Supporting Information

Enantioselective Direct Vinylogous Aldol-Cyclization Cascade Reaction between *β,γ*-Unsaturated Amides and *o*-Quinones

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1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 spectrometer and the chemical shifts in ppm downfield from tetramethylsilane (δ 0.00 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ 77.0 ppm) for ^{13}C NMR spectroscopy. IR spectra were recorded on Nicolet Magna-I 550 spectrometer. High resolution mass spectra (HRMS) were performed on an electron ionization time-of-flight (EI-TOF) mass spectrometer.

Thin-layer chromatography (TLC) was performed on 10-40 μm silica gel plates. Column chromatography was performed using silica gel (300-400 mesh) eluted with petroleum ether and ethyl acetate.

Catalysts **C1-C4**,[1] **C5-C6**,[2] **C7**,[3] and **C8-C10**[4] were prepared according to literature procedures. The *o*-quinones **2d**[5] and **2e**[6] were prepared by the known procedures.

2. General Procedure and Characterization of the Substrates

General procedure: Pyrazole (16 mmol) and β,γ-unsaturated carboxylic acid (4 mmol) were added to a CH_2Cl_2 (25 mL) solution of $SOCl_2$ (4 mmol) at room temperature and stirred for 3 h. The reaction mixture was quenched with 0.1 M HCl (5 mL) and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4, then filtered and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel.

Characterization of new substrates:

3-(3-Chlorophenyl)-1-(1*H*-pyrazol-1-yl)but-3-en-1-one (**1g**). Colorless liquid, 74% yield (0.73 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 2.8 Hz, 1H), 7.75 (s, 1H), 7.47 (s, 1H), 7.35-7.33 (m, 1H), 7.27-7.24 (m, 2H), 6.46-6.45 (m, 1H), 5.63 (s, 1H), 5.34 (s, 1H), 4.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 144.2, 141.7, 139.3, 134.4, 129.6, 128.5, 127.9, 126.1, 124.0, 118.3, 110.0, 40.0; IR (KBr, cm^{-1}): v 2975, 1735, 1635, 1383, 1351, 1191, 1088, 913, 768; HRMS (EI) calcd for $C_{13}H_{11}ClN_2O$ 246.0560, found 246.0559.

1-(1*H*-Pyrazol-1-yl)-3-(o-tolyl)but-3-en-1-one (**1i**). Colorless liquid, 50% yield (0.45 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 2.8 Hz, 1H), 7.67 (s, 1H), 7.23-7.21 (m, 1H), 7.18-7.11 (m, 3H), 6.40-6.39 (m, 1H), 5.41 (s, 1H), 5.17 (s, 1H), 4.22 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 143.9, 141.5, 141.3, 135.0, 130.2, 128.4, 128.3, 127.3, 125.5, 119.2, 110.0, 42.2, 19.8; IR (KBr, cm^{-1}): v 2922, 1735, 1635, 1383, 1351, 1191, 1088, 913, 768; HRMS (EI) calcd for $C_{14}H_{14}N_2O$ 226.1106, found 226.1105.

3-(2,4-Dimethylphenyl)-1-(1*H*-pyrazol-1-yl)but-3-en-1-one (**1j**). Yield: 46% (0.44 g), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 2.8 Hz, 1H), 7.67 (s, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H), 6.95 (d J = 7.6 Hz, 1H), 6.40-6.39 (m, 1H), 5.39 (d, J = 1.2 Hz,

1H), 5.16 (s, 1H), 4.21 (s, 2H), 2.35 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 143.9, 141.4, 138.4, 136.9, 134.9, 131.0, 128.4, 128.3, 126.2, 119.1, 110.0, 42.4, 21.0, 19.8; IR (KBr, cm^{-1}): v 1709, 1383, 1352, 1199, 913, 823, 770; HRMS (EI) calcd for $C_{15}H_{16}N_2O$ 240.1263, found 240.1263.

3-(3,5-Dimethylphenyl)-1-(1*H*-pyrazol-1-yl)but-3-en-1-one (**1k**). Colorless liquid, 74% yield (0.71 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 2.8 Hz, 1H), 7.73 (s, 1H), 7.08 (s, 2H), 6.91 (s, 1H), 6.44-6.43 (m, 1H), 5.59 (s, 1H), 5.23 (s, 1H), 4.35 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 144.0, 140.6, 139.7, 137.8, 129.5, 128.4, 123.7, 116.6, 109.7, 40.2, 21.3; IR (KBr, cm^{-1}): v 3148, 2918, 1737, 1382, 1350, 1199, 1088, 917, 770; HRMS (EI) calcd for $C_{15}H_{16}N_2O$ 240.1263, found 240.1263.

3-(Naphthalen-1-yl)-1-(1*H*-pyrazol-1-yl)but-3-en-1-one (**1l**). Colorless liquid, 64% yield (0.67 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 2.4 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 7.85-7.83 (m, 1H), 7.78-7.76 (m, 1H), 7.67(s, 1H), 7.52-7.40 (m, 4H), 6.39 (d, J = 1.2 Hz, 1H), 5.61 (s, 1H), 5.40 (s, 1H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 144.0, 140.5, 139.6, 133.7, 131.0, 128.3, 128.2, 127.8, 126.1, 125.7, 125.5, 125.2, 120.5, 109.7, 42.9, 29.7; IR (KBr, cm^{-1}): v 3052, 2919, 1708, 1384, 1201, 919, 802, 776; HRMS (EI) calcd for $C_{17}H_{14}N_2O$ 262.1106, found 262.1110.

3-(Naphthalen-2-yl)-1-(1*H*-pyrazol-1-yl)but-3-en-1-one (**1m**). Colorless liquid, 74% yield (0.78 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 2.8 Hz, 1H), 7.87 (s, 1H), 7.80-7.76 (m, 4H), 7.67-7.65 (m, 1H), 7.44-7.42 (m, 2H), 6.44-6.43 (m, 1H), 5.78 (s, 1H), 5.40 (s, 1H), 4.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 144.1, 140.3, 136.9, 133.2, 132.9, 128.5, 128.3, 128.1, 127.5, 126.2, 126.0, 124.7, 124.1, 117.6, 109.9, 40.2; IR (KBr, cm^{-1}): v 3055, 2917, 1731, 1623, 1382, 1350, 1199, 1089, 914, 861; HRMS (EI) calcd for $C_{17}H_{14}N_2O$ 262.1106, found 262.1107.

3. References

1 (a) B. Vakulya, S. Varga, A. Csámpai and T. Soós, *Org. Lett.*, 2005, **7**, 1967; (b) T.-Y. Liu, J. Long, B.-J. Li, L. Jiang, R. Li, Y. Wu, L.-S. Ding and Y.-C. Chen, *Org. Biomol. Chem.*, 2006, **4**, 2097.

2 W. Li, W. Wu, F. Yu, H. Huang, X. Liang and J. Ye, *Org. Biomol. Chem.*, 2011, **9**, 2505.

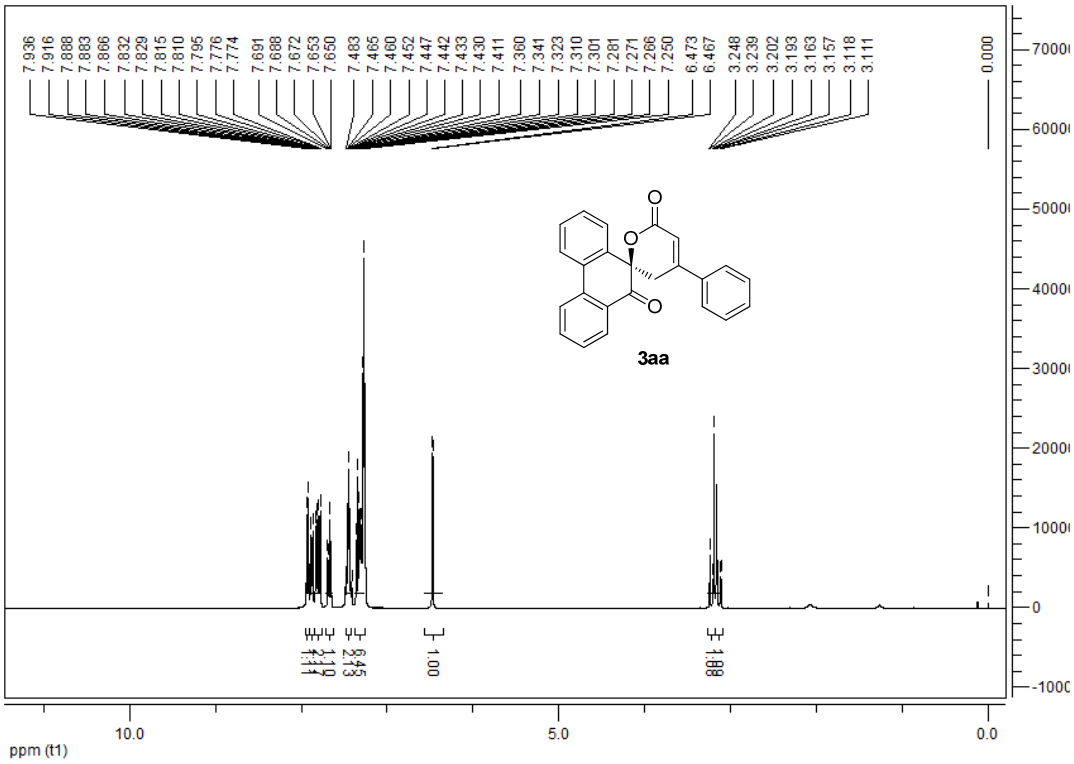
3 W. Yang and D.-M. Du, *Org. Lett.*, 2010, **12**, 5450.

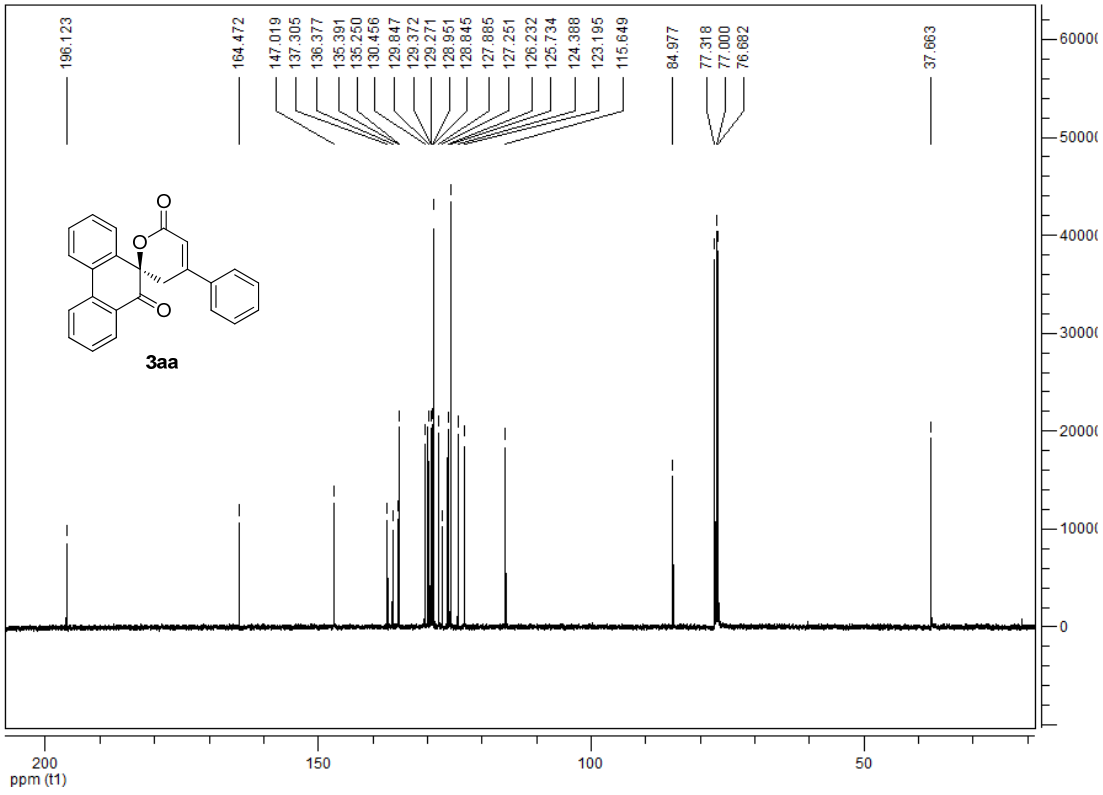
4 (a) T. Okino, Y. Hoashi, T. Furukawa, X. Xu and Y. Takemoto, *J. Am. Chem. Soc.*, 2005, **127**, 119; (b) S.-Z. Nie, Z.-P. Hu, Y.-N. Xuan, J.-J. Wang, X.-M. Li and M. Yan, *Tetrahedron: Asymmetry*, 2010, **21**, 2055.

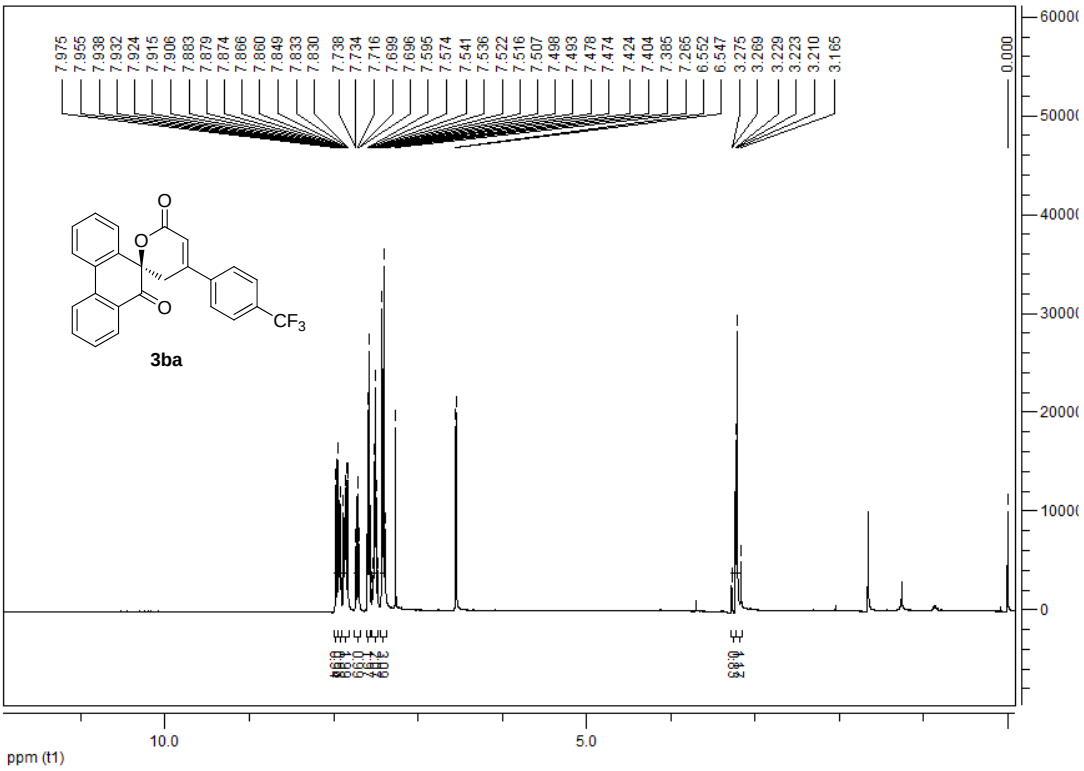
5 W. R. Carroll, P. Pellechia and K. D. Shimizu, *Org. Lett.*, 2008, **10**, 3547.

6 (a) Q. Li, J. Li, H. Ren, Z. Gao and D. Liu, *Synth. Commun.*, 2011, **41**, 3325; (b) J. Hu, D. Zhang and F. W. Harris, *J. Org. Chem.*, 2005, **70**, 707.

4. Copies of NMR Spectra of the Products



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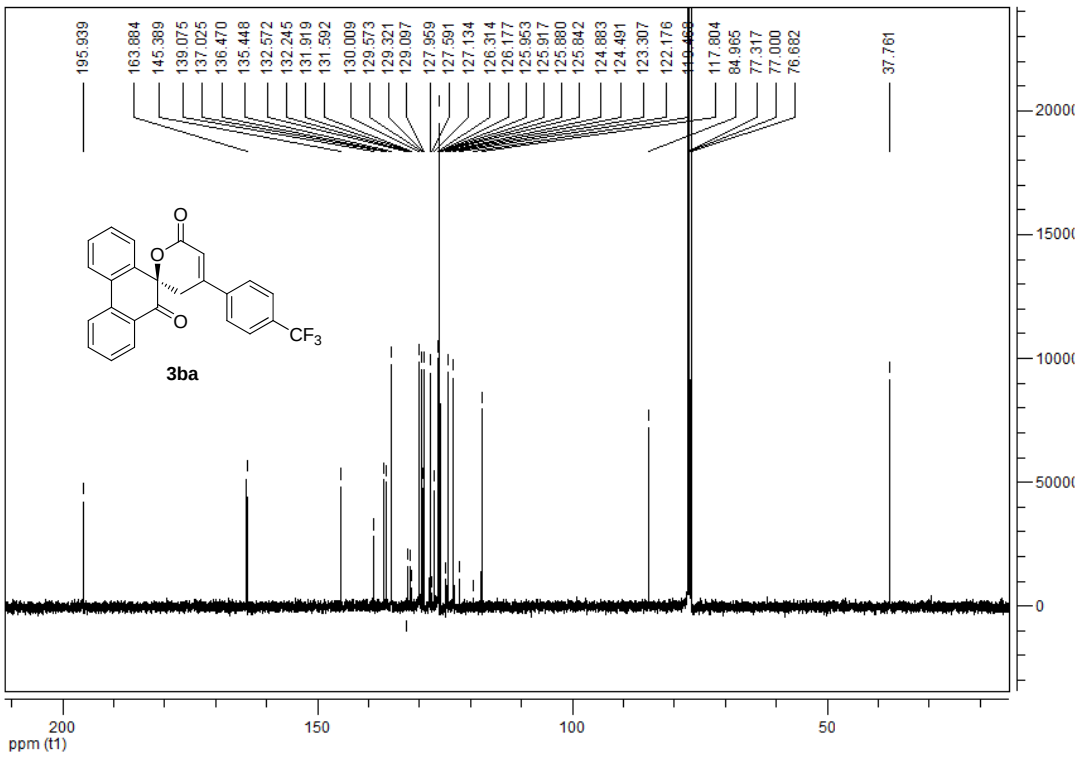
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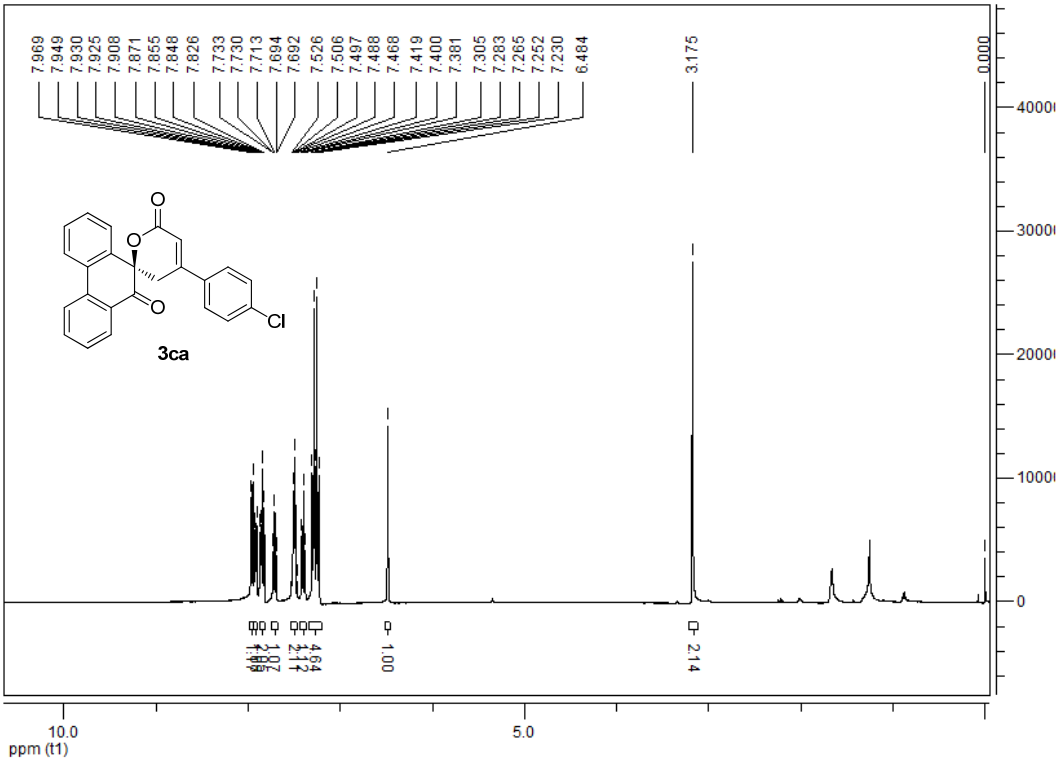
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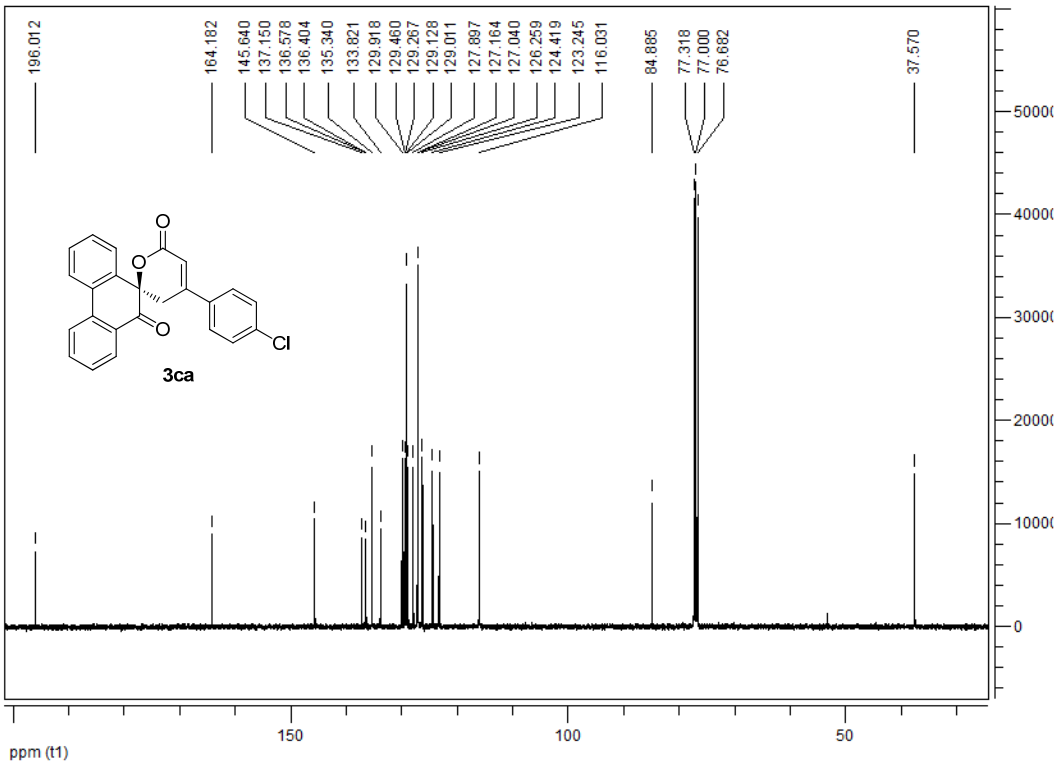
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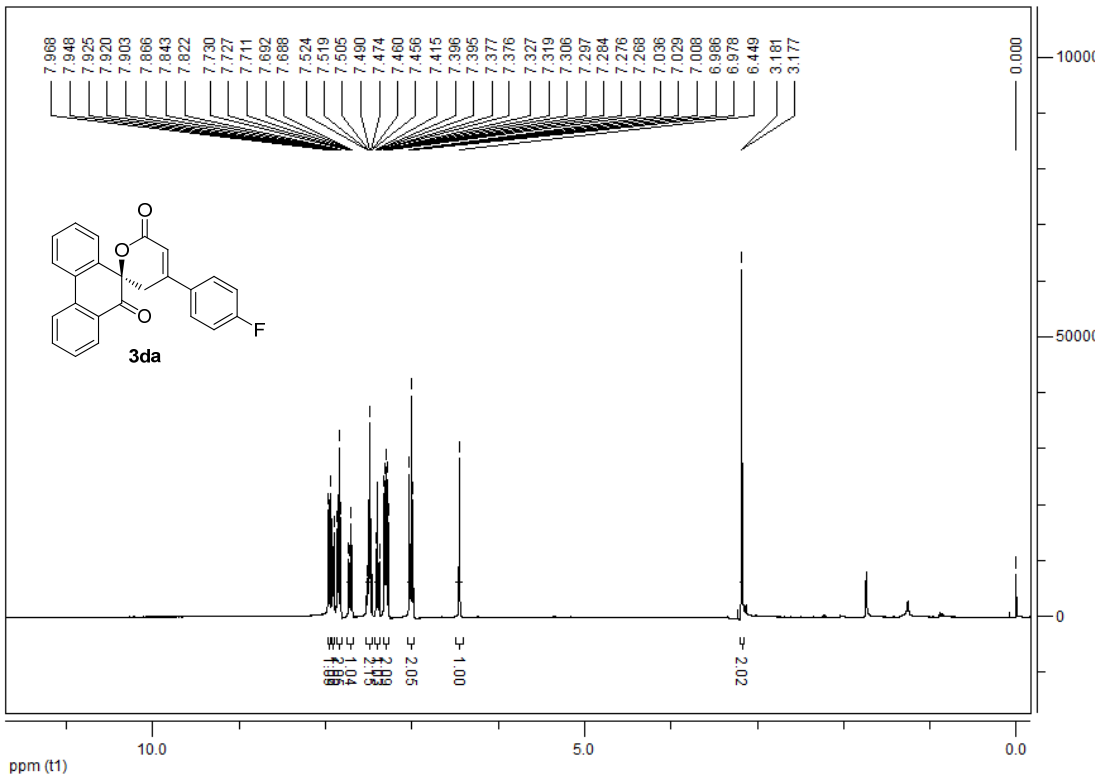
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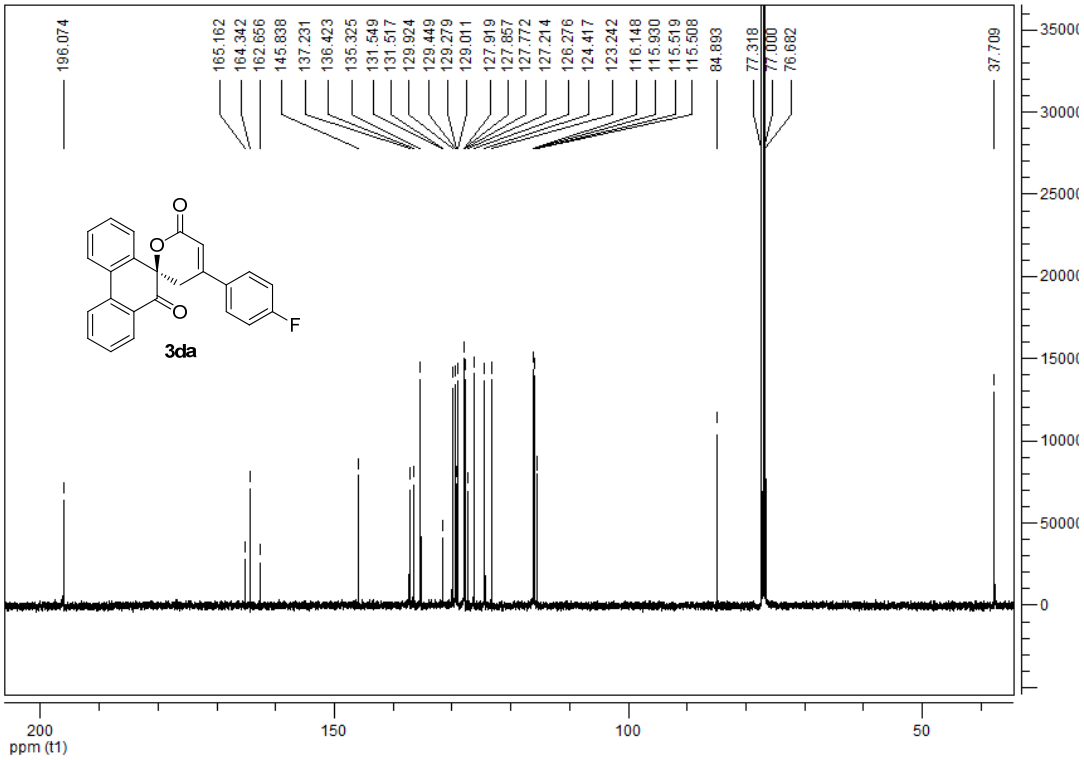
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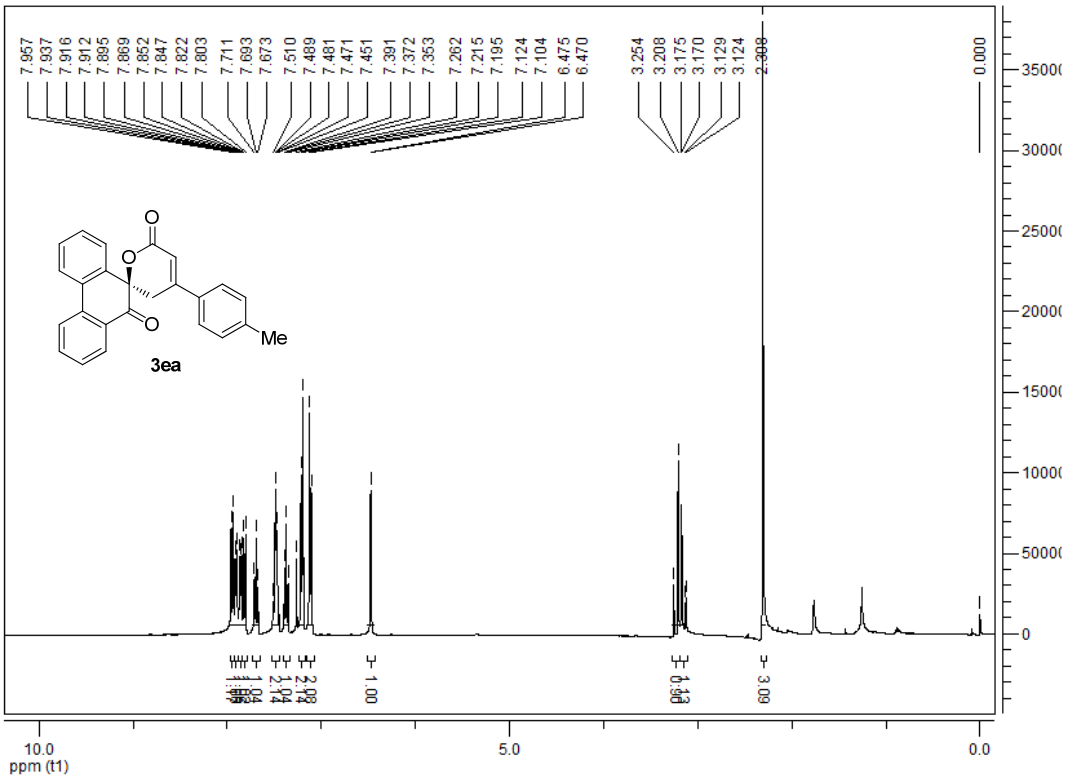
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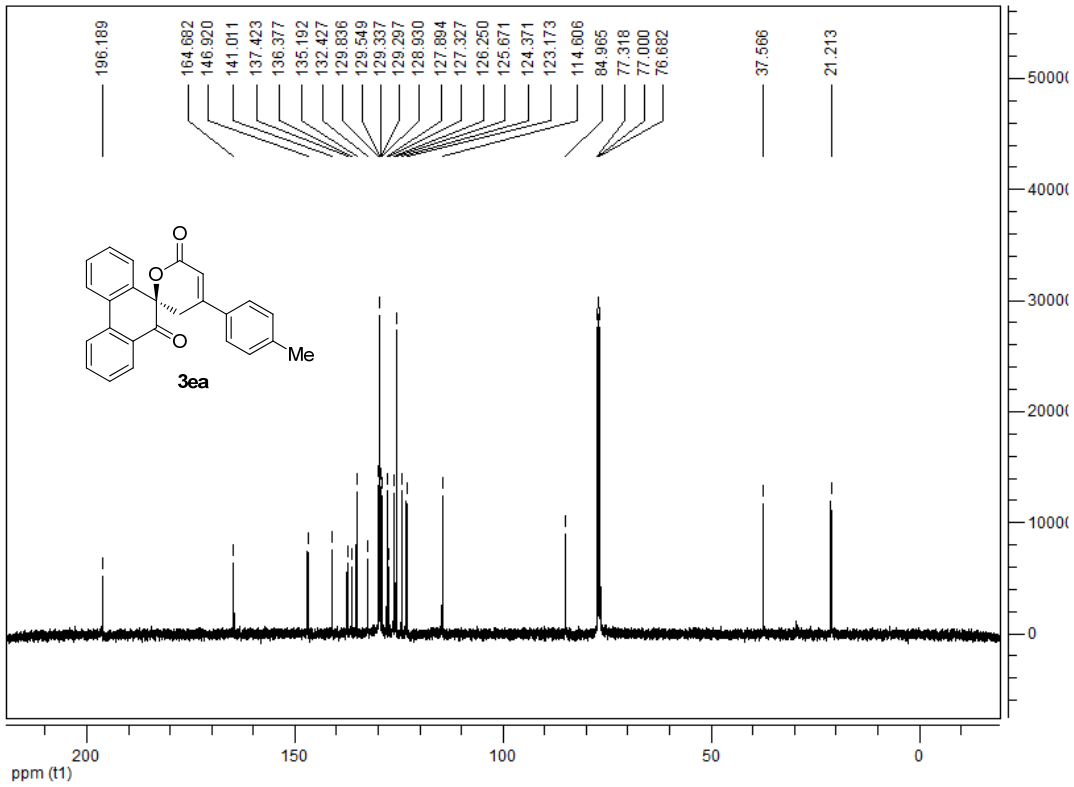
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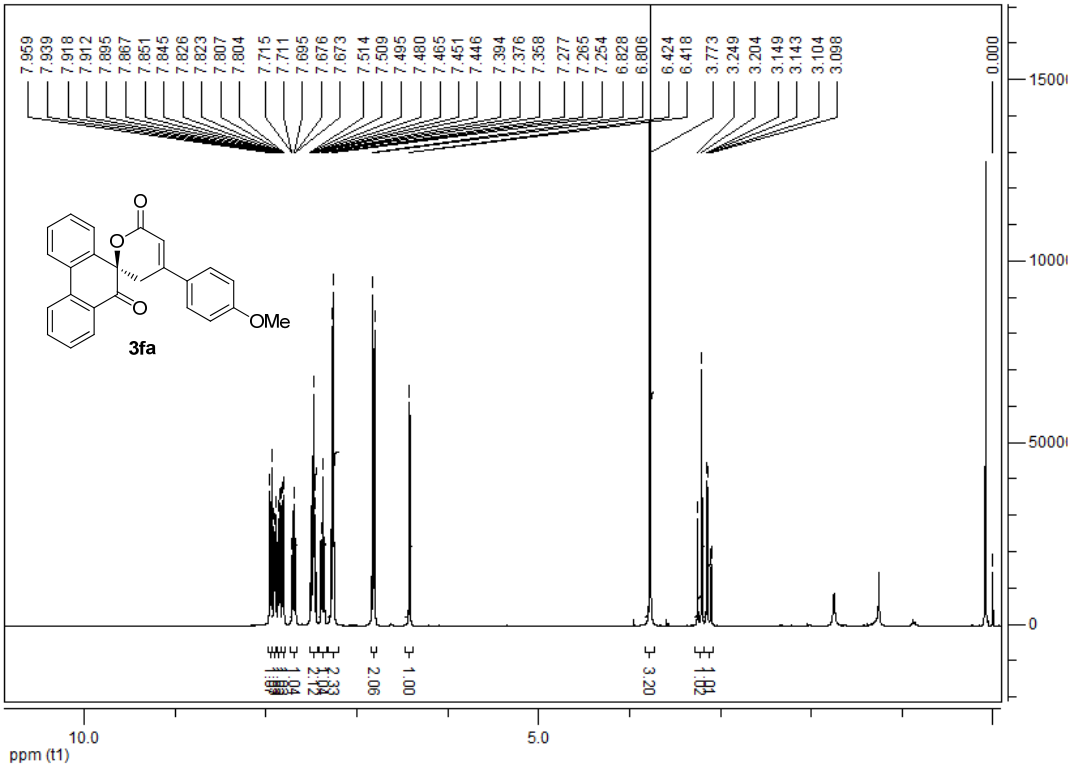
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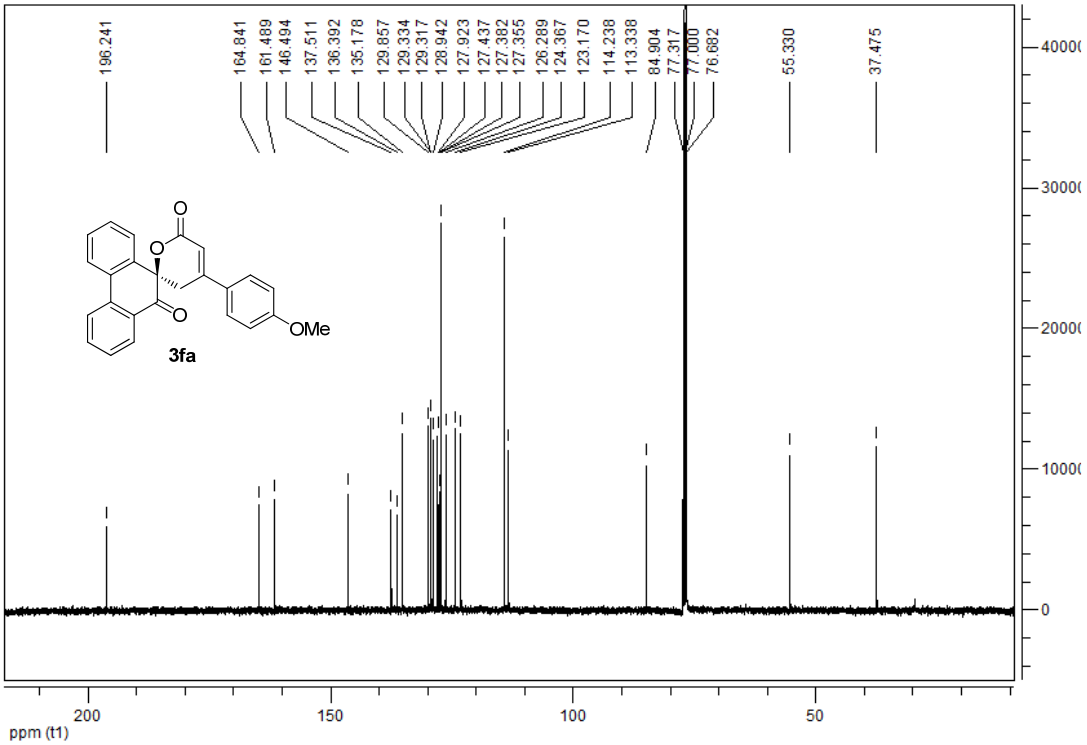
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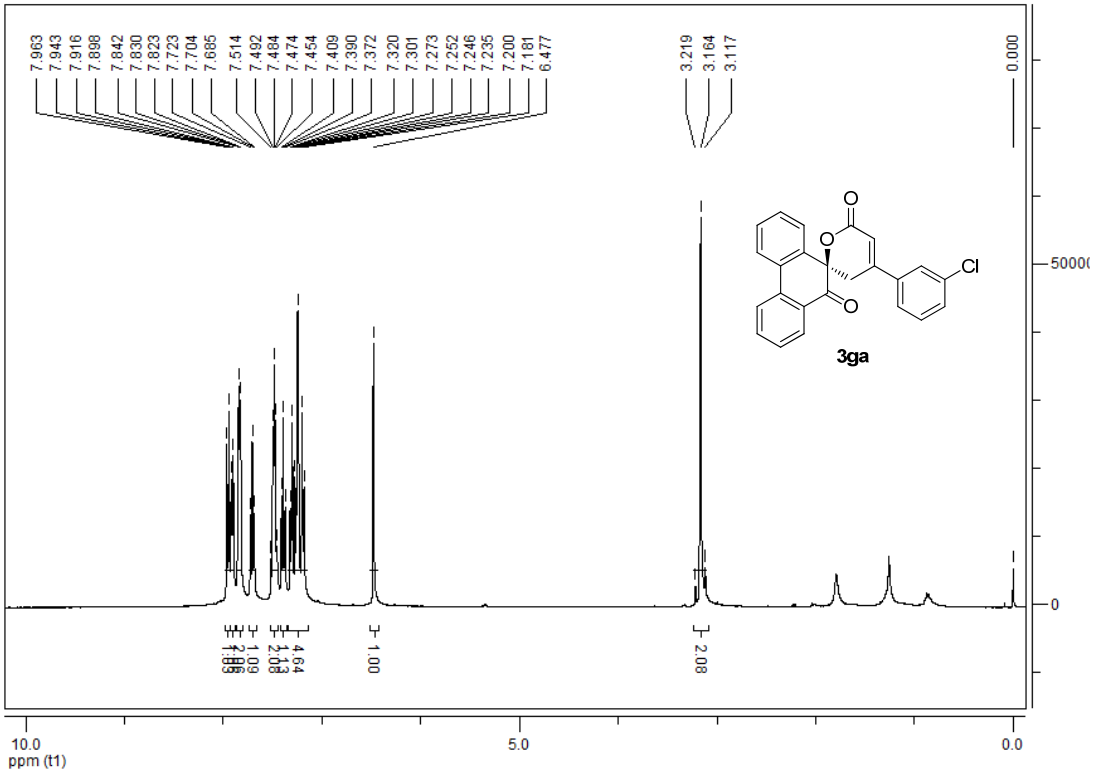
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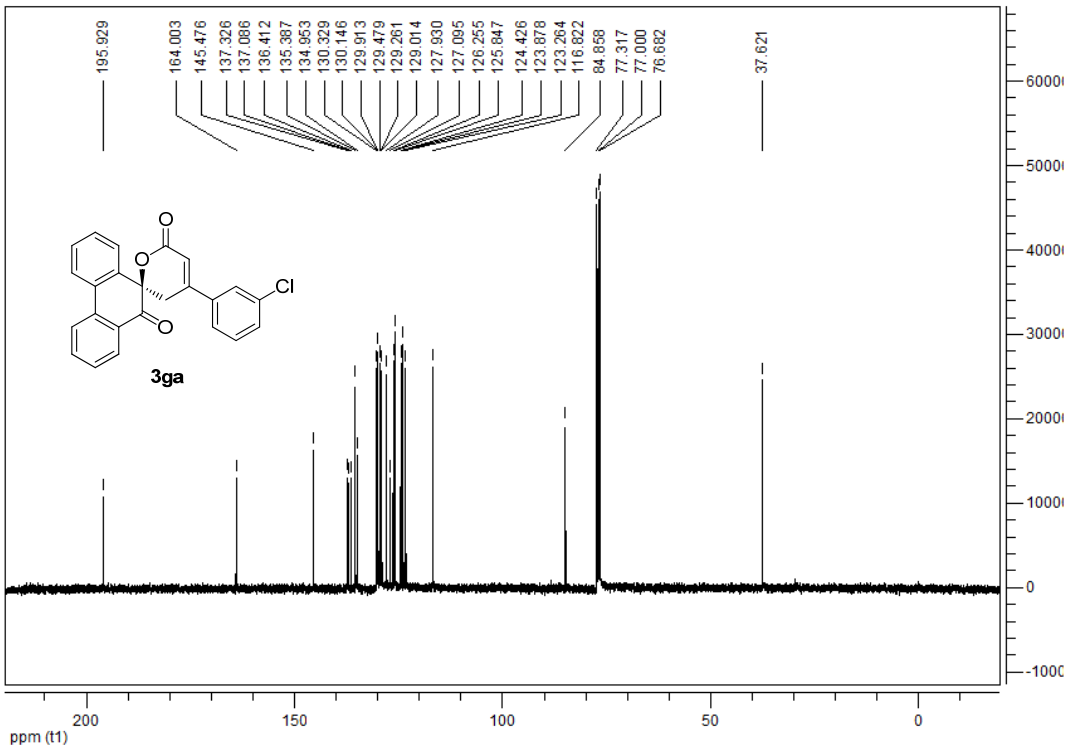
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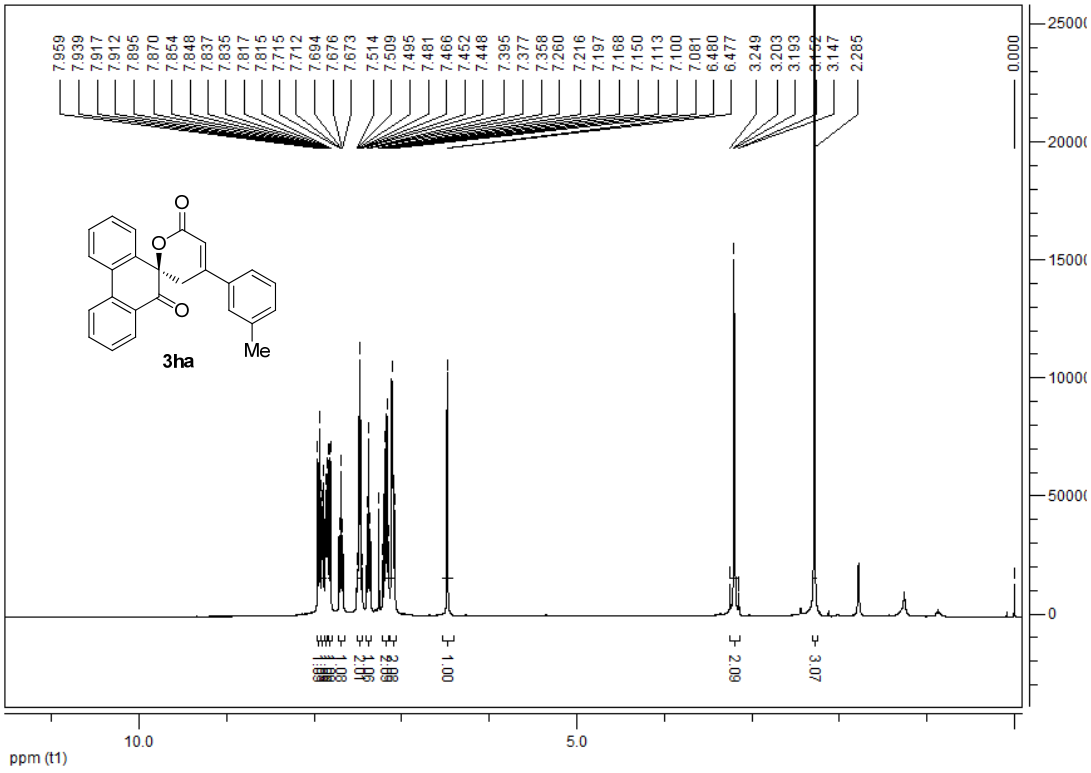
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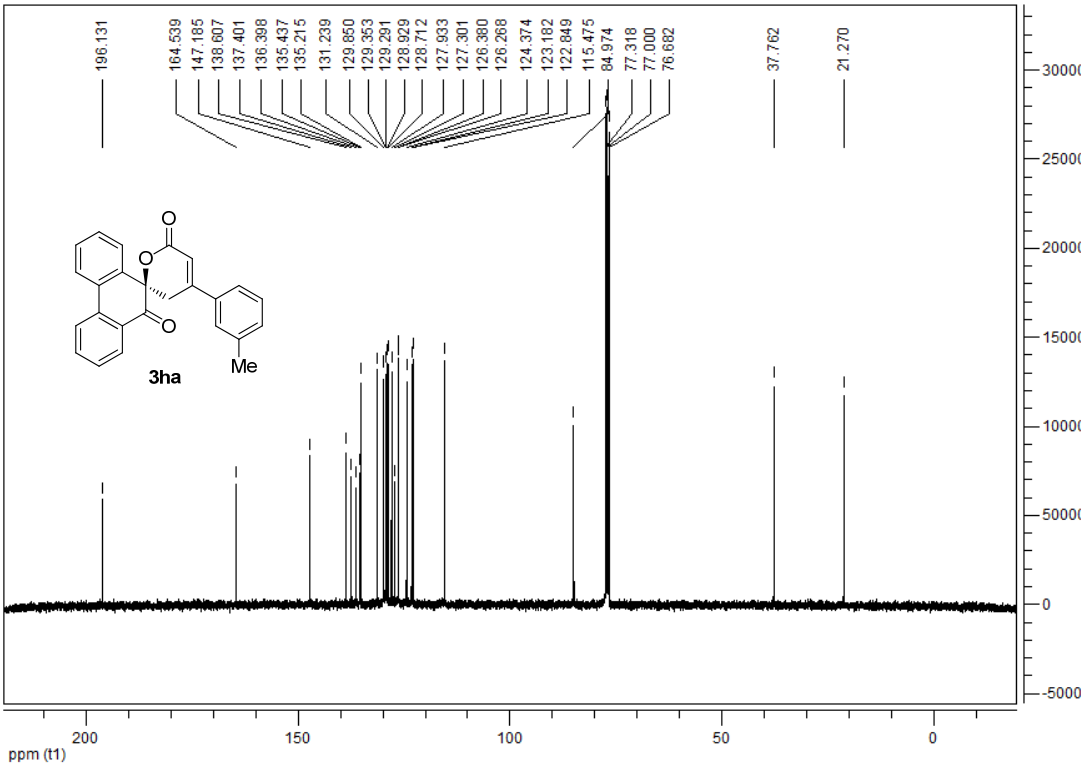
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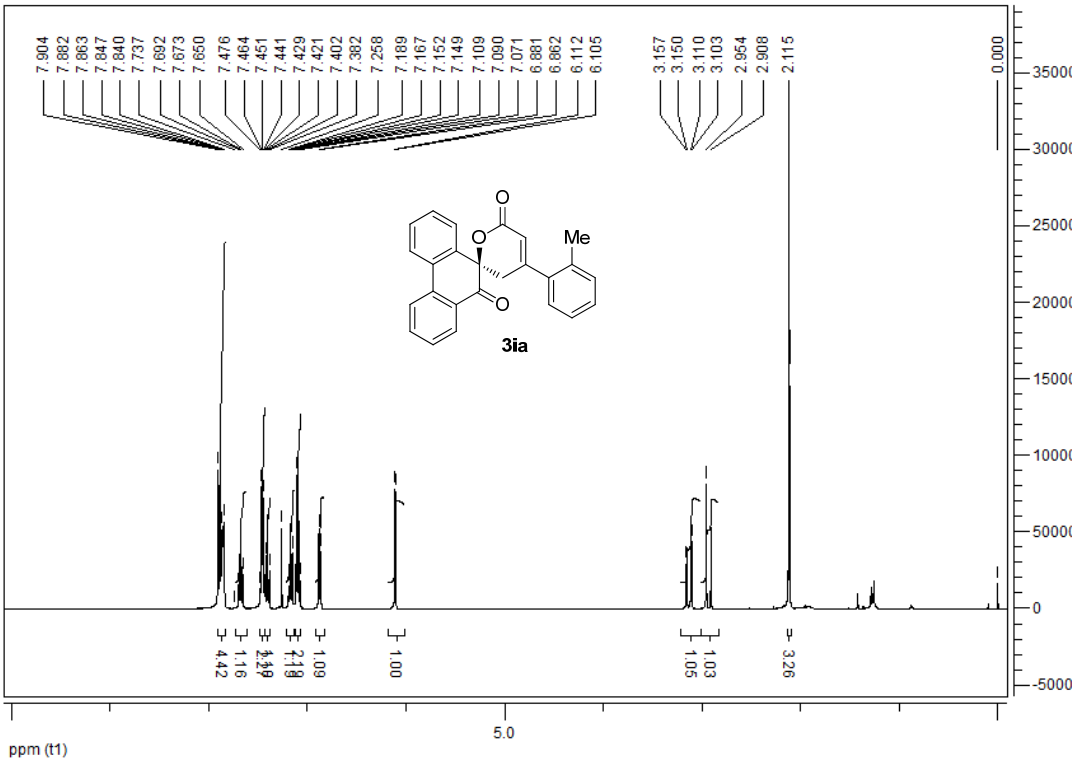
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7.451
7.441
7.429
7.421
7.402
7.382
7.258
7.189
7.167
7.152
7.149
7.109
7.090
7.071
6.881
6.862
6.112
6.105
3.157
3.150
3.110
3.103
2.954
2.908
2.115
0.000
O
O
Me
O
3ia
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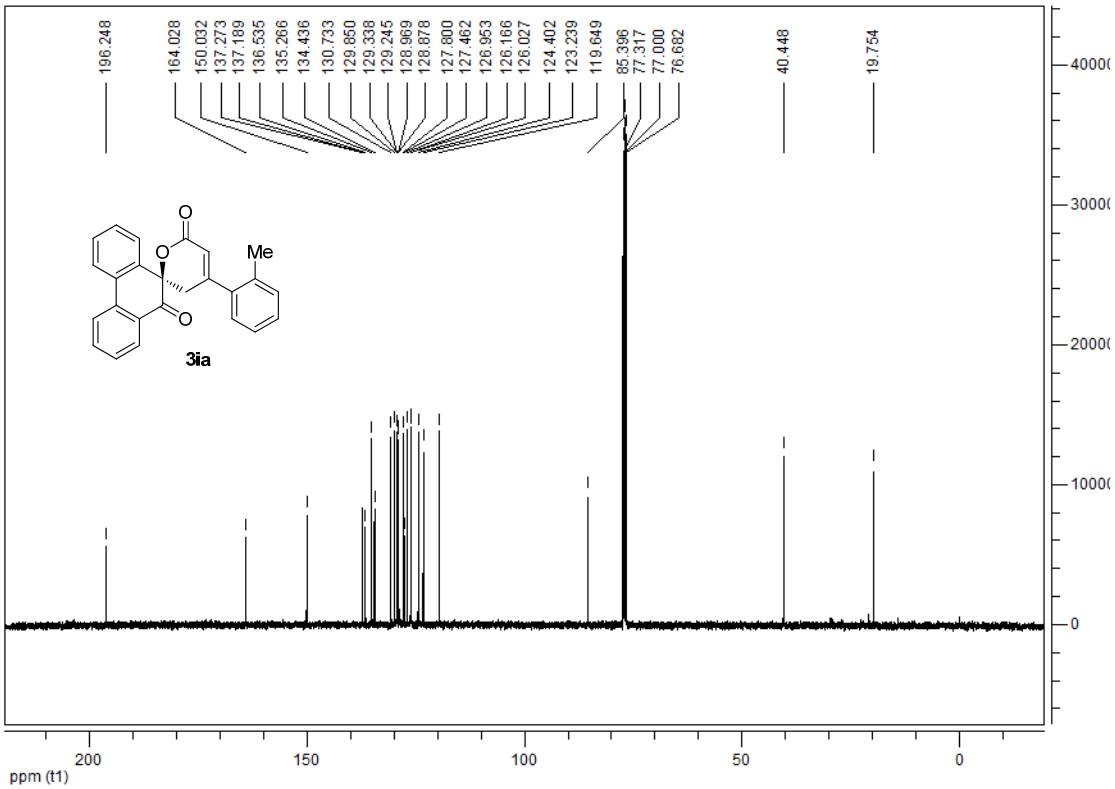
1.16
2.49
2.44
2.19
1.09
1.00
1.05
1.03
3.26
5.0
ppm (t1)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135.266
134.436
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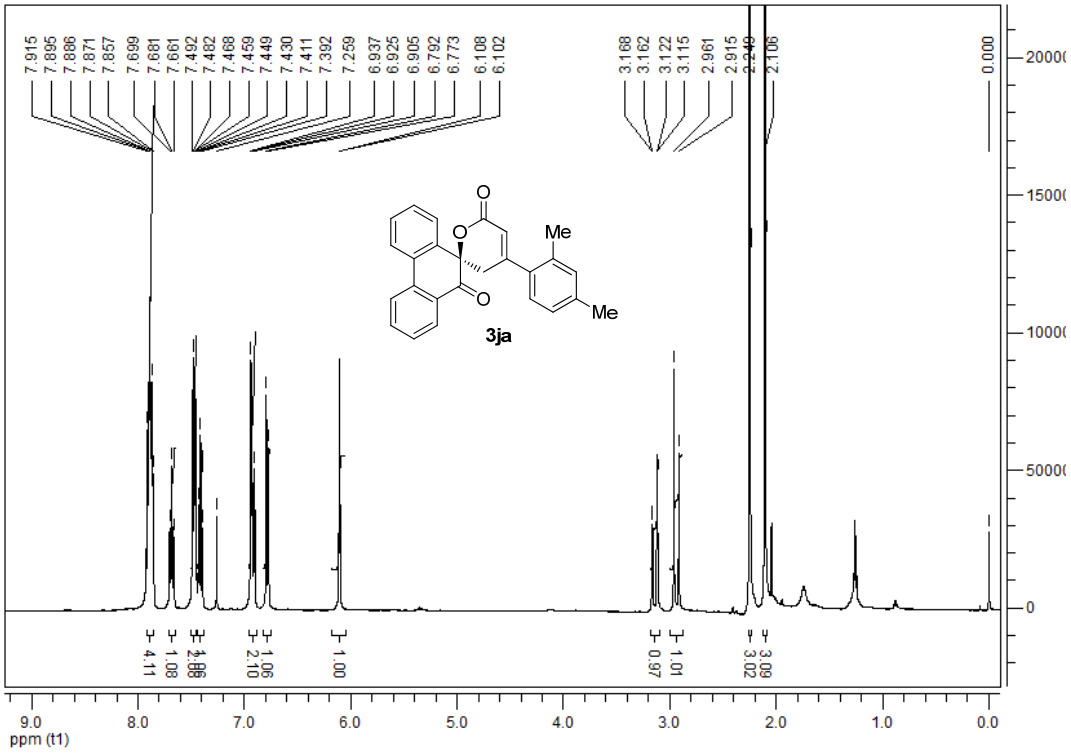
129.850
129.338
129.245
128.969
128.878
127.800
127.462
126.953
126.166
126.027
124.402
123.239
119.649
85.396
77.317
77.000
76.682
40.448
19.754
O
O
Me
O
3ia
200
150
100
50
0
ppm (t1)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7.459
7.449
7.430
7.411
7.392
7.259
6.937
6.925
6.905
6.792
6.773
6.108
6.102
3.168
3.162
3.122
3.115
2.961
2.915
2.249
2.106
0.000
O
O
O
Me
Me
3ja
4.11
1.08
2.10
1.00
0.97
1.01
3.02
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2.0
1.0
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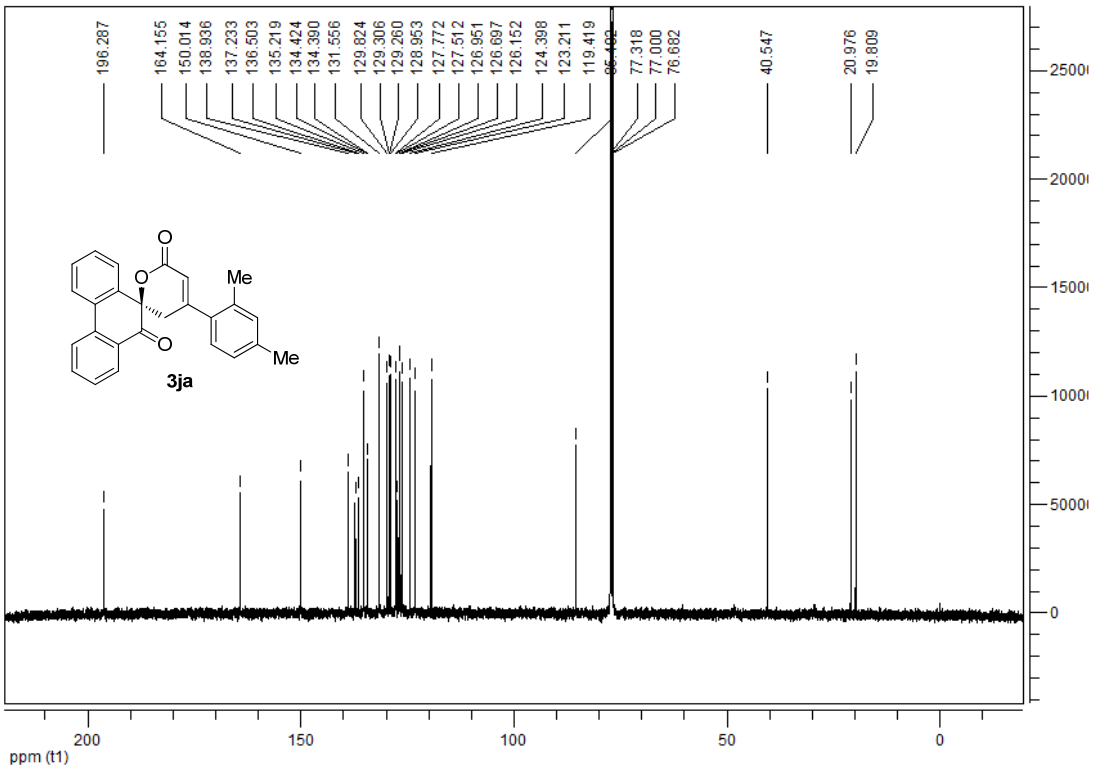
ppm (t1)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131.556
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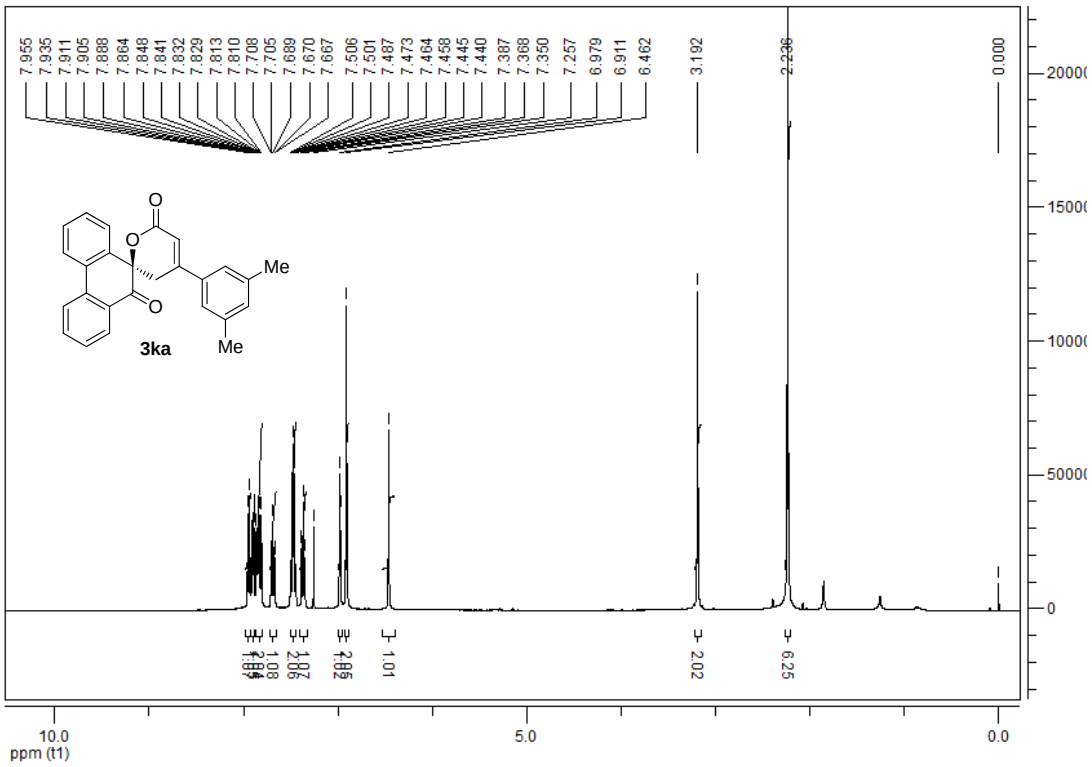
129.260
128.953
127.772
127.512
126.951
126.697
126.152
124.398
123.211
119.419
77.318
77.000
76.682
40.547
20.976
19.809
O
O
O
Me
Me
3ja
200
150
100
50
0
ppm (t1)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7.832
7.829
7.813
7.810
7.708
7.705
7.689
7.670
7.667
7.506
7.501
7.487
7.473
7.464
7.458
7.445
7.440
7.387
7.368
7.350
7.257
6.979
6.911
6.462
3.192
2.236
0.000
O
O
O
Me
Me
3ka
2000
1500
1000
5000
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1.07
2.06
2.02
1.01
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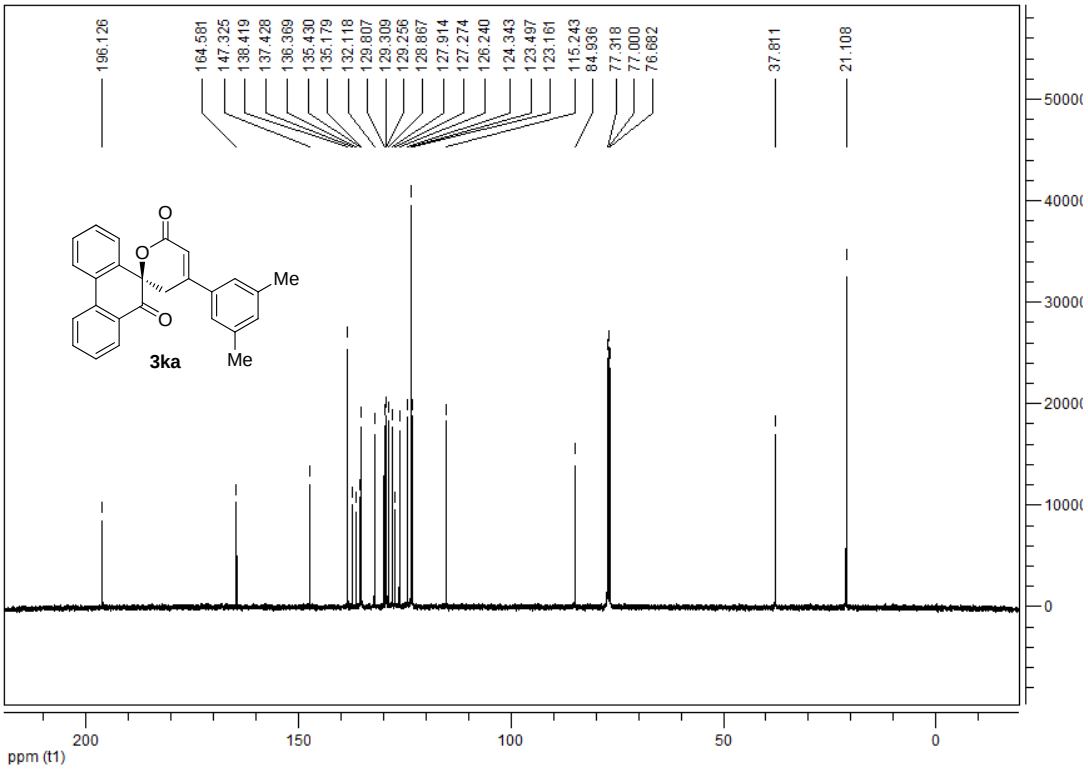
ppm (t1)
5.0
0.0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129.807
129.309
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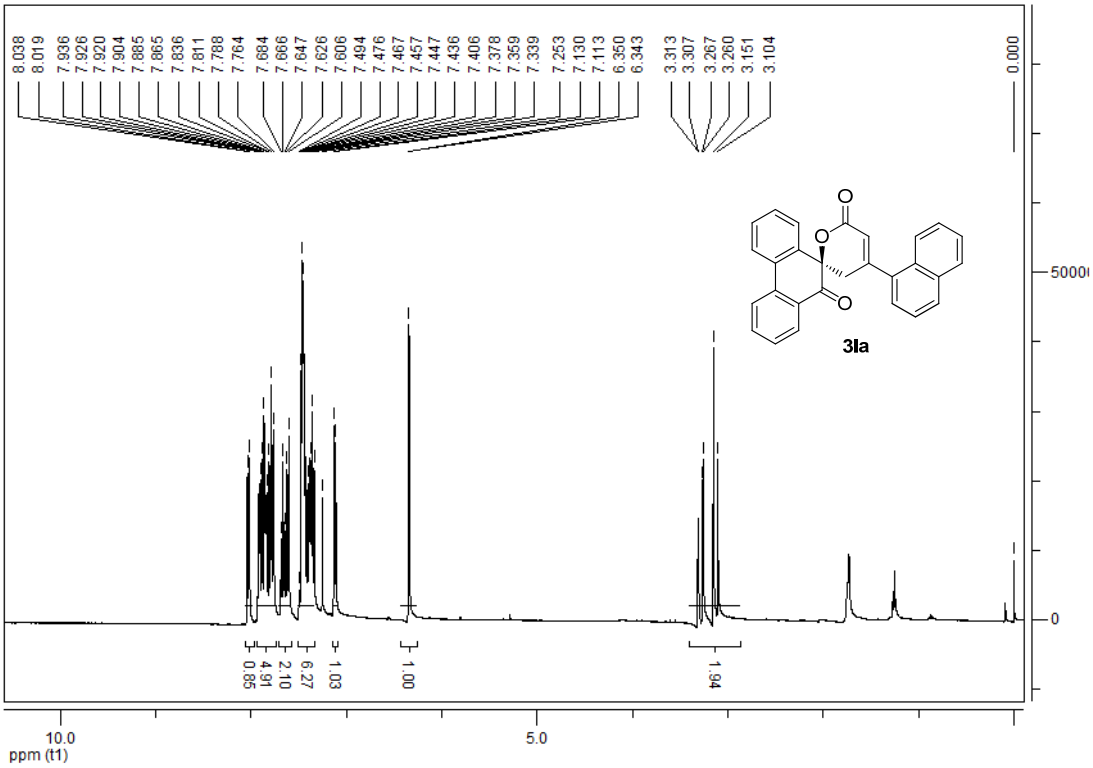
128.867
127.914
127.274
126.240
124.343
123.497
123.161
115.243
84.936
77.318
77.000
76.682
37.811
21.108
O
O
O
Me
Me
3ka
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)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7.865
7.836
7.811
7.788
7.764
7.684
7.666
7.647
7.626
7.606
7.494
7.476
7.467
7.457
7.447
7.436
7.406
7.378
7.359
7.339
7.253
7.130
7.113
6.350
6.343
3.313
3.307
3.267
3.260
3.151
3.104
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2.10
6.27
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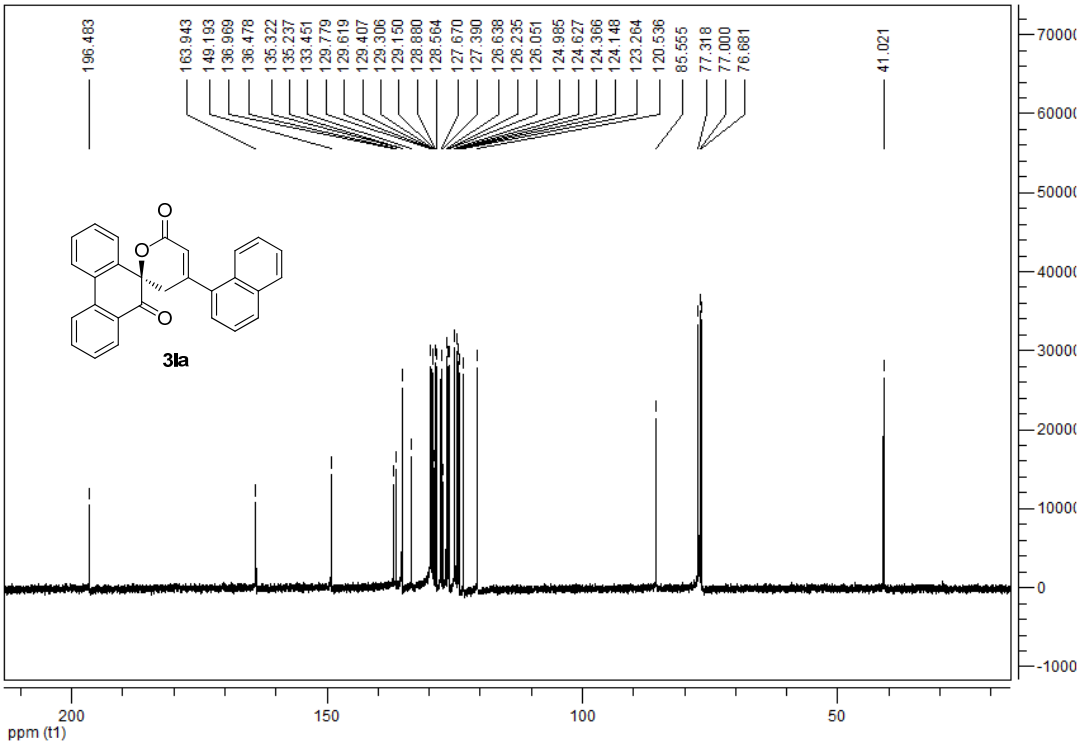
1.00
1.94
10.0
ppm (t1)
5.0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133.451
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129.150
128.880
128.564
127.670
127.390
126.638
126.235
126.051
124.985
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123.264
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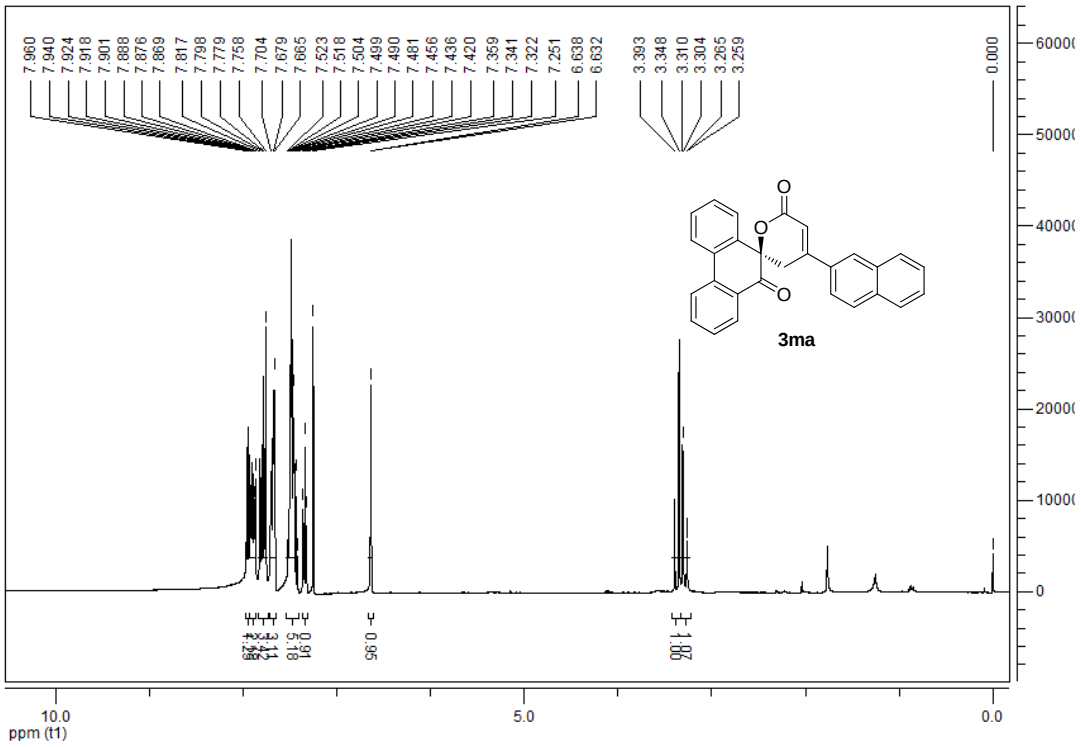
77.000
76.681
41.021
3la
ppm (t1)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7.888
7.876
7.869
7.817
7.798
7.779
7.758
7.704
7.679
7.665
7.523
7.518
7.504
7.499
7.490
7.481
7.456
7.436
7.420
7.359
7.341
7.322
7.251
6.638
6.632
3.393
3.348
3.310
3.304
3.265
3.259
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3ma
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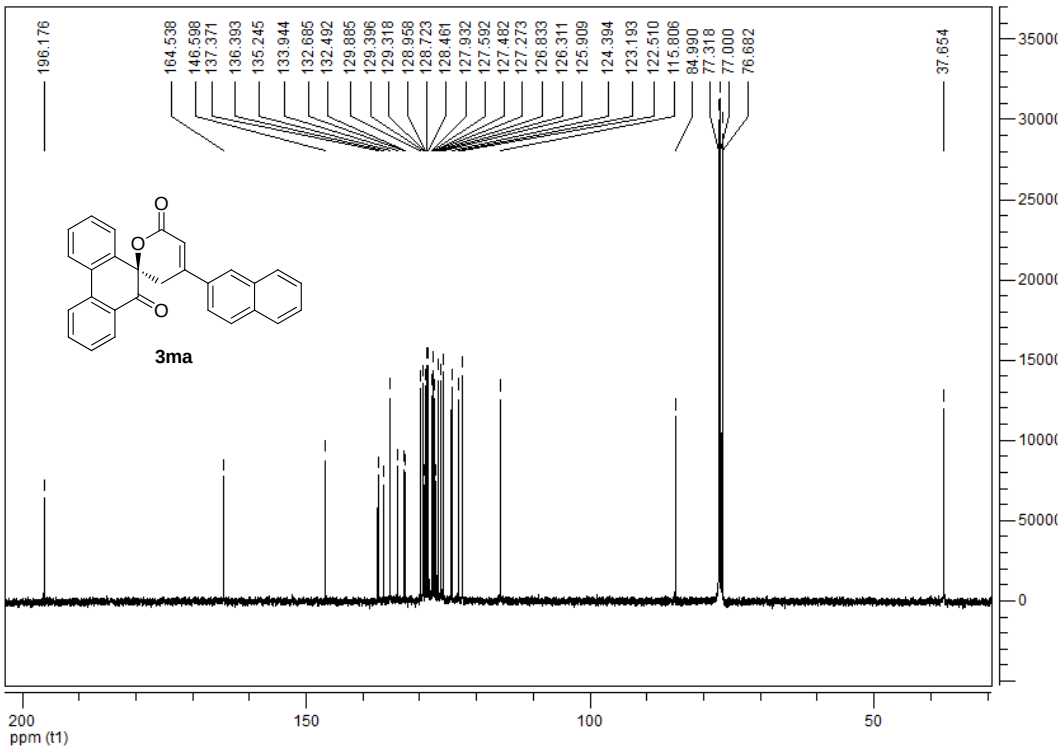
3.12
3.18
0.91
0.96
1.00
10.0
ppm (t1)
5.0
0.0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132.685
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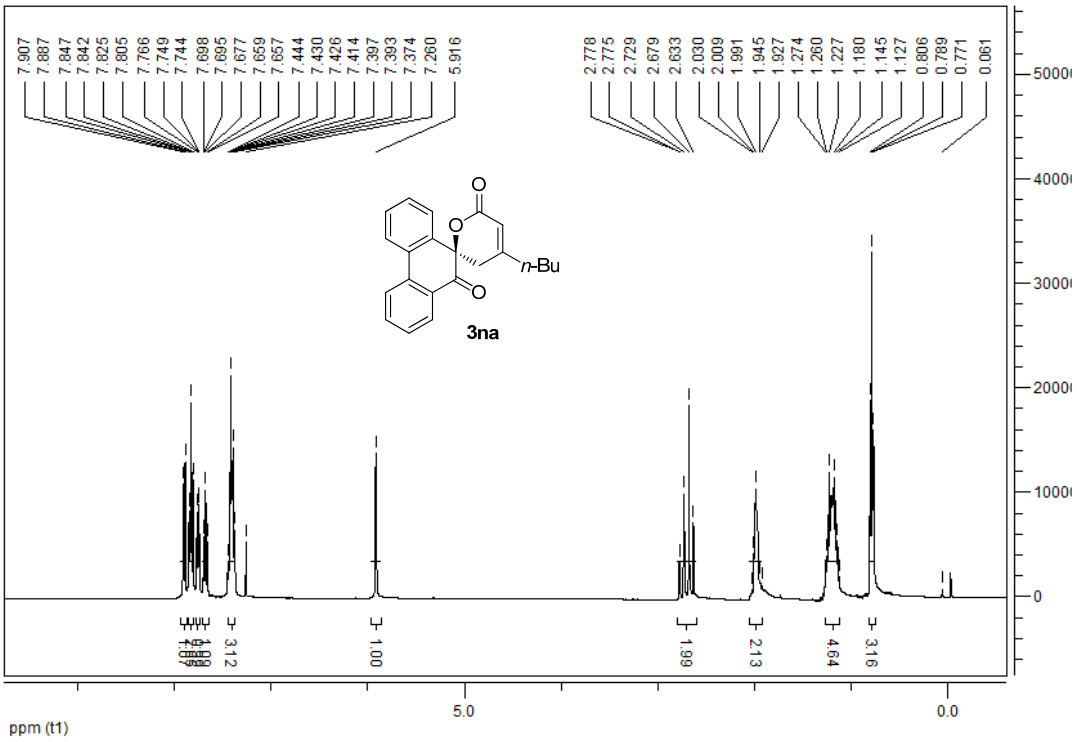
129.885
129.396
129.318
128.958
128.723
128.461
127.932
127.592
127.482
127.273
126.833
126.311
125.909
124.394
123.193
122.510
115.806
84.990
77.318
77.000
76.682
37.654
3ma
200
ppm (t1)
150
100
50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7.749
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7.698
7.695
7.677
7.659
7.657
7.444
7.430
7.426
7.414
7.397
7.393
7.374
7.260
5.916
2.778
2.775
2.729
2.679
2.633
2.030
2.009
1.991
1.945
1.927
1.274
1.260
1.227
1.180
1.145
1.127
0.806
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0.061
n-Bu
3na
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2.13
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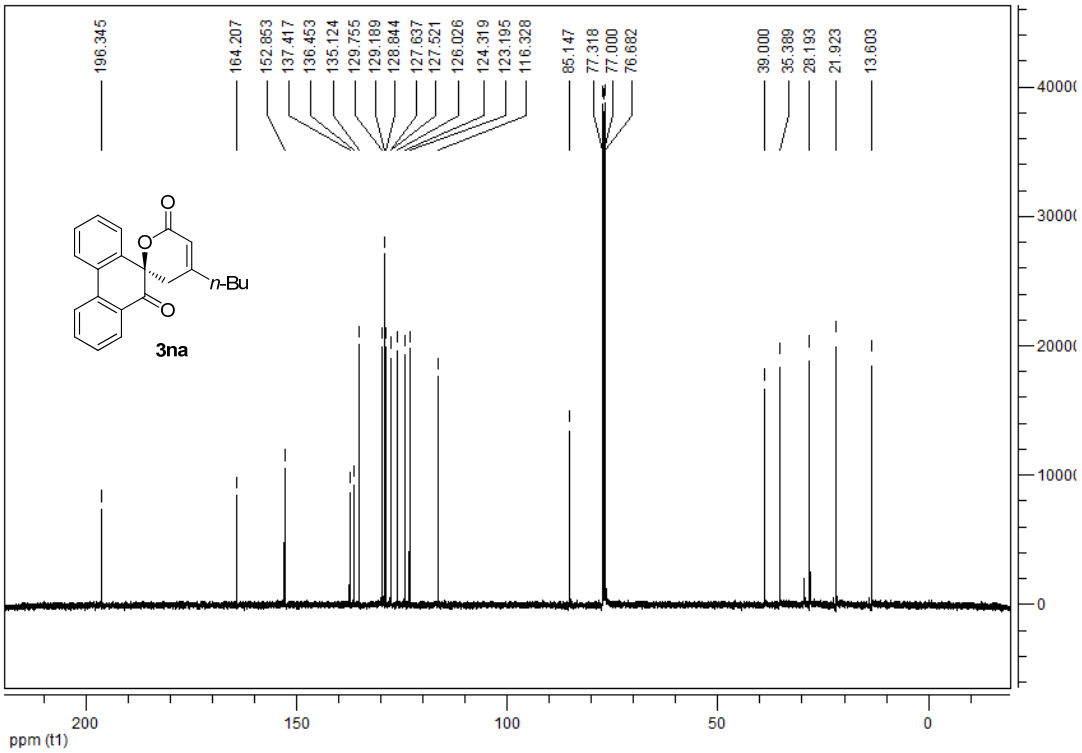
3.16
ppm (t1)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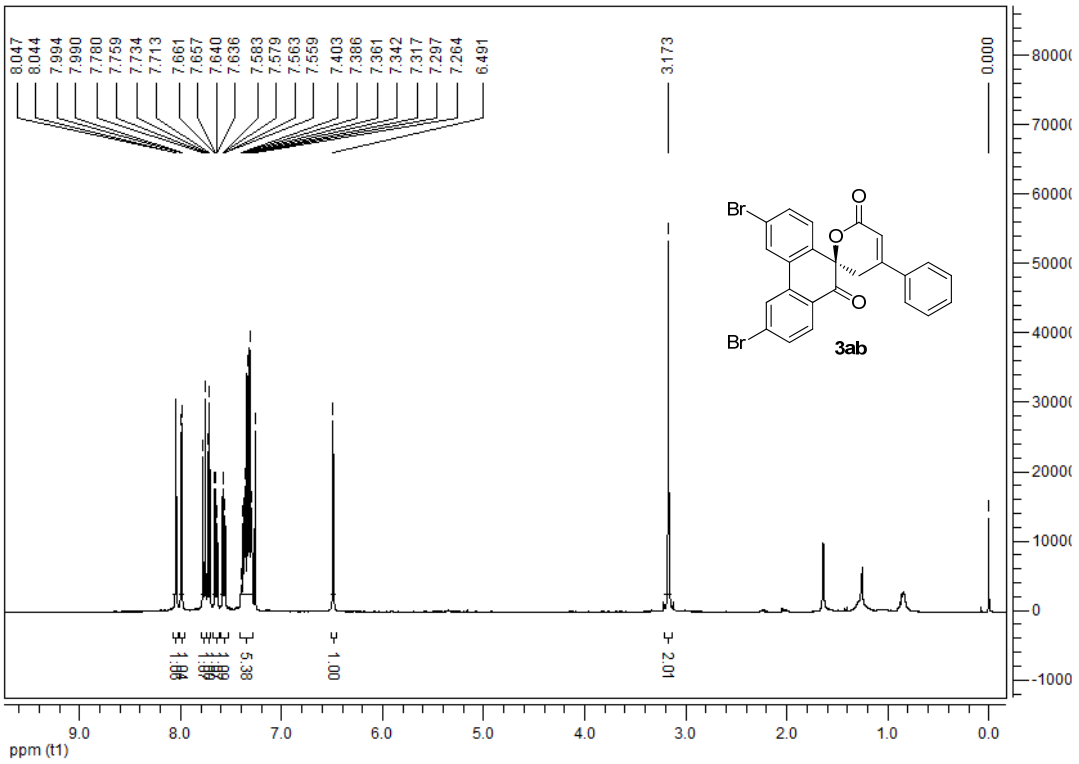
127.521
126.026
124.319
123.195
116.328
85.147
77.318
77.000
76.682
39.000
35.389
28.193
21.923
13.603
n-Bu
3na
ppm (t1)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7.759
7.734
7.713
7.661
7.657
7.640
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7.583
7.579
7.563
7.559
7.403
7.386
7.361
7.342
7.317
7.297
7.264
6.491
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Br
O
O
O
Br
3ab
2.01
1.00
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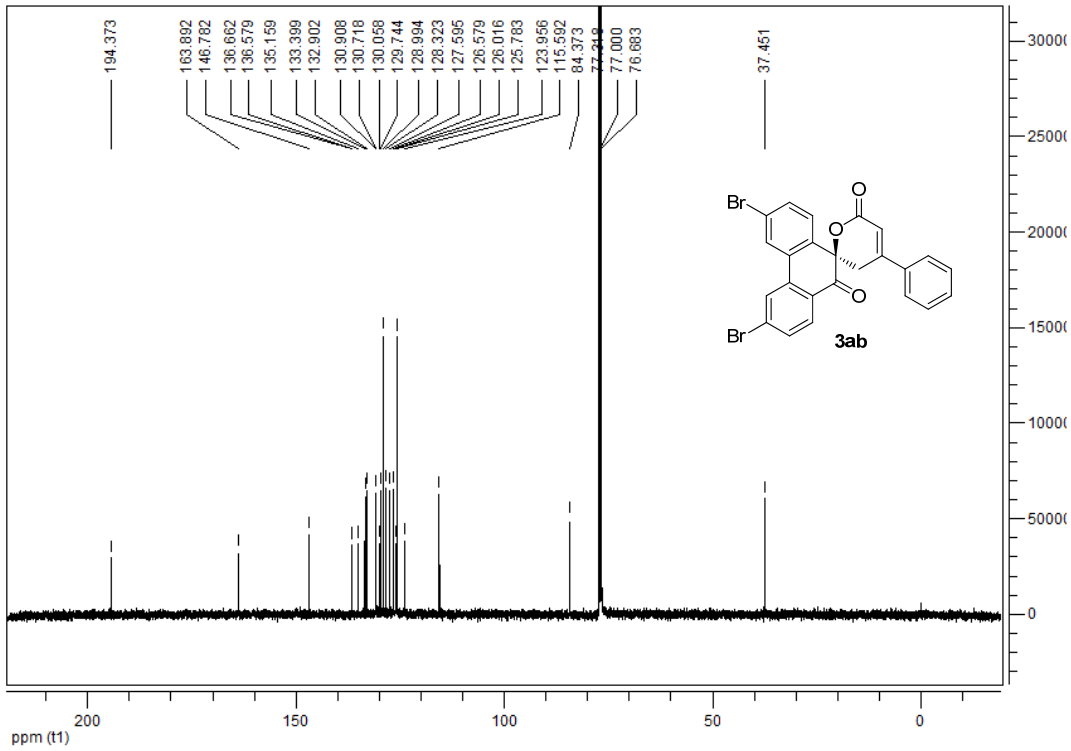
ppm (t1)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132.902
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128.994
128.323
127.595
126.579
126.016
125.783
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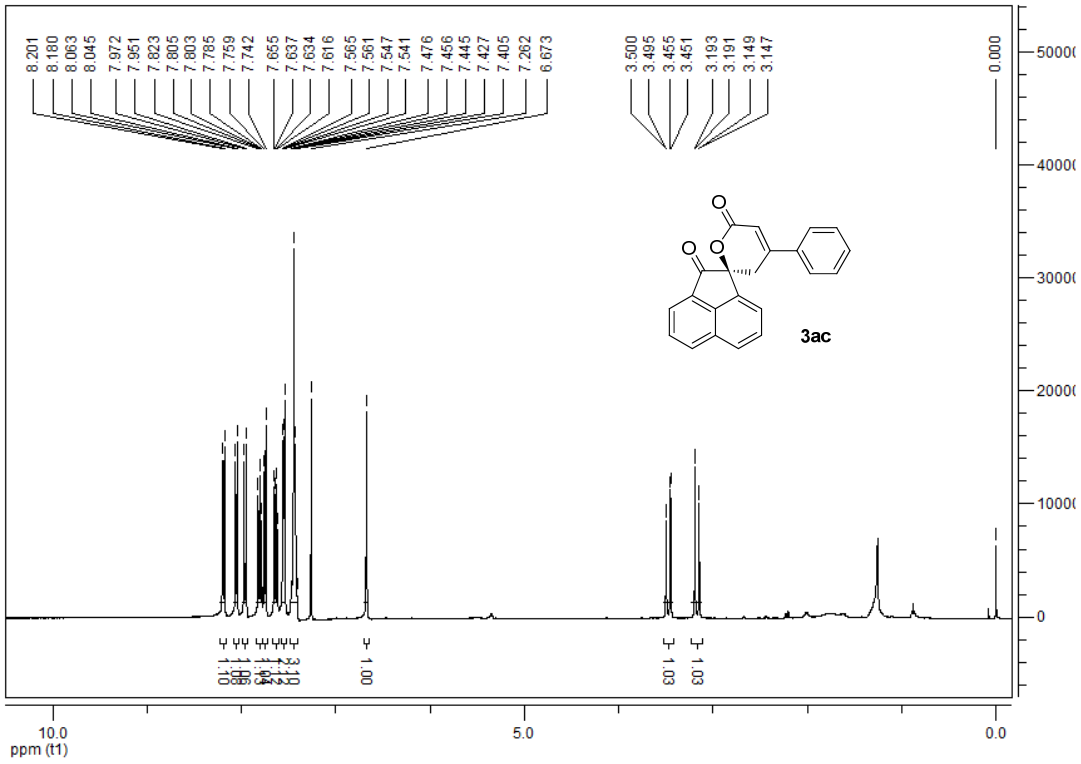
77.319
77.000
76.683
37.451
Br
O
O
O
Br
3ab
ppm (t1)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7.805
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7.759
7.742
7.655
7.637
7.634
7.616
7.565
7.561
7.547
7.541
7.476
7.456
7.445
7.427
7.405
7.262
6.673
3.500
3.495
3.455
3.451
3.193
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3.149
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0.000
3ac
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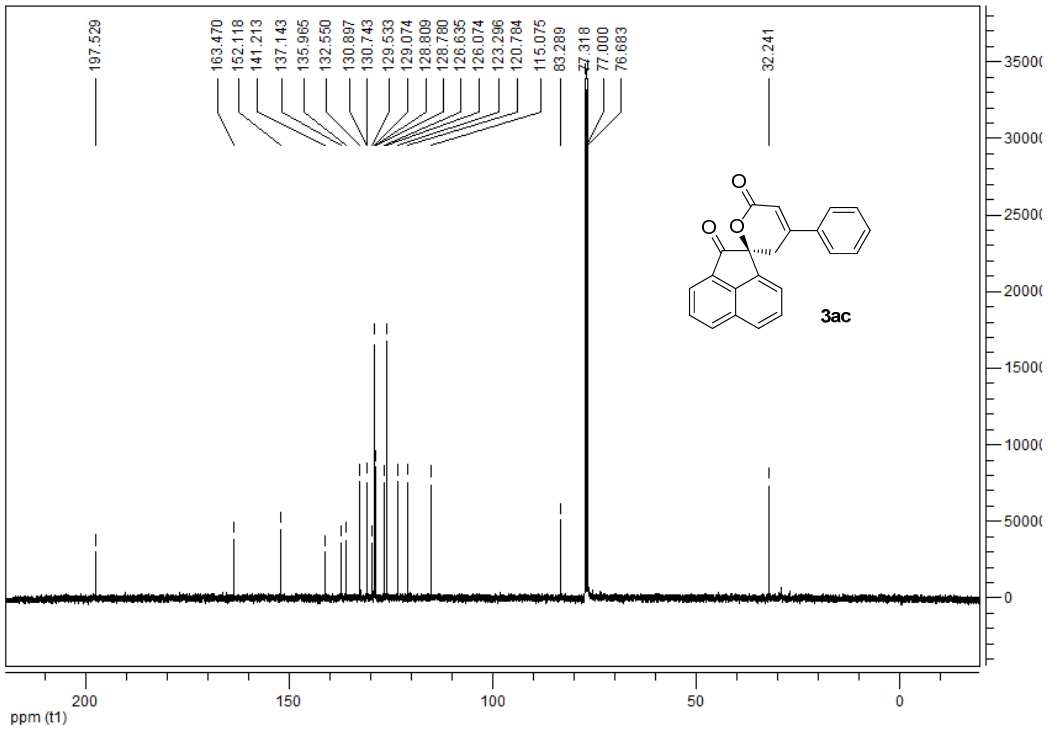
10.0
5.0
0.0
ppm (t1)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130.897
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129.533
129.074
128.809
128.780
126.635
126.074
123.296
120.784
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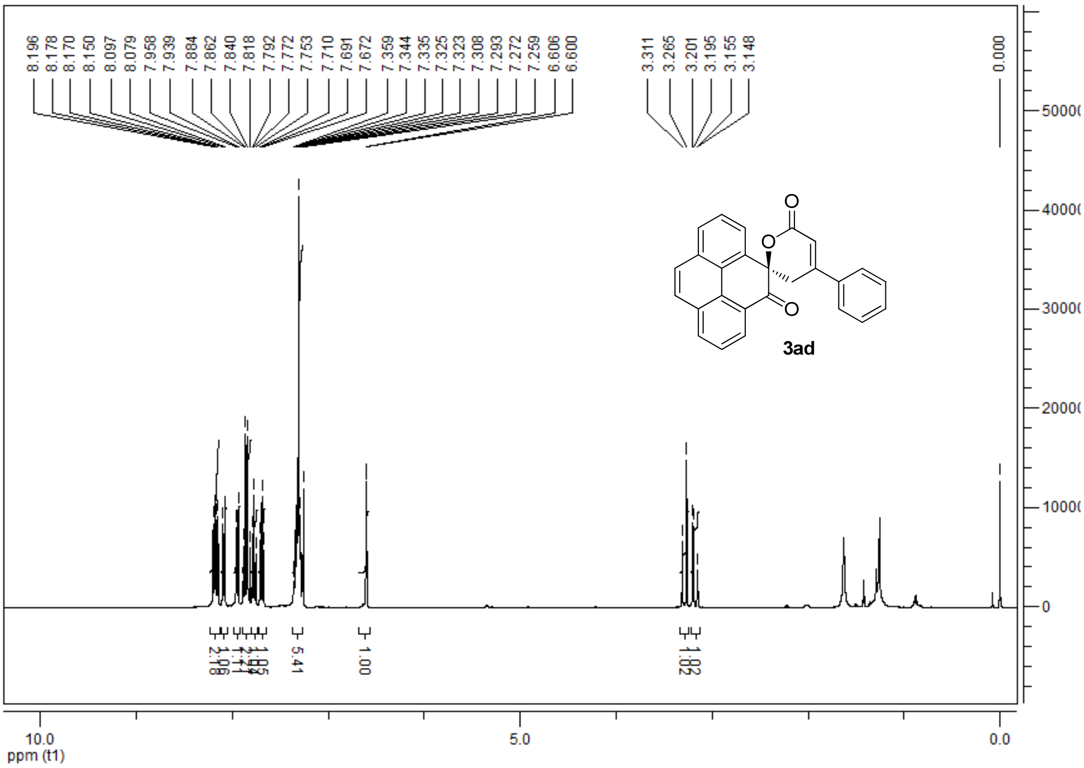
77.318
77.000
76.683
32.241
3ac
200
150
100
50
0
ppm (t1)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8.079
7.958
7.939
7.884
7.862
7.840
7.818
7.792
7.772
7.753
7.710
7.691
7.672
7.359
7.344
7.335
7.325
7.323
7.308
7.293
7.272
7.259
6.606
6.600
3.311
3.265
3.201
3.195
3.155
3.148
0.000
3ad
2.18
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1.00
1.02
10.0
5.0
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ppm (t1)
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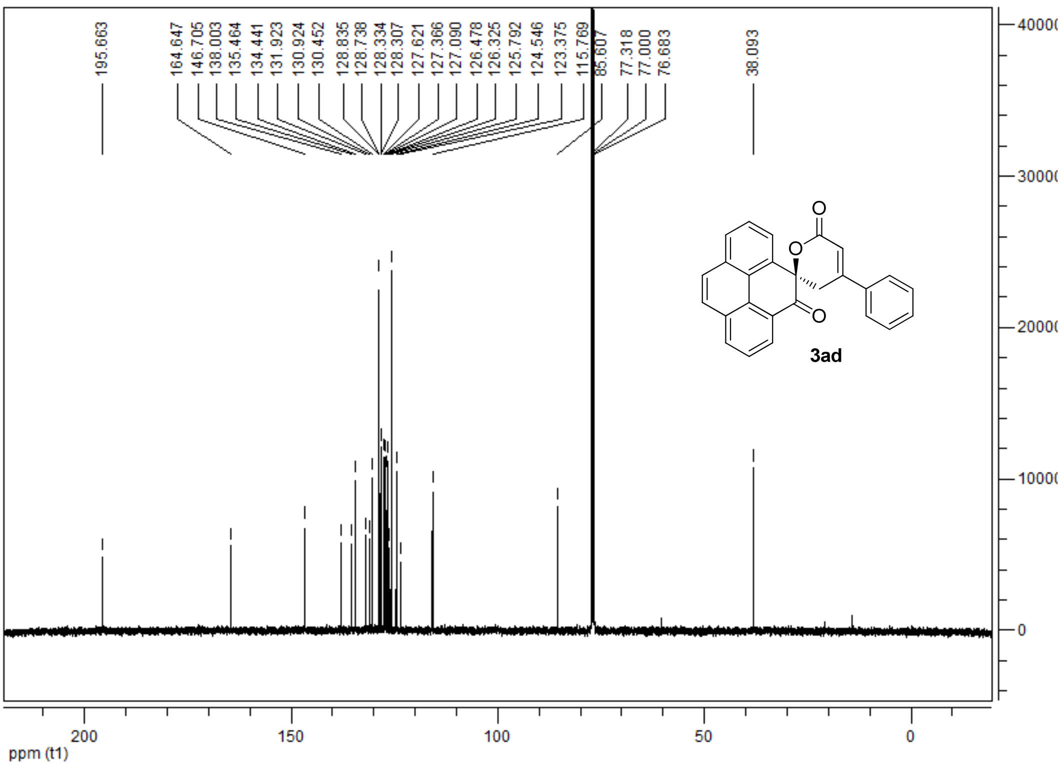
40000
30000
20000
10000
0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130.924
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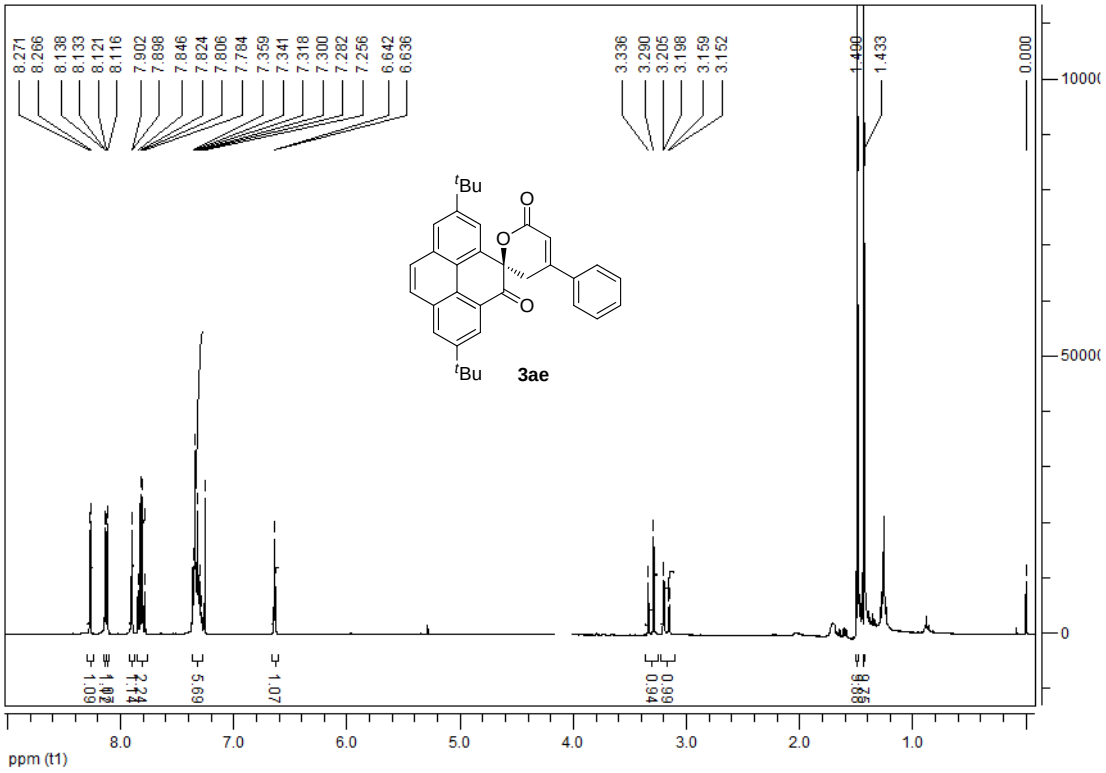
128.334
128.307
127.621
127.366
127.090
126.478
126.325
125.792
124.546
123.375
115.769
85.607
77.318
77.000
76.683
38.093
3ad
200
150
100
50
0
ppm (t1)
40000
30000
20000
10000
0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8.116
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7.898
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7.824
7.806
7.784
7.359
7.341
7.318
7.300
7.282
7.256
6.642
6.636
3.336
3.290
3.205
3.198
3.159
3.152
1.490
1.433
0.000
tBu
O
O
O
tBu
3ae
10000
50000
0
1.09
2.24
5.69
1.07
0.94
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7.0
6.0
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4.0
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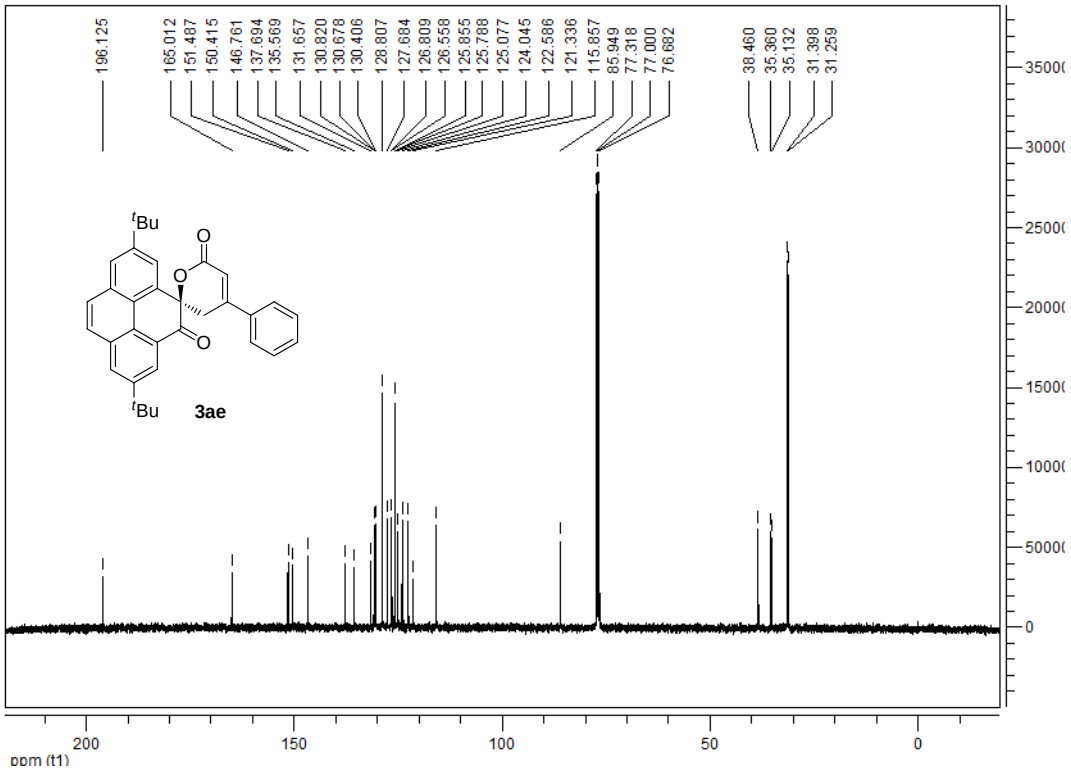
2.0
1.0
ppm (t1)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128.807
127.684
126.809
126.558
125.855
125.788
125.077
124.045
122.586
121.336
115.857
85.949
77.318
77.000
76.682
38.460
35.360
35.132
31.398
31.259
tBu
O
O
O
tBu
3ae
35000
30000
25000
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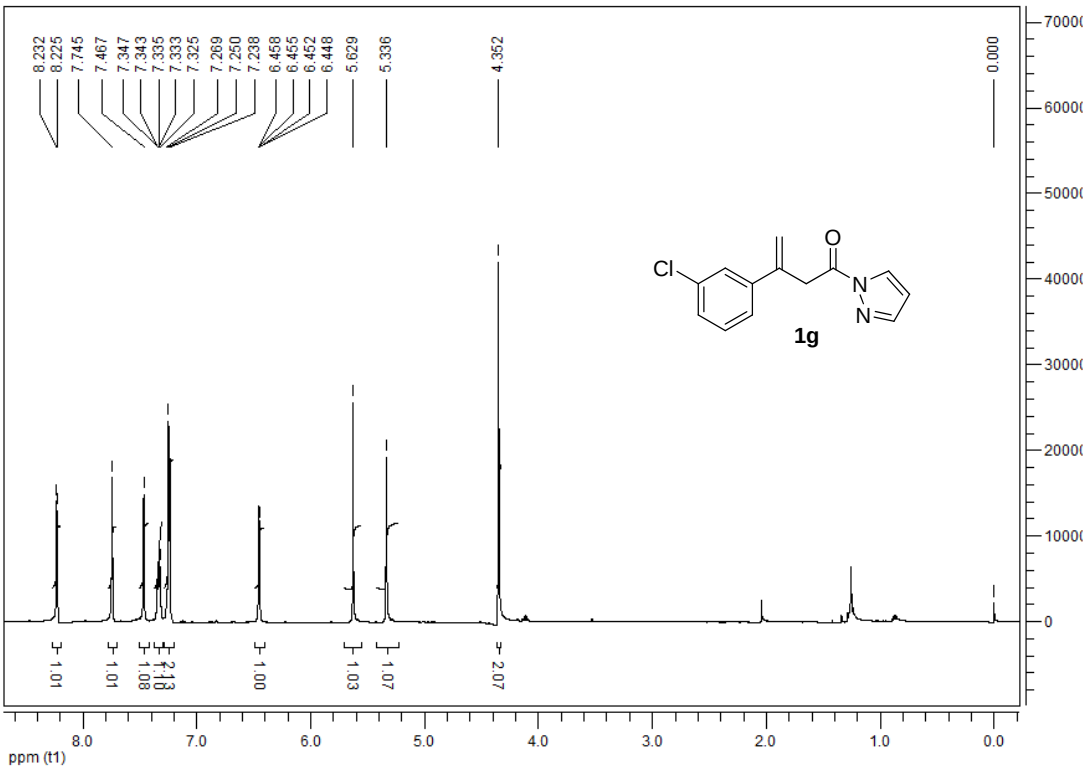
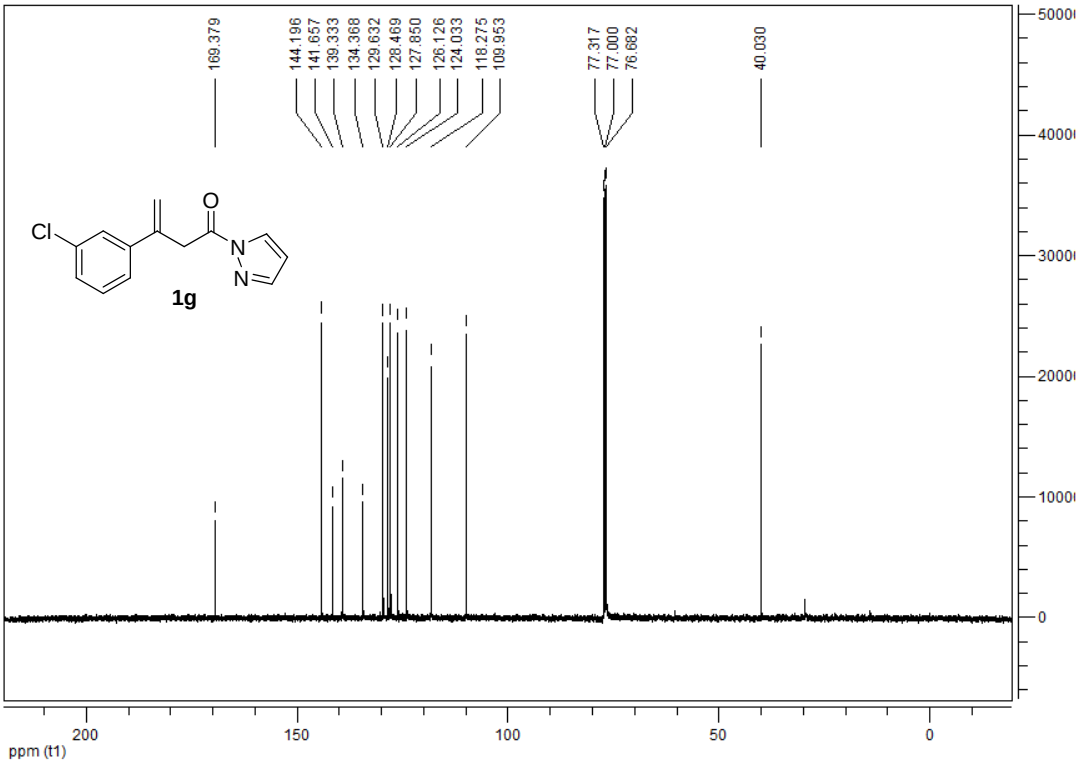
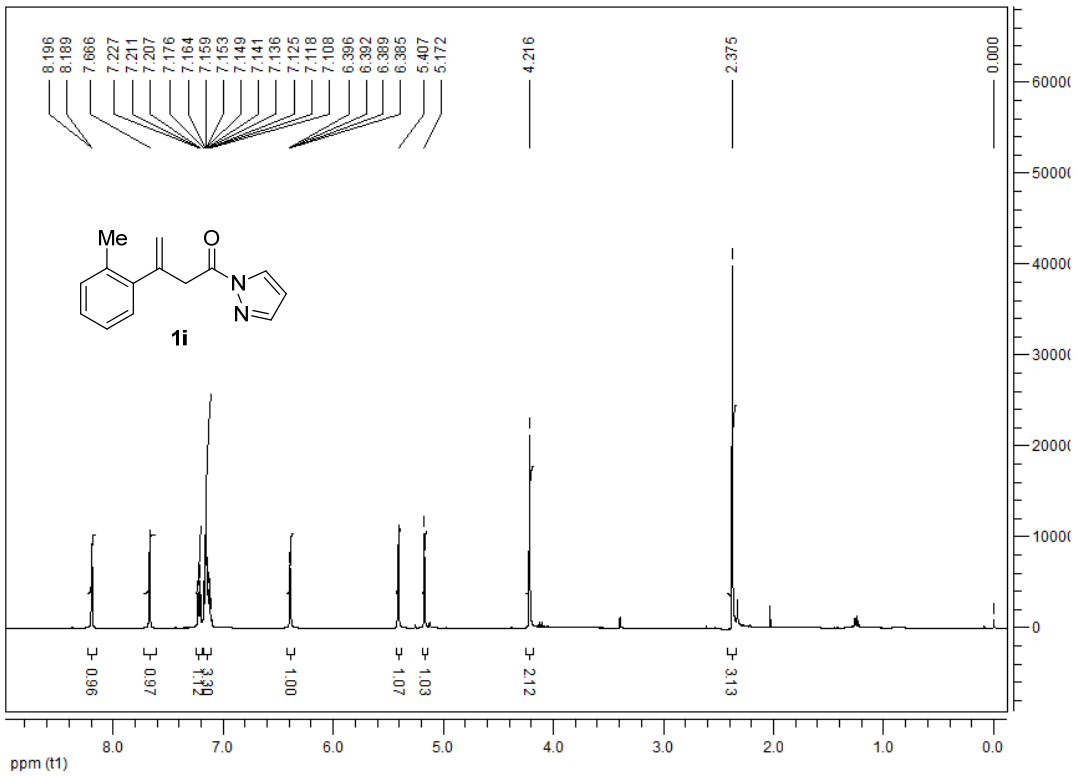
10000
5000
0
200
150
100
50
0
ppm (t1)

5. Copies of NMR Spectra of the Substrates



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7.153
7.149
7.141
7.136
7.125
7.118
7.108
6.396
6.392
6.389
6.385
5.407
5.172
4.216
2.375
0.000
Me
O
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N
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0.96
0.97
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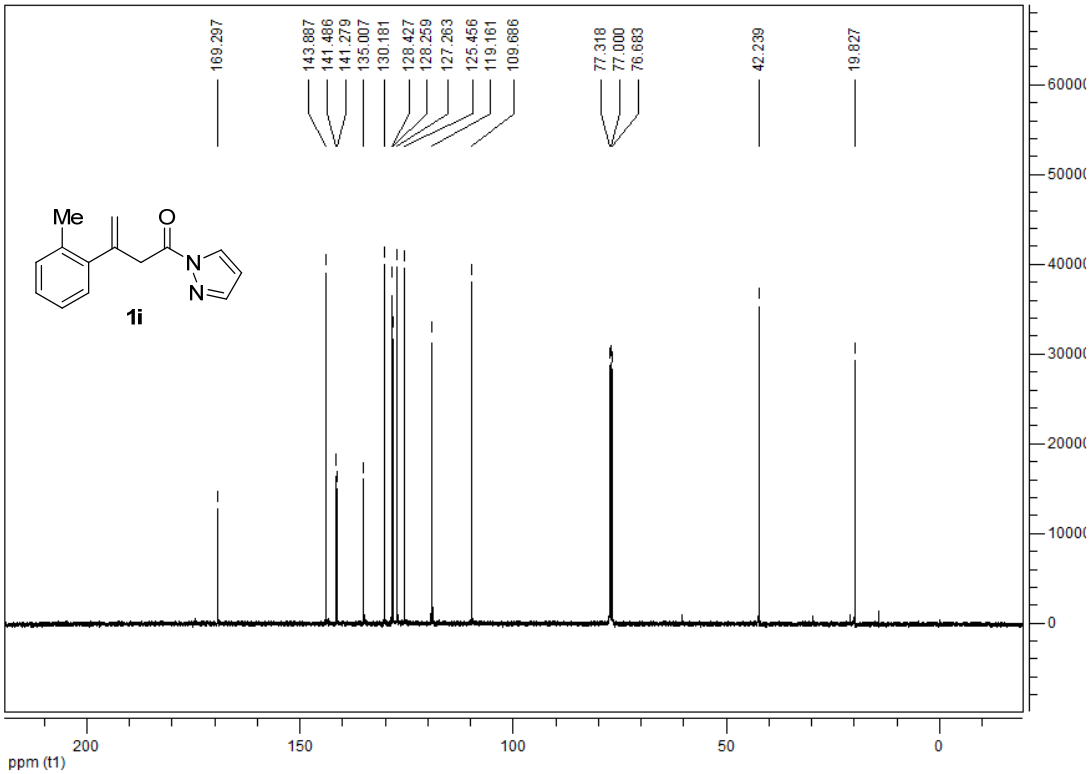
1.03
2.12
3.13
ppm (t1)


169.297
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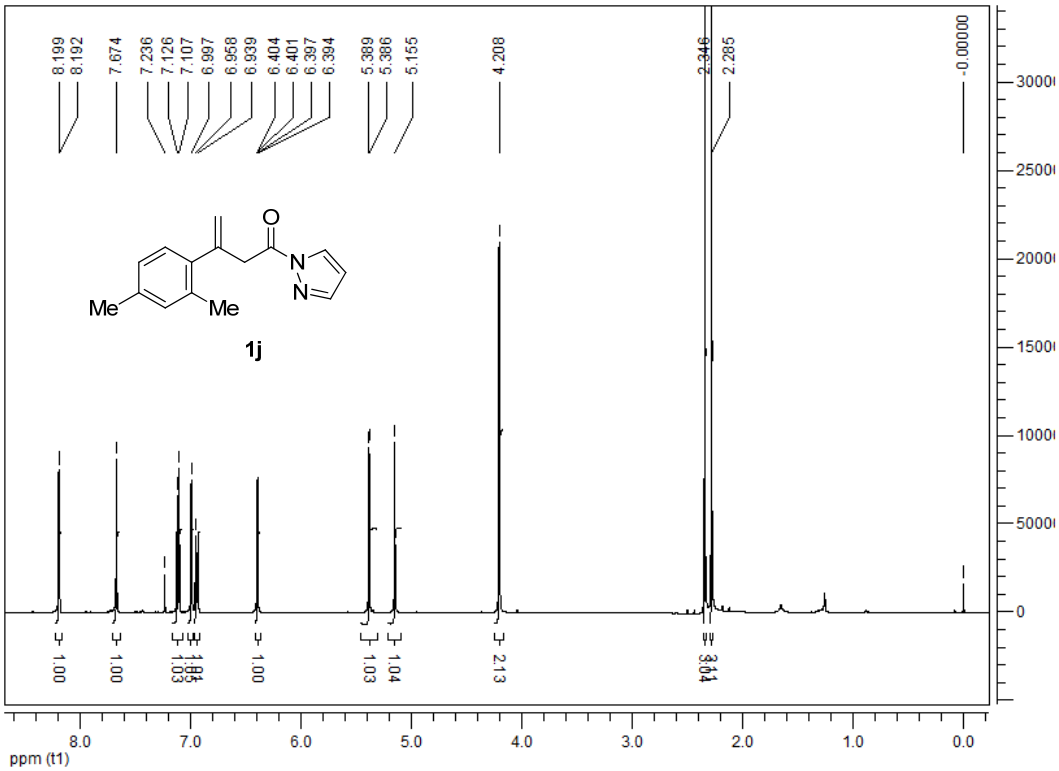
141.279
135.007
130.181
128.427
128.259
127.263
125.456
119.161
109.686
77.318
77.000
76.683
42.239
19.827
Me
O
N
N
1i
ppm (t1)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7.126
7.107
6.997
6.958
6.939
6.404
6.401
6.397
6.394
5.389
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2.285
-0.00000
O
N
N
Me
Me
1j
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1.00
1.03
1.00
1.03
1.04
2.13
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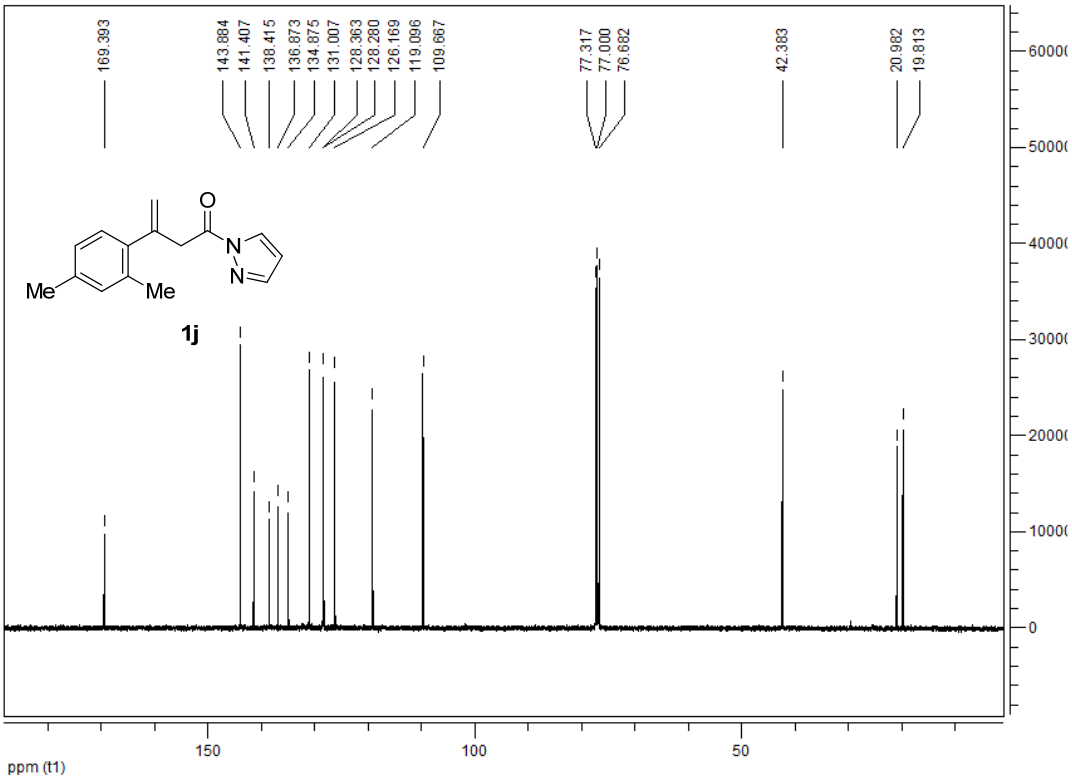
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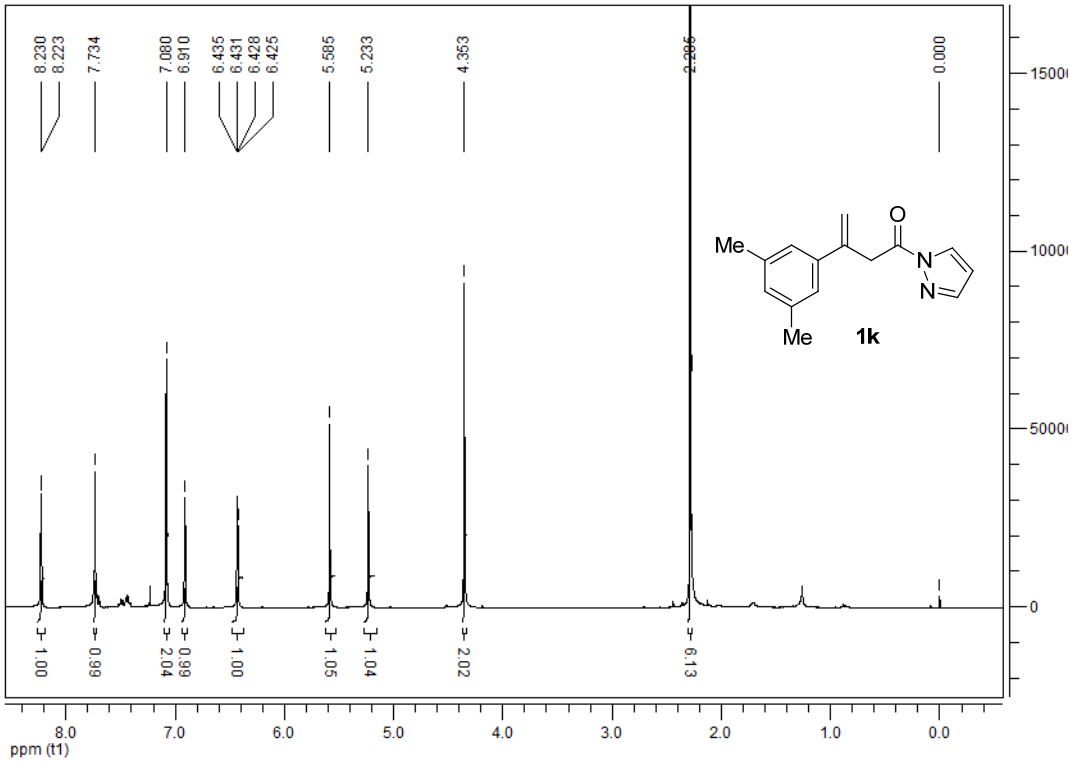
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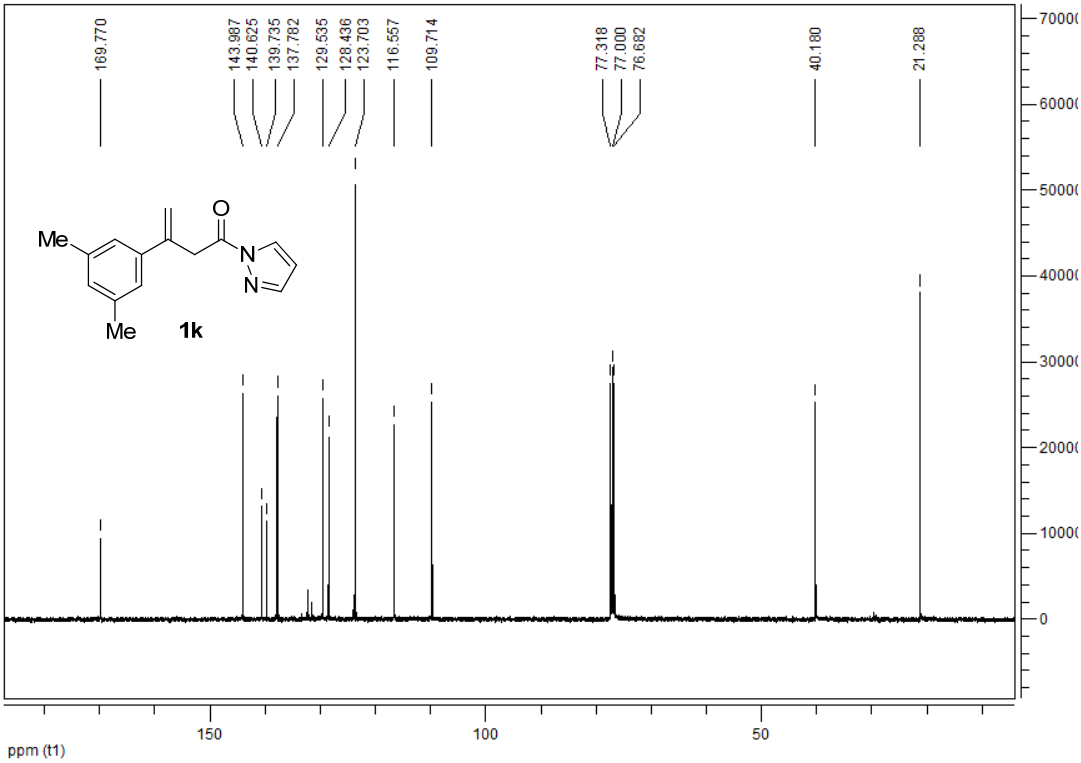
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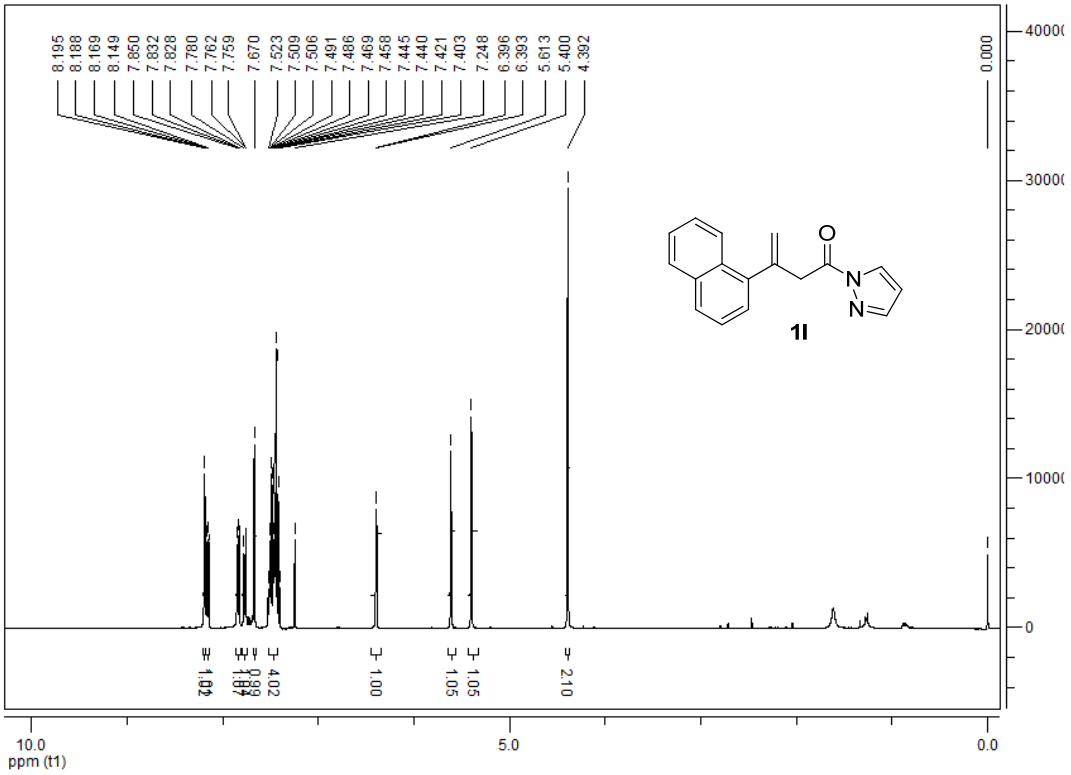
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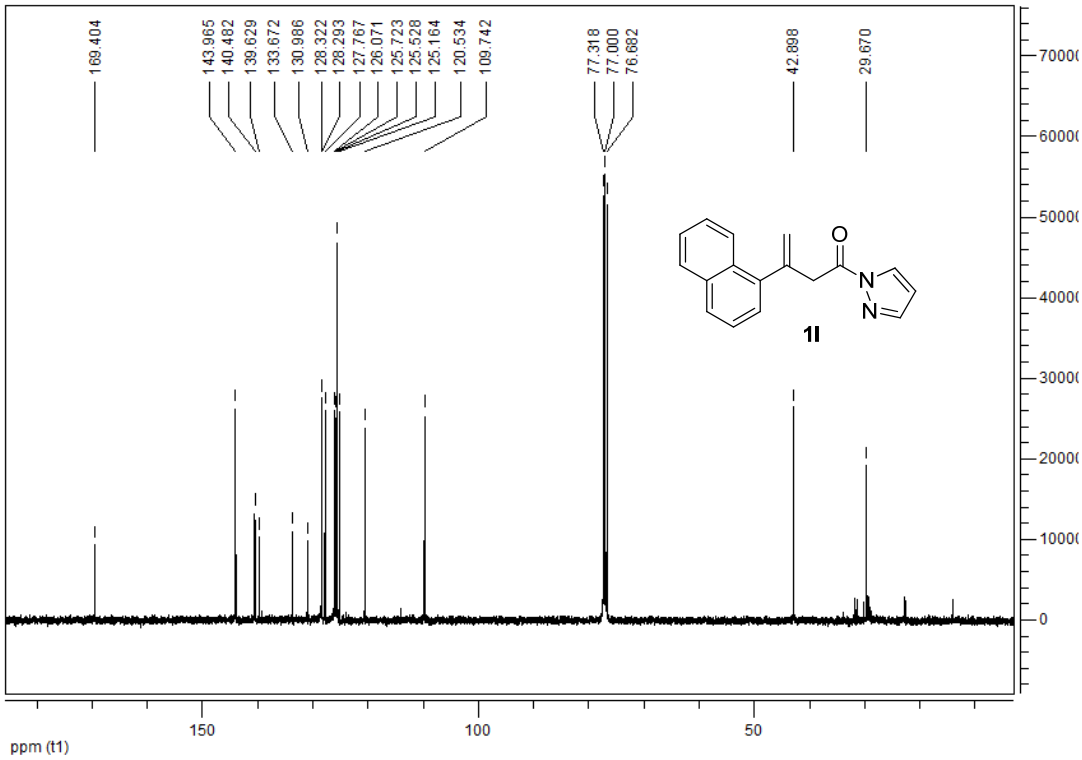
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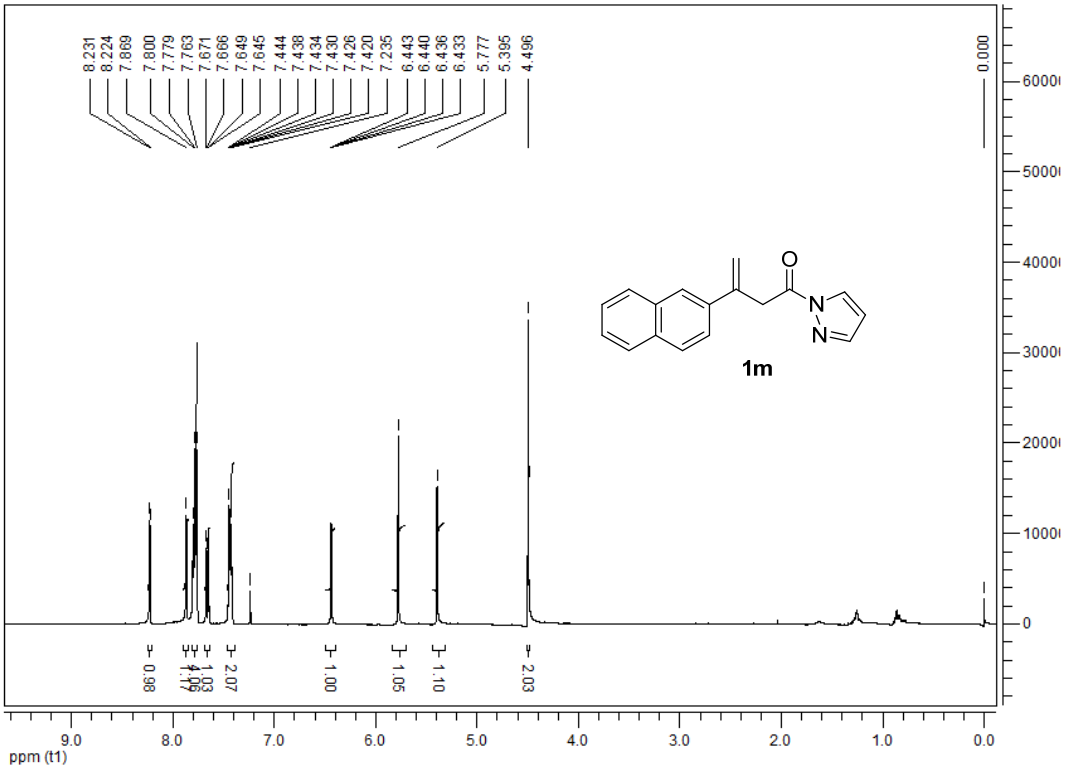
ppm (t1)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6.433
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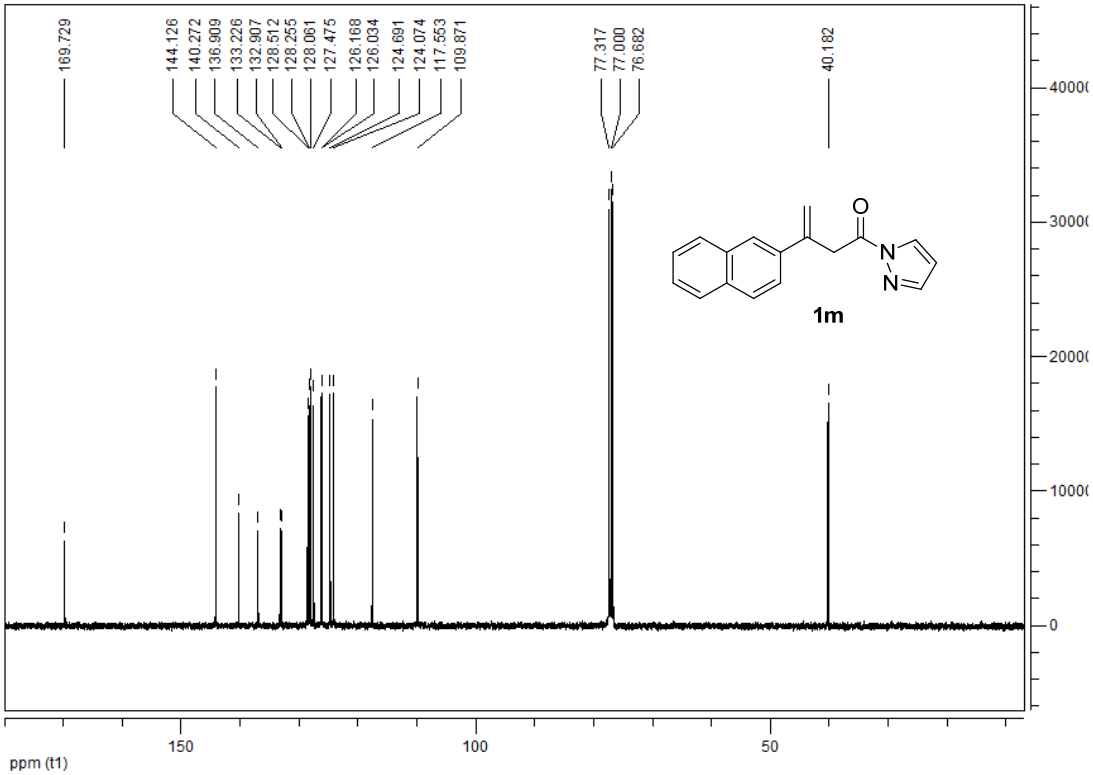
1m
ppm (t1)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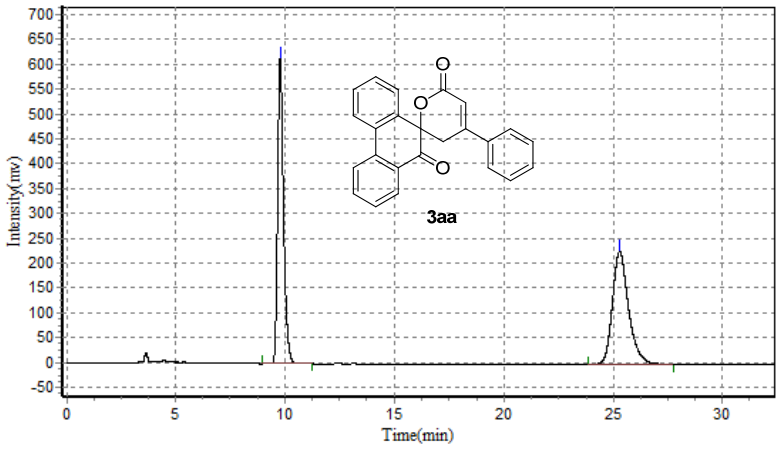
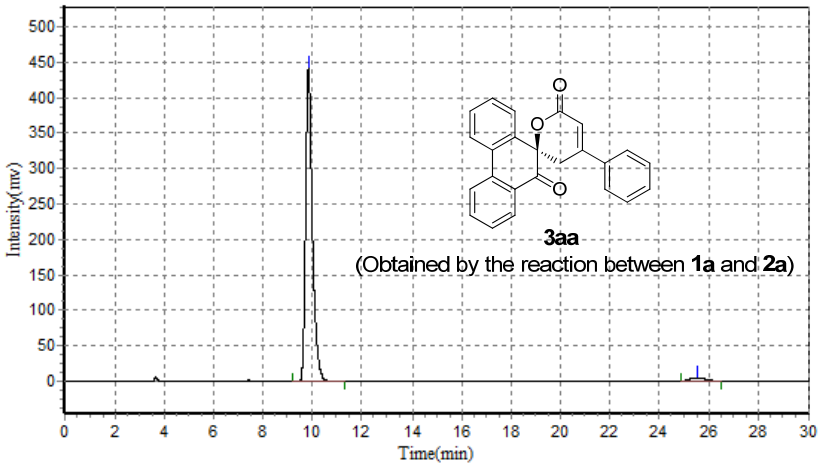
1m
ppm (t1)

6. Copies of HPLC Spectra of the Products



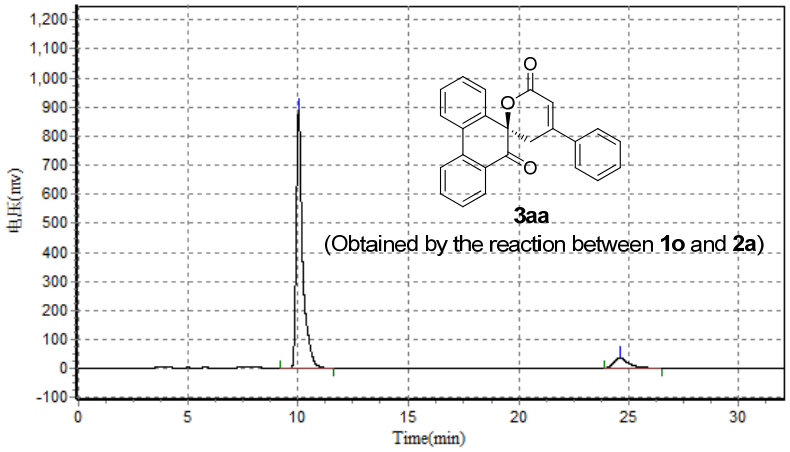
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.787	614056.625	11459768.000	49.8236
2		25.293	226565.047	11540913.000	50.1764
Total			840621.672	23000681.000	100.0000



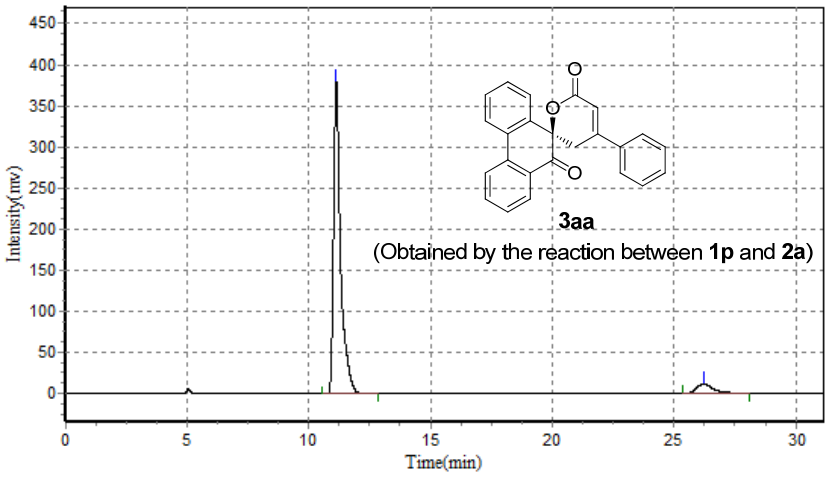
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.843	441101.438	8406273.000	97.0717
2		25.515	5494.763	253585.656	2.9283
Total			446596.201	8659858.656	100.0000



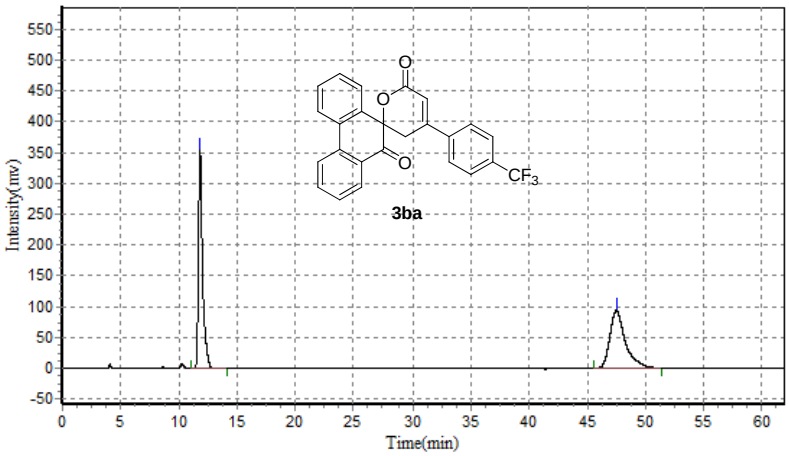
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.042	886508.875	18035906.000	91.0204
2		24.618	35451.879	1779319.750	8.9796
Total			921960.754	19815225.750	100.0000



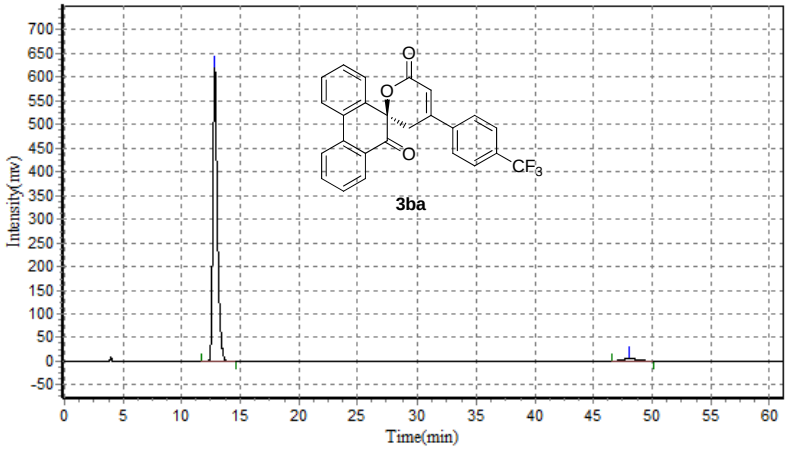
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.138	379284.938	7627287.500	92.6262
2		26.213	11842.730	607197.063	7.3738
Total			391127.668	8234484.563	100.0000



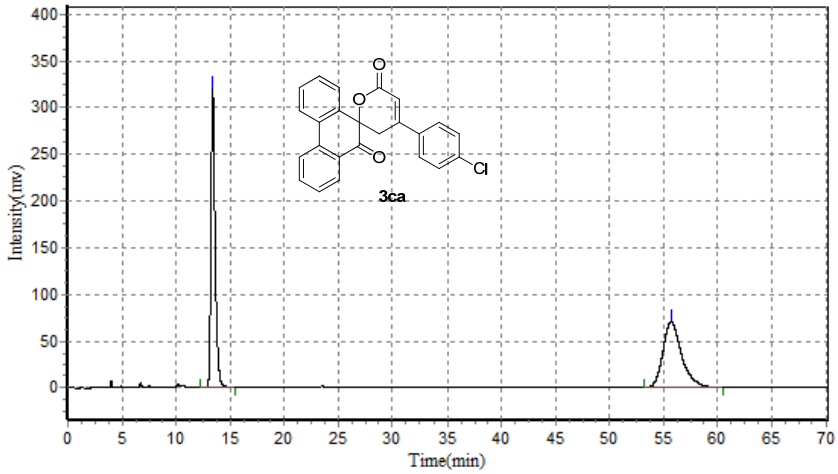
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.822	352925.500	8687303.000	49.9594
2		47.482	93399.617	8701431.000	50.0406
Total			446325.117	17388734.000	100.0000



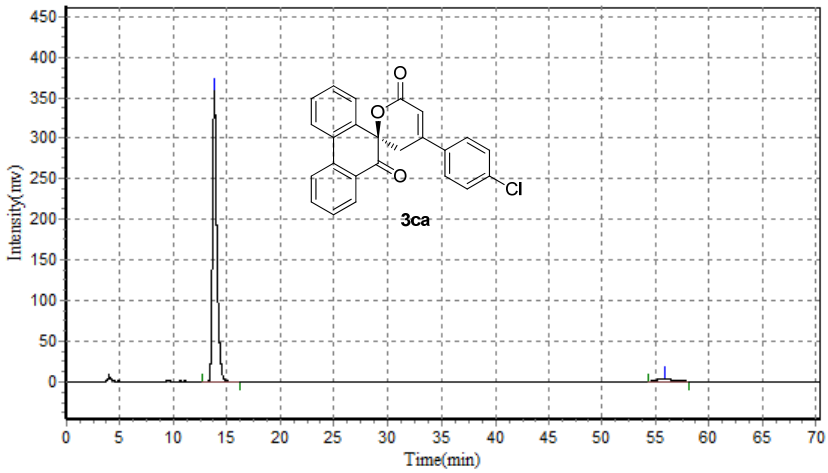
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.820	618377.063	16484476.000	97.0281
2		48.098	5188.208	504906.656	2.9719
Total			623565.270	16989382.656	100.0000



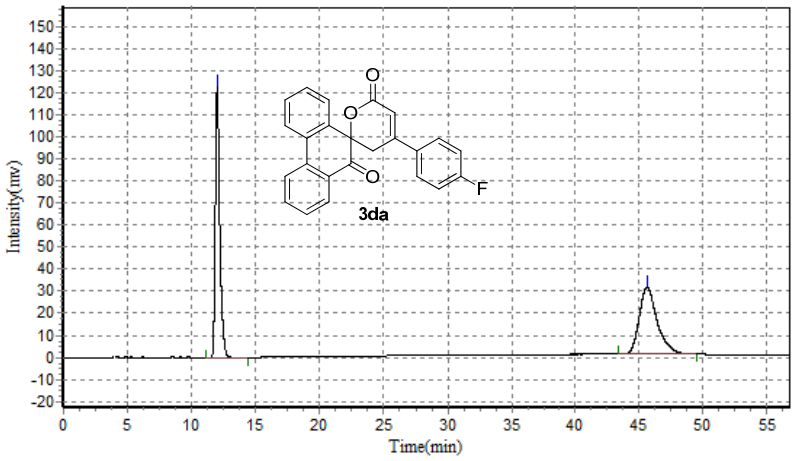
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.362	318900.938	8480727.000	50.0689
2		55.713	70531.086	8457391.000	49.9311
Total			389432.023	16938118.000	100.0000



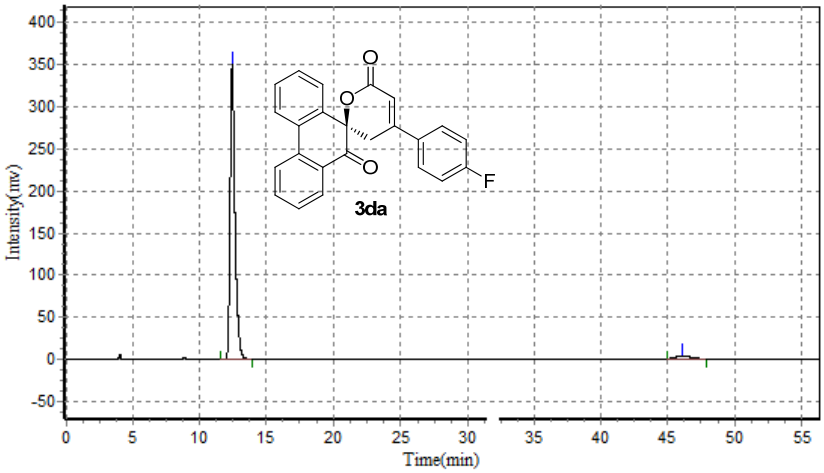
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.825	358604.813	10036490.000	96.9098
2		55.788	3146.996	320035.406	3.0902
Total			361751.809	10356525.406	100.0000



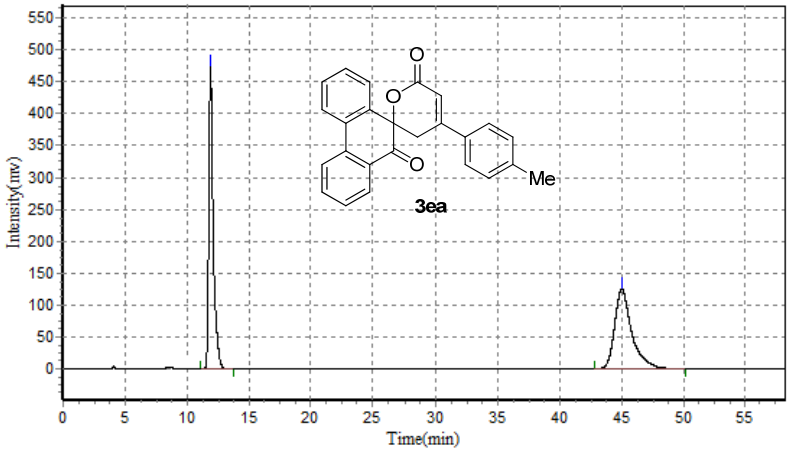
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.033	122721.438	2973482.250	49.9809
2		45.600	30417.834	2975754.500	50.0191
Total			153139.271	5949236.750	100.0000



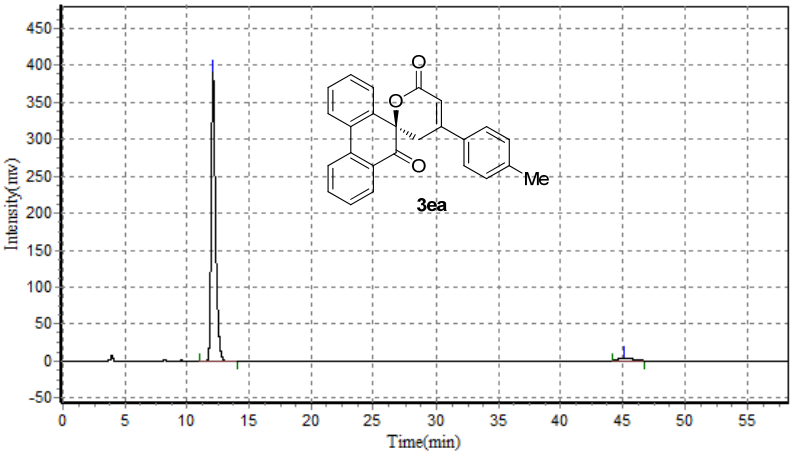
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.425	350057.000	8807251.000	96.5882
2		46.083	3812.679	311100.500	3.4118
Total			353869.679	9118351.500	100.0000



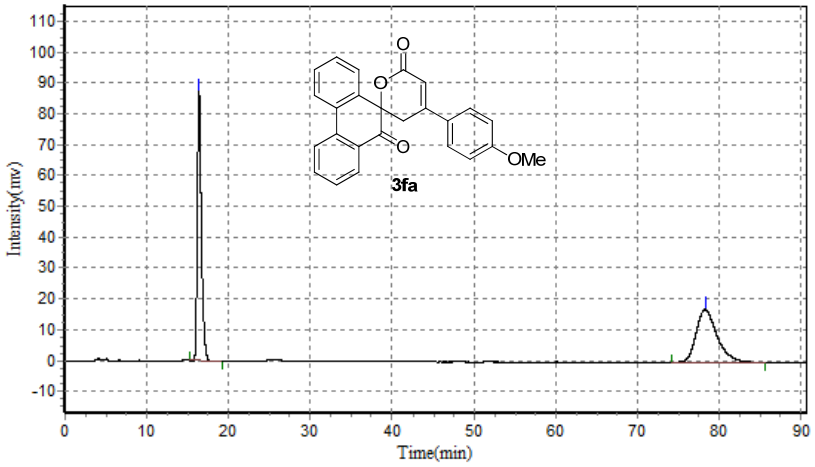
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.907	473451.594	11760662.000	49.7555
2		45.020	124794.781	11876249.000	50.2445
Total			598246.375	23636911.000	100.0000



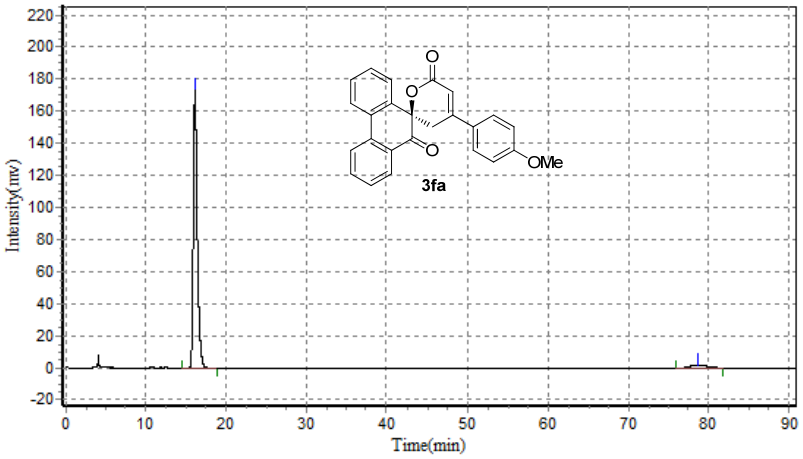
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.093	391046.250	9477957.000	97.0902
2		45.143	3629.641	284057.500	2.9098
Total			394675.891	9762014.500	100.0000



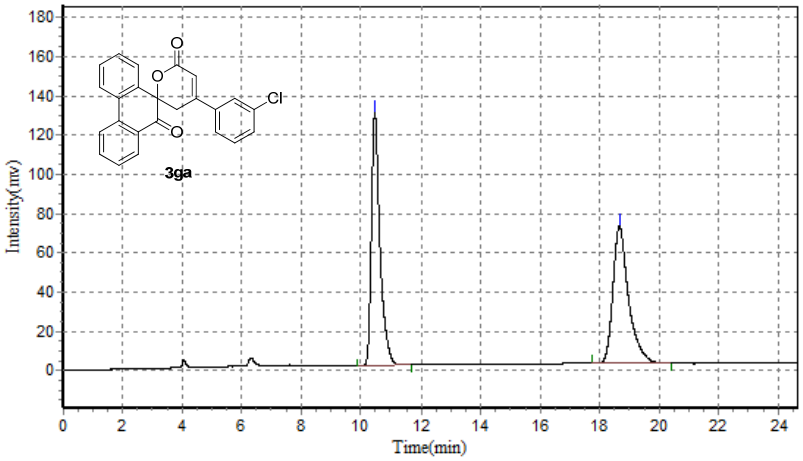
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.398	87483.570	3022968.250	49.8464
2		78.285	17184.629	3041595.750	50.1536
Total			104668.199	6064564.000	100.0000



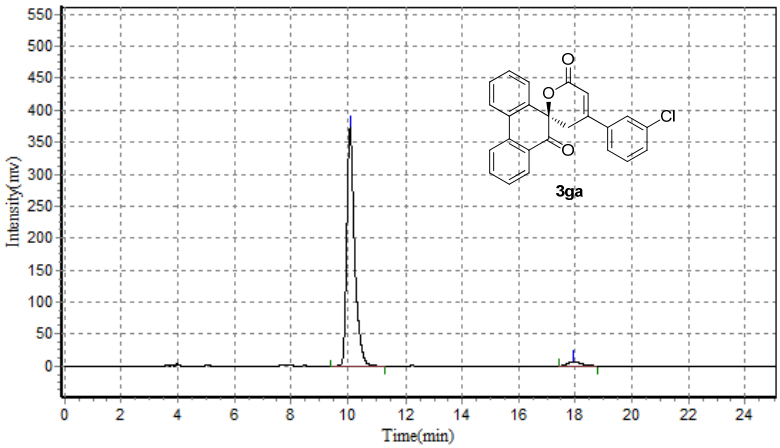
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.120	173384.625	5967257.000	94.9591
2		78.690	2010.934	316773.219	5.0409
Total			175395.559	6284030.219	100.0000



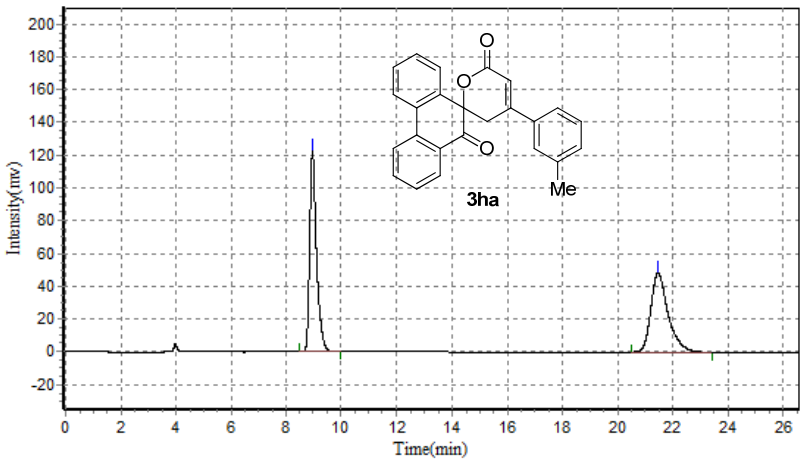
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.468	128228.156	2545953.750	50.2039
2		18.648	69484.398	2525268.750	49.7961
Total			197712.555	5071222.500	100.0000



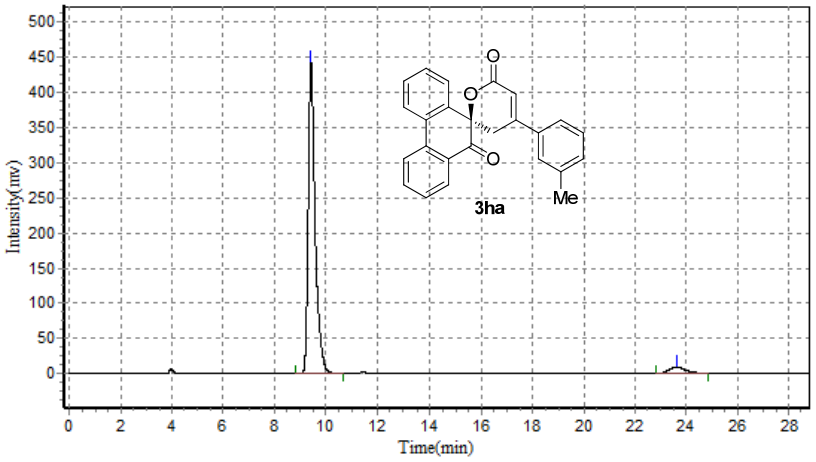
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.083	371566.625	7147675.000	96.8840
2		17.932	6964.065	229886.297	3.1160
Total			378530.690	7377561.297	100.0000



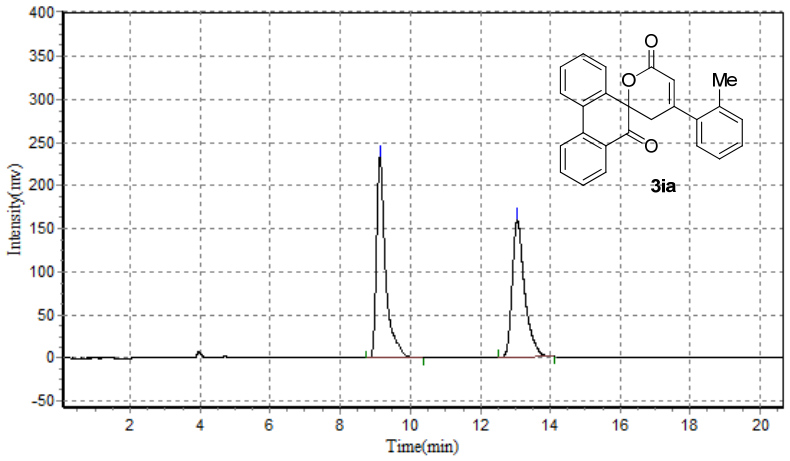
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.960	122149.836	2098938.000	50.0288
2		21.470	48166.941	2096522.625	49.9712
Total			170316.777	4195460.625	100.0000



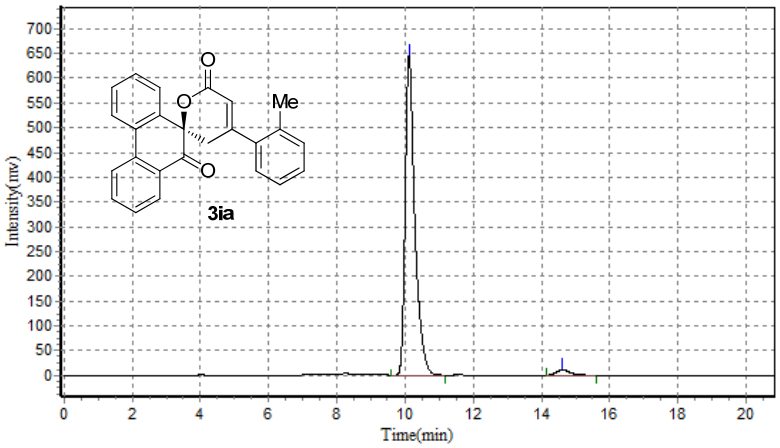
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.427	442152.469	8272815.500	94.9507
2		23.617	9367.438	439930.938	5.0493
Total			451519.906	8712746.438	100.0000



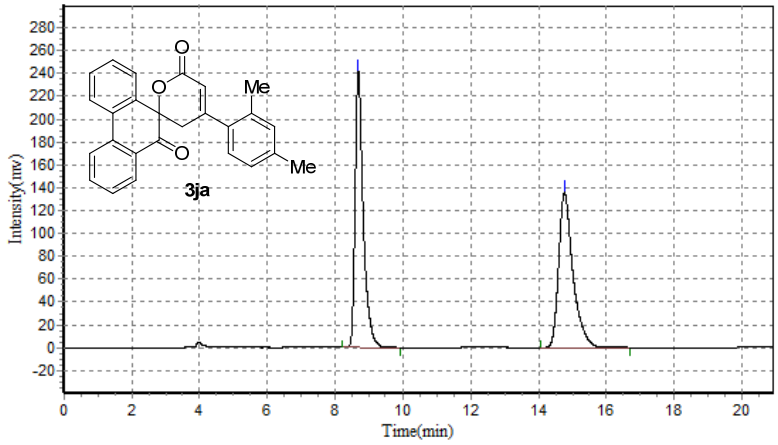
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.150	232545.734	4162264.500	51.7468
2		13.050	158516.094	3881248.250	48.2531
Total			391061.828	8043512.750	100.0000



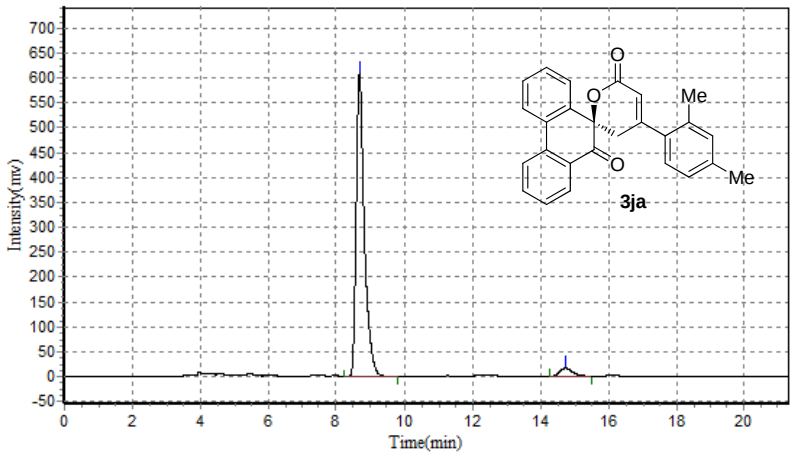
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.097	644757.625	12733394.000	97.5038
2		14.612	11252.168	325994.094	2.4962
Total			656009.793	13059388.094	100.0000



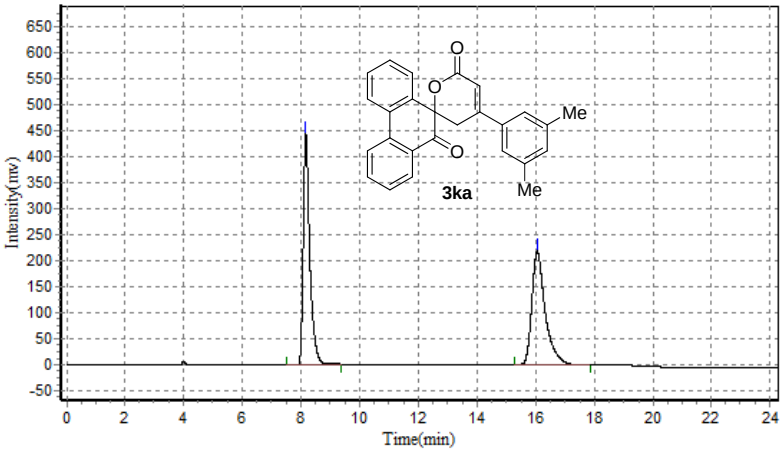
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.705	240728.969	3999984.750	49.9831
2		14.767	135655.547	4002692.250	50.0169
Total			376384.516	8002677.000	100.0000



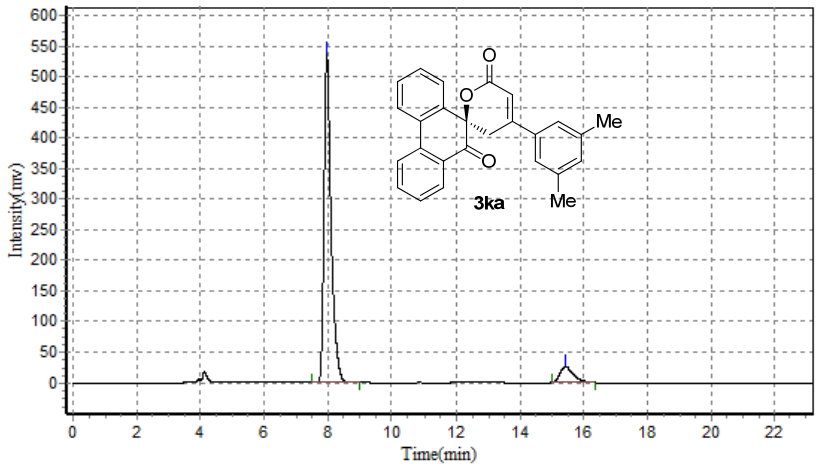
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.695	607132.188	10085407.000	95.5065
2		14.725	17143.426	474504.906	4.4935
Total			624275.613	10559911.906	100.0000



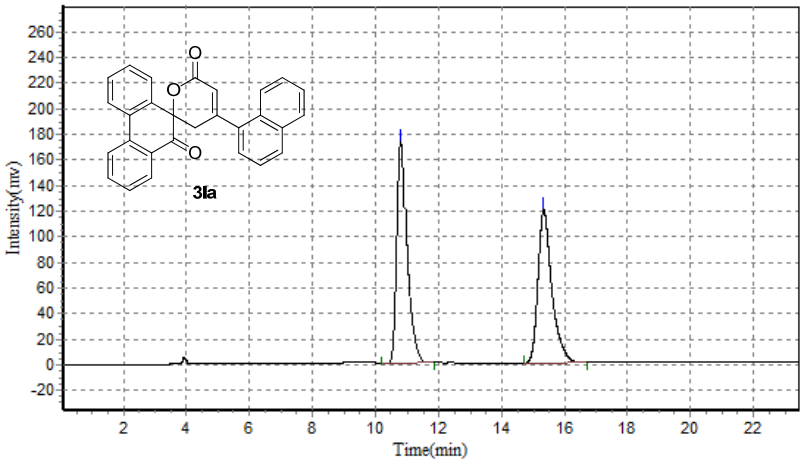
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.175	442282.250	6838692.500	49.9758
2		16.040	217645.438	6845320.500	50.0242
Total			659927.688	13684013.000	100.0000



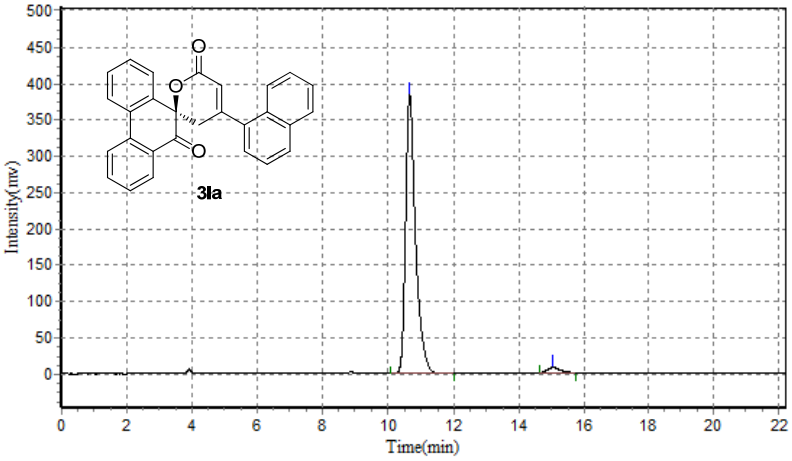
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.978	537153.500	8237559.000	91.5416
2		15.427	25817.561	761146.875	8.4584
Total			562971.061	8998705.875	100.0000



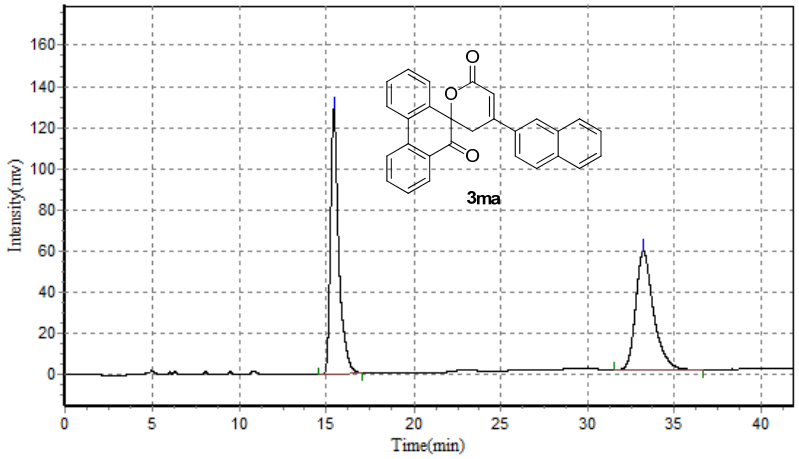
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.822	172802.094	3651731.500	49.9402
2		15.338	119222.945	3660472.750	50.0598
Total			292025.039	7312204.250	100.0000



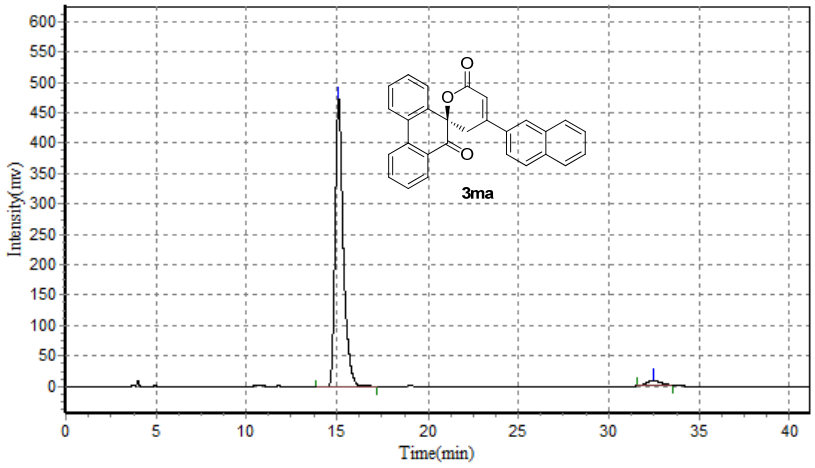
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.650	383202.250	8122290.000	97.3885
2		15.050	7759.125	217797.094	2.6114
Total			390961.375	8340087.094	100.0000



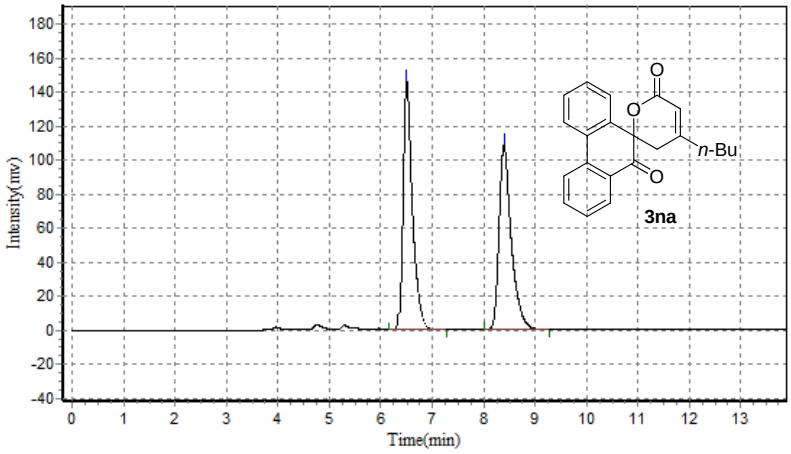
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.453	128554.656	4251031.500	50.9729
2		33.203	57484.504	4088757.250	49.0271
Total			186039.160	8339788.750	100.0000



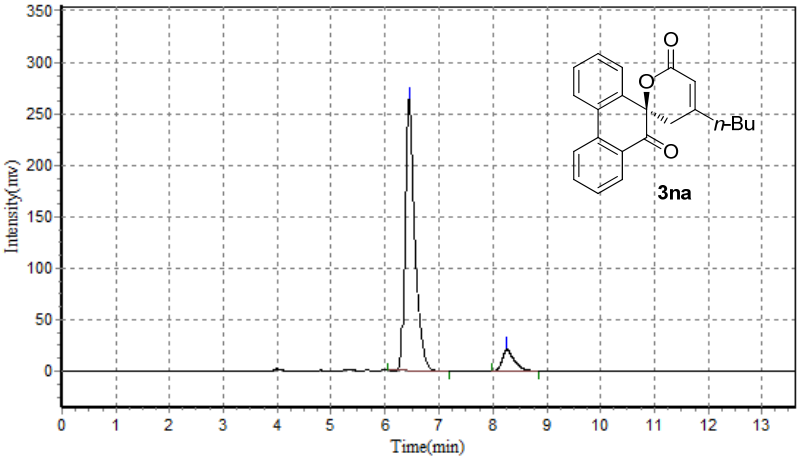
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.112	472055.219	14827618.000	97.0667
2		32.477	7806.026	448087.313	2.9333
Total			479861.245	15275705.313	100.0000



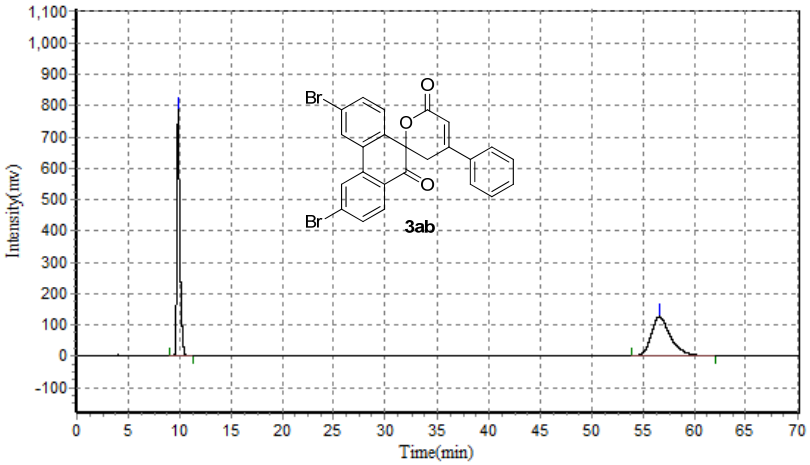
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.492	145743.969	1812056.625	50.4990
2		8.388	107784.805	1776244.375	49.5010
Total			253528.773	3588301.000	100.0000



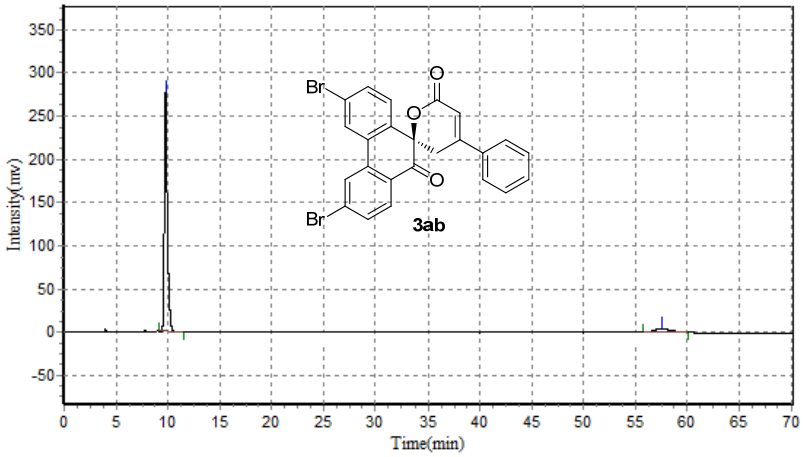
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.432	264272.781	3196601.500	90.8497
2		8.257	20618.816	321958.688	9.1503
Total			284891.598	3518560.188	100.0000



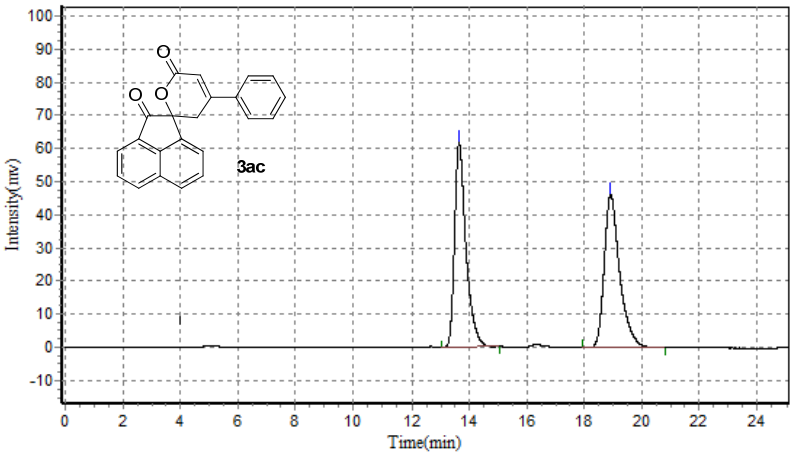
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.860	784427.000	15744093.000	49.6956
2		56.612	124367.352	15936948.000	50.3044
Total			908794.352	31681041.000	100.0000



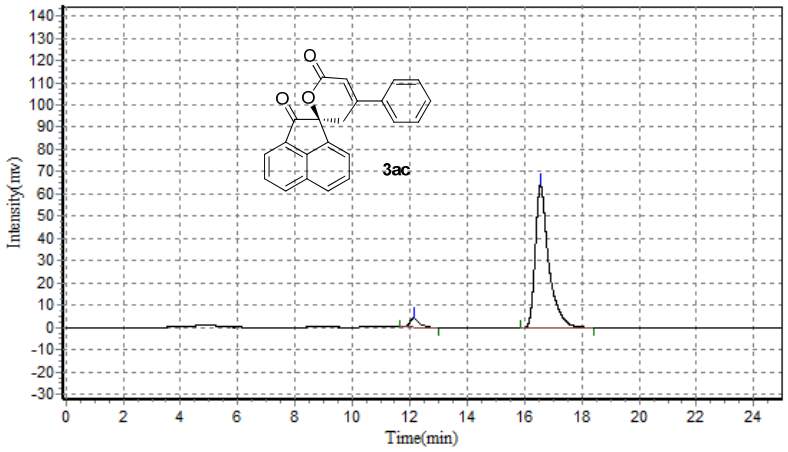
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.785	275815.781	5525684.500	91.6451
2		57.542	4347.846	503757.031	8.3550
Total			280163.627	6029441.531	100.0000



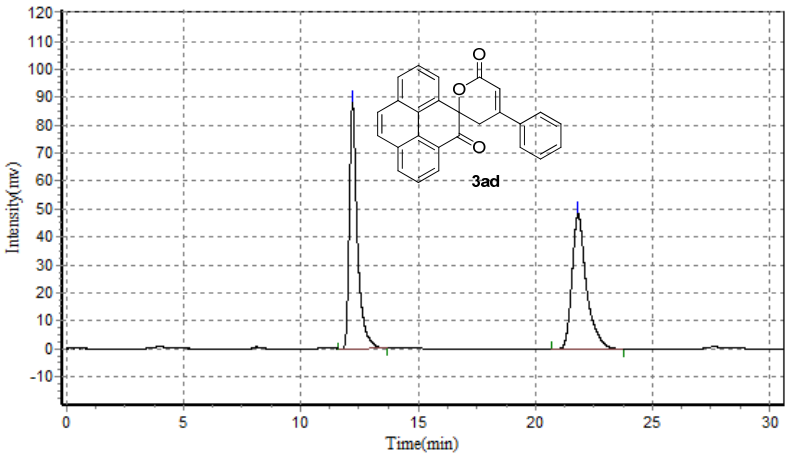
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.647	61633.969	1692879.250	49.4071
2		18.915	46321.141	1733511.625	50.5929
Total			107955.109	3426390.875	100.0000



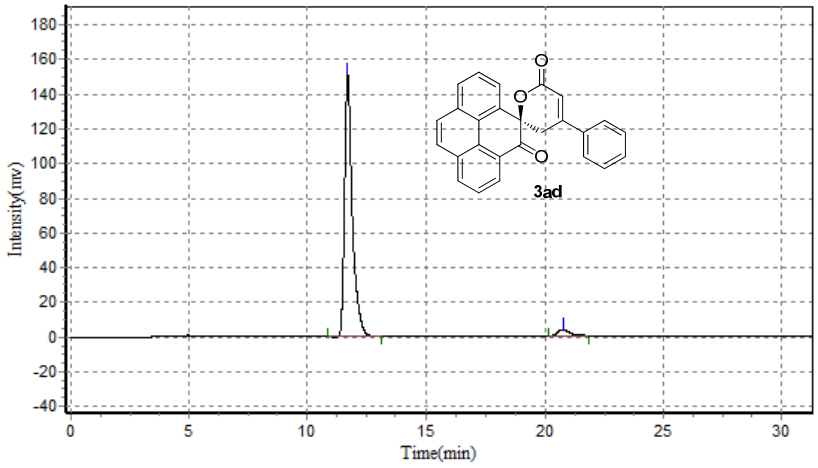
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.120	4236.203	98790.000	4.5078
2		16.550	64277.090	2092741.625	95.4922
Total			68513.293	2191531.625	100.0000



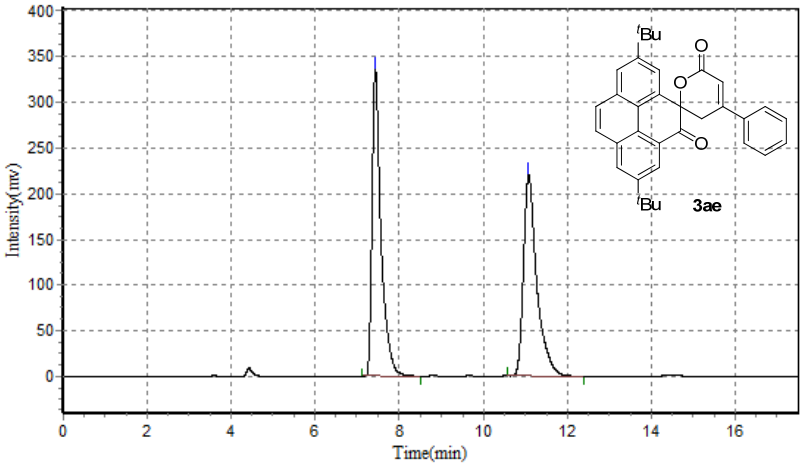
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.222	87919.195	2085330.250	50.0901
2		21.822	48294.289	2077827.625	49.9099
Total			136213.484	4163157.875	100.0000



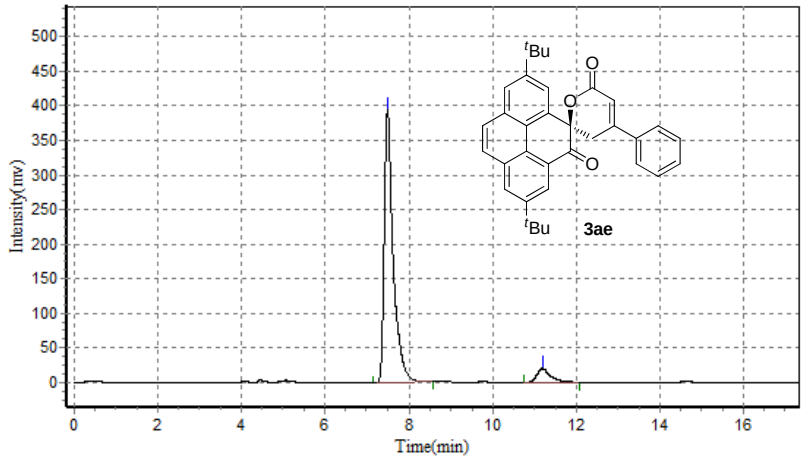
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.715	151129.656	3459215.250	95.9600
2		20.758	3619.608	145635.297	4.0400
Total			154749.264	3604850.547	100.0000



Results

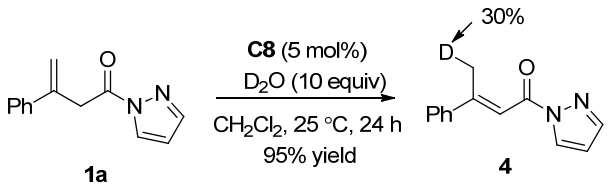
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.445	335864.563	4944200.500	50.5846
2		11.072	219642.719	4829914.500	49.4154
Total			555507.281	9774115.000	100.0000

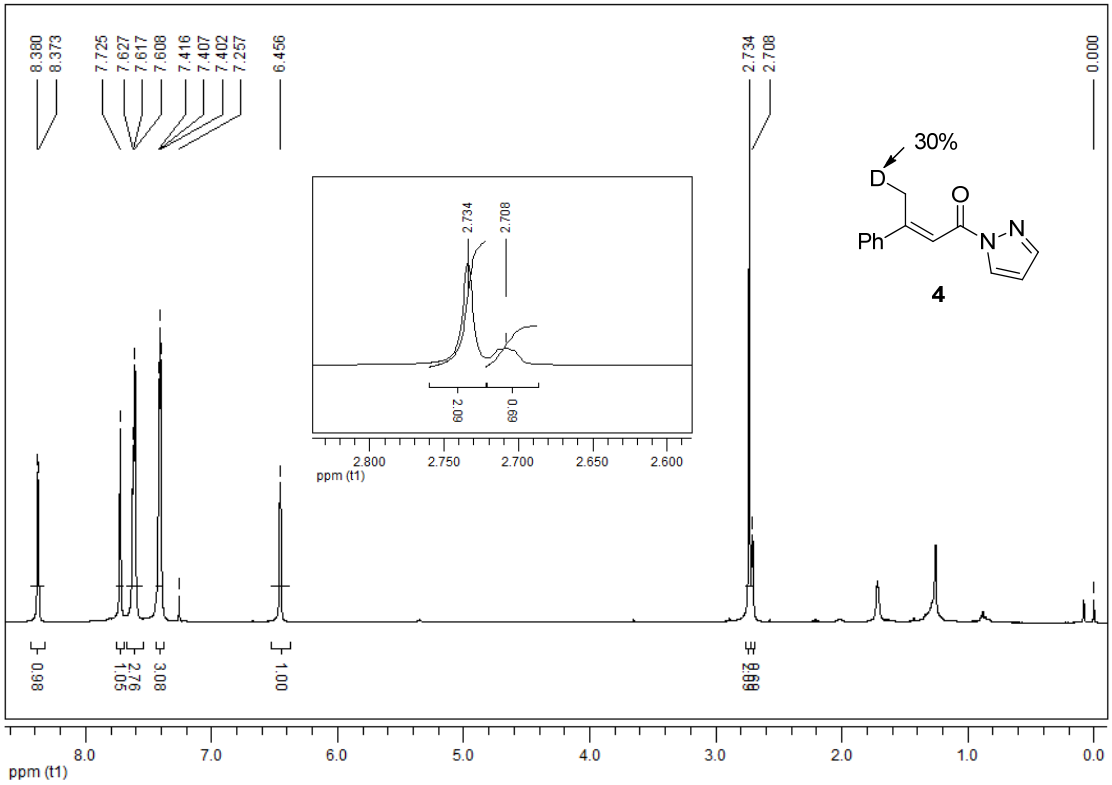


Results

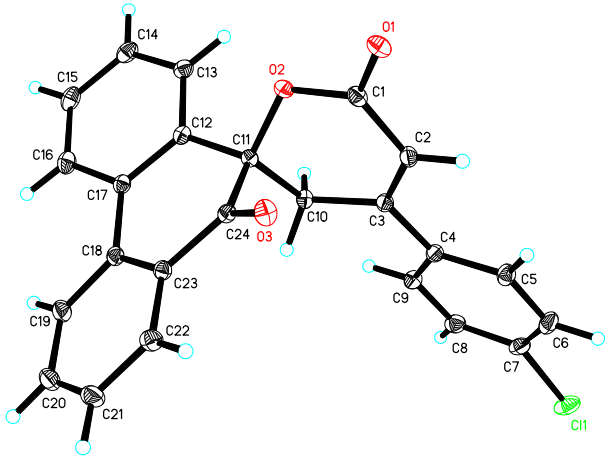
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.500	394601.781	5838946.500	92.9311
2		11.175	19954.115	444146.750	7.0689
Total			414555.896	6283093.250	100.0000

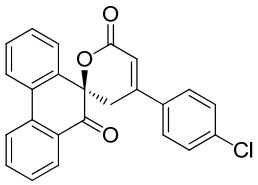
7. The Data for the Deuterium Experiment





8. X-Ray Analysis of Compound 3ca





3ca

Table 1. Crystal data and structure refinement for **3ca**

Identification code	mo_dm15338_0m	
Empirical formula	$C_{24}H_{15}ClO_3$	
Formula weight	386.81	
Temperature	130 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.5258(9) Å	a= 90°.
	b = 11.7582(10) Å	b= 90°.
	c = 14.4254(12) Å	g = 90°.
Volume	1785.4(3) $Å^3$	
Z	4	
Density (calculated)	1.439 Mg/m^3	
Absorption coefficient	0.238 mm^{-1}	
F(000)	800	
Crystal size	0.28 x 0.2 x 0.17 mm^3	
Theta range for data collection	2.235 to 30.527°.	
Index ranges	-15<=h<=14, -14<=k<=16, -20<=l<=20	
Reflections collected	18084	
Independent reflections	5459 [R(int) = 0.0255]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.7079	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5459 / 0 / 253
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0851
R indices (all data)	R1 = 0.0397, wR2 = 0.0885
Absolute structure parameter	-0.002(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.267 and -0.329 e.$Å^{-3}$