Supporting Information

Radical Addition Cascade Cyclization of 1,6-Enynes with DMSO to Access Methylsulfonylated and Carbonylated Benzofurans under Transition-Metal-Free Conditions

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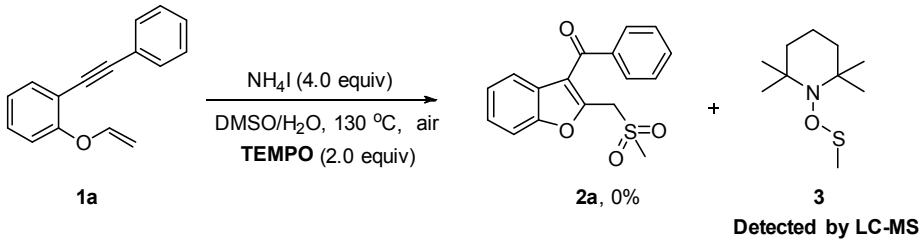
1. The control experiments

1.1. Free radical-trapping experiment A



To a sealed tube were added 1,6-enyne **1a** (0.2 mmol, 1.0 equiv), NH_4I (0.8 mmol, 4.0 equiv), TEMPO (0.4 mmol, 2.0 equiv), DMSO (1.6 mL) and H_2O (0.4 mL). The reaction mixture was stirred at 130 °C for 24 h. After the reaction was stopped, no desired product **2a** was detected by TLC and LC-MS, indicating that the reaction was completely inhibited. Meanwhile, a methylthiyl radical (MeS·) trapping product **3** was observed through the LC-MS analysis of the reaction solution (Figure S1).

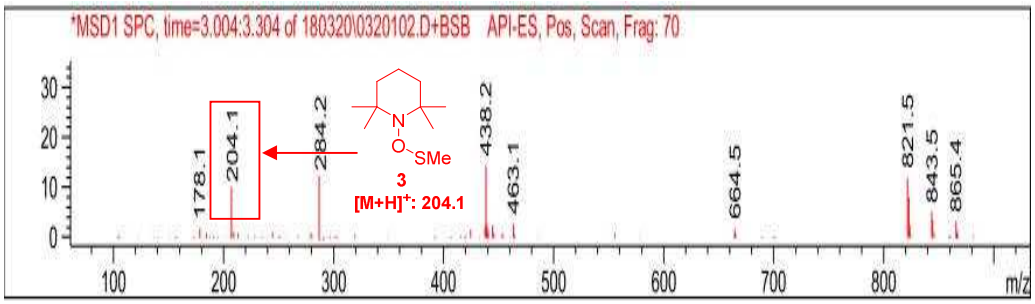
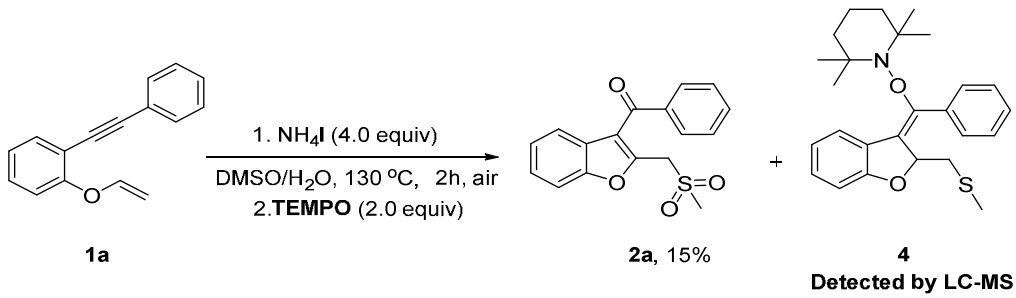


Figure S1. LC-MS analysis of the radical trapping product **3**.

1.2. Free radical-trapping experiment B



To a sealed tube were added 1,6-enyne **1a** (0.2 mmol, 1.0 equiv), NH_4I (0.8 mmol, 4.0 equiv), DMSO (1.6 mL) and H_2O (0.4 mL). The reaction mixture was stirred at 130 °C for 2 h and then TEMPO (0.4 mmol, 2.0 equiv) was added under air atmosphere. The reaction was continued for 12 h. After the reaction was stopped, the desired product **2a** was separated in 15% yields.

Meanwhile, a radical trapping product **4** was observed through LC-MS analysis of the reaction solution (Figure S2).

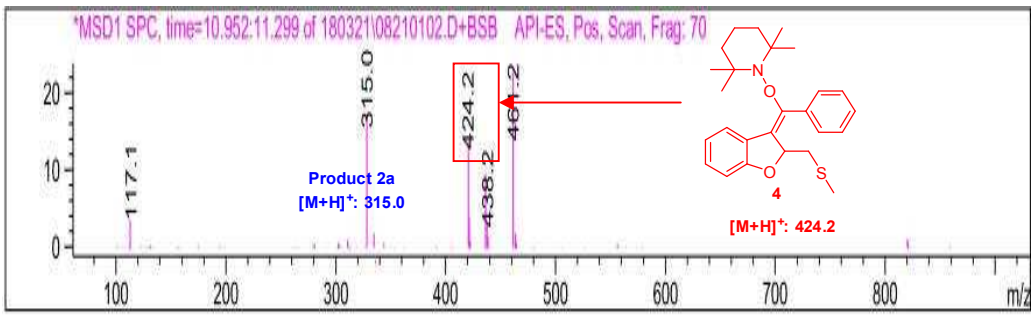
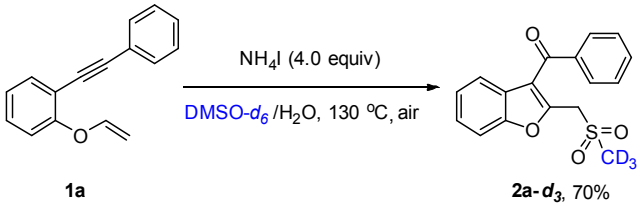


Figure S2. LC-MS analysis of the radical trapping product **4**.

1.3. The isotopic labeling experiments



The isotopic labeling experiment was performed according to the general procedure for the preparation of **2a** except changing DMSO to DMSO-d_6. The desired product **2a-*d*$_3$** was obtained in 70% yield (Figure S3).

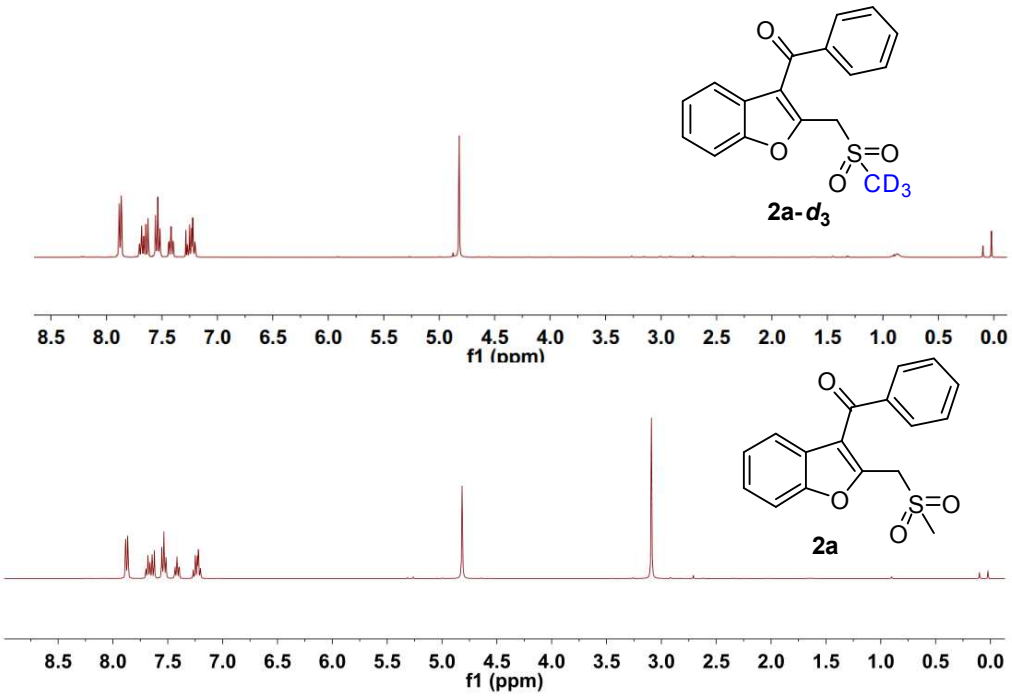
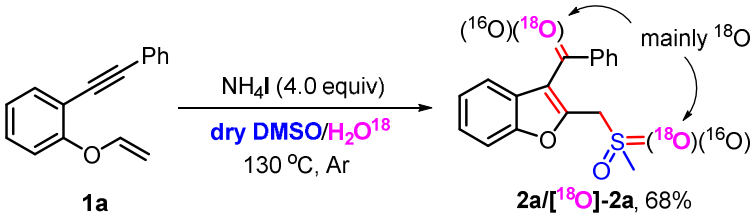


Figure S3. ^{1}H NMR analysis of **2a** and **2a-*d*$_3$**.

1.4. H_2O^{18}-isotope labeling experiment



To identify the source of oxygen in product **2a**, ^{18}O-labeling experiment was performed using H_2O^{18} under the standard condition, and the subsequent GC-MS analysis revealed that the ^{18}O-labelled **2a** was the main product (Figure S4).

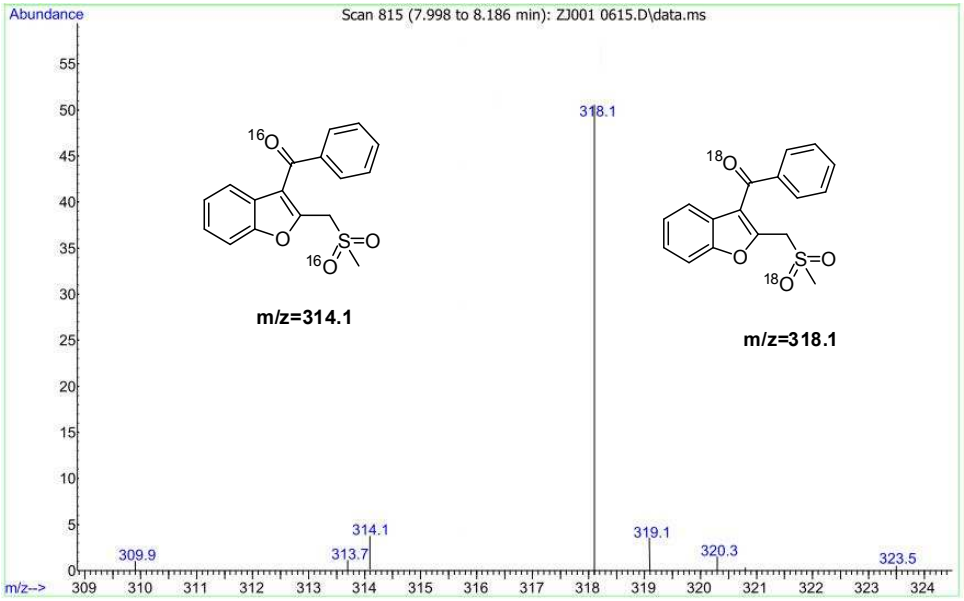
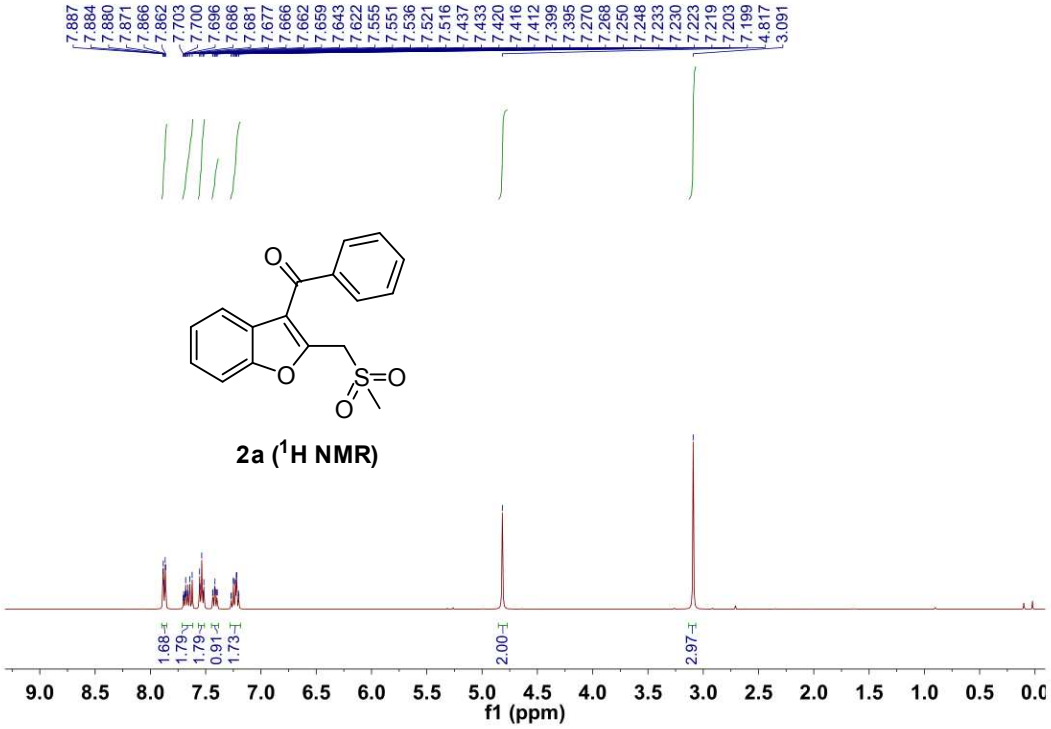
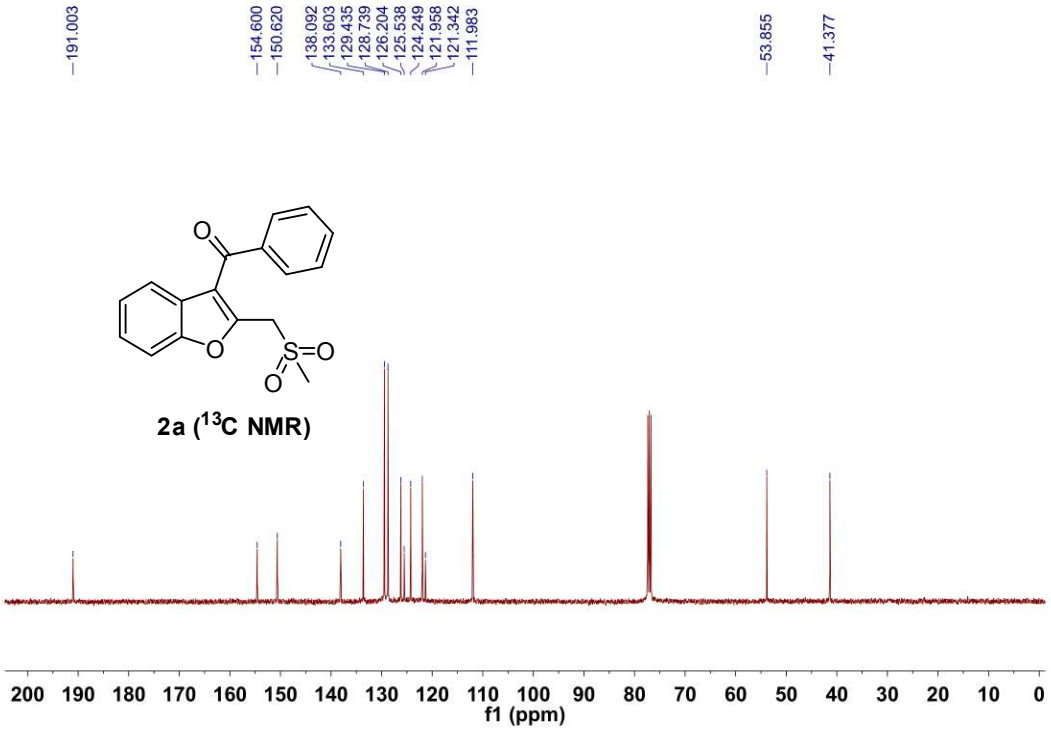


Figure S4. GC-MS analysis of ^{18}O-labelled product **2a**.

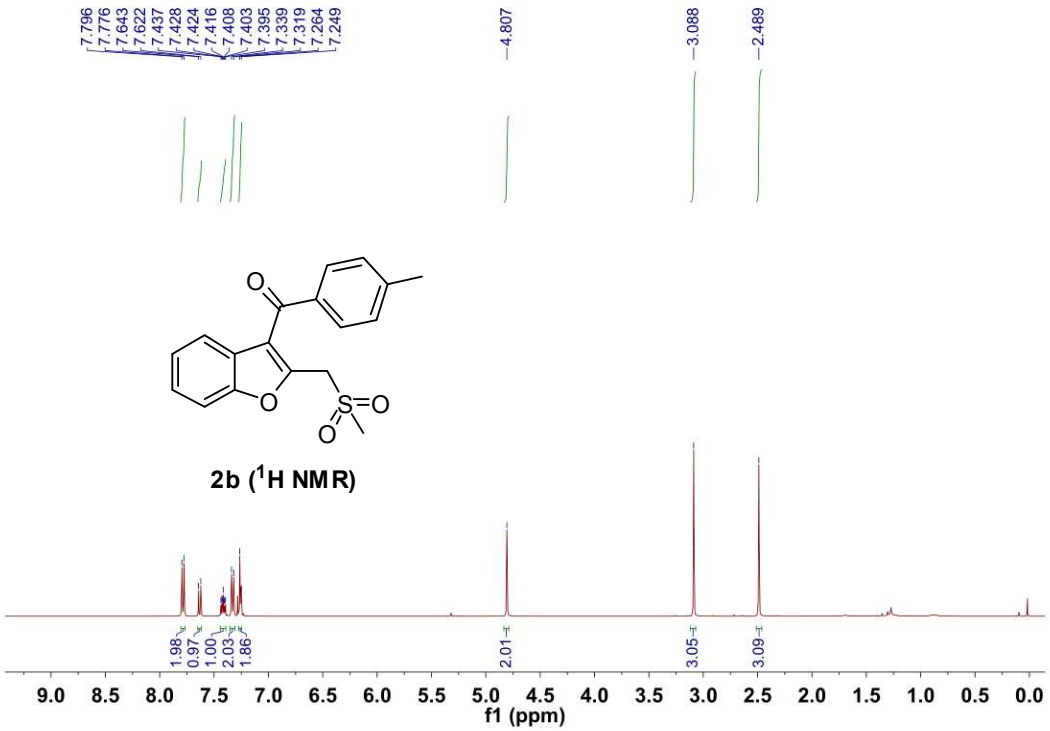
2. ^{1}H and ^{13}C NMR spectra of the products 2



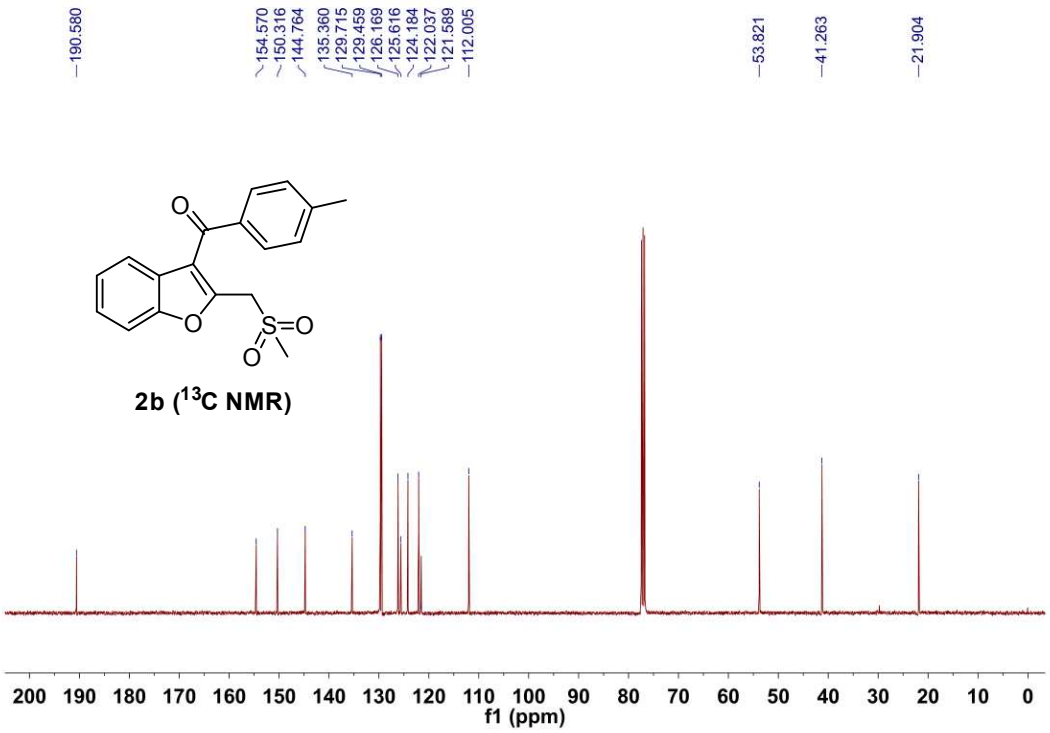
2a (^{1}H NMR)



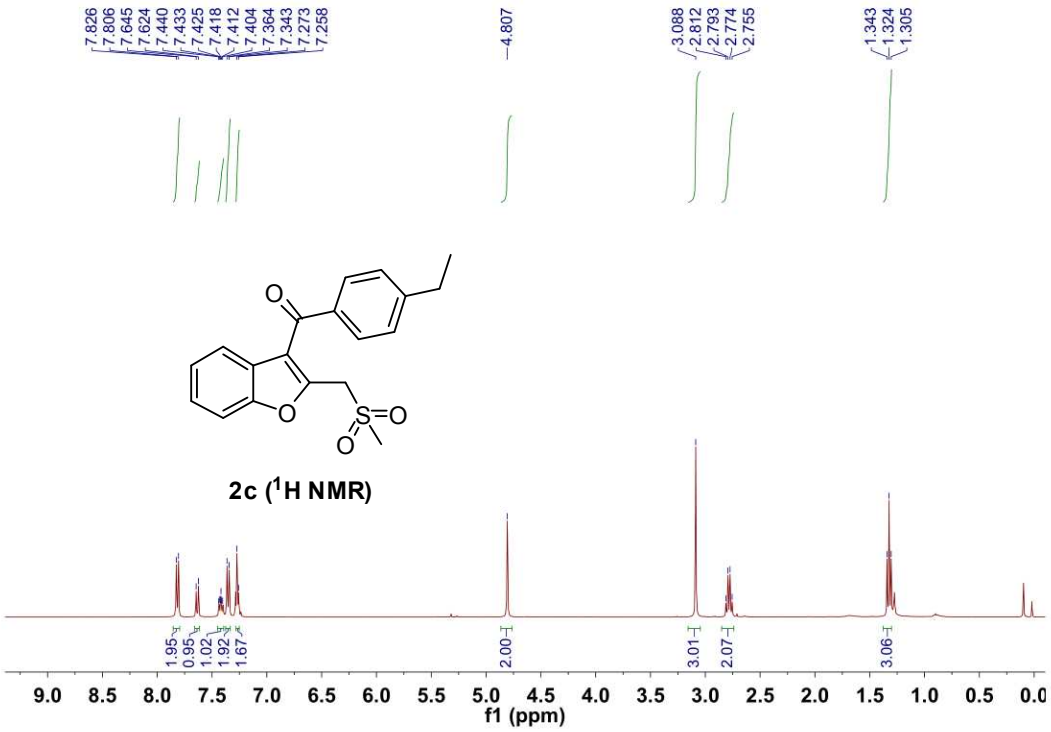
2a (^{13}C NMR)



2b (^{1}H NMR)



2b (^{13}C NMR)



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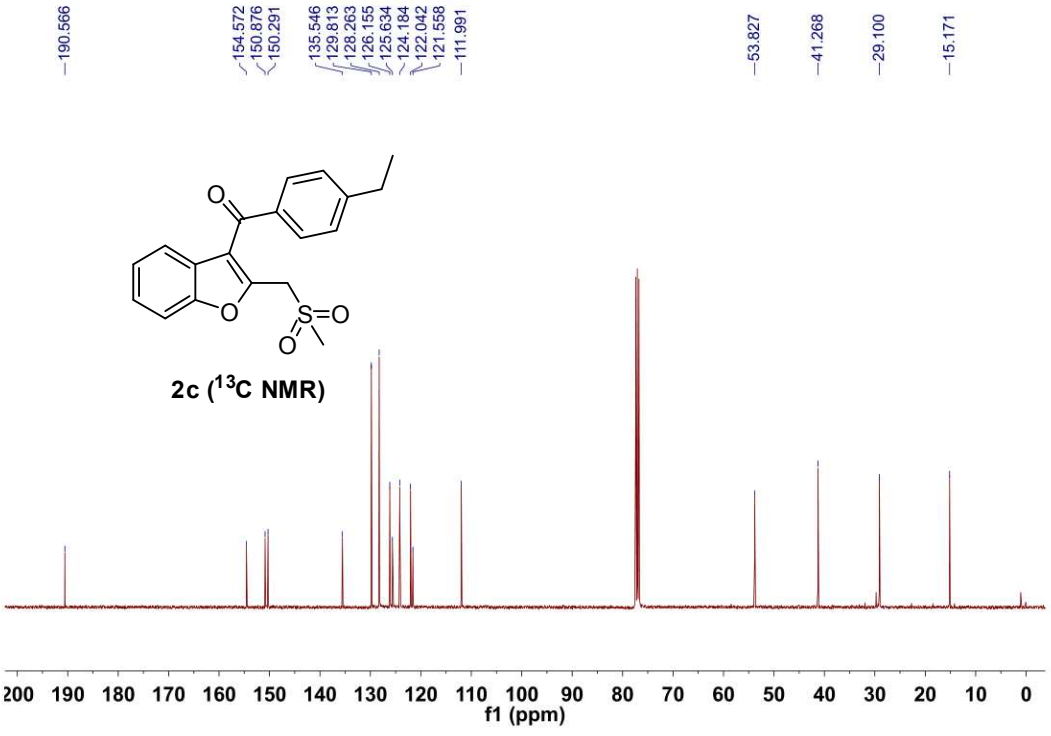

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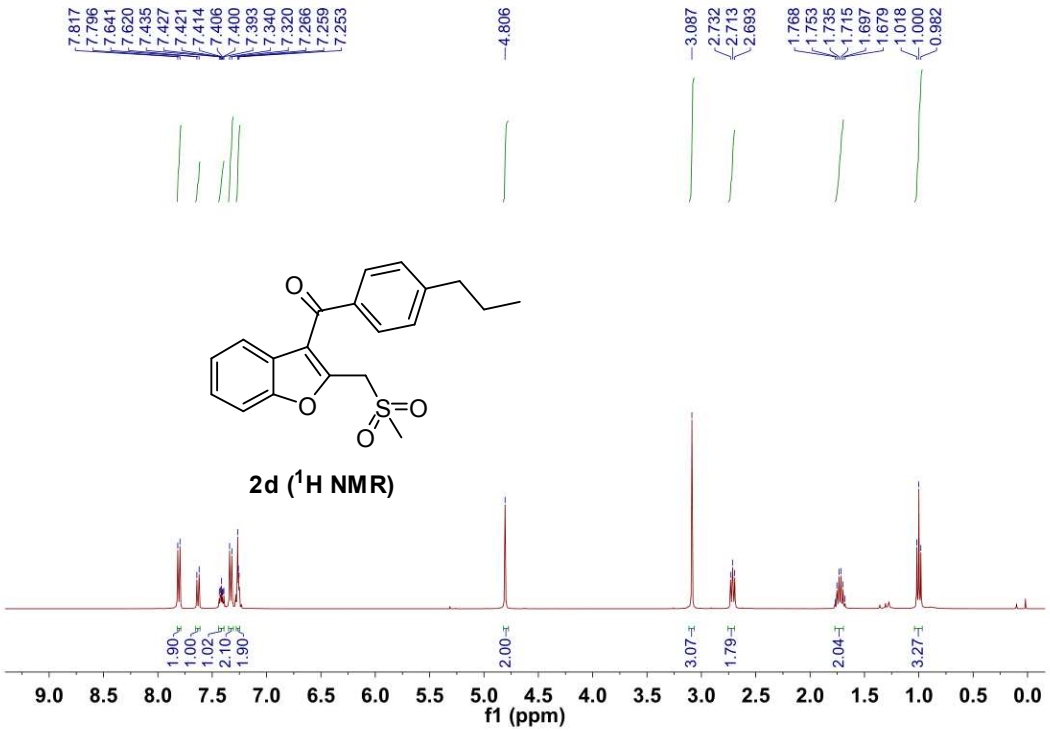

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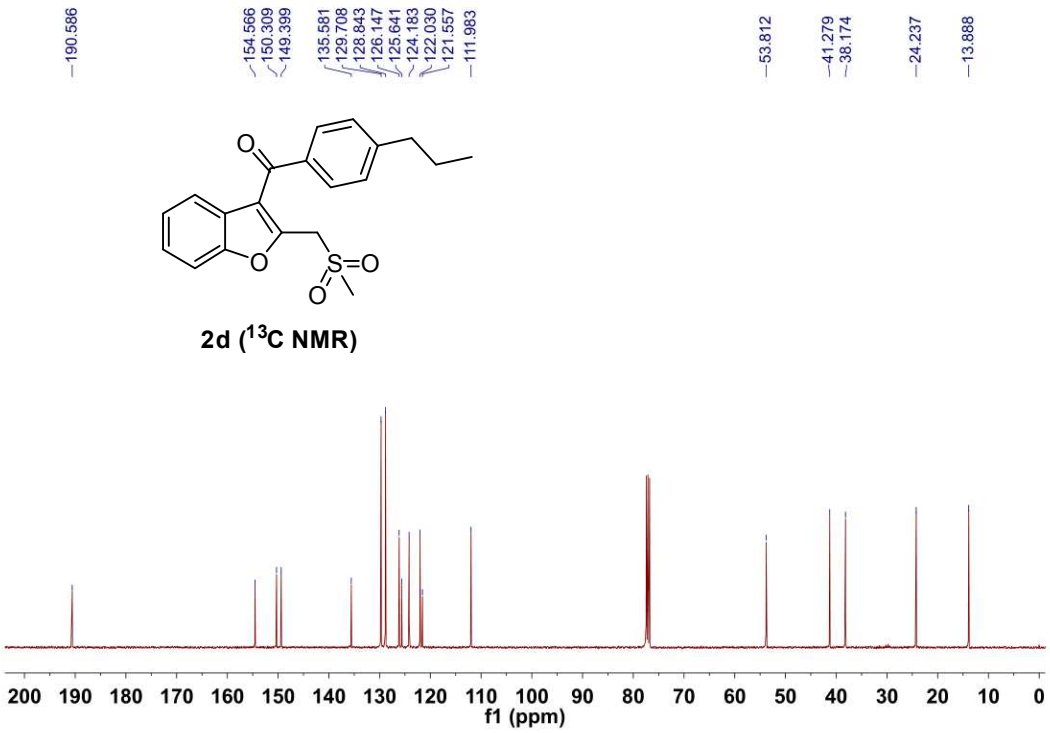

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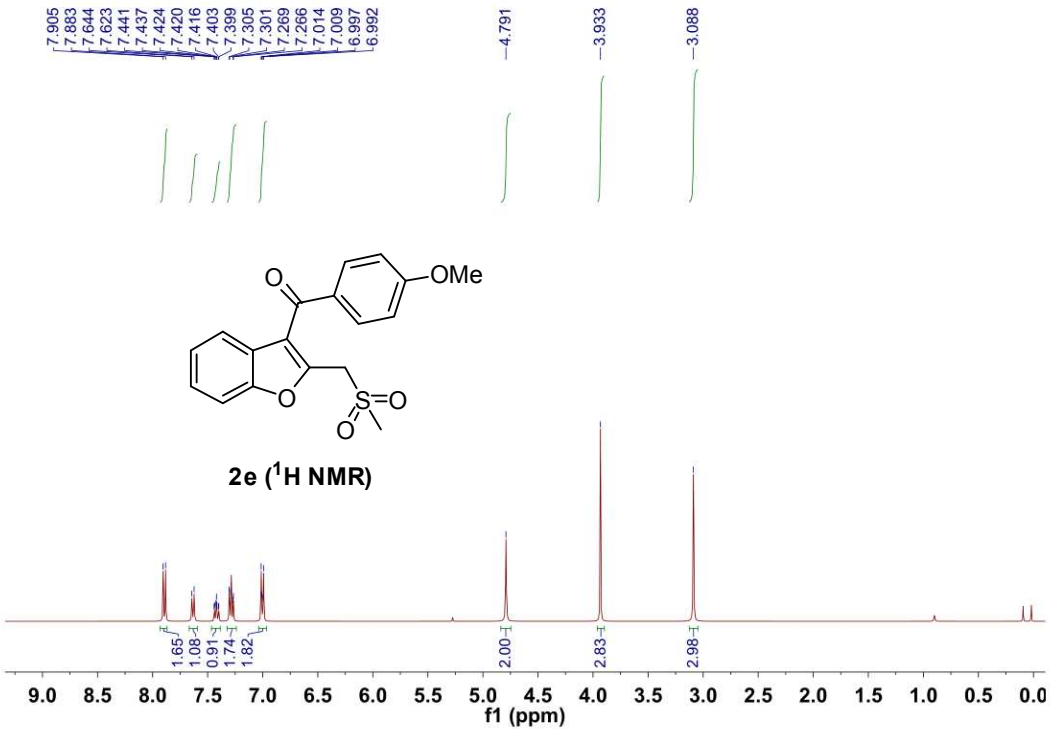

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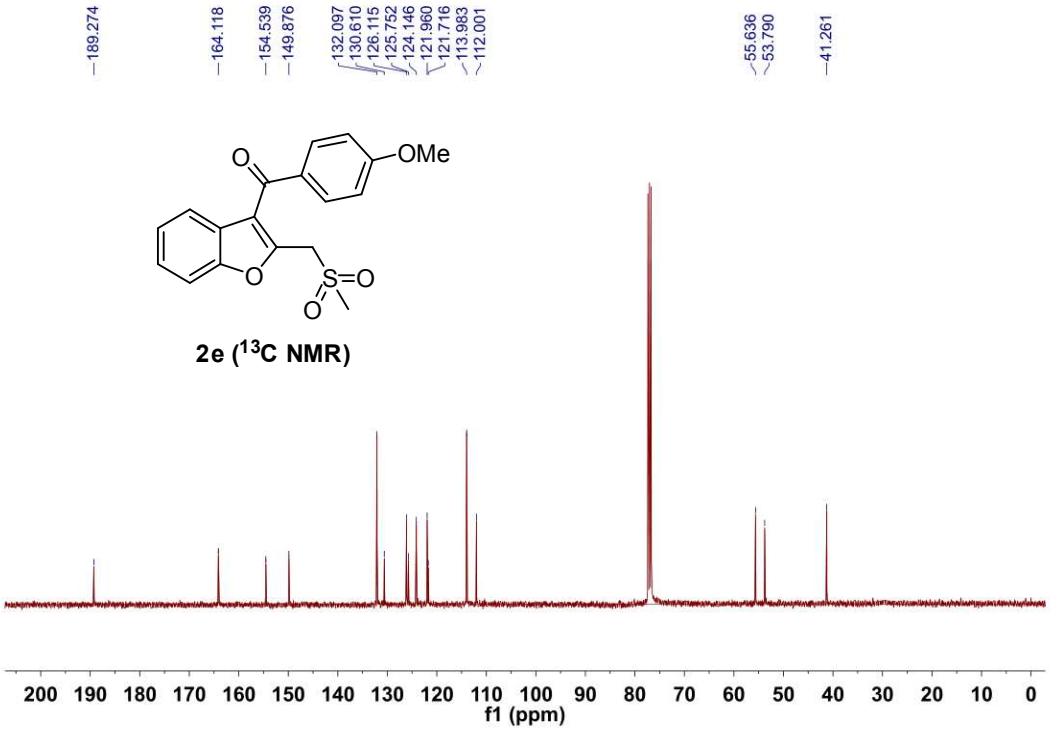

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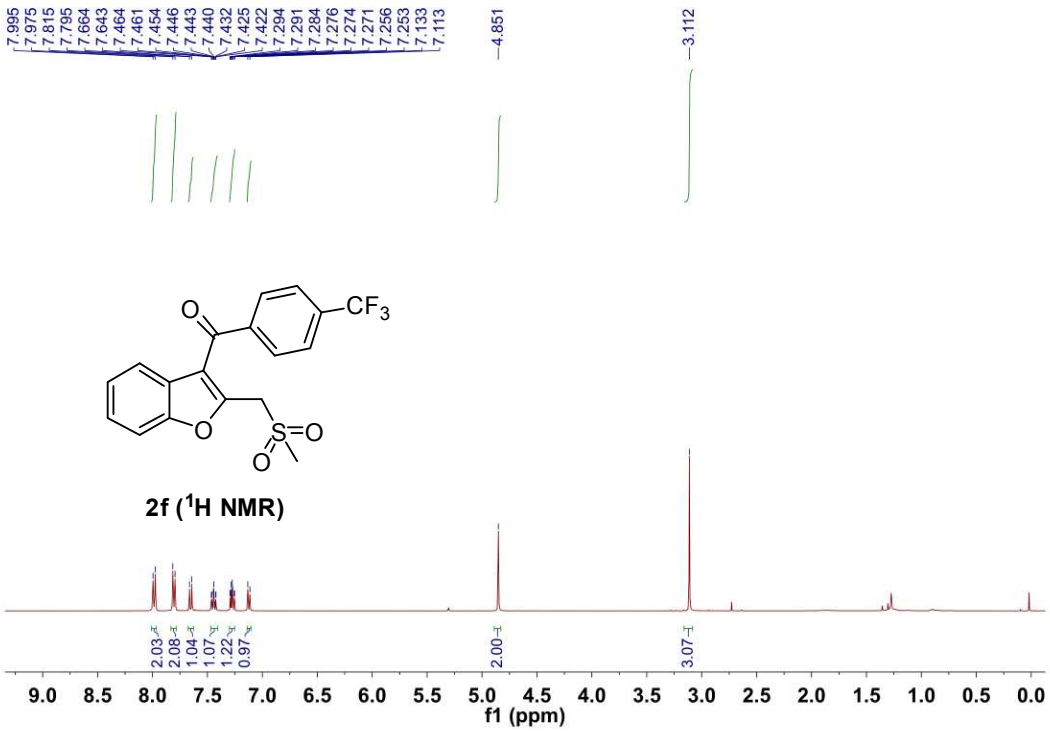
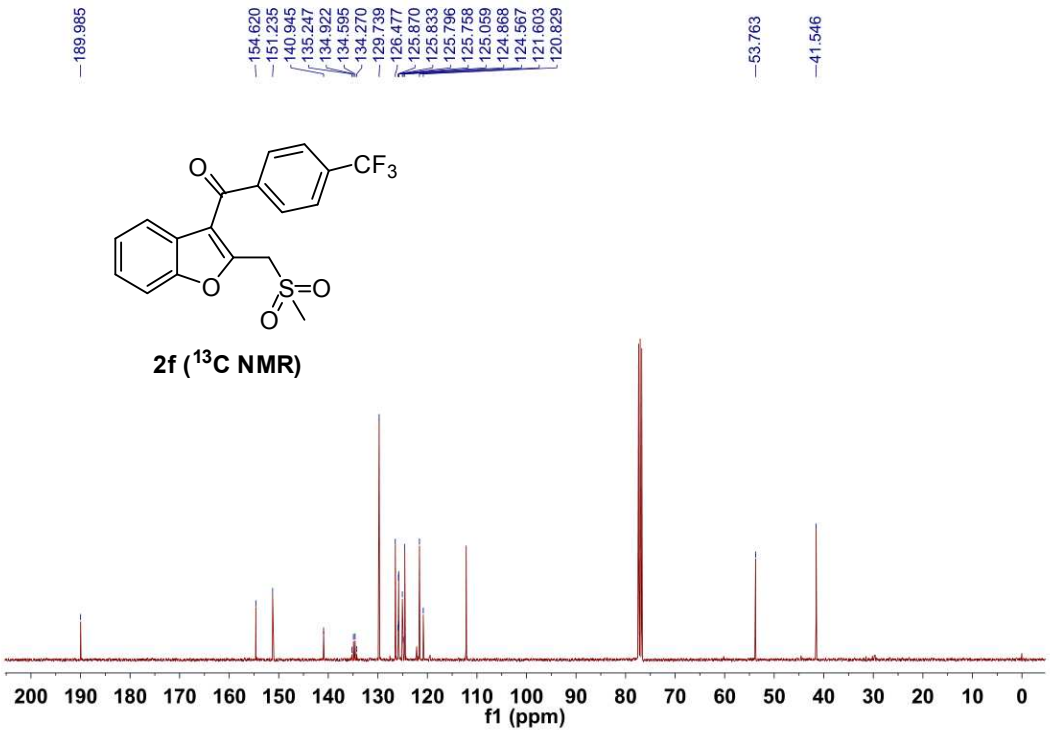


2f (^{1}H NMR)



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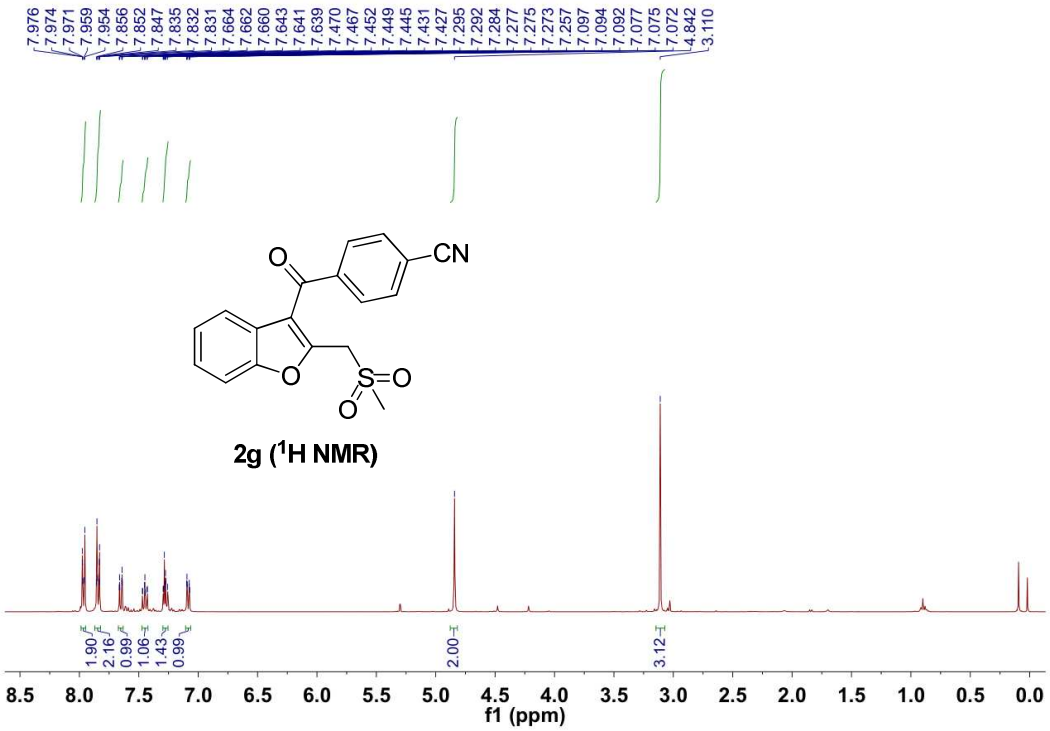

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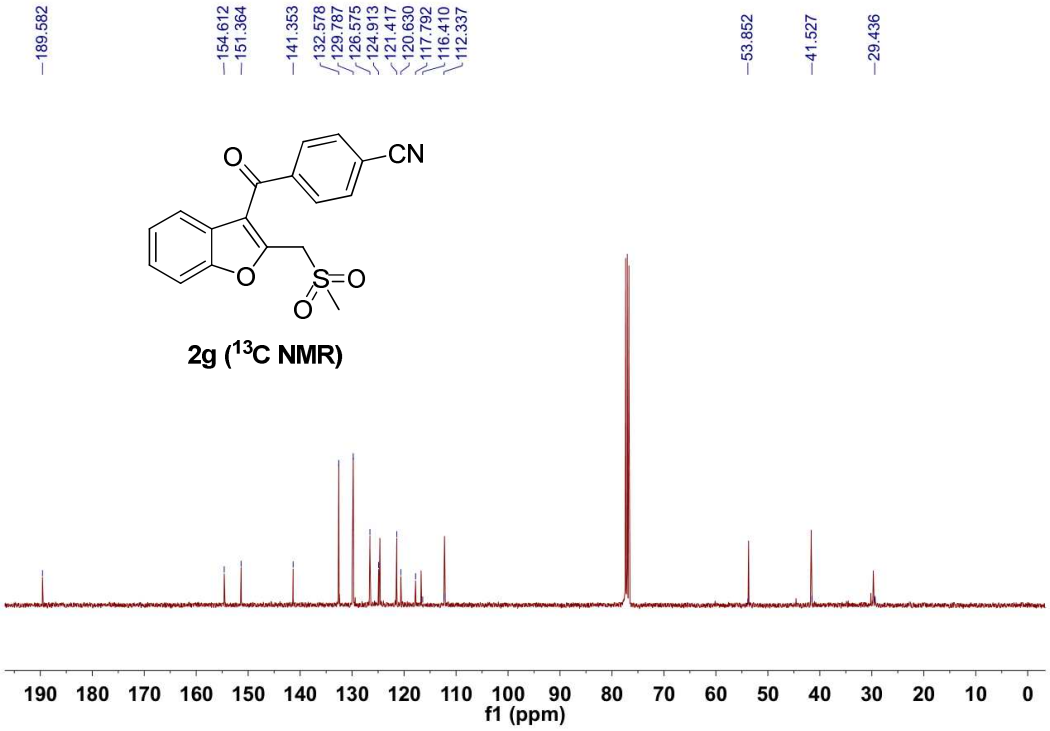
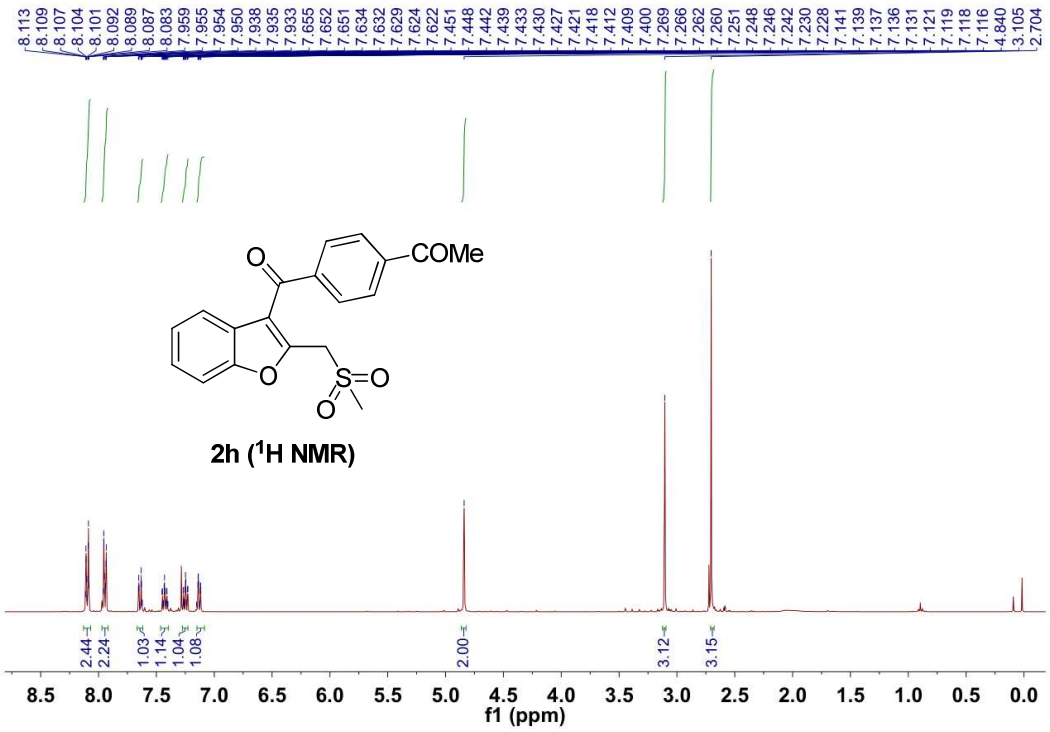


2g (^{13}C NMR)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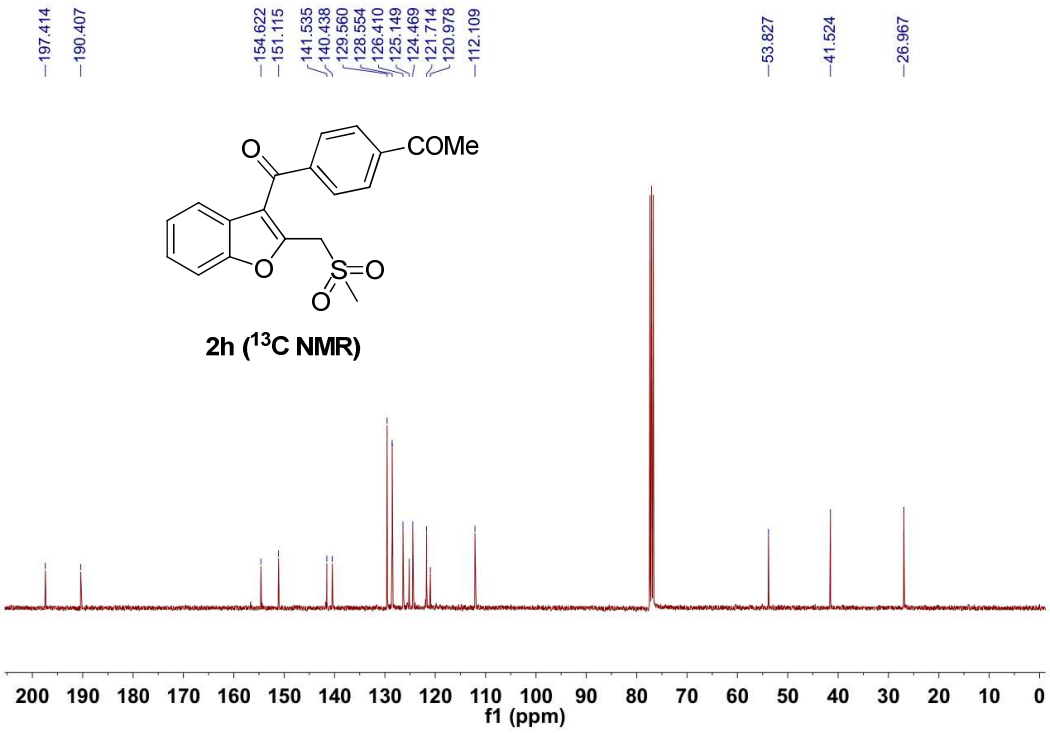
8.109
8.107
8.104
8.101
8.092
8.089
8.087
8.083
7.959
7.955
7.954
7.950
7.938
7.935
7.933
7.655
7.652
7.651
7.634
7.632
7.629
7.624
7.622
7.451
7.448
7.442
7.439
7.433
7.430
7.427
7.421
7.418
7.412
7.409
7.400
7.269
7.266
7.262
7.260
7.251
7.248
7.246
7.242
7.230
7.228
7.141
7.139
7.137
7.136
7.131
7.121
7.119
7.118
7.116
4.840
3.105
2.704
O
COMe
O
S=O
O
2h (1H NMR)
2.44
2.24
1.03
1.14
1.04
1.08
2.00
3.12
3.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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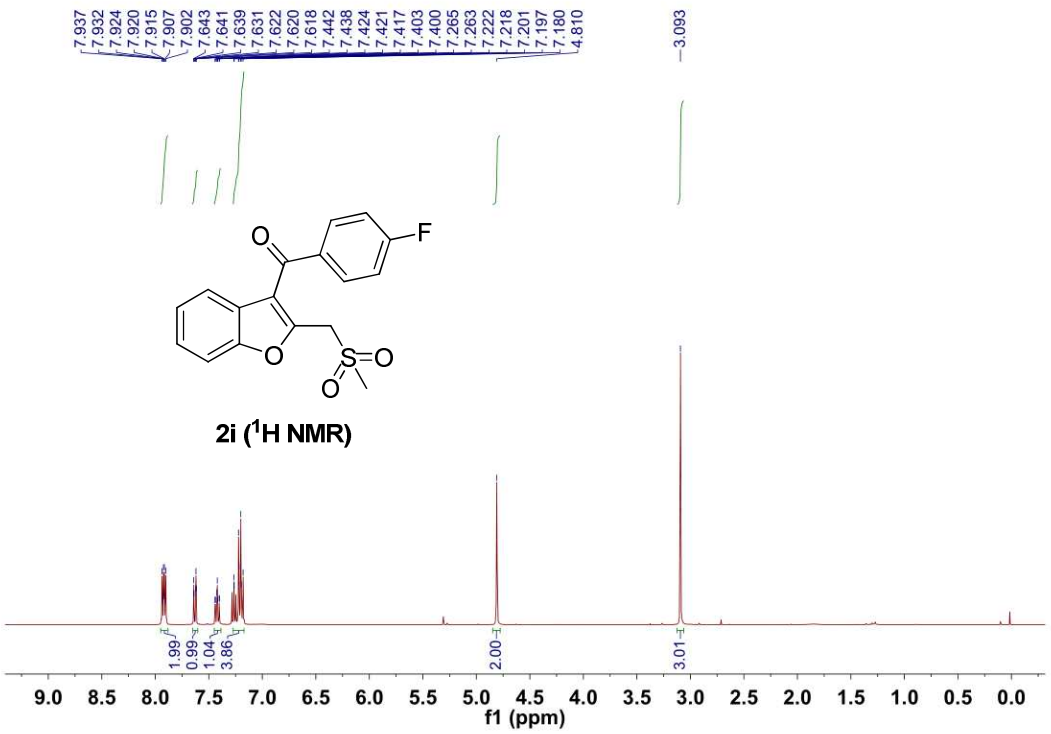
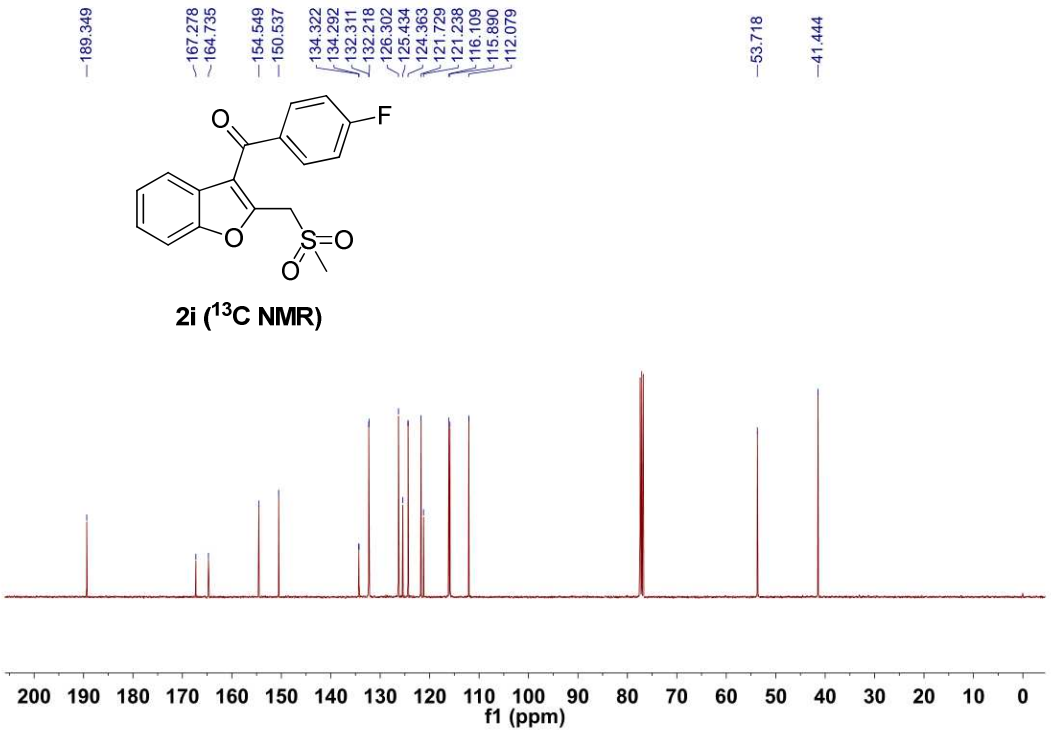
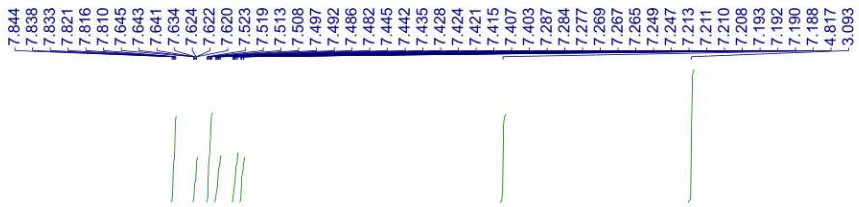
154.622
151.115
141.535
140.438
129.560
128.554
126.410
125.149
124.469
121.714
120.978
112.109
53.827
41.524
26.967
O
COMe
O
S=O
O
2h (13C NMR)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

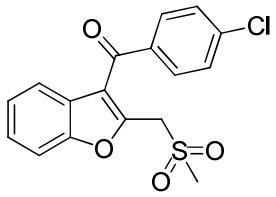


2i (^{1}H NMR)

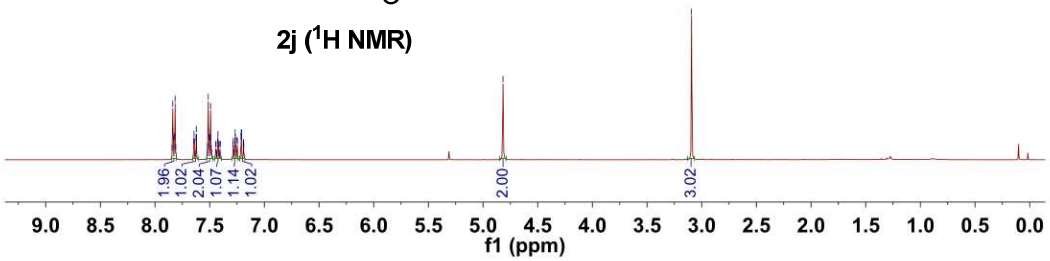


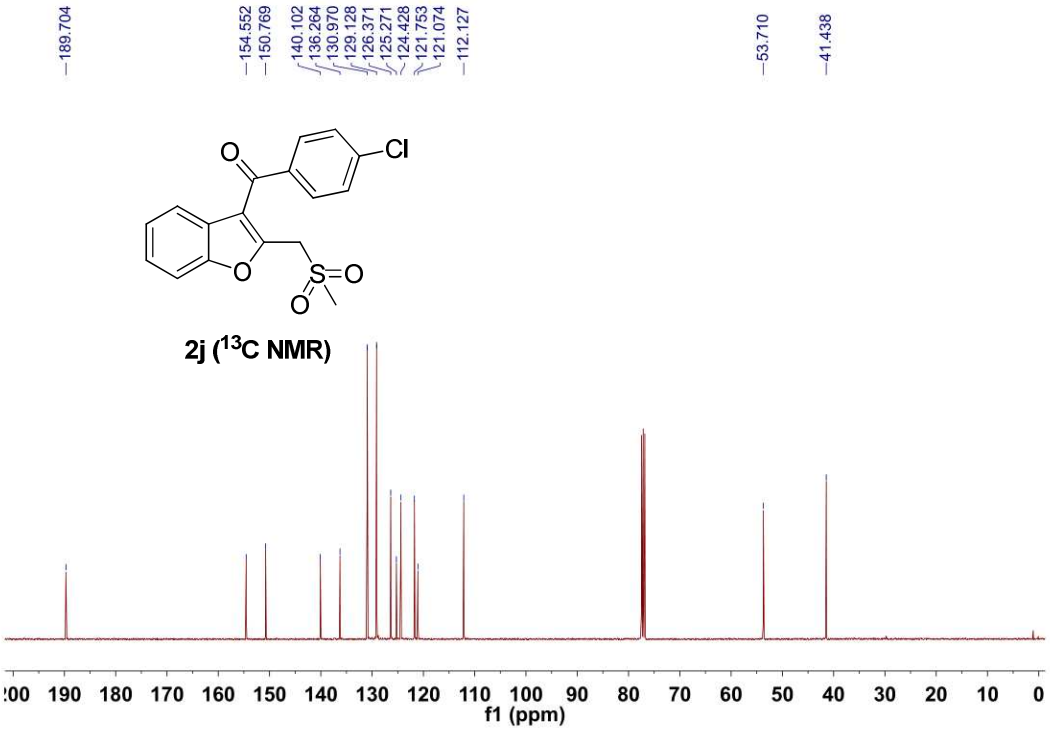
2i (^{13}C NMR)





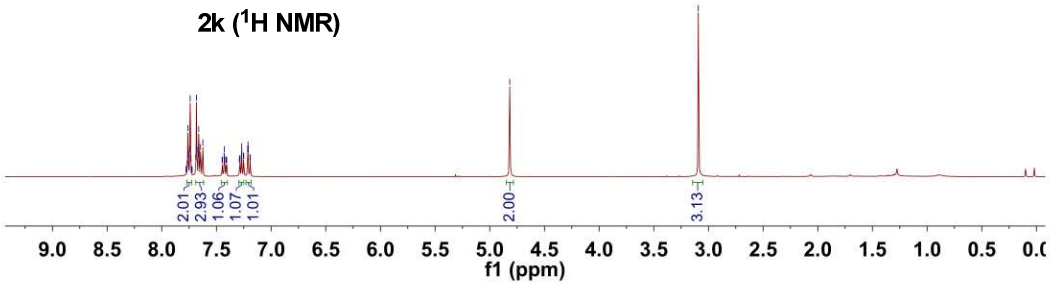
2j (^{1}H NMR)

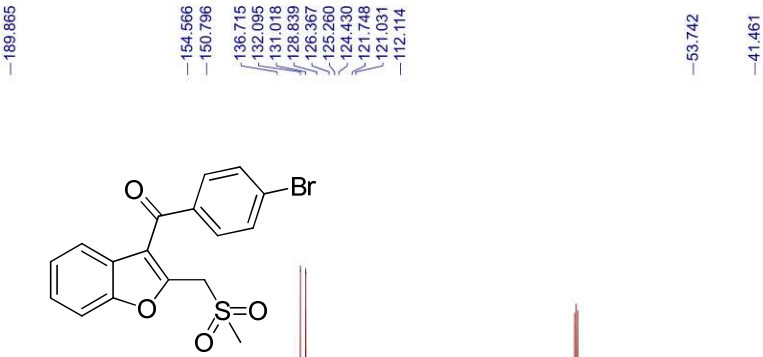




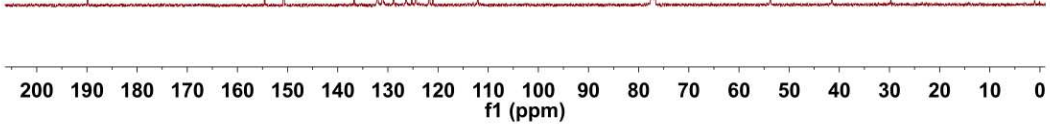
2j (^{13}C NMR)

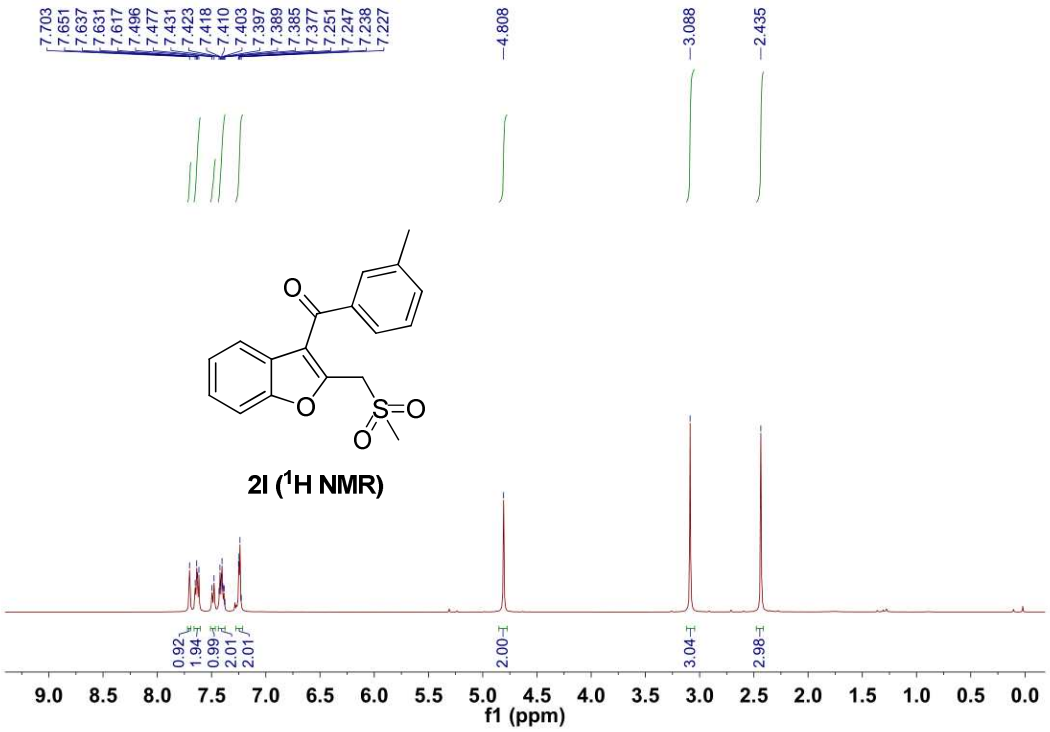
2k (^{1}H NMR)



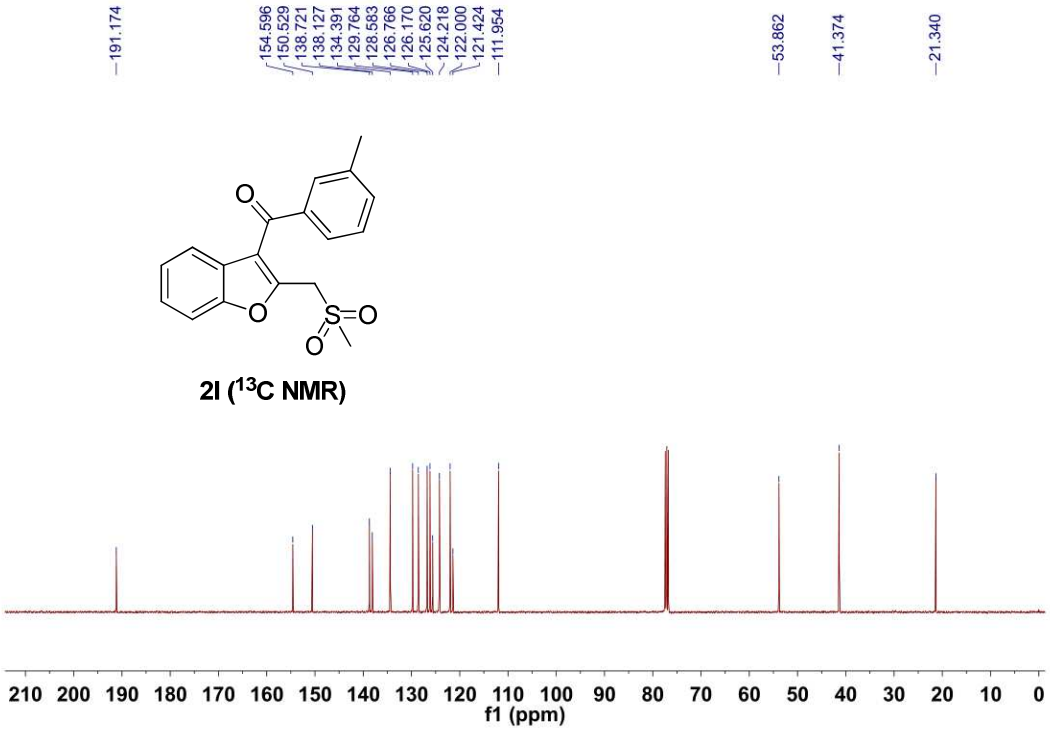


2k (^{13}C NMR)

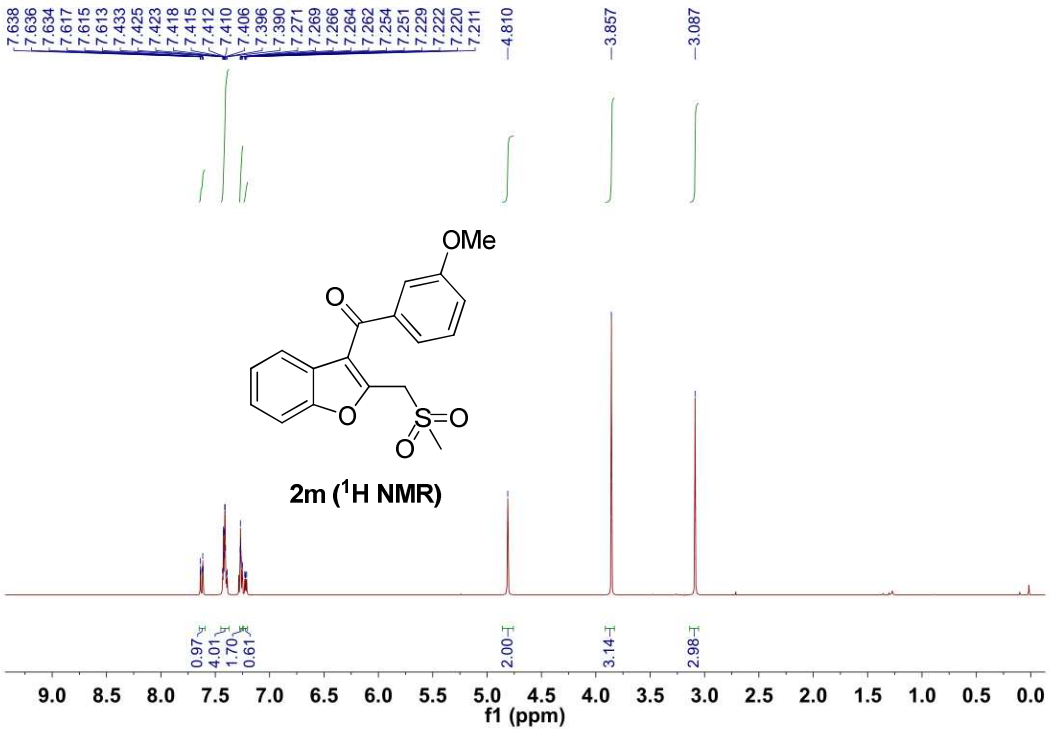




2l (^{1}H NMR)



2l (^{13}C NMR)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7.634
7.617
7.615
7.613
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7.423
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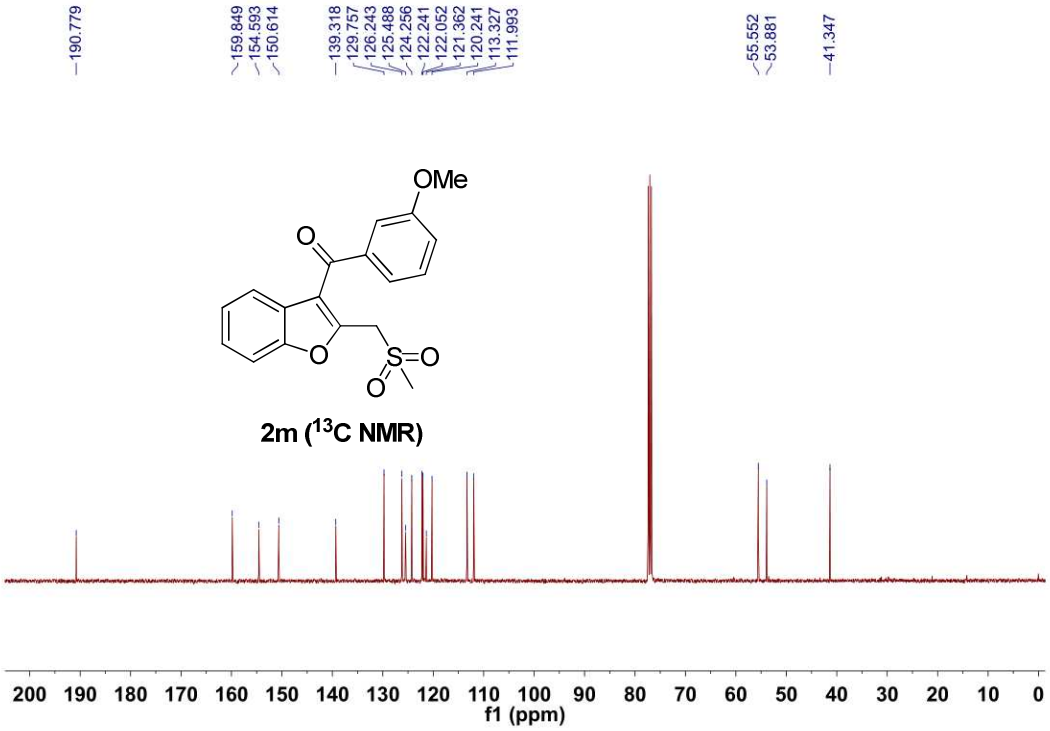
7.410
7.406
7.396
7.390
7.271
7.269
7.266
7.264
7.262
7.254
7.251
7.229
7.222
7.220
7.211
4.810
3.857
3.087
OMe
O
O
S=O
O
2m (1H NMR)
0.97
4.01
1.70
0.61
2.00
3.14
2.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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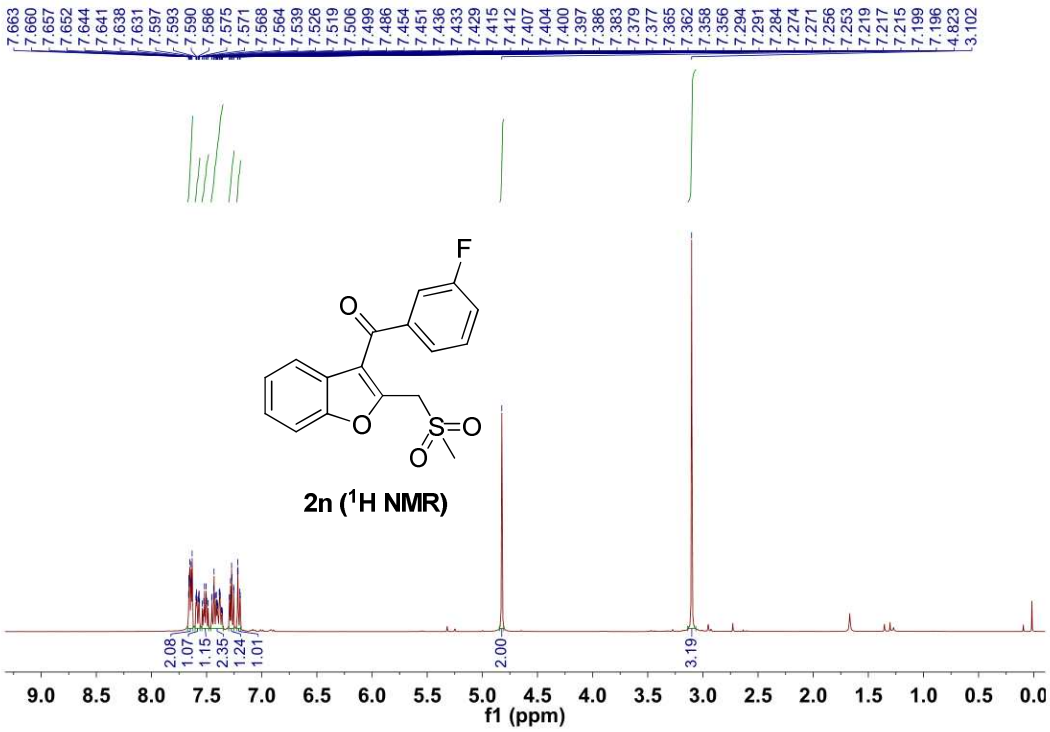
139.318
129.757
126.243
125.488
124.256
122.241
122.052
121.362
120.241
113.327
111.993
55.552
53.881
41.347
OMe
O
O
S=O
O
2m (13C NMR)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.652
7.644
7.641
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7.575
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7.539
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7.429
7.415
7.412
7.407
7.404
7.400
7.397
7.386
7.383
7.379
7.377
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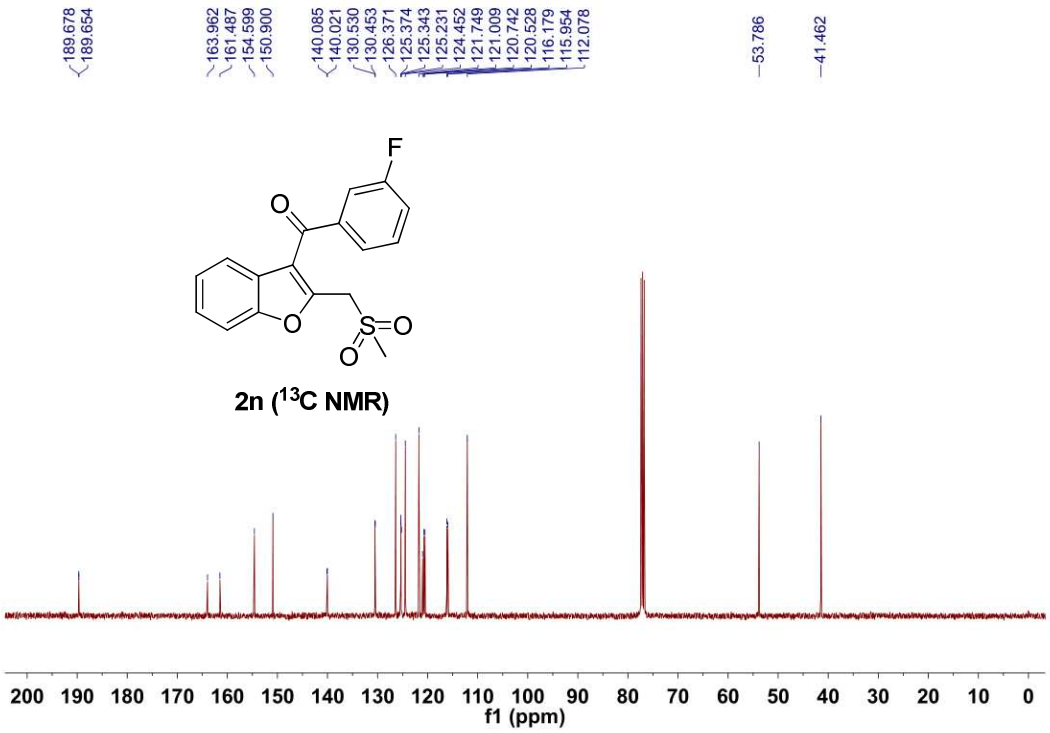
7.362
7.358
7.356
7.294
7.291
7.284
7.274
7.271
7.256
7.253
7.219
7.217
7.215
7.199
7.196
4.823
3.102
F
O
O
S=O
O
2n (1H NMR)
2.08
1.07
1.15
2.35
1.24
1.01
2.00
3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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161.487
154.599
150.900
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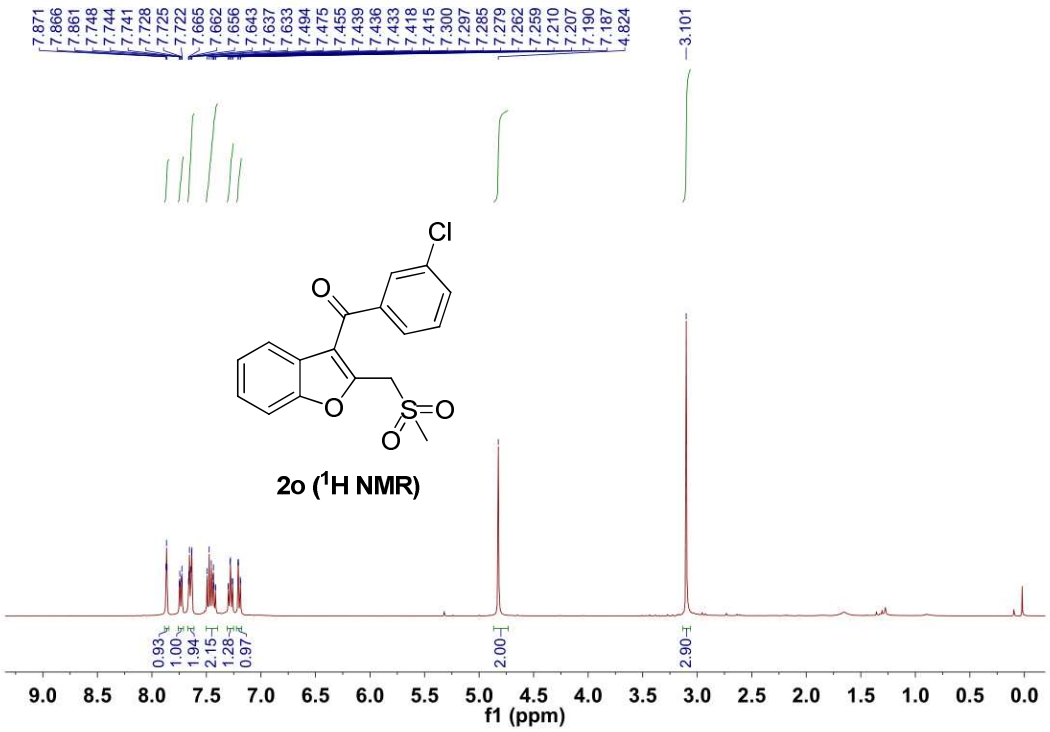
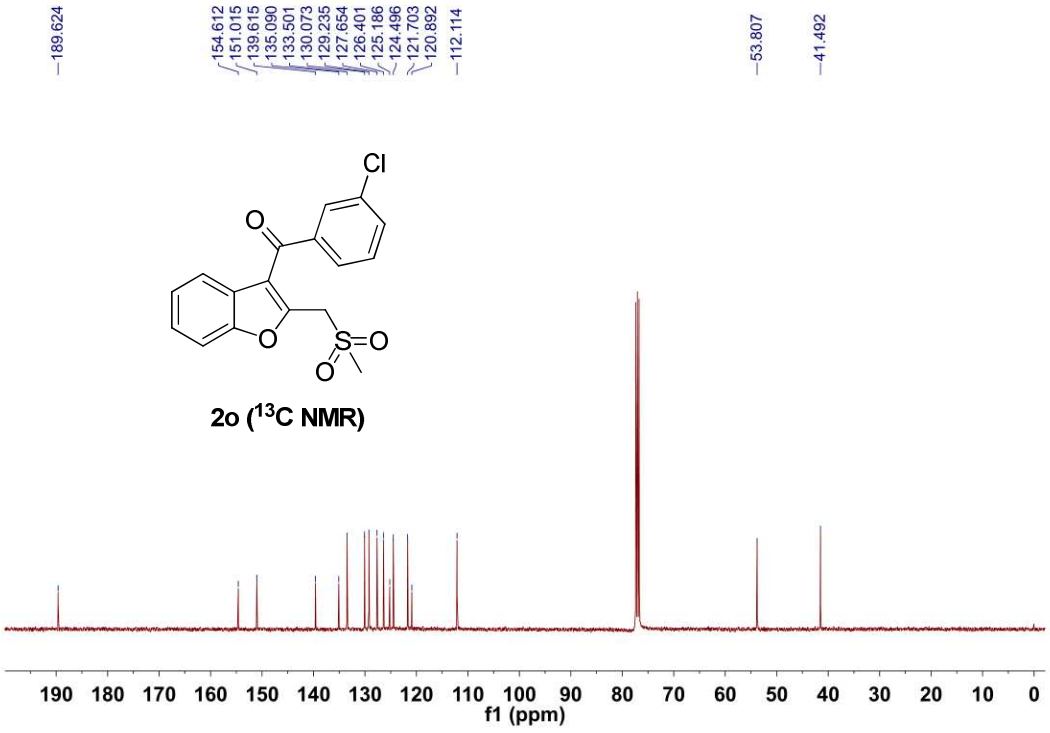
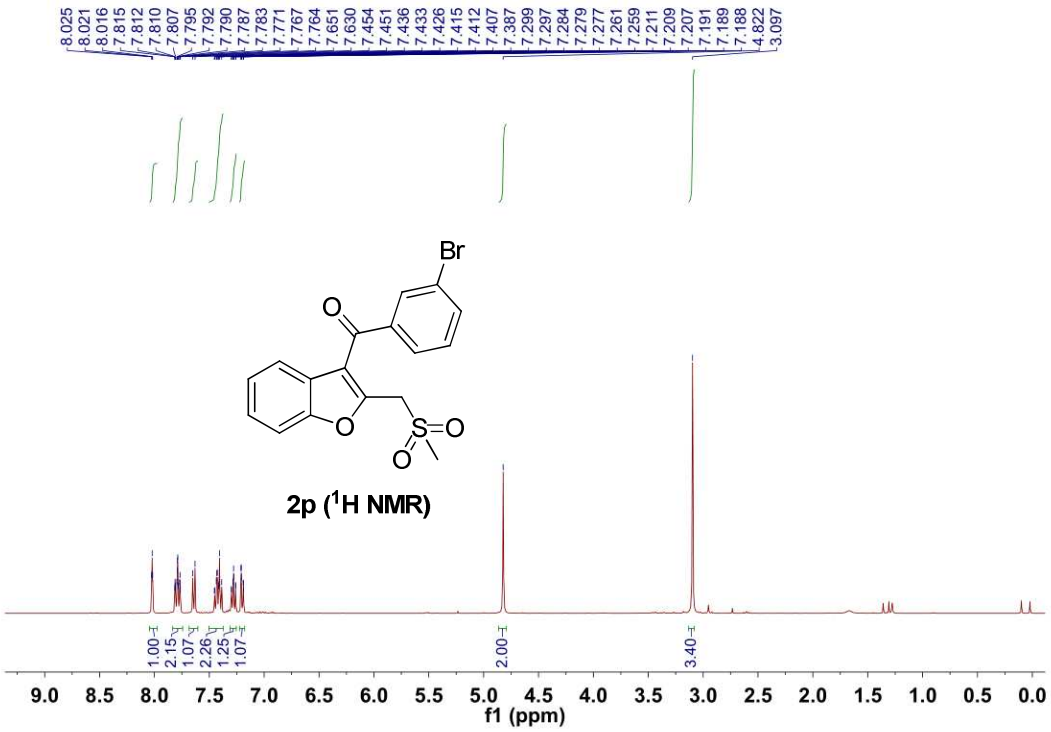
125.343
125.231
124.452
121.749
121.009
120.742
120.528
116.179
115.954
112.078
53.786
41.462
F
O
O
S=O
O
2n (13C NMR)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



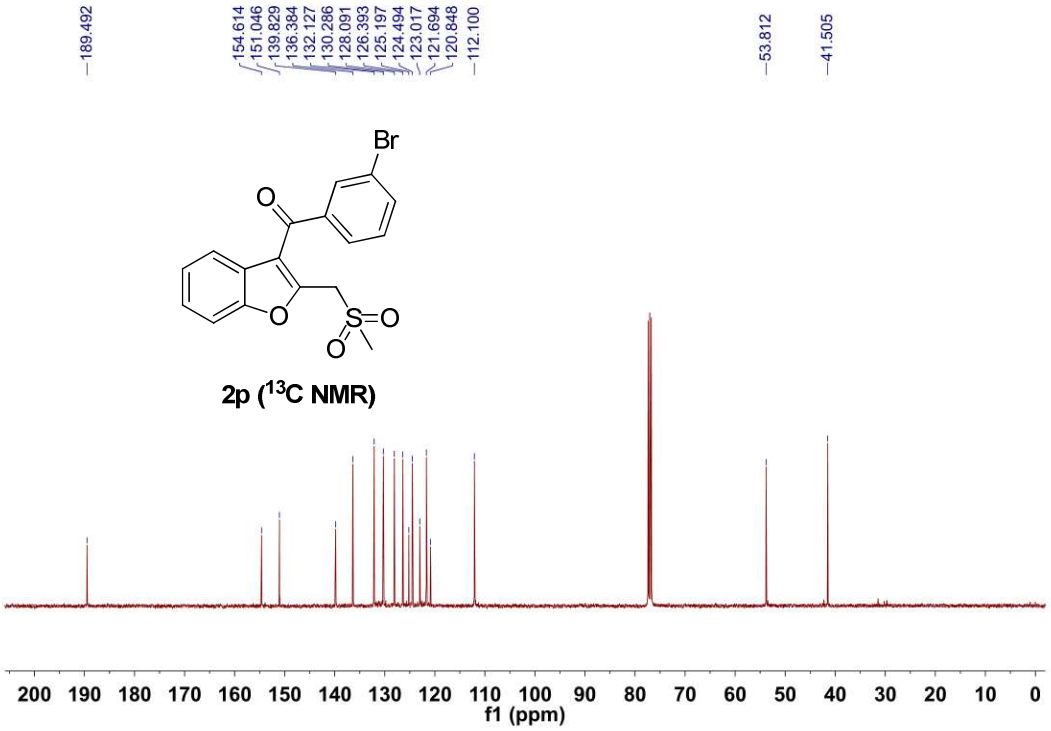
2o (^{1}H NMR)



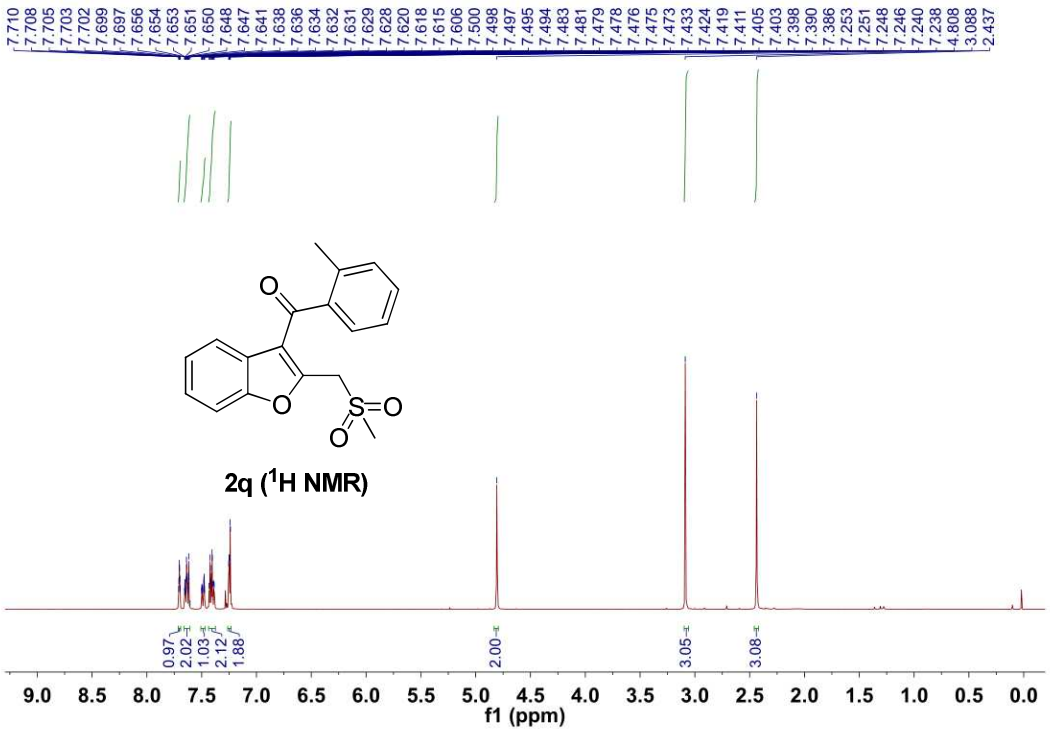
2o (^{13}C NMR)



2p (^{1}H NMR)



2p (^{13}C NMR)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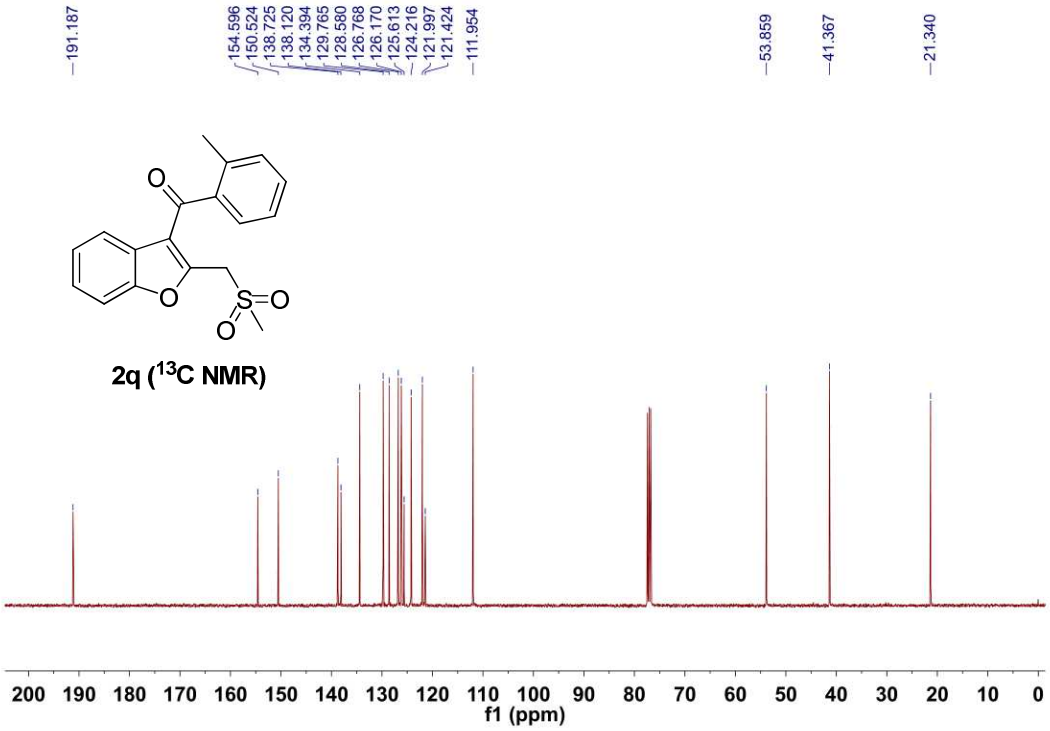
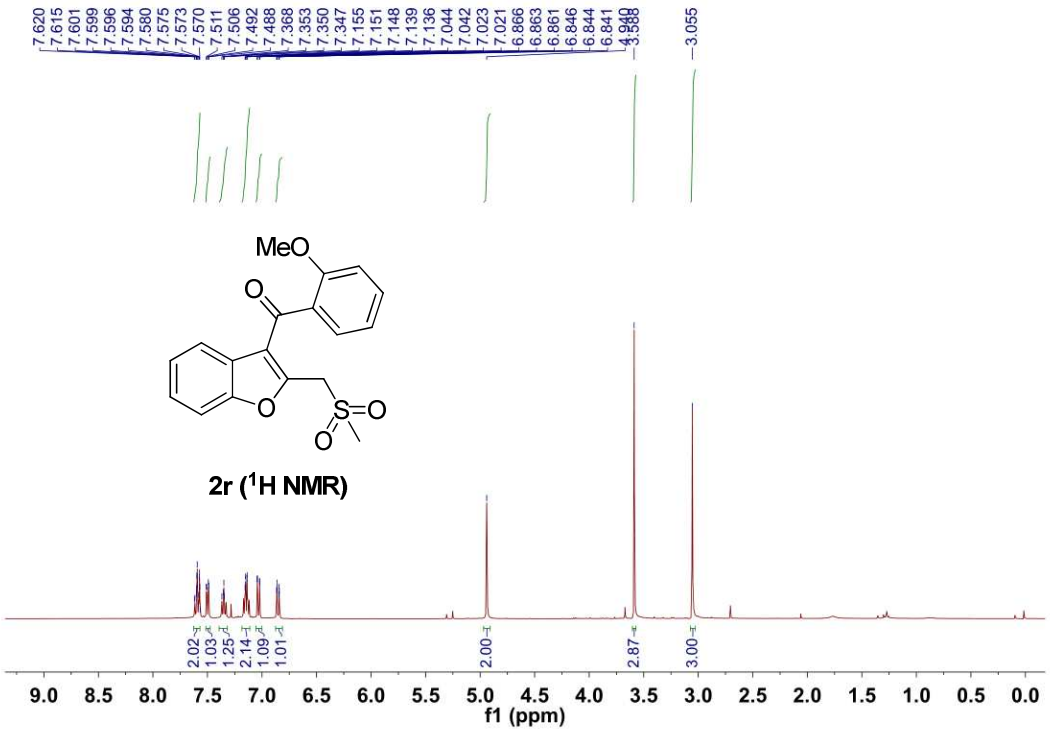
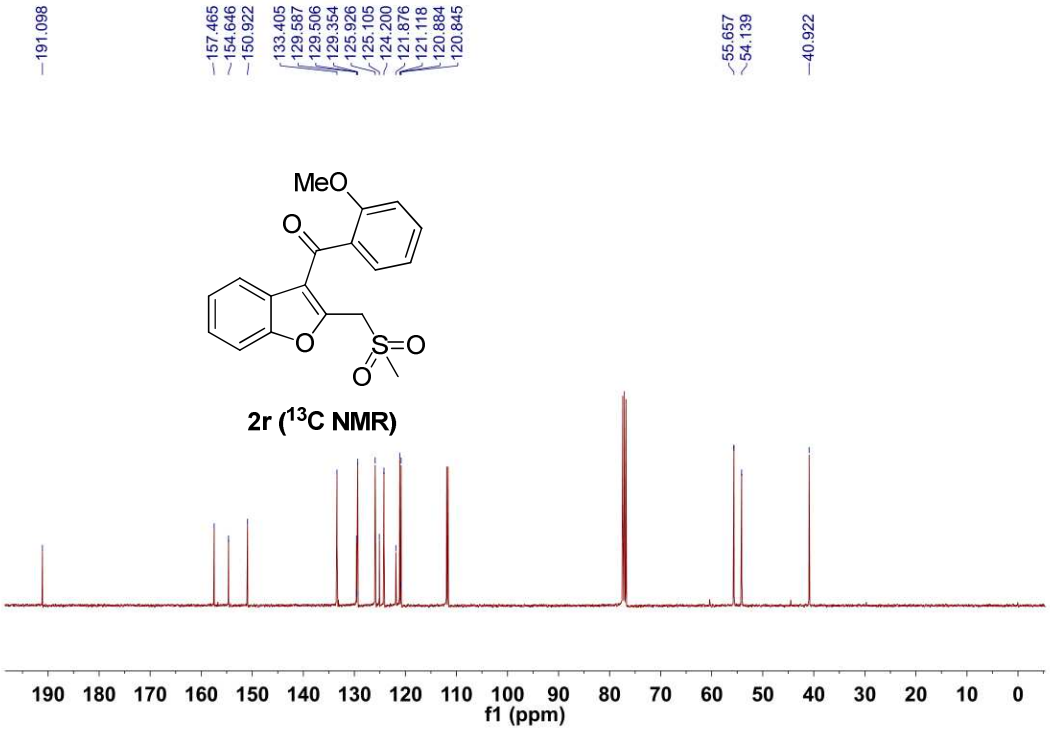
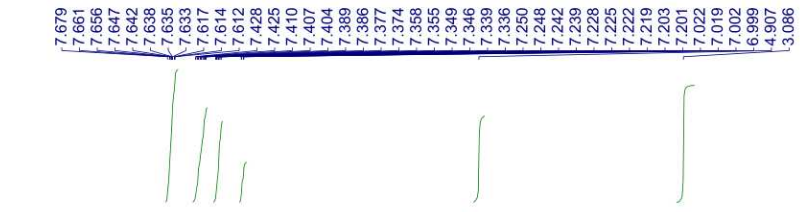
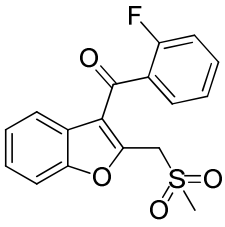
7.708
7.705
7.703
7.702
7.699
7.697
7.656
7.654
7.653
7.651
7.650
7.648
7.647
7.641
7.638
7.636
7.634
7.632
7.631
7.629
7.628
7.620
7.618
7.615
7.606
7.500
7.498
7.497
7.495
7.494
7.483
7.481
7.479
7.478
7.476
7.475
7.473
7.433
7.424
7.419
7.411
7.405
7.403
7.398
7.390
7.386
7.253
7.251
7.248
7.246
7.240
7.238
4.808
3.088
2.437
O
O
S
O
O
2q (1H NMR)
0.97
2.02
1.03
2.12
1.88
2.00
3.05
3.08
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)


191.187
154.596
150.524
138.725
138.120
134.394
129.765
128.580
126.768
126.170
125.613
124.216
121.997
121.424
111.954
53.859
41.367
21.340
O
O
S
O
O
2q (13C NMR)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

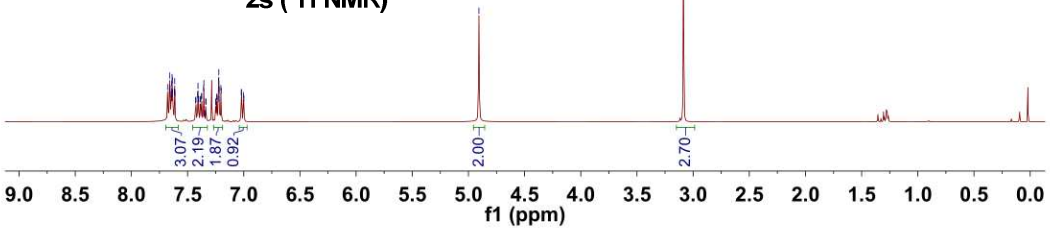

7.620
7.615
7.601
7.599
7.596
7.594
7.580
7.575
7.573
7.570
7.511
7.506
7.492
7.488
7.368
7.353
7.350
7.347
7.155
7.151
7.148
7.139
7.136
7.044
7.042
7.023
7.021
6.866
6.863
6.861
6.846
6.844
6.841
3.588
3.055
MeO
O
O
S=O
O
2r (1H NMR)
2.02
1.03
1.25
2.14
1.09
1.01
2.00
2.87
3.00
9.0 8.5 8.0 7.5 7.0 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)

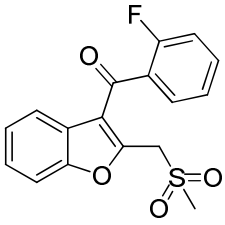

191.098
157.465
154.646
150.922
133.405
129.587
129.506
129.354
125.926
125.105
124.200
121.876
121.118
120.884
120.845
55.657
54.139
40.922
MeO
O
O
S=O
O
2r (13C NMR)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



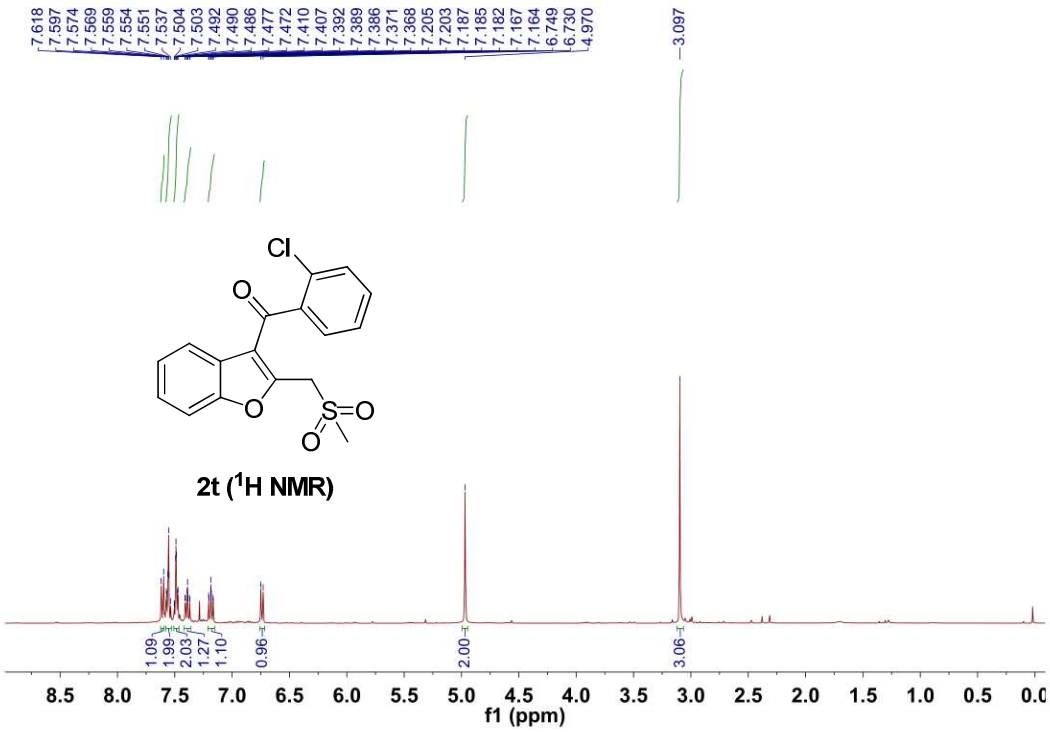


2s (^{1}H NMR)

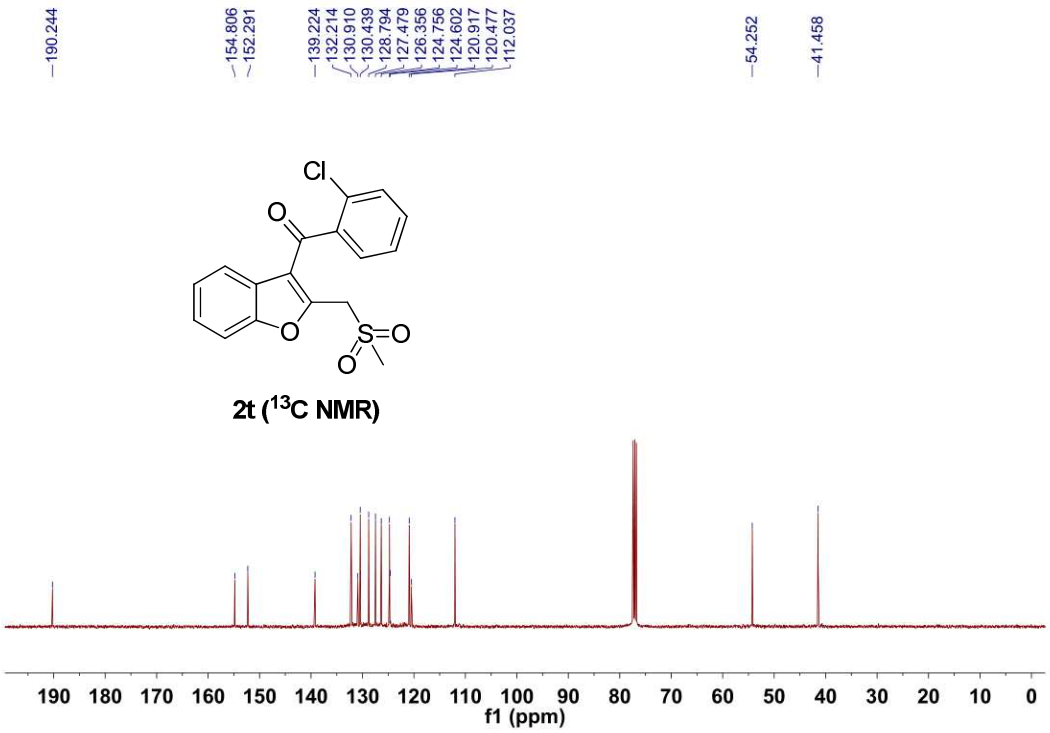




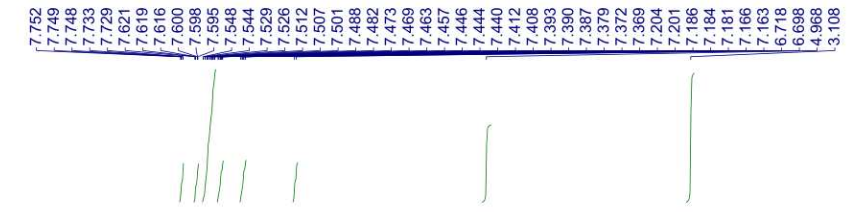
2s (^{13}C NMR)

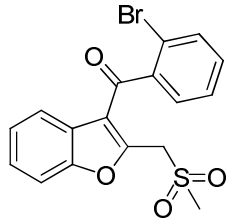


2t (^{1}H NMR)

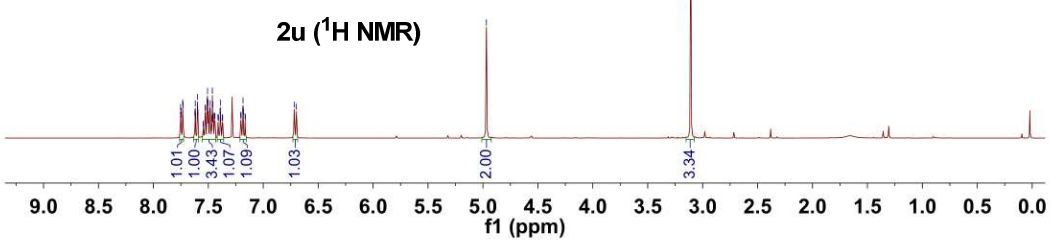


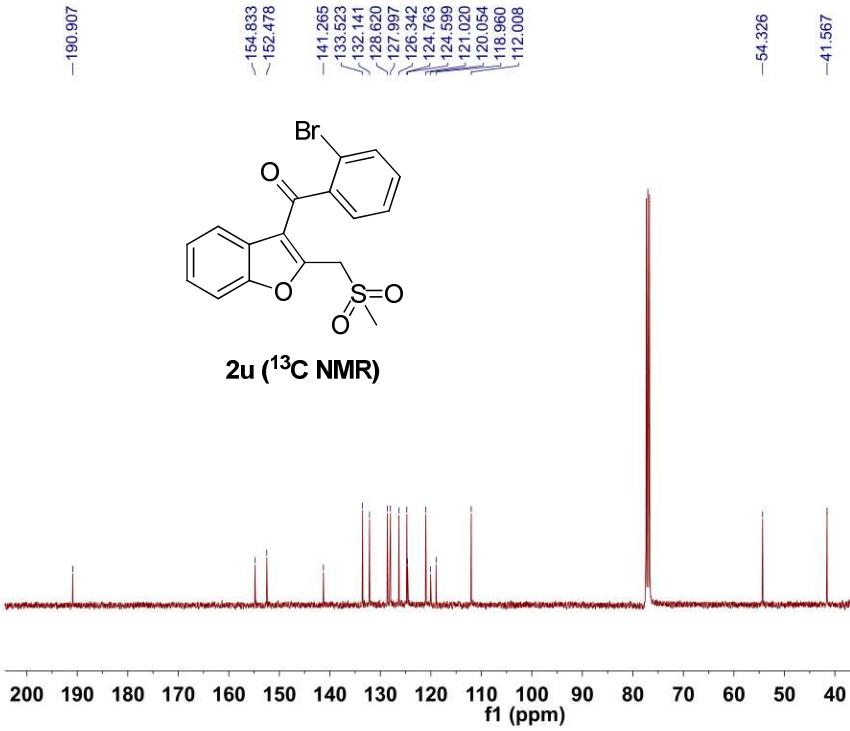
2t (^{13}C NMR)



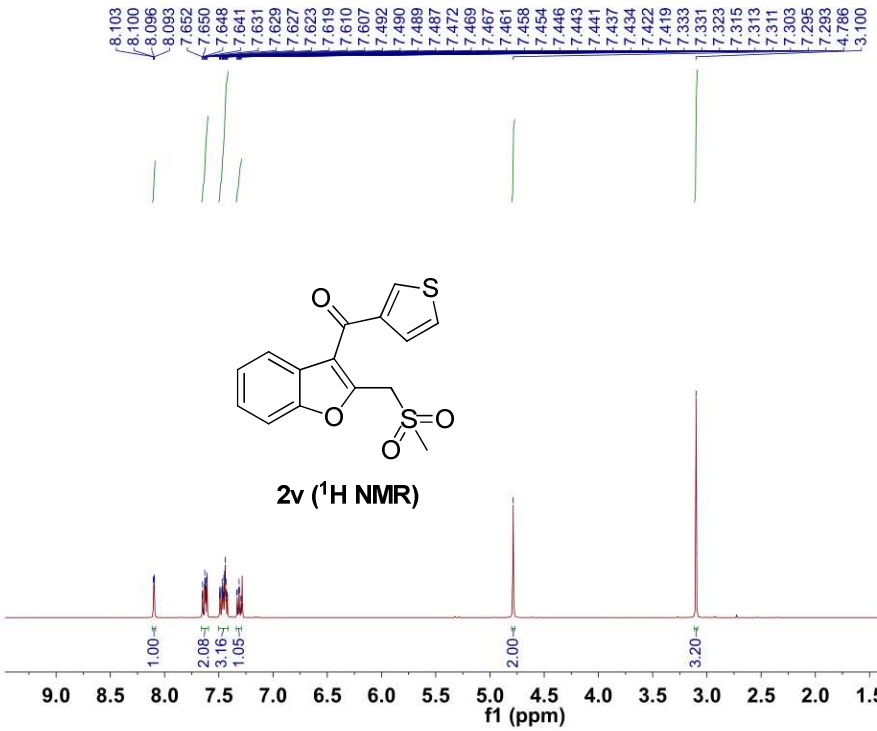


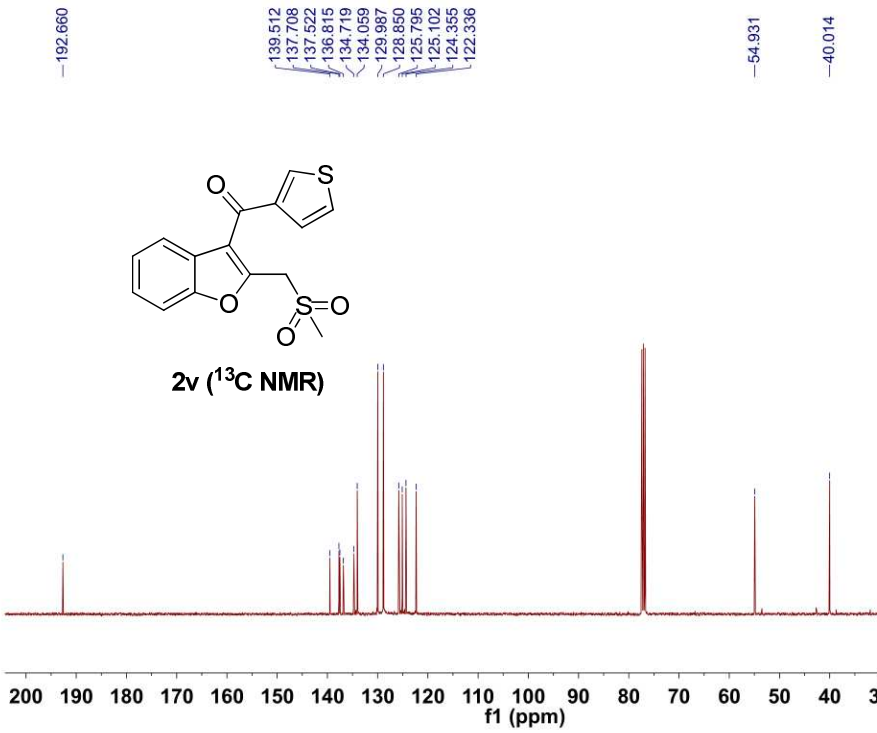
2u (^{1}H NMR)

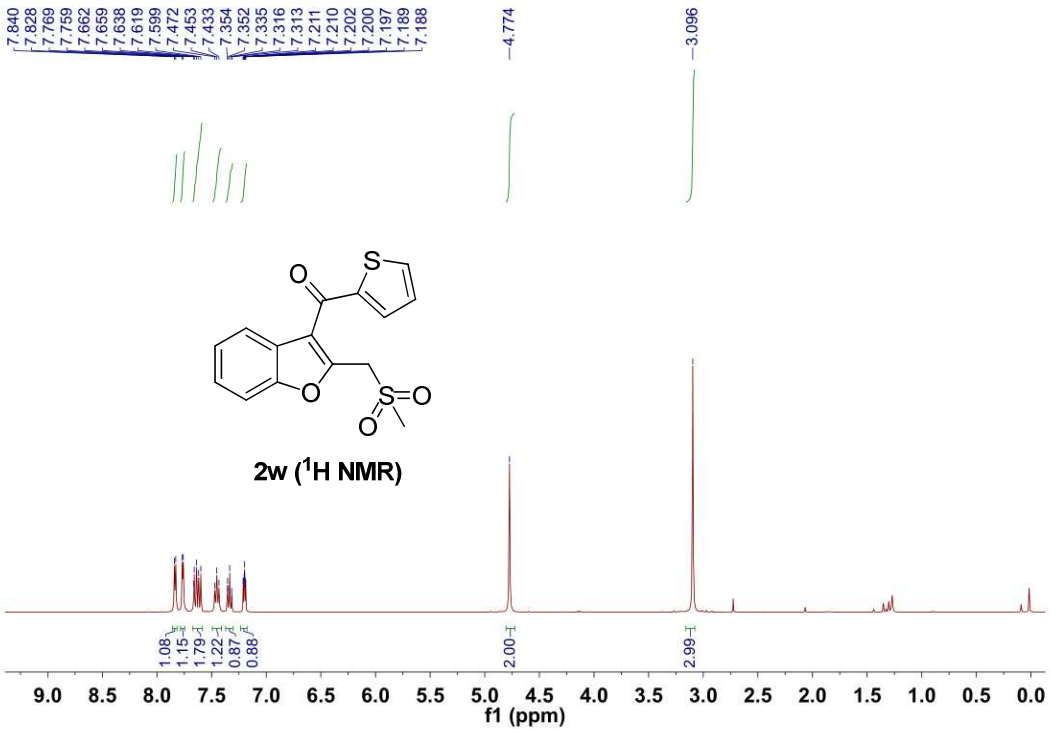




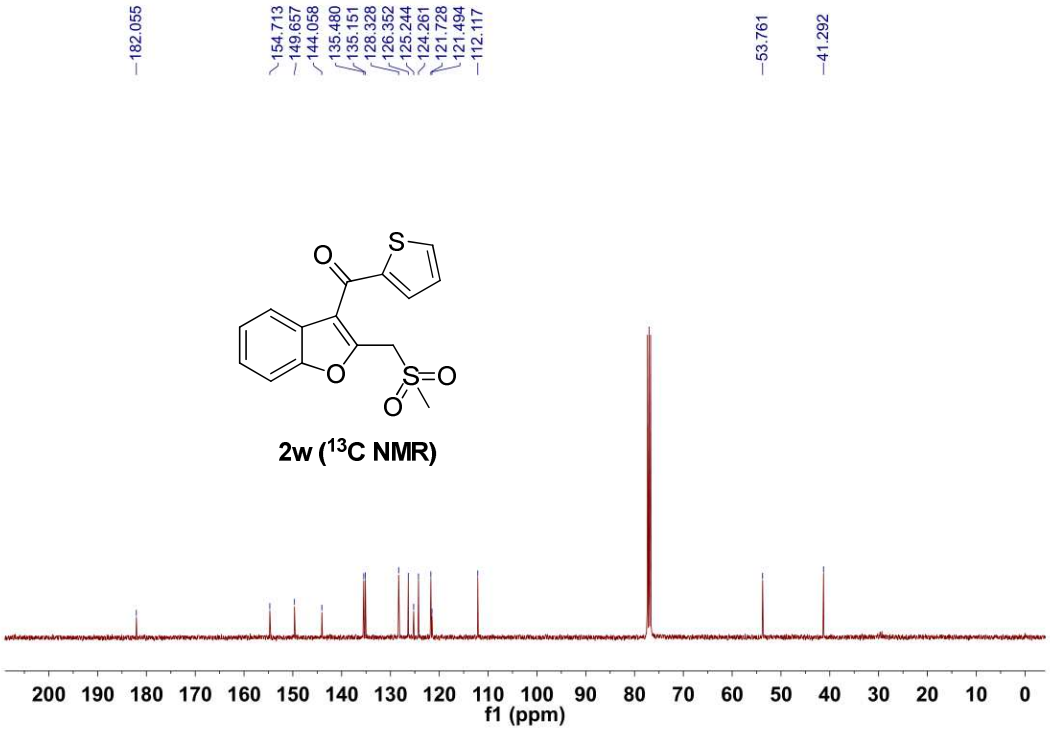
2u (^{13}C NMR)


8.103
8.100
8.096
8.093
7.652
7.650
7.648
7.641
7.631
7.629
7.627
7.623
7.619
7.610
7.607
7.492
7.490
7.489
7.487
7.472
7.469
7.467
7.461
7.458
7.454
7.446
7.443
7.441
7.437
7.434
7.422
7.419
7.333
7.331
7.323
7.315
7.313
7.311
7.303
7.295
7.293
4.786
3.100
O
S
O
O
S=O
O
2v (^{1}H NMR)
1.00
2.08
3.16
1.05
2.00
3.20
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)

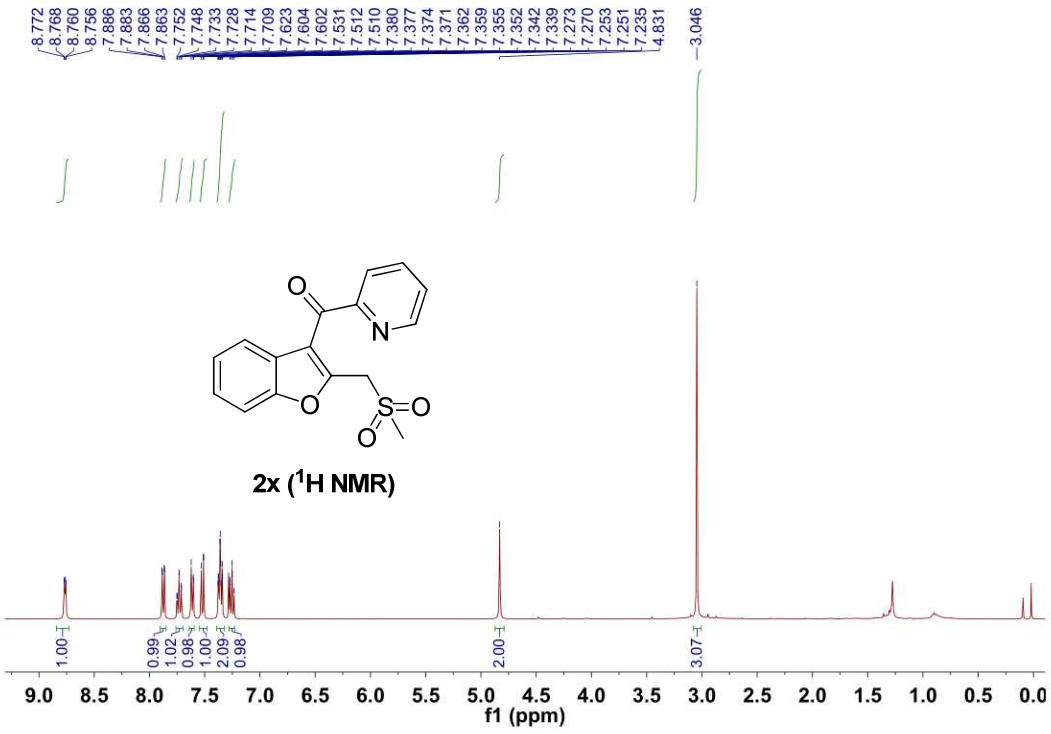

192.660
139.512
137.708
137.522
136.815
134.719
134.059
129.987
128.850
125.795
125.102
124.355
122.336
54.931
40.014
O
S
O
O
S=O
O
2v (^{13}C NMR)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



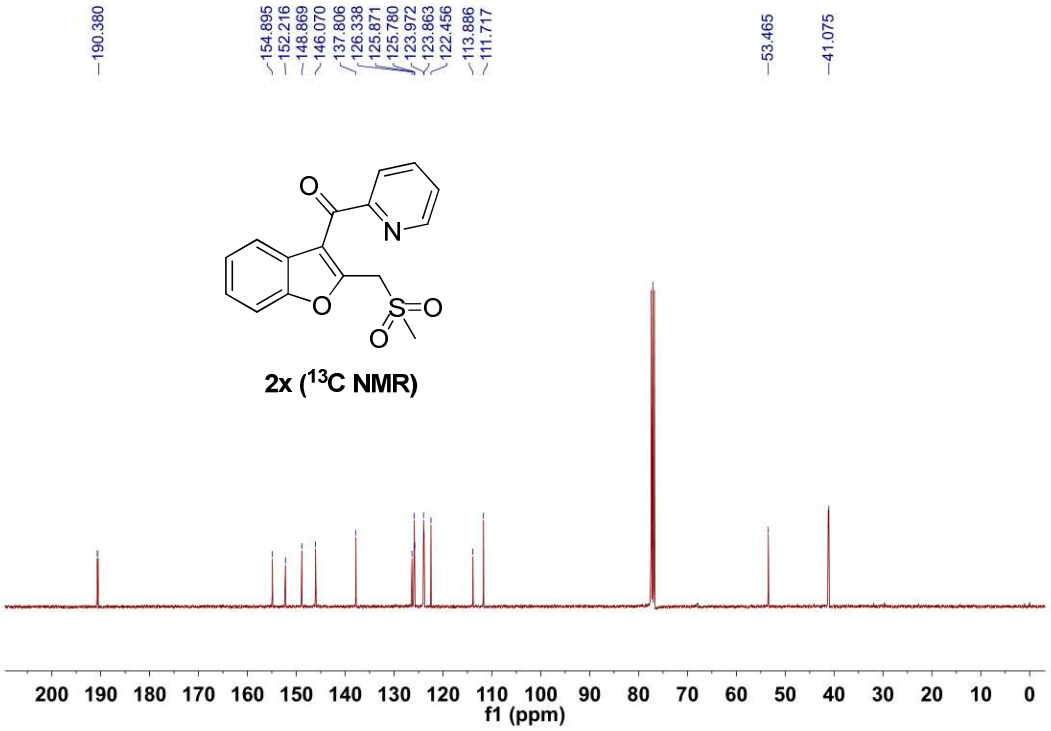
2w (^{1}H NMR)



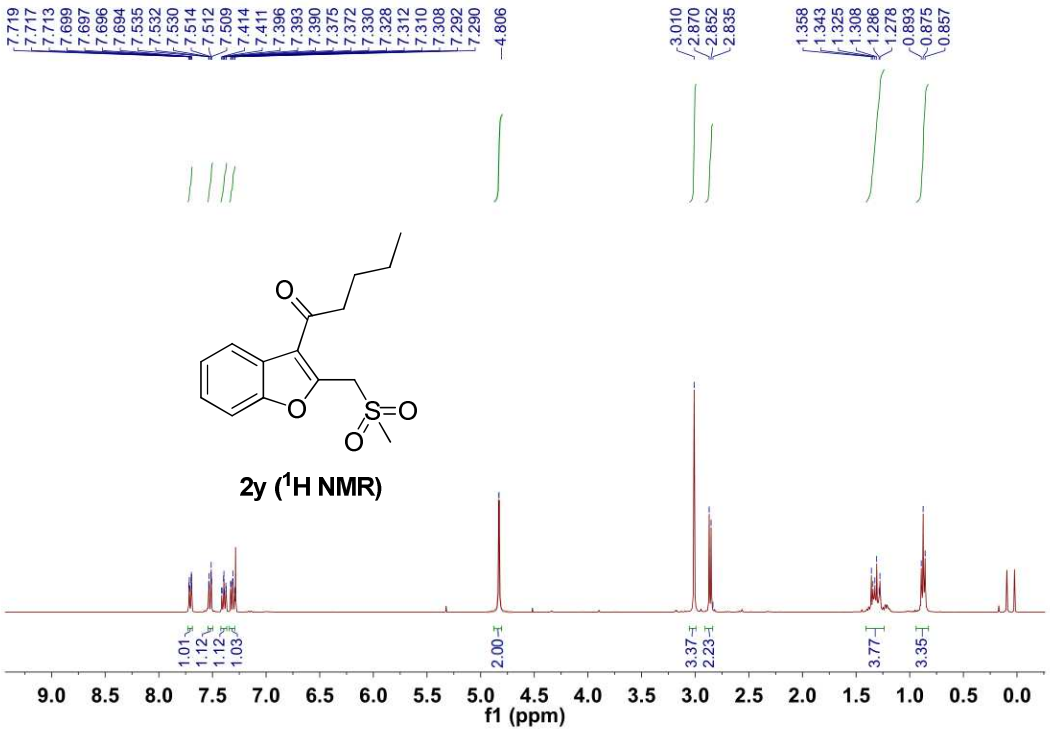
2w (^{13}C NMR)



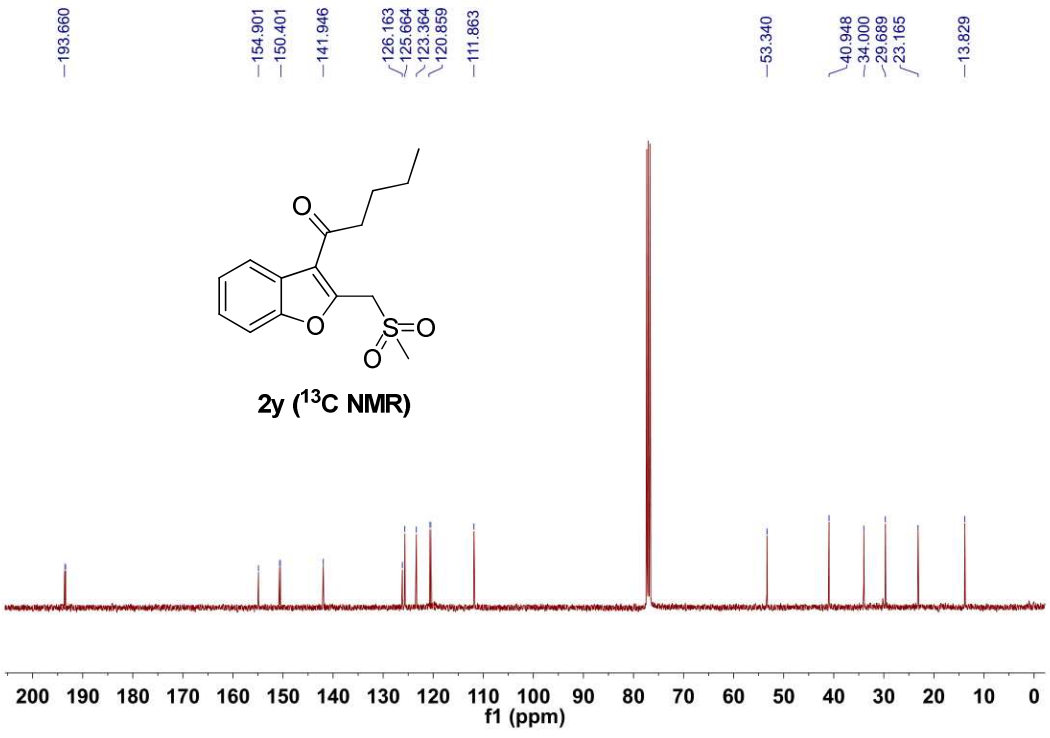
2x (^{1}H NMR)



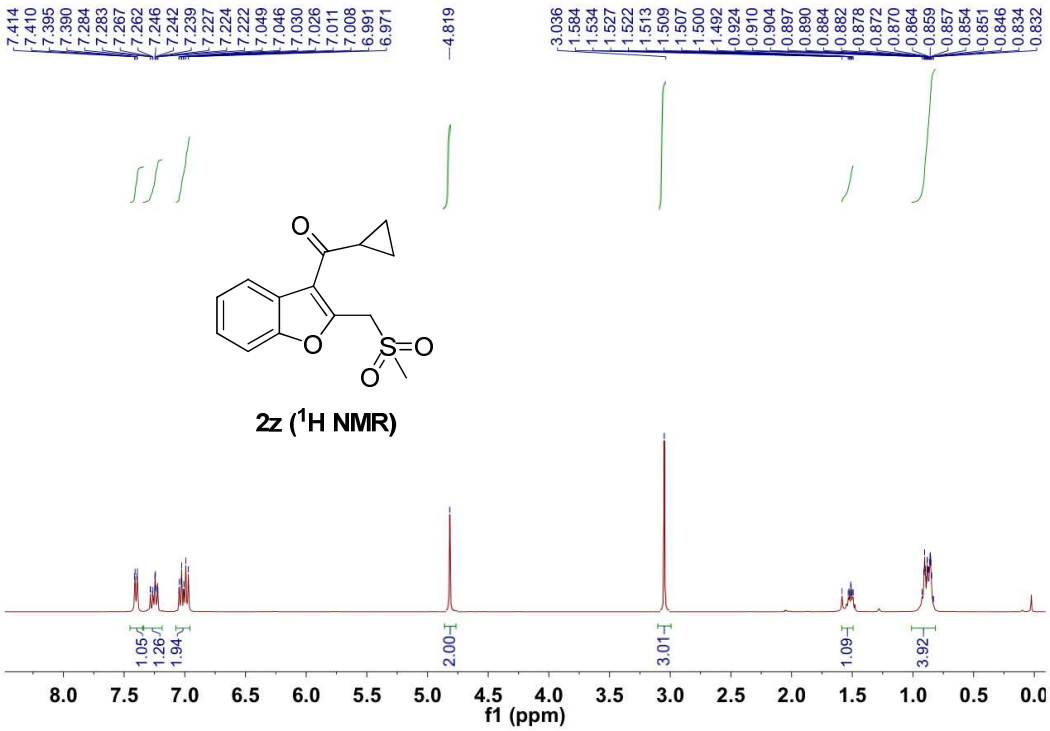
2x (^{13}C NMR)



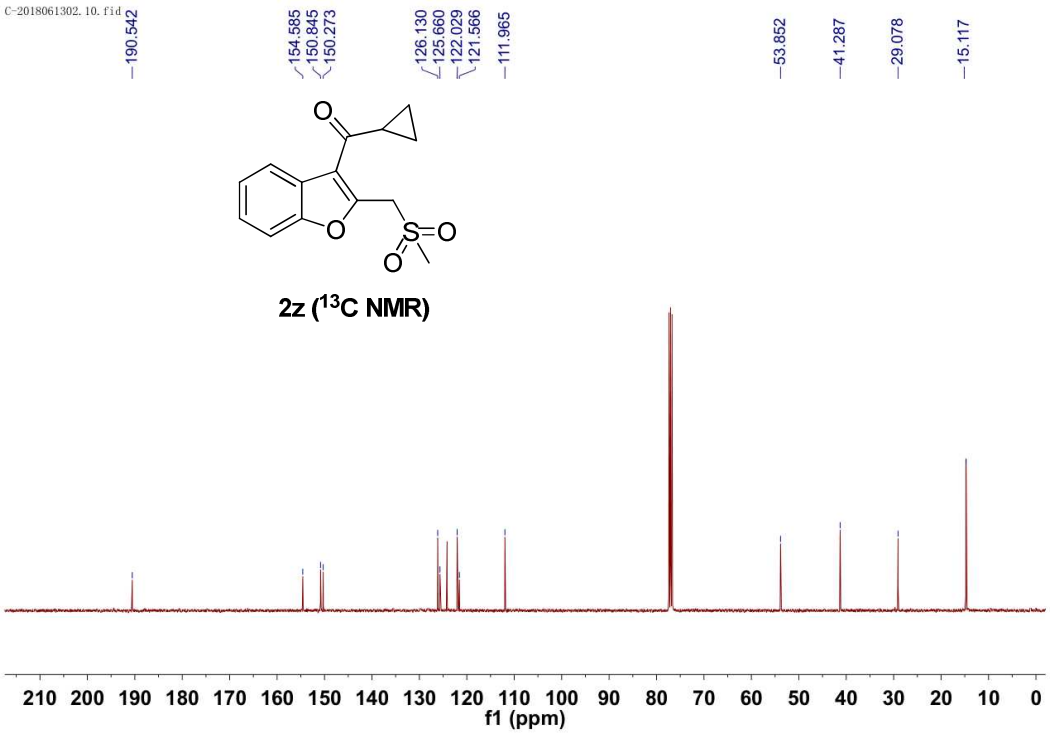
2y (^{1}H NMR)



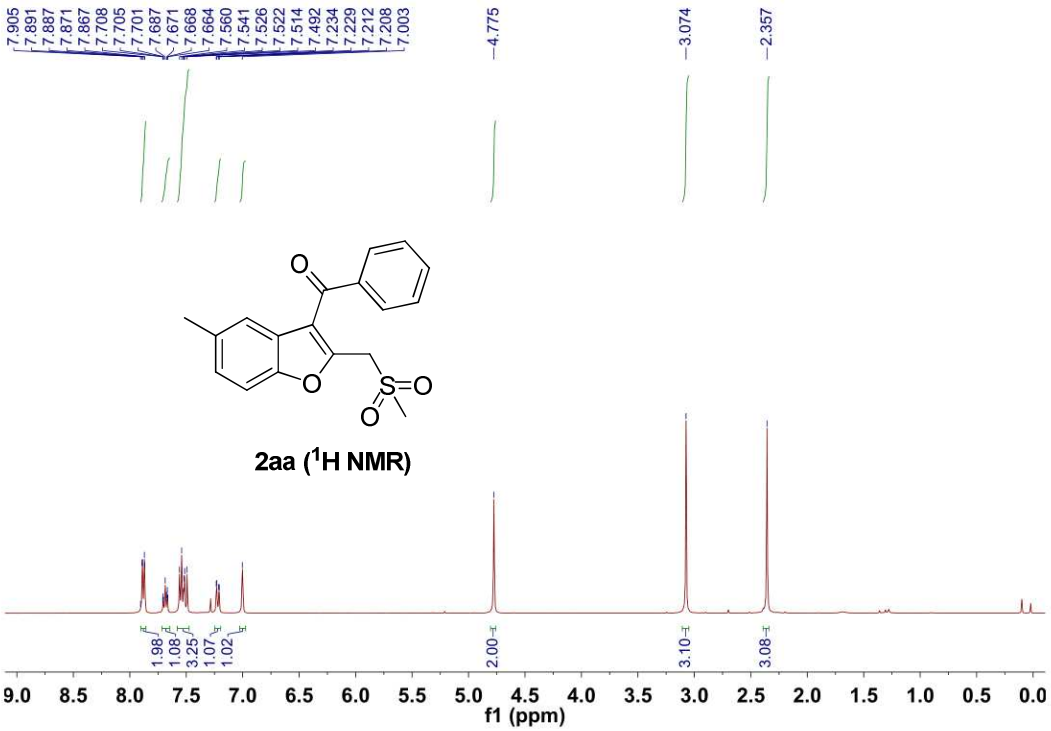
2y (^{13}C NMR)



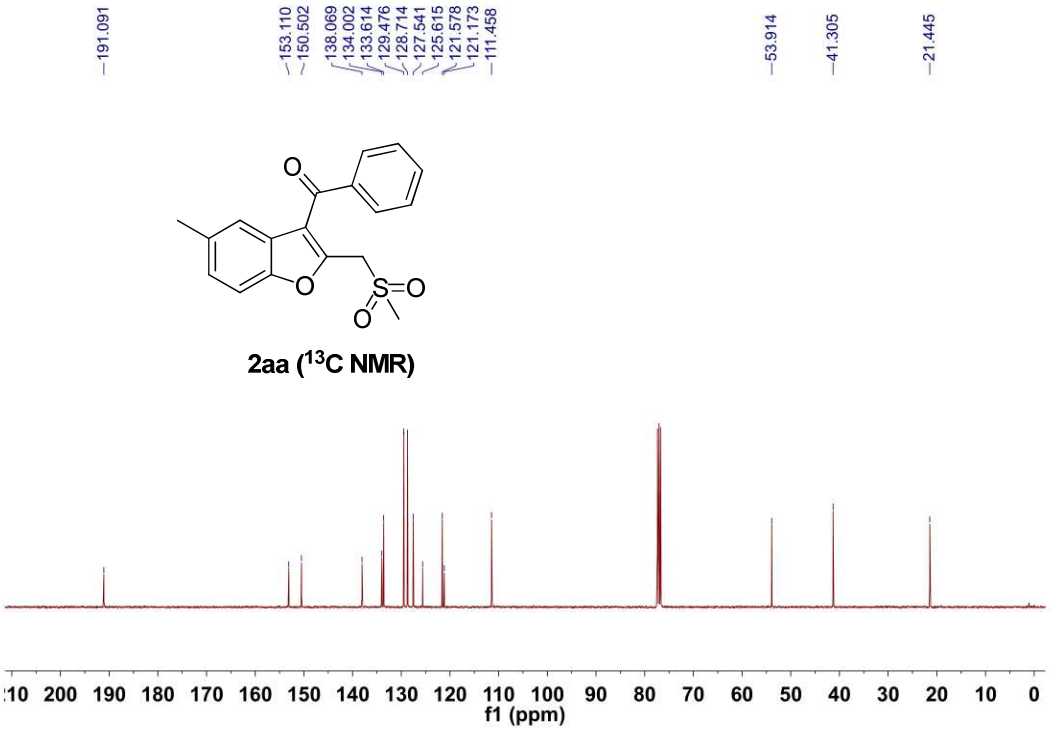
2z (^{1}H NMR)



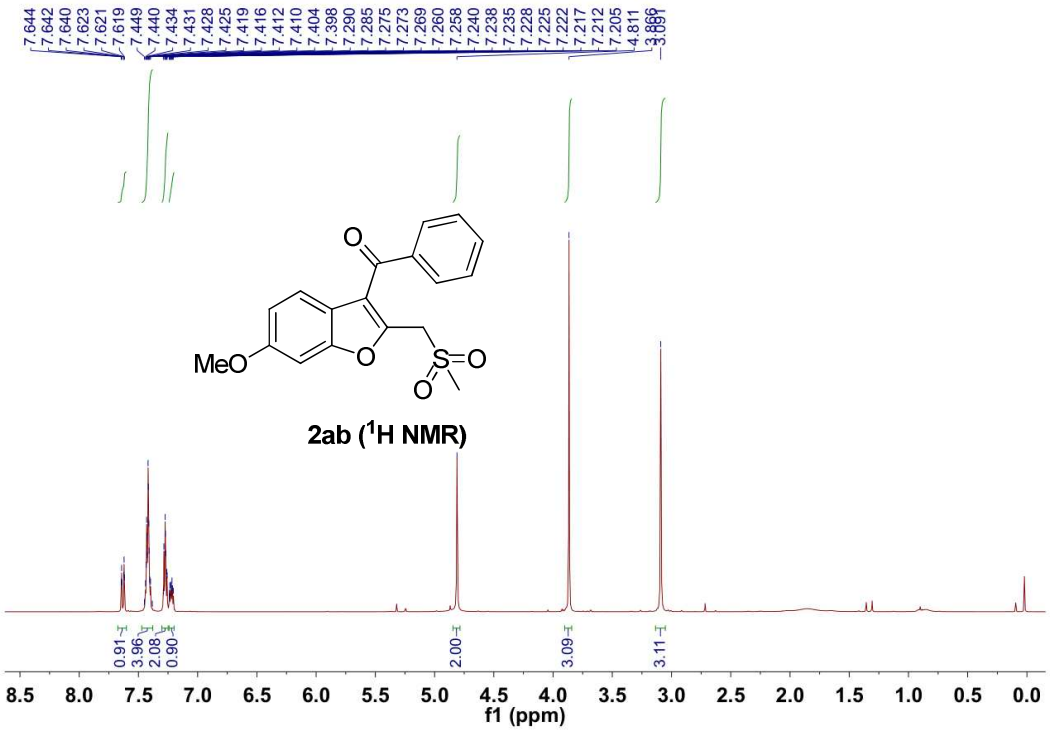
2z (^{13}C NMR)



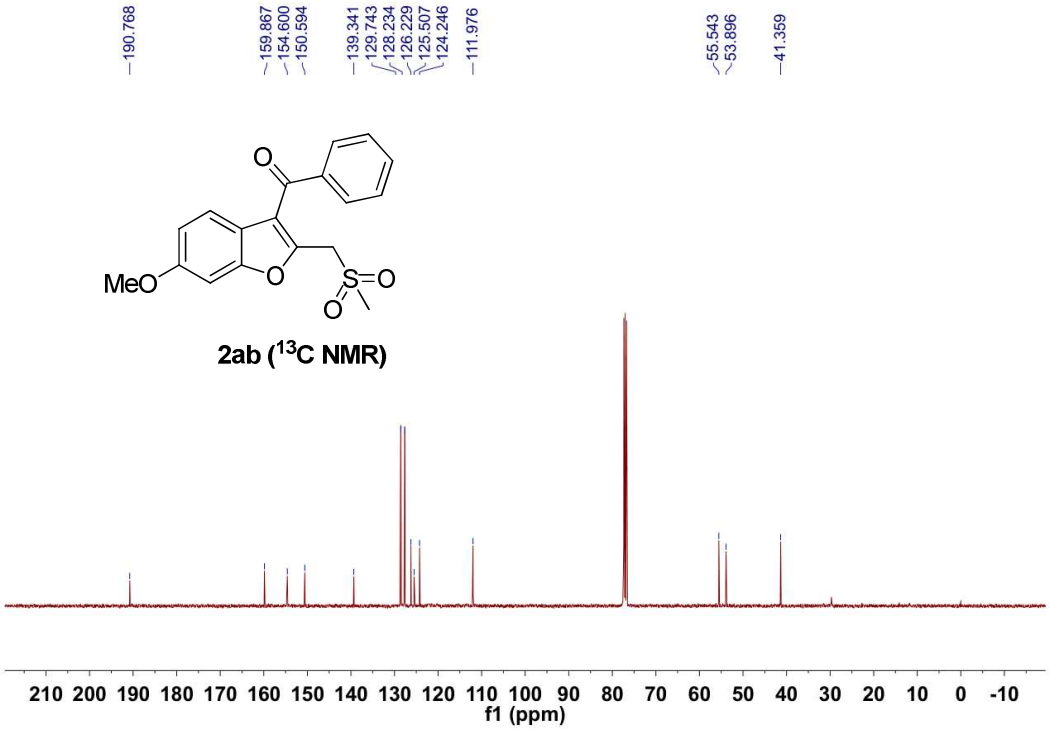
2aa (^{1}H NMR)



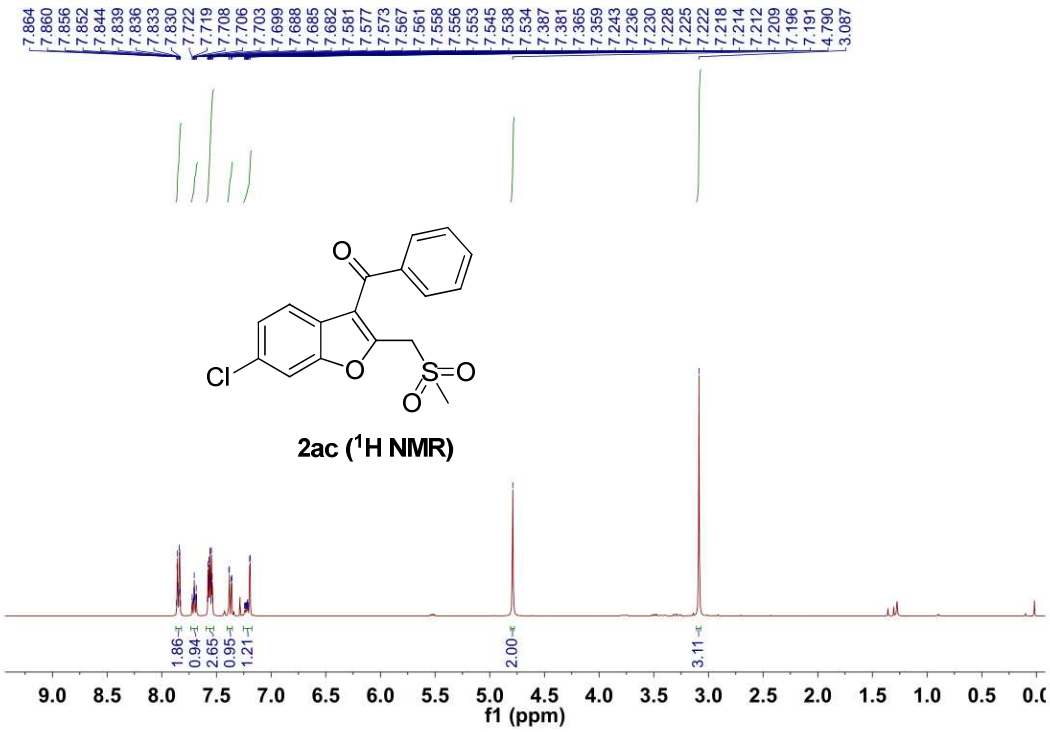
2aa (^{13}C NMR)



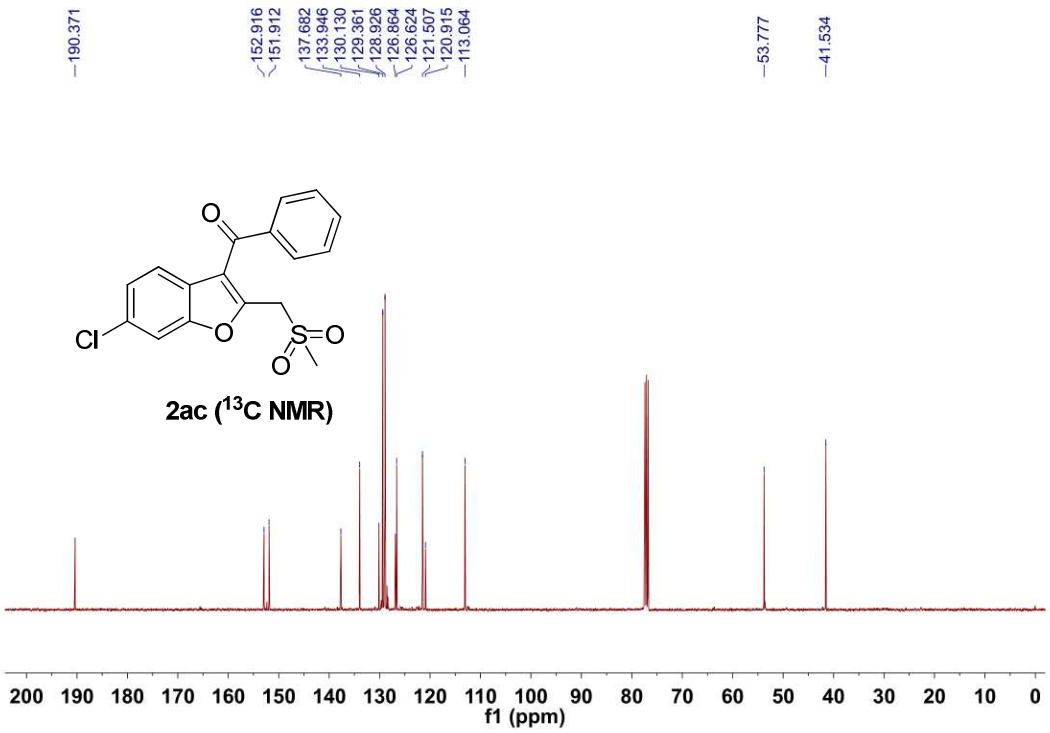
2ab (^{1}H NMR)



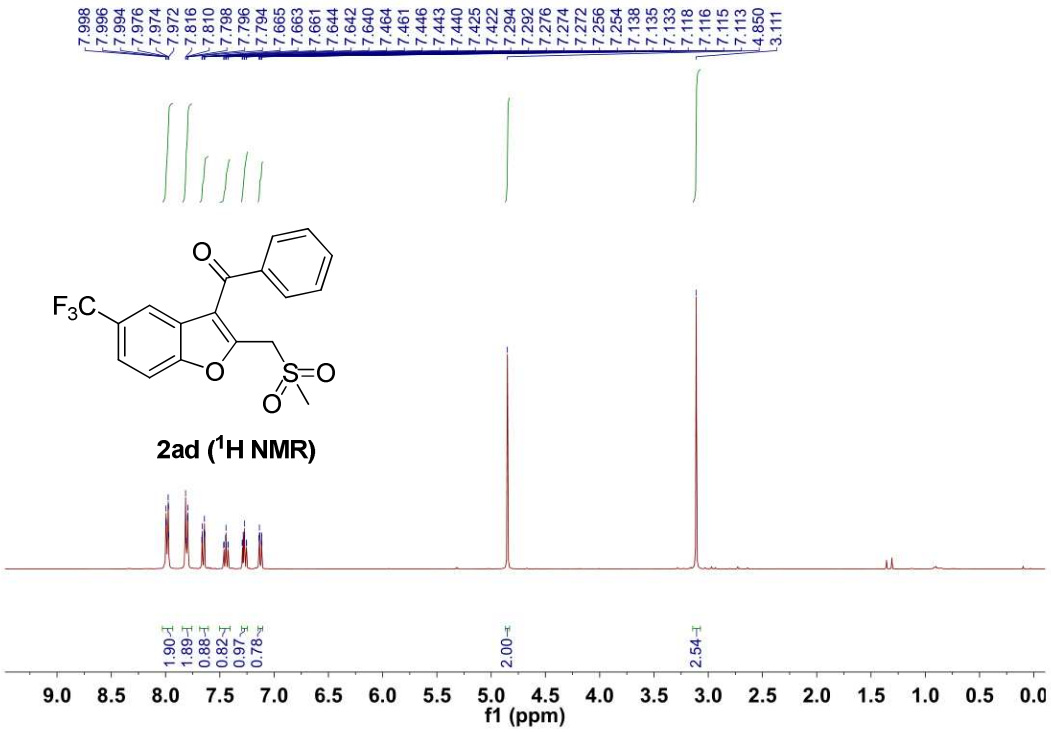
2ab (^{13}C NMR)



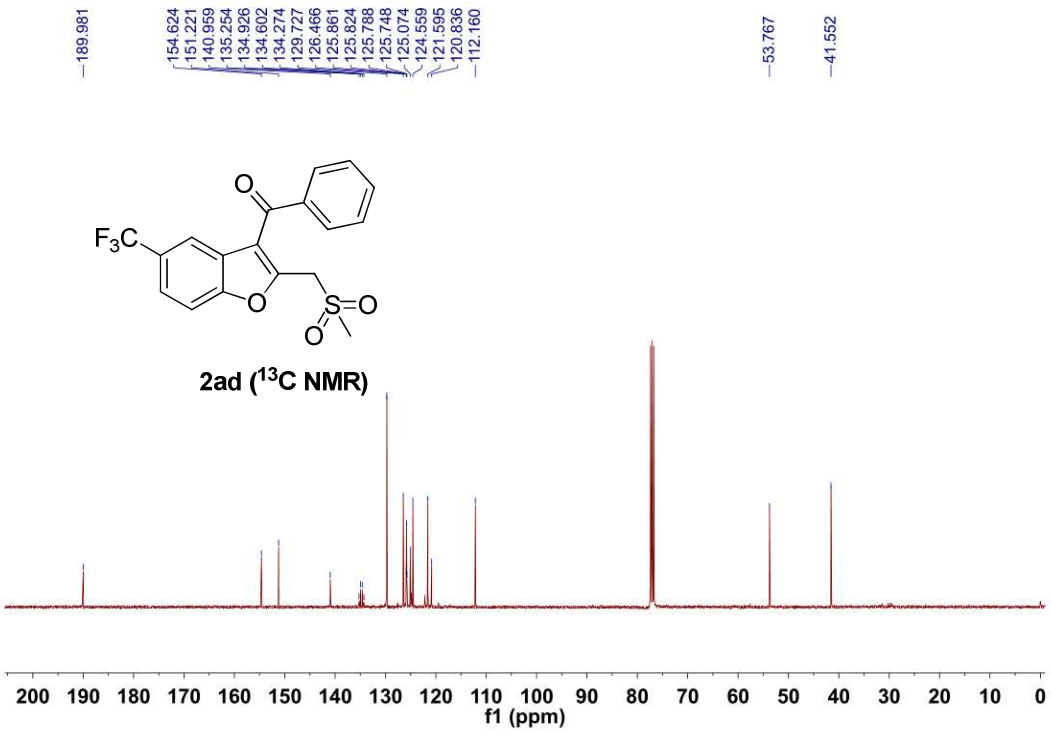
2ac (^{1}H NMR)



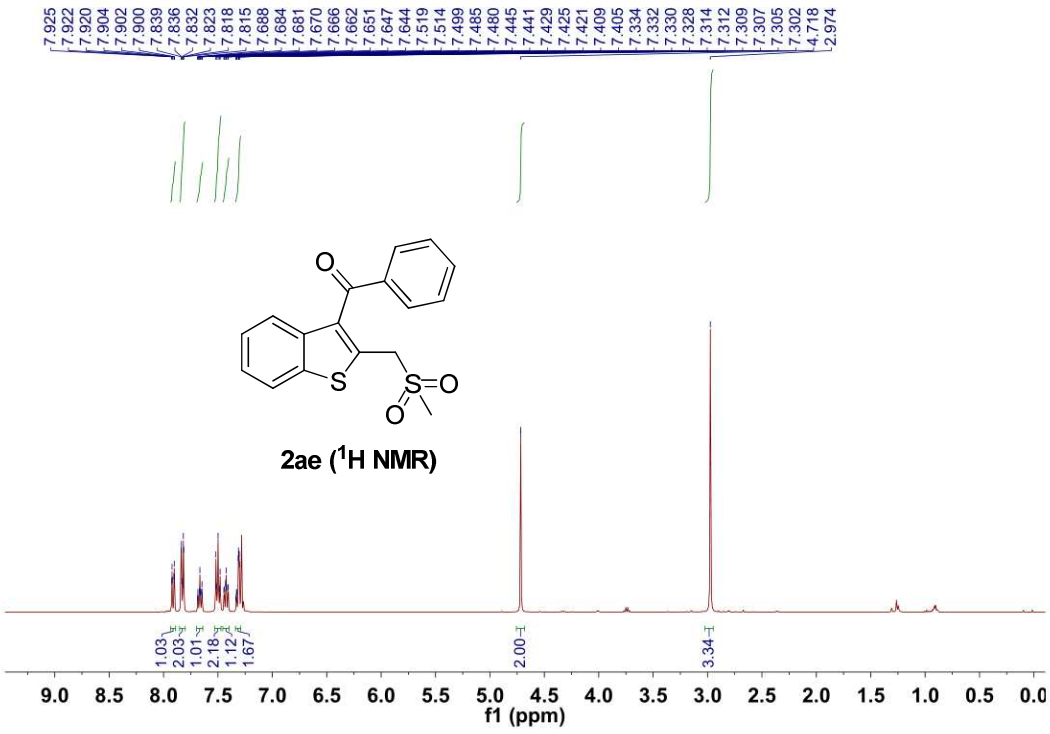
2ac (^{13}C NMR)



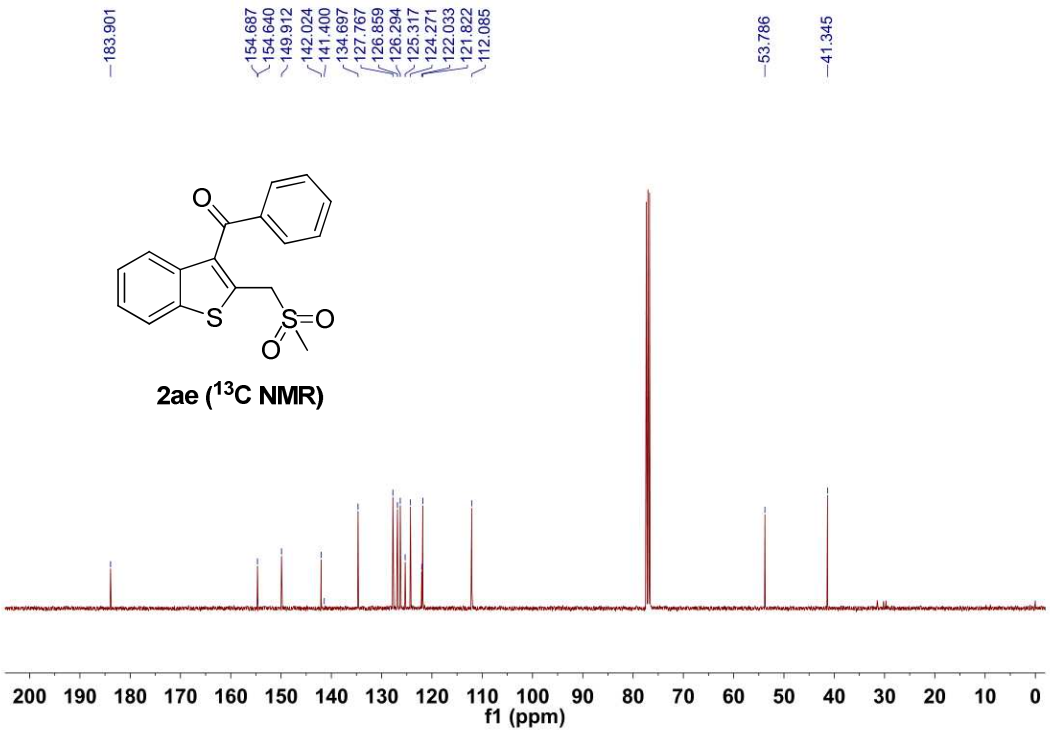
2ad (^{1}H NMR)



2ad (^{13}C NMR)



2ae (^{1}H NMR)



2ae (^{13}C NMR)