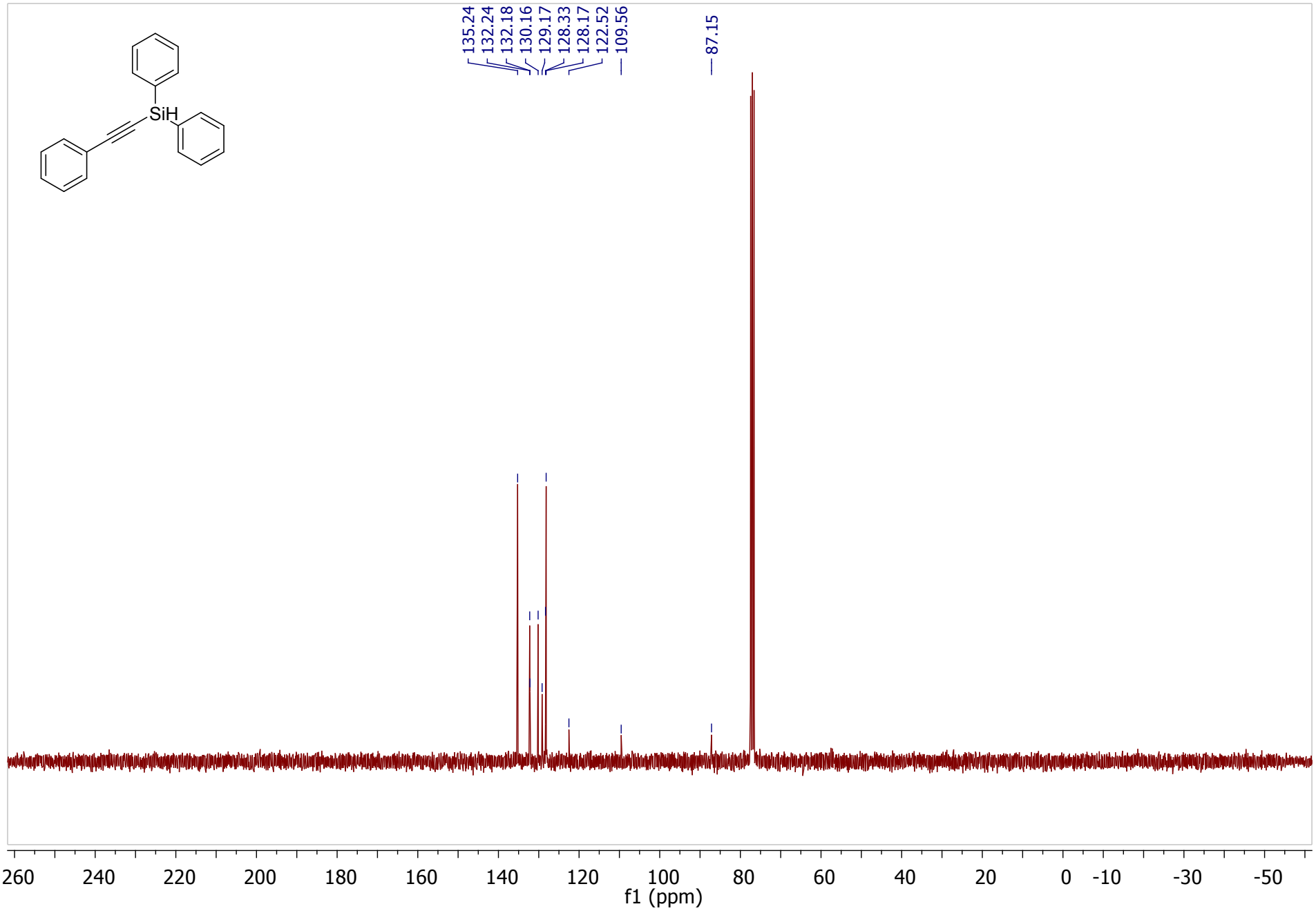
Conforms to the literature analytical data[4]

**References:**

(1) H. Q. Liu and J. F. Harrod, *Can. J. Chem.*, 1990, **68**, 1100–1105.
(2) H. Sakaba, M. Yoshida, C. Kabuto and K. Kabuto, *J. Am. Chem. Soc.*, 2005, **127**, 7276–7277.
(3) C. Conifer, C. Gunanathan, T. Rinesch, M. Hölscher and W. Leitner, *Eur. J. Inorg. Chem.*, 2015, **2015**, 333–339.
(4) P. N. Reddy, T. Hayashi, M. Tanaka and M. Itoh, *Chem. Lett.*, 2000, **29**, 254–255.

2. **Spectra of products**

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132.24
132.18
130.16
129.17
128.33
128.17
122.52
109.56
87.15
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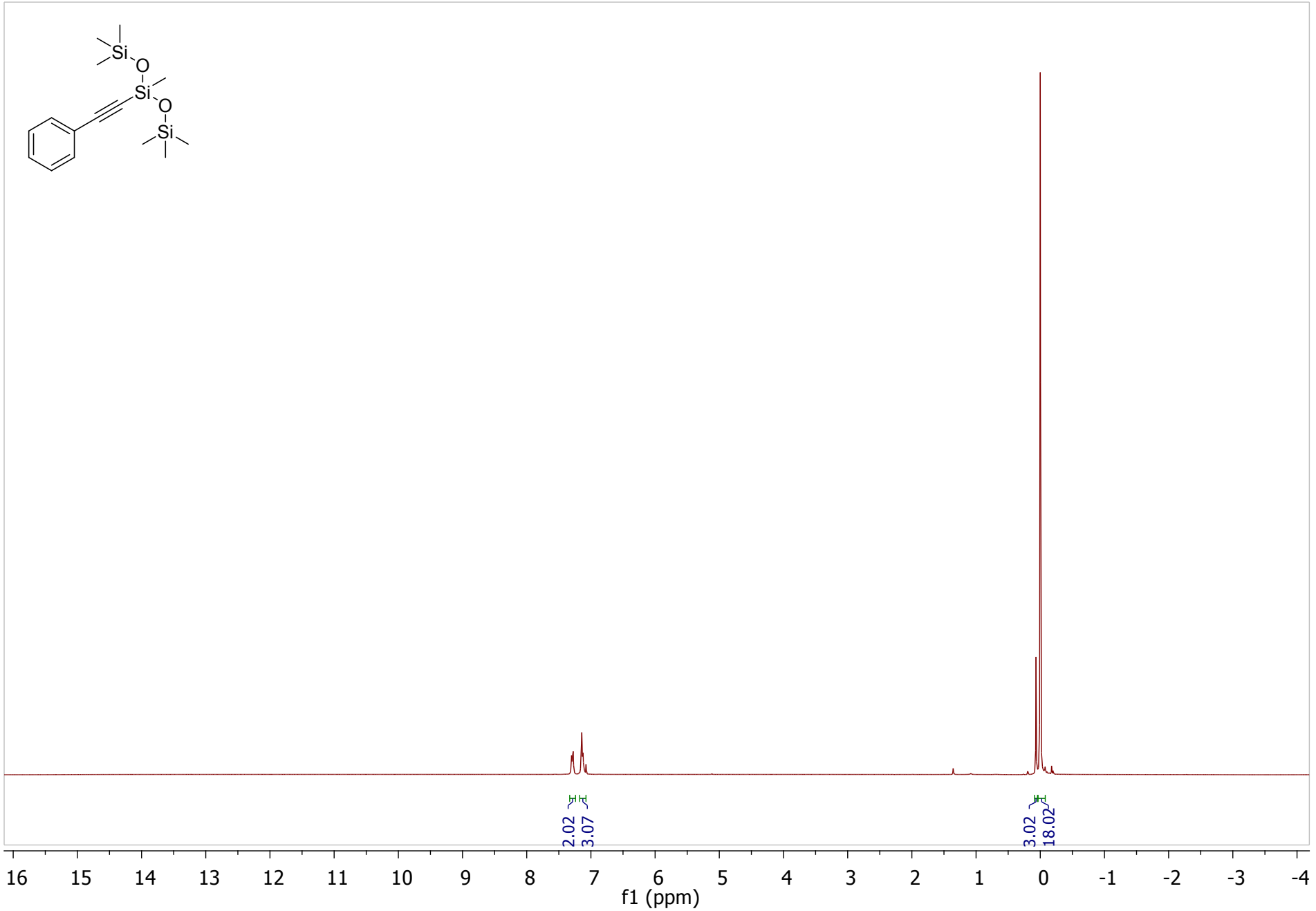
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)


Si
O
Si
O
Si
2.02
3.07
3.02
18.02
16
15
14
13
12
11
10
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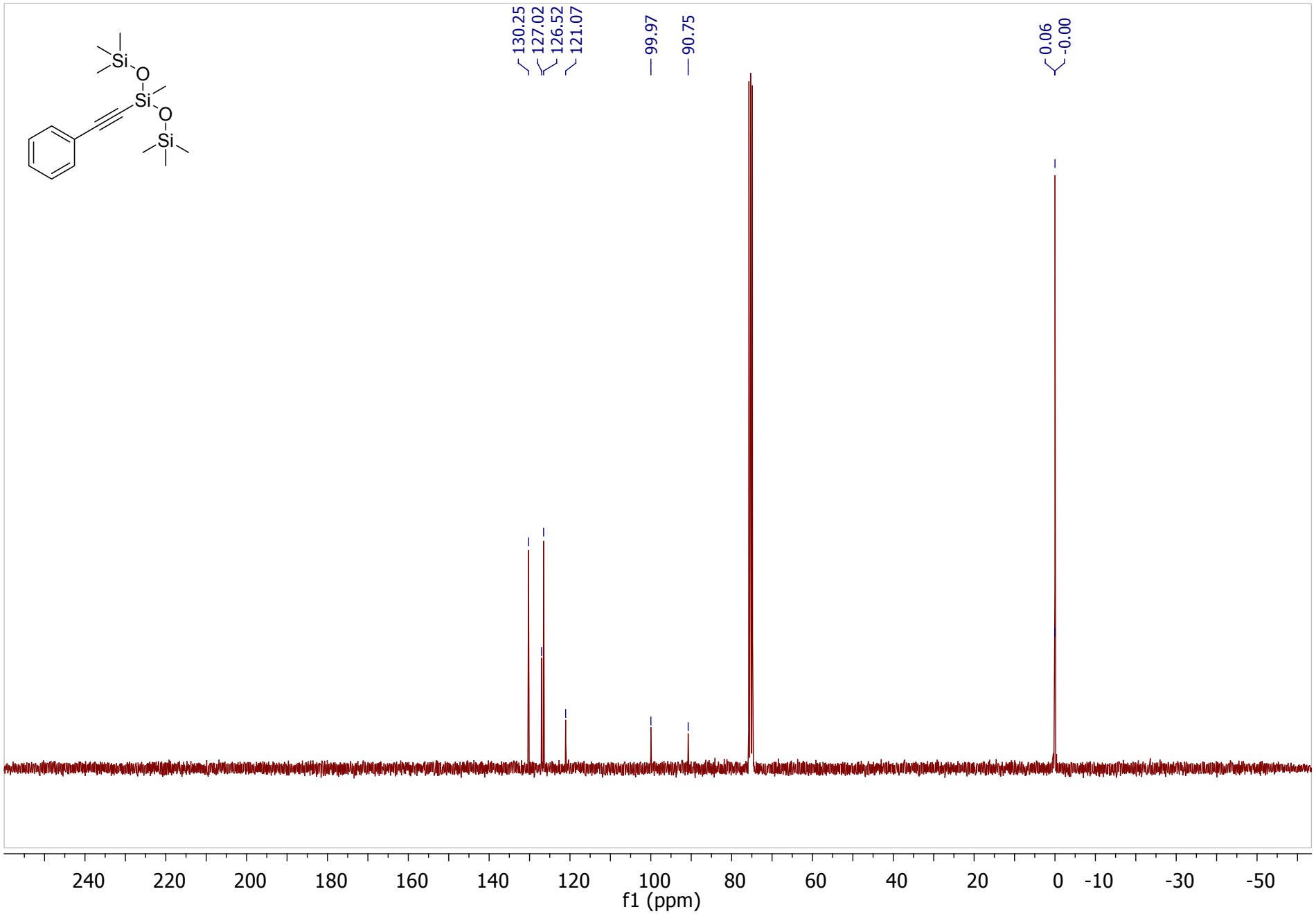
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)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127.02
126.52
121.07
99.97
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-0.00
Si
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Si
O
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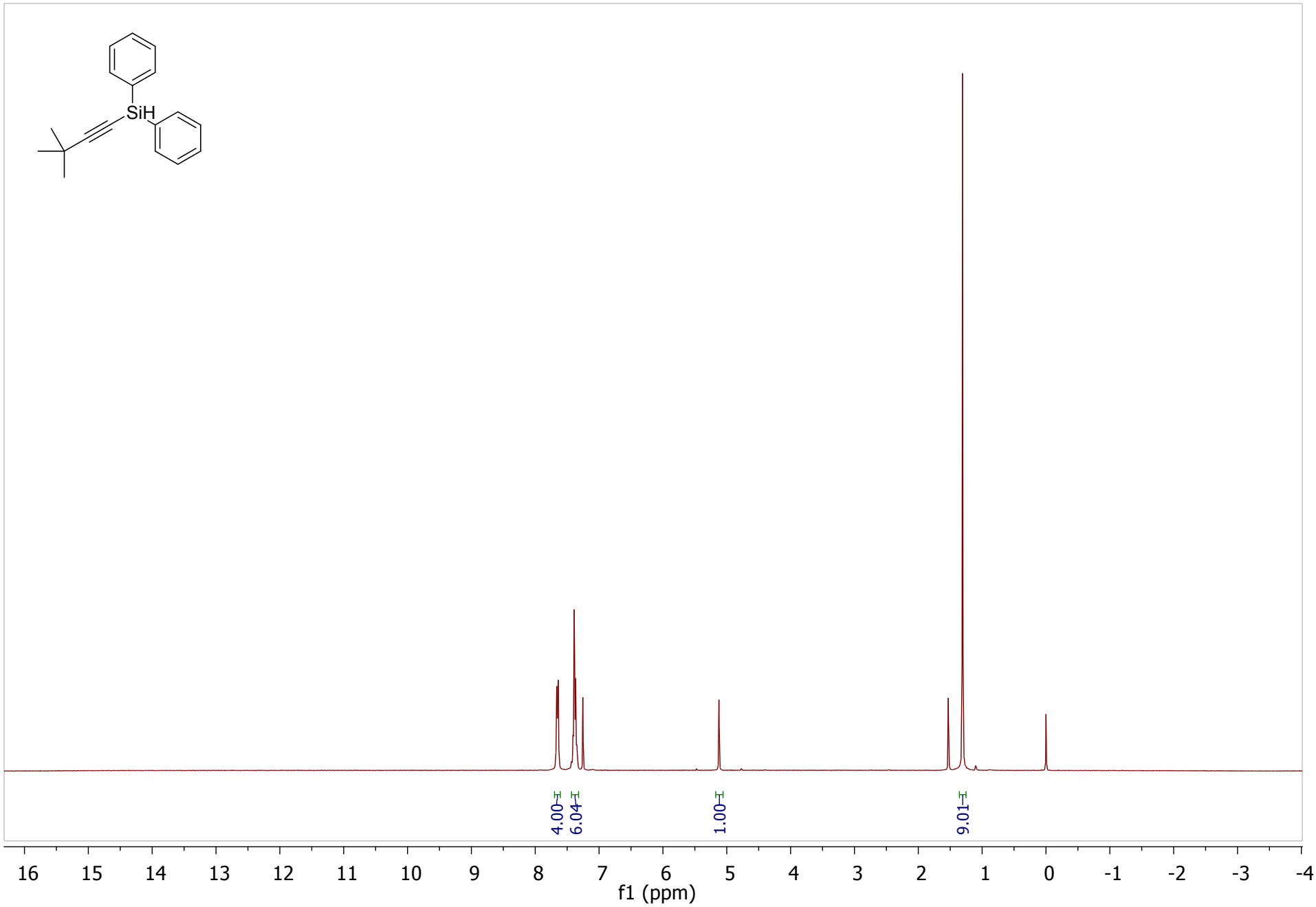
f1 (ppm)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9.01
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13
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11
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9
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7
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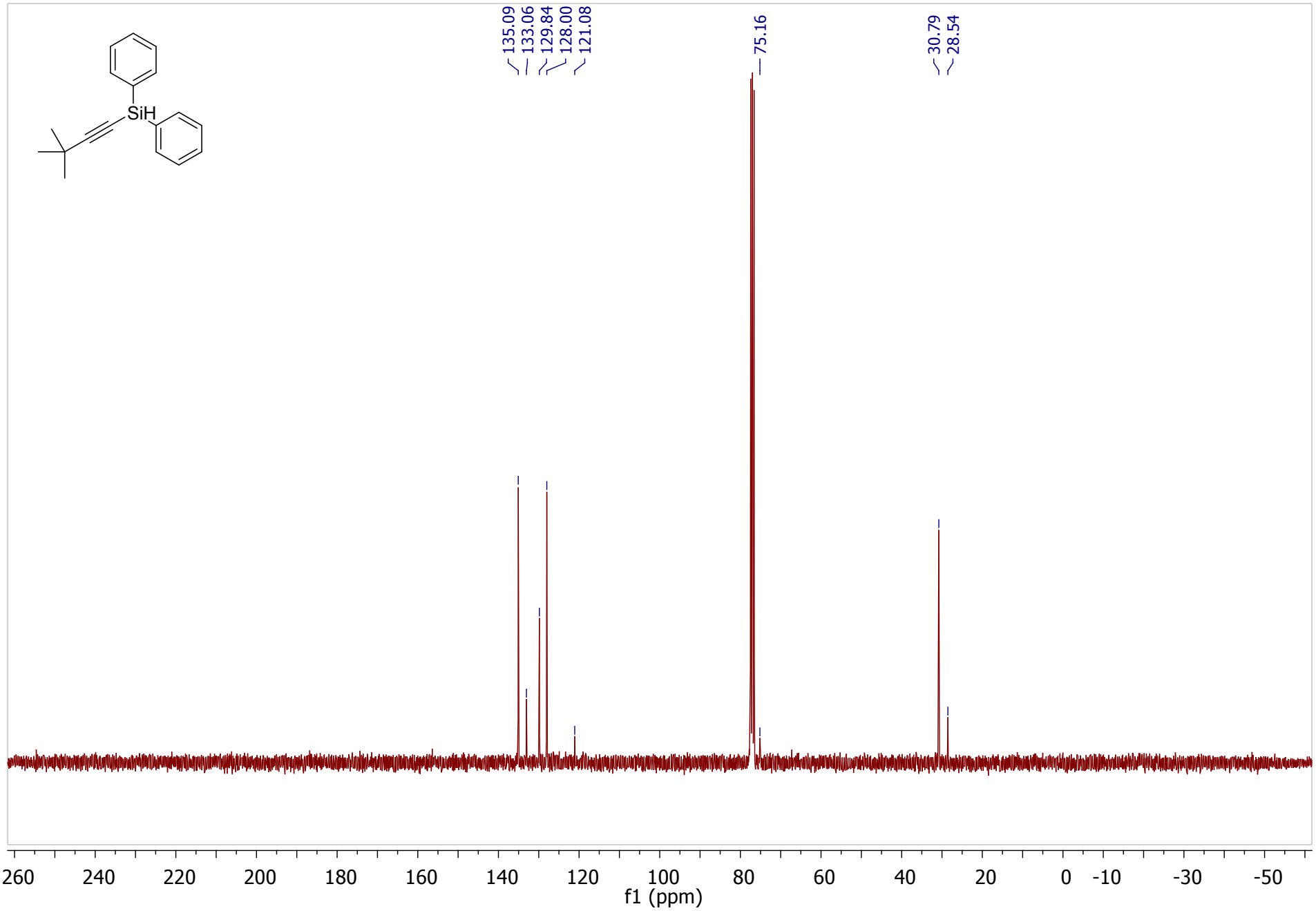
-4
f1 (ppm)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121.08
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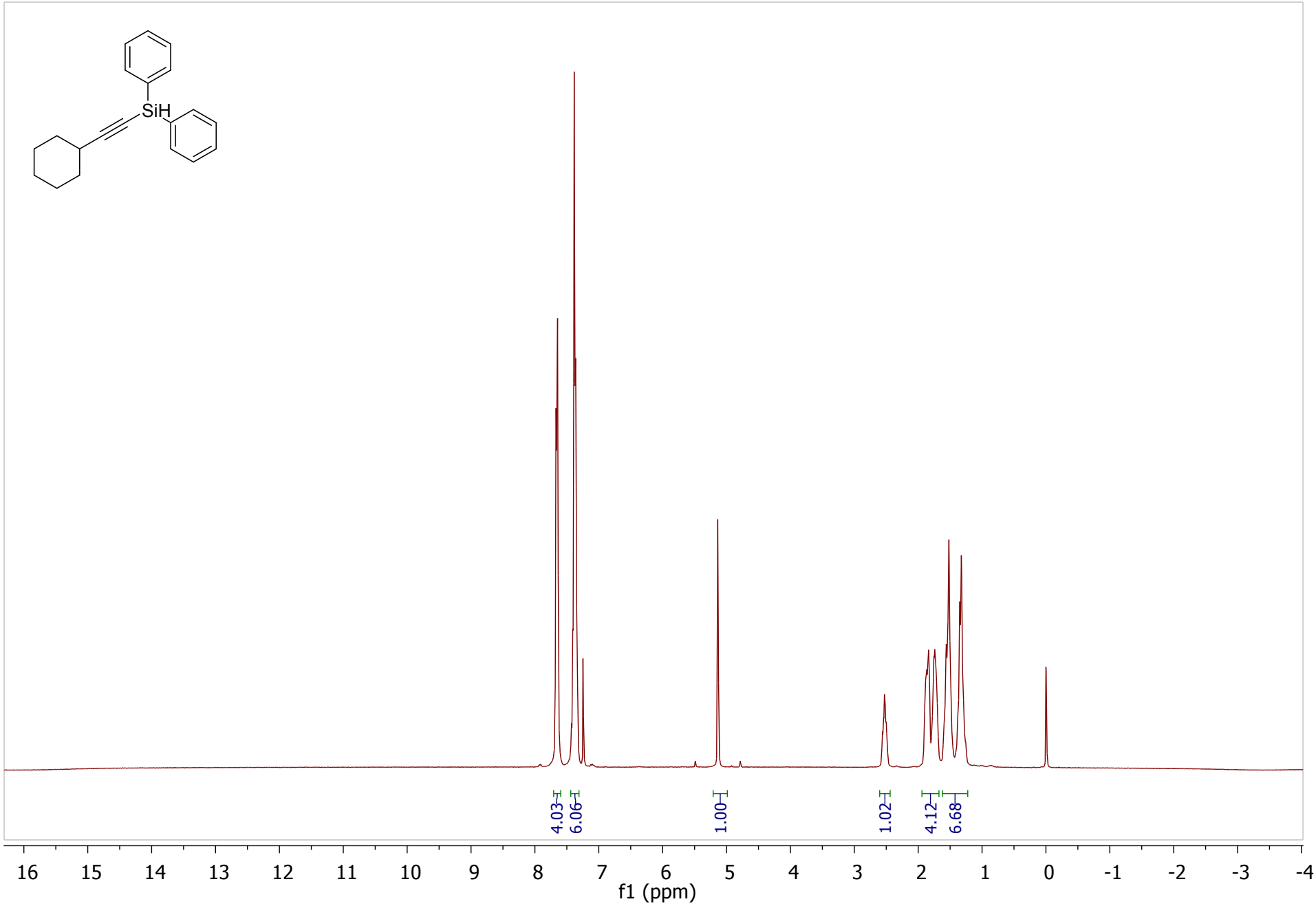
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)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7
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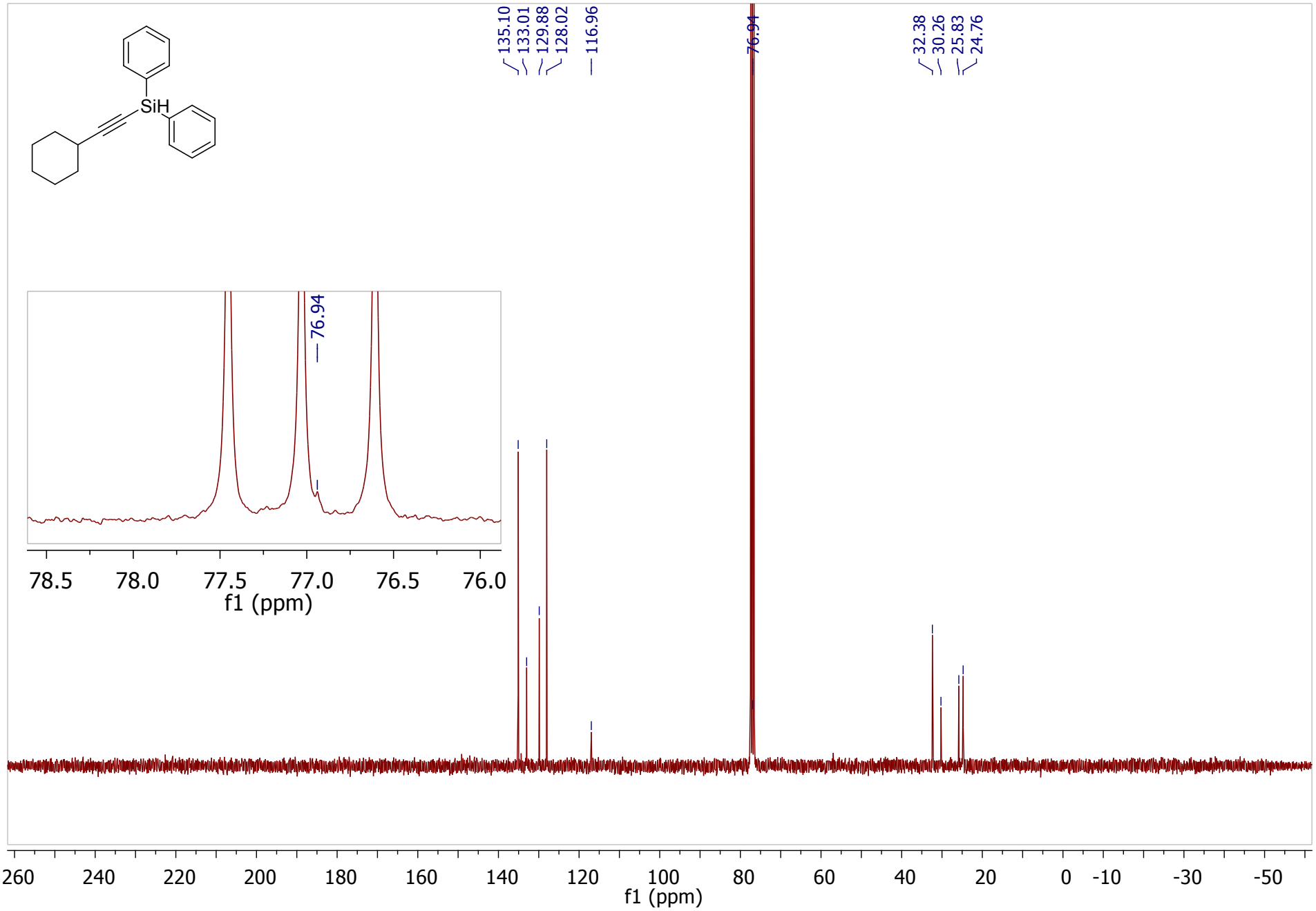
-4
f1 (ppm)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24.76
78.5
78.0
77.5
77.0
76.5
76.0
f1 (ppm)
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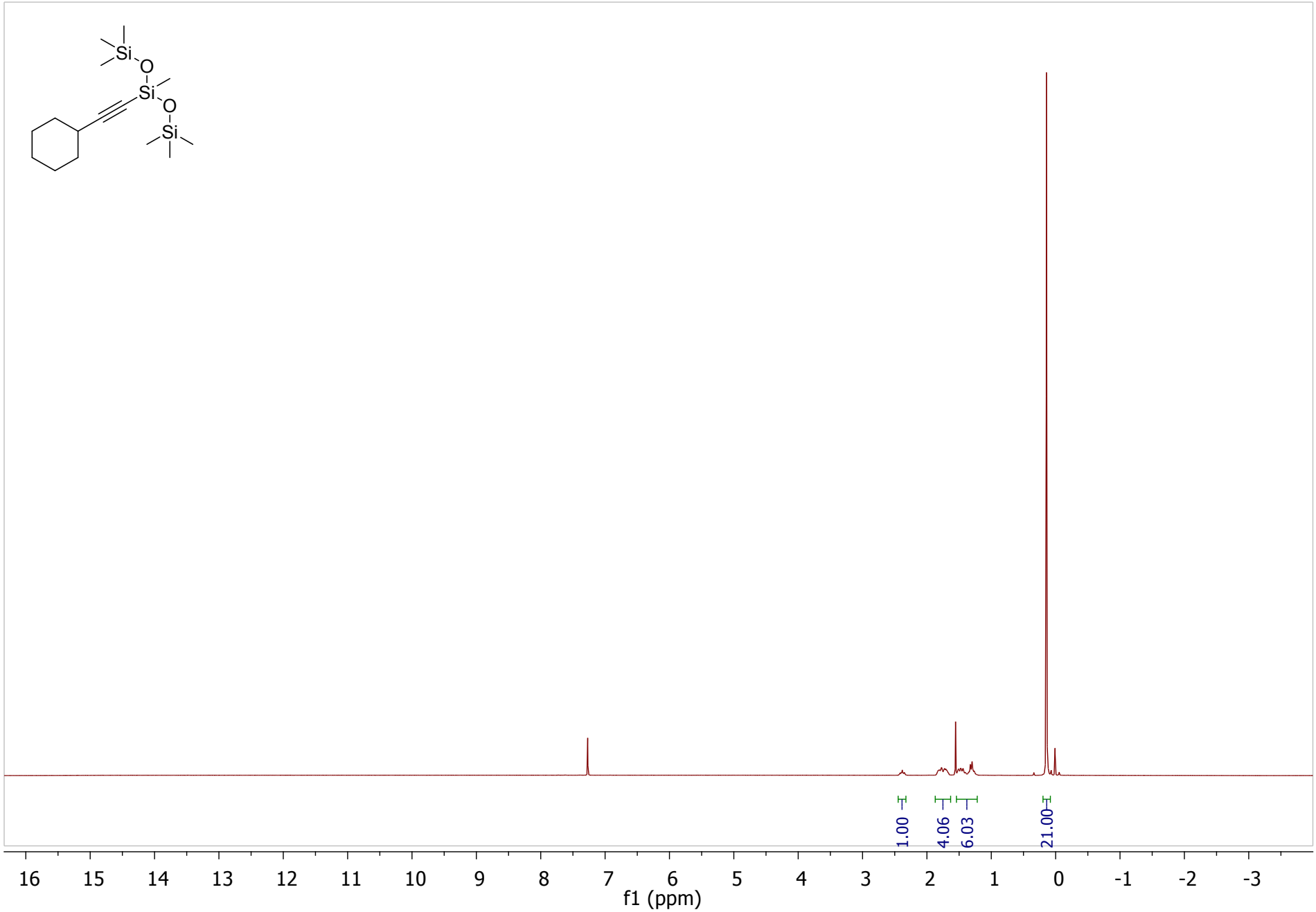
240
220
200
180
160
140
120
100
80
60
40
20
0
-10
-30
-50
f1 (ppm)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O
Si
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6.03
21.00
16
15
14
13
12
11
10
9
8
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5
4
3
2
1
0
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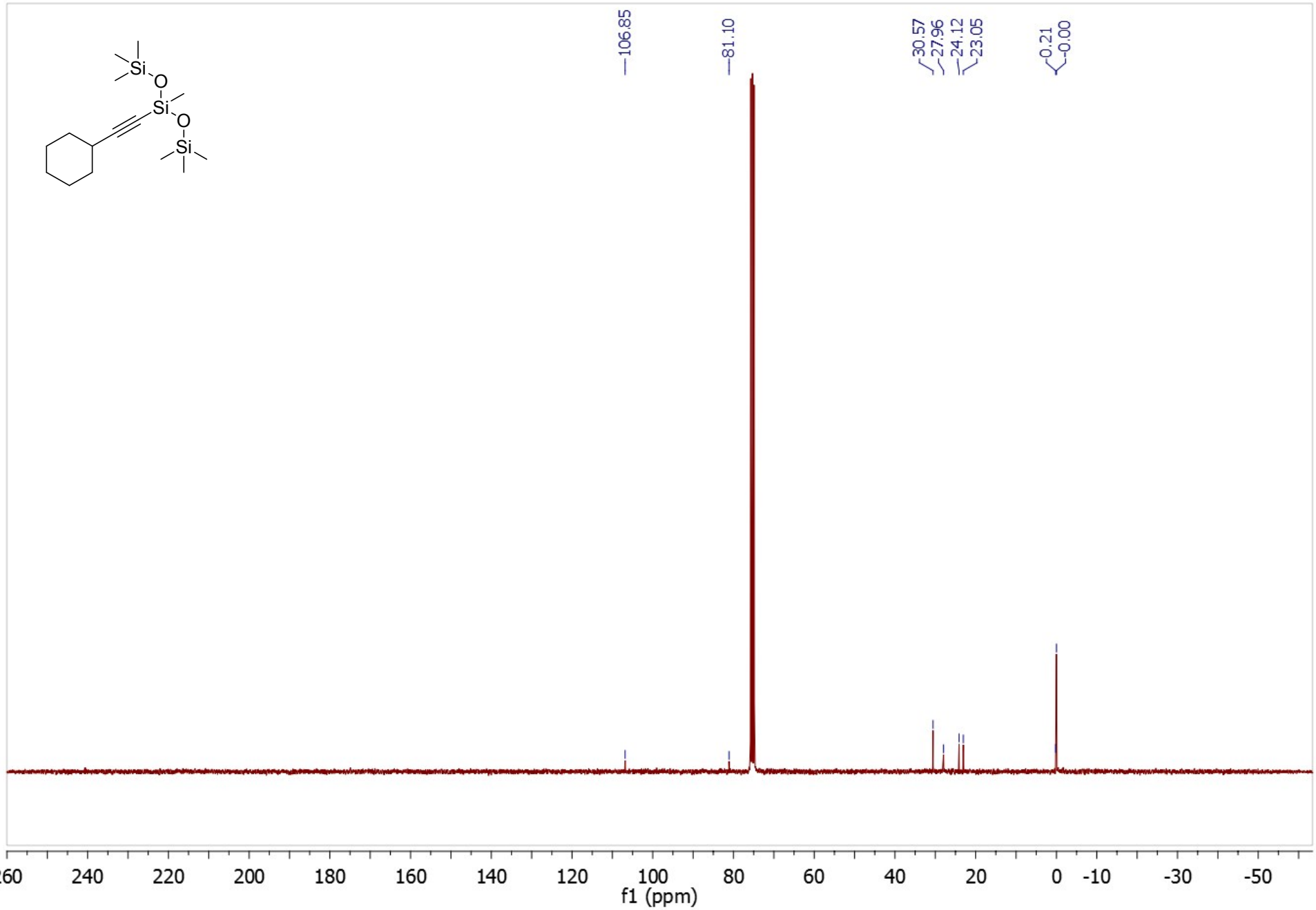
-2
-3
f1 (ppm)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Si
O
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180
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100
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60
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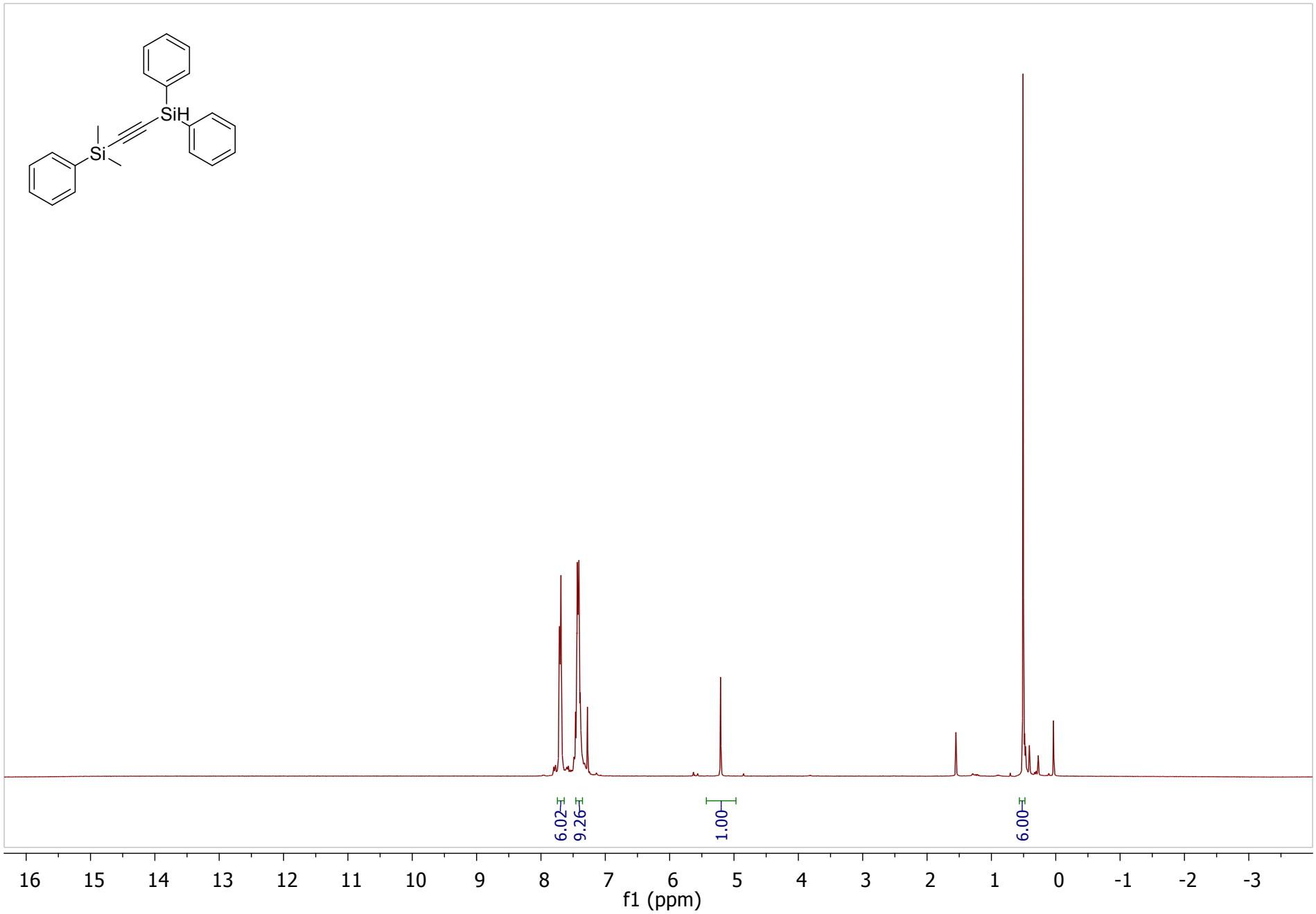
20
0
-10
-30
-50
f1 (ppm)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1.00
6.00
16
15
14
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9
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7
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5
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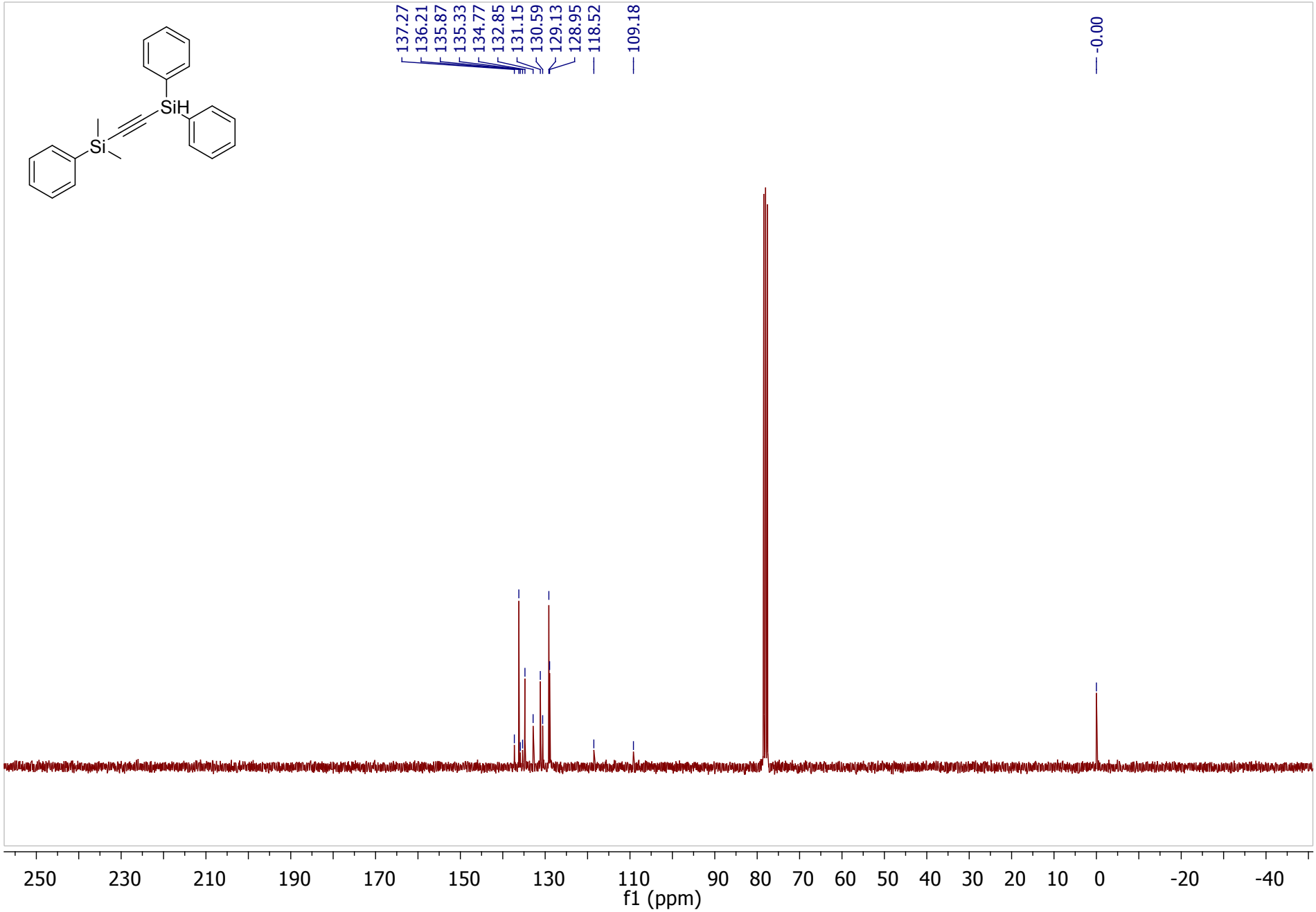
3
2
1
0
-1
-2
-3
f1 (ppm)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135.87
135.33
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132.85
131.15
130.59
129.13
128.95
118.52
109.18
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SiH
Si
250
230
210
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130
110
90
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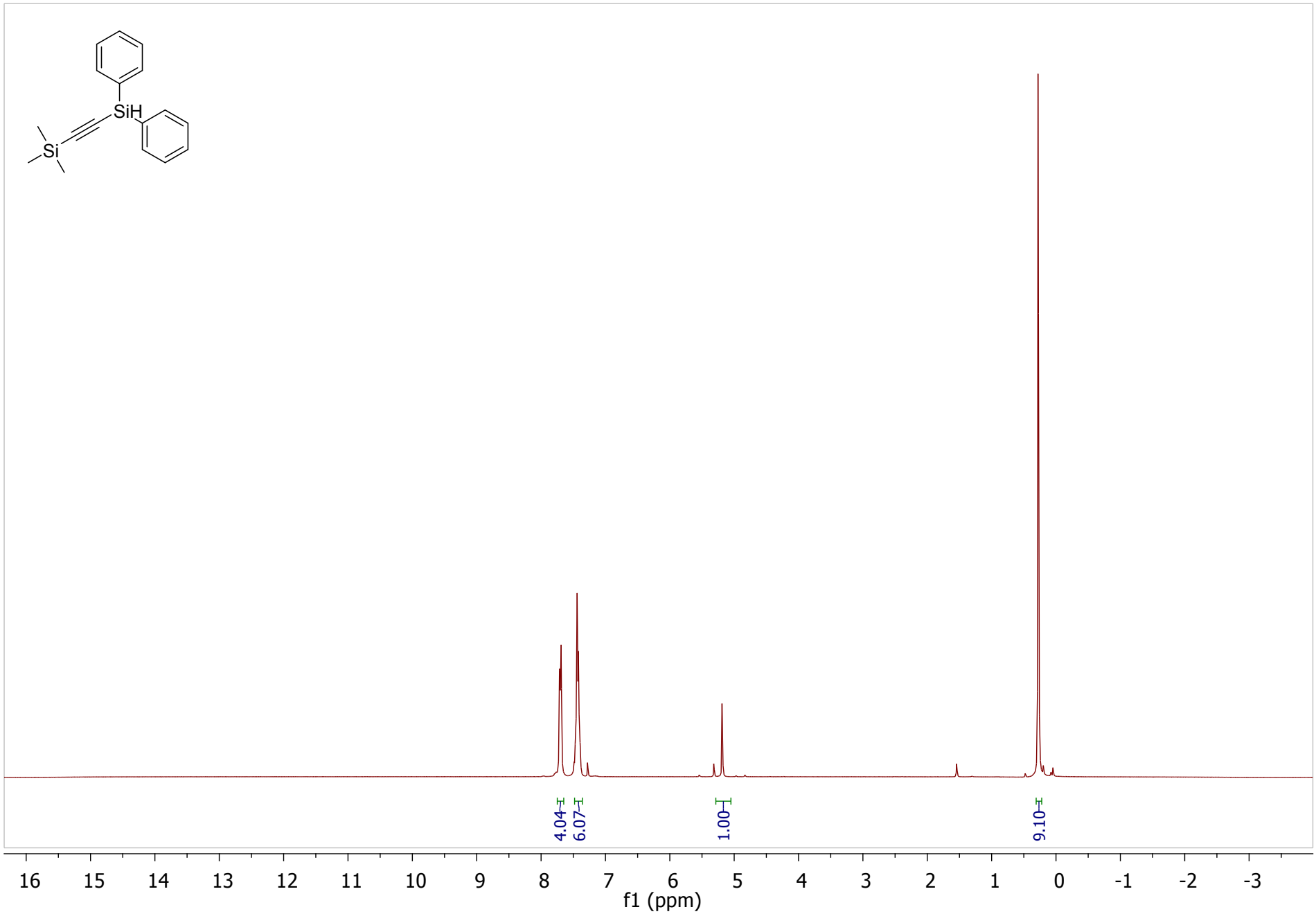
70
60
50
40
30
20
10
0
-20
-40
f1 (ppm)


SiH
Si
4.04
6.07
1.00
9.10
16
15
14
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12
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9
8
7
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5
4
3
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1
0
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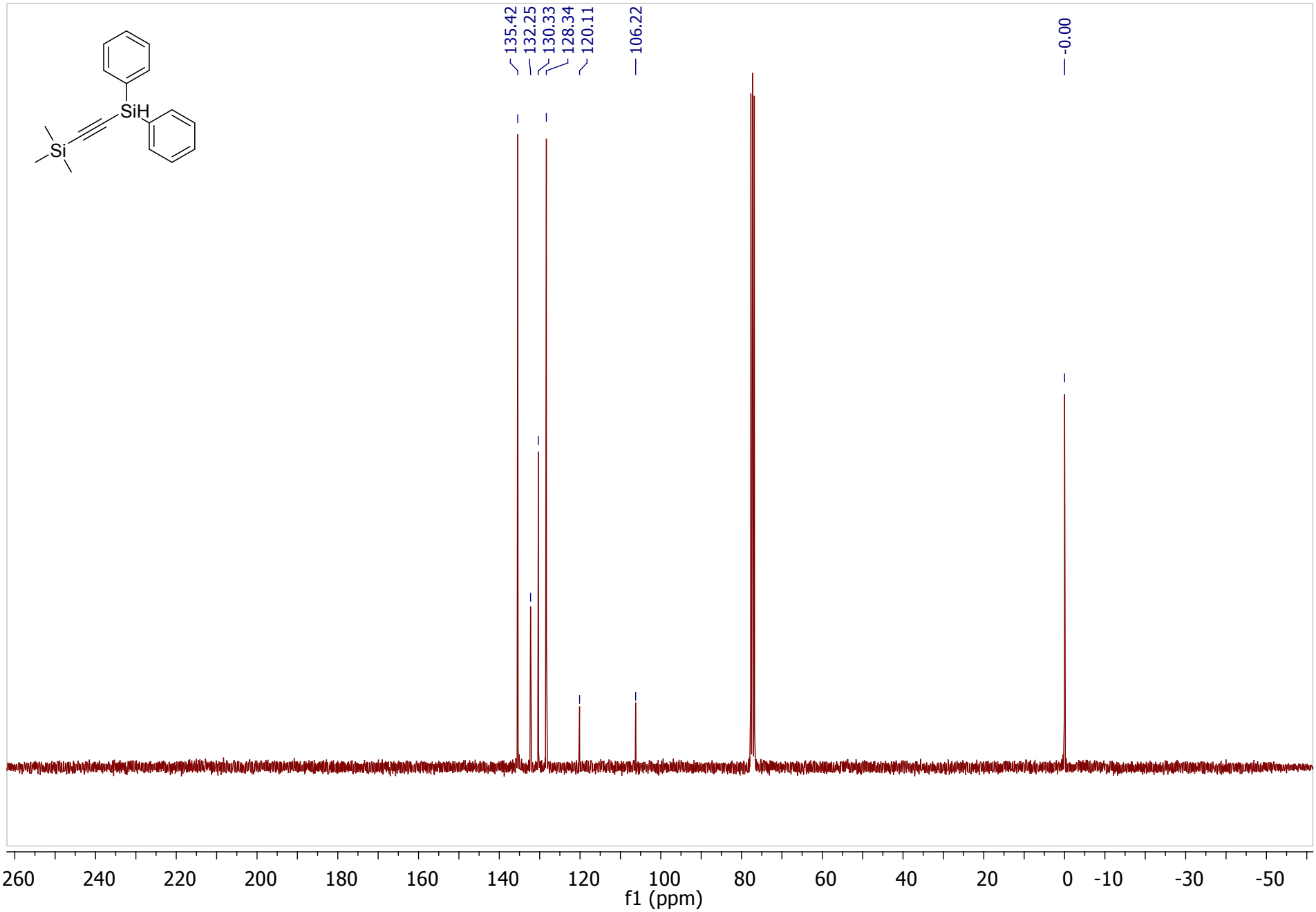
-2
-3
f1 (ppm)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106.22
-0.00
SiH
Si
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120
100
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60
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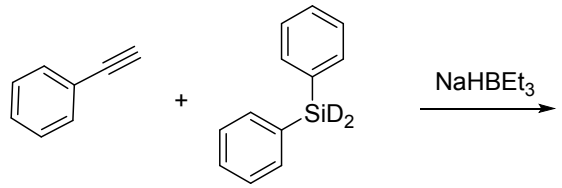
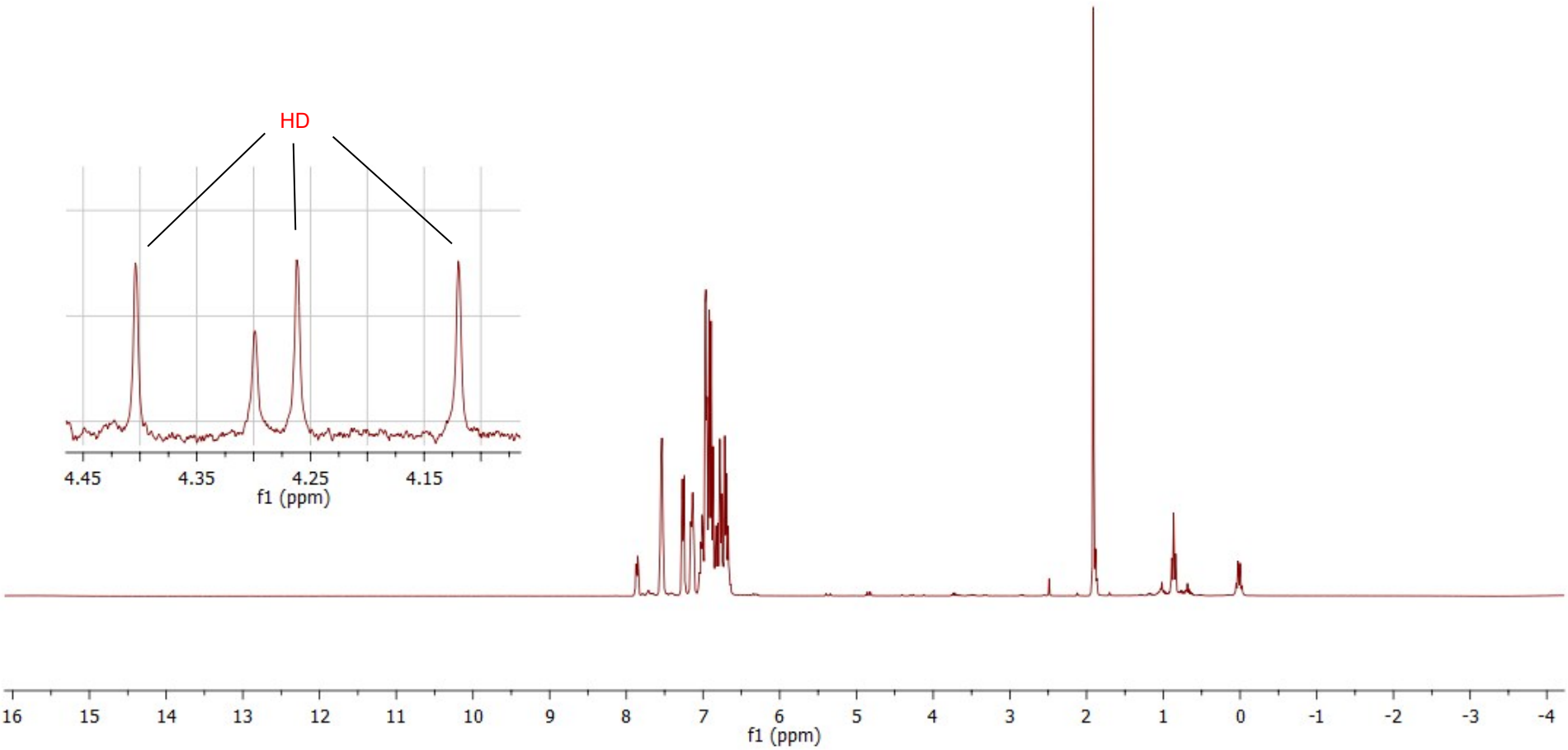
20
0
-10
-30
-50
f1 (ppm)


NaHBEt3
SiD2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4.15
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14
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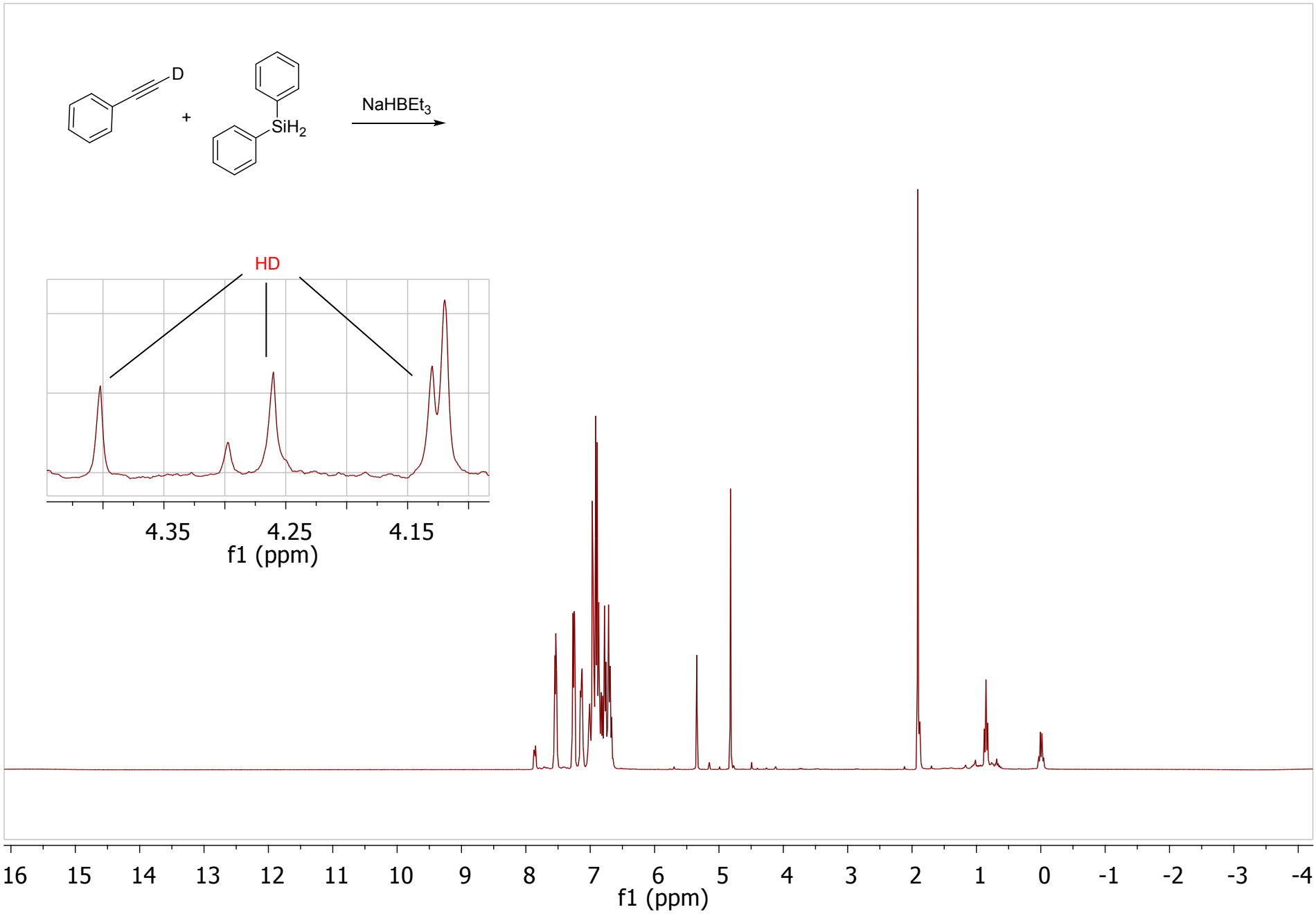
-1
-2
-3
-4
f1 (ppm)


D
+
SiH2
NaHBEt3
HD
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4.25
4.15
f1 (ppm)
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15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)