Supplementary Information

Modular Synthesis of 3-Substituted Isocoumarins *via* Silver-Catalyzed Aerobic Oxidation/*6-Endo* Heterocyclization of *ortho*-Alkynylbenzaldehydes

Hao Wu,[a] Andrey Shatskiy,[b] Yi-Chun Wang,[a] Qiu-Yan Li, [a] Jian-Quan Liu,[a,b,] Markus D. Kärkäs,[b,]* Xiang-Shan Wang[a,]**

[a] School of Chemistry and Materials Science, Jiangsu Key Laboratory of Green Synthesis for Functional Materials Jiangsu Normal University, Xuzhou, Jiangsu 221116, China

[b] Department of Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

* E-mail: liujq316@jsnu.edu.cn; karkas@kth.se; xswang1974@yahoo.com

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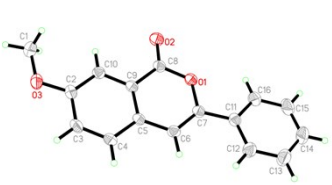
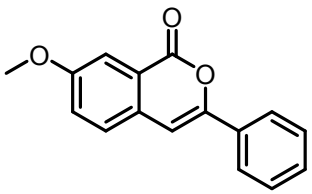
I. Crystallography

Compound **2d** (58 mg) was dissolved in a centrifuge tube with 100 μL DMF and 50 μL H_2O. Two days later, we can get the the single-crystal of **2d**. Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 296(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.[1] Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S1.

1 (*a*) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures, University of Gottingen,* Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures, University of Gottingen,* Germany, 1997.

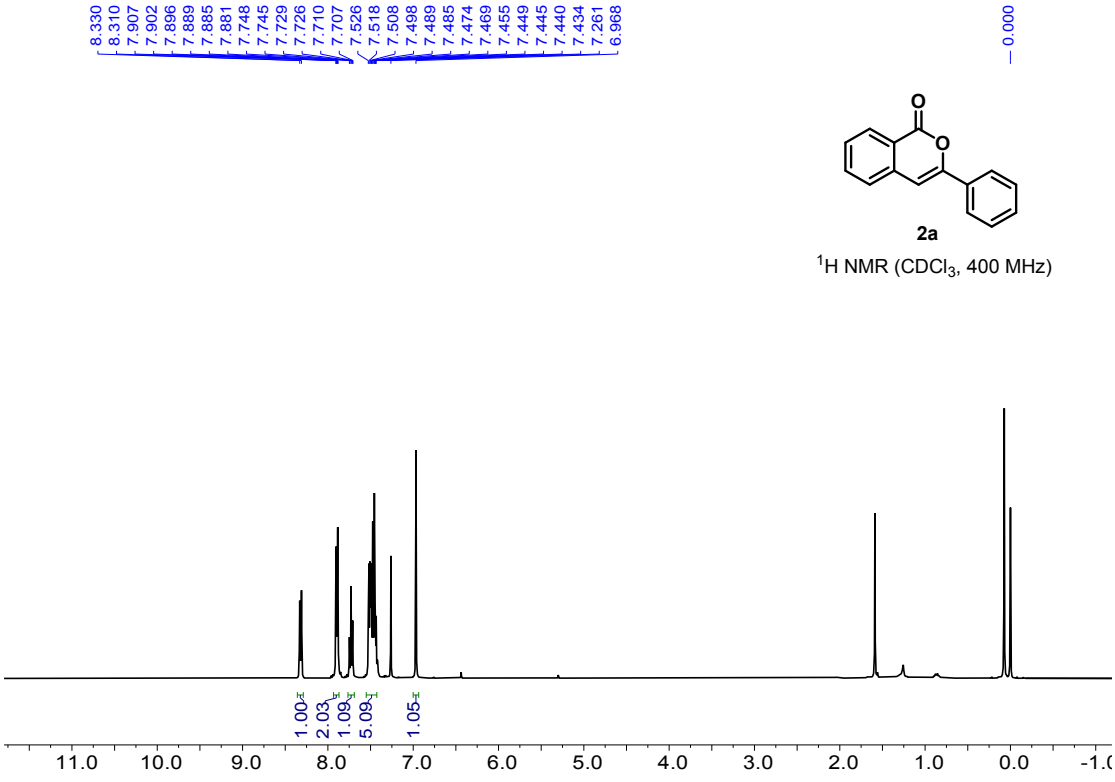
Table S1. Crystal data of **2d** with 30% probability levels and structure refinement.

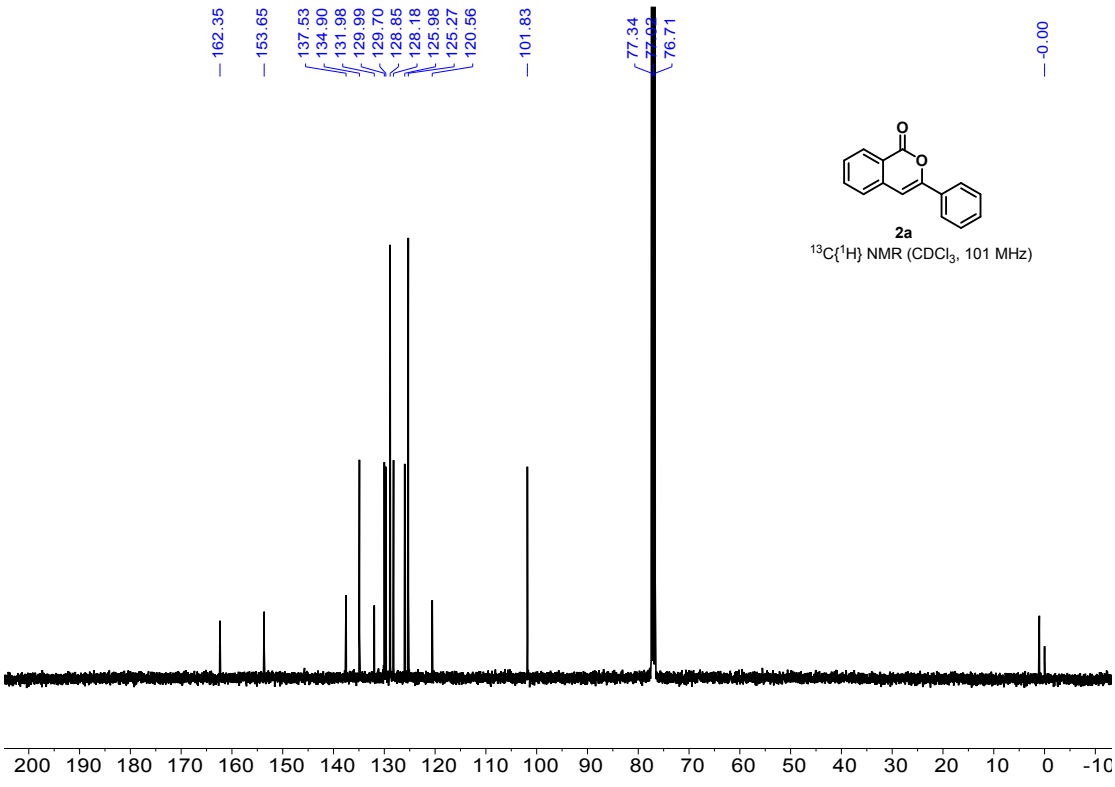


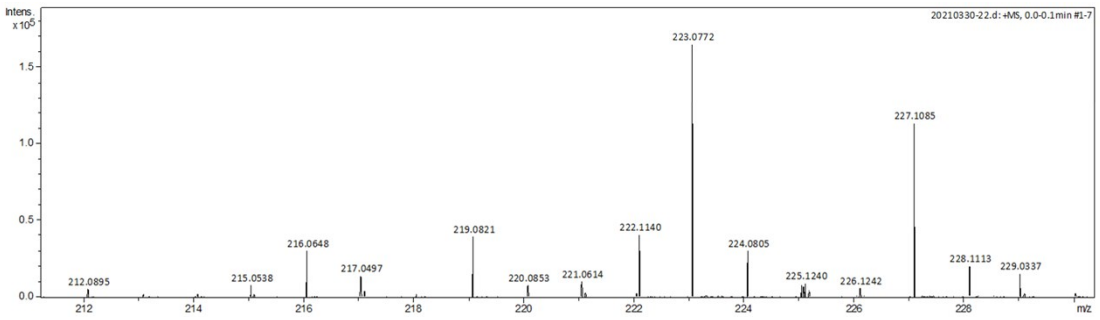


Empirical formula	$C_{16}H_{12}O_3$
Temperature	296(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 7.0451(17) Å b = 7.3918(17) Å c = 12.782(3) Å alpha = 76.201(3) deg. beta = 81.124(3) deg. gamma = 73.395(3) deg.
Volume	616.8(3) $Å^3$
Z	2
Space group	P -1
Calculated density	1.358 Mg/m^3
Absorption coefficient	0.094 mm^{-1}
F(000)	264
Crystal size	0.32 x 0.28 x 0.24 mm
Theta range for data collection	2.94 to 25.02 deg.
Reflections collected / unique	6292 / 2159 [R(int) = 0.0195]
Data / restraints / parameters	2159 / 0 / 173
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1218
R indices (all data)	R1 = 0.0507, wR2 = 0.1317

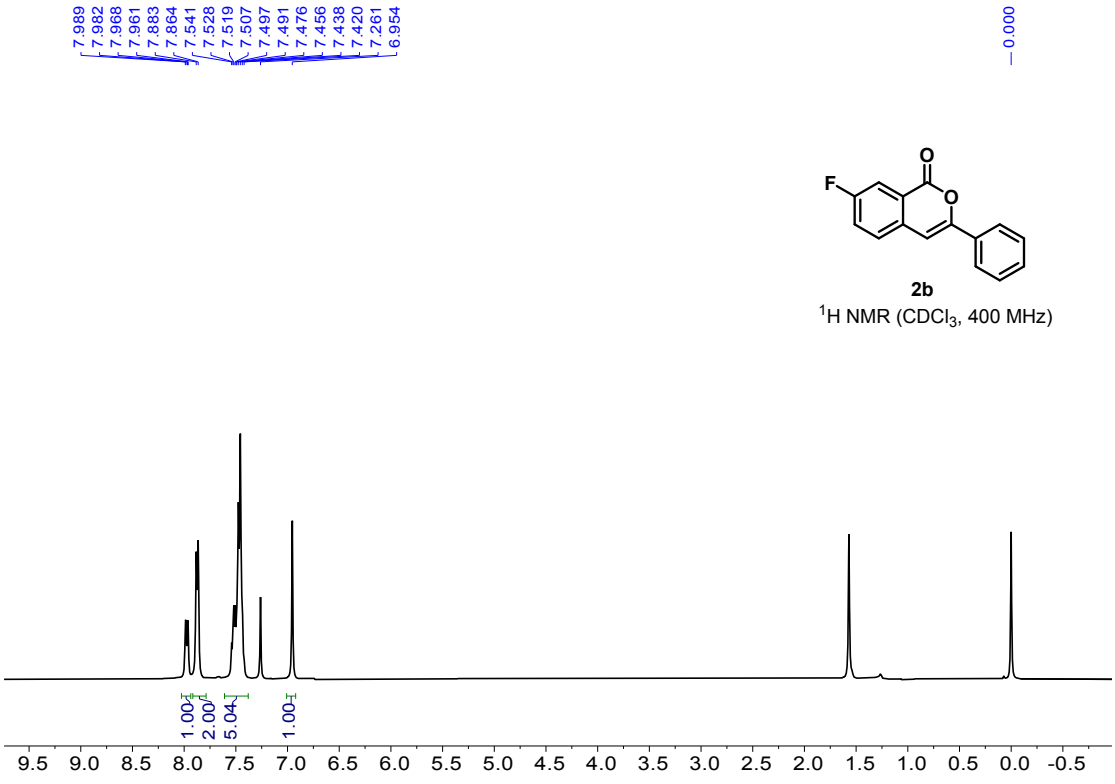
II. NMR and HRMS spectra copies of 2 and 3





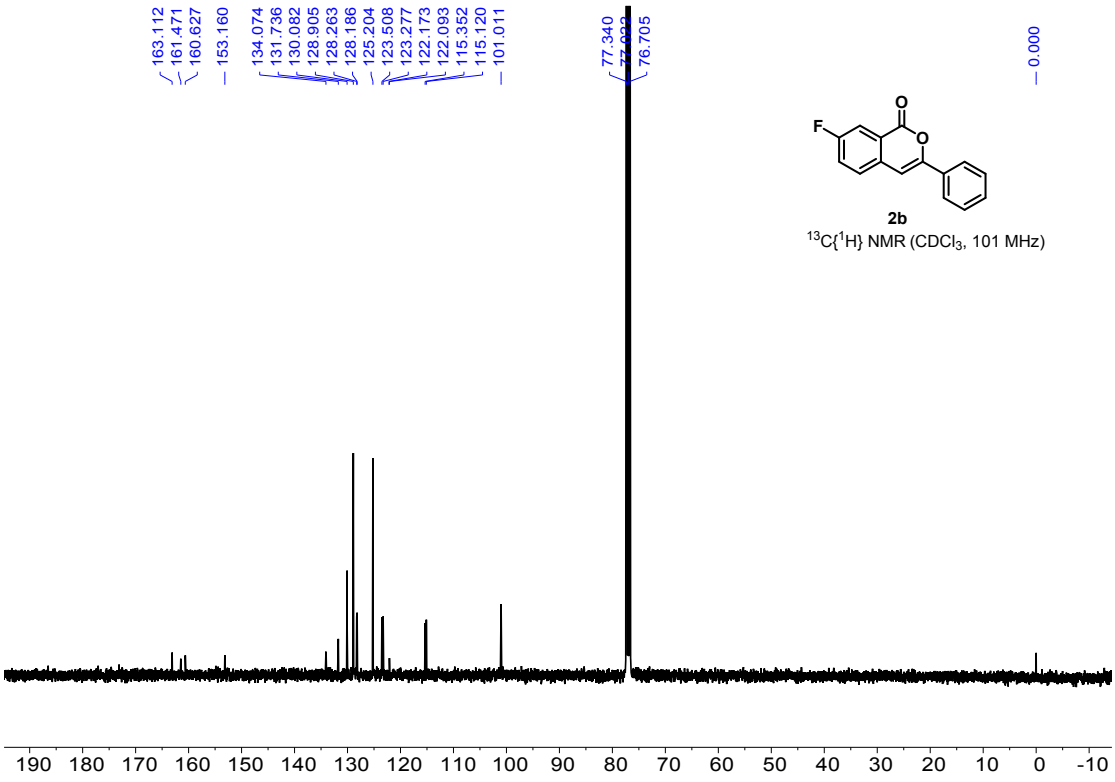


(**2a**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{11}O_2$ $[M + H]^+$: 223.0754, found 223.0772.



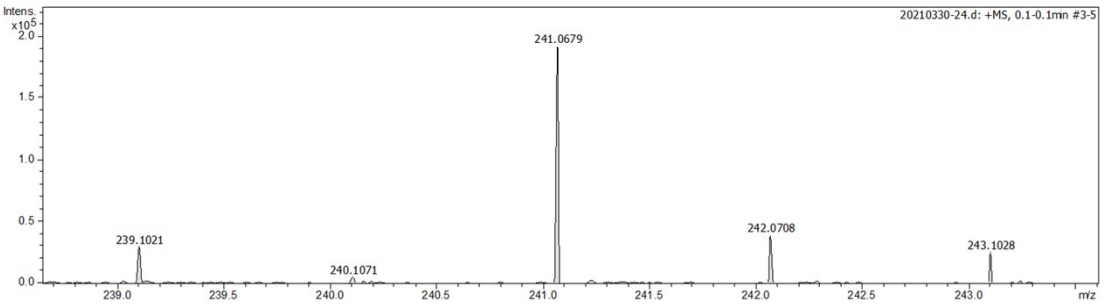
2b

^{1}H NMR ($CDCl_3$, 400 MHz)

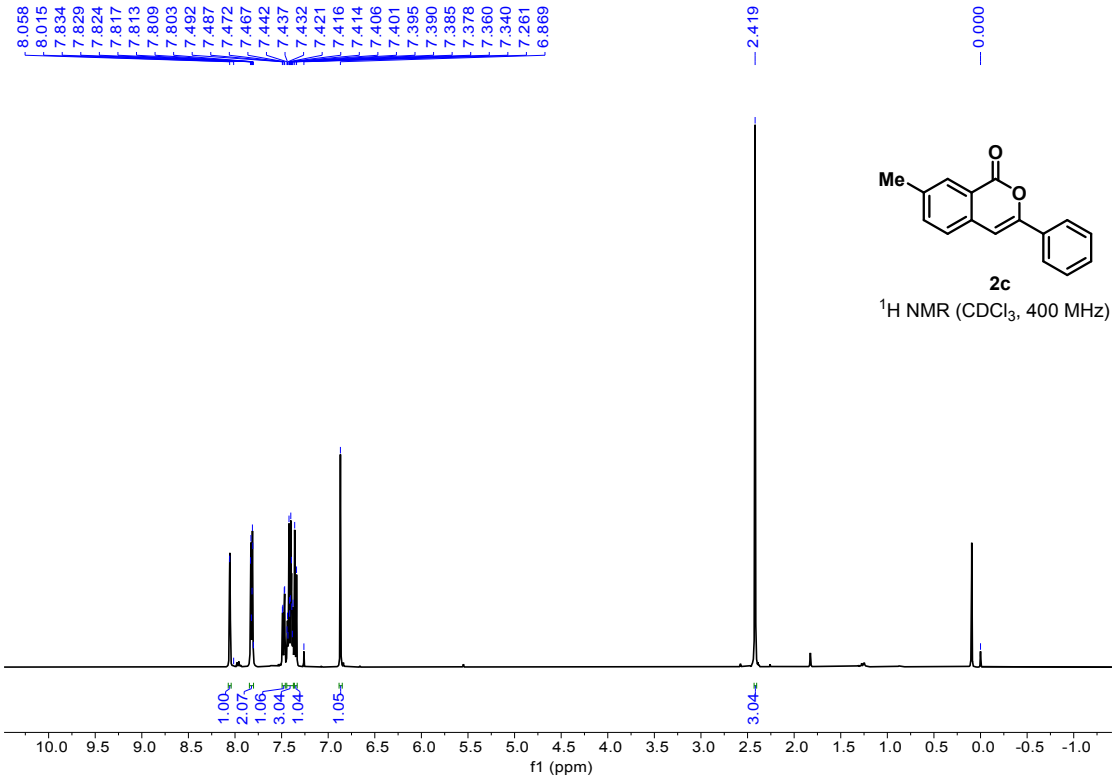


2b

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

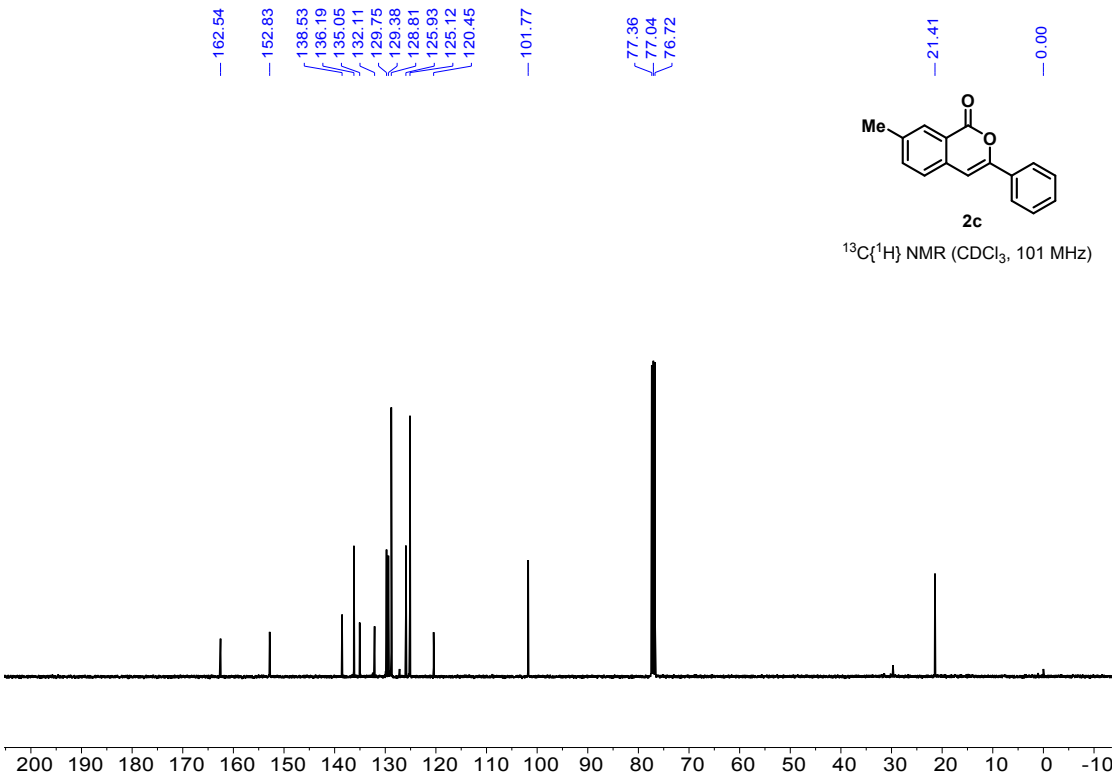


(**2b**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$: 241.0659, found 241.0679.



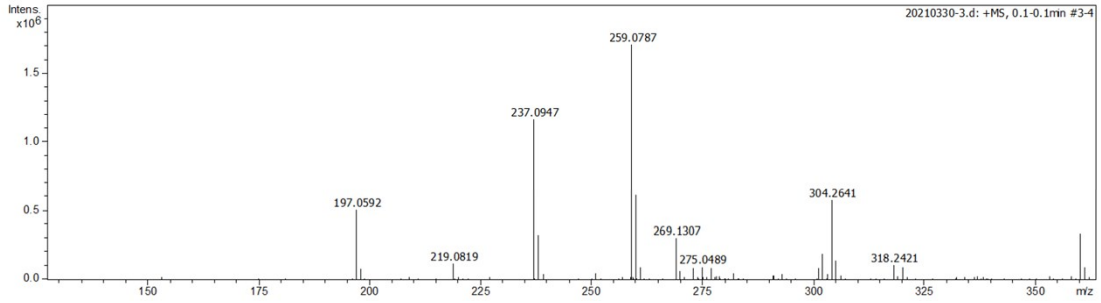
2c

^{1}H NMR ($CDCl_3$, 400 MHz)

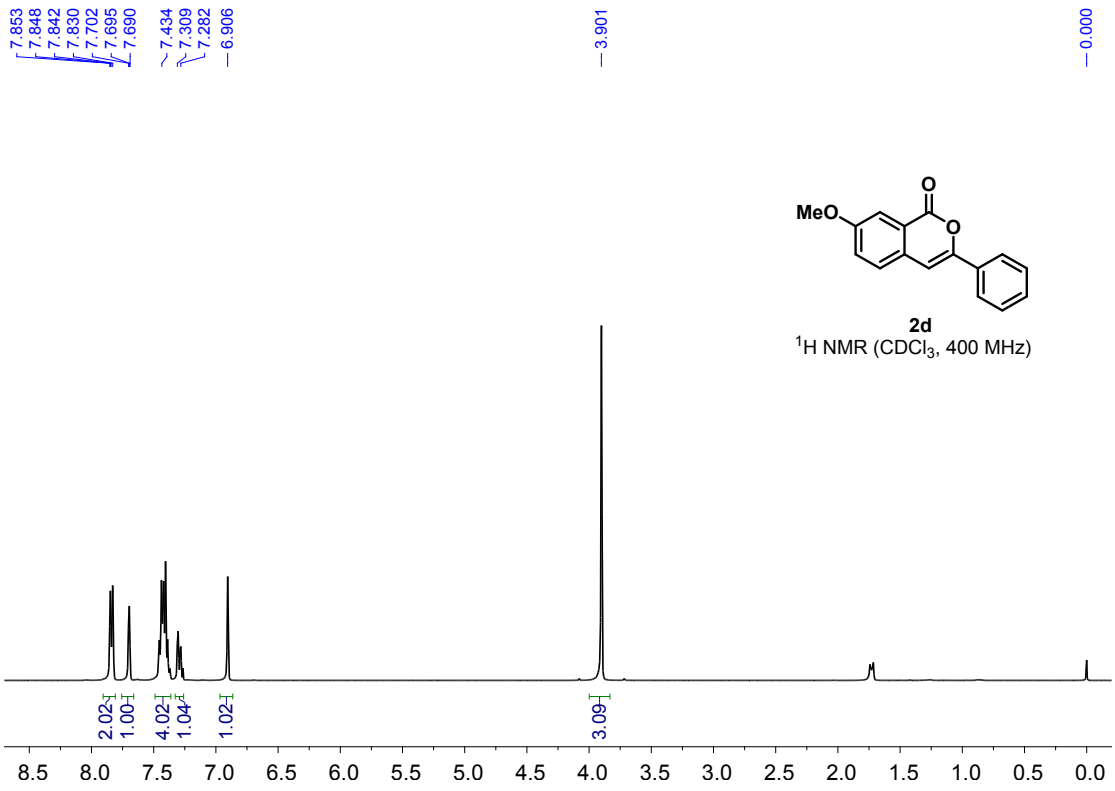


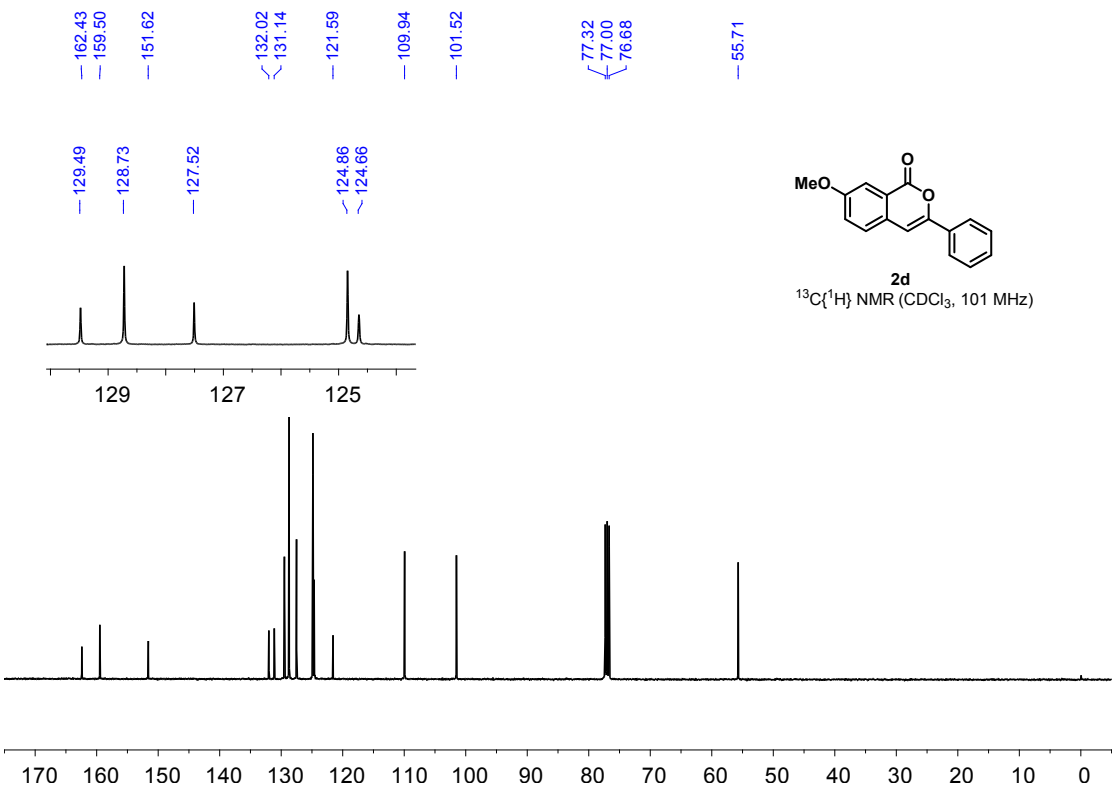
2c

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



(**2c**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0910, found 237.0947.


7.853
7.848
7.842
7.830
7.702
7.695
7.690
7.434
7.309
7.282
6.906
3.901
0.000
MeO
O
O
2d
1H NMR (CDCl3, 400 MHz)
2.02
1.00
4.02
1.04
1.02
3.09
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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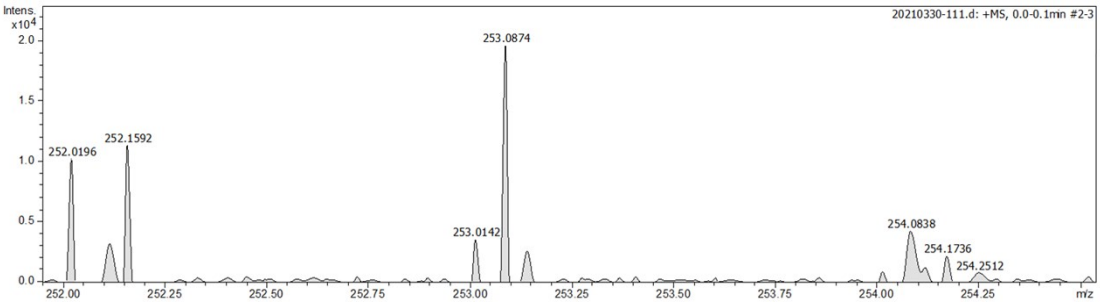
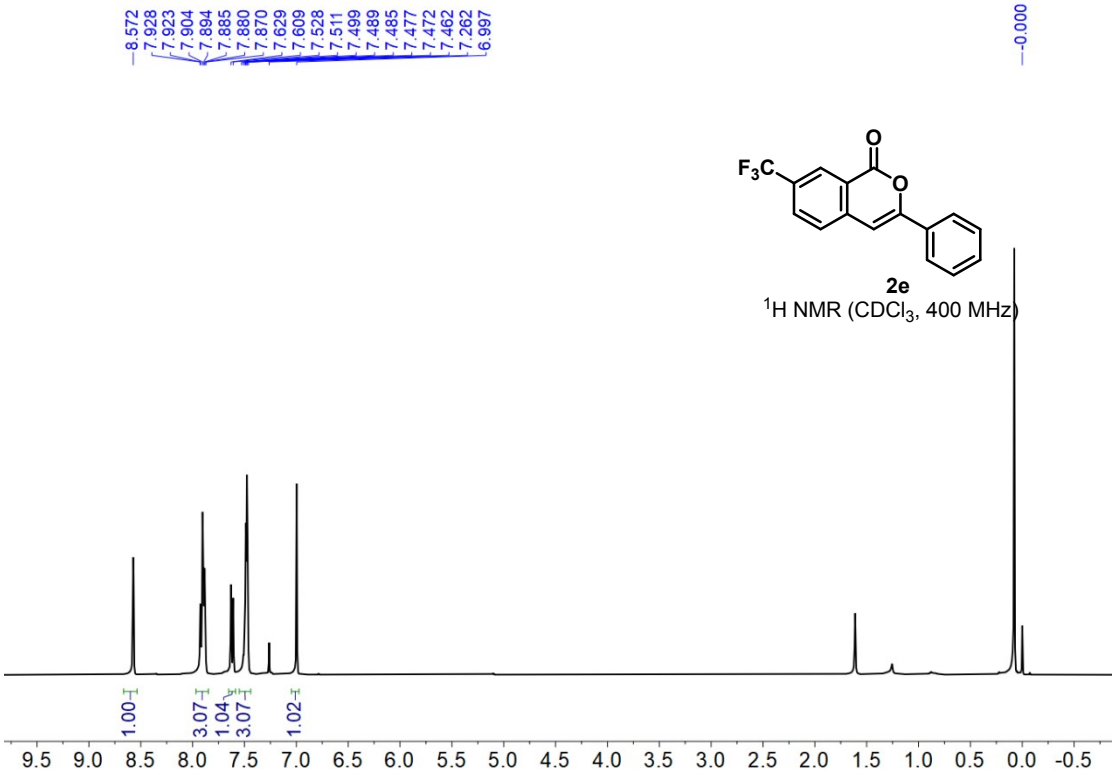
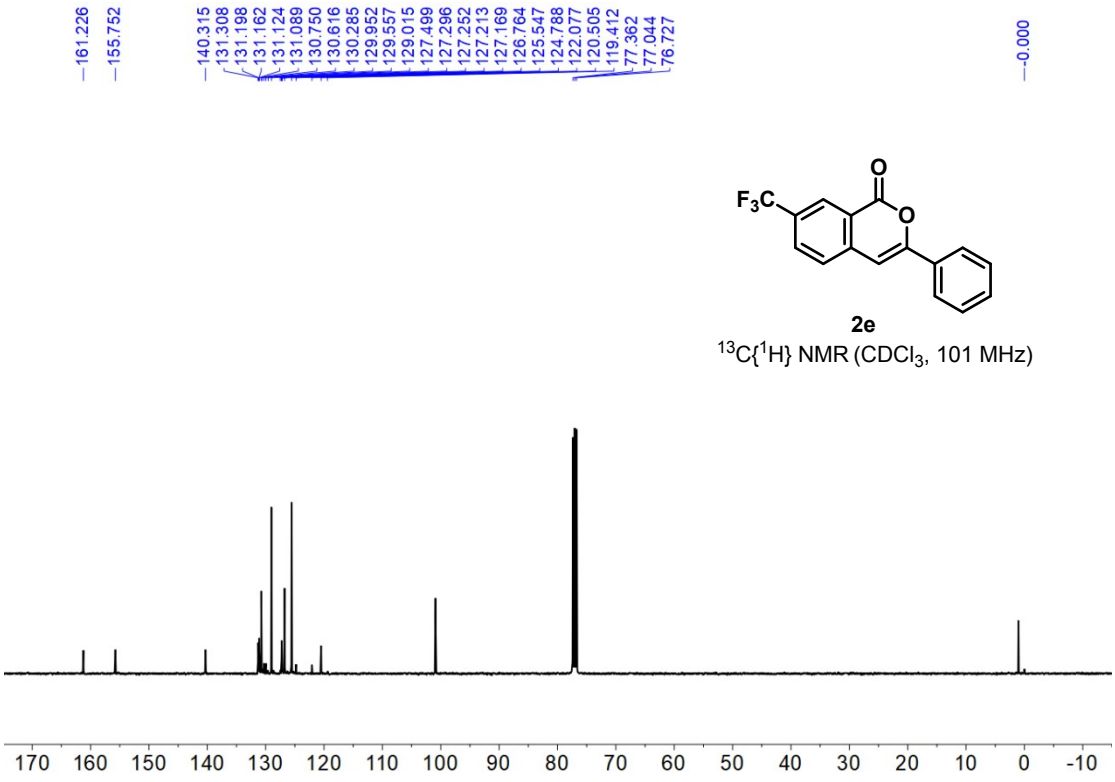
159.50
151.62
132.02
131.14
121.59
109.94
101.52
77.32
77.00
76.68
55.71
129.49
128.73
127.52
124.86
124.66
MeO
O
O
2d
13C{1H} NMR (CDCl3, 101 MHz)
129
127
125
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



(**2d**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{13}O_3$ $[M + H]^+$: 253.0859, found 253.0874.


8.572
7.928
7.923
7.904
7.894
7.885
7.880
7.870
7.629
7.609
7.528
7.511
7.499
7.489
7.485
7.477
7.472
7.462
7.262
6.997
-0.000
F3C
O
O
2e
1H NMR (CDCl3, 400 MHz)
1.00
3.07
1.04
3.07
1.02
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


161.226
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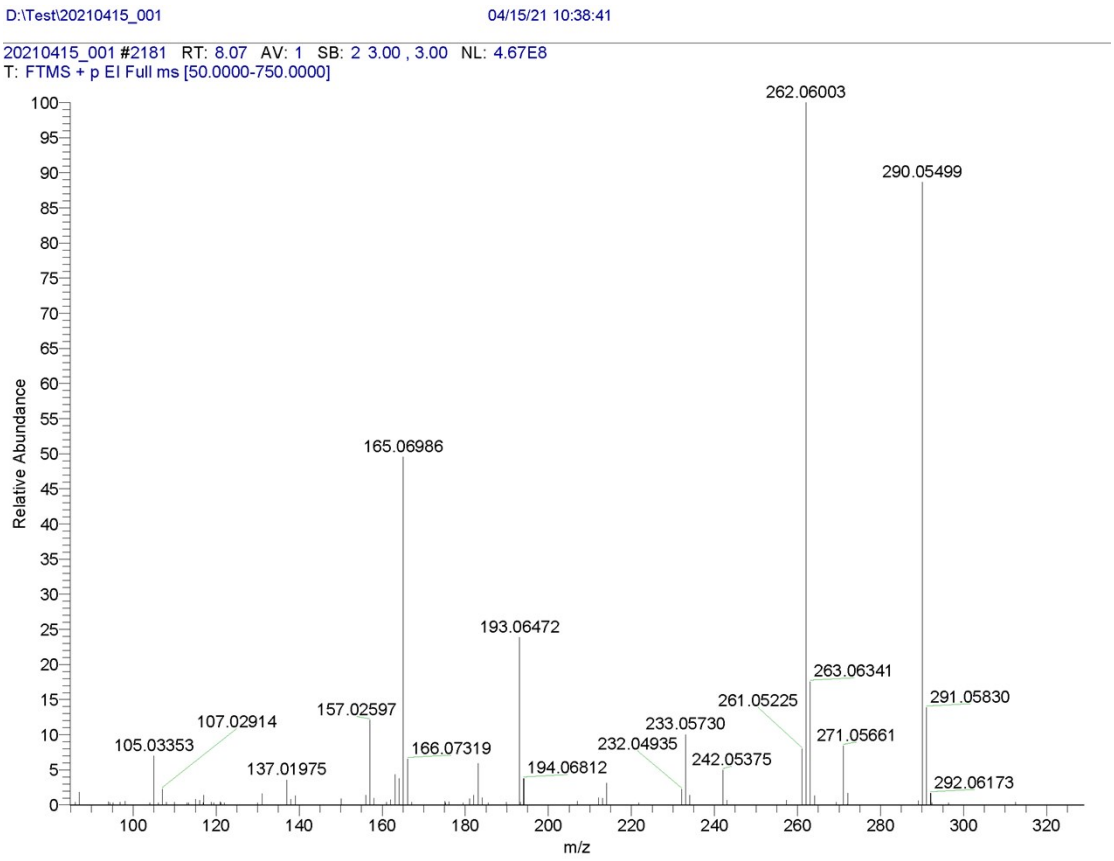
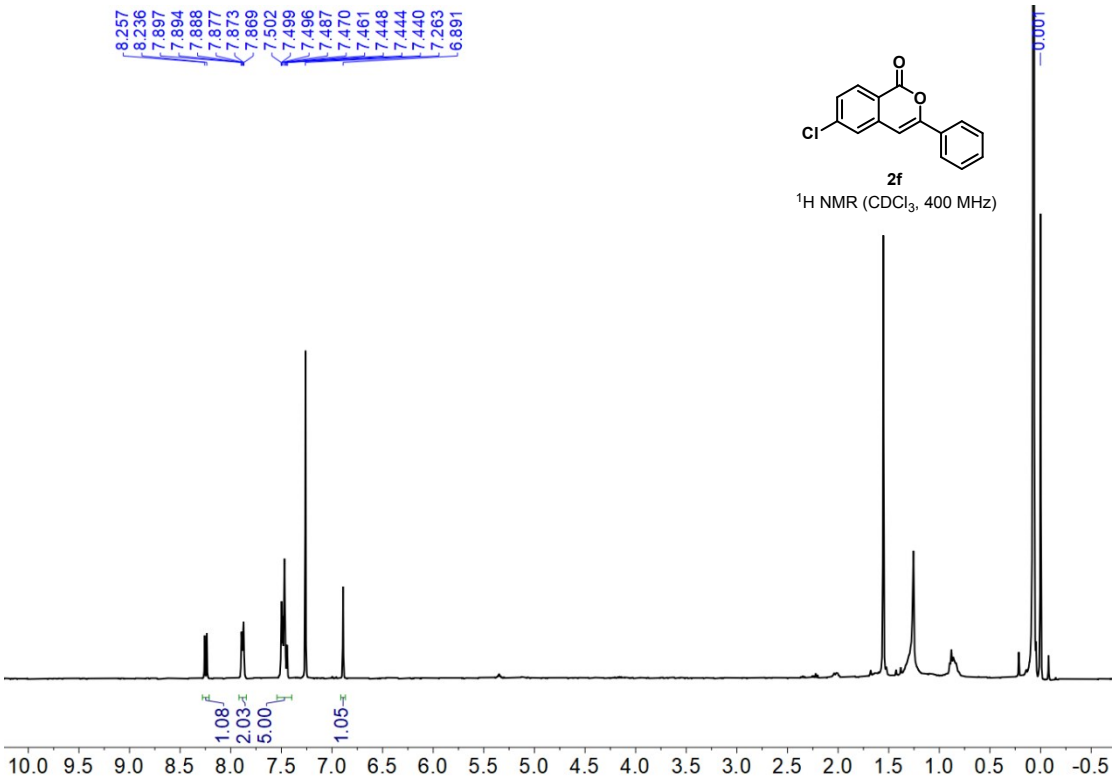
140.315
131.308
131.198
131.162
131.124
131.089
130.750
130.616
130.285
129.952
129.557
129.015
127.499
127.296
127.252
127.213
127.169
126.764
125.547
124.788
122.077
120.505
119.412
77.362
77.044
76.727
-0.000
F3C
O
O
2e
13C{1H} NMR (CDCl3, 101 MHz)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

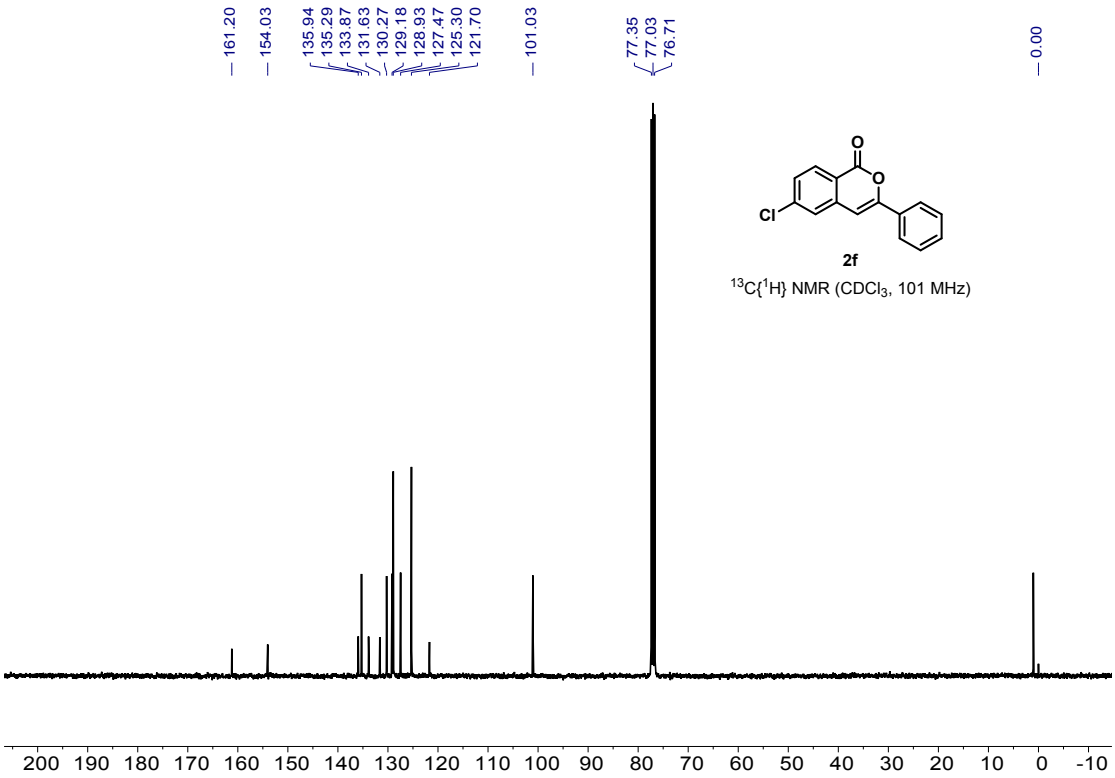


(**2e**) **HRMS** (EI) *m/z* calcd for $C_{16}H_9F_3O_2$ $[M]^+$: 290.05546, found 290.05499.



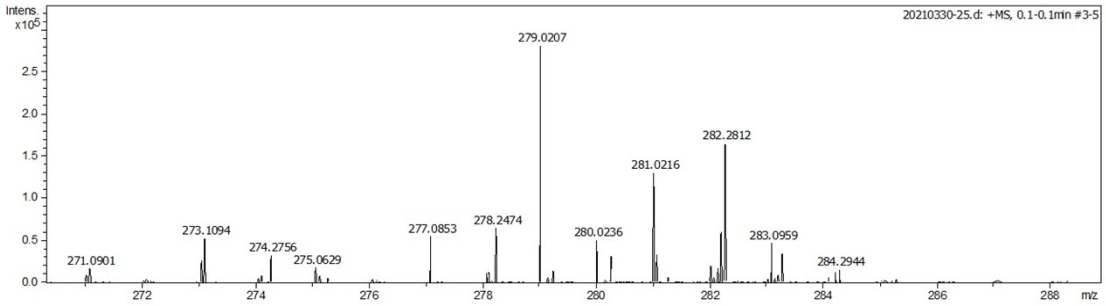
2f

^{1}H NMR ($CDCl_3$, 400 MHz)

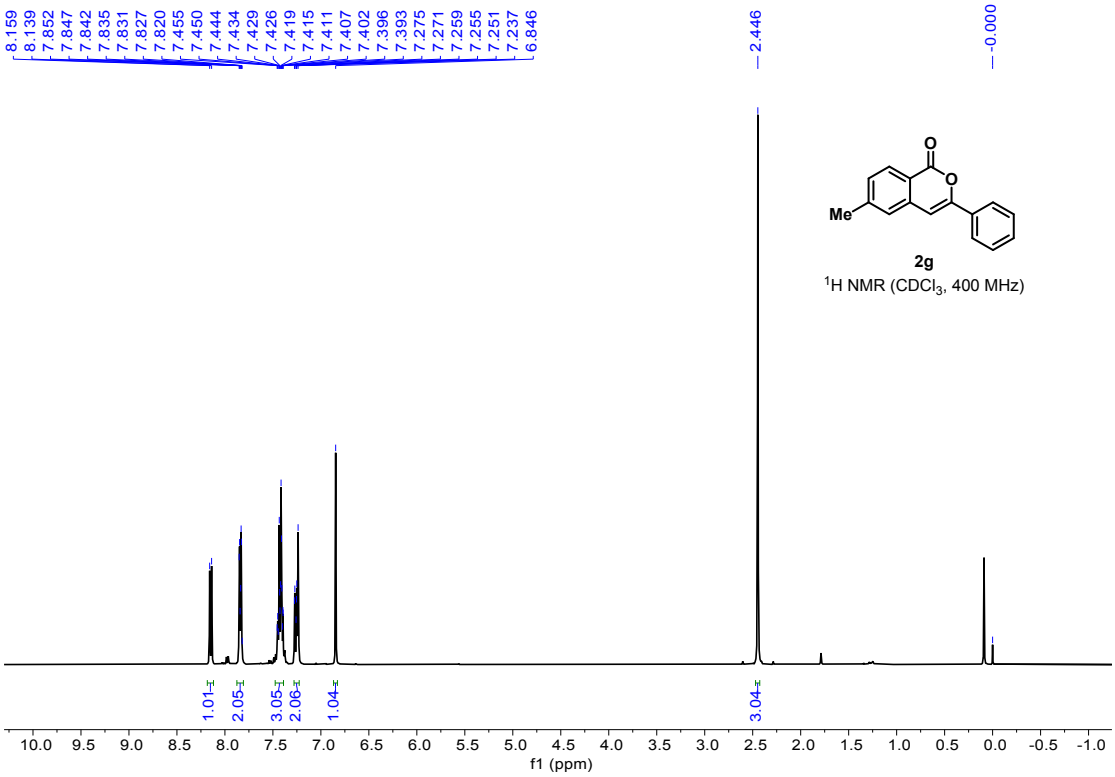


2f

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

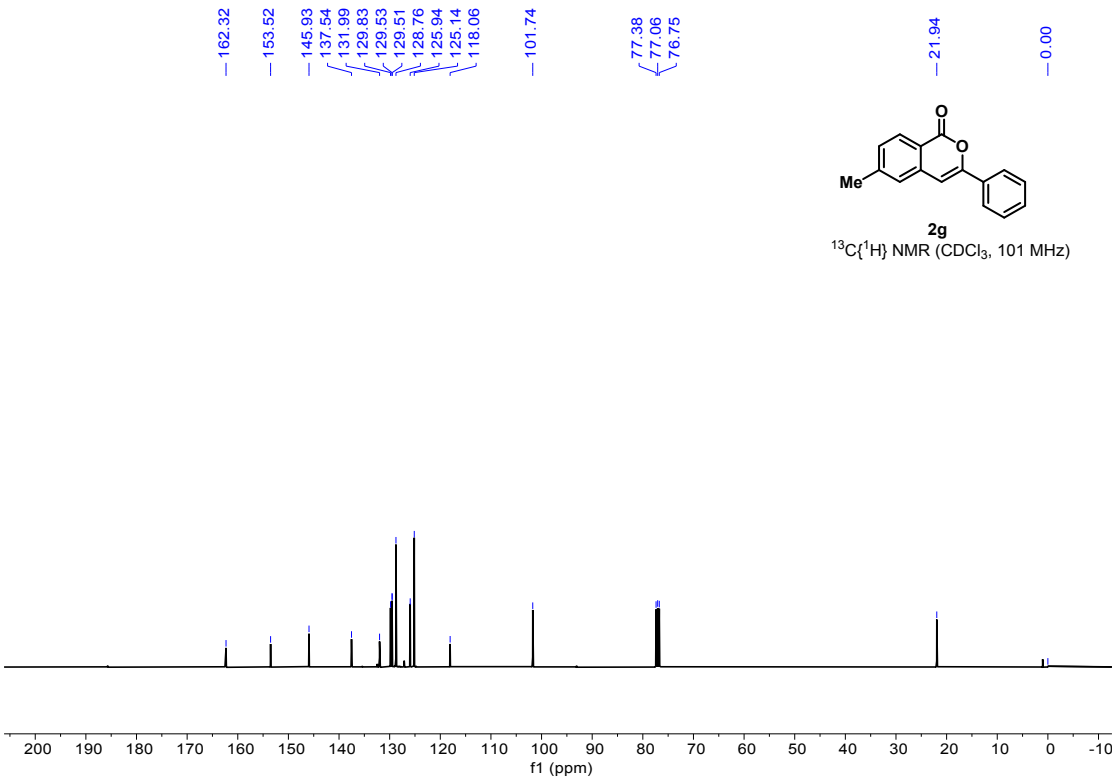


(**2f**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_9ClNaO_2$ $[M + H]^+$: 279.0183, found 279.0207.



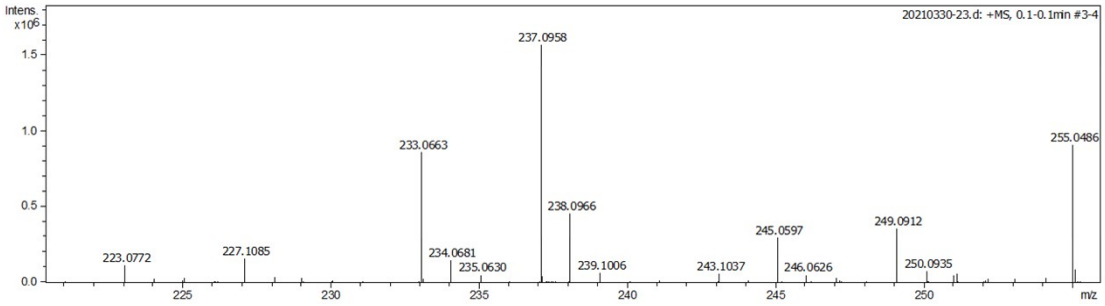
2g

^{1}H NMR ($CDCl_3$, 400 MHz)

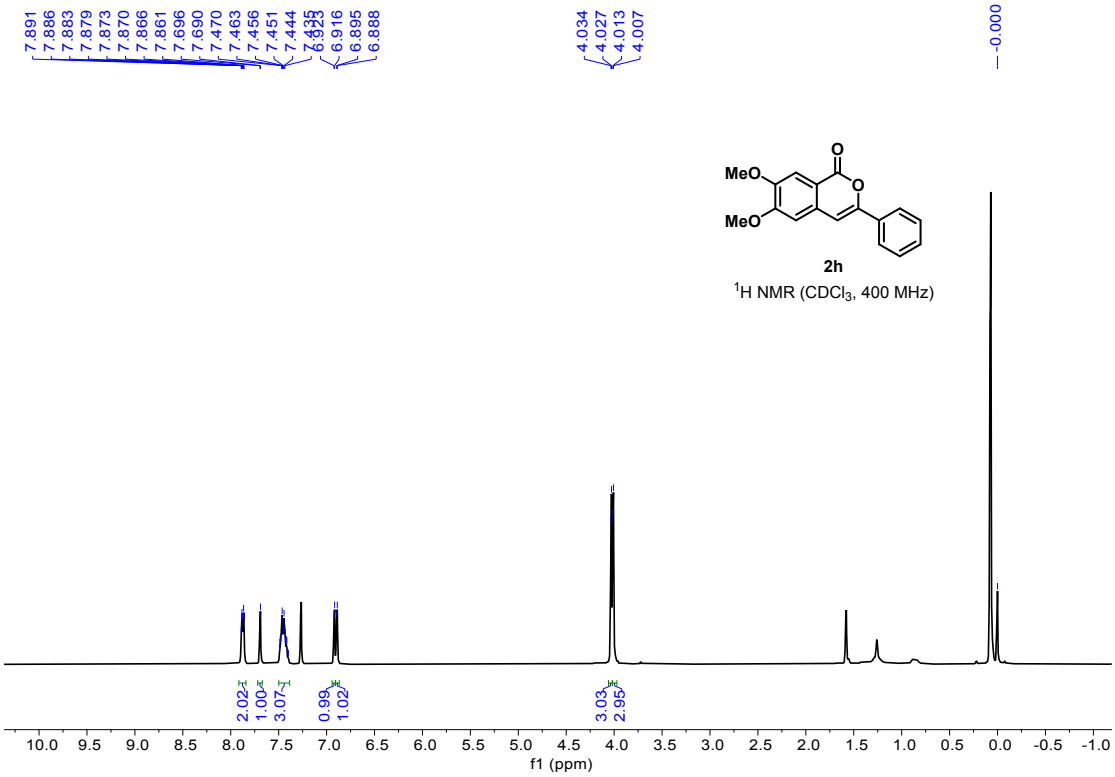


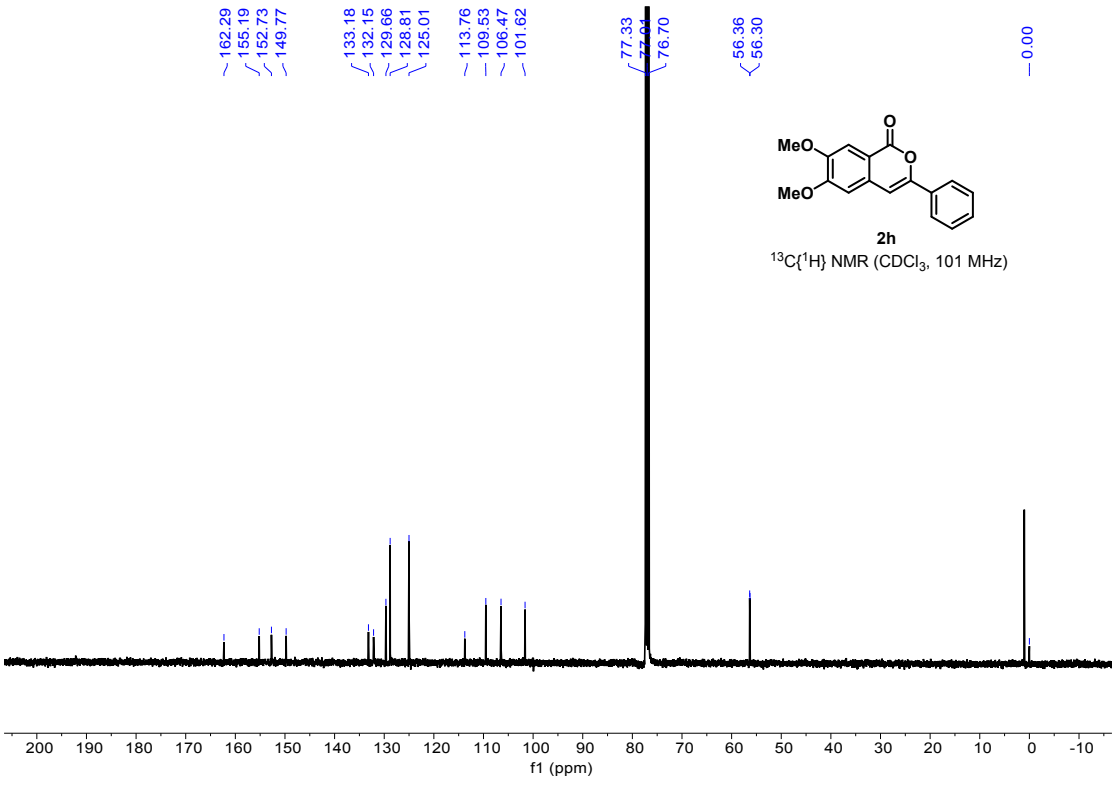
2g

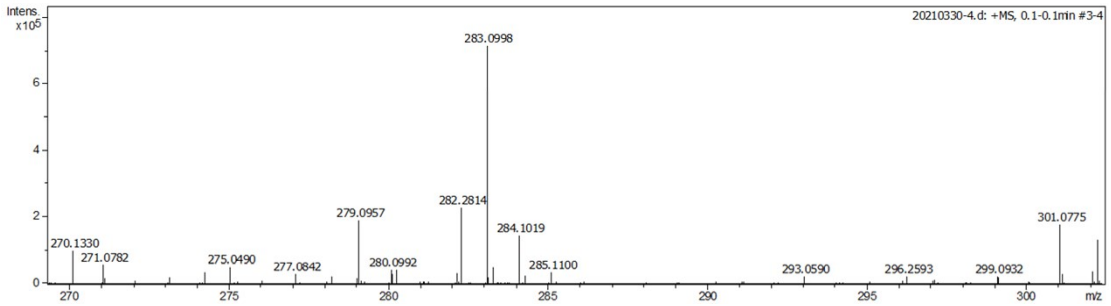
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



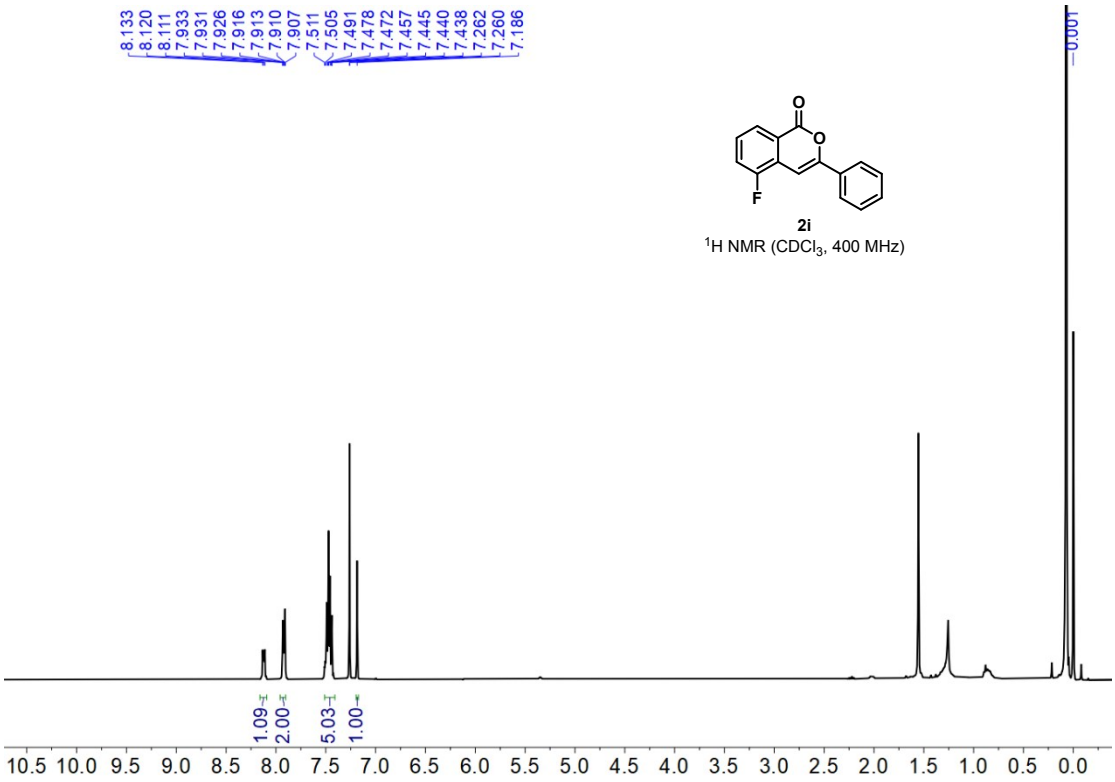
(**2g**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0910, found 237.0958.


7.891
7.886
7.883
7.879
7.873
7.870
7.866
7.861
7.696
7.690
7.470
7.463
7.456
7.451
7.444
6.916
6.895
6.888
4.034
4.027
4.013
4.007
-0.000
MeO
MeO
O
O
2h
1H NMR (CDCl3, 400 MHz)
2.02
1.00
3.07
0.99
1.02
3.03
2.95
f1 (ppm)


162.29
155.19
152.73
149.77
133.18
132.15
129.66
128.81
125.01
113.76
109.53
106.47
101.62
77.33
77.01
76.70
56.36
56.30
0.00
MeO
MeO
O
O
2h
13C{1H} NMR (CDCl3, 101 MHz)
f1 (ppm)

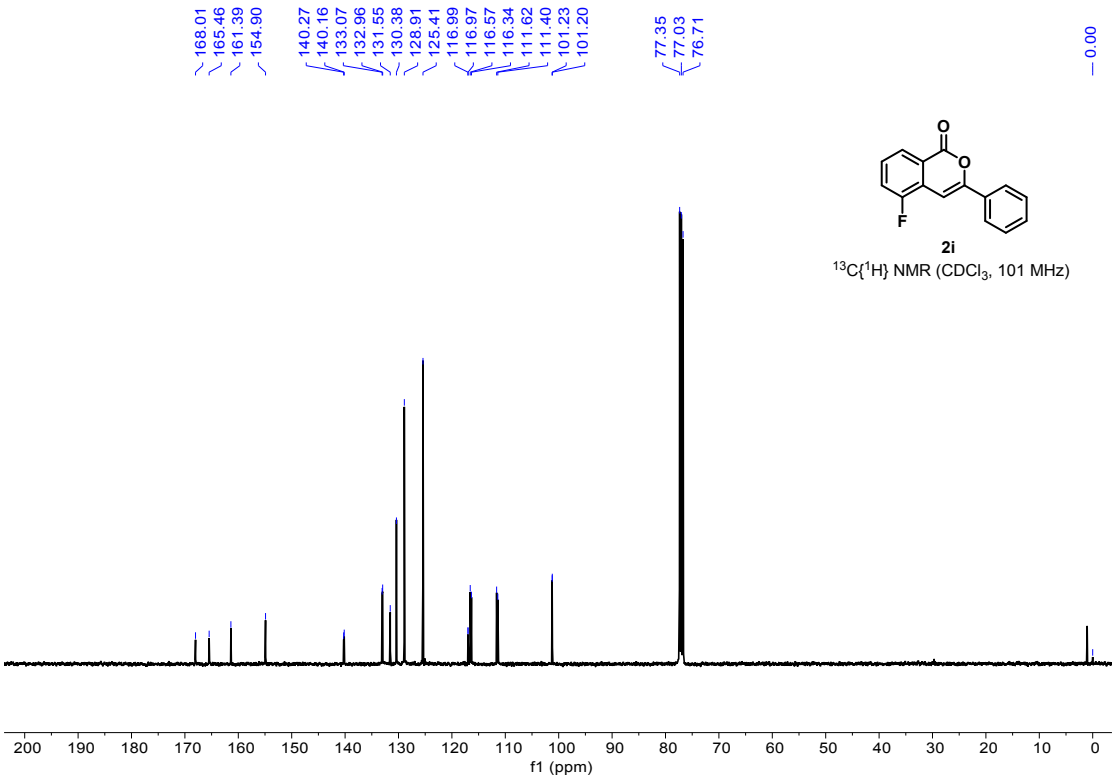


(**2h**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{15}O_4$ $[M + H]^+$: 283.0965, found 283.0998.



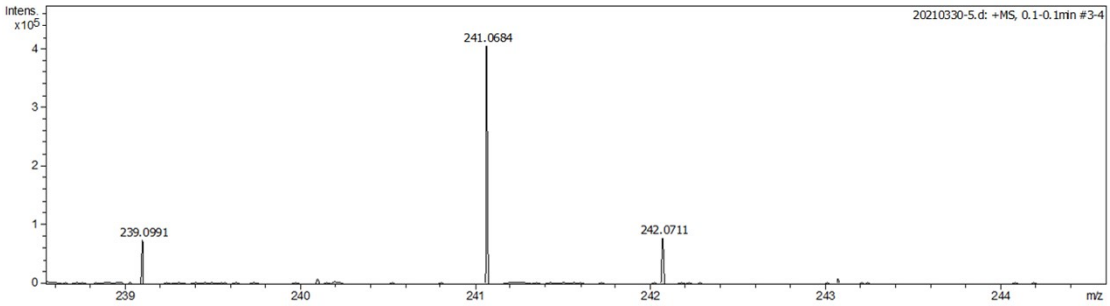
2i

^{1}H NMR ($CDCl_3$, 400 MHz)

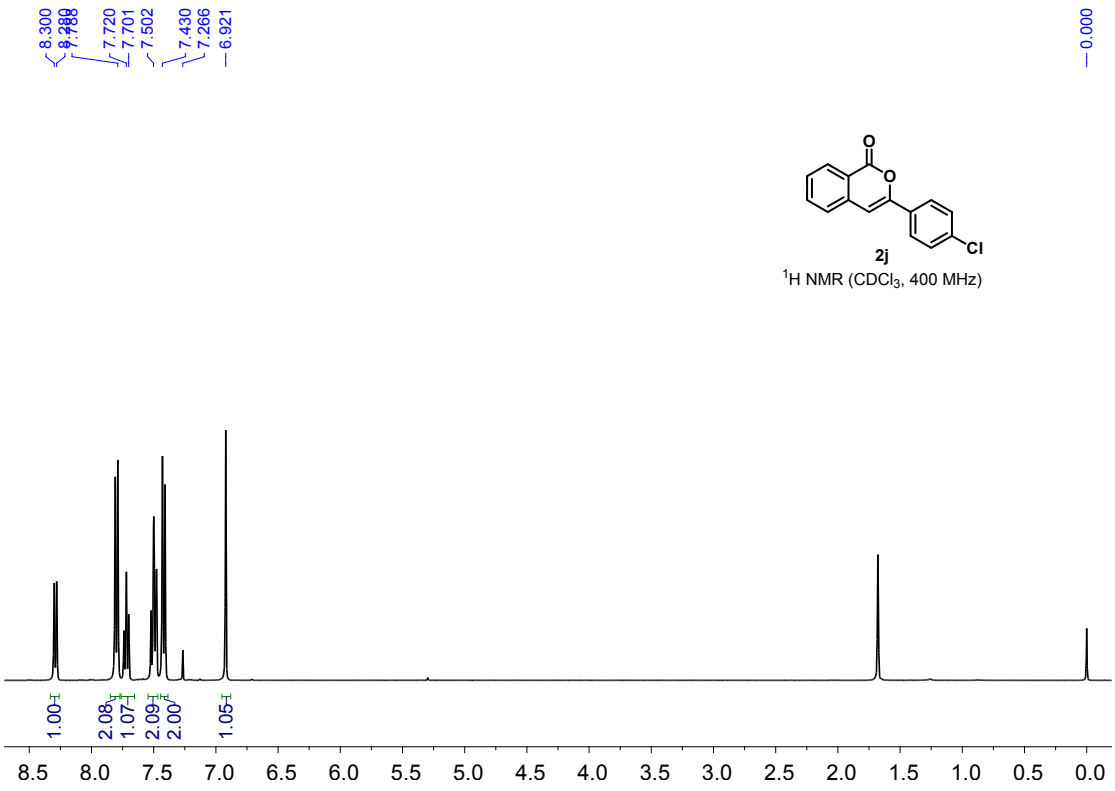


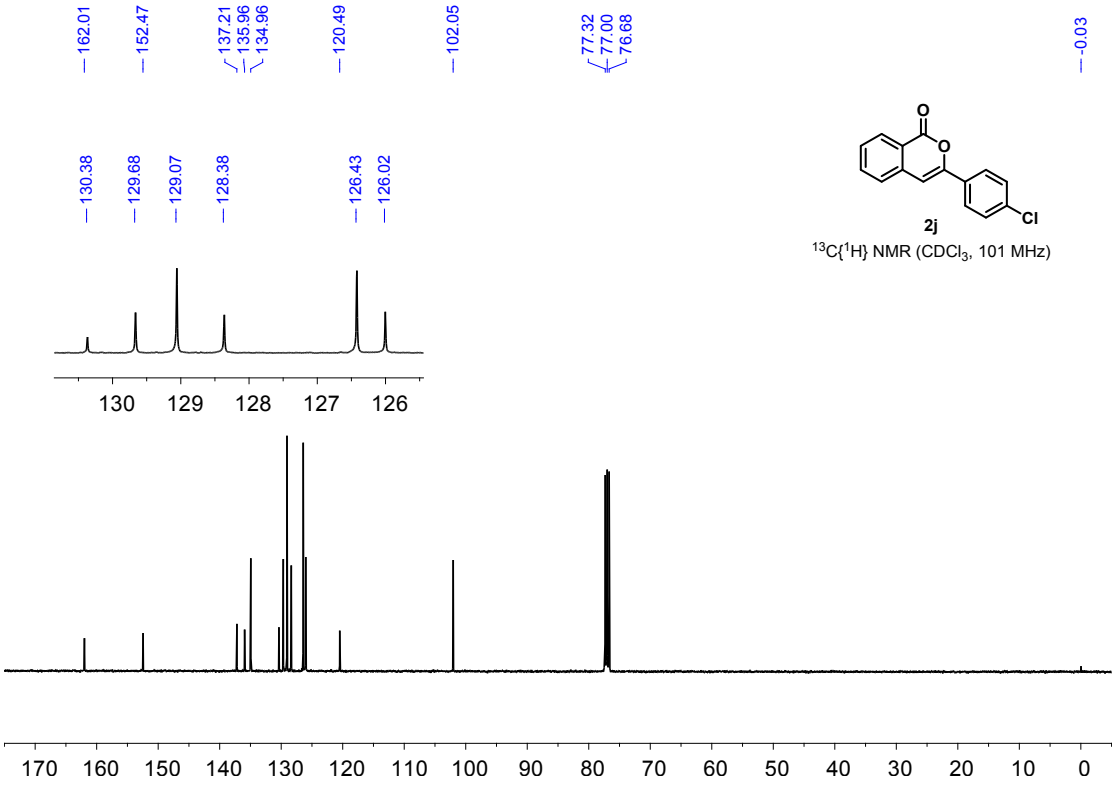
2i

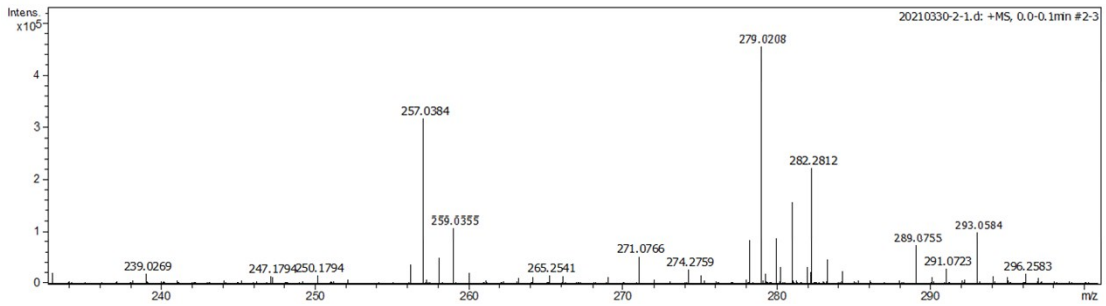
^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



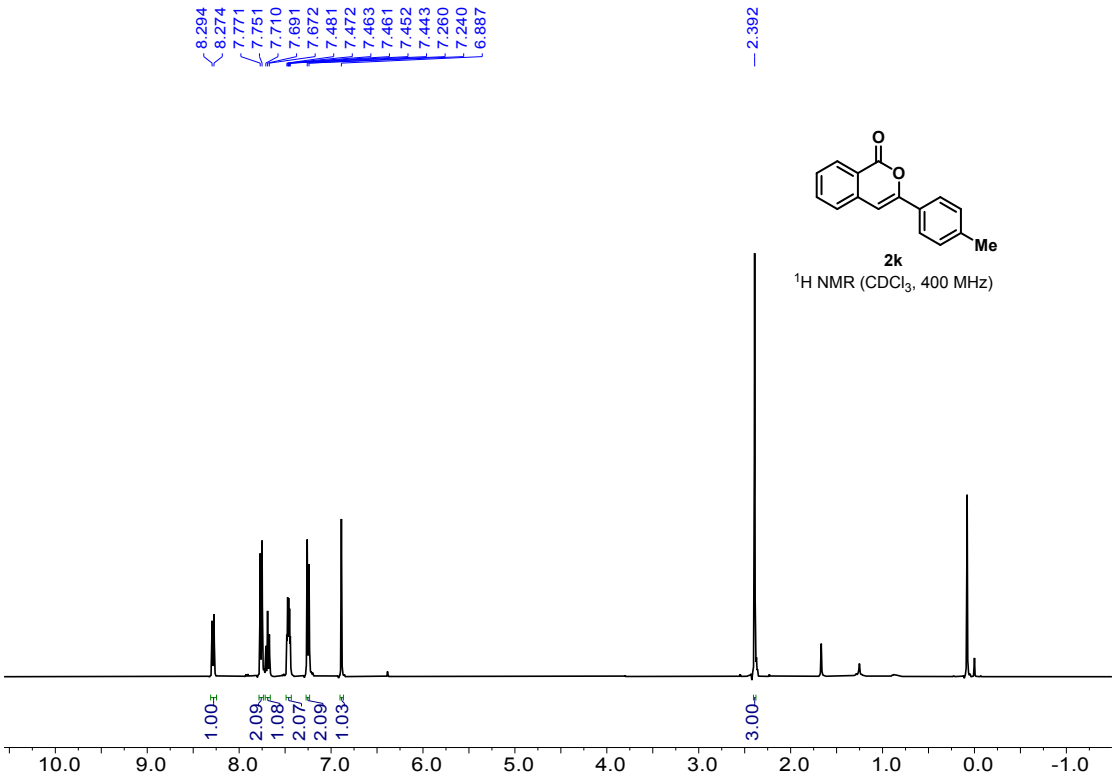
(**2i**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$: 241.0659, found 241.0684.

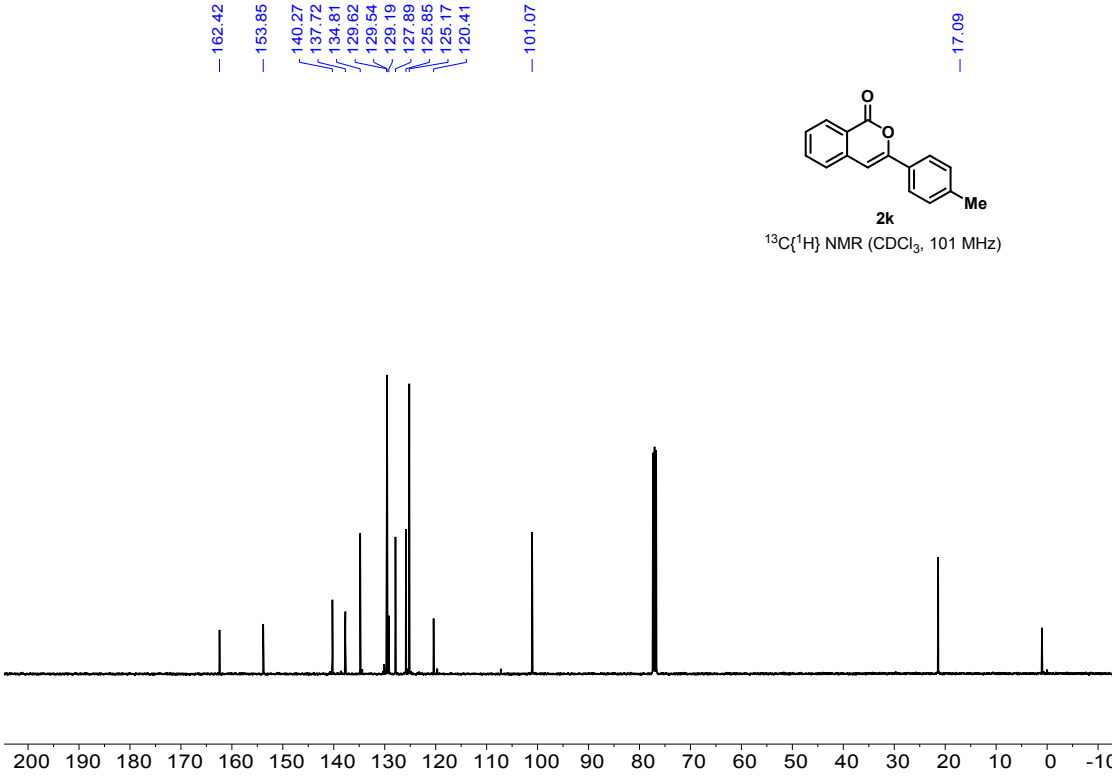

8.300
7.720
7.701
7.502
7.430
7.266
6.921
0.000
O
O
Cl
2j
^{1}H NMR ($CDCl_3$, 400 MHz)
1.00
2.08
1.07
2.09
2.00
1.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

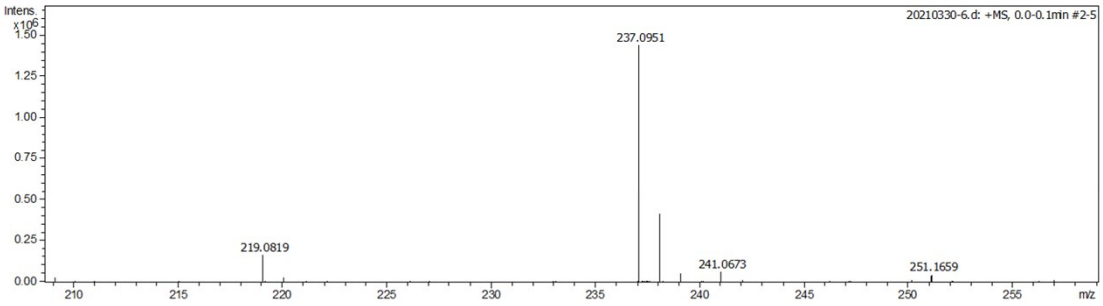

162.01
152.47
137.21
135.96
134.96
120.49
102.05
77.32
77.00
76.68
-0.03
130.38
129.68
129.07
128.38
126.43
126.02
O
O
Cl
2j
^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)
130 129 128 127 126
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



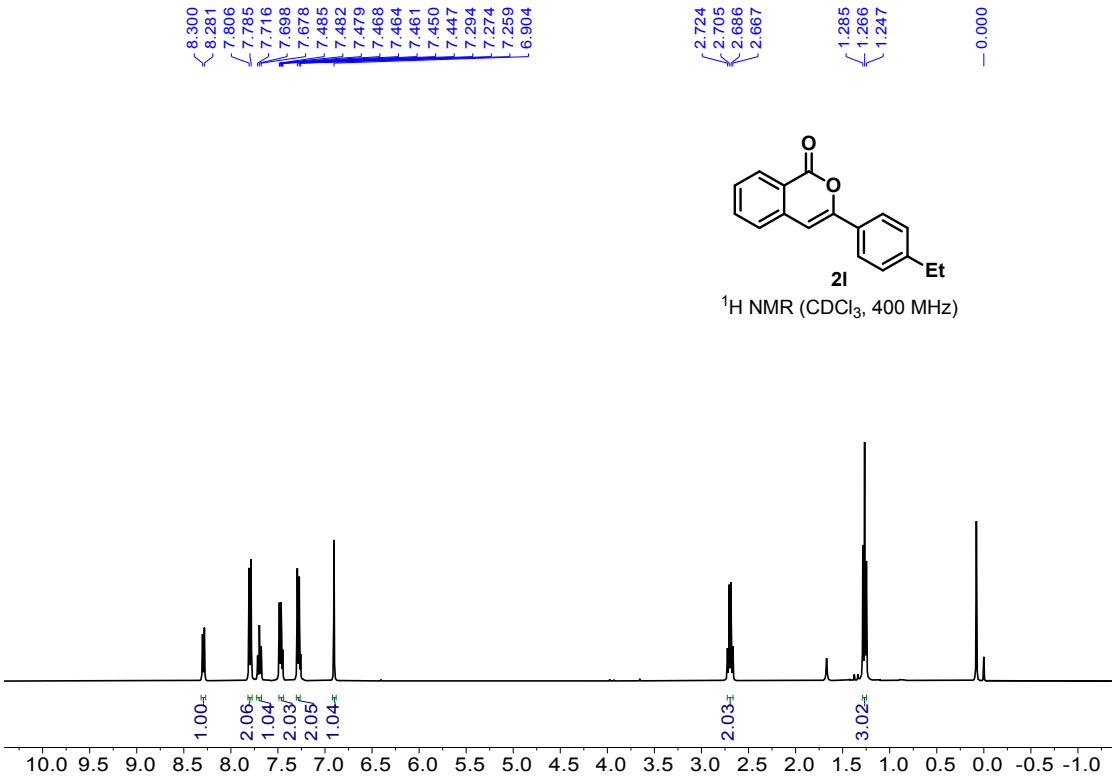
(**2j**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{20}ClO_2$ $[M + H]^+$: 257.0364, found 257.0384.


8.294
8.274
7.771
7.751
7.710
7.691
7.672
7.481
7.472
7.463
7.461
7.452
7.443
7.260
7.240
6.887
2.392
O
O
Me
2k
1H NMR (CDCl3, 400 MHz)
1.00
2.09
1.08
2.07
2.09
1.03
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0


162.42
153.85
140.27
137.72
134.81
129.62
129.54
129.19
127.89
125.85
125.17
120.41
101.07
17.09
O
O
Me
2k
13C{1H} NMR (CDCl3, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

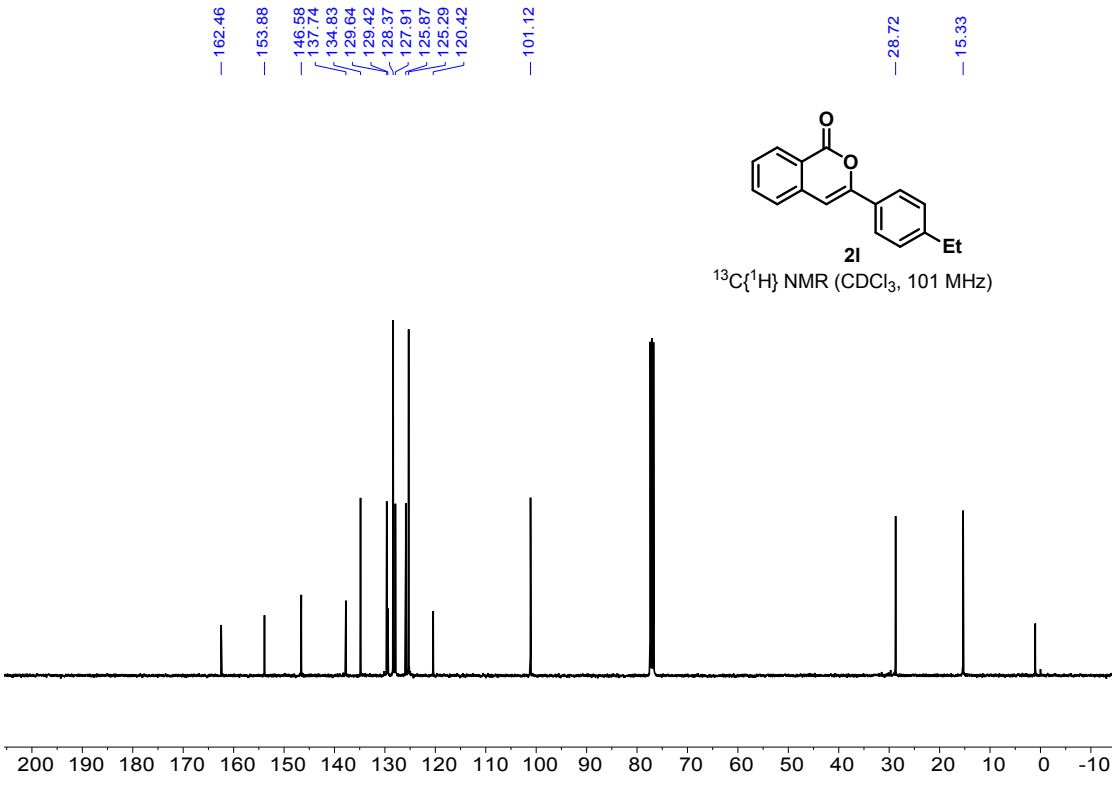


(**2k**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{13}O_2$ $[M + H]^+$: 237.0910, found 237.0951.



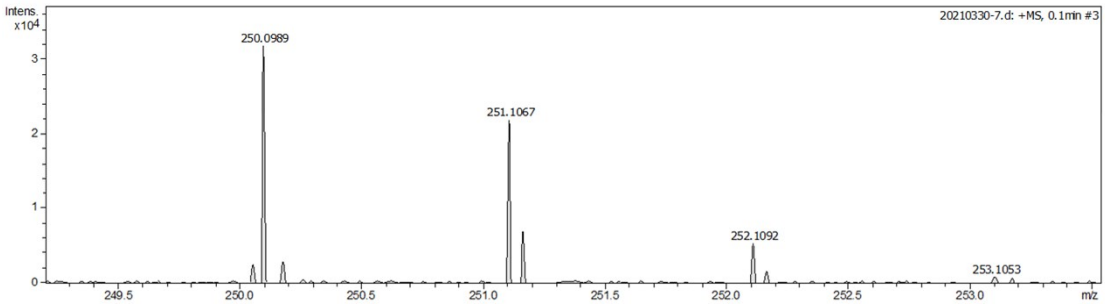
2l

^{1}H NMR ($CDCl_3$, 400 MHz)

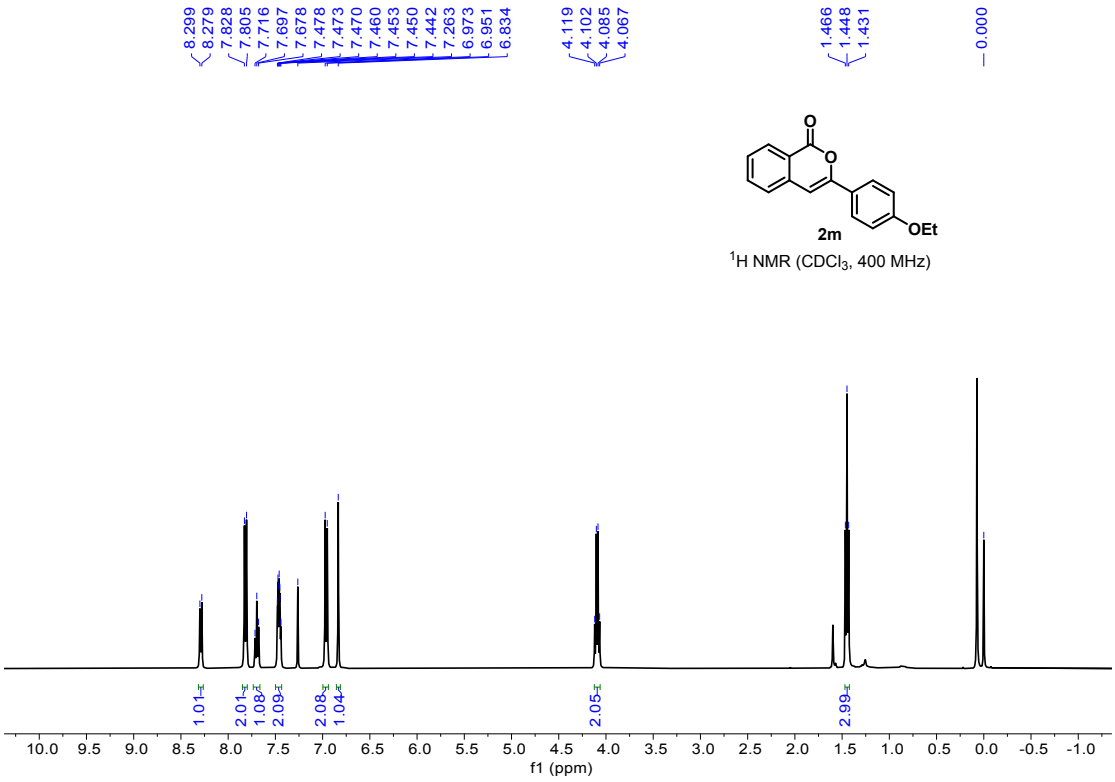


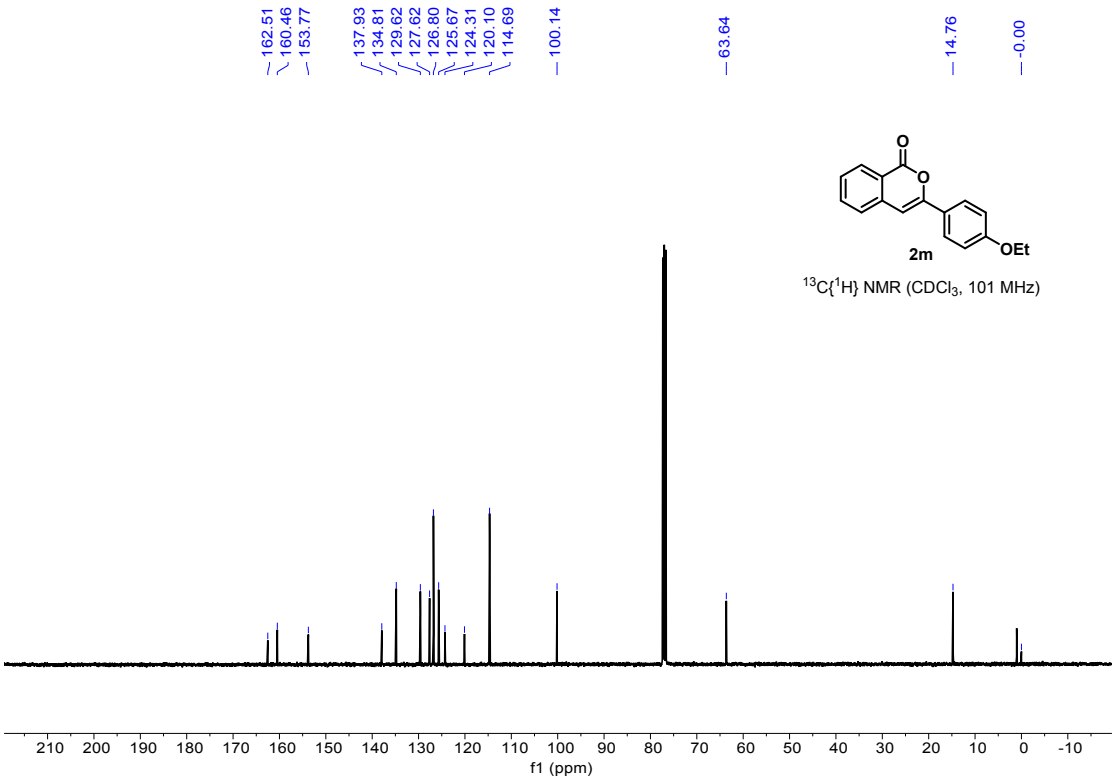
2l

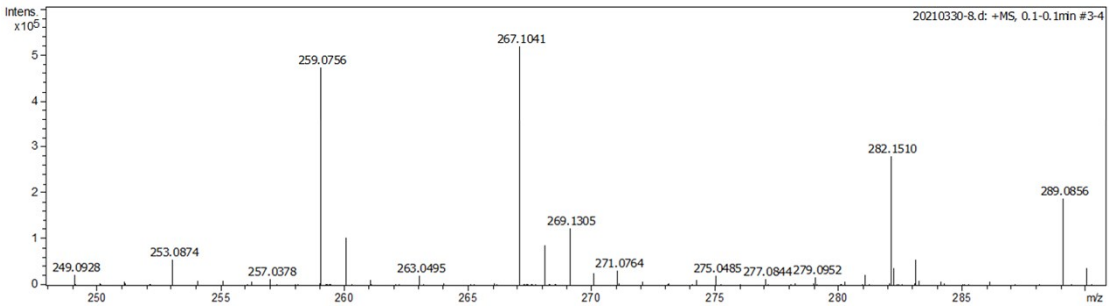
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



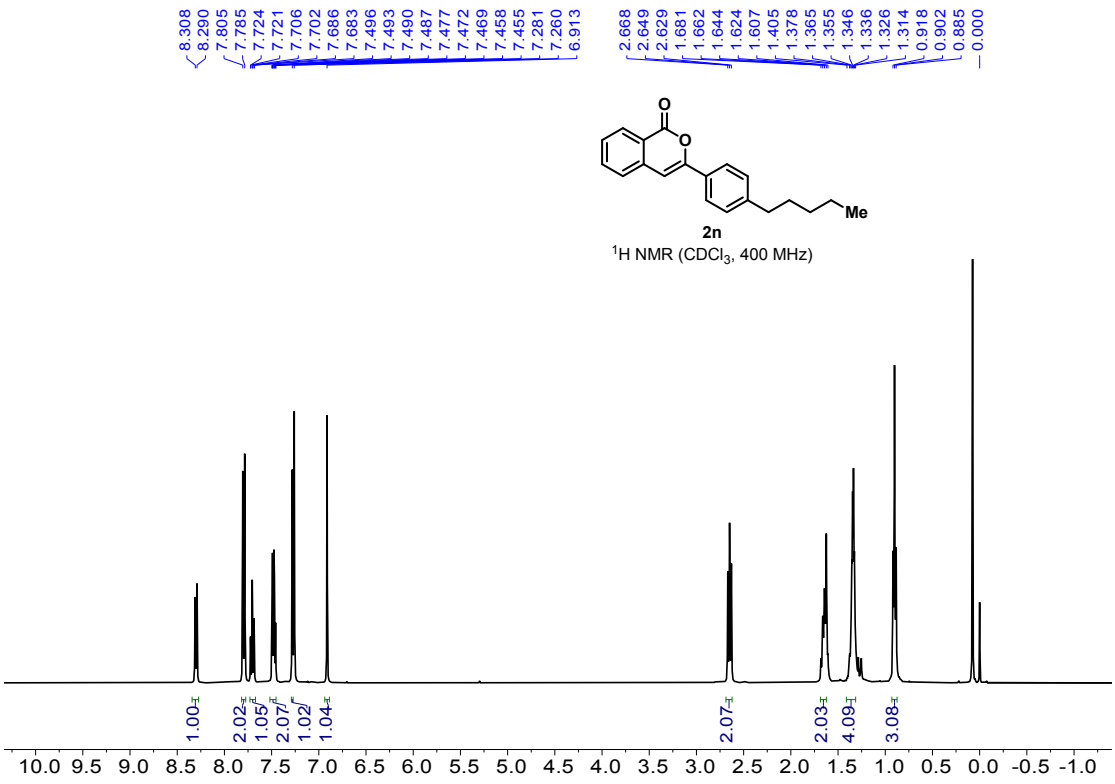
(**2l**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{15}O_3$ $[M + H]^+$: 251.1067, found 251.1067.


8.299
8.279
7.828
7.805
7.716
7.697
7.678
7.478
7.473
7.470
7.460
7.453
7.450
7.442
7.263
6.973
6.951
6.834
4.119
4.102
4.085
4.067
1.466
1.448
1.431
0.000
O
O
OEt
2m
1H NMR (CDCl3, 400 MHz)
1.01
2.01
1.08
2.09
2.08
1.04
2.05
2.99
10.0 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)


162.51
160.46
153.77
137.93
134.81
129.62
127.62
126.80
125.67
124.31
120.10
114.69
100.14
63.64
14.76
-0.00
O
O
OEt
2m
13C{1H} NMR (CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

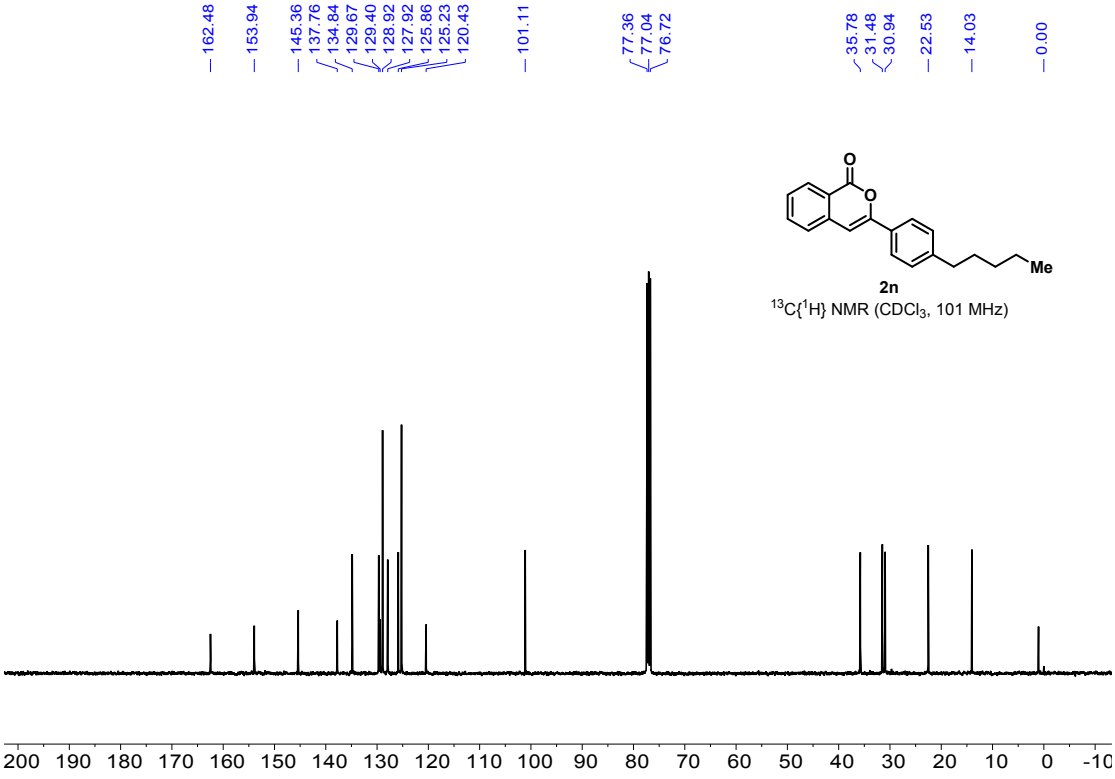


(**2m**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{17}H_{15}O_3$ $[M + H]^+$: 267.1016, found 267.1041.



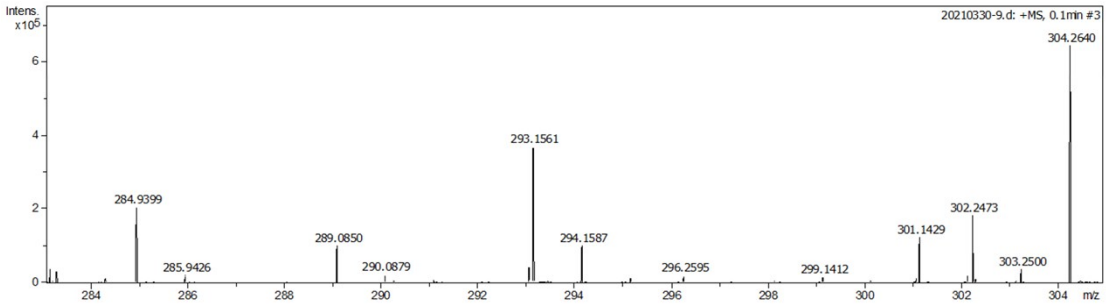
2n

^{1}H NMR ($CDCl_3$, 400 MHz)

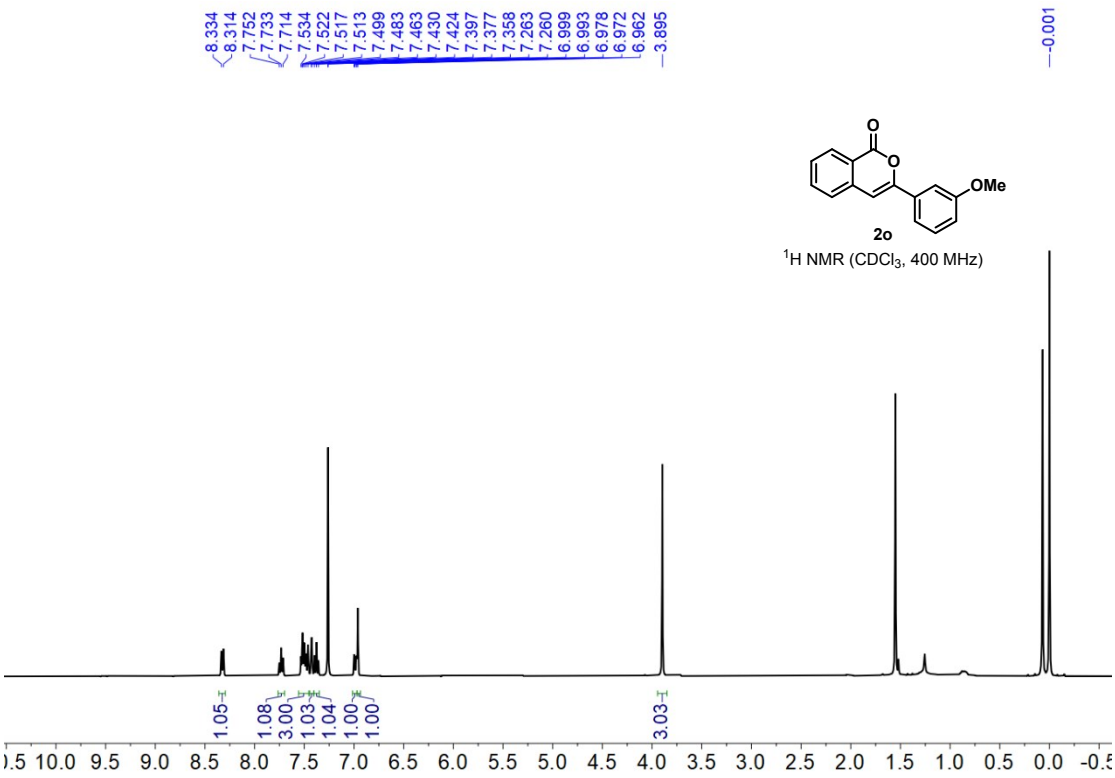


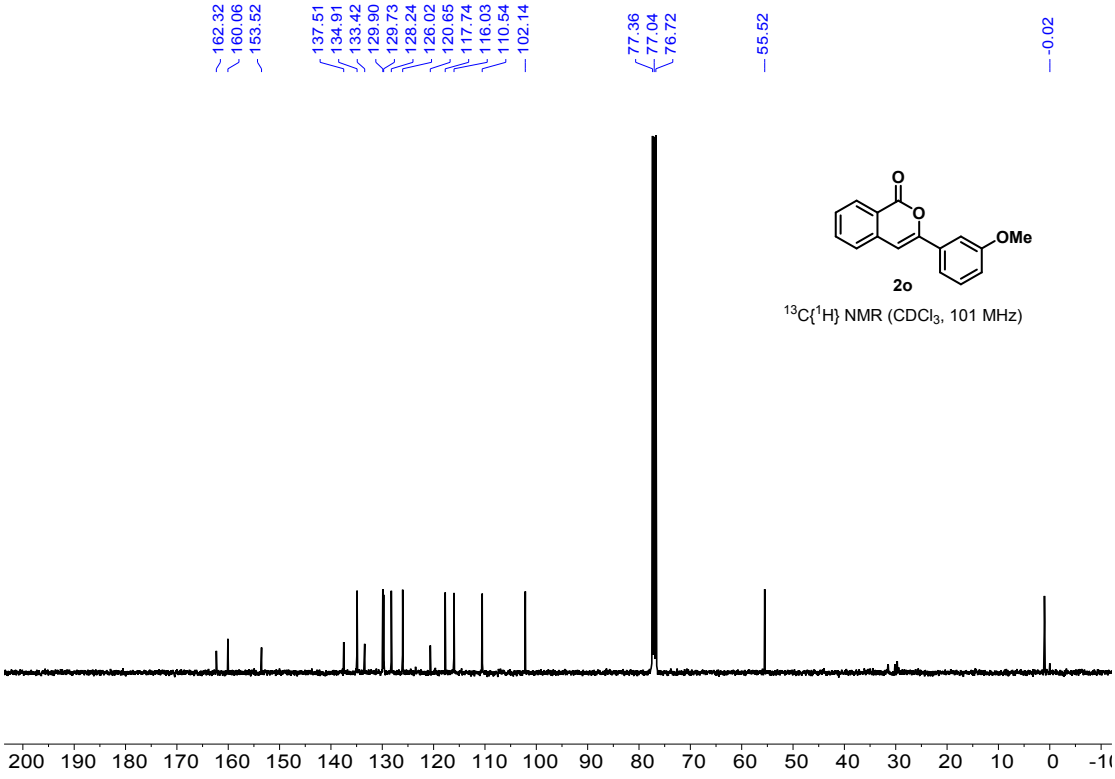
2n

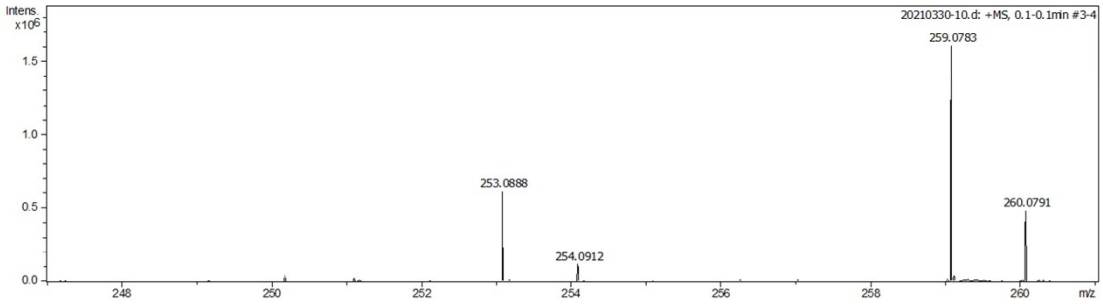
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



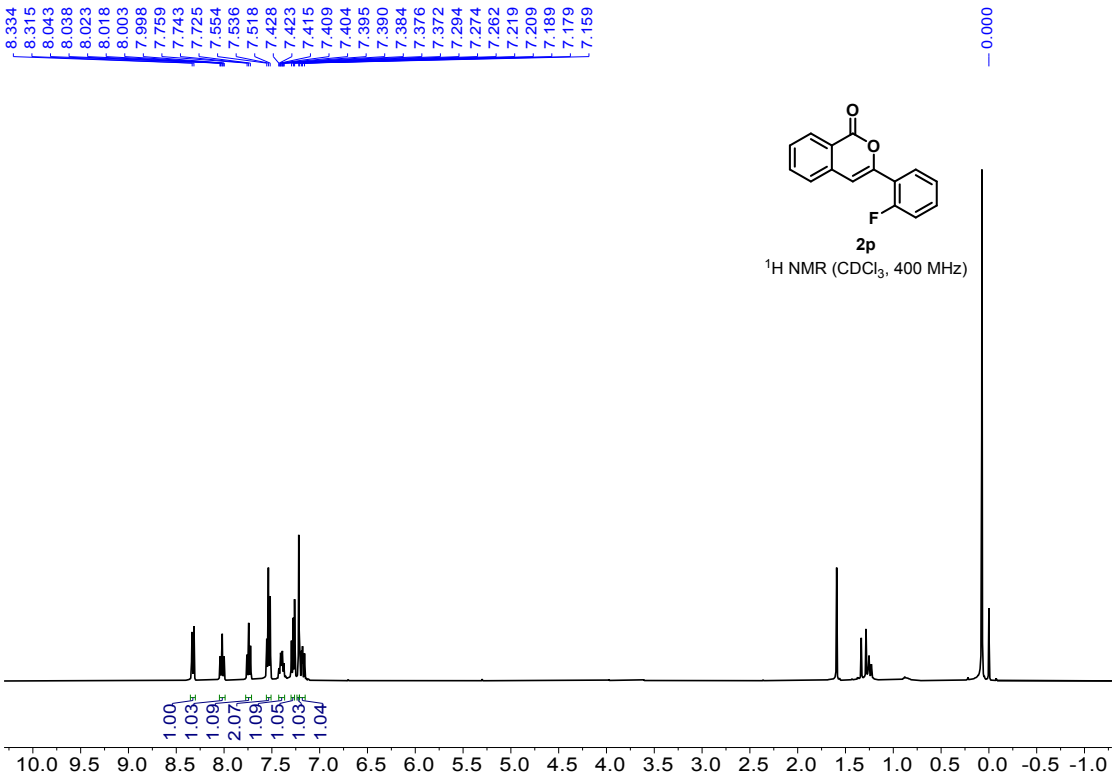
(**2n**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{20}H_{21}O_2$ $[M + H]^+$: 293.1536, found 293.1561.

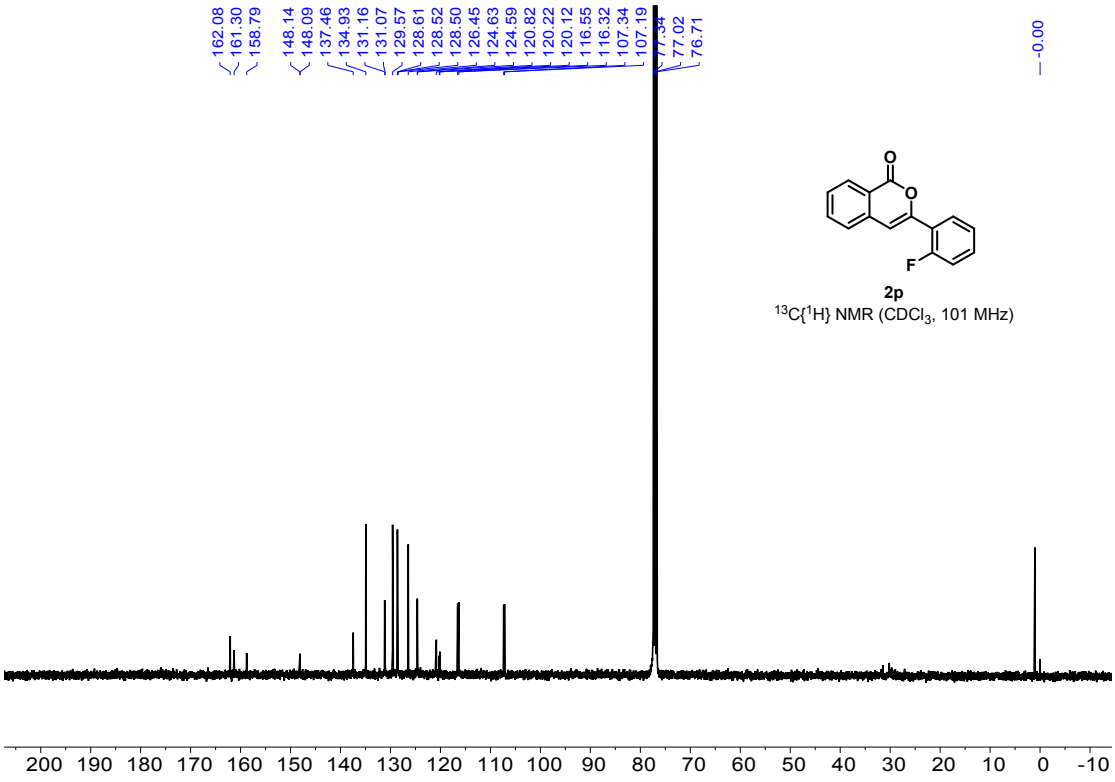

8.334
8.314
7.752
7.733
7.714
7.534
7.522
7.517
7.513
7.499
7.483
7.463
7.430
7.424
7.397
7.377
7.358
7.263
7.260
6.999
6.993
6.978
6.972
6.962
3.895
-0.001
O
O
OMe
2o
1H NMR (CDCl3, 400 MHz)
1.05
1.08
3.00
1.03
1.04
1.00
1.00
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

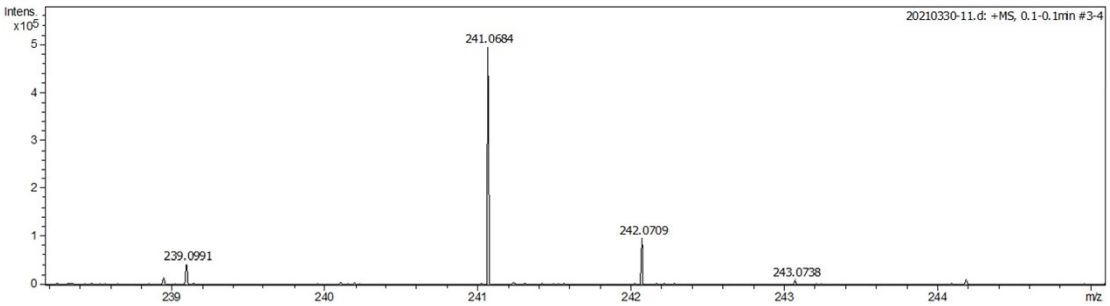

162.32
160.06
153.52
137.51
134.91
133.42
129.90
129.73
128.24
126.02
120.65
117.74
116.03
110.54
102.14
77.36
77.04
76.72
55.52
-0.02
O
O
OMe
2o
13C{1H} NMR (CDCl3, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



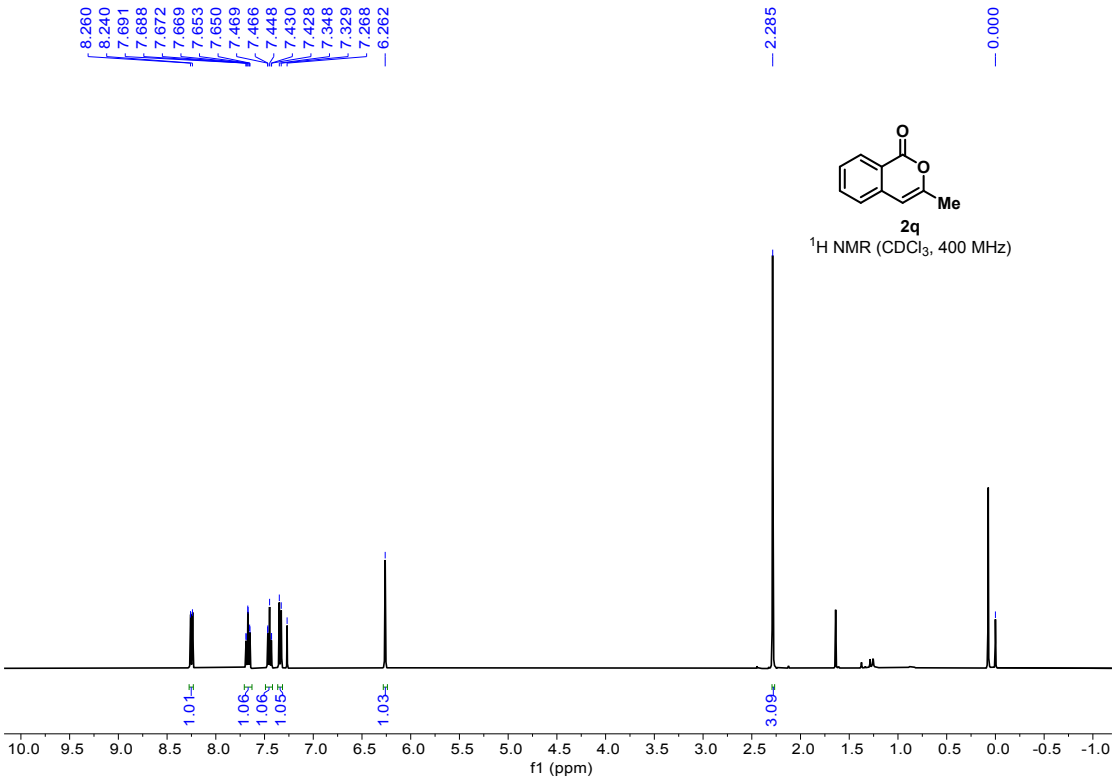
(**2o**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{16}H_{13}O_3$ $[M + H]^+$: 253.0859, found 253.0888.

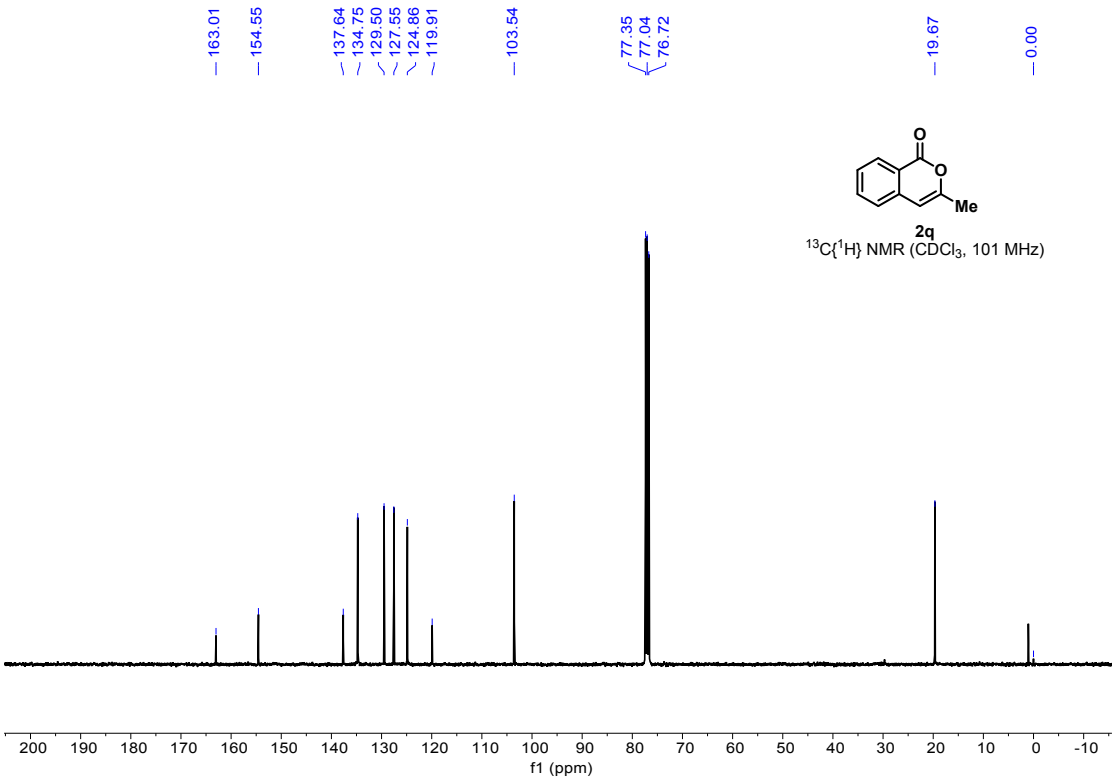

8.334
8.315
8.043
8.038
8.023
8.018
8.003
7.998
7.759
7.743
7.725
7.554
7.536
7.518
7.428
7.423
7.415
7.409
7.404
7.395
7.390
7.384
7.376
7.372
7.294
7.274
7.262
7.219
7.209
7.189
7.179
7.159
0.000
O
O
F
2p
^{1}H NMR (CDCl$_3$, 400 MHz)
1.00
1.03
1.09
2.07
1.09
1.05
1.03
1.04
10.0 9.5 9.0 8.5 8.0 7.5 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

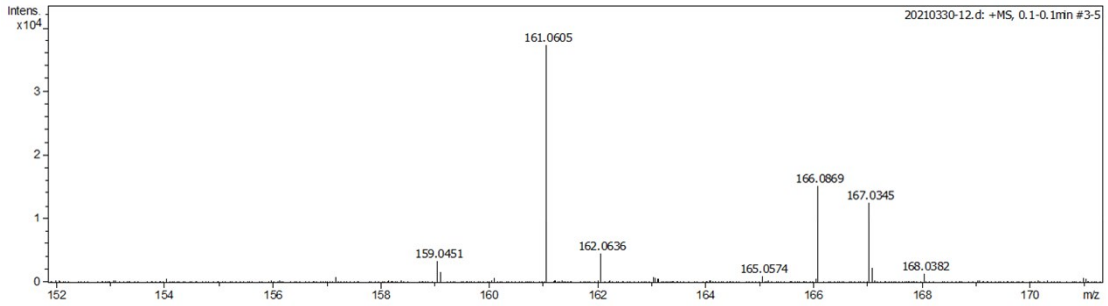

162.08
161.30
158.79
148.14
148.09
137.46
134.93
131.16
131.07
129.57
128.61
128.52
128.50
126.45
124.63
124.59
120.82
120.22
120.12
116.55
116.32
107.34
107.19
77.34
77.02
76.71
-0.00
O
O
F
2p
^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



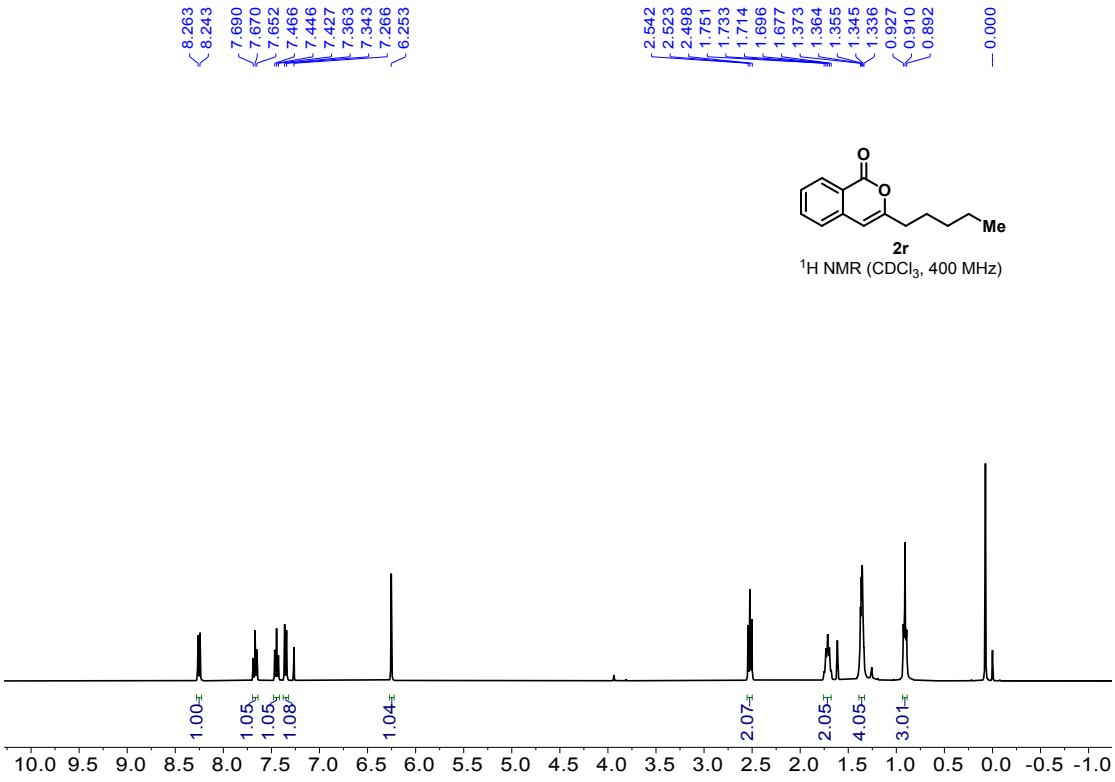
(**2p**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$: 241.0659, found 241.0684.


8.260
8.240
7.691
7.688
7.672
7.669
7.653
7.650
7.469
7.466
7.448
7.430
7.428
7.348
7.329
7.268
6.262
2.285
0.000
O
O
Me
2q
1H NMR (CDCl3, 400 MHz)
1.01
1.06
1.06
1.05
1.03
3.09
f1 (ppm)


163.01
154.55
137.64
134.75
129.50
127.55
124.86
119.91
103.54
77.35
77.04
76.72
19.67
0.00
O
O
Me
2q
13C{1H} NMR (CDCl3, 101 MHz)
f1 (ppm)

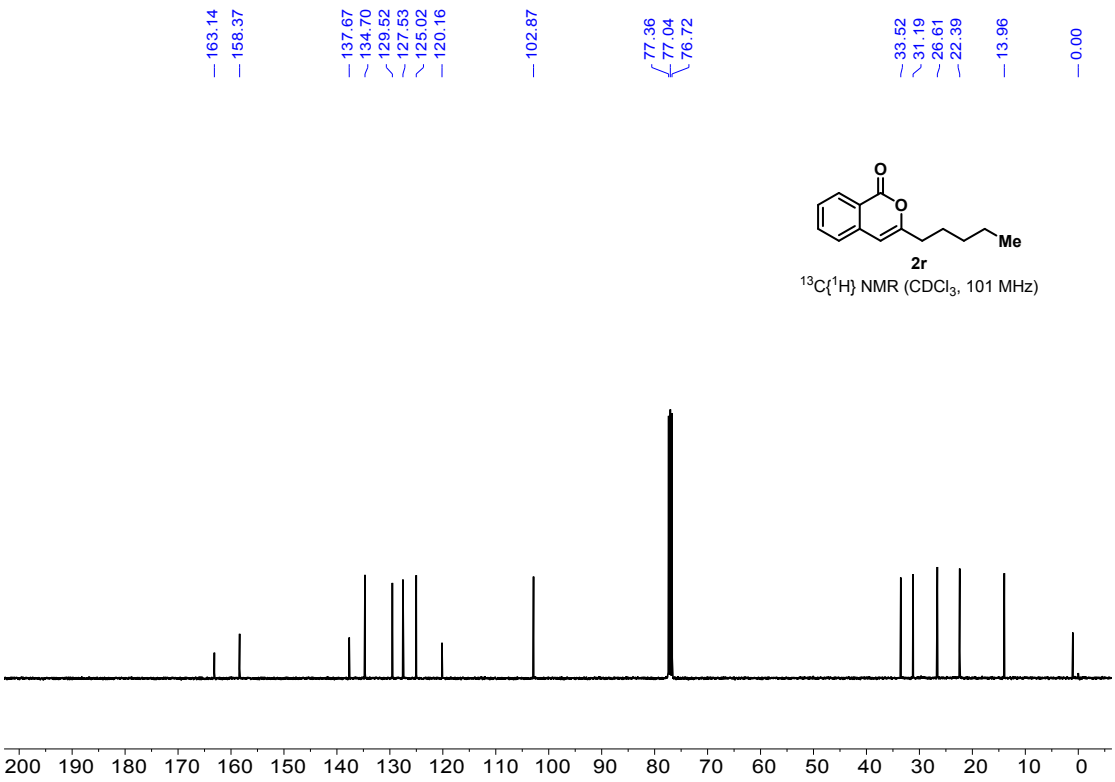


(**2q**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{10}H_9O_2$ $[M + H]^+$: 161.0597, found 161.0605.



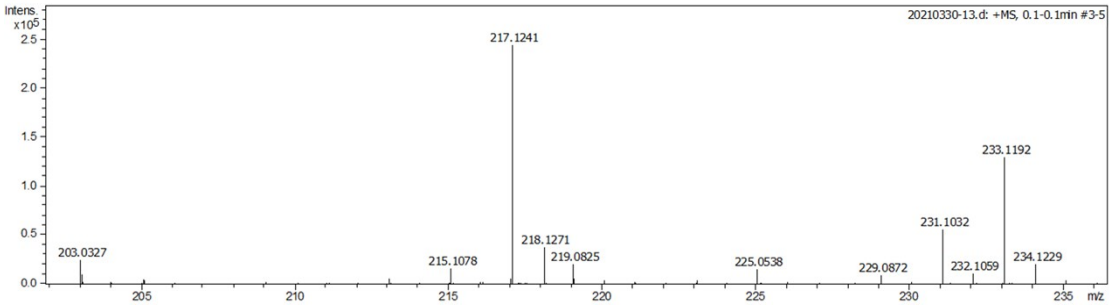
2r

^{1}H NMR ($CDCl_3$, 400 MHz)

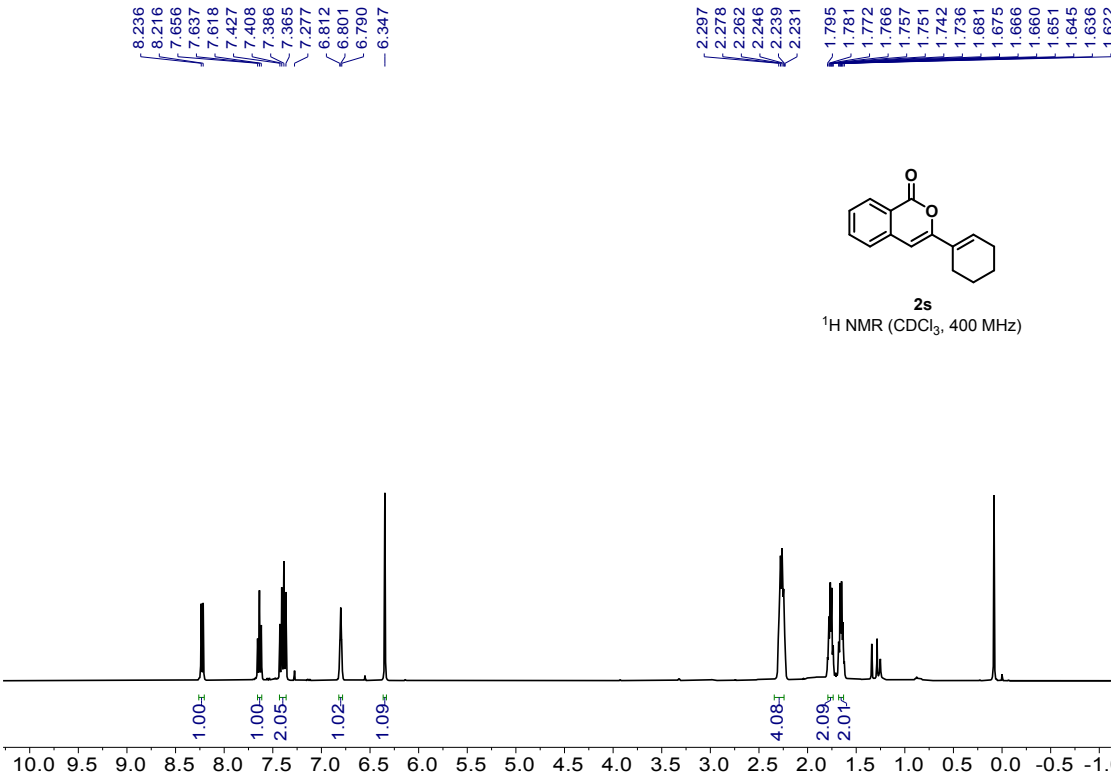


2r

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

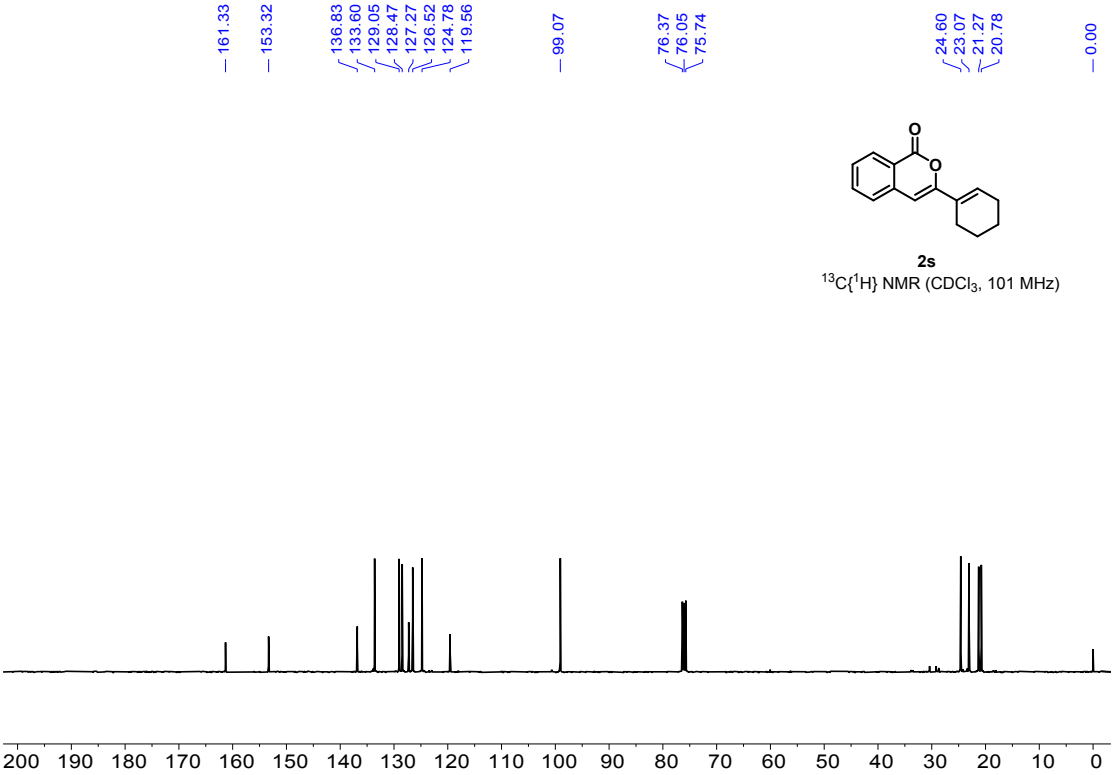


(**2r**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{17}O_2$ $[M + H]^+$: 217.1223, found 217.1241.



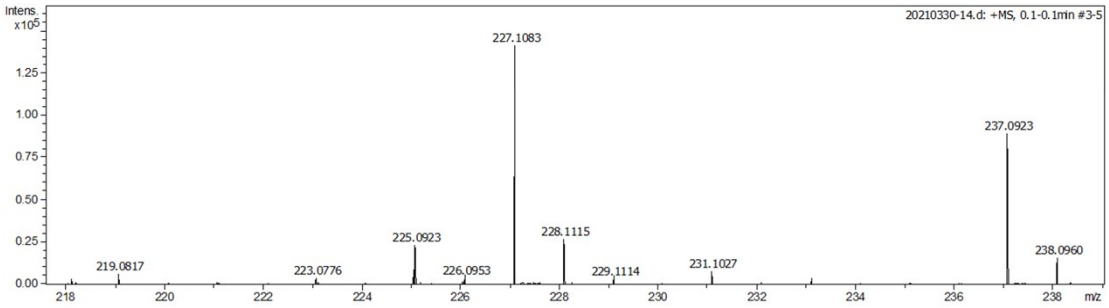
2s

^{1}H NMR ($CDCl_3$, 400 MHz)

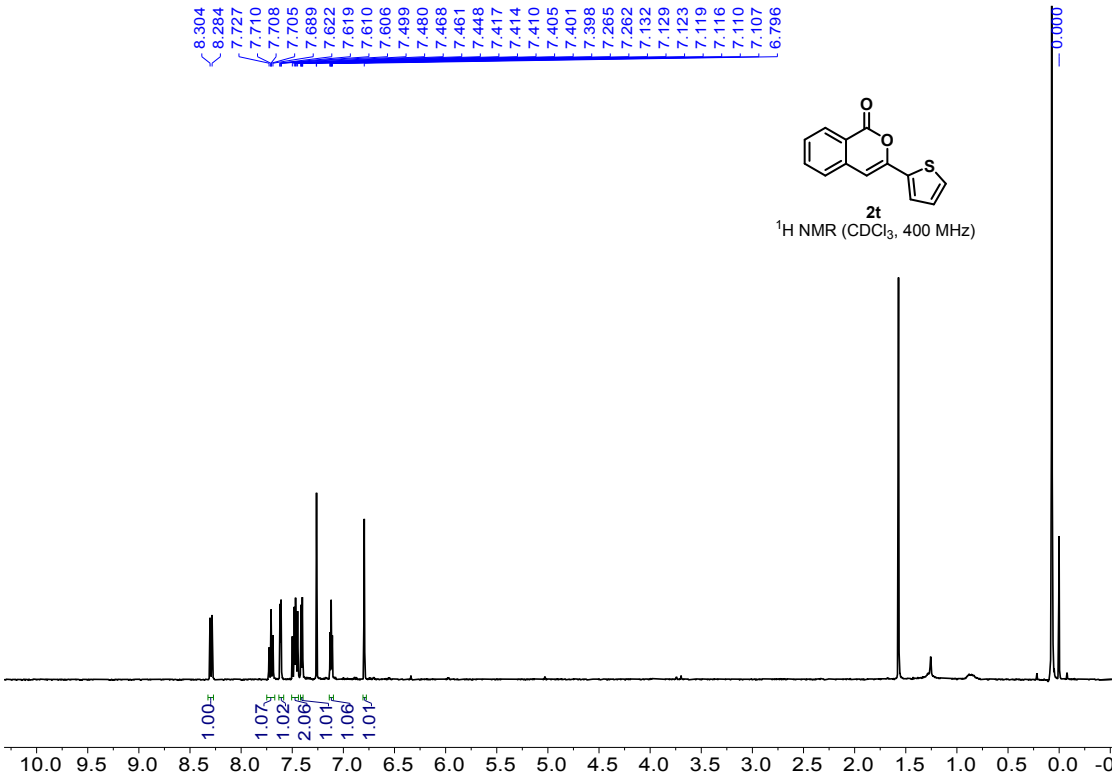


2s

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

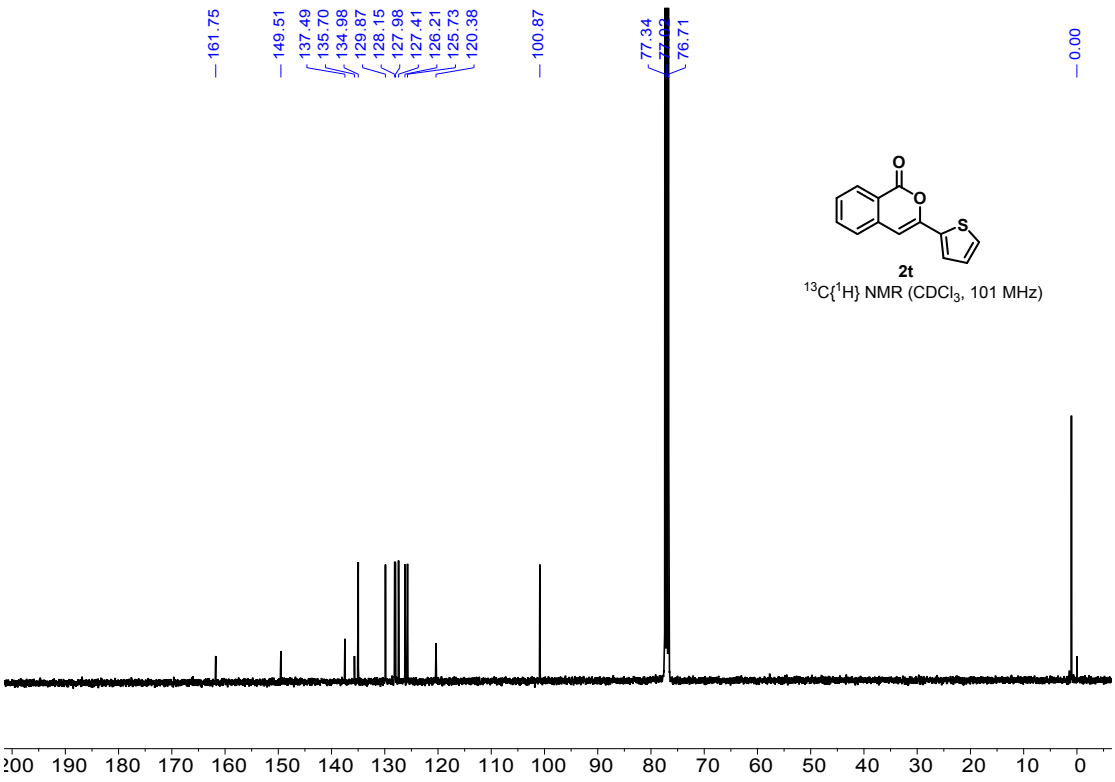


(**2s**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{15}H_{15}O_2$ $[M + H]^+$: 227.1067, found 227.1083.



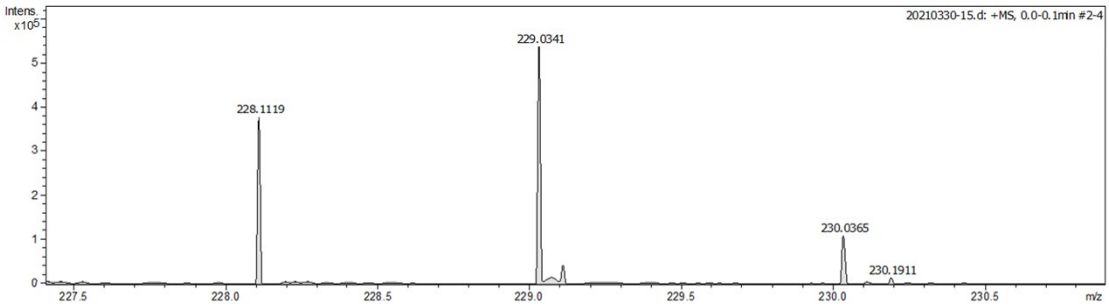
2t

^{1}H NMR ($CDCl_3$, 400 MHz)

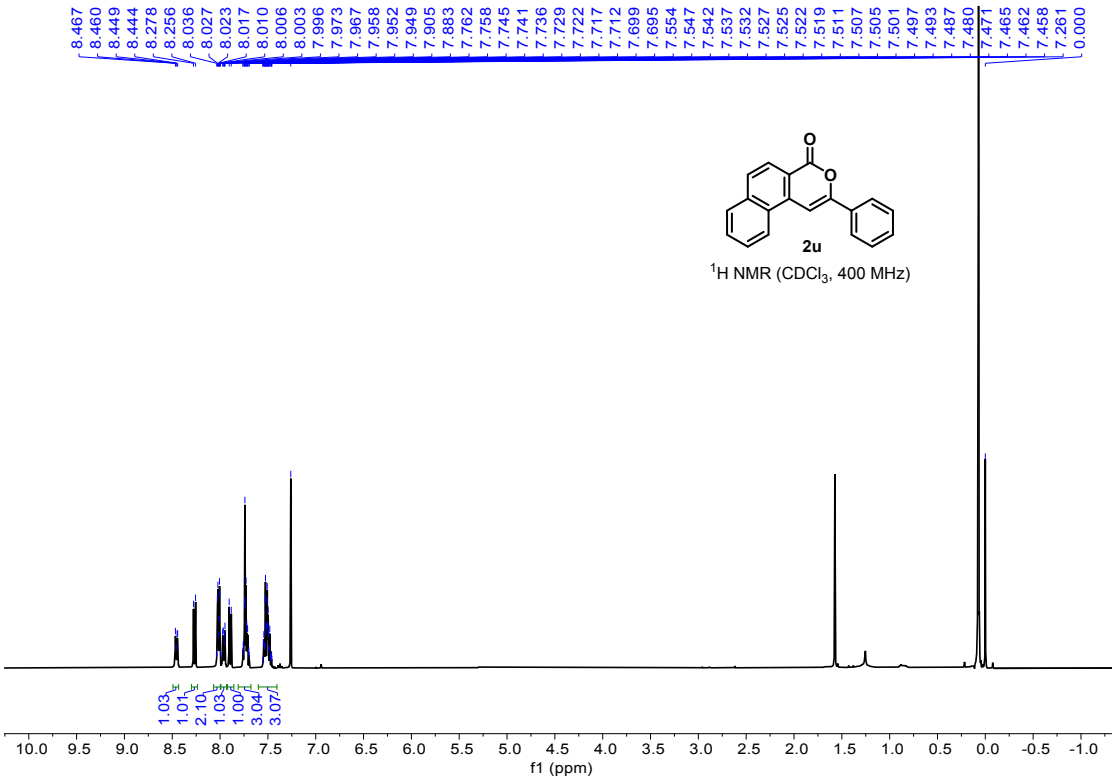


2t

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

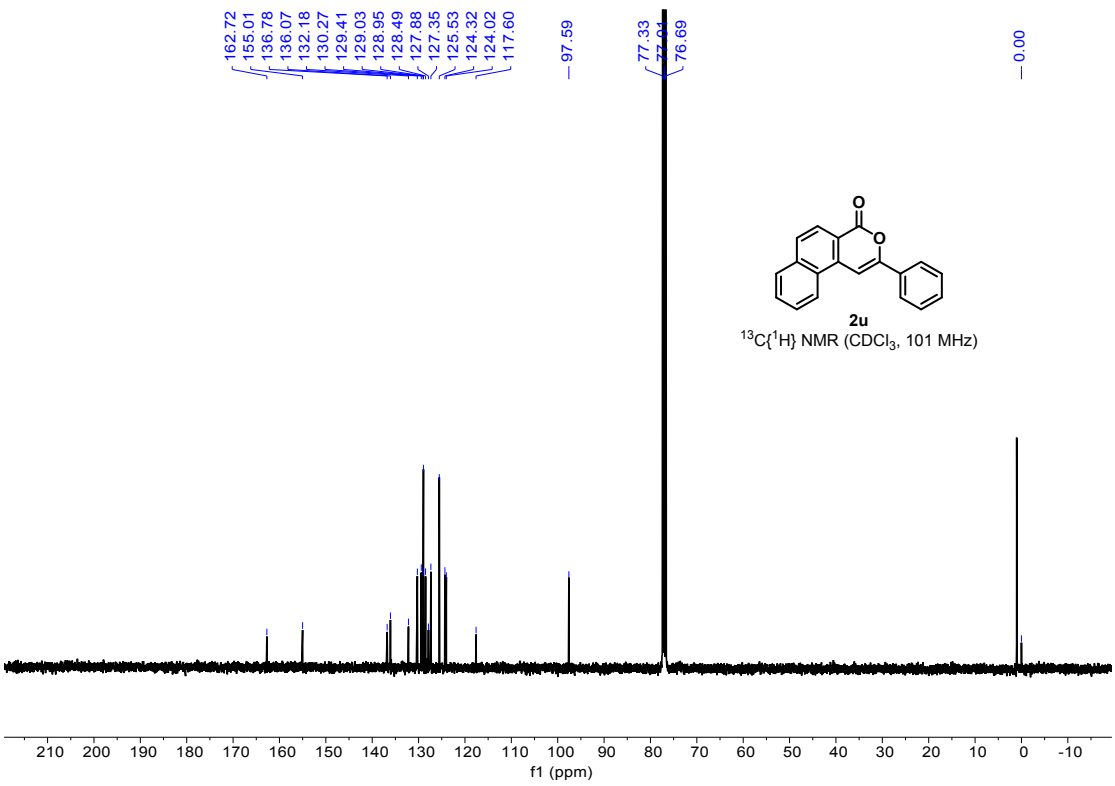


(**2t**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_9O_2S$ $[M + H]^+$: 229.0318, found 229.0341.



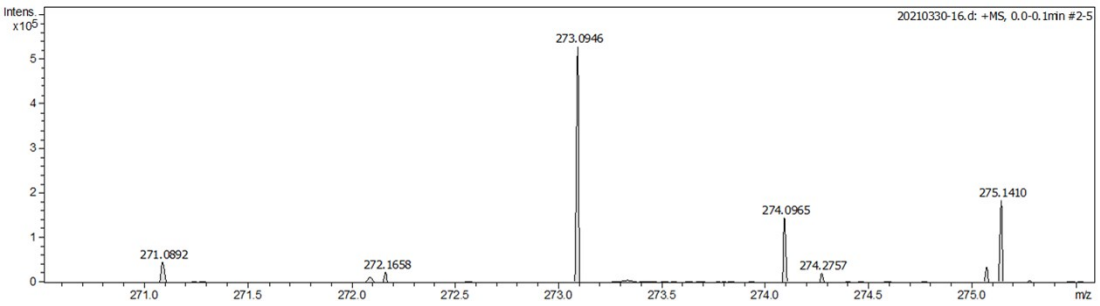
2u

^{1}H NMR ($CDCl_3$, 400 MHz)

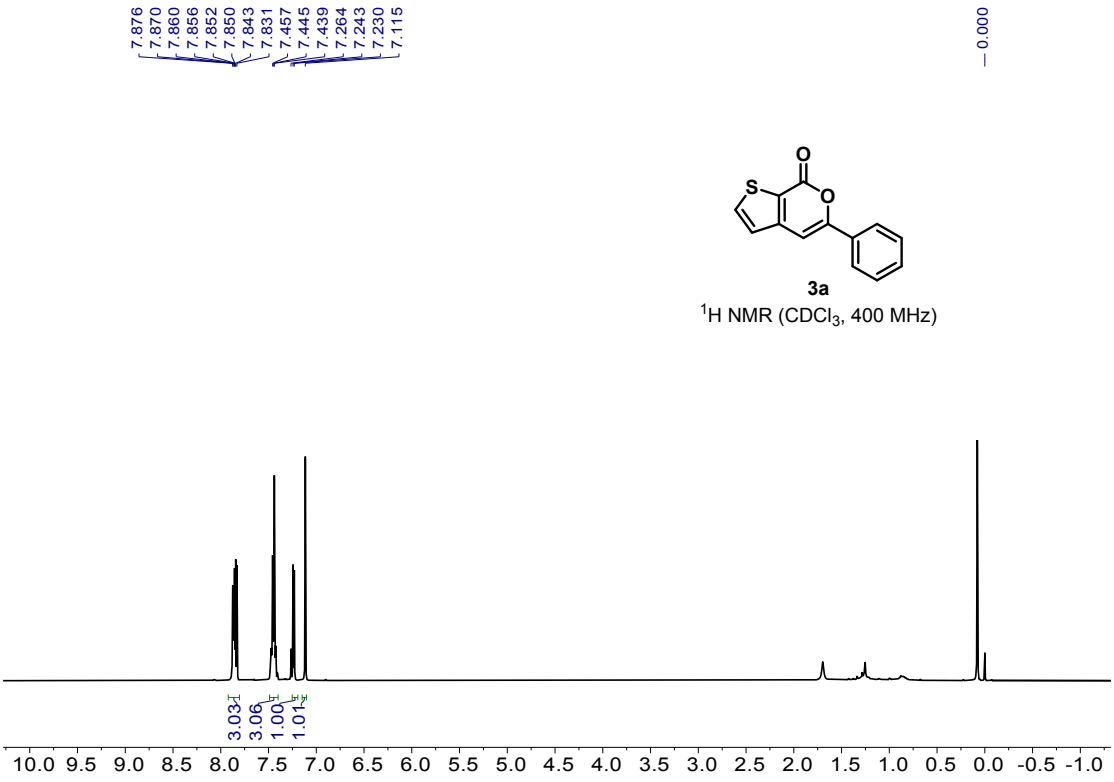


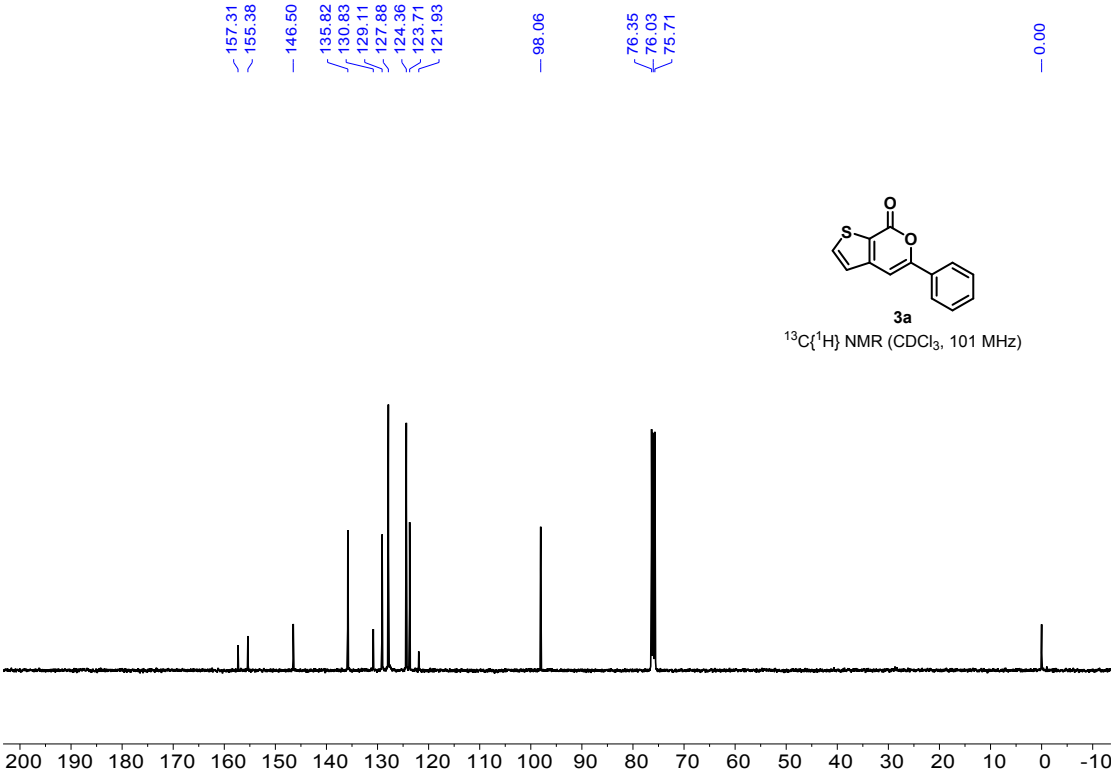
2u

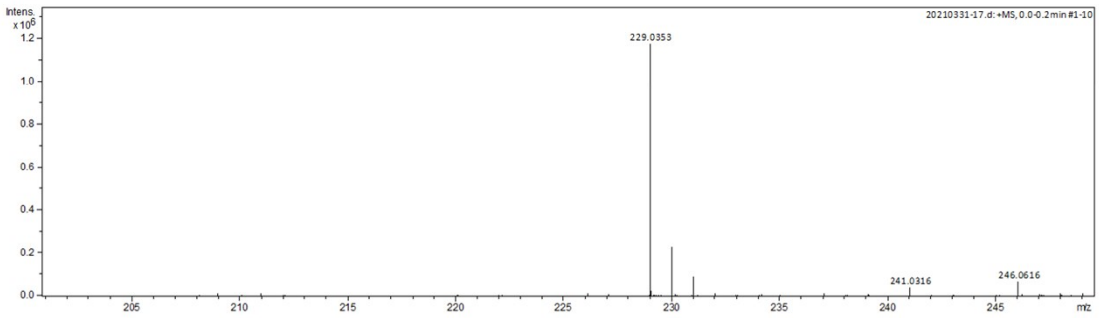
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



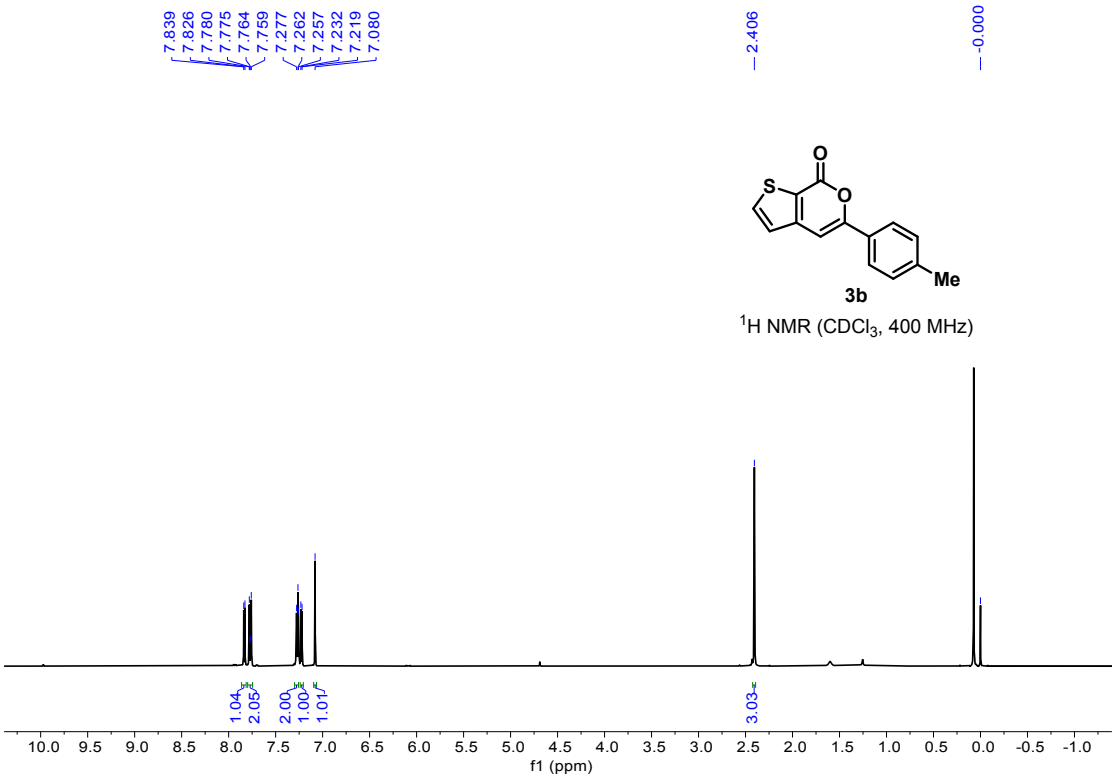
(**2u**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{19}H_{13}O_2$ $[M + H]^+$: 273.0910, found 273.0946.


7.876
7.870
7.860
7.856
7.852
7.850
7.843
7.831
7.457
7.445
7.439
7.264
7.243
7.230
7.115
0.000
O
S
O
3a
^{1}H NMR (CDCl$_3$, 400 MHz)
3.03
3.06
1.00
1.01
10.0 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

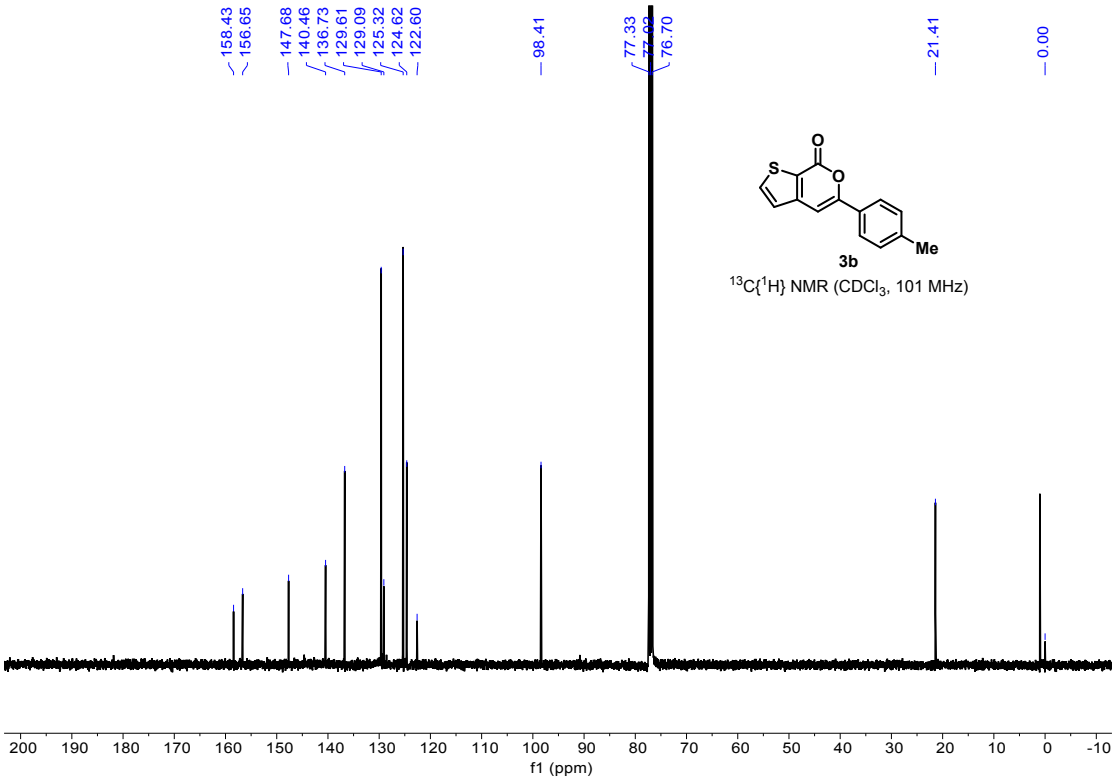

157.31
155.38
146.50
135.82
130.83
129.11
127.88
124.36
123.71
121.93
98.06
76.35
76.03
75.71
0.00
O
S
O
3a
^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



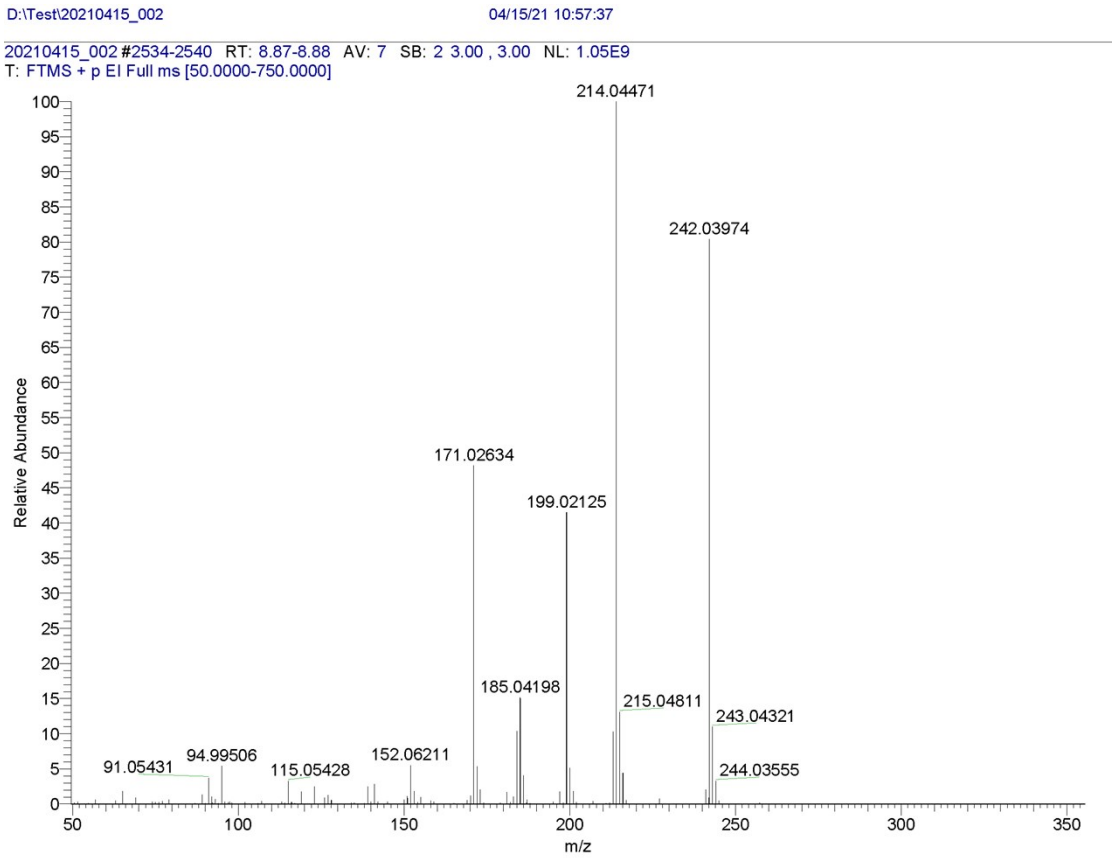
(**3a**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_9O_2S$ $[M + H]^+$: 229.0318, found 229.0353.



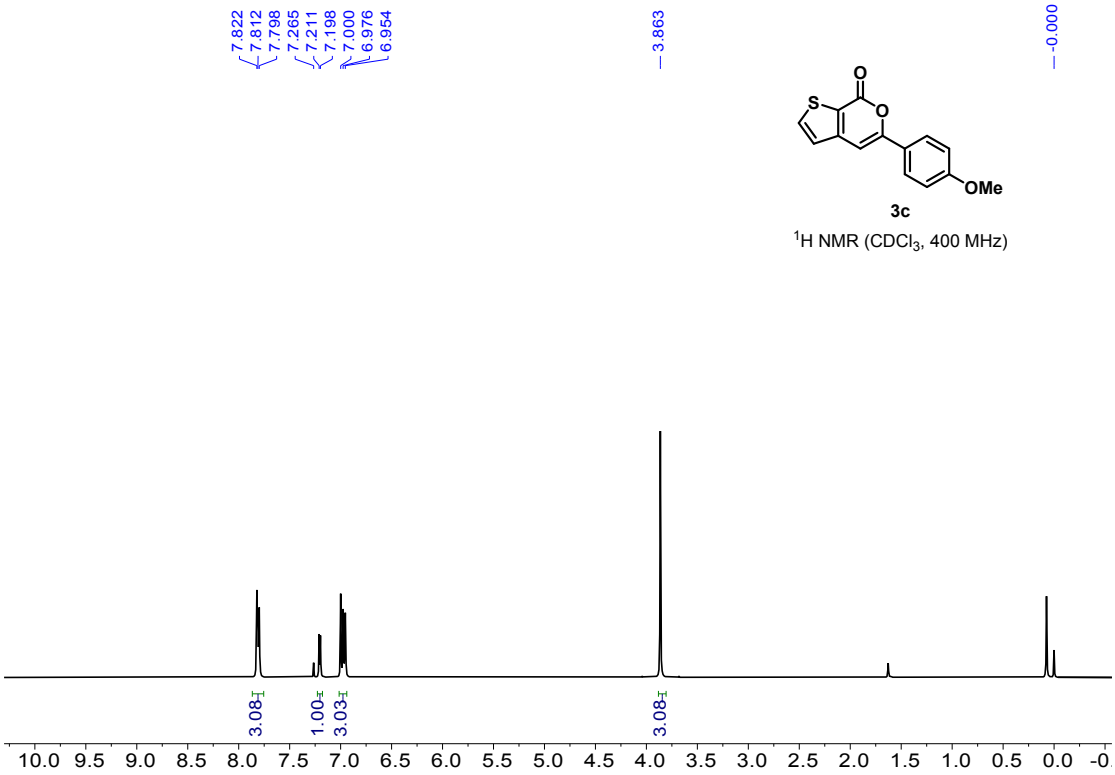
^{1}H NMR ($CDCl_3$, 400 MHz)



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

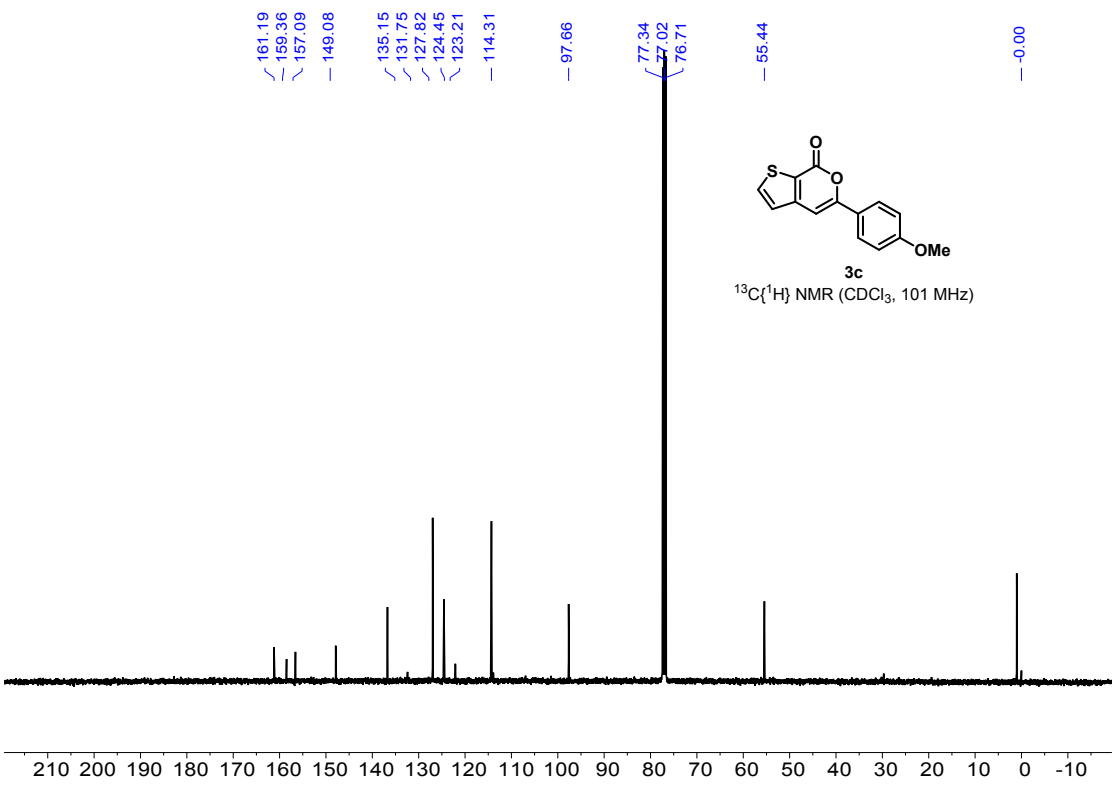


(**3b**) **HRMS** (EI) *m/z* calcd for $C_{14}H_{11}O_2S$ $[M]^+$: 242.04015, found 242.03974.



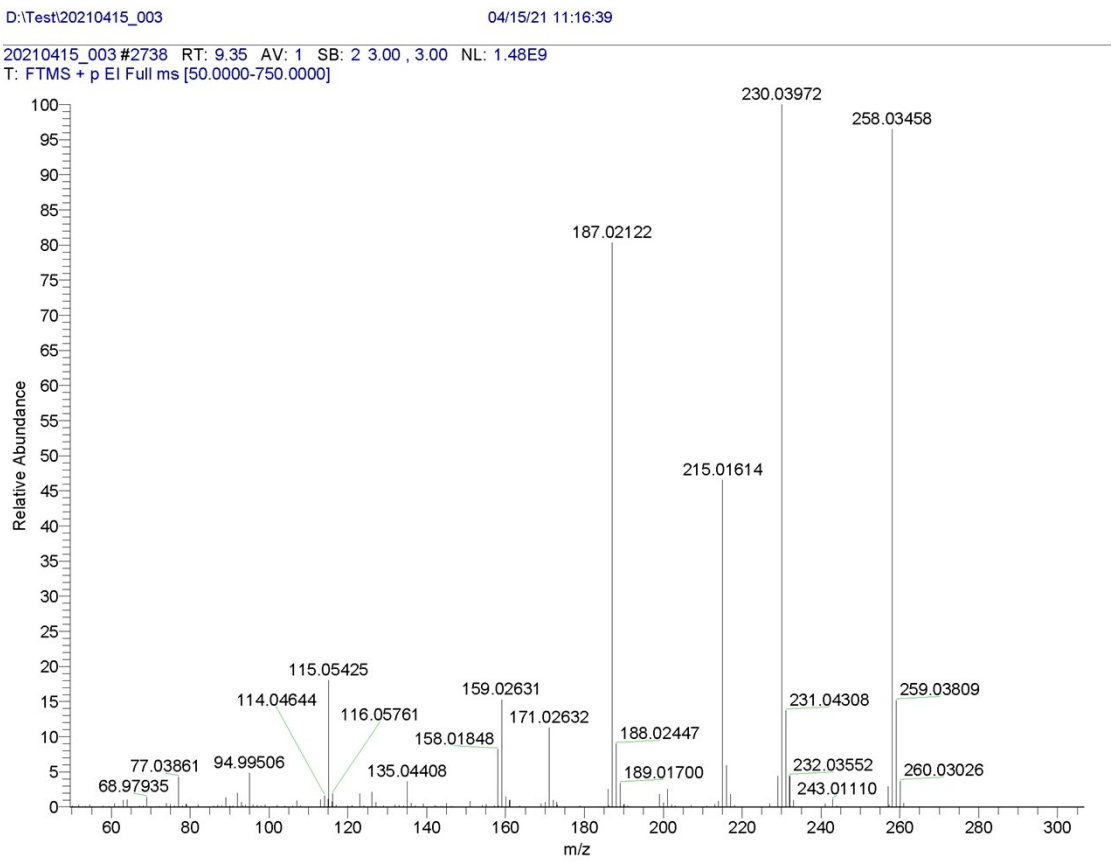
3c

^{1}H NMR ($CDCl_3$, 400 MHz)

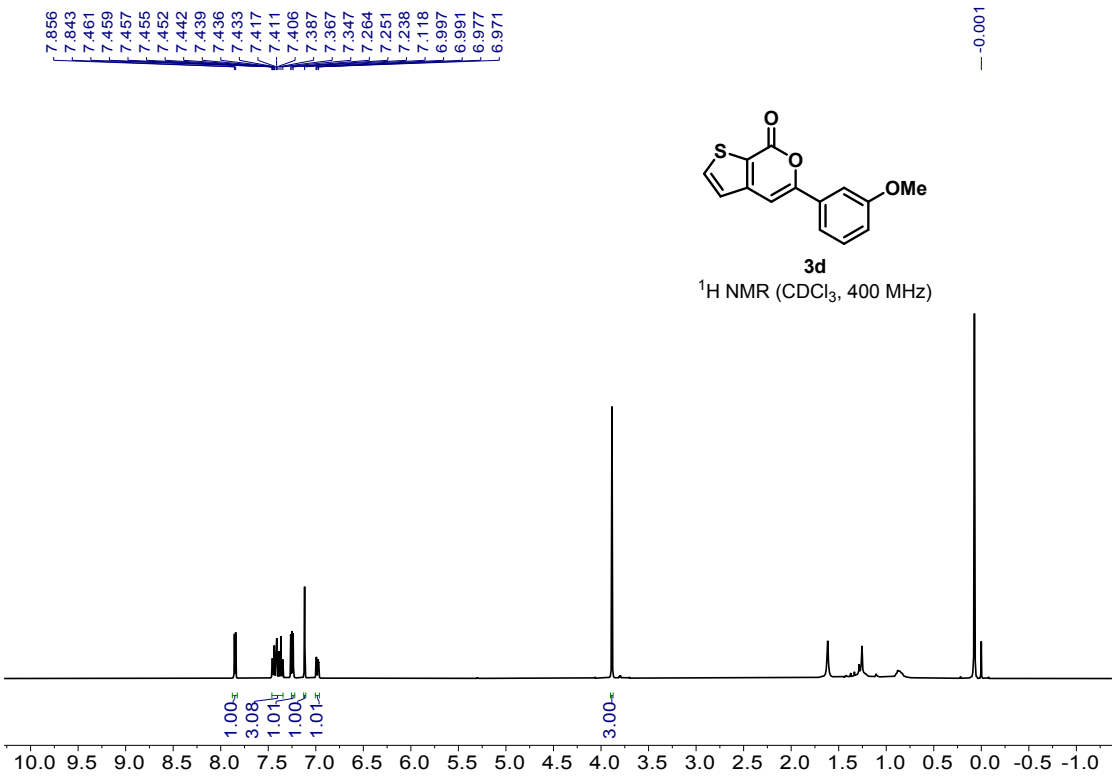


3c

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

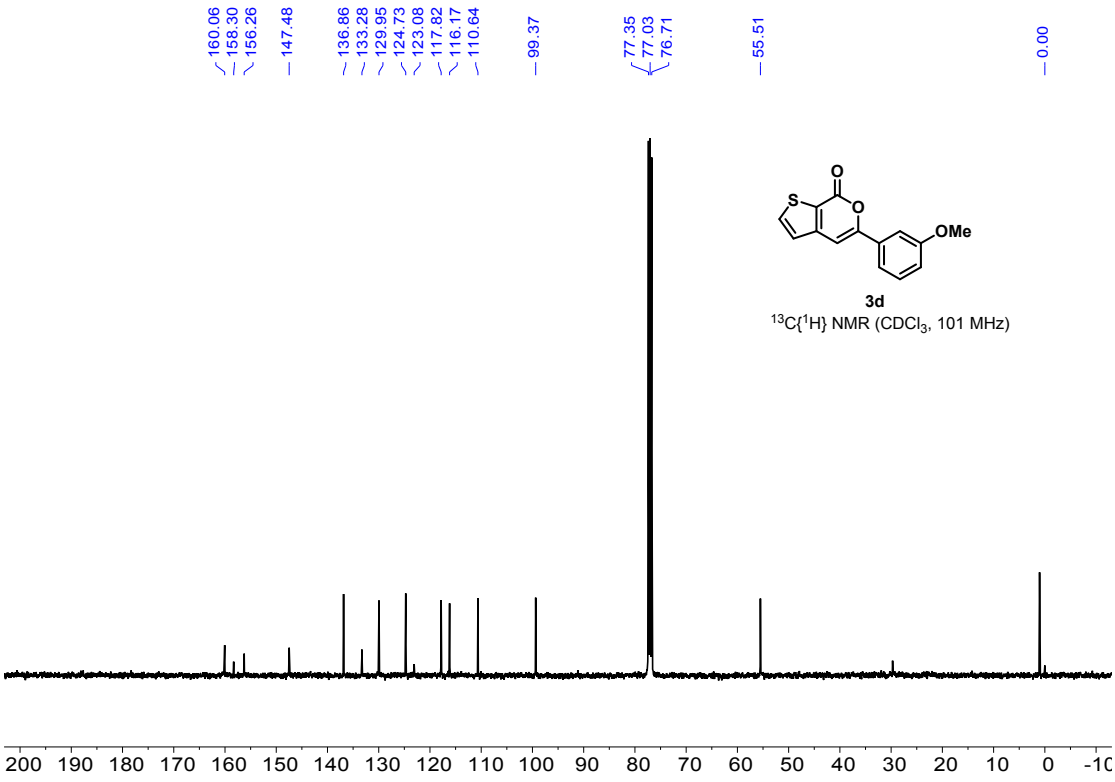


(**3c**) **HRMS** (EI) *m/z* calcd for $C_{14}H_{10}O_3S$ $[M]^+$: 258.03506, found 258.03458.



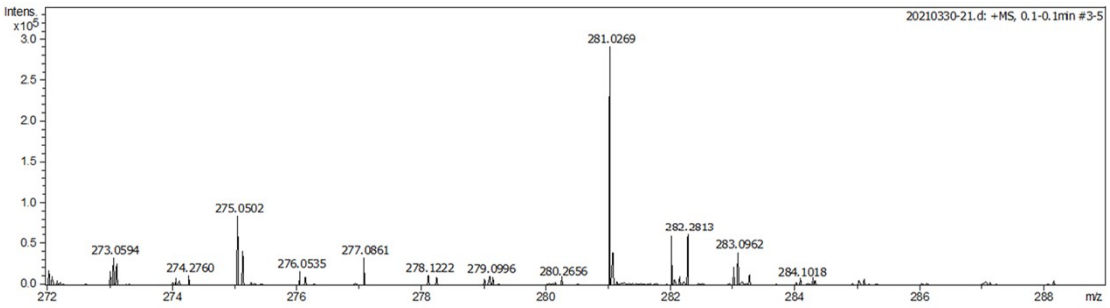
3d

^{1}H NMR ($CDCl_3$, 400 MHz)

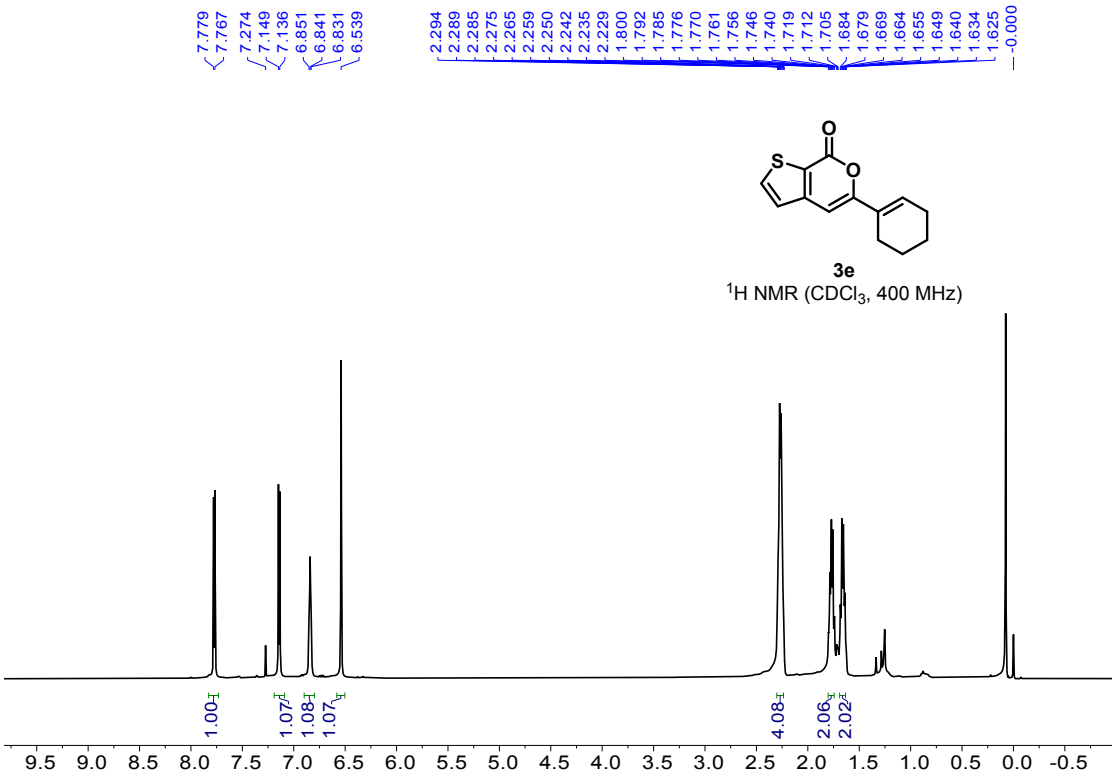


3d

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)

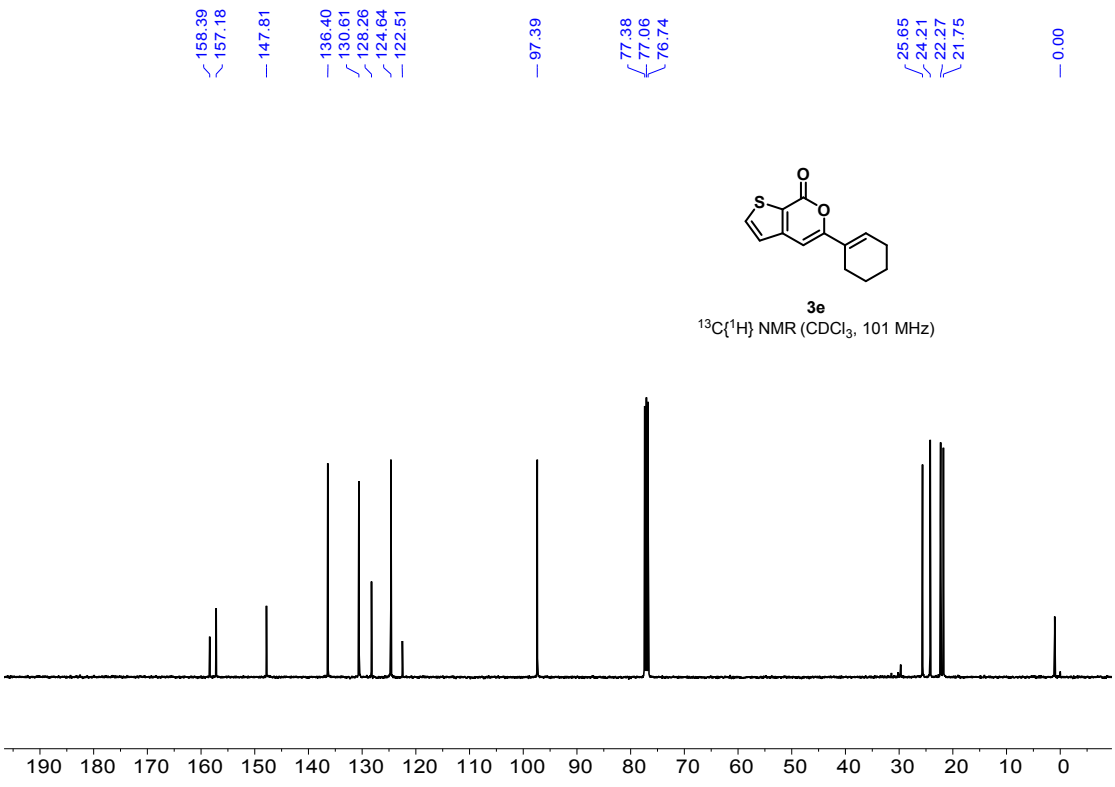


(**3d**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{10}NaO_3S$ $[M + Na]^+$: 281.0243, found 281.0269.



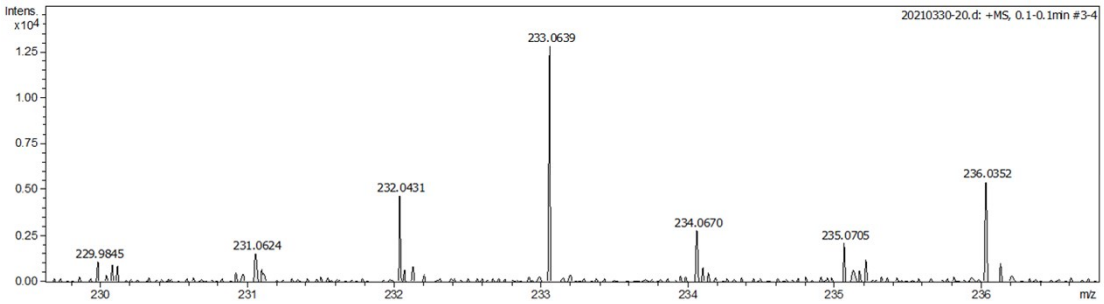
3e

^{1}H NMR ($CDCl_3$, 400 MHz)

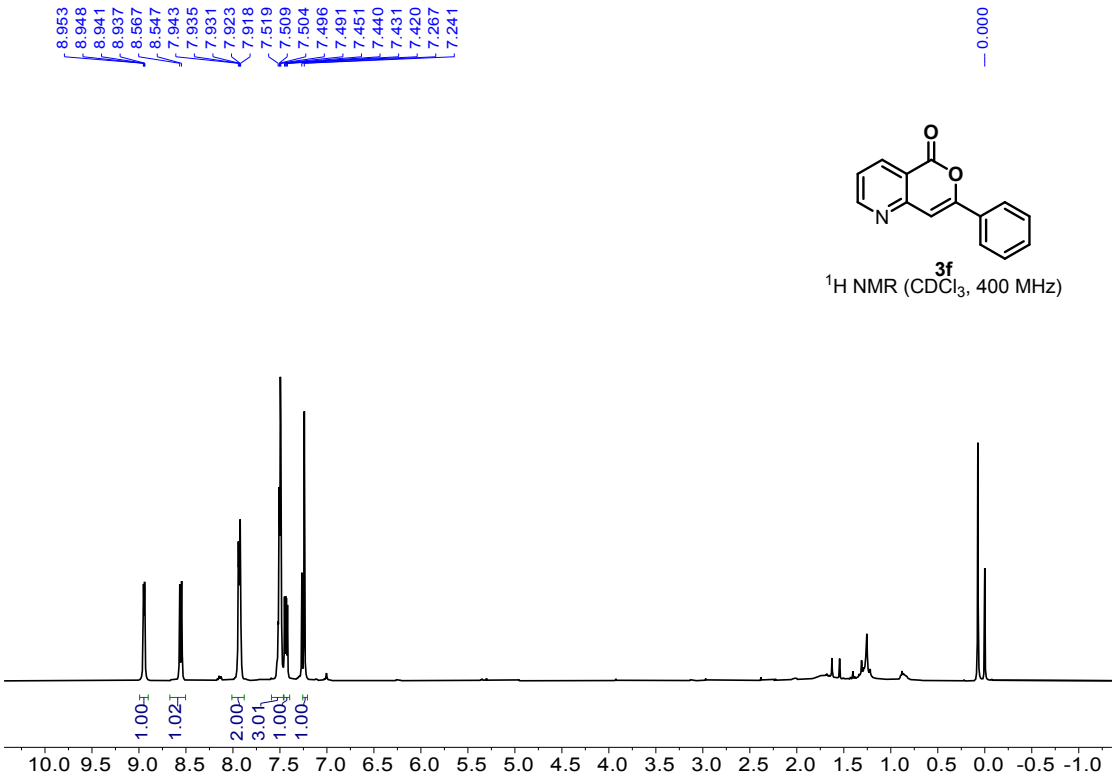


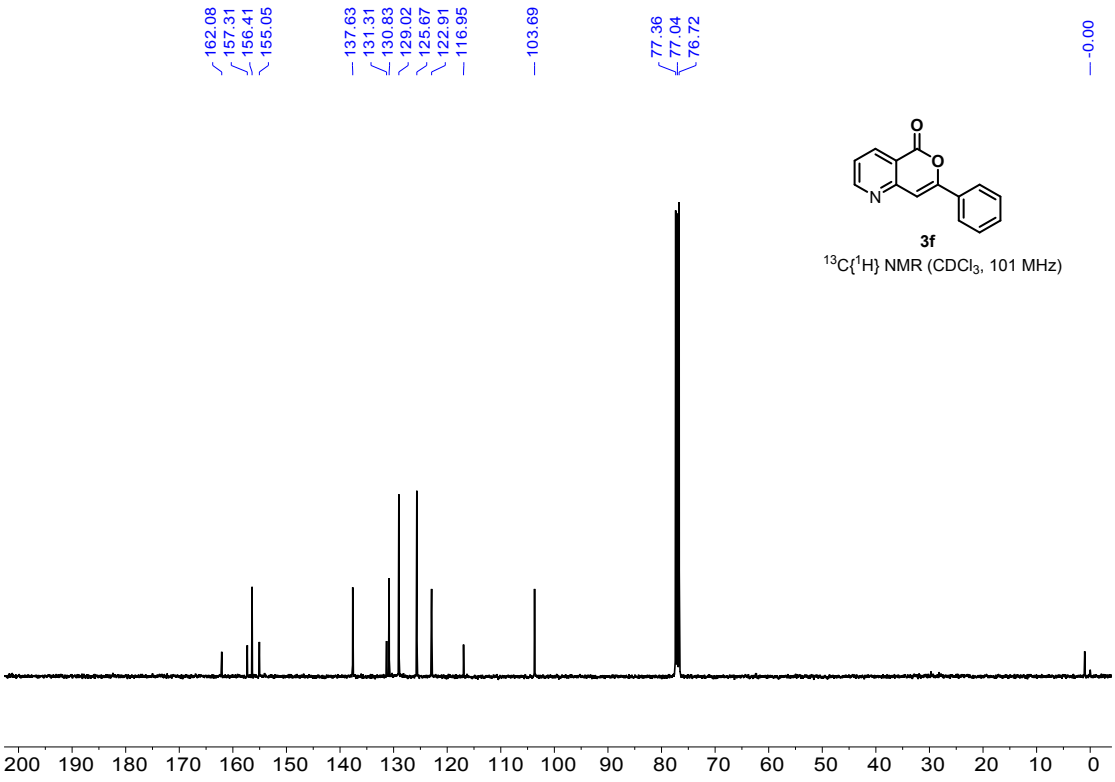
3e

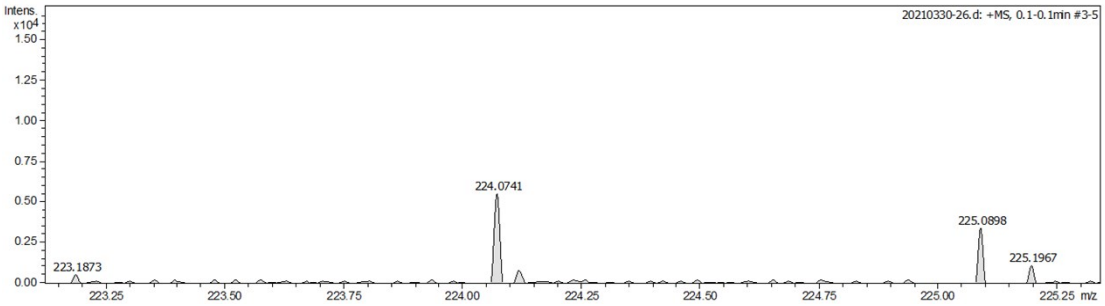
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 101 MHz)



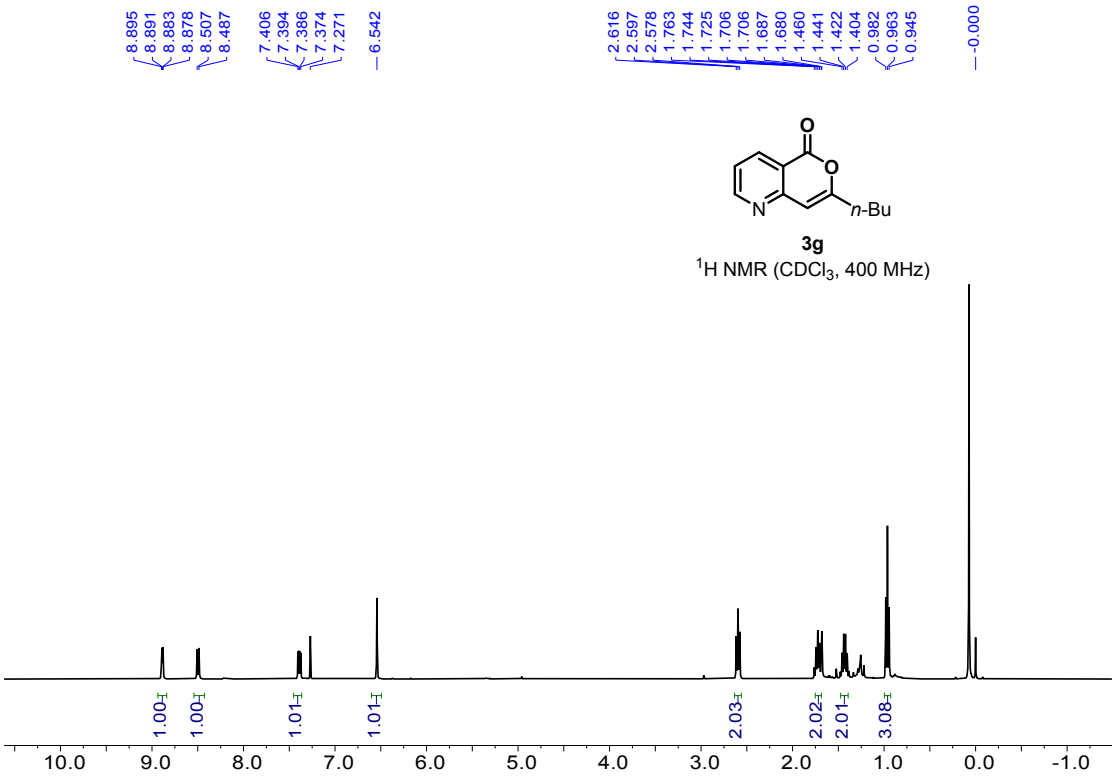
(**3e**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{13}H_{13}O_2S$ $[M + H]^+$: 233.0631, found 233.0639.


8.953
8.948
8.941
8.937
8.567
8.547
7.943
7.935
7.931
7.923
7.918
7.519
7.509
7.504
7.496
7.491
7.451
7.440
7.431
7.420
7.267
7.241
0.000
O
O
N
3f
^{1}H NMR (CDCl$_3$, 400 MHz)
1.00
1.02
2.00
3.01
1.00
1.00
10.0 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


162.08
157.31
156.41
155.05
137.63
131.31
130.83
129.02
125.67
122.91
116.95
103.69
77.36
77.04
76.72
-0.00
O
O
N
3f
^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

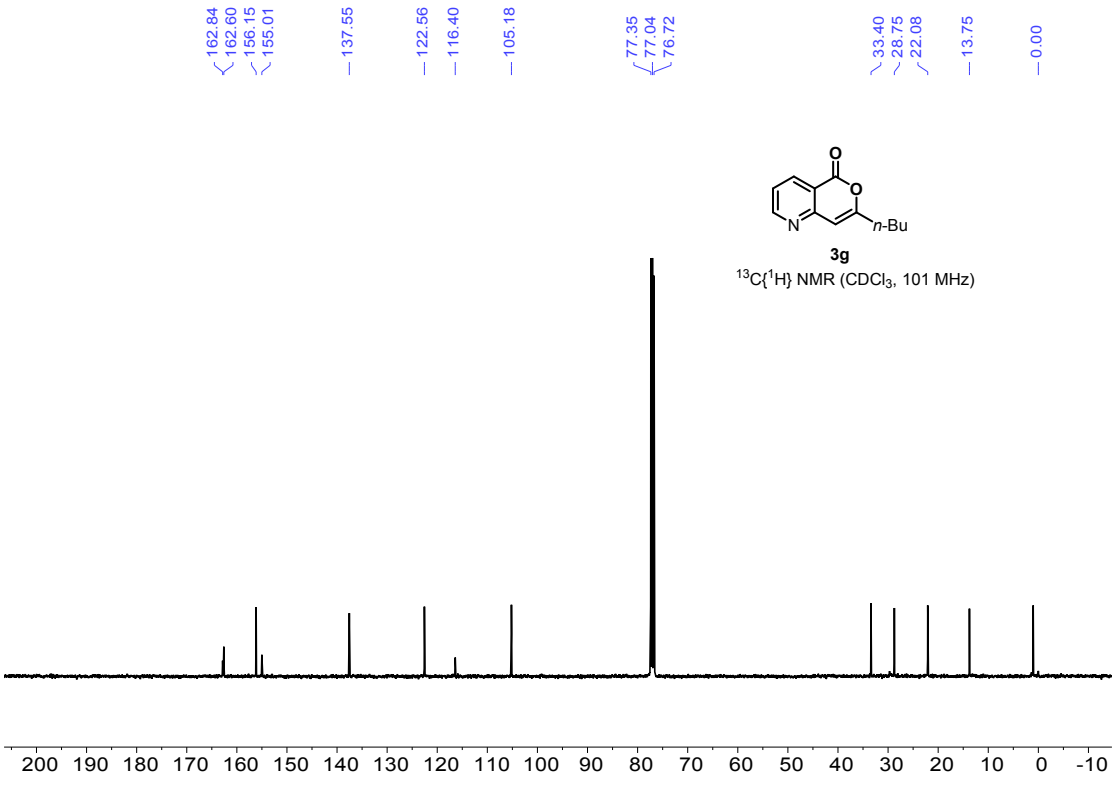


(**3f**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{14}H_{10}NO_2$ $[M + H]^+$: 224.0706, found 224.0741.



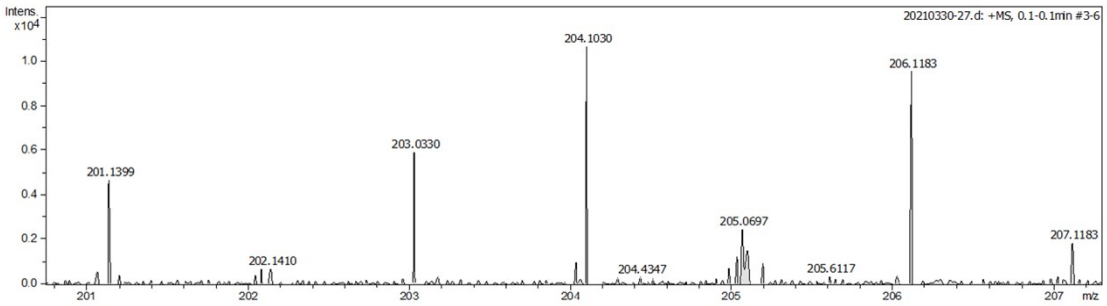
3g

^{1}H NMR ($CDCl_3$, 400 MHz)

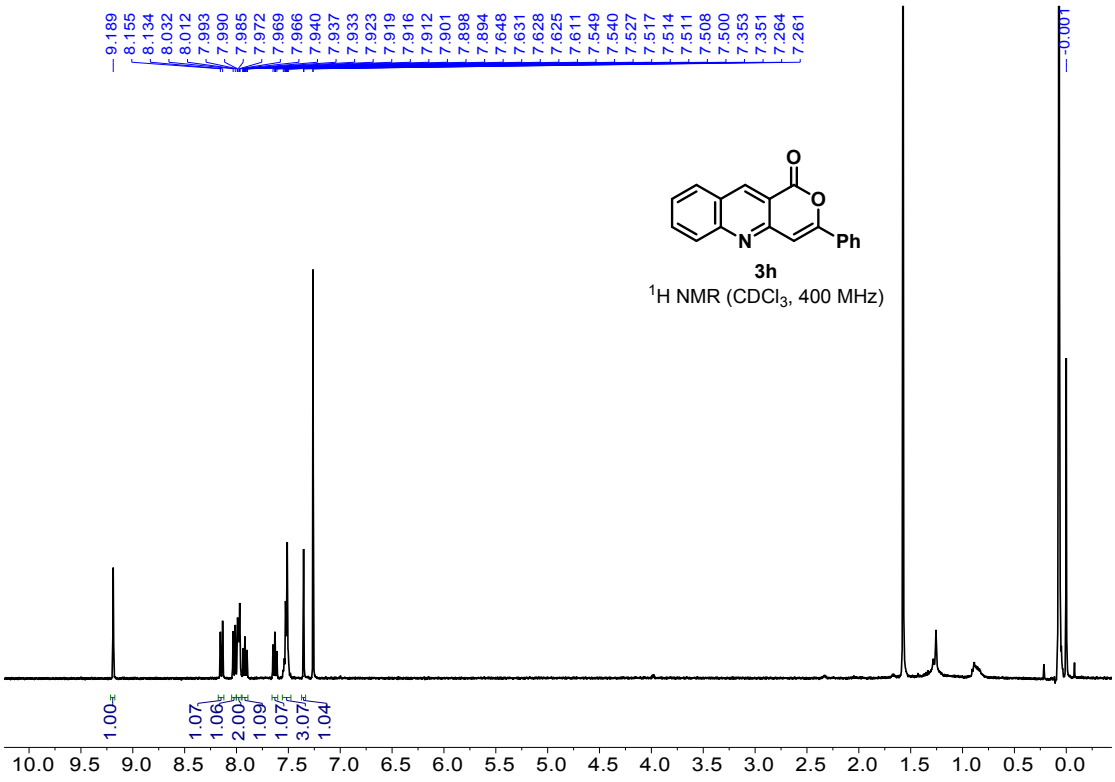


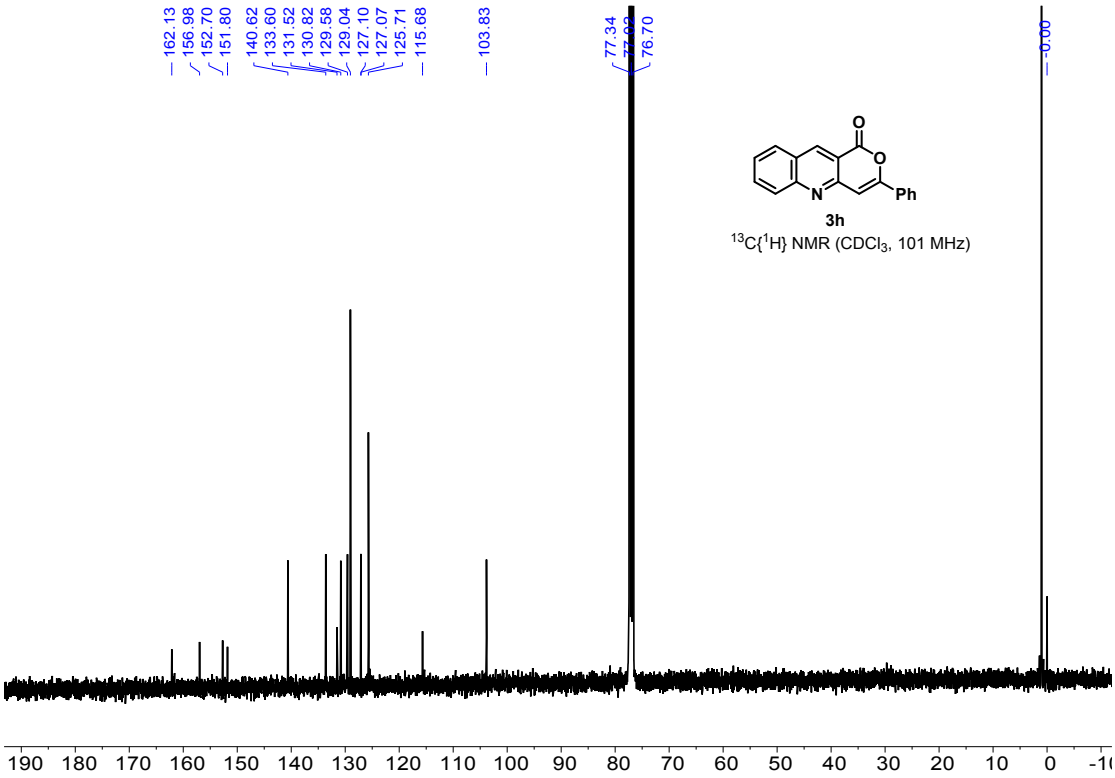
3g

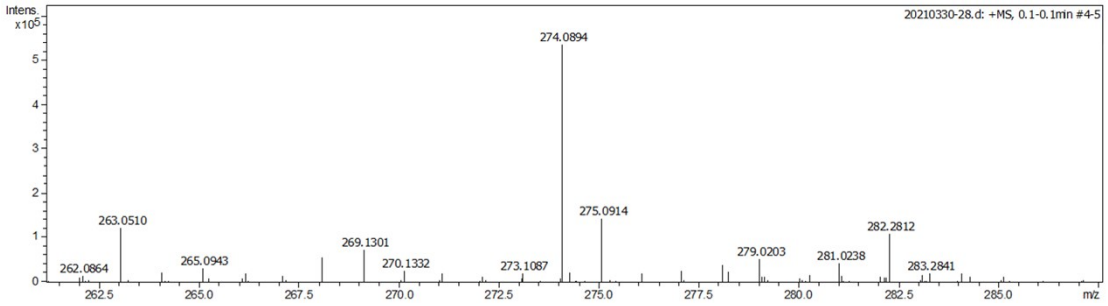
^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz)



(**3g**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{12}H_{14}NO_2$ $[M + H]^+$: 204.1019, found 204.1030.


9.189
8.155
8.134
8.032
8.012
7.993
7.990
7.985
7.972
7.969
7.966
7.940
7.937
7.933
7.923
7.919
7.916
7.912
7.901
7.898
7.894
7.648
7.631
7.628
7.625
7.611
7.549
7.540
7.527
7.517
7.514
7.511
7.508
7.500
7.353
7.351
7.264
7.261
0.001
O
O
N
Ph
3h
1H NMR (CDCl3, 400 MHz)
1.00
1.07
1.06
2.00
1.09
1.07
3.07
1.04
10.0 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


162.13
156.98
152.70
151.80
140.62
133.60
131.52
130.82
129.58
129.04
127.10
127.07
125.71
115.68
103.83
77.34
77.00
76.70
0.00
O
O
N
Ph
3h
13C{1H} NMR (CDCl3, 101 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



(**3h**) **HRMS** (ESI-TOF) *m/z* calcd for $C_{18}H_{12}NO_2$ $[M + H]^+$: 274.0863, found 274.0894.