

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 ($\lambda = 0.71073$ Å). 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 1.2*U*_{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).

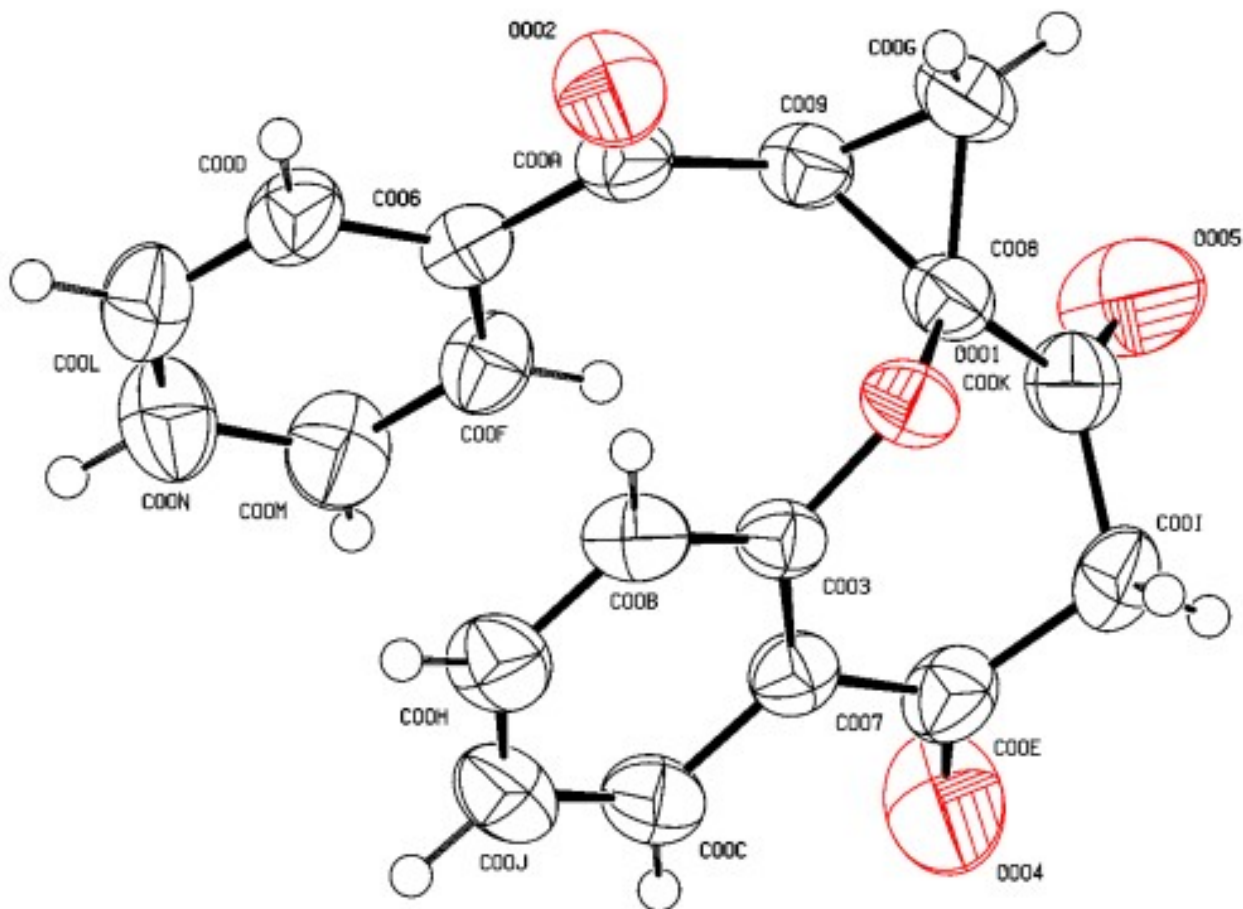


Figure S1. ORTEP diagram of compound **3aa**(CCDC 2233544), thermal ellipsoids drawn at the 50% probability level.

Table S1. Crystal data for compound 3aa.

Compound	3aa
Empirical formula	C ₁₉ H ₁₄ O ₄
Formula weight	306.32
Temperature	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 (°)	α = 85.100(6) deg.
β (°)	β = 81.305(6) deg.
γ (°)	γ = 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 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 12, -11 ≤ <i>l</i> ≤ 13
Reflections collected / unique	6876 / 3484 [R(int) = 0.0307]
Completeness to $\Theta = 25.242$	99.8 %
Max. and min. transmission	1.00000 and 0.40828
Absorption correction	none
Data / restraints / parameters	3484 / 0 / 209
Goodness-of-fit on F ²	1.0415
Final R indices [I > 2σ(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.Å ⁻³)	0.2762 and -0.2872 e.Å ⁻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 ($\lambda = 0.71073$ Å). 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).

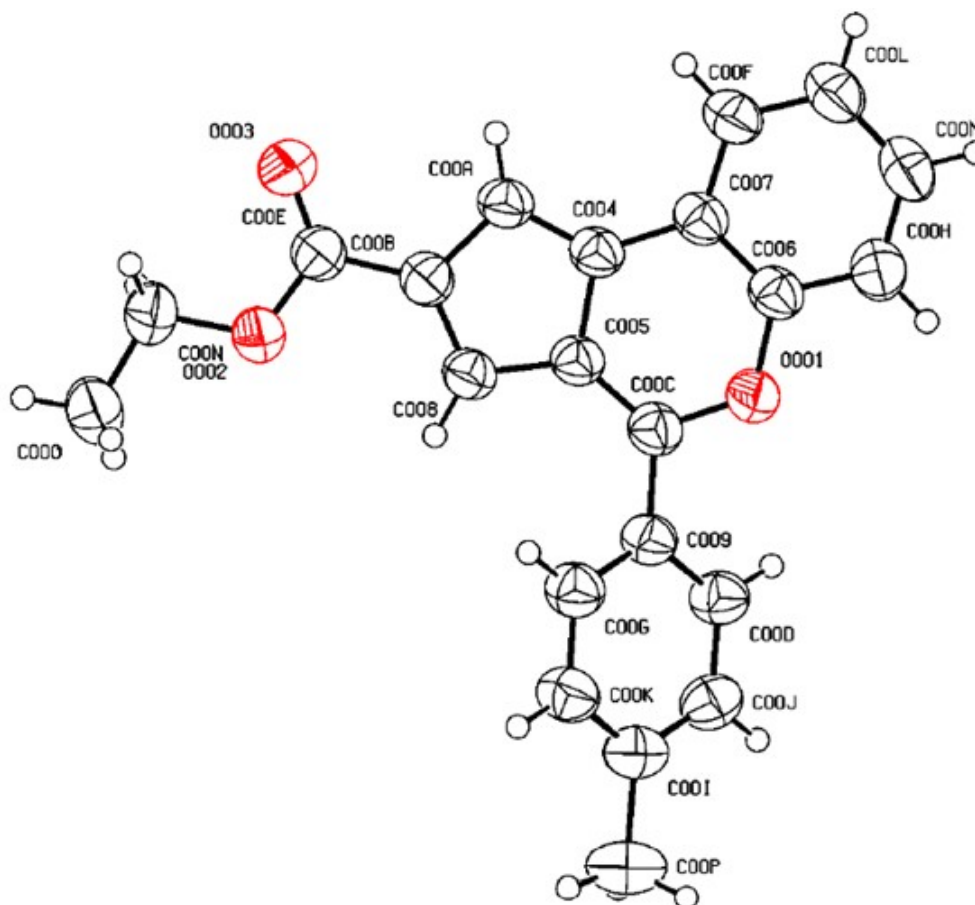
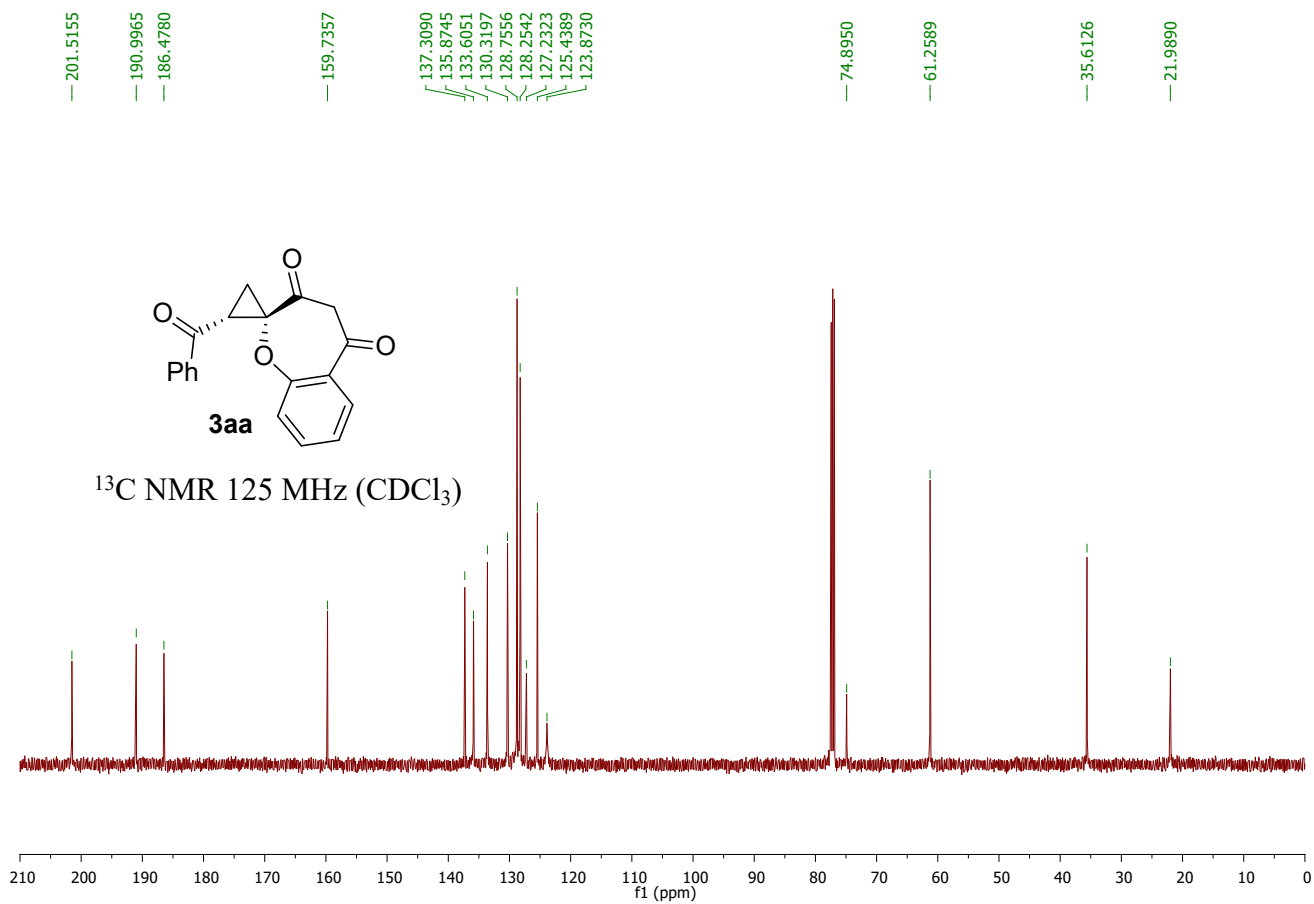
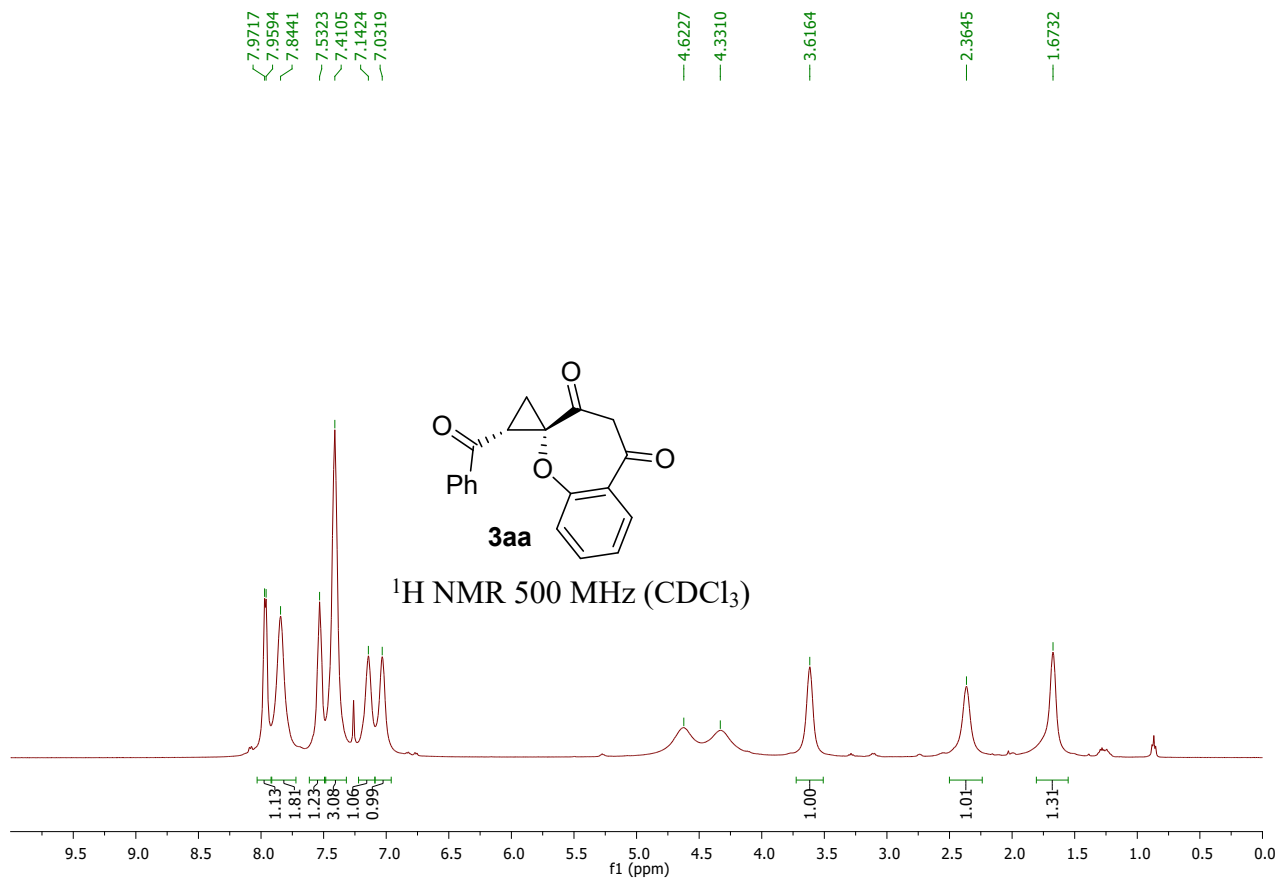
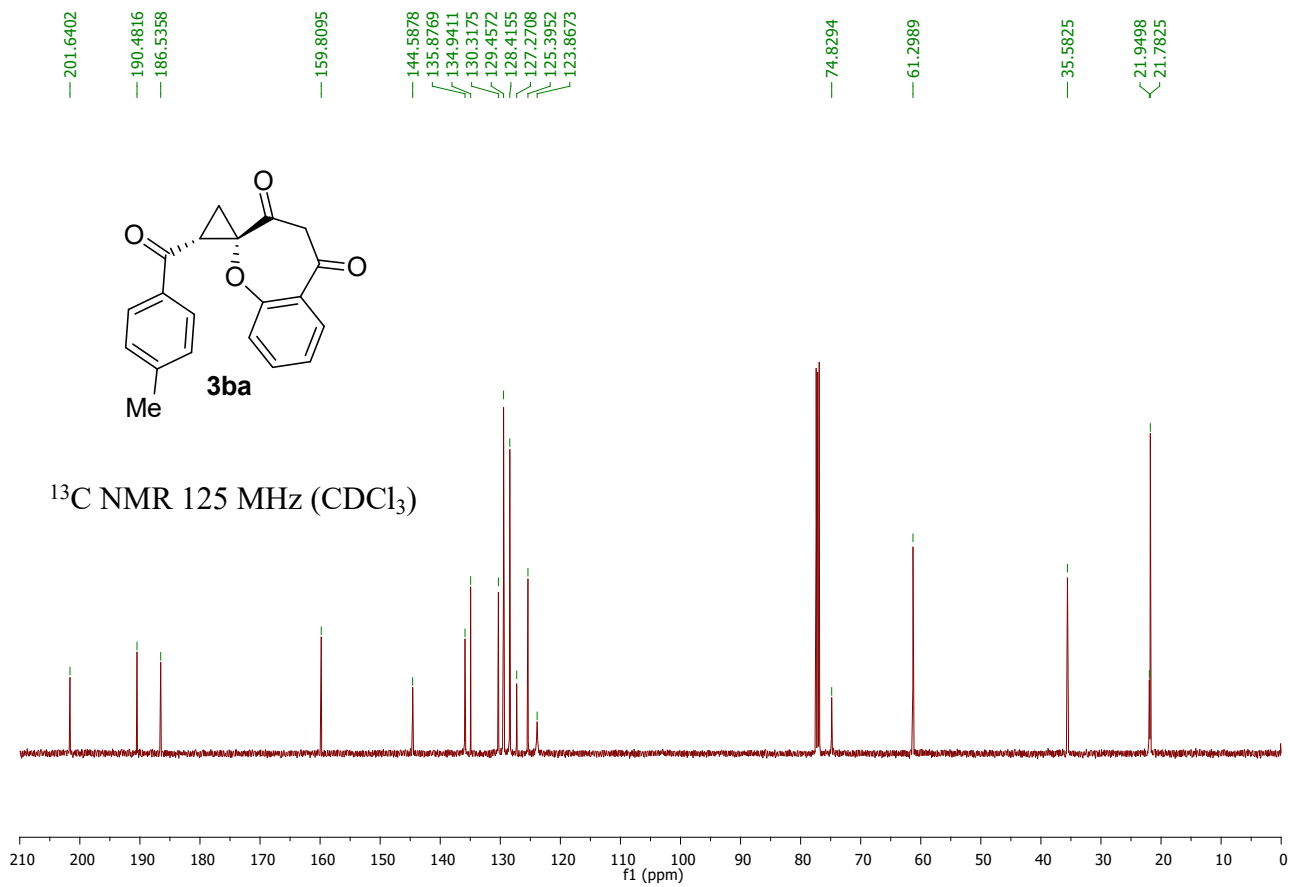
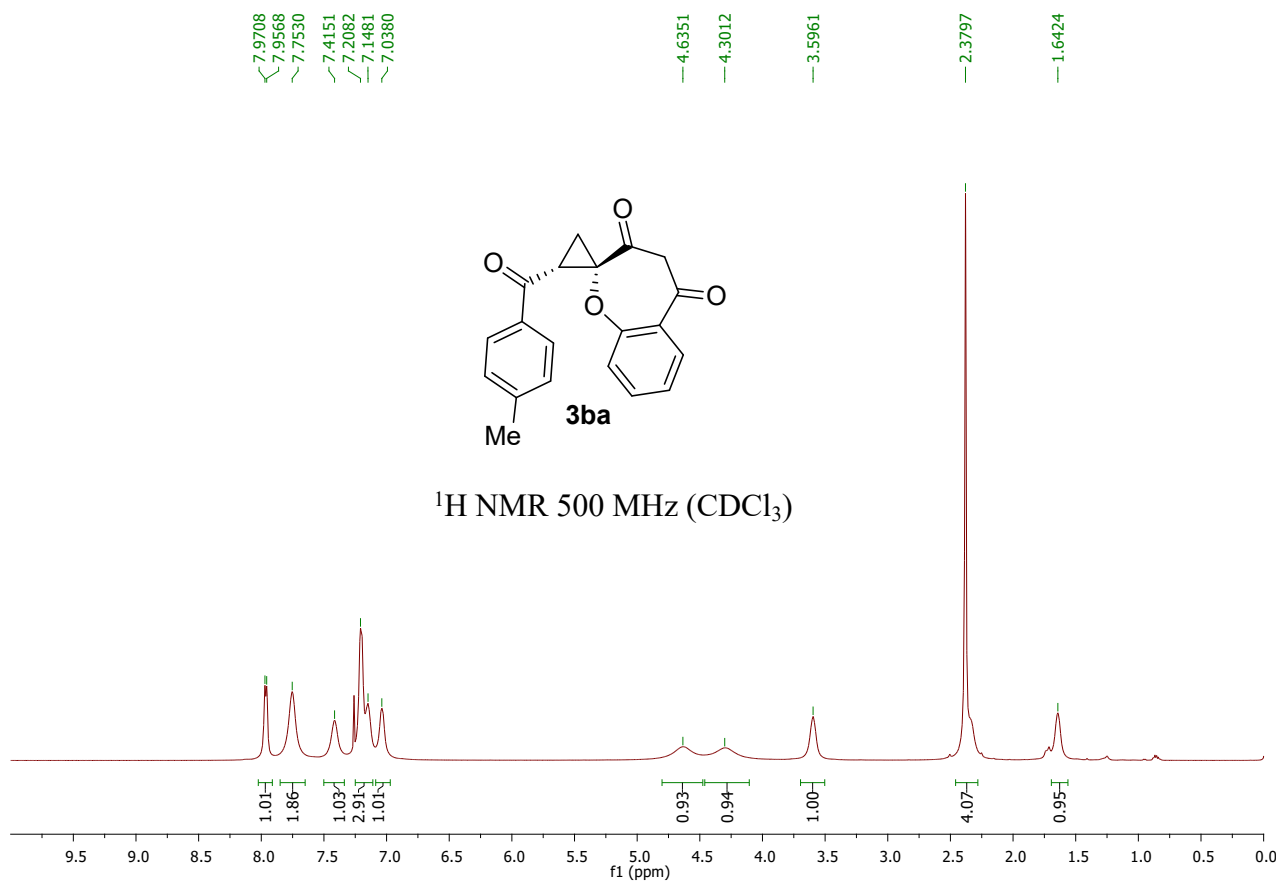


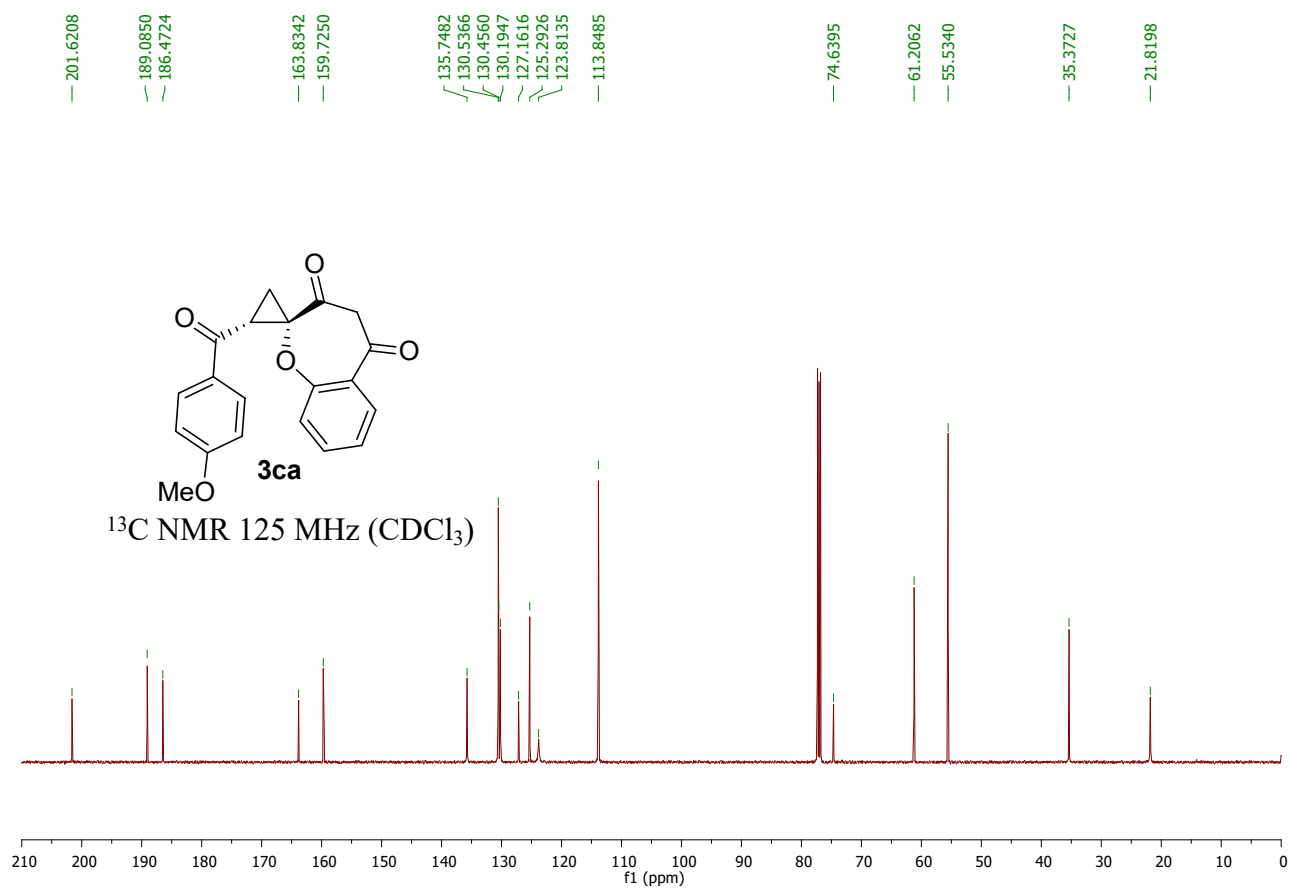
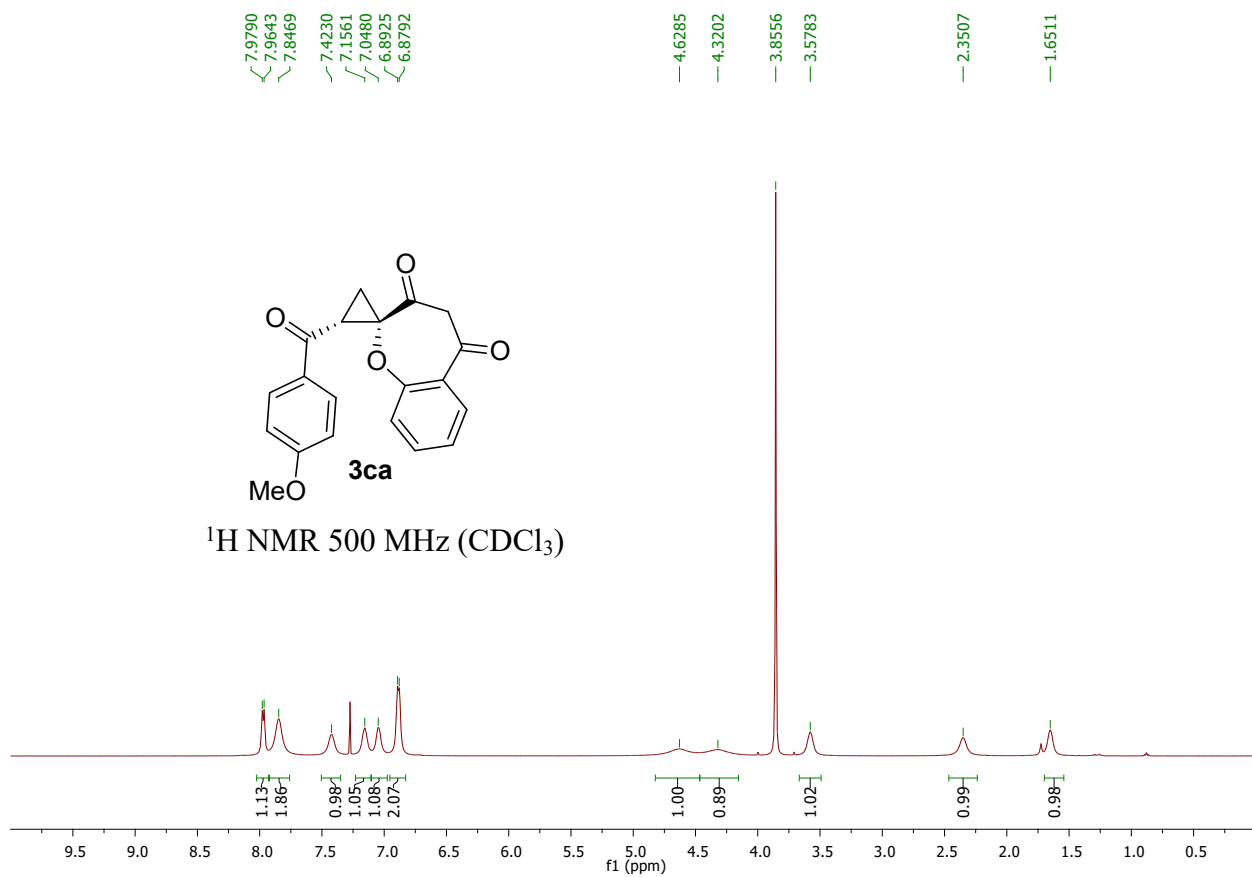
Figure S2 . ORTEP diagram of compound **5ba**, thermal ellipsoids drawn at the 50% probability level.

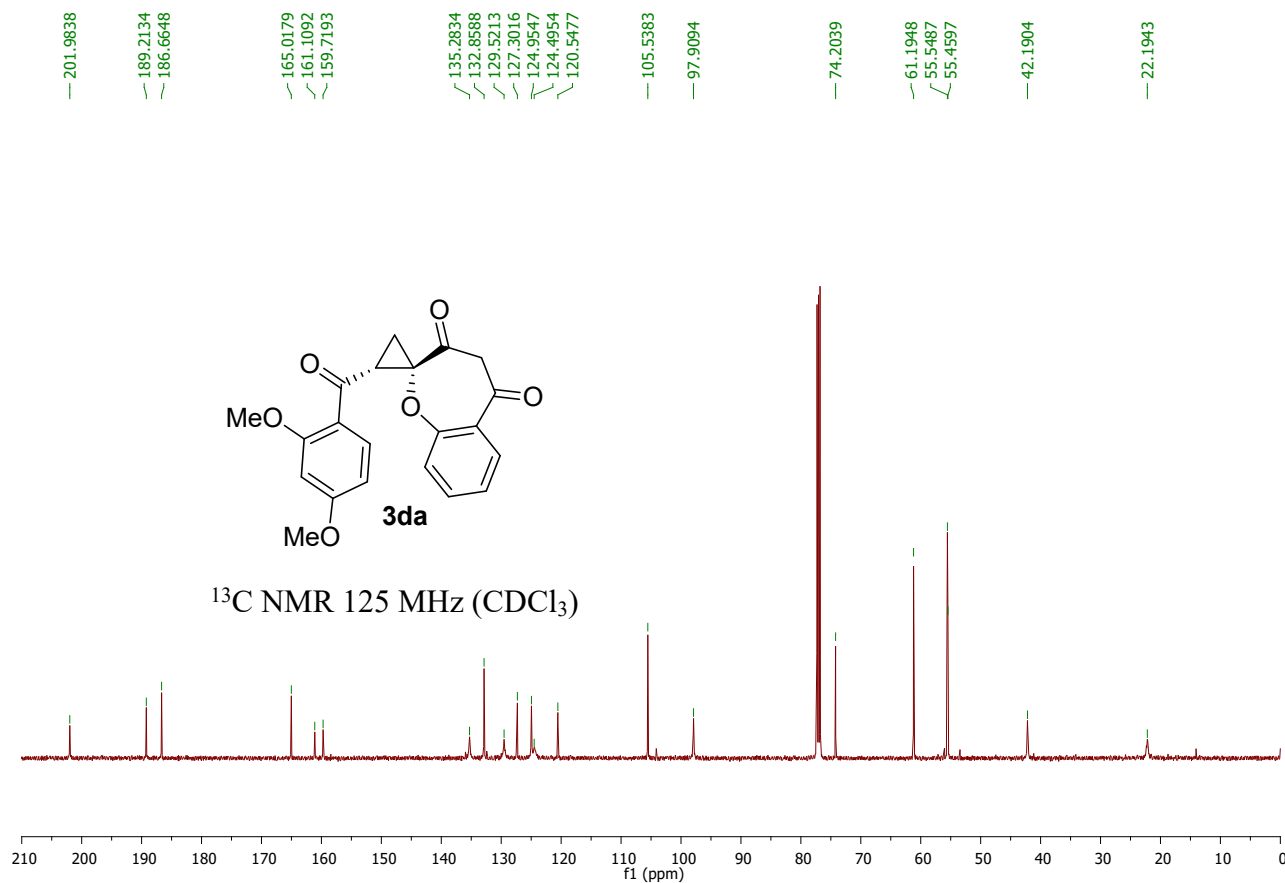
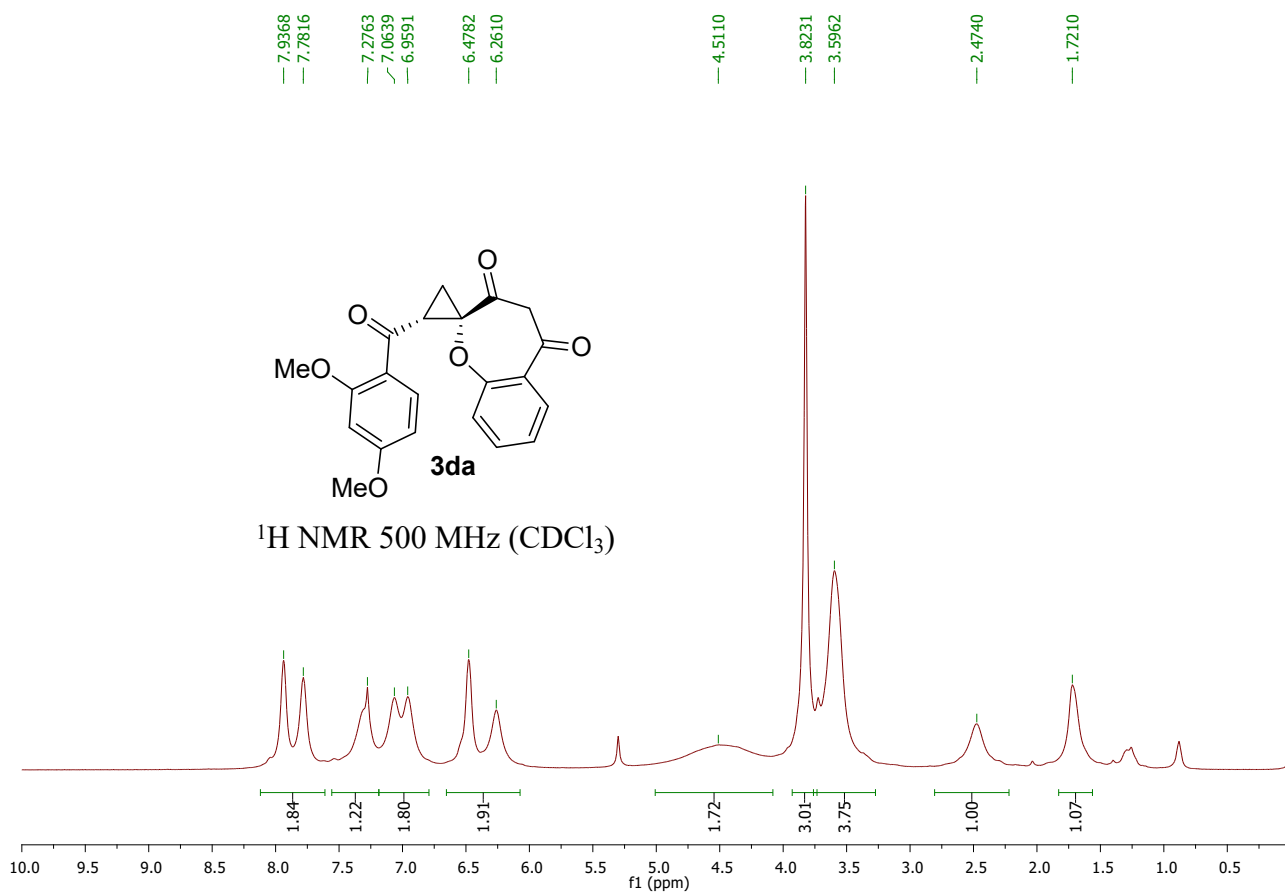
Table S2. Crystal data for compound 5ba.

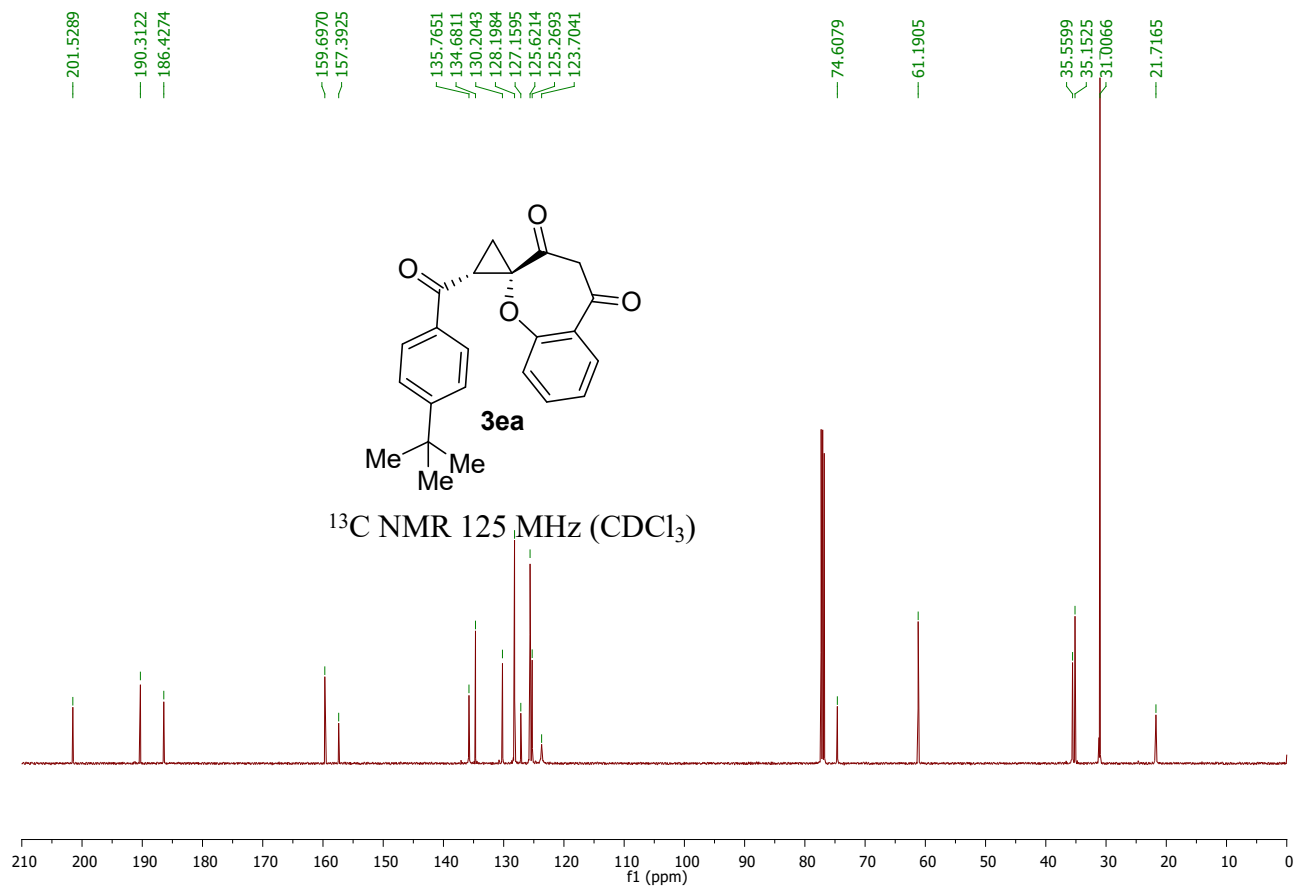
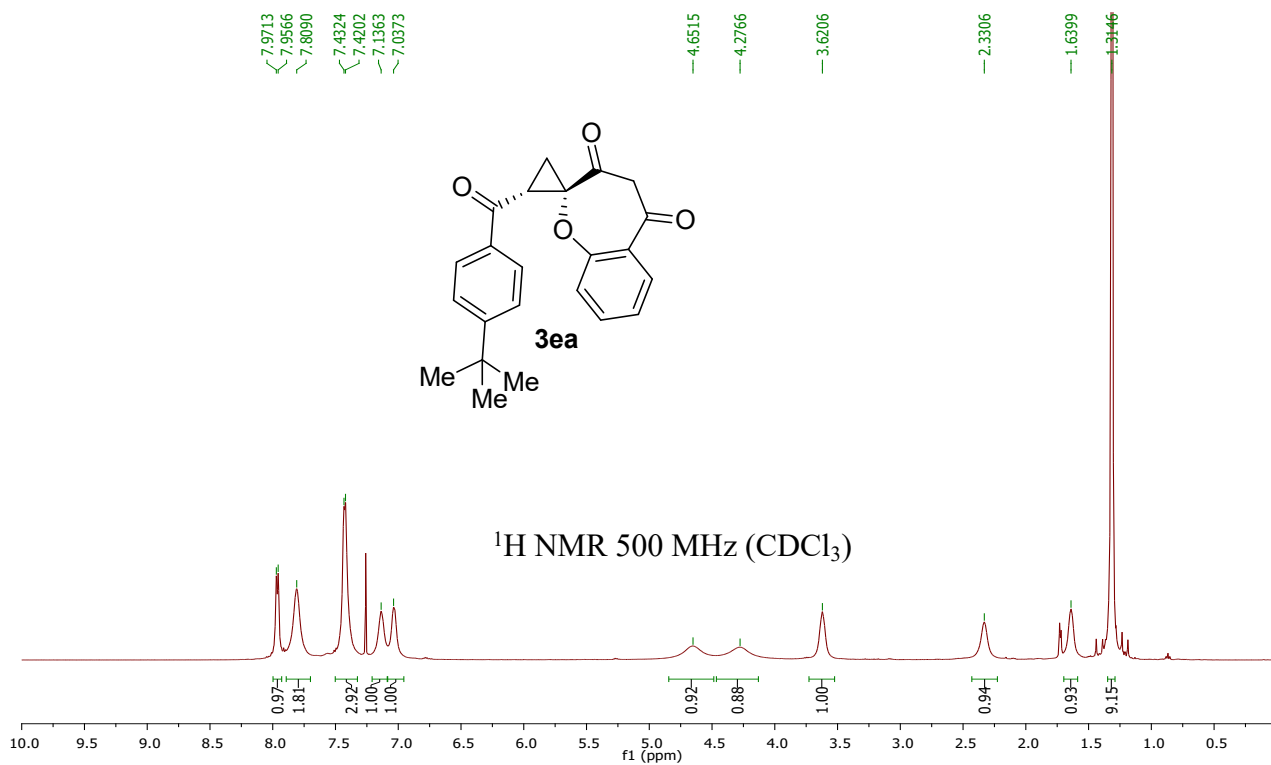
Compound	5ba
Empirical formula	C ₂₂ H ₁₈ O ₃
Formula weight	330.39
Temperature	293 K
Wave length (Å)	0.71073 Å
Crystal system, space group	Monoclinic, C 1 2/c 1
<i>a</i> (Å)	<i>a</i> = 11.8421(3) Å
<i>b</i> (Å)	<i>b</i> = 14.4124(5) Å
<i>c</i> (Å)	<i>c</i> = 20.4372(7) Å
α (°)	α = 90 deg.
β (°)	β = 101.814(3) deg.
γ (°)	γ = 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 ≤ <i>h</i> ≤ 14, -12 ≤ <i>k</i> ≤ 17, -23 ≤ <i>l</i> ≤ 25
Reflections collected / unique	12340 / 3284 [R(int) = 0.0996]
Completeness to $\Theta = 25.242$	97.9 %
Max. and min. transmission	1.00000 and 0.25768
Absorption correction	none
Data / restraints / parameters	2308 / 0 / 229
Goodness-of-fit on F ²	1.0358
Final R indices [<i>I</i> > 2σ(<i>I</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.Å ⁻³)	0.3462 and -0.2904 e.Å ⁻³
CCDC	2239029

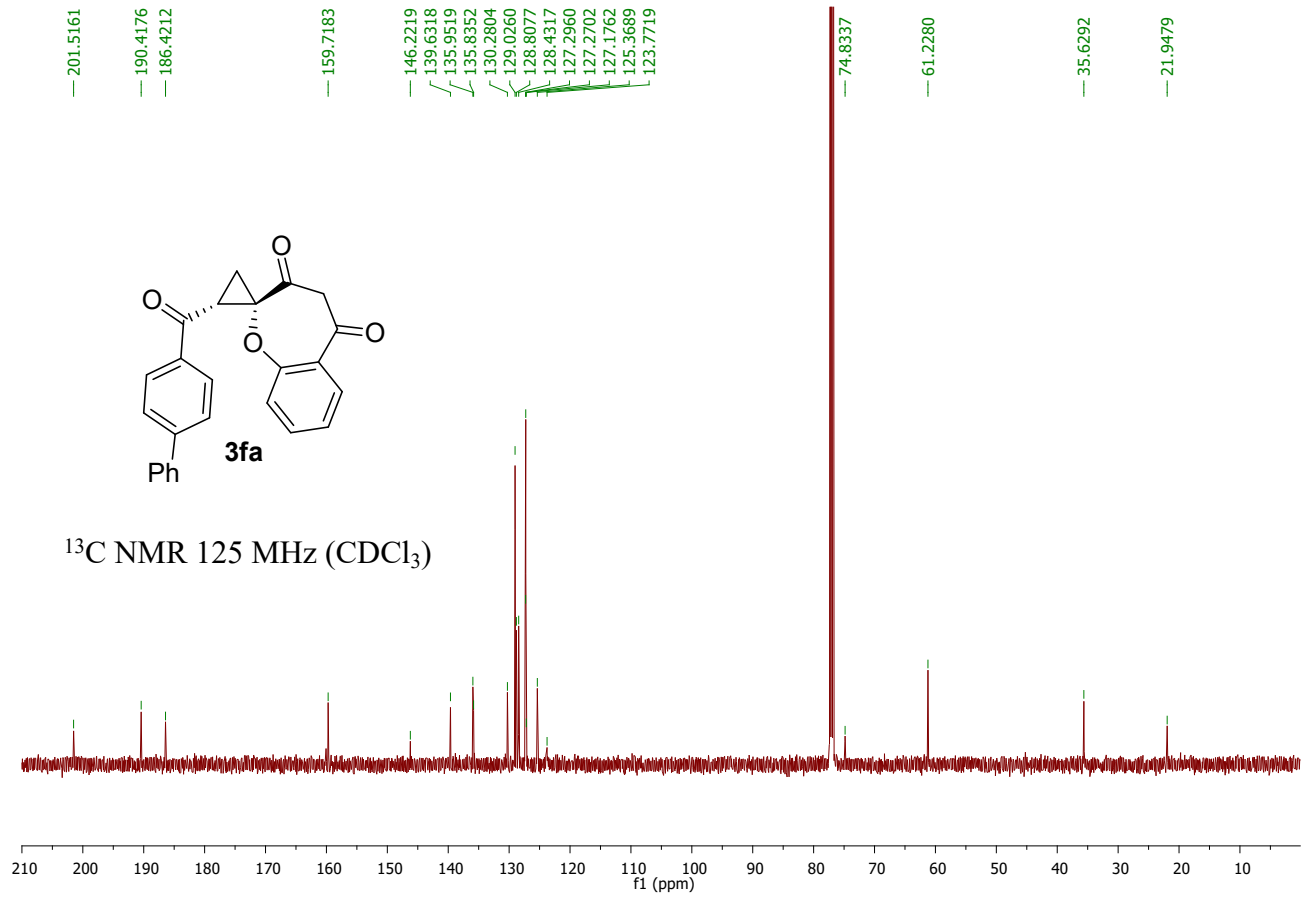
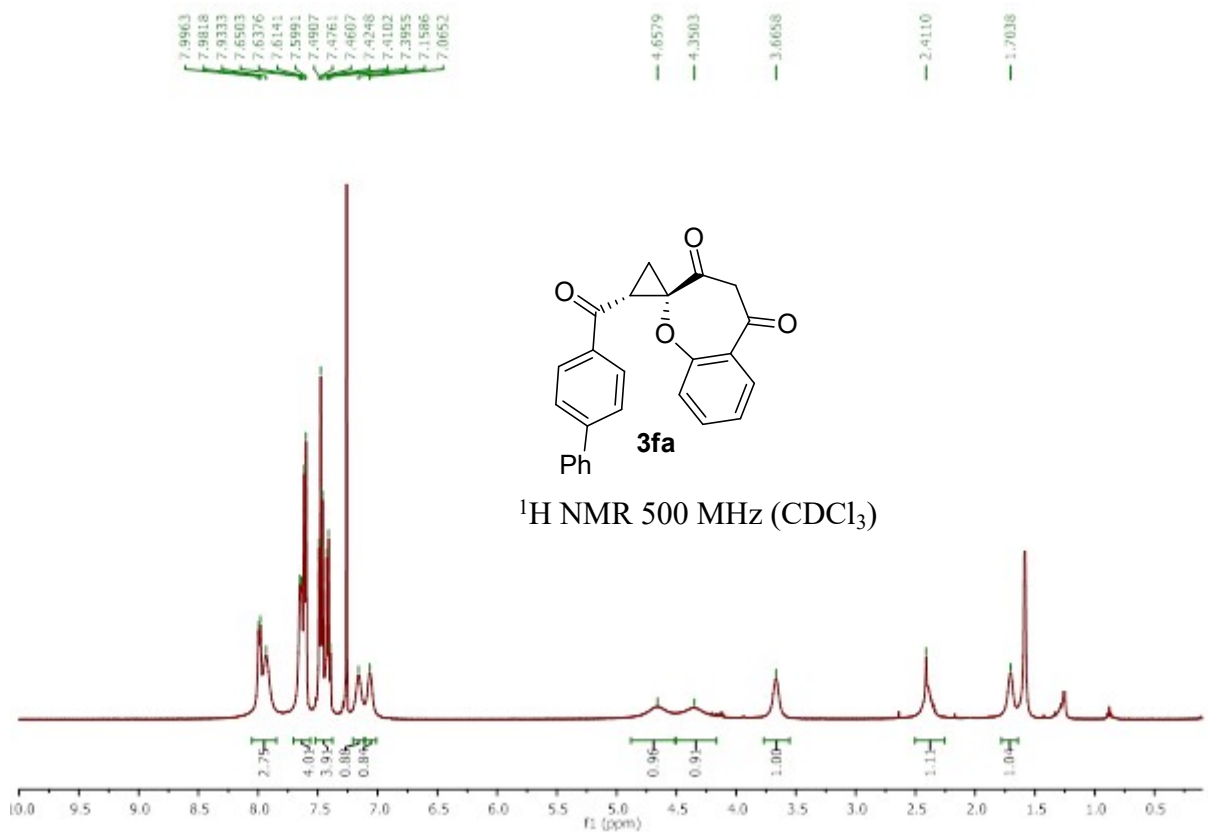


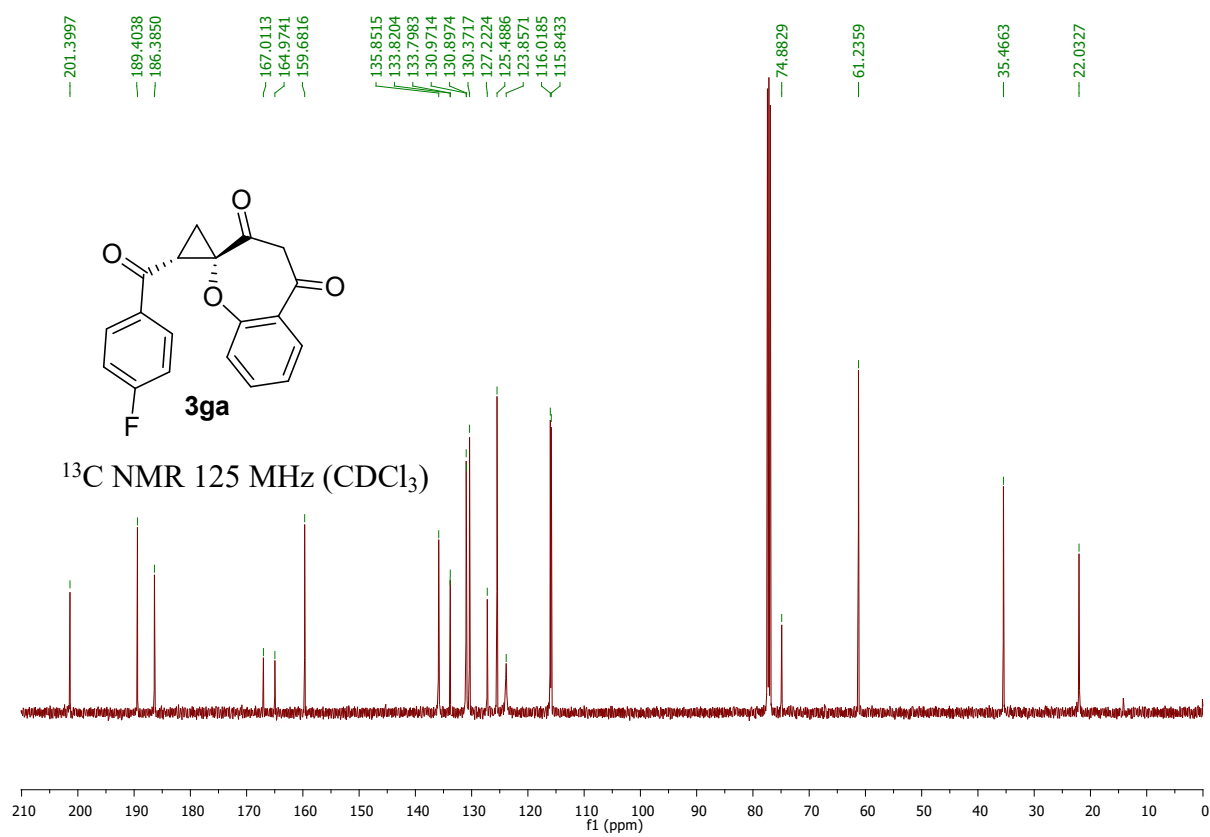
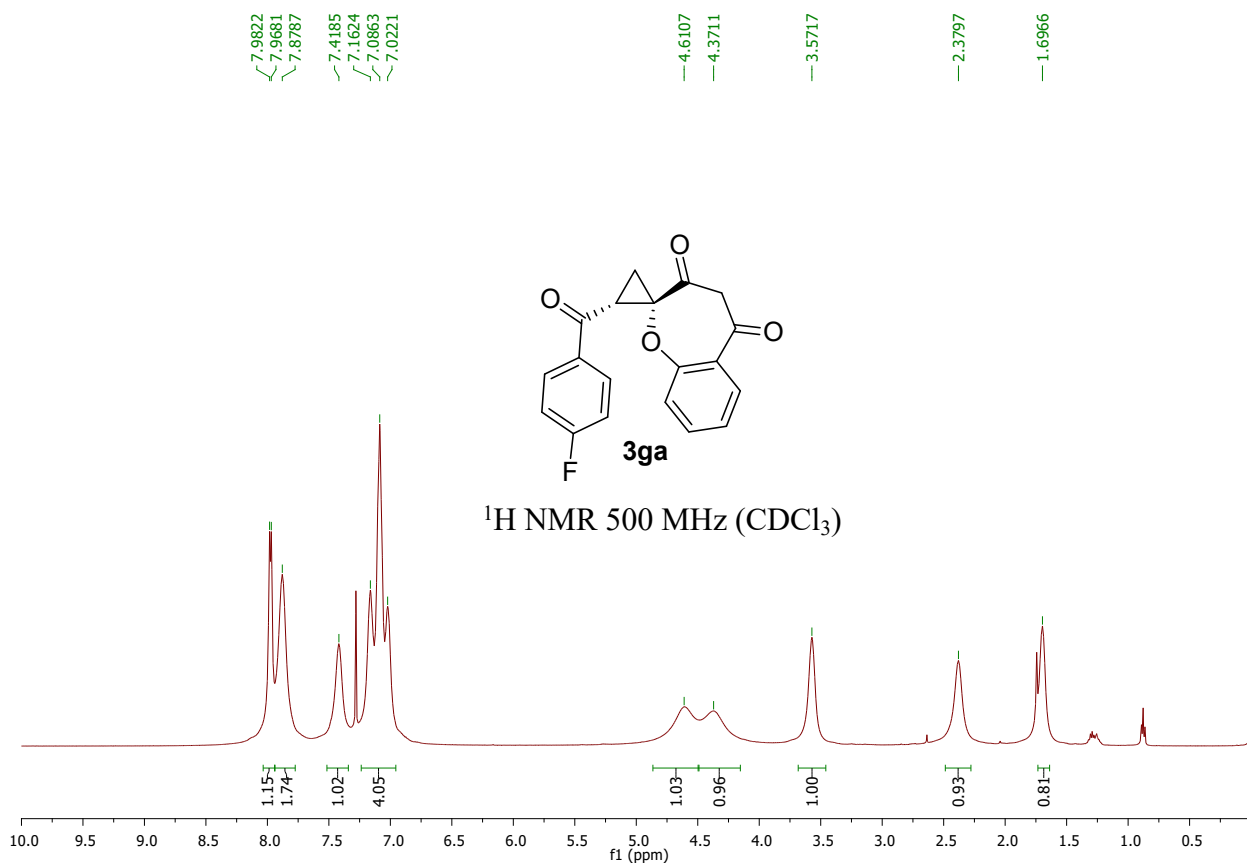


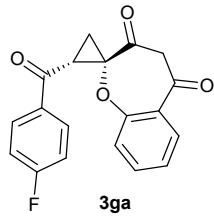




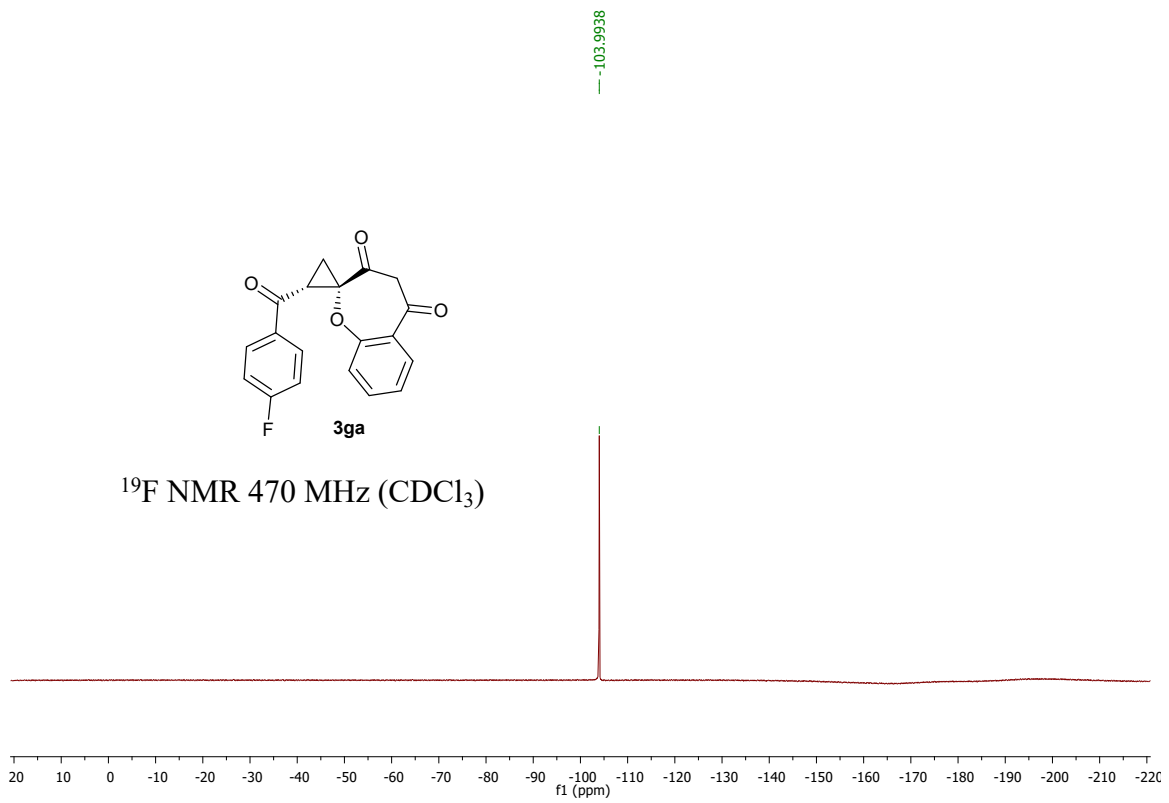


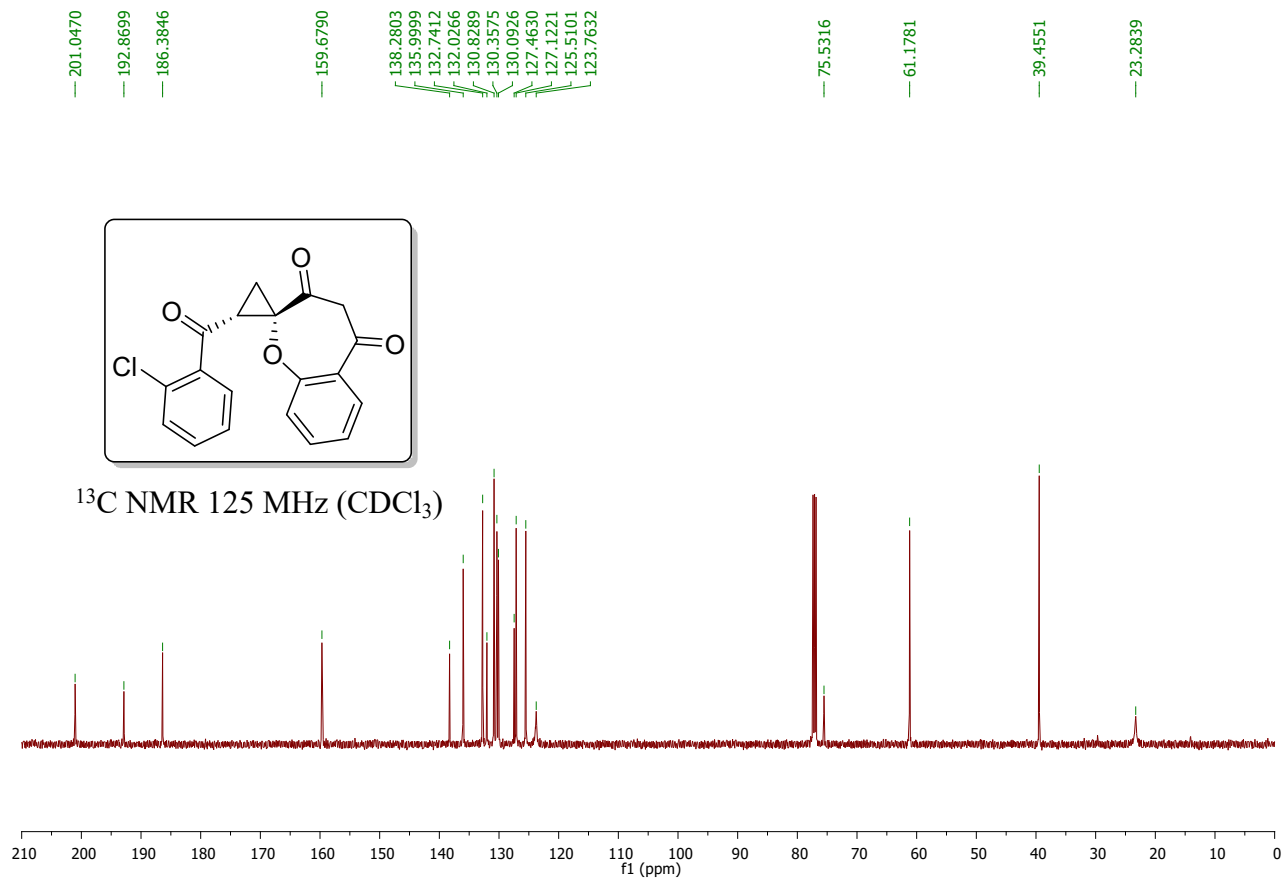
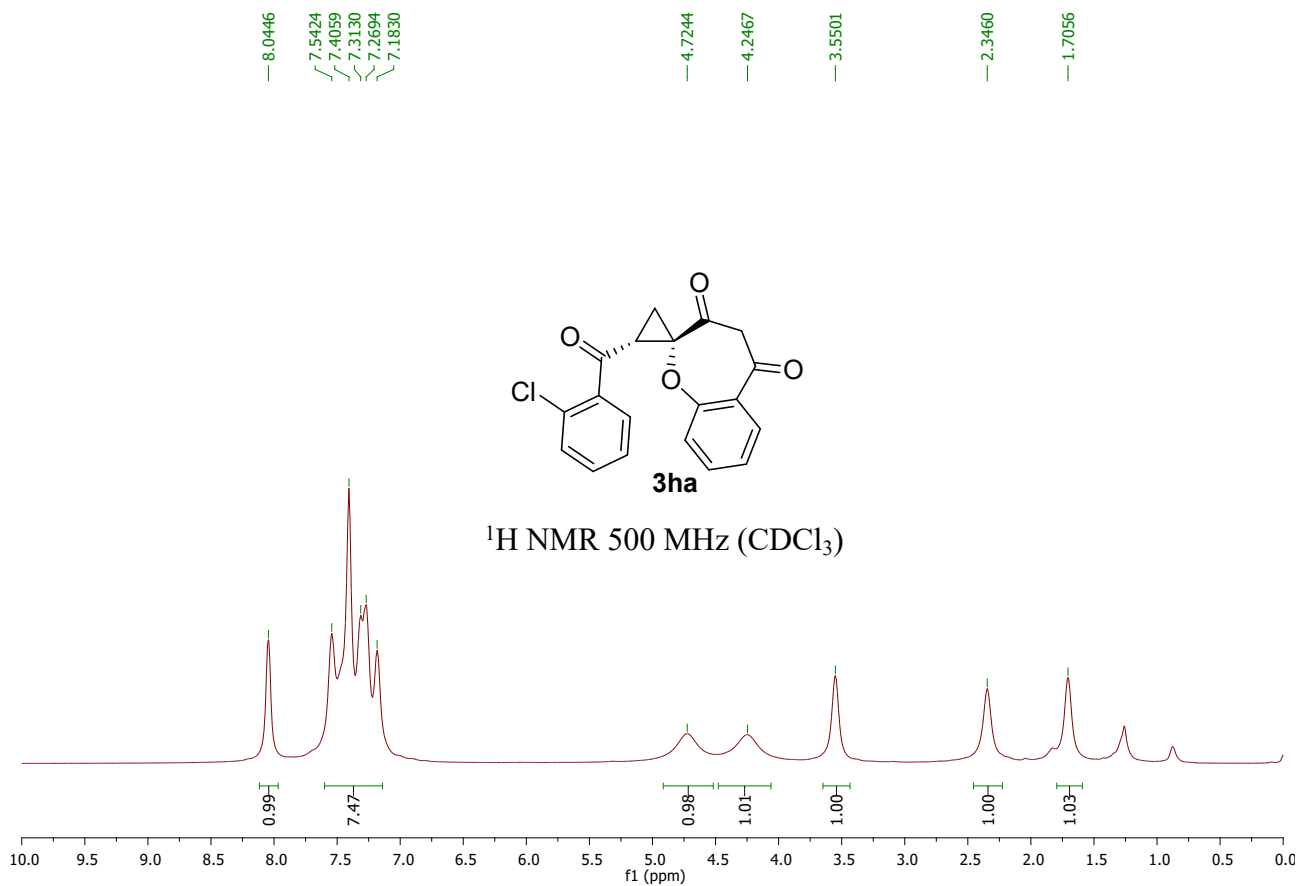






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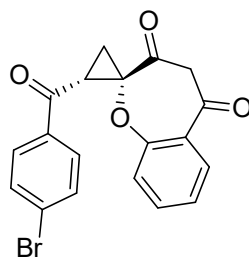
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7.4233
7.1726
7.0124

4.6054
4.3670

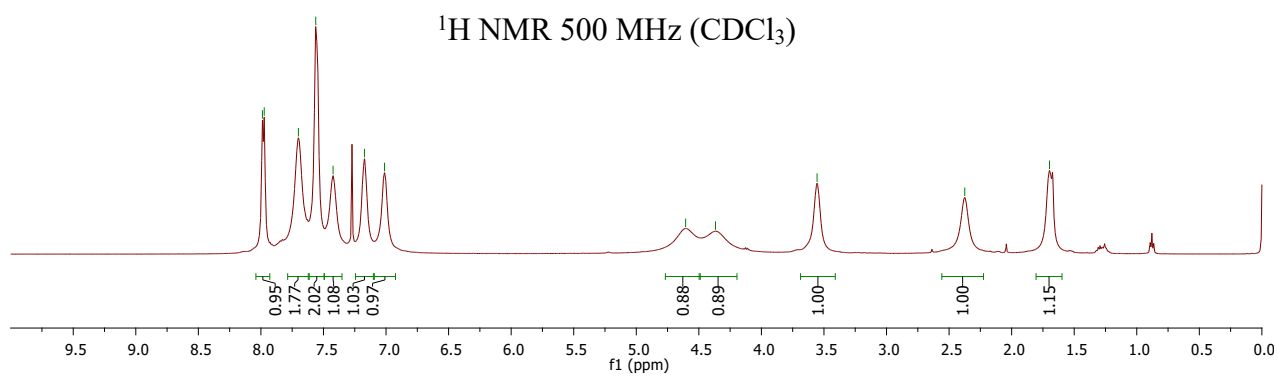
3.5550

2.3746

1.6972



^1H NMR 500 MHz (CDCl_3)



201.2443

189.9870

186.2534

159.5655

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135.8063

132.0003

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129.6093

128.8259

127.1181

125.4371

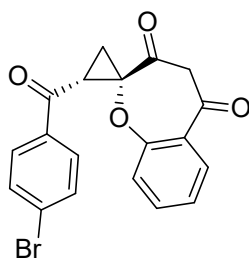
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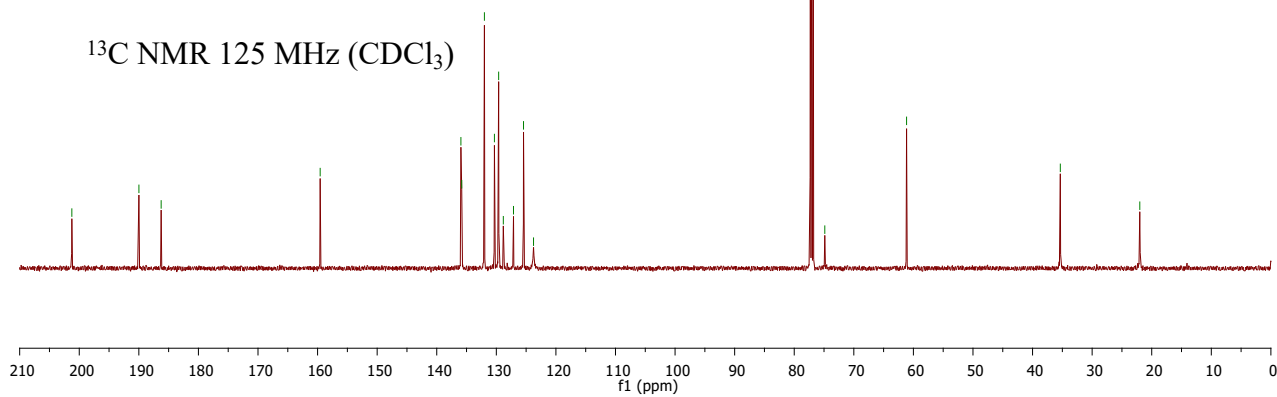
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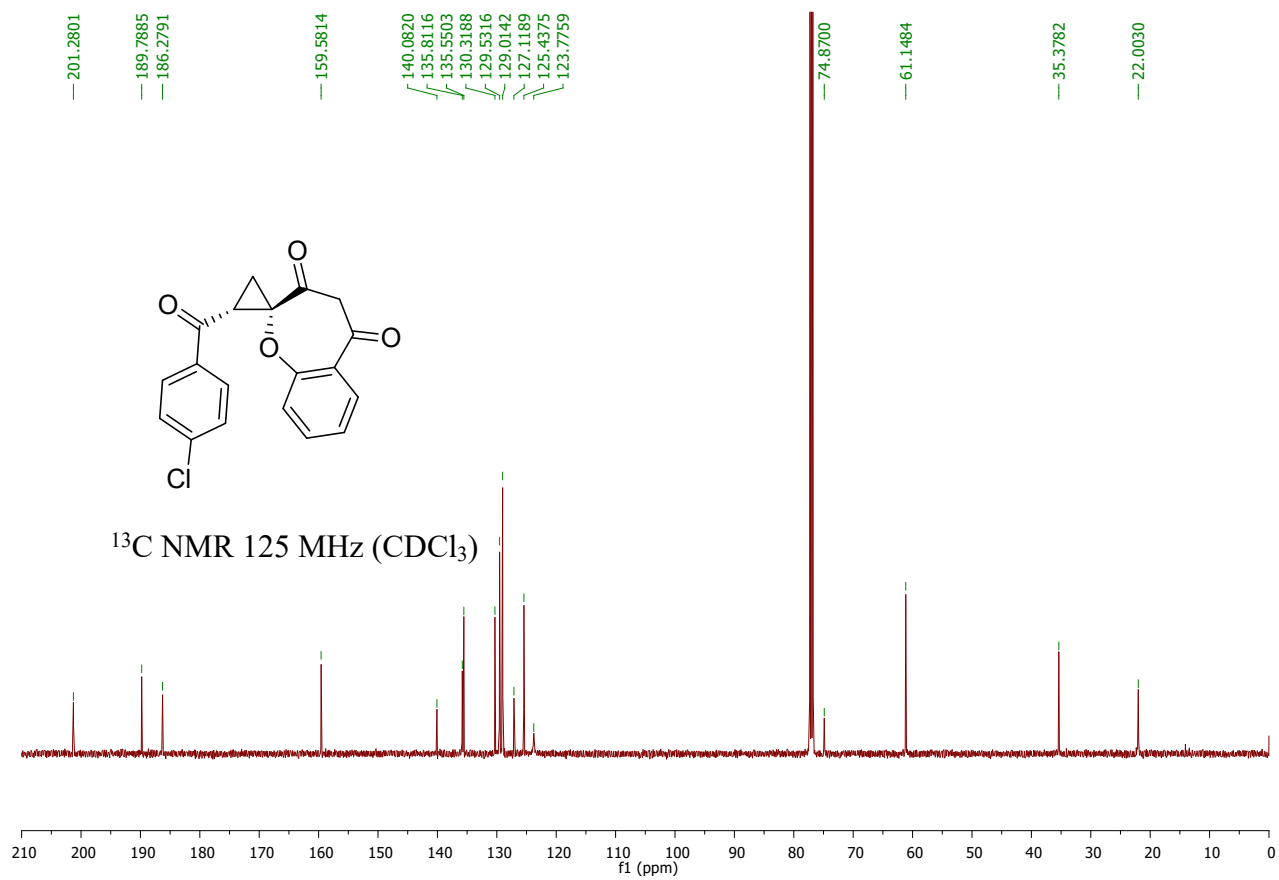
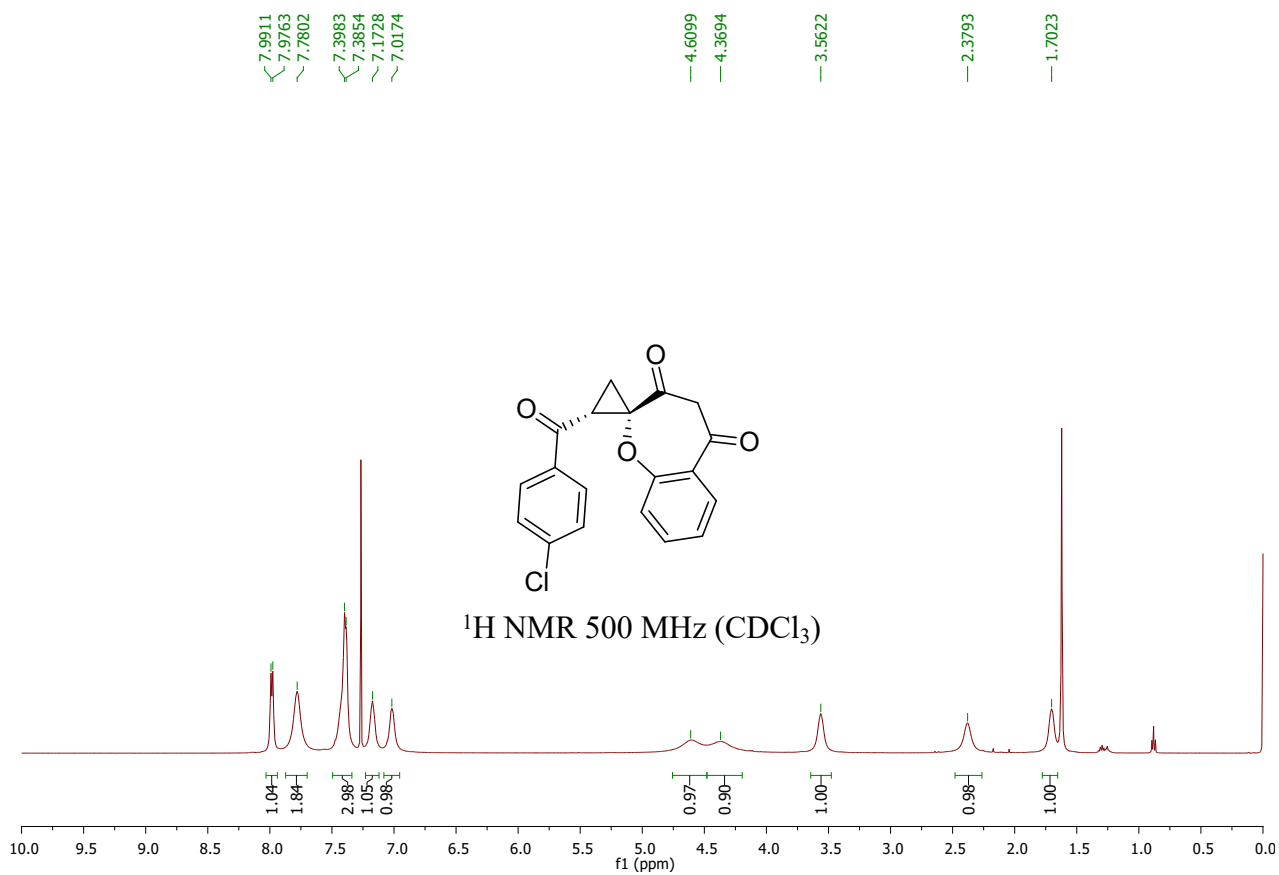
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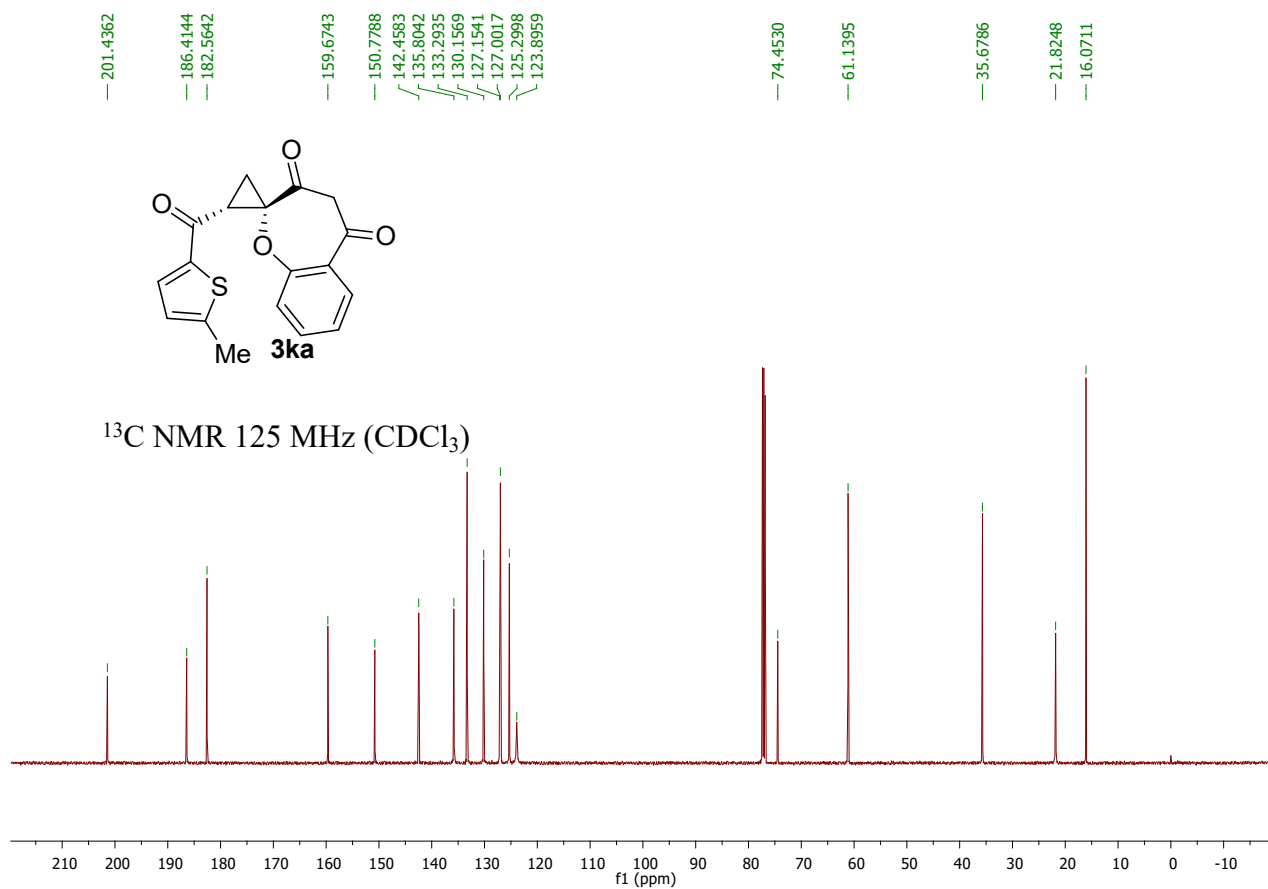
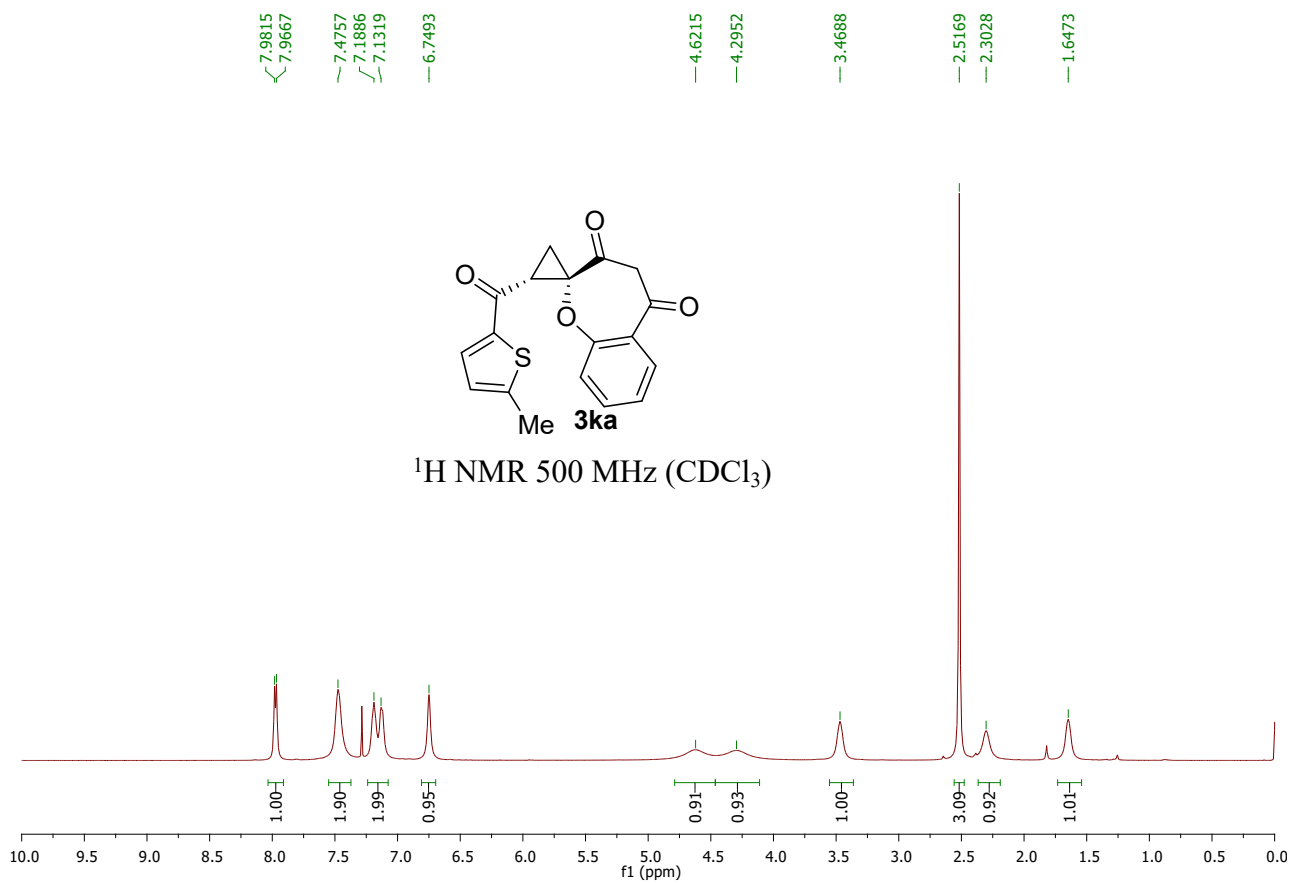
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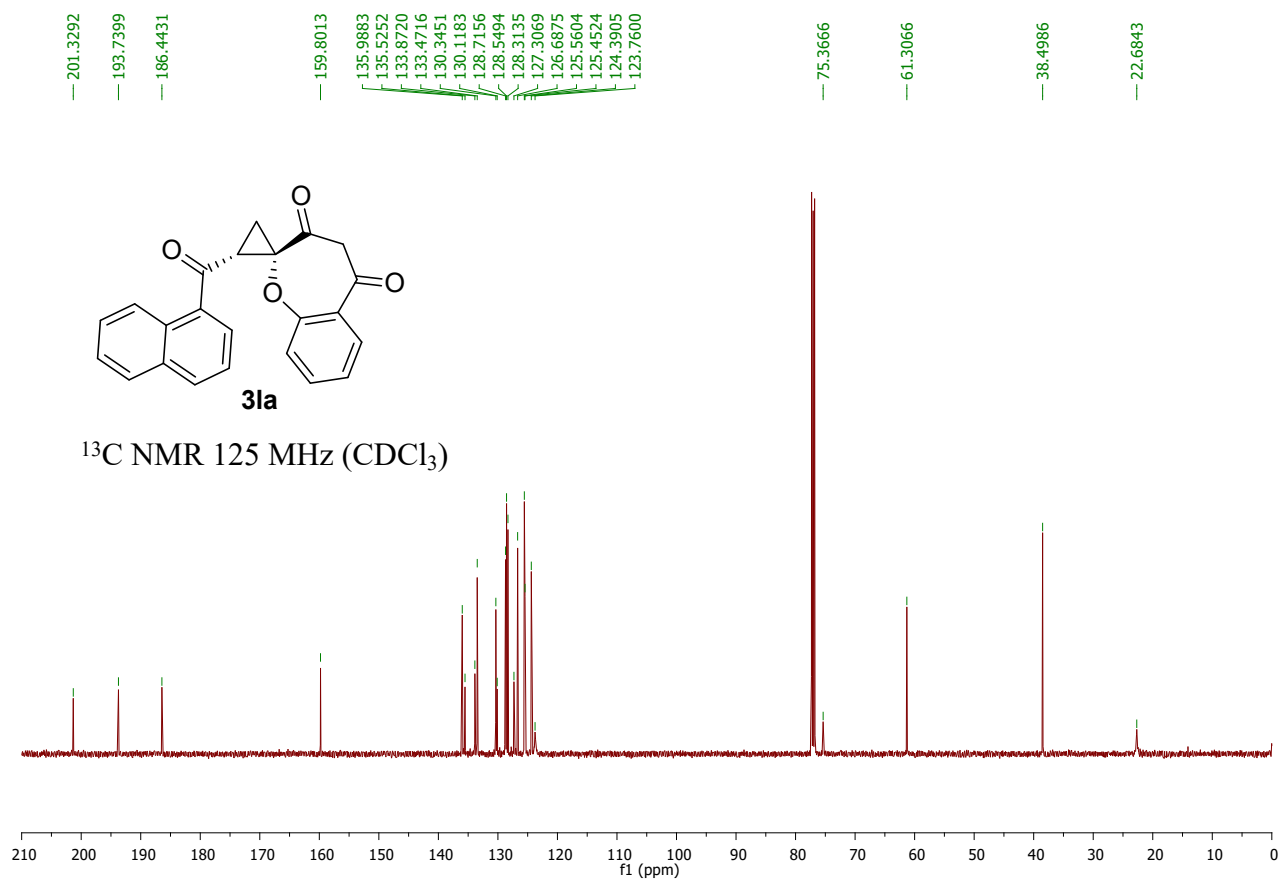
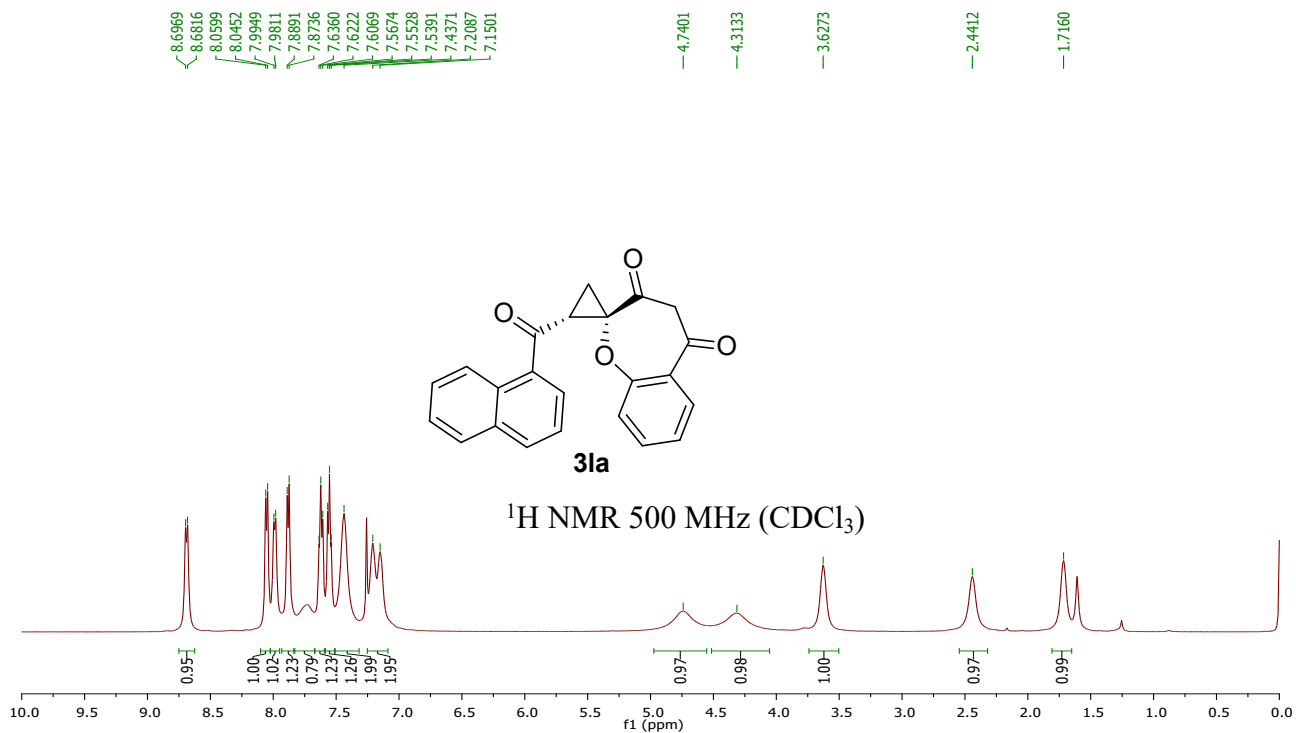


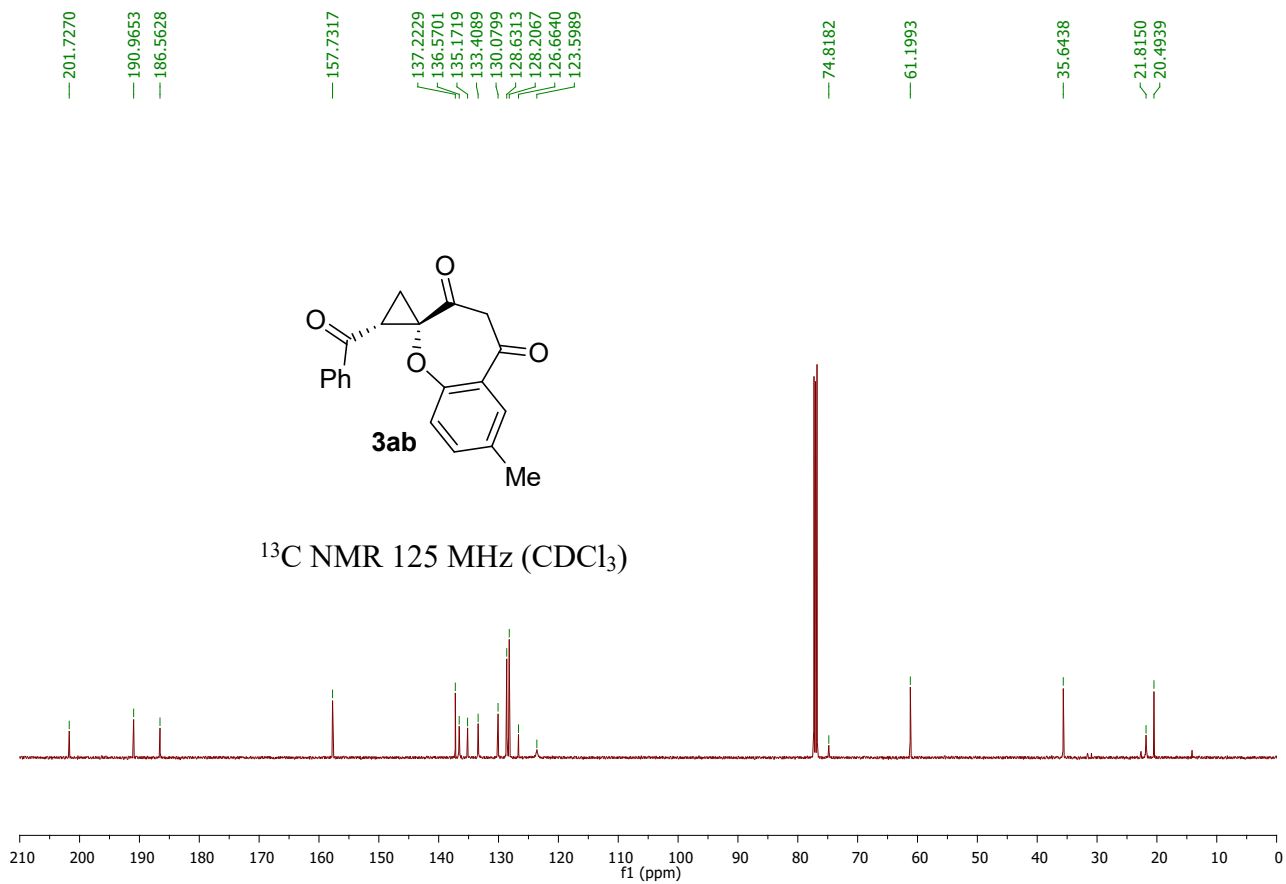
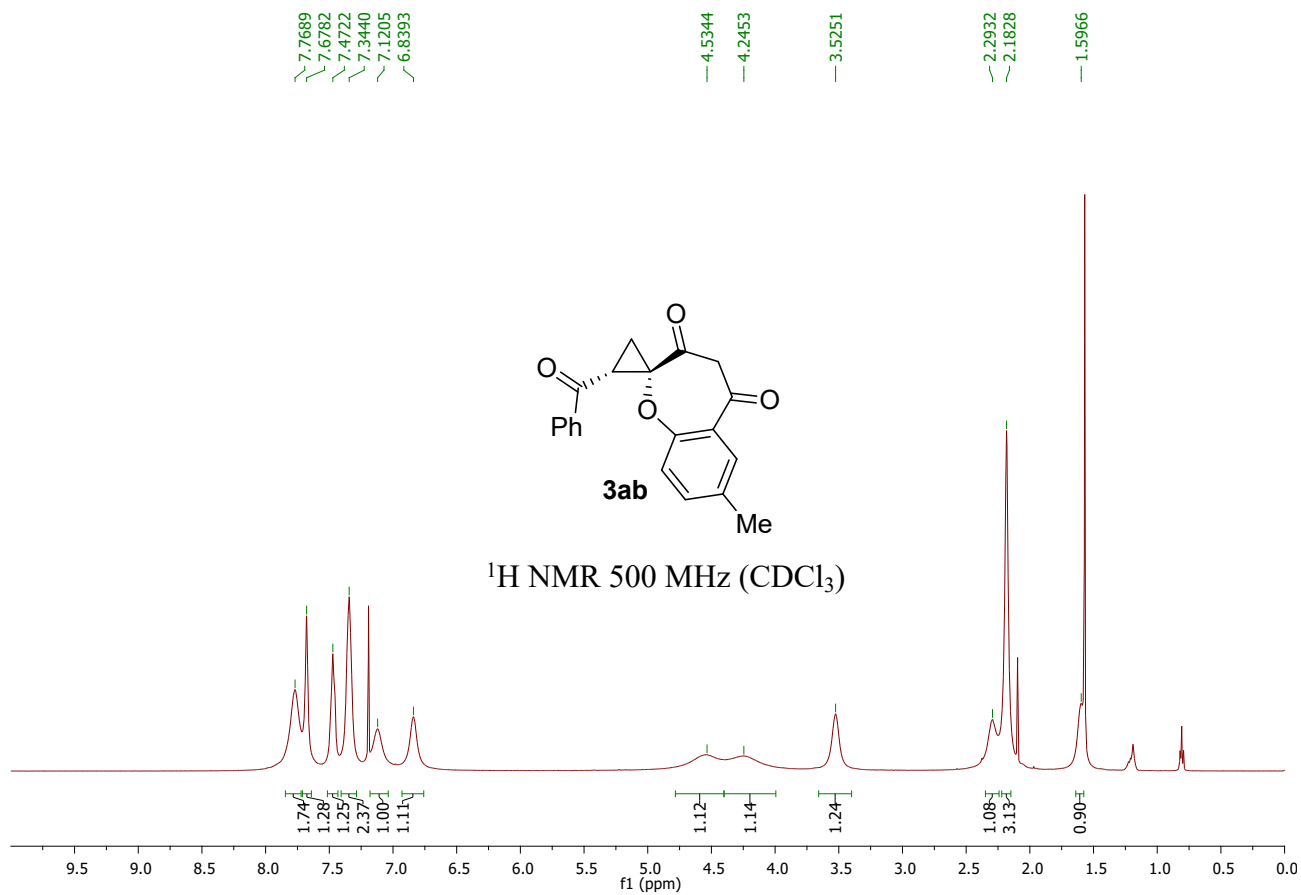
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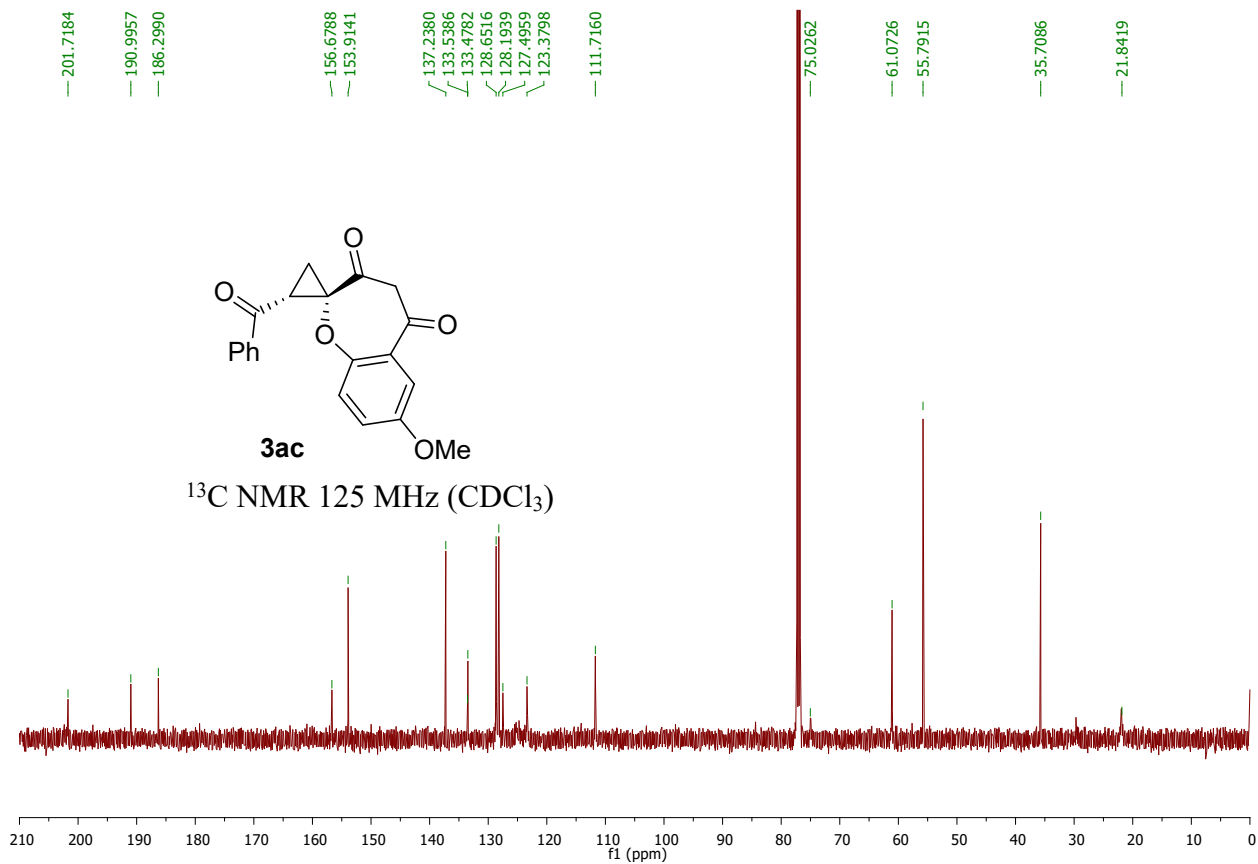
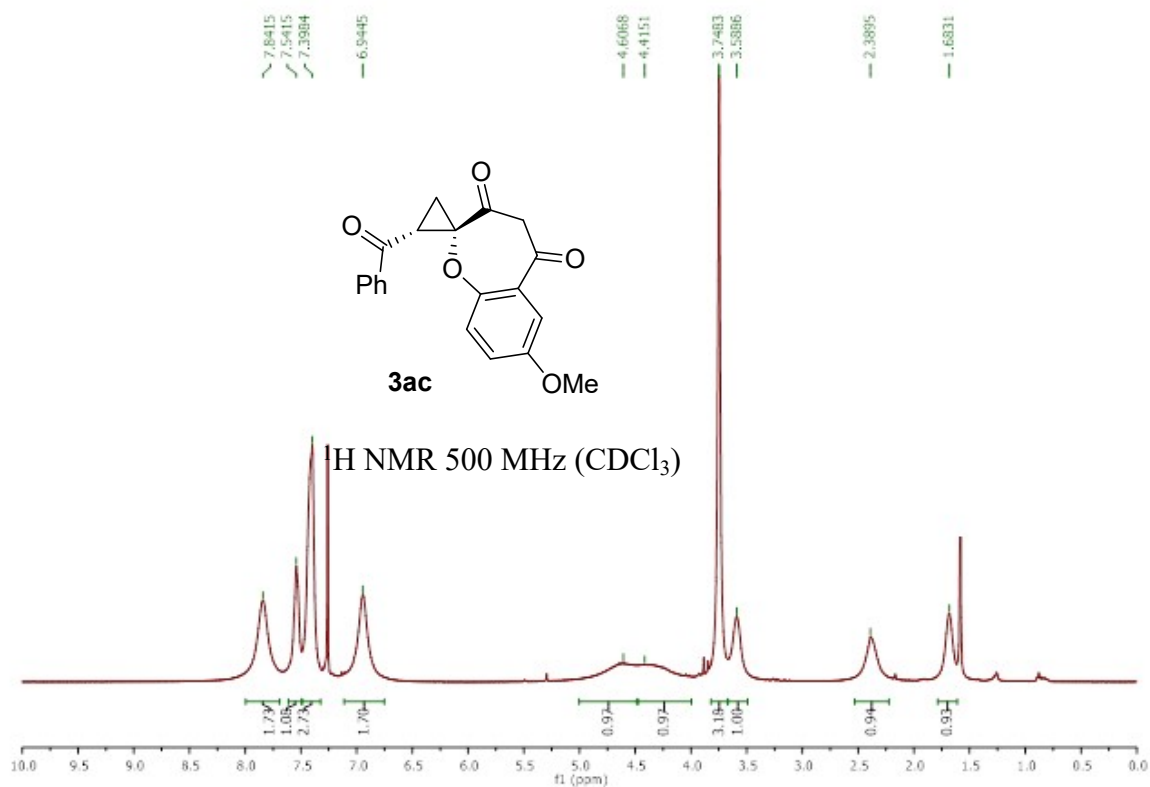


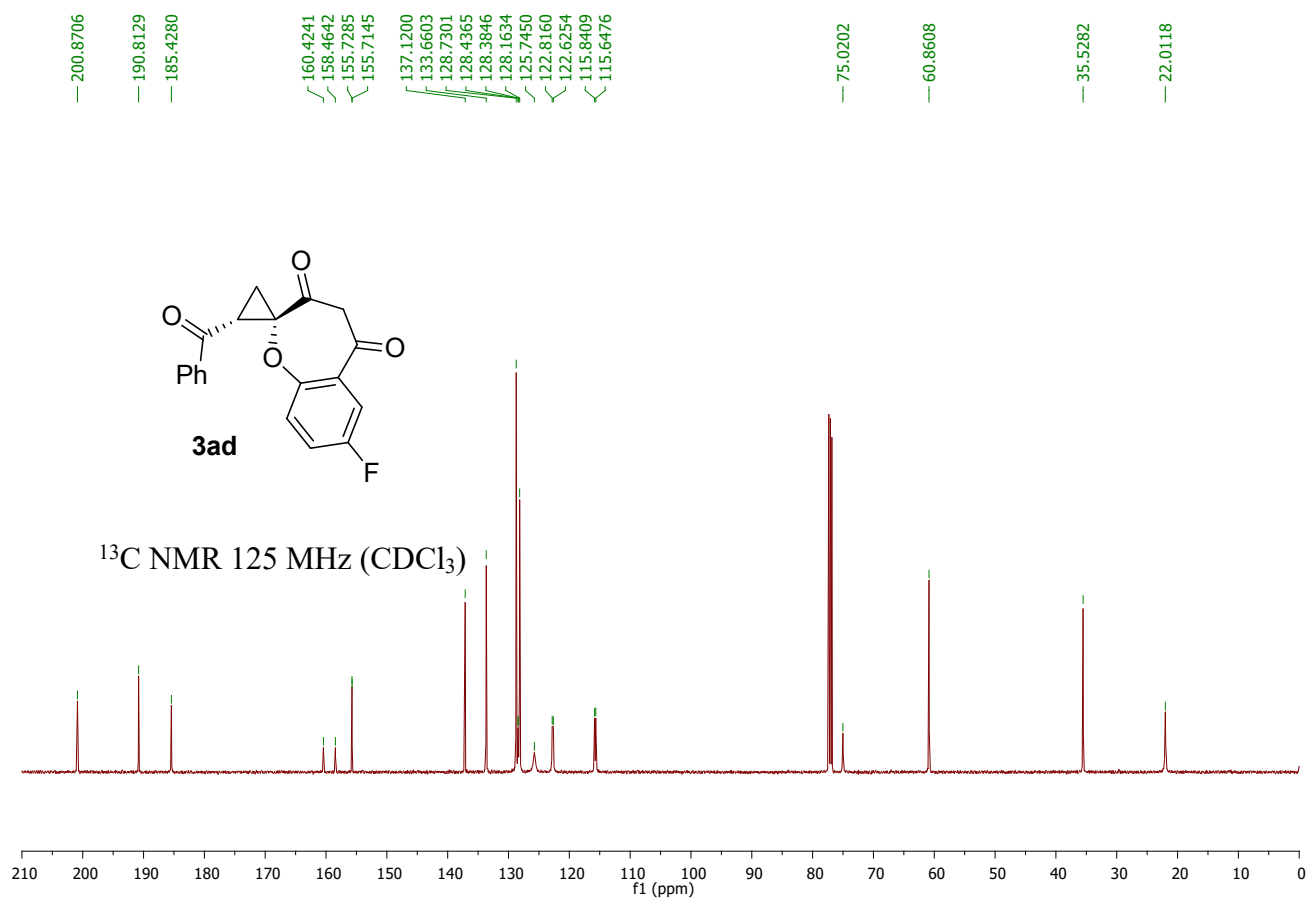
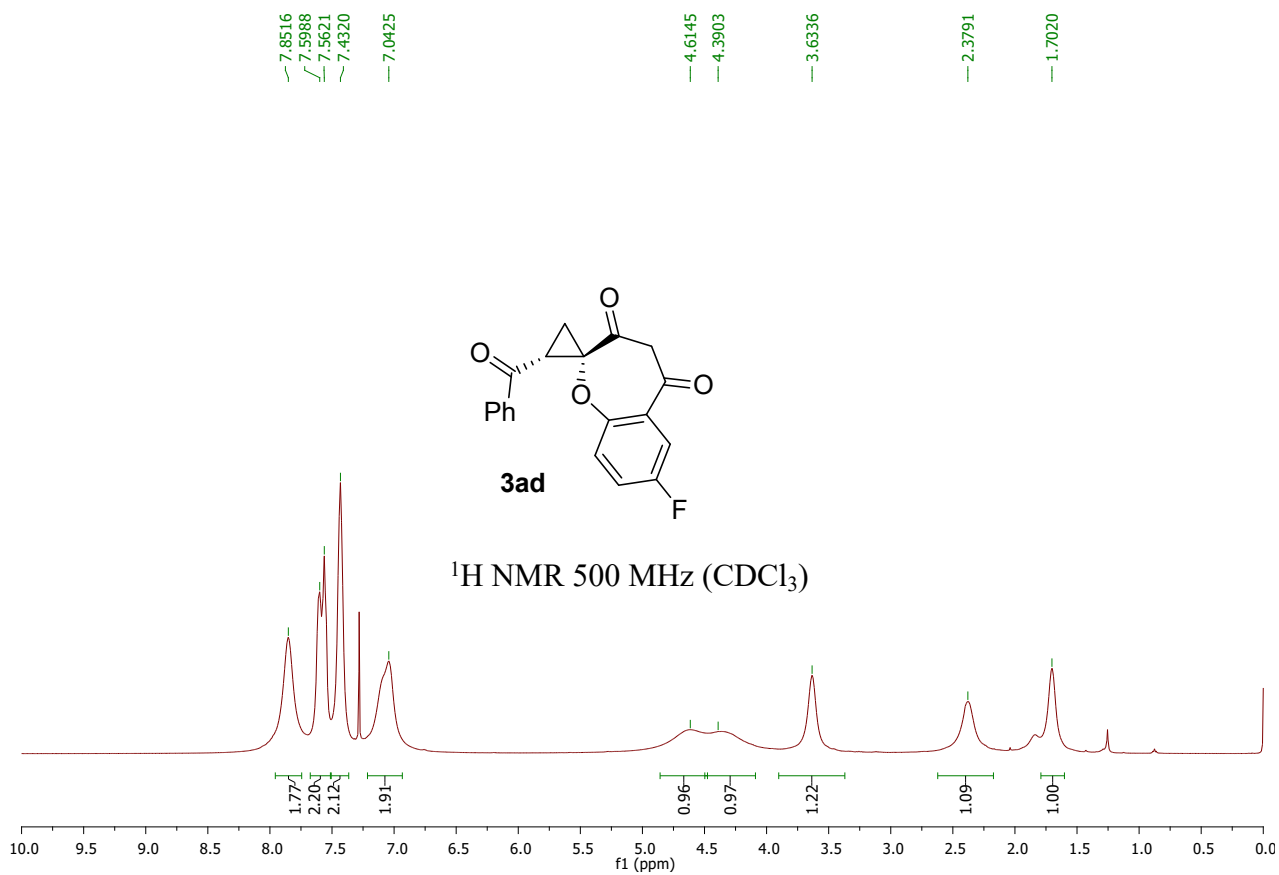


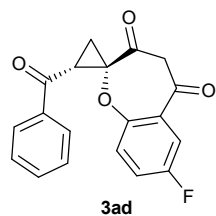




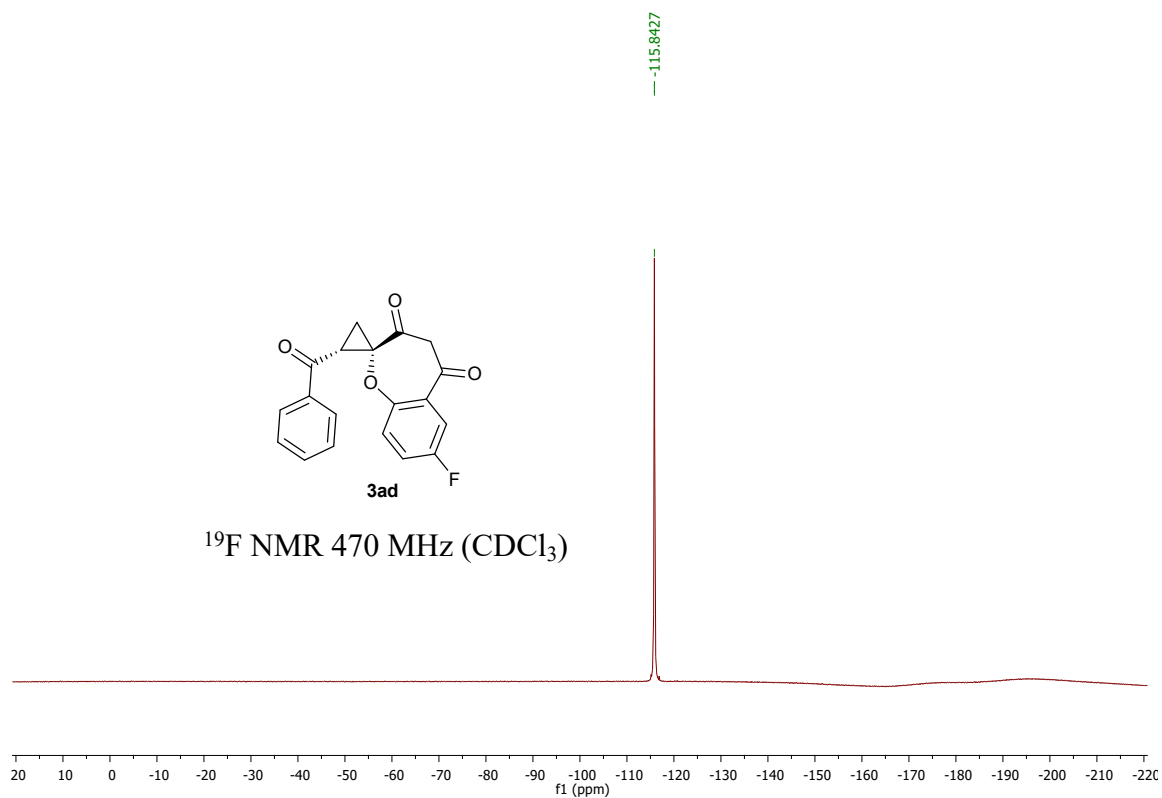


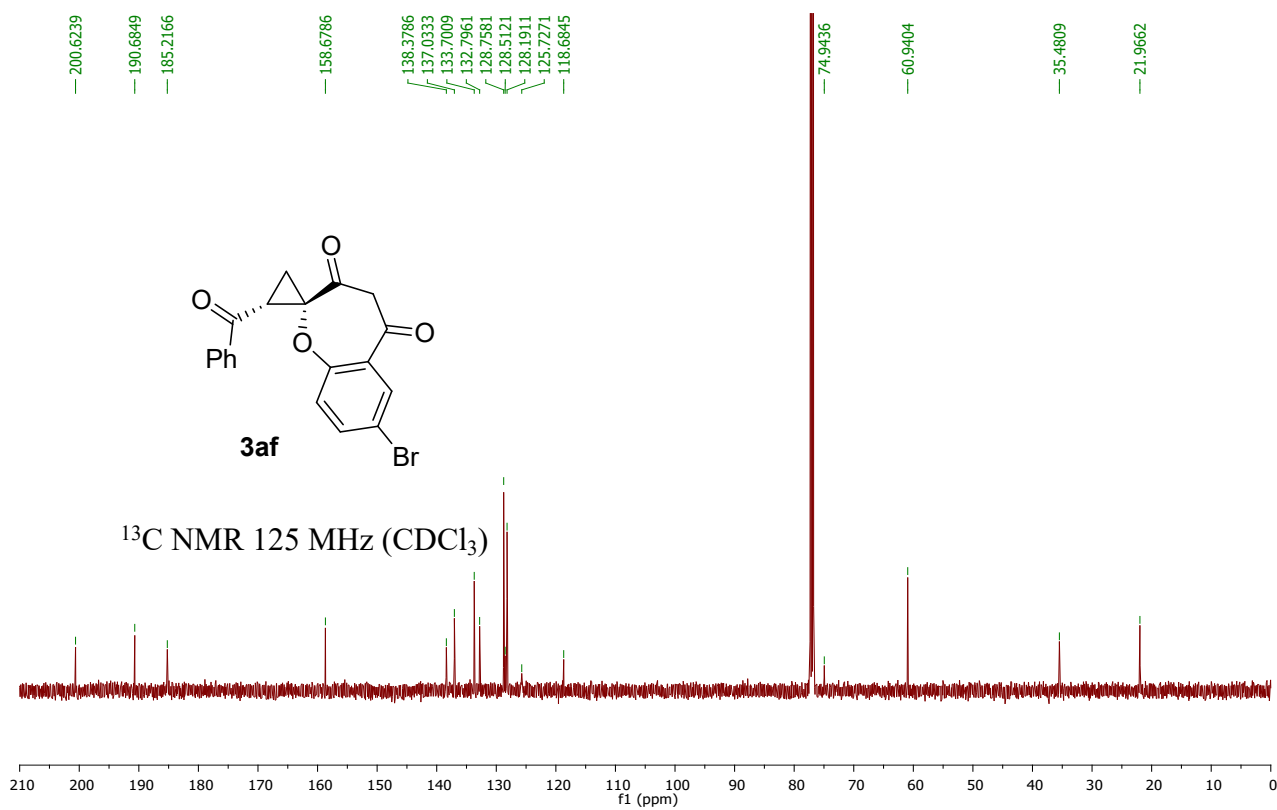
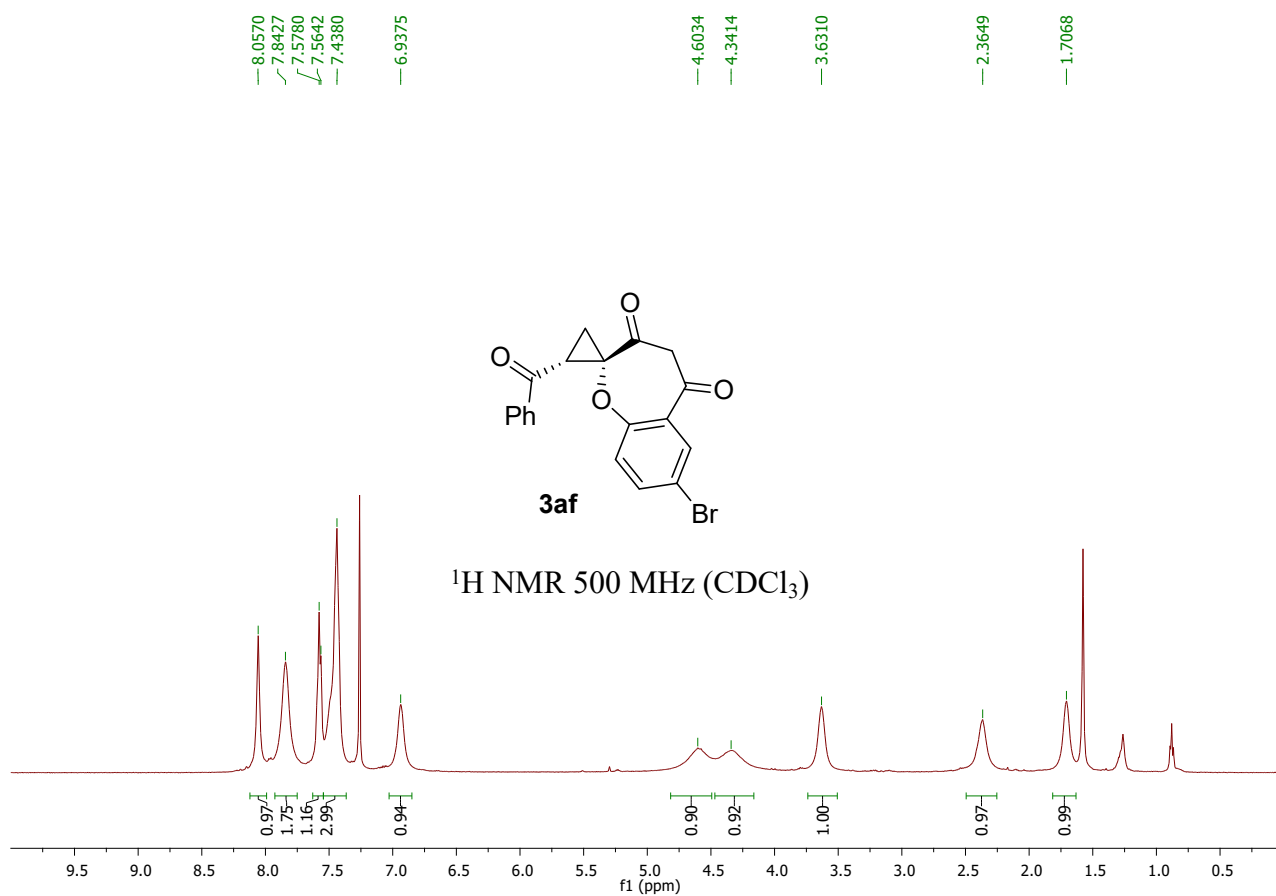


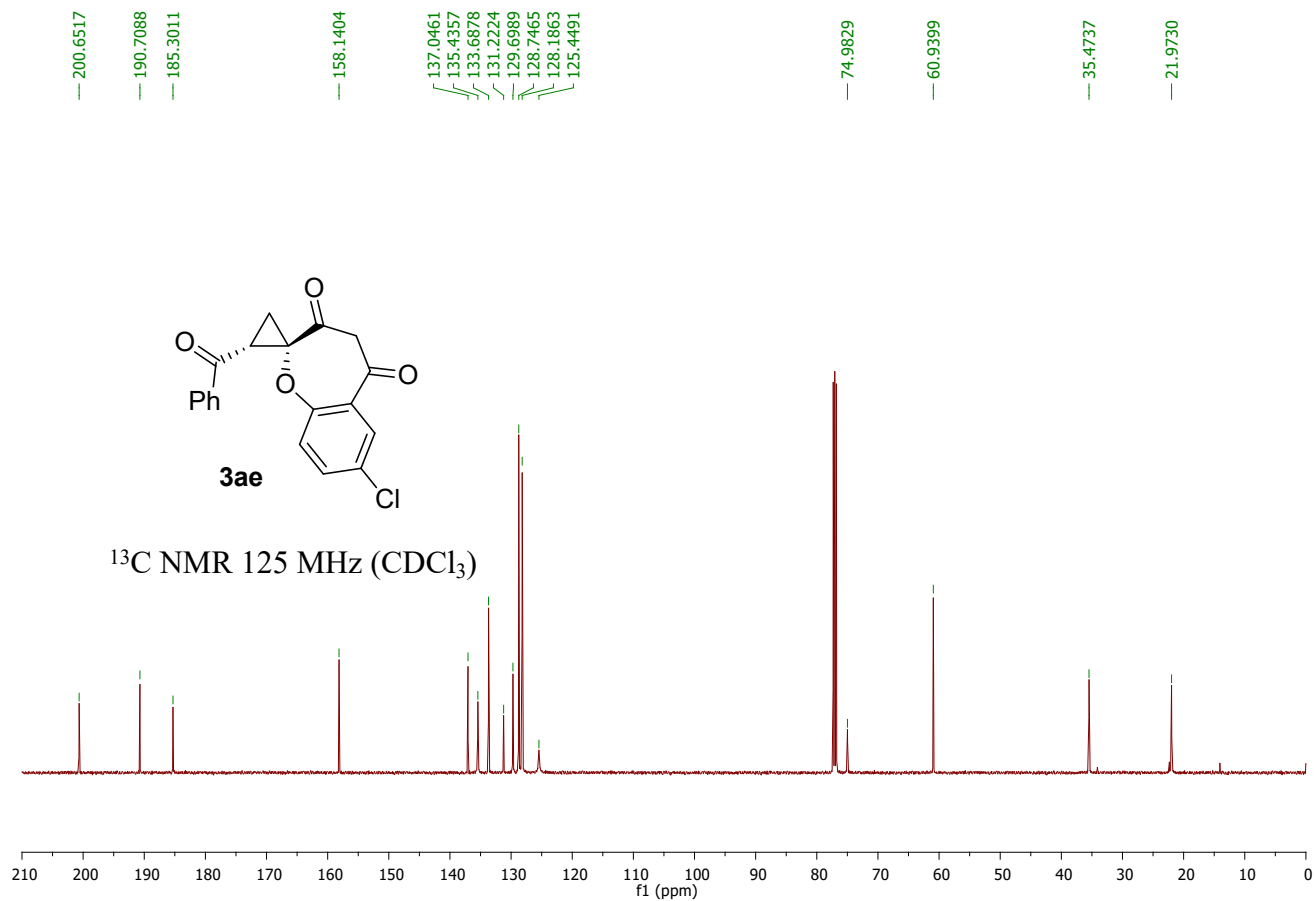
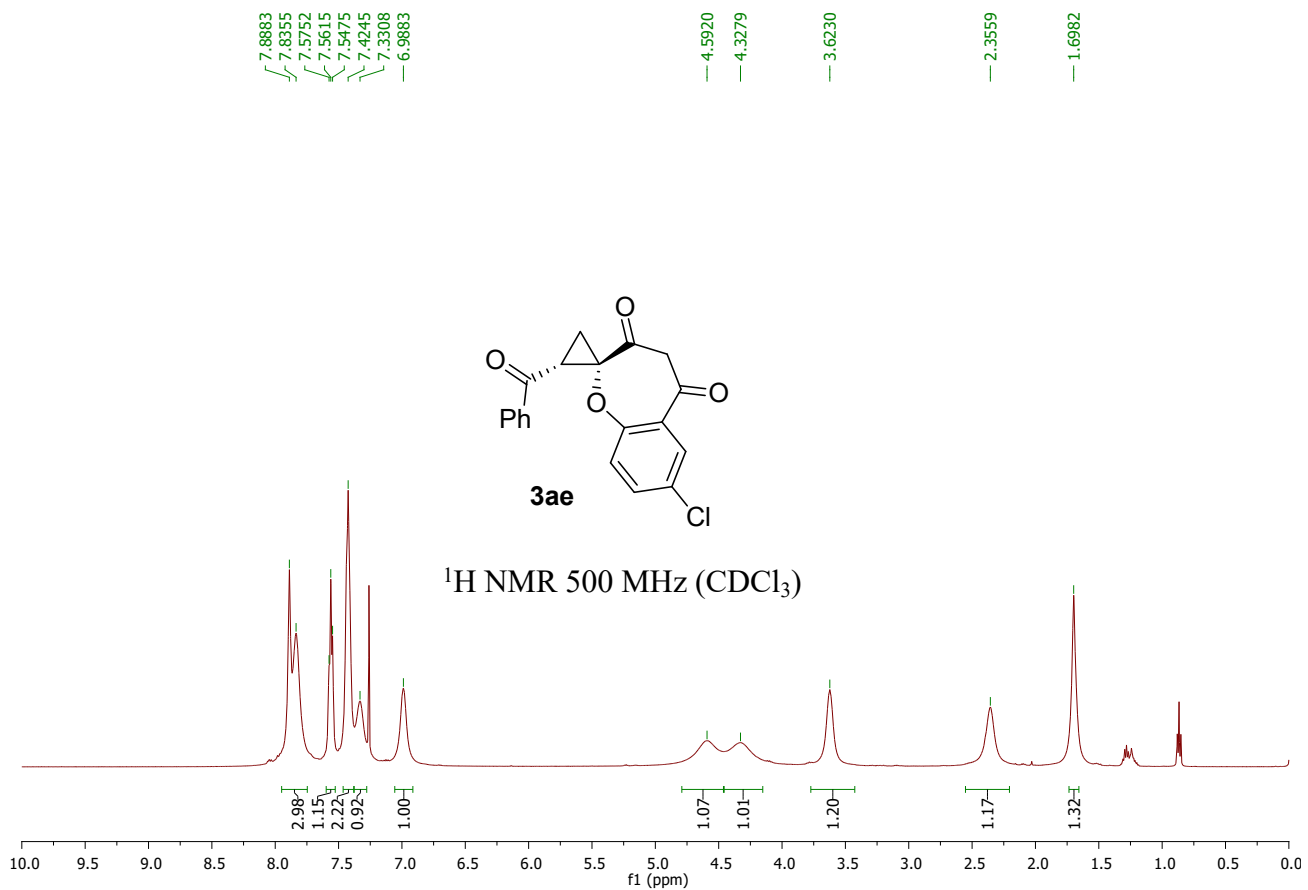


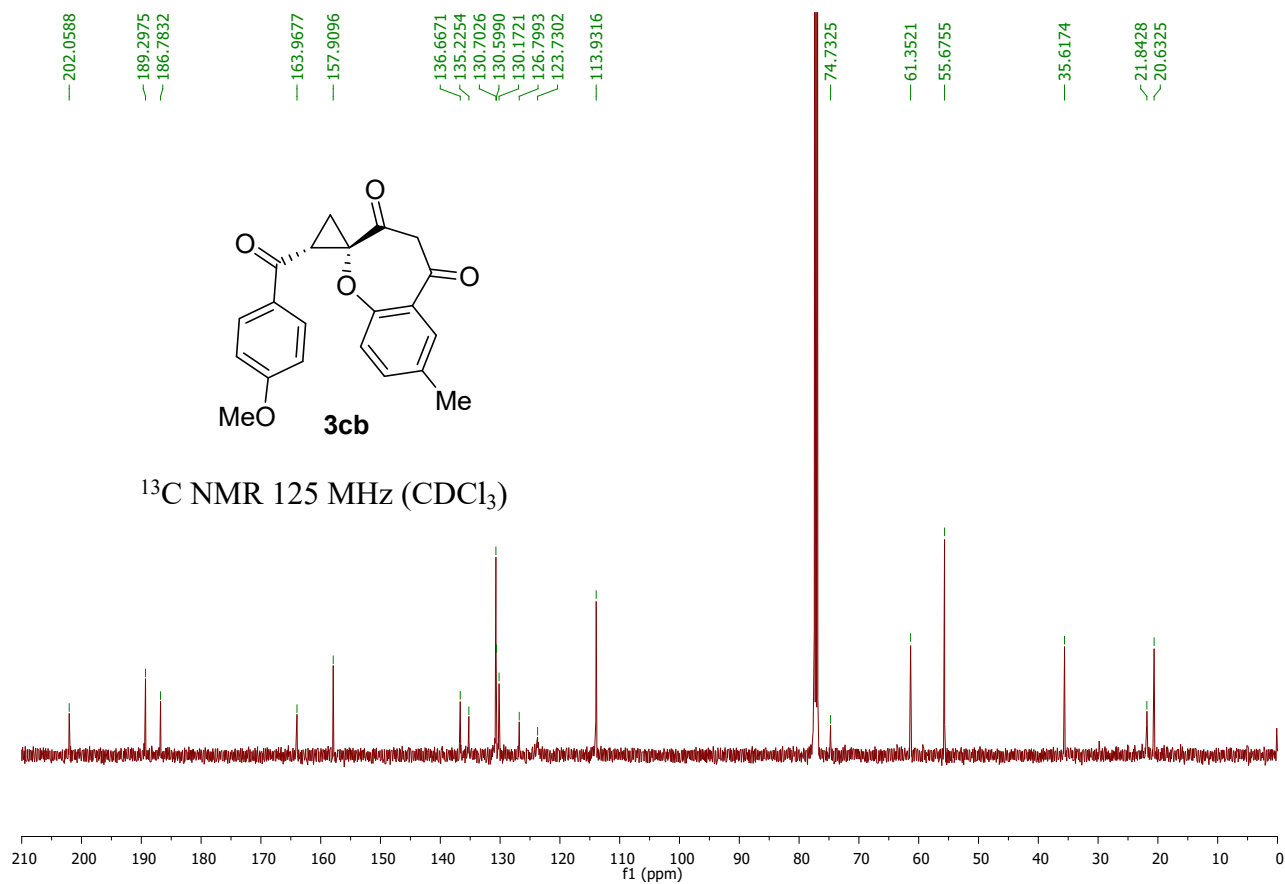
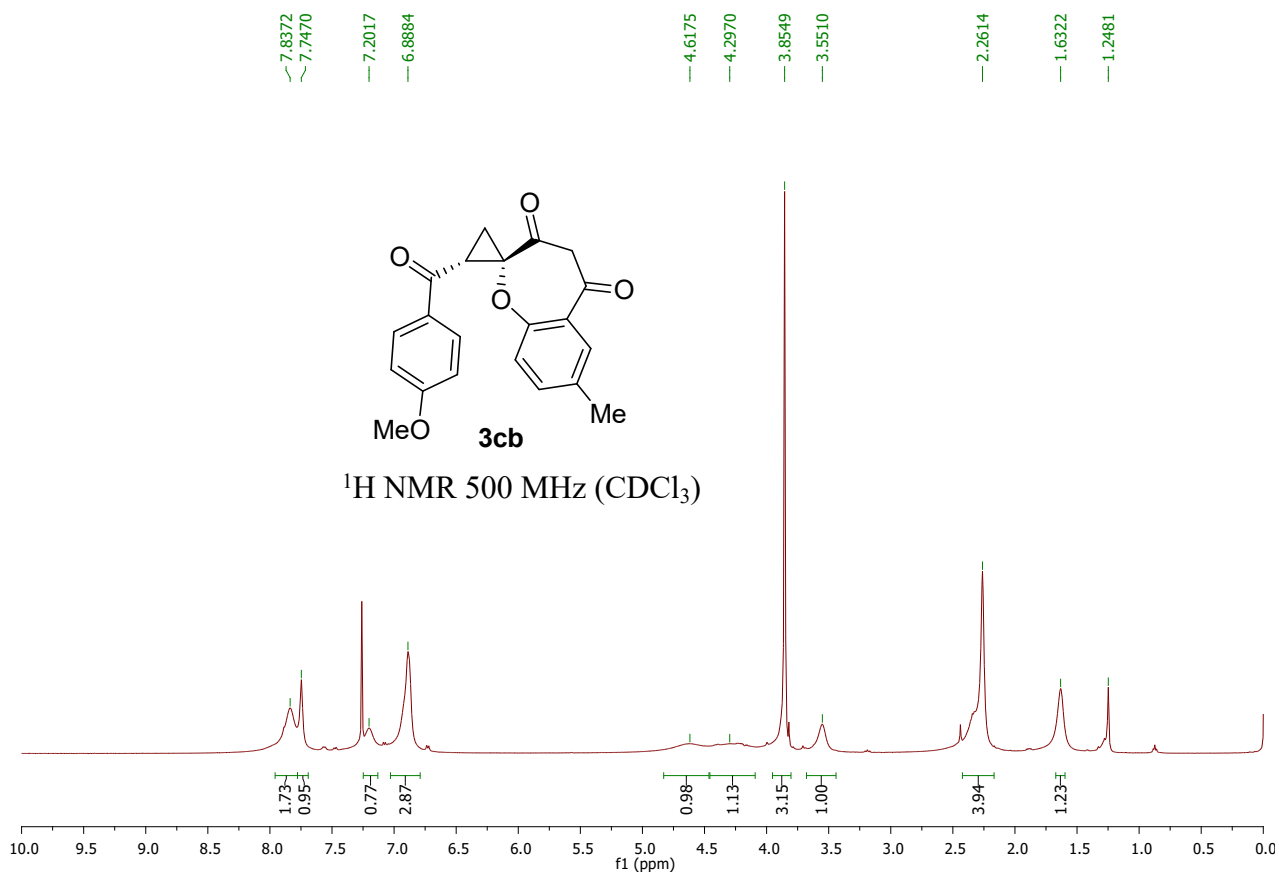


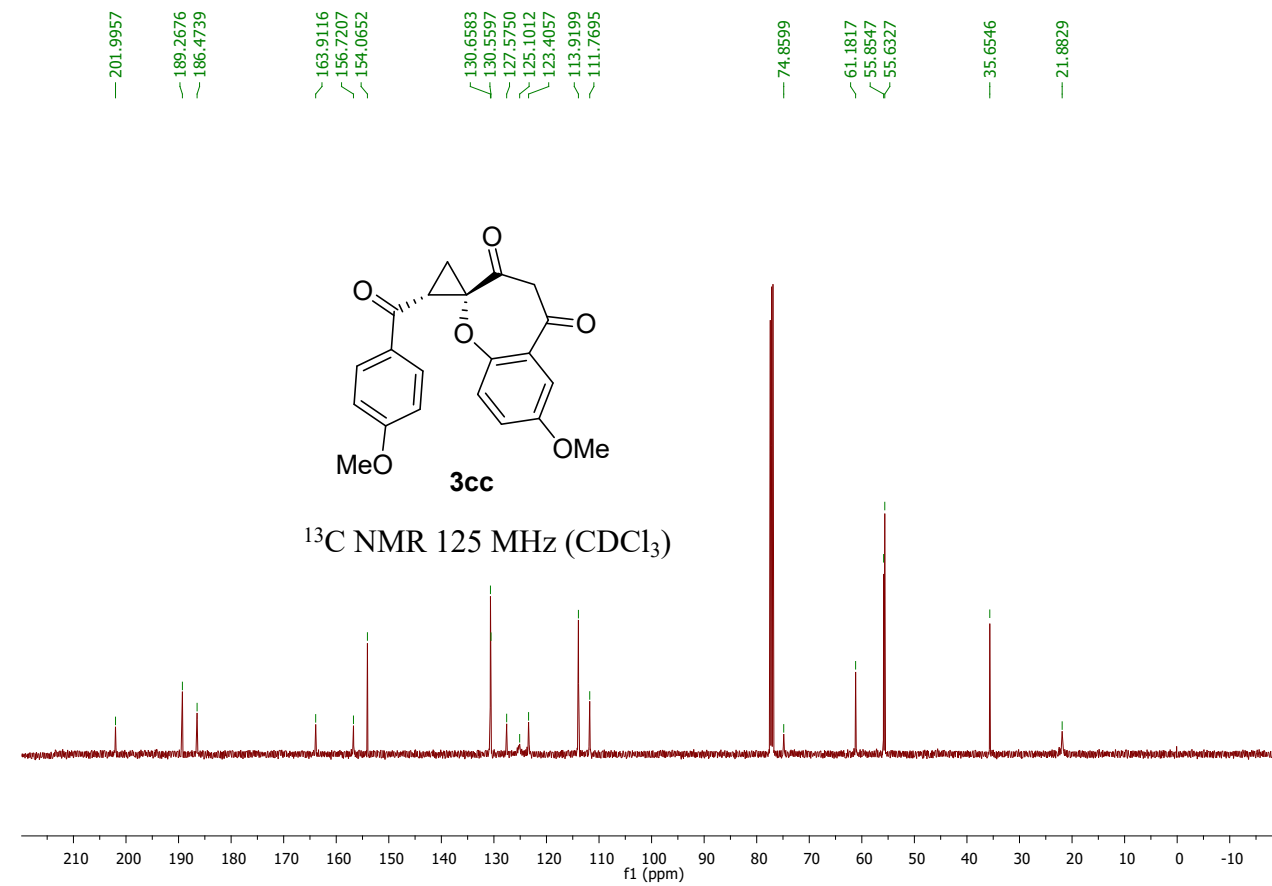
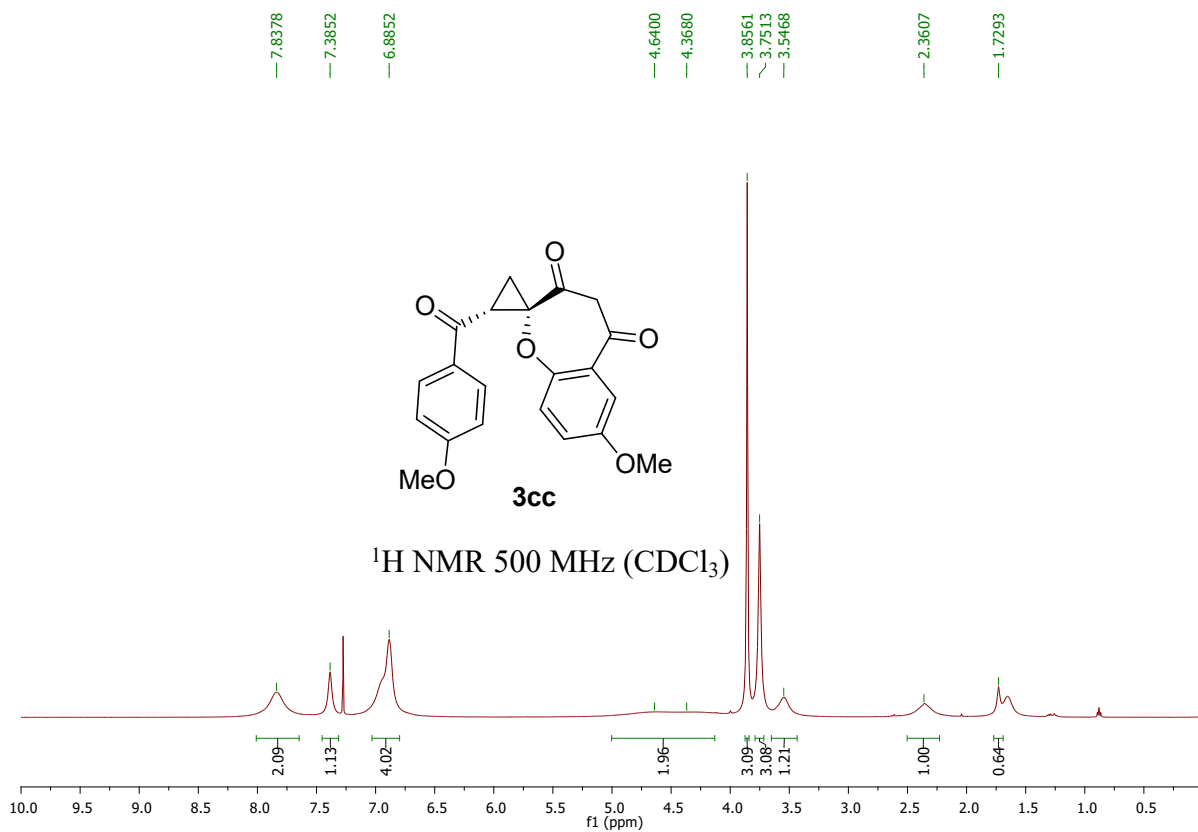
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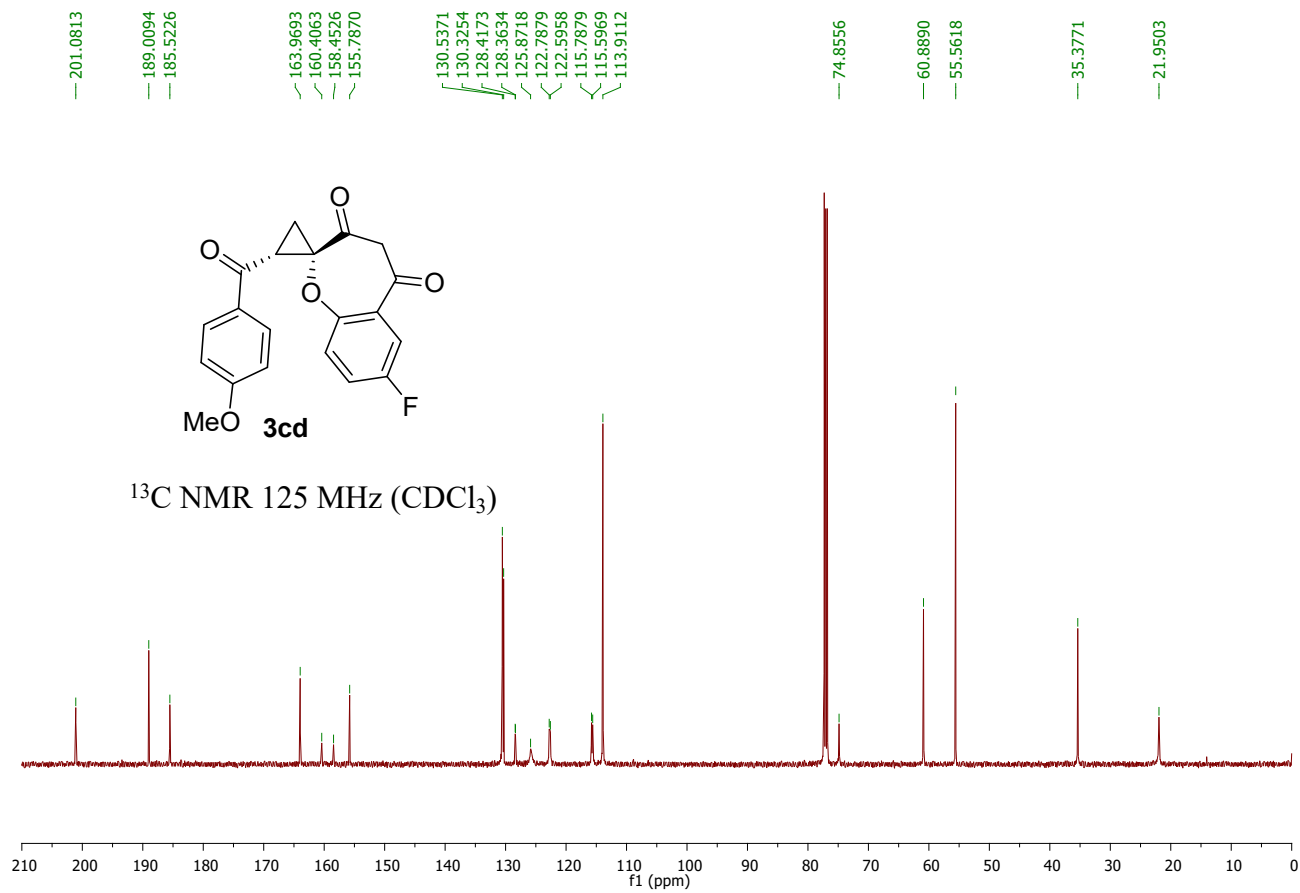
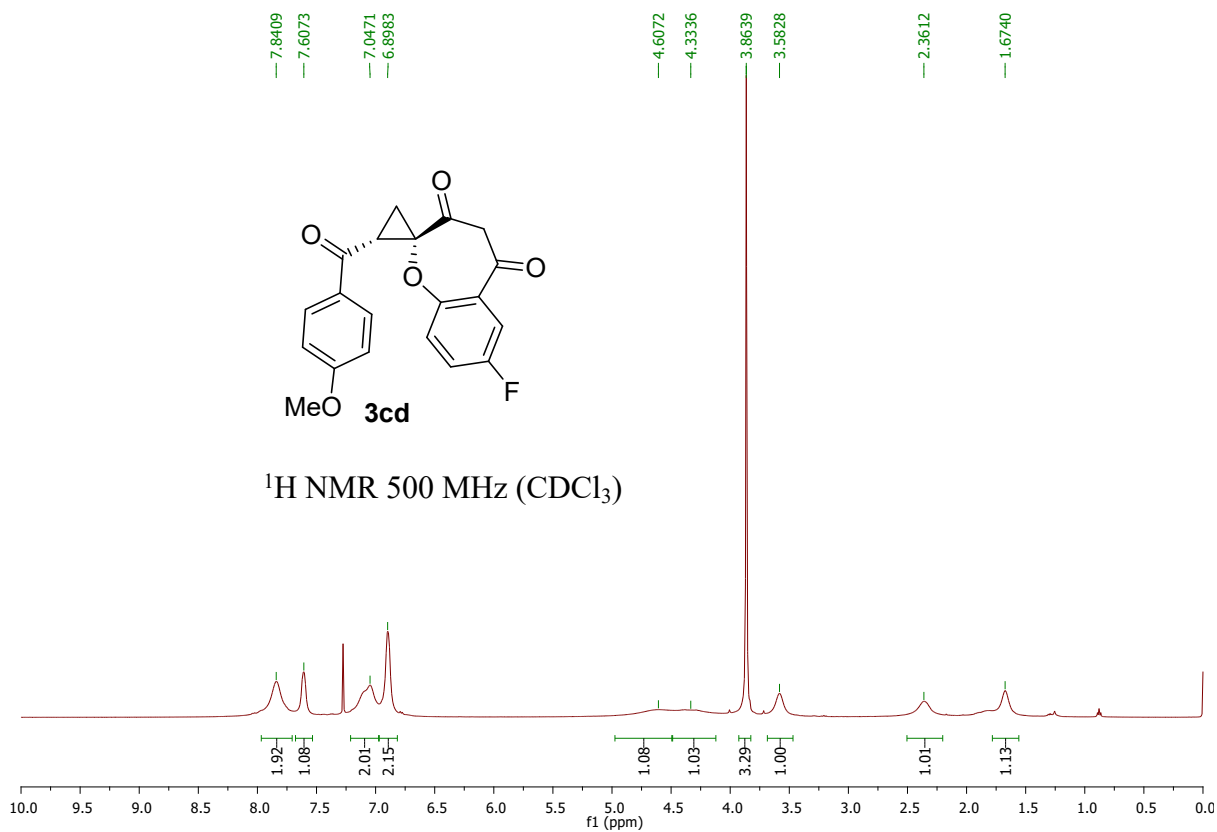


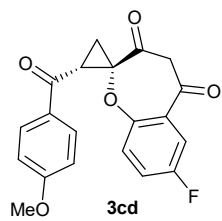




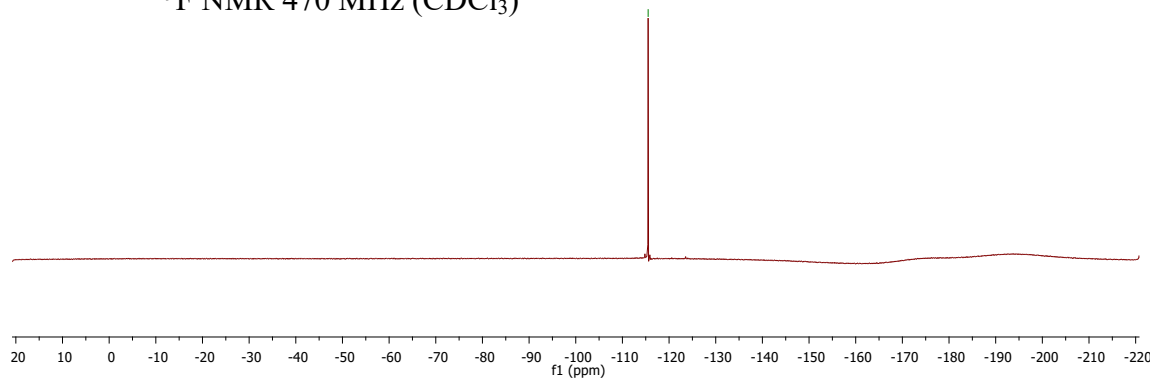


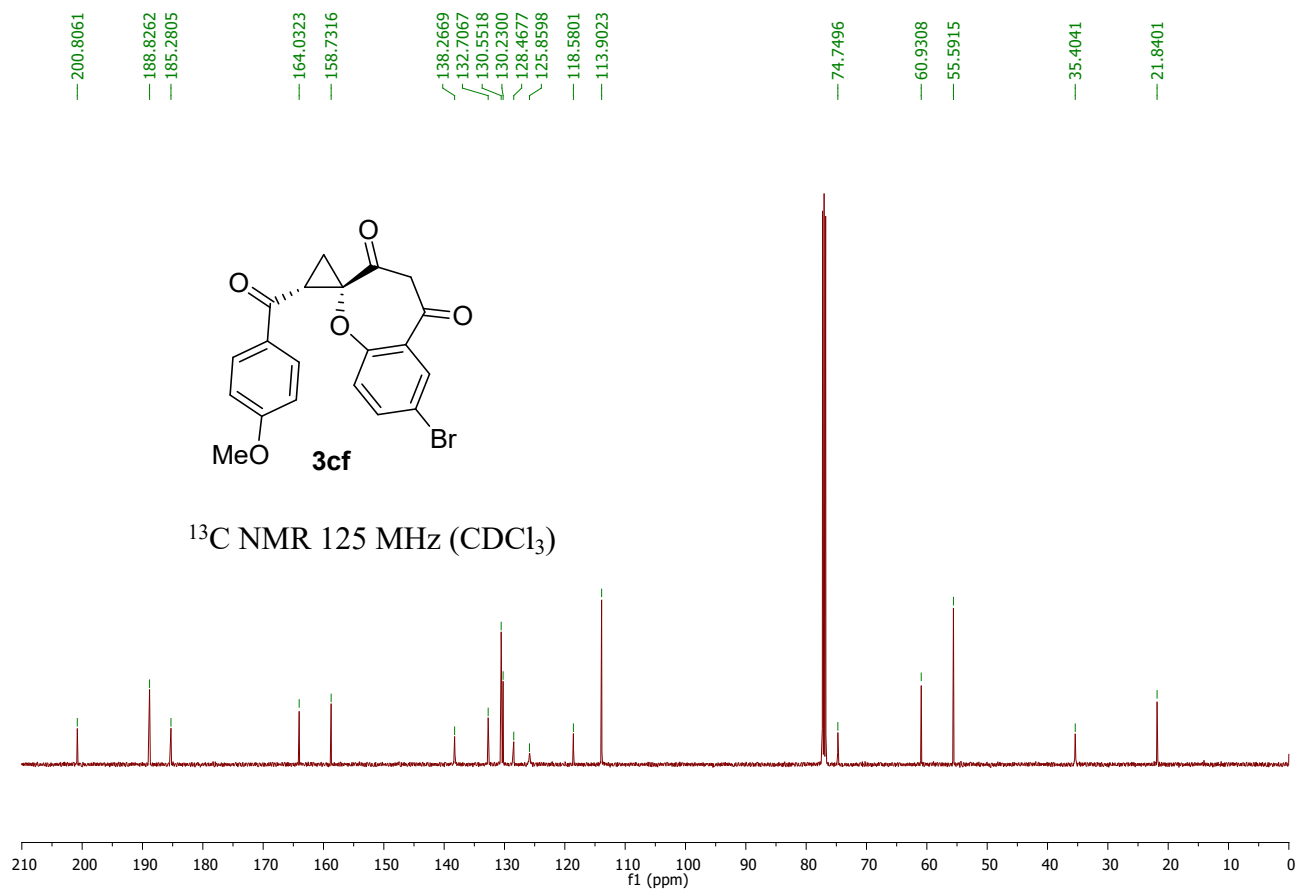
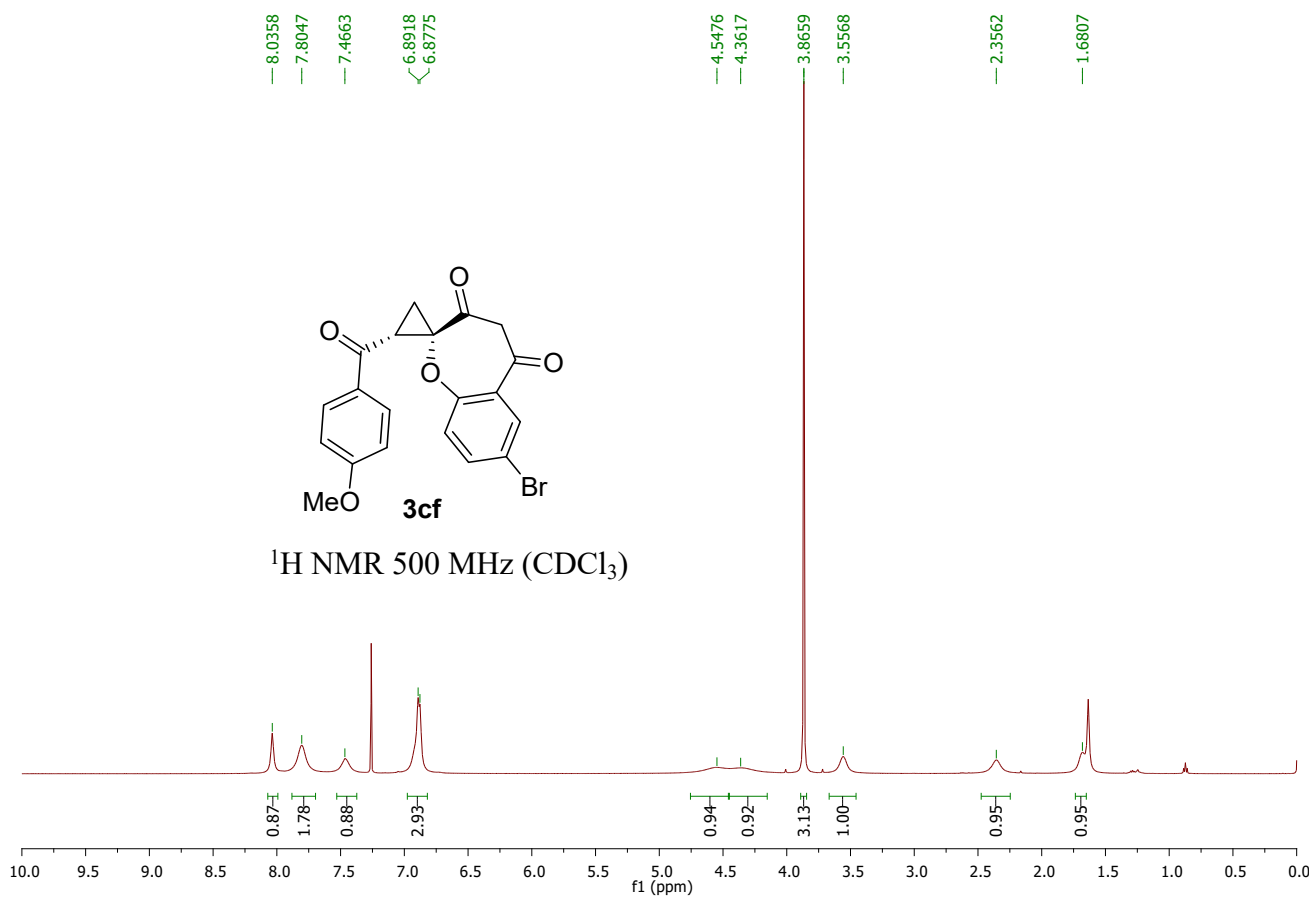


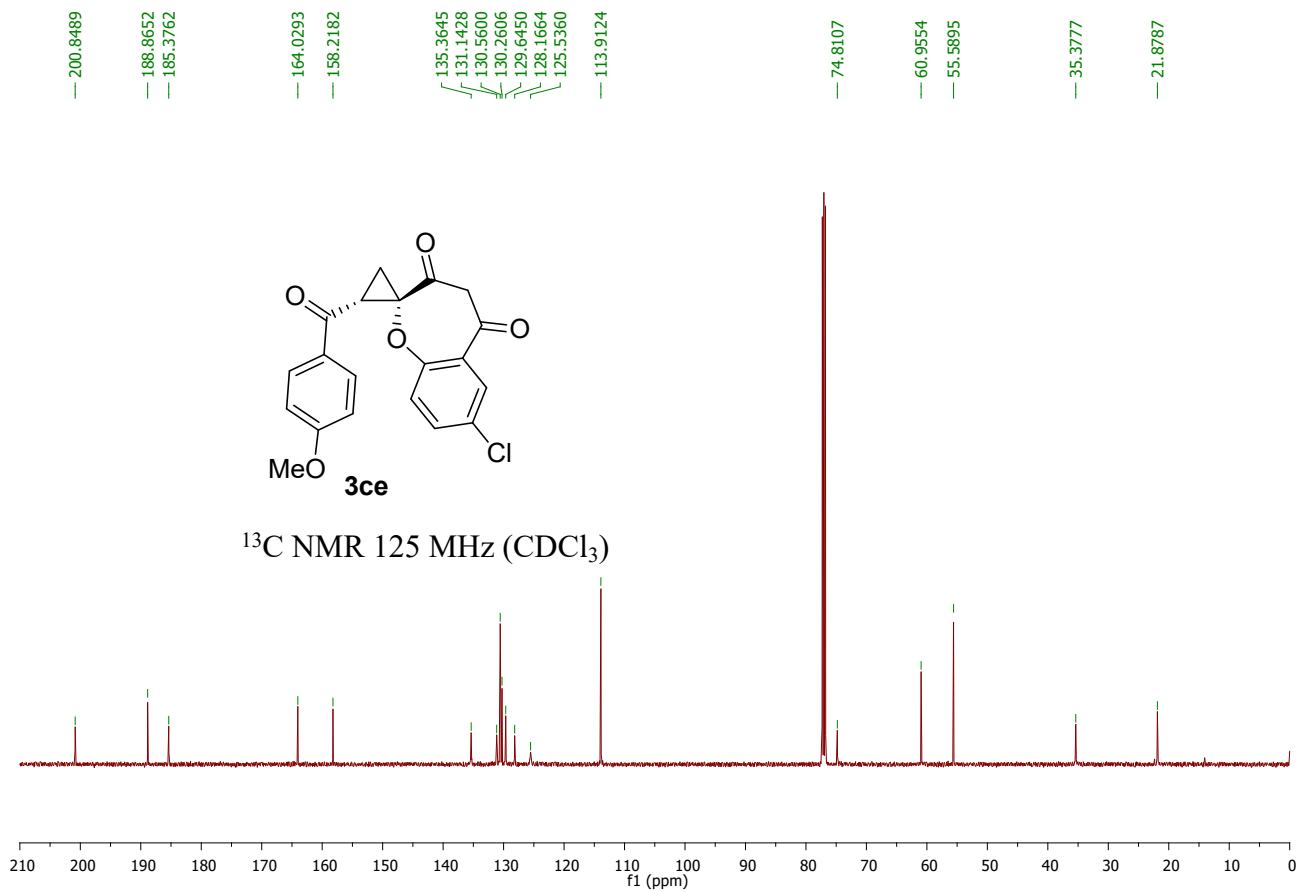
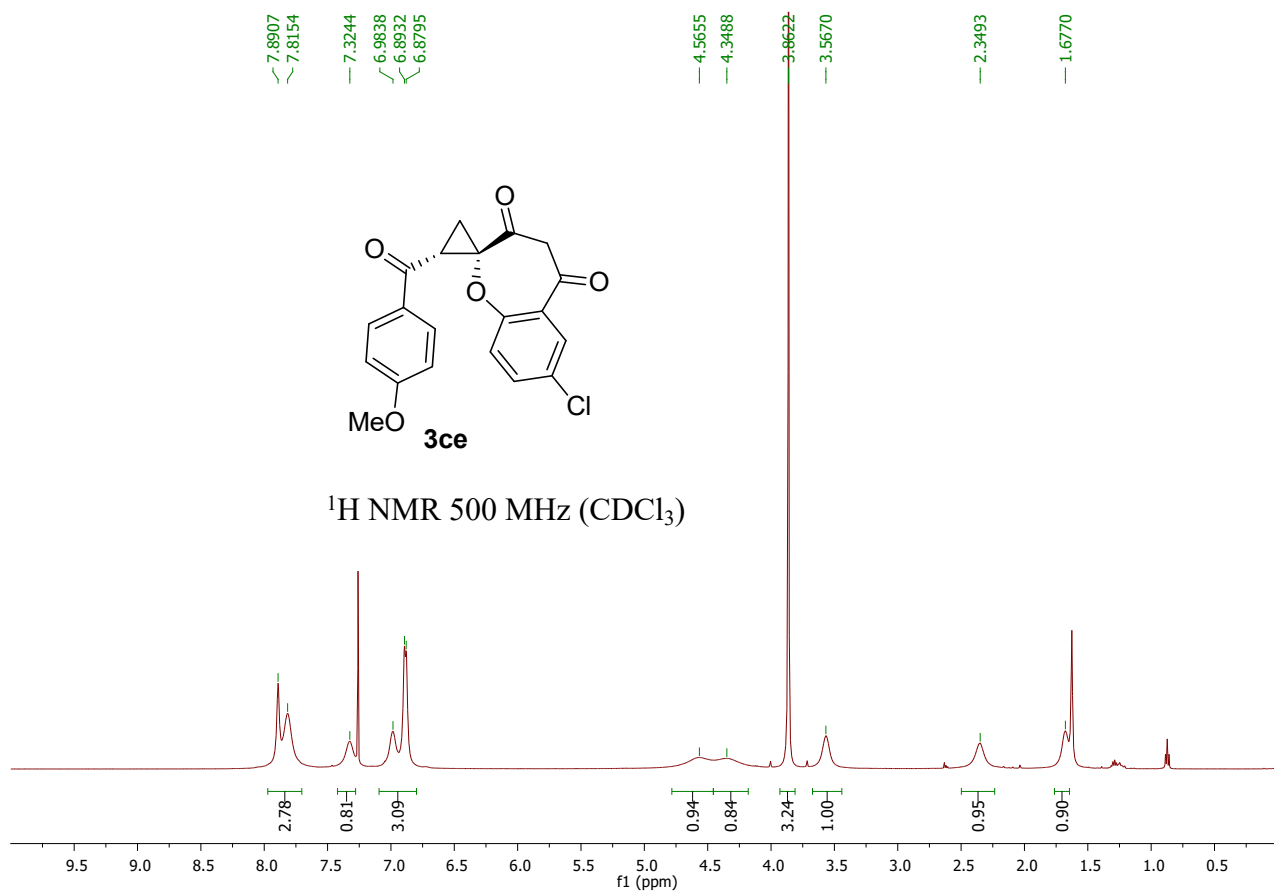


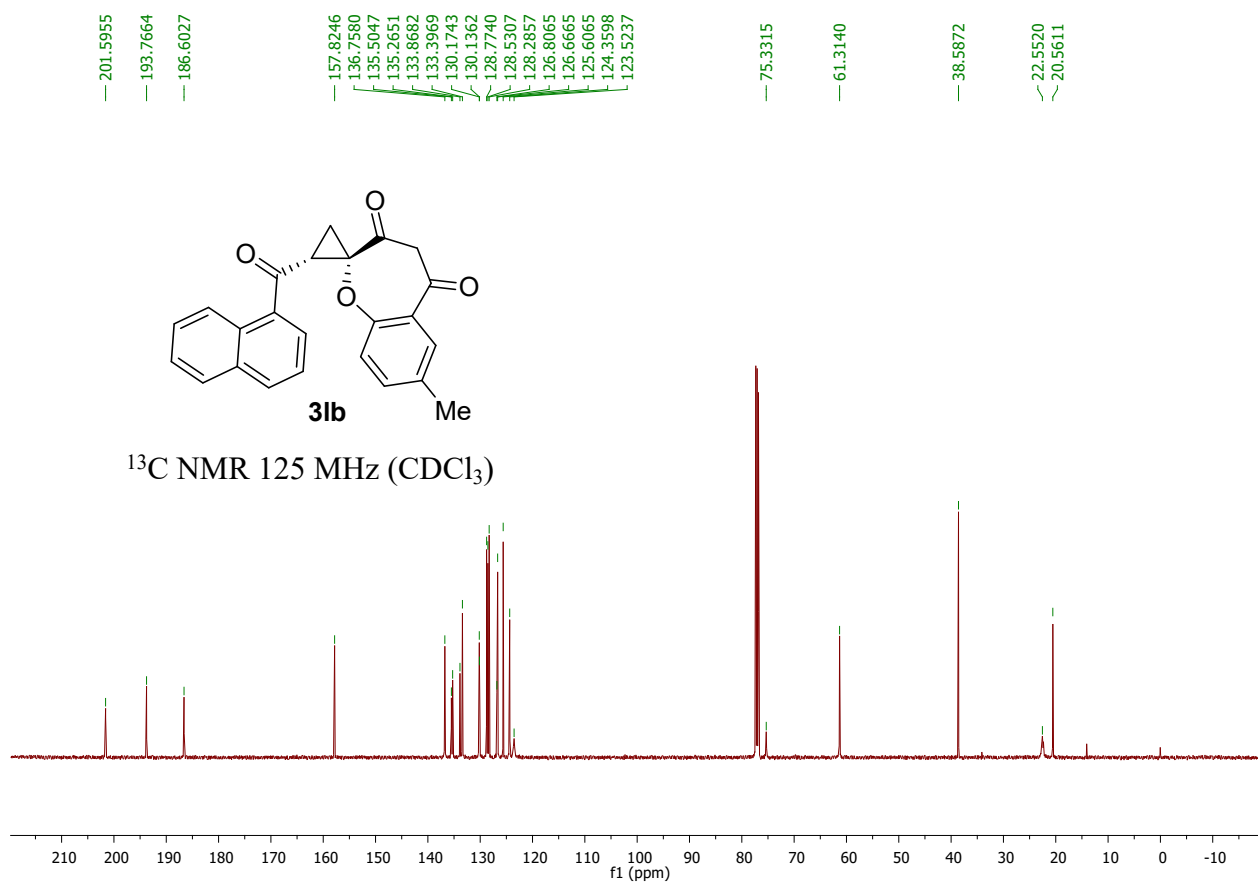
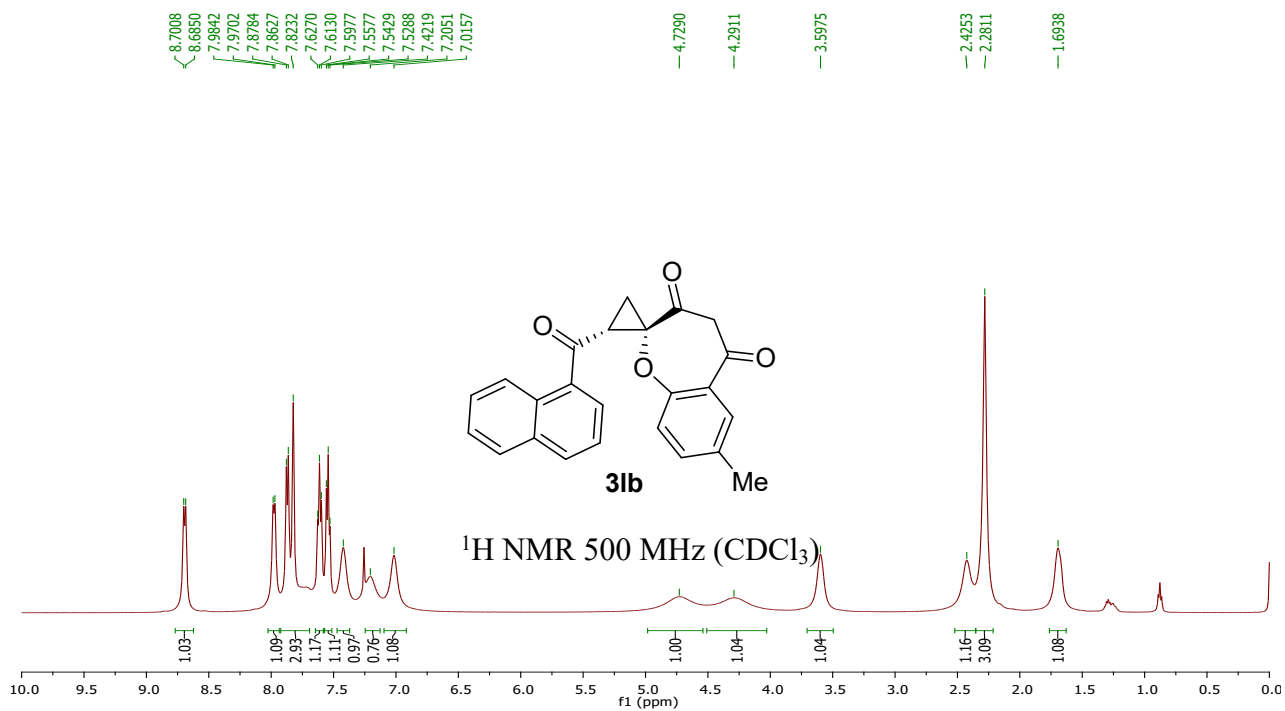


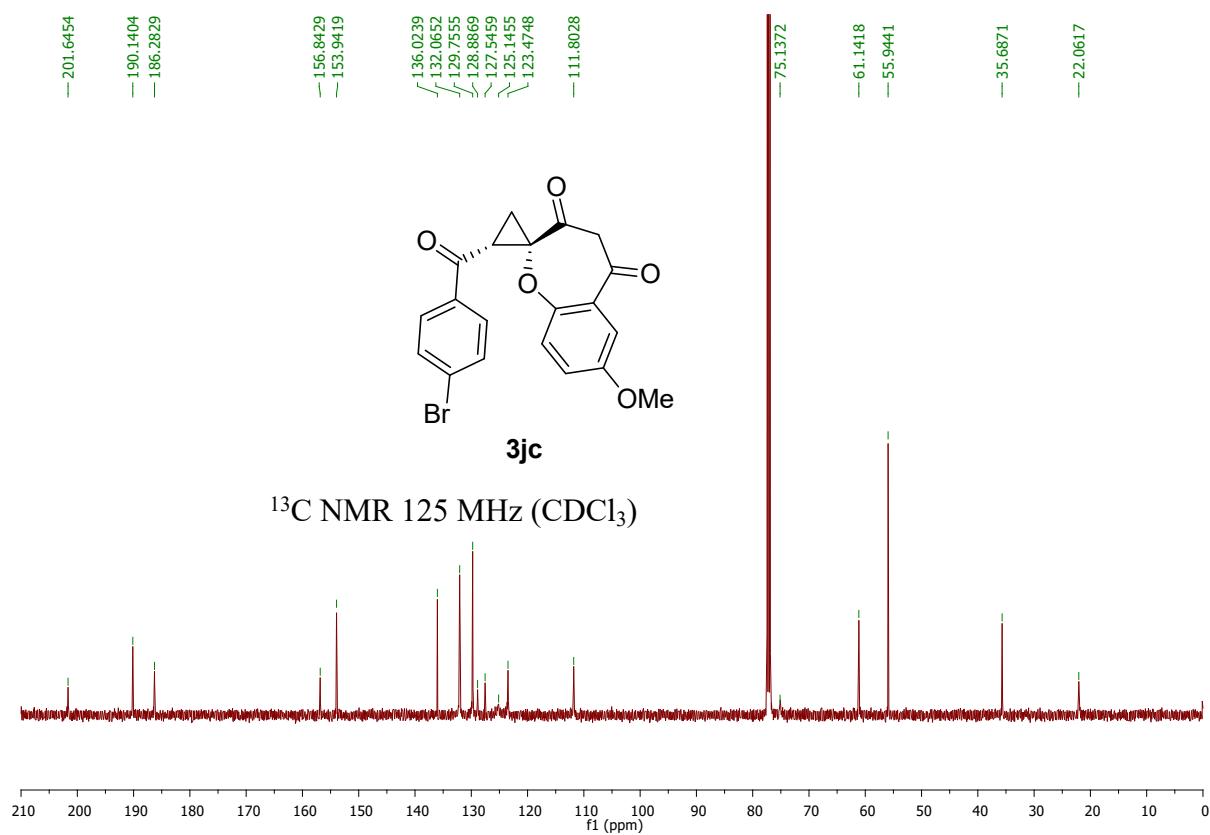
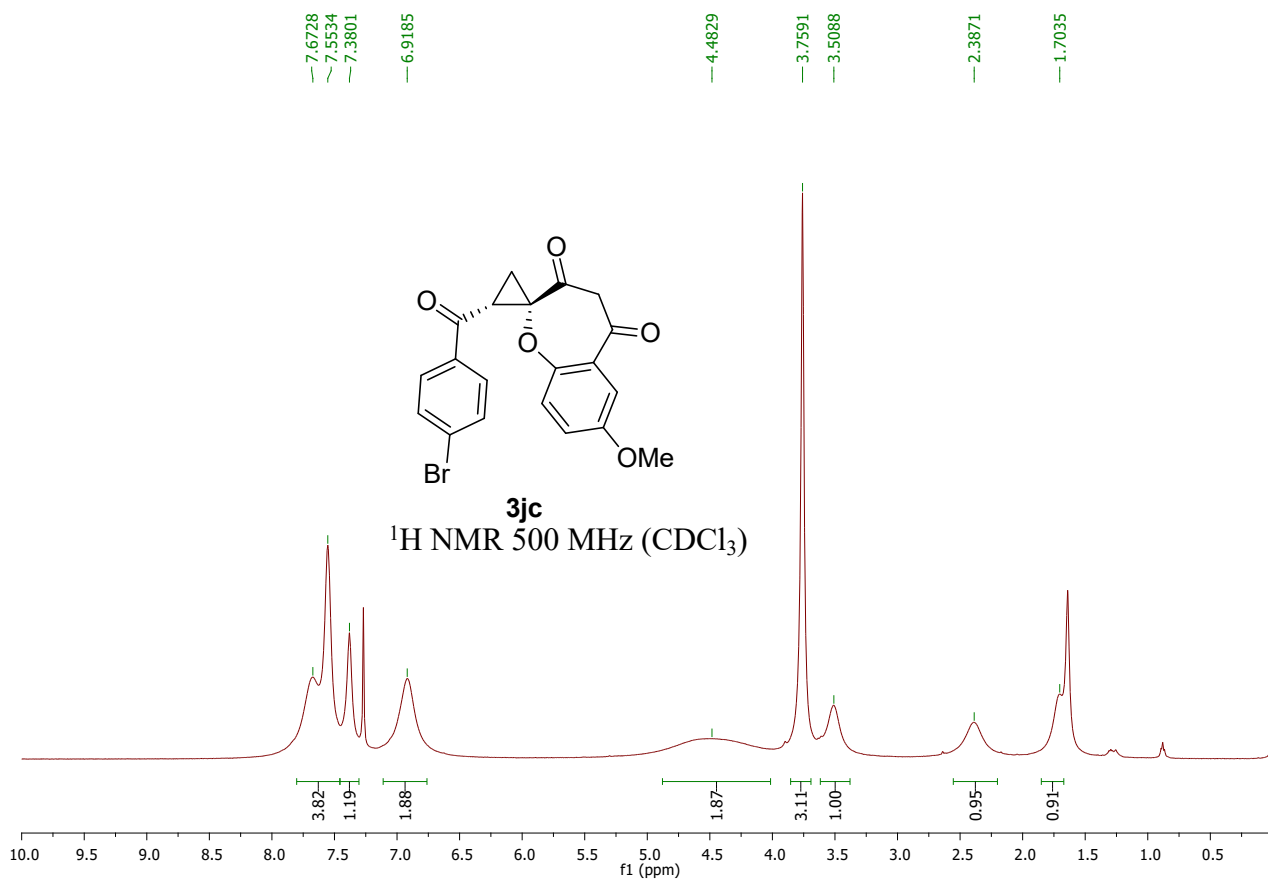
^{19}F NMR 470 MHz (CDCl_3)

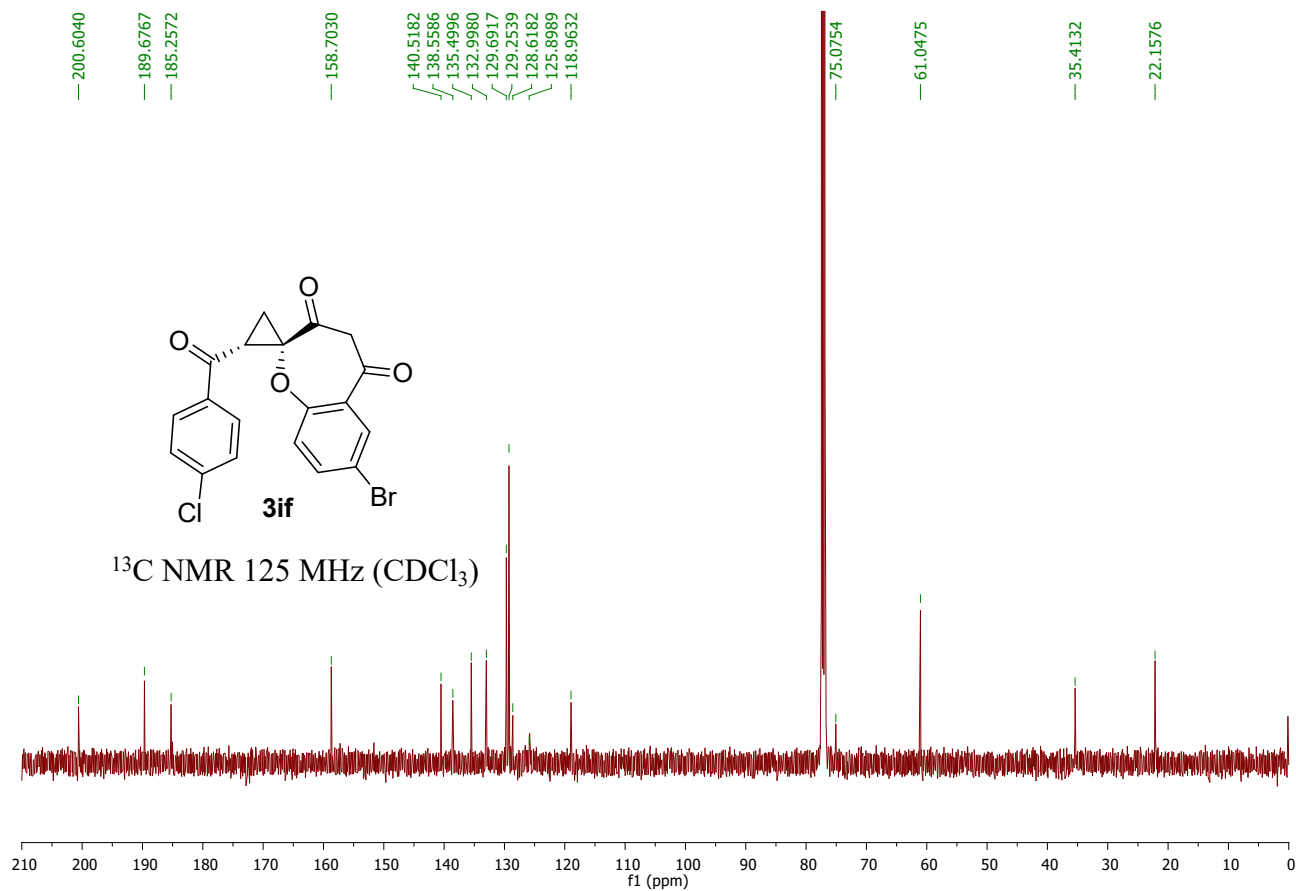
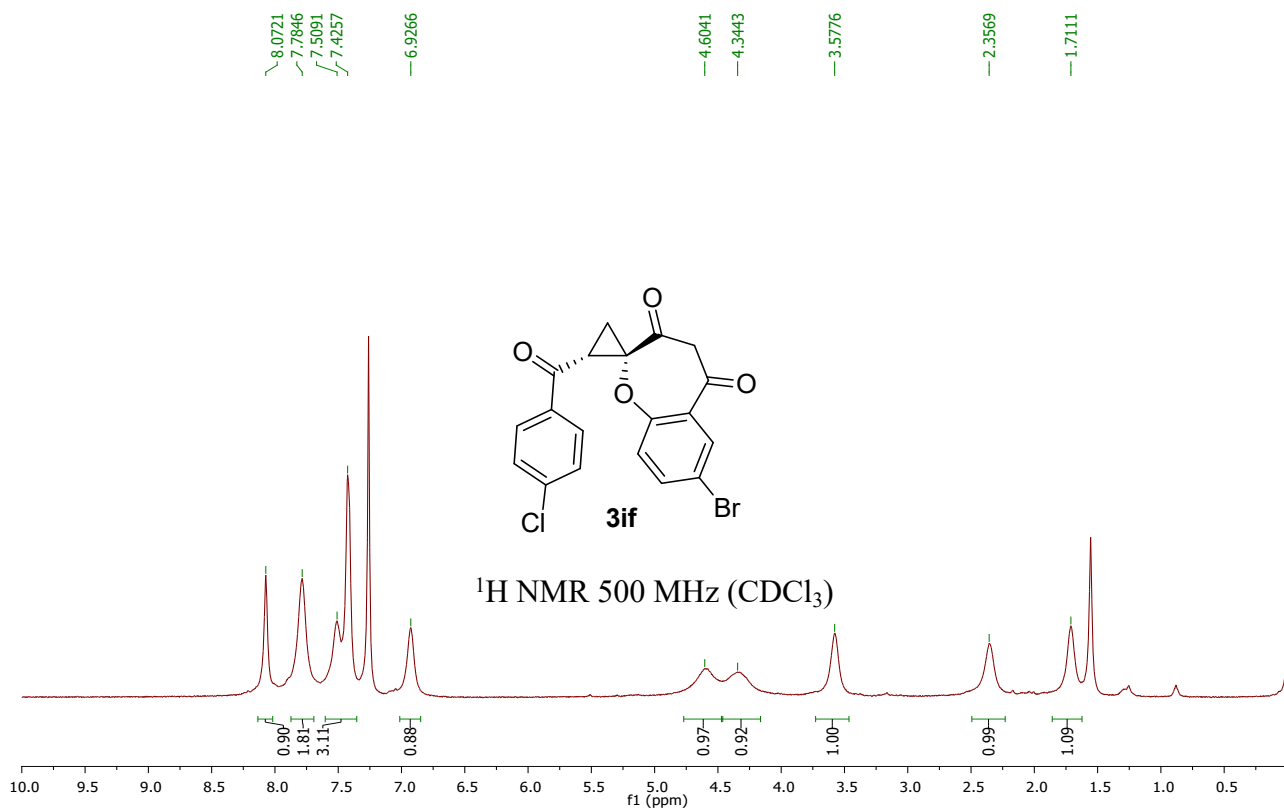


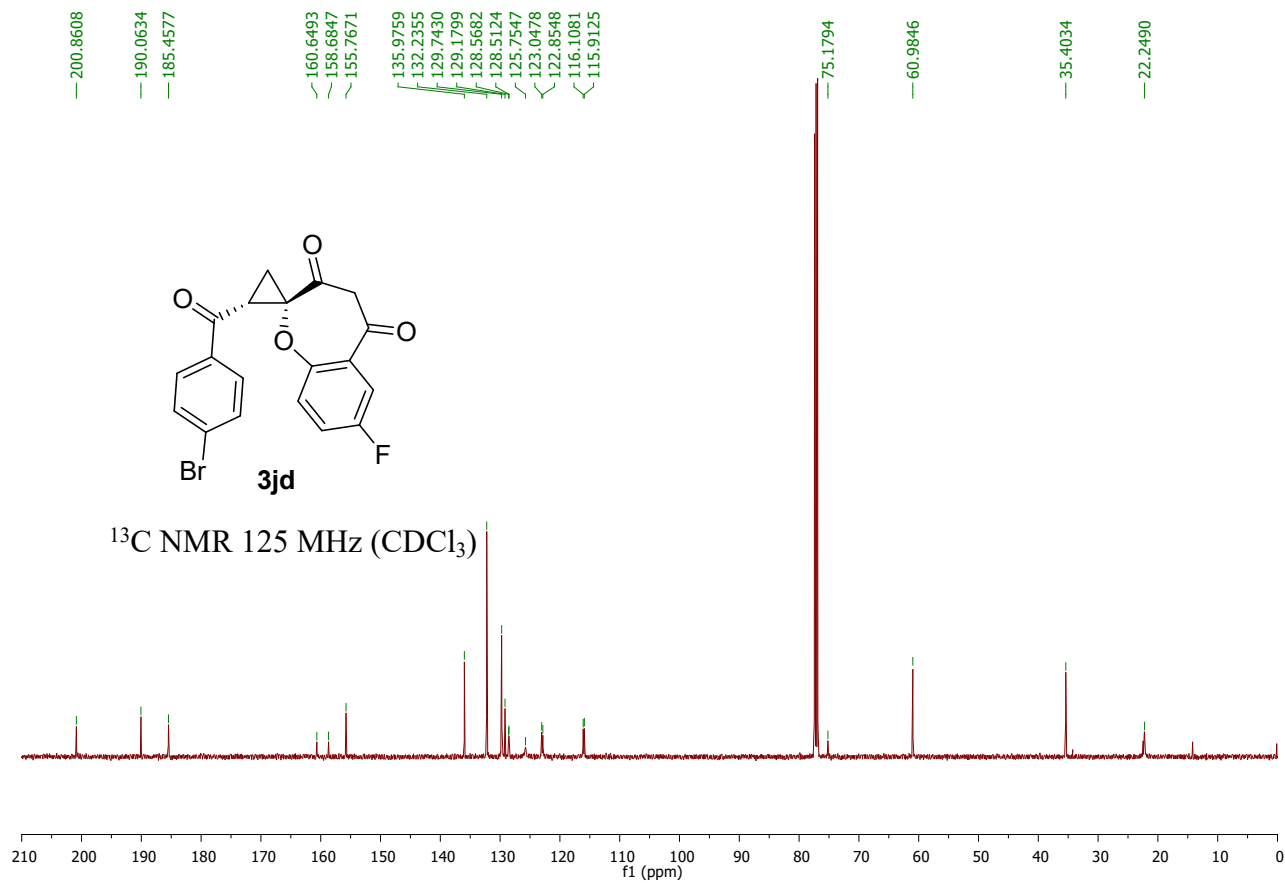
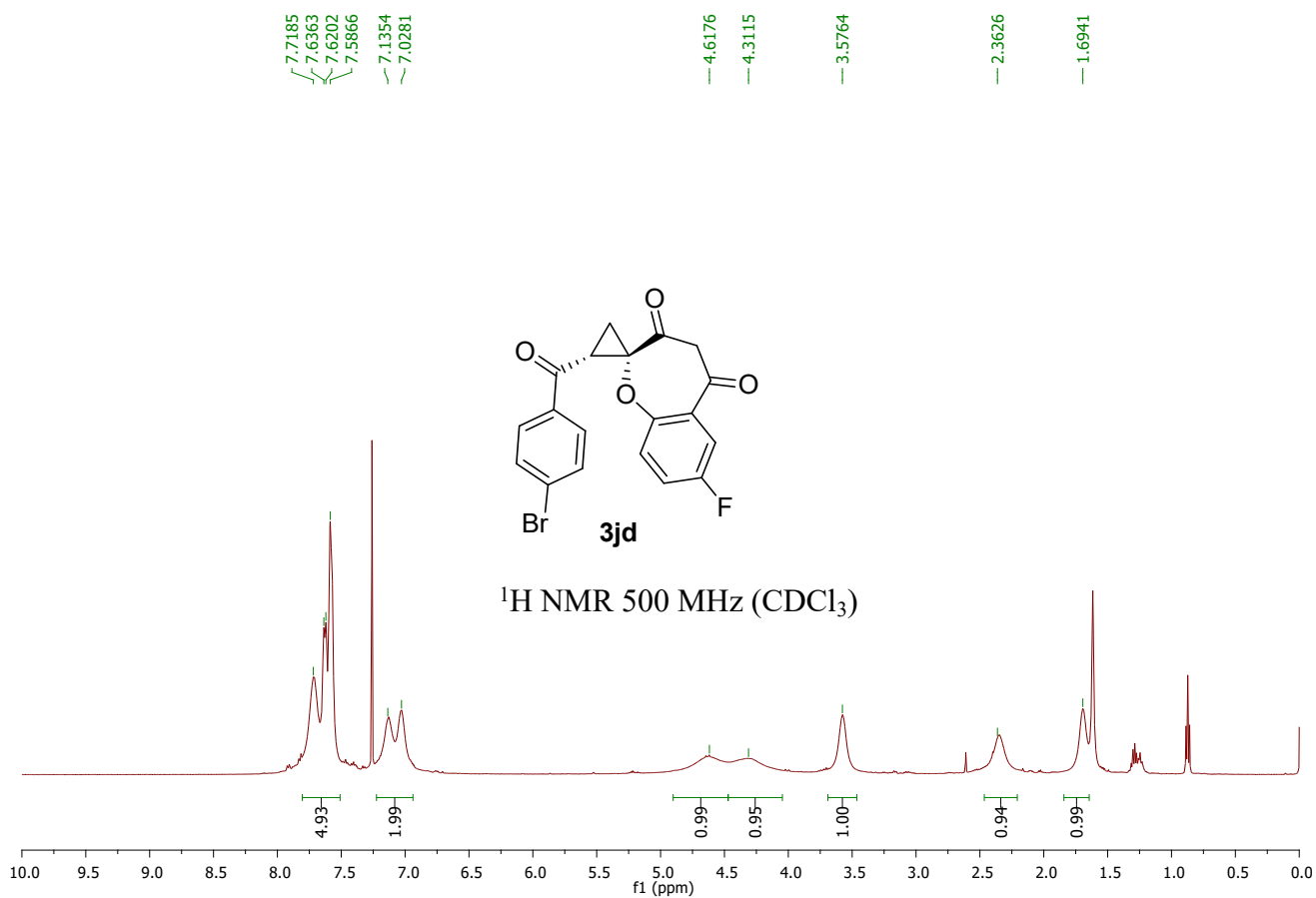


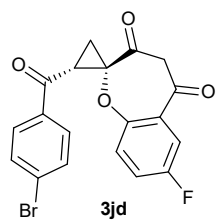




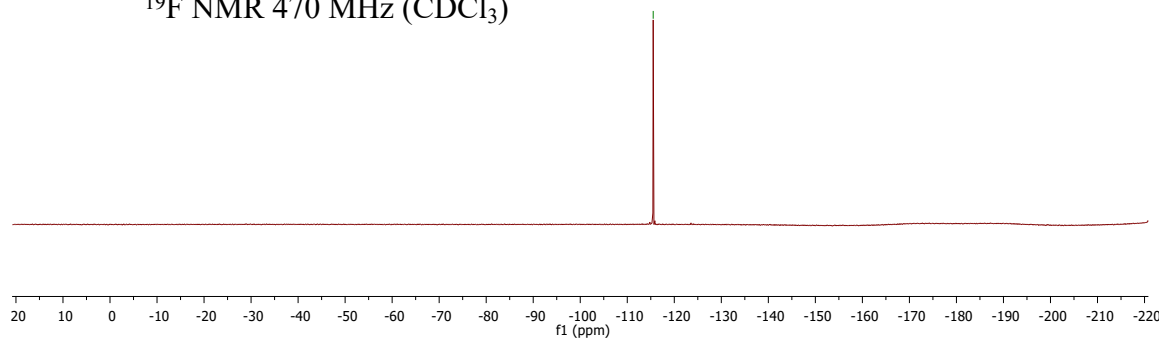


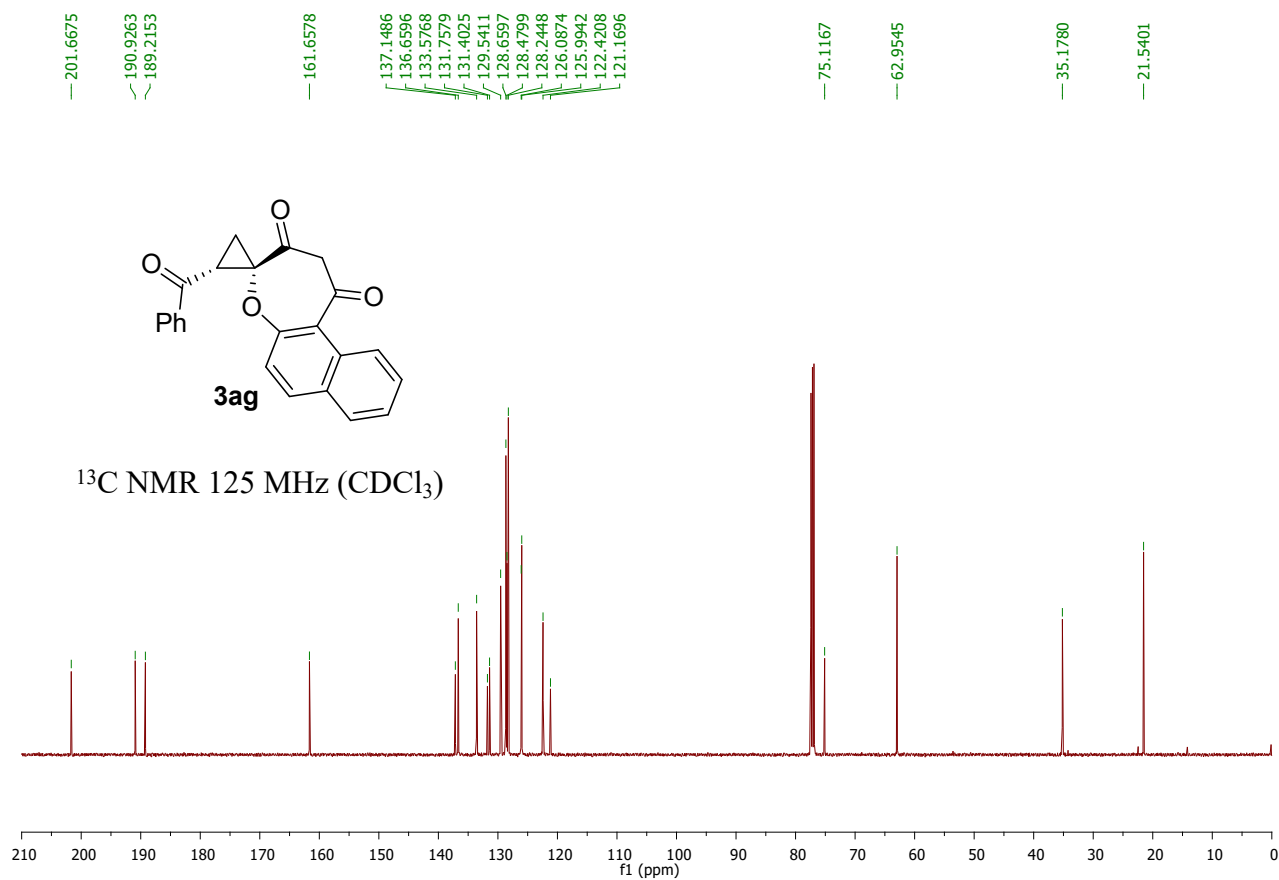
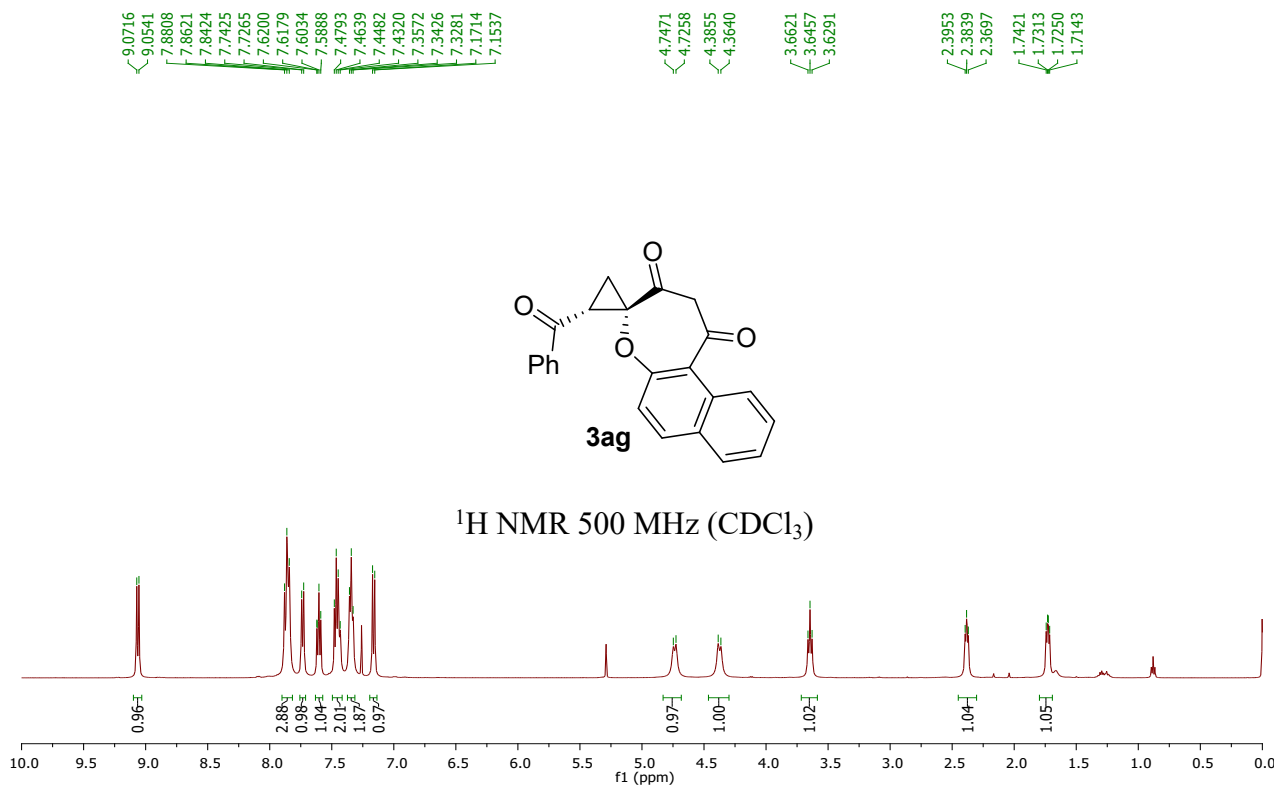


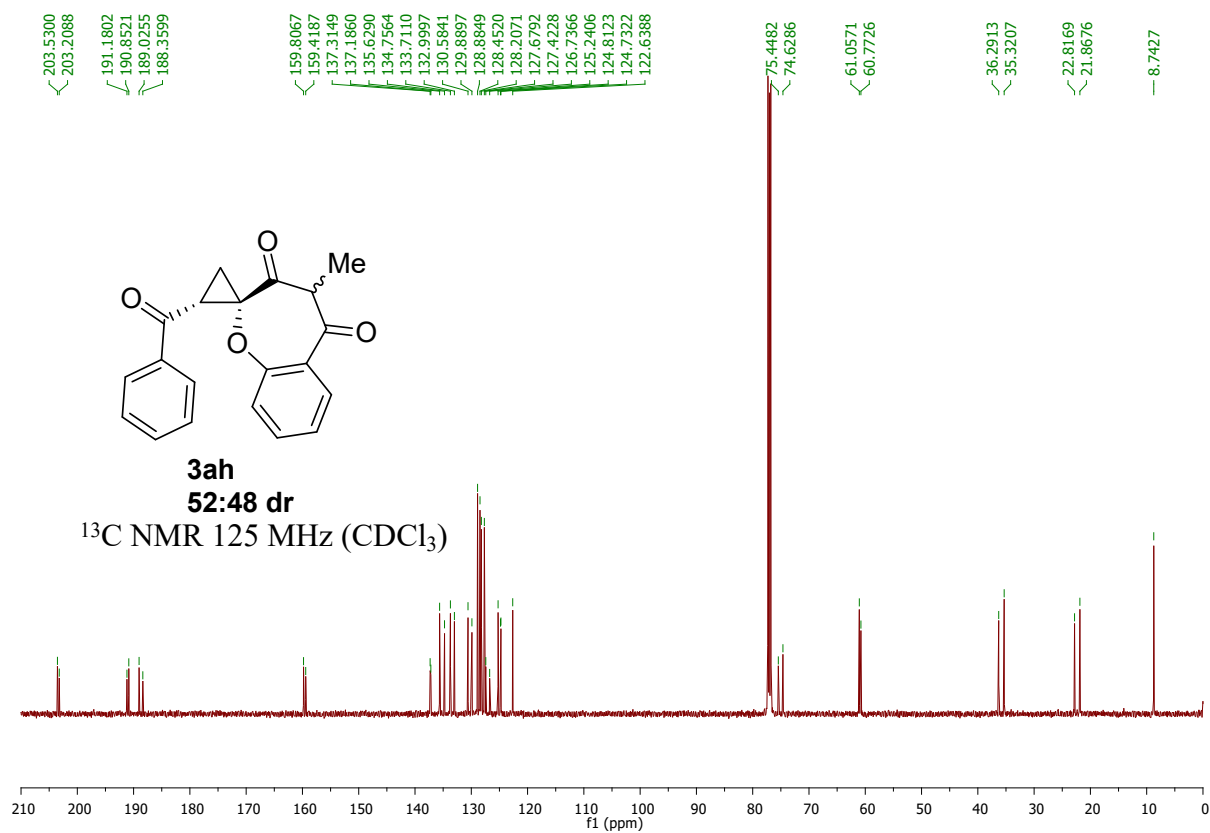
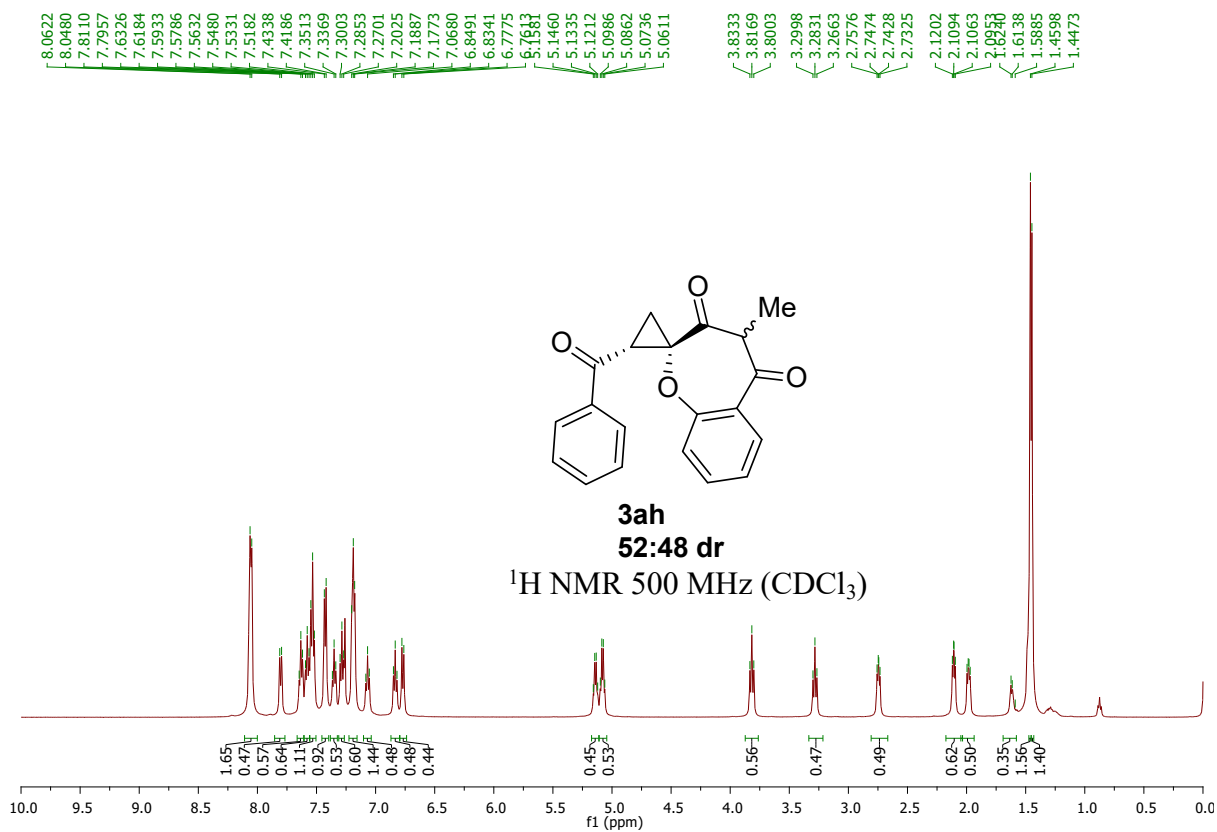


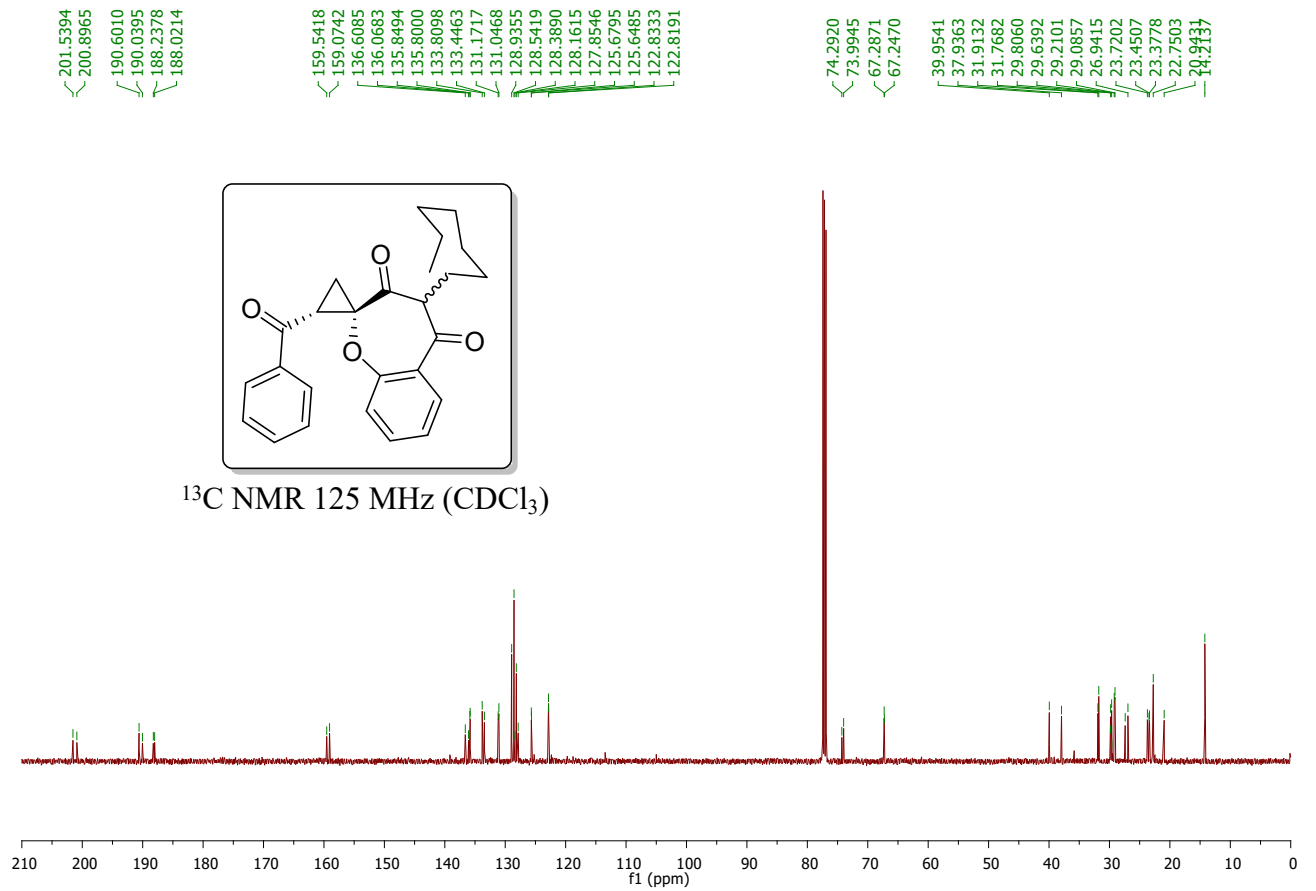
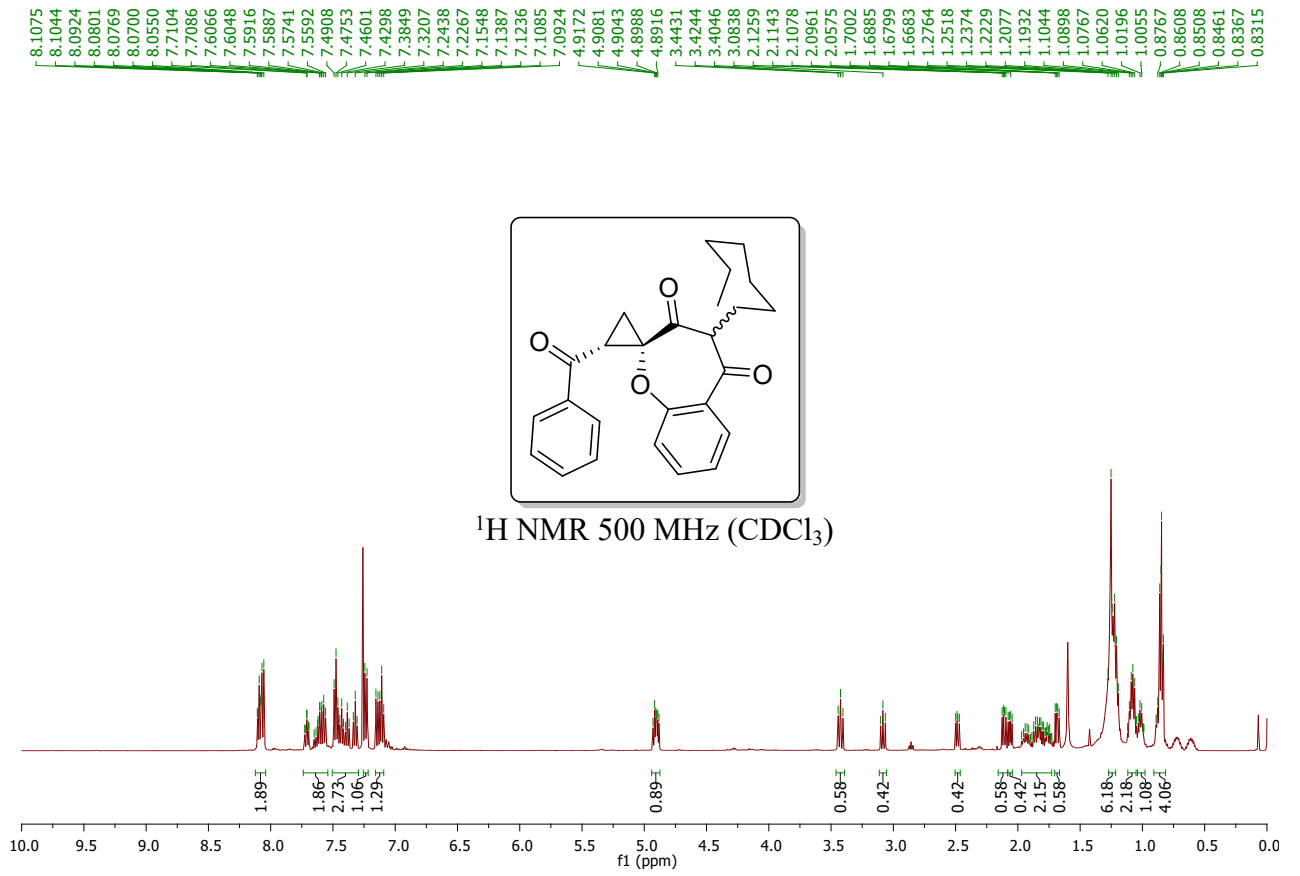


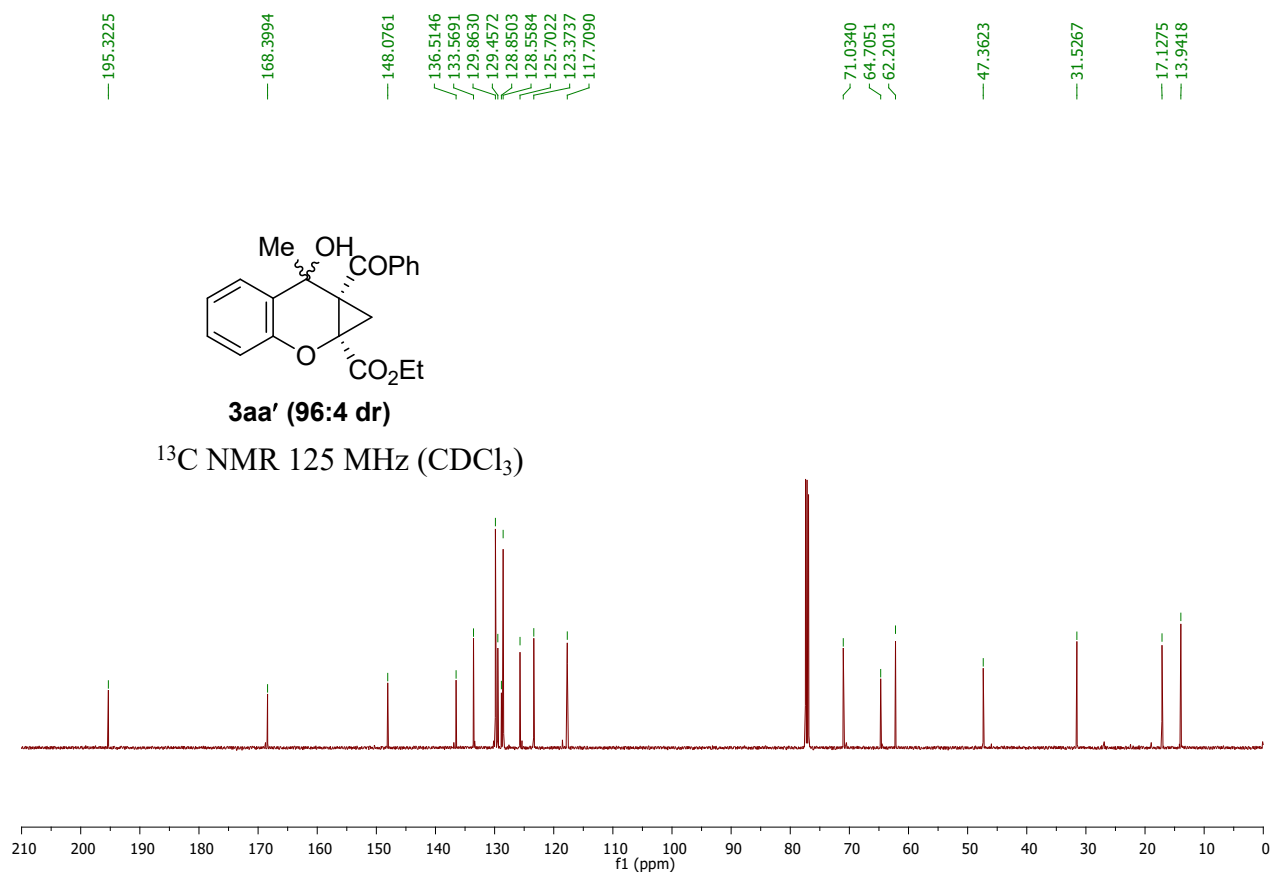
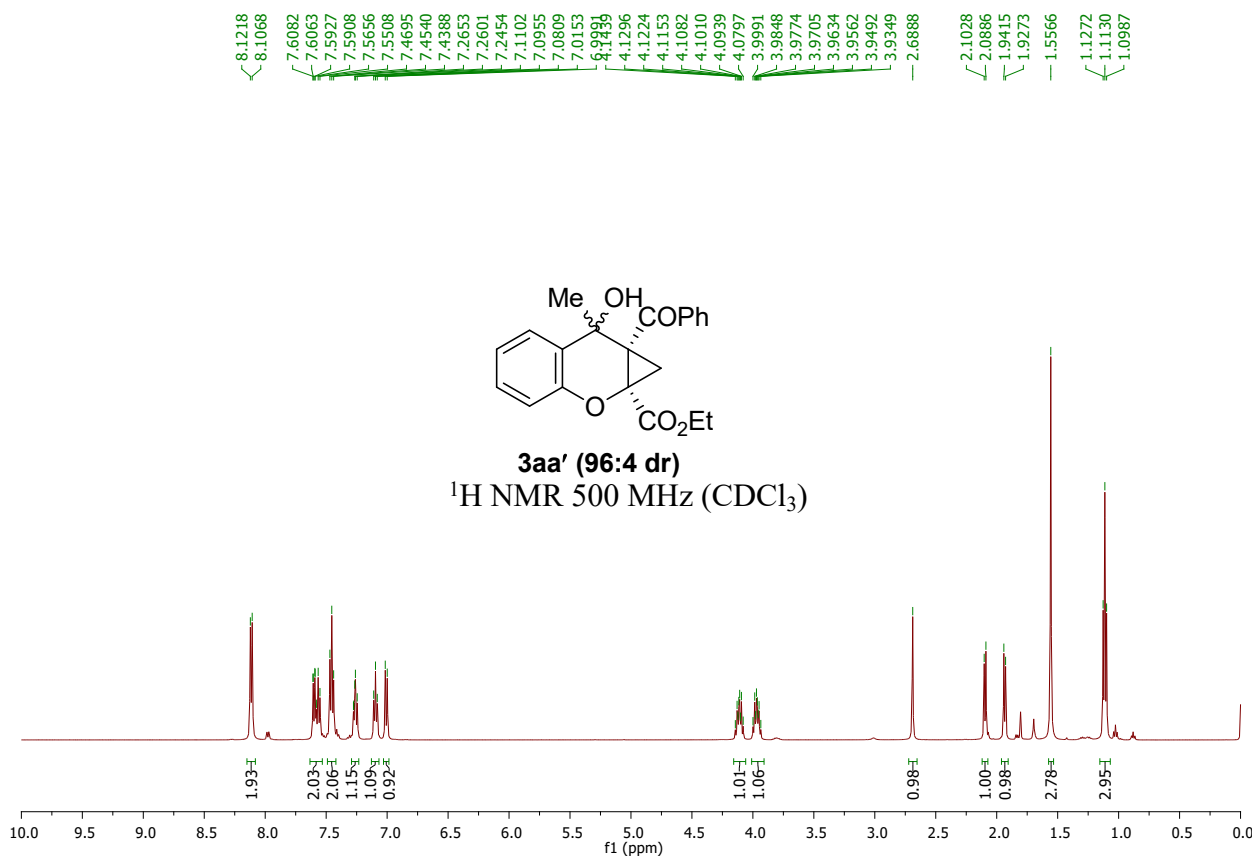
^{19}F NMR 470 MHz (CDCl_3)

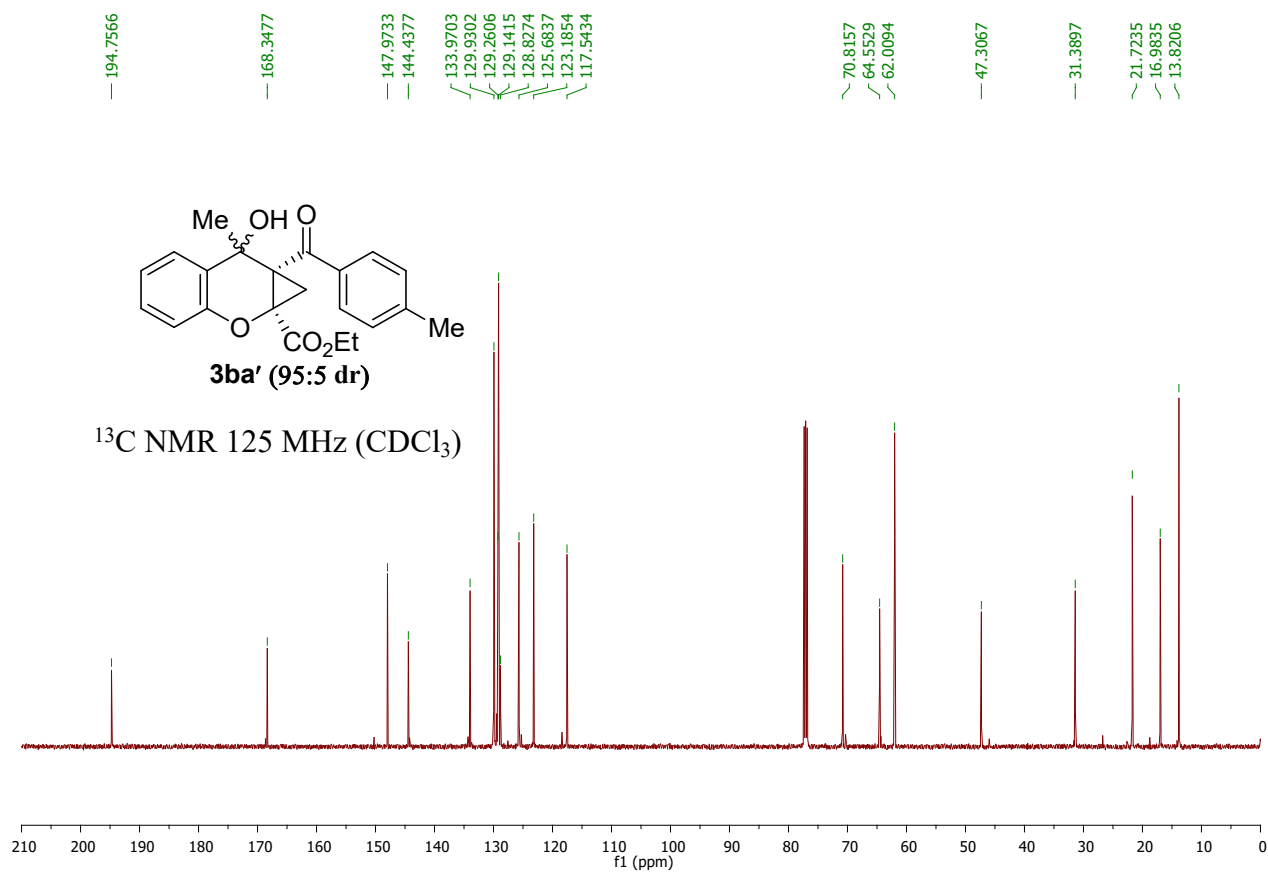
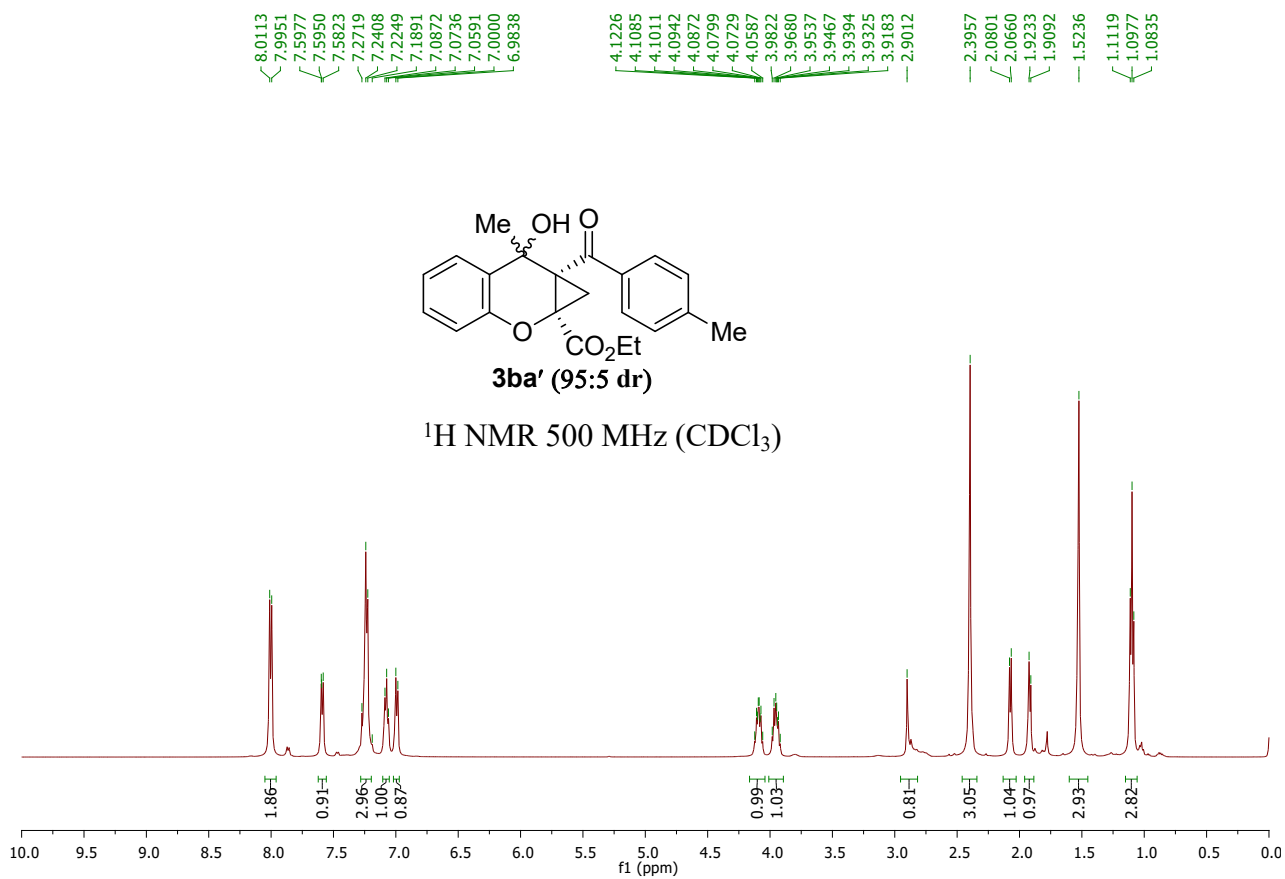


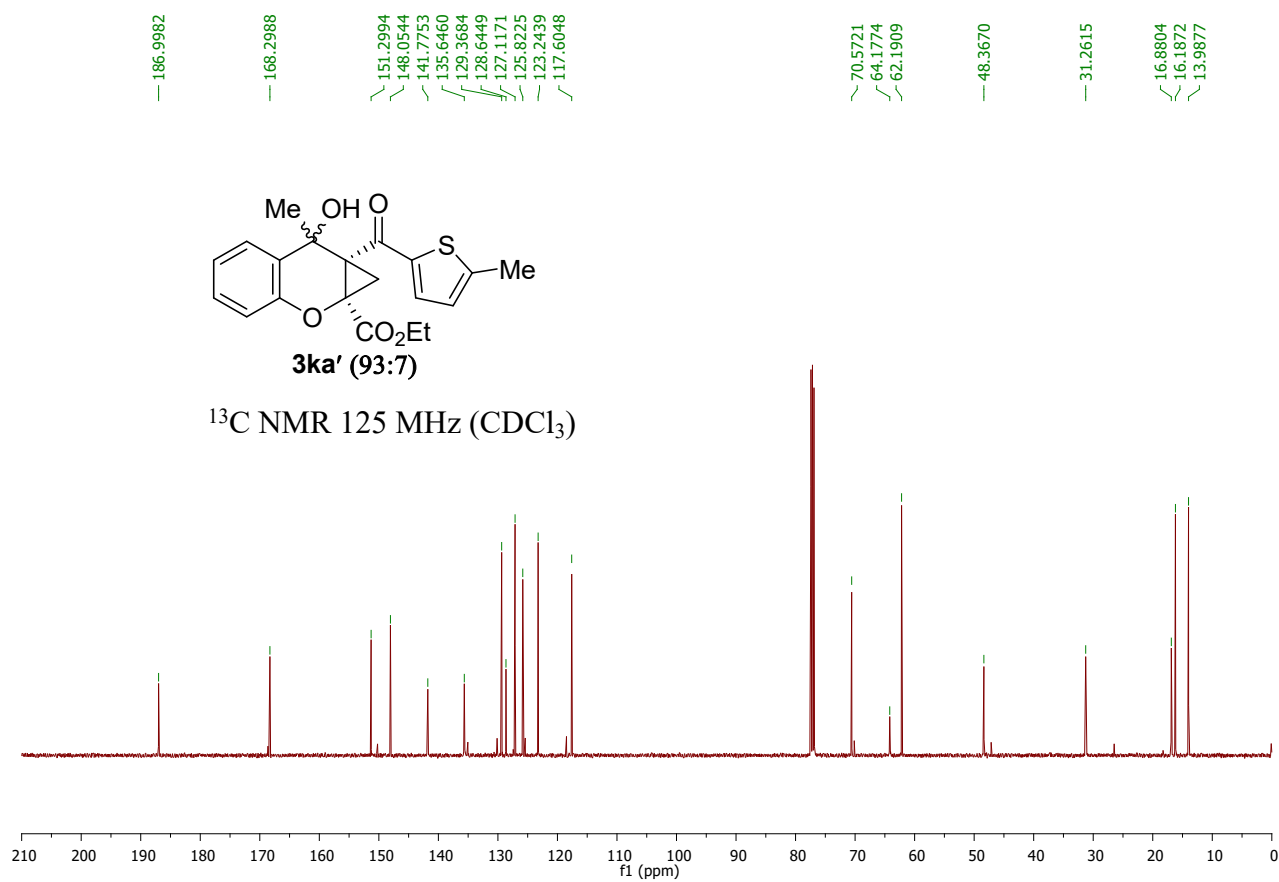
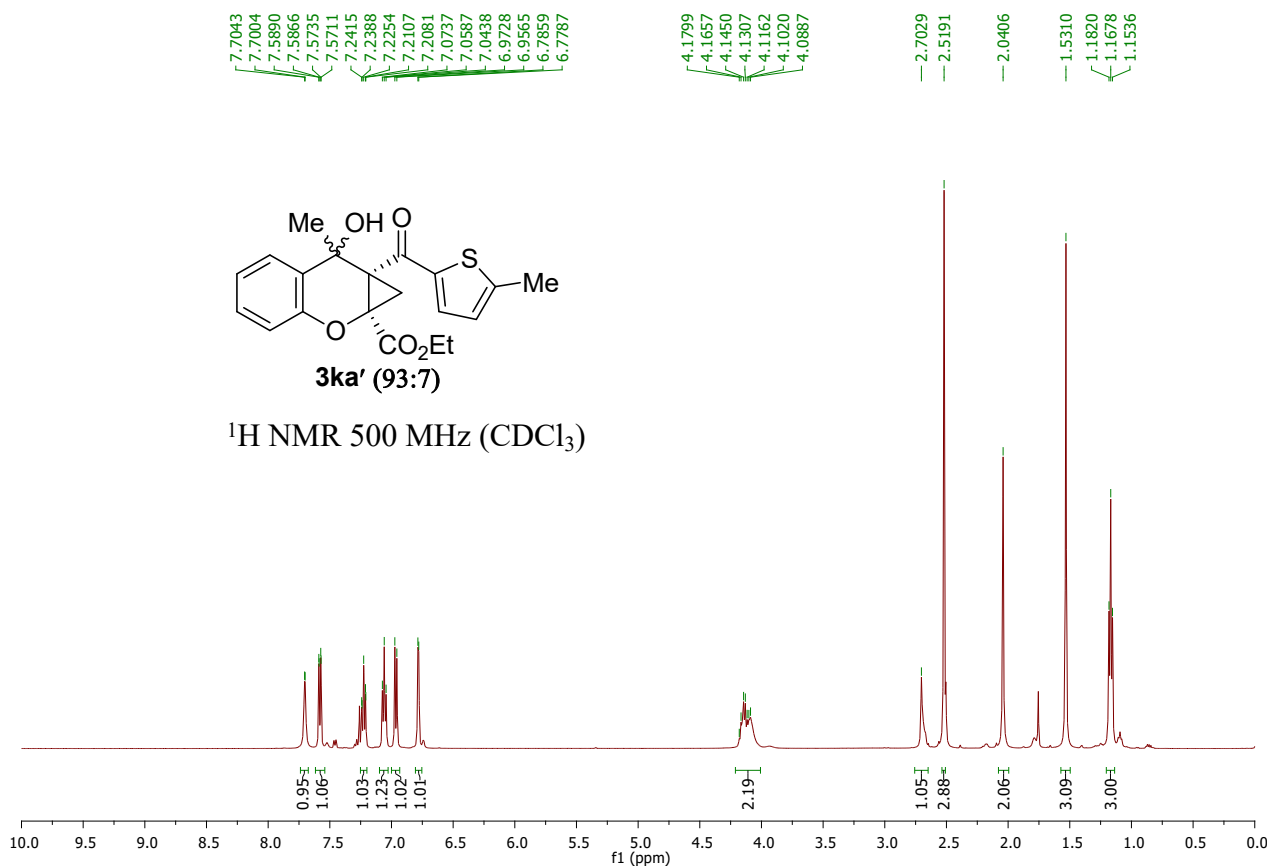


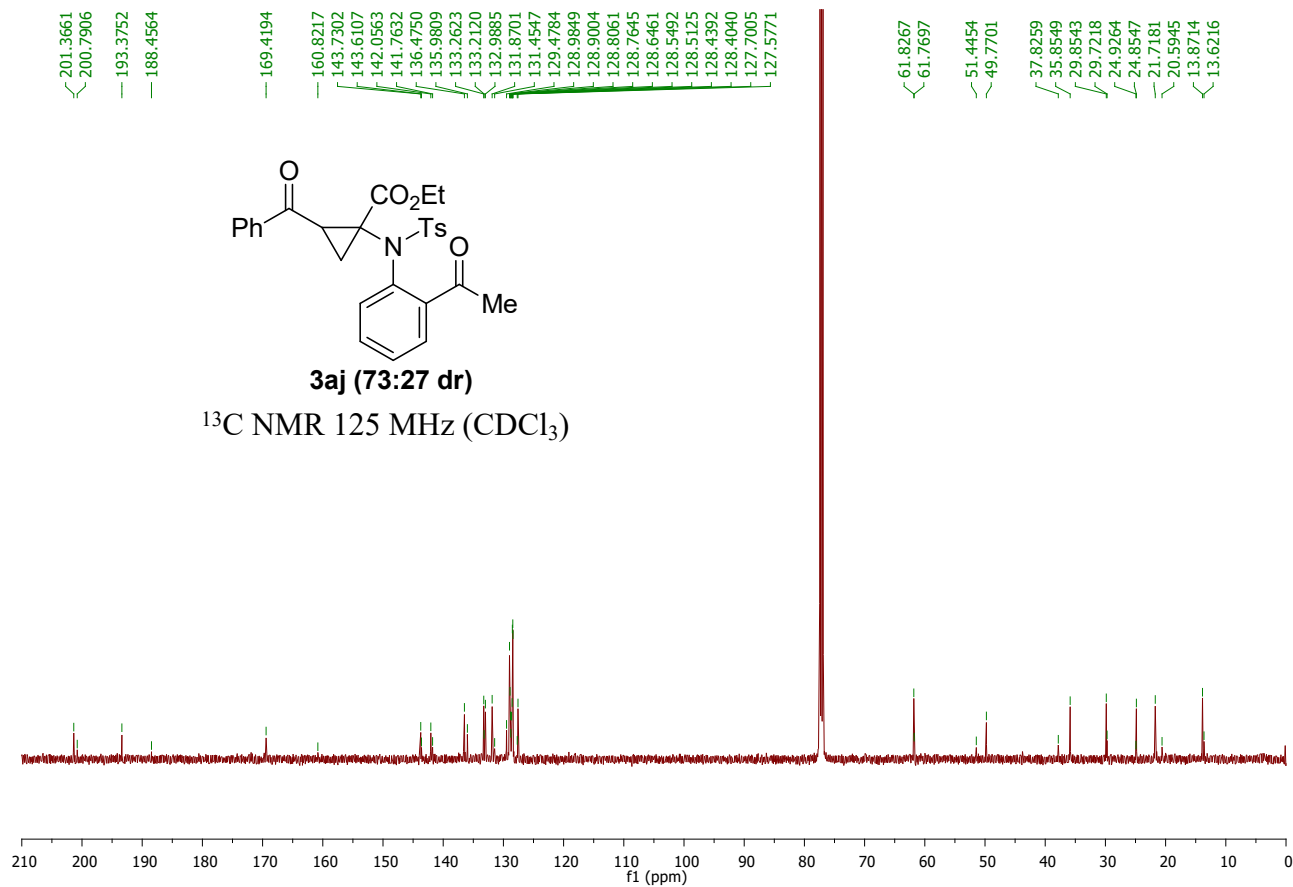
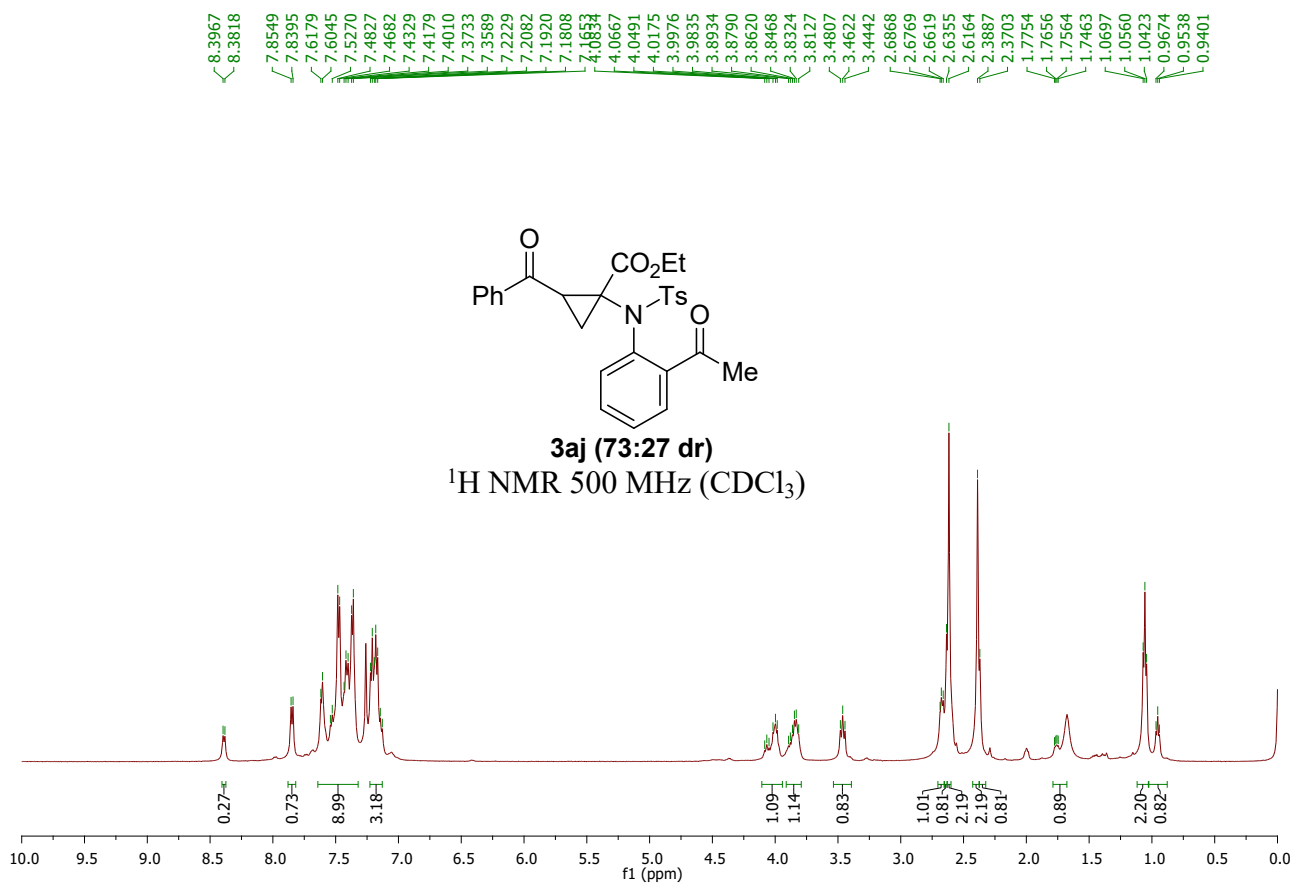


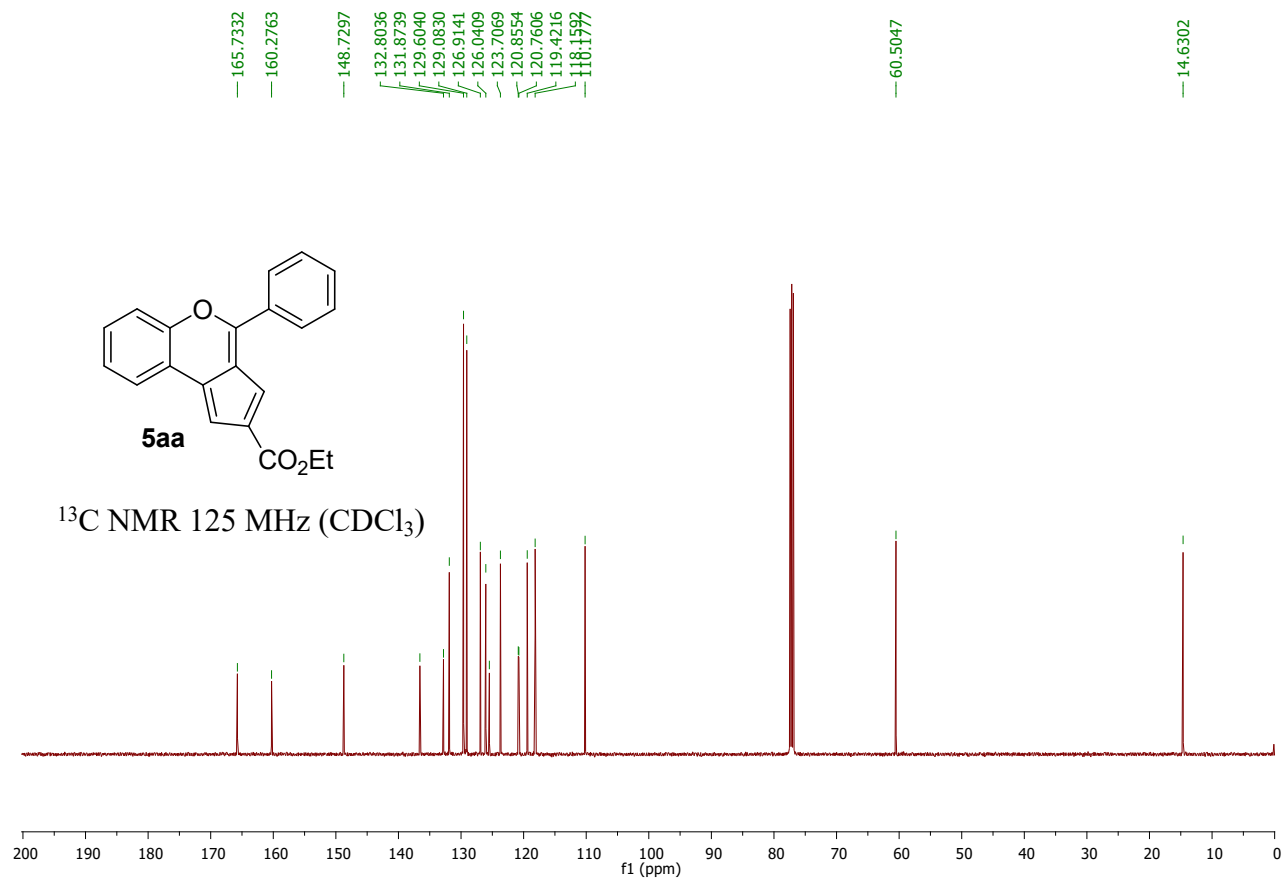
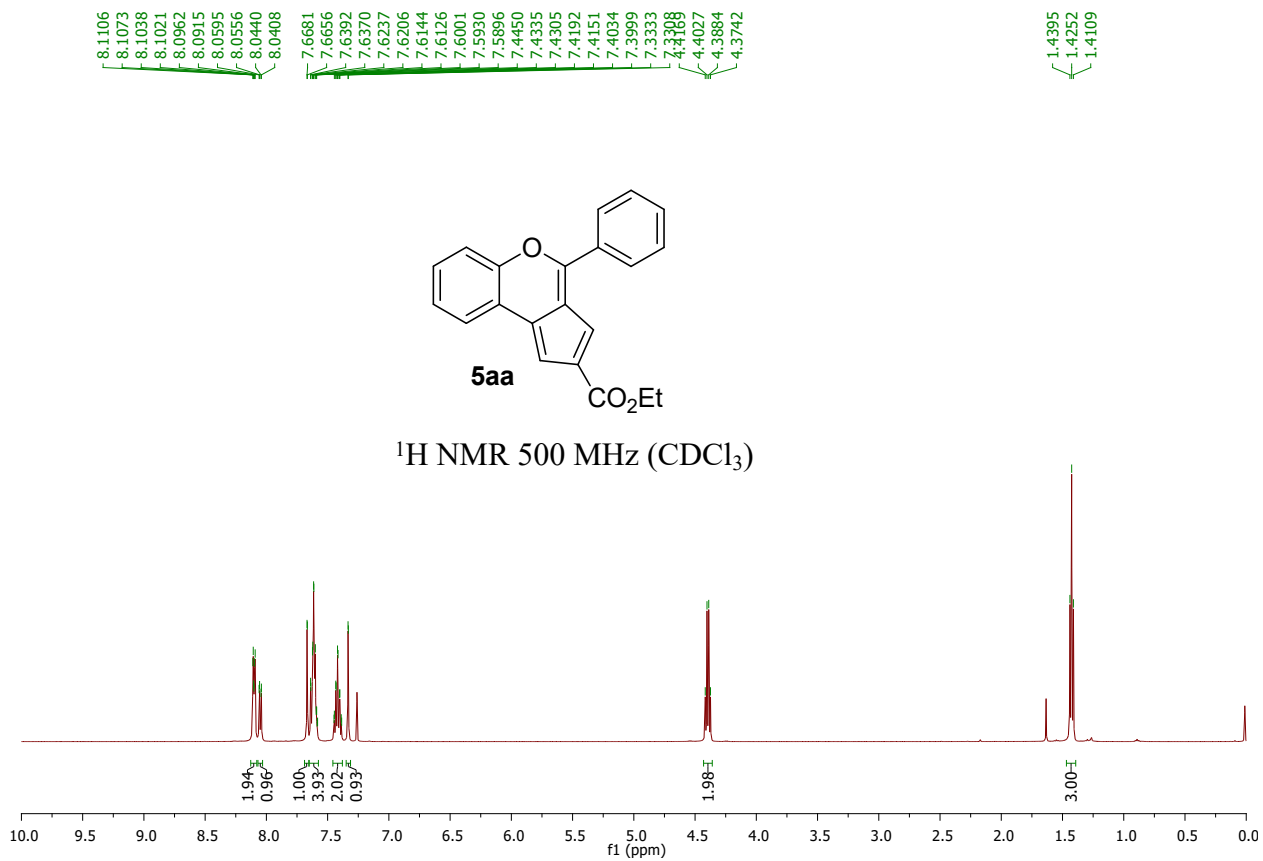


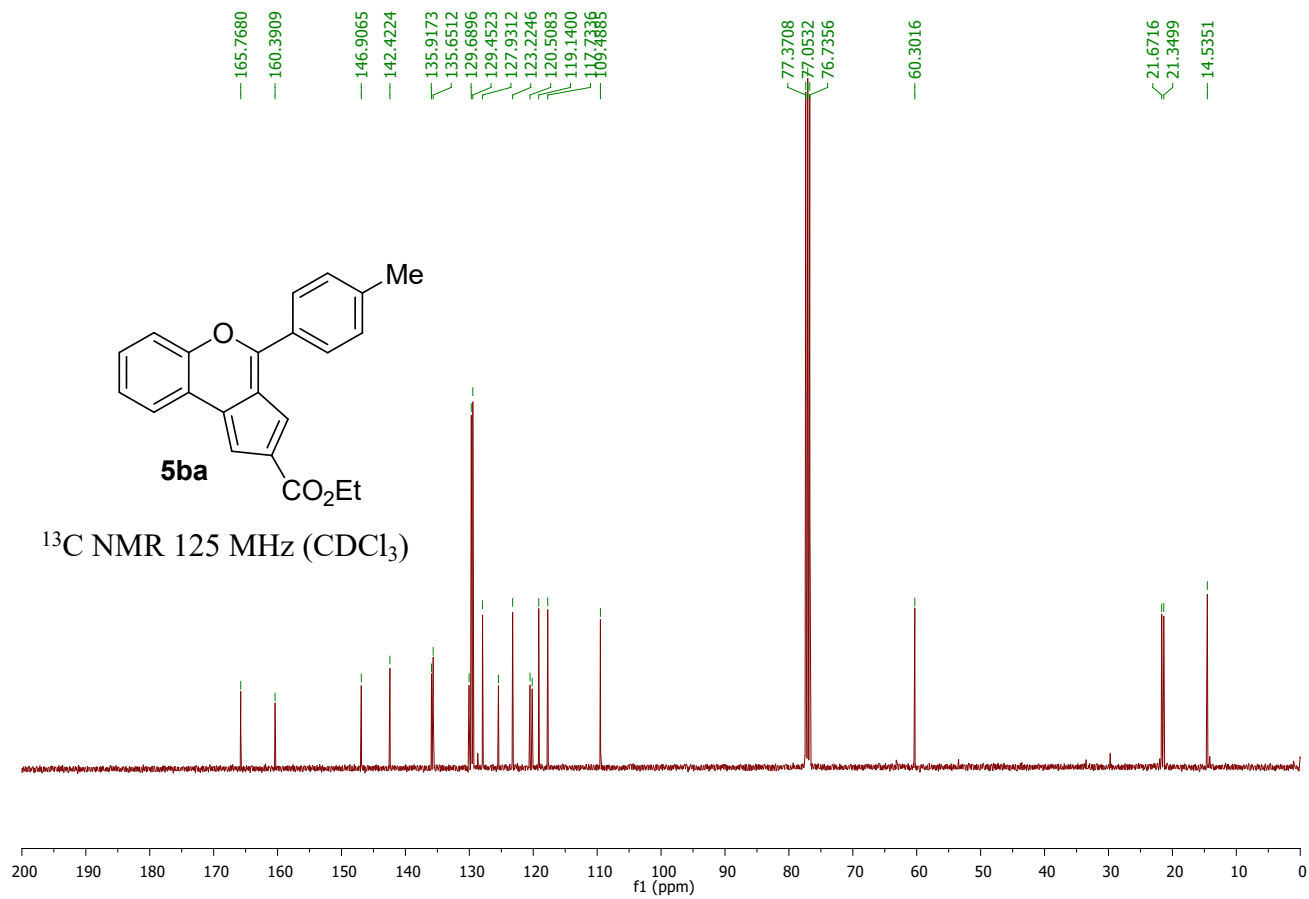
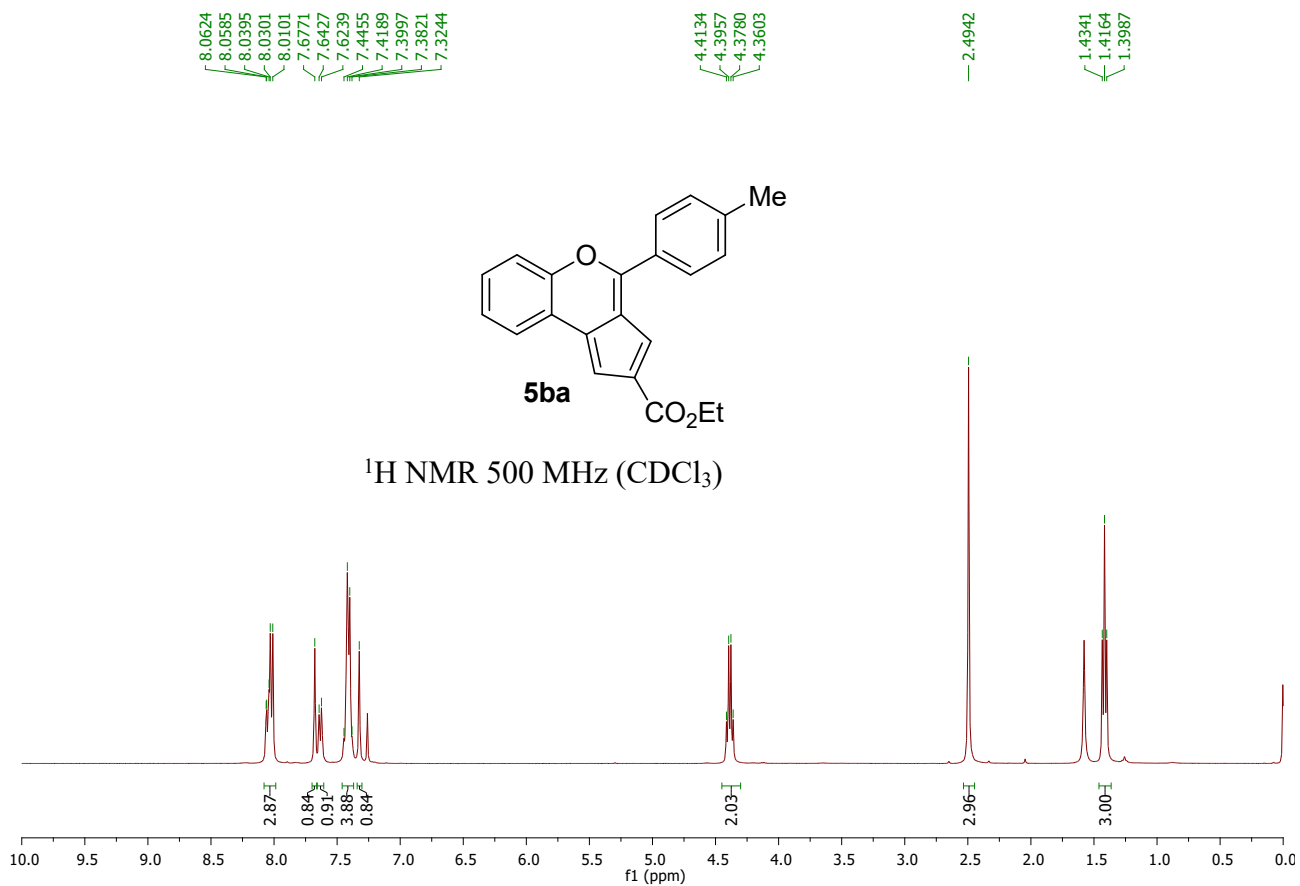


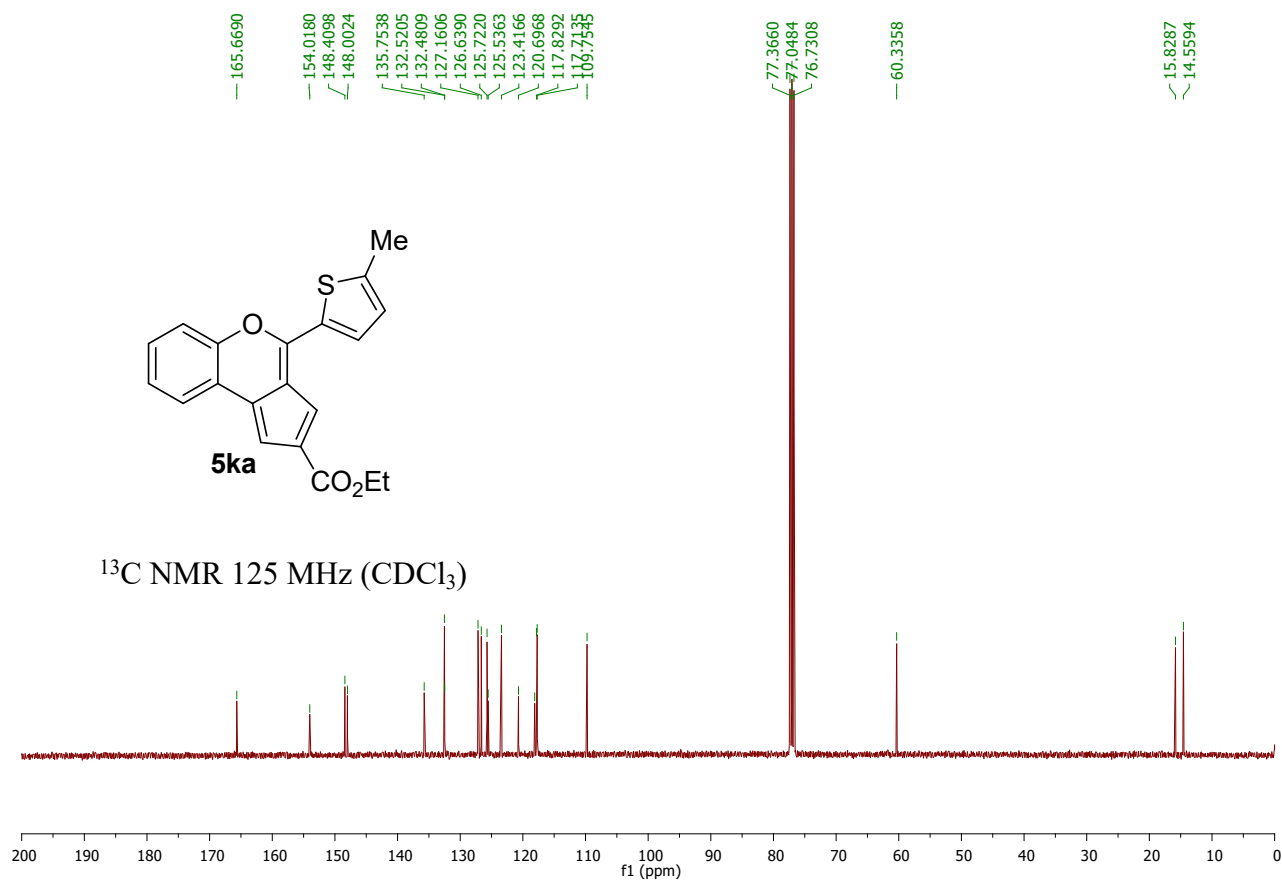
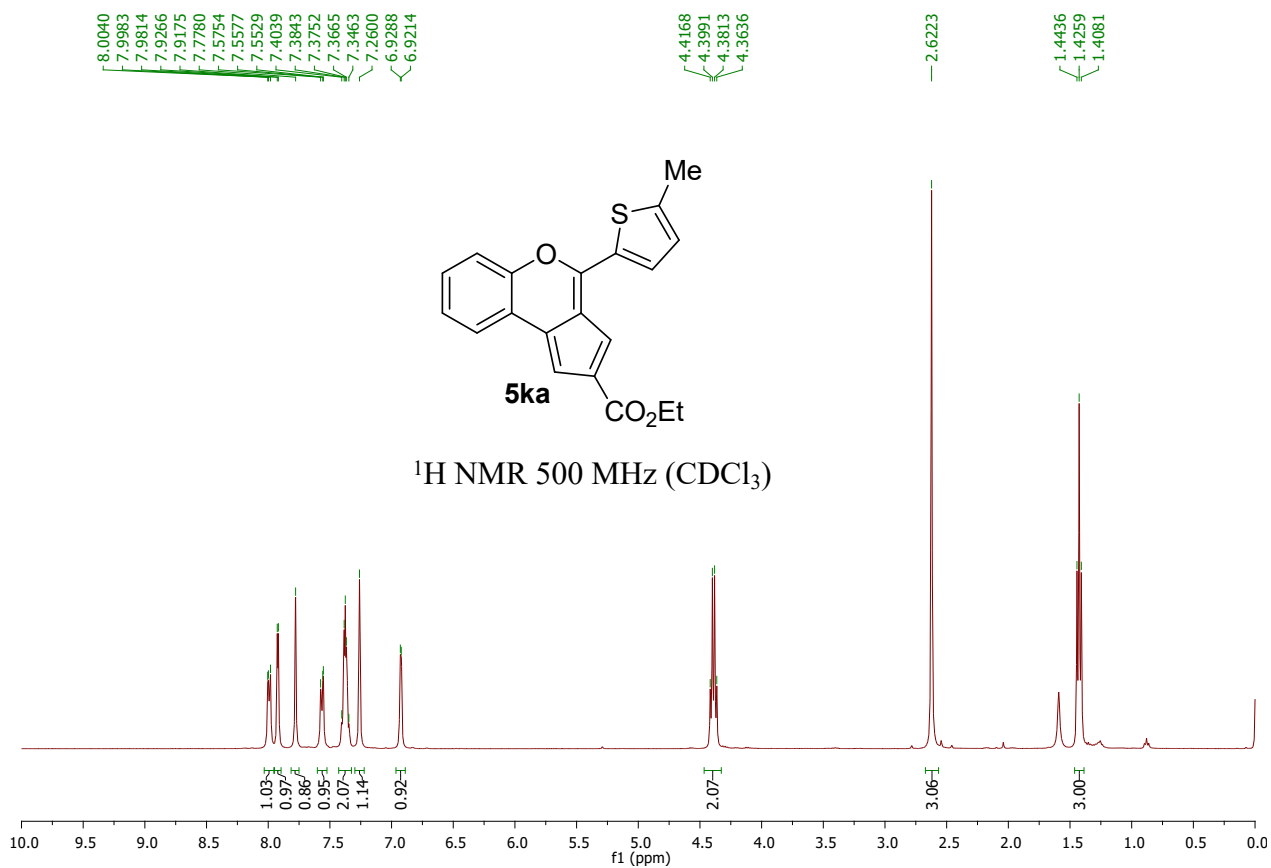


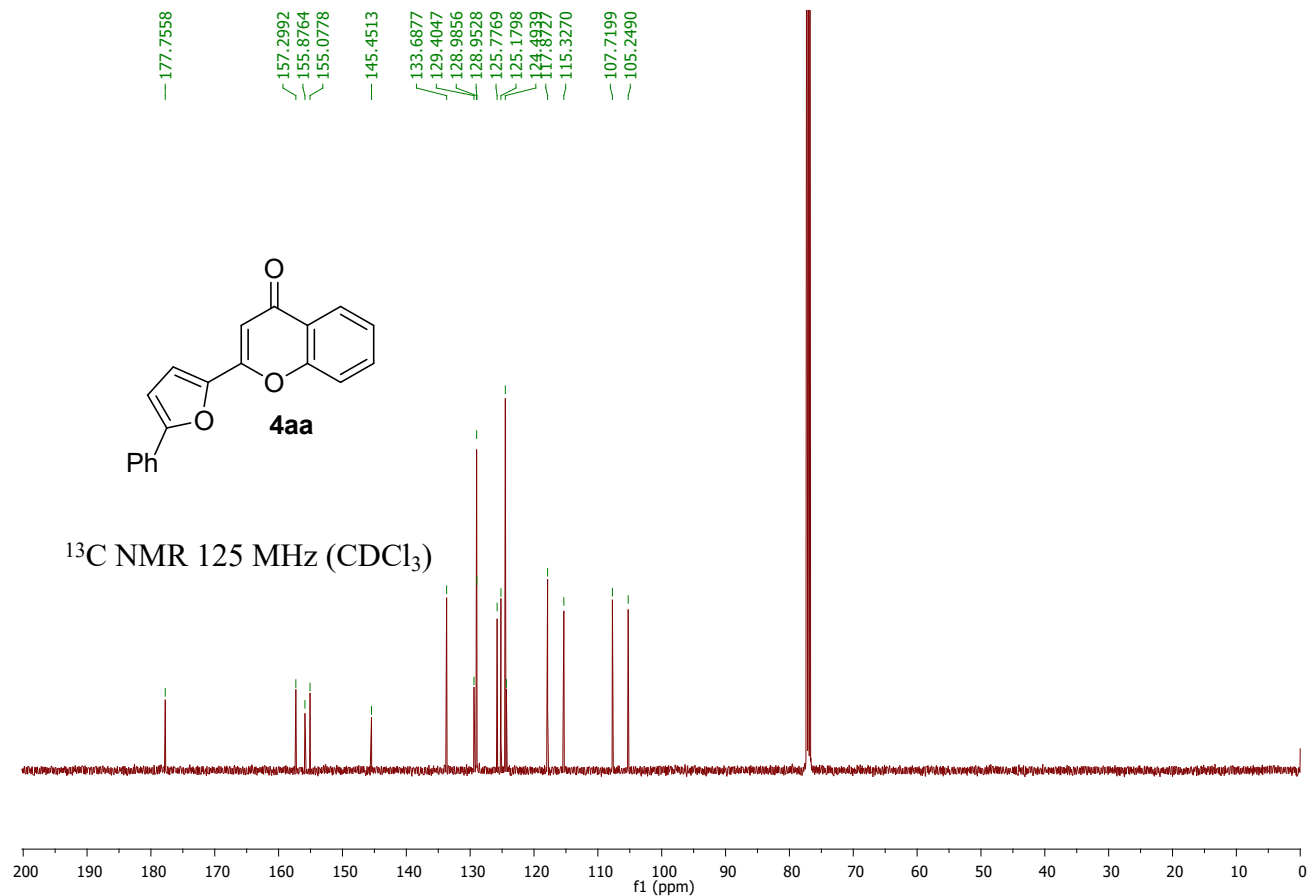
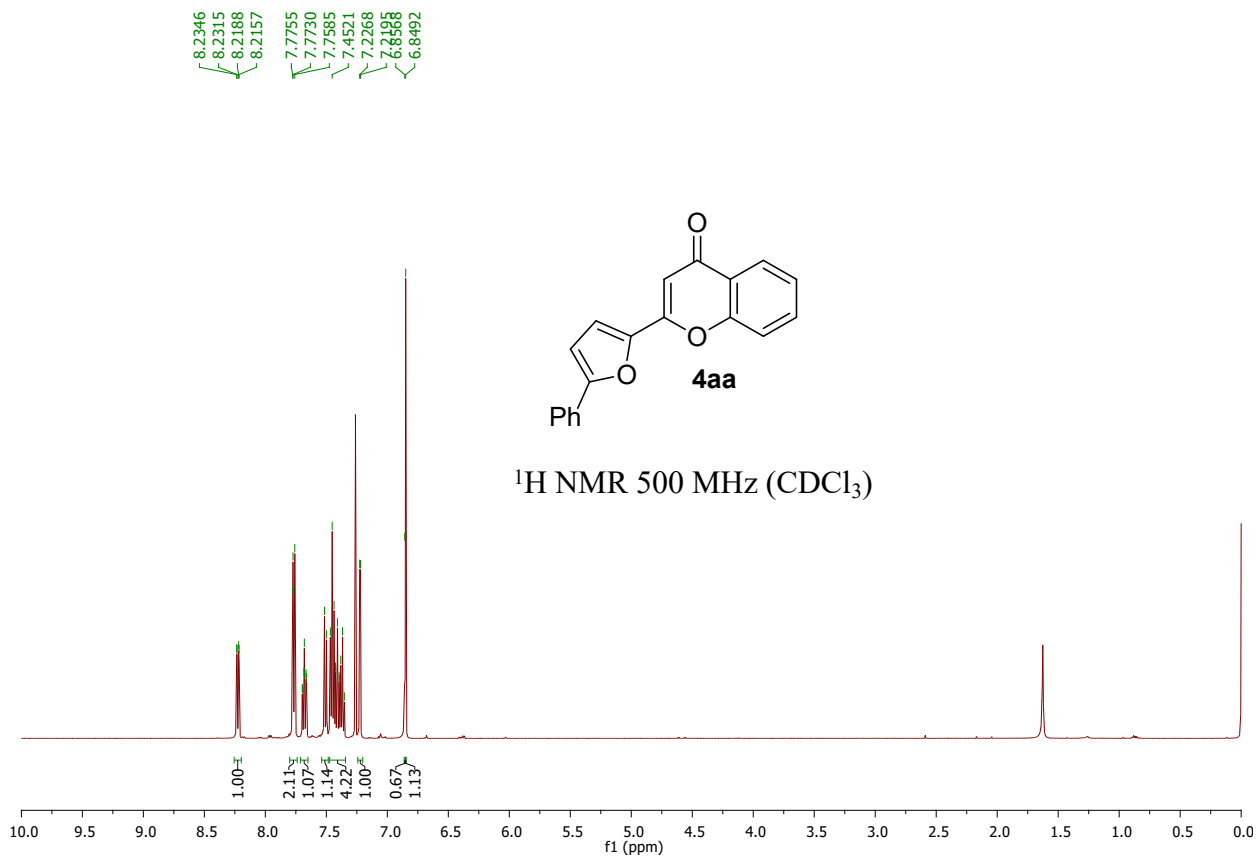




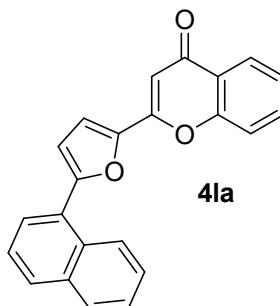




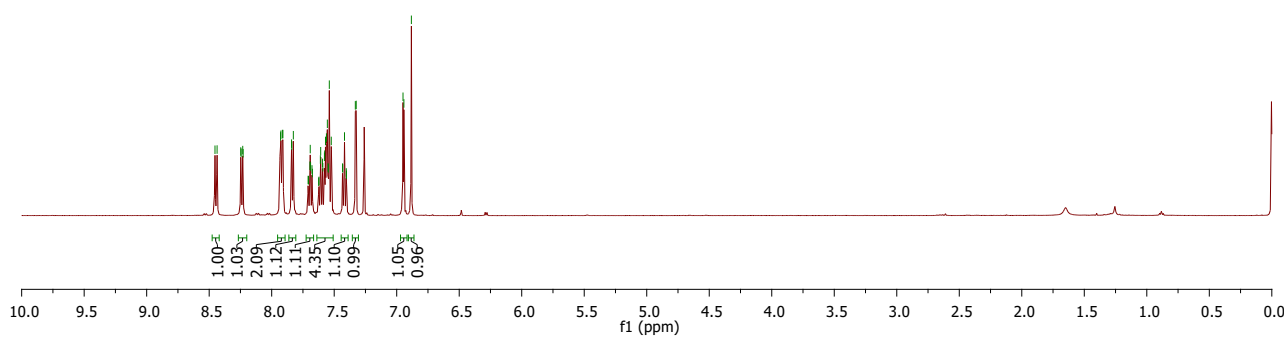




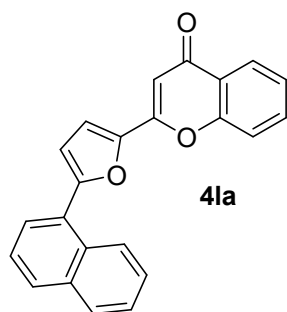
8.4536
8.4368
7.9291
7.9267
7.9147
7.9103
7.8412
7.8395
7.8268
7.6917
7.5697
7.5621
7.5547
7.5391
7.5235
7.4176
7.3310
6.9480
6.9425
6.8826



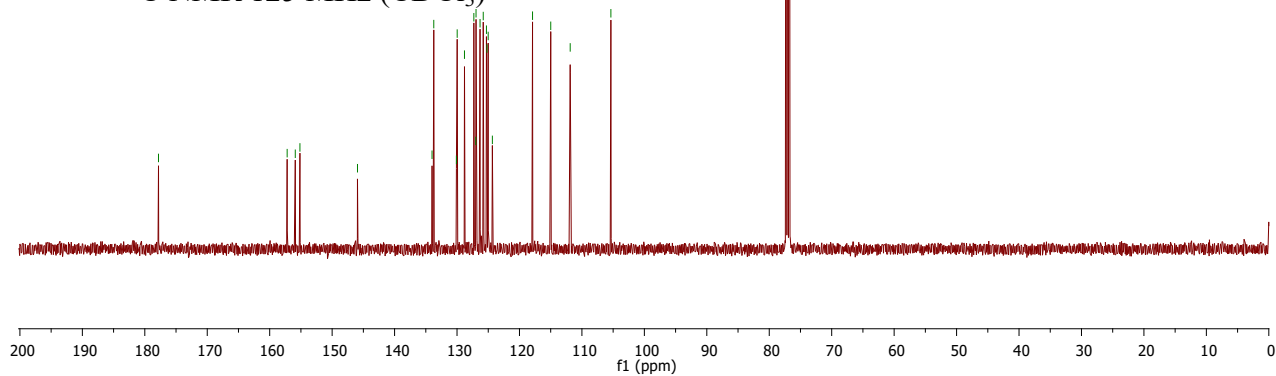
$^1\text{H NMR}$ 500 MHz (CDCl_3)

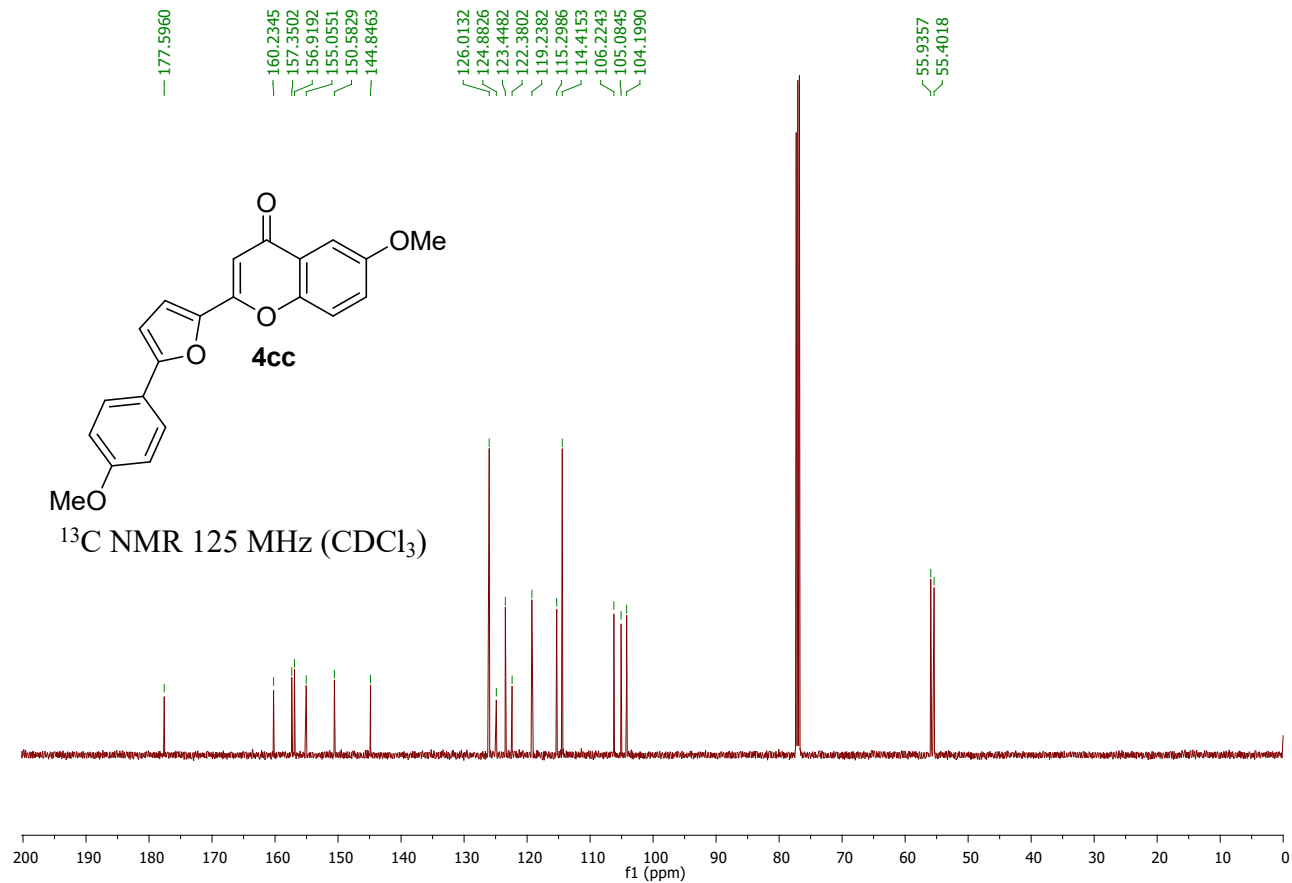
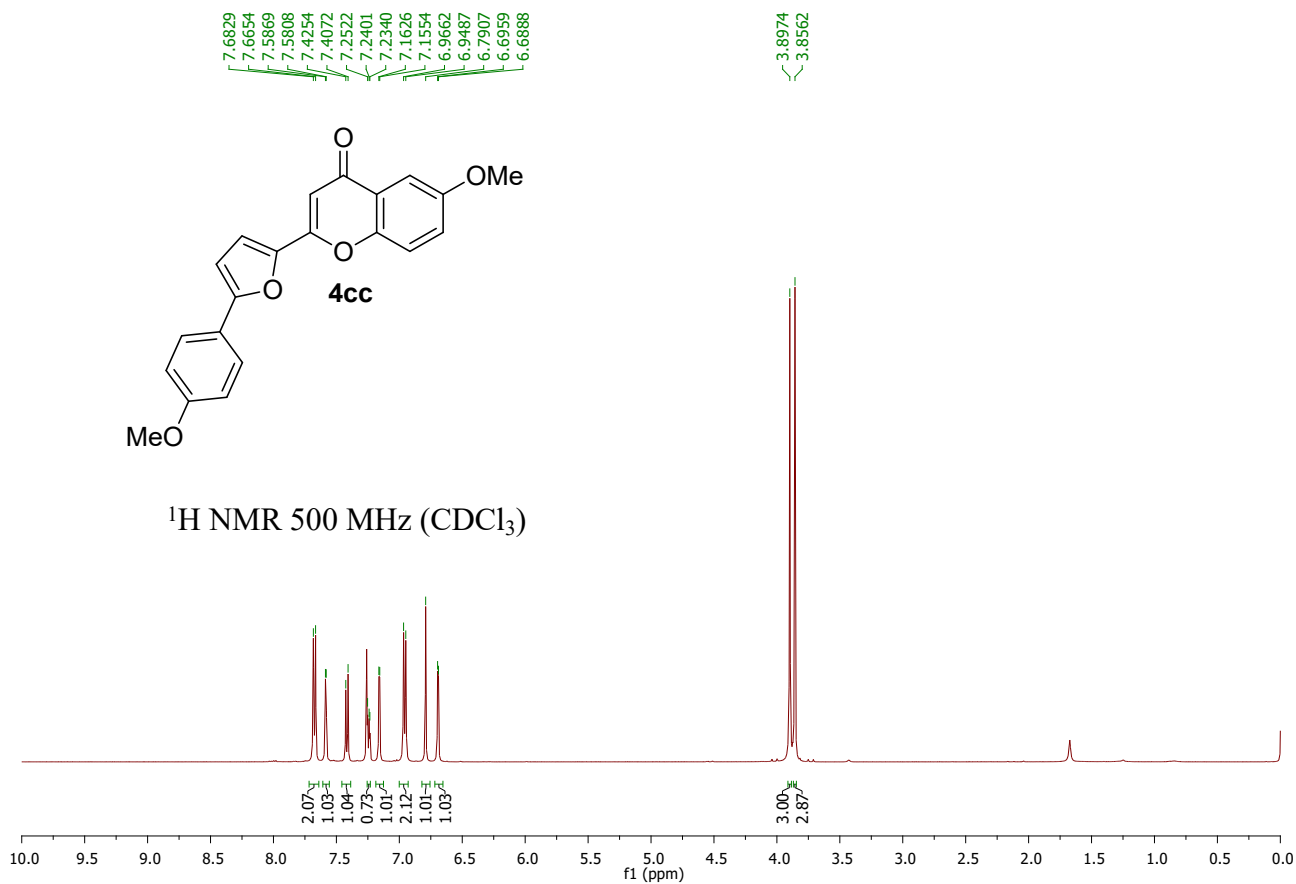


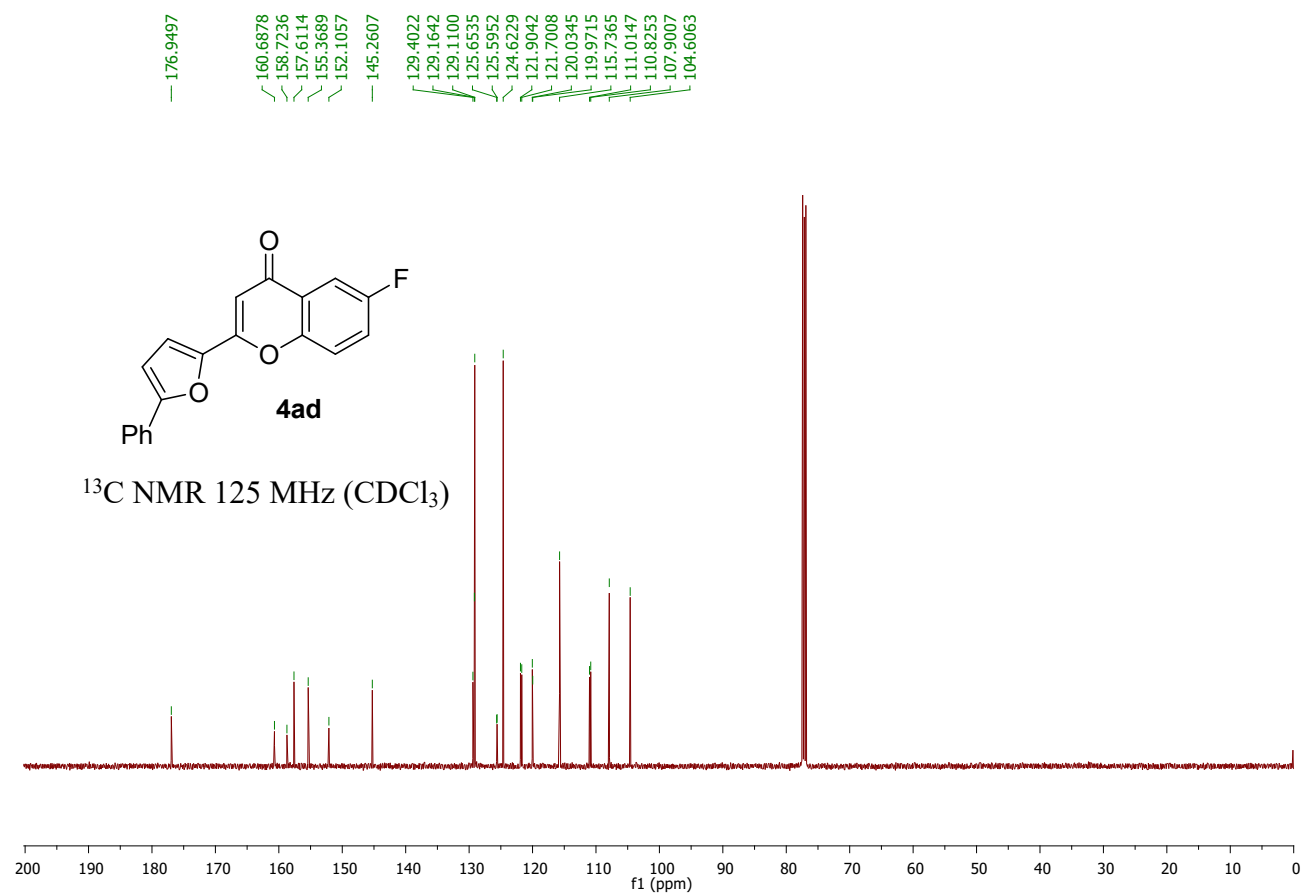
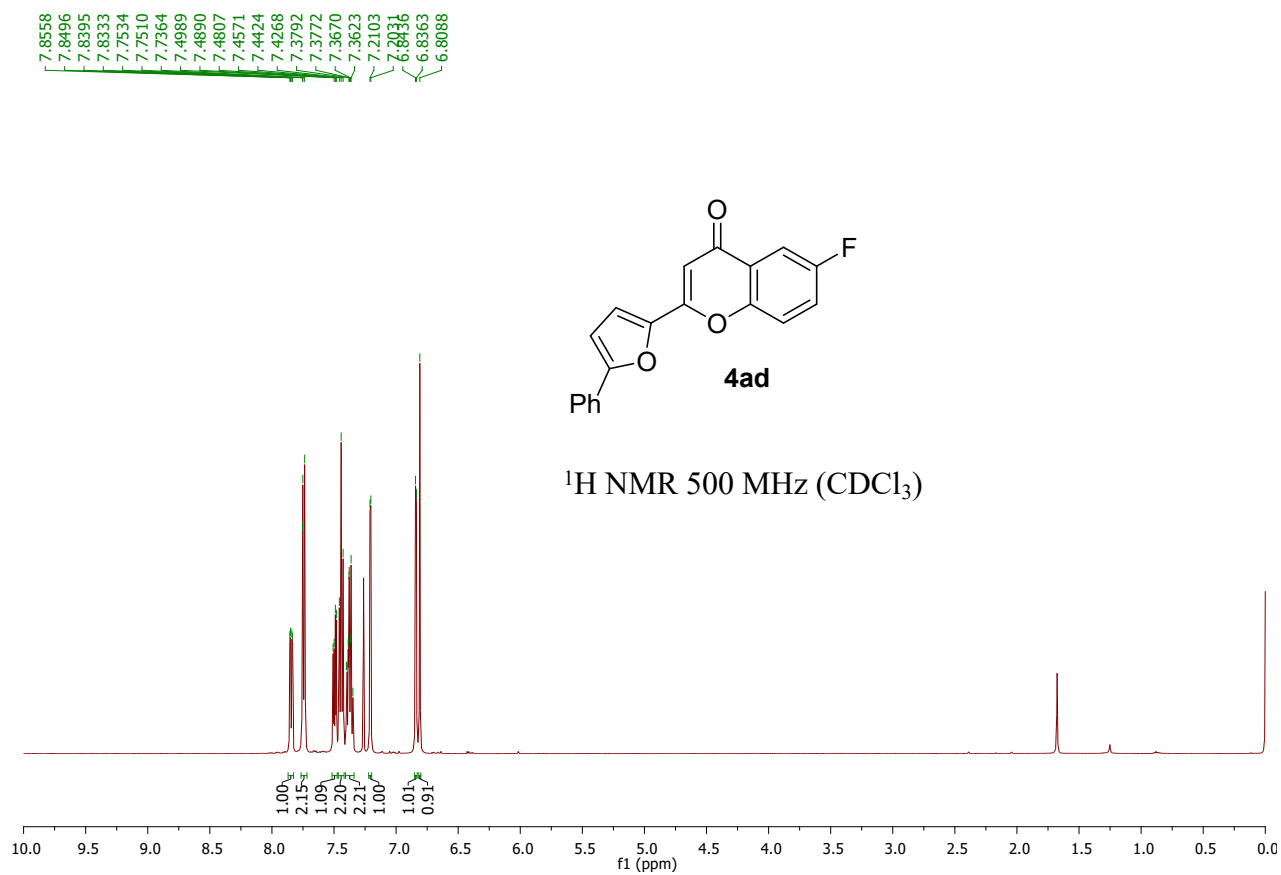
177.8074
157.2033
155.9023
155.1575
145.9390
133.7235
129.9739
127.3065
126.9564
126.3124
125.8016
125.6888
117.9888
114.9923
111.8761
105.3612

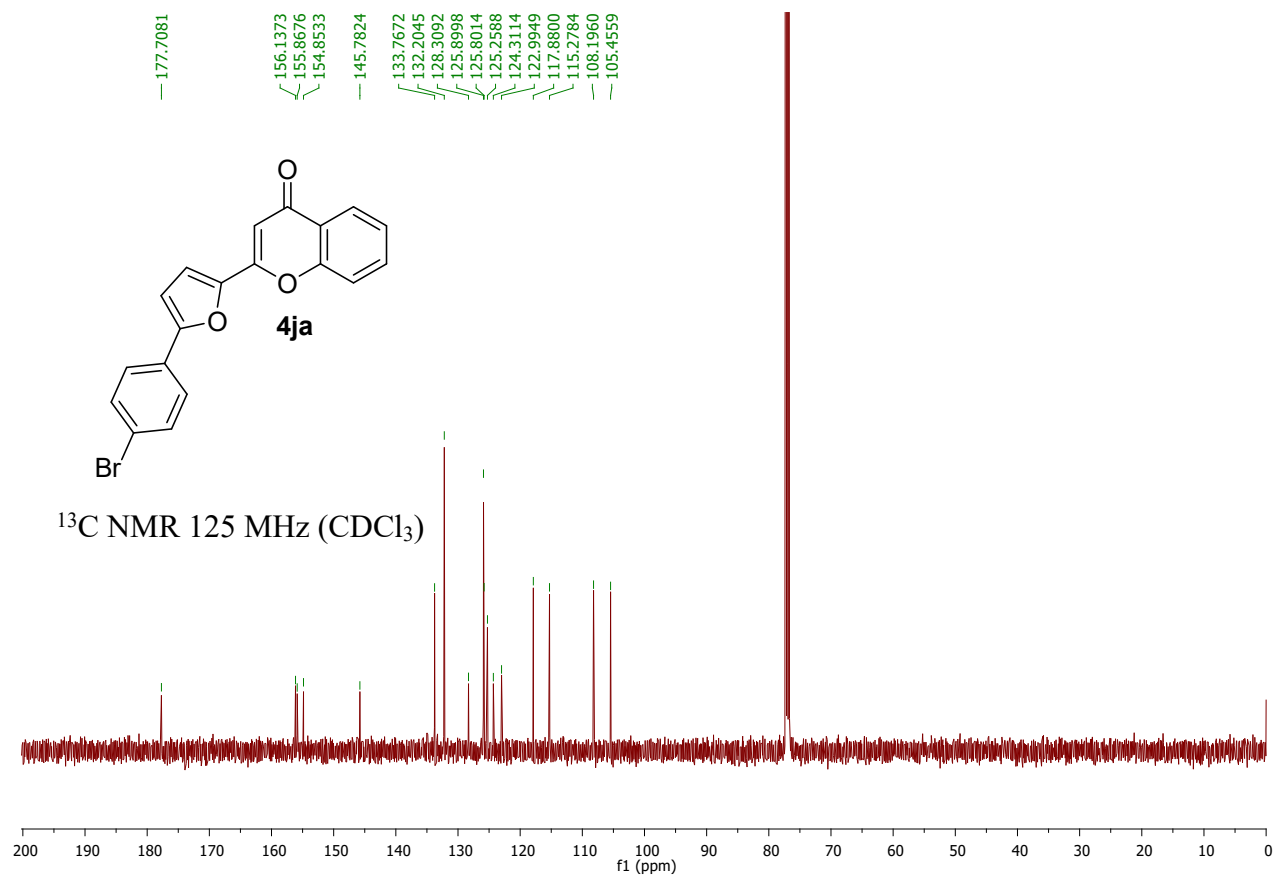
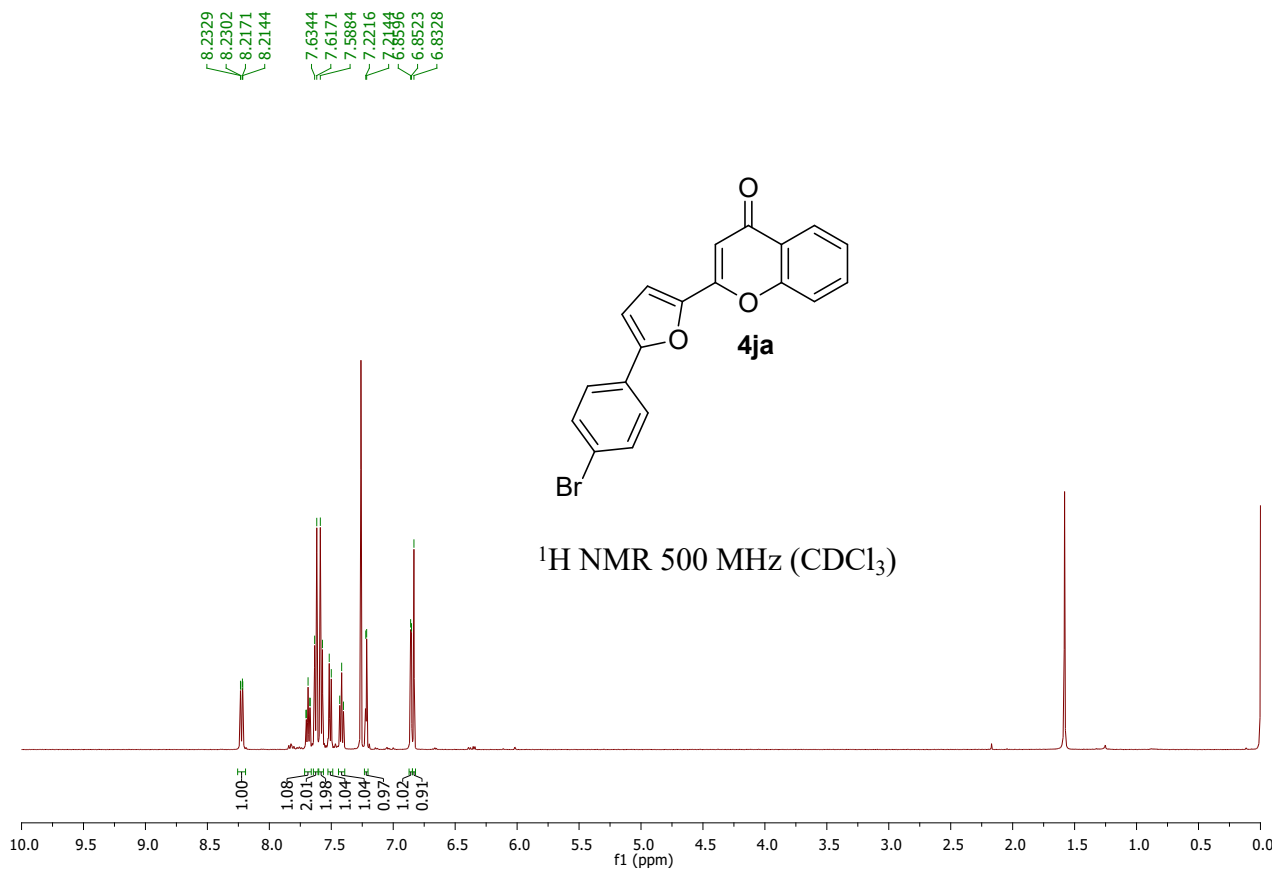


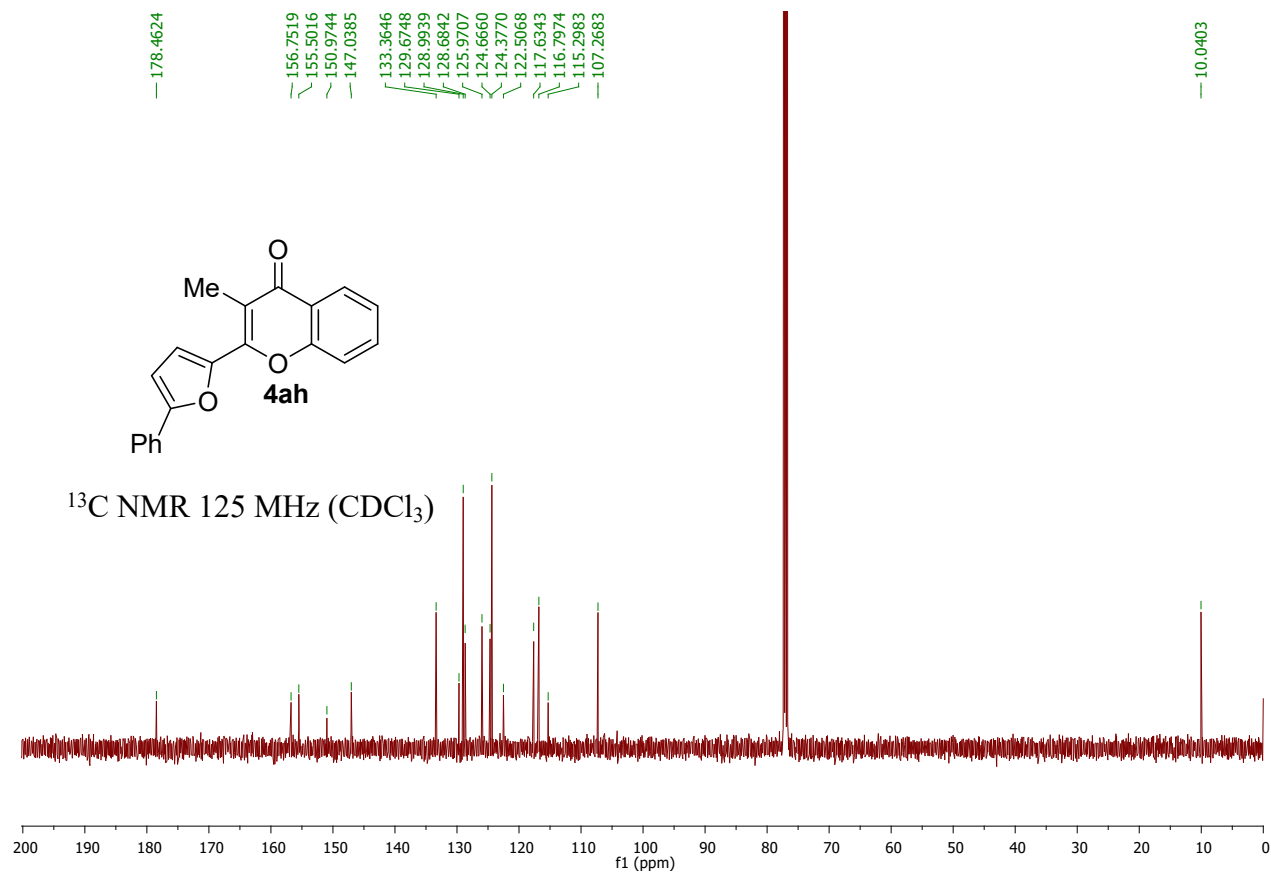
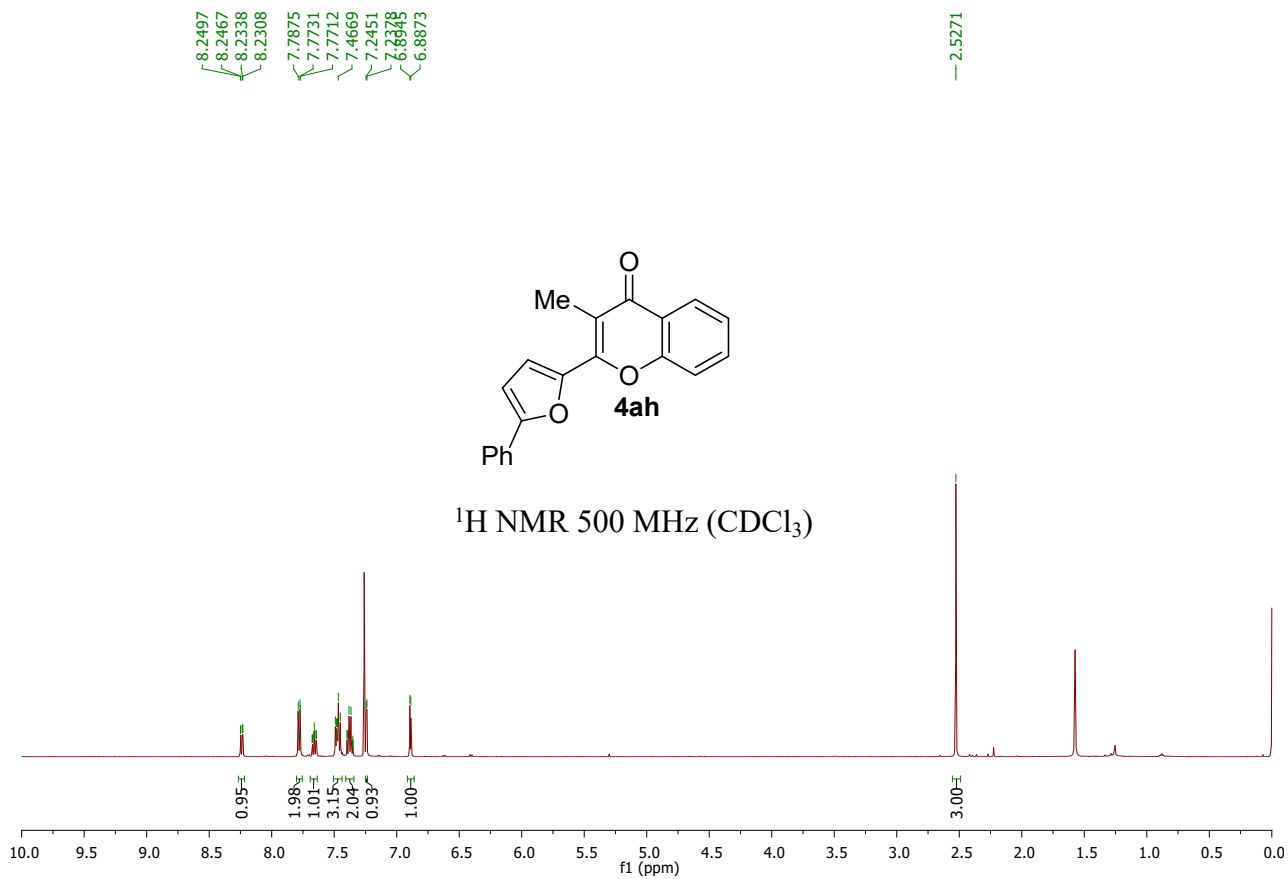
$^{13}\text{C NMR}$ 125 MHz (CDCl_3)

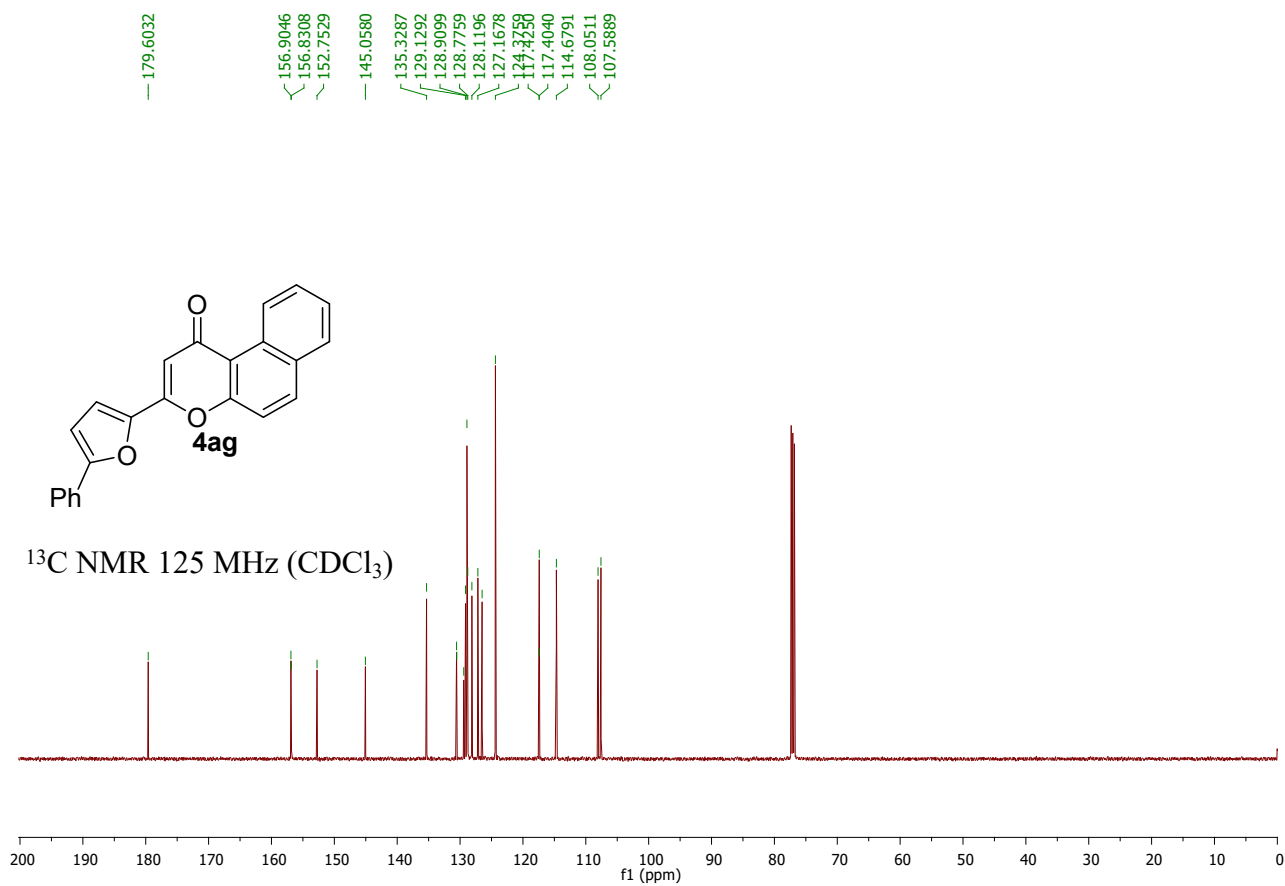
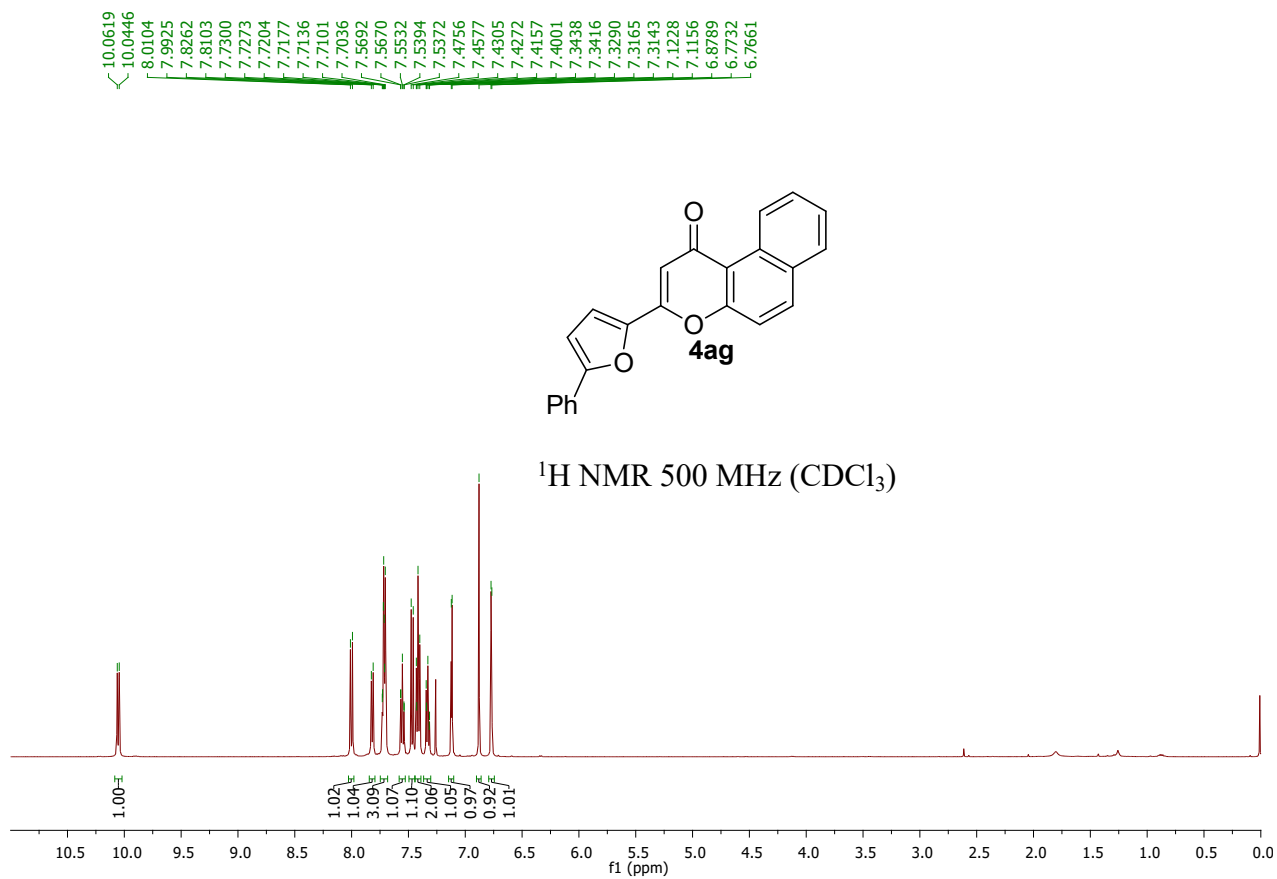


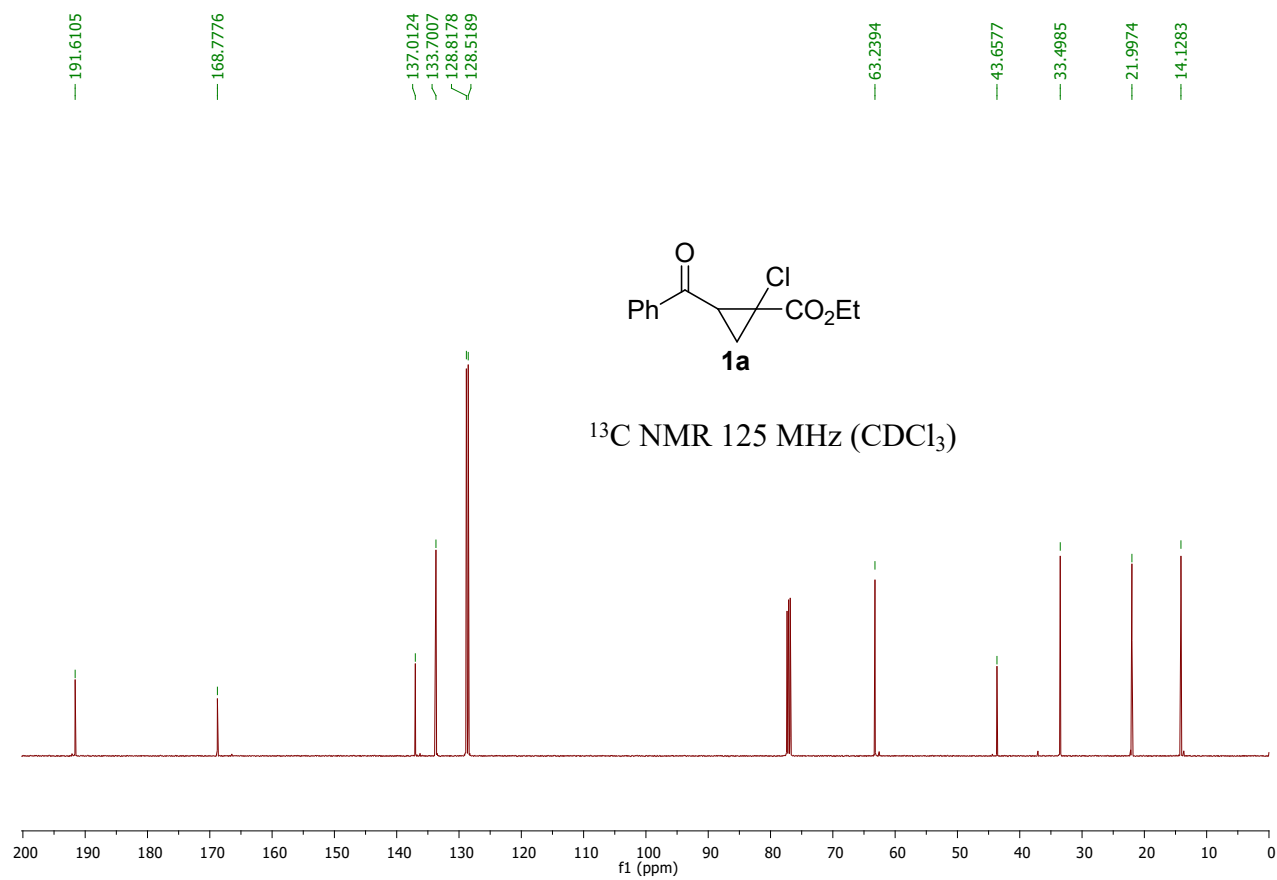
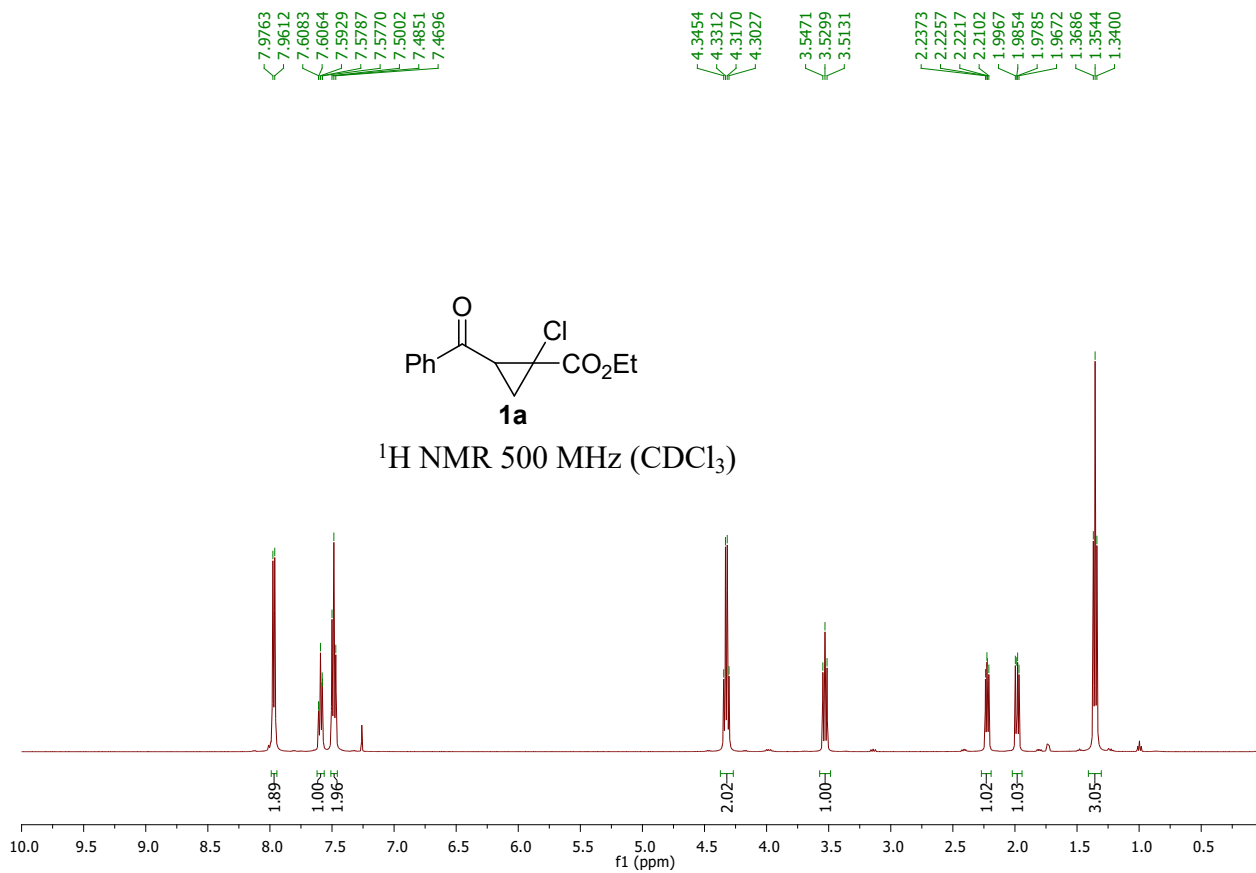










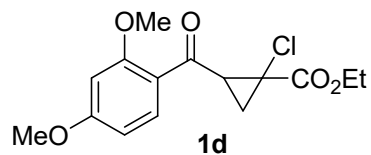


7.8884
7.8665

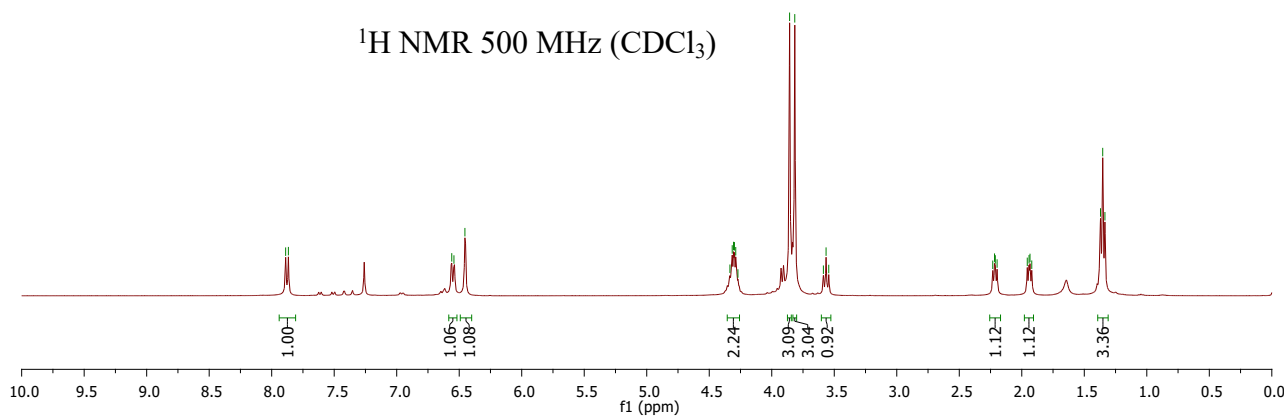
6.5597
6.5422
6.4544

4.3346
4.3163
4.3055
4.2986
4.2880
4.2706
3.8572
3.8159
3.5869
3.5655
3.5440

2.2321
2.2179
2.2118
2.1975
1.9561
1.9419
1.9342
1.9201
1.3703
1.3526
1.3349



¹H NMR 500 MHz (CDCl₃)



190.3900

169.7061
165.3559
161.7001

133.3621

120.7879

105.7583

98.5715

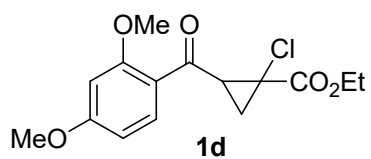
62.8232

55.8675
55.7290

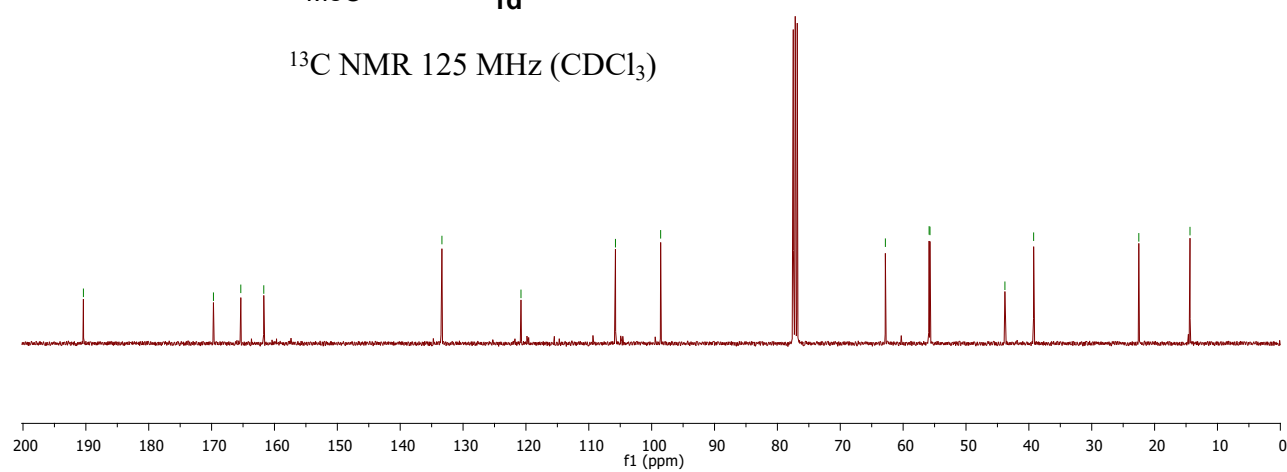
43.8098
39.2415

22.5111

14.3687



¹³C NMR 125 MHz (CDCl₃)

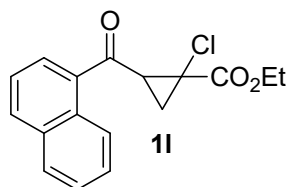


8.7264
8.7092
8.0405
8.0240
7.9731
7.9720
7.9588
7.8893
7.8831
7.6355
7.6333
7.6192
7.6048
7.6024
7.5661
7.5585
7.5519
7.5427
7.5277

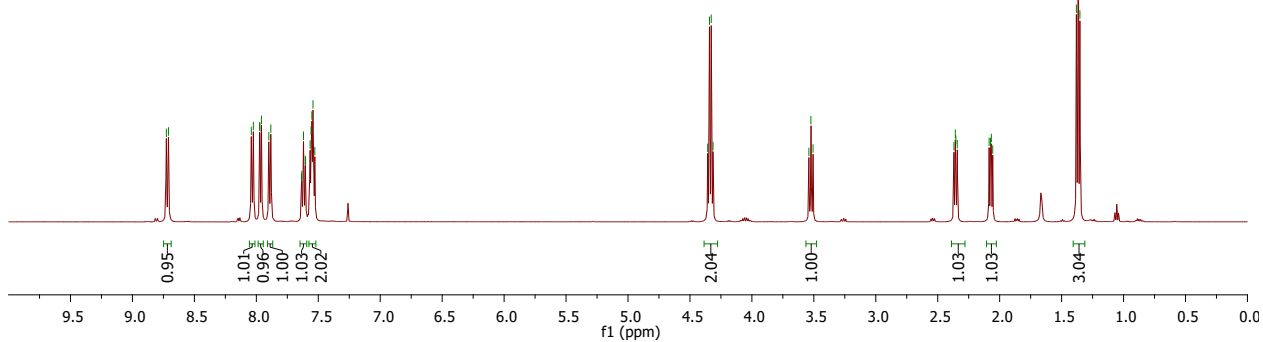
4.3566
4.3423
4.3281
4.3138

3.5400
3.5237
3.5062

2.3691
2.3578
2.3534
2.3422
2.0852
2.0740
2.0672
2.0560
1.3807
1.3664
1.3522



¹H NMR 500 MHz (CDCl₃)



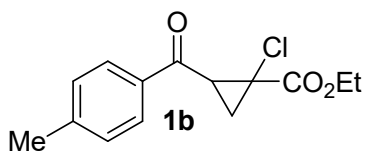
7.8895
7.8731

7.2973
7.2811

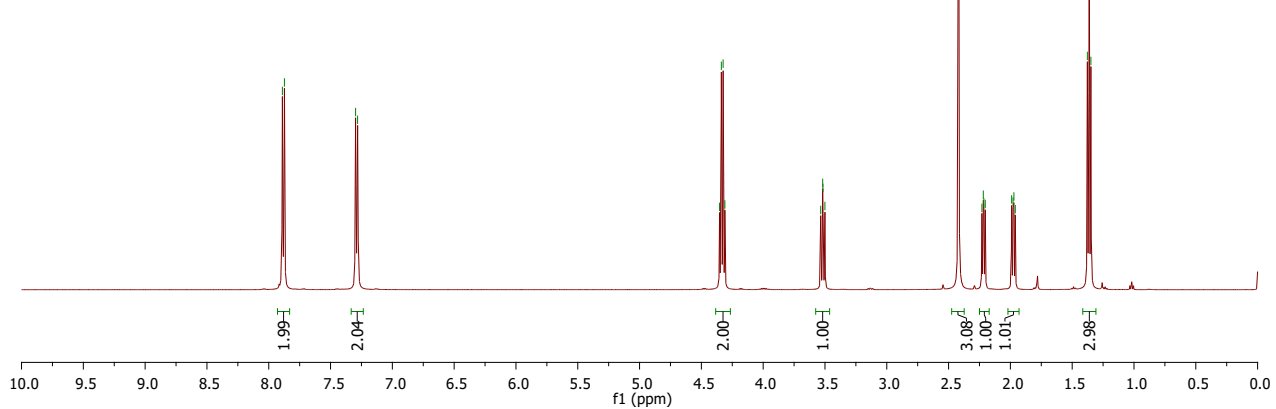
4.3526
4.3384
4.3241
4.3098

3.5346
3.5185
3.5165
3.5005

2.4196
2.2304
2.2192
2.2146
2.2034
1.9899
1.9786
1.9716
1.9604
1.3772
1.3629
1.3486



¹H NMR 500 MHz (CDCl₃)

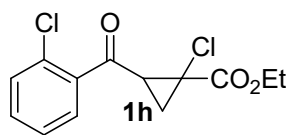


7.6070
7.5916
7.4331
7.4256
7.3668
7.3592
7.3511
7.3429
7.3344

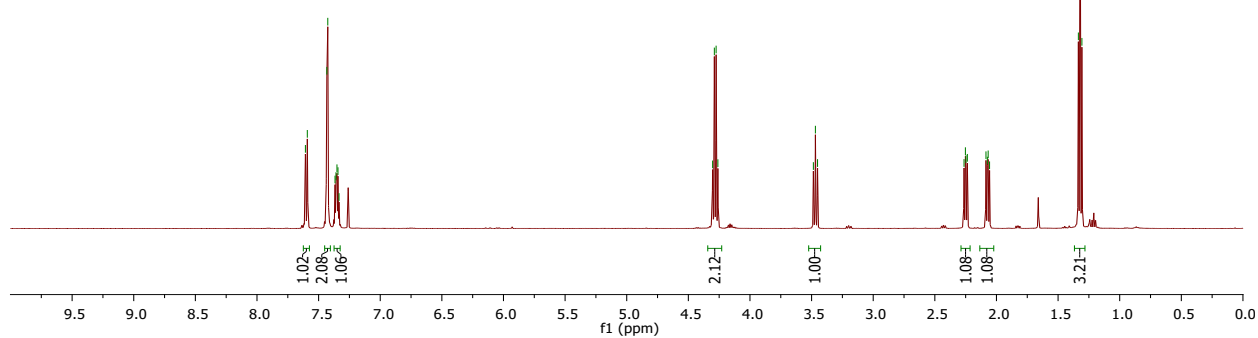
4.3031
4.2889
4.2746
4.2604

3.4854
3.4690
3.4518

2.2631
2.2519
2.2474
2.2362
2.0850
2.0739
2.0672
2.0561
1.3353
1.3210
1.3067



$^1\text{H NMR}$ 500 MHz (CDCl_3)



193.4755

168.6119

138.4787
132.8867
132.2345
130.8752
130.4149
127.2781

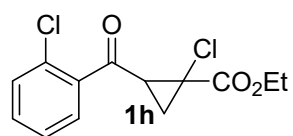
63.2486

45.7457

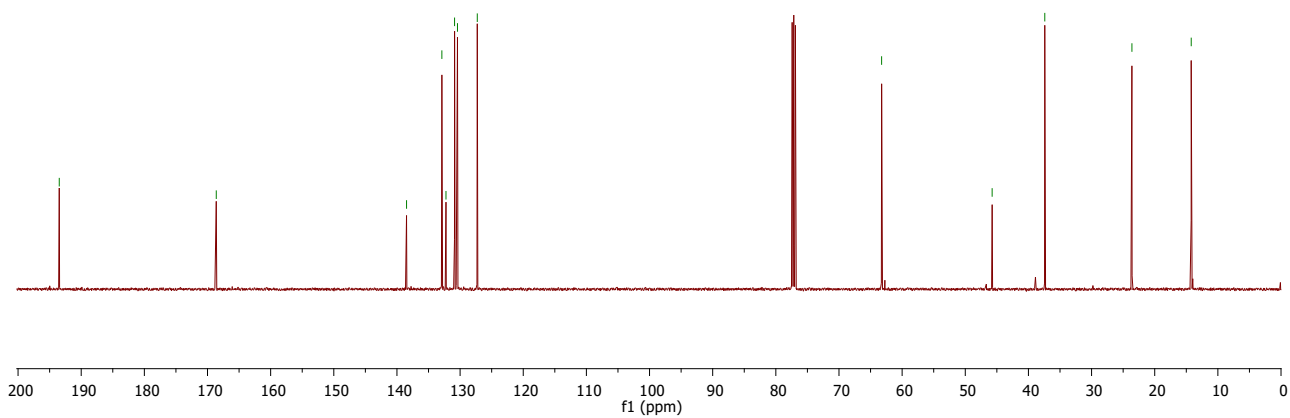
37.4100

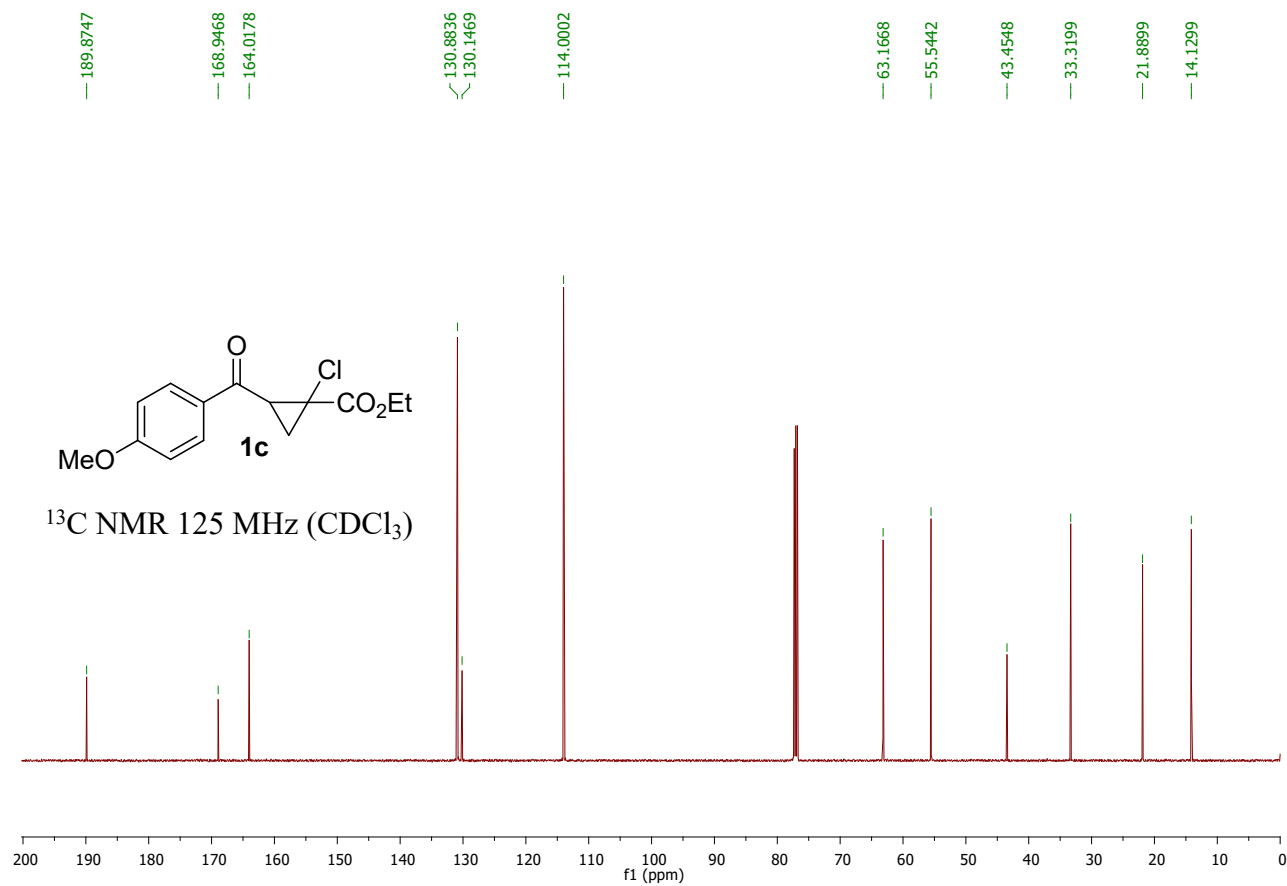
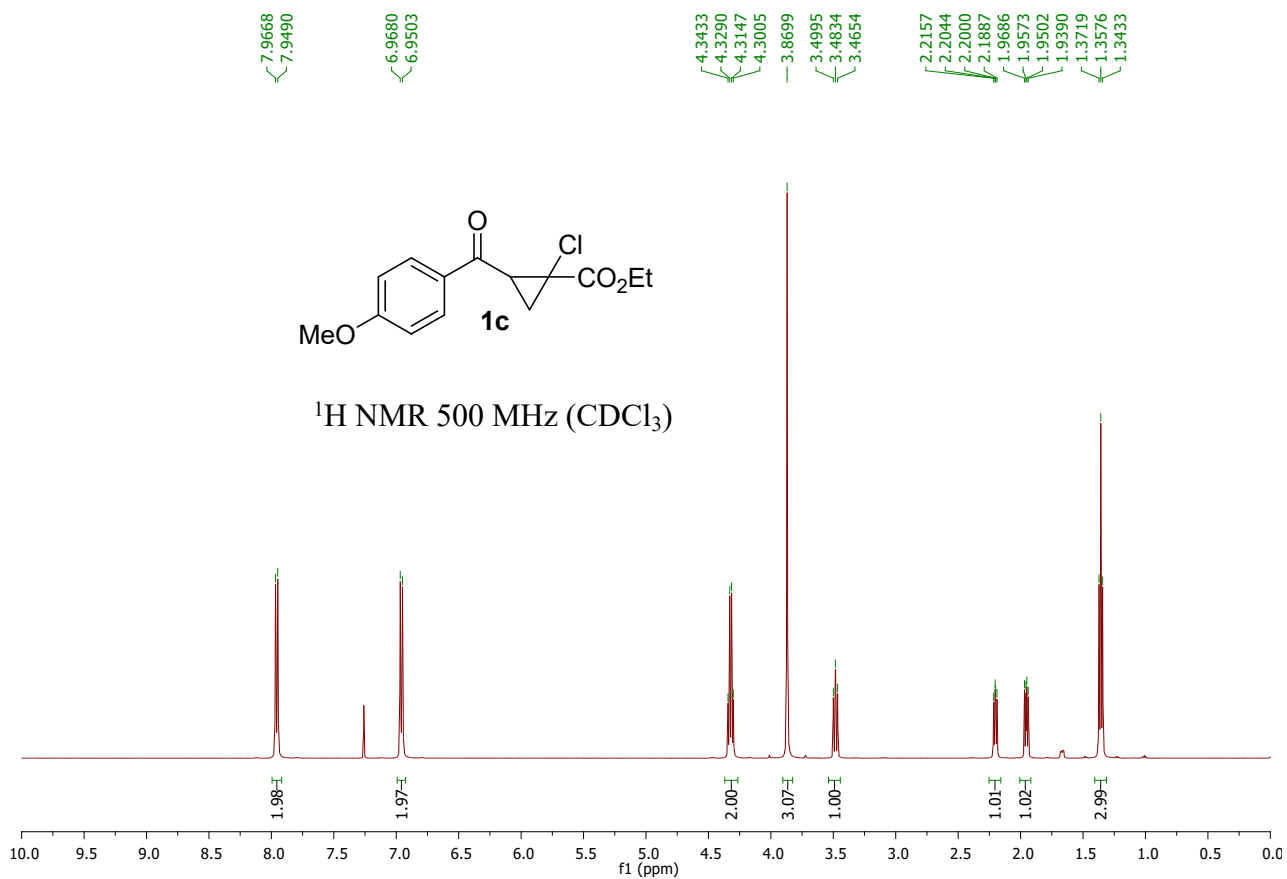
23.6104

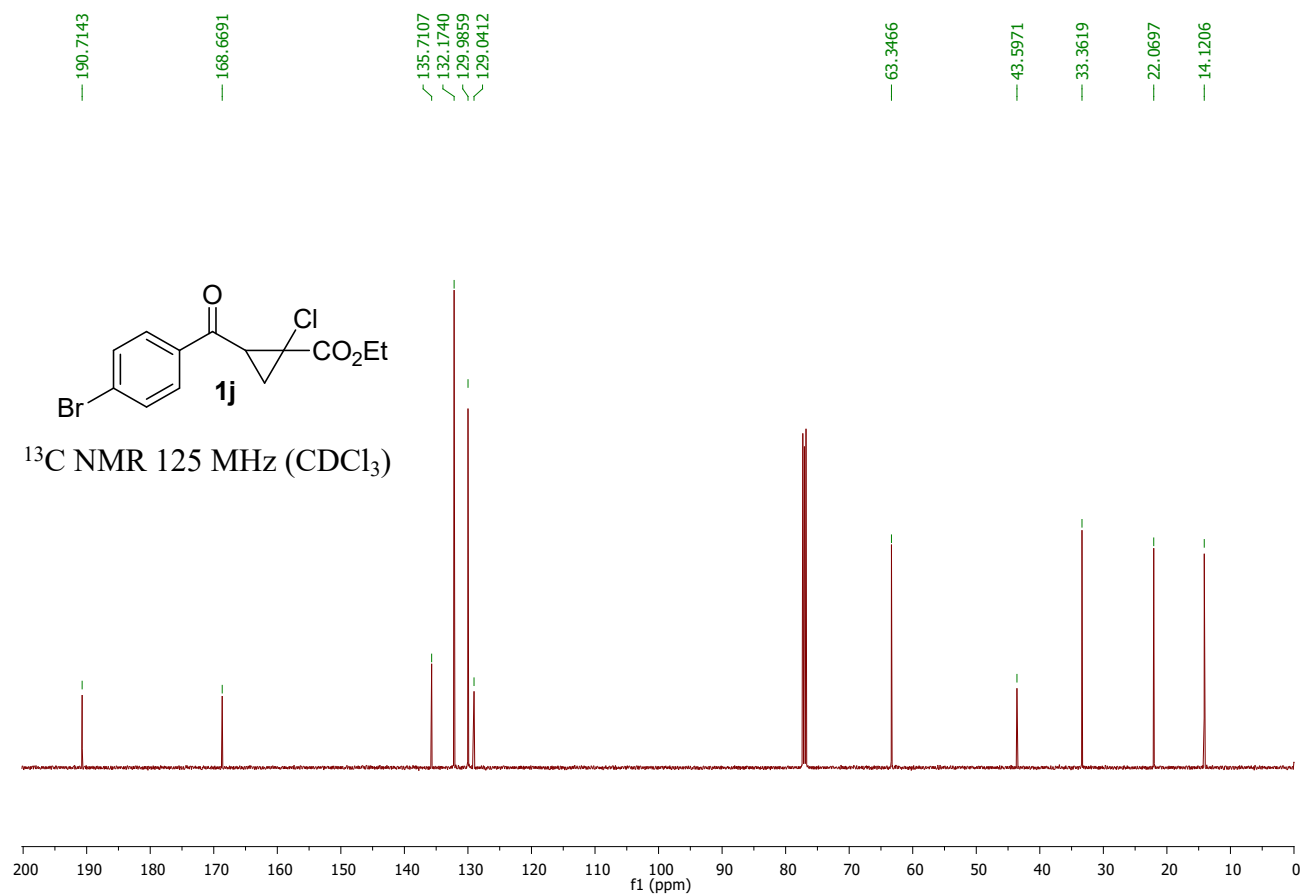
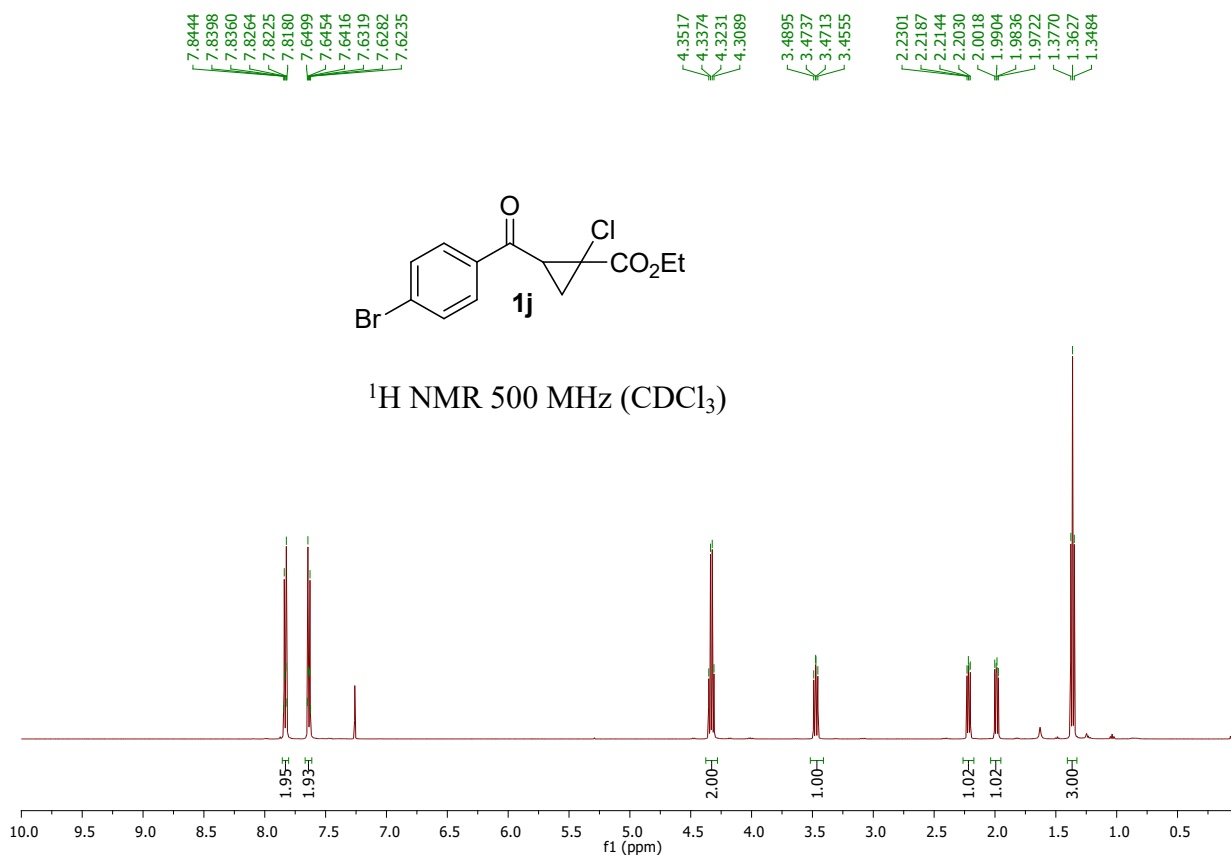
14.2196



$^{13}\text{C NMR}$ 125 MHz (CDCl_3)





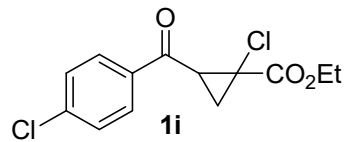


7.9189
7.9019
7.4763
7.4594

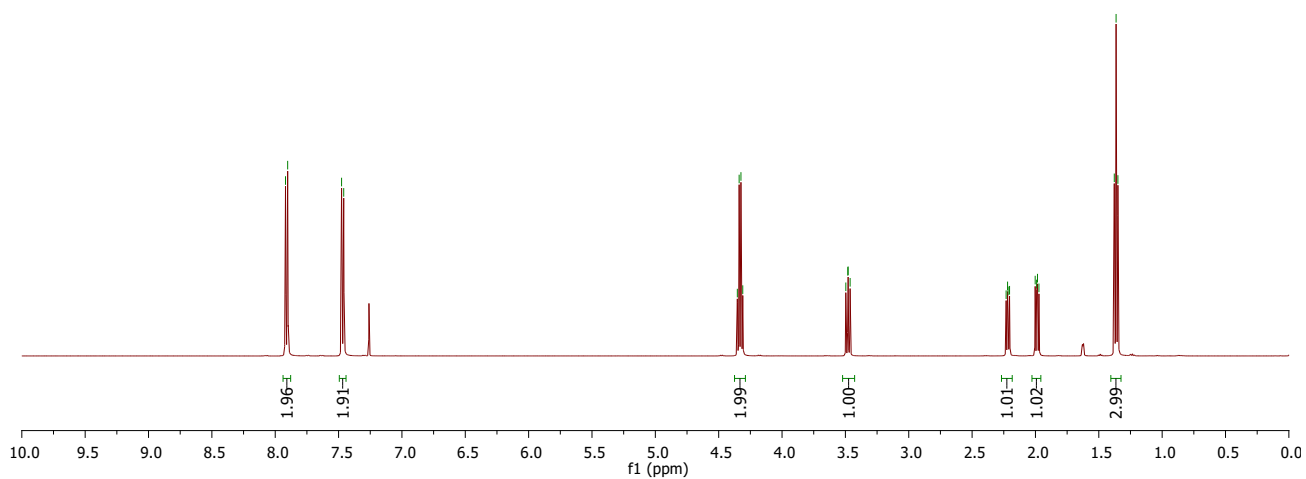
4.3529
4.3386
4.3243
4.3101

3.4966
3.4808
3.4785
3.4627

2.2315
2.2200
2.2160
2.2044
2.0022
1.9907
1.9839
1.9725
1.3778
1.3636
1.3493



^1H NMR 500 MHz (CDCl_3)



190.6129

168.7942

140.3864

135.4319

130.0241

129.2936

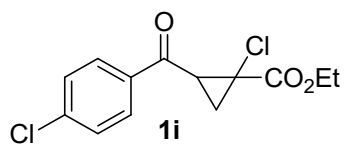
63.4557

43.7102

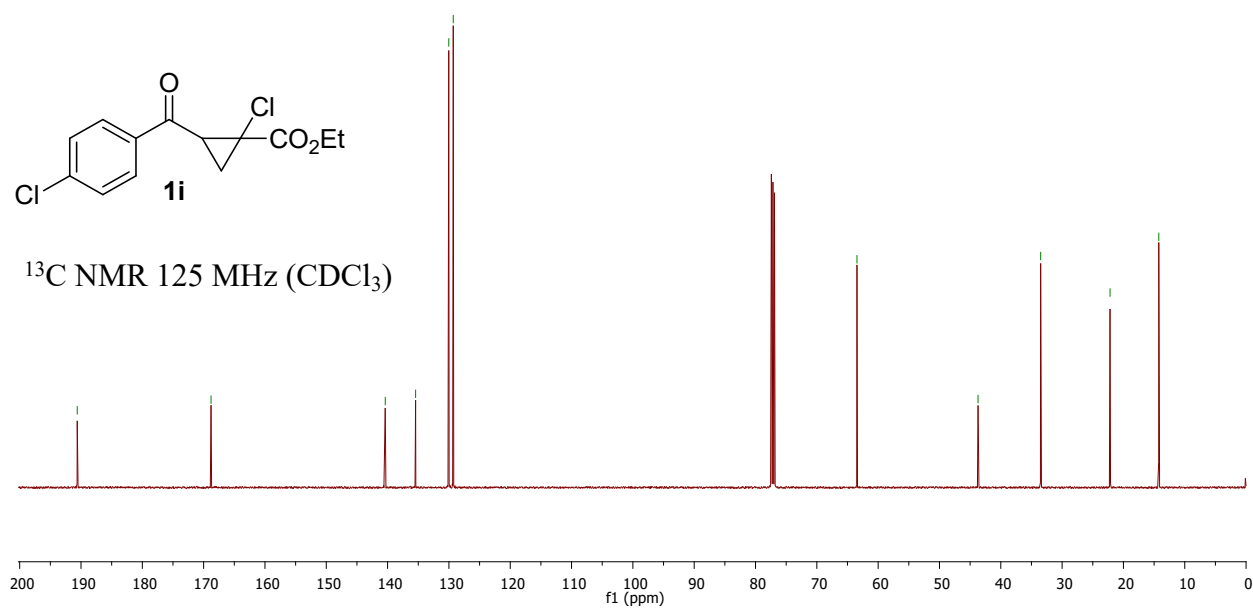
33.4988

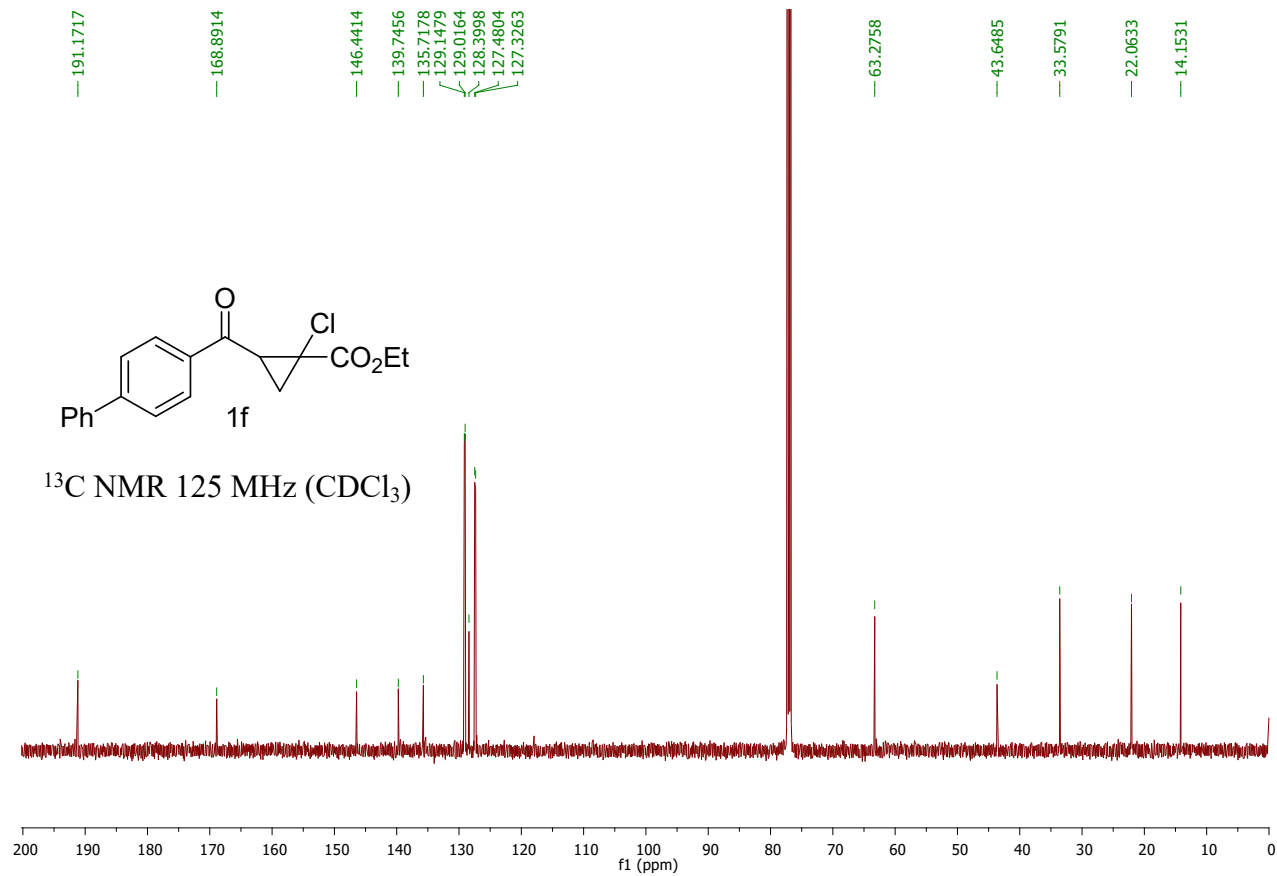
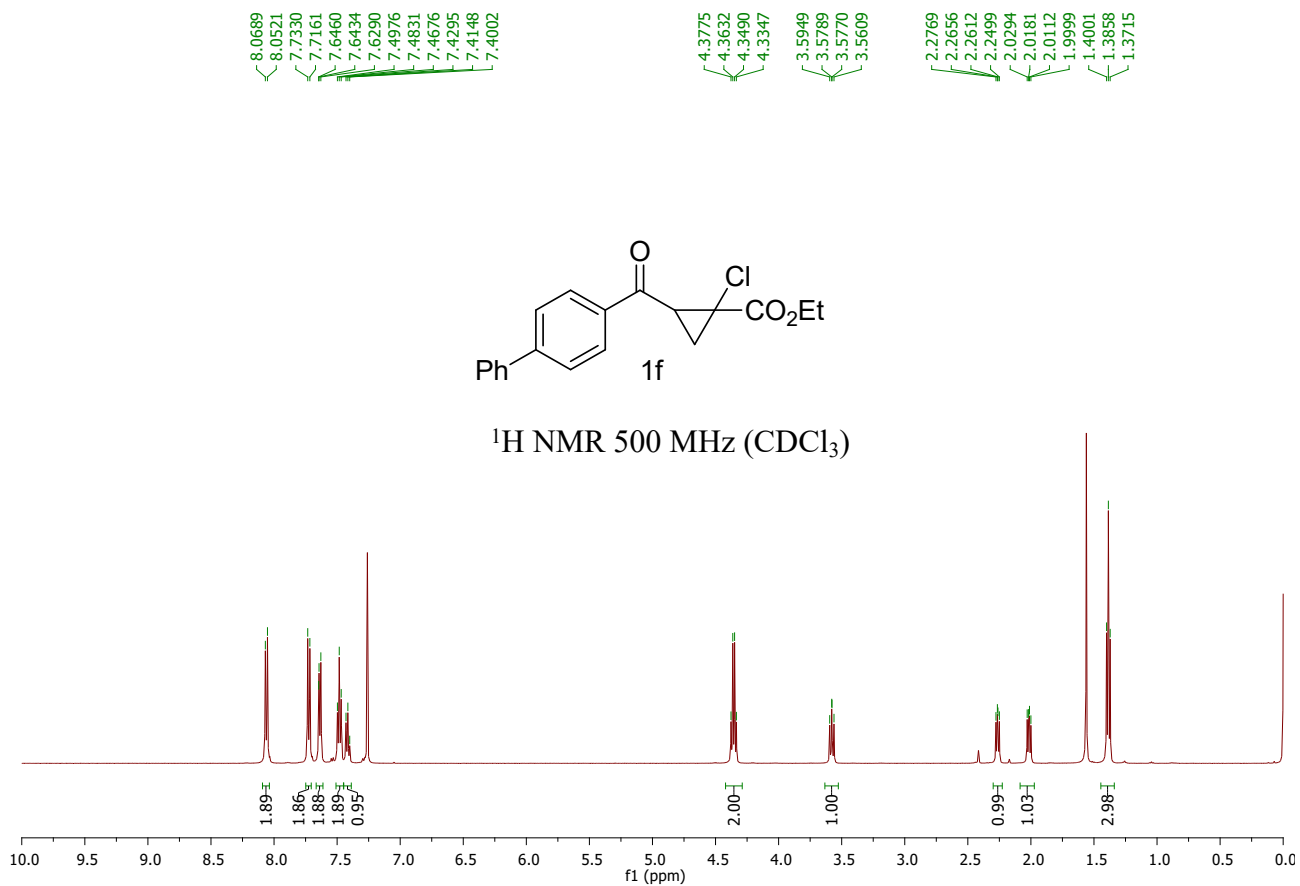
22.1838

14.2354



^{13}C NMR 125 MHz (CDCl_3)



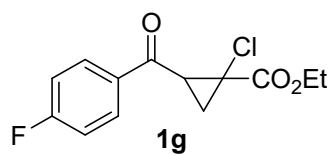


8.0151
8.0109
8.0044
8.0007
7.9974
7.9909
7.9867
7.1852
7.1795
7.1755
7.1623
7.1492
7.1451
7.1394

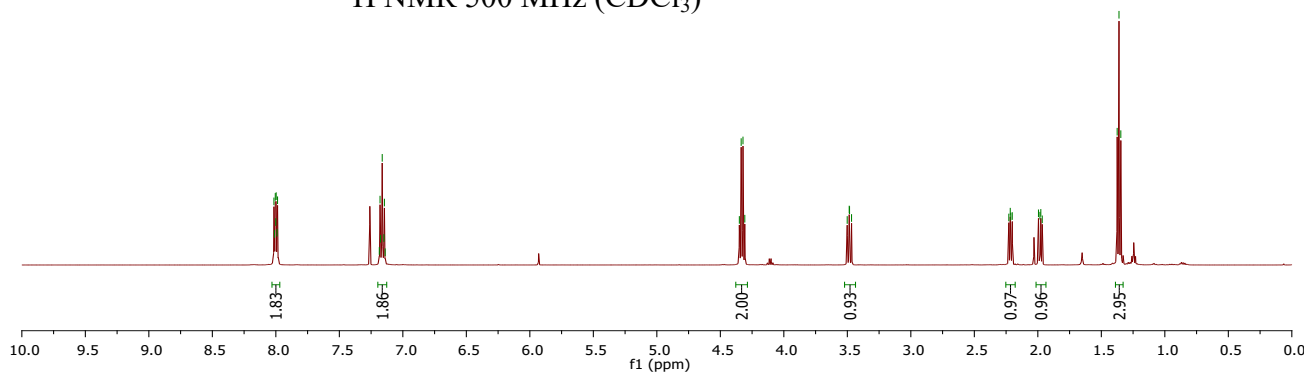
4.3502
4.3359
4.3216
4.3074

3.5009
3.4851
3.4828
3.4669

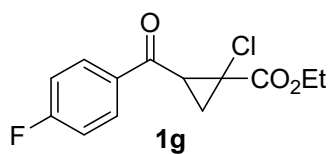
2.2284
2.2170
2.2127
2.2013
1.9947
1.9834
1.9765
1.9651
1.3752
1.3609
1.3466



^1H NMR 500 MHz (CDCl_3)



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



^{13}C NMR 125 MHz (CDCl_3)

