

Base-promoted cyclization of *ortho*-hydroxyacetophenones with *in situ* generated cyclopropenes: diastereoselective access to spirobenzo[*b*]oxepines and related precursors

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Crystallographic data: Single crystal X-ray structural of compound **3aa** was measured on the SuperNova, Dual, Mo at home/near, Eos- XRD at 150(2) K using graphite monochromated Mo K α radiation ($\lambda\alpha = 0.71073 \text{ \AA}$). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structure was solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F^2 . The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. The crystal data are summarized in Table S1. The CCDC number **2233544**) can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

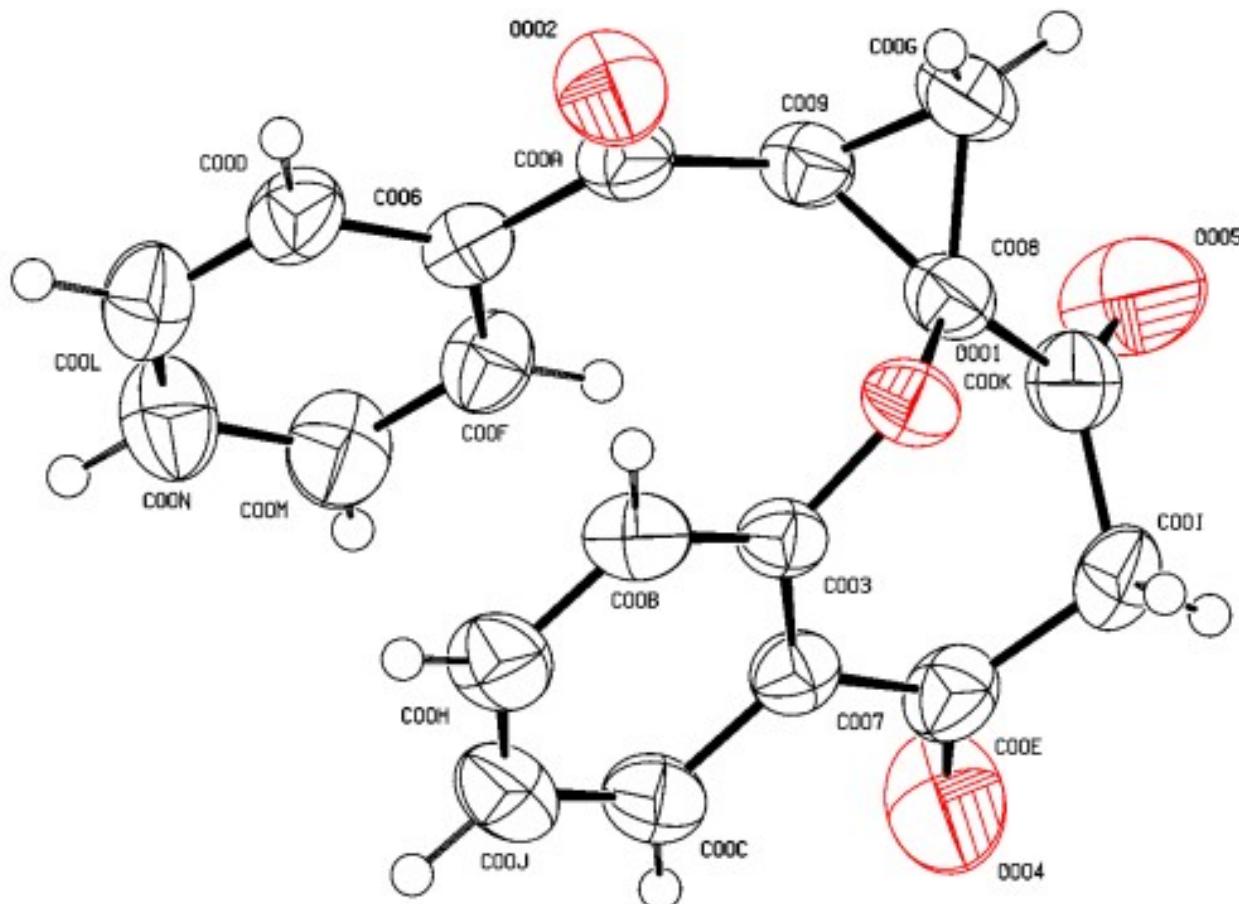


Figure S1. ORTEP diagram of compound **3aa**(CCDC **2233544**), thermal ellipsoids drawn at the 50% probability level.

Table S1. Crystal data for compound 3aa.

Compound	3aa
Empirical formula	C ₁₉ H ₁₄ O ₄
Formula weight	306.32
Temperatute	293 K
Wave length (Å)	0.71073 Å
Crystal system, space group	Triclinic, P -1
<i>a</i> (Å)	<i>a</i> = 8.5674(6) Å
<i>b</i> (Å)	<i>b</i> = 9.4995(7) Å
<i>c</i> (Å)	<i>c</i> = 9.9500(7) Å
α (°)	alpha = 85.100(6) deg.
β (°)	beta = 81.305(6) deg.
γ (°)	gamma = 68.735(7) deg.
Volume (Å ³)	745.57(10) Å ³
Z, Calculated density (mg/m ³)	2, 1.364 Mg/m ³
Absorption coefficient (mm ⁻¹)	0.096 mm ⁻¹
F(000)	320.224
Θ range (deg)	3.7130 to 28.8090 deg.
Limiting indices	-11<=h<=10, -11<=k<=12, -11<=l<=13
Reflections collected / unique	6876 / 3484 [R(int) = 0.0307]
Completeness to Θ = 25.242	99.8 %
Max. and min. transmission	1.00000 and 0.40828
Absorption correction	none
Data / restrains / parameters	3484/ 0 / 209
Goodness-of-fit on F ²	1.0415
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1447
R indices (all data)	R1 = 0.0719, wR2 = 0.1533
Extinction coefficient	n/a
Largest diff. peak and hole (e.A ⁻³)	0.2762 and -0.2872e.A ⁻³
CCDC	2233544

Crystallographic data: Single crystal X-ray structural of compound **5ba** was measured on the SuperNova, Dual, Mo at home/near, Eos- XRD at 150(2) K using graphite monochromated Mo K α radiation ($\lambda\alpha = 0.71073 \text{ \AA}$). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structure was solved by direct methods using SHELXS-97, and refined by full matrix least-squares with SHELXL-97, refining on F^2 . The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. The crystal data are summarized in Table S2. The CCDC number of compound **5ba**: 2239029 can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

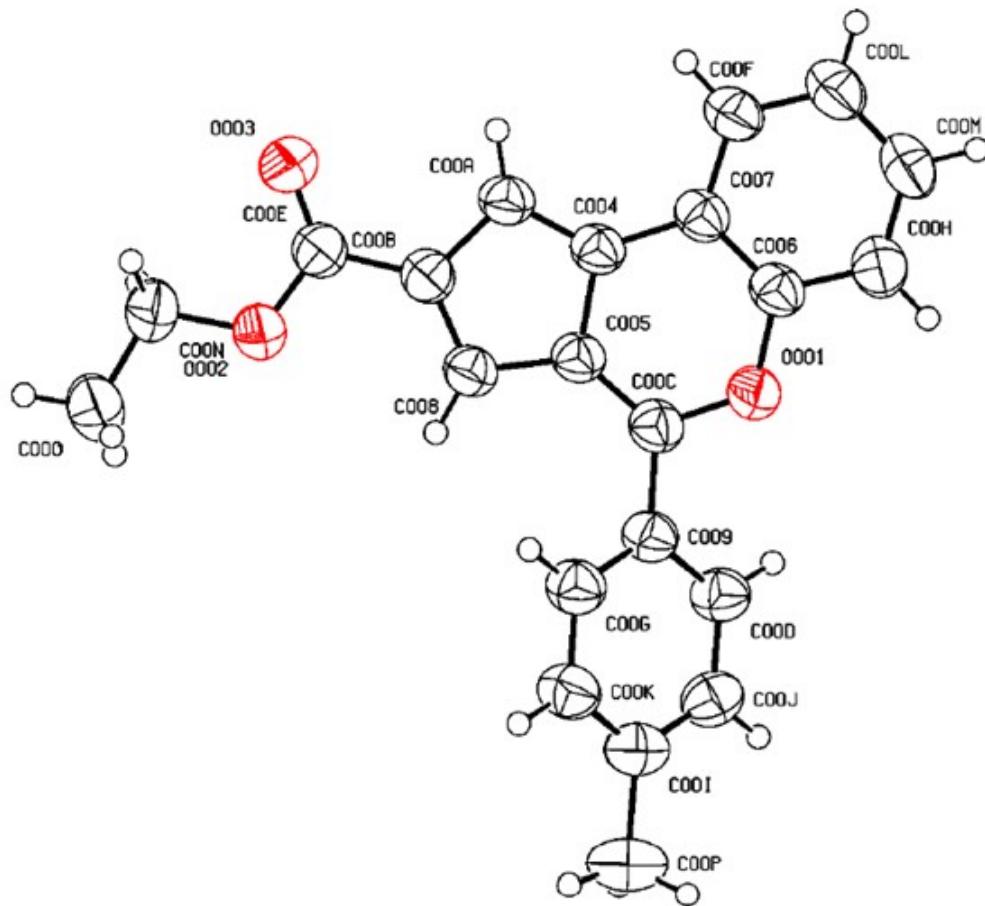
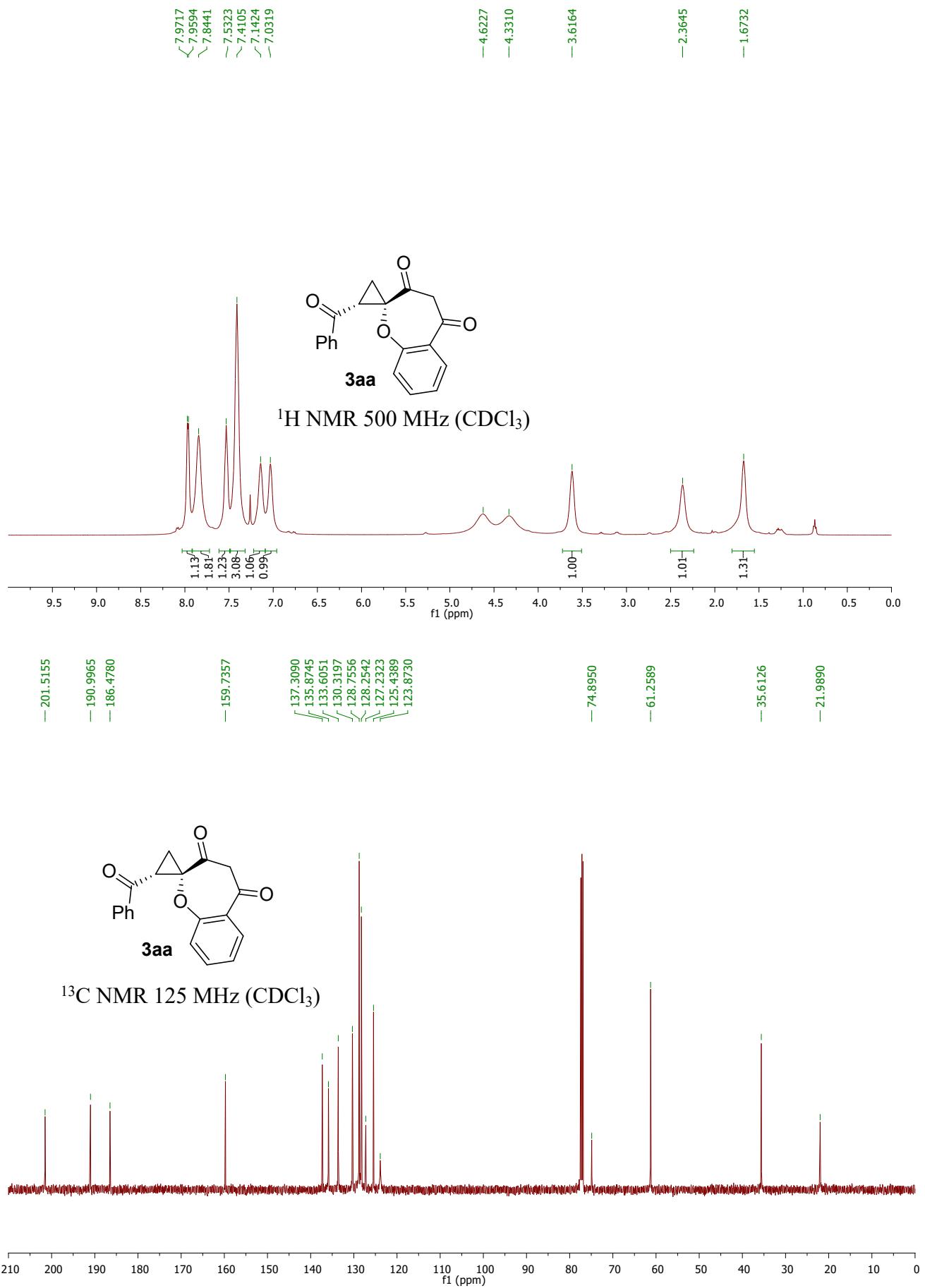


Figure S2 . ORTEP diagram of compound **5ba**, thermal ellipsoids drawn at the 50% probability level.

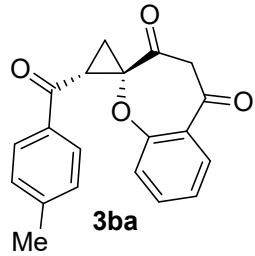
Table S2. Crystal data for compound 5ba.

Compound	5ba
Empirical formula	C ₂₂ H ₁₈ O ₃
Formula weight	330.39
Temperatute	293 K
Wave length (Å)	0.71073 Å
Crystal system, space group	Monoclinic, C 1 2/c 1
<i>a</i> (Å)	<i>a</i> = 11.8421(3) Å
<i>b</i> (Å)	<i>b</i> = 14.4124(5) Å
<i>c</i> (Å)	<i>c</i> = 20.4372(7) Å
α (°)	alpha = 90 deg.
β (°)	beta = 101.814(3) deg.
γ (°)	gamma = 90 deg.
Volume (Å ³)	3414.19(19) Å ³
Z, Calculated density (mg/m ³)	8, 1.286 Mg/m ³
Absorption coefficient (mm ⁻¹)	0.680 mm ⁻¹
F(000)	1396.638
Θ range (deg)	4.42 to 71.66 deg.
Limiting indices	-14<=h<=14, -12<=k<=17, -23<=l<=25
Reflections collected / unique	12340 / 3284 [R(int) = 0.0996]
Completeness to Θ = 25.242	97.9 %
Max. and min. transmission	1.00000 and 0.25768
Absorption correction	none
Data / restrains / parameters	2308/ 0 / 229
Goodness-of-fit on F ²	1.0358
Final R indices [I>2sigma(I)]	R1 = 0.0690, wR2 = 0.2176
R indices (all data)	R1 = 0.0876, wR2 = 0.1824
Extinction coefficient	n/a
Largest diff. peak and hole (e.A ⁻³)	0.3462 and -0.2904 e.A ⁻³
CCDC	2239029

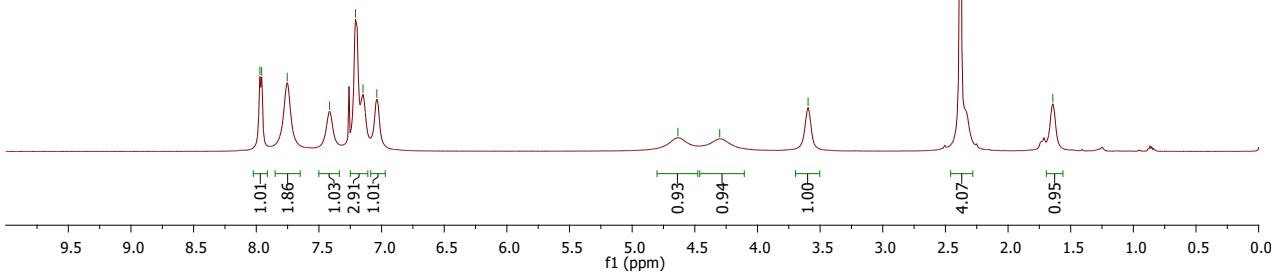


↗ 7.9708
 ↗ 7.9668
 ↗ 7.7530
 ↗ 7.4151
 ↗ 7.2082
 ↗ 7.1481
 ↗ 7.0380

— 4.6351
 — 4.3012
 — 3.5961
 — 2.3797
 — 1.6424



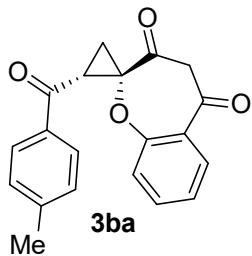
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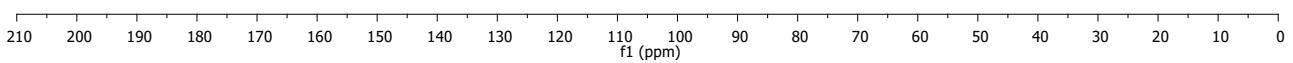
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 — 186.5358

— 159.8095
 — 144.5878
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 — 128.4155
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 — 125.3952
 — 123.8673

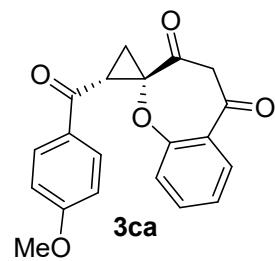
— 74.8294
 — 61.2989
 — 35.5825
 ↗ 21.7825



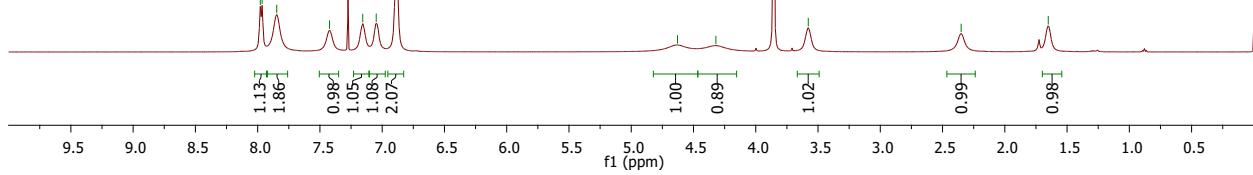
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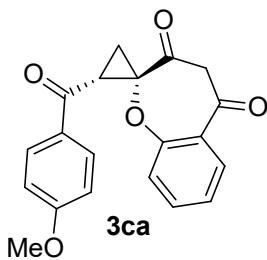
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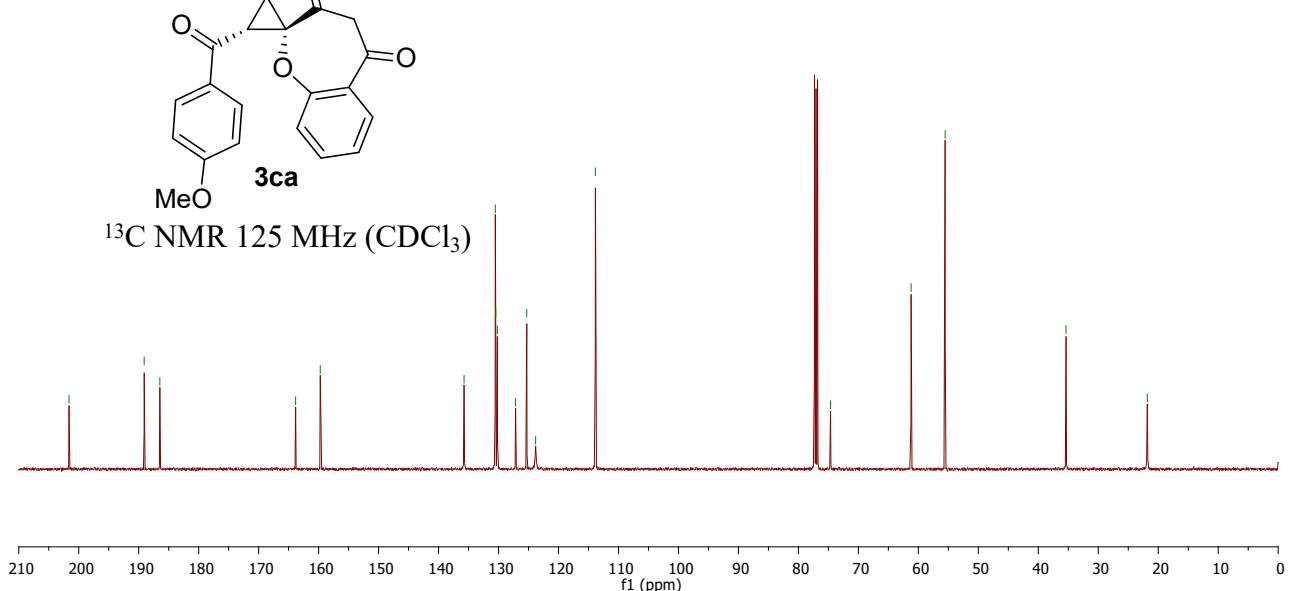
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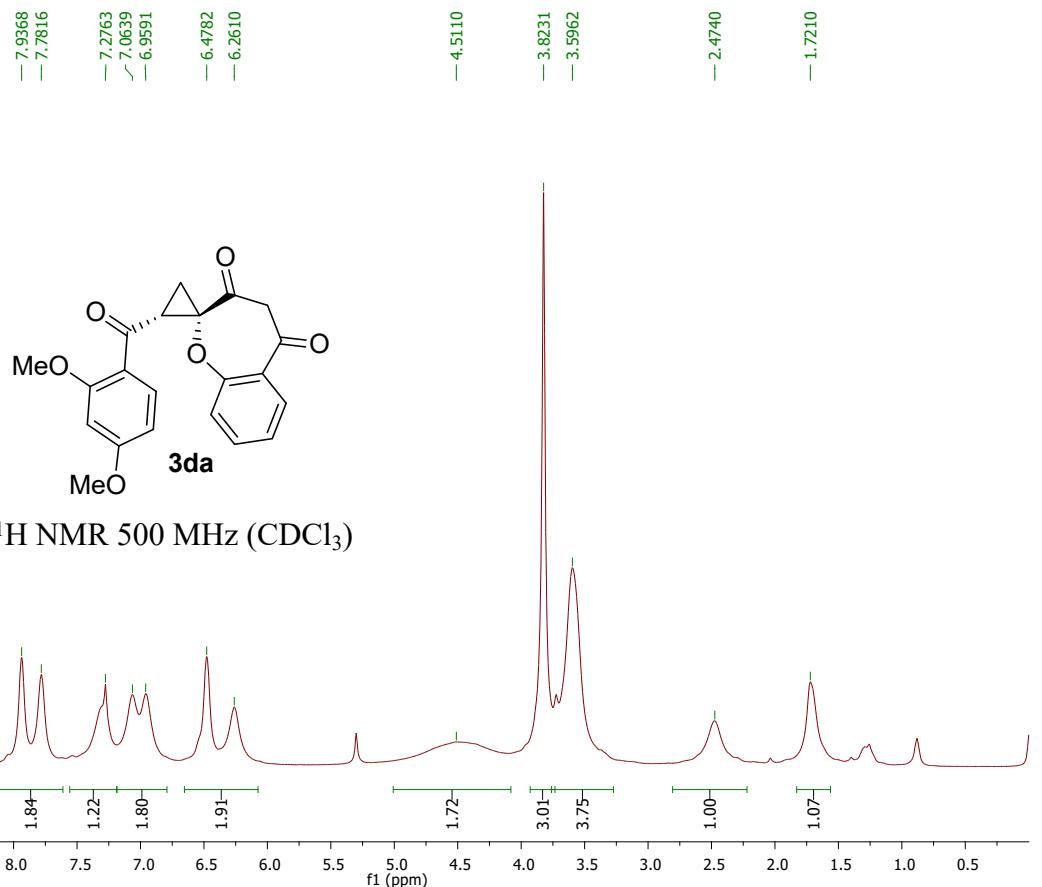


— 201.6208
 — 189.0850
 — 186.4724
 — 163.8342
 — 159.7250
 — 135.7482
 — 130.5366
 — 130.4560
 — 130.1947
 — 127.1616
 — 125.2926
 — 123.8135
 — 113.8485
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 — 21.8198

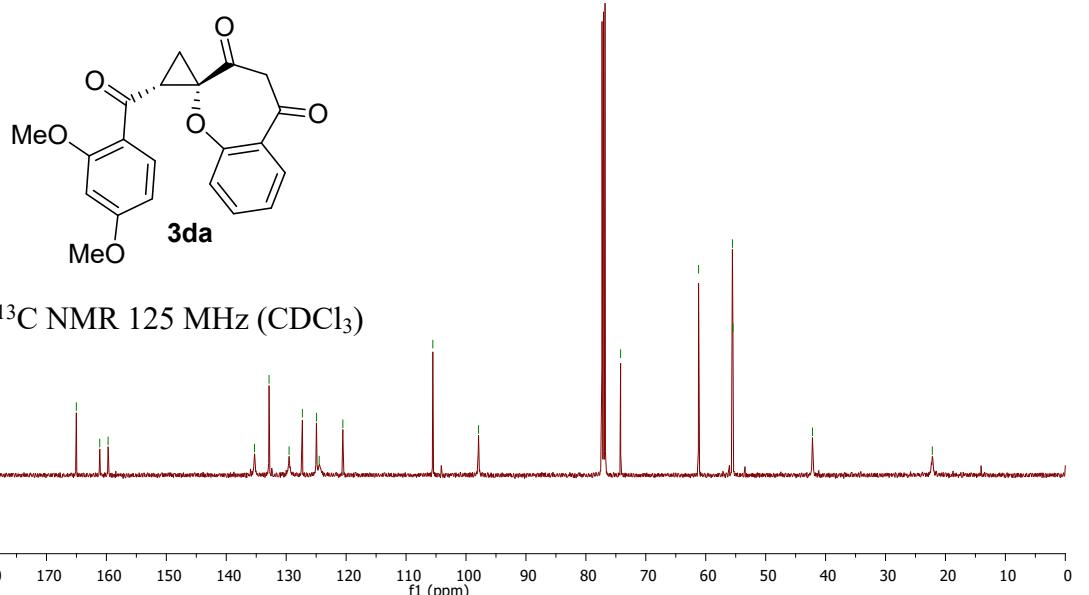


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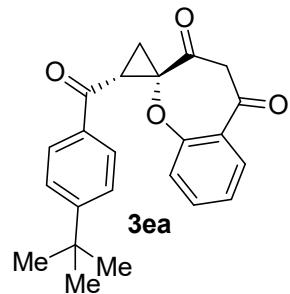




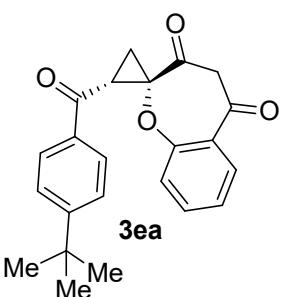
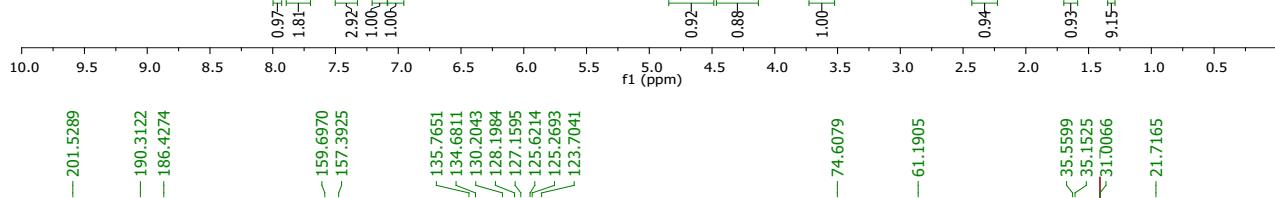
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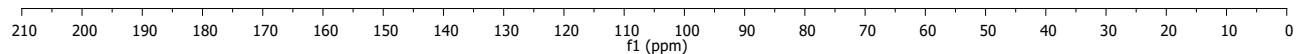
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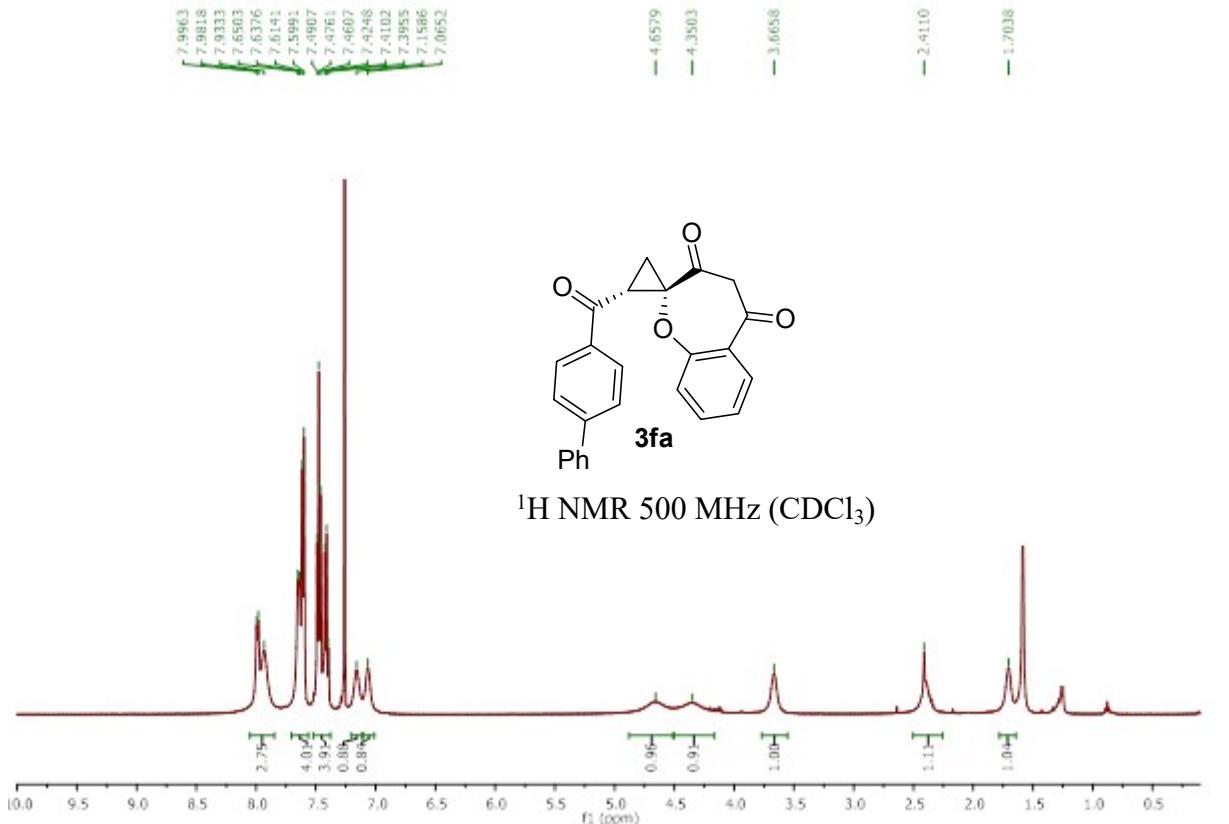


¹H NMR 500 MHz (CDCl_3)



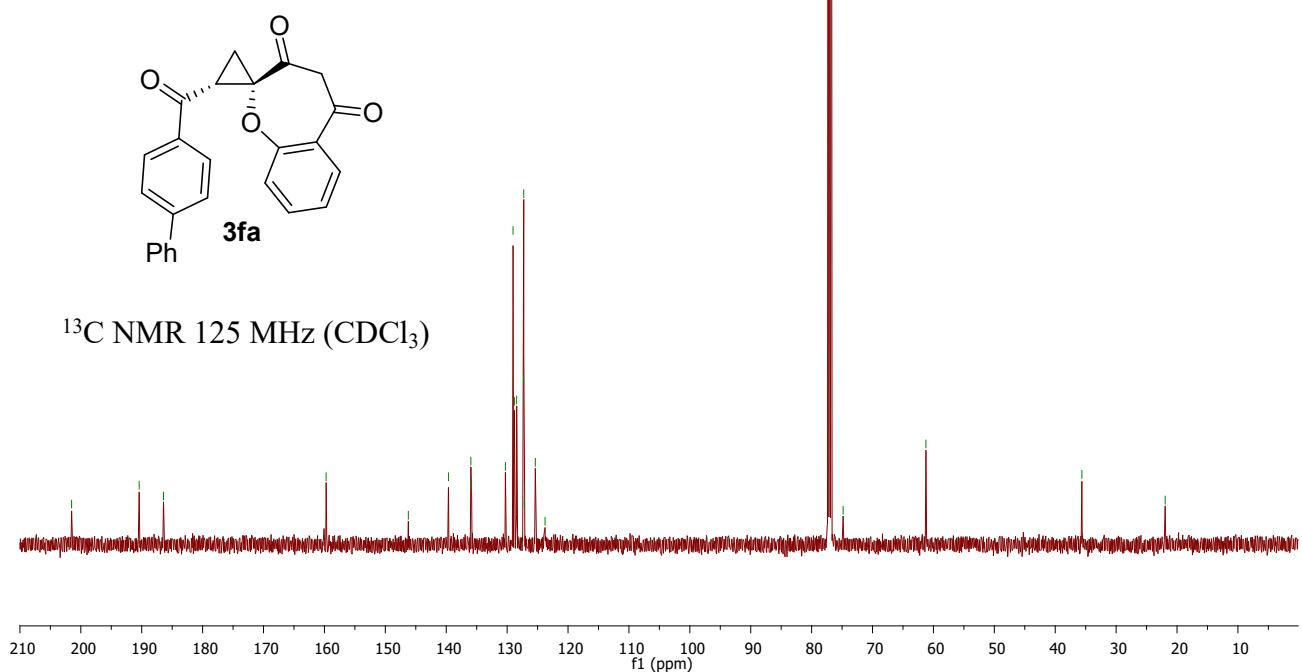
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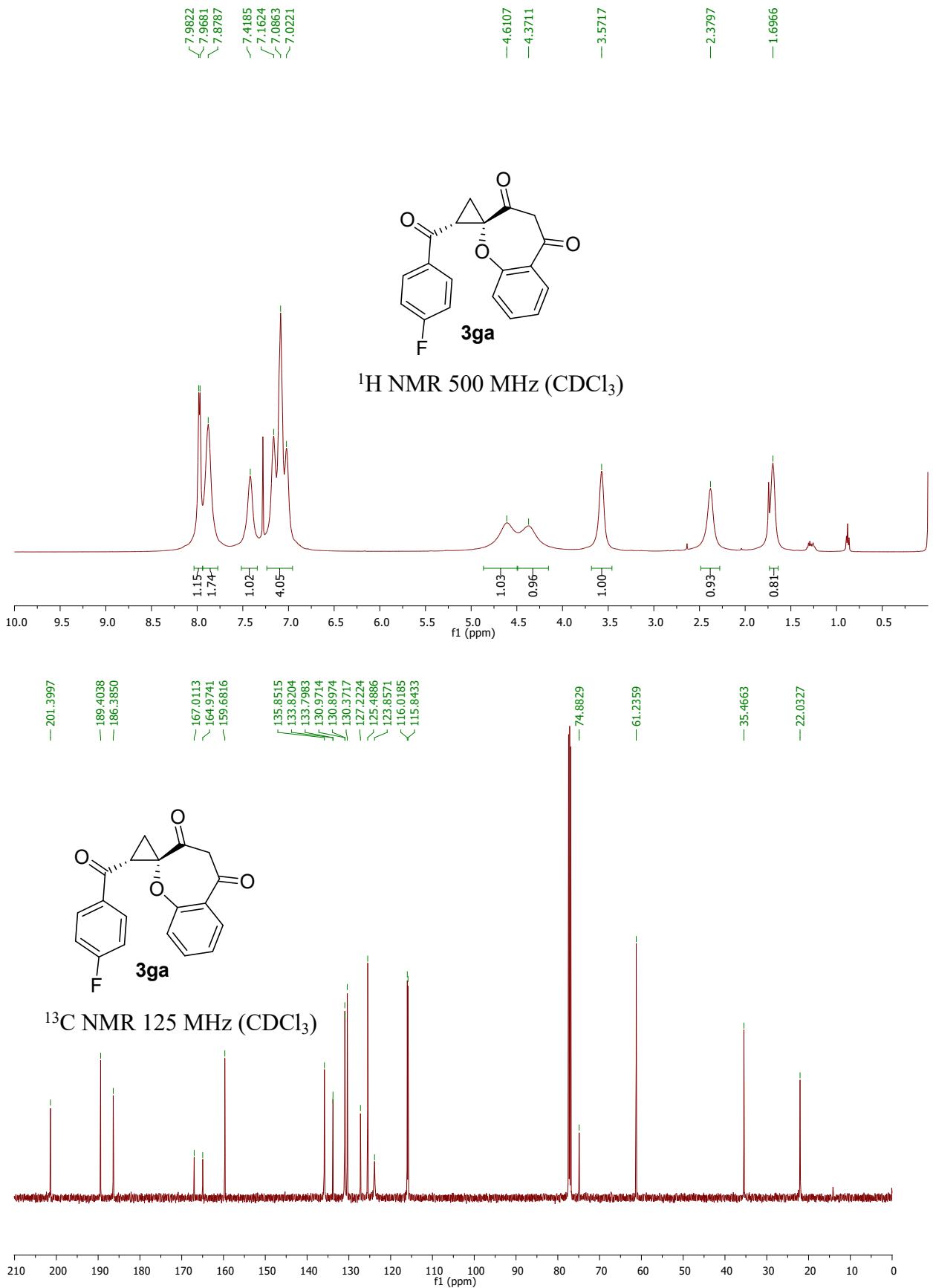




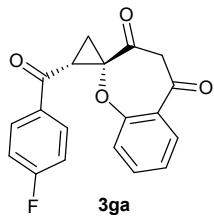
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— 159.7183
— 146.2219
— 139.6318
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— 129.0260
— 128.8077
— 128.4317
— 127.2960
— 127.2702
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— 123.7719

— 4.6779
— 4.3033
— 3.9058
— 3.8548
— 3.8458



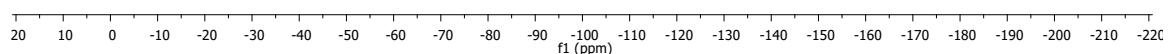


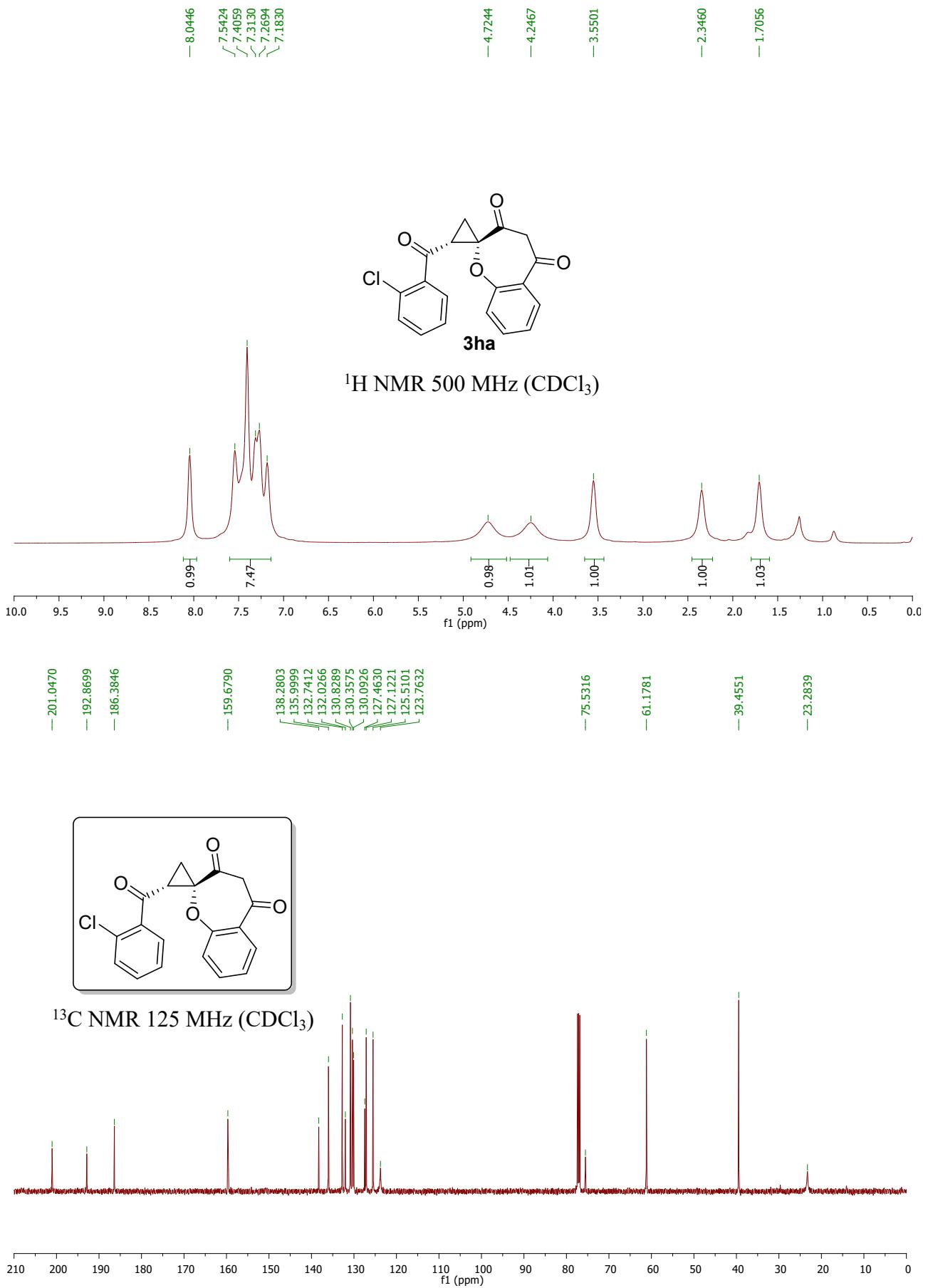
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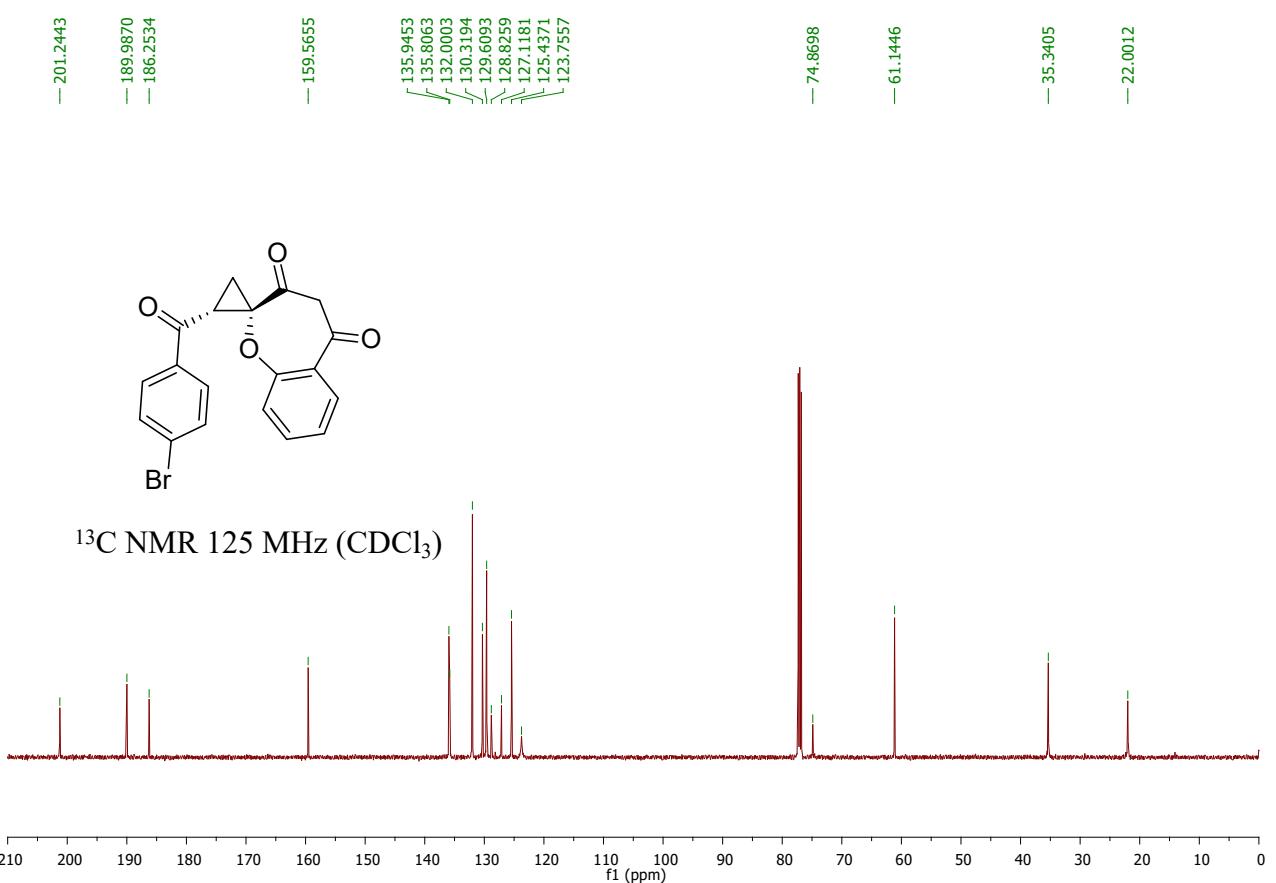
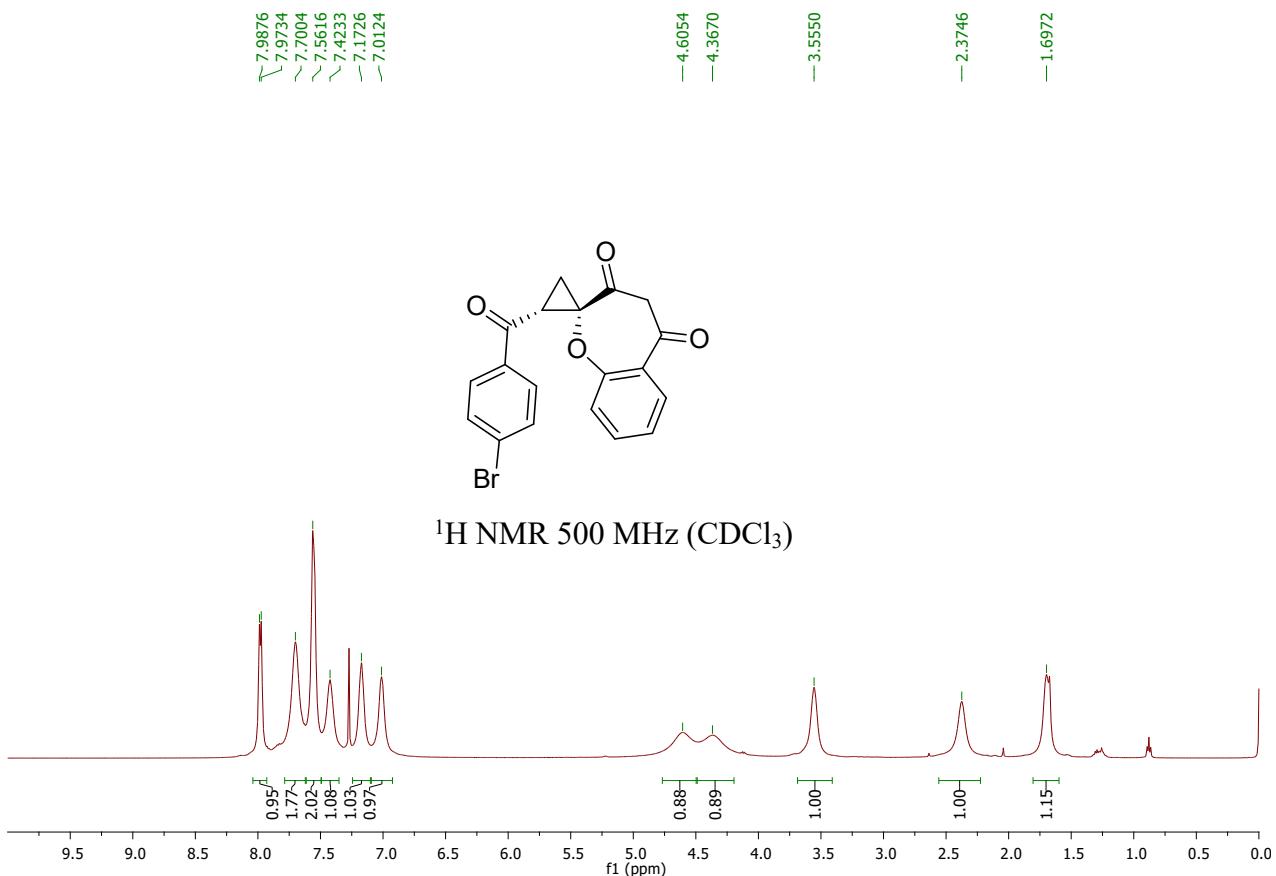


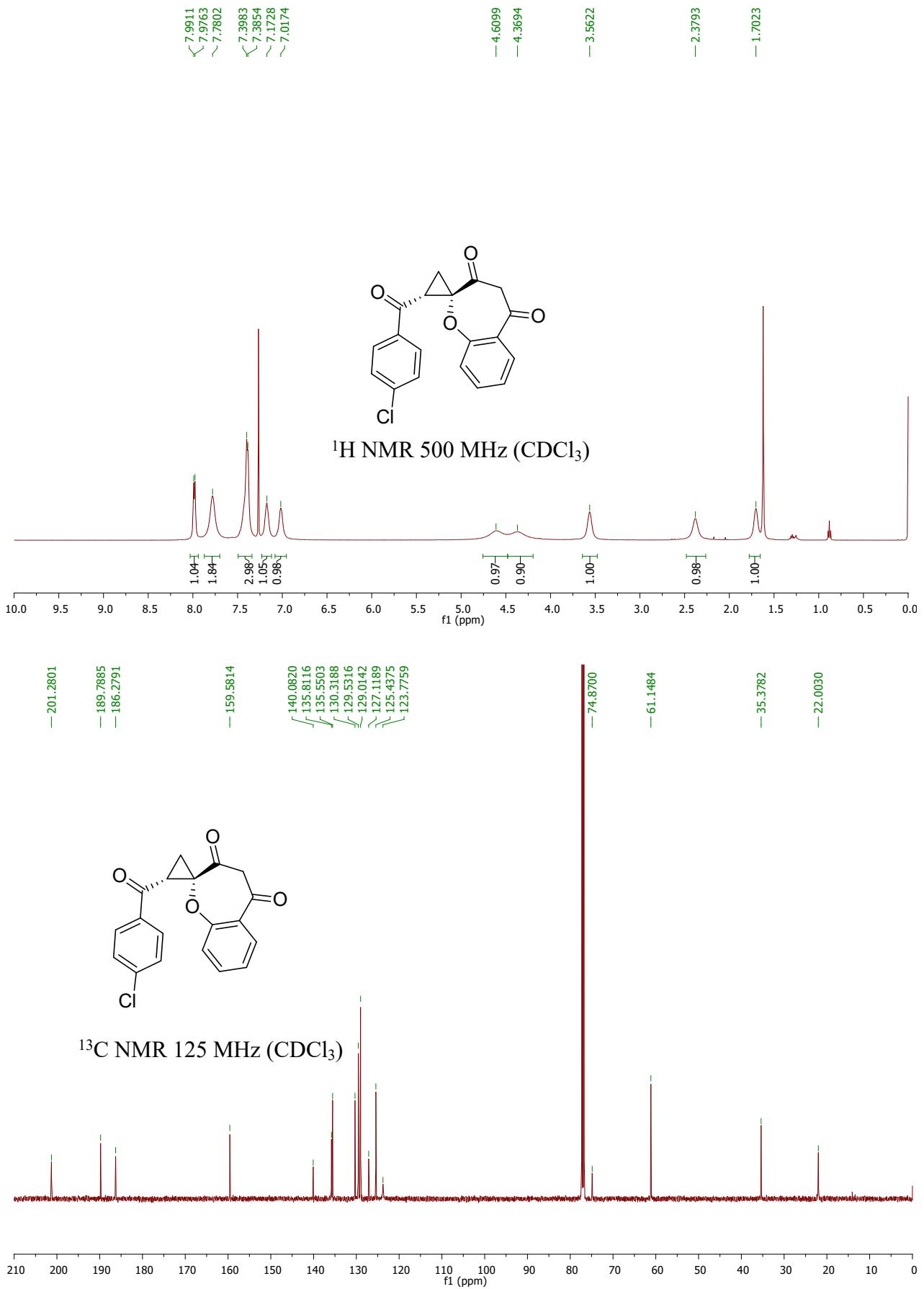
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¹⁹F NMR 470 MHz (CDCl₃)

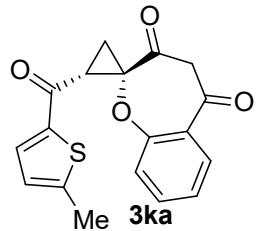




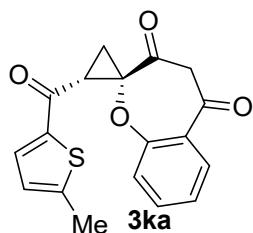
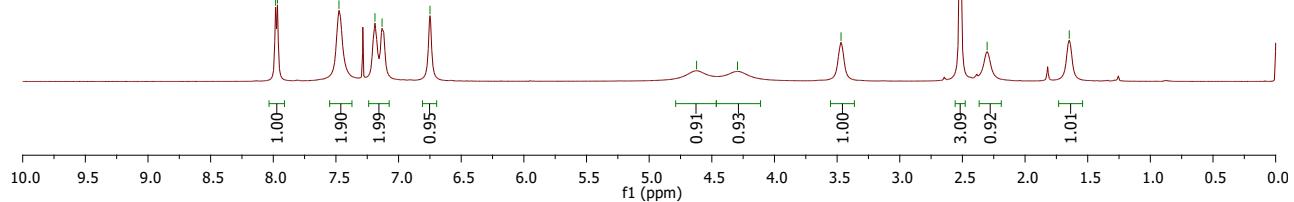




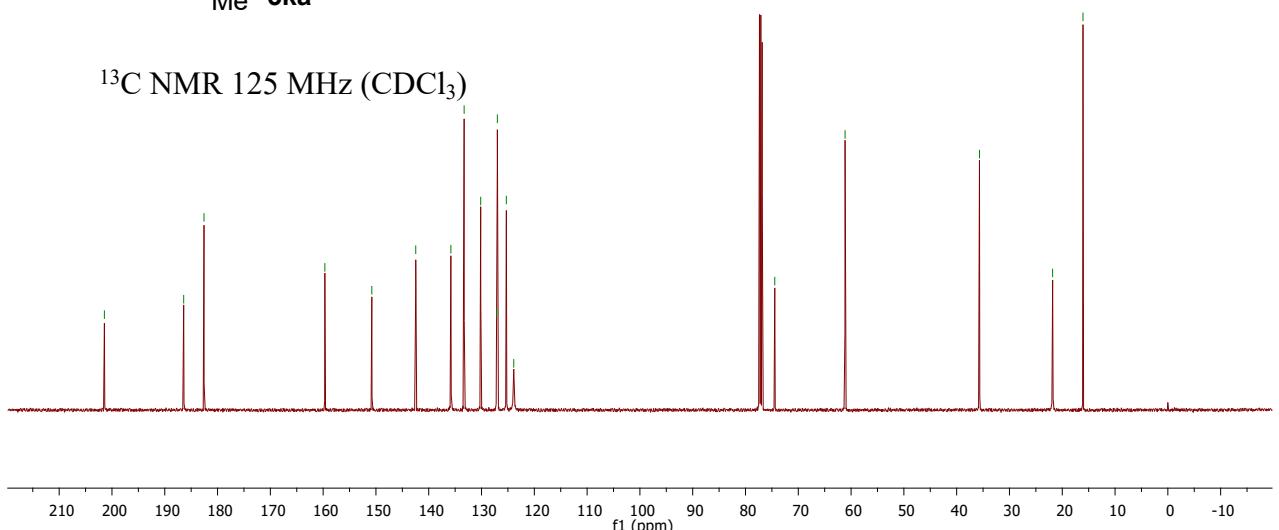
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 ∫ 7.1886
 ∫ 7.1319
 — 6.7493

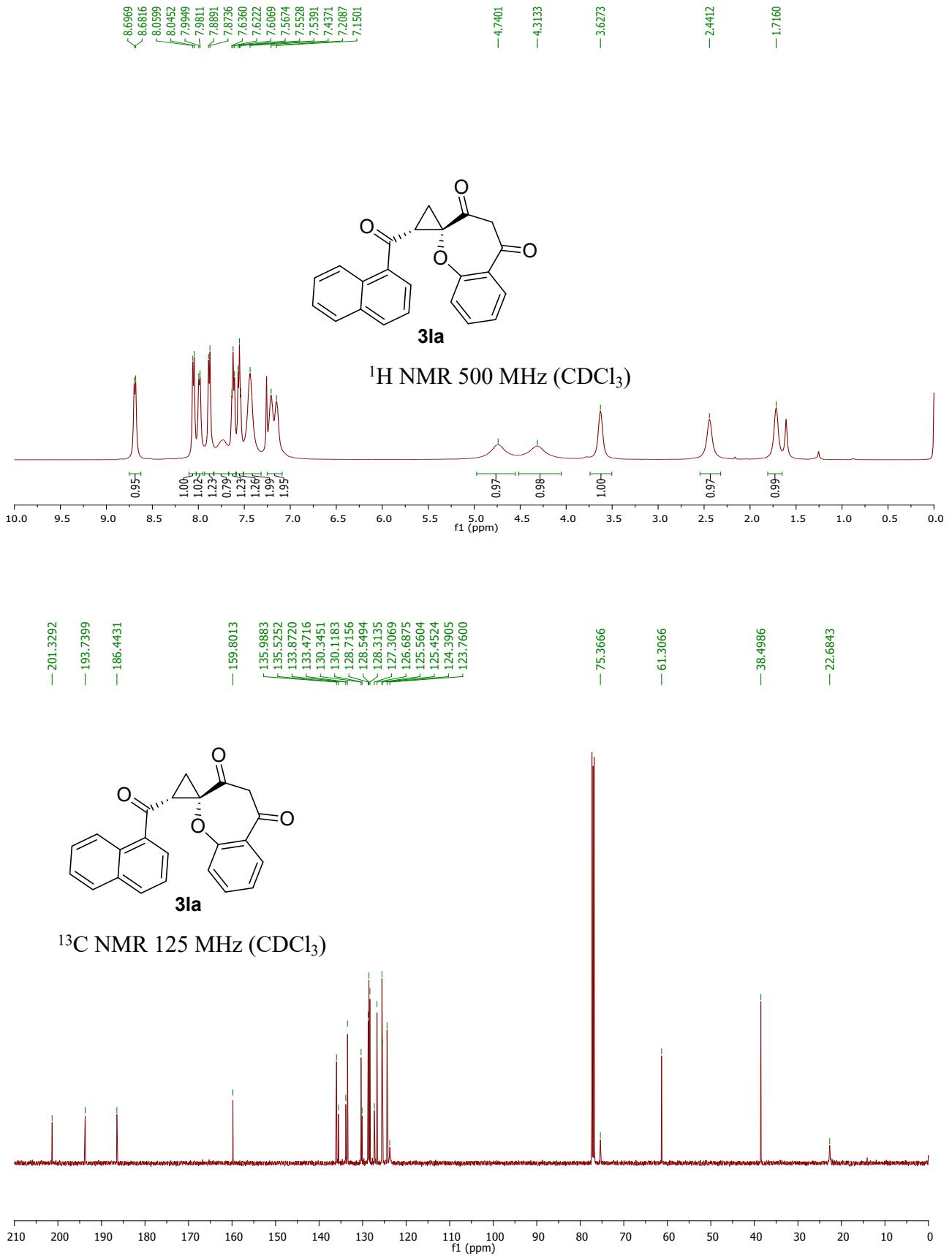


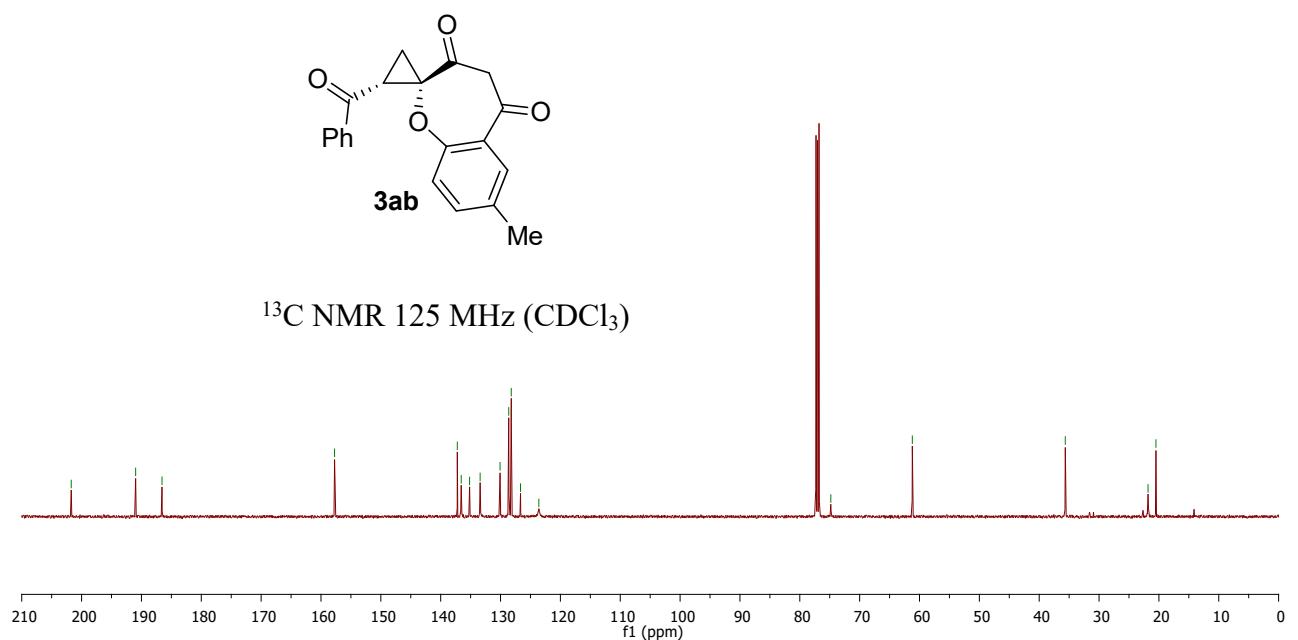
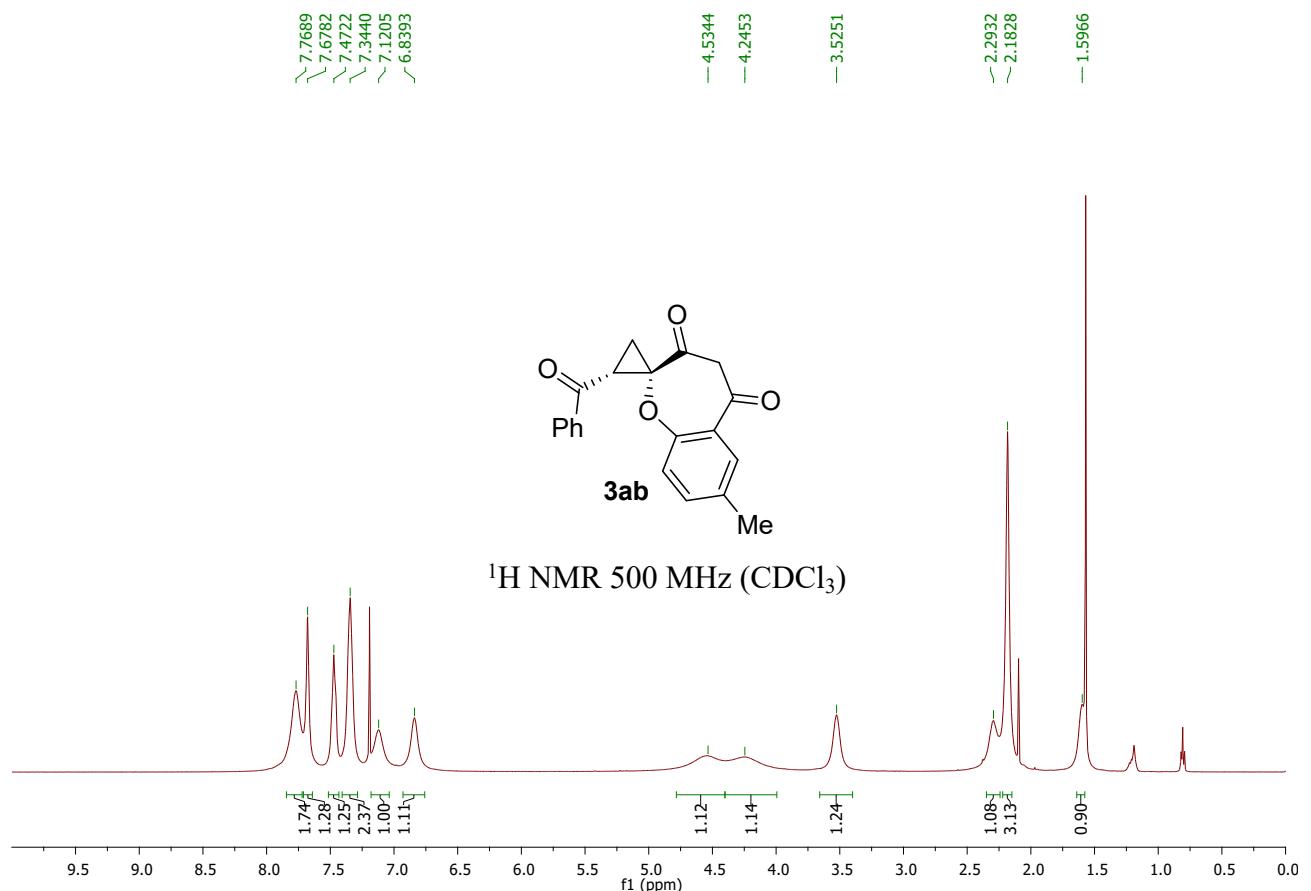
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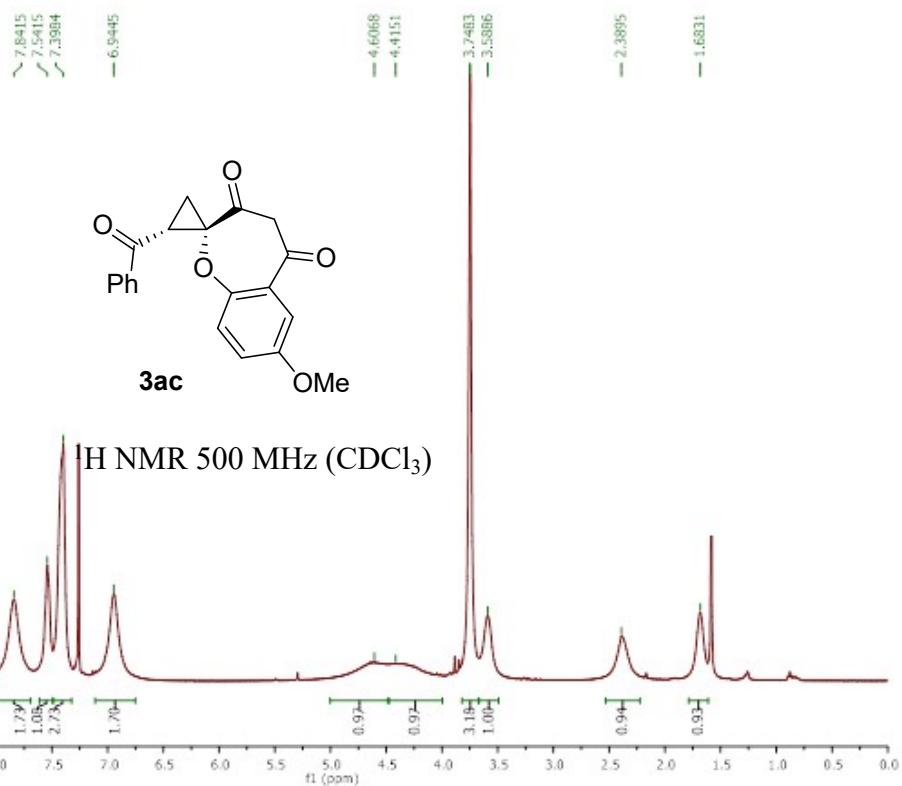


¹³C NMR 125 MHz (CDCl₃)









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— 153.9141

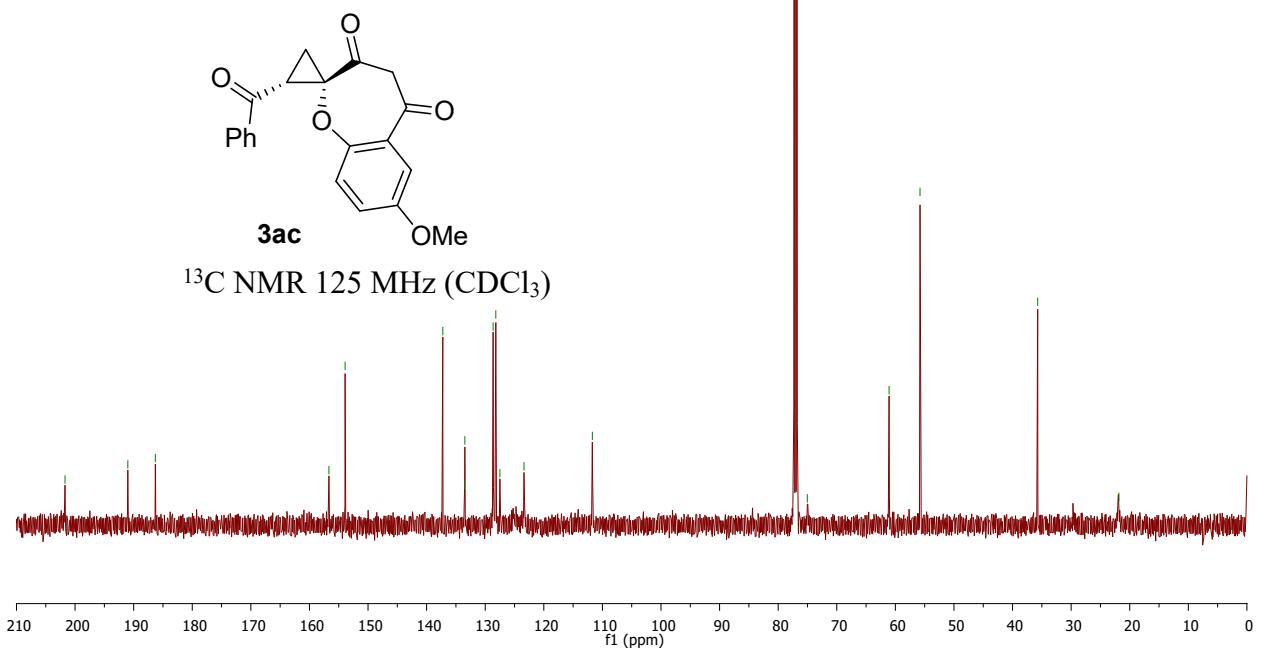
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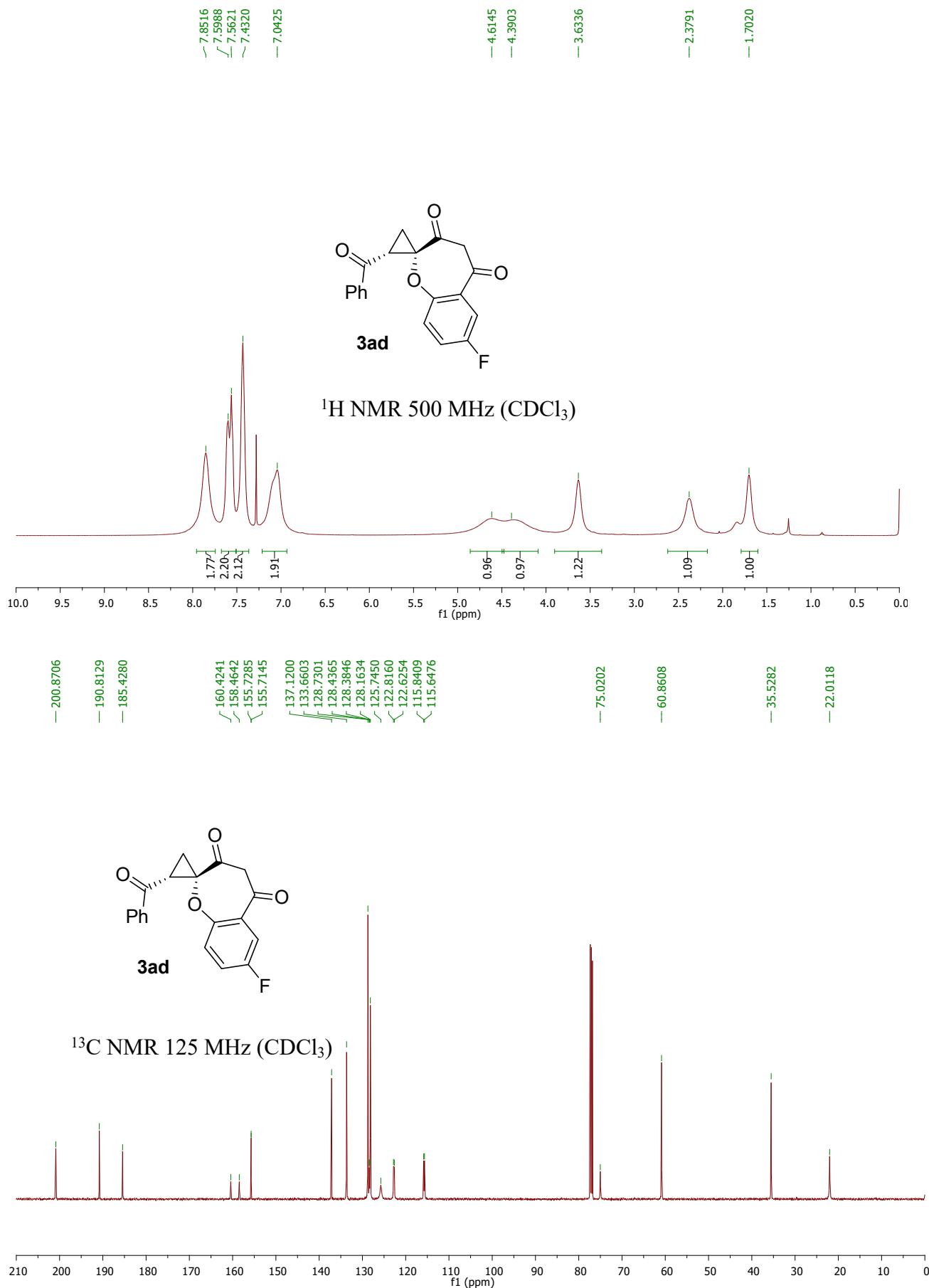
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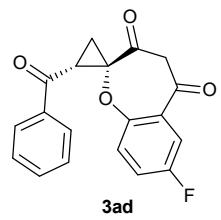
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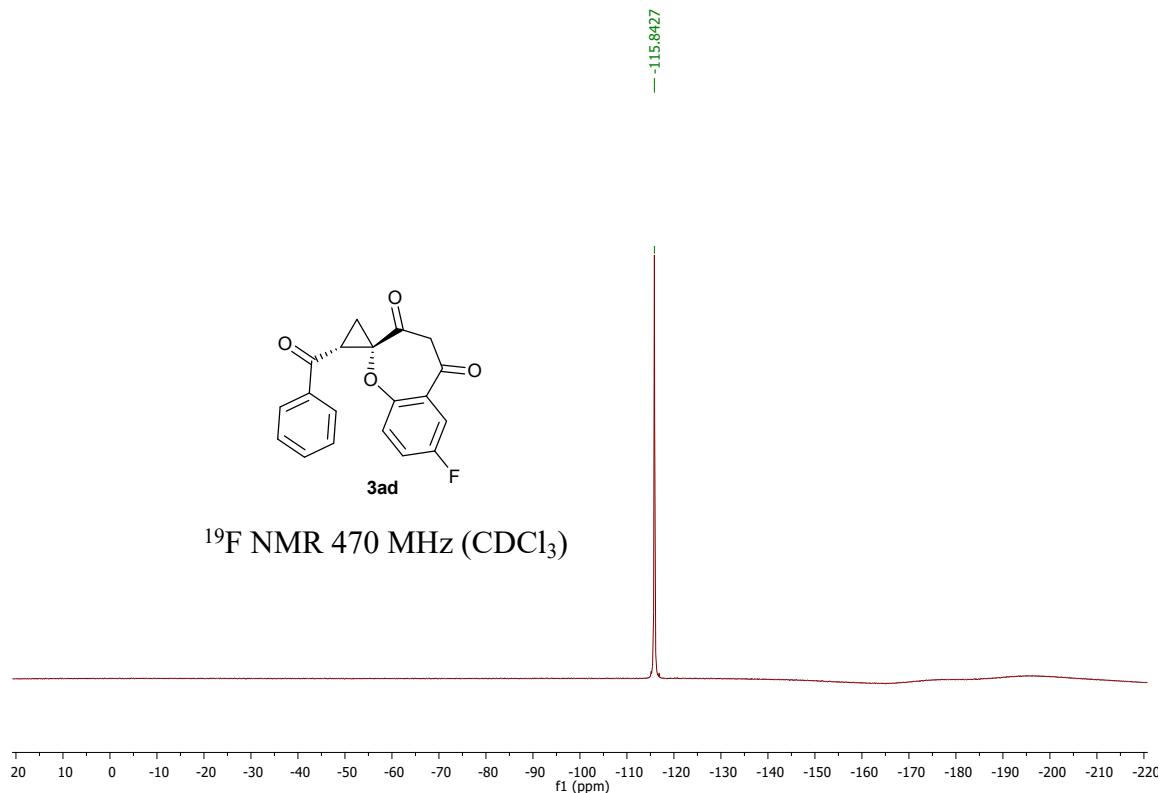
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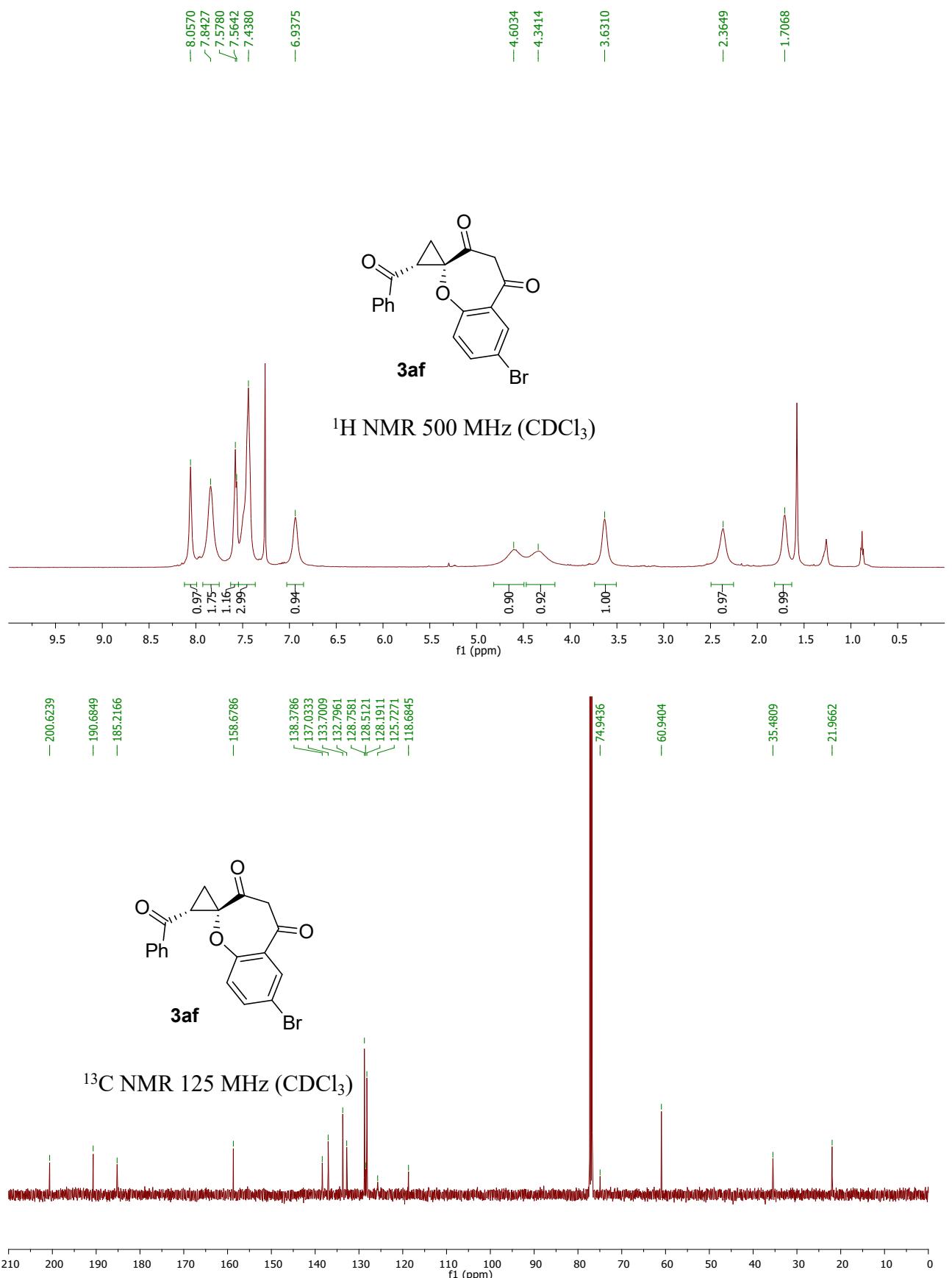


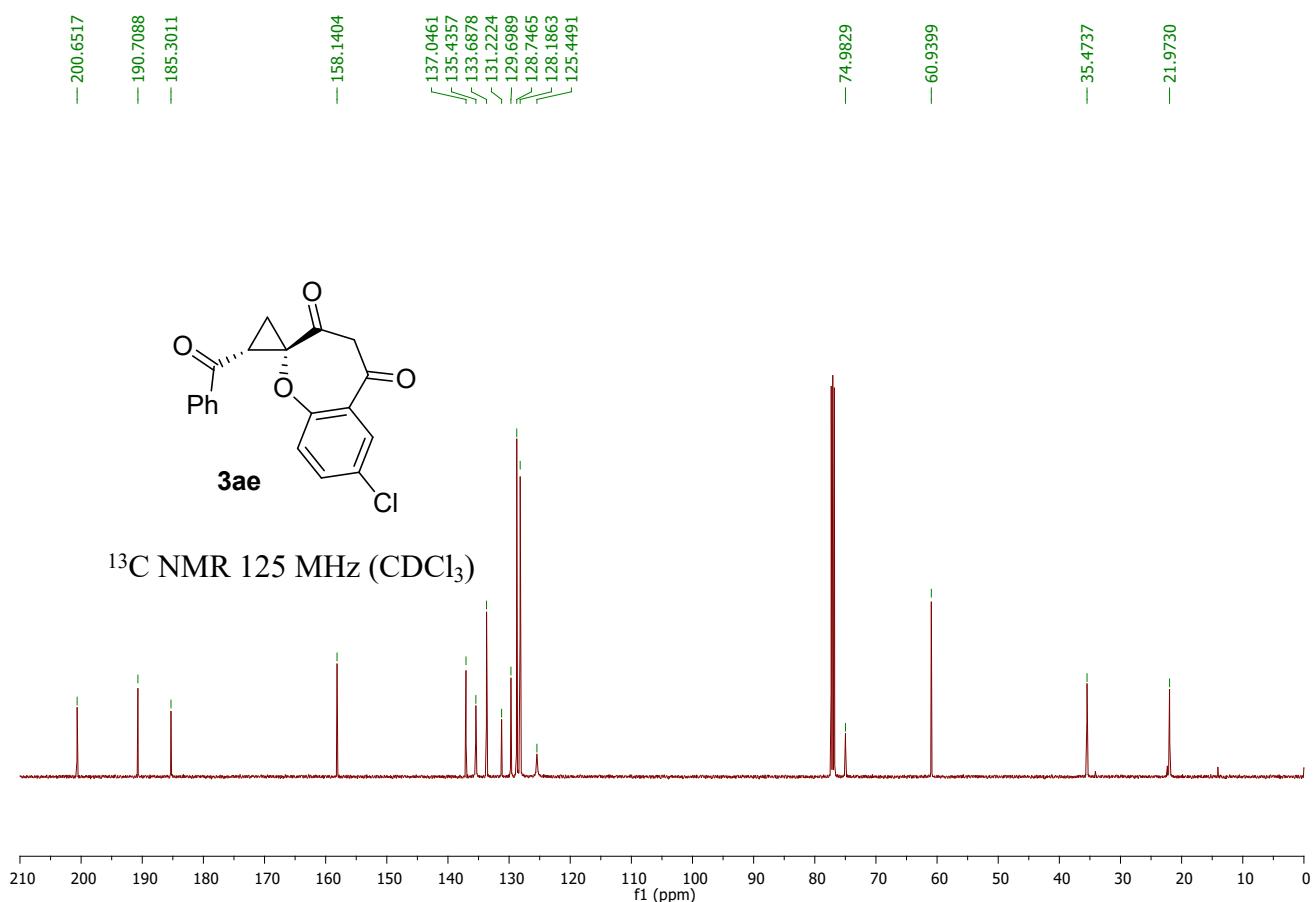
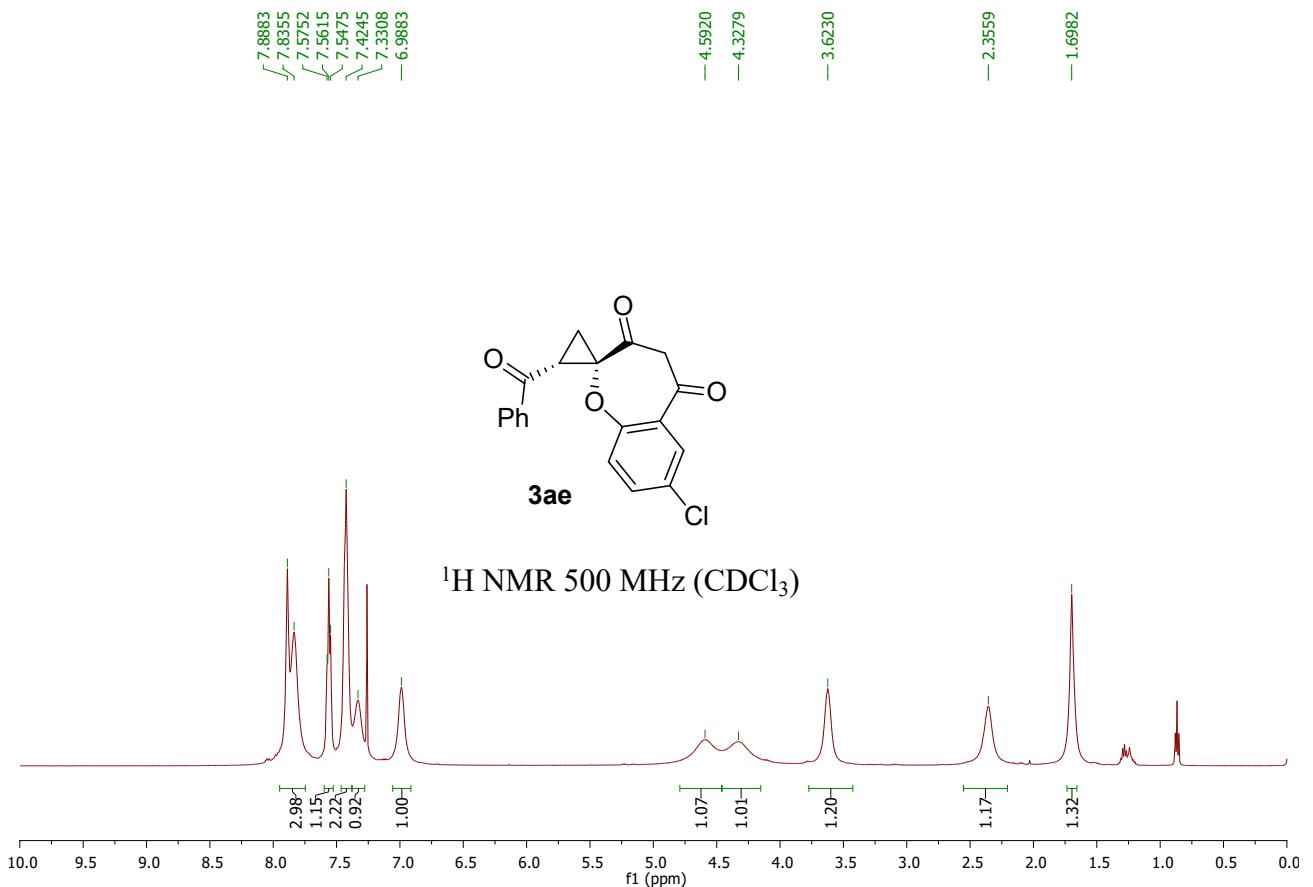


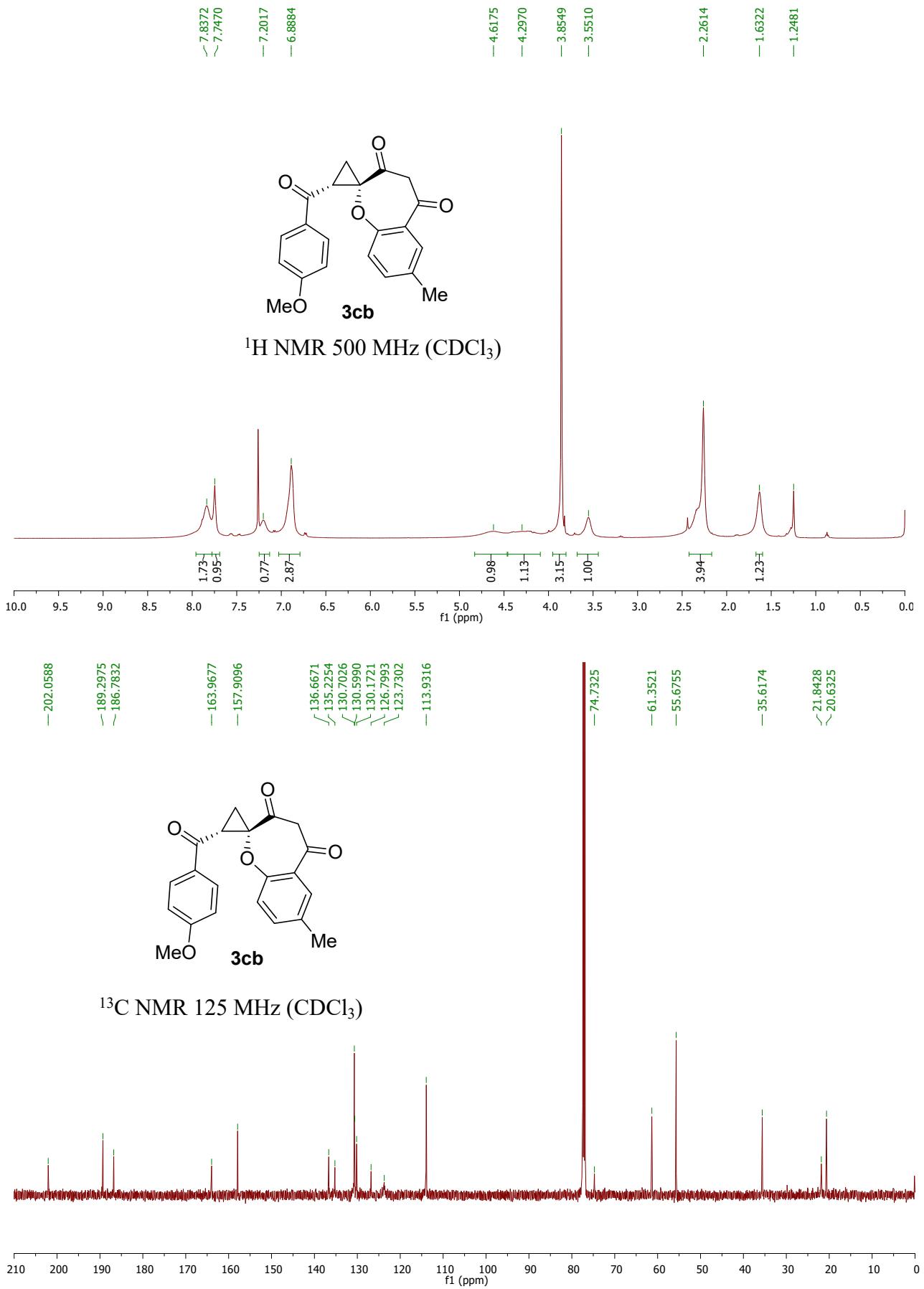


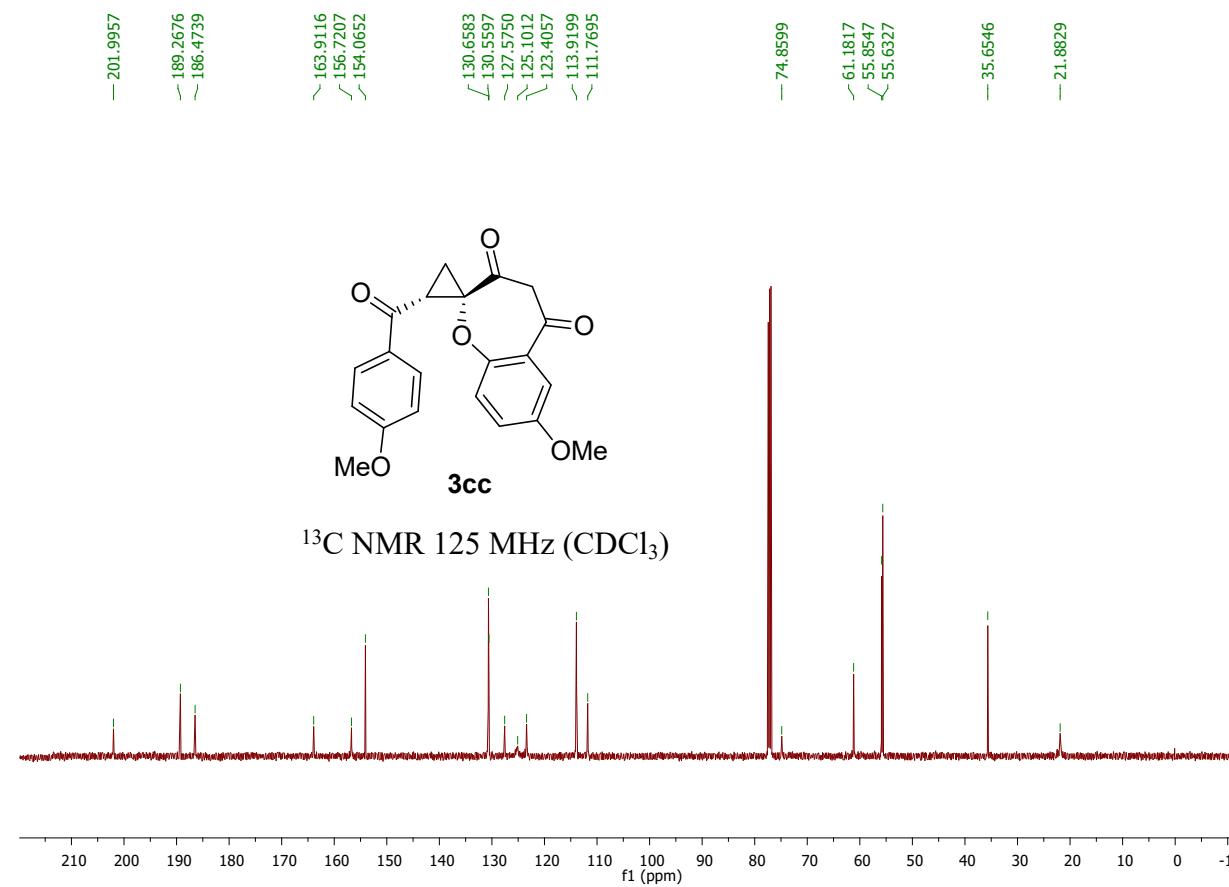
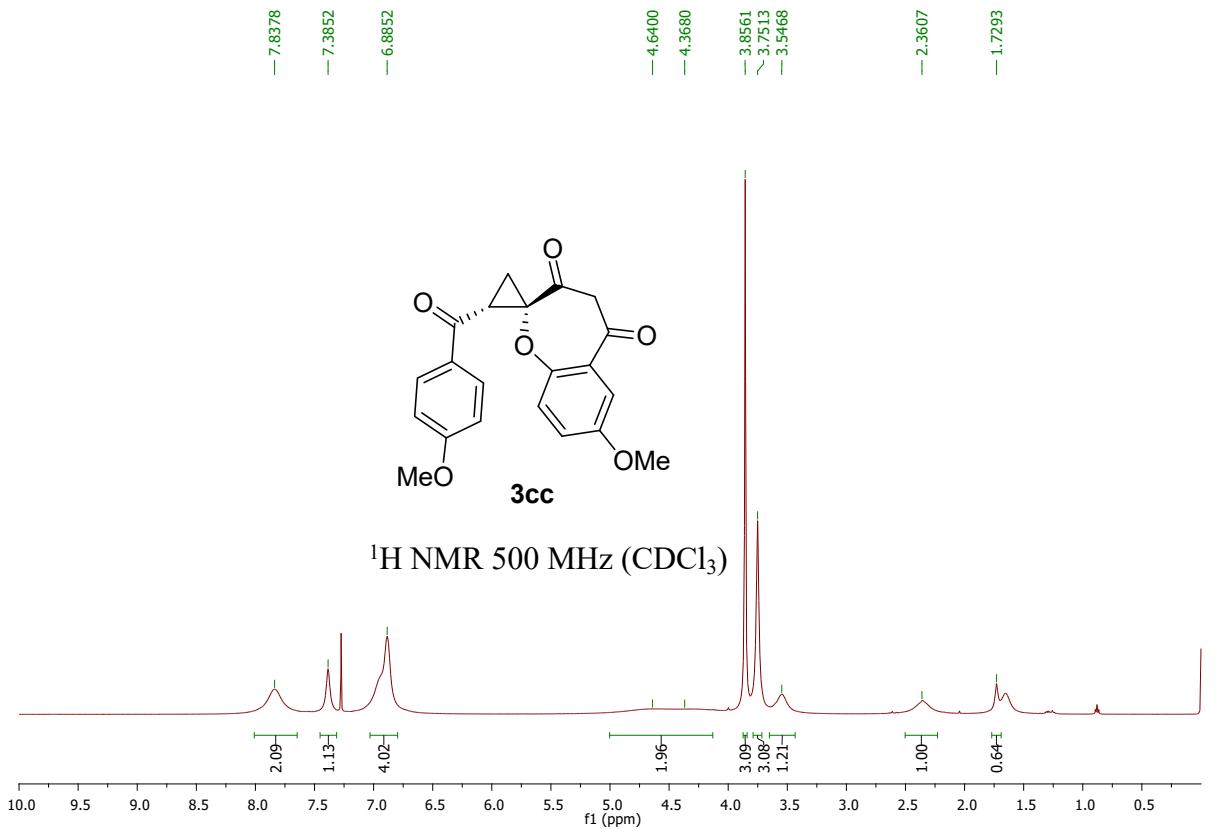
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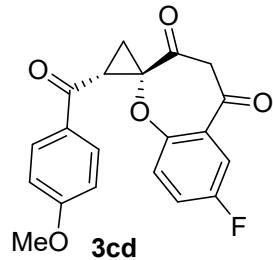




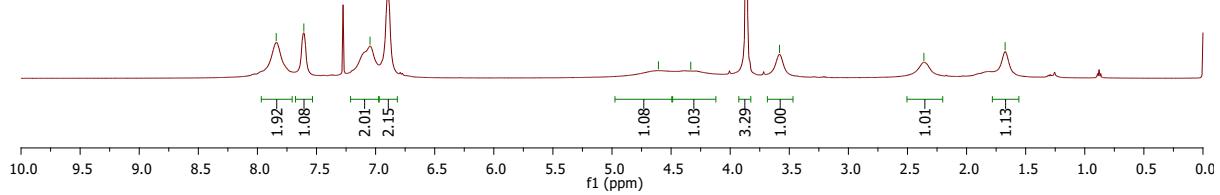




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— 7.6073
— 7.0471
— 6.8983



^1H NMR 500 MHz (CDCl_3)

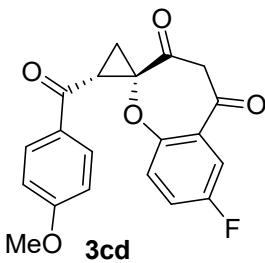


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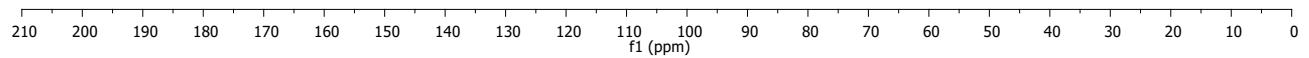
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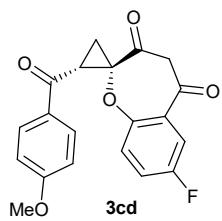
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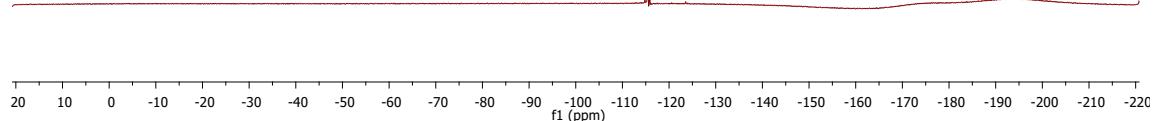
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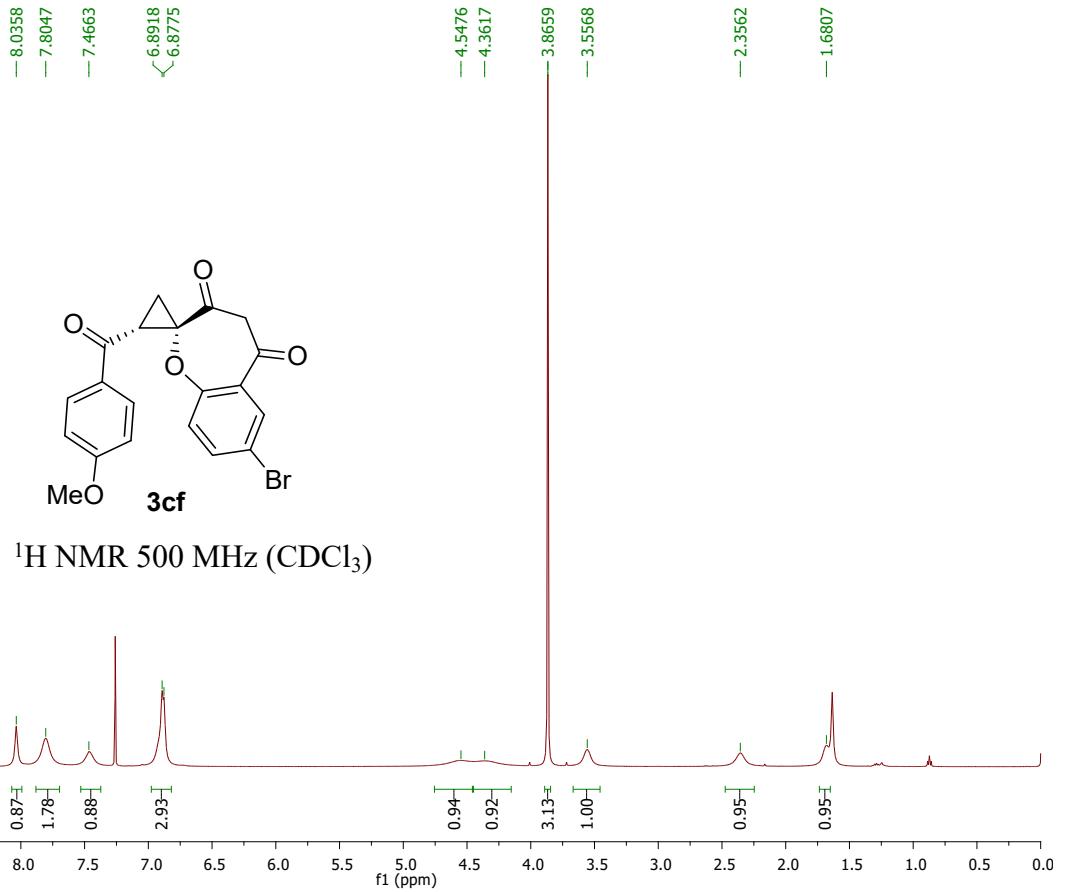


— -115.5159

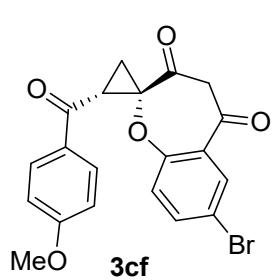


^{19}F NMR 470 MHz (CDCl_3)

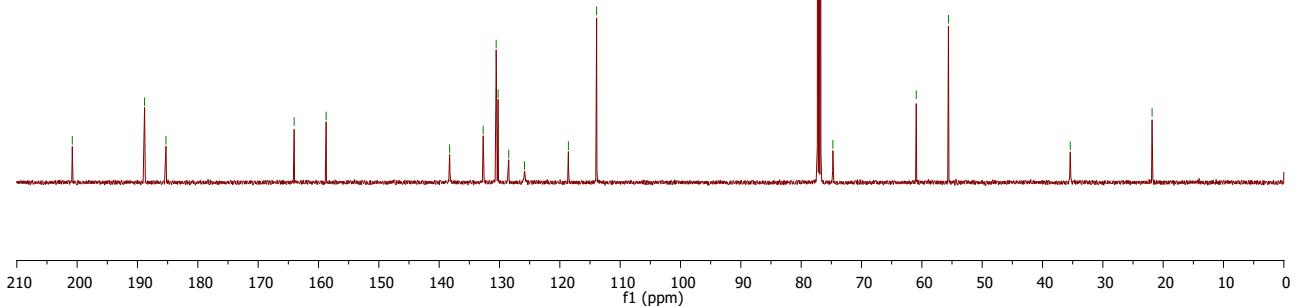




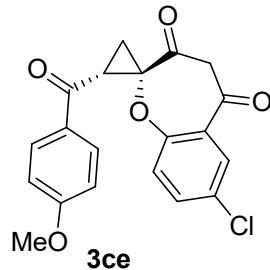
— 200.8061
 — 188.8323
 — 185.2805
 — 164.0323
 — 158.7316
 ✓ 138.2669
 ✓ 132.7067
 ✓ 130.5518
 ✓ 130.2300
 ✓ 128.4677
 ✓ 125.8598
 — 118.5801
 — 113.9023
 — 74.7496
 — 60.9308
 — 55.5915
 — 35.4041
 — 21.8401



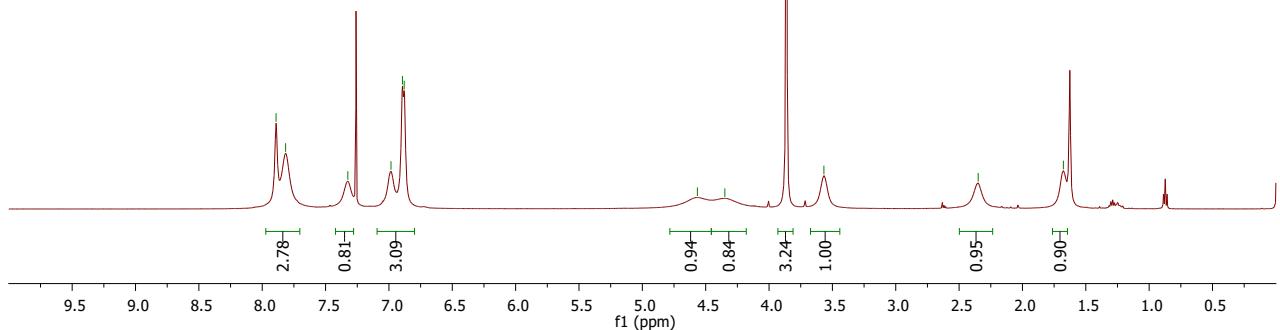
¹³C NMR 125 MHz (CDCl₃)



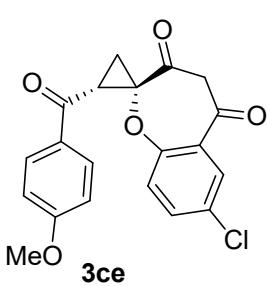
— 7.8907
 — 7.8154
 — 7.3244
 — 6.9838
 — 6.8932
 — 6.8795



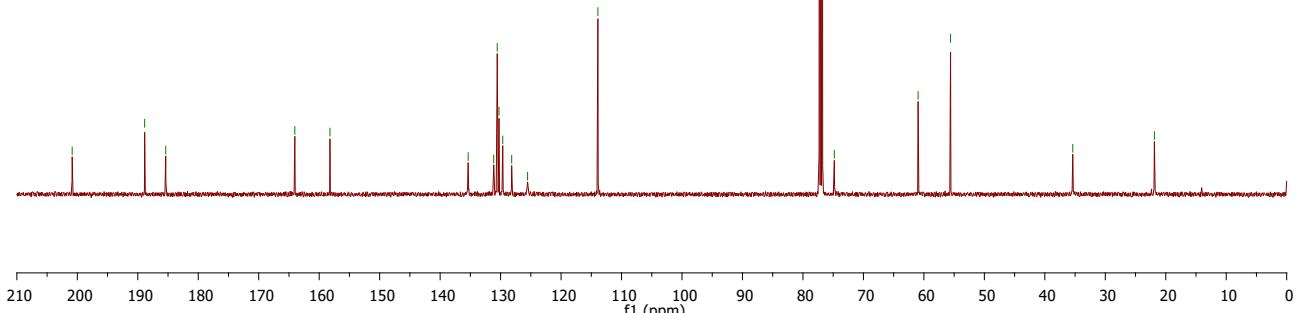
^1H NMR 500 MHz (CDCl_3)

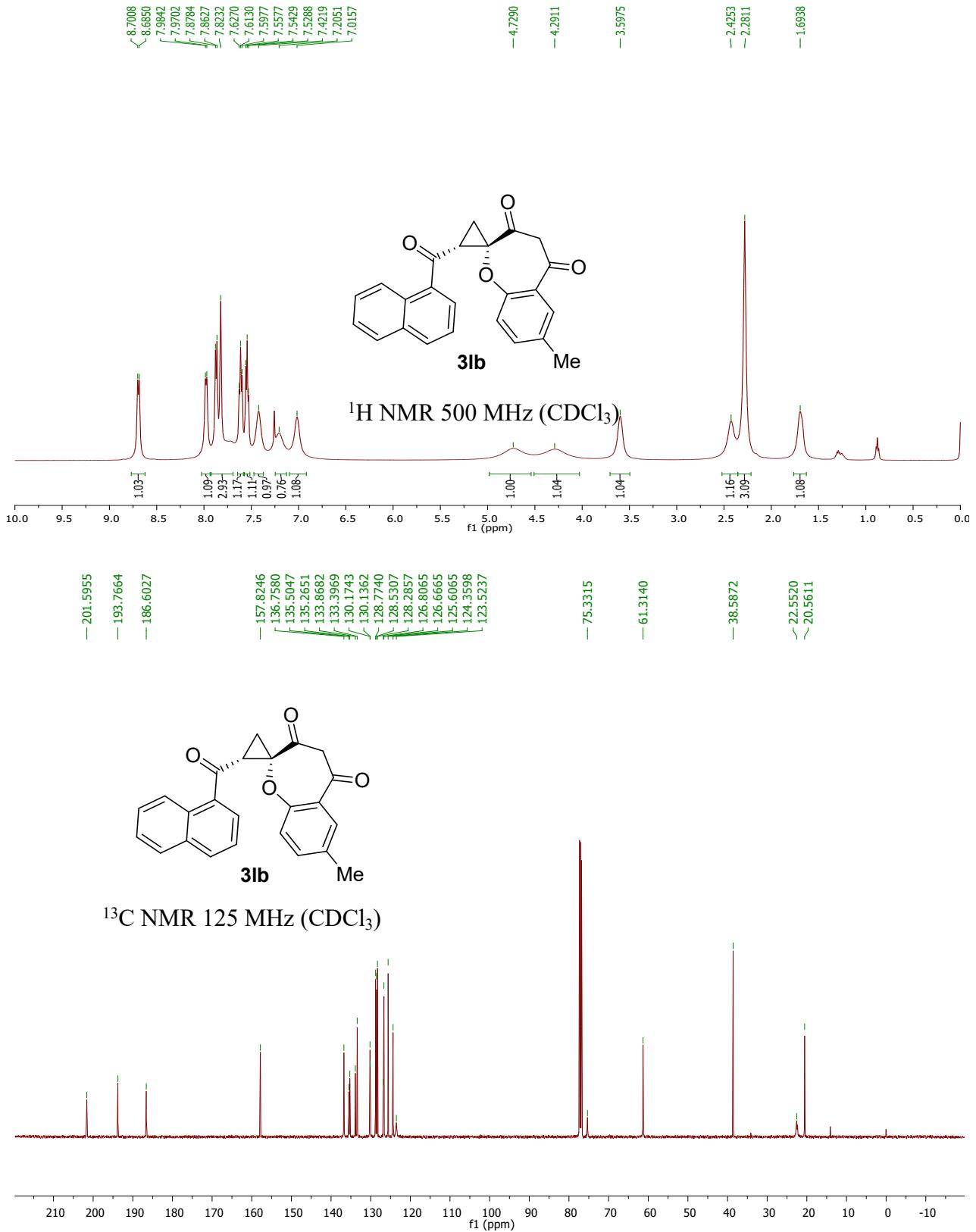


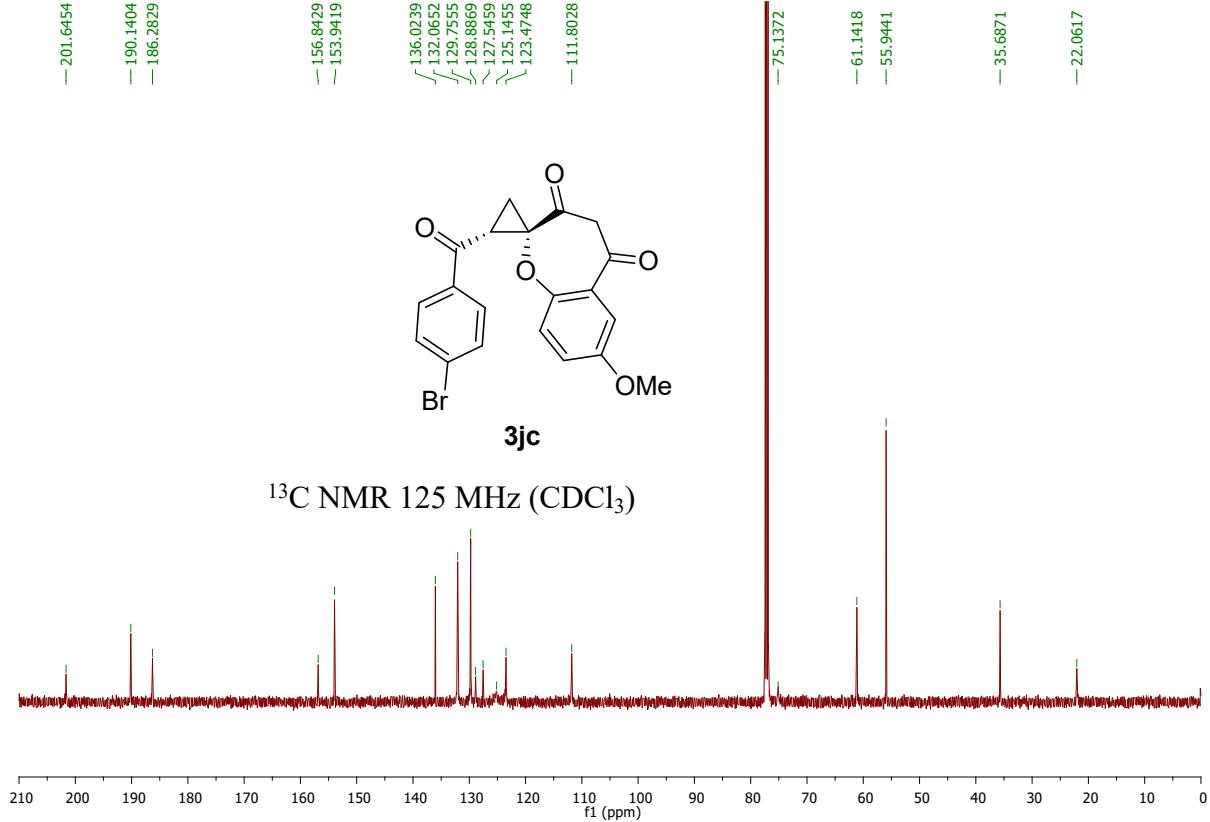
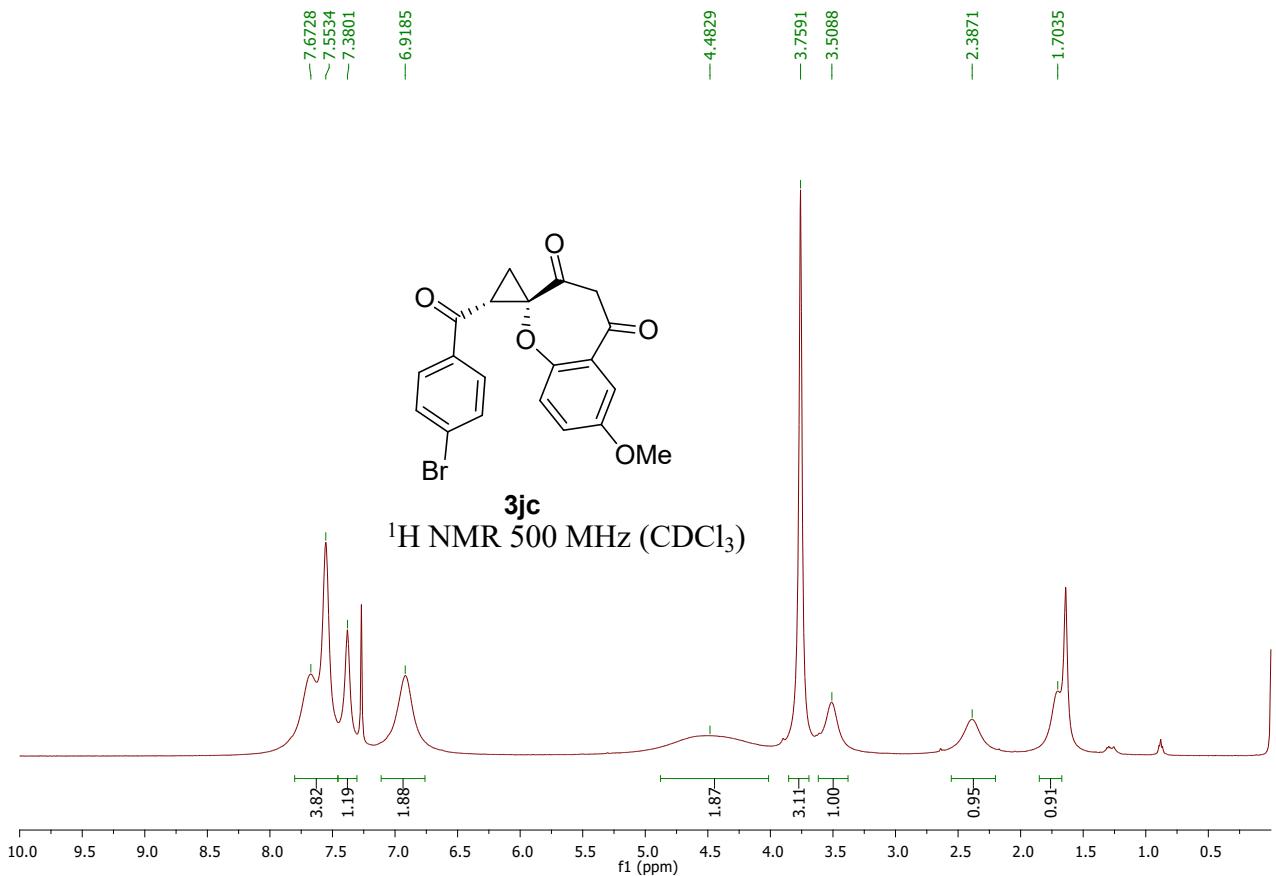
— 200.8489
 — 188.8652
 — 185.3762
 — 164.0293
 — 158.2182
 — 135.3645
 — 131.1428
 — 130.5600
 — 130.2606
 — 129.6450
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 — 74.8107
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 — 55.5895
 — 35.3777
 — 21.8787

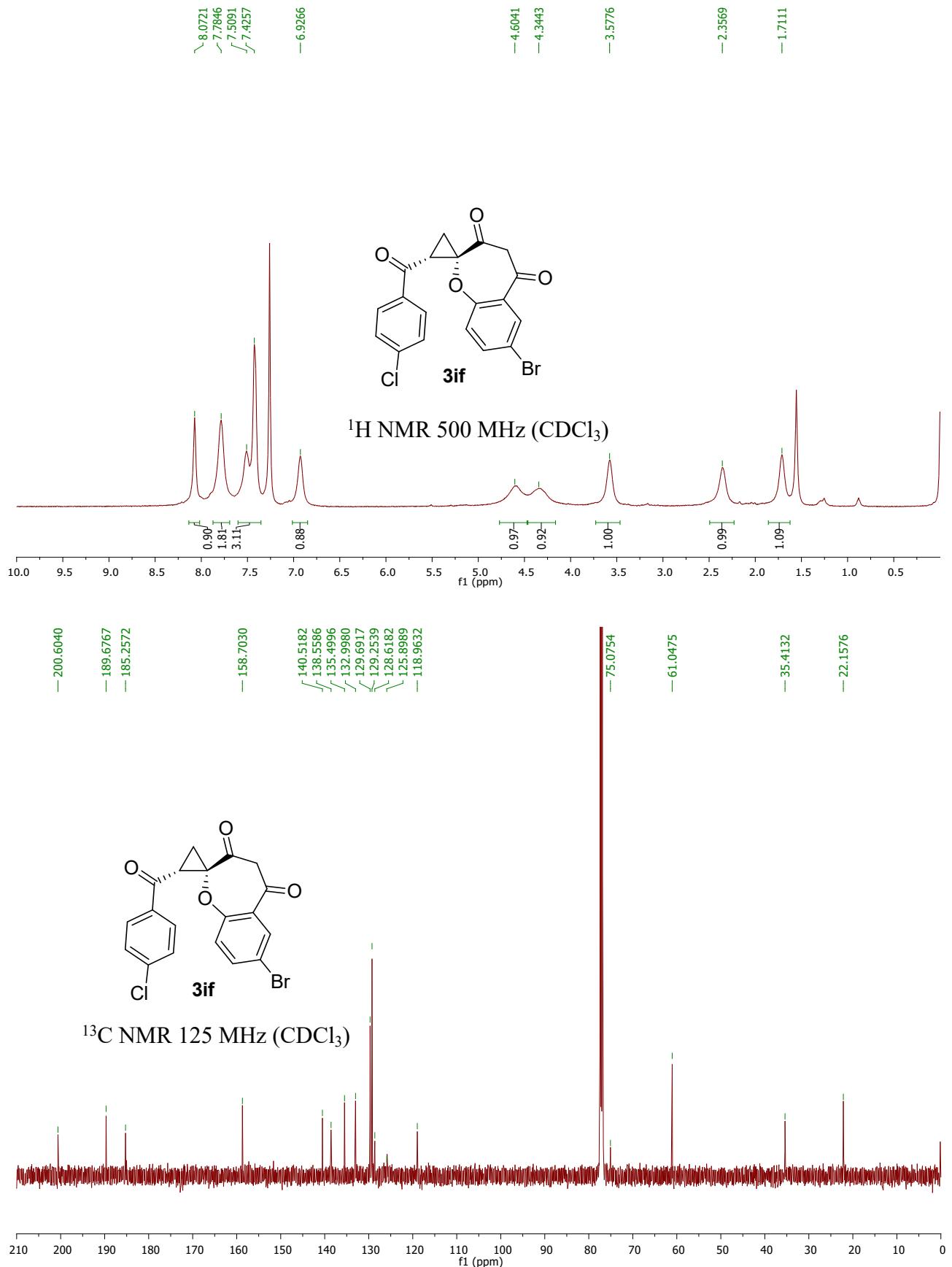


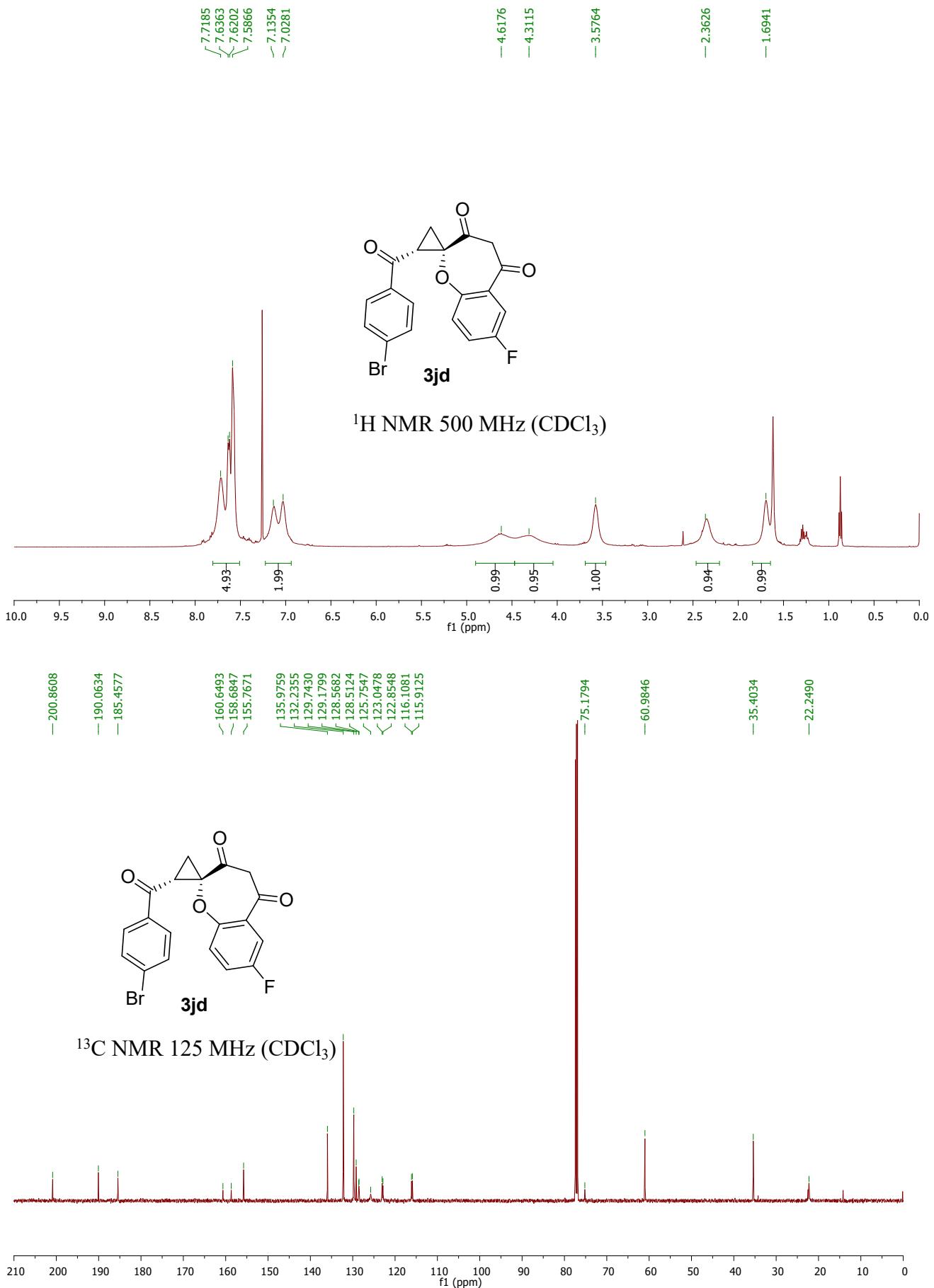
^{13}C NMR 125 MHz (CDCl_3)



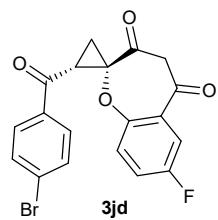




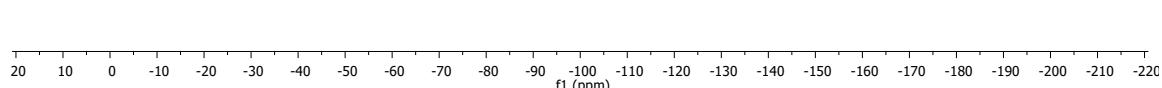


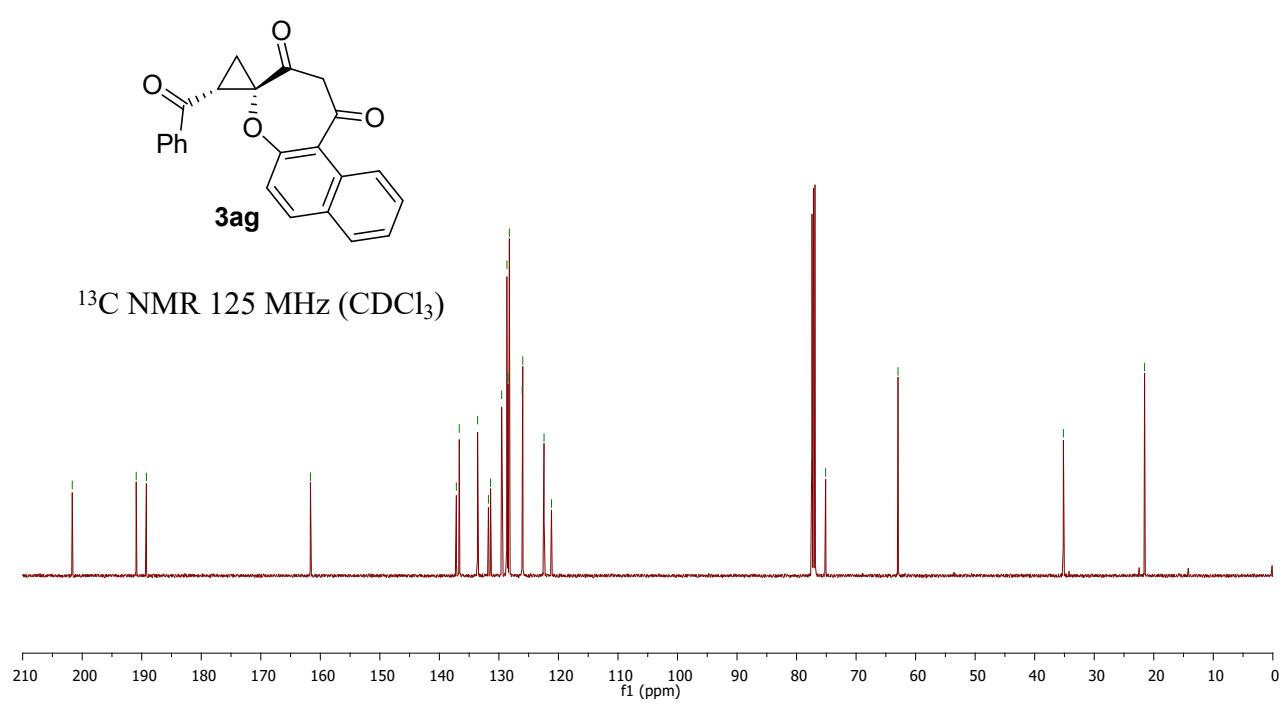
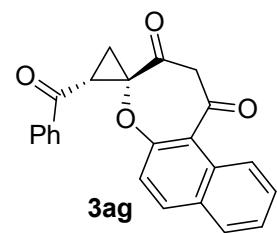
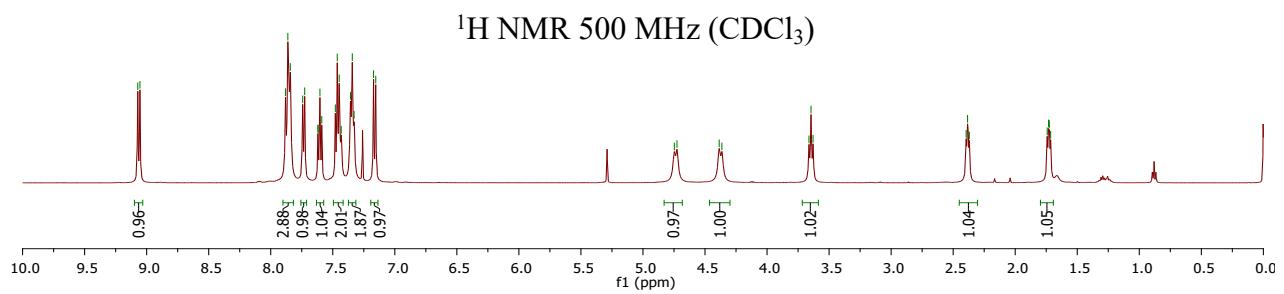


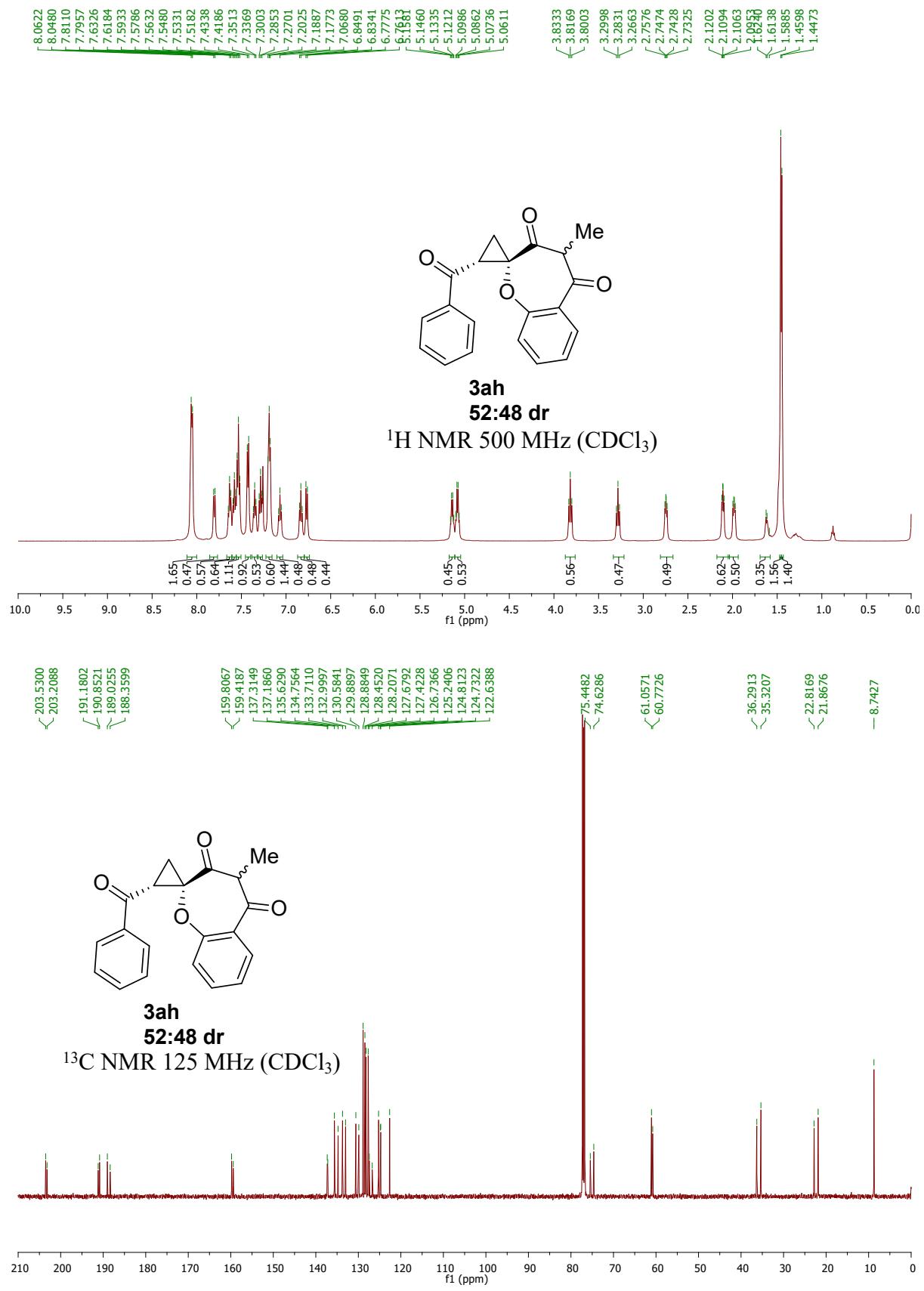
— -115.5149

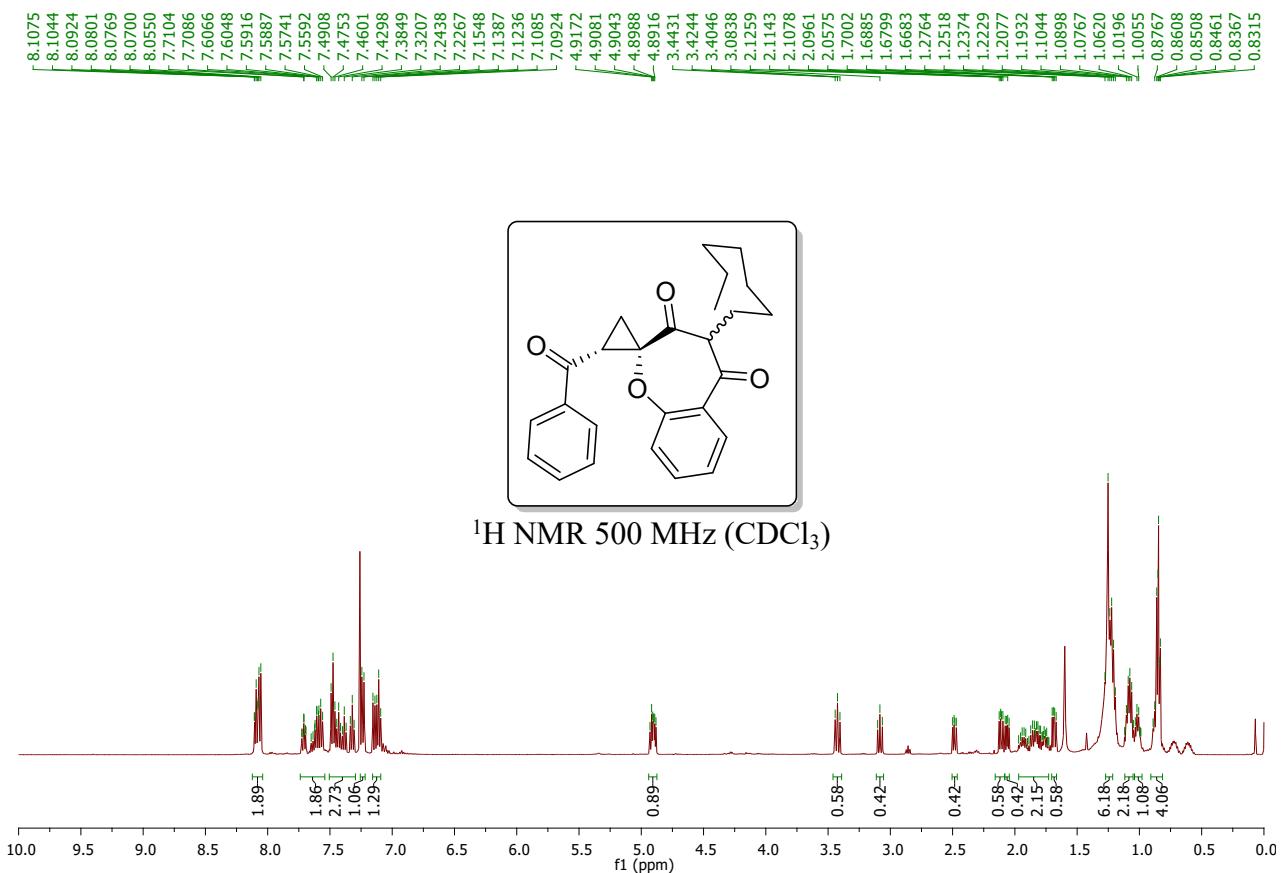


^{19}F NMR 470 MHz (CDCl_3)

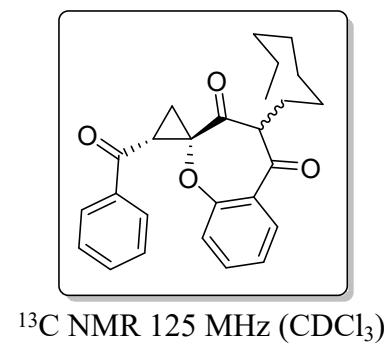




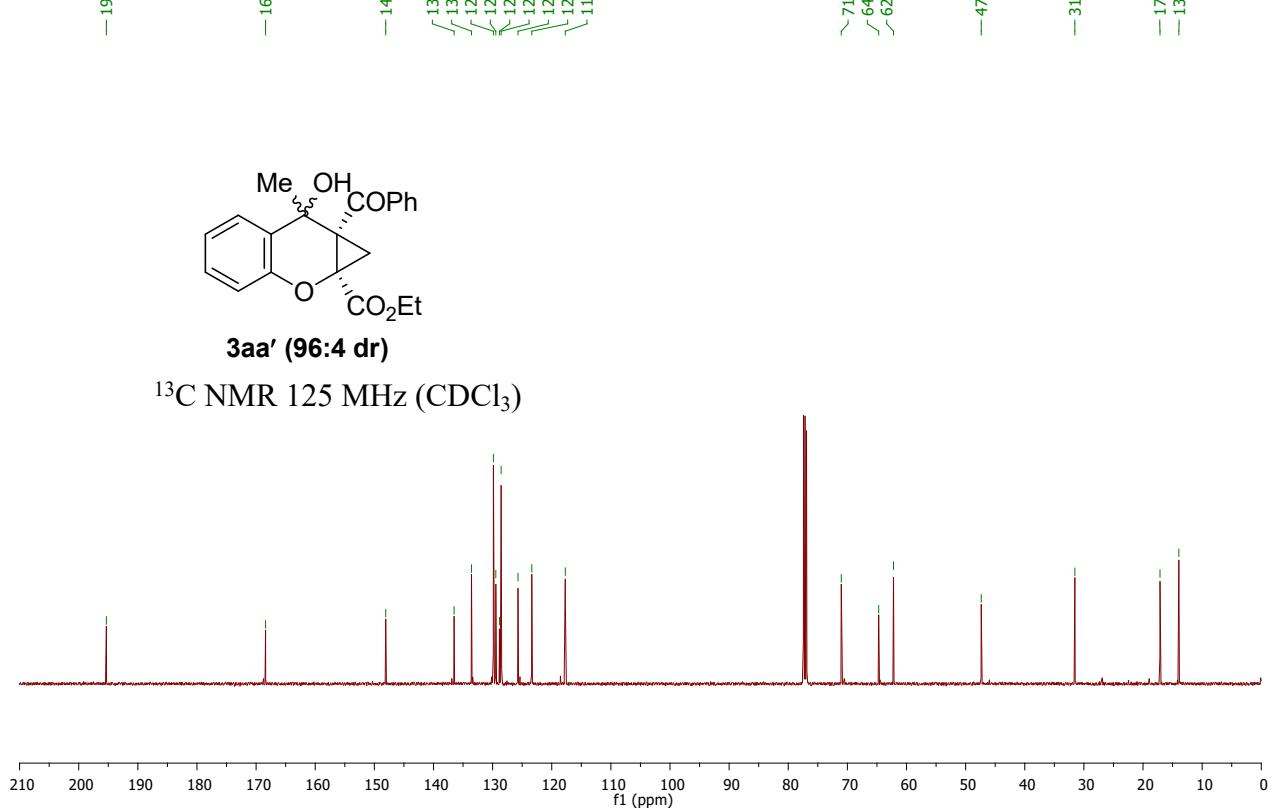
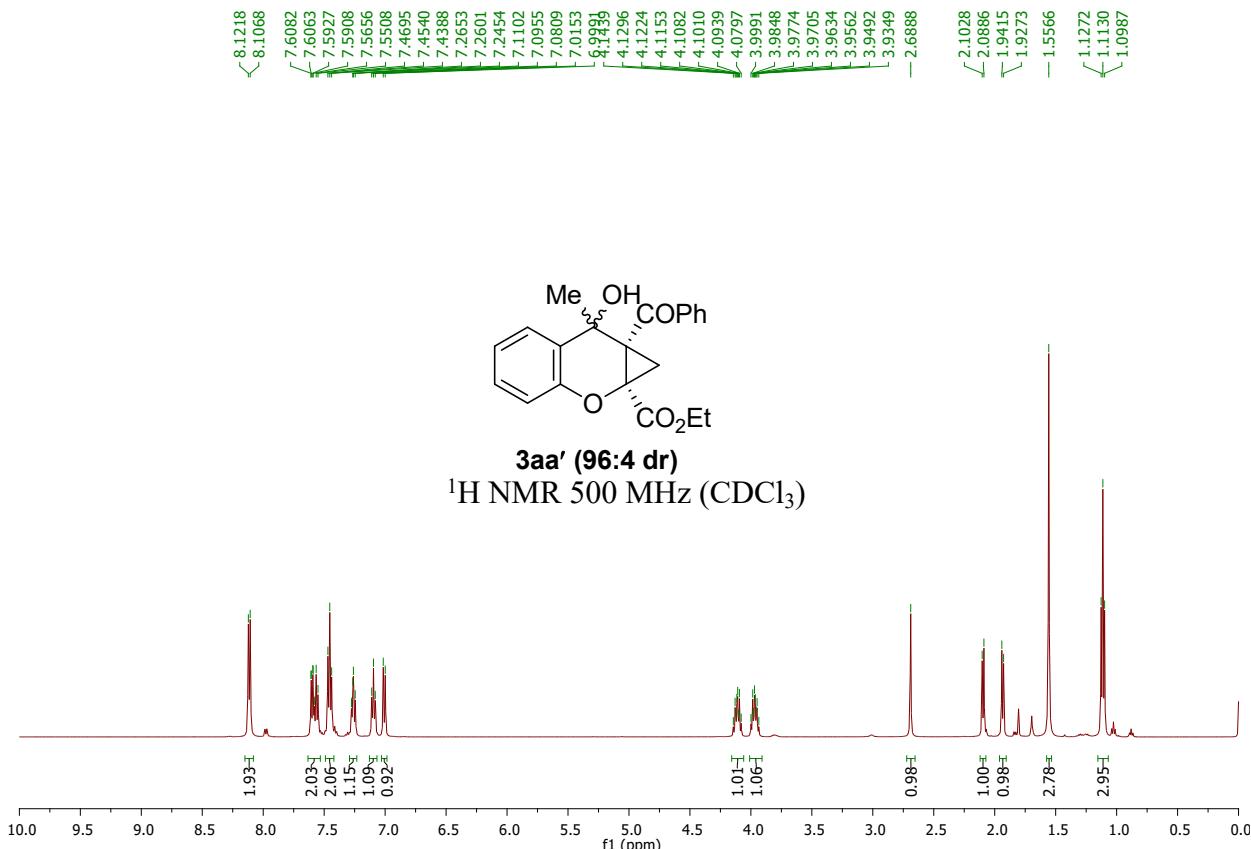


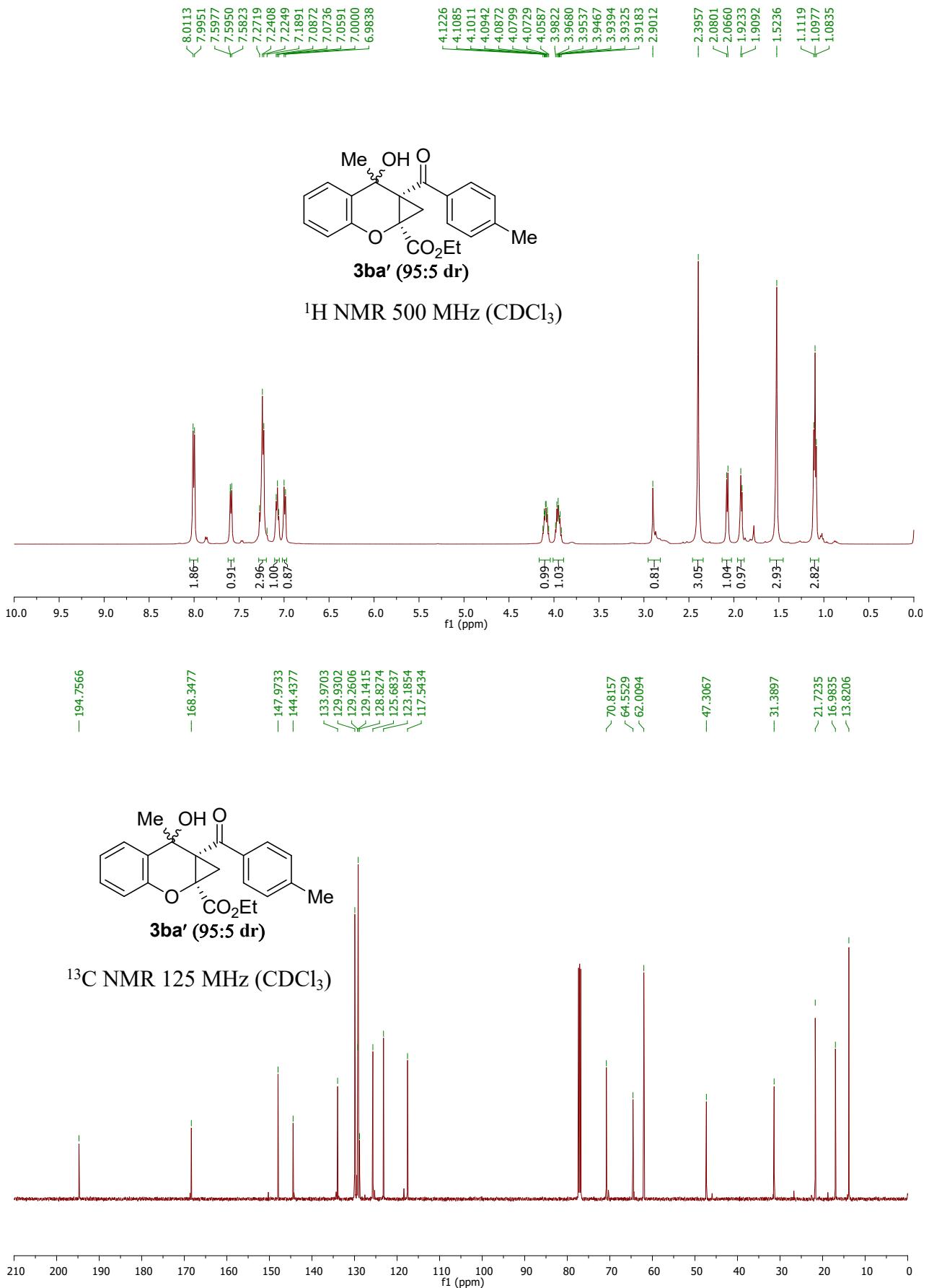


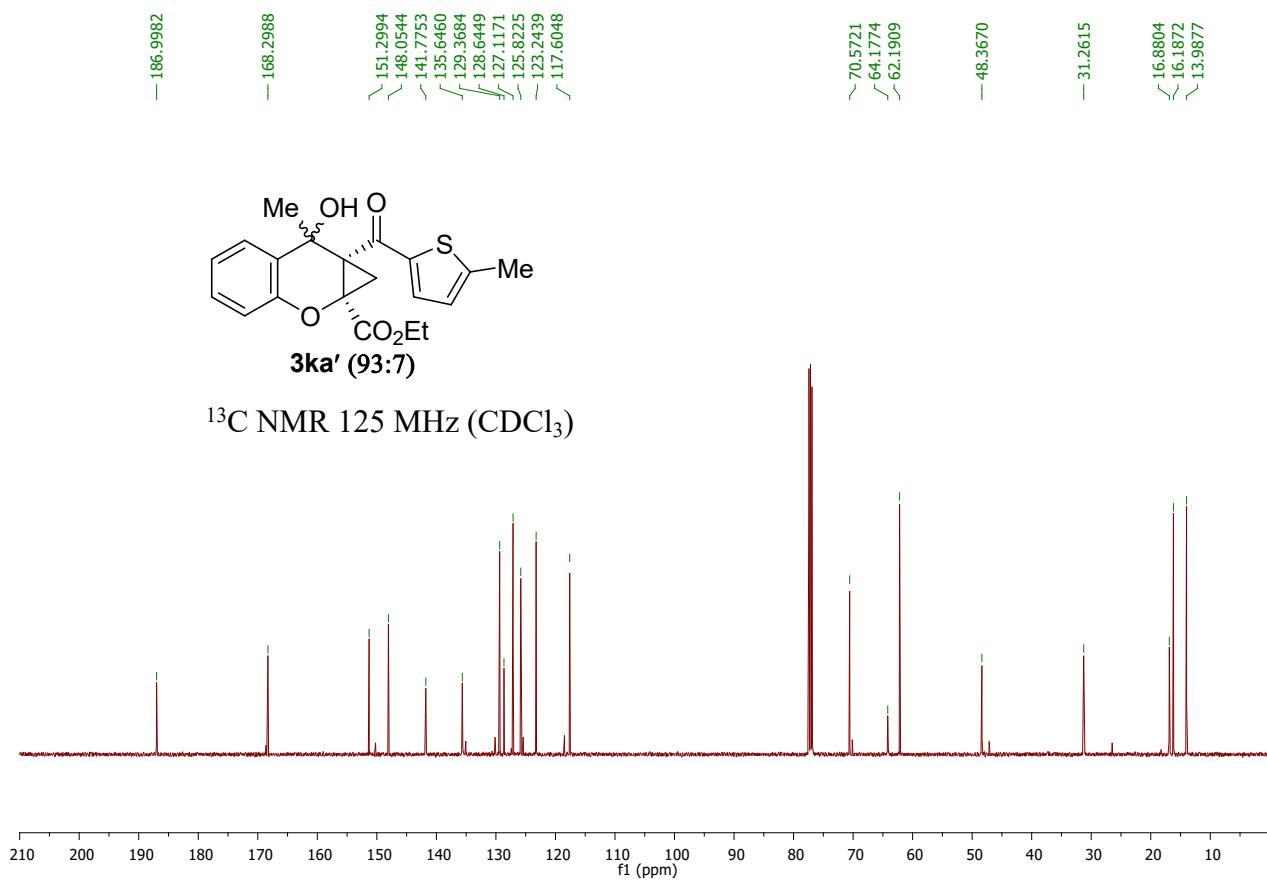
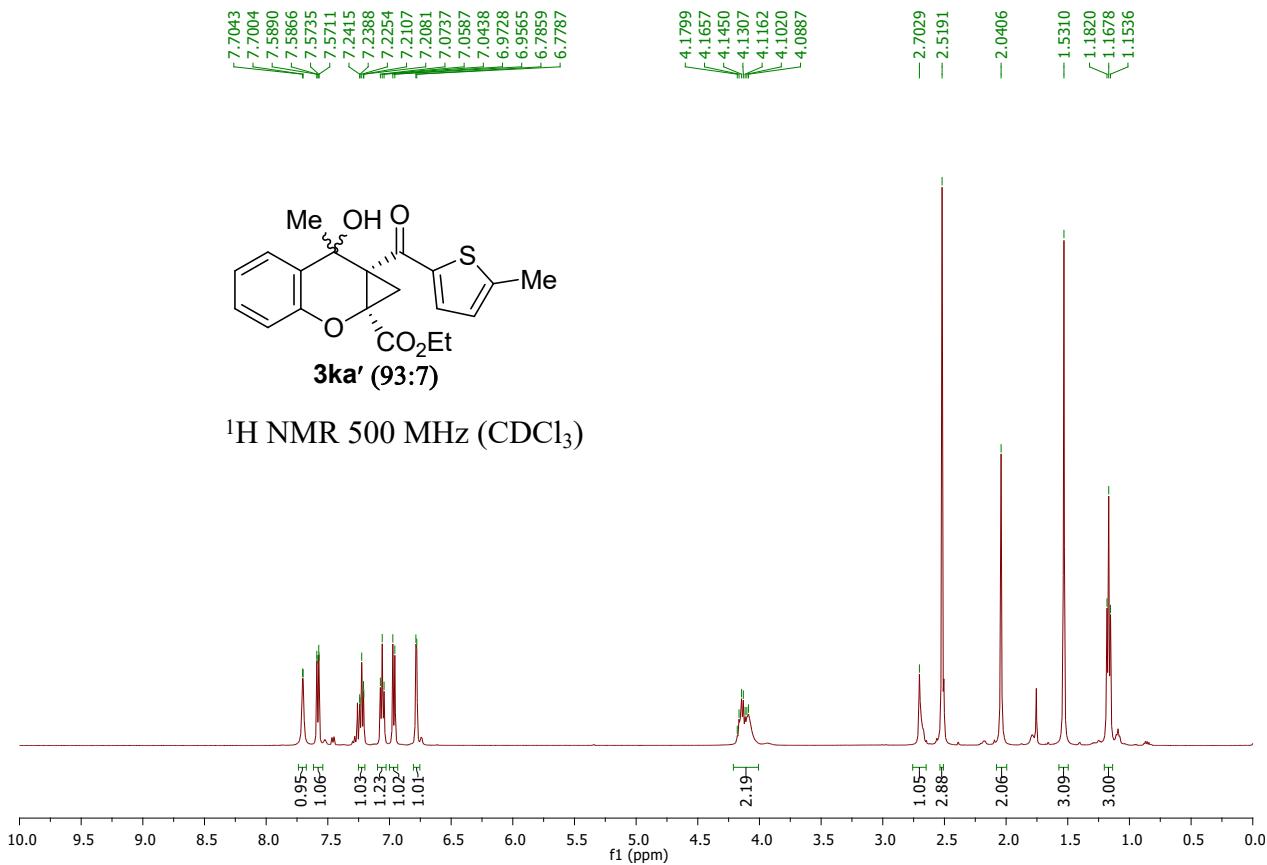
< 201.5394 < 200.8965 / 190.6010 / 190.0395 < 188.2378 < 188.0214
 < 159.5418 < 159.0742 / 136.0683 / 135.8494 / 135.8000 / 133.8098 / 133.4463 / 131.1717
 / 131.0468 / 128.9355 / 128.5419 / 128.3890 / 128.1615 / 127.8546 / 125.6795
 / 125.6485 / 122.8333 / 122.8191

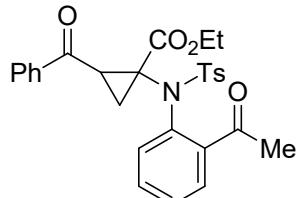


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
 f1 (ppm)

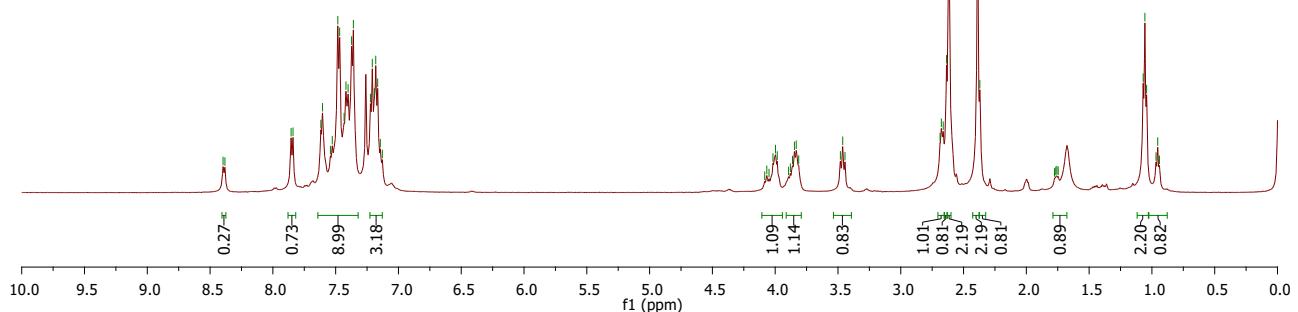




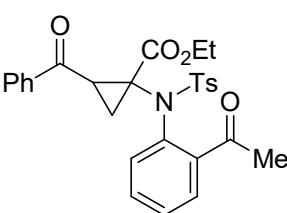




3aj (73:27 dr)
¹H NMR 500 MHz (CDCl₃)

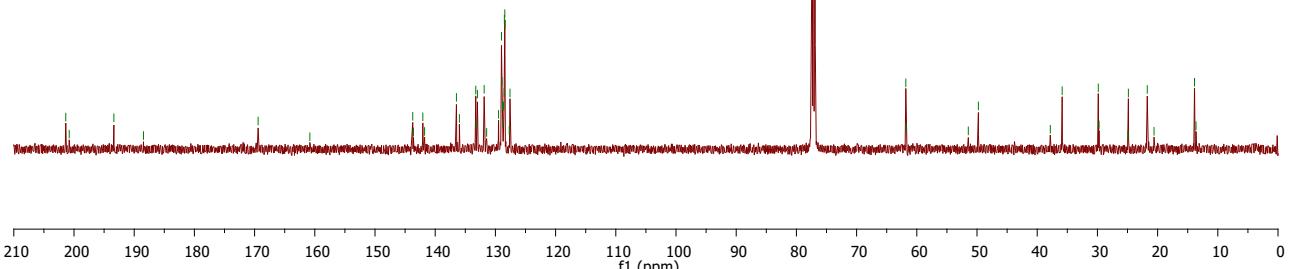


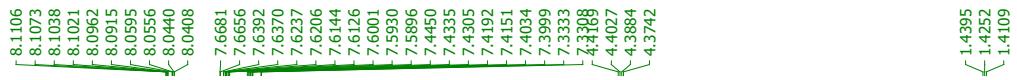
— 201.3661
< 200.7906
— 193.3752
— 188.4954



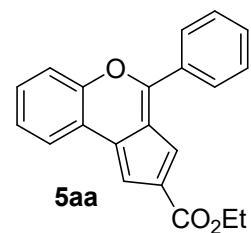
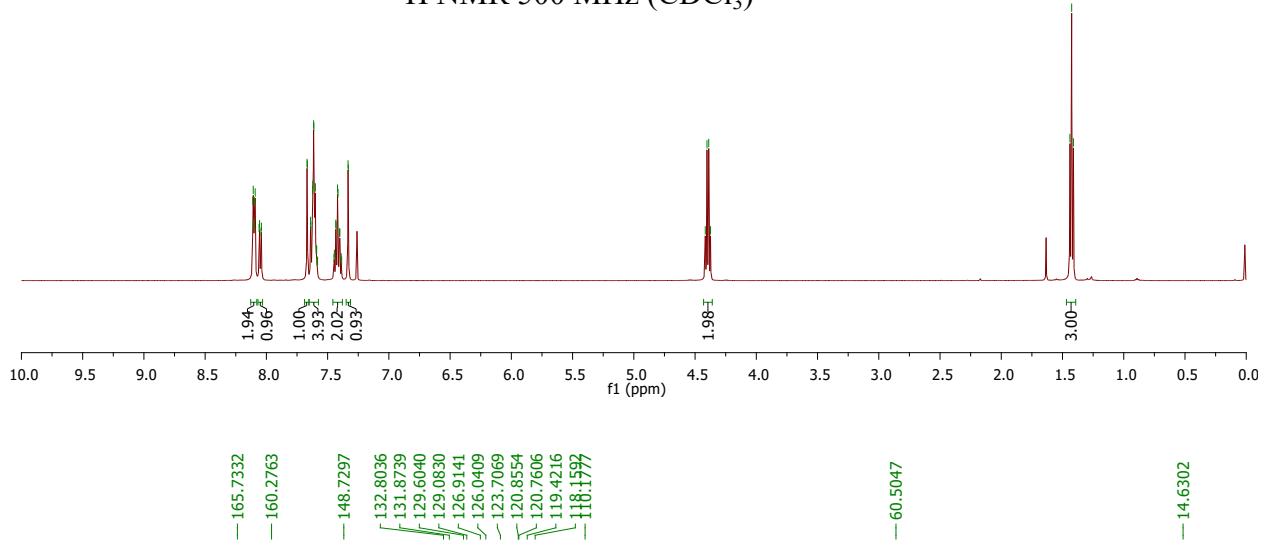
3aj (73:27 dr)

¹³C NMR 125 MHz (CDCl₃)

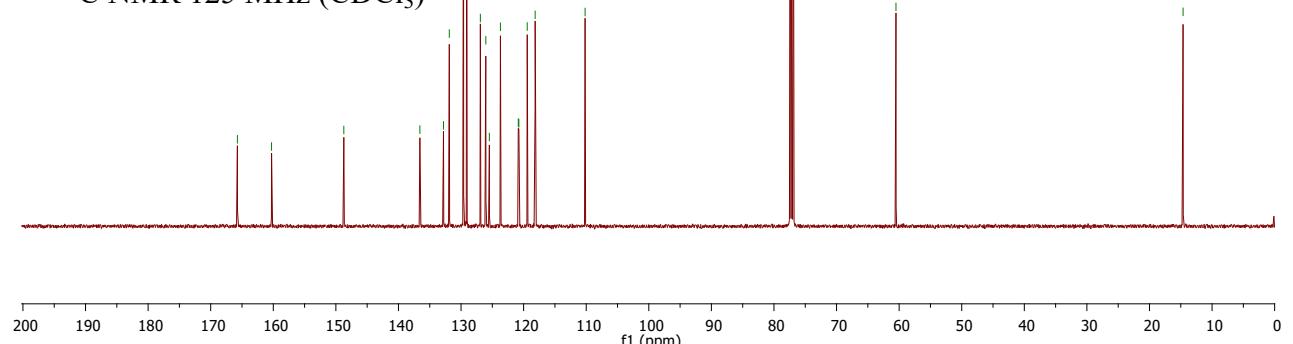


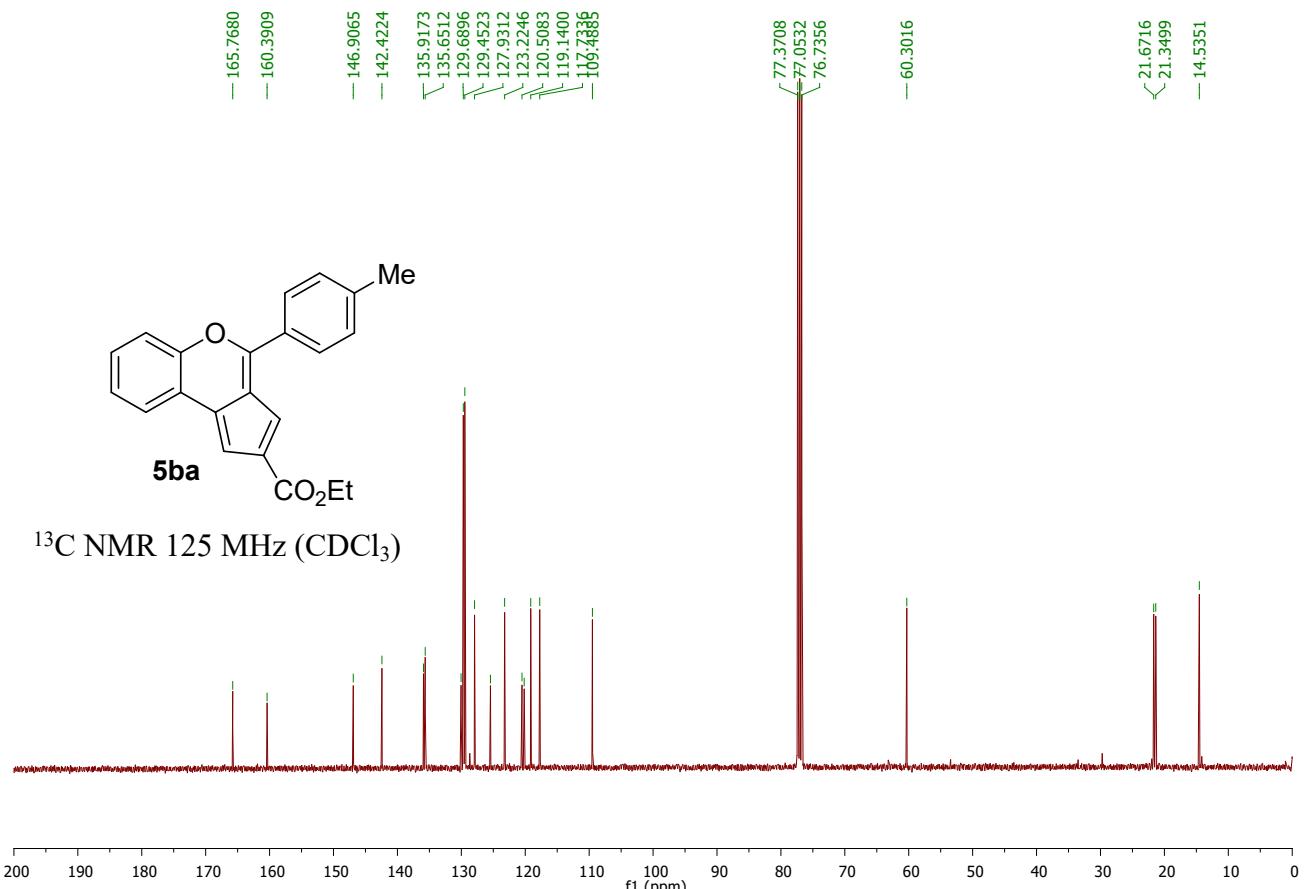
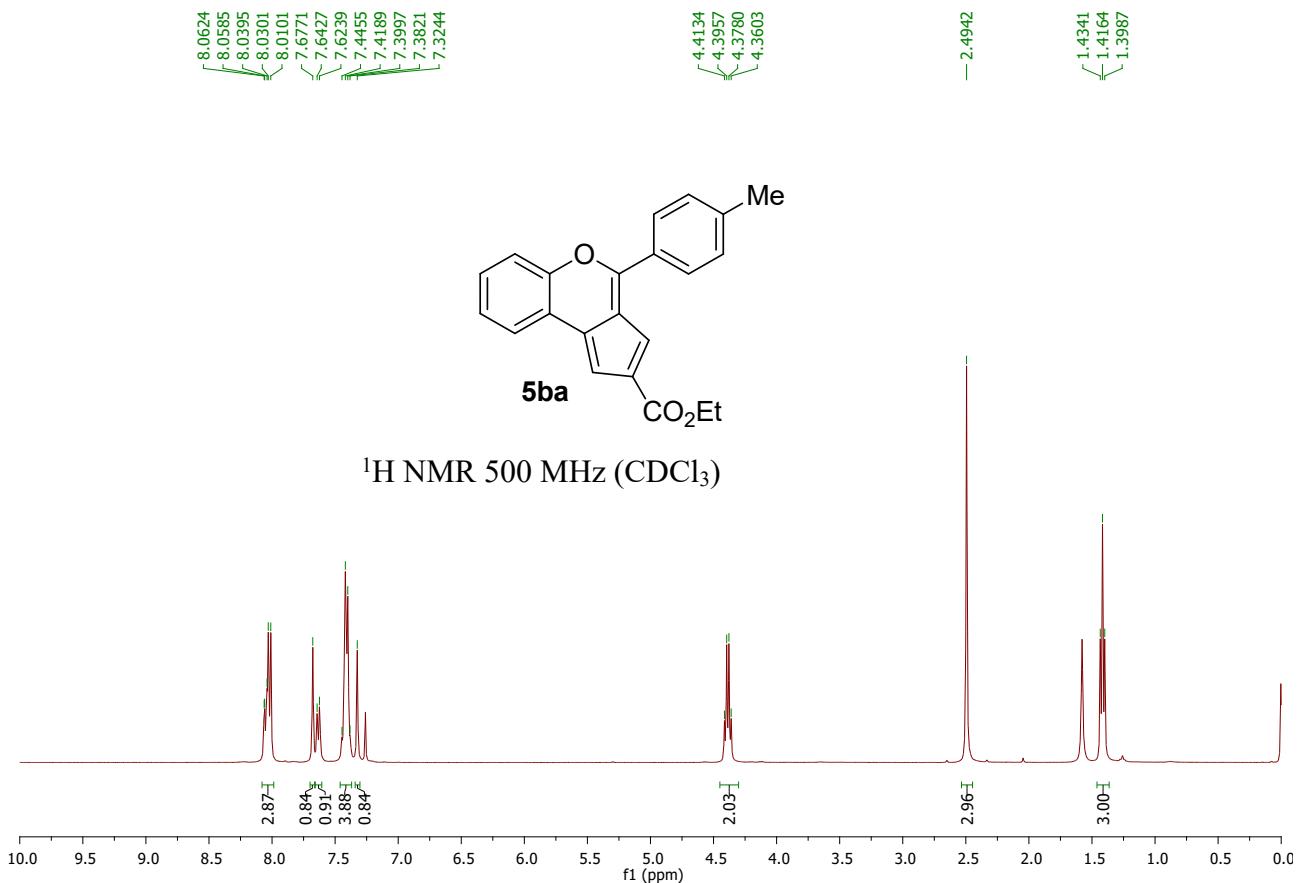


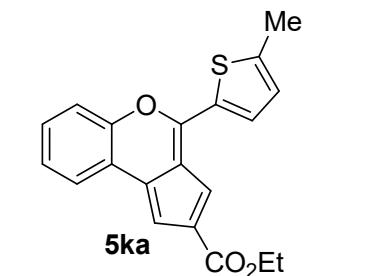
¹H NMR 500 MHz (CDCl_3)



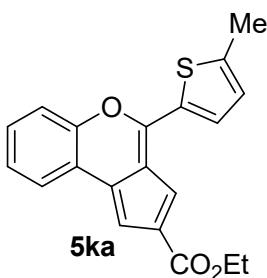
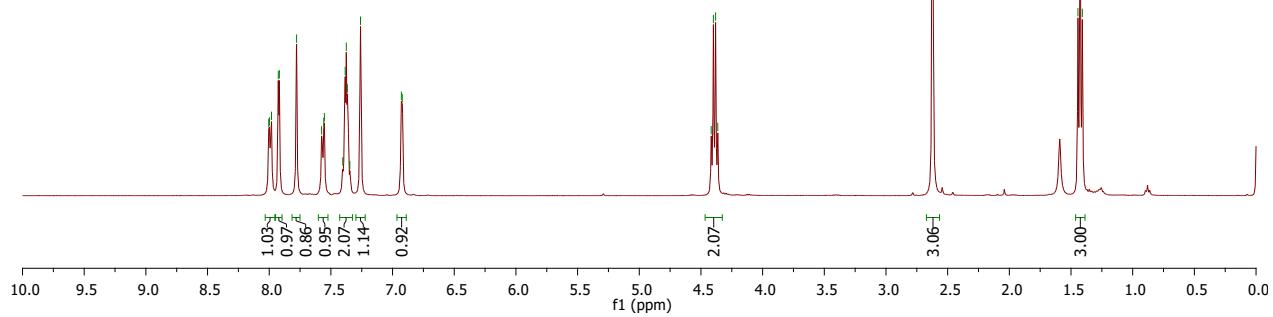
¹³C NMR 125 MHz (CDCl_3)



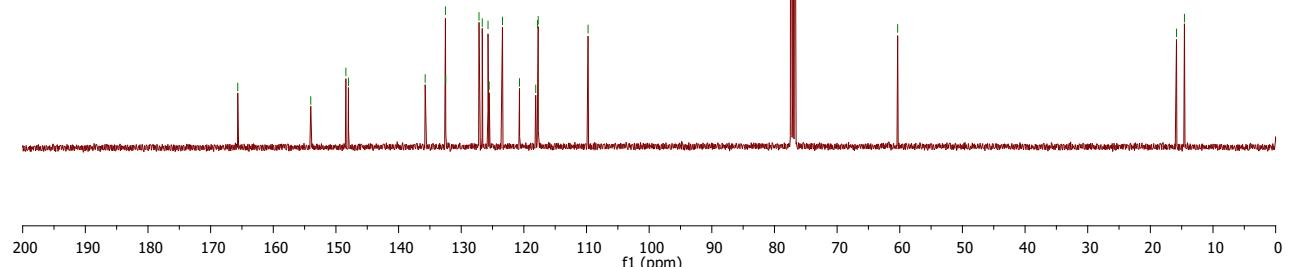


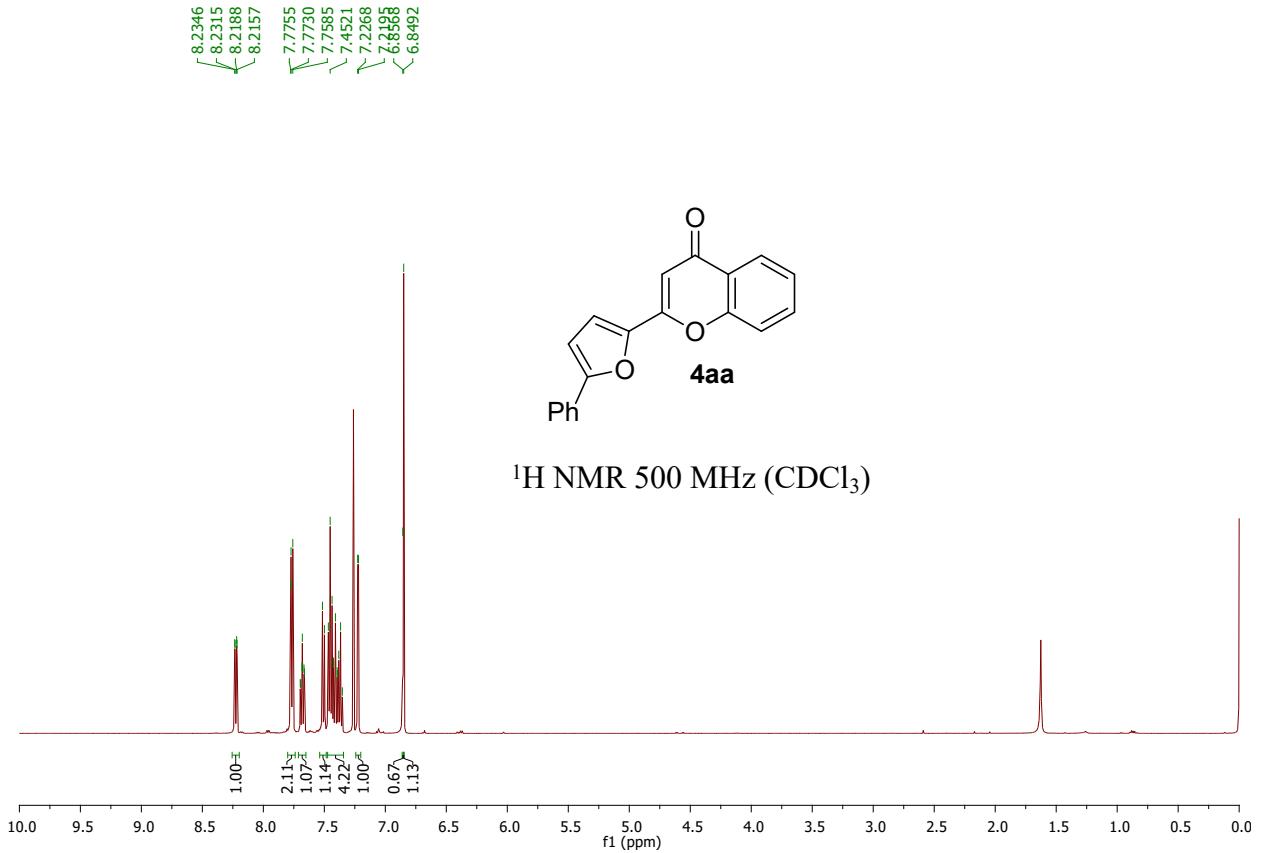


^1H NMR 500 MHz (CDCl_3)



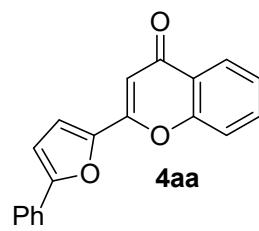
^{13}C NMR 125 MHz (CDCl_3)



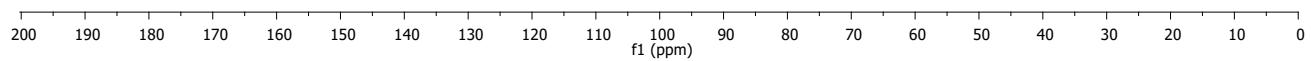


— 177.7558
 ✓ 157.2992
 ✓ 155.8764
 ✓ 155.0778
 — 145.4513

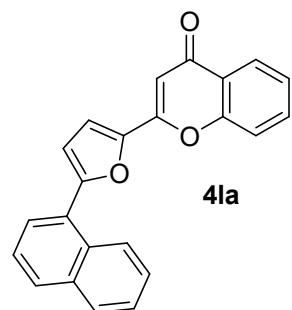
✓ 133.6877
 ✓ 129.4047
 ✓ 128.9856
 ✓ 128.9528
 ✓ 125.7769
 ✓ 125.1798
 ✓ 124.8939
 — 124.8939
 — 115.3270
 — 107.7199
 — 105.2490



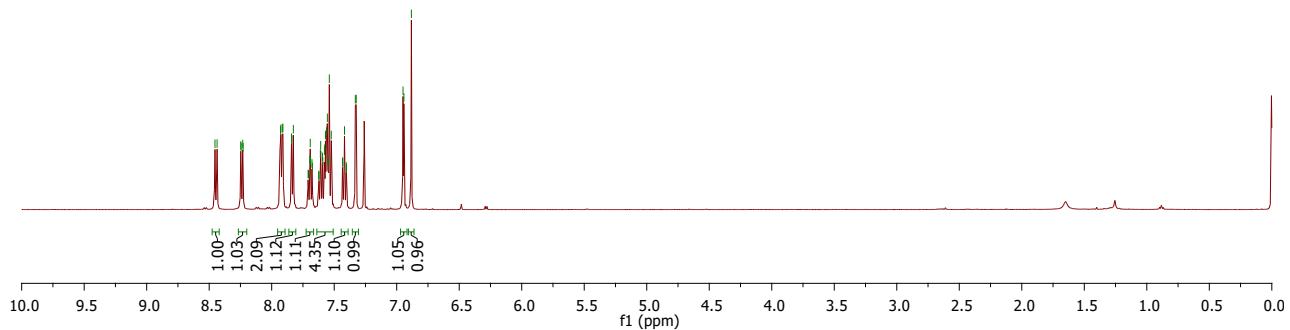
¹³C NMR 125 MHz (CDCl₃)



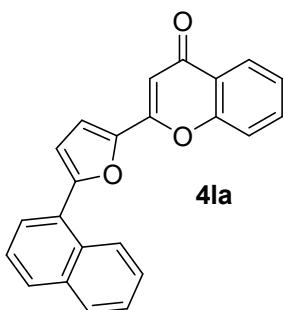
8.4336
 8.4368
 7.9291
 7.9267
 7.9147
 7.9103
 7.8912
 7.8395
 7.8268
 7.6917
 7.5697
 7.5621
 7.5547
 7.5391
 7.5335
 7.4176
 7.3310
 6.9496
 6.9425
 6.8826



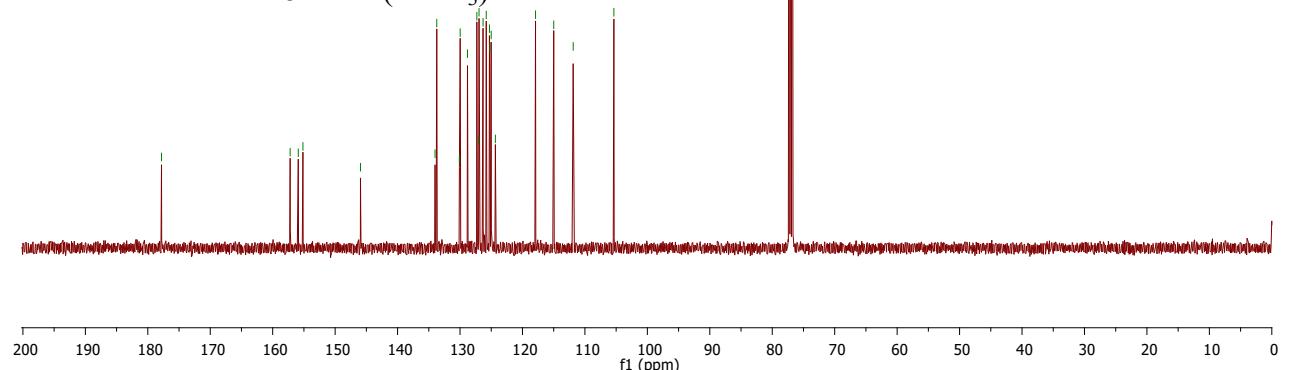
¹H NMR 500 MHz (CDCl_3)

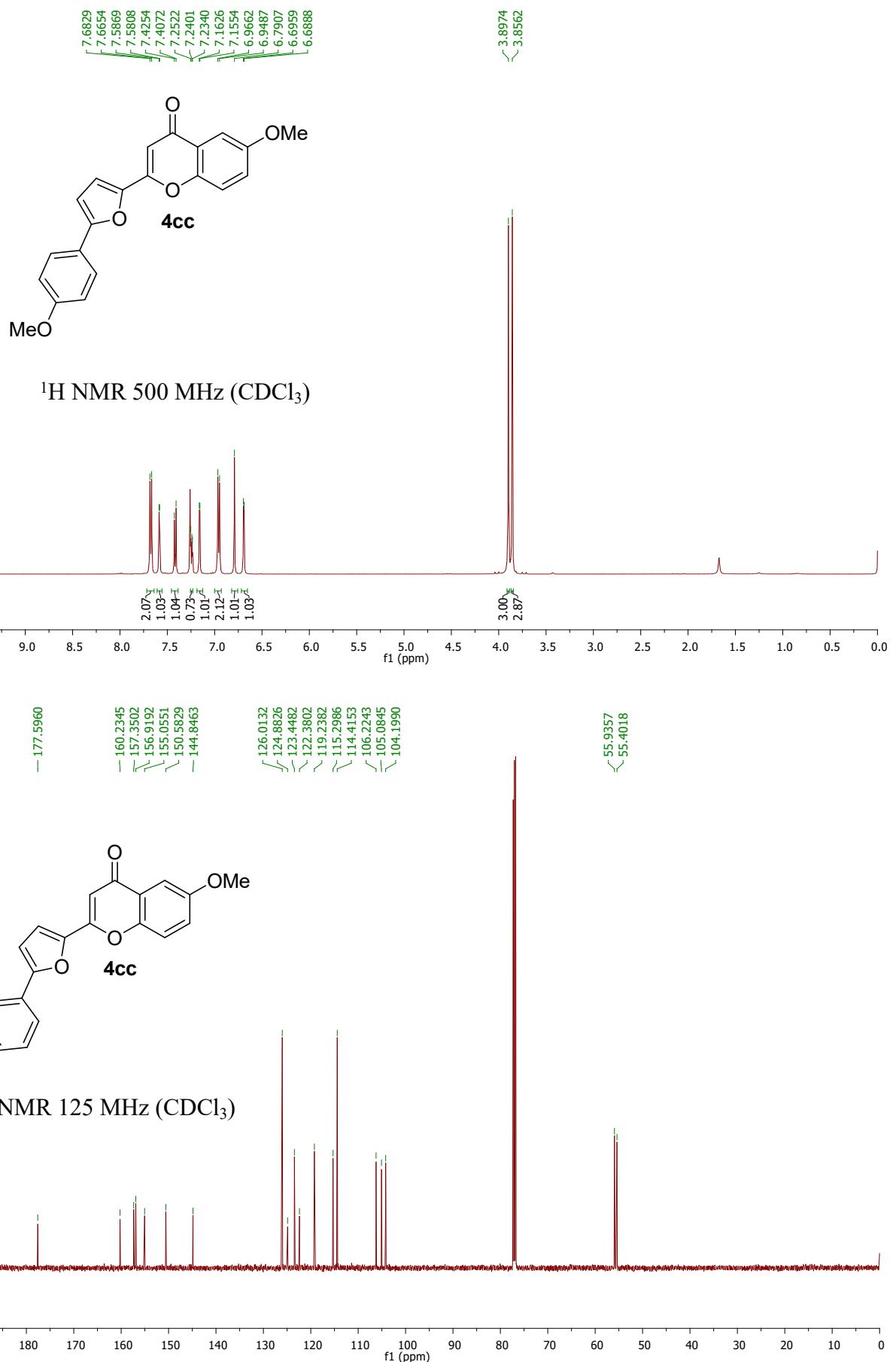


-177.8074
 157.2033
 155.9023
 155.1575
 -145.9390
 133.7235
 129.9739
 127.3065
 126.9564
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 -111.8761
 -105.3612

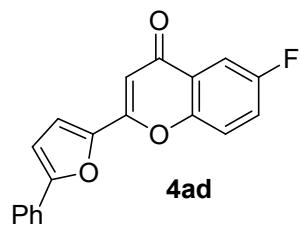


¹³C NMR 125 MHz (CDCl_3)

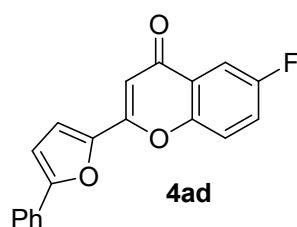
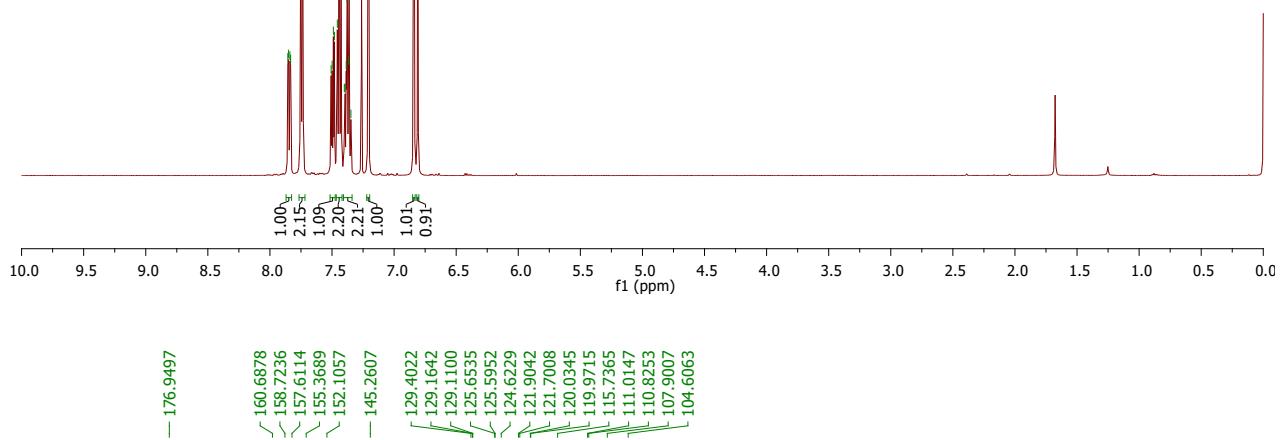




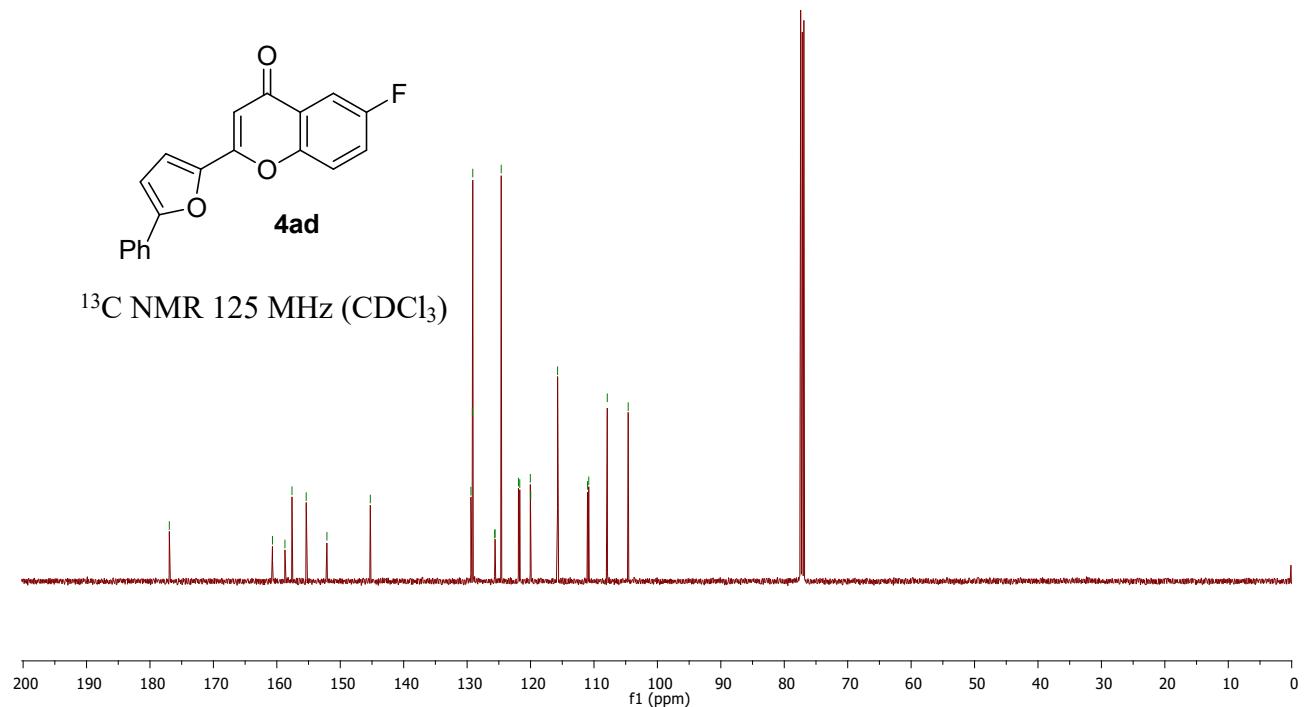
7.8558
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 7.7364
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 7.4571
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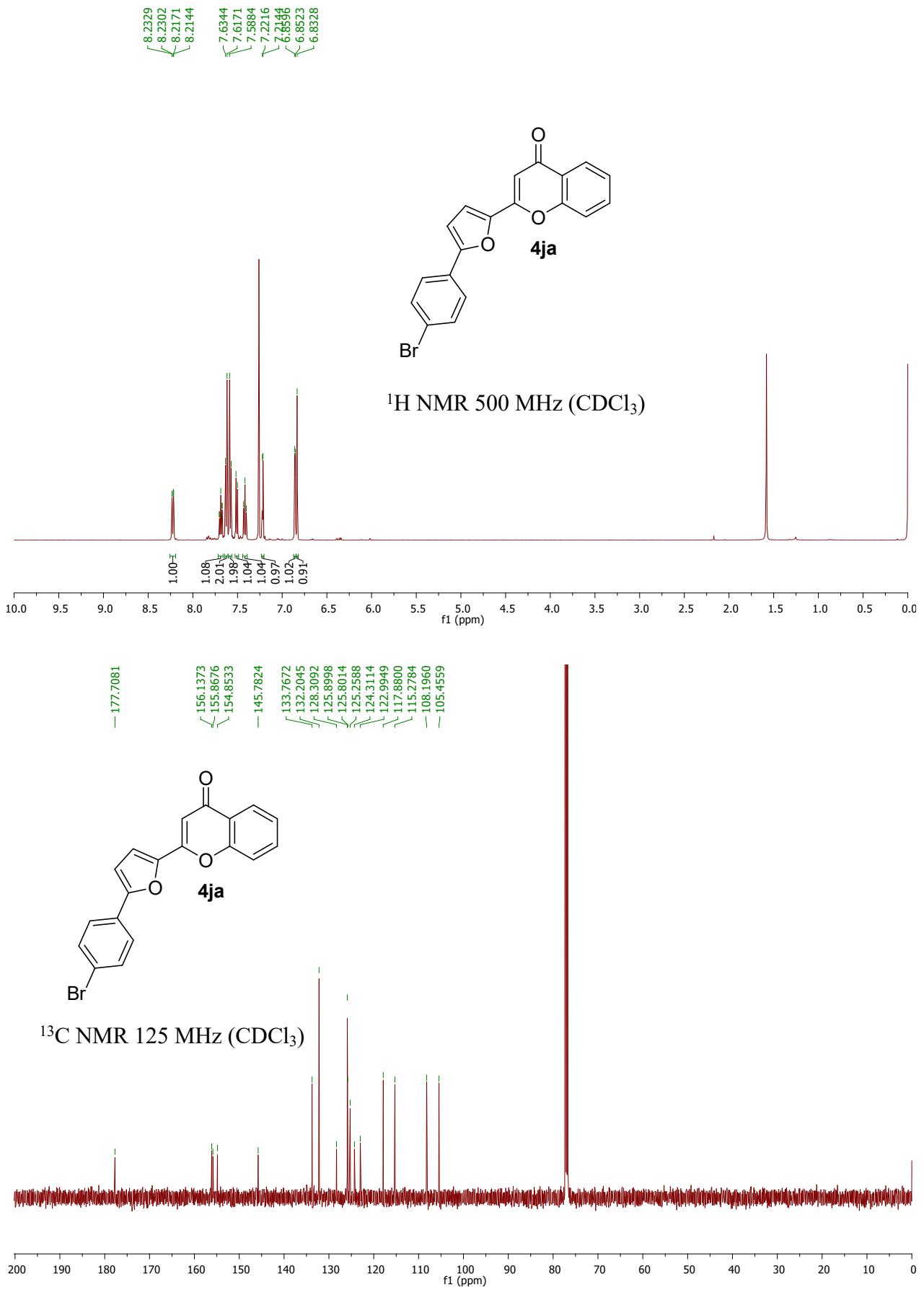


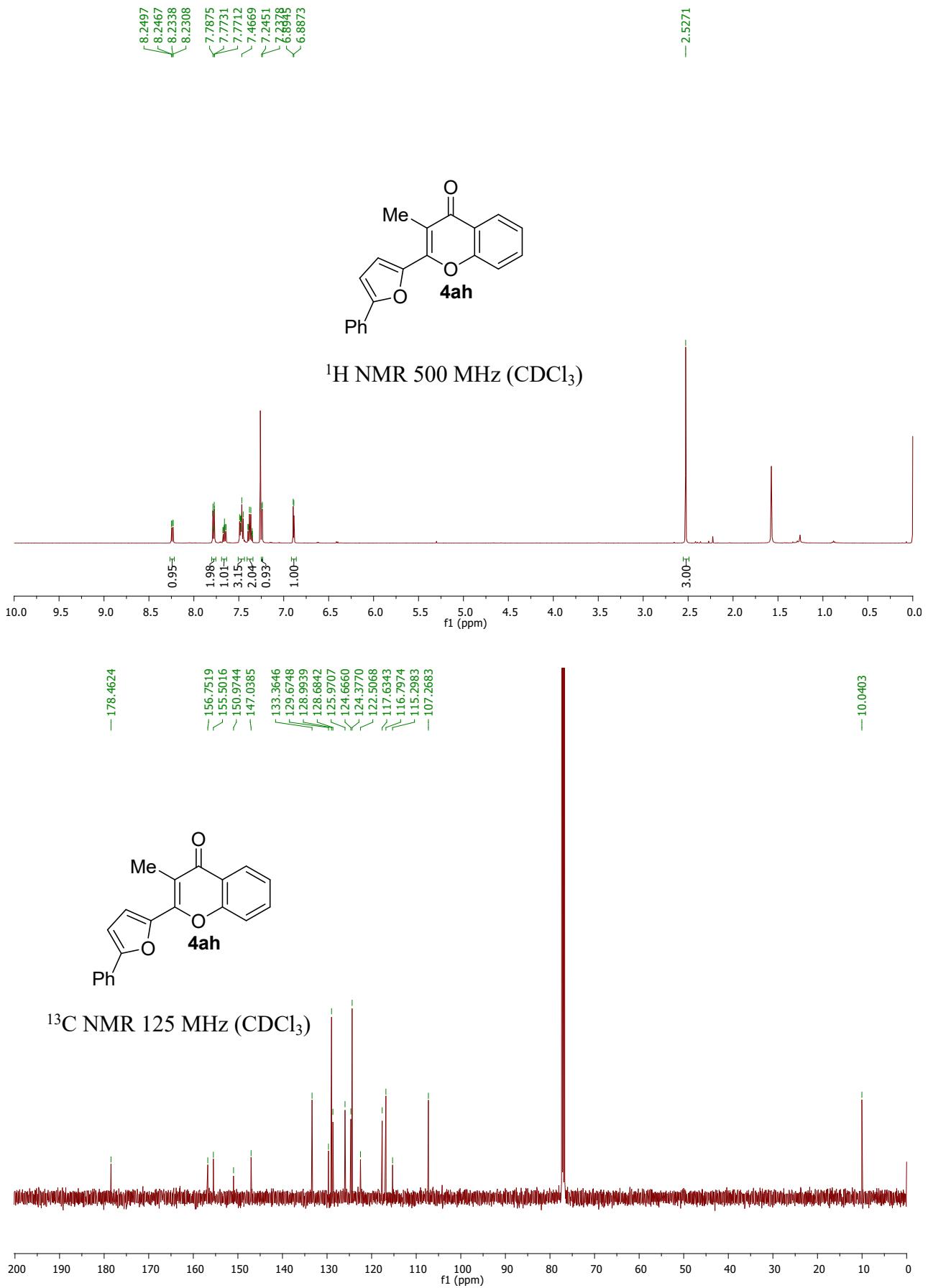
¹H NMR 500 MHz (CDCl₃)



¹³C NMR 125 MHz (CDCl₃)

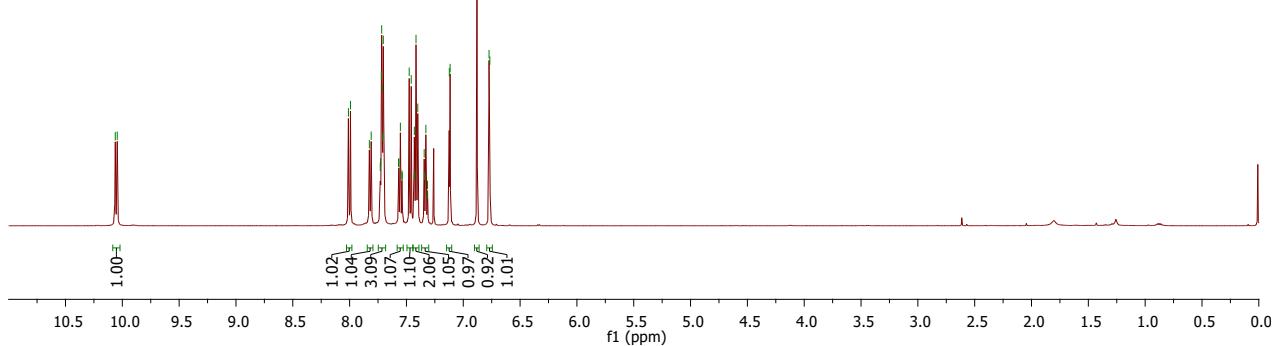




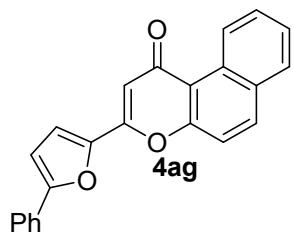




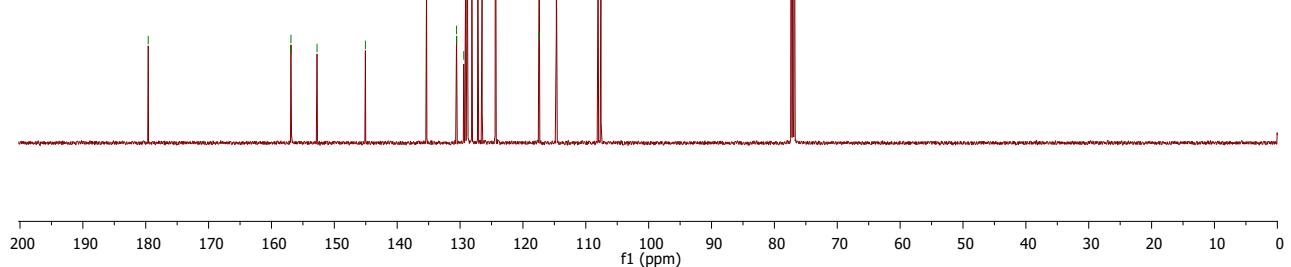
¹H NMR 500 MHz (CDCl₃)

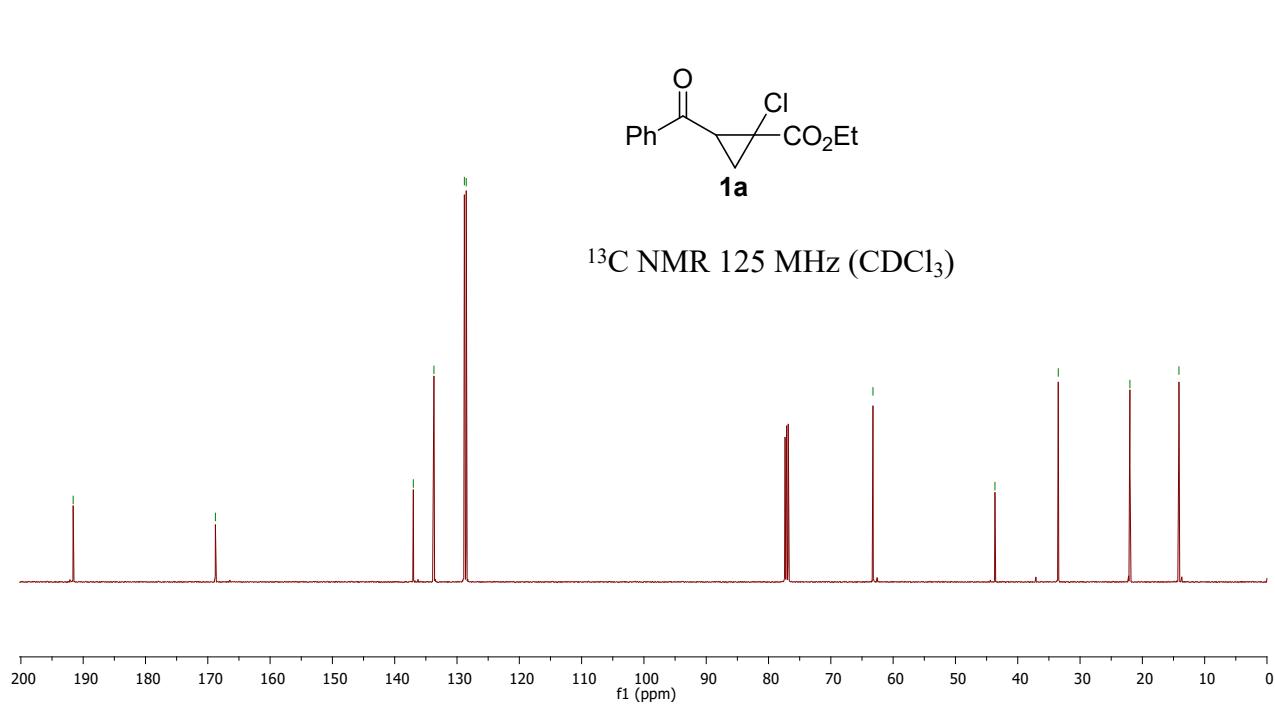
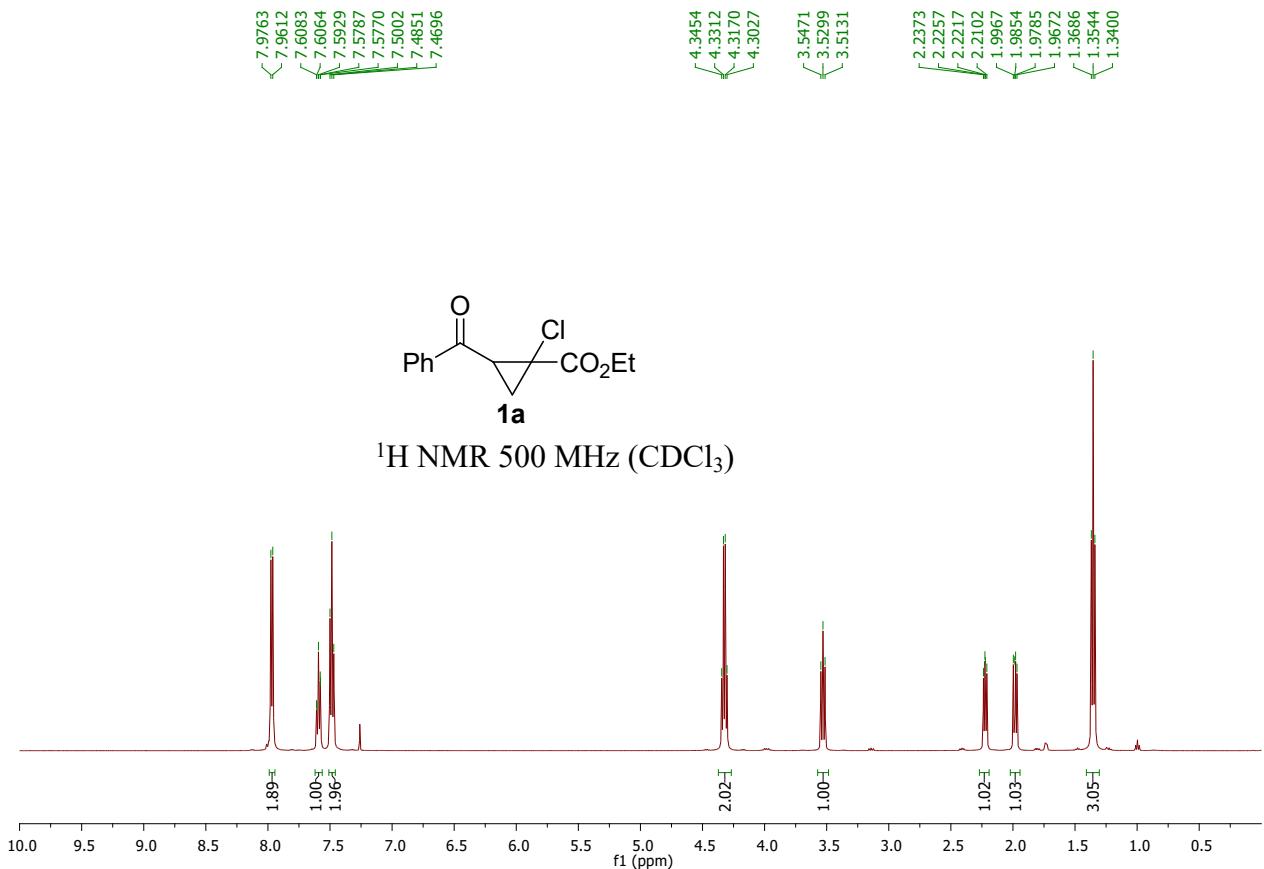


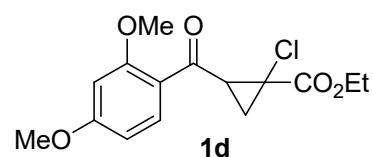
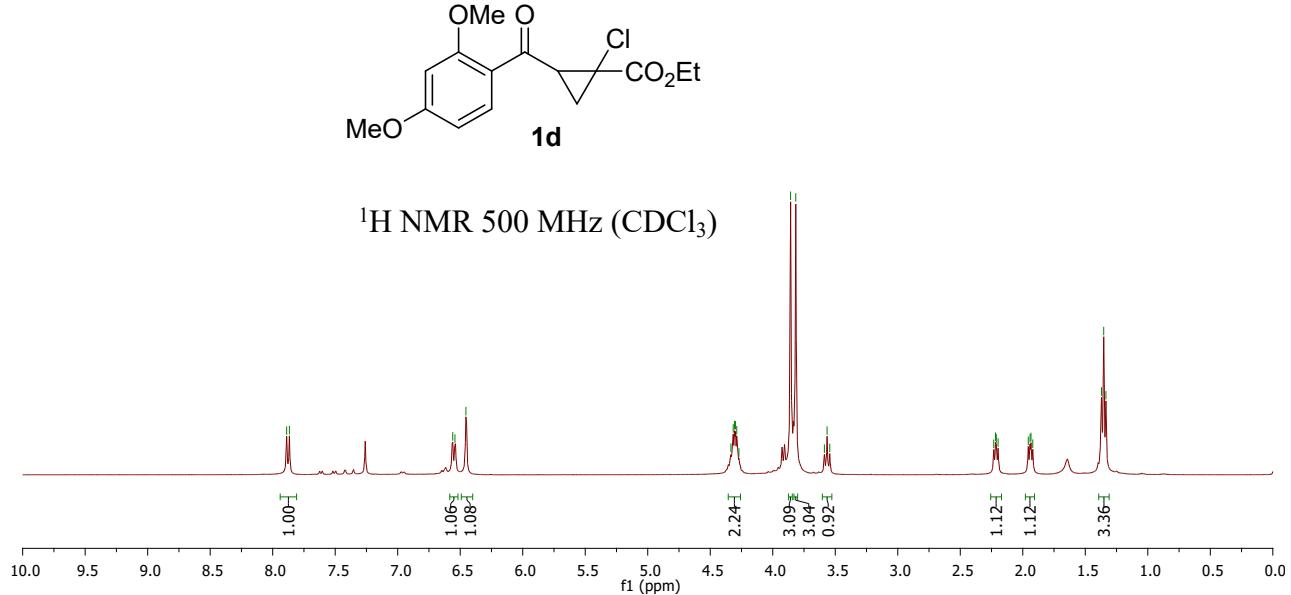
— 179.6032
— 156.9046
— 156.8308
— ~152.7529
— 145.0580
— 135.3287
— 129.1292
— 128.9099
— 128.7759
— 128.1196
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— 124.4250
— 117.4040
— 114.6791
— 108.0511
— <107.5889



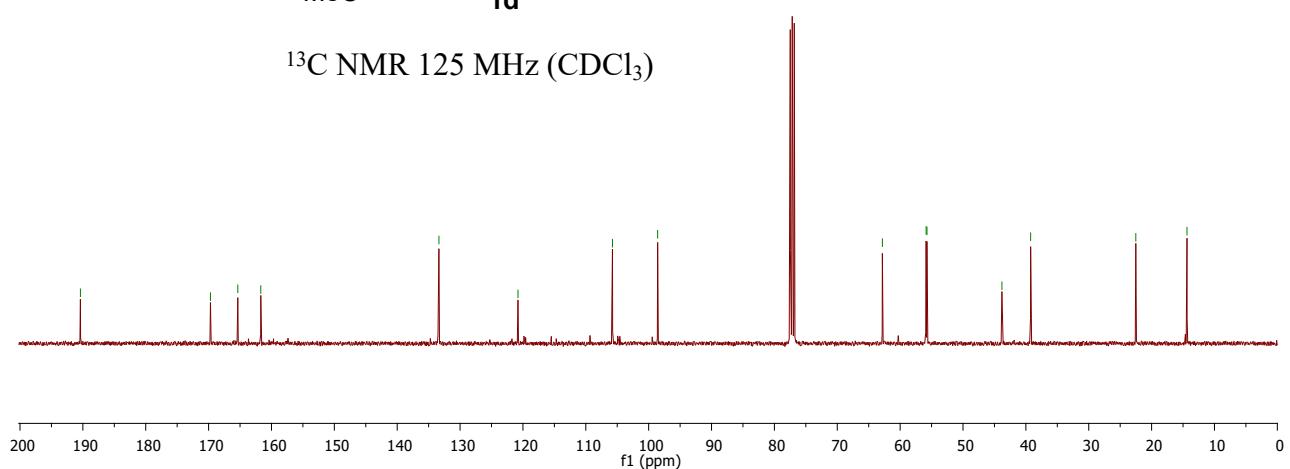
¹³C NMR 125 MHz (CDCl₃)





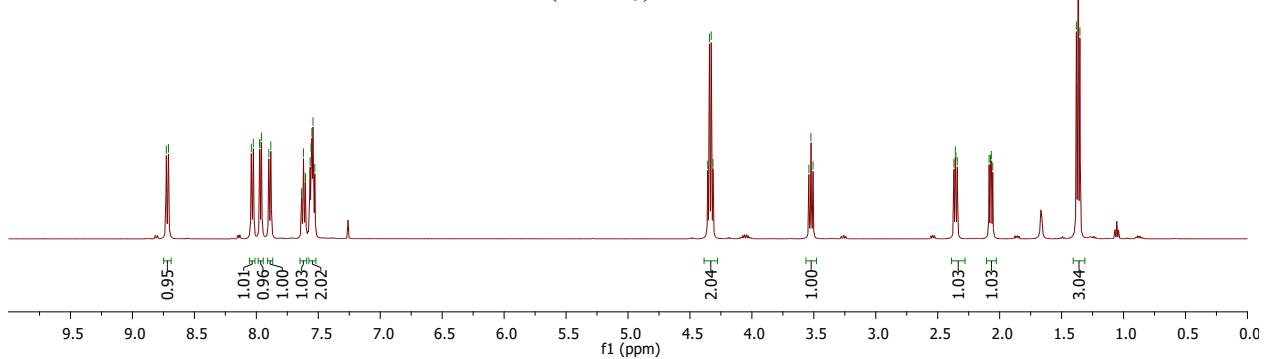


¹³C NMR 125 MHz (CDCl_3)

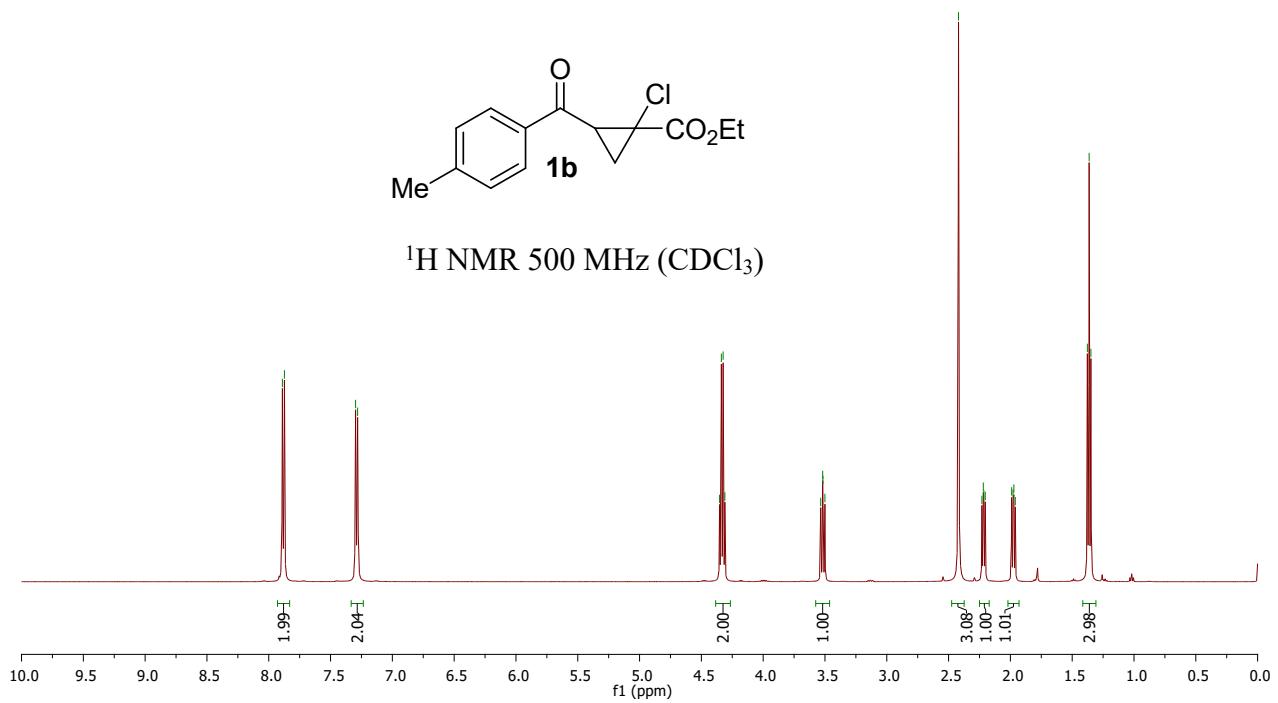


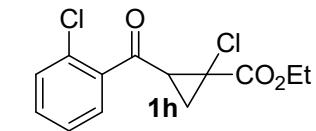


^1H NMR 500 MHz (CDCl_3)

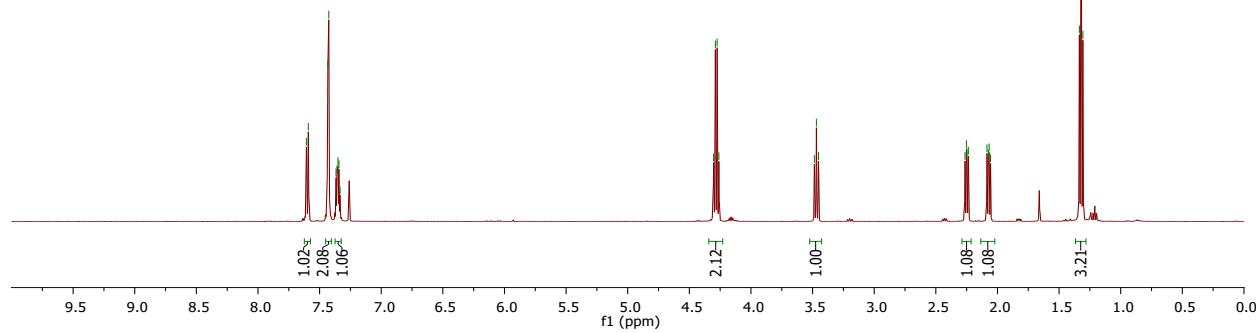


^1H NMR 500 MHz (CDCl_3)





^1H NMR 500 MHz (CDCl_3)



— 193.4755

— 168.6119

— 138.4787
— 132.8867
— 132.2345
— 130.8752
— 130.4449
— 127.2781

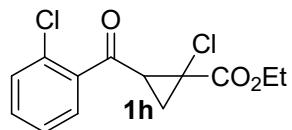
— 63.2486

— 45.7457

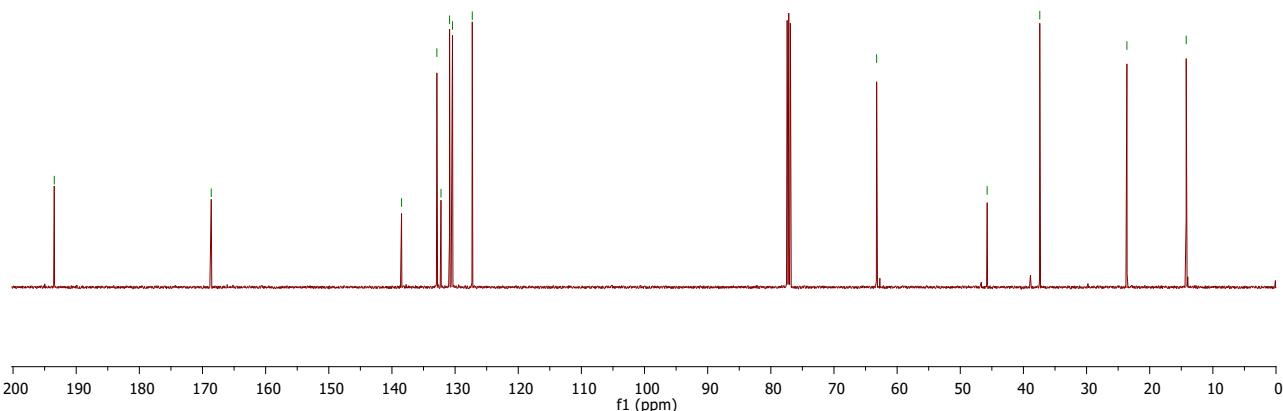
— 37.4100

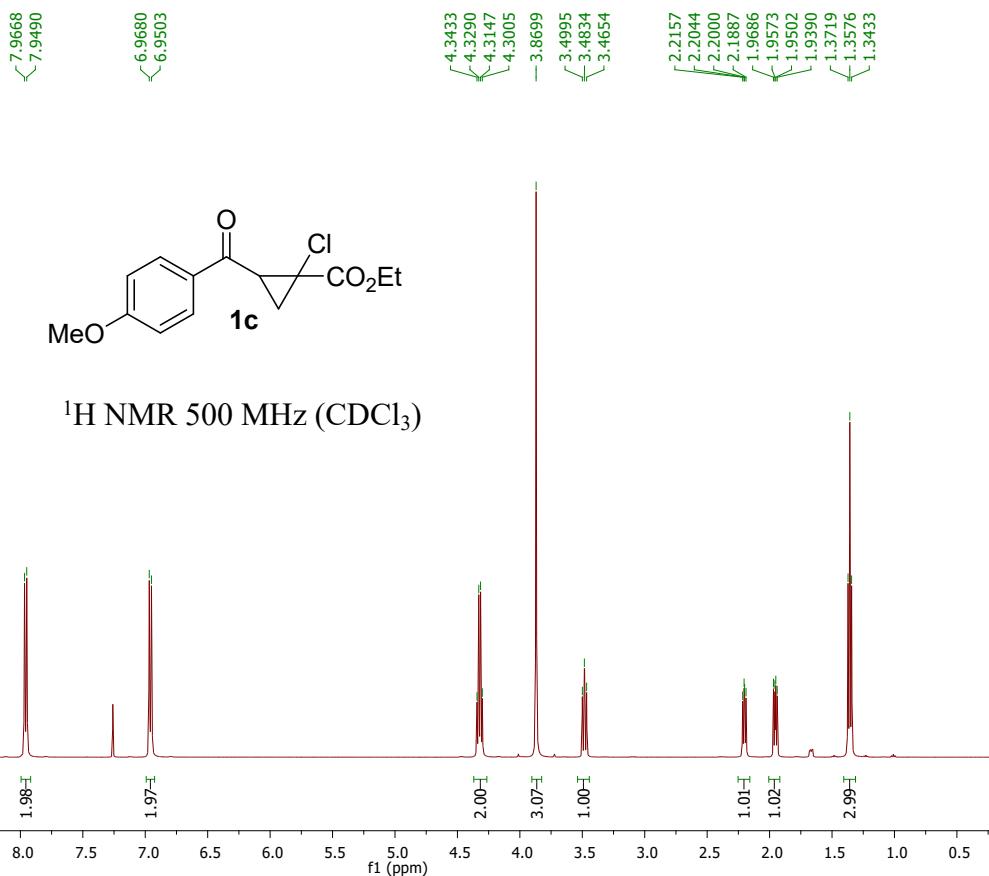
— 23.6104

— 14.2196

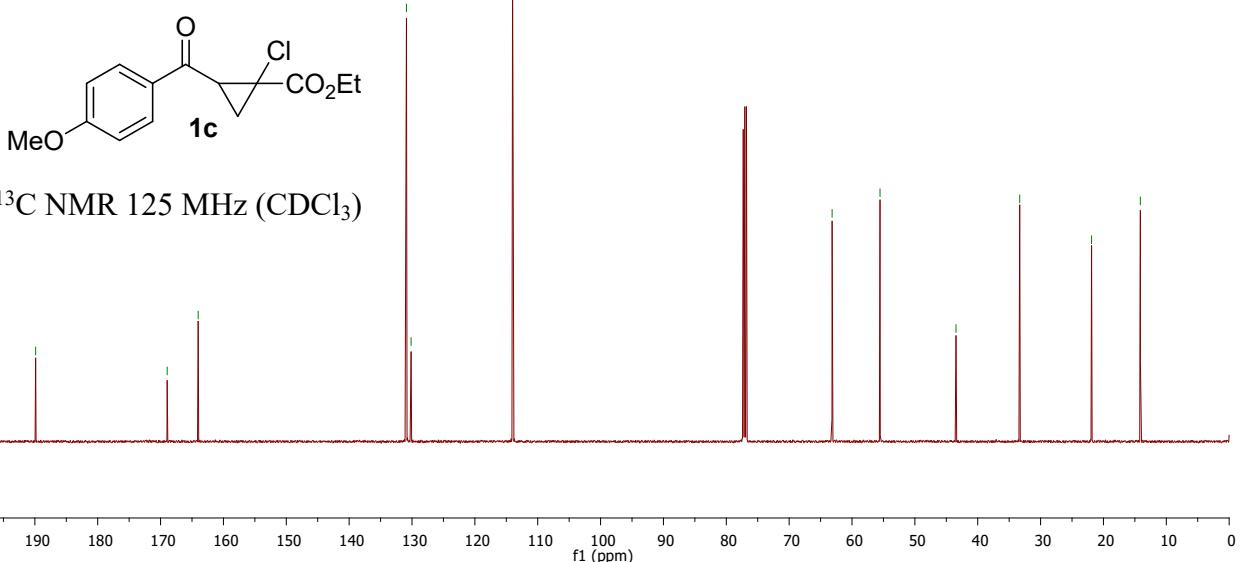


^{13}C NMR 125 MHz (CDCl_3)





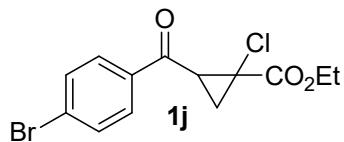
— 189.8747
 — 168.9468
 — 164.0178
 — 130.8836
 — 130.1469
 — 114.0002
 — 63.1668
 — 55.5442
 — 43.4548
 — 33.3199
 — 21.8899
 — 14.1299



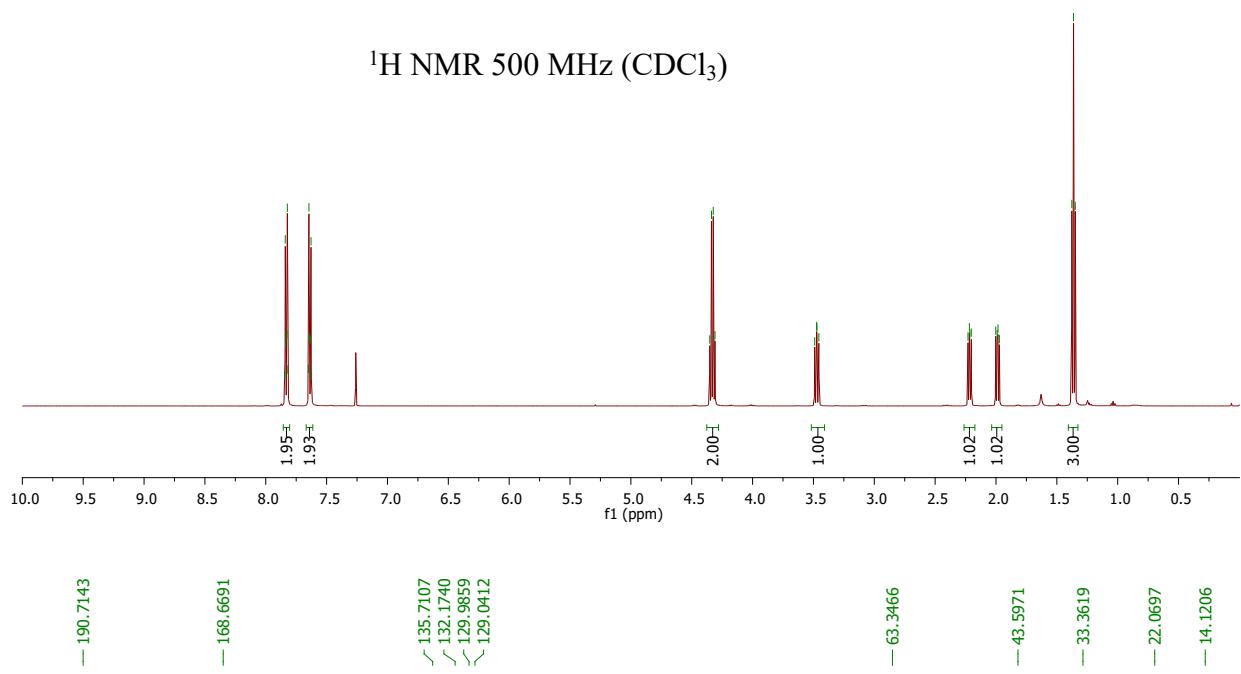
7.8944
 7.8398
 7.8360
 7.8364
 7.8225
 7.8180
 7.6999
 7.6554
 7.6416
 7.6319
 7.6282
 7.6235

4.3517
 4.3374
 4.3331
 4.3089

2.2301
 2.2187
 2.2144
 2.2030
 2.0018
 1.9904
 1.9836
 1.9722
 1.3770
 1.3627
 1.3484



¹H NMR 500 MHz (CDCl₃)



— 190.7143

— 168.6691

135.7107
 132.1740
 129.9859
 129.0412

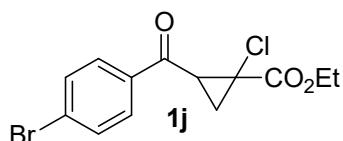
— 63.3466

— 43.5971

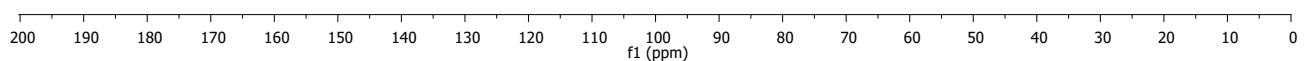
— 33.3619

— 22.0697

— 14.1206



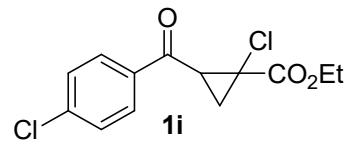
¹³C NMR 125 MHz (CDCl₃)



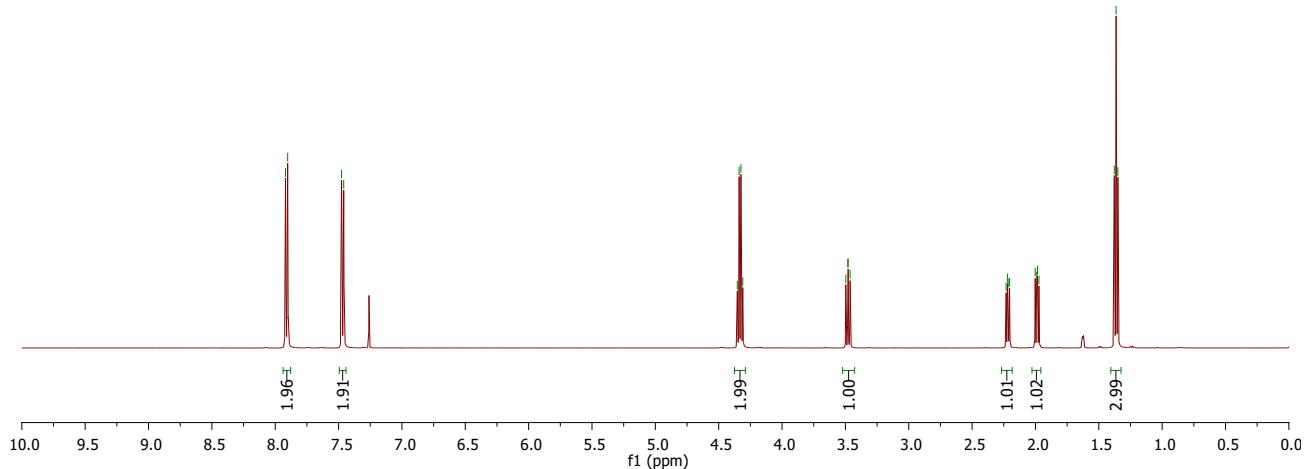
< 7.9189
 < 7.9019
 < 7.4763
 < 7.4594

4.3529
 4.3386
 4.3243
 4.3101

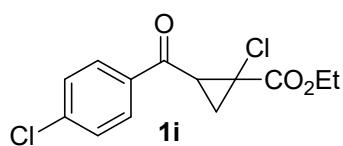
3.4966
 3.4808
 3.4785
 3.4627



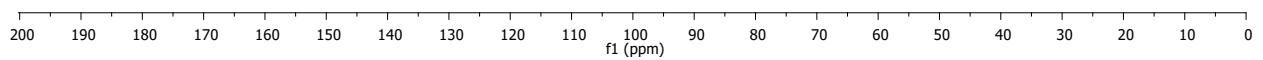
¹H NMR 500 MHz (CDCl₃)



— 190.6129
 — 168.7942
 ~ 140.3864
 ~ 135.4319
 ∫ 130.0241
 ∫ 129.2936
 — 63.4557
 — 43.7102
 — 33.4988
 — 22.1838
 — 14.2354



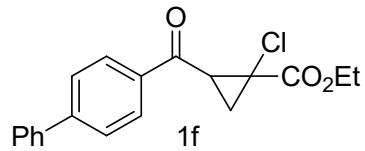
¹³C NMR 125 MHz (CDCl₃)



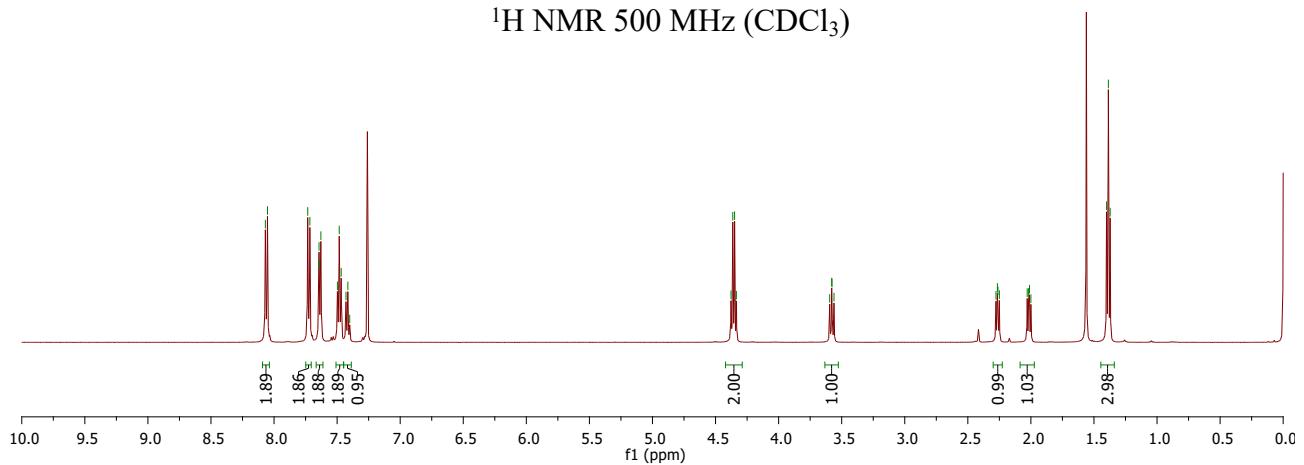
8.0689
 8.0521
 7.7330
 7.7161
 7.6660
 7.6534
 7.6334
 7.6390
 7.4976
 7.4831
 7.4676
 7.4295
 7.4148
 7.4002

4.3775
 4.3632
 4.3590
 4.3347

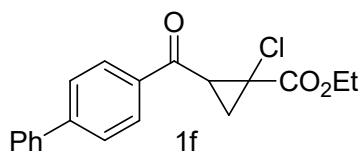
3.5949
 3.5789
 3.5770
 3.5609



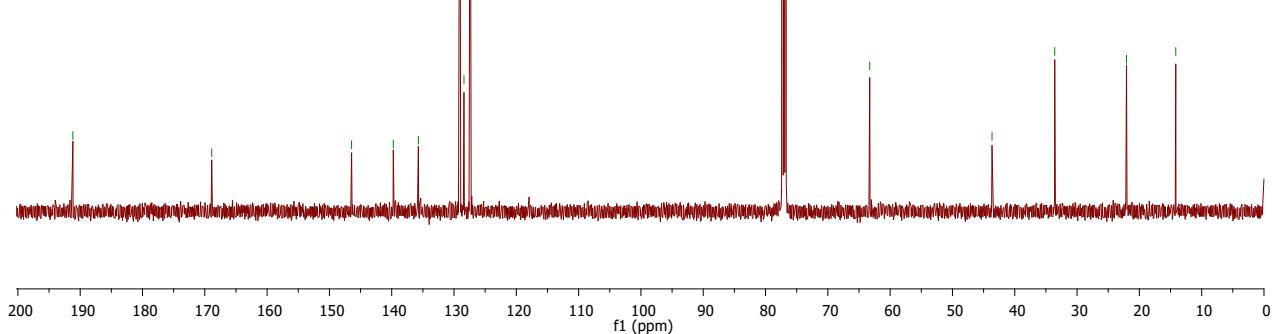
¹H NMR 500 MHz (CDCl₃)

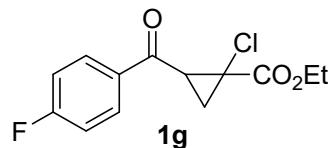


— 191.1717
 — 168.8914
 — 146.4414
 — 139.7456
 — 135.7178
 — 129.1479
 — 129.0164
 — 128.3998
 — 127.3804
 — 127.3263
 — 63.2758
 — 43.6485
 — 33.5791
 — 22.0633
 — 14.1531

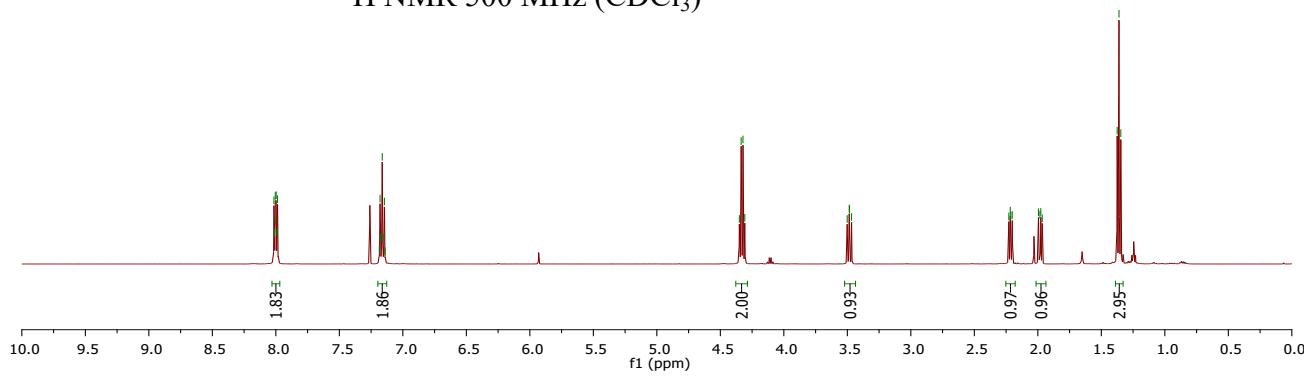


¹³C NMR 125 MHz (CDCl₃)





¹H NMR 500 MHz (CDCl₃)



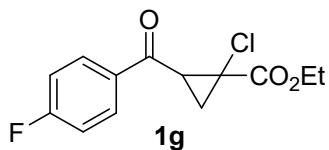
— 190.1701

— 168.8332
— 167.2391
— 165.2029

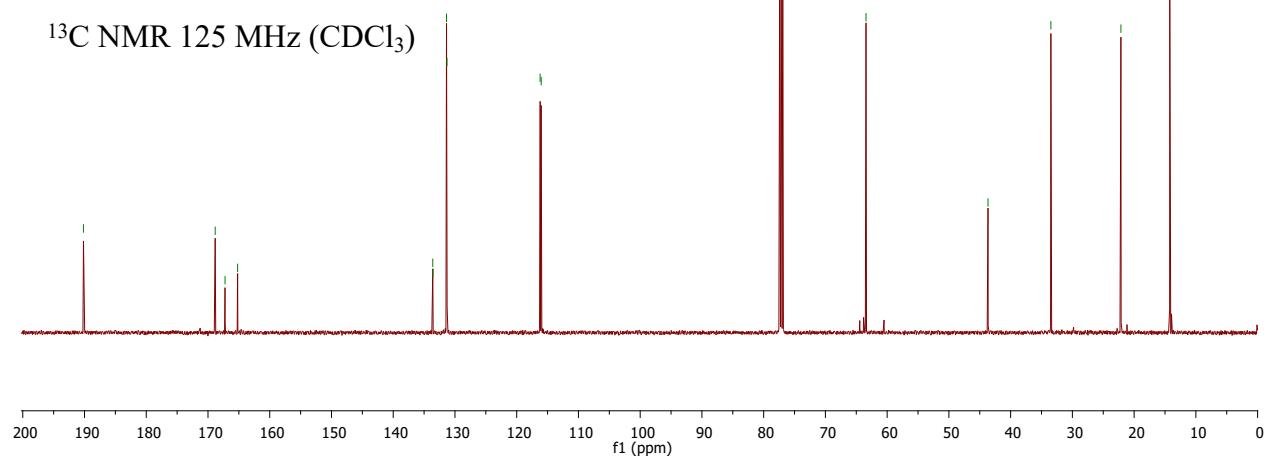
— 133.5943
— 133.5707
— 131.3660
— 131.2914

— 116.2051
— 116.0300

— 63.4230
— 43.6616
— 33.4806
— 22.1384
— 14.2249



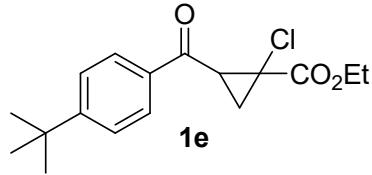
¹³C NMR 125 MHz (CDCl₃)



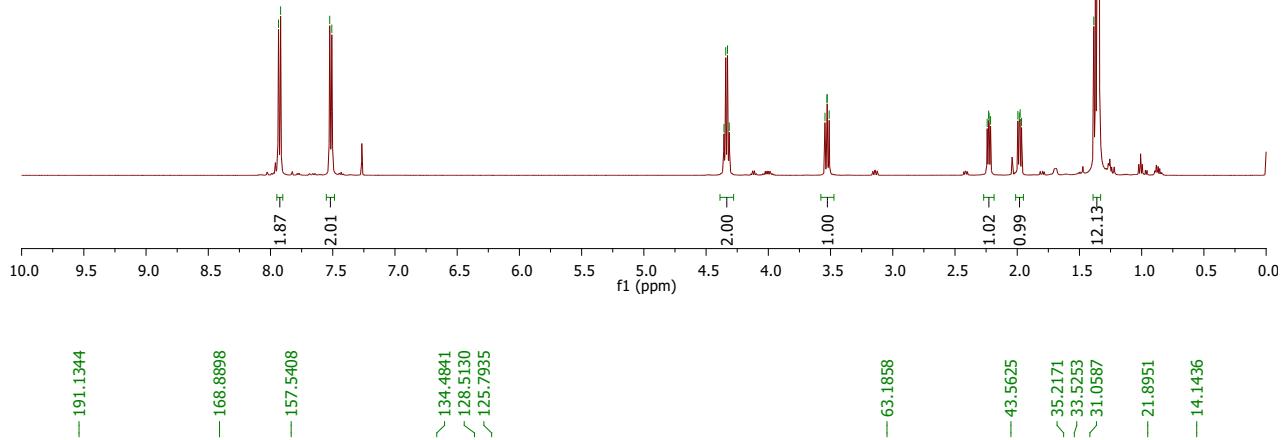
7.957
 7.9189
 7.5343
 7.5076

4.3564
 4.3222
 4.3279
 4.3137

3.549
 3.5287
 3.5269
 3.5108



¹H NMR 500 MHz (CDCl_3)



— 191.1344

— 168.8898

— 157.5408

~ 134.4841
 ✓ 128.5130
 ✓ 125.7955

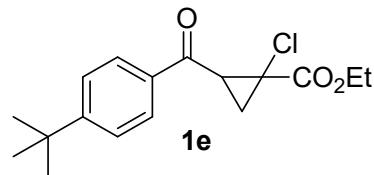
— 63.1858

— 43.5625

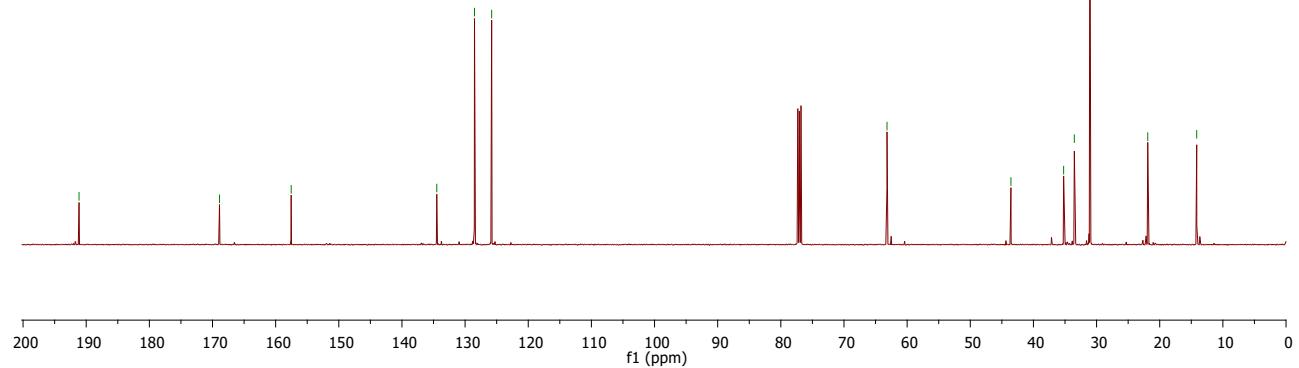
✓ 35.2171
 ✓ 33.5253
 ~ 31.0587

— 21.8951

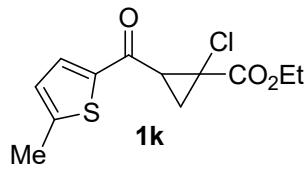
— 14.1436



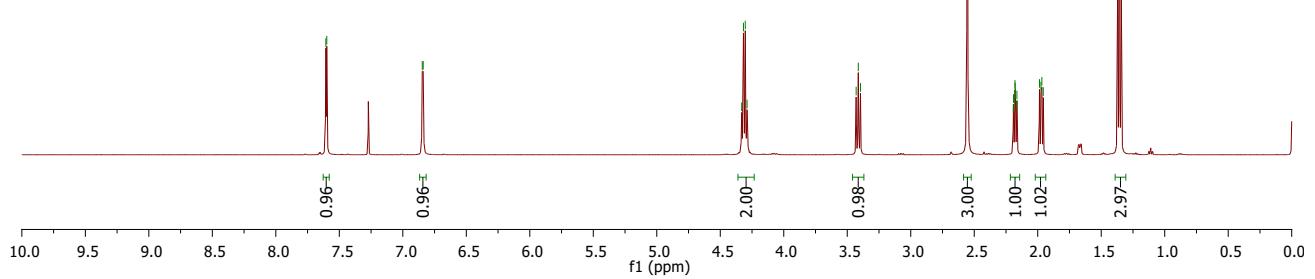
¹³C NMR 125 MHz (CDCl_3)



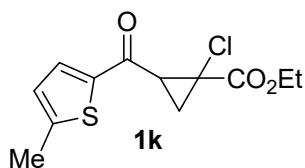
7.6061
 7.5986
 6.8468
 6.8394
 4.3314
 4.3172
 4.3031
 4.2889



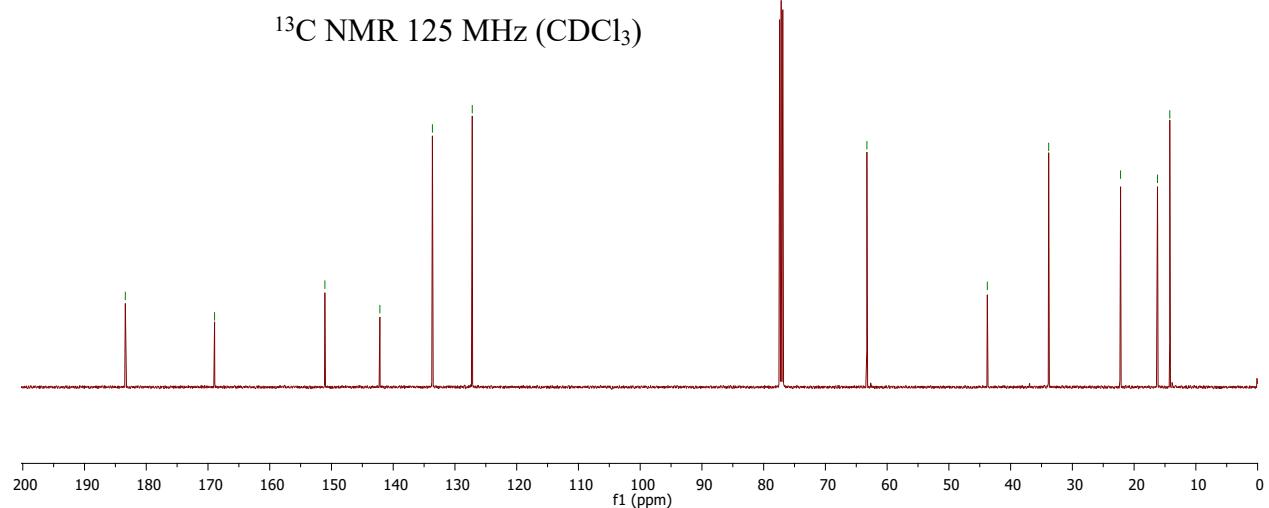
¹H NMR 500 MHz (CDCl_3)

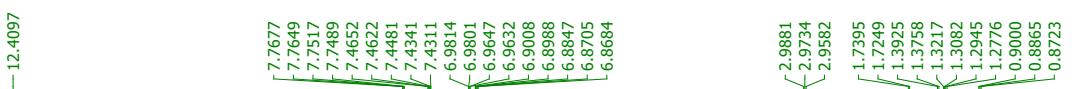


183.3919
 168.9348
 151.0685
 142.1602
 133.6507
 127.1979
 63.2813
 43.7746
 33.8381
 ~22.1983
 / 16.2118
 / 14.2229

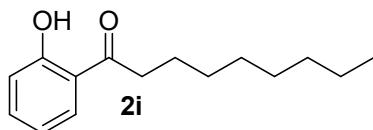
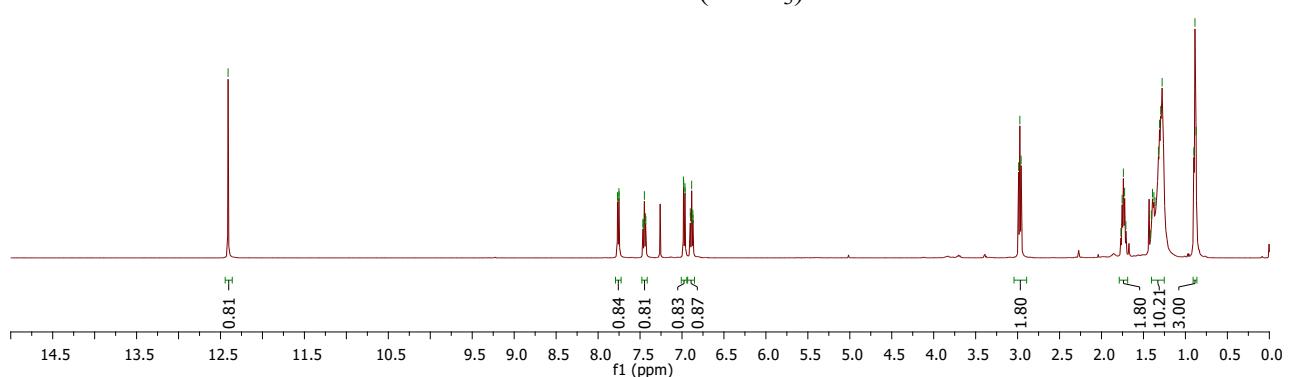


¹³C NMR 125 MHz (CDCl_3)





¹H NMR 500 MHz (CDCl₃)



¹³C NMR 125 MHz (CDCl₃)

