Supporting Information

Silica-Supported Catalysts for Ring-Closing Metathesis: Effects of Linker Group and Microenvironment on Recyclability

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General

FT-IR spectra were recorded on a Bio-rad FTS-60A spectrometer using the photoacoustic mode. Solution NMR spectra were recorded on a Bruker spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) at ambient temperature in the solvents indicated, and referenced to the solvent peaks. ^{13}C CP-MAS and ^{29}Si CP-MAS NMR spectra were recorded on a 400 MHz Bruker spectrometer for compounds immobilized onto MCF. Elemental analyses were performed with CE440 CHN Analyzer (Exeter Analytical). ICP-MS data were obtained by Elan DRC II, PerkinElmer SCIEX, USA. Mass spectra were obtained at the Elemental Analysis Laboratory, Department of Chemistry, National University of Singapore, Singapore. Conversions for RCM of dienes were determined by GC (Agilent 6890N) or LC (Agilent 1100 Series). Unless otherwise noted, reactions were performed under argon atmosphere by standard Schlenk techniques. All the chemicals were purchased from Aldrich. Solvents were either purified by passage through a column of activated alumina or purchased in sealed bottles from Aldrich. Spherical MCF microparticles were synthesized according to our published procedures.[12]

General Procedure for the Preparation of Precursors 5a–5c

A 250-ml two-necked flask equipped with a reflux condenser was charged with magnesium (21.0 mmol), iodine (trace), and dried tetrahydrofuran (THF, 50 ml), and then heated under reflux. 4-Bromo-2-isopropoxystyrene (**3**, 20.0 mmol) in THF (50 ml) was added slowly, and the resulting mixture was stirred under reflux until magnesium was nearly consumed. After cooling to room temperature, the turbid solution was added to a stirred solution of the corresponding dichloride **4** (60.0 mmol) in THF (50 ml) at 0 °C. The resulting solution was stirred for 18 h at room temperature. It was concentrated under reduced pressure, and hexane (20 ml) was added slowly under stirring. The insoluble substance was filtered off, and the filtrate was concentrated and dried under vacuum for 24 h to give the corresponding chlorosilane **5** as an oil, which was used for the next step without further purification.

The general procedure using dichlorodimethylsilane (**4a**, 20.0 mmol) gave 5.05 g (99%) of the corresponding chlorosilane **5a**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.68 (s, 6H), 1.36 (d, 6H, J = 6.0 Hz), 4.59 (septet, 1H, J = 6.0 Hz), 5.27 (dd, 1H, J = 11.2, 1.4 Hz), 5.78 (dd, 1H, J = 17.6, 1.4 Hz), 6.91 (d, 1H, J = 8.4 Hz), 7.05 (dd, 1H, J = 17.6, 11.2 Hz), 7.46 (dd, 1H, J = 8.4, 1.6 Hz), 7.69 (d, 1H, J = 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 2.2, 22.0, 70.3, 113.0, 114.5, 126.6, 127.2, 131.7, 131.8, 133.8, 156.9.

The general procedure using 1,2-bis(dichlorosilyl)ethane (**4b**, 15.0 mmol) gave 5.01 g (98%) of the corresponding chlorosilane **5b**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.30 (s, 6H), 0.42 (s, 6H), 0.76 (s, 4H), 1.39 (d, 6H, *J* = 6.0 Hz), 4.61 (septet, 1H, *J* = 6.0 Hz), 5.28 (dd, 1H, *J* = 11.2, 1.4 Hz), 5.79 (dd, 1H, *J* = 17.6, 1.4 Hz), 6.91 (d, 1H, *J* = 8.4 Hz), 7.10 (dd, 1H, *J* = 17.6, 11.2 Hz), 7.37 (dd, 1H, *J* = 8.4, 1.6 Hz), 7.61 (d, 1H, *J* = 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ -3.4, 1.0, 7.3, 11.5, 22.2, 70.3, 113.0, 114.1, 127.0, 129.1, 132.2, 132.3, 134.3, 156.1.

The general procedure using 1,6-bis(dichlorosilyl)hexane (**4c**, 20.0 mmol) gave 7.78 g (98%) of the corresponding chlorosilane **5c**. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.24 (s, 6H), 0.40 (s, 6H), 0.70–0.85 (m, 4H), 1.32 (bs, 8H), 1.37 (d, 6H, *J* = 6.0 Hz), 4.57 (septet, 1H, *J* = 6.0 Hz), 5.24 (dd, 1H, *J* = 11.2, 1.4 Hz), 5.76 (dd, 1H, *J* = 17.6, 1.4 Hz), 6.88 (d, 1H, *J* = 8.4 Hz), 7.07 (dd, 1H, *J* = 17.6, 11.2 Hz), 7.34 (dd, 1H, *J* = 8.4, 1.6 Hz), 7.59 (d, 1H, *J* = 1.6 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$): δ -2.6, 1.9, 16.1, 19.2, 22.4, 23.1, 24.0, 32.8, 33.4, 70.5, 113.2, 114.1, 127.1, 130.3, 132.3, 132.5, 134.4, 156.1.

General Procedure for the Preparation of Immobilized Ligands 6a–6c

A 100-ml Schlenk flask was charged with MCF (3.00 g, 0.80 mmol of TMS/g), and placed under vacuum for 24 h at 120 °C. The flask was purged with argon at room temperature, and charged with triethylamine (0.44 ml), dried toluene (40 ml), and the corresponding chlorosilane **5** (1.05 mmol). The resulting mixture was stirred for 24 h at room temperature. The white solid was thoroughly rinsed by toluene, DCM, methanol, and DCM (50 ml each), which was transferred to a 100-ml Schlenk flask and dried under vacuum for 12 h at 80 °C. After cooling down to room temperature, the flask was placed in liquid nitrogen bath for 10 min, and HMDS (1 ml) was added under vacuum. The flask was sealed and then kept at 80 °C for 5 h. The resulting solid was cooled to room temperature, washed thoroughly with DCM (100 ml), and then dried under vacuum for 24 h to give the corresponding immobilized ligand **6** as a white powder.

The general procedure using the corresponding precursor **5a** (1.05 mmol) gave 3.23 g of **6a**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 0.0, 20.8, 49.6, 69.7, 113.1, 128.0, 132.6, 156.9. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -108.8, -102.3, 3.32, 13.9. Elemental analysis, found: C, 8.16; H, 1.39; N, < 0.07. Loading of ligand: 0.35 mmol/g.

The general procedure using the corresponding precursor **5b** (0.70 mmol) gave 2.20 g of **6b**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 1.1, 8.9, 21.7, 50.6, 69.7, 112.7, 132.5, 157.4. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -107.0, -99.9, -1.74, 14.7. Elemental analysis, found: C, 10.99; H, 2.12; N, < 0.03. Loading of ligand: 0.32 mmol/g.

The general procedure using the corresponding precursor **5c** (1.05 mmol) gave 3.46 g of **6c**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 3.4, 20.3, 25.6, 36.0, 72.6, 115.8, 130.5, 135.6, 159.0. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -105.3, -97.5, -0.3, 17.6. Elemental analysis, found: C, 12.87; H, 2.48; N, < 0.11. Loading of ligand: 0.35 mmol/g.

General Procedure for the Preparation of Immobilized Ligands 6d–6e

A 100-ml Schlenk flask was charged with uncapped MCF (2.13 g), and placed under vacuum for 24 h at 120 °C. The flask was purged with argon at room temperature, and charged with chlorosilane **5c** (0.70 mmol) and alkylchlorosilane (**4d** or **4e**, 1.80 mmol) in the presence of triethylamine (5.00 mmol) and dried toluene (40 ml). The resulting mixture was stirred for 24 h at room temperature. The white solid was thoroughly rinsed by toluene, DCM, methanol, and DCM (50 ml each), which was transferred to a 100-ml Schlenk flask and dried under vacuum for 12 h at 80 °C. After cooling down to room temperature, the flask was placed in liquid nitrogen bath for 10 min, and HMDS (1 ml) was added under vacuum. The flask was sealed and then kept at 80 °C for 5 h. The resulting solid was cooled to room temperature, washed thoroughly with DCM (100 ml), and then dried under vacuum for 24 h to give the corresponding immobilized ligand **6** as a white powder.

The general procedure using the precursor **5c** (0.70 mmol) and chlorodimethyl(*n*-octyl)silane **4d** (1.80 mmol) gave 2.58 g of **6d**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 2.5, 15.8, 20.6, 25.8, 32.4, 35.1, 36.4, 53.7, 72.8, 114.9, 116.0, 130.7, 132.9, 135.0, 135.8, 136.7, 159.3. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -104.4, -97.1, 0.0, 18.1. Elemental analysis, found: C, 12.87; H, 2.39; N, < 0.02. Loading of ligand: 0.20 mmol/g.

The general procedure using the precursor **5c** (0.70 mmol) and chlorodimethyl(perfluorooctylethyl)silane **4e** (1.80 mmol) gave 2.96 g of **6e**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 1.7, 3.5, 10.1, 20.3, 25.8, 28.2, 36.0, 45.9, 53.4, 73.0, 114.7, 119.1, 121.4, 123.7, 132.9, 135.7, 156.2. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -105.0, -96.4, 0.0, 18.3. Elemental analysis, found: C, 12.00; H, 1.67; N, < 0.02. Loading of ligand: 0.23 mmol/g.

General Procedure for the Preparation of Catalysts 7a–7e

A 50-ml two-necked flask equipped with a reflux condenser was charged with ligand **6** (0.18 mmol), second-generation Grubbs' catalyst **1b** (0.18 mmol), copper chloride (0.18 mmol), and dried DCM (20 ml) under argon. The reaction mixture was heated for 5 h under reflux in argon. The reaction mixture gradually changed from dark brown to deep green. After cooling to room temperature, the fine powder was washed thoroughly with DCM (100 ml), and dried under vacuum for 24 h to give the immobilized catalyst **7** as a green powder.

The general procedure using the derivative of **6a** (500 mg) gave 566 mg of **7a**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 1.3, 21.0, 51.8, 60.2, 71.1, 75.6, 114.1, 129.8, 139.6, 146.2, 155.0, 209.6, 219.2. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -105.1, -98.2, 6.7, 17.6. Elemental analysis, found: C, 12.99; H, 1.97; N, 0.59. Loading of ruthenium: 0.21 mmol/g.

The general procedure using the derivative of **6b** (2.00 g) gave 2.27 g of **7b**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 2.3, 10.6, 20.8, 52.2, 60.0, 71.3, 75.4, 113.5, 129.9, 135.7, 139.7, 146.5, 154.5, 209.2, 219.1. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -104.6, -97.5, 2.1, 17.9. Elemental analysis, found: C, 14.45; H, 3.55; N, 0.62. Loading of ruthenium: 0.22 mmol/g.

The general procedure using the derivative of **6c** (2.00 g) gave 2.25 g of **7c**. ^{13}C CP-MAS NMR (100 MHz): δ (ppm) = 1.7, 19.1, 33.7, 51.4, 74.7, 113.2, 129.3, 135.3, 139.0, 145.7, 153.7. ^{29}Si CP-MAS NMR (75 MHz): δ (ppm) = -105.1, -96.8, -0.3, 17.8. Elemental analysis, found: C, 16.23; H, 2.68; N, 0.60. Loading of ruthenium: 0.21 mmol/g.

The general procedure using the derivative of **6d** (2.00 g) gave 2.16 g of **7d**. Elemental analysis, found: C, 16.30; H, 2.79; N, 0.45. Loading of ruthenium: 0.15 mmol/g.

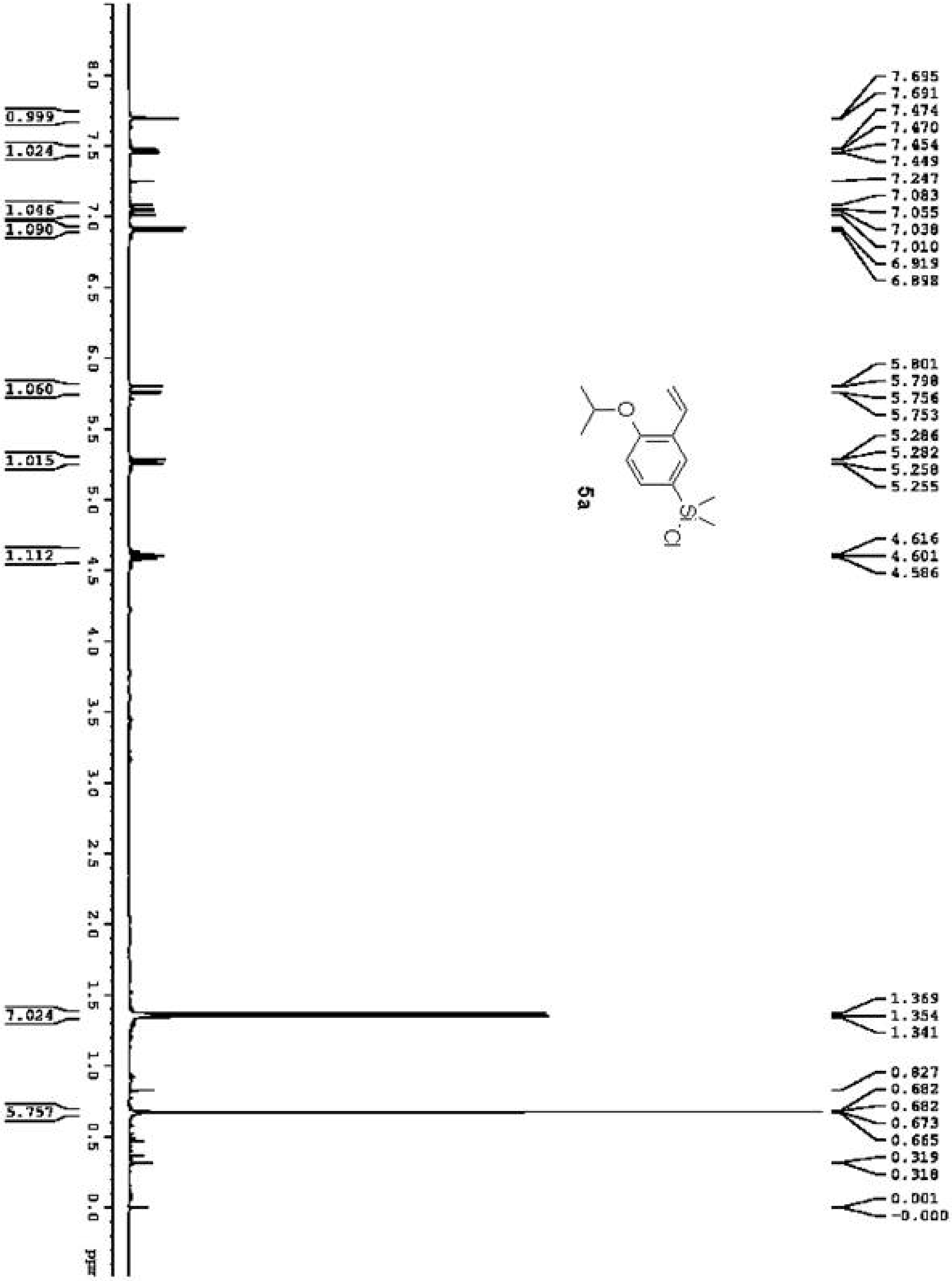
The general procedure using the derivative of **6e** (2.00 g) gave 2.15 g of **7e**. Elemental analysis, found: C, 14.04; H, 1.83; N, 0.41. Loading of ruthenium: 0.14 mmol/g.

General Procedure for Testing Catalytic Activity

Reactions were run in a vial containing a magnetic stir bar under argon. The vial was charged with catalysts **7** (5 μmol) and DCM (2 ml). A substrate (0.1 mmol) was injected, and the conversion was monitored by GC or LC after fresh filtration through a short pad of silica gel by elution with DCM.

General Procedure for Testing Catalyst Recyclability

Reactions were run in a similar manner as described above. On completion of each run, the reaction vial was centrifuged at 4000 rpm for 3 min, and the supernatant was characterized by flash column chromatography and GC for isolated yield and conversion, respectively. The vial was charged with another aliquot of DCM, stirred for 1 min, and centrifuged again. One more rinse was performed before the next run was conducted with fresh substrate.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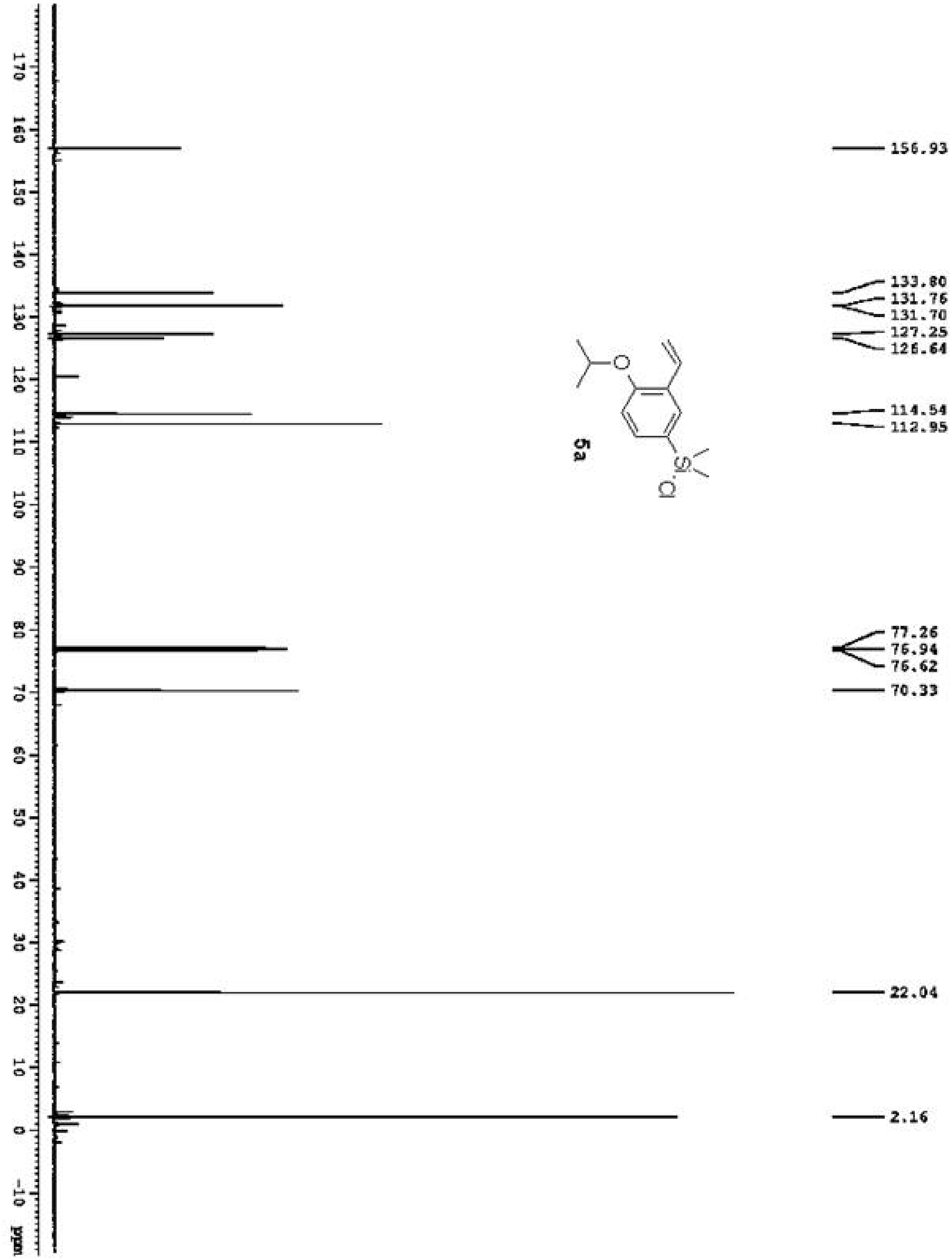
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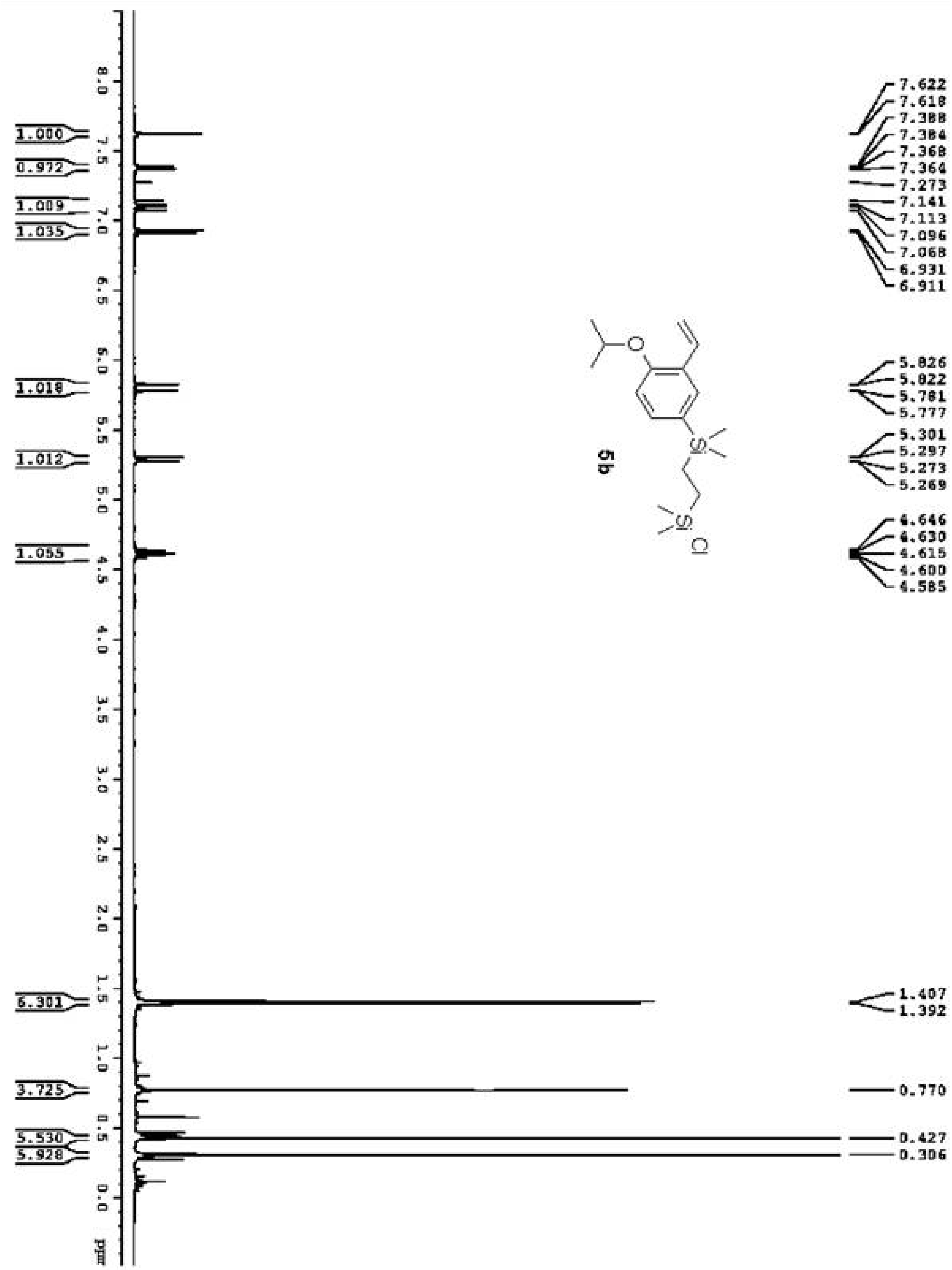
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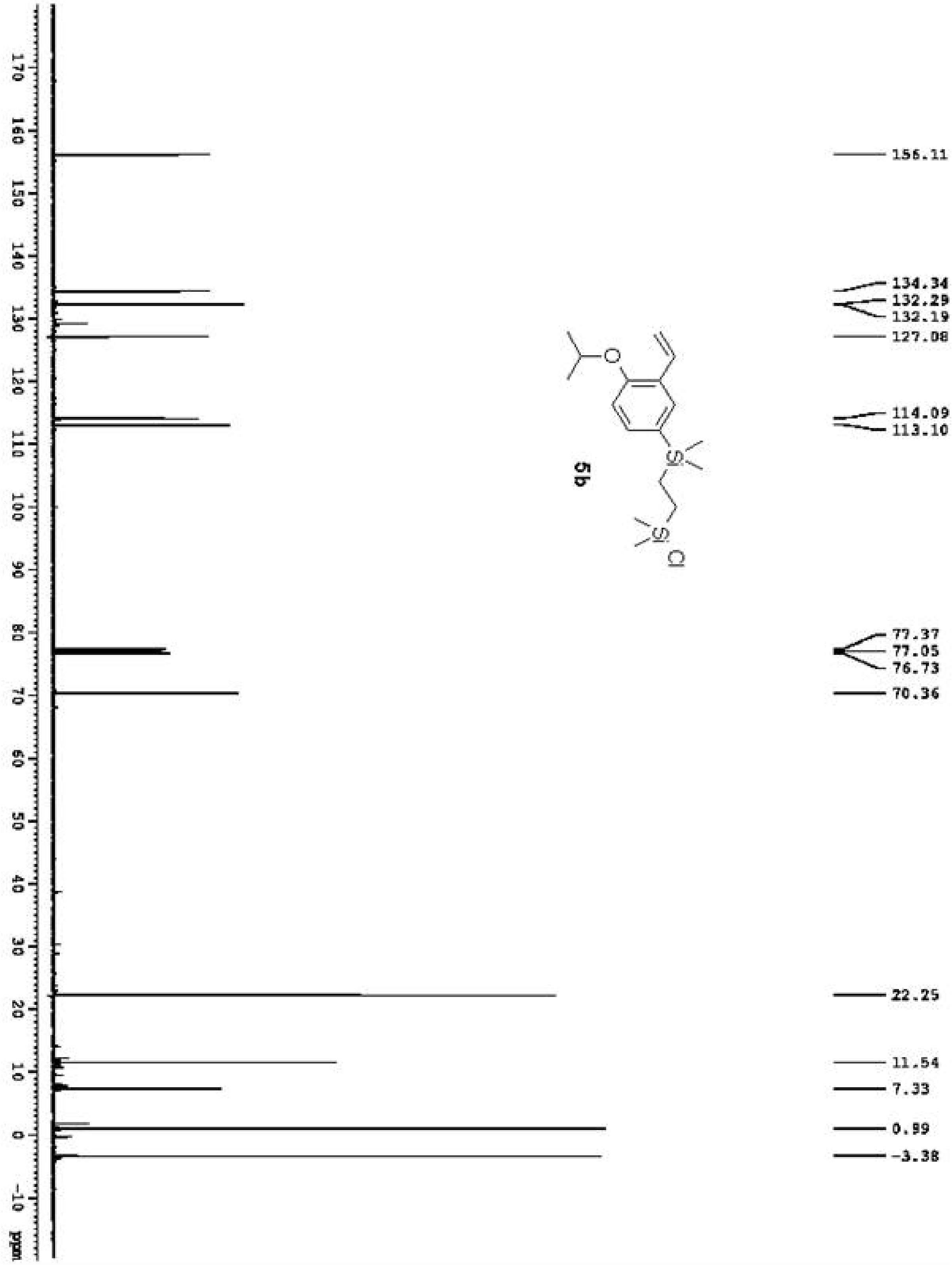
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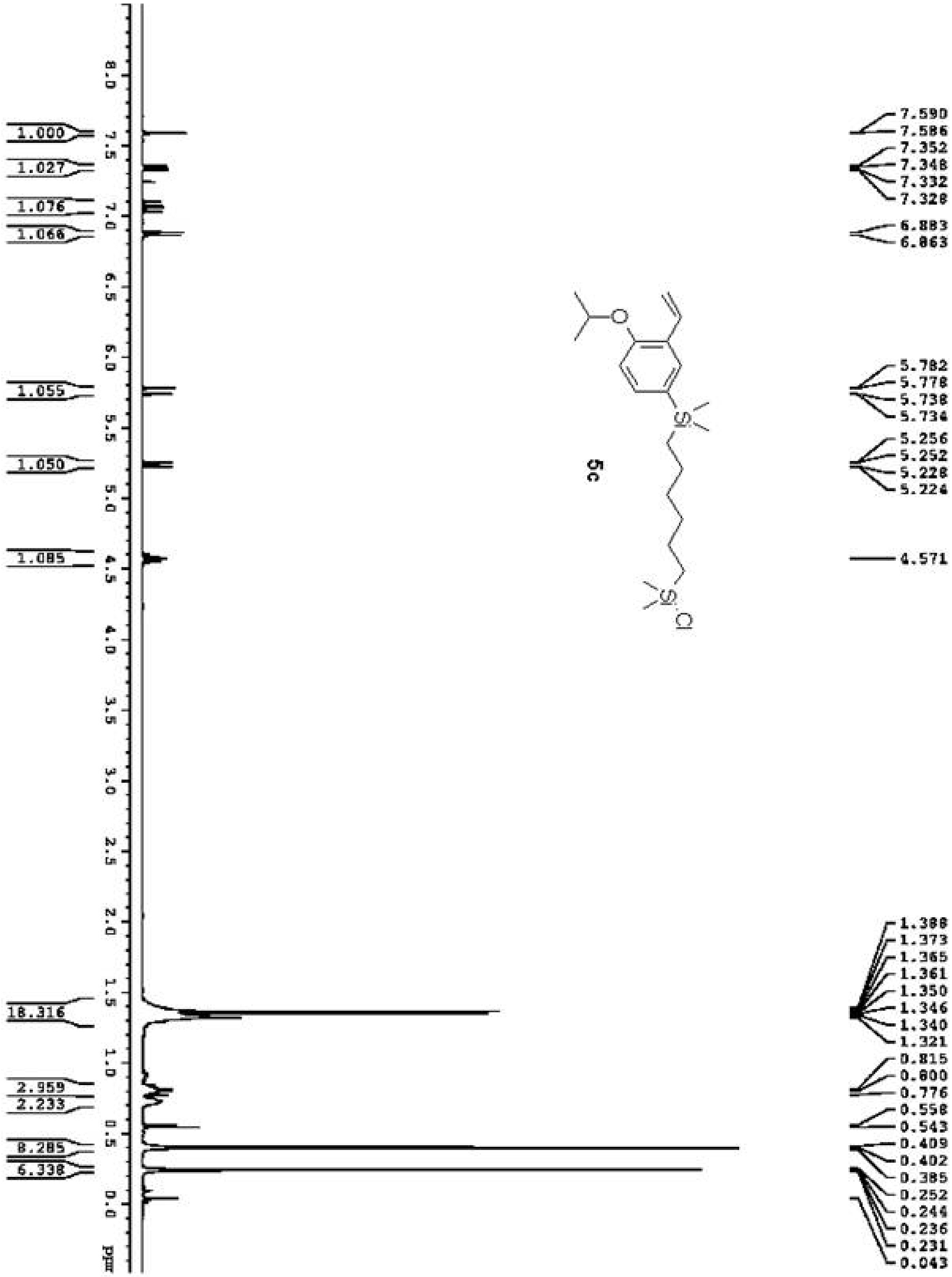
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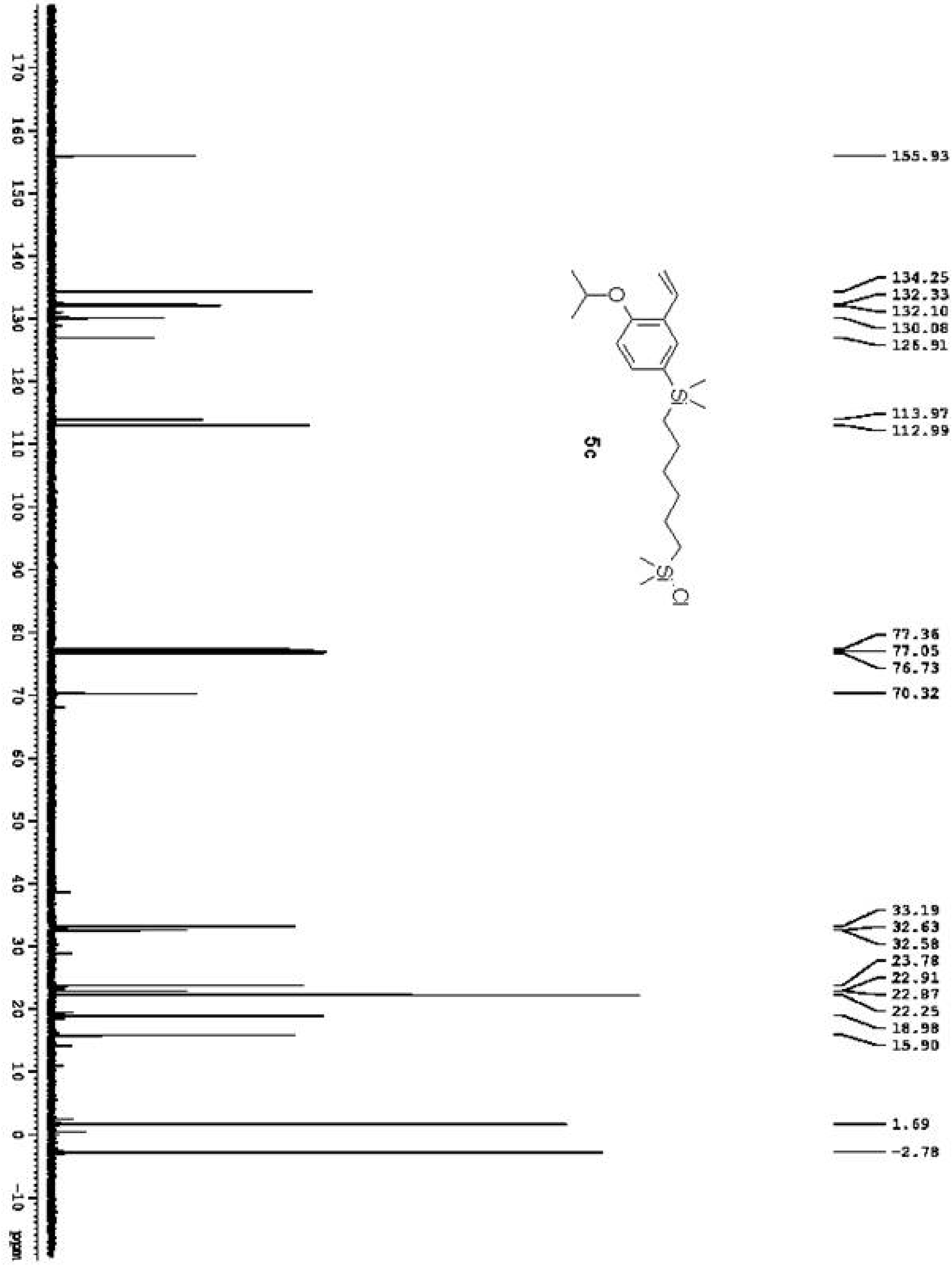
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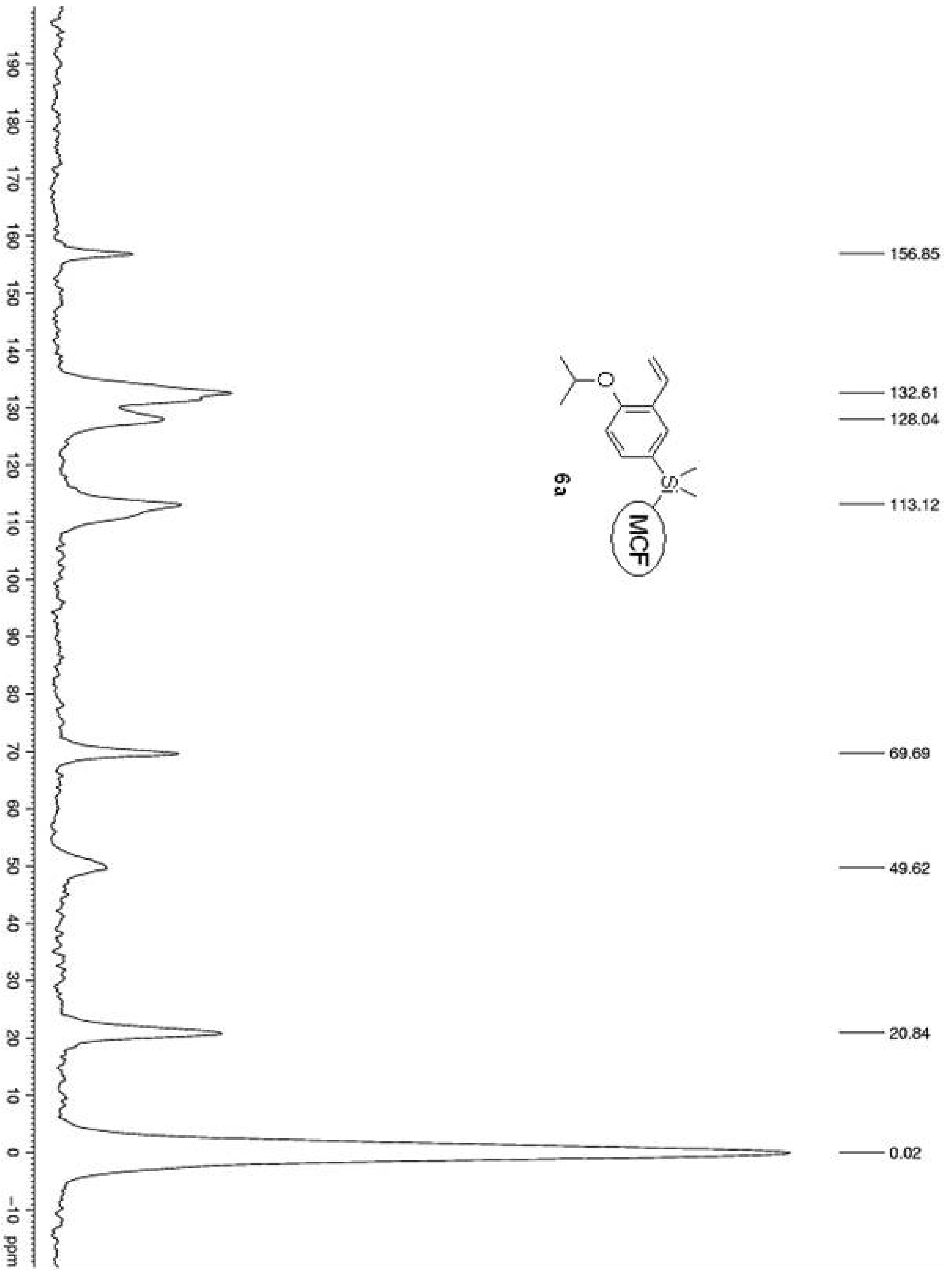
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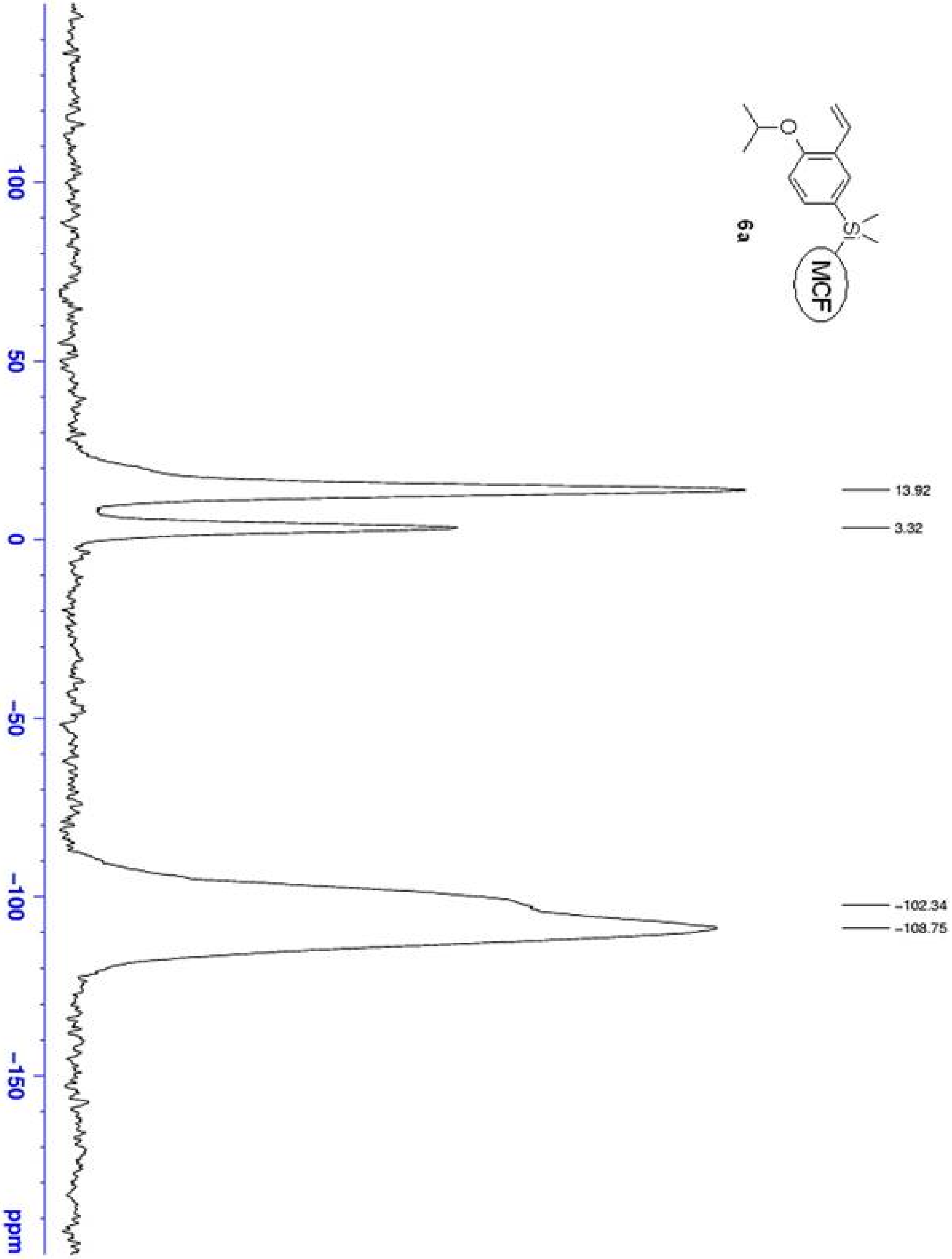
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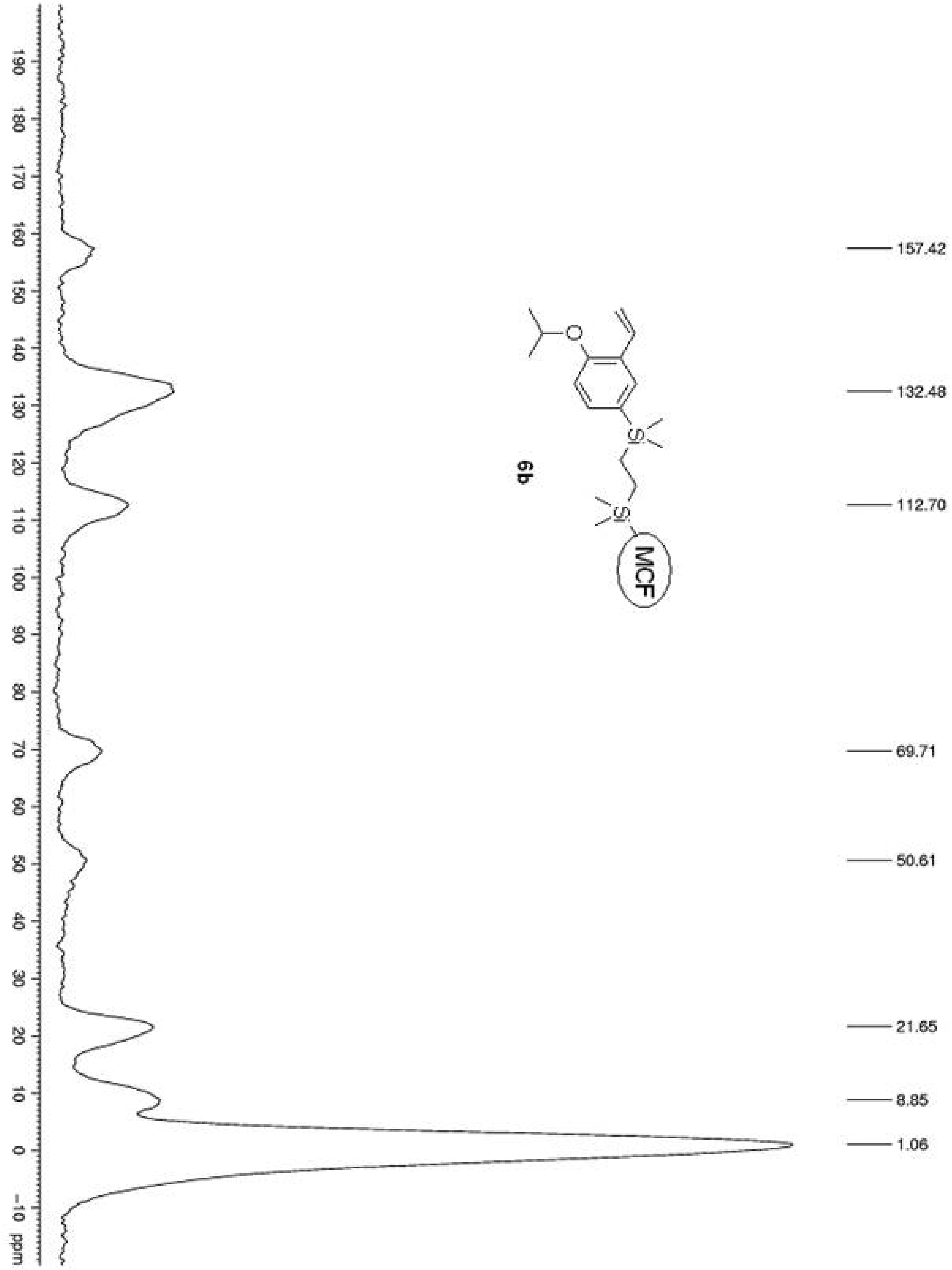
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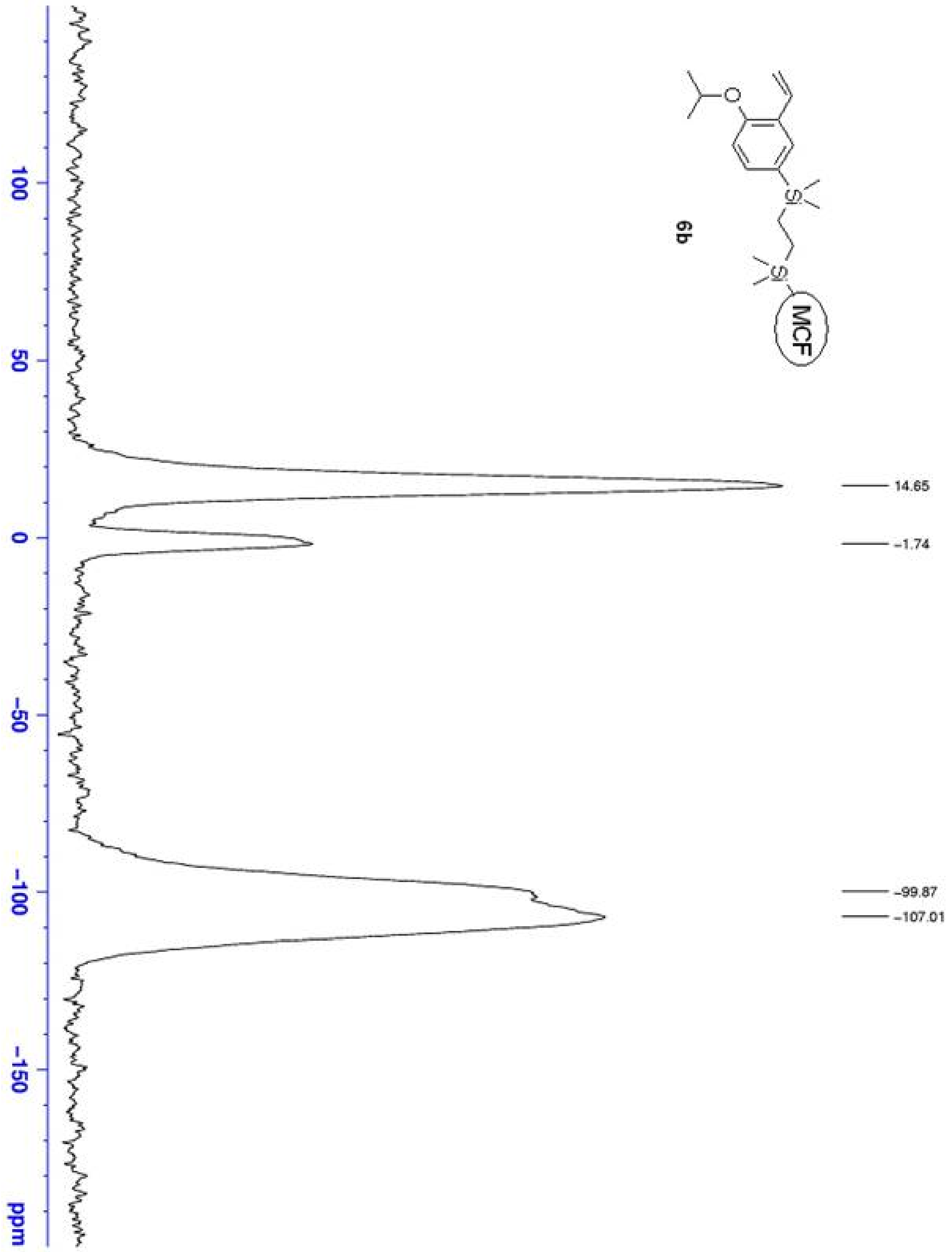
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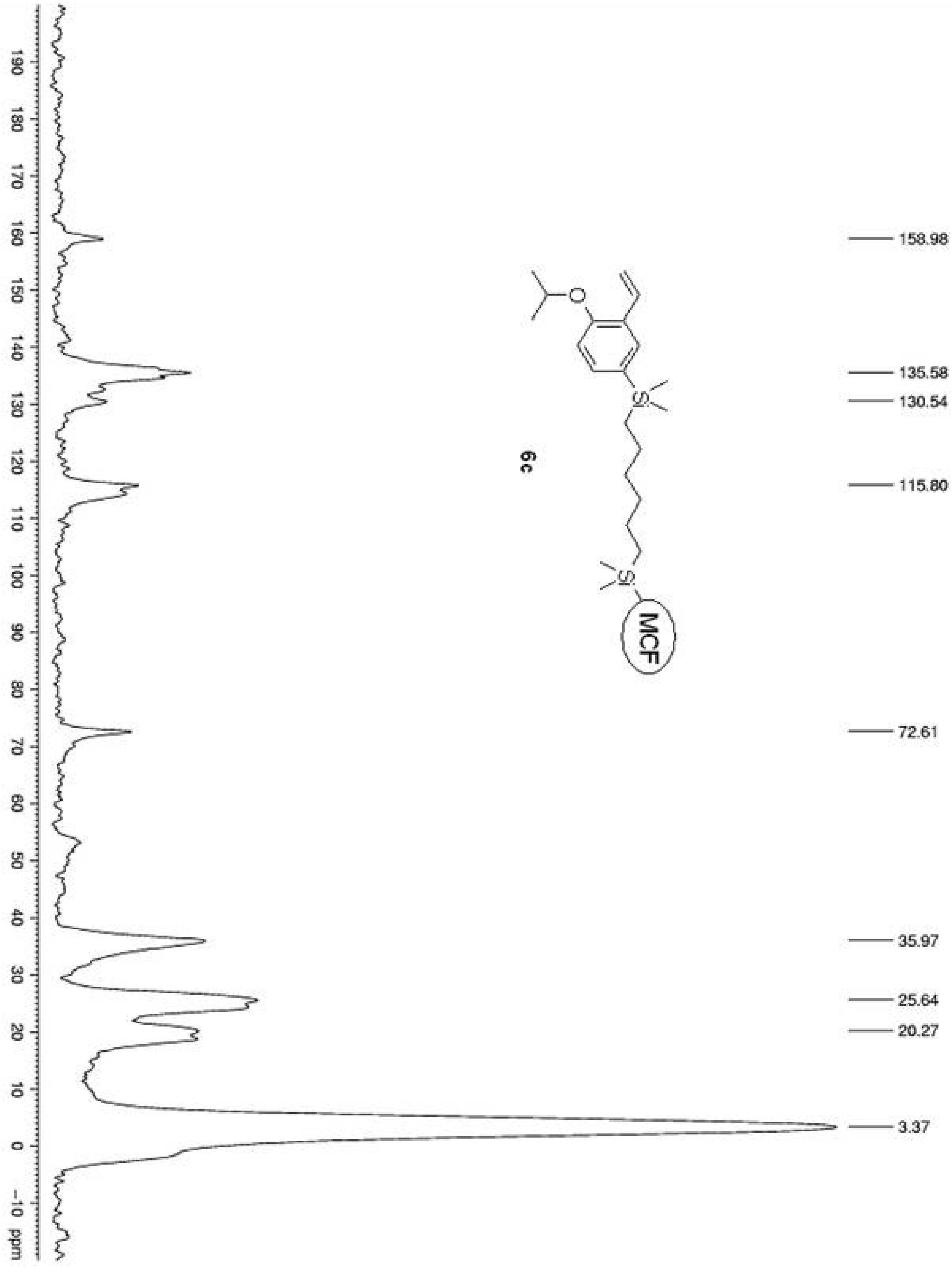
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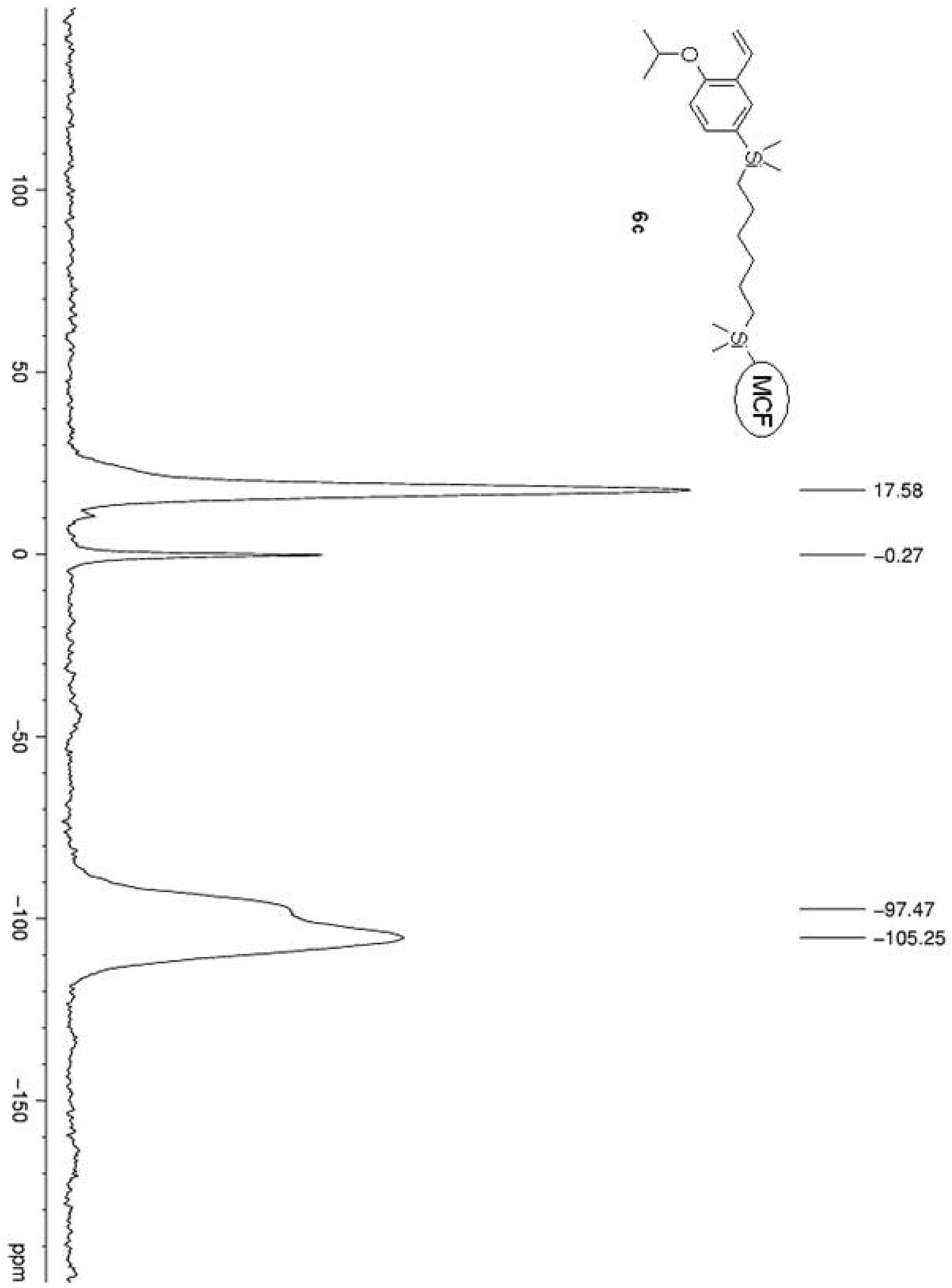
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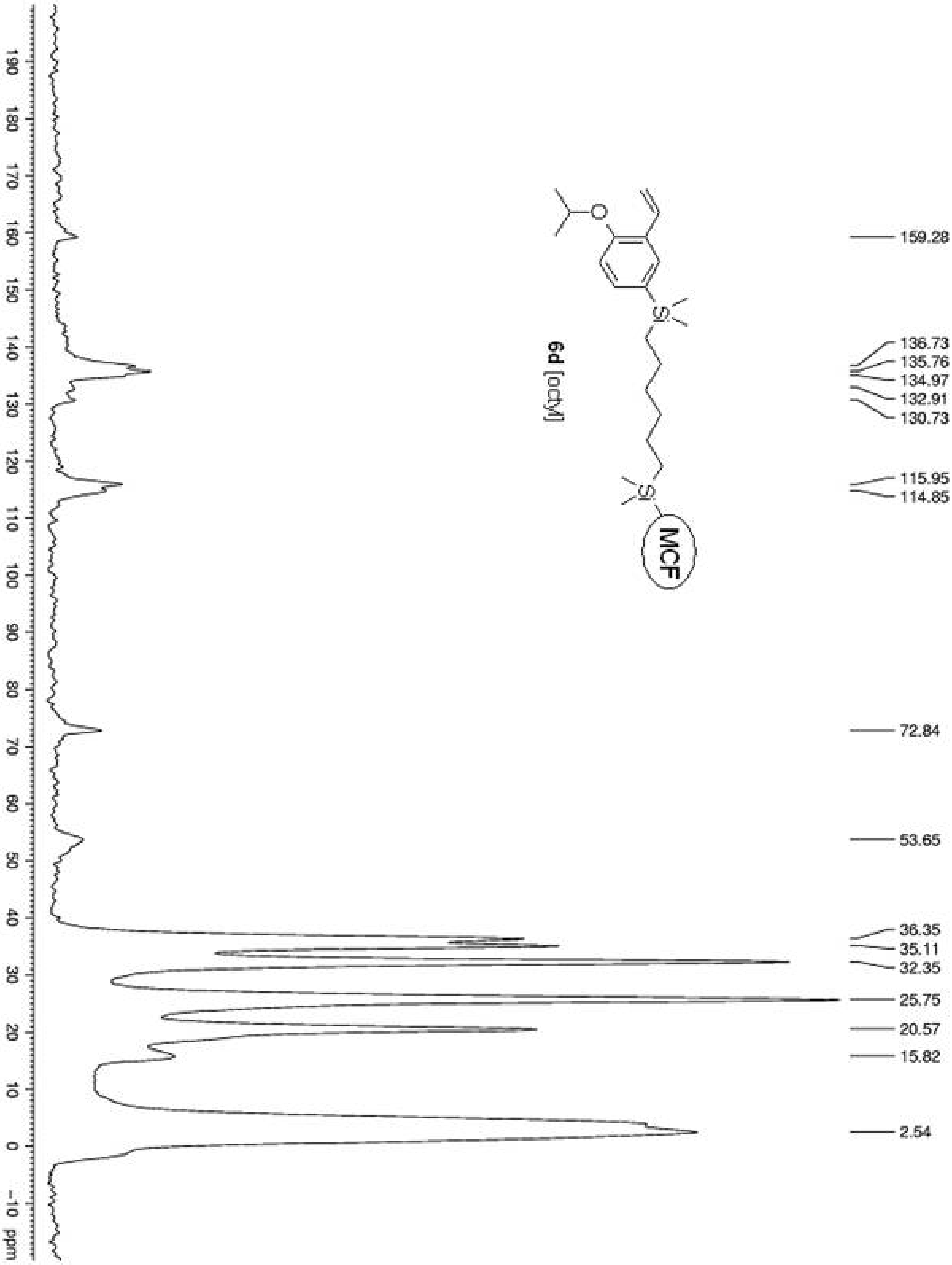
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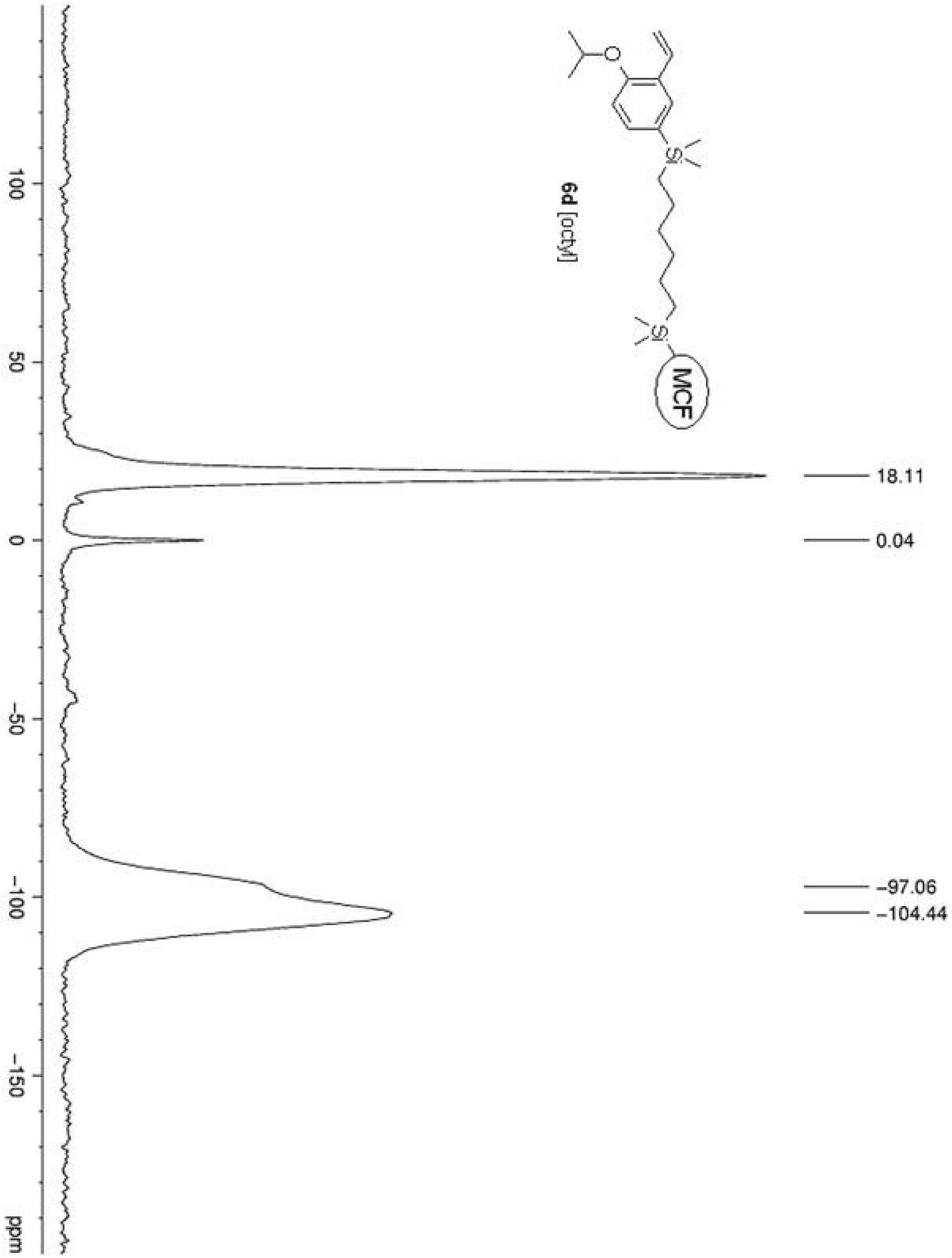
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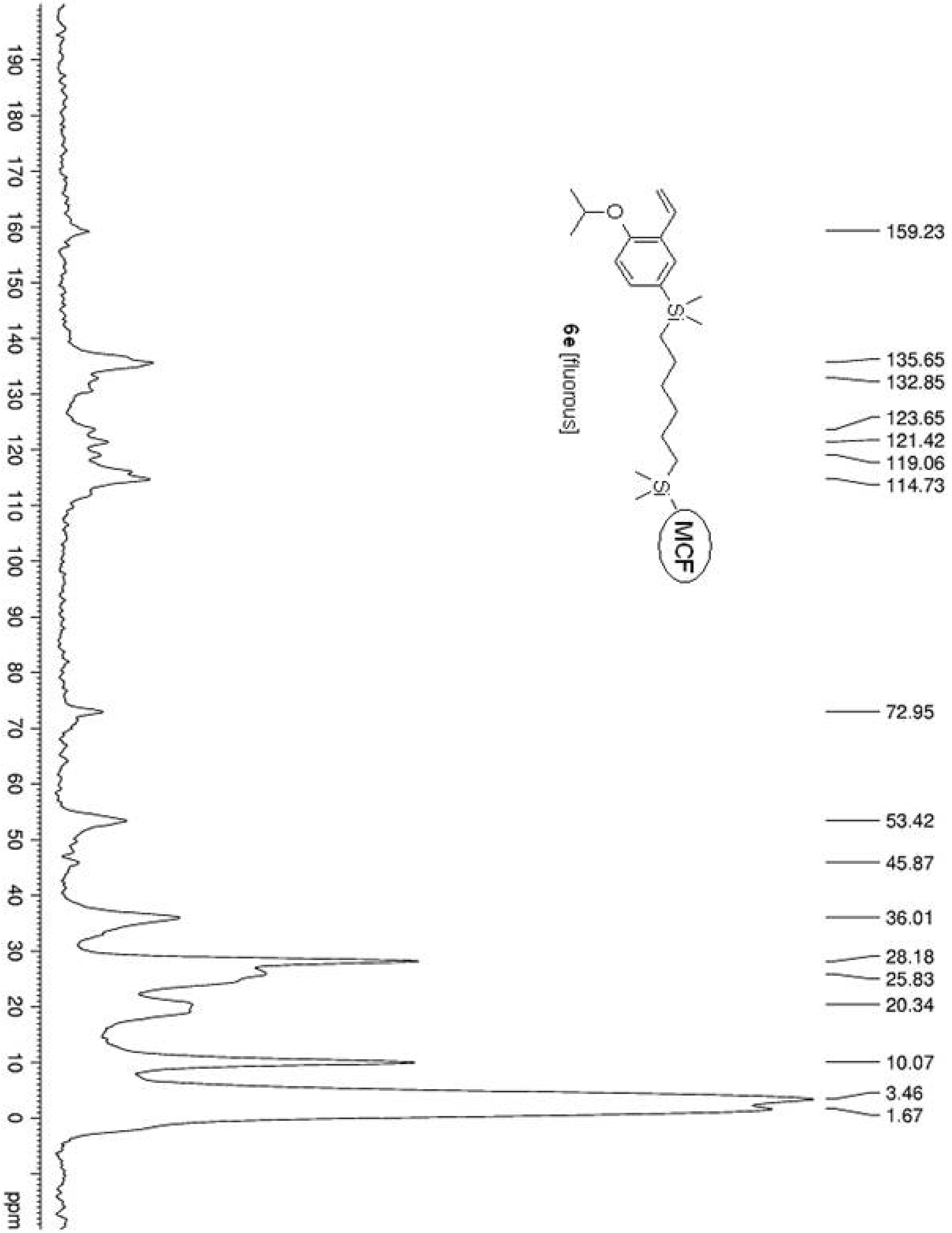
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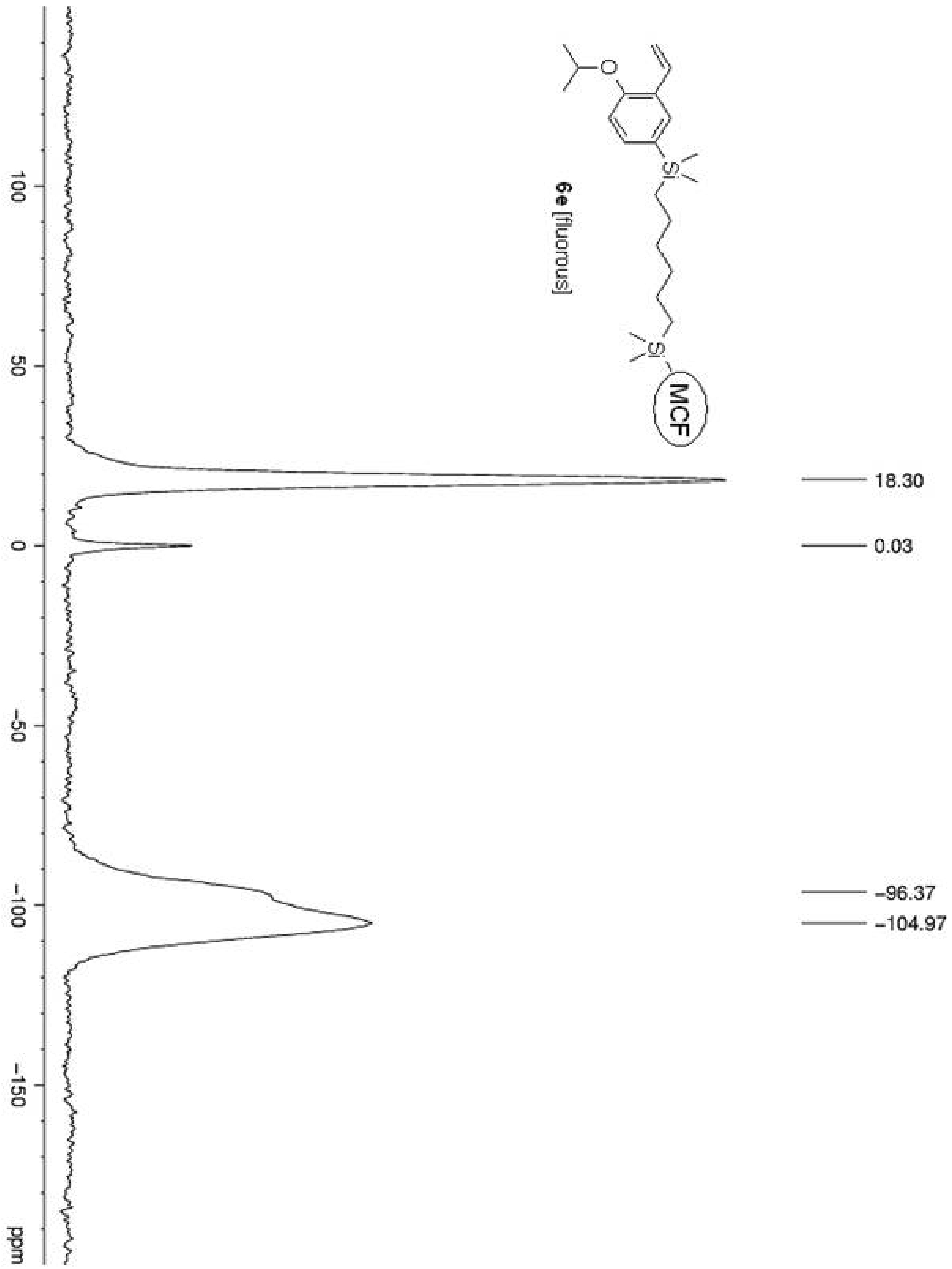
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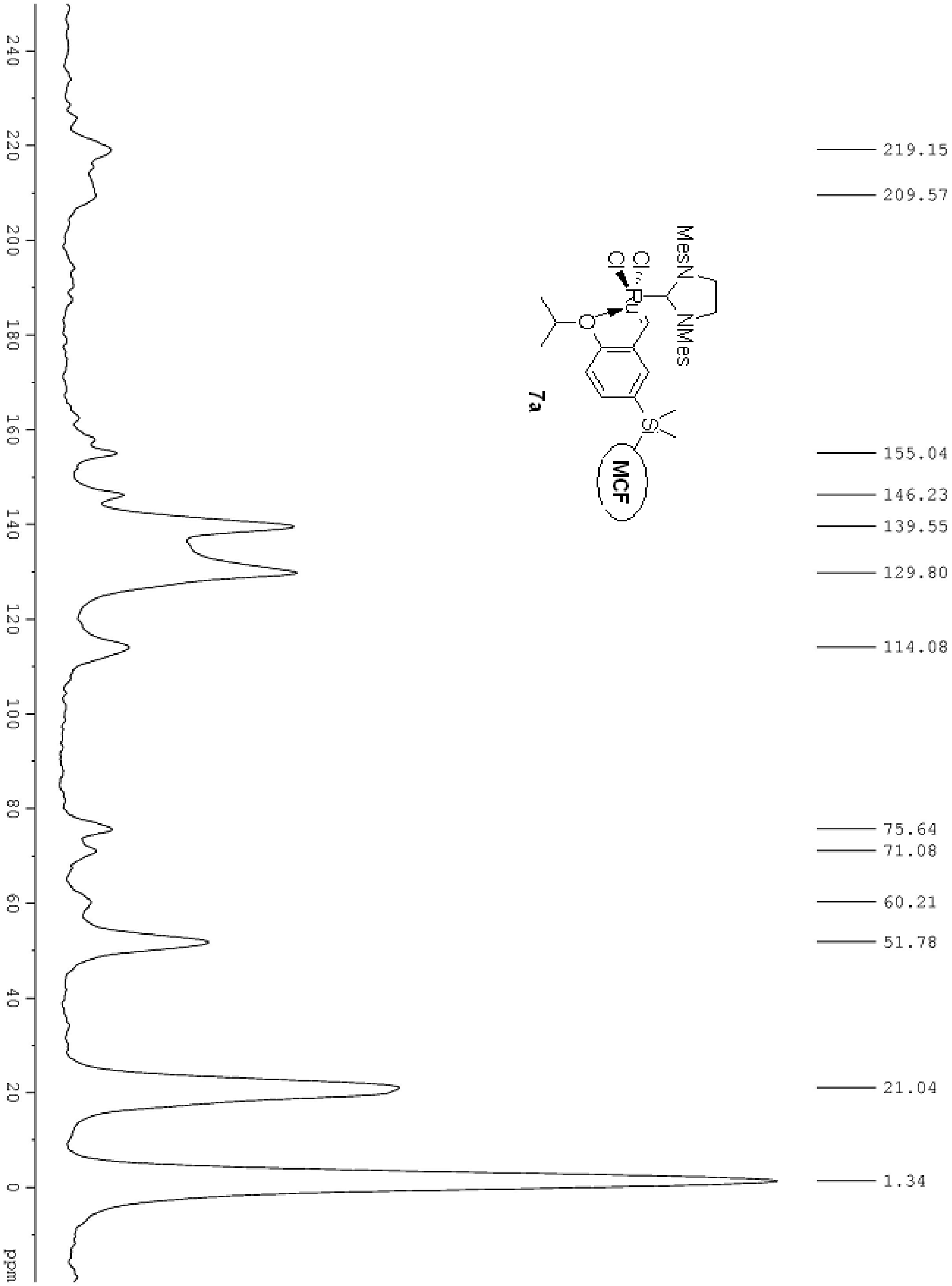
−100
−150
ppm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220
200
180
160
140
120
100
80
60
40
20
0
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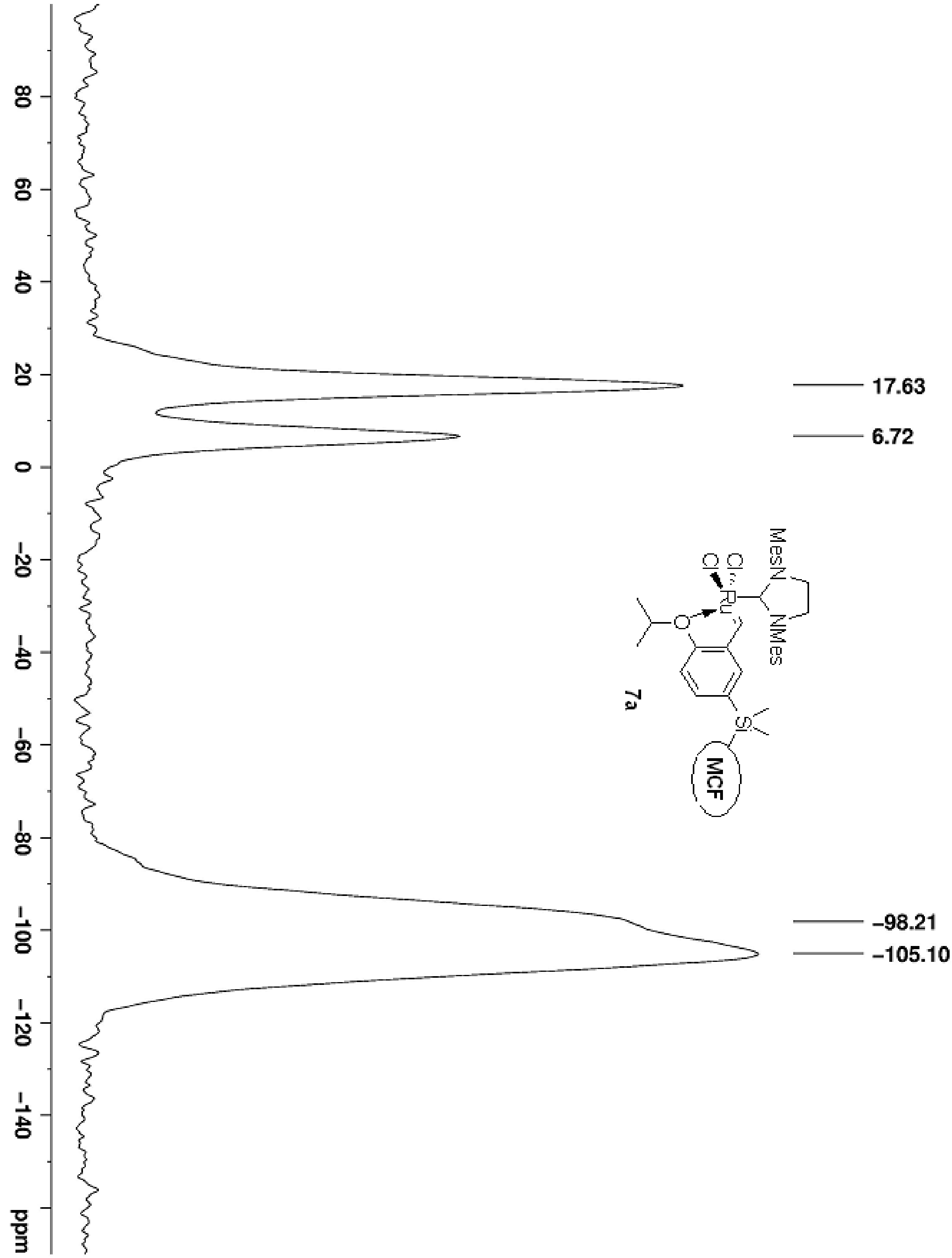
209.57
155.04
146.23
139.55
129.80
114.08
75.64
71.08
60.21
51.78
21.04
1.34
MesN
NMes
Cl
Cl
Ru
O
Si
MCF
7a


17.63
6.72
-98.21
-105.10
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
ppm
MesN
NMes
Cl
Cl
Ru
O
Si
MCF
7a

Supplementary Material (ESI) for Chemical Communications
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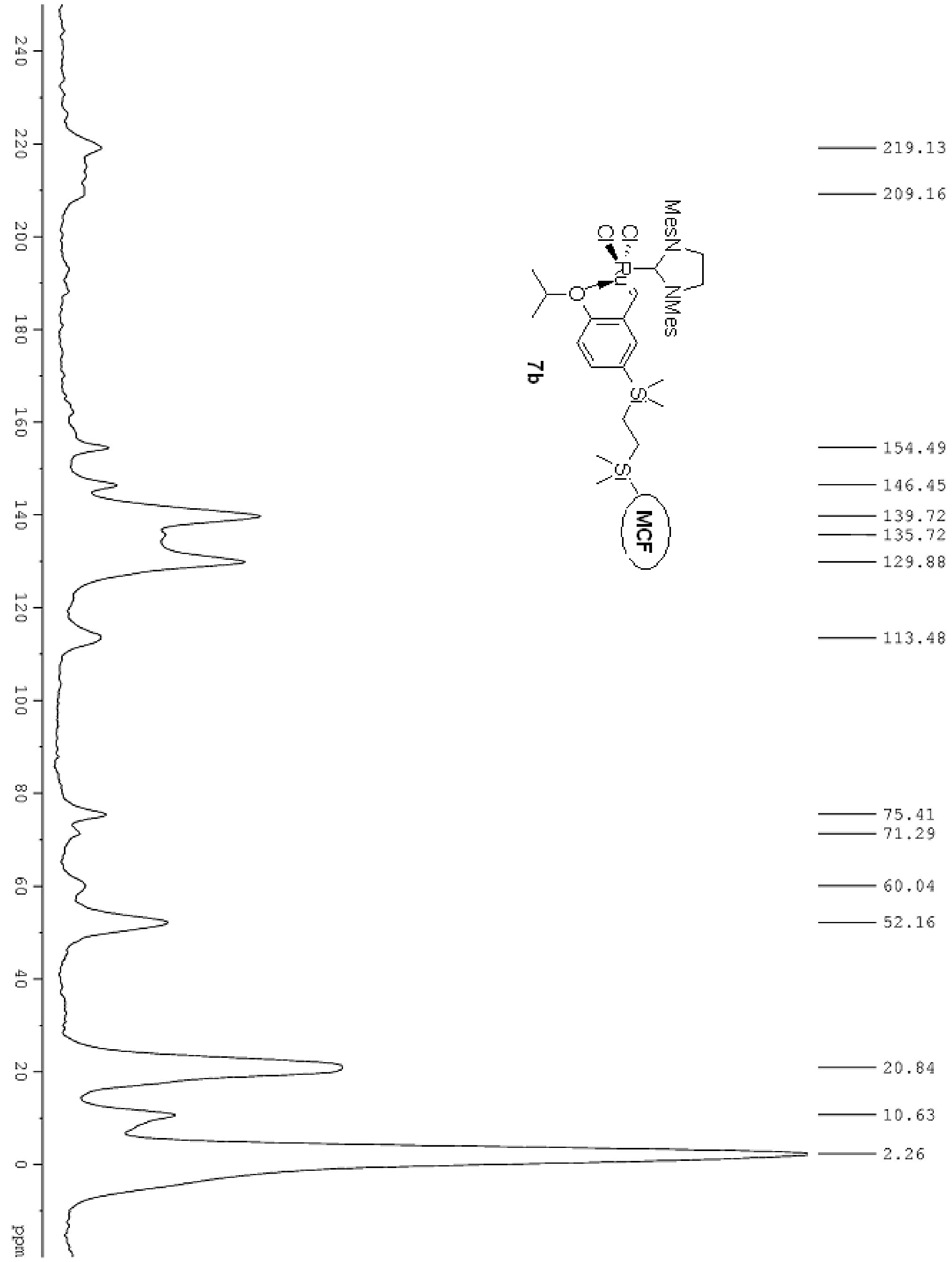

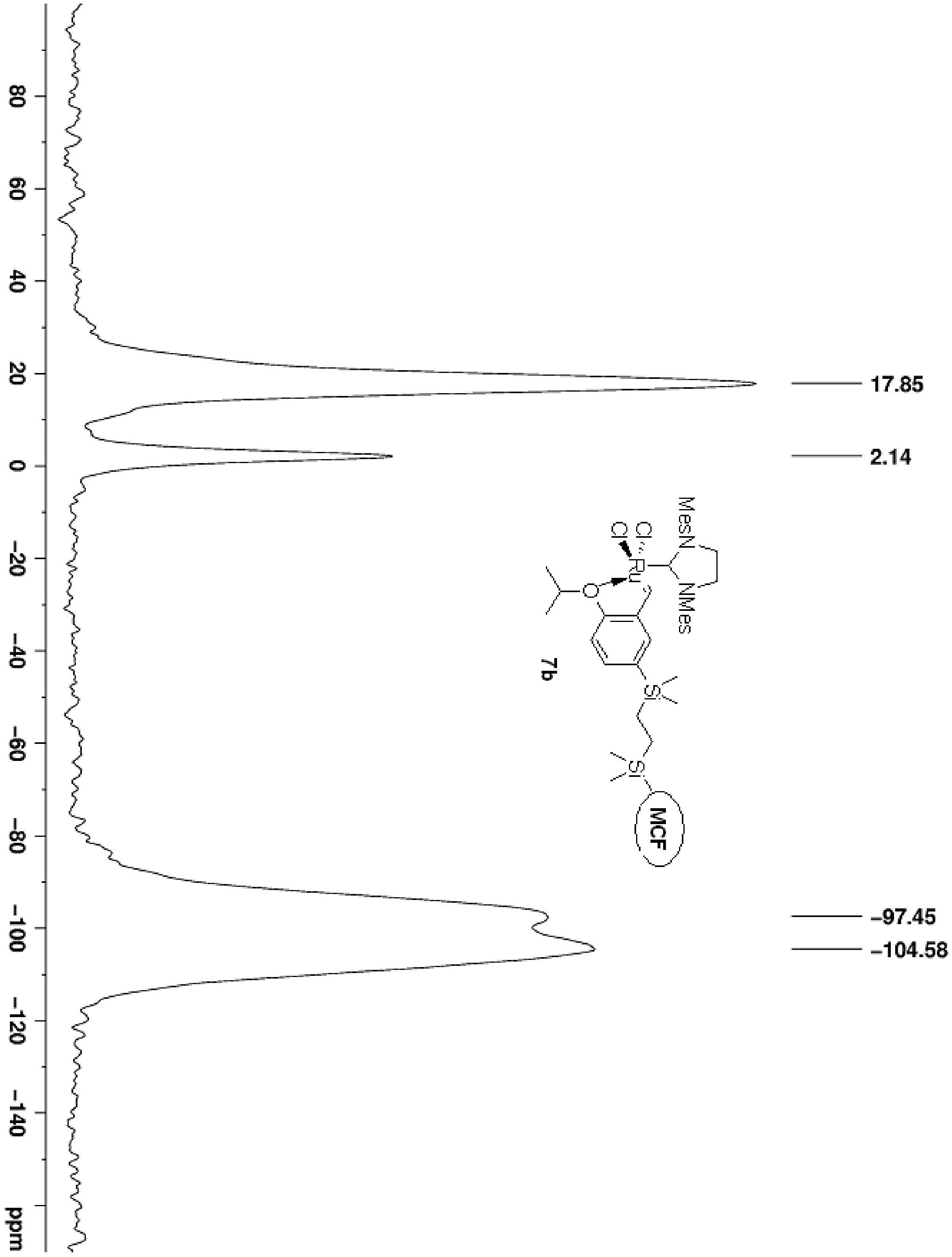
17.85
2.14
-97.45
-104.58
80
60
40
20
0
-20
-40
-60
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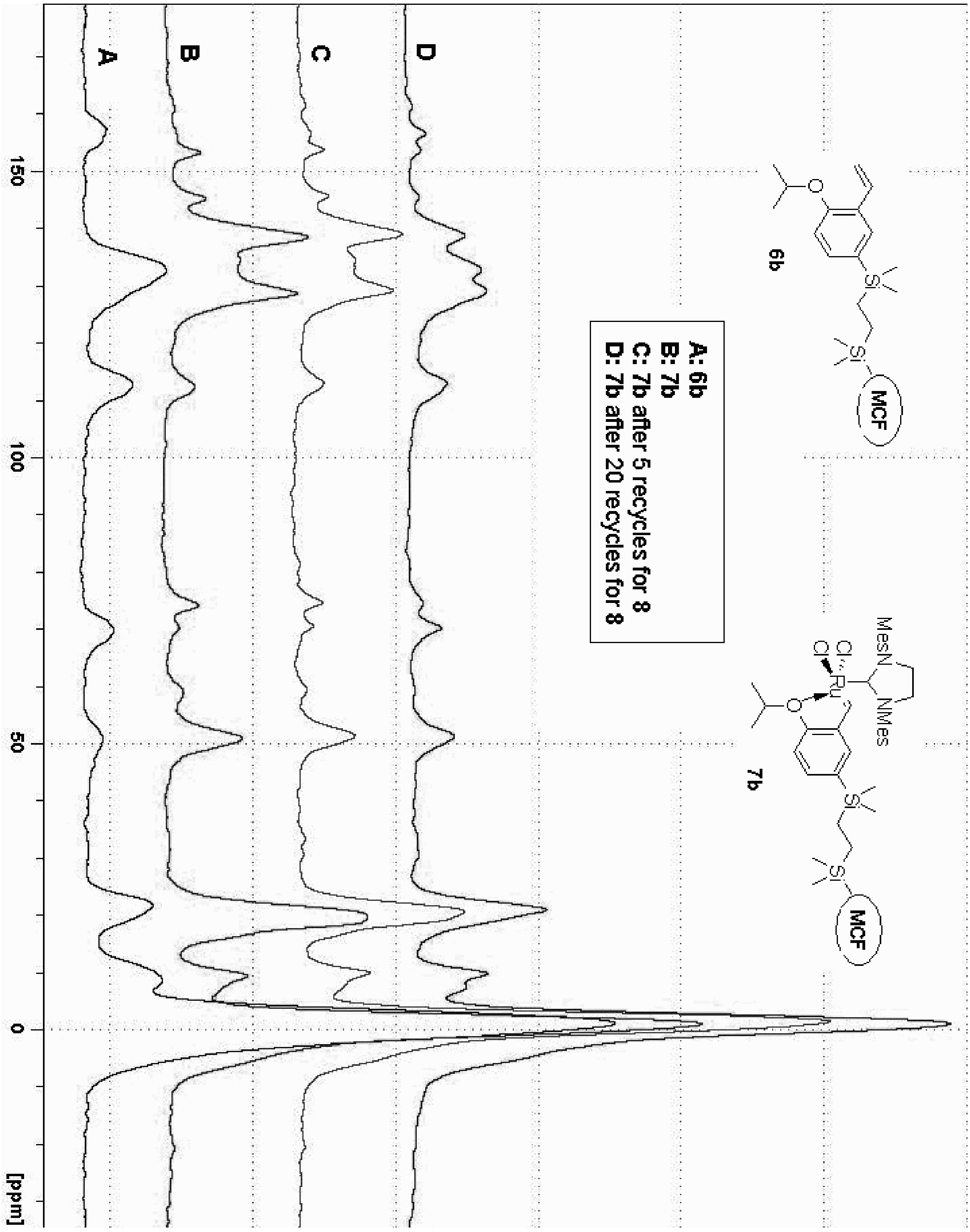
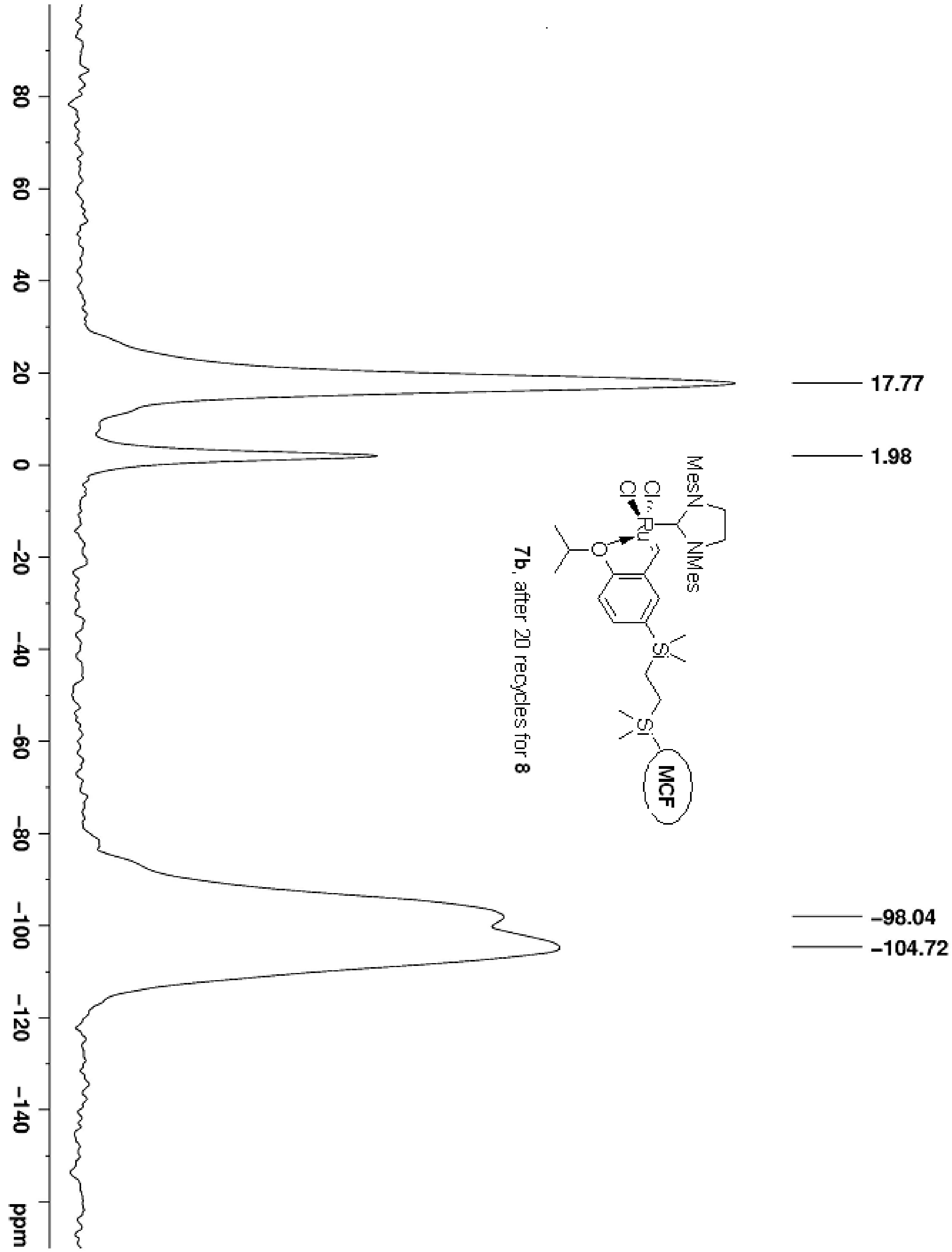
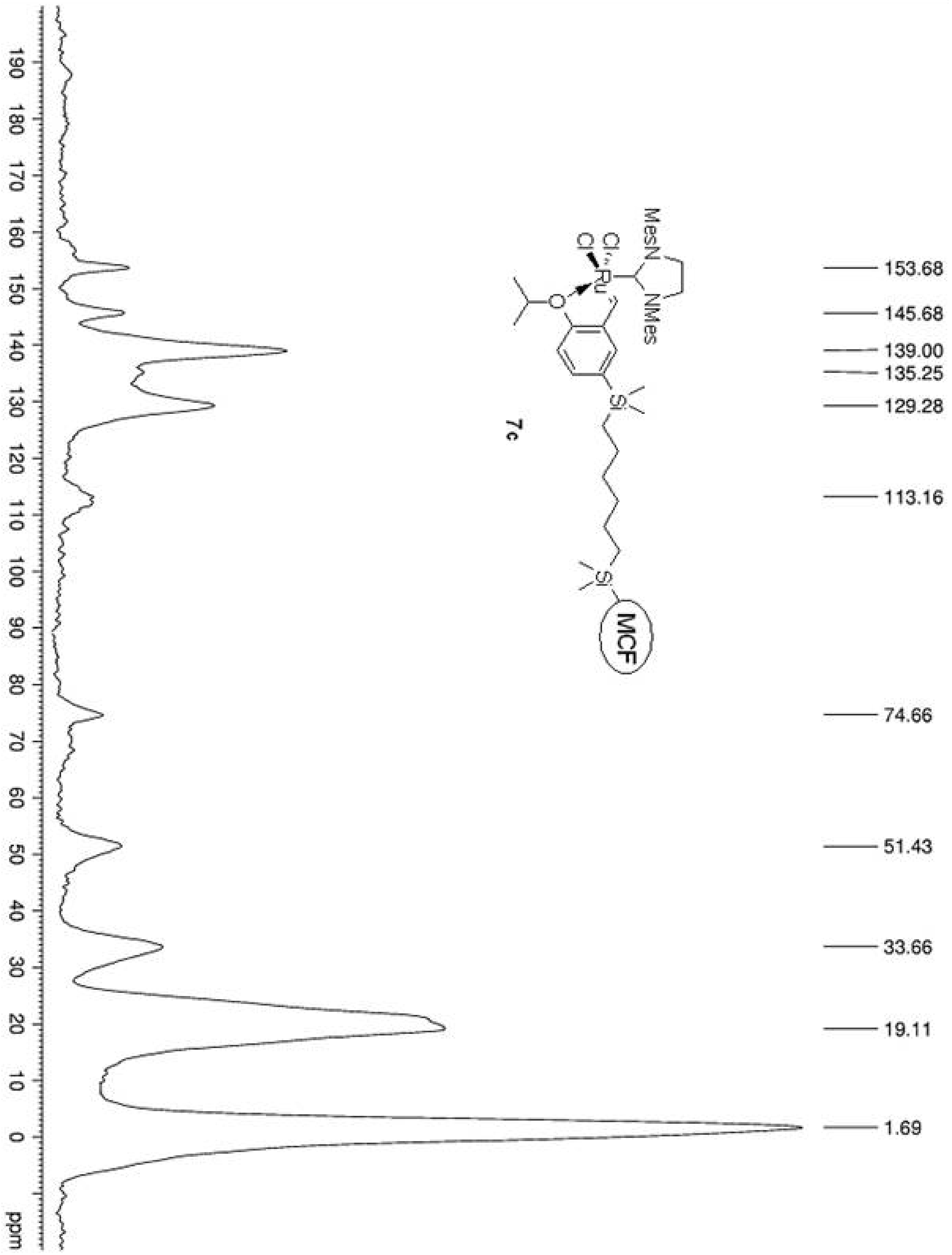
-100
-120
-140
ppm
MesN
NMes
Cl
Cl
Ru
O
Si
Si
MCF
7b

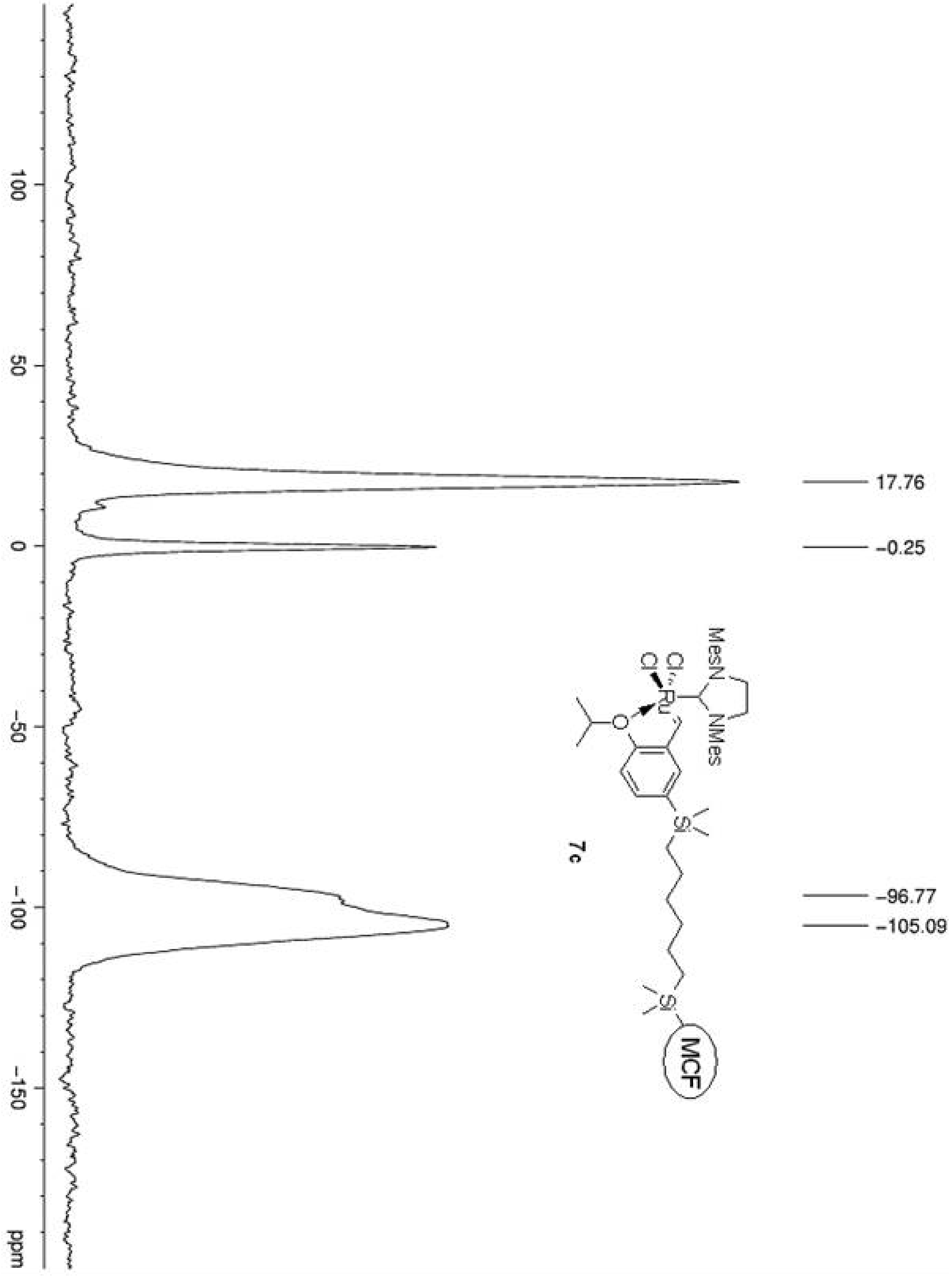

A
B
C
D
A: 6b
B: 7b
C: 7b after 5 recycles for 8
D: 7b after 20 recycles for 8
6b
7b
MCF
Si
O
MesN
NMes
Cl
Ru
150
100
50
0
[ppm]



7b, after 20 recycles for 8


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
MesN
NMes
Cl
Cl
Ru
O
Si
Si
MCF
153.68
145.68
139.00
135.25
129.28
113.16
74.66
51.43
33.66
19.11
1.69

7c



7c

100
50
0
−50
−100
−150
ppm
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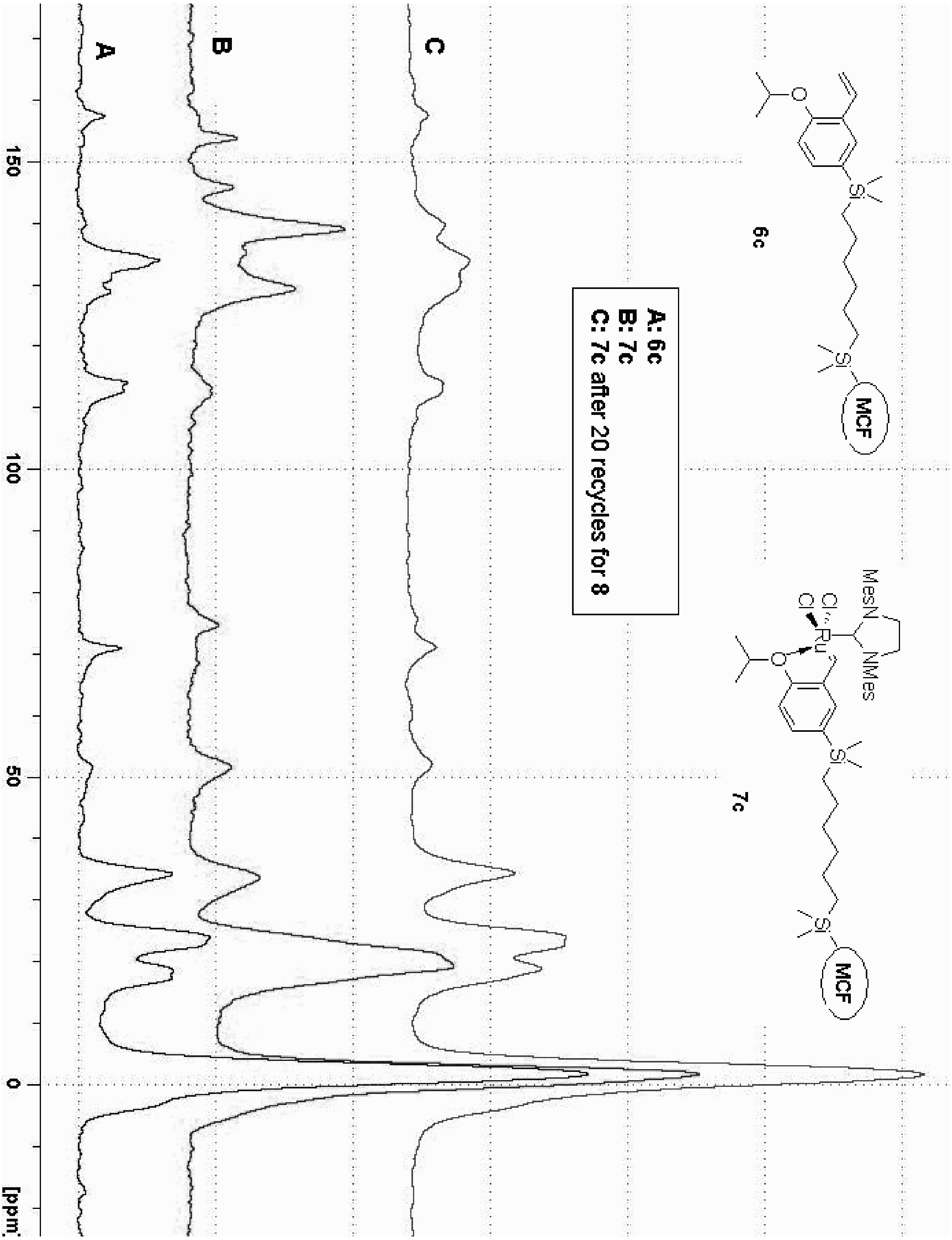
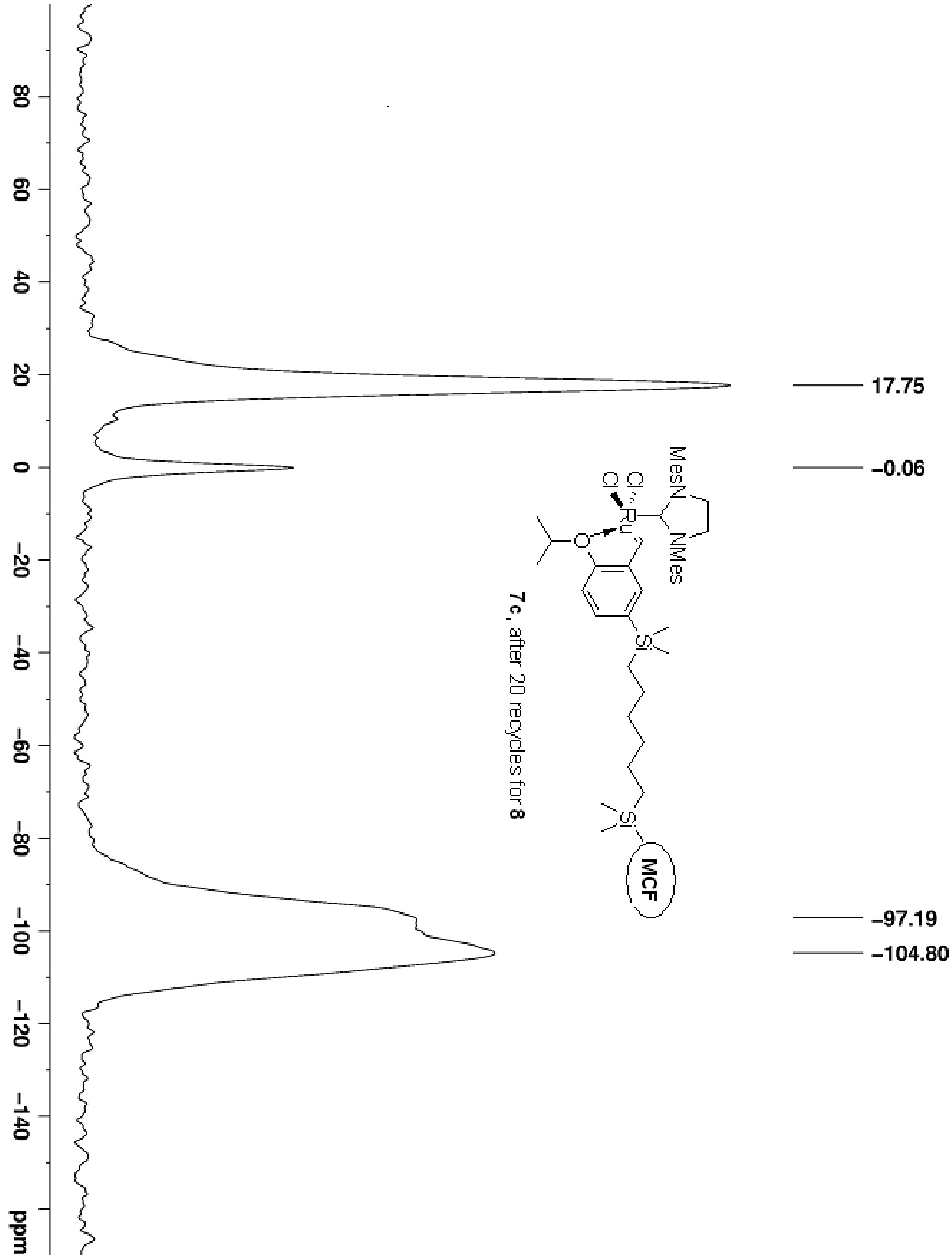
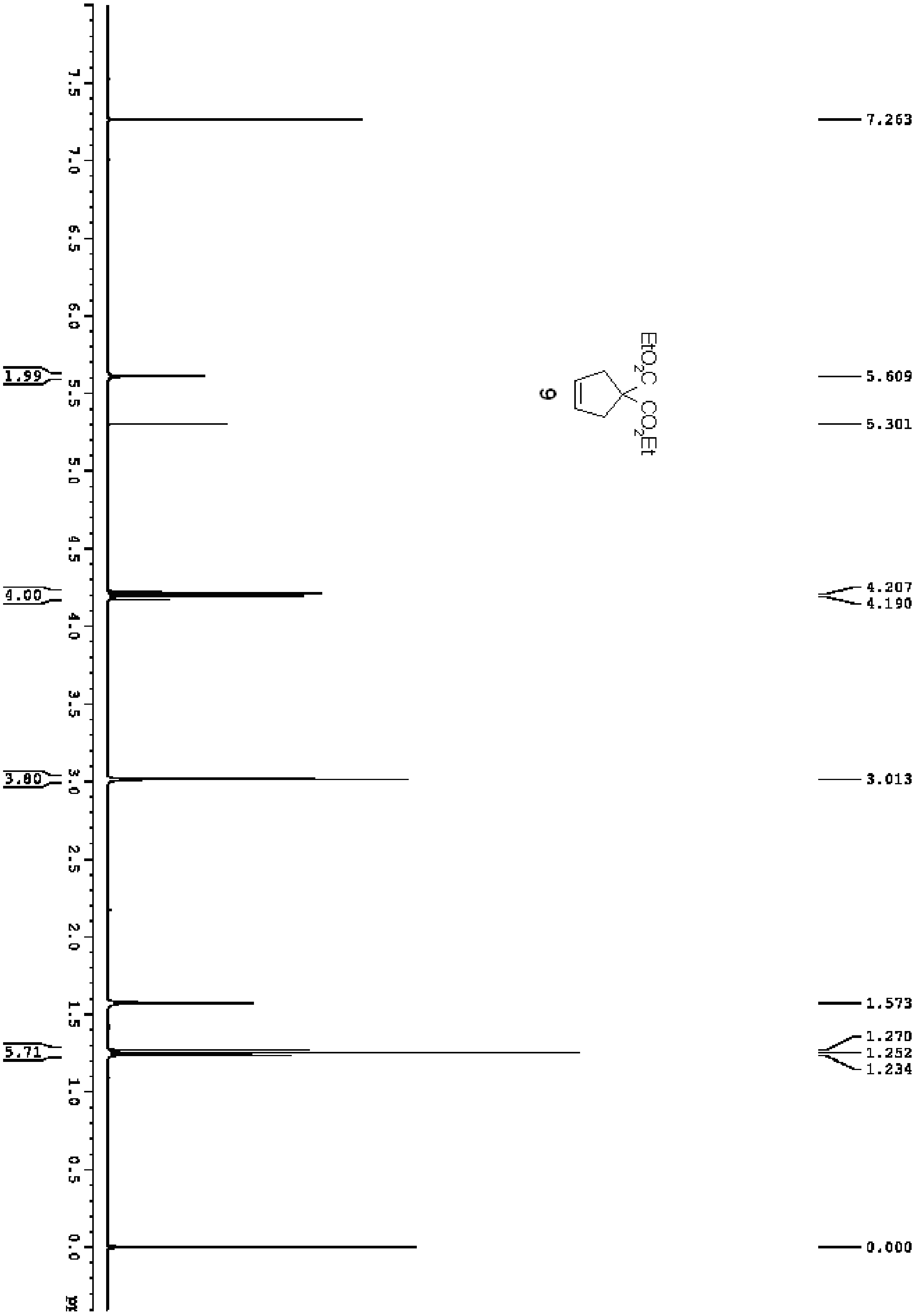
−0.25
−96.77
−105.09
MesN
NMes
Cl
Cl
Ru
O
Si
Si
MCF


A
B
C
A: 6c
B: 7c
C: 7c after 20 recycles for 8
6c
7c
Si
MCF
MesN
NMes
Cl
Ru
O
150
100
50
0
[ppm]



7c, after 20 recycles for **8**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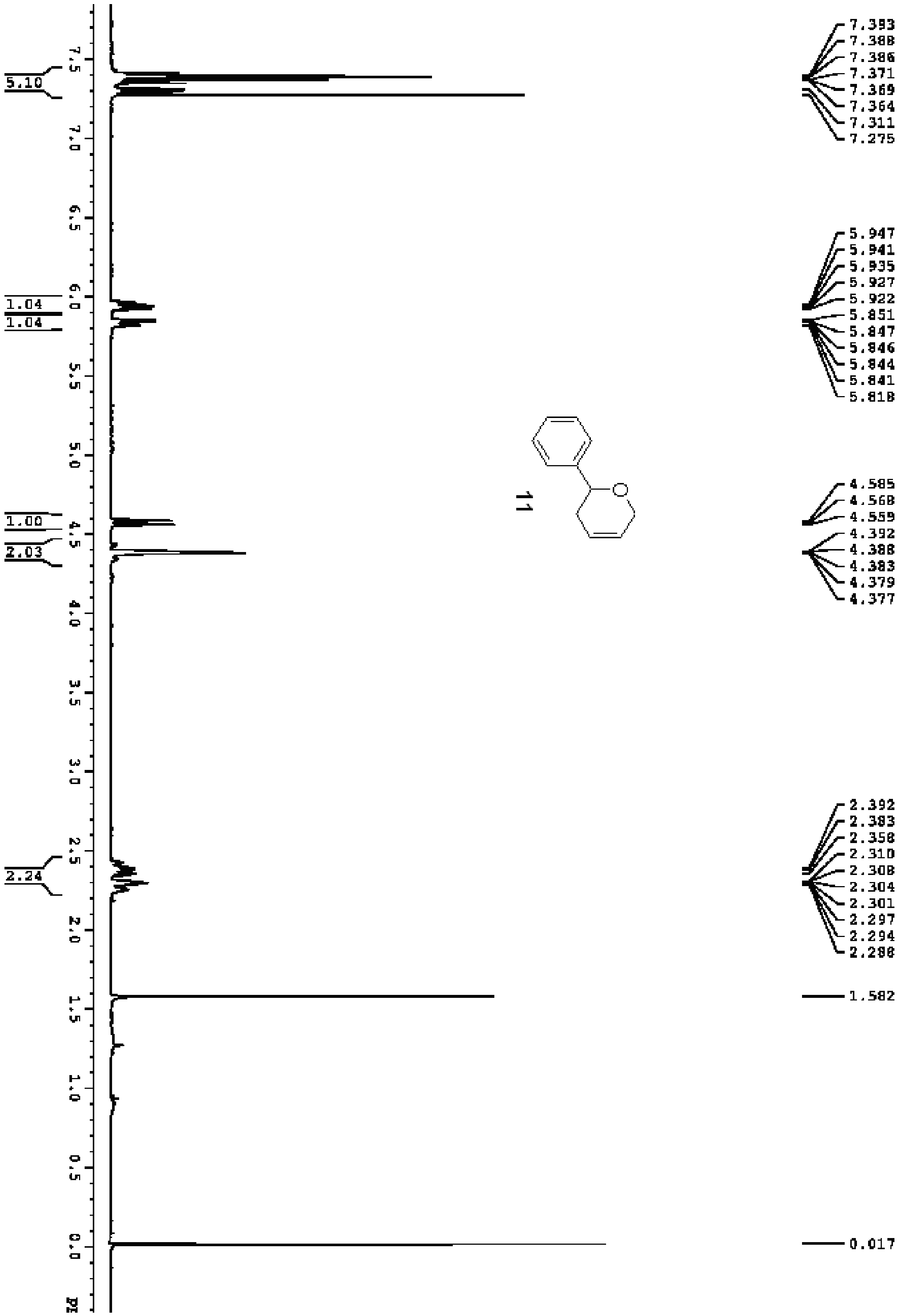
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.99
4.00
3.80
5.71
7.263
5.609
5.301
4.207
4.190
3.013
1.573
1.270
1.252
1.234
0.000
EtO$_2$C
CO$_2$Et
9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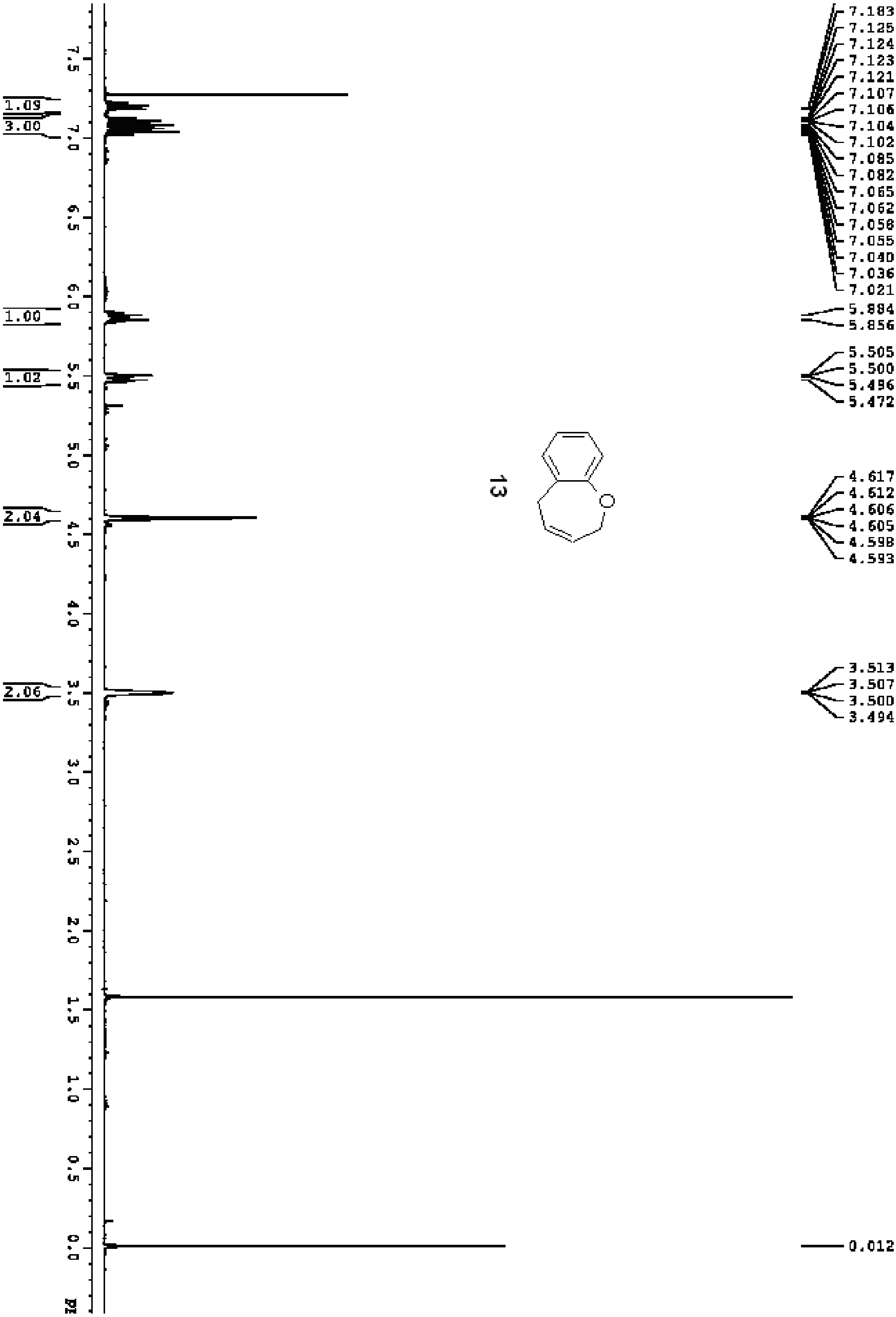
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
PPM
5.10
1.04
1.04
1.00
2.03
2.24
7.393
7.388
7.386
7.371
7.369
7.364
7.311
7.275
5.947
5.941
5.935
5.927
5.922
5.851
5.847
5.846
5.844
5.841
5.818
4.585
4.568
4.559
4.392
4.388
4.383
4.379
4.377
2.392
2.383
2.358
2.310
2.308
2.304
2.301
2.297
2.294
2.288
1.582
0.017
O
11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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
PPM
1.09
3.00
1.00
1.02
2.04
2.06
13
7.183
7.125
7.124
7.123
7.121
7.107
7.106
7.104
7.102
7.085
7.082
7.065
7.062
7.058
7.055
7.040
7.036
7.021
5.884
5.856
5.505
5.500
5.496
5.472
4.617
4.612
4.606
4.605
4.598
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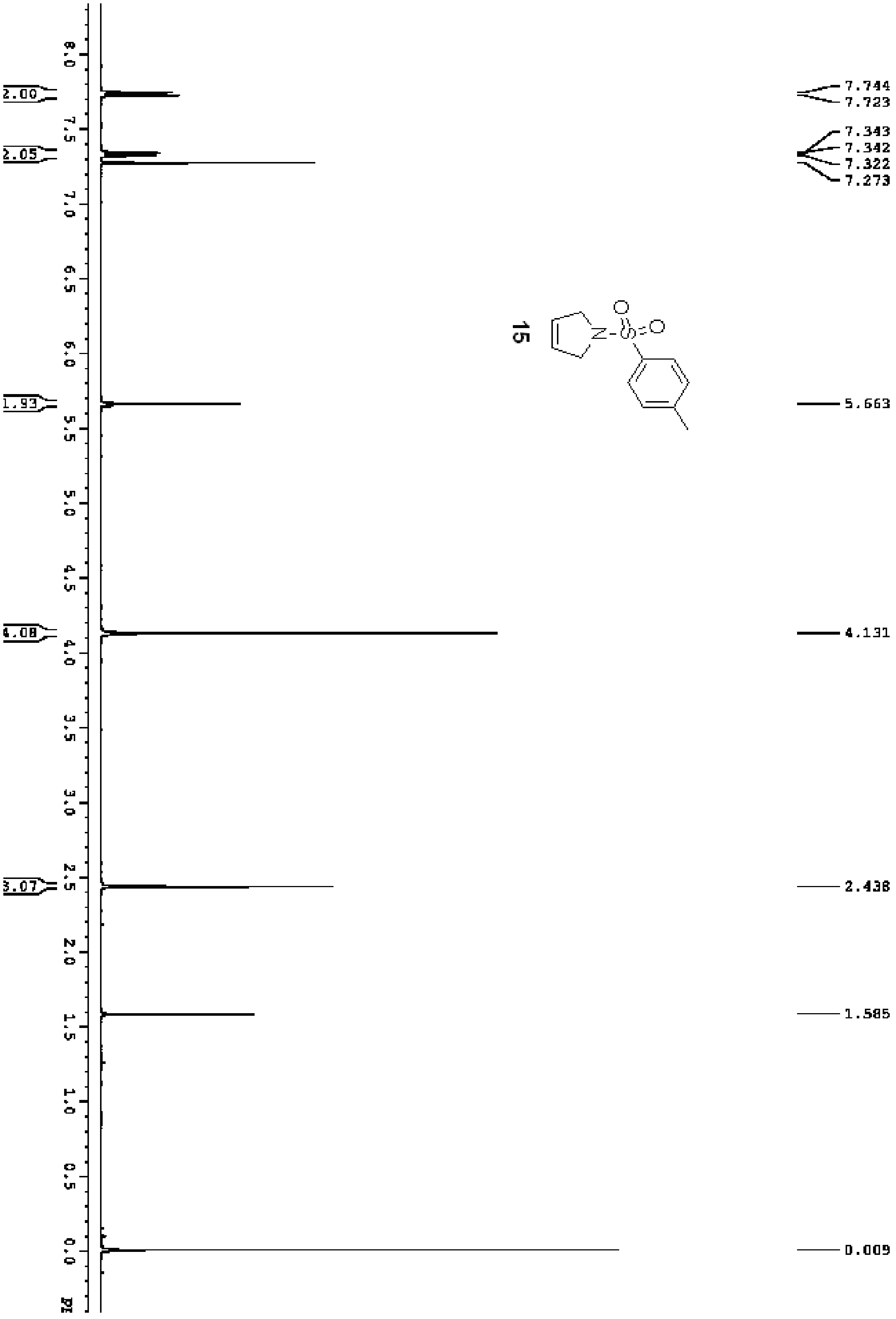
3.513
3.507
3.500
3.494
0.012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5.5
5.0
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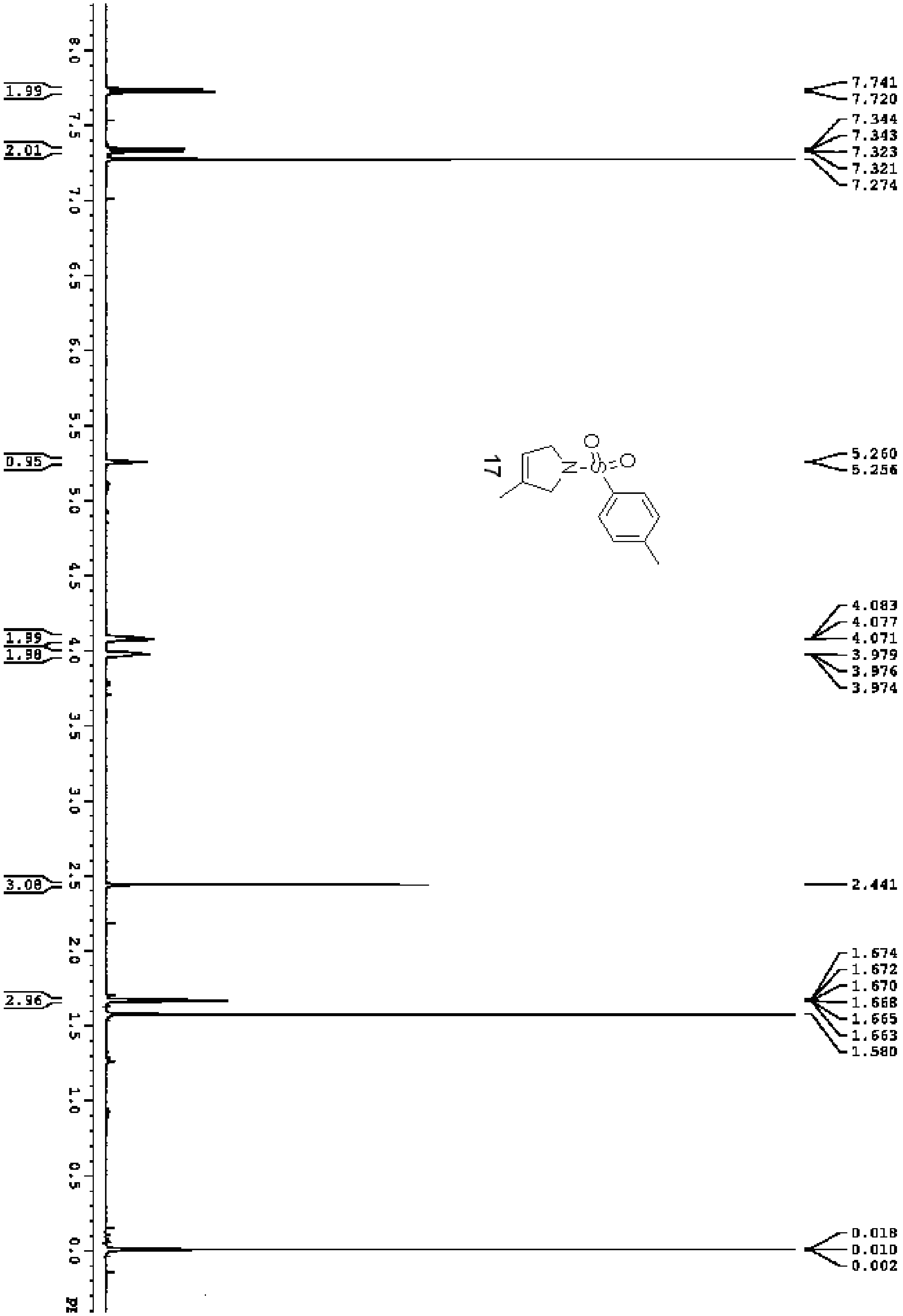
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.00
2.05
1.93
4.08
3.07
7.744
7.723
7.343
7.342
7.322
7.273
5.663
4.131
2.438
1.585
0.009
15
N
S
O
O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N
S
O
O
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.99
2.01
0.95
1.99
1.98
3.08
2.96
7.741
7.720
7.344
7.343
7.323
7.321
7.274
5.260
5.256
4.083
4.077
4.071
3.979
3.976
3.974
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1.672
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1.668
1.665
1.663
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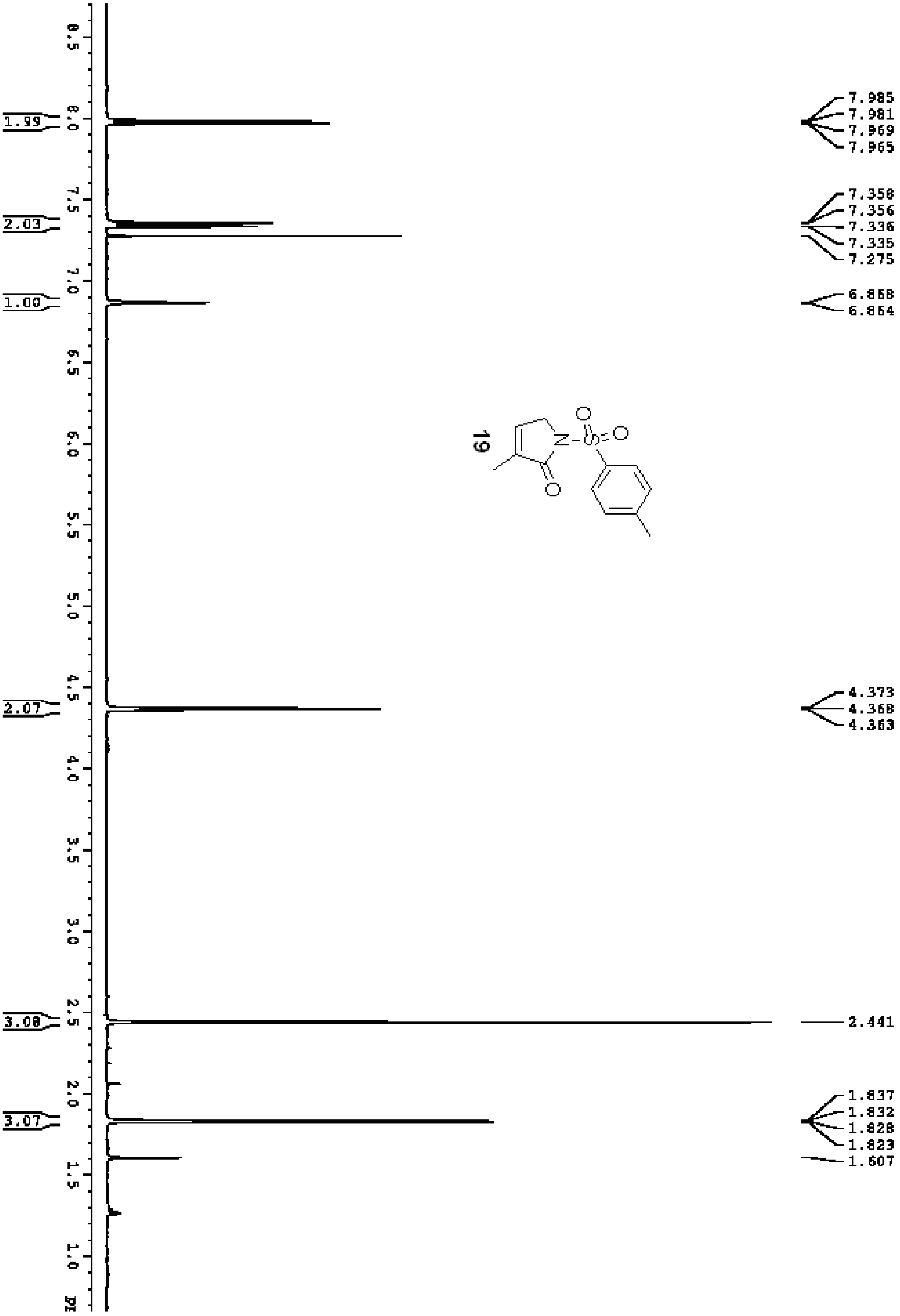
0.002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6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
2.03
1.00
2.07
3.08
3.07
7.985
7.981
7.969
7.965
7.358
7.356
7.336
7.335
7.275
6.868
6.864
4.373
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1.837
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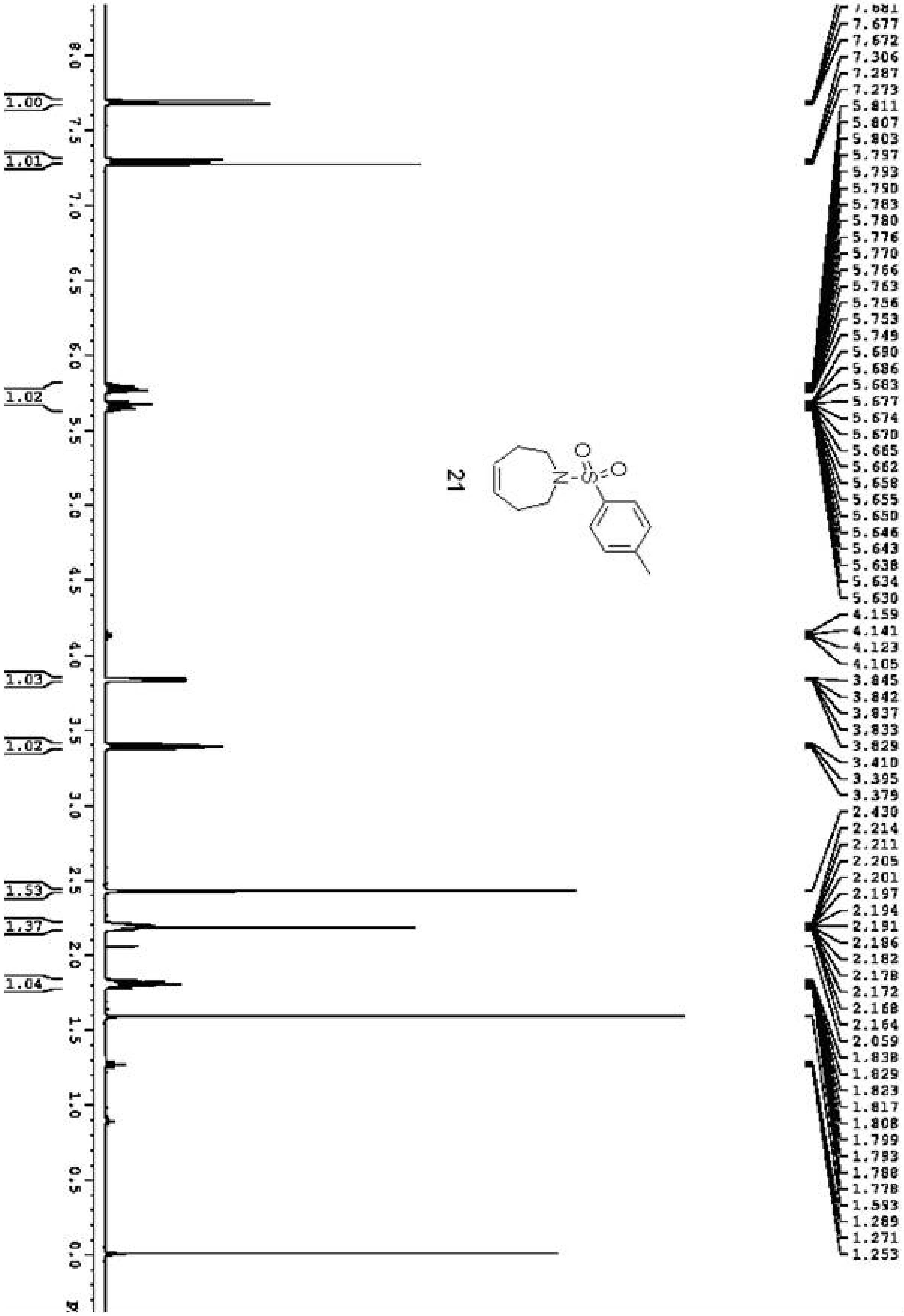
1.823
1.607
O
O
N
S
O

19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3.5
3.0
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2.0
1.5
1.0
0.5
0.0
1.00
1.01
1.02
1.03
1.02
1.53
1.37
1.04
O
S
O
N
7.681
7.677
7.672
7.306
7.287
7.273
5.811
5.807
5.803
5.797
5.793
5.790
5.783
5.780
5.776
5.770
5.766
5.763
5.756
5.753
5.749
5.690
5.686
5.683
5.677
5.674
5.670
5.665
5.662
5.658
5.655
5.650
5.646
5.643
5.638
5.634
5.630
4.159
4.141
4.123
4.105
3.845
3.842
3.837
3.833
3.829
3.410
3.395
3.379
2.430
2.214
2.211
2.205
2.201
2.197
2.194
2.191
2.186
2.182
2.178
2.172
2.168
2.164
2.059
1.838
1.829
1.823
1.817
1.808
1.799
1.793
1.788
1.778
1.593
1.289
1.271
1.253

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