

Supporting Information

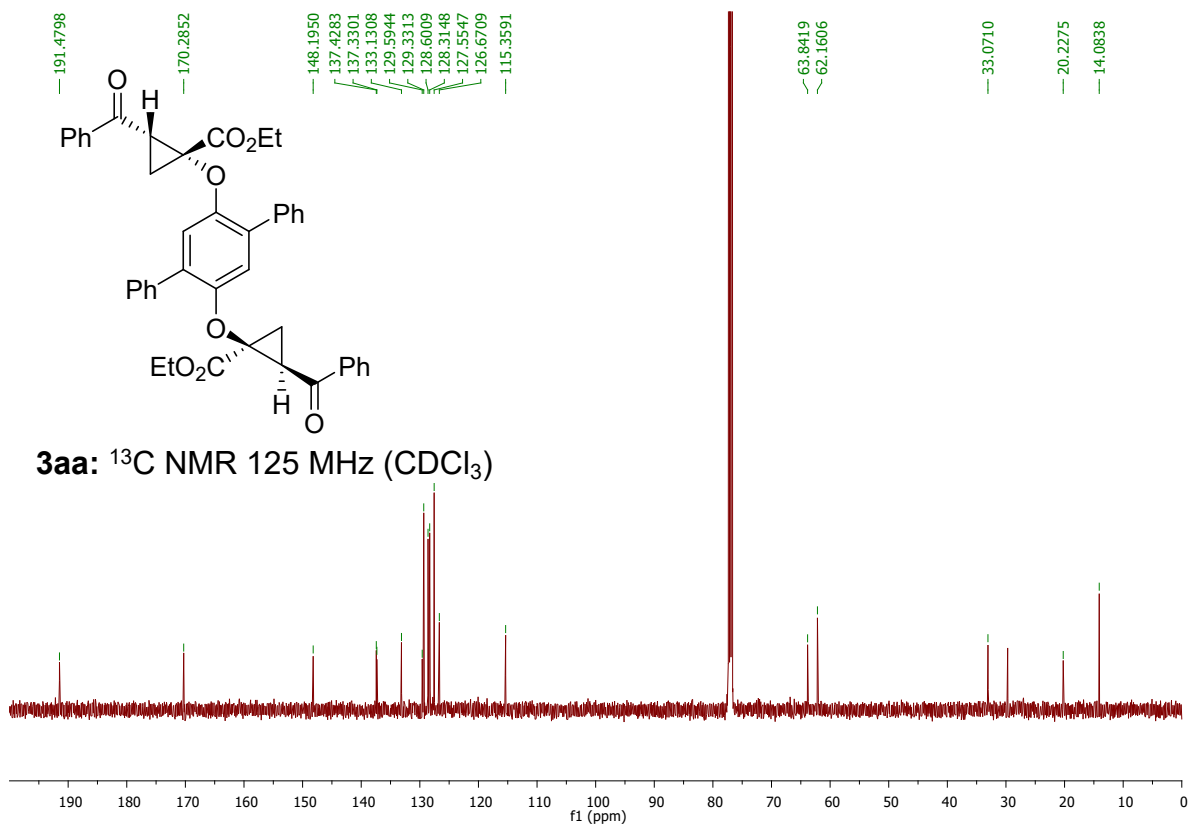
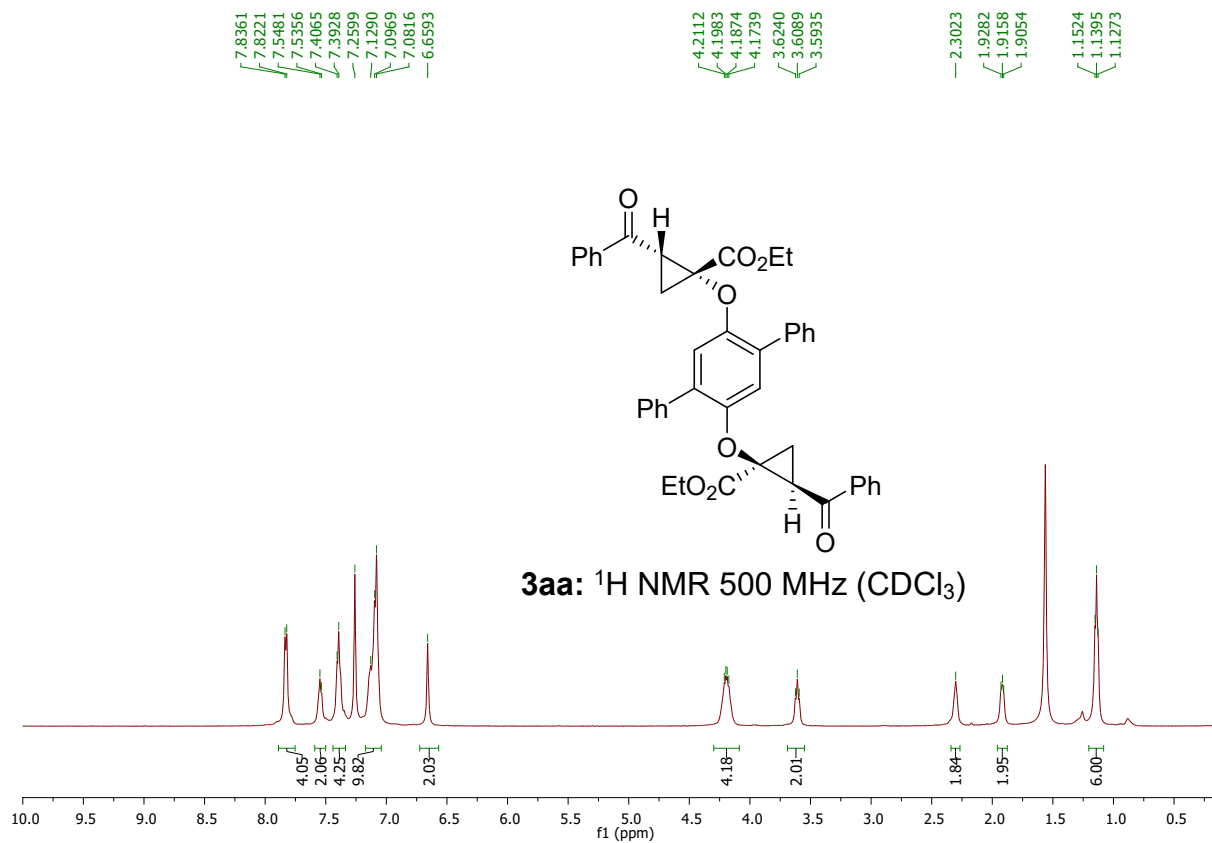
Substrate-dependent reaction of 1-aryl-2-alkyl-1,2-diketones with 2-aryl-1-chlorocyclopropanecarboxylates: selective access to 2',5'-dicyclopropoxy-1,1':4',1''-teraryls and pentafulvenes

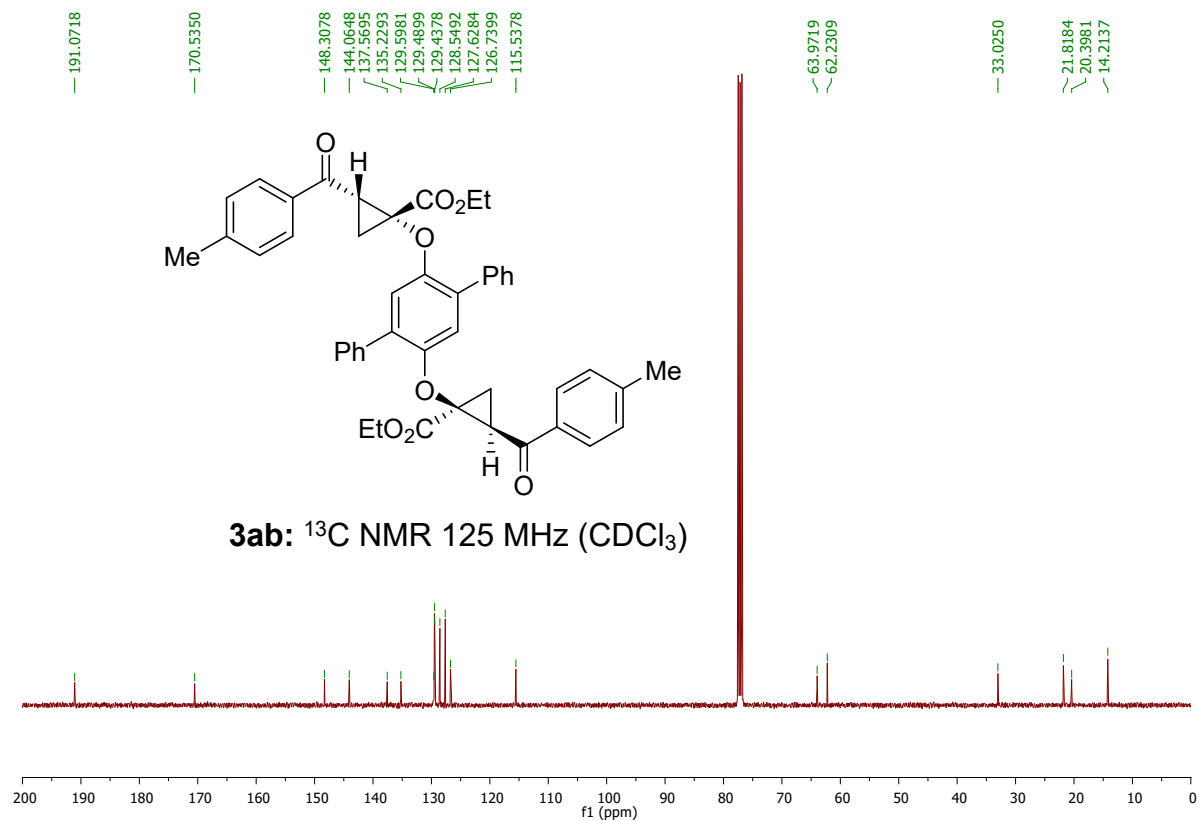
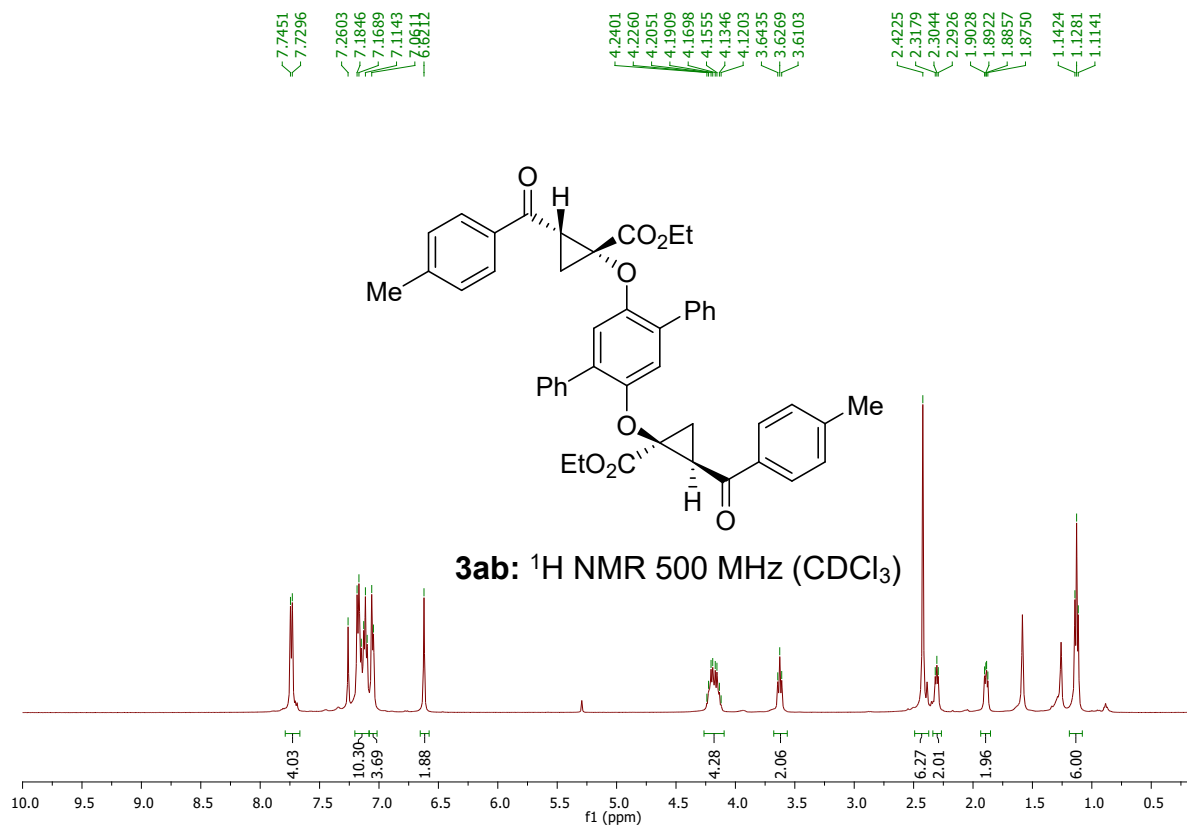
Meher Prakash, Poonam Rani and Sampak Samanta^{*,a}

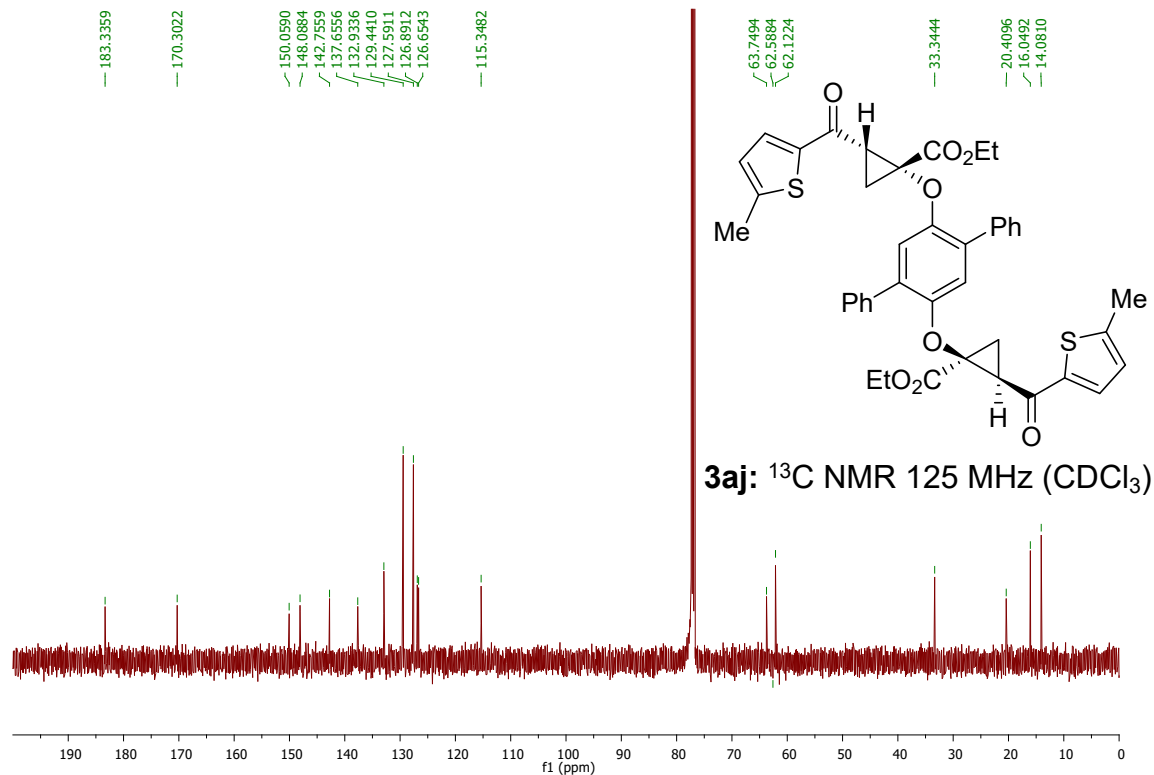
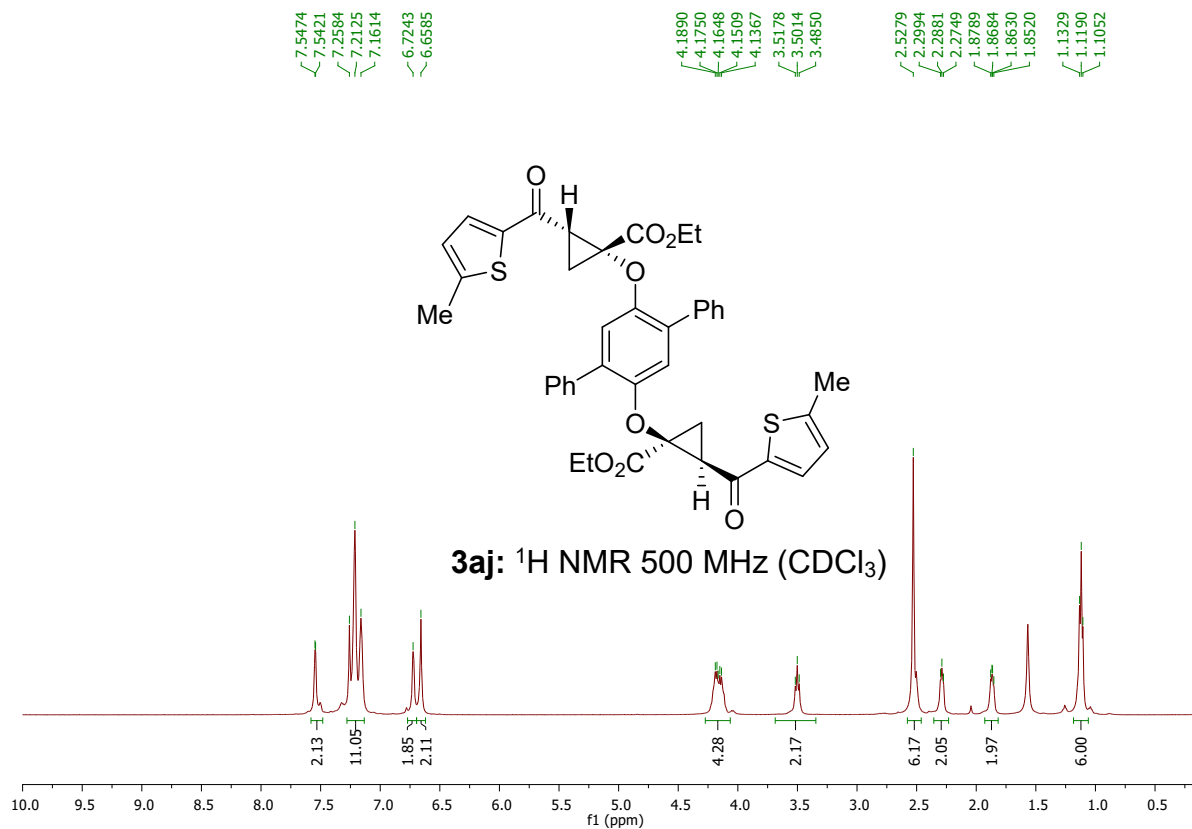
^aDepartment of Chemistry, Indian Institute of Technology Indore, Simrol, Indore-453552, Madhya Pradesh, India.

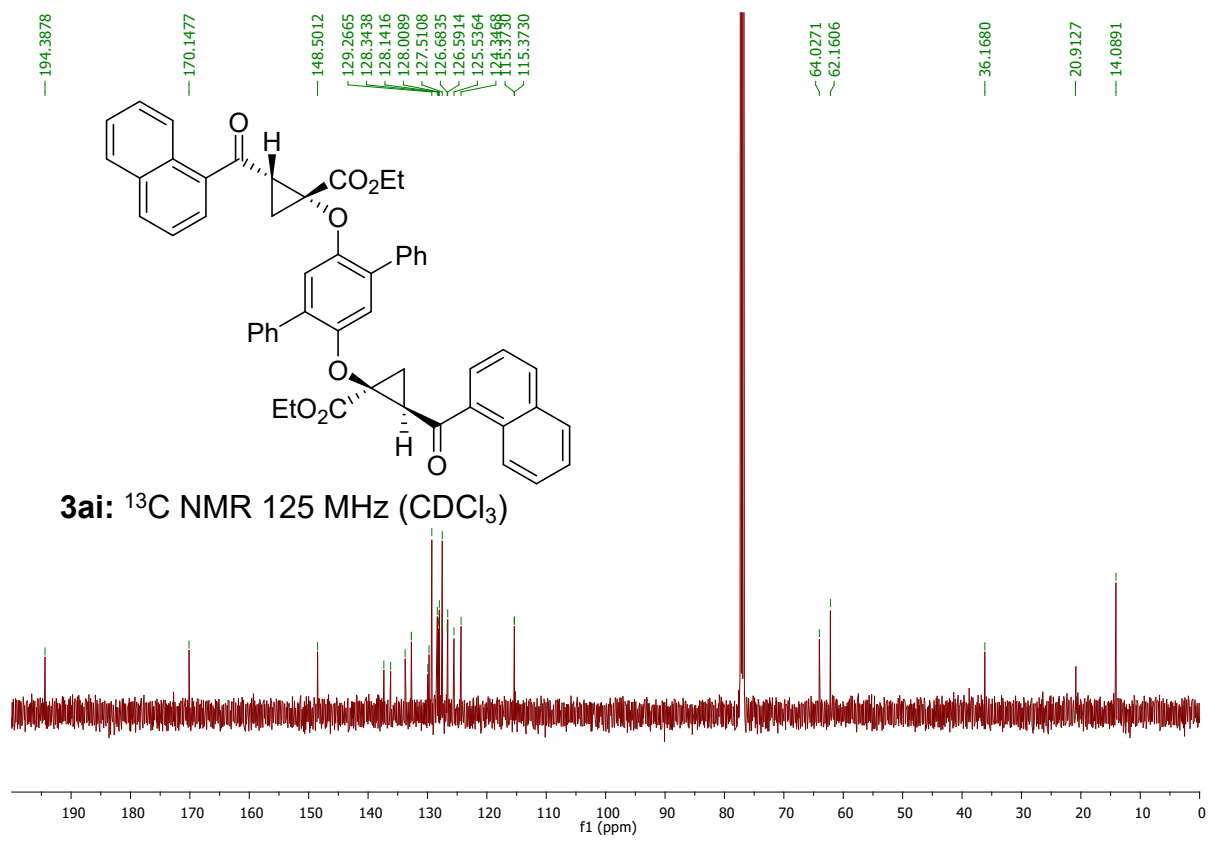
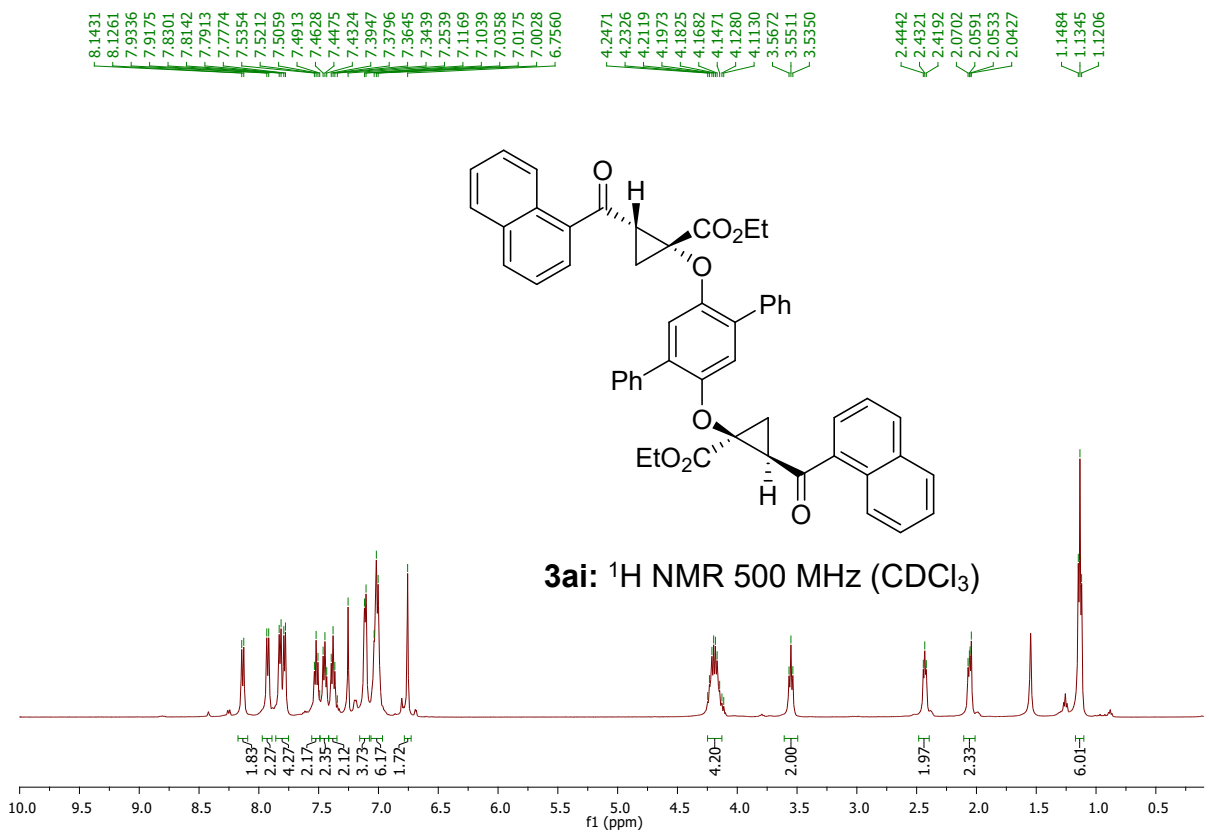
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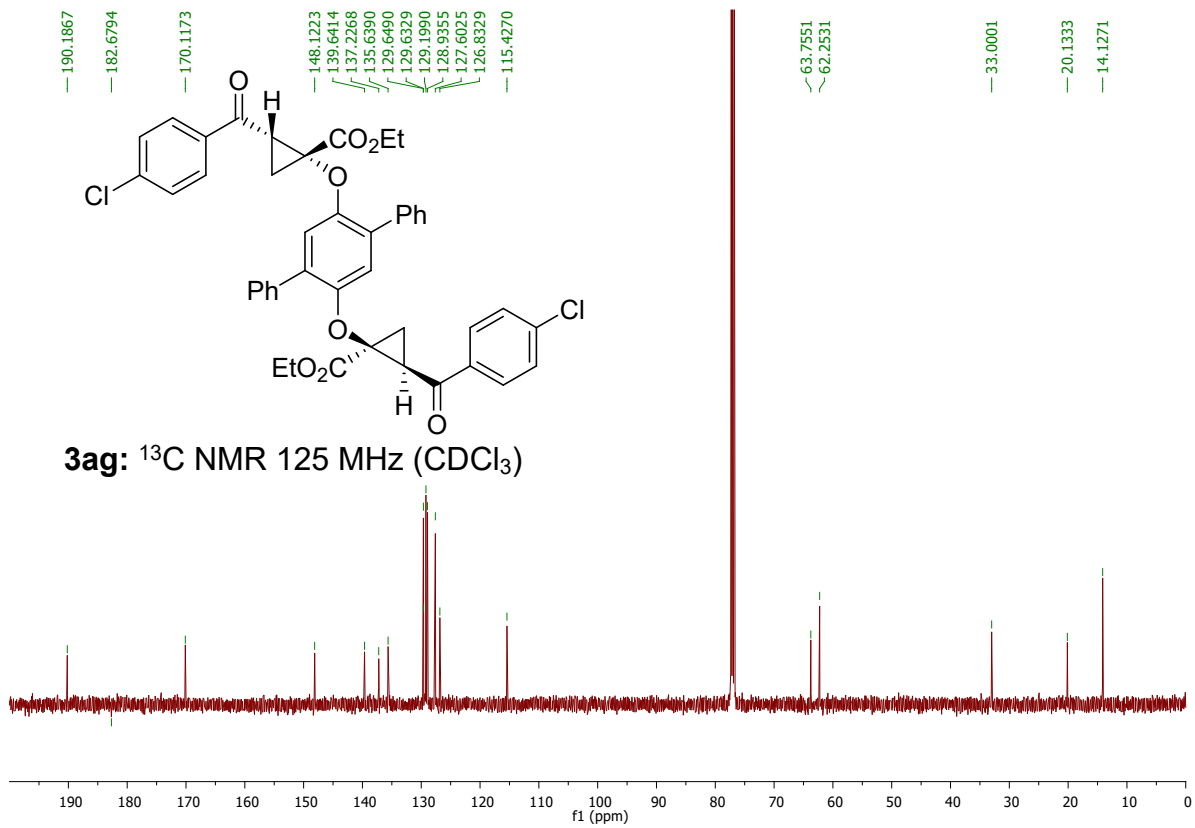
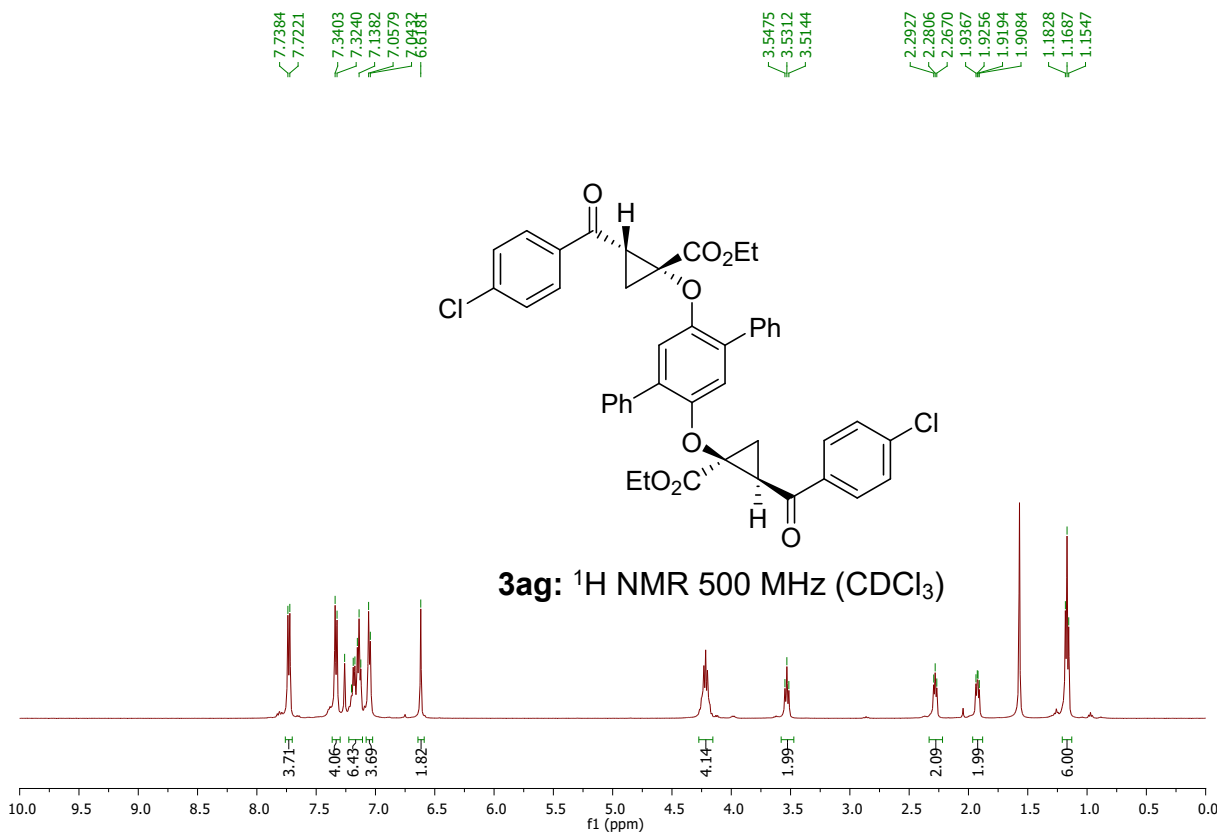
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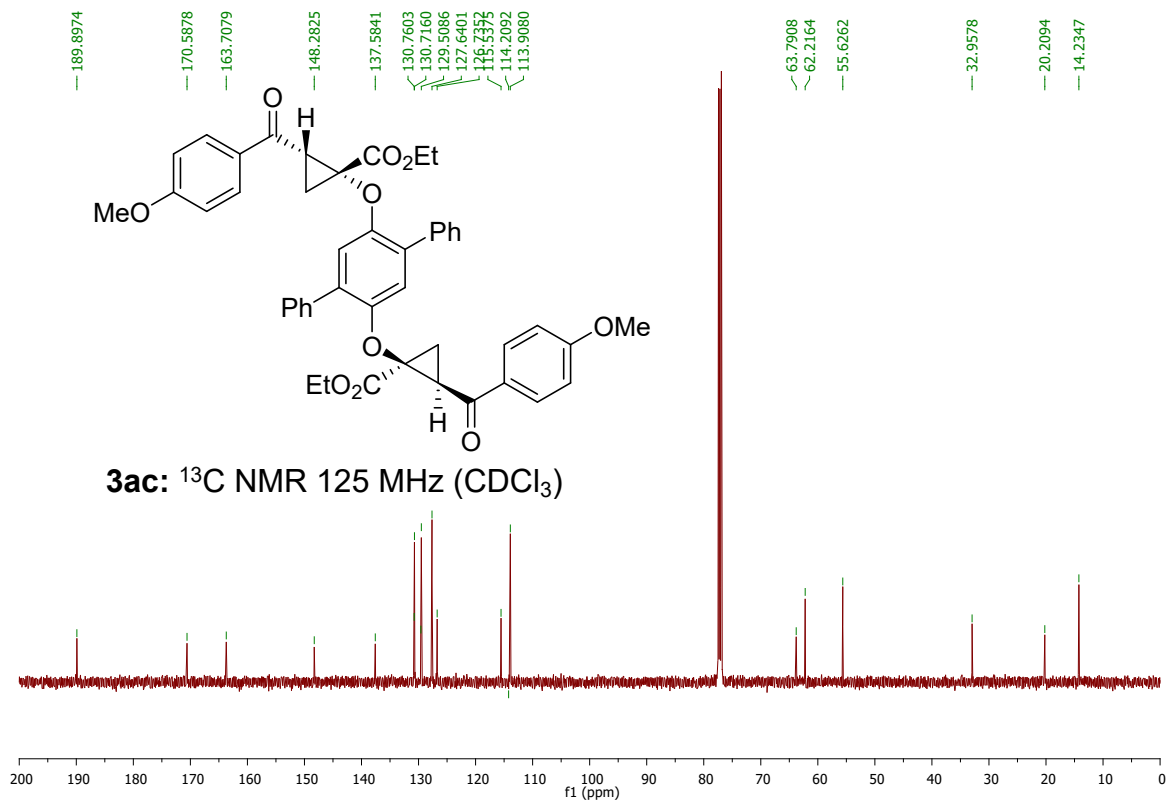
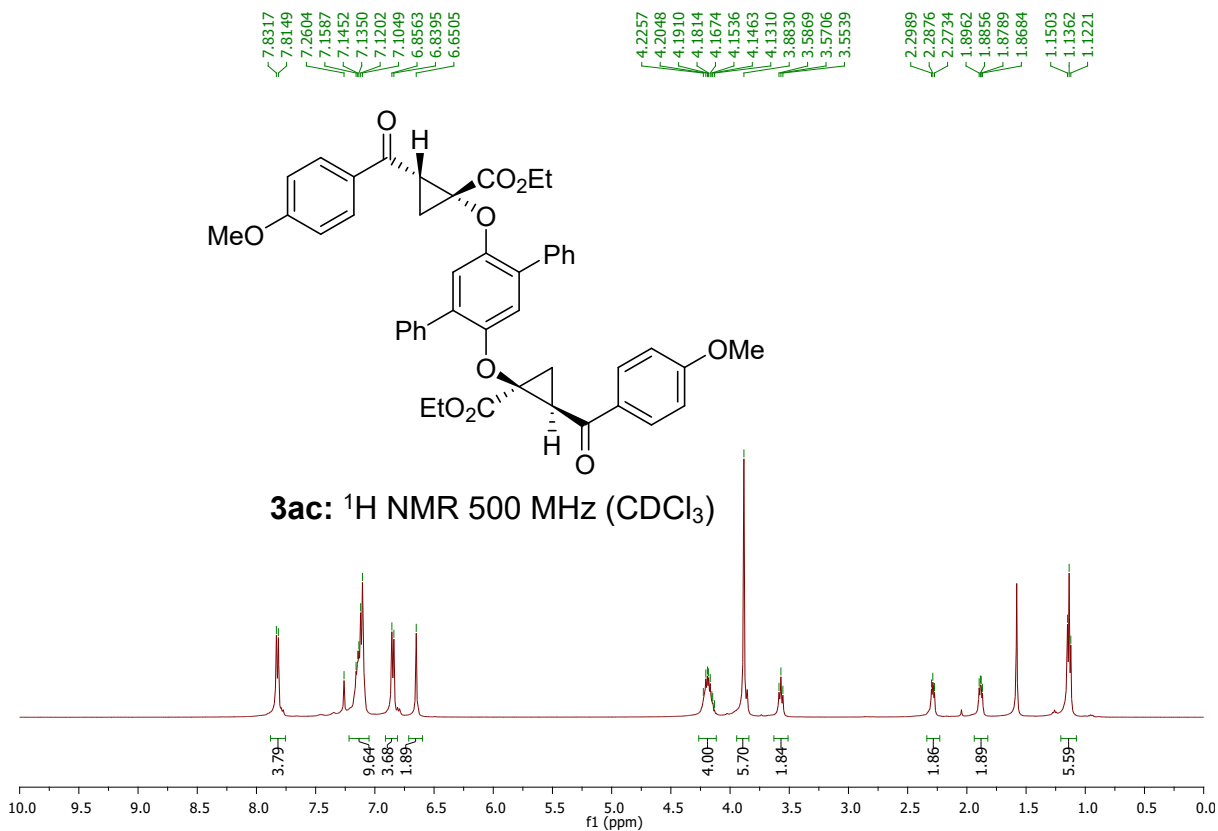


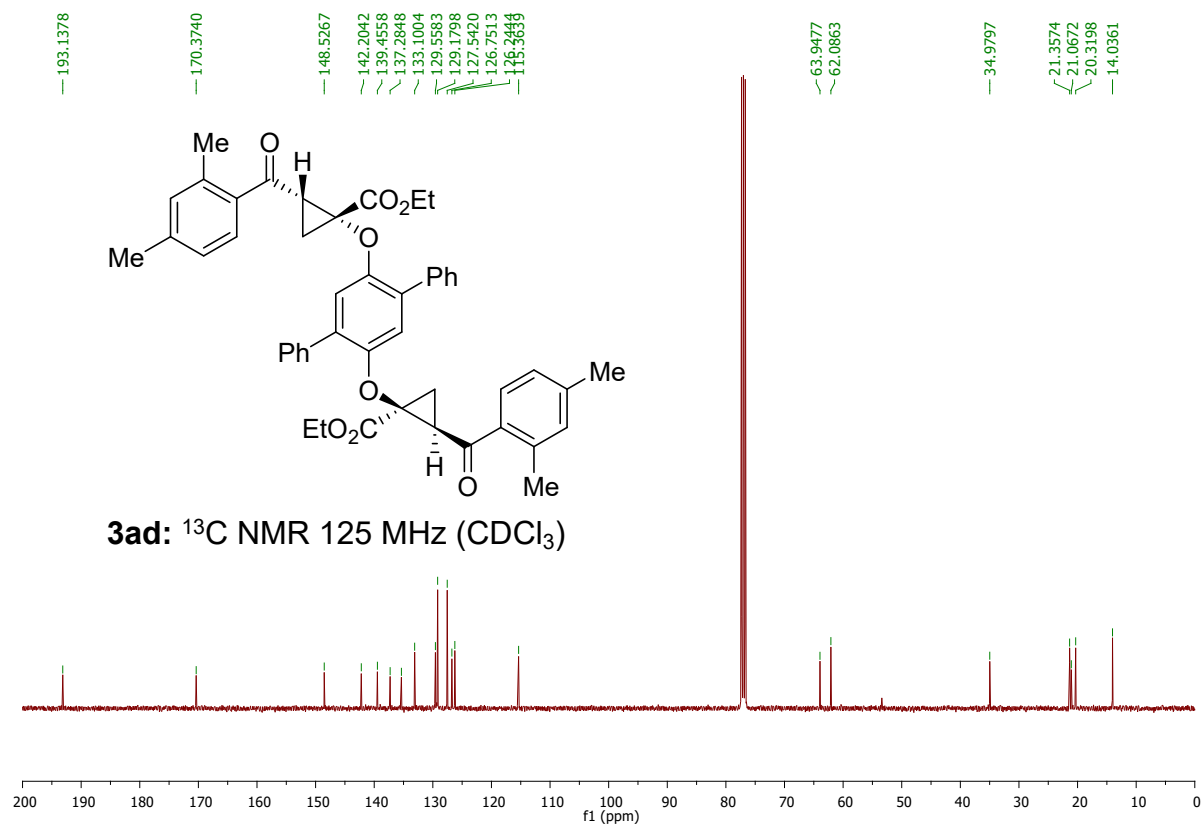
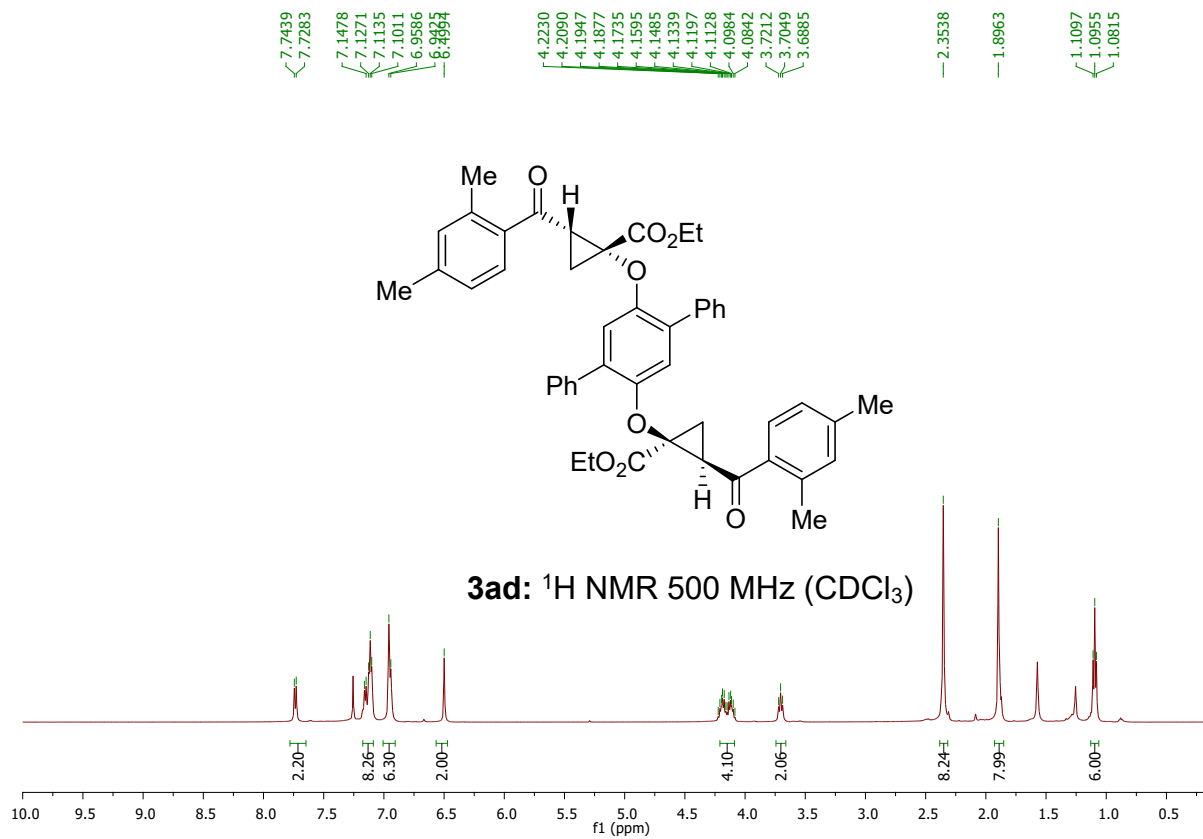


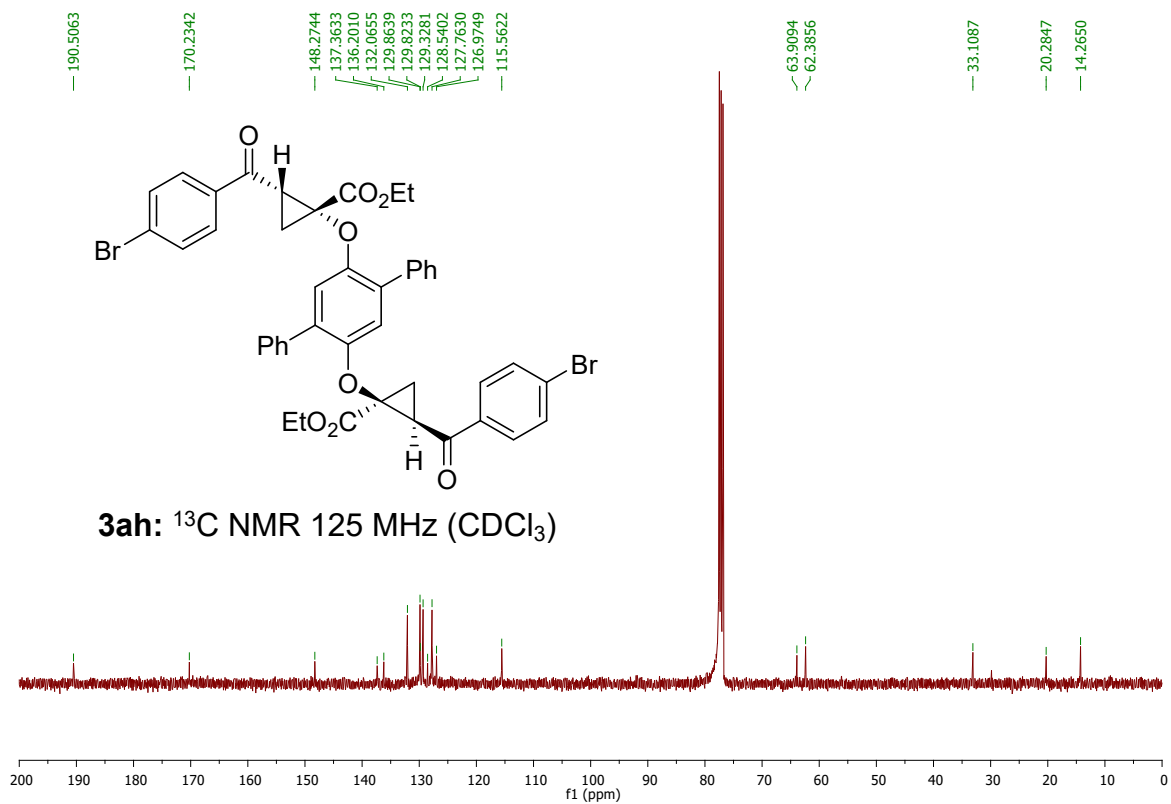
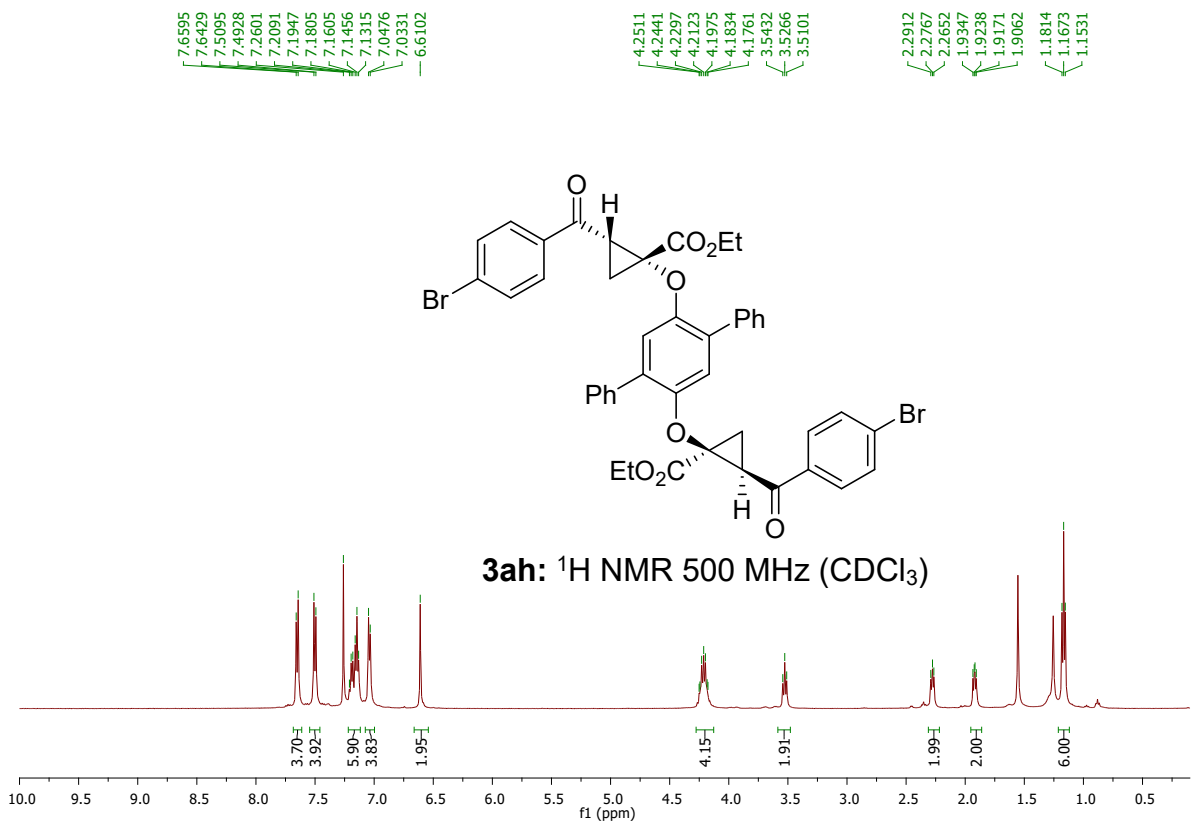


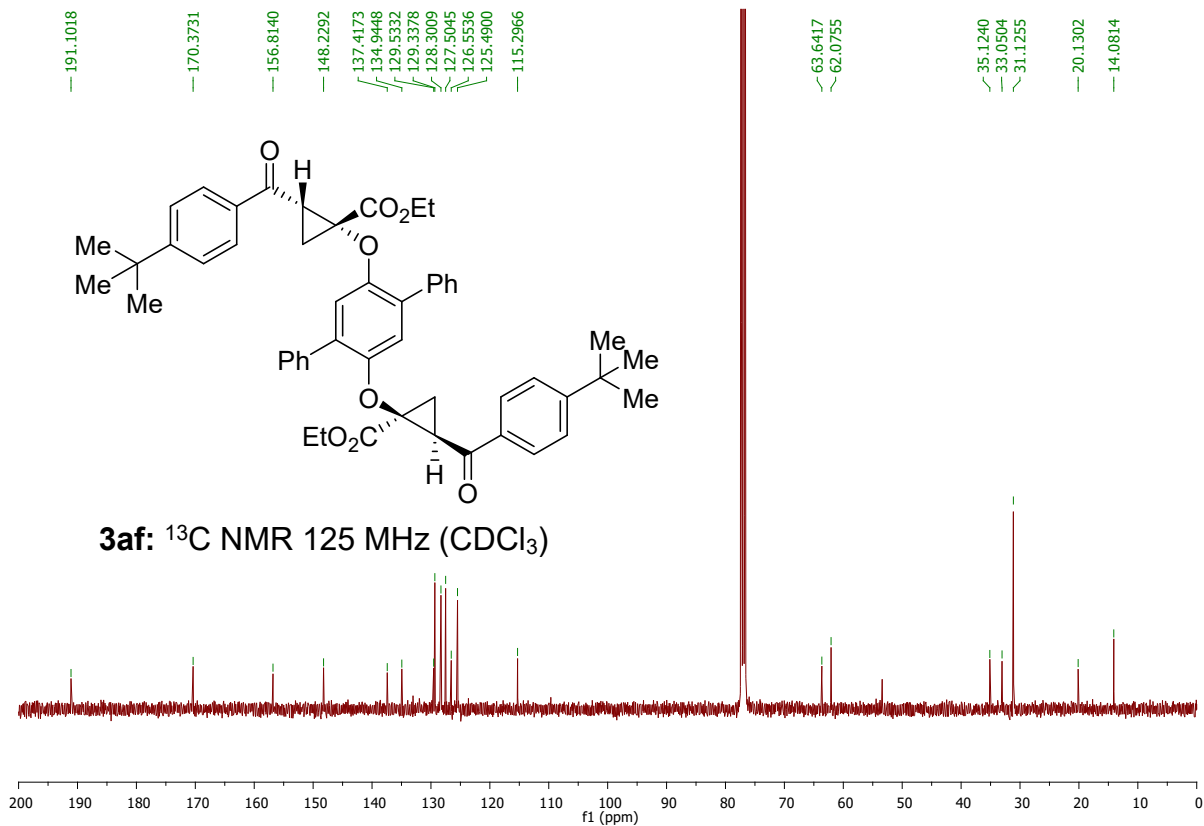
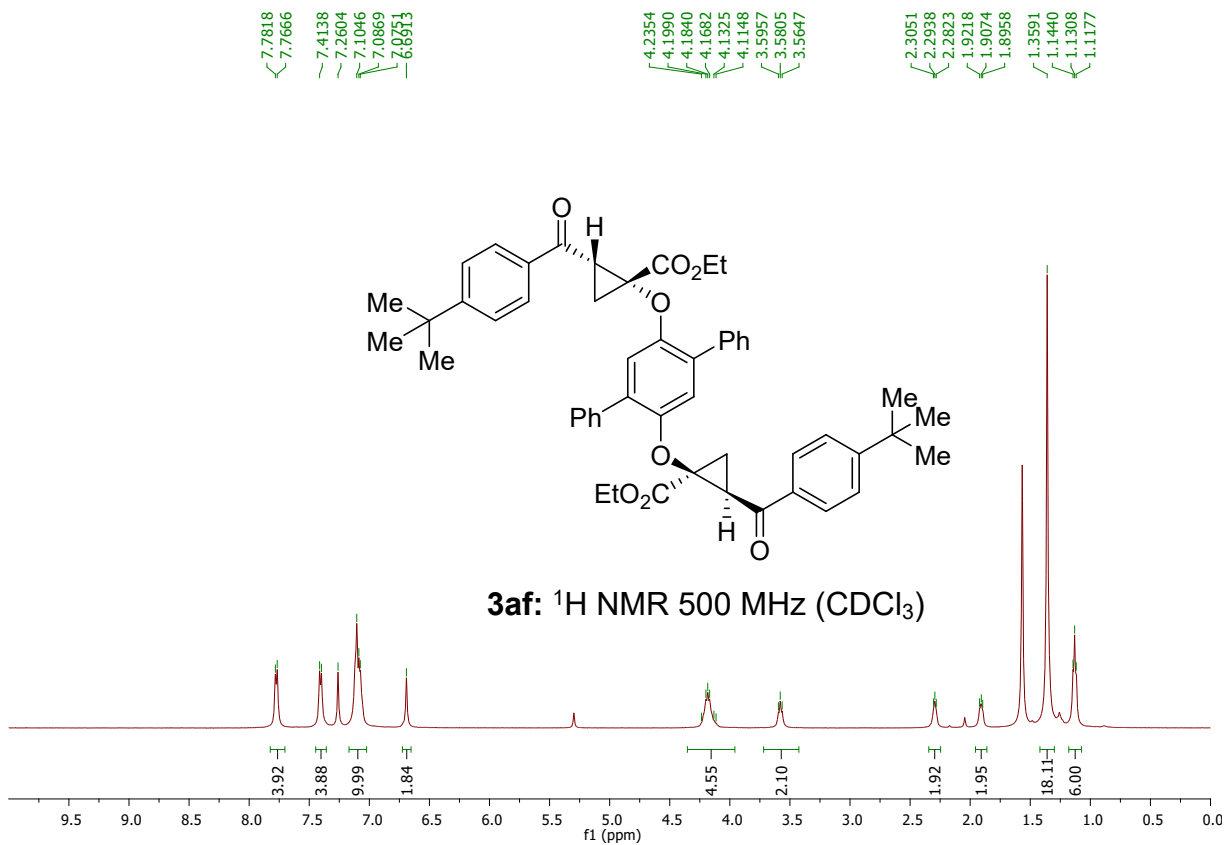


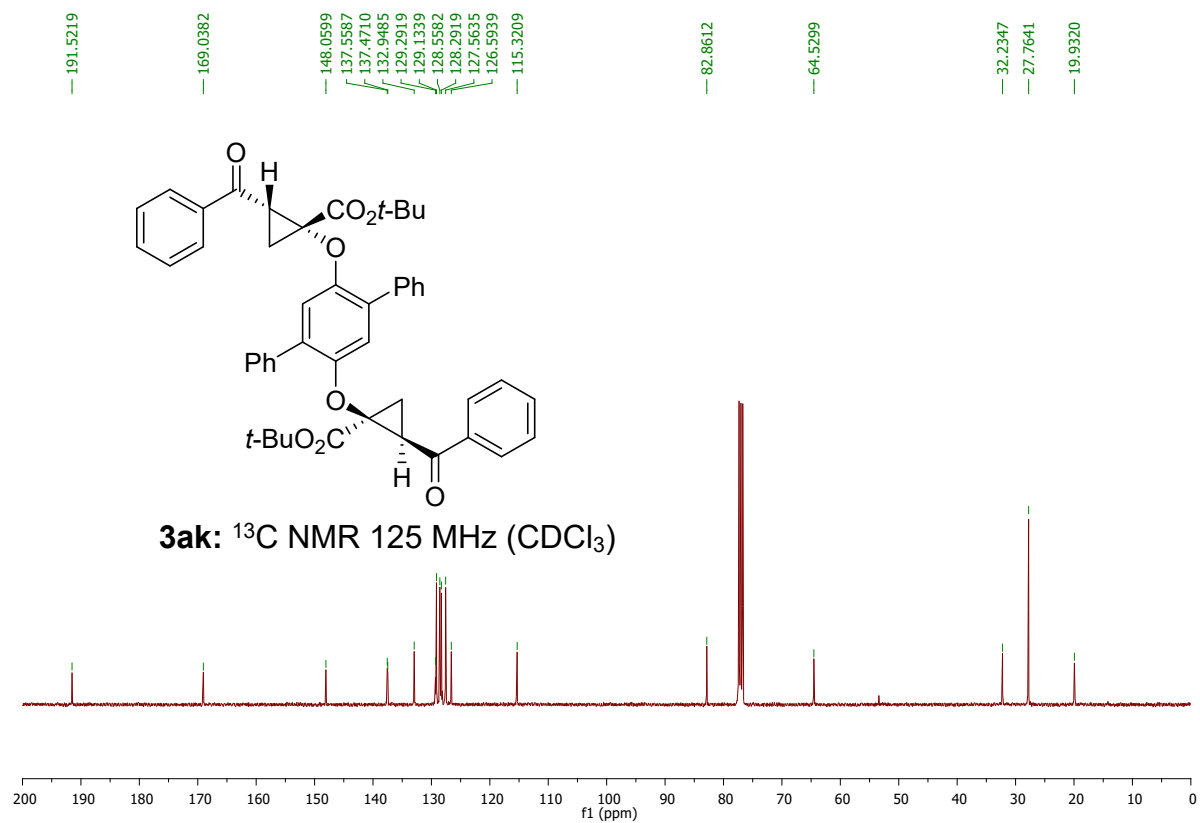
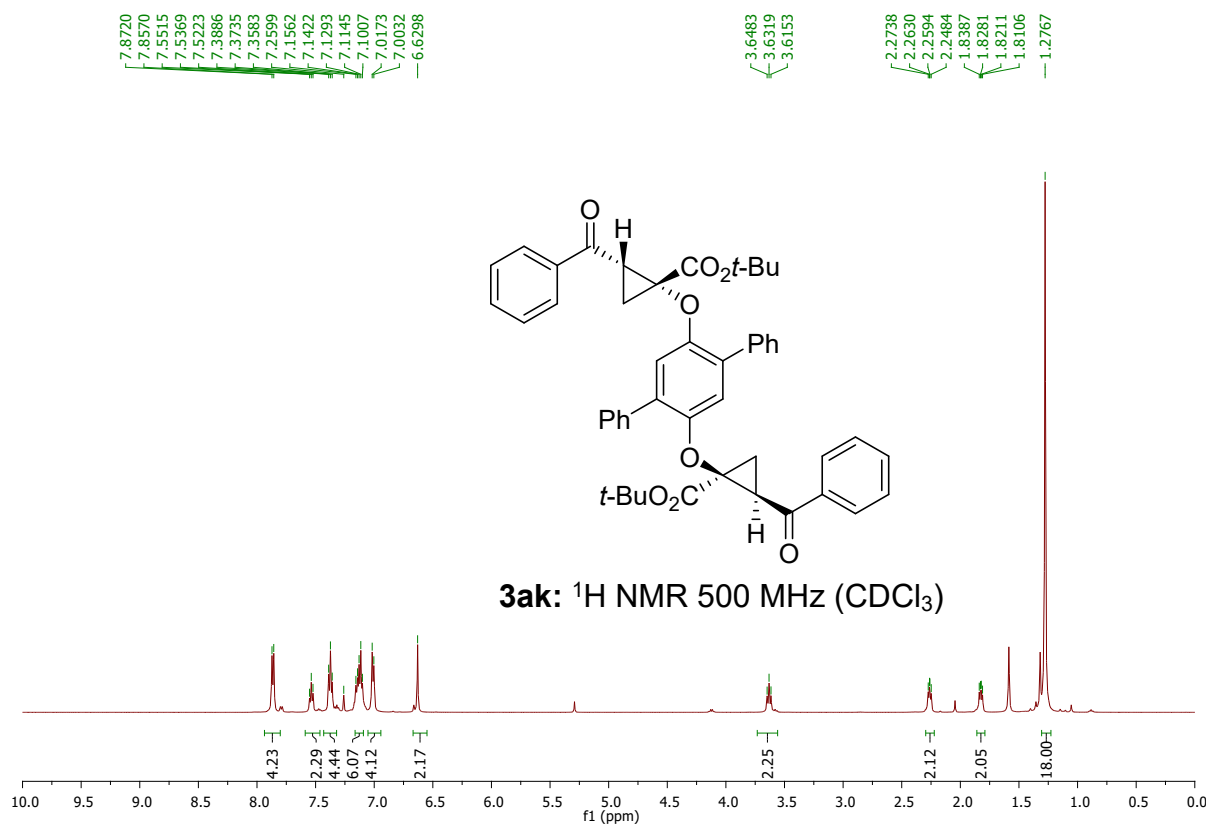


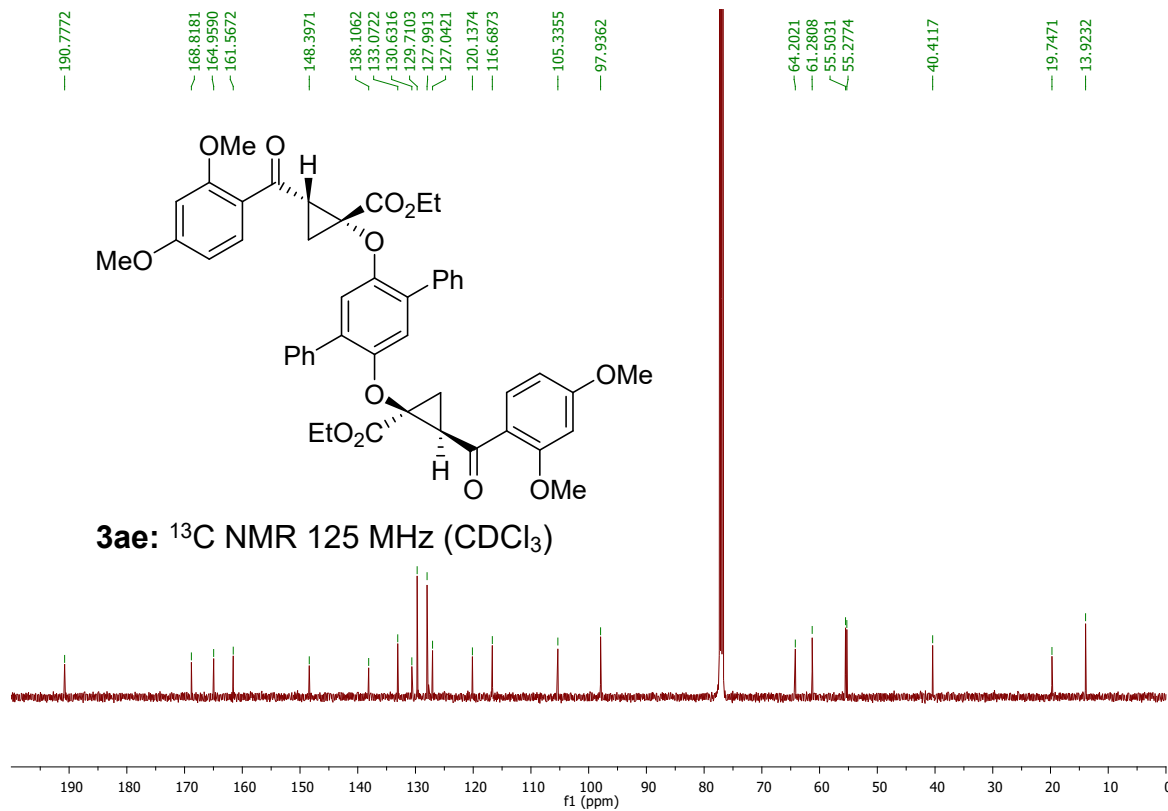
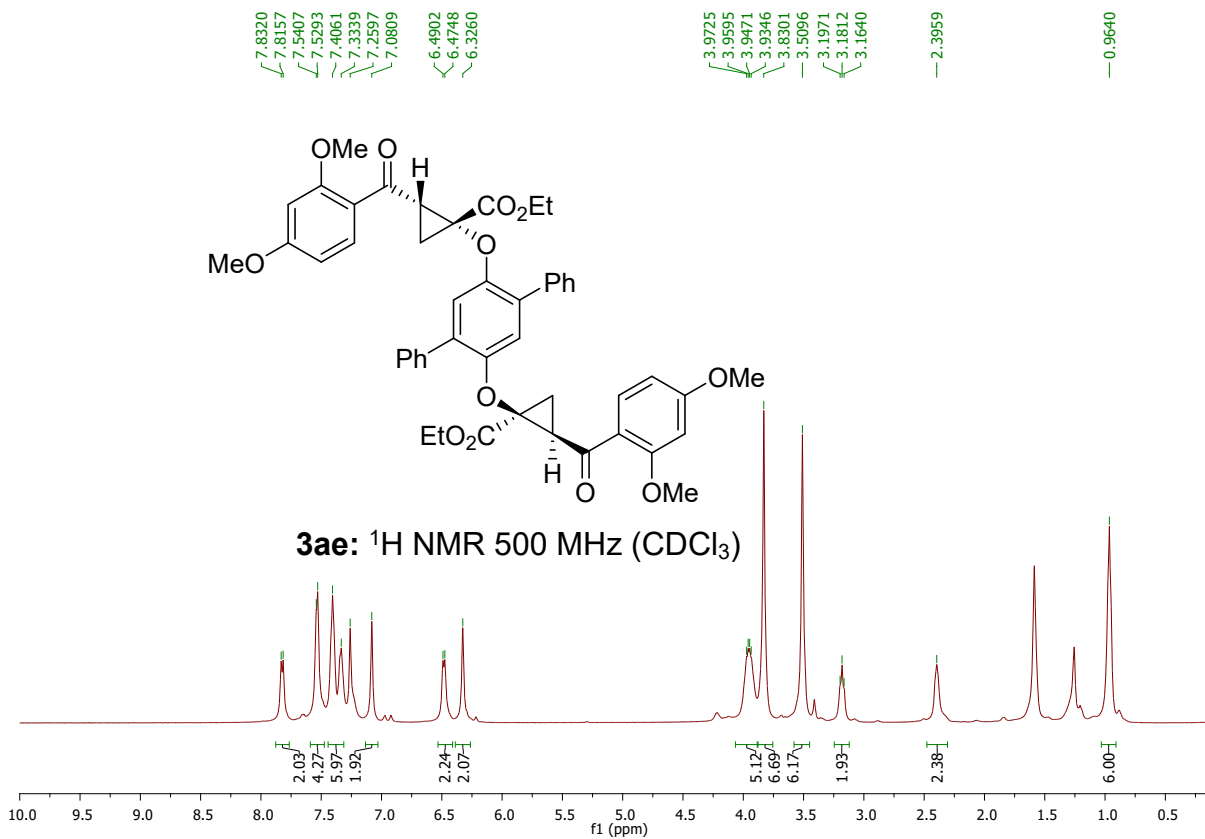


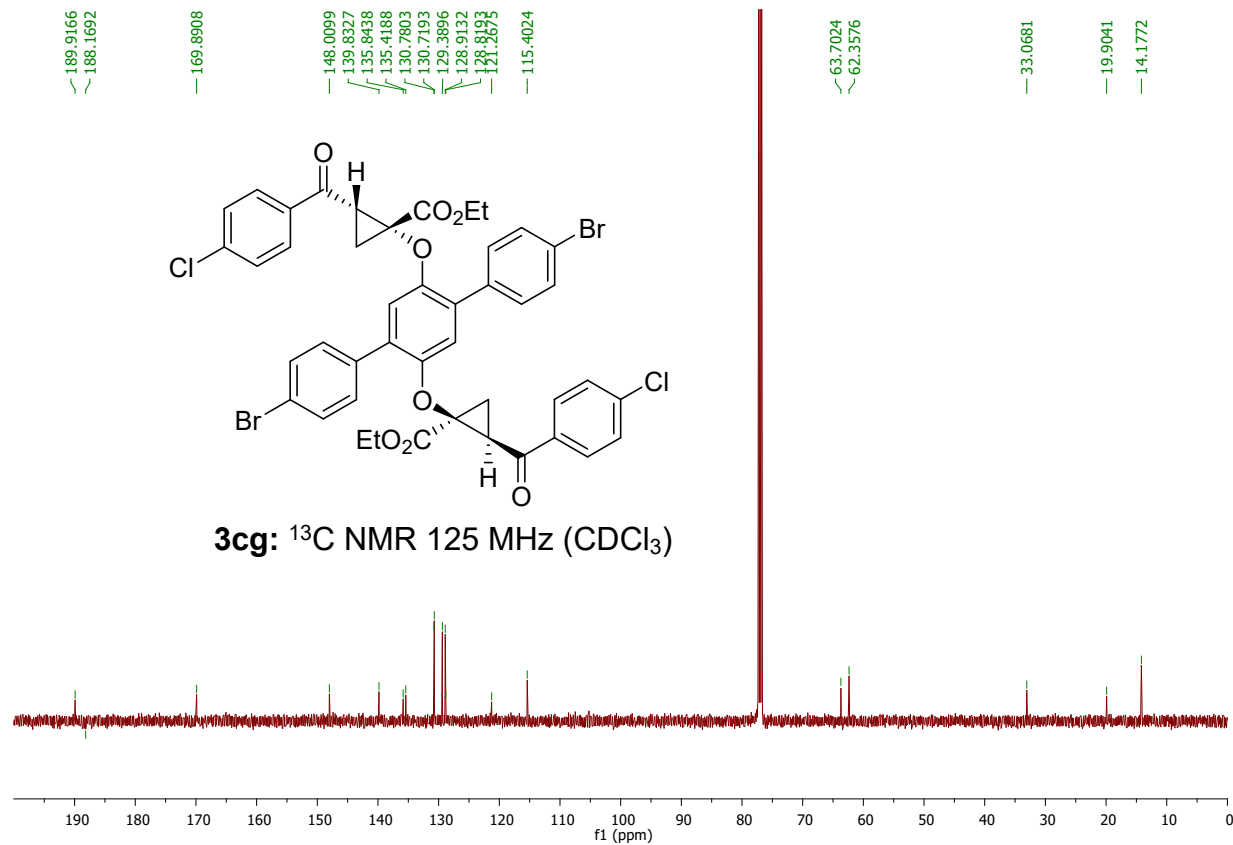
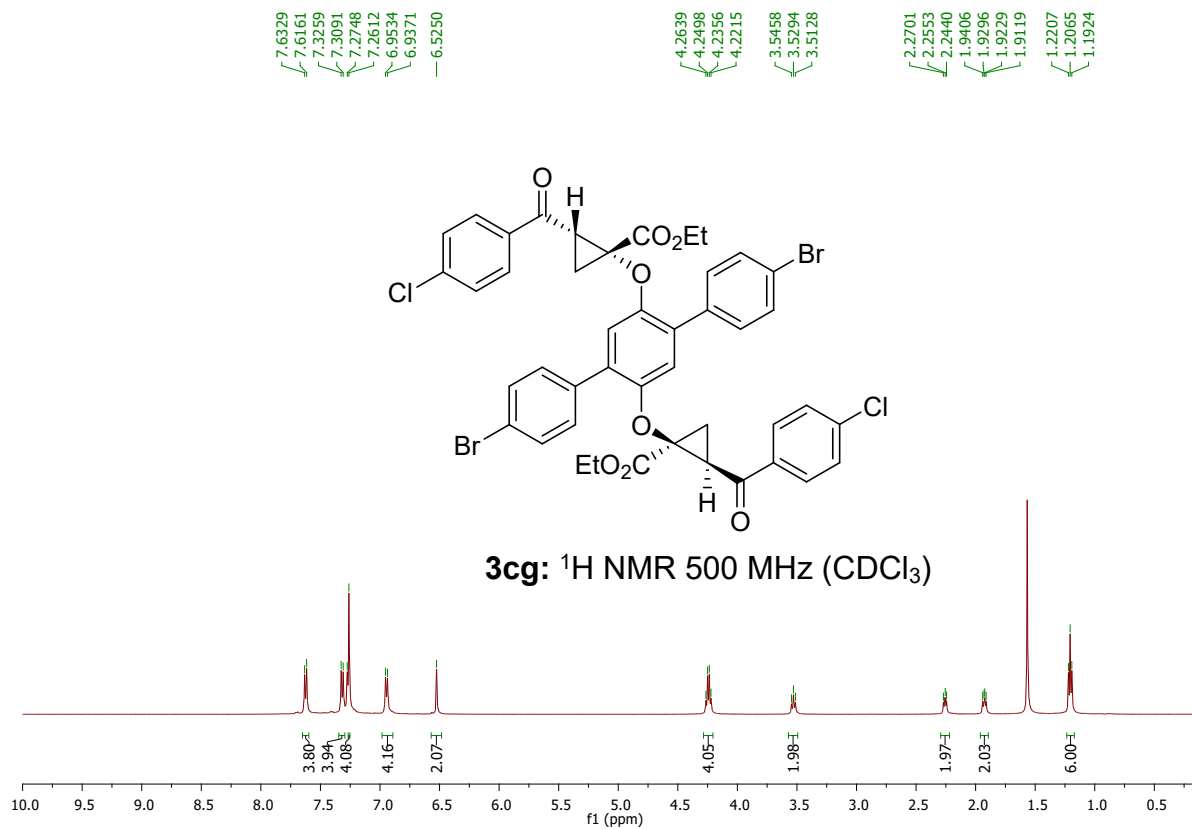


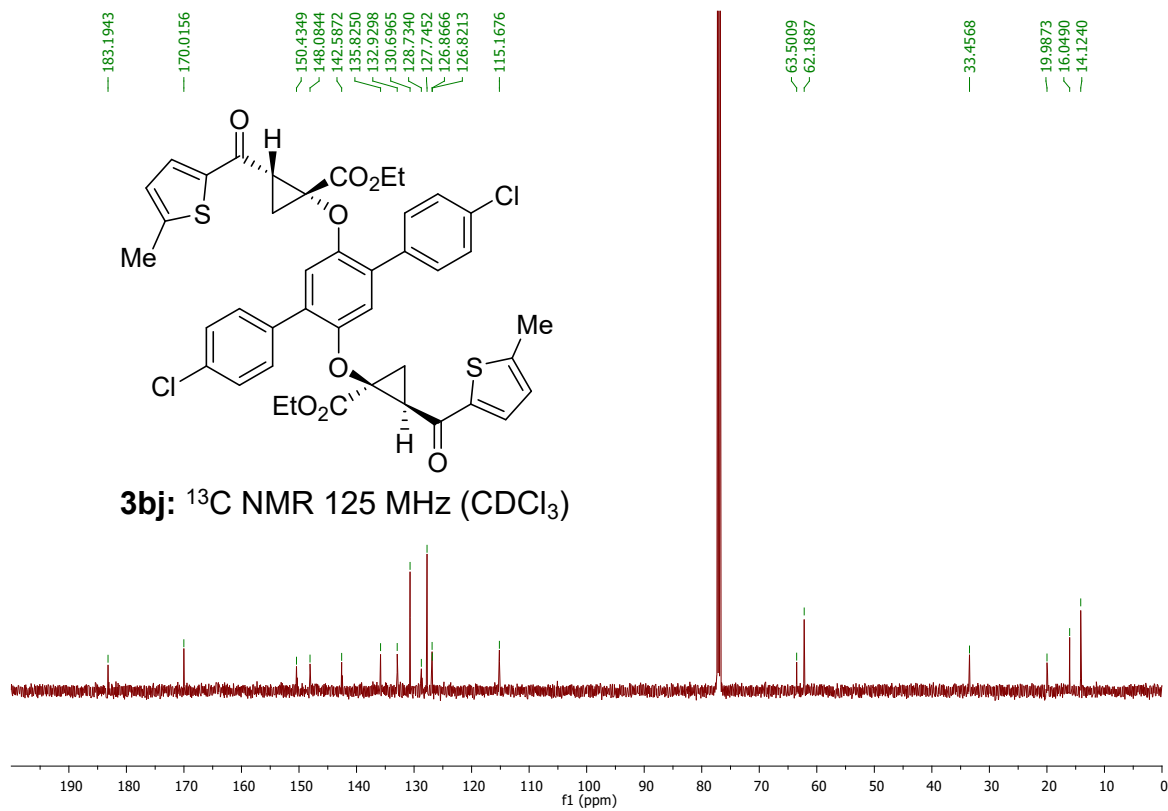
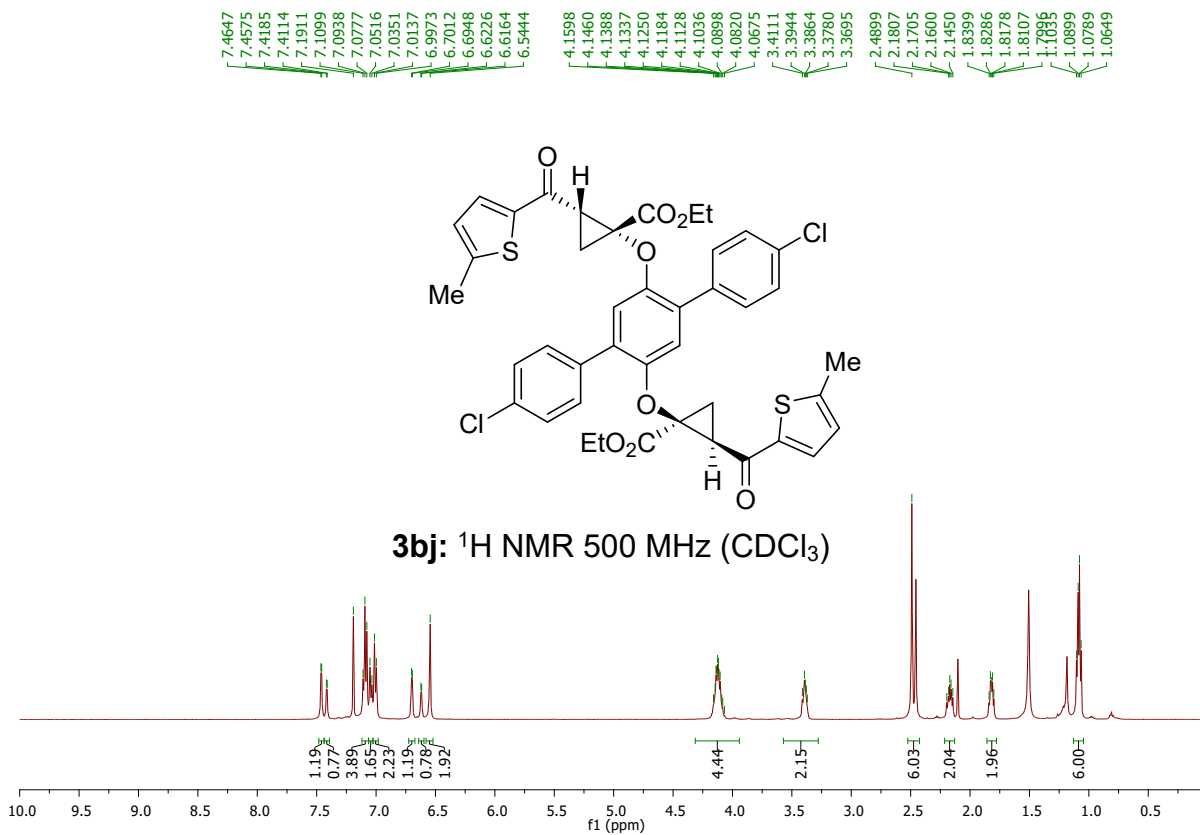


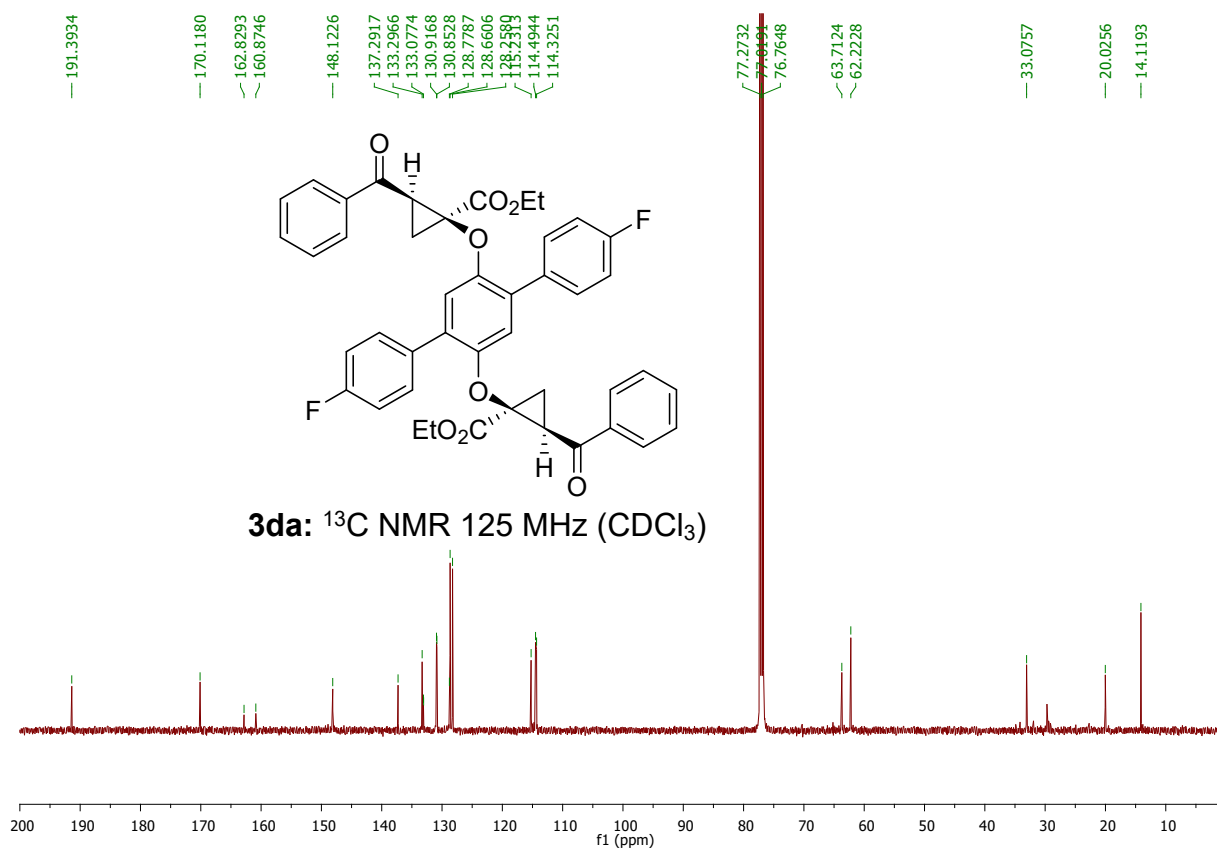
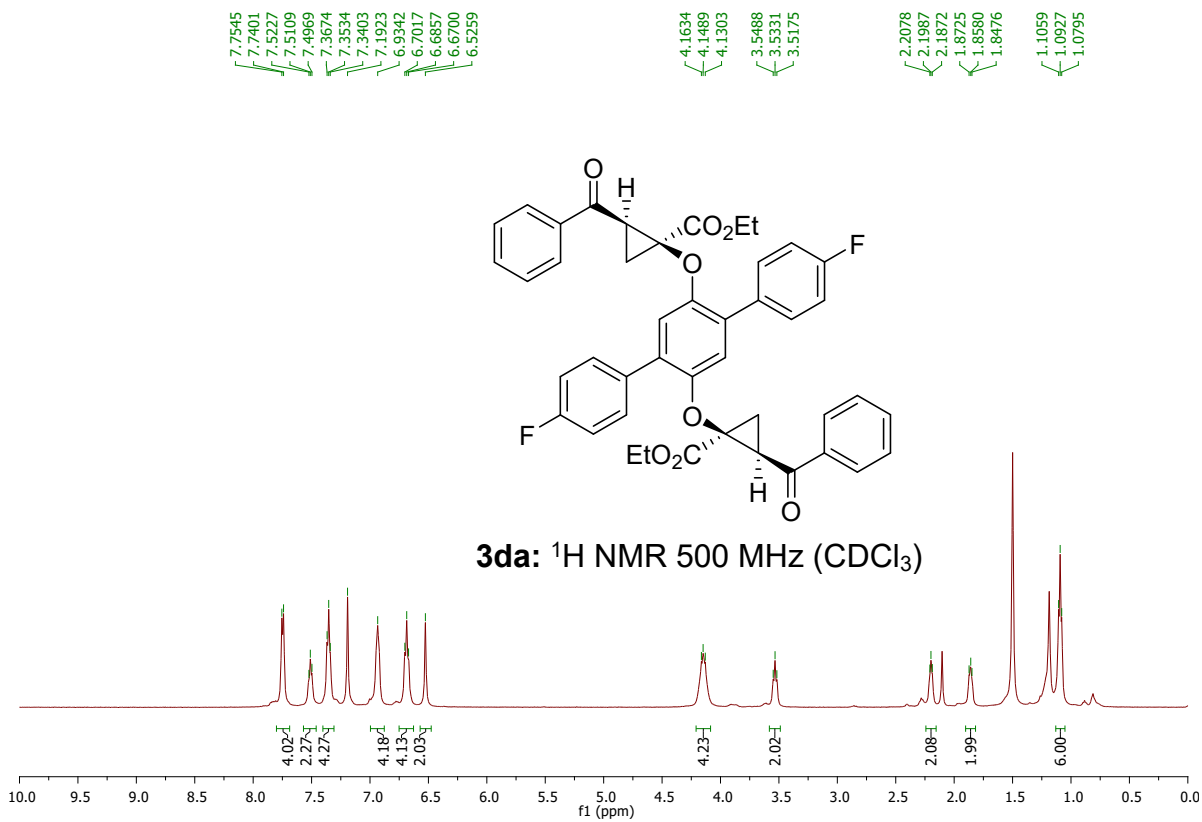


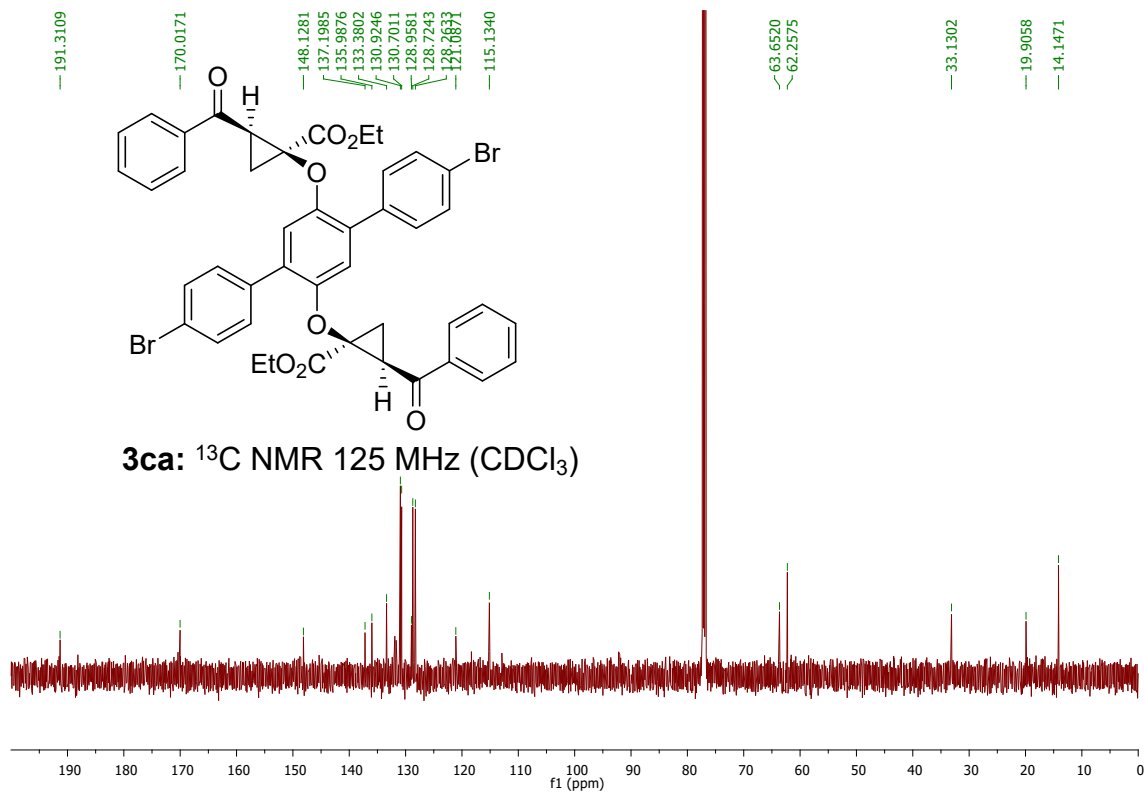
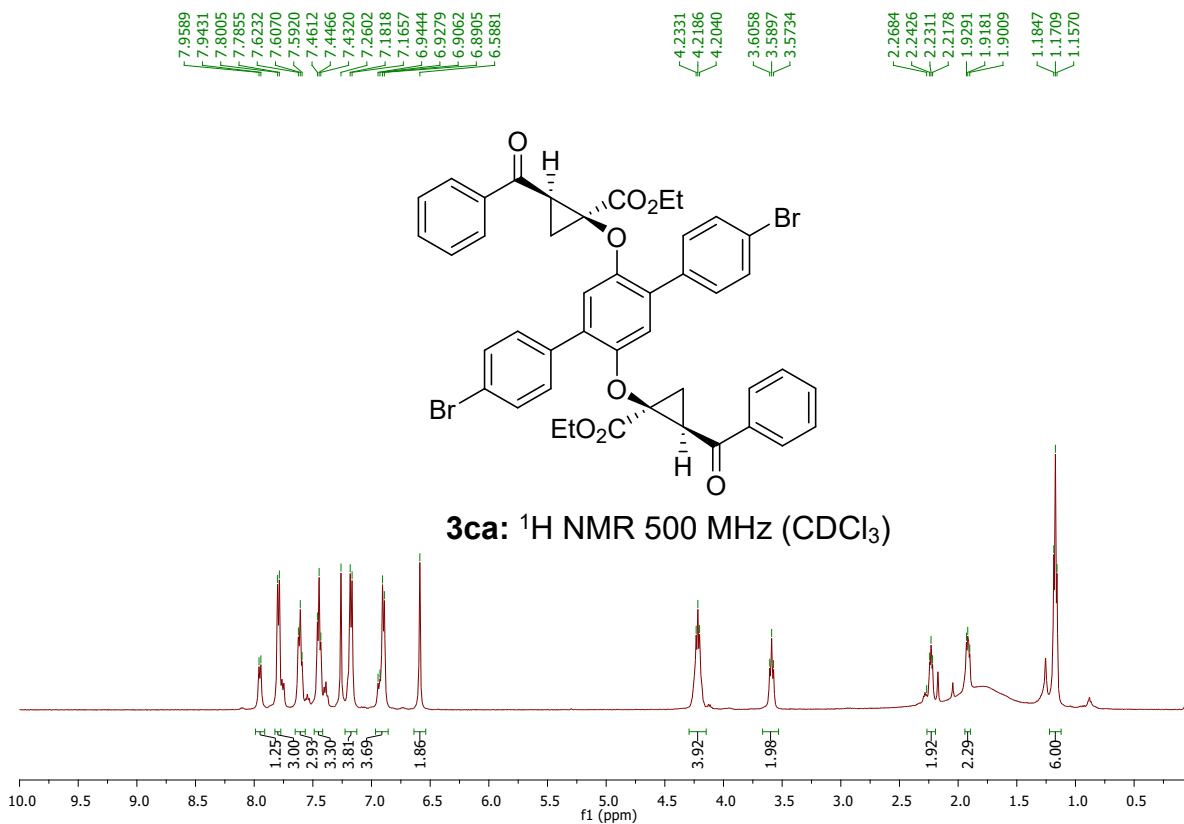


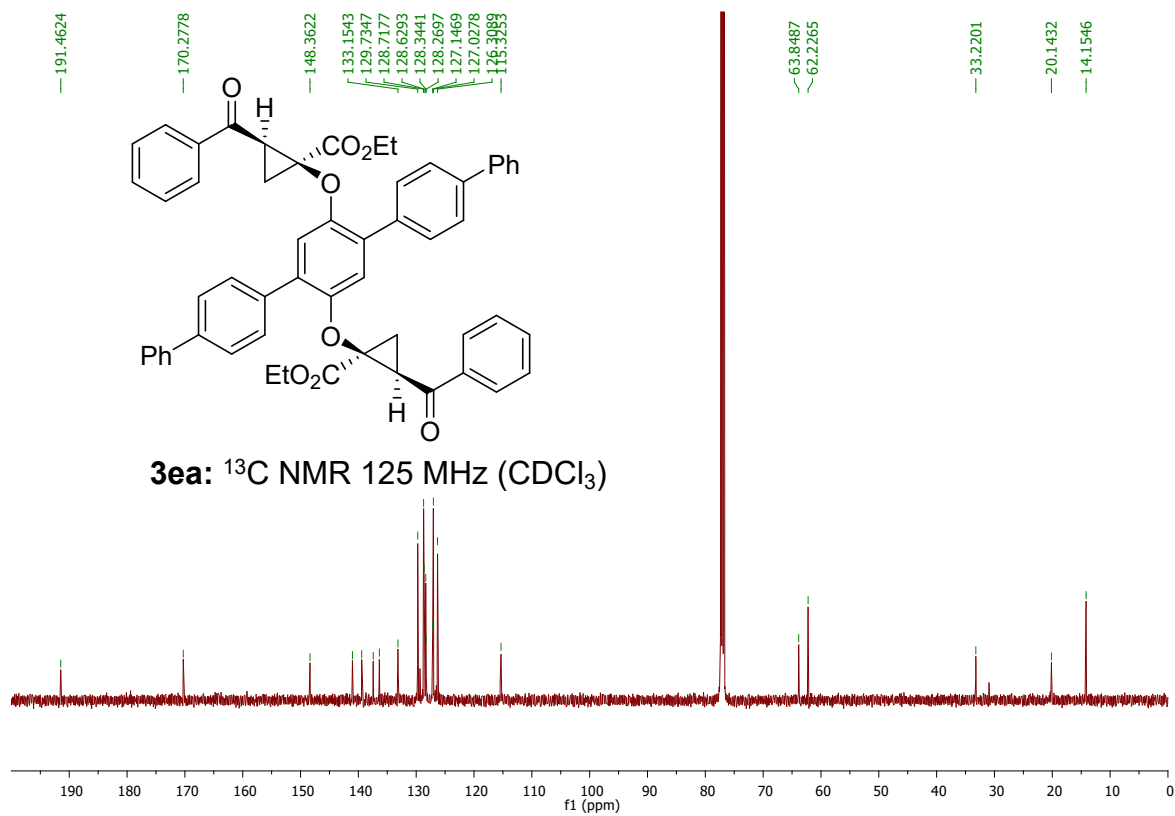
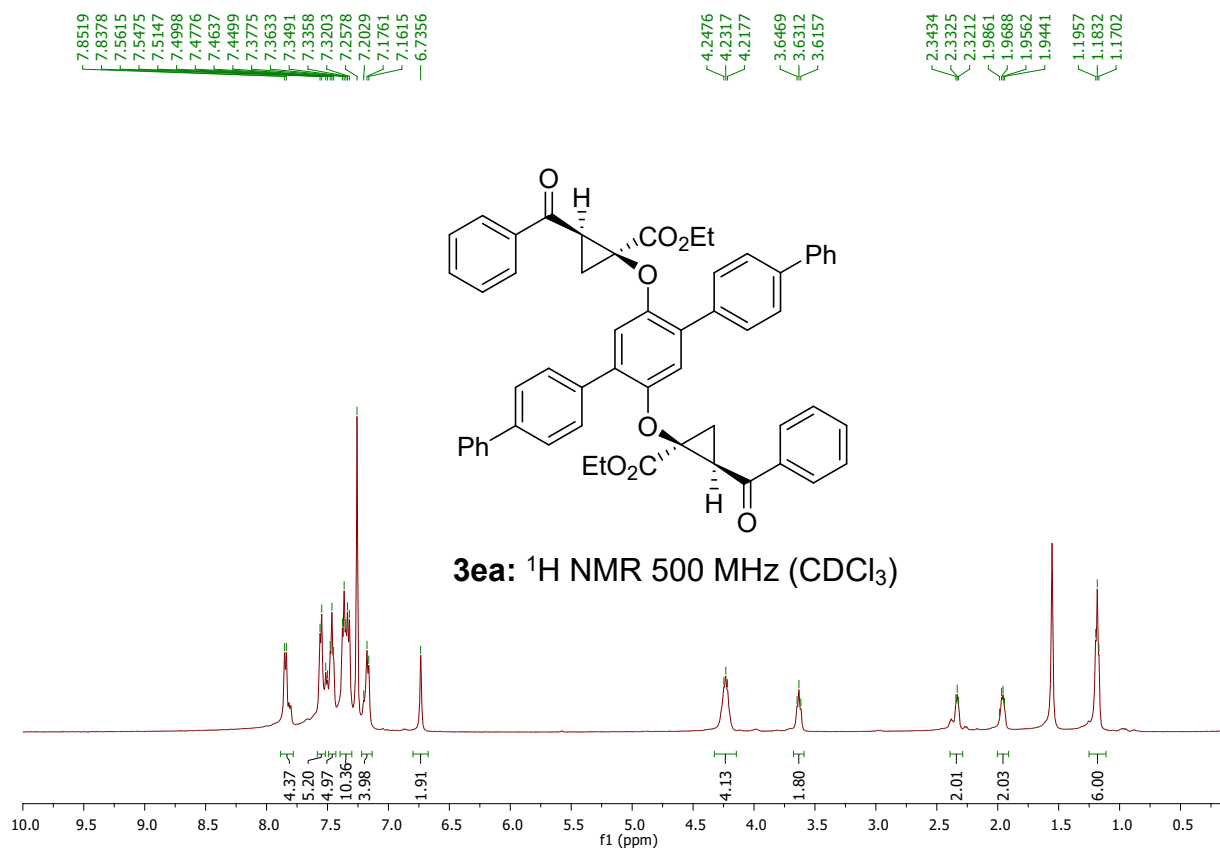


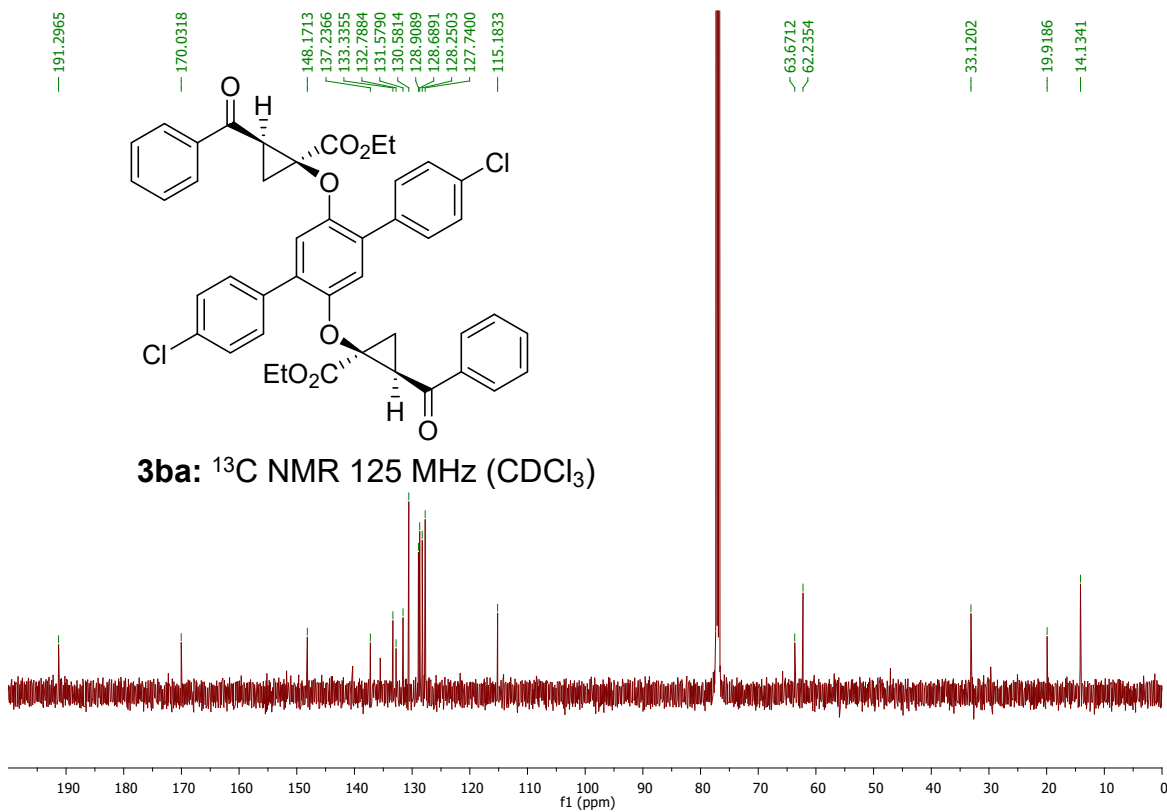
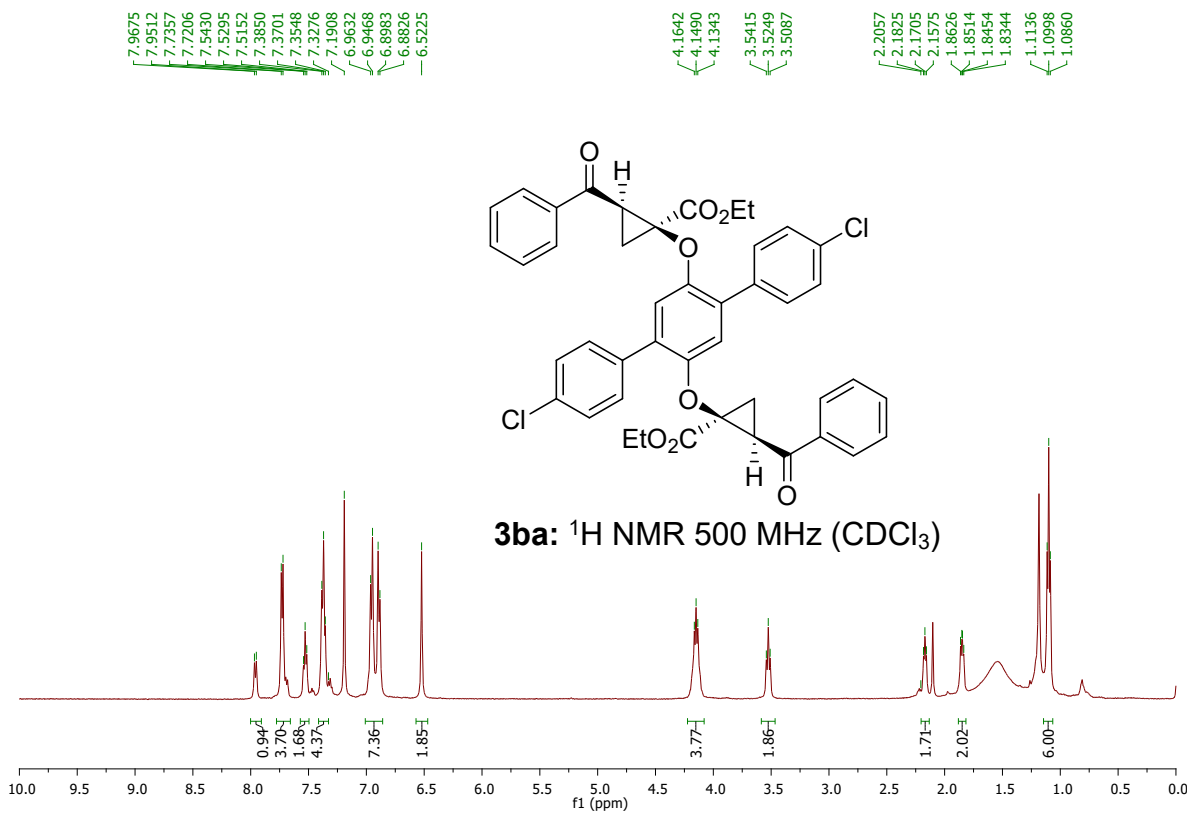


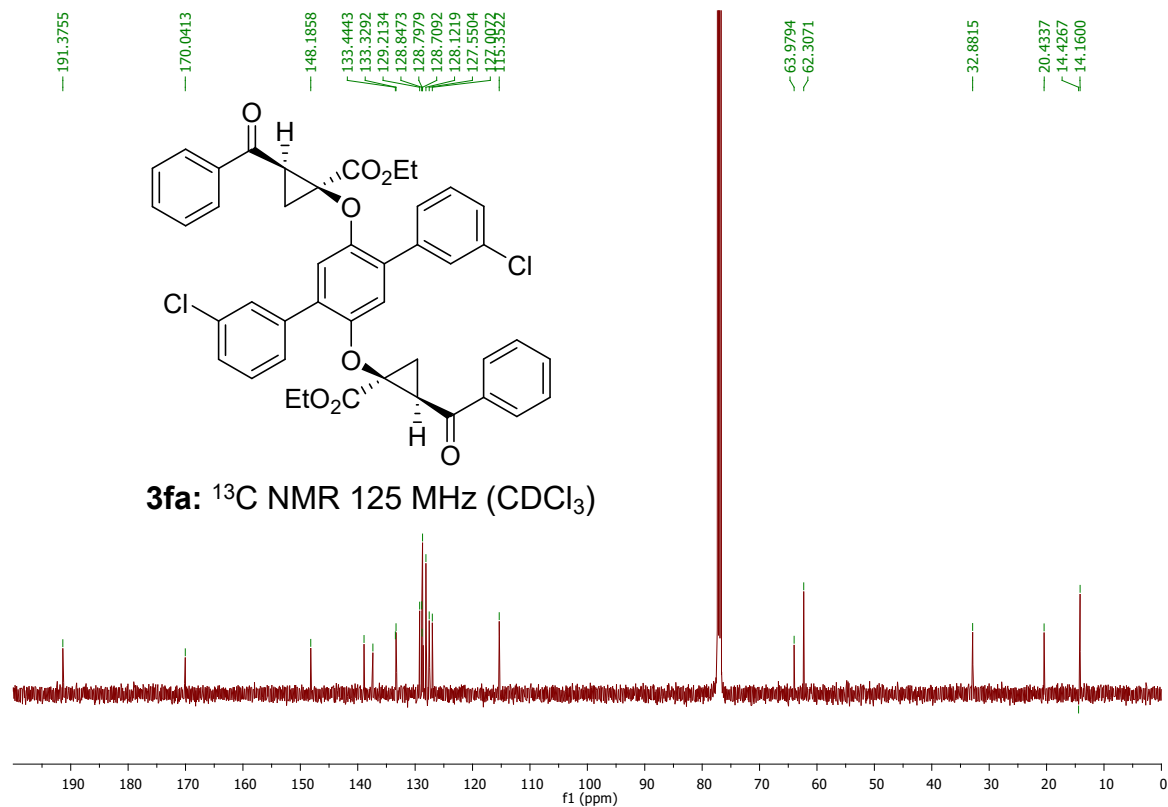
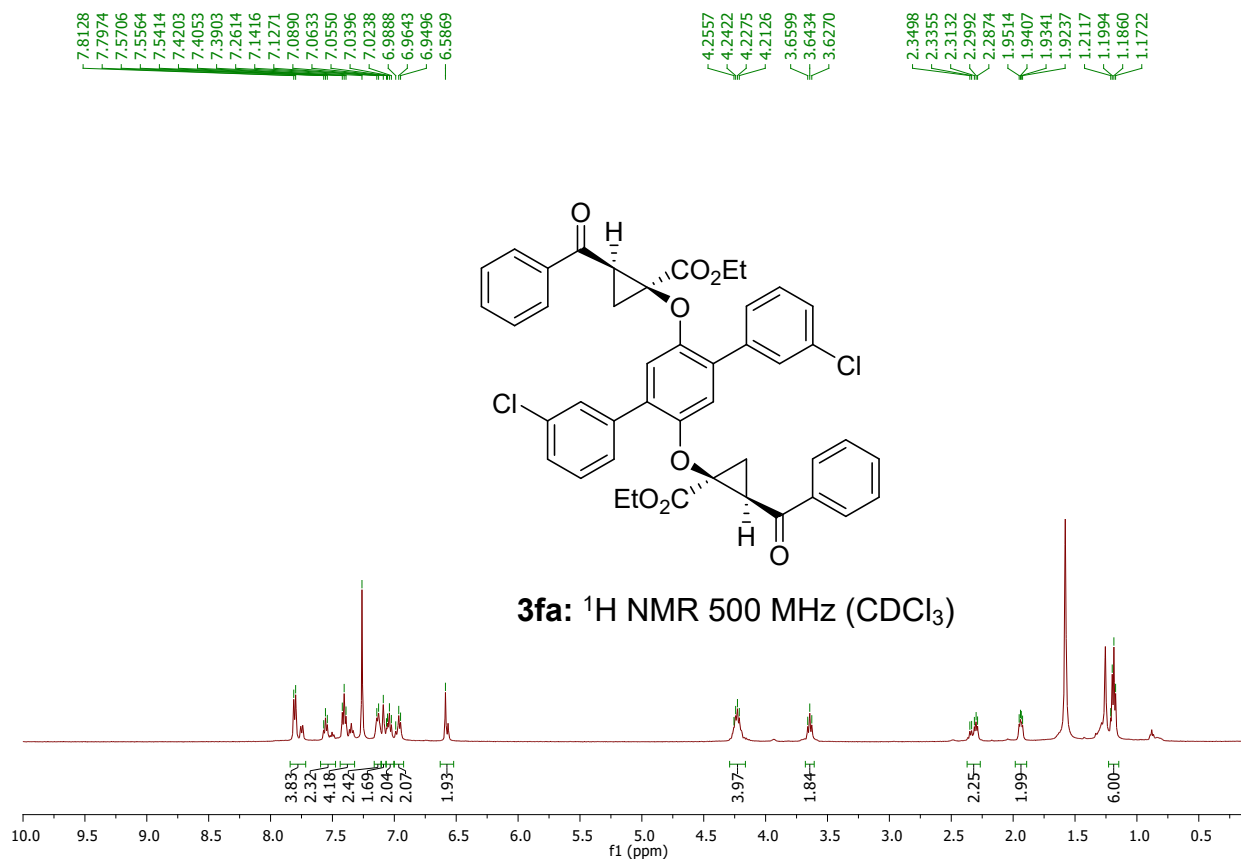


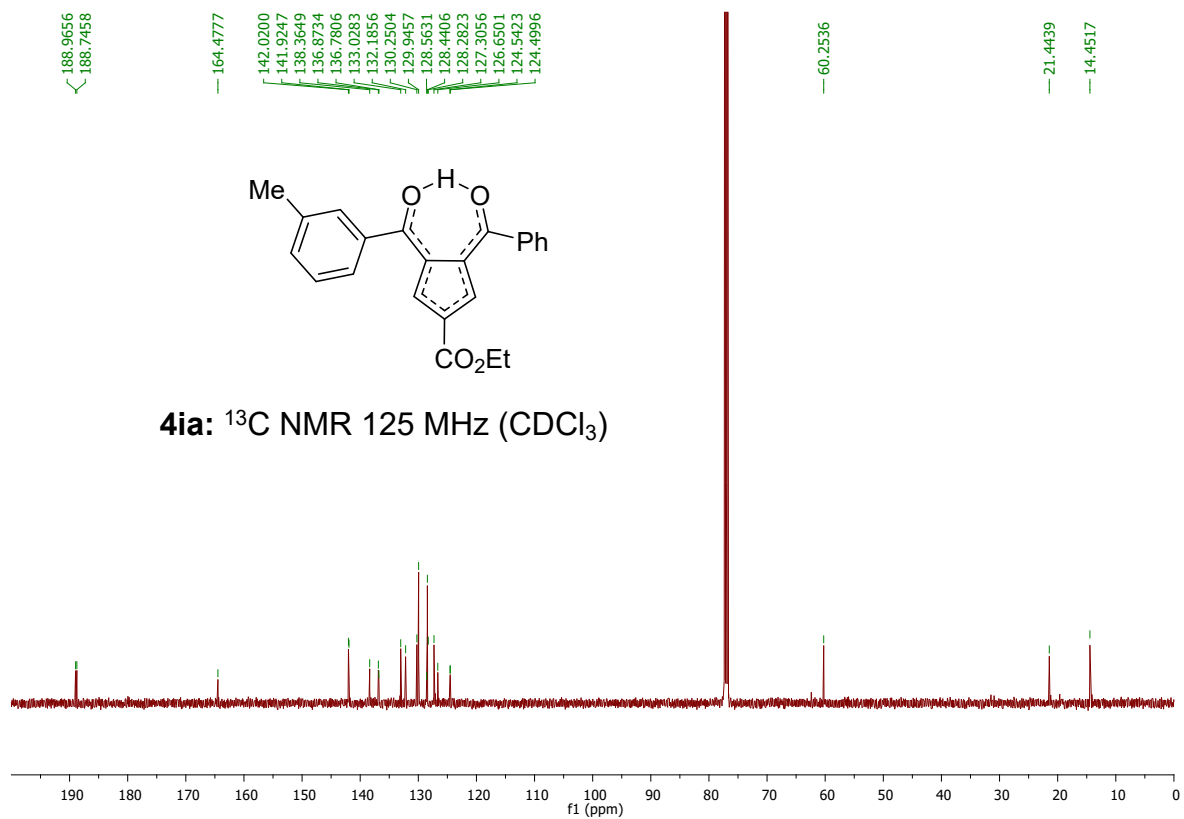
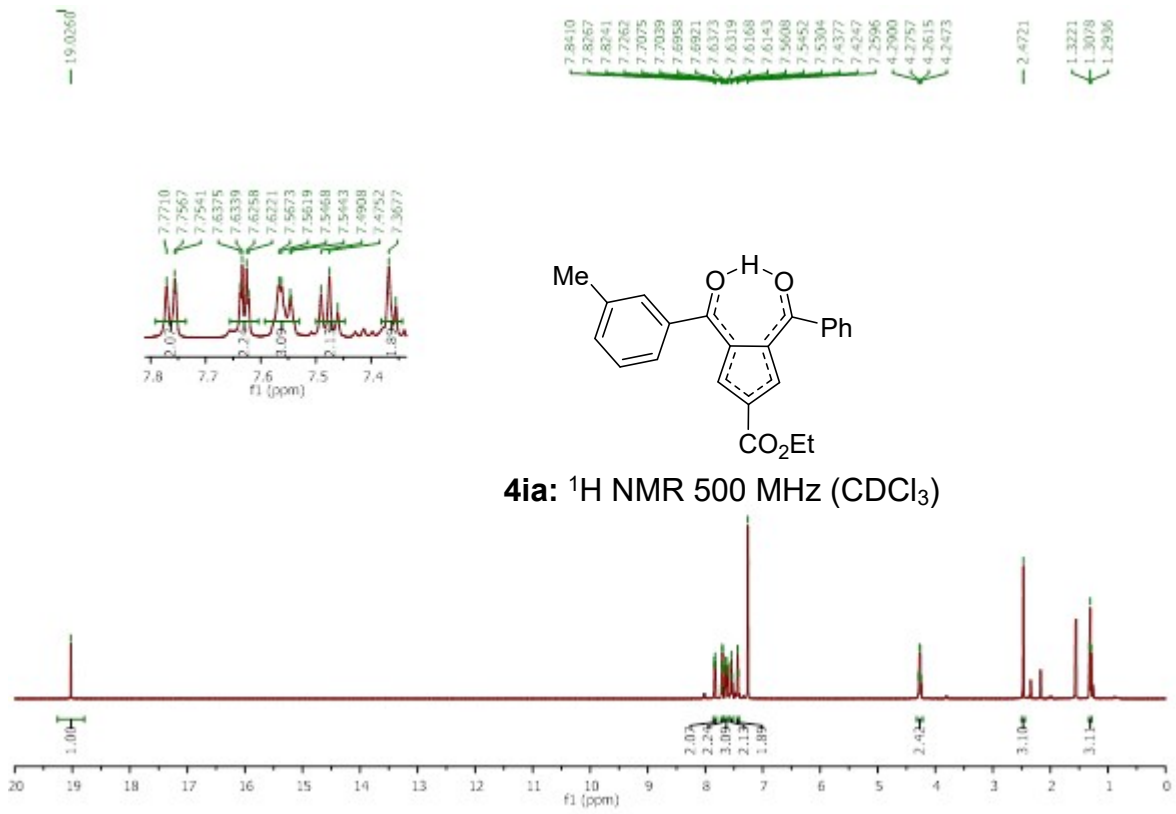


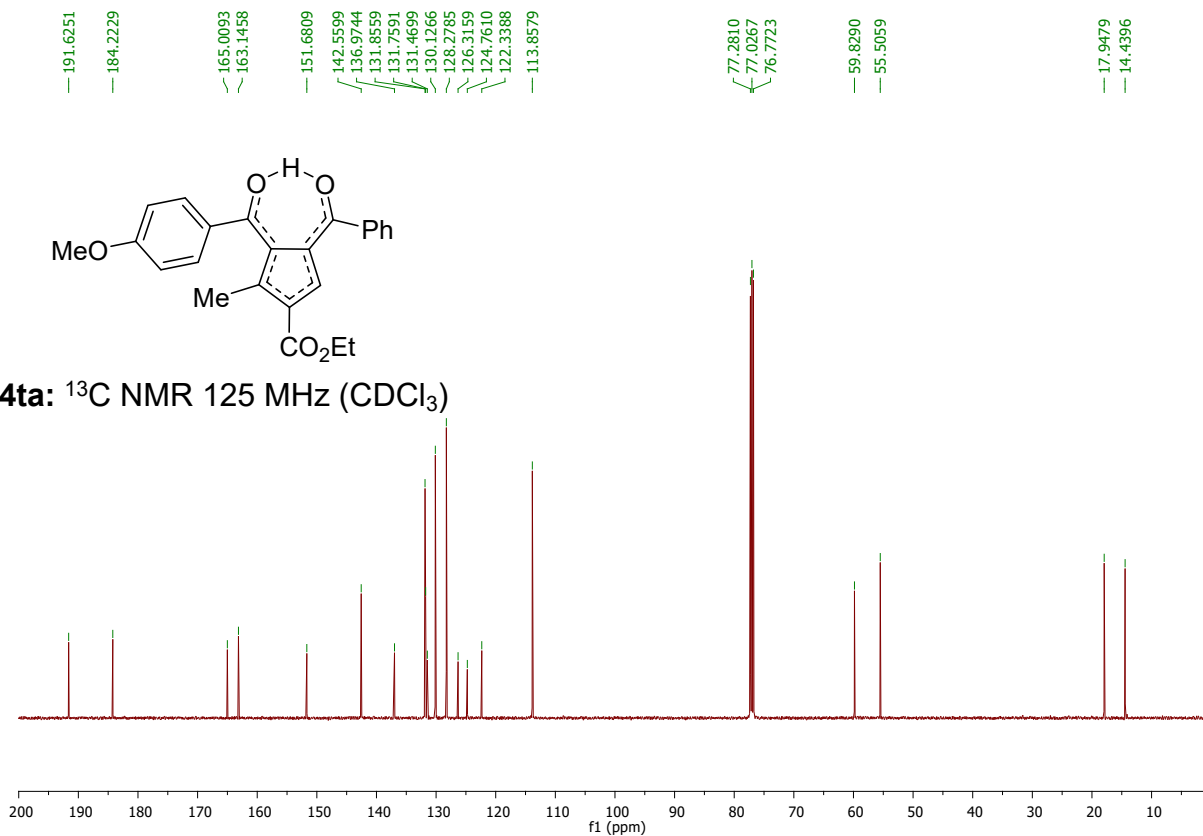
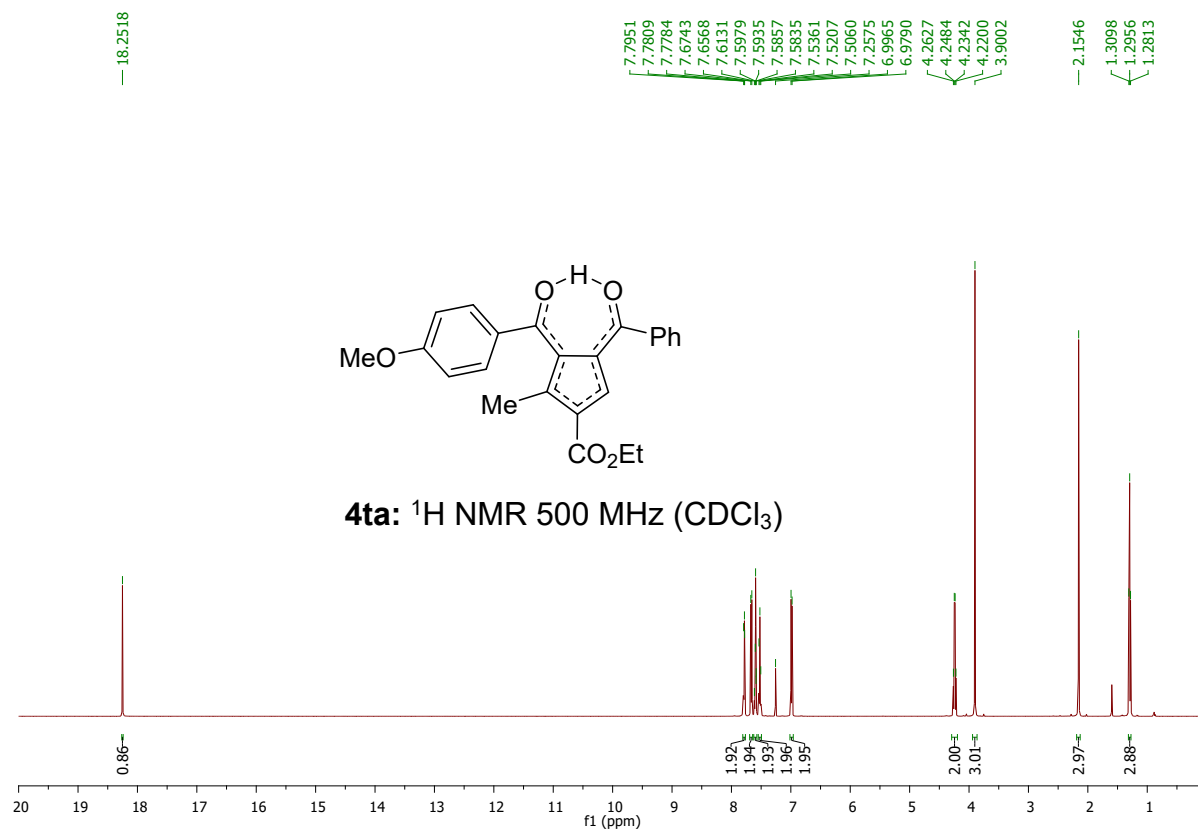


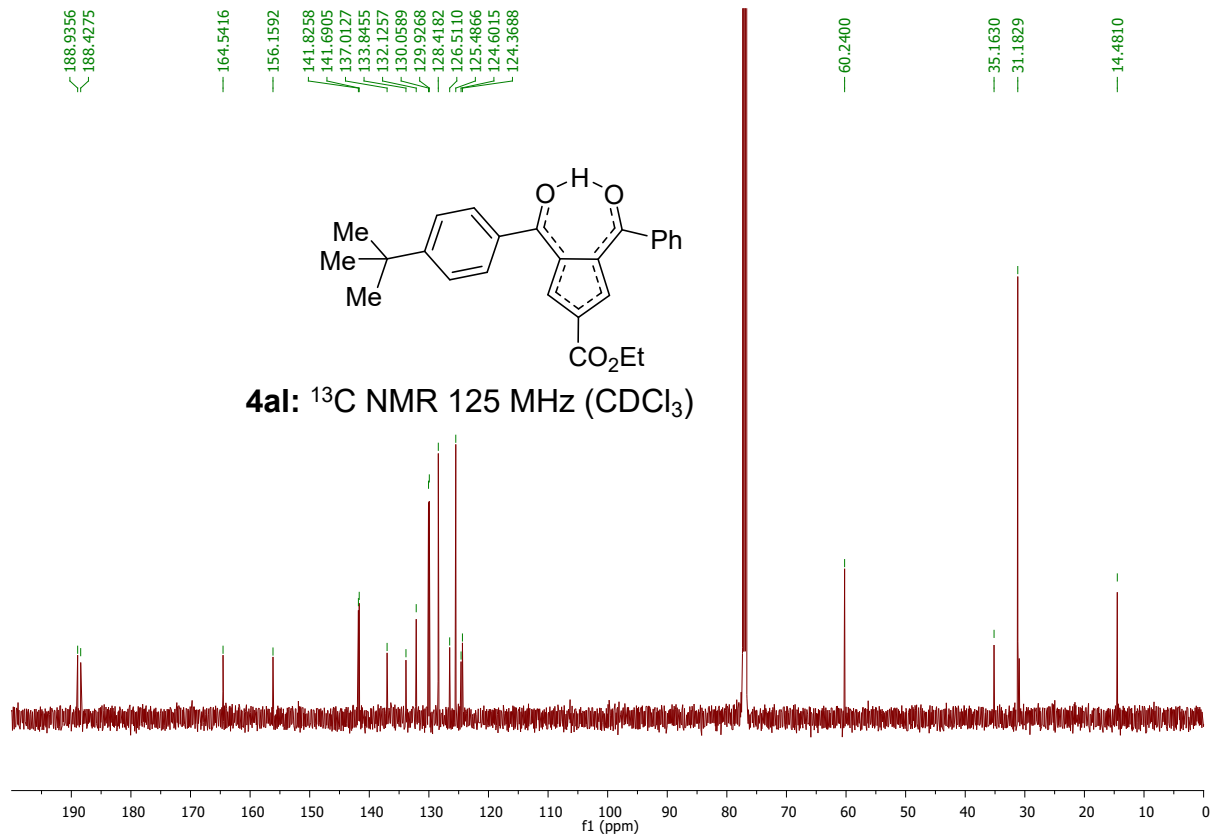
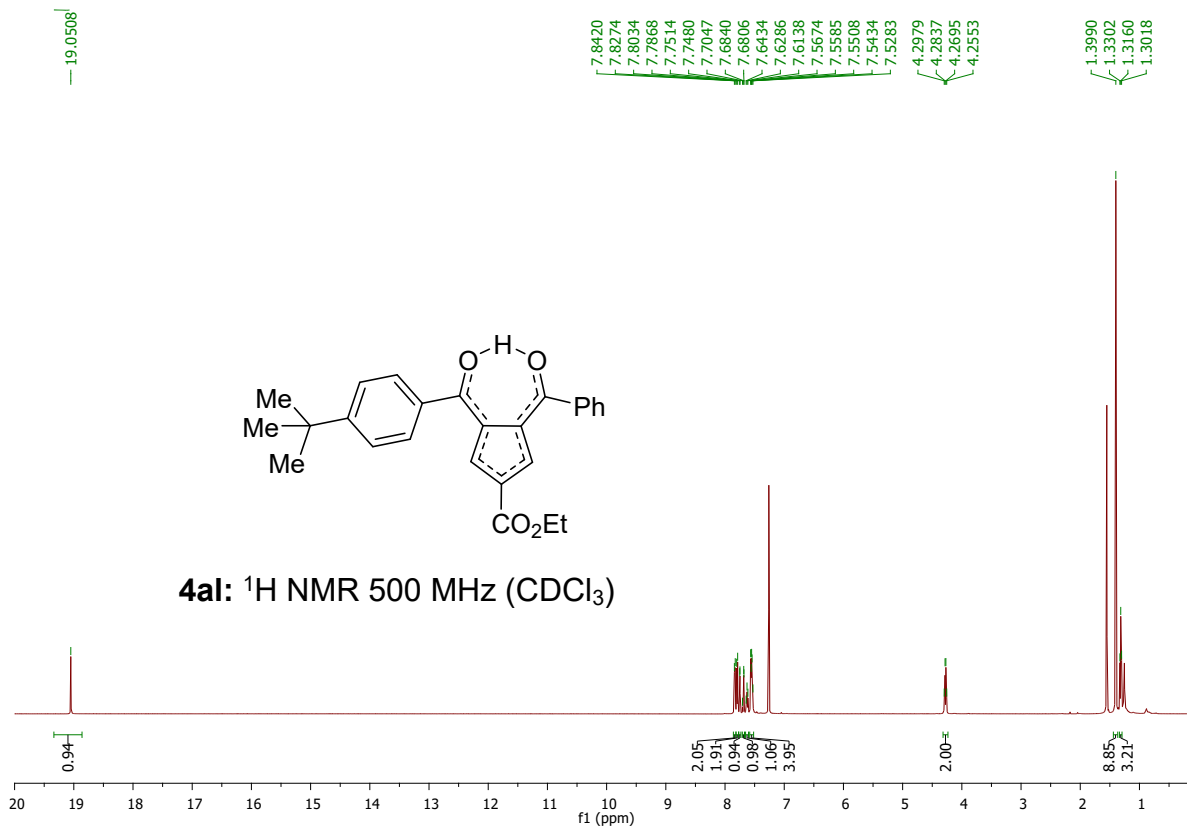


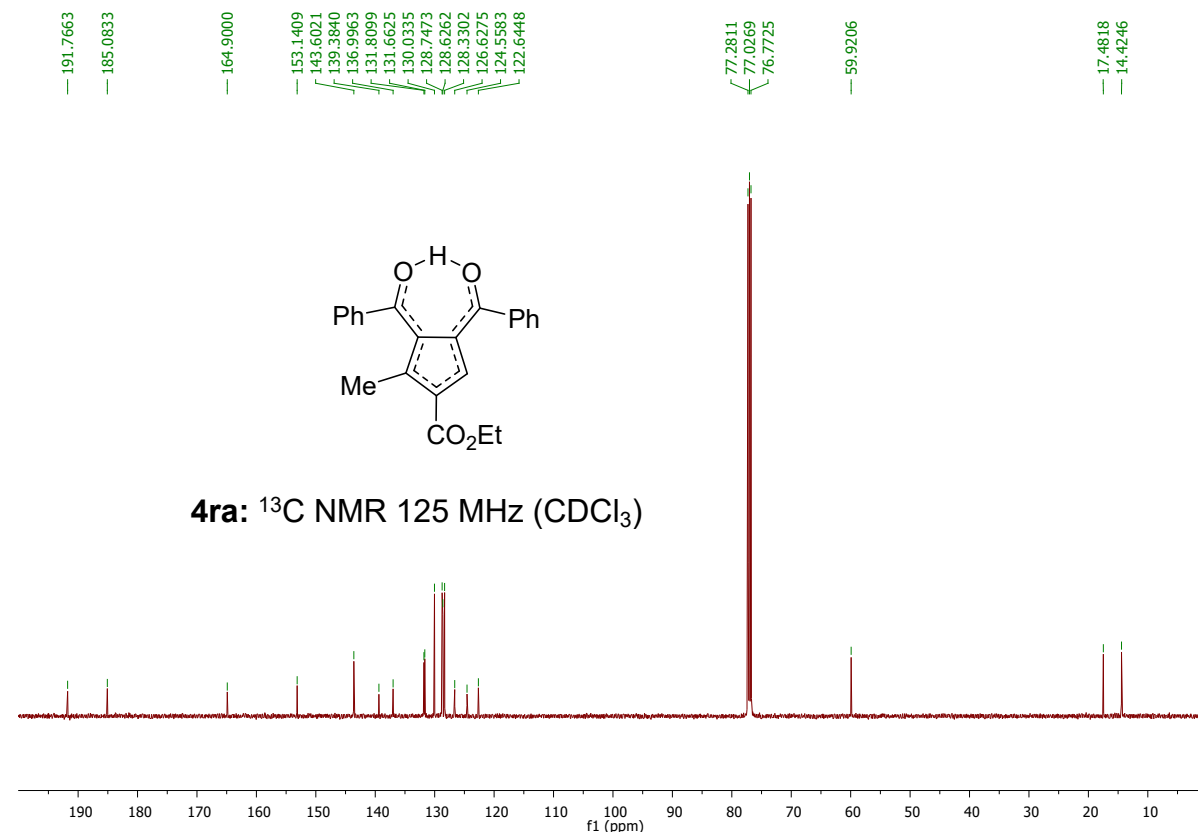
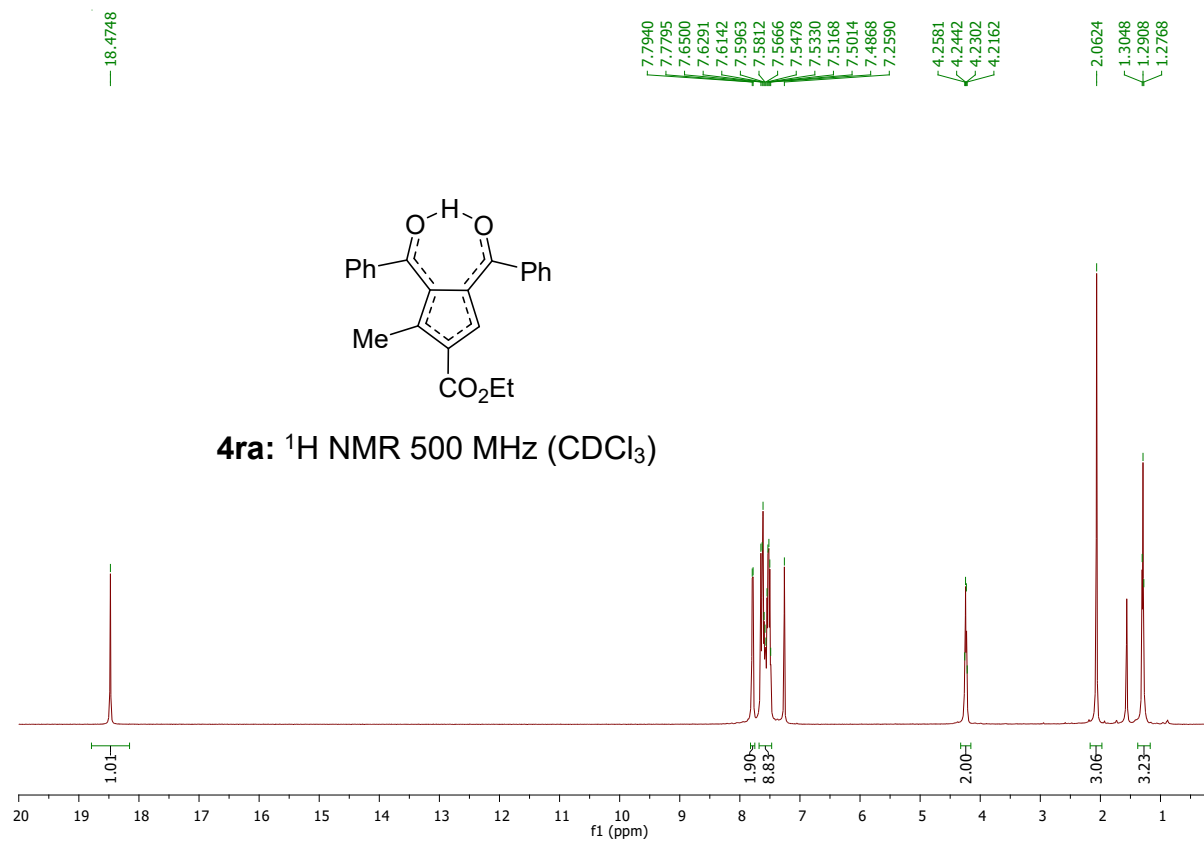


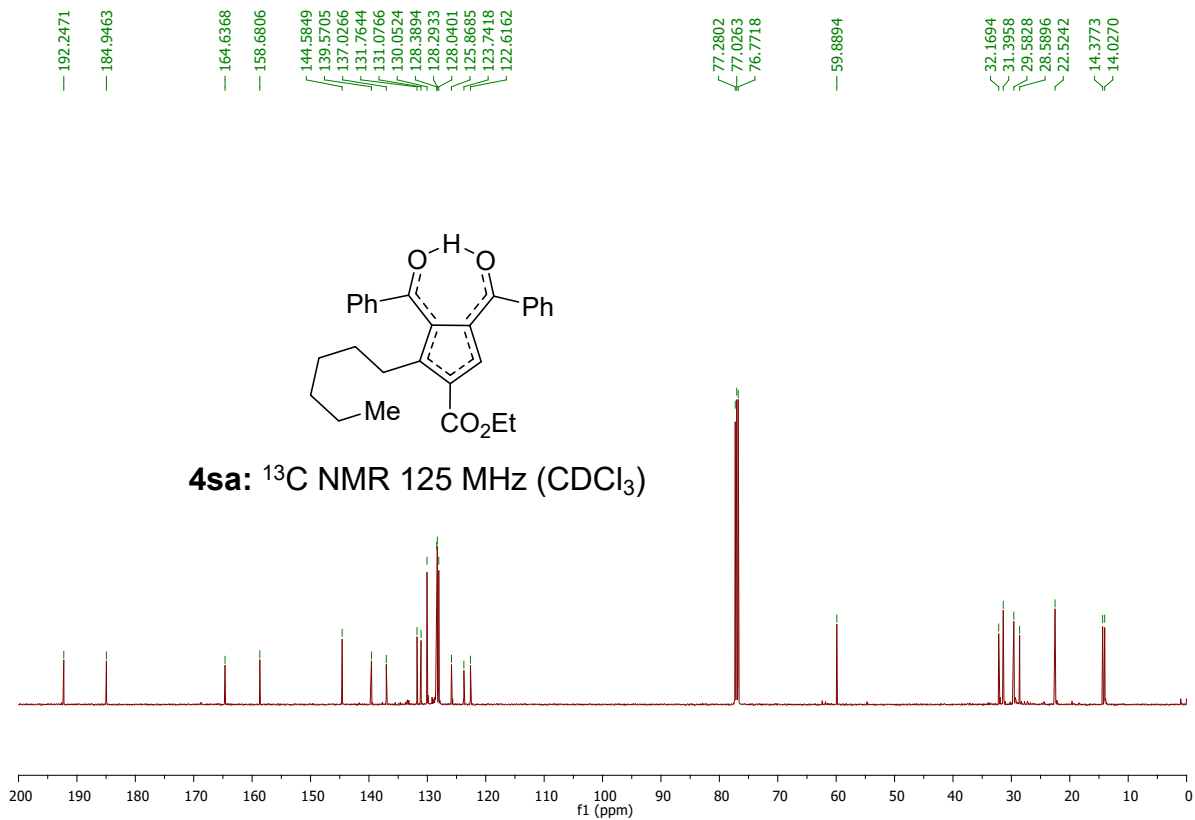
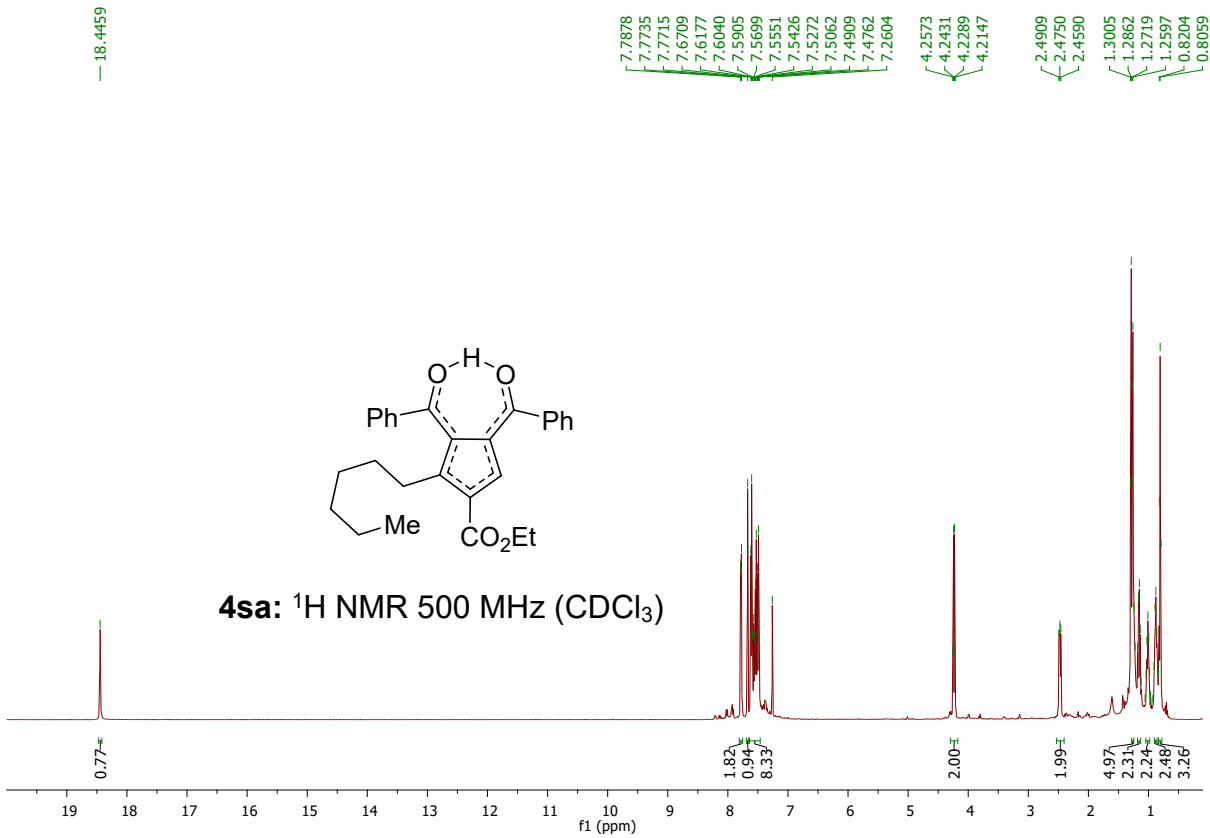


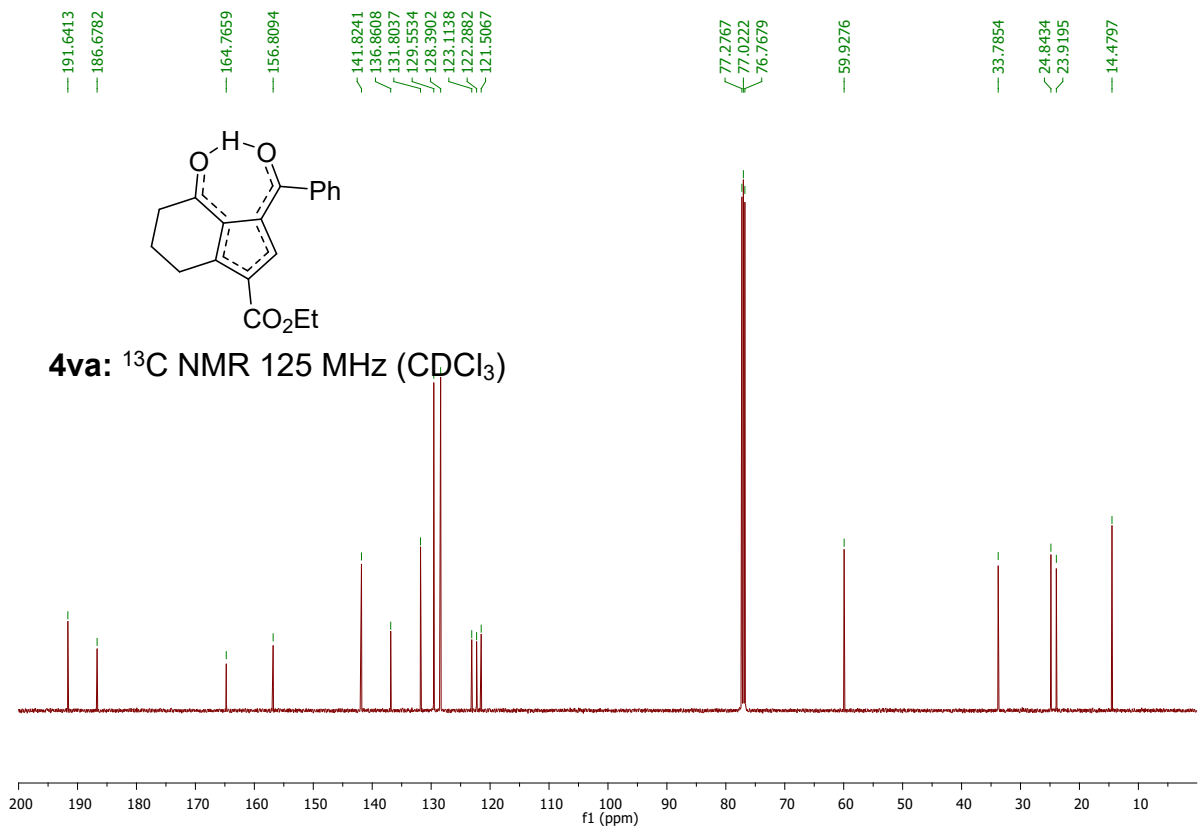
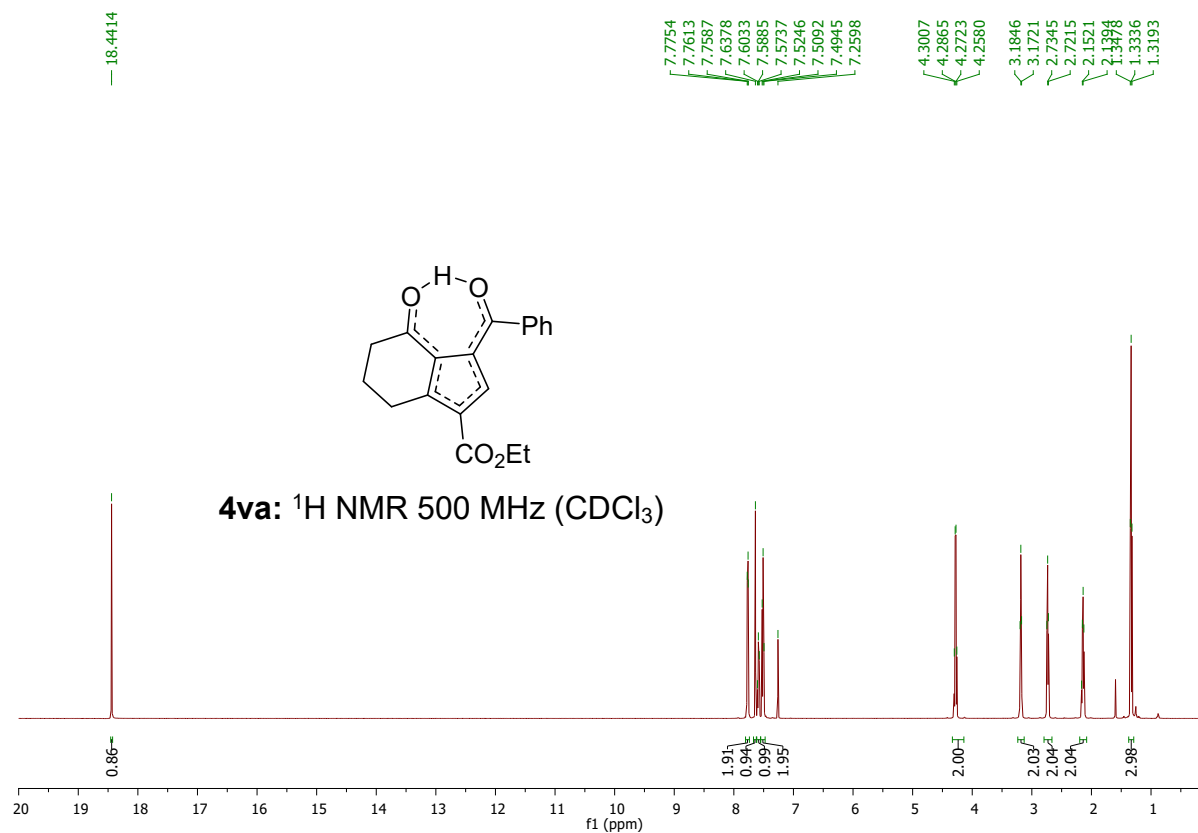


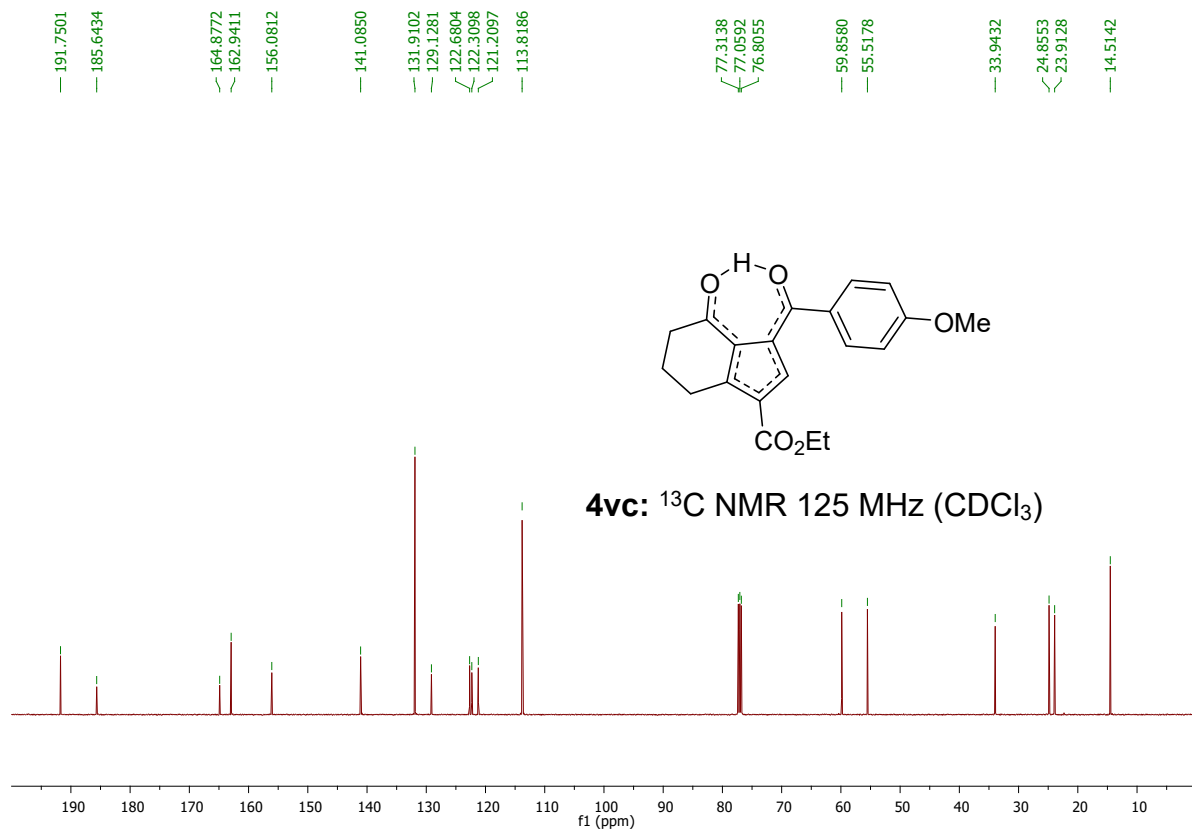
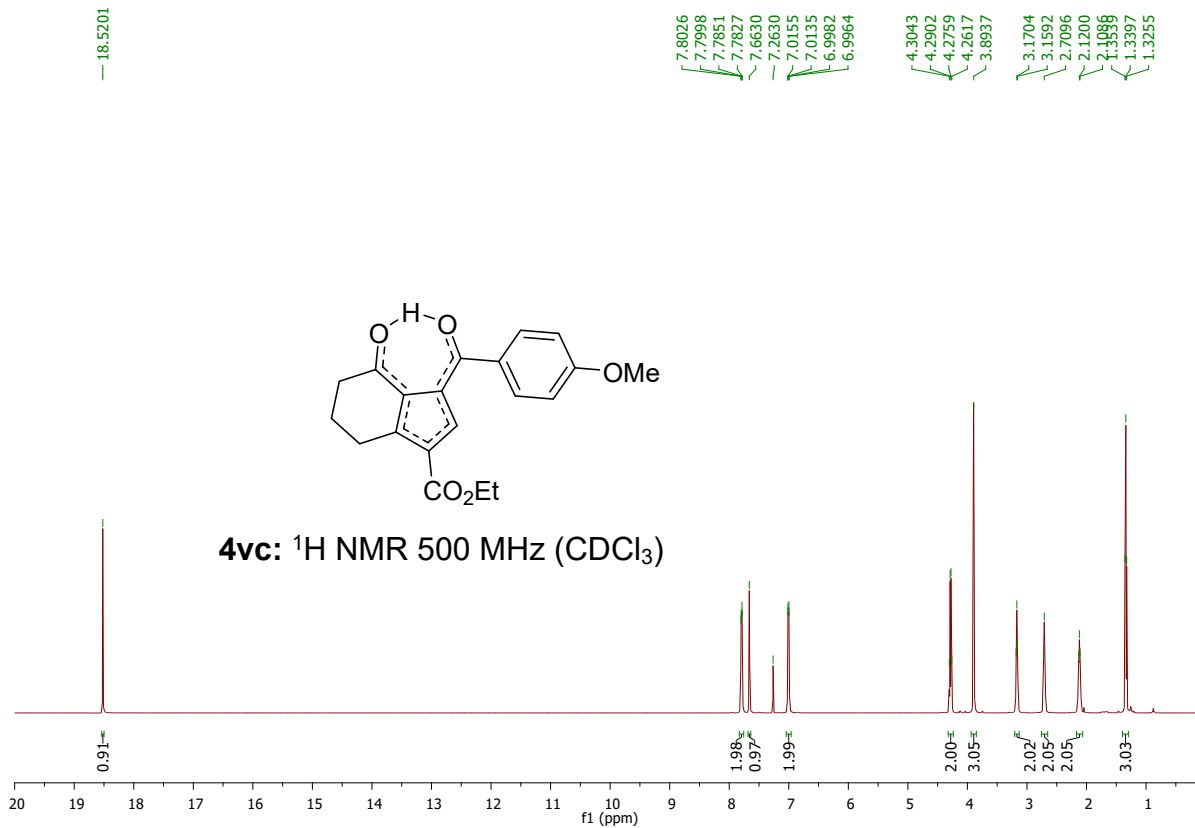








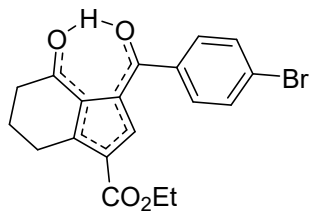




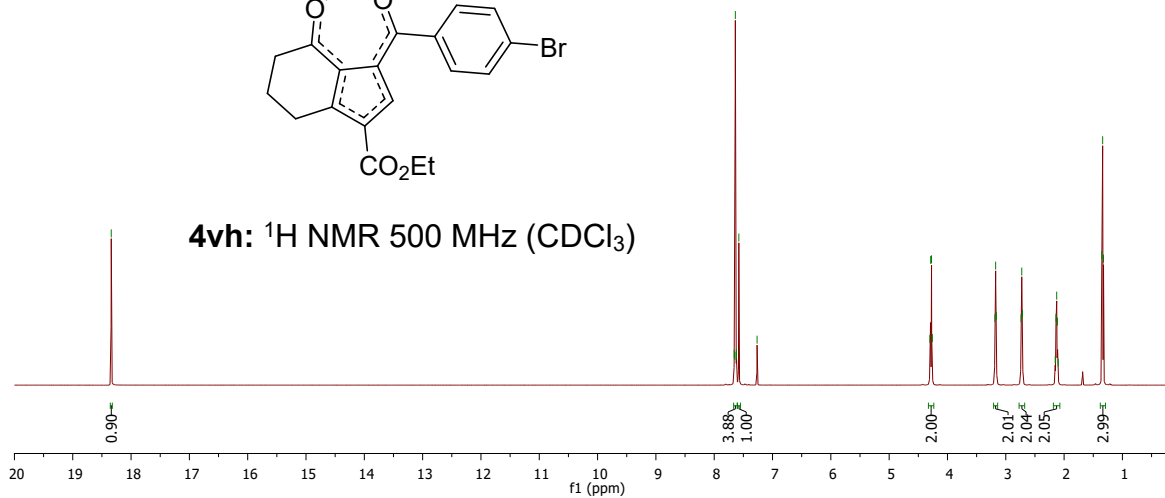
18.3397

7.6565
7.6506
7.6376
7.6243
7.6185
7.5776
7.2648

4.3019
4.2877
4.2735
4.2592
3.1739
3.1614
2.7261
2.7132
2.1396
2.1268
1.3387
1.3245



4vh: ¹H NMR 500 MHz (CDCl₃)



191.4853

185.4363

164.5794

157.1905

141.4285

135.7417

131.6711

130.9976

126.6278

123.3107

122.1552

121.4542

77.3004

77.0468

76.7928

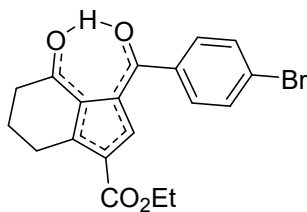
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33.6165

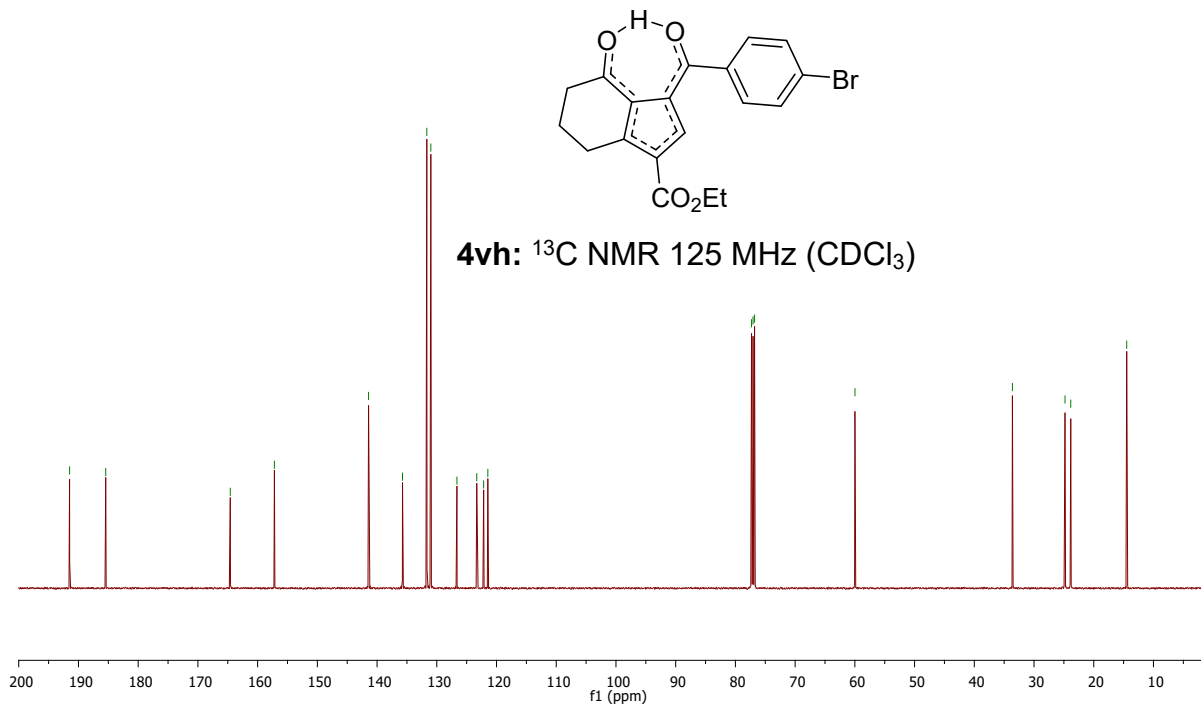
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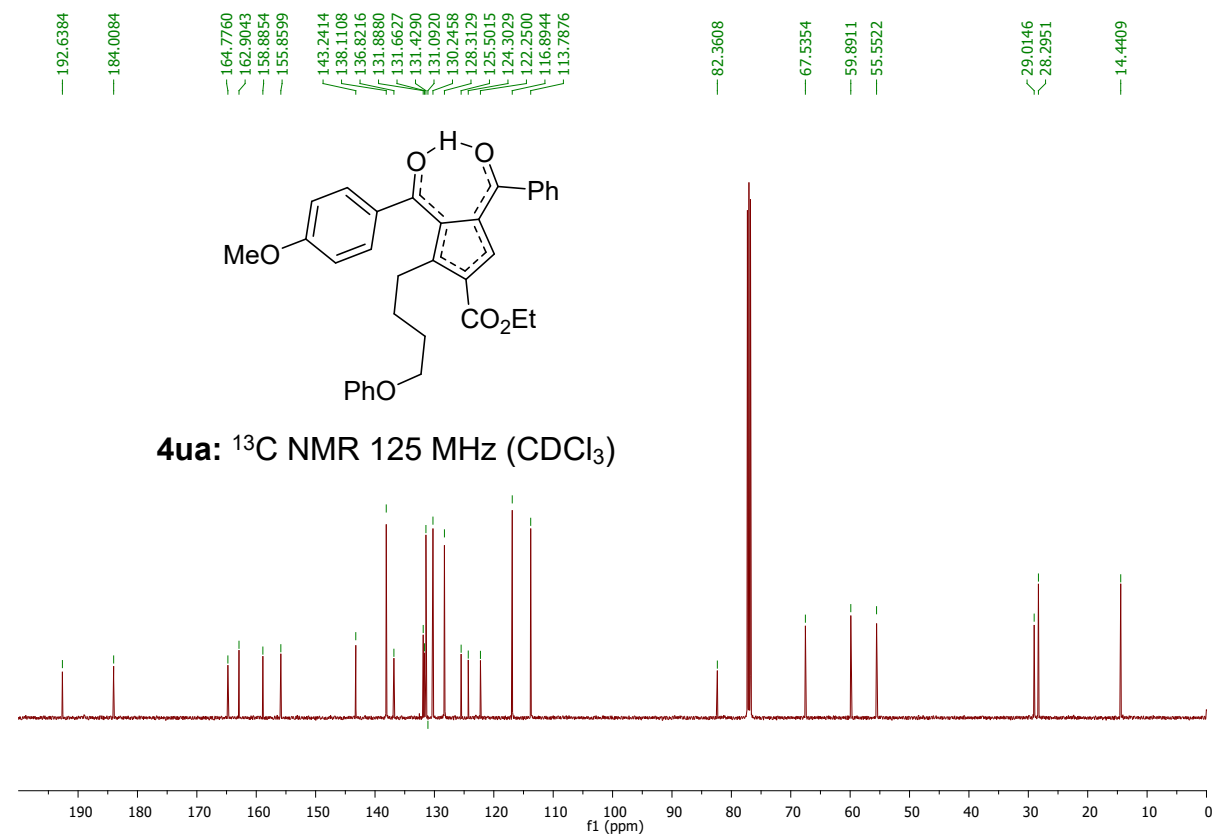
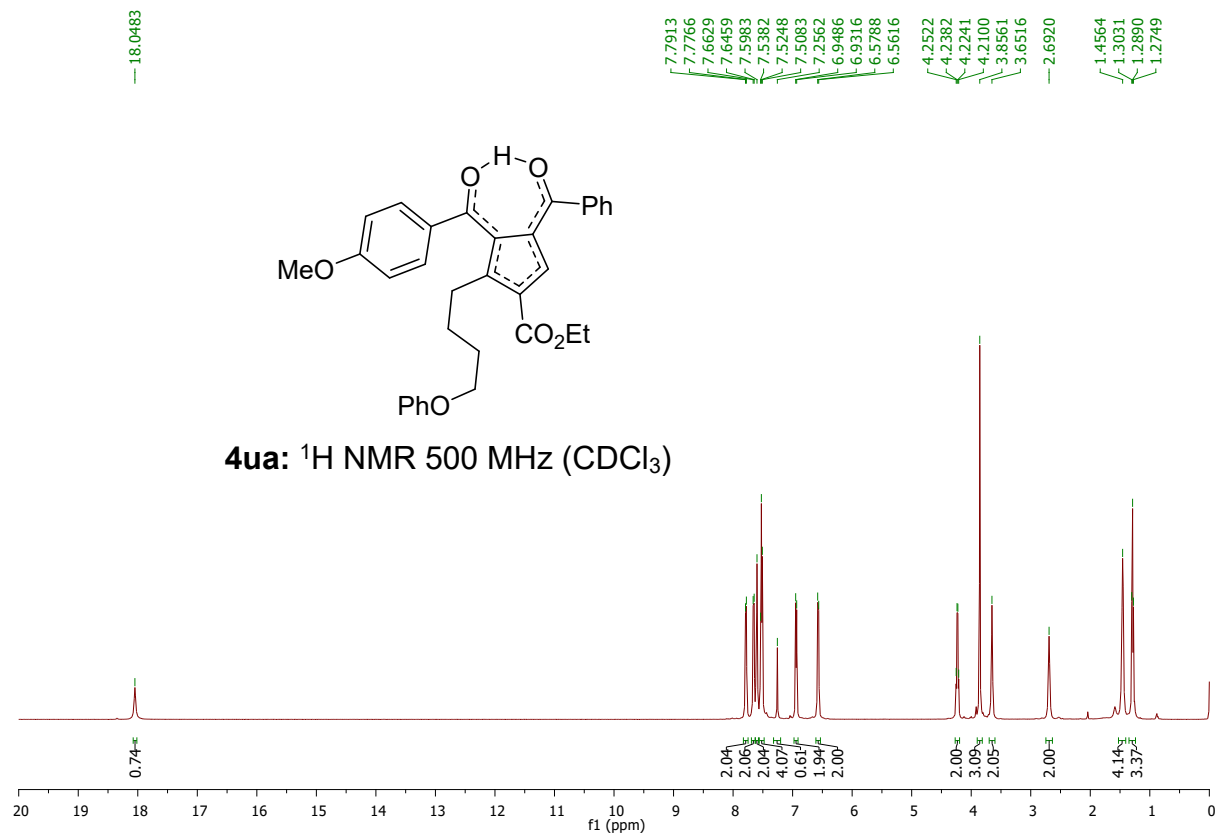
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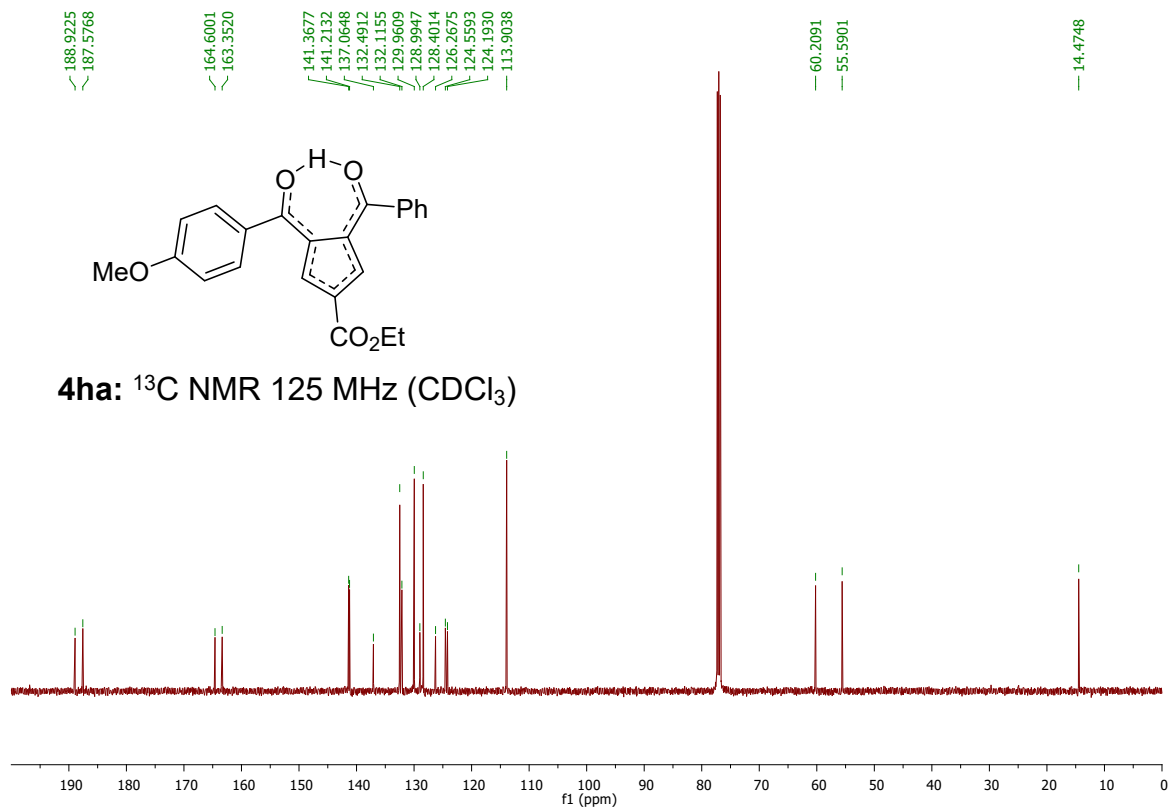
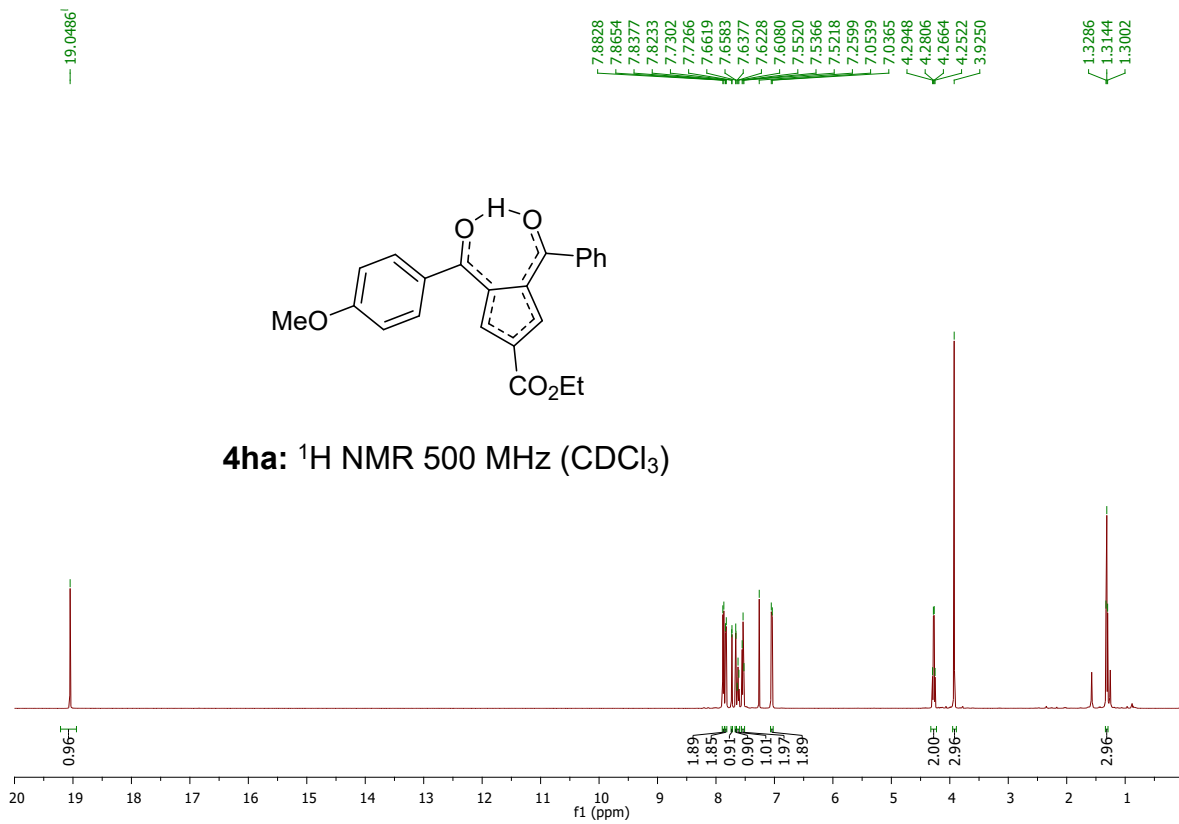
14.4788

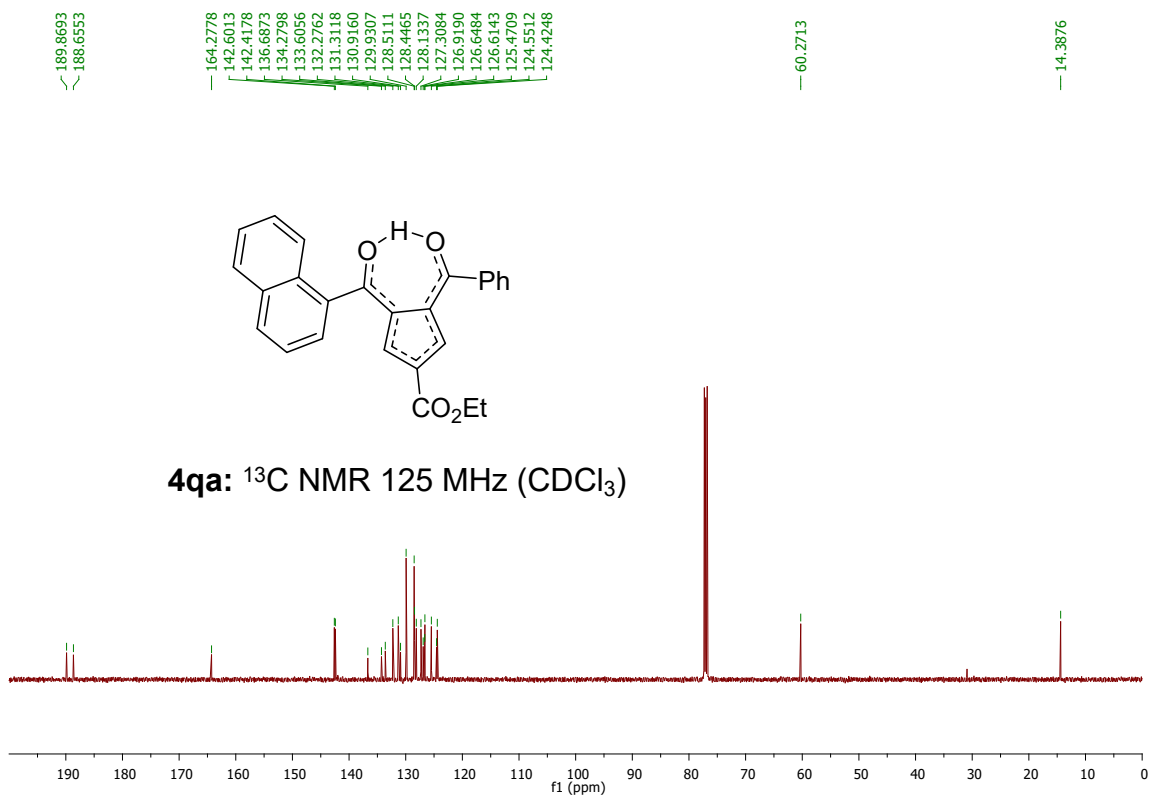
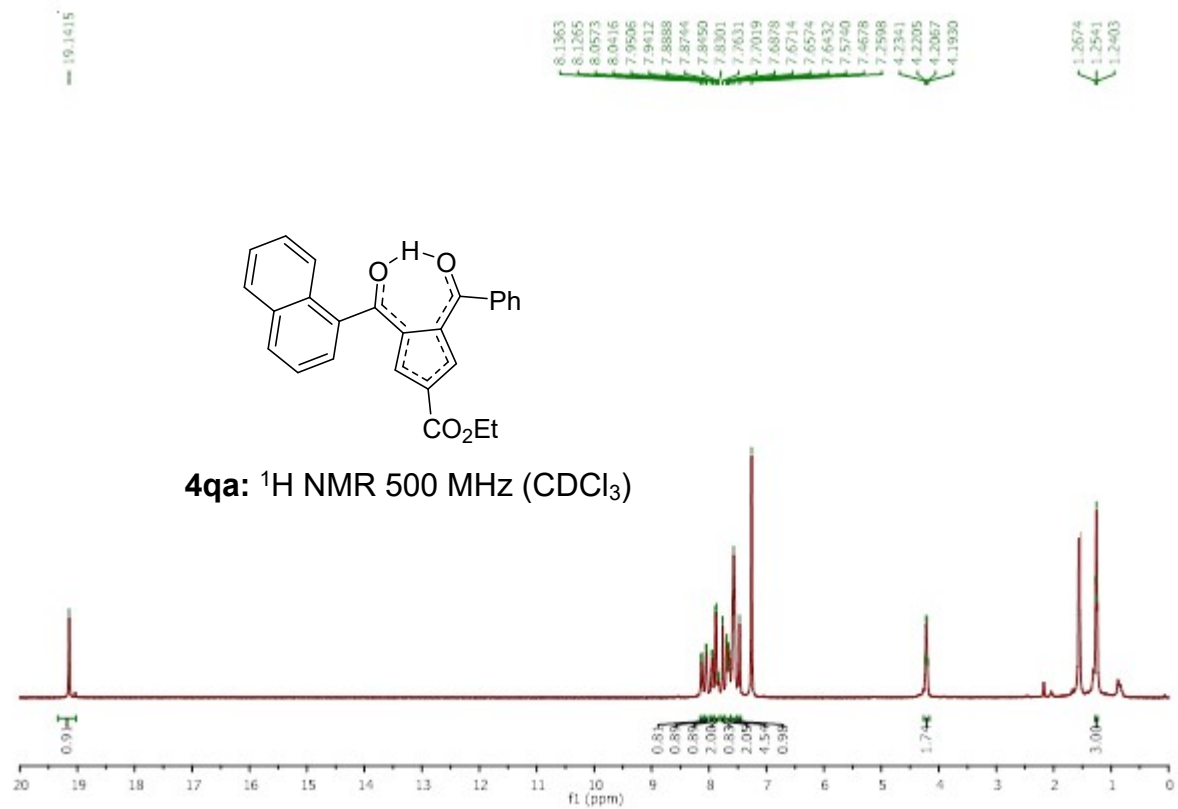


4vh: ¹³C NMR 125 MHz (CDCl₃)







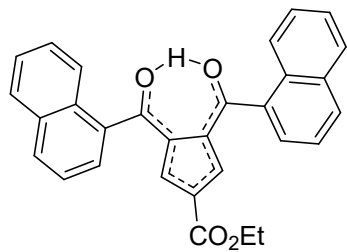


SS-M83-135

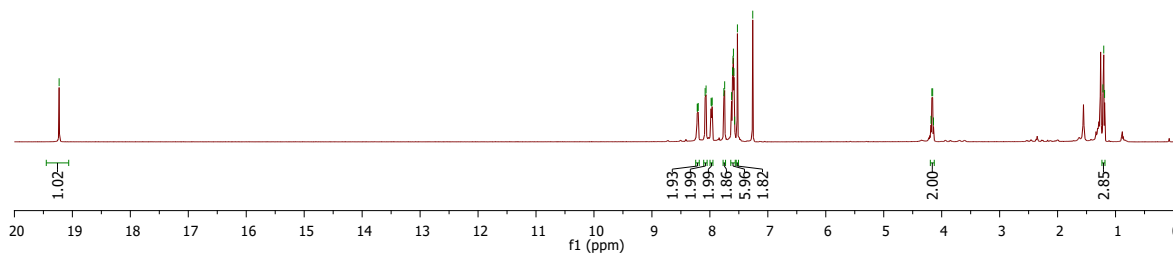
19.2288

8.2181
8.2118
8.2009
8.0819
8.0655
7.9789
7.9683
7.9608
7.7584
7.7448
7.6255
7.6097
7.6003
7.5935
7.5851
7.5727
7.5246
7.2602
4.1839
4.1697
4.1556
4.1415

1.2178
1.2036
1.1895



4qi: ¹H NMR 500 MHz (CDCl₃)



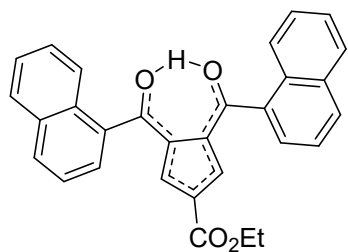
189.8141

164.1222

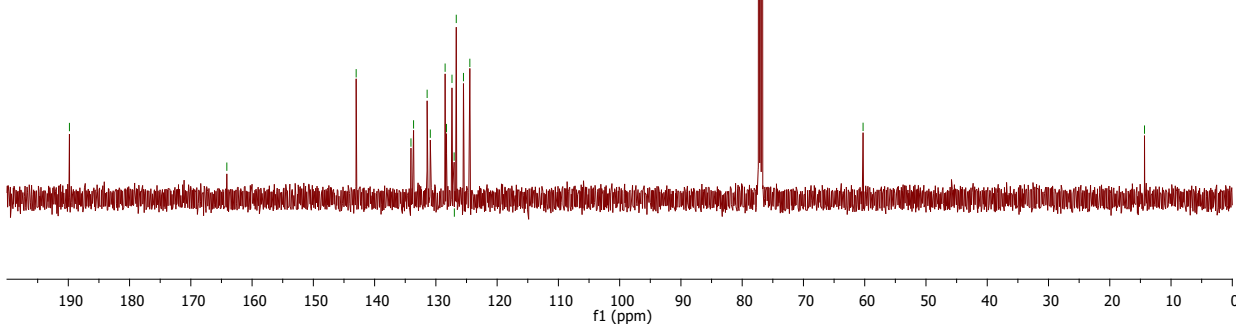
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134.0670
133.6420
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126.6723
125.4952
124.4567

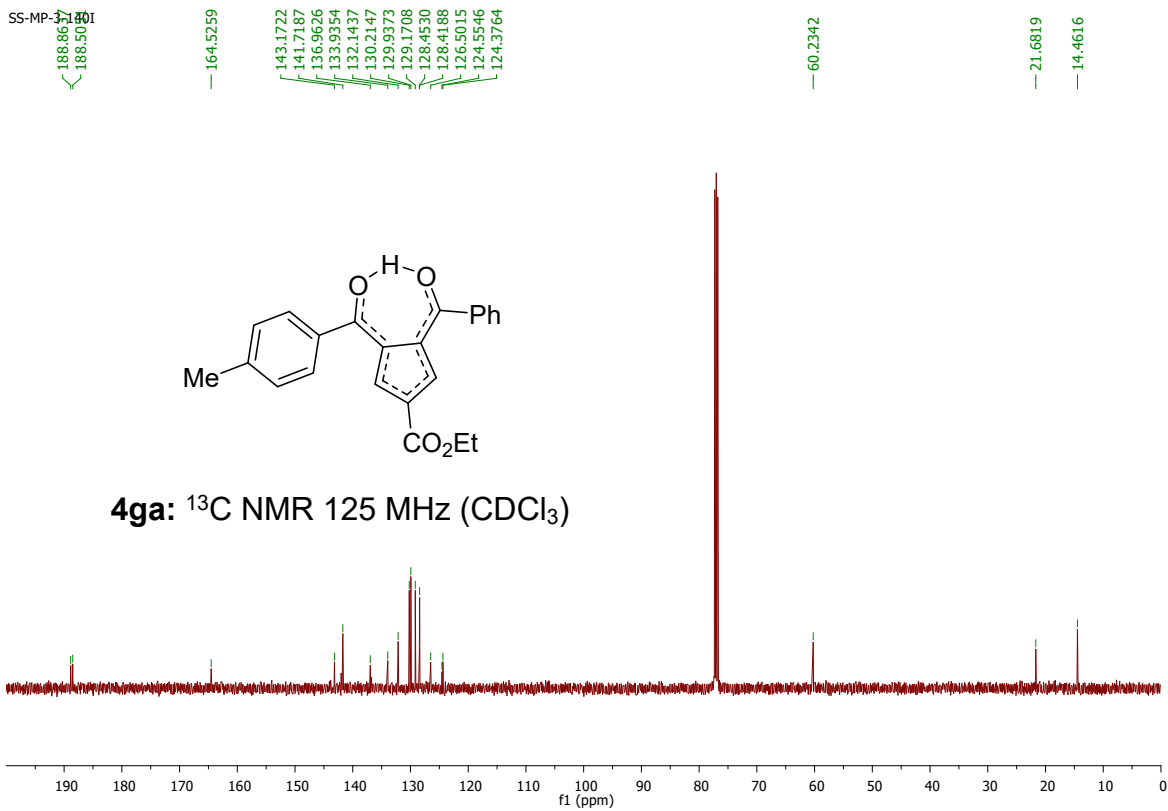
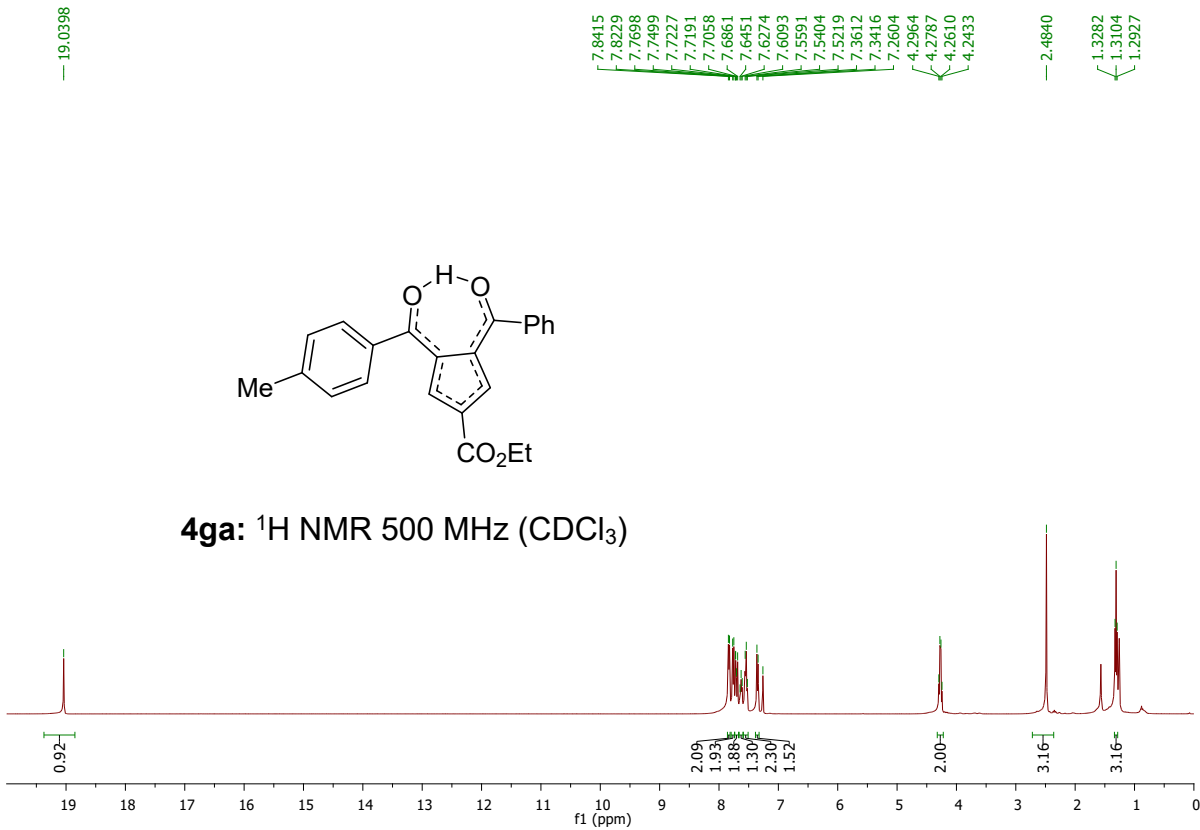
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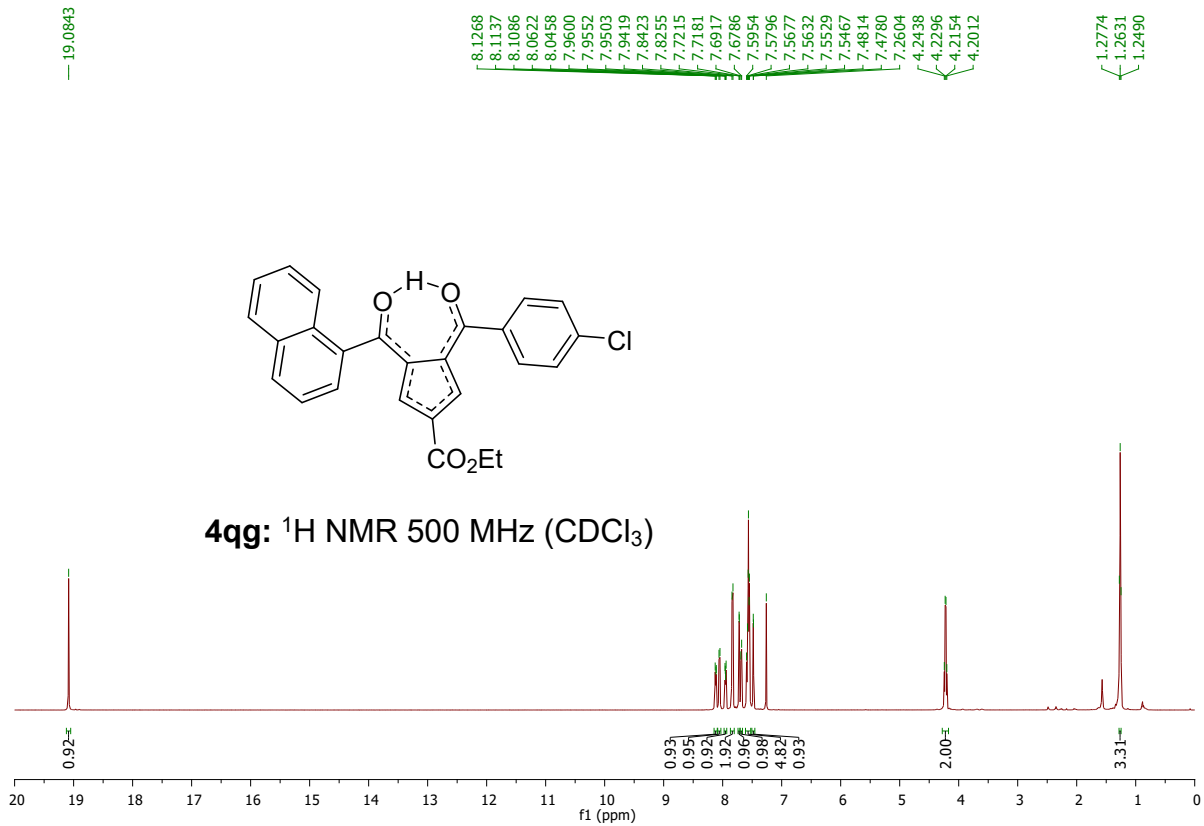
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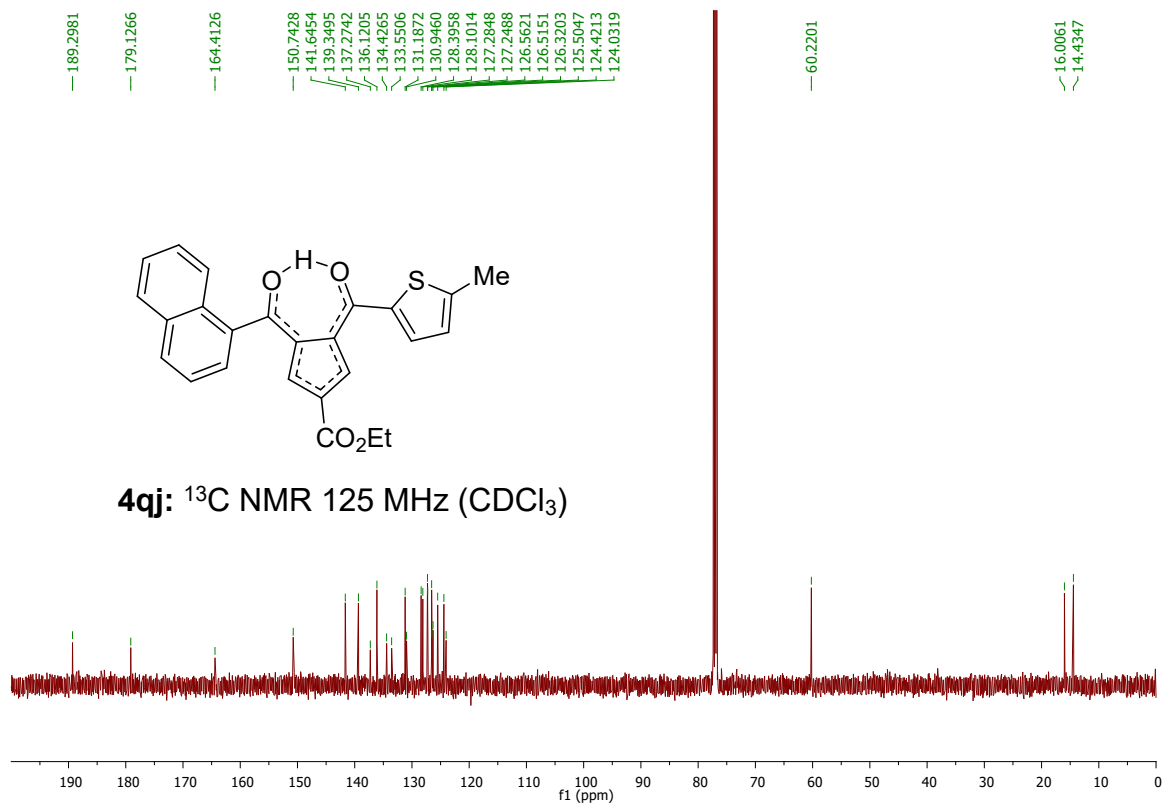
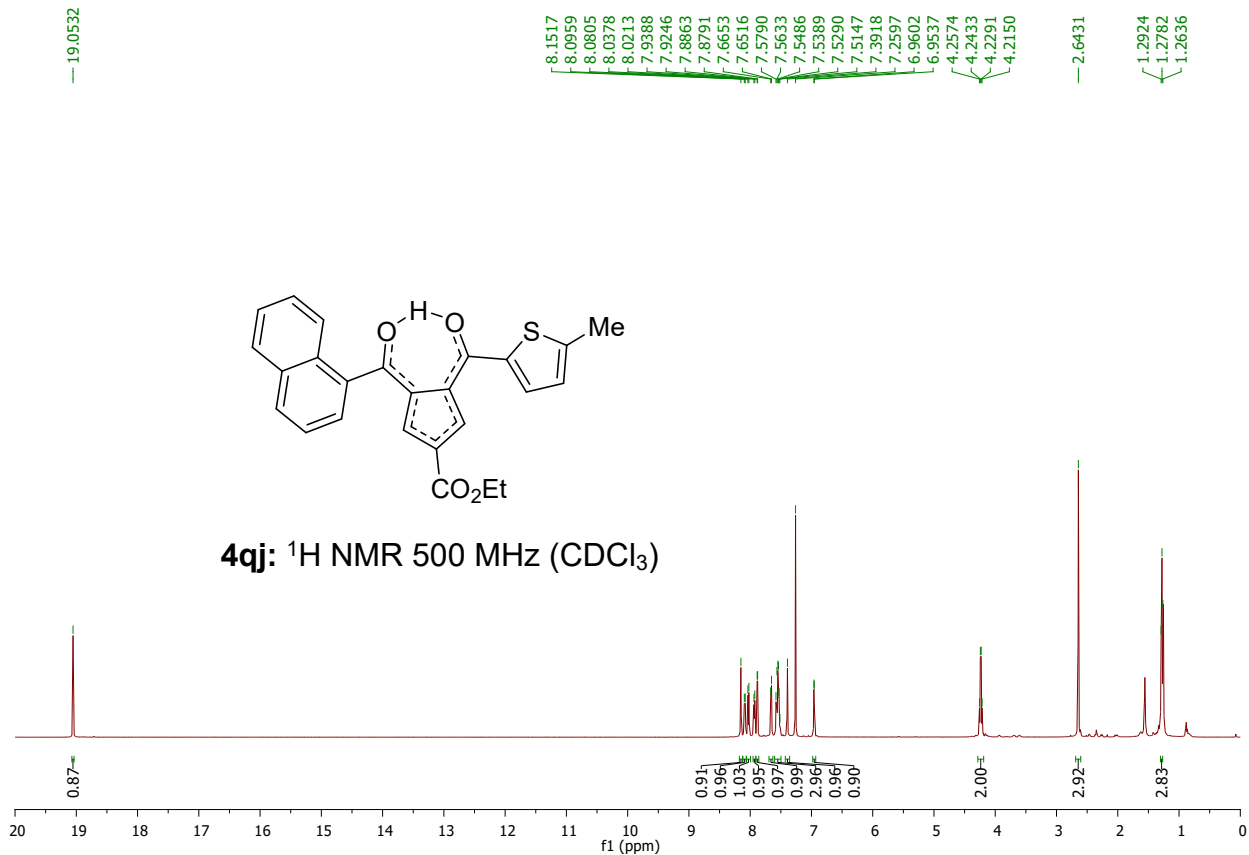


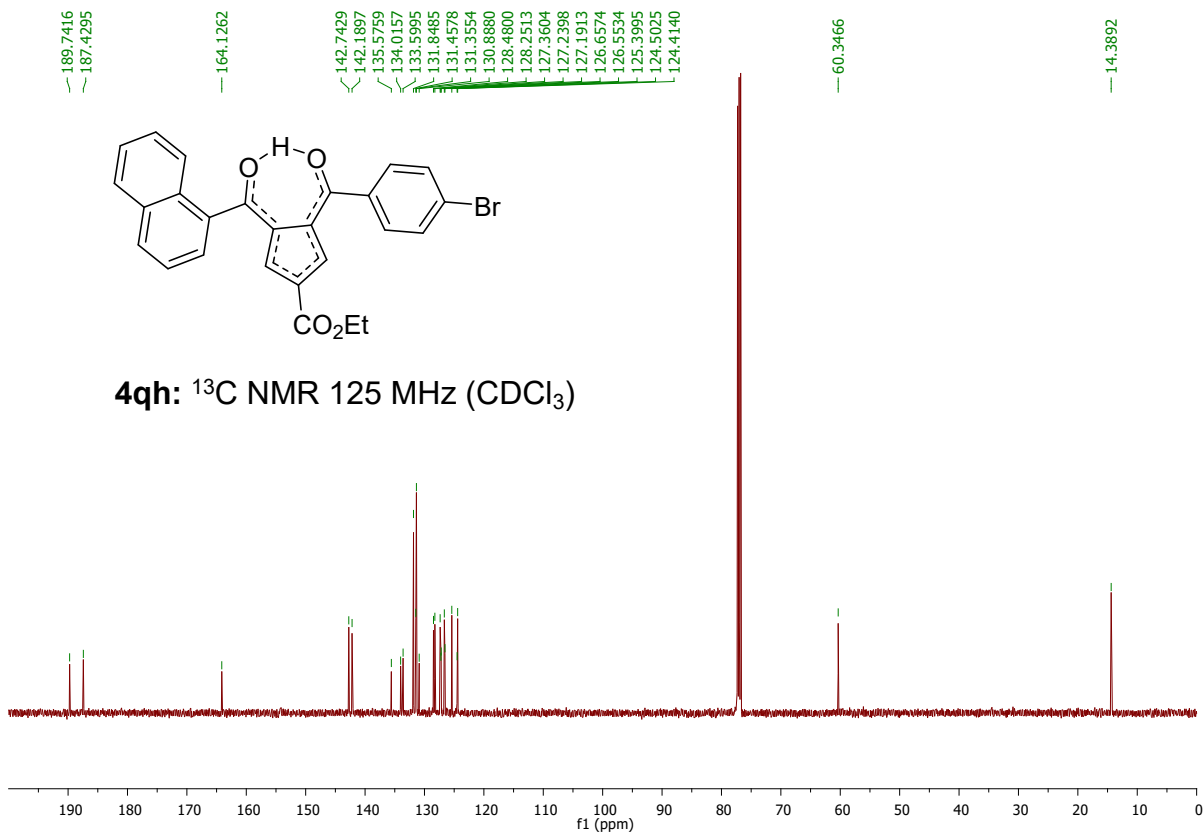
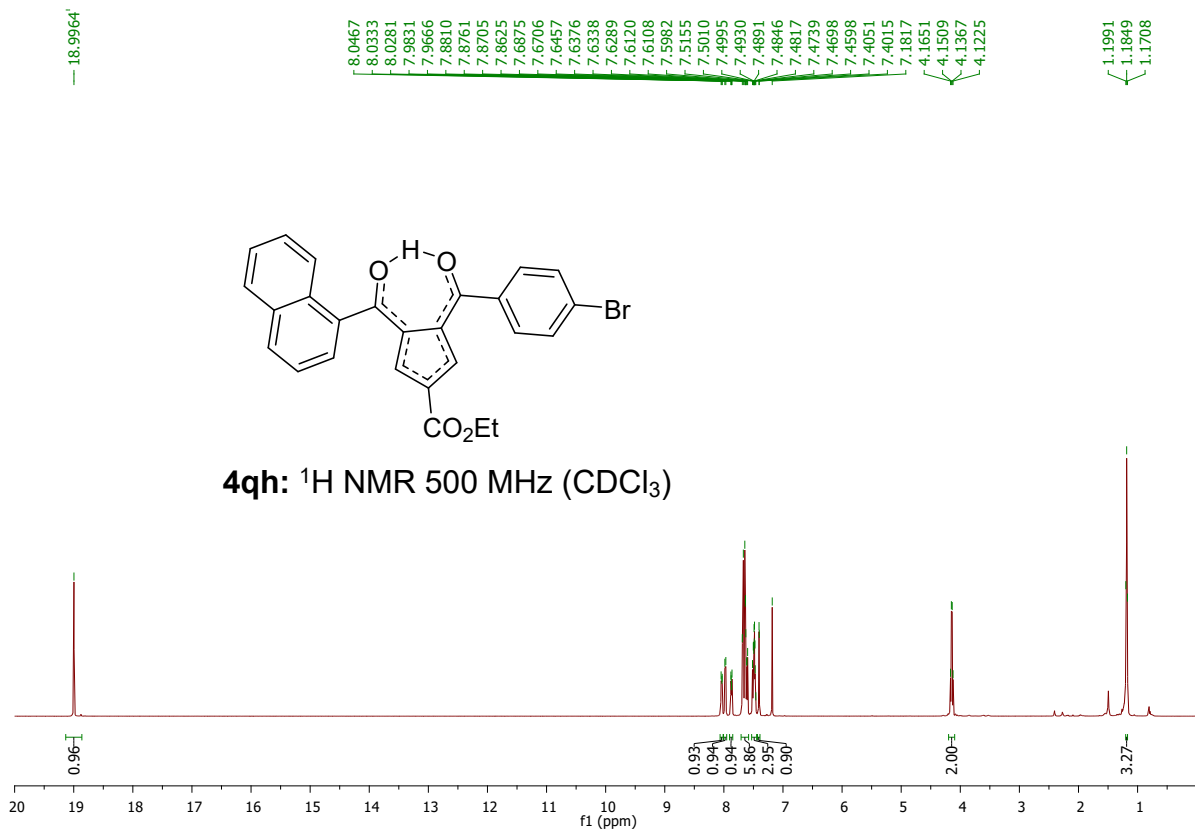
4qi: ¹³C NMR 125 MHz (CDCl₃)

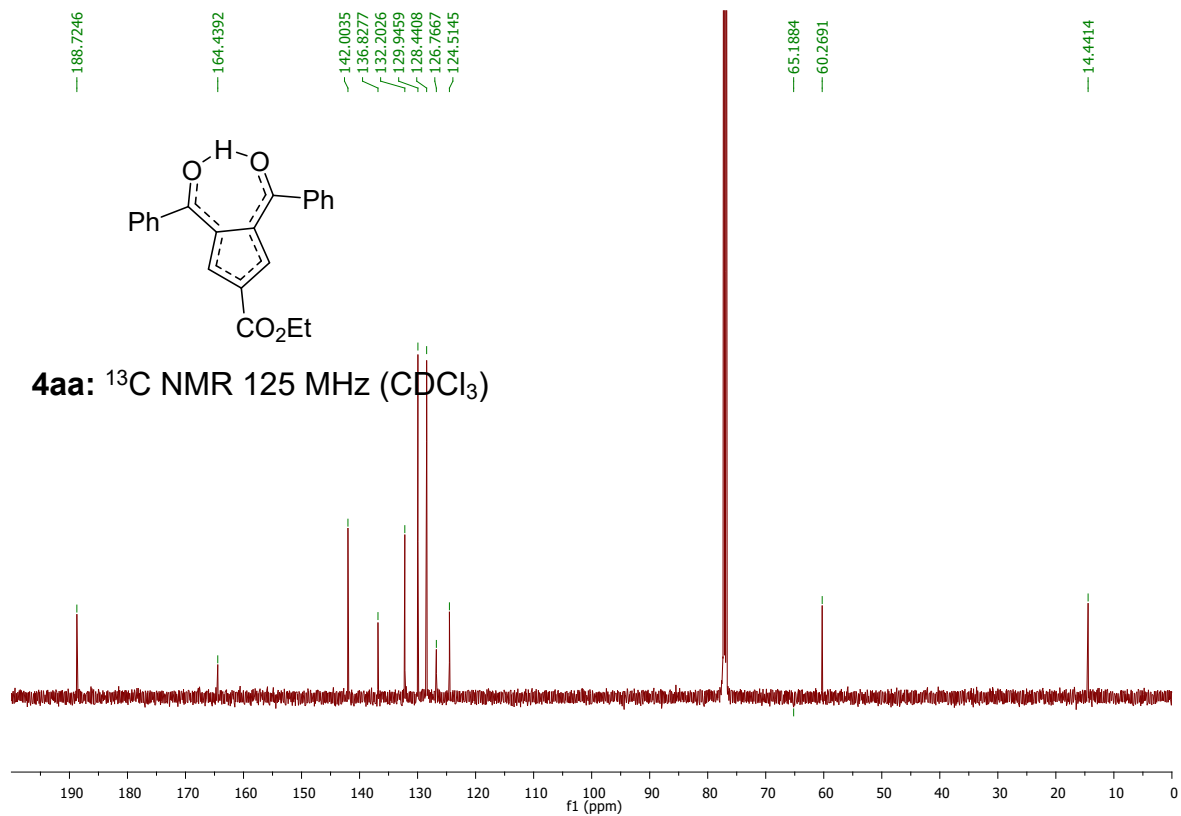
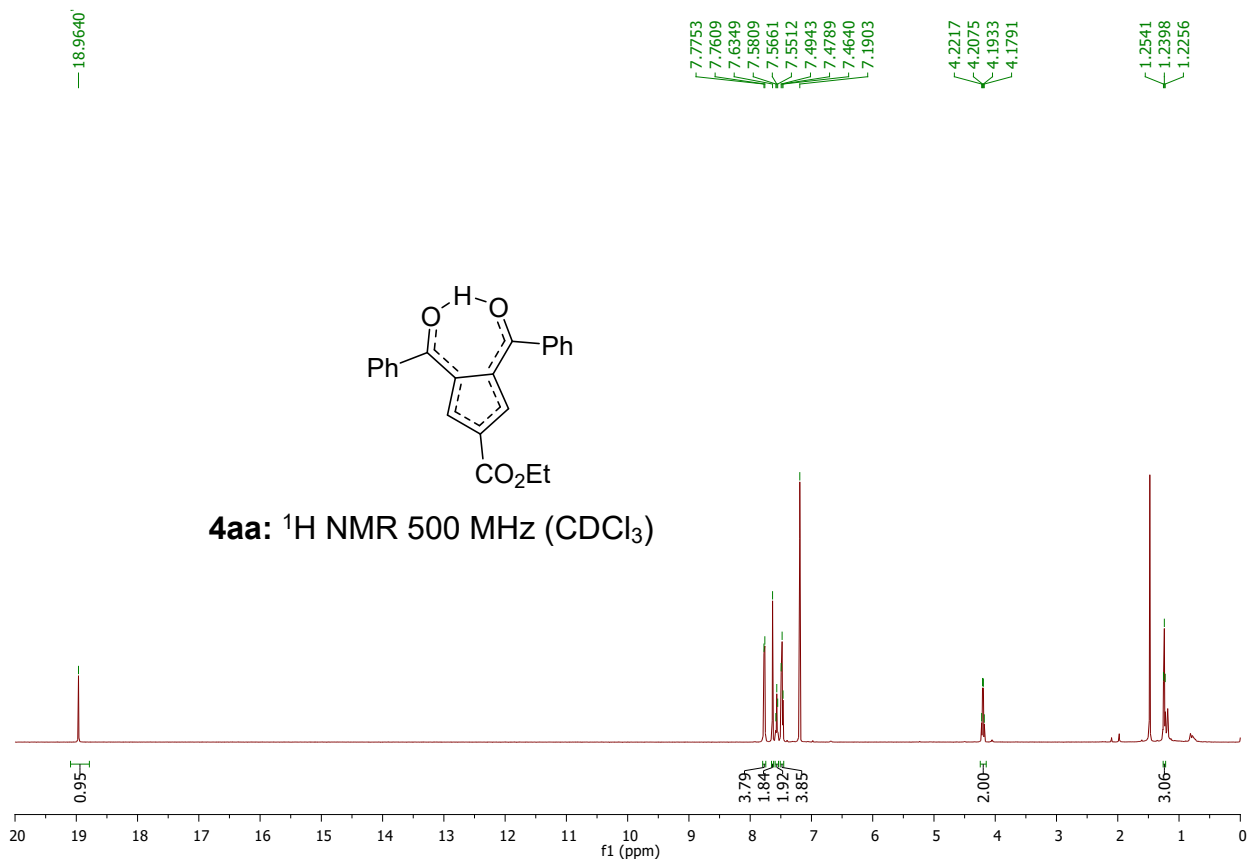








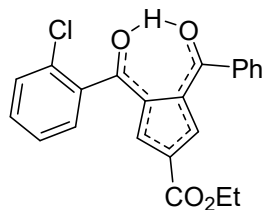




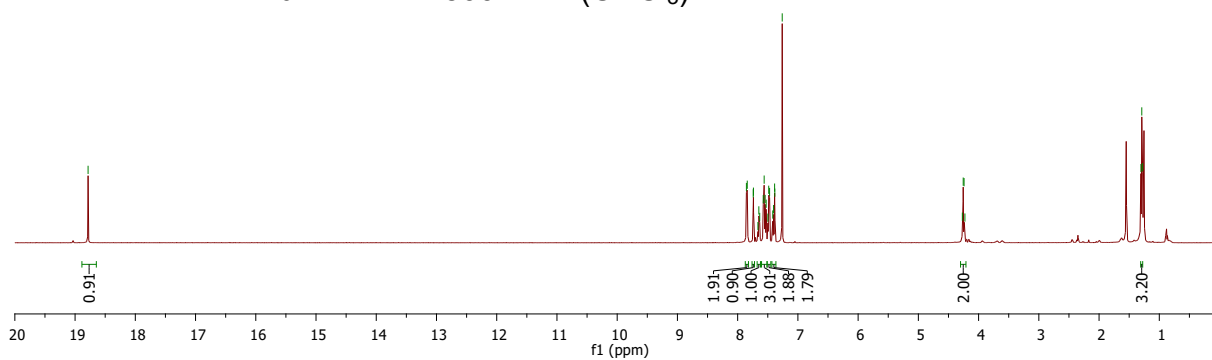
18.7841

7.8549
7.8405
7.7412
7.7380
7.6634
7.6483
7.6337
7.5753
7.5600
7.5436
7.5268
7.4978
7.4843
7.4698
7.4174
7.4037
7.3865
7.3831
7.2602
4.2697
4.2555
4.2413
4.2271

1.3050
1.2908
1.2765



4na: ¹H NMR 500 MHz (CDCl₃)



SS-MP-310

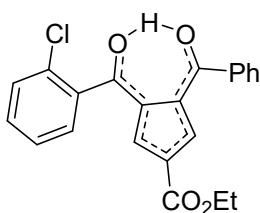
187.7340
187.6169

164.2000

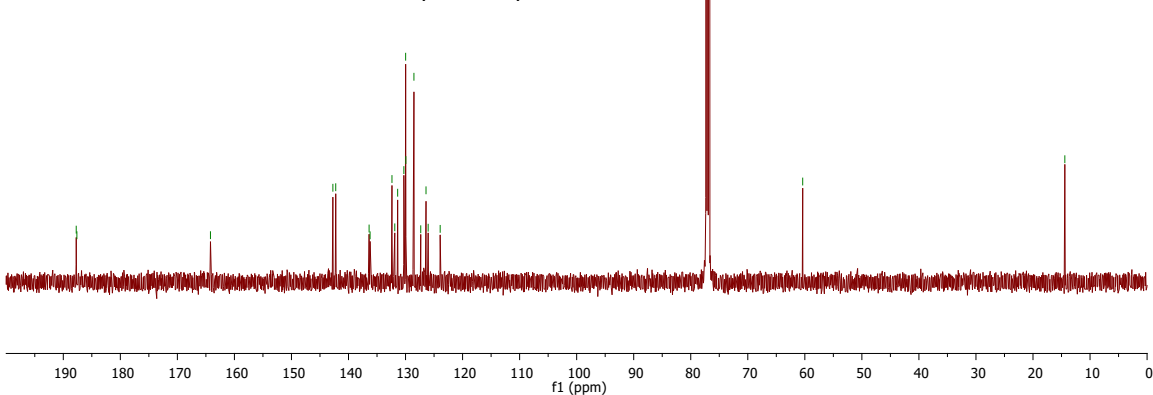
142.7381
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136.3894
136.2170
132.3799
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130.2953
129.9827
129.9502
128.5300
127.3356
126.4112
126.0351
123.9287

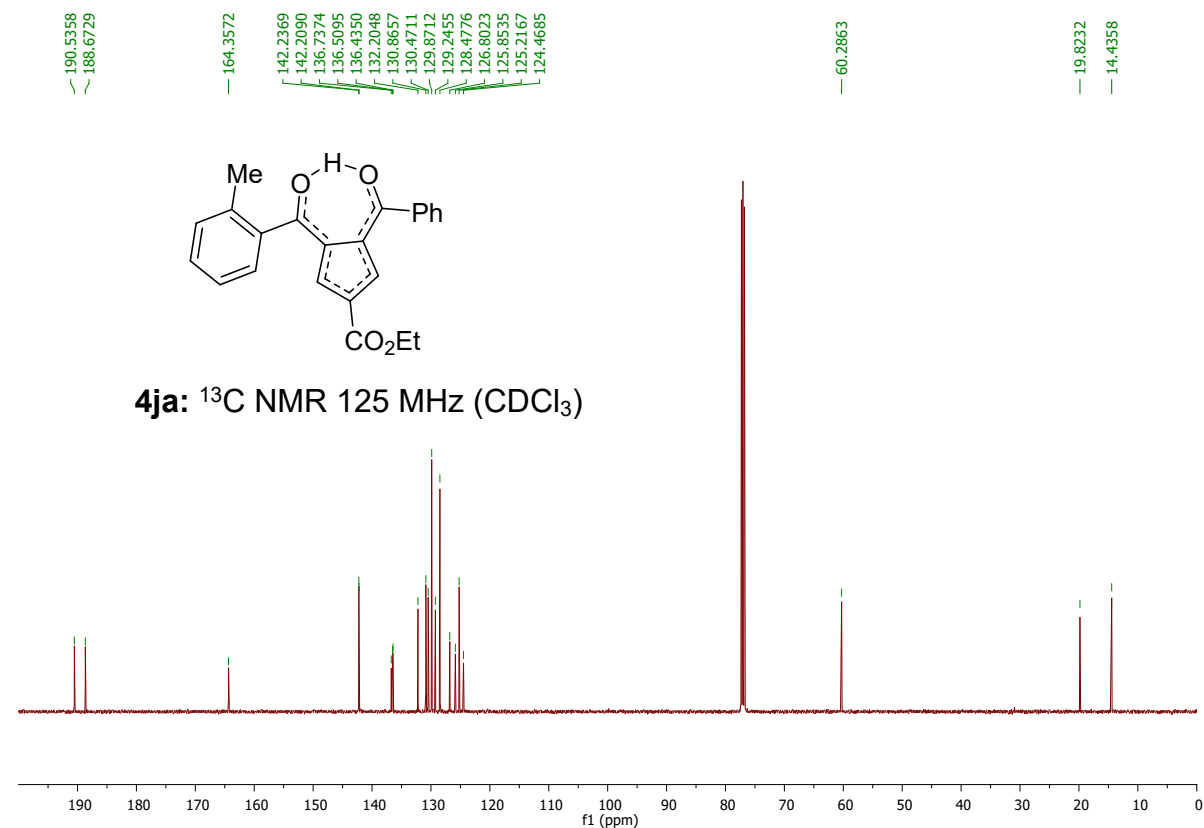
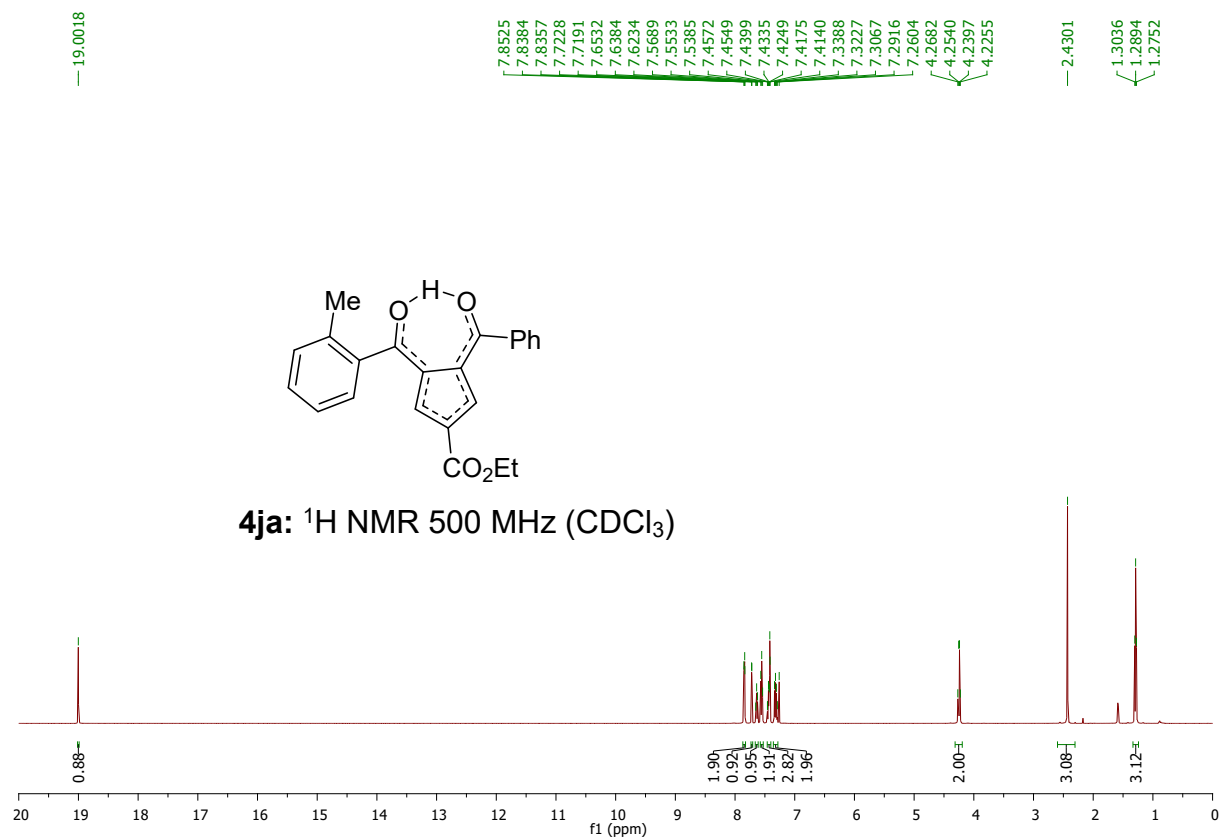
60.3734

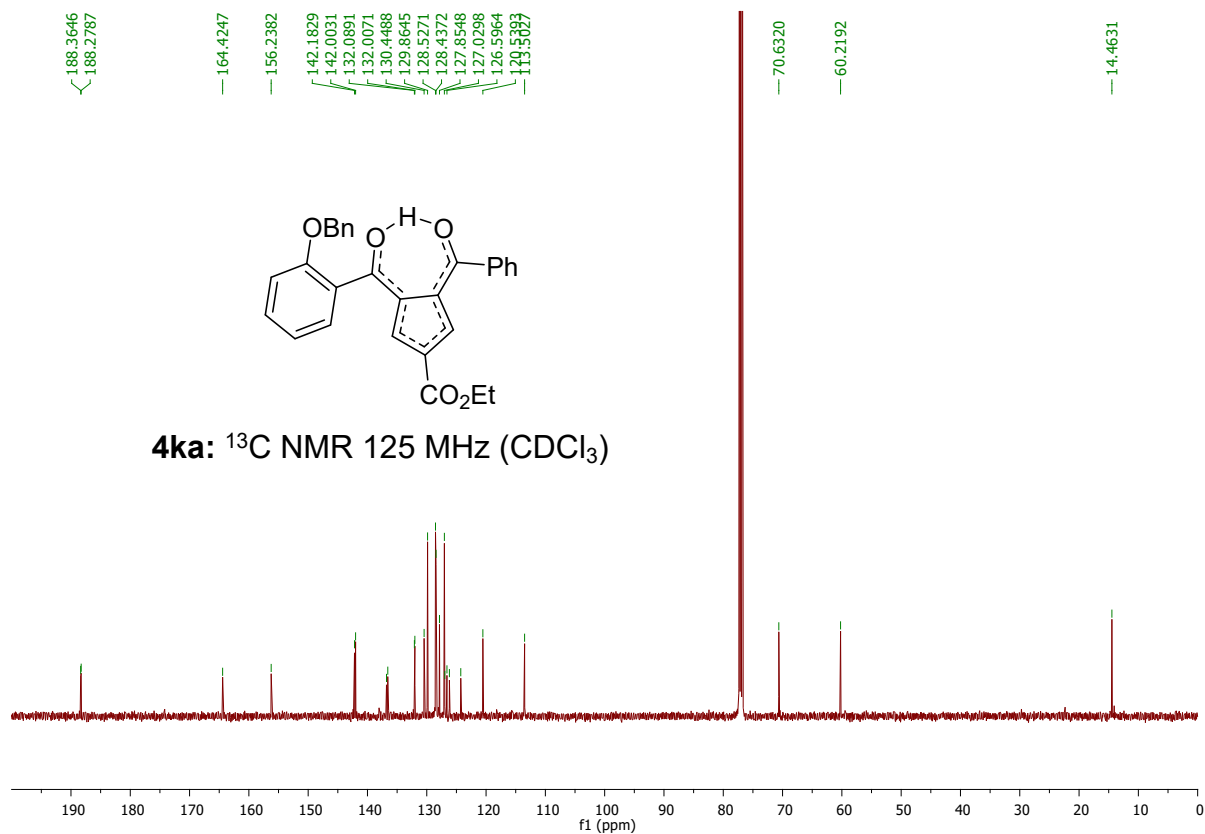
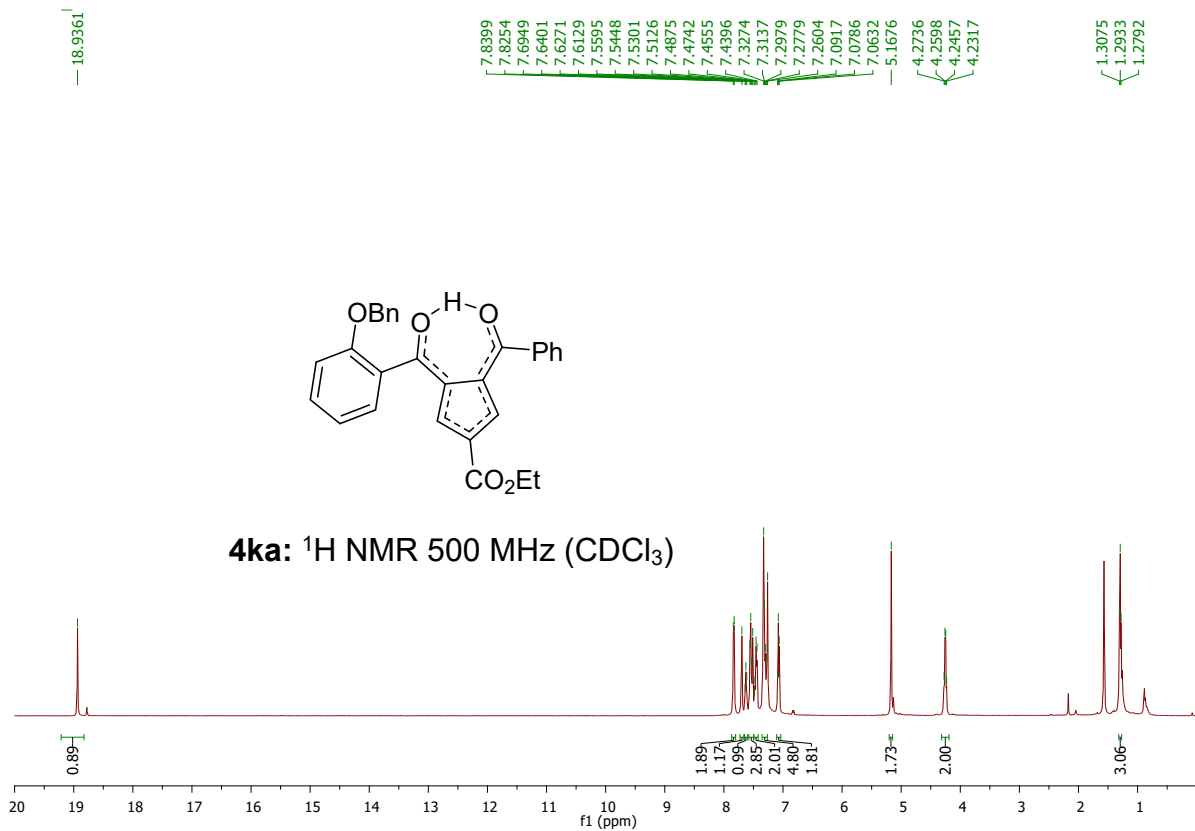
14.4186



4na: ¹³C NMR 125 MHz (CDCl₃)

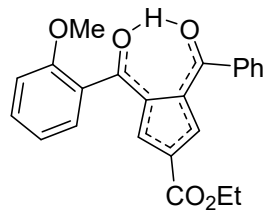




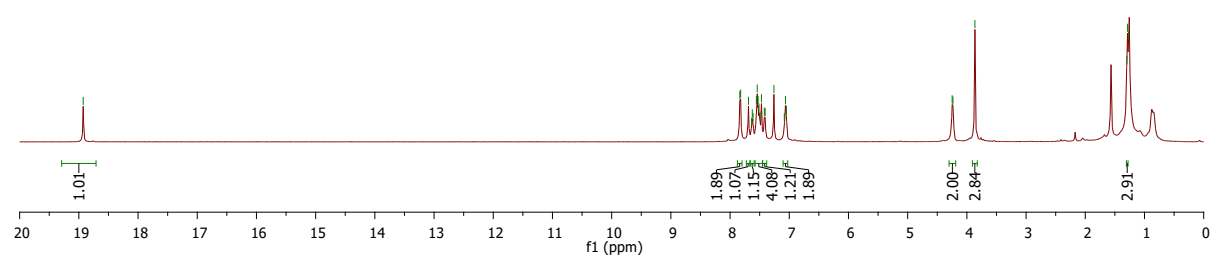


18.9264

7.8353
7.8215
7.6892
7.6364
7.6244
7.6110
7.5553
7.5414
7.5269
7.5107
7.4946
7.4697
7.4213
7.4078
7.2595
7.0837
7.0643
7.0482
4.2487
4.2352
3.8640
1.2976
1.2856
1.2696



4ma: ¹H NMR 500 MHz (CDCl₃)

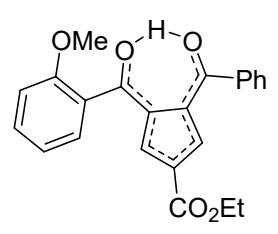


188.5066
188.2210

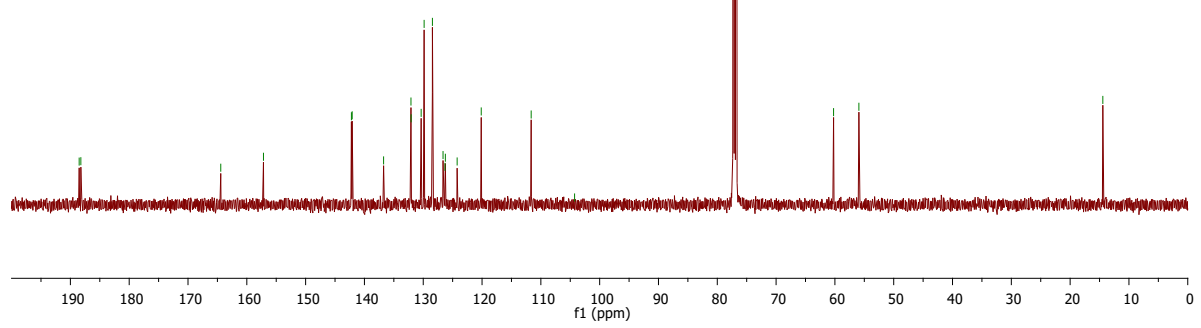
164.4301
157.1678
142.2146
142.0826
136.7413
132.0874
132.0618
130.3546
129.8491
128.4397
126.6337
126.3065
126.2382
124.2346
120.1385
111.6458
104.2653

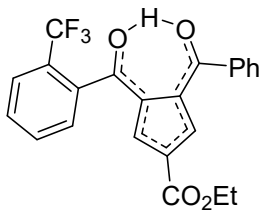
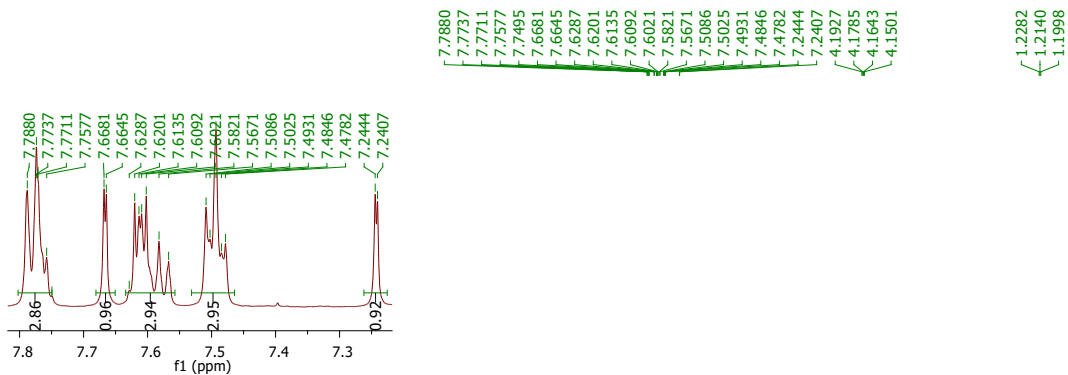
60.2260
55.9217

14.4404

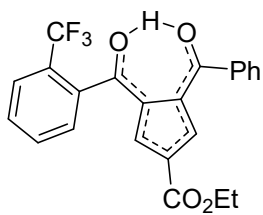
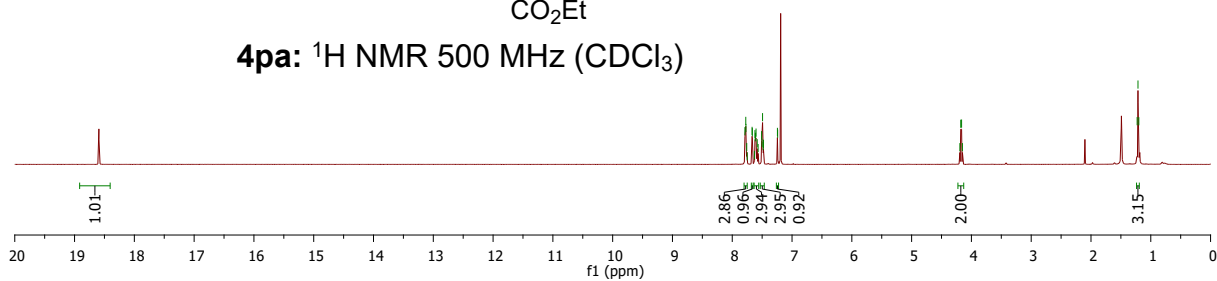


4ma: ¹³C NMR 125 MHz (CDCl₃)

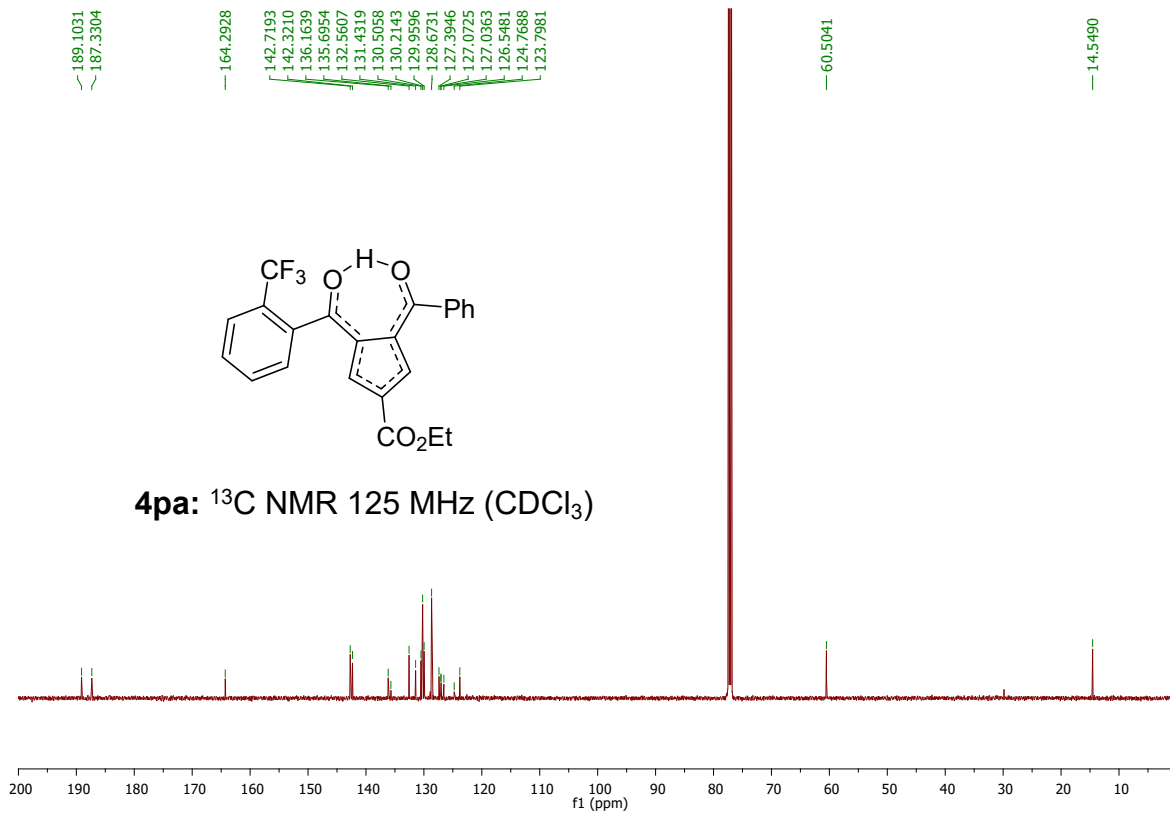


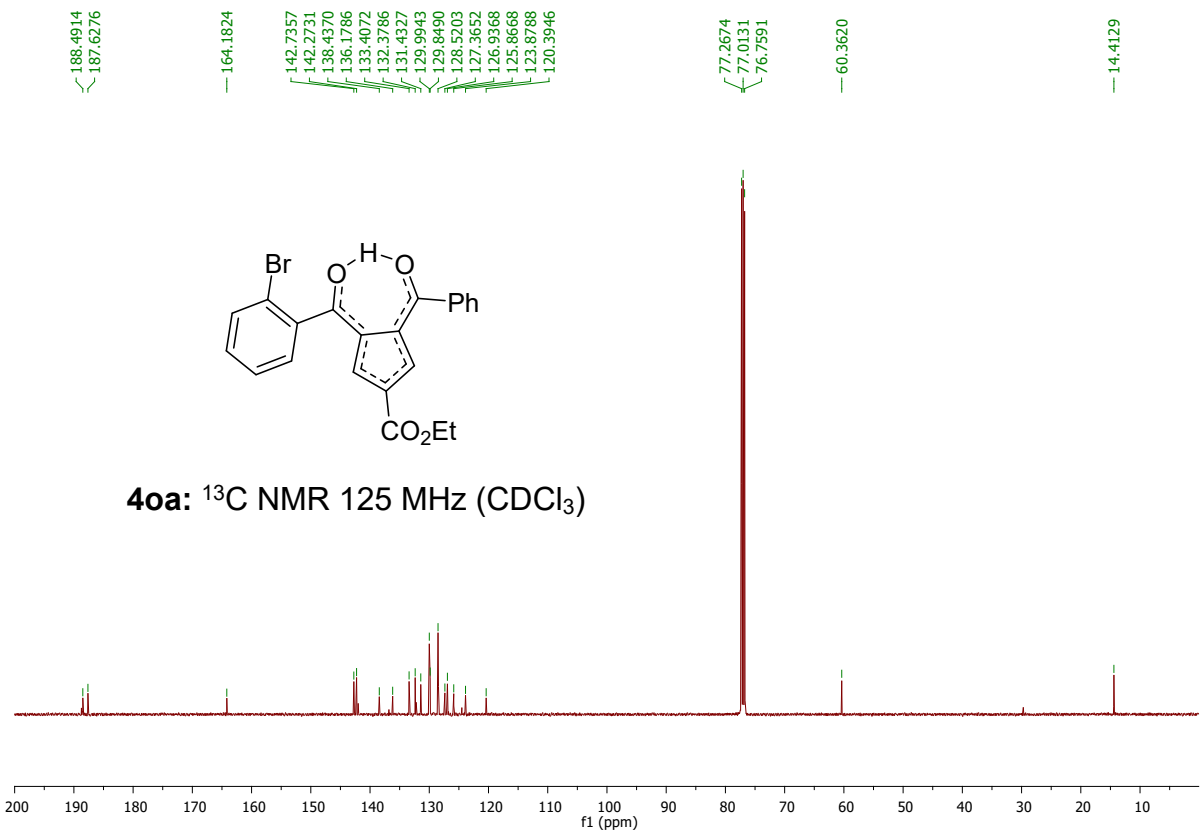
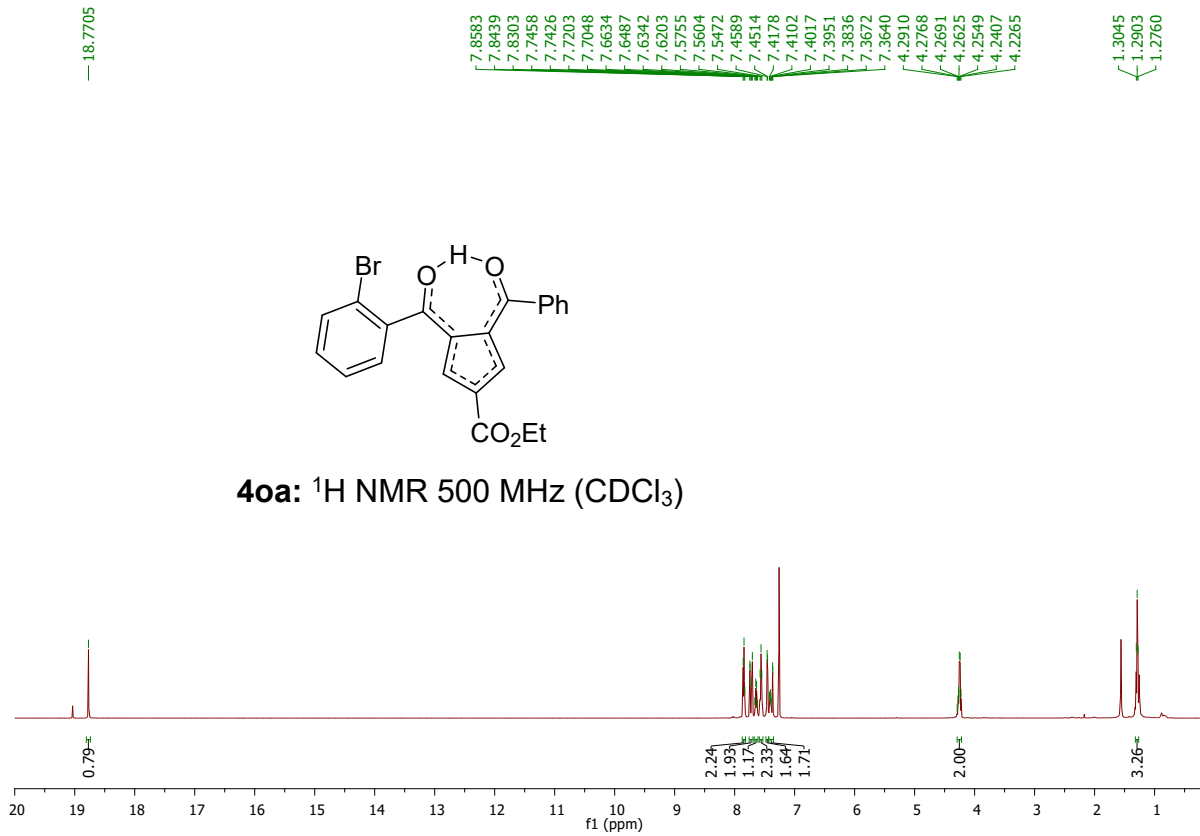


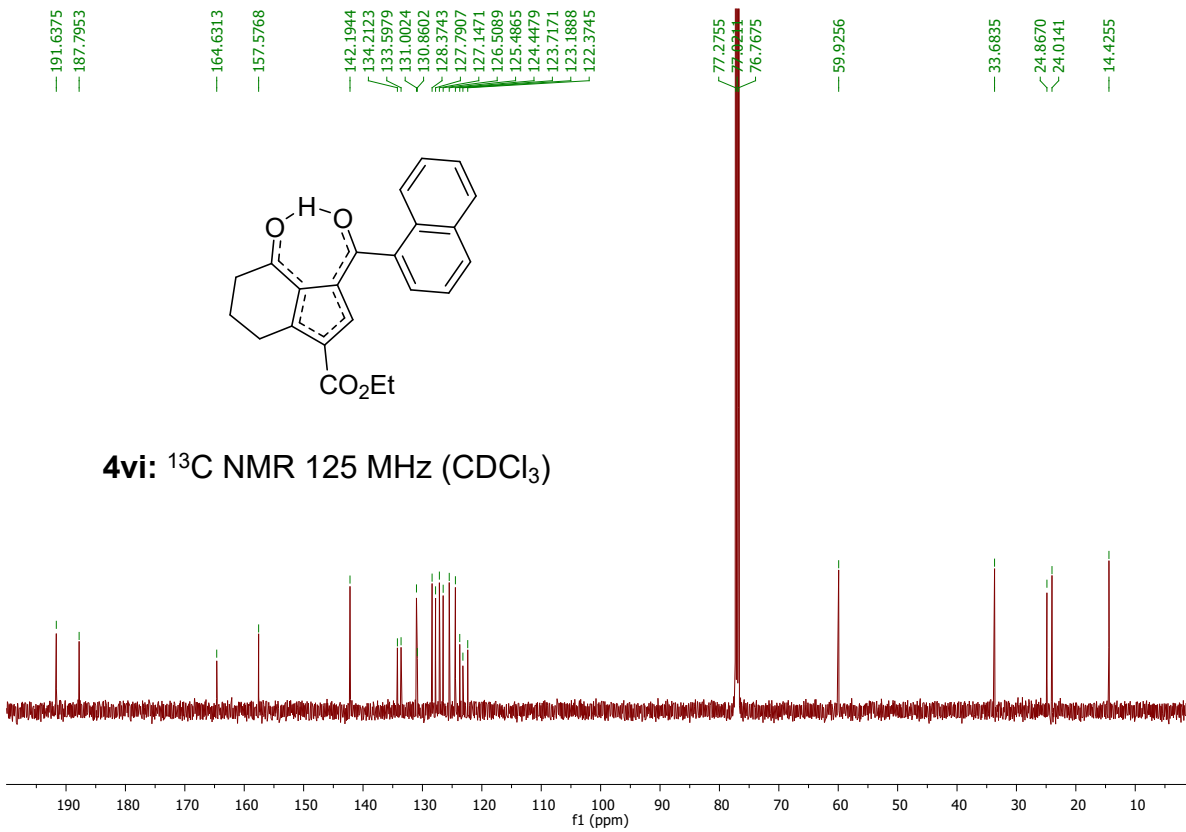
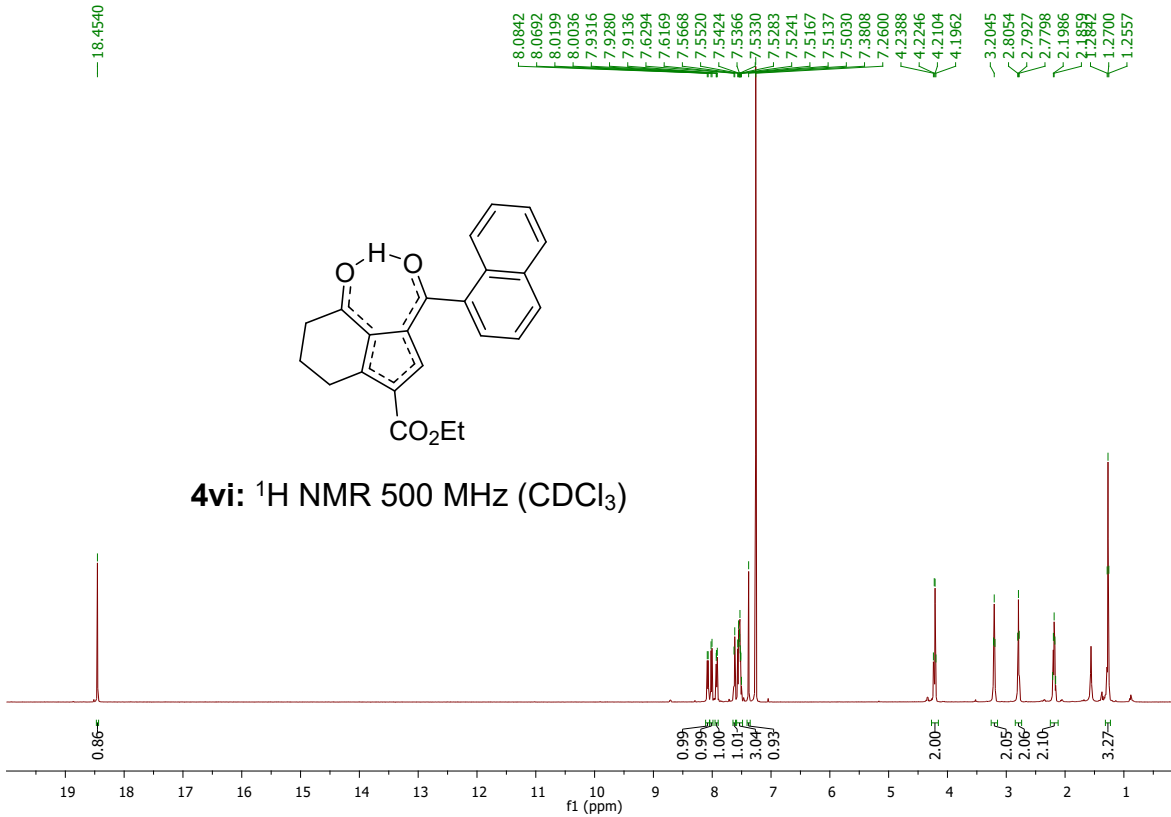
4pa: ^1H NMR 500 MHz (CDCl_3)

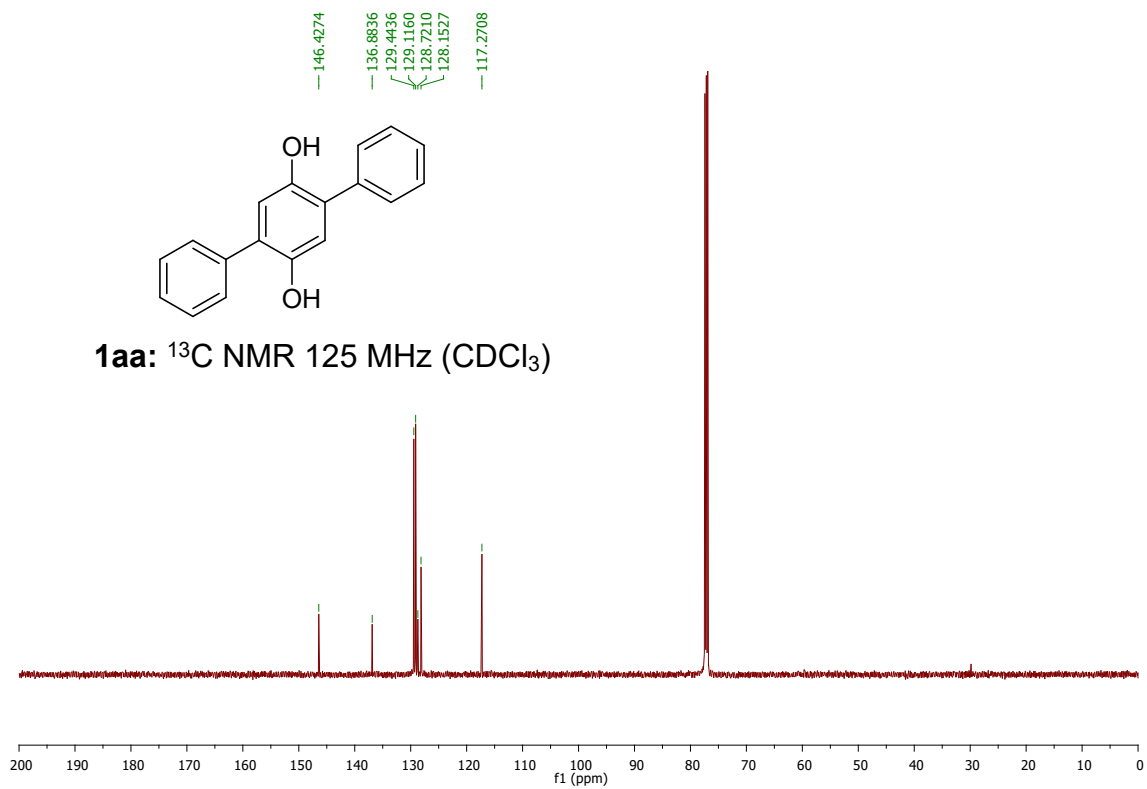
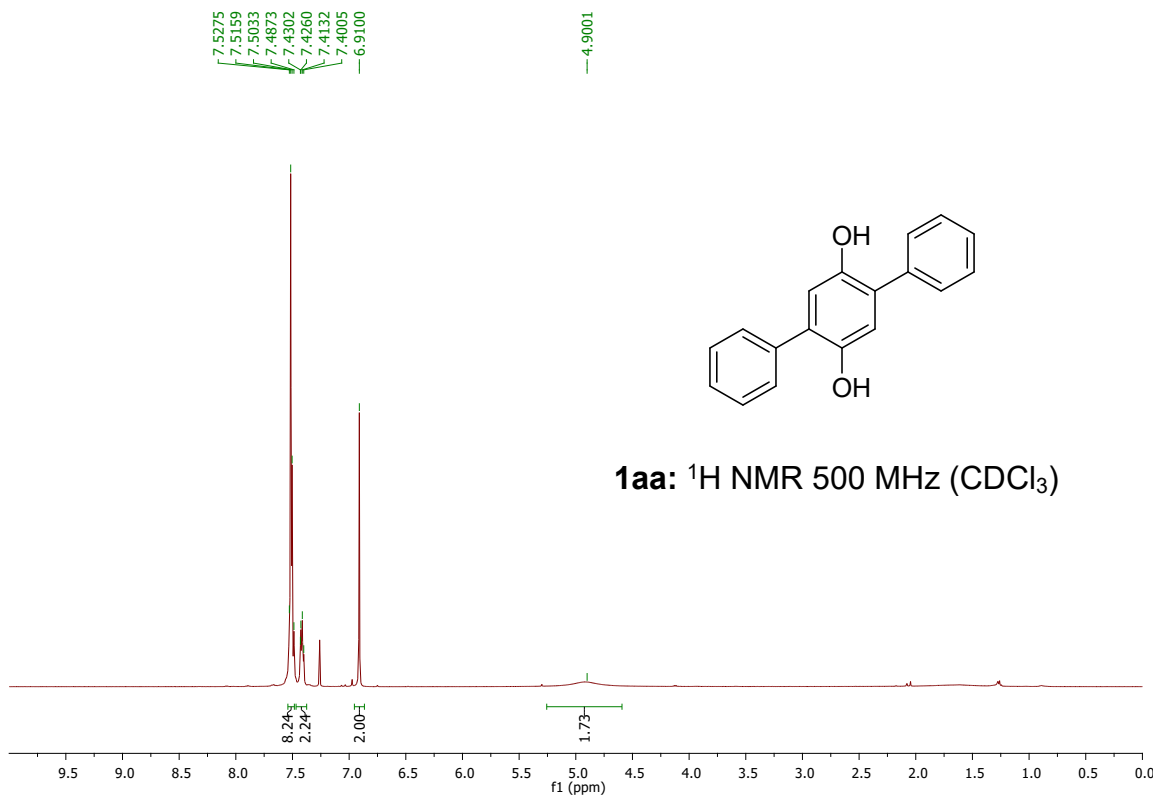


4pa: ^{13}C NMR 125 MHz (CDCl_3)





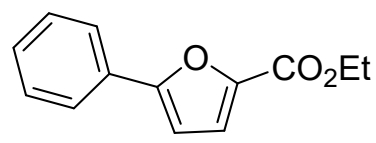




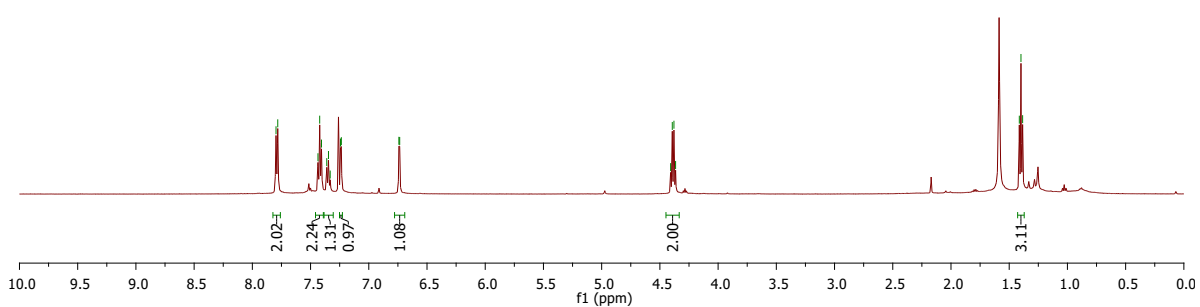
7.7967
7.7818
7.4216
7.4062
7.2427
6.7357
6.7345

4.4078
4.3935
4.3793
4.3651

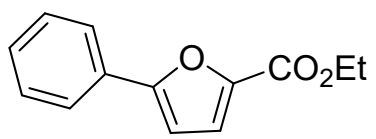
1.4132
1.3990
1.3847



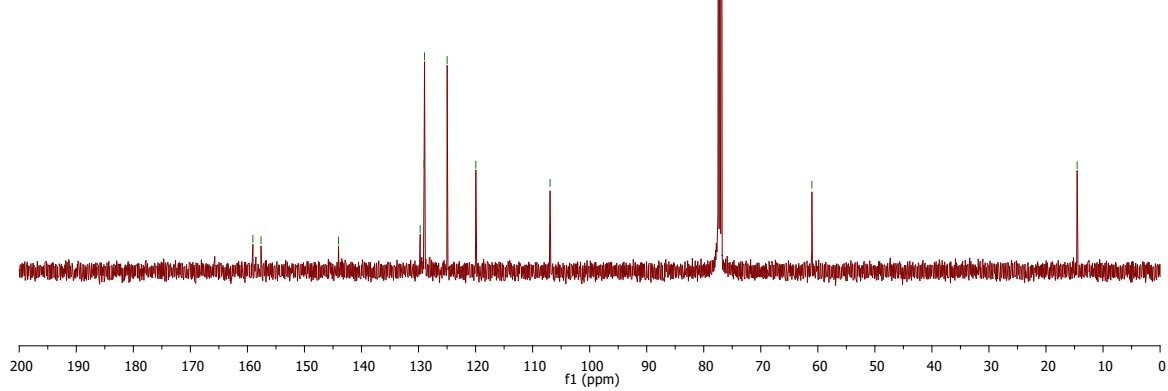
¹H NMR 500 MHz (CDCl₃)

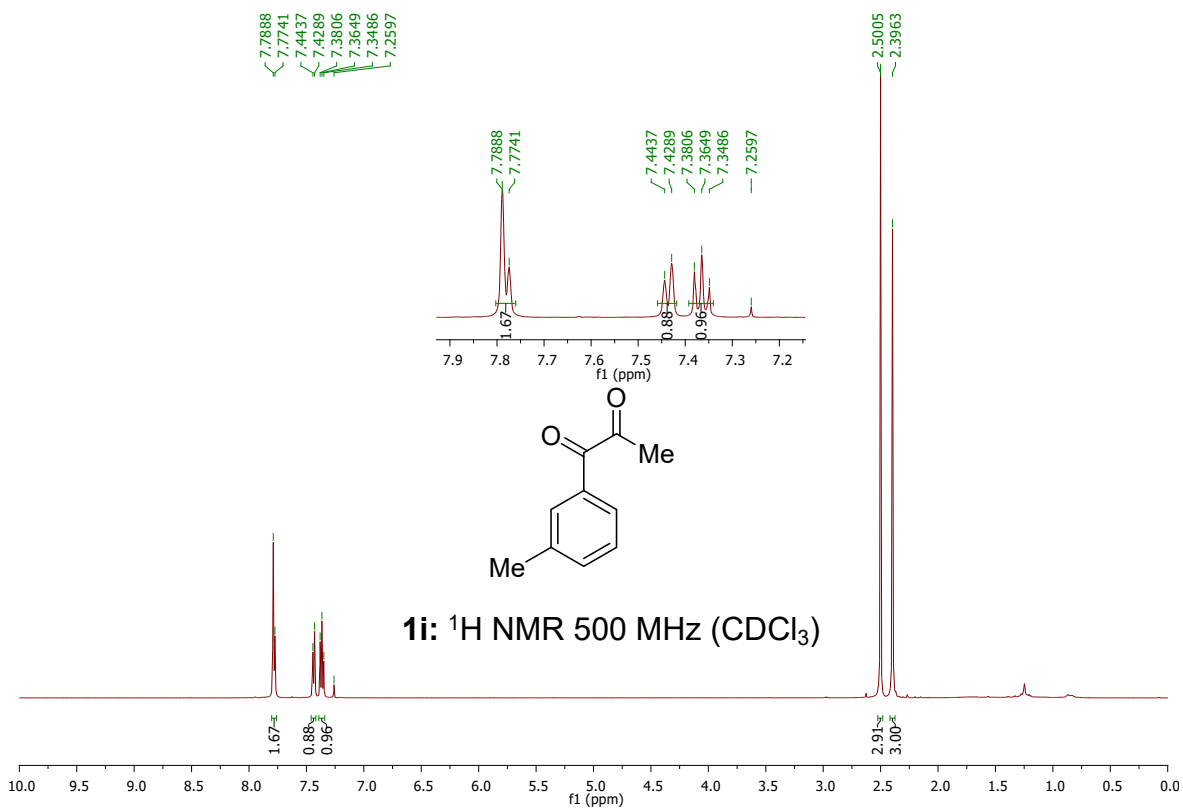
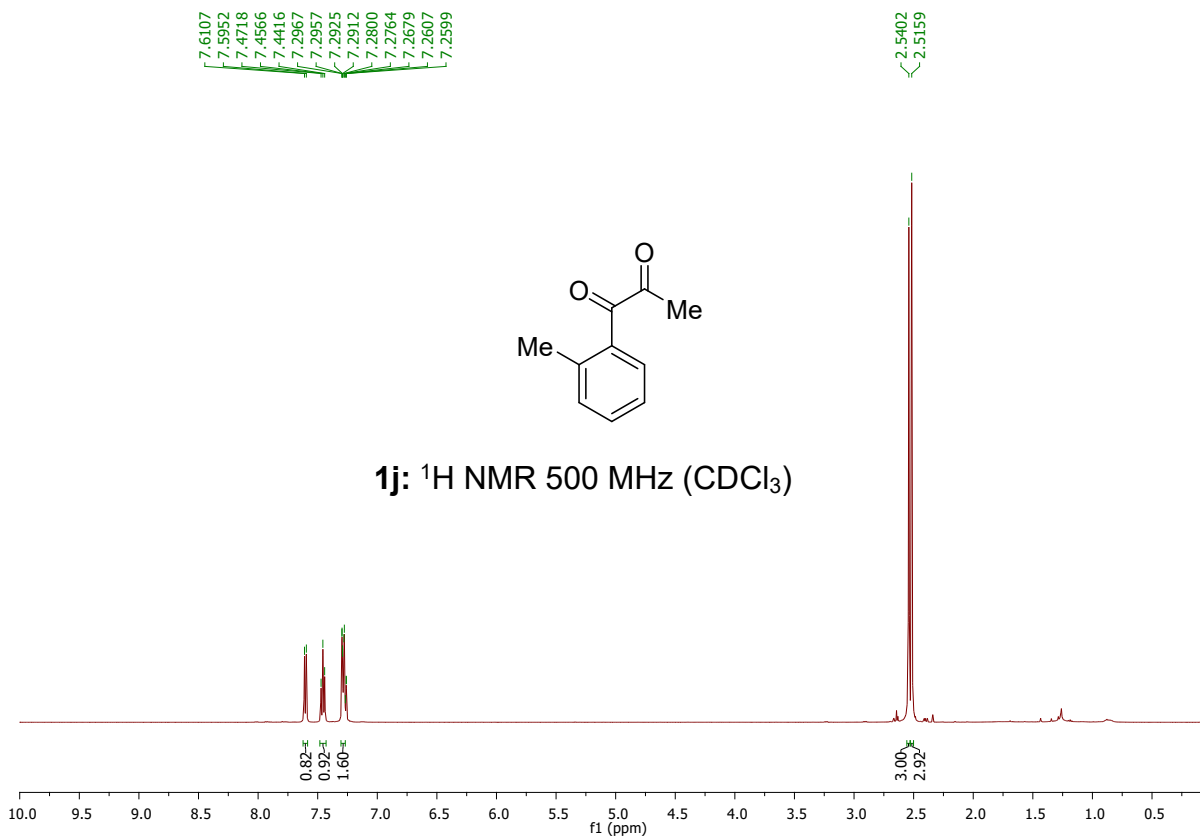


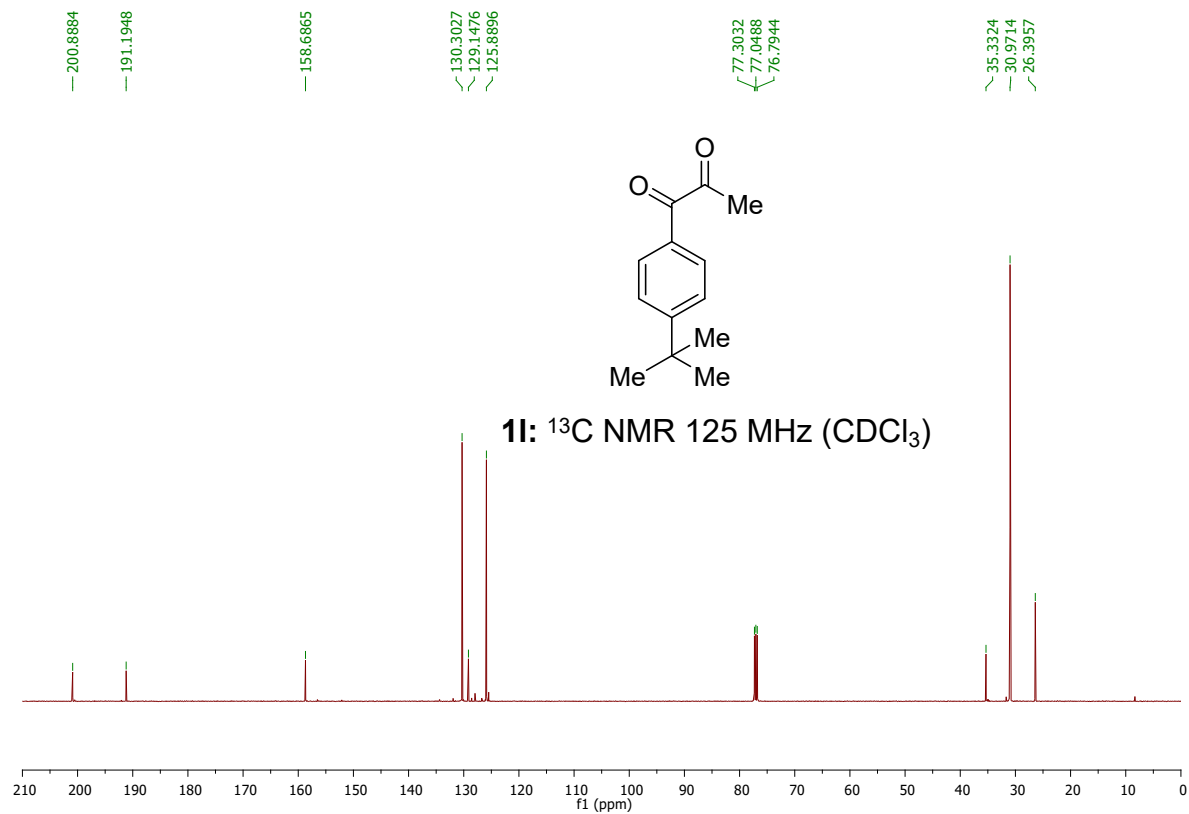
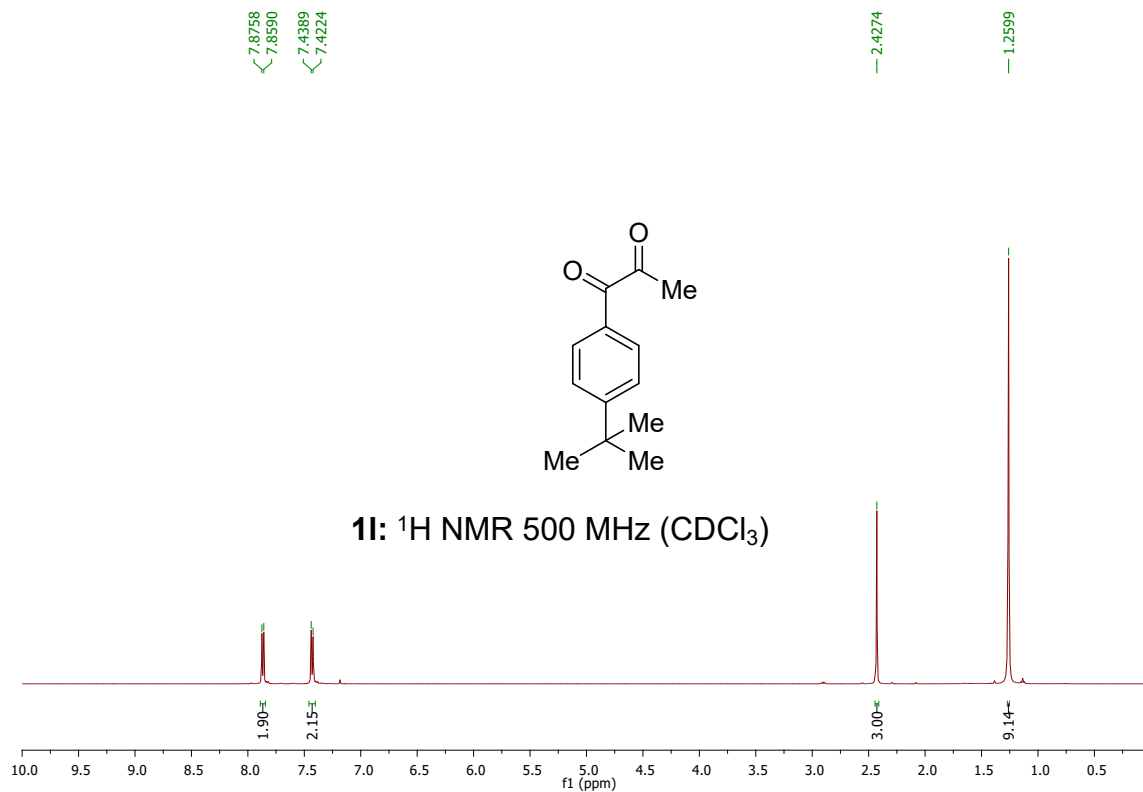
159.0386
157.6209
144.0274
129.7099
129.0313
128.9498
124.9819
119.9542
106.9433
61.0451
14.5419

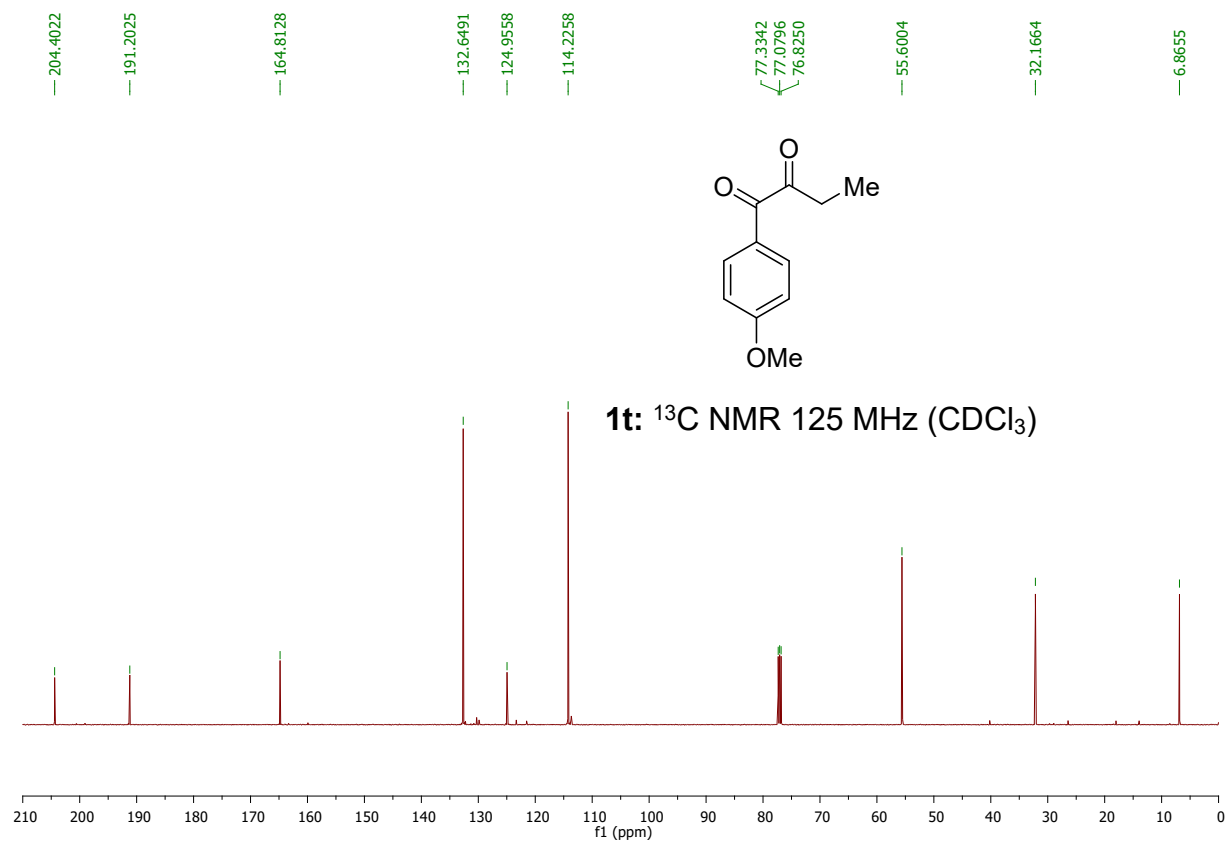
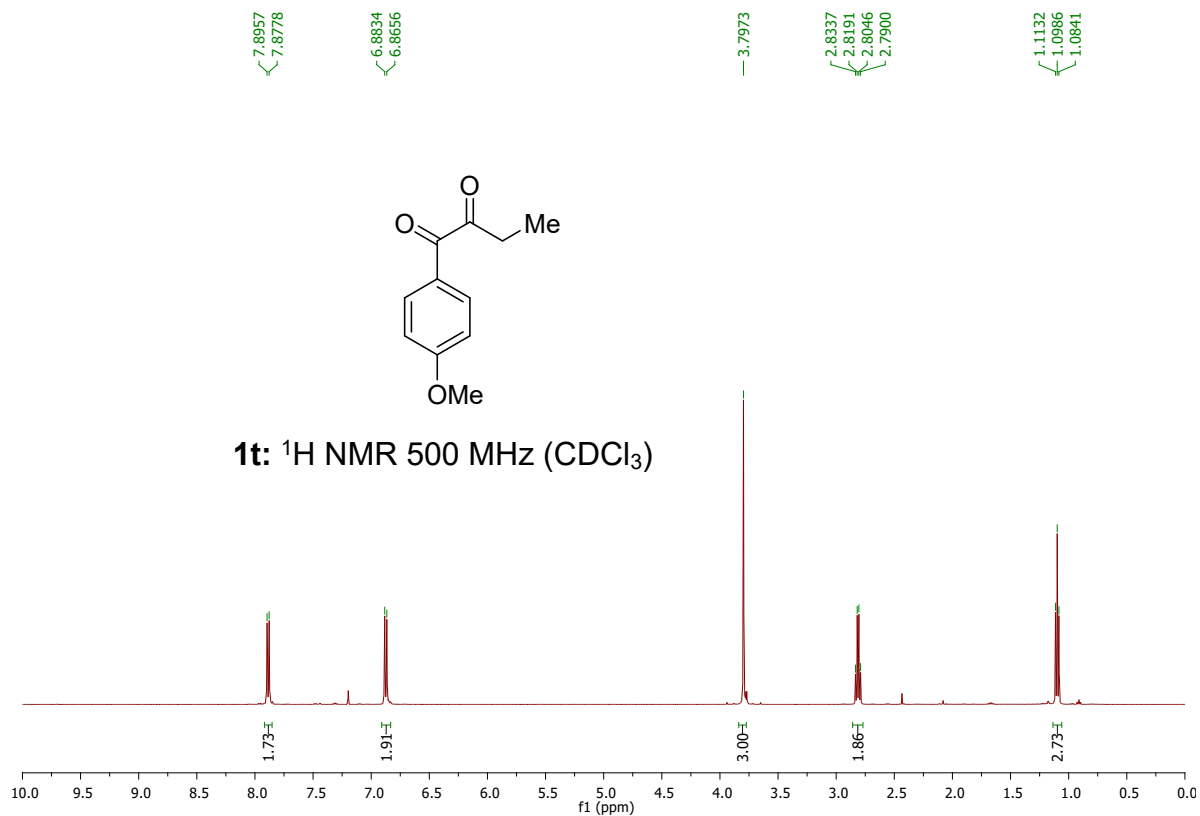


¹³C NMR 125 MHz (CDCl₃)





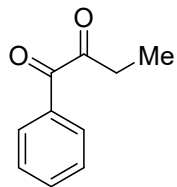




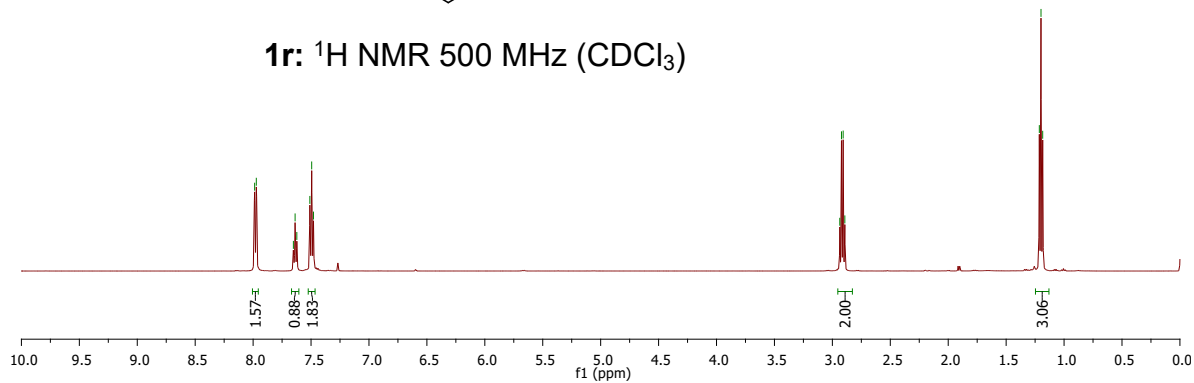
7.9869
7.9725
7.6524
7.6376
7.6227
7.5103
7.4945
7.4791

2.9359
2.9214
2.9068
2.8923

1.2136
1.1991
1.1845



1r: ¹H NMR 500 MHz (CDCl₃)



203.8442

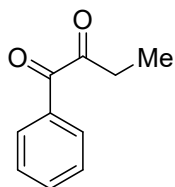
192.5773

134.5807
132.0194
130.1490
128.8537

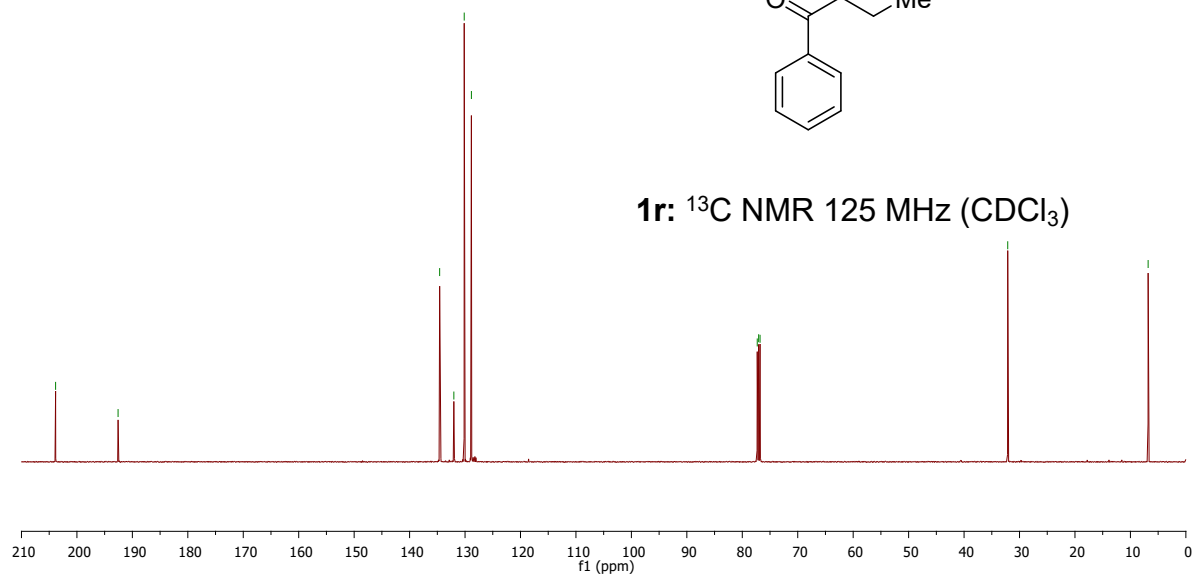
77.3019
77.0477
76.7932

32.1260

6.8051

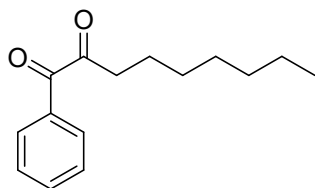


1r: ¹³C NMR 125 MHz (CDCl₃)

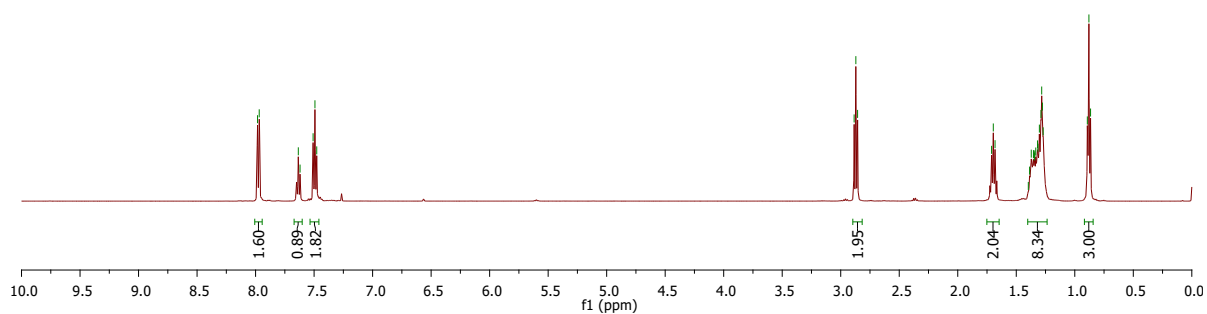


7.9833
7.9689
7.6348
7.6199
7.5086
7.4927
7.4774

2.8855
2.8708
2.8559
1.6962
1.6814
1.3182
1.3144
1.3025
1.2887
1.2827
1.2765
0.8597
0.8492
0.8451



1s: ^1H NMR 500 MHz (CDCl_3)



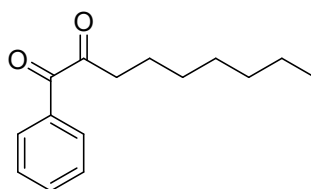
203.5504

192.6055

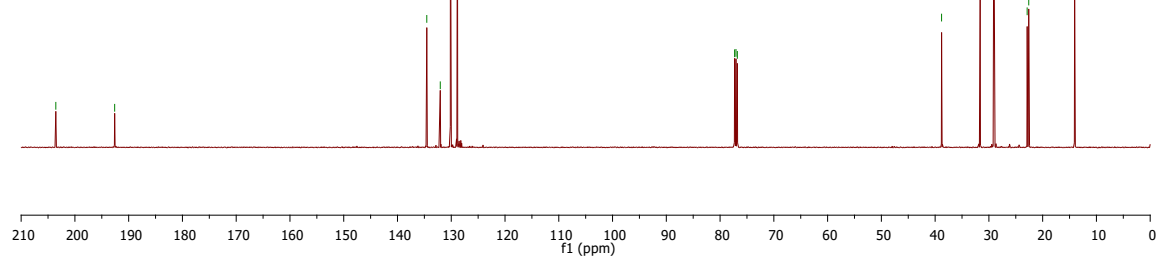
134.5509
132.0423
130.1573
128.8489

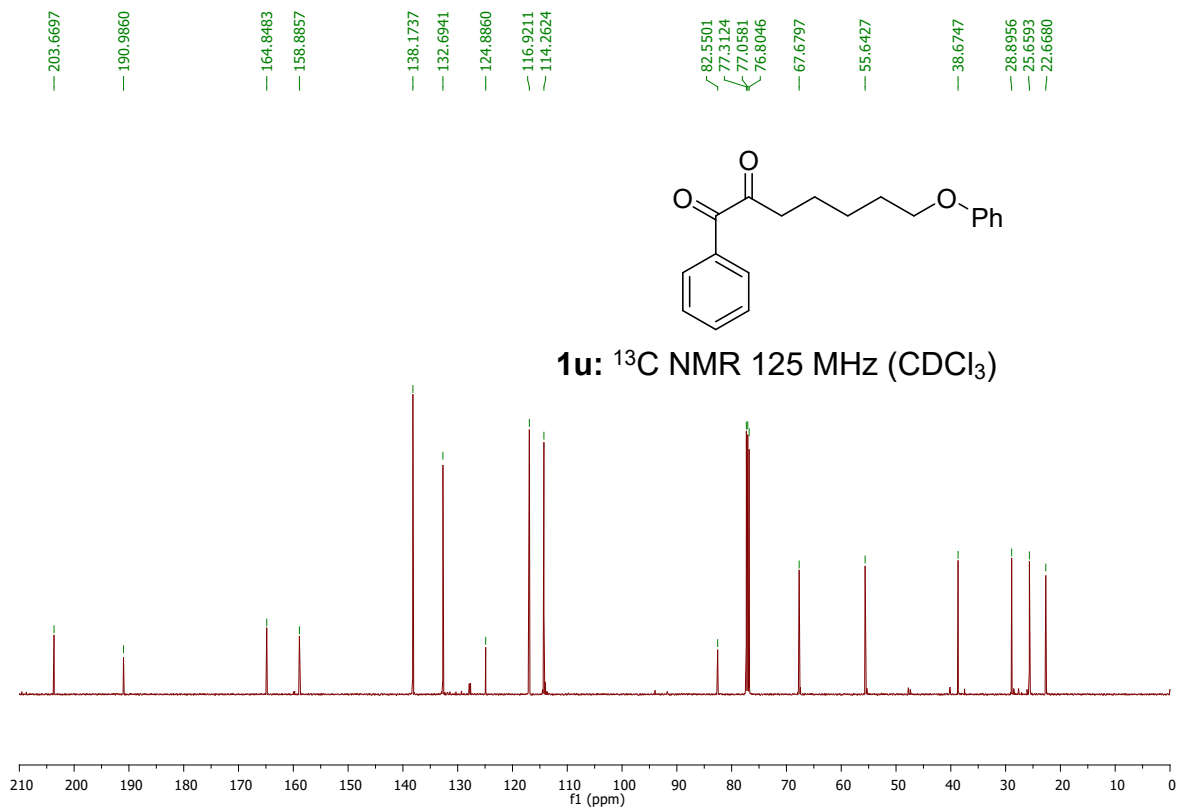
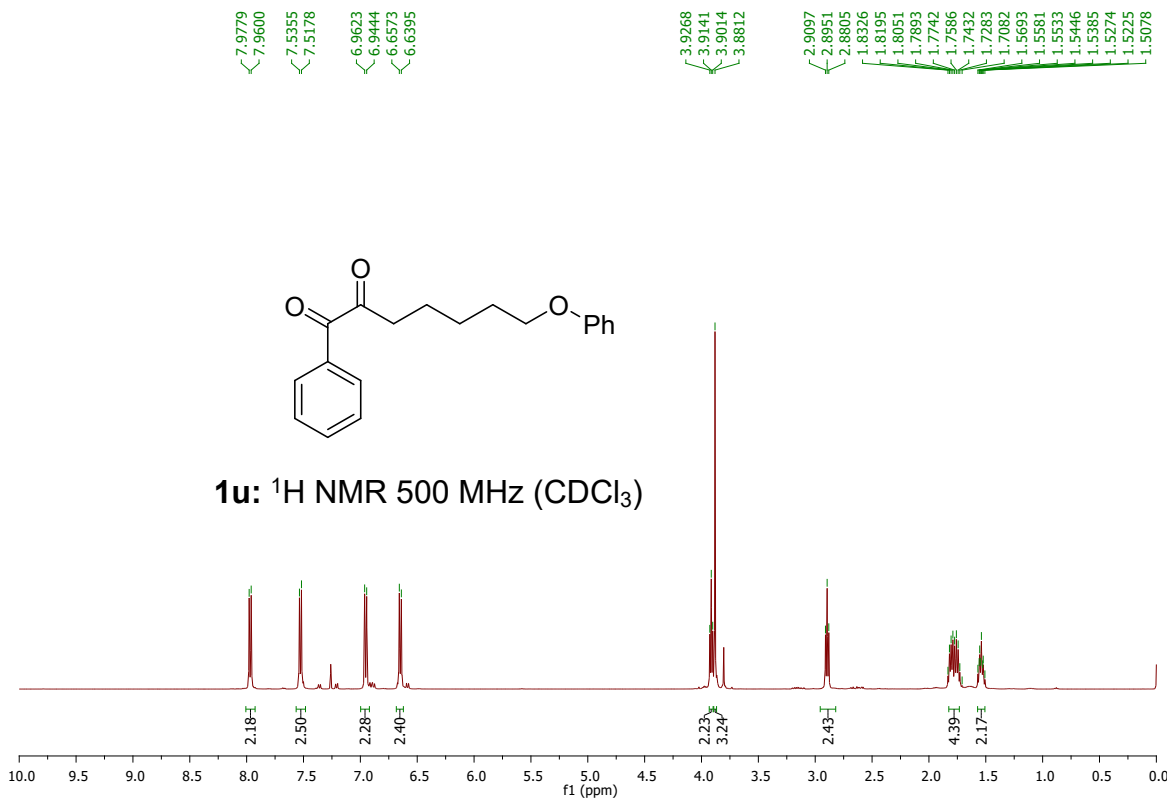
77.2974
77.0431
76.7890

38.8020
31.6212
29.1299
28.9977
22.8849
22.5878
14.0535



1s: ^{13}C NMR 125 MHz (CDCl_3)

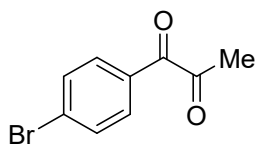




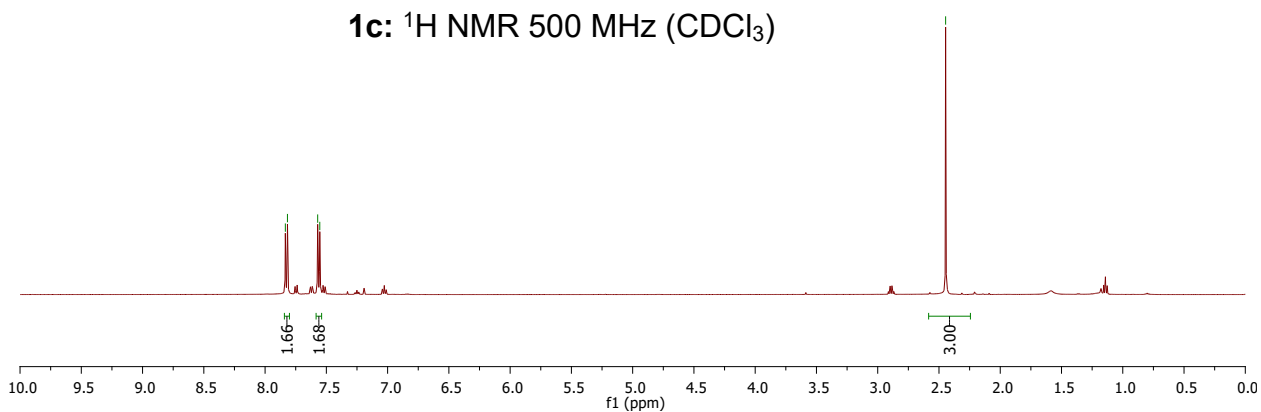
SS-MP-BR-DIKETO

7.8346
7.8175
7.5708
7.5536

2.4458



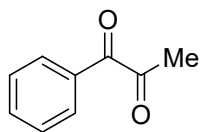
1c: ^1H NMR 500 MHz (CDCl_3)



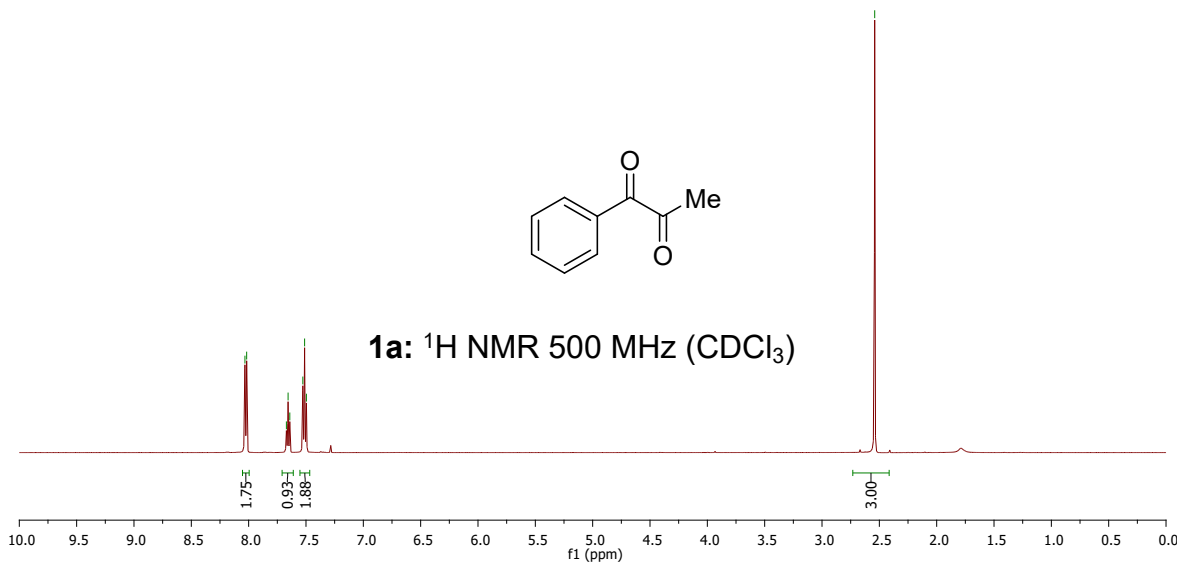
SS-MP-DIKETO

8.0323
8.0174
7.6709
7.6561
7.6411
7.5275
7.5120
7.4964

2.5405



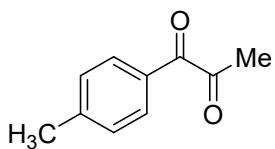
1a: ^1H NMR 500 MHz (CDCl_3)



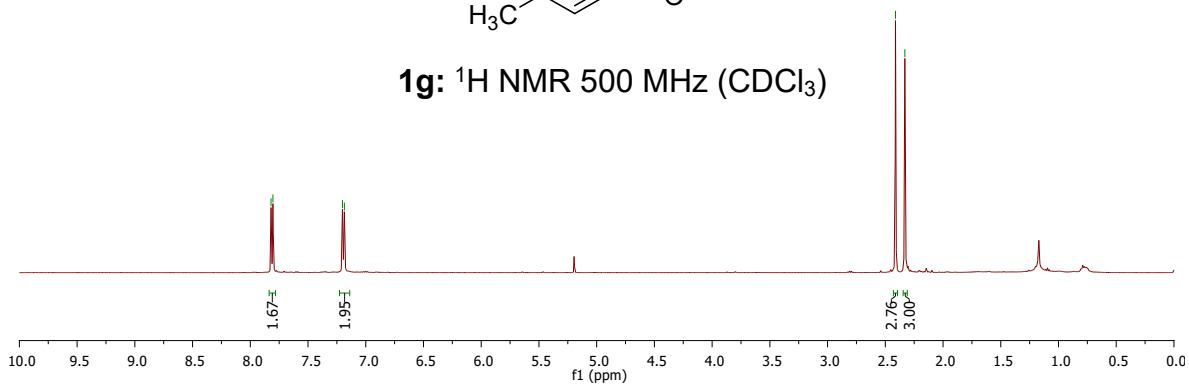
SS-MP-DIKETO-1

7.8203
7.8039
7.2018
7.1852

2.4119
2.3308

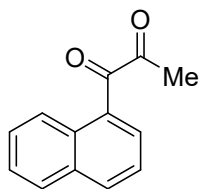


1g: ¹H NMR 500 MHz (CDCl₃)

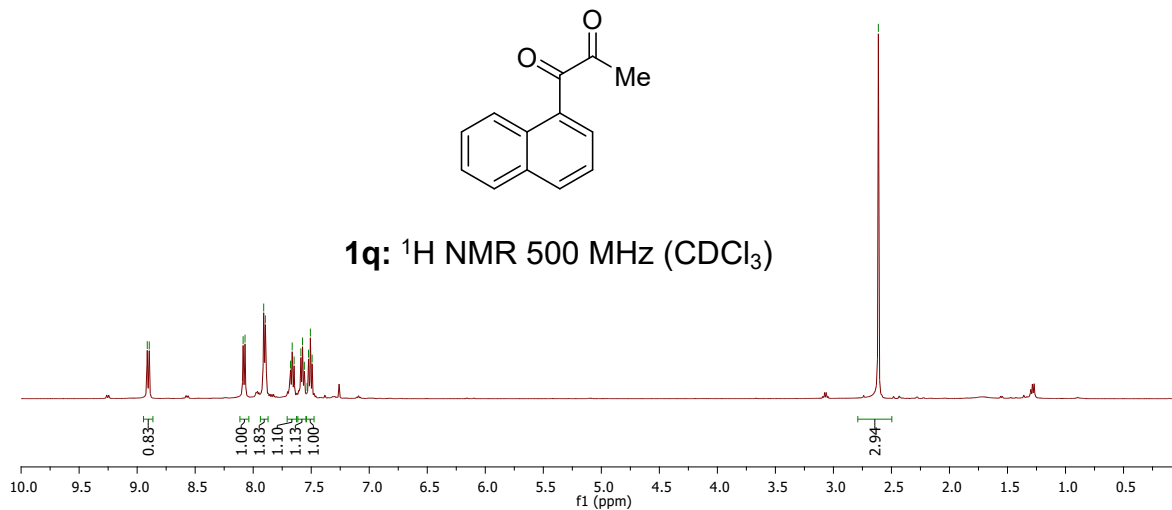


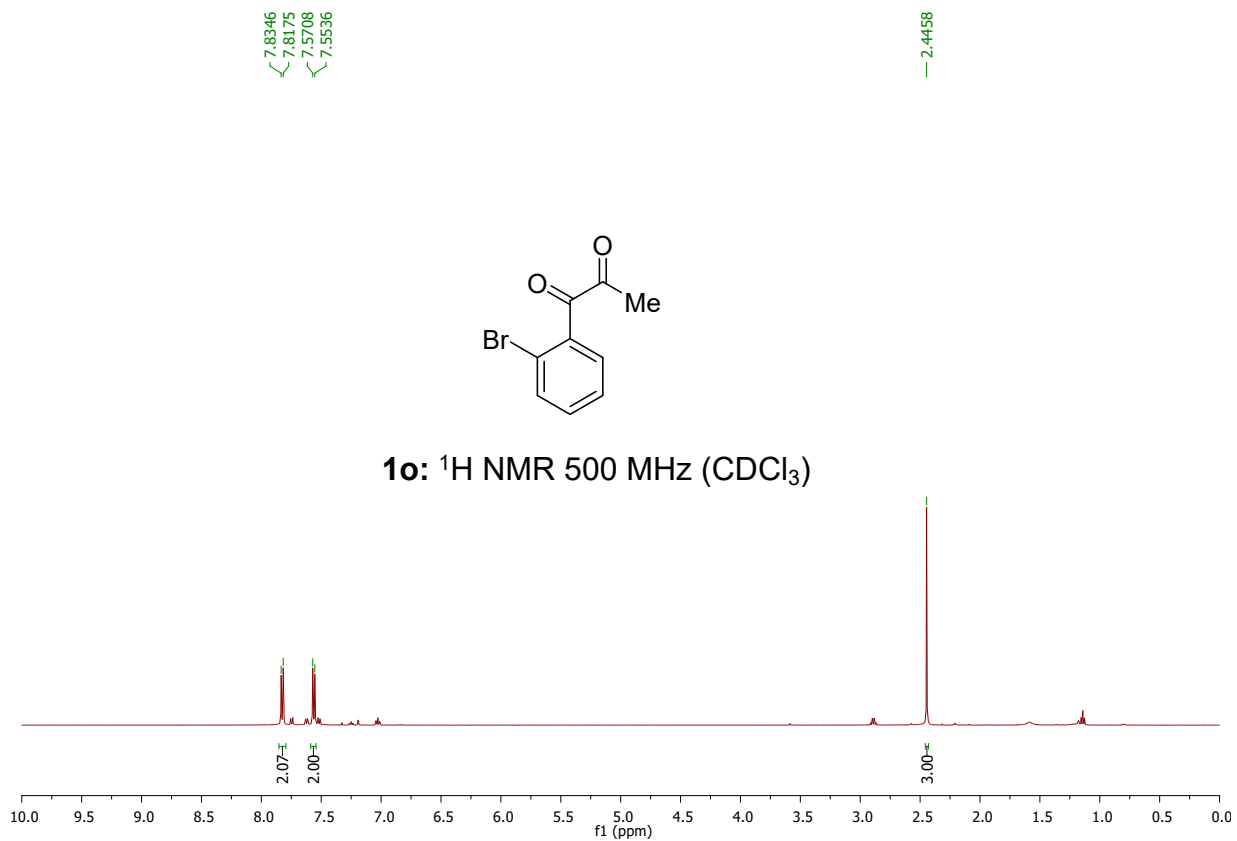
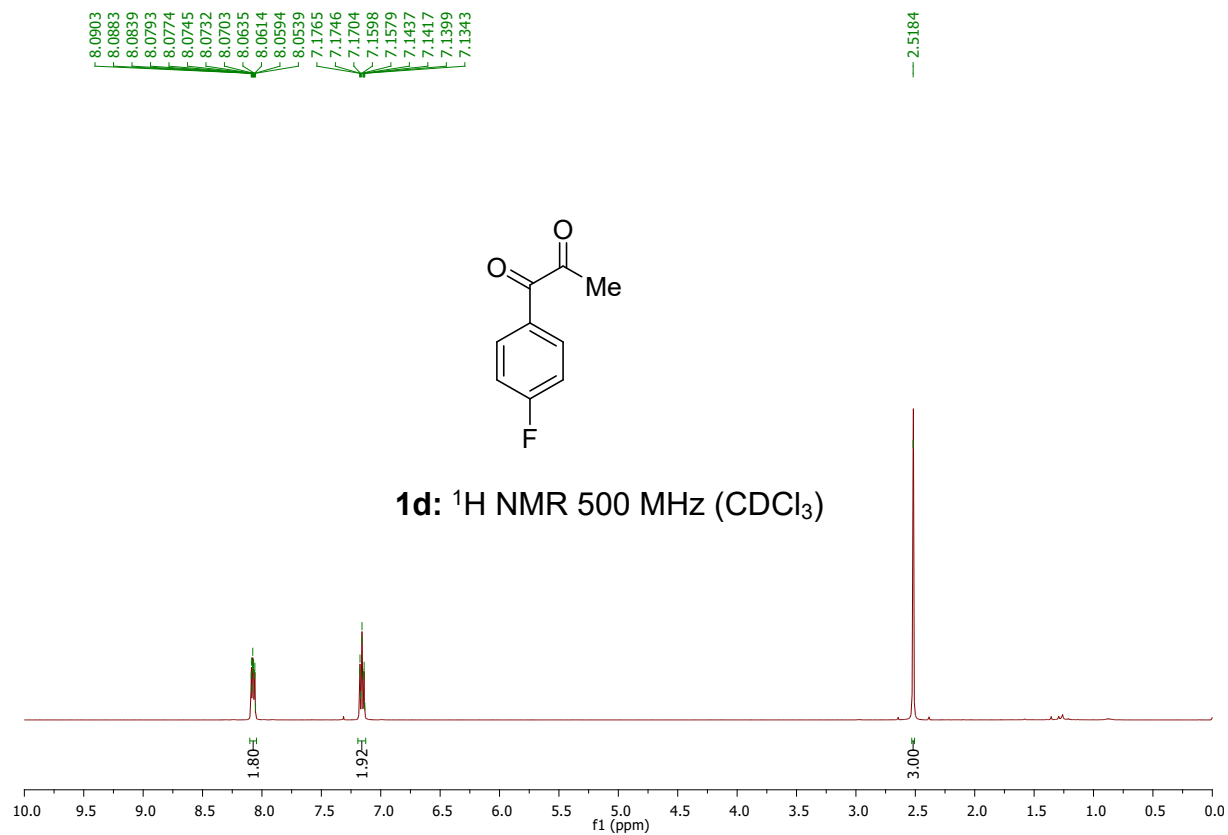
8.9127
8.8955
8.0867
8.0703
7.9096
7.8952
7.6783
7.6641
7.6474
7.5891
7.5748
7.5592
7.5351
7.5231
7.5072
7.4922

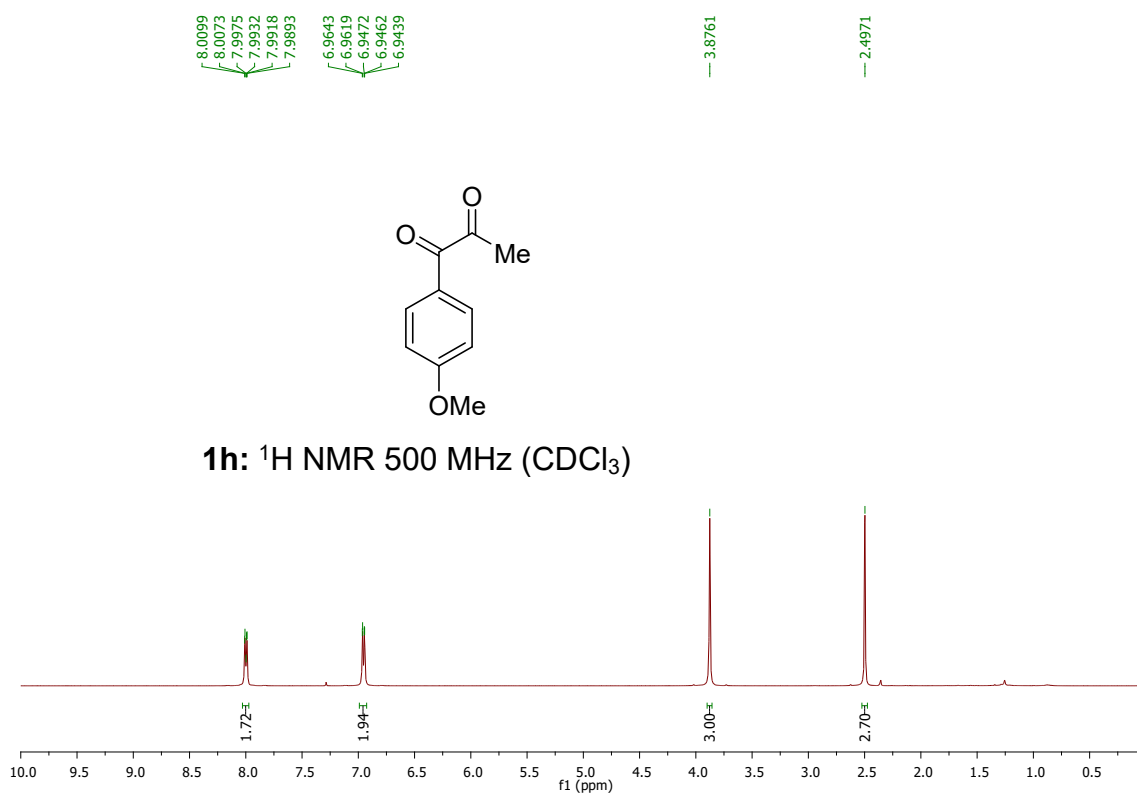
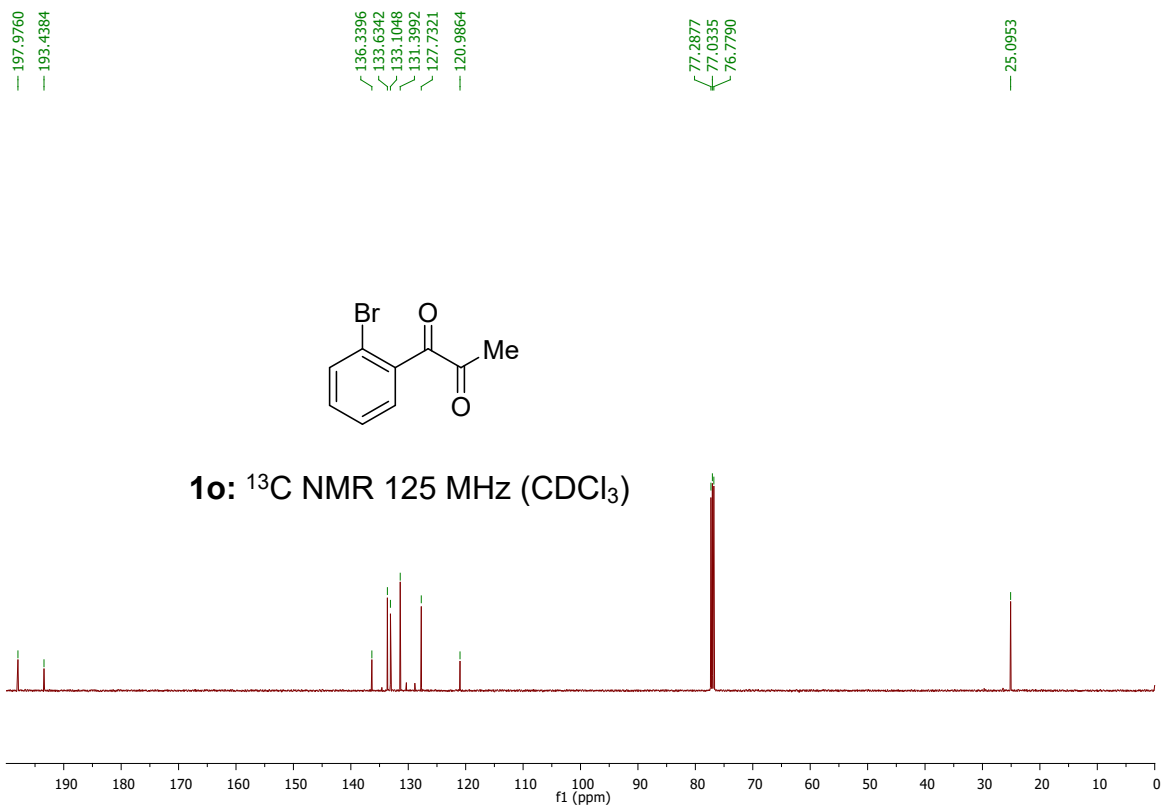
2.6127

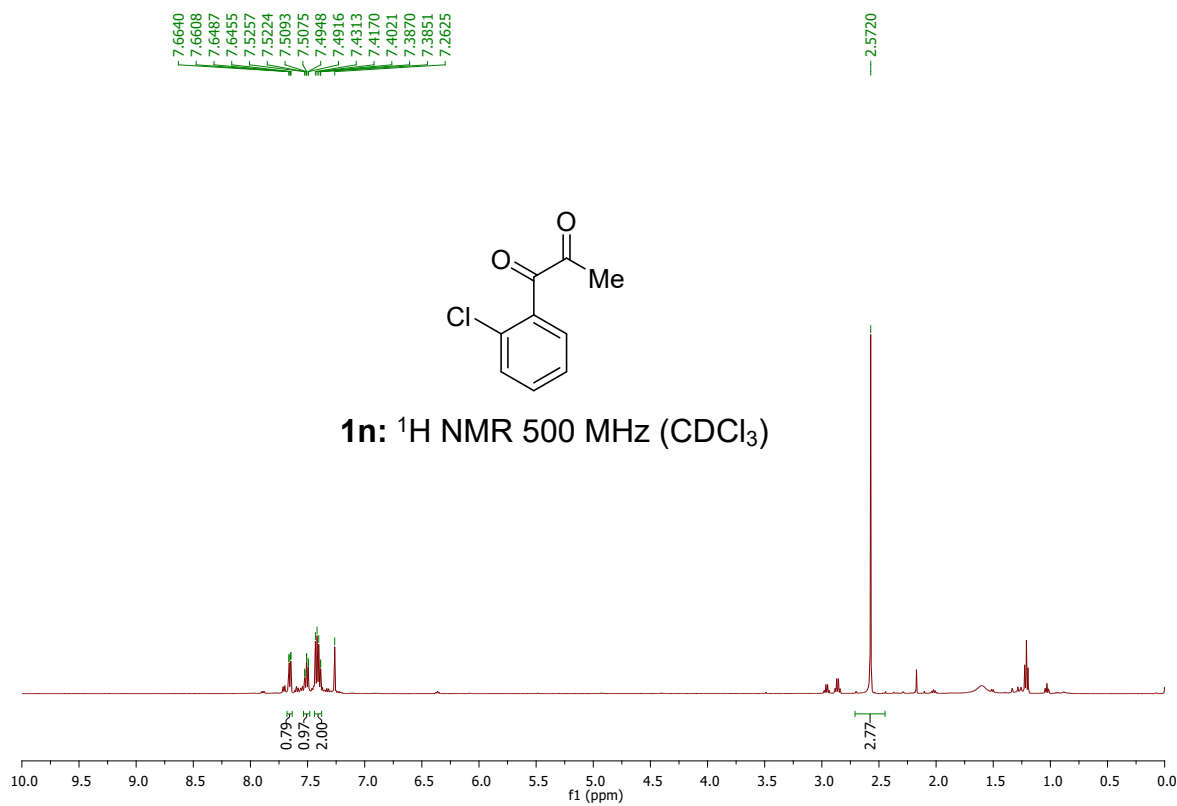
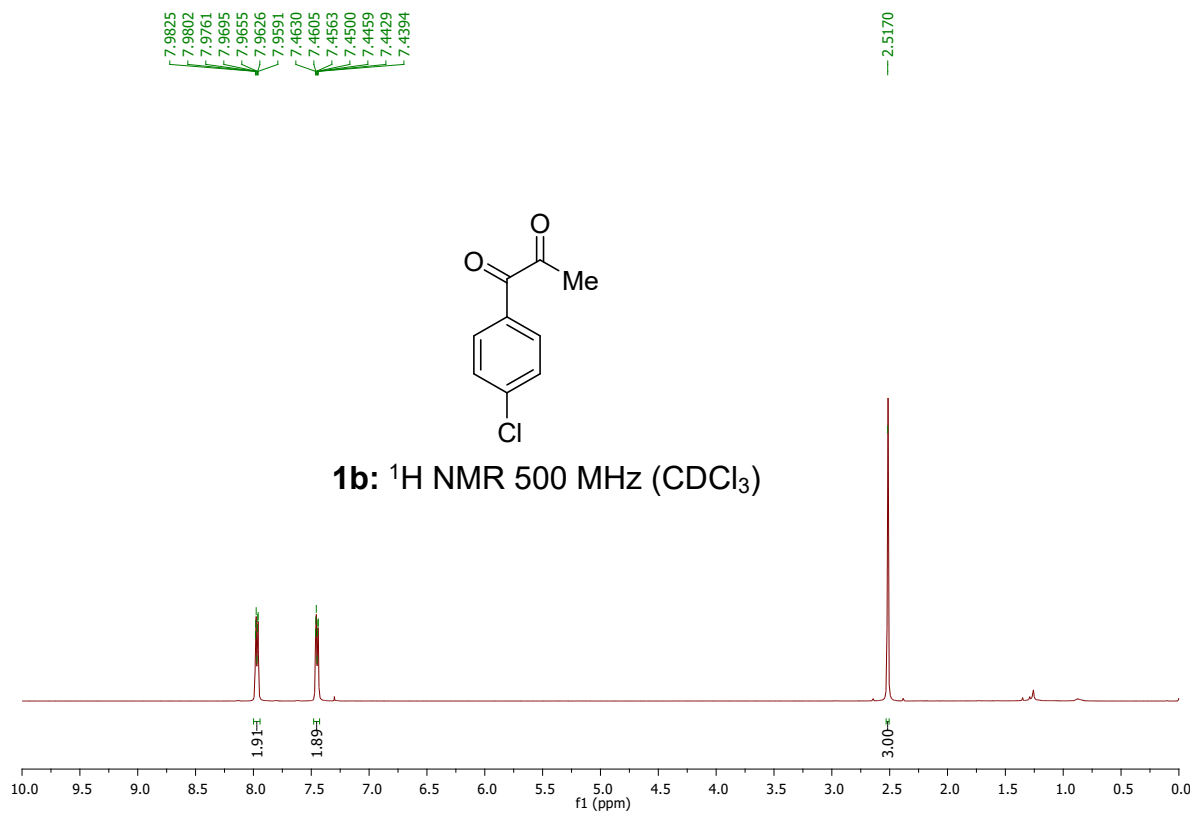


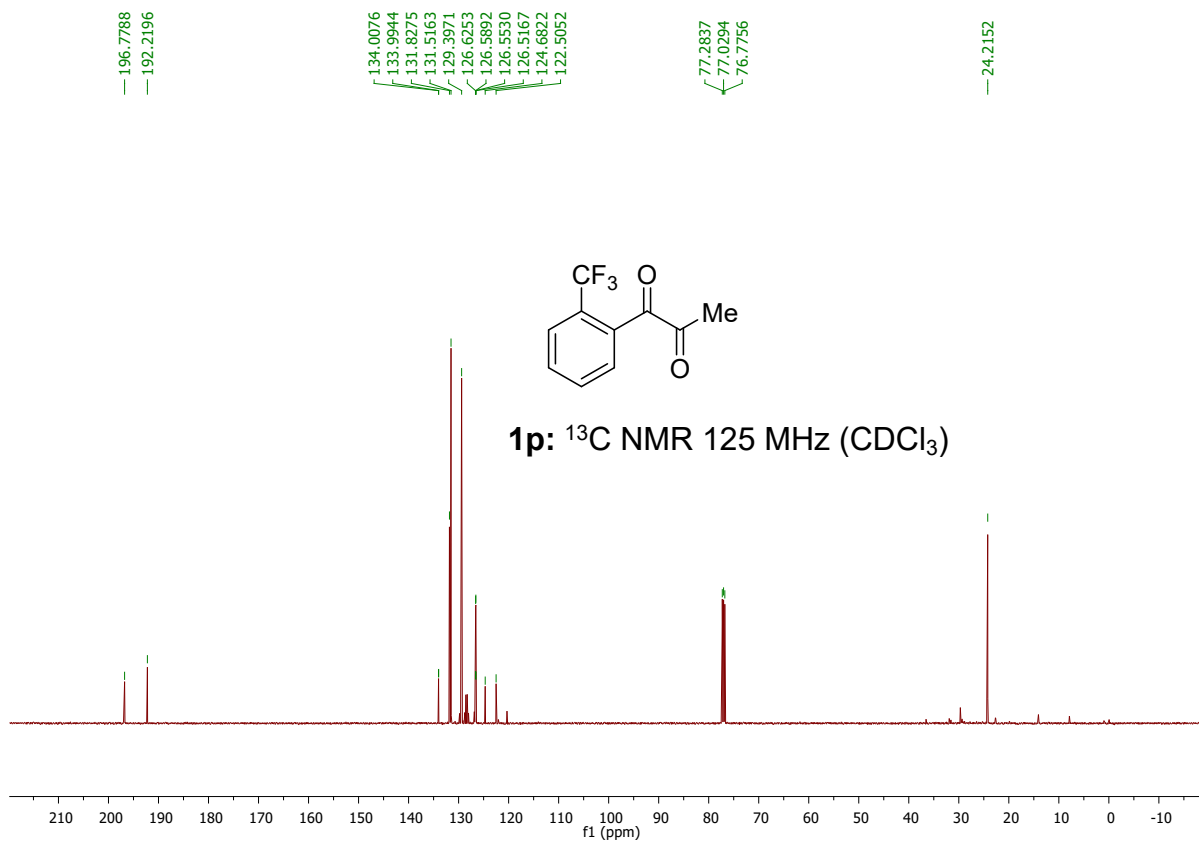
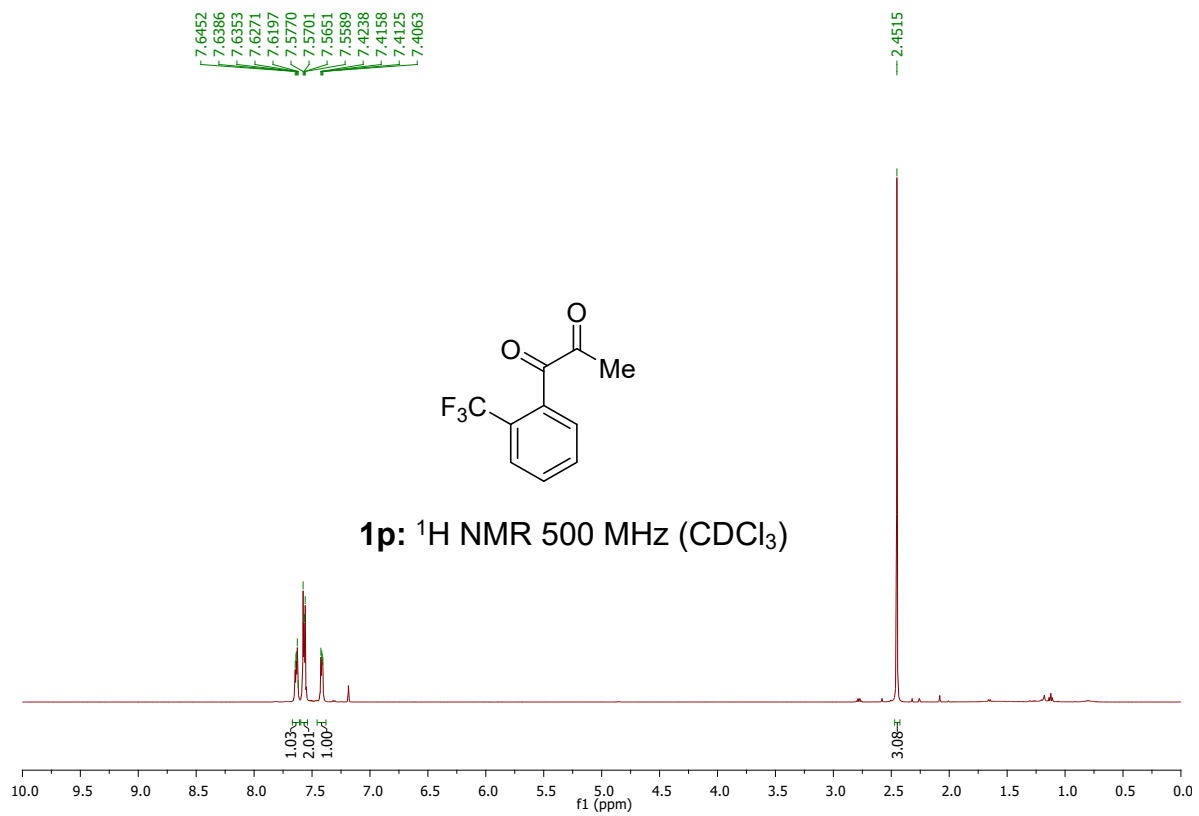
1q: ¹H NMR 500 MHz (CDCl₃)

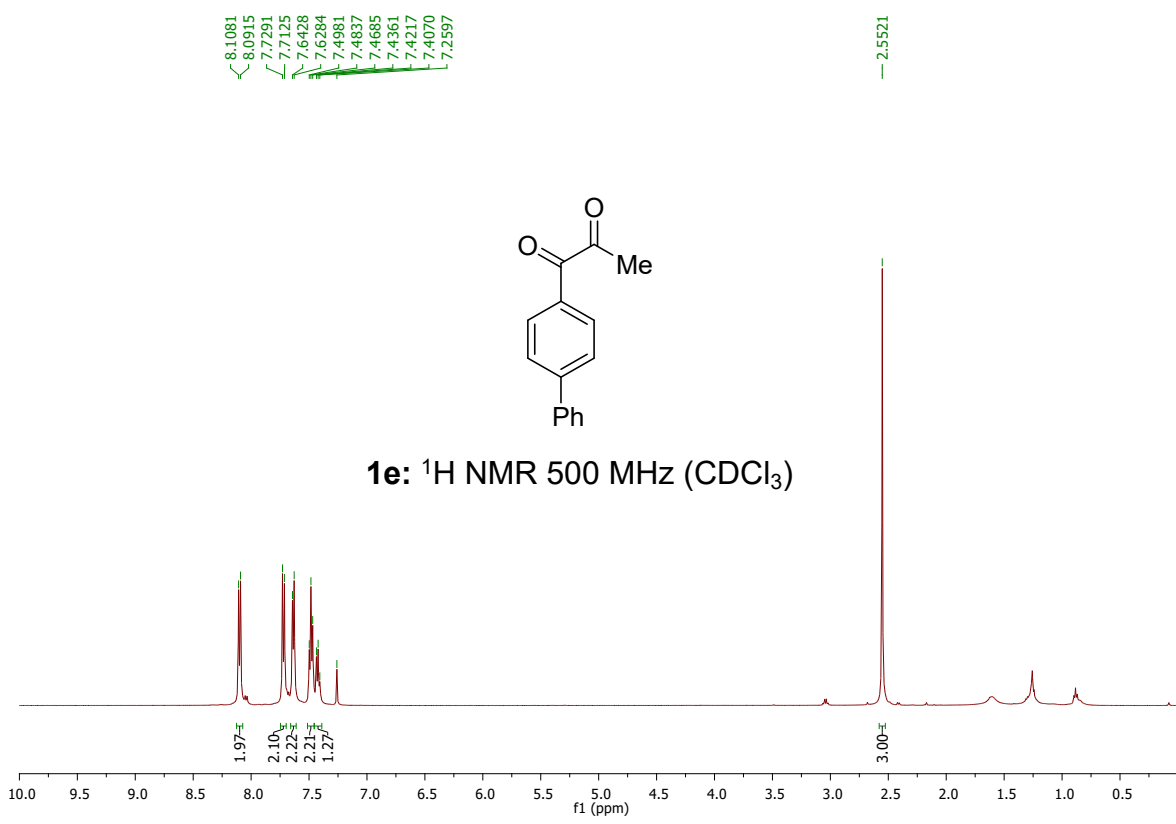
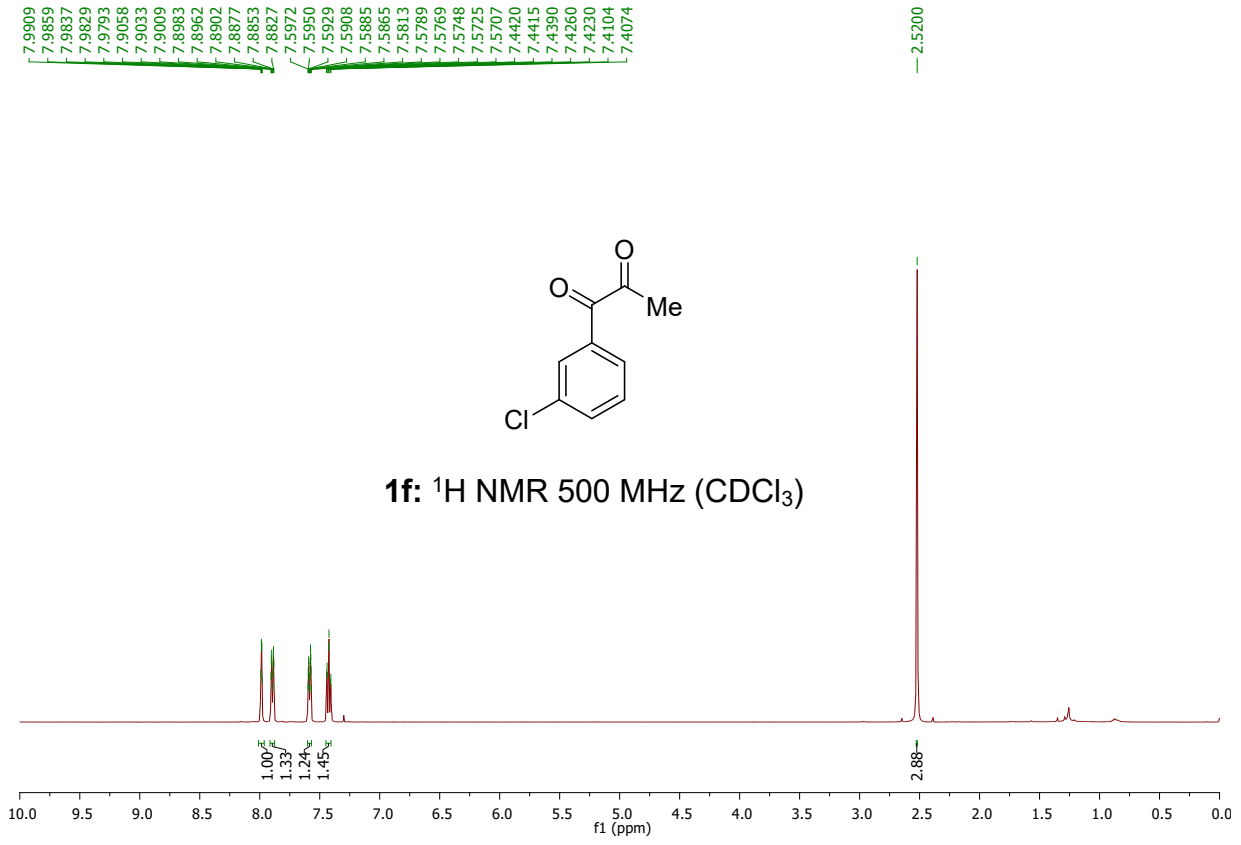


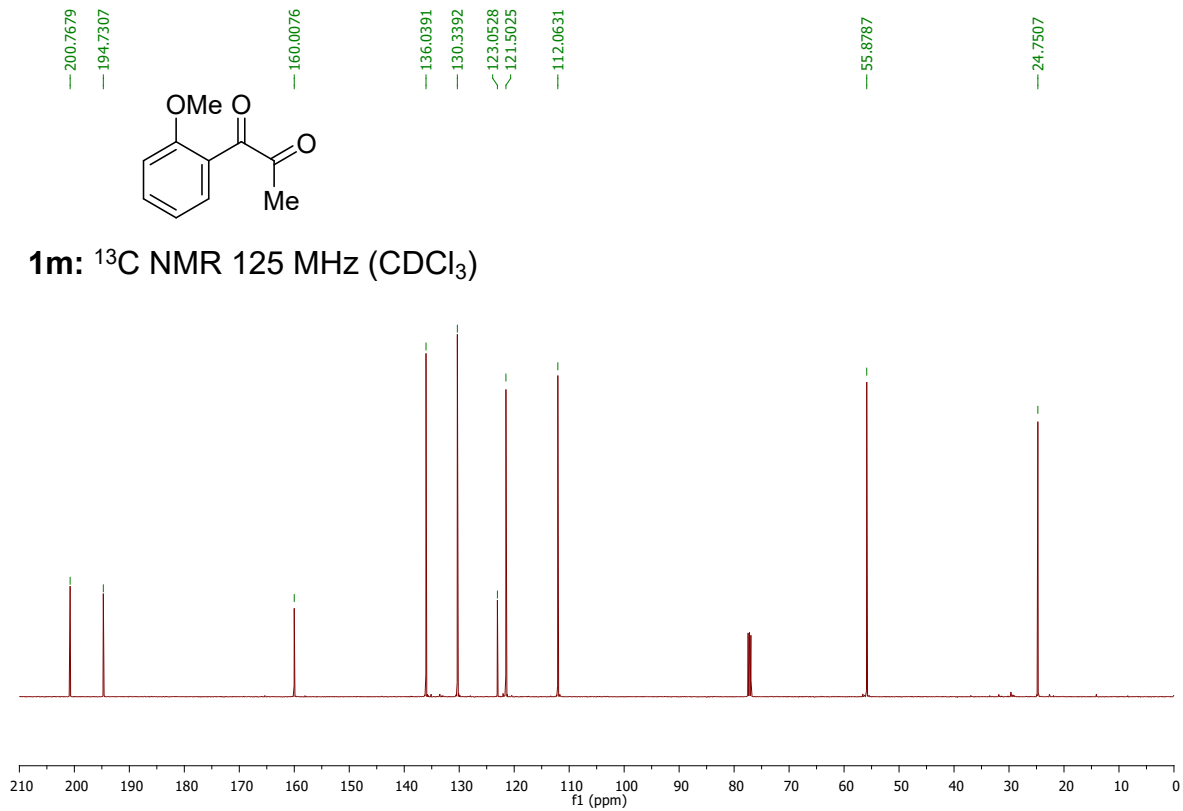
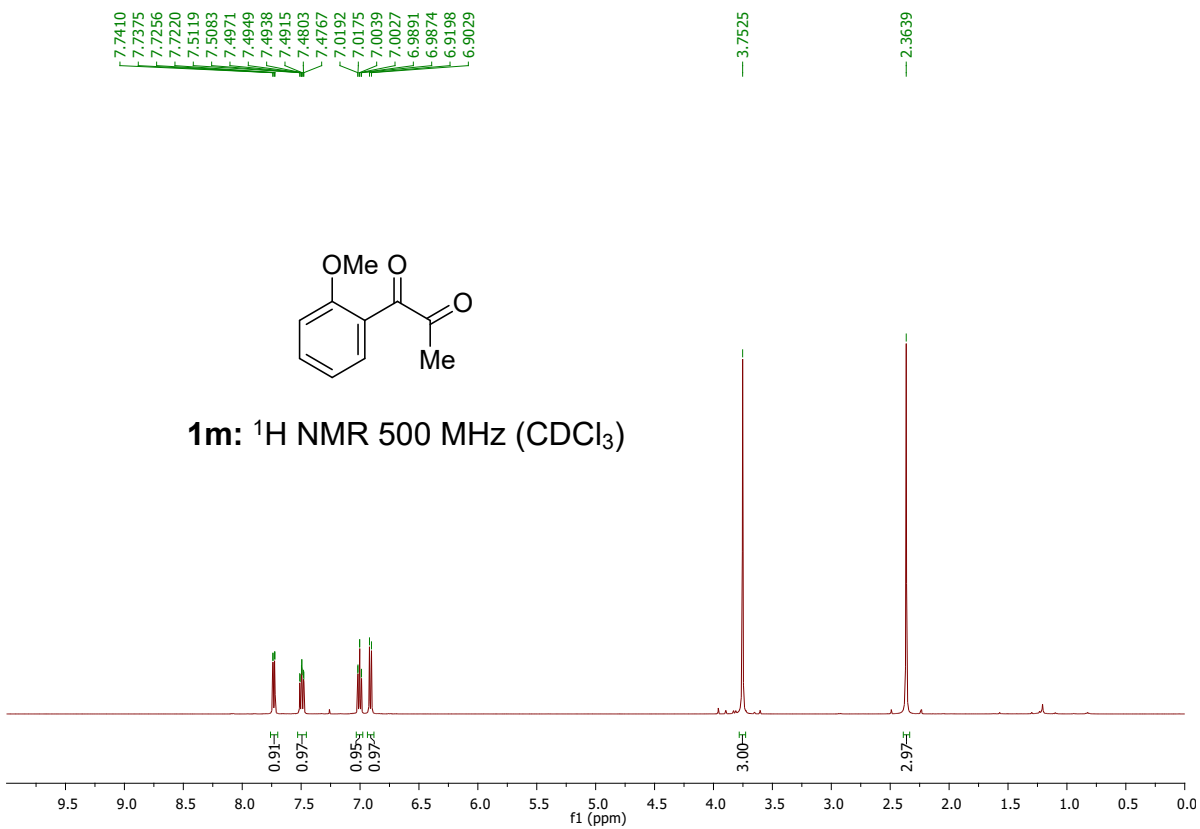


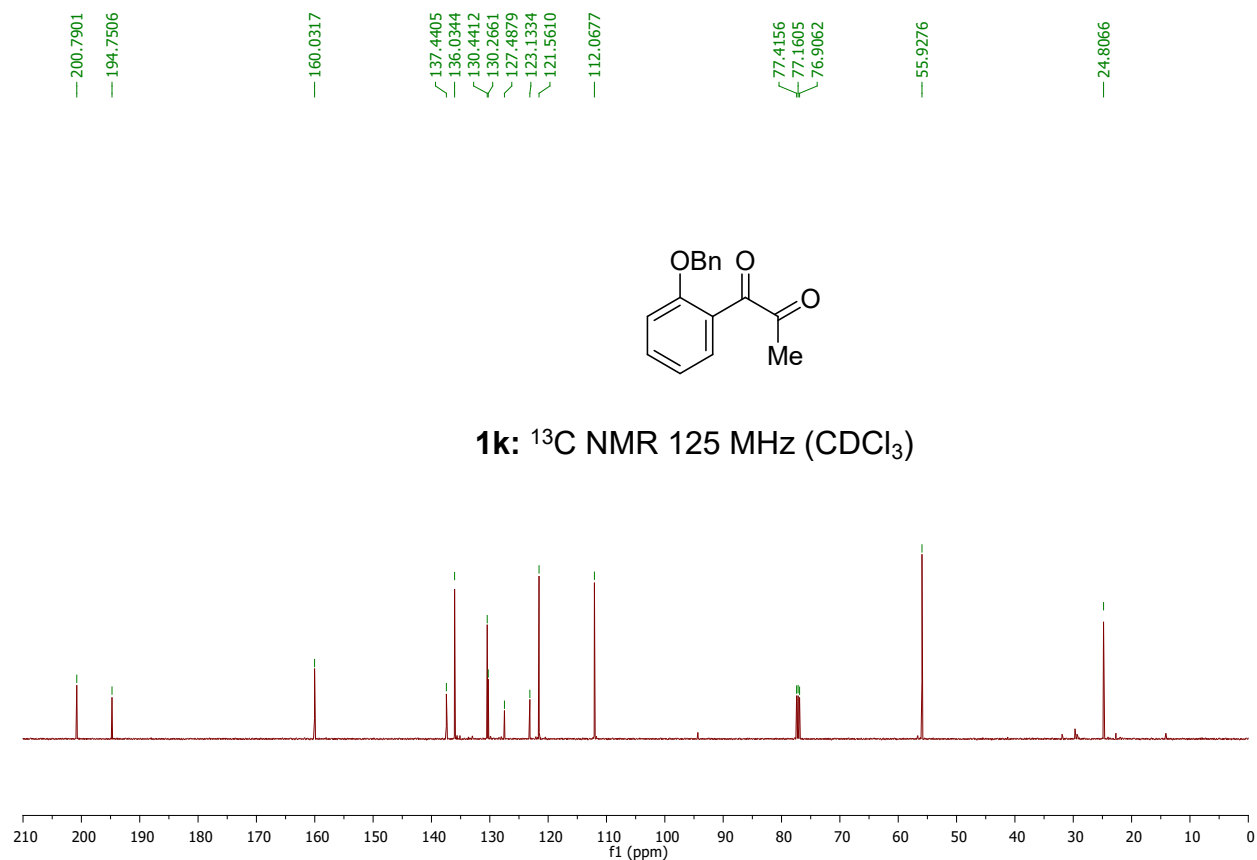
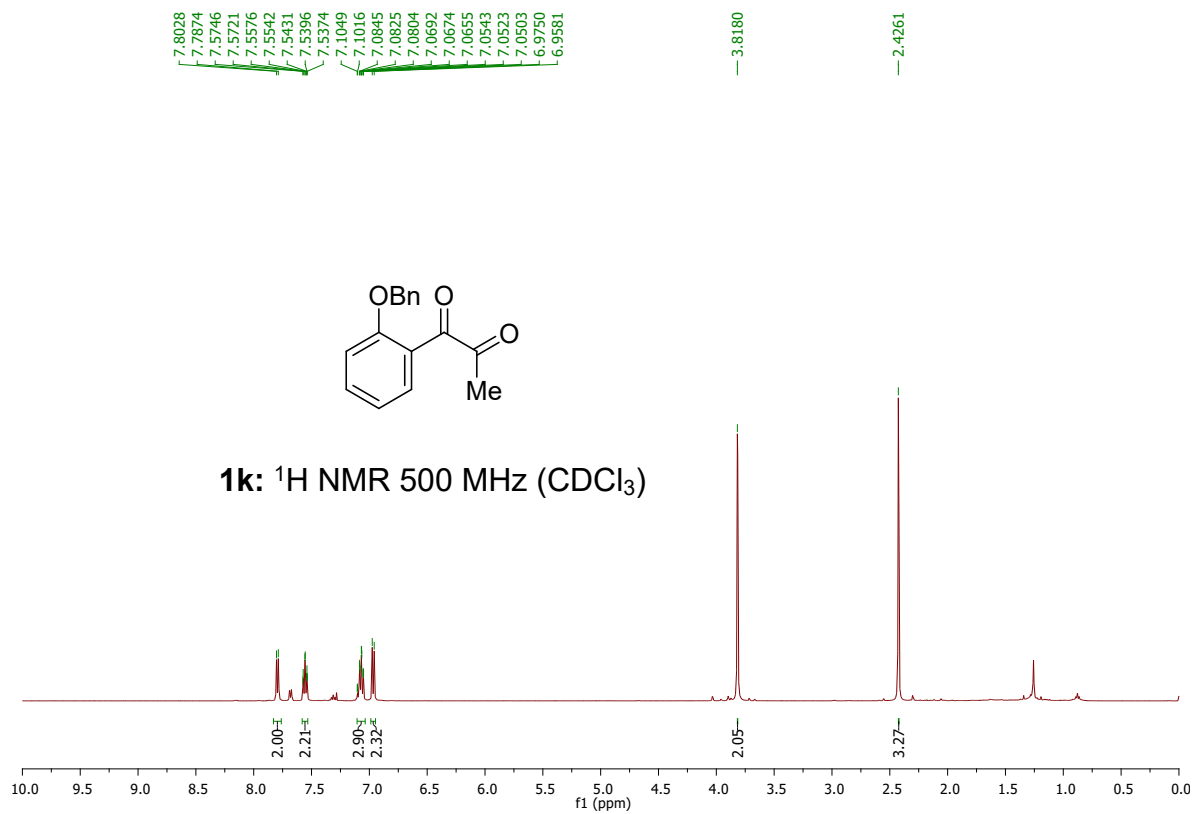


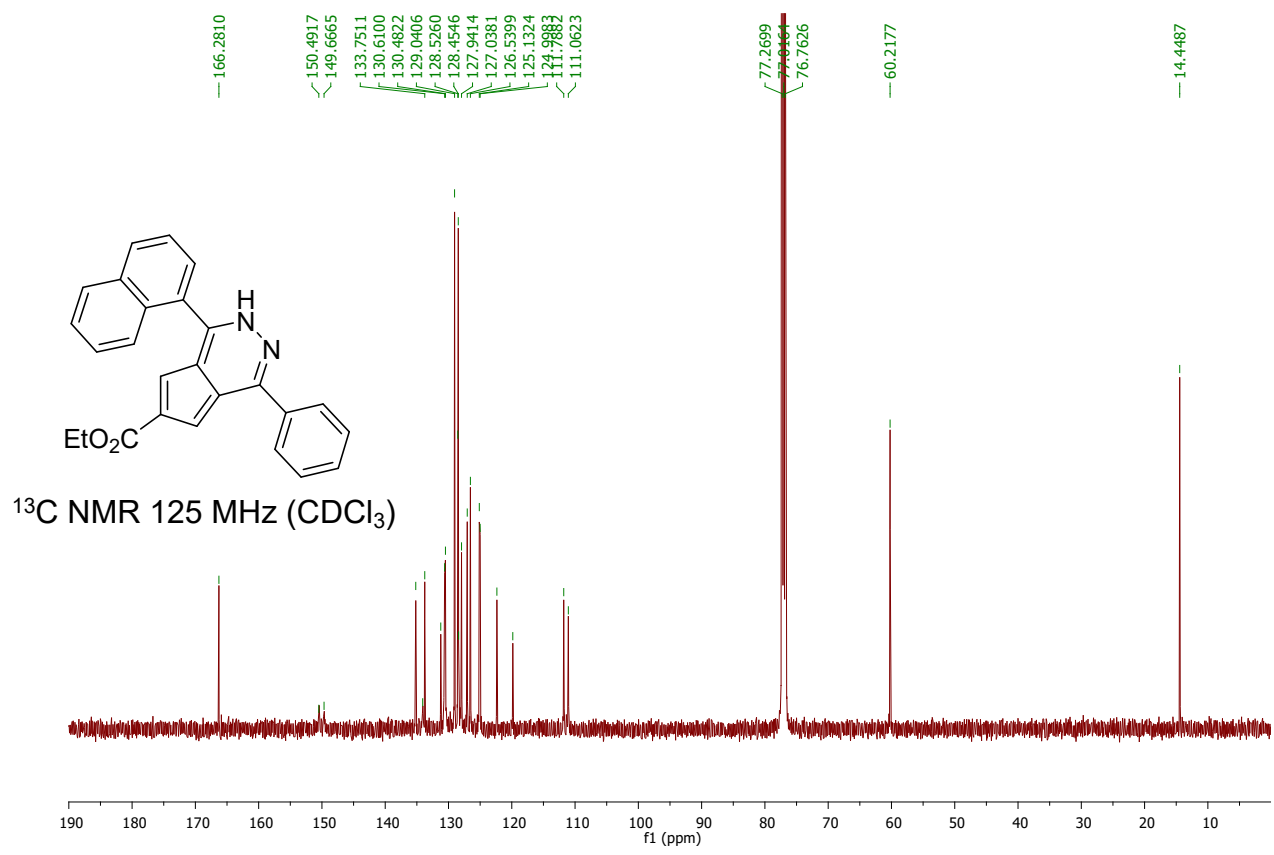
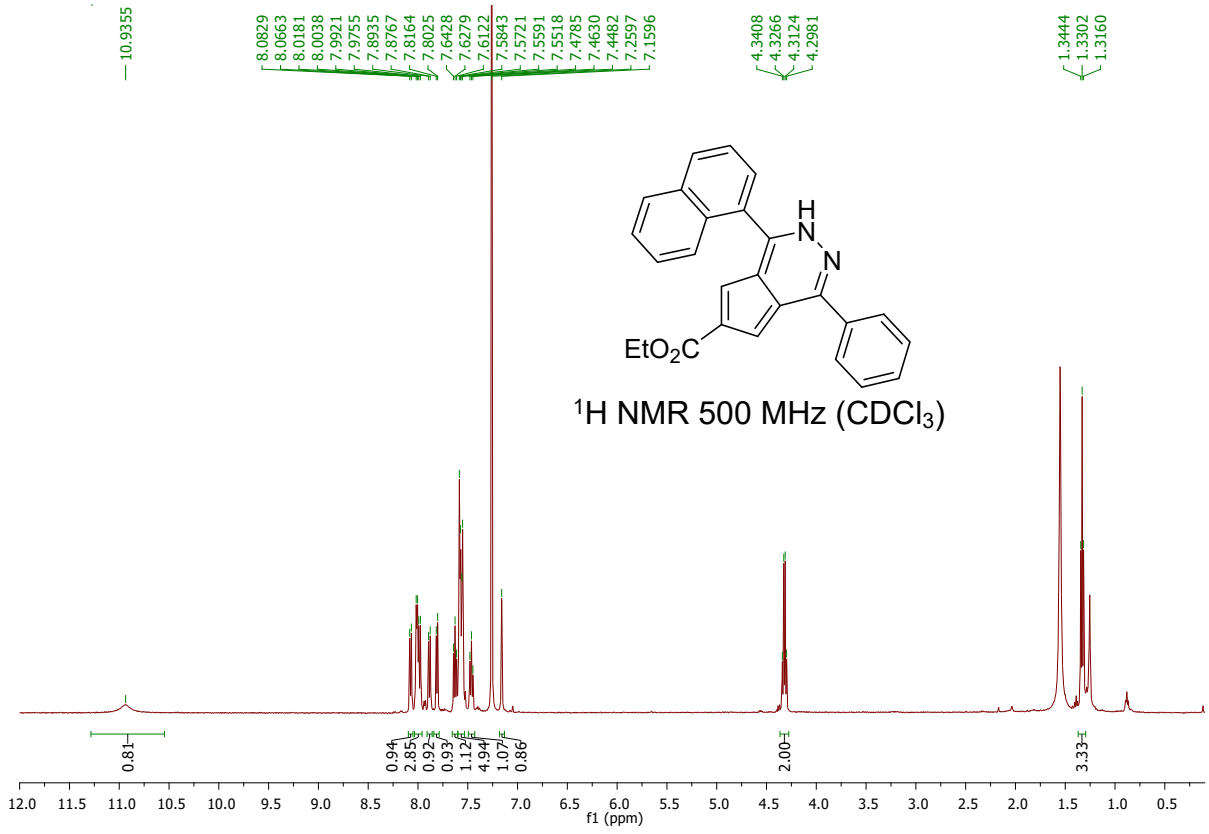












Crystallographic data: Single crystal X-ray structural of compound **3aj** was measured on the Bruker D8 Quest Single Crystal - XRD at 150(2) K using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. 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 S1. The **CCDC** number of compound **3aj** (**2169277**) 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).

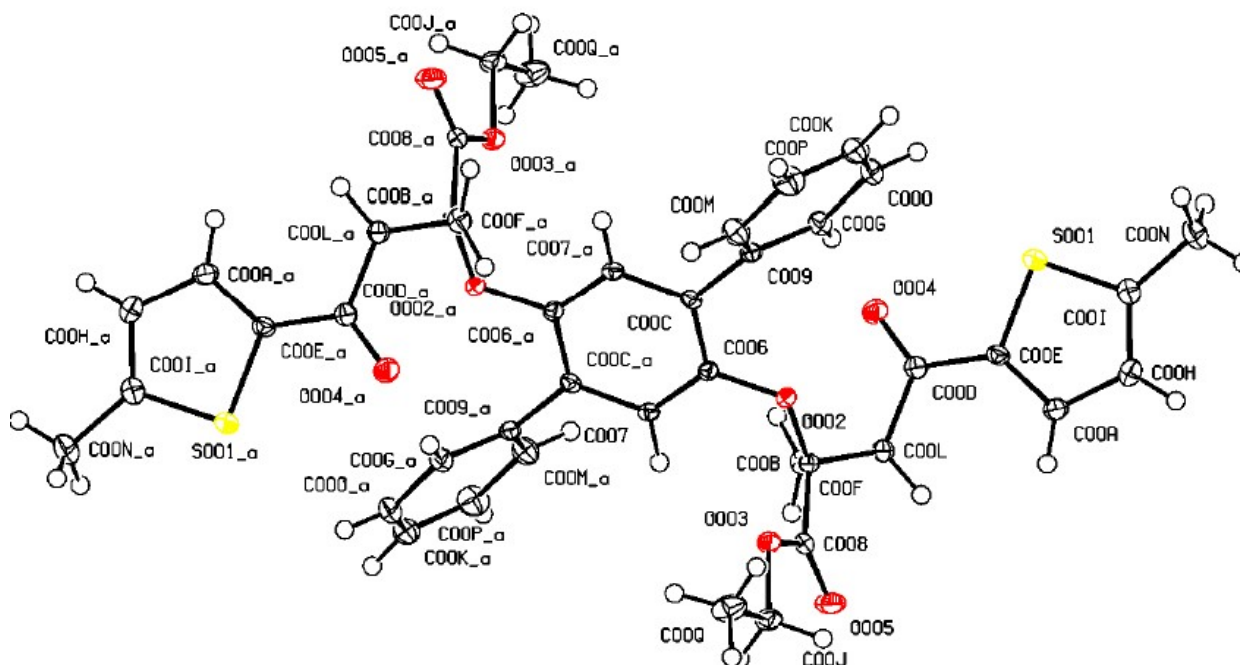


Figure S1 . ORTEP diagram of compound **3aj** (CCDC 2169277), thermal ellipsoids drawn at the 50% probability level.

Table S1. Crystal data for compound 3aj

Compound	3aj
Empirical formula	C ₂₁ H ₁₉ O ₄ S
Formula weight	367.42
Temperature	273.15 K
Wave length (Å)	0.71073 Å
Crystal system, space group	Triclinic, P -1
<i>a</i> (Å)	<i>a</i> = 8.6775(6) Å
<i>b</i> (Å)	<i>b</i> = 9.7016(6) Å
<i>c</i> (Å)	<i>c</i> = 11.8817(8) Å
α (°)	α = 86.390(2) deg.
β (°)	β = 79.605(2) deg.
γ (°)	γ = 66.426(2) deg.
Volume (Å ³)	901.70(10) Å ³
Z, Calculated density (mg/m ³)	2, 1.353 Mg/m ³
Absorption coefficient (mm ⁻¹)	0.203 mm ⁻¹
F(000)	386
Θ range (deg)	2.68 to 28.22 deg.
Limiting indices	-11 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 12, -15 ≤ <i>l</i> ≤ 15
Reflections collected / unique	20304 / 4474 [R(int) = 0.0447]
Completeness to $\Theta = 25.242$	99.6 %
Max. and min. transmission	0.746 and 0.665
Absorption correction	none
Data / restraints / parameters	4474/ 0 / 241
Goodness-of-fit on F ²	1.100
Final R indices [I > 2σ(I)]	R1 = 0.0367, wR2 = 0.0981
R indices (all data)	R1 = 0.0440, wR2 = 0.1084
Extinction coefficient	n/a
Largest diff. peak and hole (e.Å ⁻³)	0.399 and -0.310 e.Å ⁻³
CCDC	2169277

Crystallographic data: Single crystal X-ray structural of compound **4qa** was measured on the Bruker D8 Quest Single Crystal - 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 **4qa** (**2169276**) 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).

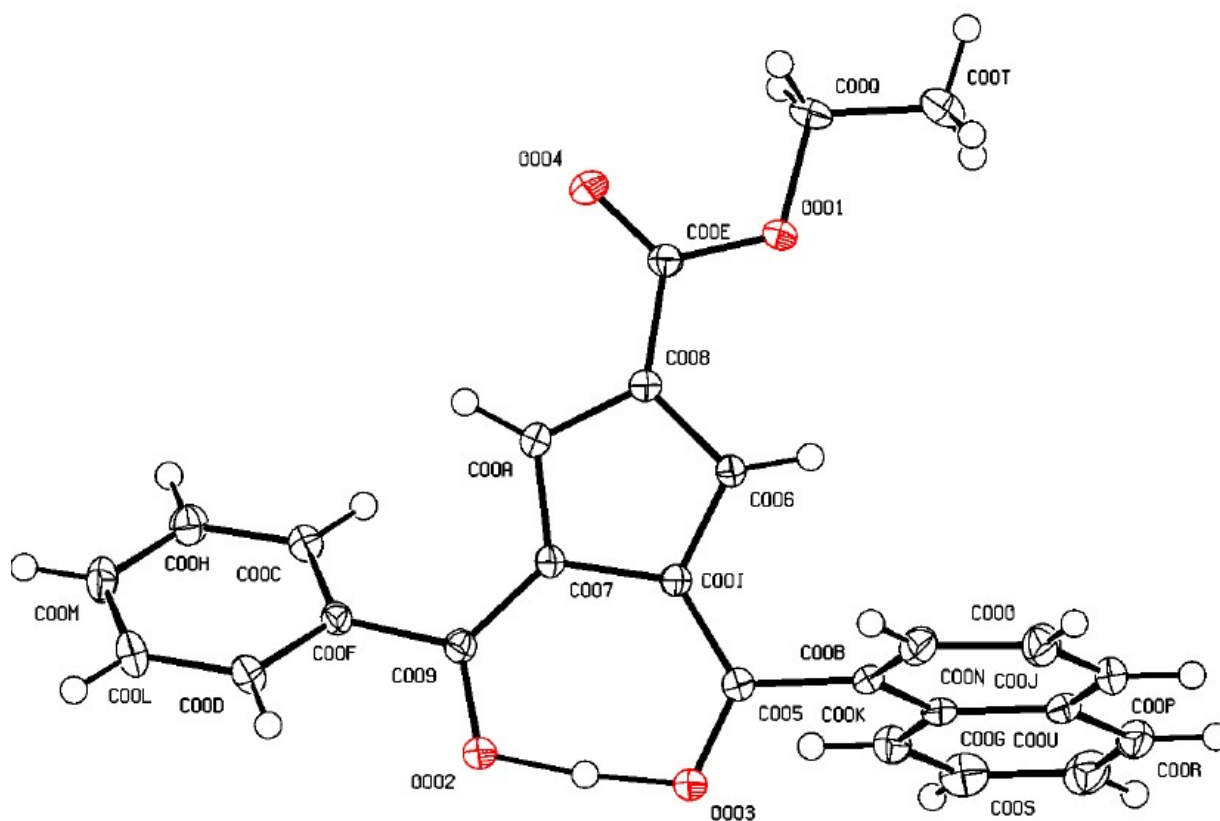


Figure S2. ORTEP diagram of compound **4qa** (CCDC 2169276), thermal ellipsoids drawn at the 50% probability level.

Table S2. Crystal data for compound 4qa.

Compound	4qa
Empirical formula	C ₂₆ H ₂₀ O ₄
Formula weight	396.42
Temperature	273.15 K
Wave length (Å)	0.71073 Å
Crystal system, space group	Monoclinic, P 1 2 ₁ /n 1
<i>a</i> (Å)	<i>a</i> = 7.3447(5)Å
<i>b</i> (Å)	<i>b</i> = 21.7403(15)Å
<i>c</i> (Å)	<i>c</i> = 12.7291(10) Å
α (°)	alpha = 90 deg.
β (°)	beta = 103.687(2)deg.
γ (°)	gamma = 90 deg.
Volume (Å ³)	1974.8(2) Å ³
Z, Calculated density (mg/m ³)	4, 1.333 Mg/m ³
Absorption coefficient (mm ⁻¹)	0.089 mm ⁻¹
F(000)	832
Θ range (deg)	2.495 to 28.309 deg.
Limiting indices	-9<= <i>h</i> <=9, -28<= <i>k</i> <=28, -16<= <i>l</i> <=16
Reflections collected / unique	31839 / 4896 [R(int) = 0.0536]
Completeness to $\Theta = 25.242$	99.8 %
Max. and min. transmission	0.7457 and 0.7019
Absorption correction	multi-scan
Data / restraints / parameters	4896 / 0 / 276
Goodness-of-fit on F ²	1.190
Final R indices [I>2 σ (I)]	R1 = 0.0453, wR2 = 0.1469
R indices (all data)	R1 = 0.0573, wR2 = 0.1621
Extinction coefficient	n/a
Largest diff. peak and hole (e.Å ⁻³)	0.360 and -0.242 e.Å ⁻³
CCDC	2169276

Crystallographic data: Single crystal X-ray structural of compound **4vh** 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 1.2Ueq of their parent atoms. The crystal data are summarized in Table S3. The CCDC number of compound **4vh** (**2169275**) 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).

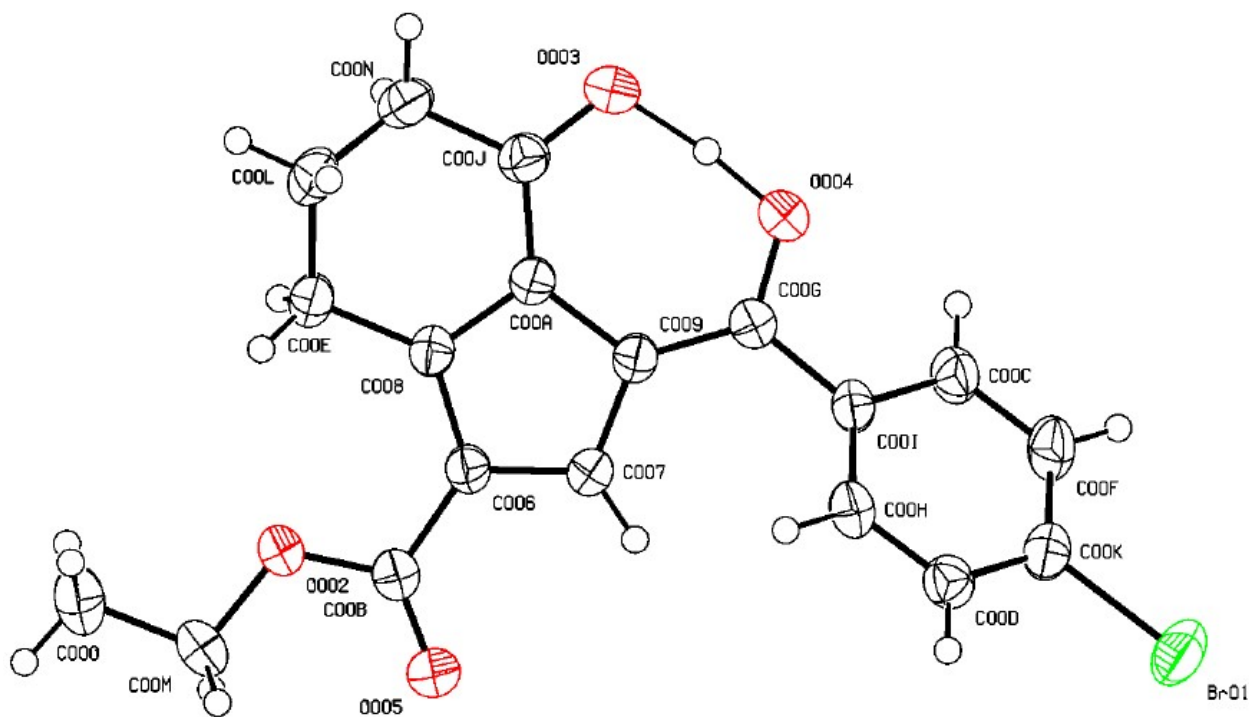


Figure S3. ORTEP diagram of compound **4vh** (CCDC 2169275), thermal ellipsoids drawn at the 50% probability level.

Table S3. Crystal data for compound 4vh.

Compound	4vh
Empirical formula	C ₁₉ H ₁₇ Br O ₄
Formula weight	389.23
Temperature	293 K
Wave length (Å)	0.71073 Å
Crystal system, space group	Monoclinic, P 21/c
<i>a</i> (Å)	a = 8.8846(3) Å
<i>b</i> (Å)	b = 10.4690(6) Å
<i>c</i> (Å)	c = 18.3384(9) Å
α (°)	alpha = 90(4) deg.
β (°)	beta = 79.975 deg.
γ (°)	gamma = 90 (4) deg.
Volume (Å ³)	1679.66(14) Å ³
Z, Calculated density (mg/m ³)	4, 1.539 Mg/m ³
Absorption coefficient (mm ⁻¹)	2.467 mm ⁻¹
F(000)	792
Θ range (deg)	3.3510 to 28.5250 deg.
Limiting indices	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -24 ≤ l ≤ 24
Reflections collected / unique	19410 / 4138 [R(int) = 0.0444]
Completeness to $\Theta = 25.242$	99.9 %
Max. and min. transmission	35 and 25
Absorption correction	none
Data / restraints / parameters	4138/ 0 / 223
Goodness-of-fit on F ²	1.039
Final R indices [I > 2σ(I)]	R1 = 0.0346, wR2 = 0.0793
R indices (all data)	R1 = 0.0504, wR2 = 0.0874
Extinction coefficient	n/a
Largest diff. peak and hole (e.Å ⁻³)	0.385 and -0.469 e.Å ⁻³
CCDC	2169275