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An Unprecedented Use for Glycerol: Chemoselective Reducing Agent for Sulfoxides

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Electronic Supplementary Information

Index

General methods 2

General procedures for the reduction of sulfoxides 3

General procedure for the Mo-catalyzed oxidation of glycerol with bis(*p*-tolyl)sulfoxide 4

General procedure for the reduction of sulfoxides using oxidation products from glycerol as reducing agents 4

NMR studies and spectra for the determination of glycerol oxidation products in the process 5

NMR spectra of products obtained after extraction in Table 2 and Schemes 1, 2 and 3 13

General methods: All reactions were assembled under air atmosphere unless otherwise noted. All reaction temperatures 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 catalyst, $MoO_2Cl_2(dmf)_2$, was prepared as previously reported.[2] Solvents were dried by standard methods. 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 ^1H NMR spectroscopy[3] 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).

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

[2] R. Sanz, J. Escribano, R. Aguado, M. R. Pedrosa, and F. J. Arnáiz, *Synthesis,* 2004, 1629–1632.

[3] 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.

General procedures for the reduction of sulfoxides:

Method A: A mixture of glycerol (921 mg, 10 equiv.), sulfoxide (1 mmol) and $MoO_2Cl_2(dmf)_2$ (17 mg, 5 mol%) was heated at 170 °C overnight. The reaction mixture was cooled to room temperature and Et_2O (20 mL) and water (20 mL) were added. The layers were separated and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvents were removed under reduced pressure. The corresponding sulfide was obtained in almost pure form without further purification in the yields reported in Table 2.

Method B: A mixture of glycerol (921 mg, 10 equiv.), sulfoxide (1 mmol) and $MoO_2Cl_2(dmf)_2$ (9 mg, 2.5 mol%) was heated at 200 °C for 2–4 h. The reaction mixture was cooled to room temperature and Et_2O (20 mL) and water (20 mL) were added. The layers were separated and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvents were removed under reduced pressure. The corresponding sulfide was obtained in almost pure form without further purification in the yields reported in Table 2.

Method C: A mixture of glycerol (111 mg, 1.2 equiv.), sulfoxide (1 mmol) and $MoO_2Cl_2(dmf)_2$ (9 mg, 2.5 mol%) in toluene (1 mL) was irradiated in a sealed tube in the microwave cavity at 230 °C for 5 min. The reaction mixture was cooled to room temperature and Et_2O (20 mL) and water (20 mL) were added. The layers were separated and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvents were removed under reduced pressure. The corresponding sulfide was obtained in almost pure form without further purification in the yields reported in Table 2.

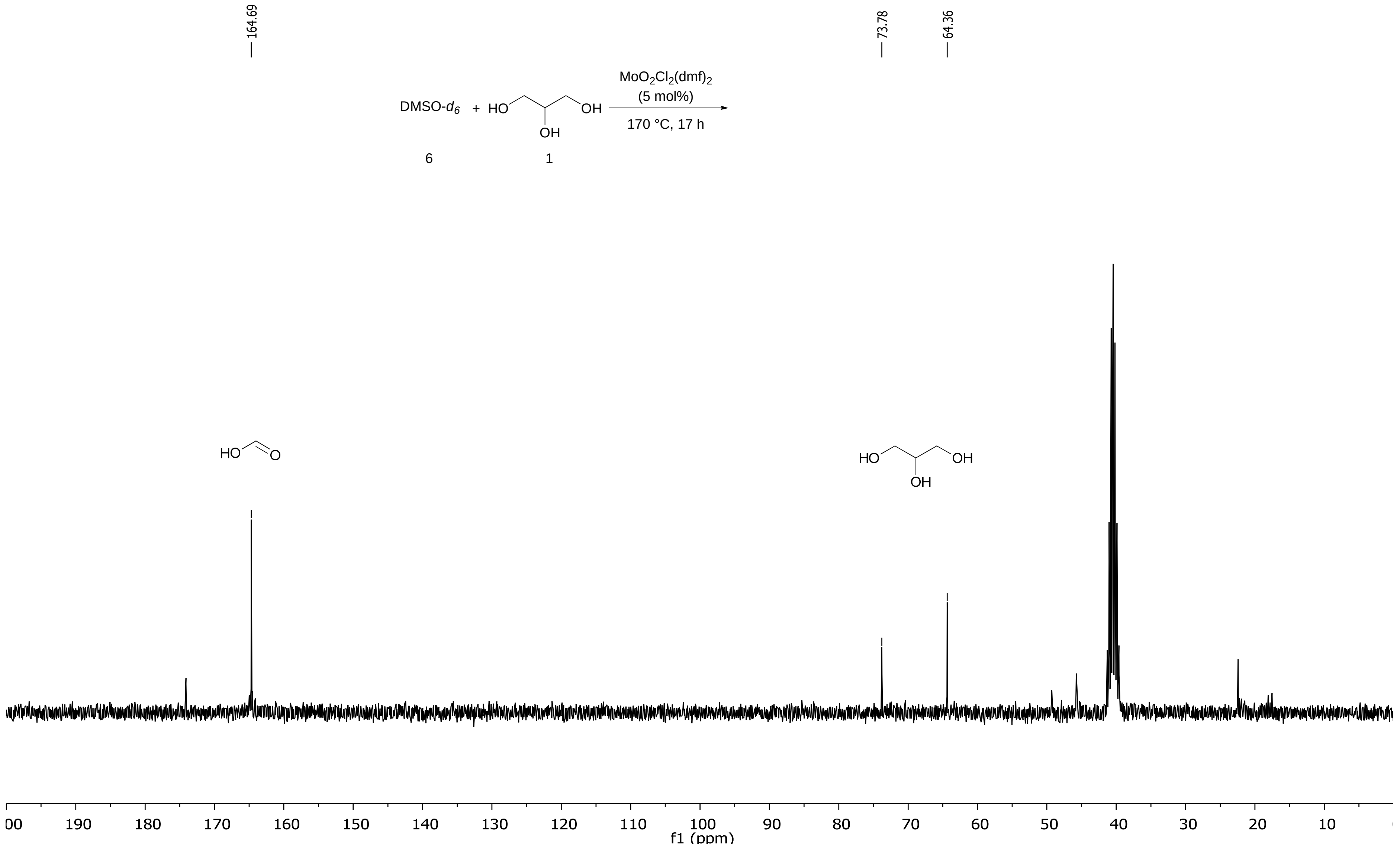
Recycling study: A mixture of glycerol (92 g, 100 equiv.), bis(*p*-tolyl)sulfoxide (2.3 g, 10 mmol) and $MoO_2Cl_2(dmf)_2$ (90 mg, 2.5 mol%) was heated at 200 °C for 4–6 h. The reaction mixture was cooled to 100 °C and extracted with hot toluene (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvents were removed under reduced pressure. Bis(*p*-tolyl)sulfide was obtained in almost pure form without further purification in the yields reported in Scheme 2. The glycerolic phase was reused in the next cycle.

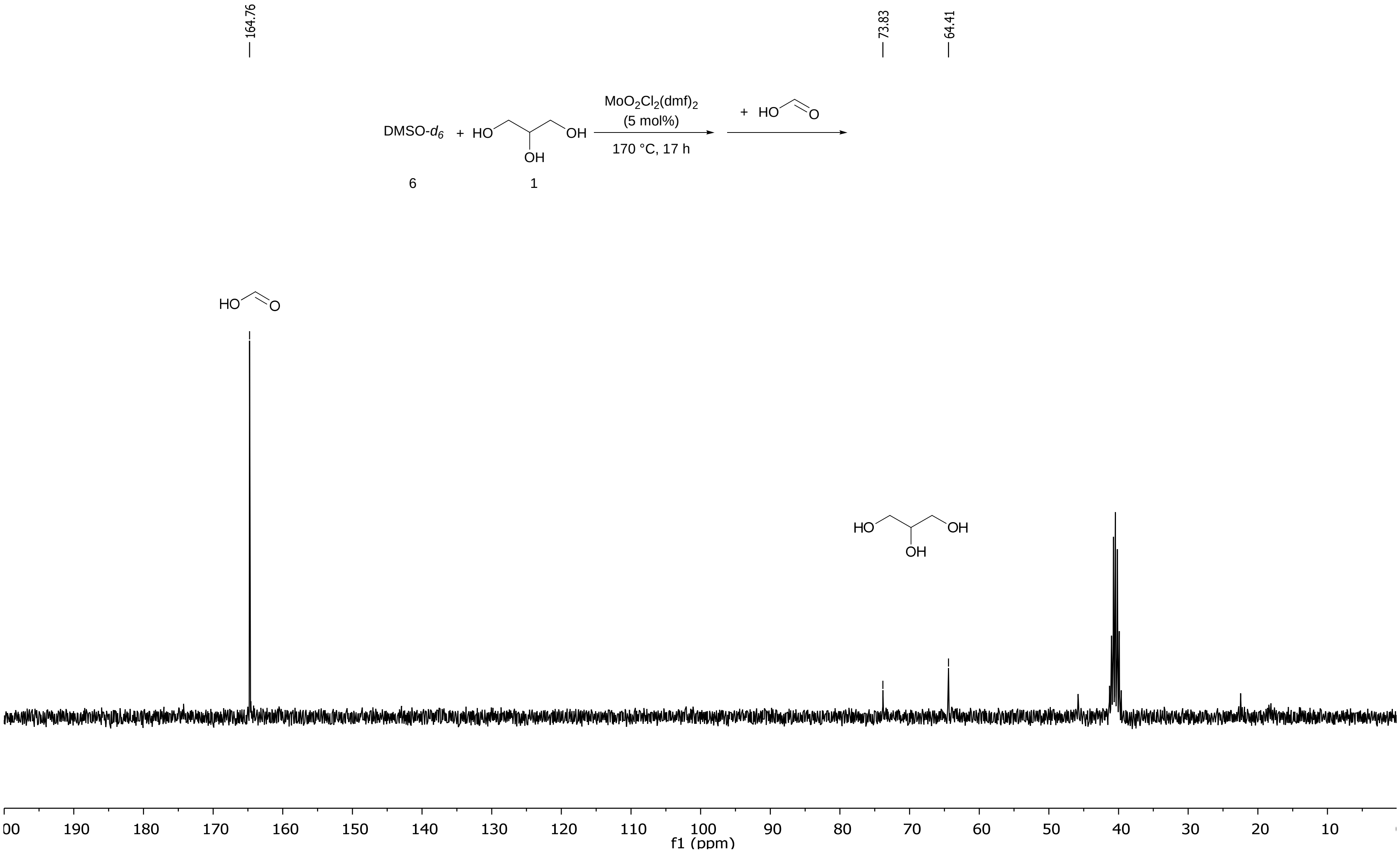
Using crude glycerol: A mixture of crude glycerol (2.36 g, ca. 5–8% purity, ca. 2 equiv.), sulfoxide (1 mmol) and $MoO_2Cl_2(dmf)_2$ (9 mg, 2.5 mol%) was heated at 200 °C for 2–7 h in an open flask until complete consumption of the starting material (determined by GC-MS analysis). The reaction mixture was cooled to room temperature and Et_2O (20 mL) and H_2O (20 mL) were added. The layers were separated and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvents were removed under reduced pressure. The corresponding sulfide was obtained in almost pure form without further purification in the yields reported in Scheme 3.

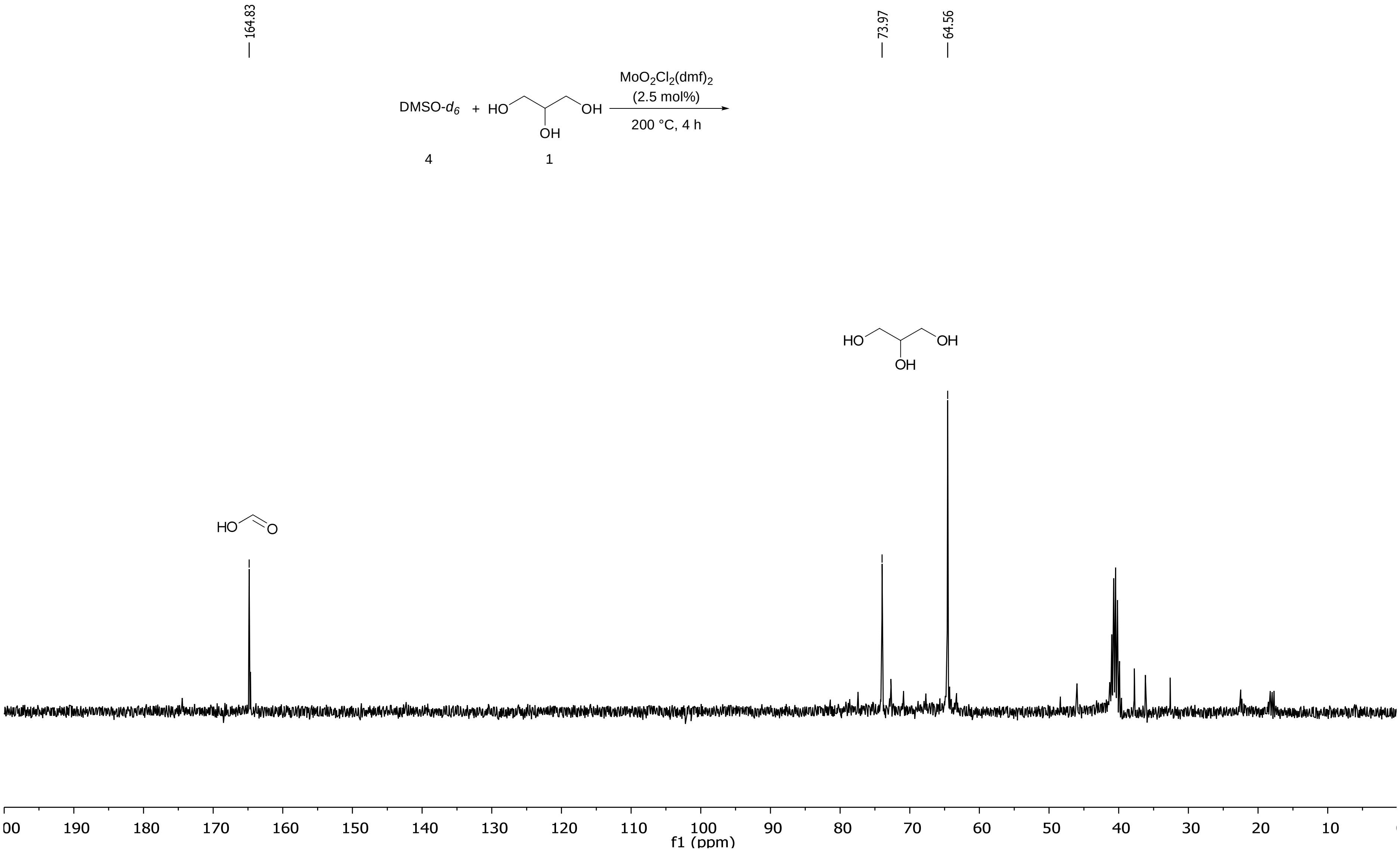
General procedure for the Mo-catalyzed oxidation of glycerol with bis(*p*-tolyl)sulfoxide: A mixture of bis(*p*-tolyl)sulfoxide (230 mg, 1 mmol), the appropriate amount of glycerol (1–8 equiv.), $MoO_2Cl_2(dmf)_2$ (9 mg, 2.5 mol%) in mesitylene (2 mL) was heated at 200 °C for 9 h. The reaction mixture was cooled to room temperature and Et_2O (20 mL) and water (20 mL) were added. The layers were separated and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvents were removed under reduced pressure. Bis(*p*-tolyl)sulfide was formed in the conversions estimated by ^1H NMR (300 MHz) reported in Scheme 4.

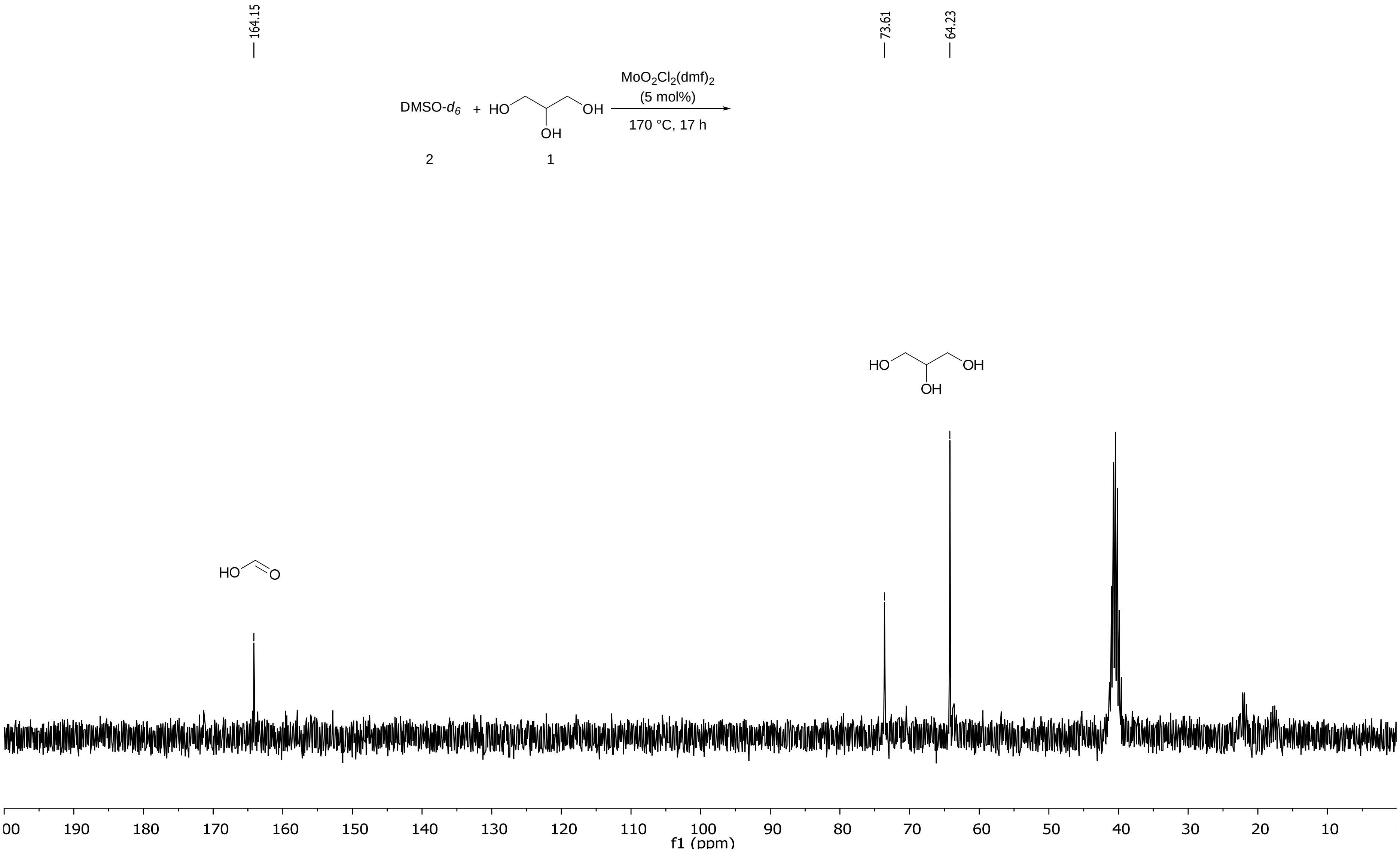
General procedure for the reduction of sulfoxides using oxidation products from glycerol as reducing agents: A mixture of bis(*p*-tolyl)sulfoxide (230 mg, 1 mmol), the appropriate amount of reducing agent (1–6 equiv.), and $MoO_2Cl_2(dmf)_2$ (9 mg, 2.5 mol%) in toluene (1 mL) was irradiated in a sealed tube in the microwave cavity at 180 or 230 °C for 5 min. The reaction mixture was cooled to room temperature and Et_2O (20 mL) and H_2O (20 mL) were added. The layers were separated and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvents were removed under reduced pressure to give bis(*p*-tolyl)sulfide in the conversions and yields reported in Table 3.

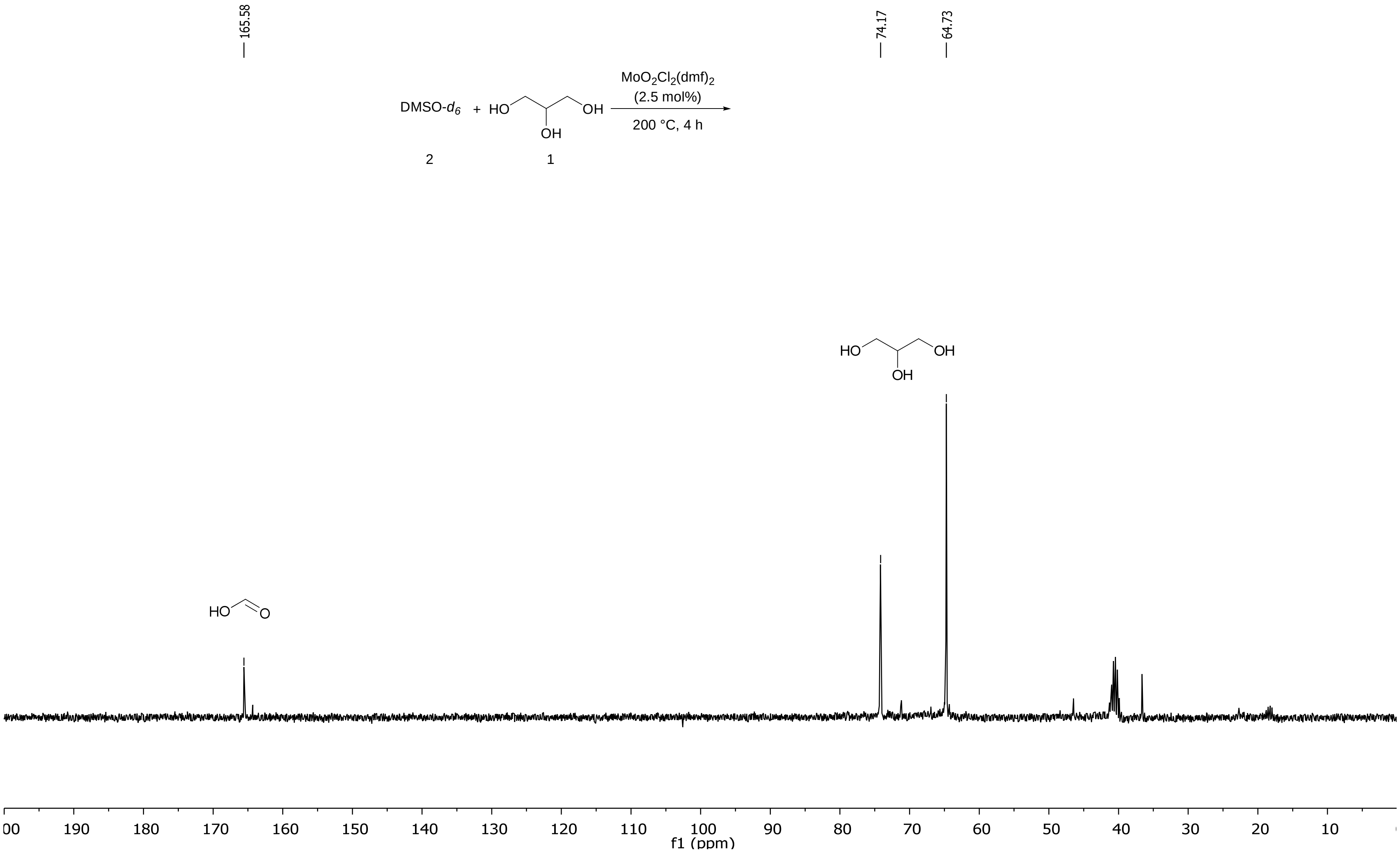
NMR studies and spectra for the determination of glycerol oxidation products in the process: A mixture glycerol (276 mg, 3 mmol), the appropriate amount of DMSO-d_6 (1 to 6 equiv.), and $MoO_2Cl_2(dmf)_2$ (9–17 mg, 2.5–5.0 mol%) was heated at 170 °C overnight or at 200 °C for 4 h. After cooling, the crude reaction mixture was homogenized, if necessary, by adding additional DMSO-d_6 and its ^{13}C NMR was measured. In the spectra reported below of all the experiments performed we could observe the signals corresponding to the formation of formic acid (δ = 167.7) as main product as well as variable amounts of remaining glycerol (δ = 73.8 and 64.4).

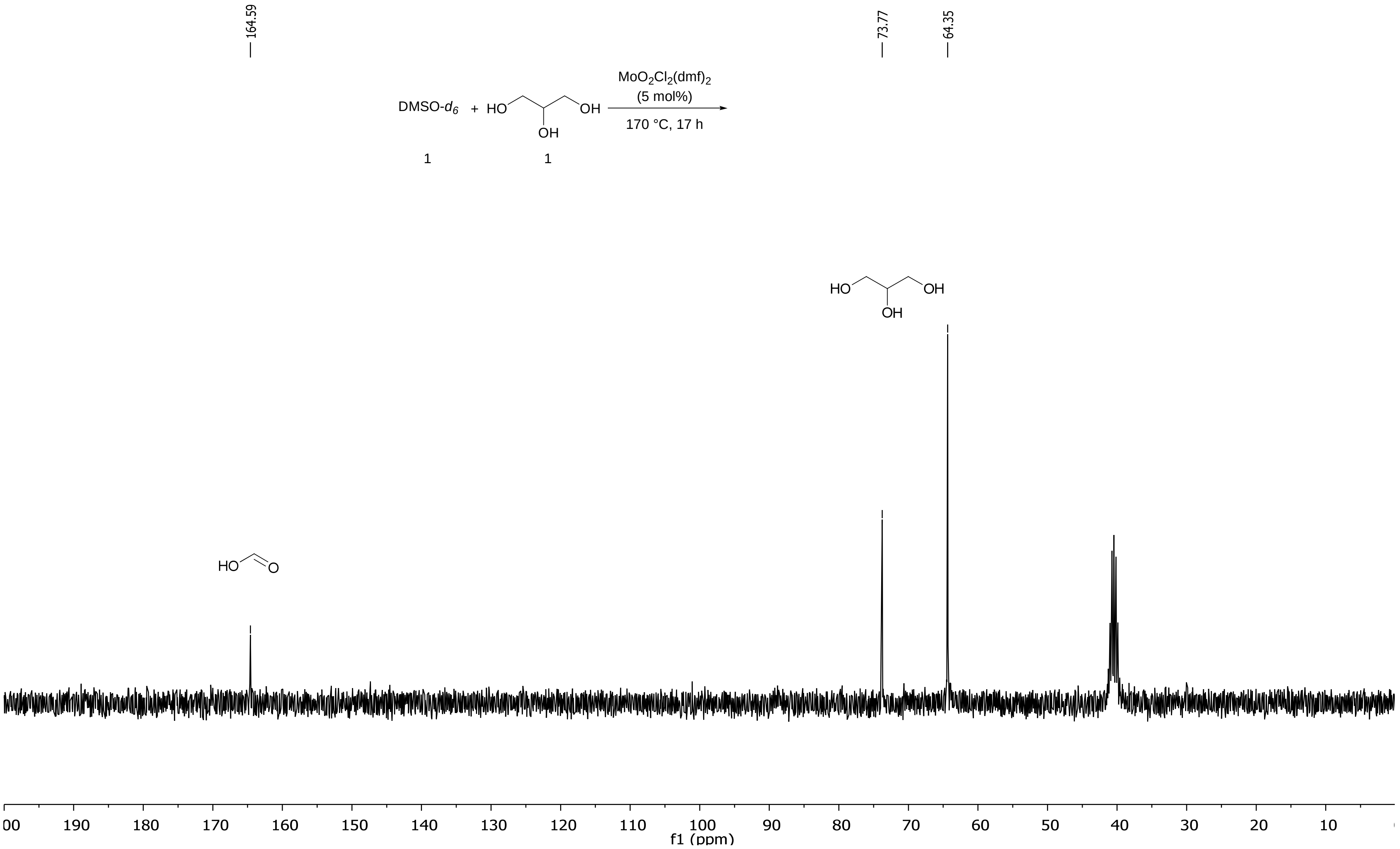

164.69
73.78
64.36
DMSO-d_6
HO
OH
OH
$MoO_2Cl_2(dmf)_2$
(5 mol%)
170 °C, 17 h
6
1
HO
O
HO
OH
OH
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

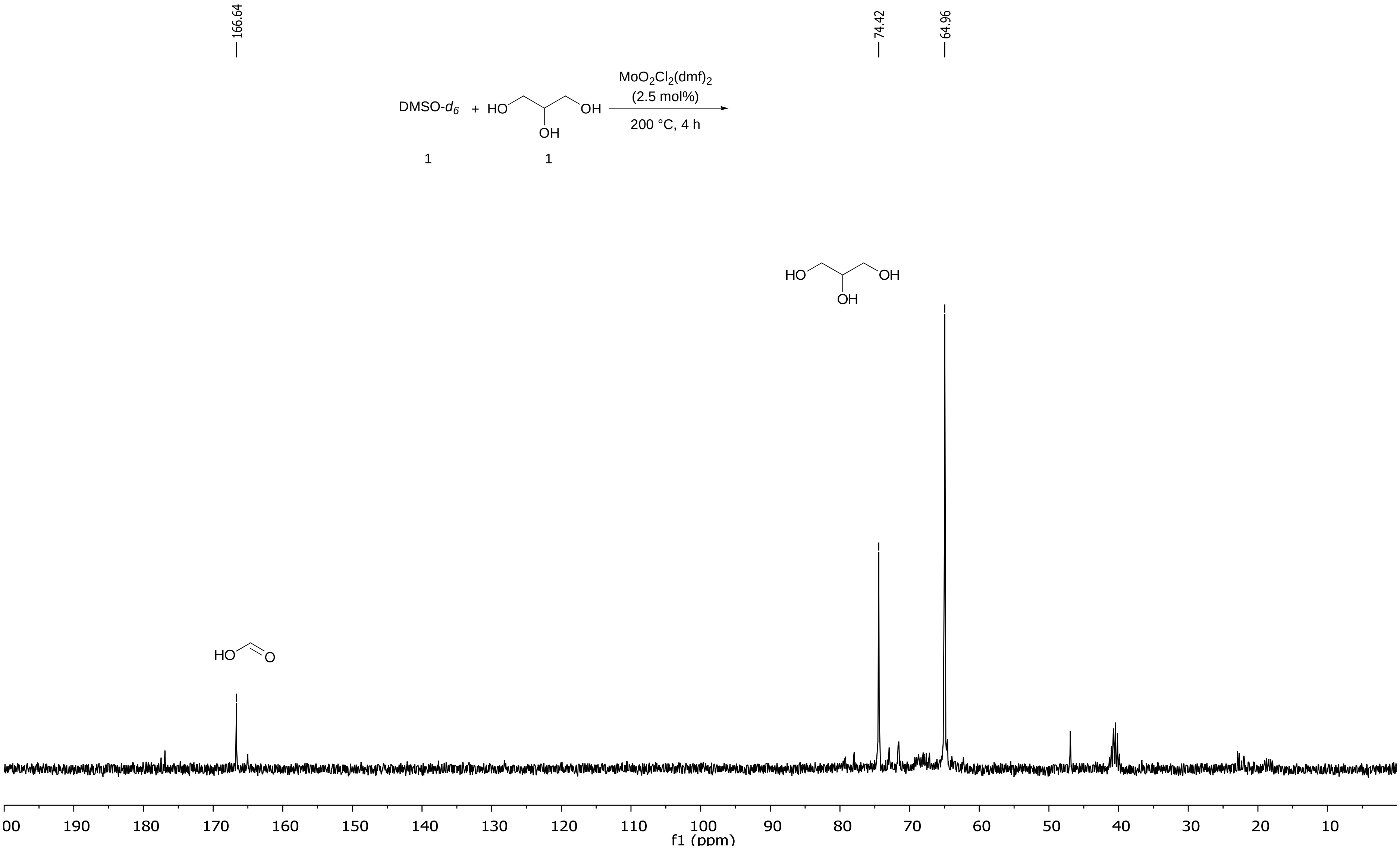

164.76
73.83
64.41
$MoO_2Cl_2(dmf)_2$
(5 mol%)
DMSO-d_6 + HO OH
OH
170 °C, 17 h
+ HO O
6
1
HO O
HO OH
OH
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


164.83
73.97
64.56
DMSO-d_6 + HO OH OH
4
1
$MoO_2Cl_2(dmf)_2$
(2.5 mol%)
200 °C, 4 h
HO OH OH
HO O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

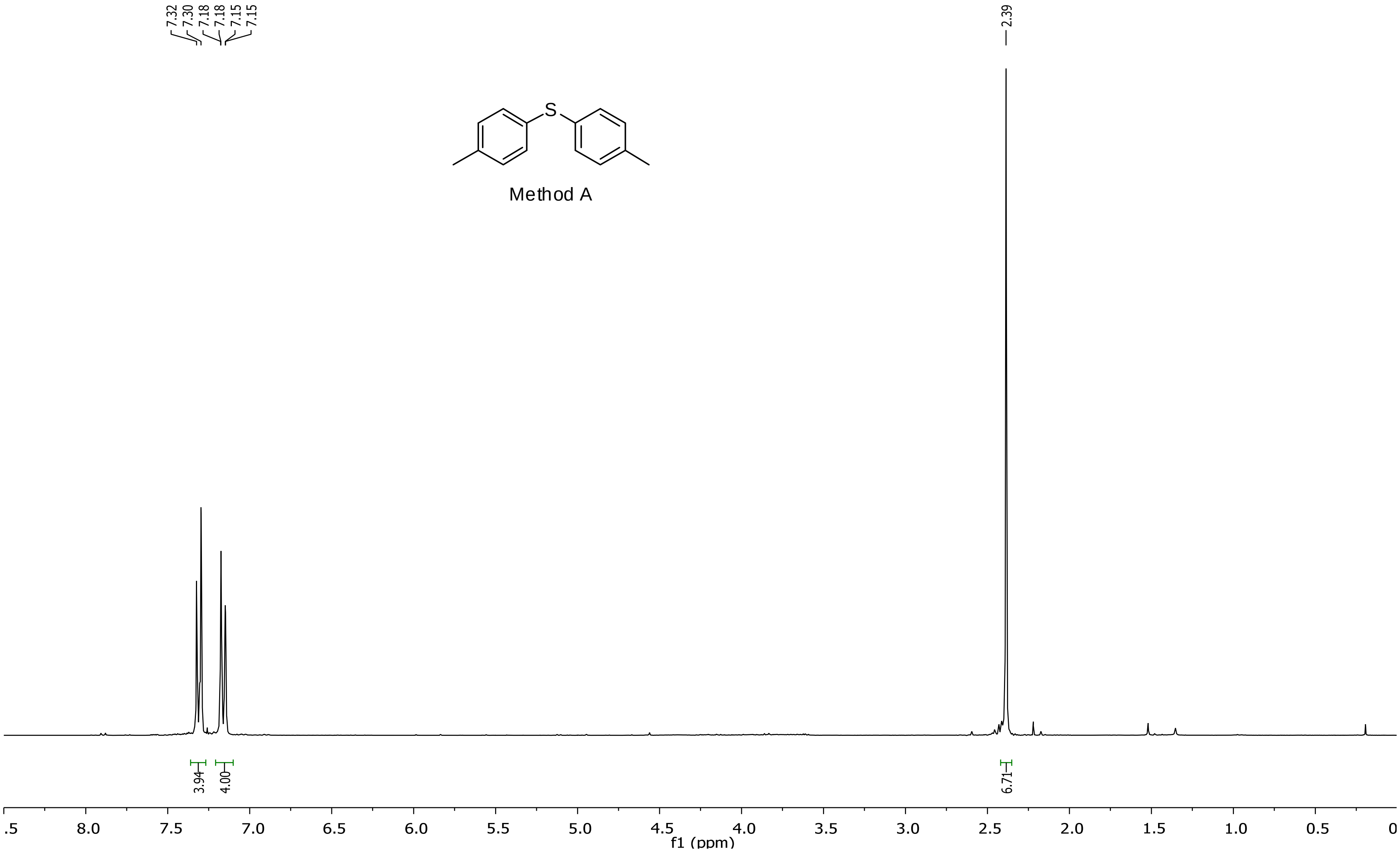

164.15
73.61
64.23
DMSO-d_6 + HO OH OH
2
1
$MoO_2Cl_2(dmf)_2$
(5 mol%)
170 °C, 17 h
HO O
HO OH OH
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

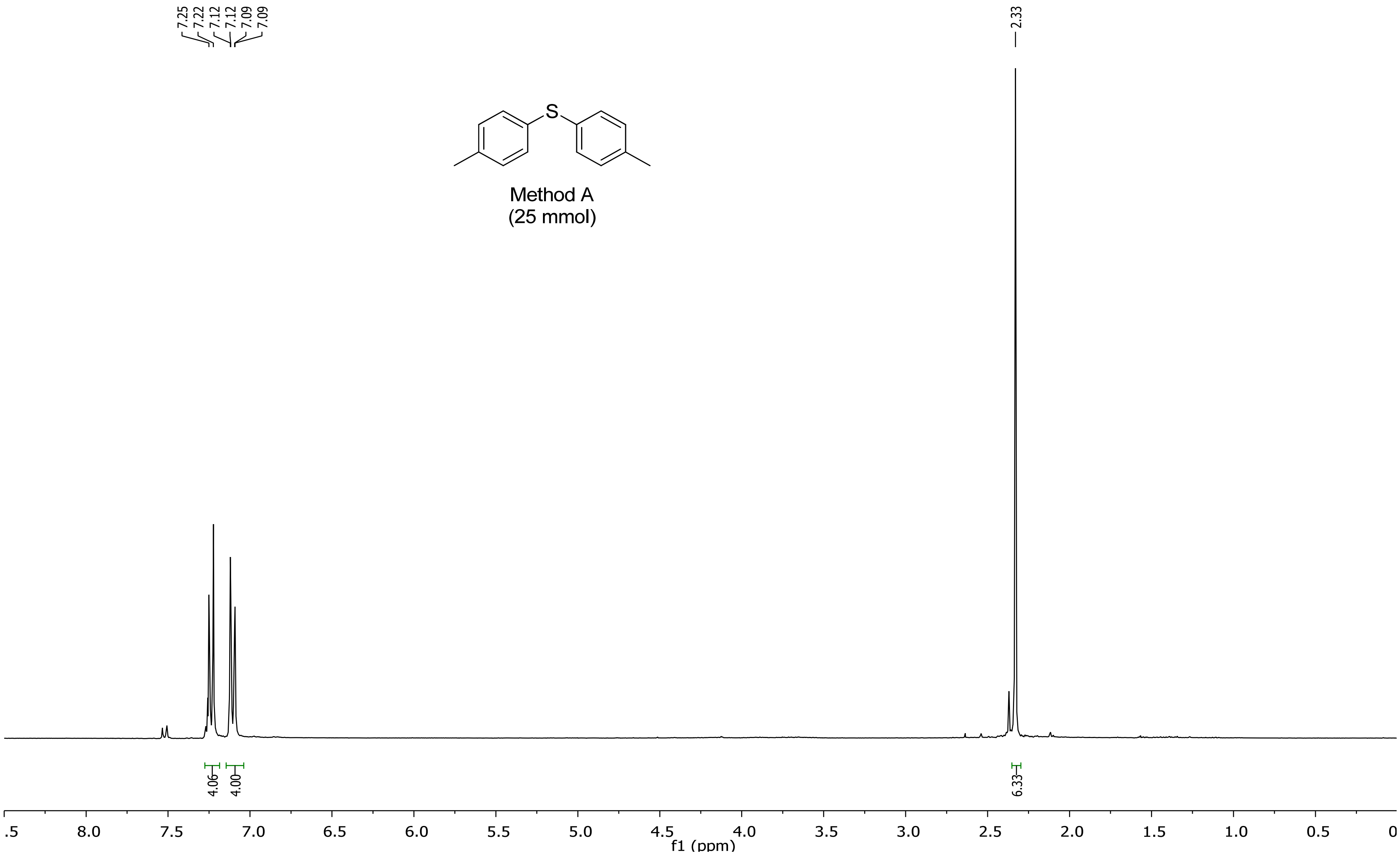

165.58
74.17
64.73
DMSO-d_6 + HO OH OH
$MoO_2Cl_2(dmf)_2$
(2.5 mol%)
200 °C, 4 h
2
1
HO OH OH
HO O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


164.59
73.77
64.35
DMSO-d_6 + HO OH OH
1
1
$MoO_2Cl_2(dmf)_2$
(5 mol%)
170 °C, 17 h
HO OH OH
HO O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

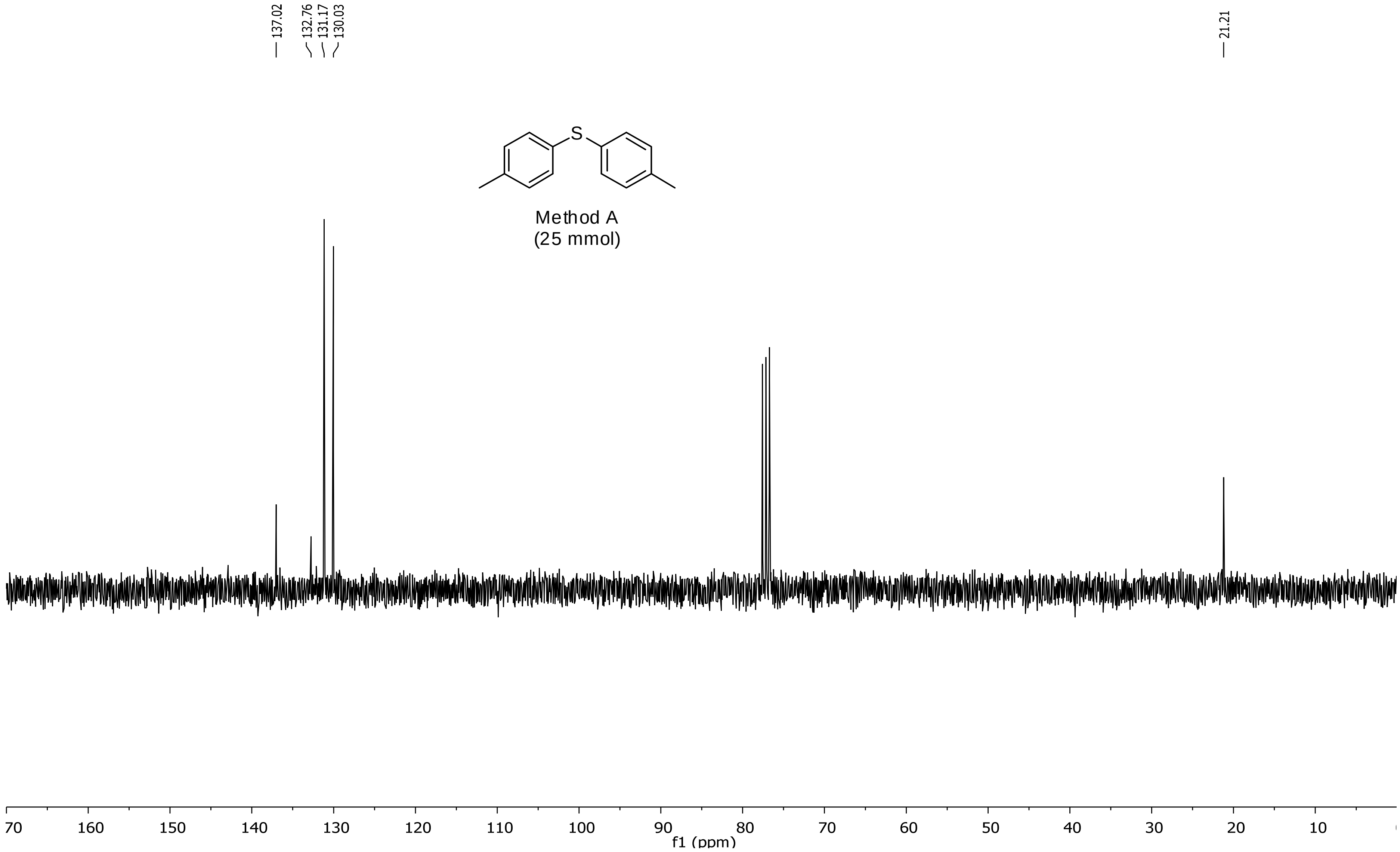

166.64
74.42
64.96
DMSO-d_6
+
HO
OH
OH
1
1
$MoO_2Cl_2(dmf)_2$
(2.5 mol%)
200 °C, 4 h
HO
OH
OH
HO
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

NMR spectra of products obtained after extraction in Table 2 and Schemes 1, 2 and 3

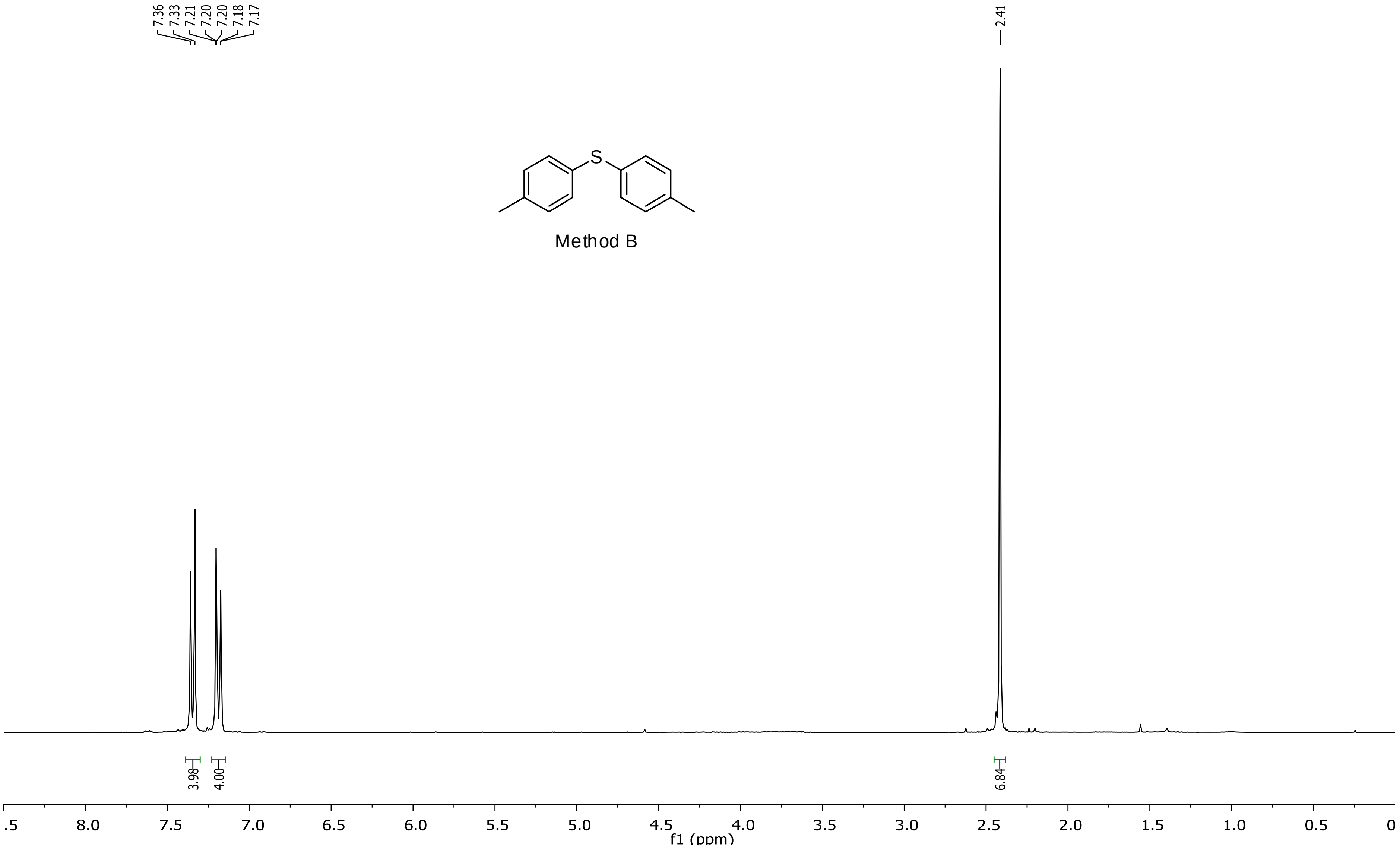

7.32
7.30
7.18
7.18
7.15
7.15
2.39
S
Method A
3.94
4.00
6.71
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

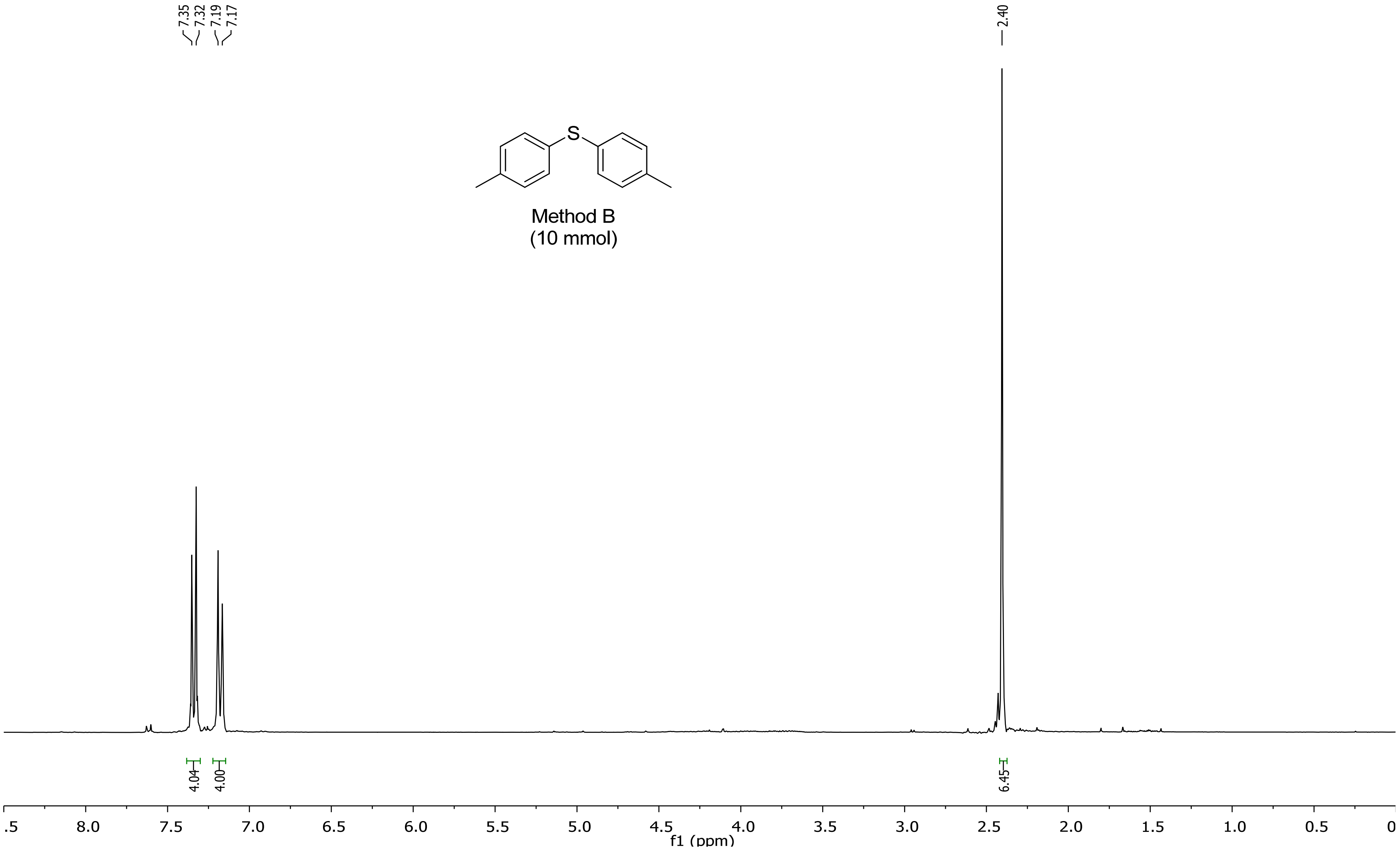


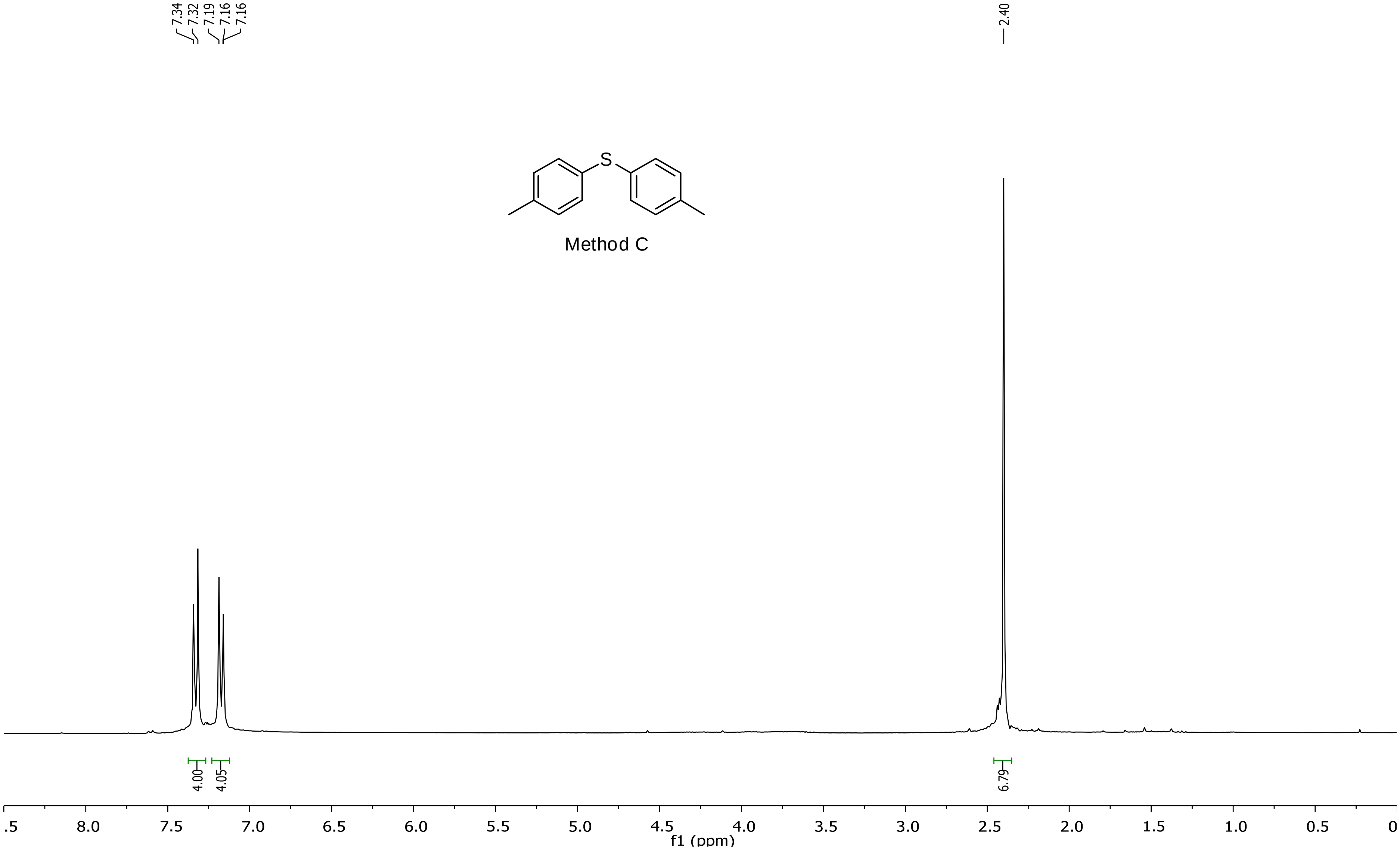
Method A
(25 mmol)

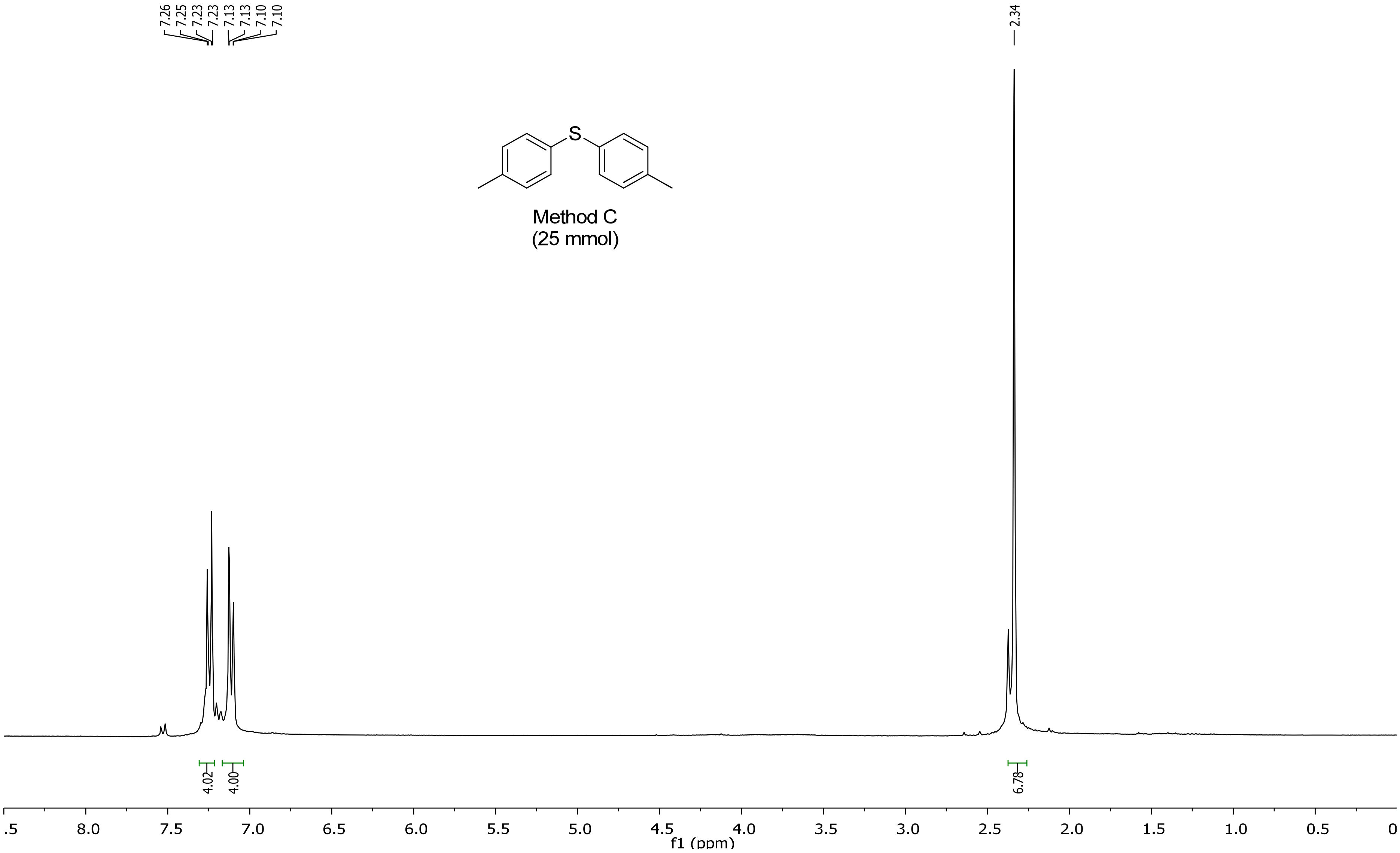


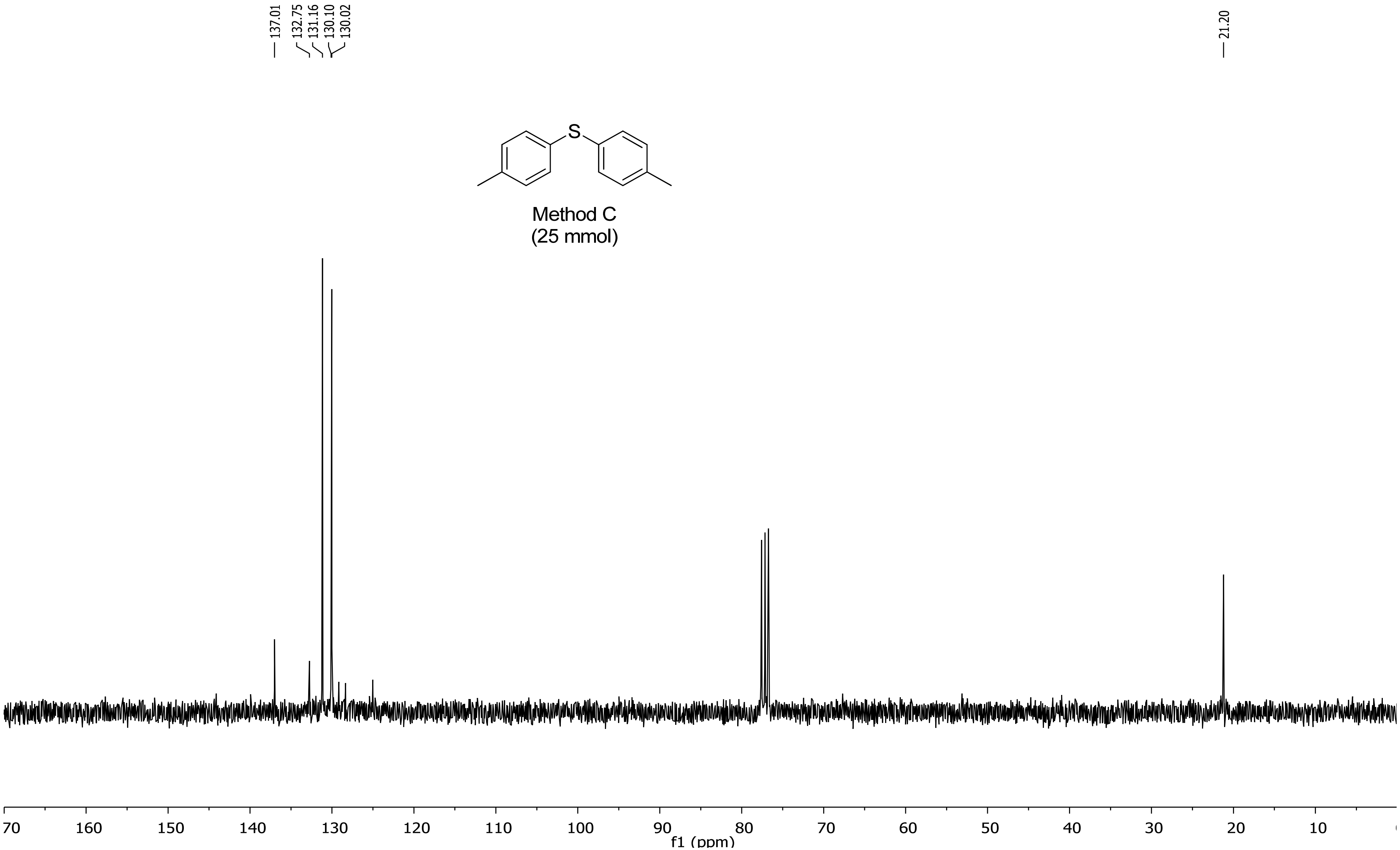
Method A
(25 mmol)

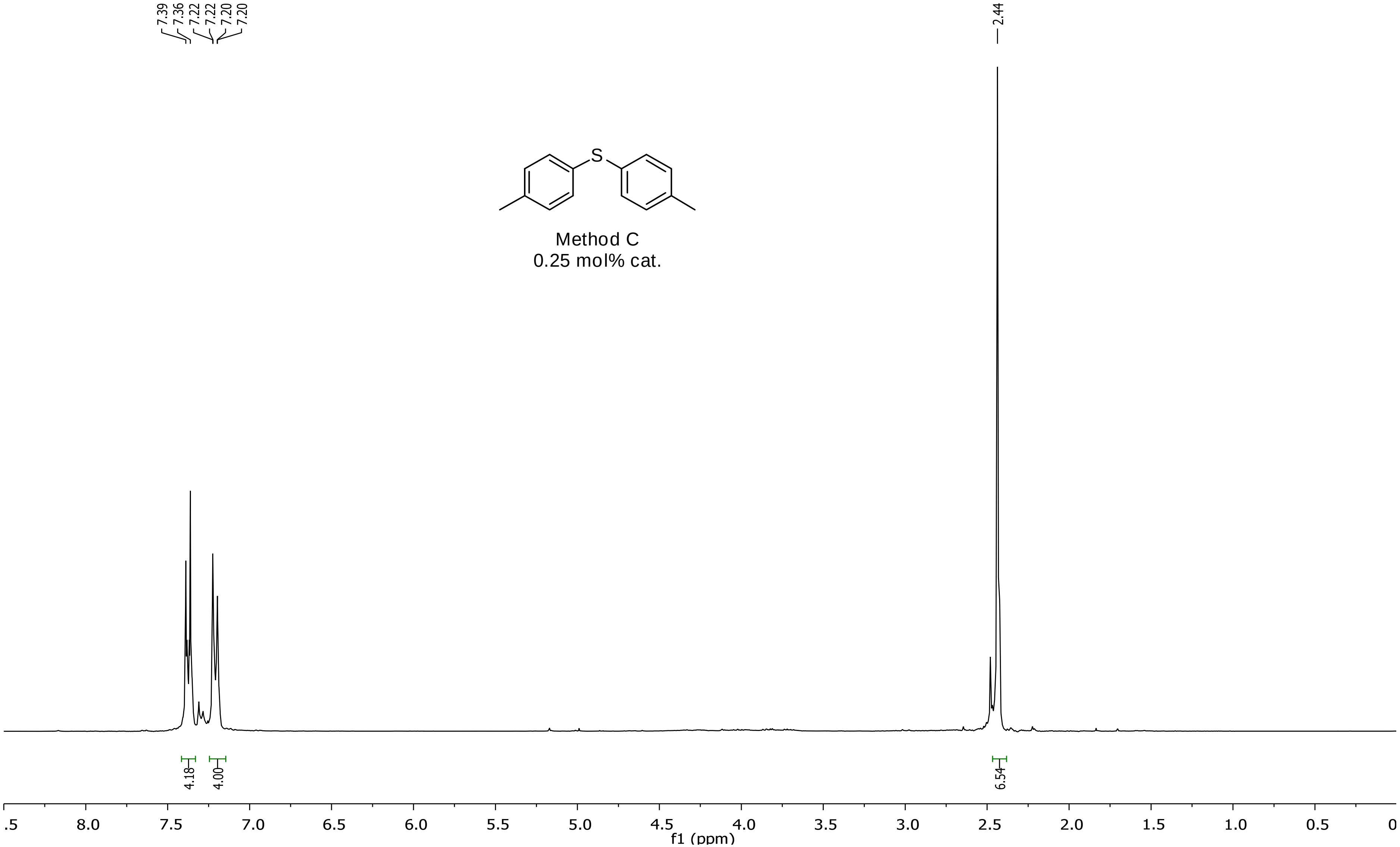

7.36
7.33
7.21
7.20
7.20
7.18
7.17
2.41
S
Method B
3.98
4.00
6.84
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

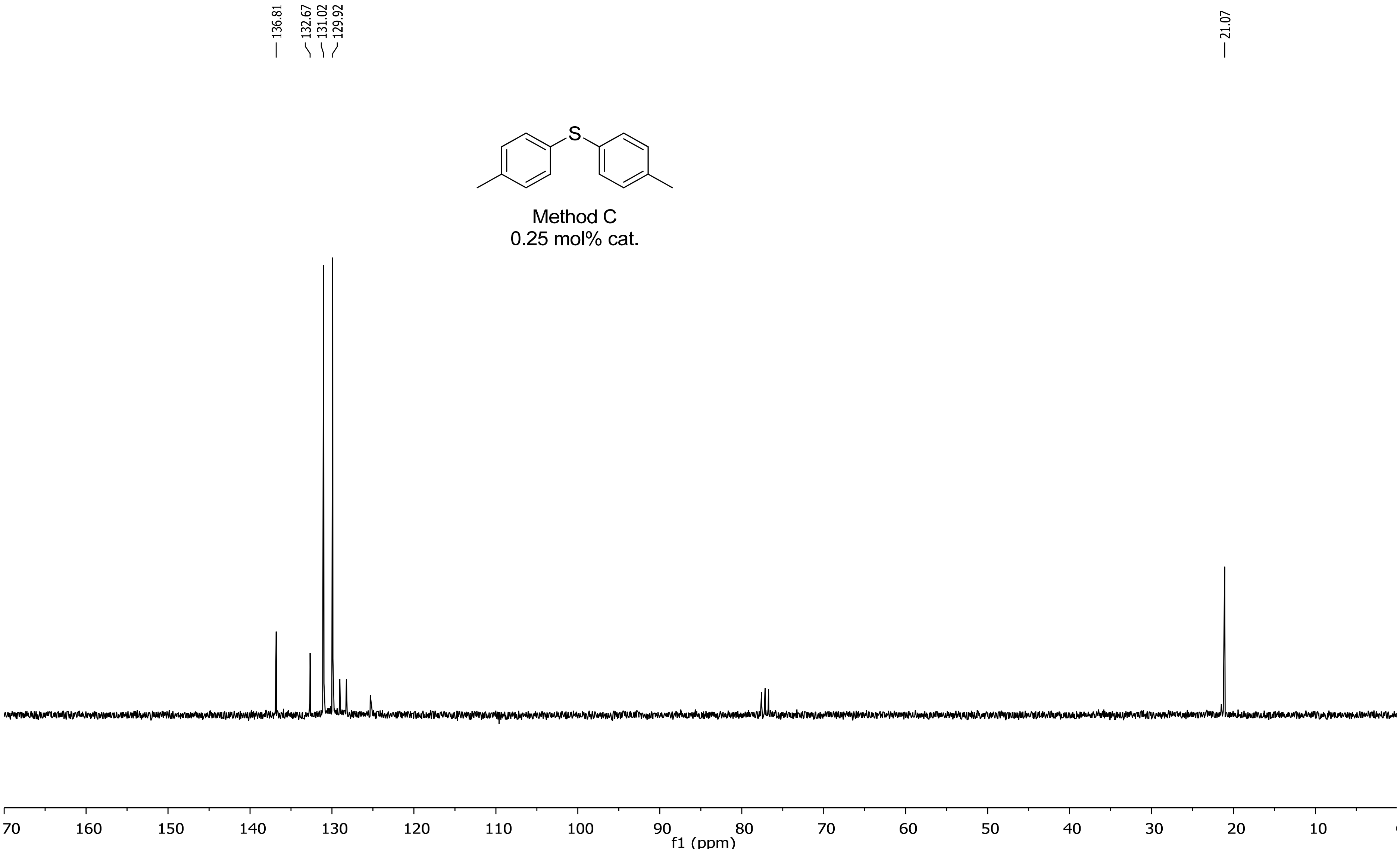

7.35
7.32
7.19
7.17
2.40
S
Method B
(10 mmol)
4.04
4.00
6.45
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


7.34
7.32
7.19
7.16
7.16
2.40
S
Method C
4.00
4.05
6.79
.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)

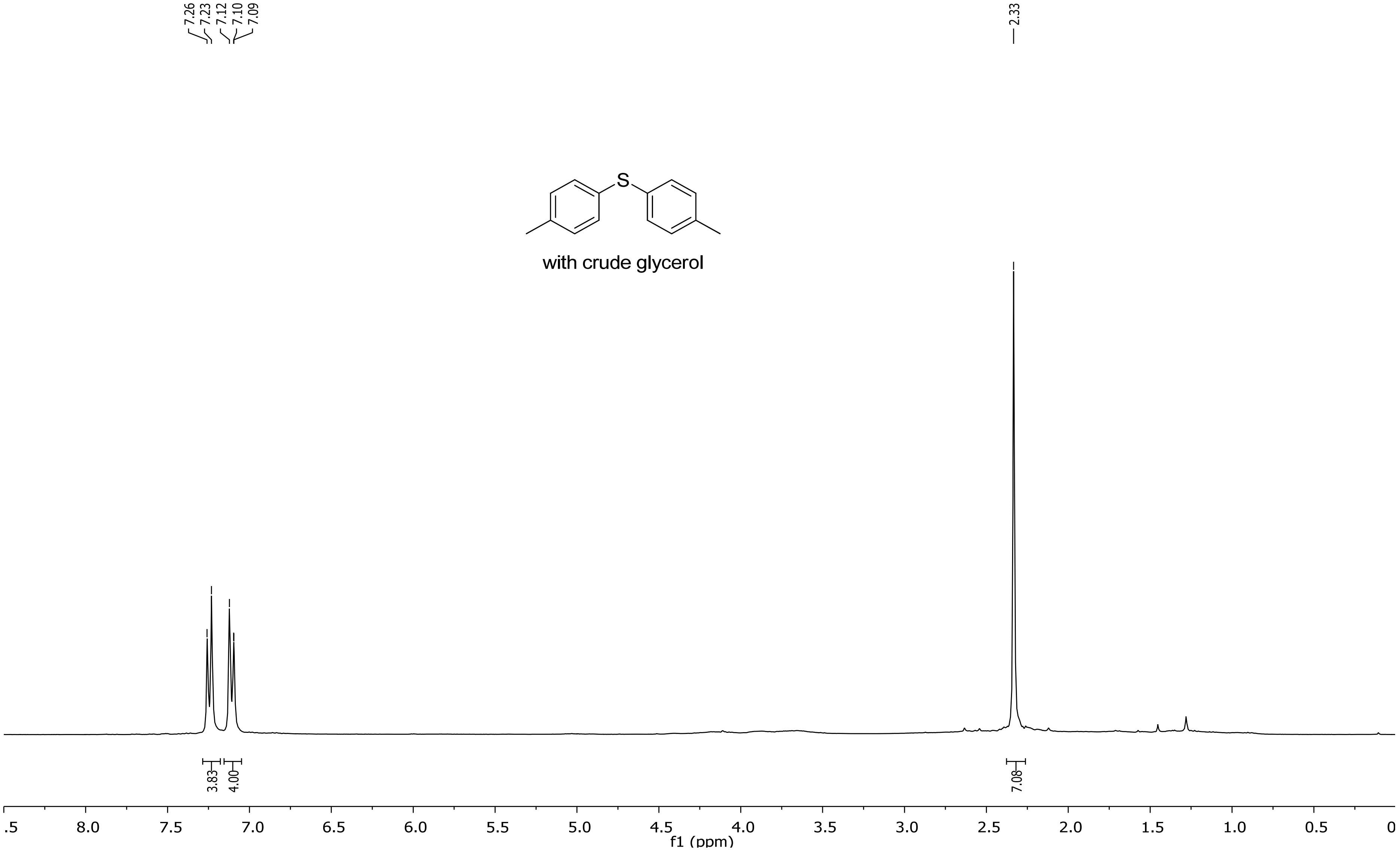

7.26
7.25
7.23
7.23
7.13
7.13
7.10
7.10
2.34
S
Method C
(25 mmol)
4.02
4.00
6.78
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

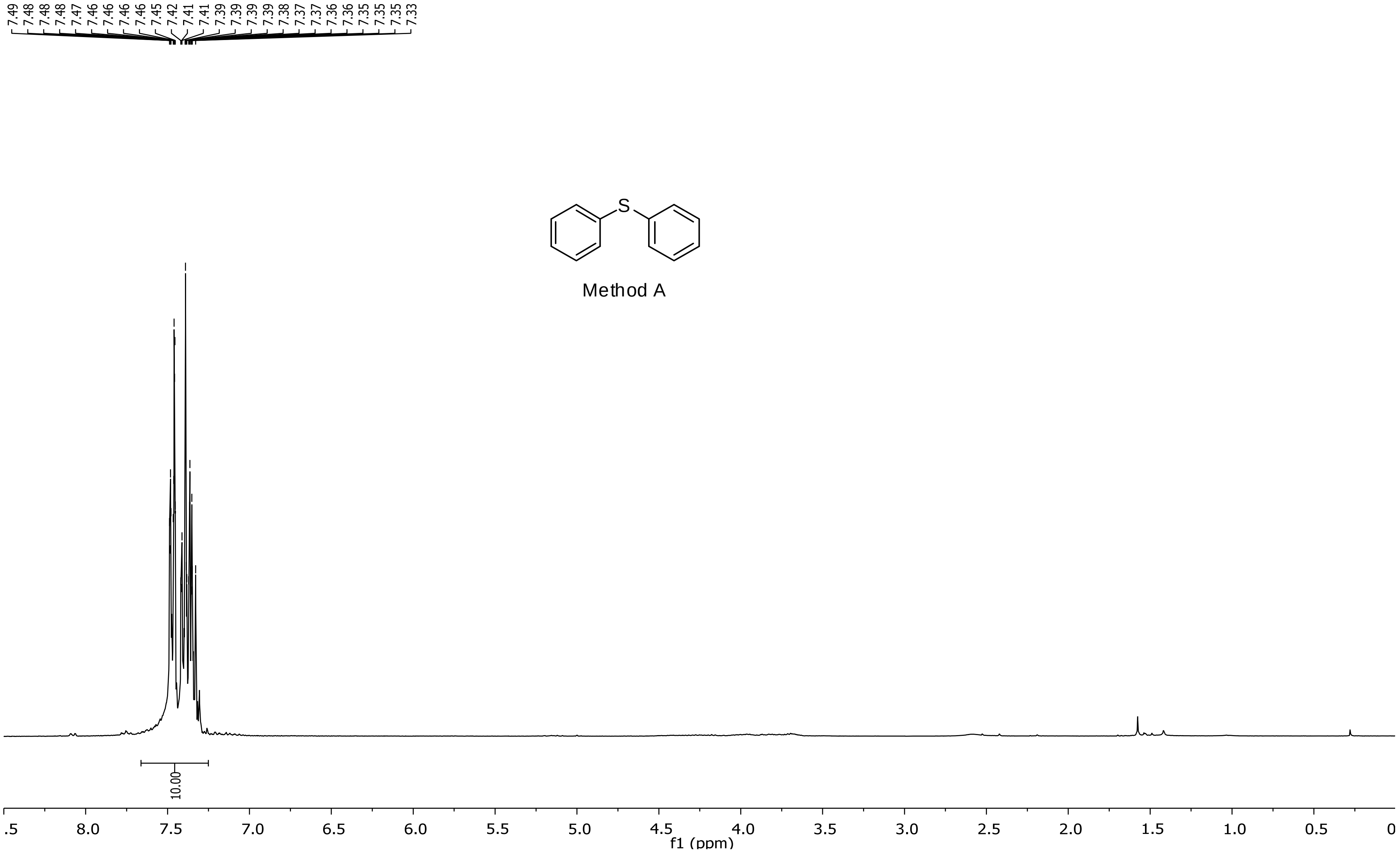

137.01
132.75
131.16
130.10
130.02
21.20
S
Method C
(25 mmol)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

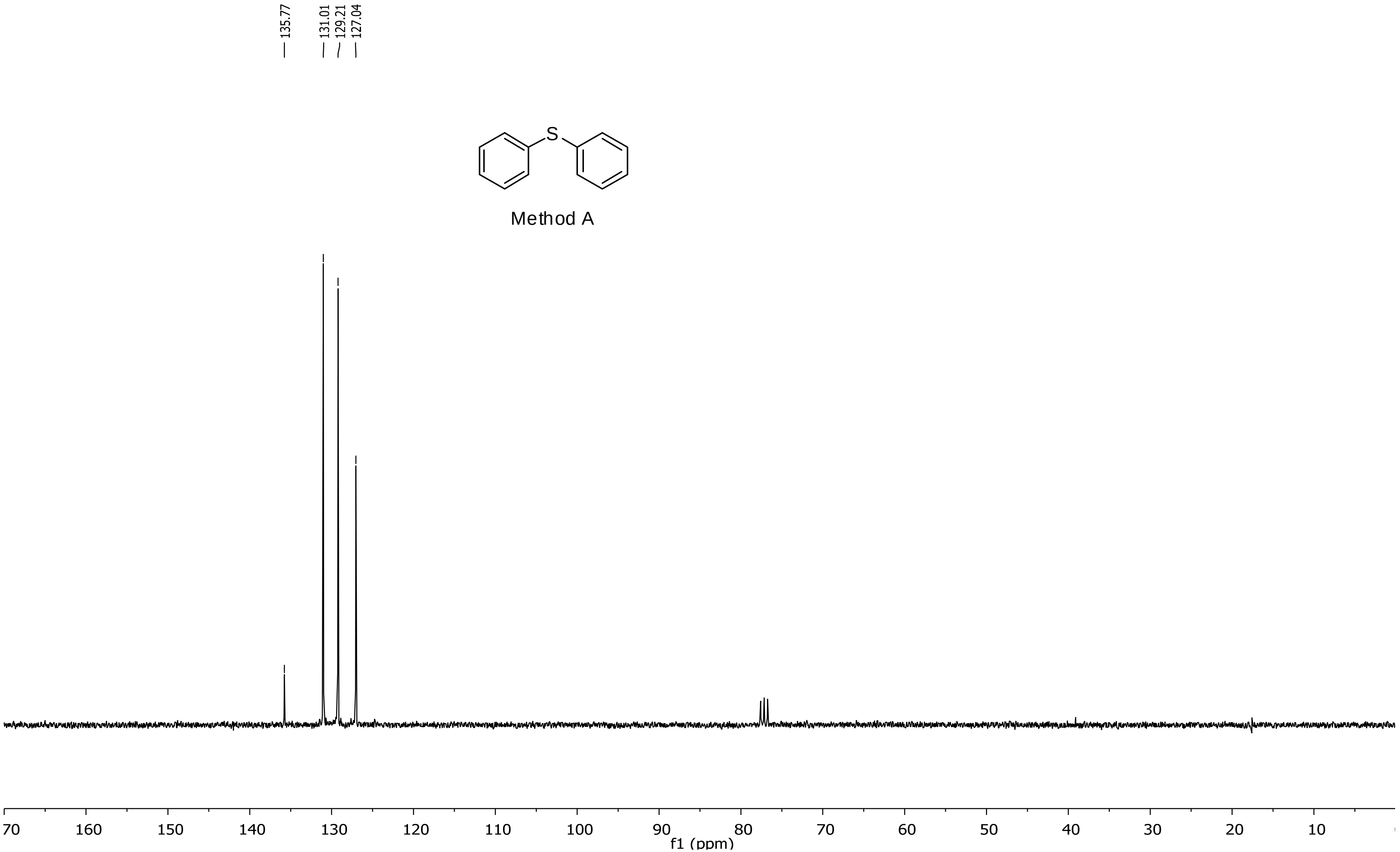

7.39
7.36
7.22
7.22
7.20
7.20
2.44
S
Method C
0.25 mol% cat.
4.18
4.00
6.54
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

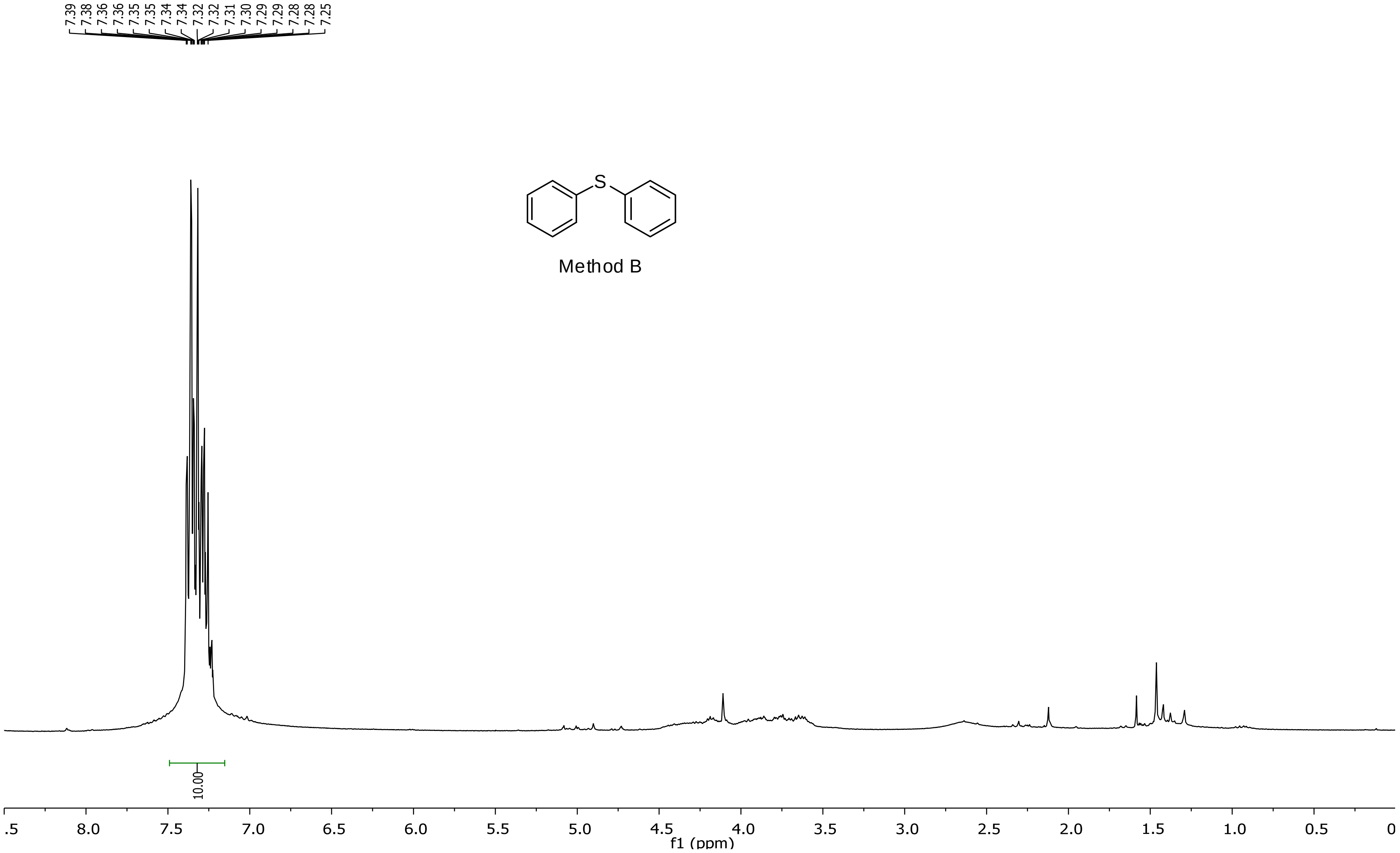


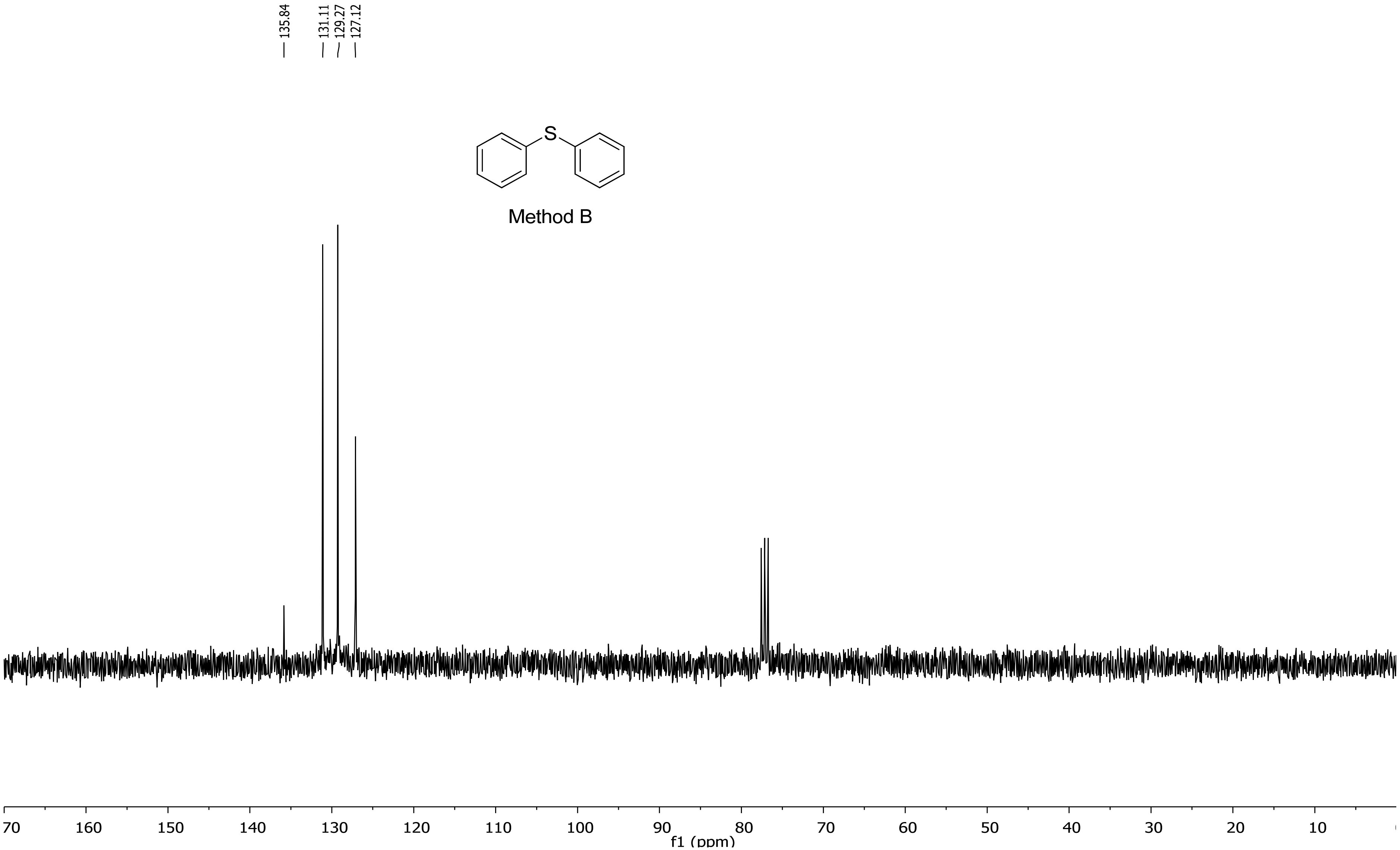
Method C
0.25 mol% cat.

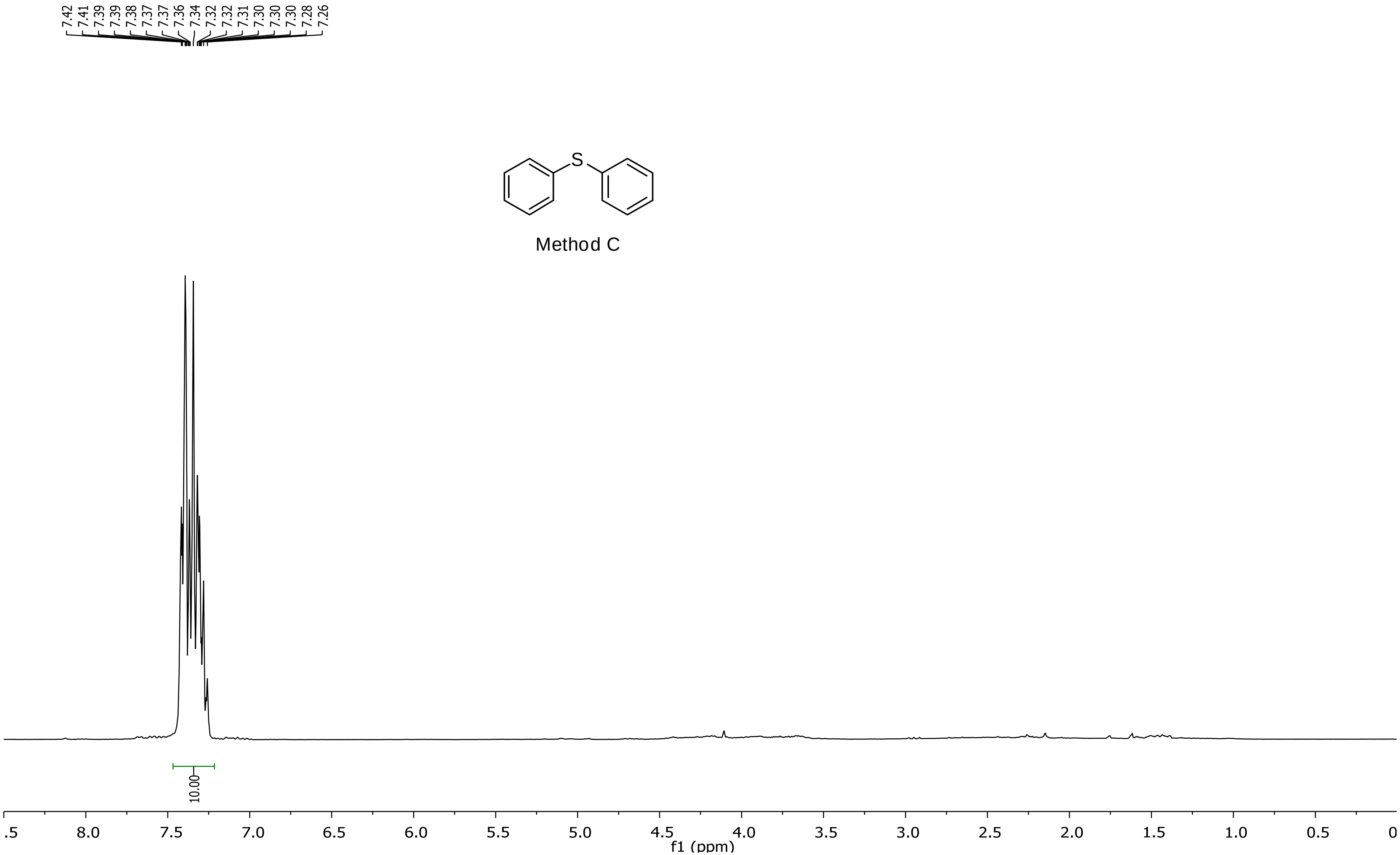

7.26
7.23
7.12
7.10
7.09
2.33
S
with crude glycerol
3.83
4.00
7.08
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

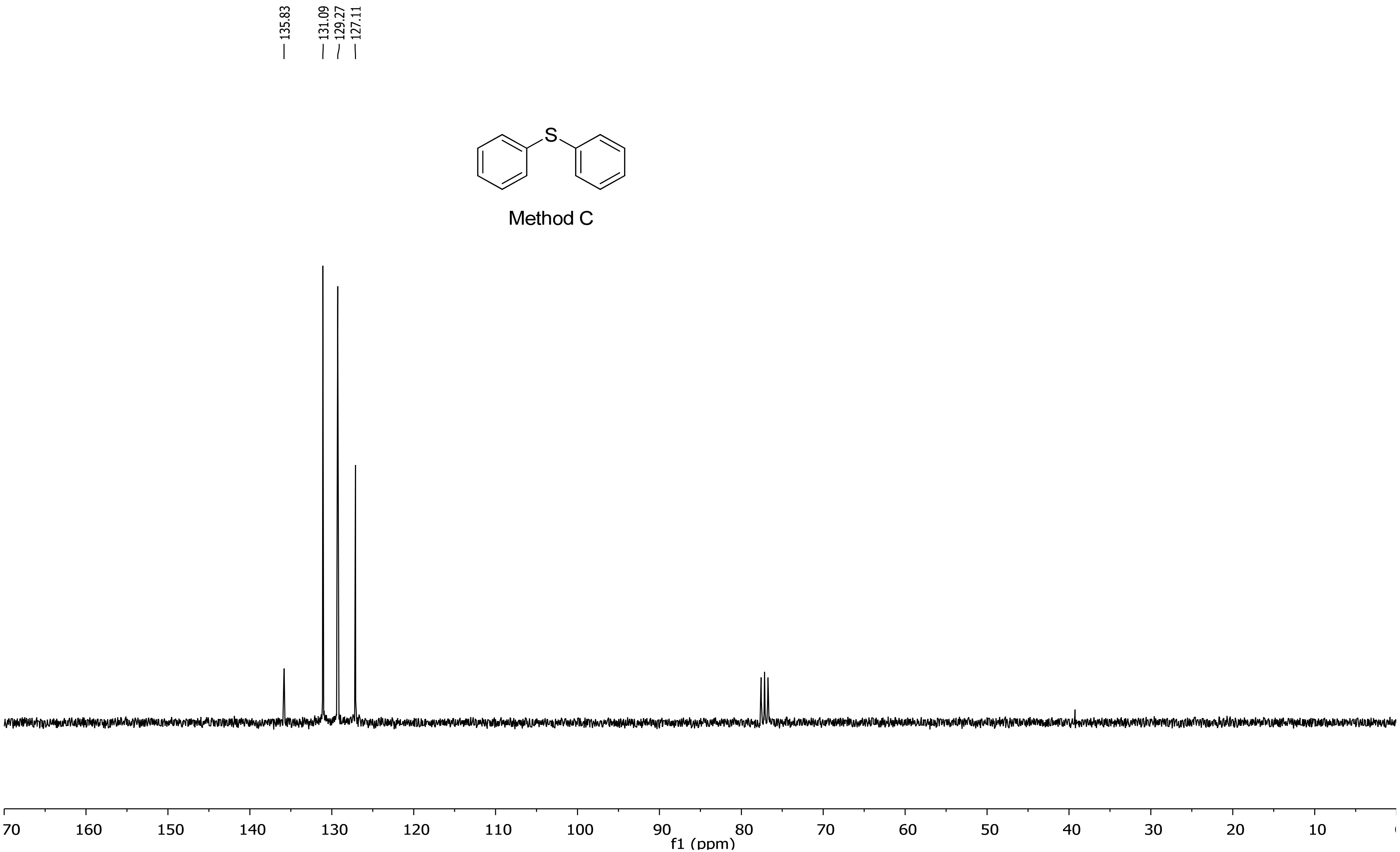

7.49
7.48
7.48
7.48
7.47
7.46
7.46
7.46
7.45
7.42
7.41
7.41
7.39
7.39
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.33
S
Method A
10.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

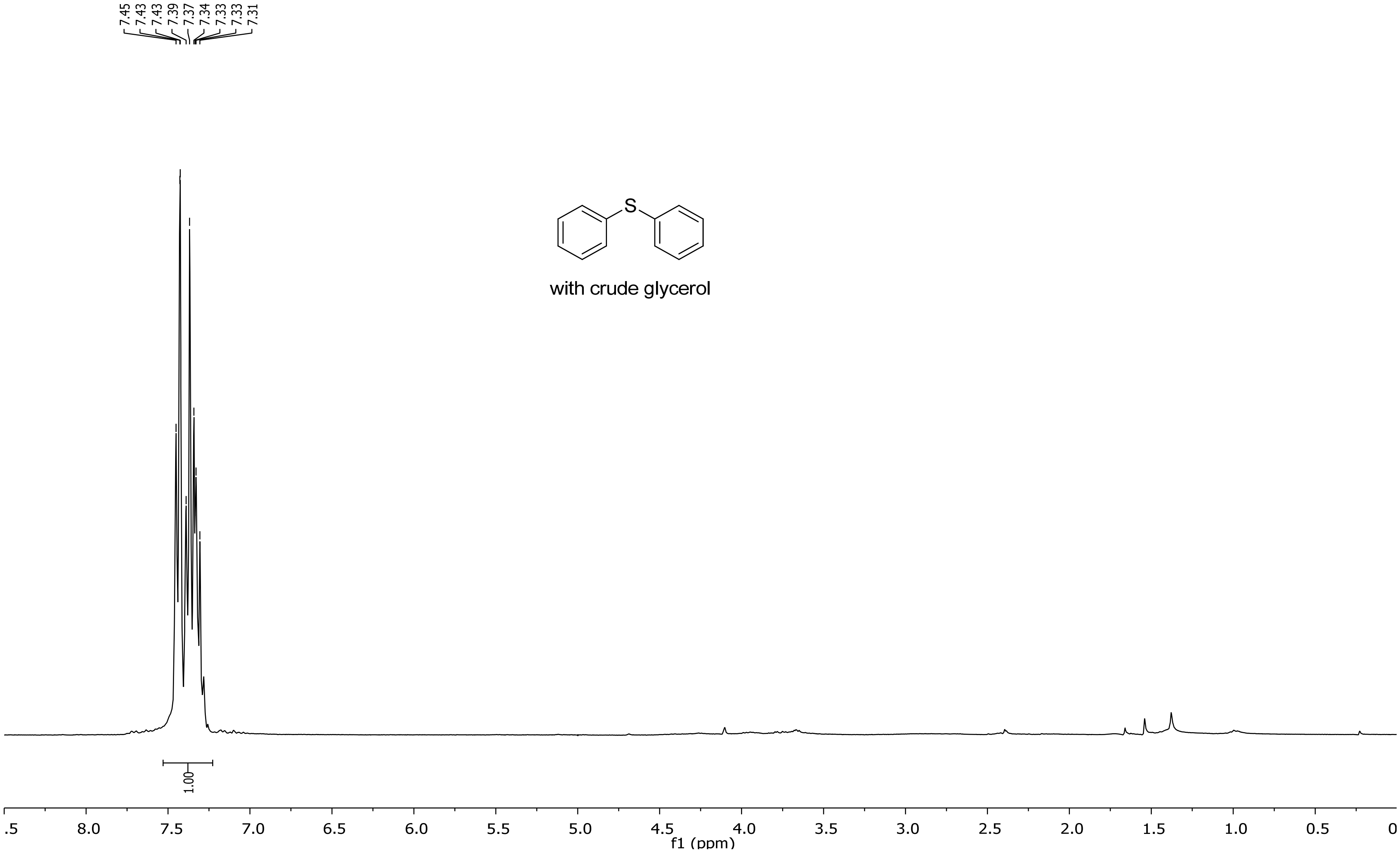

135.77
131.01
129.21
127.04
S
Method A
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

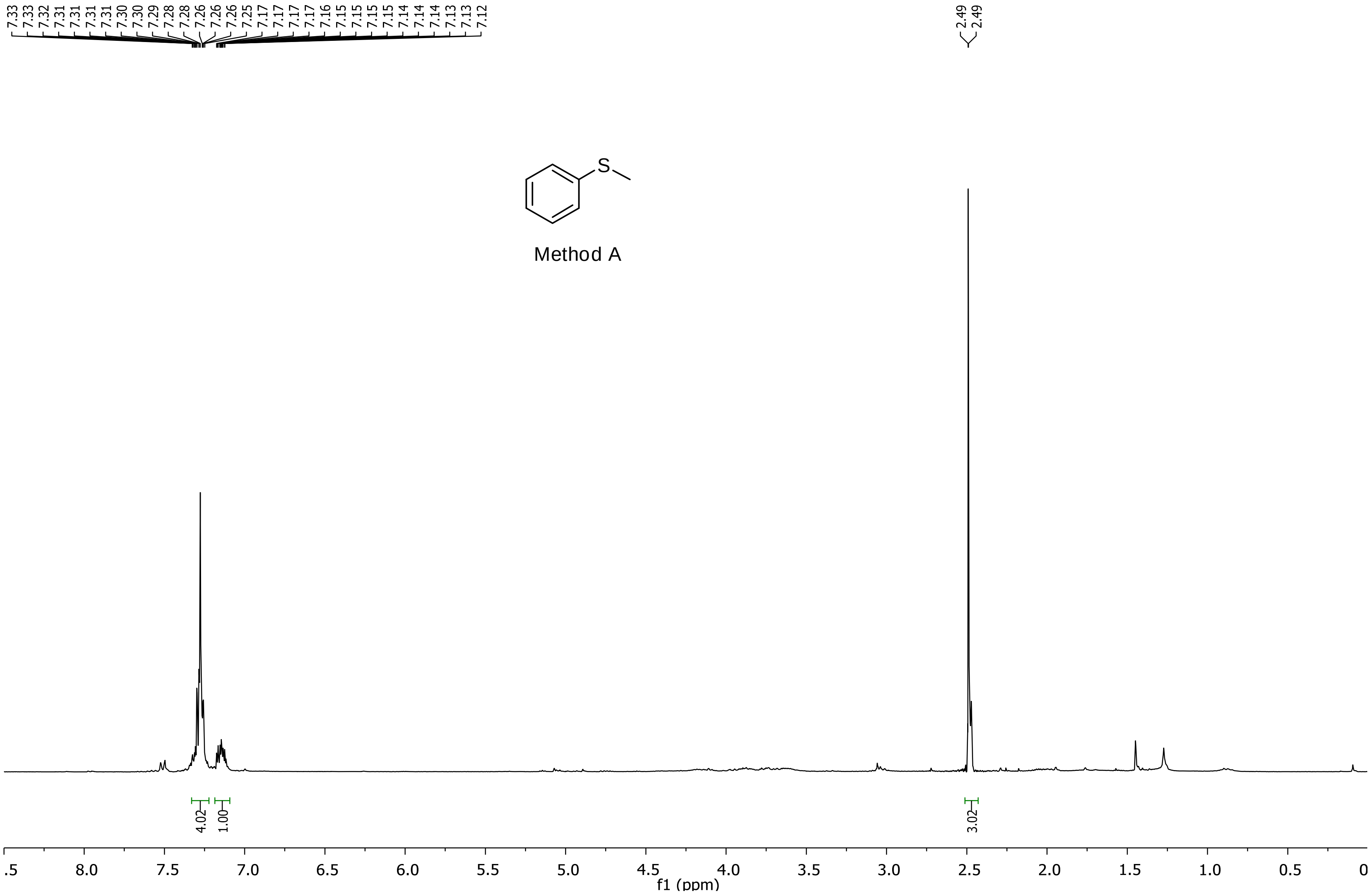

7.39
7.38
7.36
7.36
7.35
7.35
7.34
7.34
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.25
S
Method B
10.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


135.84
131.11
129.27
127.12
S
Method B
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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
S
Method C
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)


135.83
131.09
129.27
127.11
S
Method C
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.45
7.43
7.43
7.39
7.37
7.34
7.33
7.33
7.31
S
with crude glycerol
1.00
.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)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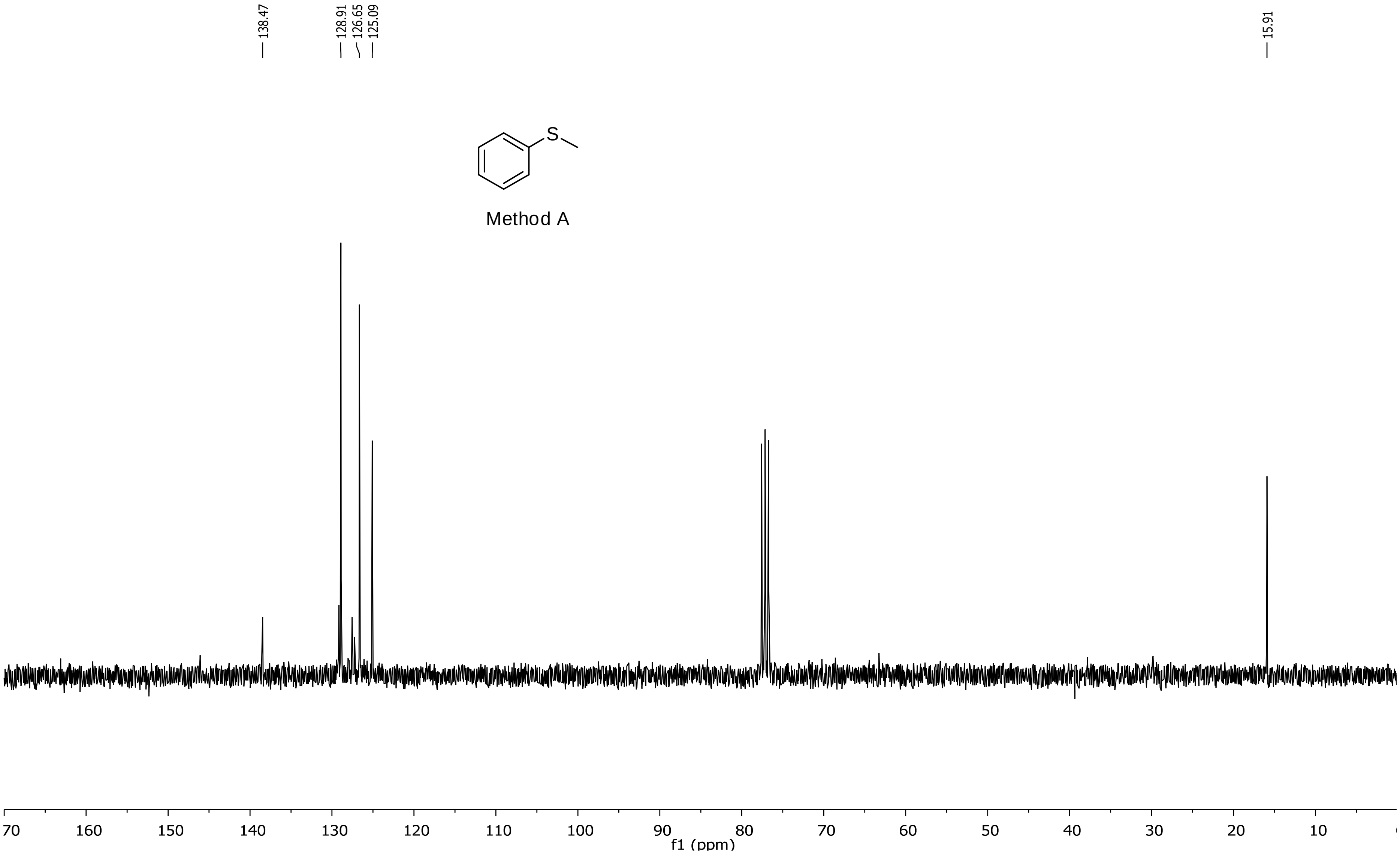
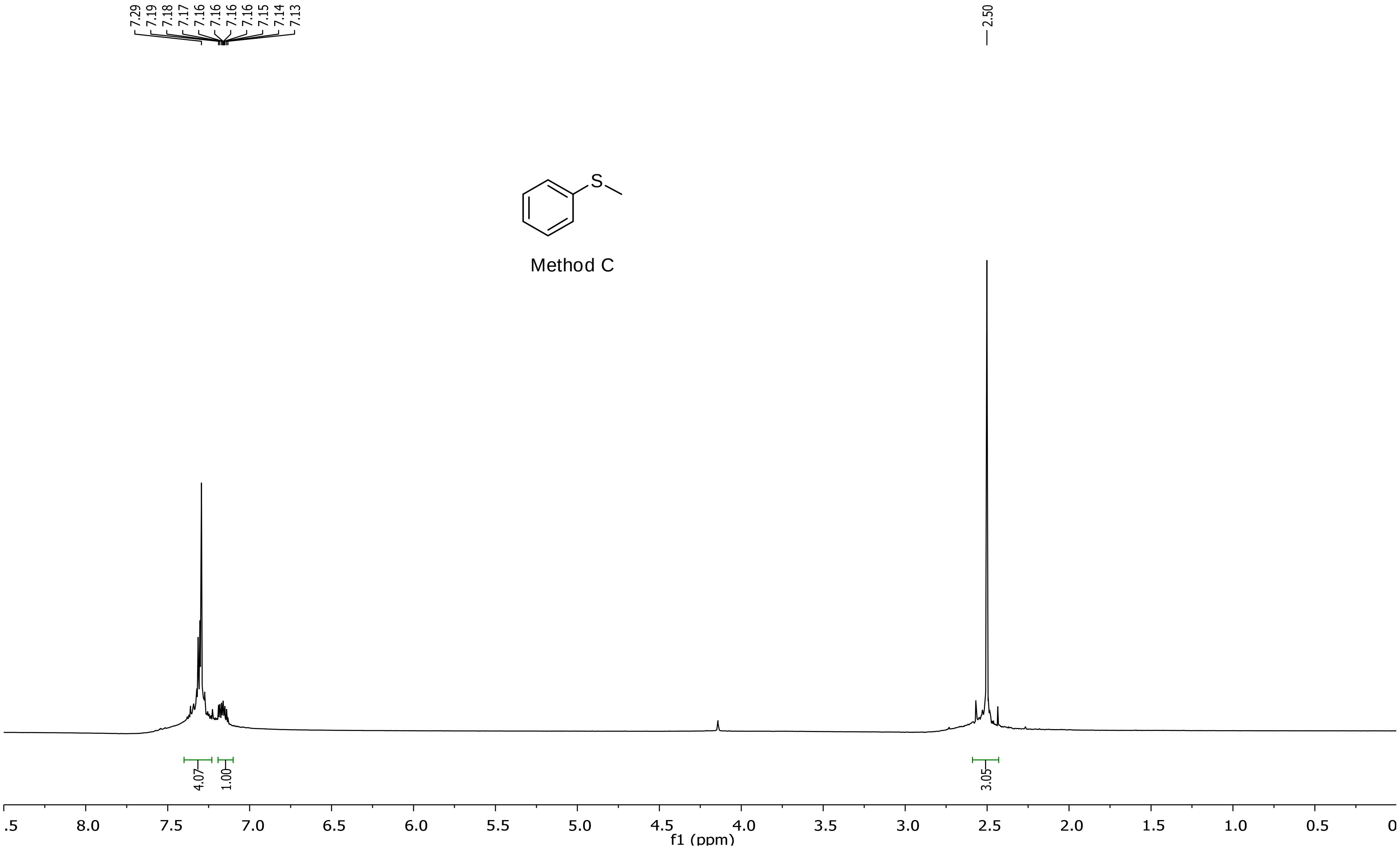
7.33
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.26
7.26
7.26
7.25
7.17
7.17
7.17
7.17
7.16
7.15
7.15
7.15
7.15
7.14
7.14
7.14
7.13
7.13
7.12
2.49
2.49
S
4.02
1.00
3.02
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

Method A


138.47
128.91
126.65
125.09
15.91
S
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Method A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7.18
7.17
7.16
7.16
7.16
7.16
7.15
7.14
7.13
2.50
S
Method C
4.07
1.00
3.05
.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
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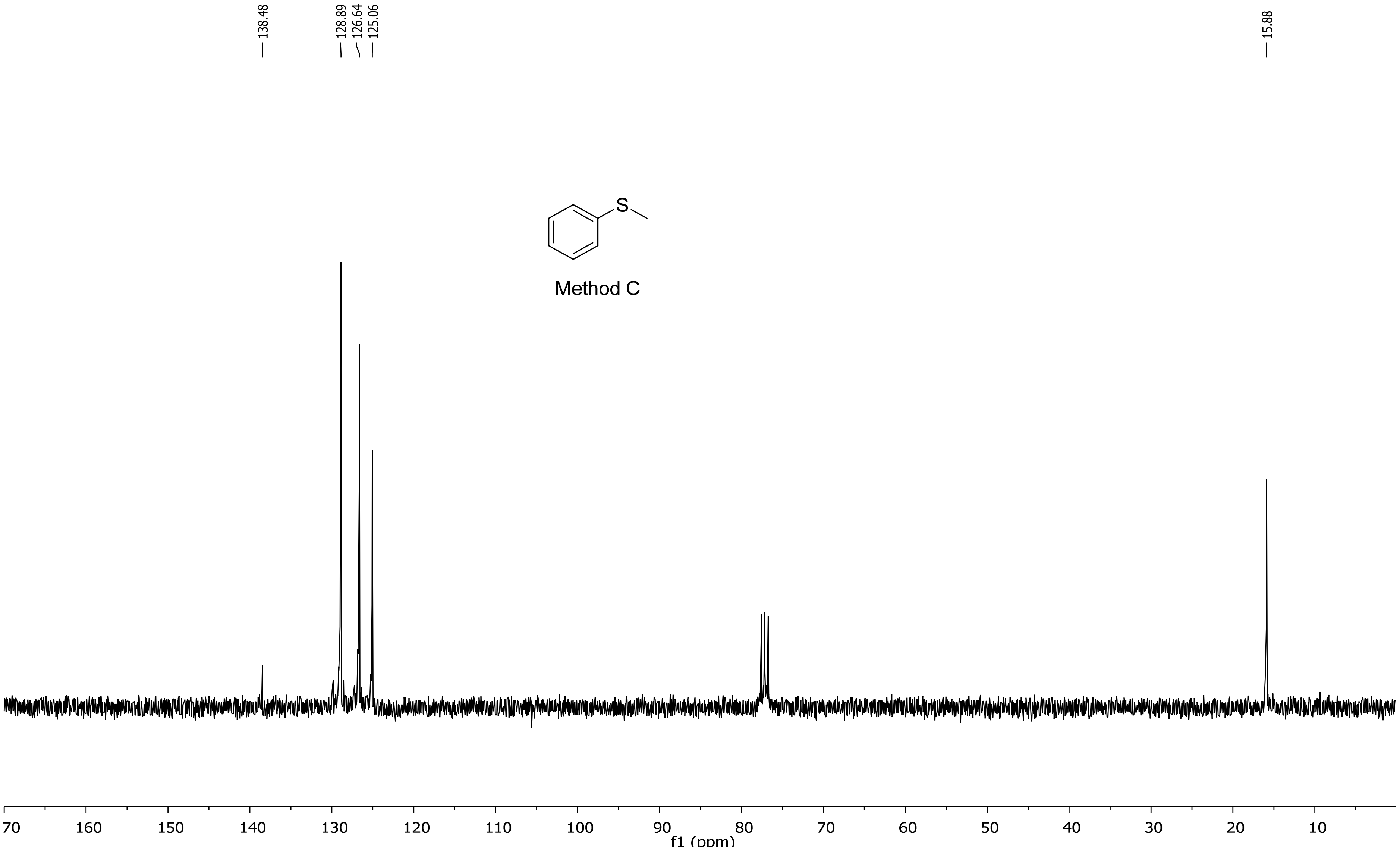
0
f1 (ppm)


138.48
128.89
126.64
125.06
15.88
S
Method C
70
160
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100
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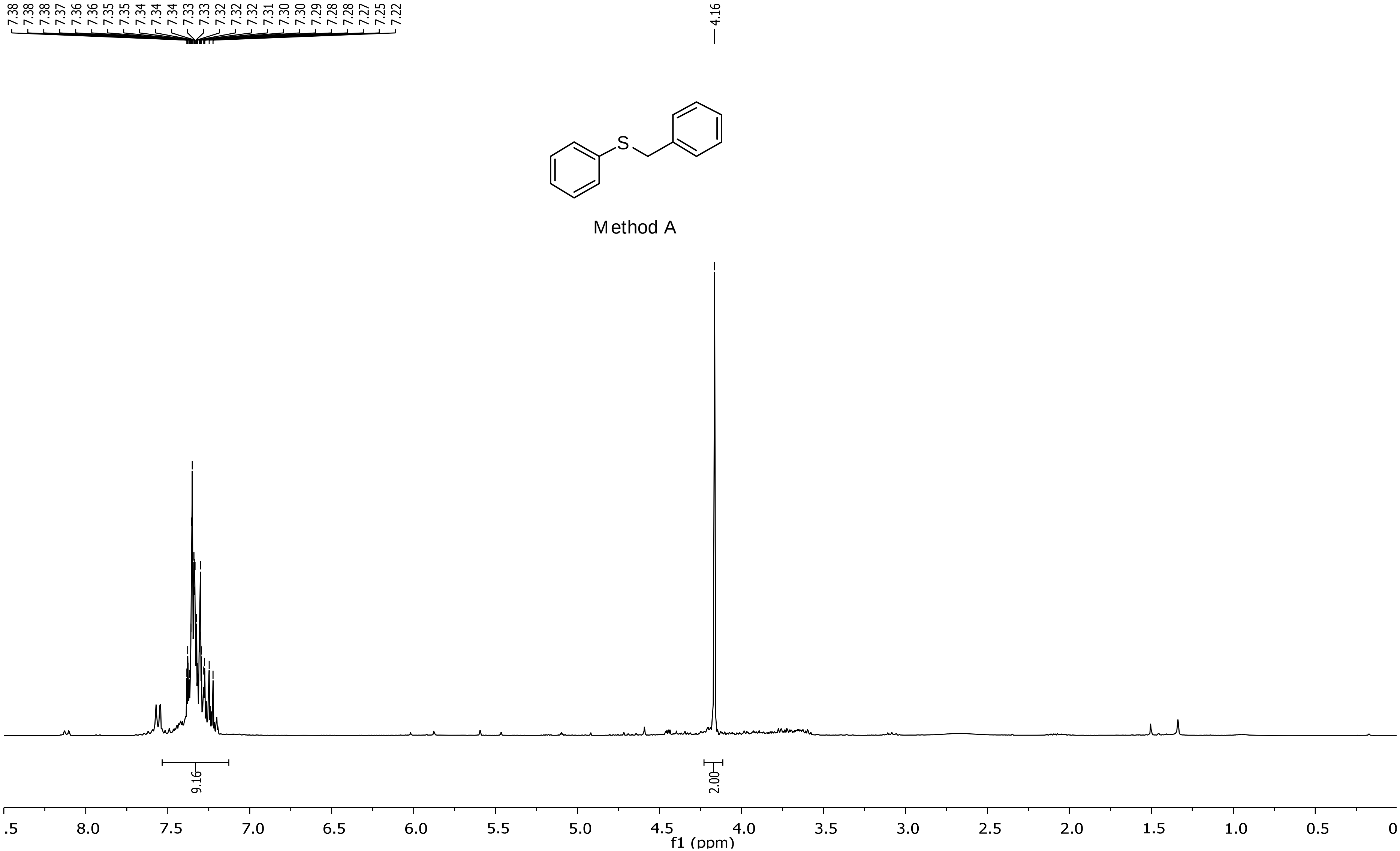
80
70
60
50
40
30
20
10
f1 (ppm)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7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.25
7.22
4.16
S
Method A
9.16
2.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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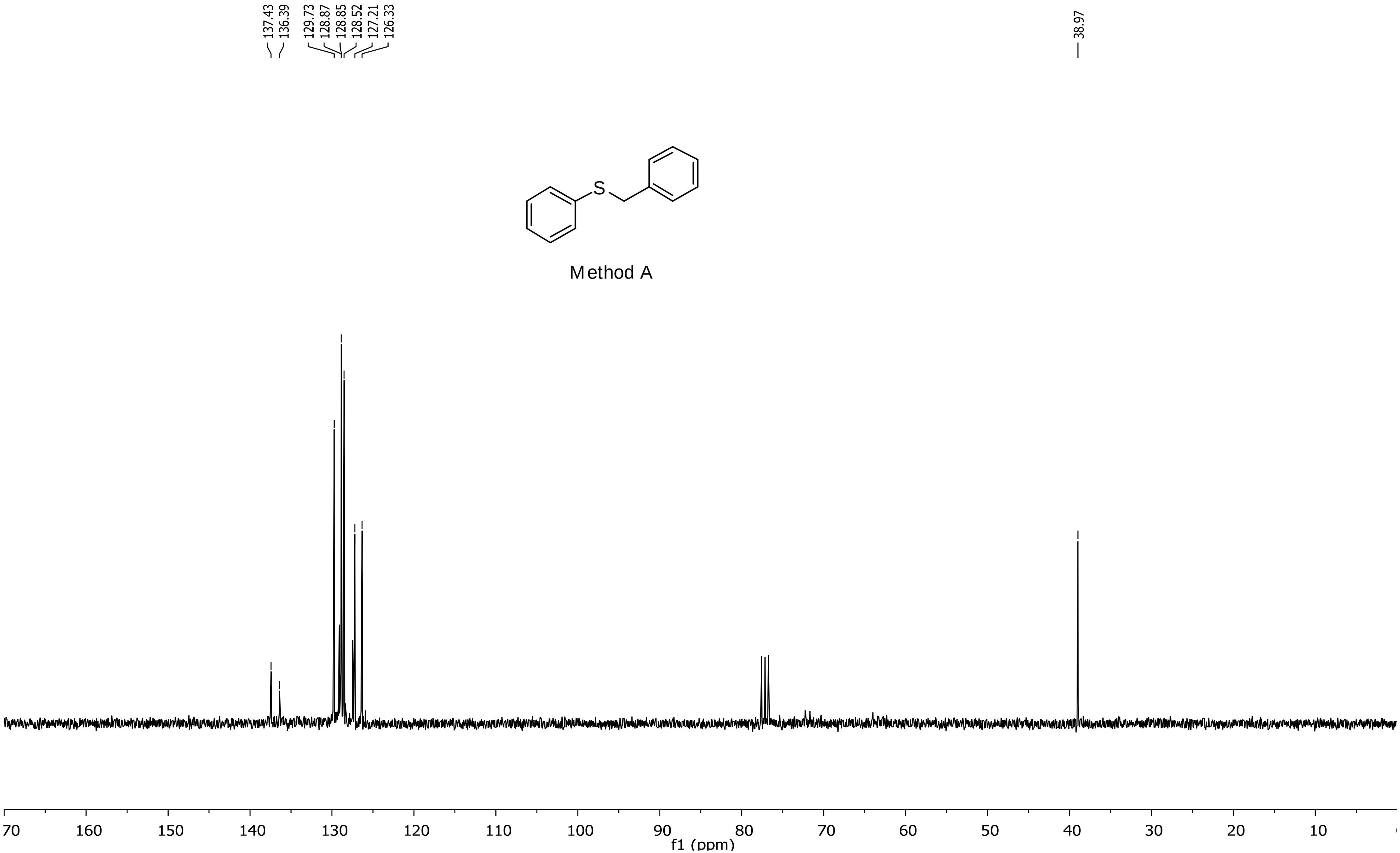
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


137.43
136.39
129.73
128.87
128.85
128.52
127.21
126.33
38.97
S
Method A
70
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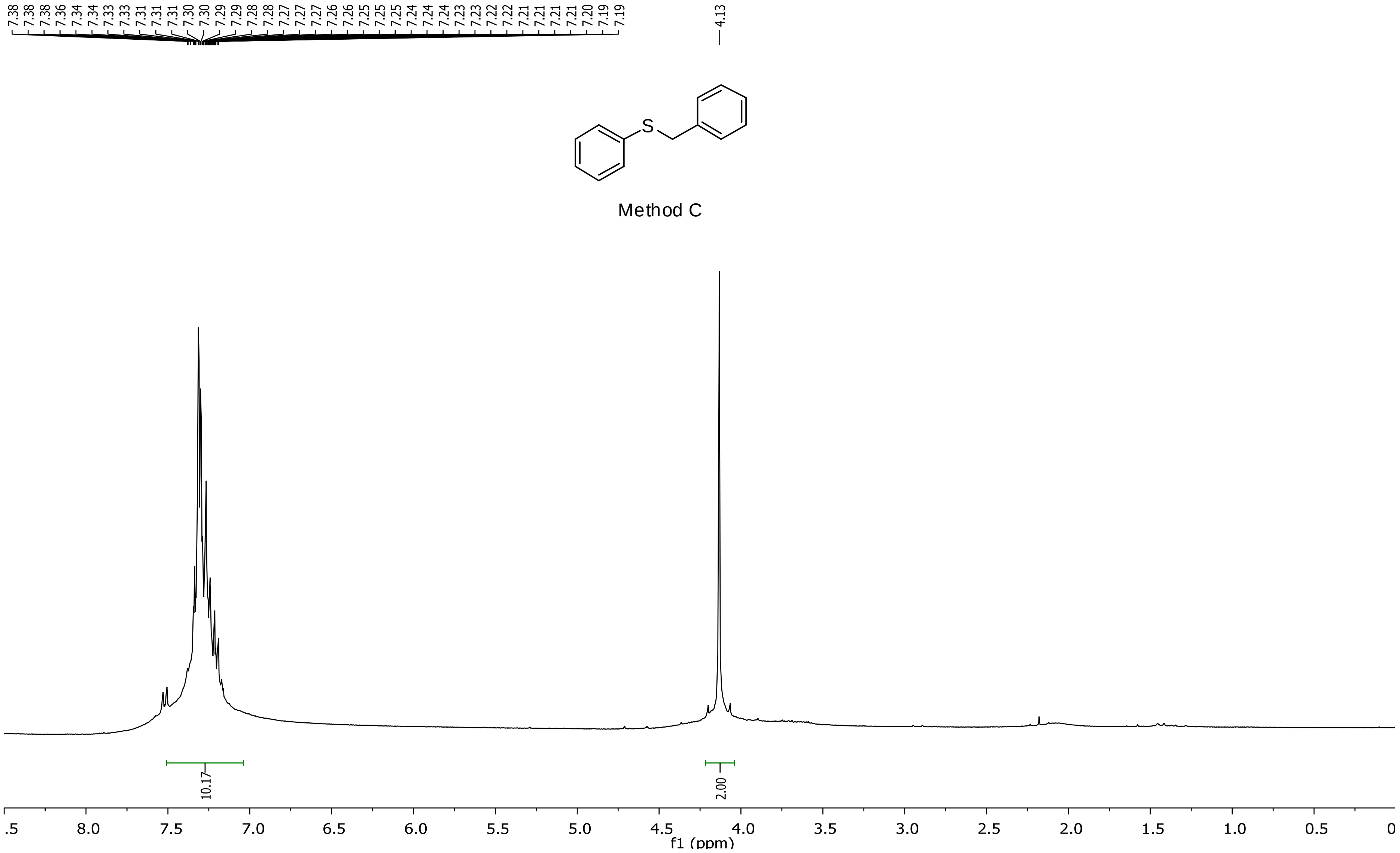
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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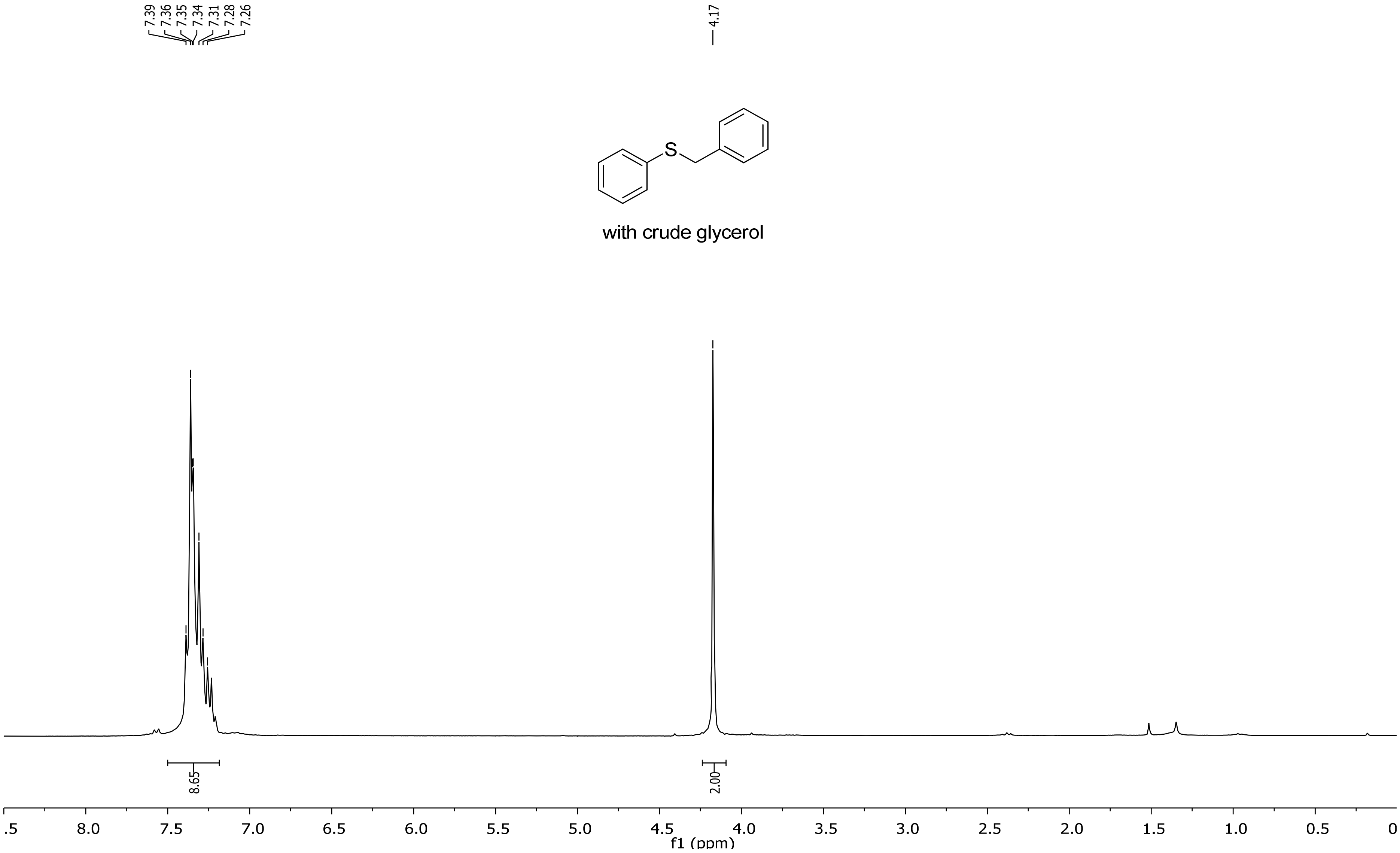
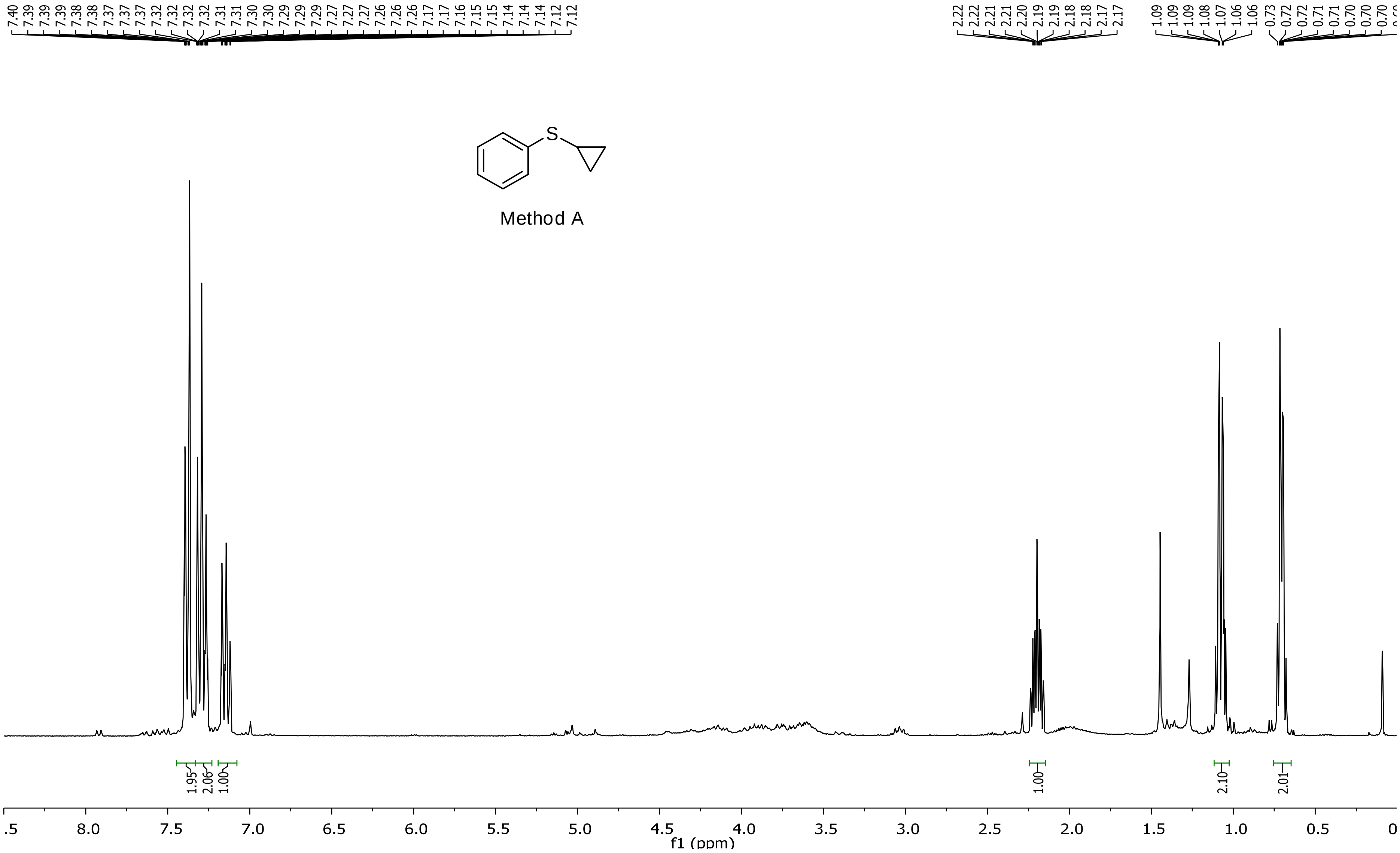
7.34
7.33
7.33
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.21
7.20
7.19
7.19
4.13
S
Method C
10.17
2.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


with crude glycerol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7.37
7.37
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7.32
7.32
7.32
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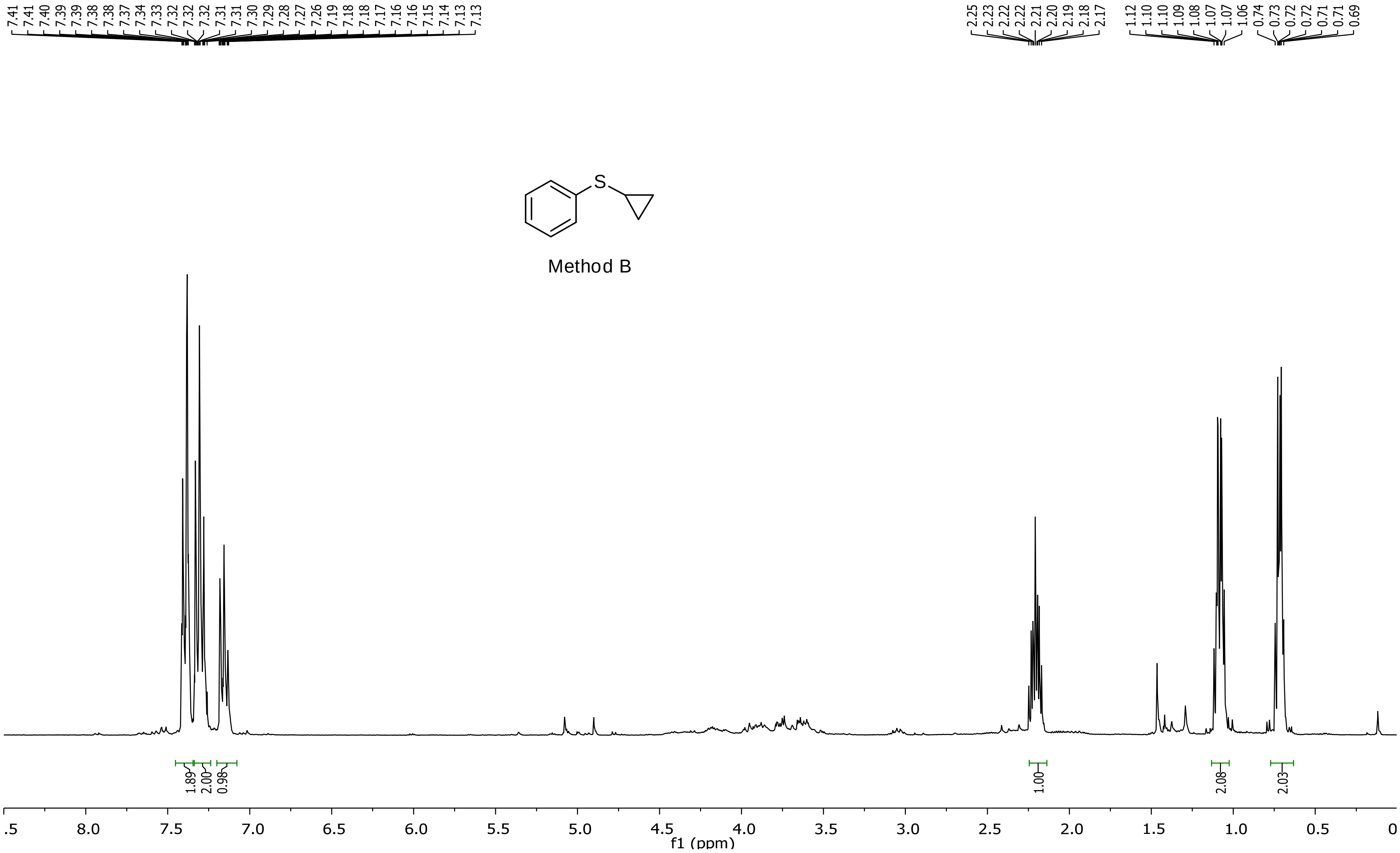
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.27
7.27
7.27
7.26
7.26
7.26
7.17
7.17
7.16
7.15
7.15
7.14
7.14
7.14
7.12
7.12
2.22
2.22
2.21
2.21
2.20
2.19
2.19
2.18
2.18
2.17
2.17
1.09
1.09
1.09
1.08
1.07
1.06
1.06
0.73
0.72
0.72
0.71
0.70
0.70
0.70
S
Method A
1.95
2.06
1.00
1.00
2.10
2.01
.5
8.0
7.5
7.0
6.5
6.0
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)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7.37
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7.33
7.32
7.32
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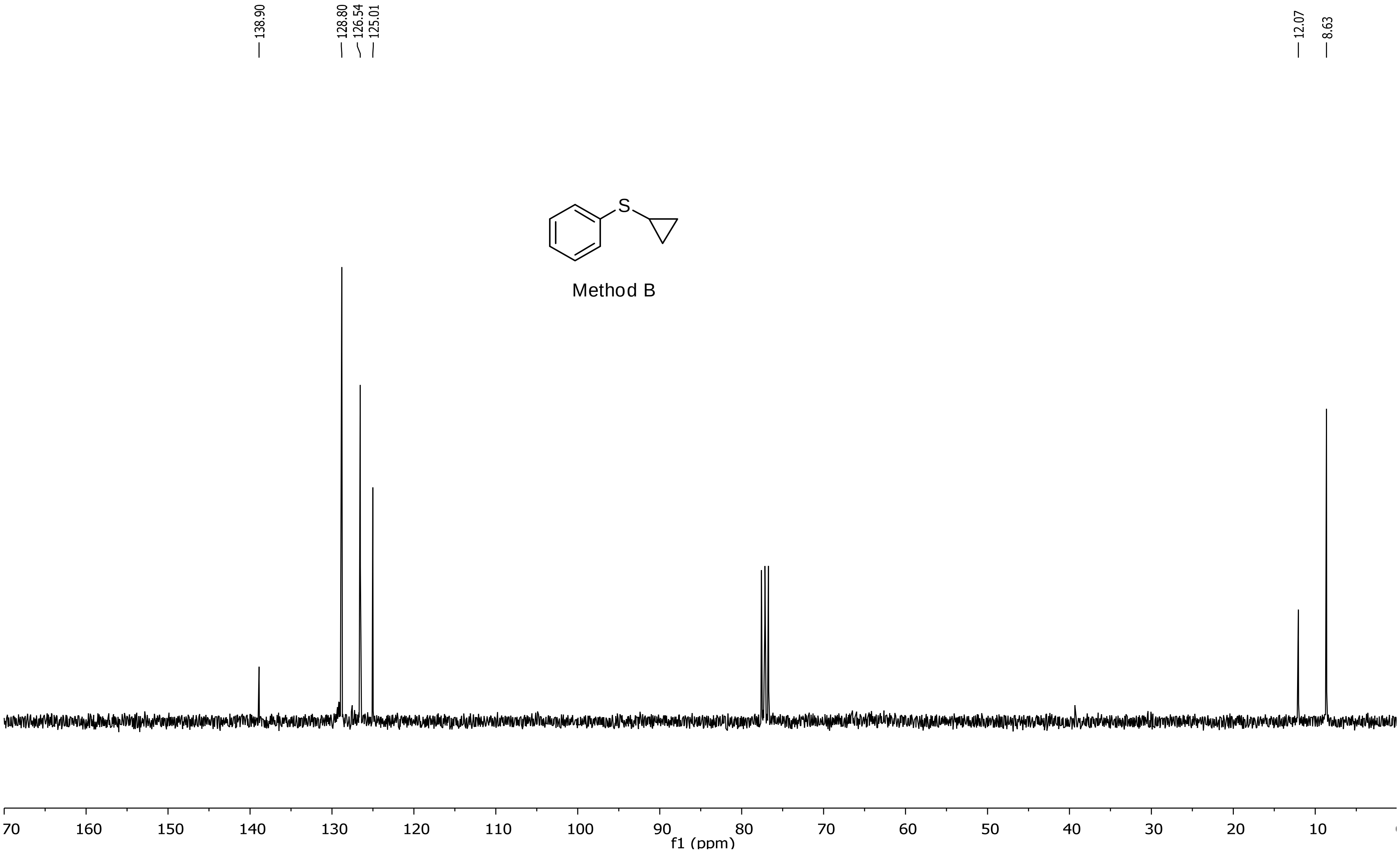
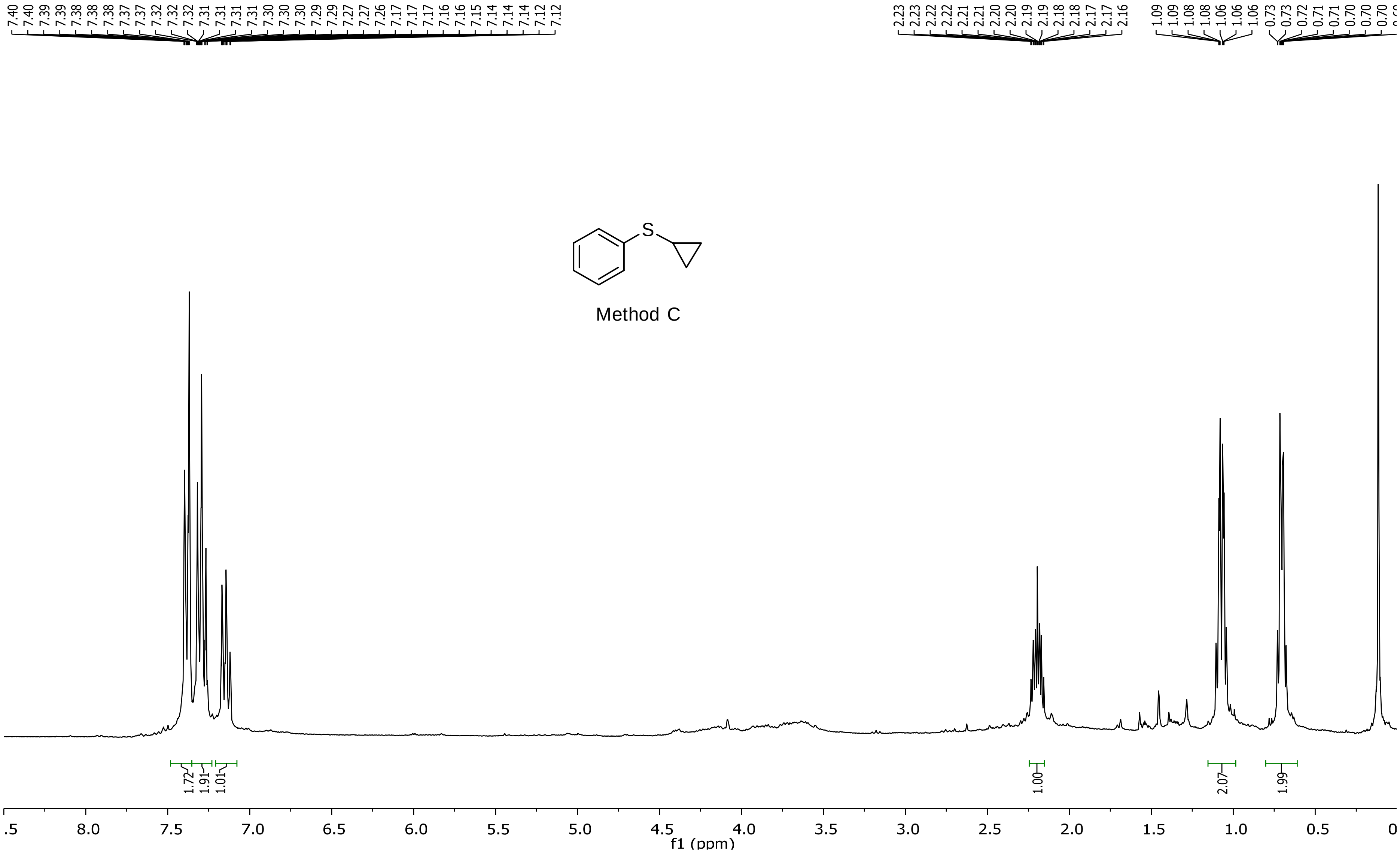
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.14
7.13
7.13
2.25
2.23
2.22
2.22
2.21
2.20
2.19
2.18
2.17
1.12
1.10
1.10
1.09
1.08
1.07
1.07
1.06
0.74
0.73
0.72
0.72
0.71
0.71
0.69
S
Method B
1.89
2.00
0.98
1.00
2.08
2.03
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


138.90
128.80
126.54
125.01
12.07
8.63
S
Method B
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.32
7.32
7.32
7.31
7.31
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7.31
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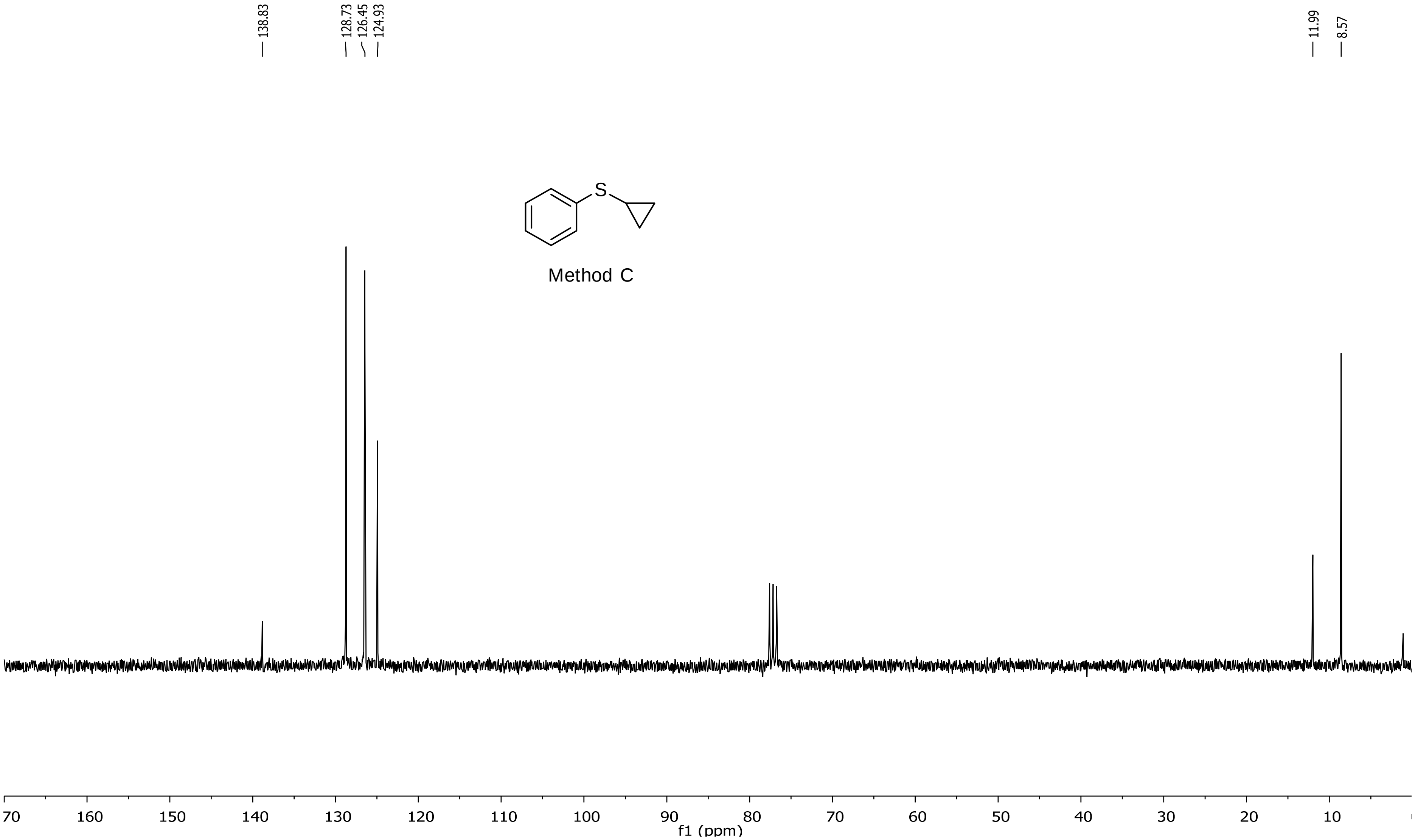
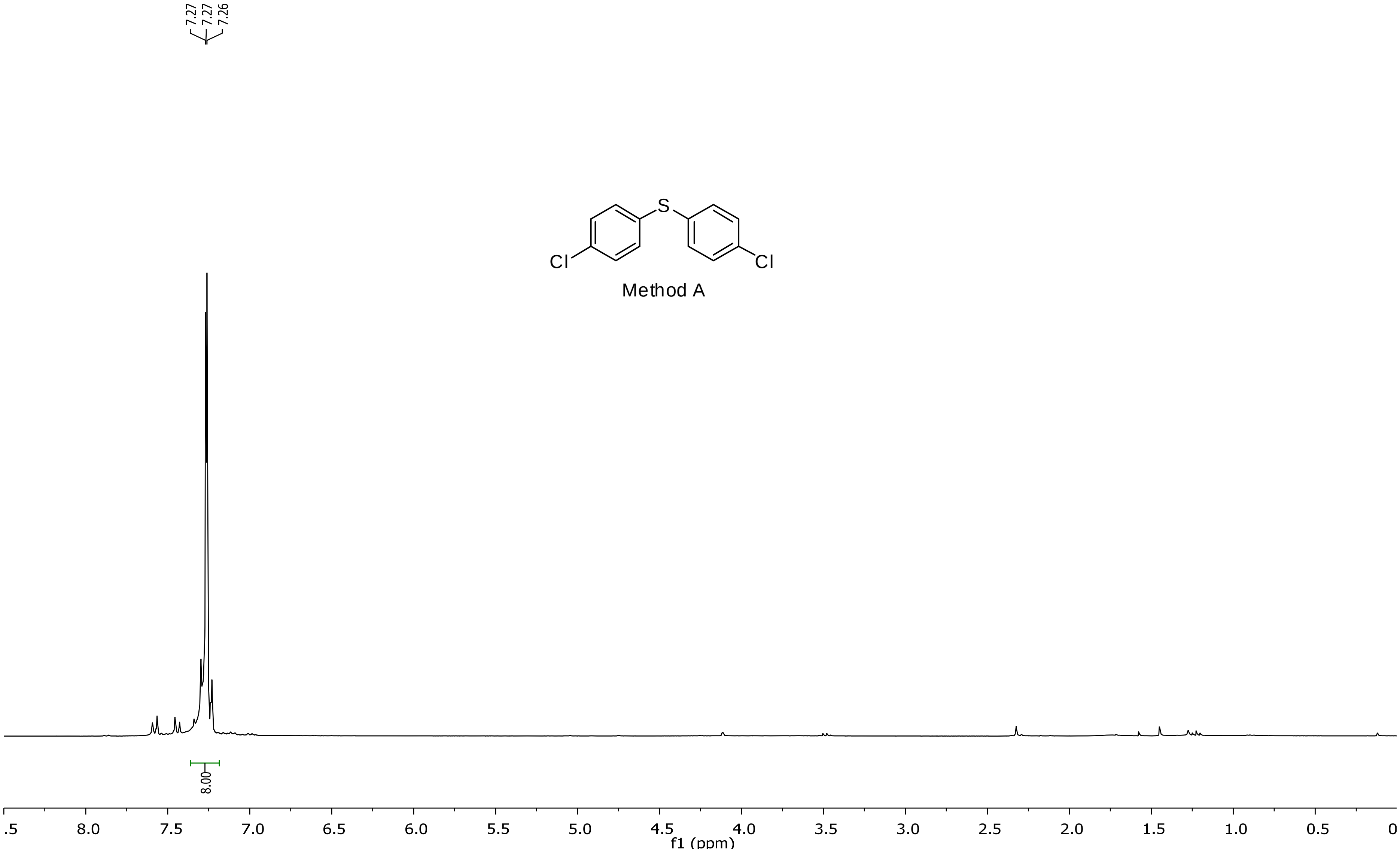
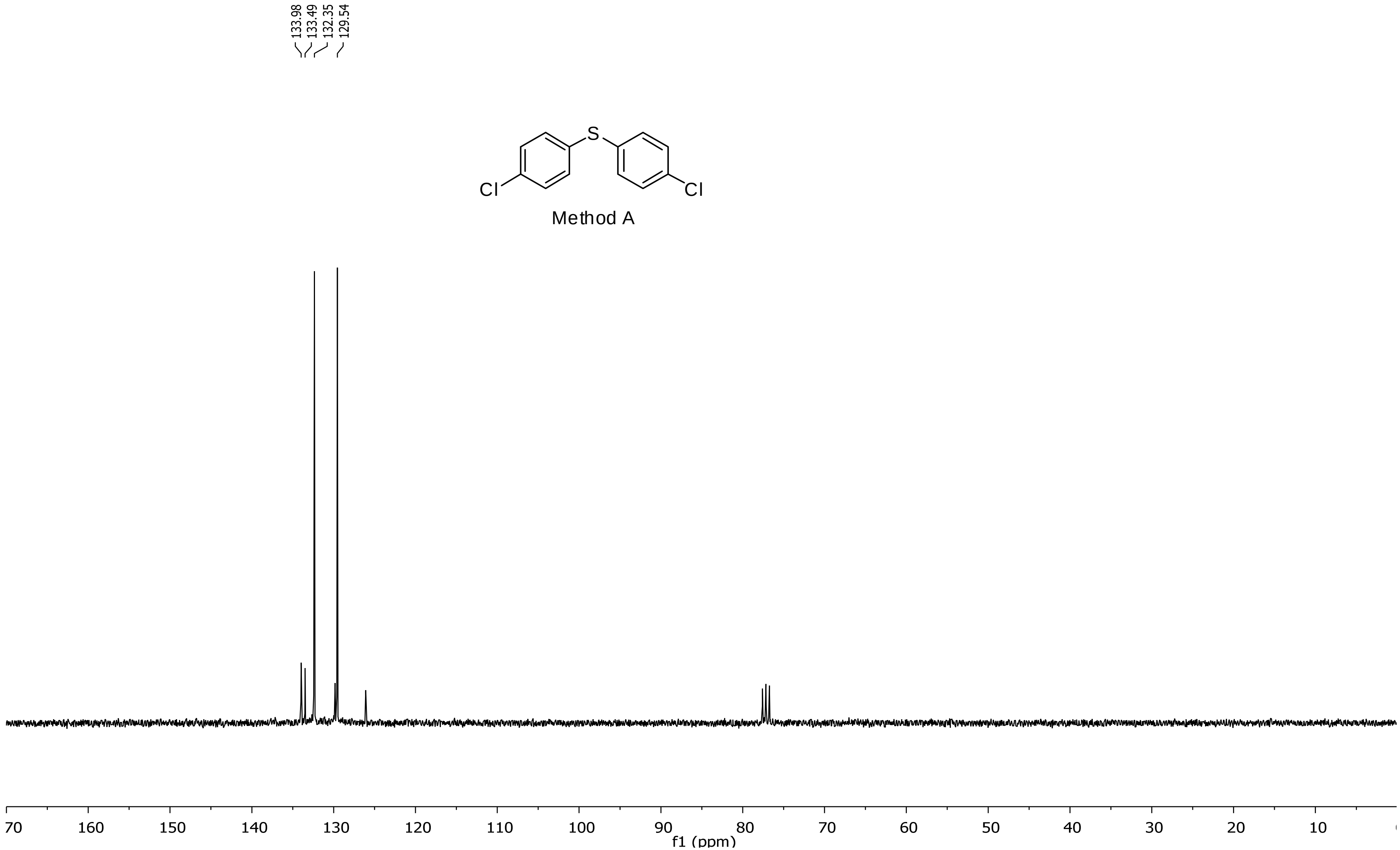
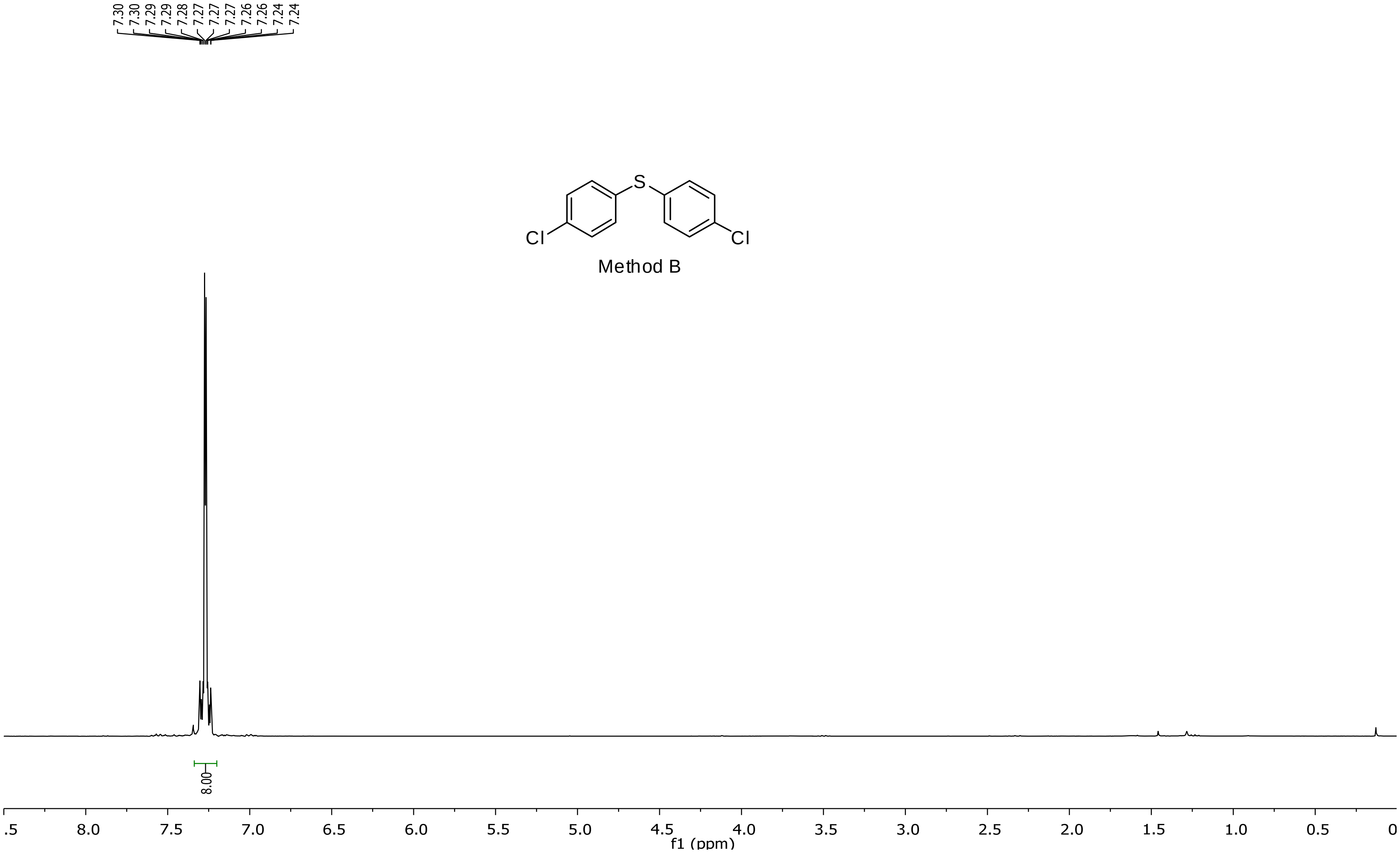
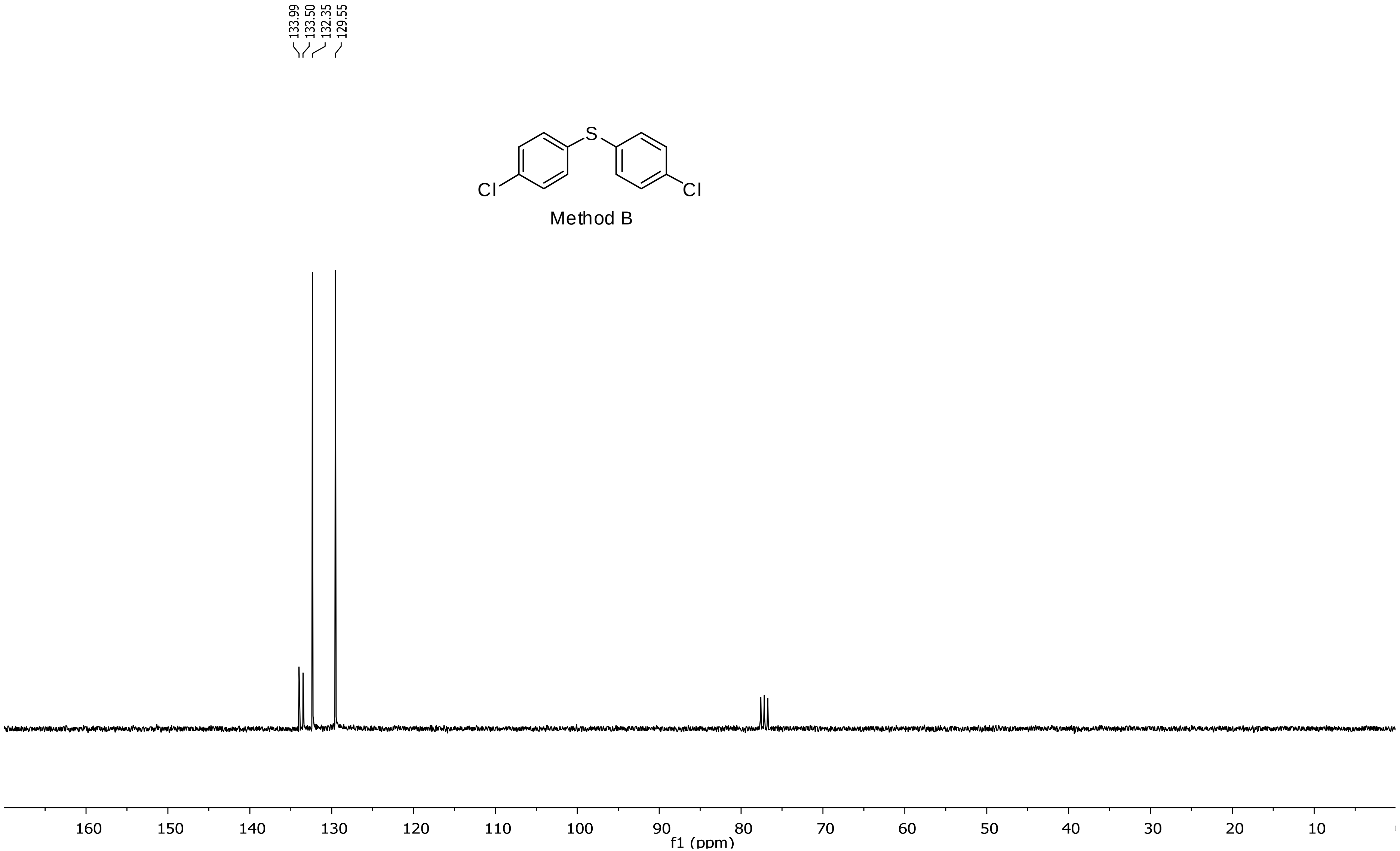
7.30
7.29
7.29
7.27
7.27
7.26
7.17
7.17
7.17
7.17
7.16
7.16
7.15
7.14
7.14
7.14
7.12
7.12
2.23
2.23
2.22
2.22
2.21
2.21
2.20
2.20
2.19
2.19
2.18
2.18
2.17
2.17
2.16
1.09
1.09
1.08
1.08
1.06
1.06
1.06
0.73
0.73
0.72
0.71
0.70
0.70
0.70
S
Method C
1.72
1.91
1.01
1.00
2.07
1.99
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

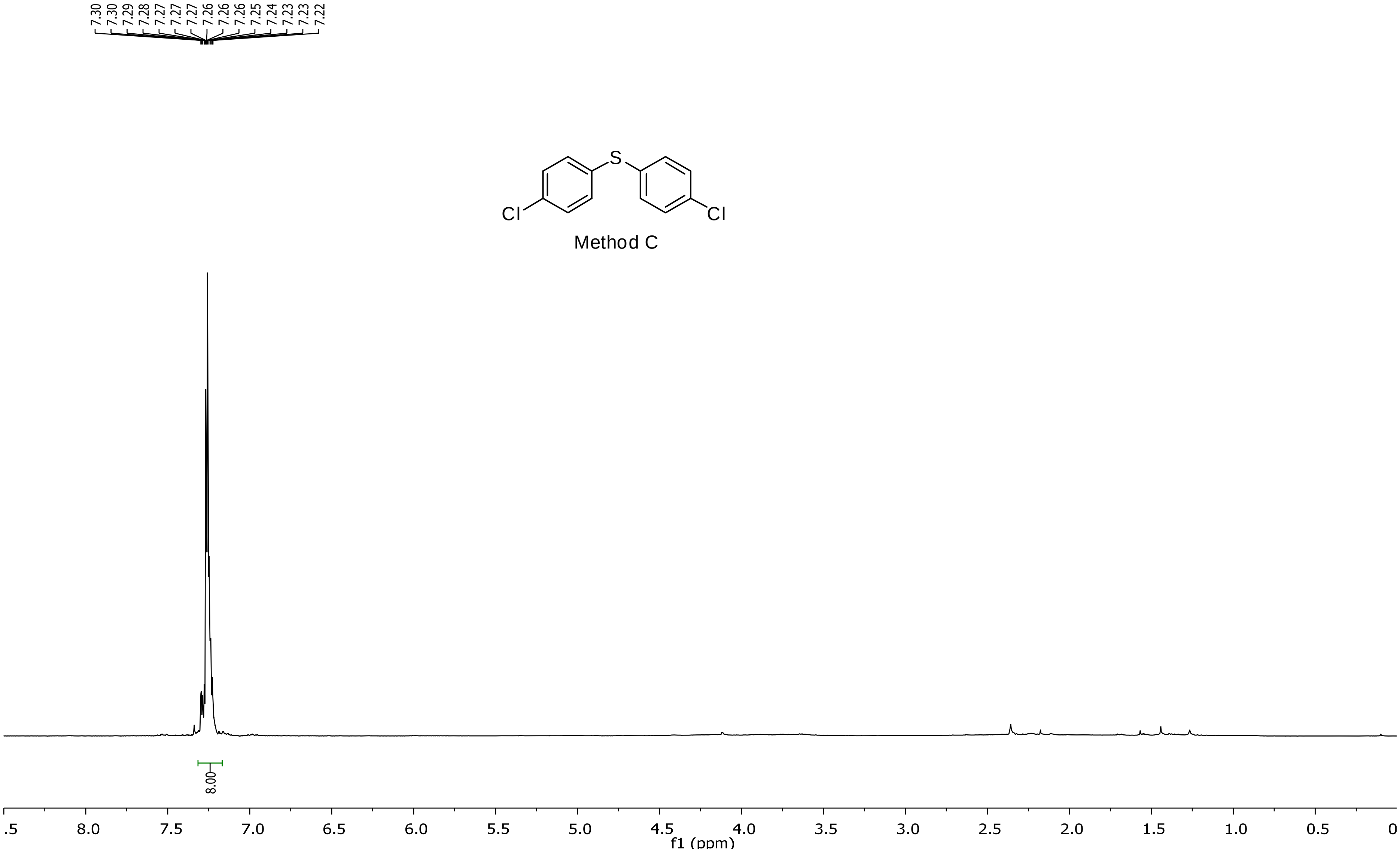

138.83
128.73
126.45
124.93
11.99
8.57
S
Method C
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.27
7.27
7.26
S
Cl
Cl
Method A
8.00
.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)

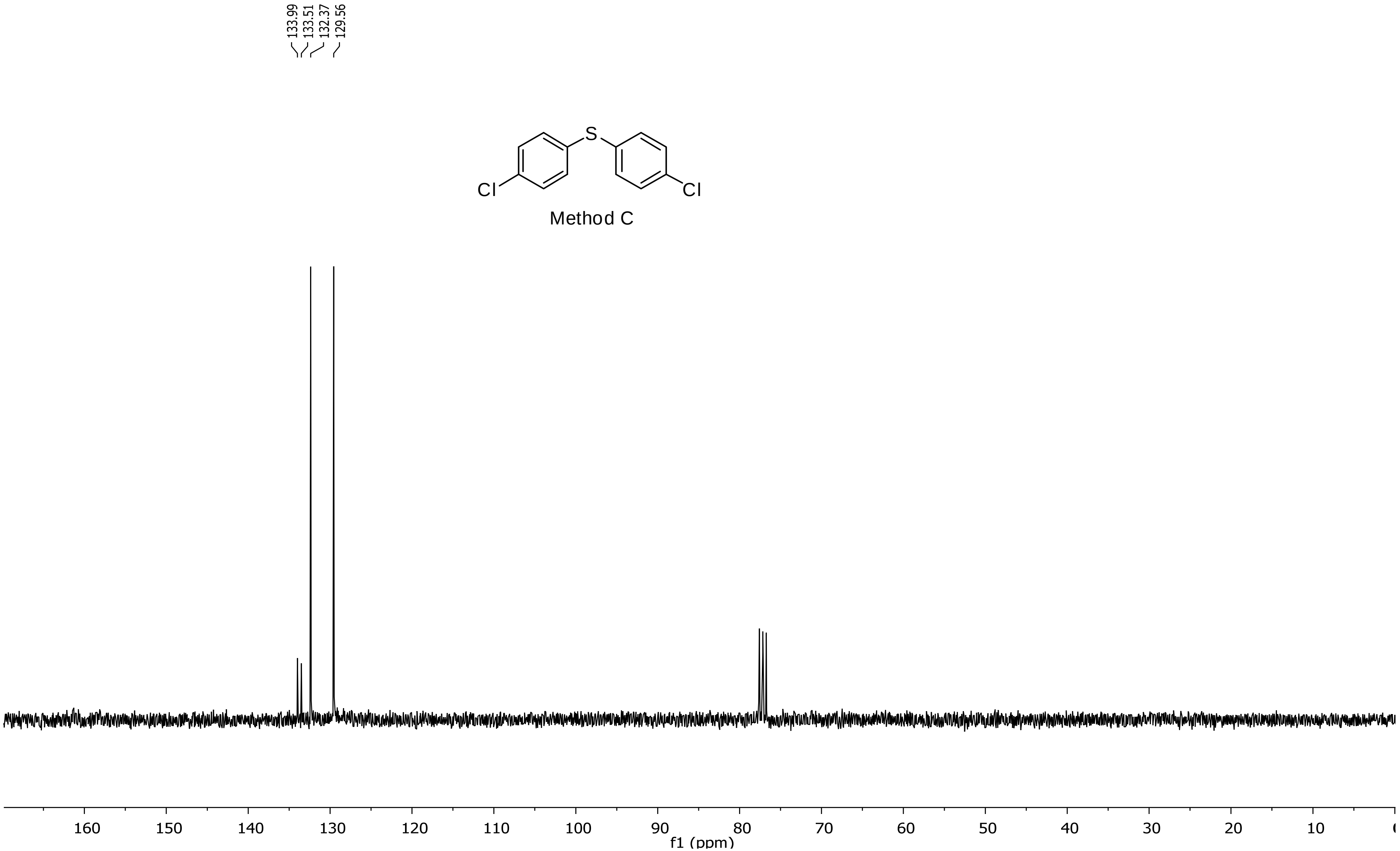

133.98
133.49
132.35
129.54
S
Cl
Cl
Method A
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

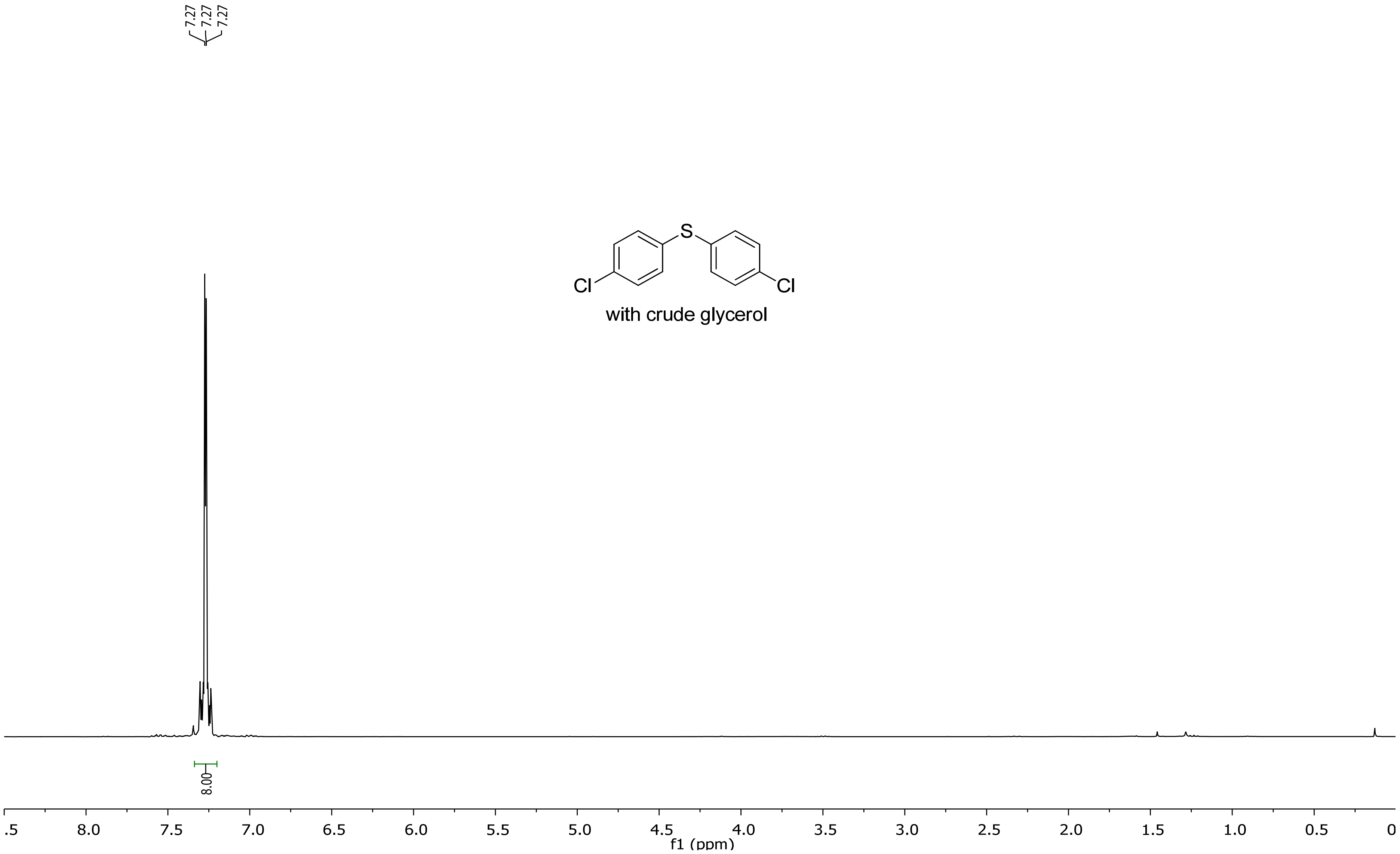

7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.27
7.26
7.26
7.24
7.24
S
Cl
Cl
Method B
8.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

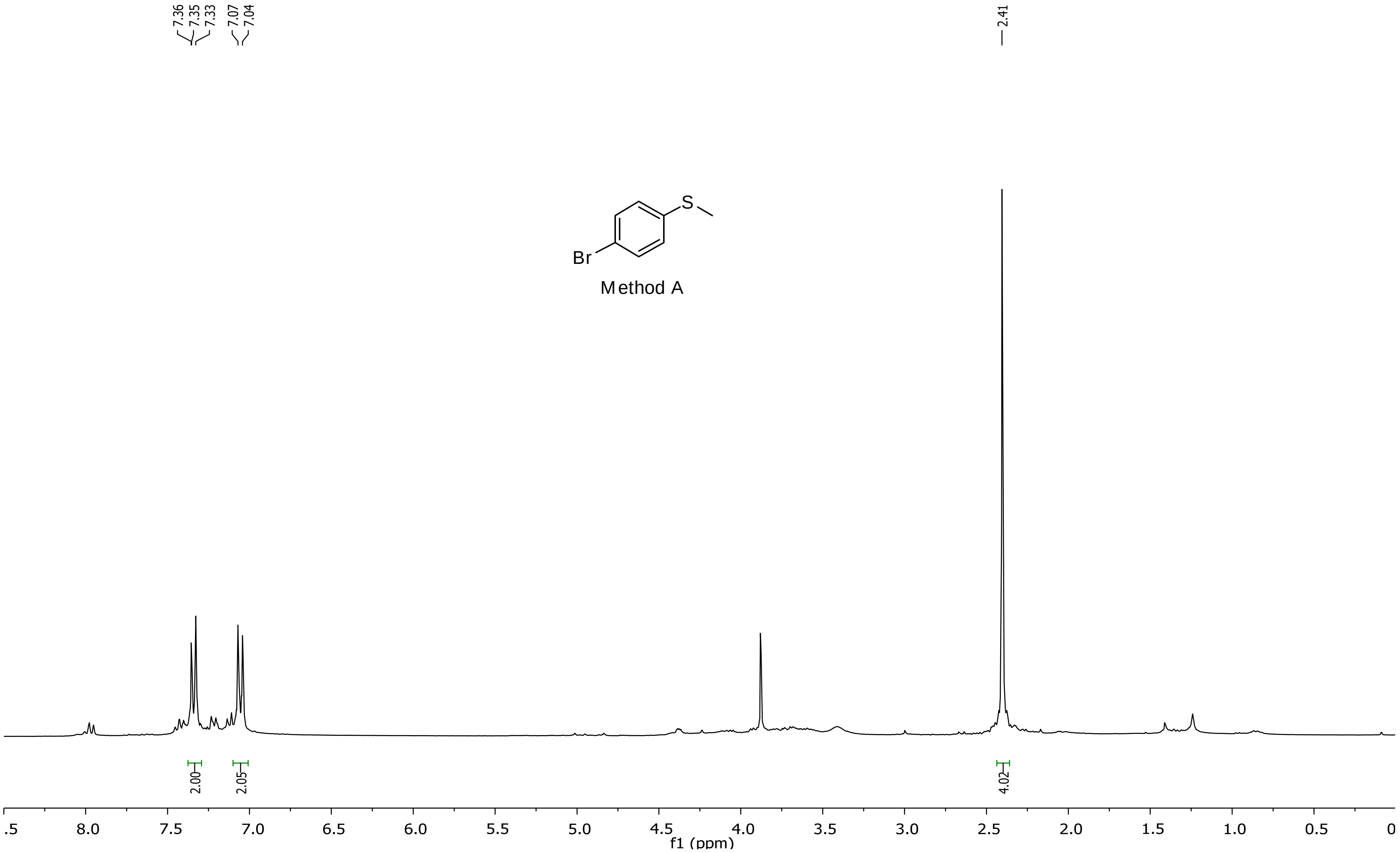

133.99
133.50
132.35
129.55
S
Cl
Cl
Method B
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

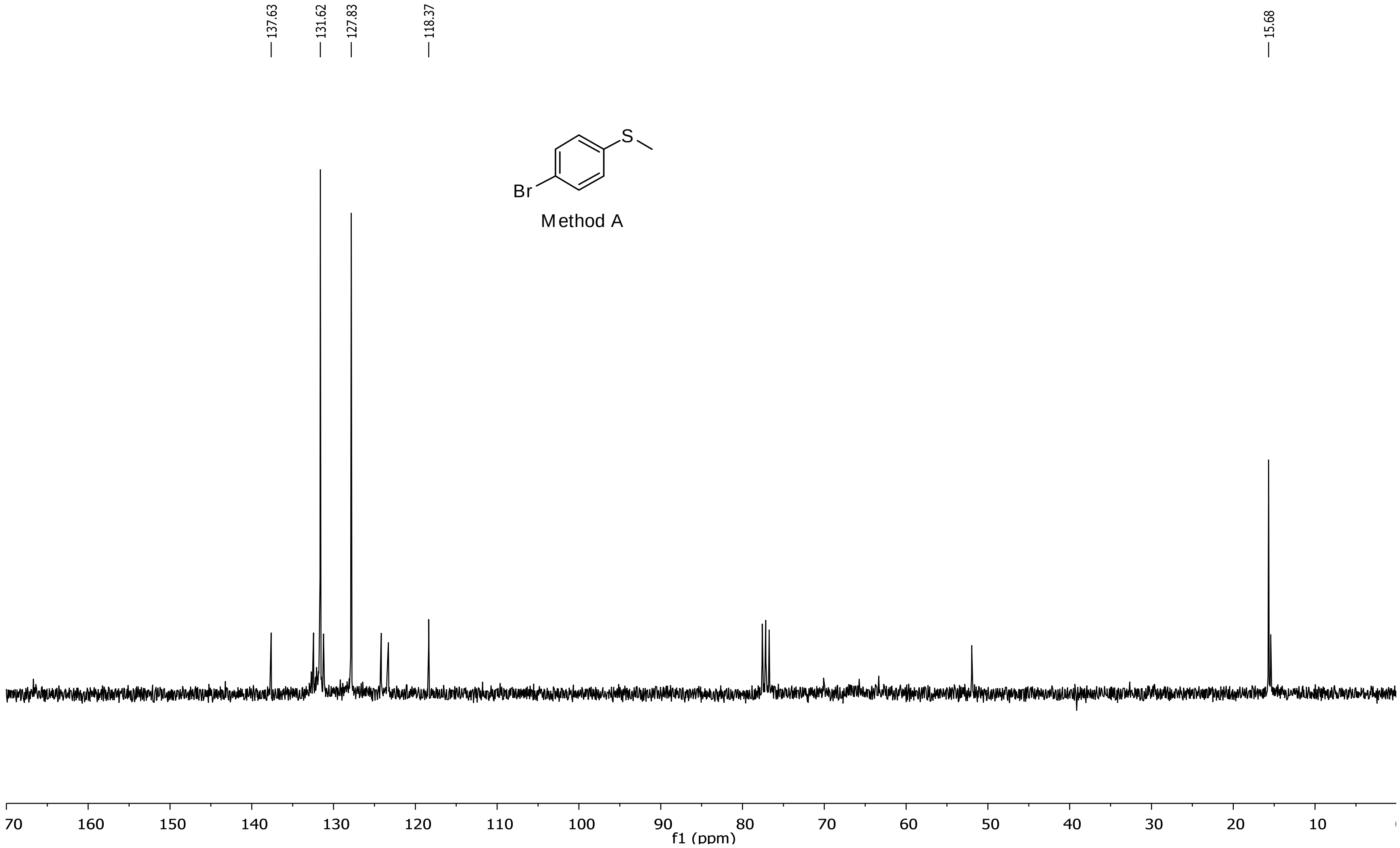

7.30
7.30
7.29
7.28
7.27
7.27
7.27
7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.22
S
Cl
Cl
8.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

Method C


133.99
133.51
132.37
129.56
S
Cl
Cl
Method C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.27
7.27
7.27
S
Cl
Cl
with crude glycerol
8.00
.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)


7.36
7.35
7.33
7.07
7.04
2.41
S
Br
Method A
2.00
2.05
4.02
.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)


137.63
131.62
127.83
118.37
15.68
S
Br
Method A
70
160
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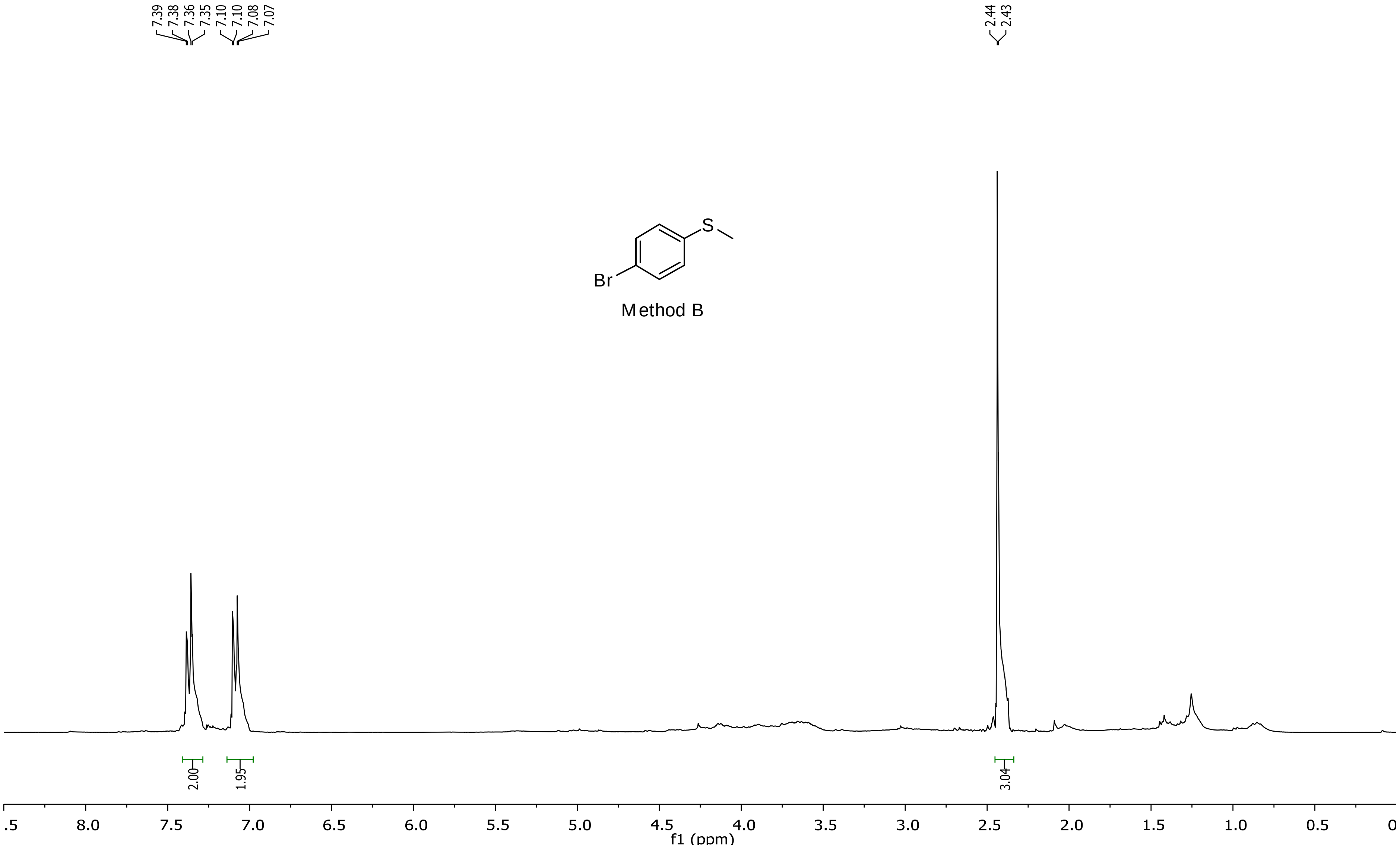
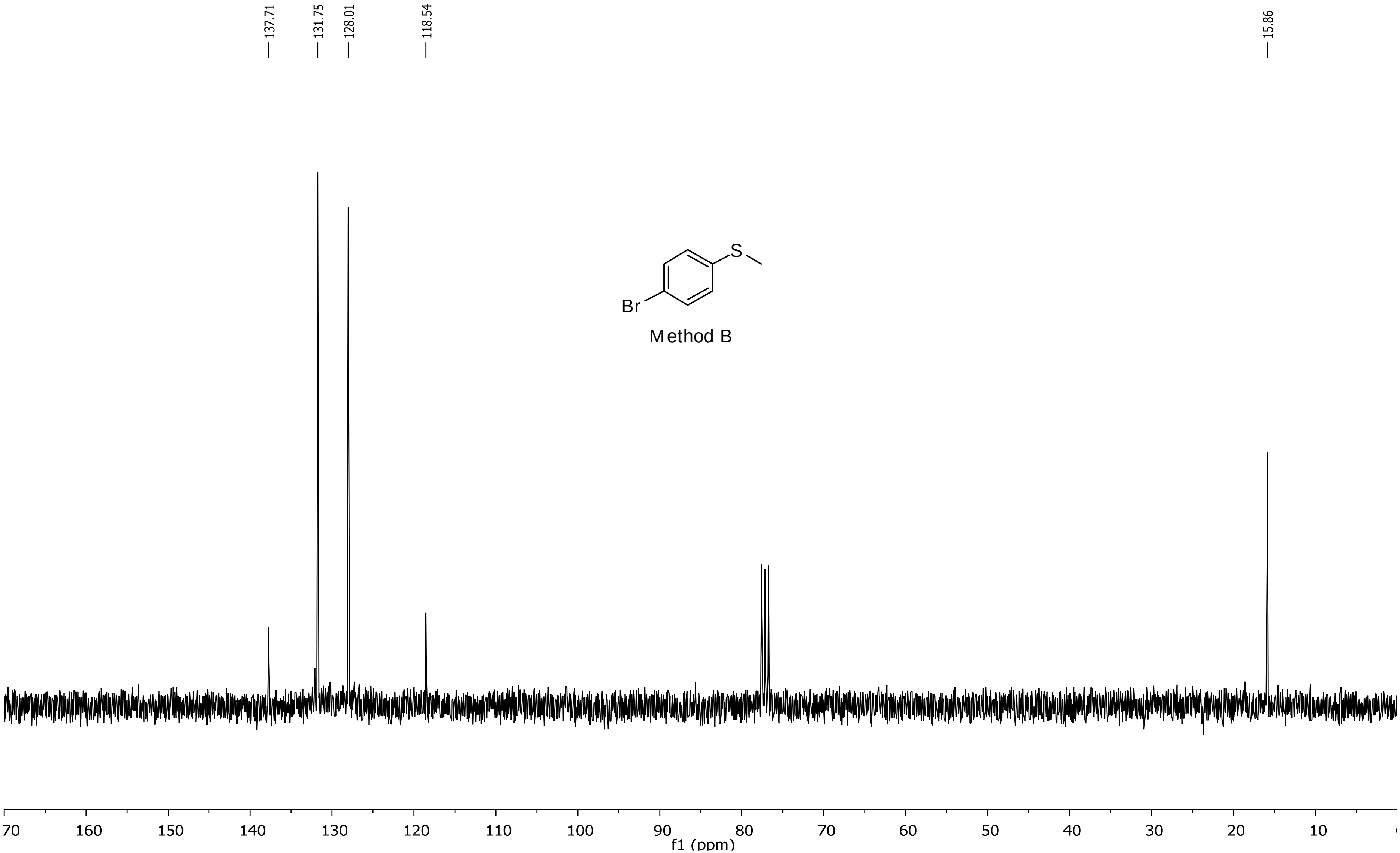
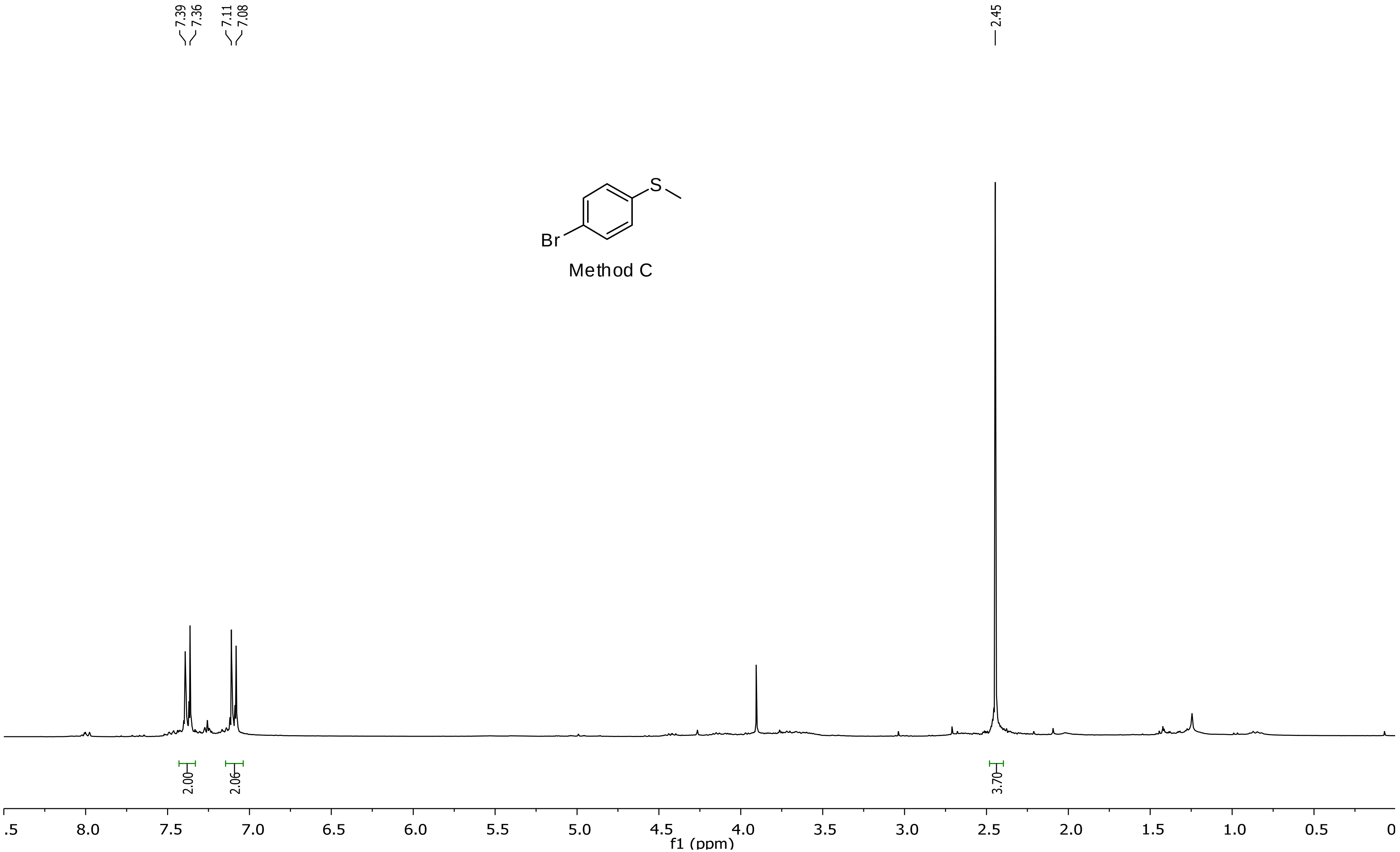
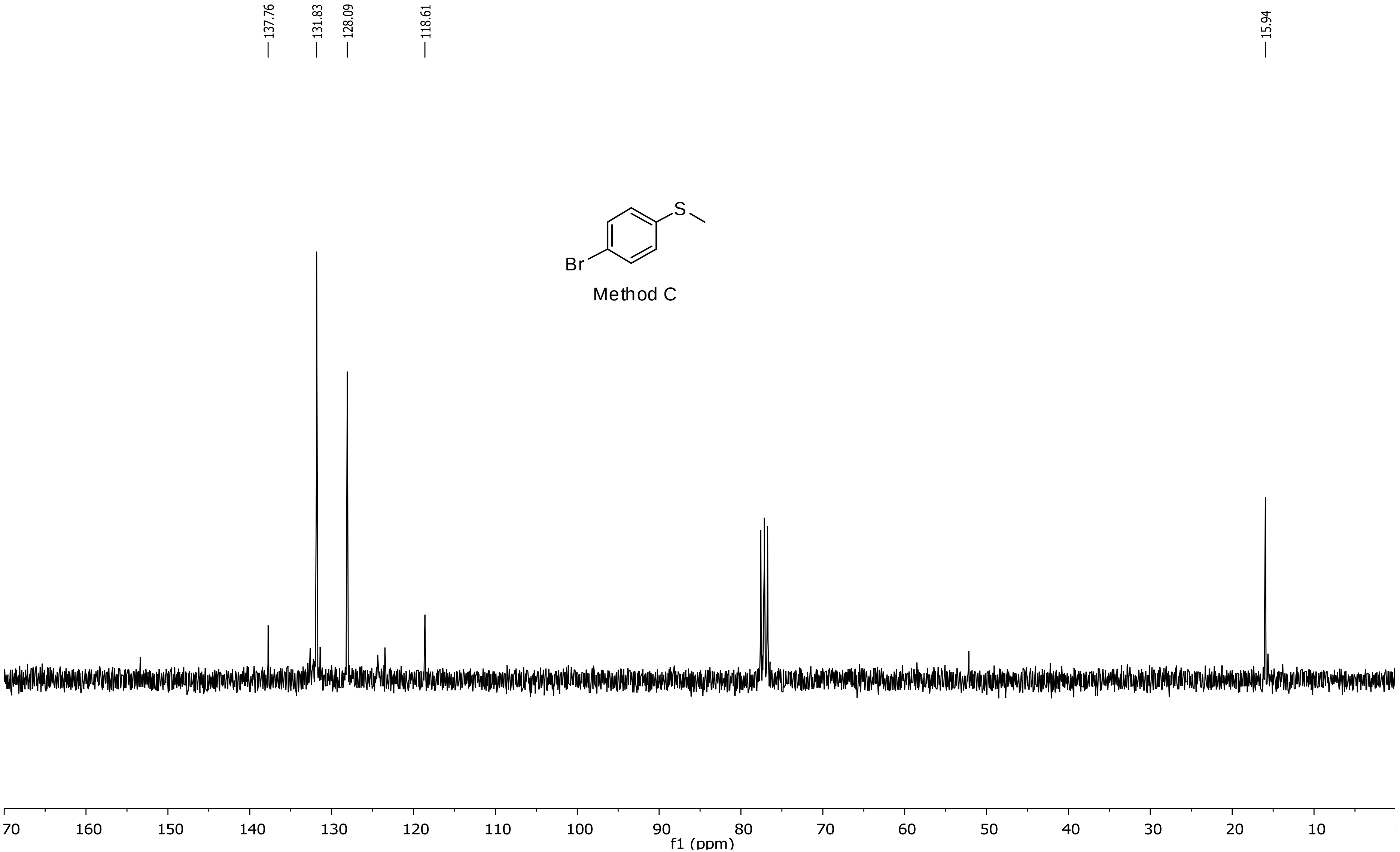
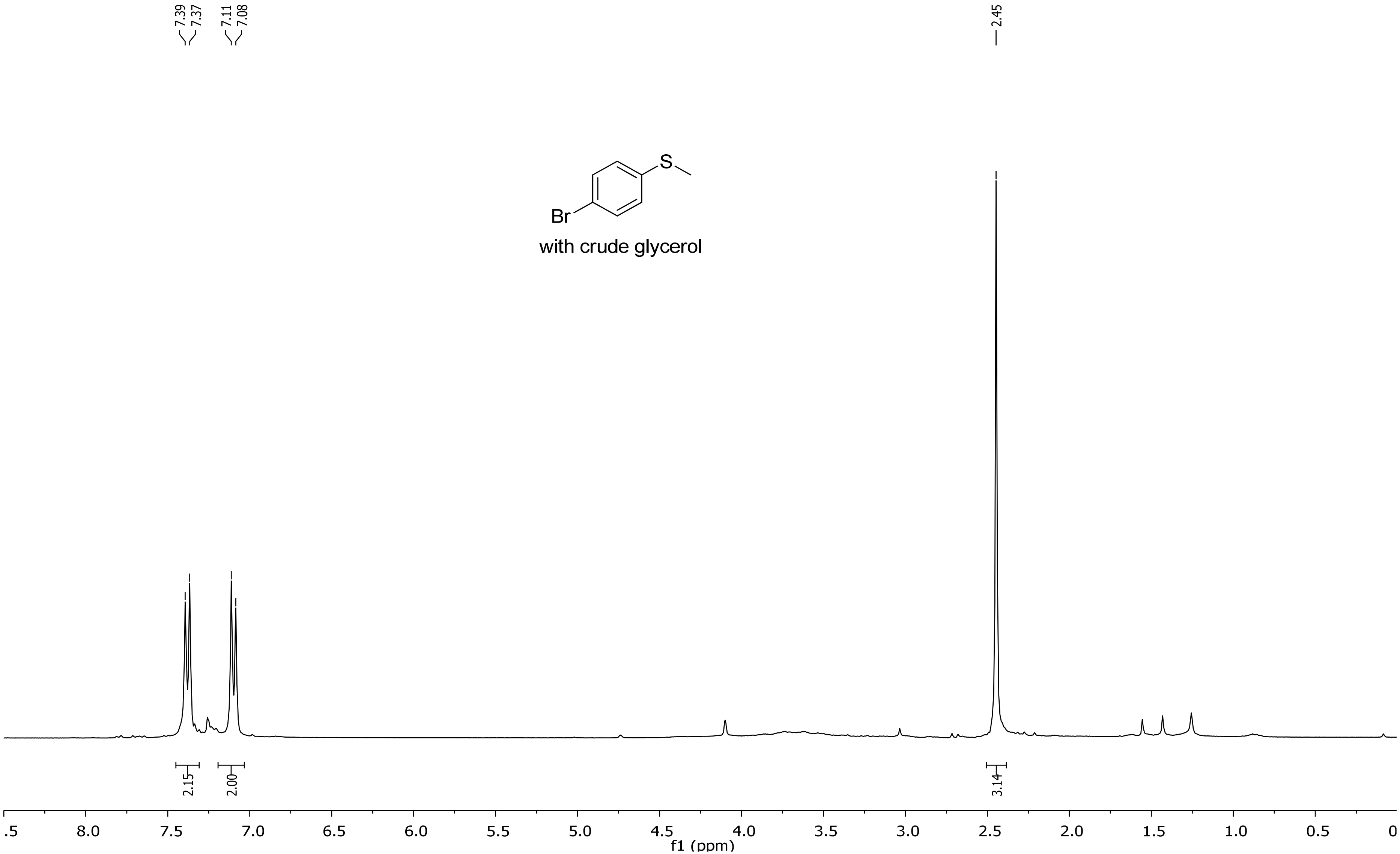
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

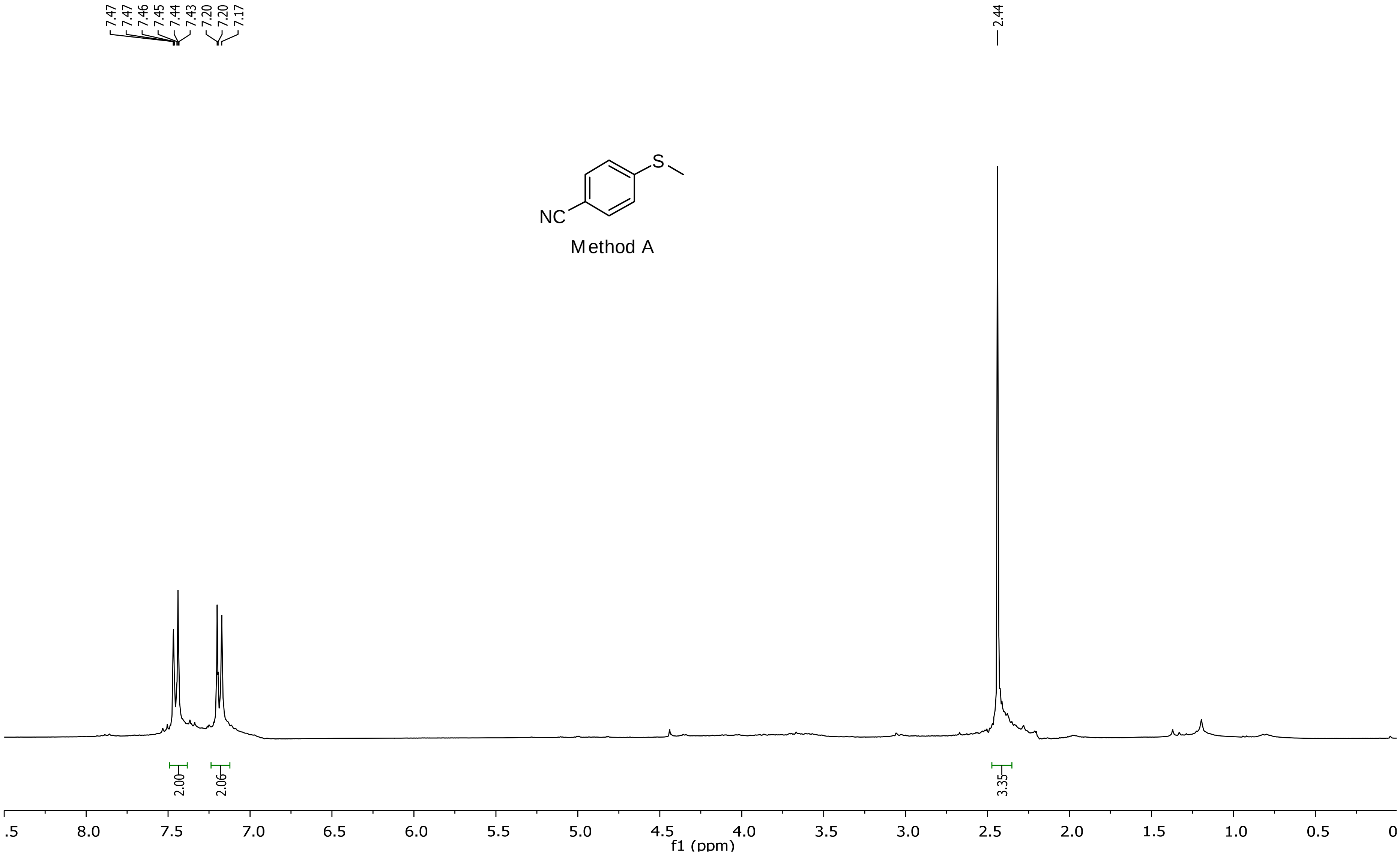

7.39
7.38
7.36
7.35
7.10
7.10
7.08
7.07
2.44
2.43
S
Br
Method B
2.00
1.95
3.04
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

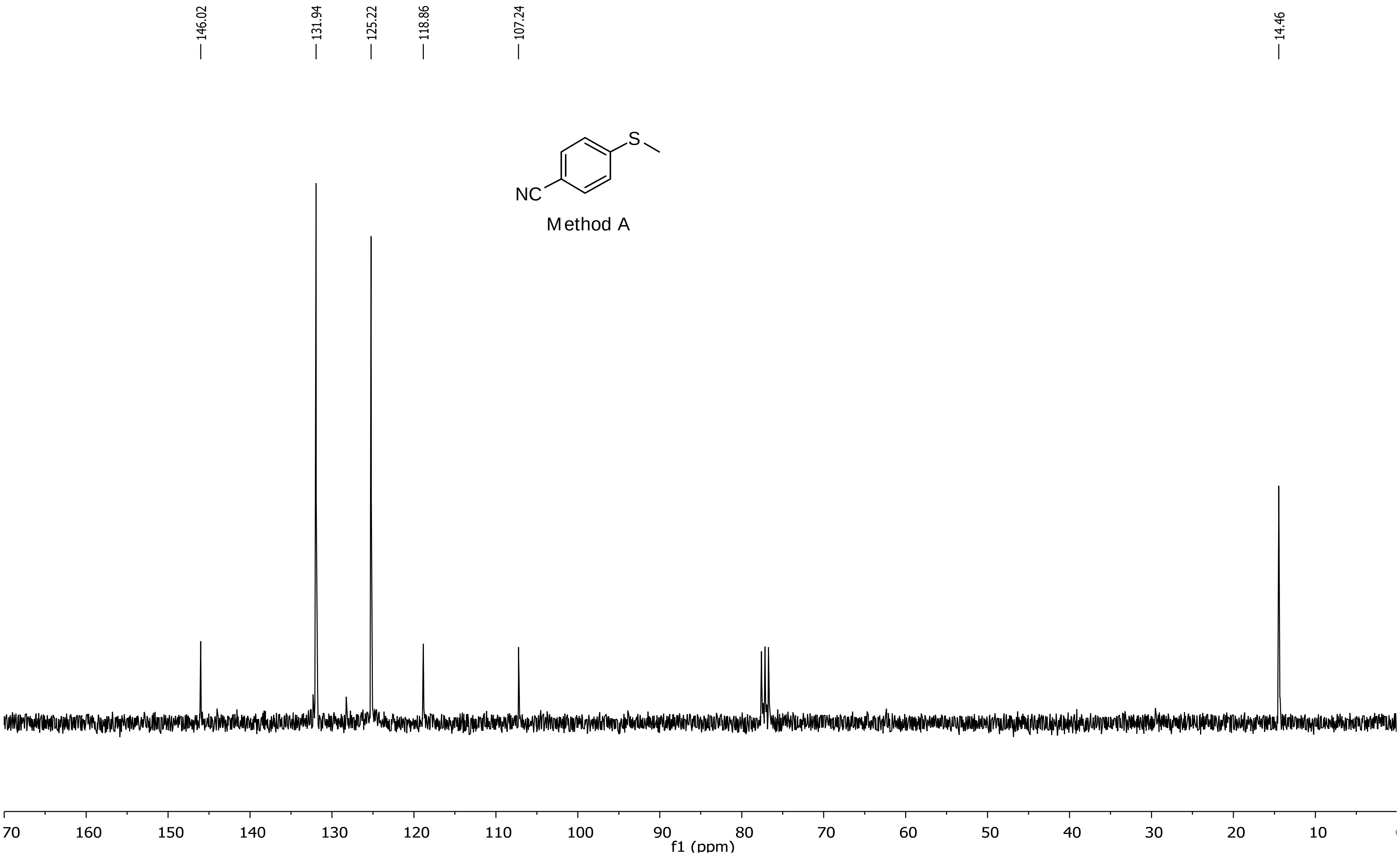

137.71
131.75
128.01
118.54
15.86
Br
S
Method B
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.39
7.36
7.11
7.08
2.45
Br
S
Method C
2.00
2.06
3.70
.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)


137.76
131.83
128.09
118.61
15.94
S
Br
Method C
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.39
7.37
7.11
7.08
2.45
S
Br
with crude glycerol
2.15
2.00
3.14
.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)


7.47
7.47
7.46
7.45
7.44
7.43
7.20
7.20
7.17
2.44
NC
S
Method A
2.00
2.06
3.35
.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)


146.02
131.94
125.22
118.86
107.24
14.46
S
NC
Method A
70
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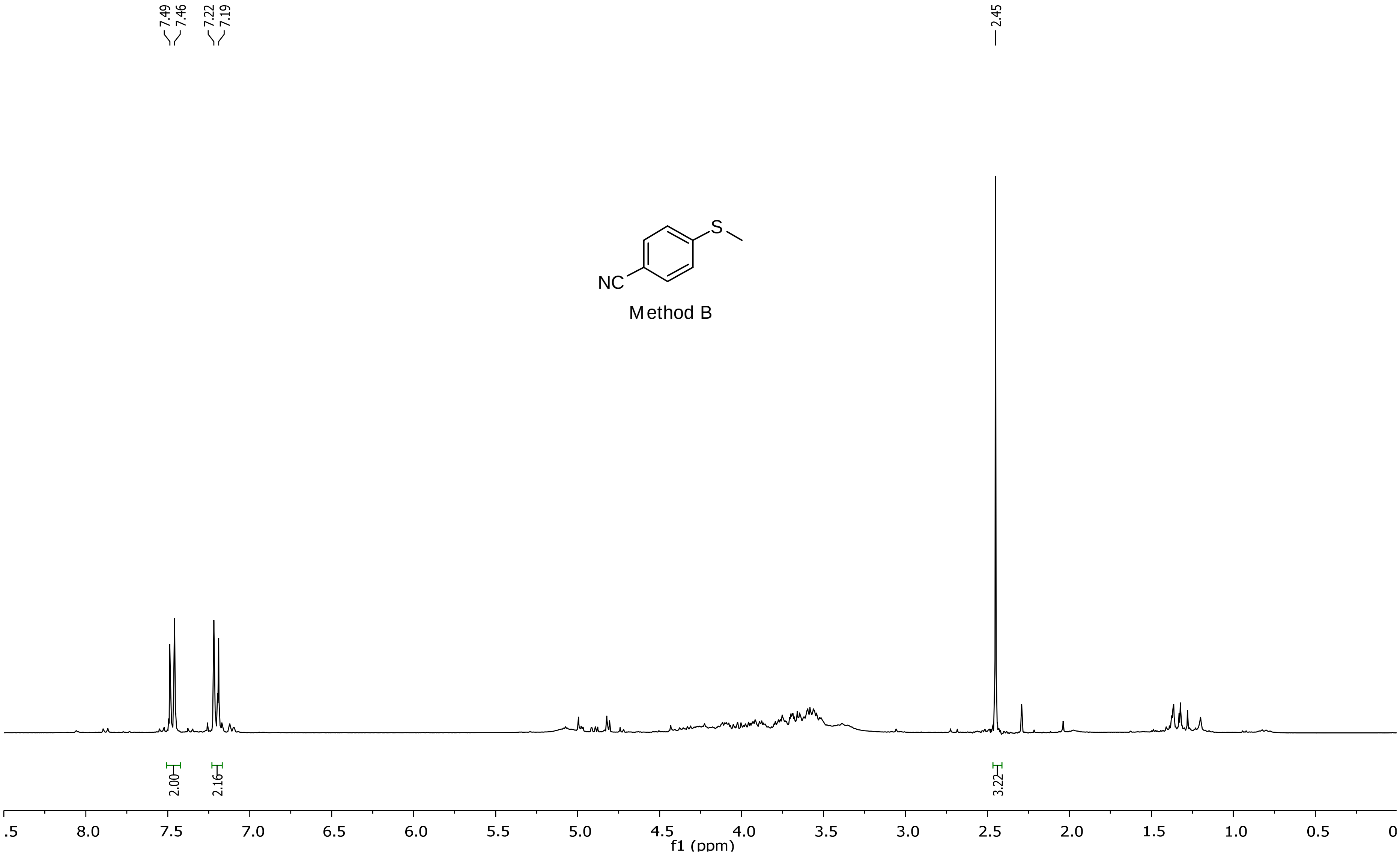
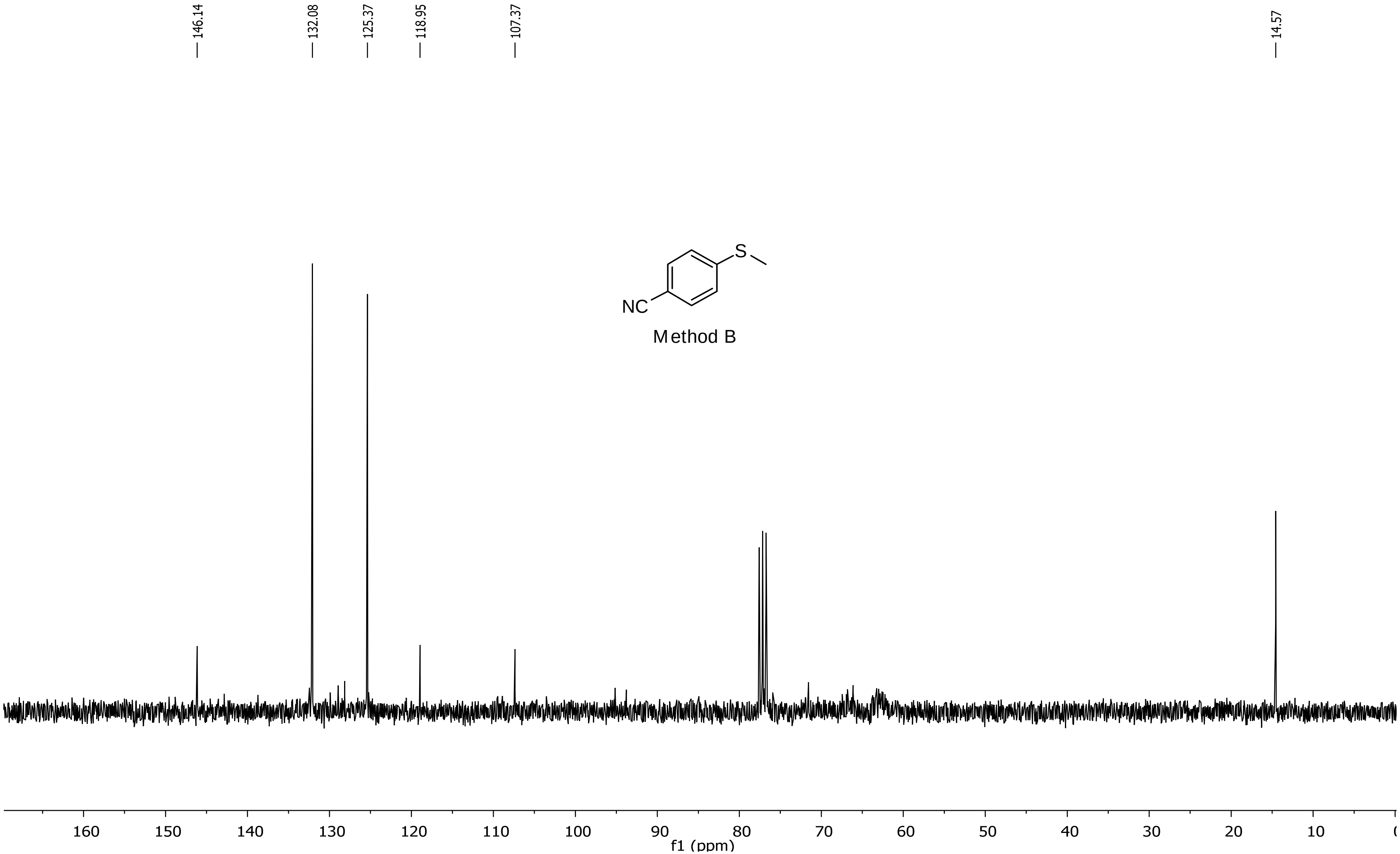
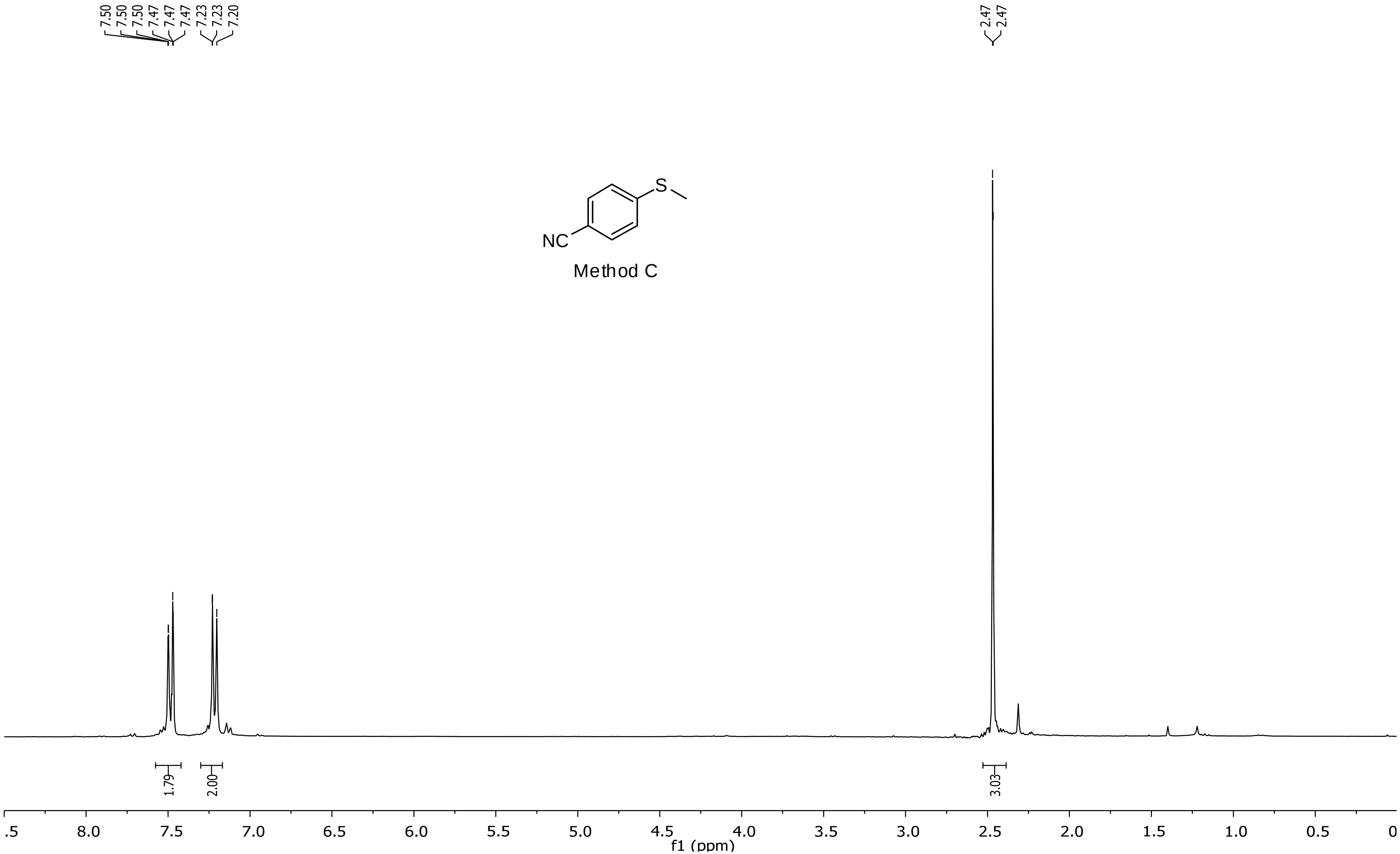
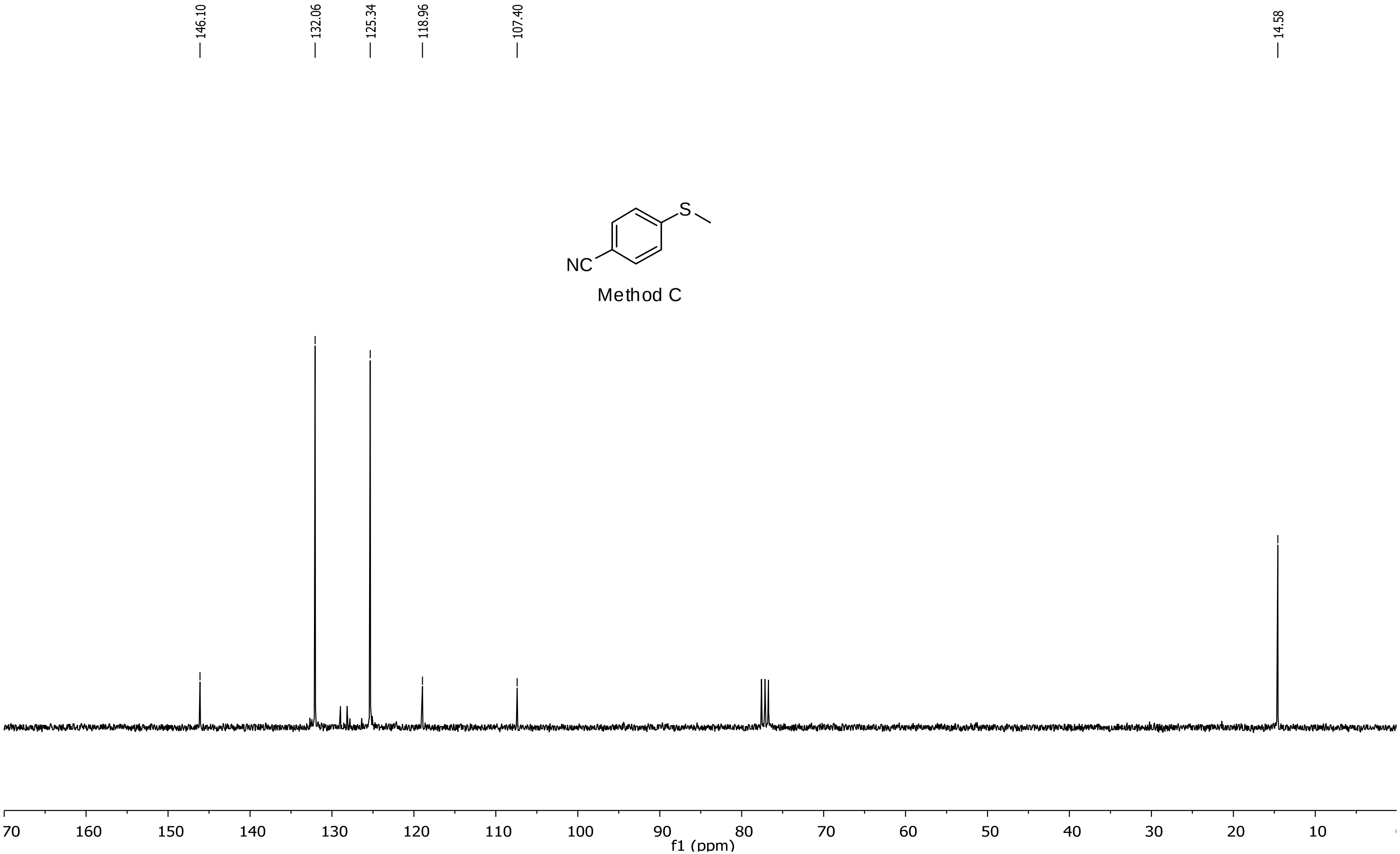
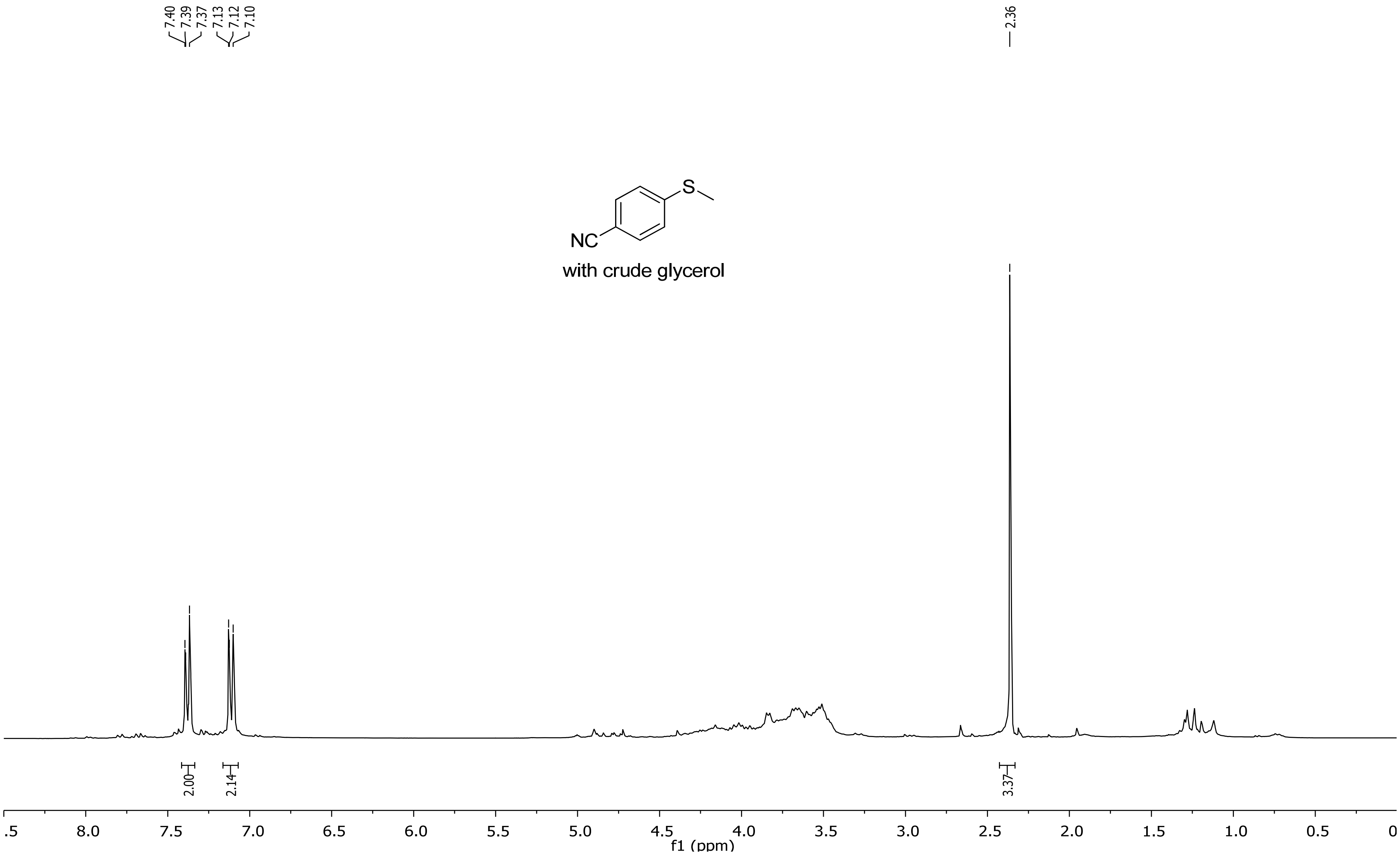
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.49
7.46
7.22
7.19
2.45
S
NC
Method B
2.00
2.16
3.22
.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)

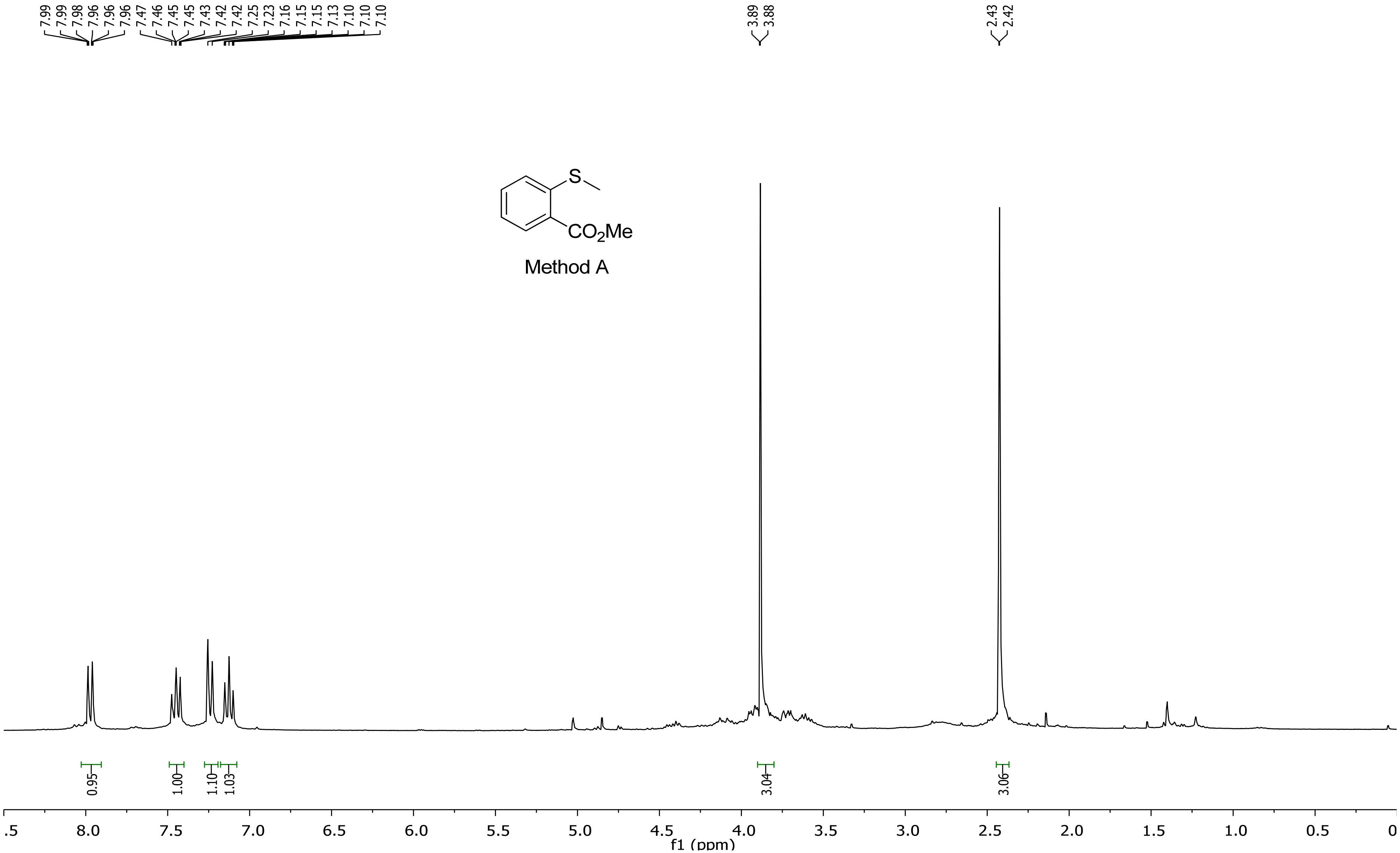

146.14
132.08
125.37
118.95
107.37
14.57
NC
S
Method B
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

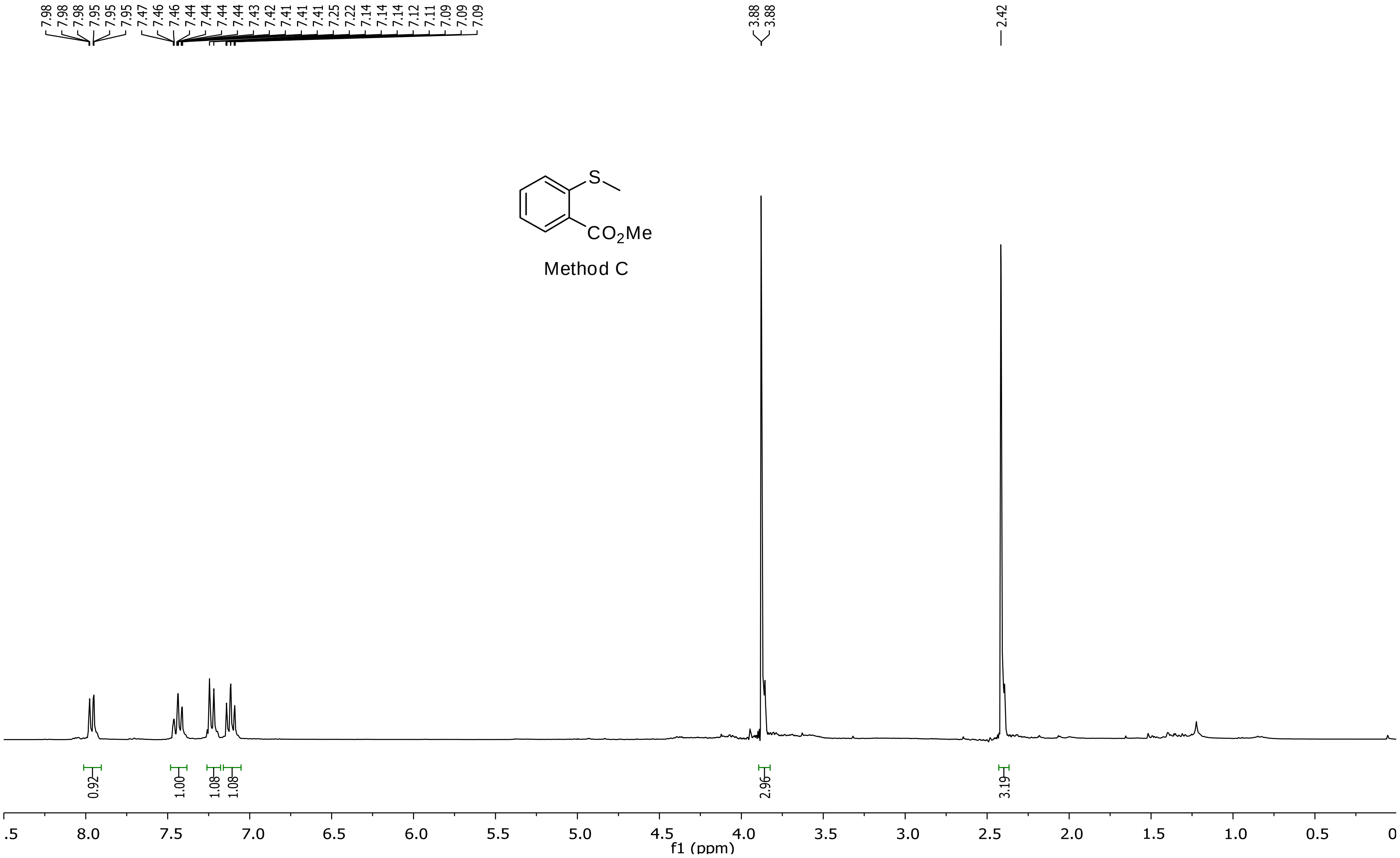

7.50
7.50
7.50
7.47
7.47
7.47
7.23
7.23
7.20
2.47
2.47
S
NC
Method C
1.79
2.00
3.03
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

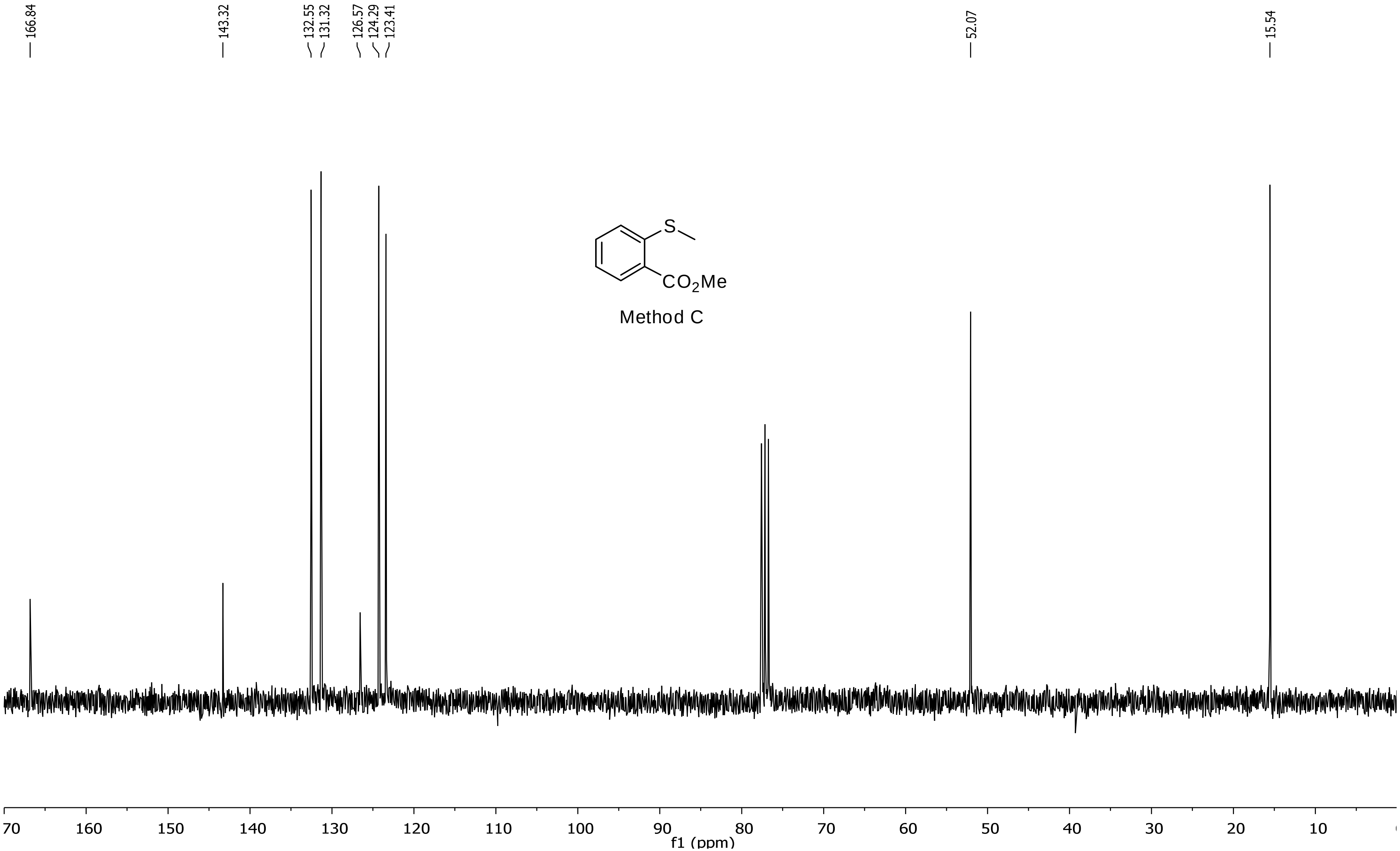

146.10
132.06
125.34
118.96
107.40
14.58
S
NC
Method C
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

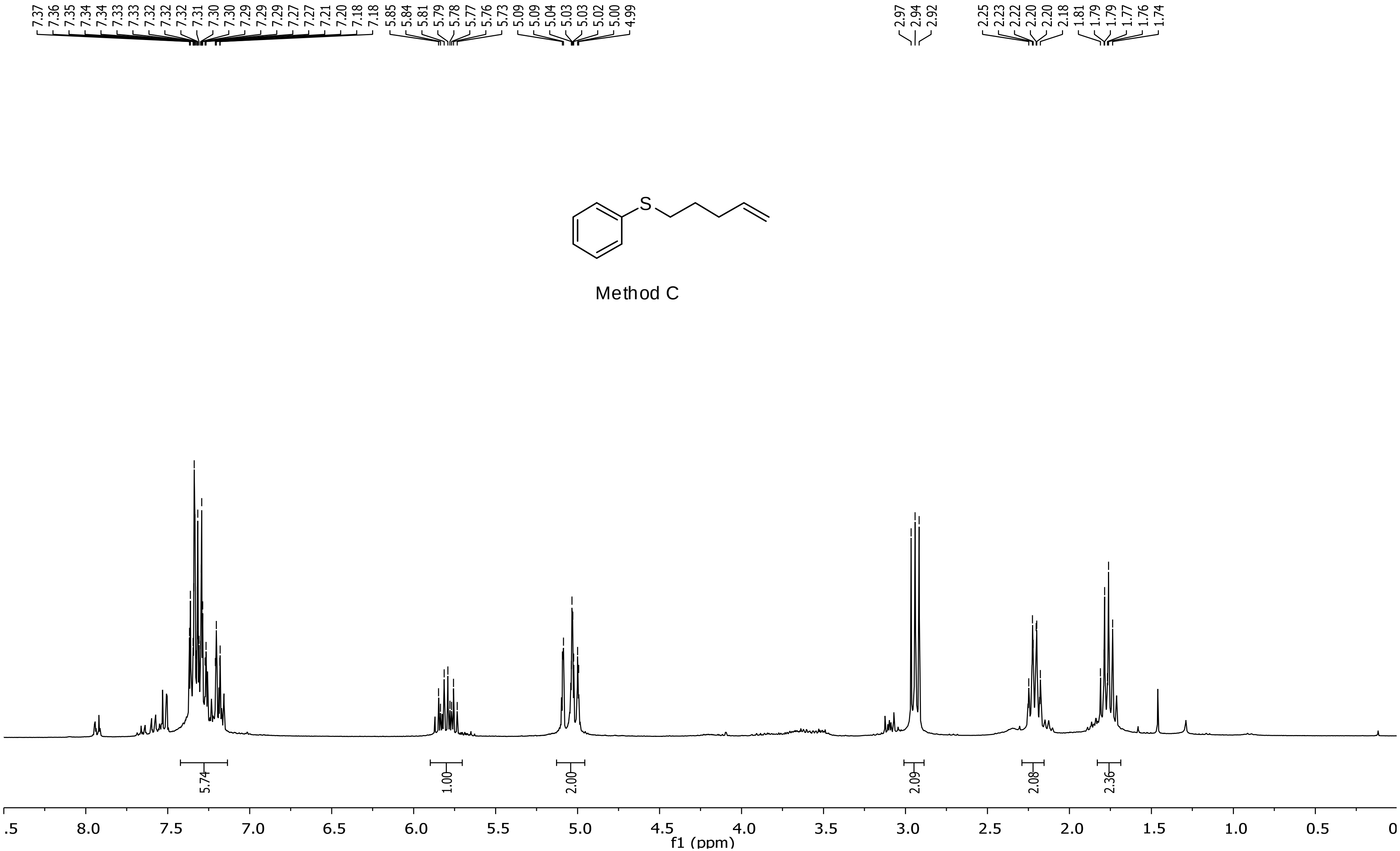


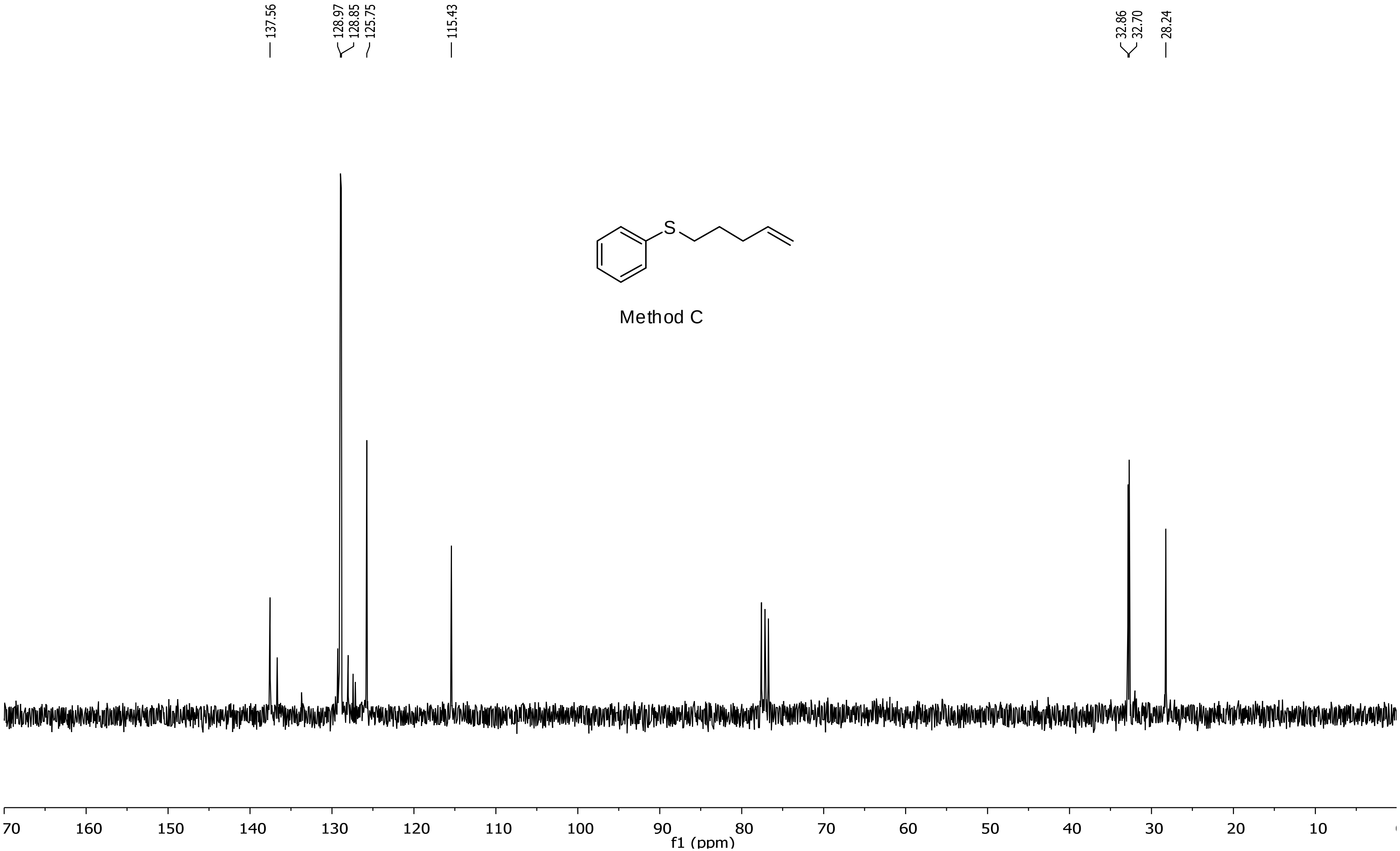
with crude glycerol

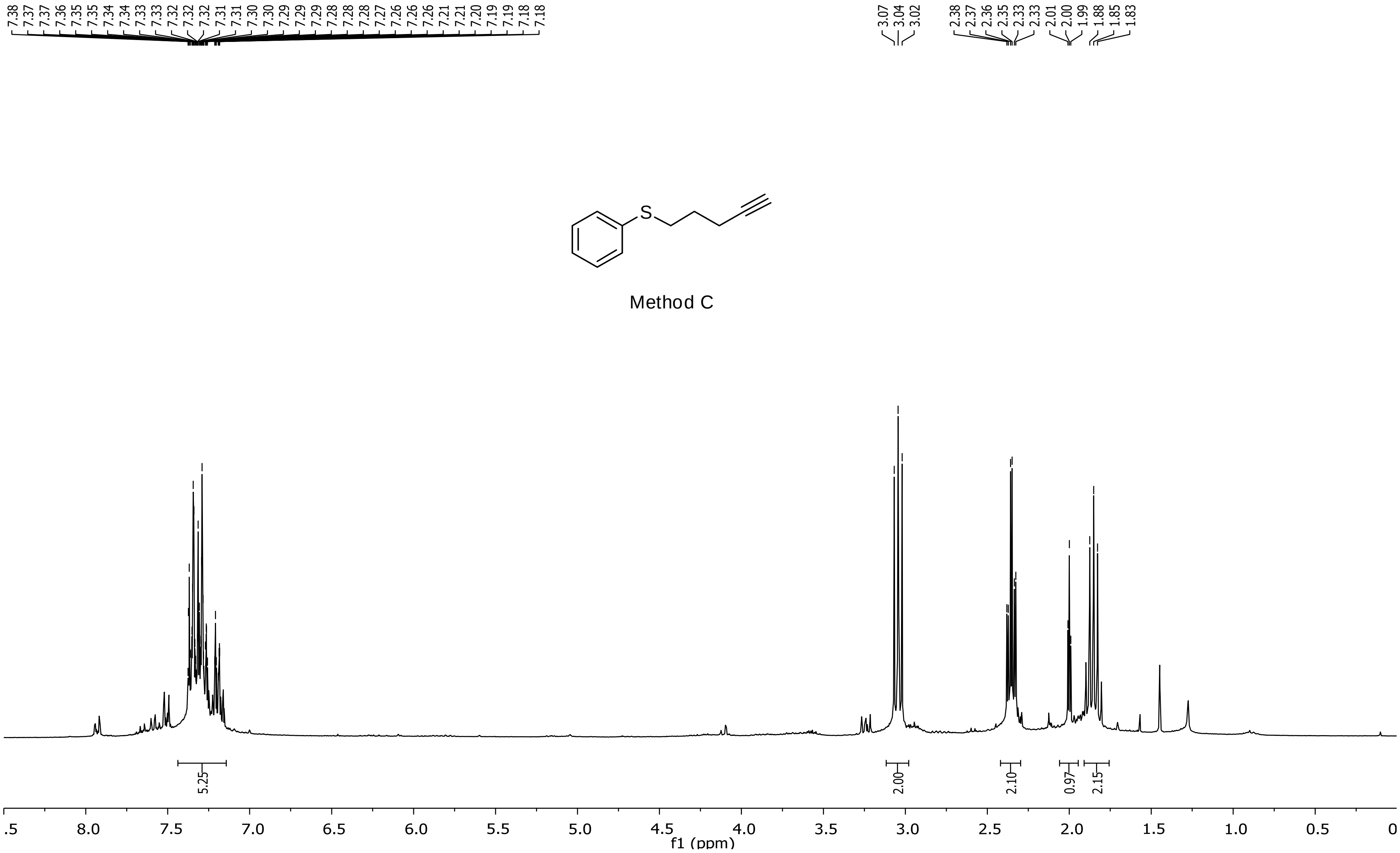

7.99
7.99
7.98
7.96
7.96
7.96
7.47
7.46
7.45
7.45
7.43
7.42
7.42
7.25
7.23
7.16
7.15
7.15
7.13
7.10
7.10
7.10
3.89
3.88
2.43
2.42
S
CO2Me
Method A
0.95
1.00
1.10
1.03
3.04
3.06
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

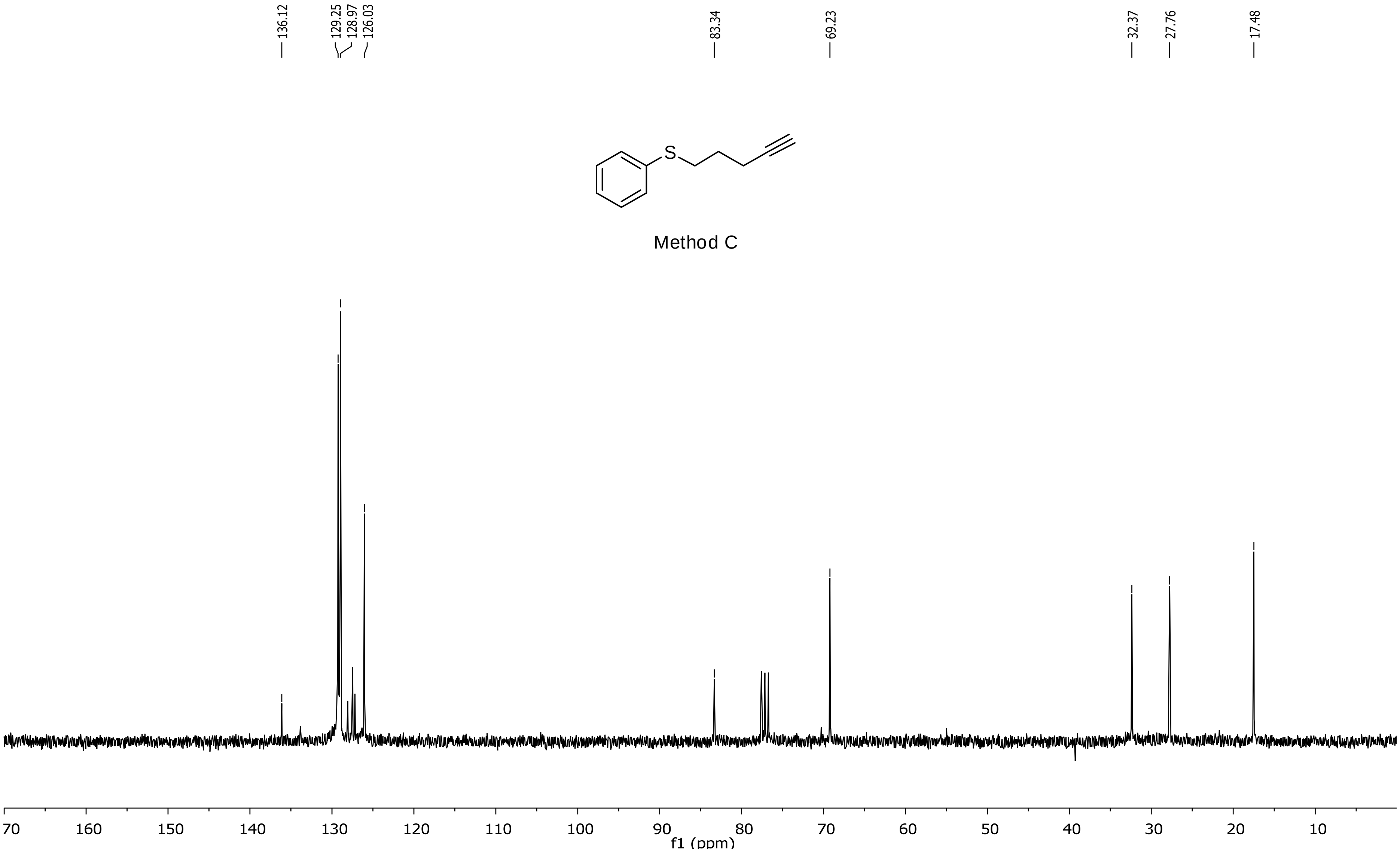

7.98
7.98
7.98
7.95
7.95
7.95
7.47
7.46
7.46
7.44
7.44
7.44
7.44
7.43
7.42
7.41
7.41
7.41
7.25
7.22
7.14
7.14
7.14
7.12
7.11
7.09
7.09
7.09
3.88
3.88
2.42
S
CO2Me
Method C
0.92
1.00
1.08
1.08
2.96
3.19
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

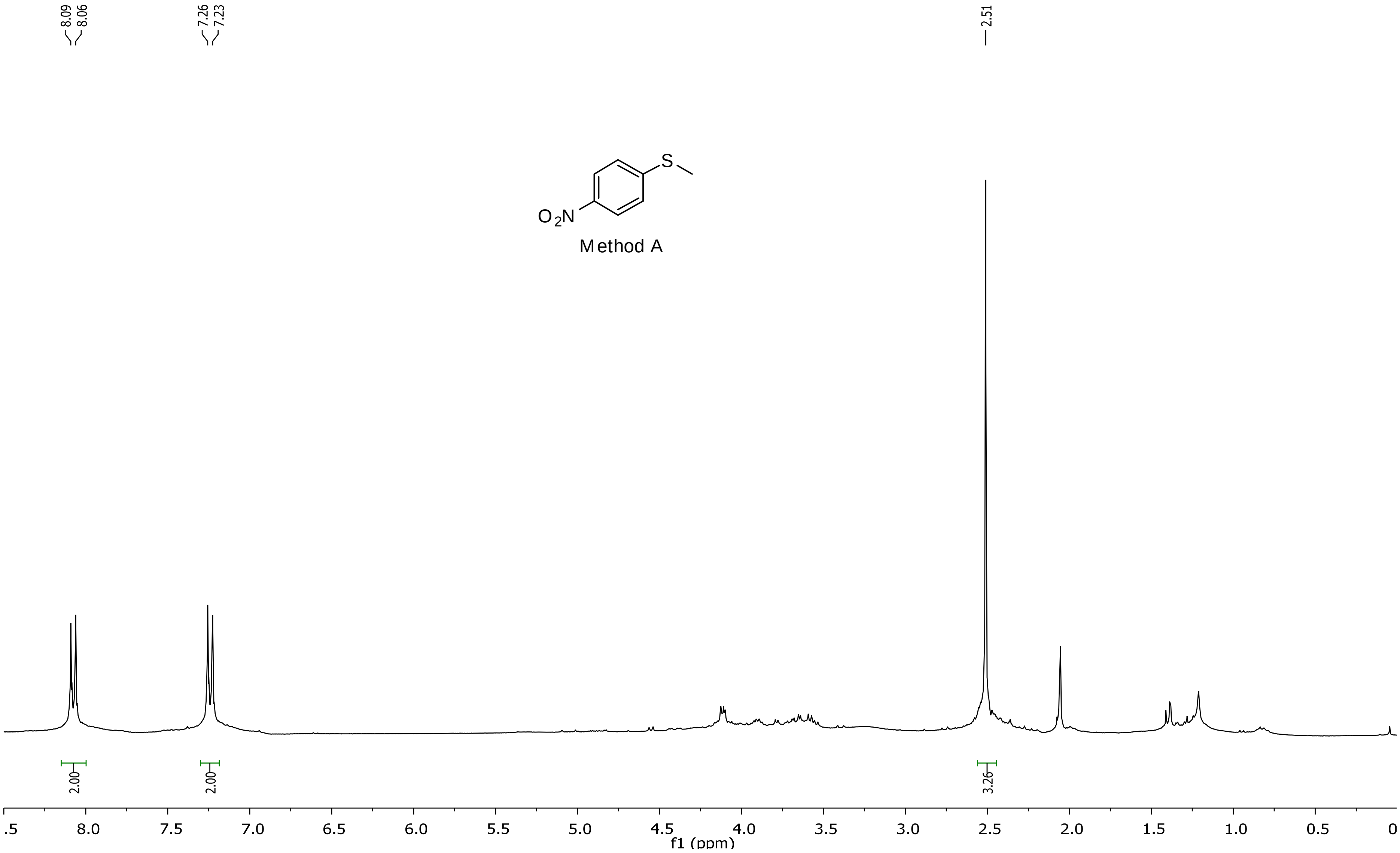

166.84
143.32
132.55
131.32
126.57
124.29
123.41
52.07
15.54
S
CO2Me
Method C
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

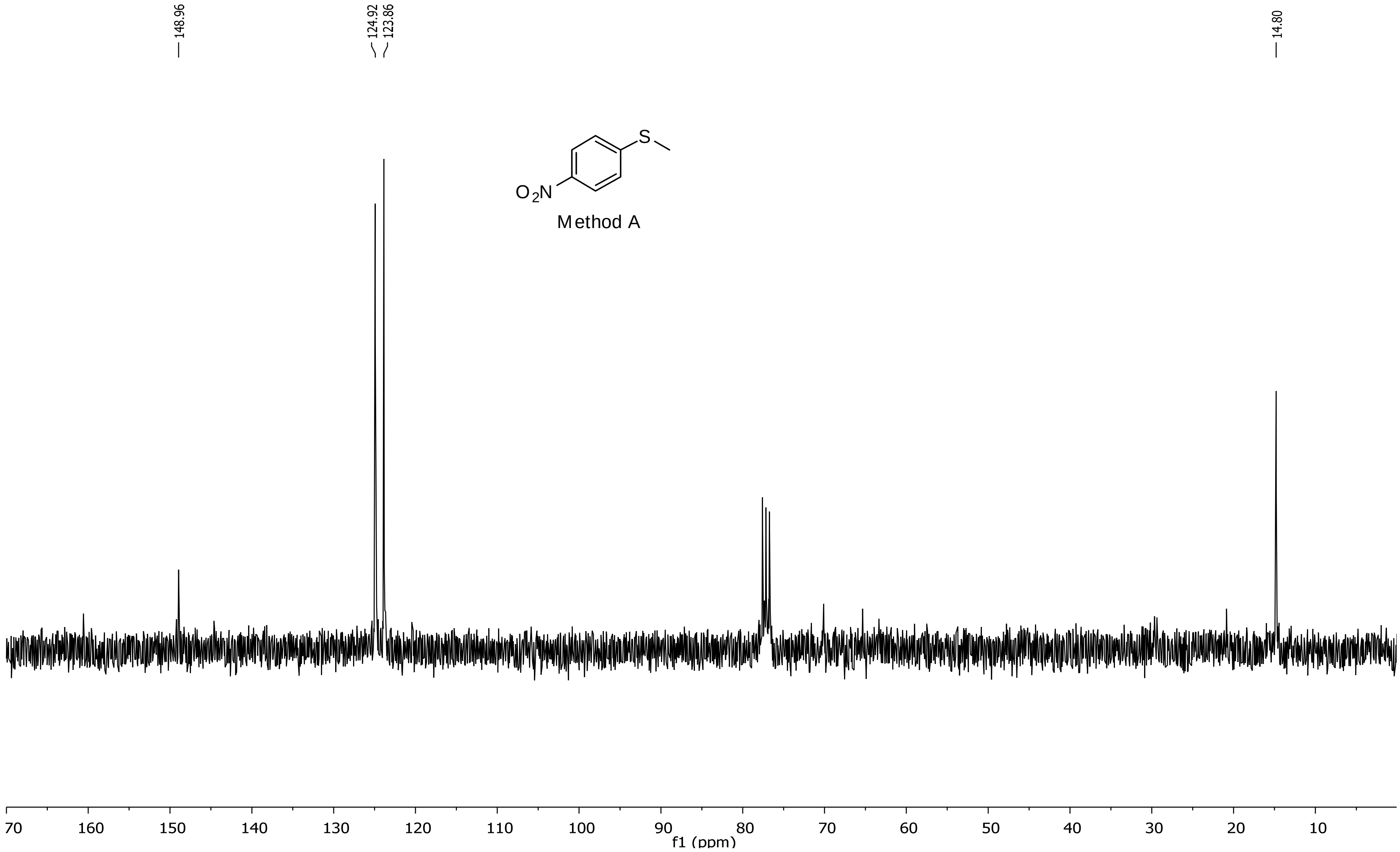

7.37
7.36
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.29
7.27
7.27
7.21
7.20
7.18
5.85
5.84
5.81
5.79
5.78
5.77
5.76
5.73
5.09
5.09
5.04
5.03
5.03
5.02
5.00
4.99
2.97
2.94
2.92
2.25
2.23
2.22
2.20
2.20
2.18
1.81
1.79
1.79
1.77
1.76
1.74
S
Method C
5.74
1.00
2.00
2.09
2.08
2.36
.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)

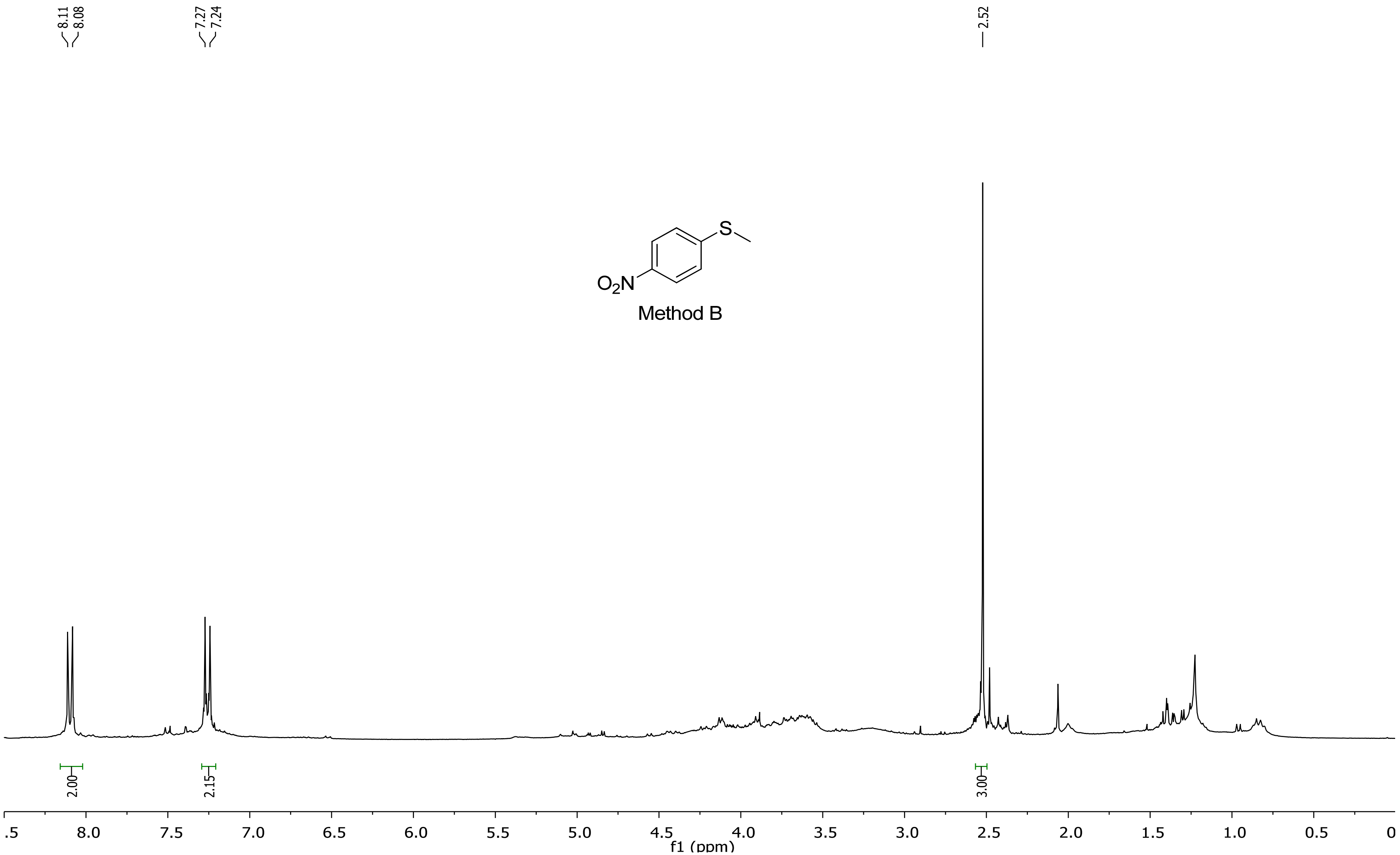

137.56
128.97
128.85
125.75
115.43
32.86
32.70
28.24
S
Method C
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

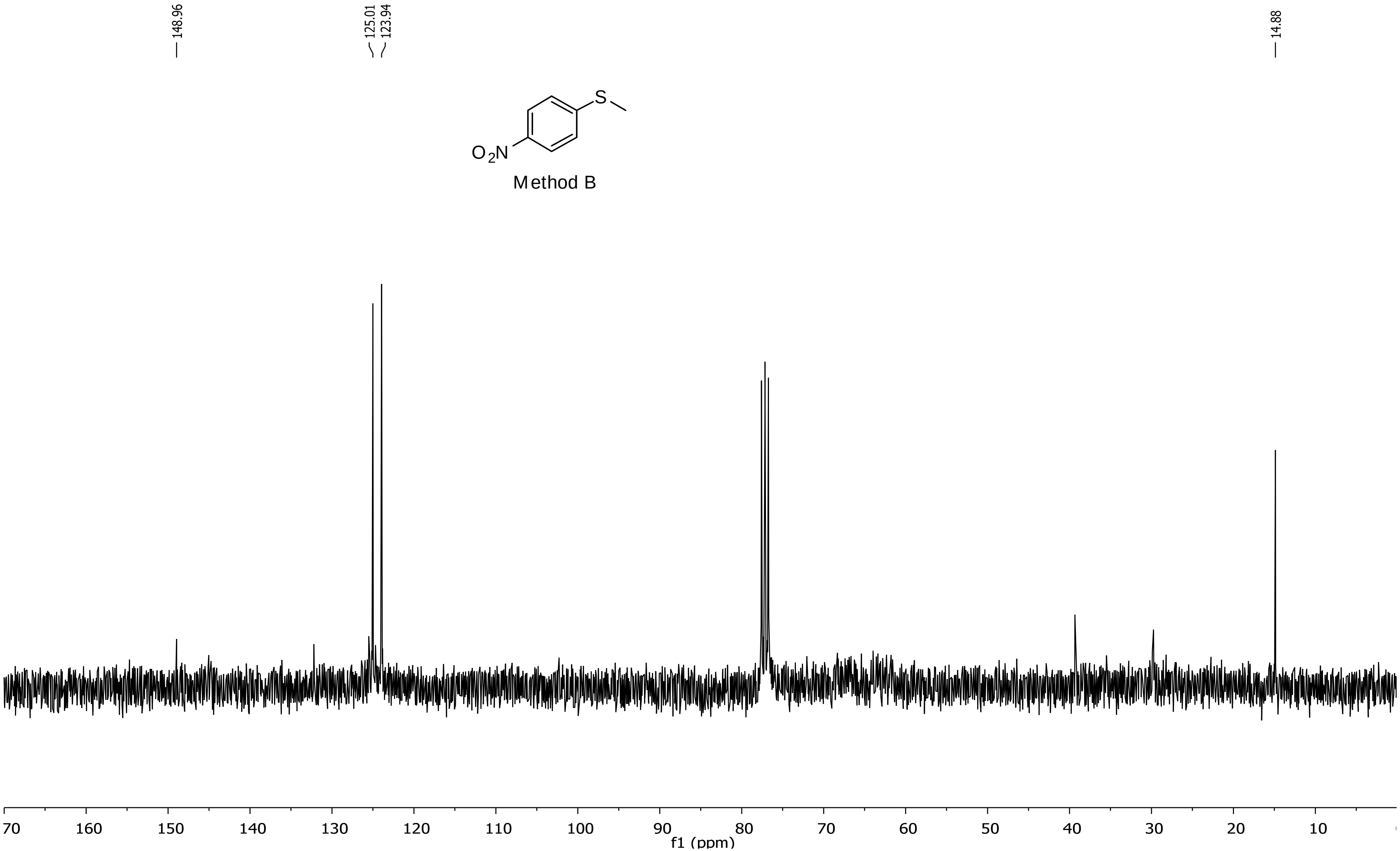

7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.27
7.26
7.26
7.26
7.21
7.21
7.20
7.19
7.19
7.18
7.18
3.07
3.04
3.02
2.38
2.37
2.36
2.35
2.33
2.33
2.01
2.00
1.99
1.88
1.85
1.83
S
Method C
5.25
2.00
2.10
0.97
2.15
.5
8.0
7.5
7.0
6.5
6.0
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)

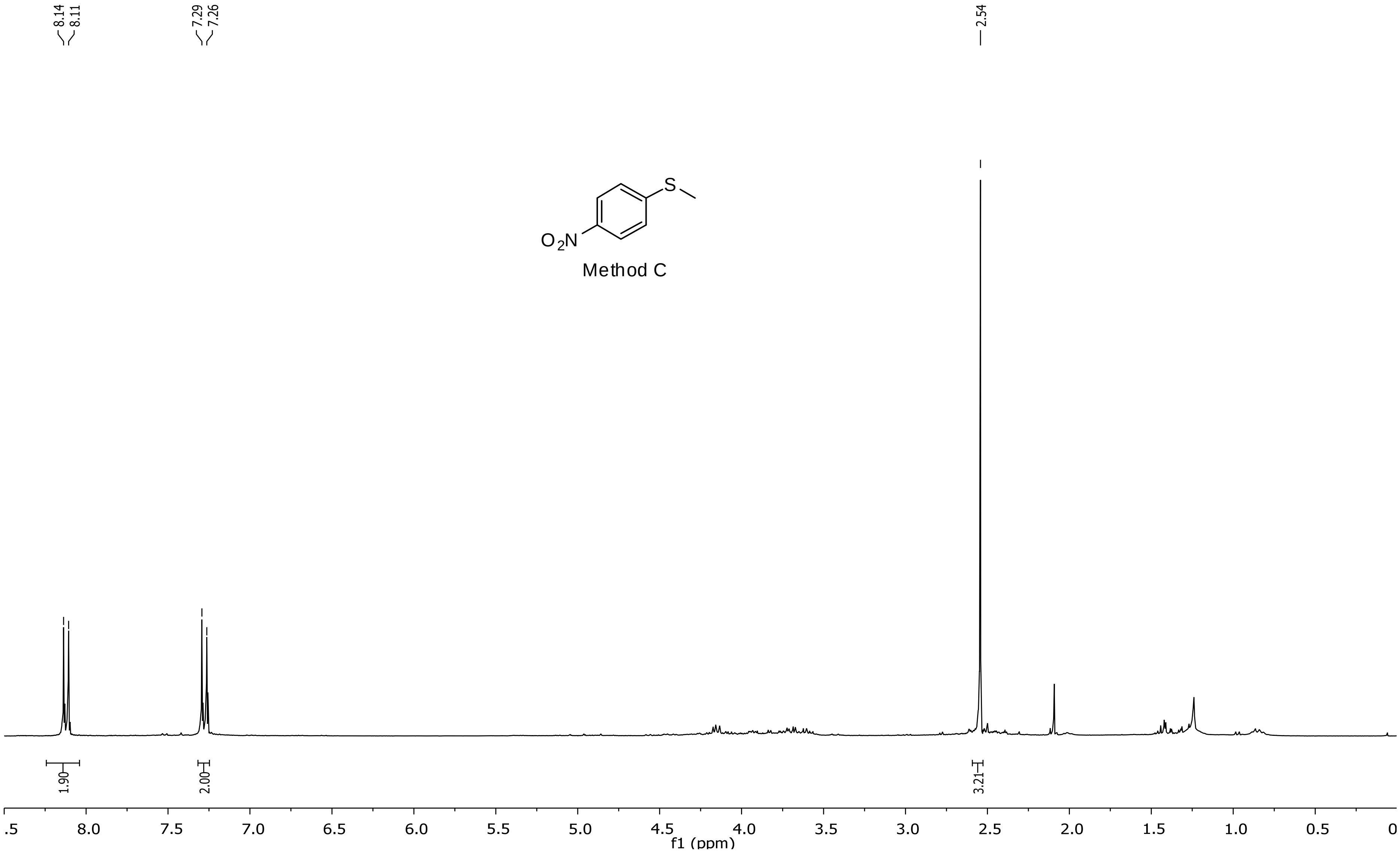

136.12
129.25
128.97
126.03
83.34
69.23
32.37
27.76
17.48
S
Method C
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

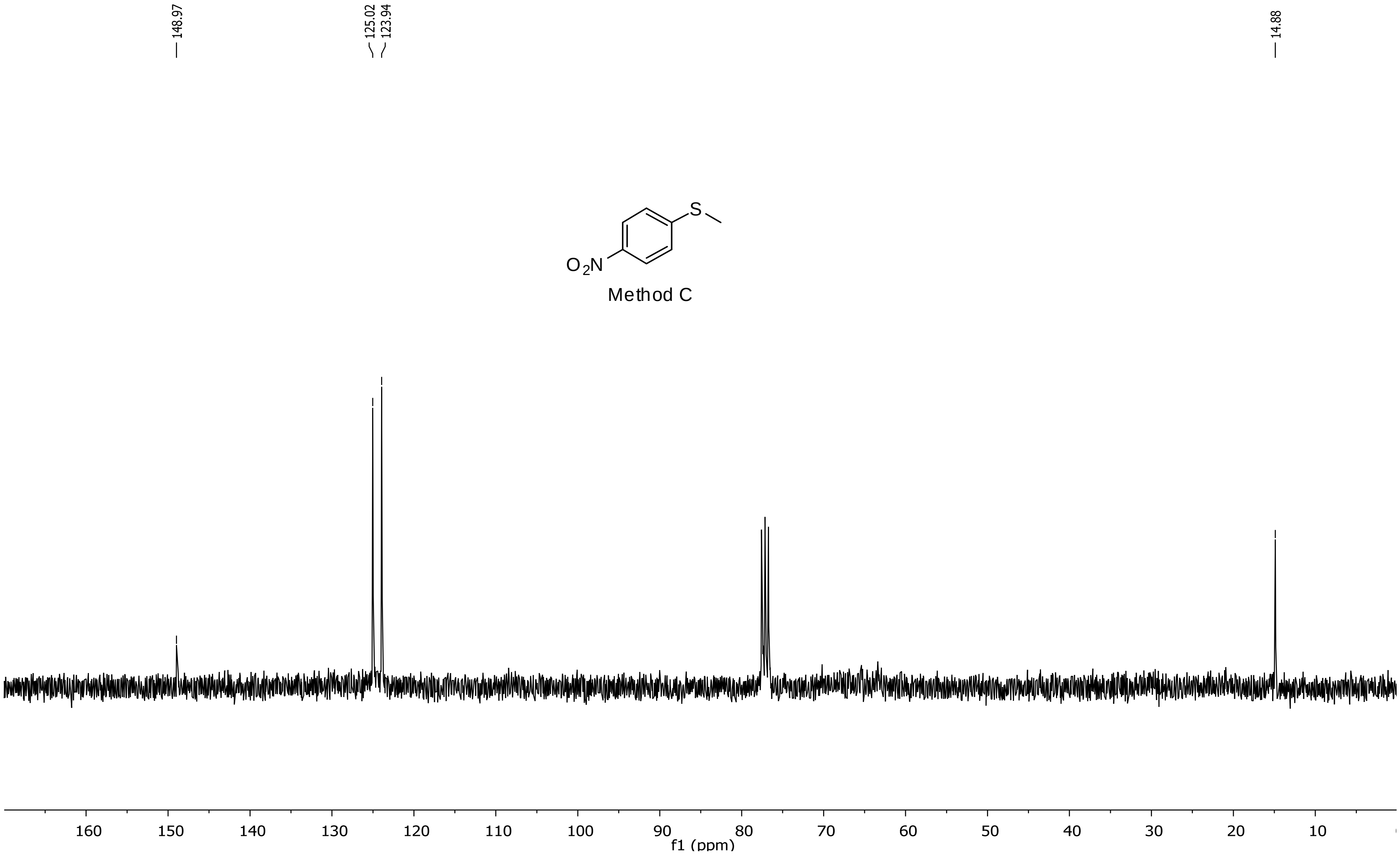

8.09
8.06
7.26
7.23
2.51
O_2N
S
Method A
2.00
2.00
3.26
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

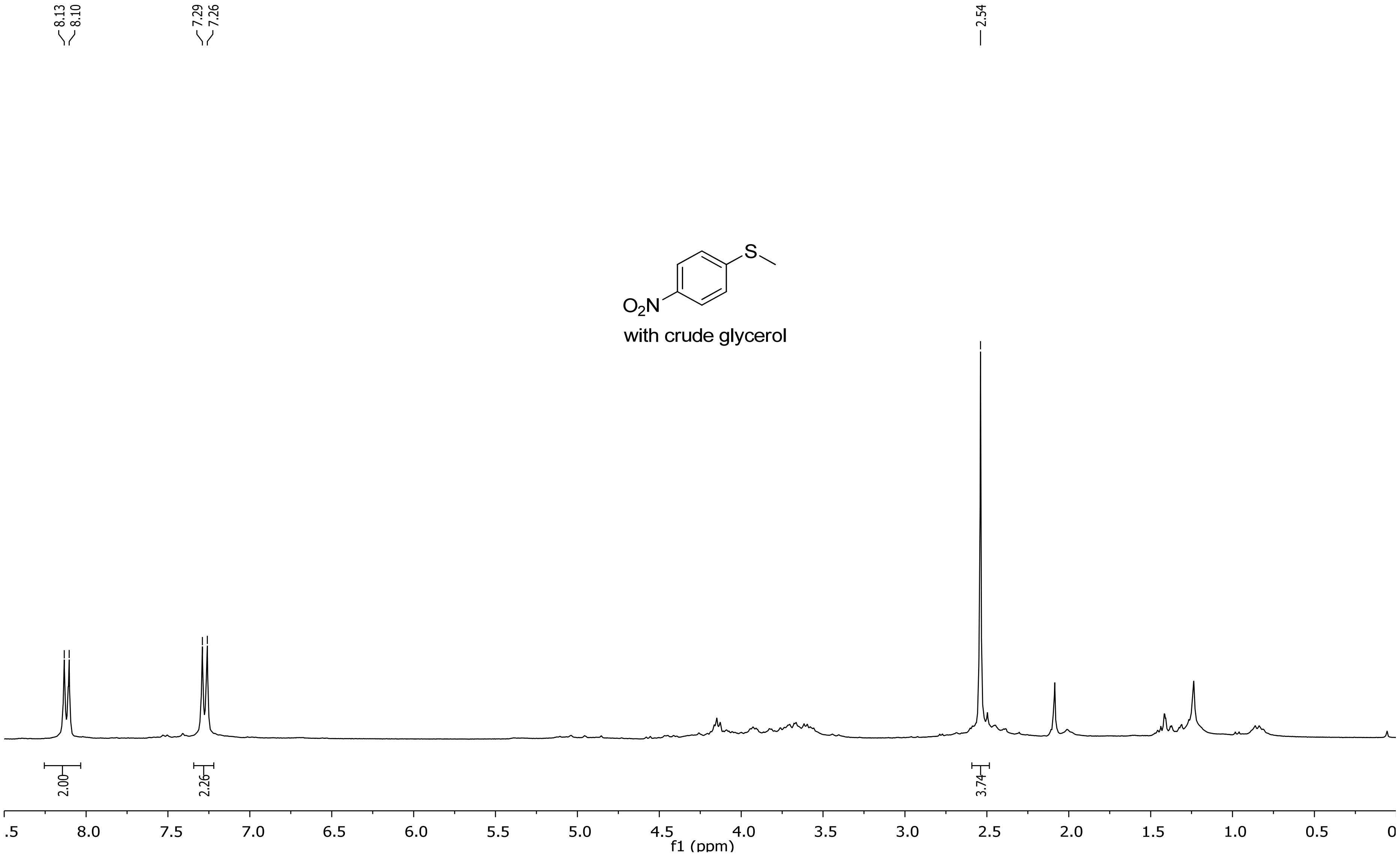

148.96
124.92
123.86
14.80
S
O2N
Method A
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

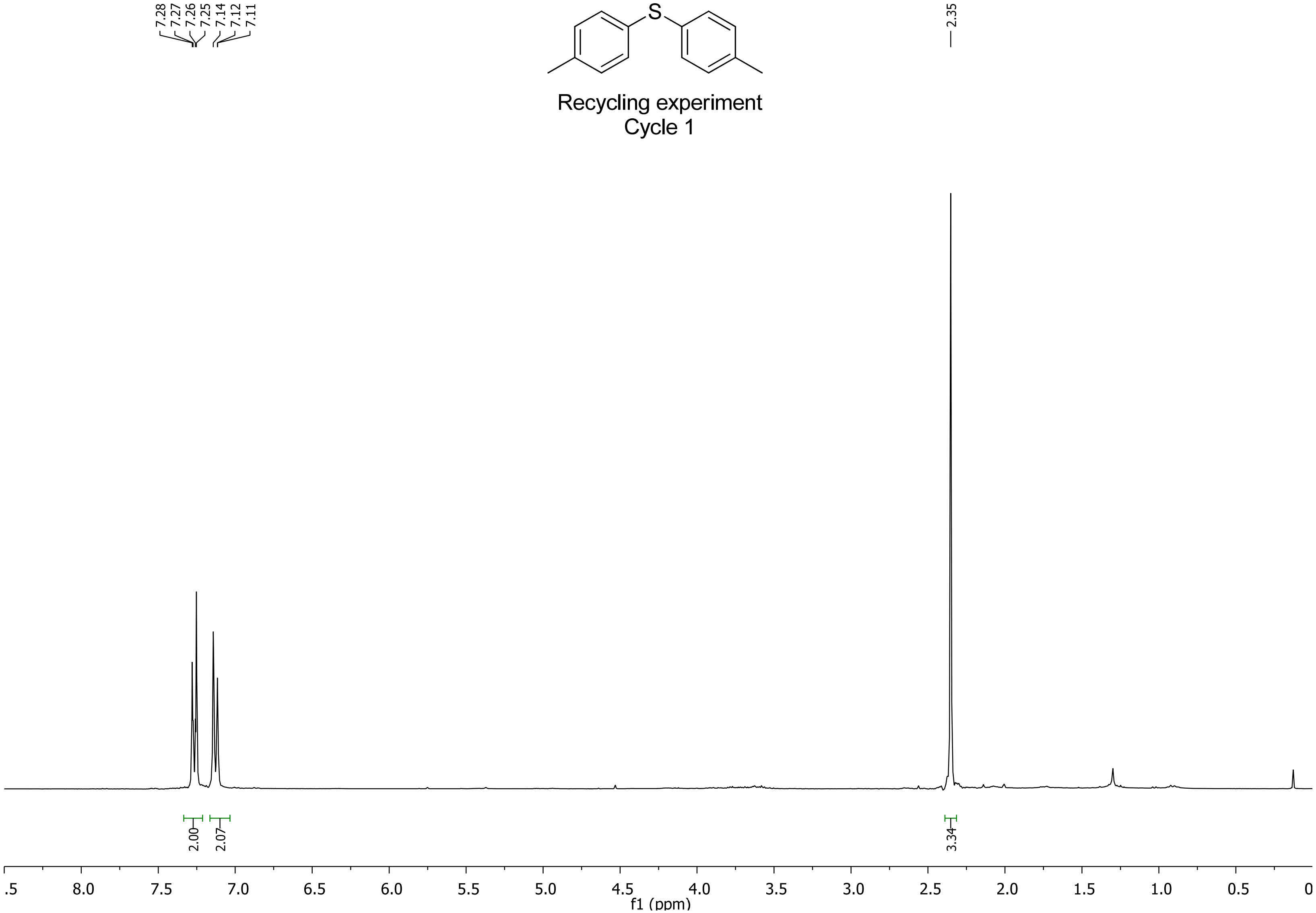

8.11
8.08
7.27
7.24
2.52
S
O_2N
Method B
2.00
2.15
3.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

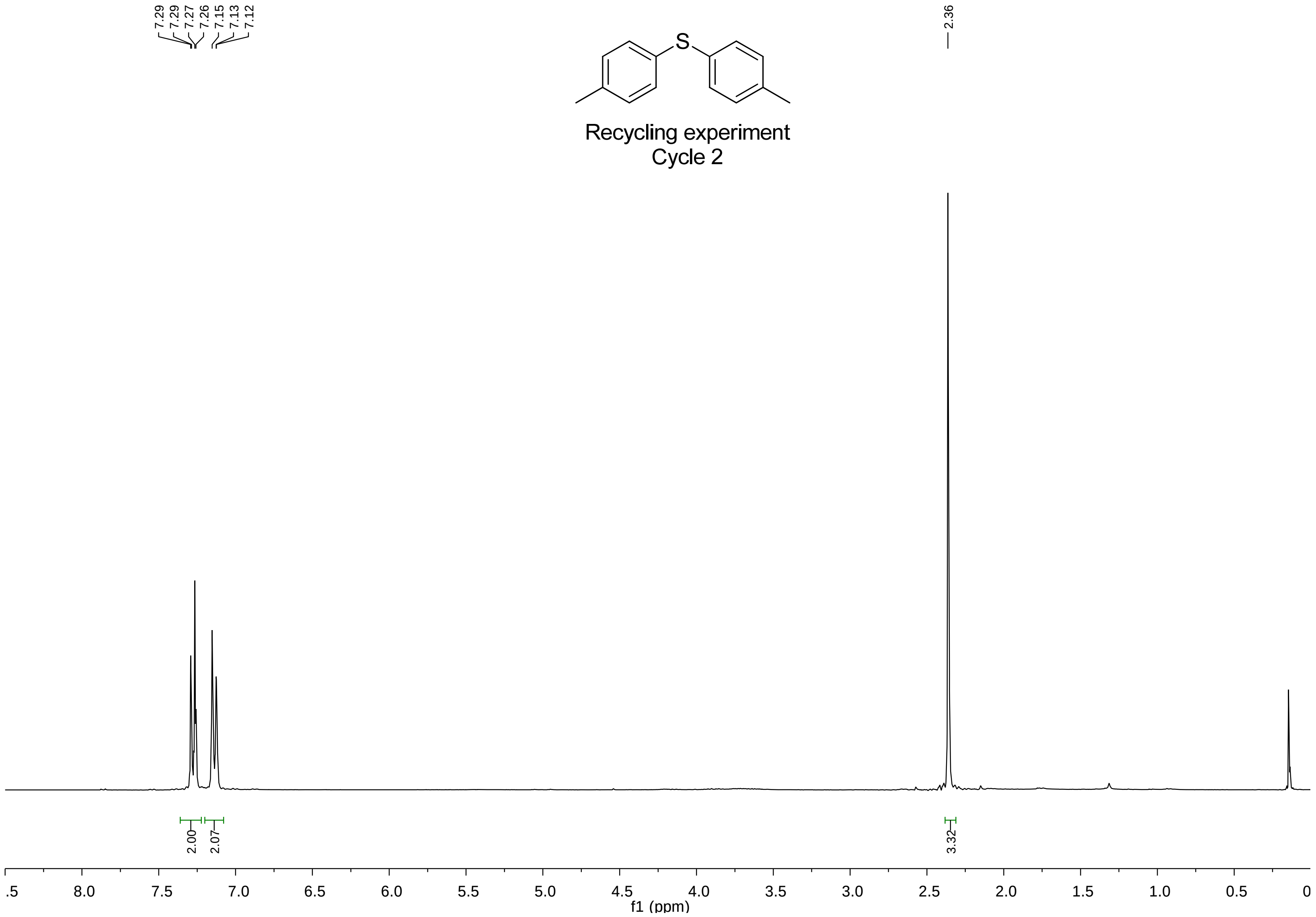

148.96
125.01
123.94
14.88
S
O2N
Method B
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

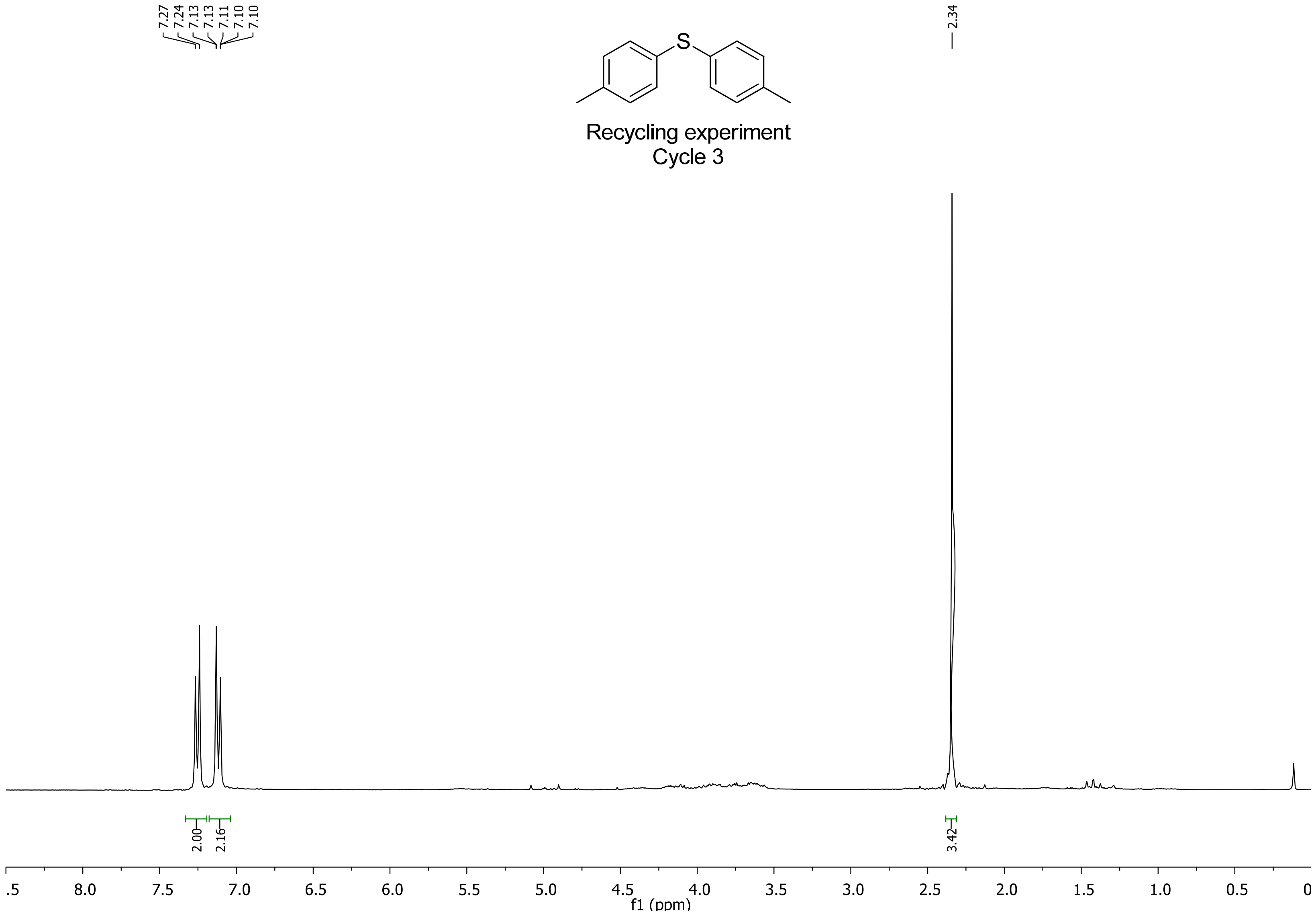

8.14
8.11
7.29
7.26
2.54
S
O2N
Method C
1.90
2.00
3.21
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

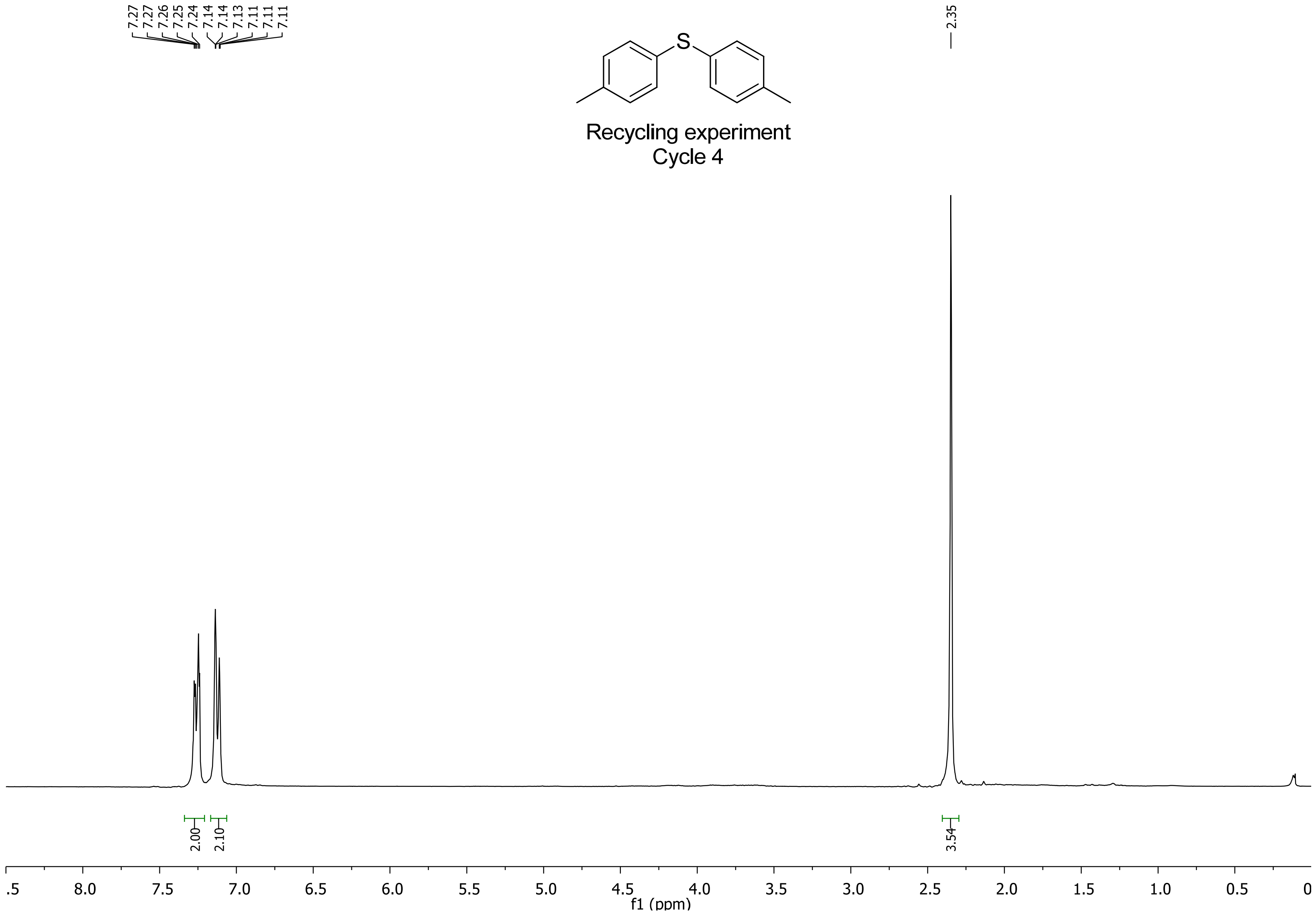

148.97
125.02
123.94
14.88
S
O2N
Method C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.13
8.10
7.29
7.26
2.54
S
O_2N
with crude glycerol
2.00
2.26
3.74
.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)

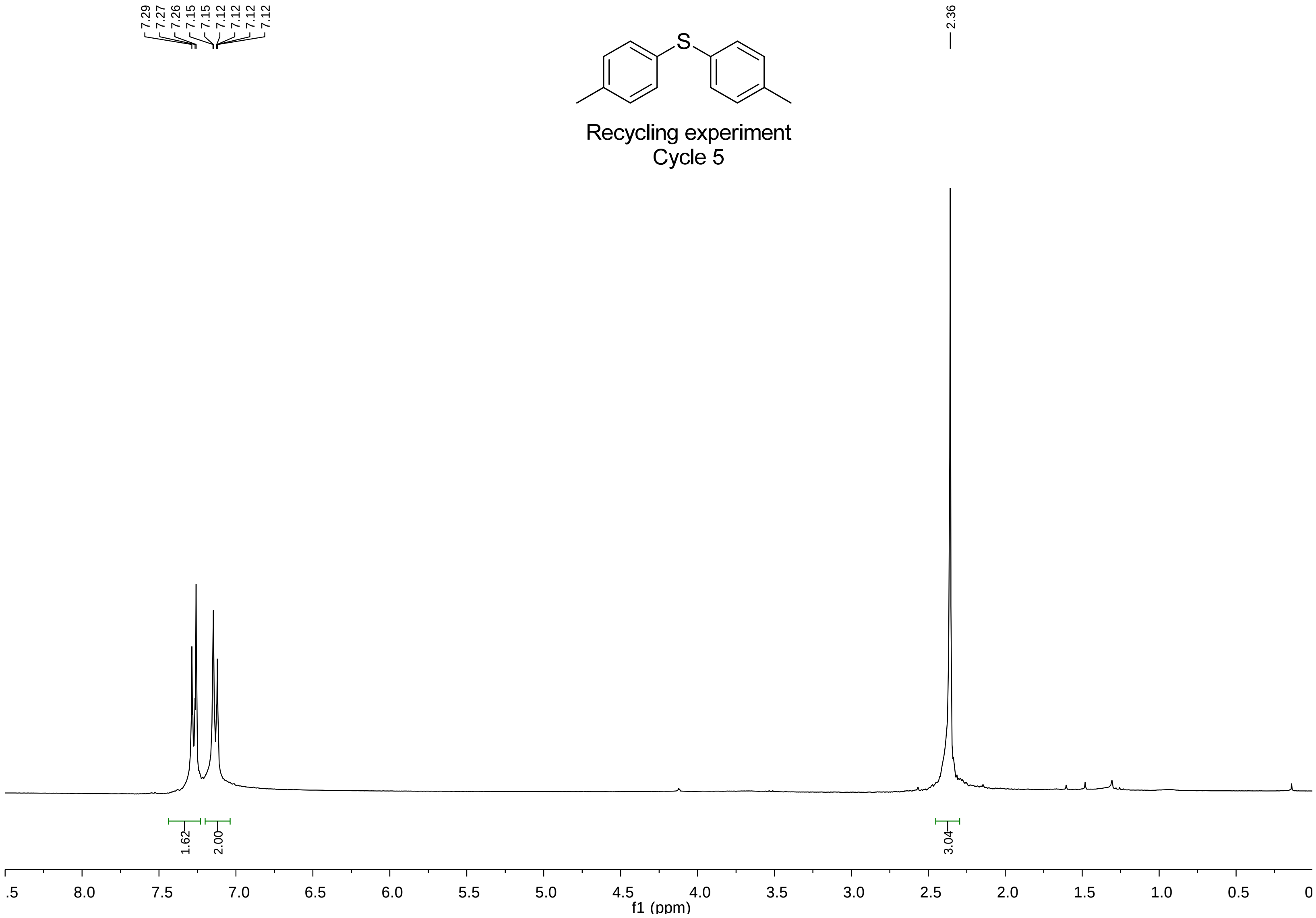

7.28
7.27
7.26
7.25
7.14
7.12
7.11
2.35
S
Recycling experiment
Cycle 1
2.00
2.07
3.34
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

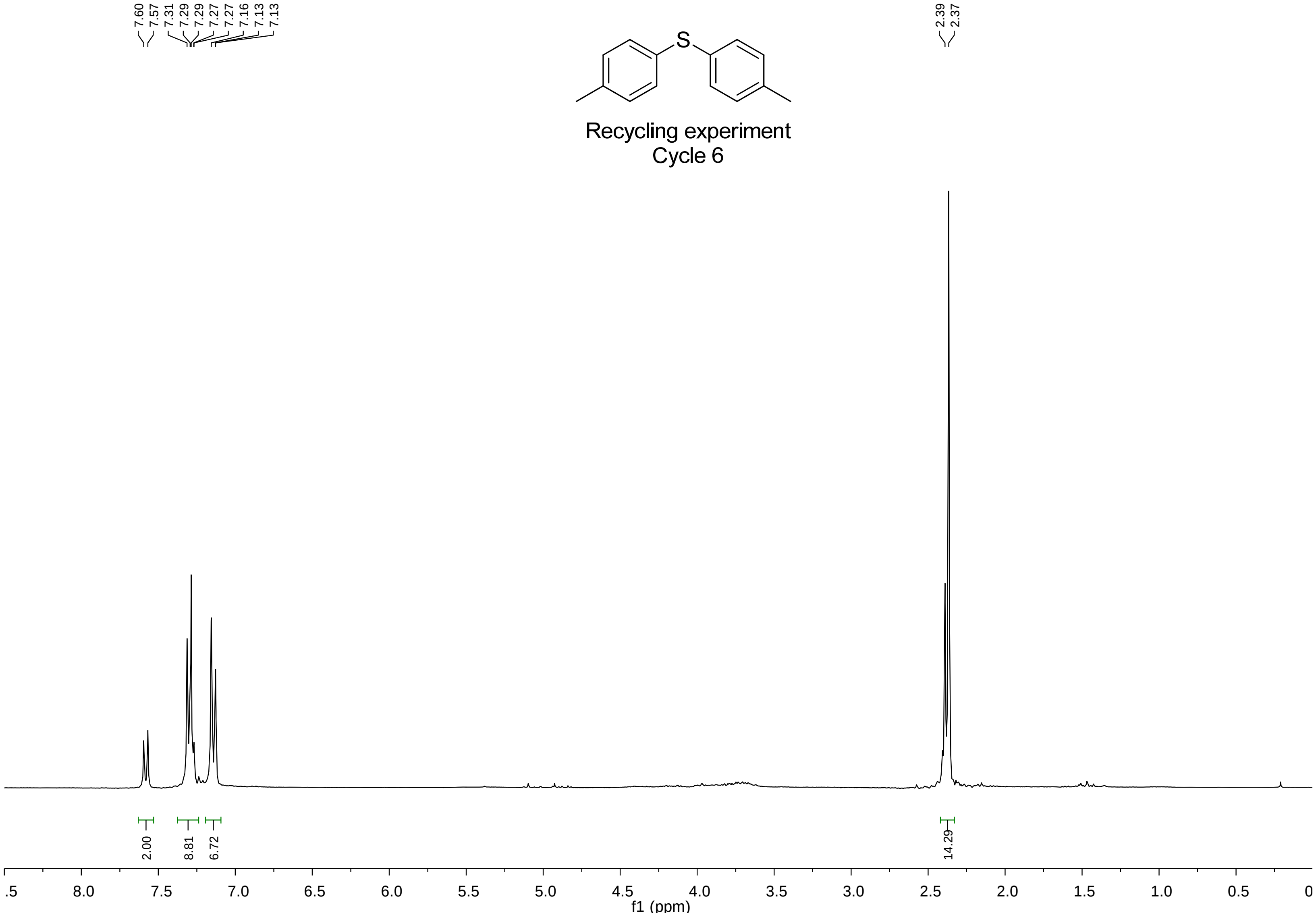

7.29
7.29
7.27
7.26
7.15
7.13
7.12
2.36
S
Recycling experiment
Cycle 2
2.00
2.07
3.32
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


7.27
7.24
7.13
7.13
7.11
7.10
7.10
2.34
S
Recycling experiment
Cycle 3
2.00
2.16
3.42
.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)


7.27
7.27
7.26
7.25
7.24
7.14
7.14
7.13
7.11
7.11
7.11
2.35
S
Recycling experiment
Cycle 4
2.00
2.10
3.54
.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)

Recycling experiment
Cycle 5




7.60
7.57
7.31
7.29
7.29
7.27
7.27
7.16
7.13
7.13
2.39
2.37
S
Recycling experiment
Cycle 6
2.00
8.81
6.72
14.29
.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)