

Supporting information

Electrochemical Metal-, Oxidant-free Synthesis of S-Thiocarbamates

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1. Experimental Setup for electro batch condition



Fig. S1 IKA ElectraSyn 2.0 for batch process



Fig. S2 10 ml reaction vessel with graphite & Pt electrodes

Experimental Setup for electro flow condition



Fig. S3 IKA ElectraSyn 2.0 as power supply (left), μ -EFR (middle), syringe pump (right).

2. Evaluation of reaction optimization experiment with μ -EFR.

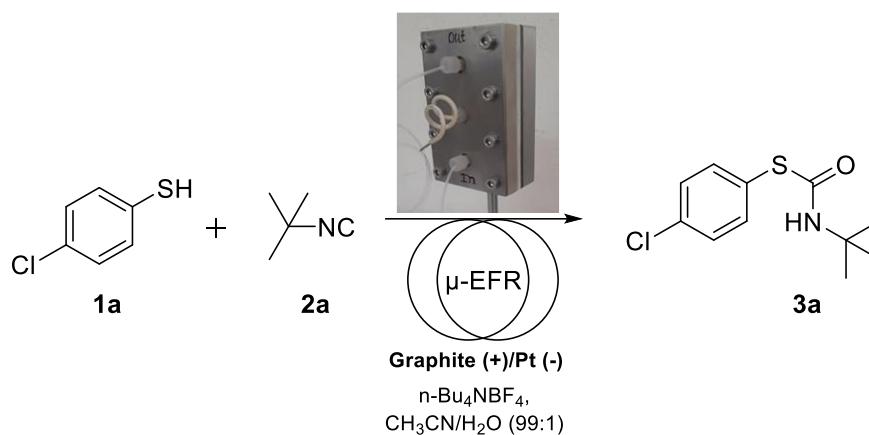


Table S1:

Entry	Concentration [mol/L]	Flow rate [ml/min]	Current density [mA/cm ²]	Current [F/mol]	Conversion % (yield %) ^a
1.	0.2	0.005	0.87	3.0	>99 (62)
2.	0.2	0.01	0.87	3.0	>99 (77)
3.	0.2	0.02	0.87	3.0	>99 (85)
4.	0.2	0.03	0.87	3.0	>85 (52)
5.	0.33	0.02	0.87	3.0	>90 (78)
6.	0.17	0.02	0.87	3.0	>99 (80)

3. Pt@Cu cathode preparation: Modified phosphates bath-based method has been used



for deposition of Pt over the Cu plate cathode. In this method, stock electrolytic solution containing mixture of Pt(IV) chlorides 150 mg, diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ 80 mg, disodium hydrogen phosphate $(\text{Na})_2\text{HPO}_4$ 200 mg, ammonium chloride 50 mg, and water 10 mL, was pumped with fix flow rate of $100 \mu\text{L min}^{-1}$ for 2h at 70°C under current density of 0.003 A/cm^2 , which typically led to the generation of a silver-black colored patterning, and then washed with water thoroughly to remove any unreacted salt and nanoparticle.

Reference - Raub, J.; Baumgärtner, ME. *Platinum Metals Rev.* **1988**, 32, 188.

4. Fabrication of micro-electrolysis flow reactor (μ -EFR)

Micro electro-flow outer body was fabricated using a stainless-steel body jacket (**A1**: 100 mm length x 64 mm width x 3 mm thickness) and second layer was fabricated 10 mm thickness high dens nylon plate (**A2**: 100 mm length x 64 mm width), it has a hole in the middle that allows an easy connection of the electrodes to the power supply by a copper wire and also has 2 holes, one for the inlet and one for the outlet of the reaction solution. The third layer was fabricated with teflon (**A3**: 100 mm length x 64 mm width x 0.5 mm thickness) layer made with laser cutter for protecting the nylon and stainless steel from the corrosive acid base and insulator for the current flow. Fourth layer copper electrode was customized as per the reactor size (**A4**: 72 mm length x 38 mm width x 1 mm thickness) these are fitted in same size rectangular shape groove, 1mm thickness PTFE core plate. For the solution flow under the constant current, fifth layer consisted of a laser cutted PTFE plate (**A5**: 100 mm x 64 mm x 1 mm thickness) zigzag groove with rectangular shape (2 mm x 350 mm x 1 mm = 700 μ L vol.), exposed electrode surface: 7 cm². Next, graphite anode was customized as per the reactor size (**A6**; 100 mm length x 64 mm width x 2 mm thickness). Last layer aluminium body (**A7**: 100 mm length x 64 mm width x 15 mm thickness). After fabrication of each layer and to align the patterns order **A1** to **A7**. Thereafter, both the electrodes were sandwiched by 2 mm teflon zig-zag channel sheets with identical dimension to fit groove channels and coupled to each other by inserting metal allenkey bolts through the eight holes on aluminium body plate. Finally, the metal holder was tightly pressed by help of allenkey driver to seal the device with no leak (**Fig. S4, S5, S6, S7**).

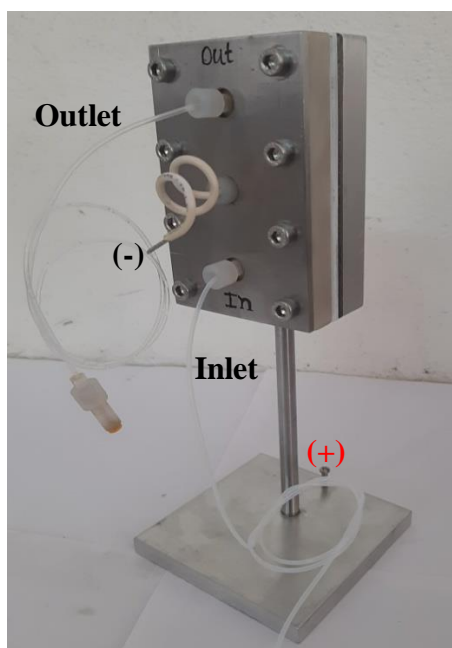


Fig. S4. Original Image of μ -EFR

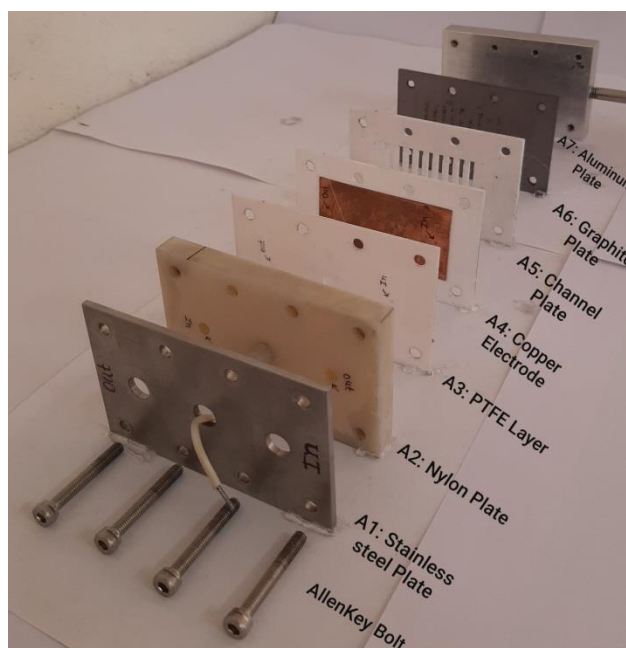
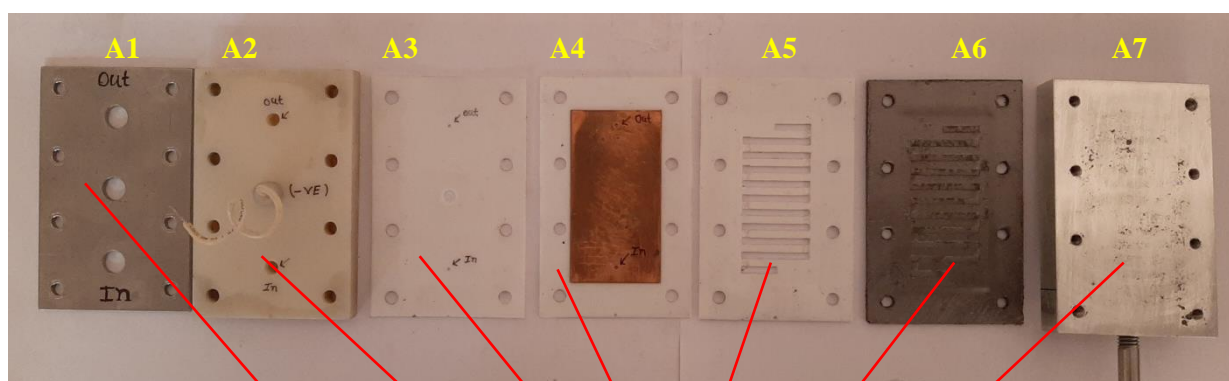


Fig. S5. Components of μ -EFR



- A1: Stainless steel plate**
- A2: Nylon plate**
- A3: PTFE plate**
- A4: PTFE core copper plate**
- A5: PTFE channel plate**
- A6: Graphite plate**
- A7: Aluminum plate with ϕ 5mm thread**

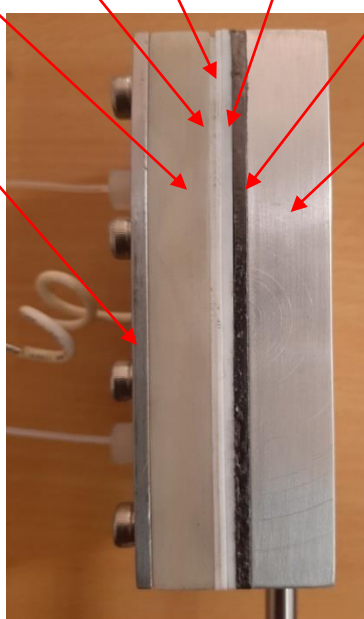


Fig. S6, S7

B series NMR
B-13

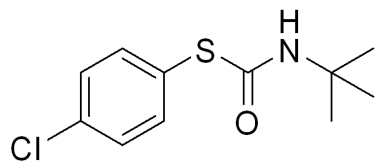
7.461
7.456
7.445
7.440
7.433
7.380
7.375
7.369
7.358
7.353
7.347
7.265

5.205

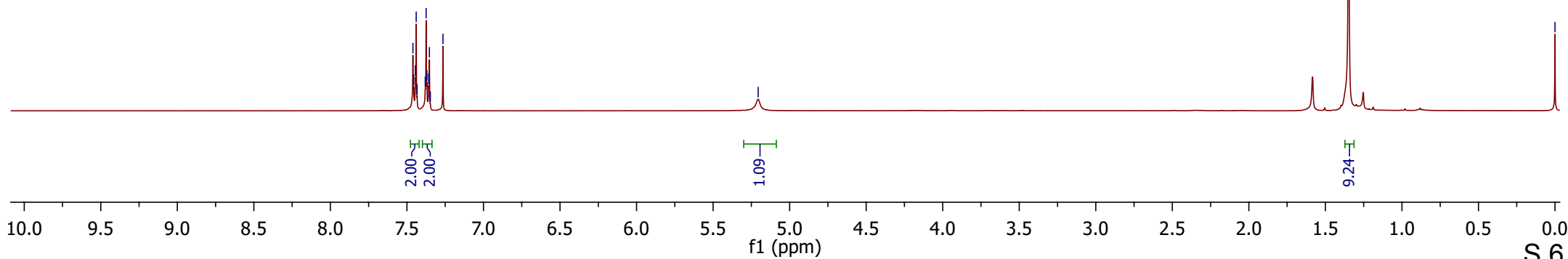
1.348

0.000

^1H NMR (400 MHz, CDCl_3) in Batch Process



(3a)



B series NMR
B-13

—163.14

—136.54
—135.63

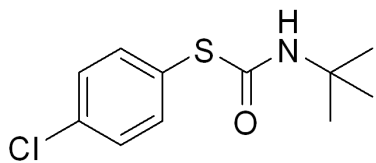
—129.30
—127.30

77.32
77.00
76.68

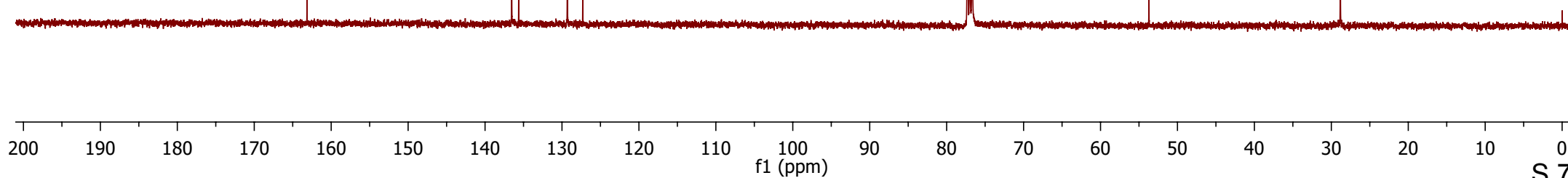
—53.70

—28.83

¹³C NMR (100 MHz, CDCl₃) in Batch Process

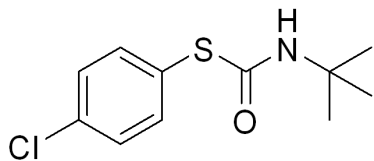


(3a)



New NMR
b-13

¹H NMR (400 MHz, CDCl₃) in Flow Process



(3a)

7.461
7.455
7.450
7.439
7.434
7.427
7.375
7.369
7.364
7.353
7.348
7.341
7.260

5.210

1.342

||

~

2.06
2.02

1.00

9.20

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 0.5 0.0
f1 (ppm)

163.14

136.54
135.63

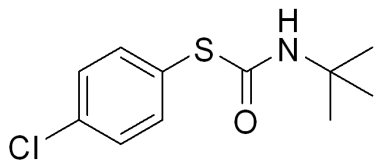
129.30
127.30

77.32
77.00
76.68

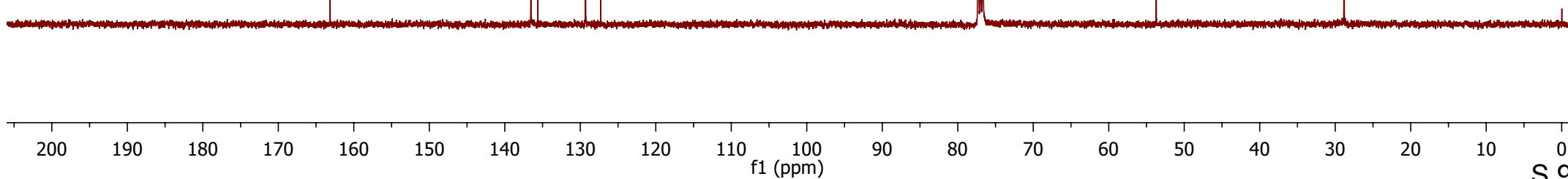
53.70

28.83

¹³C NMR (100 MHz, CDCl₃) in Flow Process



(3a)



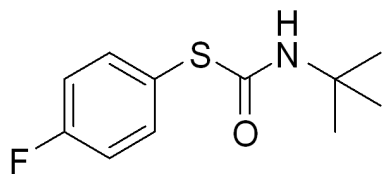
B series NMR
B-05

7.513
7.508
7.500
7.497
7.494
7.491
7.483
7.478
7.260
7.114
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7.101
7.090
7.085
7.080
7.069
7.063
7.056

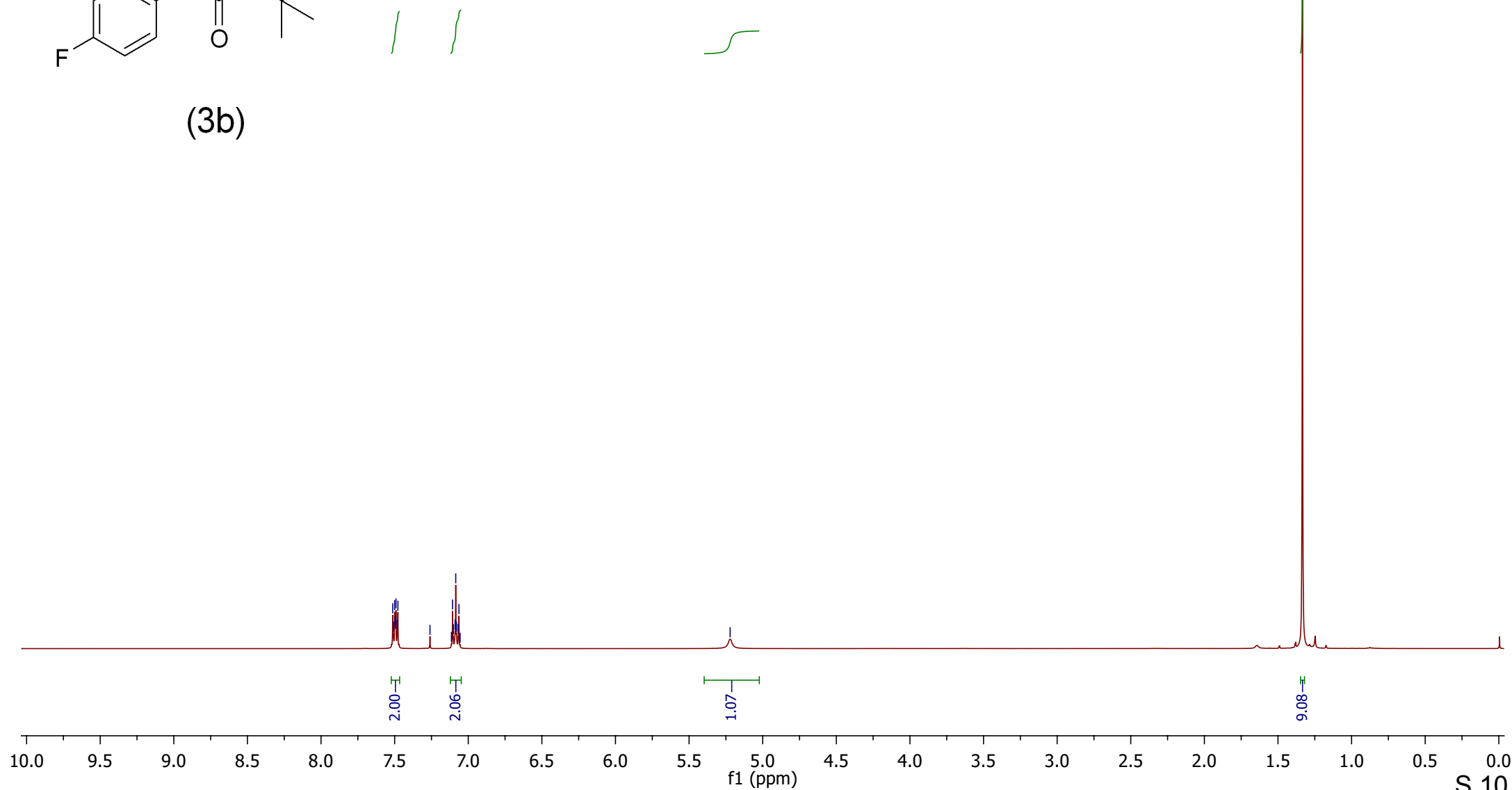
5.221

1.334

¹H NMR (400 MHz, CDCl₃)



(3b)



B series NMR
B-05

164.632
163.676
162.149

137.519
137.434

124.174
124.141

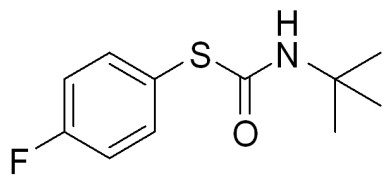
116.413
116.194

77.318
77.000
76.683

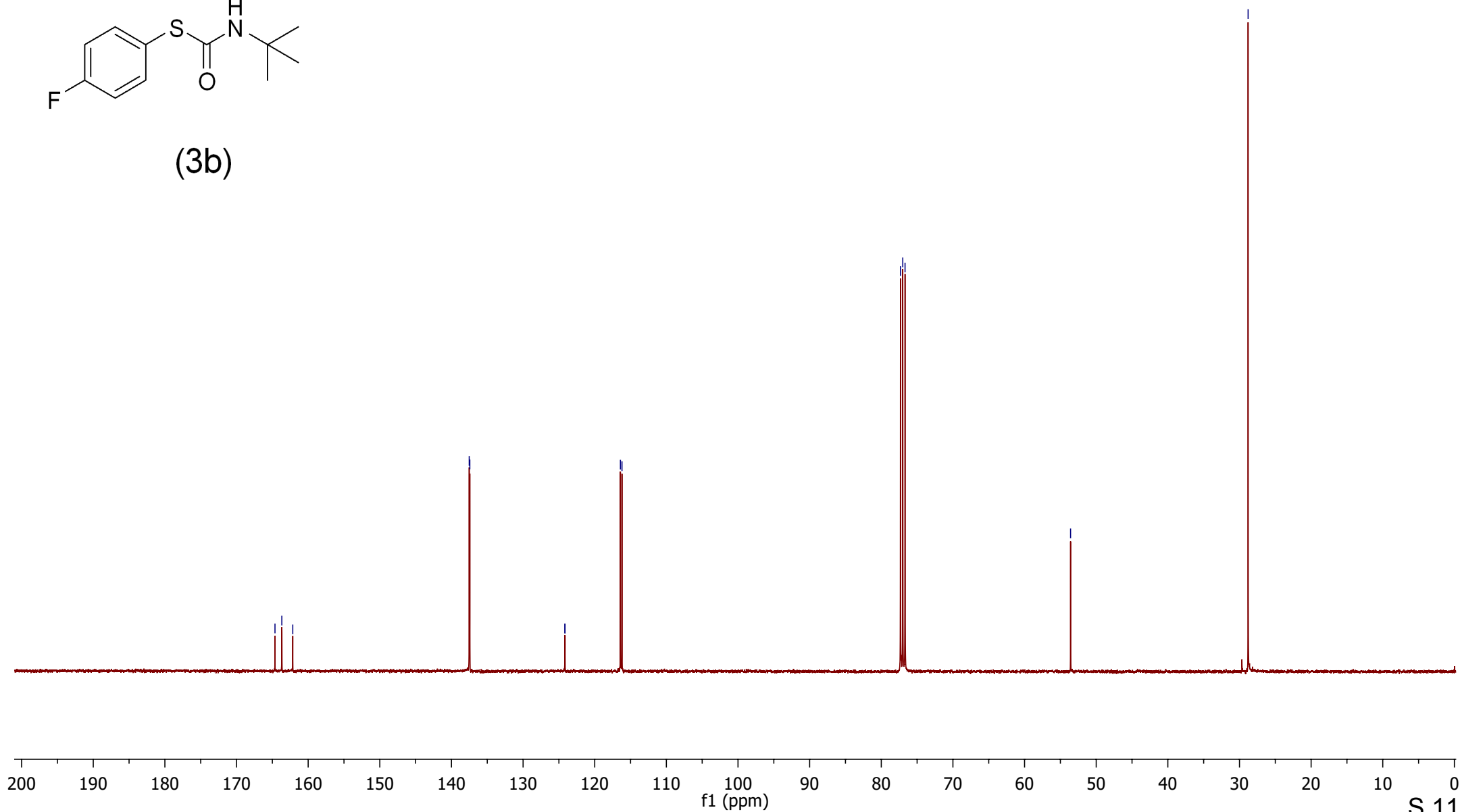
53.578

28.795

^{13}C NMR (100 MHz, CDCl_3)

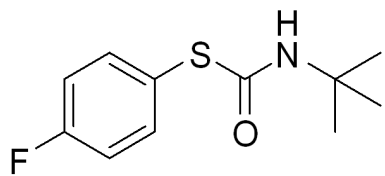


(3b)



F-NMR
B-05

^{19}F NMR (376 MHz, CDCl_3)



(3b)

-111.42

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

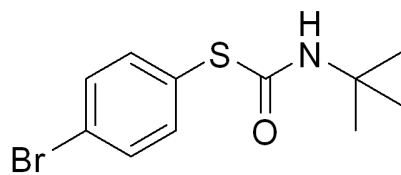
New NMR
b-17

7.530
7.523
7.519
7.507
7.502
7.496
7.391
7.385
7.380
7.368
7.363
7.357
7.260

5.228

1.341

¹H NMR (400 MHz, CDCl₃)



(3c)

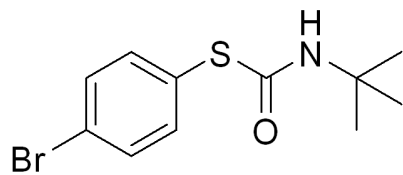
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f1 (ppm)

1.00

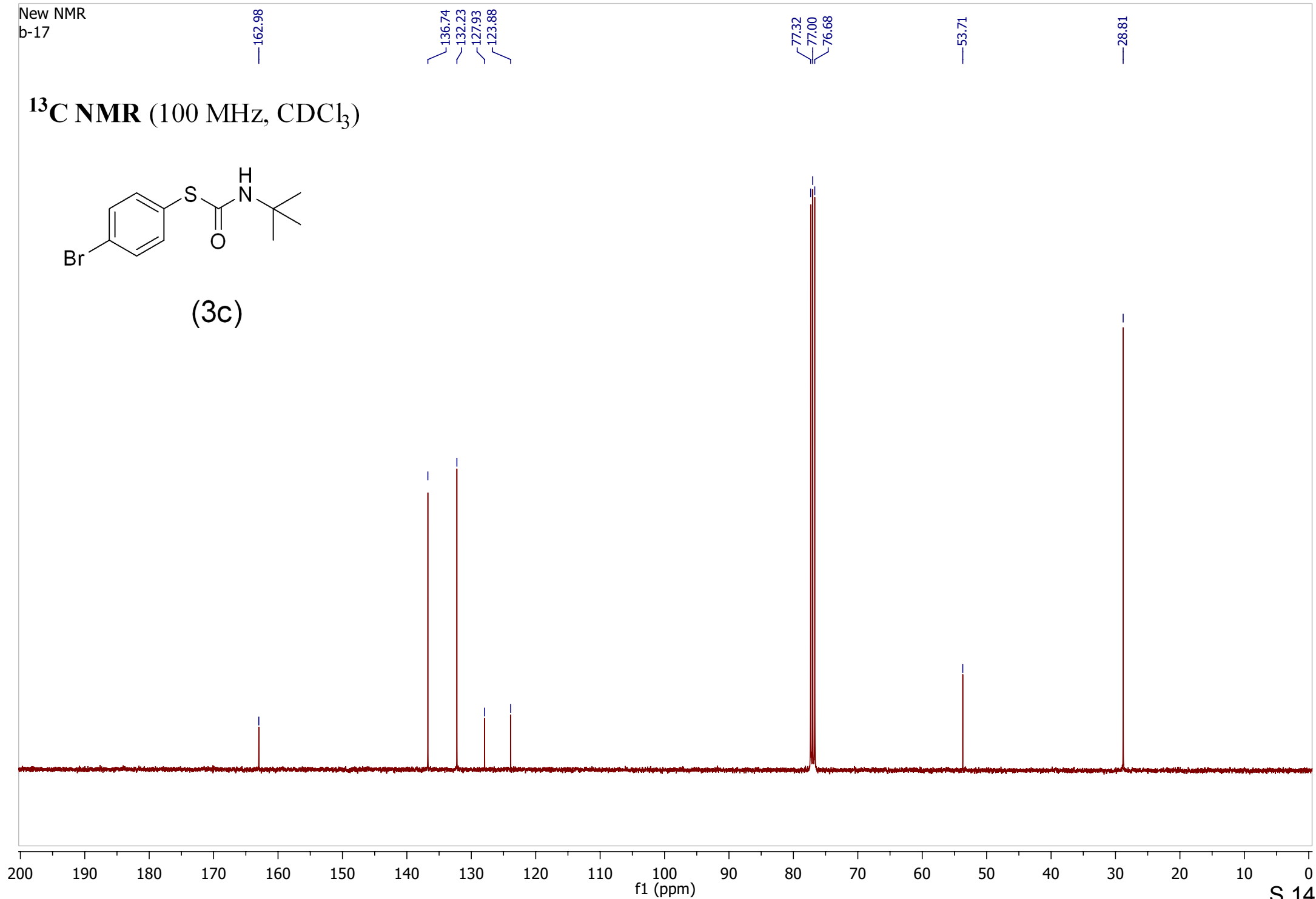
9.12

New NMR
b-17

^{13}C NMR (100 MHz, CDCl_3)



(3c)



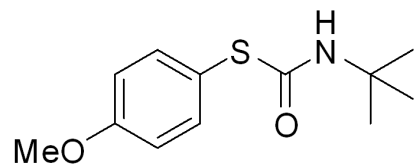
7.461
7.453
7.448
7.436
7.431
7.423
7.260
6.935
6.928
6.922
6.911
6.905
6.898

5.223

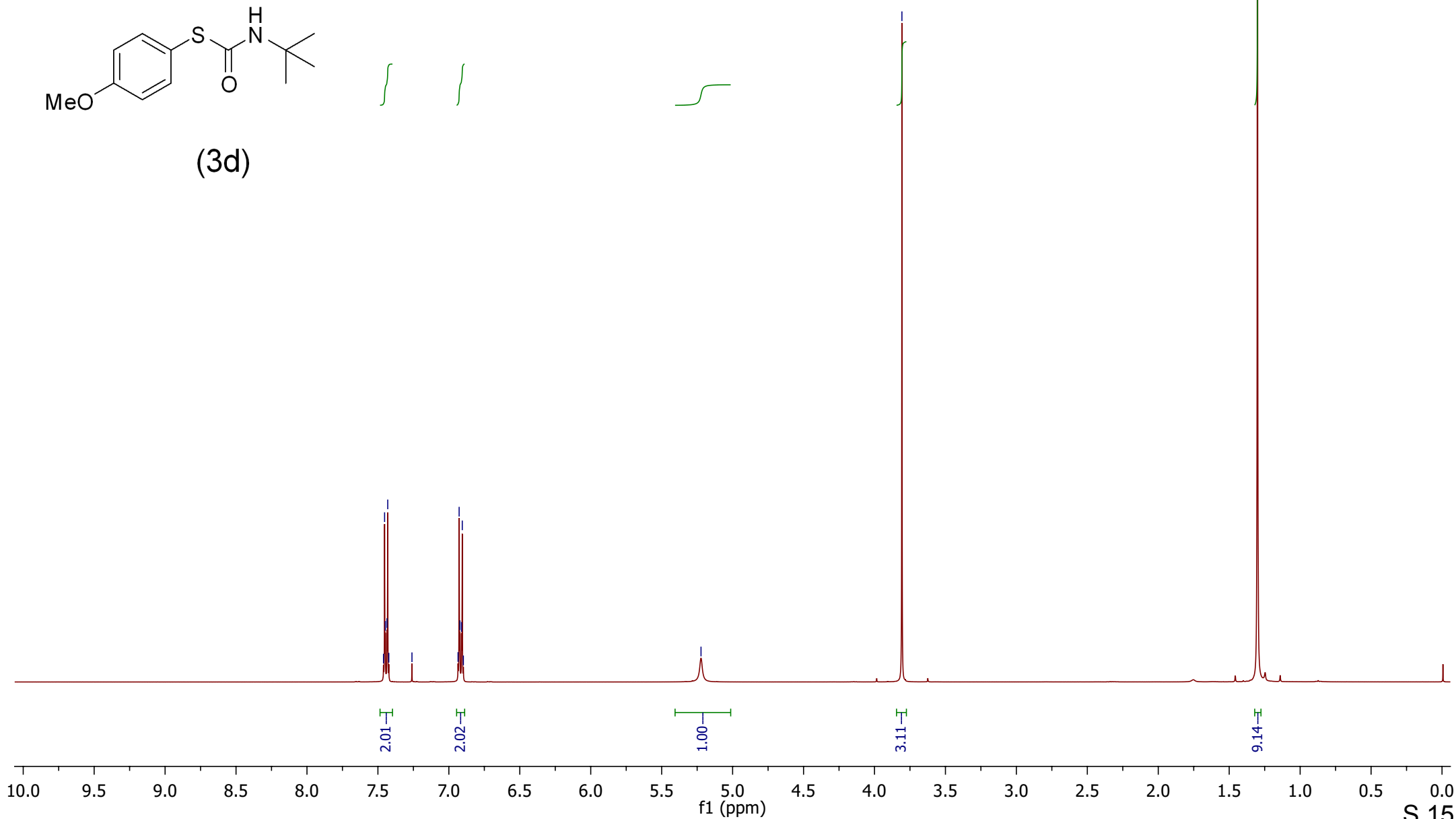
3.807

1.301

¹H NMR (400 MHz, CDCl₃)



(3d)



164.8

160.58

137.08

119.74

114.80

77.32

77.00

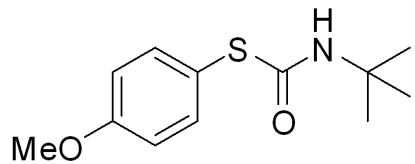
76.68

55.27

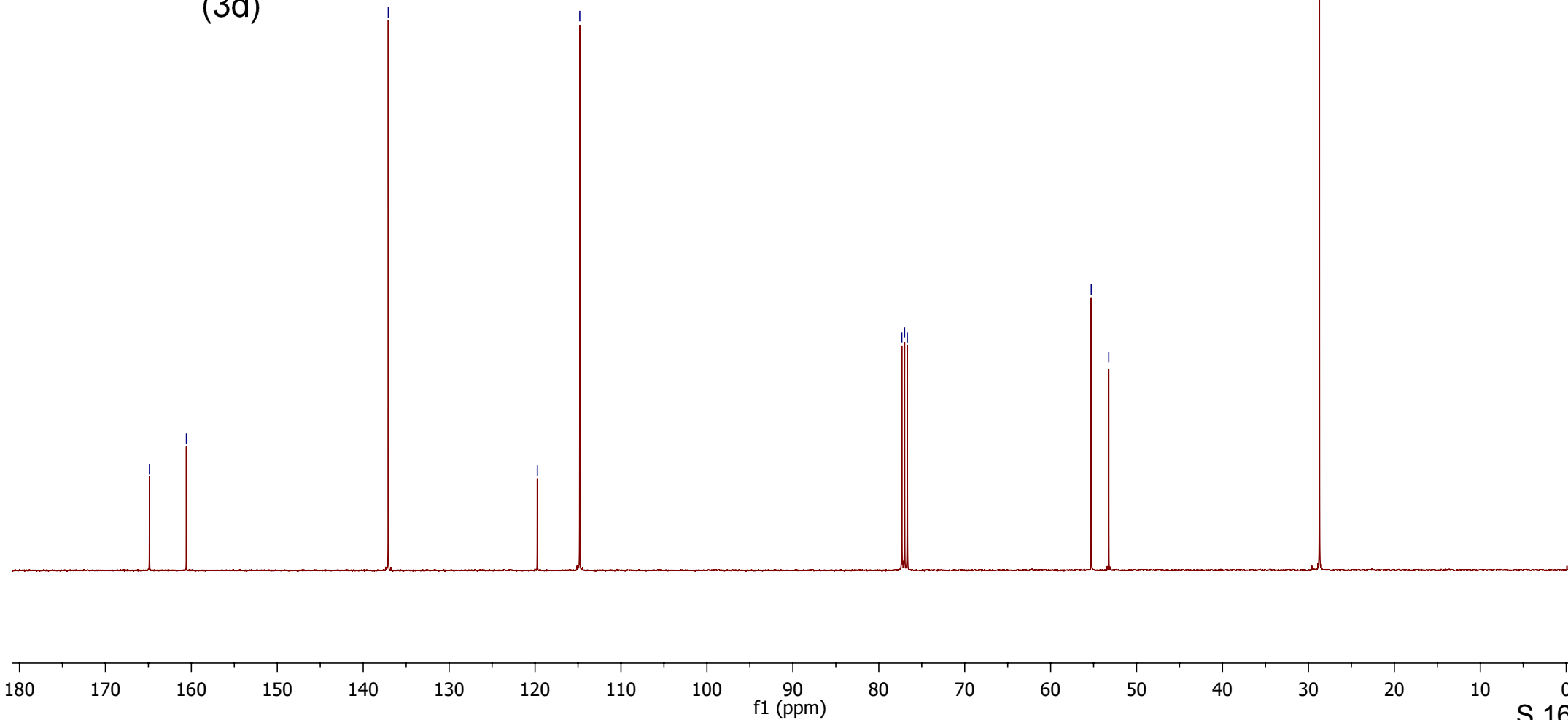
53.23

28.72

^{13}C NMR (100 MHz, CDCl_3)



(3d)



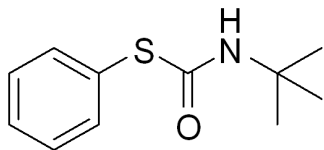
New NMR
b-02

7.544
7.541
7.539
7.536
7.531
7.527
7.524
7.520
7.417
7.407
7.404
7.401
7.399
7.396
7.395
7.391
7.387
7.260

5.193

1.323

¹H NMR (400 MHz, CDCl₃)



(3e)

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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 0.5 0.0
f1 (ppm)

2.00
3.11

1.07

9.11

—163.97

—135.33

129.28

129.19

128.97

77.32

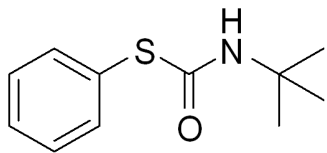
77.00

76.68

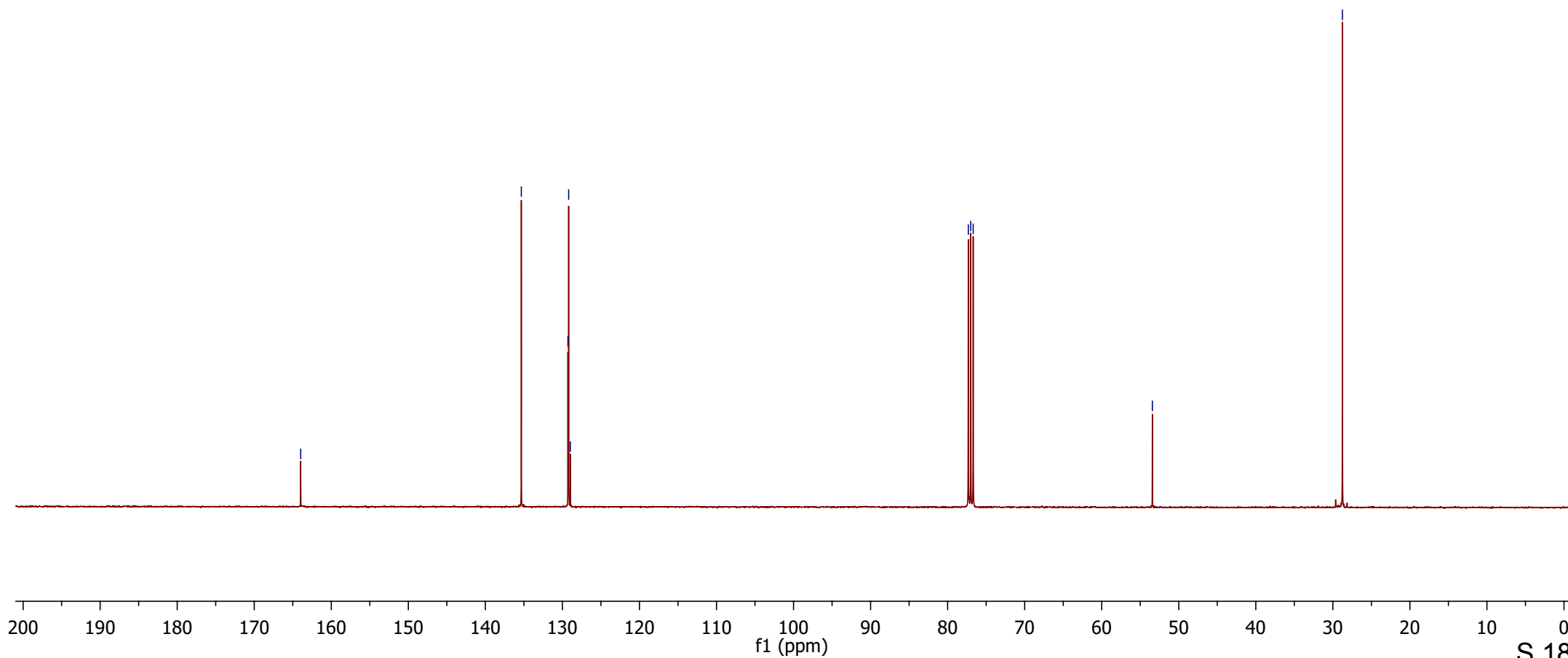
—53.43

—28.76

¹³C NMR (100 MHz, CDCl₃)



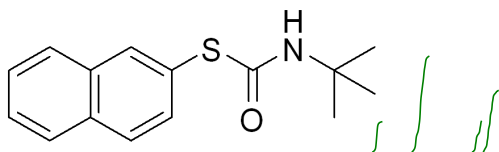
(3e)



New NMR
b-21

8.060
8.056
7.872
7.857
7.851
7.844
7.840
7.834
7.827
7.590
7.585
7.568
7.564
7.534
7.529
7.520
7.510
7.505
7.260

^1H NMR (400 MHz, CDCl_3)



(3f)

5.266

1.332

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 0.5 0.0
f1 (ppm)

1.00

3.13

1.03

2.02

1.03

9.04

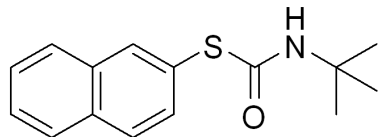
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133.49
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126.32

77.32
77.00
76.68

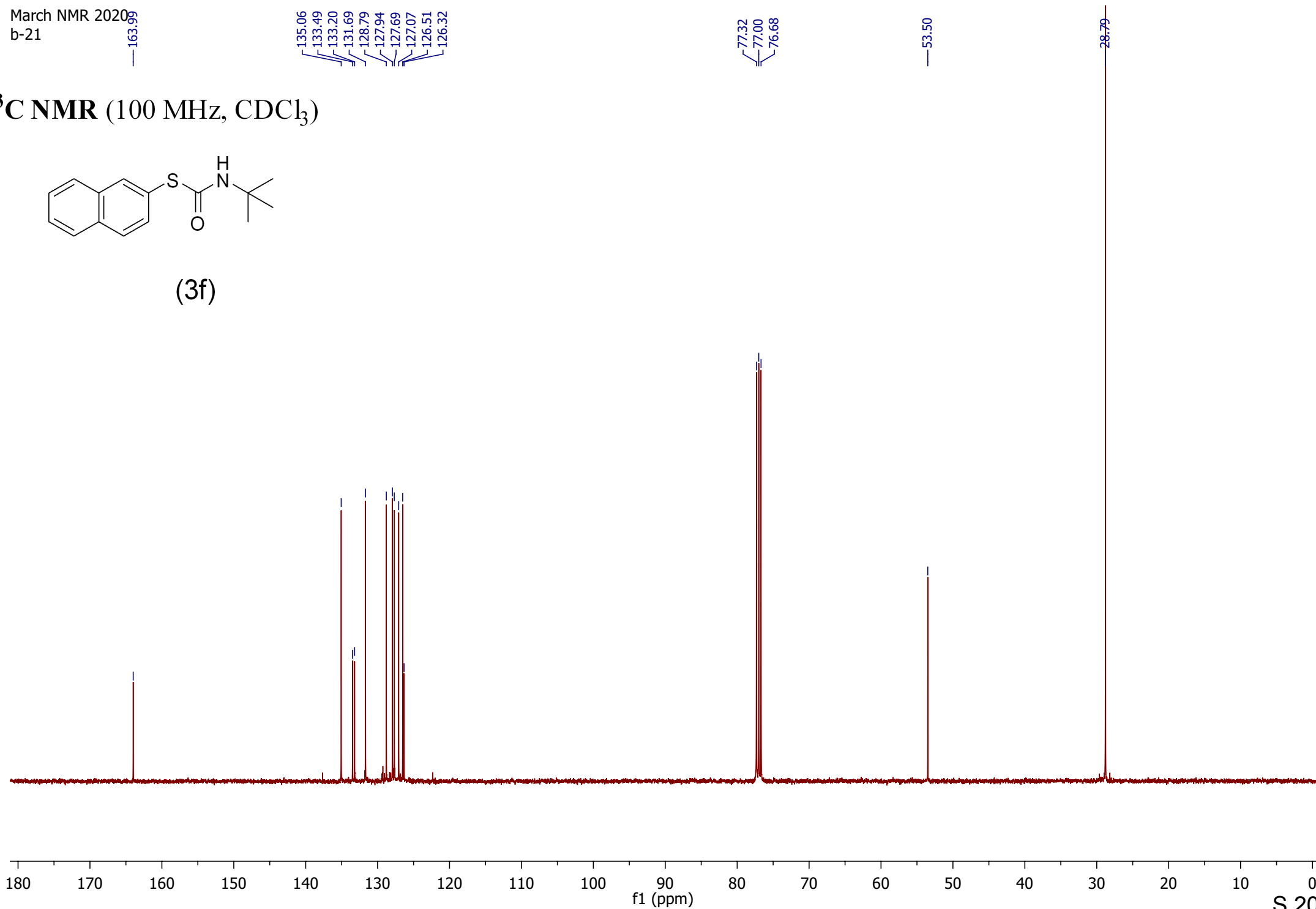
53.50

28.79

¹³C NMR (100 MHz, CDCl₃)



(3f)



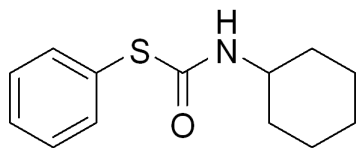
7.565
7.560
7.551
7.542
7.429
7.419
7.413
7.408
7.405
7.403
7.397
7.394
7.260

5.182

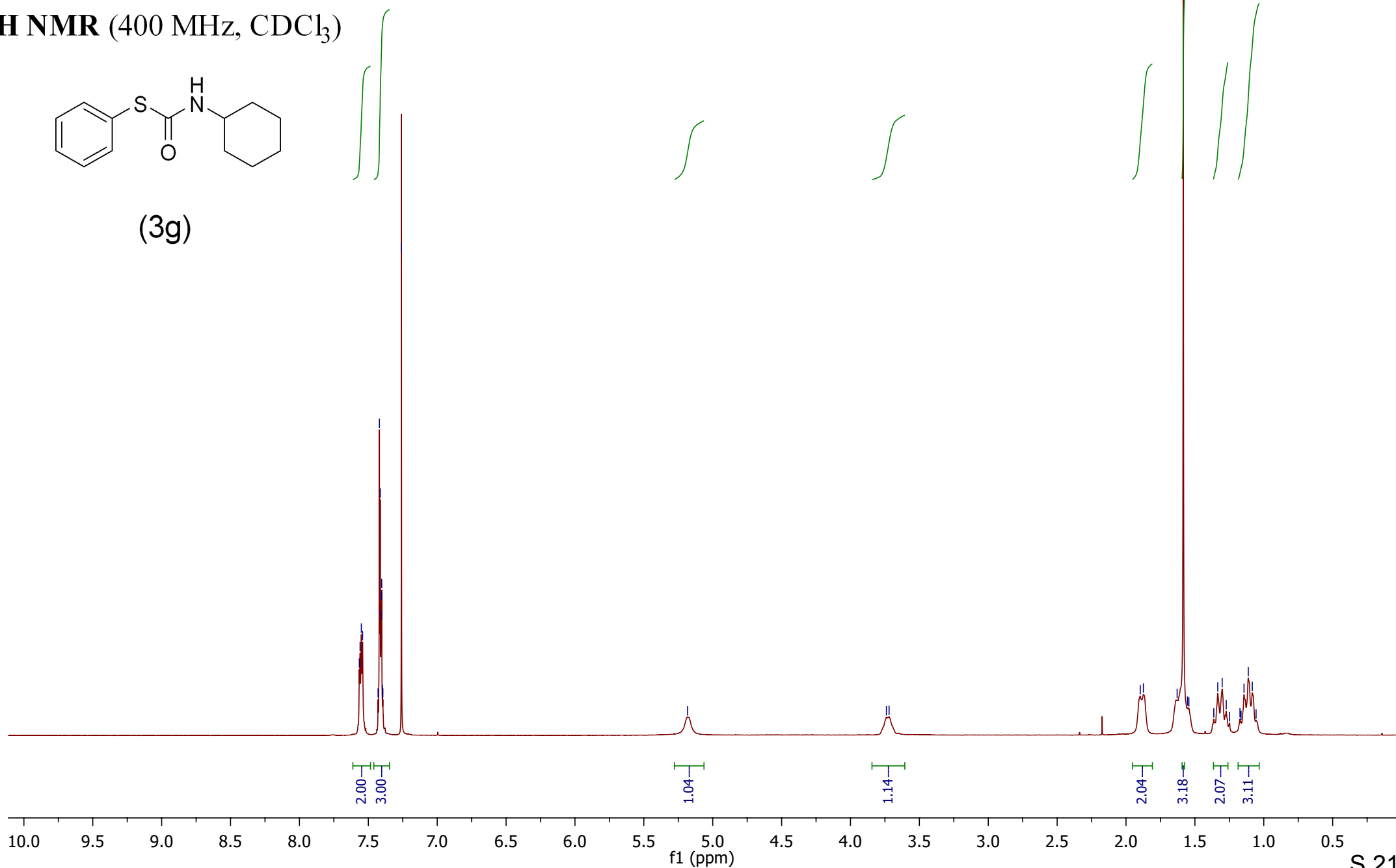
3.739
3.720

1.897
1.874
1.629
1.584
1.553
1.544
1.363
1.334
1.302
1.272
1.173
1.165
1.144
1.113
1.083
1.056

¹H NMR (400 MHz, CDCl₃)



(3g)



164.93

135.41

129.55

129.39

128.81

77.32

77.00

76.68

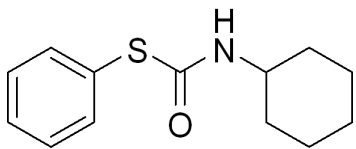
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32.83

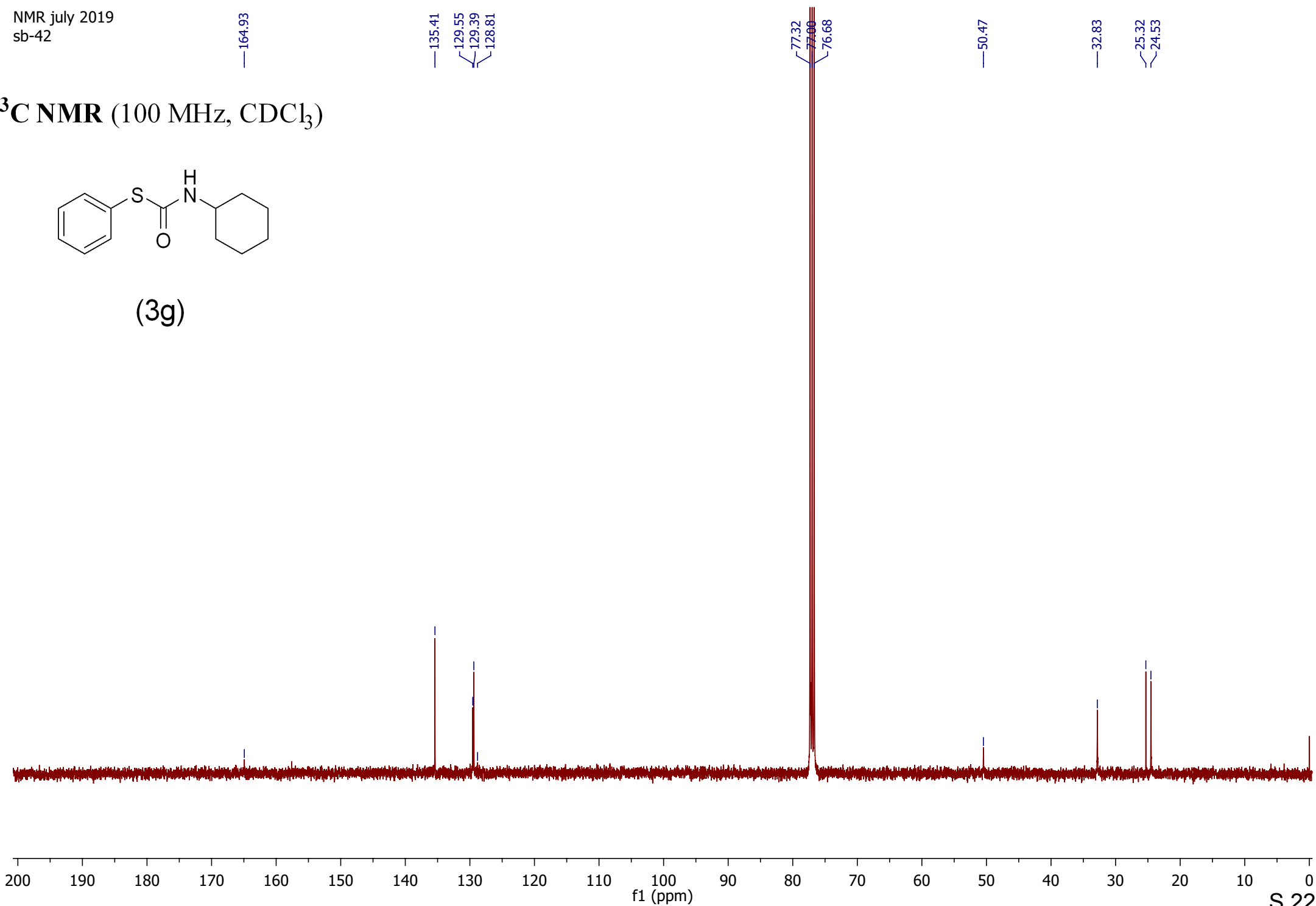
25.32

24.53

^{13}C NMR (100 MHz, CDCl_3)



(3g)



B series mahesh
B-06

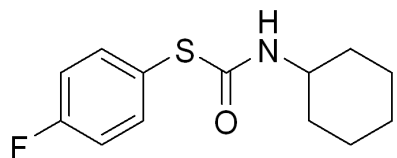
7.528
7.514
7.506
7.493
7.260
7.111
7.090
7.069

5.255

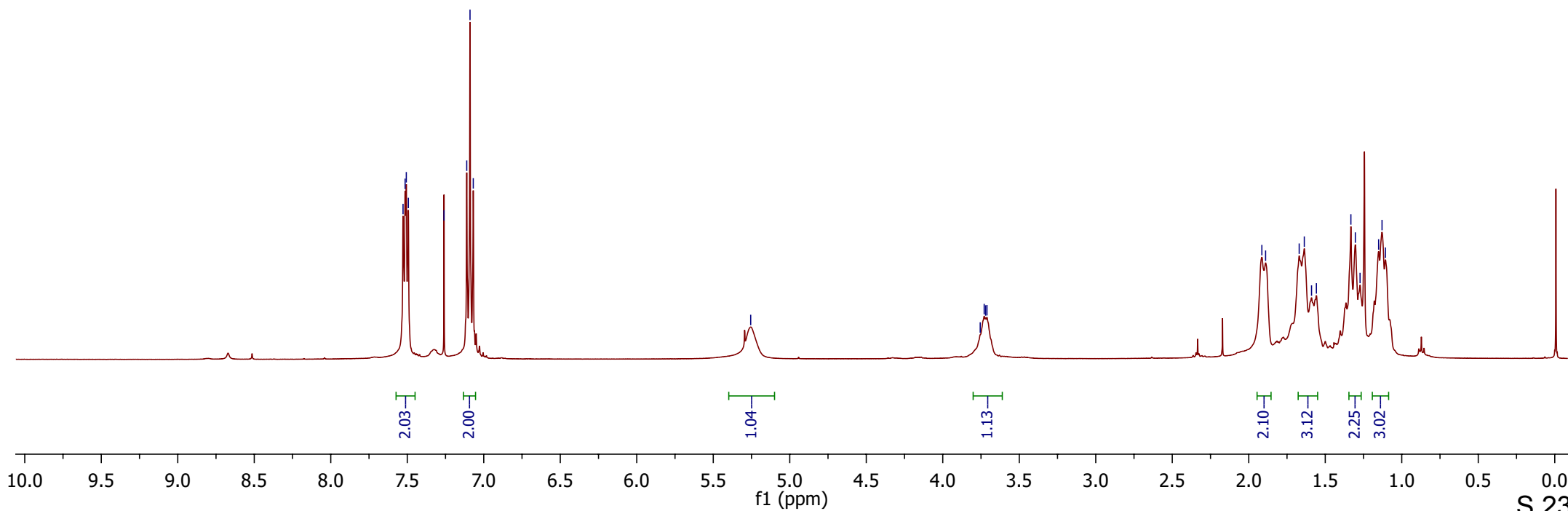
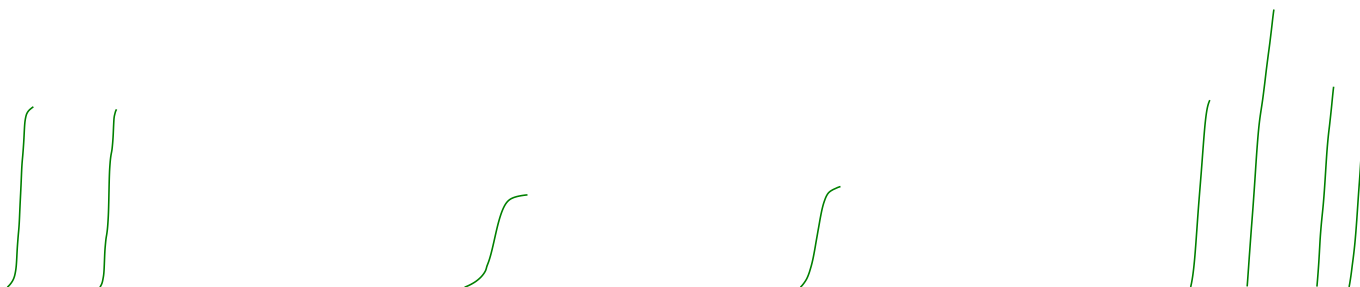
3.755
3.729
3.720
3.711

1.914
1.890
1.670
1.637
1.590
1.558
1.333
1.303
1.273
1.151
1.129
1.107

^1H NMR (400 MHz, CDCl_3)



(3h)



B series NMR
B-06

164.71
164.56
162.23

137.52
137.44

123.97

116.54
116.32

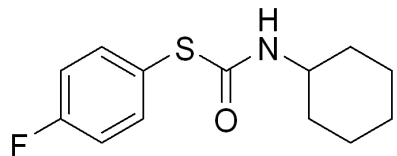
77.32
77.00
76.68

50.68

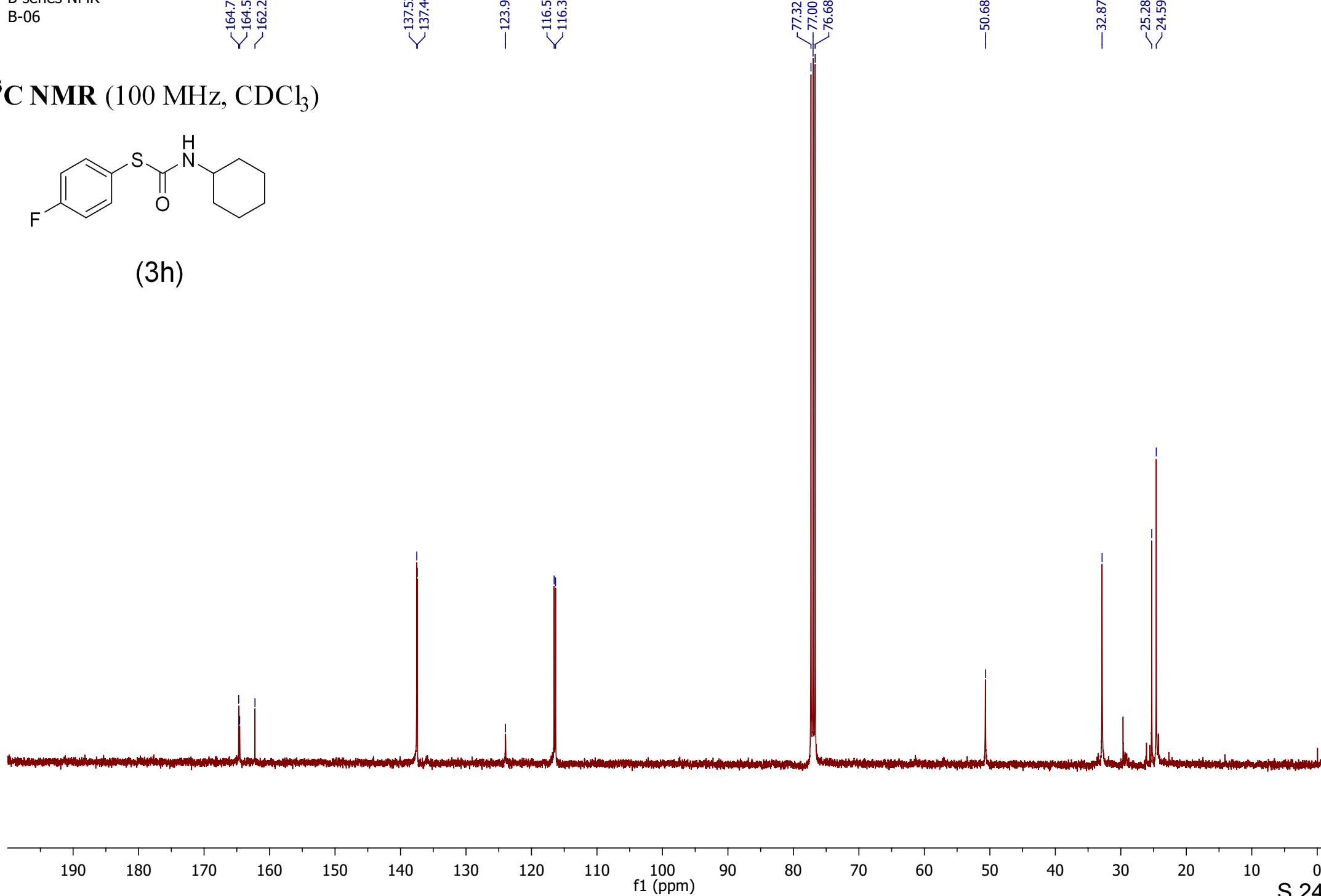
32.87

25.28
24.59

^{13}C NMR (100 MHz, CDCl_3)

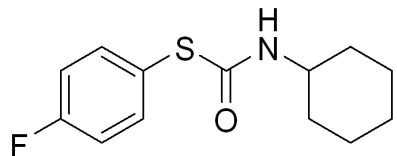


(3h)

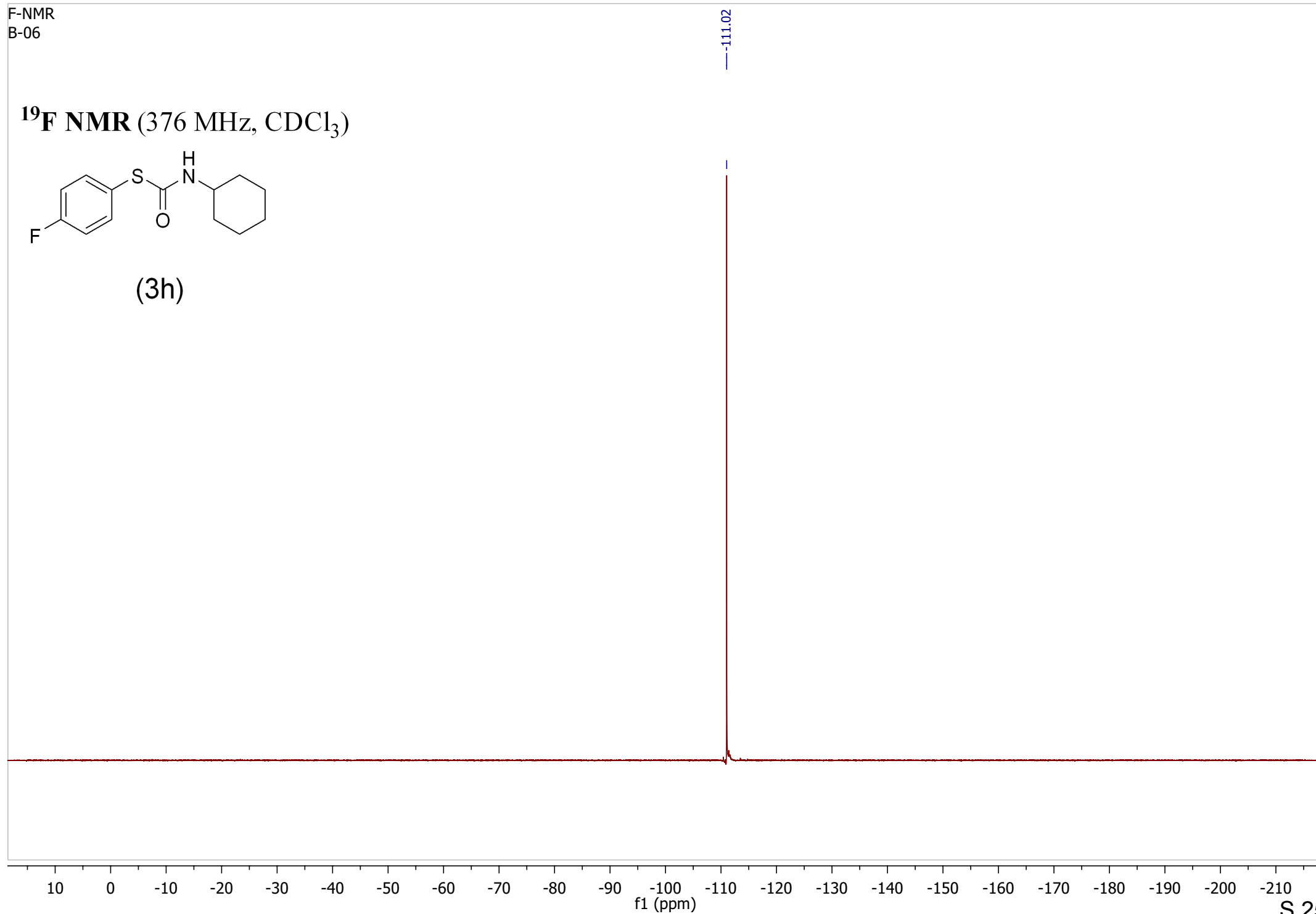


F-NMR
B-06

^{19}F NMR (376 MHz, CDCl_3)



(3h)



B series mahesh
B-18

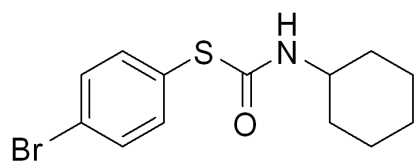
7.54
7.53
7.52
7.51
7.50
7.41
7.40
7.39
7.38
7.38
7.37
7.26

5.23

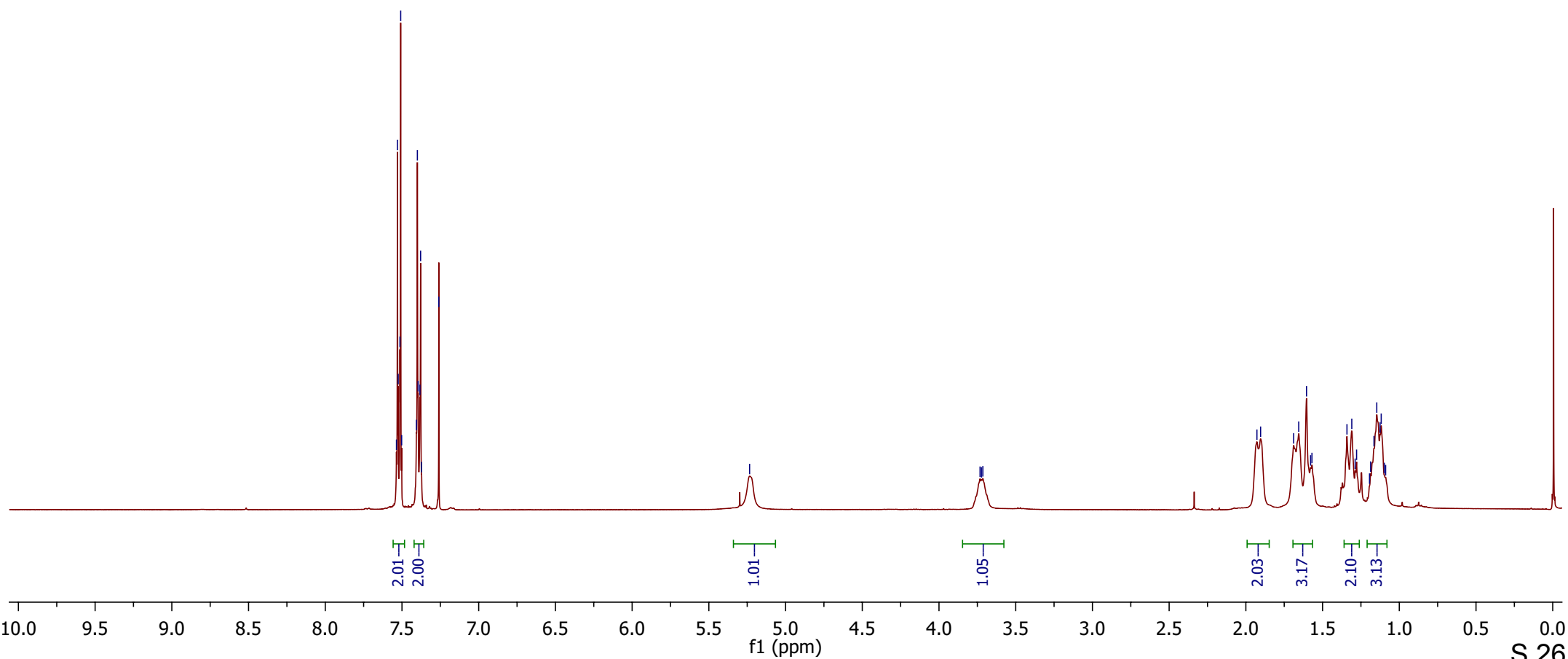
3.73
3.72
3.71

1.93
1.90
1.69
1.66
1.60
1.58
1.57
1.34
1.31
1.29
1.28
1.19
1.19
1.16
1.15
1.13
1.12
1.10
1.09

¹H NMR (400 MHz, CDCl₃)



(3i)



B series NMR
B-18

163.84

136.68

132.34

127.75

124.02

77.32

77.00

76.68

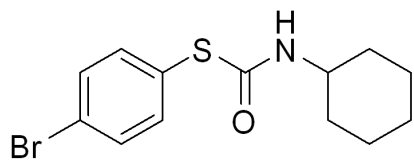
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32.90

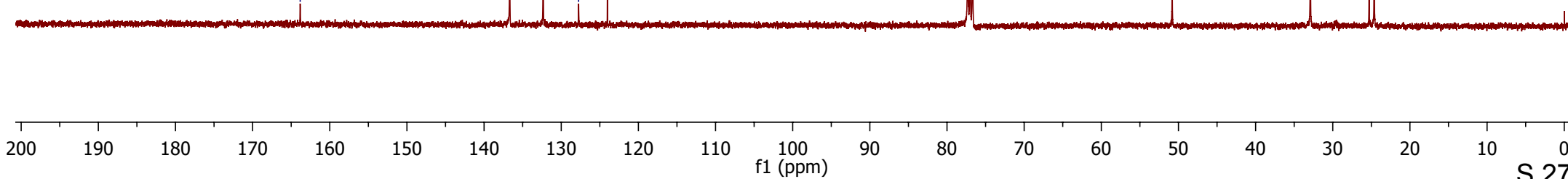
25.28

24.63

^{13}C NMR (100 MHz, CDCl_3)



(3i)



New NMR
b-45

7.464
7.457
7.451
7.440
7.435
7.427
7.260
6.943
6.936
6.930
6.919
6.914
6.906

5.135

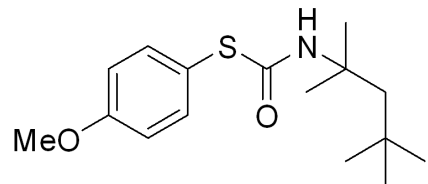
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1.645

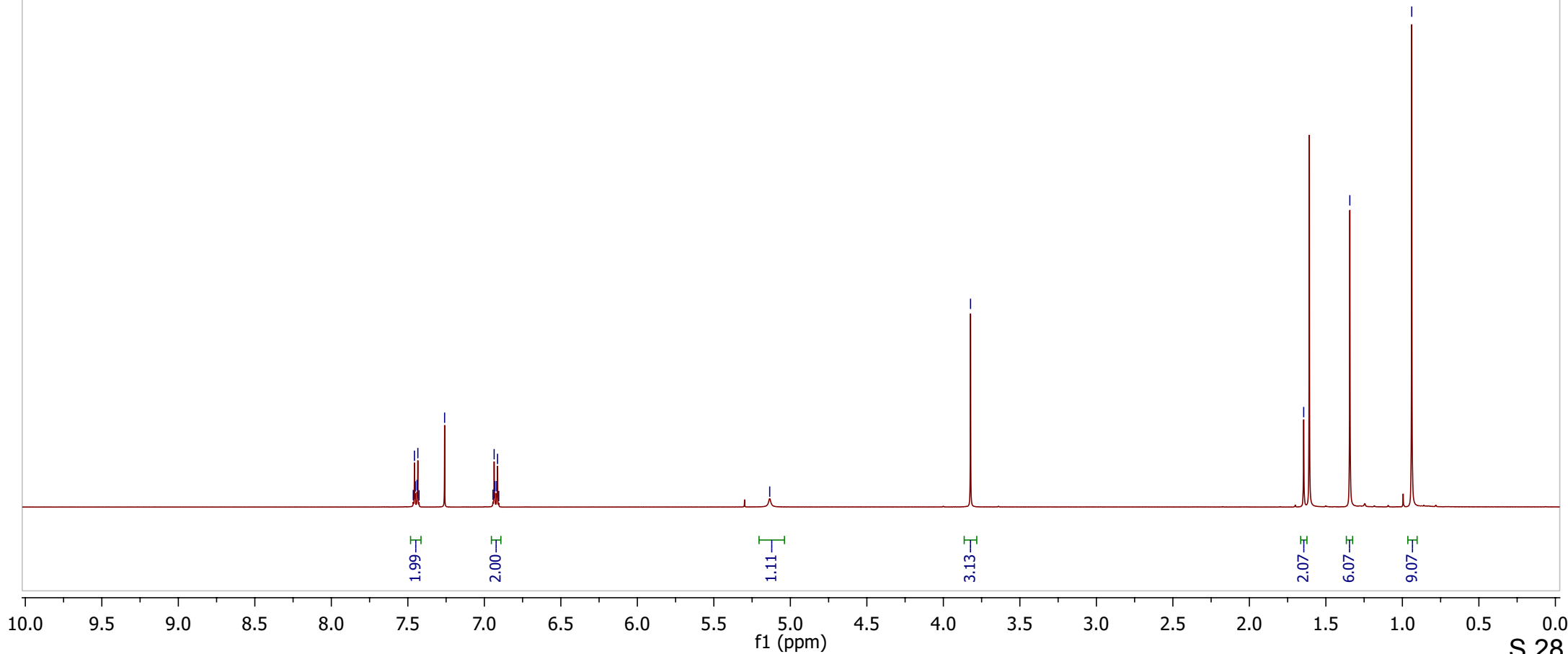
1.344

0.939

¹H NMR (400 MHz, CDCl₃)



(3j)



164.69

160.63

137.18

119.83

114.82

77.32

77.00

76.68

56.92

55.22

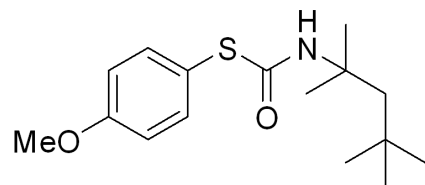
51.50

31.36

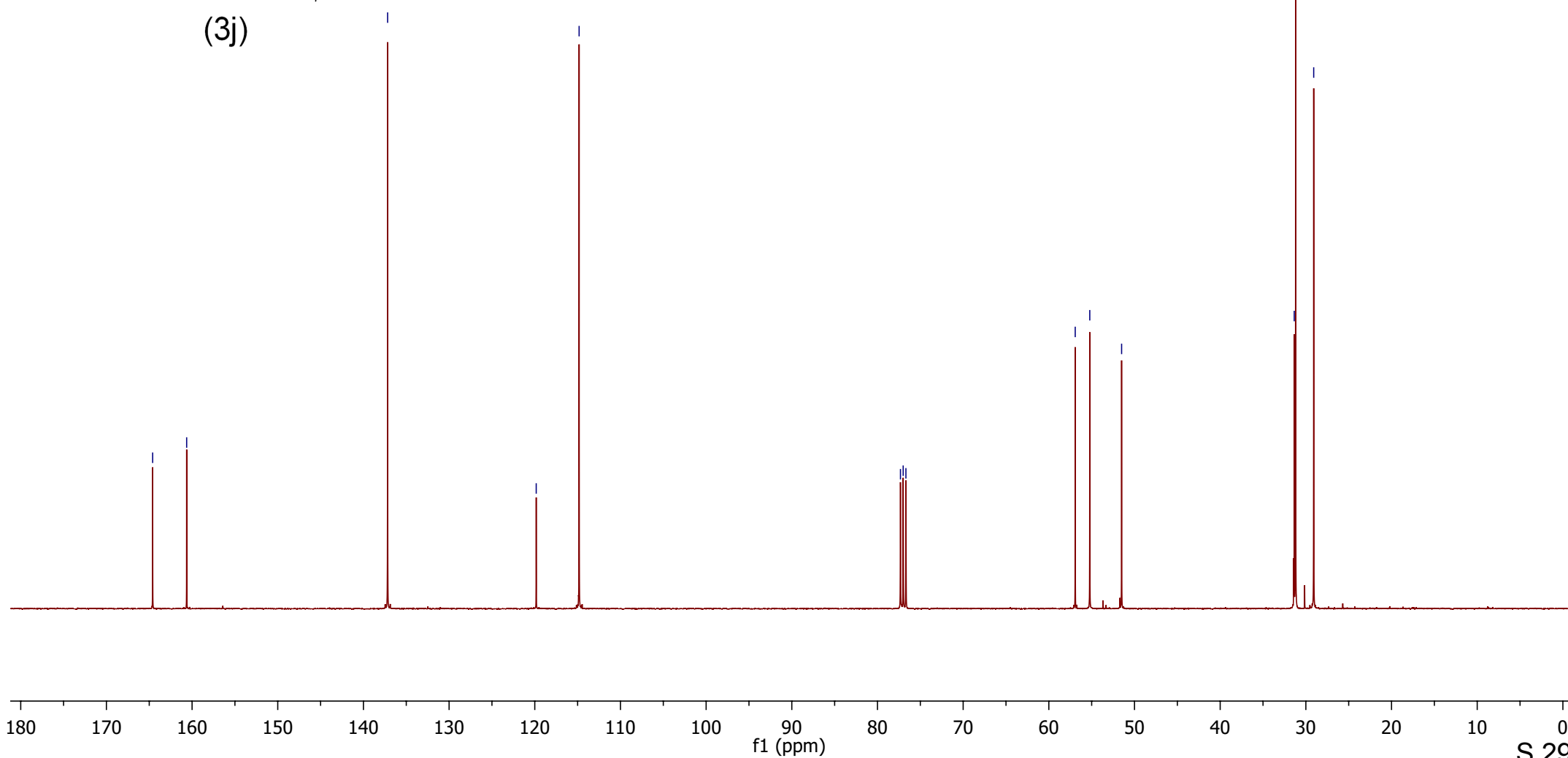
31.19

29.08

¹³C NMR (100 MHz, CDCl₃)

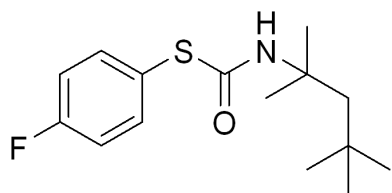


(3j)



New NMR
b-08

¹H NMR (400 MHz, CDCl₃)



(3k)

7.493
7.260
7.088

5.155

1.673

1.373

0.971

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 0.5 0.0

f1 (ppm)

S 30

2.06

2.00

1.12

2.03

6.08

9.14

B series NMR
B-08

164.64
163.44
162.15

137.62
137.54

124.29
124.26

116.44
116.22

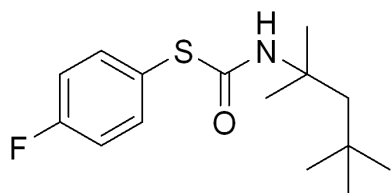
77.32
77.00
76.68

57.30

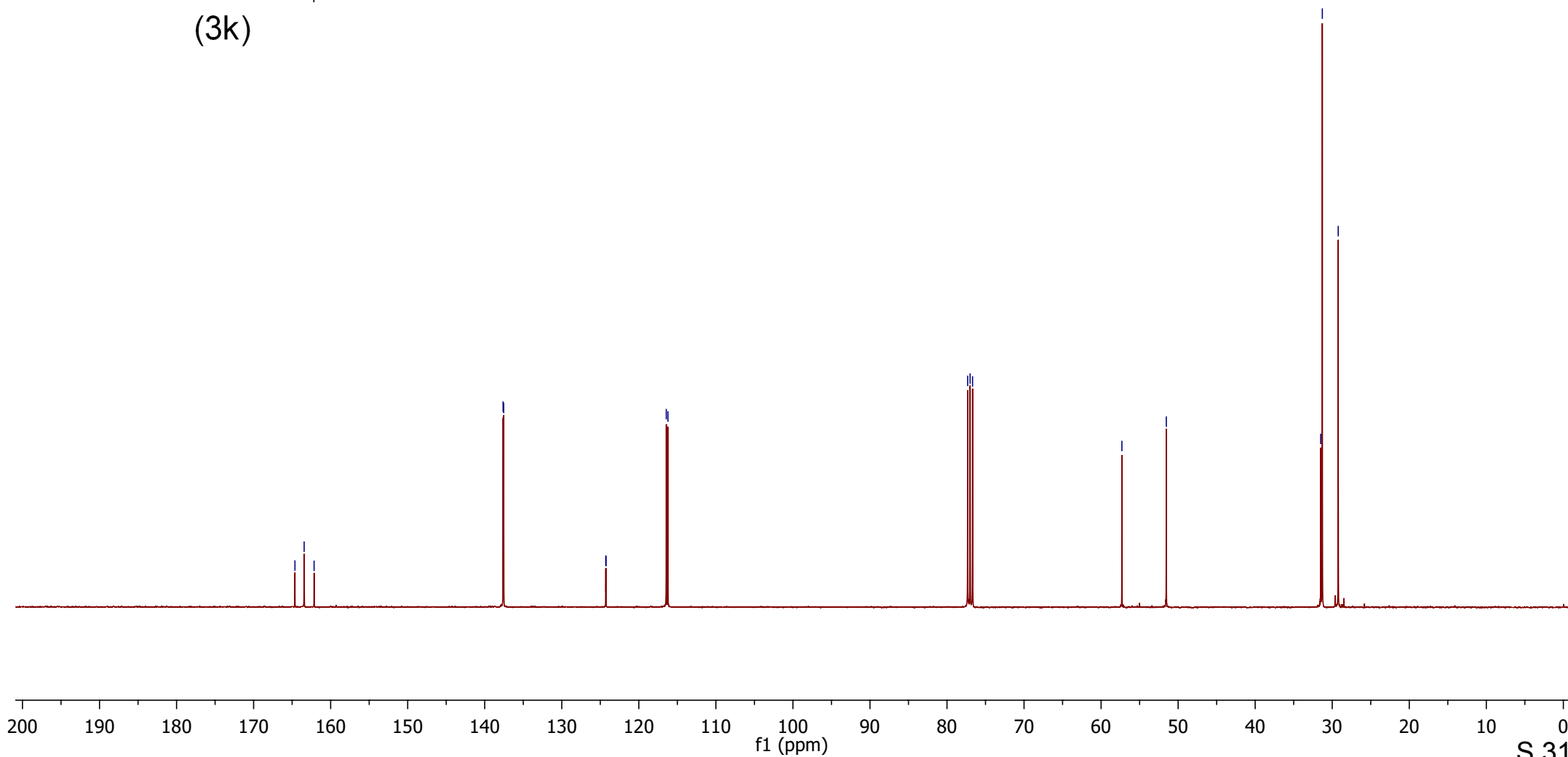
51.54

31.50
31.28
29.22

^{13}C NMR (100 MHz, CDCl_3)

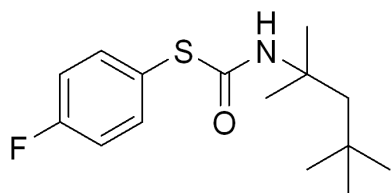


(3k)



F-NMR
B-08

^{19}F NMR (376 MHz, CDCl_3)



(3k)

-111.23

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

B series NMR
B-16

7.456
7.450
7.445
7.434
7.429
7.423
7.374
7.368
7.363
7.352
7.347
7.341
7.260

5.172

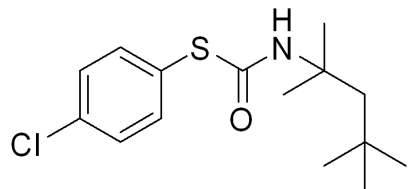
1.684

1.378

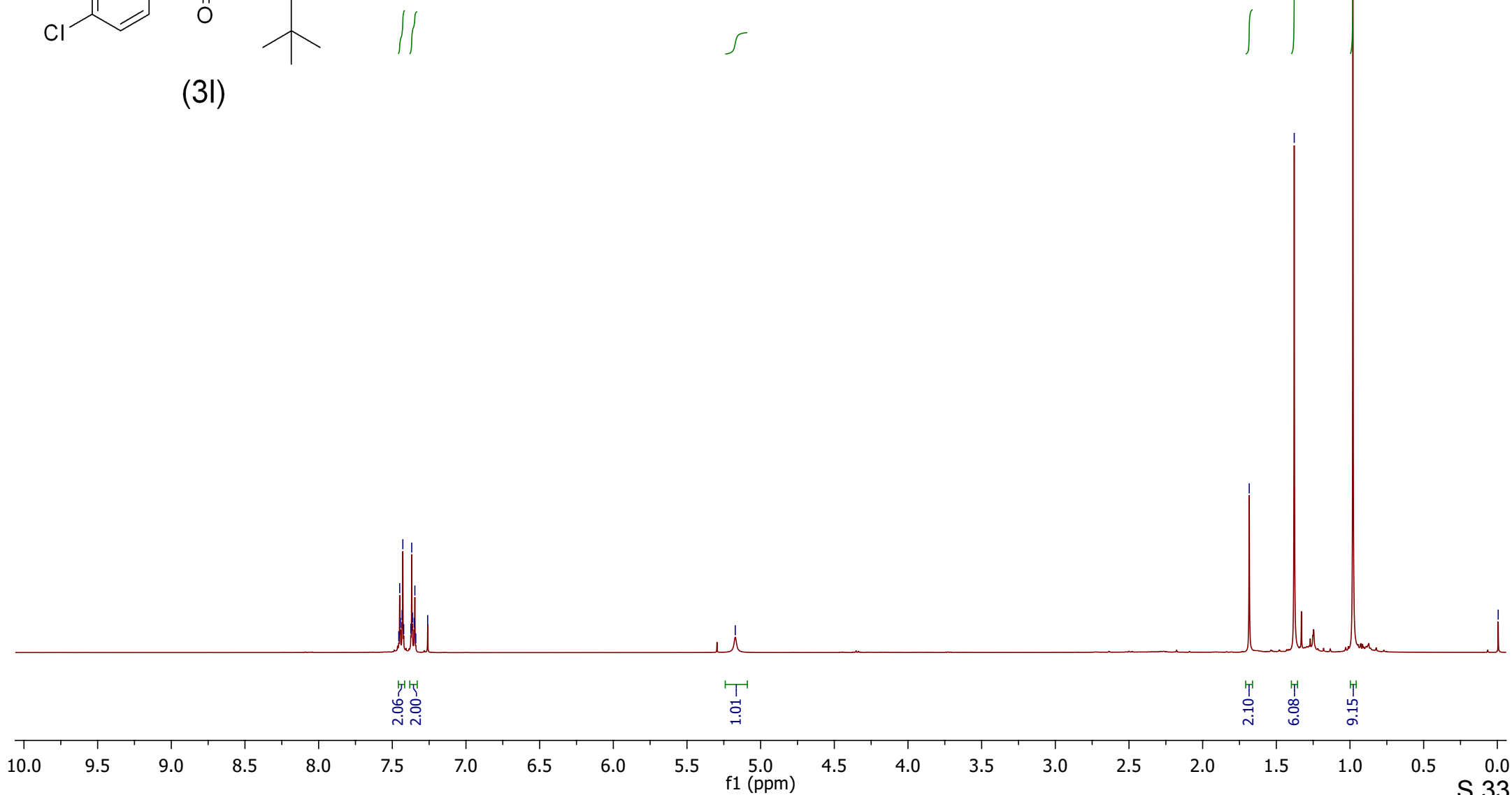
0.980

0.006

^1H NMR (400 MHz, CDCl_3)



(3)



B series NMR
B-16

162.95

136.65
135.70

129.34
127.37

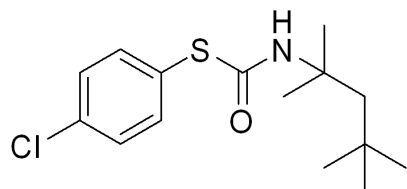
77.32
77.00
76.68

57.46

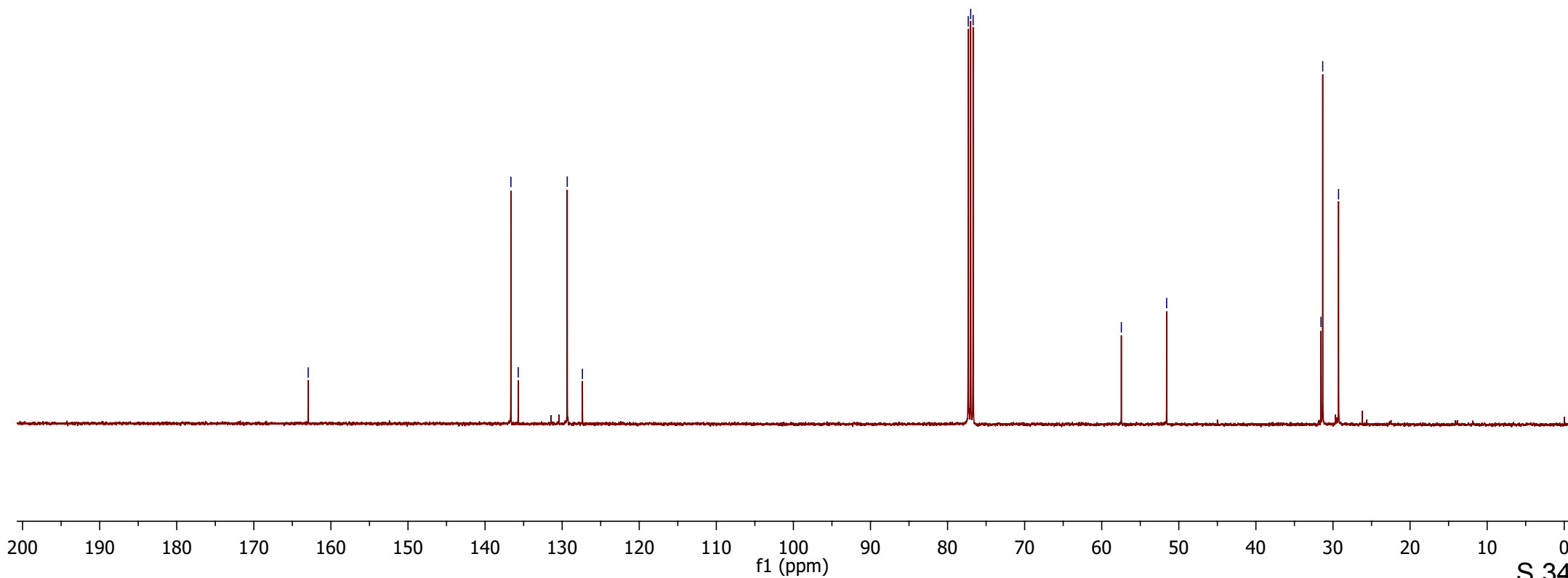
51.58

31.55
31.33
29.28

^{13}C NMR (100 MHz, CDCl_3)

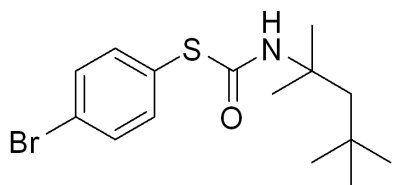


(3I)



New NMR
b-20

¹H NMR (400 MHz, CDCl₃)



(3m)

7.532
7.526
7.521
7.510
7.505
7.499
7.387
7.381
7.376
7.364
7.359
7.353
7.260

5.161

1.686

1.382

0.983

2.00

2.00

1.06

2.02

6.08

9.09

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 0.5 0.0

f1 (ppm)

March NMR 2020
b-20

162.76

136.85

132.31

128.09

123.98

77.32

77.00

76.68

57.51

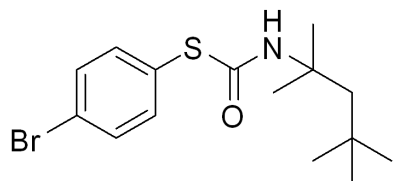
51.70

31.58

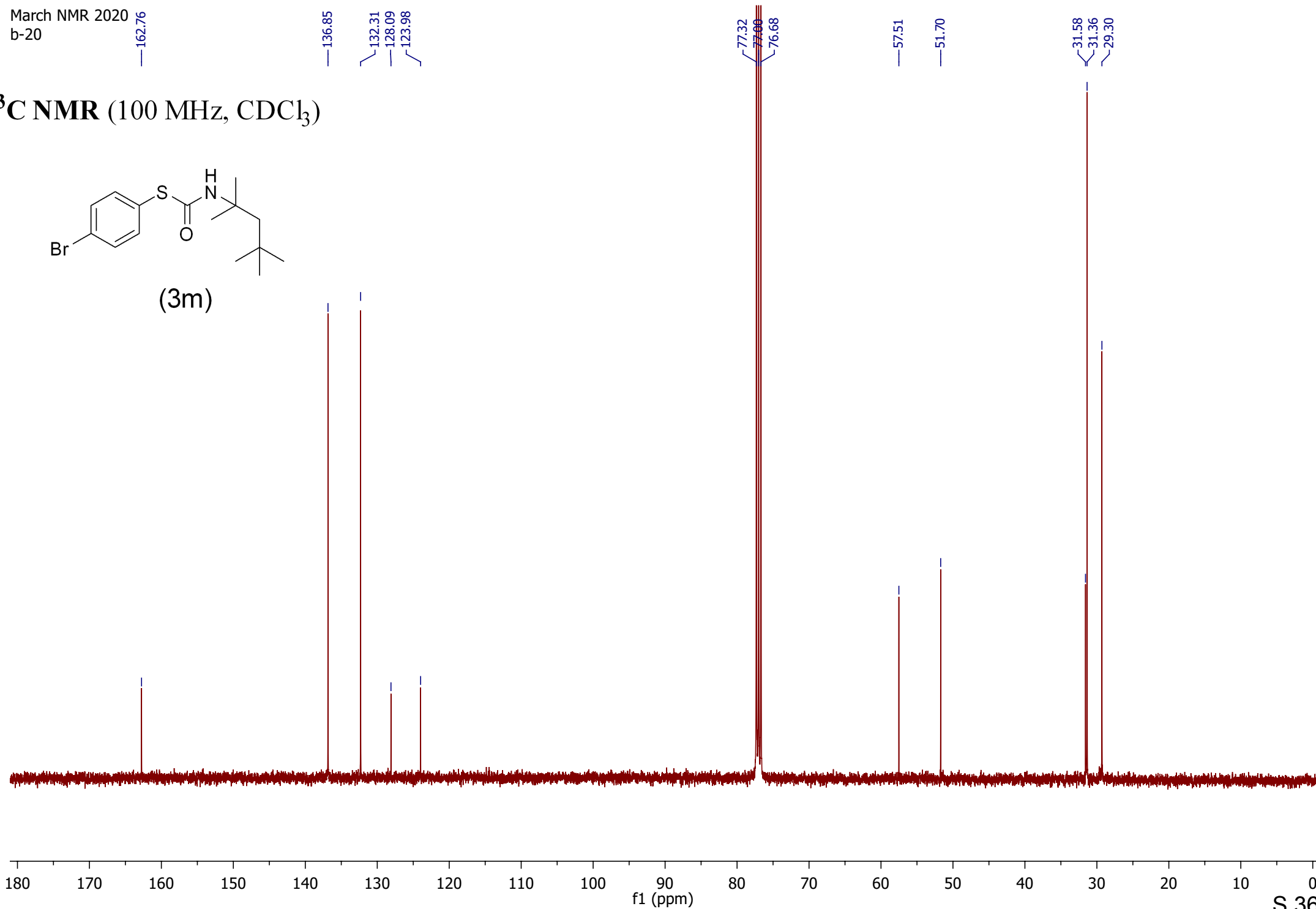
31.36

29.30

¹³C NMR (100 MHz, CDCl₃)



(3m)



B series NMR
b-03

7.563
7.557
7.548
7.539
7.416
7.407
7.401
7.391
7.260

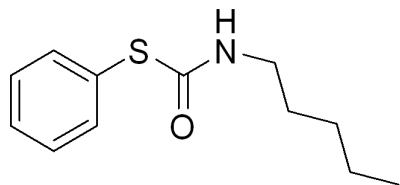
5.595

5.273

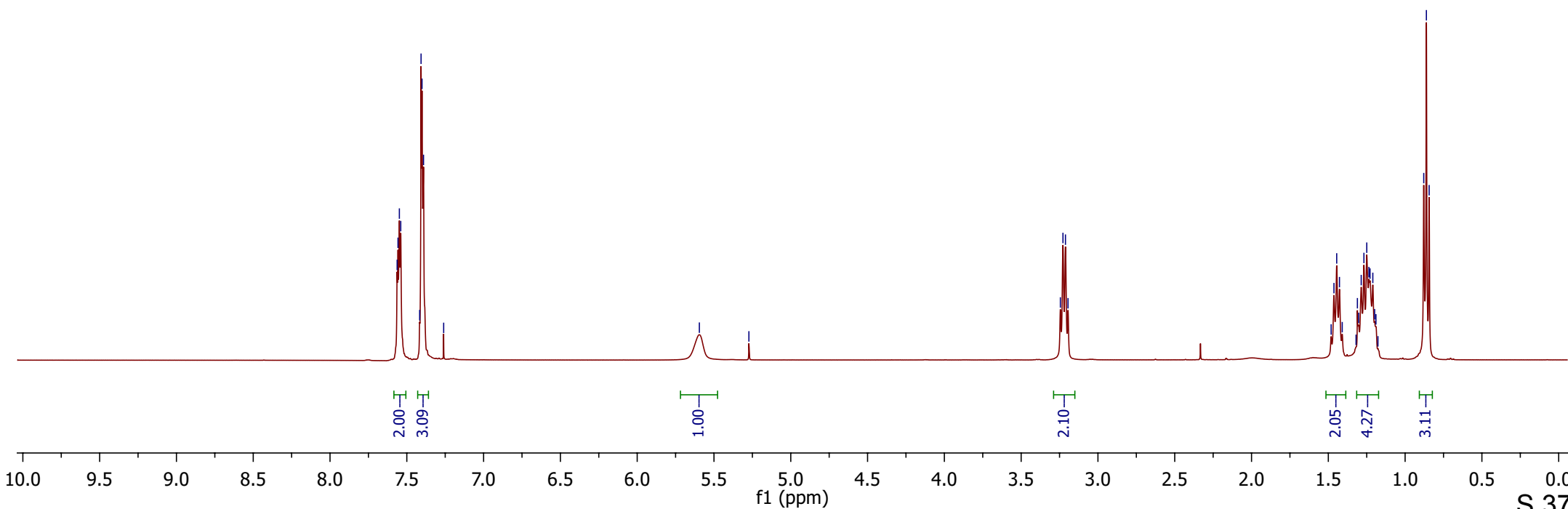
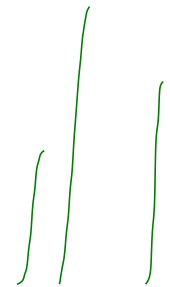
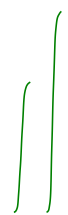
3.245
3.228
3.212
3.195

1.482
1.463
1.445
1.427
1.409
1.319
1.311
1.303
1.286
1.268
1.250
1.236
1.228
1.210
1.199
0.879
0.861
0.843

¹H NMR (400 MHz, CDCl₃)



(3n)



B series NMR
b-03

—165.87

—135.33

129.42

129.26

128.59

77.32

77.00

76.68

—41.39

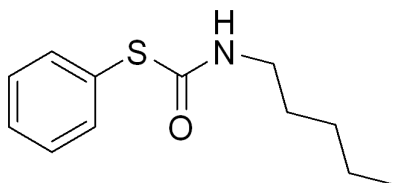
29.01

28.68

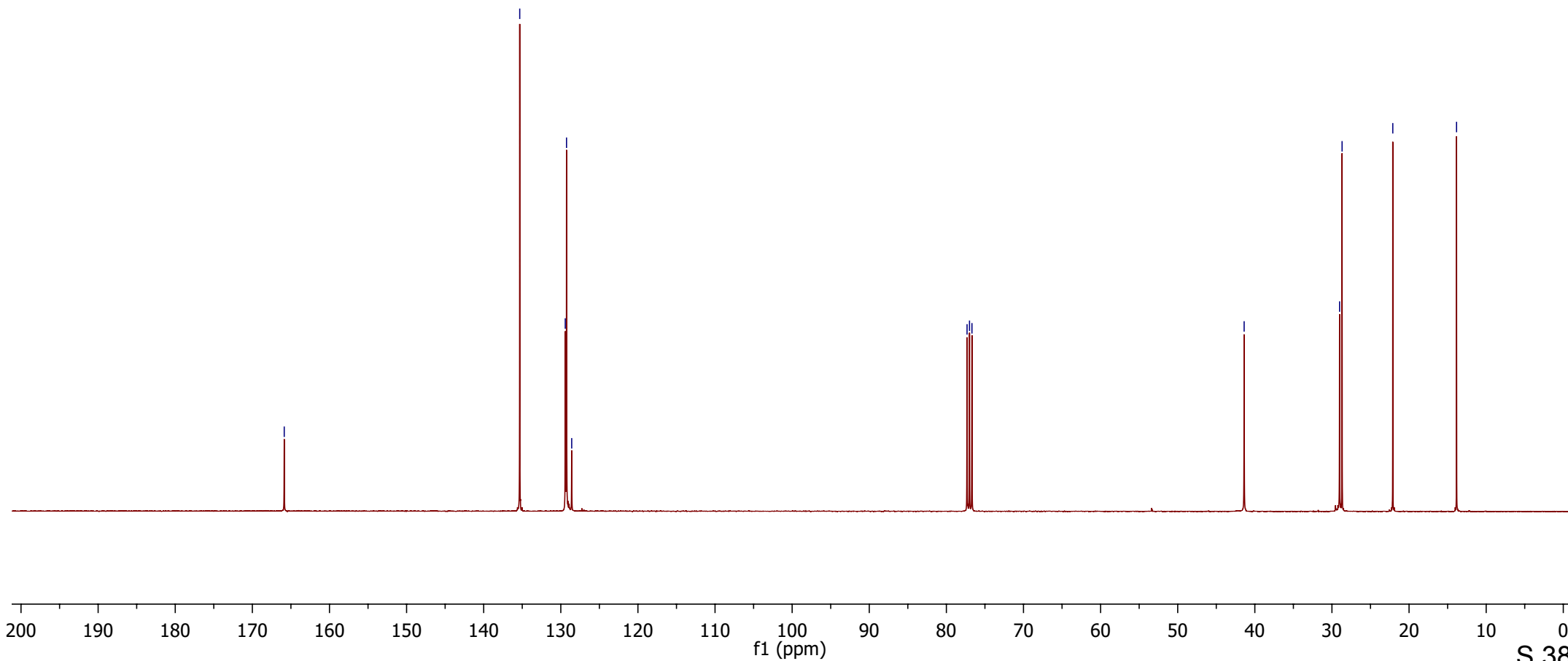
—22.11

—13.84

¹³C NMR (100 MHz, CDCl₃)



(3n)



7.450
7.428

6.910
6.888

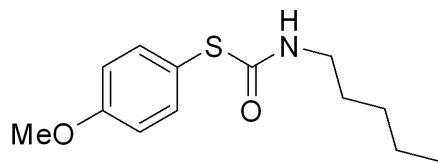
5.595

3.783

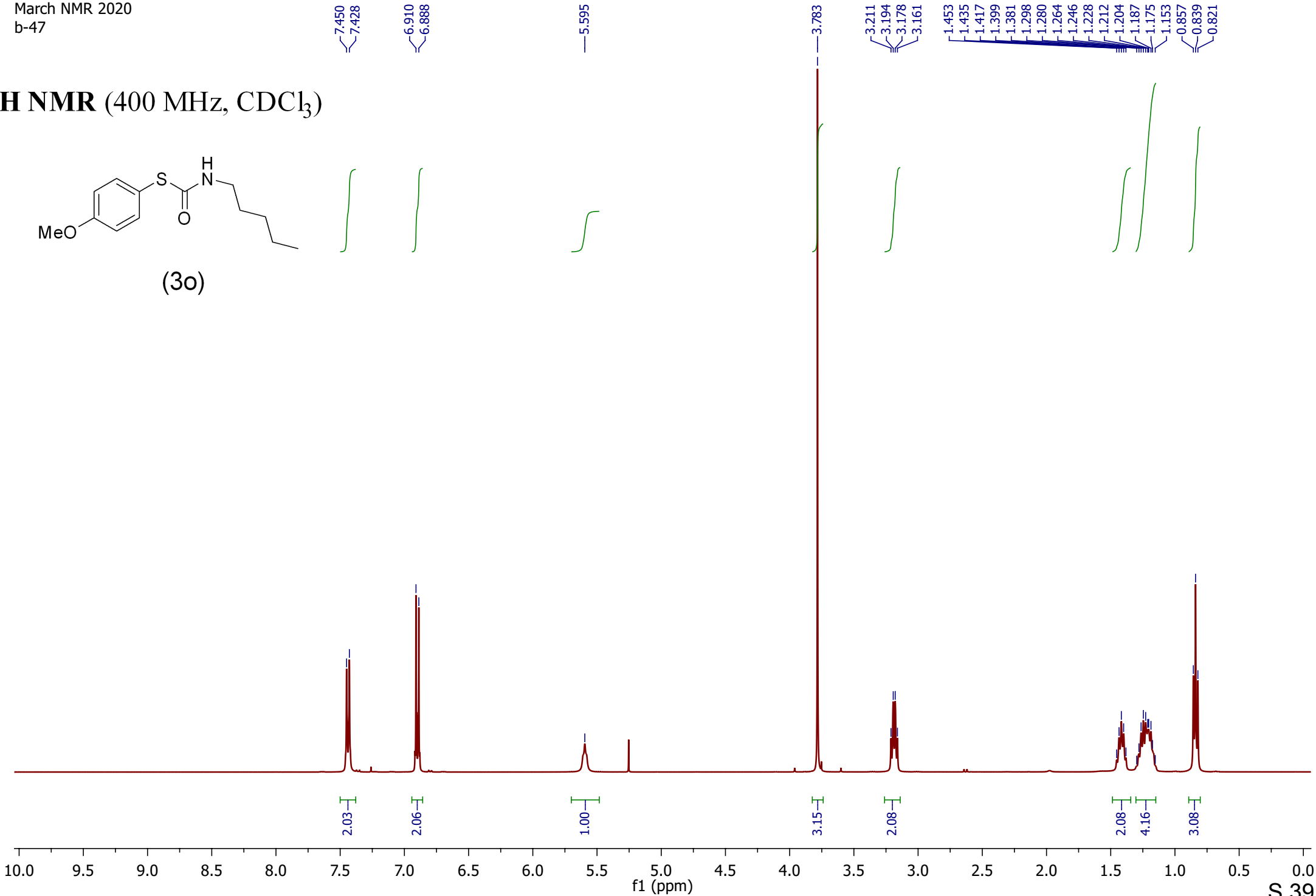
3.211
3.194
3.178
3.161

1.453
1.435
1.417
1.399
1.381
1.298
1.280
1.264
1.246
1.228
1.212
1.204
1.187
1.175
1.153
0.857
0.839
0.821

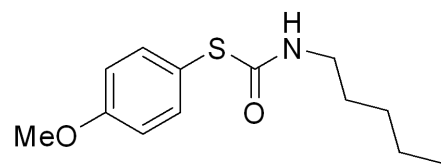
¹H NMR (400 MHz, CDCl₃)



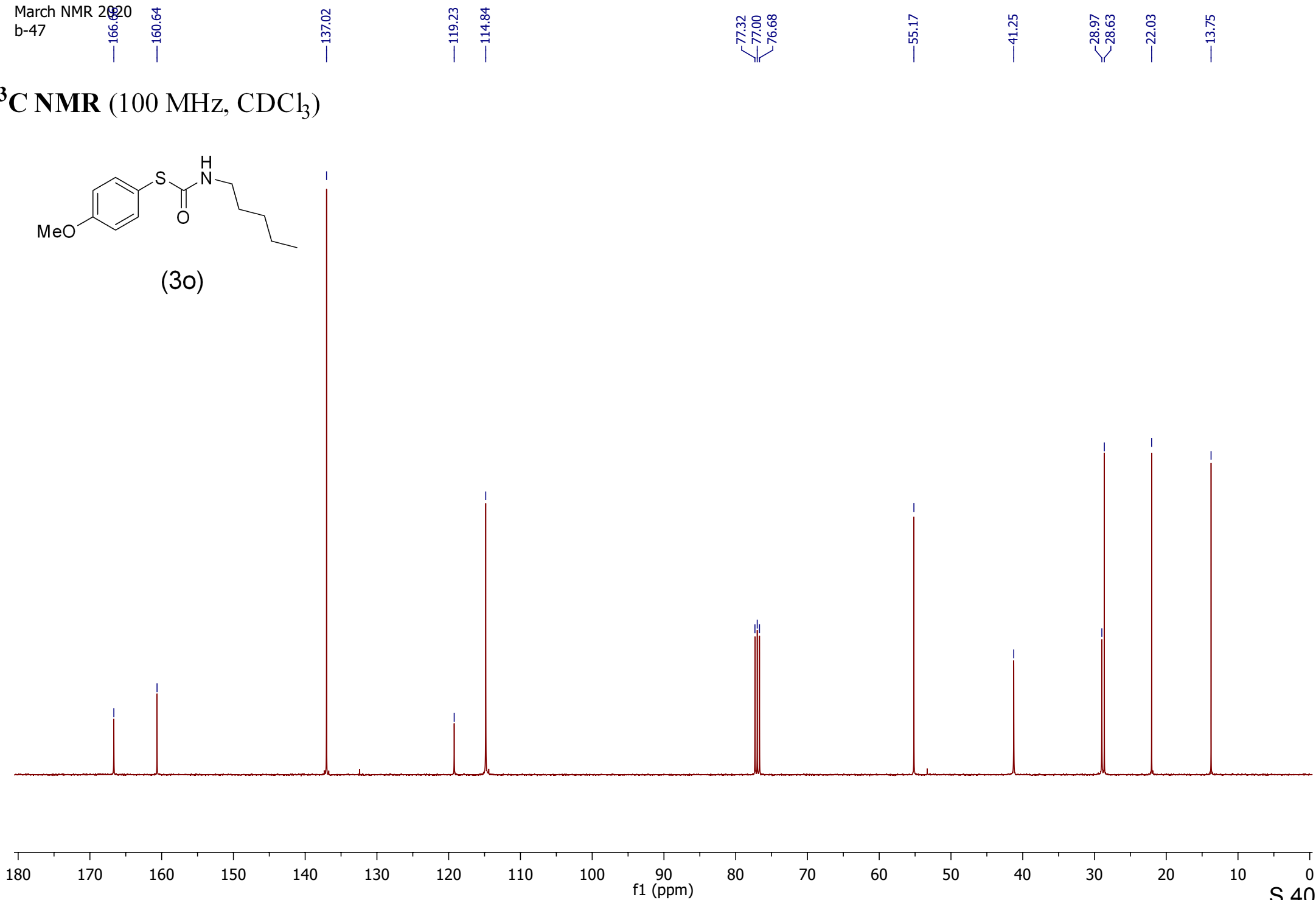
(3o)



March NMR 2020
b-47



(3o)



B series NMR
B-07

7.54
7.52
7.52
7.50
7.26
7.12
7.10
7.08

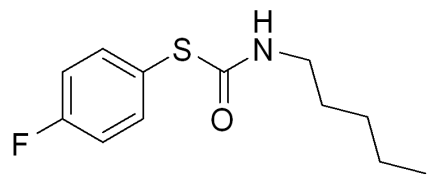
5.37

3.28
3.26
3.25
3.23

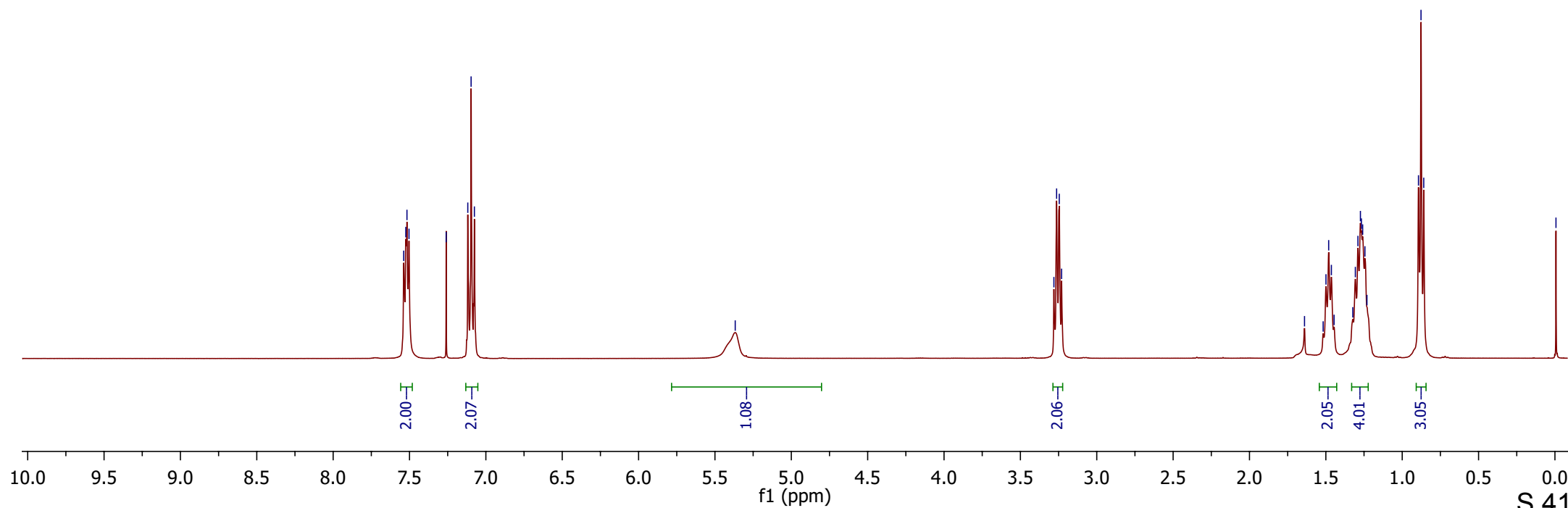
1.64
1.52
1.50
1.48
1.46
1.45
1.32
1.31
1.29
1.27
1.26
1.24
1.23
0.89
0.88
0.86

-0.01

^1H NMR (400 MHz, CDCl_3)



(3p)



B series NMR
B-07

165.61
164.77
162.28

137.60
137.51

123.82

116.61
116.40

77.32
77.00
76.68

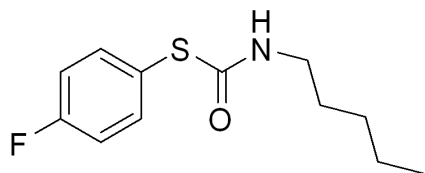
41.60

29.18
28.80

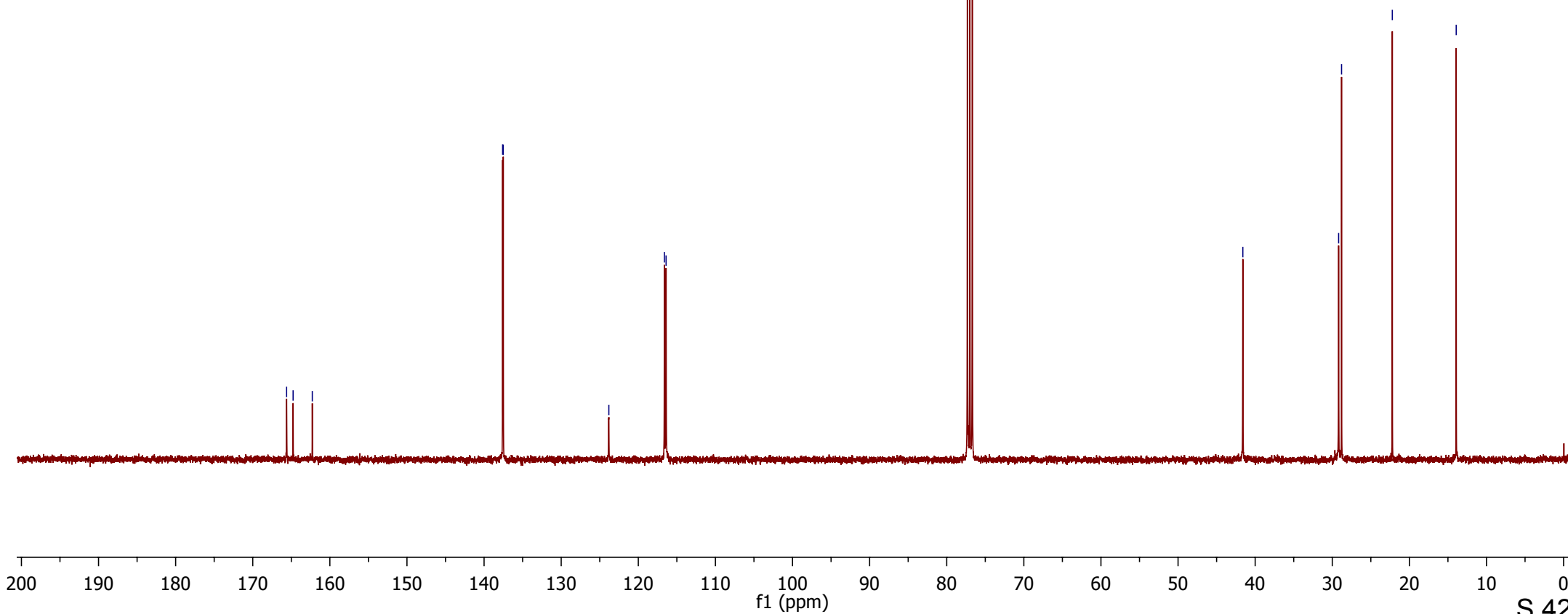
22.21

13.93

^{13}C NMR (100 MHz, CDCl_3)

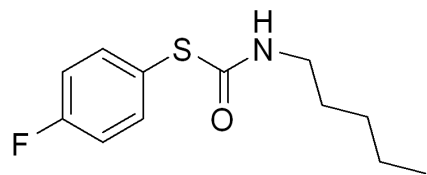


(3p)



F-NMR
B-07

^{19}F NMR (376 MHz, CDCl_3)



(3p)

-110.95

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

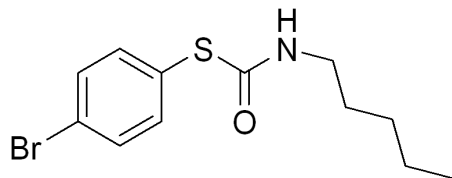
7.529
7.508
7.404
7.383
7.260

5.444

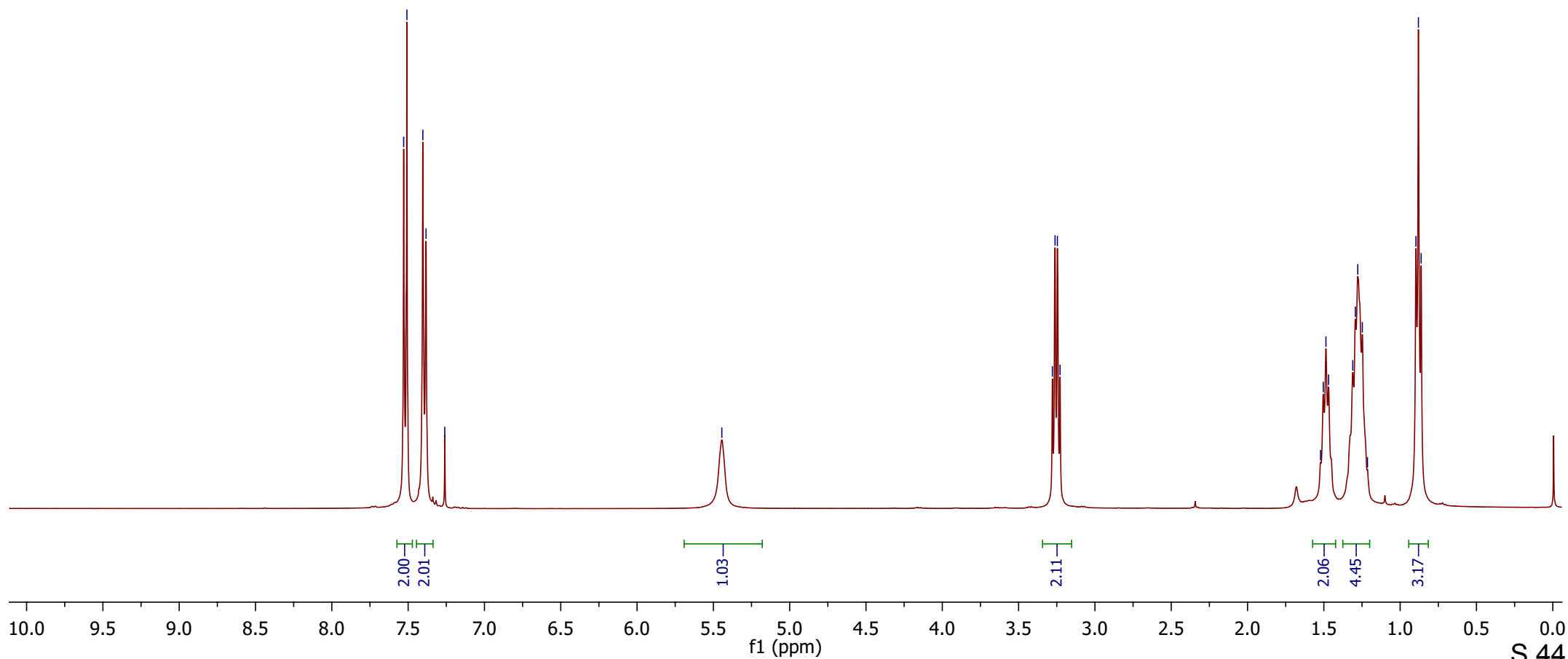
3.279
3.261
3.246
3.228

1.521
1.504
1.486
1.469
1.310
1.294
1.278
1.248
1.214
0.897
0.880
0.862

¹H NMR (400 MHz, CDCl₃)



(3q)



164.89

136.73

132.37

127.65

124.07

77.32

77.00

76.68

41.66

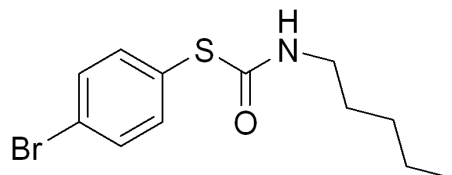
29.17

28.79

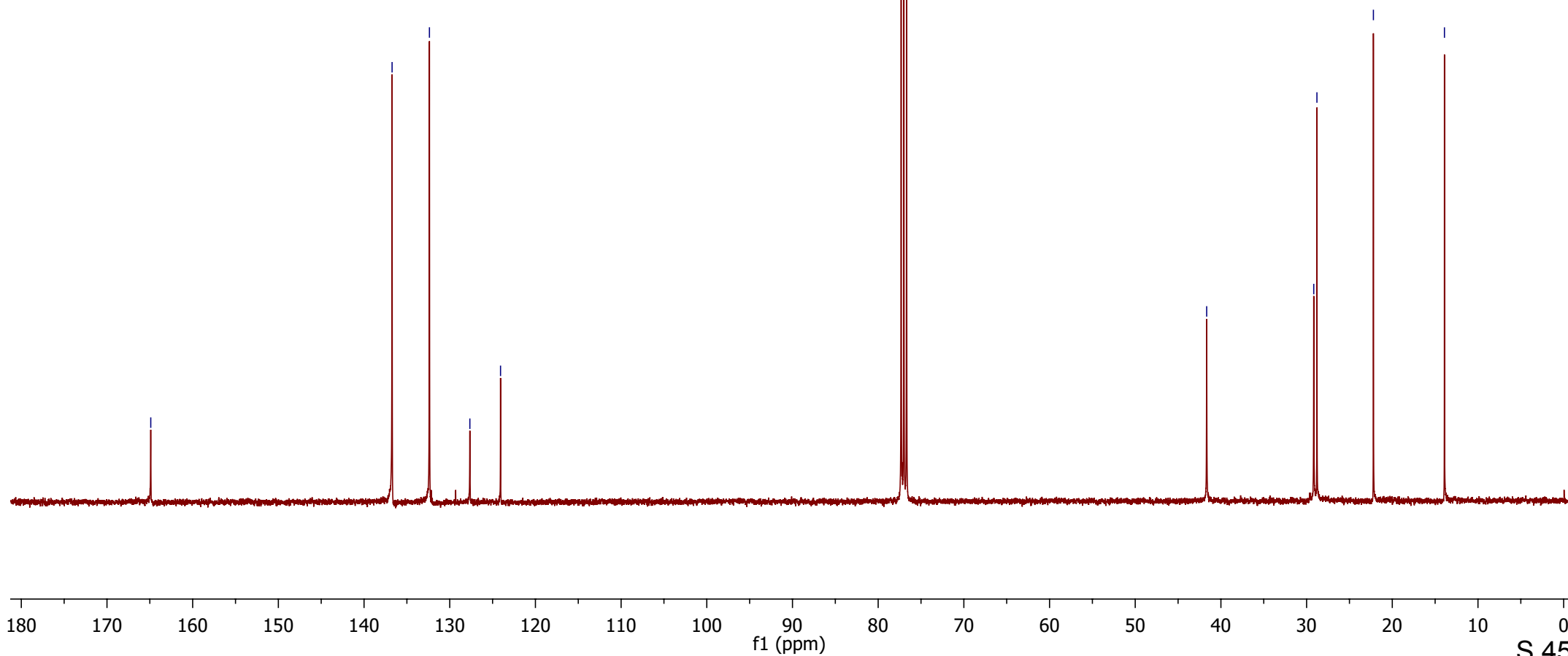
22.20

13.91

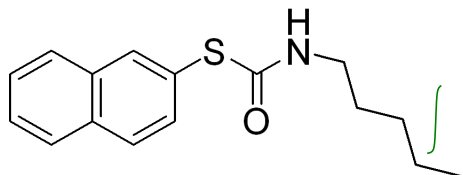
¹³C NMR (100 MHz, CDCl₃)



(3q)



¹H NMR (400 MHz, CDCl₃)



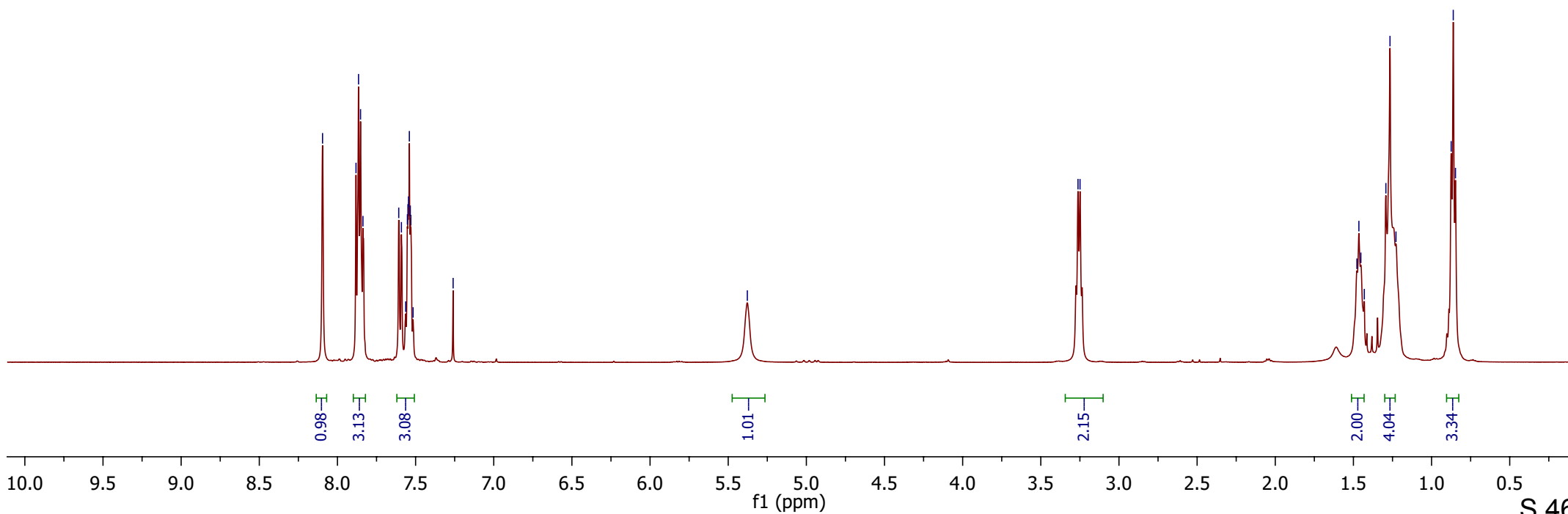
(3r)

8.095
7.881
7.865
7.852
7.837
7.608
7.591
7.563
7.552
7.549
7.545
7.540
7.534
7.530
7.516
7.260

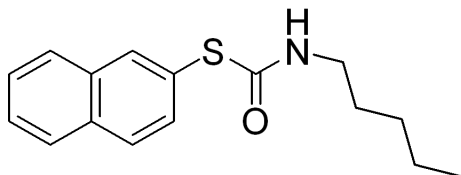
5.378

3.262
3.249

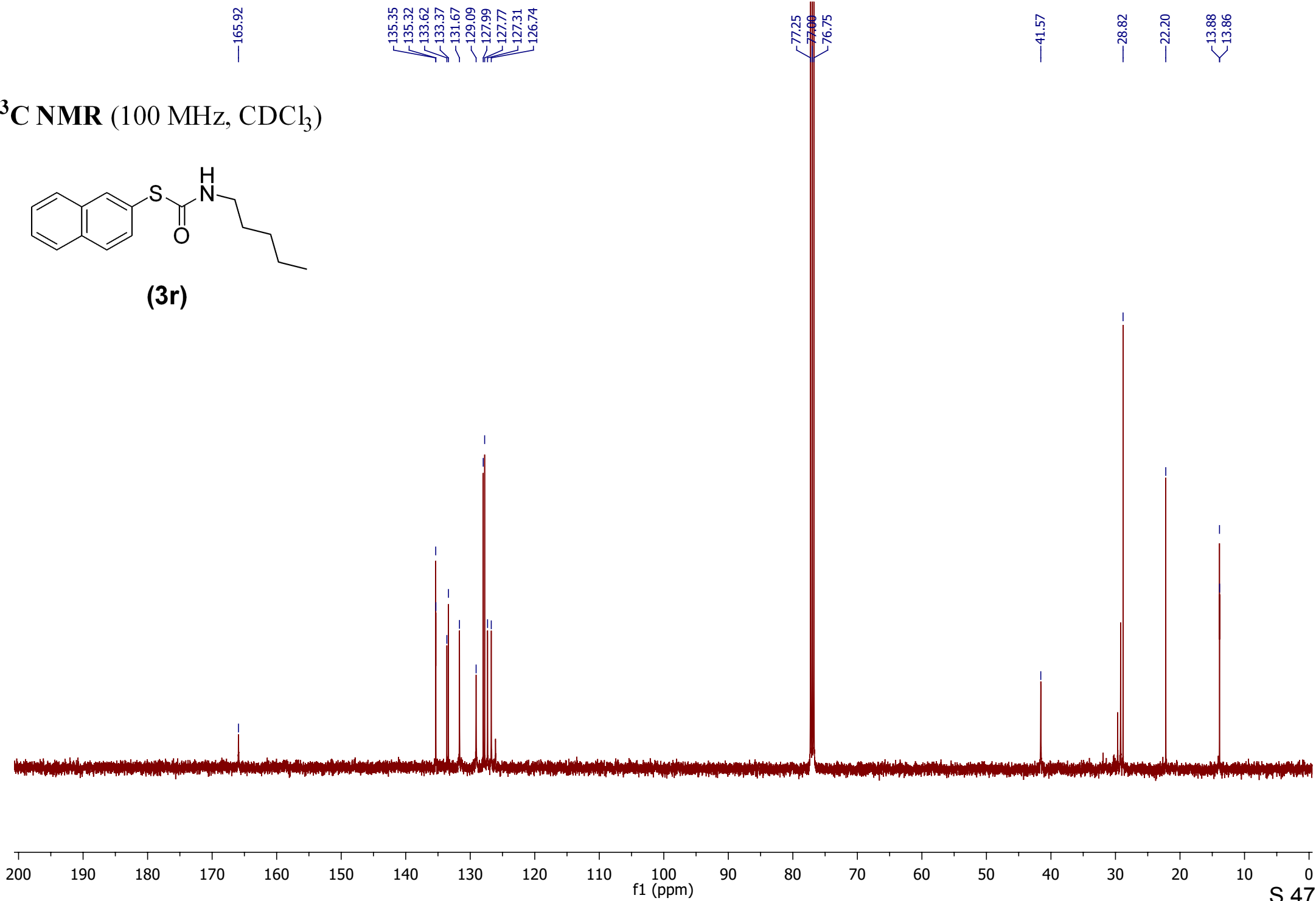
1.478
1.465
1.452
1.430
1.292
1.266
1.228
0.875
0.861
0.847



^{13}C NMR (100 MHz, CDCl_3)

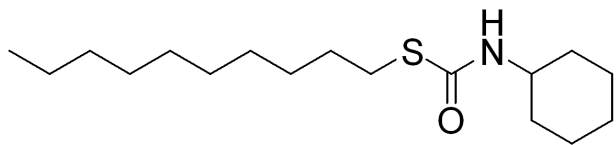


(3r)

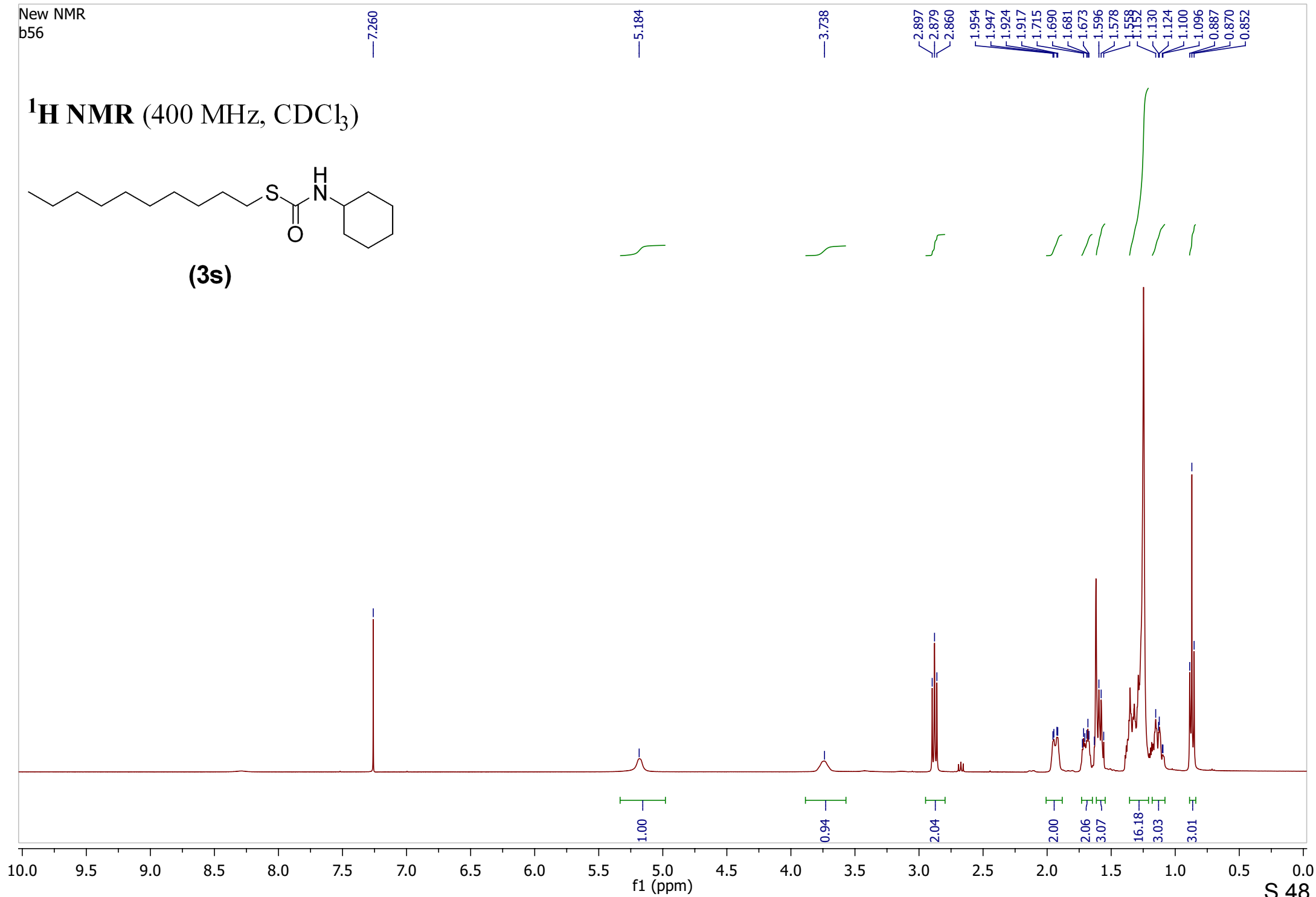


New NMR
b56

^1H NMR (400 MHz, CDCl_3)

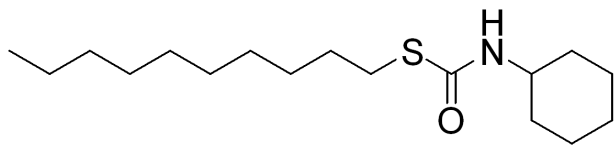


(3s)

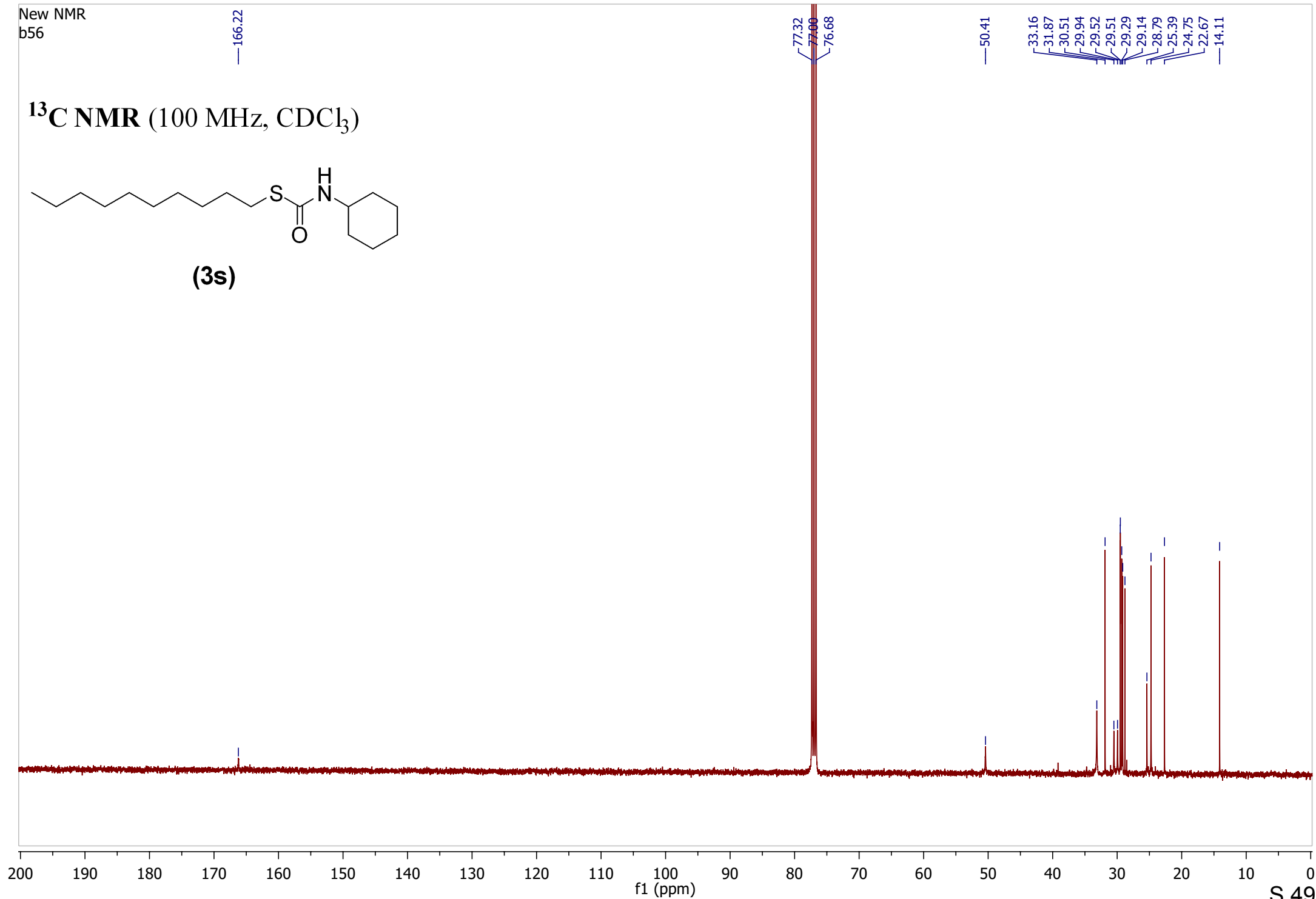


New NMR
b56

^{13}C NMR (100 MHz, CDCl_3)

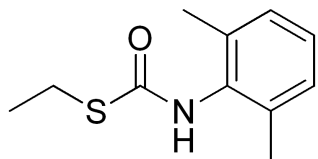


(3s)



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^1H NMR (400 MHz, CDCl_3)



(3u)

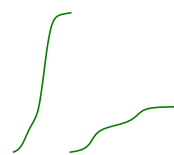
7.260
7.182
7.101
6.876
6.659

2.973
2.841

2.306

1.676

1.333
1.286
1.255
1.237



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 0.5 0.0

f1 (ppm)

S 50

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BKS-51

171.23

165.90

138.18

135.64

132.79

128.82

128.36

127.47

77.32

77.00

76.68

24.56

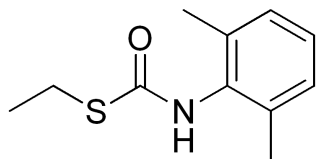
24.07

18.35

15.63

15.24

^{13}C NMR (100 MHz, CDCl_3)



(3u)

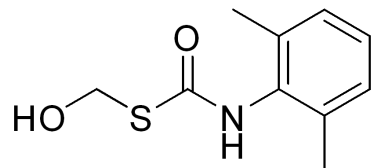
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S 51

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BKS-50

^1H NMR (400 MHz, CDCl_3)



(3v)

7.260
7.230
7.213
7.196
7.130
7.112
7.079
6.886
6.691

3.395
3.388
3.266

2.304
2.246

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 0.5 0.0
f1 (ppm)

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BKS-50

169.70

164.54

138.42

135.76

132.36

129.37

128.79

127.96

77.54

77.33

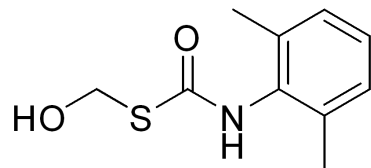
76.91

33.12

32.58

19.60

^{13}C NMR (100 MHz, CDCl_3)



(3v)

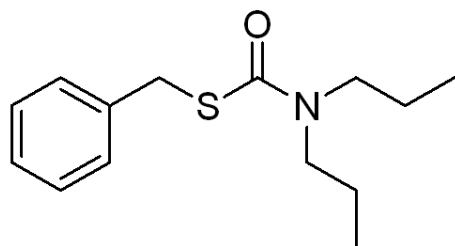
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

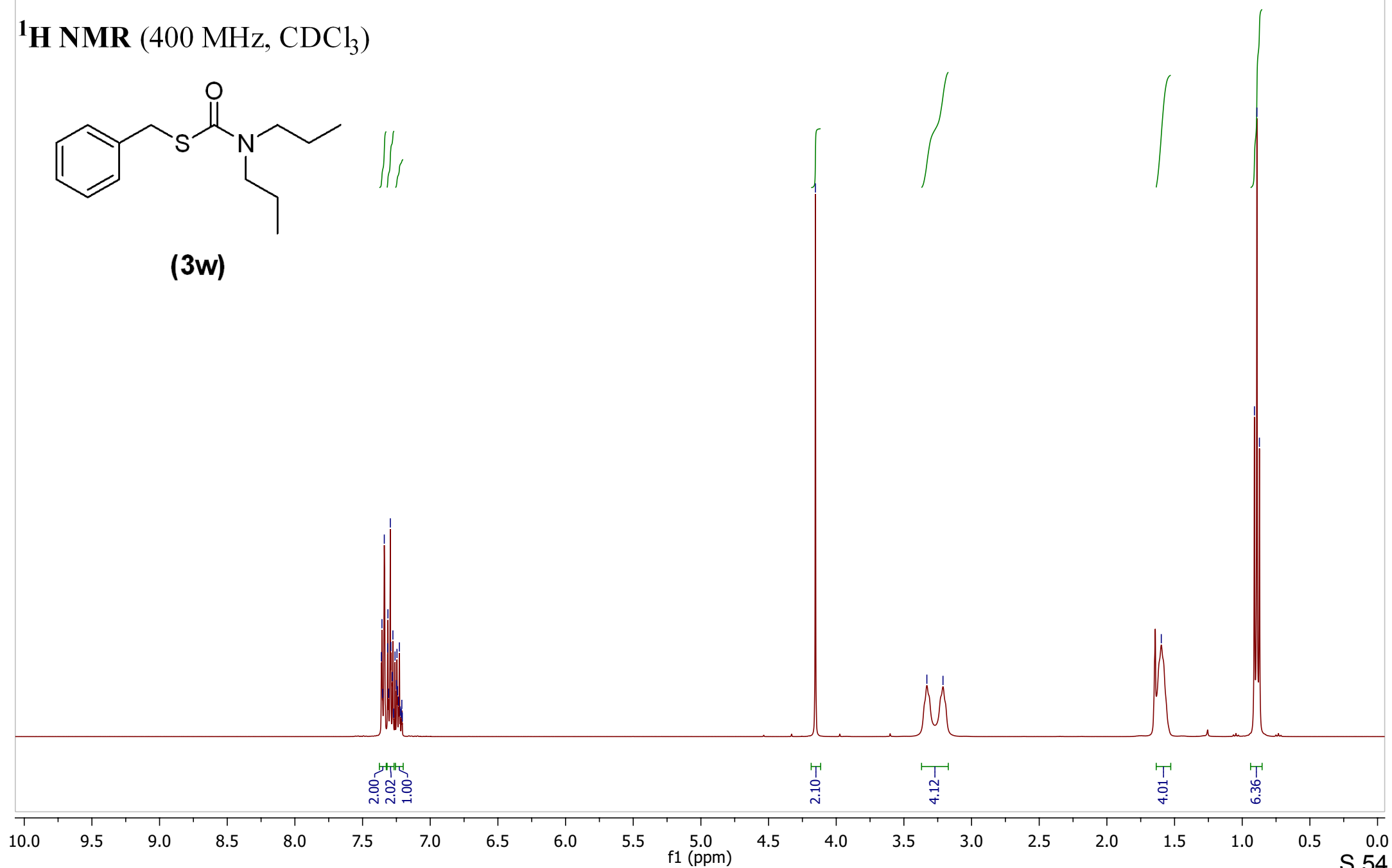
Aug25-2021
BKS-55

7.361
7.357
7.352
7.339
7.315
7.312
7.308
7.295
7.291
7.280
7.276
7.271
7.260
7.249
7.246
7.242
7.234
7.228
7.221
7.213
7.210
7.206

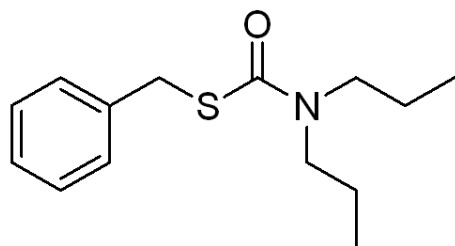
¹H NMR (400 MHz, CDCl₃)



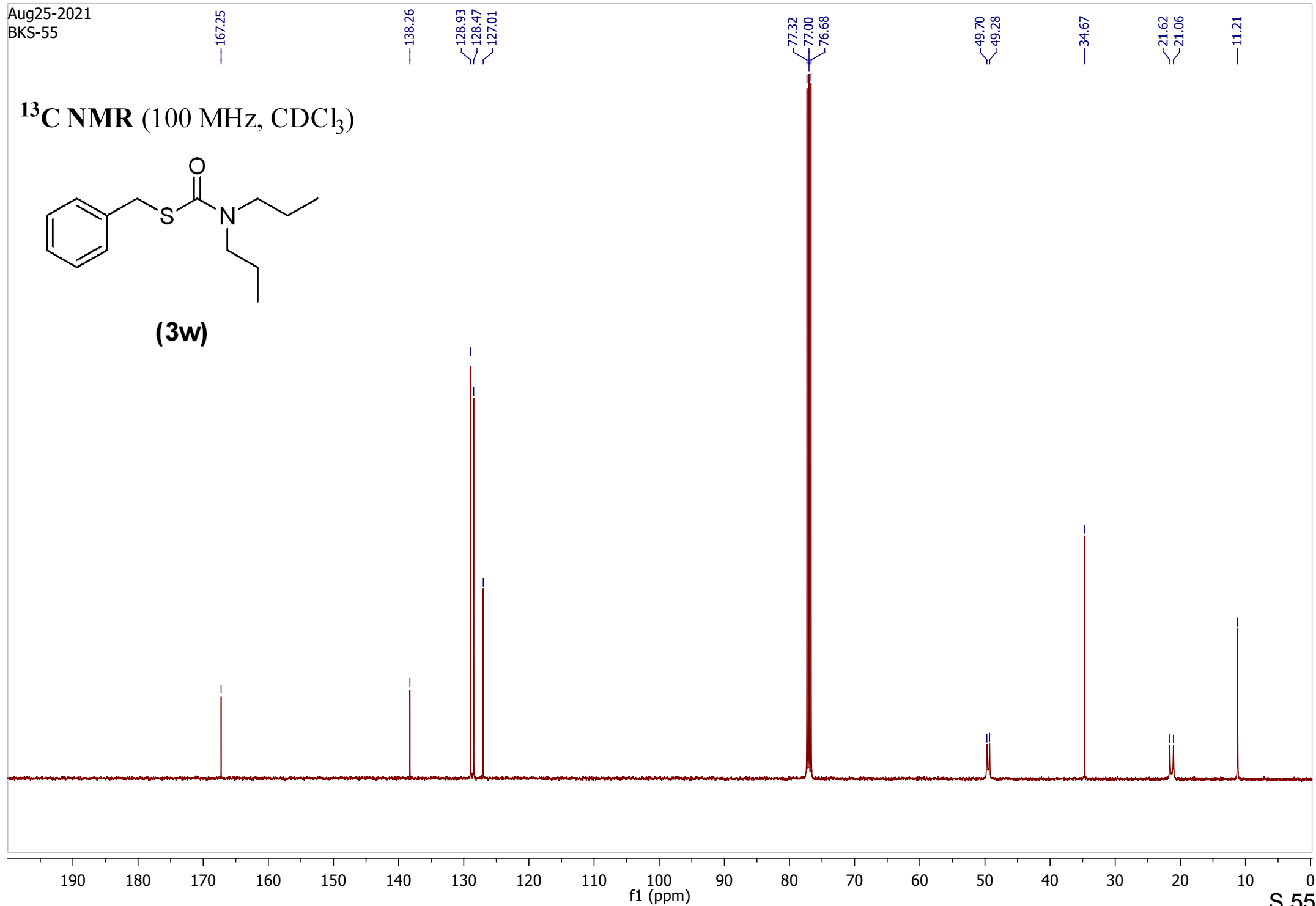
(3w)



^{13}C NMR (100 MHz, CDCl_3)

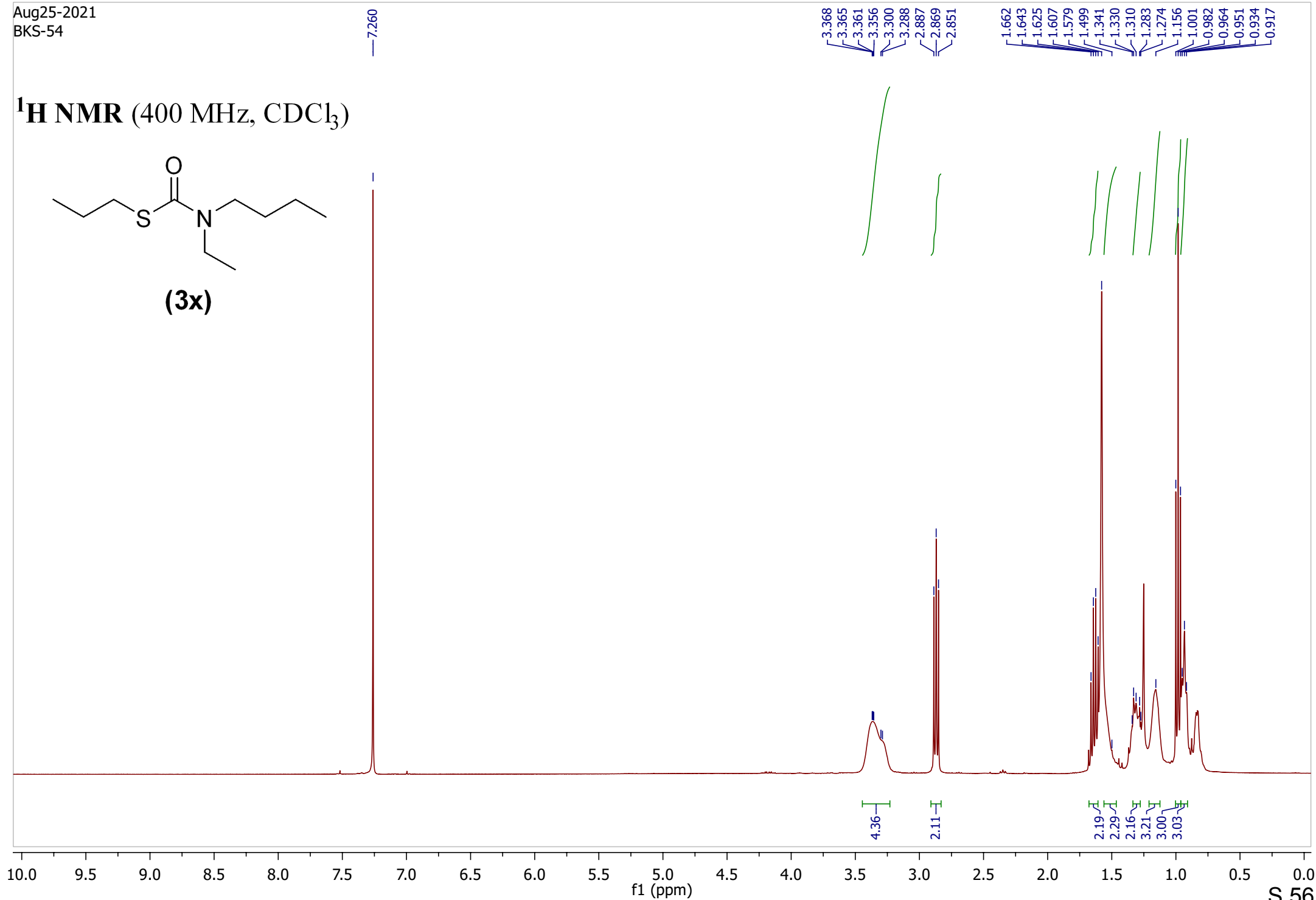
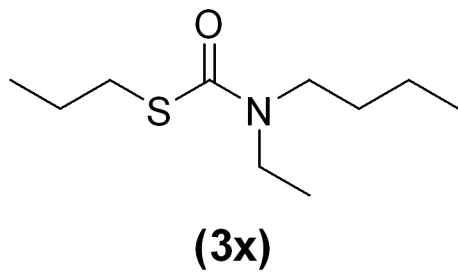


(3w)



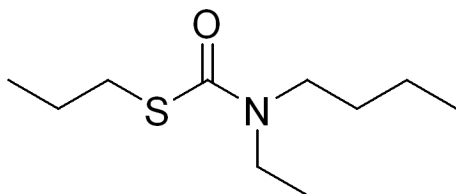
Aug25-2021
BKS-54

^1H NMR (400 MHz, CDCl_3)



Aug25-2021
BKS-54

^{13}C NMR (100 MHz, CDCl_3)



(3x)

—167.55

77.32
77.00
76.68

—32.15

—23.59

—20.09

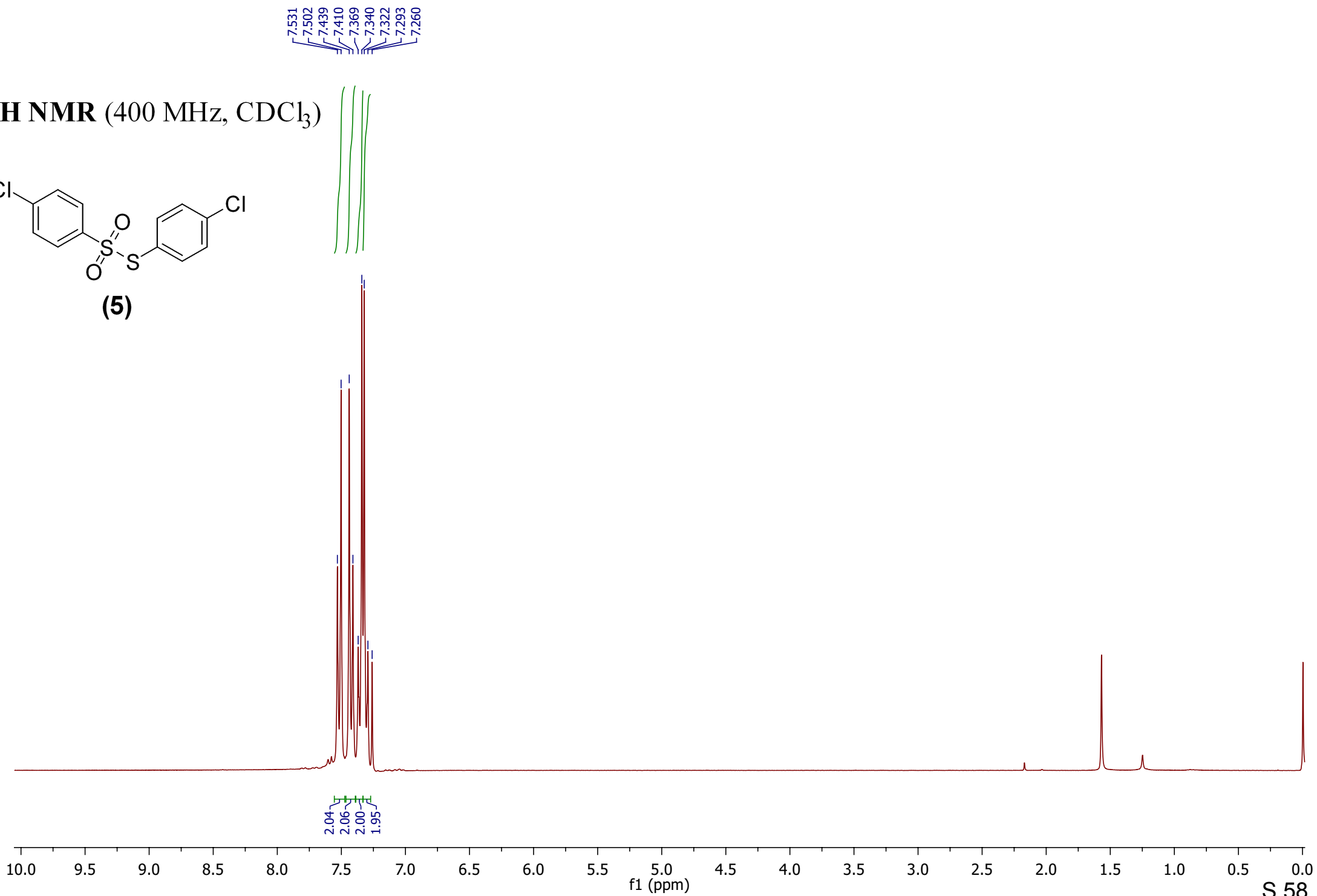
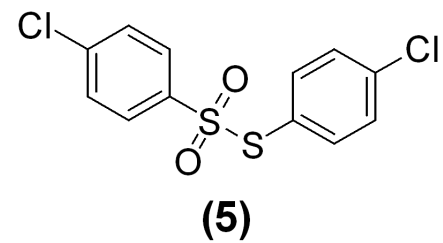
13.81

13.43

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

f1 (ppm)

¹H NMR (400 MHz, CDCl₃)



¹³C NMR (100 MHz, CDCl₃)

