Supporting Information

Synthesis of indoline-fused eight-membered azaheterocycles through Zn-catalyzed dearomatization of indoles and subsequent base-promoted C–C activation

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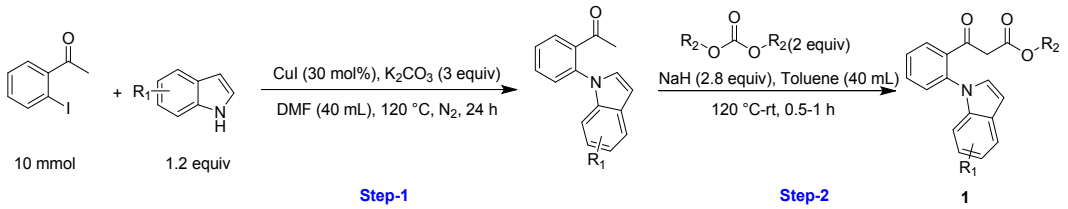
1. Typical procedure for the synthesis of 1 and 2



The benzoates tethered with ortho-indole moiety **1** were prepared according to the reference.[1, 2]

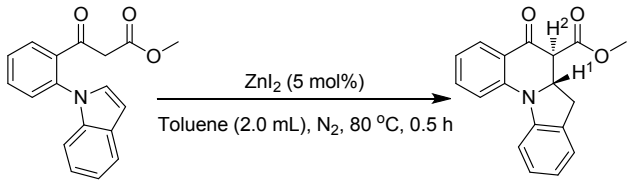
Step-1 To a DMF solution containing 1-(2-iodophenyl)ethanone (10.0 mmol, 2.46 g), indoles (12.0 mmol, 1.41 g) and CuI (3.0 mmol, 571.3 mg) was added K_2CO_3 (30.0 mmol, 4.15 g) under nitrogen. The reaction mixture was stirred for 24 h at 120 ^oC. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with H_2O (10 mL), and extracted with EA (40 mL ×3). The organic layer was washed with brine, dried with anhydrous Na_2SO_4, and concentrated under vacuum to give the crude product. The residue was purified by silica gel column with petroleum ether/EA as the eluent to give the analytical pure 1-(2-(1*H*-indol-1-yl)phenyl)ethenone.

Step-2 To a dried 25-mL RBF was added NaH (28 mmol, 60% dispersion in mineral oil, 1.12 g), dimethyl carbonate (20 mmol, 1.7 mL) and toluene (10 mL) under nitrogen. After the mixture was heated to reflux, a solution of 1-(2-(1*H*-indol-1-yl) phenyl)ethanone (10 mmol, 2.35 g) in toluene (5 mL) was added dropwise over 0.5 h. After the evolution of hydrogen ceased (15-20 min), the reaction was cooled down to room temperature. After cooling, the reaction mixture was poured into ice-water (10 mL), acidified with aqueous HCl (3 M) to PH 2~3 and extracted with EA (40 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel with petroleum ether/EA as the eluent to give the yellow oil methyl-3-(2-(1*H*-indol-1-yl)phenyl)-3-oxopropanoate **1a**.

The ynones **2** are known compounds and the spectroscopic data in

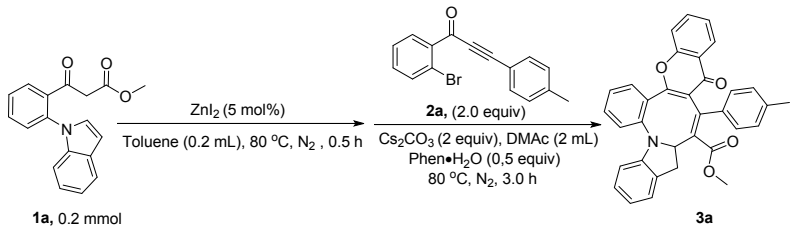
agreement with that previously reported[3].

2. Synthesis of 4a



In a schlenk tube methyl 3-(2-(1*H*-indol-1-yl)phenyl)-3-oxopropanoate **1a** (0.20 mmol, 58.6 mg), ZnI_2 (0.01 mmol, 3.2 mg) and toluene (2.0 mL) were stirred at 80 °C for 0.5 h under N_2. After the reaction was completed as monitored by thin-layer chromatography, water was then added to the reaction mixture, and the water layer was extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) afforded desired compound **4a** (yellow solid, 56.9 mg, 97% yield). The stereochemistry of **4a** was assigned on the basis of its spectral data (J_{H1H2} = 13.2 Hz).[4]

3. Synthesis of 3a



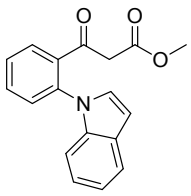
In a schlenk tube methyl 3-(2-(1*H*-indol-1-yl)phenyl)-3-oxopropanoate **1a** (0.20 mmol, 58.7 mg), ZnI_2 (0.01 mmol, 3.2 mg) and toluene (0.2 mL) were stirred at 80 °C under N_2. After 0.5 h, 1-(2-bromophenyl)-3-(p-tolyl)prop-2-yn-1-one **2a** (0.4 mmol, 119.7 mg), Cs_2CO_3 (0.4 mmol, 130.3 mg), phen·H_2O (0.1 mmol, 19.8 mg) and DMAc (2.0 mL) were added. After the completion of the addition, the reaction mixture was allowed to react at 80 °C for 3 h in N_2. Then, the reaction mixture was cooled to room

temperature and treated with H_2O, then extracted with EA and dried over anhydrous Na_2SO_4. After removal of the EA, the residue was purified by chromatography on basic silica gel (PE/EA = 10:1) to afford **3a** (yellow solid, 78.9 mg, 77%).

4. References

1. (a) S. E. Kiruthika, A. Nandakumar and P. T. Perumal, *Org Lett.,* **2014,** *16*, 4424. (b) T. Y. Ko and S. W. Youn, *Adv Synth Catal.,* **2016,** *358*, 2059.
2. (a) W. Tang, W. Wang, Y. Chi and X. Tang, *Angew. Chem. Int. Ed*., **2003,** *42*, 3509. (b) J. Sun, X. Zhen, H. Ge, G. Zhang, X. An and Y. Du, *Beilstein J. Org. Chem.,* **2018,** *14,* 1452.
3. (a) Y. Zhou, X. Tao, Q. Yao, Y. Zhao and Y. Li, *Chem. Eur. J*., **2016**, *22*, 17936. (b) M. Wang, L. Kong, Y. Wang, B. Song, Y. Sun, R. Tang and Y. Li, *Org. Lett*., **2018**, *20*, 6130. (c) M. Wang, Y. Yang, B. Song, L. Yin, S. Yan and Y. Li, *Org. Lett.,* **2020,** *22*, 155. (d) Y. Yuan, Z. Guo, Y. Mu, Y. Wang, M. Xu and Y. Li, *Adv Synth Catal.,* **2020,** *362*, 1298.
4. S. Mühmel, D. Alpers, F. Hoffmann, and M. Brasholz, *Chem. Eur. J*., **2015**, *21*, 12308-12312.

5. Copies of spectra of new products



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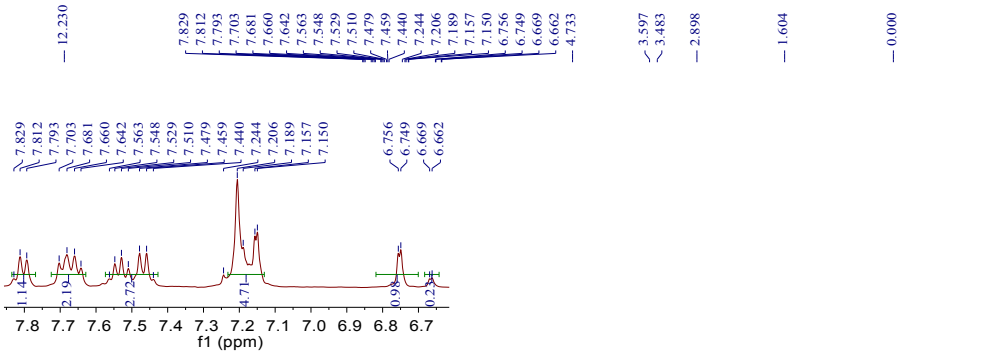

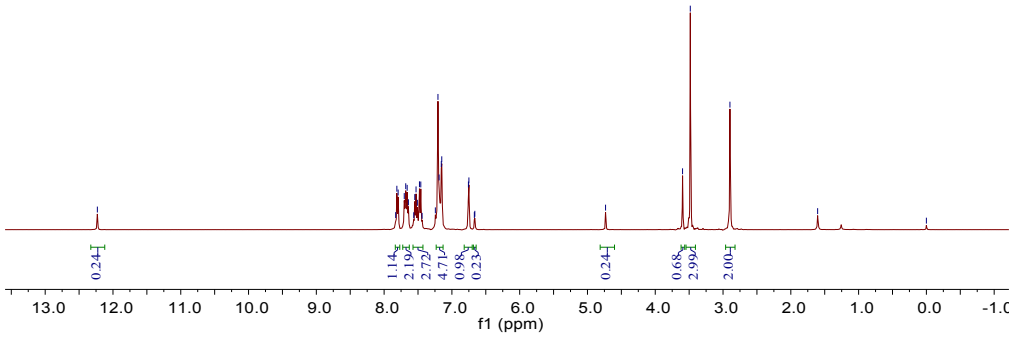

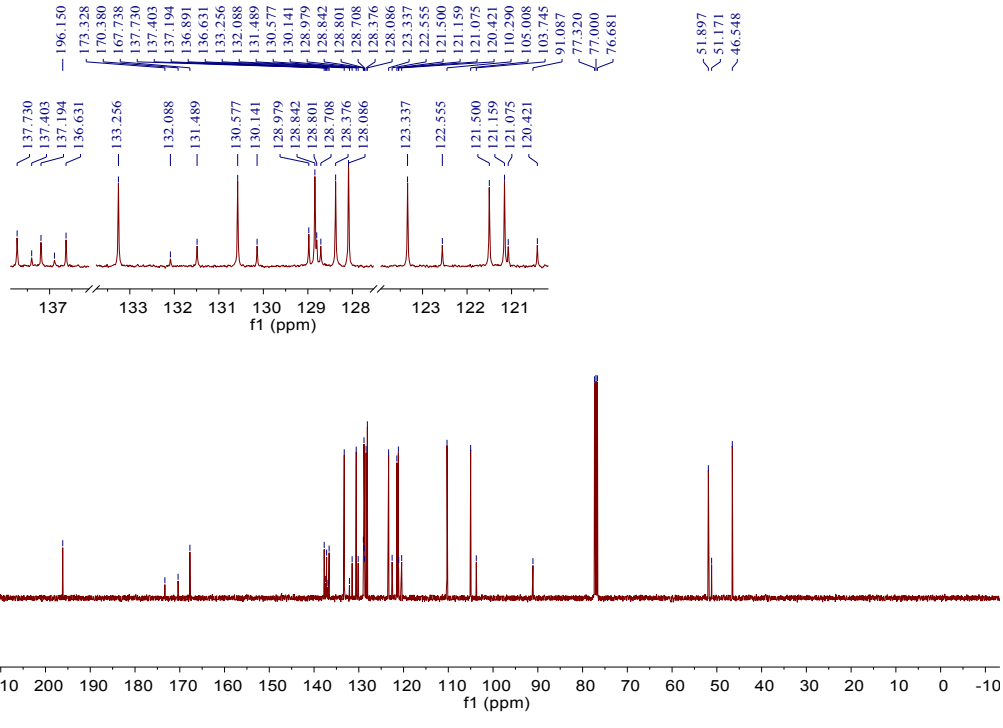

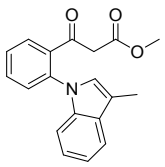

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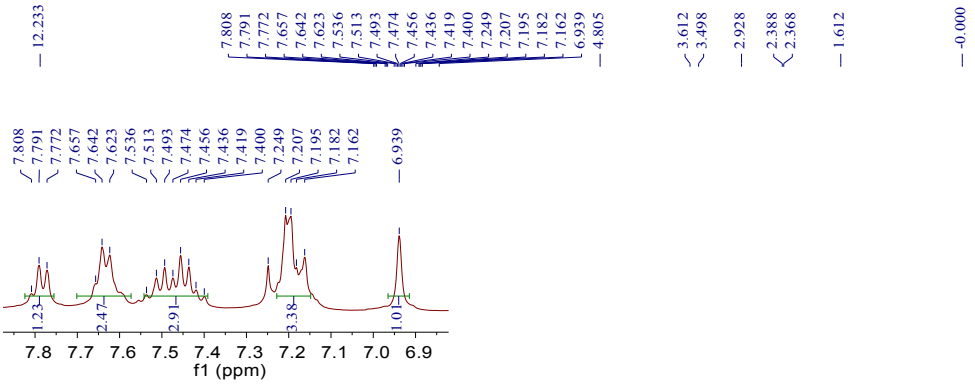
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7.436
7.419
7.400
7.249
7.207
7.195
7.182
7.162
6.939
4.805
3.612
3.498
2.928
2.388
2.368
1.612
0.000
1.23
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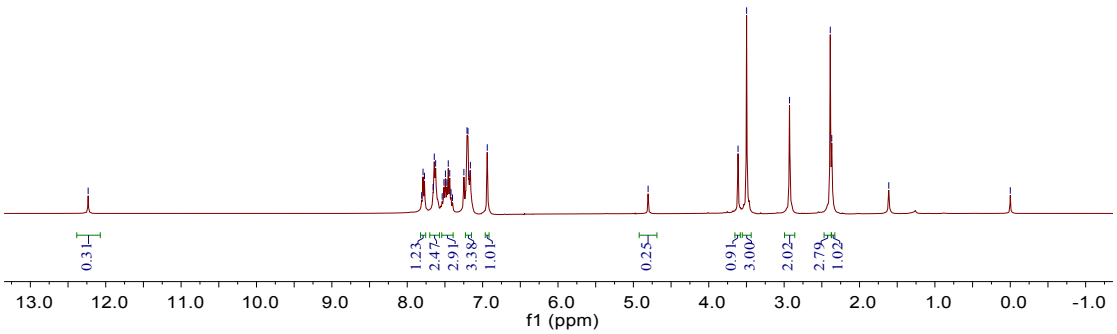
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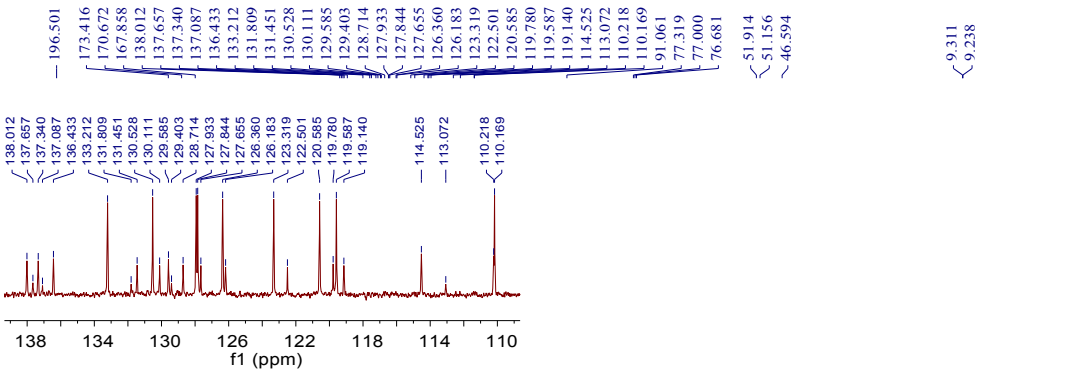
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126.183
123.319
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119.587
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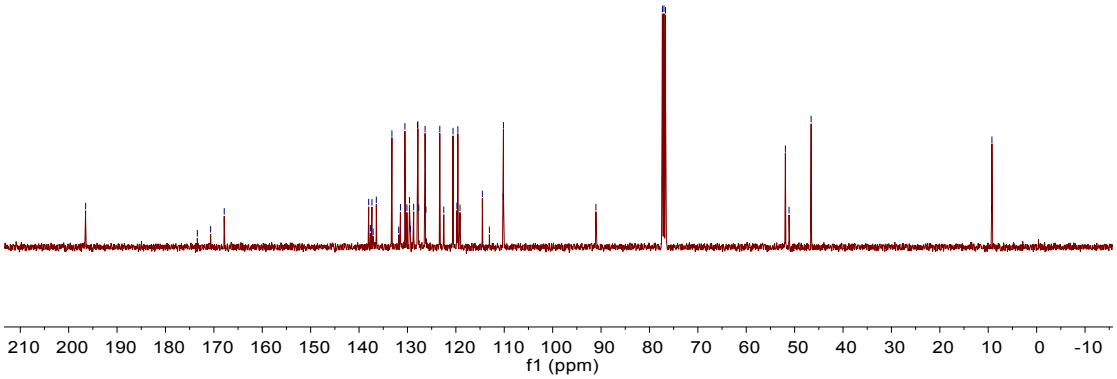
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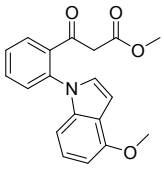

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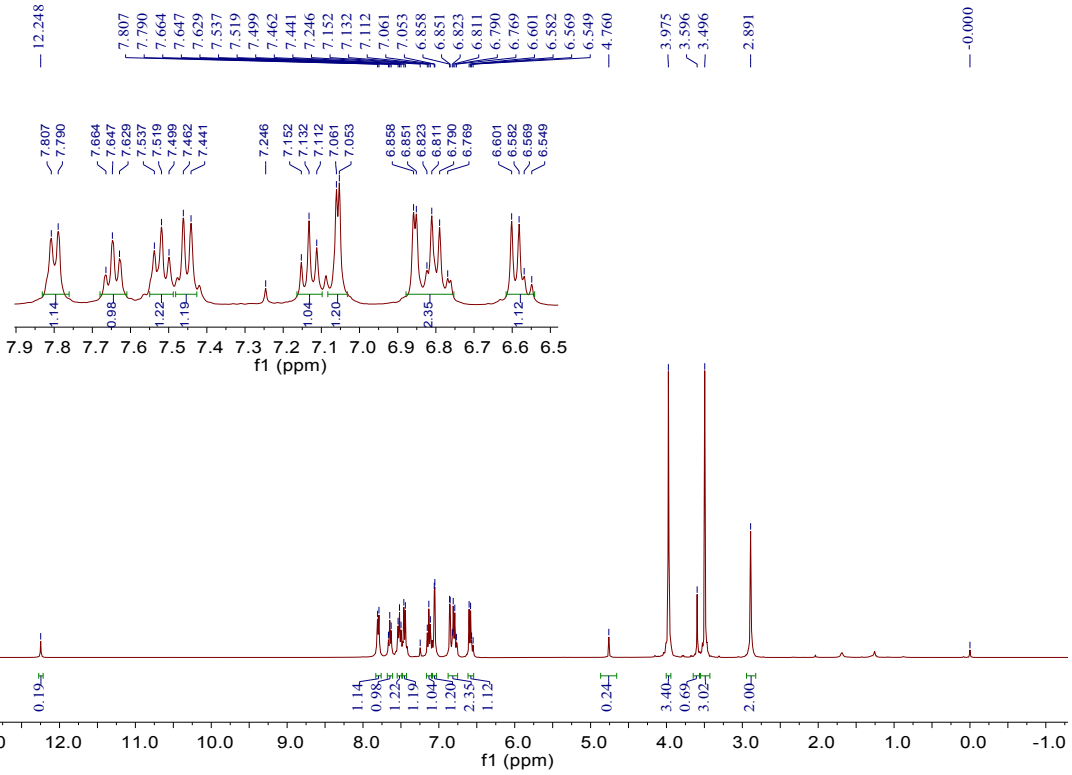
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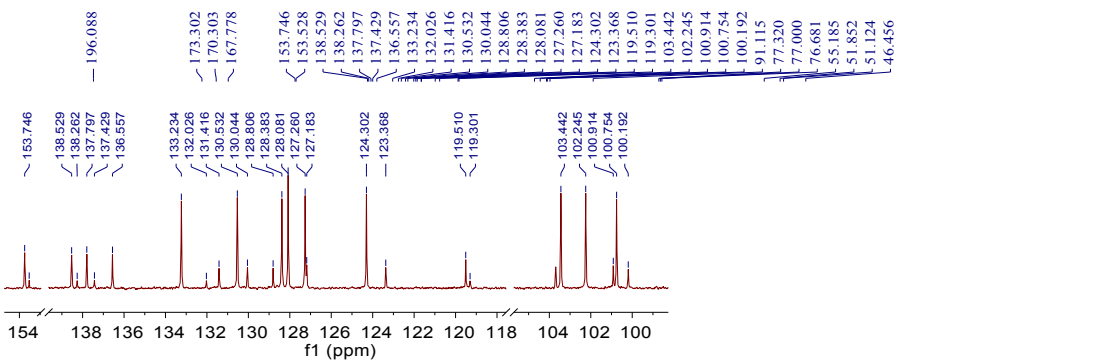
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124.302
123.368
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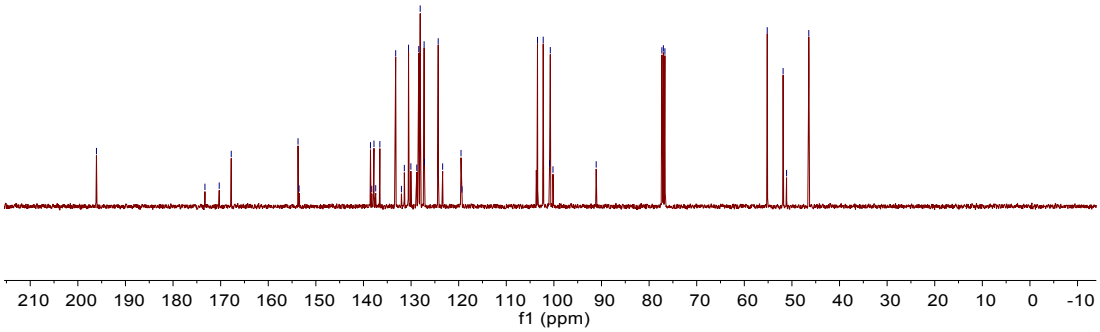
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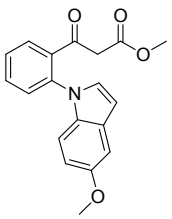

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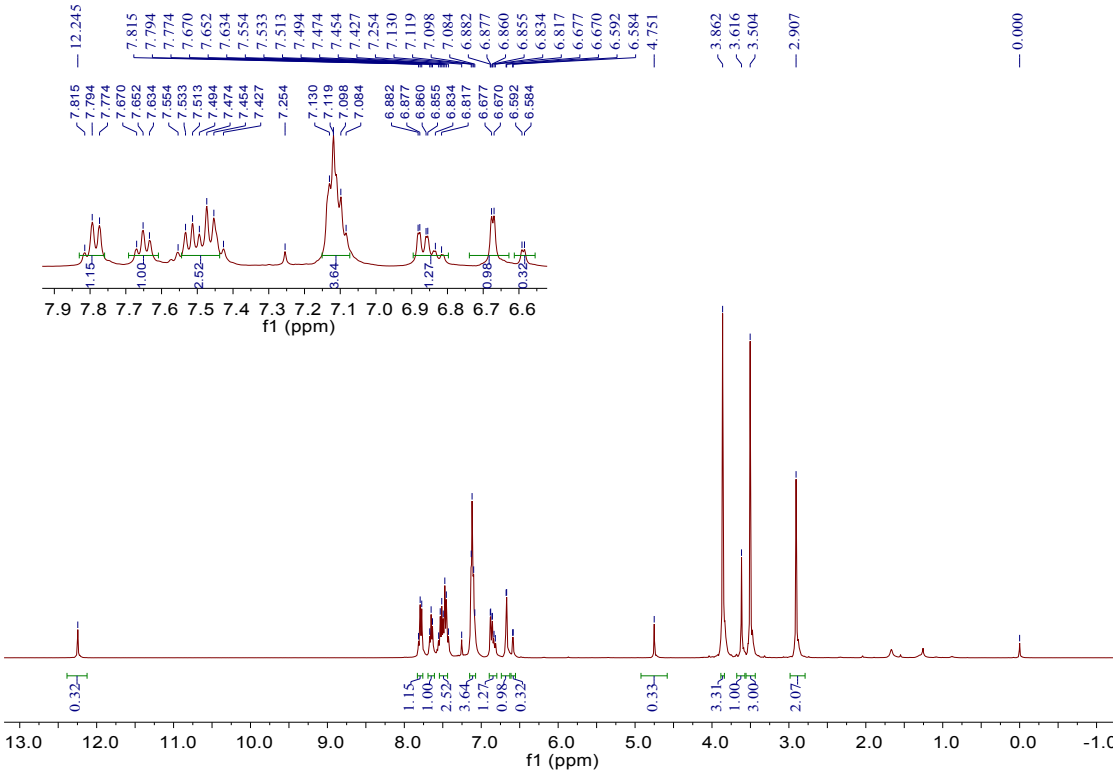

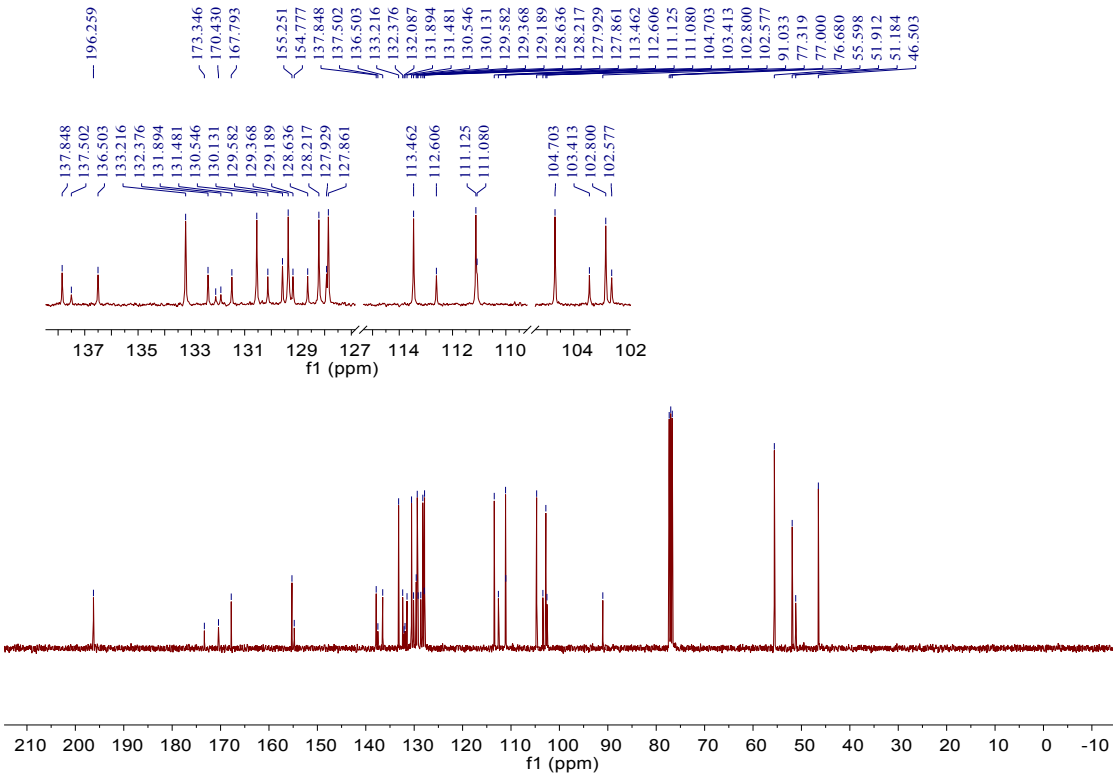

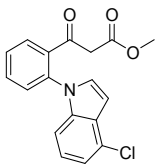
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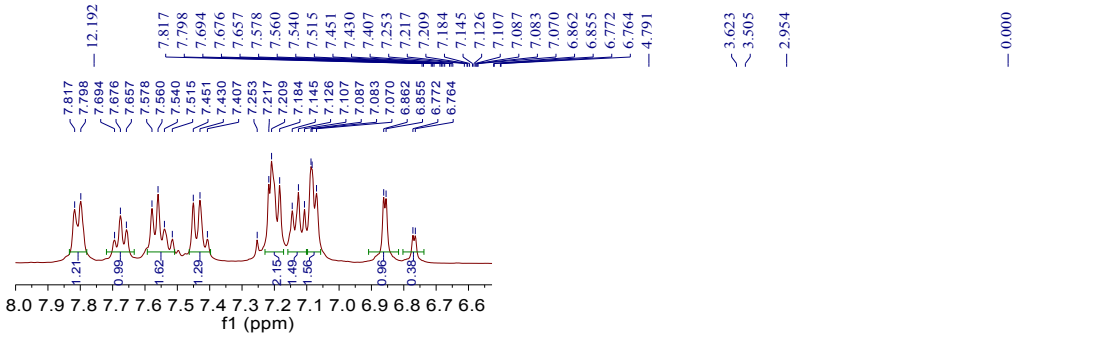
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2.15
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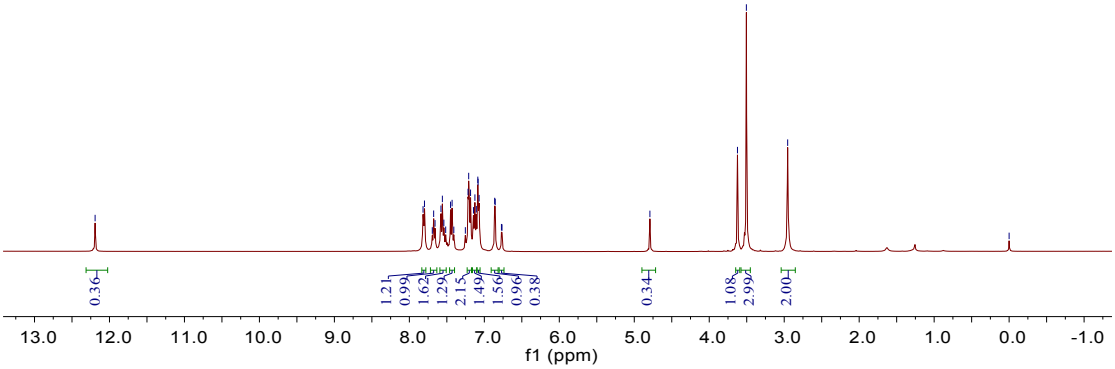
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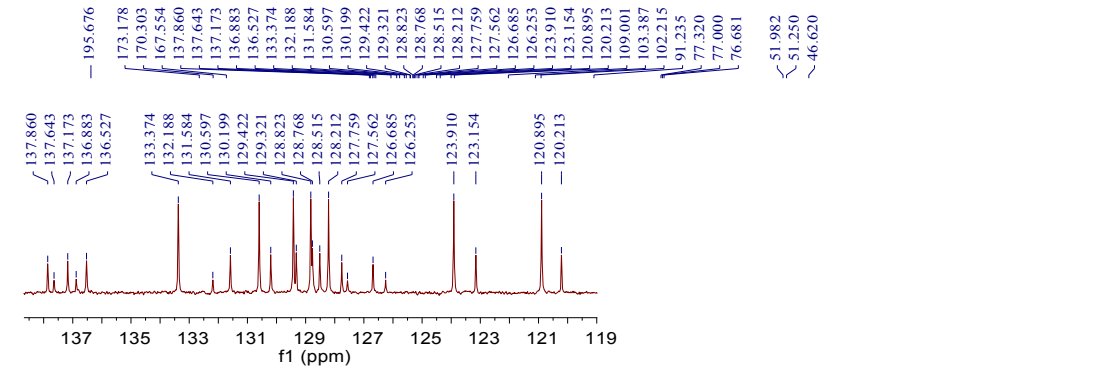
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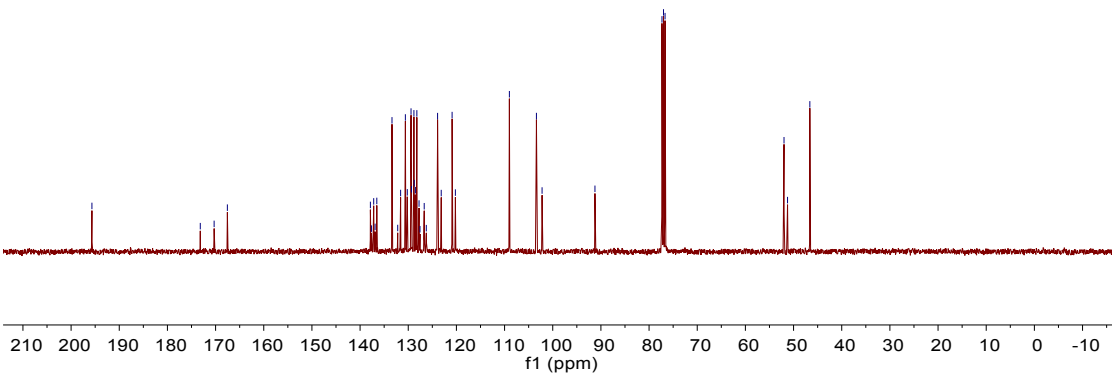
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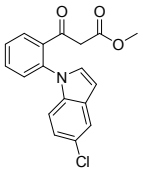
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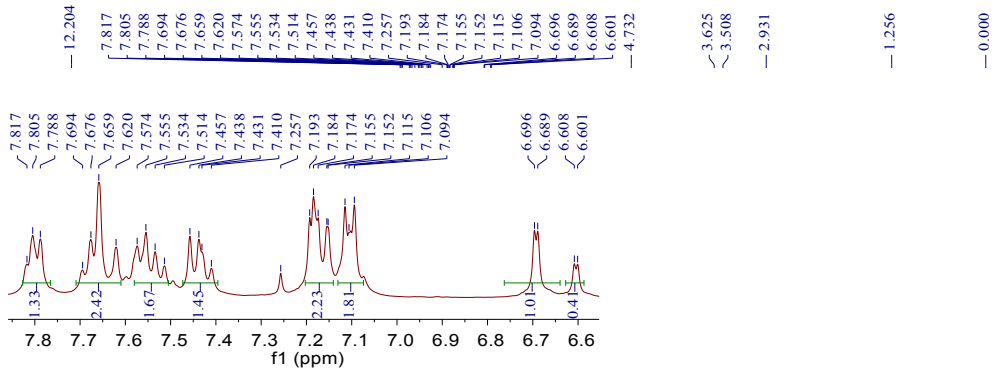
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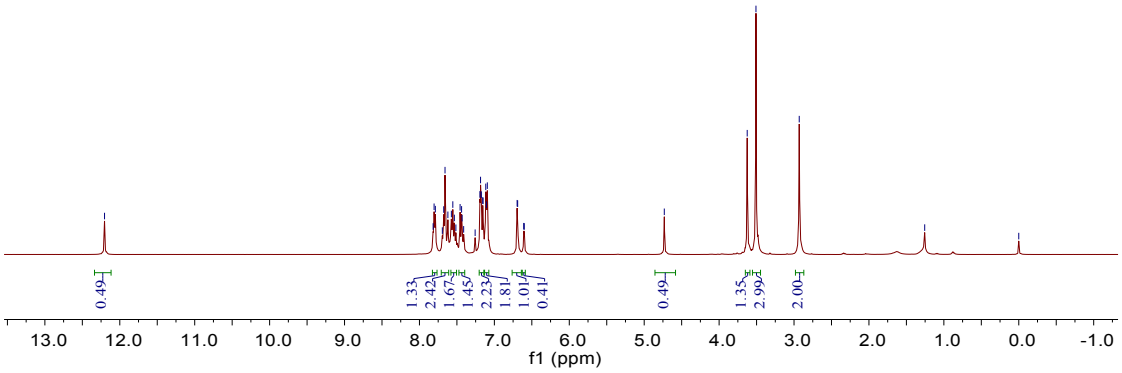
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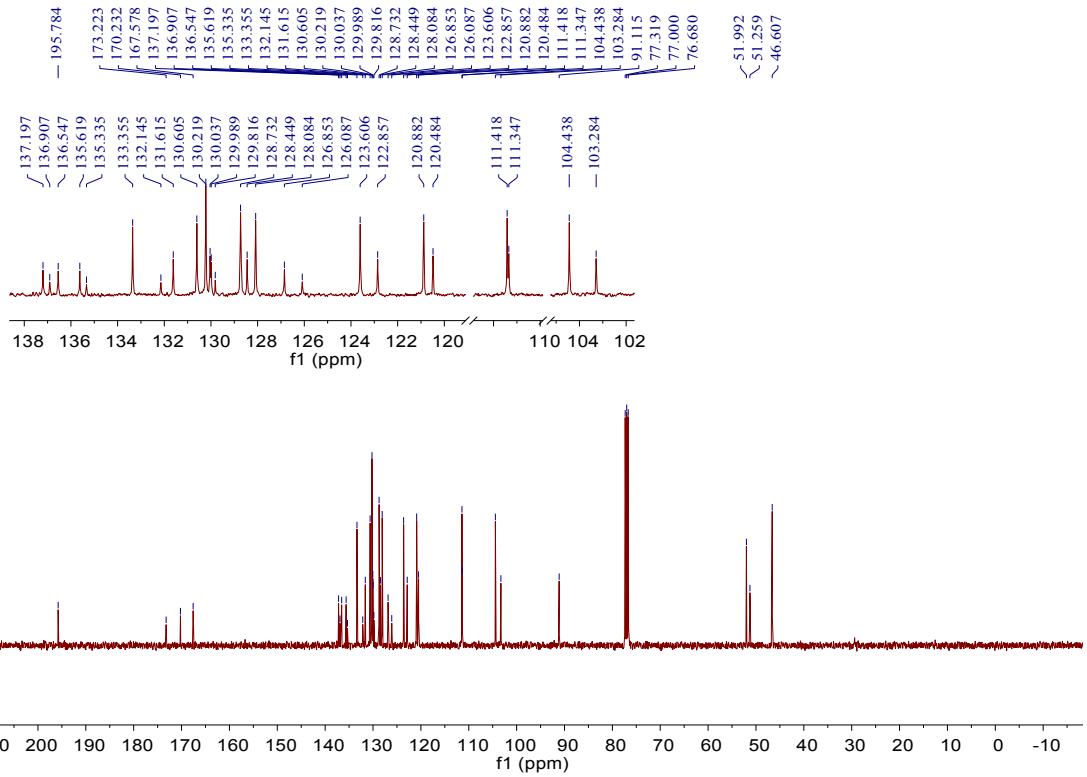
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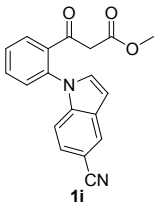
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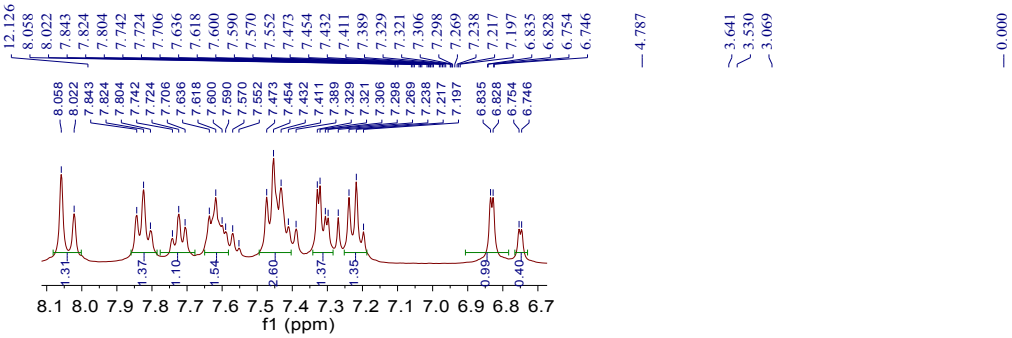
CN

1i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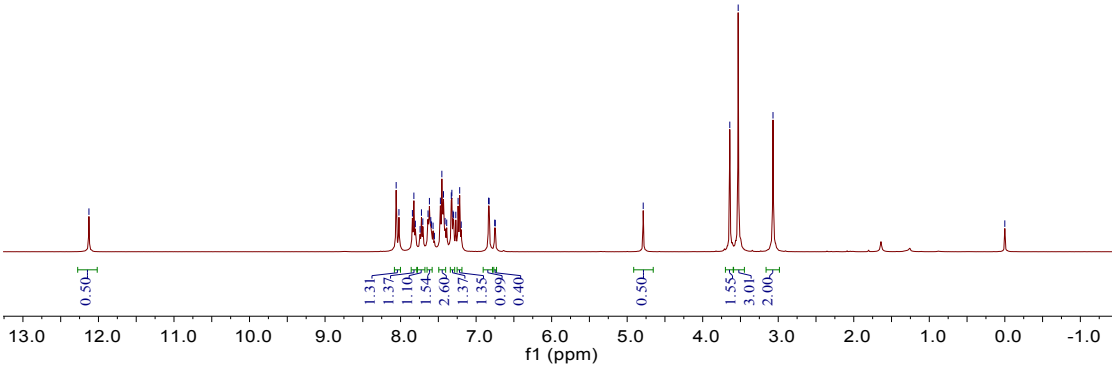
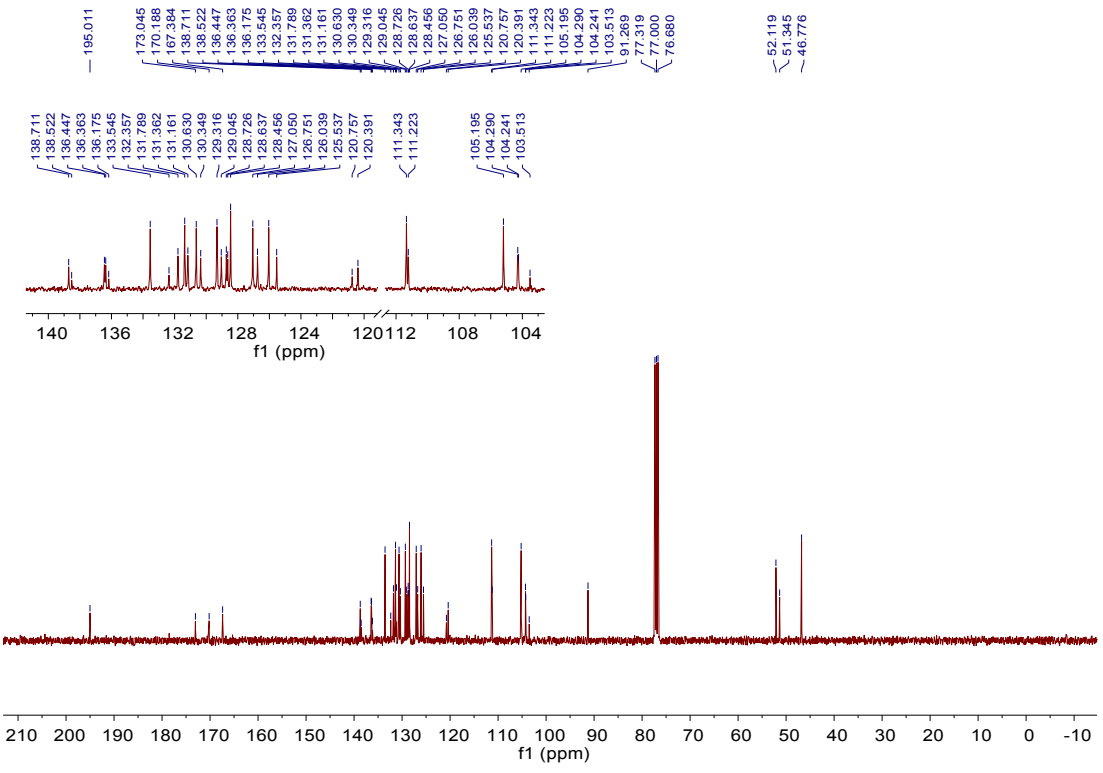
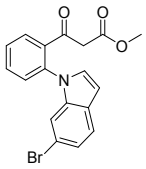
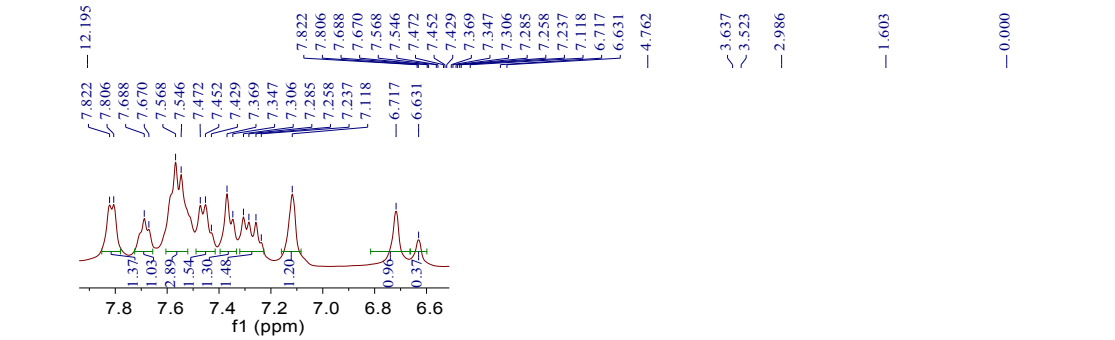
1.54
2.60
1.37
1.35
0.99
0.40
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)

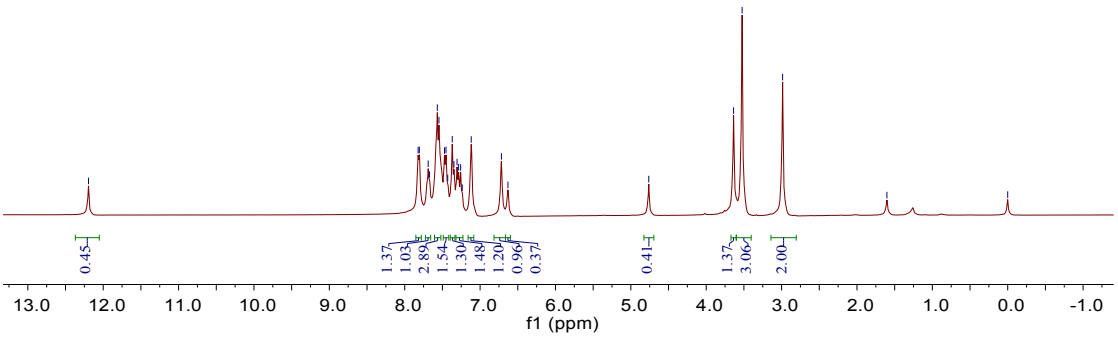

0.50
1.31
1.37
1.10
1.54
2.60
1.37
1.35
0.99
0.40
0.50
1.55
3.01
2.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

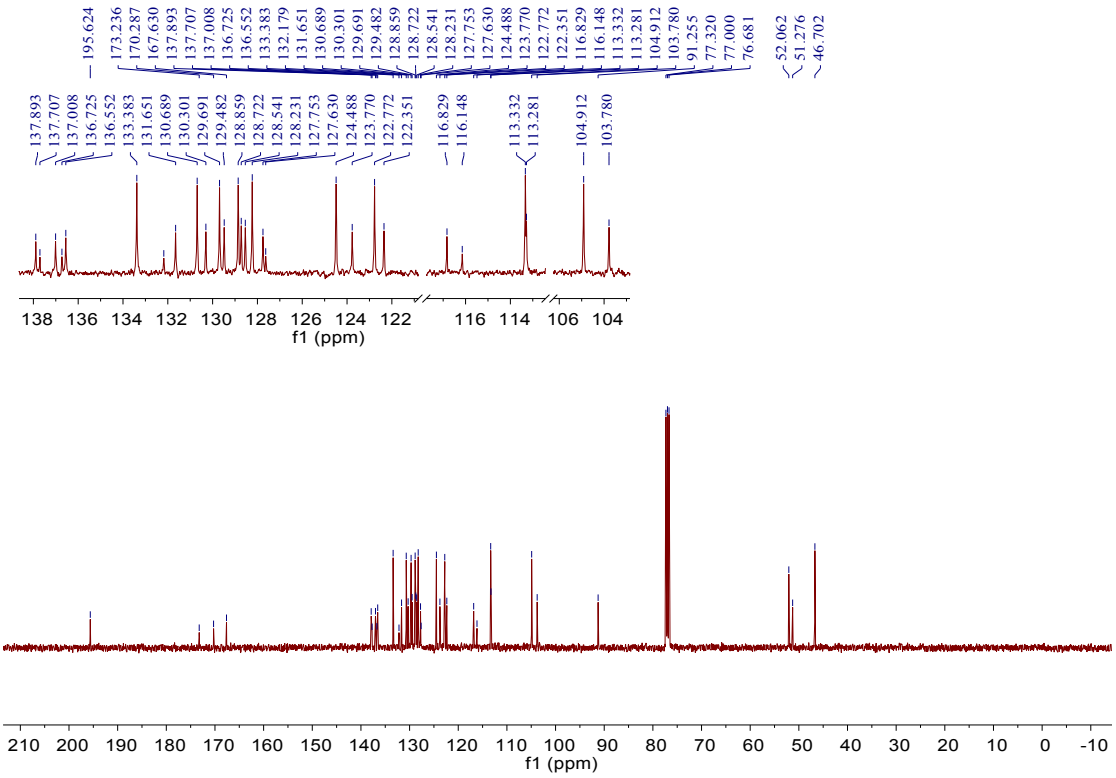

195.011
173.045
170.188
167.384
138.711
138.522
136.447
136.363
136.175
133.545
132.357
131.789
131.362
131.161
130.630
130.349
129.316
129.045
128.726
128.637
128.456
127.050
126.751
126.039
125.537
120.757
120.391
111.343
111.223
105.195
104.290
104.241
103.513
91.269
77.319
77.000
76.680
52.119
51.345
46.776
140 136 132 128 124 120112 108 104
f1 (ppm)
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)

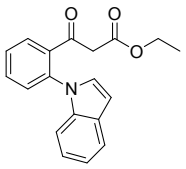

O
O
O
N
Br

1j

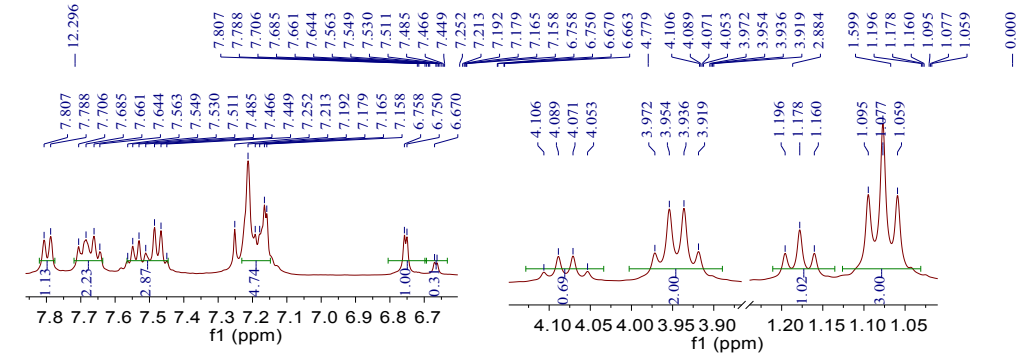

12.195
7.822
7.806
7.688
7.670
7.568
7.546
7.472
7.452
7.429
7.369
7.347
7.306
7.285
7.258
7.237
7.118
6.717
6.631
4.762
3.637
3.523
2.986
1.603
0.000
1.37
1.03
2.89
1.54
1.30
1.48
1.20
0.96
0.37
7.8
7.6
7.4
7.2
7.0
6.8
6.6
f1 (ppm)

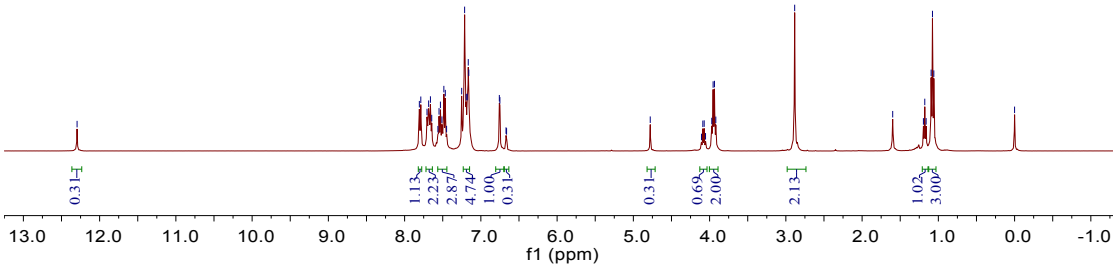

0.45
1.37
1.03
2.89
1.54
1.30
1.48
1.20
0.96
0.37
0.41
1.37
3.06
2.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

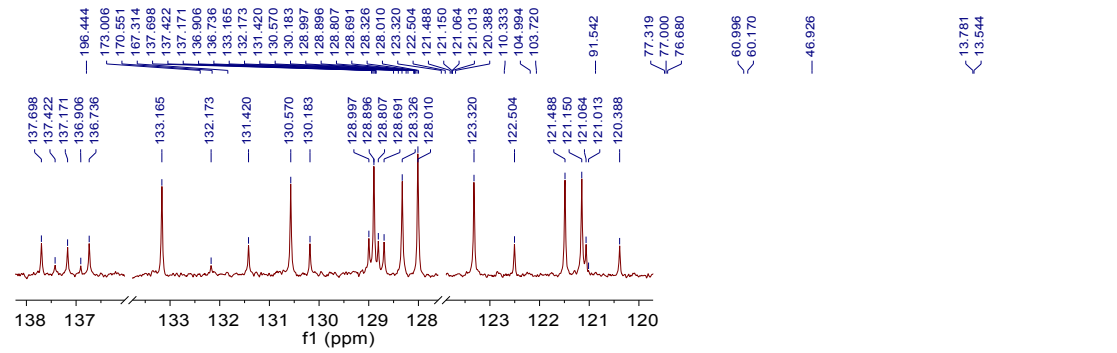

195.624
173.236
170.287
167.630
137.893
137.707
137.008
136.725
136.552
133.383
132.179
131.651
130.689
130.301
129.691
129.482
128.859
128.722
128.541
128.231
127.753
127.630
124.488
123.770
122.772
122.351
116.829
116.148
113.332
113.281
104.912
103.780
91.255
77.320
77.000
76.681
52.062
51.276
46.702
138
136
134
132
130
128
126
124
122
116
114
106
104
f1 (ppm)
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)

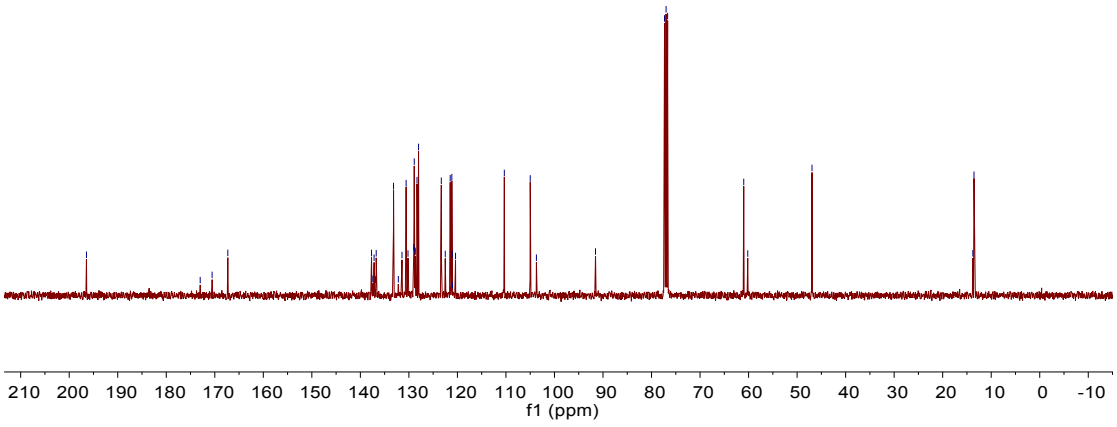


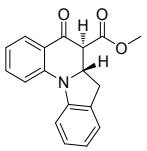
1k



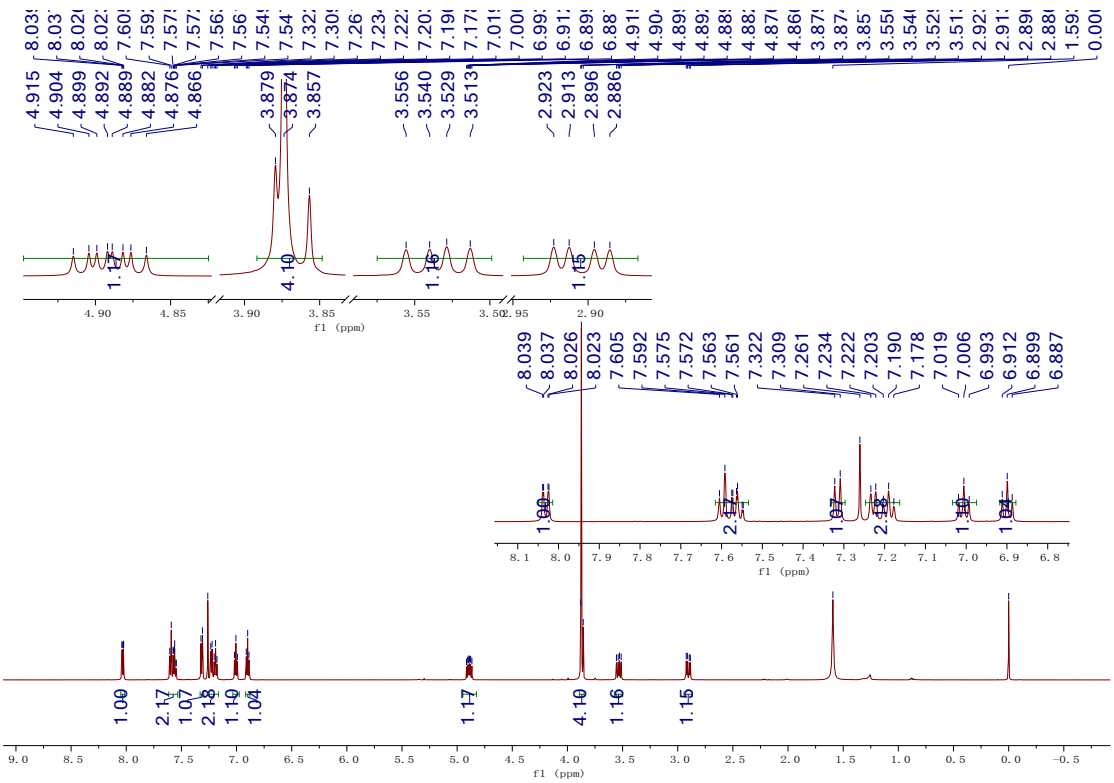


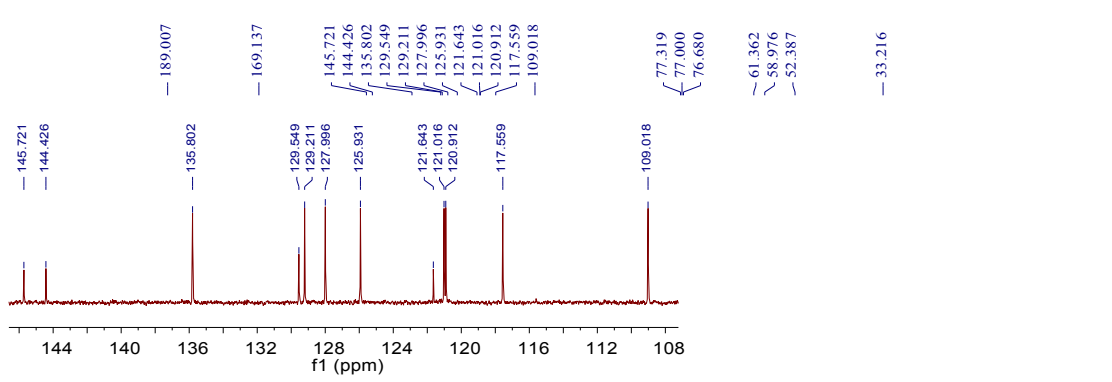


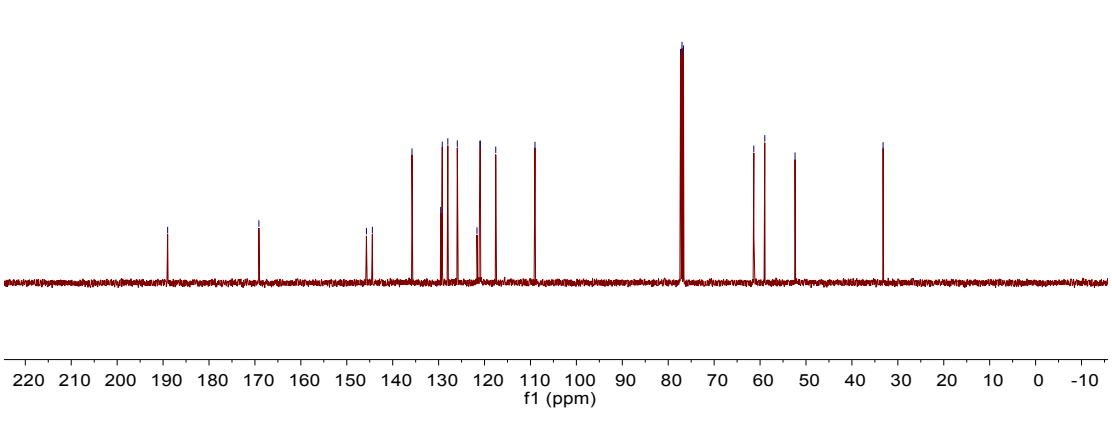


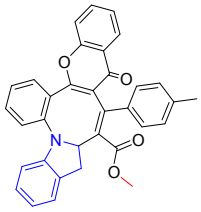


4a

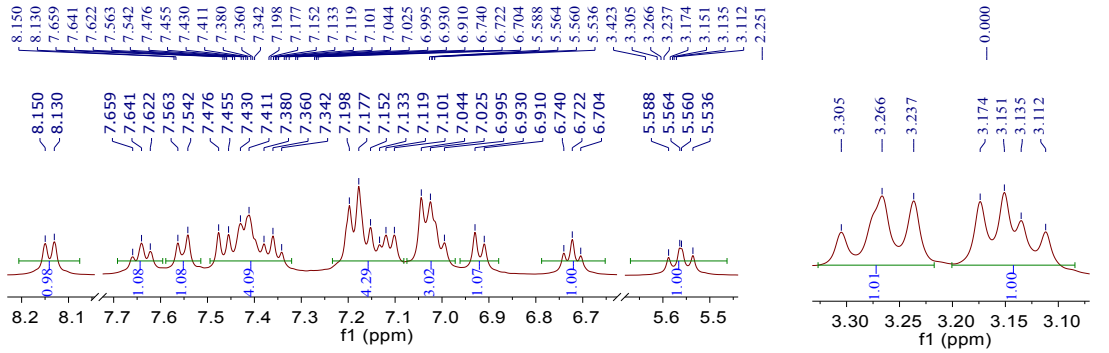


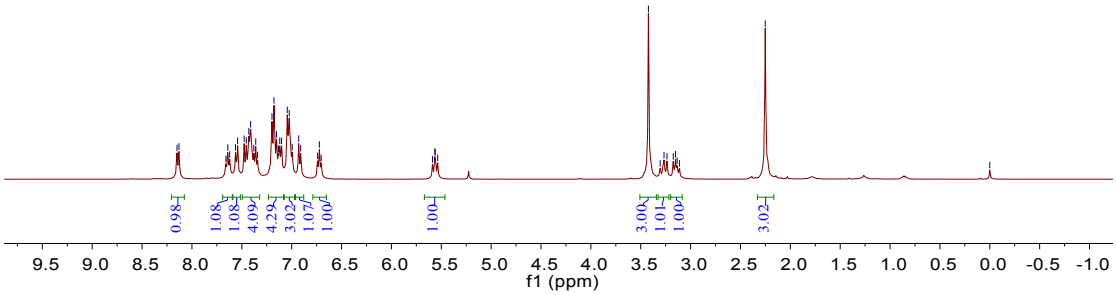


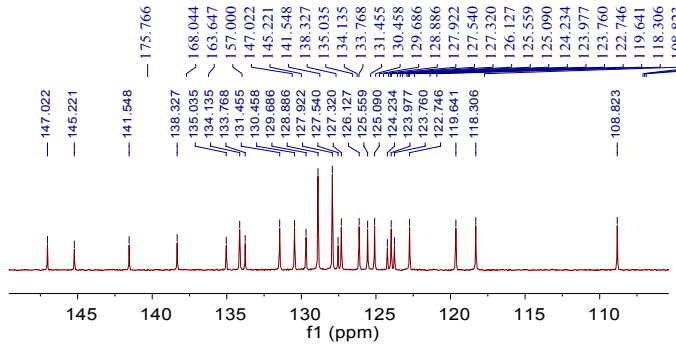


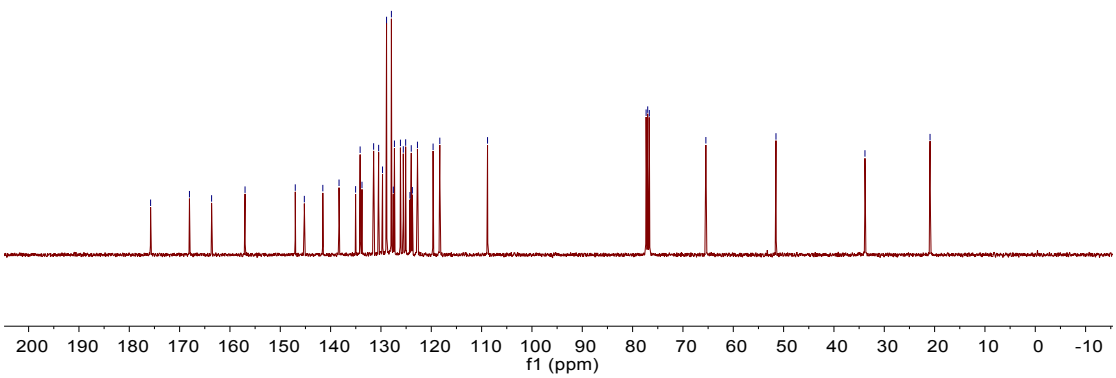


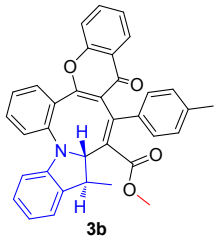
3a



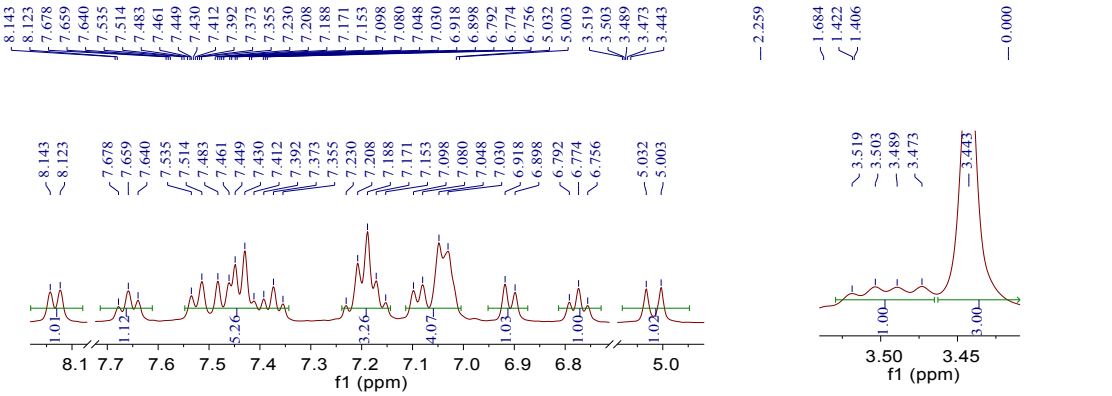


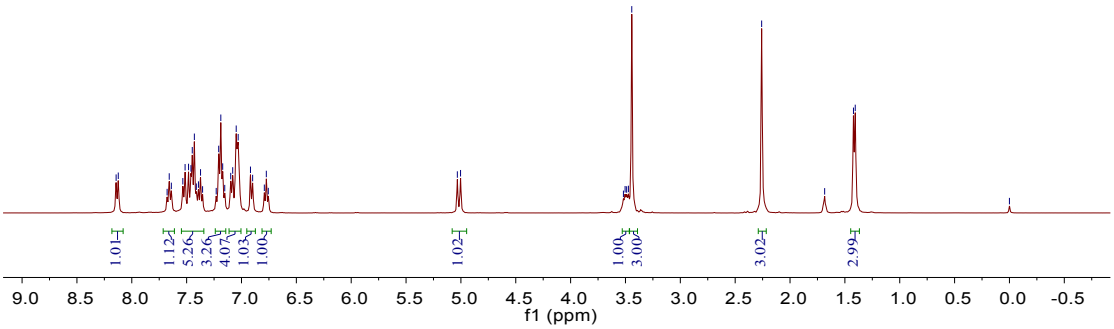


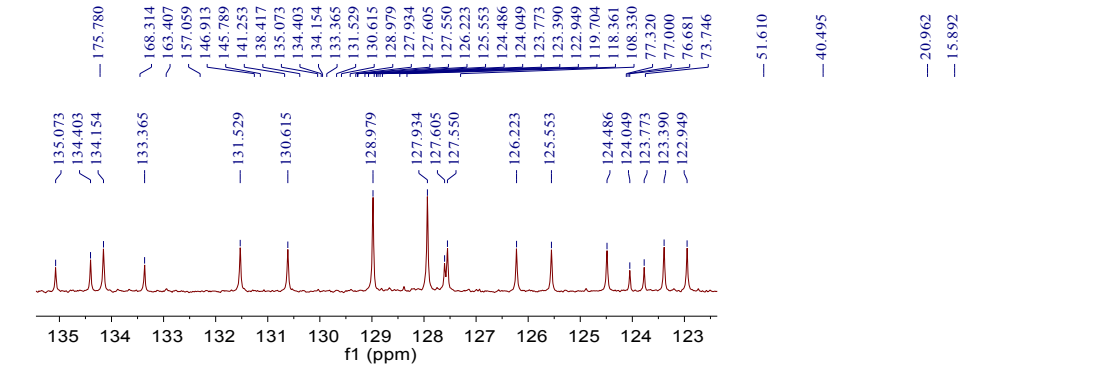



O
O
H
N
O
O
H

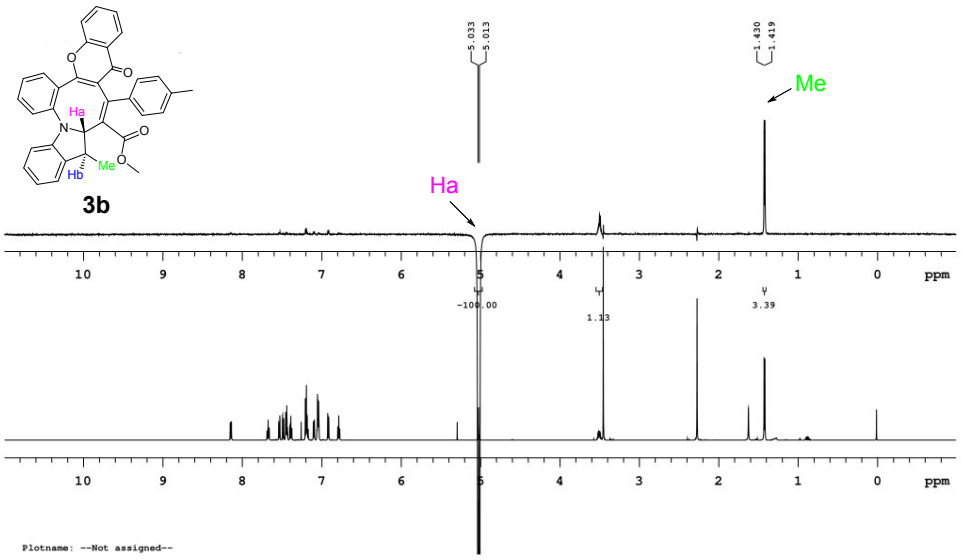
3b


8.143
8.123
7.678
7.659
7.640
7.535
7.514
7.483
7.461
7.449
7.430
7.412
7.392
7.373
7.355
7.230
7.208
7.188
7.171
7.153
7.098
7.080
7.048
7.030
6.918
6.898
6.792
6.774
6.756
5.032
5.003
3.519
3.503
3.489
3.473
3.443
2.259
1.684
1.422
1.406
0.000
1.01
1.12
5.26
3.26
4.07
1.03
1.00
1.02
1.00
3.00
f1 (ppm)

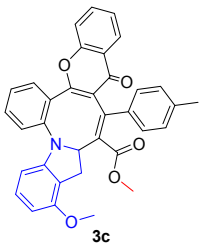

1.01
1.12
5.26
3.26
4.07
1.03
1.00
1.02
1.00
3.00
3.02
2.99
f1 (ppm)


175.780
168.314
163.407
157.059
146.913
145.789
141.253
138.417
135.073
134.403
134.154
133.365
133.529
131.529
130.615
128.979
127.934
127.605
127.550
126.223
125.553
124.486
124.049
123.773
123.390
122.949
119.704
118.361
108.330
77.320
77.000
76.681
73.746
51.610
40.495
20.962
15.892
f1 (ppm)

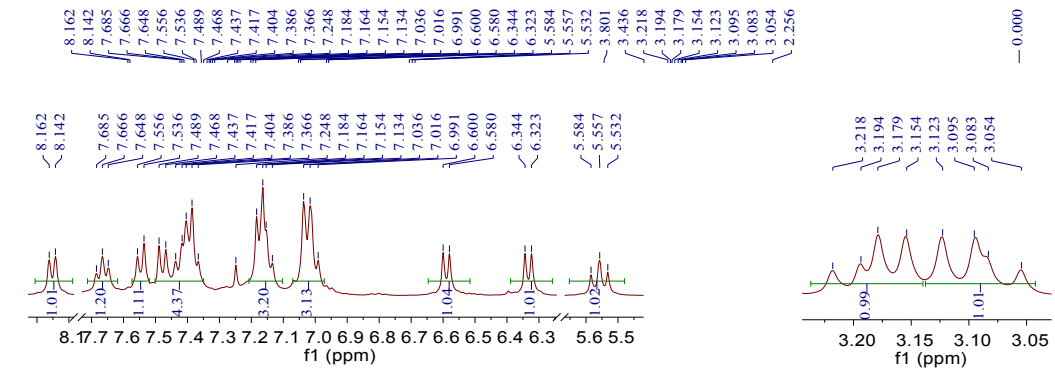
6. The 1D NOESY spectra of 3b

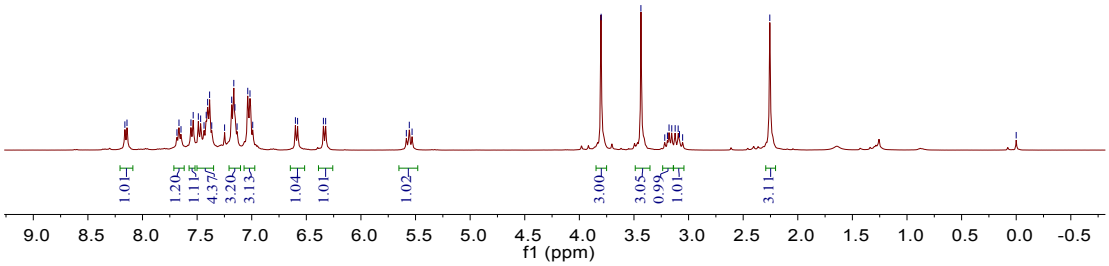


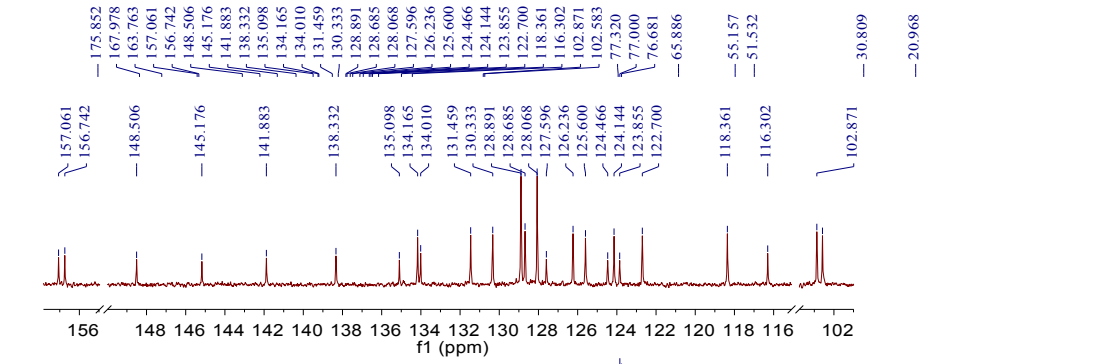
NOE enhancement = 3.39%

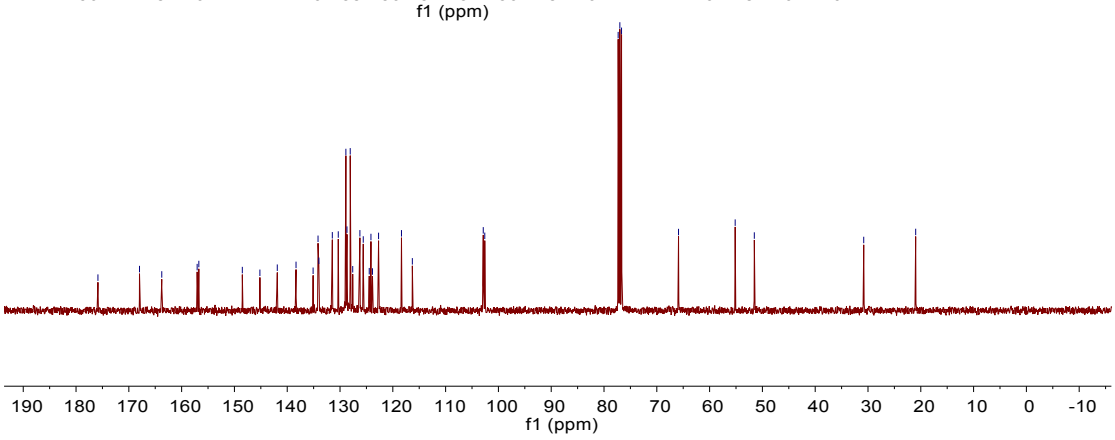


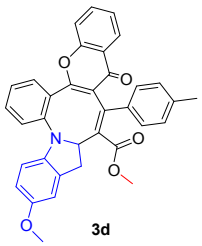
3c



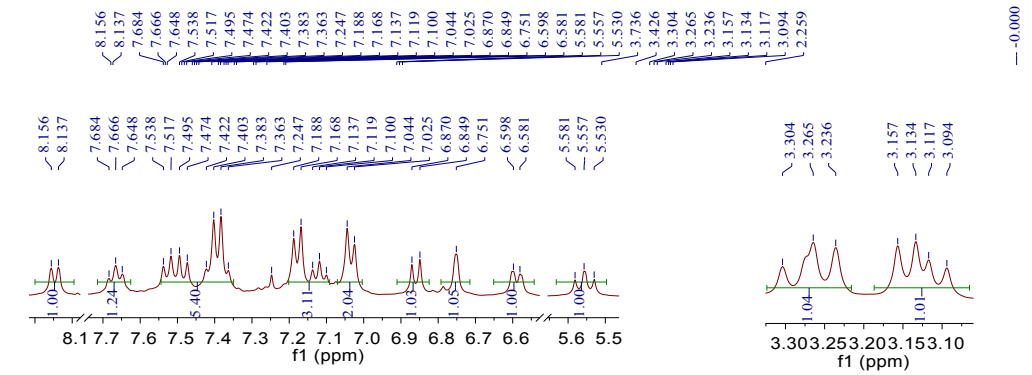


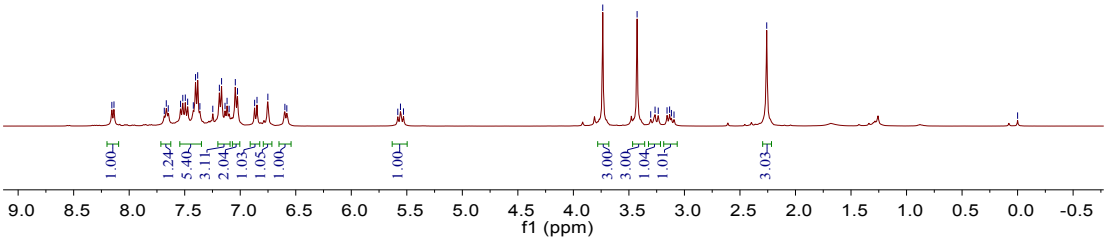


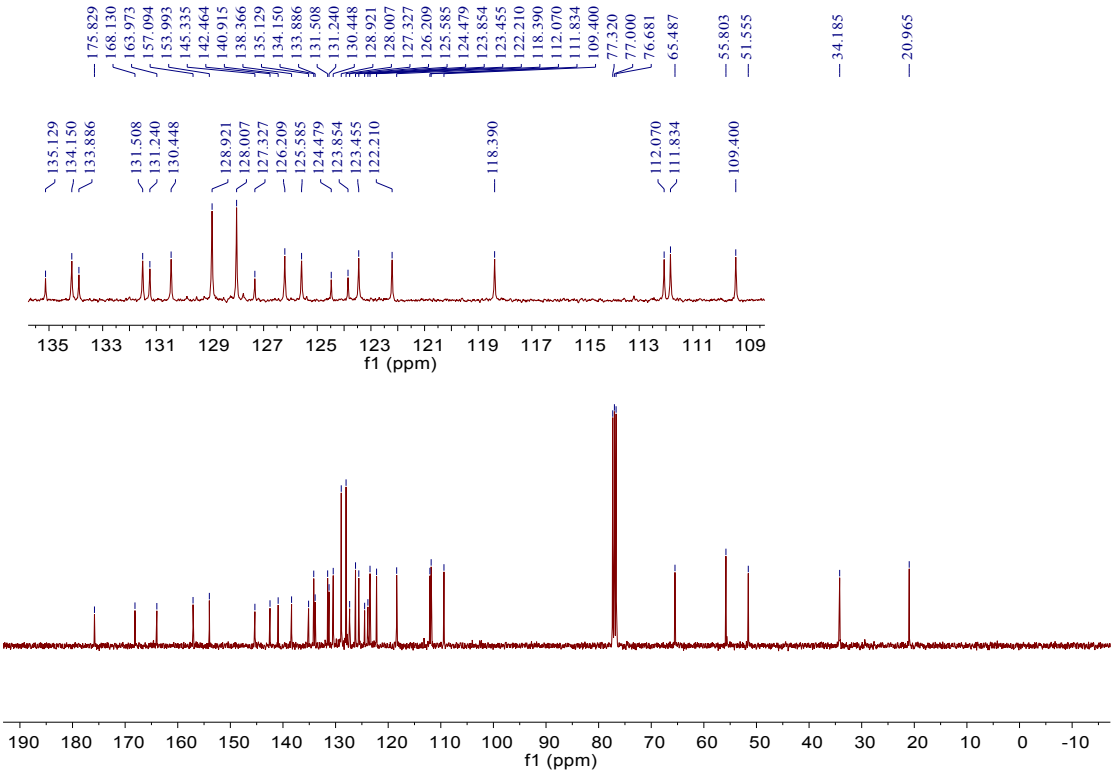


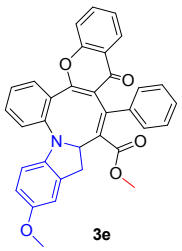

O
O
N
O
O
O

3d

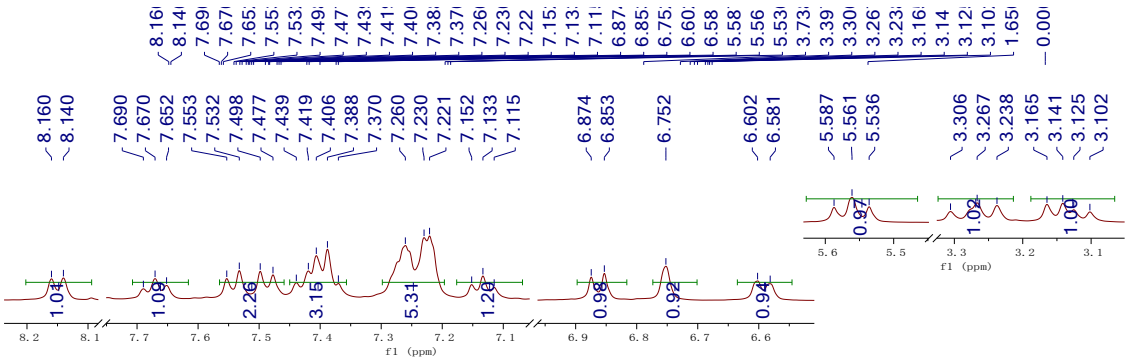

8.156
8.137
7.684
7.666
7.648
7.538
7.517
7.495
7.474
7.422
7.403
7.383
7.363
7.247
7.188
7.168
7.137
7.119
7.100
7.044
7.025
6.870
6.849
6.751
6.598
6.581
5.581
5.557
5.530
3.736
3.426
3.304
3.265
3.236
3.157
3.134
3.117
3.094
2.259
-0.000
1.00
1.24
5.40
3.11
2.04
1.03
1.05
1.00
1.00
1.04
1.01
8.1 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 5.6 5.5
3.30 3.25 3.20 3.15 3.10
f1 (ppm)

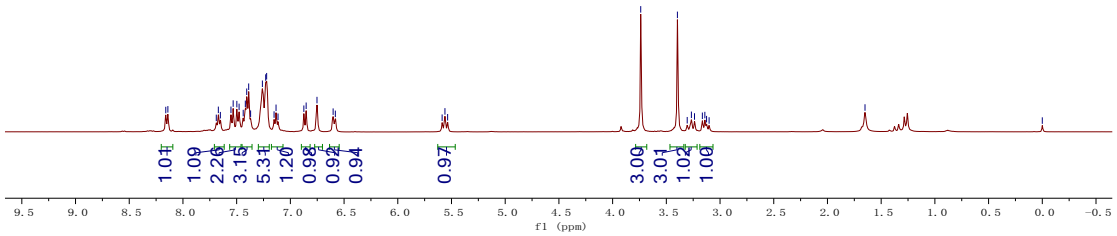

1.00
1.24
5.40
3.11
2.04
1.03
1.05
1.00
1.00
3.00
3.00
1.04
1.01
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

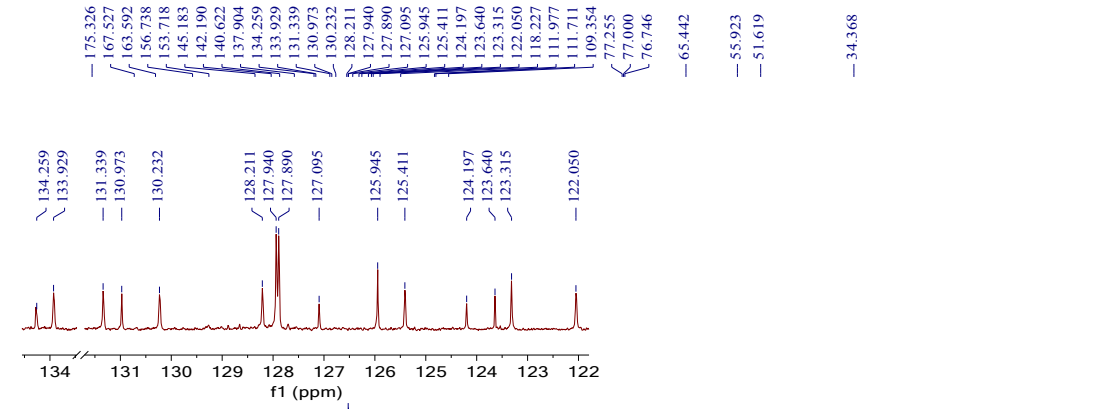

175.829
168.130
163.973
157.094
153.993
145.335
142.464
140.915
138.366
135.129
134.150
133.886
131.508
131.240
130.448
128.921
128.007
127.327
126.209
125.585
124.479
123.854
123.455
122.210
118.390
112.070
111.834
109.400
77.320
77.000
76.681
65.487
55.803
51.555
34.185
20.965
135 133 131 129 127 125 123 121 119 117 115 113 111 109
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

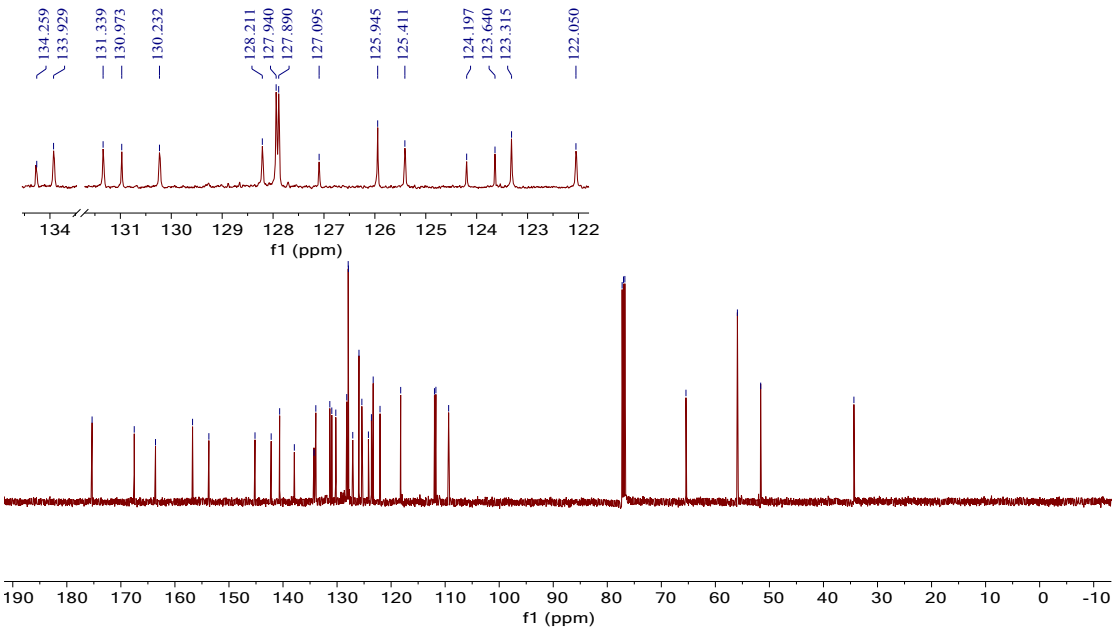


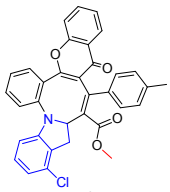
3e



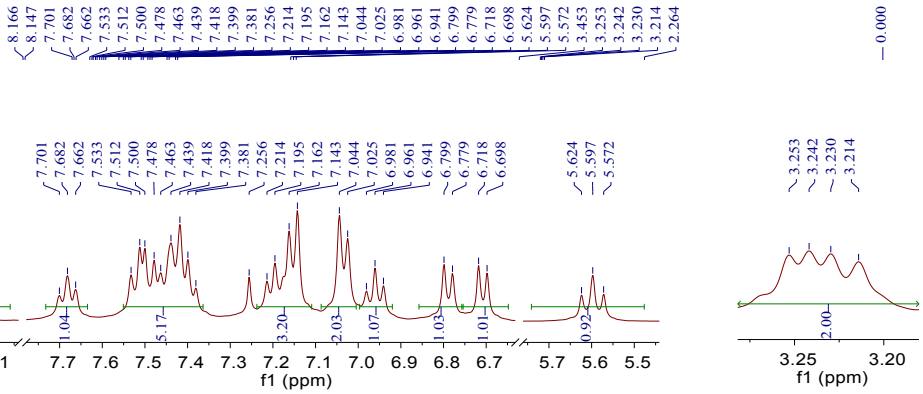


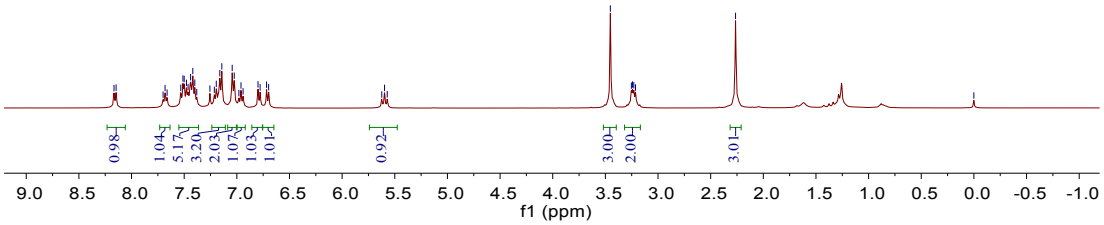


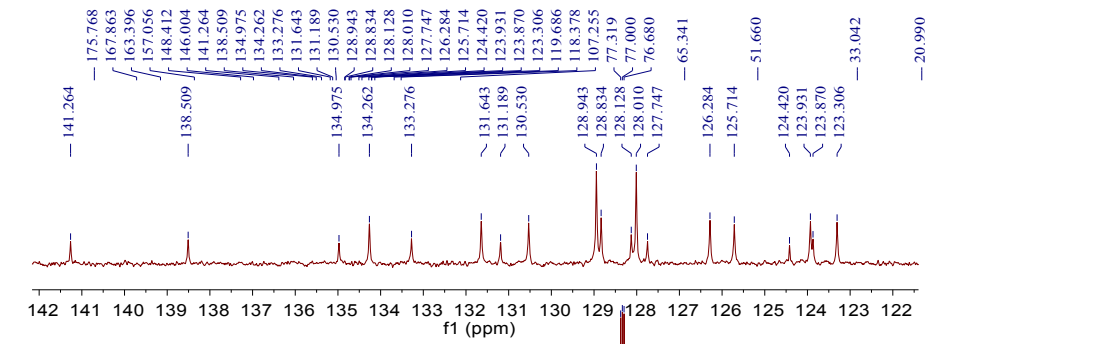


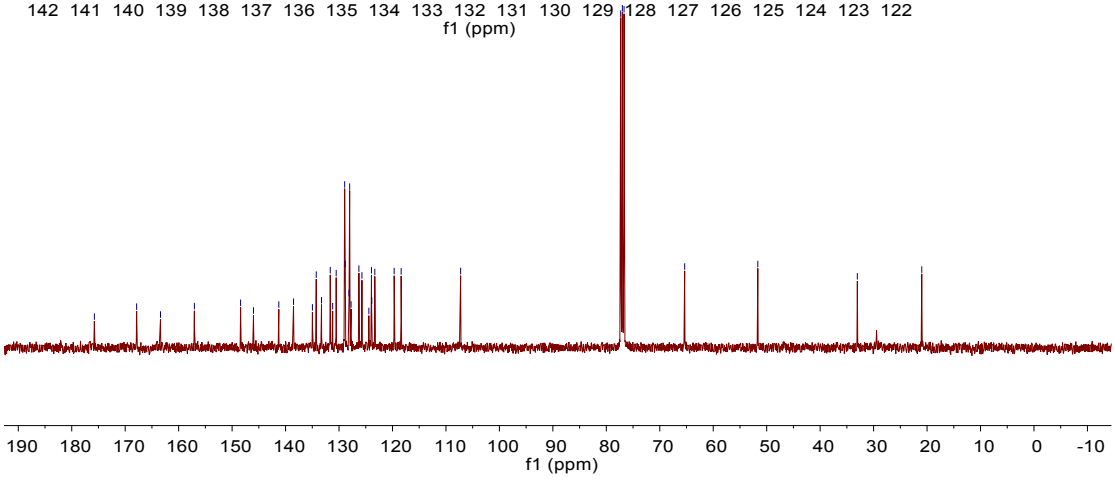


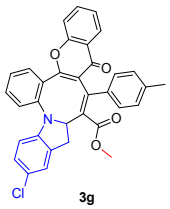
3f



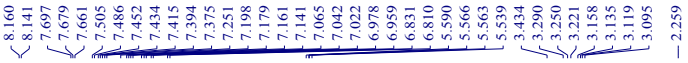







O
O
O
O
N
Cl

3g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7.486
7.452
7.434
7.415
7.394
7.375
7.251
7.198
7.179
7.161
7.141
7.065
7.042
7.022
6.978
6.959
6.831
6.810
5.590
5.566
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5.539
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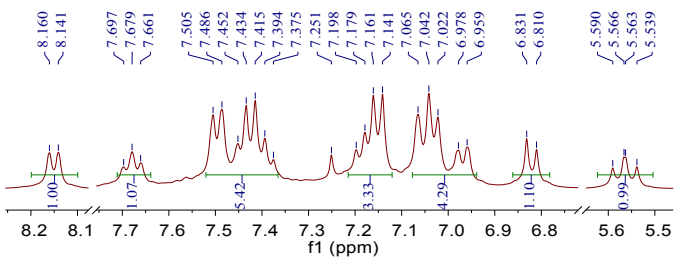
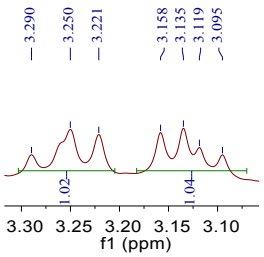
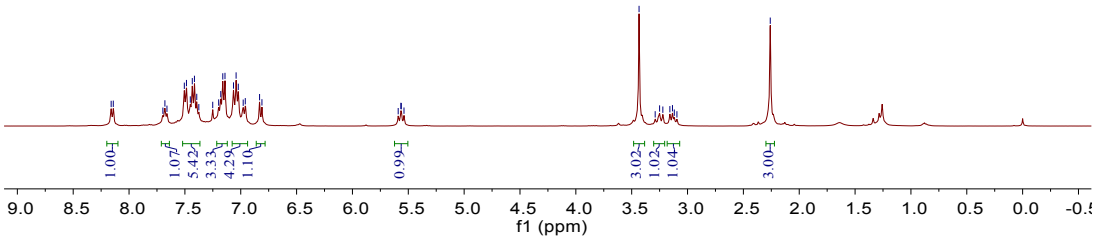
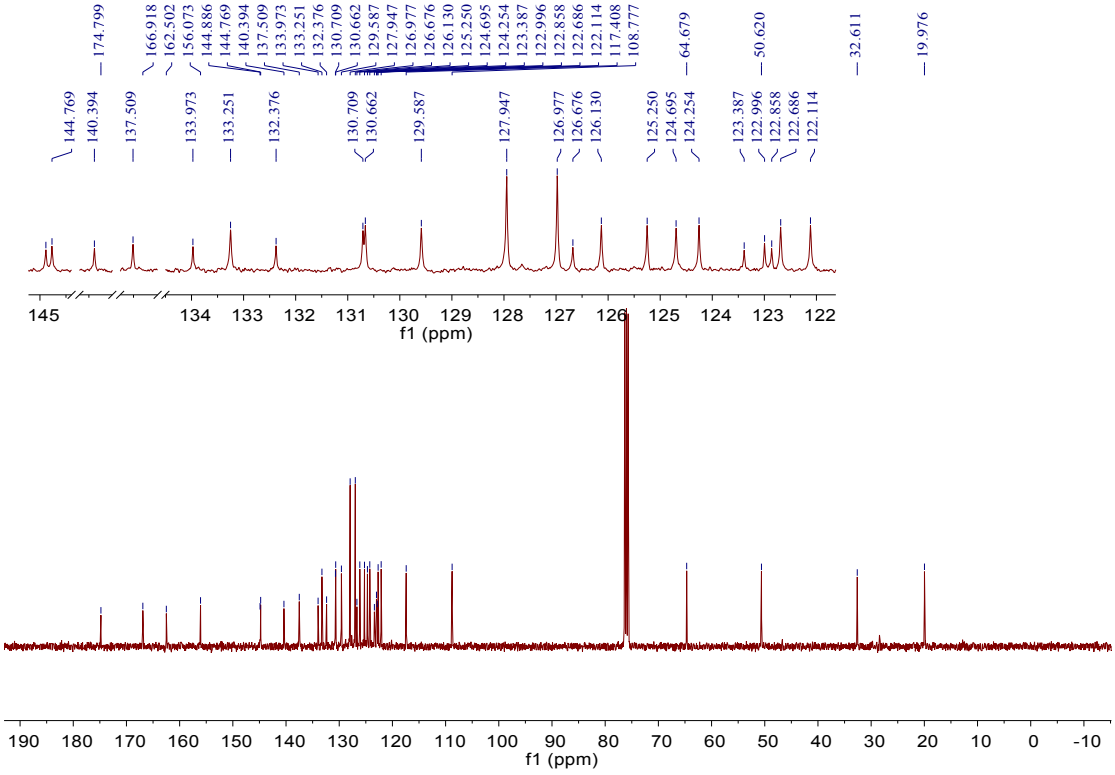
3.250
3.221
3.158
3.135
3.119
3.095
2.259


1.00
1.07
5.42
3.33
4.29
1.10
0.99
8.2 8.1 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 5.6 5.5
f1 (ppm)


1.02
1.04
3.30 3.25 3.20 3.15 3.10
f1 (ppm)


1.00
1.07
5.42
3.33
4.29
1.10
0.99
3.02
1.02
1.04
3.00
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)


174.799
166.918
162.502
156.073
144.886
144.769
140.394
137.509
133.973
133.251
132.376
130.709
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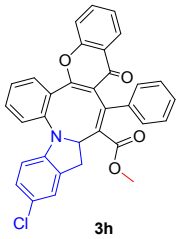
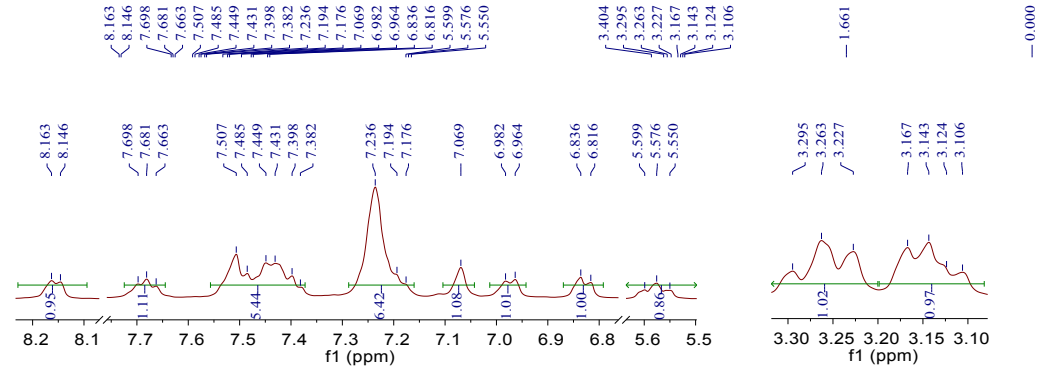
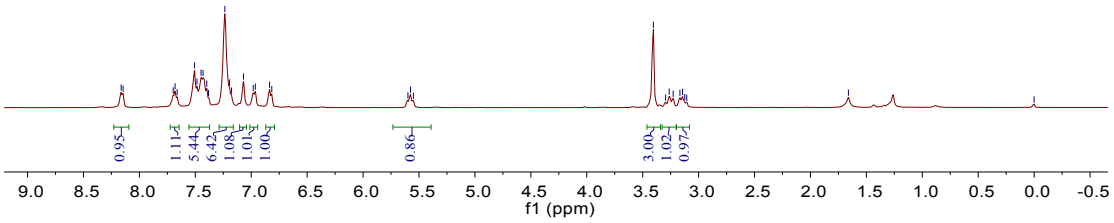
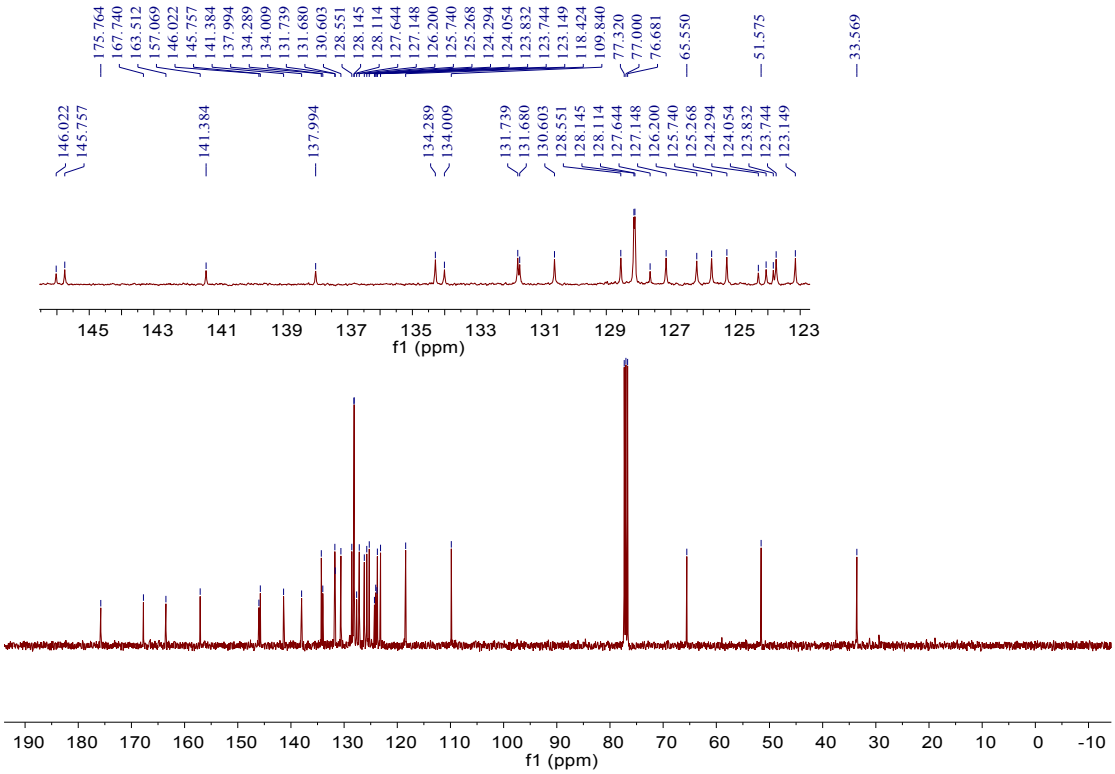
129.587
127.947
126.977
126.676
126.130
125.250
124.695
124.254
123.387
122.996
122.858
122.686
122.114
117.408
108.777
64.679
50.620
32.611
19.976
145 134 133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
O
O
N
Cl

3h


8.163
8.146
7.698
7.681
7.663
7.507
7.485
7.449
7.431
7.398
7.382
7.236
7.194
7.176
7.069
6.982
6.964
6.836
6.816
5.599
5.576
5.550
3.404
3.295
3.263
3.227
3.167
3.143
3.124
3.106
1.661
0.000
0.95
1.11
5.44
6.42
1.08
1.01
1.00
0.86
1.02
0.97
f1 (ppm)


0.95
1.11
5.44
6.42
1.08
1.01
1.00
0.86
3.00
1.02
0.97
f1 (ppm)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163.512
157.069
146.022
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141.384
137.994
134.289
134.009
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131.680
130.603
128.551
128.145
128.114
127.644
127.148
126.200
125.740
125.268
124.294
124.054
123.832
123.744
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118.424
109.840
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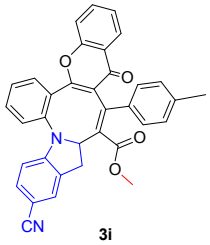
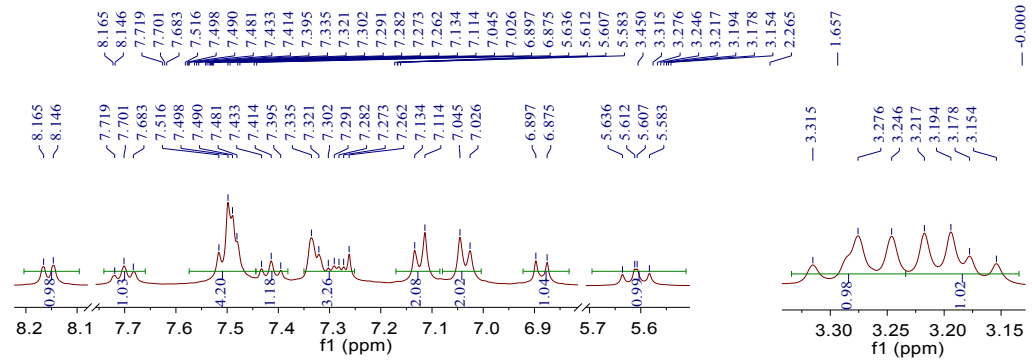
77.000
76.681
65.550
51.575
33.569
f1 (ppm)


O
O
N
O
O
CN

3i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7.719
7.701
7.683
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7.490
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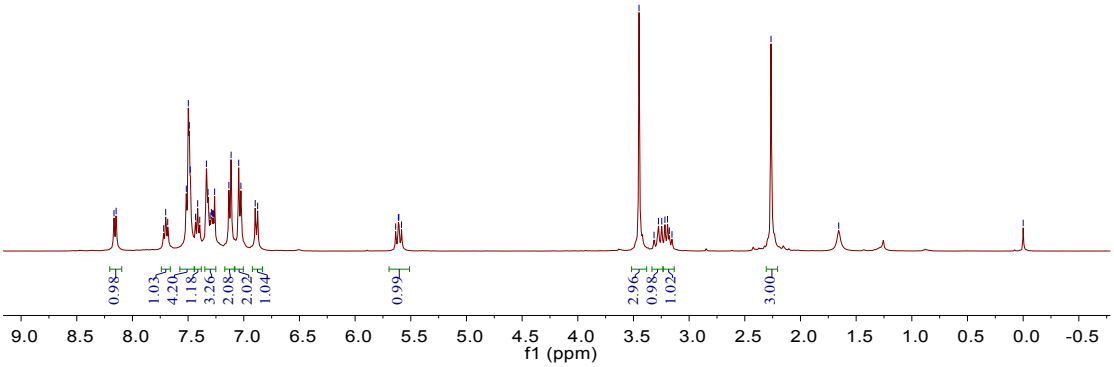
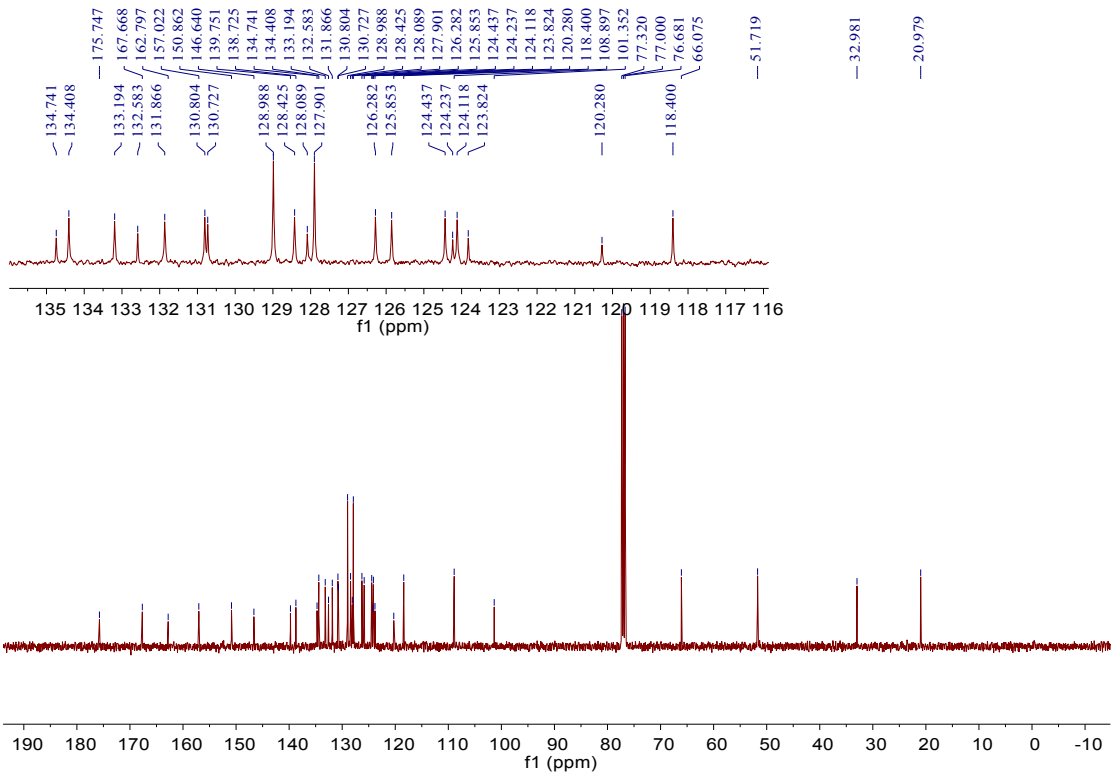
7.433
7.414
7.395
7.335
7.321
7.302
7.291
7.282
7.273
7.262
7.134
7.114
7.045
7.026
6.897
6.875
5.636
5.612
5.607
5.583
3.450
3.315
3.276
3.246
3.217
3.194
3.178
3.154
2.265
1.657
-0.000
0.98
1.03
4.20
1.18
3.26
2.08
2.02
1.04
0.99
0.98
1.02
f1 (ppm)


0.98
1.03
4.20
1.18
3.26
2.08
2.02
1.04
0.99
2.96
0.98
1.02
3.00
f1 (ppm)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146.640
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138.725
134.741
134.408
133.194
132.583
131.866
130.804
130.727
128.988
128.425
128.089
127.901
126.282
125.853
124.437
124.237
124.118
123.824
120.280
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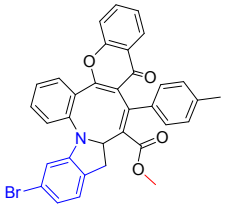
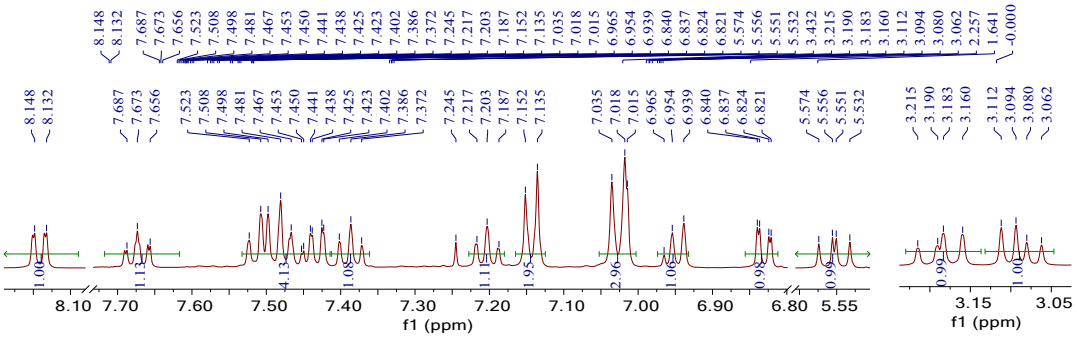
108.897
101.352
77.320
77.000
76.681
66.075
51.719
32.981
20.979
f1 (ppm)


O
O
N
O
O
Br

3j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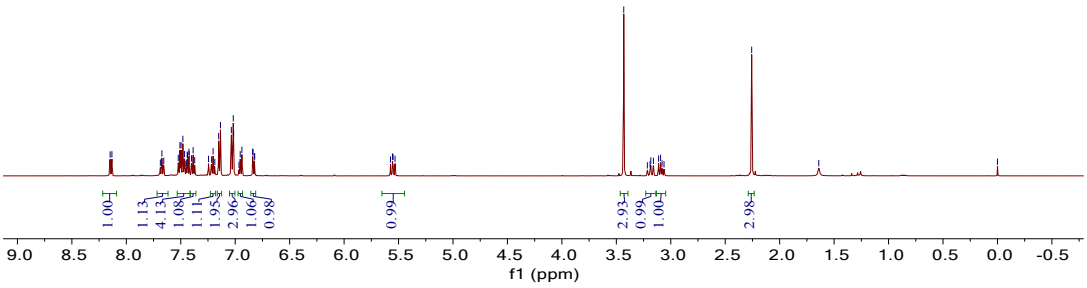
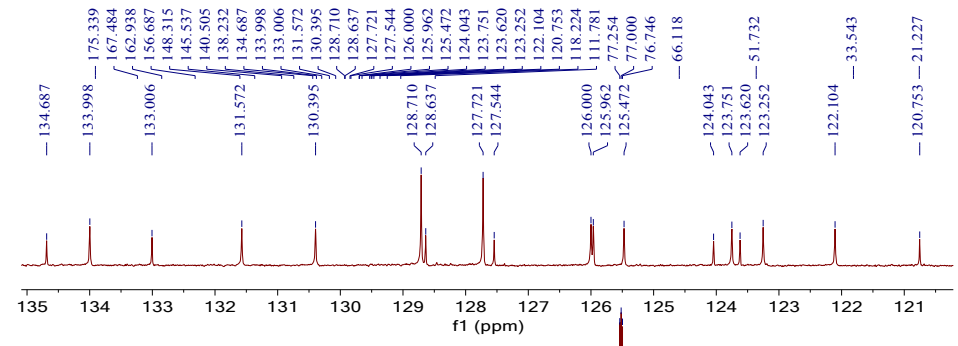
7.450
7.441
7.438
7.425
7.423
7.402
7.386
7.372
7.245
7.217
7.203
7.187
7.152
7.135
7.035
7.018
7.015
6.965
6.954
6.939
6.840
6.837
6.824
6.821
5.574
5.556
5.551
5.532
3.215
3.190
3.183
3.160
3.112
3.094
3.080
3.062
2.257
1.641
-0.000
1.00
1.13
4.13
1.08
1.11
1.95
2.96
1.06
0.98
0.99
2.93
0.99
1.00
2.98
8.10 7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80 5.55
f1 (ppm)
3.15 3.05
f1 (ppm)


1.00
1.13
4.13
1.08
1.11
1.95
2.96
1.06
0.98
0.99
2.93
0.99
1.00
2.98
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
f1 (ppm)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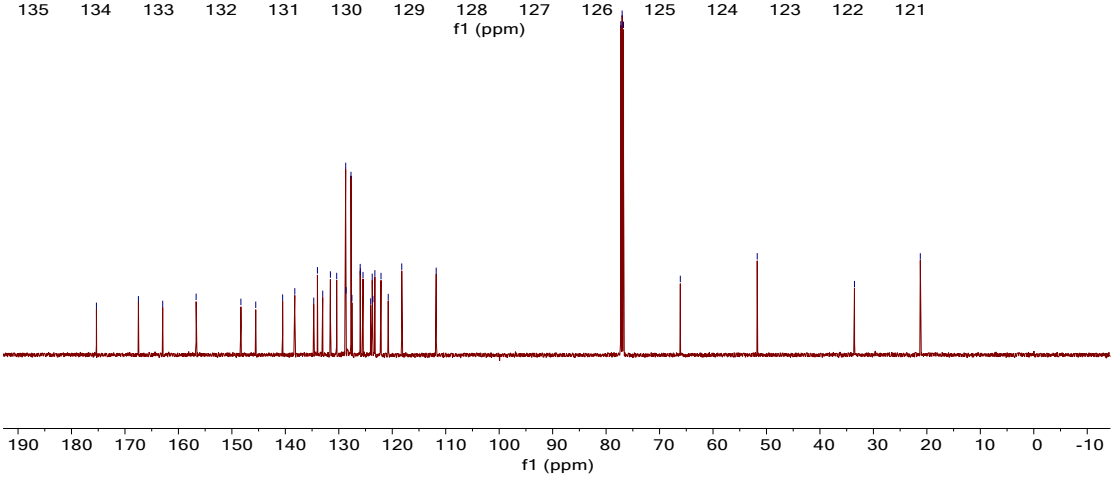
145.537
140.505
138.232
134.687
133.998
133.006
131.572
130.395
128.710
128.637
127.721
127.544
126.000
125.962
125.472
124.043
123.751
123.620
123.252
122.104
120.753
118.224
111.781
77.254
77.000
76.746
66.118
51.732
33.543
21.227
135 134 133 132 131 130 129 128 127 126 125 124 123 122 121
f1 (ppm)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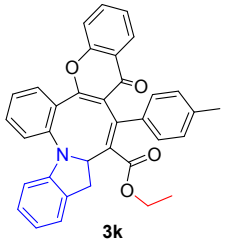
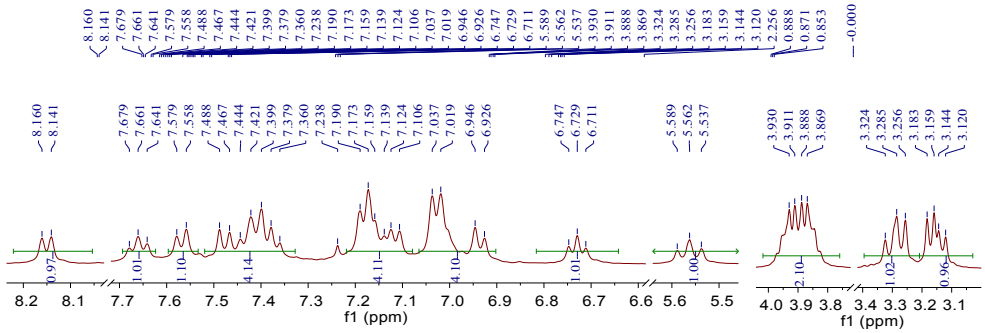
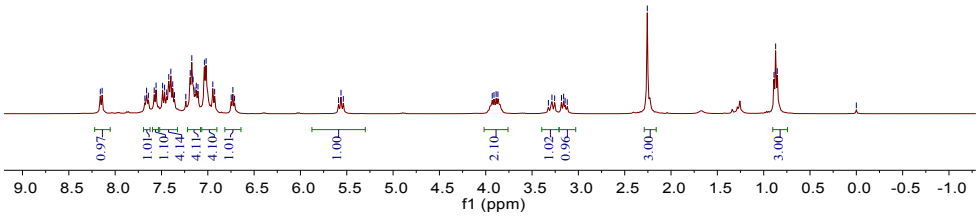
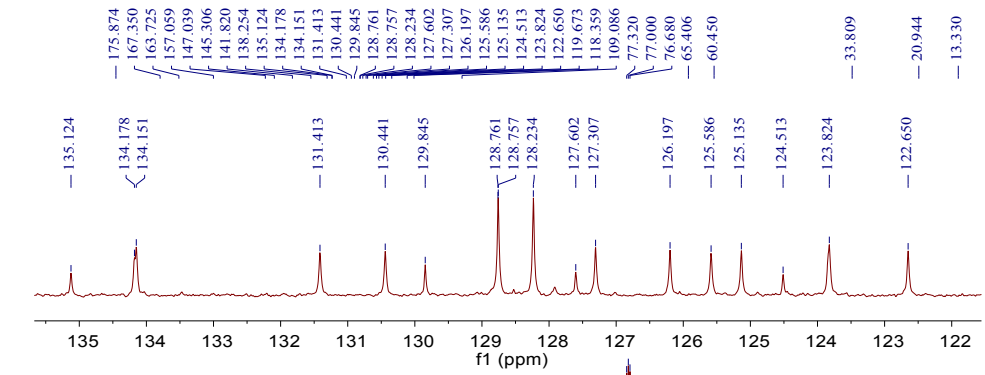
f1 (ppm)

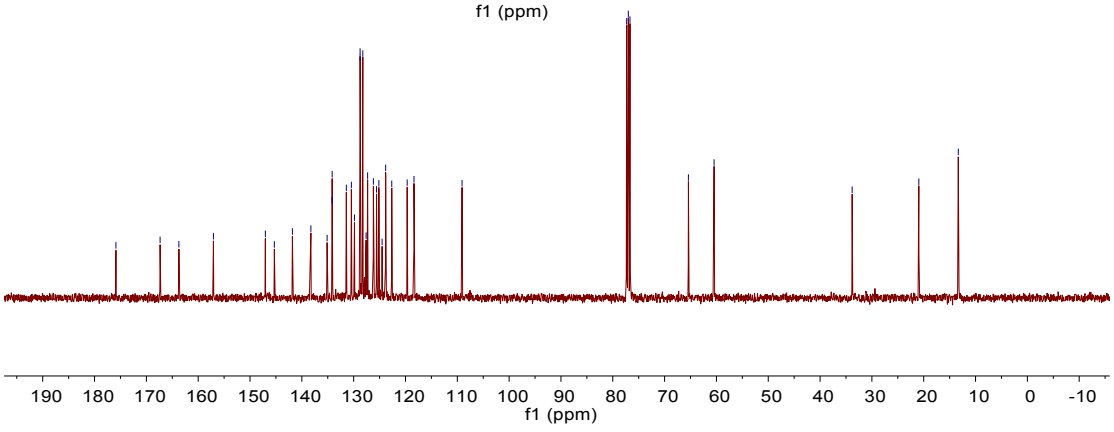


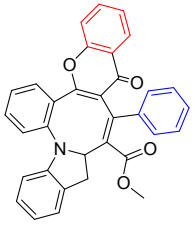
3k











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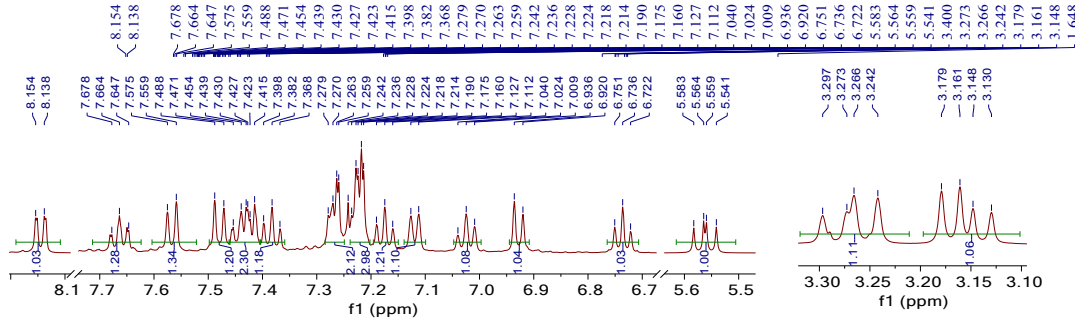

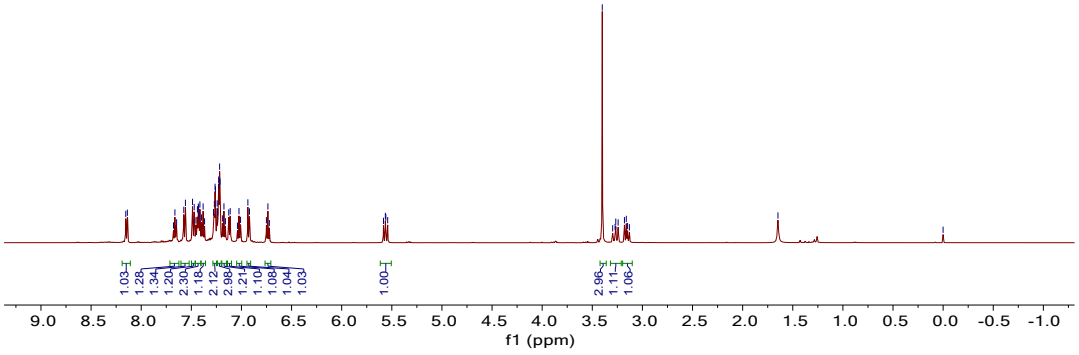

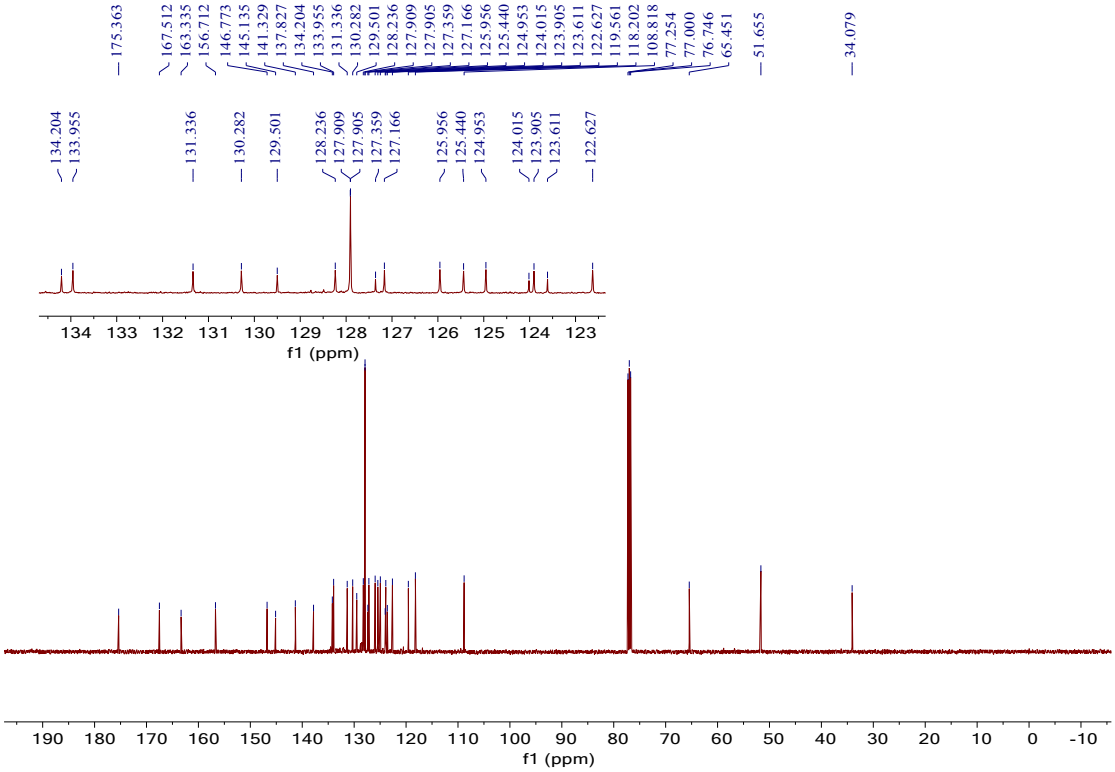

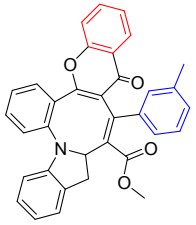

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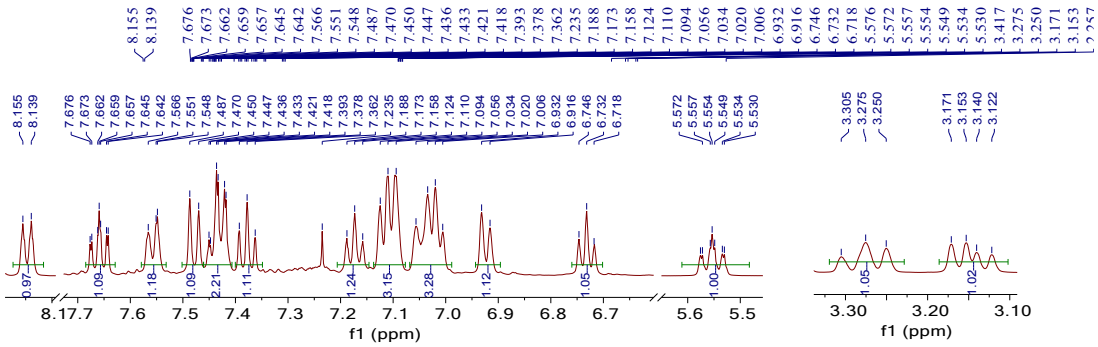

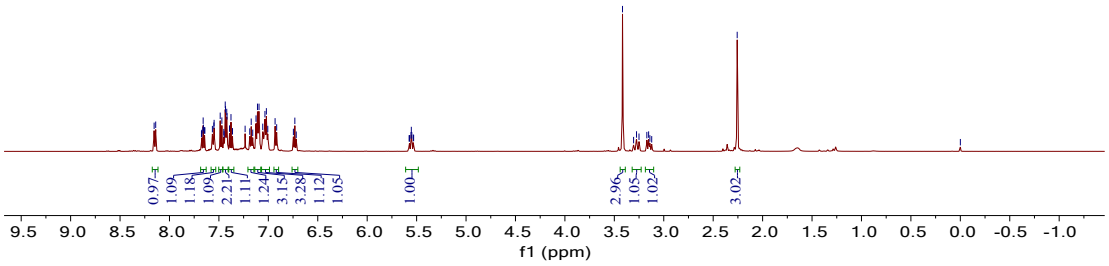

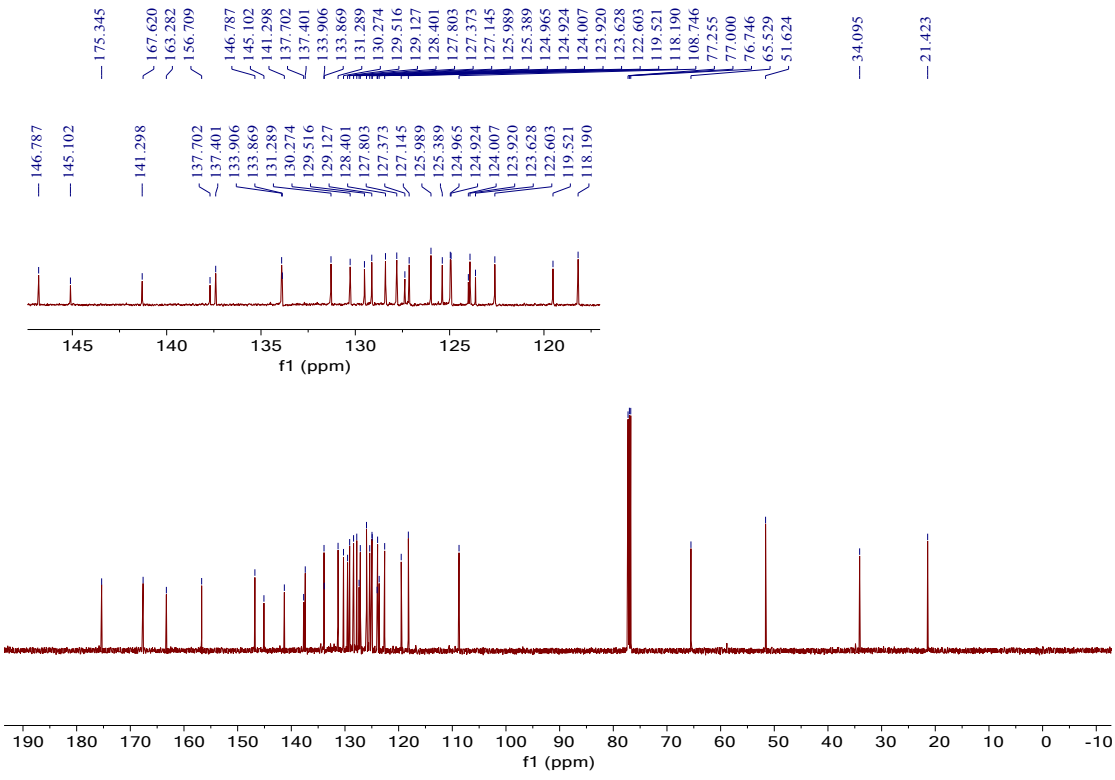

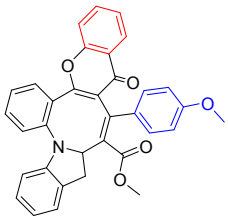

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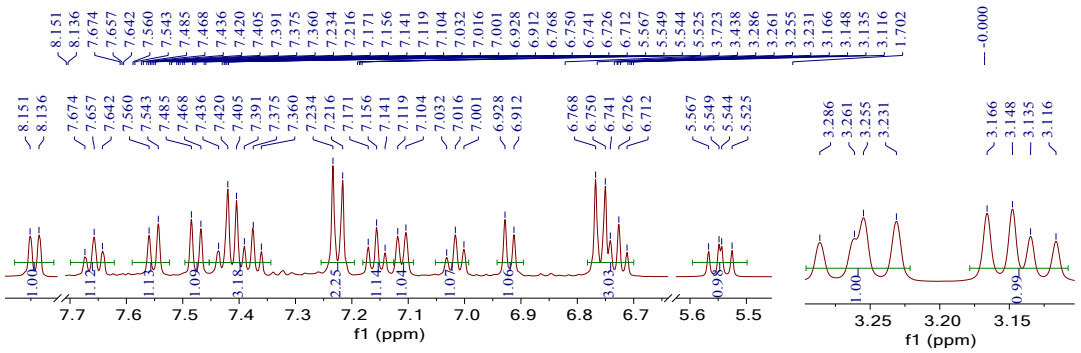

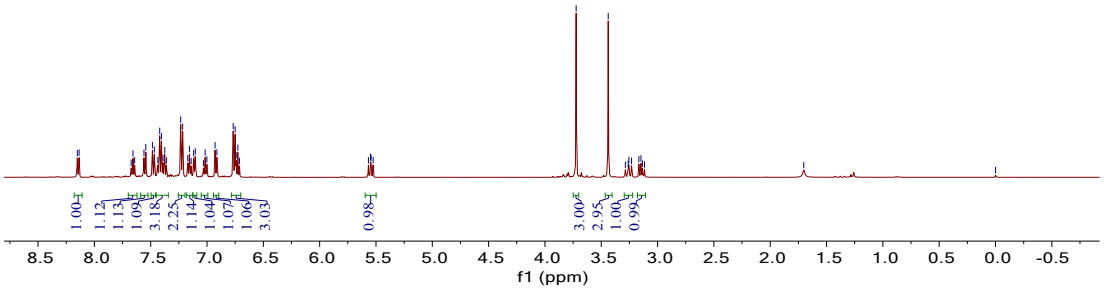

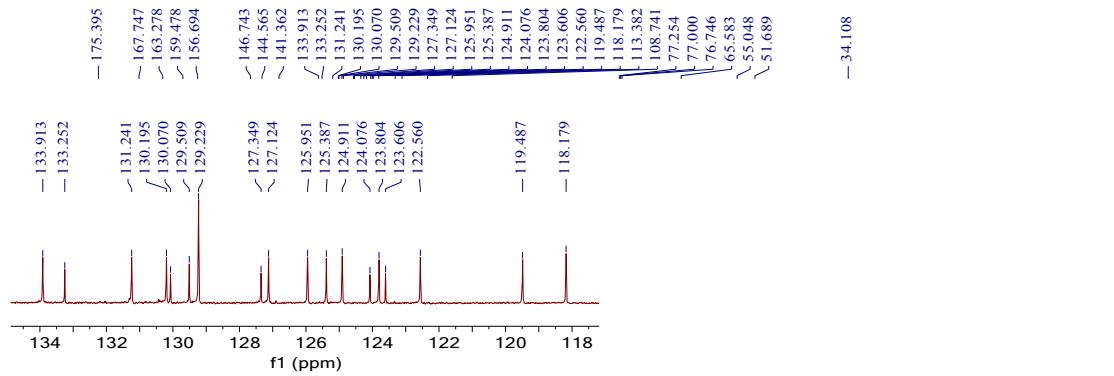

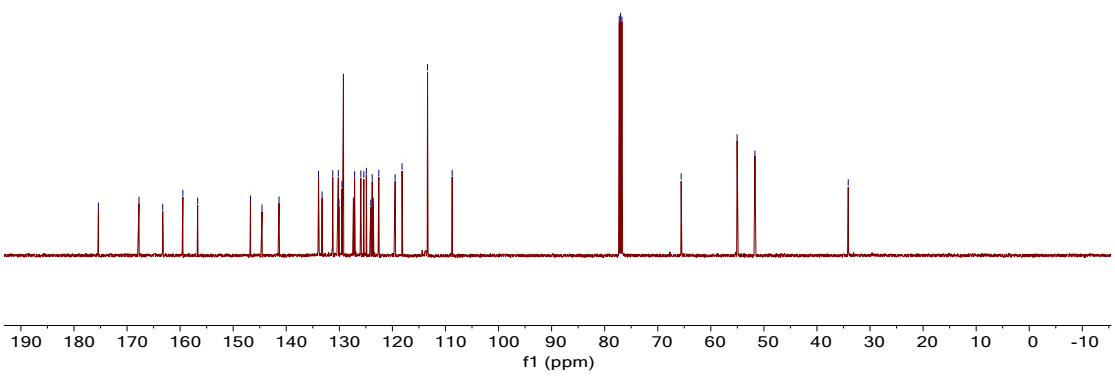

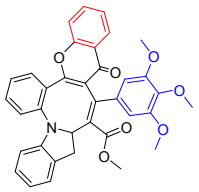

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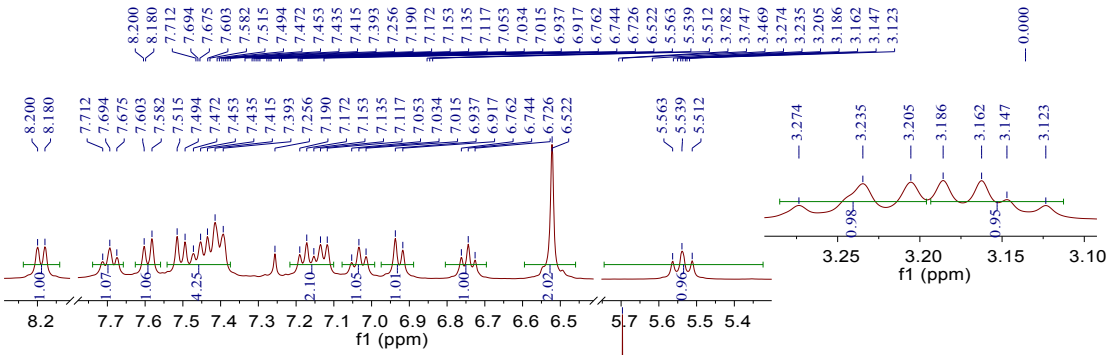

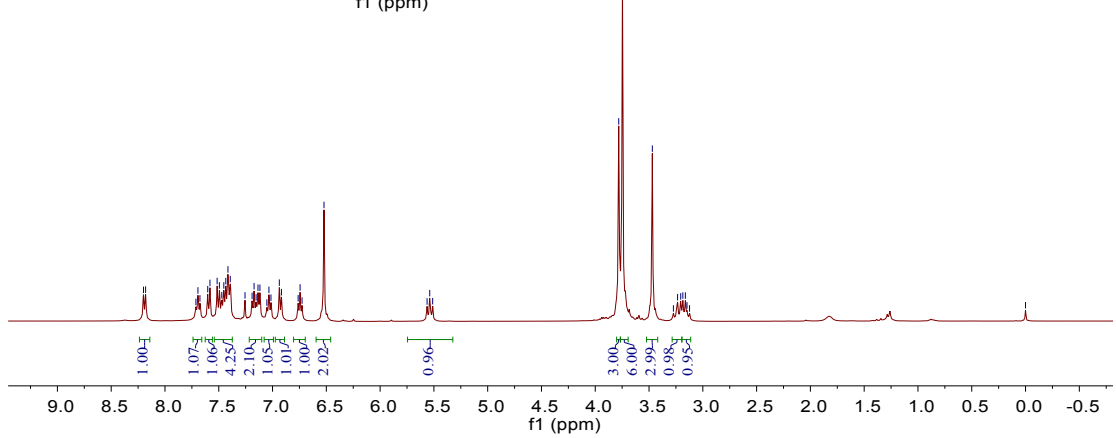

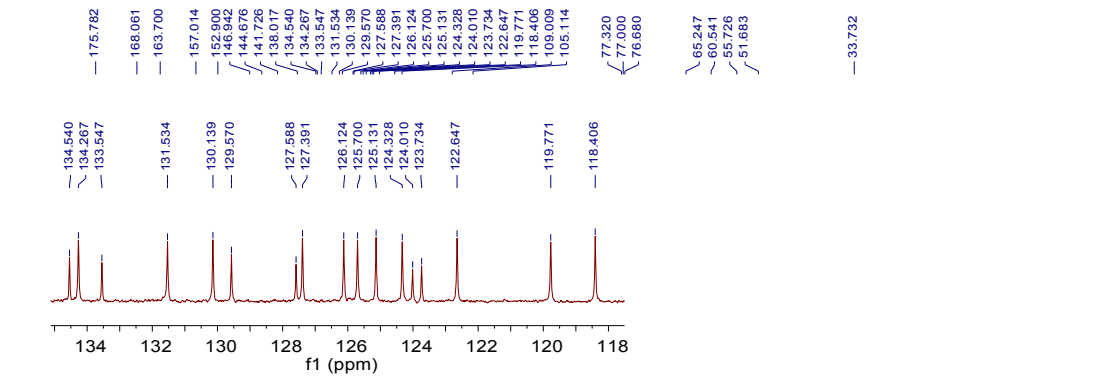

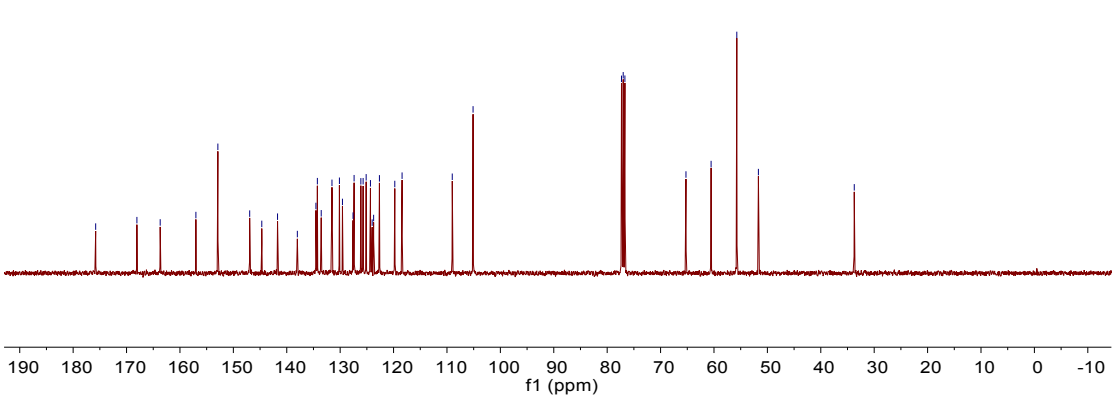

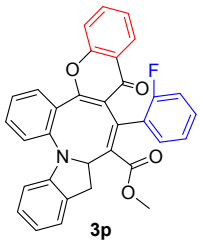
O
O
F
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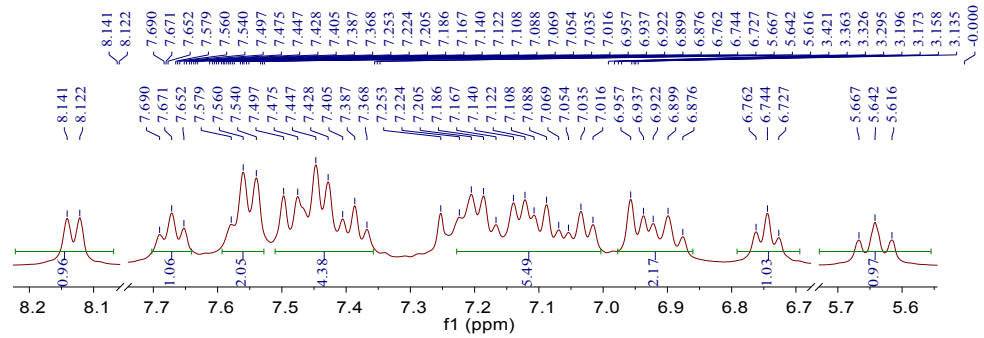
O
O

3p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7.405
7.387
7.368
7.253
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7.205
7.186
7.167
7.140
7.122
7.108
7.088
7.069
7.054
7.035
7.016
6.957
6.937
6.922
6.899
6.876
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6.744
6.727
5.667
5.642
5.616
3.421
3.363
3.326
3.295
3.196
3.173
3.158
3.135
-0.000
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2.05
4.38
5.49
2.17
1.03
0.97
3.00
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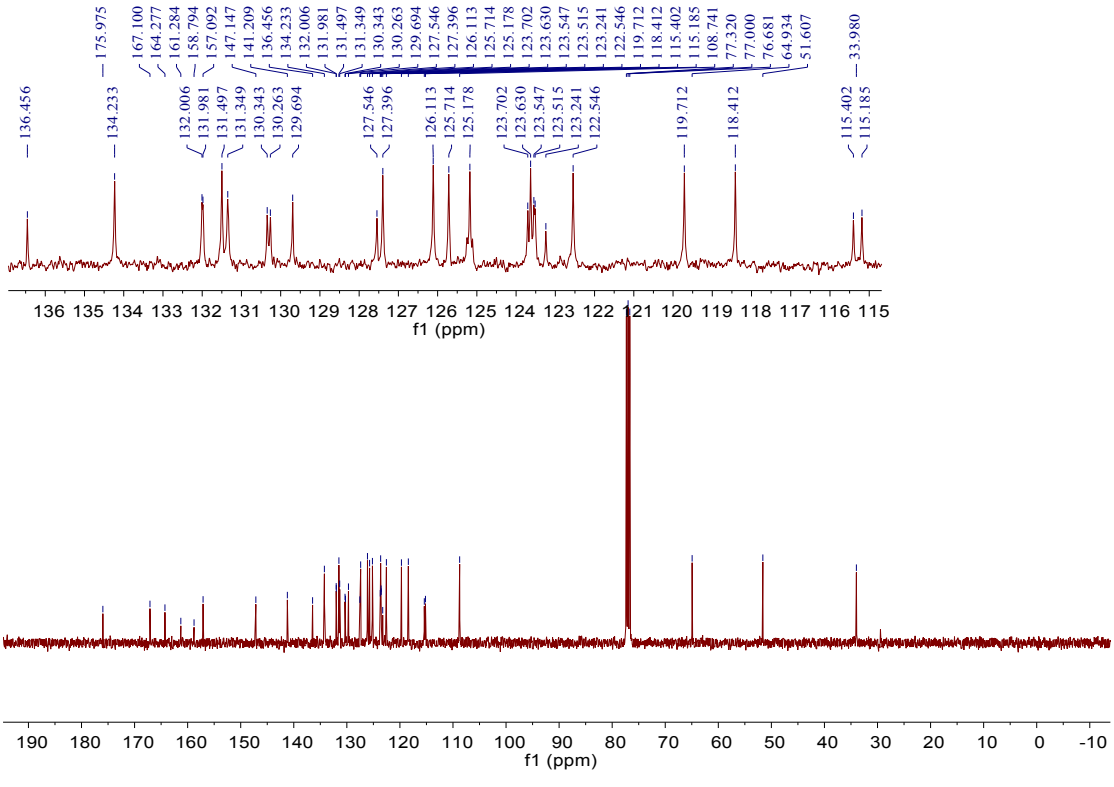
1.01
f1 (ppm)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130.343
130.263
129.694
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127.396
126.113
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125.178
123.702
123.630
123.547
123.515
123.241
122.546
119.712
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77.000
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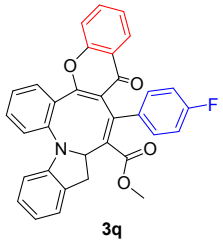
51.607
33.980
f1 (ppm)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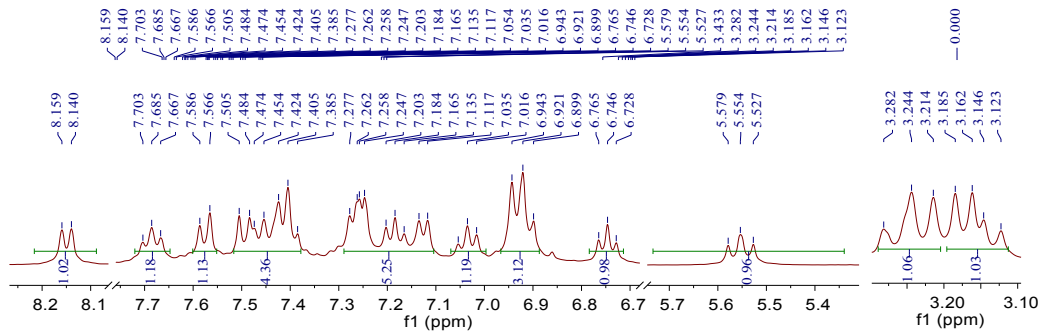
O
F
N
O
O

3q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7.667
7.586
7.566
7.505
7.484
7.474
7.454
7.424
7.405
7.385
7.277
7.262
7.258
7.247
7.203
7.184
7.165
7.135
7.117
7.054
7.035
7.016
6.943
6.921
6.899
6.765
6.746
6.728
5.579
5.554
5.527
3.433
3.282
3.244
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3.185
3.162
3.146
3.123
0.000
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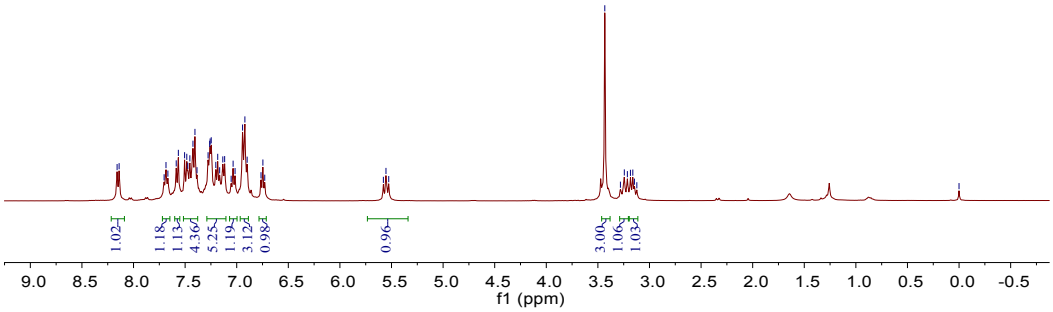
1.18
1.13
4.36
5.25
1.19
3.12
0.98
0.96
1.06
1.03
f1 (ppm)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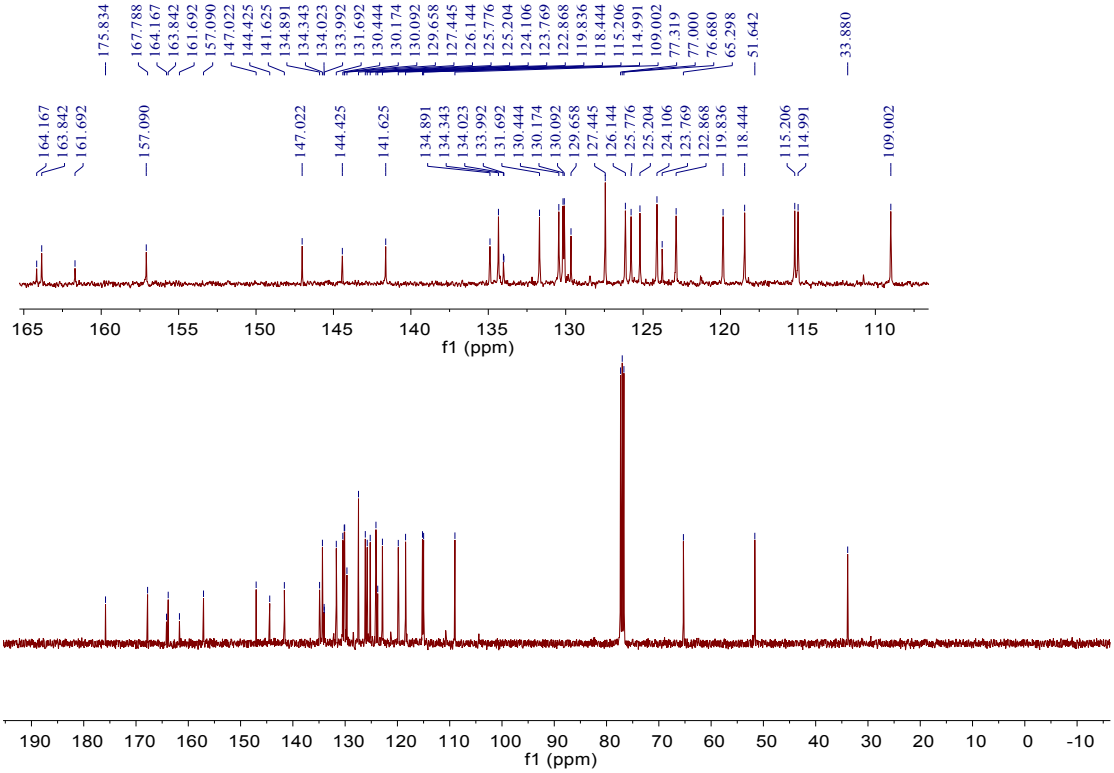
1.18
1.13
4.36
5.25
1.19
3.12
0.98
0.96
3.00
1.06
1.03
f1 (ppm)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144.425
141.625
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133.992
131.692
130.444
130.174
130.092
129.658
127.445
126.144
125.776
125.204
124.106
123.769
122.868
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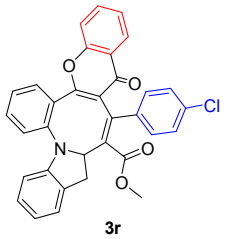
77.000
76.680
65.298
51.642
33.880
f1 (ppm)



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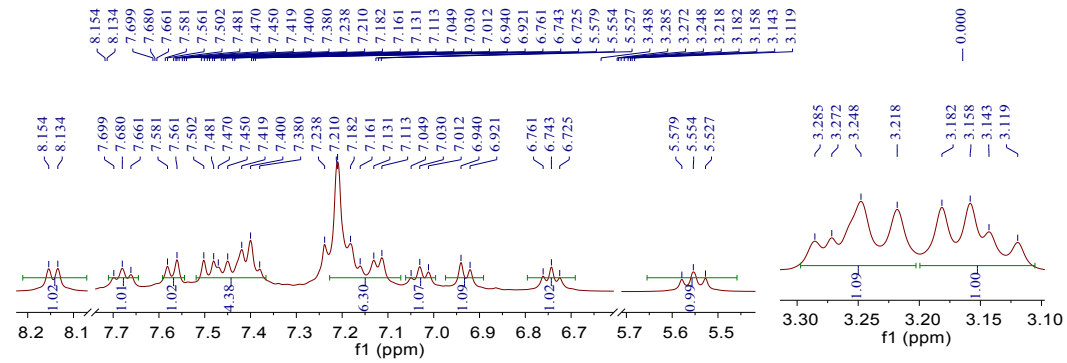

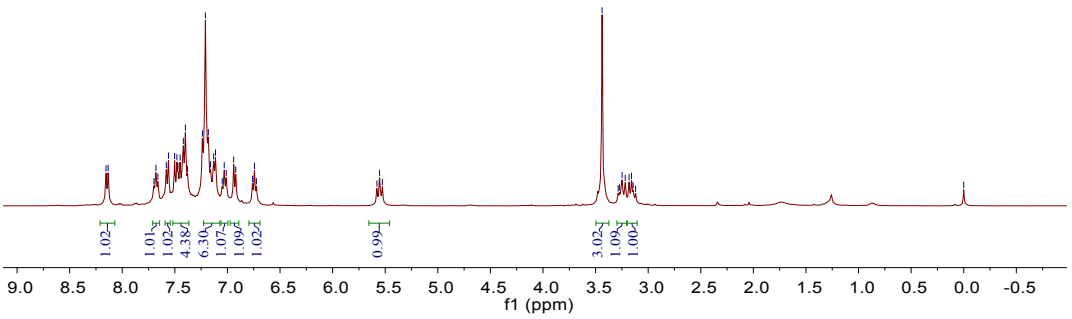

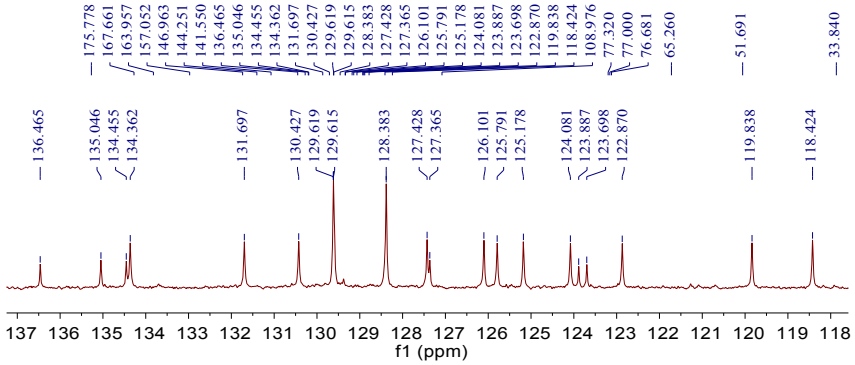

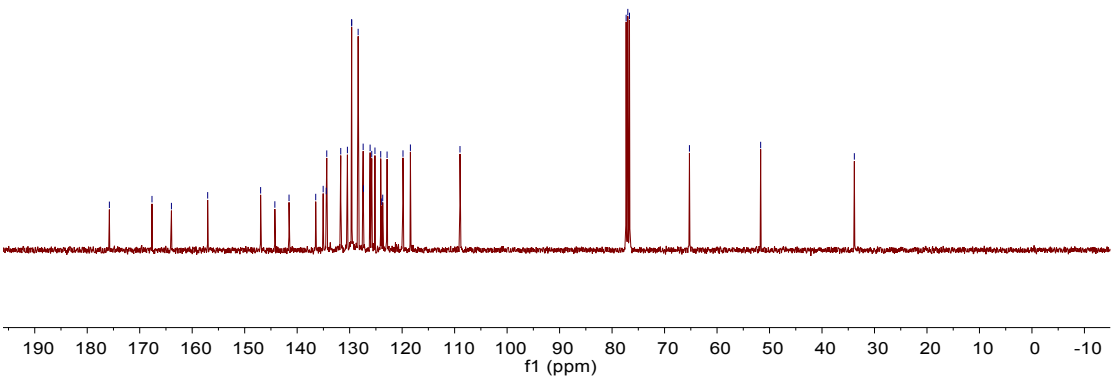

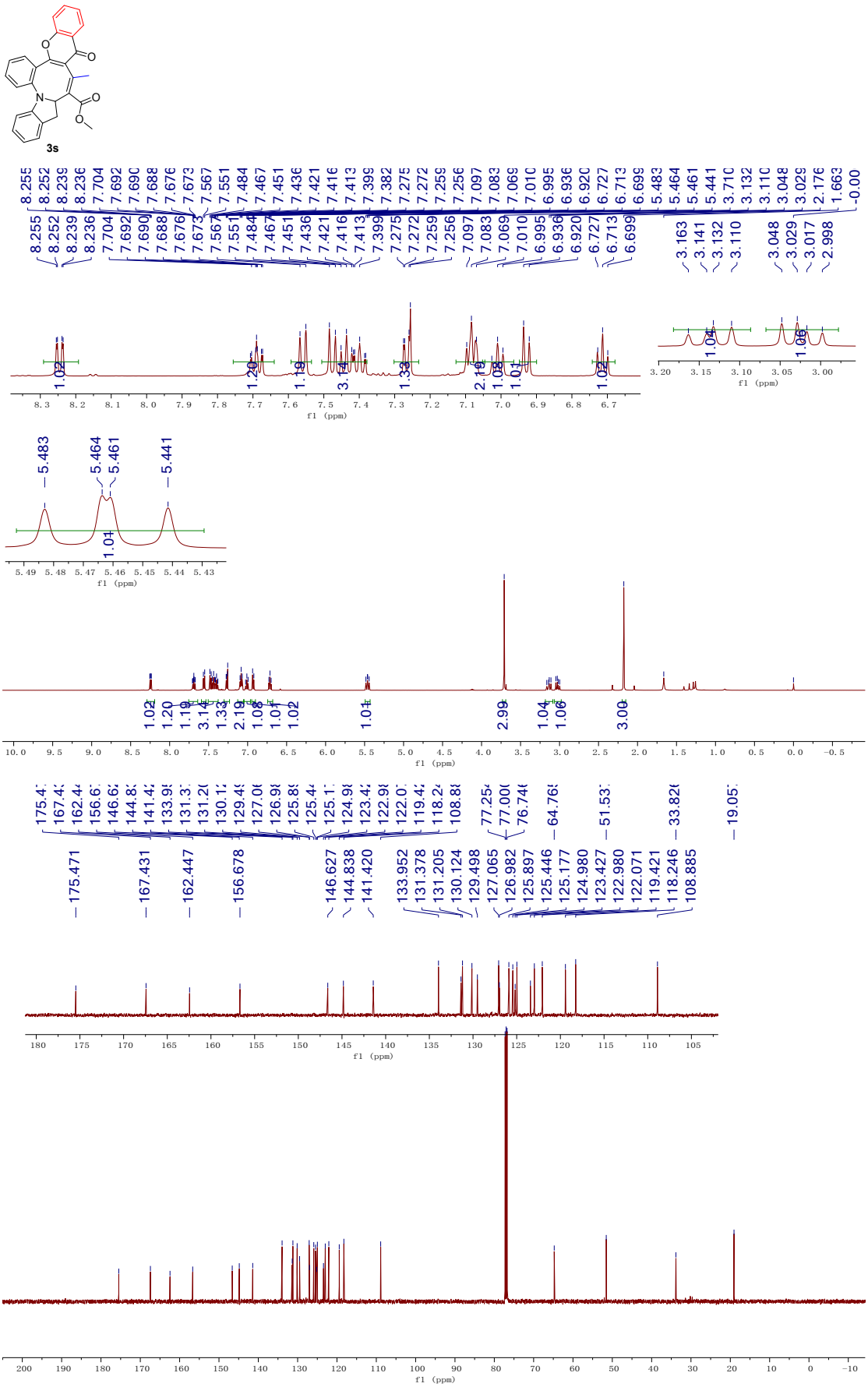
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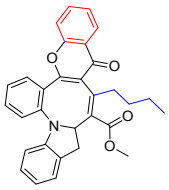

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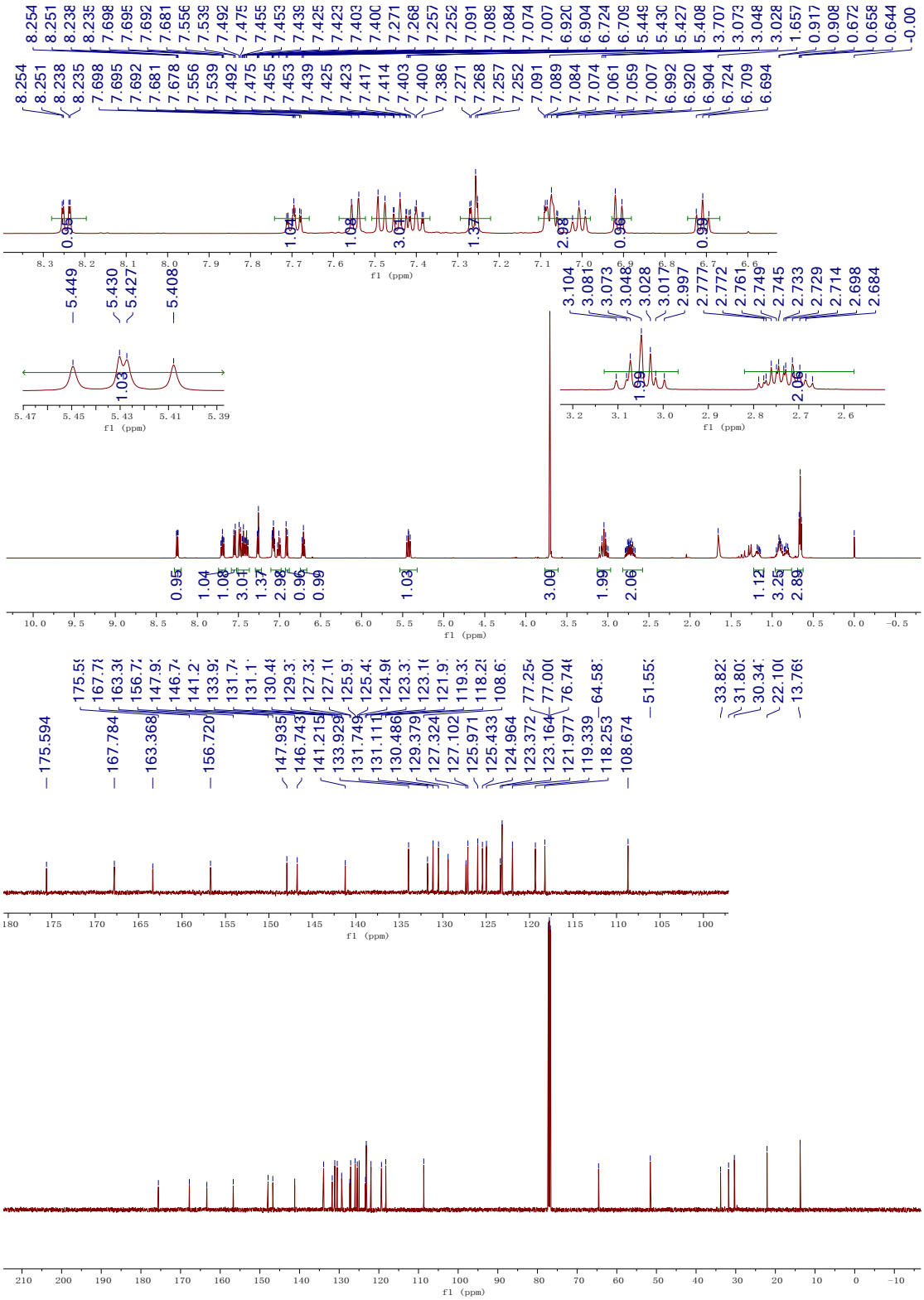

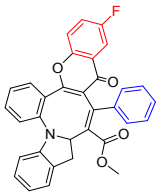

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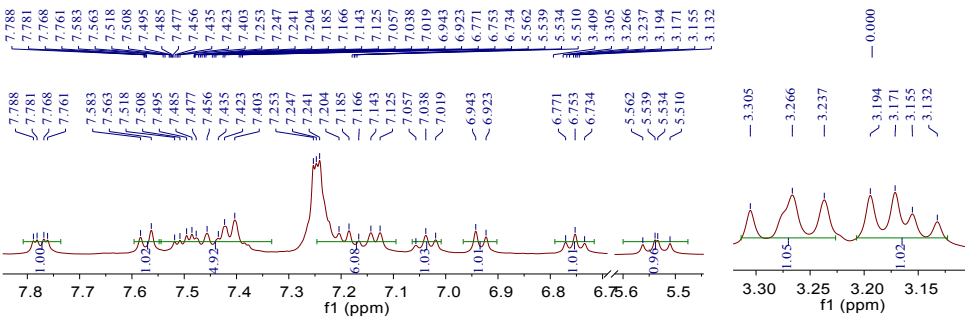

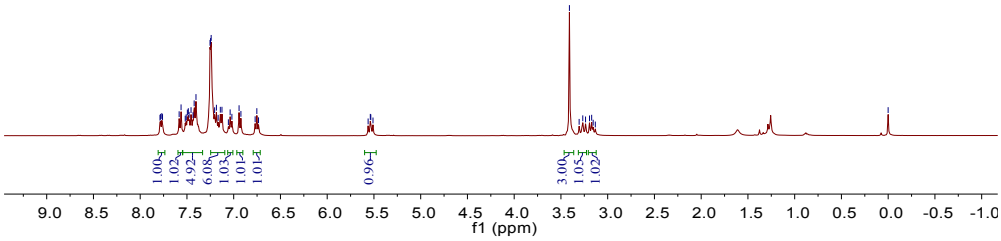

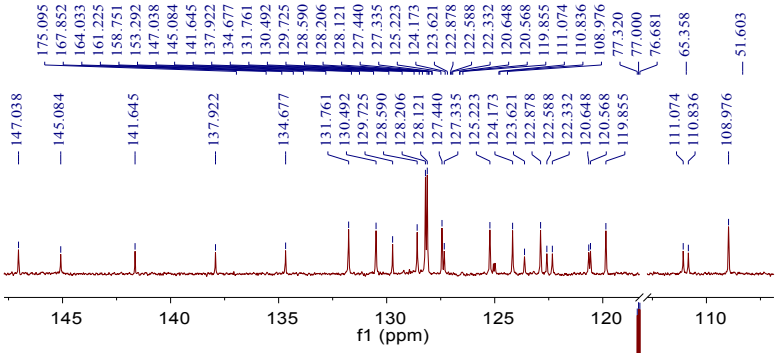

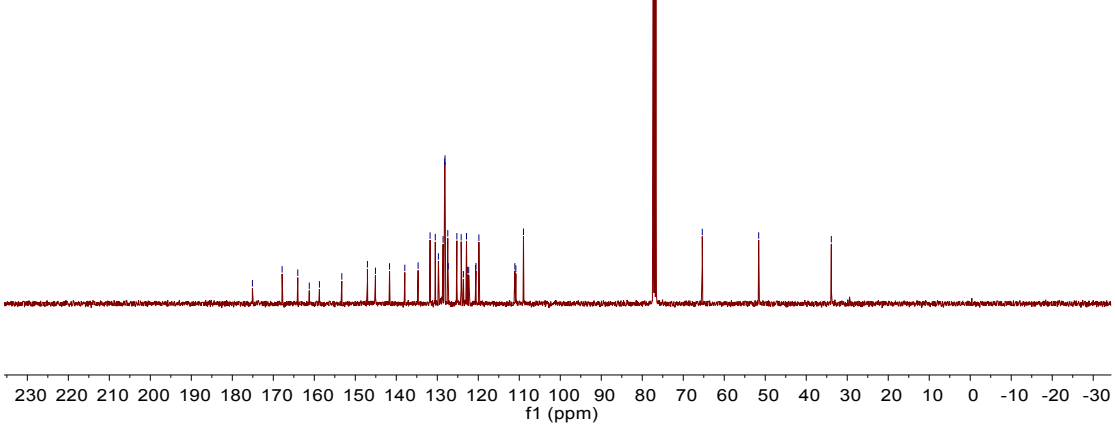

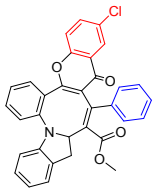

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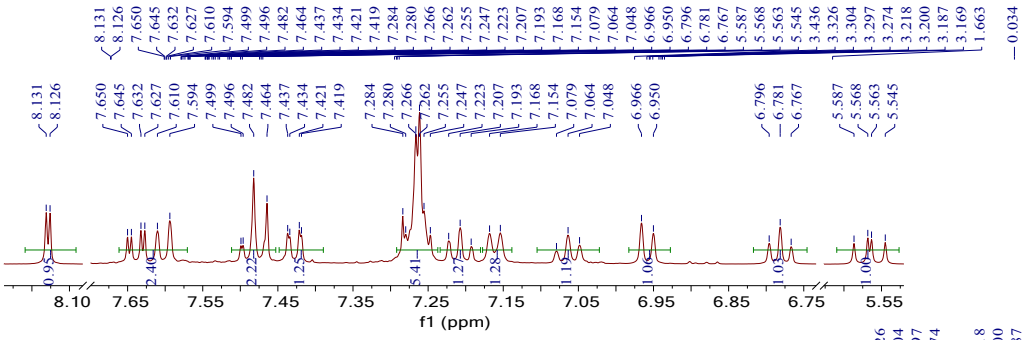
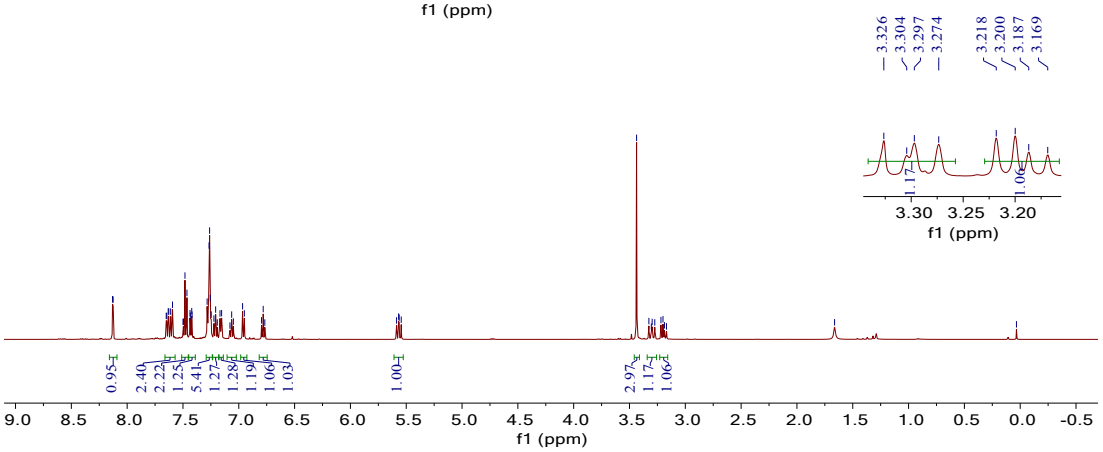
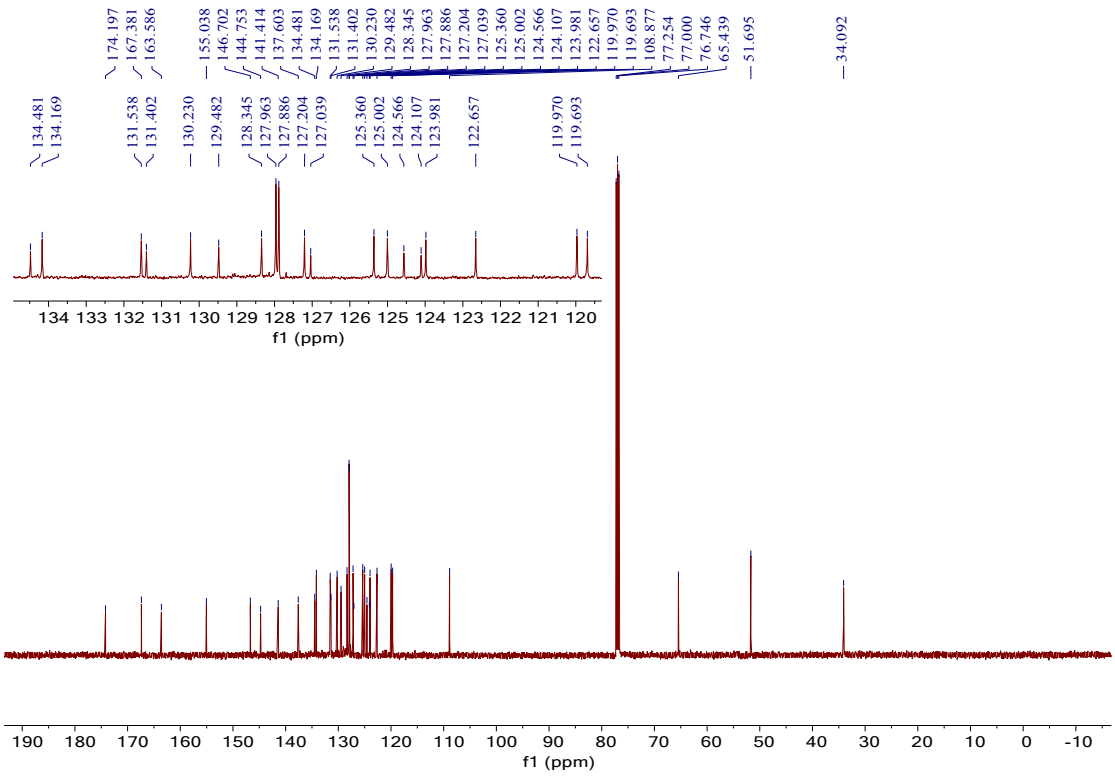
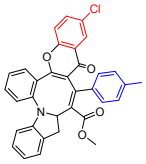
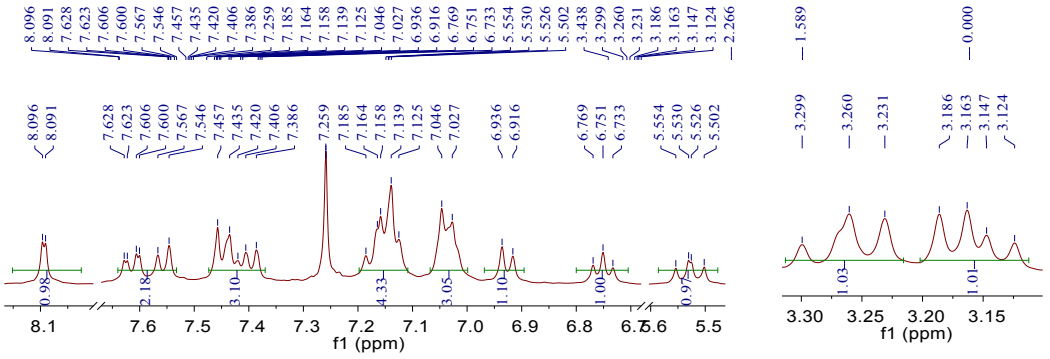







Cl
O
O
N
O
O

3w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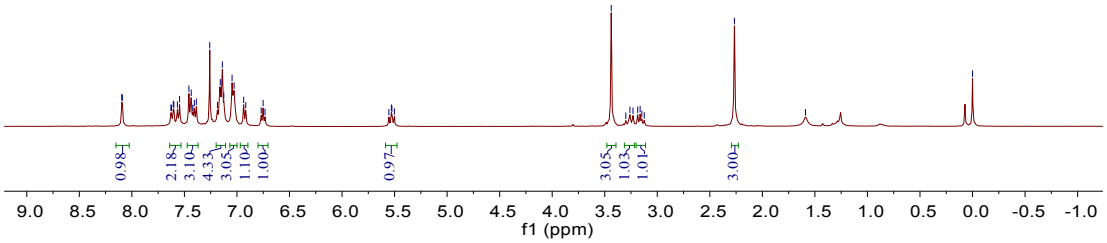
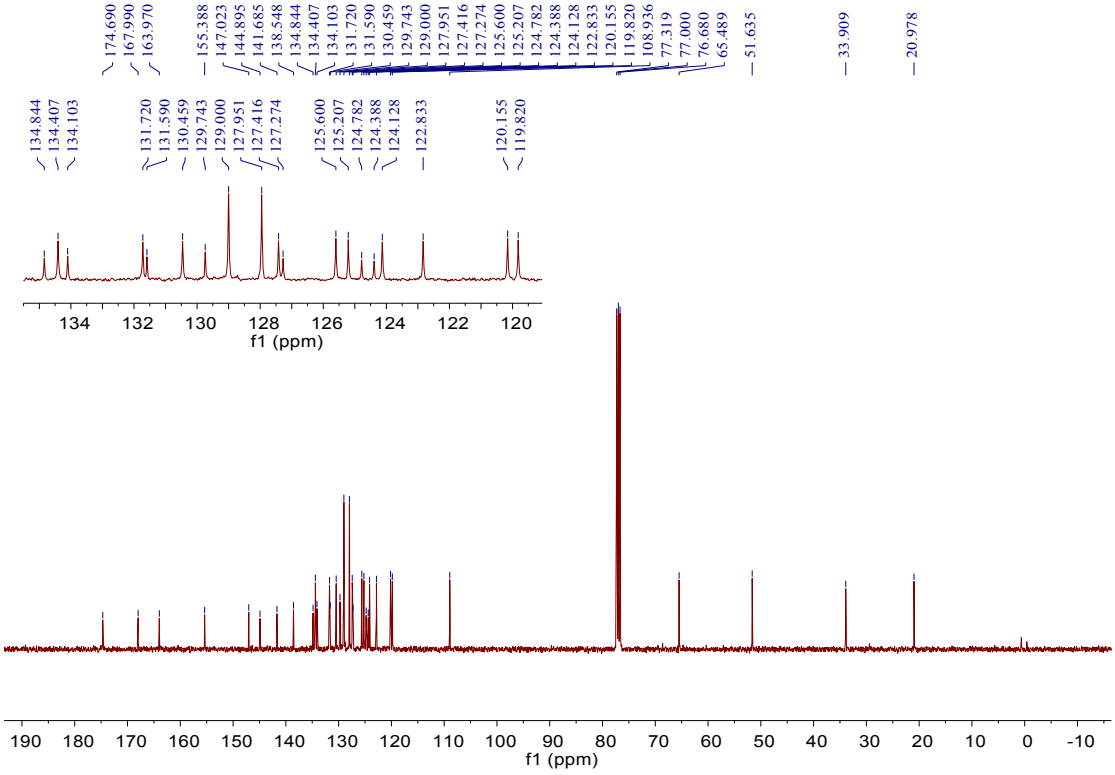
0.98 2.18 3.10 4.33 3.05 1.10 1.00 0.97
1.03 1.01
f1 (ppm)


0.98 2.18 3.10 4.33 3.05 1.10 1.00 0.97 3.05 1.03 1.01 3.00
f1 (ppm)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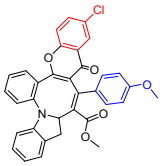
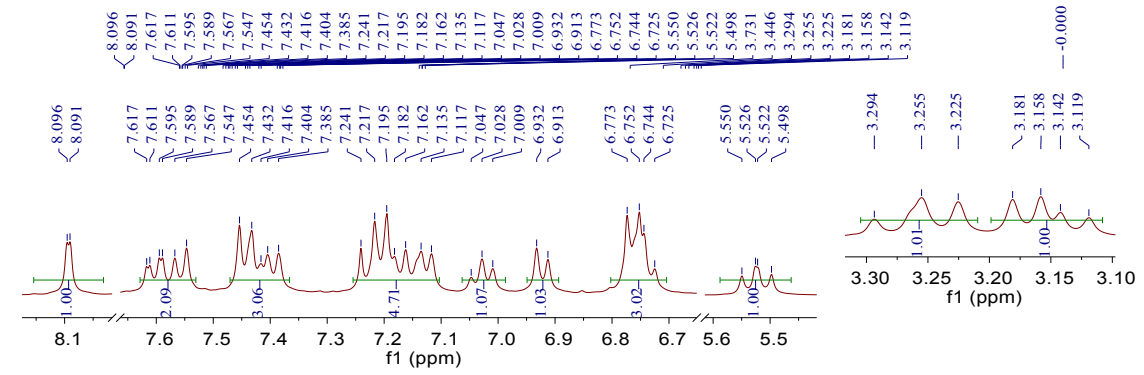
f1 (ppm)


Cl
O
O
O
N
O
O

3x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7.416
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7.385
7.241
7.217
7.195
7.182
7.162
7.135
7.117
7.047
7.028
7.009
6.932
6.913
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6.752
6.744
6.725
5.550
5.526
5.522
5.498
3.294
3.255
3.225
3.181
3.158
3.142
3.119
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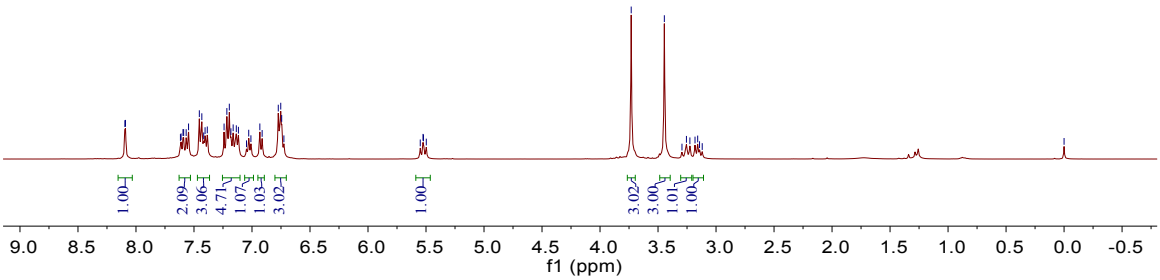
3.06
4.71
1.07
1.03
3.02
1.00
1.01
1.00
f1 (ppm)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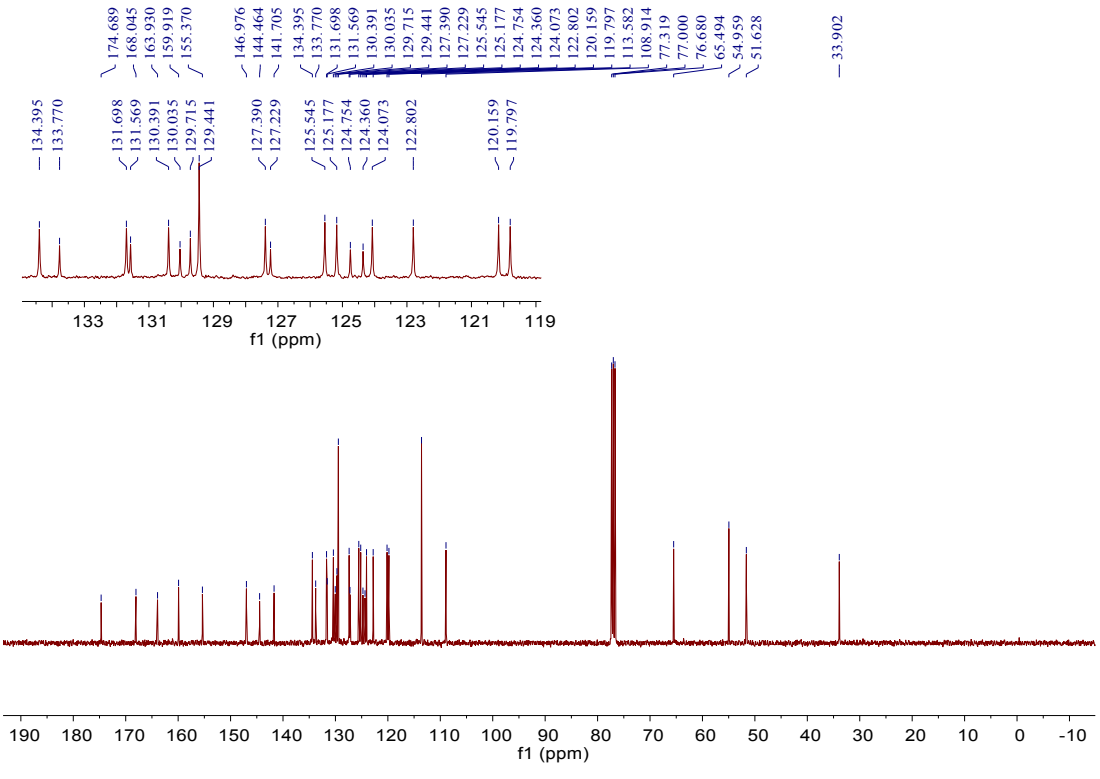
3.06
4.71
1.07
1.03
3.02
1.00
3.02
3.00
1.01
1.00
f1 (ppm)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159.919
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129.715
129.441
127.390
127.229
125.545
125.177
124.754
124.360
124.073
122.802
120.159
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77.000
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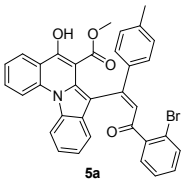
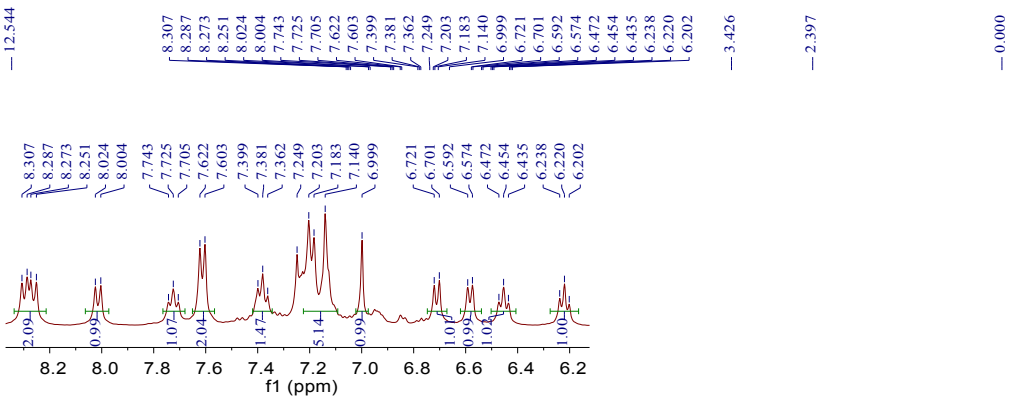
65.494
54.959
51.628
33.902
f1 (ppm)


OH
O
O
N
O
Br

5a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8.024
8.004
7.743
7.725
7.705
7.622
7.603
7.399
7.381
7.362
7.249
7.203
7.183
7.140
6.999
6.721
6.701
6.592
6.574
6.472
6.454
6.435
6.238
6.220
6.202
3.426
2.397
0.000
2.09
0.99
1.07
2.04
1.47
5.14
0.99
1.01
0.99
1.02
1.00
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8.0
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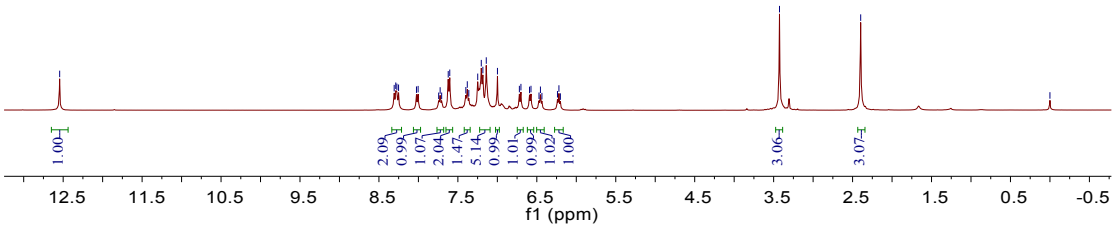
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
f1 (ppm)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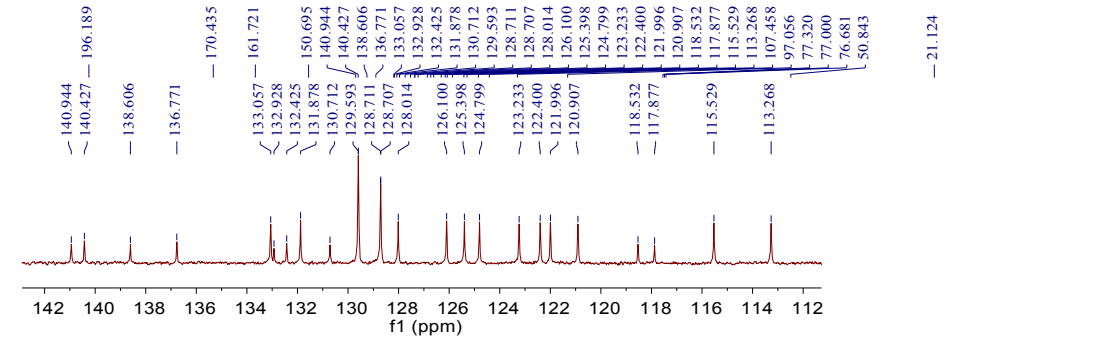
2.09
0.99
1.07
2.04
1.47
5.14
0.99
1.01
0.99
1.02
1.00
3.06
3.07
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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140.427
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136.771
133.057
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132.425
131.878
130.712
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128.711
128.707
128.014
126.100
125.398
124.799
123.233
122.400
121.996
120.907
118.532
117.877
115.529
113.268
107.458
97.056
77.320
77.000
76.681
50.843
21.124
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130
128
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122
120
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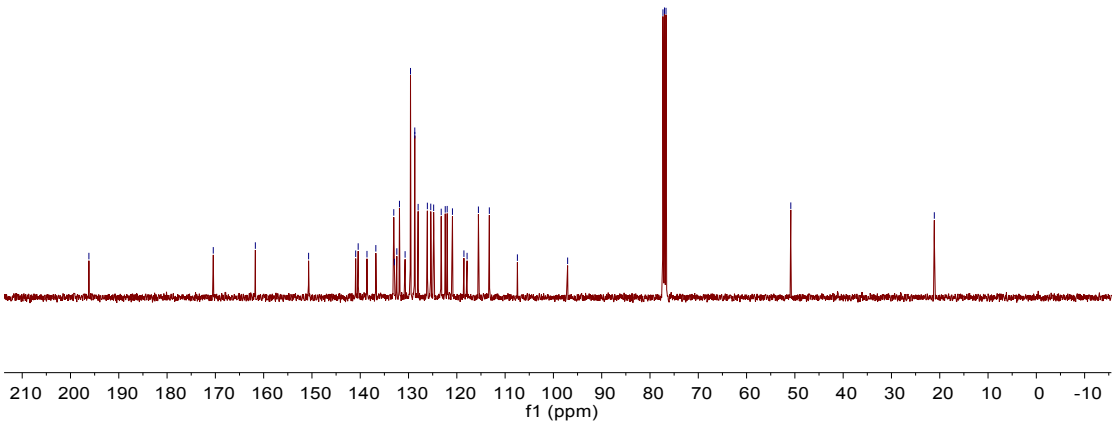
116
114
112
f1 (ppm)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130
120
110
100
90
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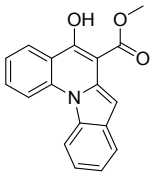
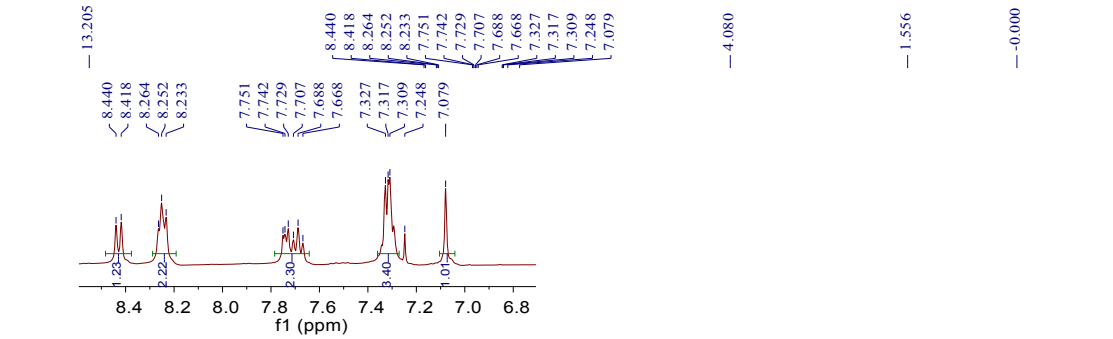
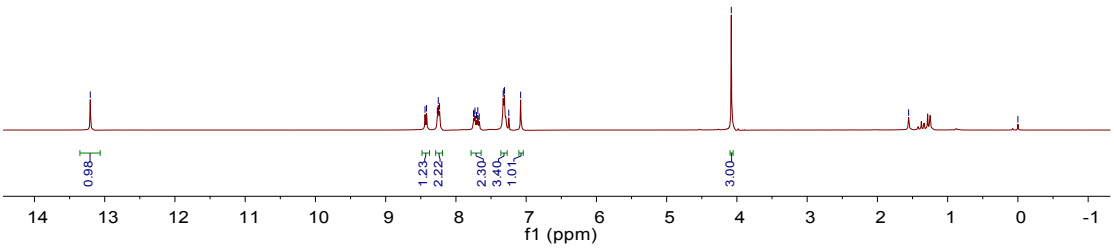
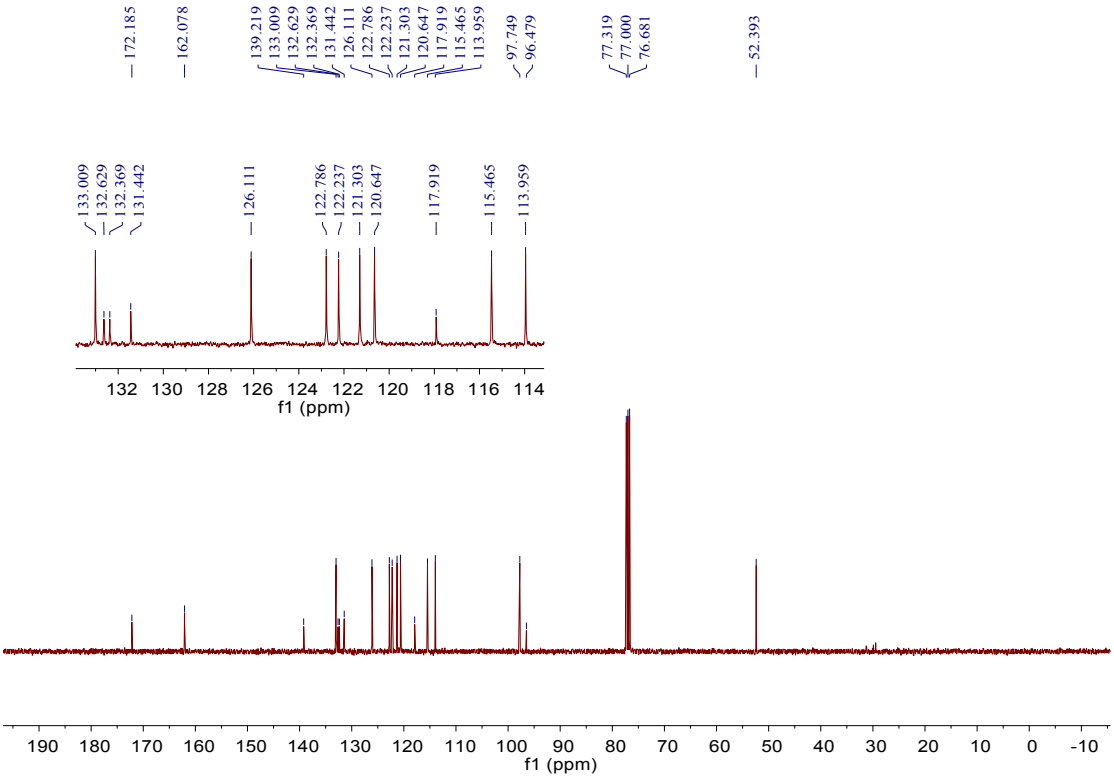
60
50
40
30
20
10
0
-10
f1 (ppm)


OH
O
O
N

6a


13.205
8.440
8.418
8.264
8.252
8.233
7.751
7.742
7.729
7.707
7.688
7.668
7.327
7.317
7.309
7.248
7.079
4.080
1.556
-0.000
1.23
2.22
2.30
3.40
1.01
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8
f1 (ppm)

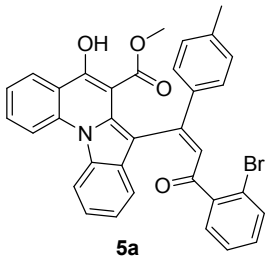

0.98
1.23
2.22
2.30
3.40
1.01
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


172.185
162.078
139.219
133.009
132.629
132.369
131.442
126.111
122.786
122.237
121.303
120.647
117.919
115.465
113.959
97.749
96.479
77.319
77.000
76.681
52.393
132 130 128 126 124 122 120 118 116 114
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

7. X-ray crystallography of 5a

(Z)-methyl 7-(3-(2-bromophenyl)-3-oxo-1-(p-tolyl)prop-1-en-1-yl)-5-hydroxyindolo[1,2-a]quinoline-6-carboxylate (5a, mo_d8v19220_0m)

(Ortep ellipsoids are depicted at the 50% level)

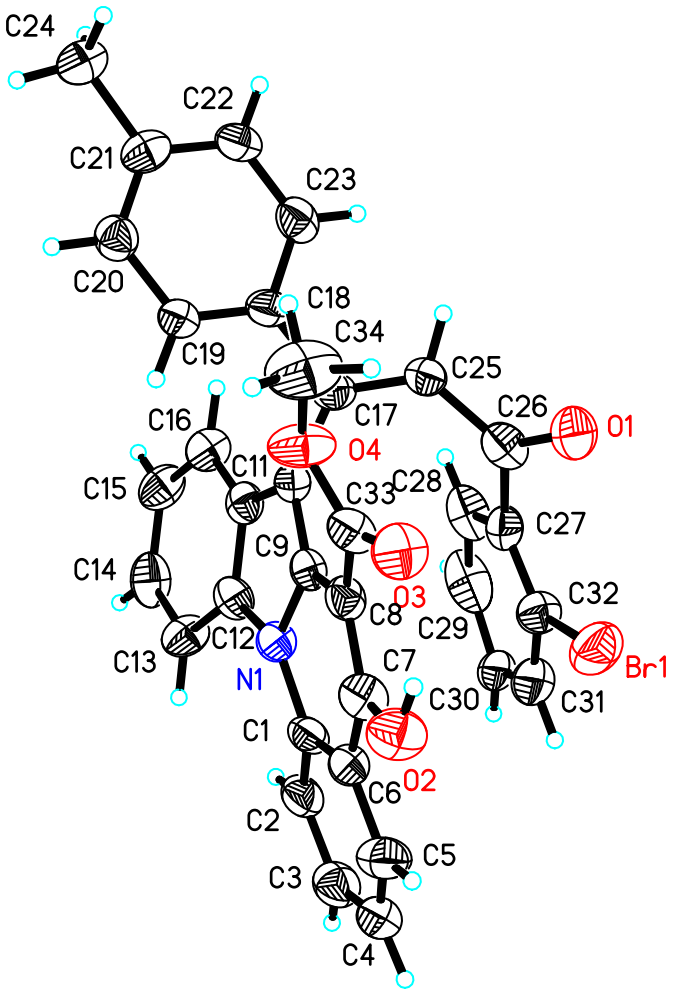


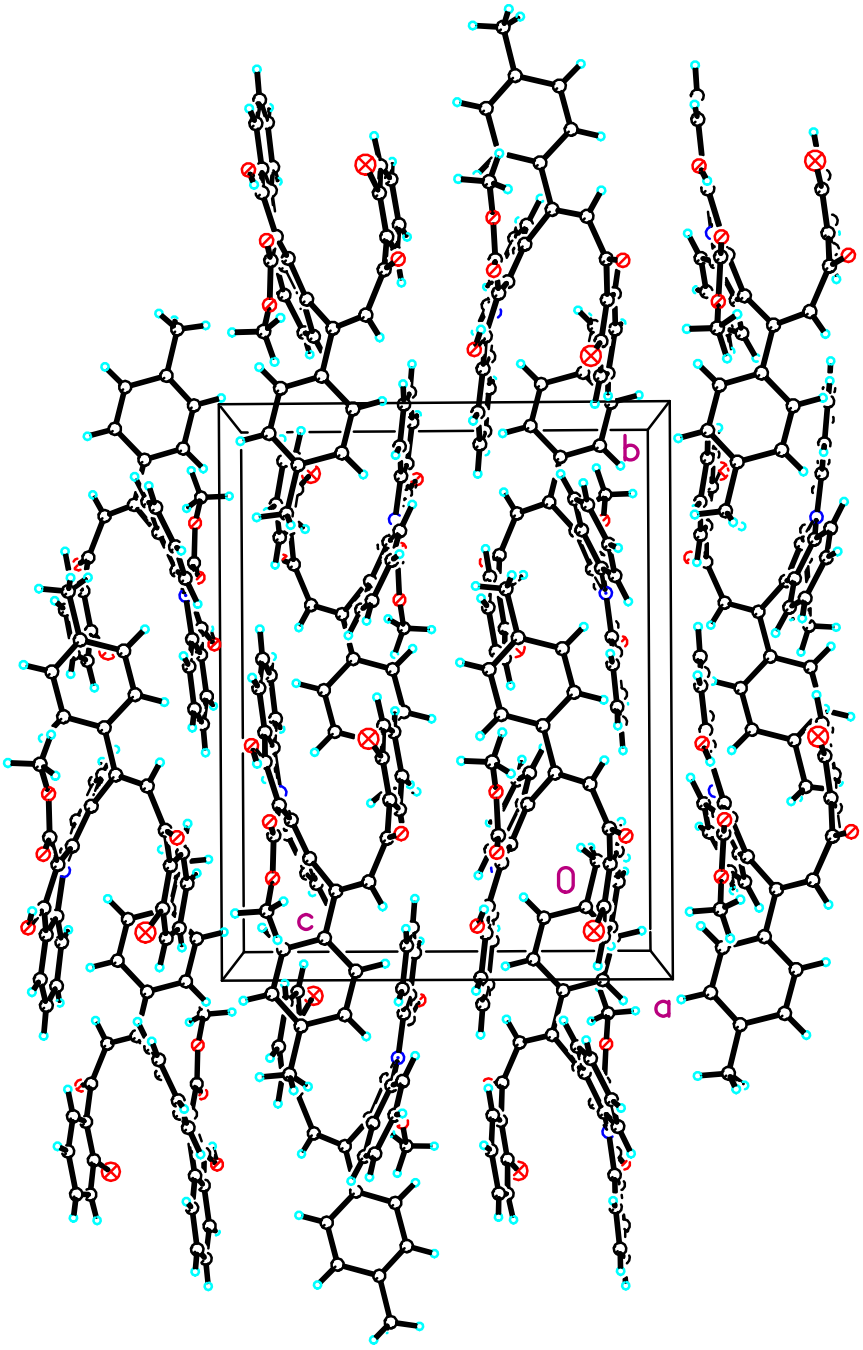
5a

Table S1. Crystal data and structure refinement for **5a**.

Identification code	**5a**
Empirical formula	$C_{34}H_{24}BrNO_4$
Formula weight	590.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 11.571(3) Å, α = 90°.
	b = 17.156(5) Å, β = 91.359(9)°.
	c = 13.431(4) Å, γ = 90°.
Volume	2665.5(14) $Å^3$
Z	4
Density (calculated)	1.471 Mg/m^3
Absorption coefficient	1.584 mm^{-1}
F(000)	1208
Crystal size	0.150 x 0.100 x 0.080 mm^3
Theta range for data collection	2.296 to 25.000°.
Index ranges	-13<=h<=13, -20<=k<=20, -15<=l<=15
Reflections collected	33030

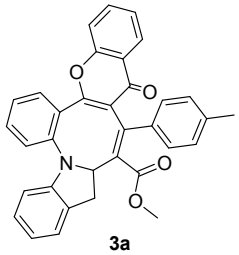
Independent reflections	4672 [R(int) = 0.1610]
Completeness to theta = 25.242°	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4758
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4672 / 0 / 366
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.1027, wR2 = 0.2623
R indices (all data)	R1 = 0.1810, wR2 = 0.3215
Extinction coefficient	0.019(3)
Largest diff. peak and hole	0.667 and -0.570 e.$Å^{-3}$


C24
C22
C21
C23
C20
C18
C34
C19
C25
C16
C17
C26
O1
O4
C11
C15
C33
C28
C27
C9
C14
O3
C8
C32
C12
C29
Br1
C13
N1
C7
C30
C31
C1
O2
C6
C2
C5
C3
C4


b
0
c
a

8. X-ray crystallography of 3a

(E)-methyl 13-oxo-12-(p-tolyl)-10a,13-dihydro-10*H*-benzo[7,8]chromeno[3',2':5, 6]azocino[1,2-a]indole-11-carboxylate(3a, mo_d8v19221_0m)
(Ortep ellipsoids are depicted at the 50% level)

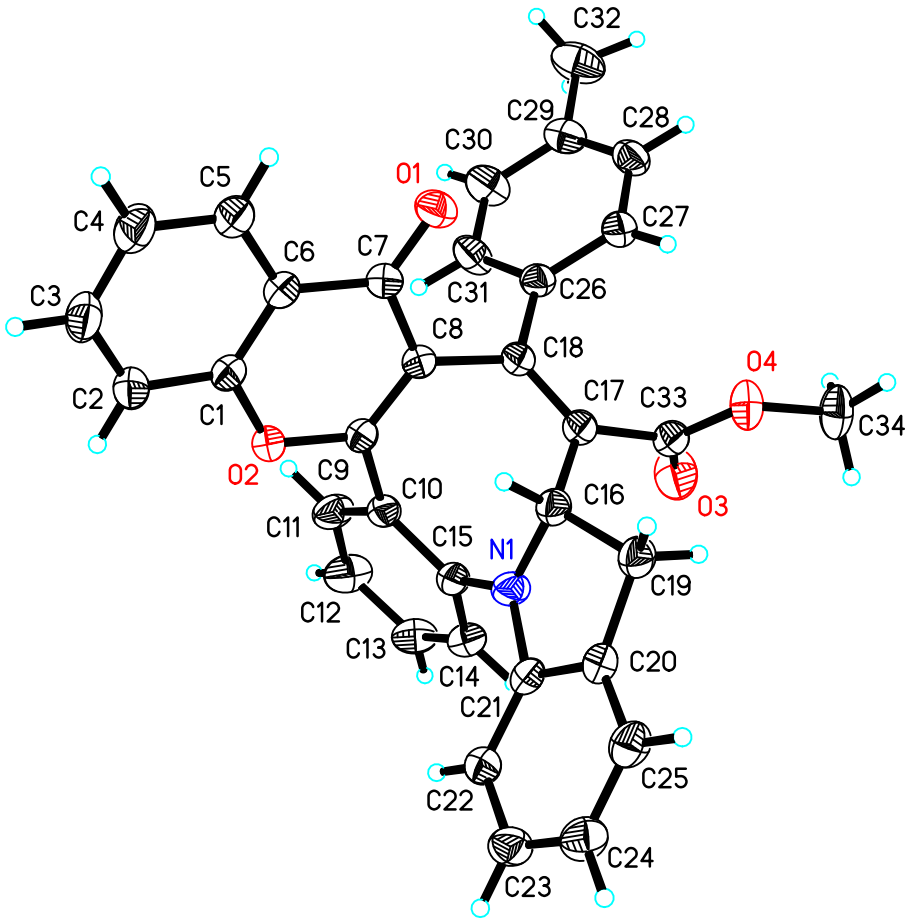


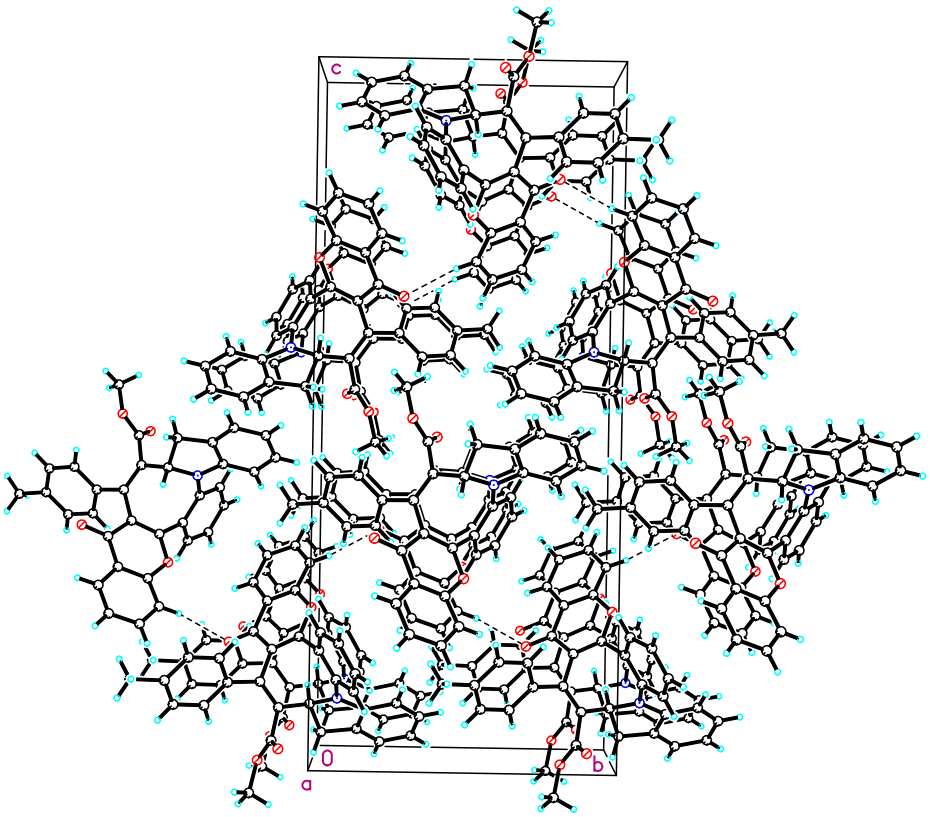
3a

Table S2. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	$C_{34}H_{25}NO_4$
Formula weight	511.55
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 7.2273(3) Å, α = 90°.
	b = 12.6042(5) Å, β = 90°.
	c = 29.1348(12) Å, γ = 90°.
Volume	2654.02(19) $Å^3$
Z	4
Density (calculated)	1.280 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F(000)	1072
Crystal size	0.200 x 0.160 x 0.130 mm^3
Theta range for data collection	2.648 to 25.991°.
Index ranges	-8<=h<=8, -15<=k<=15, -35<=l<=24
Reflections collected	13426

Independent reflections	5164 [R(int) = 0.0285]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6689
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5164 / 0 / 355
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0837
R indices (all data)	R1 = 0.0514, wR2 = 0.0931
Absolute structure parameter	0.4(5)
Extinction coefficient	0.037(4)
Largest diff. peak and hole	0.142 and -0.116 e.$Å^{-3}$




c
0
b
a