Supplementary Information

Intermolecular Sulfenoamination of Alkenes with Sulfonylamides and N-Sulfanylsuccinimides for the Synthesis of β-Sulfonylamino sulfides and Dihydrobenzothiazines

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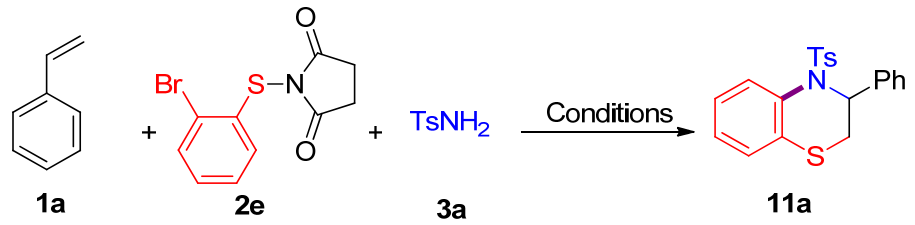
Table S1. Optimization of reaction conditions for the synthesis of 11a[a]



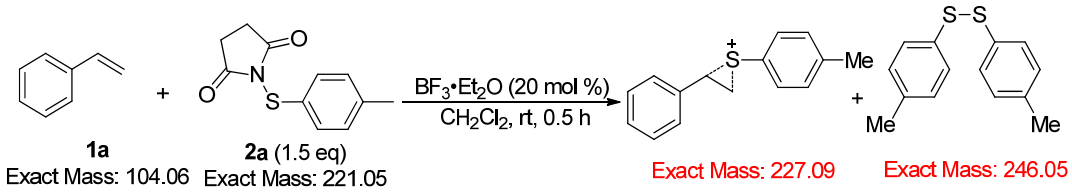
1a 2e 3a 11a

Entry	Conditions	Yield (%)[b]
1	1) TfOH (20 mol %), CH_2Cl_2 (1 mL), 60 °C; 2) $Pd(OAc)_2$ (20 mol %), BINAP (40 mol %), K_2CO_3 (2.5 eq), Toluene, 110 °C	0
2	1) TfOH (20 mol %), Toluene (1 mL), 60 °C; 2) $Pd(OAc)_2$ (20 mol %), BINAP (40 mol %), K_2CO_3 (2.5 eq), Toluene, 110 °C	0
3	1) TfOH (20 mol %), CH_2Cl_2 (1 mL), 60 °C; 2) CuI (10 mol %), ethylenediamine (20 mol %), K_2CO_3 (2.0 eq), 1,4-Dioxane, 100 °C	0
4	1) TfOH (20 mol %), CH_2Cl_2 (1 mL), 60 °C; 2) Cu (1.1 eq), DMF (1 mL), N_2, 120 °C	27
5	1) TfOH (20 mol %), DCE (1 mL), 60 °C; 2) Cu (1.1 eq), DMF (1 mL), N_2, 120 °C	0
6	1) TfOH (20 mol %), Toluene (1 mL), 60 °C; 2) Cu (1.1 eq), DMF (1 mL), N_2, 120 °C	66
7	1) TfOH (20 mol %), Toluene (0.5 mL), 60 °C; 2) Cu (1.1 eq), DMF (1 mL), N_2, 120 °C	72
8	1) $BF_3 \cdot Et_2O$ (20 mol %), Toluene (1 mL), 60 °C; 2) Cu (1.1 eq), DMF (1 mL), N_2, 120 °C	54

[a] Reaction conditions: **1a** (0.2 mmol), **2e** (0.3 mmol), and **3a** (0.22 mmol) was subjected to the indicated conditions. [b] Isolated yield.

MS on Mechanism Study

Mass spectroscopy (MALDI) for the reaction of 1a with 2a



1a
Exact Mass: 104.06

2a (1.5 eq)
Exact Mass: 221.05

Exact Mass: 227.09

Exact Mass: 246.05

Testing Report

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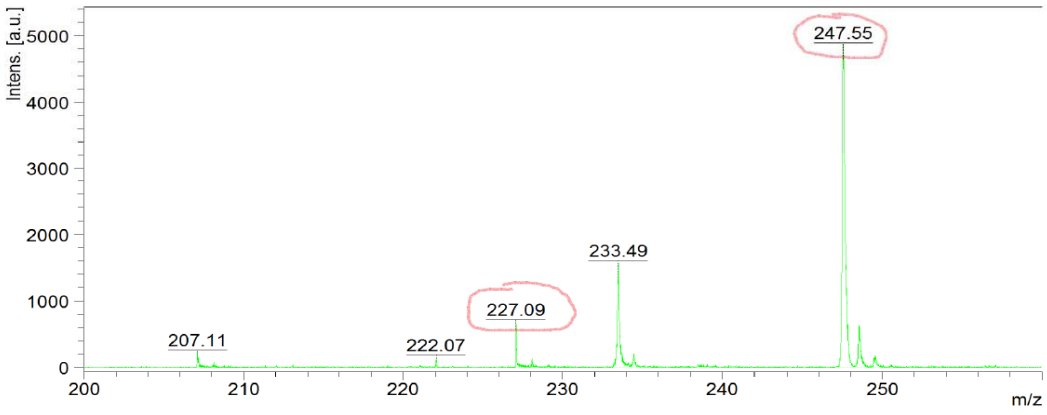
Processing method	
File Name	D:\Data\20161208\2-hcca\0_B13\3



Instrument

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Name of computer	UTX-00589
Operator ID or name	BDAL@DE
flexControl version	flexControl 3.4.135.0
flexAnalysis version	3.4.76.0

Target

Target type	0280784
Target serial number	1112383
Position	B13

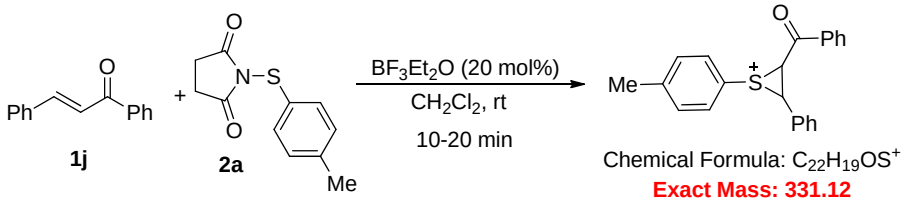
Spectrometer

positive voltage polarity	POS
PIE delay	100 ns
Ion source voltage 1	20 kV
Ion source voltage 2	17.75 kV
Lens voltage	7 kV
Linear detector voltage	2.85 kV
Deflection on	
Deflection mass	

Laser

Laser beam attenuation	95
Laser beam focus	36
Laser repetition rate	2000 Hz
Number of shots	3000

Mass spectroscopy (MALDI) for the reaction of 1j with 2a



Chemical Formula: $C_{22}H_{19}OS^+$

Exact Mass: 331.12

Testing Report

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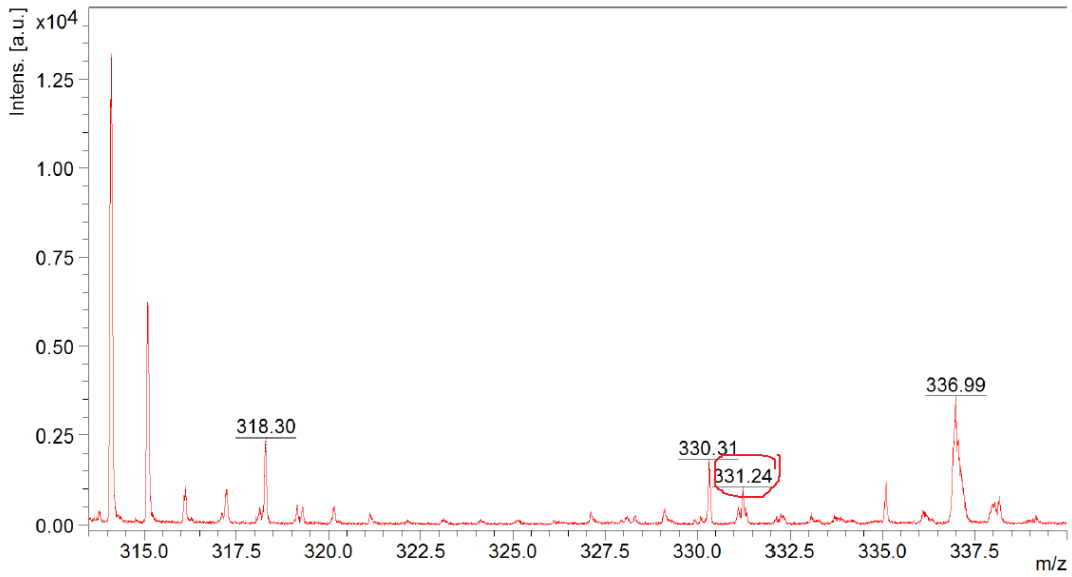

Instrument

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Name of computer	UTX-00589
Operator ID or name	BDAL@DE
flexControl version	flexControl 3.4.135.0
flexAnalysis version	3.4.76.0

Target

Target type	0280784
Target serial number	1112383
Position	A19

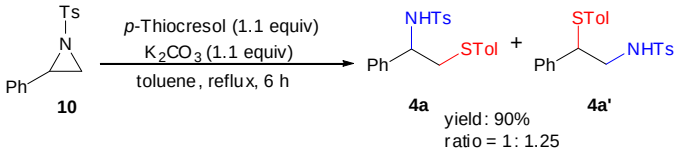
Spectrometer

positive voltage polarity	POS
PIE delay	100 ns
Ion source voltage 1	20 kV
Ion source voltage 2	17.75 kV
Lens voltage	7 kV
Linear detector voltage	2.838 kV
Deflection on	
Deflection mass	

Laser

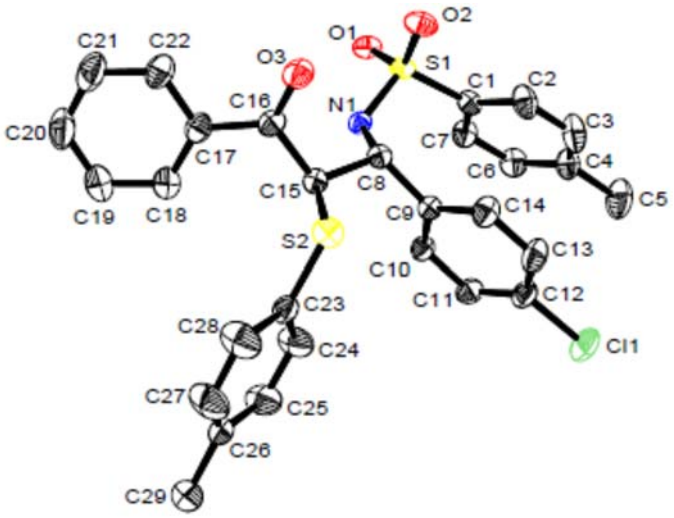
Laser beam attenuation	99
Laser beam focus	36
Laser repetition rate	1000 Hz
Number of shots	1500

Synthesis of β-Sulfonamino Sulfides through Ring Opening of Phenyl N-tosylaziridine with *p*-Thiocresol



Crystal Structure of 4m and the Corresponding Data

ORTEP drawing of 4m (CCDC 1528230); thermal ellipsoids are set at a 30% probability level



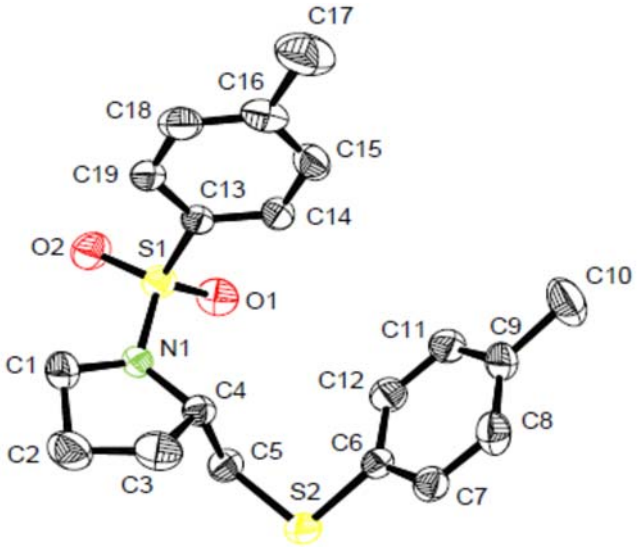
Crystal Structure Information of 4m

Crystal data	
Chemical formula	$C_{29}H_{27}ClNO_3S_2$
M_r	537.08
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	290
a, b, c (Å)	10.7451 (4), 24.1196 (8), 10.5407 (4)
β (°)	100.488 (1)
V (Å^3)	2686.17 (17)
Z	4
Radiation type	Mo $K\alpha$

μ (mm^{-1})	0.33
Crystal size (mm)	0.25 × 0.20 × 0.10
Data collection	
Diffractometer	Bruker *APEX*-II CCD diffractometer
Absorption correction	Multi-scan *SADABS*
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25814, 6640, 4696
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.157, 1.06
No. of reflections	6640
No. of parameters	327
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.32, −0.51

Crystal Structure of 9 and the Corresponding Data

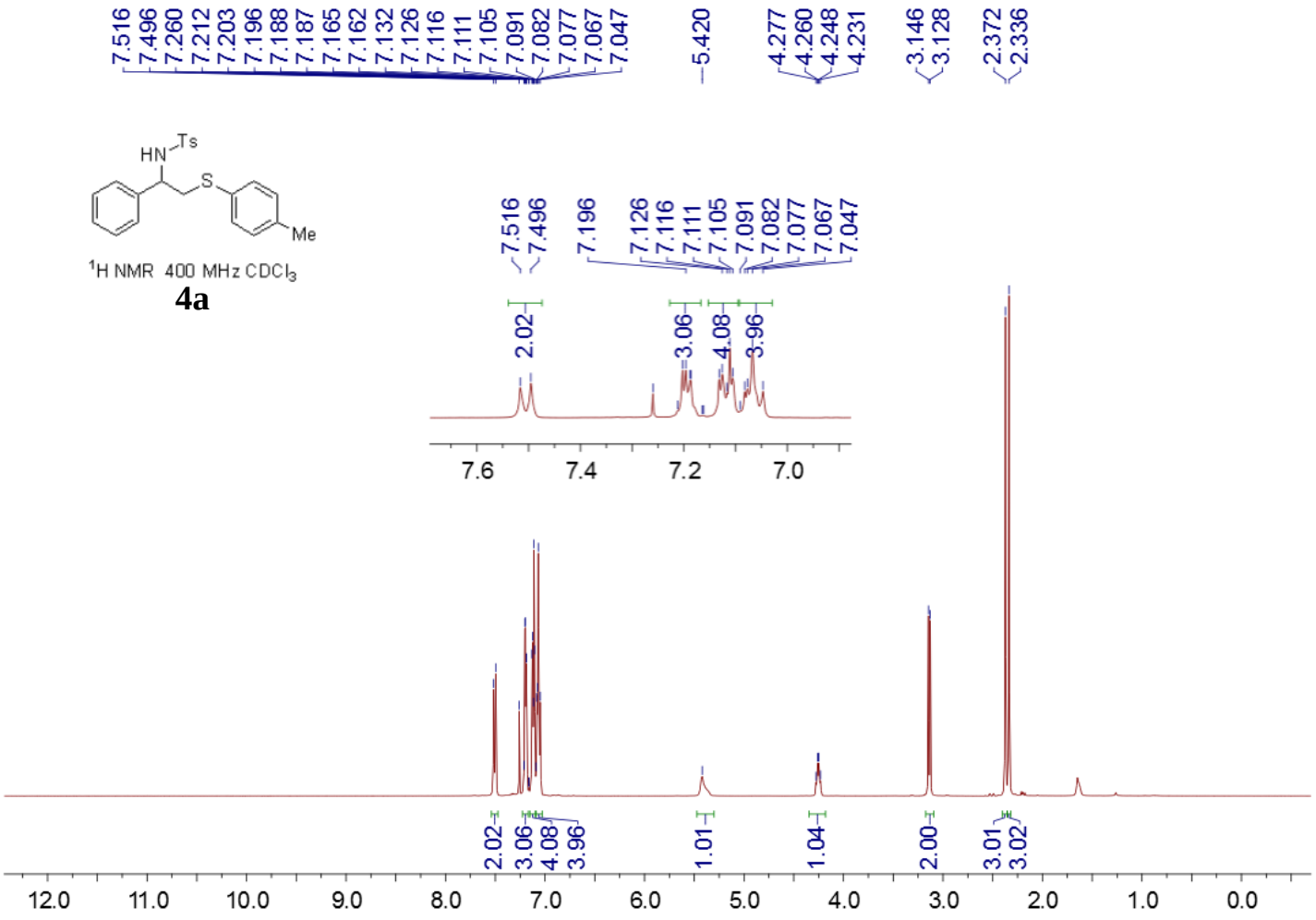
ORTEP drawing of 9 (CCDC 1528231); thermal ellipsoids are set at a 30% probability level

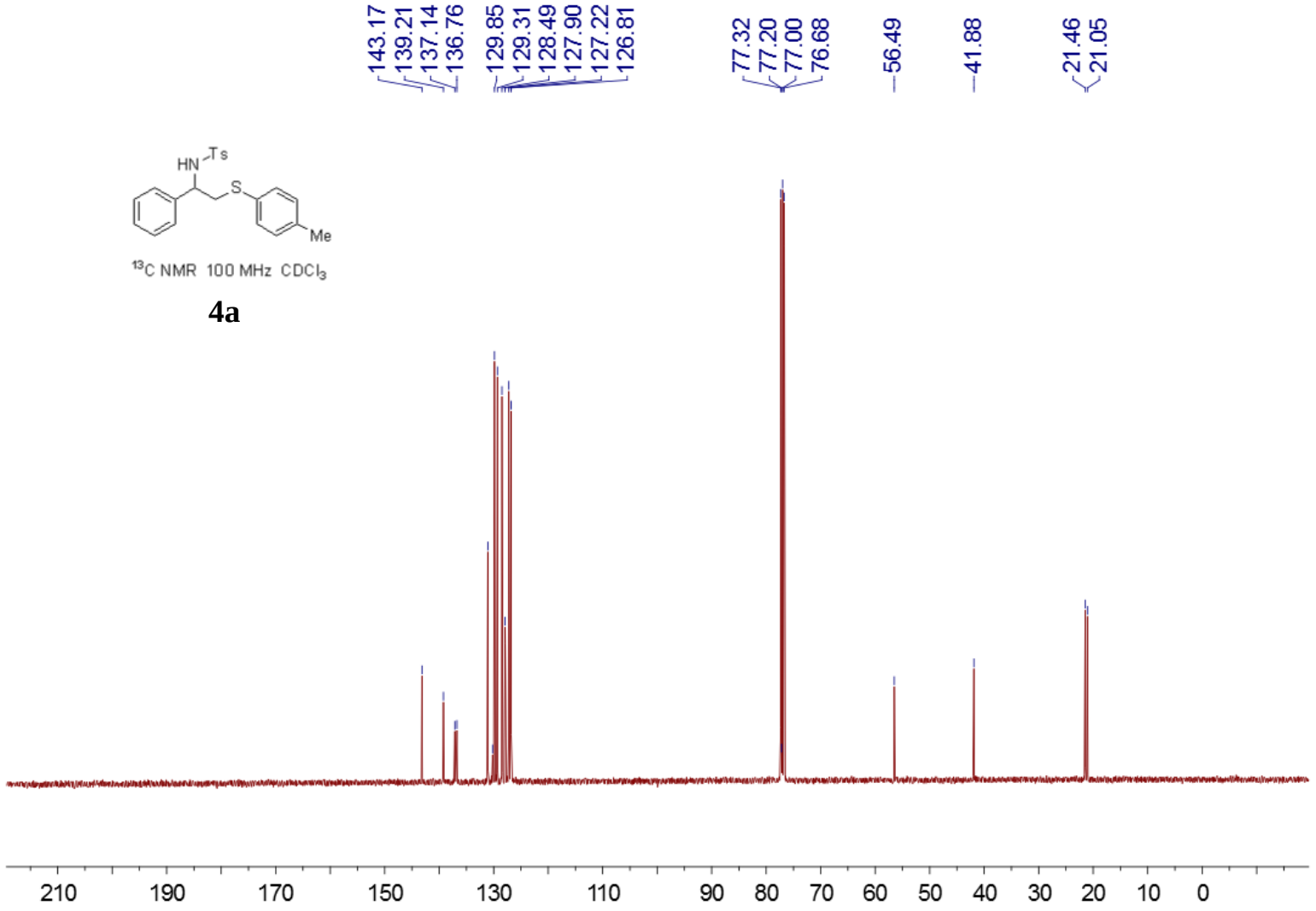


Crystal Structure Information of 9

Crystal data	
Chemical formula	$C_{19}H_{23}NO_2S_2$
M_r	361.50
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	284
a, b, c (Å)	10.7682 (5), 18.6312 (8), 10.2412 (5)
β (°)	110.113 (1)
V (Å^3)	1929.34 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.29
Crystal size (mm)	0.30 × 0.25 × 0.18
Data collection	
Diffractometer	Bruker *APEX*-II CCD diffractometer
Absorption correction	Multi-scan *SADABS*
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18068, 4730, 3414
R_{int}	0.031
(sin θ/λ)max (Å−1)	0.666
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.163, 1.01
No. of reflections	4730
No. of parameters	219
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.42

NMR Spectra of Products

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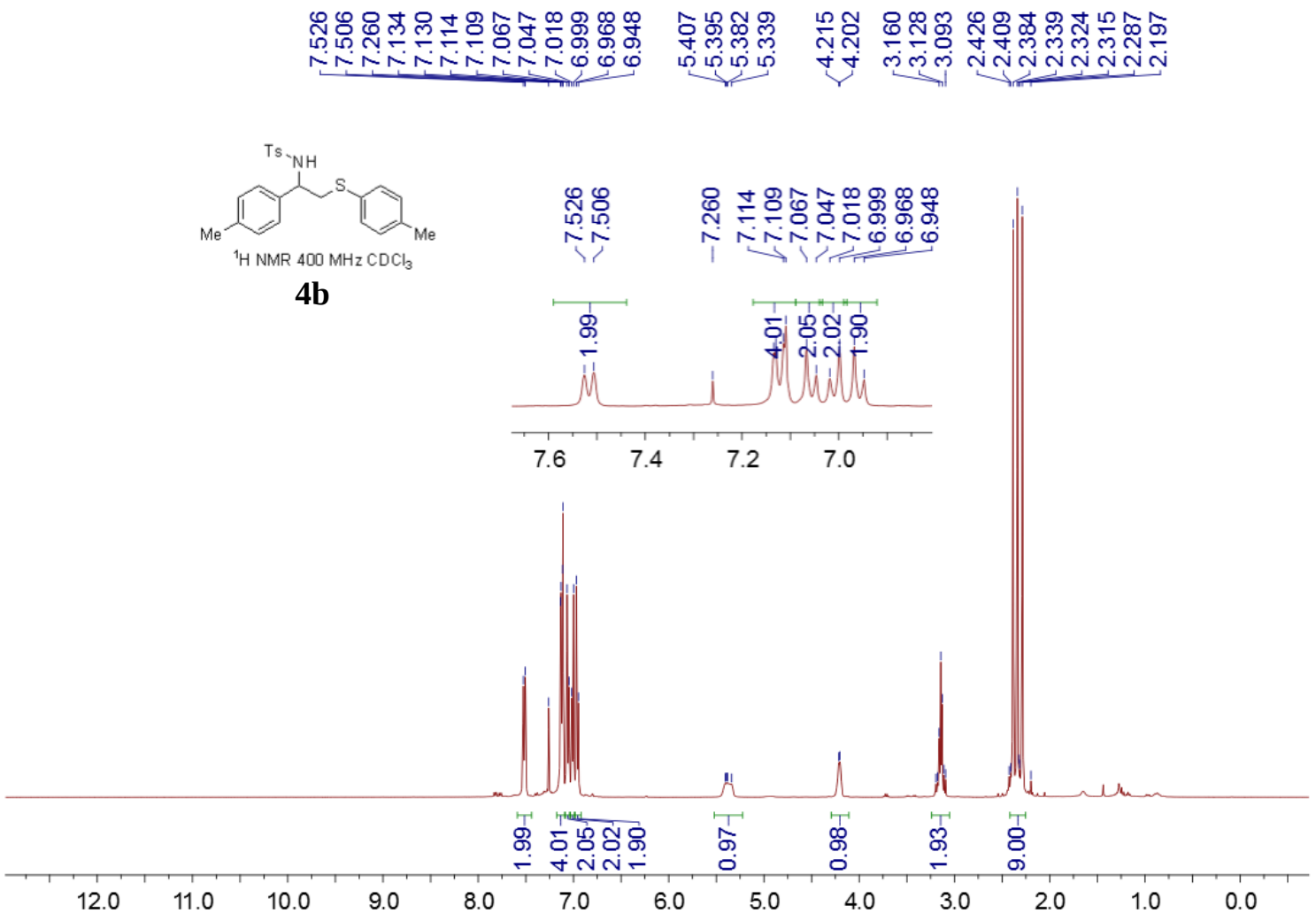
139.21
137.14
136.76
129.85
129.31
128.49
127.90
127.22
126.81
77.32
77.20
77.00
76.68
56.49
41.88
21.46
21.05
HN
Ts
S
Me
^{13}C NMR 100 MHz $CDCl_3$
4a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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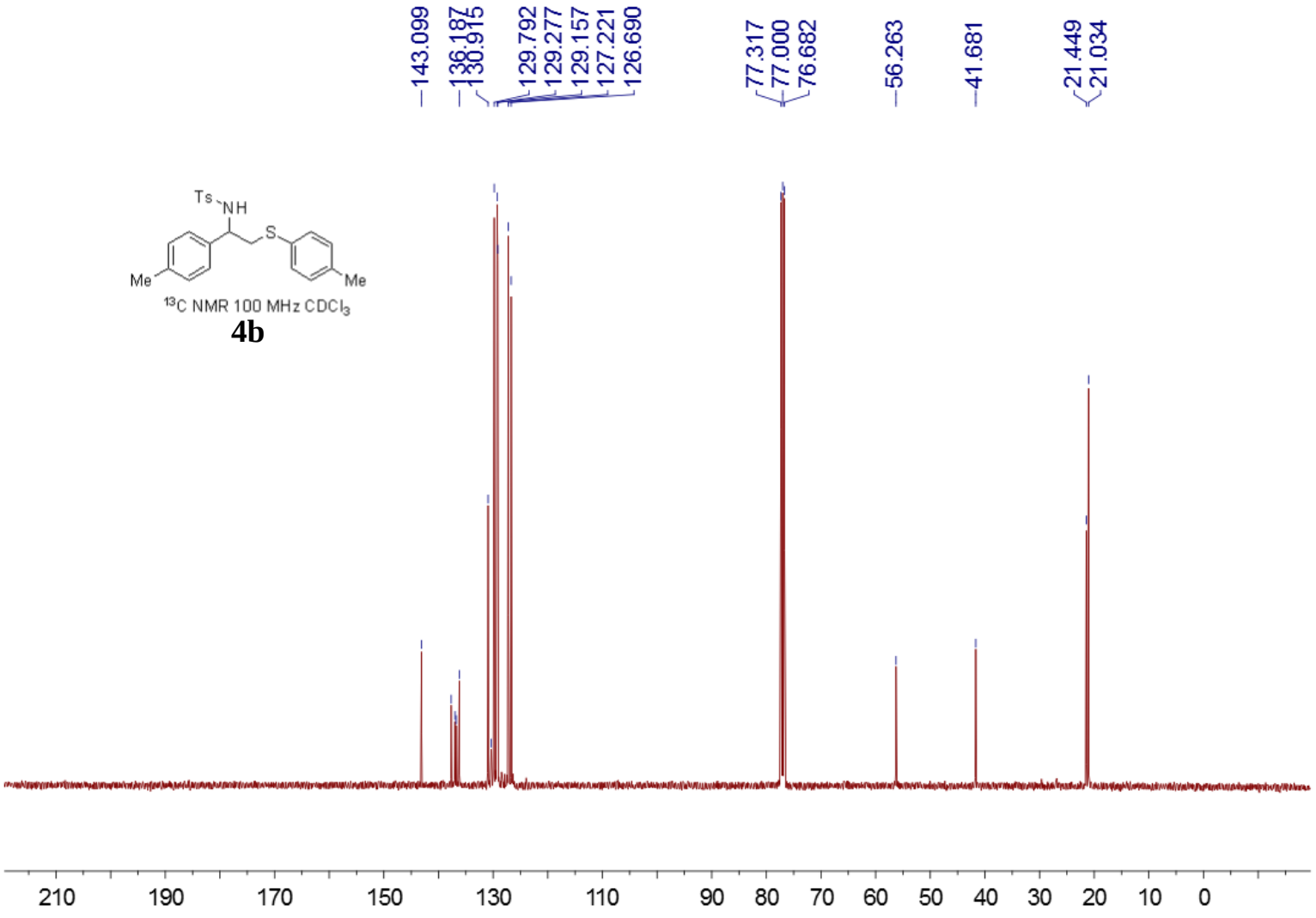
7.506
7.260
7.134
7.130
7.114
7.109
7.067
7.047
7.018
6.999
6.968
6.948
5.407
5.395
5.382
5.339
4.215
4.202
3.160
3.128
3.093
2.426
2.409
2.384
2.339
2.324
2.315
2.287
2.197
Ts
NH
S
Me
Me
1H NMR 400 MHz CDCl3
4b
1.99
4.01
2.05
2.02
1.90
0.97
0.98
1.93
9.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.6
7.4
7.2
7.0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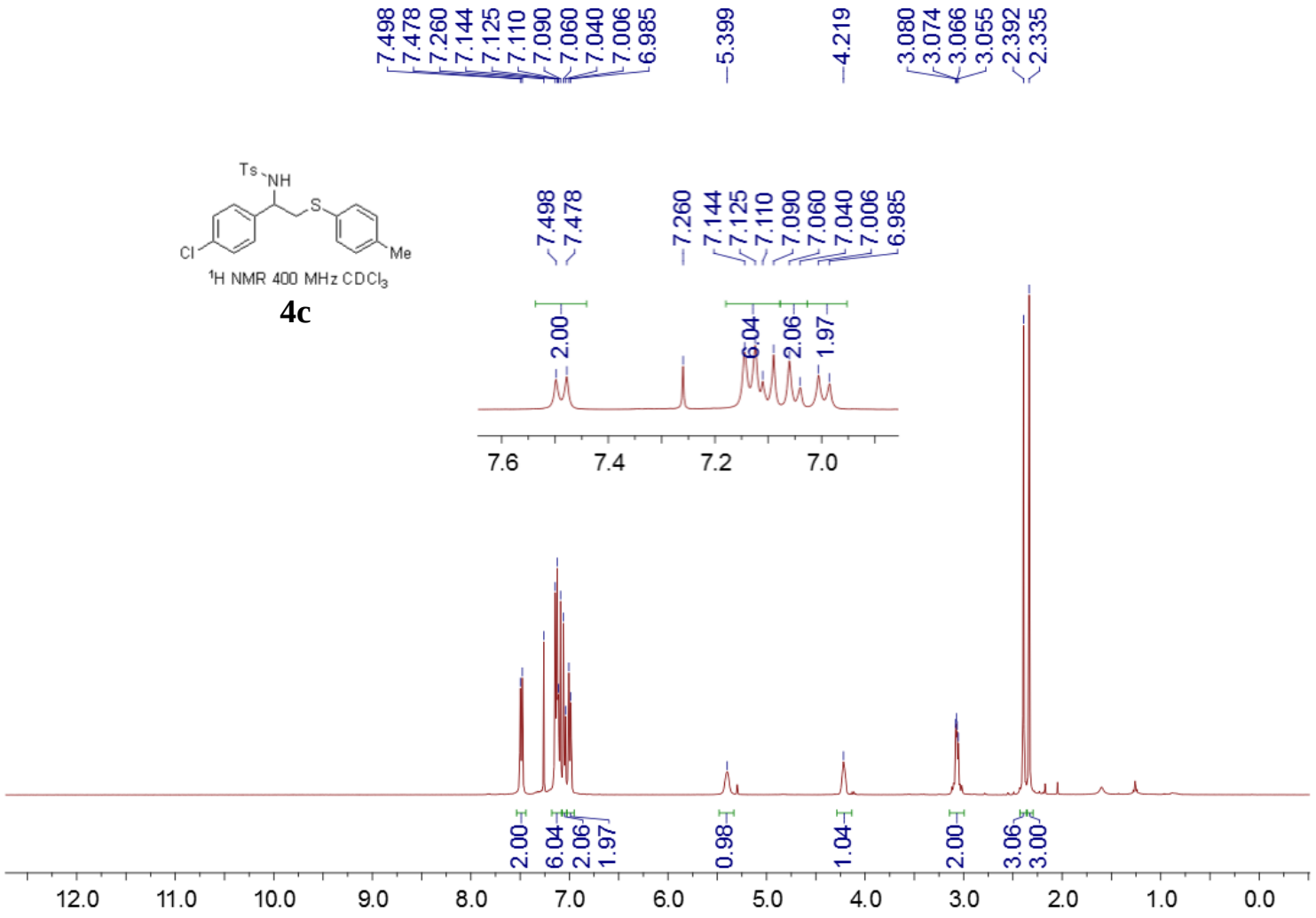
136.187
130.915
129.792
129.277
129.157
127.221
126.690
77.317
77.000
76.682
56.263
41.681
21.449
21.034
Ts
NH
S
Me
Me
13C NMR 100 MHz CDCl3
4b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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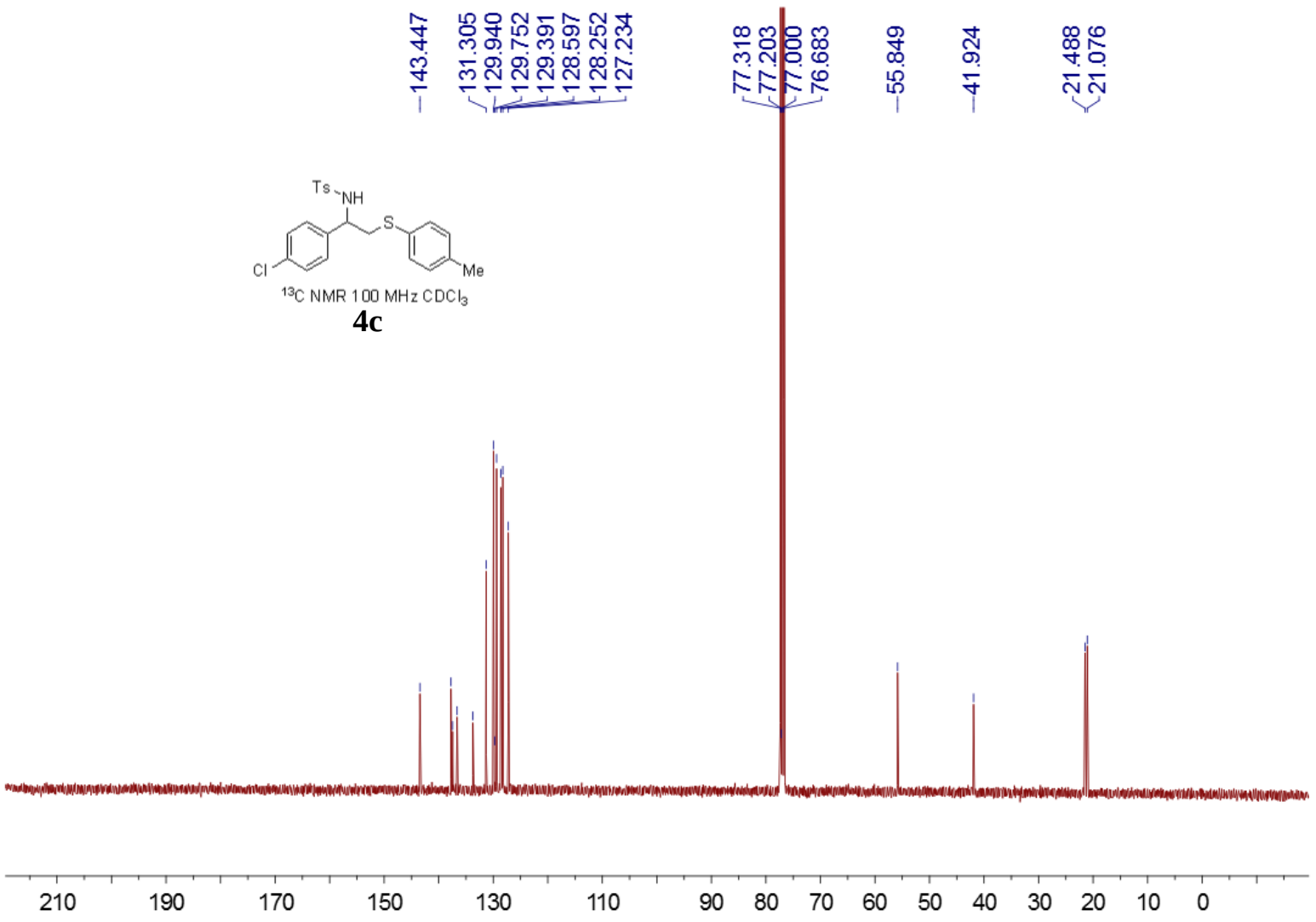
7.478
7.260
7.144
7.125
7.110
7.090
7.060
7.040
7.006
6.985
5.399
4.219
3.080
3.074
3.066
3.055
2.392
2.335
Ts
NH
S
Cl
Me
1H NMR 400 MHz CDCl3
4c
2.00
6.04
2.06
1.97
7.6
7.4
7.2
7.0
2.00
6.04
2.06
1.97
0.98
1.04
2.00
3.06
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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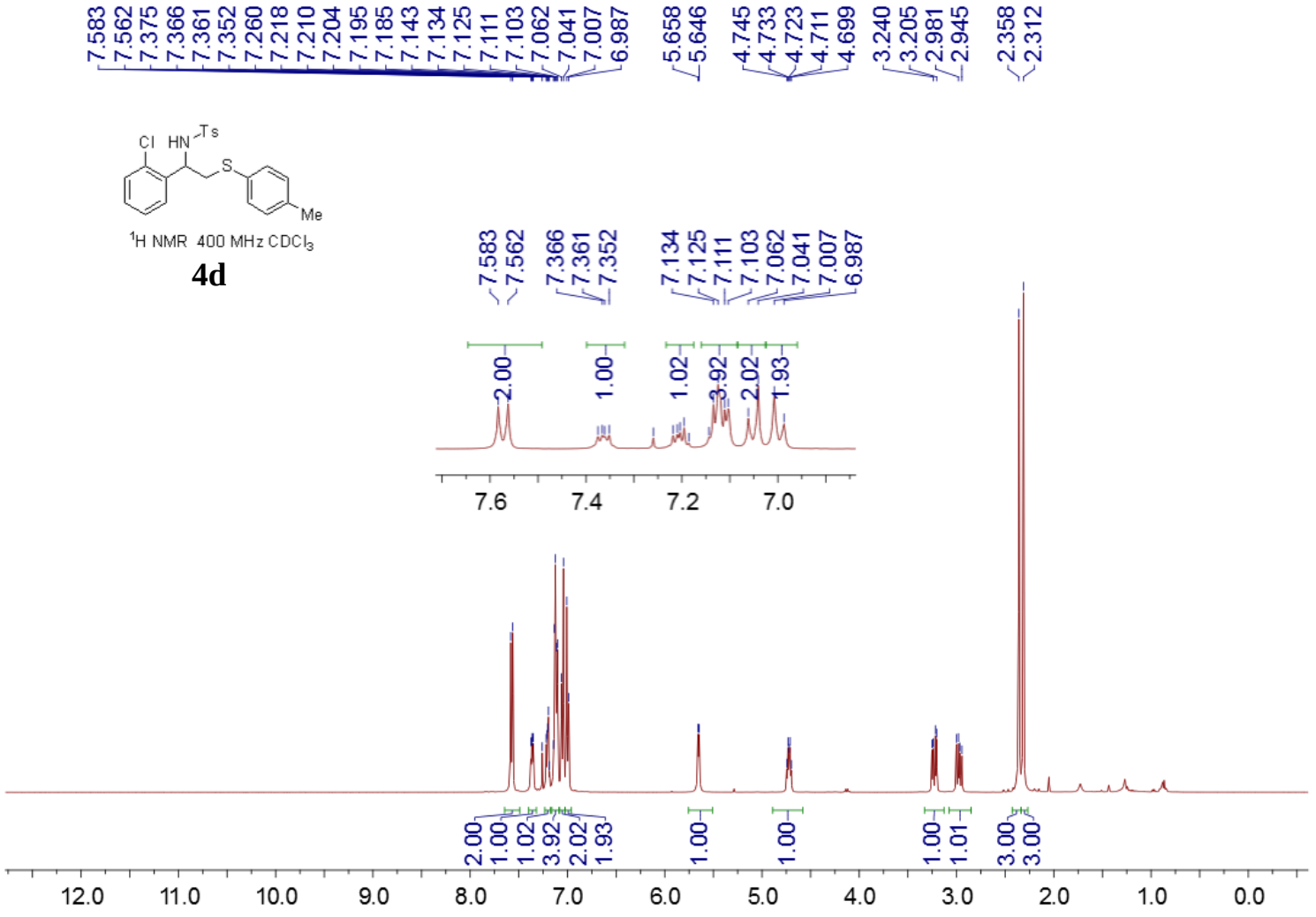
129.940
129.752
129.391
128.597
128.252
127.234
77.318
77.203
77.000
76.683
55.849
41.924
21.488
21.076
Ts
NH
S
Cl
Me
13C NMR 100 MHz CDCl3
4c
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0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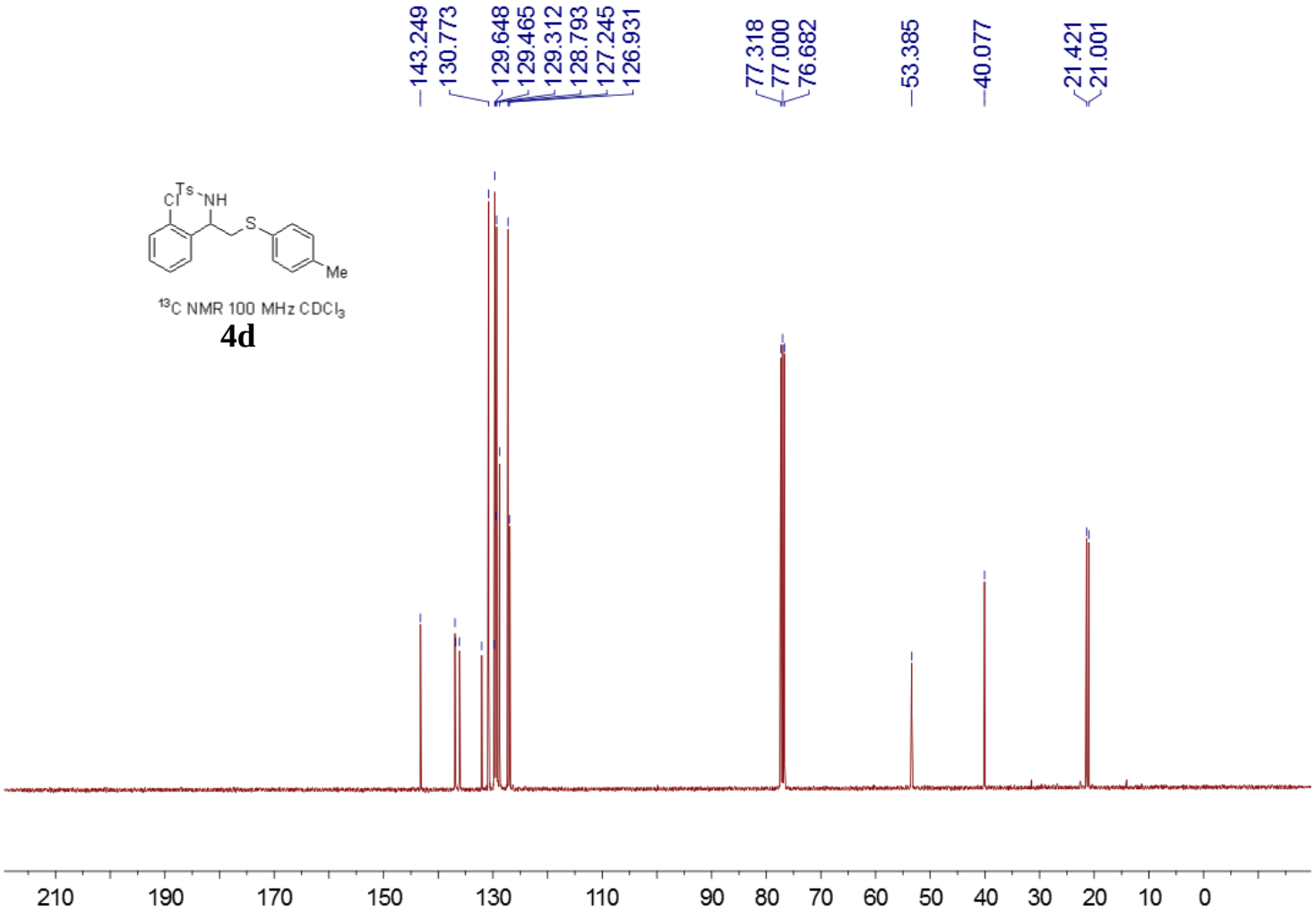
7.375
7.366
7.361
7.352
7.260
7.218
7.210
7.204
7.195
7.185
7.143
7.134
7.125
7.111
7.103
7.062
7.041
7.007
6.987
5.658
5.646
4.745
4.733
4.723
4.711
4.699
3.240
3.205
2.981
2.945
2.358
2.312
Cl
HN
Ts
S
Me
^{1}H NMR 400 MHz CDCl$_3$
4d
2.00
1.00
1.02
3.92
2.02
1.93
7.6
7.4
7.2
7.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


143.249
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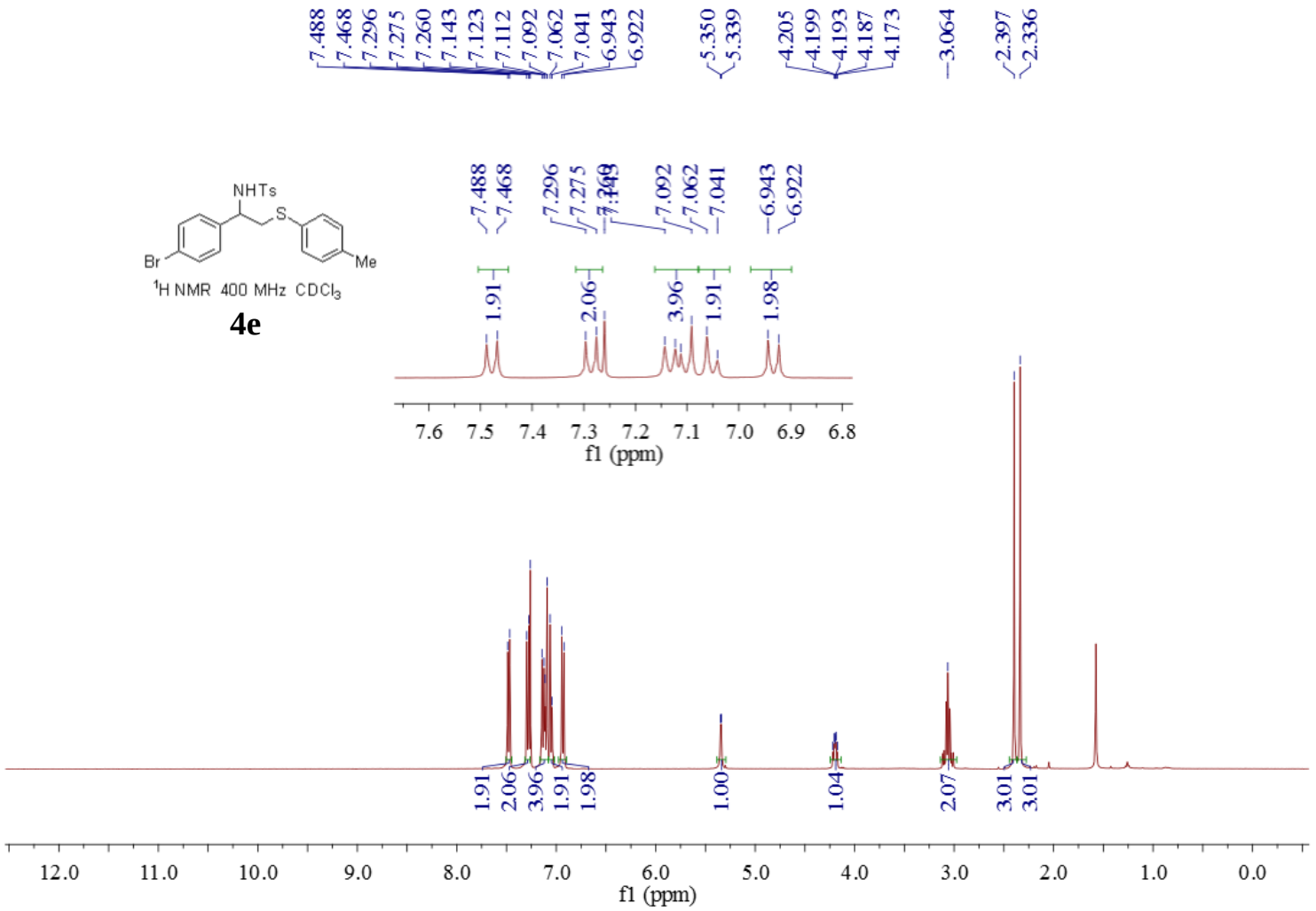
129.648
129.465
129.312
128.793
127.245
126.931
77.318
77.000
76.682
53.385
40.077
21.421
21.001
Cl
Ts
NH
S
Me
13C NMR 100 MHz CDCl3
4d
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


NHTs
S
Br
Me
^{1}H NMR 400 MHz CDCl$_3$
4e
7.488
7.468
7.296
7.275
7.260
7.143
7.123
7.112
7.092
7.062
7.041
6.943
6.922
5.350
5.339
4.205
4.199
4.193
4.187
4.173
3.064
2.397
2.336
1.91
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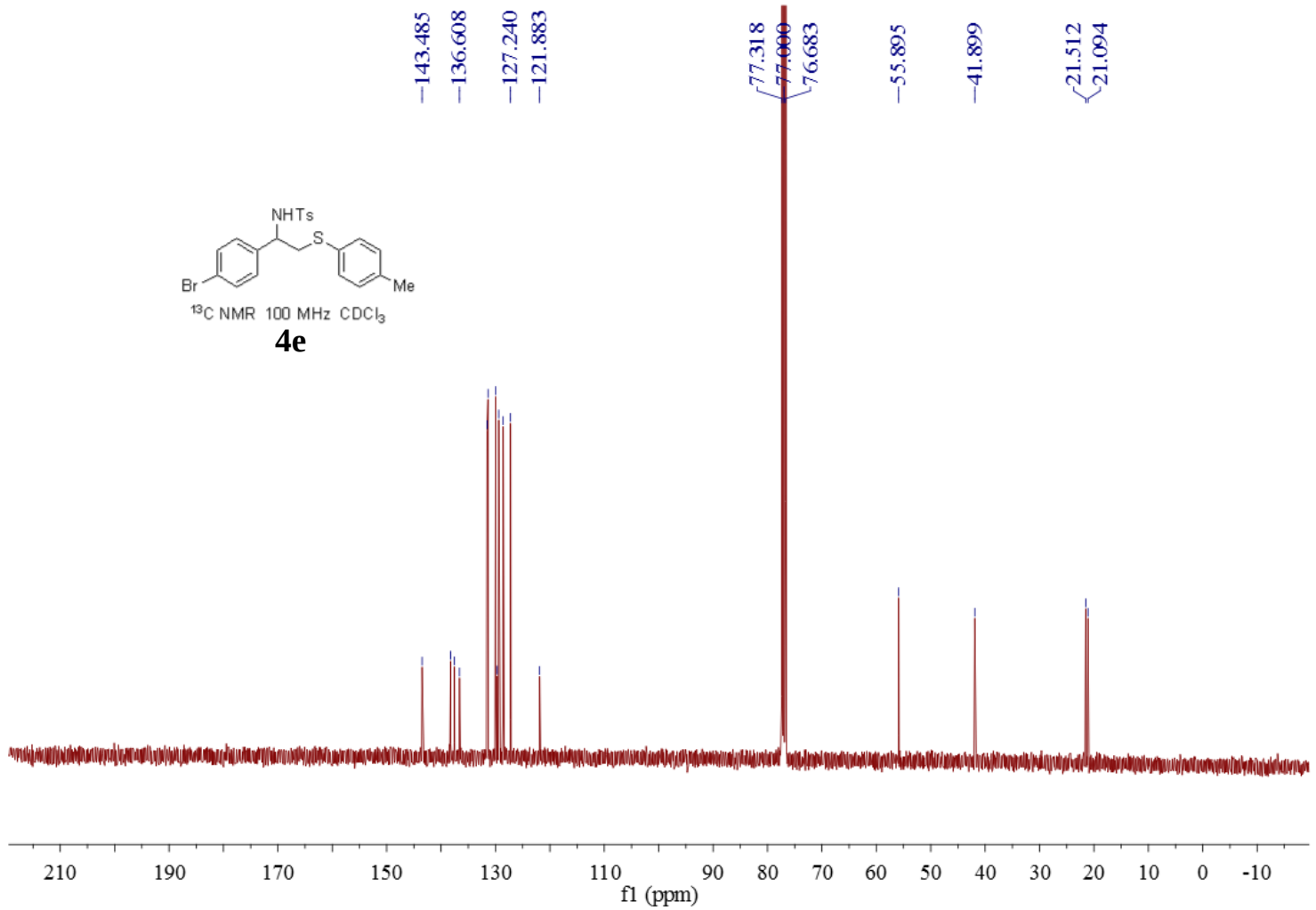
3.96
1.91
1.98
1.00
1.04
2.07
3.01
3.01
f1 (ppm)


143.485
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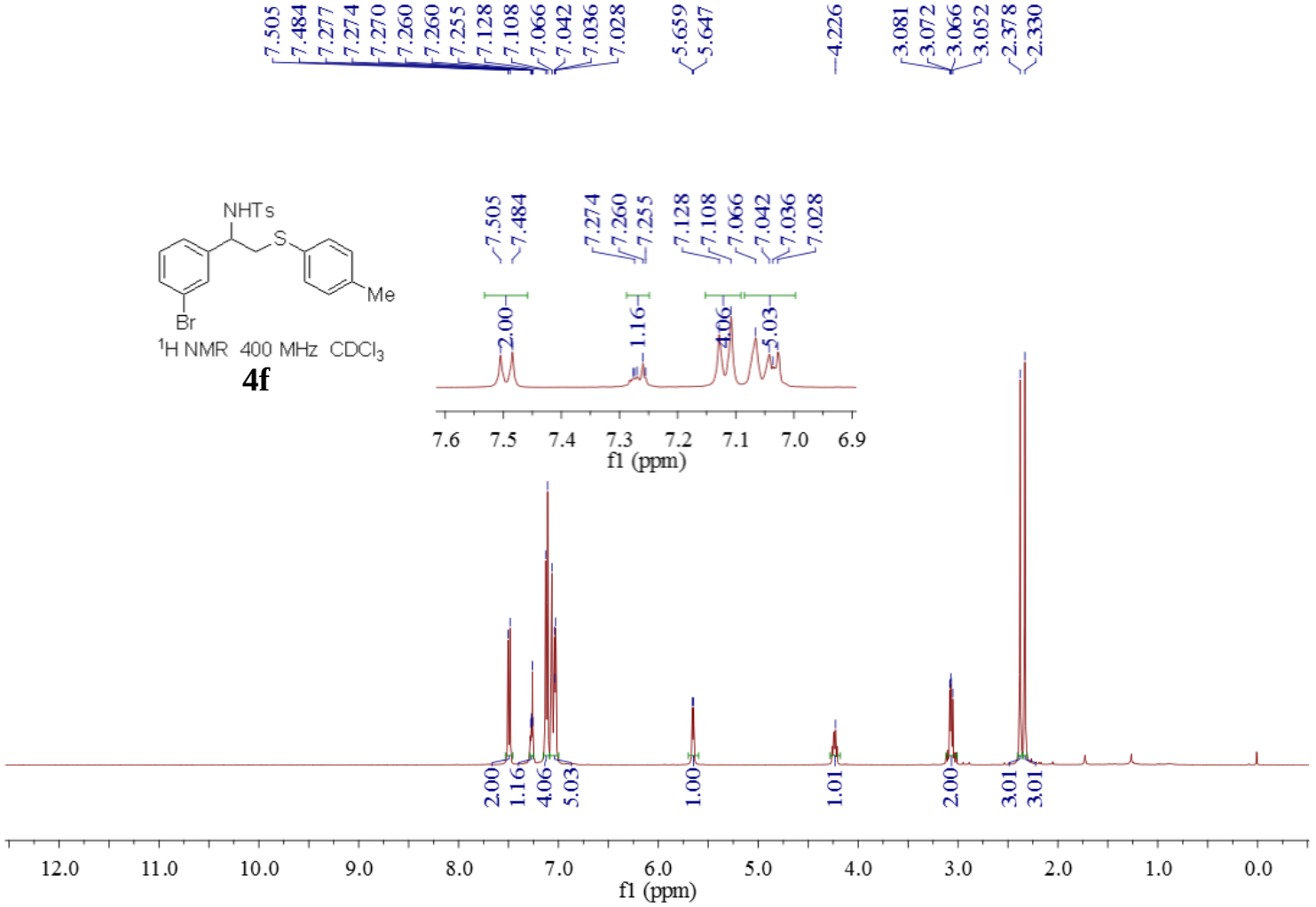
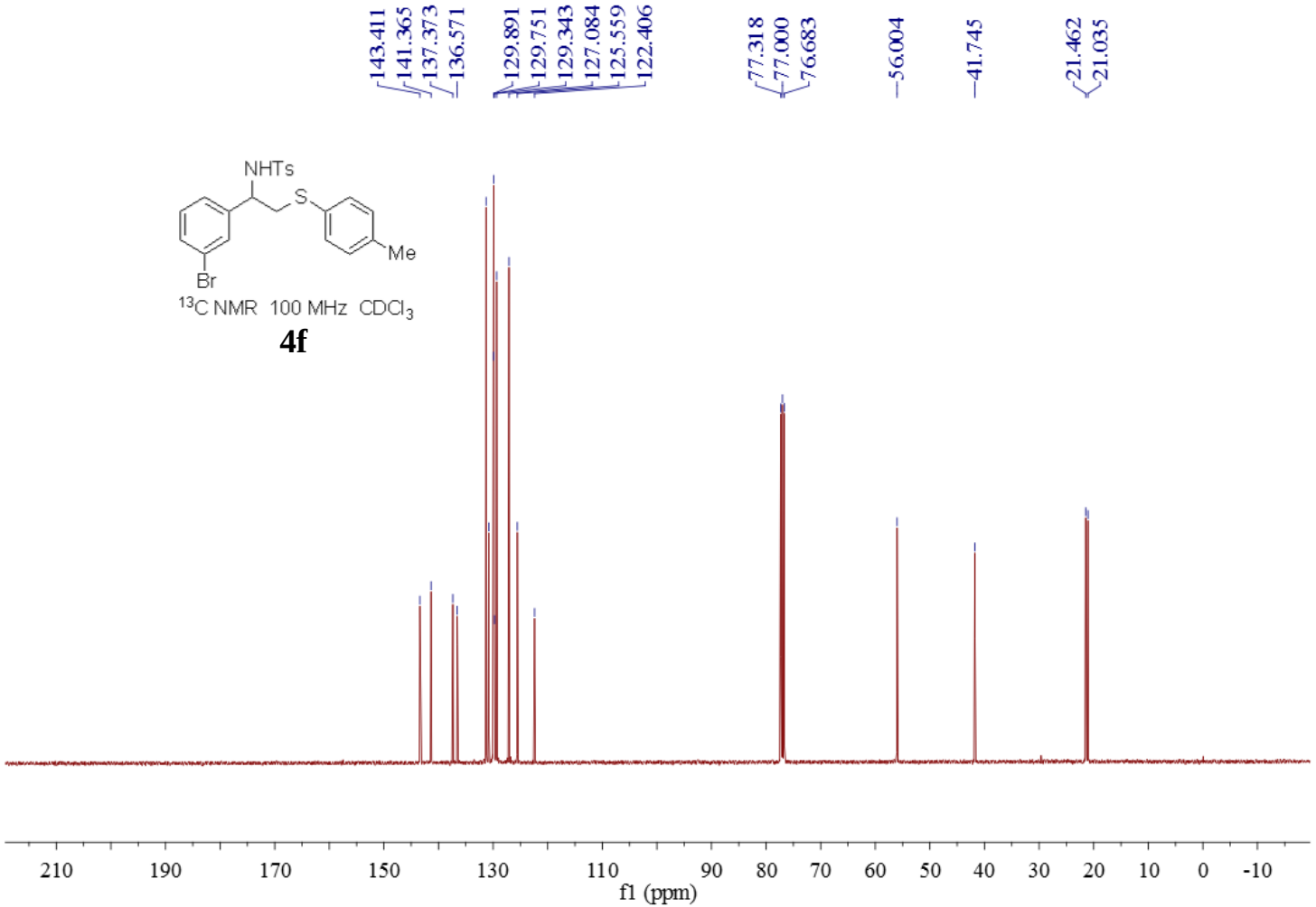
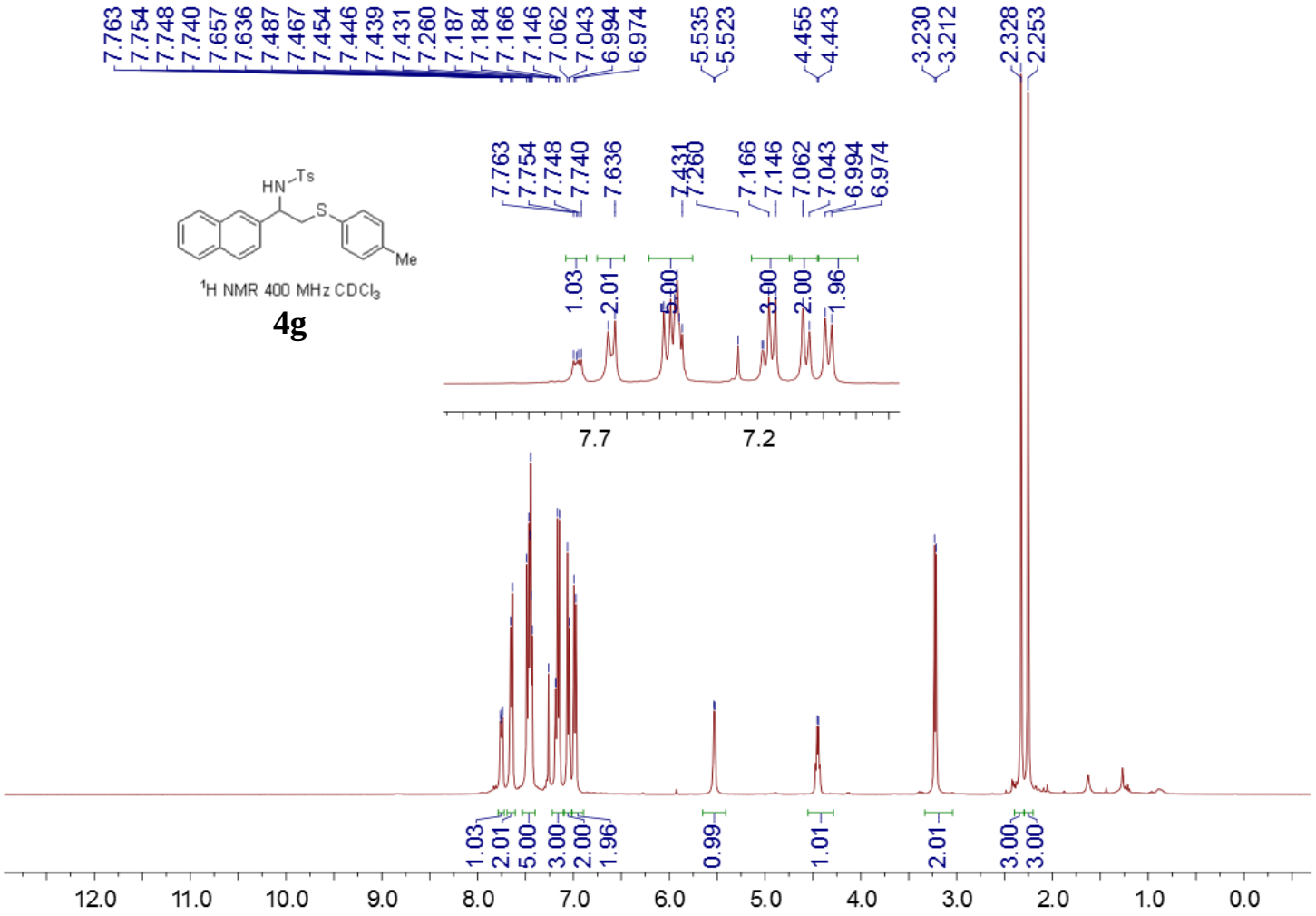
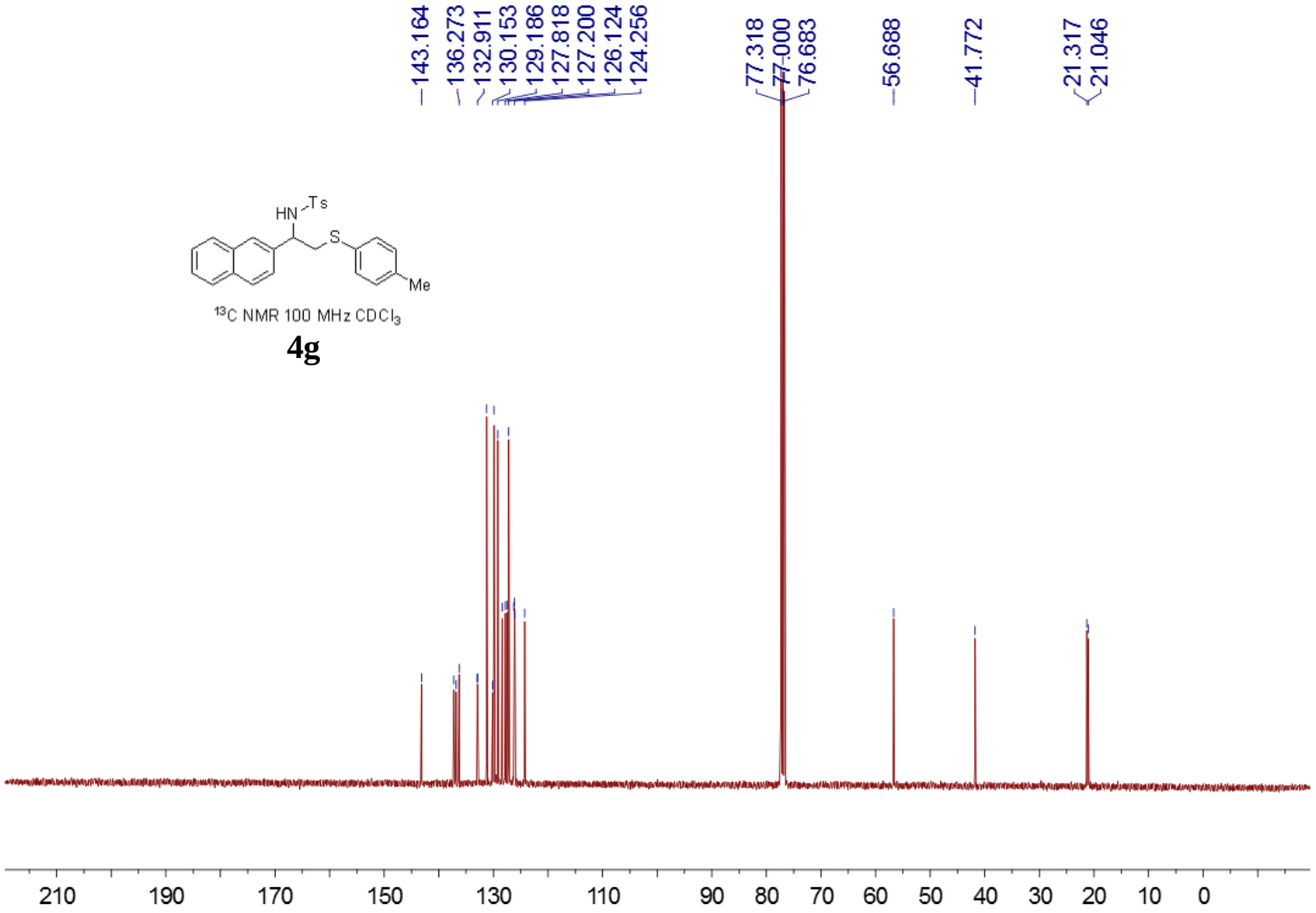
127.240
121.883
77.318
77.000
76.683
55.895
41.899
21.512
21.094
NHTs
S
Br
Me
13C NMR 100 MHz CDCl3
4e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.505
7.484
7.277
7.274
7.270
7.260
7.260
7.255
7.128
7.108
7.066
7.042
7.036
7.028
5.659
5.647
4.226
3.081
3.072
3.066
3.052
2.378
2.330
NHTs
S
Me
Br
1H NMR 400 MHz CDCl3
4f
2.00
1.16
4.06
5.03
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.00
1.16
4.06
5.03
1.00
1.01
2.00
3.01
3.01
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


143.411
141.365
137.373
136.571
129.891
129.751
129.343
127.084
125.559
122.406
77.318
77.000
76.683
56.004
41.745
21.462
21.035
NHTs
S
Me
Br
^{13}C NMR 100 MHz CDCl$_3$
4f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HN
Ts
S
Me
^{1}H NMR 400 MHz $CDCl_3$
4g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136.273
132.911
130.153
129.186
127.818
127.200
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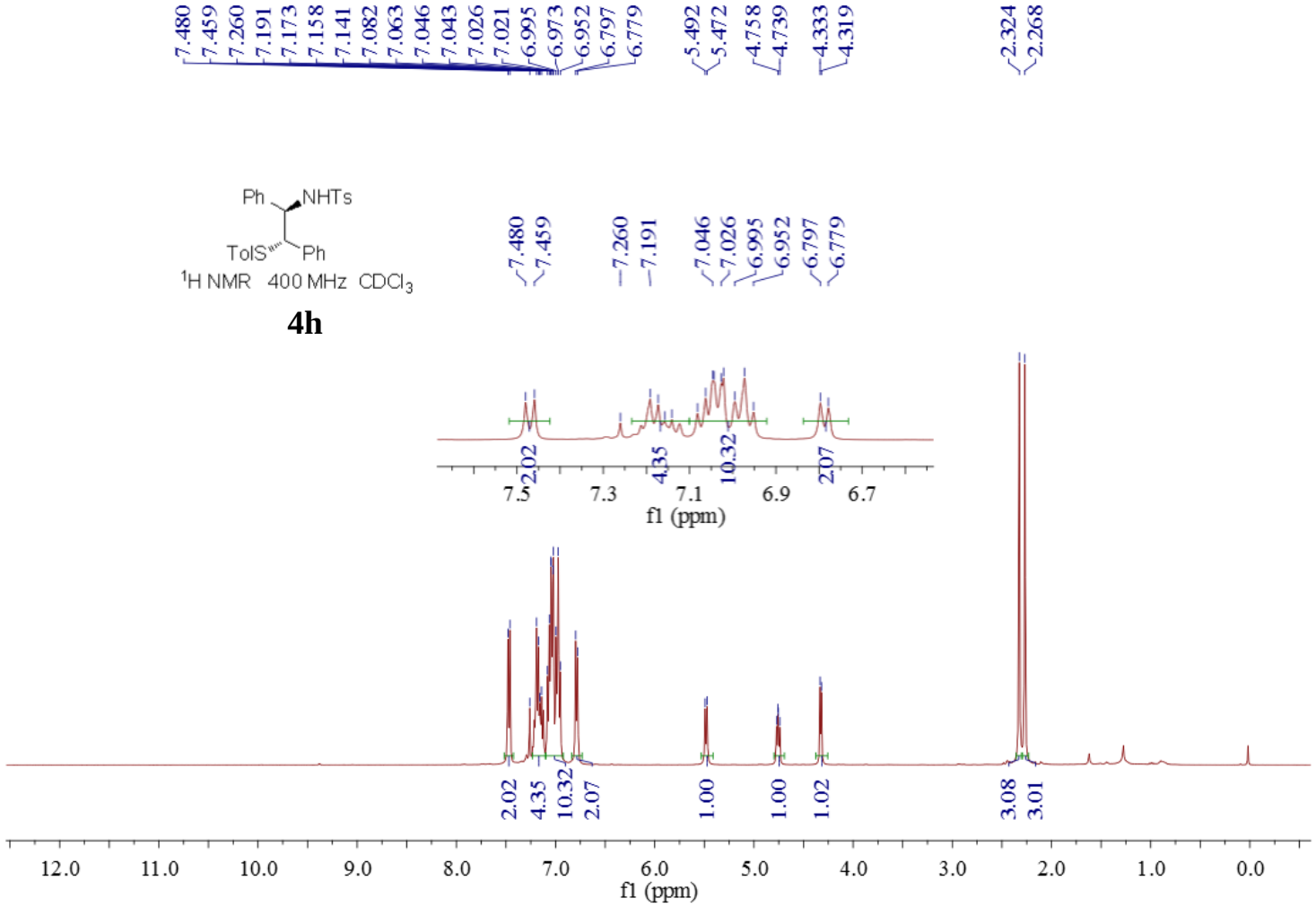
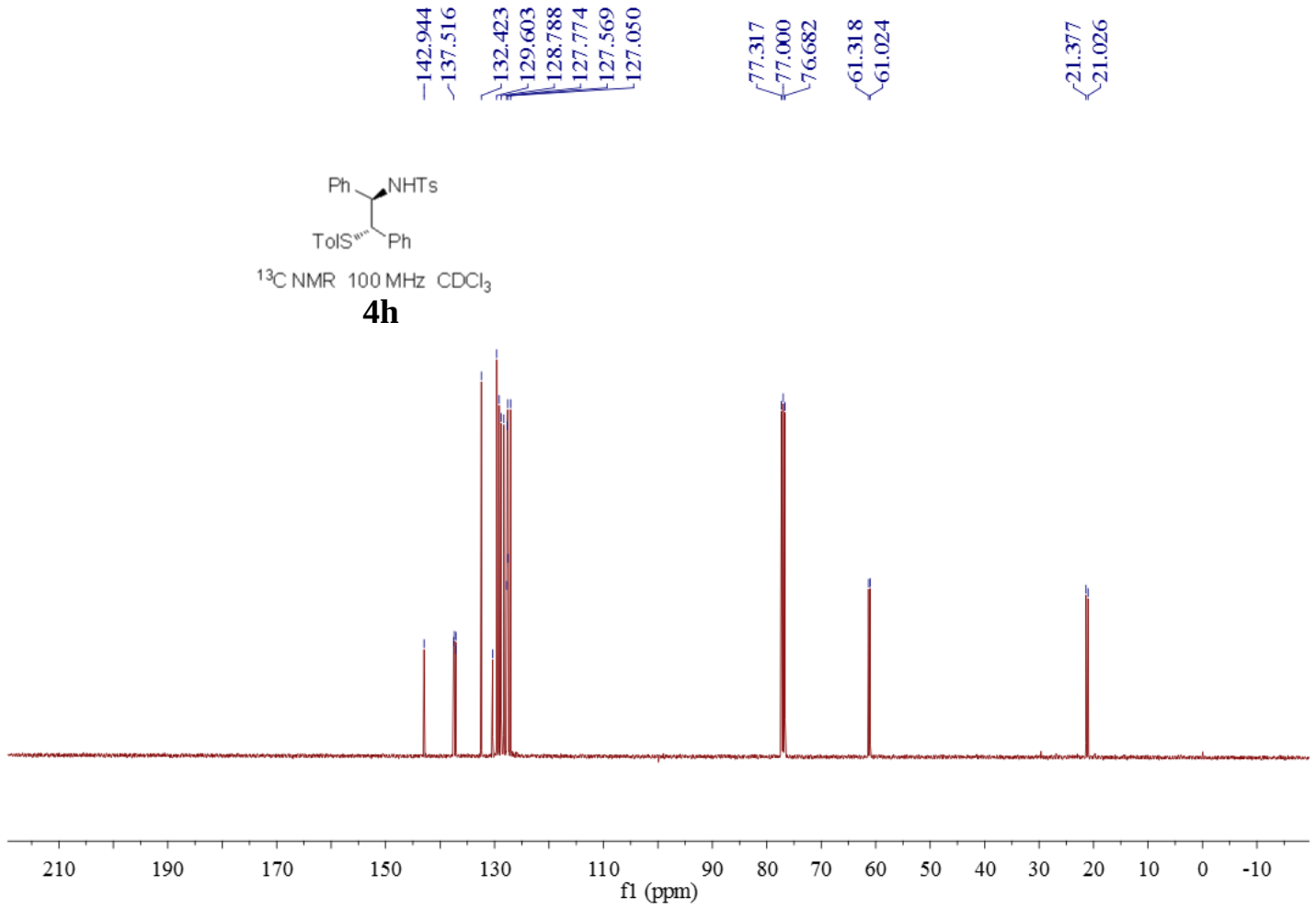
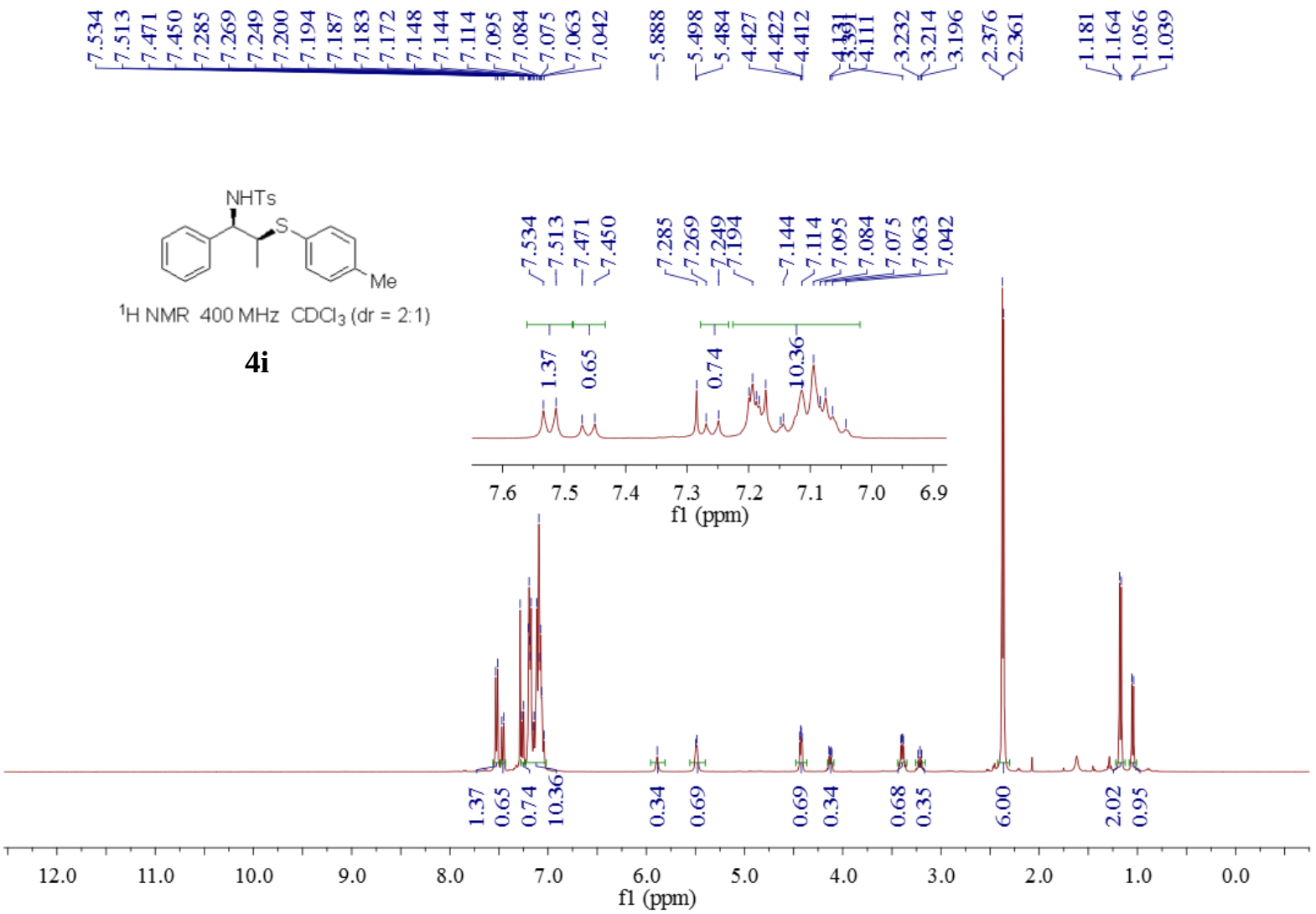
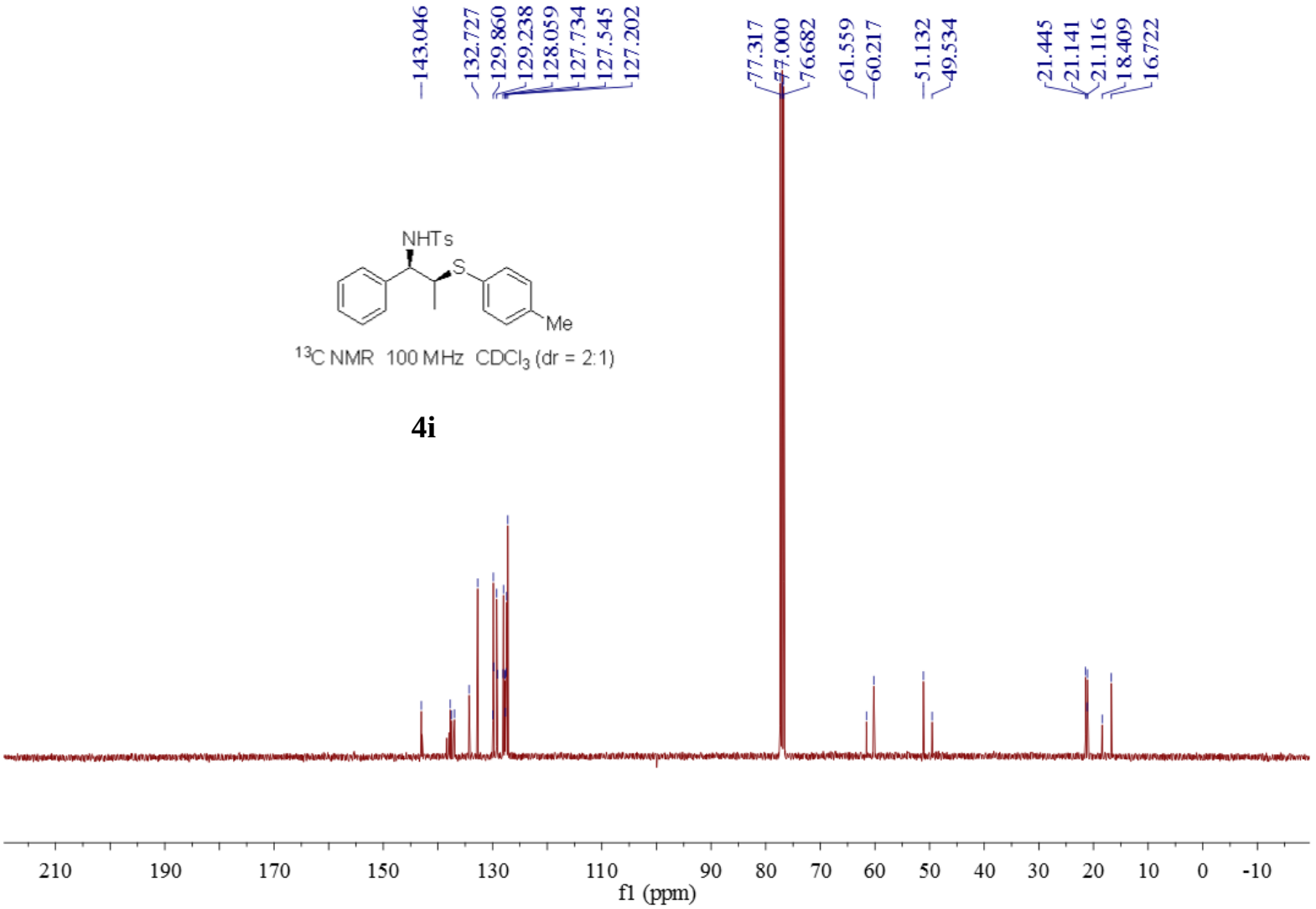
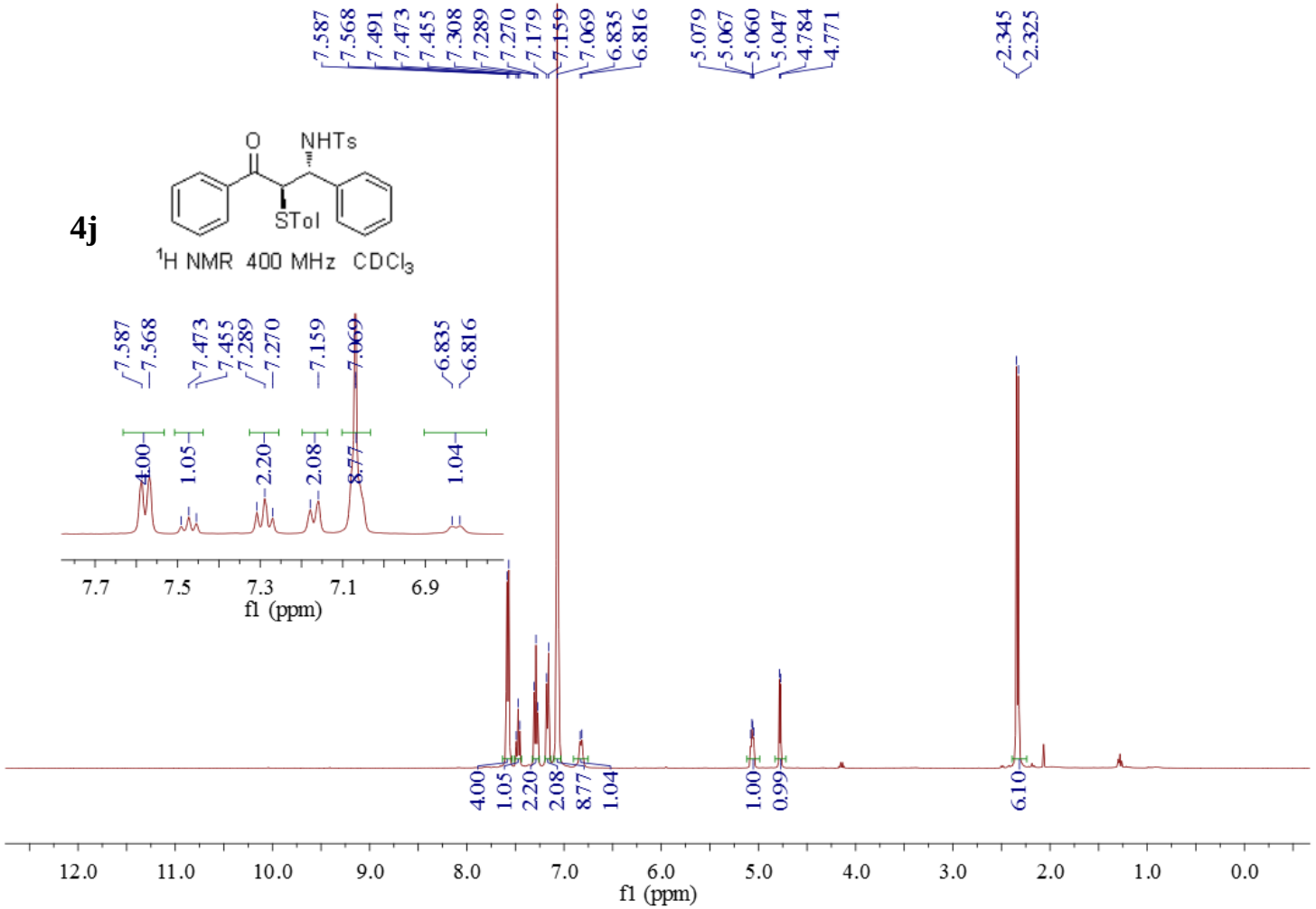
77.318
77.000
76.683
56.688
41.772
21.317
21.046
HN
Ts
S
Me
13C NMR 100 MHz CDCl3
4g
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

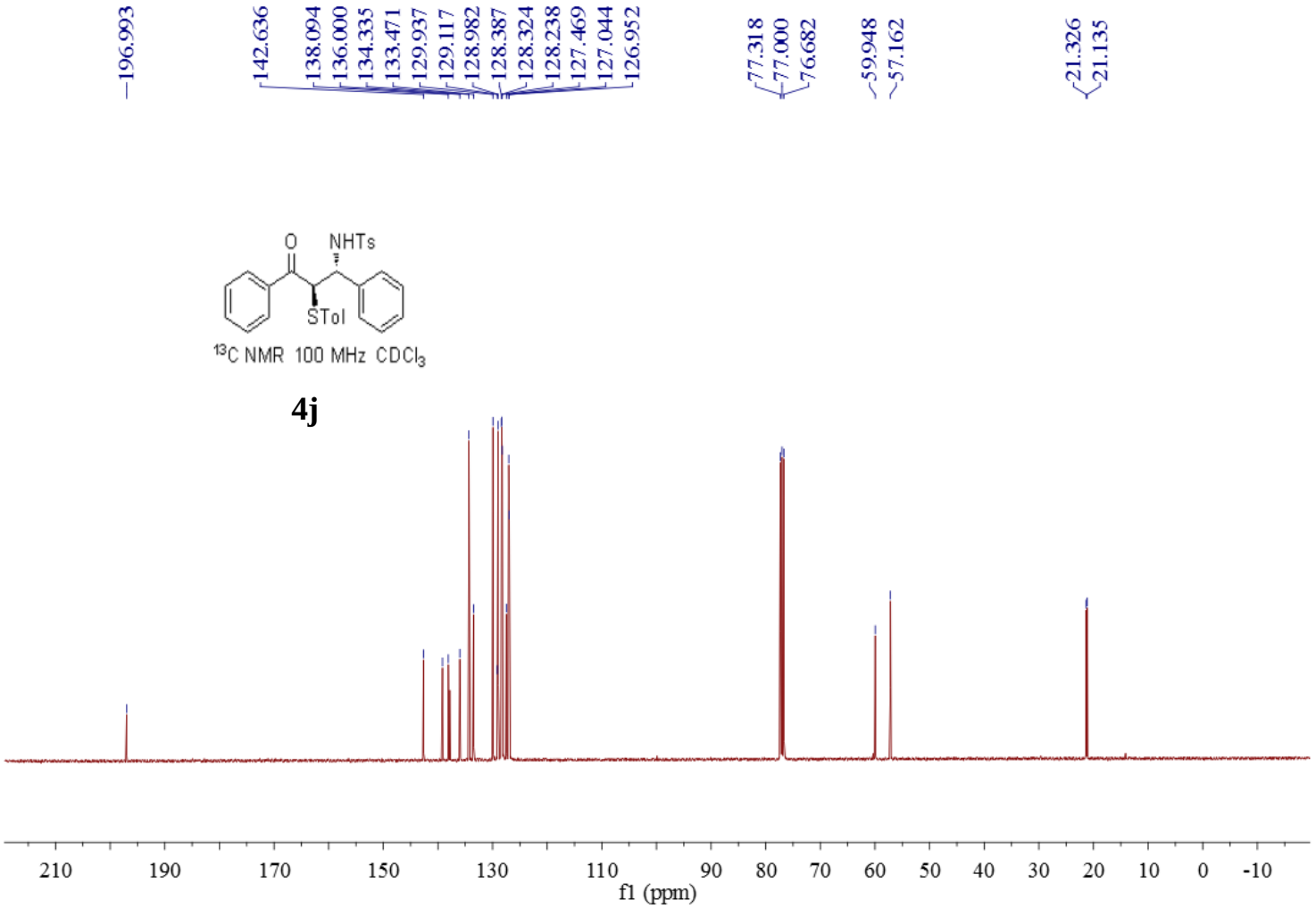

7.480
7.459
7.260
7.191
7.173
7.158
7.141
7.082
7.063
7.046
7.043
7.026
7.021
6.995
6.973
6.952
6.797
6.779
5.492
5.472
4.758
4.739
4.333
4.319
2.324
2.268
Ph
NHTs
TolS
Ph
1H NMR 400 MHz CDCl3
4h
2.02
4.35
10.32
2.07
1.00
1.00
1.02
3.08
3.01
f1 (ppm)

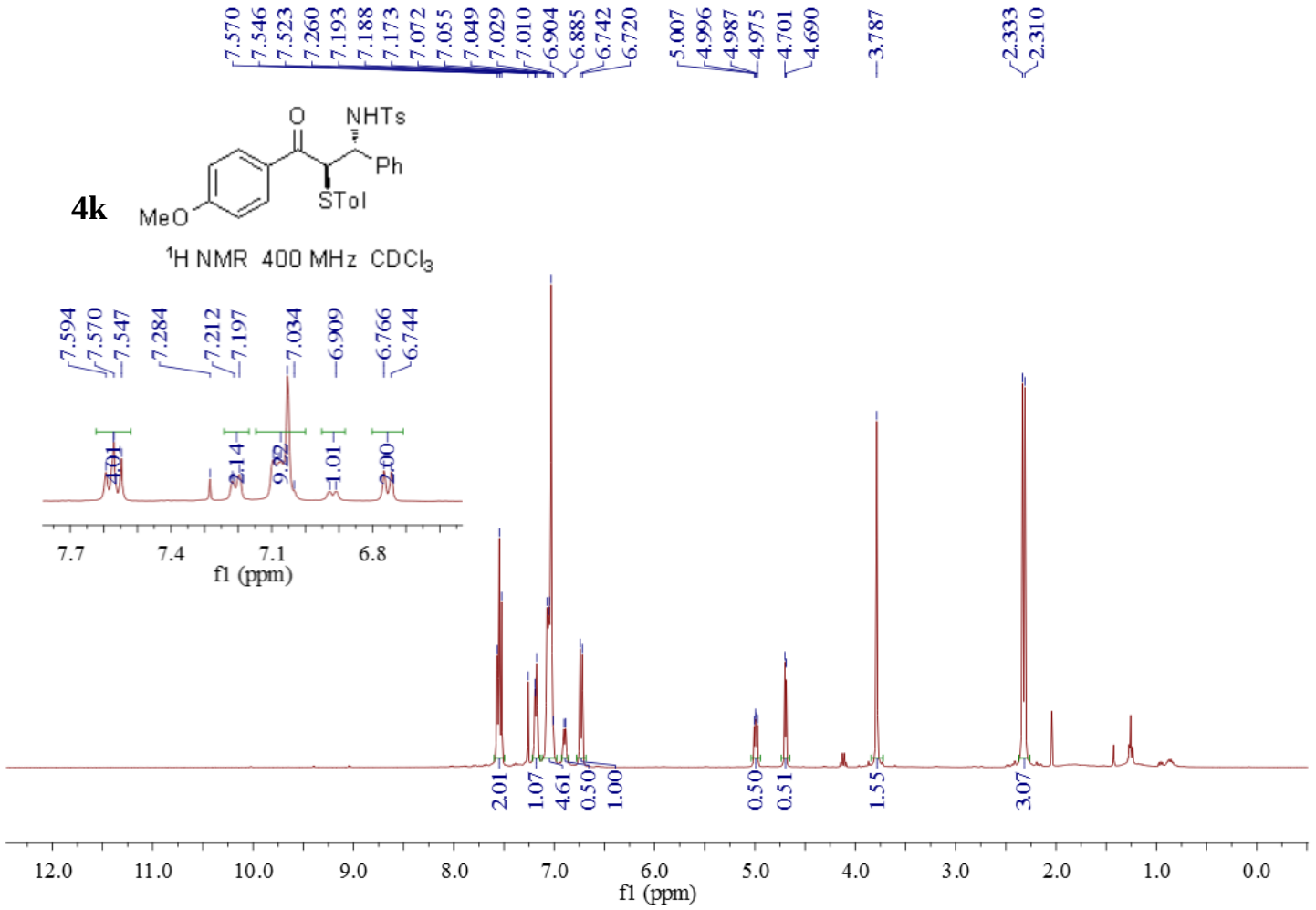

142.944
137.516
132.423
129.603
128.788
127.774
127.569
127.050
77.317
77.000
76.682
61.318
61.024
21.377
21.026
Ph
NHTs
TolS
Ph
13C NMR 100 MHz CDCl3
4h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

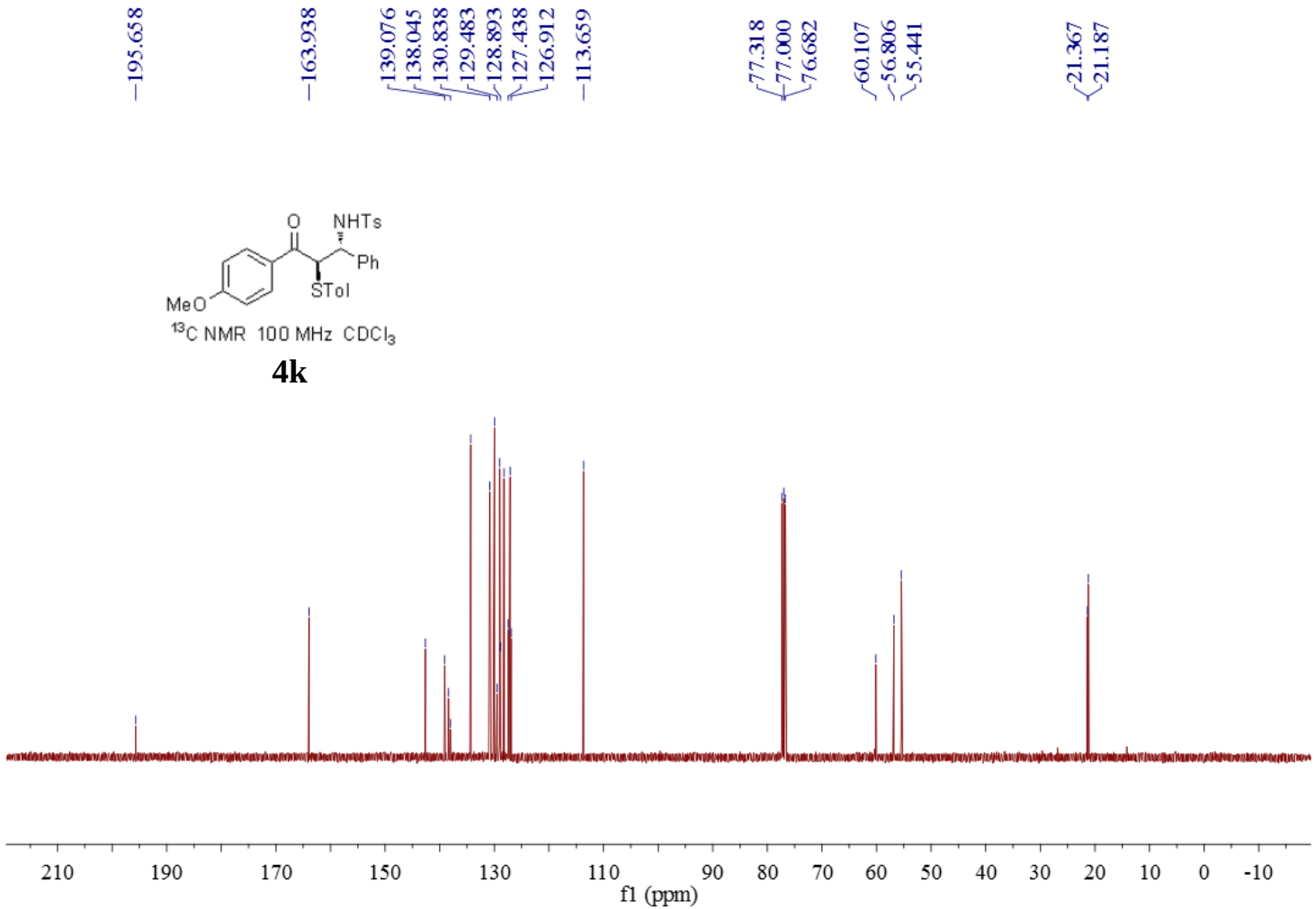

7.534
7.513
7.471
7.450
7.285
7.269
7.249
7.200
7.194
7.187
7.183
7.172
7.148
7.144
7.114
7.095
7.084
7.075
7.063
7.042
5.888
5.498
5.484
4.427
4.422
4.412
4.131
4.111
3.232
3.214
3.196
2.376
2.361
1.181
1.164
1.056
1.039
NHTs
S
Me
1H NMR 400 MHz CDCl3 (dr = 2:1)
4i
1.37
0.65
0.74
10.36
0.34
0.69
0.69
0.34
0.68
0.35
6.00
2.02
0.95
f1 (ppm)

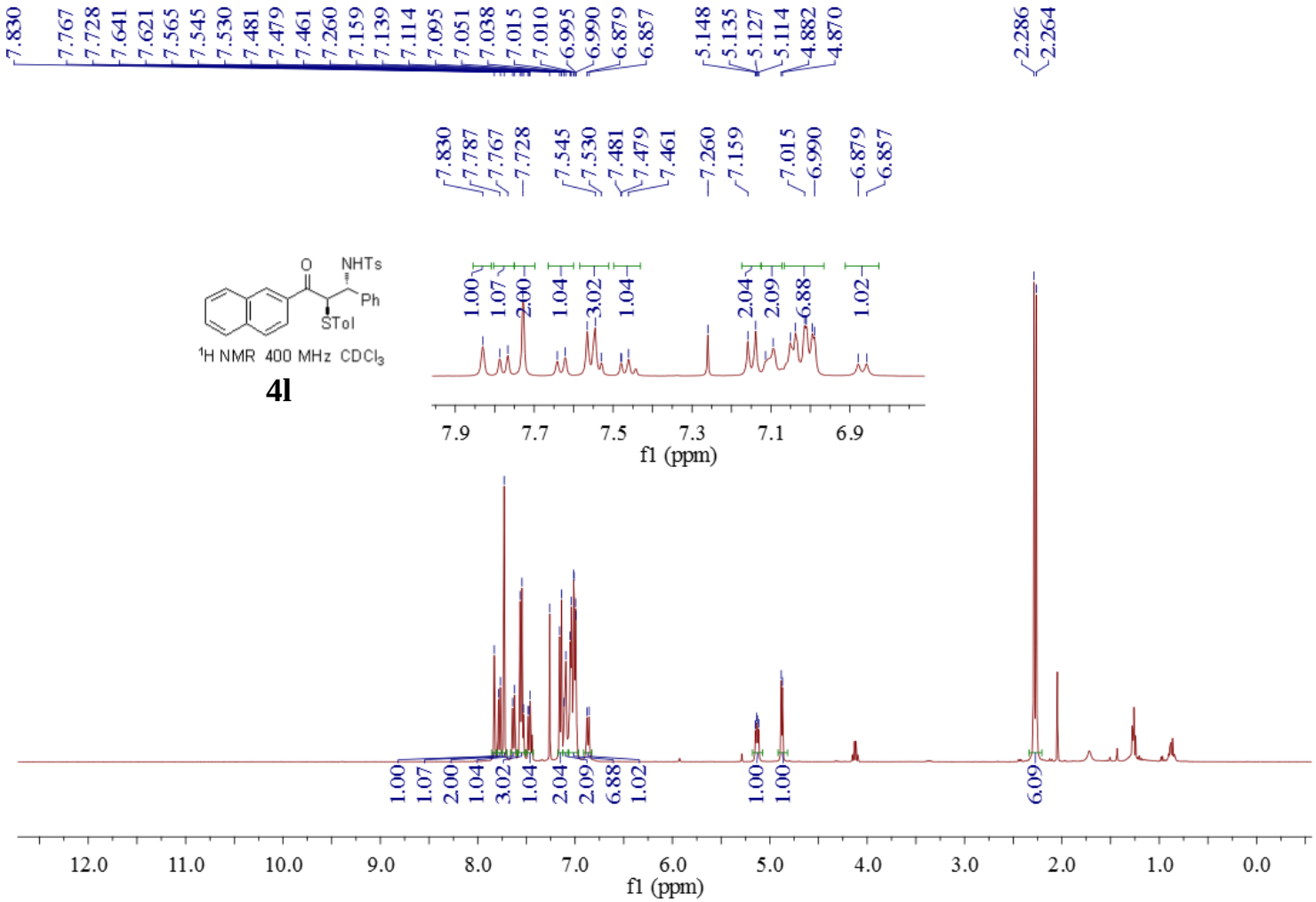

143.046
132.727
129.860
129.238
128.059
127.734
127.545
127.202
77.317
77.000
76.682
61.559
60.217
51.132
49.534
21.445
21.141
21.116
18.409
16.722
NHTs
S
Me
13C NMR 100 MHz CDCl3 (dr = 2:1)
4i
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

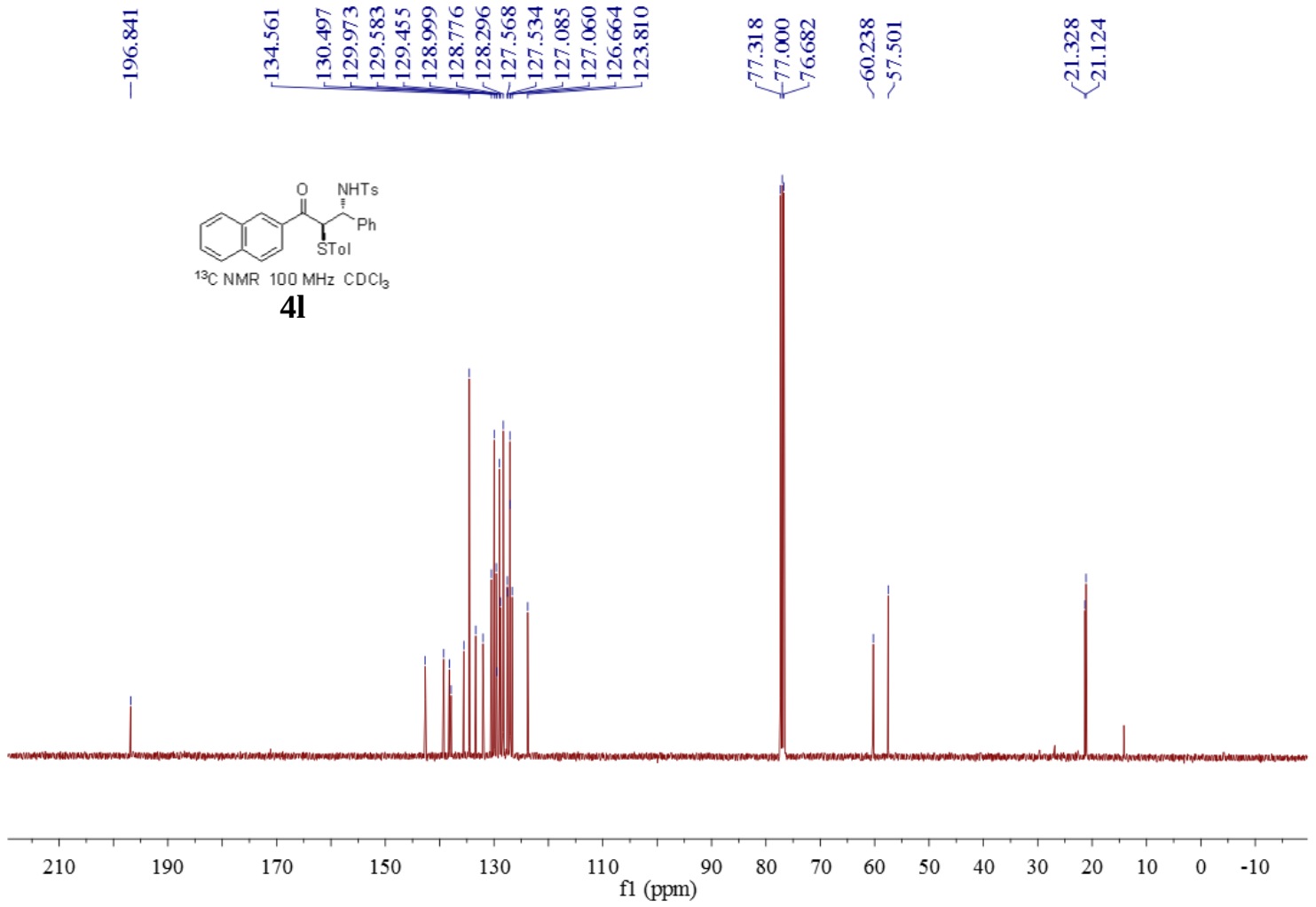

4j
O
NHTs
STol
^{1}H NMR 400 MHz $CDCl_3$
7.587
7.568
7.491
7.473
7.455
7.308
7.289
7.270
7.179
7.159
7.069
6.835
6.816
5.079
5.067
5.060
5.047
4.784
4.771
2.345
2.325
4.00
1.05
2.20
2.08
8.77
1.04
1.00
0.99
6.10
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
7.7
7.5
7.3
7.1
6.9
f1 (ppm)

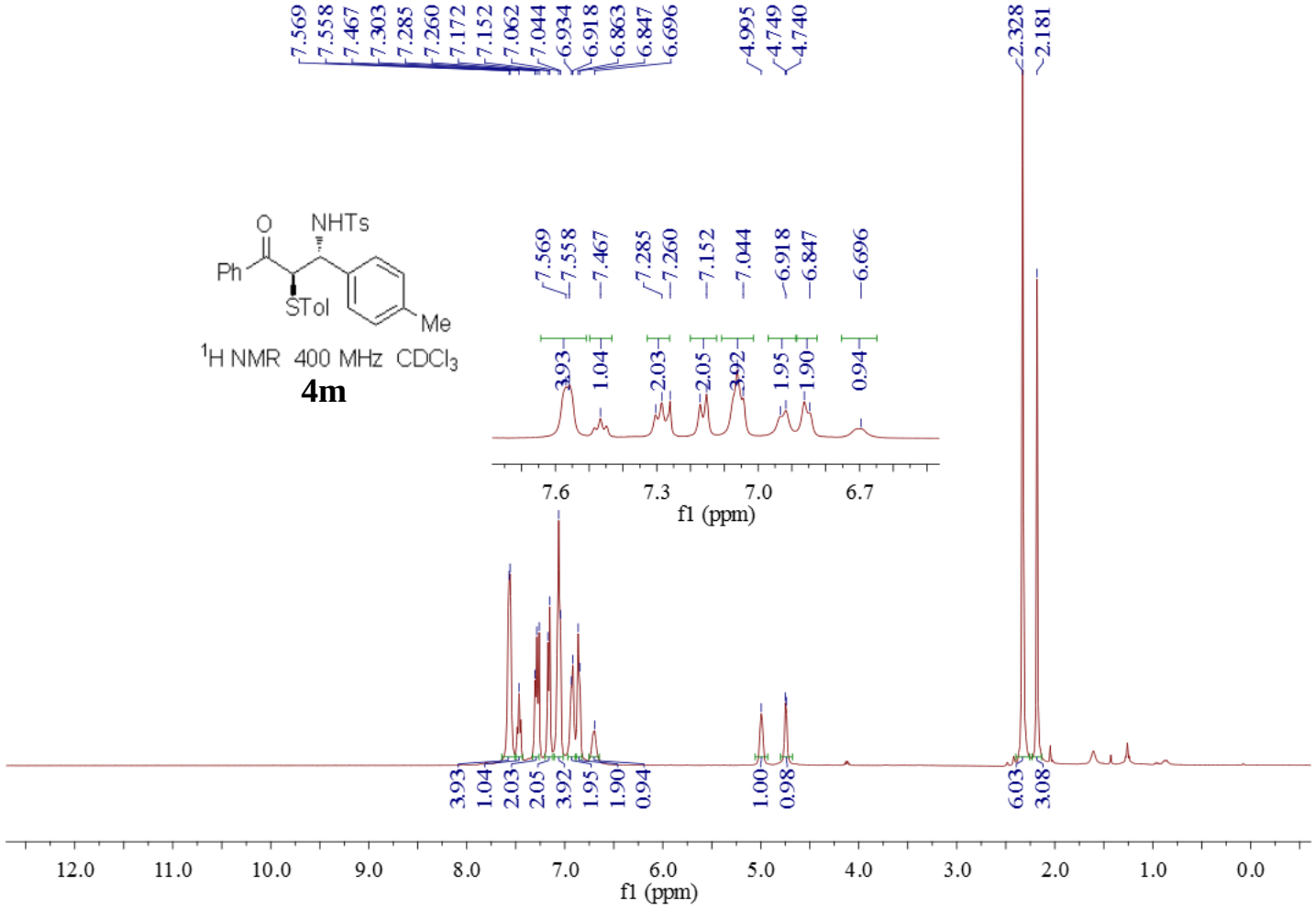

196.993
142.636
138.094
136.000
134.335
133.471
129.937
129.117
128.982
128.387
128.324
128.238
127.469
127.044
126.952
77.318
77.000
76.682
59.948
57.162
21.326
21.135
O
NHTs
STol
13C NMR 100 MHz CDCl3
4j
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

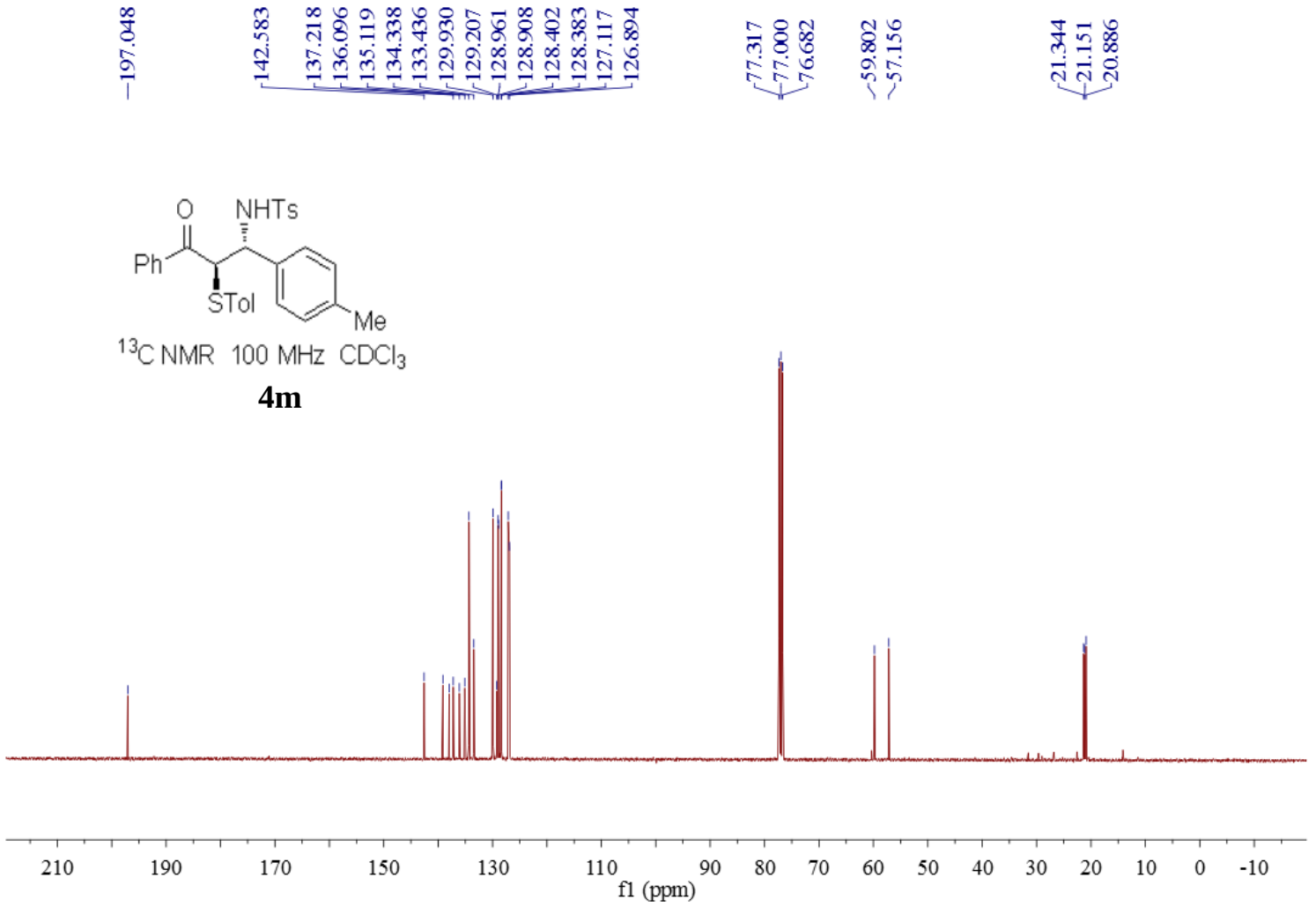

4k
MeO
O
NHTs
Ph
STol
^{1}H NMR 400 MHz $CDCl_3$
7.570
7.546
7.523
7.260
7.193
7.188
7.173
7.072
7.055
7.049
7.029
7.010
6.904
6.885
6.742
6.720
5.007
4.996
4.987
4.975
4.701
4.690
3.787
2.333
2.310
2.01
1.07
4.61
0.50
1.00
0.50
0.51
1.55
3.07
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
7.594
7.570
7.547
7.284
7.212
7.197
7.034
6.909
6.766
6.744
4.01
2.14
9.22
1.01
2.00
7.7
7.4
7.1
6.8
f1 (ppm)

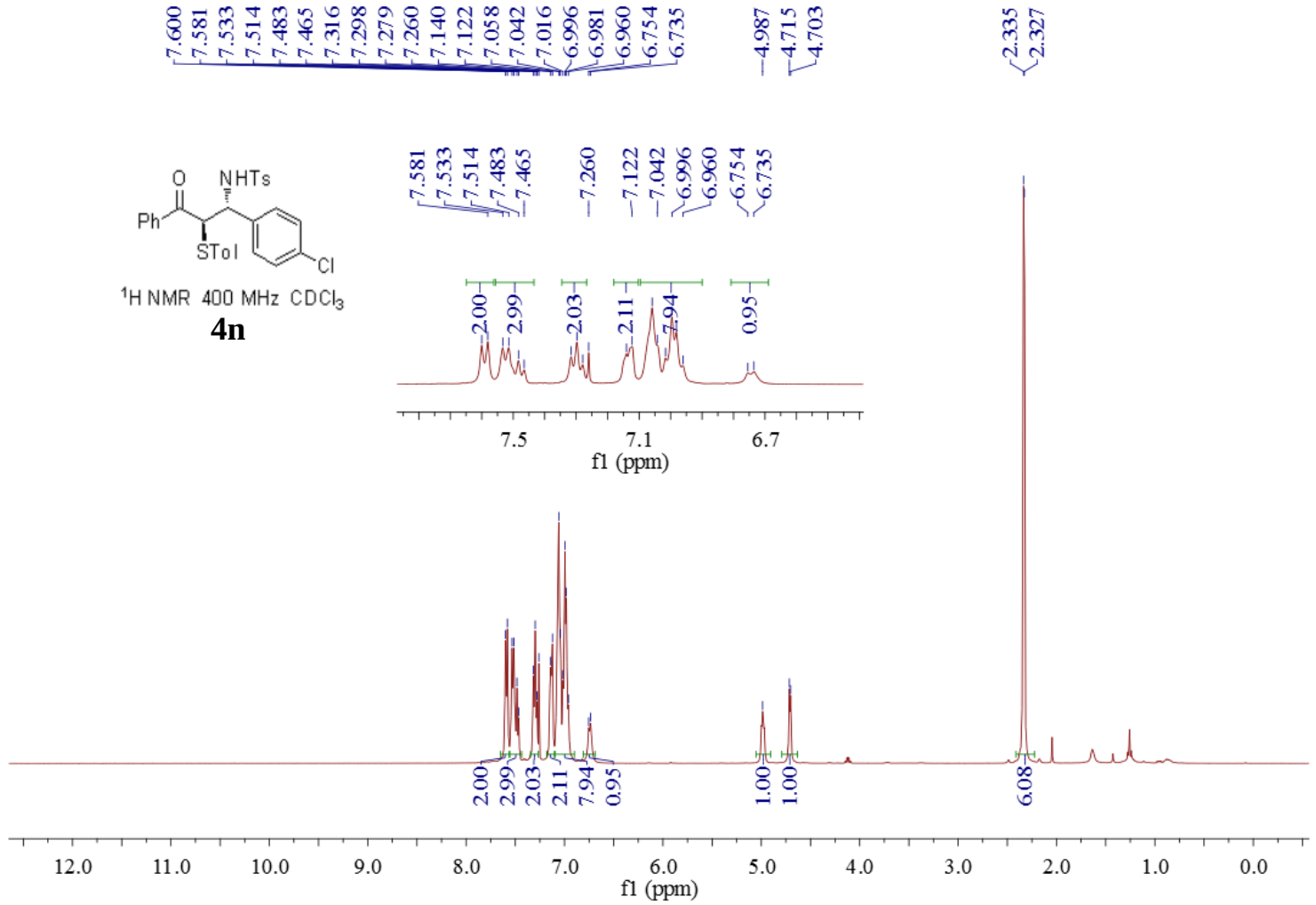

195.658
163.938
139.076
138.045
130.838
129.483
128.893
127.438
126.912
113.659
77.318
77.000
76.682
60.107
56.806
55.441
21.367
21.187
O
NHTs
Ph
STol
MeO
13C NMR 100 MHz CDCl3
4k
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

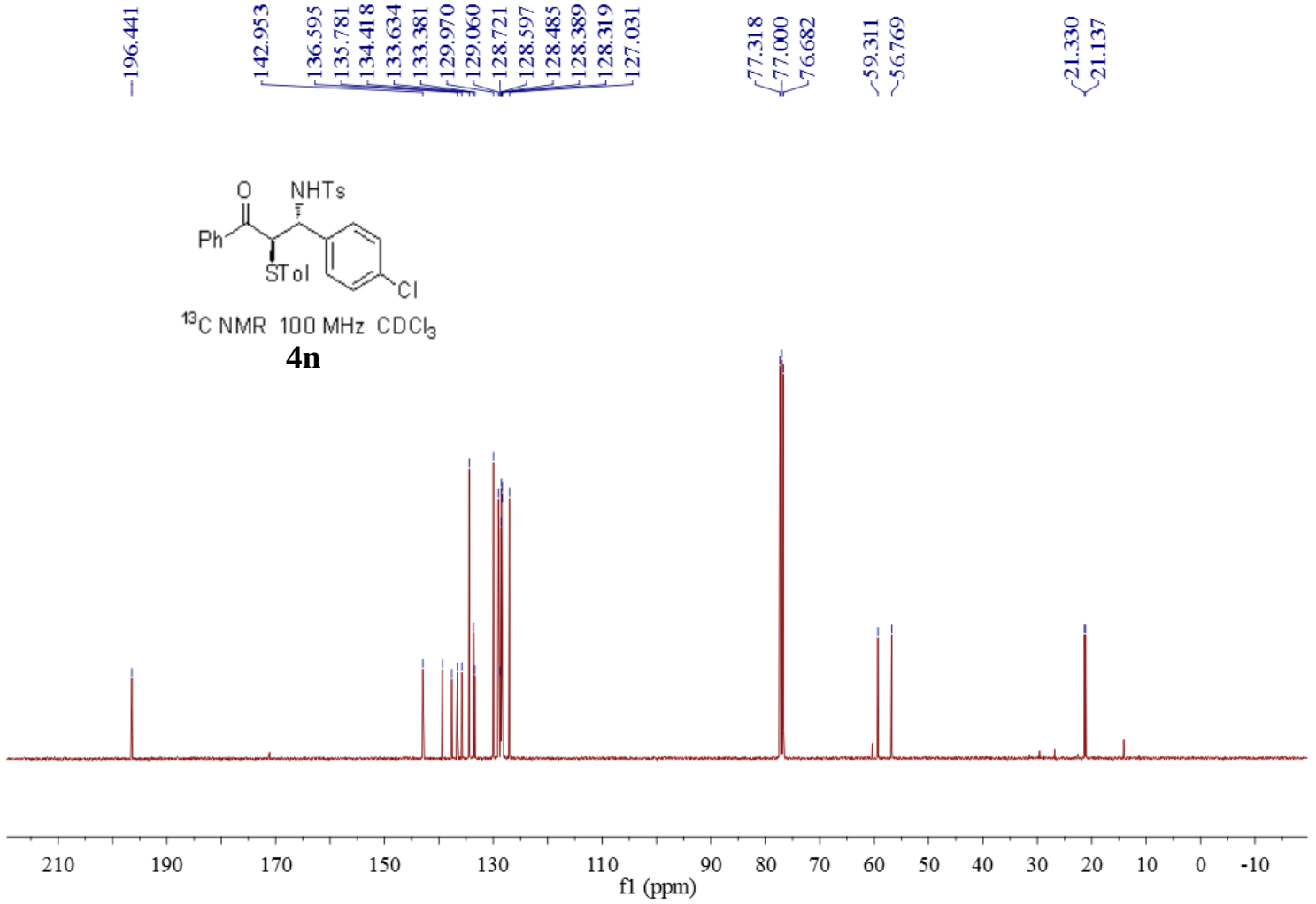

7.830
7.767
7.728
7.641
7.621
7.565
7.545
7.530
7.481
7.479
7.461
7.260
7.159
7.139
7.114
7.095
7.051
7.038
7.015
7.010
6.995
6.990
6.879
6.857
5.148
5.135
5.127
5.114
4.882
4.870
2.286
2.264
O
NHTs
Ph
STol
1H NMR 400 MHz CDCl3
4l
1.00
1.07
2.00
1.04
3.02
1.04
2.04
2.09
6.88
1.02
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
1.00
1.07
2.00
1.04
3.02
1.04
2.04
2.09
6.88
1.02
1.00
1.00
6.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

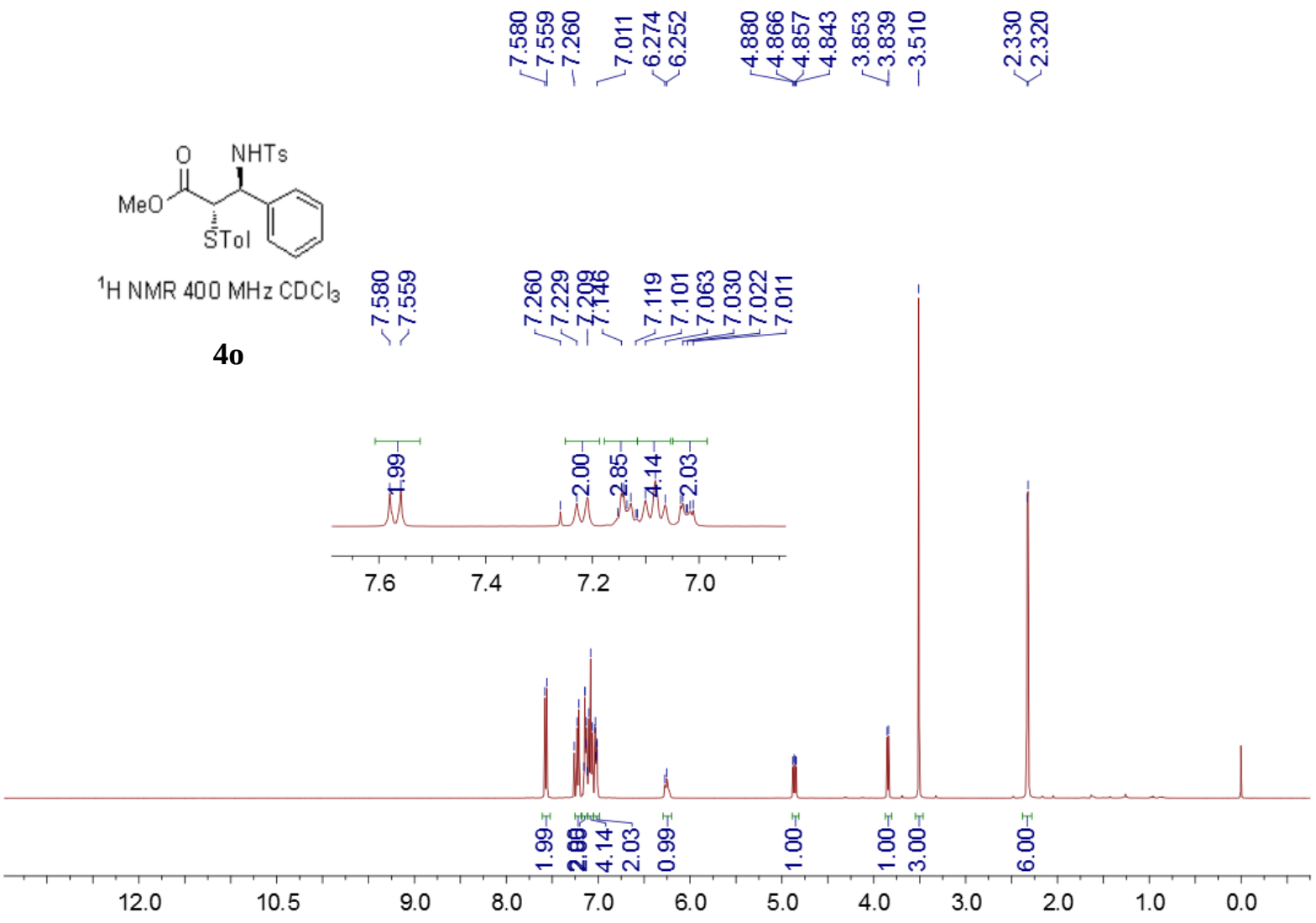

196.841
134.561
130.497
129.973
129.583
129.455
128.999
128.776
128.296
127.568
127.534
127.085
127.060
126.664
123.810
77.318
77.000
76.682
60.238
57.501
21.328
21.124
O
NHTs
Ph
STol
13C NMR 100 MHz CDCl3
4l
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

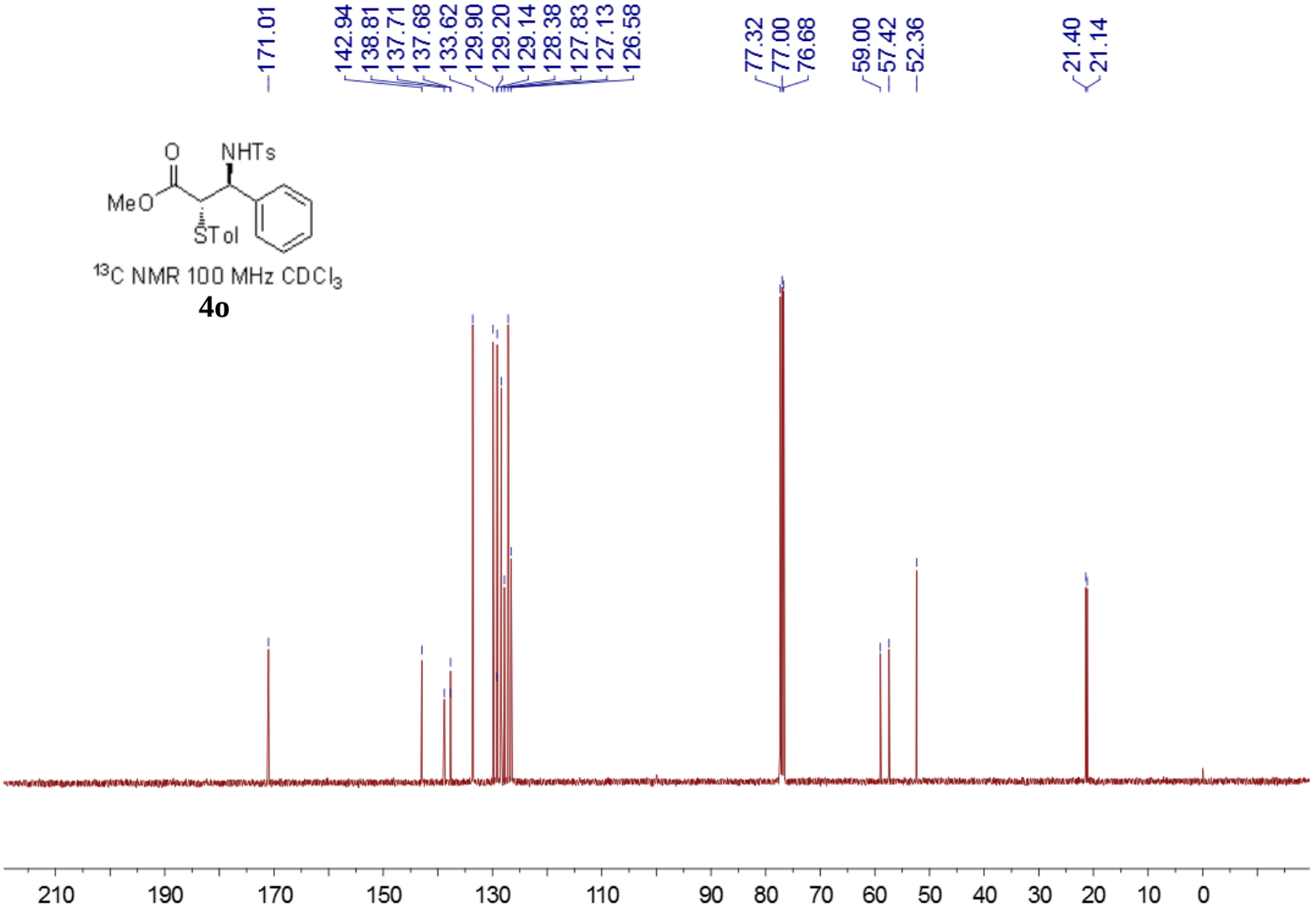

7.569
7.558
7.467
7.303
7.285
7.260
7.172
7.152
7.062
7.044
6.934
6.918
6.863
6.847
6.696
4.995
4.749
4.740
2.328
2.181
O
NHTs
Ph
STol
Me
1H NMR 400 MHz CDCl3
4m
3.93
1.04
2.03
2.05
3.92
1.95
1.90
0.94
1.00
0.98
6.03
3.08
f1 (ppm)


197.048
142.583
137.218
136.096
135.119
134.338
133.436
129.930
129.207
128.961
128.908
128.402
128.383
127.117
126.894
77.317
77.000
76.682
59.802
57.156
21.344
21.151
20.886
O
NHTs
Ph
STol
Me
13C NMR 100 MHz CDCl3
4m
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.600
7.581
7.533
7.514
7.483
7.465
7.316
7.298
7.279
7.260
7.140
7.122
7.058
7.042
7.016
6.996
6.981
6.960
6.754
6.735
4.987
4.715
4.703
2.335
2.327
O
NHTs
Ph
STol
Cl
1H NMR 400 MHz CDCl3
4n
2.00
2.99
2.03
2.11
7.94
0.95
7.5
7.1
6.7
f1 (ppm)
1.00
1.00
6.08
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

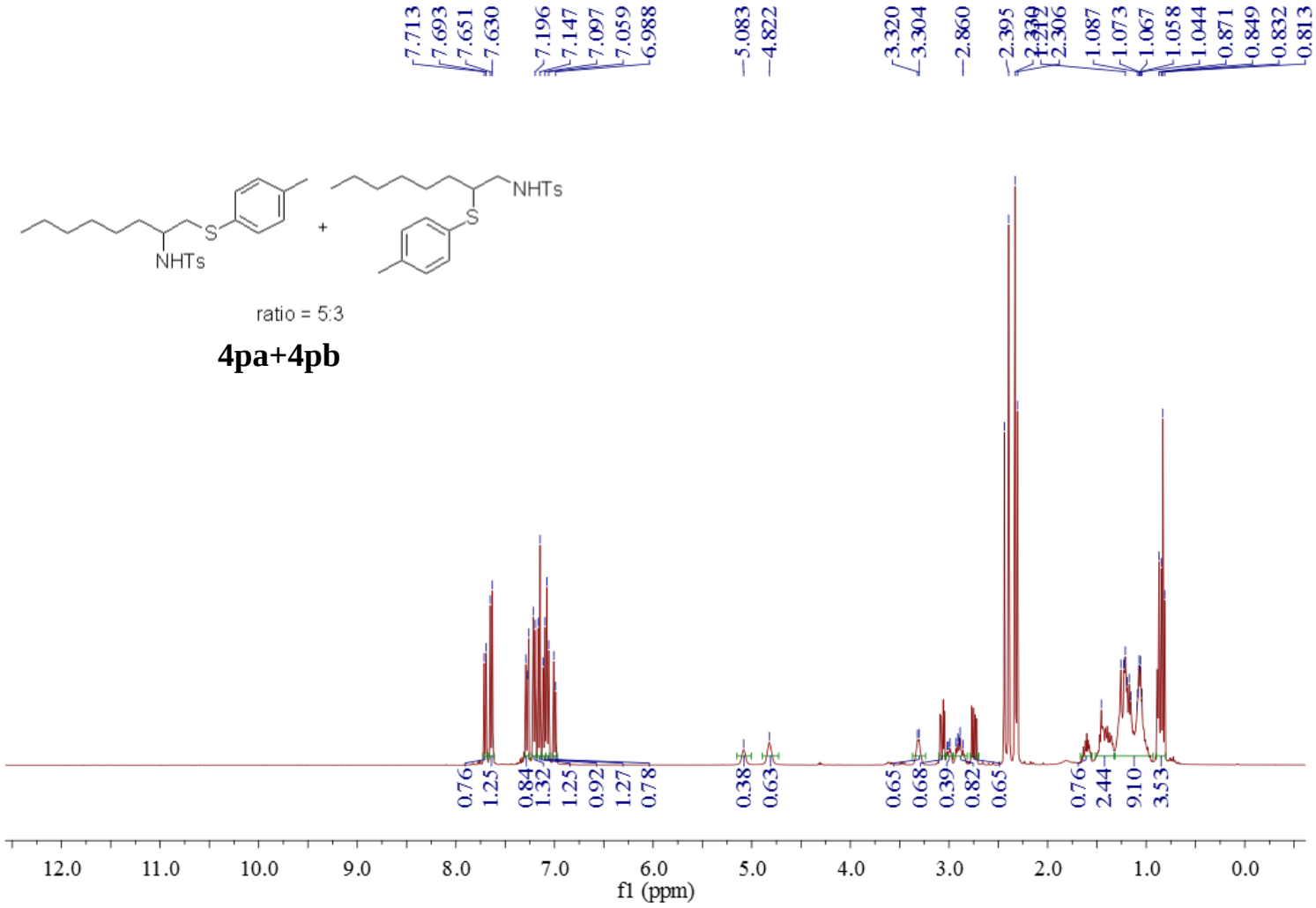

196.441
142.953
136.595
135.781
134.418
133.634
133.381
129.970
129.060
128.721
128.597
128.485
128.389
128.319
127.031
77.318
77.000
76.682
59.311
56.769
21.330
21.137
O
NHTs
Ph
STol
Cl
13C NMR 100 MHz CDCl3
4n
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

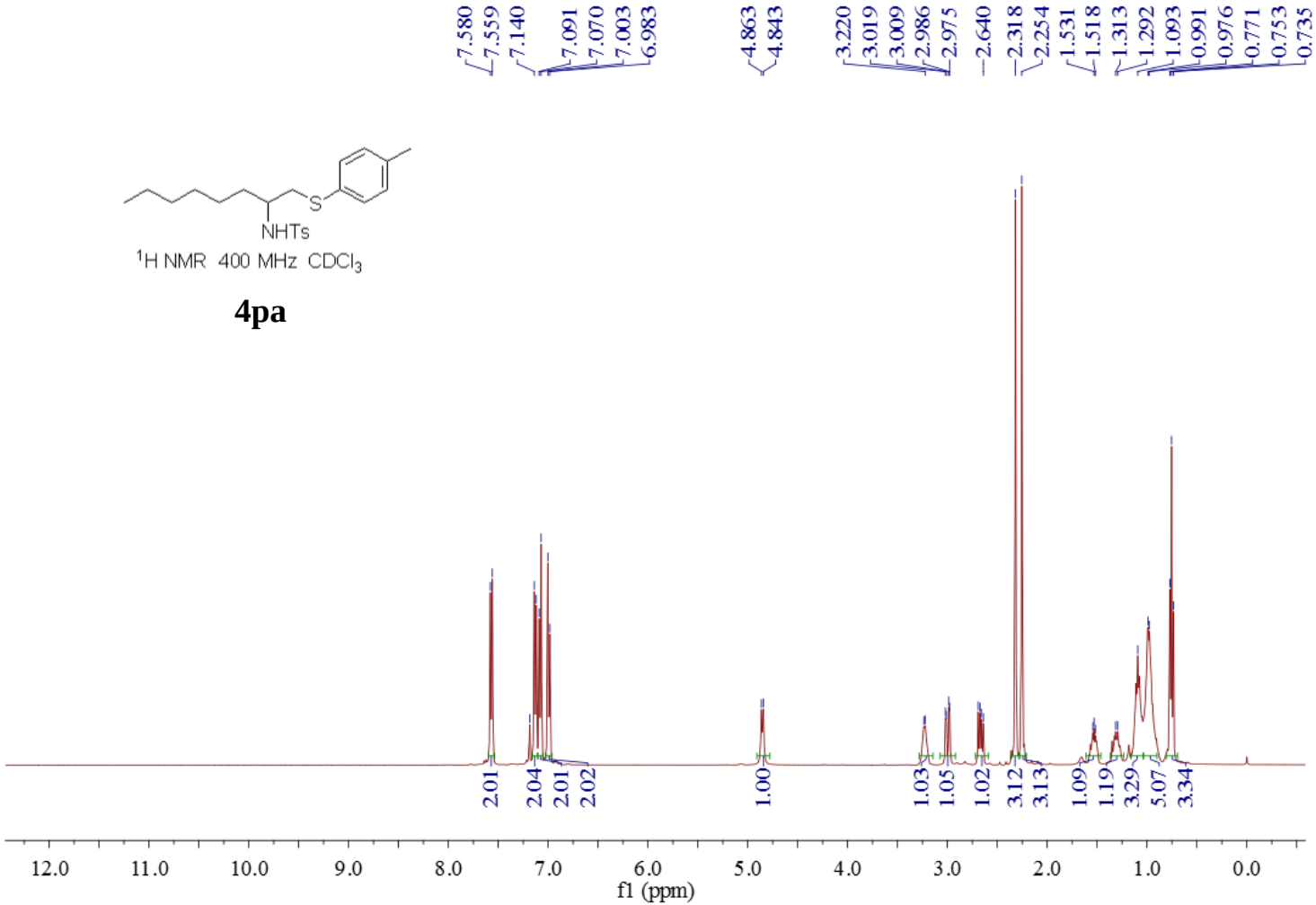

7.580
7.559
7.260
7.011
6.274
6.252
4.880
4.866
4.857
4.843
3.853
3.839
3.510
2.330
2.320
O
NHTs
MeO
STol
^{1}H NMR 400 MHz CDCl$_3$
4o
7.580
7.559
7.260
7.229
7.209
7.146
7.119
7.101
7.063
7.030
7.022
7.011
1.99
2.00
2.85
4.14
2.03
7.6
7.4
7.2
7.0
1.99
4.14
2.03
0.99
1.00
1.00
3.00
6.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0



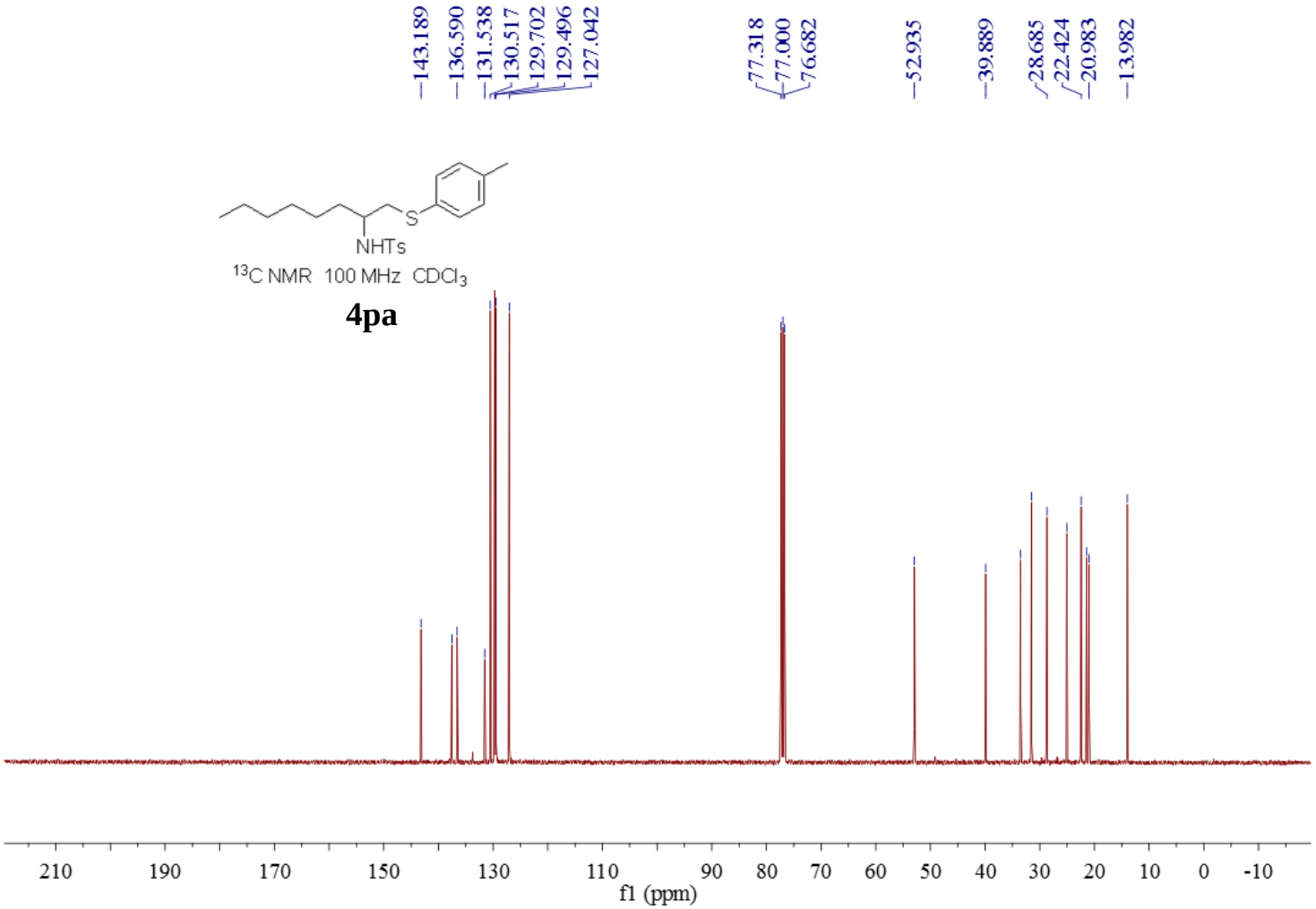
^{13}C NMR 100 MHz $CDCl_3$

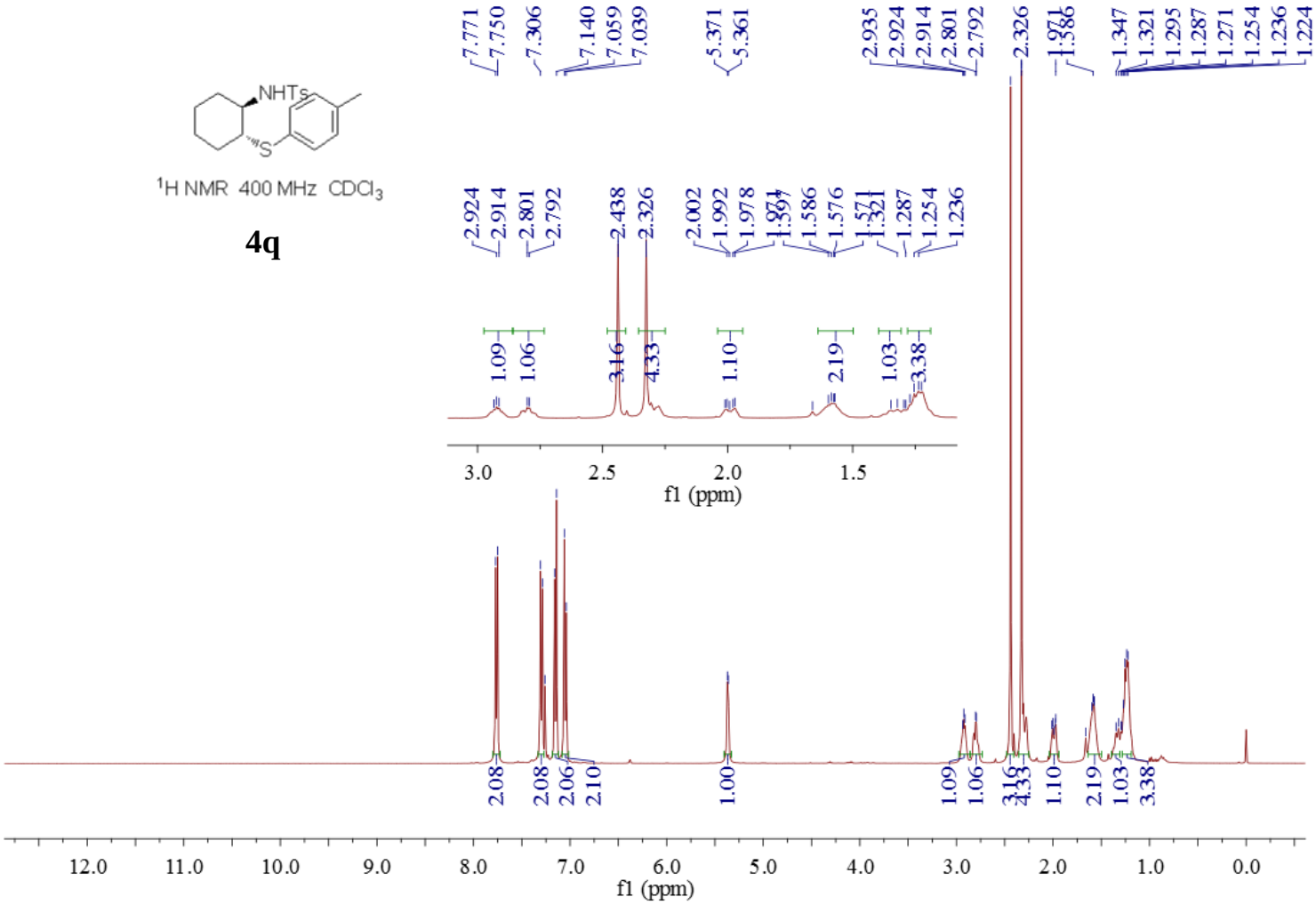
4o

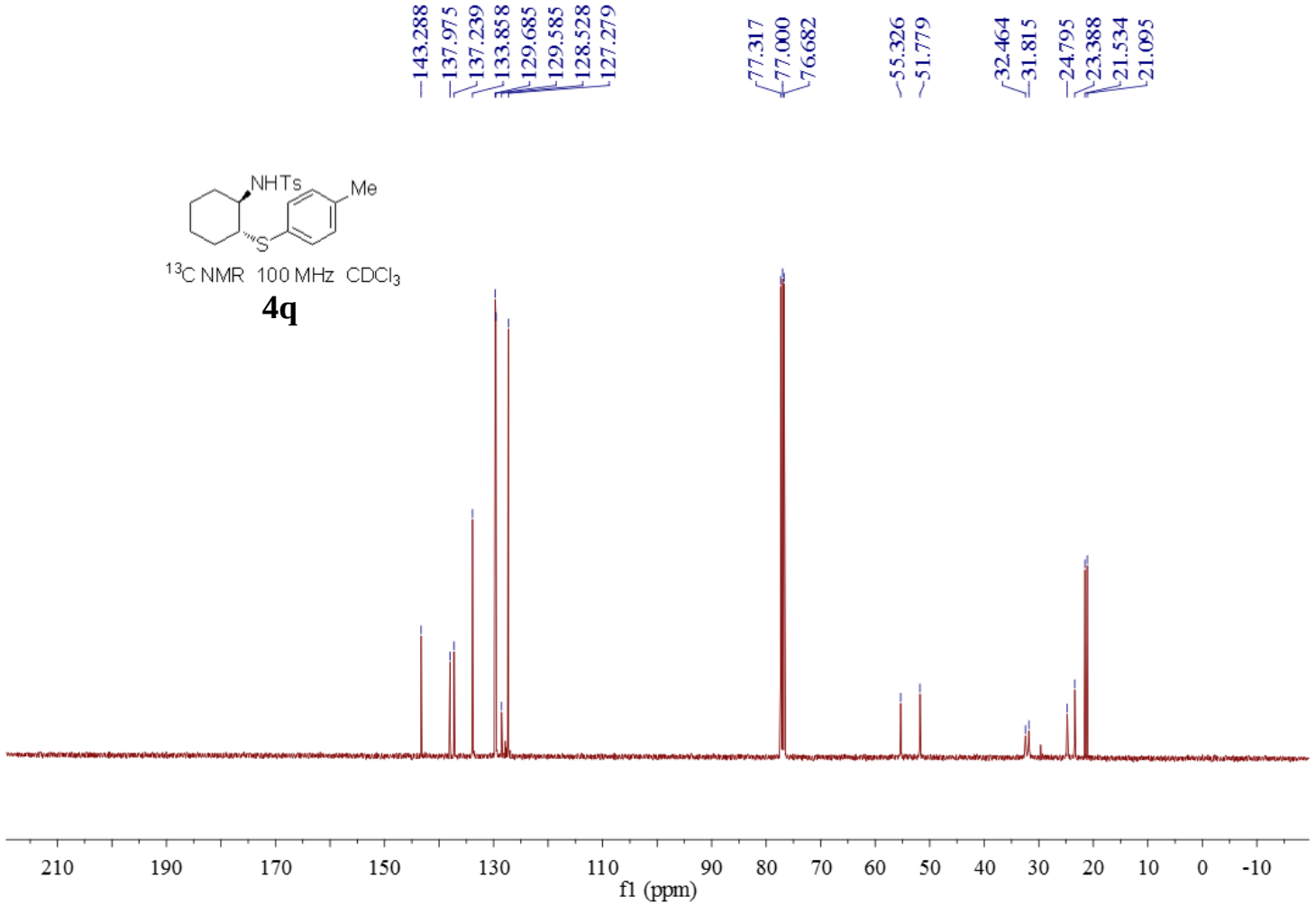

7.713
7.693
7.651
7.630
7.196
7.147
7.097
7.059
6.988
5.083
4.822
3.320
3.304
2.860
2.395
2.306
1.087
1.073
1.067
1.058
1.044
0.871
0.849
0.832
0.813
NHTs
S
NHTs
S
+
ratio = 5:3
4pa+4pb
0.76
1.25
0.84
1.32
1.25
0.92
1.27
0.78
0.38
0.63
0.65
0.68
0.39
0.82
0.65
0.76
2.44
9.10
3.53
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

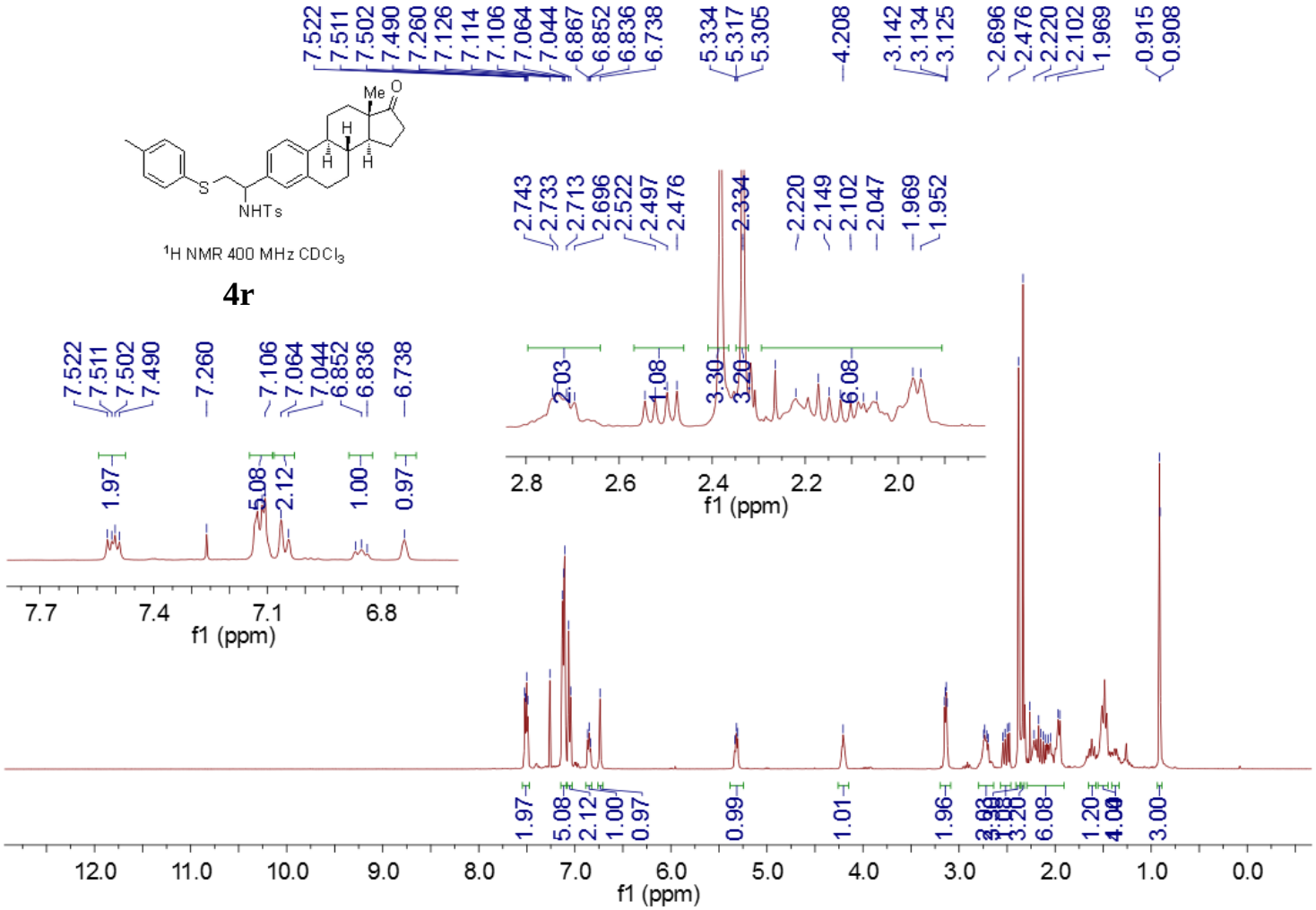

7.580
7.559
7.140
7.091
7.070
7.003
6.983
4.863
4.843
3.220
3.019
3.009
2.986
2.975
2.640
2.318
2.254
1.531
1.518
1.313
1.292
1.093
0.991
0.976
0.771
0.753
0.735
S
NHTs
1H NMR 400 MHz CDCl3
2.01
2.04
2.01
2.02
1.00
1.03
1.05
1.02
3.12
3.13
1.09
1.19
3.29
5.07
3.34
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

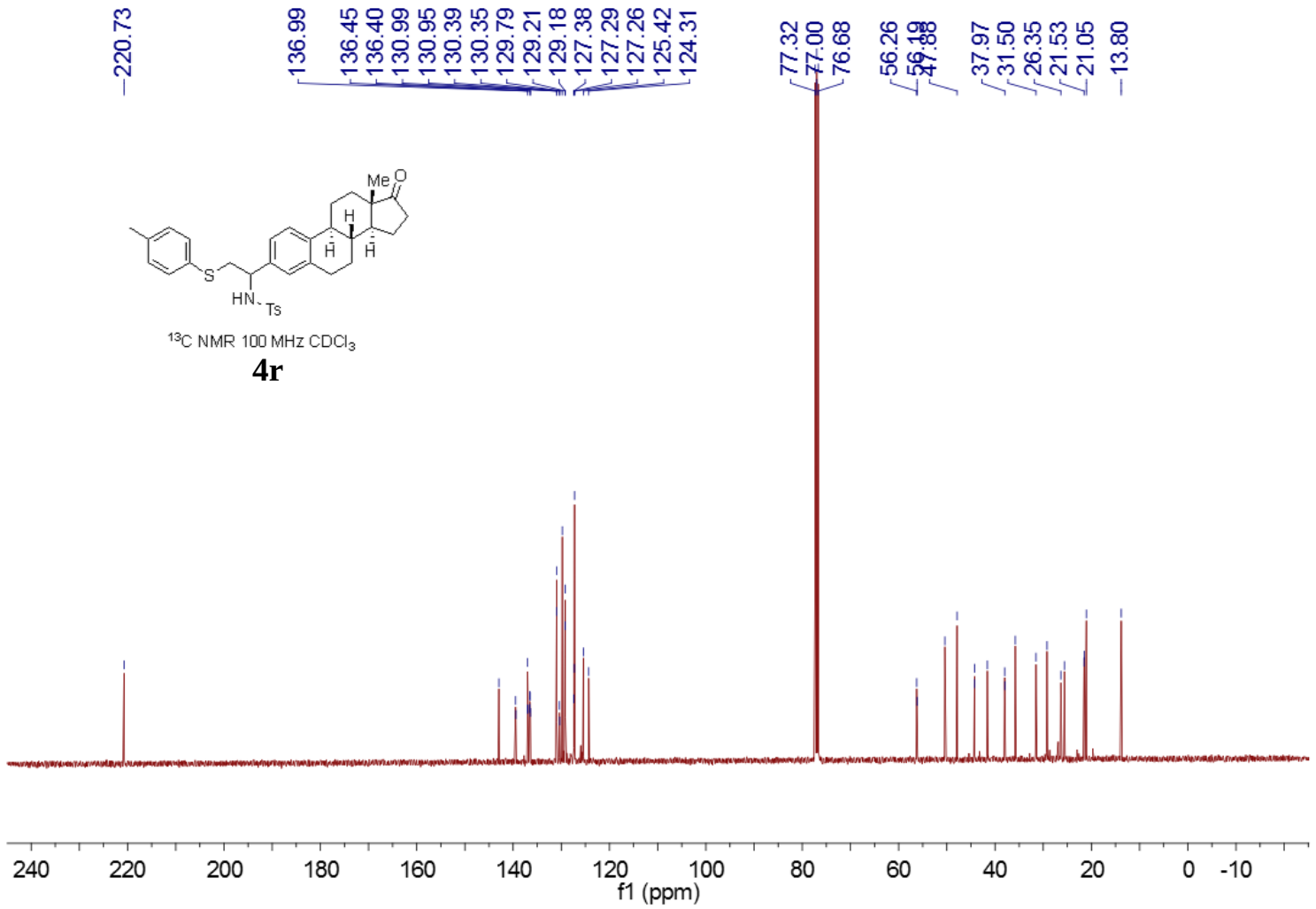
4pa


143.189
136.590
131.538
130.517
129.702
129.496
127.042
77.318
77.000
76.682
52.935
39.889
28.685
22.424
20.983
13.982
S
NHTs
13C NMR 100 MHz CDCl3
4pa
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


NHTs
S
^{1}H NMR 400 MHz $CDCl_3$
4q
f1 (ppm)

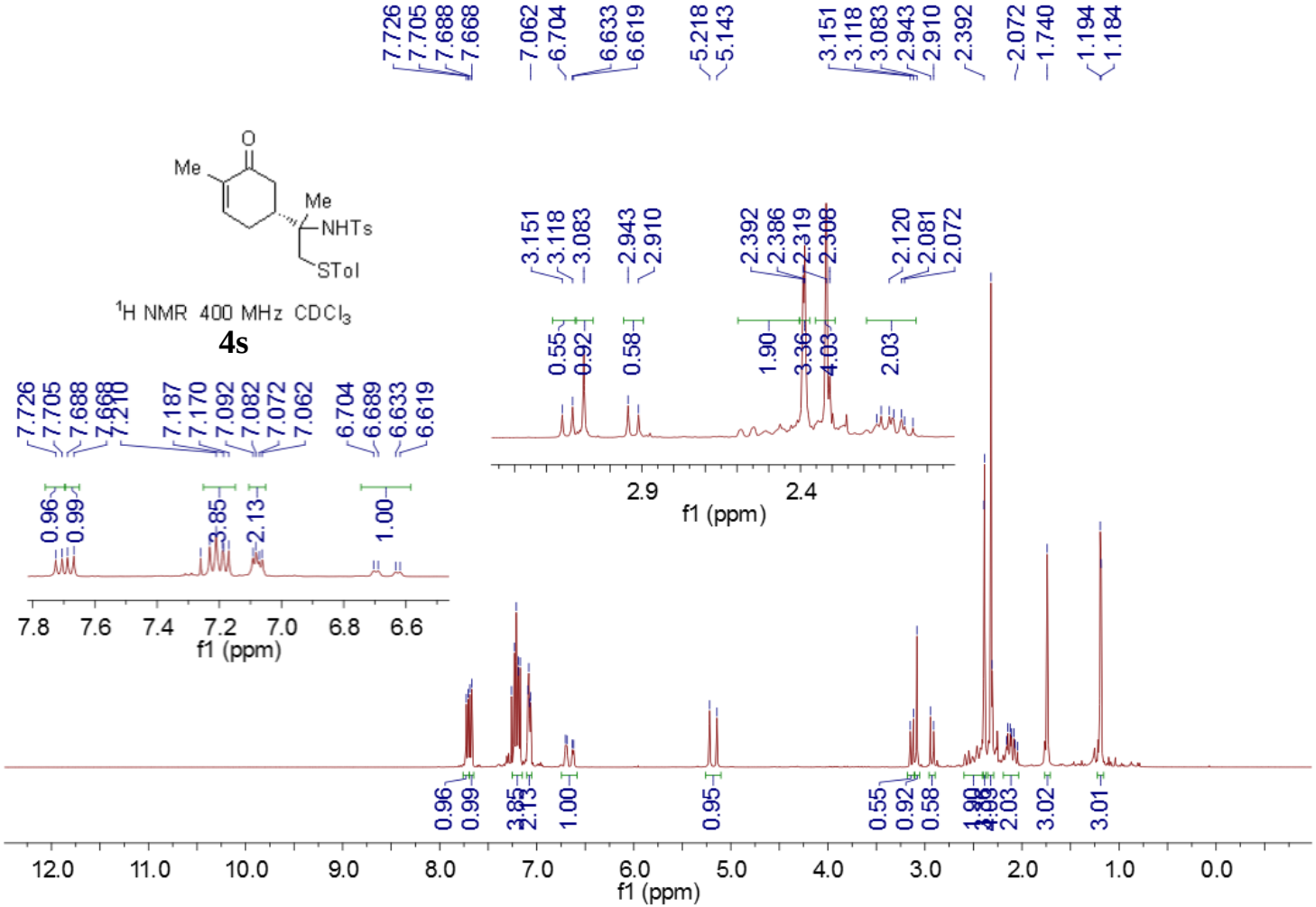

143.288
137.975
137.239
133.858
129.685
129.585
128.528
127.279
77.317
77.000
76.682
55.326
51.779
32.464
31.815
24.795
23.388
21.534
21.095
NHTs
Me
S
13C NMR 100 MHz CDCl3
4q
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

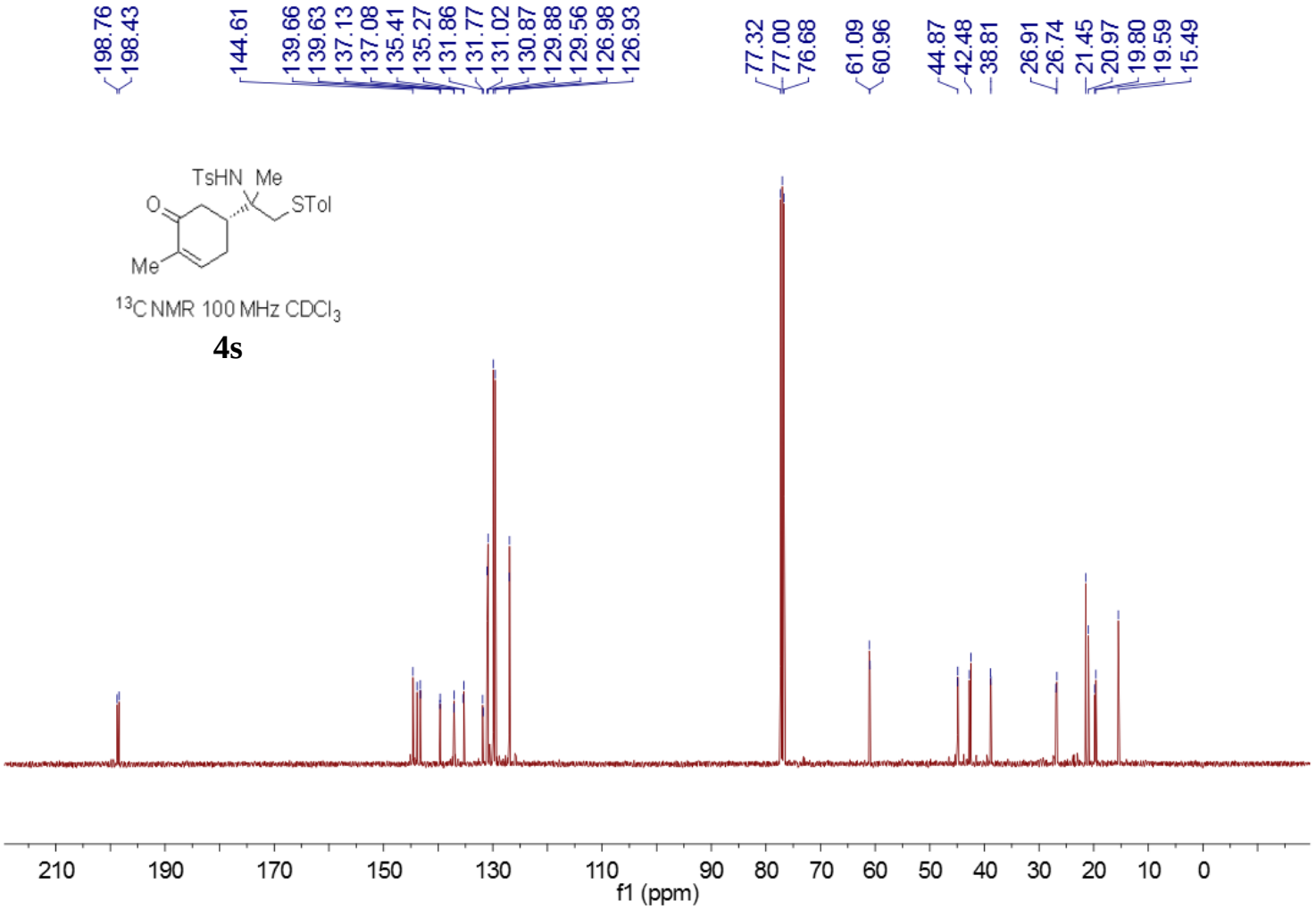

Me
O
H
H
H
S
NHTs
1H NMR 400 MHz CDCl3
4r
7.522
7.511
7.502
7.490
7.260
7.126
7.114
7.106
7.064
7.044
6.867
6.852
6.836
6.738
5.334
5.317
5.305
4.208
3.142
3.134
3.125
2.696
2.476
2.220
2.102
1.969
0.915
0.908
2.743
2.733
2.713
2.696
2.522
2.497
2.476
2.334
2.220
2.149
2.102
2.047
1.969
1.952
2.03
1.08
3.30
3.20
6.08
2.8
2.6
2.4
2.2
2.0
f1 (ppm)
1.97
5.08
2.12
1.00
0.97
7.7
7.4
7.1
6.8
f1 (ppm)
1.97
5.08
2.12
1.00
0.97
0.99
1.01
1.96
6.08
1.20
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



^{13}C NMR 100 MHz $CDCl_3$

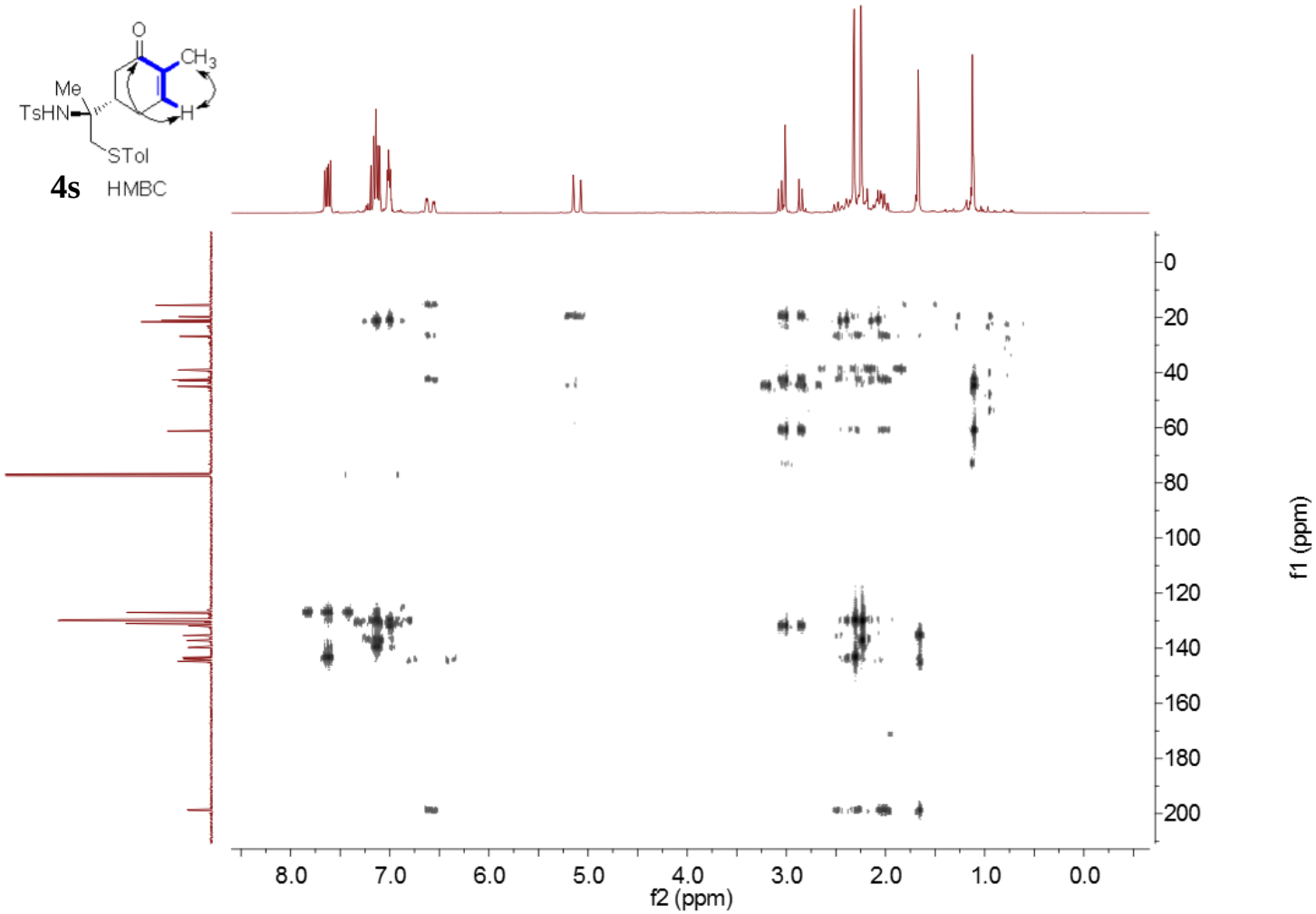
4r

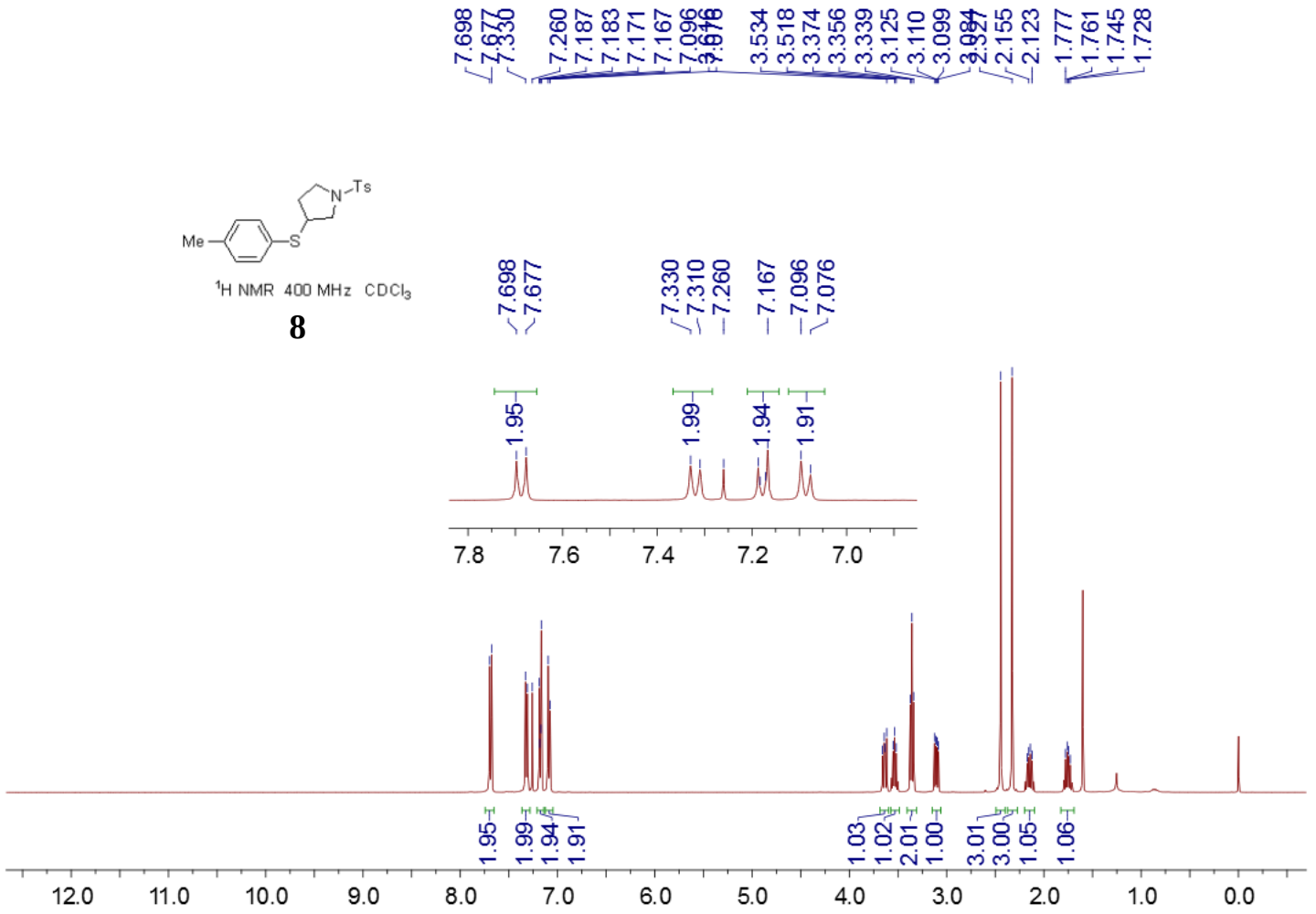

Me
O
Me
NHTs
STol
^{1}H NMR 400 MHz $CDCl_3$
4s
f1 (ppm)

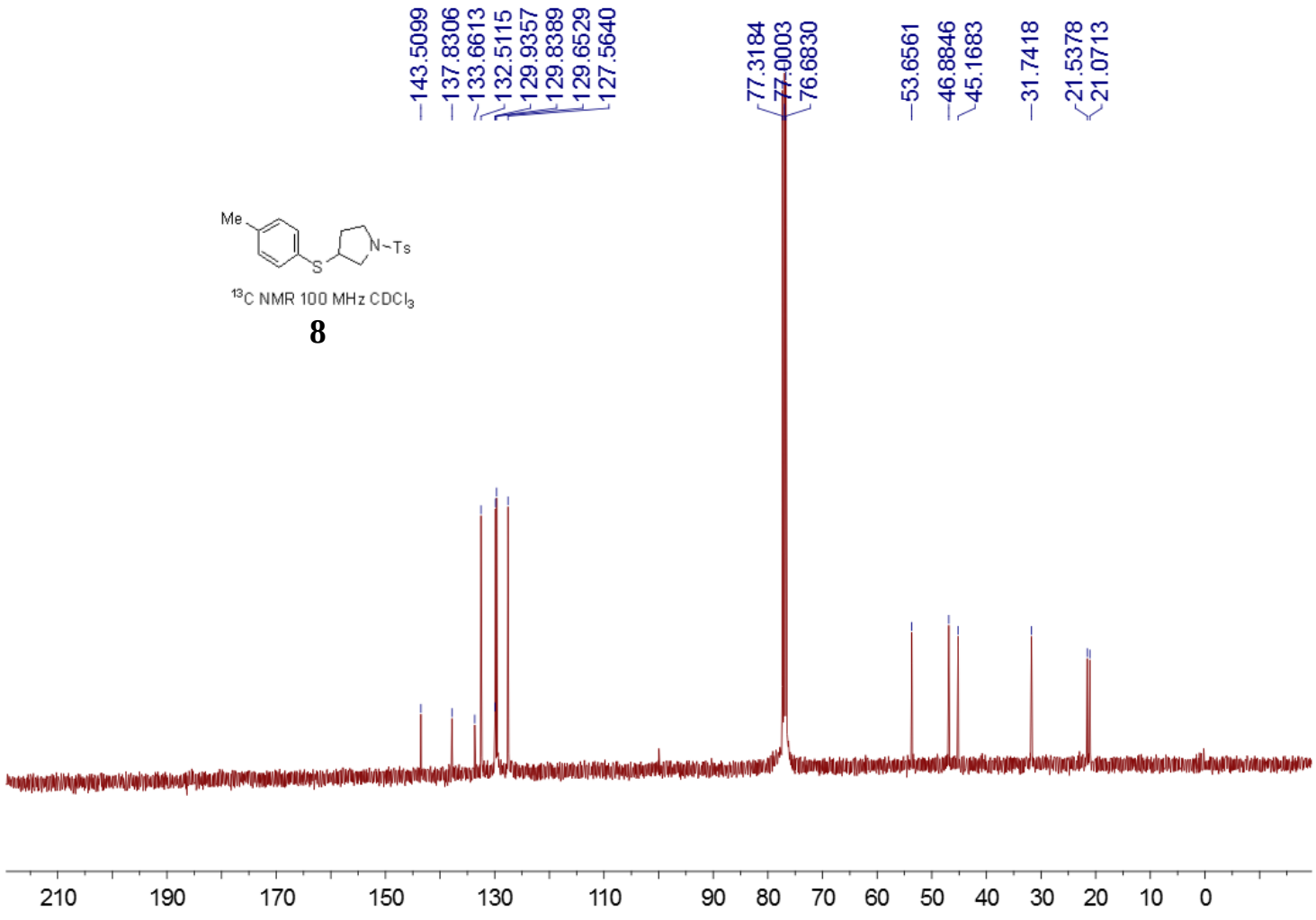


^{13}C NMR 100 MHz $CDCl_3$

4s

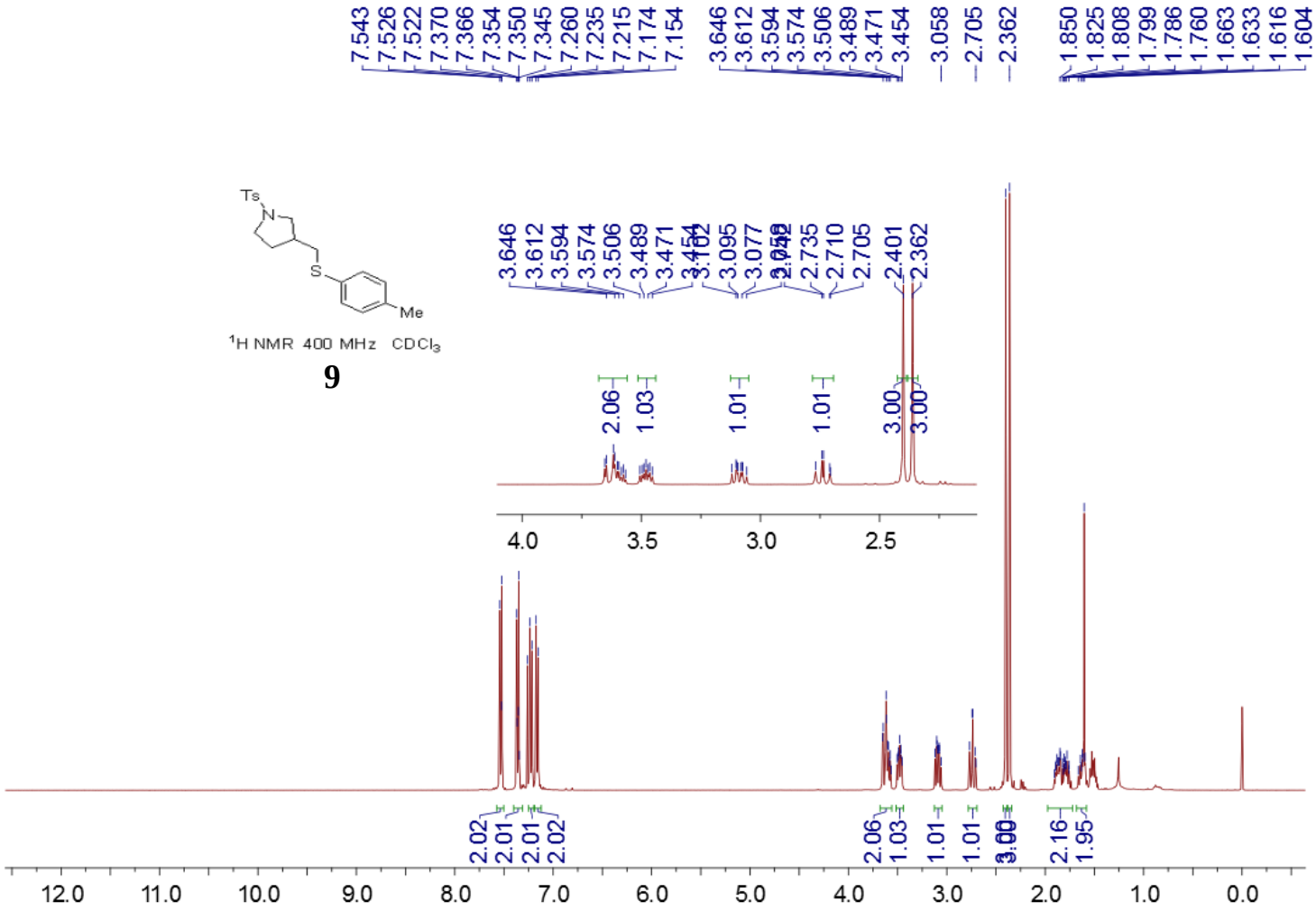

O
CH3
Me
TsHN
H
STol
4s HMBC
0
20
40
60
80
100
120
140
160
180
200
f1 (ppm)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f2 (ppm)

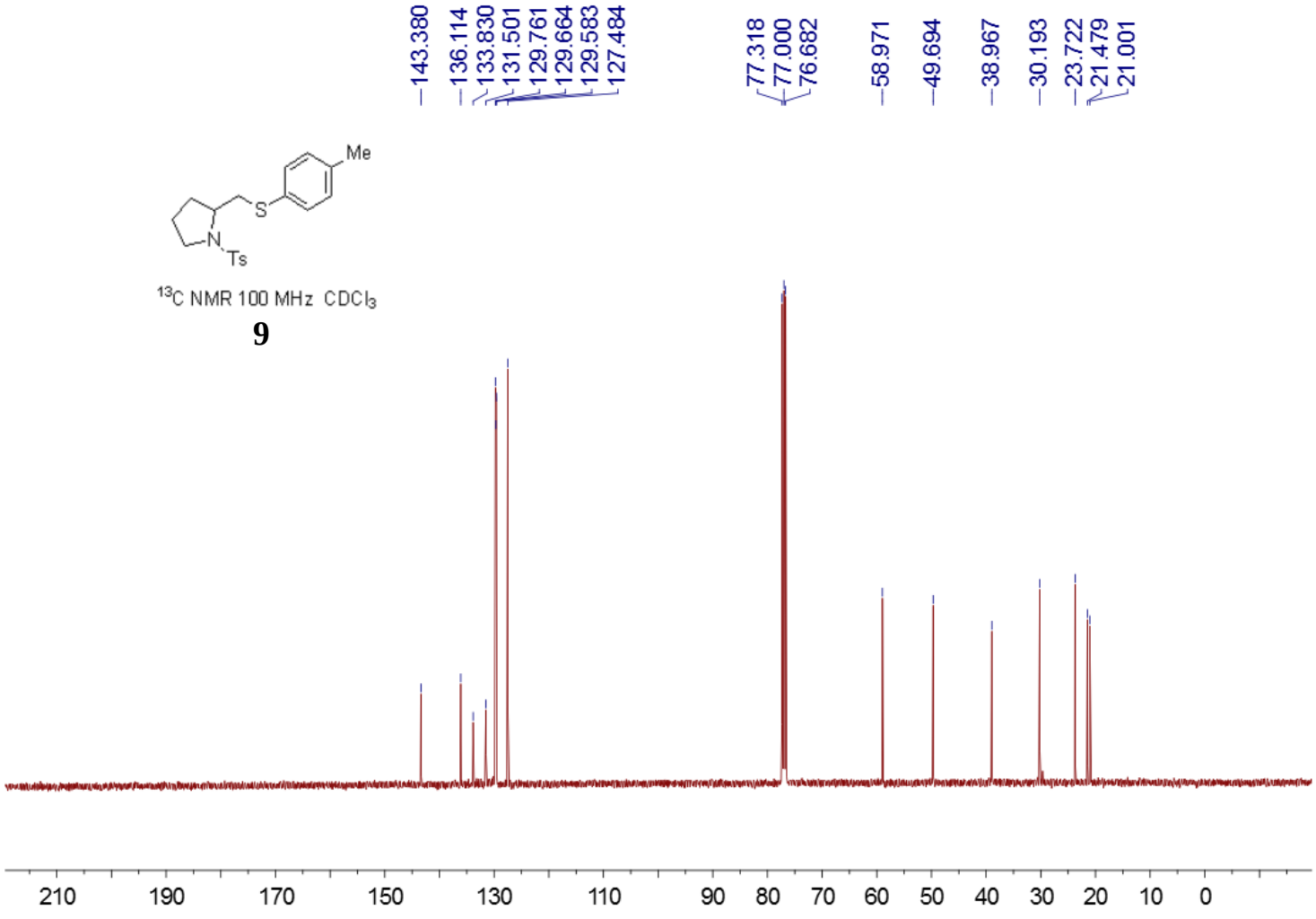

Me
S
N
Ts
^{1}H NMR 400 MHz CDCl$_3$
8
7.698
7.677
7.330
7.310
7.260
7.167
7.096
7.076
1.95
1.99
1.94
1.91
7.8
7.6
7.4
7.2
7.0
1.03
1.02
2.01
1.00
3.01
3.00
1.05
1.06
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

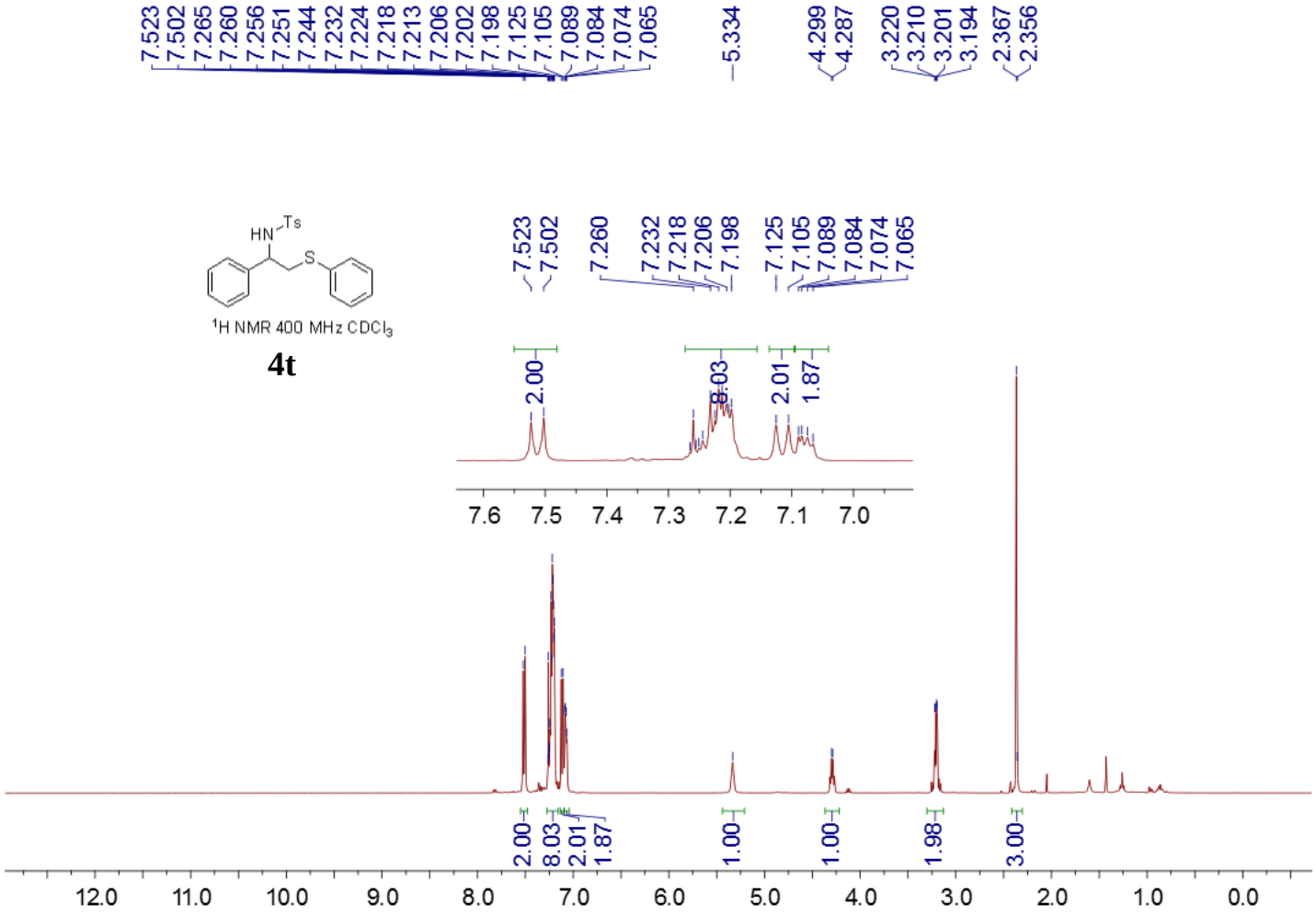


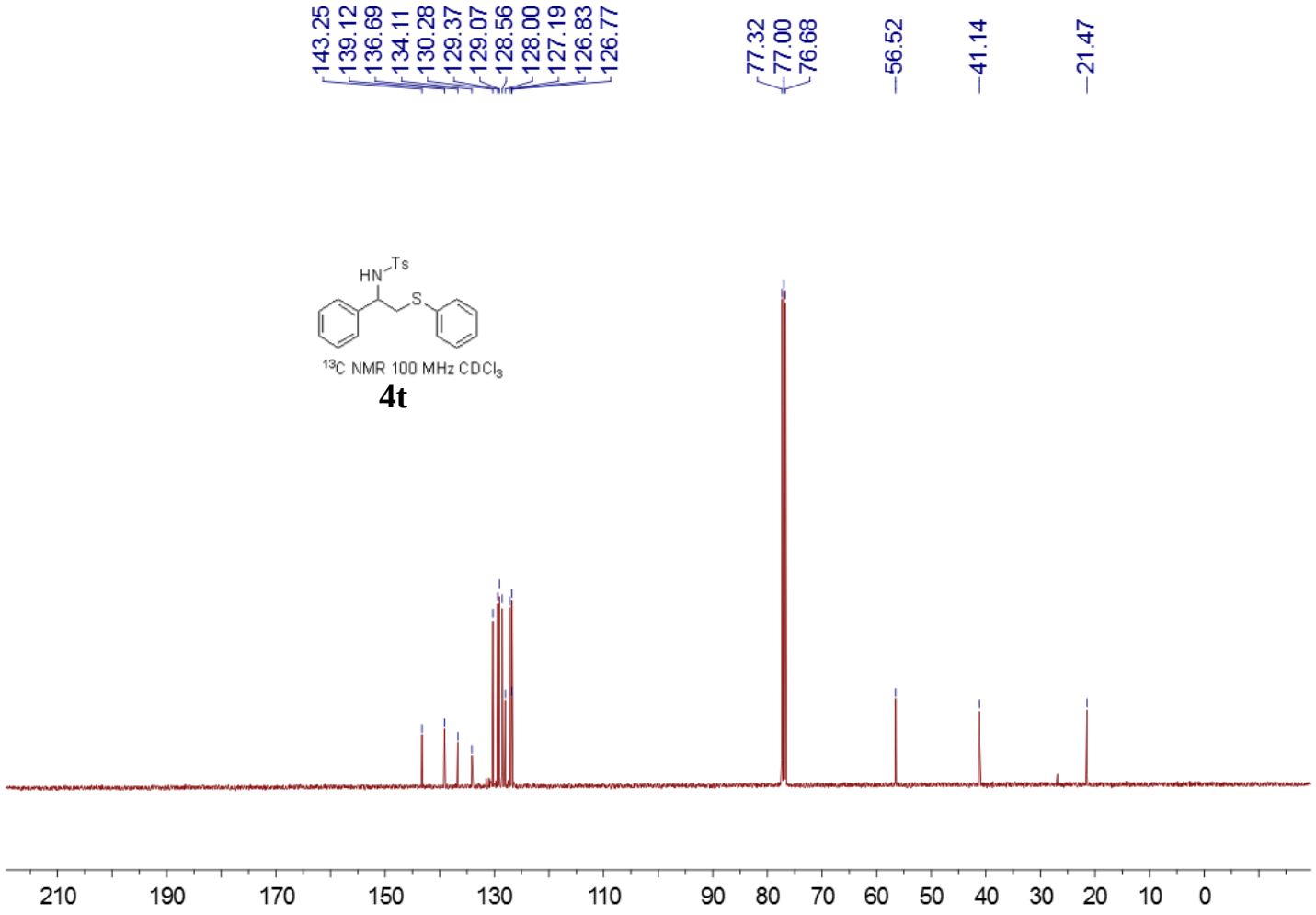
^{13}C NMR 100 MHz $CDCl_3$

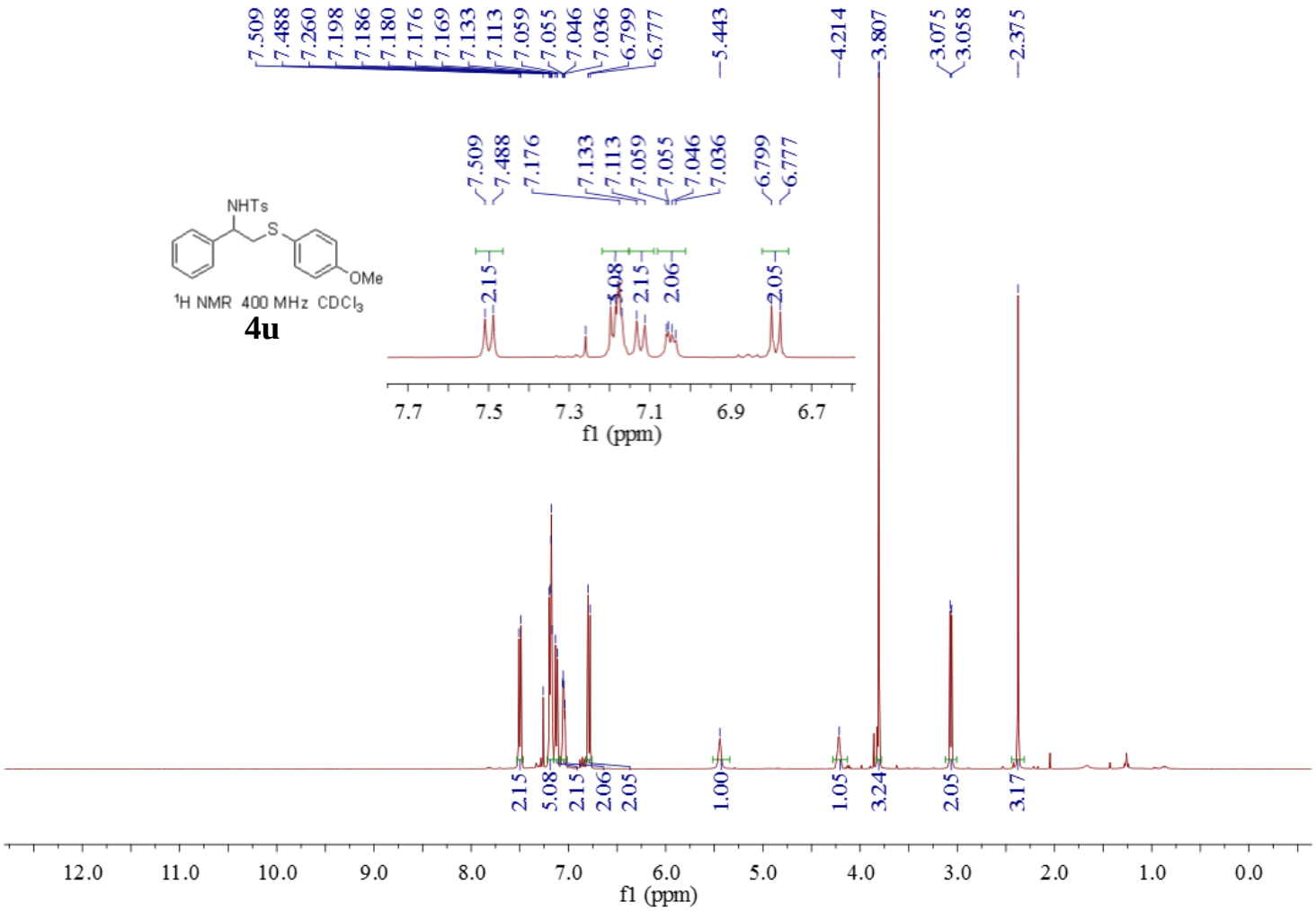
8

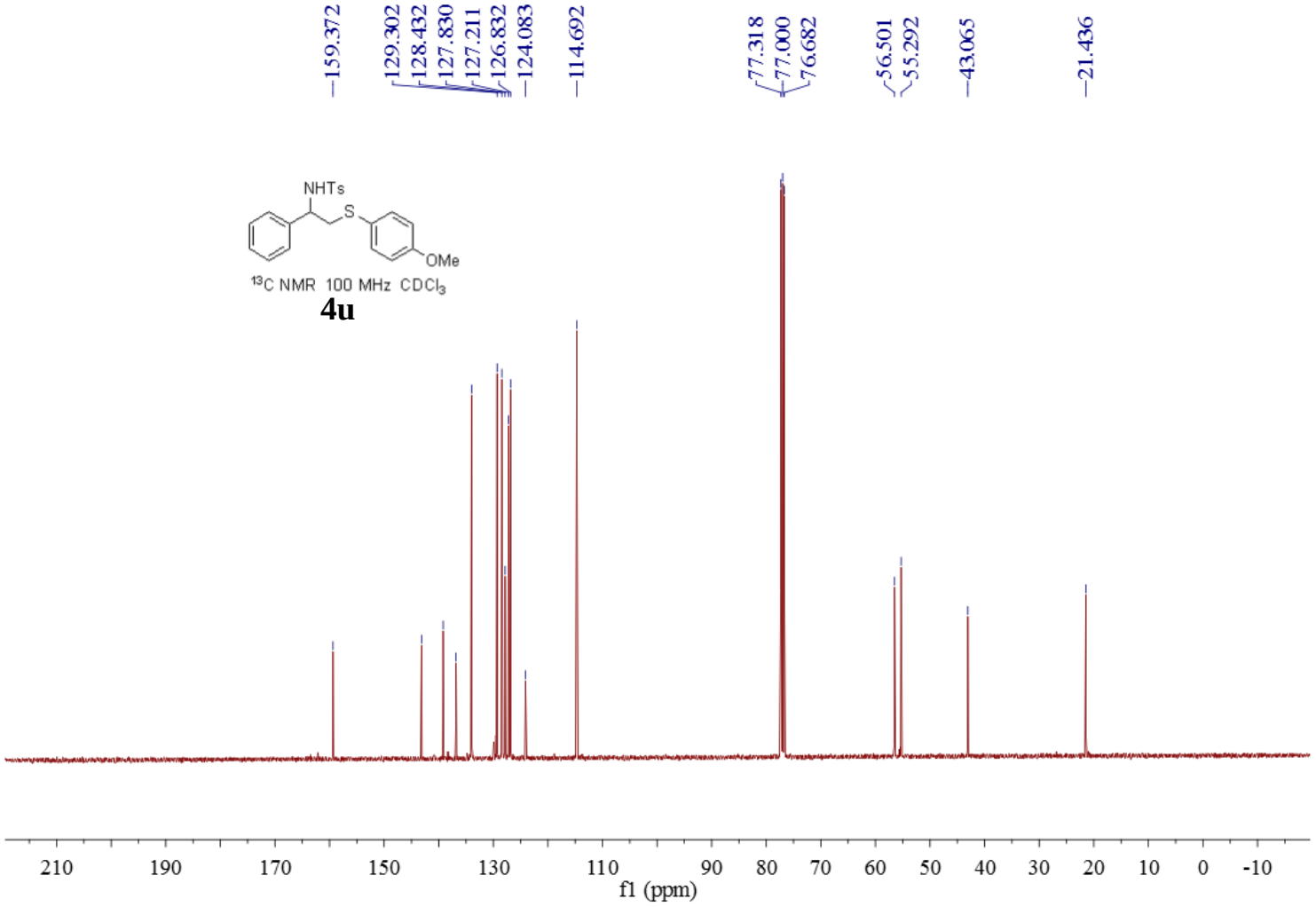

Ts
N
S
Me
^{1}H NMR 400 MHz CDCl$_3$
9

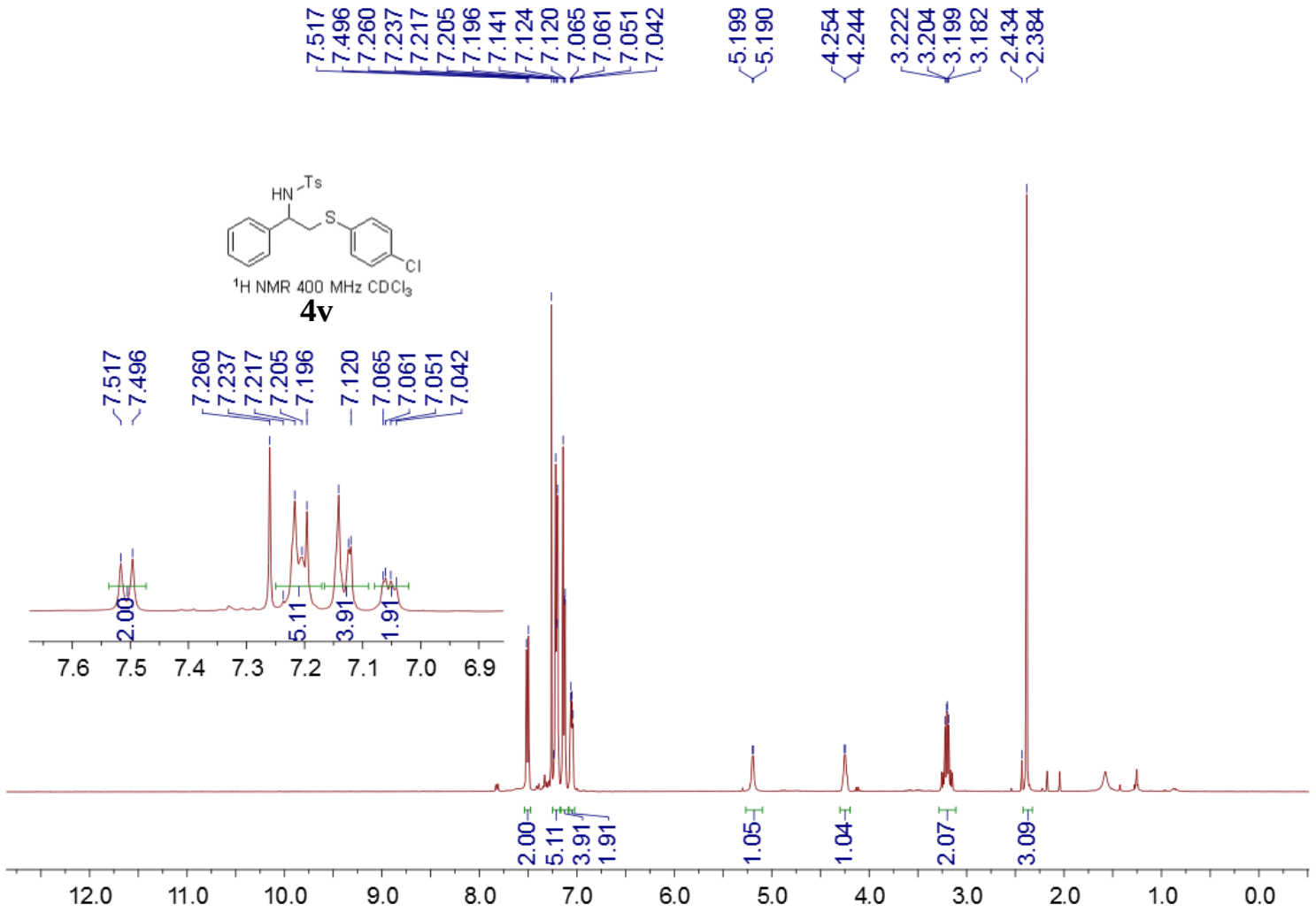

143.380
136.114
133.830
131.501
129.761
129.664
129.583
127.484
77.318
77.000
76.682
58.971
49.694
38.967
30.193
23.722
21.479
21.001
Me
S
N
Ts
^{13}C NMR 100 MHz CDCl$_3$
9
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

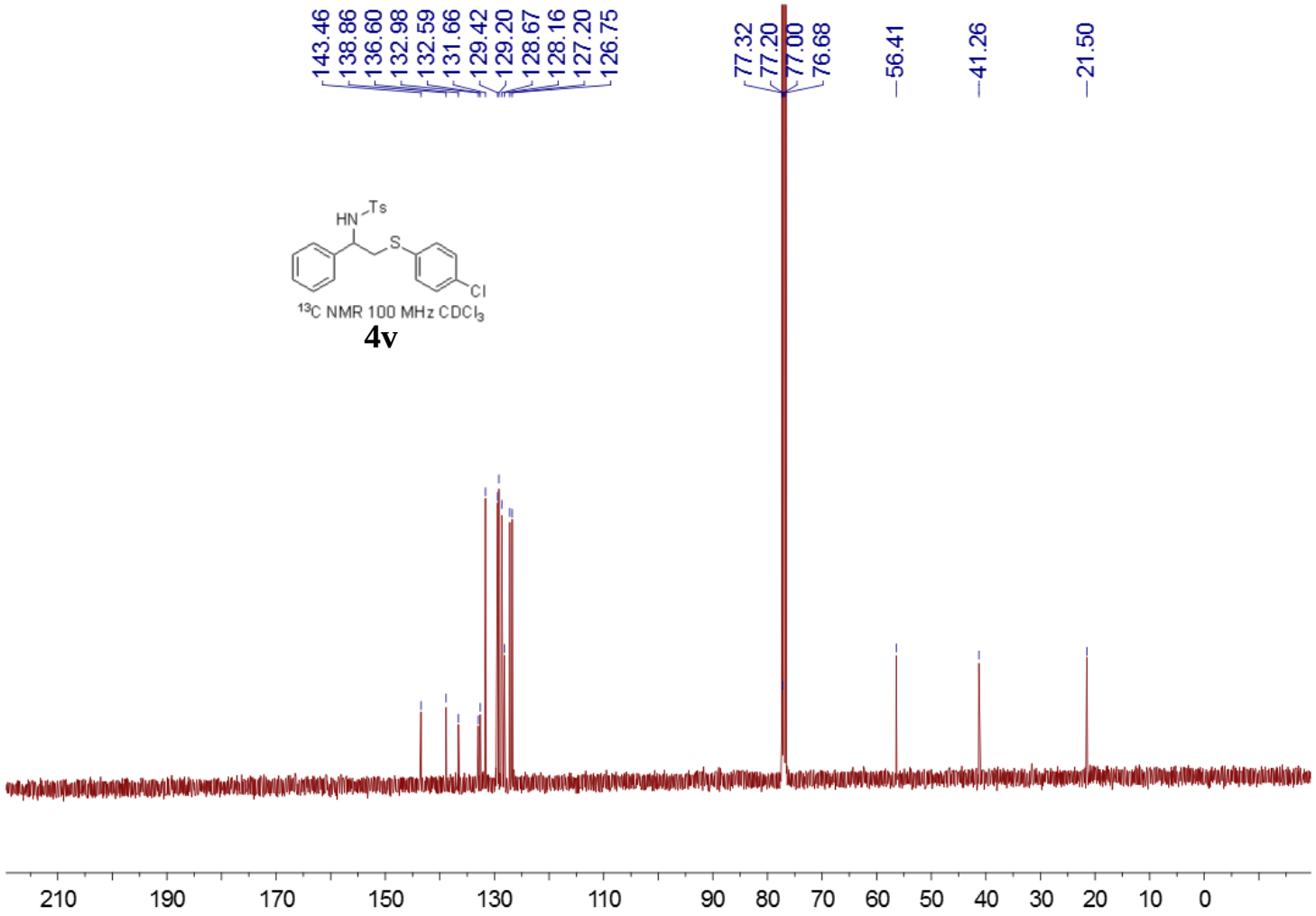

7.523
7.502
7.265
7.260
7.256
7.251
7.244
7.232
7.224
7.218
7.213
7.206
7.202
7.198
7.125
7.105
7.089
7.084
7.074
7.065
5.334
4.299
4.287
3.220
3.210
3.201
3.194
2.367
2.356
HN
Ts
S
1H NMR 400 MHz CDCl3
4t
2.00
8.03
2.01
1.87
7.6
7.5
7.4
7.3
7.2
7.1
7.0
1.00
1.00
1.98
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

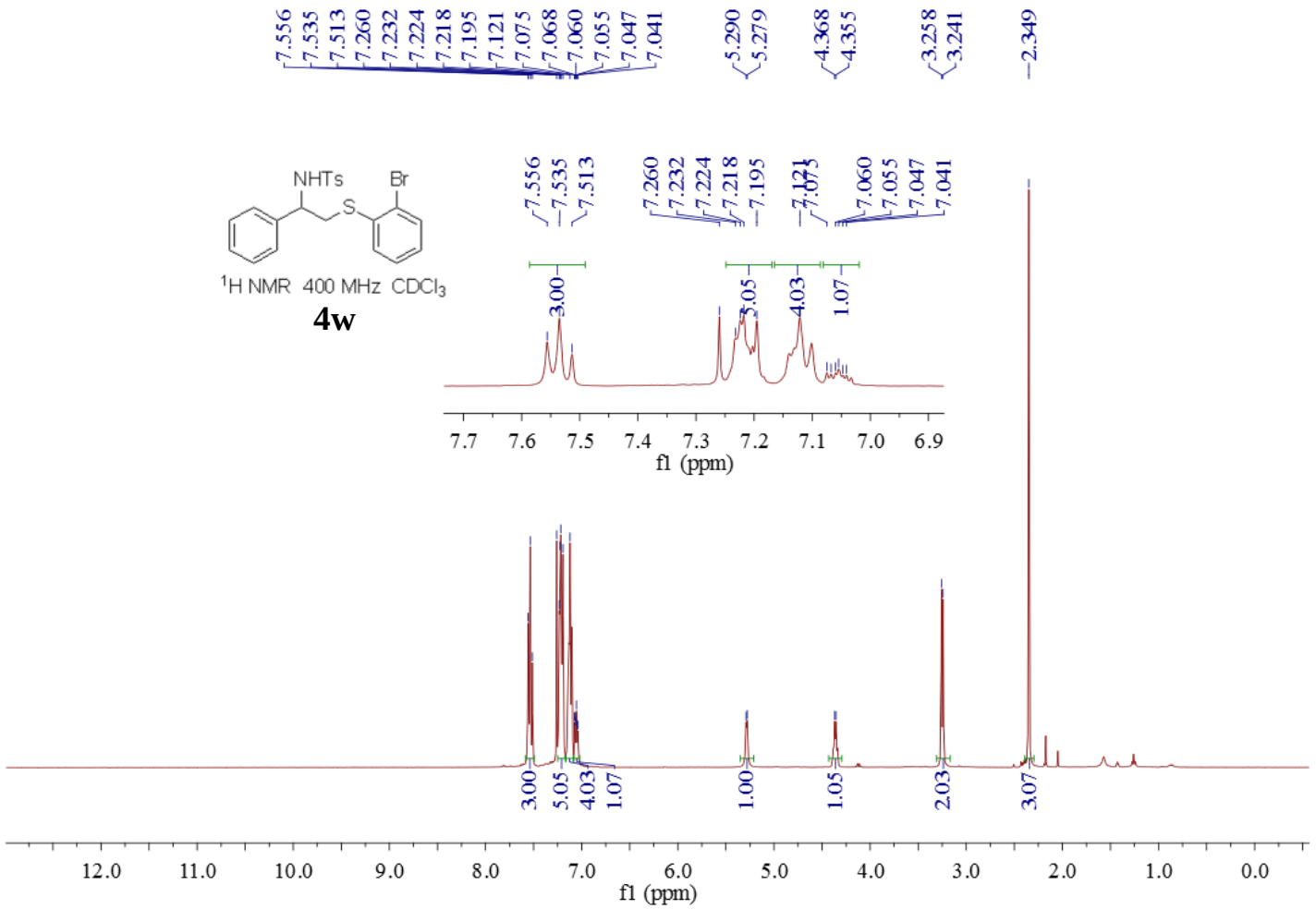

143.25
139.12
136.69
134.11
130.28
129.37
129.07
128.56
128.00
127.19
126.83
126.77
77.32
77.00
76.68
56.52
41.14
21.47
HN
Ts
S
13C NMR 100 MHz CDCl3
4t
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

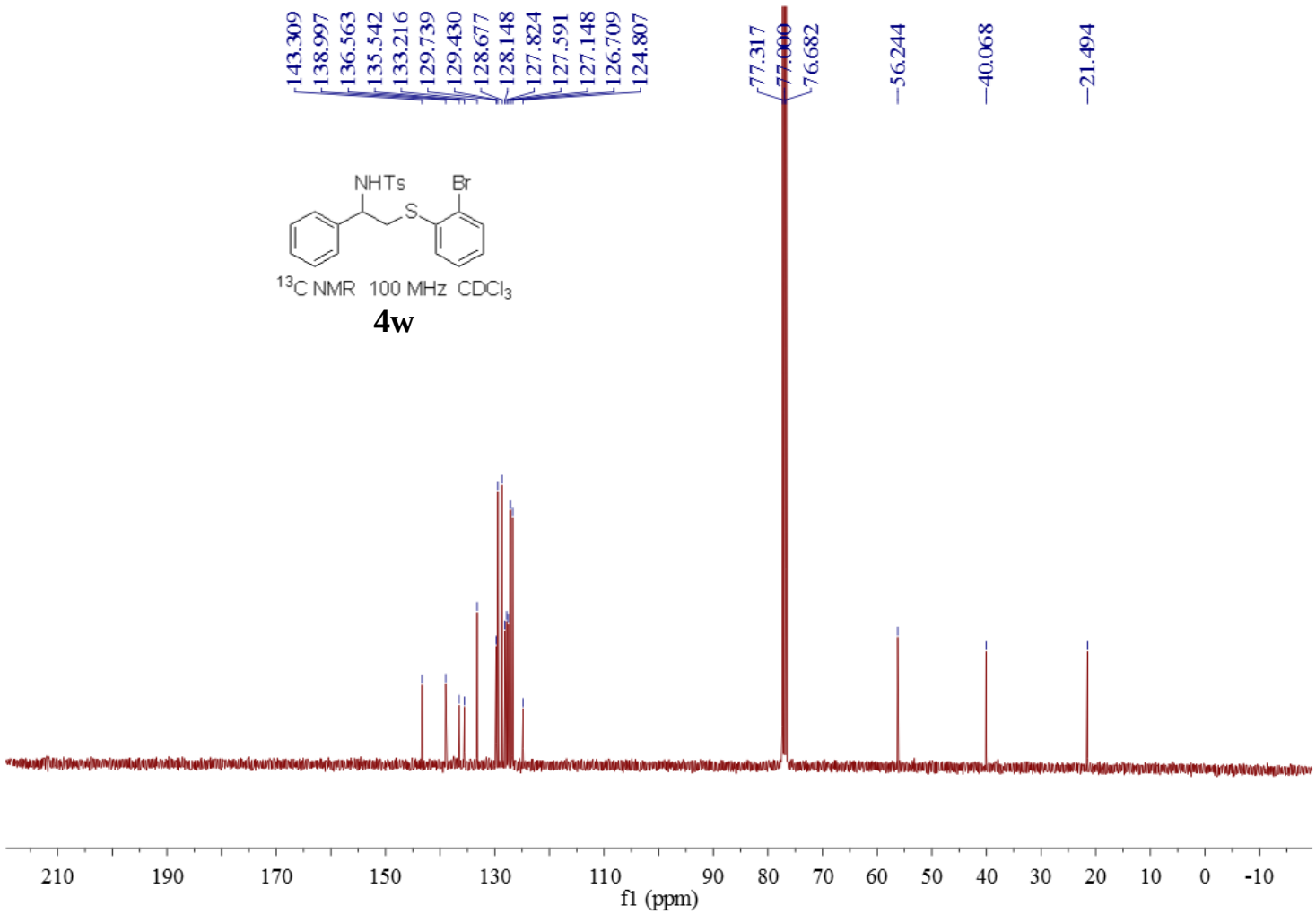

NHTs
S
OMe
^{1}H NMR 400 MHz CDCl$_3$
4u
7.509
7.488
7.260
7.198
7.186
7.180
7.176
7.169
7.133
7.113
7.059
7.055
7.046
7.036
6.799
6.777
5.443
4.214
3.807
3.075
3.058
2.375
2.15
5.08
2.15
2.06
2.05
1.00
1.05
3.24
2.05
3.17
f1 (ppm)

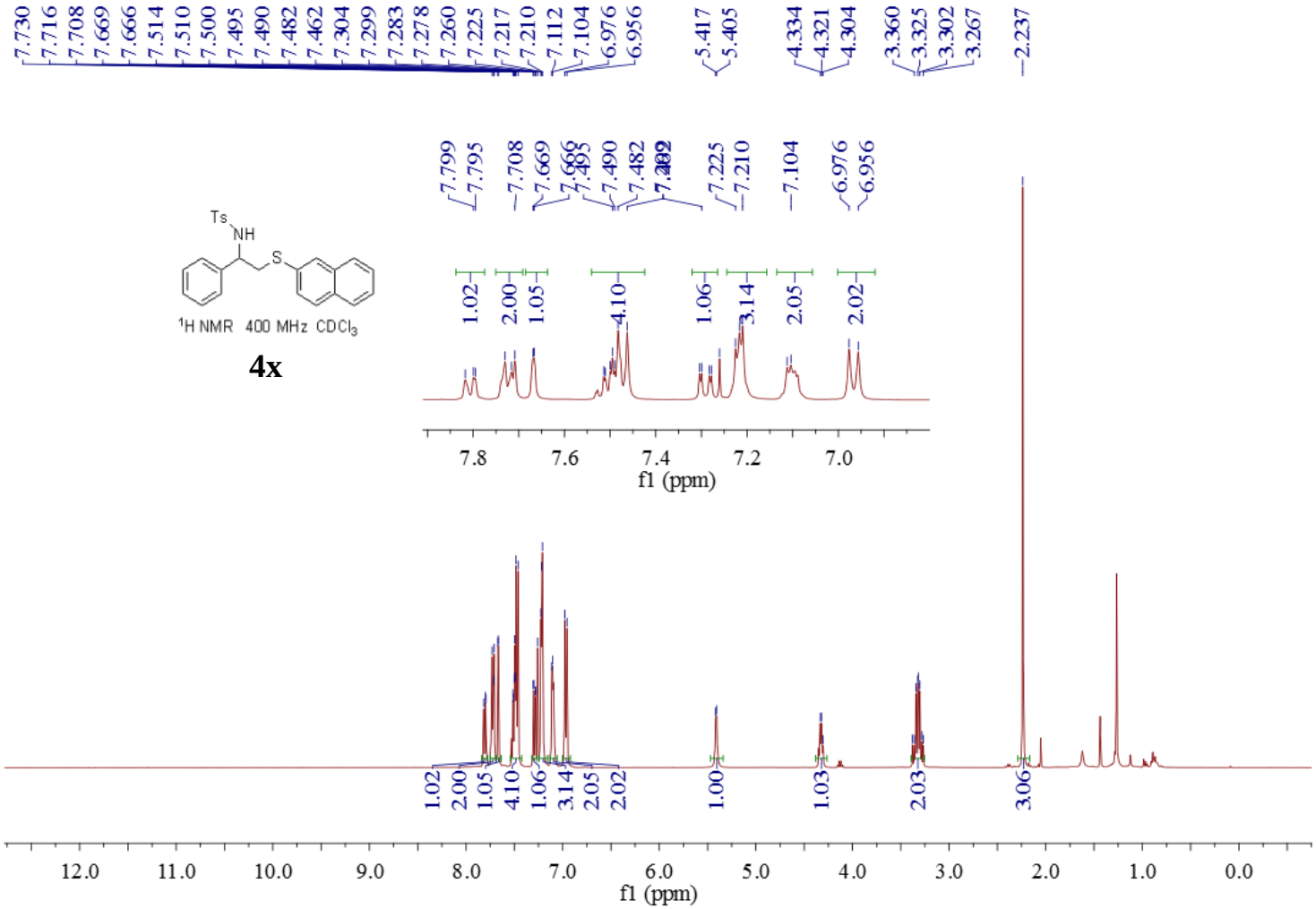

159.372
129.302
128.432
127.830
127.211
126.832
124.083
114.692
77.318
77.000
76.682
56.501
55.292
43.065
21.436
NHTs
S
OMe
13C NMR 100 MHz CDCl3
4u
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

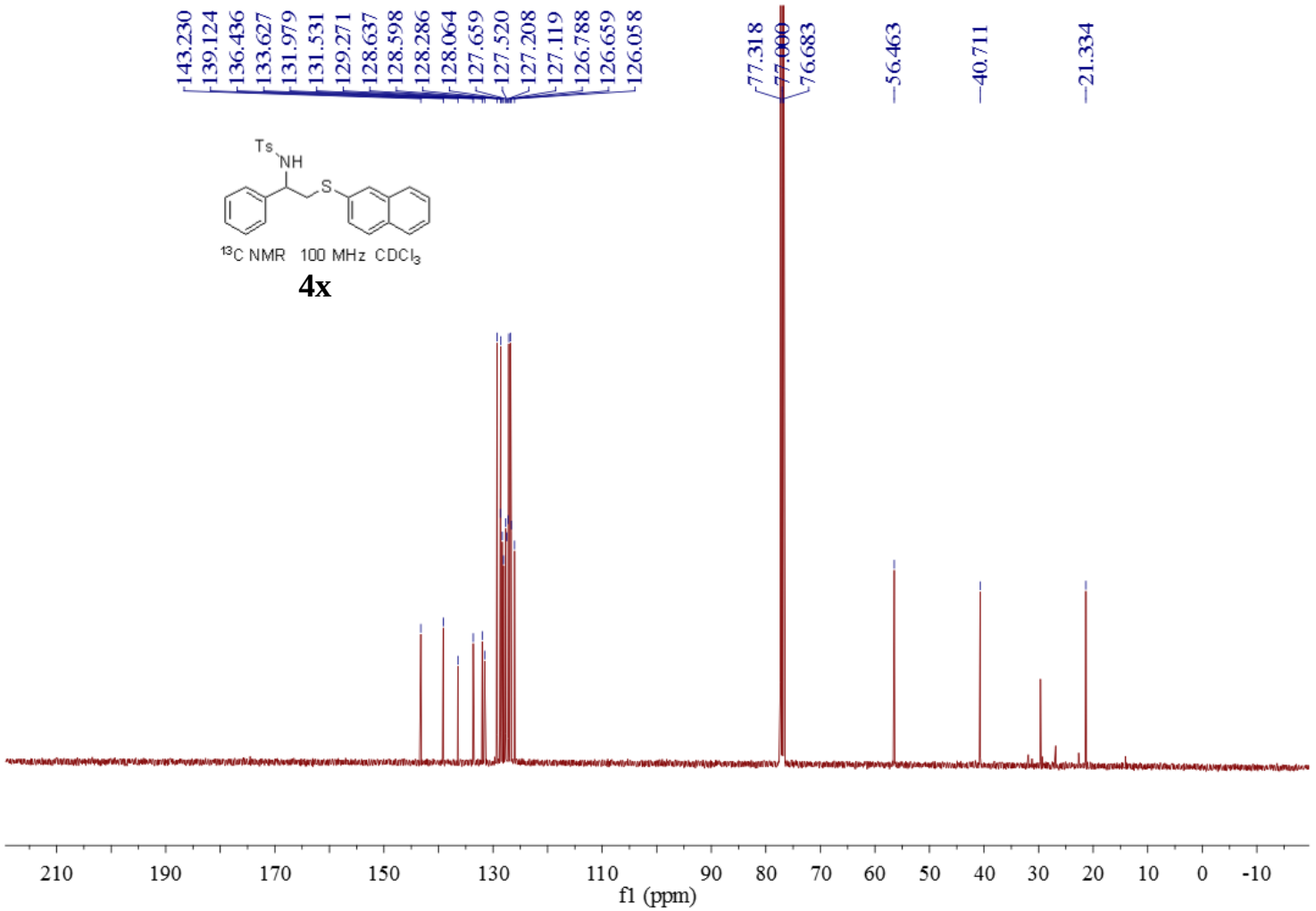

7.517
7.496
7.260
7.237
7.217
7.205
7.196
7.141
7.124
7.120
7.065
7.061
7.051
7.042
5.199
5.190
4.254
4.244
3.222
3.204
3.199
3.182
2.434
2.384
HN
Ts
S
Cl
1H NMR 400 MHz CDCl3
4v
2.00
5.11
3.91
1.91
1.05
1.04
2.07
3.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9

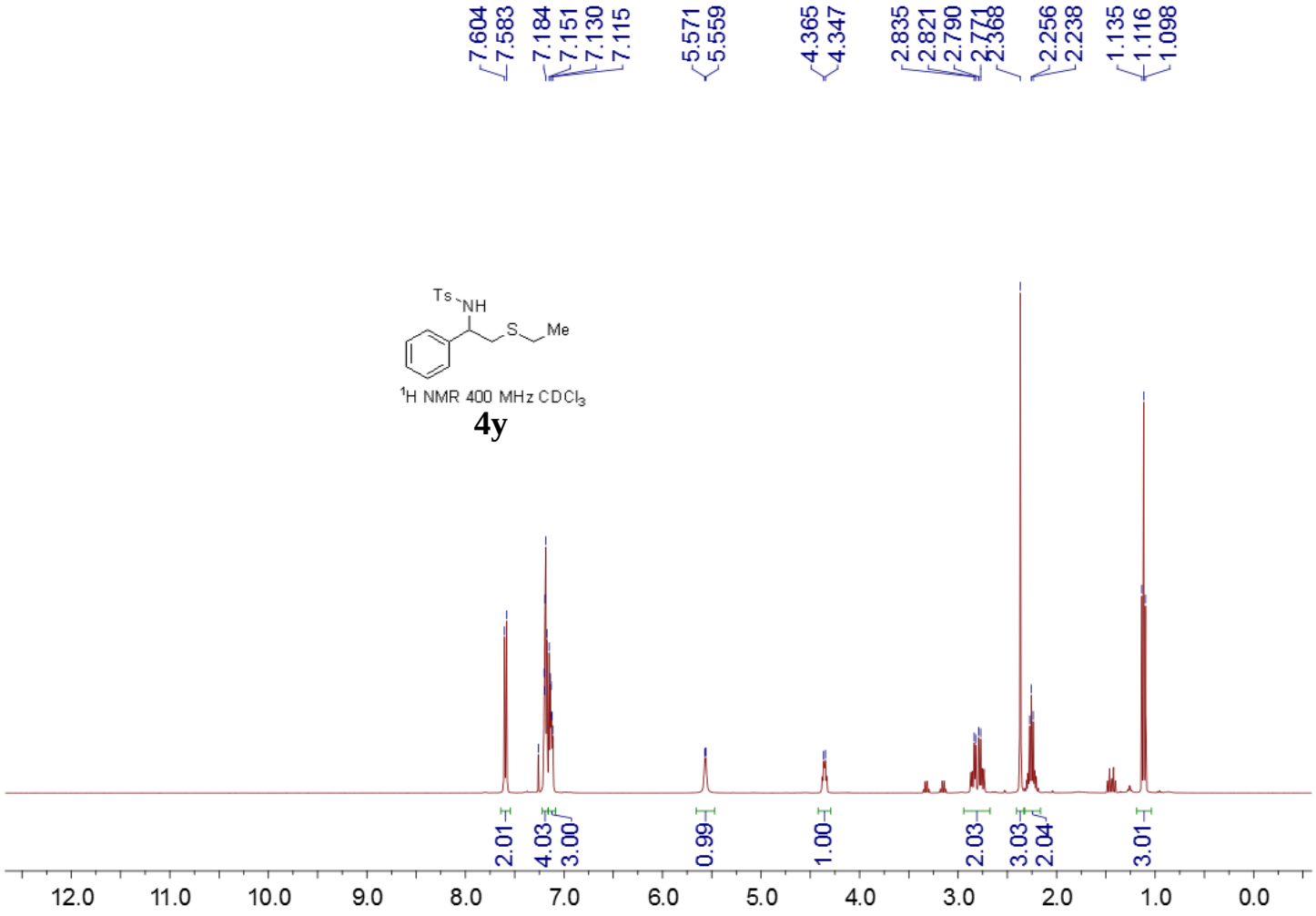

143.46
138.86
136.60
132.98
132.59
131.66
129.42
129.20
128.67
128.16
127.20
126.75
77.32
77.20
77.00
76.68
56.41
41.26
21.50
HN
Ts
S
Cl
13C NMR 100 MHz CDCl3
4v
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

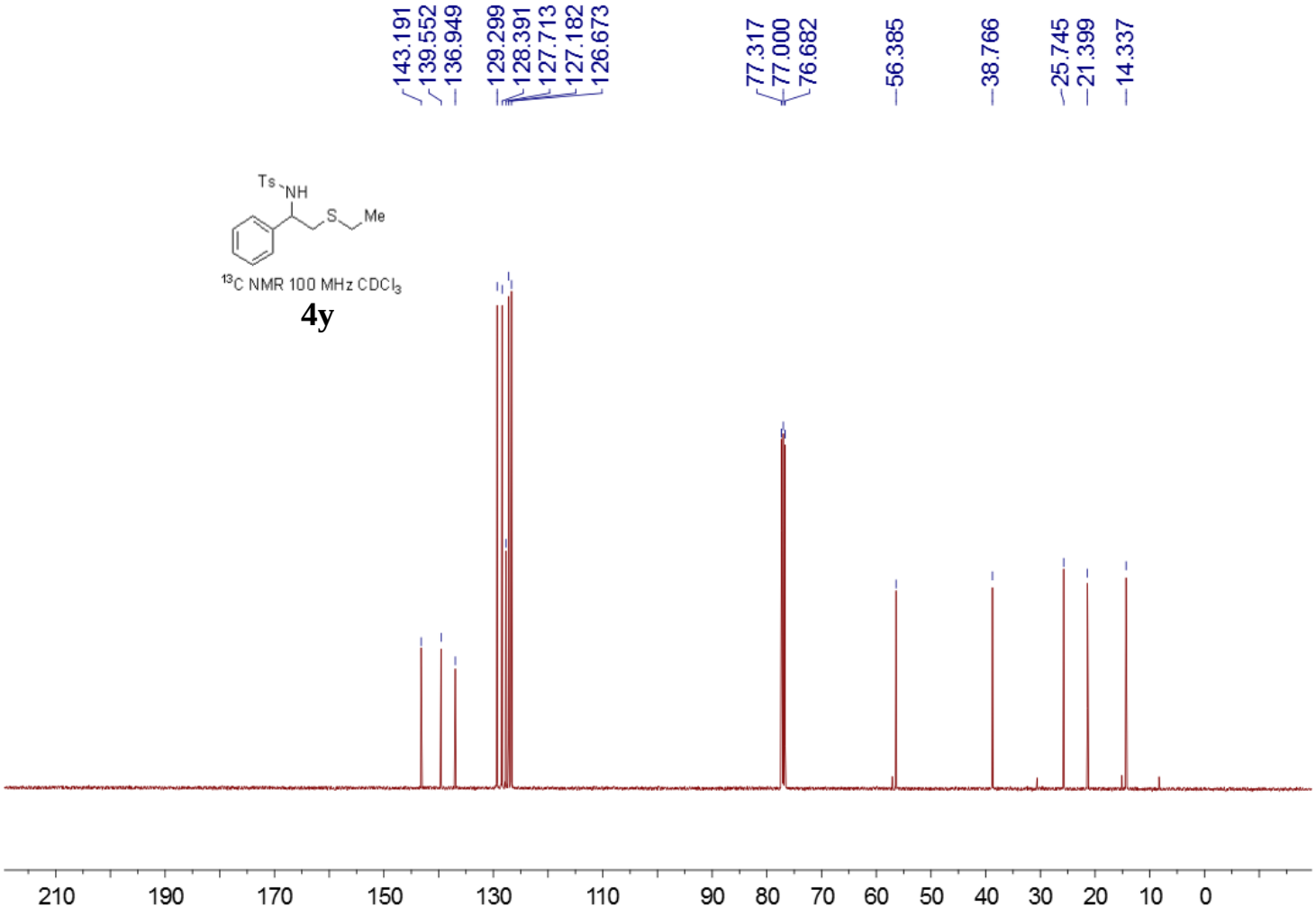

NHTs
Br
S
^{1}H NMR 400 MHz CDCl$_3$
4w
7.556
7.535
7.513
7.260
7.232
7.224
7.218
7.195
7.121
7.075
7.068
7.060
7.055
7.047
7.041
5.290
5.279
4.368
4.355
3.258
3.241
2.349
3.00
5.05
4.03
1.07
1.00
1.05
2.03
3.07
f1 (ppm)

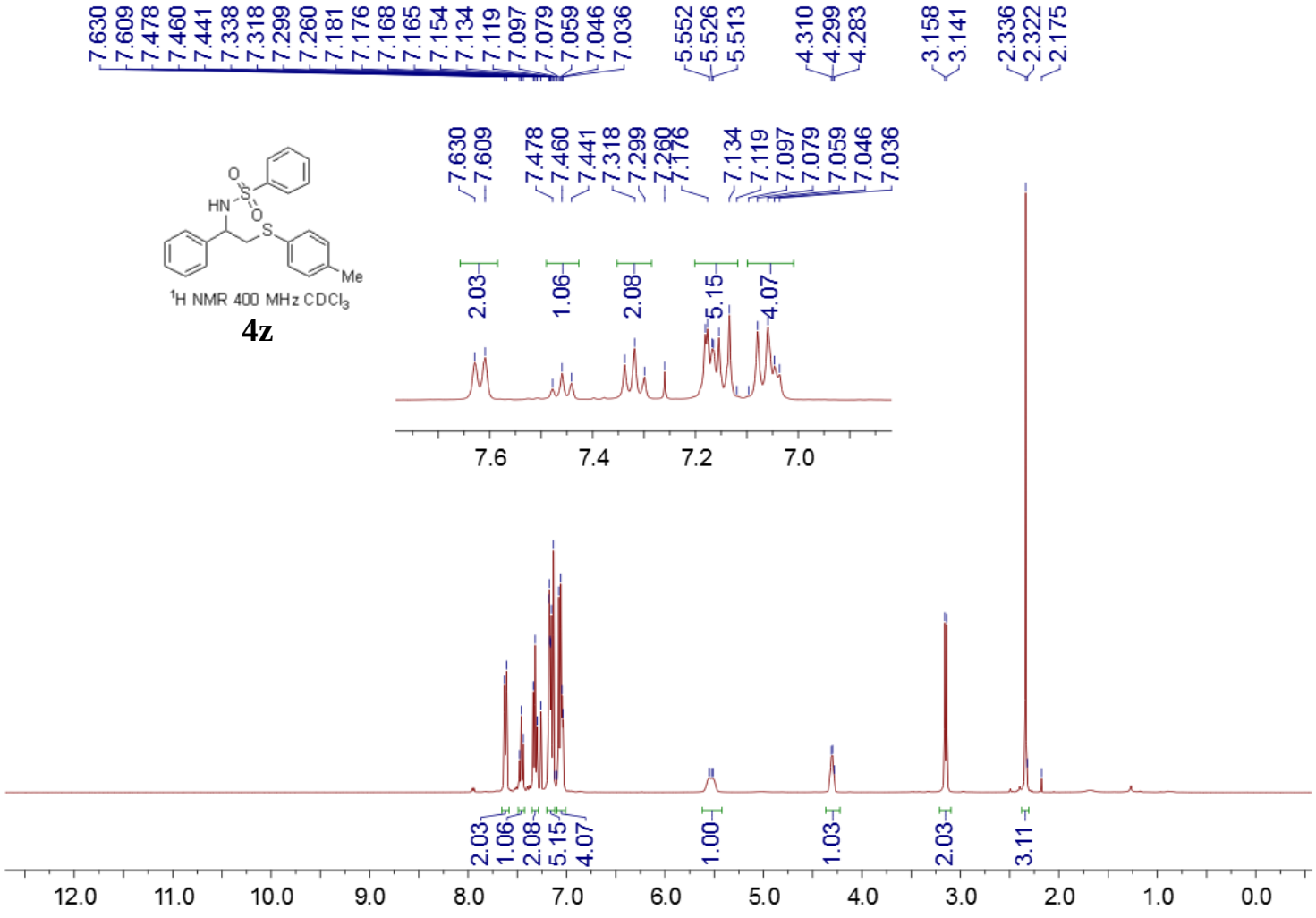

143.309
138.997
136.563
135.542
133.216
129.739
129.430
128.677
128.148
127.824
127.591
127.148
126.709
124.807
77.317
77.000
76.682
56.244
40.068
21.494
NHTs
Br
S
13C NMR 100 MHz CDCl3
4w
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

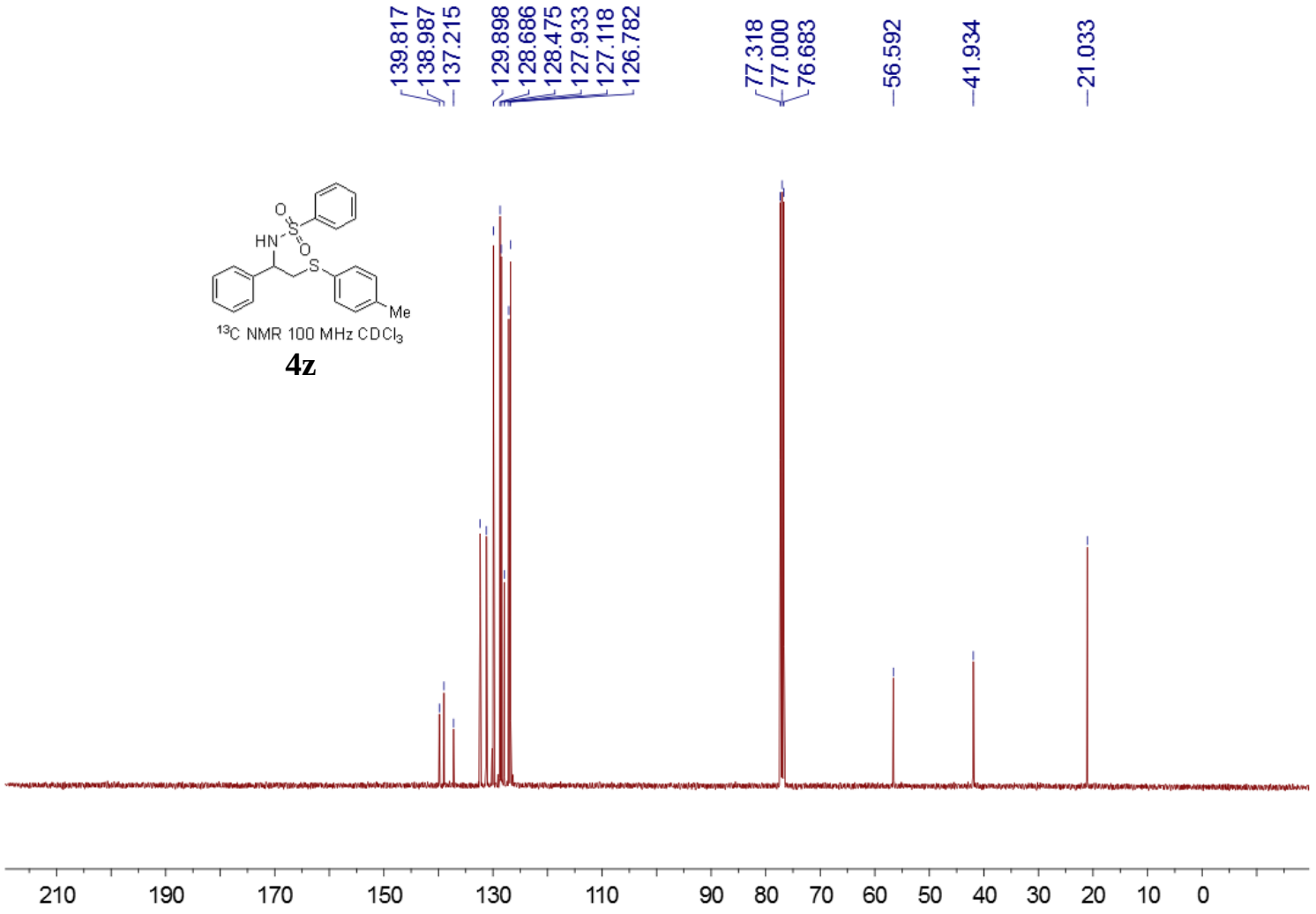

7.730
7.716
7.708
7.669
7.666
7.514
7.510
7.500
7.495
7.490
7.482
7.462
7.304
7.299
7.283
7.278
7.260
7.225
7.217
7.210
7.112
7.104
6.976
6.956
5.417
5.405
4.334
4.321
4.304
3.360
3.325
3.302
3.267
2.237
Ts
NH
S
1H NMR 400 MHz CDCl3
4x
1.02
2.00
1.05
4.10
1.06
3.14
2.05
2.02
1.00
1.03
2.03
3.06
f1 (ppm)


143.230
139.124
136.436
133.627
131.979
131.531
129.271
128.637
128.598
128.286
128.064
127.659
127.520
127.208
127.119
126.788
126.659
126.058
77.318
77.000
76.683
56.463
40.711
21.334
Ts
NH
S
13C NMR 100 MHz CDCl3
4x
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.604
7.583
7.184
7.151
7.130
7.115
5.571
5.559
4.365
4.347
2.835
2.821
2.790
2.771
2.368
2.256
2.238
1.135
1.116
1.098
Ts
NH
S
Me
1H NMR 400 MHz CDCl3
4y
2.01
4.03
3.00
0.99
1.00
2.03
3.03
2.04
3.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

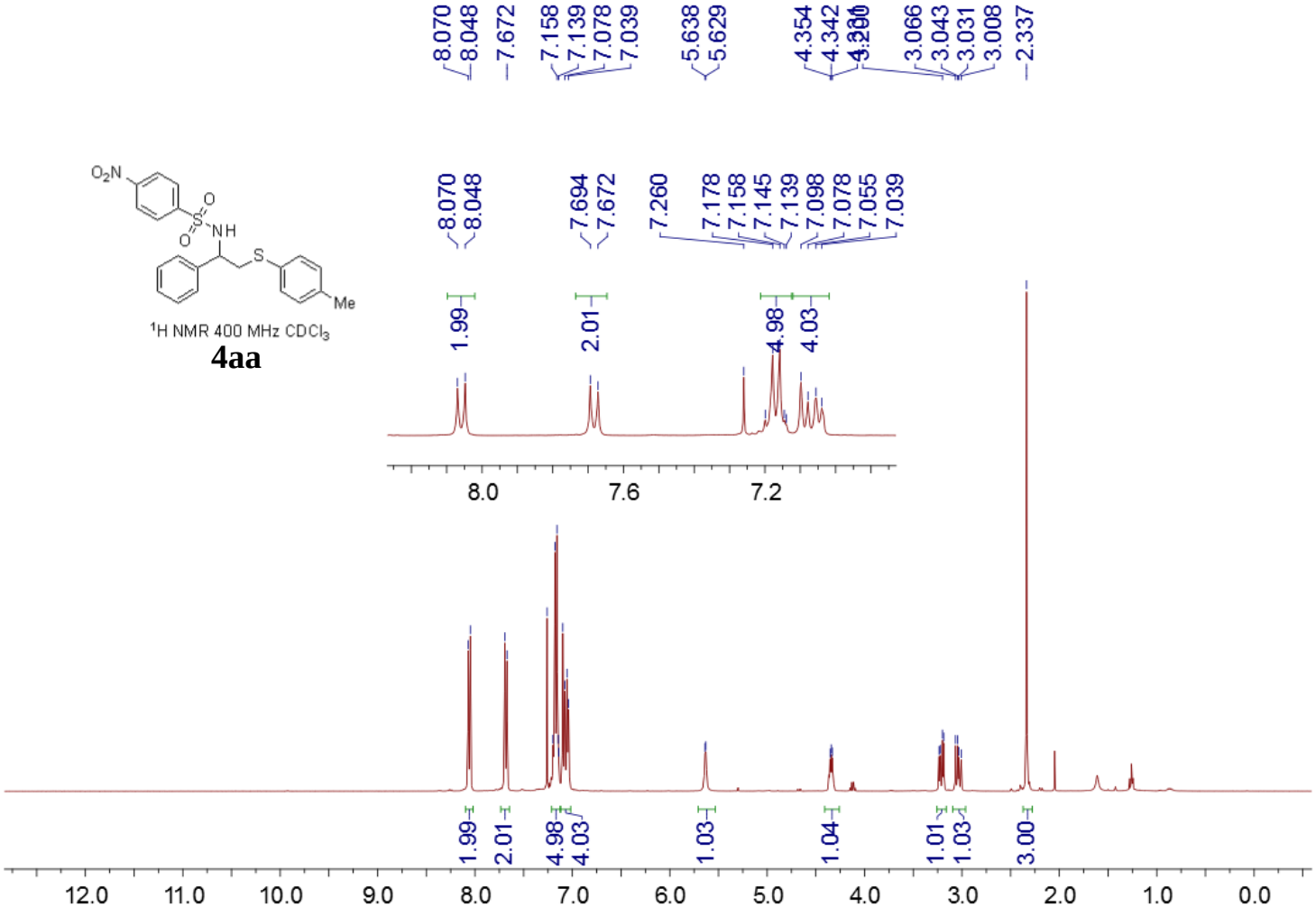

143.191
139.552
136.949
129.299
128.391
127.713
127.182
126.673
77.317
77.000
76.682
56.385
38.766
25.745
21.399
14.337
Ts
NH
S
Me
13C NMR 100 MHz CDCl3
4y
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

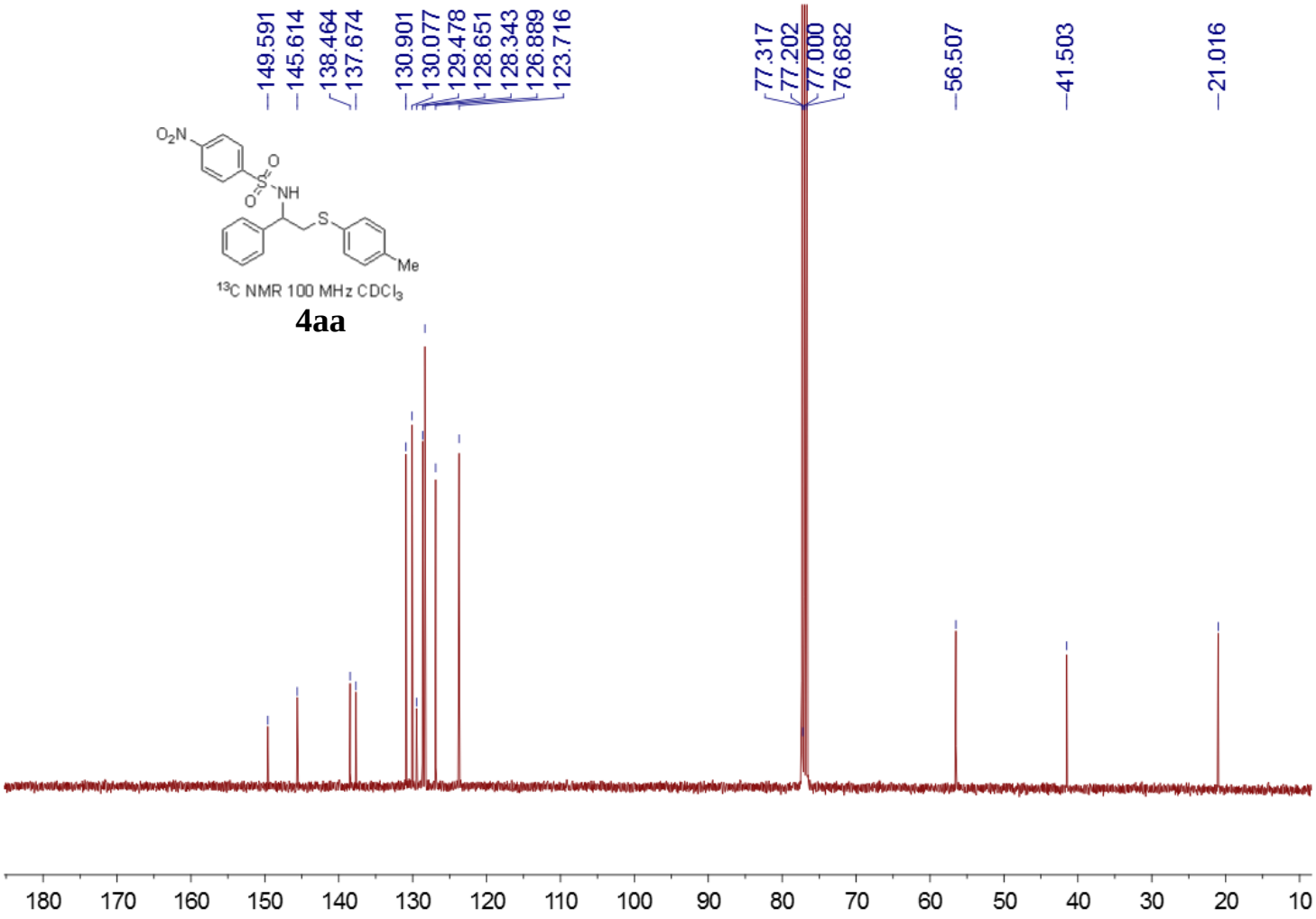

7.630
7.609
7.478
7.460
7.441
7.338
7.318
7.299
7.260
7.181
7.176
7.168
7.165
7.154
7.134
7.119
7.097
7.079
7.059
7.046
7.036
5.552
5.526
5.513
4.310
4.299
4.283
3.158
3.141
2.336
2.322
2.175
HN
O
S
O
S
Me
1H NMR 400 MHz CDCl3
4z
2.03
1.06
2.08
5.15
4.07
7.6
7.4
7.2
7.0
1.00
1.03
2.03
3.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

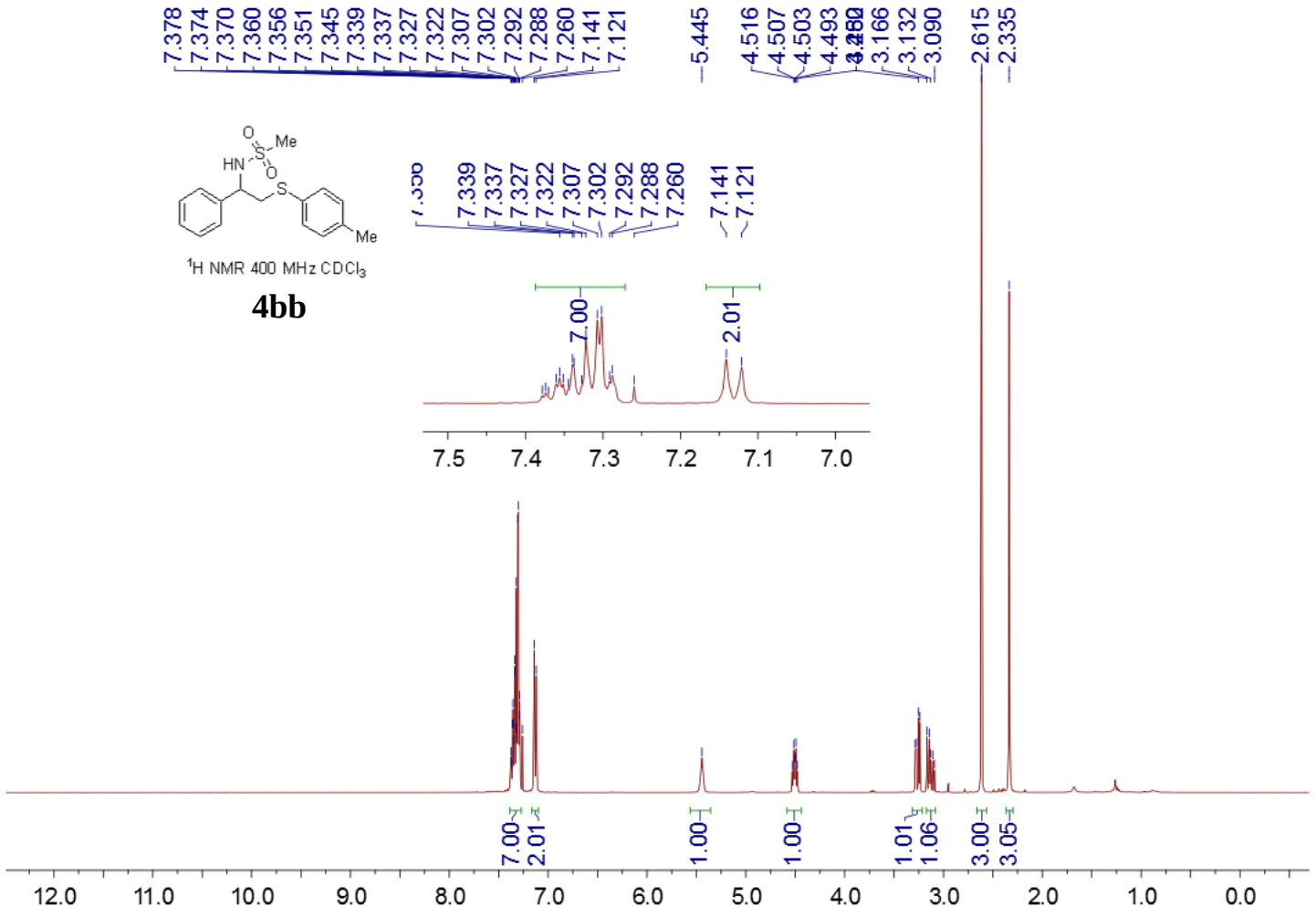


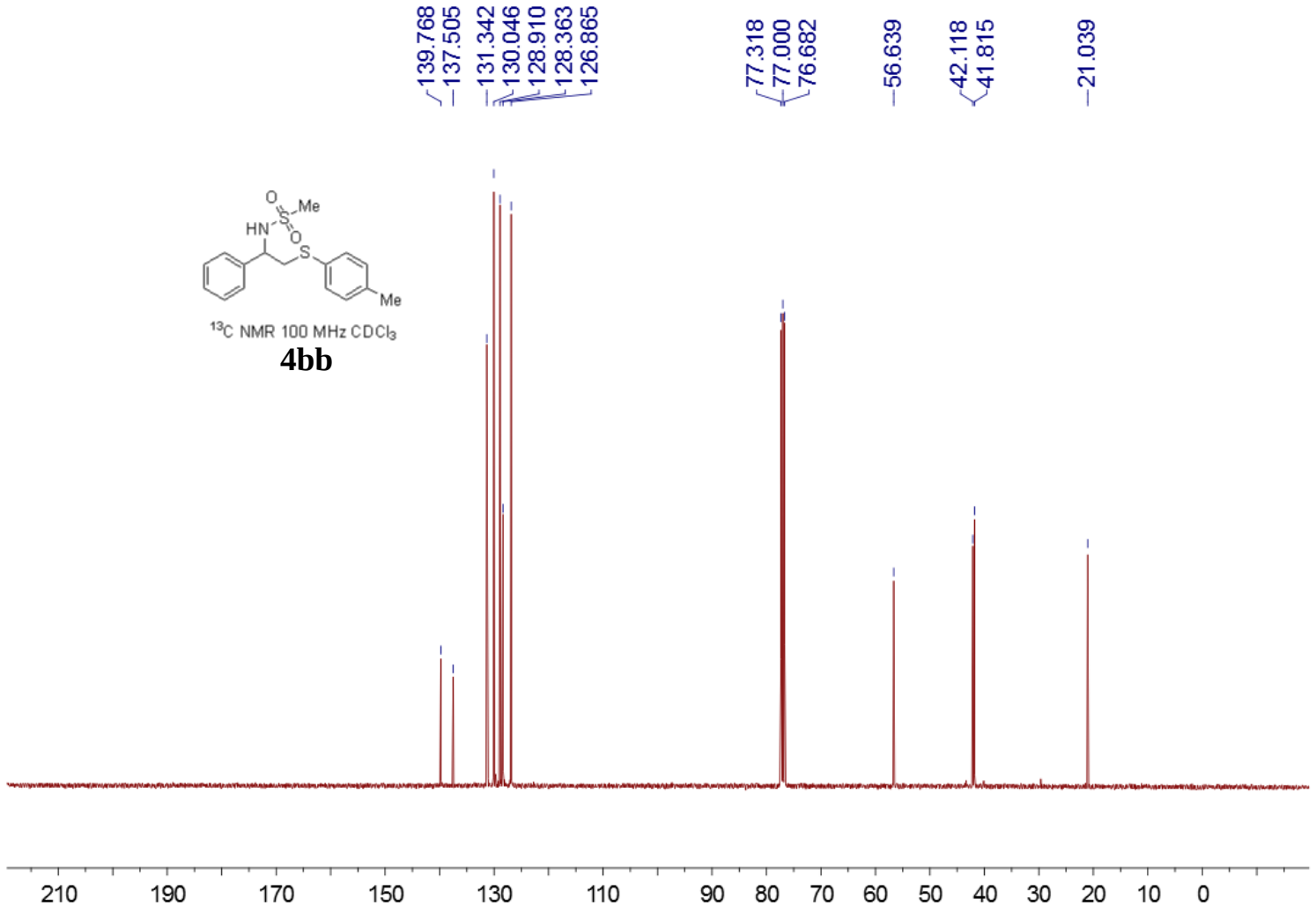
^{13}C NMR 100 MHz $CDCl_3$

4z


8.070
8.048
7.672
7.158
7.139
7.078
7.039
5.638
5.629
4.354
4.342
3.066
3.043
3.031
3.008
2.337
O2N
NH
S
Me
1H NMR 400 MHz CDCl3
4aa
7.694
7.672
7.260
7.178
7.158
7.145
7.139
7.098
7.078
7.055
7.039
1.99
2.01
4.98
4.03
8.0
7.6
7.2
1.99
2.01
4.98
4.03
1.03
1.04
1.01
1.03
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

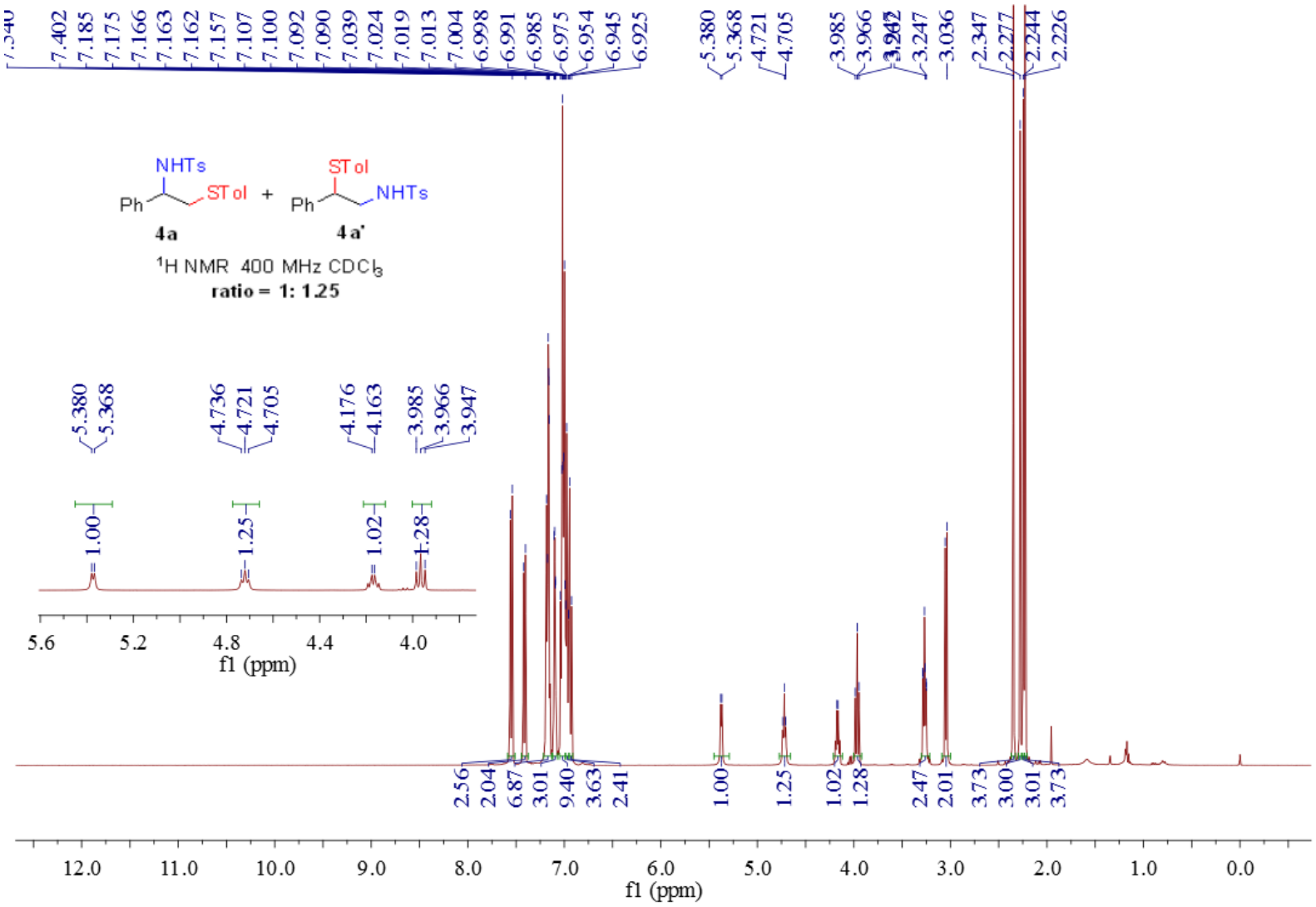

149.591
145.614
138.464
137.674
130.901
130.077
129.478
128.651
128.343
126.889
123.716
77.317
77.202
77.000
76.682
56.507
41.503
21.016
O2N
O
S
O
NH
S
Me
13C NMR 100 MHz CDCl3
4aa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

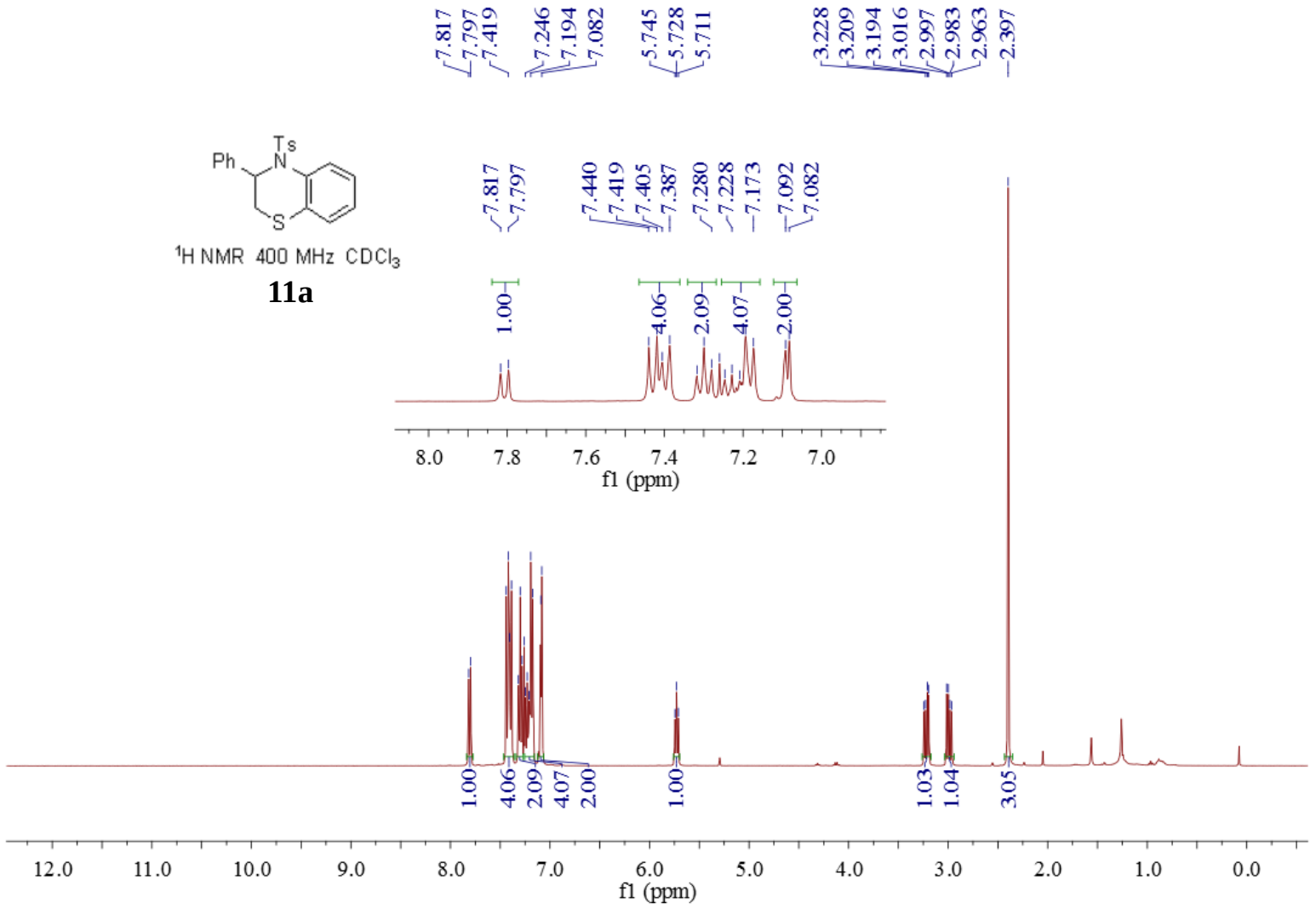

7.378
7.374
7.370
7.360
7.356
7.351
7.345
7.339
7.337
7.327
7.322
7.307
7.302
7.292
7.288
7.260
7.141
7.121
5.445
4.516
4.507
4.503
4.493
3.166
3.132
3.090
2.615
2.335
Me
HN
S
O
S
Me
1H NMR 400 MHz CDCl3
4bb
7.00
2.01
7.5
7.4
7.3
7.2
7.1
7.0
7.00
2.01
1.00
1.00
1.01
1.06
3.00
3.05
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

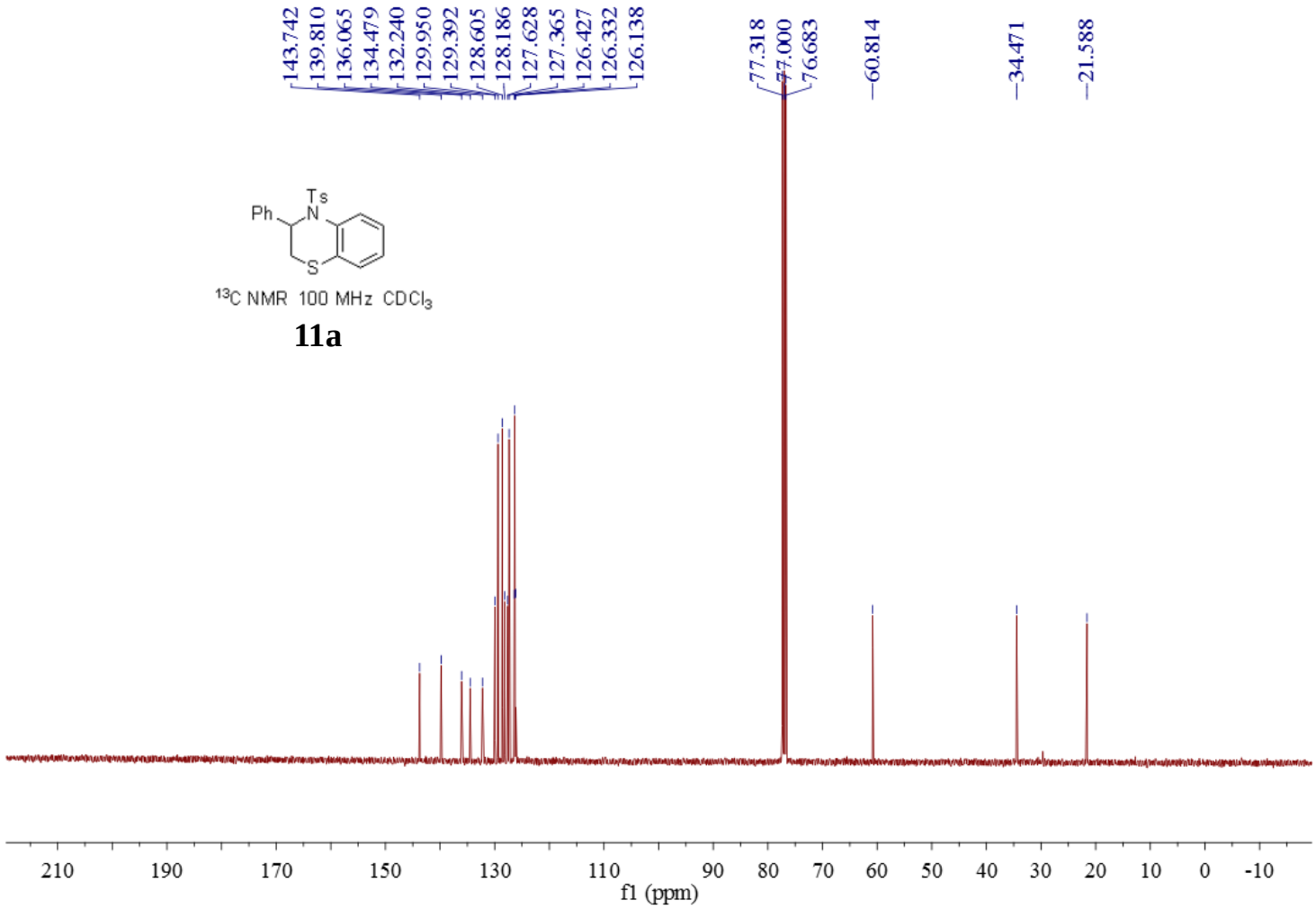


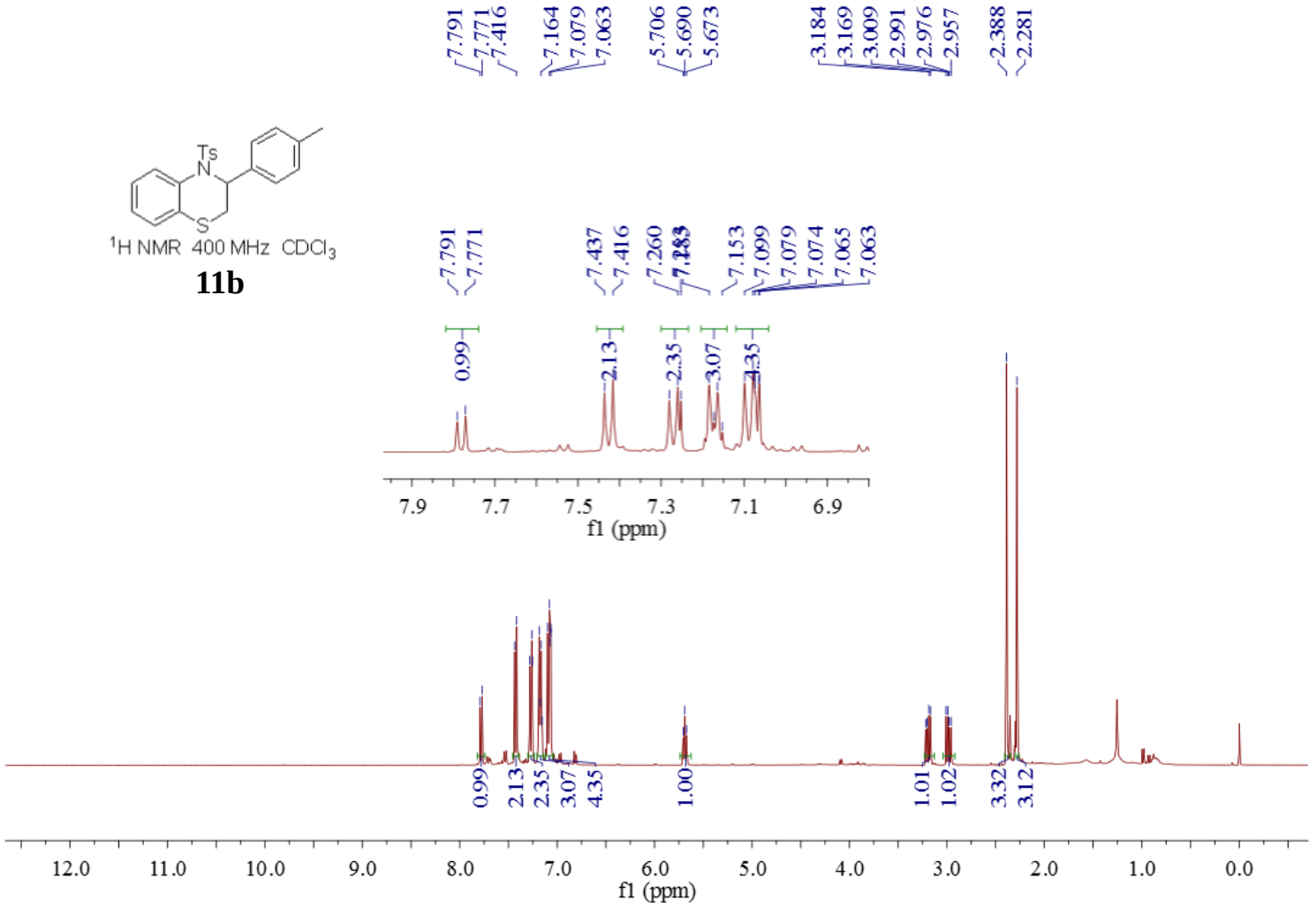
^{13}C NMR 100 MHz $CDCl_3$

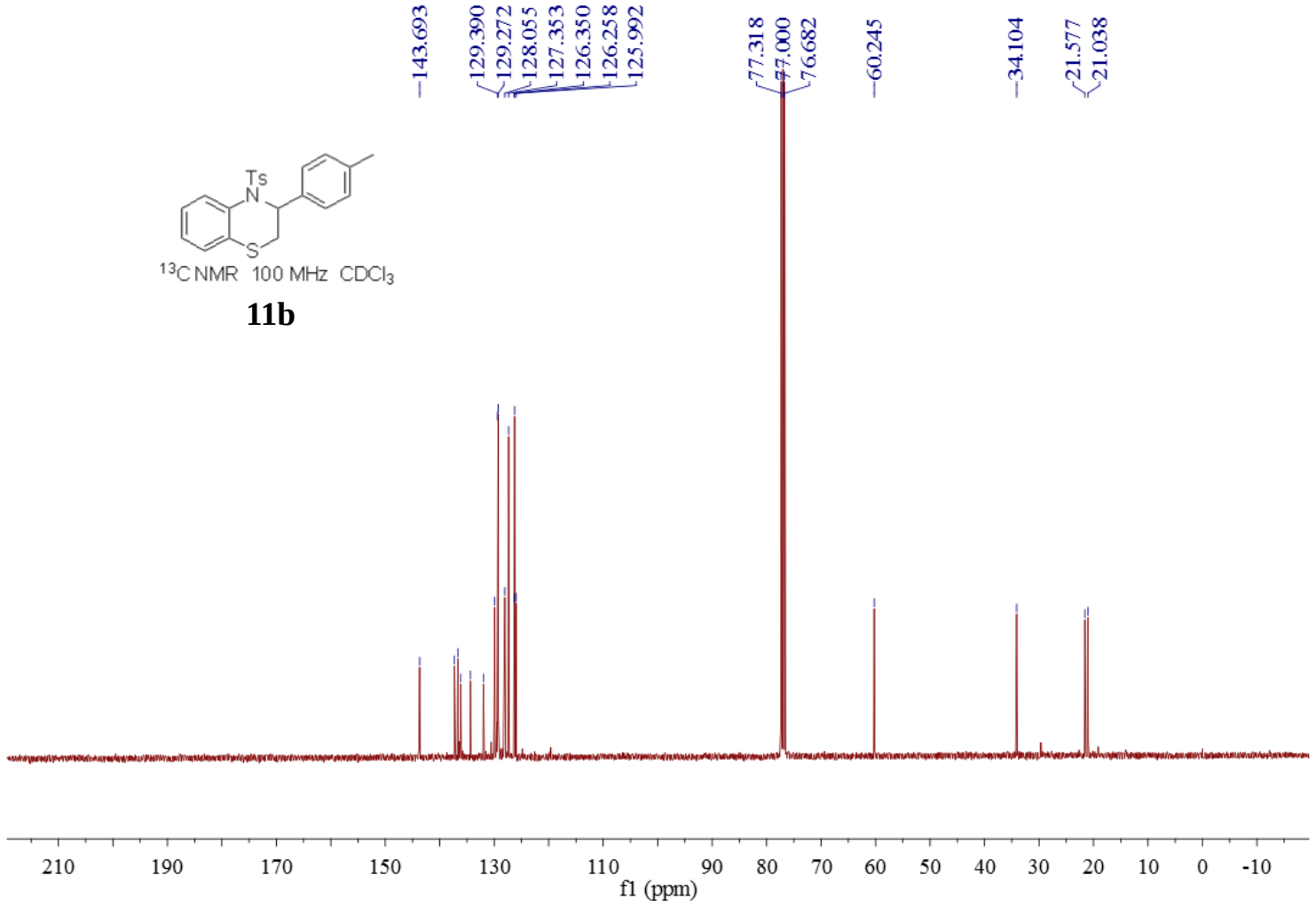
4bb

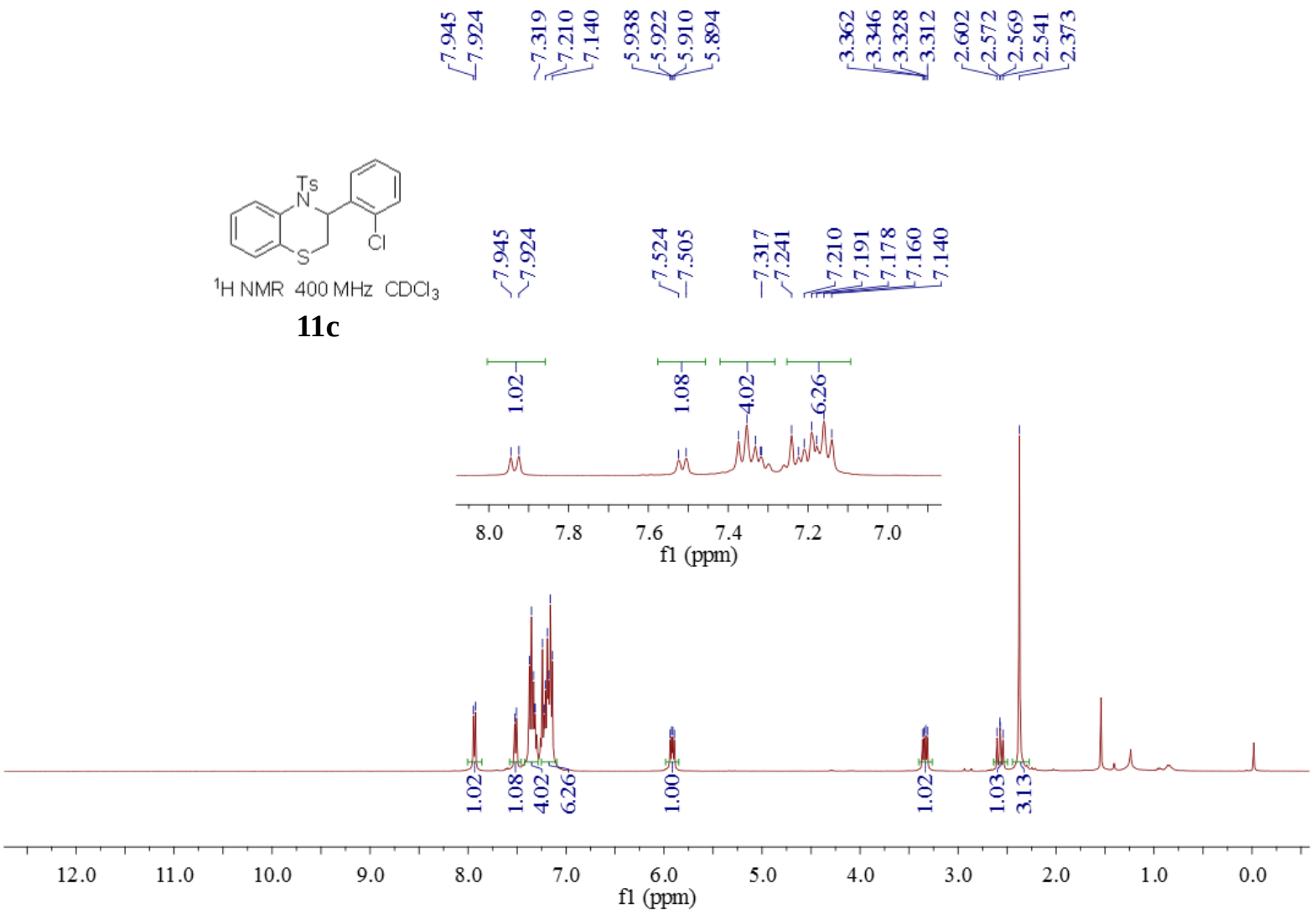

NHTs
STol
Ph
+
STol
NHTs
Ph
4a
4a'
^{1}H NMR 400 MHz CDCl$_3$
ratio = 1: 1.25
f1 (ppm)
f1 (ppm)

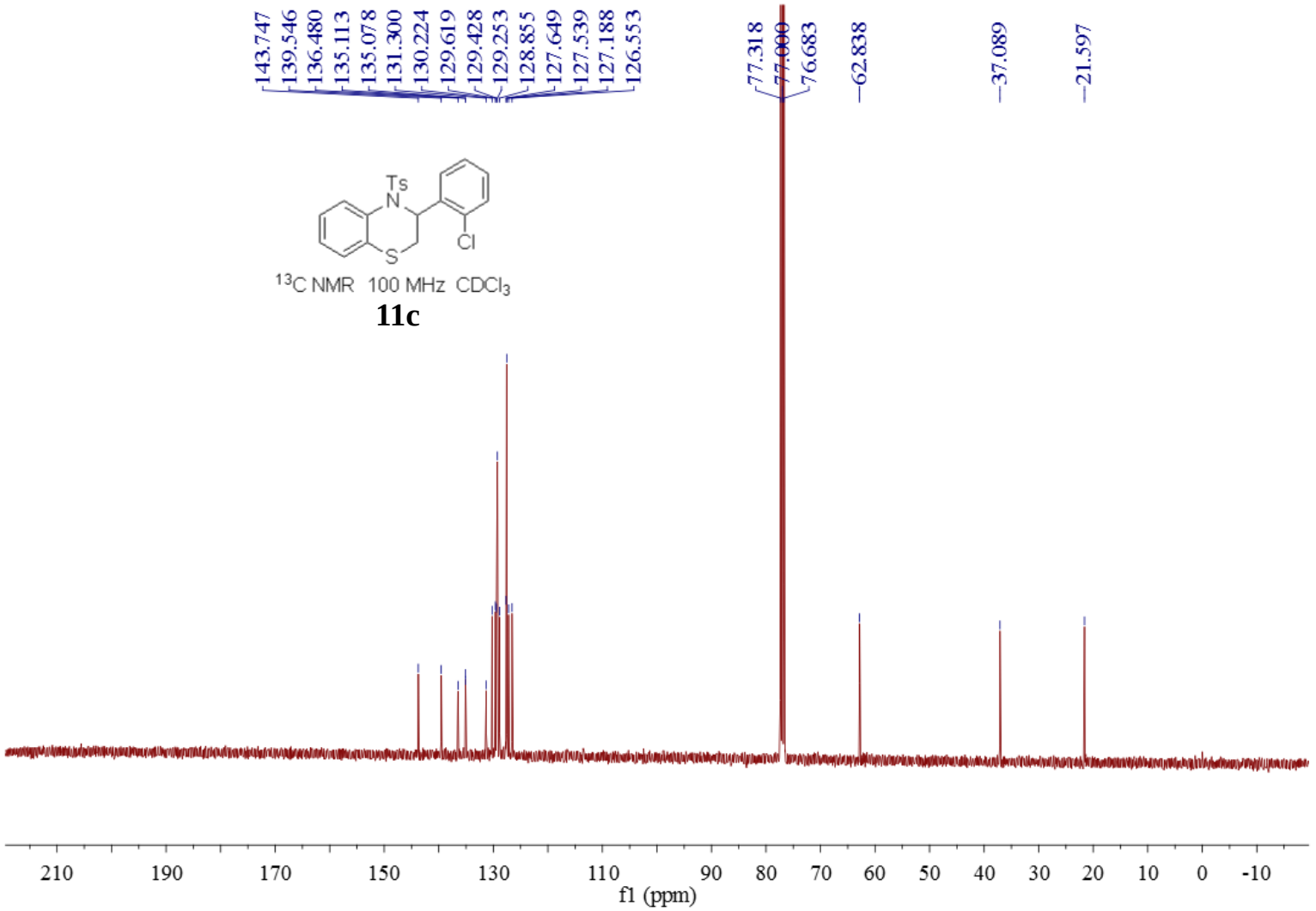

Ts
Ph
N
S
^{1}H NMR 400 MHz $CDCl_3$
11a
7.817
7.797
7.419
7.246
7.194
7.082
5.745
5.728
5.711
3.228
3.209
3.194
3.016
2.997
2.983
2.963
2.397
1.00
4.06
2.09
4.07
2.00
1.03
1.04
3.05
f1 (ppm)

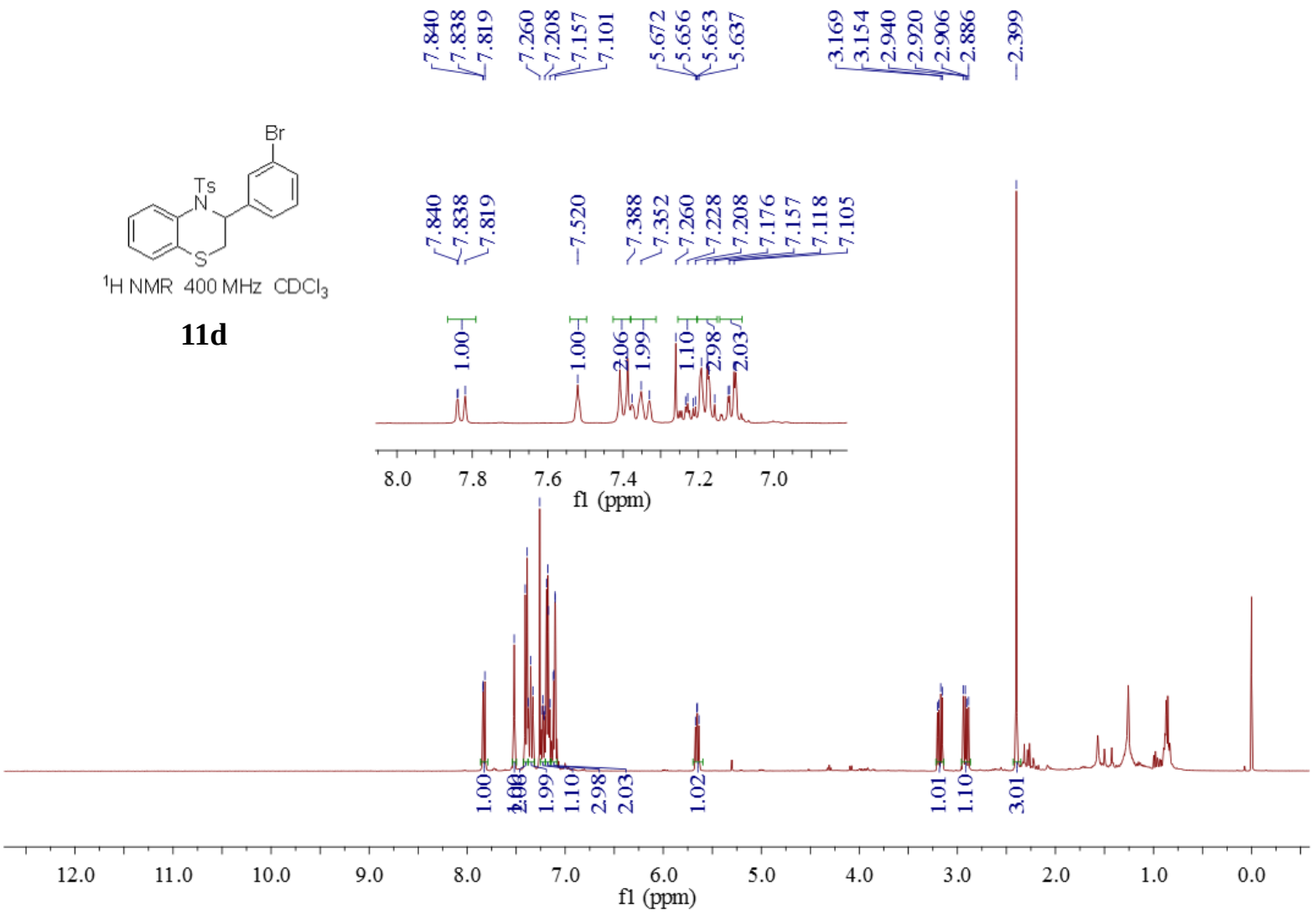

143.742
139.810
136.065
134.479
132.240
129.950
129.392
128.605
128.186
127.628
127.365
126.427
126.332
126.138
77.318
77.000
76.683
60.814
34.471
21.588
Ts
N
Ph
S
13C NMR 100 MHz CDCl3
11a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

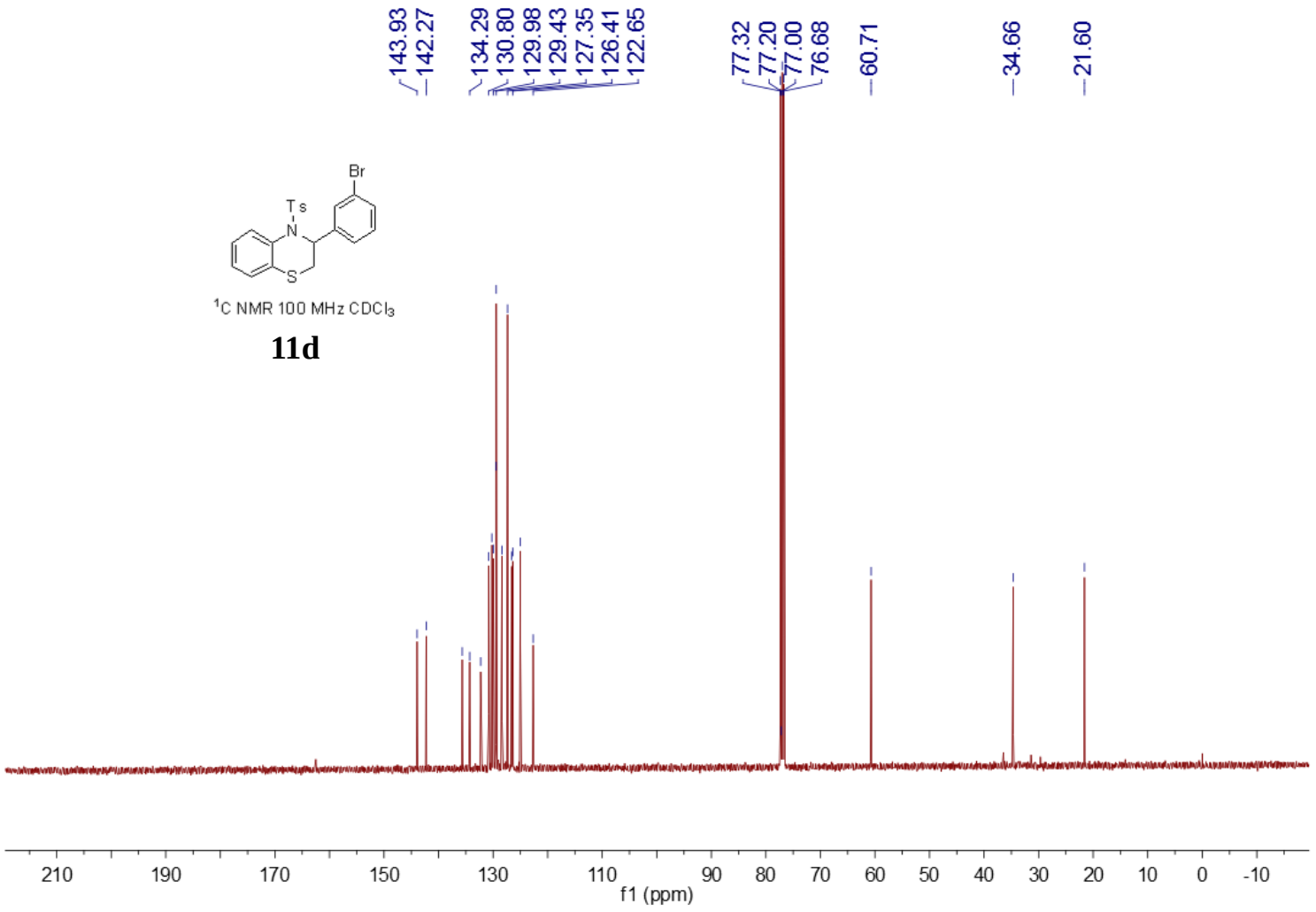

Ts
N
S
1H NMR 400 MHz CDCl3
11b
7.791
7.771
7.416
7.164
7.079
7.063
5.706
5.690
5.673
3.184
3.169
3.009
2.991
2.976
2.957
2.388
2.281
7.437
7.260
7.153
7.099
7.079
7.074
7.065
7.063
0.99
2.13
2.35
3.07
2.35
7.9
7.7
7.5
7.3
7.1
6.9
f1 (ppm)
0.99
2.13
2.35
3.07
4.35
1.00
1.01
1.02
3.32
3.12
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

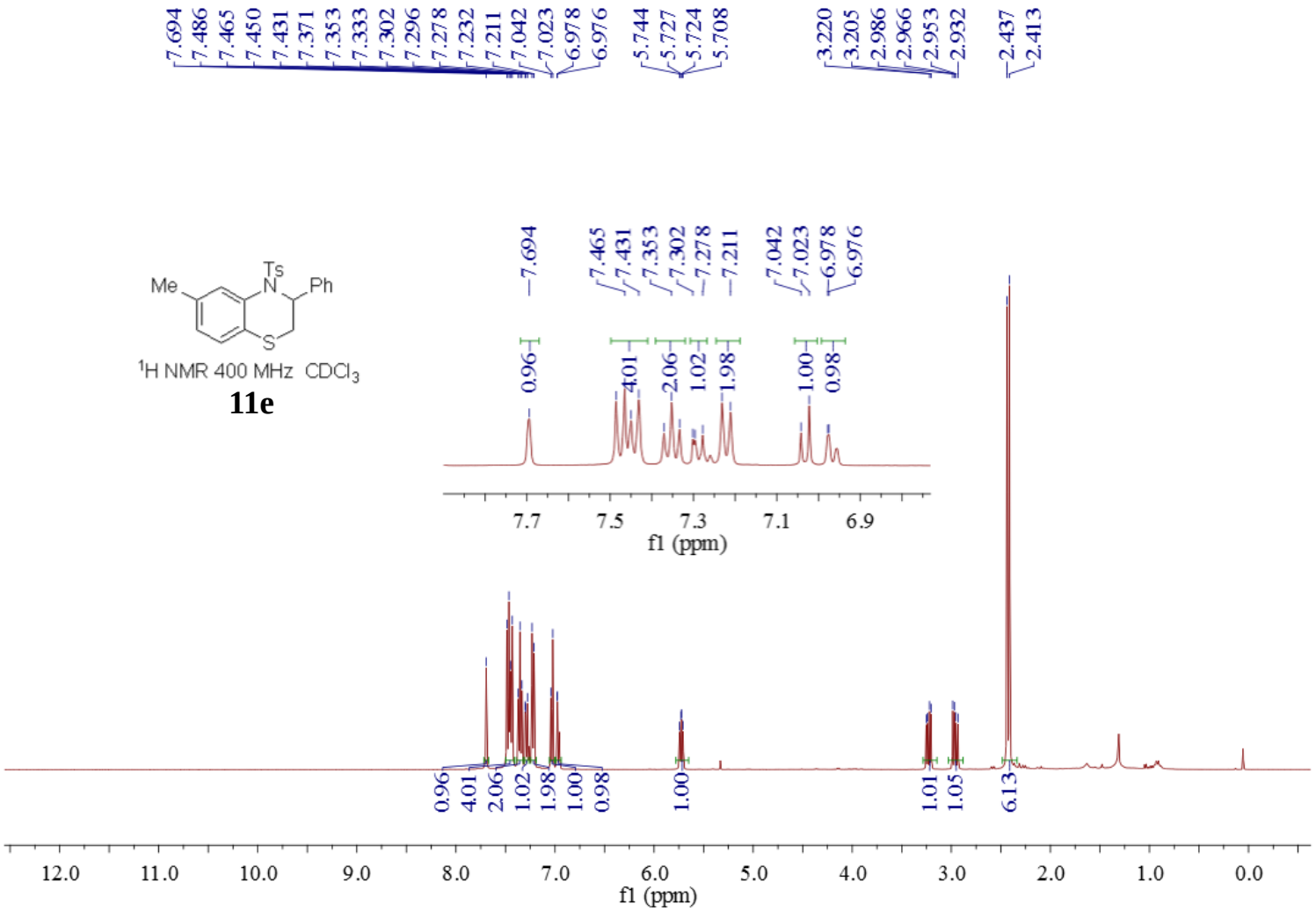

143.693
129.390
129.272
128.055
127.353
126.350
126.258
125.992
77.318
77.000
76.682
60.245
34.104
21.577
21.038
Ts
N
S
13C NMR 100 MHz CDCl3
11b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

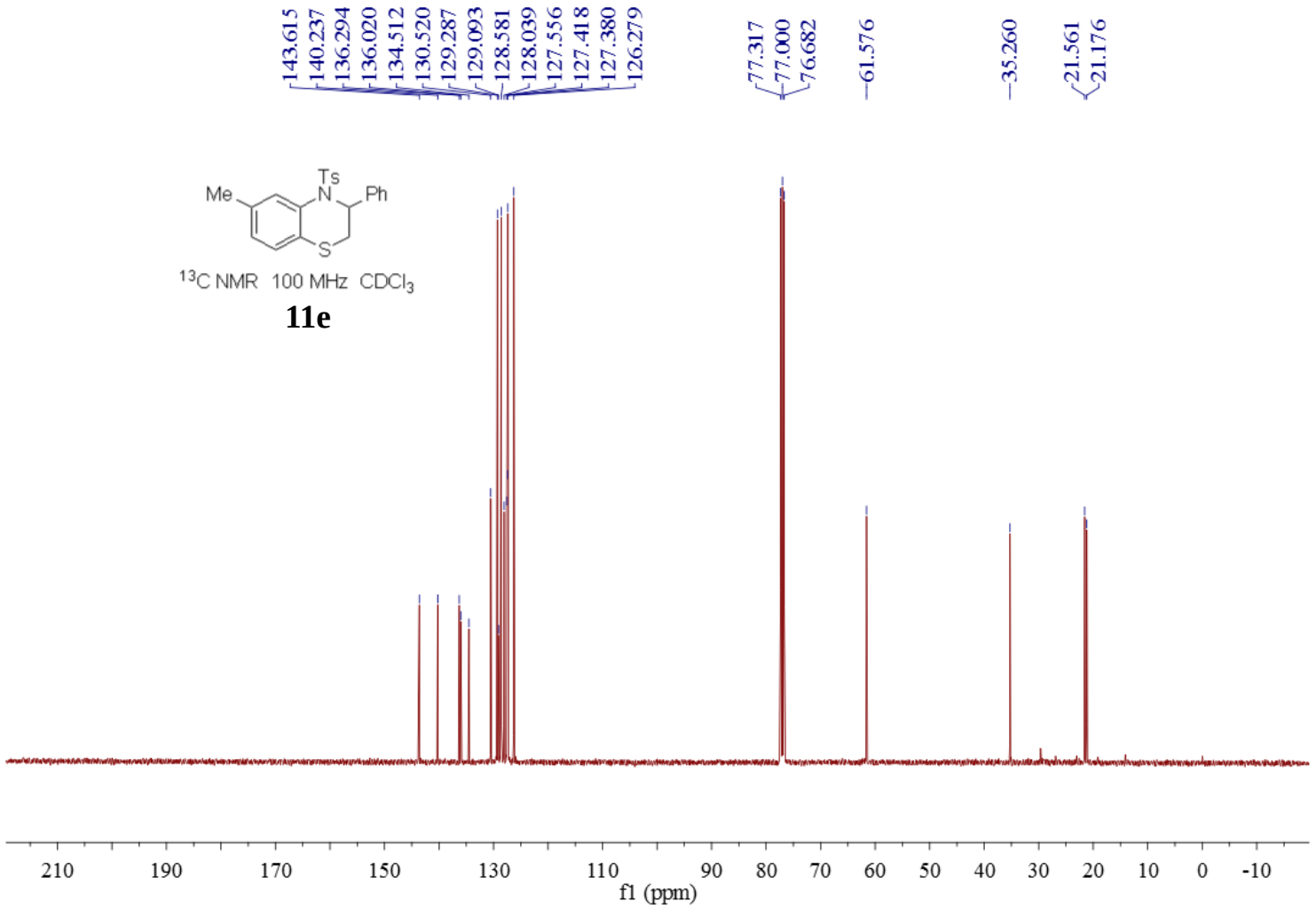

7.945
7.924
7.319
7.210
7.140
5.938
5.922
5.910
5.894
3.362
3.346
3.328
3.312
2.602
2.572
2.569
2.541
2.373
Ts
N
S
Cl
1H NMR 400 MHz CDCl3
11c
7.945
7.924
7.524
7.505
7.317
7.241
7.210
7.191
7.178
7.160
7.140
1.02
1.08
4.02
6.26
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
1.02
1.08
4.02
6.26
1.00
1.02
1.03
3.13
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

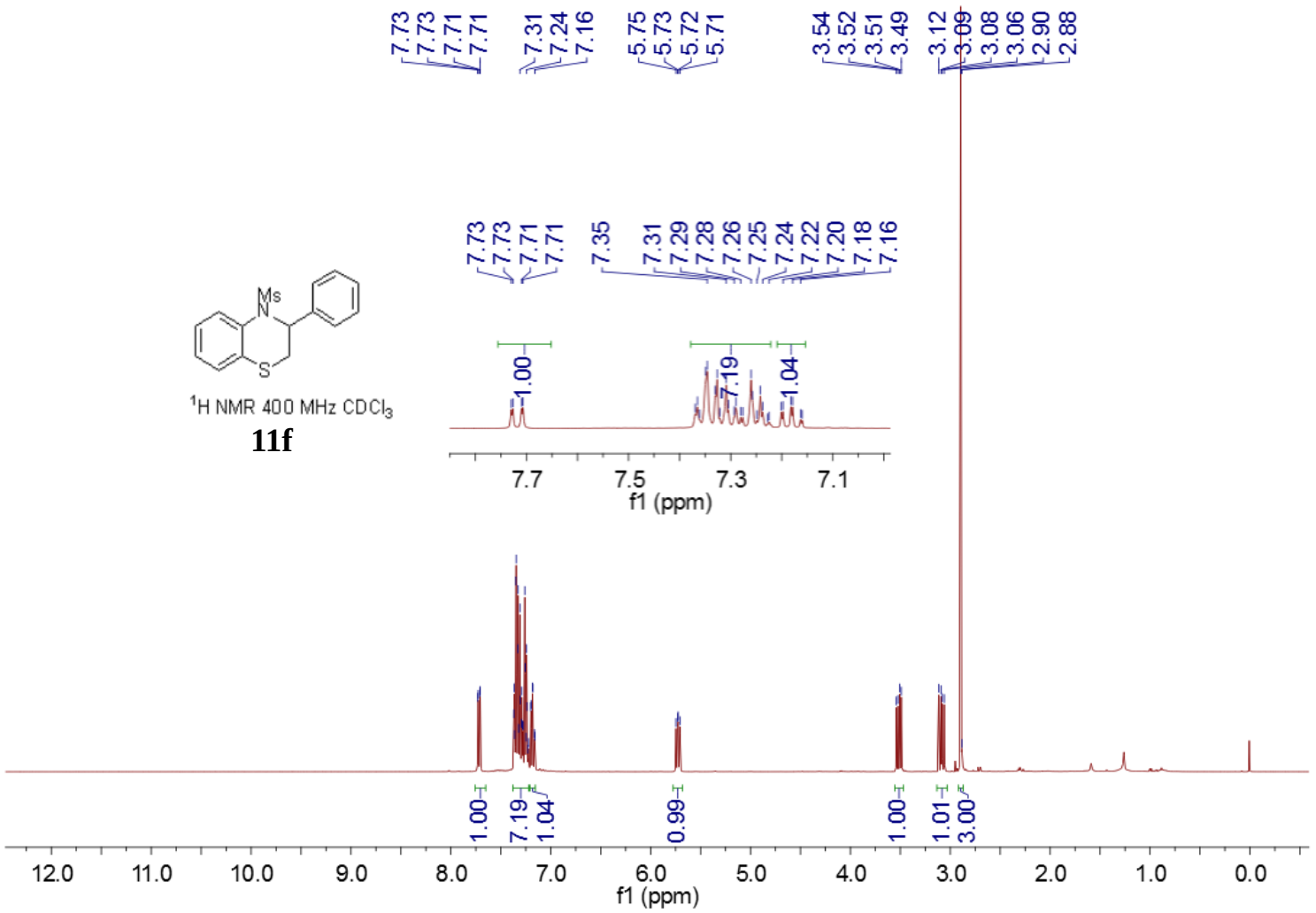

143.747
139.546
136.480
135.113
135.078
131.300
130.224
129.619
129.428
129.253
128.855
127.649
127.539
127.188
126.553
77.318
77.000
76.683
62.838
37.089
21.597
Ts
N
S
Cl
13C NMR 100 MHz CDCl3
11c
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

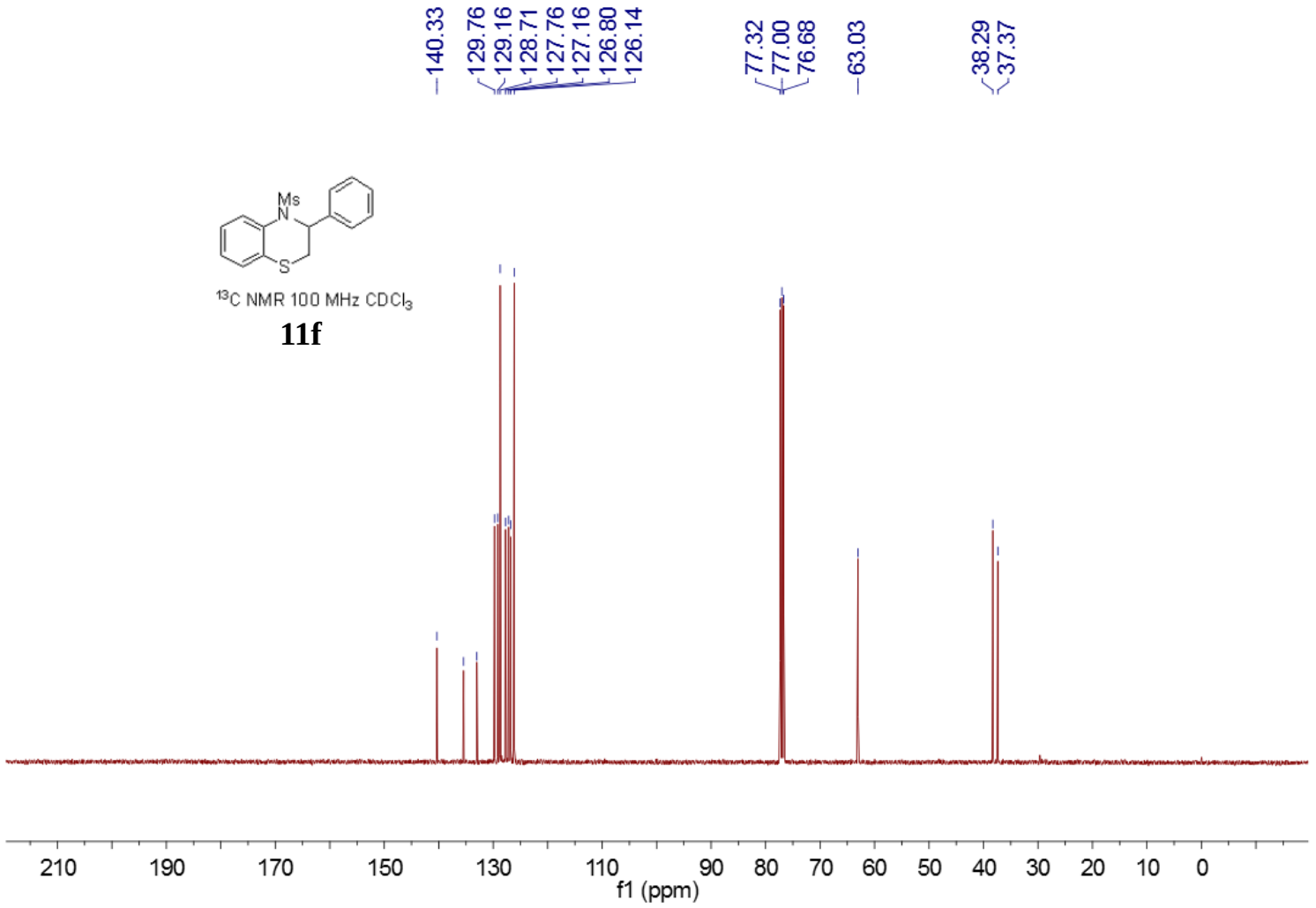

Br
Ts
N
S
1H NMR 400 MHz CDCl3
11d
7.840
7.838
7.819
7.260
7.208
7.157
7.101
5.672
5.656
5.653
5.637
3.169
3.154
2.940
2.920
2.906
2.886
2.399
7.520
7.388
7.352
7.260
7.228
7.208
7.176
7.157
7.118
7.105
1.00
1.00
2.06
1.99
1.10
2.98
2.03
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
1.00
1.99
1.10
2.98
2.03
1.02
1.01
1.10
3.01
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

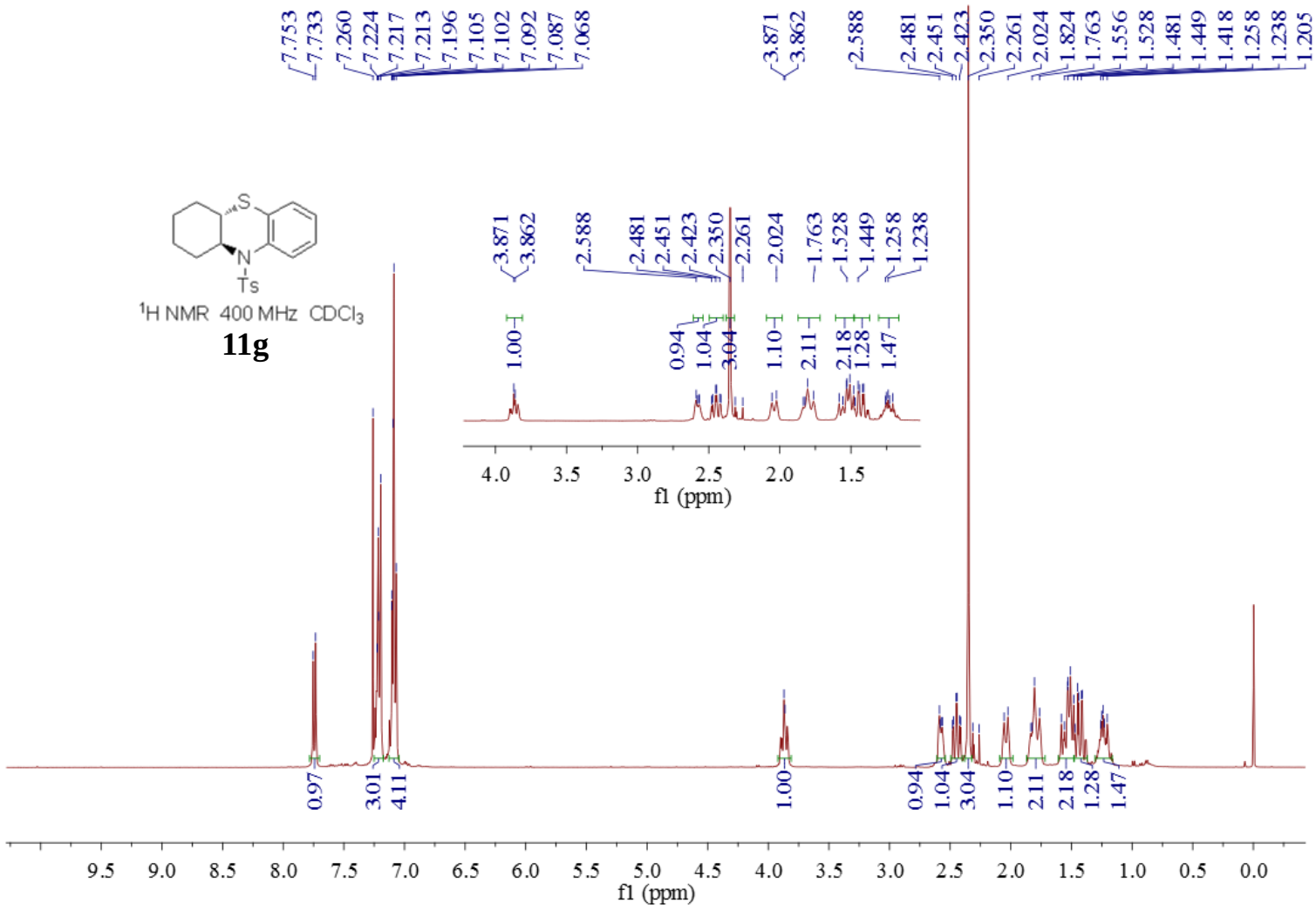

143.93
142.27
134.29
130.80
129.98
129.43
127.35
126.41
122.65
77.32
77.20
77.00
76.68
60.71
34.66
21.60
Br
Ts
N
S
^{1}C NMR 100 MHz CDCl$_3$
11d
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

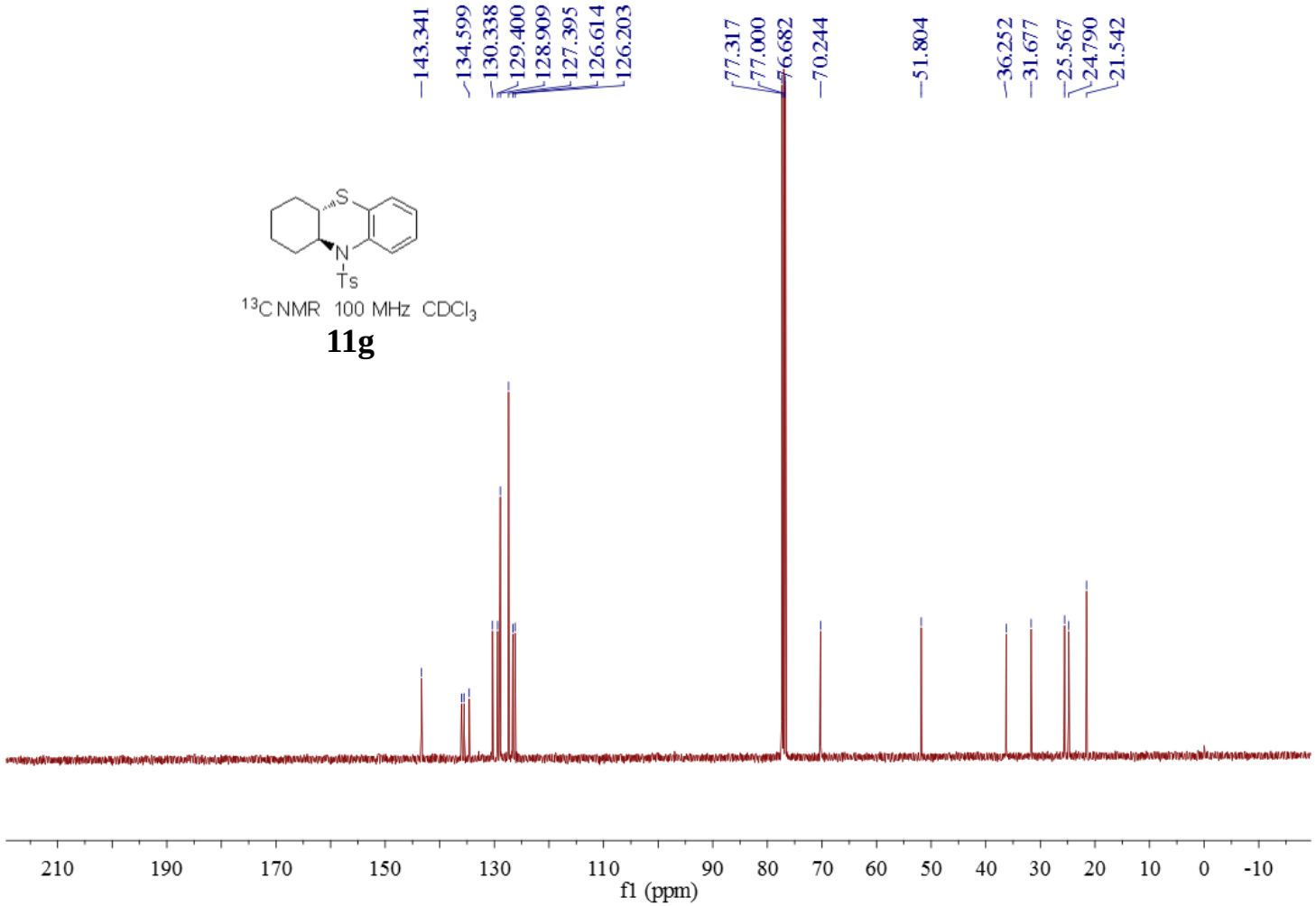

7.694
7.486
7.465
7.450
7.431
7.371
7.353
7.333
7.302
7.296
7.278
7.232
7.211
7.042
7.023
6.978
6.976
5.744
5.727
5.724
5.708
3.220
3.205
2.986
2.966
2.953
2.932
2.437
2.413
Ts
N
Me
Ph
S
^{1}H NMR 400 MHz CDCl$_3$
11e
0.96
4.01
2.06
1.02
1.98
1.00
0.98
1.00
1.01
1.05
6.13
f1 (ppm)

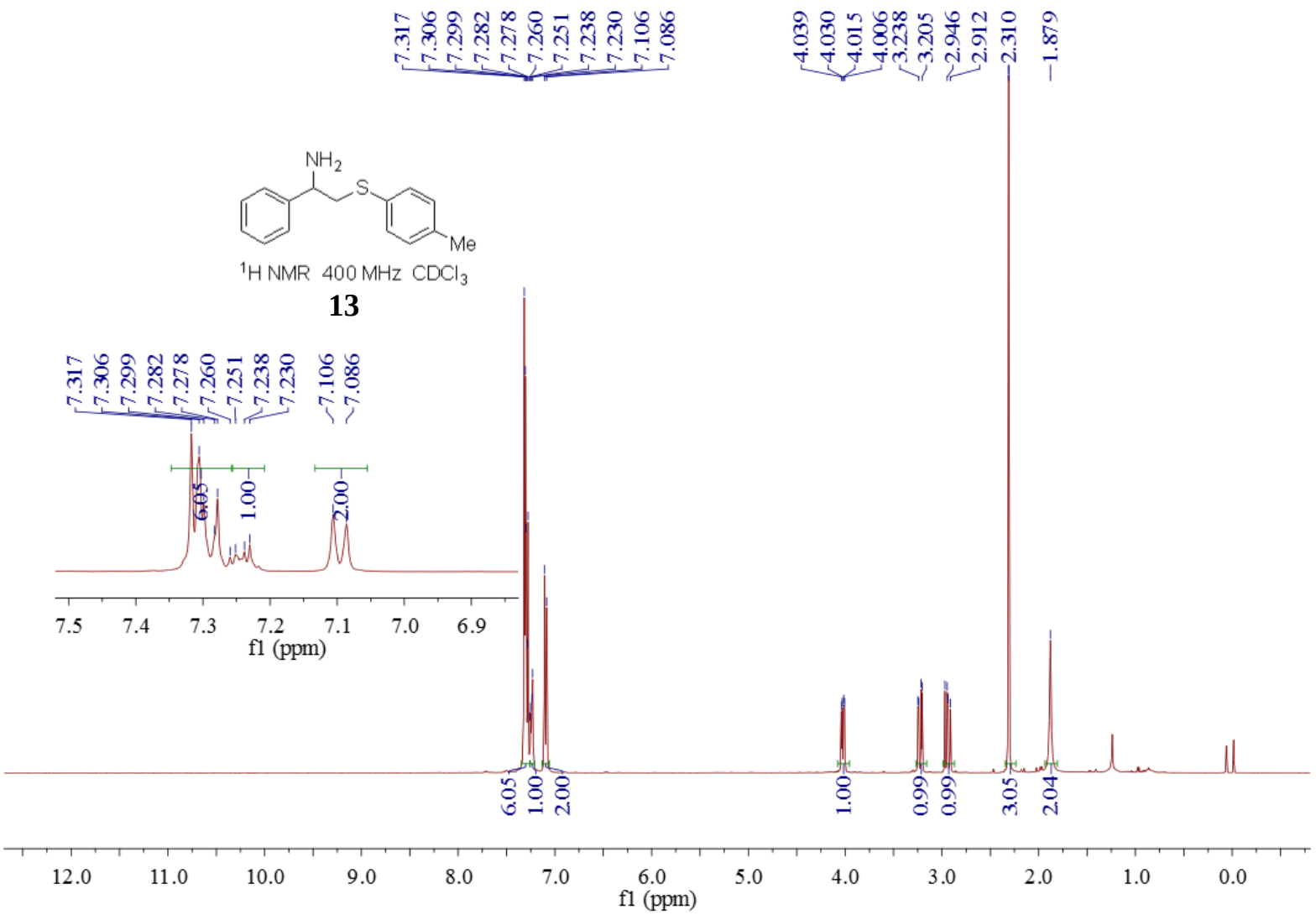

143.615
140.237
136.294
136.020
134.512
130.520
129.287
129.093
128.581
128.039
127.556
127.418
127.380
126.279
77.317
77.000
76.682
61.576
35.260
21.561
21.176
Ts
N
Me
Ph
S
13C NMR 100 MHz CDCl3
11e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

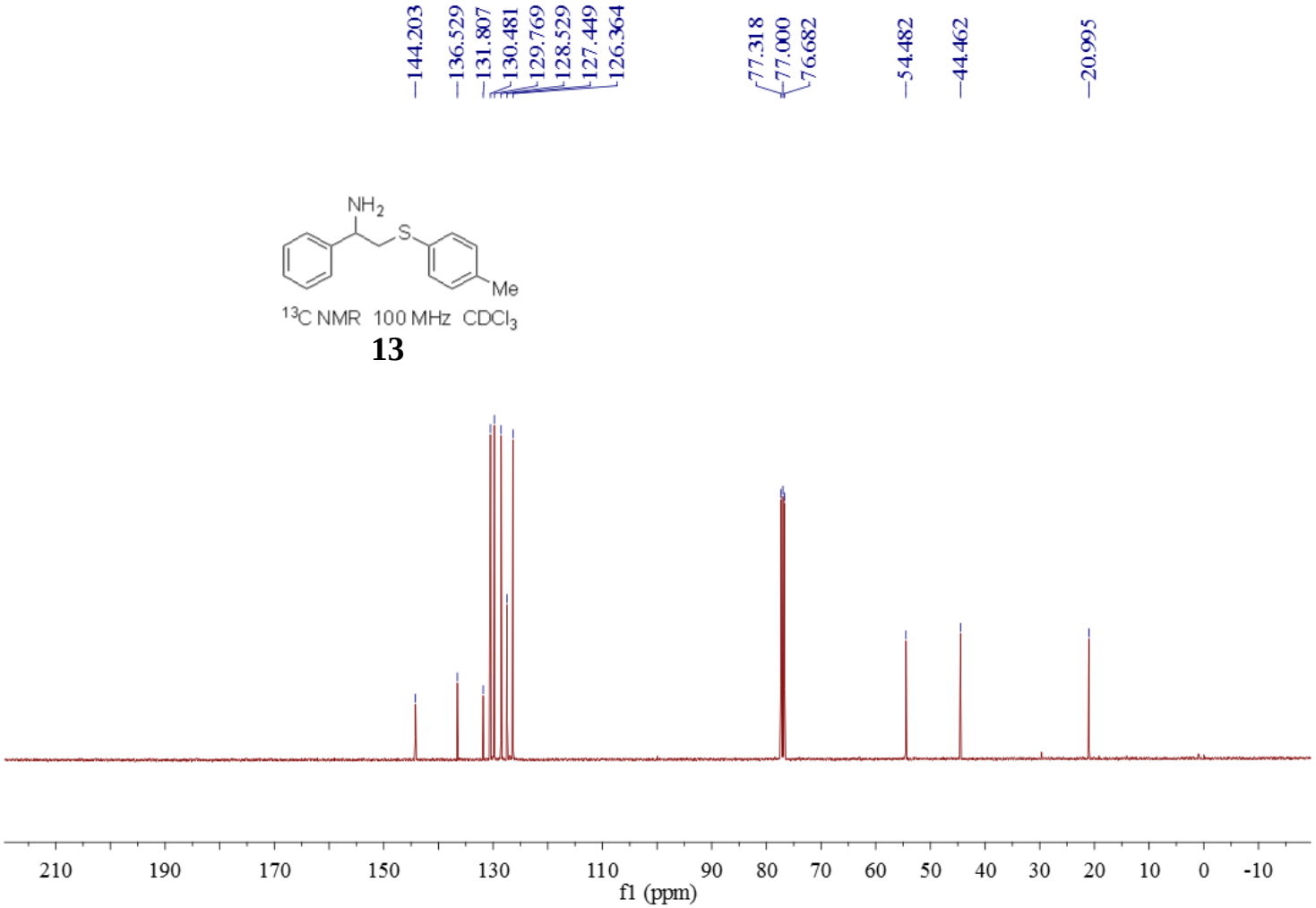

Ms
N
S
^{1}H NMR 400 MHz $CDCl_3$
11f
7.73
7.73
7.71
7.71
7.31
7.24
7.16
5.75
5.73
5.72
5.71
3.54
3.52
3.51
3.49
3.12
3.09
3.08
3.06
2.90
2.88
7.35
7.29
7.28
7.26
7.25
7.22
7.20
7.18
1.00
7.19
1.04
7.7
7.5
7.3
7.1
f1 (ppm)
1.00
7.19
1.04
0.99
1.00
1.01
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


140.33
129.76
129.16
128.71
127.76
127.16
126.80
126.14
77.32
77.00
76.68
63.03
38.29
37.37
Ms
N
S
13C NMR 100 MHz CDCl3
11f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

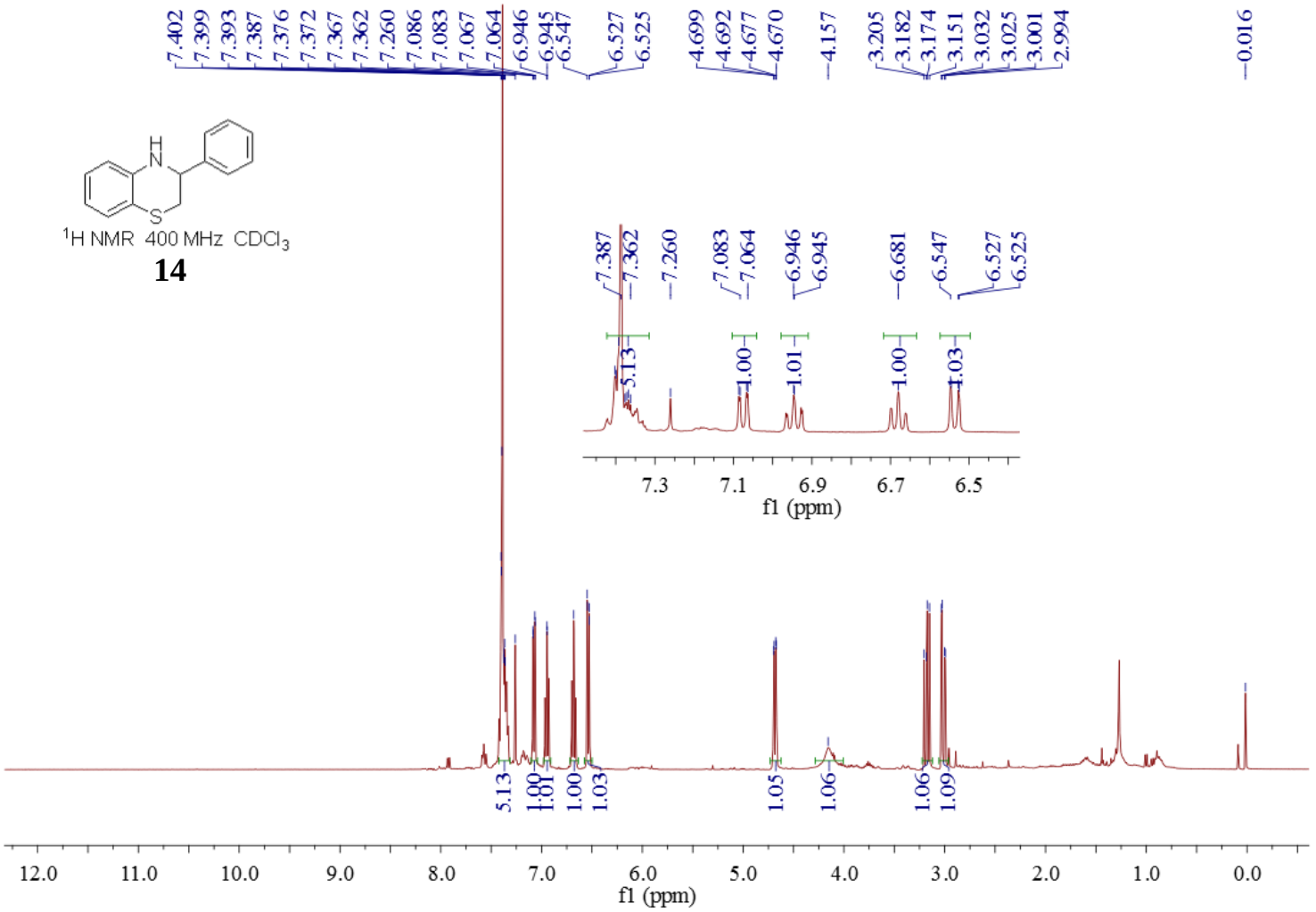

7.753
7.733
7.260
7.224
7.217
7.213
7.196
7.105
7.102
7.092
7.087
7.068
3.871
3.862
2.588
2.481
2.451
2.423
2.350
2.261
2.024
1.824
1.763
1.556
1.528
1.481
1.449
1.418
1.258
1.238
1.205
S
N
Ts
1H NMR 400 MHz CDCl3
11g
0.97
3.01
4.11
1.00
0.94
1.04
3.04
1.10
2.11
2.18
1.28
1.47
f1 (ppm)

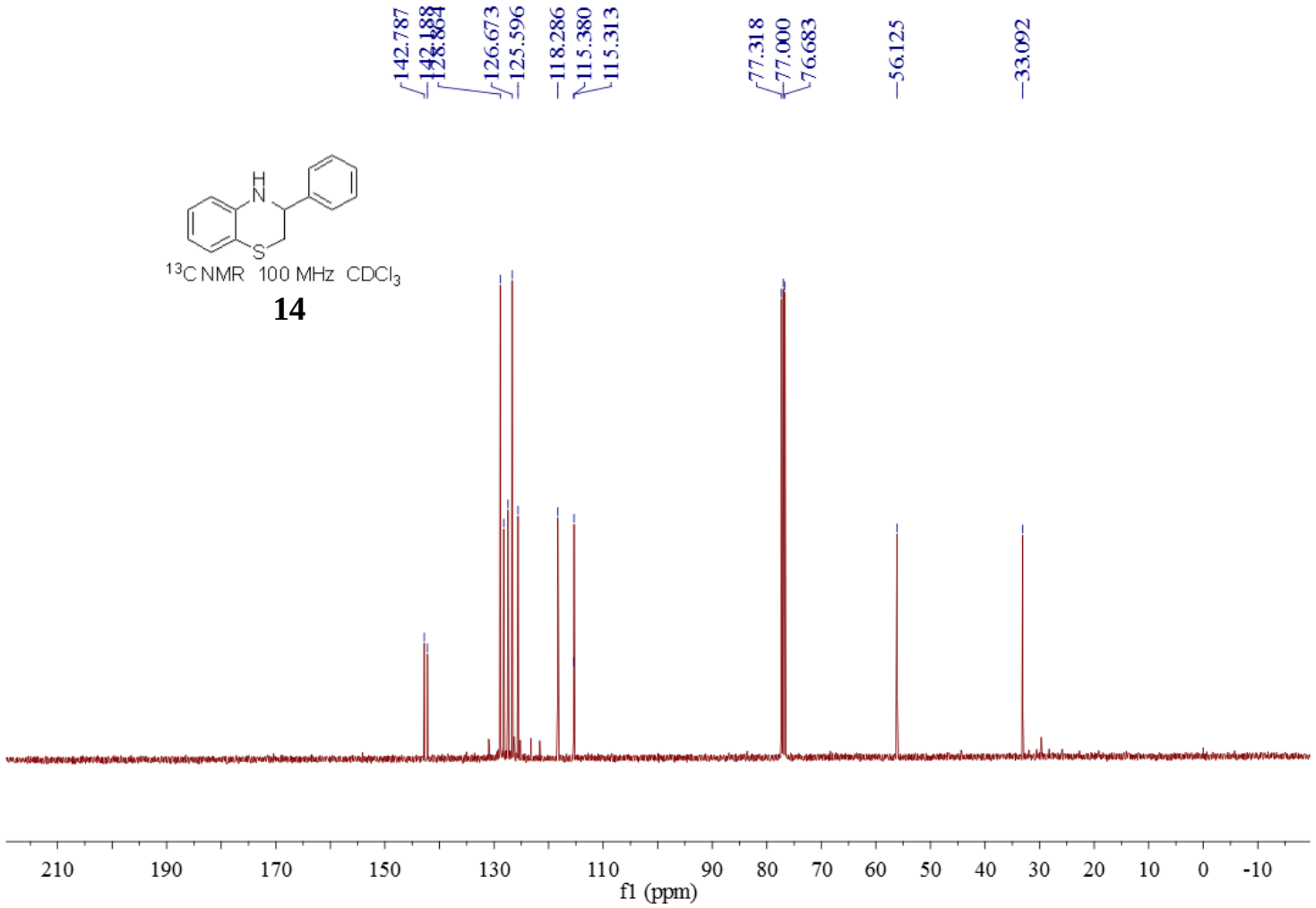

143.341
134.599
130.338
129.400
128.909
127.395
126.614
126.203
77.317
77.000
76.682
70.244
51.804
36.252
31.677
25.567
24.790
21.542
S
N
Ts
13C NMR 100 MHz CDCl3
11g
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.317
7.306
7.299
7.282
7.278
7.260
7.251
7.238
7.230
7.106
7.086
4.039
4.030
4.015
4.006
3.238
3.205
2.946
2.912
2.310
1.879
NH2
S
Me
1H NMR 400 MHz CDCl3
13
6.05
1.00
2.00
1.00
0.99
0.99
3.05
2.04
f1 (ppm)
f1 (ppm)


144.203
136.529
131.807
130.481
129.769
128.529
127.449
126.364
77.318
77.000
76.682
54.482
44.462
20.995
NH2
S
Me
13C NMR 100 MHz CDCl3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

13


7.402
7.399
7.393
7.387
7.376
7.372
7.367
7.362
7.260
7.086
7.083
7.067
7.064
6.946
6.945
6.547
6.527
6.525
4.699
4.692
4.677
4.670
4.157
3.205
3.182
3.174
3.151
3.032
3.025
3.001
2.994
0.016
H
N
S
1H NMR 400 MHz CDCl3
14
7.387
7.362
7.260
7.083
7.064
6.946
6.945
6.681
6.547
6.527
6.525
5.13
1.00
1.01
1.00
1.03
7.3
7.1
6.9
6.7
6.5
f1 (ppm)
5.13
1.00
1.01
1.00
1.03
1.05
1.06
1.06
1.09
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


142.787
126.673
125.596
118.286
115.380
115.313
77.318
77.000
76.683
56.125
33.092
^{13}C NMR 100 MHz CDCl$_3$
14
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)