Cs_2CO_3 promoted [3+4] annulation of sulfur ylides and alkenyl thiazolones: synthesis of 5,8-dihydrooxepino[2,3-d]thiazole derivatives

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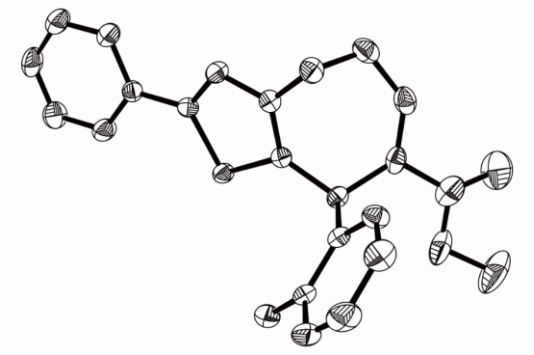
Contents

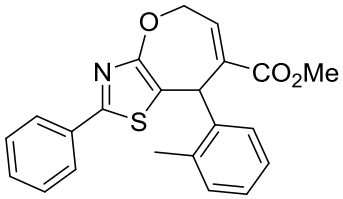
1. General information and materials

All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers (Aldrich, TCI or Alfa Aesar) and used without further purification. All solvents were purified and dried according to standard methods prior to use. TLC monitored all reactions with silica gel-coated plates. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H- and ^{13}C-NMR spectrum was recorded at ambient temperature on Bruker 400 instruments. All spectra were referenced to $CDCl_3$ (^{1}H δ 7.26 ppm and ^{13}C NMR δ 77.00 ppm). HRMS were obtained on Waters Xevo Q-TOF MS with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. Compound **1** was synthesized according to literature.[1]

1 L. Lin, Y. Yang, M. Wang, L. Lai, Y. Guo, R. Wang, *Chem. Commun.* **2015**, *51*, 8134-8137

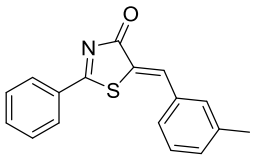
2 Crystal structure of 3j





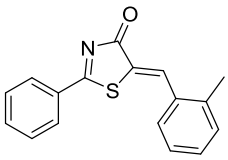
3 Characterization of all new compounds

(Z)-5-(3-methylbenzylidene)-2-phenylthiazol-4(5H)-one (1h)



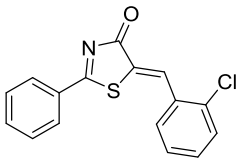
Yellow solid; Yield 19%; m.p. 83-85 ℃; IR (KBr)**:** 3021, 2961, 1689, 1598, 1578, 1505, 1481, 1443, 920, 776, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.4 Hz, 2H), 8.05 (s, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.53 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.18, 183.15, 139.03, 138.78, 135.01, 133.73, 131.96, 131.81, 131.27, 129.15, 129.10, 128.80, 127.81, 126.11, 21.38 ppm; ESI-HRMS calcd. for $C_{17}H_{13}NOS$+H 280.0791, found 280.0799.

(Z)-5-(2-methylbenzylidene)-2-phenylthiazol-4(5H)-one (1j)



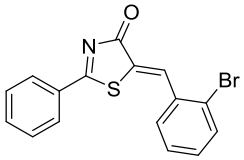
Yellow solid; Yield 41%; m.p. 140-141 ℃; IR (KBr)**:** 3055, 3008, 1701, 1591, 1521, 1482, 850, 769, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.31 (s, 1H), 8.18 – 8.24 (m, 2H), 7.66 – 7.72 (m, 2H), 7.53 – 7.58 (m, 2H), 7.32 – 7.37 (m, 2H), 7.27 – 7.31 (m, 1H), 2.51 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.86, 182.73, 139.78, 136.22, 135.04, 133.01, 131.77, 131.06, 130.89, 129.13, 128.71, 128.04, 127.77, 126.53, 20.01 ppm; ESI-HRMS calcd. for $C_{17}H_{13}NOS$+H 280.0791, found 280.0803.

(Z)-5-(2-chlorobenzylidene)-2-phenylthiazol-4(5H)-one (1k)



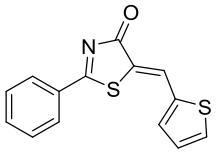
Yellow solid; Yield 46%; m.p. 167-168 ℃; IR (KBr): 3059, 3025, 1706, 1606, 1527, 763, 679 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 8.17 – 8.24 (m, 2H), 7.75 – 7.80 (m, 1H), 7.68 – 7.74 (m, 1H), 7.54 – 7.59 (m, 2H), 7.48 – 7.53 (m, 1H), 7.37 – 7.44 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.45, 182.42, 136.60, 135.27, 134.18, 132.50, 131.70, 131.67, 130.50, 129.39, 129.34, 129.23, 128.88, 127.25 ppm; ESI-HRMS calcd. for $C_{16}H_{10}NOSCl$+H 300.0244, found 300.0255.

(Z)-5-(2-bromobenzylidene)-2-phenylthiazol-4(5H)-one (1l)



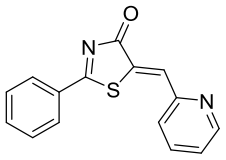
Yellow solid; Yield 39%; m.p. 177-178 ℃; IR (KBr)**:** 3025, 1716, 1595, 1529, 804, 758, 680, 553 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.38 (s, 1H), 8.17 – 8.23 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.73 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.31 (td, *J* = 7.6 , 1.2 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.55, 182.30, 136.82, 135.28, 134.37, 133.82, 131.75, 131.73, 129.67, 129.50, 129.24, 128.88, 127.87, 126.92 ppm; ESI-HRMS calcd. for $C_{16}H_{10}NOSBr$+H 343.9739, found 343.9748.

(Z)-2-phenyl-5-(thiophen-2-ylmethylene)thiazol-4(5H)-one (1m)



Yellow solid; Yield 59%; m.p. 159-160 ℃; IR (KBr)**:** 3100, 3083, 3010, 1694, 1586, 1526, 1485, 765, 677 m^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.17 – 8.26 (m, 3H), 7.66 – 7.72 (m, 2H), 7.53 – 7.59 (m, 2H), 7.50 – 7.53 (m, 1H), 7.19 – 7.24 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.88, 182.83, 139.09, 134.97, 134.56, 132.63, 131.68, 130.56, 129.15, 128.92, 128.78, 124.83 ppm; ESI-HRMS calcd. for $C_{14}H_9NOS_2$+H 272.0198, found 272.0207.

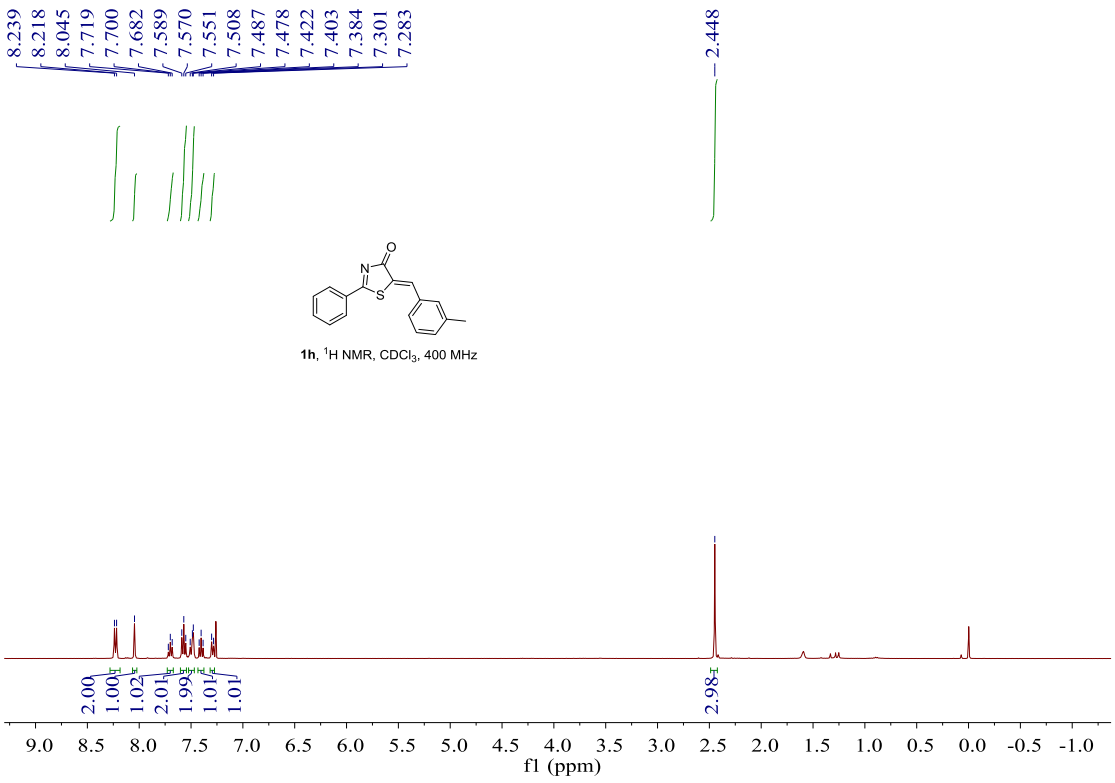
(Z)-2-phenyl-5-(pyridin-2-ylmethylene)thiazol-4(5H)-one (1n)



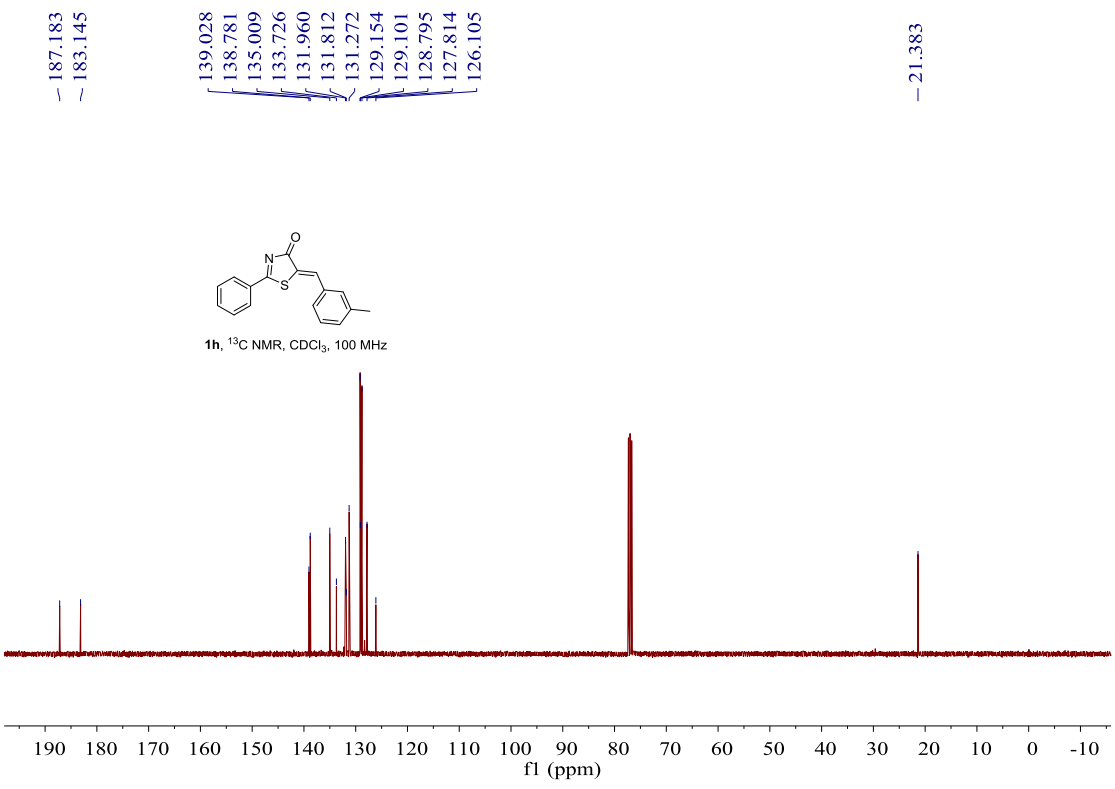
Yellow solid; Yield 26%; m.p. 184-185 ℃; IR (KBr)**:** 3047, 1698, 1610, 1579, 1525, 781, 738, 683 m^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.82 (d, *J* = 4.4 Hz, 1H), 8.23 – 8.35 (m, 2H), 7.96 (s, 1H), 7.80 (td, *J* = 7.7, 1.7 Hz, 1H), 7.69 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.53 – 7.60 (m, 3H), 7.32 (ddd, *J* = 7.6, 4.6, 1.0 Hz, 1H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.55, 183.39, 151.36, 149.65, 136.95, 134.97, 133.88, 132.15, 130.49, 129.03, 128.83, 127.78, 124.04 ppm; ESI-HRMS calcd. for $C_{15}H_{10}N_2OS$+H 267.0587, found 267.0598.

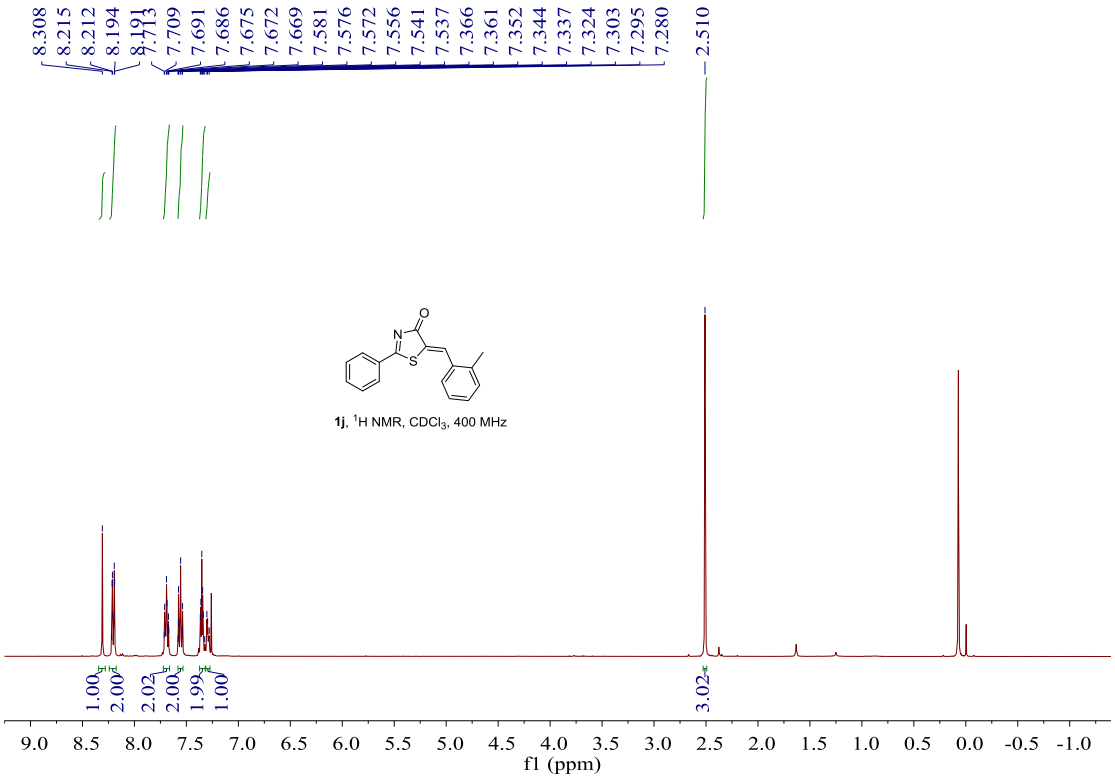
4 NMR spectra of all new compounds



1h, ^{1}H NMR, $CDCl_3$, 400 MHz



1h, ^{13}C NMR, $CDCl_3$, 100 MHz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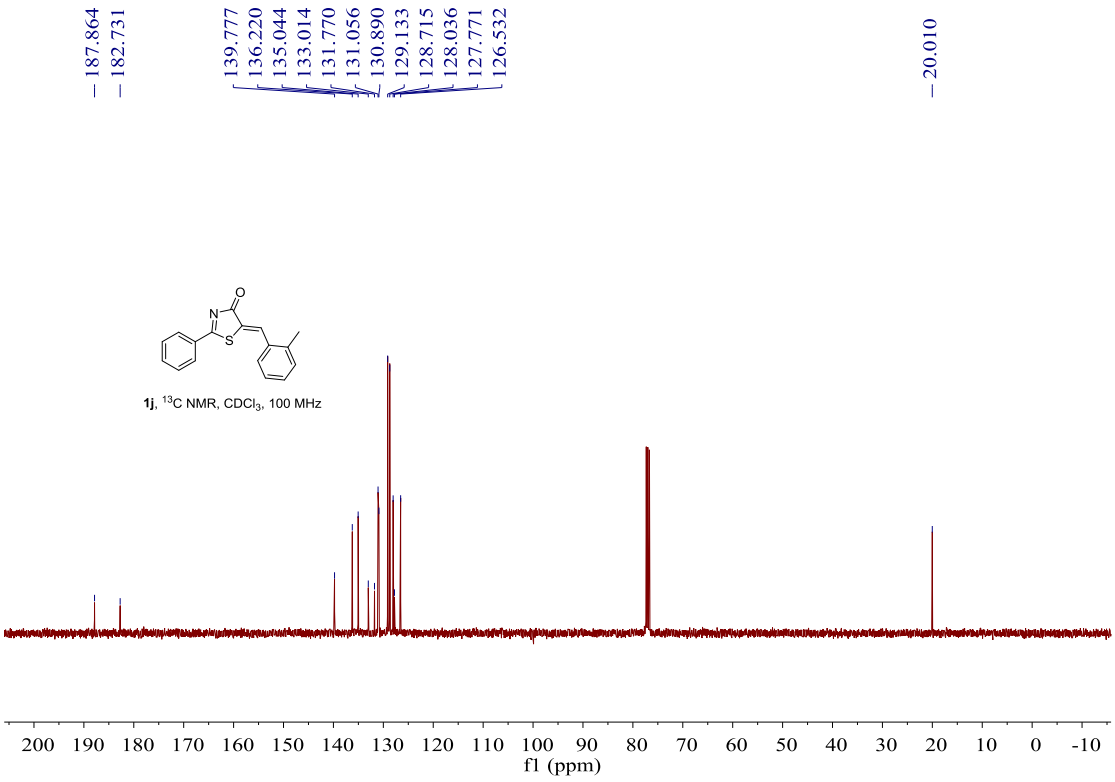
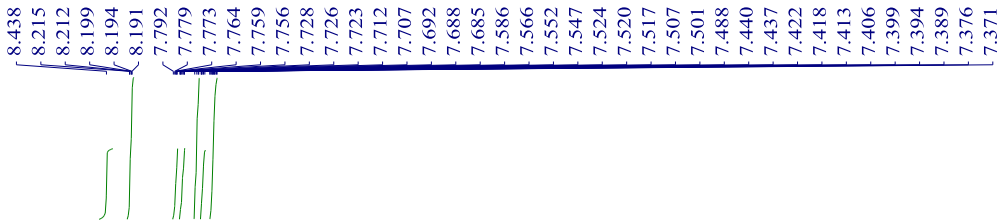
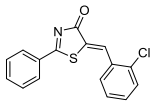
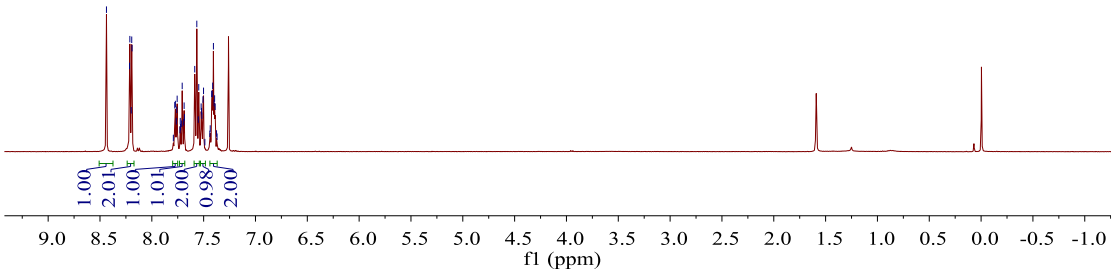
8.215
8.212
8.194
8.191
7.713
7.709
7.691
7.686
7.675
7.672
7.669
7.581
7.576
7.572
7.556
7.541
7.537
7.366
7.361
7.352
7.344
7.337
7.324
7.303
7.295
7.280
2.510
1j, 1H NMR, CDCl3, 400 MHz
1.00
2.00
2.02
2.00
1.99
1.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

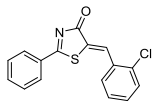

187.864
182.731
139.777
136.220
135.044
133.014
131.770
131.056
130.890
129.133
128.715
128.036
127.771
126.532
20.010
1j, 13C NMR, CDCl3, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



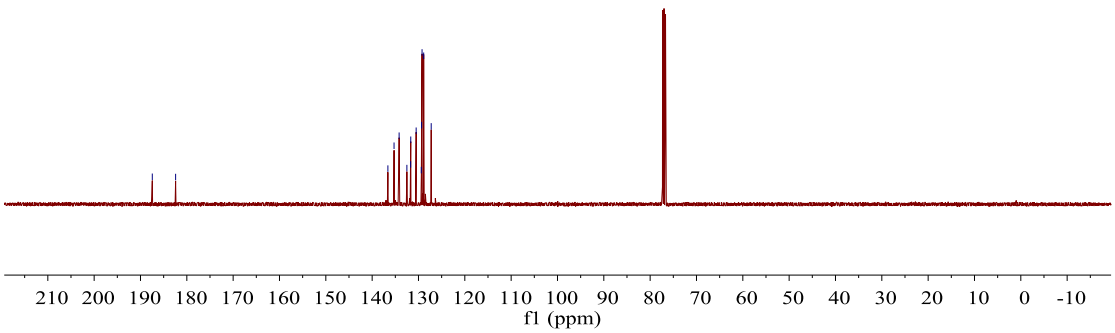


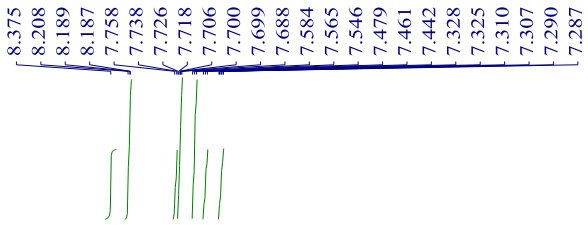
1k, ^{1}H NMR, $CDCl_3$, 400 MHz

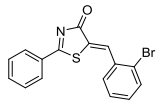




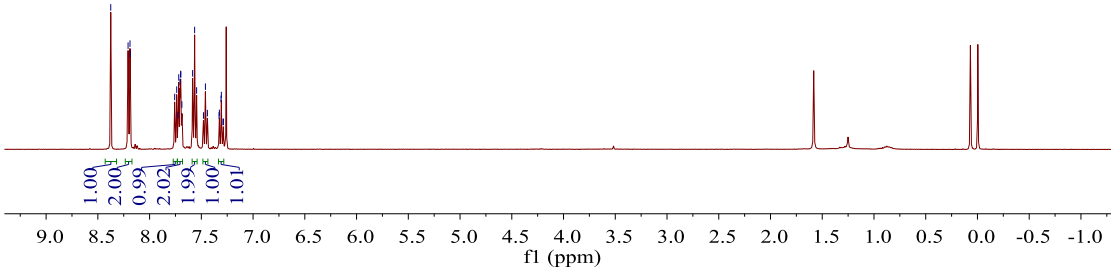
1k, ^{13}C NMR, $CDCl_3$, 100 MHz

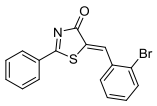




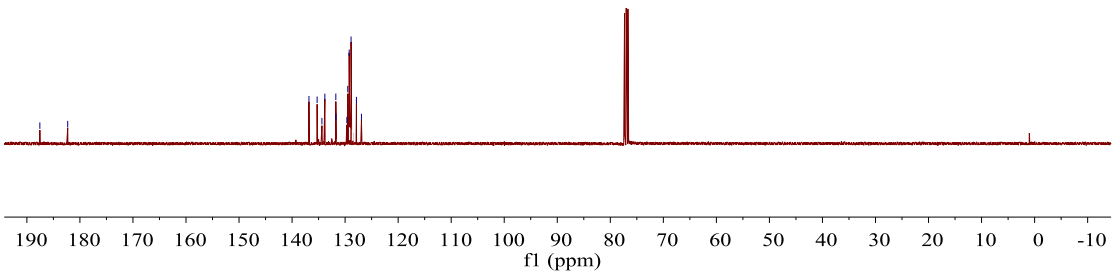


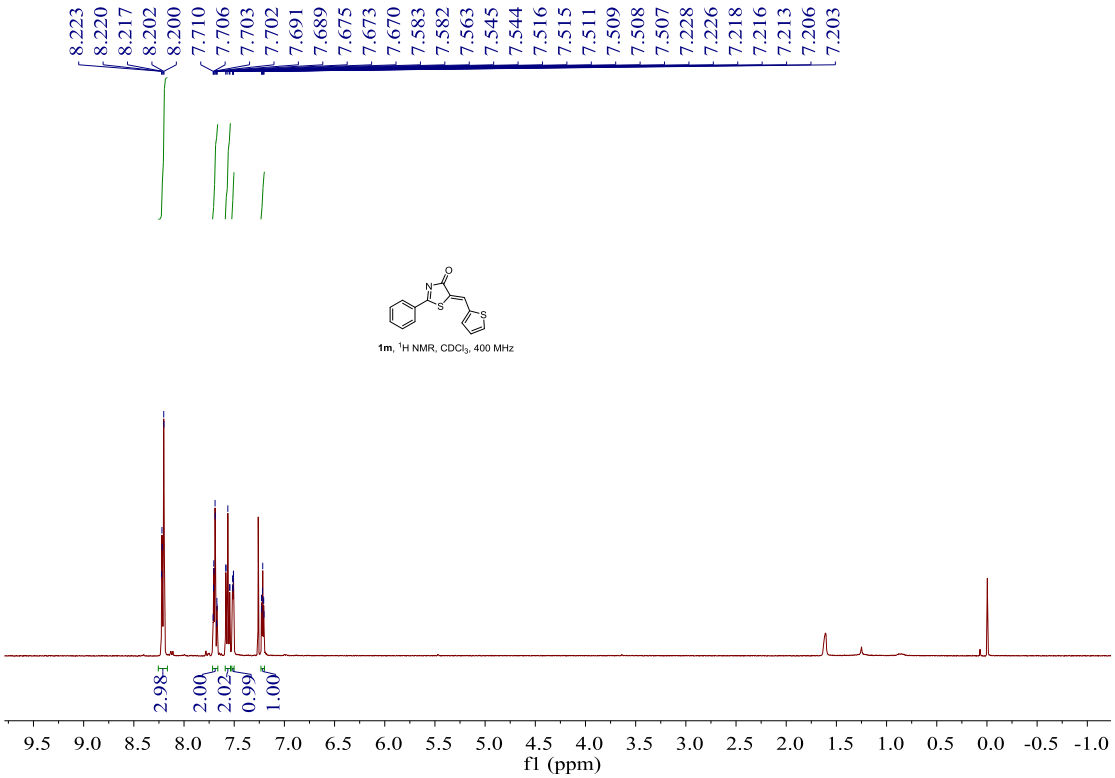
1l, ^{1}H NMR, $CDCl_3$, 400 MHz





1l, ^{13}C NMR, $CDCl_3$, 100 MHz

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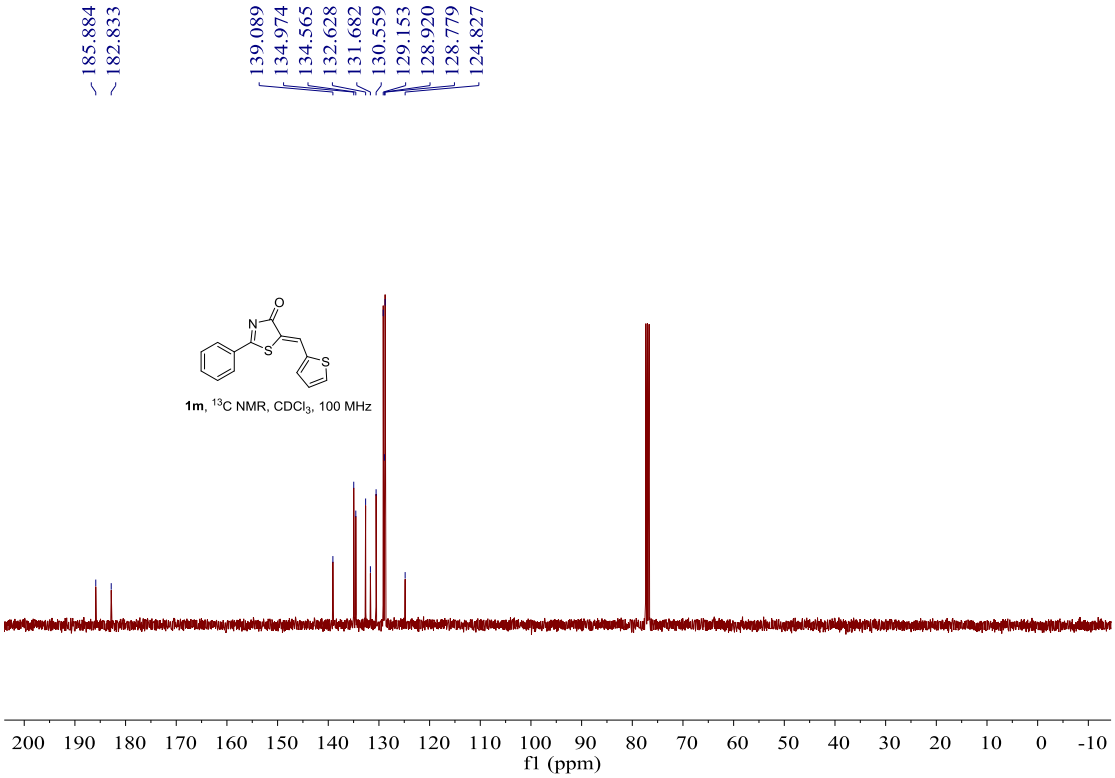
8.220
8.217
8.202
8.200
7.710
7.706
7.703
7.702
7.691
7.689
7.675
7.673
7.670
7.583
7.582
7.563
7.545
7.544
7.516
7.515
7.511
7.509
7.508
7.507
7.228
7.226
7.218
7.216
7.213
7.206
7.203
1m, 1H NMR, CDCl3, 400 MHz
2.98
2.00
2.02
0.99
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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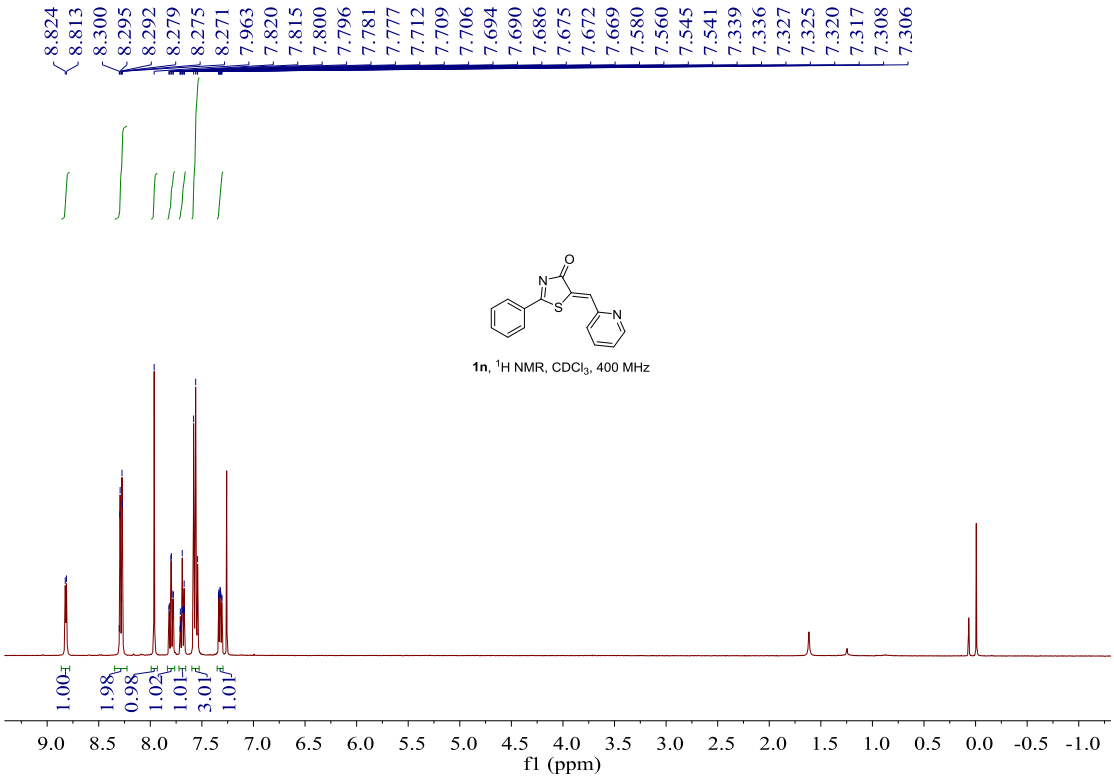
182.833
139.089
134.974
134.565
132.628
131.682
130.559
129.153
128.920
128.779
124.827
1m, 13C NMR, CDCl3, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.295
8.292
8.279
8.275
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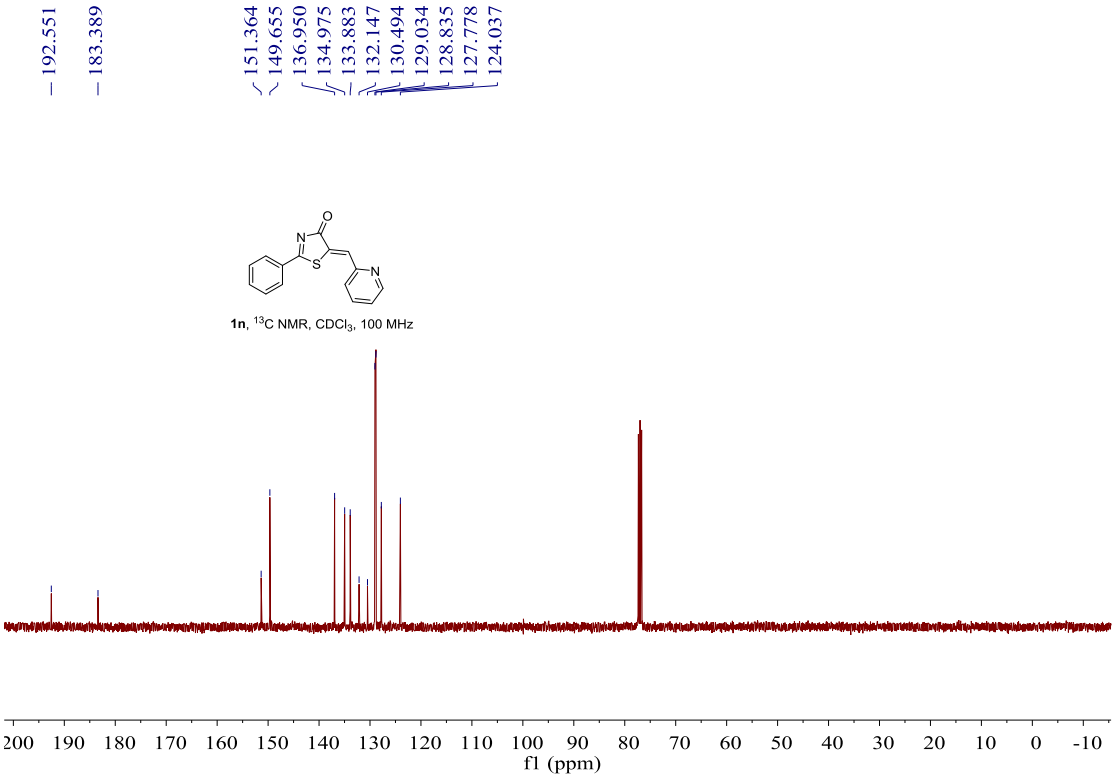
7.796
7.781
7.777
7.712
7.709
7.706
7.694
7.690
7.686
7.675
7.672
7.669
7.580
7.560
7.545
7.541
7.339
7.336
7.327
7.325
7.320
7.317
7.308
7.306
O
N
S
N
1n, 1H NMR, CDCl3, 400 MHz
1.00
1.98
0.98
1.02
1.01
3.01
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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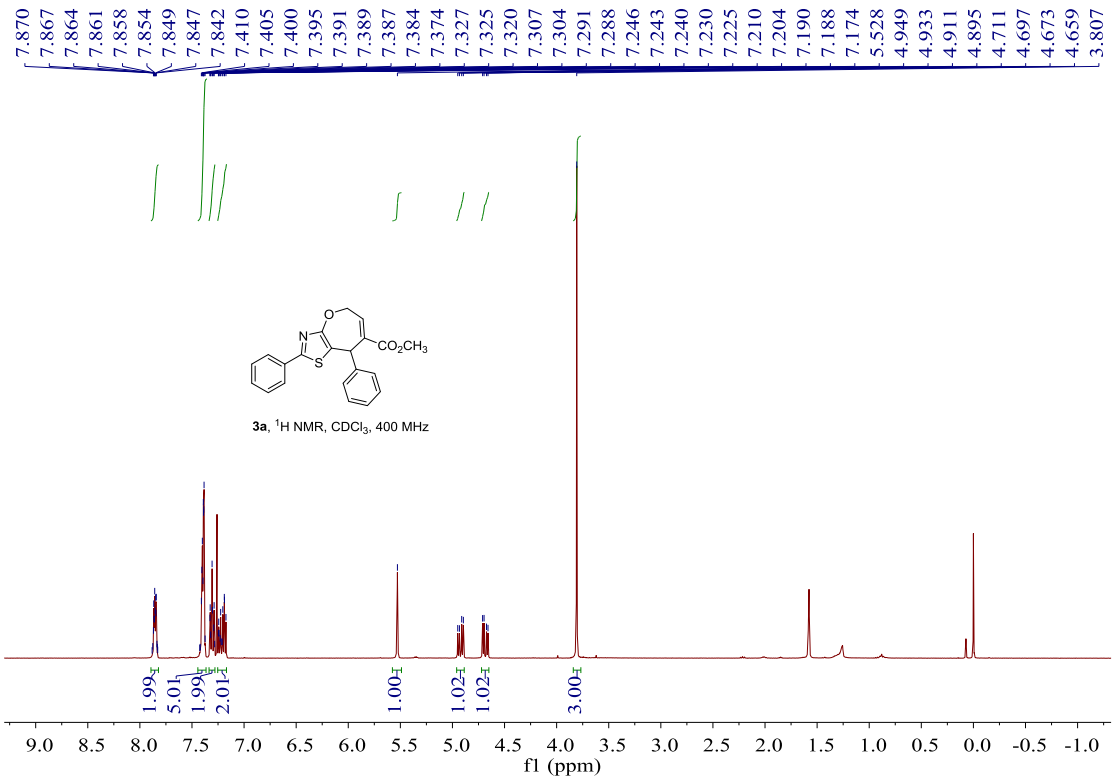
183.389
151.364
149.655
136.950
134.975
133.883
132.147
130.494
129.034
128.835
127.778
124.037
O
N
S
N
1n, 13C NMR, CDCl3, 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.858
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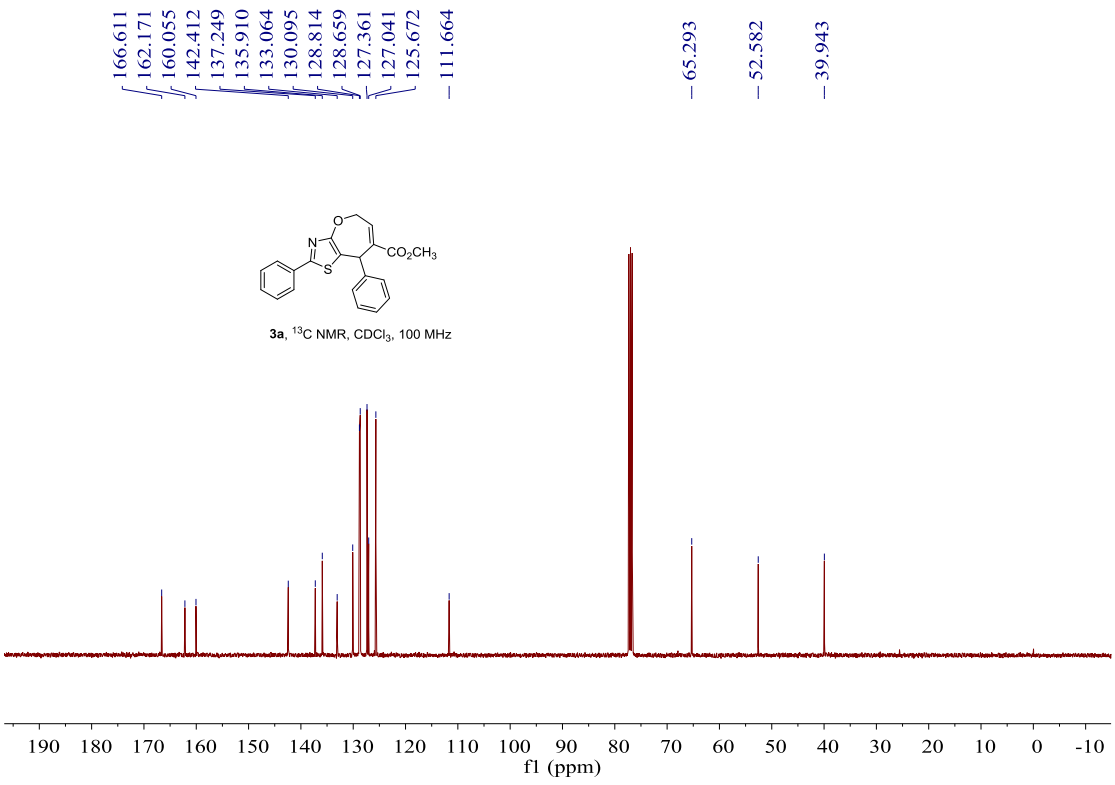
7.405
7.400
7.395
7.391
7.389
7.387
7.384
7.374
7.327
7.325
7.320
7.307
7.304
7.291
7.288
7.246
7.243
7.240
7.230
7.225
7.210
7.204
7.190
7.188
7.174
5.528
4.949
4.933
4.911
4.895
4.711
4.697
4.673
4.659
3.807
CO2CH3
3a, 1H NMR, CDCl3, 400 MHz
1.99
5.01
1.99
2.01
1.00
1.02
1.02
3.00
9.0 8.5 8.0 7.5 7.0 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 -0.5 -1.0
f1 (ppm)


166.611
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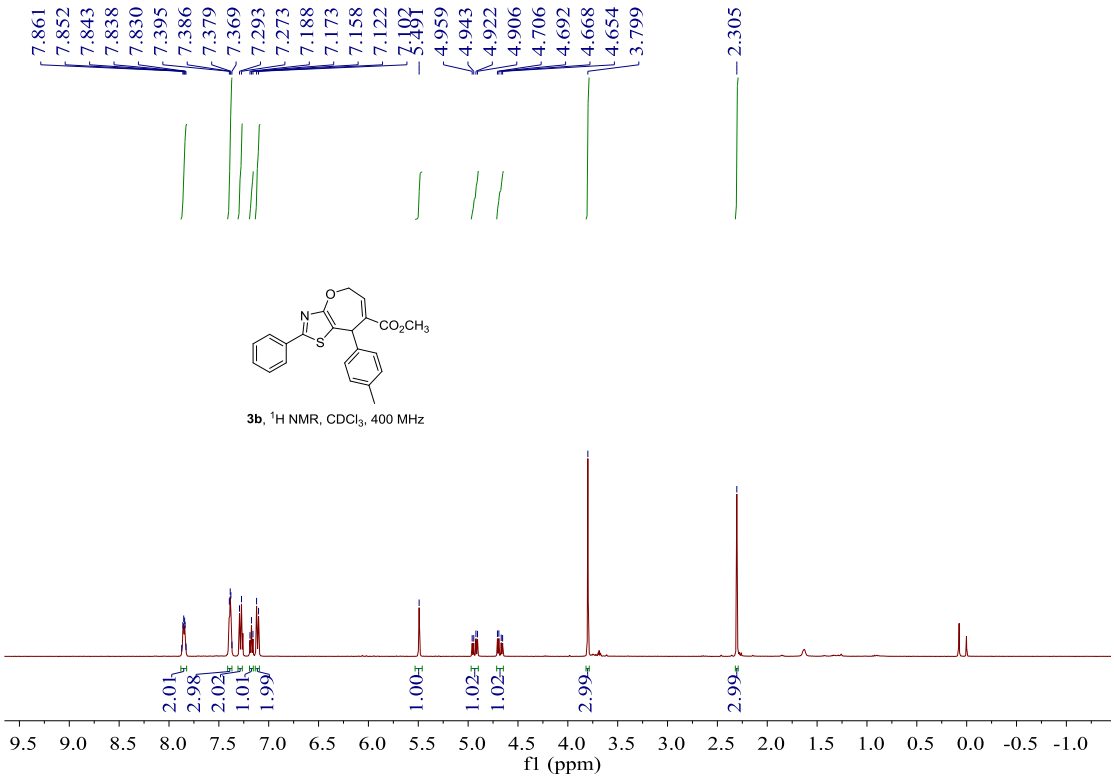
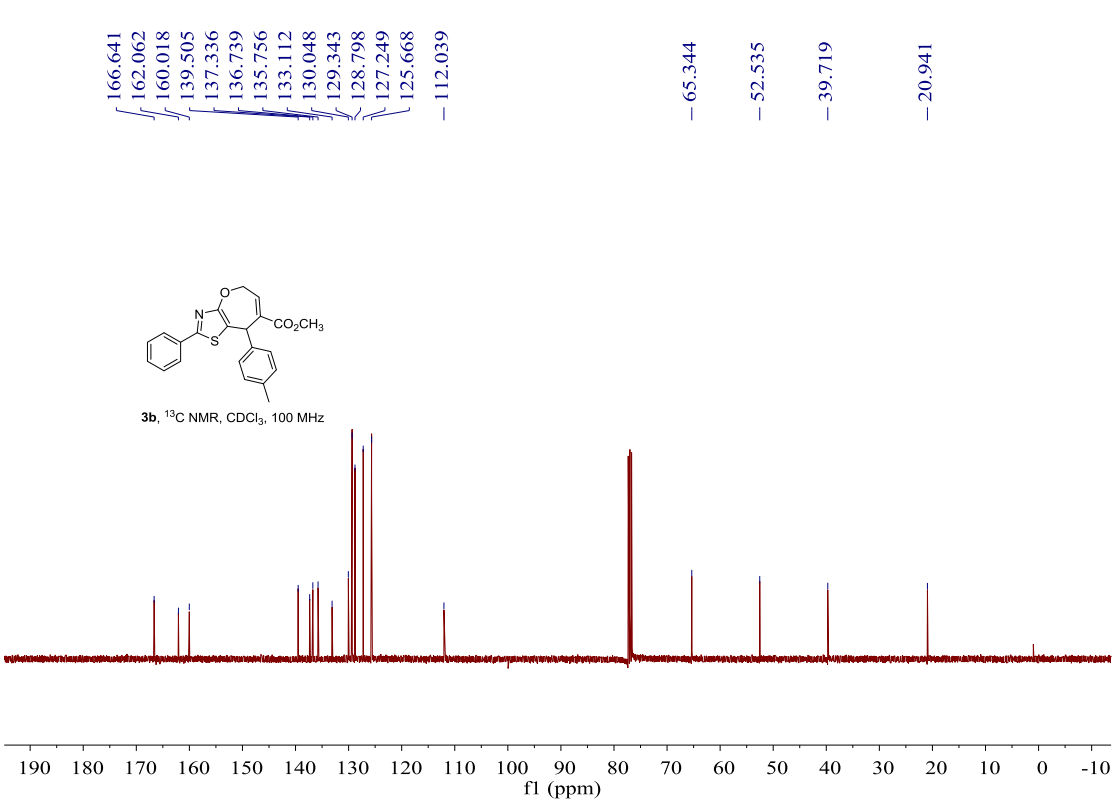
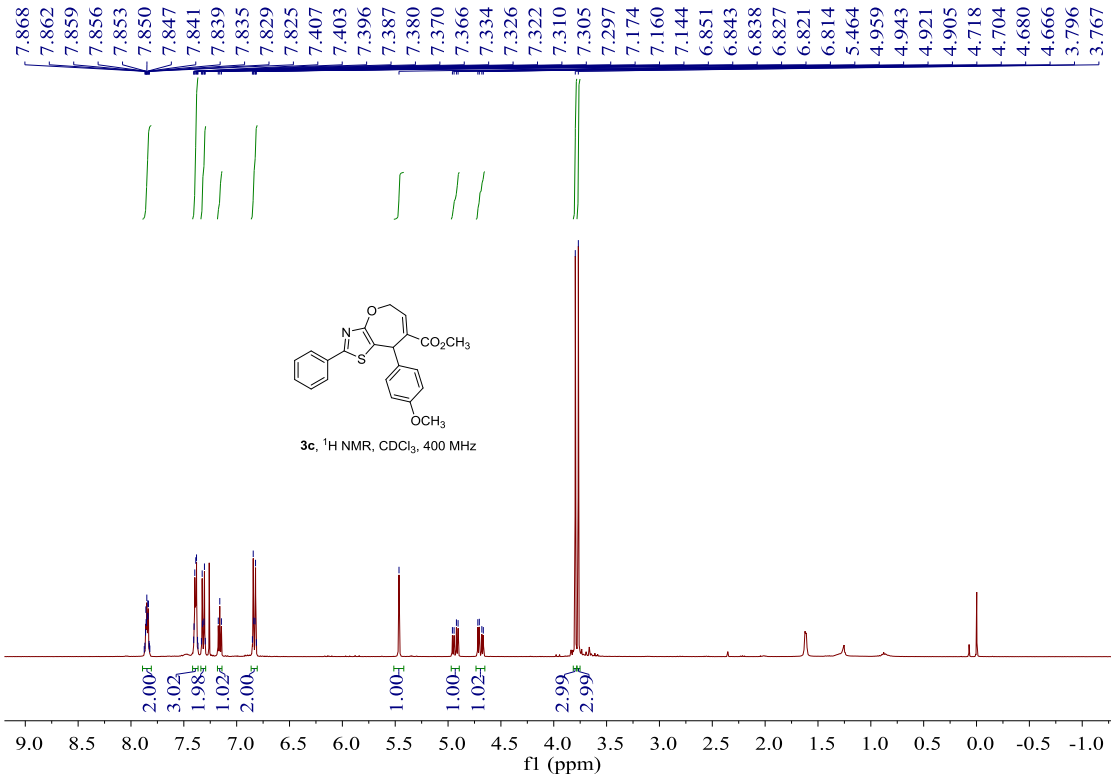
160.055
142.412
137.249
135.910
133.064
130.095
128.814
128.659
127.361
127.041
125.672
111.664
65.293
52.582
39.943
CO2CH3
3a, 13C NMR, CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



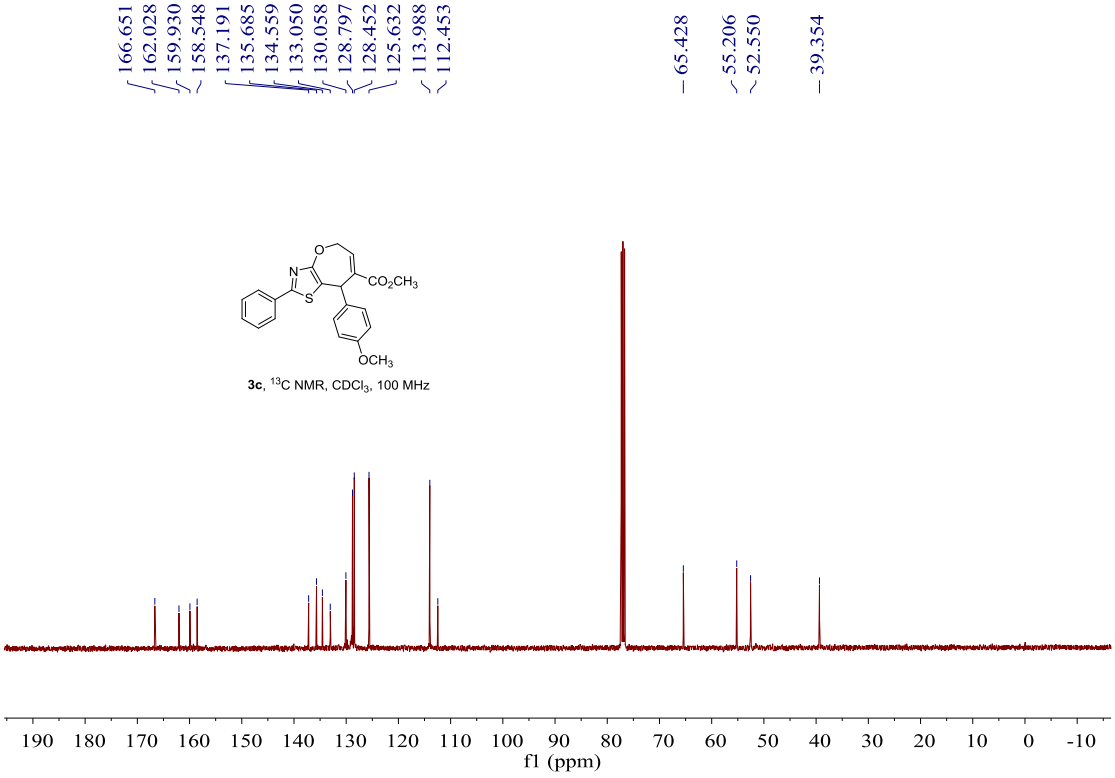
3b, ^{1}H NMR, $CDCl_3$, 400 MHz



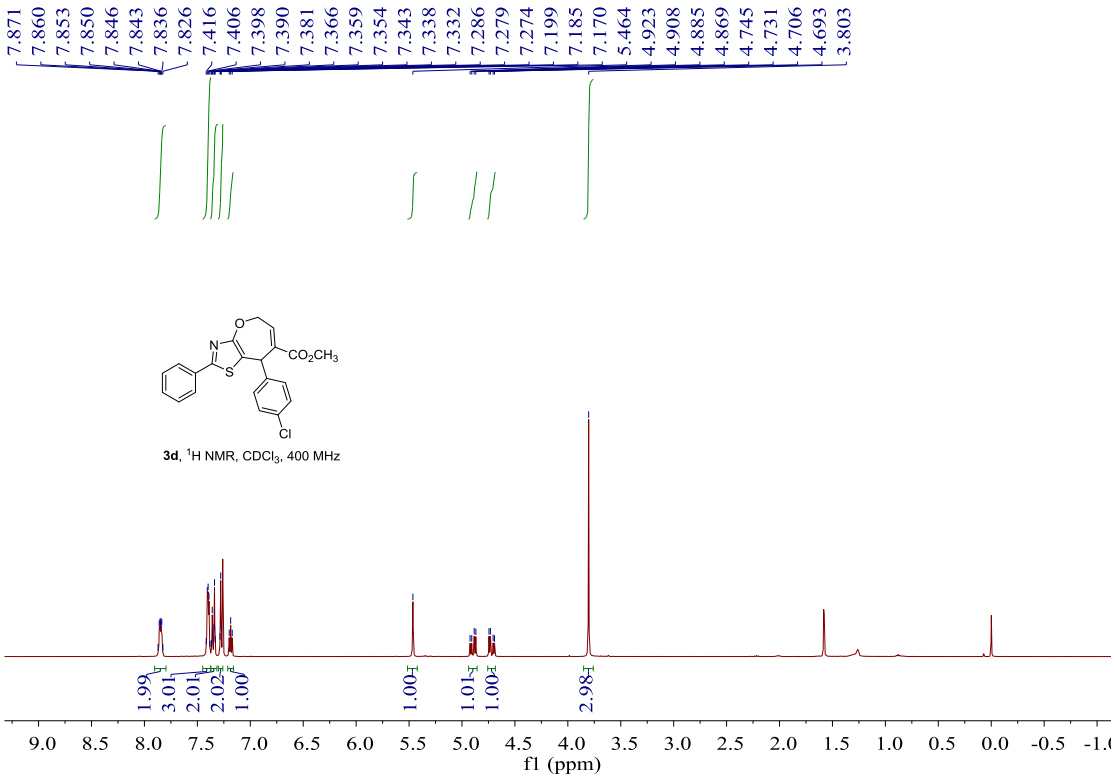
3b, ^{13}C NMR, $CDCl_3$, 100 MHz



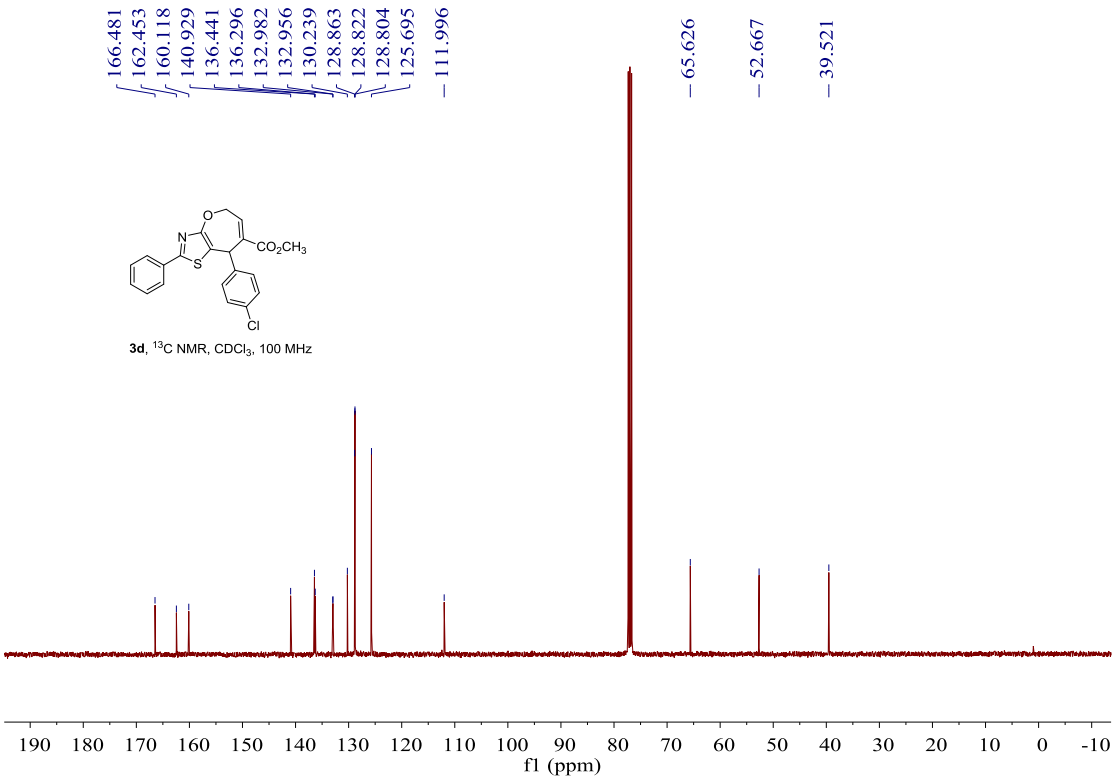
3c, ^{1}H NMR, $CDCl_3$, 400 MHz



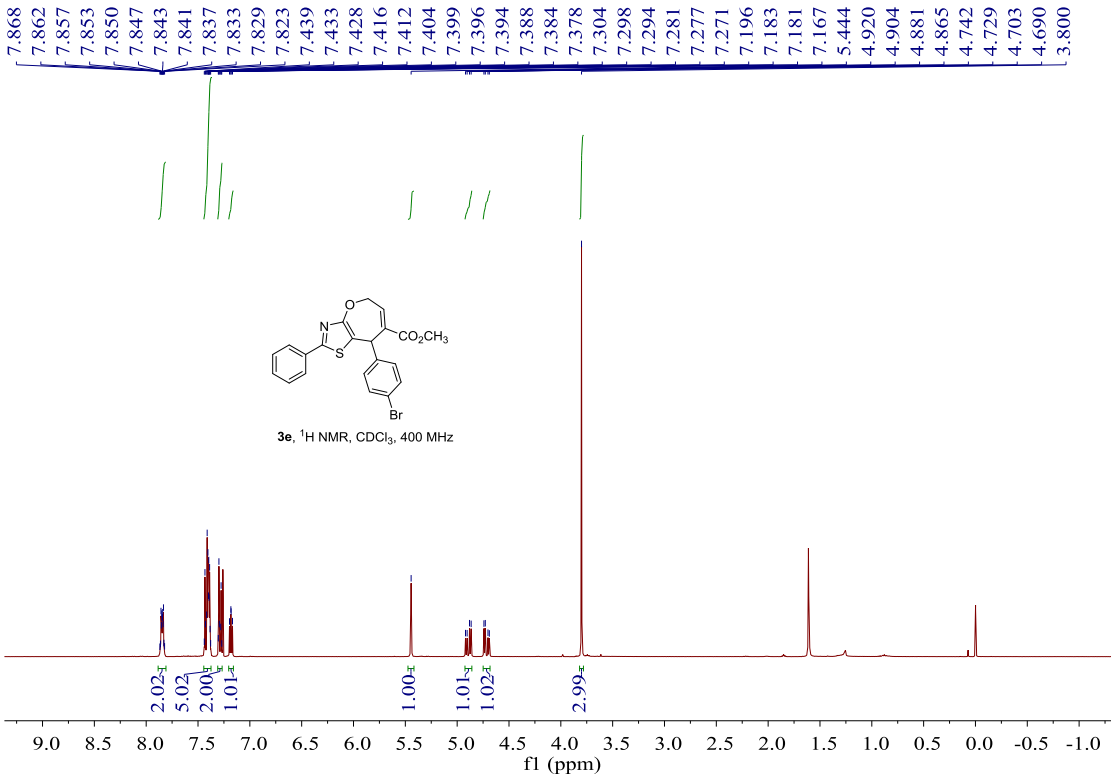
3c, ^{13}C NMR, $CDCl_3$, 100 MHz



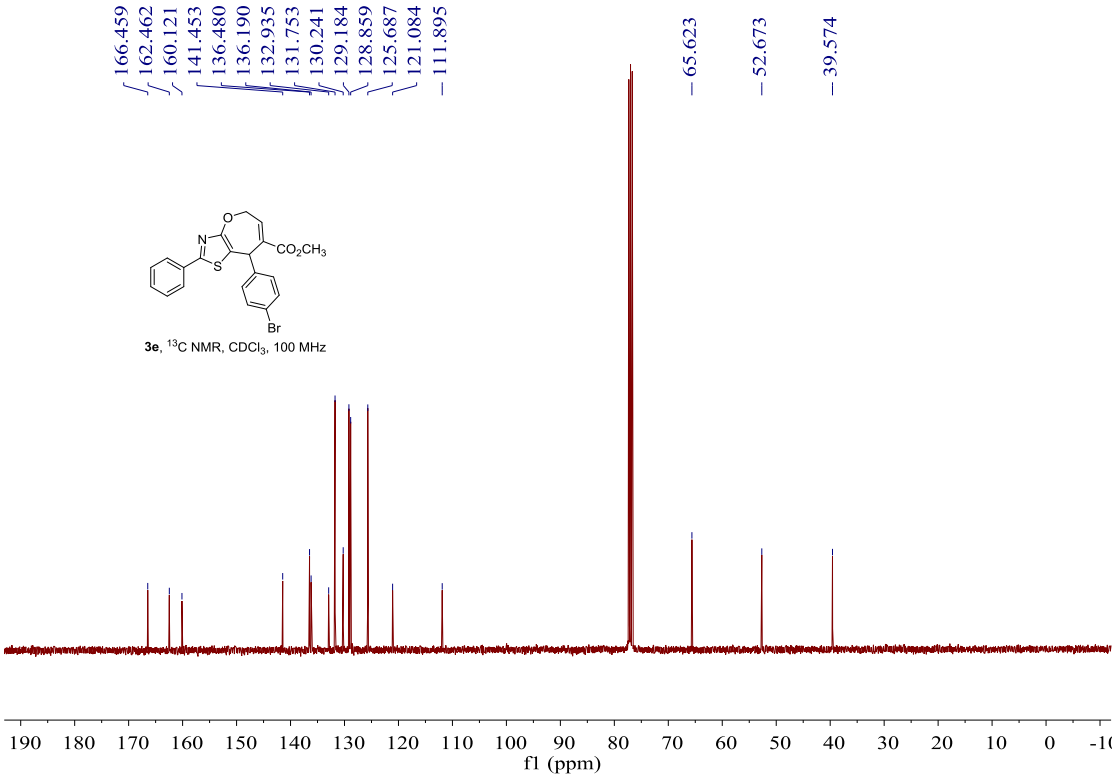
3d, ^{1}H NMR, $CDCl_3$, 400 MHz



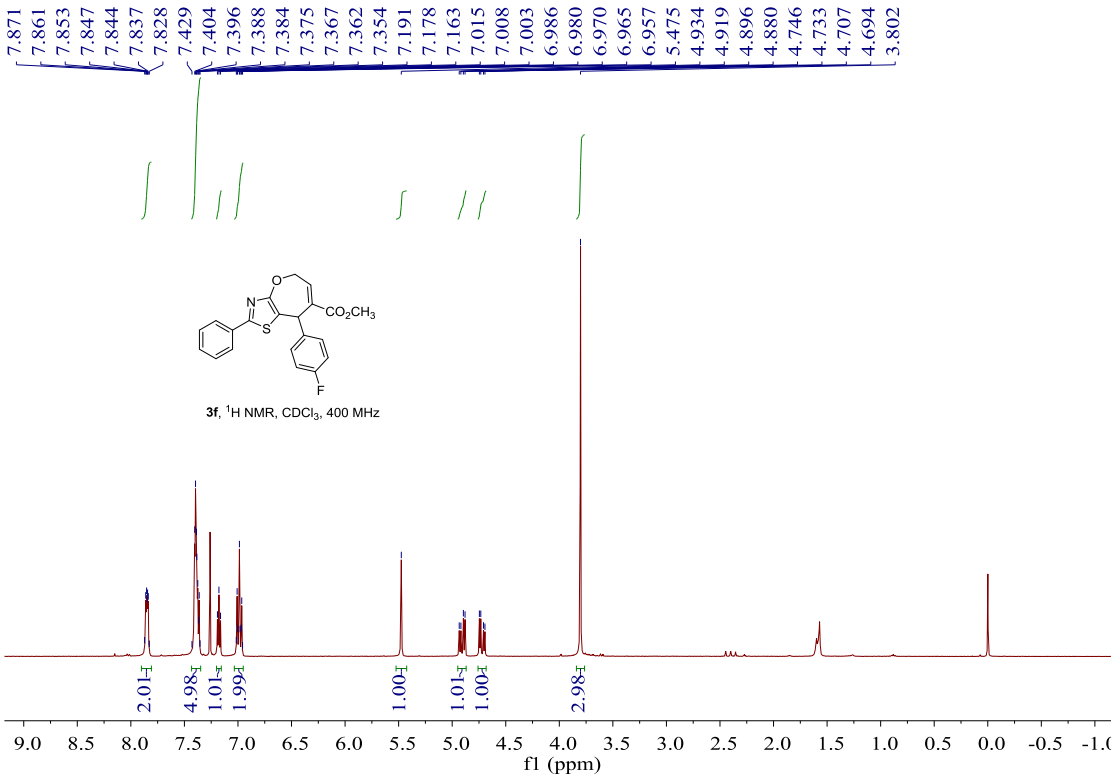
3d, ^{13}C NMR, $CDCl_3$, 100 MHz



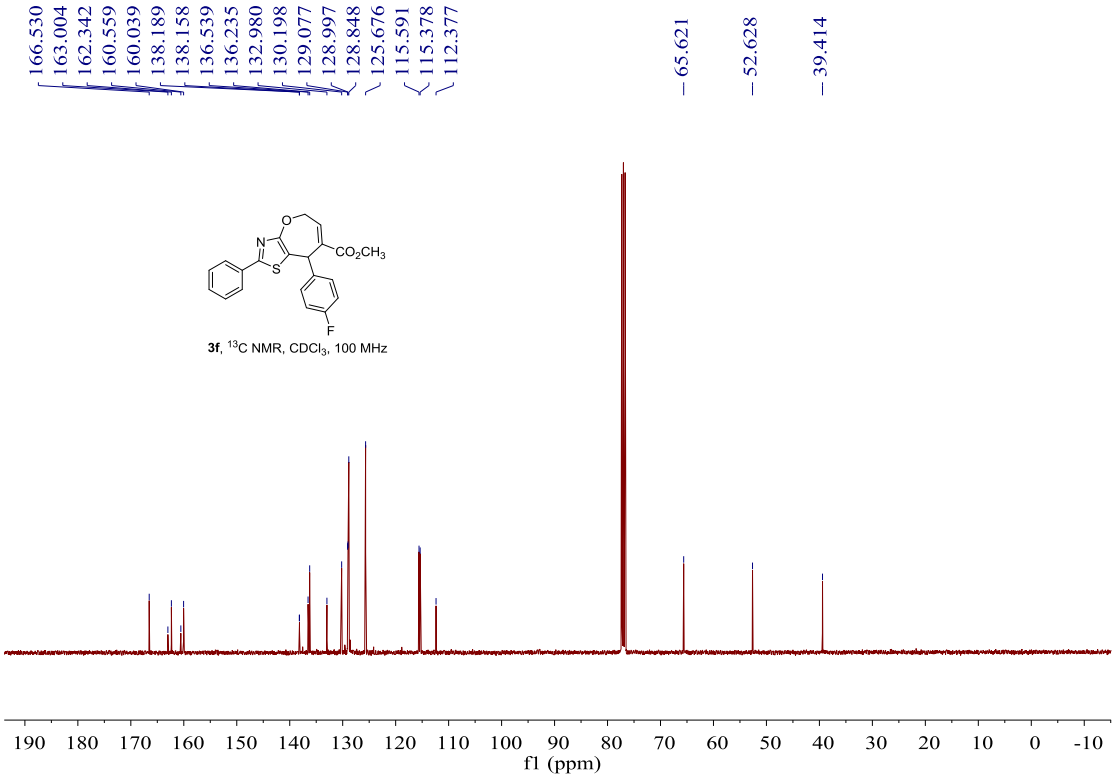
3e, ^{1}H NMR, $CDCl_3$, 400 MHz



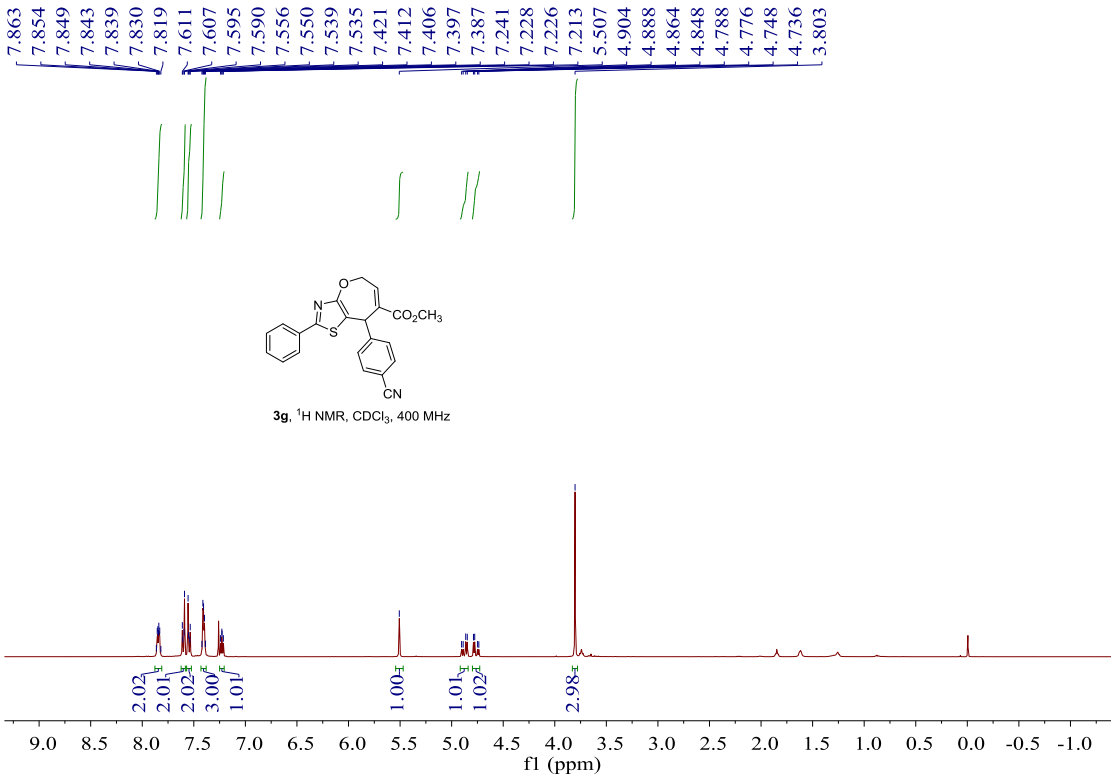
3e, ^{13}C NMR, $CDCl_3$, 100 MHz



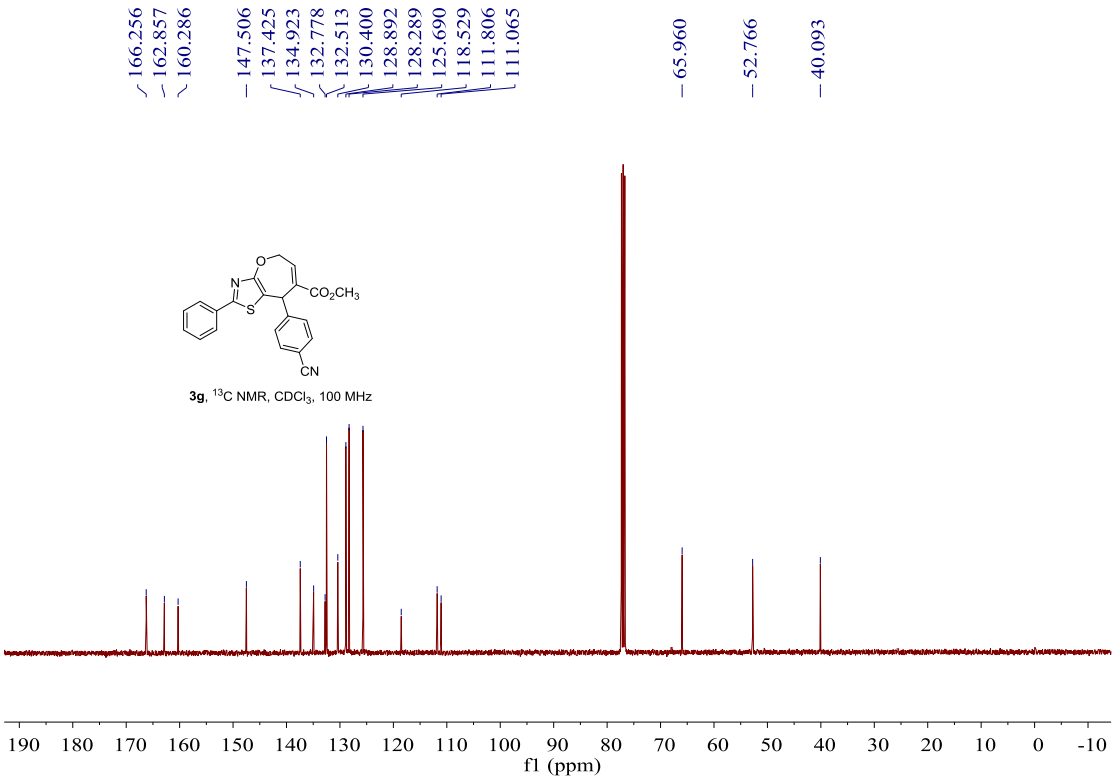
3f, ^{1}H NMR, $CDCl_3$, 400 MHz



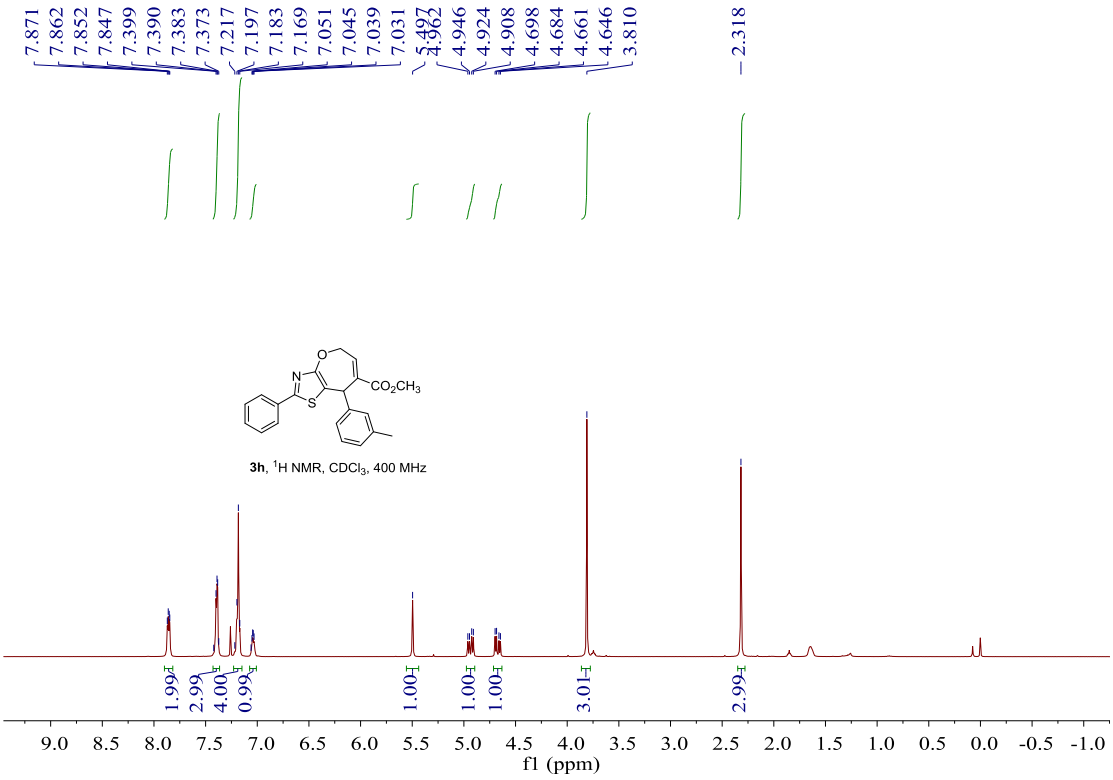
3f, ^{13}C NMR, $CDCl_3$, 100 MHz

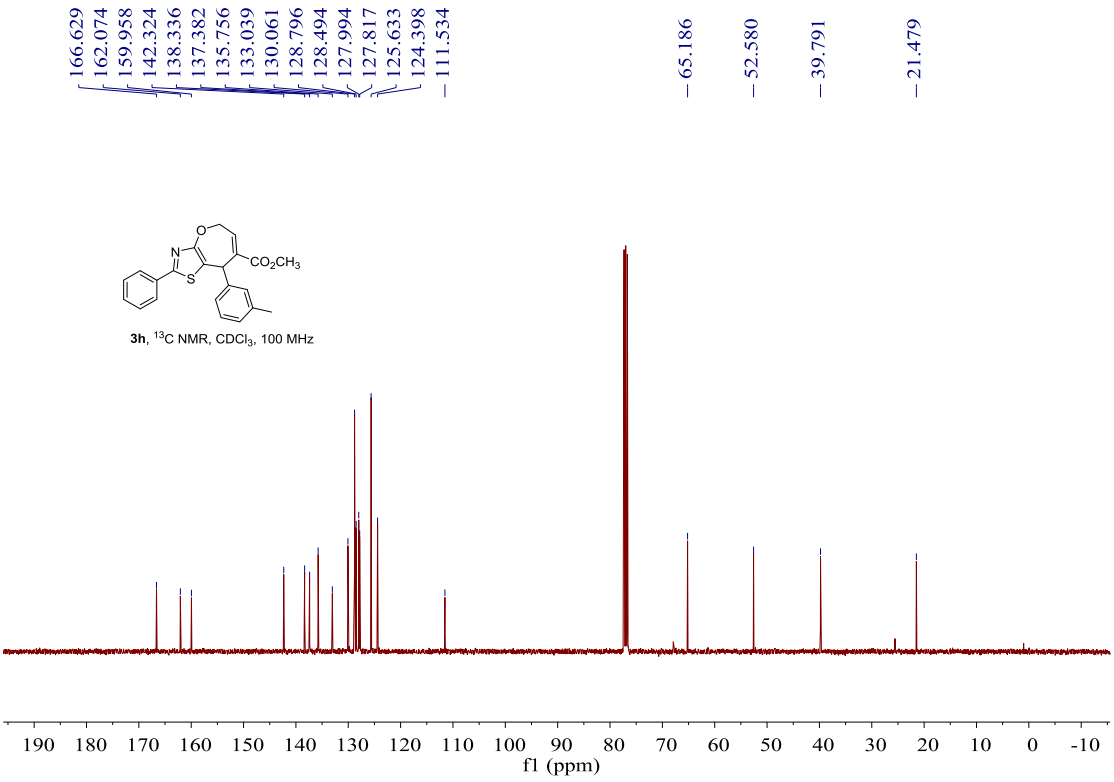


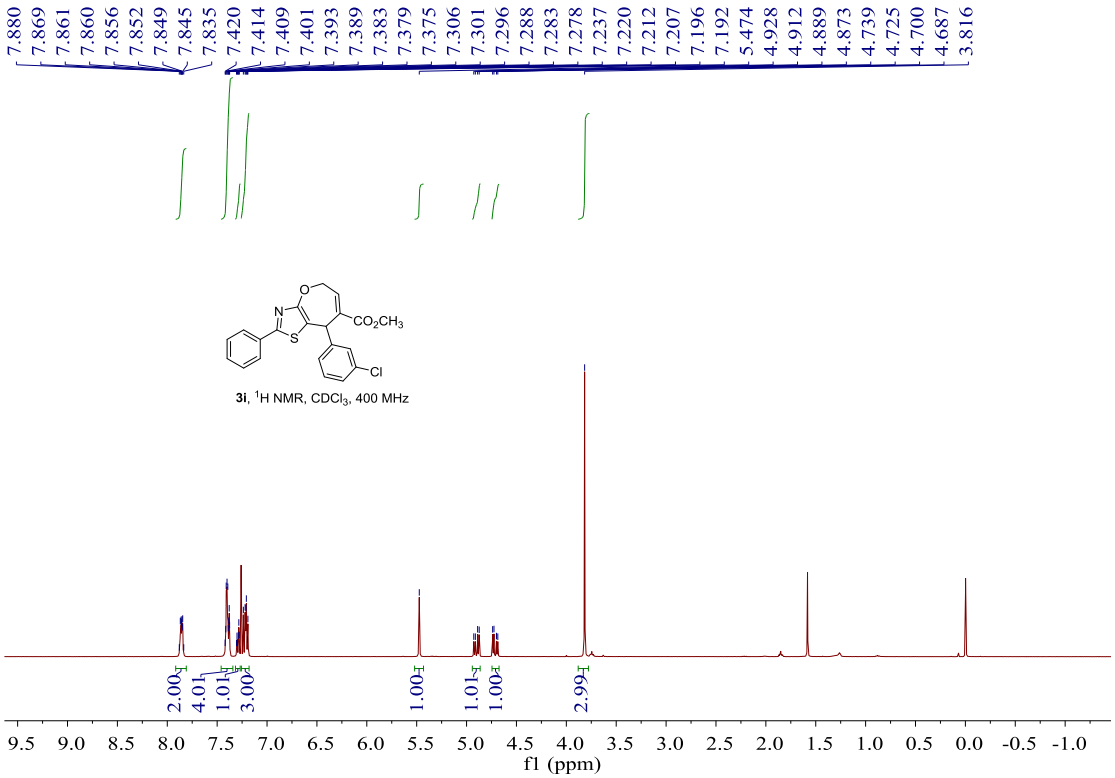
3g, ^{1}H NMR, $CDCl_3$, 400 MHz



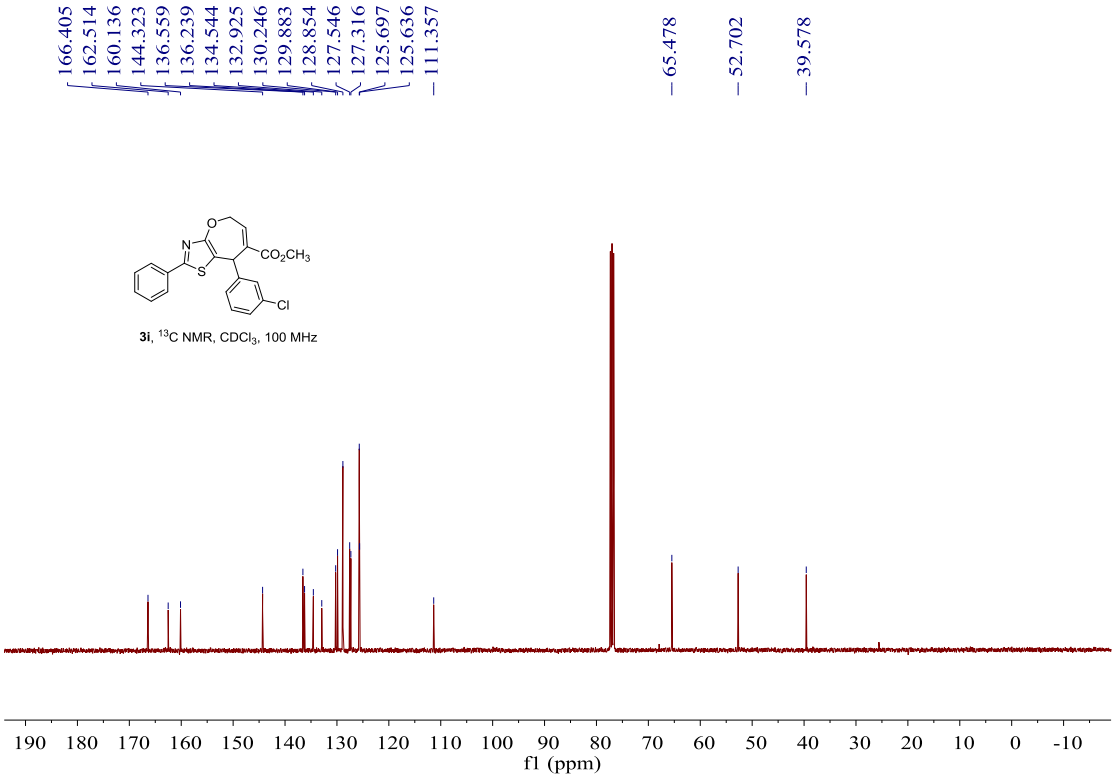
3g, ^{13}C NMR, $CDCl_3$, 100 MHz


7.871
7.862
7.852
7.847
7.399
7.390
7.383
7.373
7.217
7.197
7.183
7.169
7.051
7.045
7.039
7.031
5.497
4.962
4.946
4.924
4.908
4.698
4.684
4.661
4.646
3.810
2.318
O
N
S
CO2CH3
3h, 1H NMR, CDCl3, 400 MHz
1.99
2.99
4.00
0.99
1.00
1.00
1.00
3.01
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

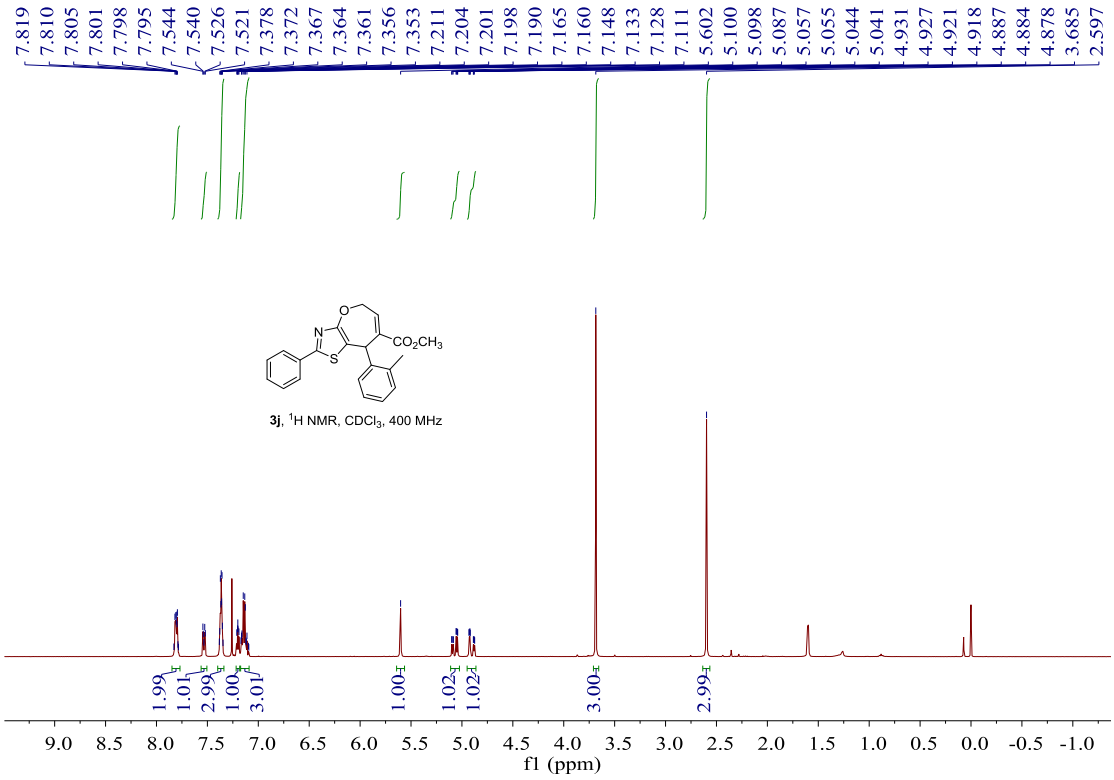

166.629
162.074
159.958
142.324
138.336
137.382
135.756
133.039
130.061
128.796
128.494
127.994
127.817
125.633
124.398
111.534
65.186
52.580
39.791
21.479
O
N
S
CO2CH3
3h, 13C NMR, CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



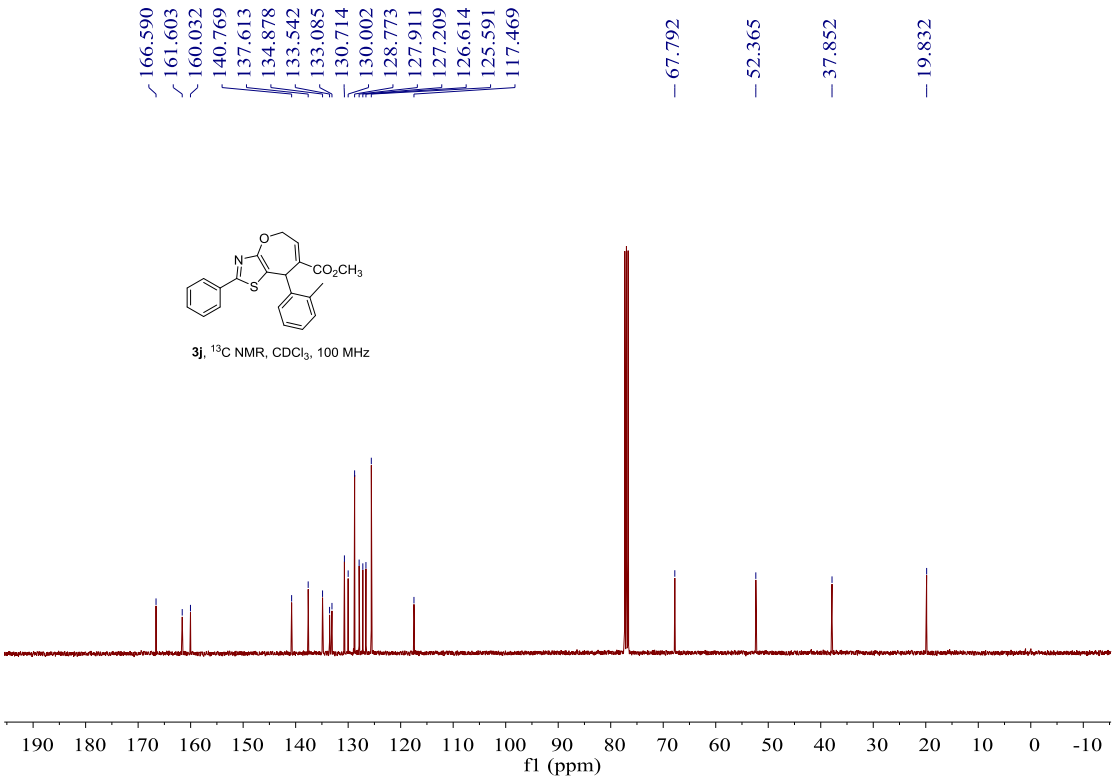
3i, ^{1}H NMR, $CDCl_3$, 400 MHz



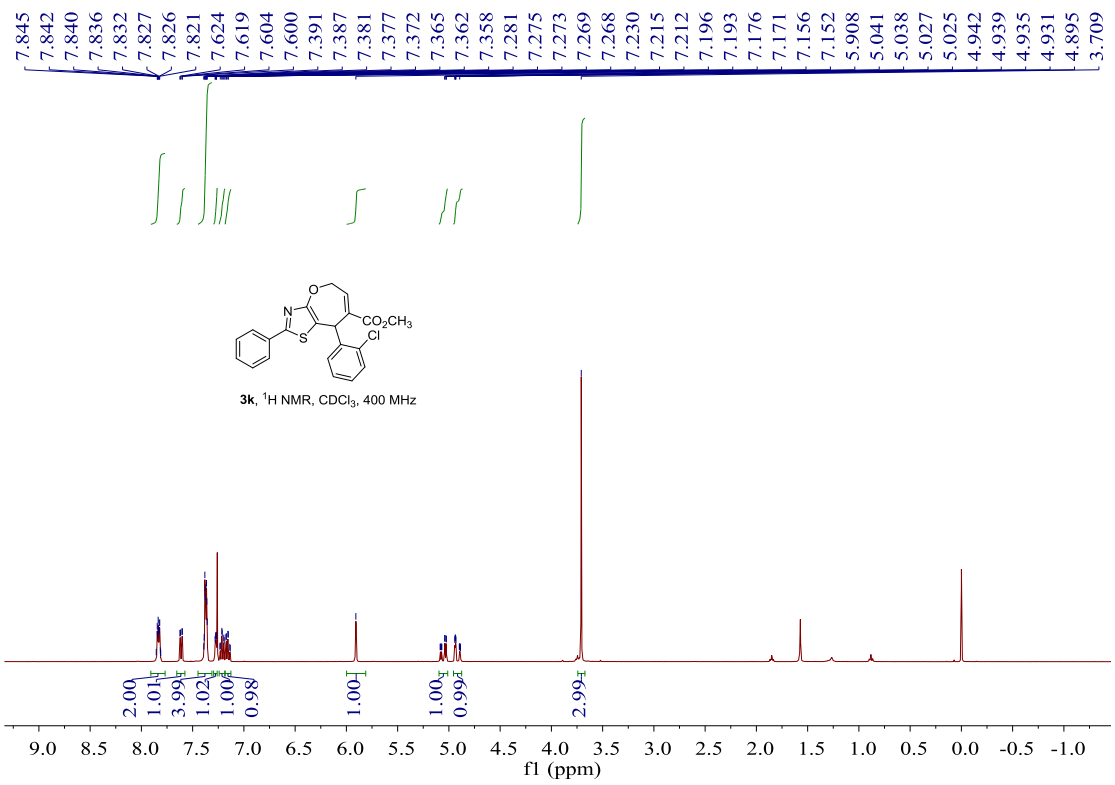
3i, ^{13}C NMR, $CDCl_3$, 100 MHz



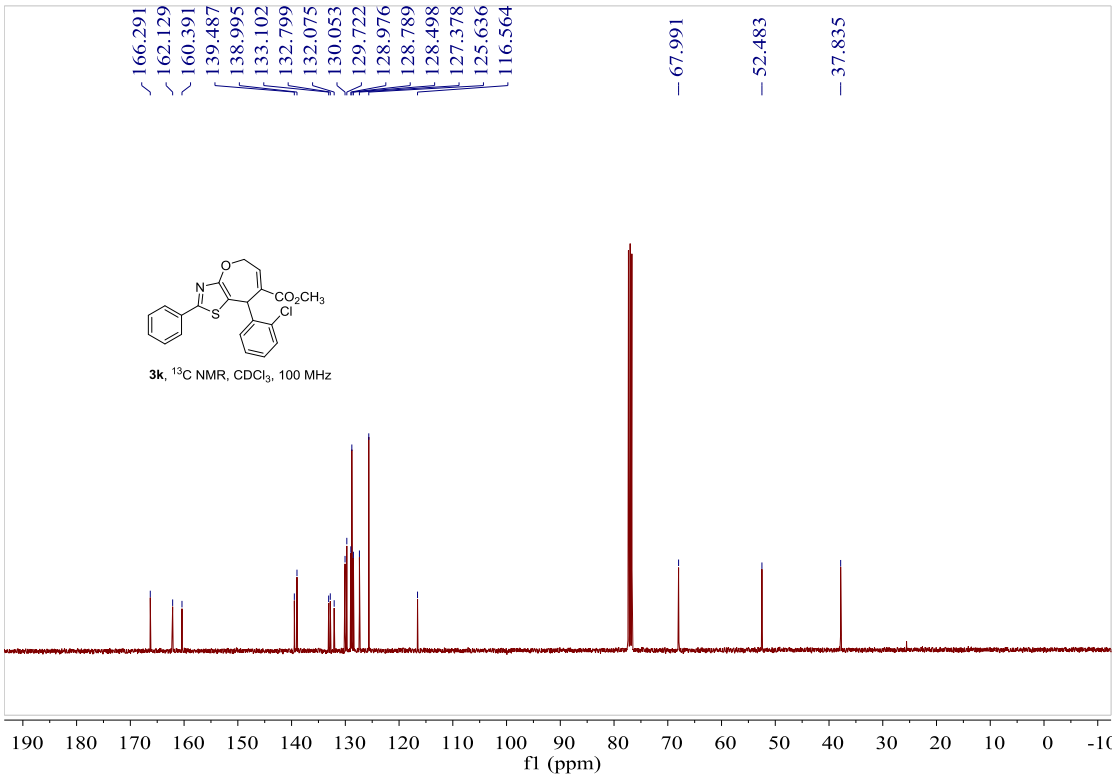
3j, ^{1}H NMR, $CDCl_3$, 400 MHz



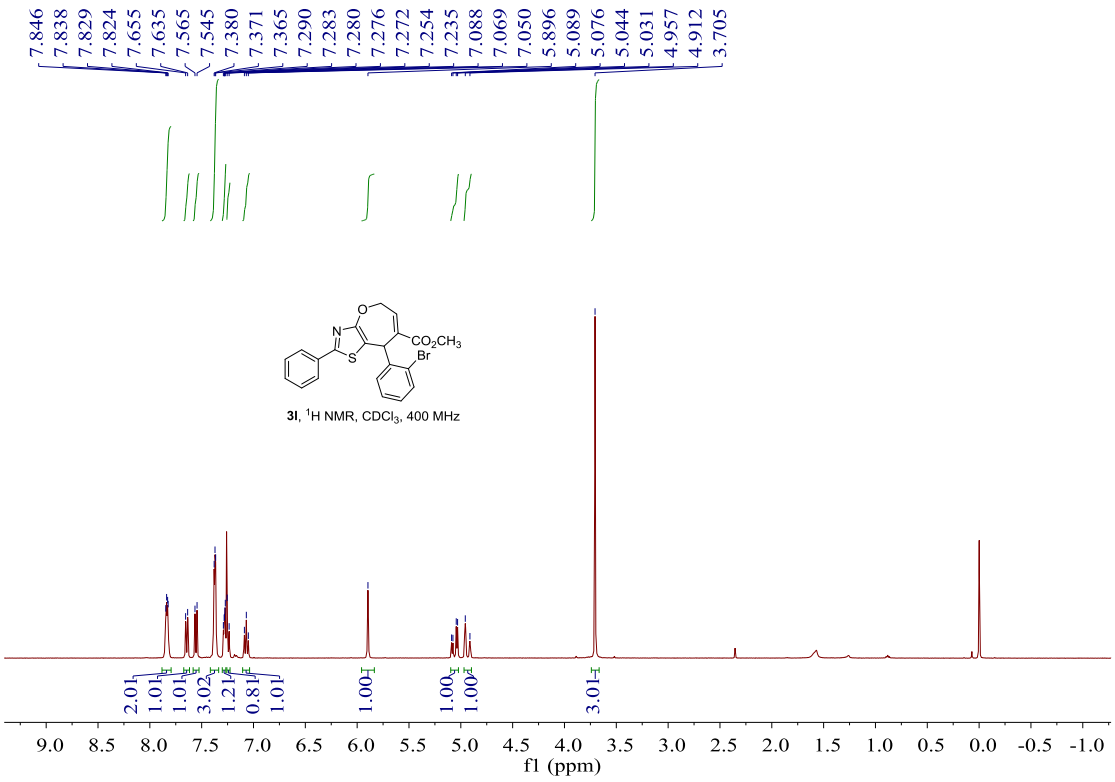
3j, ^{13}C NMR, $CDCl_3$, 100 MHz



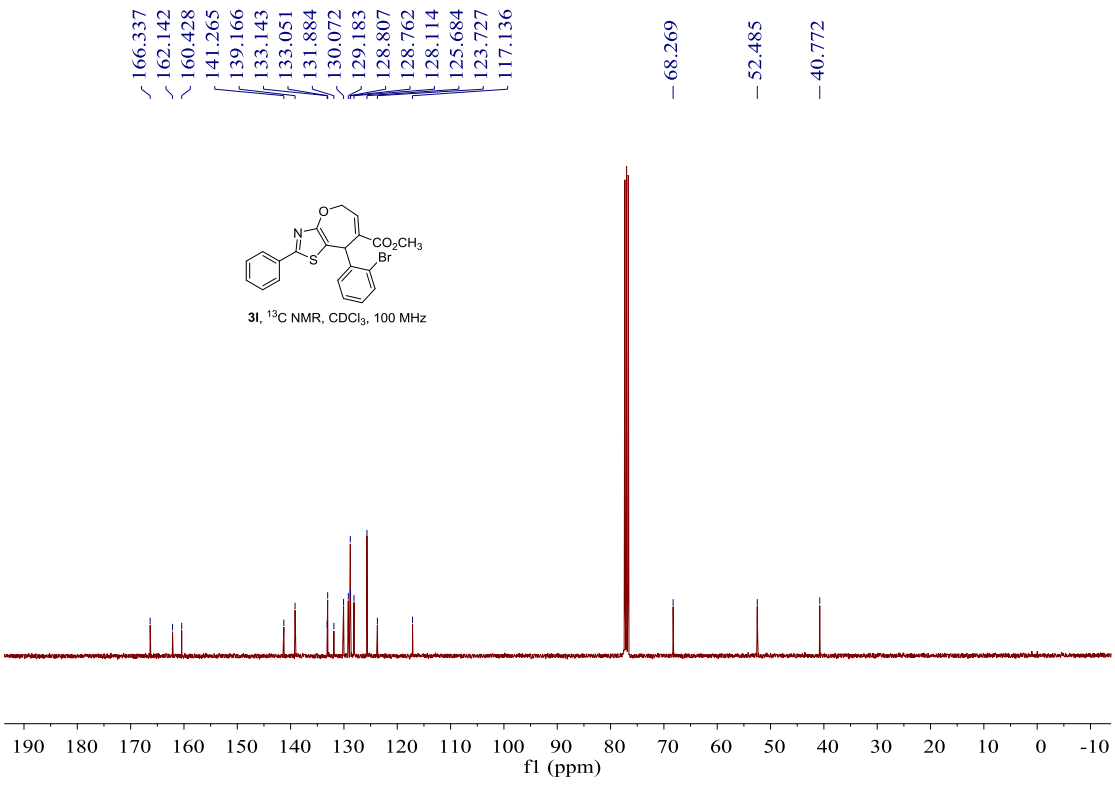
3k, ^{1}H NMR, $CDCl_3$, 400 MHz



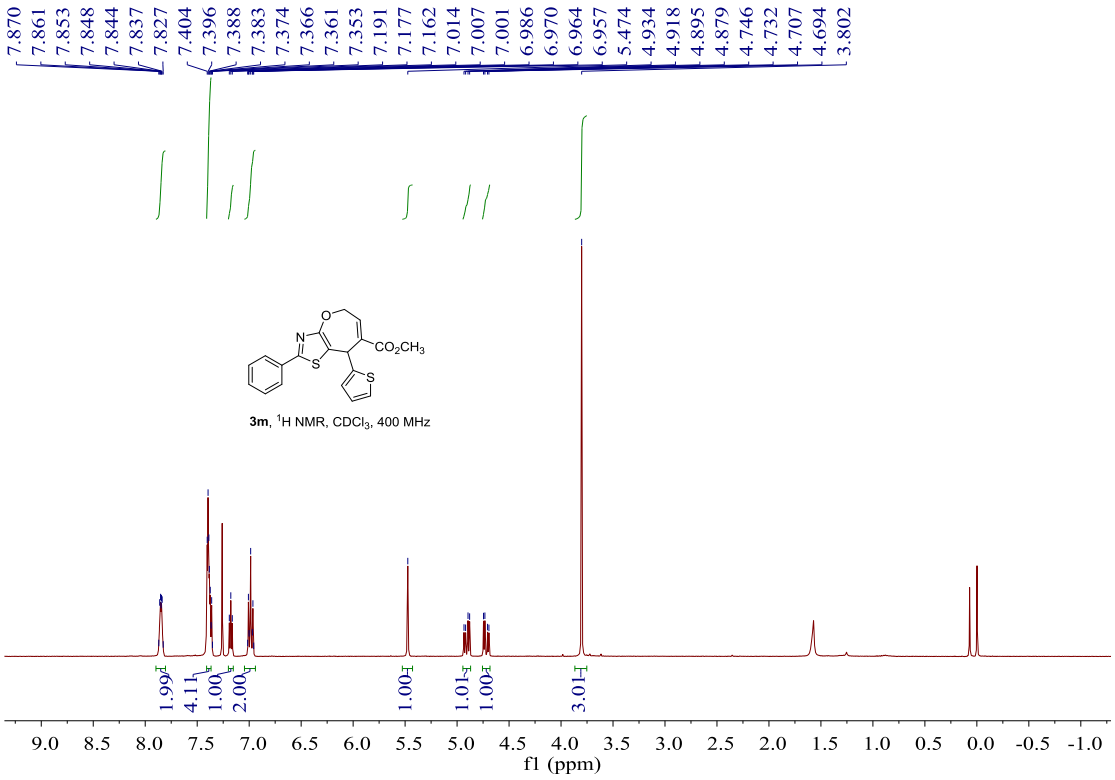
3k, ^{13}C NMR, $CDCl_3$, 100 MHz



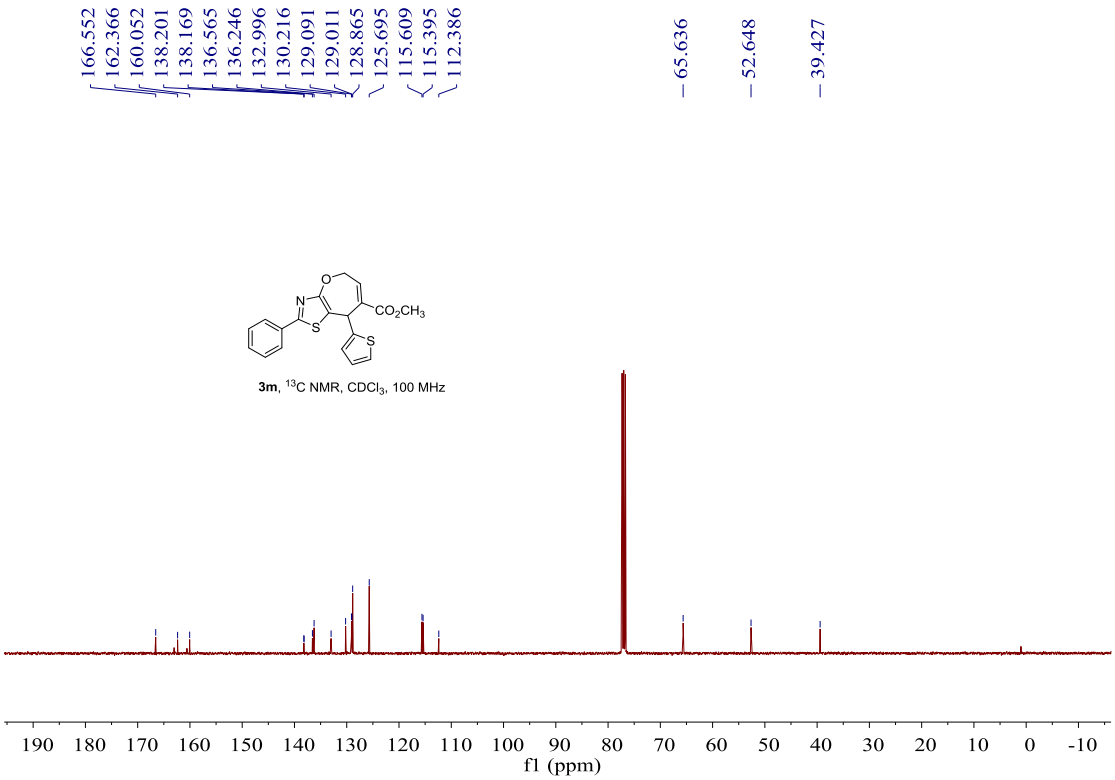
3l, ^{1}H NMR, $CDCl_3$, 400 MHz



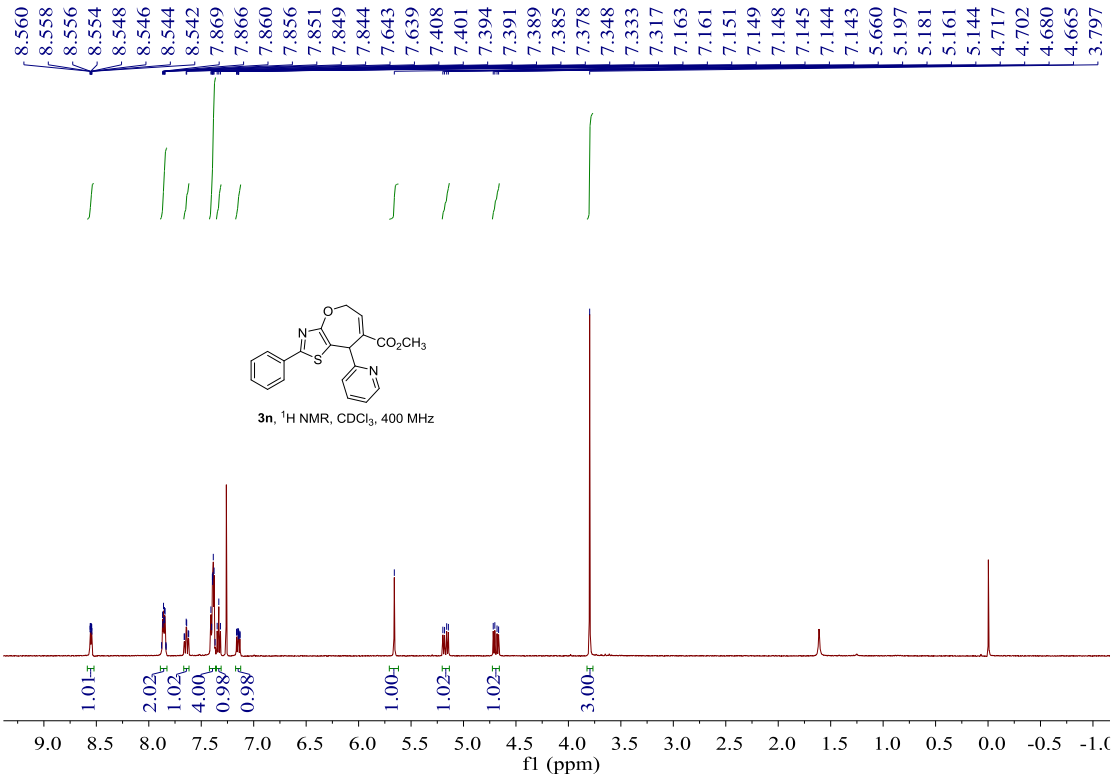
3l, ^{13}C NMR, $CDCl_3$, 100 MHz

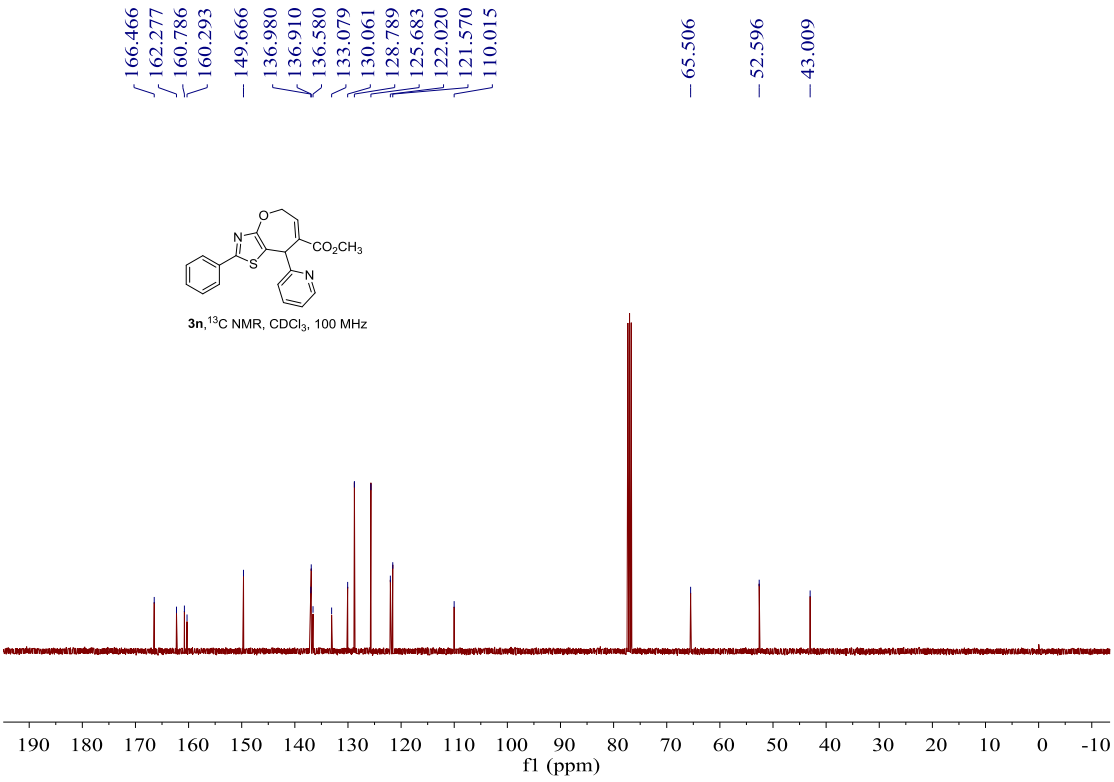


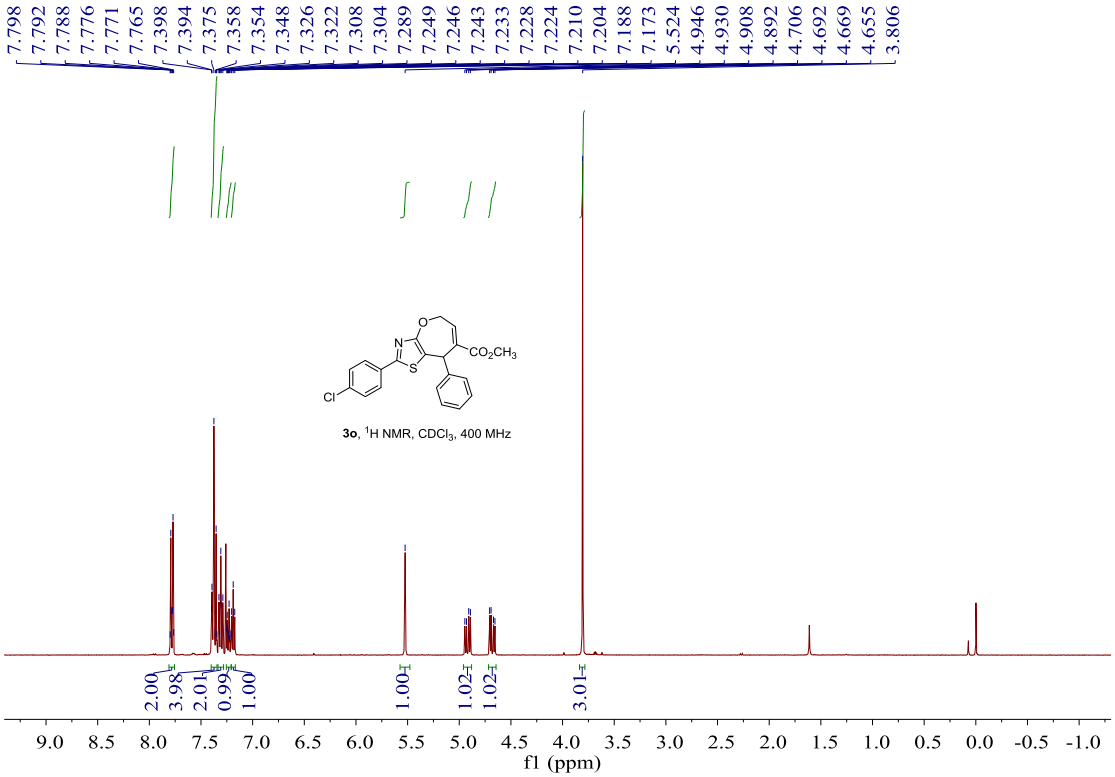
3m, ^{1}H NMR, $CDCl_3$, 400 MHz



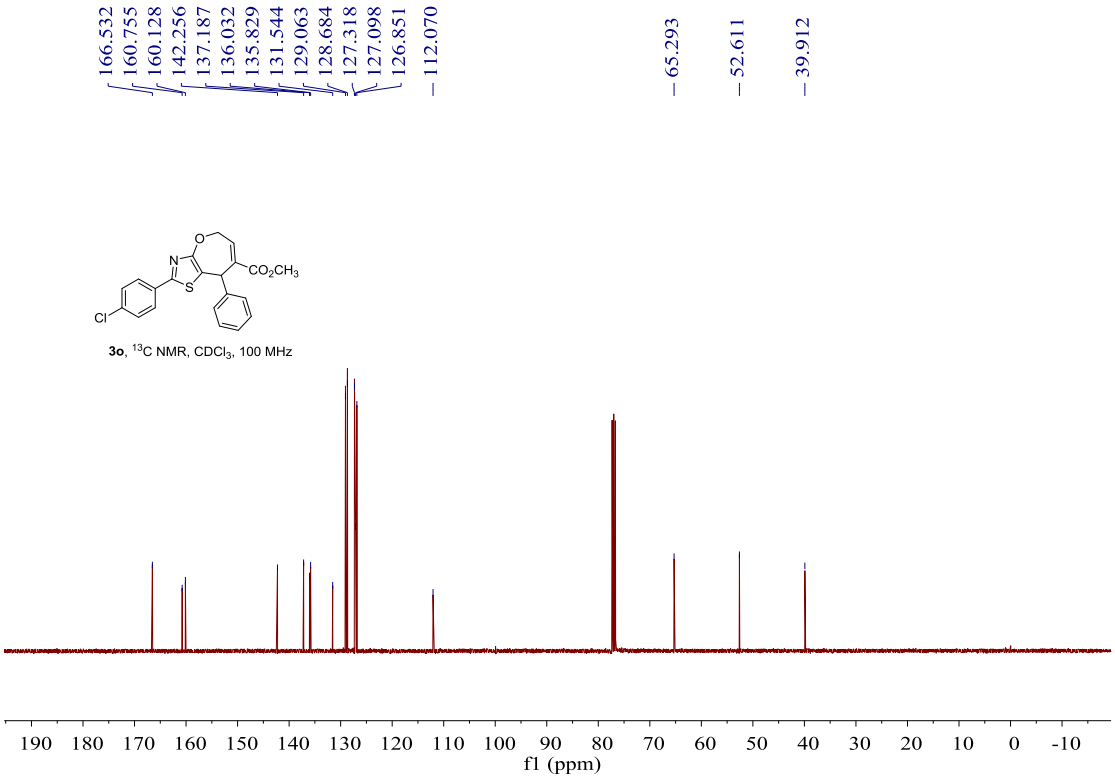
3m, ^{13}C NMR, $CDCl_3$, 100 MHz


8.560
8.558
8.556
8.554
8.548
8.546
8.544
8.542
7.869
7.866
7.860
7.856
7.851
7.849
7.844
7.643
7.639
7.408
7.401
7.394
7.391
7.389
7.385
7.378
7.348
7.333
7.317
7.163
7.161
7.151
7.149
7.148
7.145
7.144
7.143
5.660
5.197
5.181
5.161
5.144
4.717
4.702
4.680
4.665
3.797
O
N
S
CO2CH3
N
3n, 1H NMR, CDCl3, 400 MHz
1.01
2.02
1.02
4.00
0.98
0.98
1.00
1.02
1.02
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 -0.5
f1 (ppm)

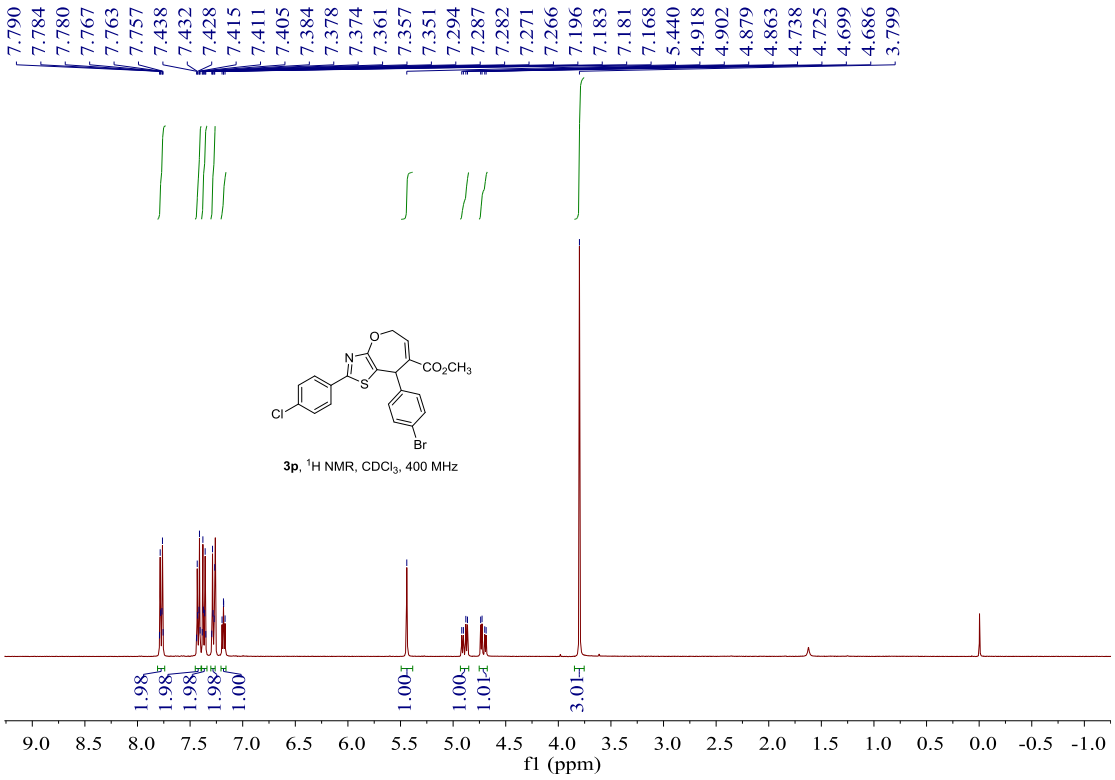

166.466
162.277
160.786
160.293
149.666
136.980
136.910
136.580
133.079
130.061
128.789
125.683
122.020
121.570
110.015
65.506
52.596
43.009
O
N
S
CO2CH3
N
3n,13C NMR, CDCl3, 100 MHz
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



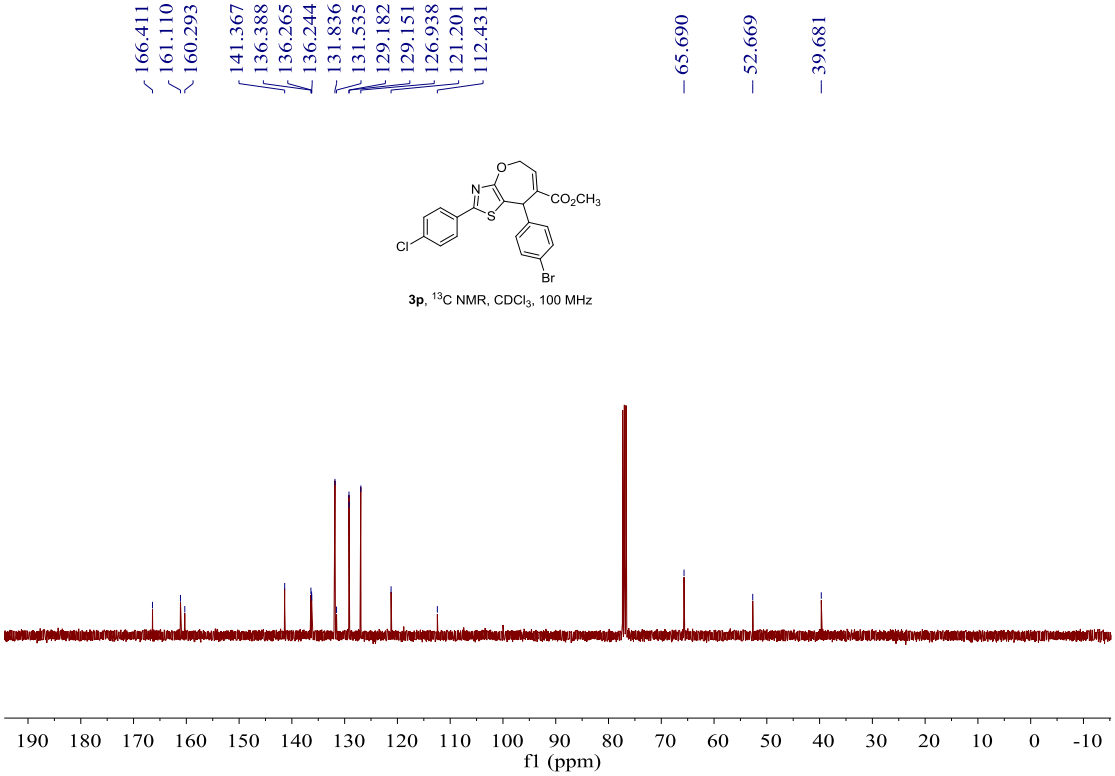
3o, ^{1}H NMR, $CDCl_3$, 400 MHz



3o, ^{13}C NMR, $CDCl_3$, 100 MHz



3p, ^{1}H NMR, $CDCl_3$, 400 MHz



3p, ^{13}C NMR, $CDCl_3$, 100 MHz