ESI for:

Recyclable $(PhSe)_2$-Catalyzed Selective Oxidation of Isatin by H_2O_2: A Practical and Waste-Free Access to Isatoic Anhydride under Mild and Neutral Conditions

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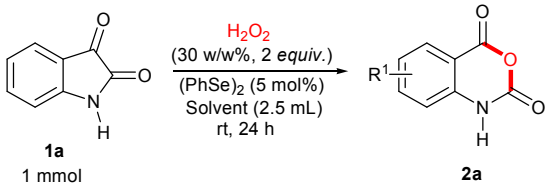
Contents

Detailed conditional optimization tables

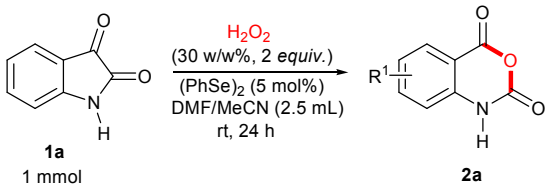
Table S1. Optimization of Solvents.[a]



Entry	solvent	yield (%)[b]
1	**MeCN**	**72**
2	*t*-BuOH	40
3	*i*-PrOH	42
4	EtOH	43
5	MeOH	40
6	H_2O	11
7	**DMF**	**65**
8	NMP	23
9	DMSO	0
10	THF	30

[a] 1 mmol of **1a**, 2 mmol of H_2O_2, 0.05 mmol of $(PhSe)_2$ and 2.5 mL of solvent were stirred at room temperature (25 °C) for 24 h; [b] Isolated yields.

Table S2. DMF concentration effect test.[a]

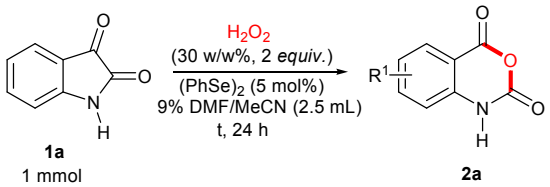


Entry	DMF (%)[b]	yield (%)[c]
1	0	72
2	3	82

3	6	86
4	**9**	**88**
5	12	87
6	21	83
7	30	75
8	60	66
9	100	65

[a] 1 mmol of **1a**, 2 mmol of H_2O_2, 0.05 mmol of $(PhSe)_2$ and 2.5 mL of solvent were stirred at room temperature (25 °C) for 24 h; [b] Volume concentration; [c] Isolated yields.

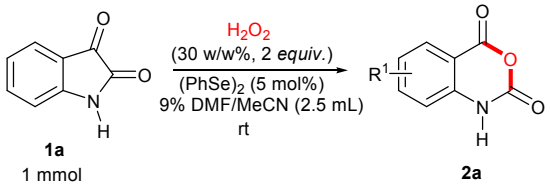
Table S3. Temperature effect test.[a]



Entry	t (°C)	Yield (%)[b]
1	**25**	**88**
2	40	78
3	60	67
4	80	62

[a] 1 mmol of **1a**, 2 mmol of H_2O_2, 0.05 mmol of $(PhSe)_2$ and 2.5 mL of 9% DMF/MeCN were stirred at different temperatures for 24 h; [b] Isolated yields.

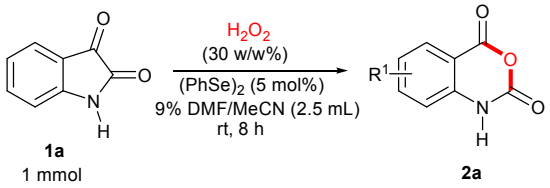
Table S4. Time effect test.[a]



Entry	t (h)	Yield (%)[b]
1	4	54
2	6	68
3	**8**	**88**
4	12	88
5	24	87

[a] 1 mmol of **1a**, 2 mmol of H_2O_2, 0.05 mmol of $(PhSe)_2$ and 2.5 mL of 9% DMF/MeCN were stirred at room temperature (25 °C) for different times; [b] Isolated yields.

Table S5. H_2O_2 dosage effect test.[a]

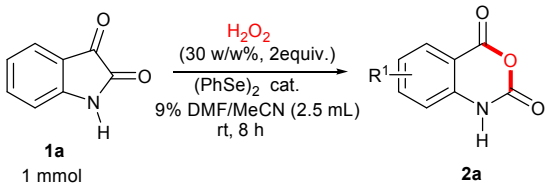


Entry	H_2O_2 Dosage (mol%)	Yield (%)[b]
1	50	40
2	100	62
3	150	73
4	**200**	**88**

5	300	82

[a] 1 mmol of **1a**, H_2O_2, 0.05 mmol of $(PhSe)_2$ and 2.5 mL of 9% DMF/MeCN were stirred at room temperature (25 °C) for 8 h; [b] Isolated yields.

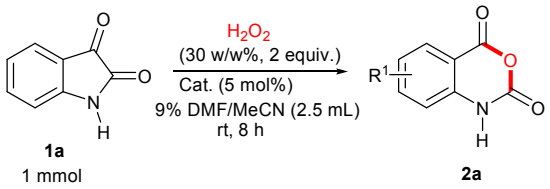
Table S6. $(PhSe)_2$ loading effect test.[a]



Entry	$(PhSe)_2$ /mol%	Yield(%)[b]
1	1	78
2	3	84
3	**5**	**88**
4	10	86
5	15	77

[a] 1 mmol of **1a**, 2 mmol of H_2O_2, catalytic $(PhSe)_2$ and 2.5 mL of 9% DMF/MeCN were stirred at room temperature (25 °C) for 8 h; [b] Isolated yields.

Table S7. Catalyst screenings.[a]

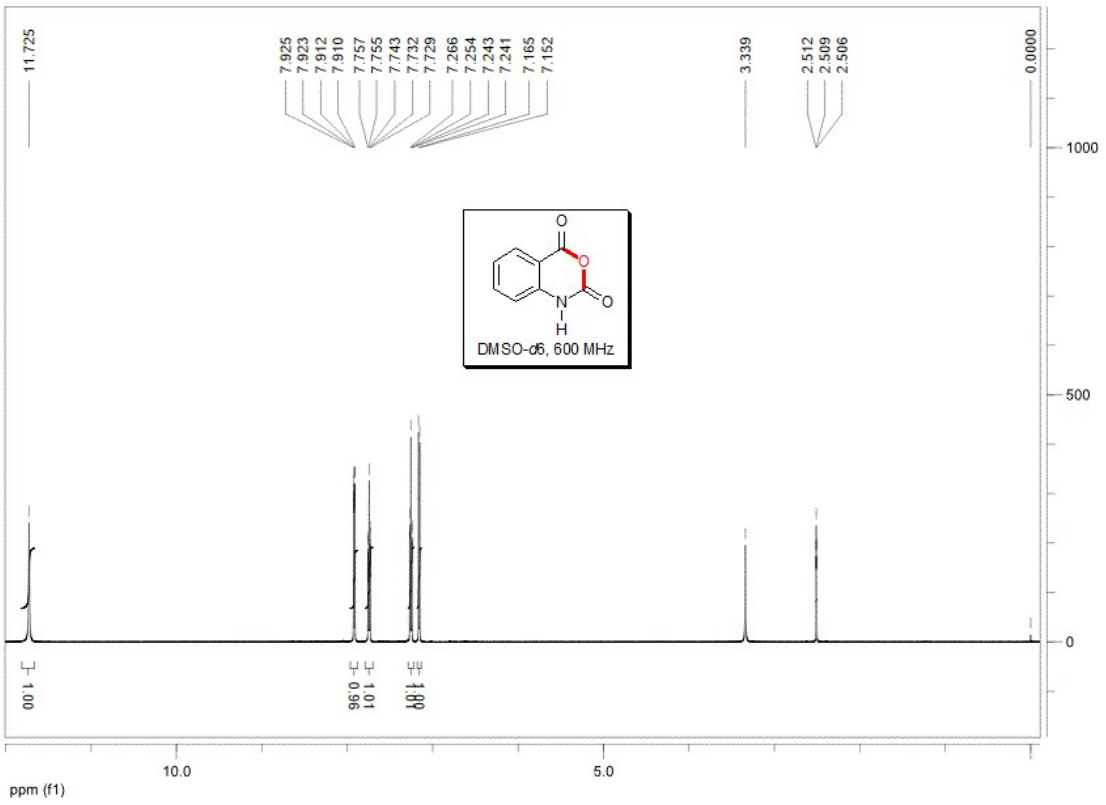


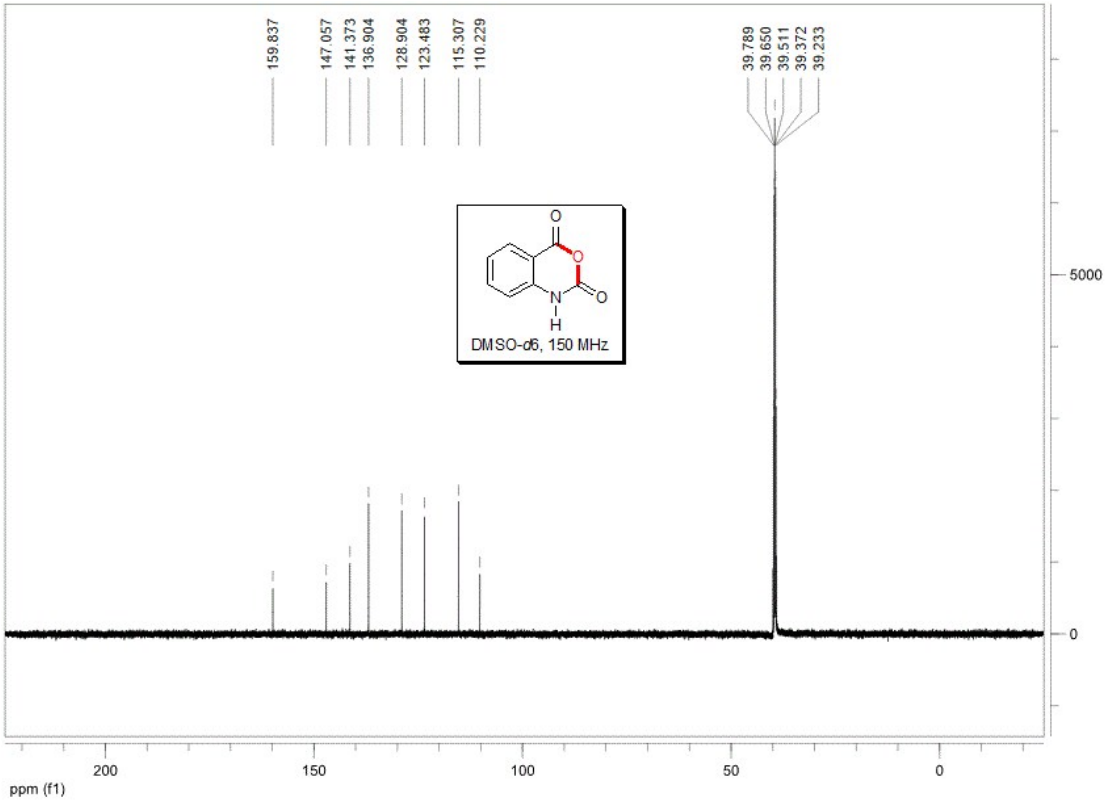
Entry	Cat.	Yield(%)[b]
1	**$(PhSe)_2$**	**88**
2	$(p\text{-}CH_3OC_6H_4Se)_2$	82
3	$[p\text{-}(CH_3)_2NC_6H_4Se]_2$	70
4	$(m\text{-}CH_3OC_6H_4Se)_2$	80

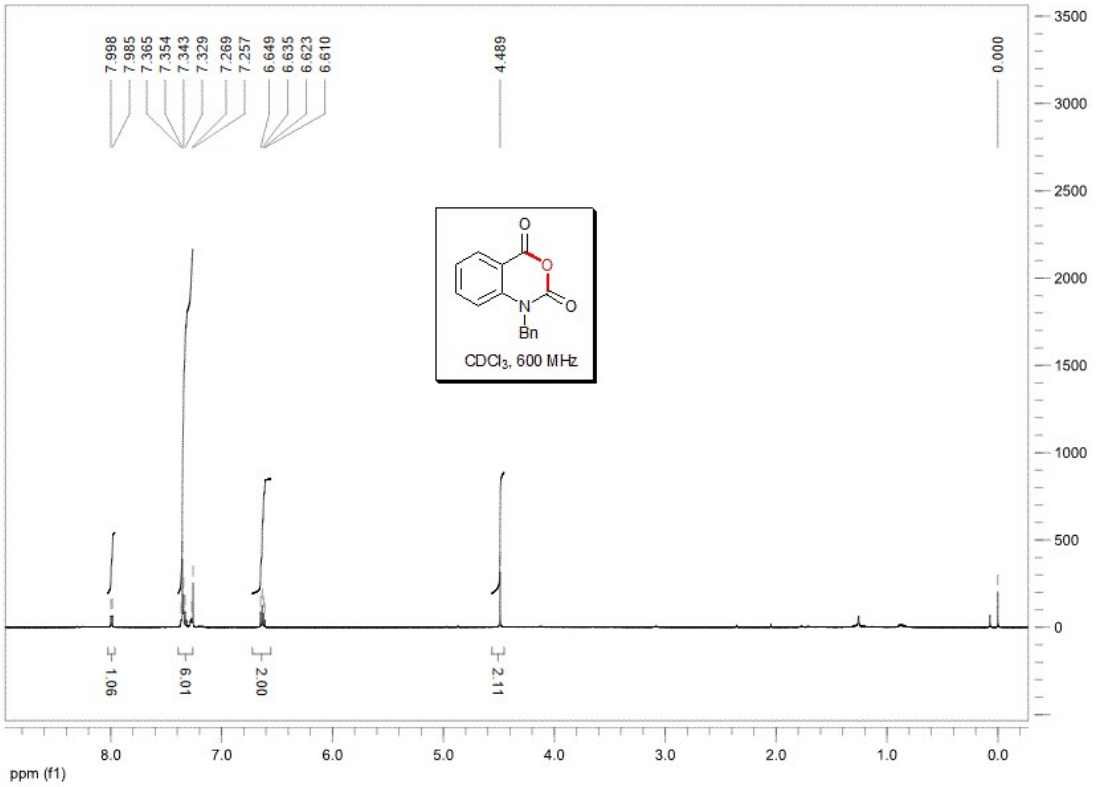
5	(*m*-$ClC_6H_4Se)_2$	78
6	(*m*-$FC_6H_4Se)_2$	82
7	[3,5-$(CF_3)_2C_6H_3Se]_2$	69
8	EtSePh	62
9	*i*-PrSePh	68
10	*c*-C_6H_{11}SePh	64
11	PhSePh	38
12	PhSeOOH	80
13	PhSeBr	78
14	SeO_2	3
15	$(PhS)_2$	18
16	$(PhTe)_2$	22
17	-	0

[a] 1 mmol of **1a**, 2 equiv. H_2O_2, 0.05 mmol of catalyst and 2.5 mL of 9% DMF/MeCN were stirred at room temperature (25 ^oC) for 8 h; [b] Isolated yields.

^{1}H and ^{13}C NMR Spectra of Products (for samples in DMSO-*d*6 solution, the peaks around 3.4 ppm and 2.5 ppm are inevitable solvent peaks)



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7.365
7.354
7.343
7.329
7.269
7.257
6.649
6.635
6.623
6.610
4.489
0.000
CDCl3, 600 MHz
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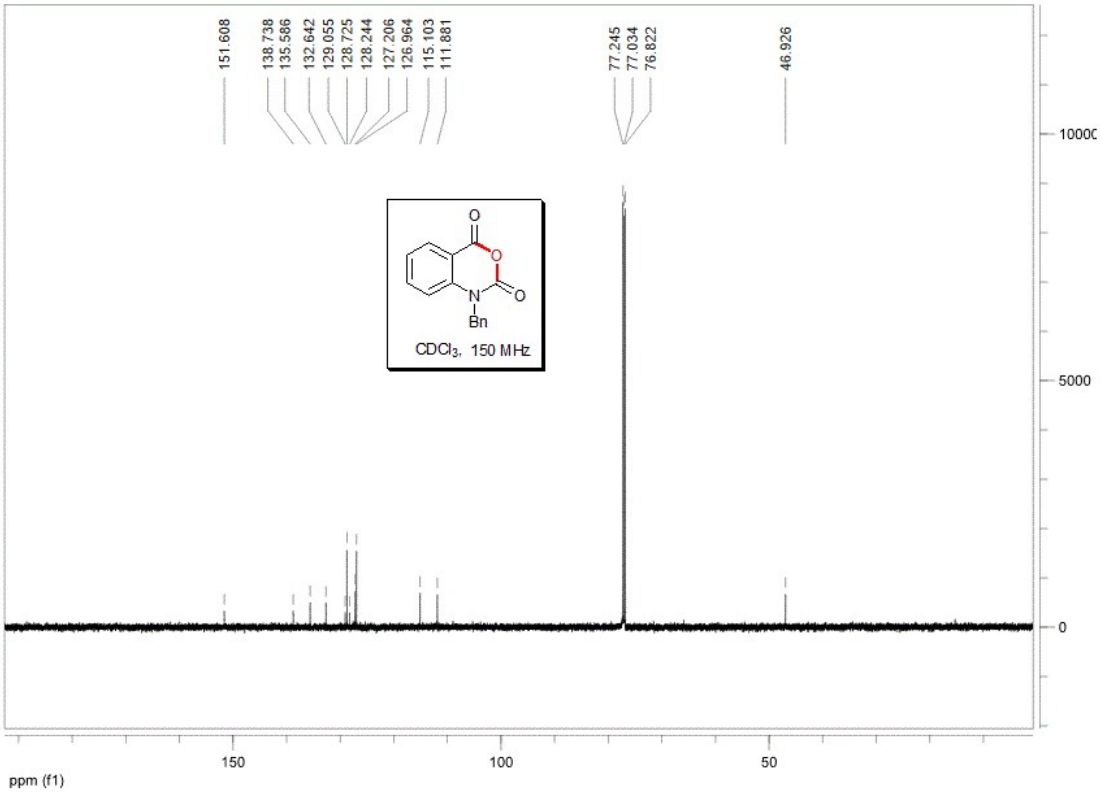
1.01
2.00
2.11
ppm (f1)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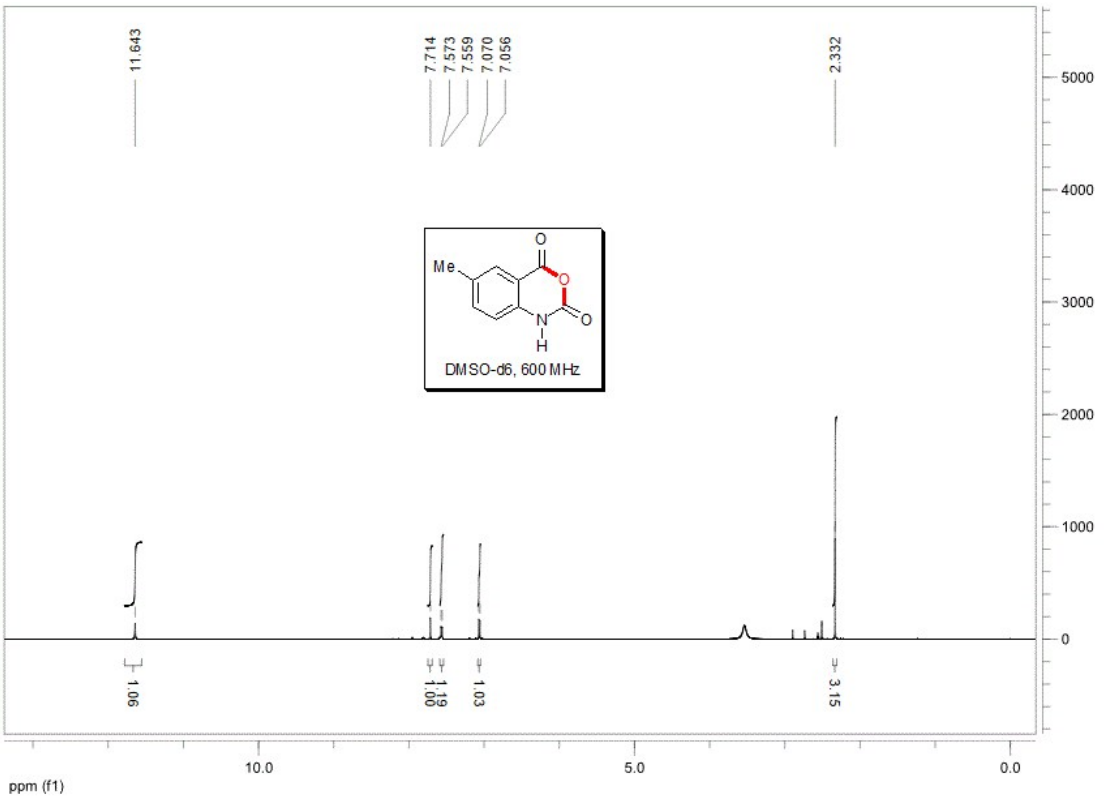
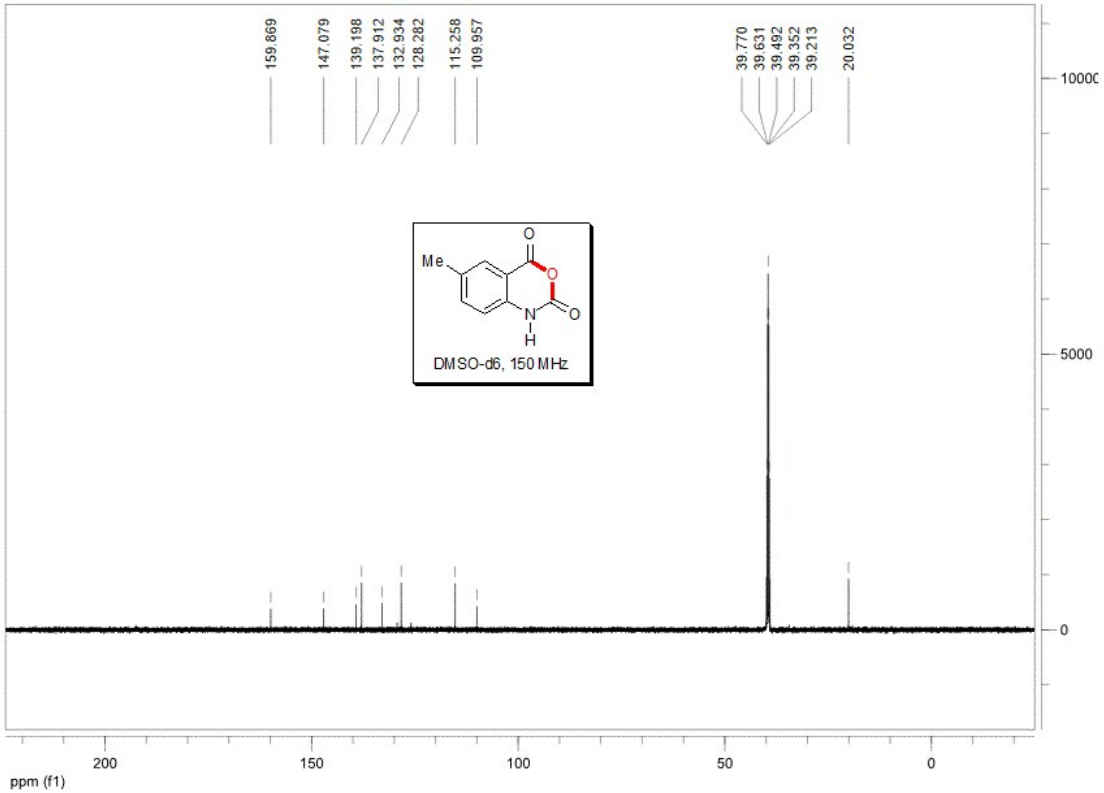
138.738
135.586
132.642
129.055
128.725
128.244
127.206
126.964
115.103
111.881
77.245
77.034
76.822
46.926
CDCl3, 150 MHz
ppm (f1)


11.643
7.714
7.573
7.559
7.070
7.056
2.332
Me
O
O
N
H
O
DMSO-d6, 600 MHz
1.06
1.19
1.00
1.03
3.15
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)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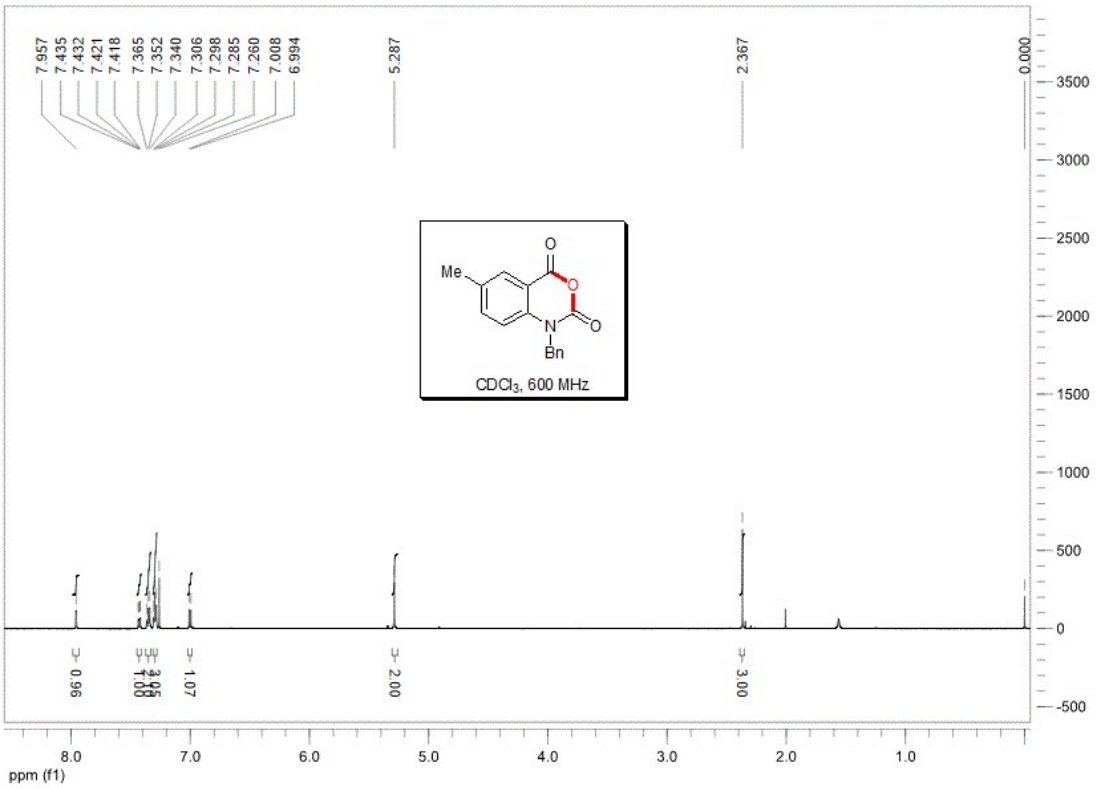
147.079
139.198
137.912
132.934
128.282
115.258
109.957
39.770
39.631
39.492
39.352
39.213
20.032
Me
O
O
N
H
O
DMSO-d6, 150 MHz
10000
5000
0
200
150
100
50
0
ppm (f1)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7.432
7.421
7.418
7.365
7.352
7.340
7.306
7.298
7.285
7.260
7.008
6.994
5.287
2.367
0.000
Me
O
O
N
O
Bn
CDCl3, 600 MHz
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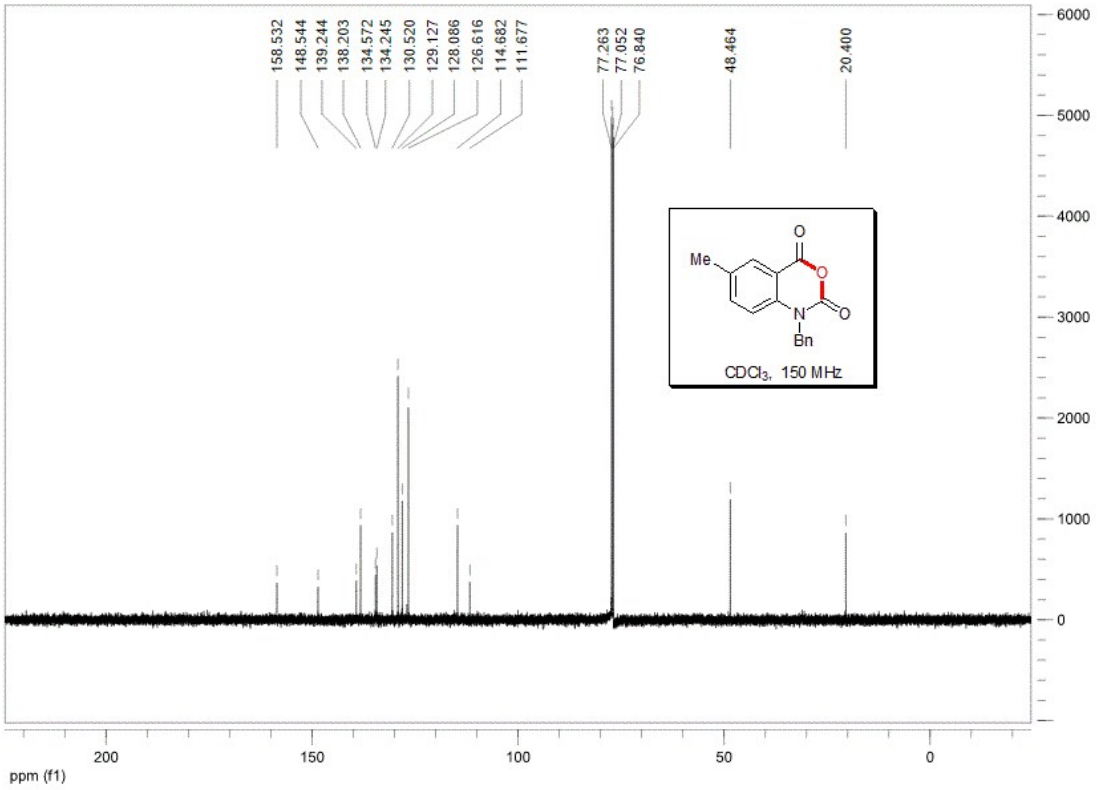
2.00
1.07
3.00
ppm (f1)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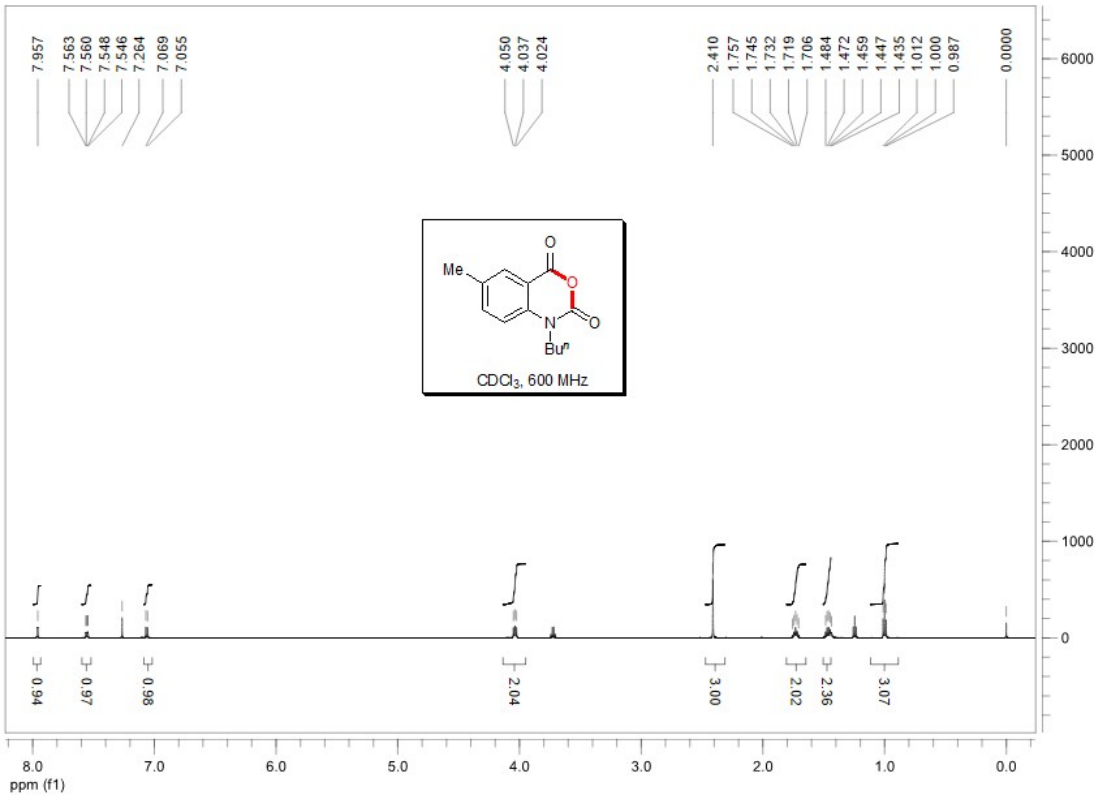
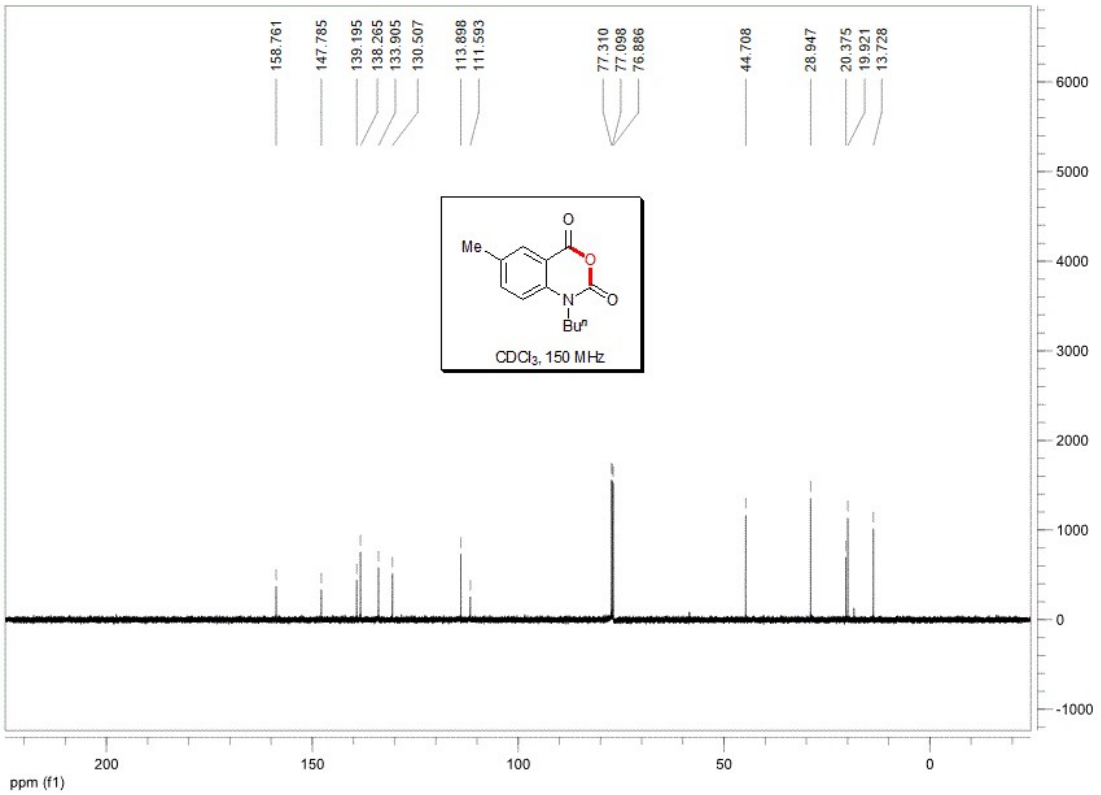
148.544
139.244
138.203
134.572
134.245
130.520
129.127
128.086
126.616
114.682
111.677
77.263
77.052
76.840
48.464
20.400
Me
O
O
N
O
Bn
CDCl3, 150 MHz
ppm (f1)


7.957
7.563
7.560
7.548
7.546
7.264
7.069
7.055
4.050
4.037
4.024
2.410
1.757
1.745
1.732
1.719
1.706
1.484
1.472
1.459
1.447
1.435
1.012
1.000
0.987
0.0000
Me
O
O
N
O
Bu^n
CDCl3, 600 MHz
0.94
0.97
0.98
2.04
3.00
2.02
2.36
3.07
ppm (f1)


158.761
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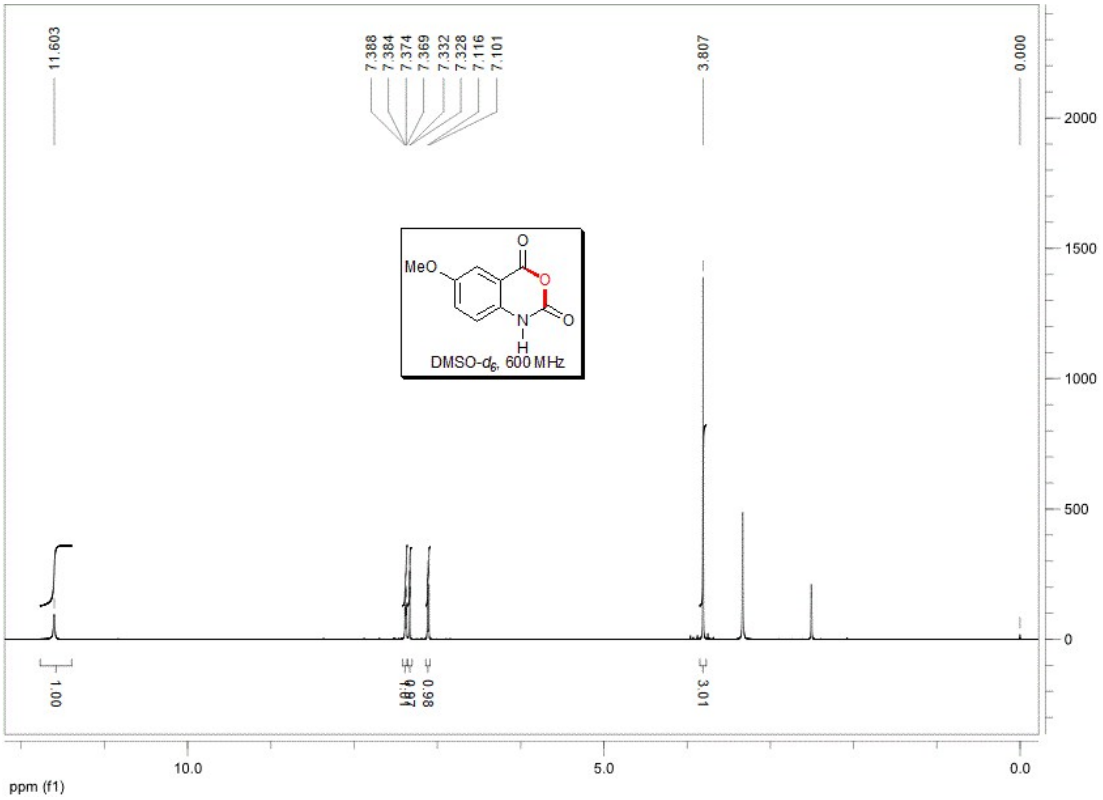
139.195
138.265
133.905
130.507
113.898
111.593
77.310
77.098
76.886
44.708
28.947
20.375
19.921
13.728
Me
O
O
N
O
Bu^n
CDCl3, 150 MHz
ppm (f1)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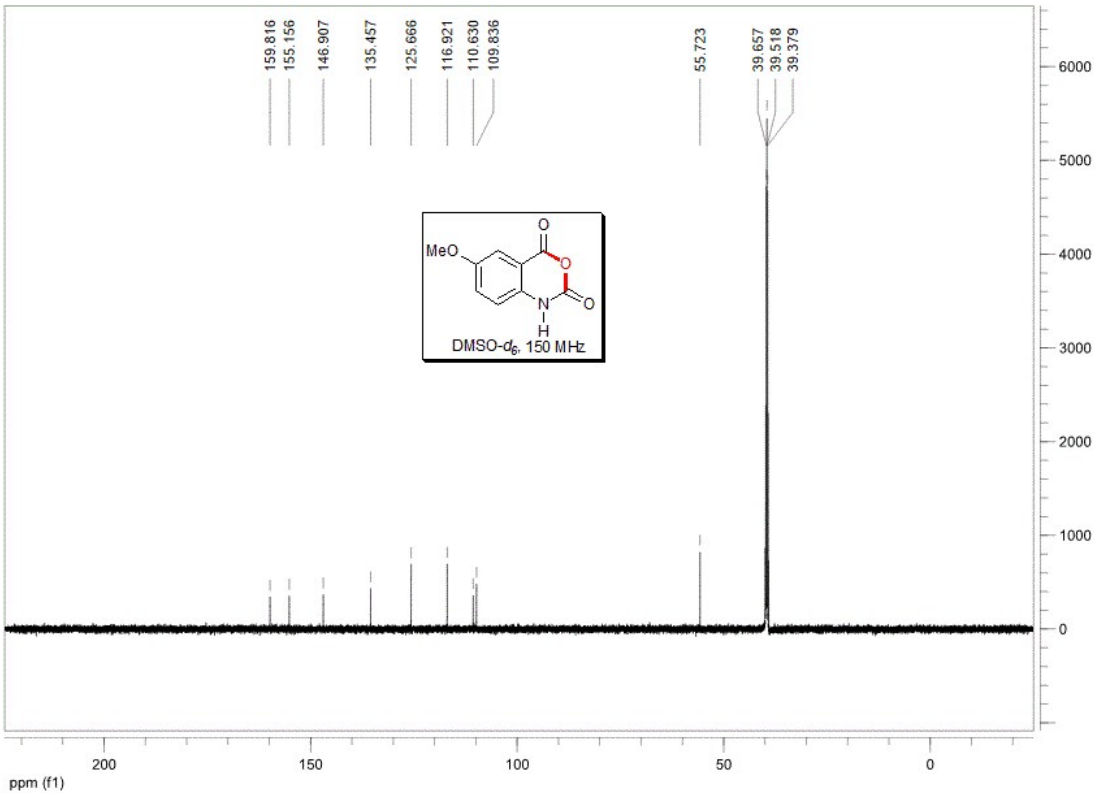
7.388
7.384
7.374
7.369
7.332
7.328
7.116
7.101
3.807
0.000
MeO
O
O
N
H
O
DMSO-d_6, 600 MHz
2000
1500
1000
500
0
1.00
0.98
3.01
10.0
5.0
0.0
ppm (f1)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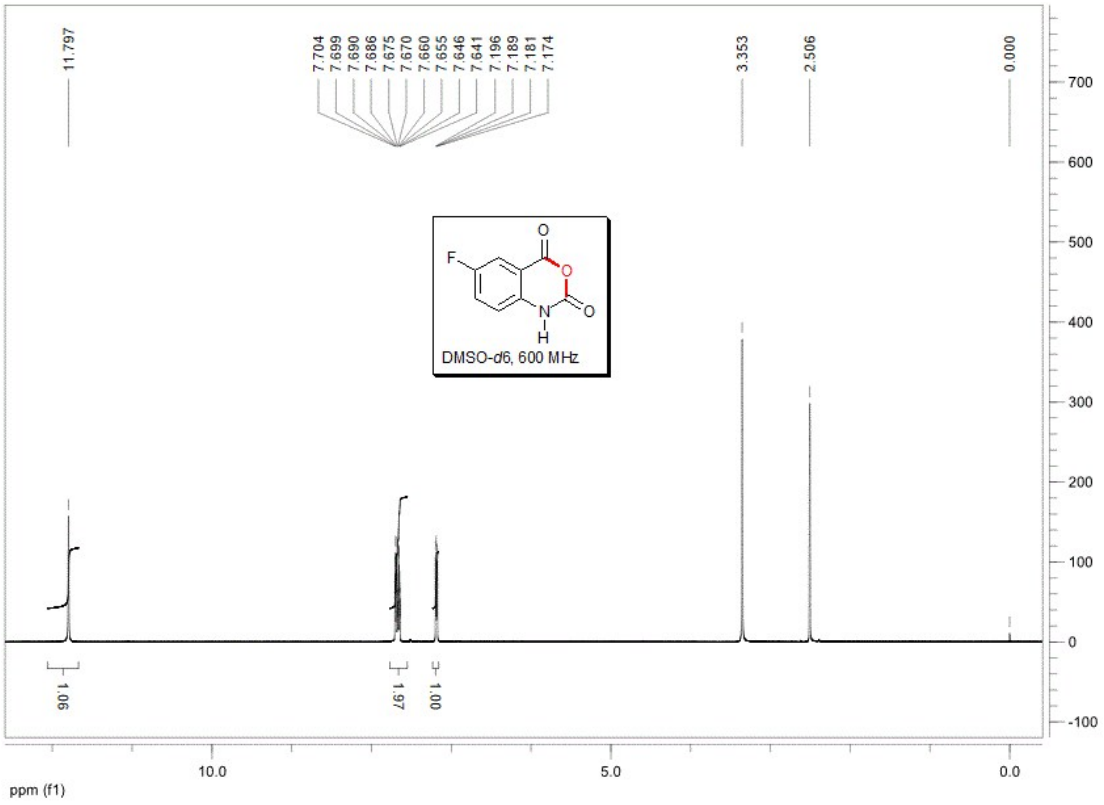
155.156
146.907
135.457
125.666
116.921
110.630
109.836
55.723
39.657
39.518
39.379
MeO
O
O
N
H
O
DMSO-d_6, 150 MHz
6000
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)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7.690
7.686
7.675
7.670
7.660
7.655
7.646
7.641
7.196
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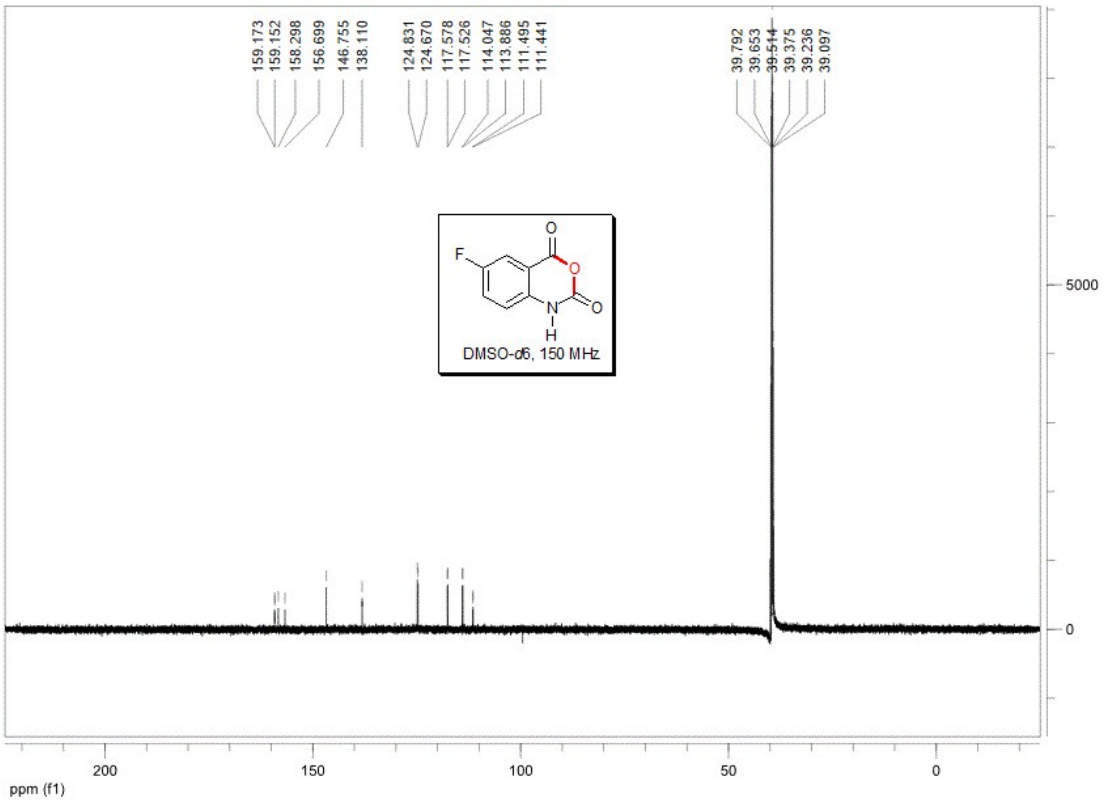
7.181
7.174
3.353
2.506
0.000
DMSO-d6, 600 MHz
1.06
1.97
1.00
ppm (f1)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158.298
156.699
146.755
138.110
124.831
124.670
117.578
117.526
114.047
113.886
111.495
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39.792
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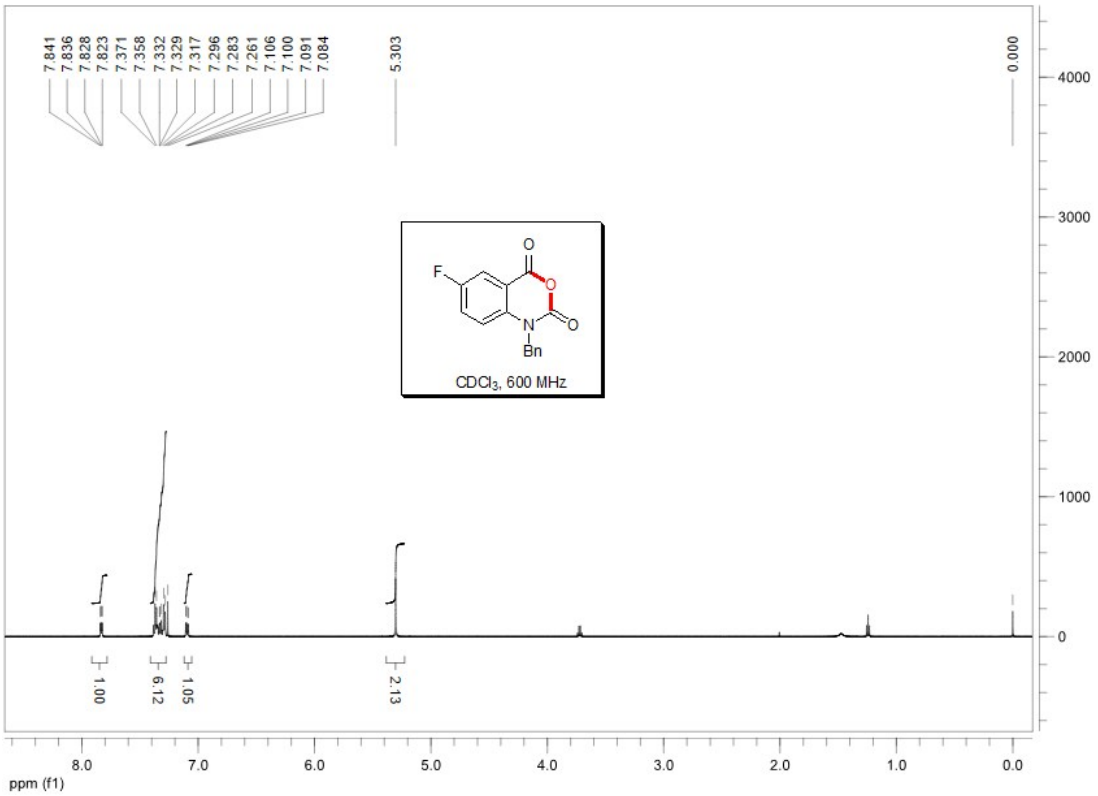
39.514
39.375
39.236
39.097
DMSO-d6, 150 MHz
ppm (f1)


7.841
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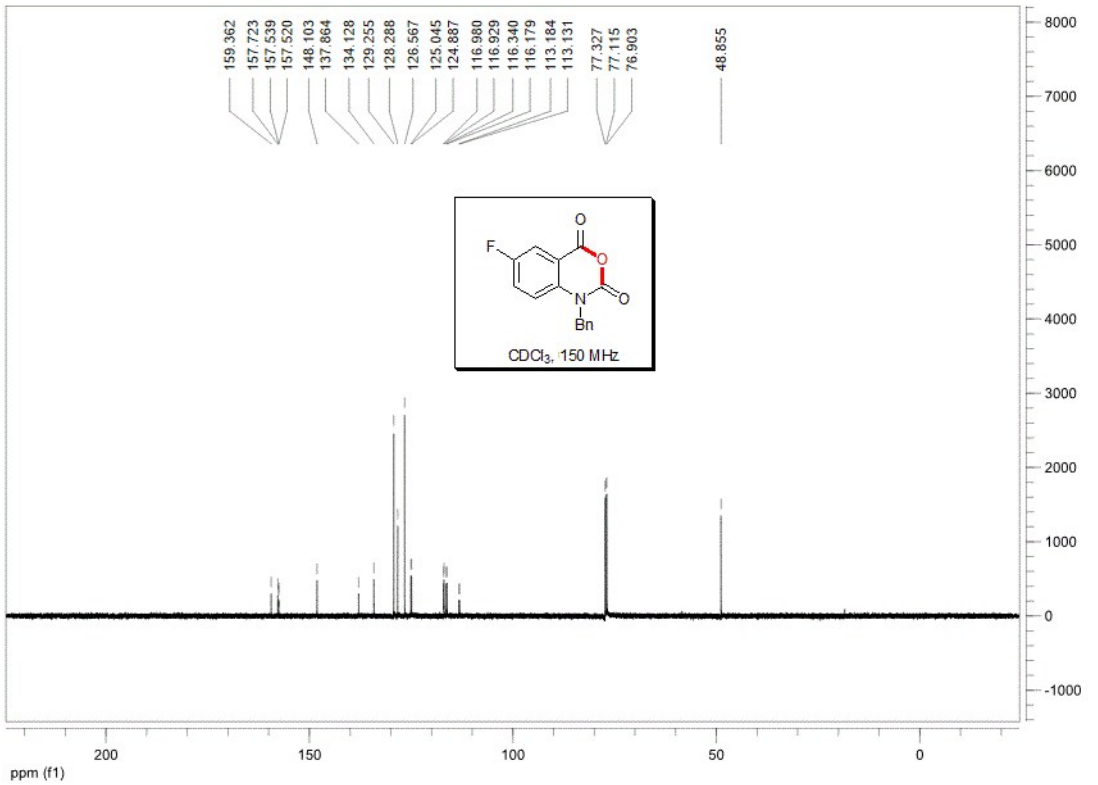
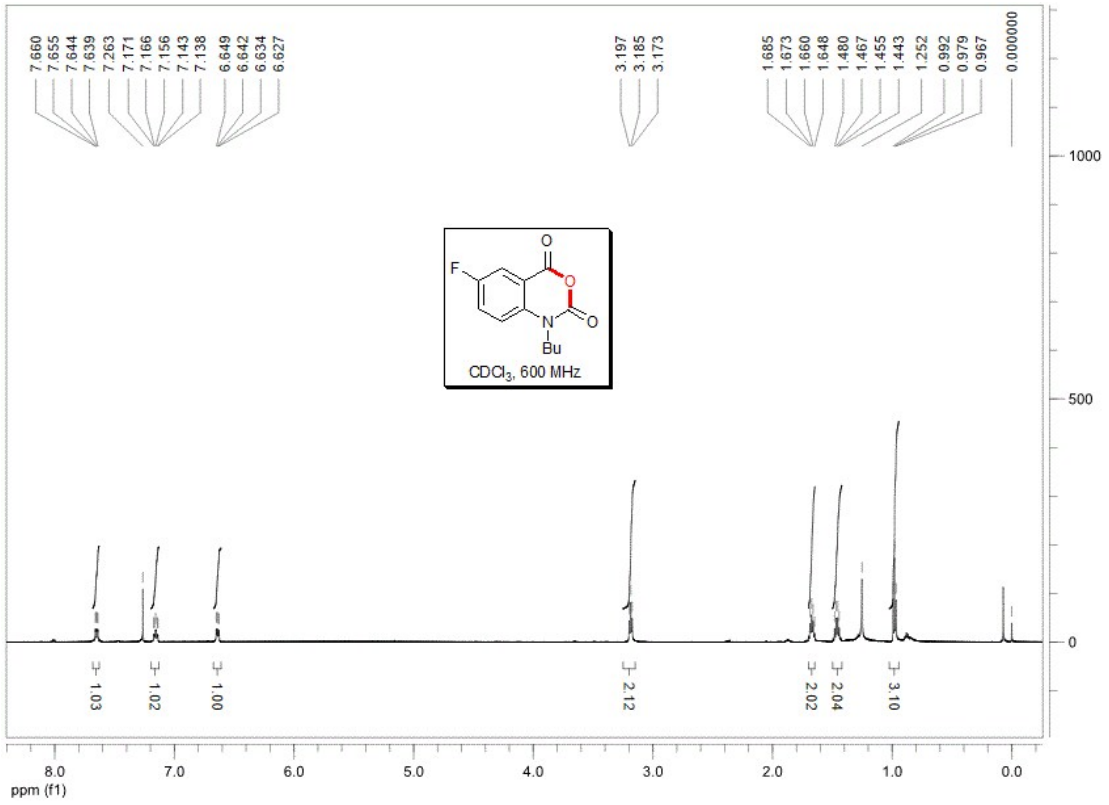
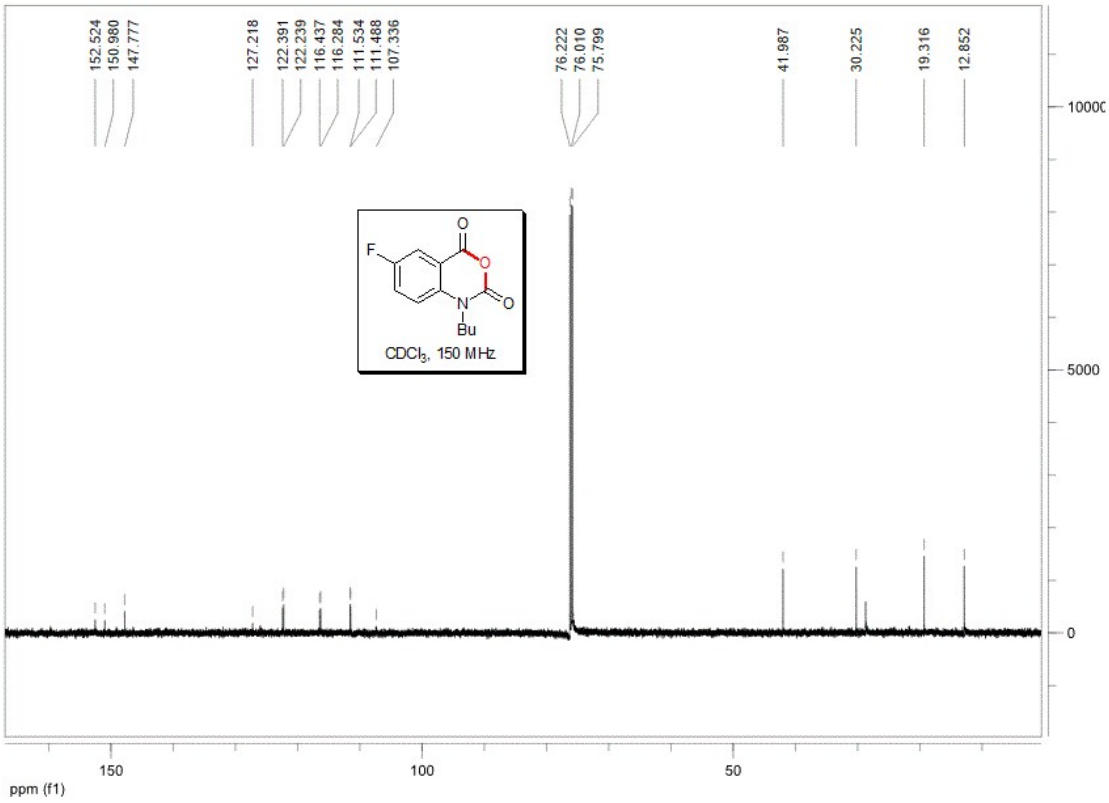
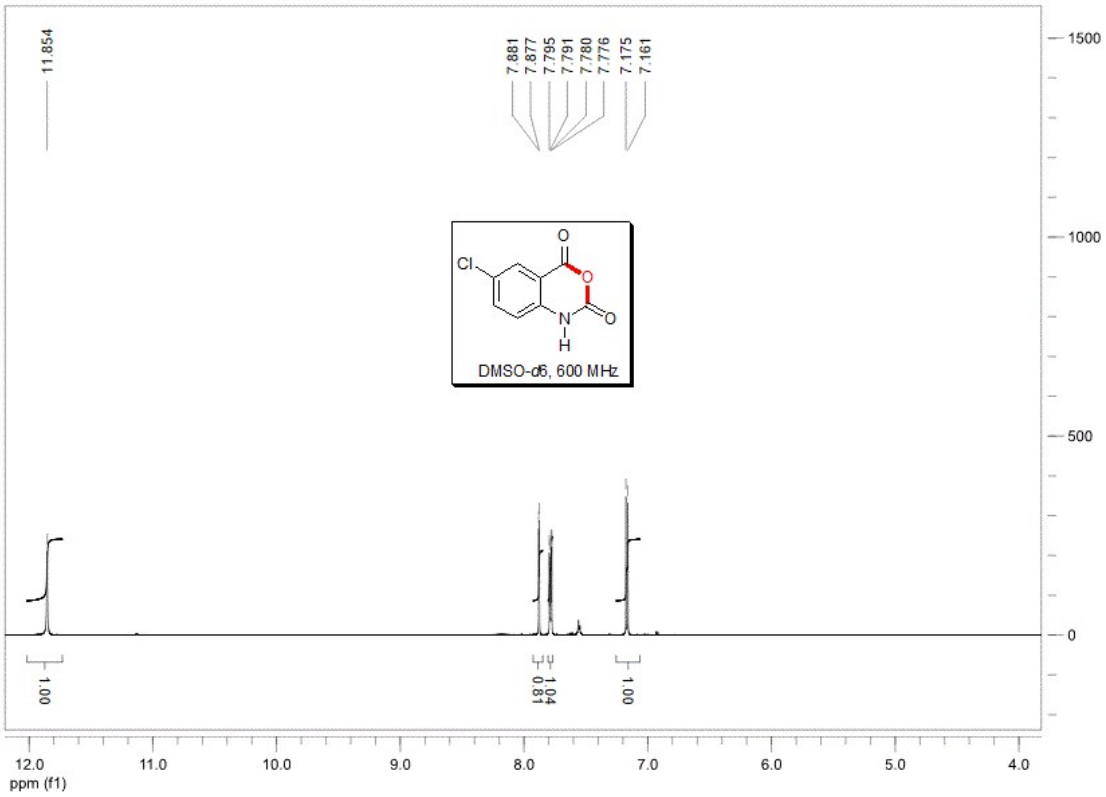
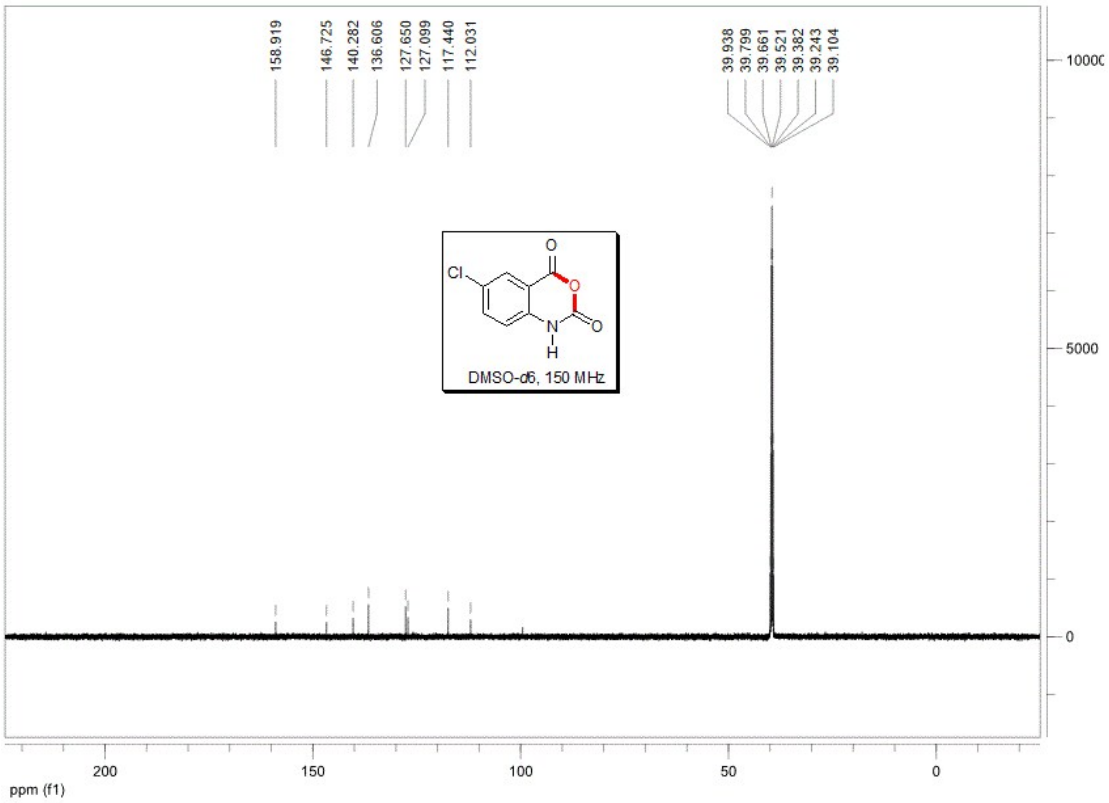
7.823
7.371
7.358
7.332
7.329
7.317
7.296
7.283
7.261
7.106
7.100
7.091
7.084
5.303
0.000
F
O
O
N
O
Bn
CDCl3, 600 MHz
1.00
6.12
1.05
2.13
ppm (f1)


159.362
157.723
157.539
157.520
148.103
137.864
134.128
129.255
128.288
126.567
125.045
124.887
116.980
116.929
116.340
116.179
113.184
113.131
77.327
77.115
76.903
48.855
F
O
O
N
O
Bn
CDCl3, 150 MHz
ppm (f1)


7.660
7.655
7.644
7.639
7.263
7.171
7.166
7.156
7.143
7.138
6.649
6.642
6.634
6.627
3.197
3.185
3.173
1.685
1.673
1.660
1.648
1.480
1.467
1.455
1.443
1.252
0.992
0.979
0.967
0.000000
1000
500
0
1.03
1.02
1.00
2.12
2.02
2.04
3.10
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
F
O
O
N
O
Bu
CDCl3, 600 MHz


152.524
150.980
147.777
127.218
122.391
122.239
116.437
116.284
111.534
111.488
107.336
76.222
76.010
75.799
41.987
30.225
19.316
12.852
10000
5000
0
150
100
50
ppm (f1)
F
O
O
N
O
Bu
CDCl3, 150 MHz


11.854
7.881
7.877
7.795
7.791
7.780
7.776
7.175
7.161
Cl
O
O
N
H
O
DMSO-d6, 600 MHz
1.00
1.04
0.81
1.00
1500
1000
500
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
ppm (f1)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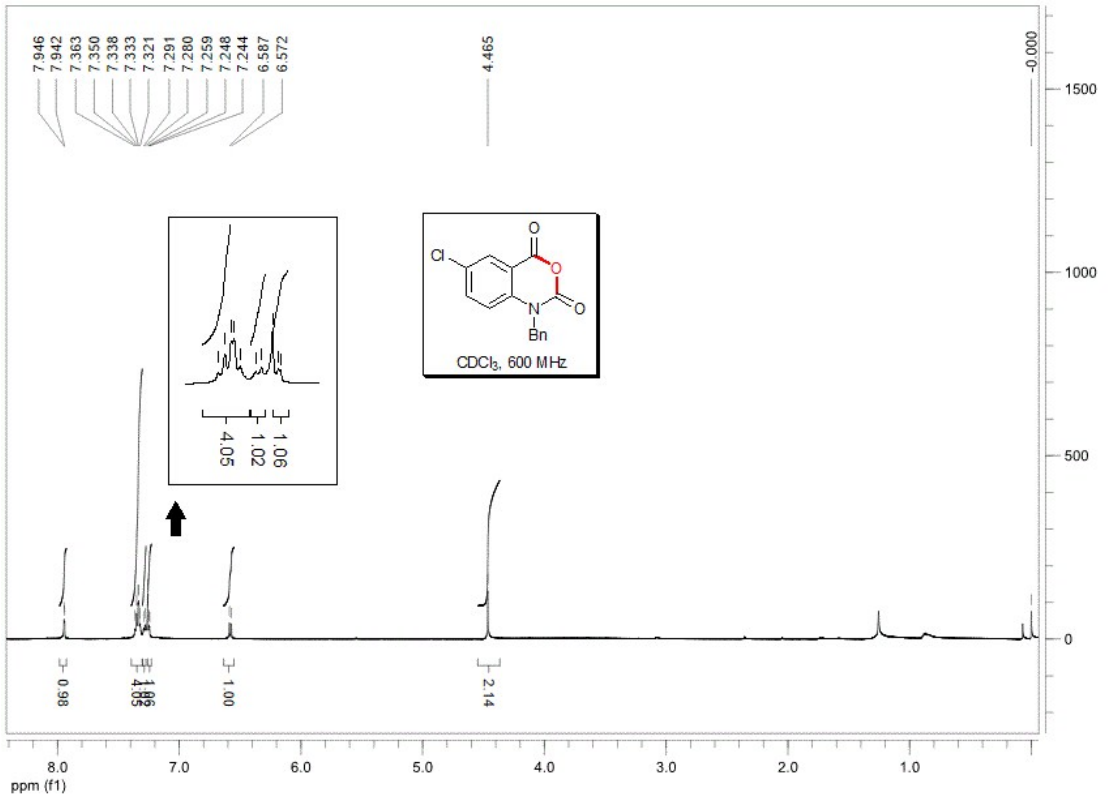
146.725
140.282
136.606
127.650
127.099
117.440
112.031
39.938
39.799
39.661
39.521
39.382
39.243
39.104
Cl
O
O
N
H
O
DMSO-d6, 150 MHz
10000
5000
0
200
150
100
50
0
ppm (f1)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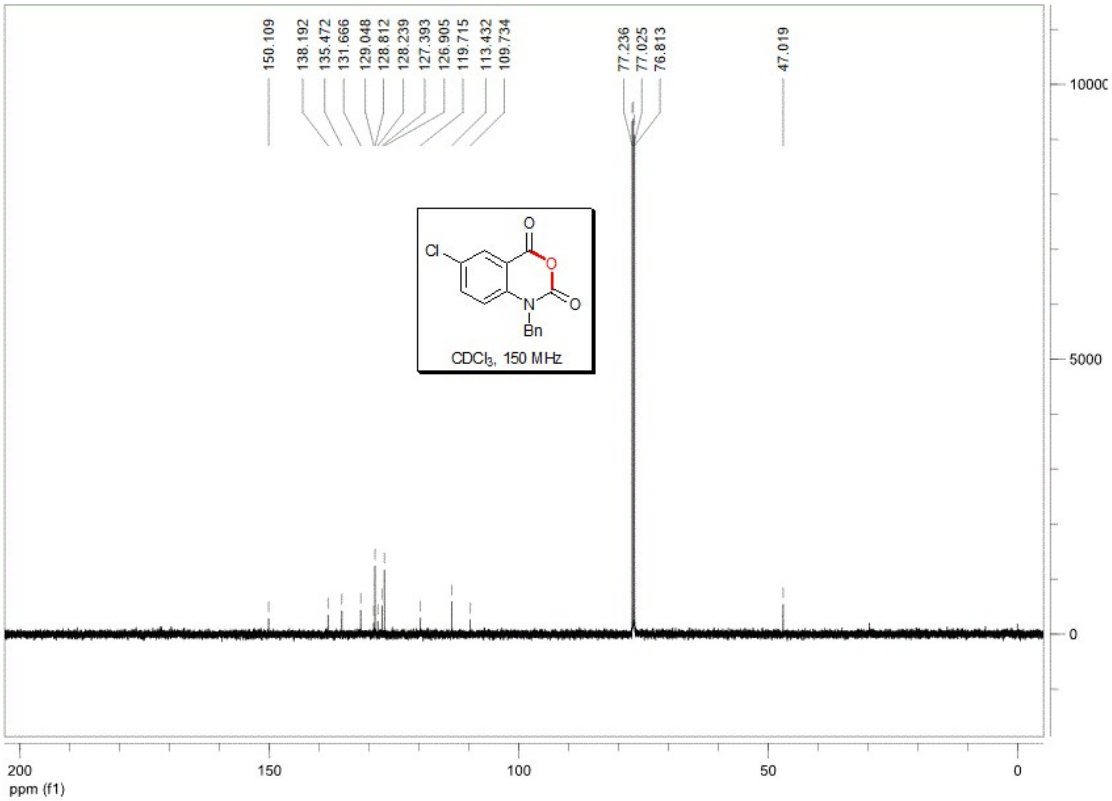
7.363
7.350
7.338
7.333
7.321
7.291
7.280
7.259
7.248
7.244
6.587
6.572
4.465
-0.000
1500
1000
500
0
4.05
1.02
1.06
0.98
1.00
2.14
CDCl3, 600 MHz
Cl
O
N
Bn
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


150.109
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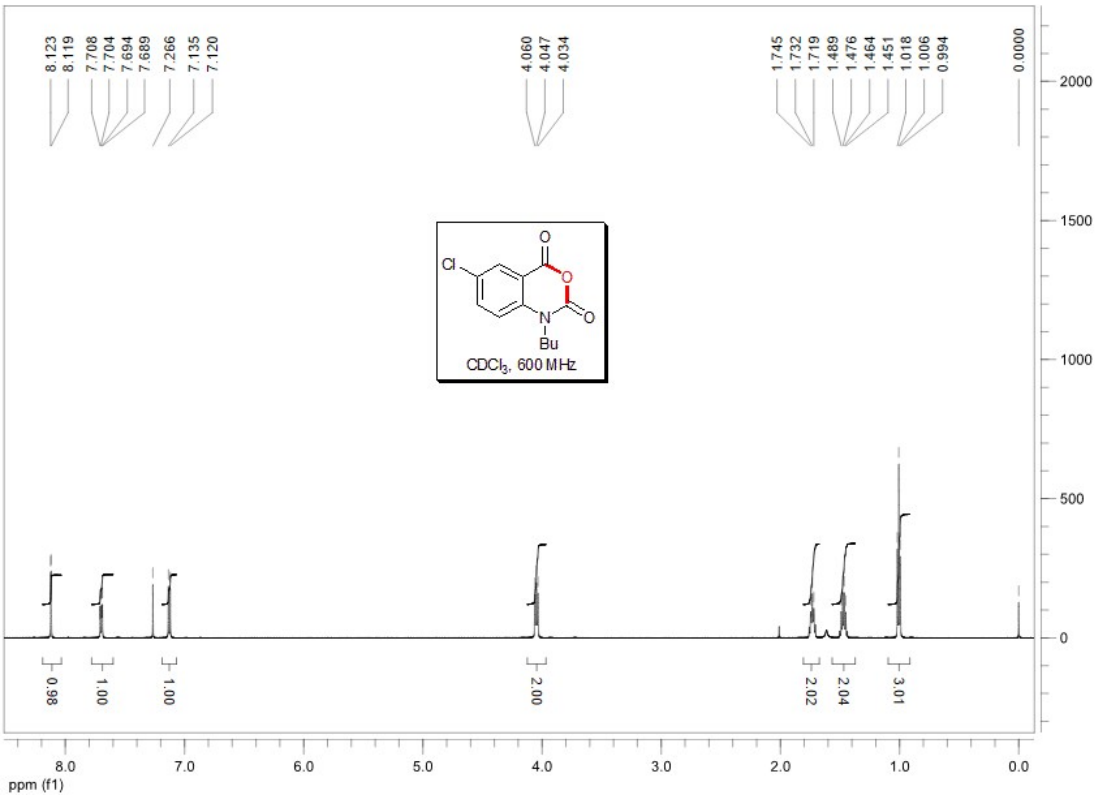
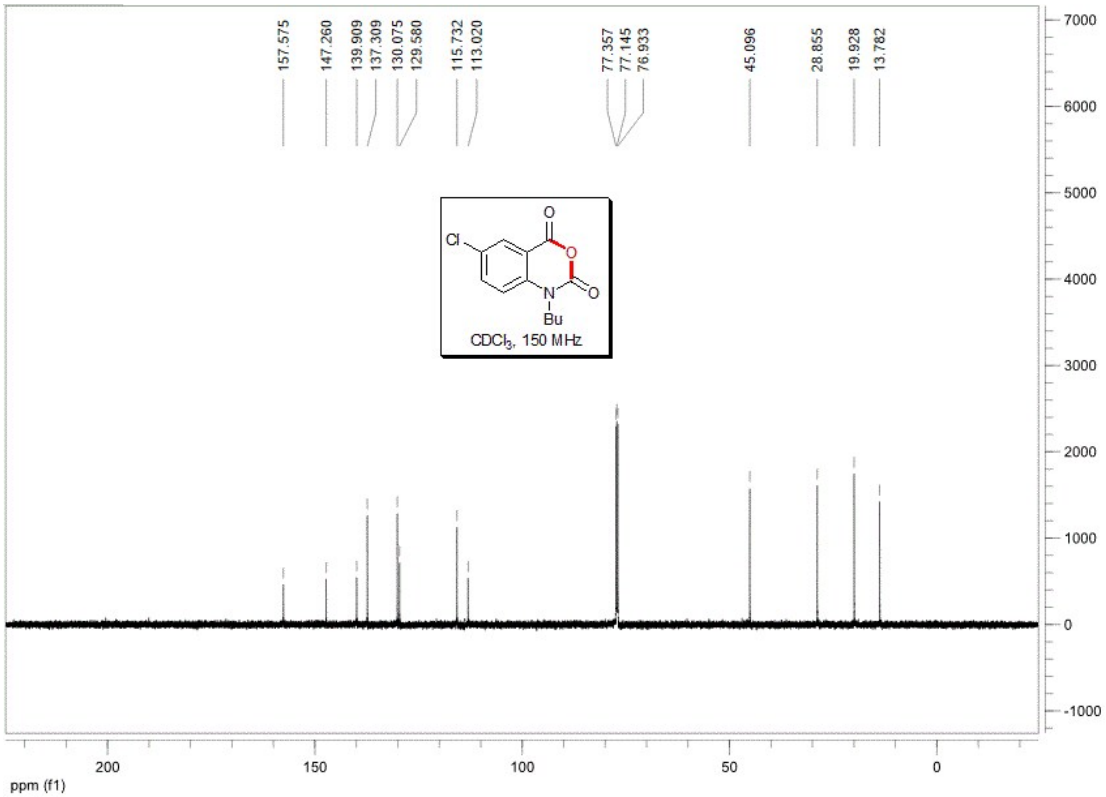
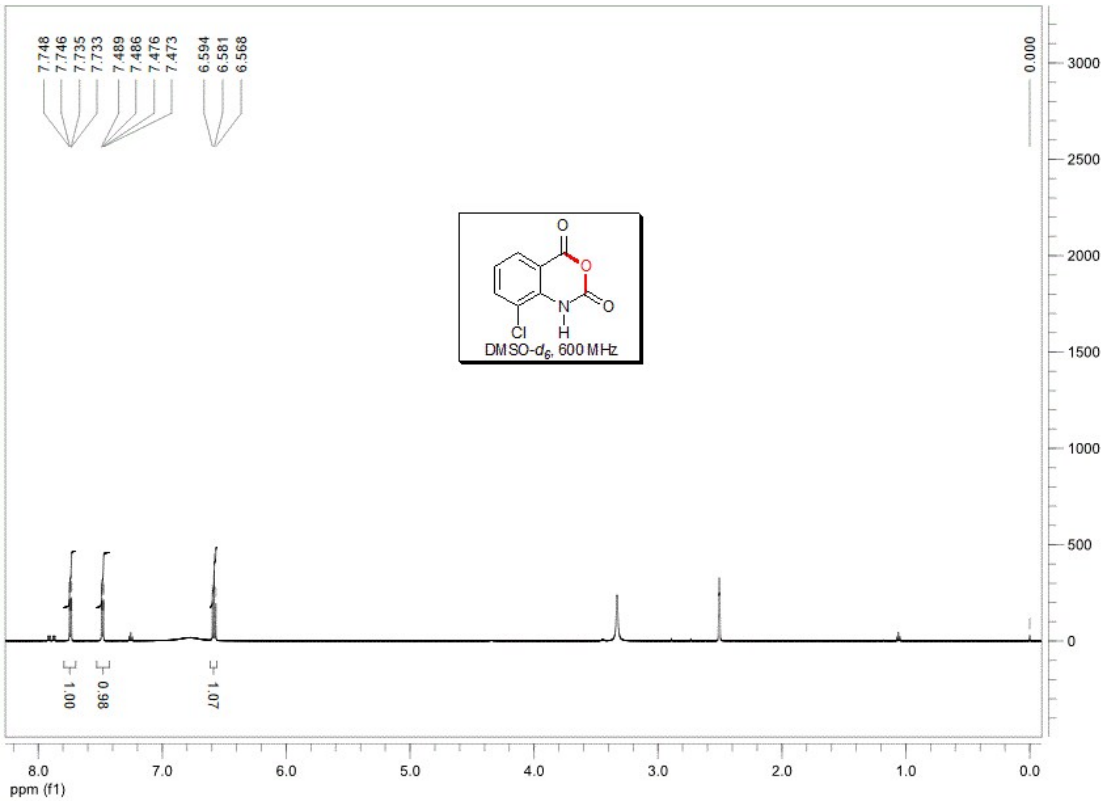
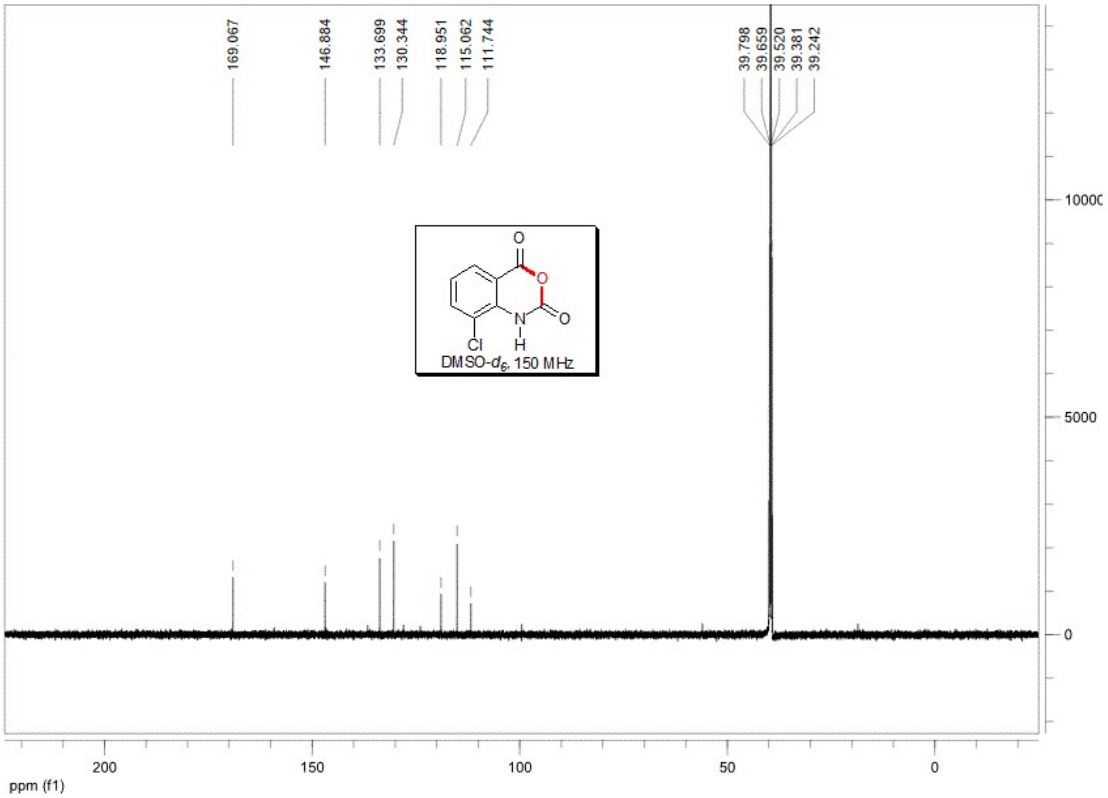
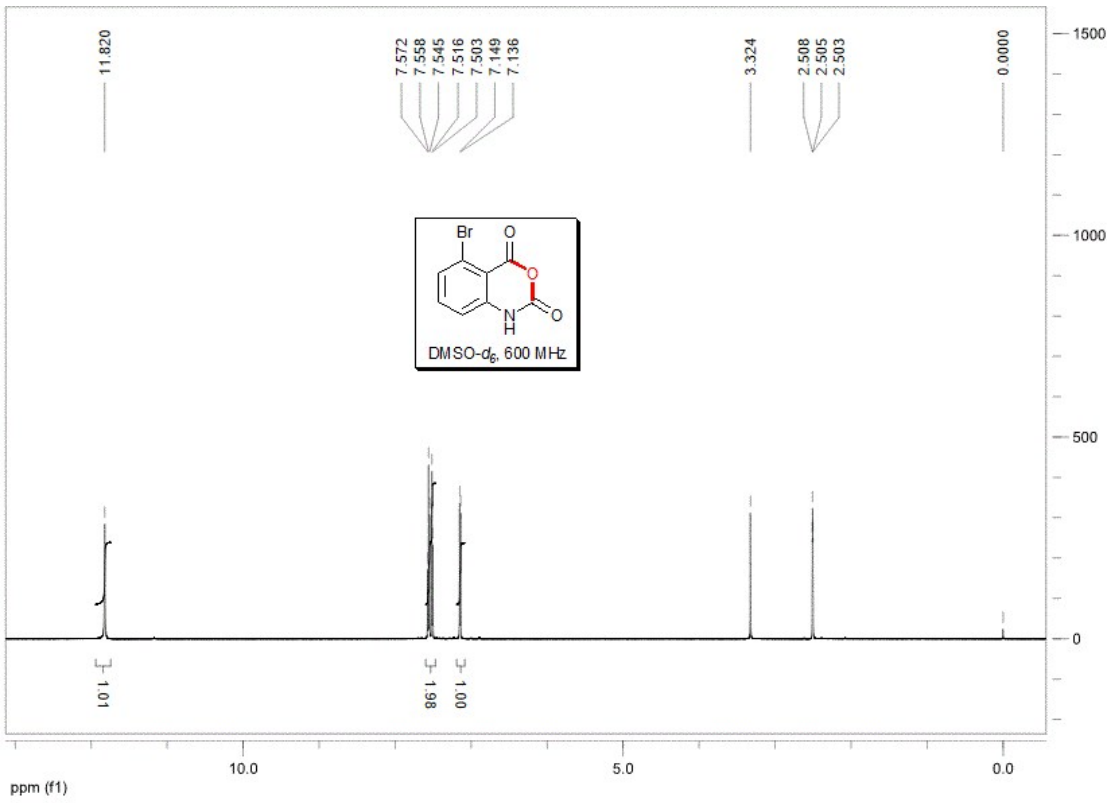
135.472
131.666
129.048
128.812
128.239
127.393
126.905
119.715
113.432
109.734
77.236
77.025
76.813
47.019
10000
5000
0
CDCl3, 150 MHz
Cl
O
N
Bn
200
150
100
50
0
ppm (f1)

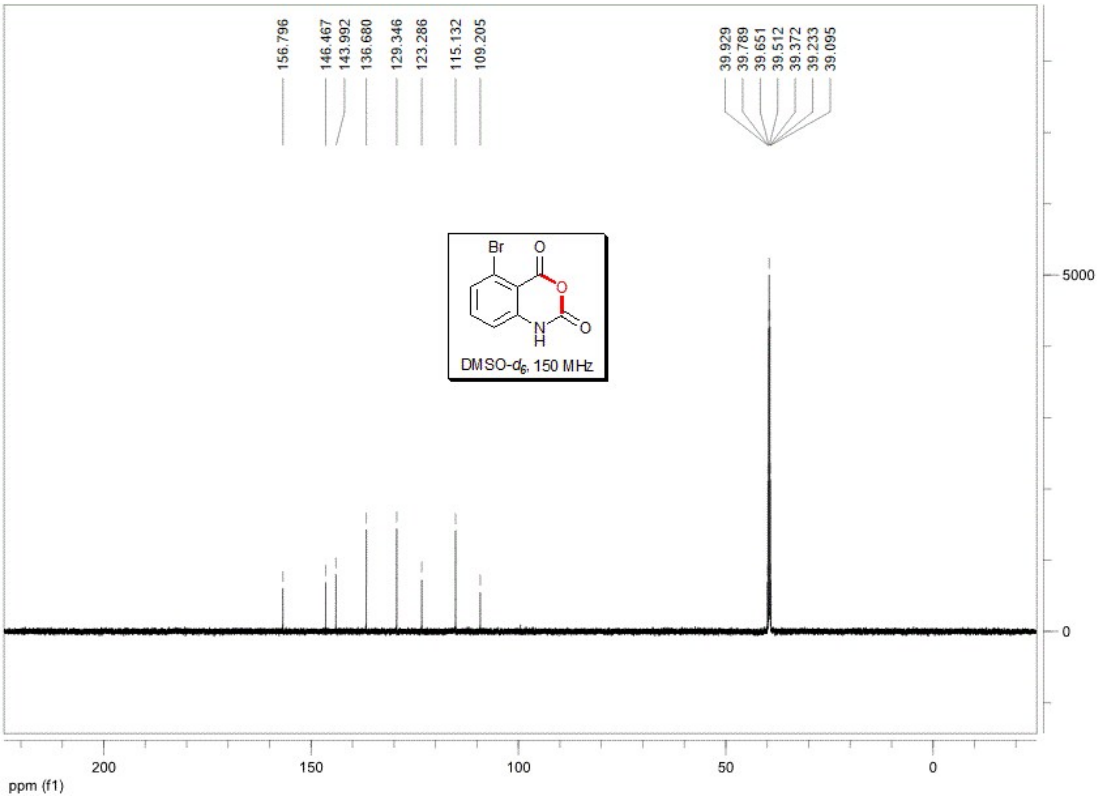

8.123
8.119
7.708
7.704
7.694
7.689
7.266
7.135
7.120
4.060
4.047
4.034
1.745
1.732
1.719
1.489
1.476
1.464
1.451
1.018
1.006
0.994
0.0000
Cl
O
O
N
O
Bu
CDCl3, 600 MHz
0.98
1.00
1.00
2.00
2.02
2.04
3.01
ppm (f1)

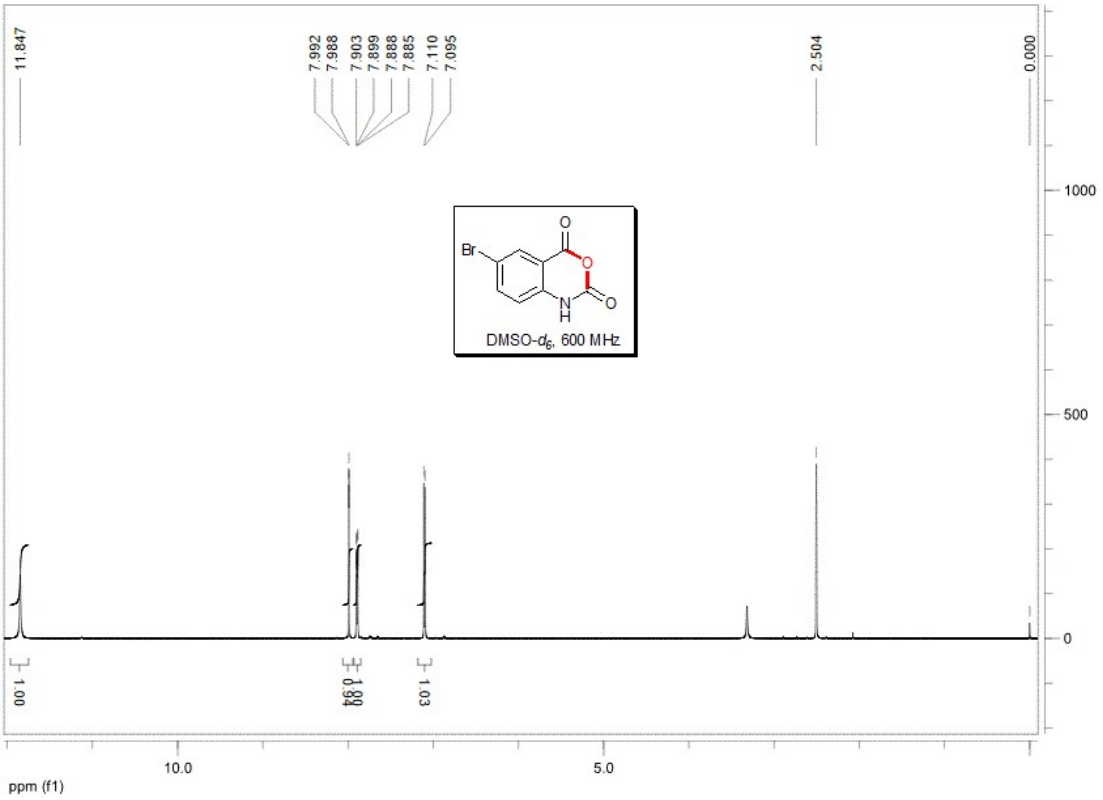

157.575
147.260
139.909
137.309
130.075
129.580
115.732
113.020
77.357
77.145
76.933
45.096
28.855
19.928
13.782
Cl
O
O
N
O
Bu
CDCl3, 150 MHz
ppm (f1)

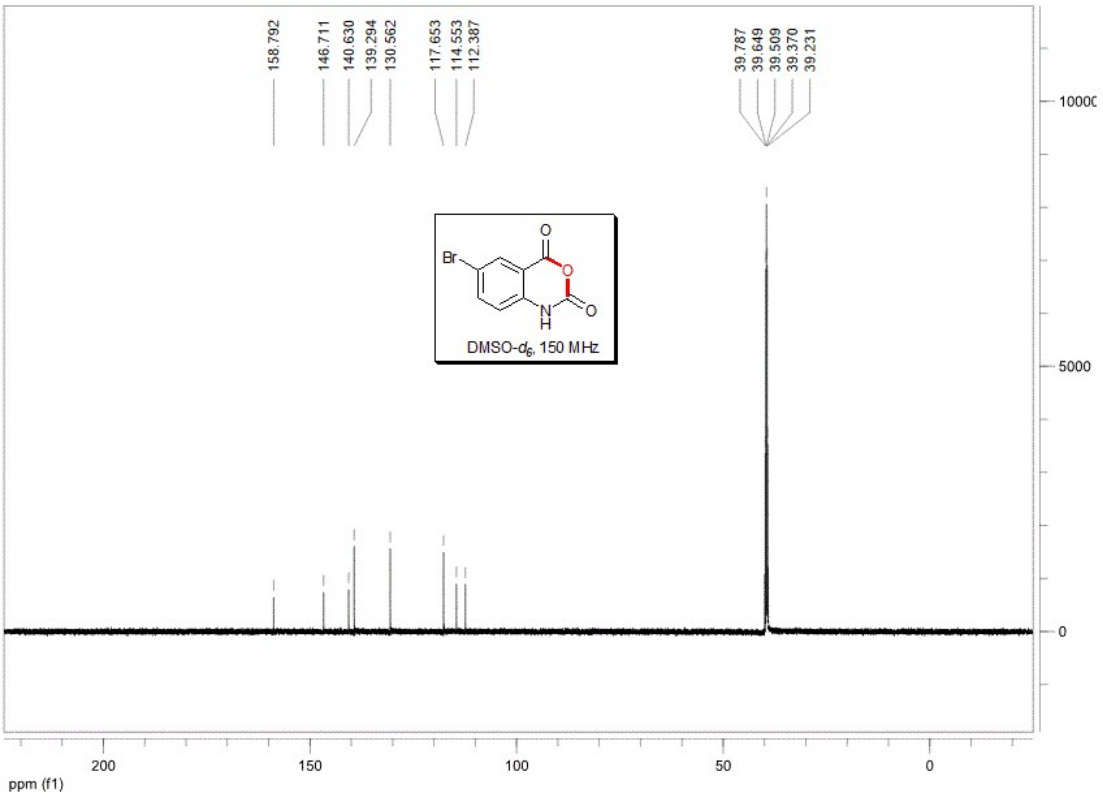

7.748
7.746
7.735
7.733
7.489
7.486
7.476
7.473
6.594
6.581
6.568
0.000
DMSO-d_6, 600 MHz
1.00
0.98
1.07
ppm (f1)

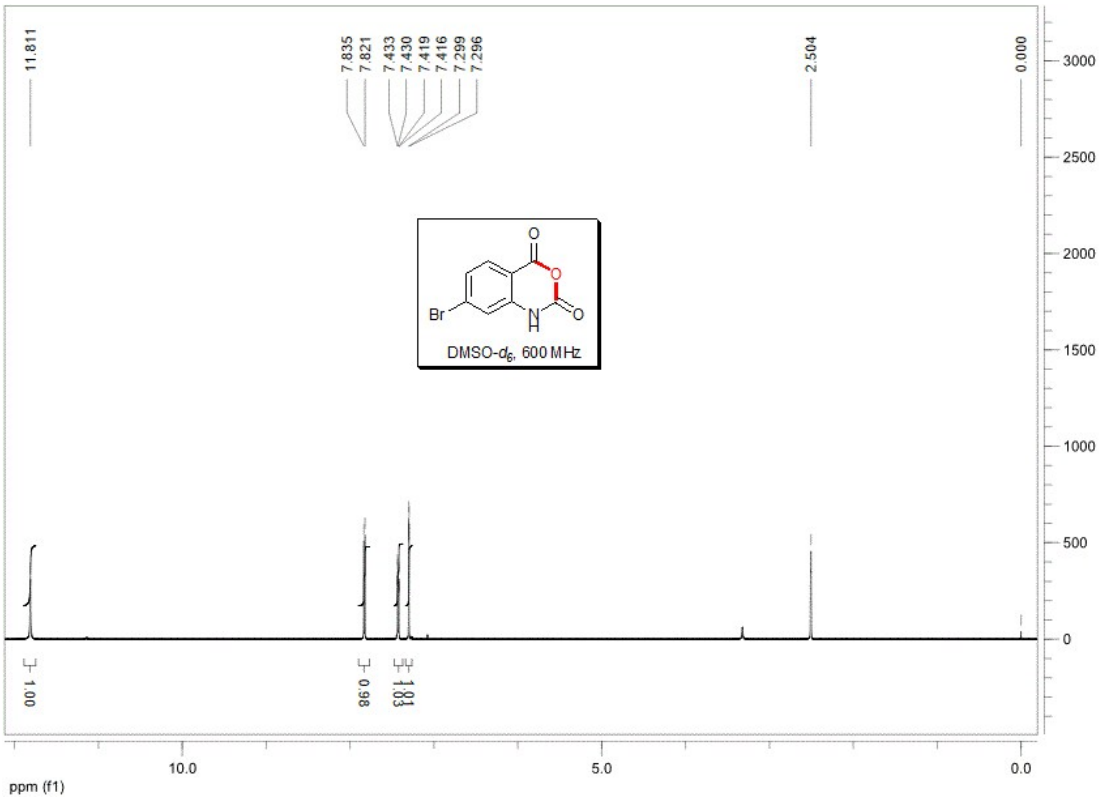

169.067
146.884
133.699
130.344
118.951
115.062
111.744
39.798
39.659
39.520
39.381
39.242
DMSO-d_6, 150 MHz
ppm (f1)

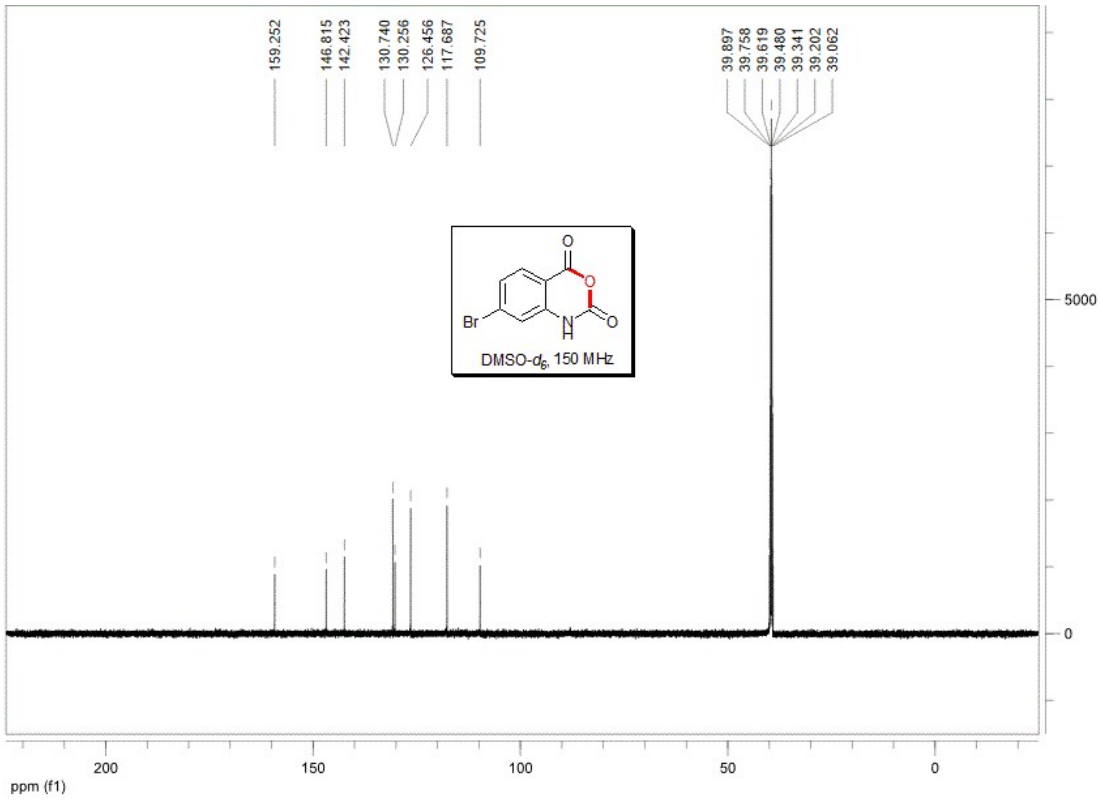

11.820
7.572
7.558
7.545
7.516
7.503
7.149
7.136
3.324
2.508
2.505
2.503
0.0000
Br
O
O
N
H
O
DMSO-d_6, 600 MHz
1500
1000
500
0
1.01
1.98
1.00
10.0
5.0
0.0
ppm (f1)

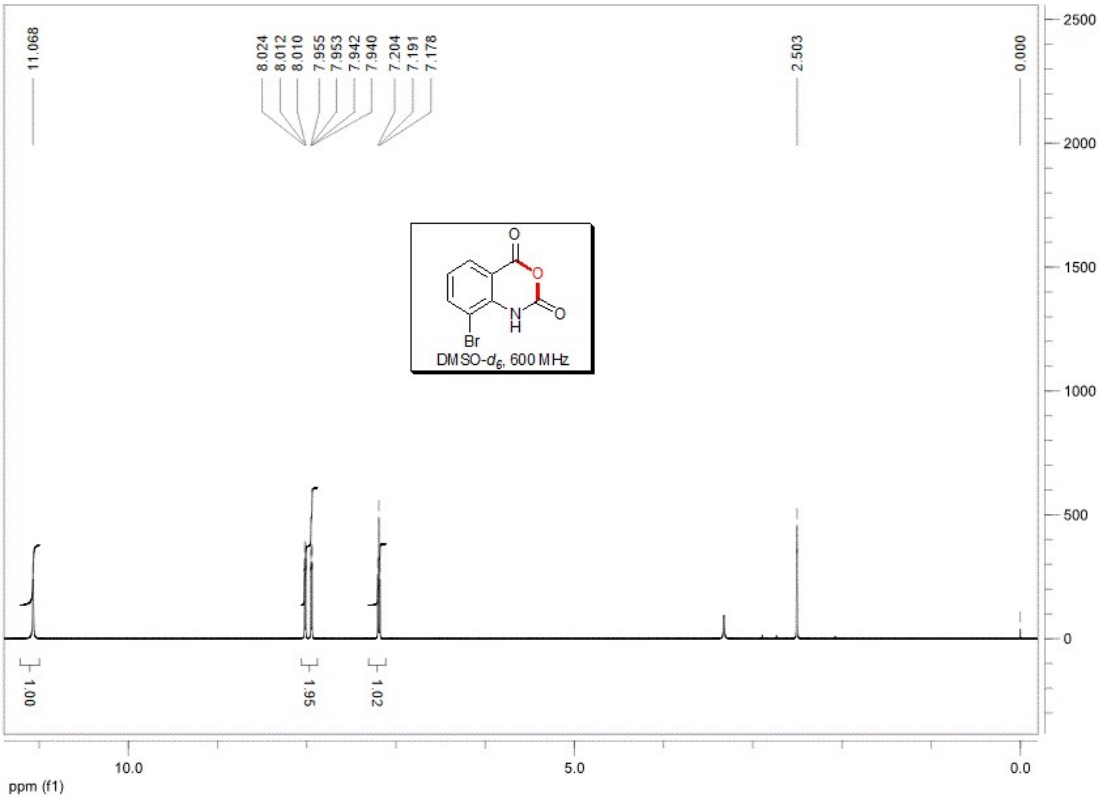

156.796
146.467
143.992
136.680
129.346
123.286
115.132
109.205
39.929
39.789
39.651
39.512
39.372
39.233
39.095
Br
O
O
N
H
O
DMSO-d_6, 150 MHz
5000
0
200
150
100
50
0
ppm (f1)

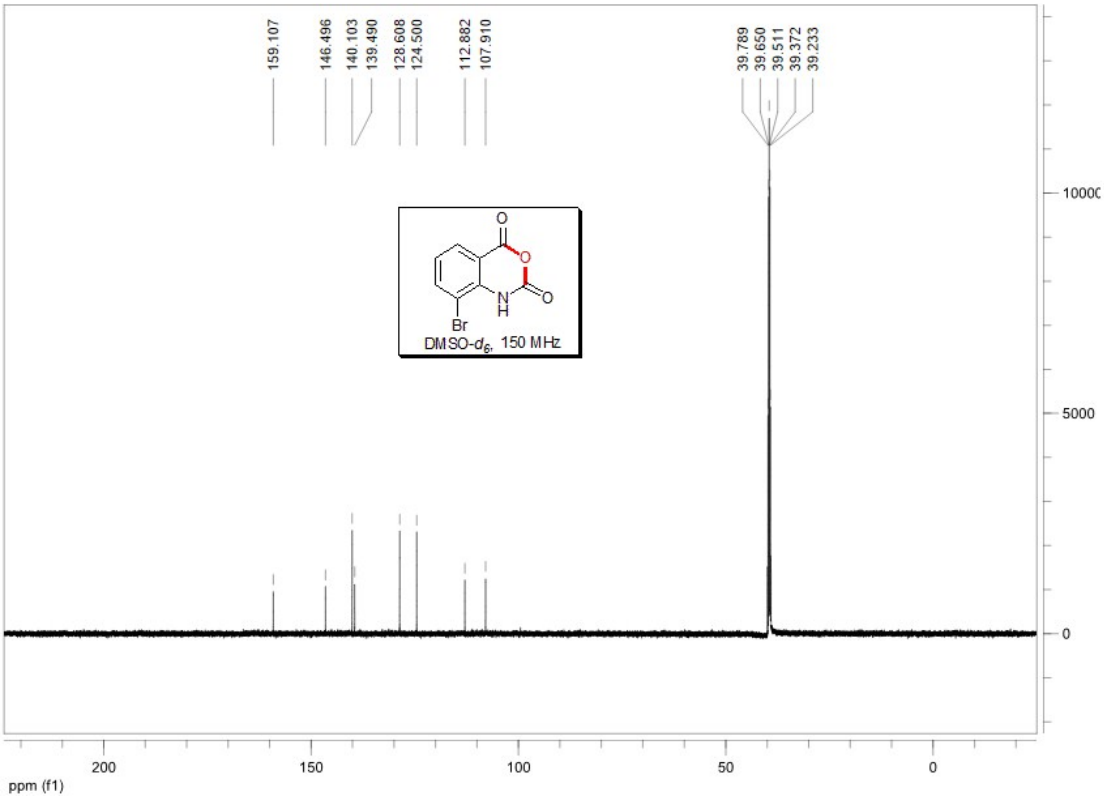

11.847
7.992
7.988
7.903
7.899
7.888
7.885
7.110
7.095
2.504
0.000
Br
O
O
N
H
O
DMSO-d_6, 600 MHz
1000
500
0
1.00
2.00
1.03
10.0
5.0
ppm (f1)


158.792
146.711
140.630
139.294
130.562
117.653
114.553
112.387
39.787
39.649
39.509
39.370
39.231
Br
O
O
N
H
O
DMSO-d_6, 150 MHz
10000
5000
0
200
150
100
50
0
ppm (f1)


11.811
7.835
7.821
7.433
7.430
7.419
7.416
7.299
7.296
2.504
0.000
DMSO-d_6, 600 MHz
1.00
0.98
1.83
ppm (f1)


159.252
146.815
142.423
130.740
130.256
126.456
117.687
109.725
39.897
39.758
39.619
39.480
39.341
39.202
39.062
DMSO-d_6, 150 MHz
ppm (f1)


11.068
8.024
8.012
8.010
7.955
7.953
7.942
7.940
7.204
7.191
7.178
2.503
0.000
DMSO-d_6, 600 MHz
1.00
1.95
1.02
ppm (f1)


159.107
146.496
140.103
139.490
128.608
124.500
112.882
107.910
39.789
39.650
39.511
39.372
39.233
DMSO-d_6, 150 MHz
ppm (f1)