Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Chromophoric Materials Derived from a Natural Azulene: Syntheses, Halochromism and One- and Two-Photon Microlithography

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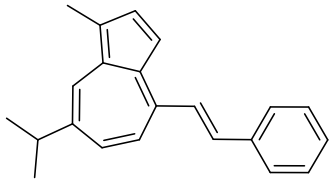


3a

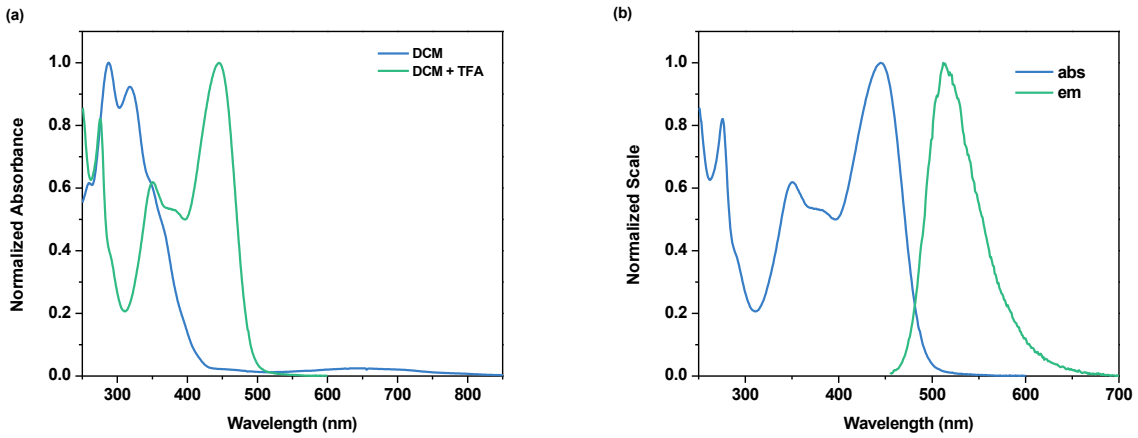
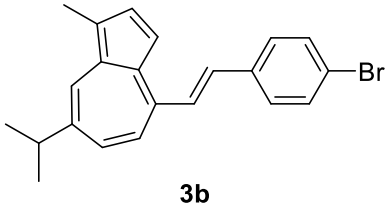


Figure S1. (a) Normalized absorbance spectra of **3a** in DCM, λ_{max} = 318 nm, and DCM:TFA (10%), λ_{max} = 445 nm. (b) Normalized abs and em spectra of **3a** in DCM:TFA (10%), λ_{ex} = 445 nm, λ_{max} = 512 nm, QY = 0.03 (referenced to CV in MeOH).



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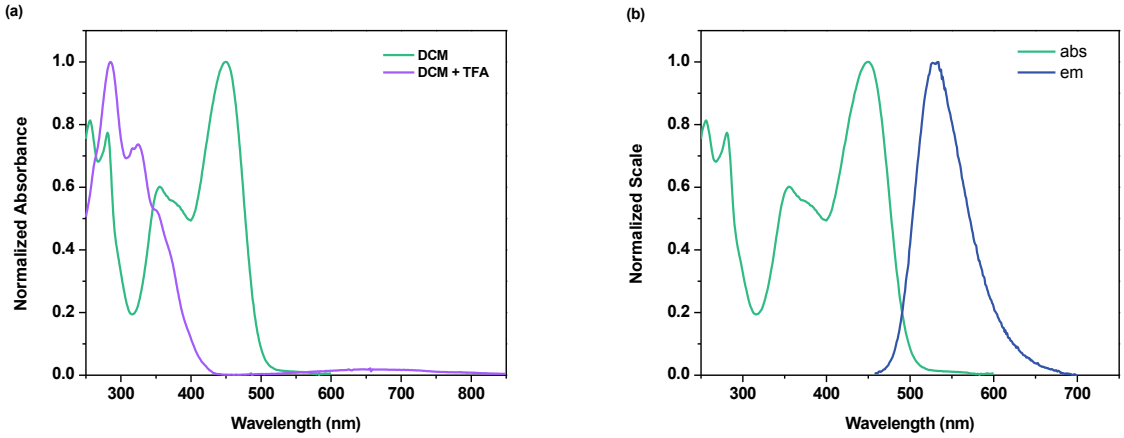
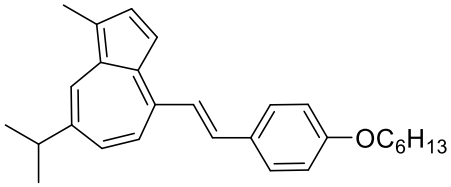


Figure S2. (a) Normalized absorbance spectra of **3b** in DCM, λ_{max} = 318 nm, and DCM:TFA (10%), λ_{max} = 450 nm. (b) Normalized abs and em spectra of **3b** in DCM:TFA (10%), λ_{ex} = 445 nm, λ_{max} = 534 nm, QY = 0.05 (referenced to CV in MeOH).



3c

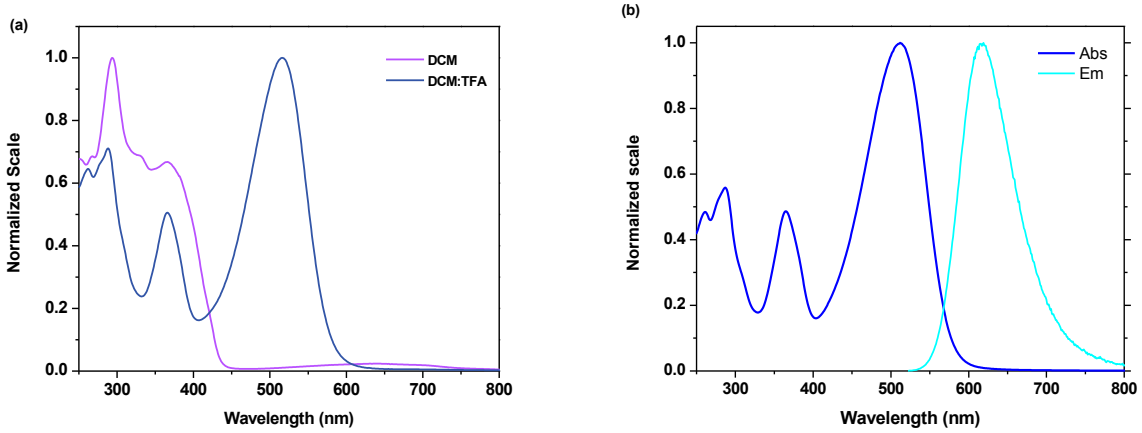
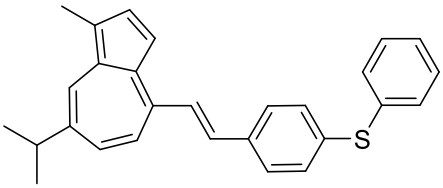


Figure S3. (a) Normalized absorbance spectra of **3c** in DCM, λ_{max} = 367 nm, and DCM:TFA (10%), λ_{max} = 516 nm. (b) Normalized abs and em spectra of **3c** in DCM:TFA (10%), λ_{ex} = 445 nm, λ_{max} = 534 nm, QY = 0.12 (referenced to CV in MeOH).



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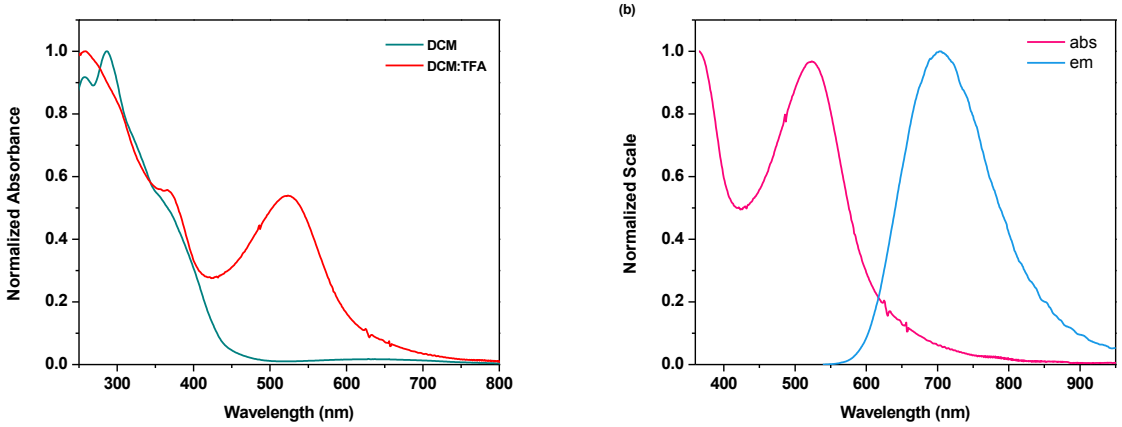
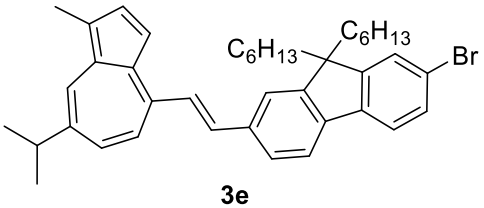


Figure S4. (a) Normalized absorbance spectra of **3d** in DCM, λ_{max} = 370 nm, and DCM:TFA (10%), λ_{max} = 523 nm. (b) Normalized abs and em spectra of **3d** in DCM:TFA (10%), λ_{ex} = 523 nm, λ_{max} = 705 nm, QY = 0.11 (referenced to CV in MeOH).



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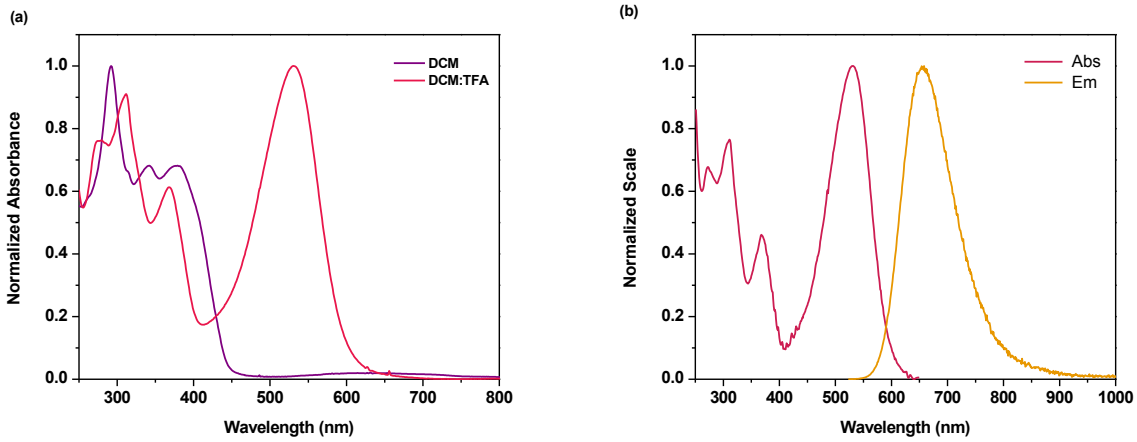
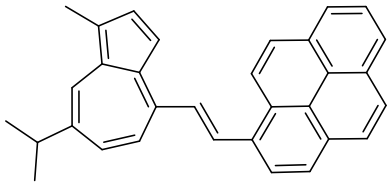


Figure S5. (a) Normalized absorbance spectra of **3e** in DCM, λ_{max} = 379 nm, and DCM:TFA (10%), λ_{max} = 530 nm. (b) Normalized abs and em spectra of **3e** in DCM:TFA (10%), λ_{ex} = 530 nm, λ_{max} = 656 nm, QY = 0.70 (referenced to Rh6G in EtOH).



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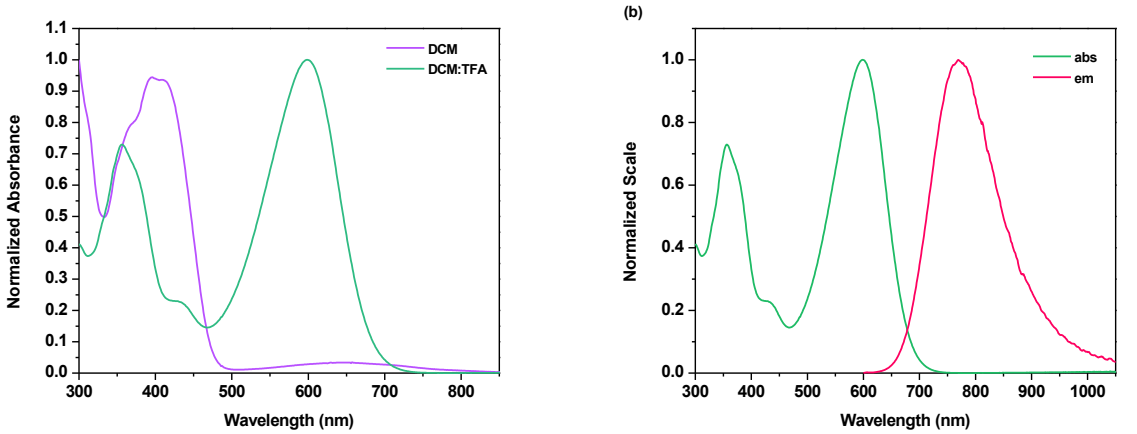
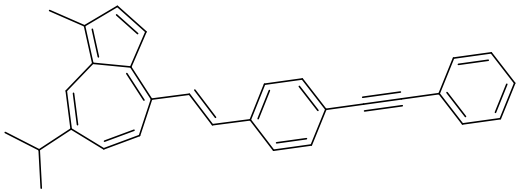


Figure S6. (a) Normalized absorbance spectra of **3f** in DCM, λ_{max} = 405 nm, and DCM:TFA (10%), λ_{max} = 599 nm. (b) Normalized abs and em spectra of **3f** in DCM:TFA (10%), λ_{ex} = 600 nm, λ_{max} = 768 nm, QY = 0.05 (referenced to CV in MeOH).



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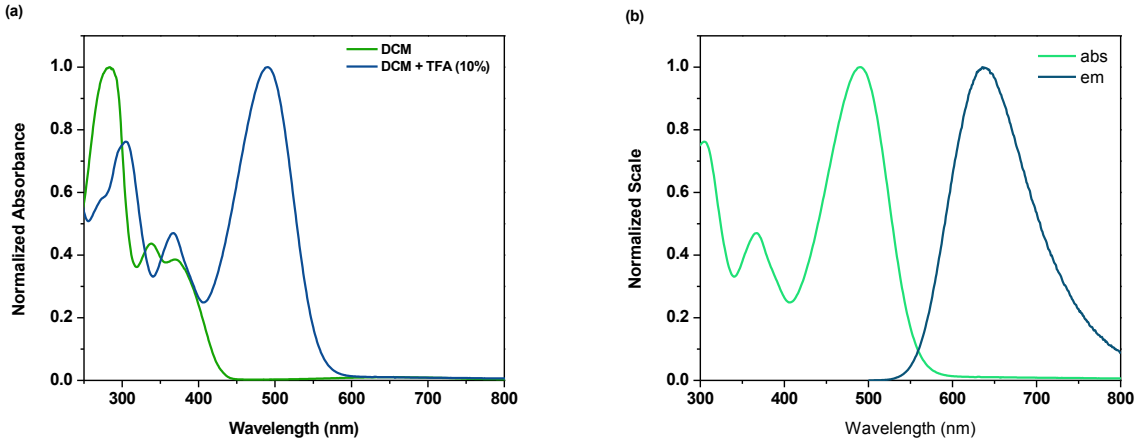
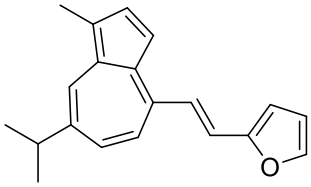


Figure S7. (a) Normalized absorbance spectra of **3g** in DCM, λ_{max} = 369 nm, and DCM:TFA (10%), λ_{max} = 490 nm. (b) Normalized abs and em spectra of **3g** in DCM:TFA (10%), λ_{ex} = 490 nm, λ_{max} = 636 nm, QY = 0.55 (referenced to CV in MeOH).



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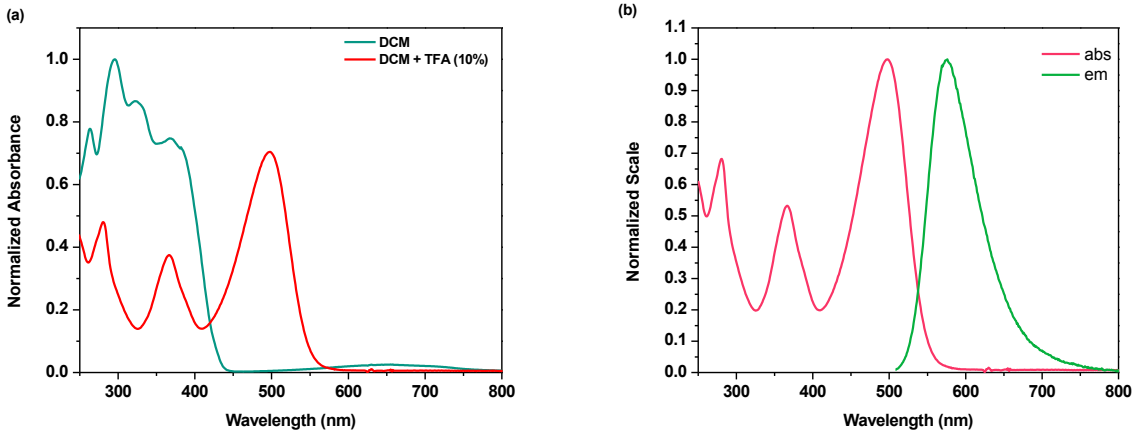
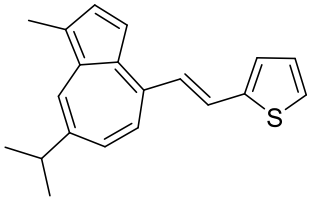


Figure S8. (a) Normalized absorbance spectra of **3h** in DCM, λ_{max} = 332 nm, and DCM:TFA (10%), λ_{max} = 498 nm. (b) Normalized abs and em spectra of **3h** in DCM:TFA (10%), λ_{ex} = 498 nm, λ_{max} = 576 nm, QY = 0.19 (referenced to CV in MeOH).



3i

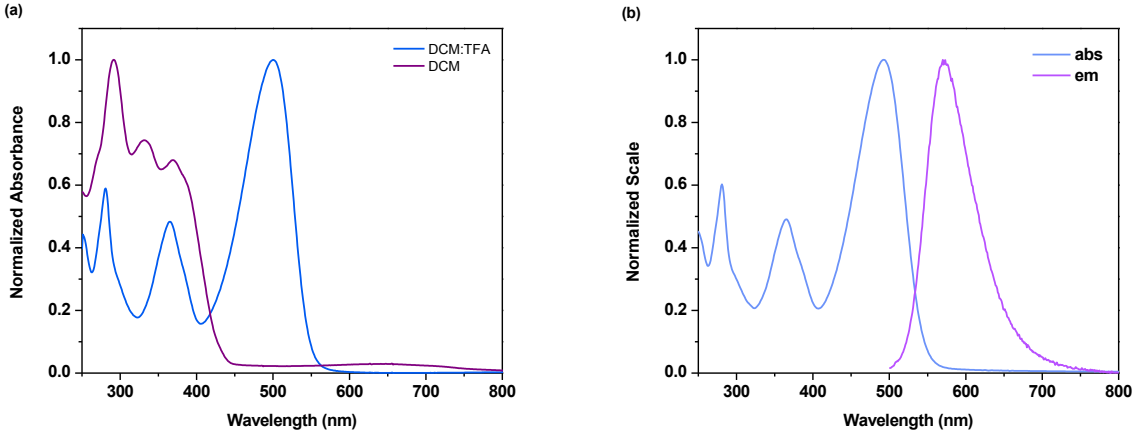
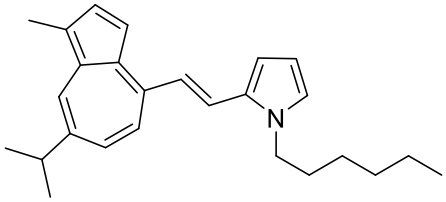


Figure S9. (a) Normalized absorbance spectra of **3i** in DCM, λ_{max} = 332 nm, and DCM:TFA (10%), λ_{max} = 493 nm. (b) Normalized abs and em spectra of **3i** in DCM:TFA (10%), λ_{ex} = 493 nm, λ_{max} = 570 nm, QY = 0.02 (referenced to CV in MeOH).



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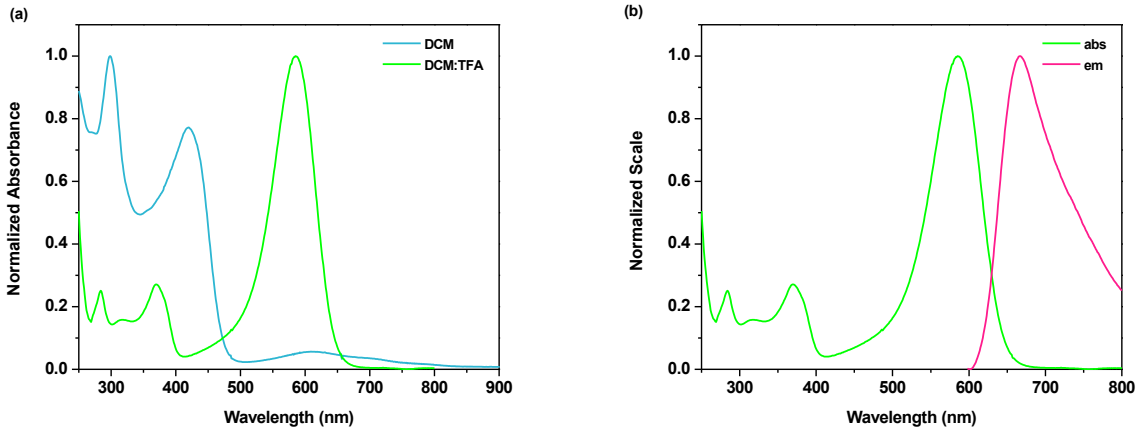
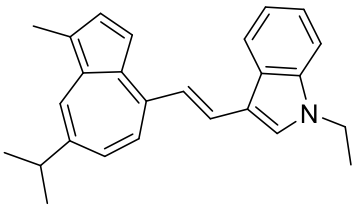


Figure S10. (a) Normalized absorbance spectra of **3j** in DCM, λ_{max} = 420 nm, and DCM:TFA (10%), λ_{max} = 587 nm. (b) Normalized abs and em spectra of **3j** in DCM:TFA (10%), λ_{ex} = 587 nm, λ_{max} = 663 nm, QY = 0.01 (referenced to CV in MeOH).



3k

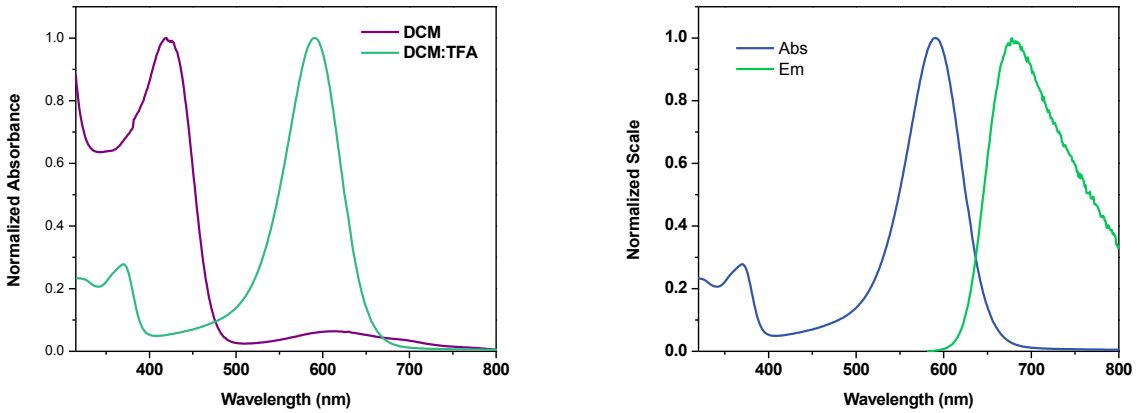
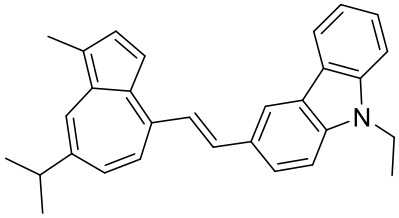


Figure S11. (a) Normalized absorbance spectra of **3k** in DCM, λ_{max} = 425 nm, and DCM:TFA (10%), λ_{max} = 590 nm. (b) Normalized abs and em spectra of **3k** in DCM:TFA (10%), λ_{ex} = 590 nm, λ_{max} = 678 nm.



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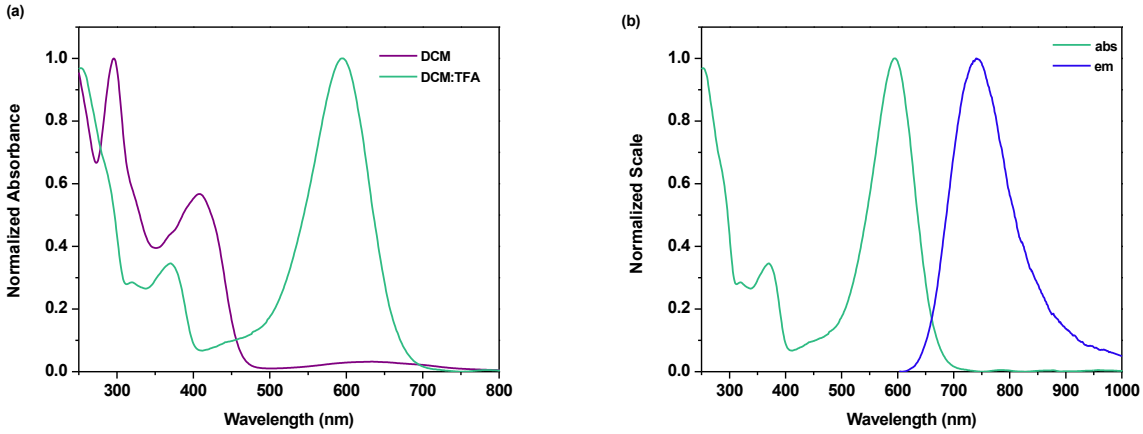
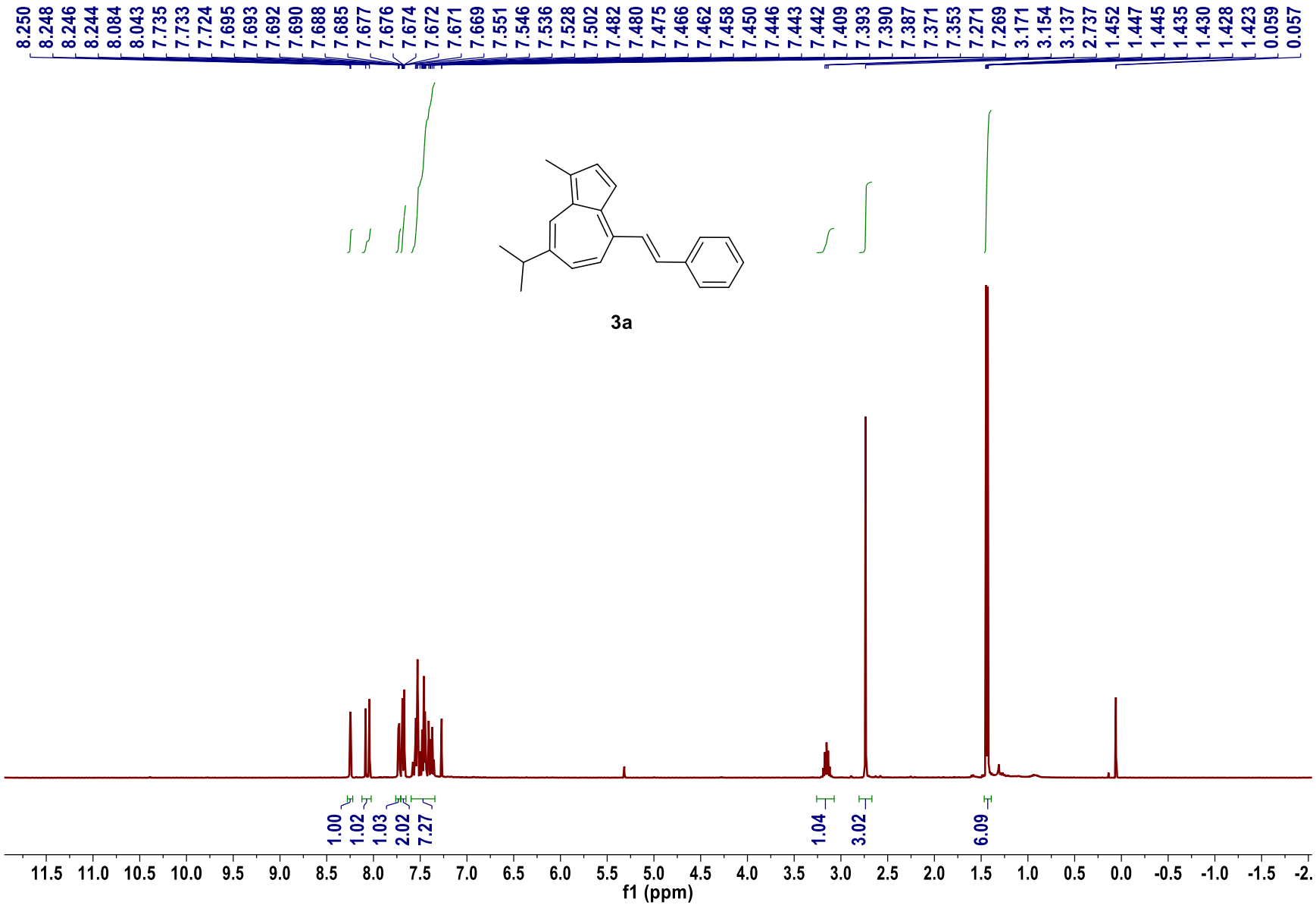


Figure S12. (a) Normalized absorbance spectra of **3l** in DCM, λ_{max} = 407 nm, and DCM:TFA (10%), λ_{max} = 595 nm. (b) Normalized abs and em spectra of **3l** in DCM:TFA (10%), λ_{ex} = 593 nm, λ_{max} = 744 nm.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7.690
7.688
7.685
7.677
7.676
7.674
7.672
7.671
7.669
7.551
7.546
7.536
7.528
7.502
7.482
7.480
7.475
7.466
7.462
7.458
7.450
7.446
7.443
7.442
7.409
7.393
7.390
7.387
7.371
7.353
7.271
7.269
3.171
3.154
3.137
2.737
1.452
1.447
1.445
1.435
1.430
1.428
1.423
0.059
0.057
3a
1.00
1.02
1.03
2.02
7.27
1.04
3.02
6.09
11.5 11.0 10.5 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 -0.5 -1.0 -1.5 -2.
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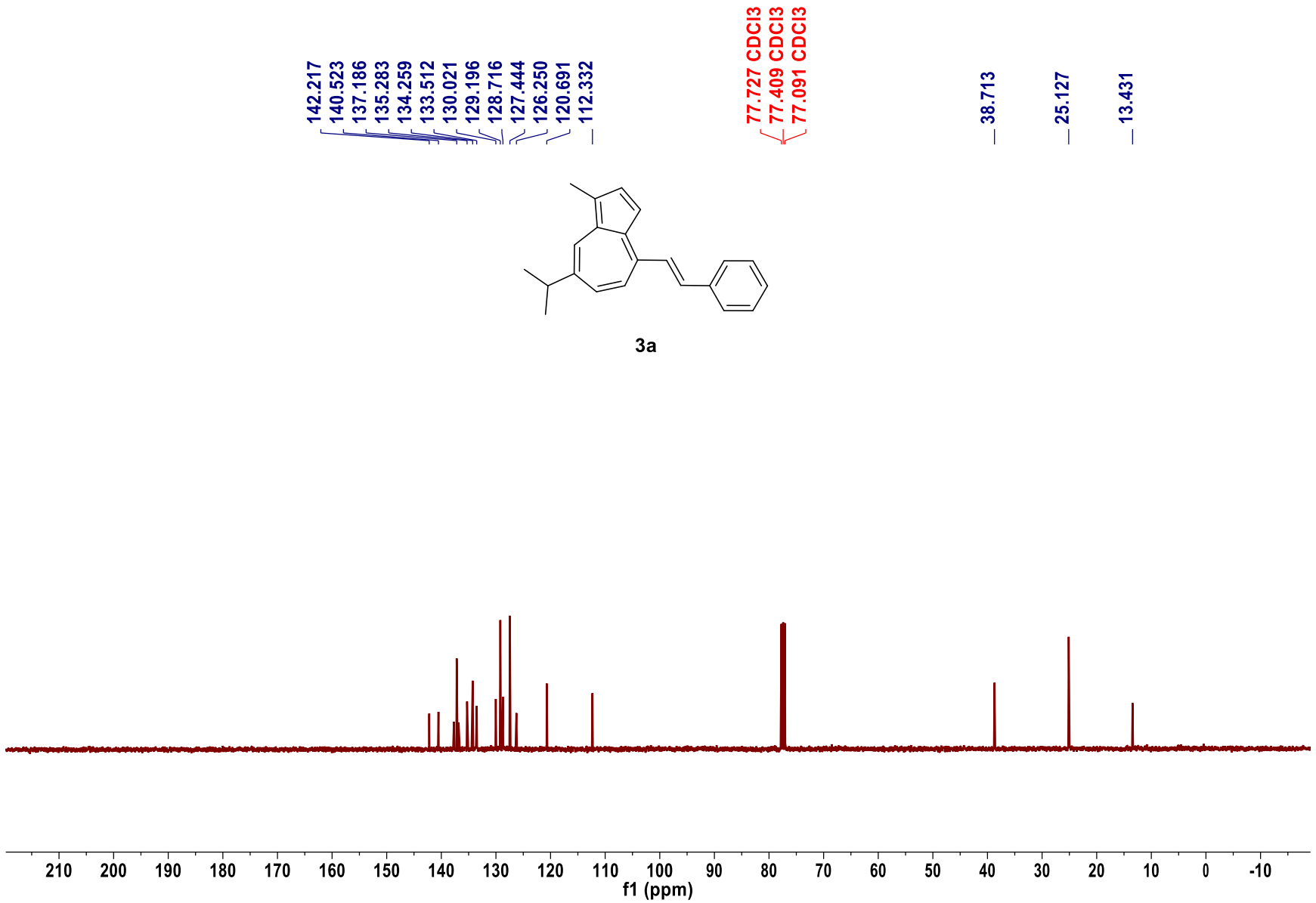
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120.691
112.332
77.727 CDCl3
77.409 CDCl3
77.091 CDCl3
38.713
25.127
13.431
3a
210
200
190
180
170
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150
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110
100
90
80
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30
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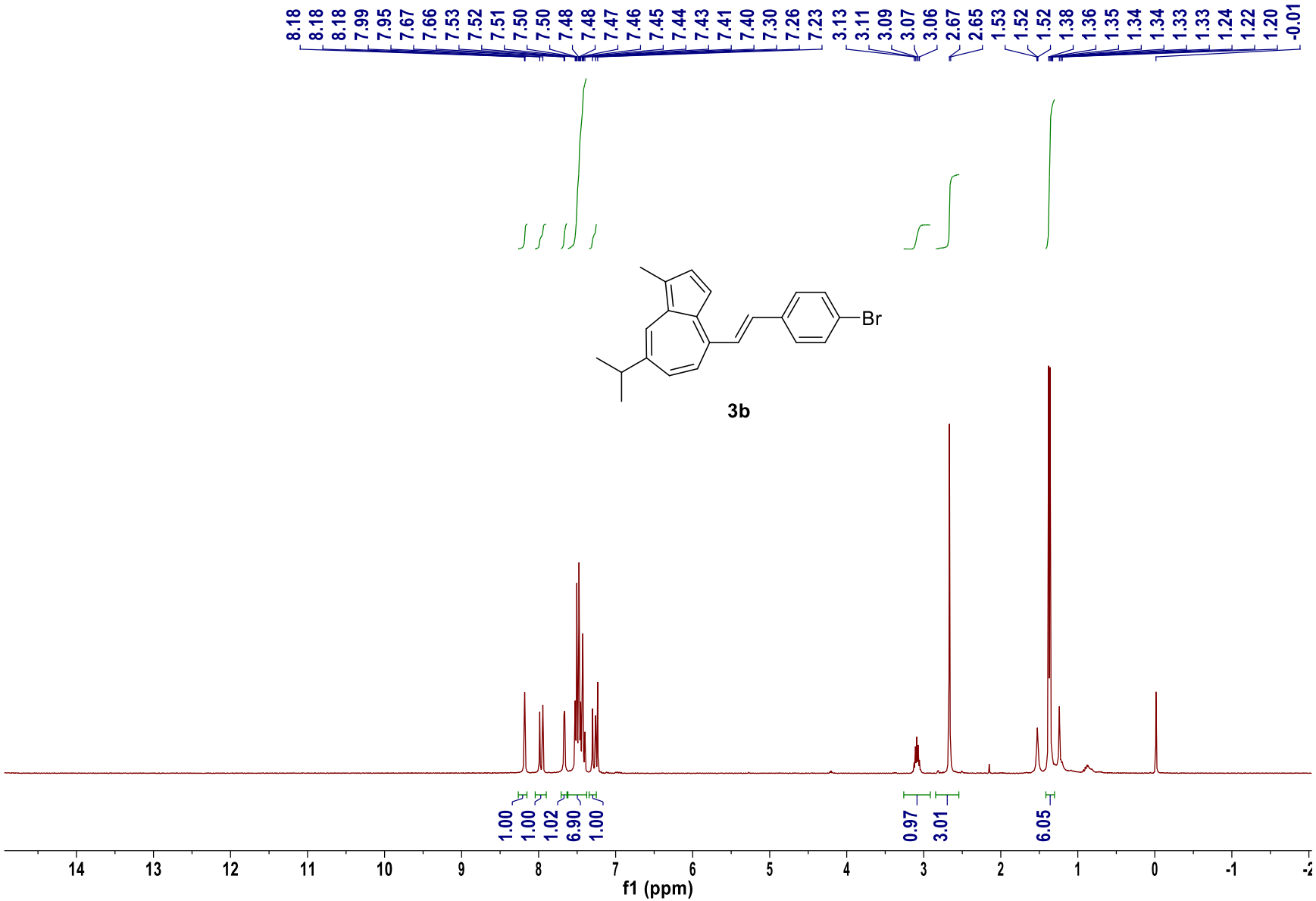
0
-10
f1 (ppm)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7.48
7.47
7.46
7.45
7.44
7.43
7.41
7.40
7.30
7.26
7.23
3.13
3.11
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3.07
3.06
2.67
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1.33
1.24
1.22
1.20
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3b
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1.00
1.02
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1.00
0.97
3.01
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8
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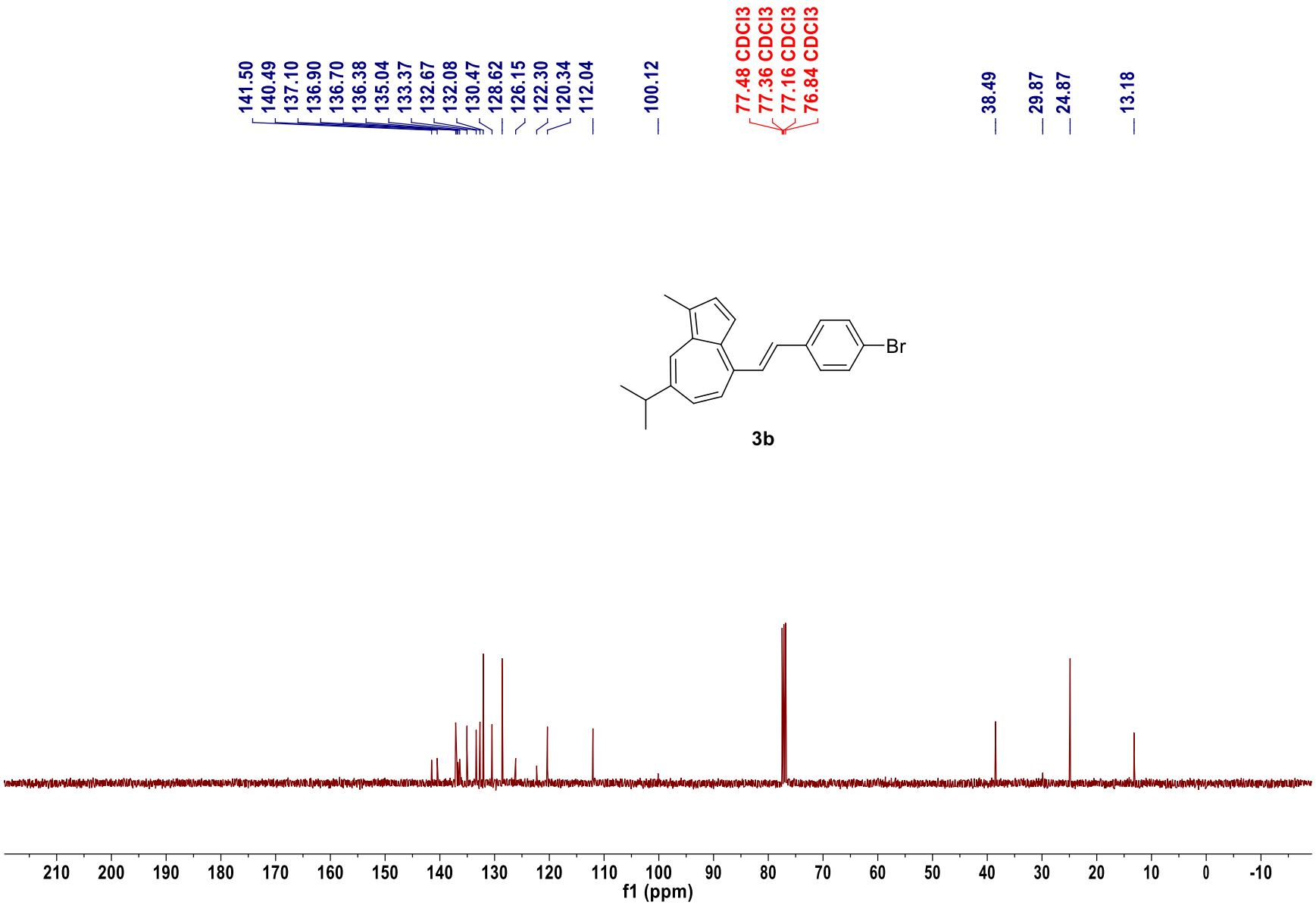
4
3
2
1
0
-1
f1 (ppm)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136.38
135.04
133.37
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130.47
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122.30
120.34
112.04
100.12
77.48 CDCl3
77.36 CDCl3
77.16 CDCl3
76.84 CDCl3
38.49
29.87
24.87
13.18
Br
3b
210
200
190
180
170
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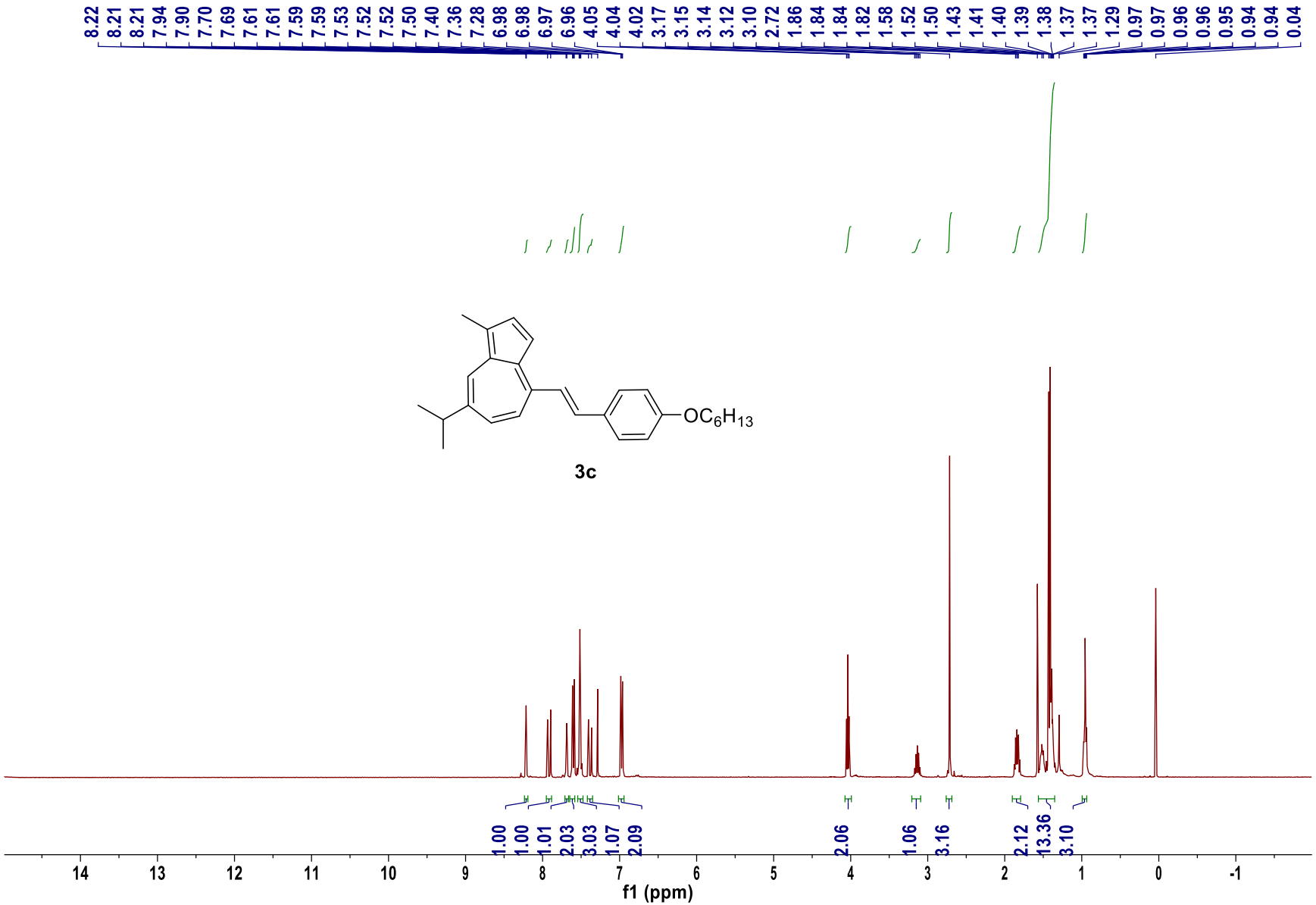
f1 (ppm)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OC6H13
3c
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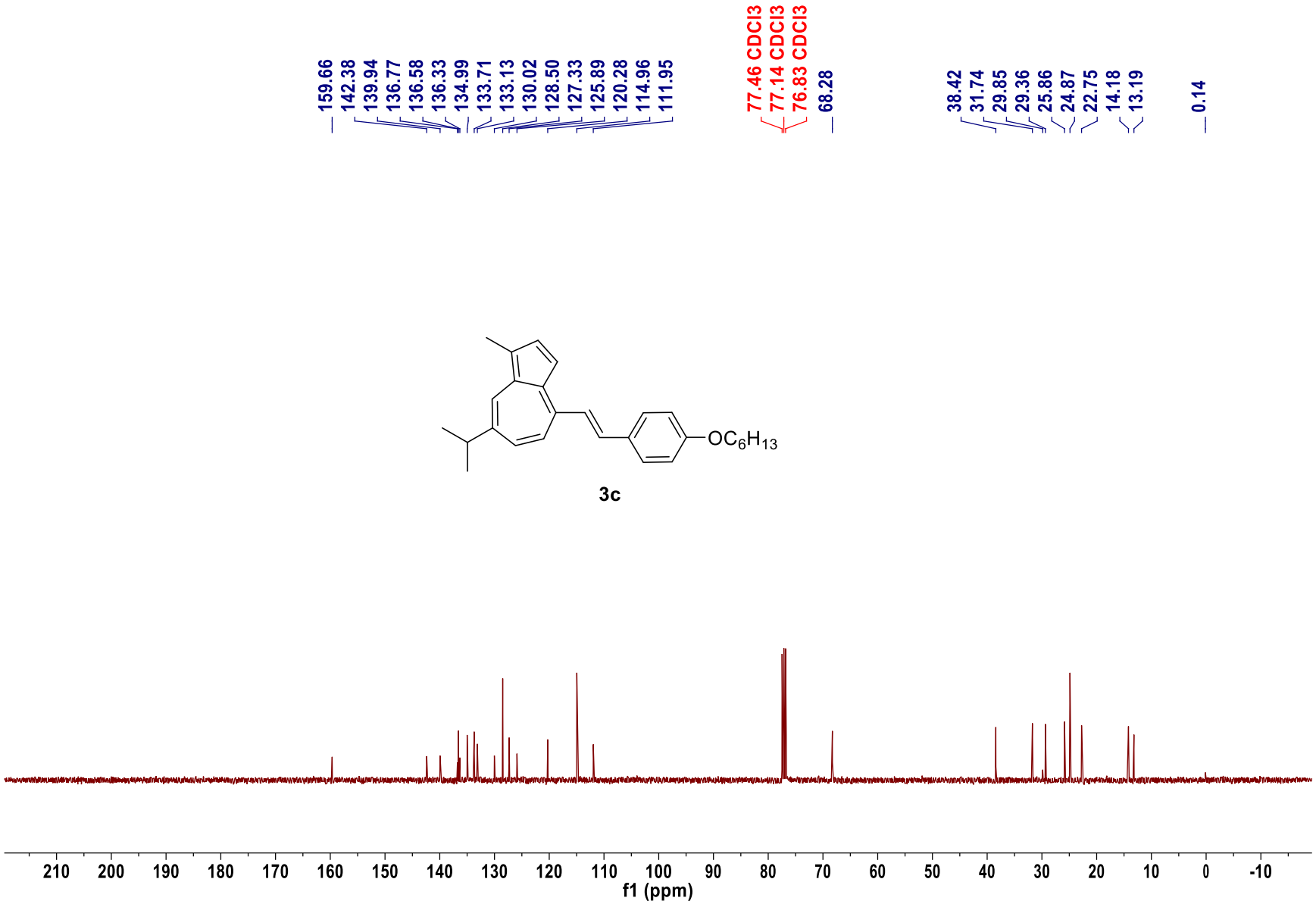
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136.33
134.99
133.71
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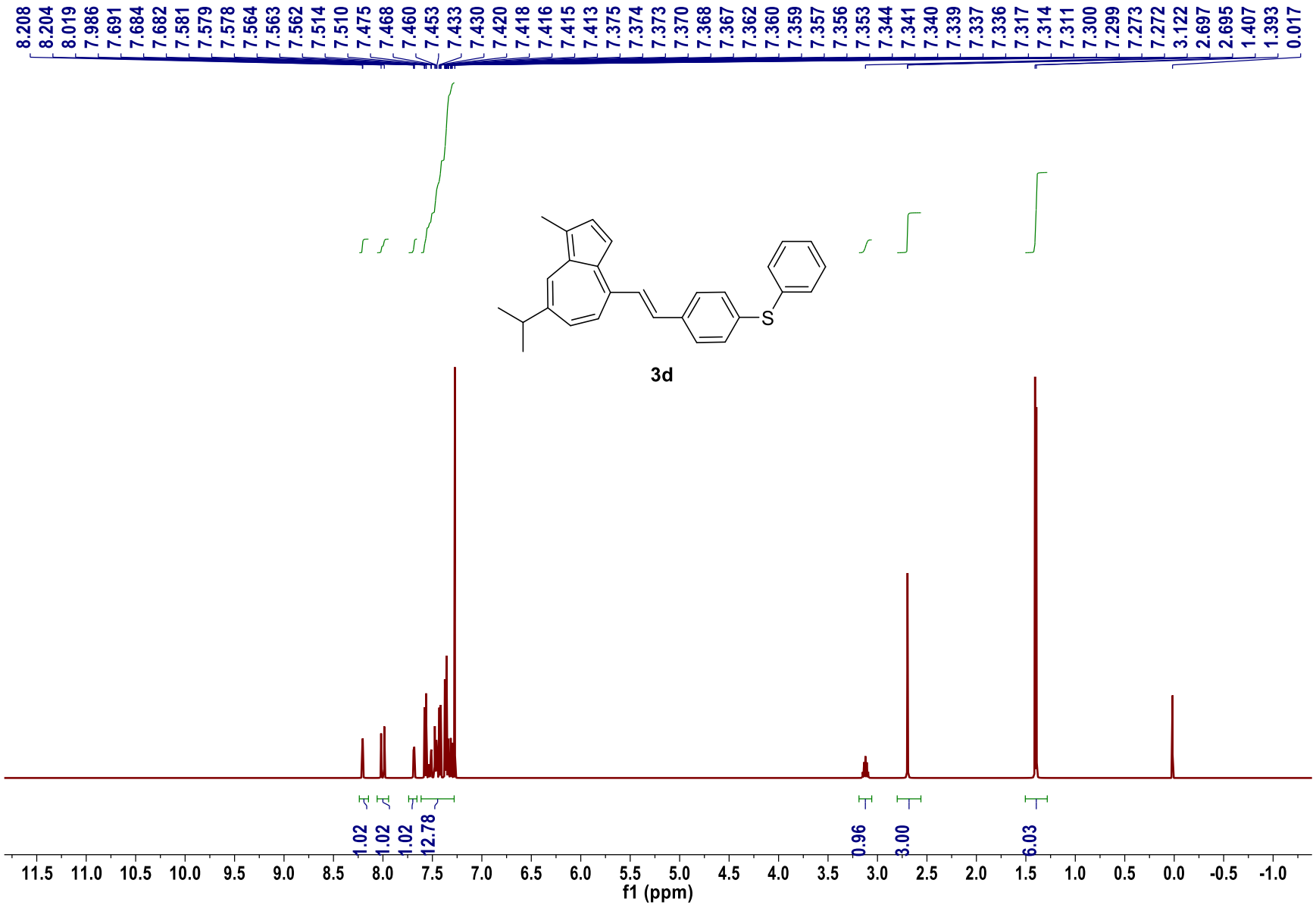
130.02
128.50
127.33
125.89
120.28
114.96
111.95
77.46 CDCl3
77.14 CDCl3
76.83 CDCl3
68.28
38.42
31.74
29.85
29.36
25.86
24.87
22.75
14.18
13.19
0.14
OC6H13
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.317
7.314
7.311
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7.299
7.273
7.272
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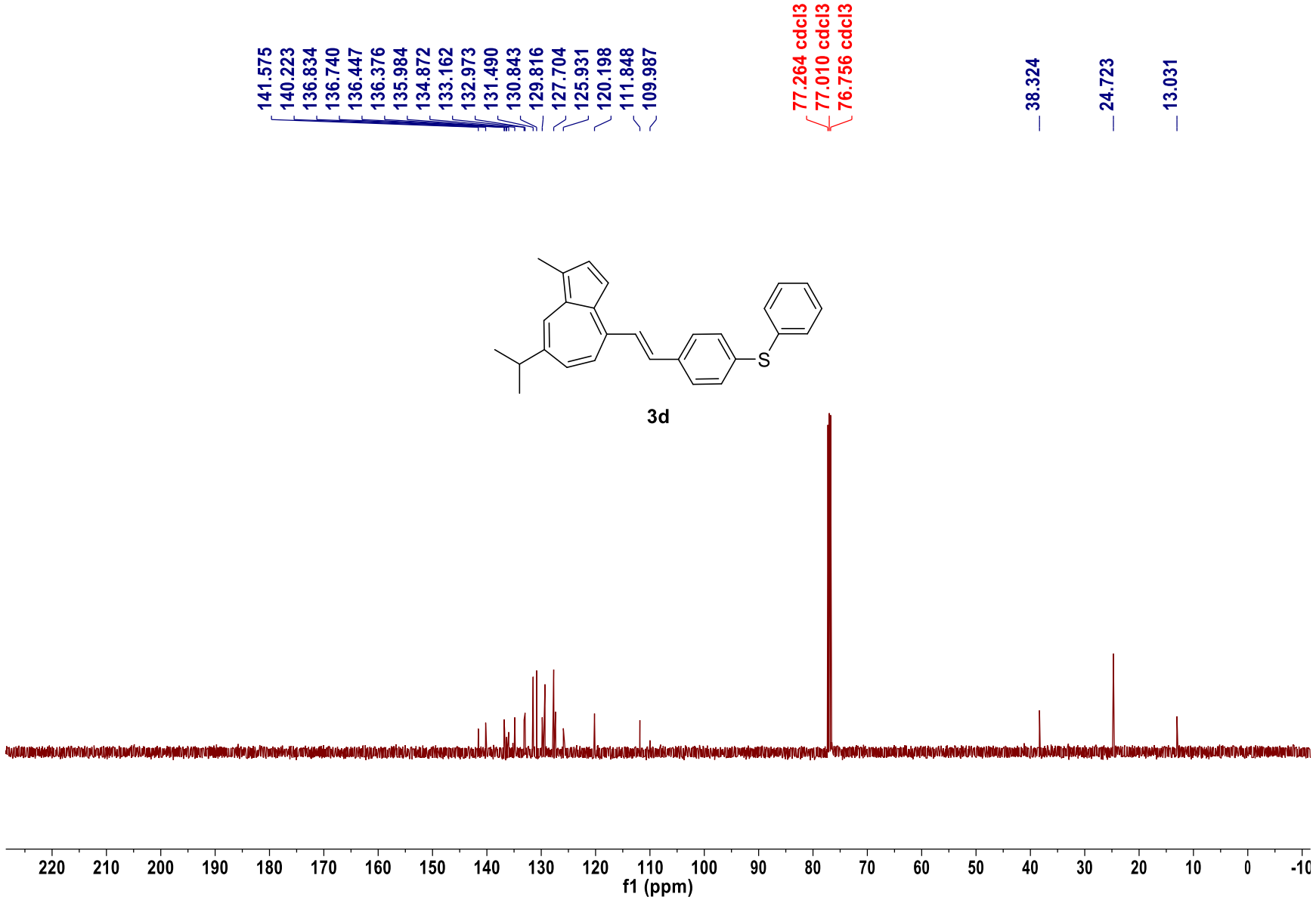
2.697
2.695
1.407
1.393
0.017
S
3d
1.02
1.02
1.02
12.78
0.96
3.00
6.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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129.816
127.704
125.931
120.198
111.848
109.987
77.264 cdcl3
77.010 cdcl3
76.756 cdcl3
38.324
24.723
13.031
S
3d
220
210
200
190
180
170
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100
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40
30
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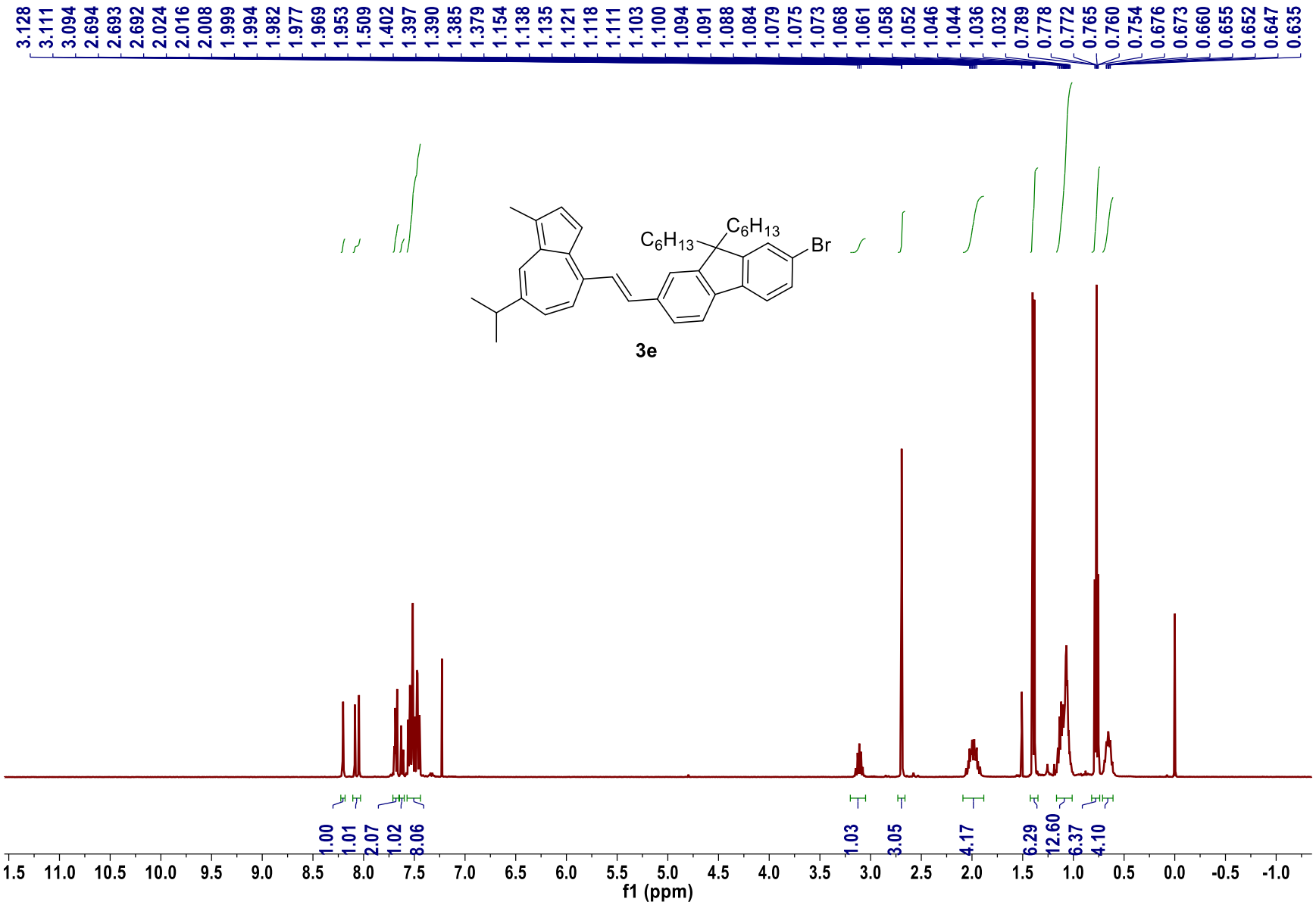
f1 (ppm)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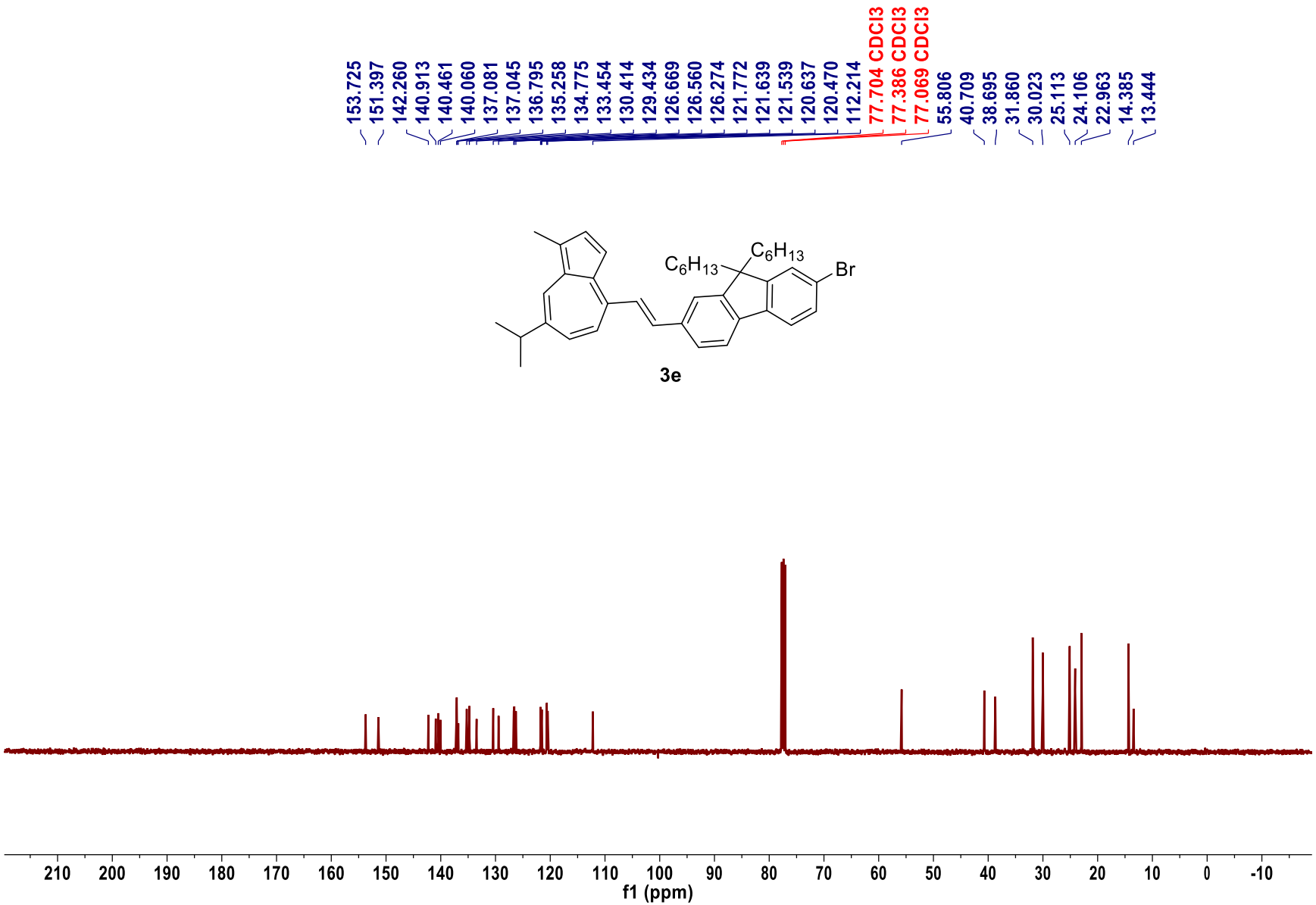
C6H13
C6H13
Br
3e
1.00 1.01 2.07 1.02 8.06 1.03 3.05 4.17 6.29 12.60 6.37 4.10
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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133.454
130.414
129.434
126.669
126.560
126.274
121.772
121.639
121.539
120.637
120.470
112.214
77.704 CDCl3
77.386 CDCl3
77.069 CDCl3
55.806
40.709
38.695
31.860
30.023
25.113
24.106
22.963
14.385
13.444
C6H13
C6H13
Br
3e
210
200
190
180
170
160
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140
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120
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100
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80
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60
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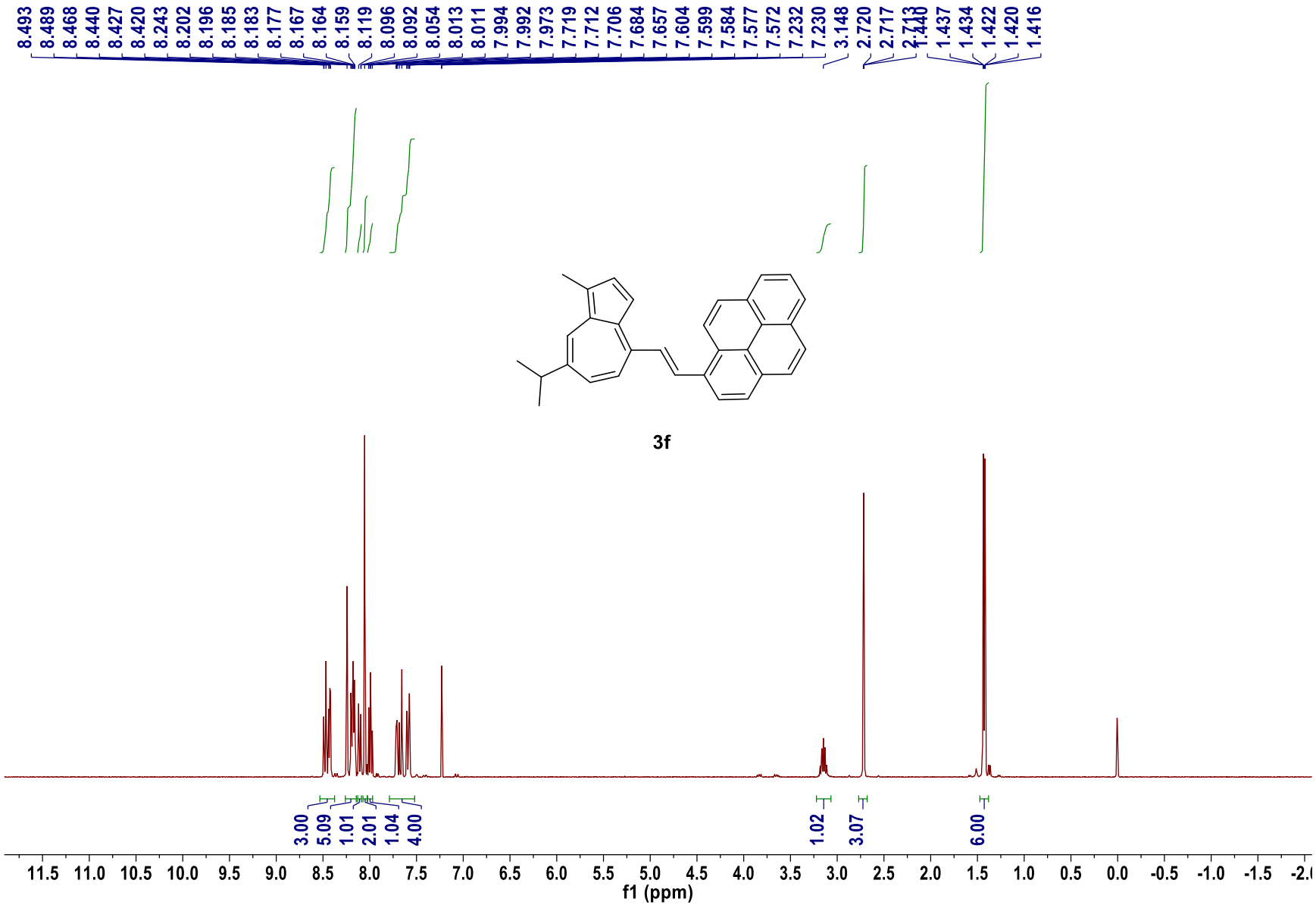
30
20
10
0
-10
f1 (ppm)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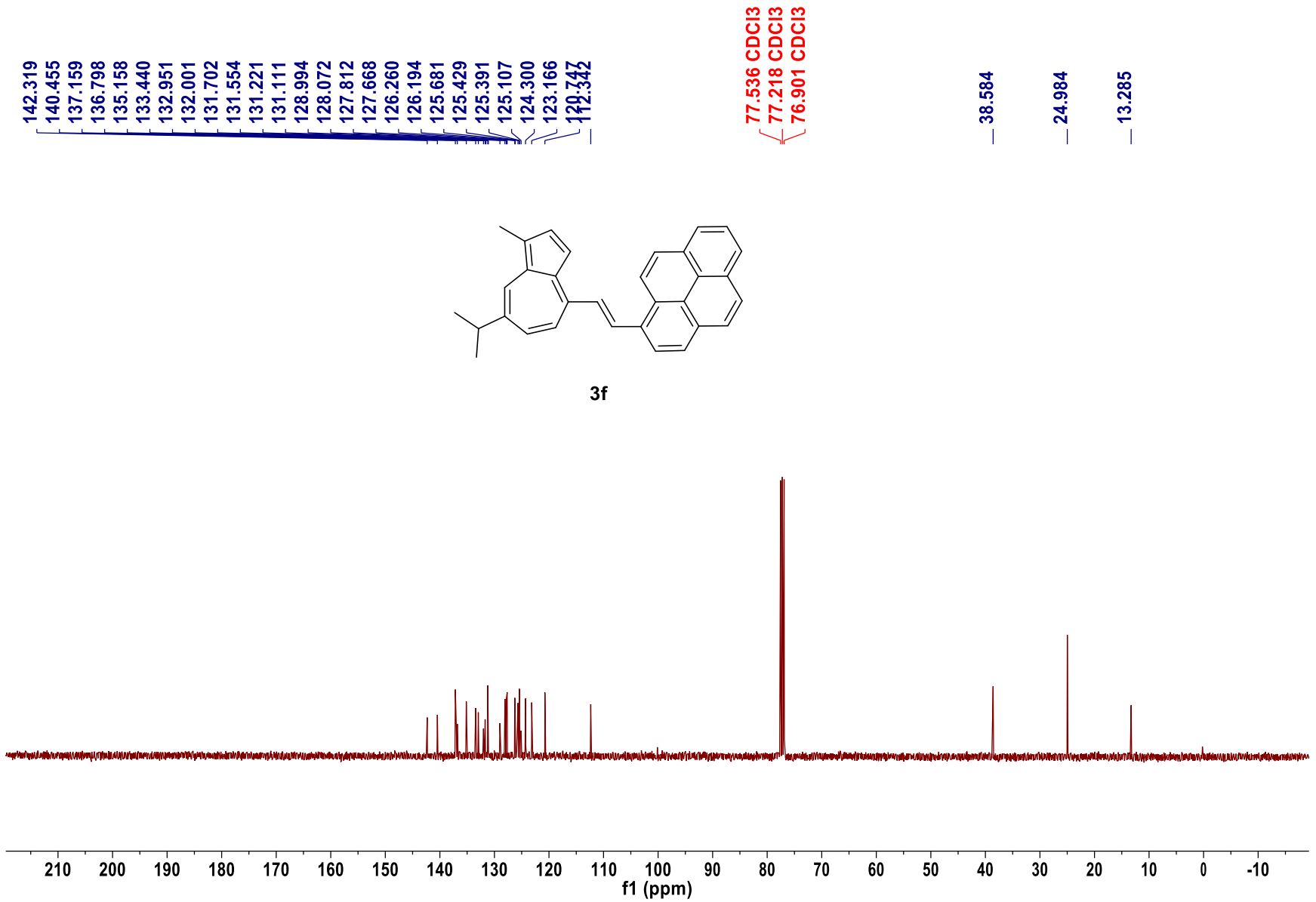
8.427
8.420
8.243
8.202
8.196
8.185
8.183
8.177
8.167
8.164
8.159
8.119
8.096
8.092
8.054
8.013
8.011
7.994
7.992
7.973
7.719
7.712
7.706
7.684
7.657
7.604
7.599
7.584
7.577
7.572
7.232
7.230
3.148
2.720
2.717
1.440
1.437
1.434
1.422
1.420
1.416
3f
3.00
5.09
1.01
2.01
1.04
4.00
1.02
3.07
6.00
f1 (ppm)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137.159
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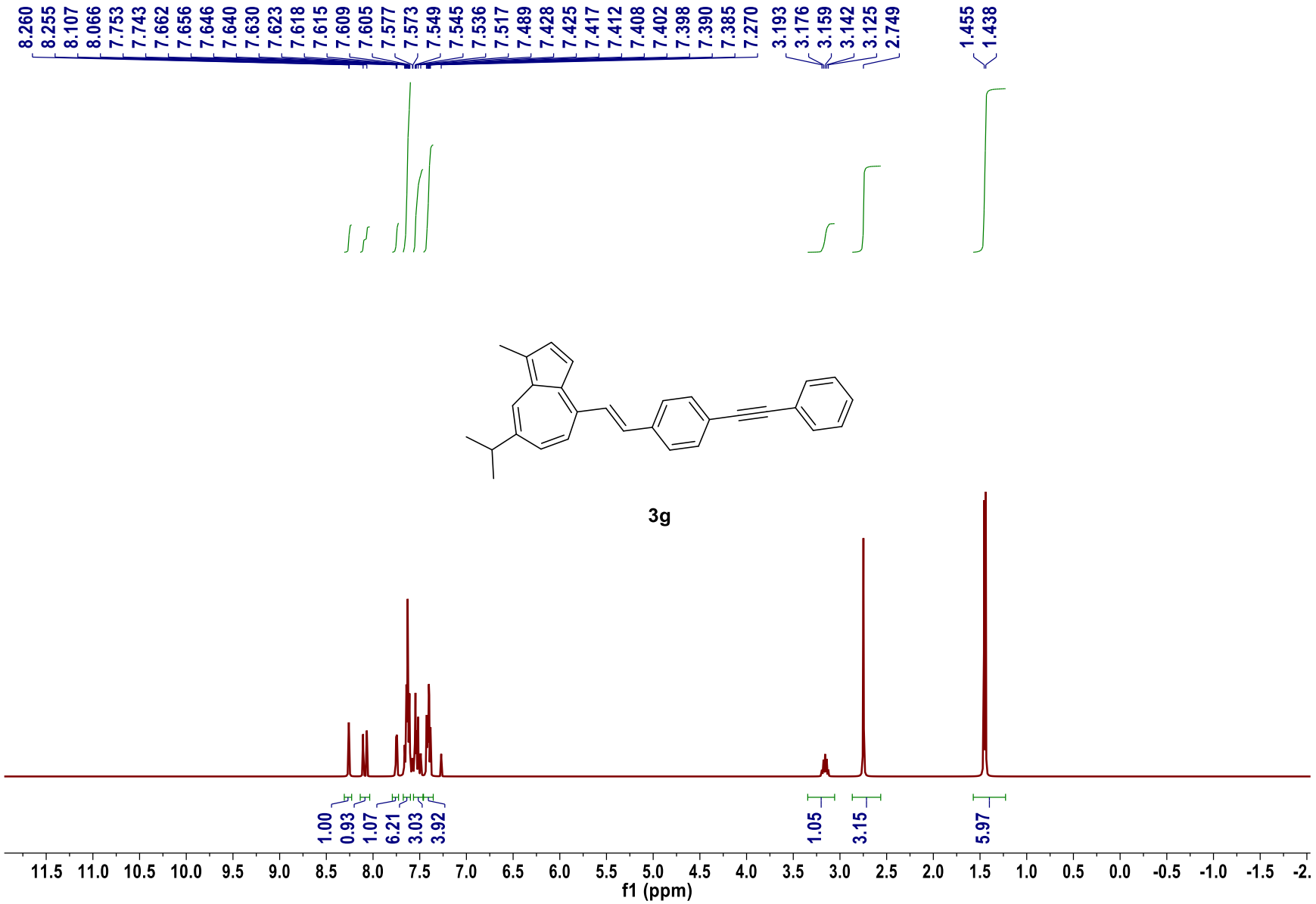
133.440
132.951
132.001
131.702
131.554
131.221
131.111
128.994
128.072
127.812
127.668
126.260
126.194
125.681
125.429
125.391
125.107
124.300
123.166
77.536 CDCl3
77.218 CDCl3
76.901 CDCl3
38.584
24.984
13.285
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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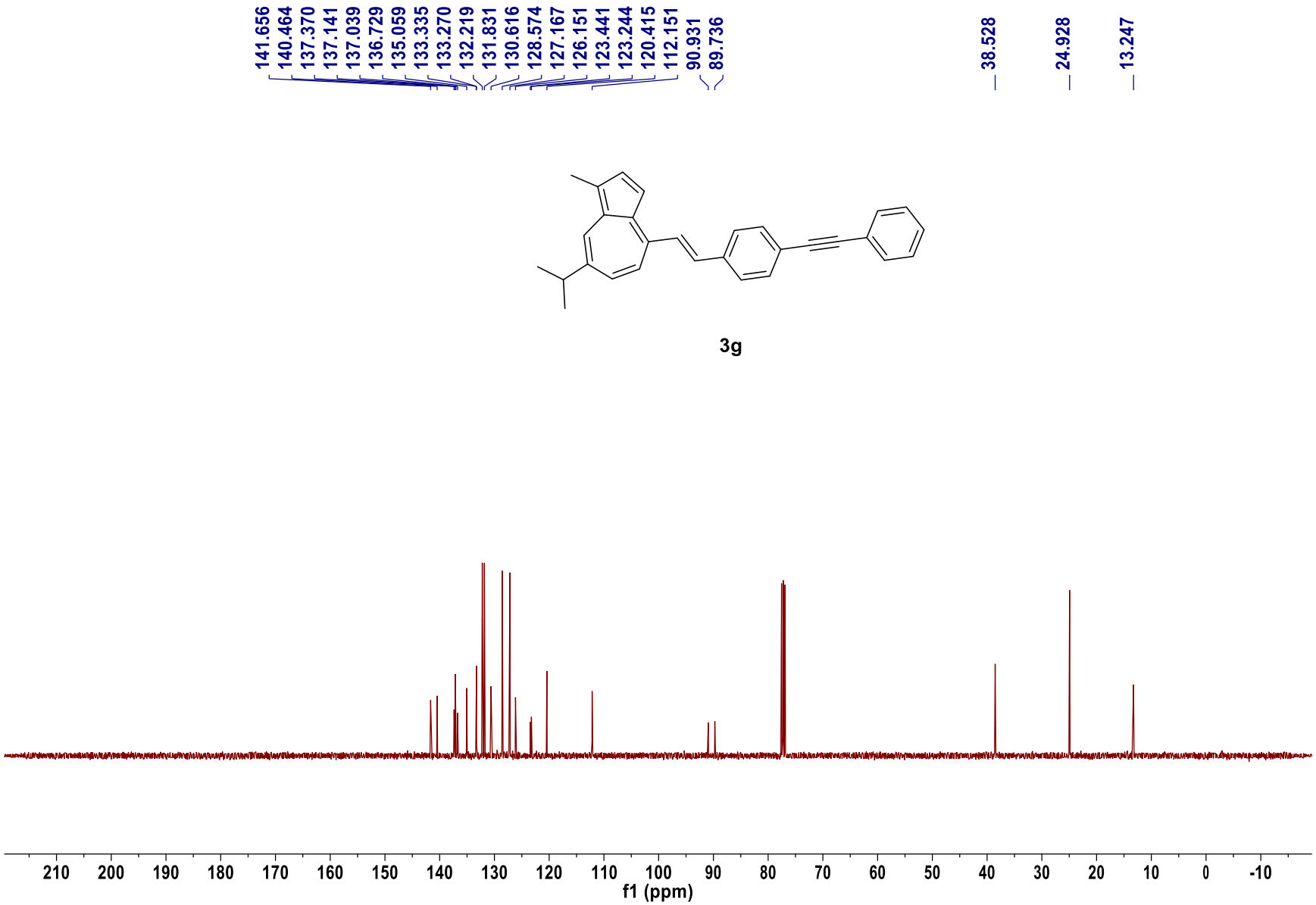
8.255
8.107
8.066
7.753
7.743
7.662
7.656
7.646
7.640
7.630
7.623
7.618
7.615
7.609
7.605
7.577
7.573
7.549
7.545
7.536
7.517
7.489
7.428
7.425
7.417
7.412
7.408
7.402
7.398
7.390
7.385
7.270
3.193
3.176
3.159
3.142
3.125
2.749
1.455
1.438
3g
1.00
0.93
1.07
6.21
3.03
3.92
1.05
3.15
5.97
f1 (ppm)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137.141
137.039
136.729
135.059
133.335
133.270
132.219
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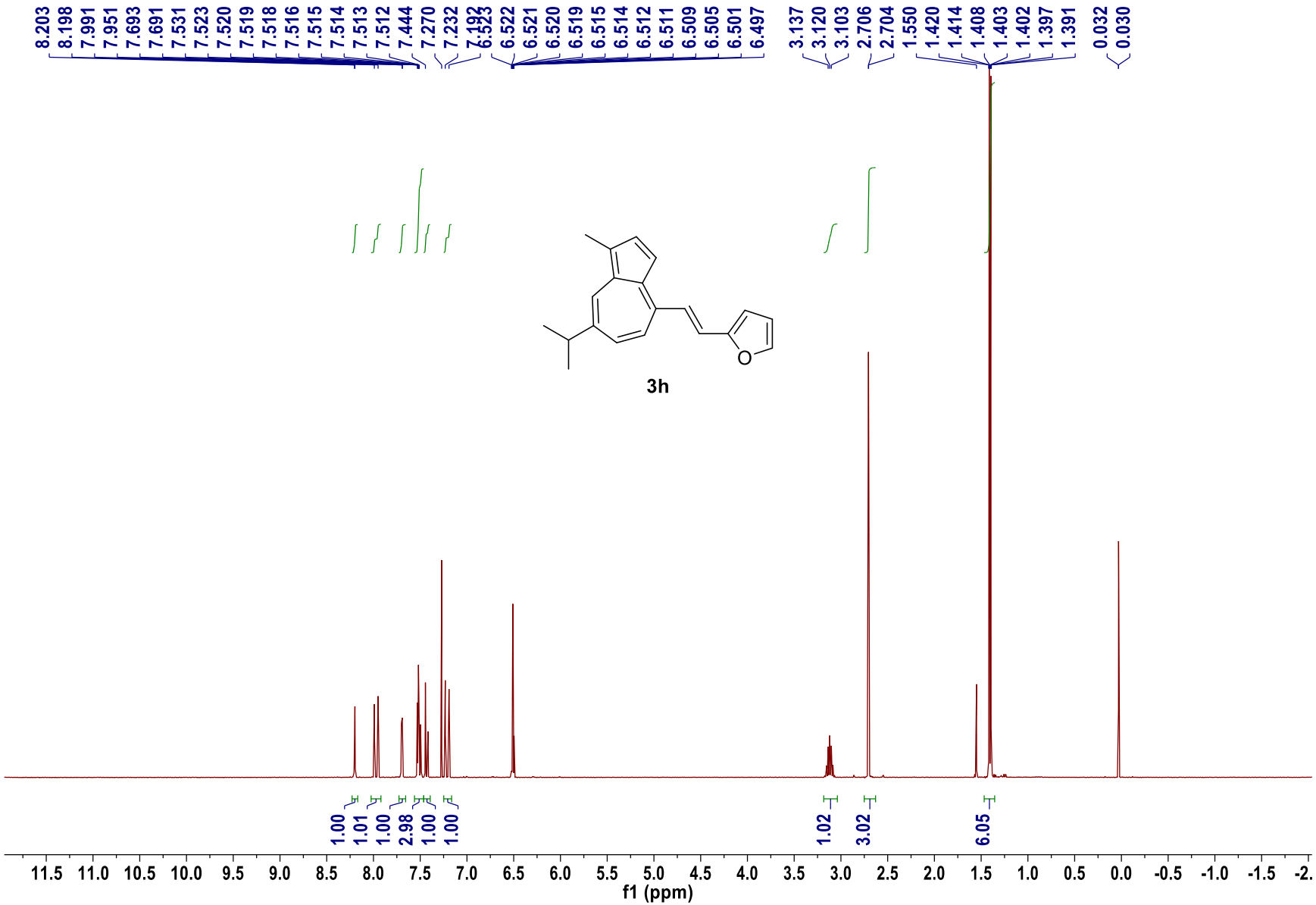
130.616
128.574
127.167
126.151
123.441
123.244
120.415
112.151
90.931
89.736
38.528
24.928
13.247
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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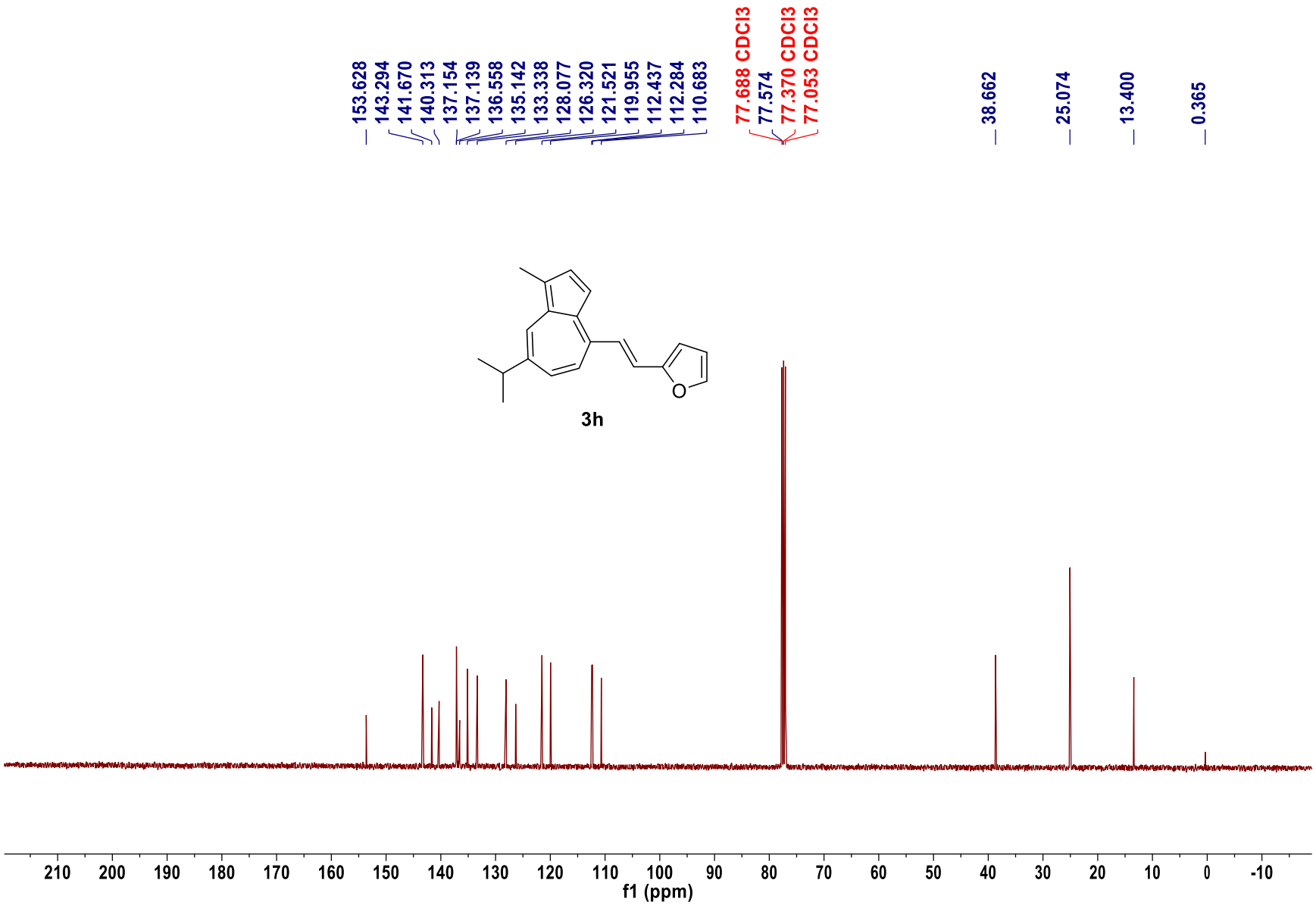
8.198
7.991
7.951
7.693
7.691
7.531
7.523
7.520
7.519
7.518
7.516
7.515
7.514
7.513
7.512
7.444
7.270
7.232
6.522
6.521
6.520
6.519
6.515
6.514
6.512
6.511
6.509
6.505
6.501
6.497
3.137
3.120
3.103
2.706
2.704
1.550
1.420
1.414
1.408
1.403
1.402
1.397
1.391
0.032
0.030
3h
1.00
1.01
1.00
2.98
1.00
1.00
1.02
3.02
6.05
f1 (ppm)


153.628
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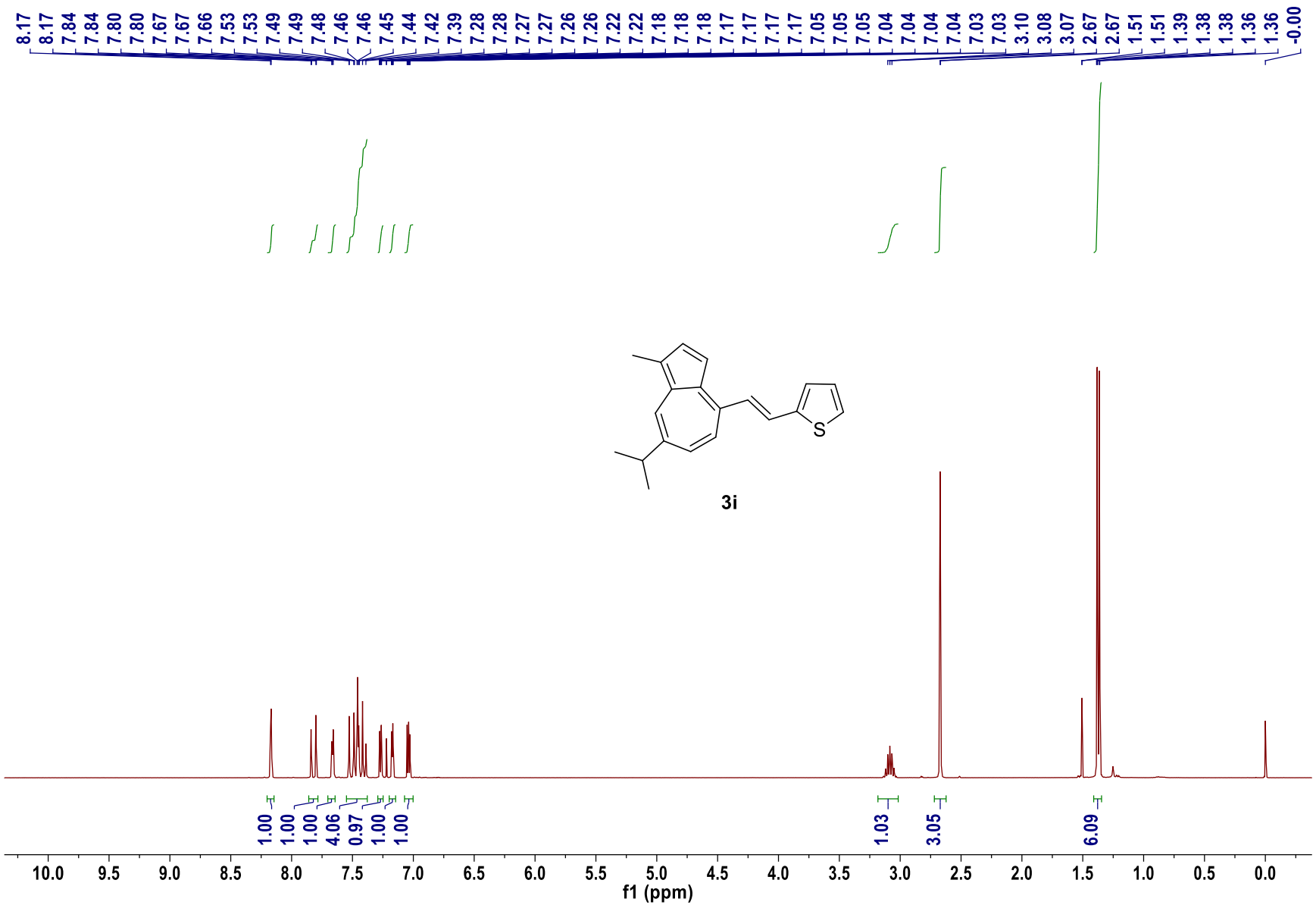
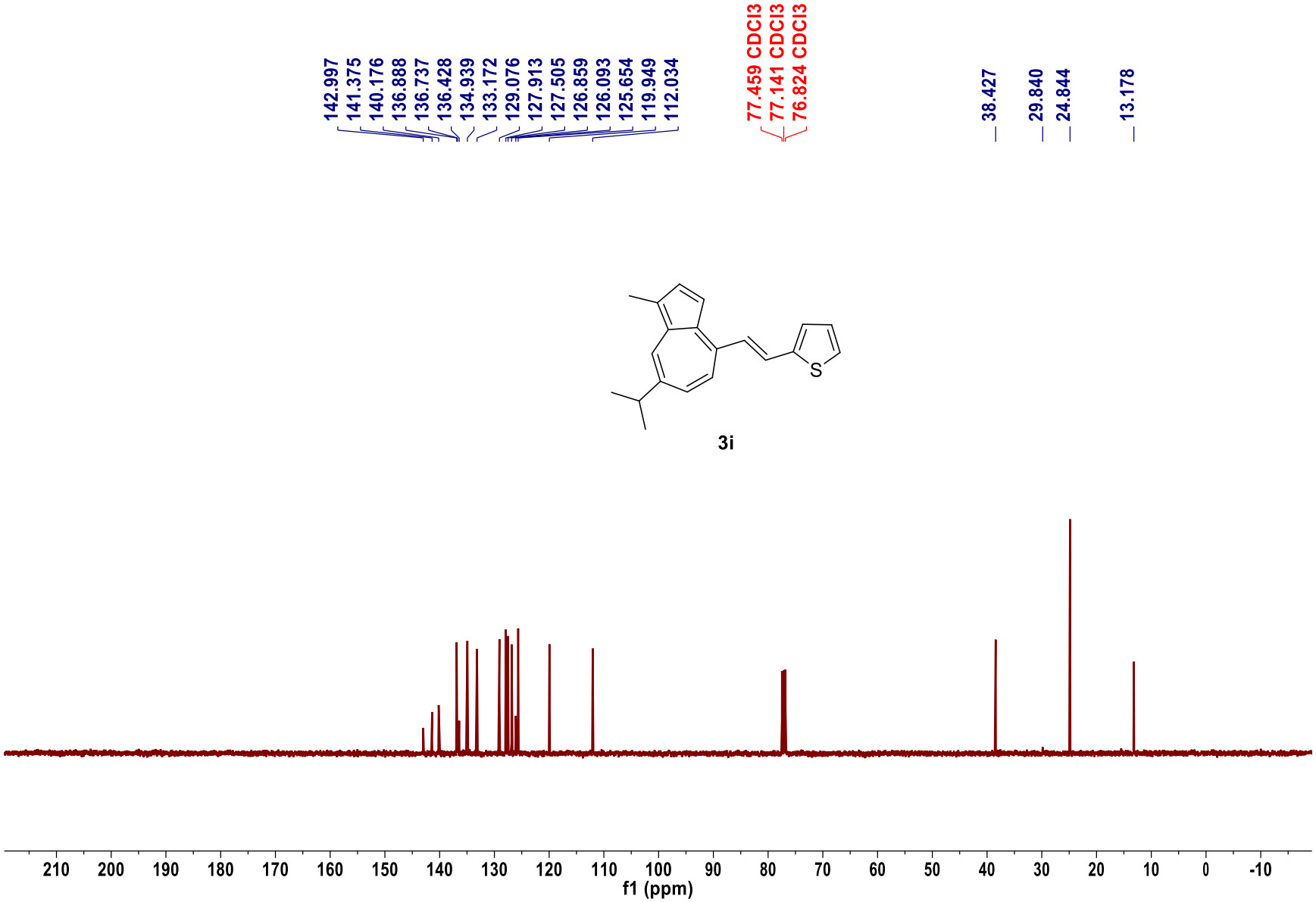
140.313
137.154
137.139
136.558
135.142
133.338
128.077
126.320
121.521
119.955
112.437
112.284
110.683
77.688 CDCl3
77.574
77.370 CDCl3
77.053 CDCl3
38.662
25.074
13.400
0.365
O
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.17 8.17 7.84 7.84 7.80 7.80 7.67 7.67 7.66 7.53 7.53 7.49 7.49 7.48 7.46 7.46 7.45 7.44 7.42 7.39 7.28 7.28 7.27 7.27 7.26 7.26 7.22 7.22 7.18 7.18 7.18 7.17 7.17 7.17 7.17 7.05 7.05 7.05 7.04 7.04 7.04 7.04 7.03 7.03 3.10 3.08 3.07 2.67 2.67 1.51 1.51 1.39 1.38 1.38 1.36 1.36 -0.00
S
3i
1.00 1.00 1.00 4.06 0.97 1.00 1.00 1.03 3.05 6.09
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)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141.375
140.176
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136.737
136.428
134.939
133.172
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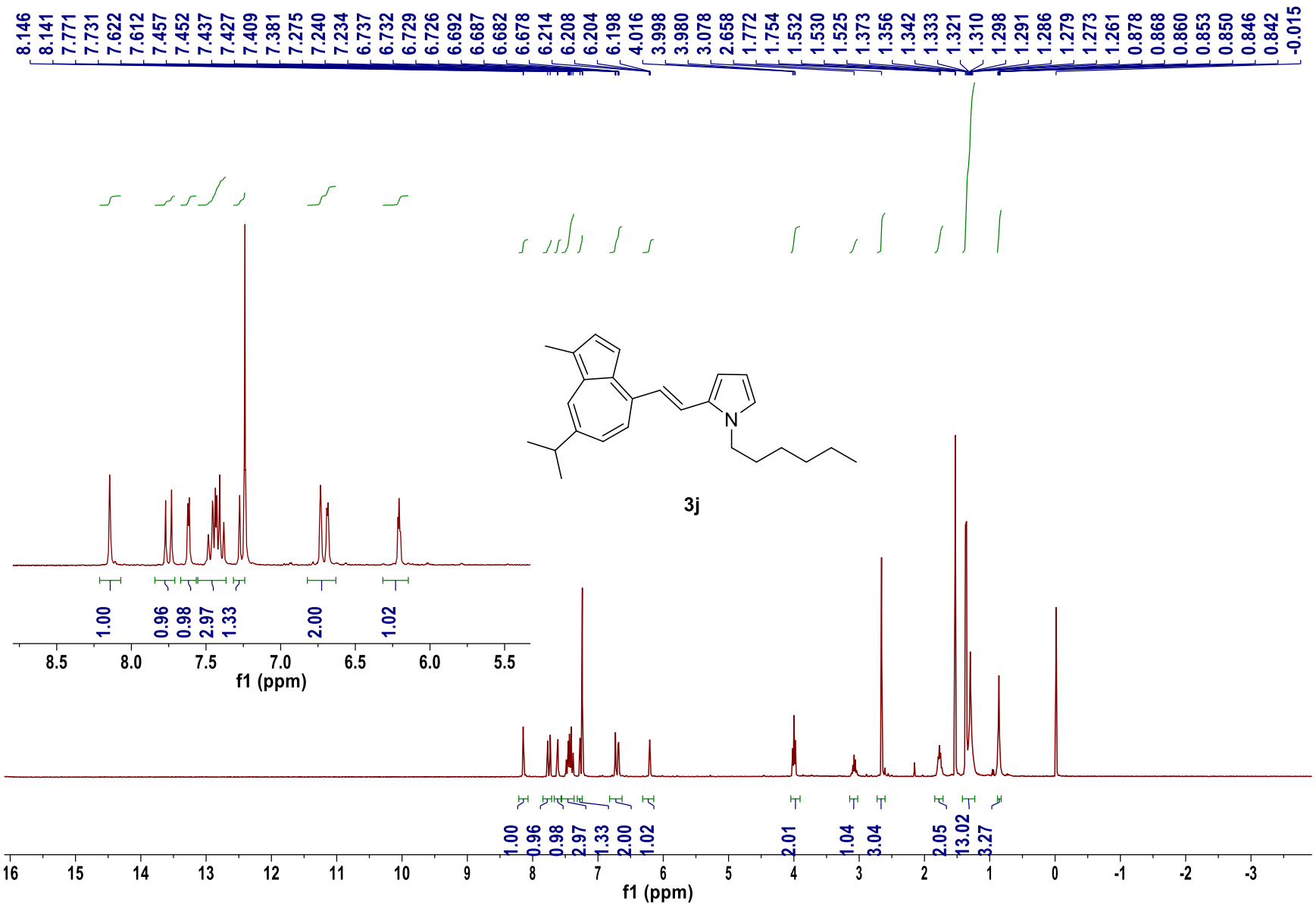
127.913
127.505
126.859
126.093
125.654
119.949
112.034
77.459 CDCl3
77.141 CDCl3
76.824 CDCl3
38.427
29.840
24.844
13.178
S
3i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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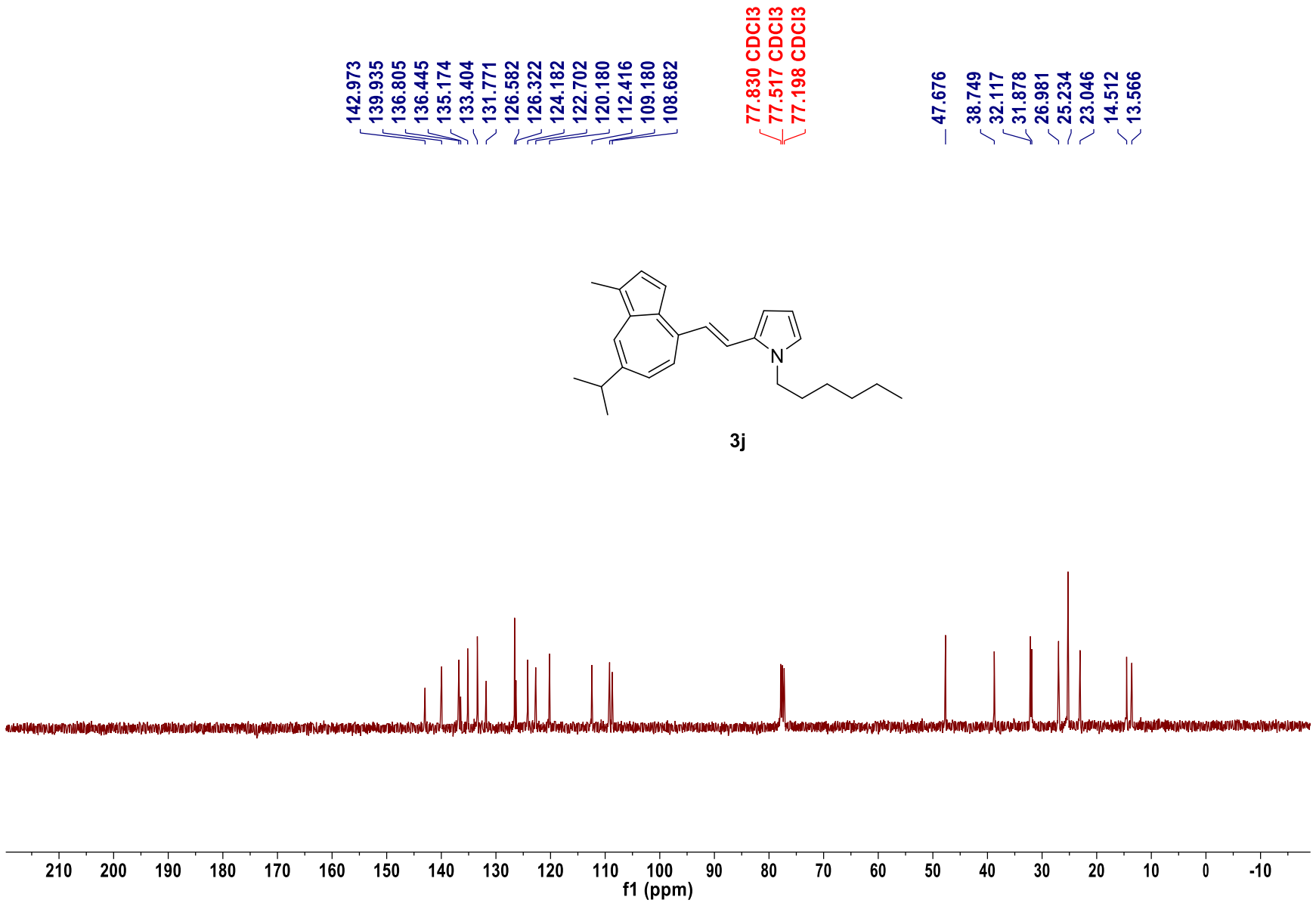
7.731
7.622
7.612
7.457
7.452
7.437
7.427
7.409
7.381
7.275
7.240
7.234
6.737
6.732
6.729
6.726
6.692
6.687
6.682
6.678
6.214
6.208
6.204
6.198
4.016
3.998
3.980
3.078
2.658
1.772
1.754
1.532
1.530
1.525
1.373
1.356
1.342
1.333
1.321
1.310
1.298
1.291
1.286
1.279
1.273
1.261
0.878
0.868
0.860
0.853
0.850
0.846
0.842
-0.015
N
3j
1.00
0.96
0.98
2.97
1.33
2.00
1.02
2.01
1.04
3.04
2.05
13.02
3.27
f1 (ppm)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139.935
136.805
136.445
135.174
133.404
131.771
126.582
126.322
124.182
122.702
120.180
112.416
109.180
108.682
77.830 CDCl3
77.517 CDCl3
77.198 CDCl3
47.676
38.749
32.117
31.878
26.981
25.234
23.046
14.512
13.566
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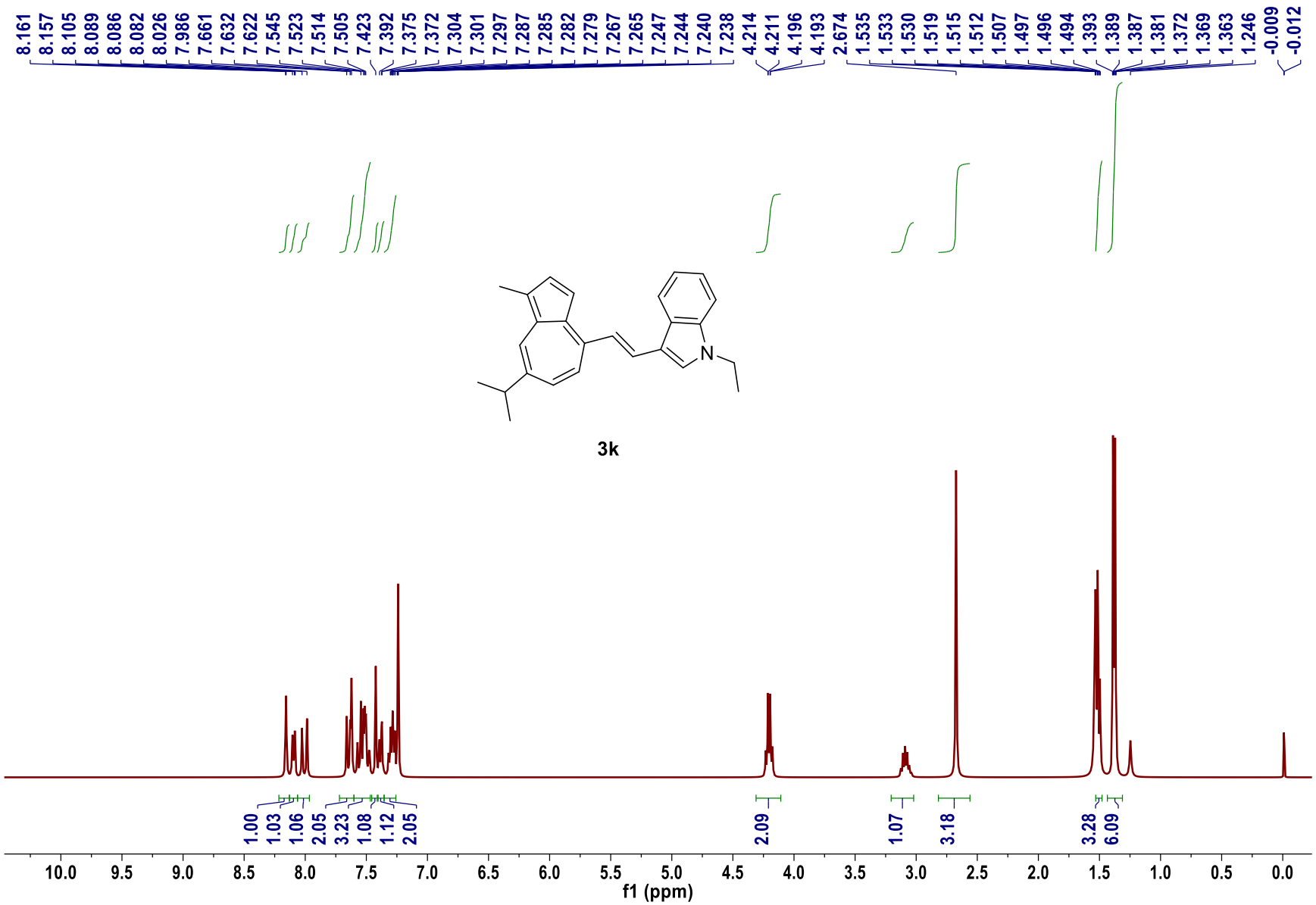
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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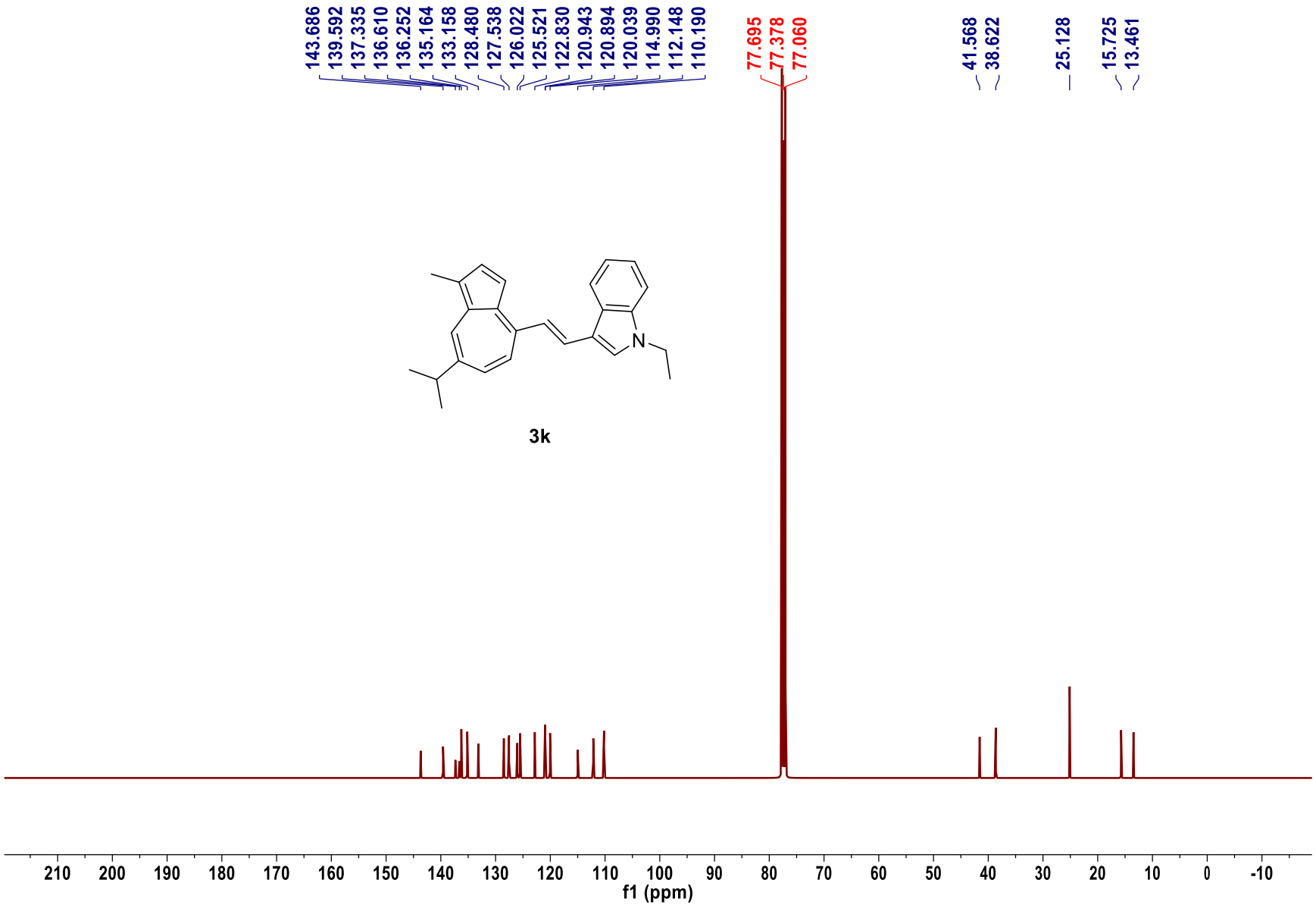
8.089
8.086
8.082
8.026
7.986
7.661
7.632
7.622
7.545
7.523
7.514
7.505
7.423
7.392
7.375
7.372
7.304
7.301
7.297
7.287
7.285
7.282
7.279
7.267
7.265
7.247
7.244
7.240
7.238
4.214
4.211
4.196
4.193
2.674
1.535
1.533
1.530
1.519
1.515
1.512
1.507
1.497
1.496
1.494
1.393
1.389
1.387
1.381
1.372
1.369
1.363
1.246
-0.009
-0.012
N
3k
1.00
1.03
1.06
2.05
3.23
1.08
1.12
2.05
2.09
1.07
3.18
3.28
6.09
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)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135.164
133.158
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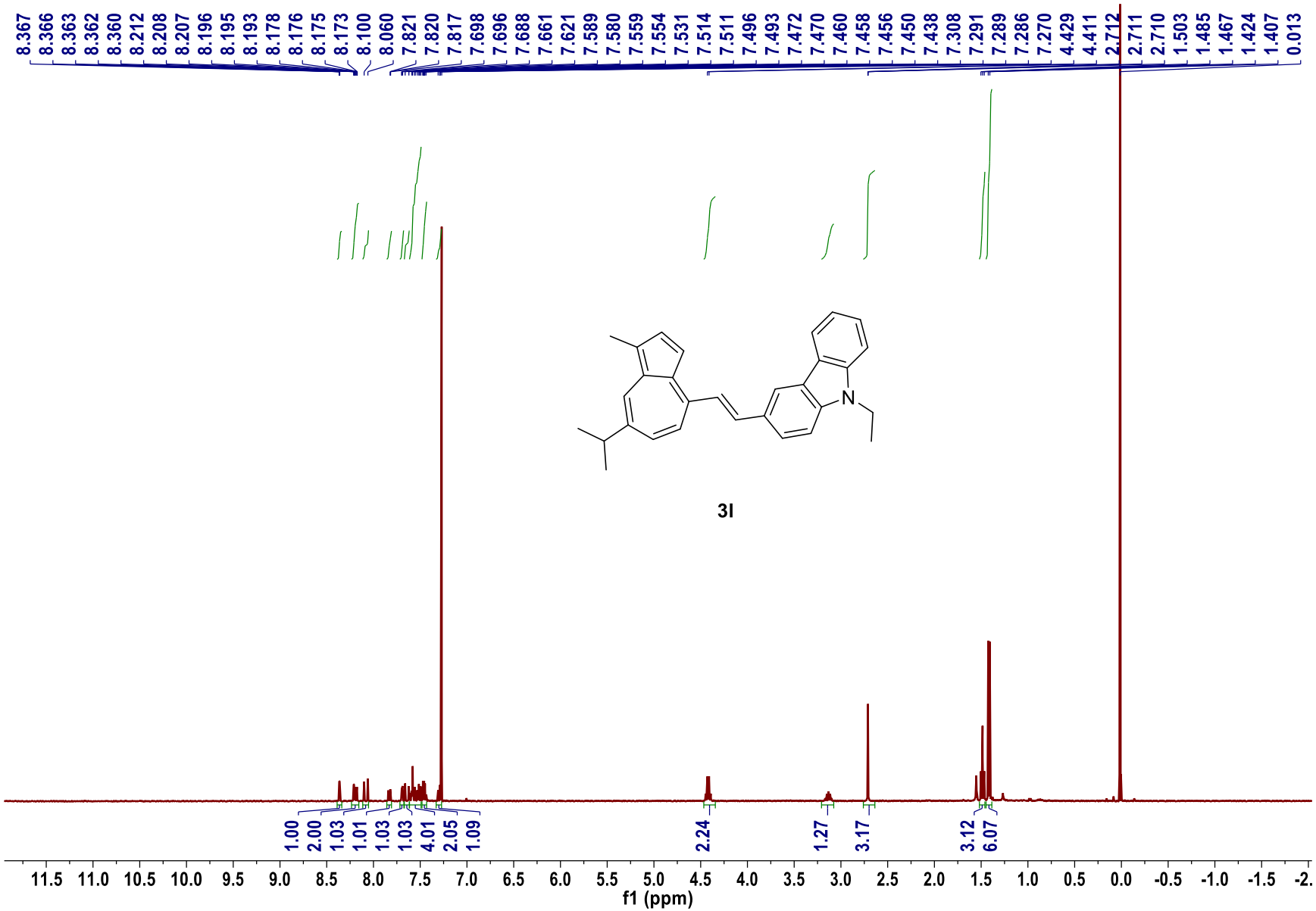
127.538
126.022
125.521
122.830
120.943
120.894
120.039
114.990
112.148
110.190
77.695
77.378
77.060
41.568
38.622
25.128
15.725
13.461
N
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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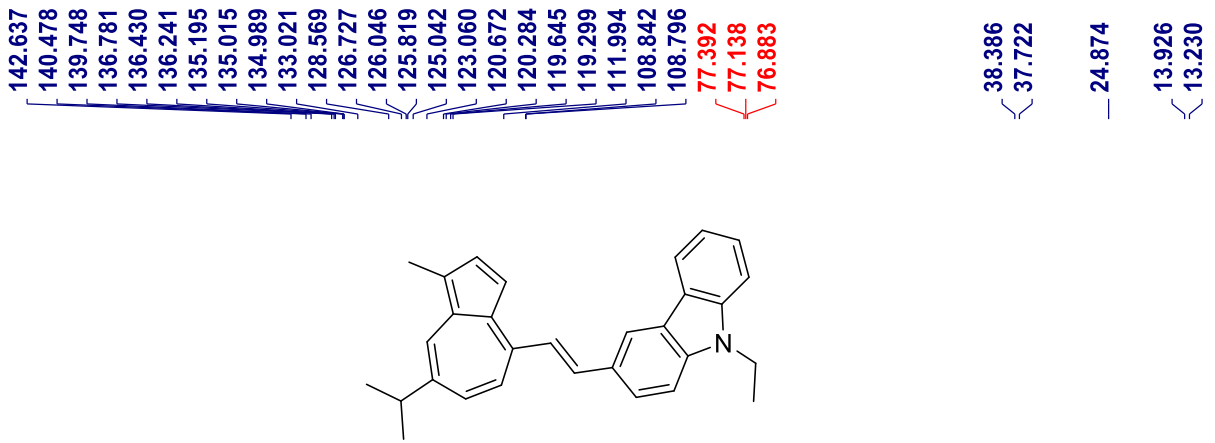
8.207
8.196
8.195
8.193
8.178
8.176
8.175
8.173
8.100
8.060
7.821
7.820
7.817
7.698
7.696
7.688
7.661
7.621
7.589
7.580
7.559
7.554
7.531
7.514
7.511
7.496
7.493
7.472
7.470
7.460
7.458
7.456
7.450
7.438
7.308
7.291
7.289
7.286
7.270
4.429
4.411
2.712
2.711
2.710
1.503
1.485
1.467
1.424
1.407
0.013
N
3l
1.00
2.00
1.03
1.01
1.03
1.03
4.01
2.05
1.09
2.24
1.27
3.17
3.12
6.07
11.5 11.0 10.5 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 -0.5 -1.0 -1.5 -2.
f1 (ppm)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135.015
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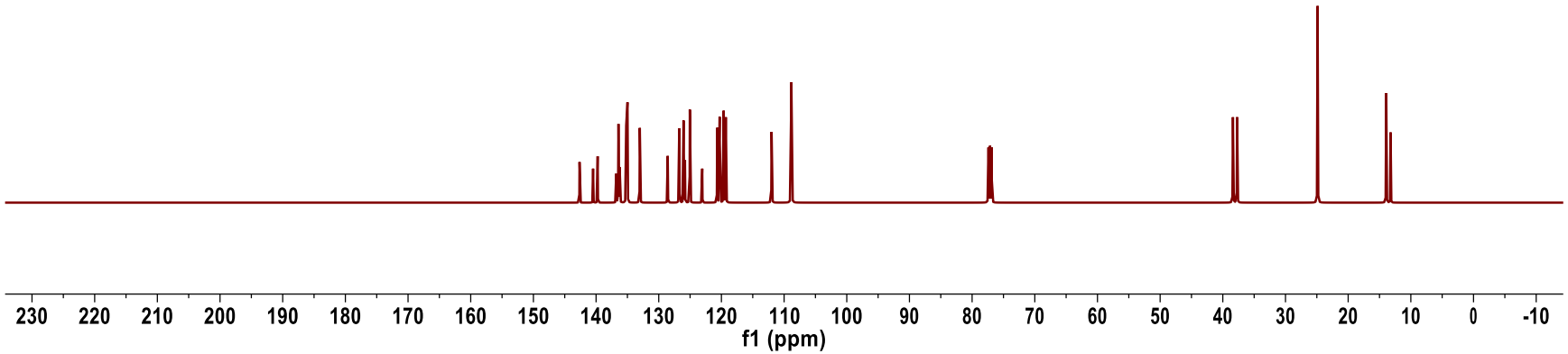
133.021
128.569
126.727
126.046
125.819
125.042
123.060
120.672
120.284
119.645
119.299
111.994
108.842
108.796
77.392
77.138
76.883
38.386
37.722
24.874
13.926
13.230
N

3l


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)