Practical and Chemoselective Mo-Catalysed Sulfoxide Reduction Protocol using 3-Mercaptopropyl-functionalized Silica Gel (MPS)

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Electronic Supplementary Information

Index

General methods: All reactions were assembled under air atmosphere unless otherwise noted. Reaction temperatures of experiments conducted under conventional heating refer to bath temperatures. All common reagents and solvents were obtained from commercial suppliers and used without any further purification. Non commercially available sulfoxides were prepared by oxidizing the precursor sulfide with $NaIO_4$ (1 equiv) or with H_2O_2 according to established procedures.[1] Sulfides precursors of 1-(pent-4-enylsulfinyl)benzene and 1-(pent-4-ynylsulfinyl)benzene were synthesized from thiophenol and the corresponding alkyl bromide in the presence of a base. The Mo(VI) catalysts were prepared as previously reported.[2] As solid-supported reducing agent both commercial available Quadrasil® MP and synthesized MPS,[3] were

[1] W. L. Xu, Y. Z. Li, Q. S. Zhang and H. S. Zhu *Synthesis,* 2004, 227.

[2] F. J. Arnáiz, R. Aguado, M. R. Pedrosa and A. De Cian, *Inorg. Chim. Acta* 2003, **347**, 33.

[3] (a) R. Gupta, S. Paul and R. Gupta, *J. Mol. Catal. A: Chem.,* 2007, **266**, 50; (b) B. Karimi and M. Khalkhali, *J. Mol. Catal. A: Chem.,* 2007, **271**, 75; (c) P. Gupta, V. Kumar and S. Paul, *J. Braz. Chem. Soc.,* 2010, **21**, 349.

indistinctly employed. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator; the chromatograms were visualized under ultraviolet light and/or by staining with a Ce/Mo reagent and subsequent heating. NMR spectra were measured on Varian Mercury-Plus 300 MHz and Varian Inova-400 MHz spectrometers. GC-MS were recorded on an Agilent 6890N/5973 Network GC System, equipped with a HP-5MS column. Products were isolated in greater than 95% purity, as determined by ^{1}H NMR spectroscopy[4] and capillary gas chromatography (GC). The microwave heating was performed in a microwave reactor (CEM Discover S-Class) with a single-mode microwave cavity producing continuous irradiation (Temperature measurements were conducted using an IR sensor located below the microwave cavity floor, and reaction times refer to the total hold time at the indicated temperature. The maximum wattage supplied was 300 W).

General procedures for the reduction of sulfoxides:

Method A: A mixture of the silica gel-supported reagent (Quadrasil® MP or synthesized MPS) (458 mg, 0.55 mmol), the appropriate sulfoxide (0.5 mmol) and $MoO_2Cl_2(dmf)_2$ (3.5 mg, 2.0 mol%) in toluene (1 mL) was irradiated in a sealed tube in the microwave cavity at 140 °C for 10 min. Then, the reaction mixture was cooled to room temperature and the silica gel was removed by filtration and washed with Et_2O (2 x 5 mL). The solvents of the filtrate were removed under reduced pressure to yield the corresponding sulfide in pure form in the yields reported in Table 2.

Method B: A mixture of the silica gel-supported reagent (Quadrasil® MP or synthesized MPS) (458 mg, 0.55 mmol), the appropriate sulfoxide (0.5 mmol) and $MoO_2Cl_2(dmf)_2$ (3.5 mg, 2.0 mol%) in toluene (1 mL) was heated for 1 h. Then, the reaction mixture was cooled to room temperature and the silica gel was removed by filtration and washed with Et_2O (2 x 5 mL). The solvents of the filtrate were removed under reduced pressure to yield the corresponding sulfide in pure form in the yields reported in Table 2 (entries 3, 5, 7).

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[4] Spectroscopical data of the synthesized sulfides were identical to those previously reported: N. García, P. García-García, M. A. Fernández-Rodríguez, R. Rubio, M. R. Pedrosa, F. J. Arnáiz and R. Sanz, *Adv. Synth. Catal.,* 2012, **354**, 321–327.
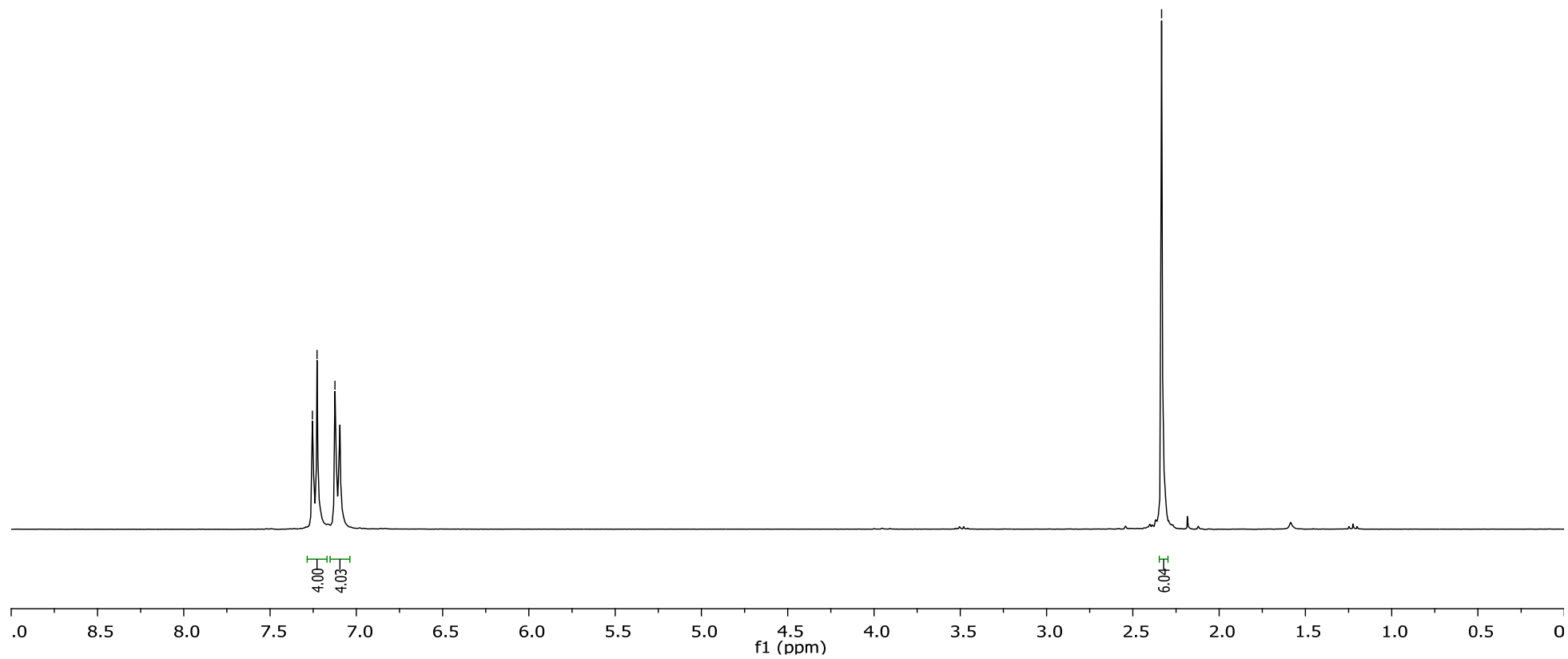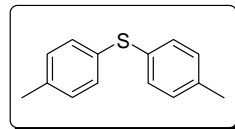
NMR spectra of products in Table 2 after filtration
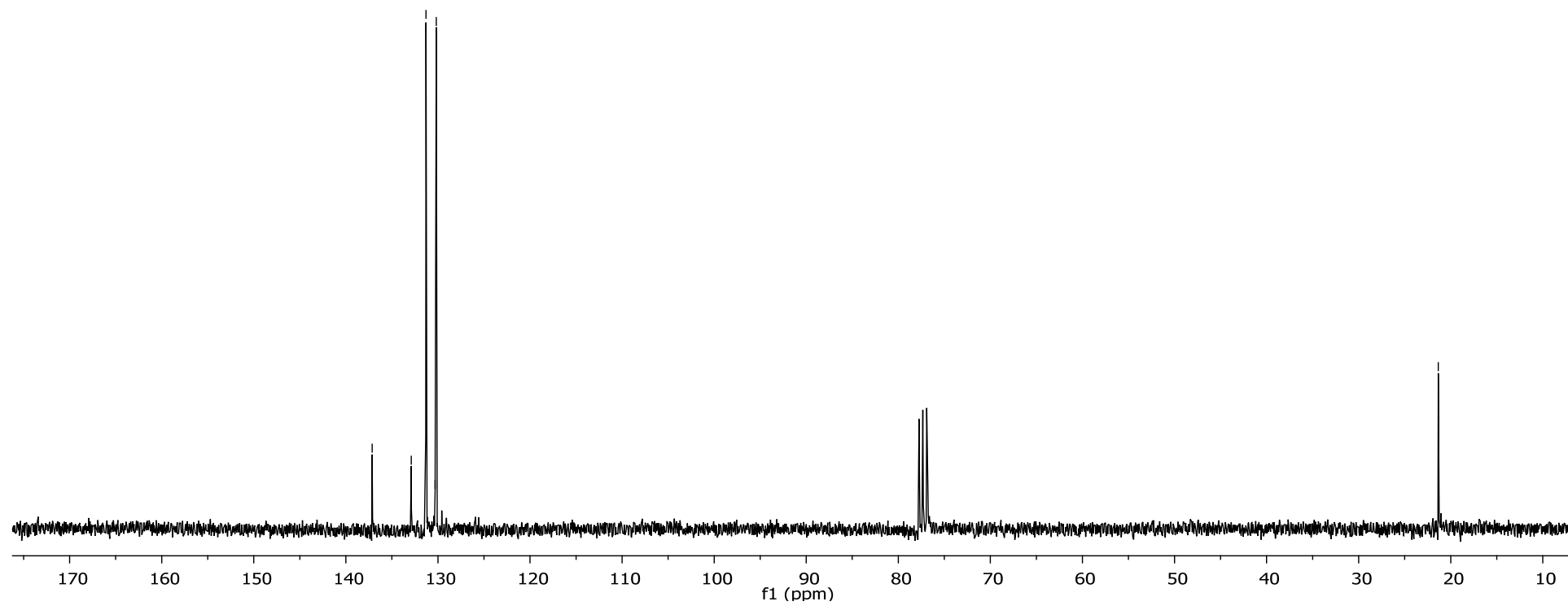
Table 2, Entry 1

^{1}H-NMR (CDCl$_3$, 300 MHz)

4.00
4.03

6.04

.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
f1 (ppm)

137.14
132.90
131.30
130.30
130.18

21.36

Table 2, Entry 1

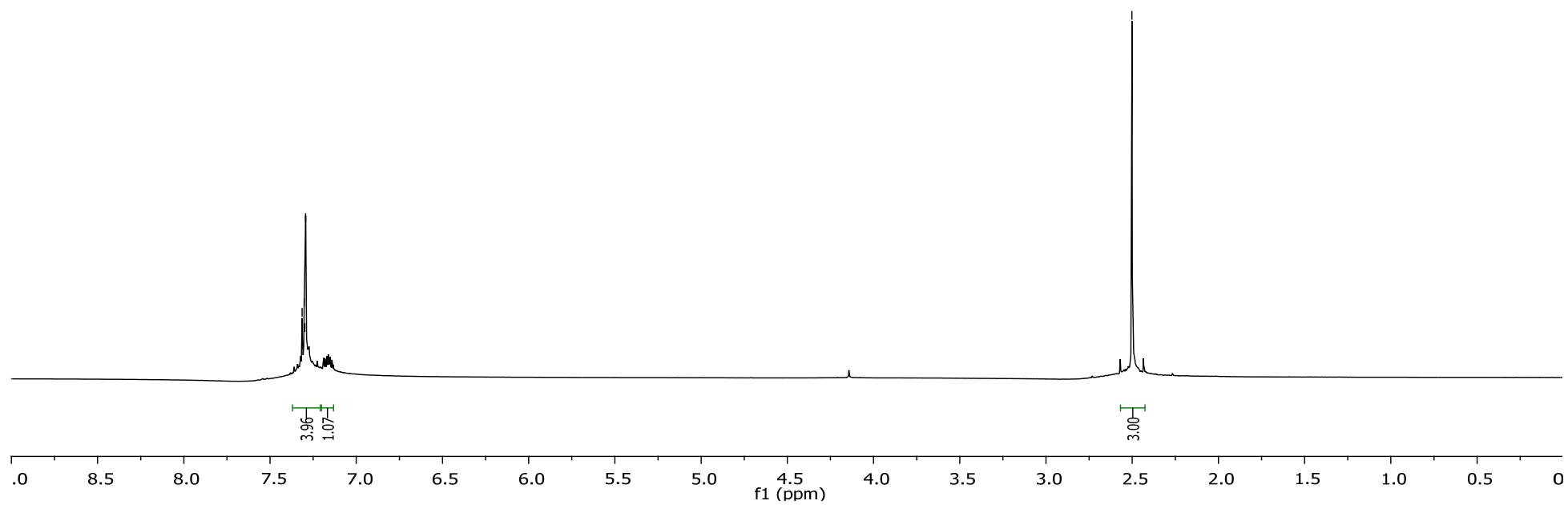^{13}C-NMR (CDCl$_3$, 75.4 MHz)

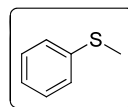170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10
f1 (ppm)
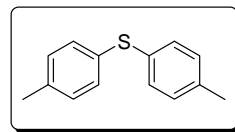
Table 2, Entry 2

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.25
7.23
7.12

2.33

4.00
4.03

6.04

.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
f1 (ppm)
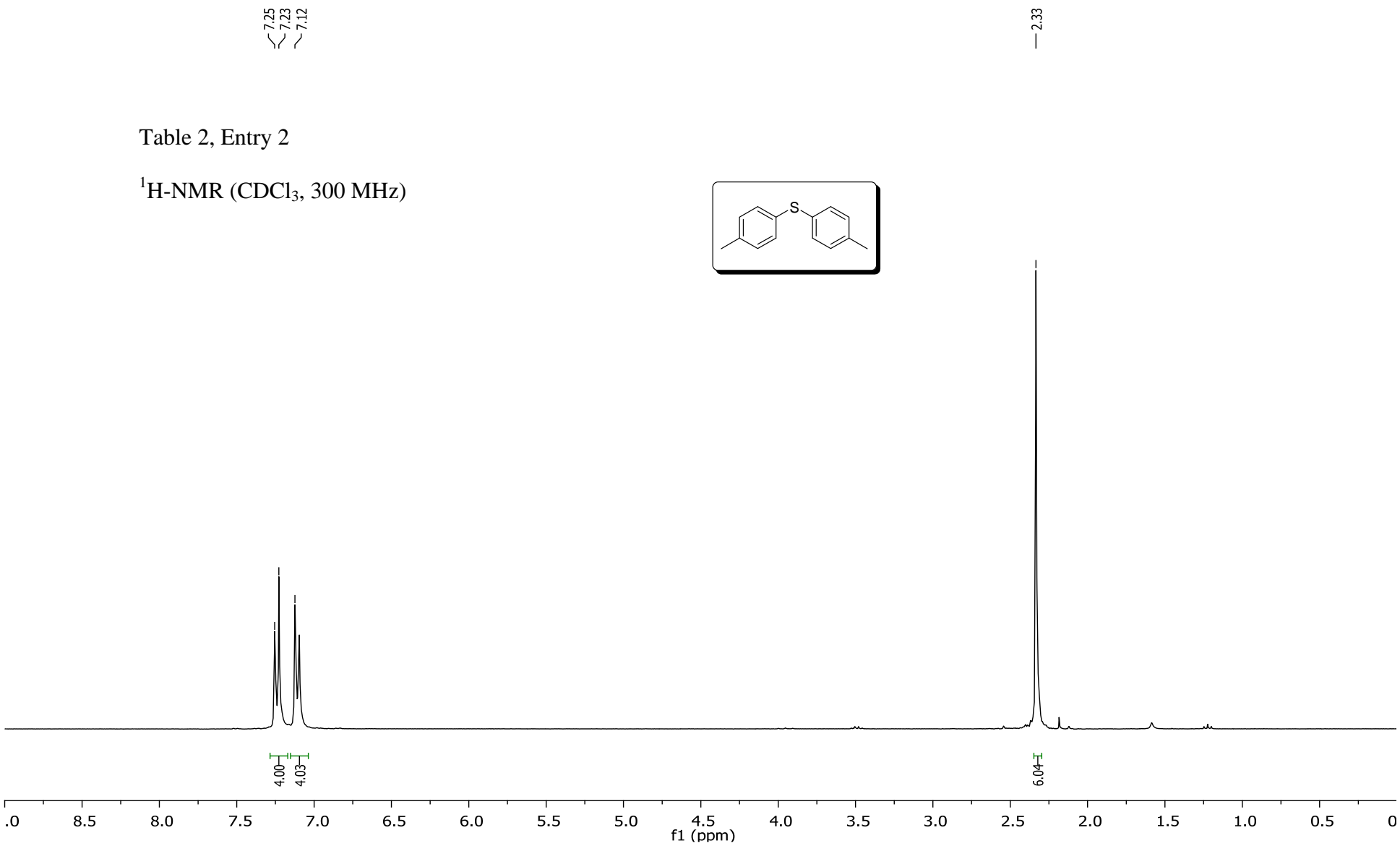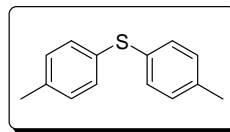
Table 2, Entry 3

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.25
7.22
7.12
7.09

2.33

4.05
4.00

6.05

.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
f1 (ppm)
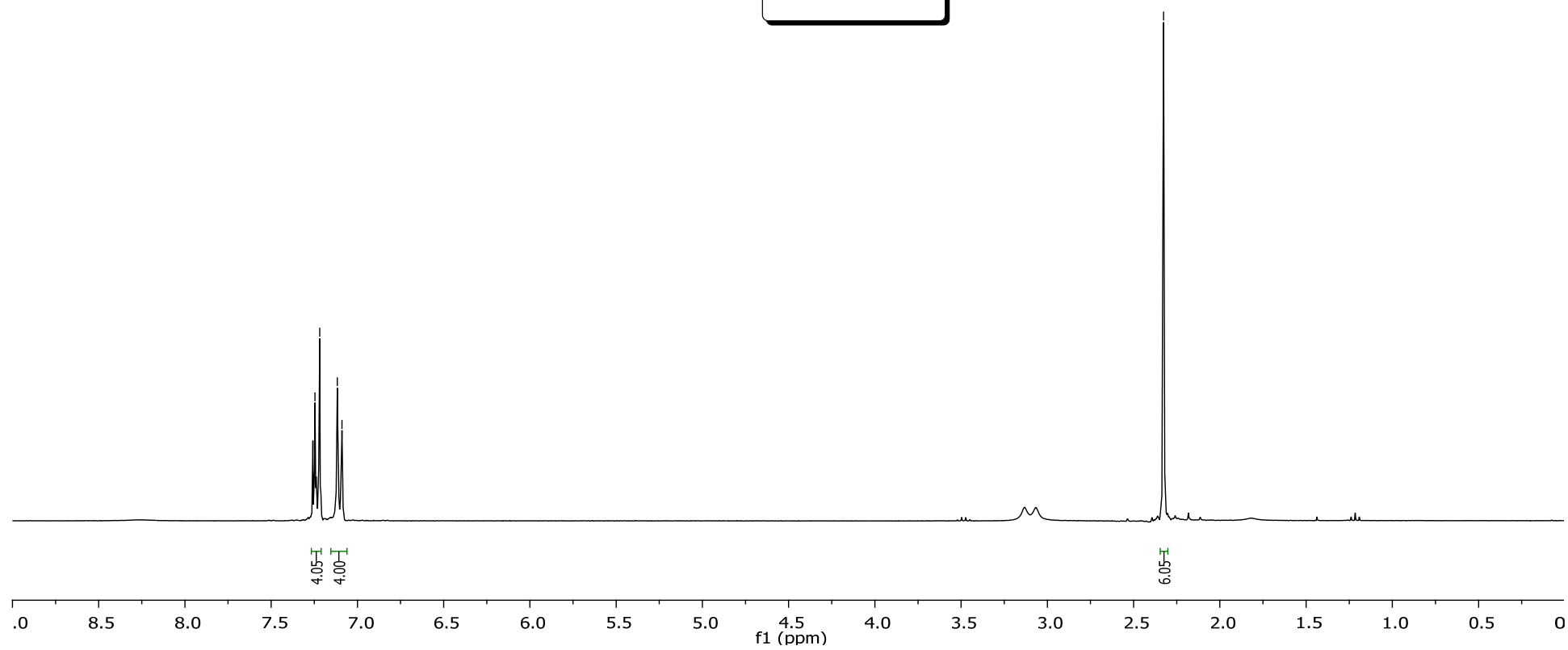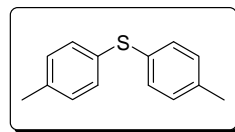
Table 2, Entry 4

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.46
7.46
7.46
7.39

10.00

f1 (ppm)

0.0 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

8
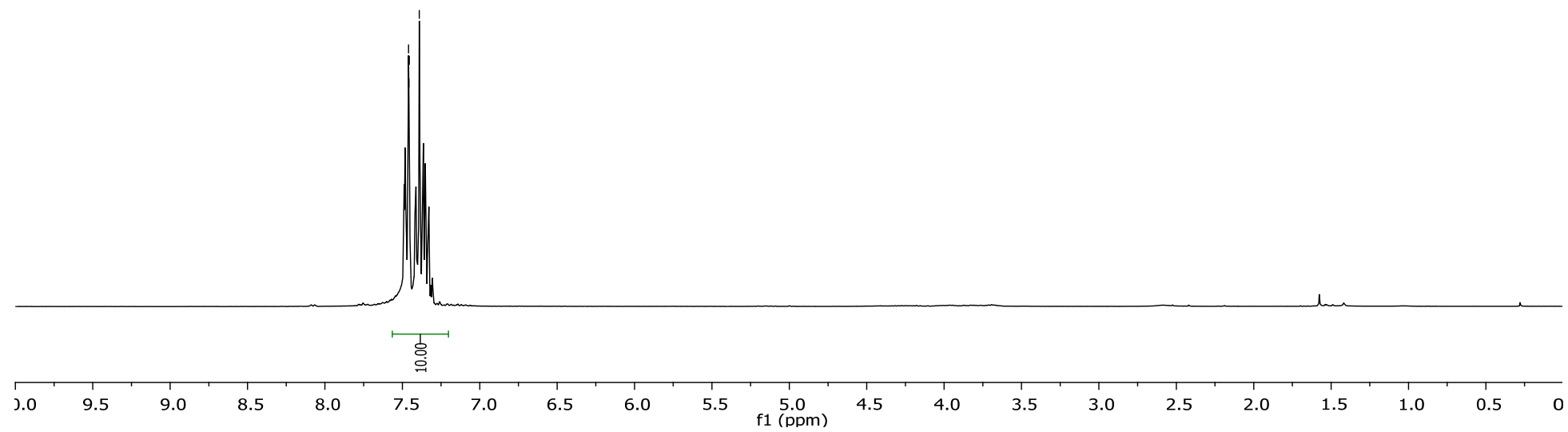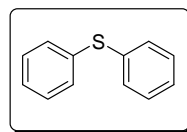
136.16
131.40
129.60
127.43

Table 2, Entry 4

^{13}C-NMR (CDCl$_3$, 75.4 MHz)

f1 (ppm)
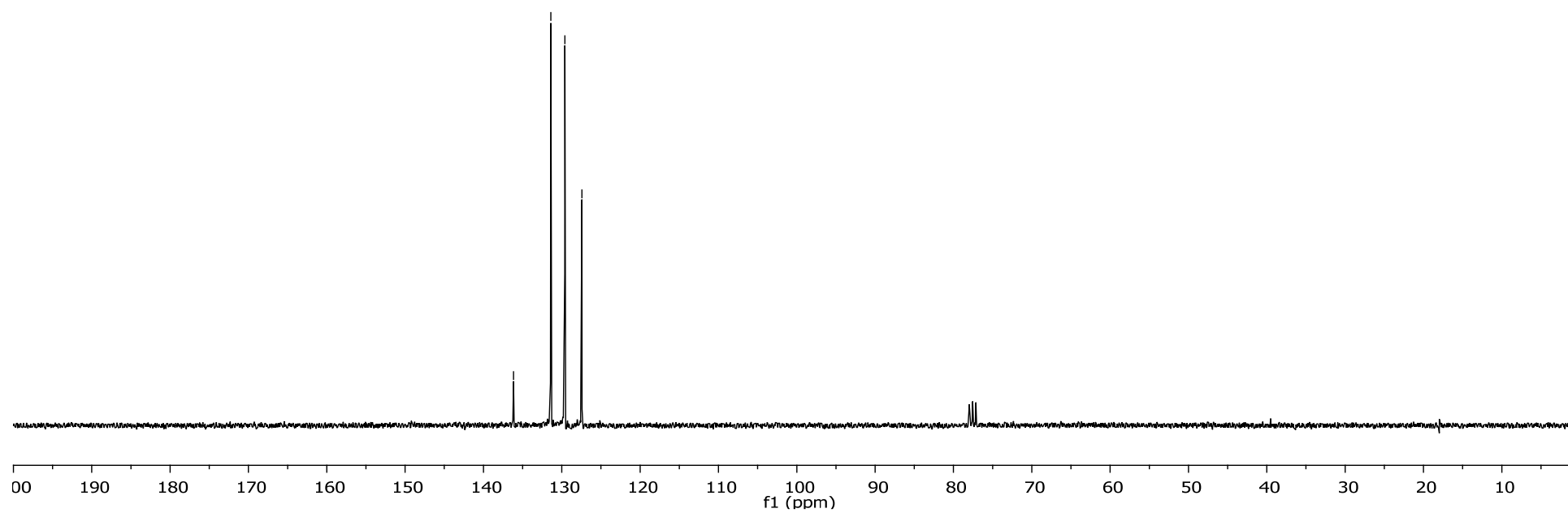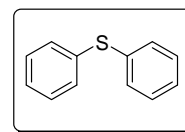
7.42
7.41
7.39
7.39
7.38
7.37
7.37
7.36
7.34
7.32
7.32
7.31
7.30
7.30
7.30
7.28
7.26

Table 2, Entry 5

^{1}H-NMR (CDCl$_3$, 300 MHz)

10.00

.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
f1 (ppm)

Table 2, Entry 6
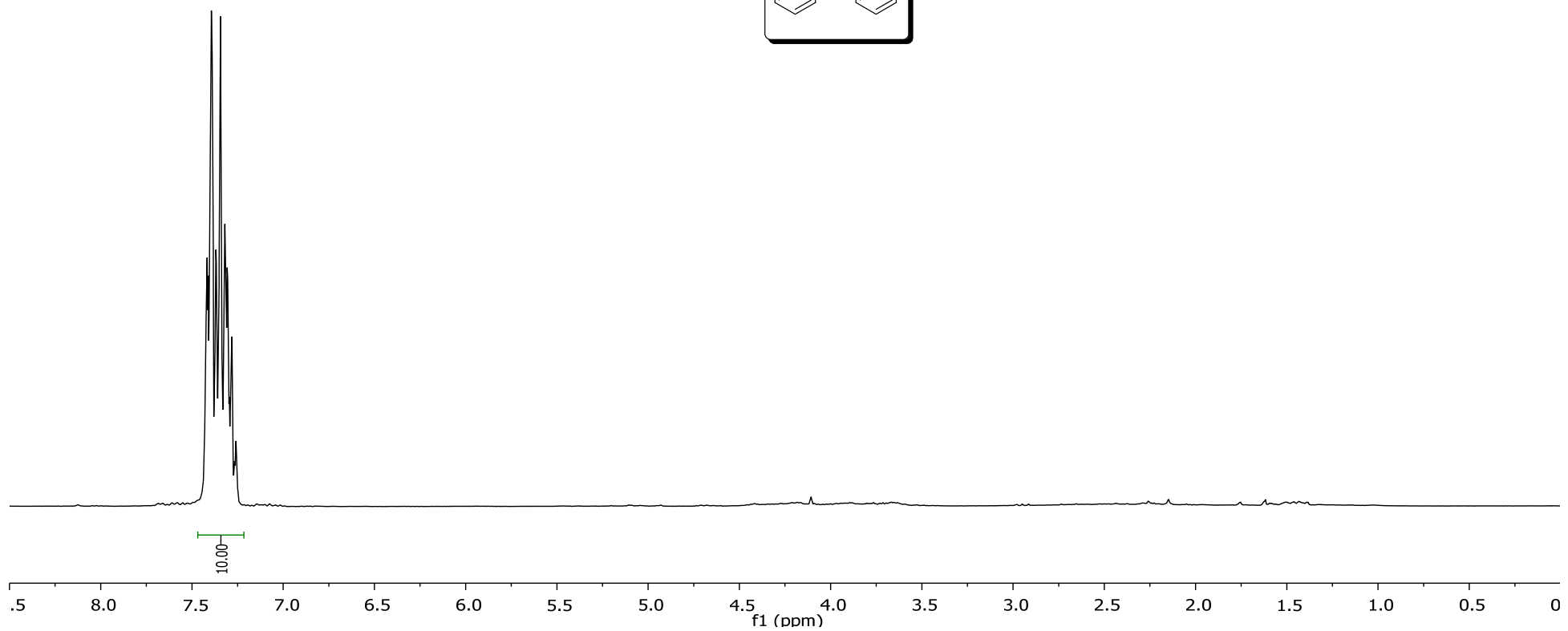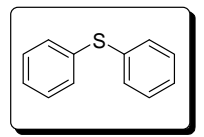
^{1}H-NMR (CDCl$_3$, 300 MHz)

7.29 7.19 7.18 7.17 7.16 7.16 7.16 7.15 7.14 7.13

2.50

4.07 1.00

3.05

f1 (ppm)
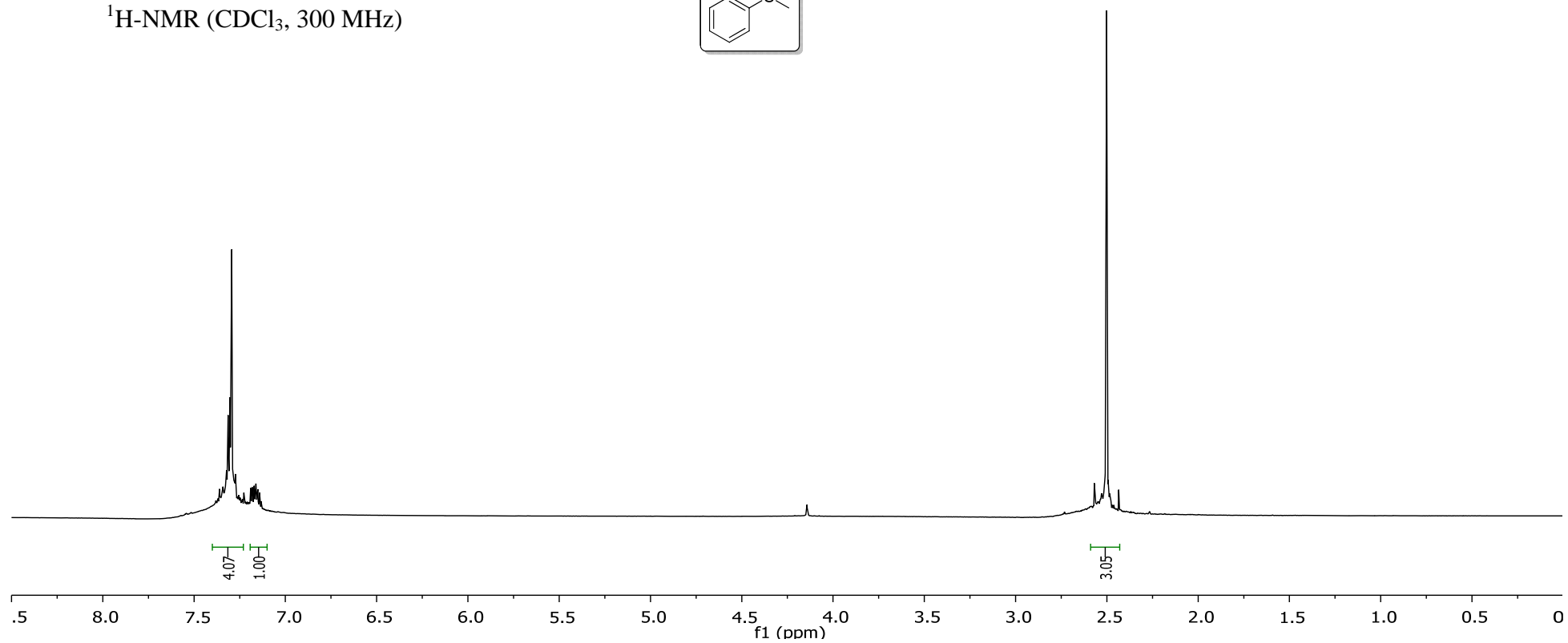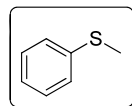
7.31
7.30
7.30
7.29

2.50

Table 2, Entry 7

^{1}H-NMR (CDCl$_3$, 300 MHz)

3.96
1.07

3.00

.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
                                              f1 (ppm)

Table 2, Entry 8

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.31
7.31
7.29

4.13

10.00

2.16
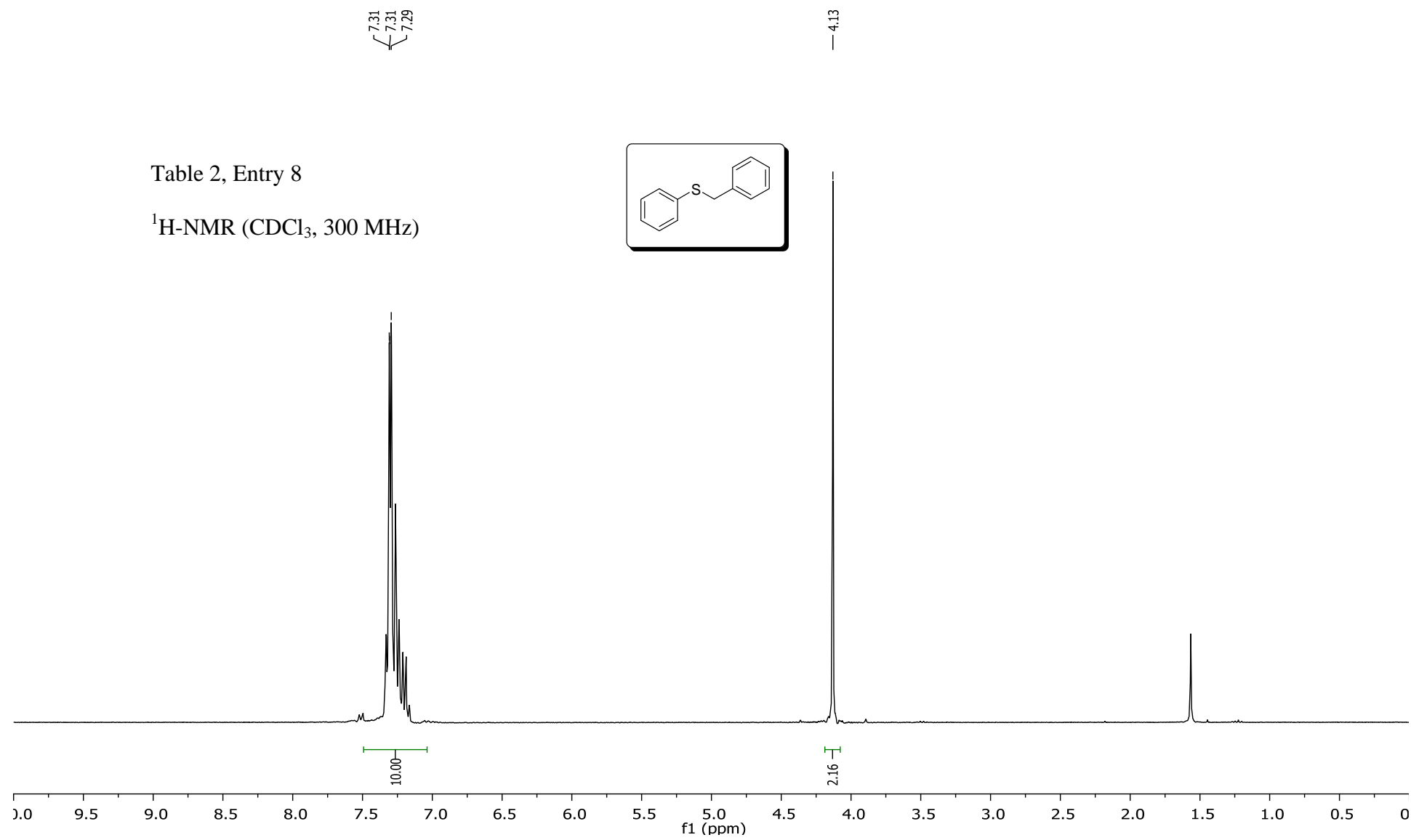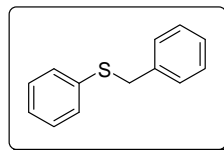
137.65
136.57
130.00
129.08
129.06
128.73
127.42
126.56

39.24

Table 2, Entry 8

^{13}C-NMR (CDCl$_3$, 75.4 MHz)

f1 (ppm)

14

Table 2, Entry 9
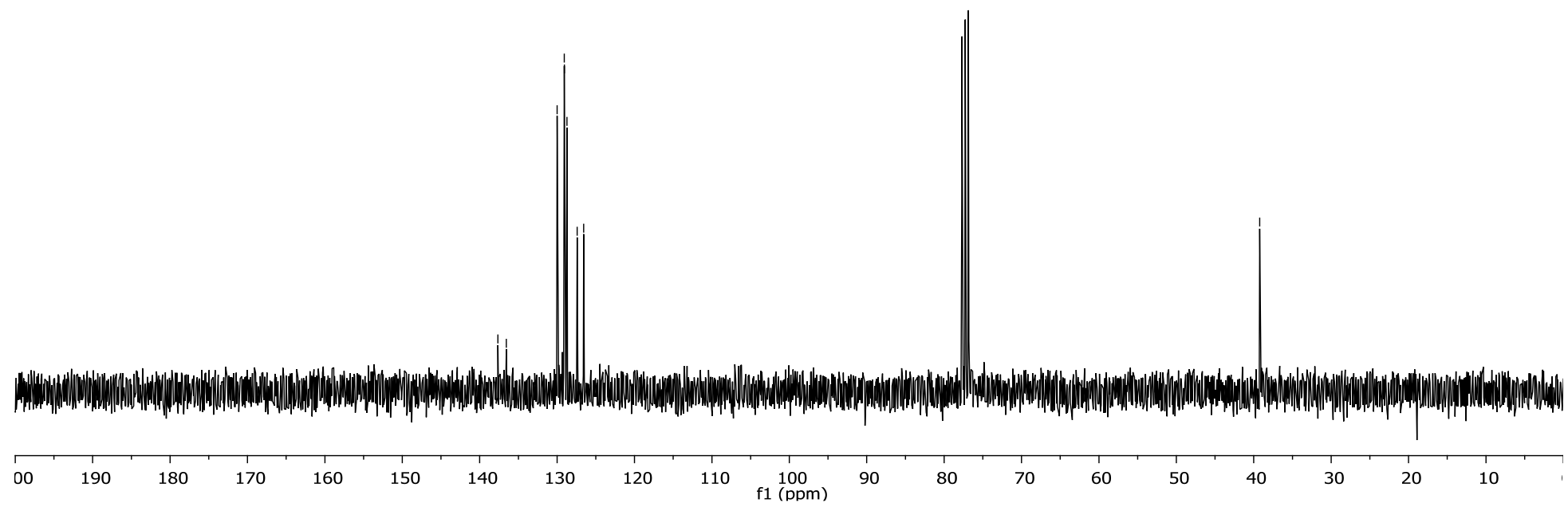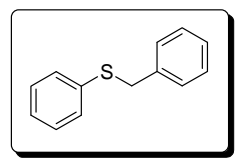
^{1}H-NMR (CDCl$_3$, 300 MHz)

7.38, 7.38, 7.37, 7.37, 7.30, 7.15

2.21, 2.20, 2.19, 2.18

1.08, 1.07

0.71, 0.70

3.96   0.91   1.00   2.12   2.12

Table 2, Entry 9

^{13}C-NMR (CDCl$_3$, 75.4 MHz)
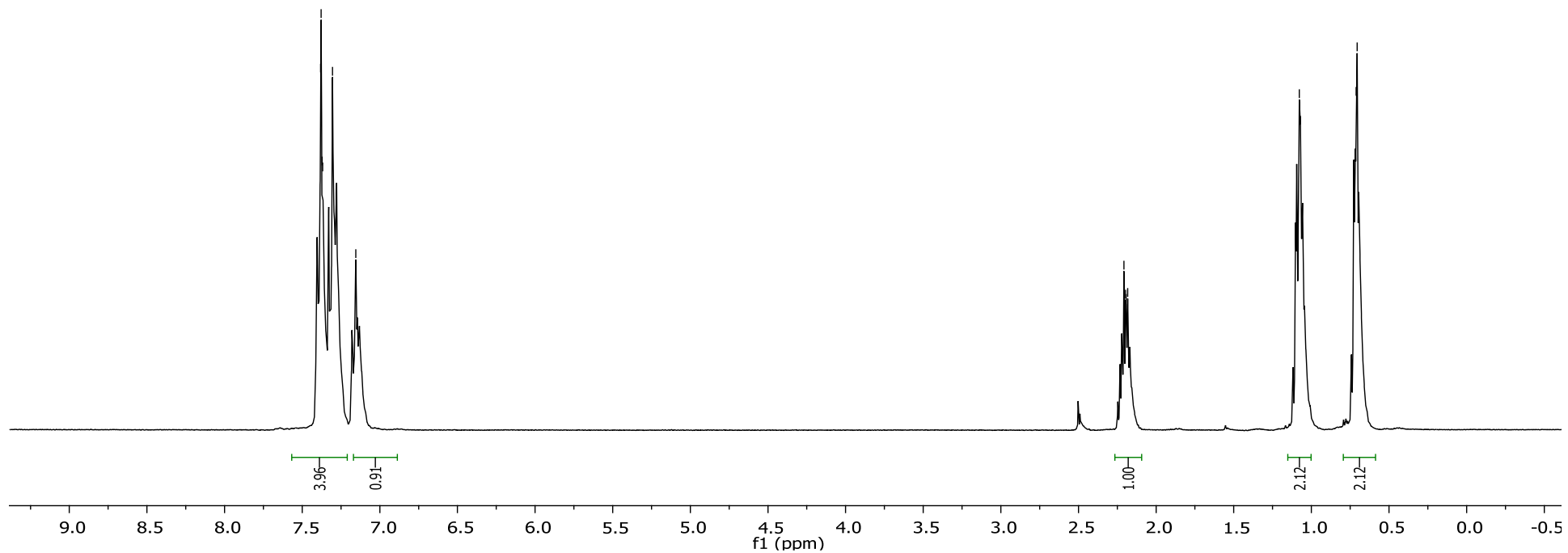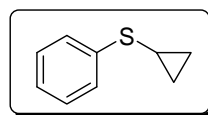
139.07
128.96
126.70
125.16
12.23
8.80

190   180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10   0
f1 (ppm)

16
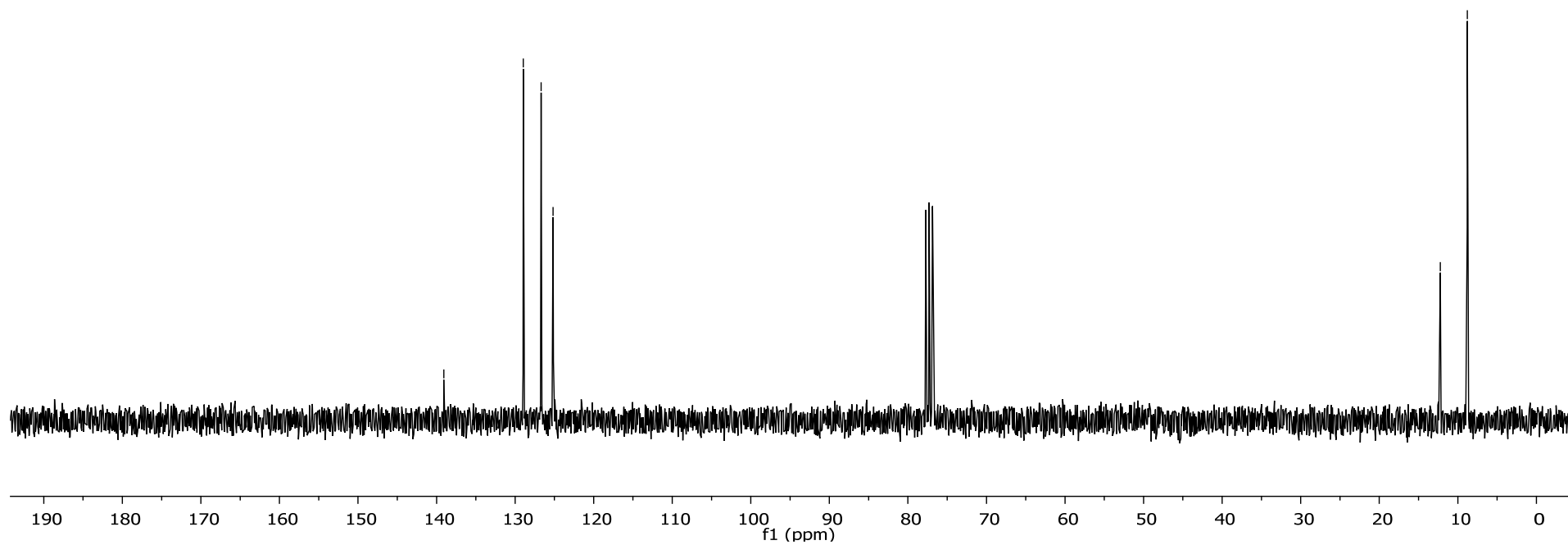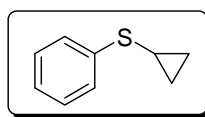
Table 2, Entry 10

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.53
7.52
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35

1.29

2.00
3.07

10.99

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
f1 (ppm)
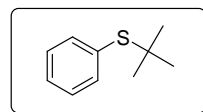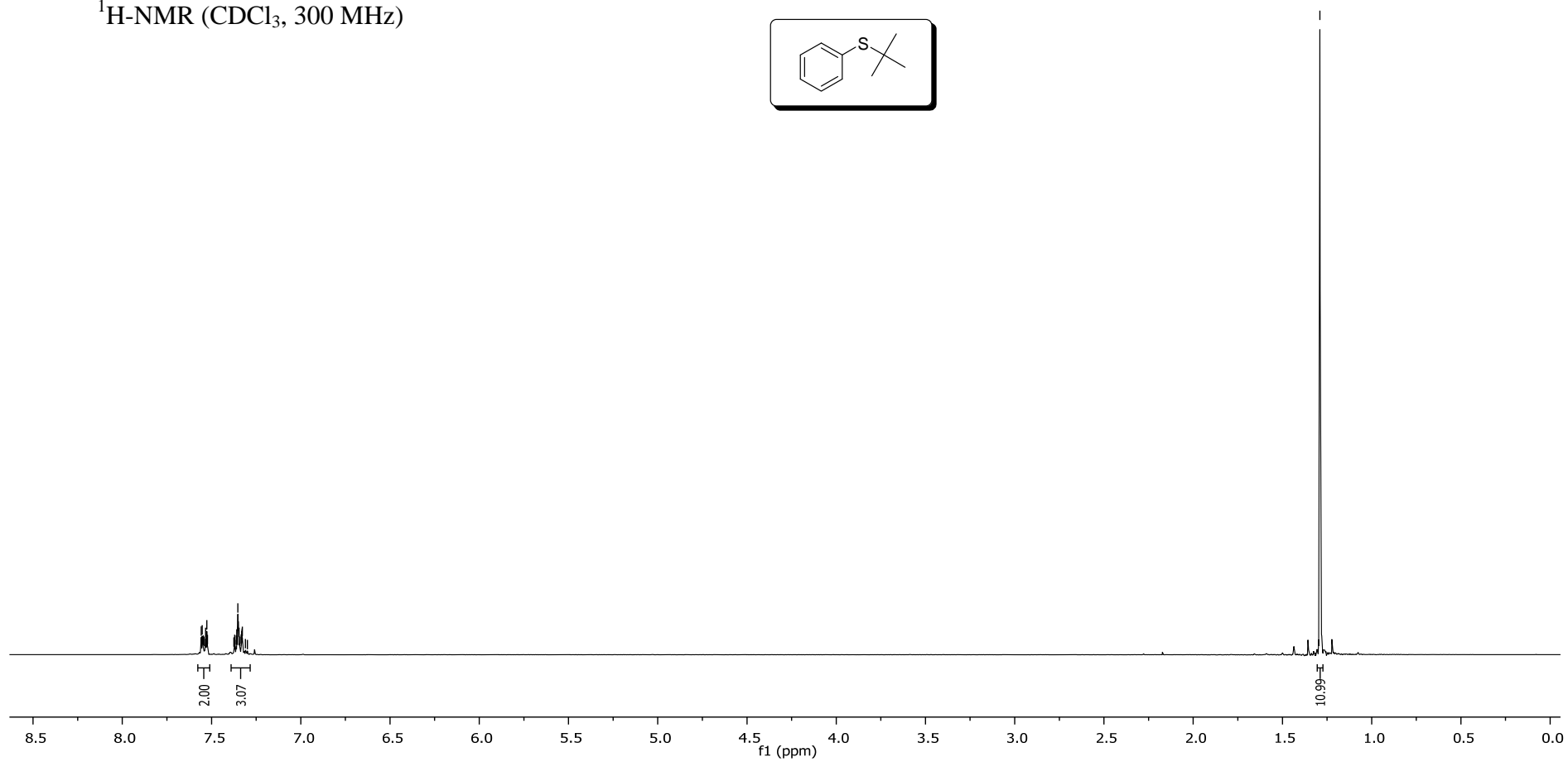
Table 2, Entry 11

^{1}H-NMR (CDCl$_3$, 300 MHz)

2.479
2.455
2.431

1.563
1.539
1.515
1.490
1.466
1.415
1.391
1.367
1.342
1.318
1.295

0.889
0.865
0.841

4.00

4.06
4.48

5.97

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
ppm
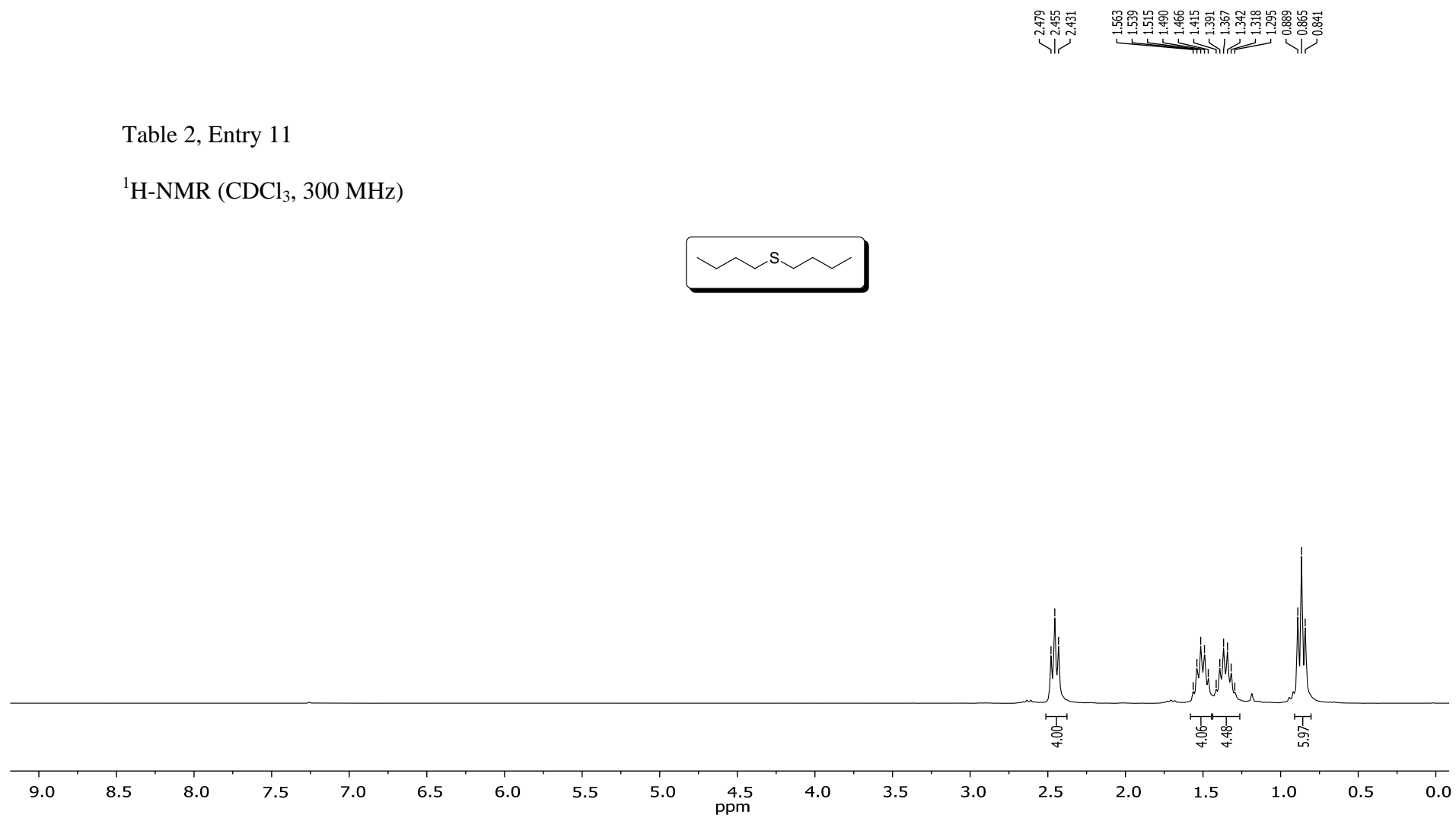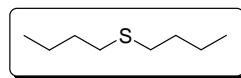
7.27
7.26

Table 2, Entry 12

^{1}H-NMR (CDCl$_3$, 300 MHz)

8.00

.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
f1 (ppm)
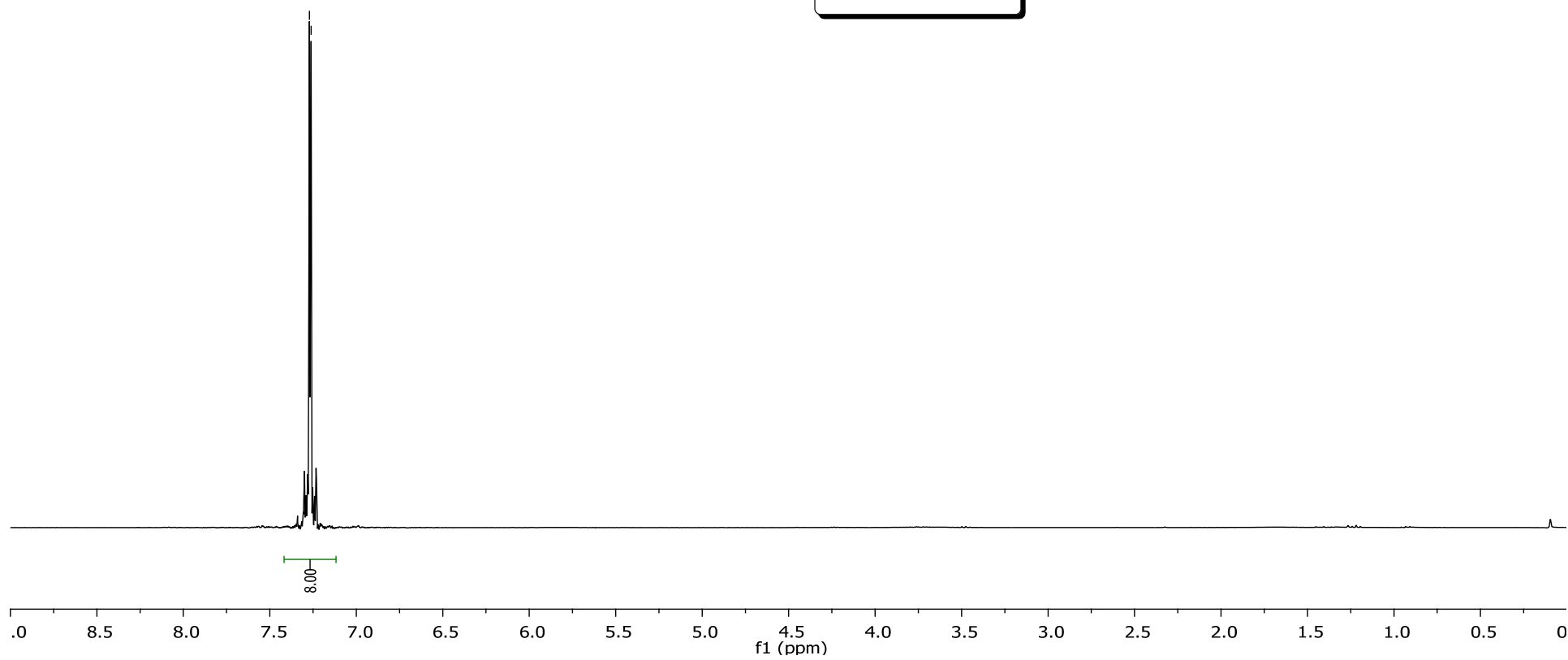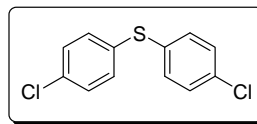
134.16
133.69
132.53
129.72

Table 2, Entry 12

^{13}C-NMR (CDCl$_3$, 75.4 MHz)

f1 (ppm)
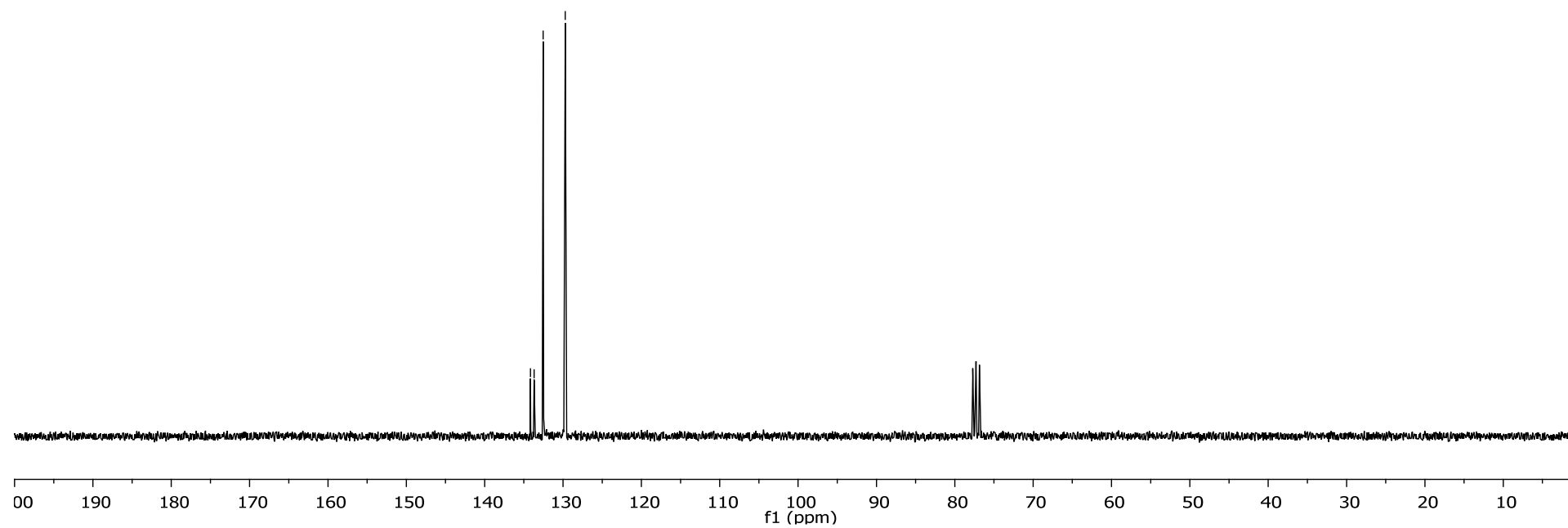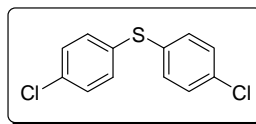
Table 2, Entry 13

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.39
7.36
7.11
7.08

2.45

2.00
2.06
3.70

Table 2, Entry 13
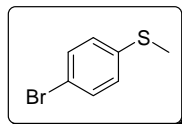
^{13}C-NMR (CDCl$_3$, 75.4 MHz)

137.91
132.99
132.00
128.26
123.01
118.79
16.12

Table 2, Entry 14
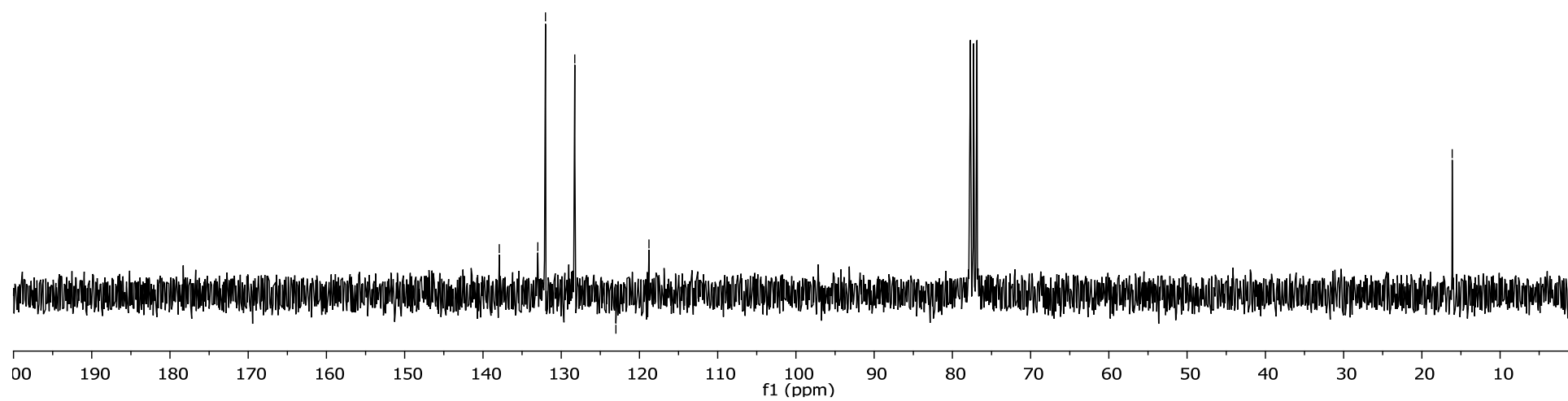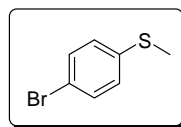
^{1}H-NMR (CDCl$_3$, 300 MHz)

7.50
7.33
7.23
7.13

5.83

5.02

2.96

2.20

1.76

5.26

1.00

2.05

2.44

2.09

2.28

f1 (ppm)
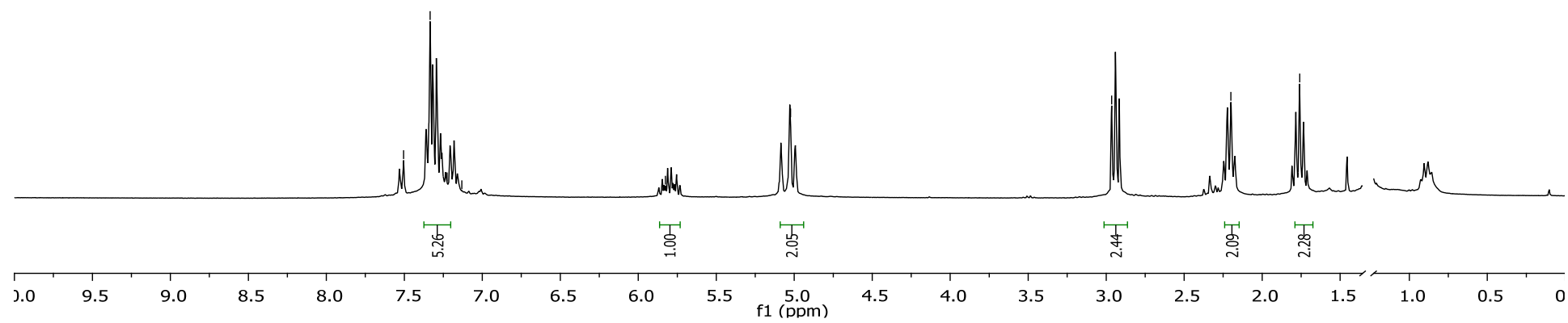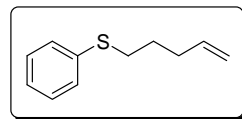
Table 2, Entry 15

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.34
7.29
7.26

3.04

2.36
2.35
2.33

1.85

1.21
1.21

4.98

2.07

2.00

1.35

1.89

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
f1 (ppm)
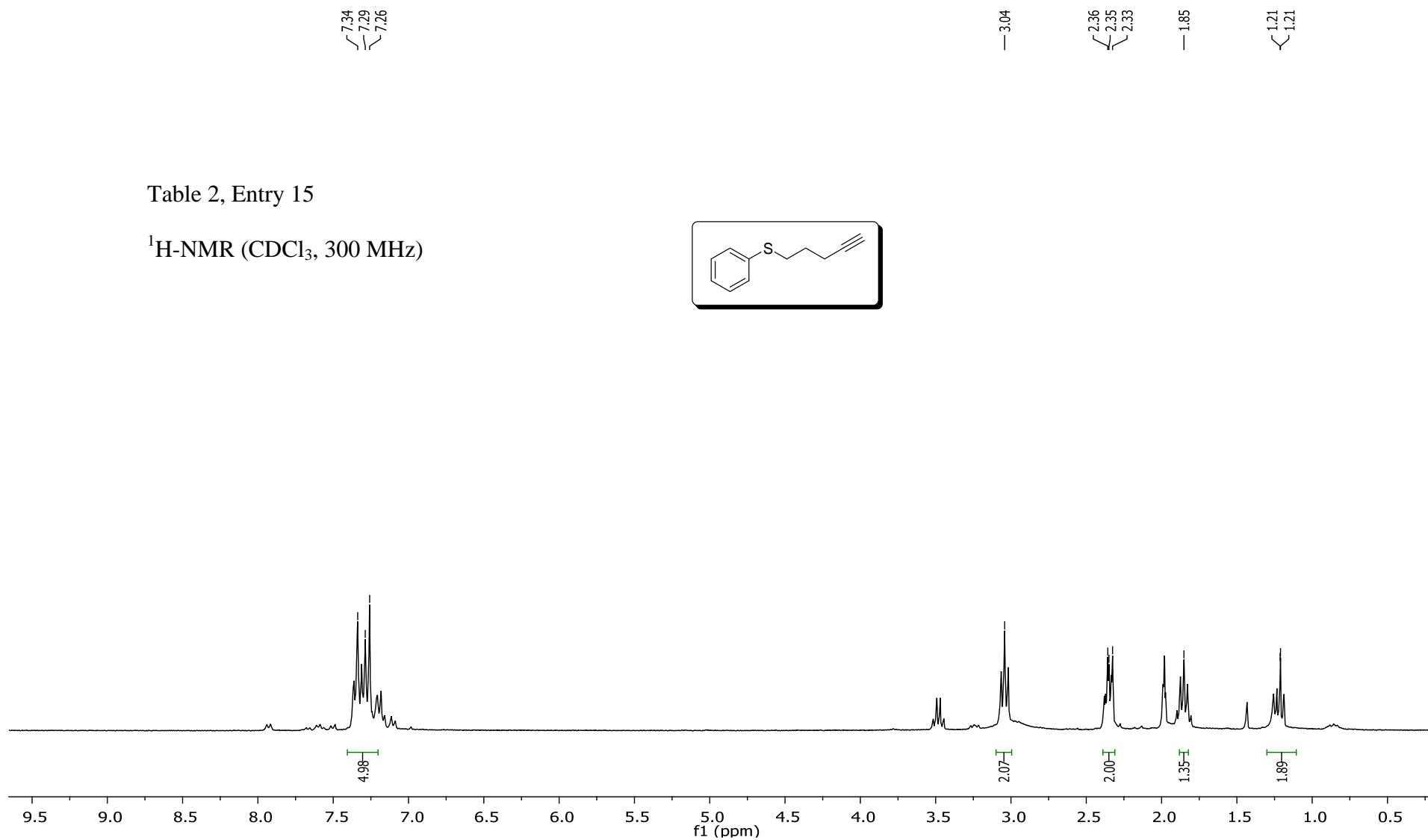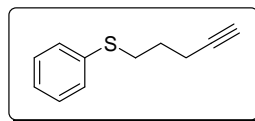
Table 2, Entry 16

^{1}H-NMR (CDCl$_3$, 300 MHz)

9.90

7.76
7.73

7.31
7.28

2.51

1.05 2.05 2.00 3.00

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
f1 (ppm)
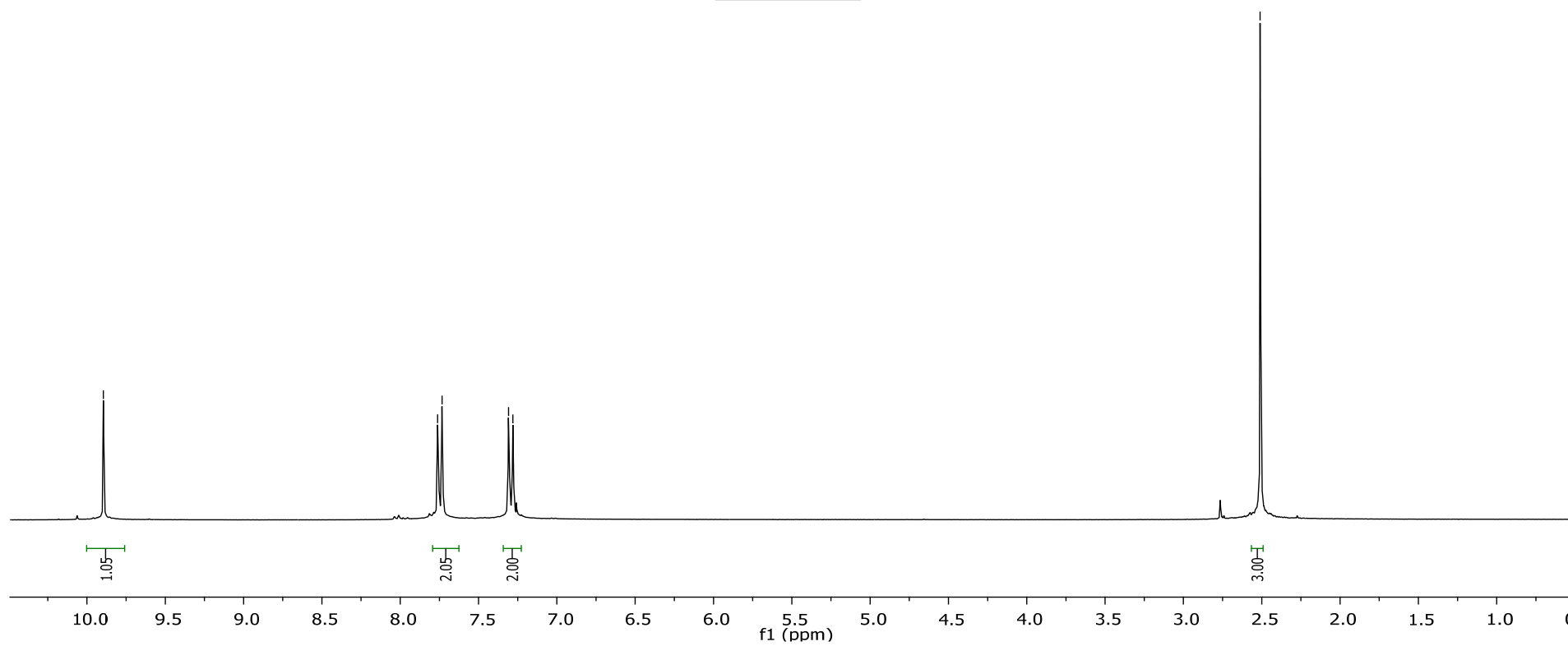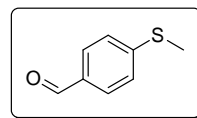
191.51

148.15

133.09
130.22
125.35

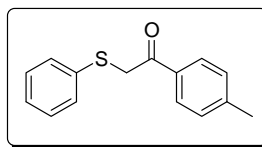14.89

Table 2, Entry 16

^{13}C-NMR (CDCl$_3$, 75.4 MHz)

190   180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10   0
f1 (ppm)

Table 2, Entry 17

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.87
7.84
7.28
7.28
7.26
4.27
4.26
2.43
2.42

1.86
1.92
4.03
2.01
3.00
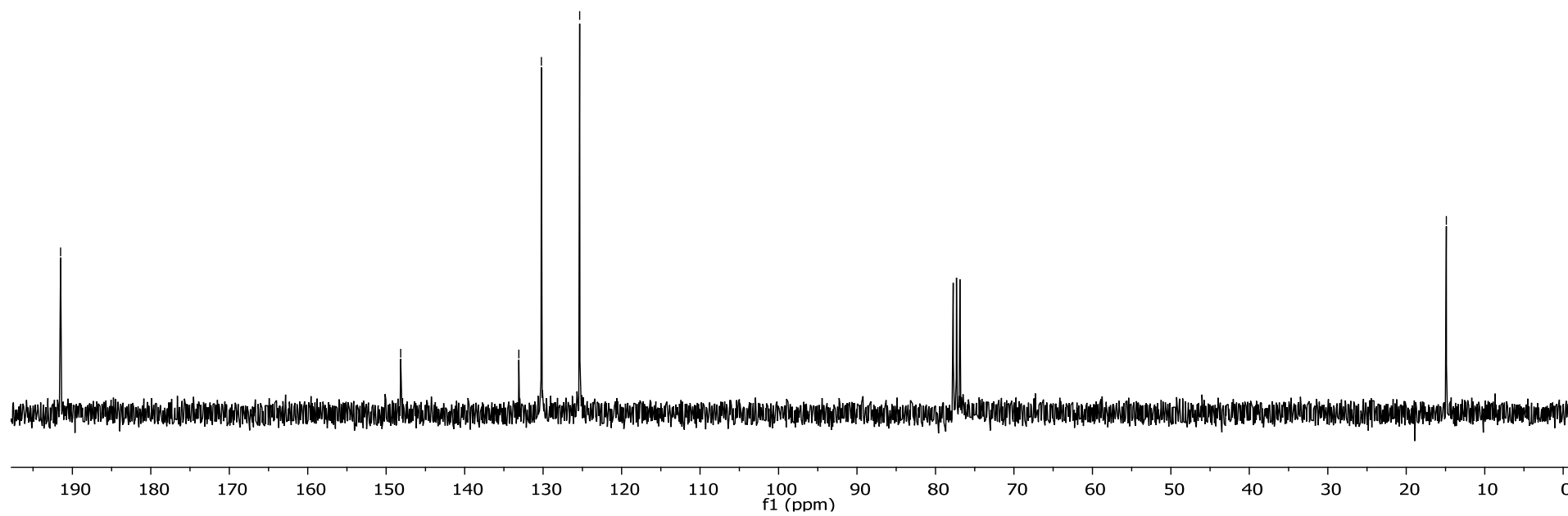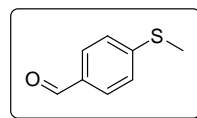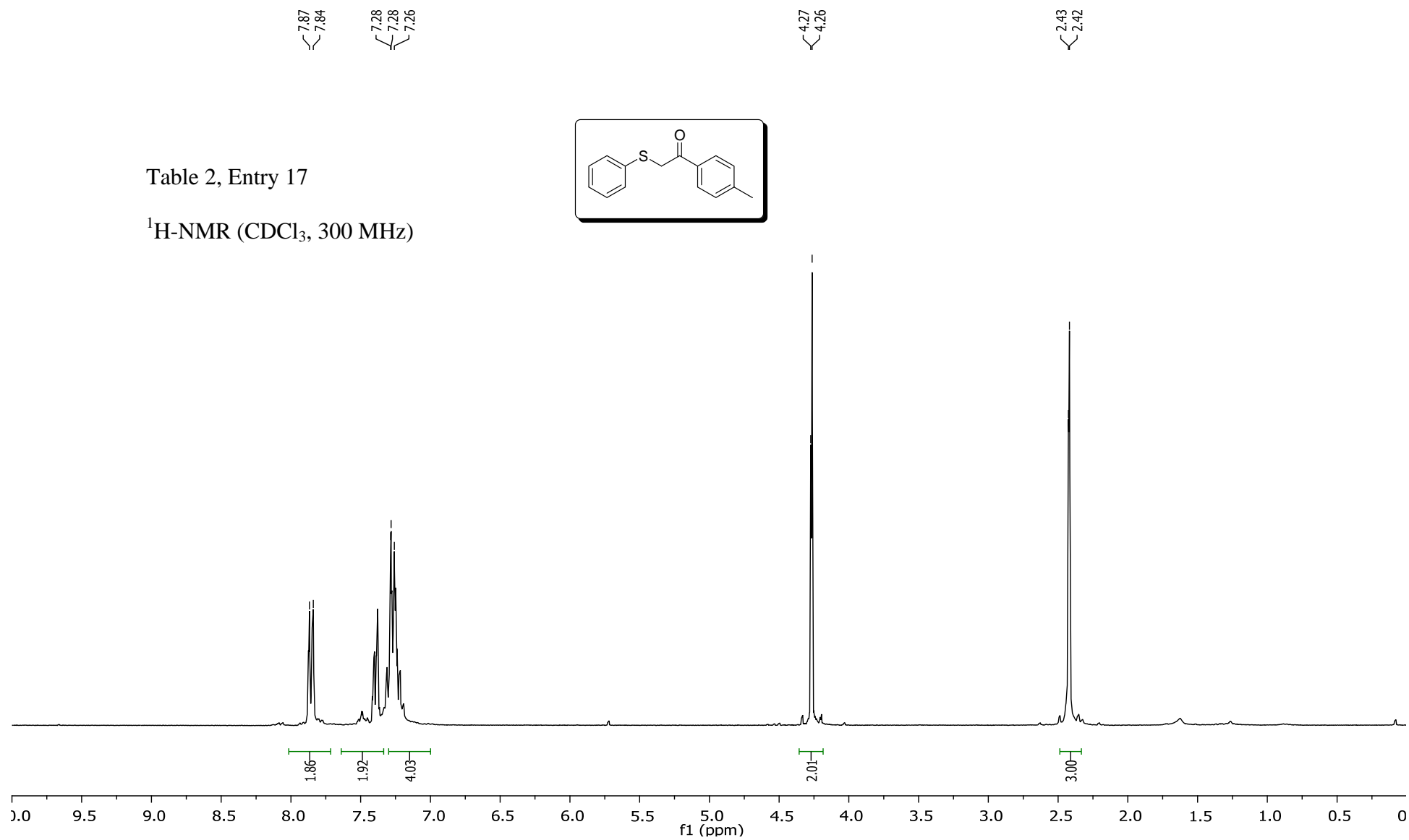
193.99

144.70
135.15
133.07
130.59
129.63
129.29
129.05
127.23

41.38

21.98

Table 2, Entry 17

^{13}C-NMR (CDCl$_3$, 75.4 MHz)

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Table 2, Entry 17

^{1}H-NMR (CDCl$_3$, 300 MHz)

8.01
8.01
7.99
7.98
7.47
7.28
7.26
7.26
7.15
7.15
3.91
3.91
2.45

1.00
1.01
1.06
1.02
3.06
3.20

f1 (ppm)

Table 2, Entry 18

^{13}C-NMR (CDCl$_3$, 75.4 MHz)

143.56 — 167.07

132.75 131.56 124.53 123.65

52.30

15.80

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Table 2, Entry 19
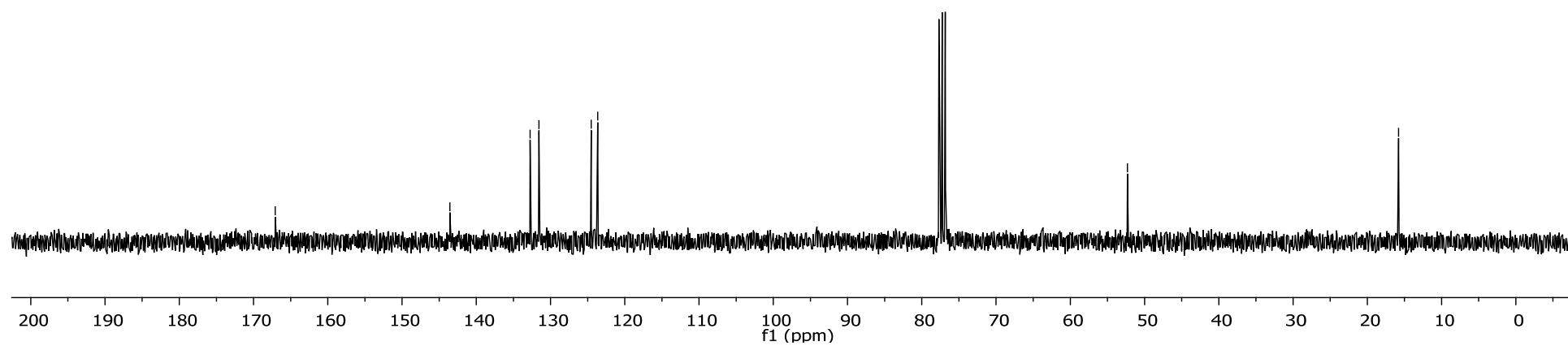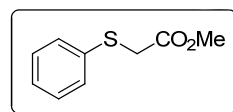
^{1}H-NMR (CDCl$_3$, 300 MHz)

7.99
7.98
7.47
7.28
7.26
7.26
7.15
7.15
7.15

3.91
3.91

2.45

1.00

1.06
1.22
1.06

3.26

3.26

.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
f1 (ppm)

Table 2, Entry 19
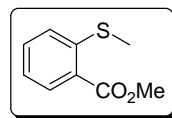
^{13}C-NMR (CDCl$_3$, 75.4 MHz)
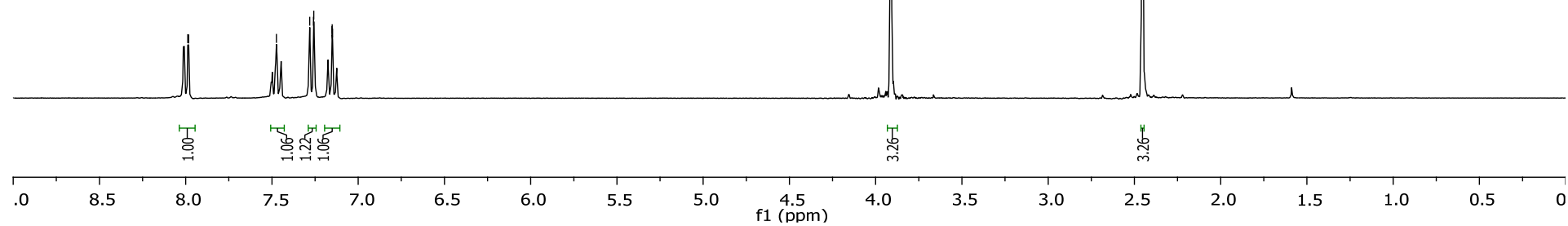
167.07
143.56
132.75
131.56
124.53
123.65
52.30
15.80

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7.55
7.38
7.38

3.56
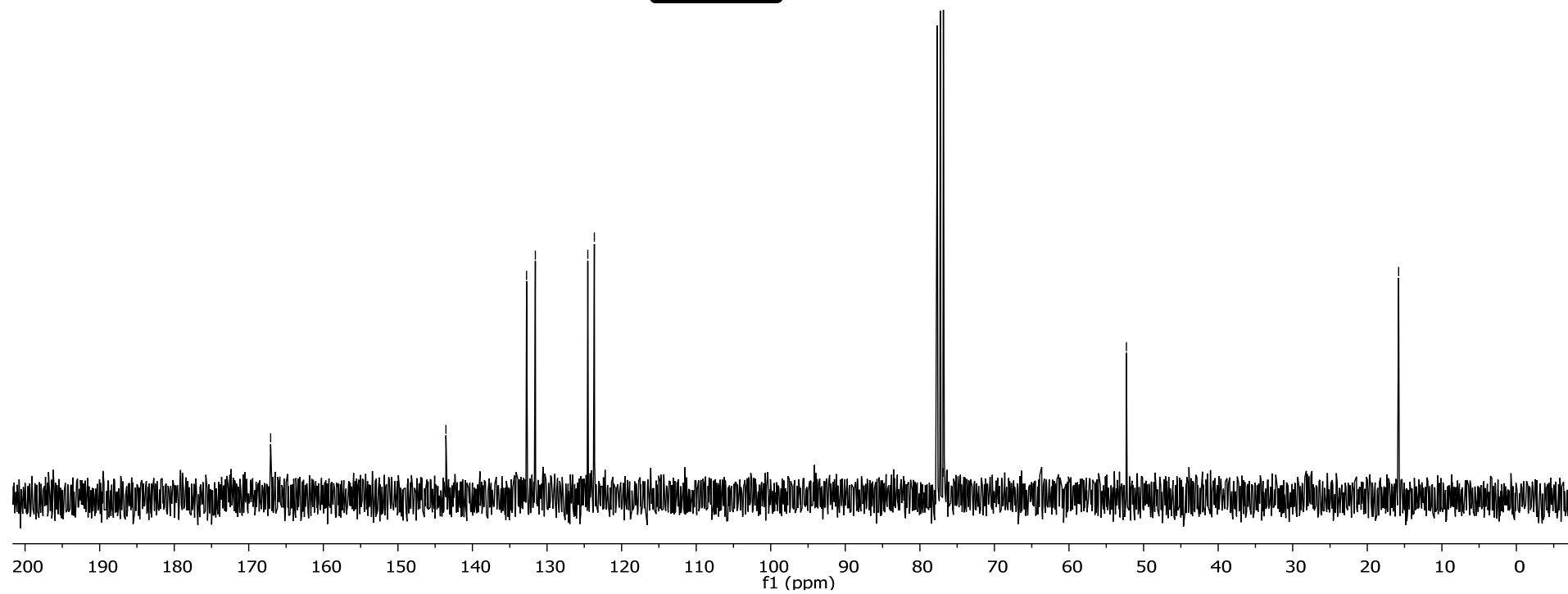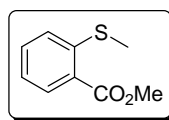
Table 2, Entry 20

^{1}H-NMR (CDCl$_3$, 300 MHz)

2.00
3.06

2.31

f1 (ppm)

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
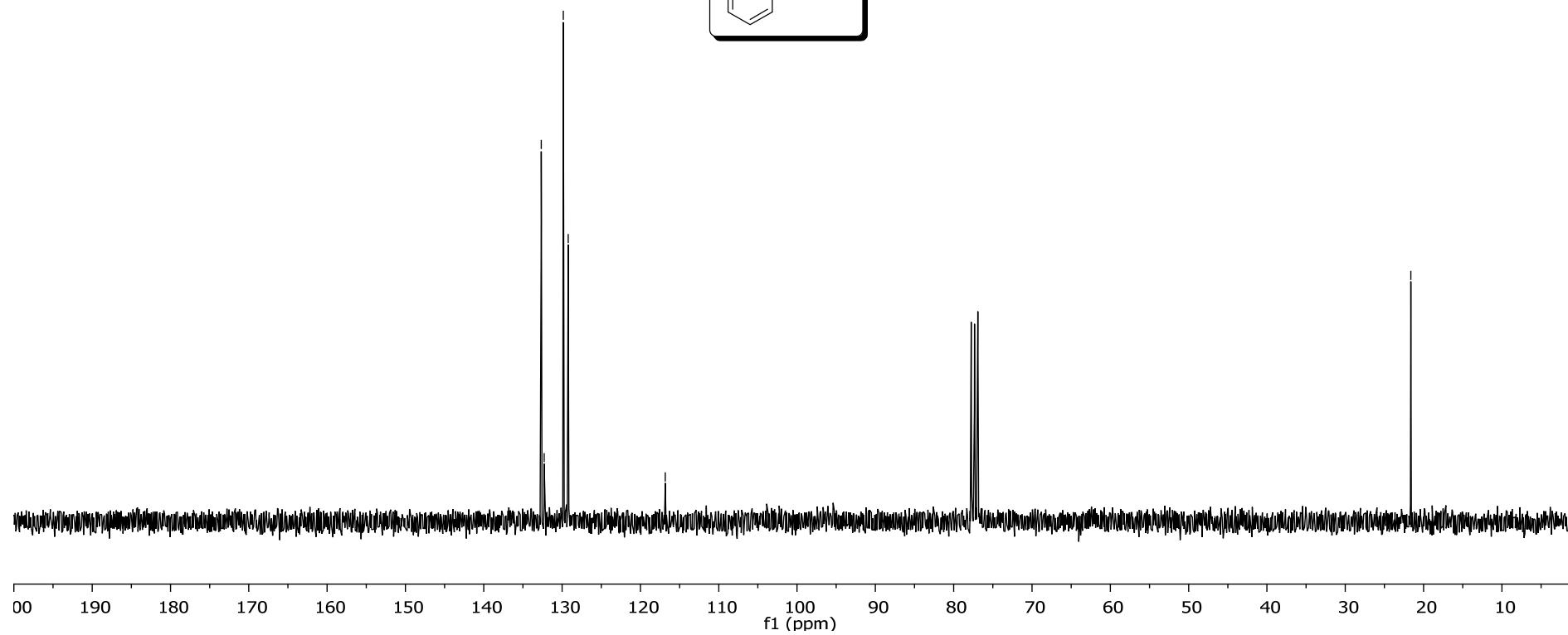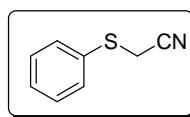
Table 2, Entry 20

^{13}C-NMR (CDCl$_3$, 75.4 MHz)
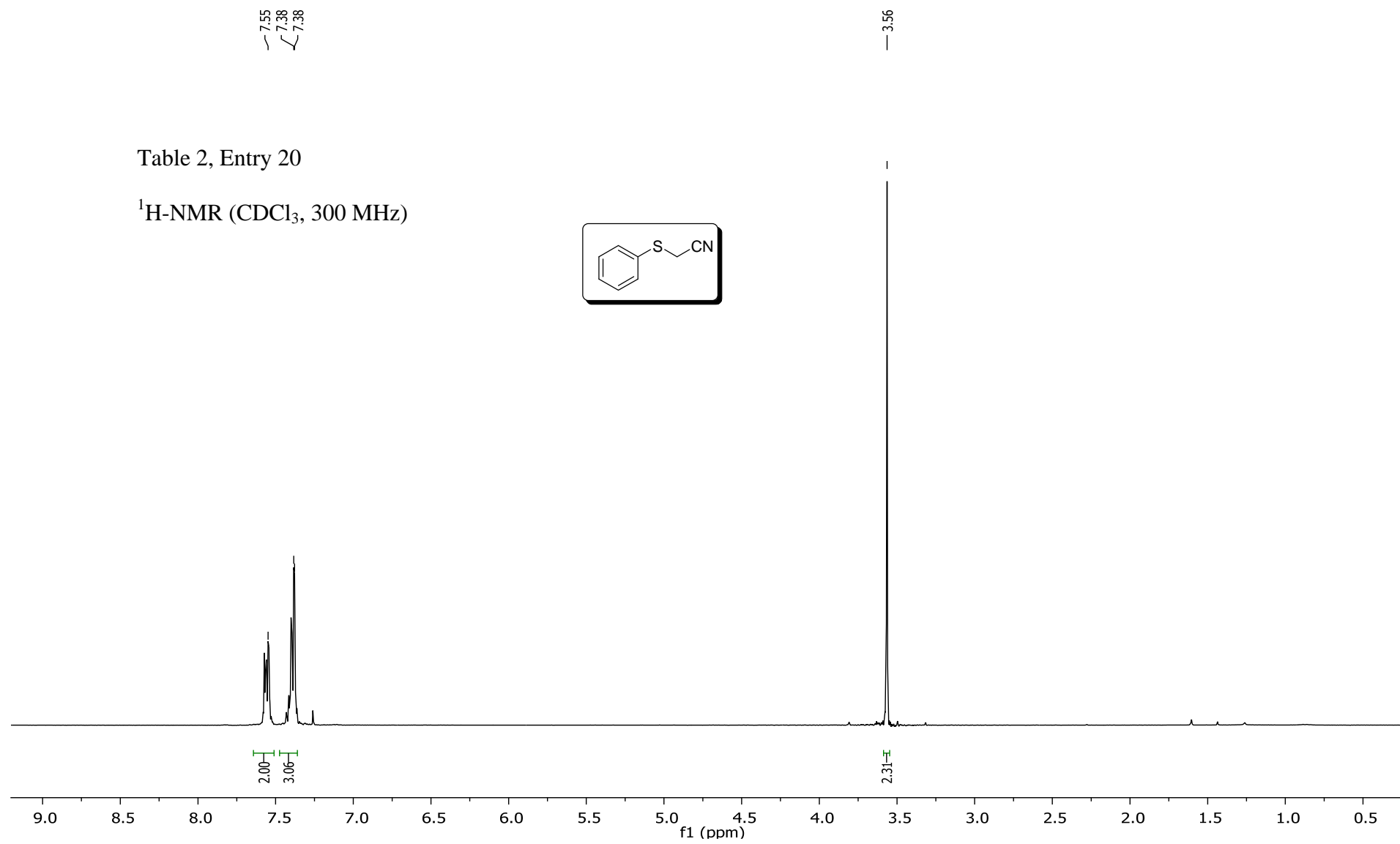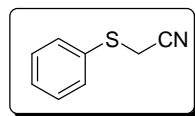
132.66
132.28
129.85
129.22
116.82
21.63

Table 2, Entry 21

^{1}H-NMR (CDCl$_3$, 300 MHz)

7.52
7.49
7.25
7.22

2.48

2.00
1.96

3.00

f1 (ppm)

Table 2, Entry 21

^{13}C-NMR (CDCl$_3$, 75.4 MHz)
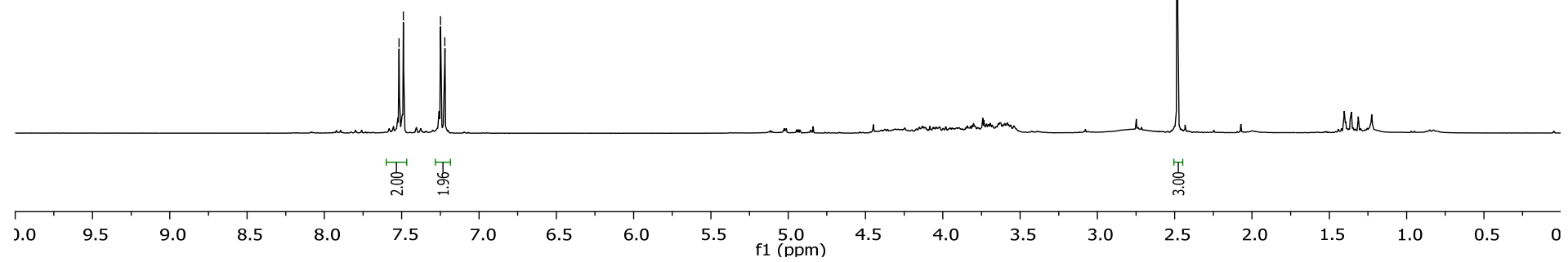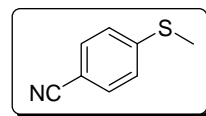
146.38
132.37
125.69
119.21
107.76
14.89

190   180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10   0
f1 (ppm)
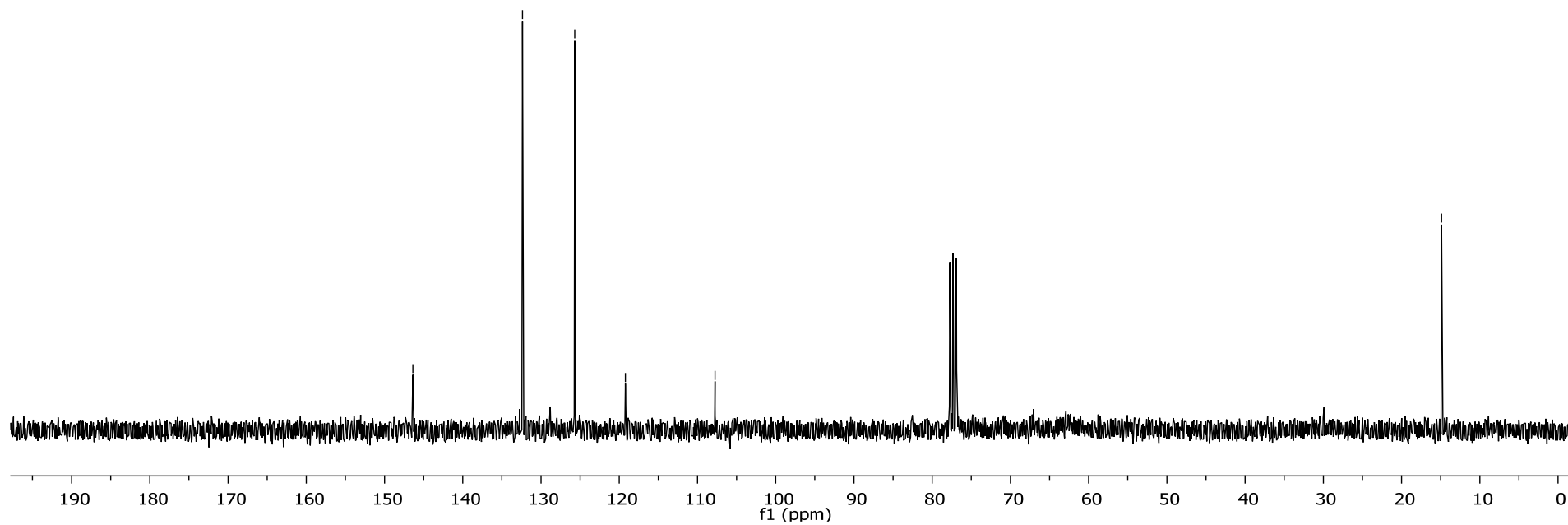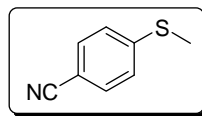
8.10
8.07
7.27
7.24
2.52

Table 2, Entry 22

^{1}H-NMR (CDCl$_3$, 300 MHz)

1.91
2.00
3.53

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

f1 (ppm)
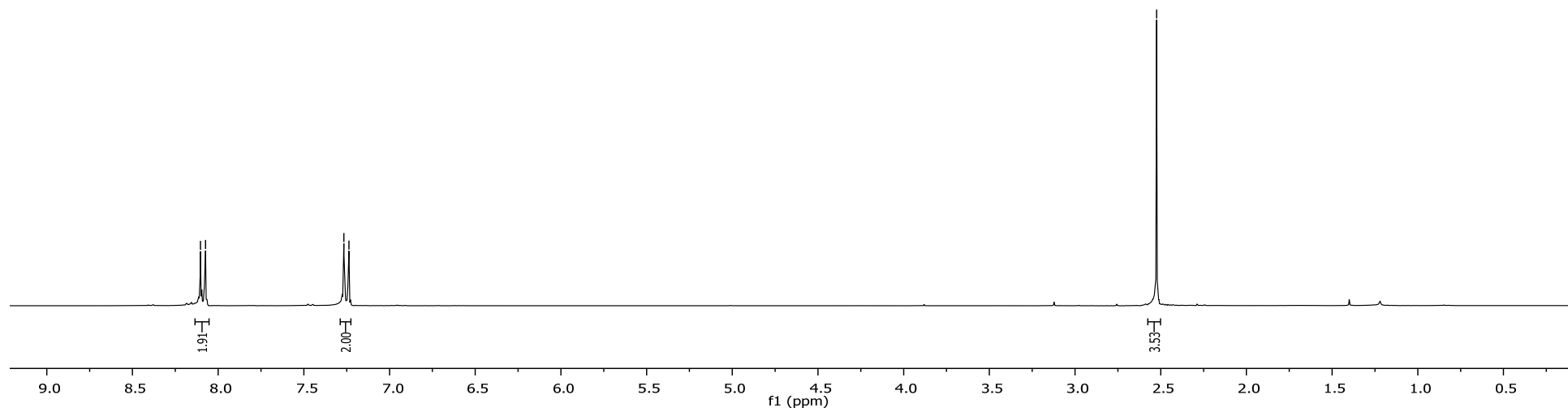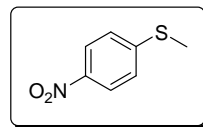
149.13

125.18
124.10

15.04

Table 2, Entry 22

^{13}C-NMR (CDCl$_3$, 75.4 MHz)

f1 (ppm)