Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Synthesis of Symmetrical Disulfides by Reacting Organic Halides with $Na_2S_2O_3 \cdot 5H_2O$ in DMSO

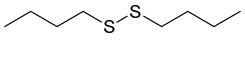
A typical scale-up procedure:

A mixture of well-powdered $Na_2S_2O_3.5H_2O$ (30 mmol, 7.445 g) and *o*-chlorobenzyl chloride (30.75 mmol, 4.952 g) in wet DMSO (30 mL DMSO + 3 mL H_2O) was stirred magnetically at 60-70 °C. The progress of the reaction was checked by litmus paper. After stirring for 4h, the color of litmus paper changed from yellow to red. The stirring was continued for further 2h under such conditions. Then the reaction was worked up by adding H_2O (10 mL) and extracted with 1:1 *n*-hexane/EtOAc (3×15 mL). The product was further purified by recrystallization from *n*-hexane to afford pure bis(2-chlorobenzyl) disulfide in 4.162 g, 88% yield.

General Procedure:

A mixture of an alkyl halide (2-2.1 mmol) and well-powdered $Na_2S_2O_3{\cdot}5H_2O$ (2 mmol) in wet DMSO (2 mL DMSO + 0.2 mL H_2O) was stirred magnetically at 60-70 ˚C. The progress of the reaction was checked by litmus paper. After changing the color of litmus paper from yellow to red (0.5-10 h), the stirring was continued for further 2h under such conditions to ensure the reaction completion. Next, the reaction was worked up by dilution with water (2 mL). The crude product was extracted and was further purified by recrystallization or chromatography on silica gel.

In this line, the oily products including **1**, **2**, **3**, **4**, **9**, **10**, **12**, **13**, **14**, **15**, **17** were extracted from the corresponding reaction mixtures using *n*-hexane in good purities and were further purified by chromatography on silica gel using *n*-hexane as eluent. Also, the solid disulfides including **5**, **6**, **8**, **11**, and **16** were extracted with 1:1 *n*-hexane/EtOAc and subjected to recrystallization in 20:1 *n*-hexane/EtOAc to afford the corresponding disulfides in high purity. The crystalline disulfide **7** was obtained in 60% yield after extraction with 1:1 *n*-hexane/EtOAc and chromatography on silica gel using 5:1 *n*-hexane/EtOAc as eluent.



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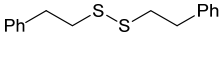

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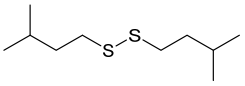

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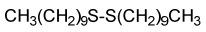

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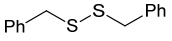

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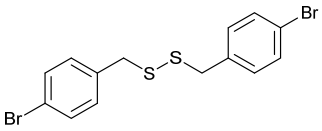

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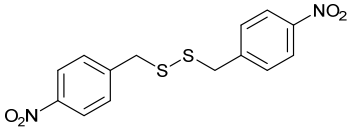

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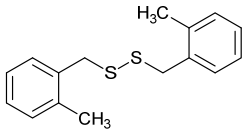

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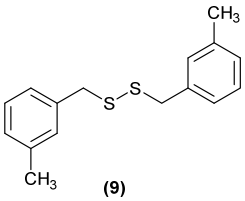

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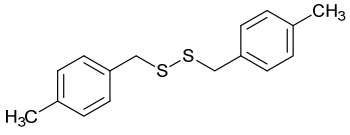

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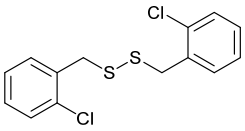

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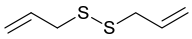

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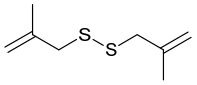

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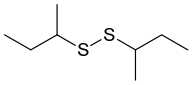

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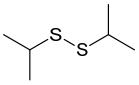

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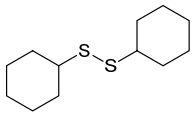

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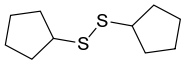


(17)

Spectral Data & Analysis

Dibutyl disulfide (1):

Colorless oil; ^{1}HNMR (250 MHz, $CDCl_3$): δ 2.69 (t, *J* = 7.4 Hz, 4H), 1.71-1.66 (m, 4H), 1.48-1.40 (m, 4H), 0.93 (t, *J* = 7.3 Hz, 6H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 39.3, 31.7, 22.0, 14.0. Anal. Calcd for $C_8H_{18}S_2$: C, 53.88; H, 10.17; S, 35.95. Found: C, 53.73; H, 10.29; S, 35.98.

Decyl disulfide (4):

Colorless oil; ^{1}HNMR (250 MHz, $CDCl_3$): δ 0.80-0.85 (m, 6H), 1.21-1.35 (m, 28H), 1.59-1.73 (m, 4H), 2.64 (t, *J* = 7.3 Hz, 4H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 39.2, 31.8, 29.6, 29.5, 29.3, 29.2, 29.0, 28.5, 22.8, 14.2; Anal. Calcd for $C_{20}H_{42}S_2$: C, 69.29; H, 12.21; S, 18.50 %. Found: C, 69.35; H, 12.29; S, 18.36 %.

Dibenzyl disulfide (5):

White crystals; m.p. 68 – 70 (Lit.[3] 68-70 °C); ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.34-7.26 (m, 10 H), 3.61 (s, 4H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 138.6, 130.7, 129.7, 128.7, 44.5. Anal. Calcd for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73; S, 26.02%. Found: C, 68.39; H, 5.66; S, 25.95%.

Bis(4-Bromobenzyl) disulfide (6):

Yellow crystals; m.p. 87–89 °C (Lit.[2] 88-89 °C); ^{1}HNMR (250 MHz, $CDCl_3$): δ 7.34-7.27 (m, 4H), 6.98-6.89 (m, 4H), 3.46 (s, 4H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 136.3, 131.6, 131.2, 121.5, 42.5; Anal. Calcd for $C_{14}H_{12}Br_2S_2$: C, 41.60; H, 2.99; S, 15.86. Found: C, 41.65; H, 3.10; S, 15.77.

Bis(2-methylbenzyl) disulfide (8):

Withe crystals; m.p.71-73 °C; ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.26-7.13 (m, 8H), 3.67 (s, 4H), 2.38 (s, 6H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 135.8, 134.0, 129.5, 129.4, 126.7, 124.9, 40.5, 18.2. Anal. Calcd for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61; S, 23.37 %. Found: C, 69.91; H, 6.55; S, 23.54 %.

Bis(3-methylbenzyl) disulfide (9):

Colorless oil; ^{1}HNMR (250 MHz, $CDCl_3$): δ 7.30-7.07 (m, 8H), 3.62 (s, 4H), 2.39 (s, 6H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 138.1, 137.3, 130.2, 128.4, 128.2, 126.5, 43.3, 21.4. Anal. Calcd for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61; S, 23.37 %. Found: C, 69.97; H, 6.77; S, 23.26 %.

Bis(2-chlorobenzyl) disulfide (11):

Yellow crystals; m.p.70-72 °C (Lit.[4] 74 °C); ^{1}HNMR (250 MHz, $CDCl_3$): δ 7.40-7.18 (m, 8H), 3.79 (s, 4H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 135.0, 134.1, 131.6, 129.7, 128.9, 126.7, 41.1. Anal. Calcd for $C_{14}H_{12}Cl_2S_2$: C, 53.34; H, 3.84; S, 20.34%. Found: C, 53.44; H, 3.96; S, 20.19%.

Bis(2-methyl-2-propenyl) disulfide (13):

Colorless oil; ^{1}HNMR (250 MHz, $CDCl_3$): δ 1.80 (s, 6H), 3.27 (s, 4H), 4.77-4.86 (m, 4H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 141.0, 115.1, 46.6, 20.7; Anal. Calcd for $C_8H_{14}S_2$: C, 55.12; H, 8.09; S, 36.79 %. Found: C, 55.25; H, 8.01; S, 36.74 %.

***iso*-Propyl disulfide (15):**

Colorless oil; ^{1}HNMR (250 MHz, $CDCl_3$): δ 1.30 (d, J = 6.9 Hz, 12H), 2.97 (m, 2H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 22.6, 41.4; Anal. Calcd for $C_6H_{14}S_2$: C, 47.95; H, 9.39; S, 42.66. Found: C, 47.85; H, 9.44; S, 42.71 %.

Cyclohexyl disulfide (16):

White solid; m.p. 123-125°C (Lit.[1] 124-129 °C); ^{1}HNMR (250 MHz, $CDCl_3$): δ 1.17-1.31 (m, 10H), 1.52-1.64 (m, 2H), 1.70-1.82 (m, 4H), 1.99-2.06 (m, 4H), 2.64-2.73 (m, 2H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 50.1, 32.7, 26.1, 25.7; Anal. Calcd for $C_{12}H_{22}S_2$: C, 62.55; H, 9.62; S, 27.83. Found: C, 62.43; H, 9.77; S, 27.80 %.

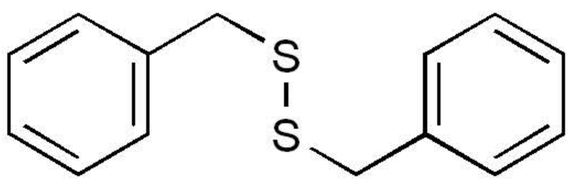
Cyclopentyl disulfide (17):

Colorless oil; ^{1}HNMR (250 MHz, $CDCl_3$): δ 3.45-3.39 (m, 2H), 1.97-1.94 (m, 4H), 1.69-1.51 (m, 12H); ^{13}CNMR (62.5 MHz, $CDCl_3$): δ 50.7, 32.9, 24.7; Anal. Calcd for $C_{10}H_{18}S_2$: C, 59.35; H, 8.97; S, 31.68. Found: C, 59.50; H, 9.01; S, 31.49%.

References:

1) Hajipour, A. R.; Mostafavi, M.; Ruoho, A. E.; *Phosphorus*, *Sulfur*, *Silicon* Relat. Elem. **2009**, *184*; 1920 – 1923.
2) Snyder, H. R.; Handrick; G. R. *J. Am. Chem. Soc*. **1944,** *66*; 1860-1863.,1862.
3) Soleiman-Beigi, M.; Mohammadi, F. *Synlett* **2015**, 911 – 914.
4) Srivastava, S. K.; Rastogi, R.; Rajaram, P.; Butcher, R. J.; Jasinski, J. P. *Phosphorus, Sulfur, Silicon Relat. Elem*. **2010**, *185*; 455-462.

Spectra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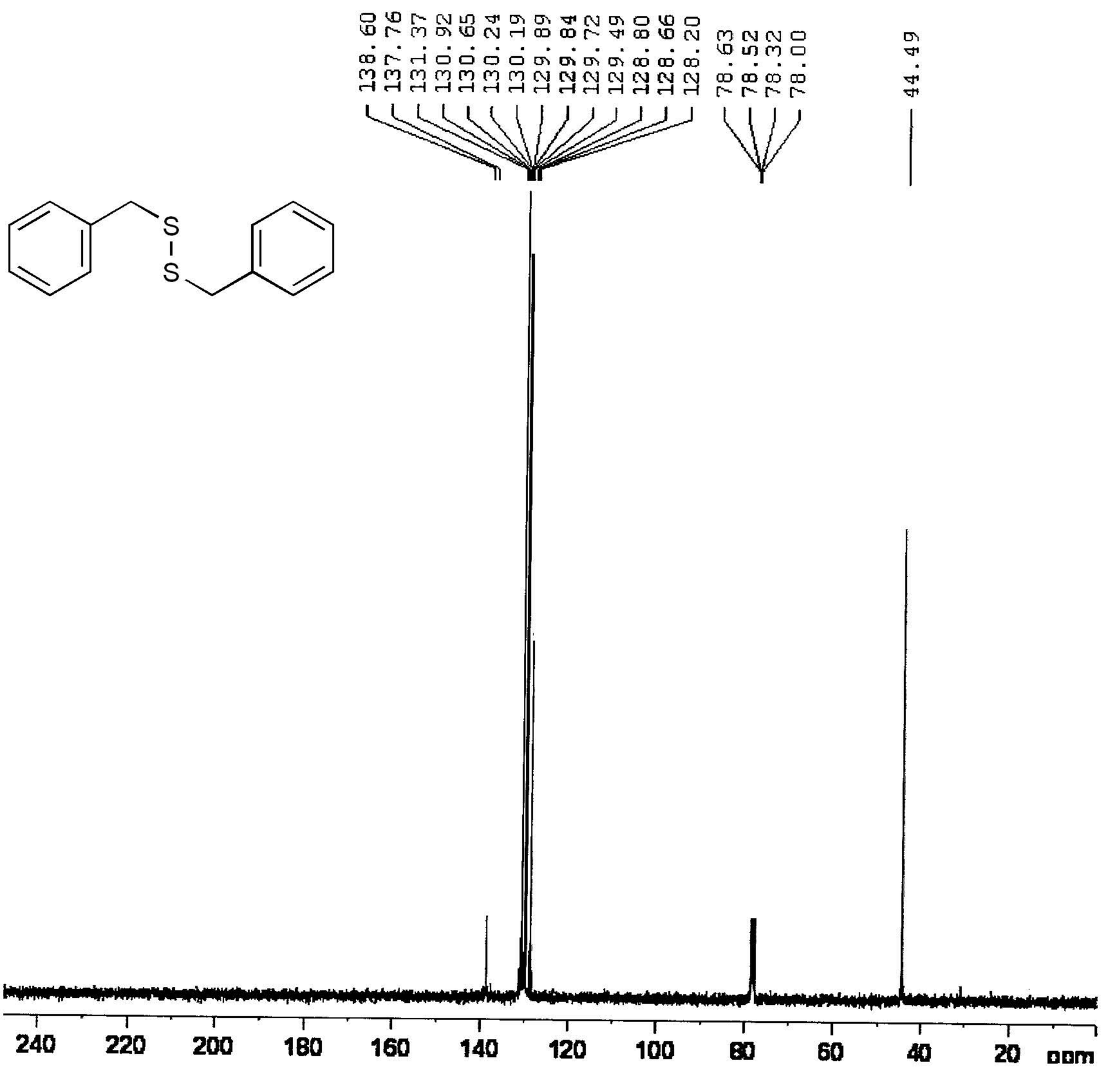
2.00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128.20
78.63
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S
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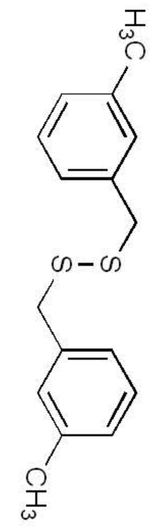
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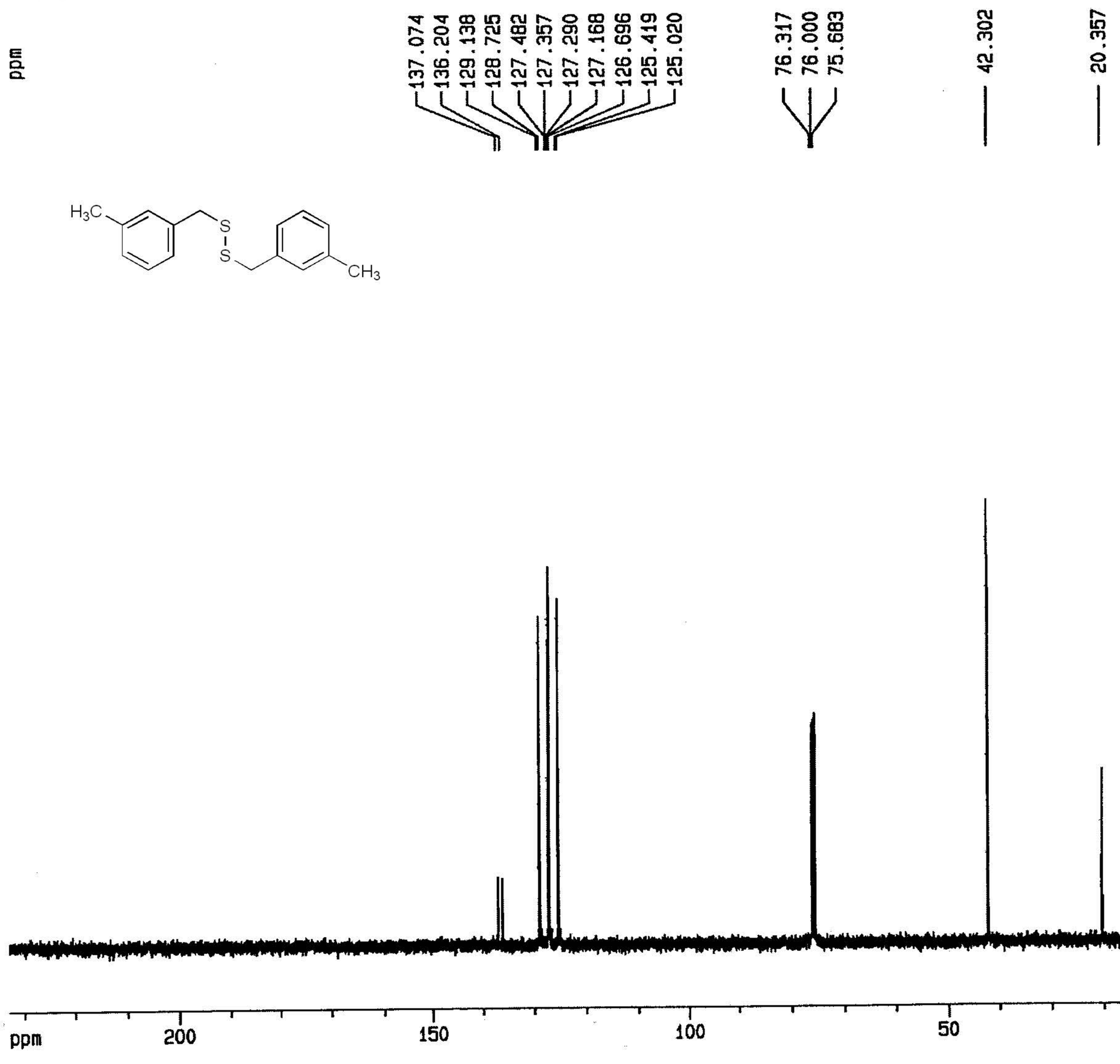
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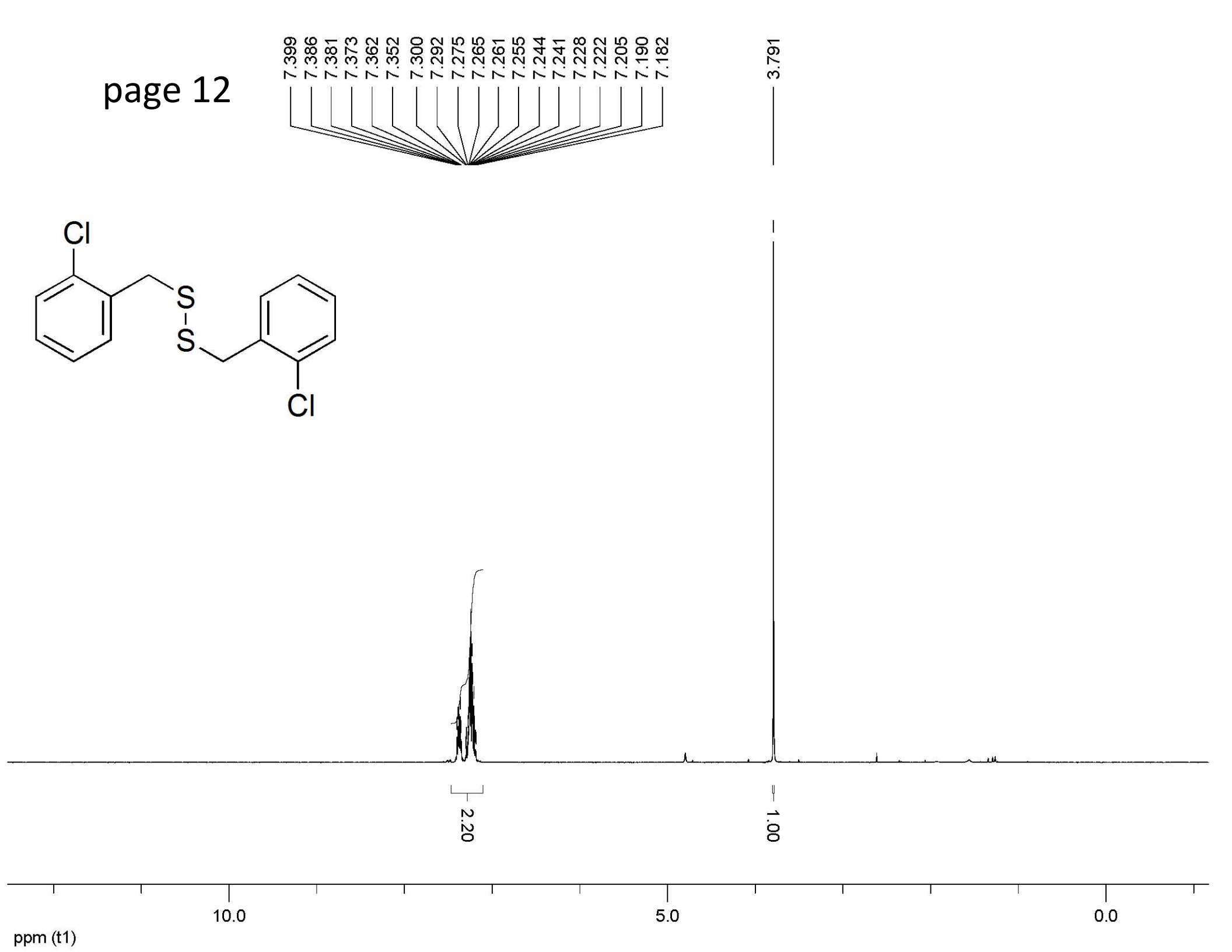
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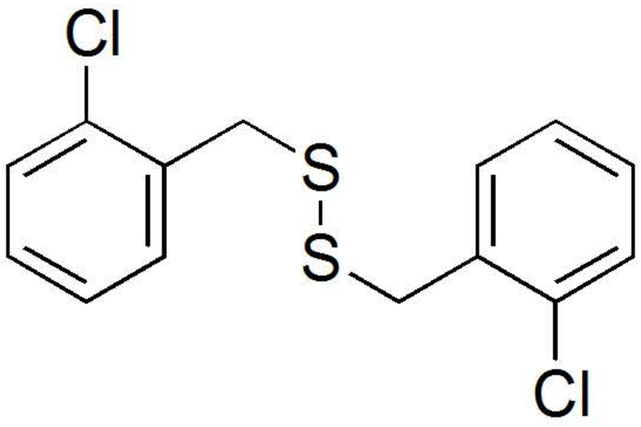
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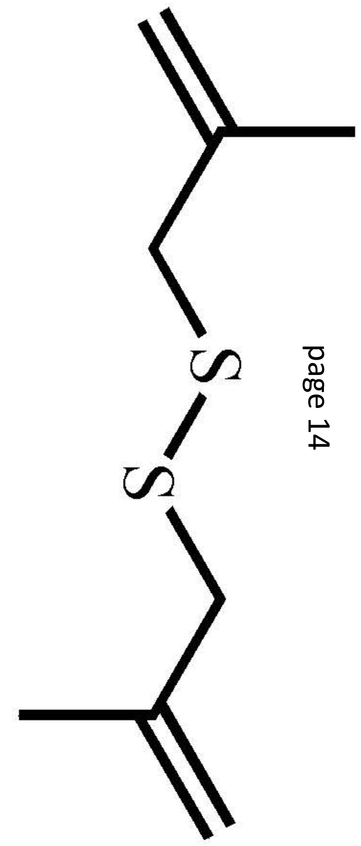

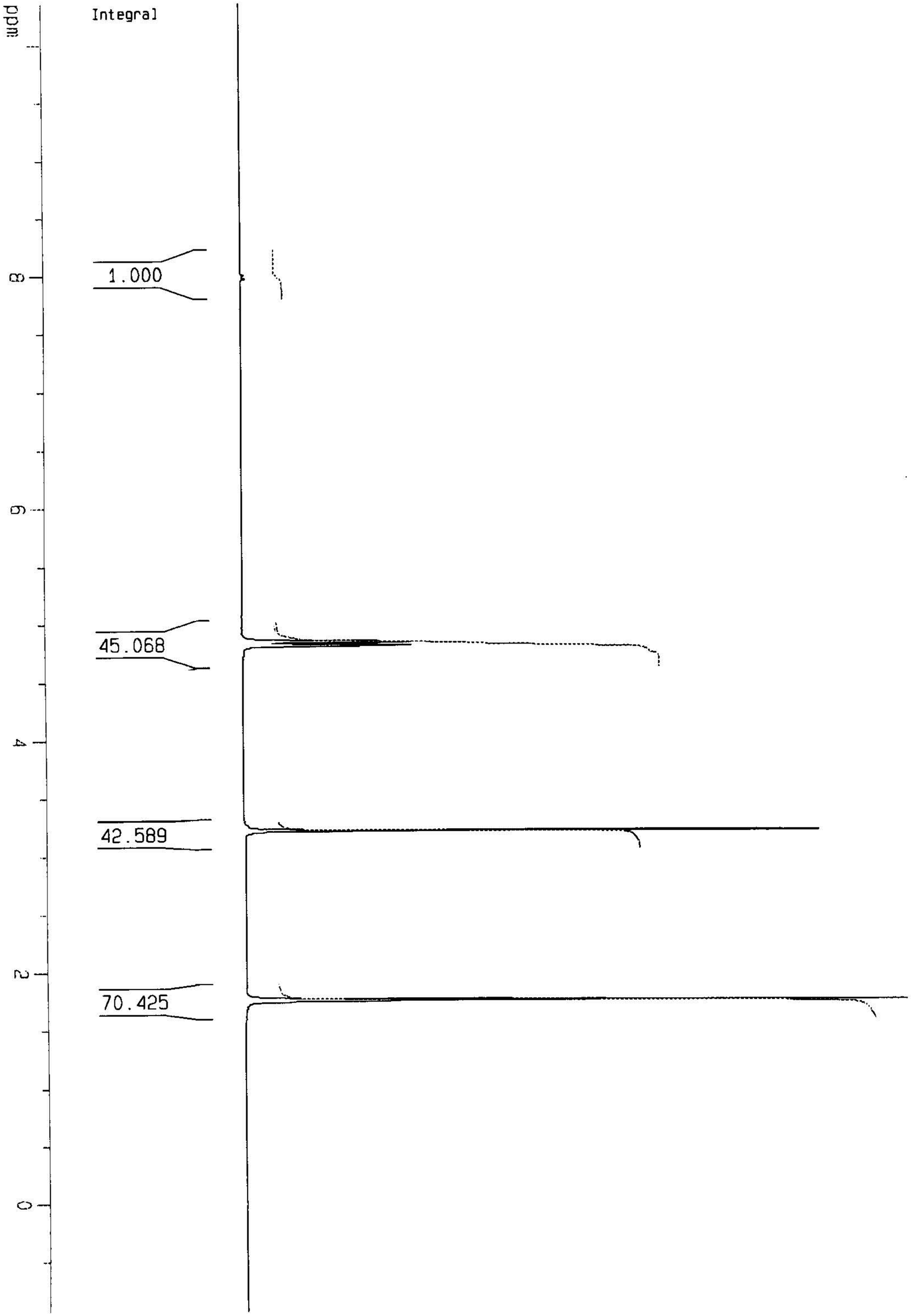

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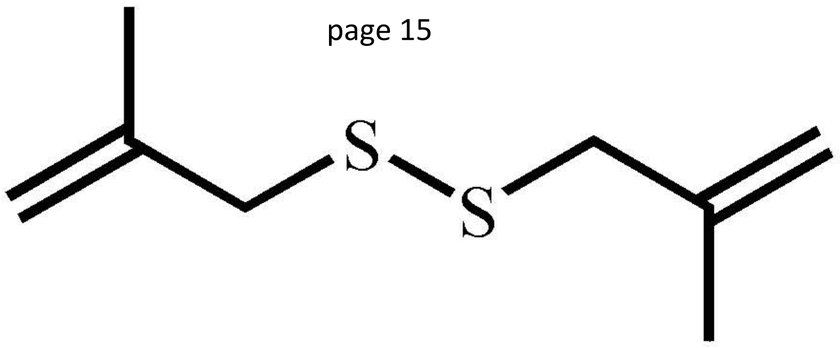
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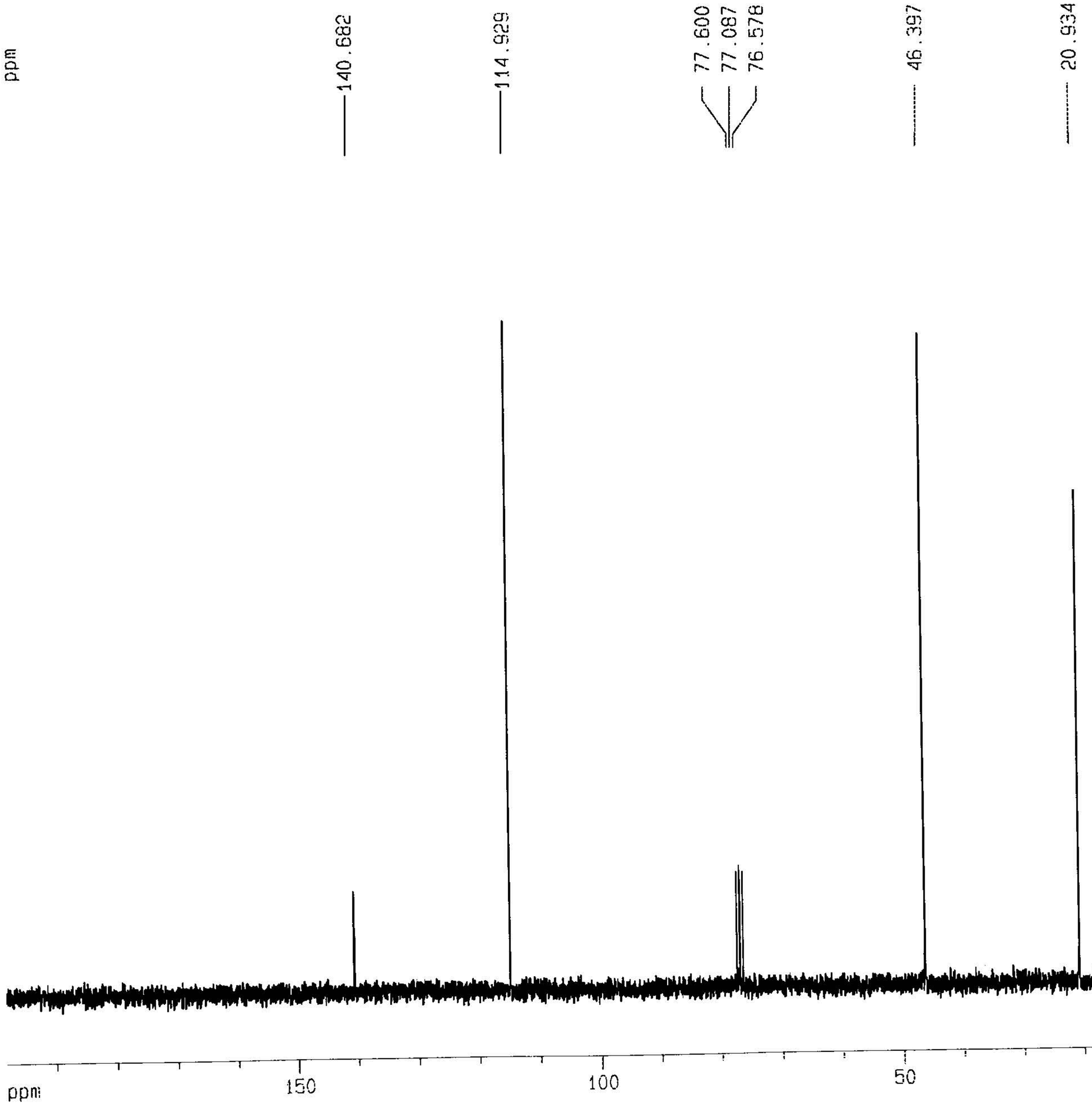
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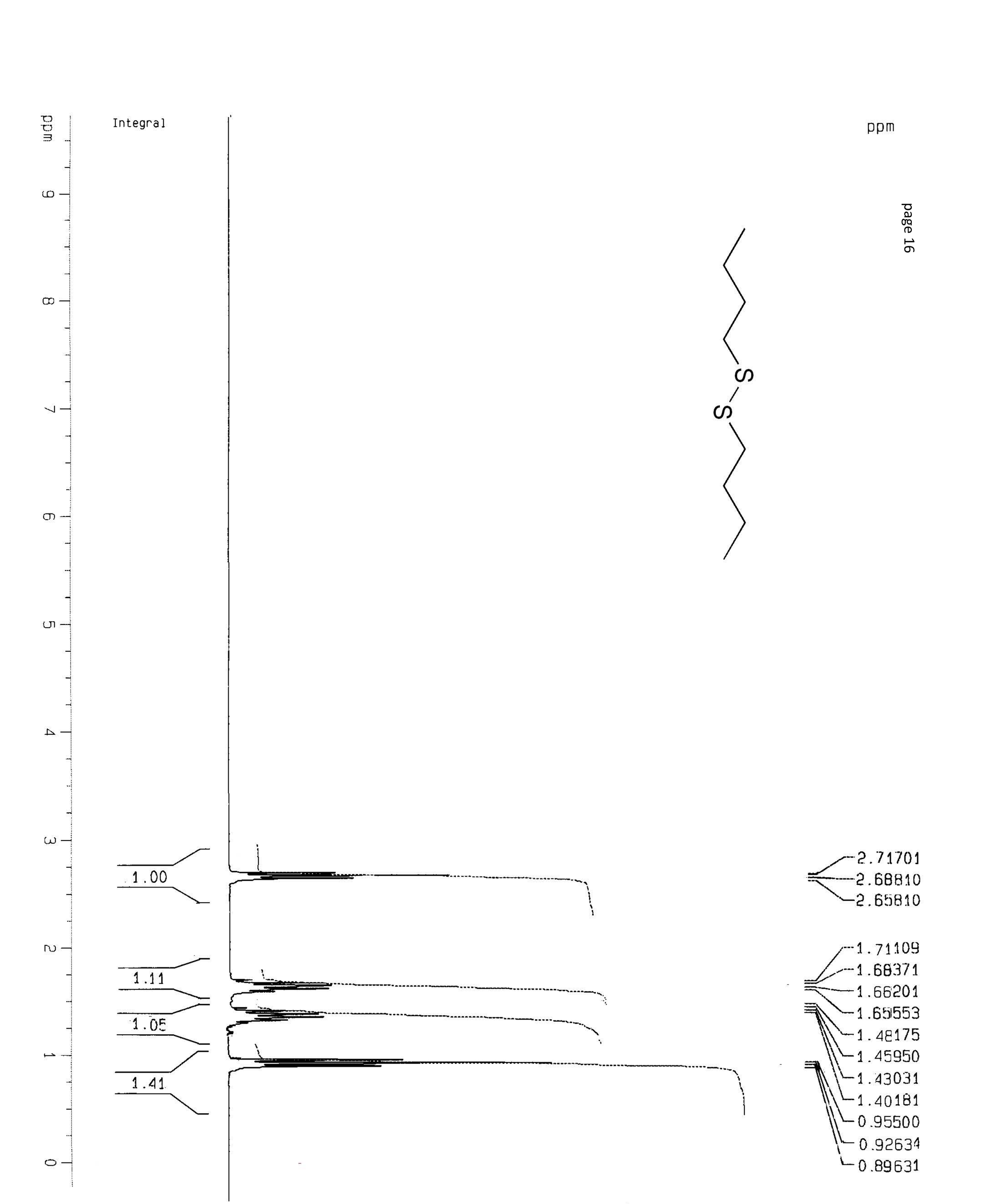
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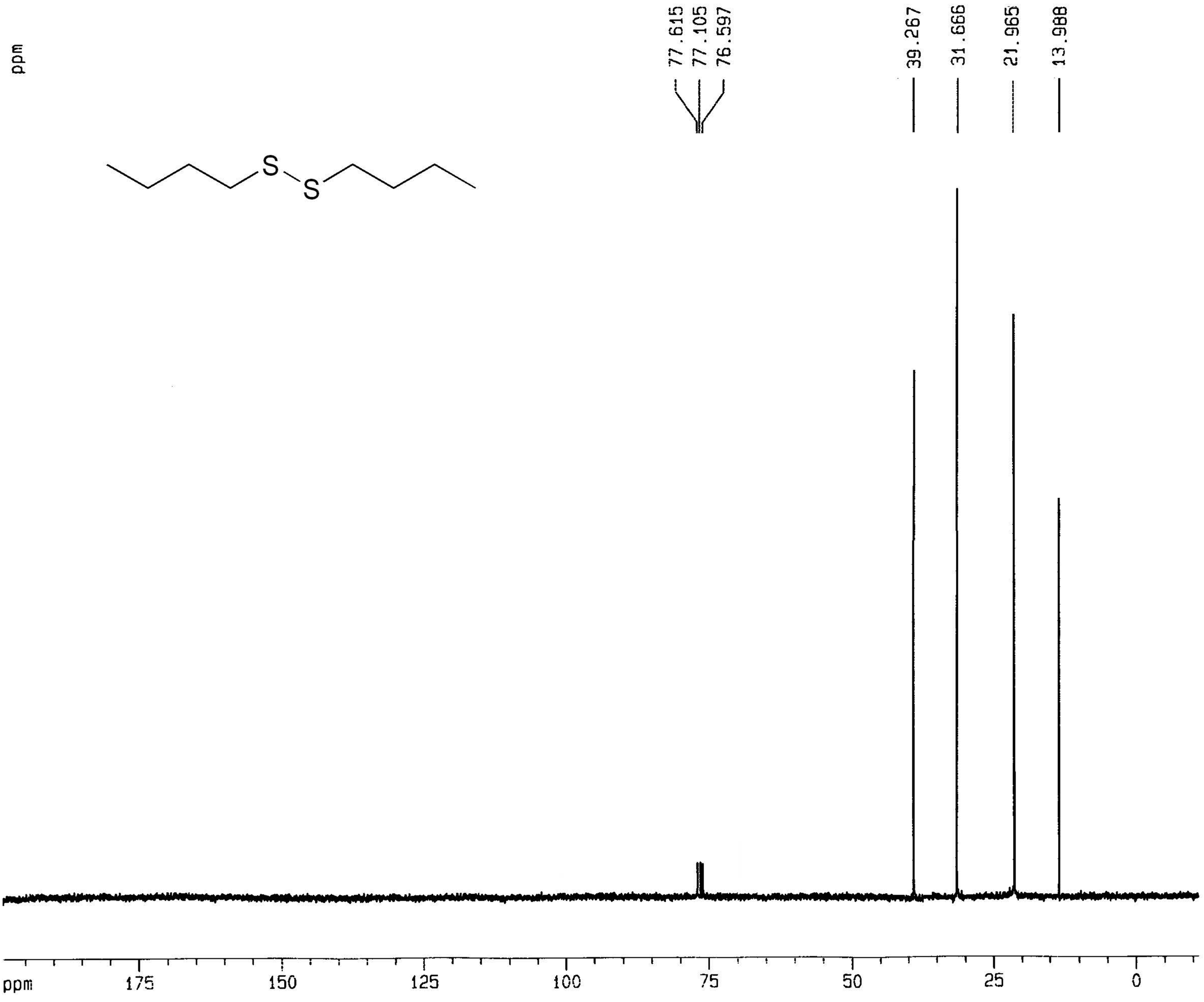
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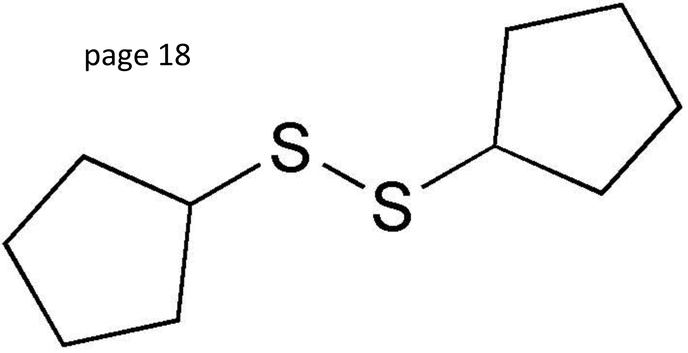
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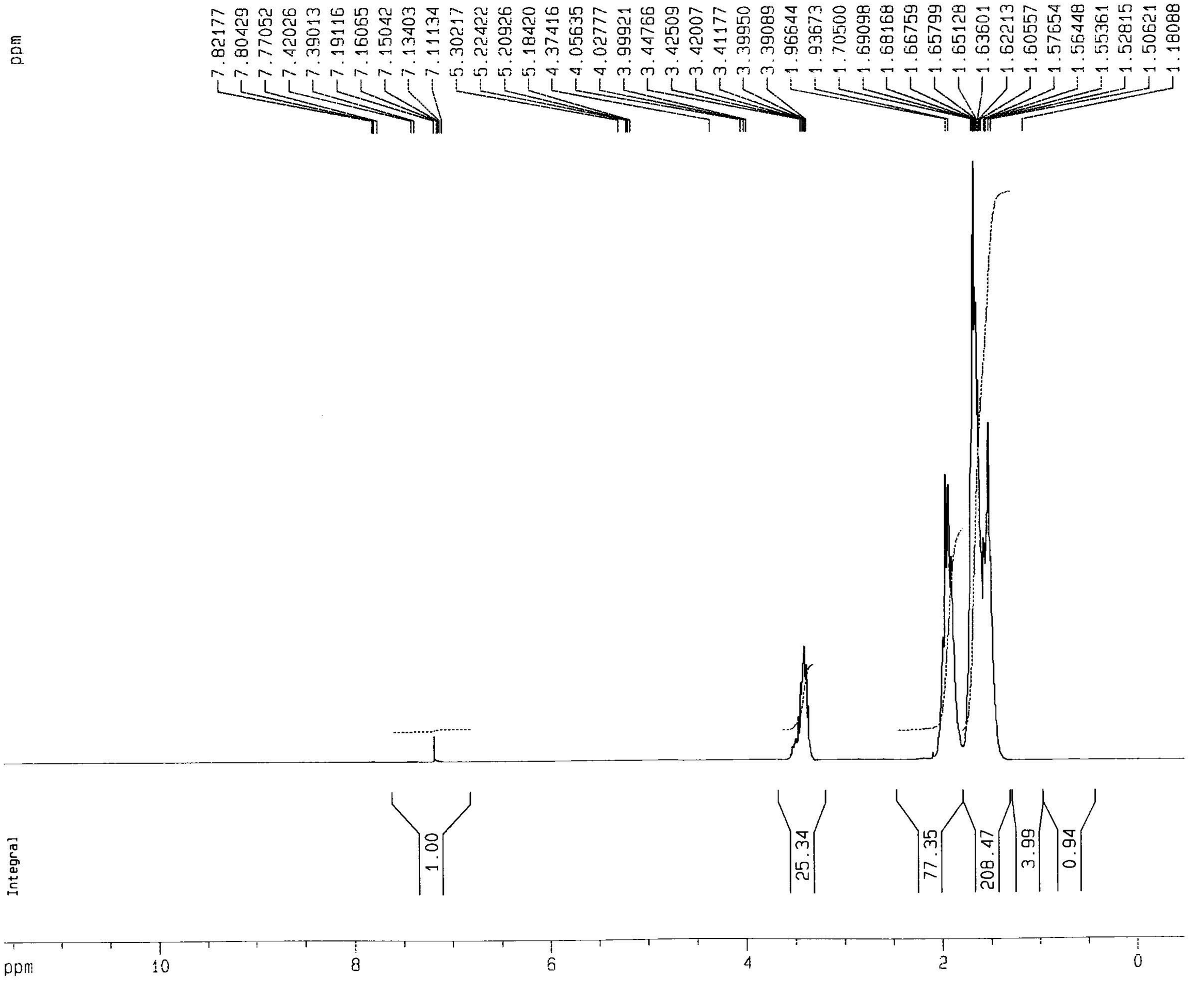
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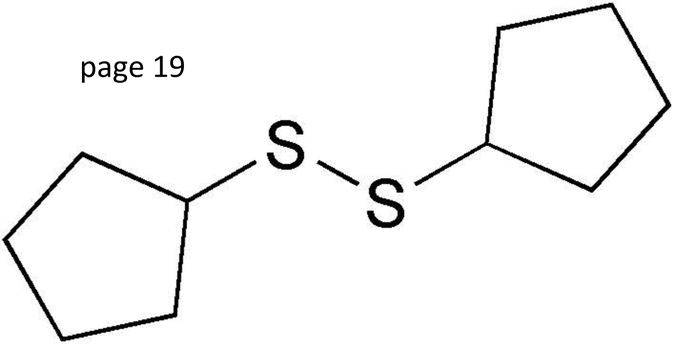
7.39013
7.19116
7.16065
7.15042
7.13403
7.11134
5.30217
5.22422
5.20926
5.18420
4.37416
4.05635
4.02777
3.99921
3.44766
3.42509
3.42007
3.41177
3.39950
3.39089
1.96644
1.93673
1.70500
1.69098
1.68168
1.66759
1.65799
1.65128
1.63601
1.62213
1.60557
1.57654
1.56448
1.55361
1.52815
1.50621
1.18088
Integral
1.00
25.34
77.35
208.47
3.99
0.94
ppm
10
8
6
4
2
0



ppm

77.551
77.043
76.534

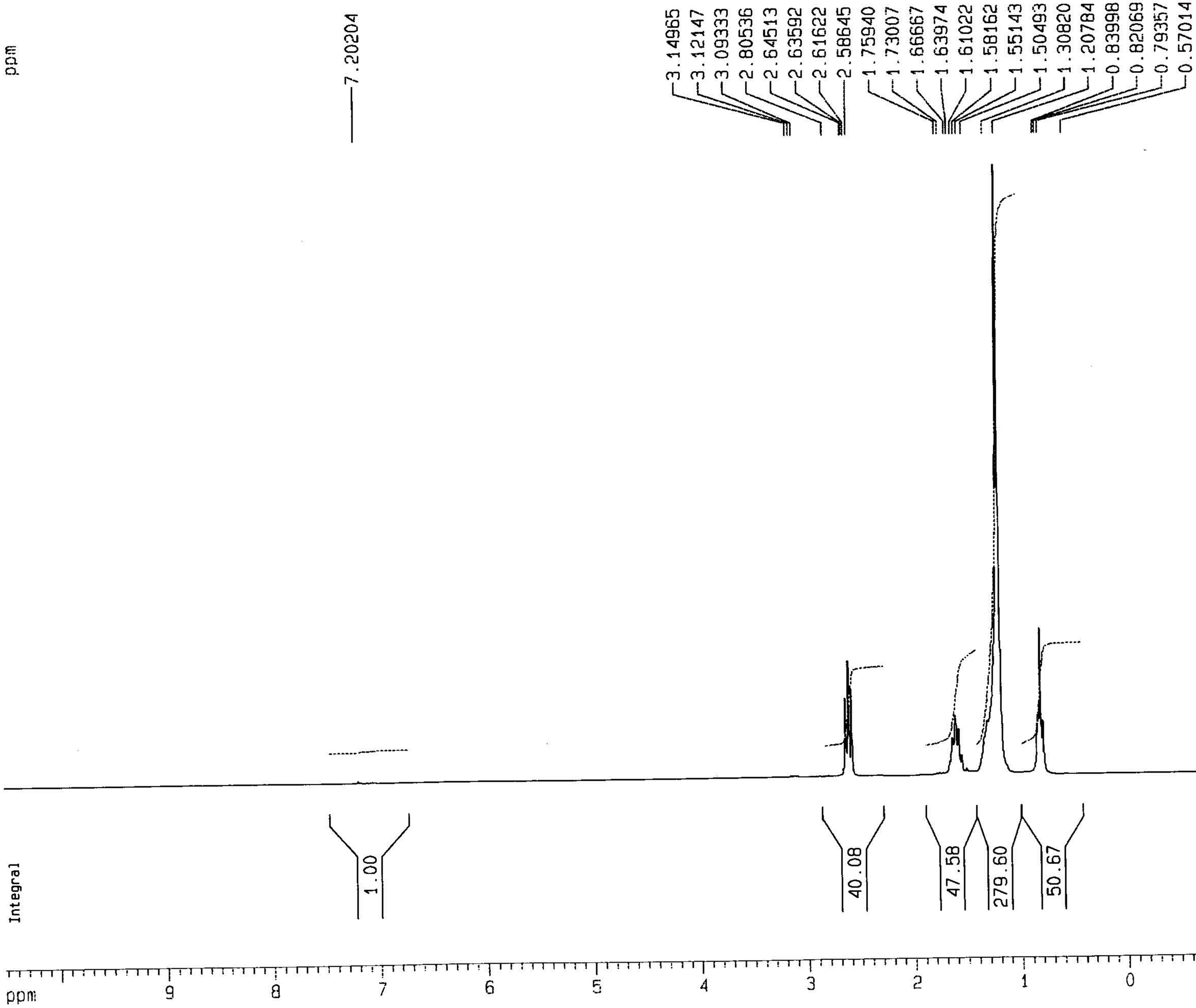
50.675

32.945

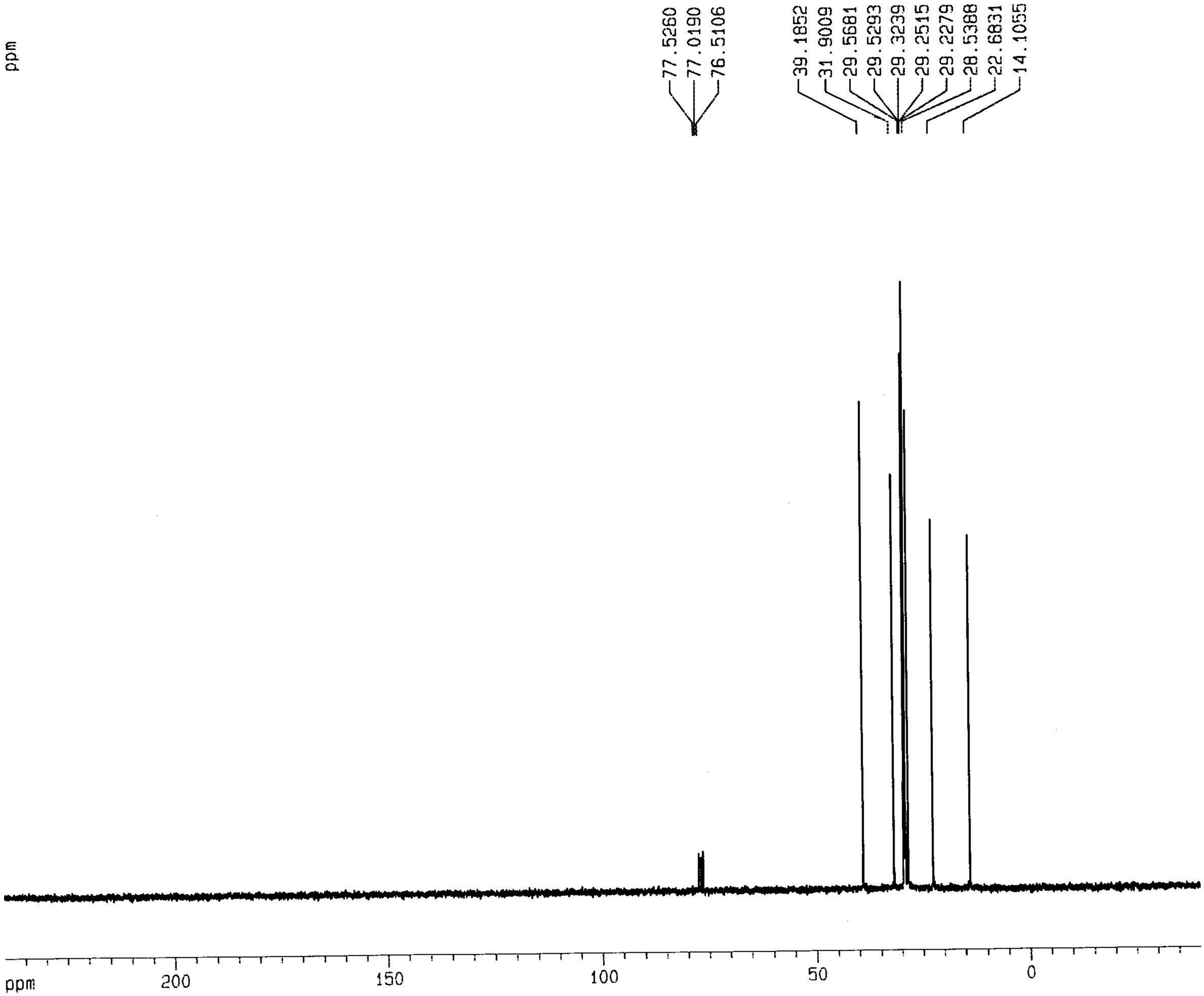
24.744

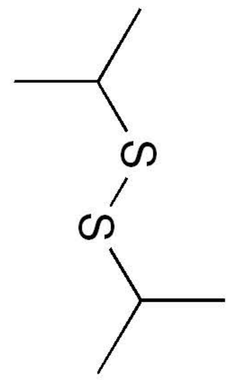
ppm
150
100
50
0

n-$C_{10}H_{21}$ S-S $C_{10}H_{21}$-n

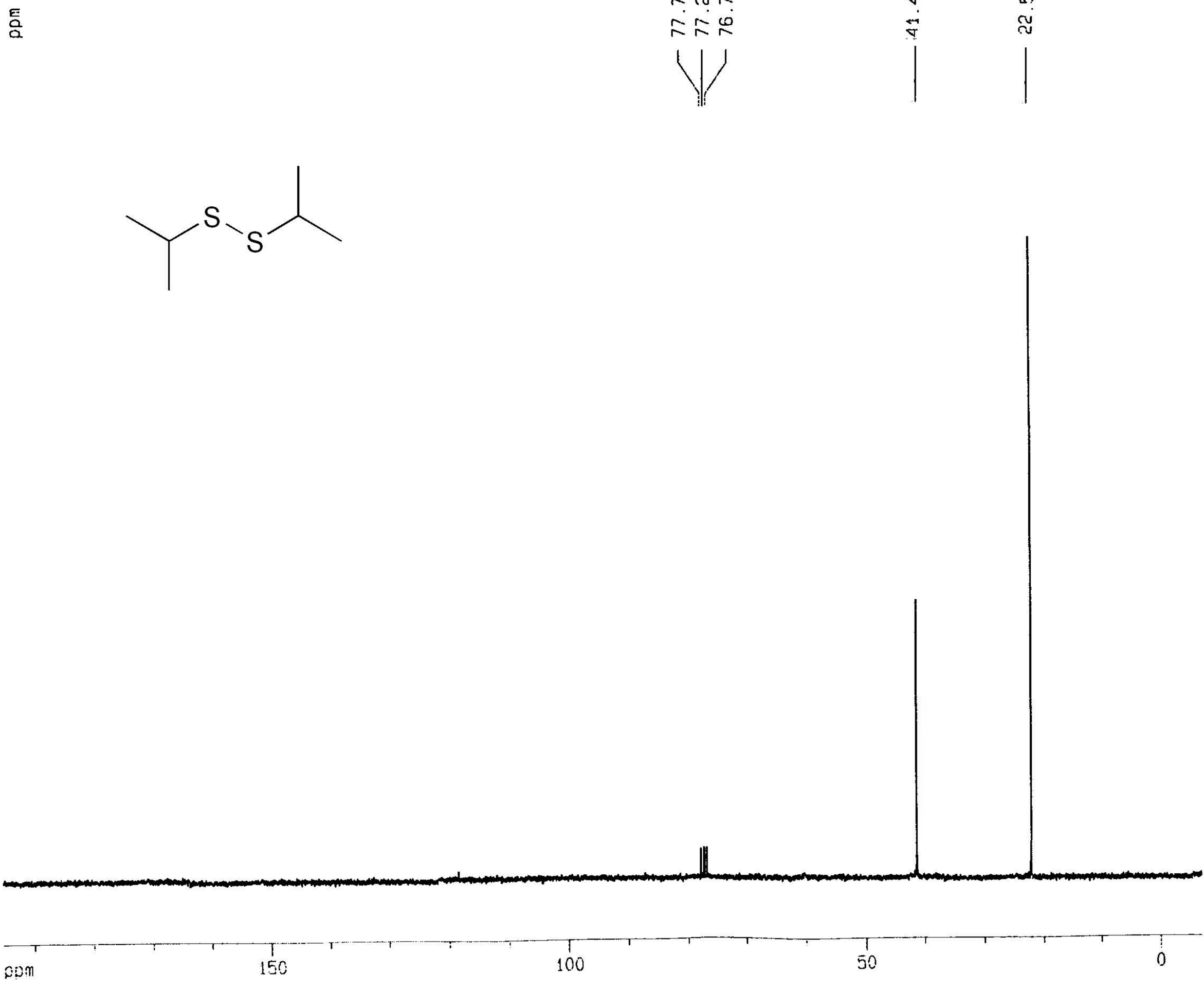


n-$C_{10}H_{21}$ S-S $C_{10}H_{21}$-n





ppm
Integral
8
6
4
2
0
1.00
6.68
3.0481
3.0214
2.9935
2.9670
2.9329
2.9120
2.8852
1.5548
1.5477
1.5248
1.4948
1.2967
1.2692
1.1976
0.8376
0.8300
0.8127
0.7854


ppm
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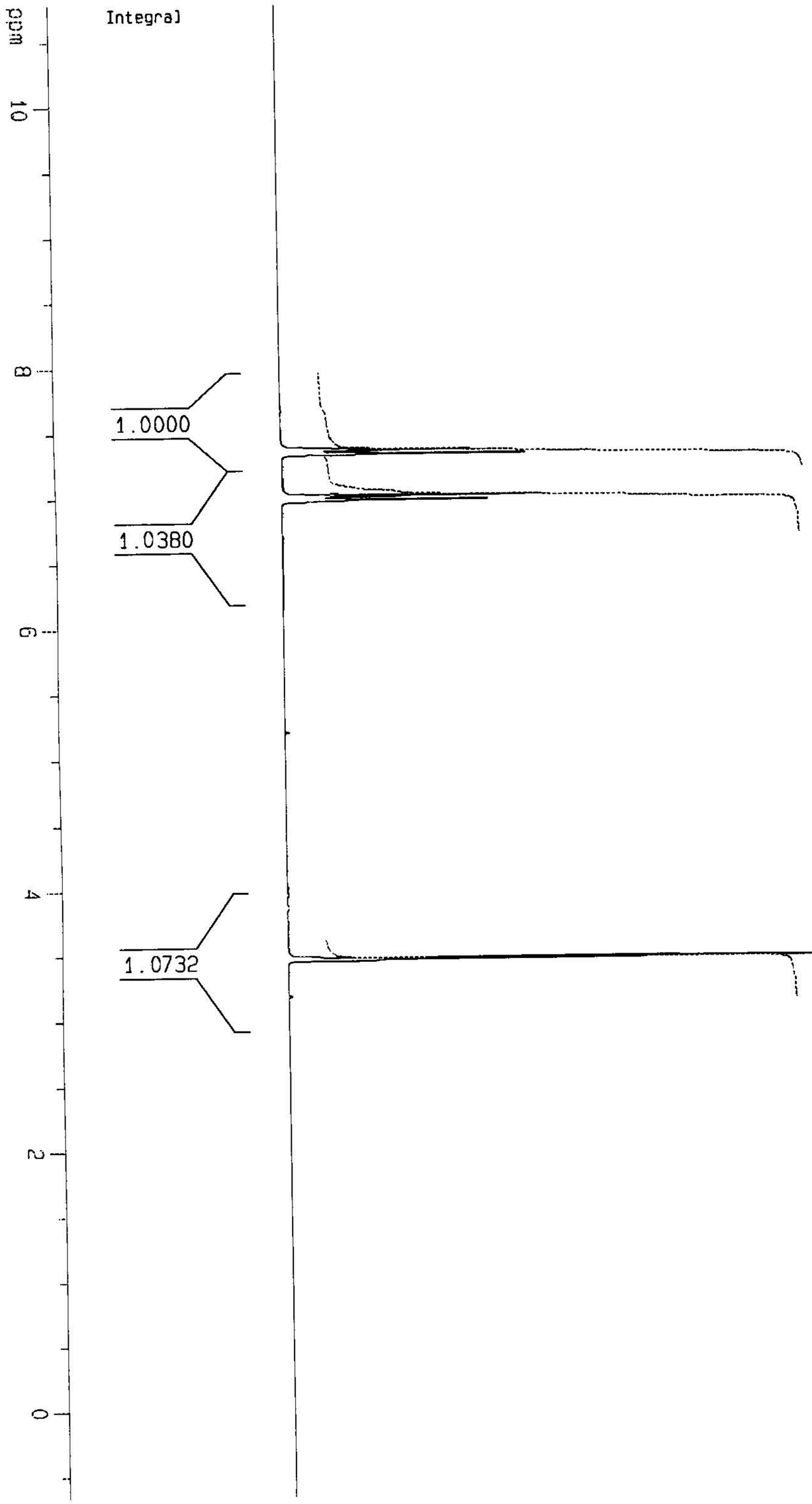
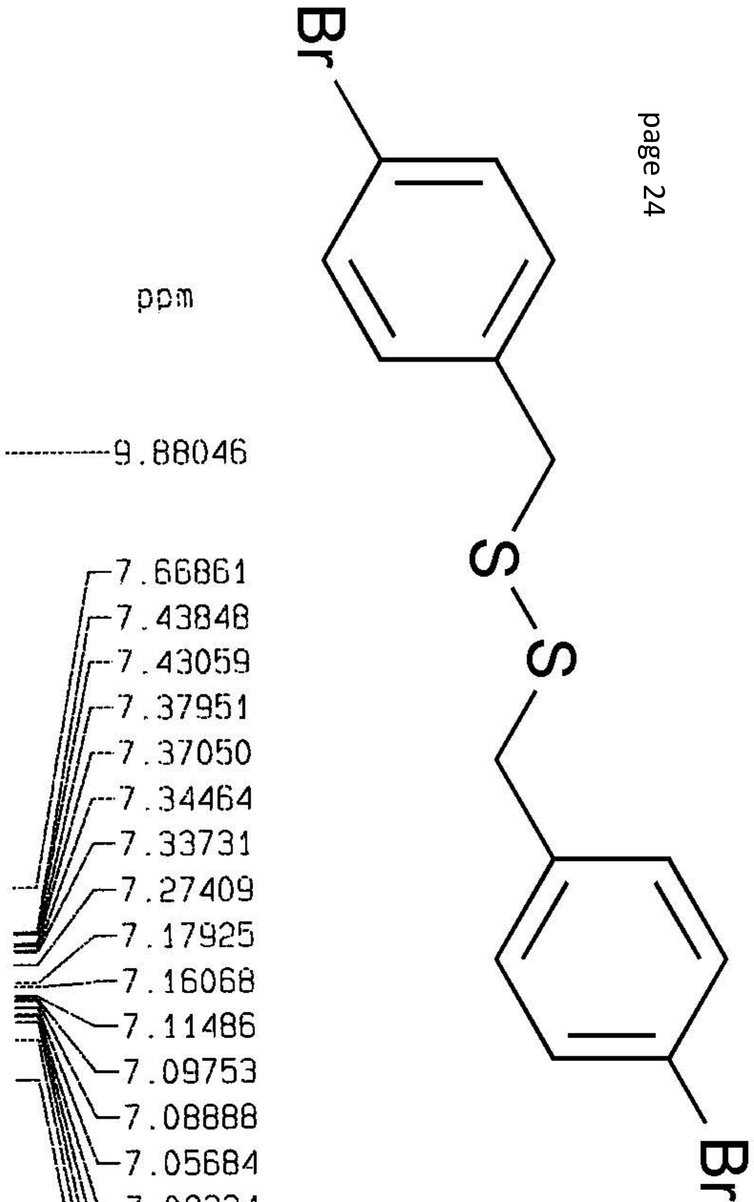
77.264
76.756
41.421
22.586
S
S
ppm
150
100
50
0

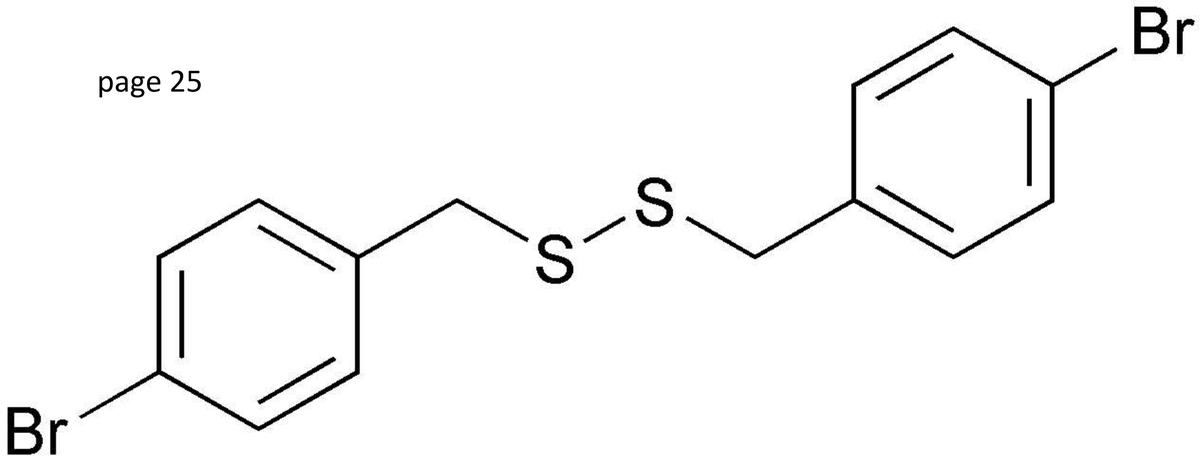




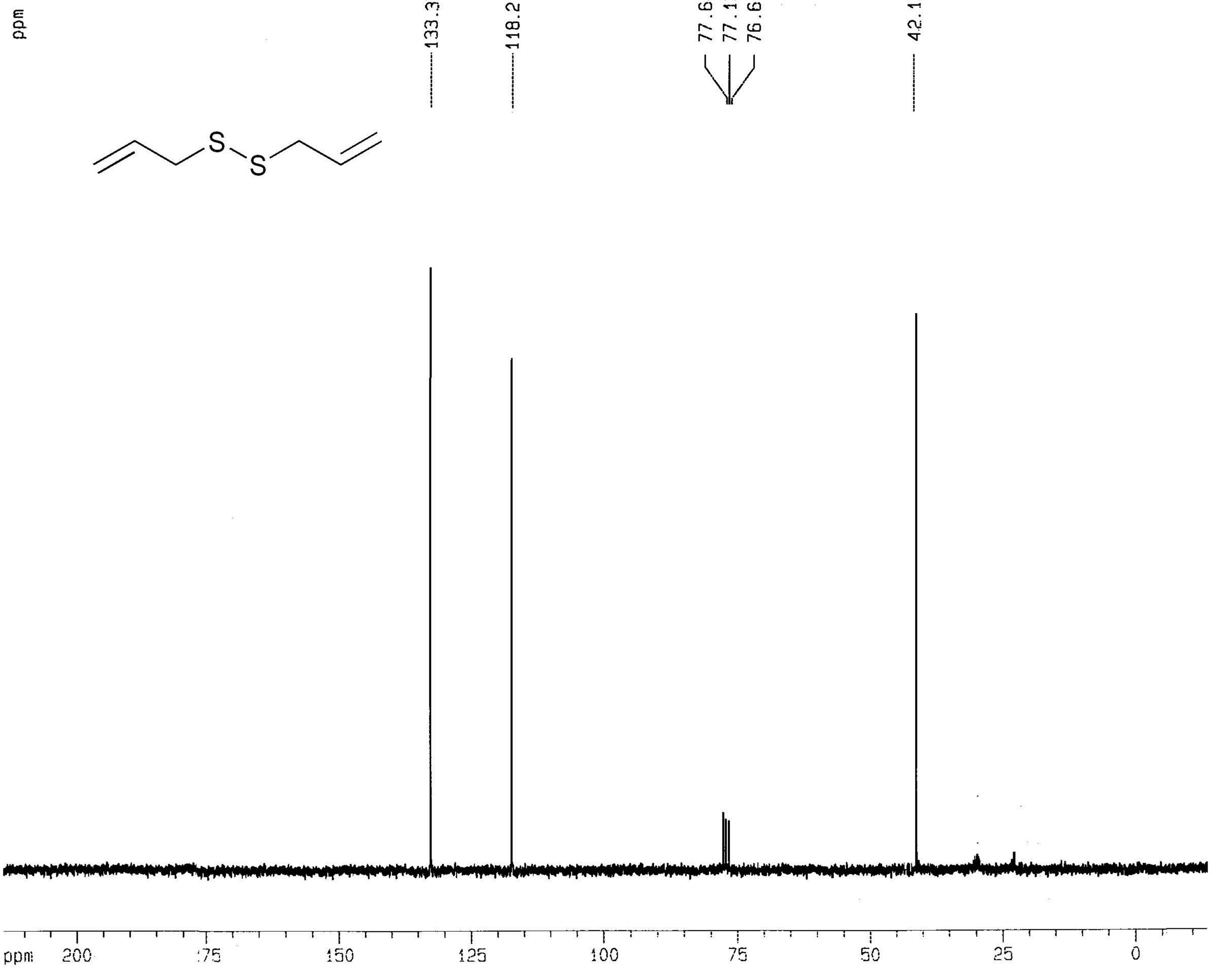
ppm

9.88046

7.66861
7.43848
7.43059
7.37951
7.37050
7.34464
7.33731
7.27409
7.17925
7.16068
7.11486
7.09753
7.08888
7.05684
7.02334
7.01371
6.98044
6.88822
6.68885
5.19697
4.26593
4.01810
3.96497
3.86437
3.74720
3.71291
3.70123
3.60290
3.54746
3.53699
3.46400
3.42423
3.36420
3.17790
2.07778
1.95846
1.51838
1.17373
1.14346
0.79836
0.77060
0.74617
0.00000

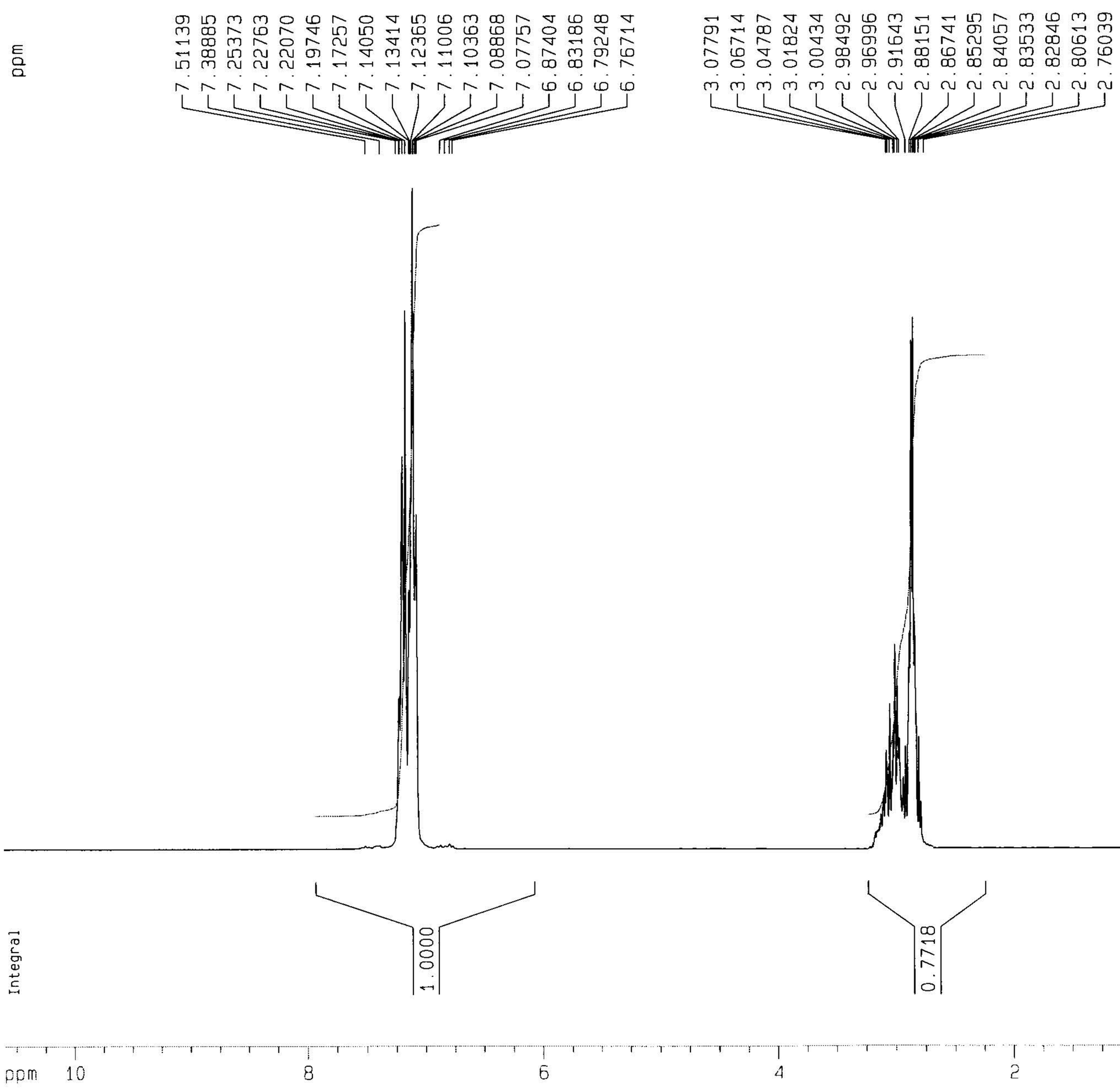

Br
S
S
Br

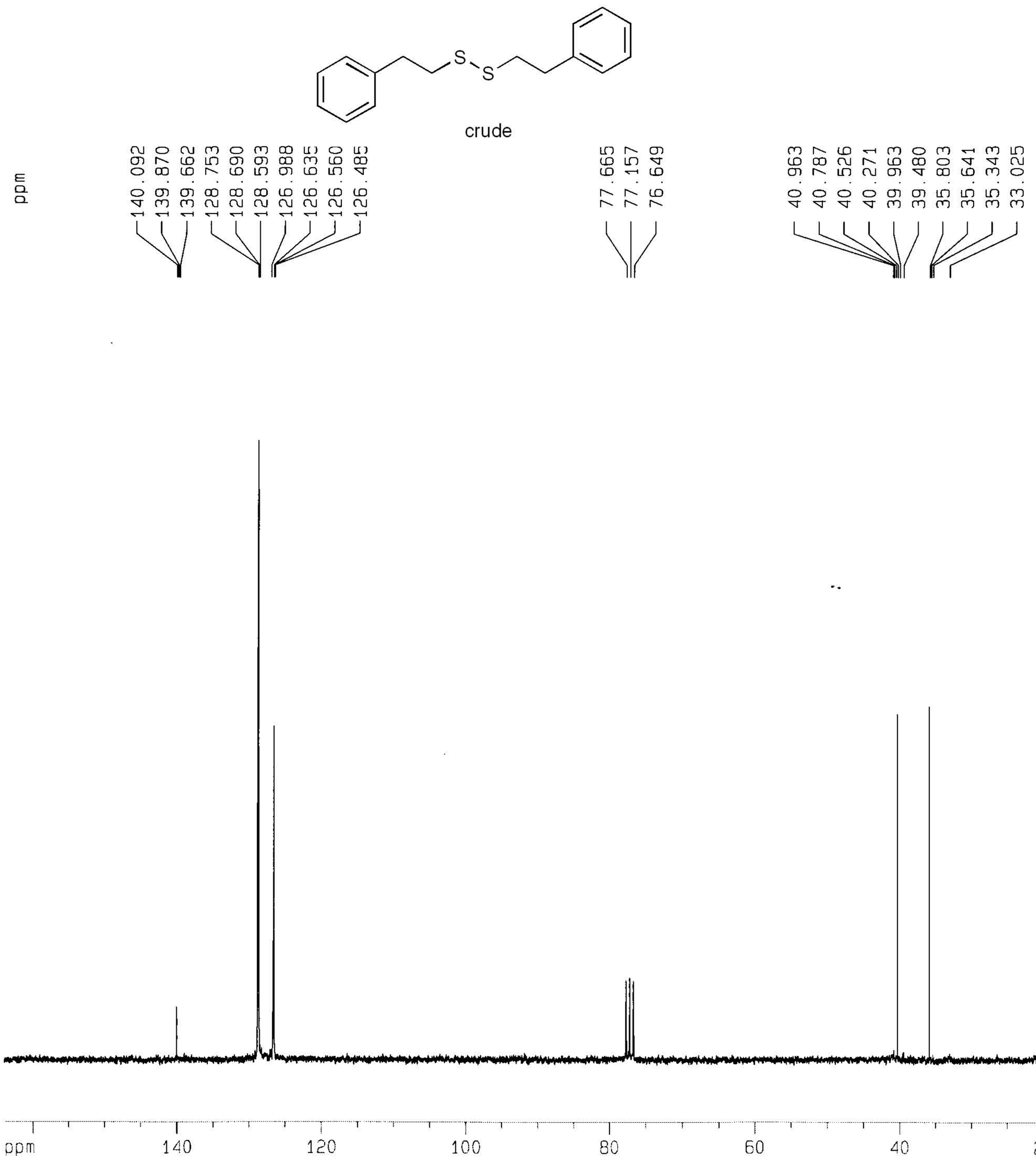
ppm
136.323
131.648
131.235
121.503
77.600
77.087
76.578
42.524
ppm
160
140
120
100
80
60
40
20
0

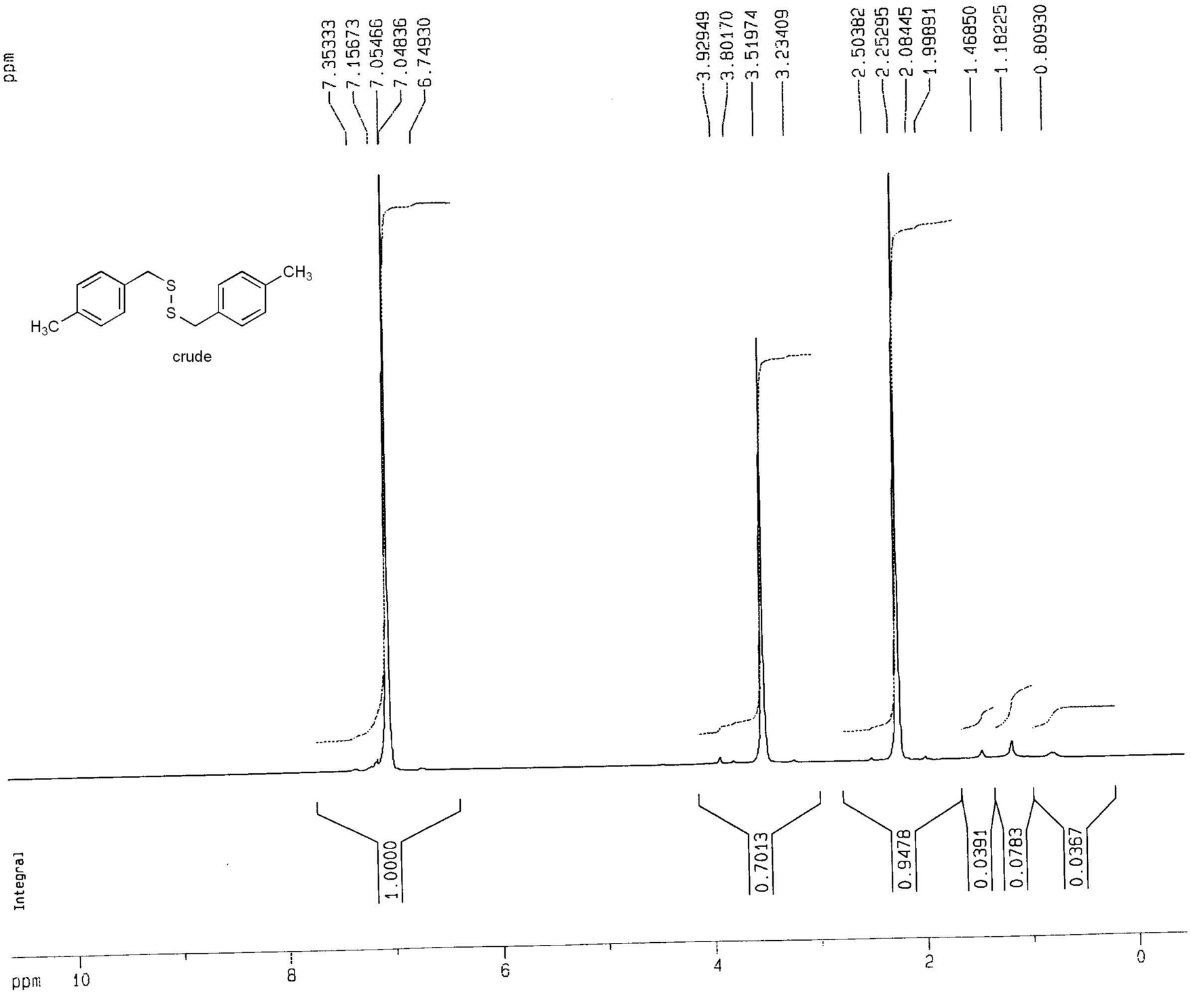

ppm
133.371
118.216
77.640
77.130
76.619
42.166
S
S
ppm 200 175 150 125 100 75 50 25 0

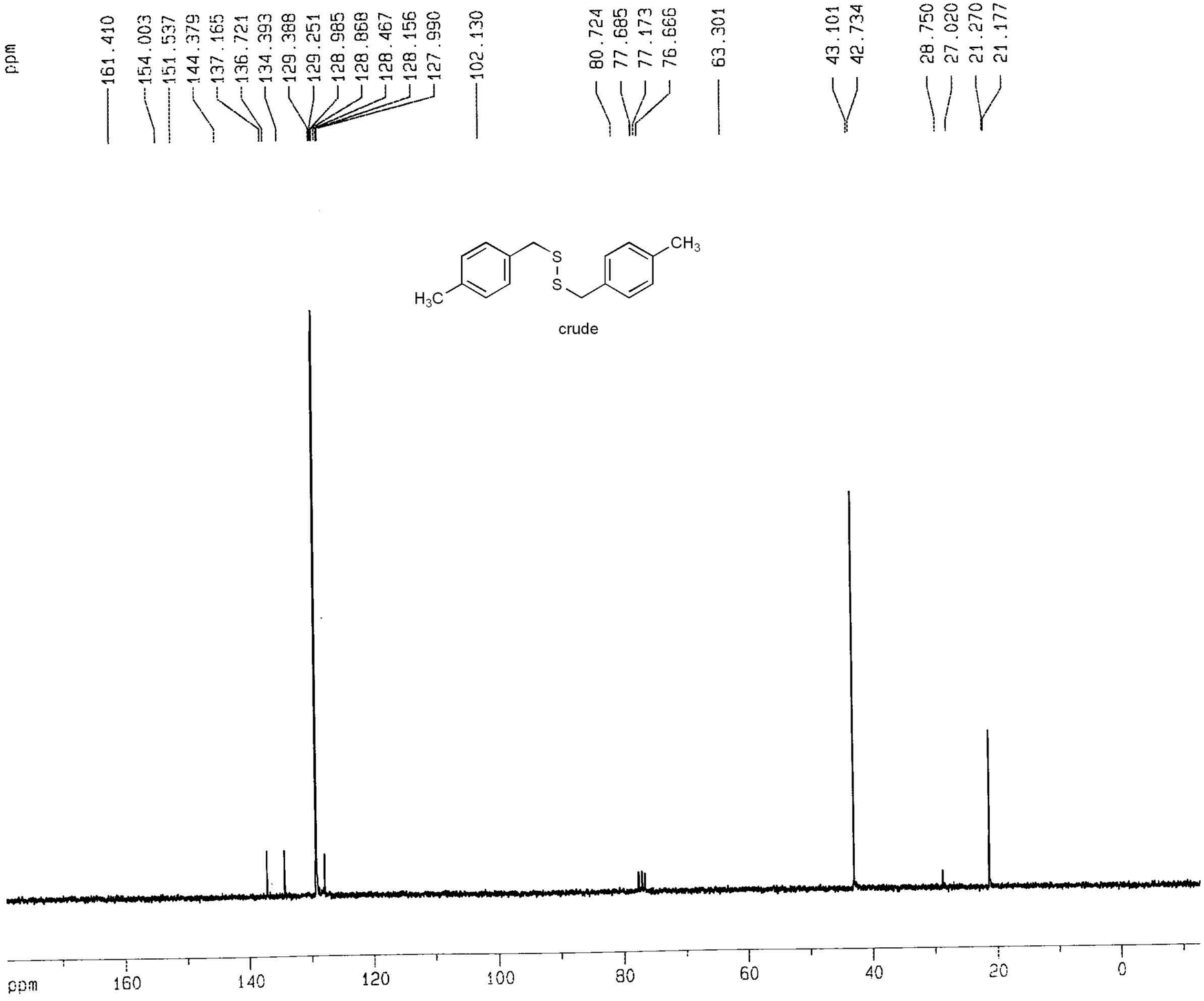

S
S

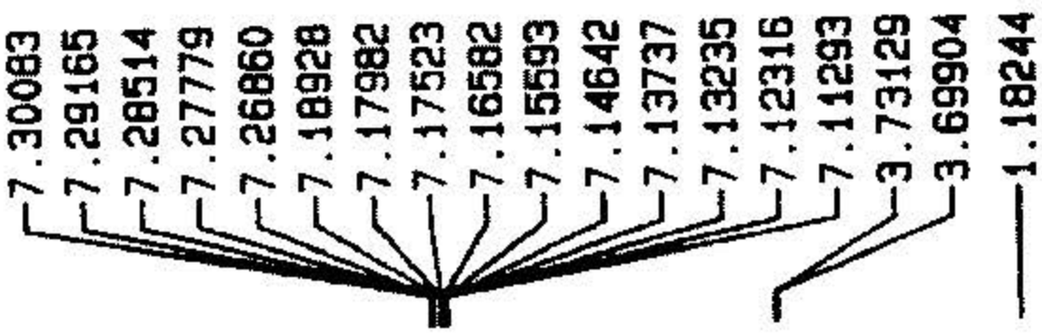
crude

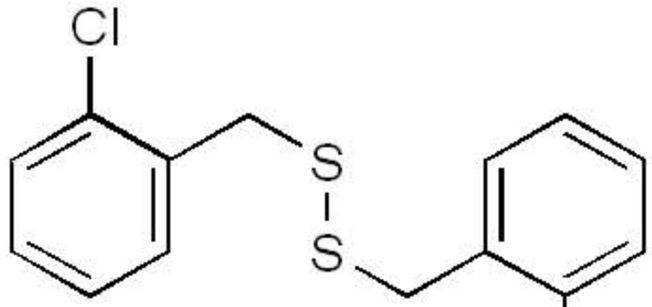

ppm
7.51139
7.38885
7.25373
7.22763
7.22070
7.19746
7.17257
7.14050
7.13414
7.12365
7.11006
7.10363
7.08868
7.07757
6.87404
6.83186
6.79248
6.76714
3.07791
3.06714
3.04787
3.01824
3.00434
2.98492
2.96996
2.91643
2.88151
2.86741
2.85295
2.84057
2.83533
2.82846
2.80613
2.76039
Integral
1.0000
0.7718
ppm 10
8
6
4
2
0


crude
ppm
140.092
139.870
139.662
128.753
128.690
128.593
126.988
126.635
126.560
126.485
77.665
77.157
76.649
40.963
40.787
40.526
40.271
39.963
39.480
35.803
35.641
35.343
33.025
ppm
140
120
100
80
60
40
20
0

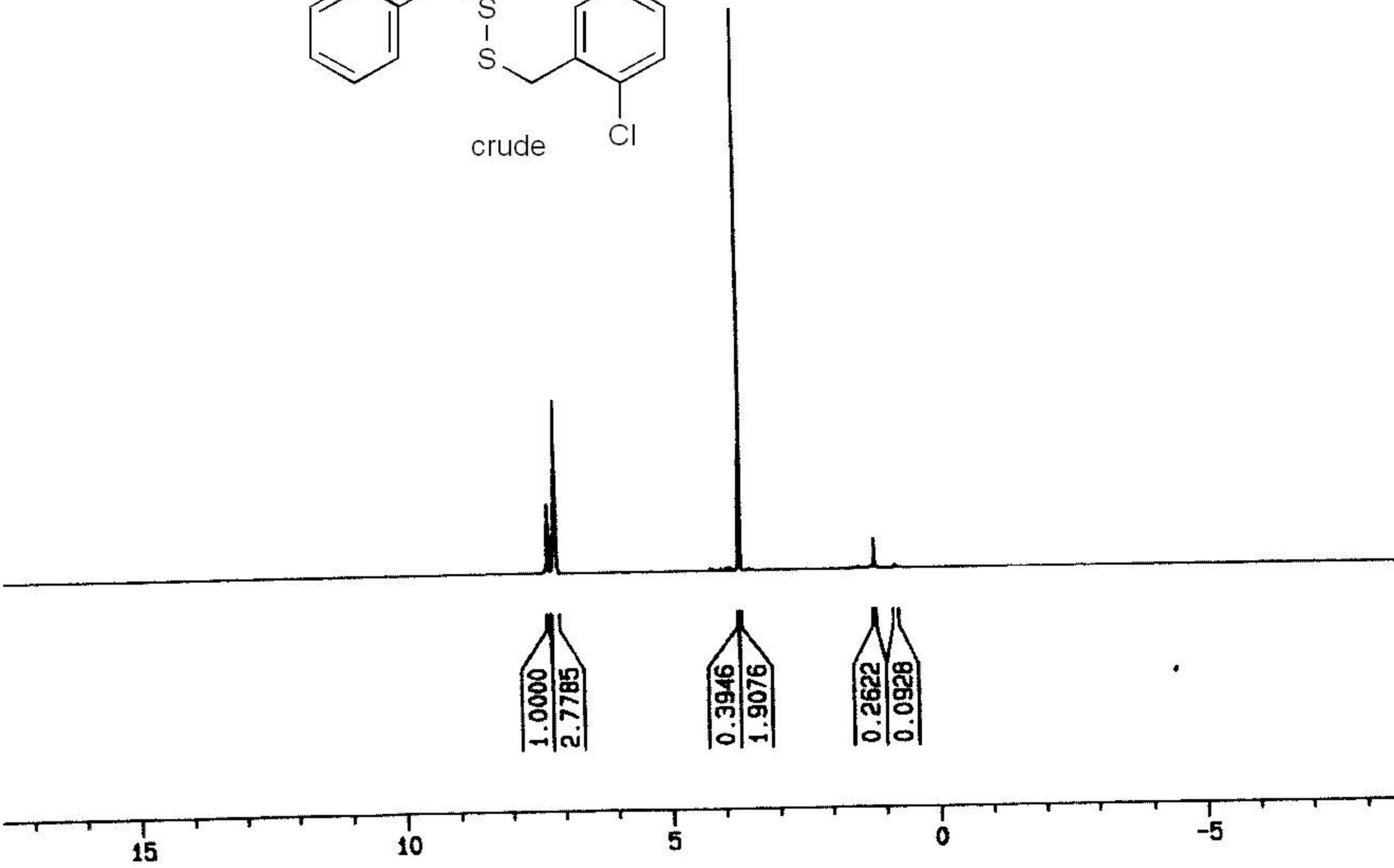

ppm
7.35333
7.15673
7.05466
7.04836
6.74930
3.92949
3.80170
3.51974
3.23409
2.50382
2.25295
2.08445
1.99891
1.46850
1.18225
0.80930
H_3C
S
S
CH_3
crude
Integral
1.0000
0.7013
0.9478
0.0391
0.0783
0.0367
ppm
10
8
6
4
2
0

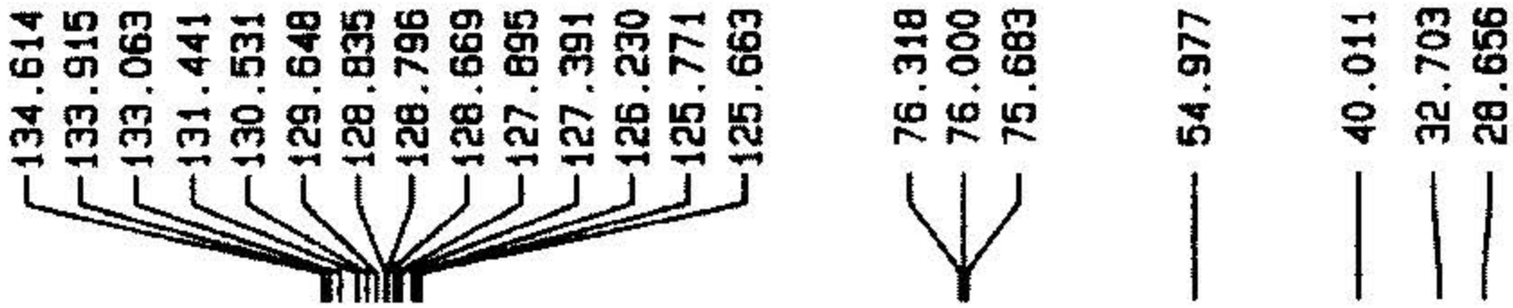

ppm
161.410
154.003
151.537
144.379
137.165
136.721
134.393
129.388
129.251
128.985
128.868
128.467
128.156
127.990
102.130
80.724
77.685
77.173
76.666
63.301
43.101
42.734
28.750
27.020
21.270
21.177
H_3C
S
S
CH_3
crude
ppm
160
140
120
100
80
60
40
20
0

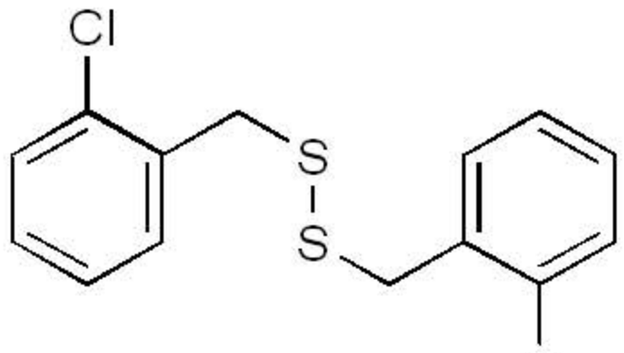

7.30083
7.29165
7.28514
7.27779
7.26860
7.18928
7.17982
7.17523
7.16582
7.15593
7.14642
7.13737
7.13235
7.12316
7.11293
3.73129
3.69904
1.18244


Cl
S
S
Cl

crude

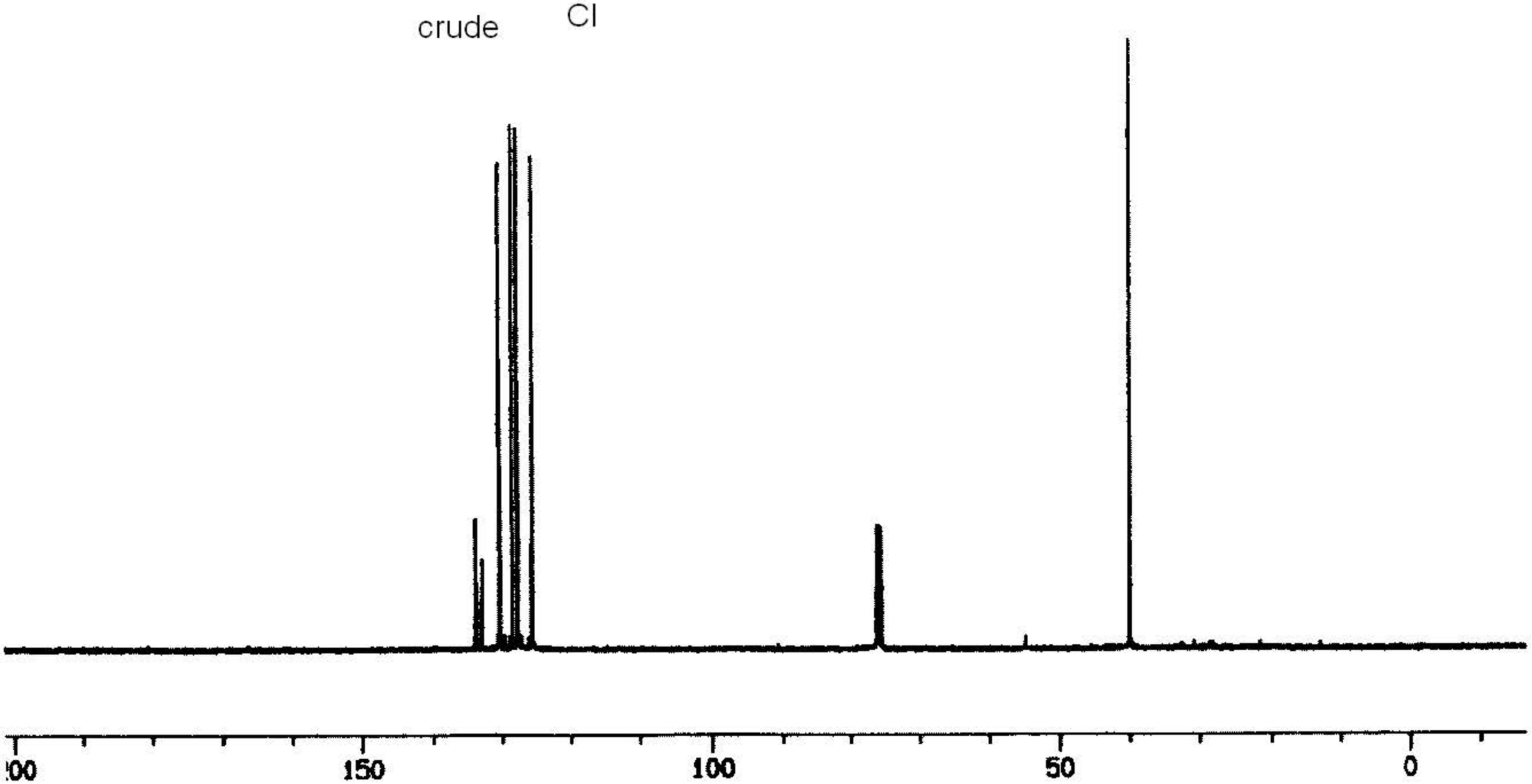

1.0000
2.7785
0.3946
1.9076
0.2622
0.0928
15
10
5
0
-5


134.614
133.915
133.063
131.441
130.531
129.648
128.835
128.796
128.669
127.895
127.391
126.230
125.771
125.663
76.318
76.000
75.683
54.977
40.011
32.703
28.656


Cl
S
S

crude

Cl

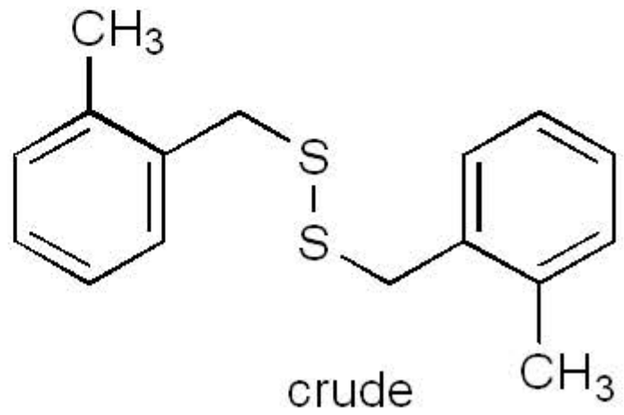

200
150
100
50
0

701 CDC13

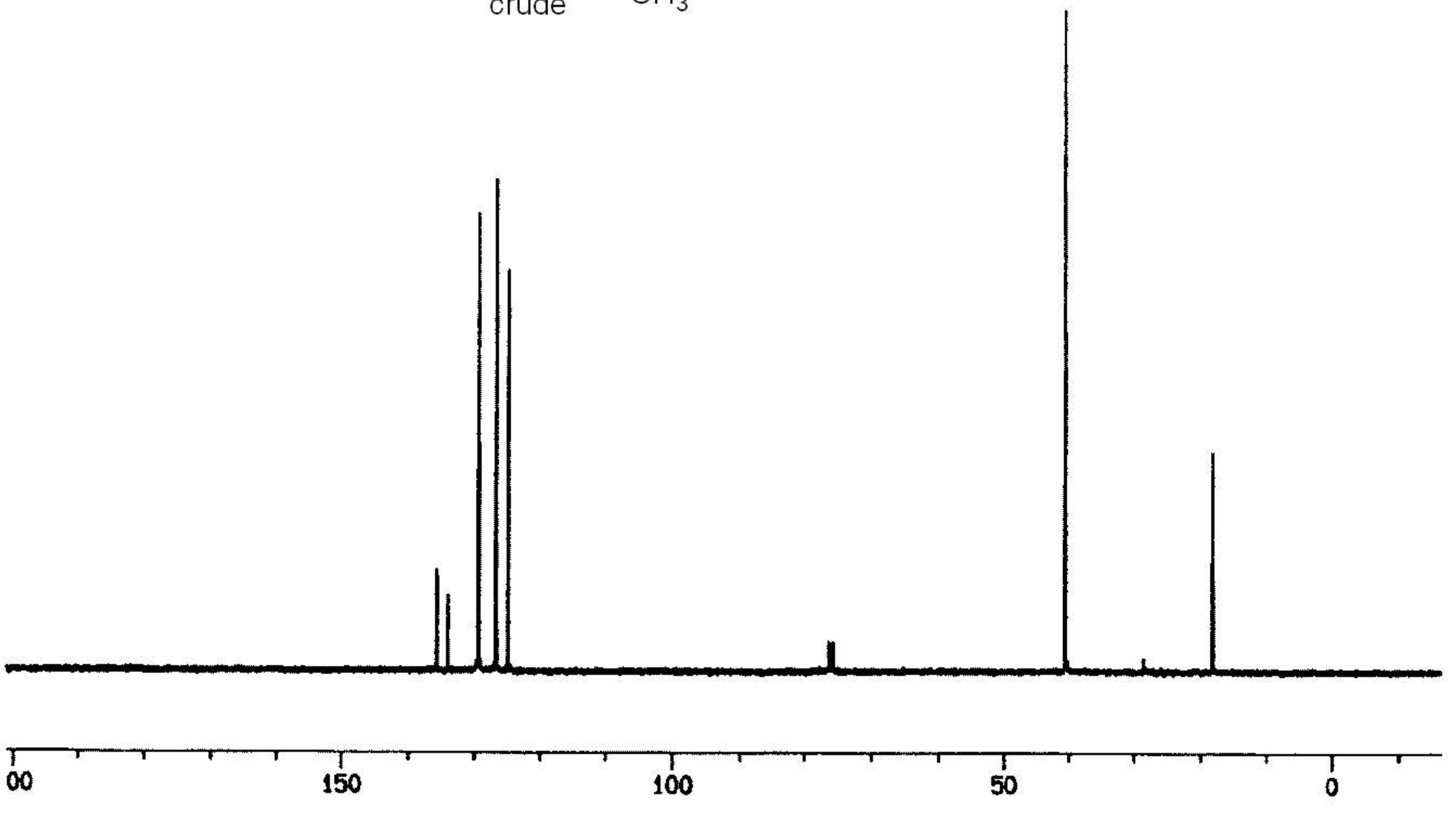
135.760
133.998
129.490
129.450
126.730
124.859

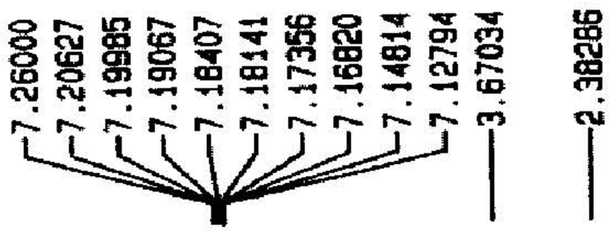
76.320
76.000
75.686

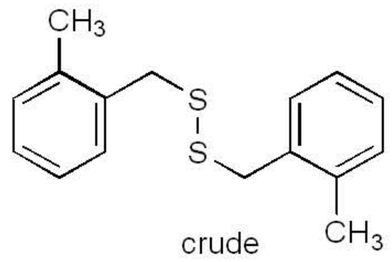
40.544
28.666
18.249



crude

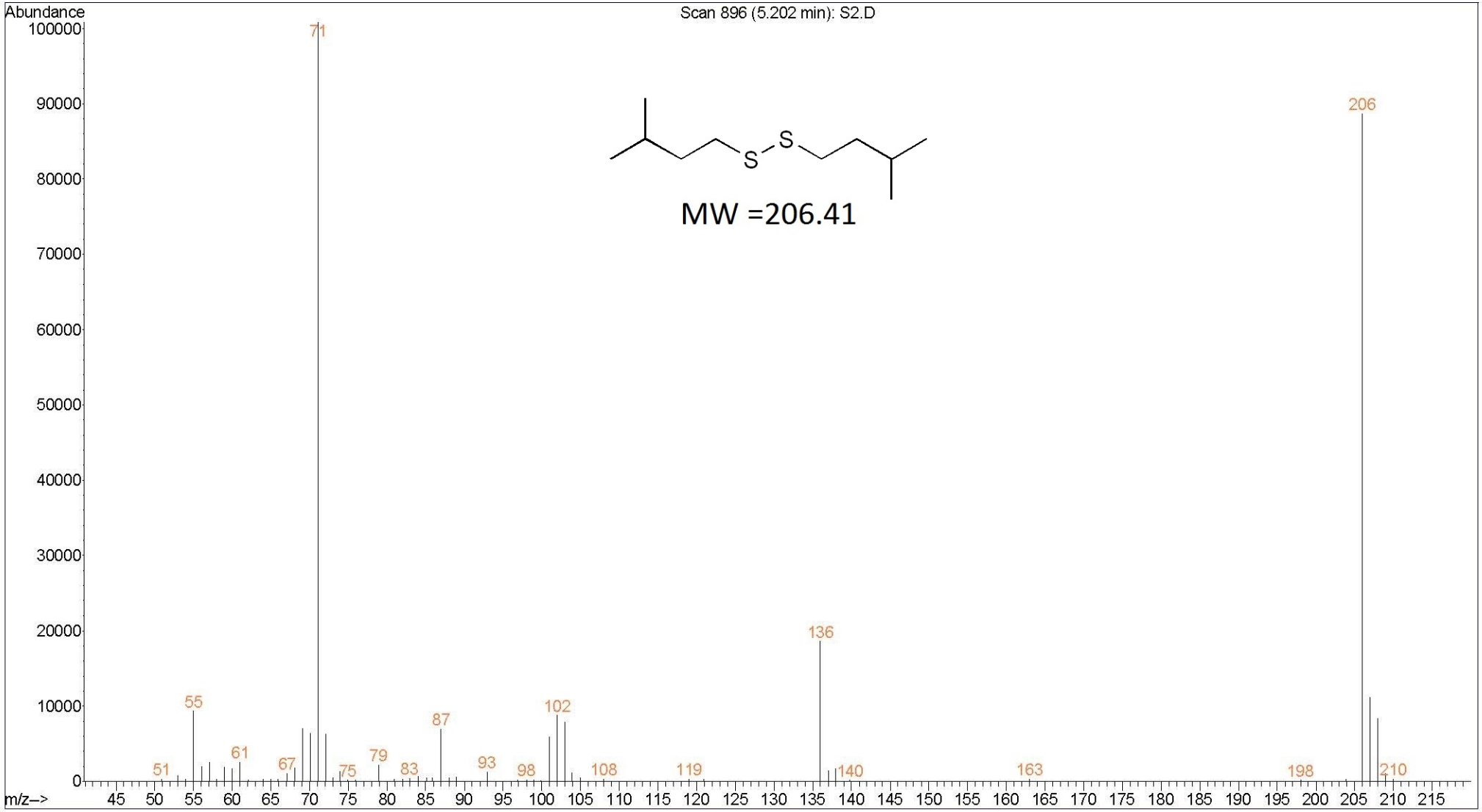


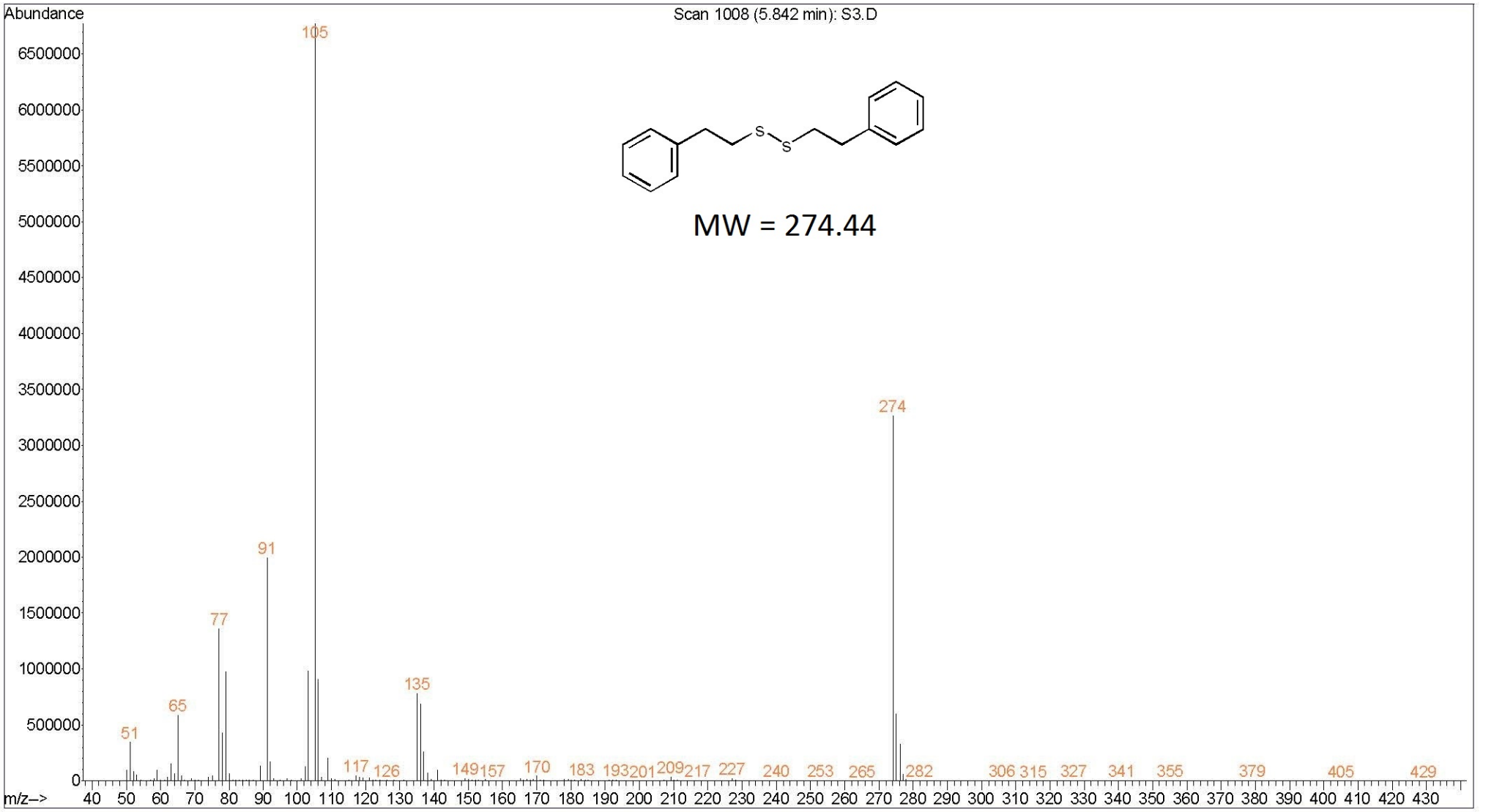

7.26000
7.20627
7.19985
7.19067
7.18407
7.18141
7.17356
7.16820
7.14814
7.12794
3.67034
2.38286

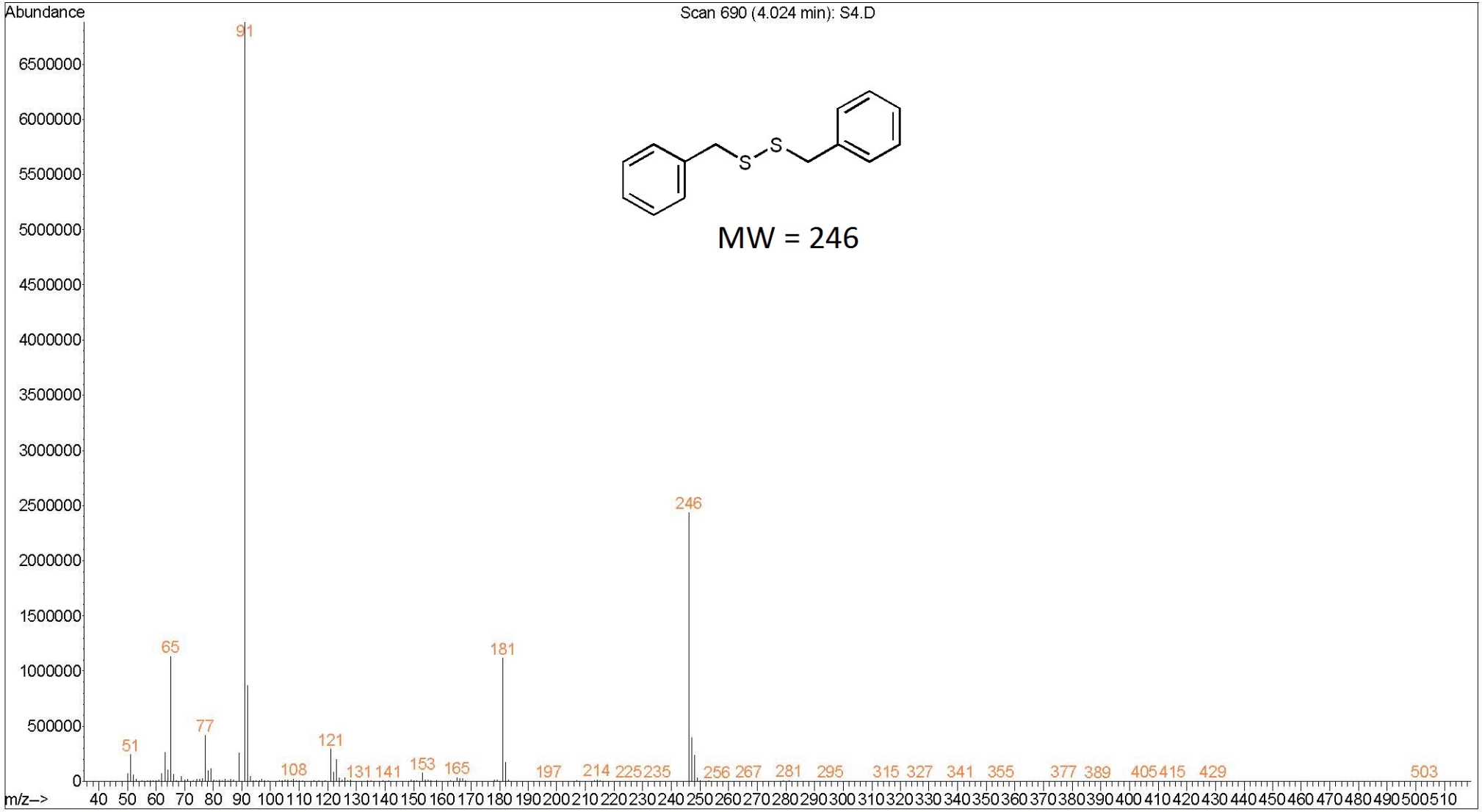

CH3
S
S
CH3

crude

5.1775
3.0000
4.1528
15
10
5
0
-5


Abundance
Scan 896 (5.202 min): S2.D
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
m/z-->
71
206
136
55
102
87
61
79
51
67
75
83
93
98
108
119
140
163
198
210
S
S
MW =206.41


Abundance
Scan 1008 (5.842 min): S3.D
105
274
91
77
135
65
51
117
126
149
157
170
183
193
201
209
217
227
240
253
265
282
306
315
327
341
355
379
405
429
m/z-->
S
S
MW = 274.44


Abundance
Scan 690 (4.024 min): S4.D
91
246
65
181
77
121
51
108
131 141
153
165
197
214 225 235
256 267
281
295
315 327
341
355
377 389
405 415
429
503
m/z-->
MW = 246