

Electronic Supplementary Information

Divergent synthesis of 3,4-dihydrodibenzo[*b,d*]furan-1(2*H*)-ones and isocoumarins via additive-controlled chemoselective C-C or C-N bond cleavage

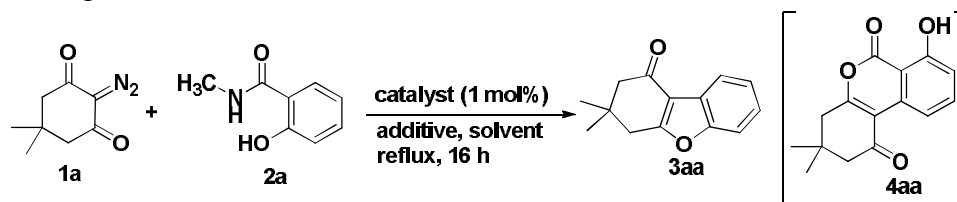
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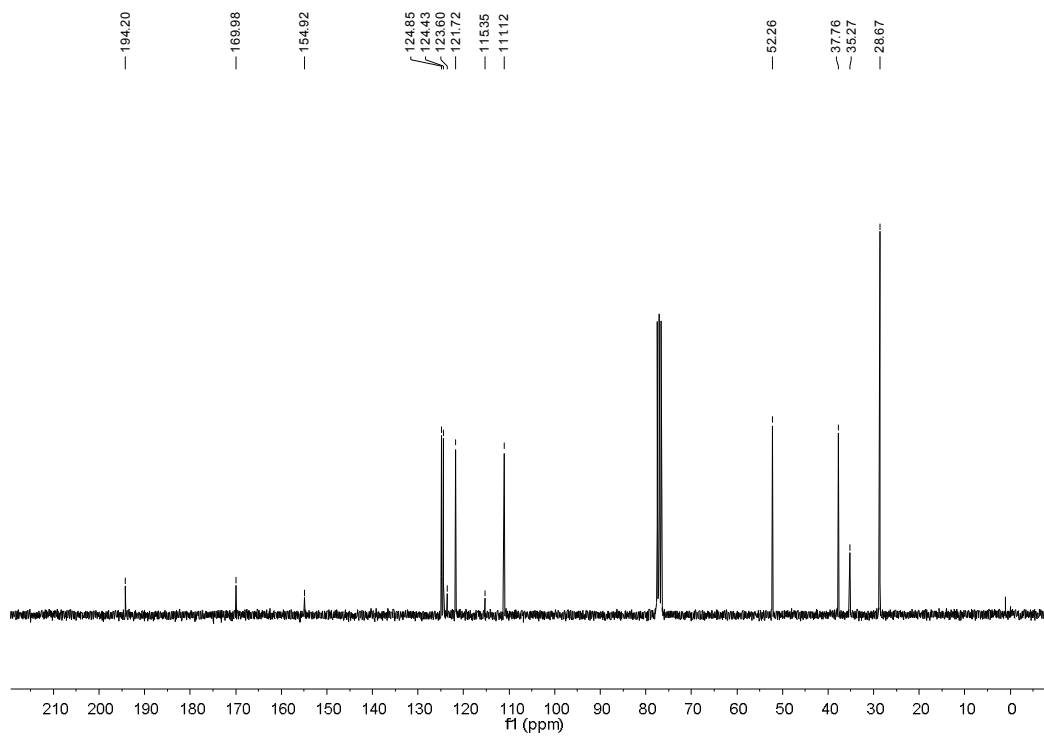
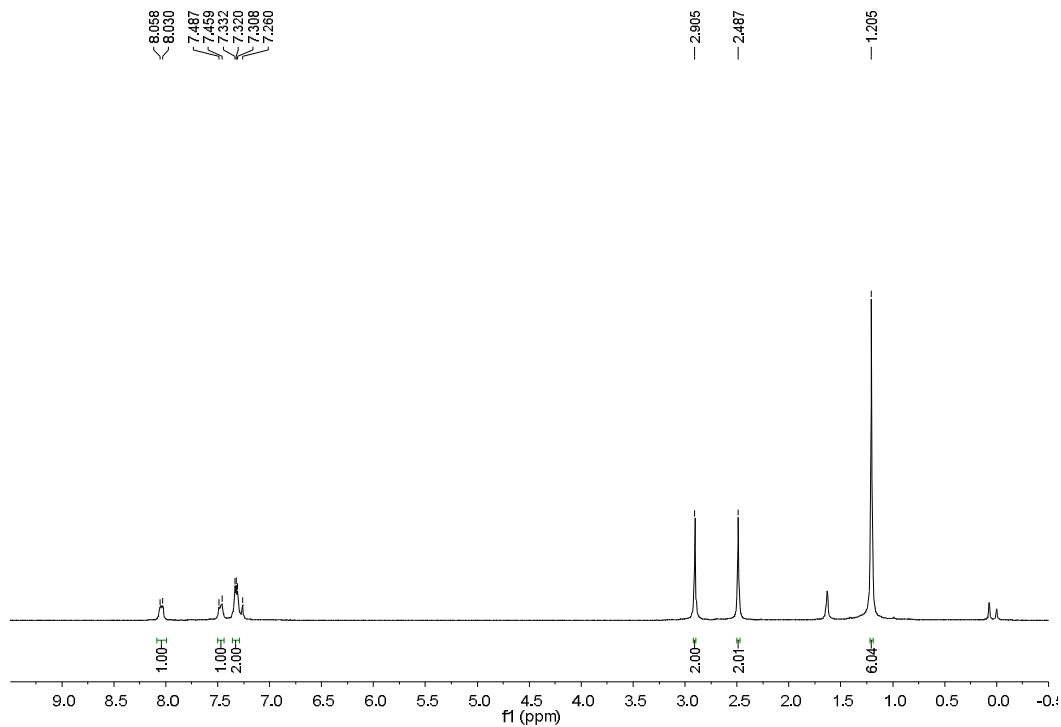
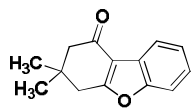
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Table S1 Optimization of the Reaction Conditions^a

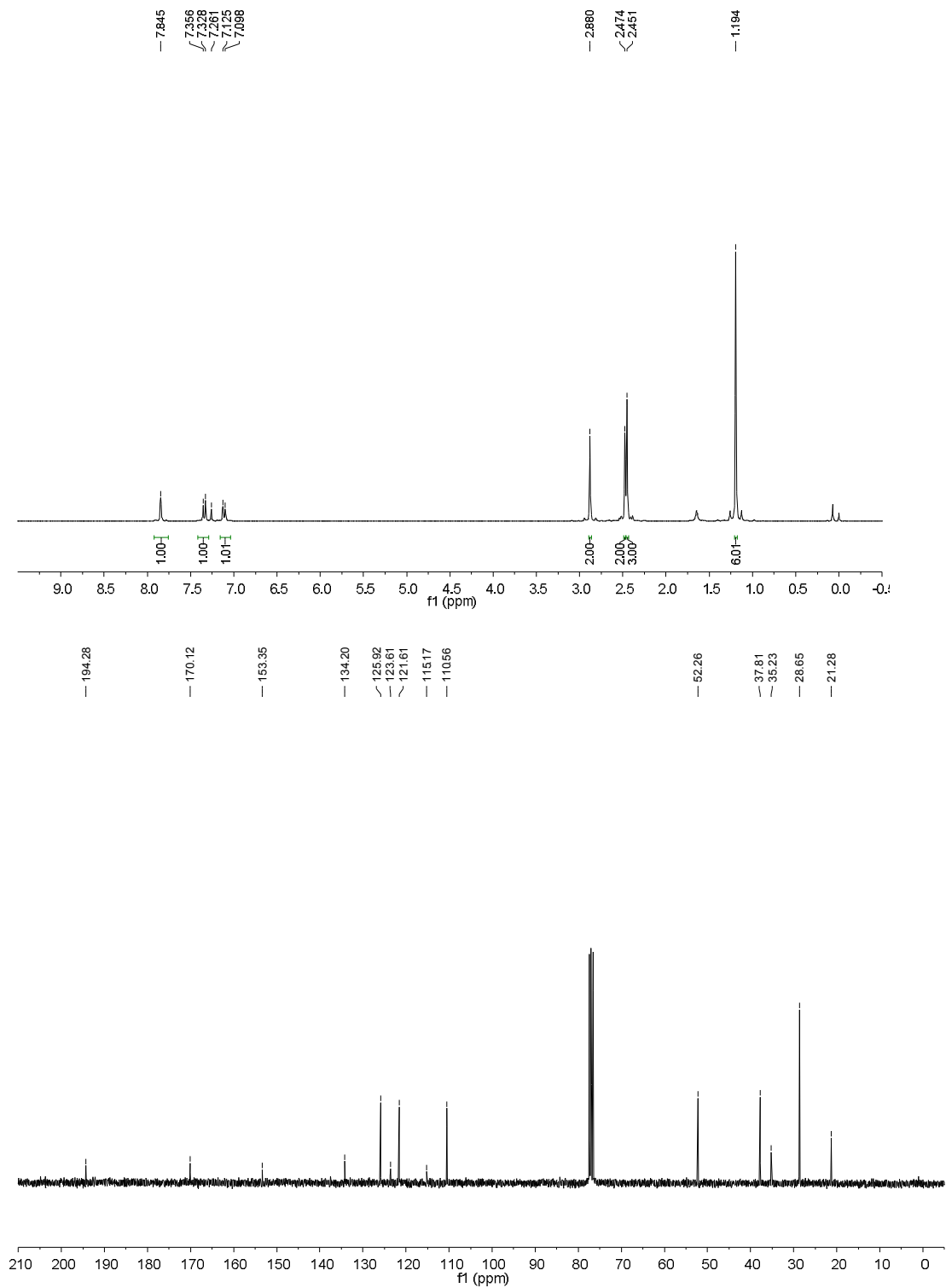
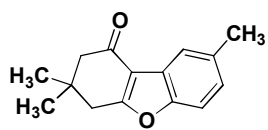
entry	catalyst	additive (mol%)	solvent	Temp (°C)	Yield ^b (%)
1	[(<i>p</i> -cymene)RuCl ₂] ₂	AgNTf ₂ (10)	MeOH	reflux	trace
2	Ru(PPh ₃)Cl ₂	AgNTf ₂ (10)	MeOH	reflux	trace
3	Pd(OAc) ₂	AgNTf ₂ (10)	MeOH	reflux	trace
4	CuI	AgNTf ₂ (10)	MeOH	reflux	trace
5	[Cp*RhCl ₂] ₂	CsOPiv (10)	MeOH	reflux	trace
6	[Cp*RhCl ₂] ₂	AgOAc (10)	MeOH	reflux	trace
7	[Cp*RhCl ₂] ₂	CsOAc (10)	MeOH	reflux	trace
8	[Cp*RhCl ₂] ₂	AgSbF ₆ (10)	MeOH	reflux	trace
9 ^c	[Cp*RhCl ₂] ₂	AgNTf ₂ (10)	MeOH	reflux	74
10 ^d	[Cp*RhCl ₂] ₂	AgNTf ₂ (10)	MeOH	reflux	67
11 ^e	[Cp*RhCl ₂] ₂	AgNTf ₂ (10)	MeOH	reflux	53

^a Reaction conditions: 2-diazo-2,2,6,6-tetramethylcyclohexane-1,3-dione **1a** (0.5 mmol), 2-hydroxy-N-methylbenzamide **2a** (0.5 mmol), solvent (3 mL), and catalyst (1.0 mol%), under argon atmosphere. ^b Isolated yields of compound **3aa**. ^c Reaction time was 20 h. ^d Reaction time was 10 h. ^e Reaction time was 8 h.

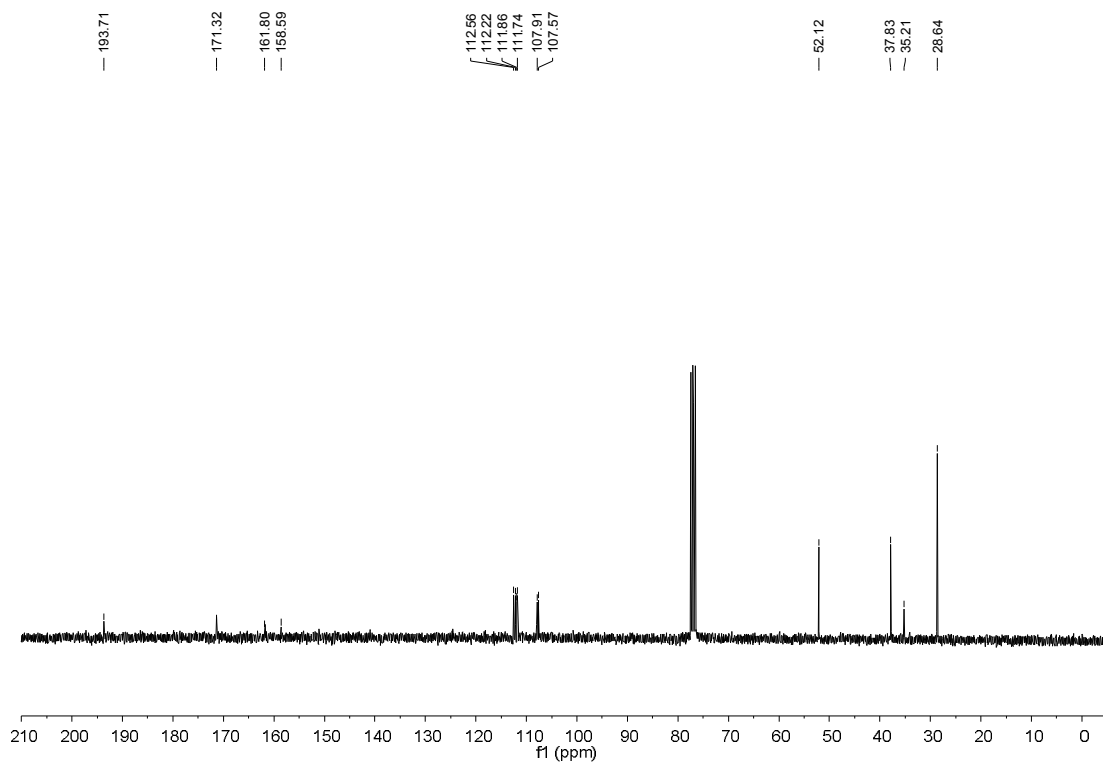
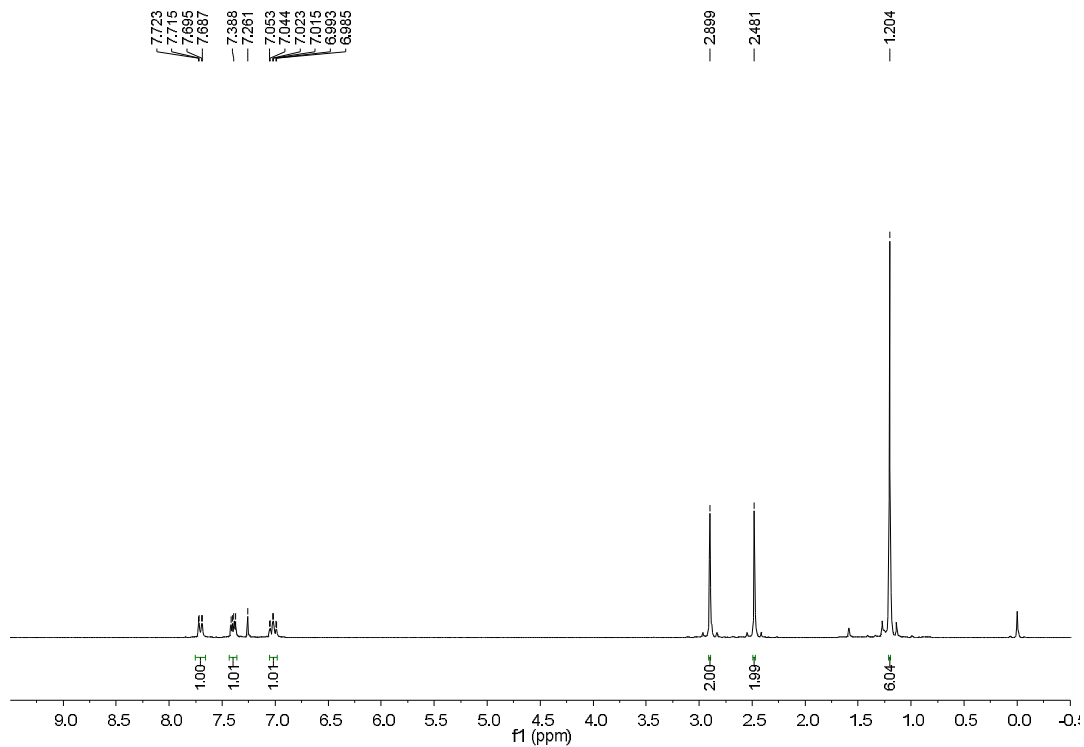
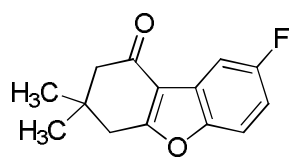
^1H NMR and ^{13}C NMR Spectra of Compound 3aa



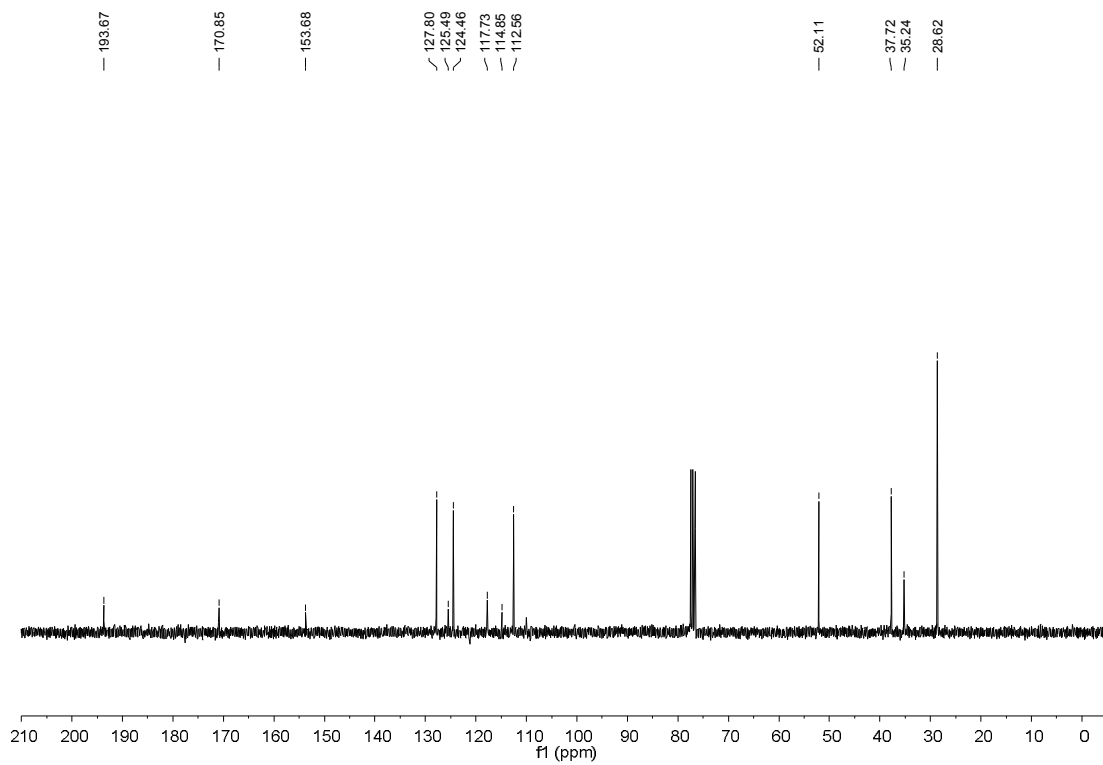
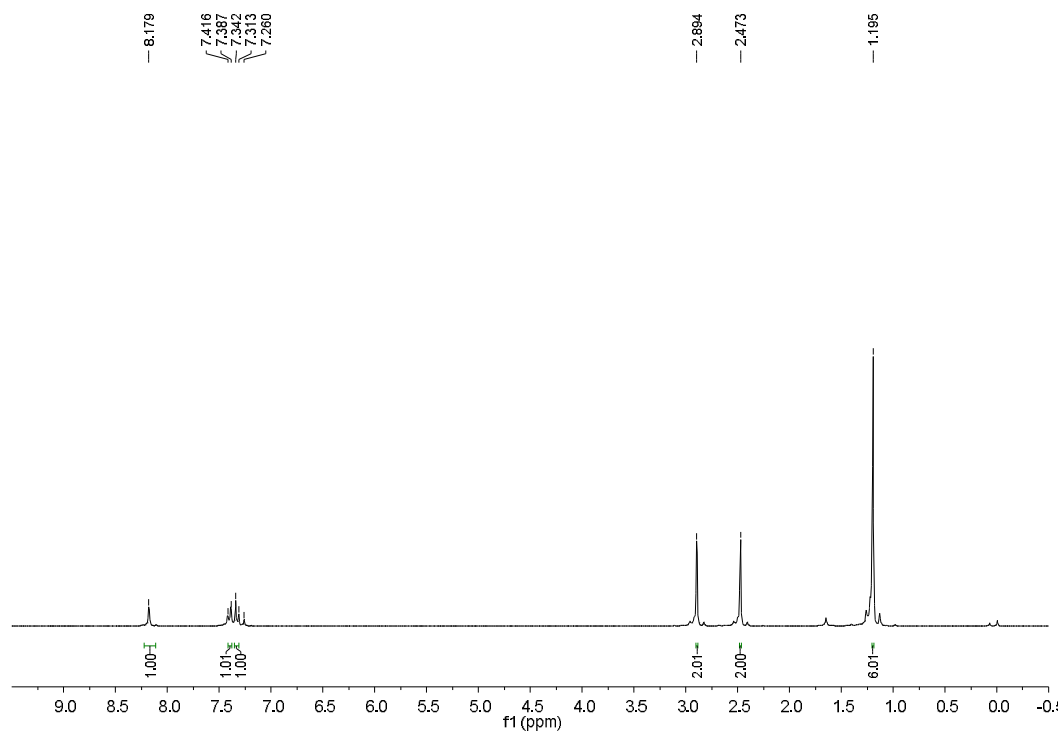
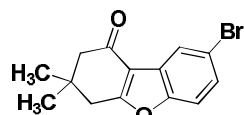
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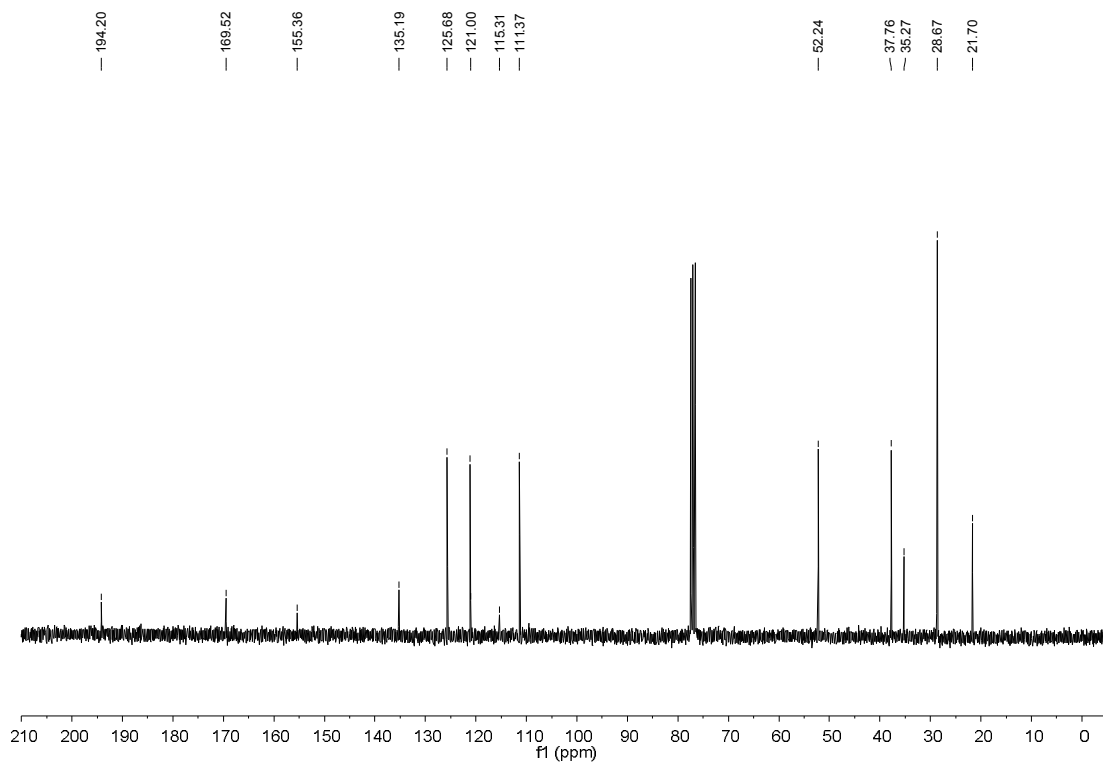
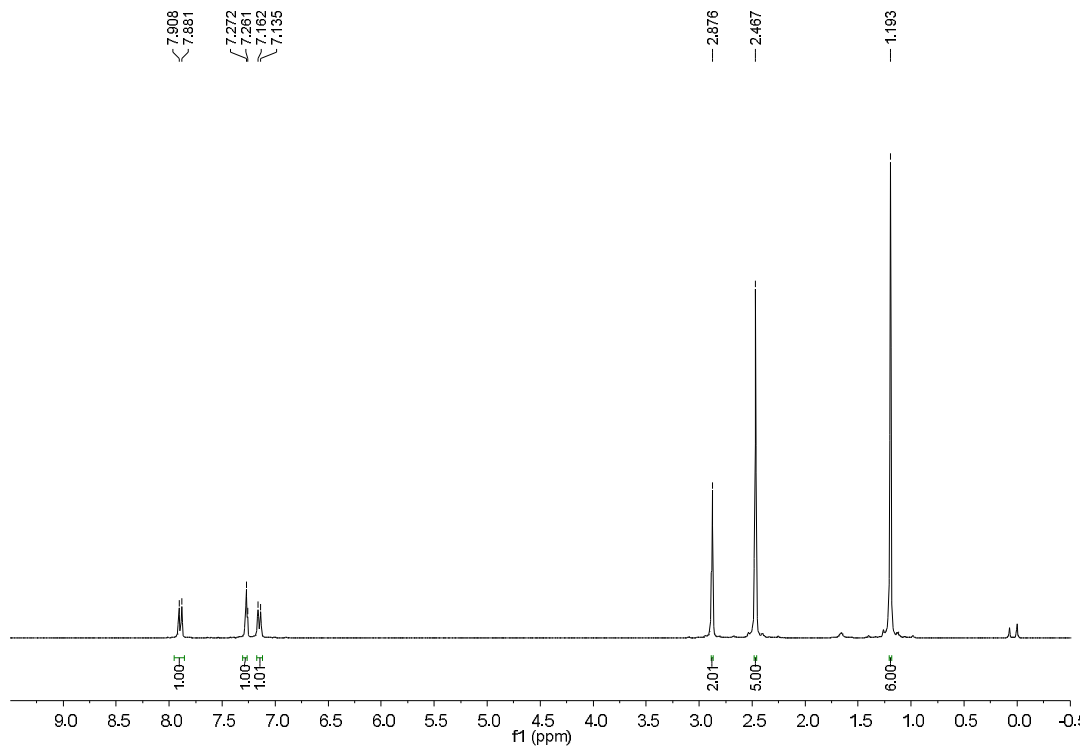
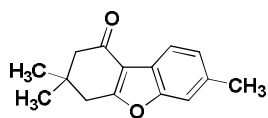
¹H NMR and ¹³C NMR Spectra of Compound 3ac



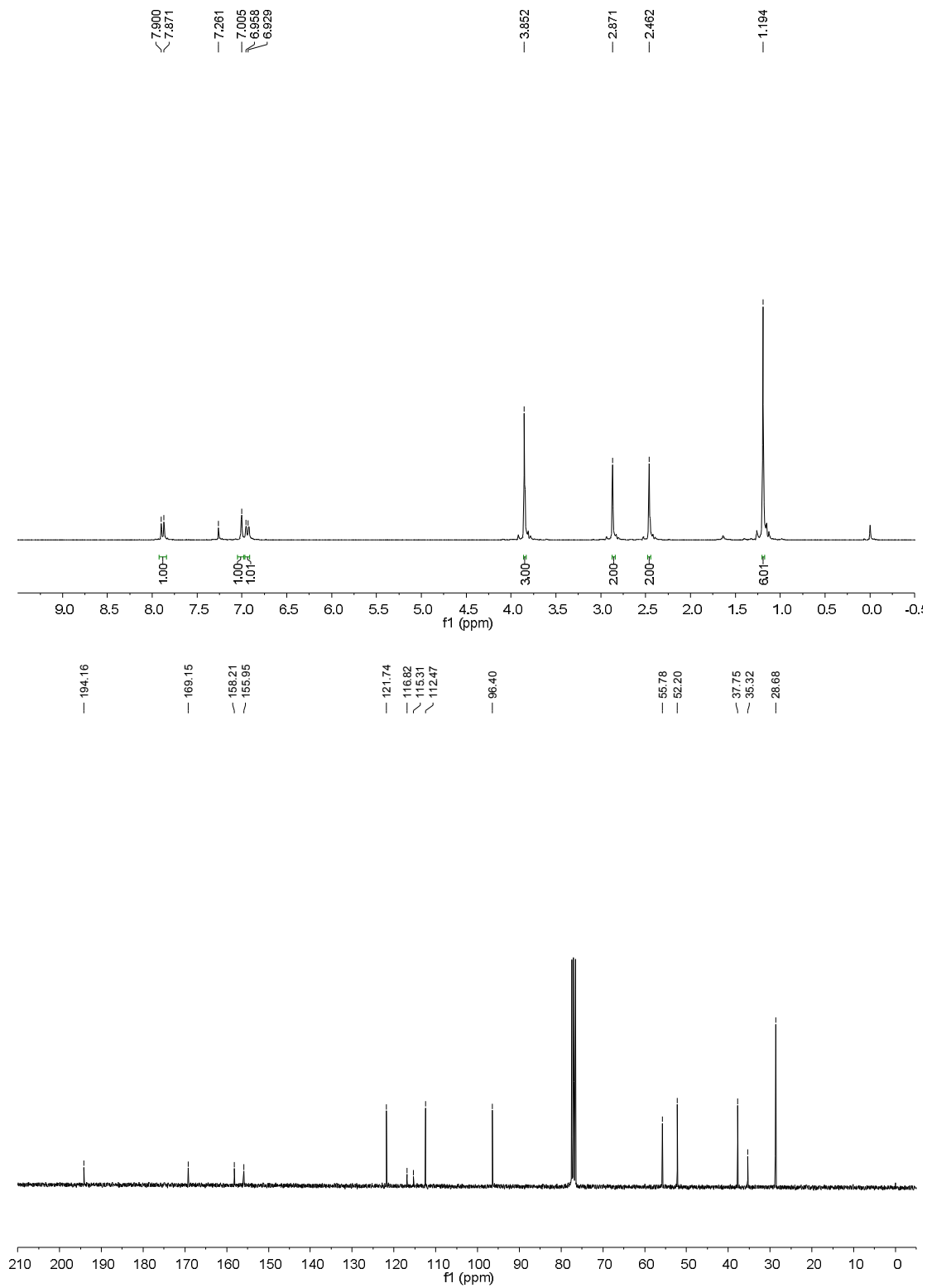
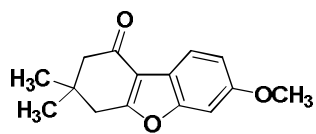
^1H NMR and ^{13}C NMR Spectra of Compound 3ad



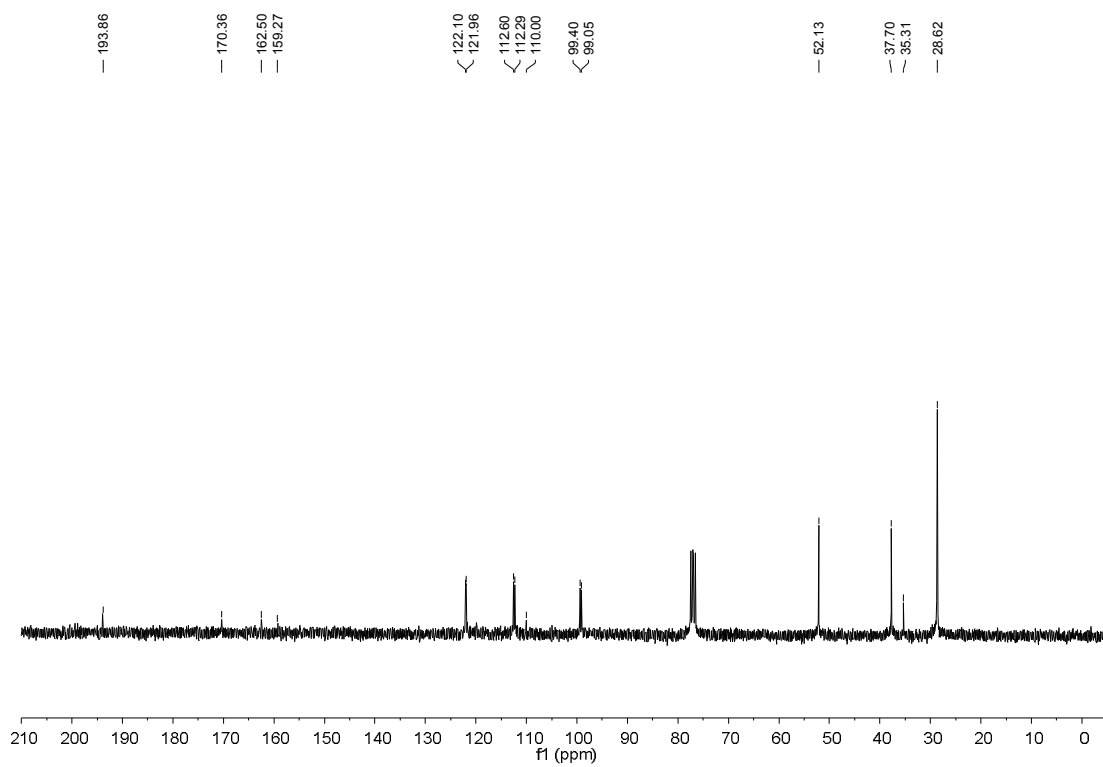
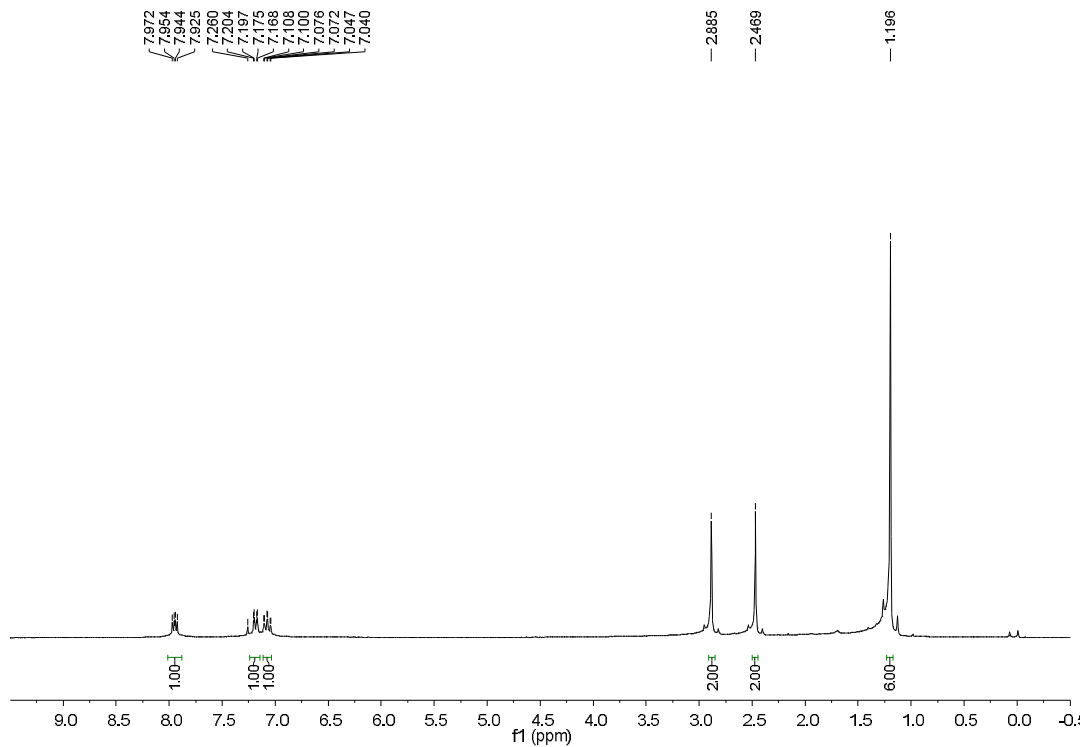
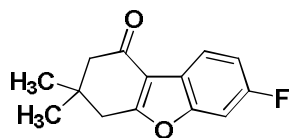
^1H NMR and ^{13}C NMR Spectra of Compound 3ae



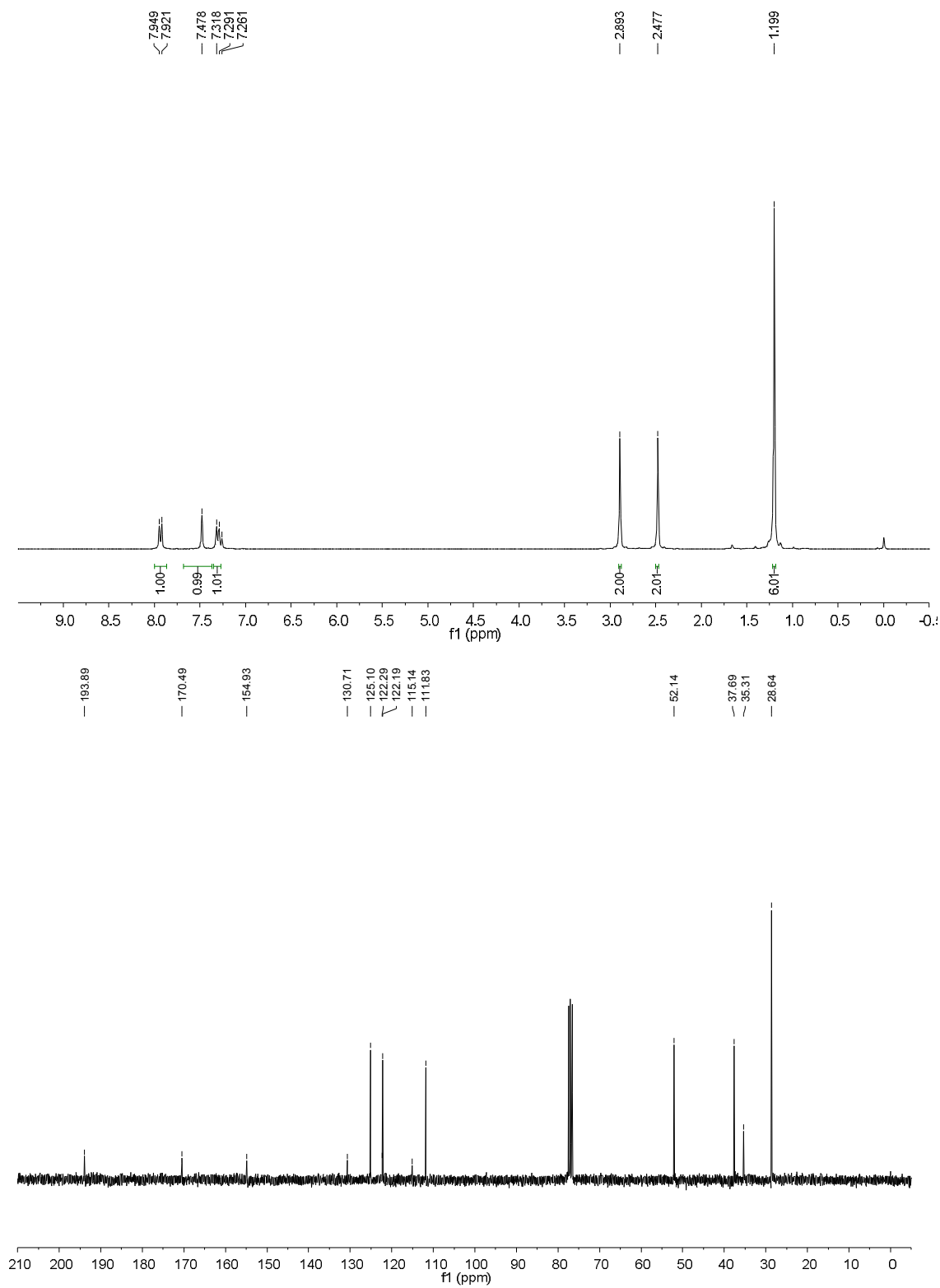
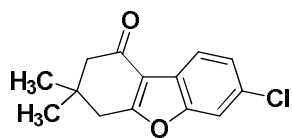
¹H NMR and ¹³C NMR Spectra of Compound 3af



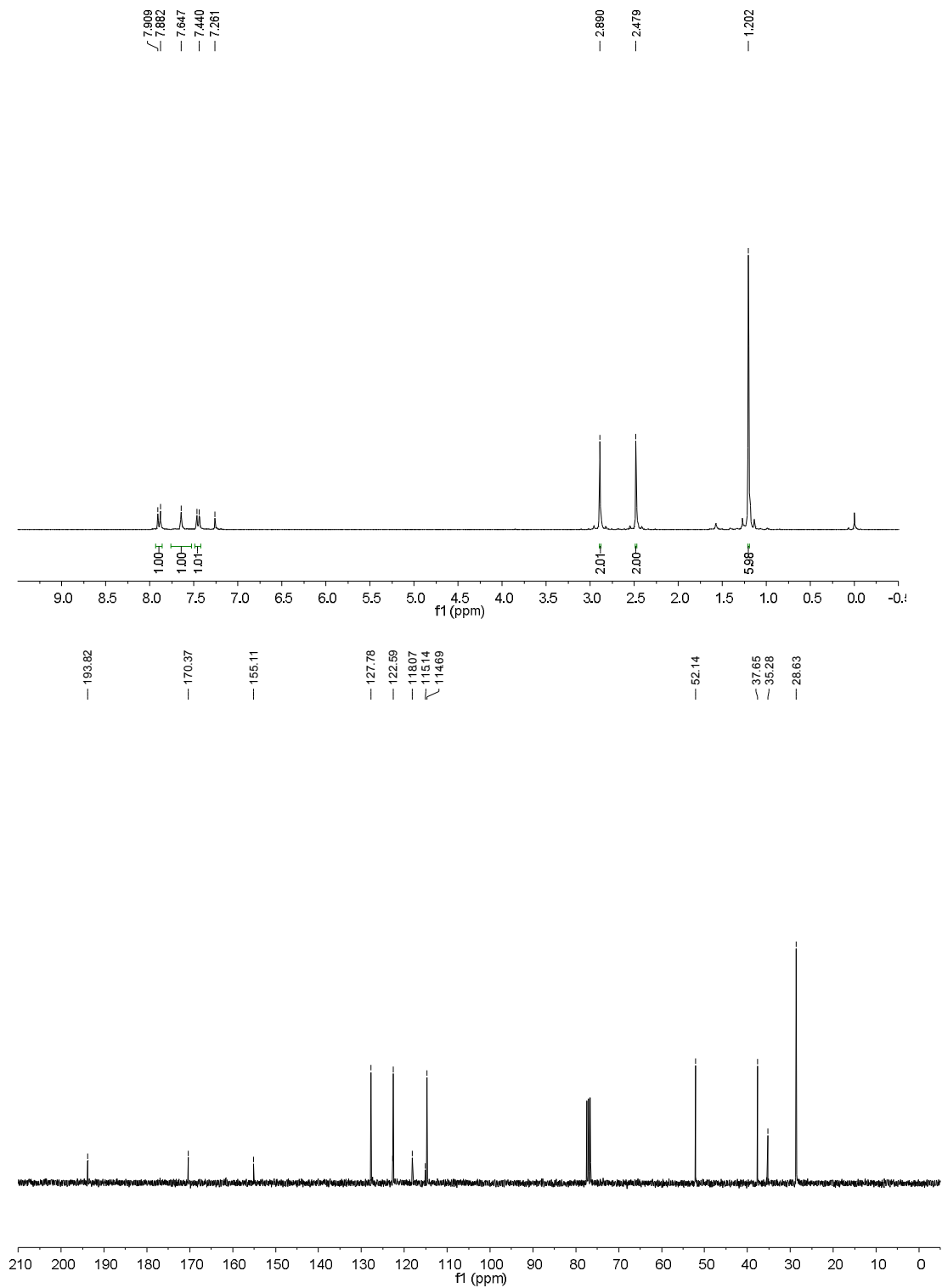
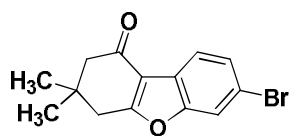
^1H NMR and ^{13}C NMR Spectra of Compound 3ag



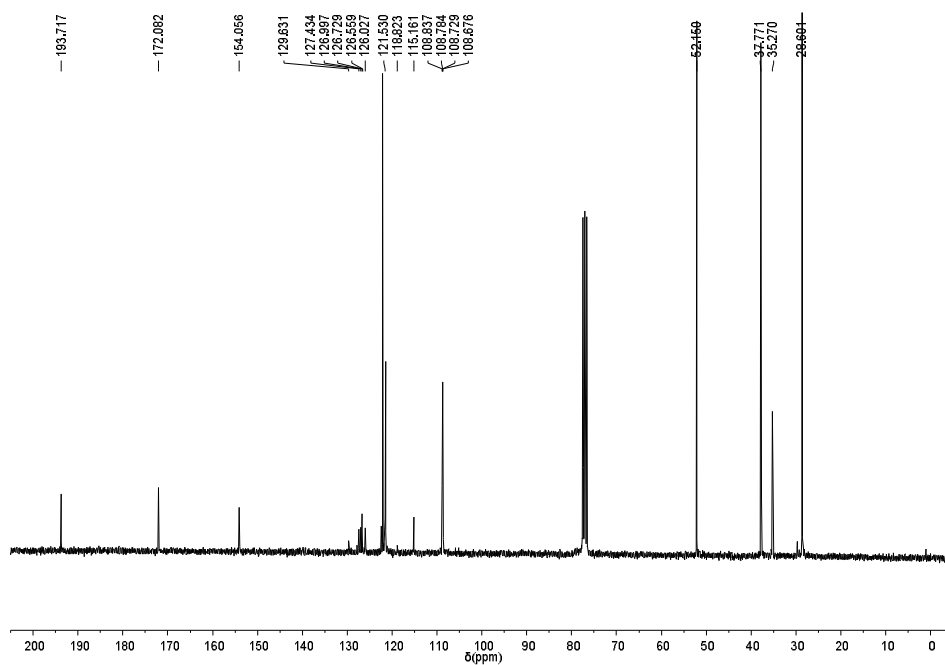
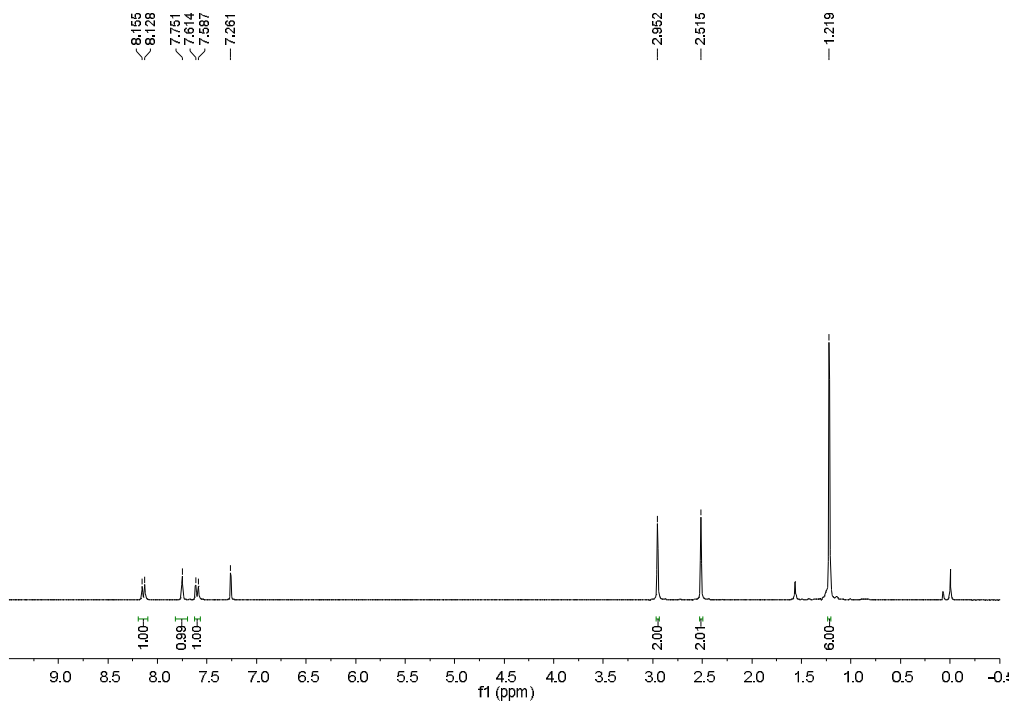
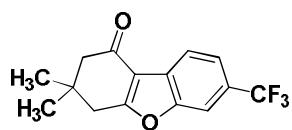
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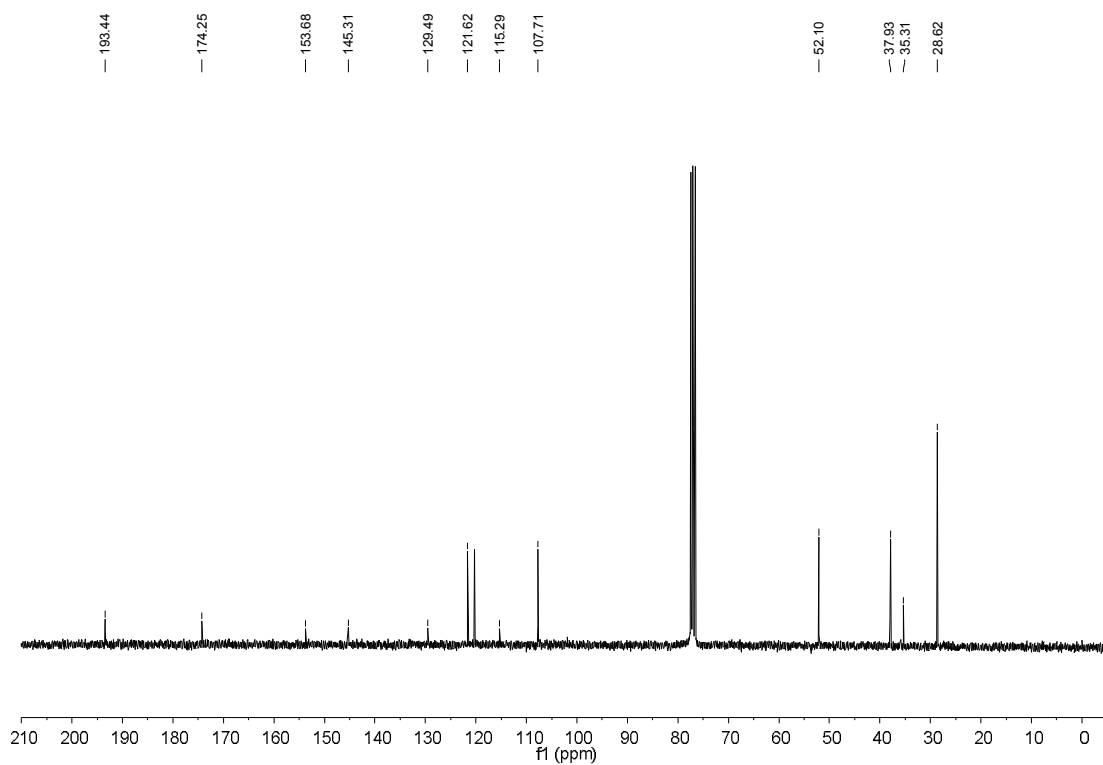
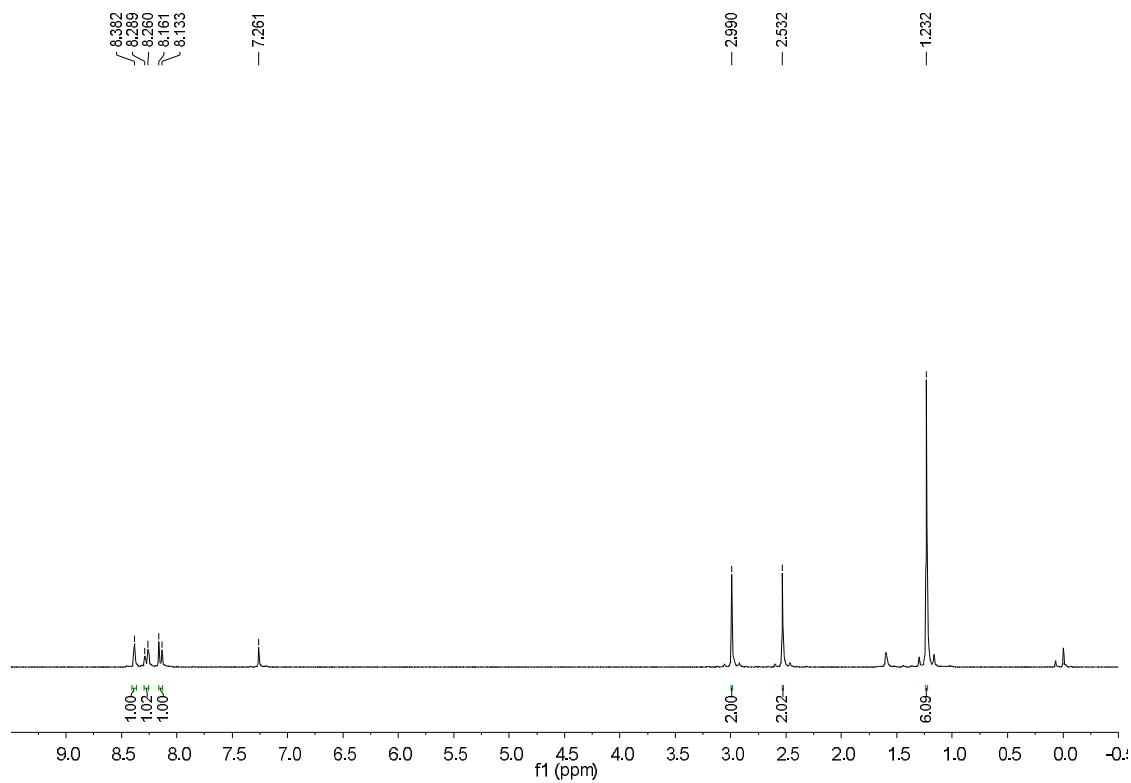
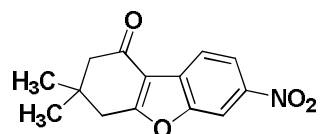
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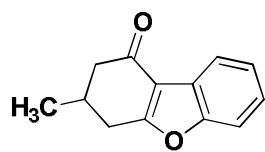
¹H NMR and ¹³C NMR Spectra of Compound 3aj



¹H NMR and ¹³C NMR Spectra of Compound 3ak

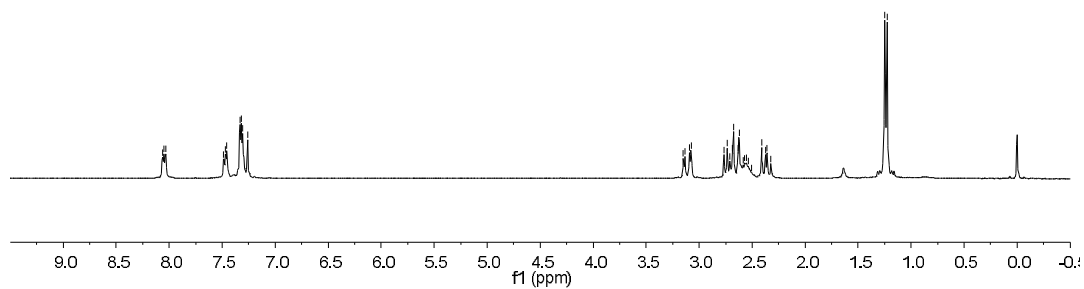


^1H NMR and ^{13}C NMR Spectra of Compound 3ba

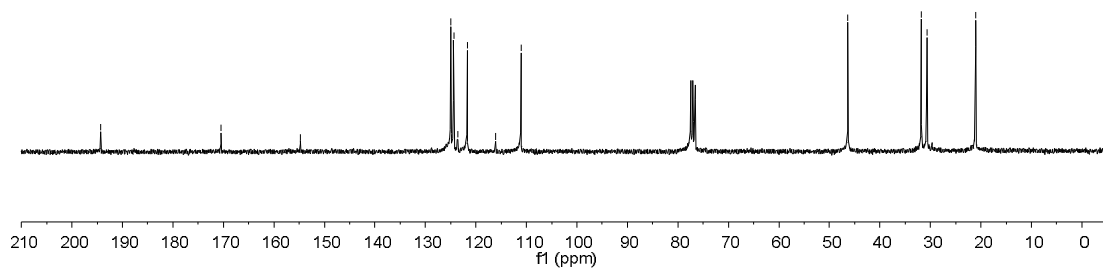


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7.455
7.333
7.318
7.304
7.261

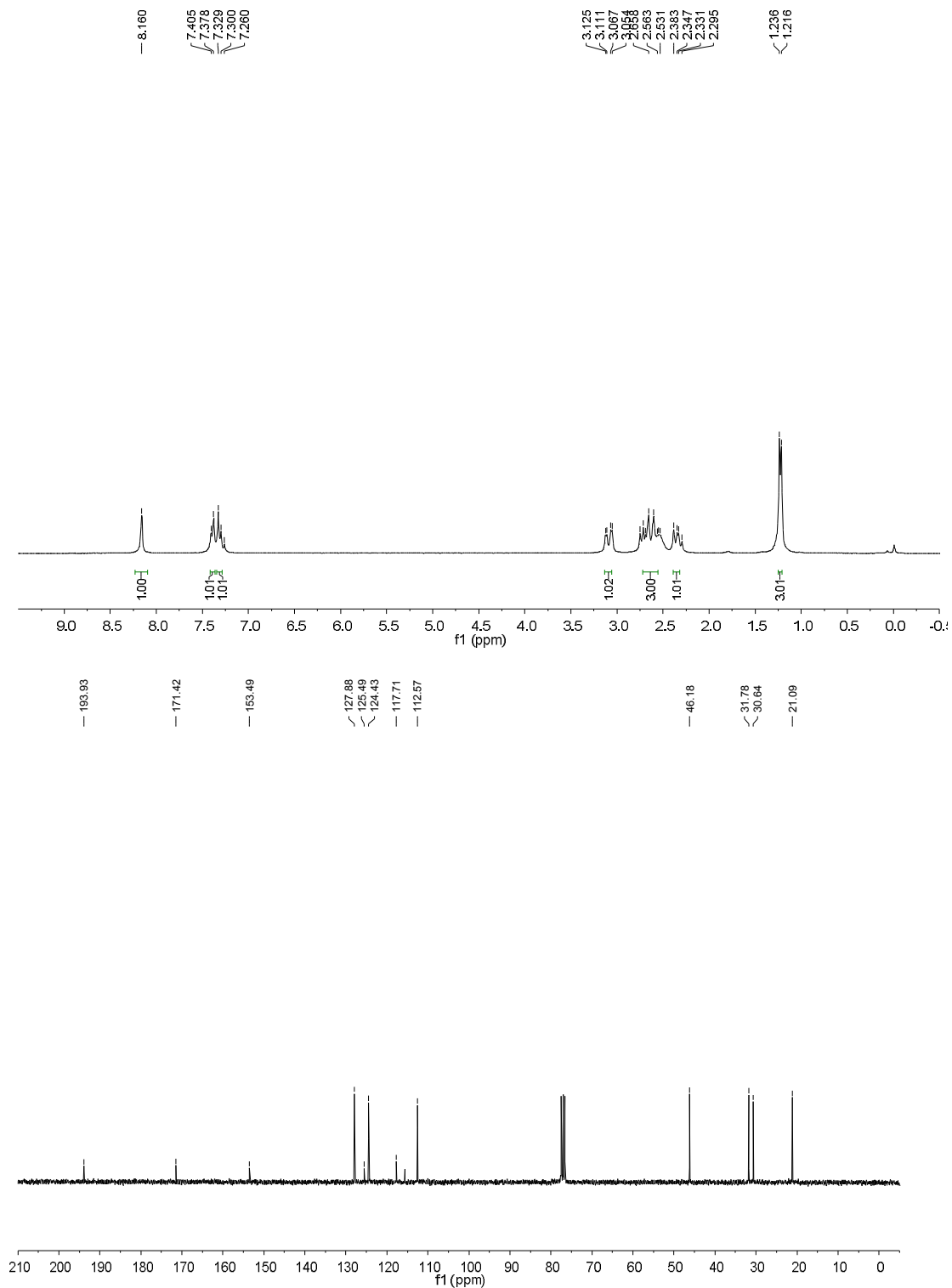
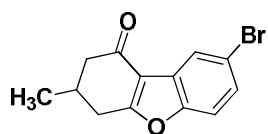
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2.503
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2.322
1.249
1.228



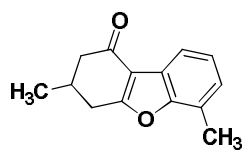
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170.44
154.75
124.91
124.40
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116.16
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31.79
30.69
21.06



¹H NMR and ¹³C NMR Spectra of Compound 3bb



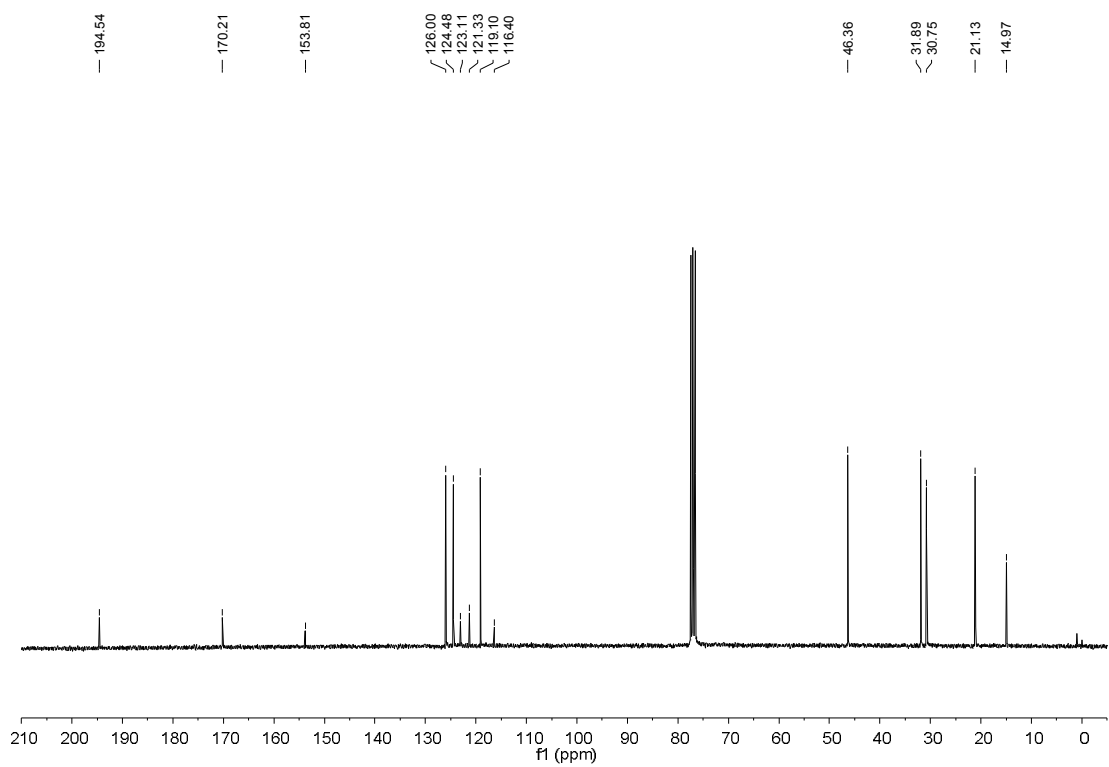
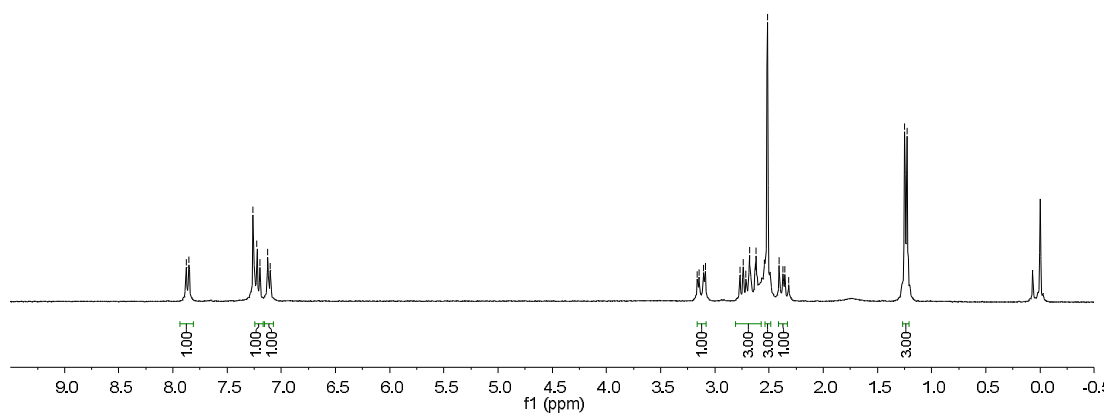
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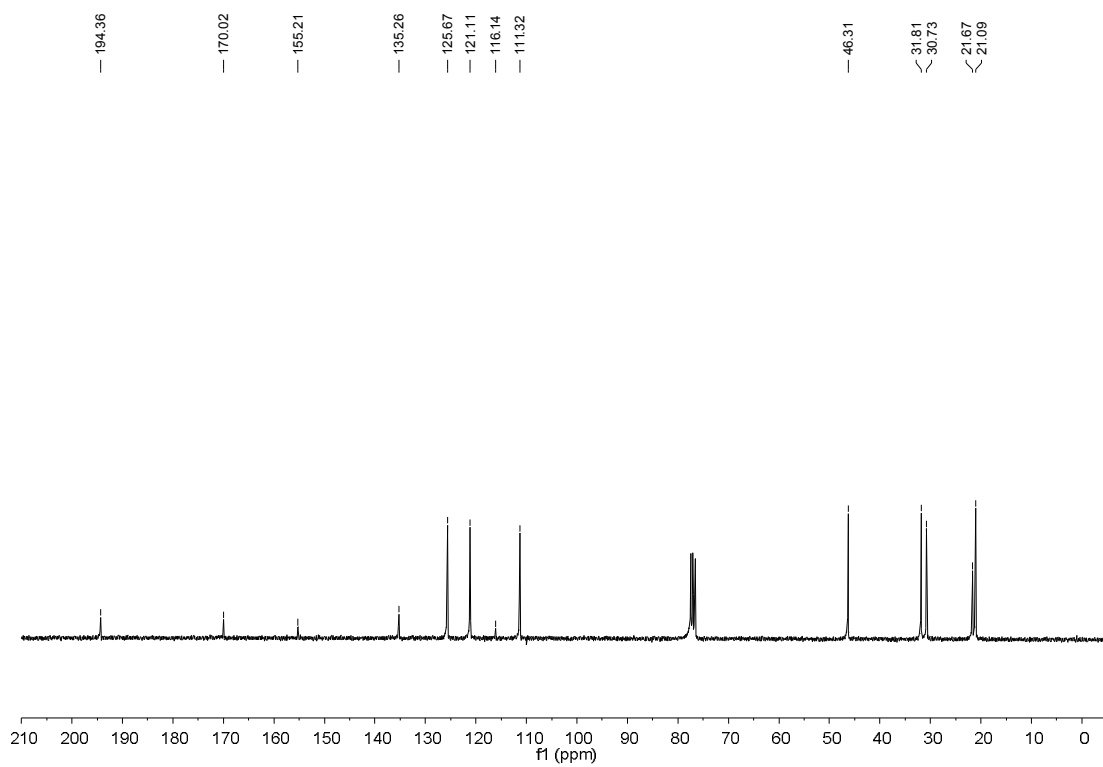
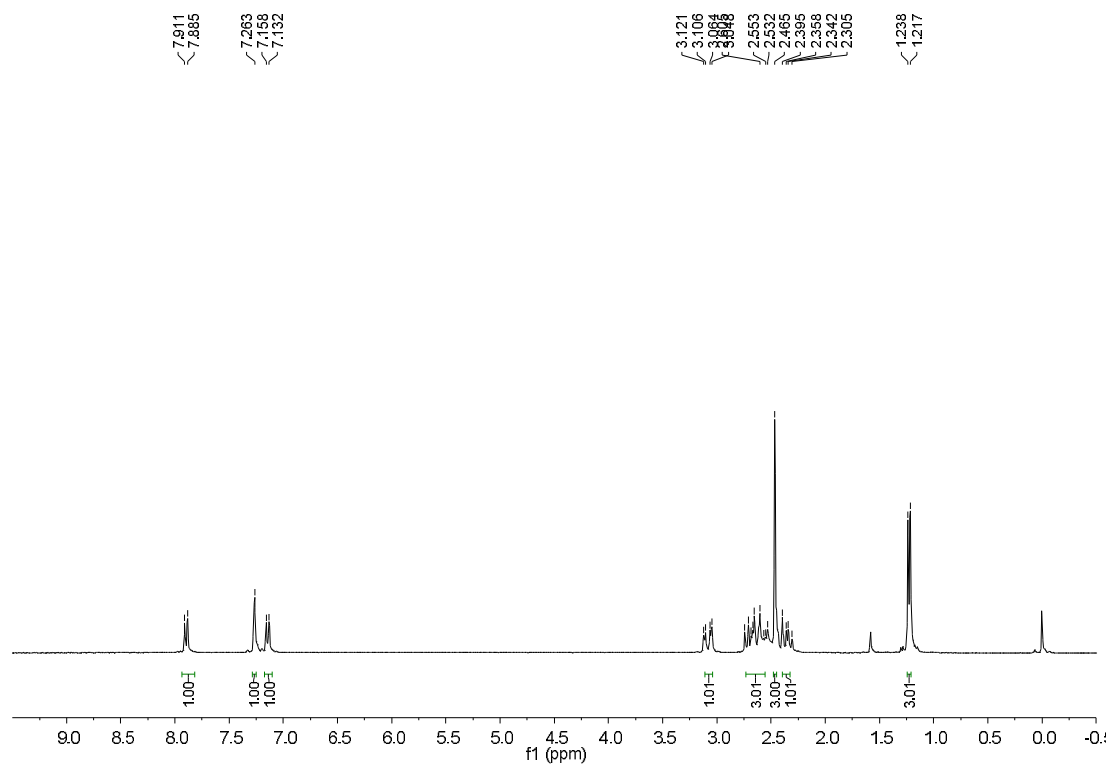
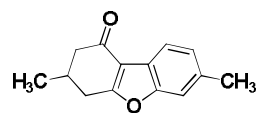
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7.281
7.224
7.199
7.126
7.101

3.163
3.147
3.105
3.090
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2.629
2.619
2.516
2.408
2.372
2.355
2.319

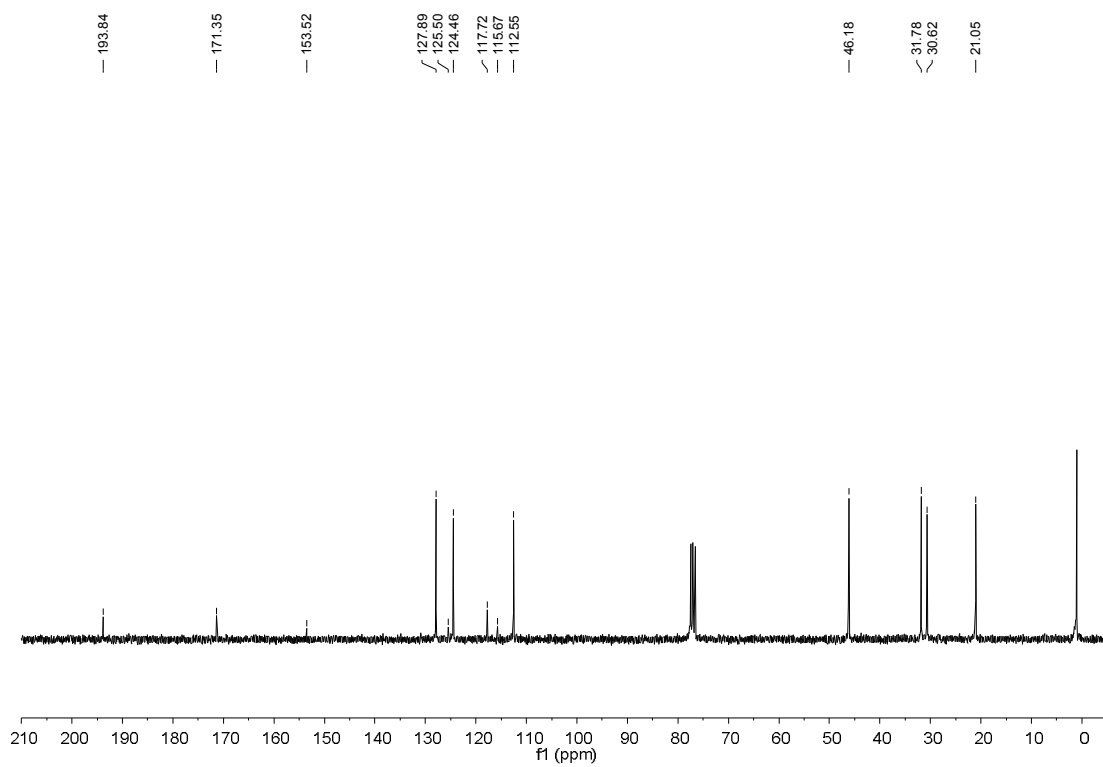
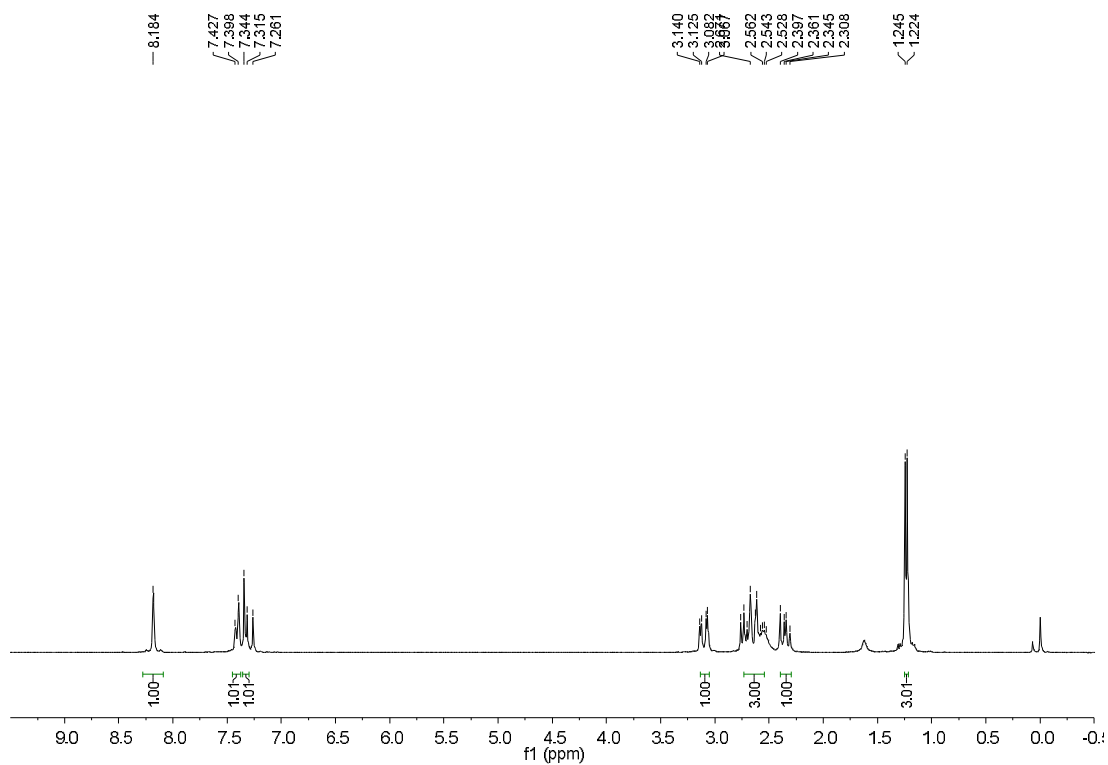
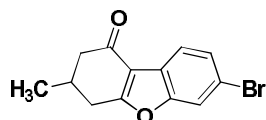
1.249
1.227



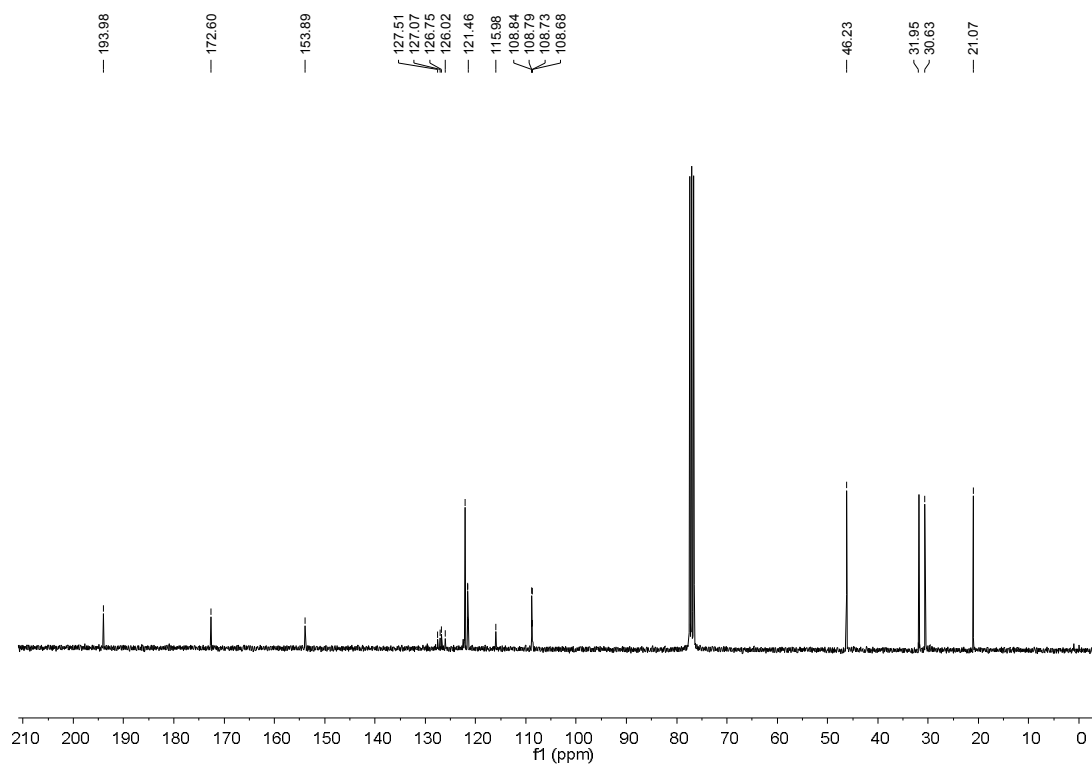
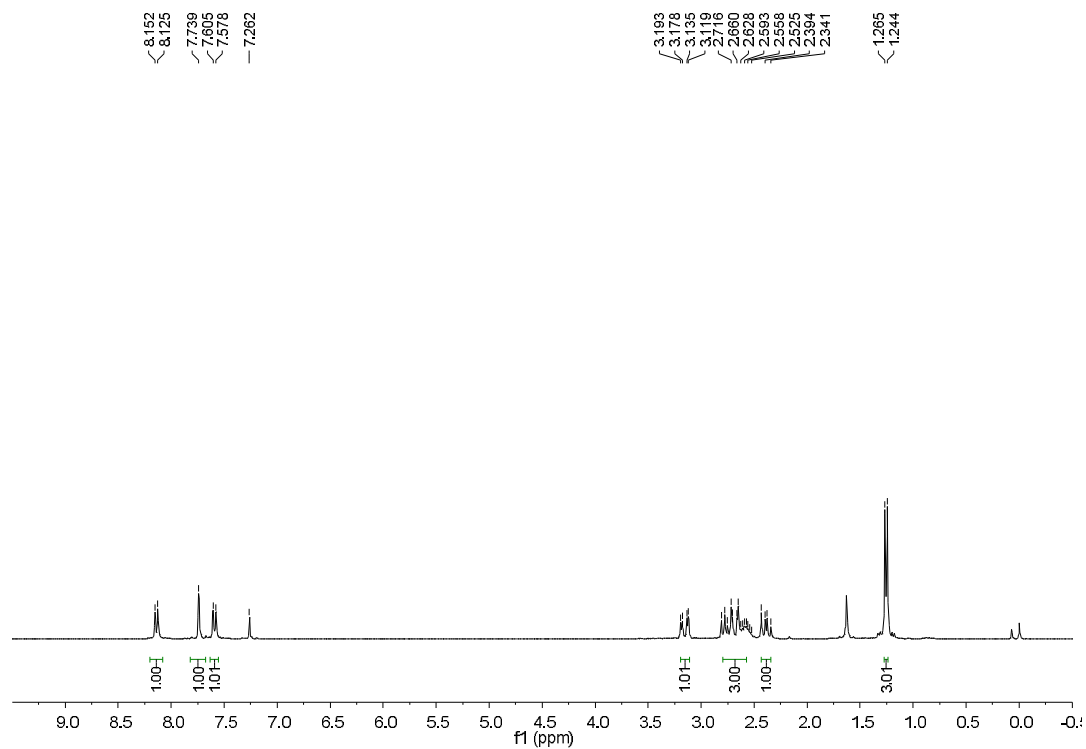
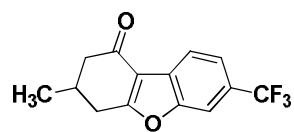
¹H NMR and ¹³C NMR Spectra of Compound 3bd



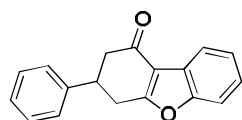
^1H NMR and ^{13}C NMR Spectra of Compound 3be



¹H NMR and ¹³C NMR Spectra of Compound 3bf

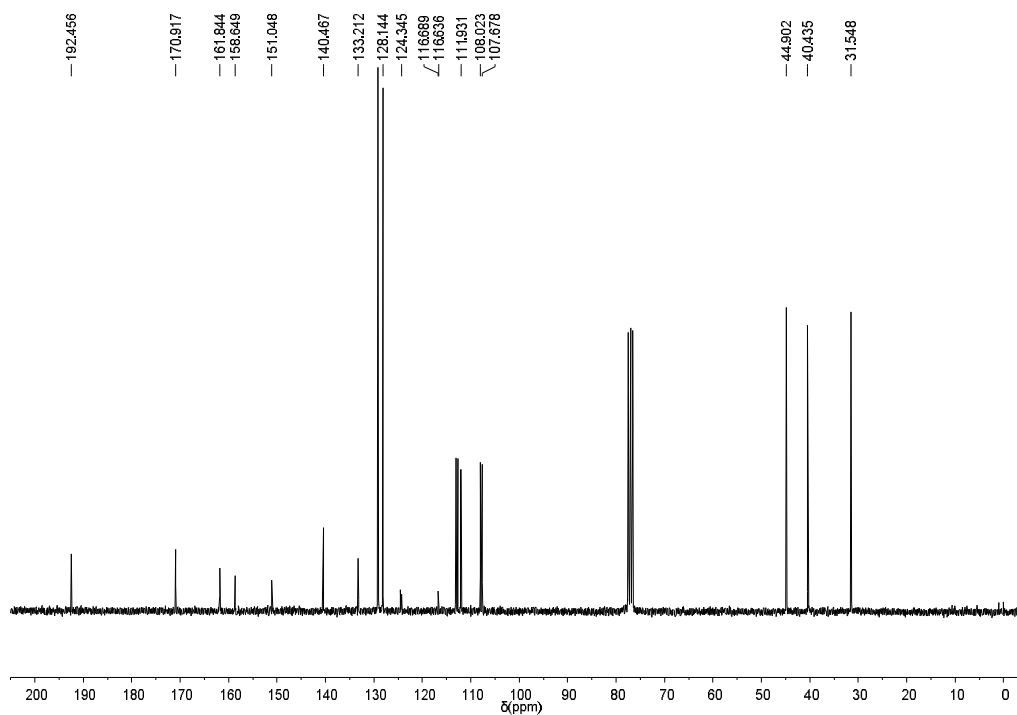
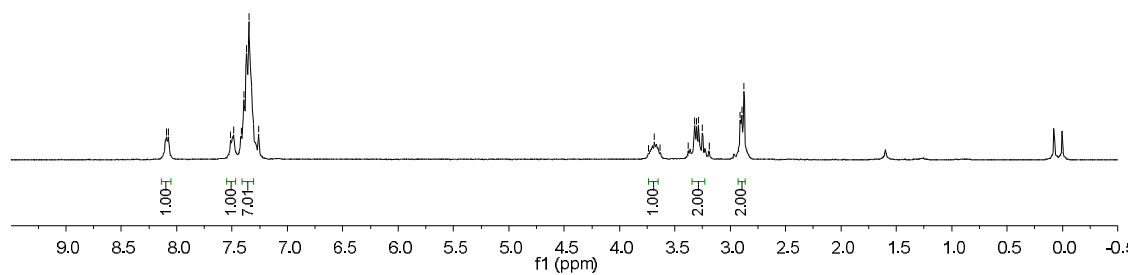


^1H NMR and ^{13}C NMR Spectra of Compound 3ca

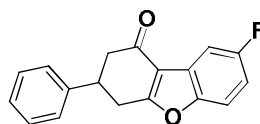


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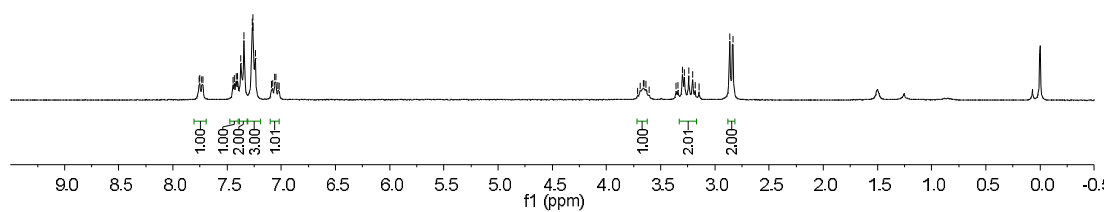


^1H NMR and ^{13}C NMR Spectra of Compound 3cb

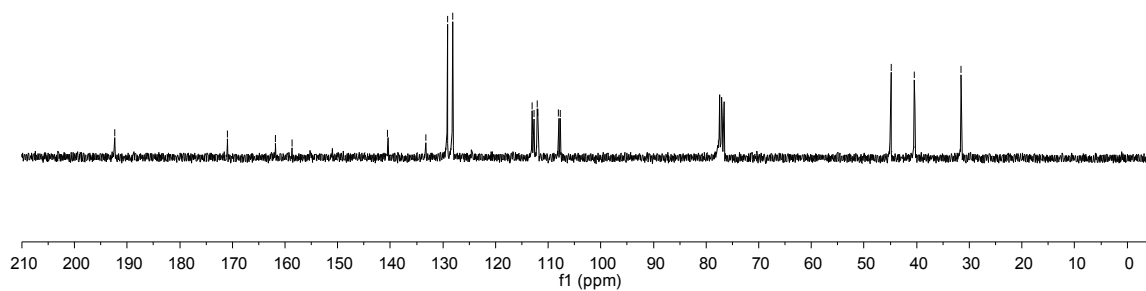


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7.052
7.031
7.022

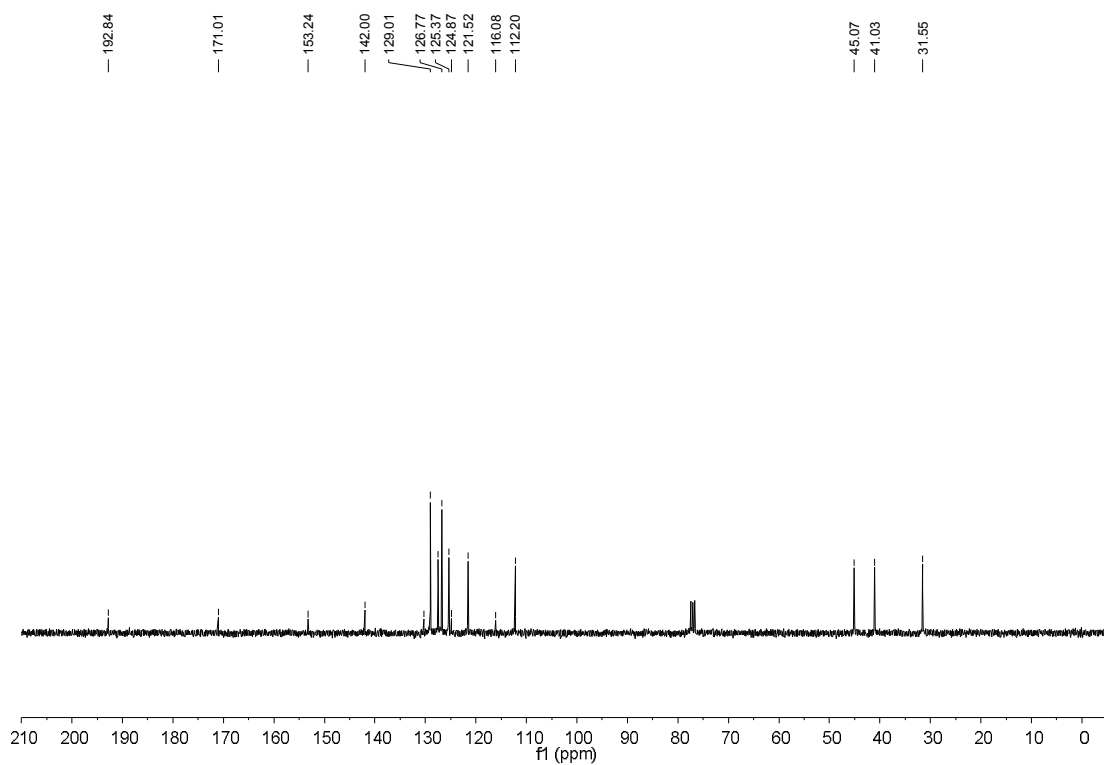
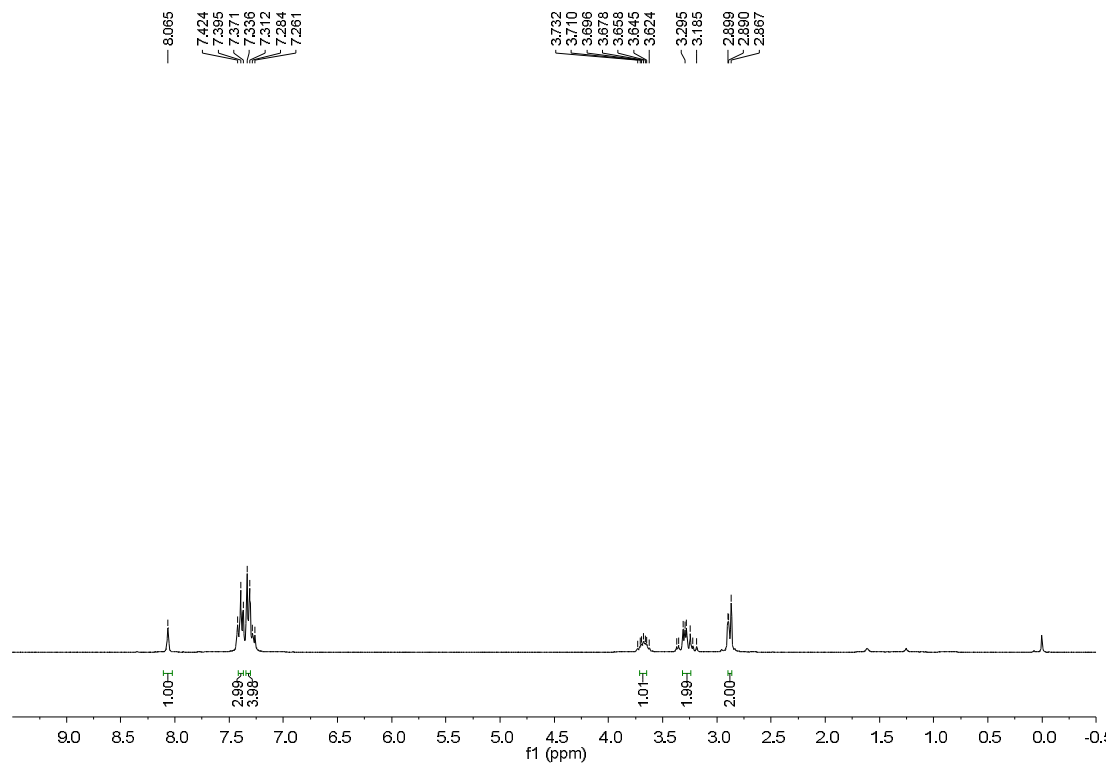
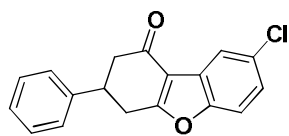
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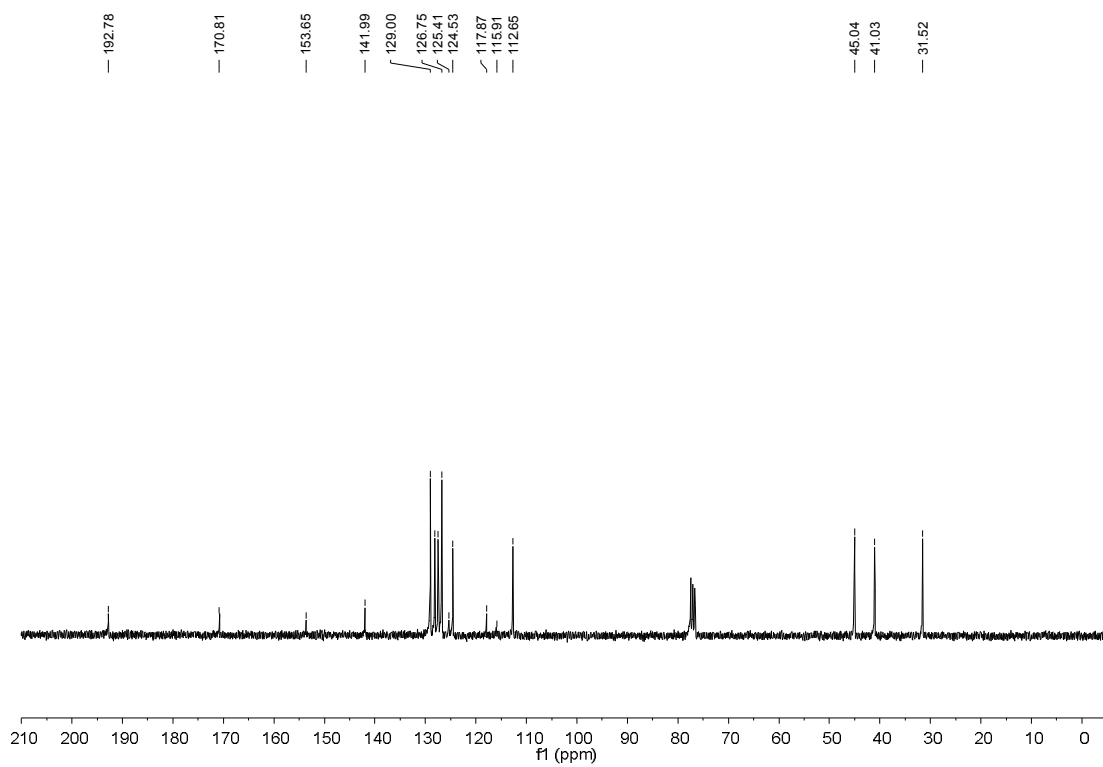
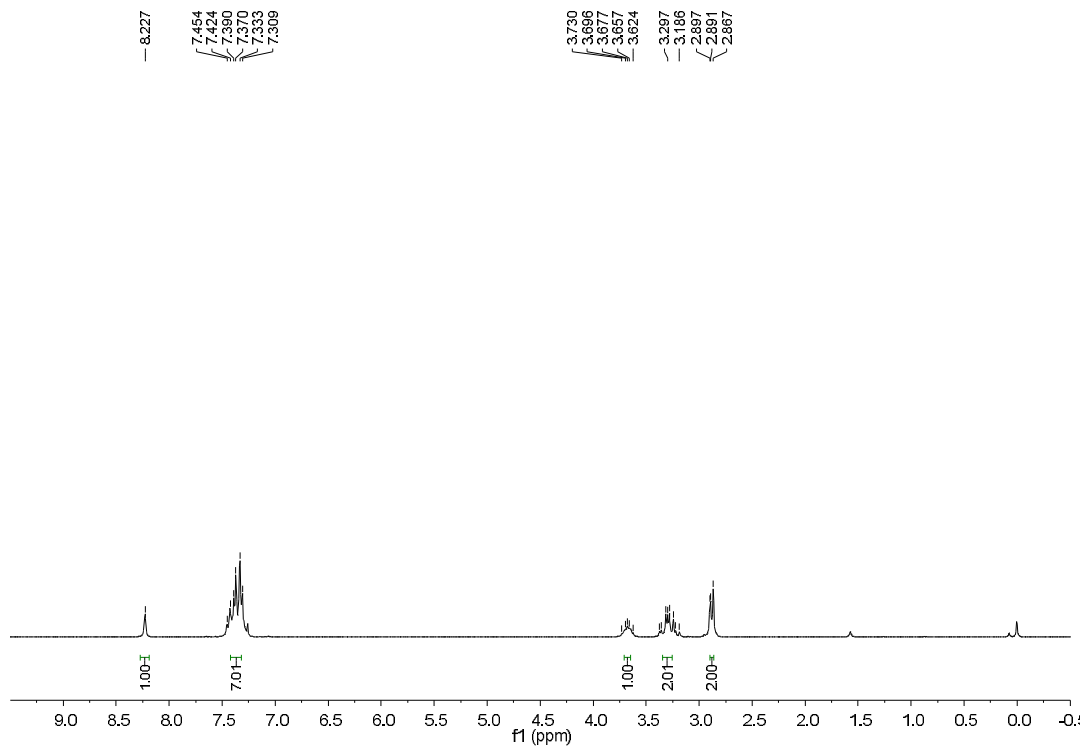
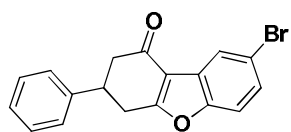
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40.42
31.52



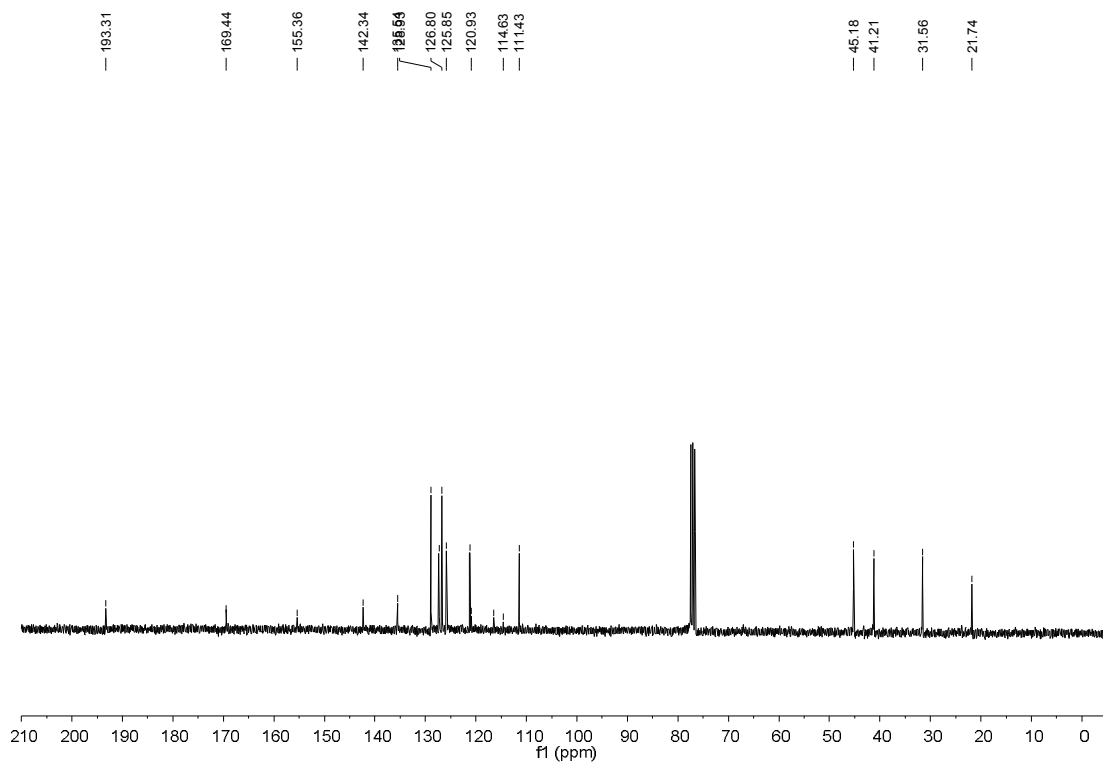
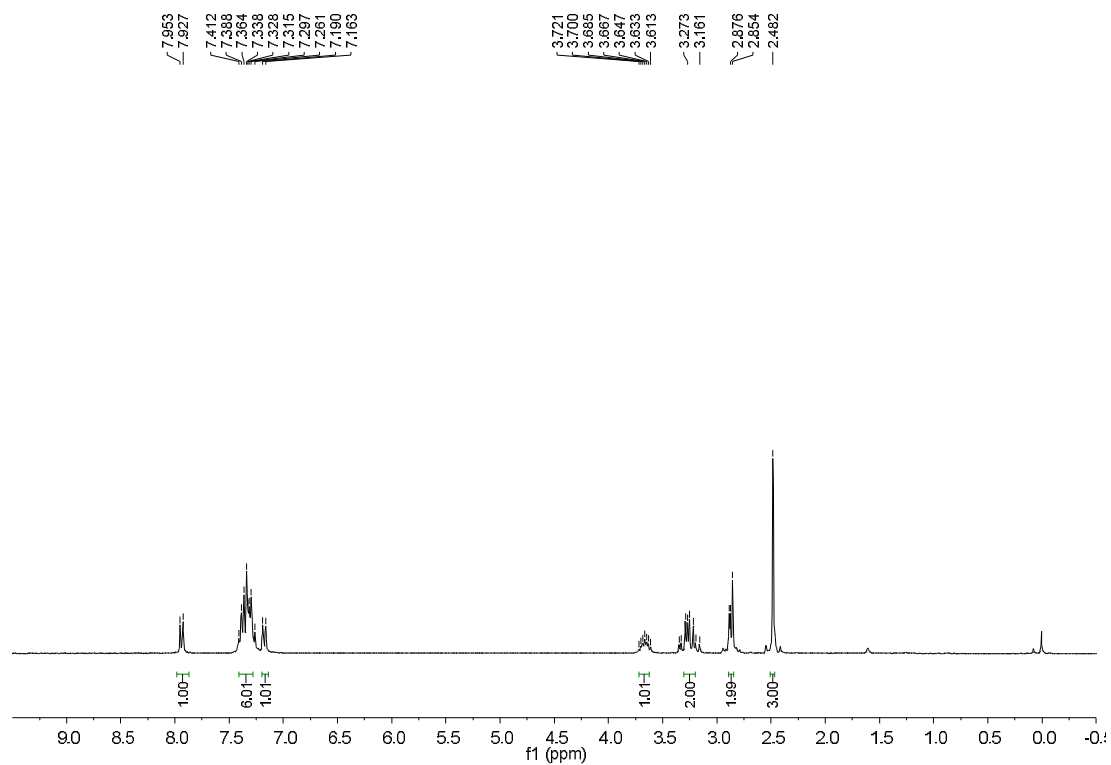
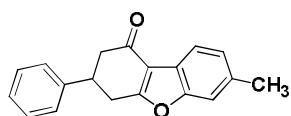
¹H NMR and ¹³C NMR Spectra of Compound 3cc



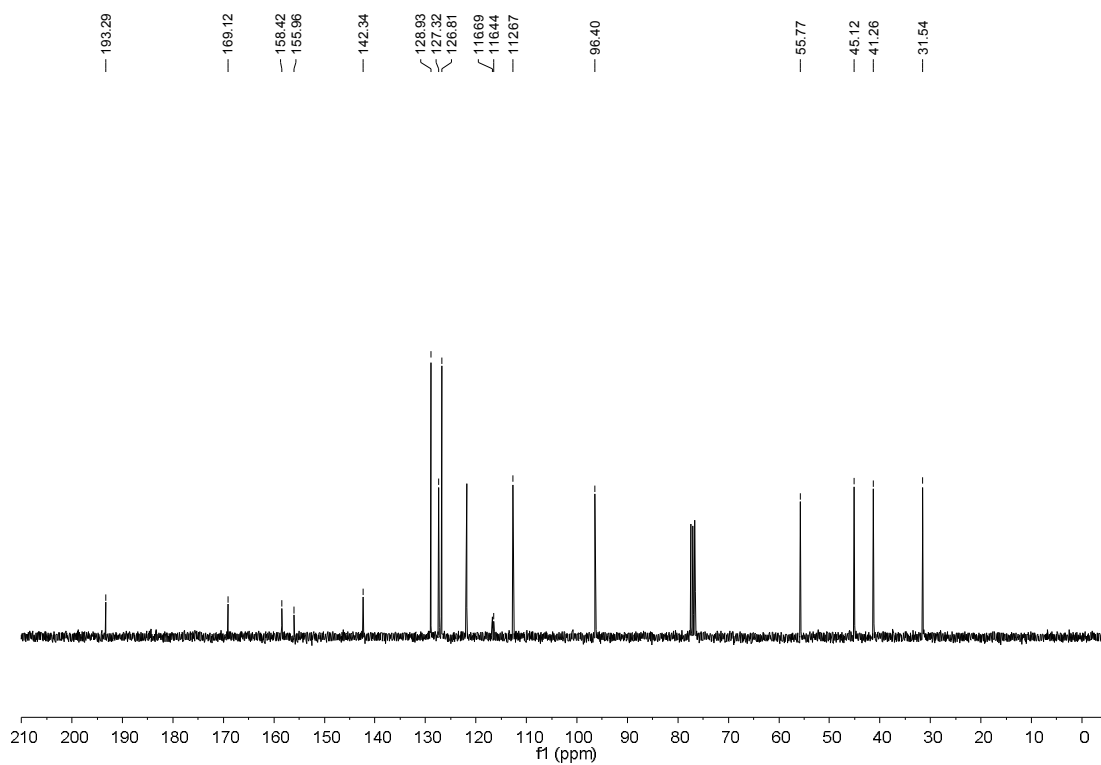
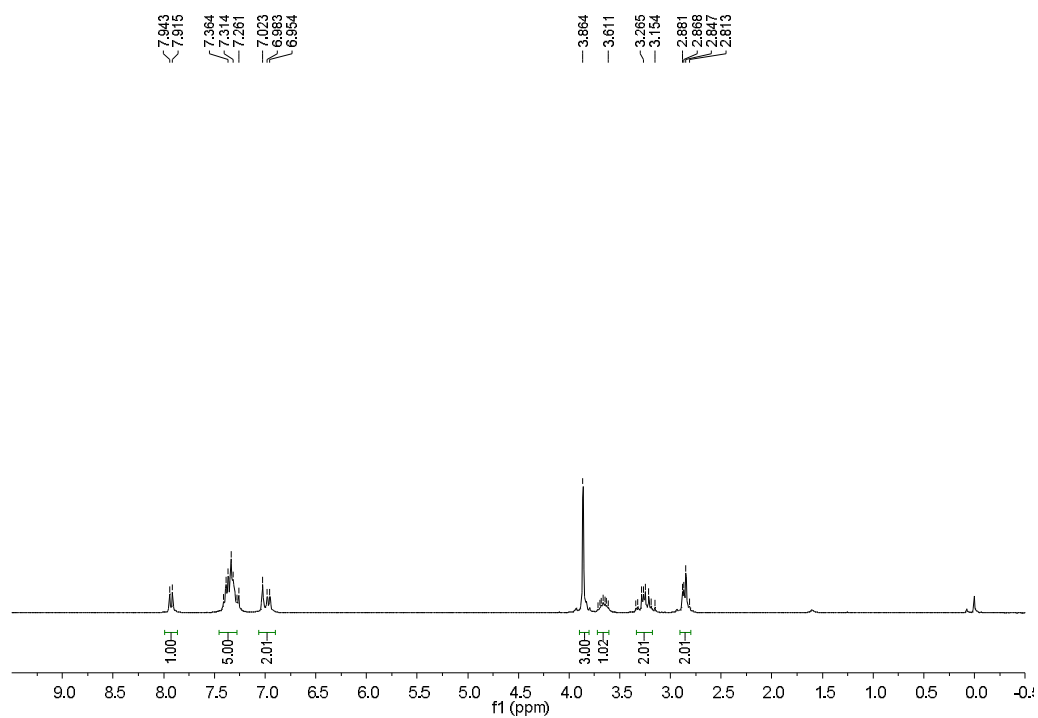
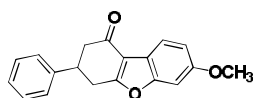
^1H NMR and ^{13}C NMR Spectra of Compound 3cd



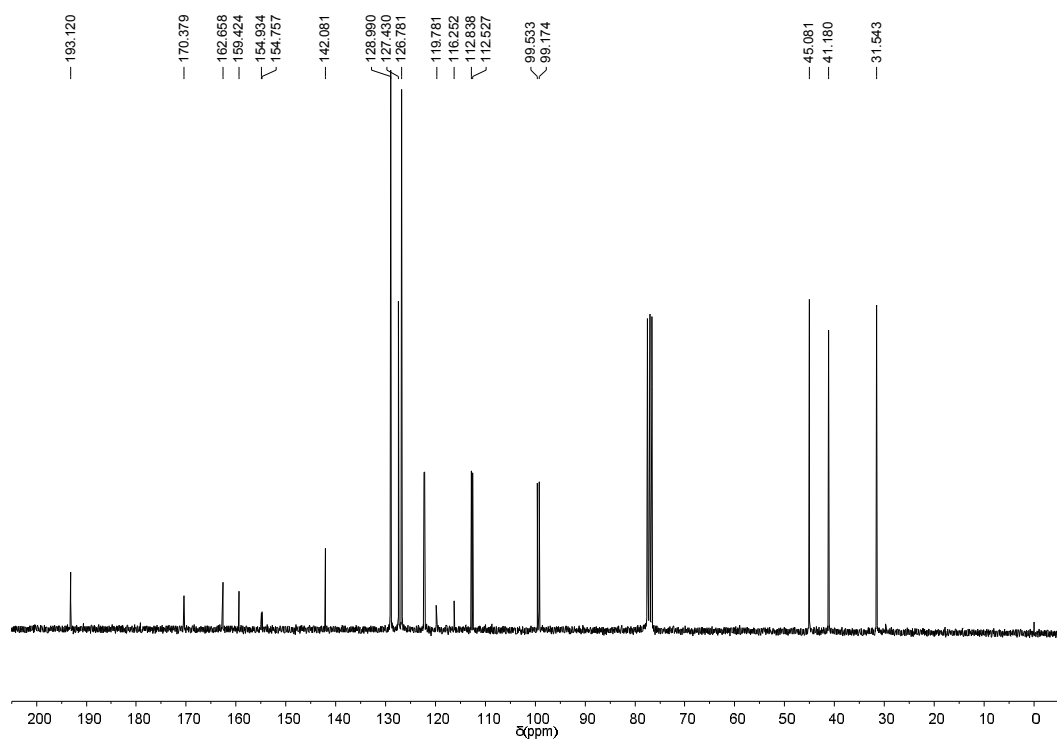
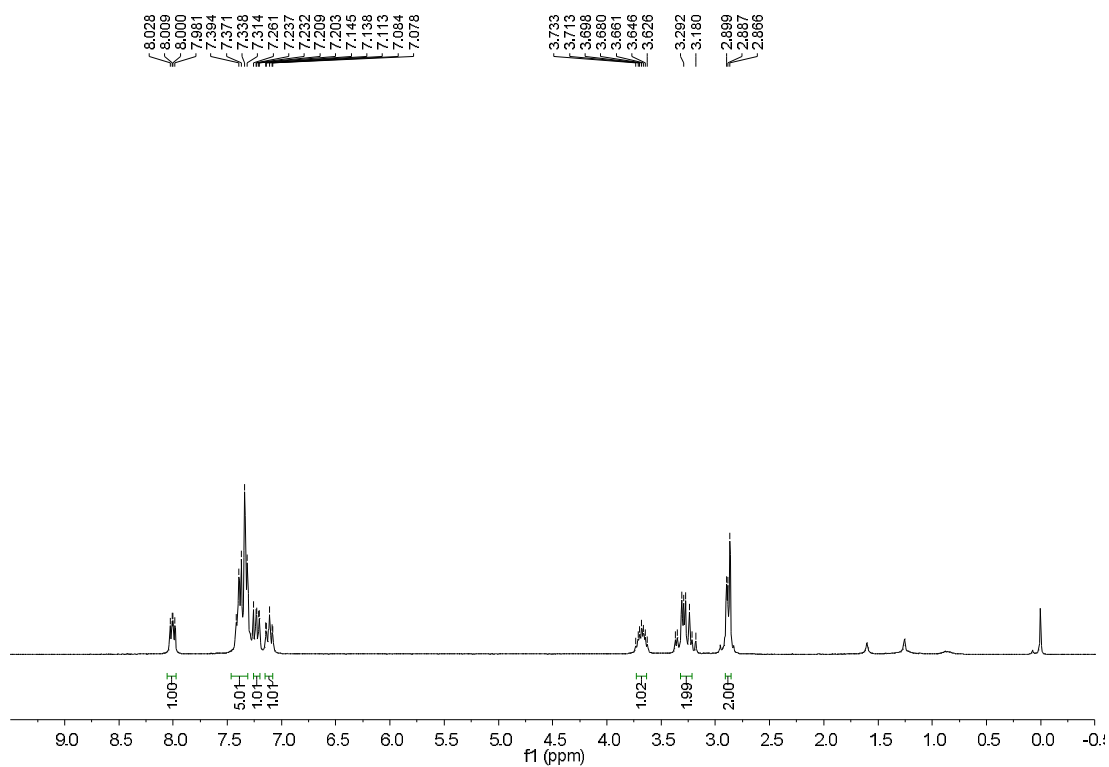
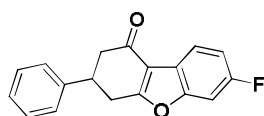
^1H NMR and ^{13}C NMR Spectra of Compound 3ce



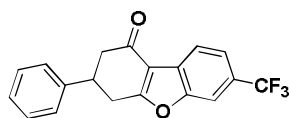
¹H NMR and ¹³C NMR Spectra of Compound 3cf



¹H NMR and ¹³C NMR Spectra of Compound 3cg

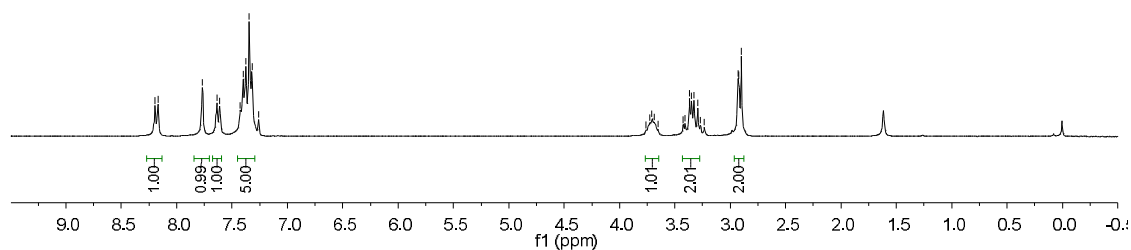


¹H NMR and ¹³C NMR Spectra of Compound 3ch

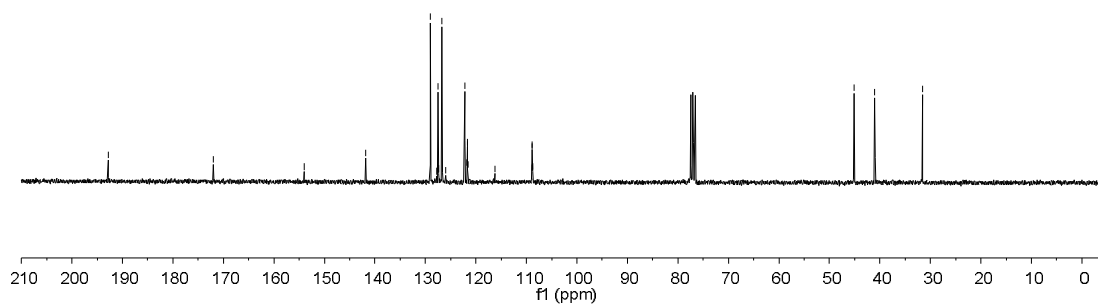


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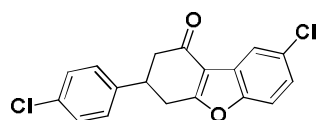
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3.233
2.930
2.923
2.899



192.84
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154.05
141.84
129.03
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108.87
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45.12
41.01
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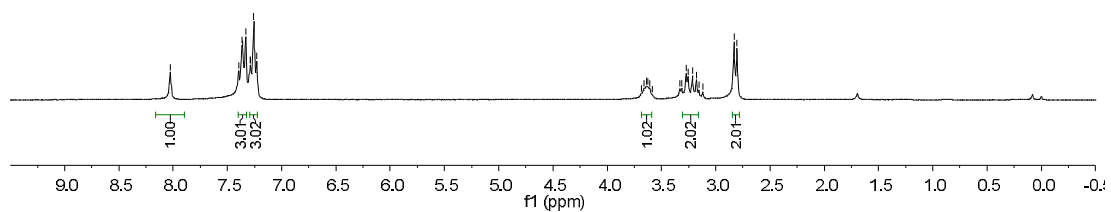


¹H NMR and ¹³C NMR Spectra of Compound 3da

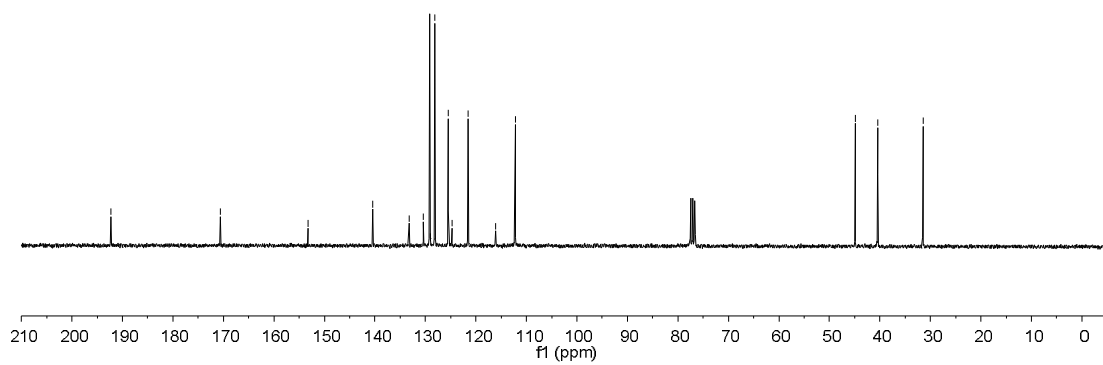


8.028
7.598
7.588
7.589
7.581
7.592
7.587
7.257
7.229

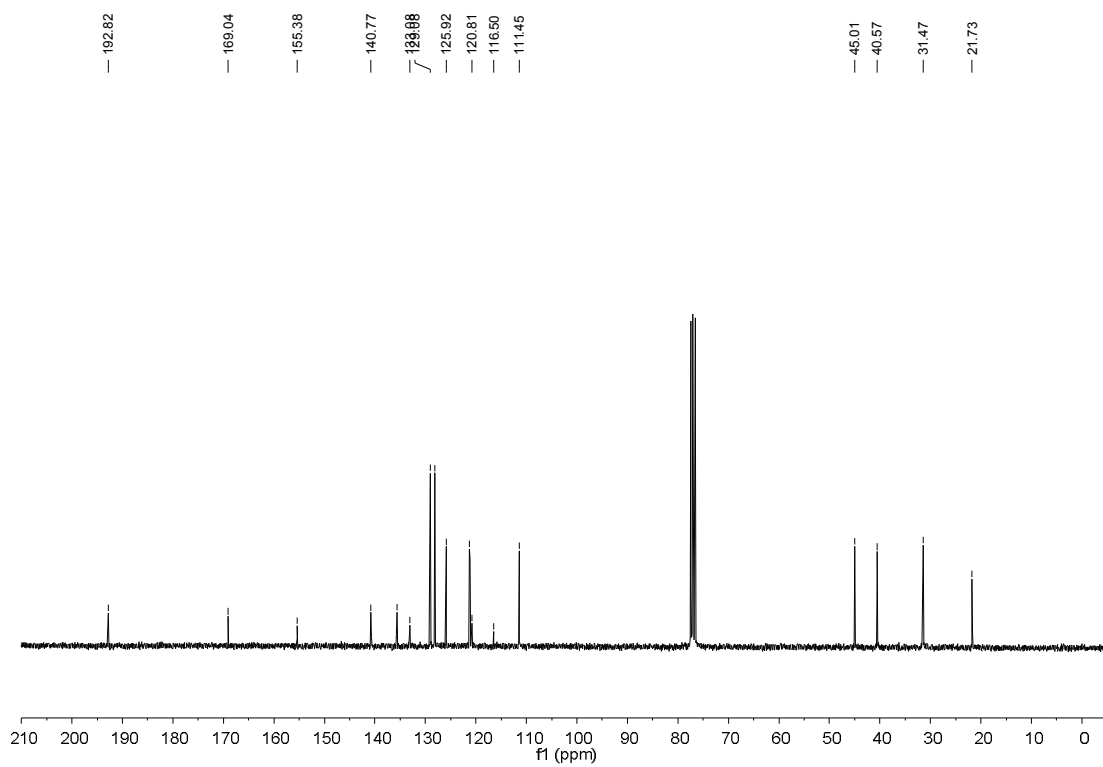
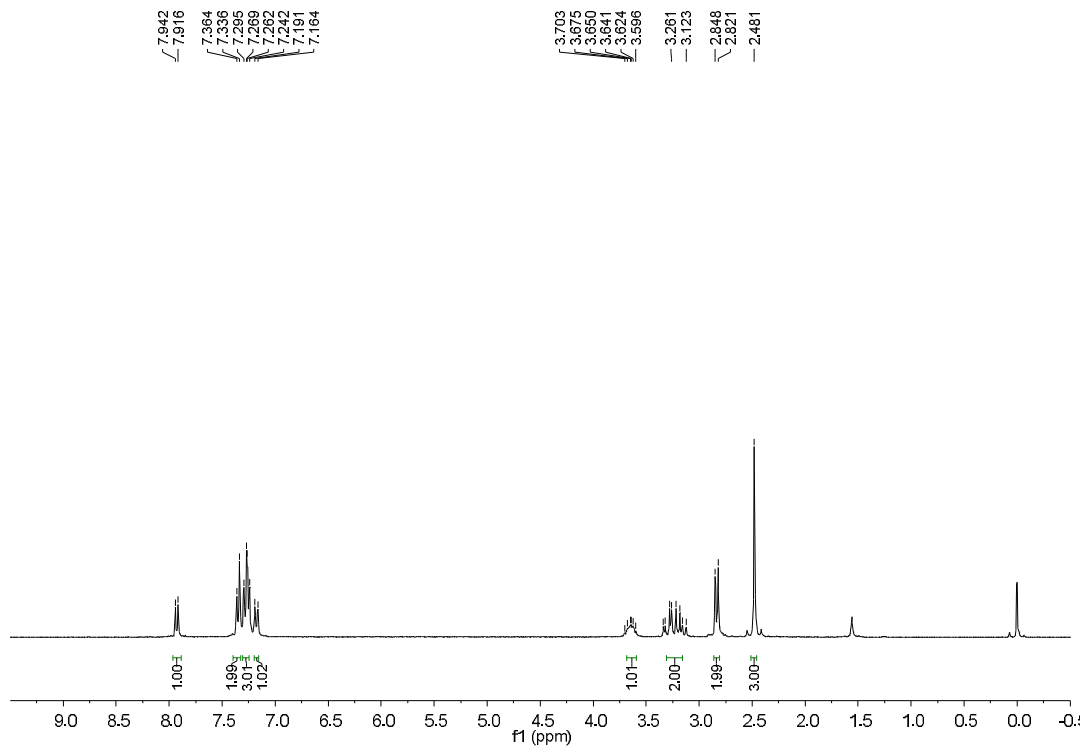
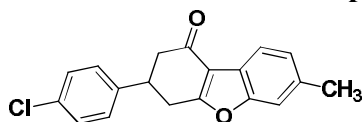
3.687
3.660
3.635
3.627
3.610
3.593
3.255
3.156
2.981
2.804



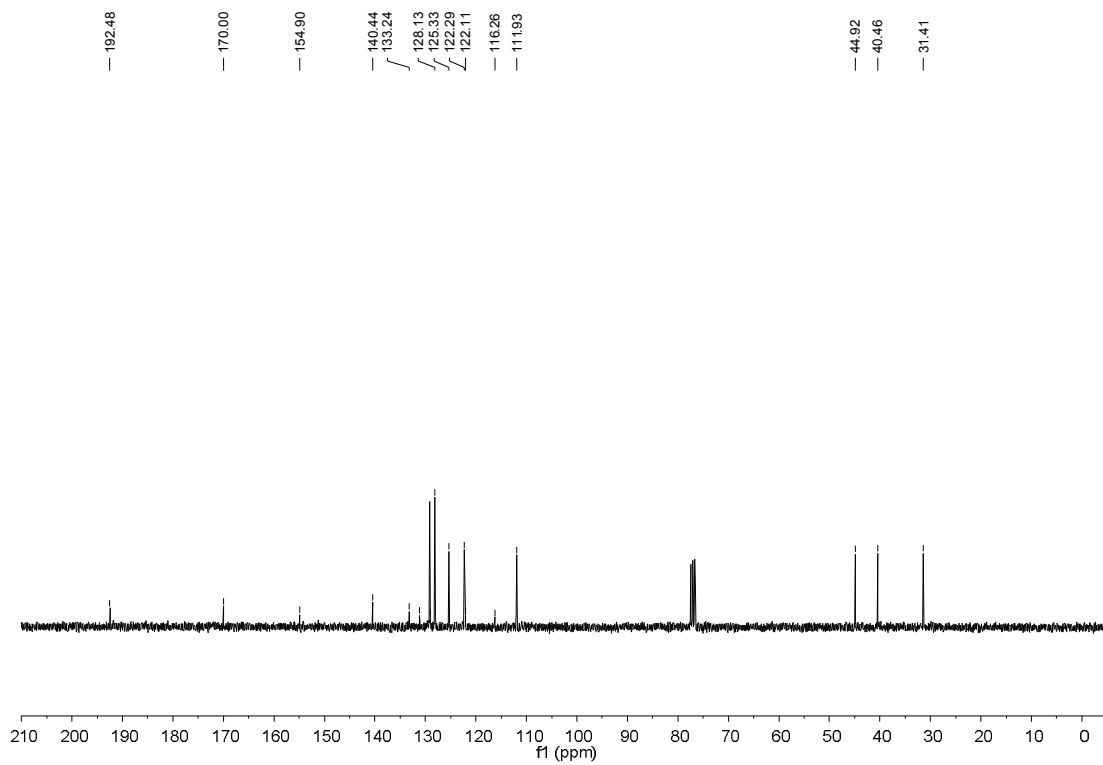
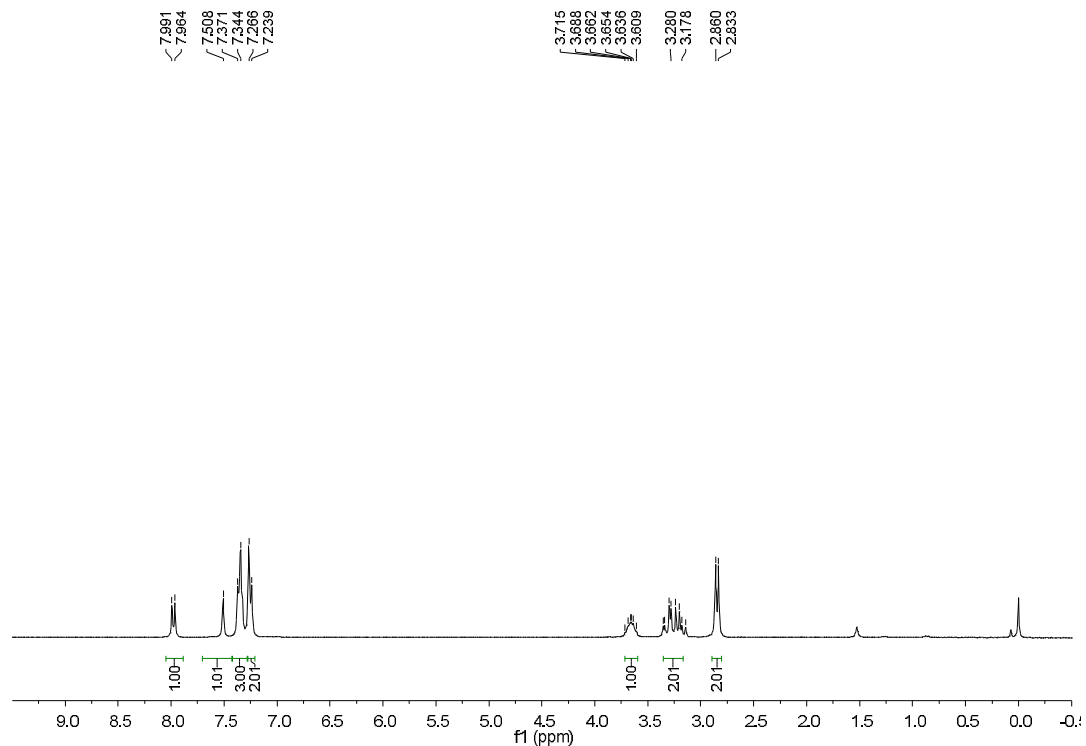
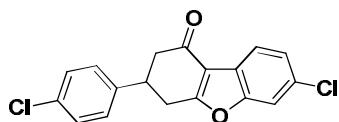
192.31
170.56
153.24
140.43
130.42
128.13
125.47
124.75
121.51
116.09
112.22
44.87
40.40
31.45



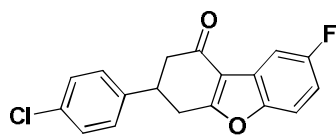
¹H NMR and ¹³C NMR Spectra of Compound 3db



¹H NMR and ¹³C NMR Spectra of Compound 3dd

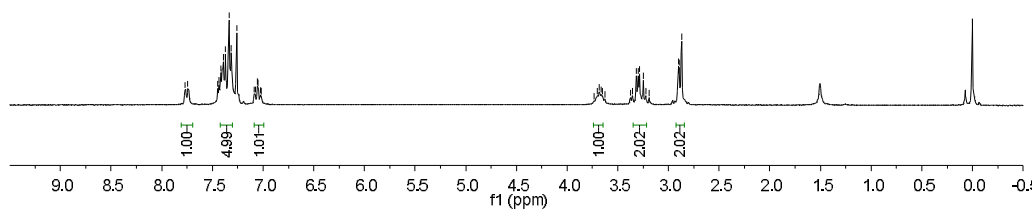


¹H NMR and ¹³C NMR Spectra of Compound 3de

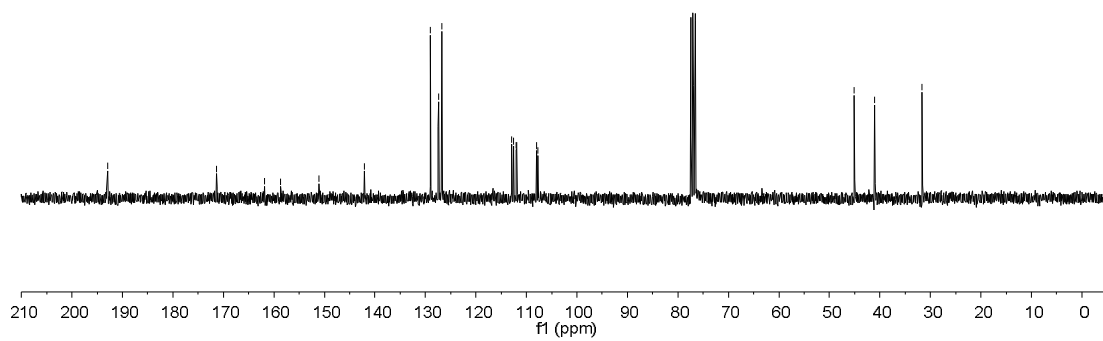


7.769
7.742
7.734
7.337
7.261
7.056
7.056
7.056
7.048
7.026
7.018

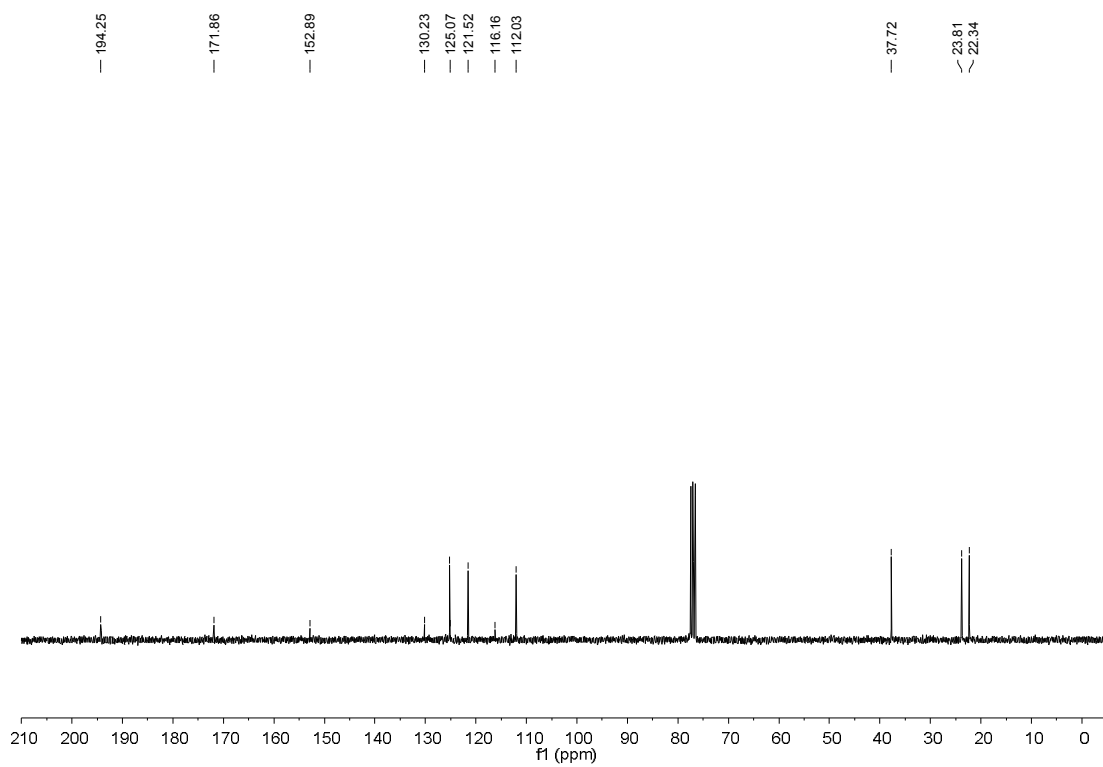
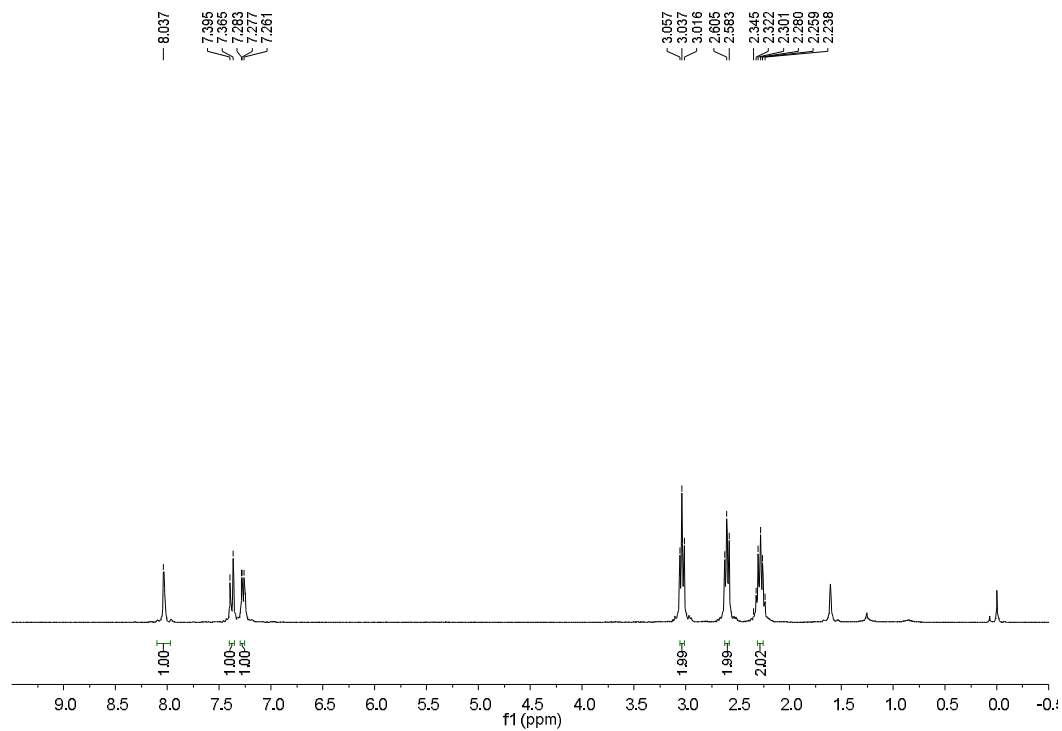
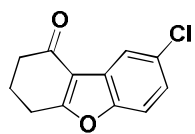
3.737
3.702
3.663
3.663
3.651
3.629
3.298
3.190
2.903
2.895
2.871



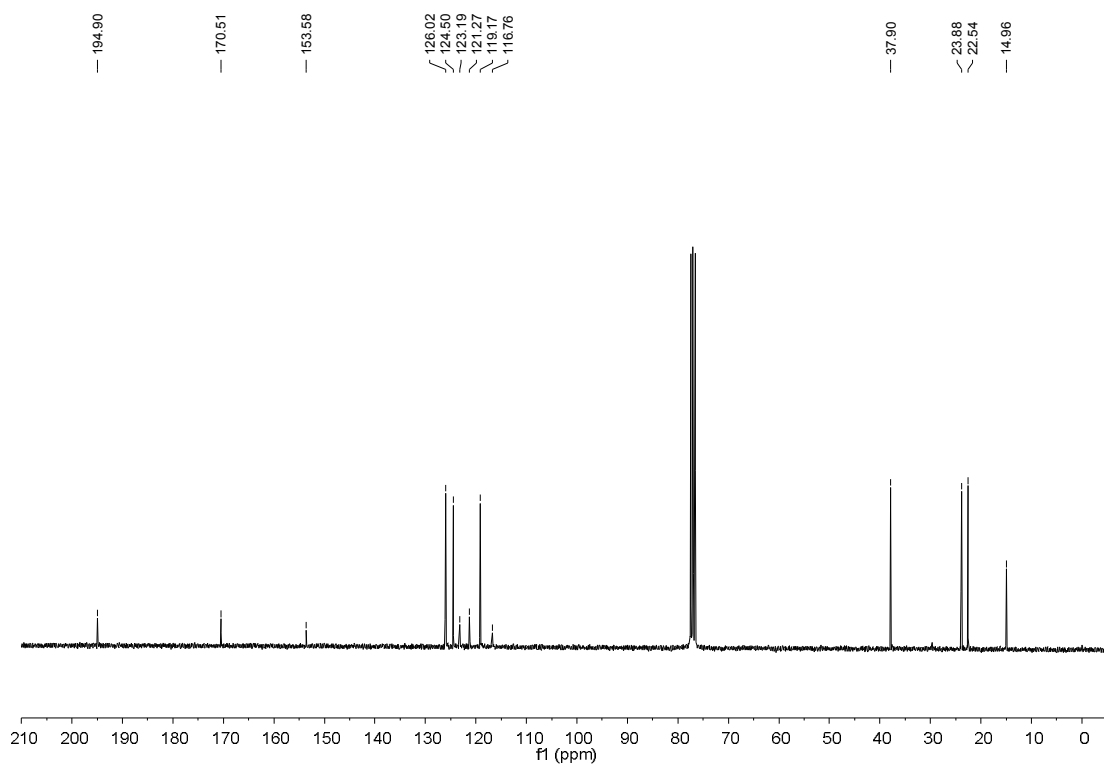
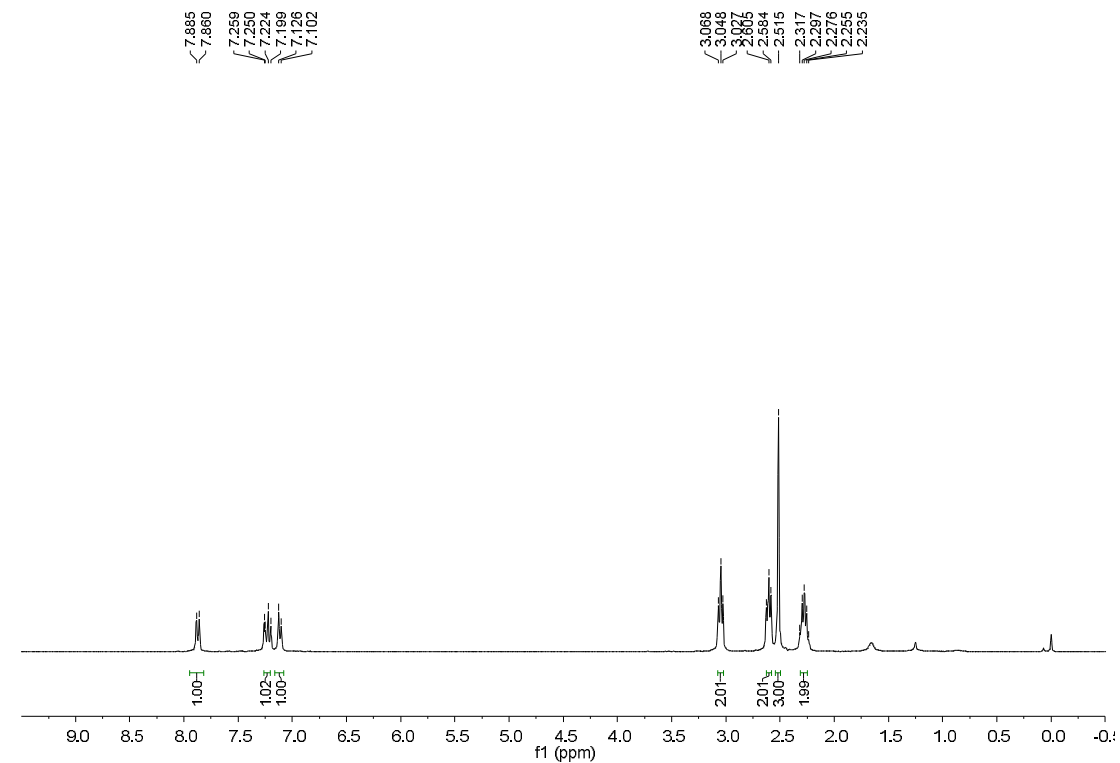
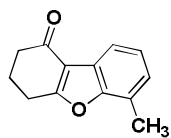
192.91
171.33
161.83
158.66
151.06
142.06
128.99
127.43
126.76
112.92
112.00
111.86
108.02
107.68
45.07
41.06
31.63



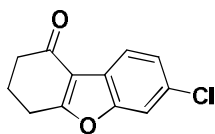
^1H NMR and ^{13}C NMR Spectra of Compound 3ea



¹H NMR and ¹³C NMR Spectra of Compound 3eb

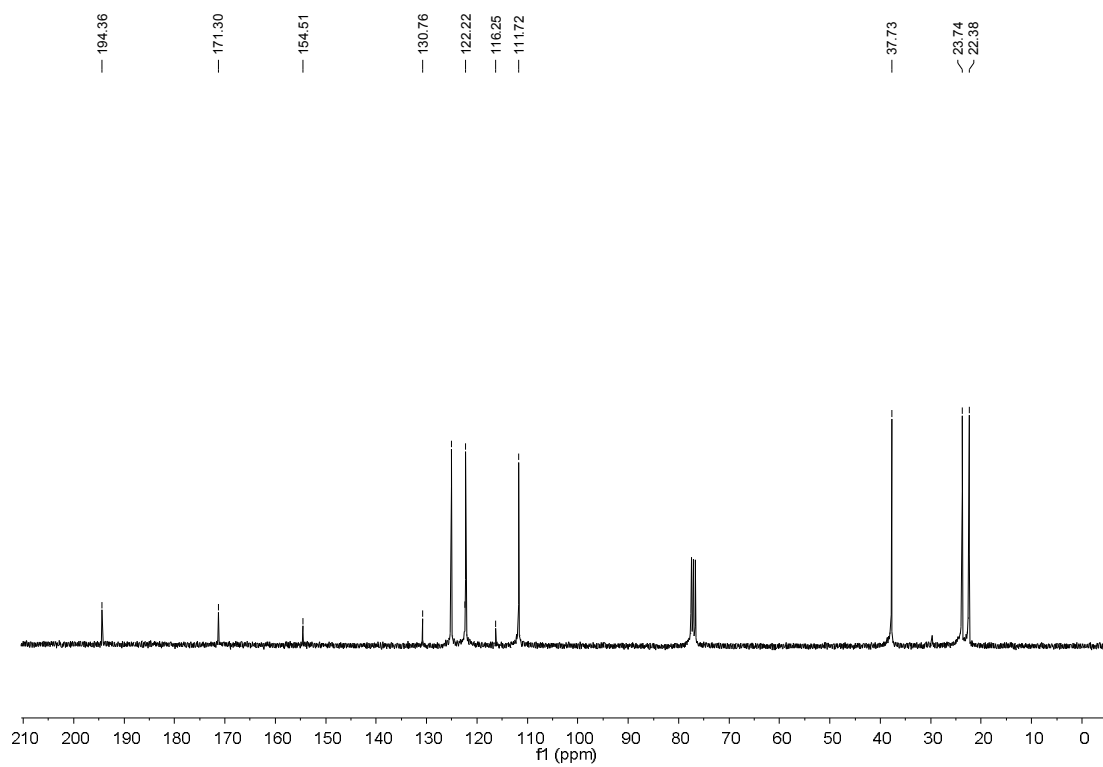
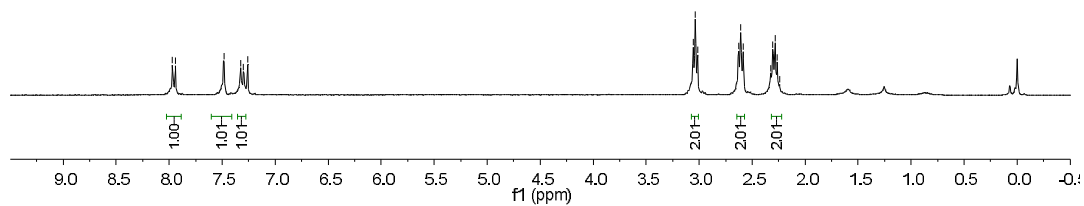


¹H NMR and ¹³C NMR Spectra of Compound 3ec

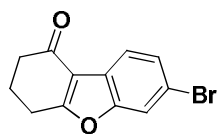


7.969
7.941
7.482
7.527
7.299
7.261

3.057
3.036
3.015
2.608
2.585
2.326
2.305
2.284
2.262
2.241

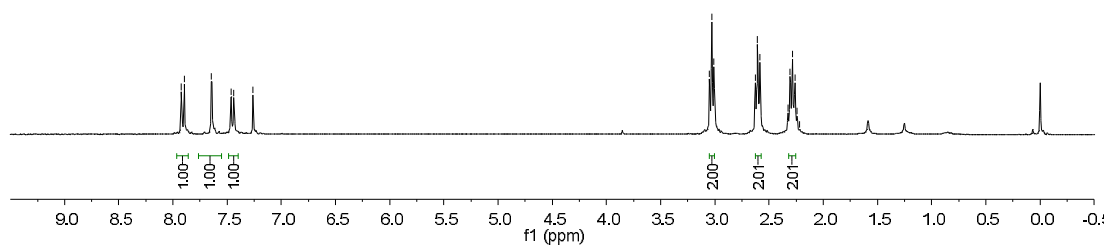


^1H NMR and ^{13}C NMR Spectra of Compound 3ed

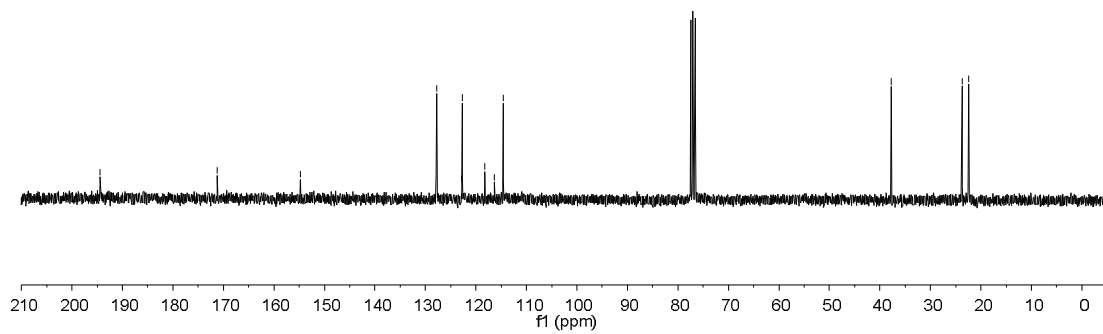


7.922
7.895
7.644
7.438
7.261

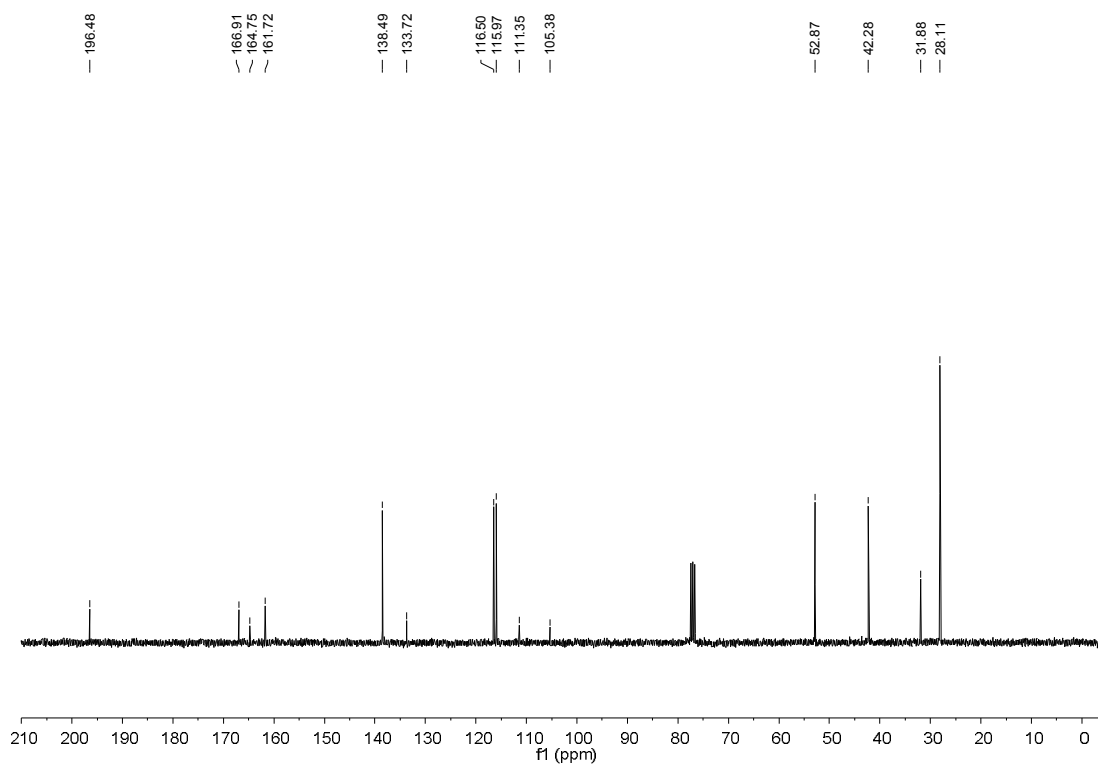
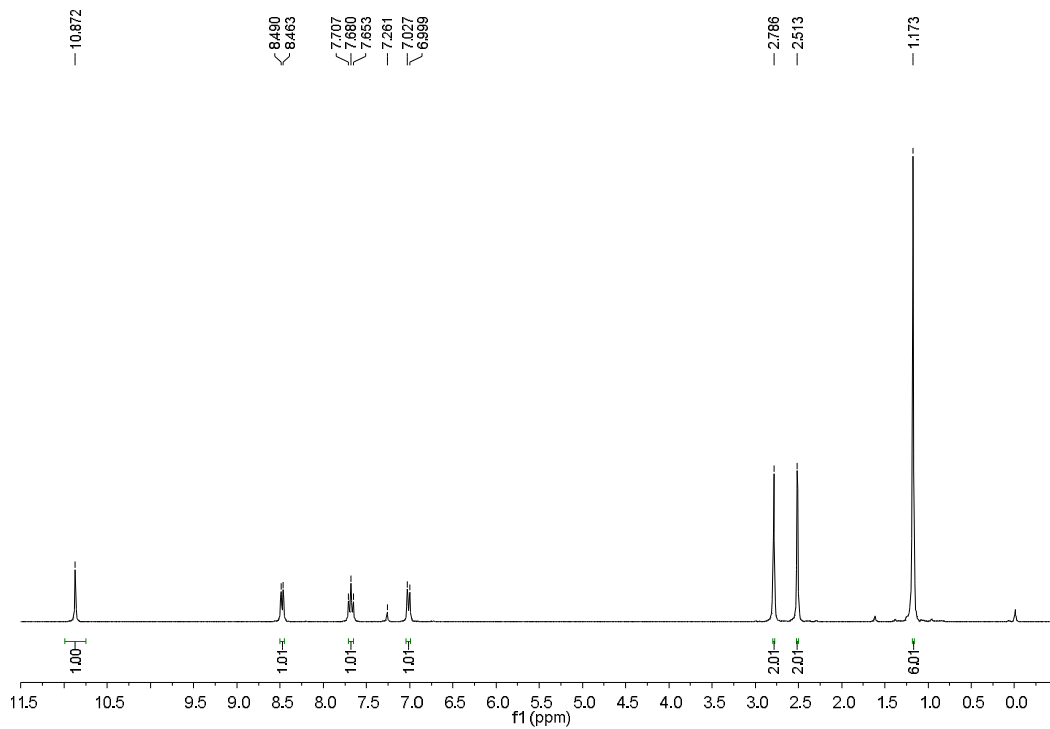
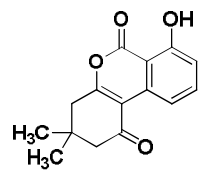
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3.028
3.008
2.606
2.584
2.326
2.305
2.284
2.262
2.241
2.218



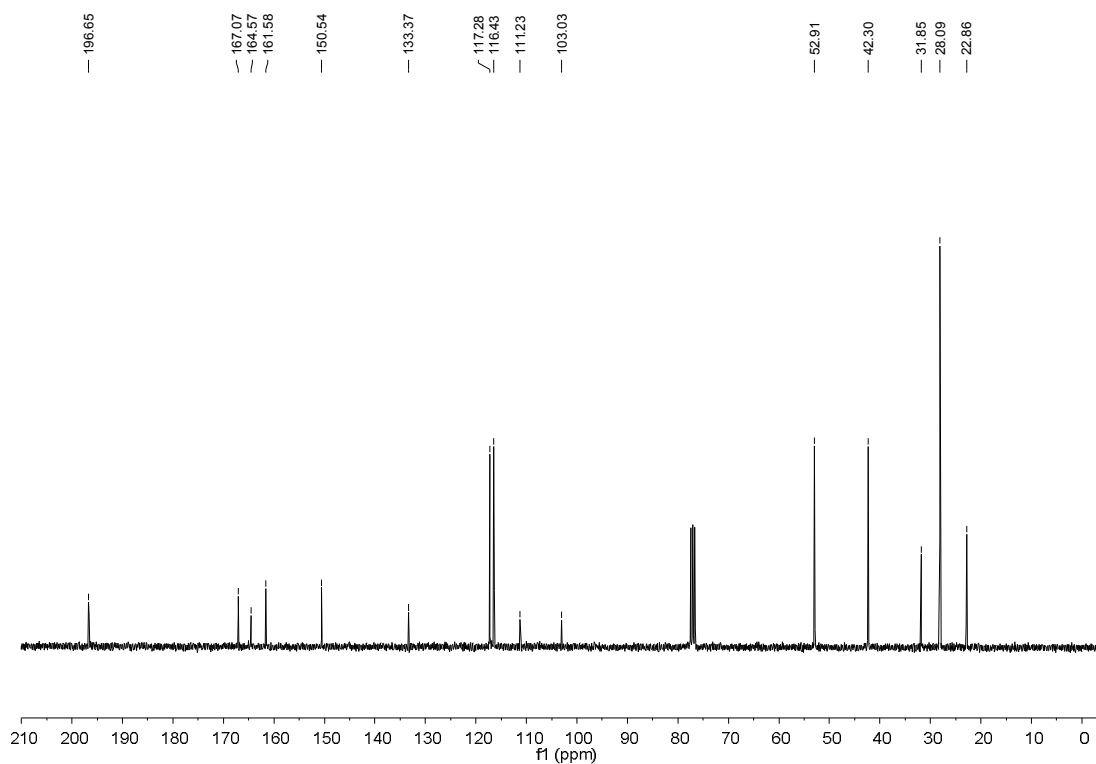
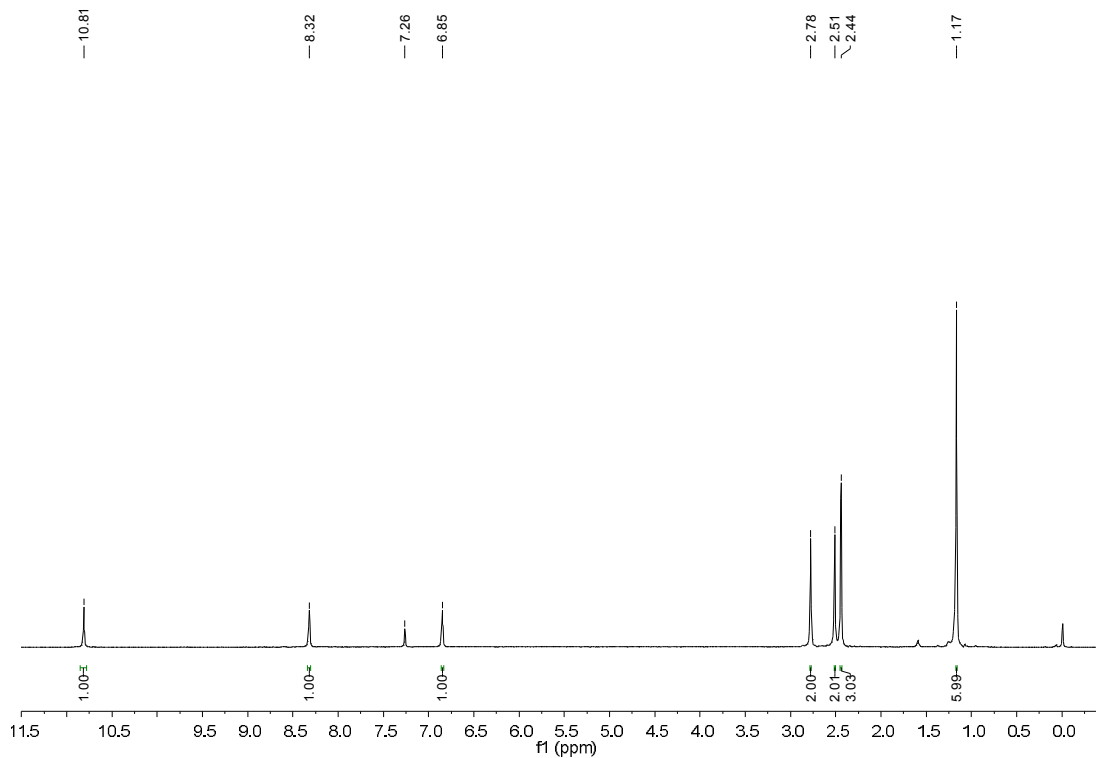
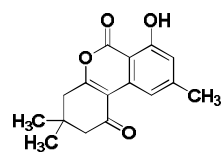
194.41
171.21
154.73
127.82
122.68
118.19
116.32
114.63
37.77
23.75
22.39



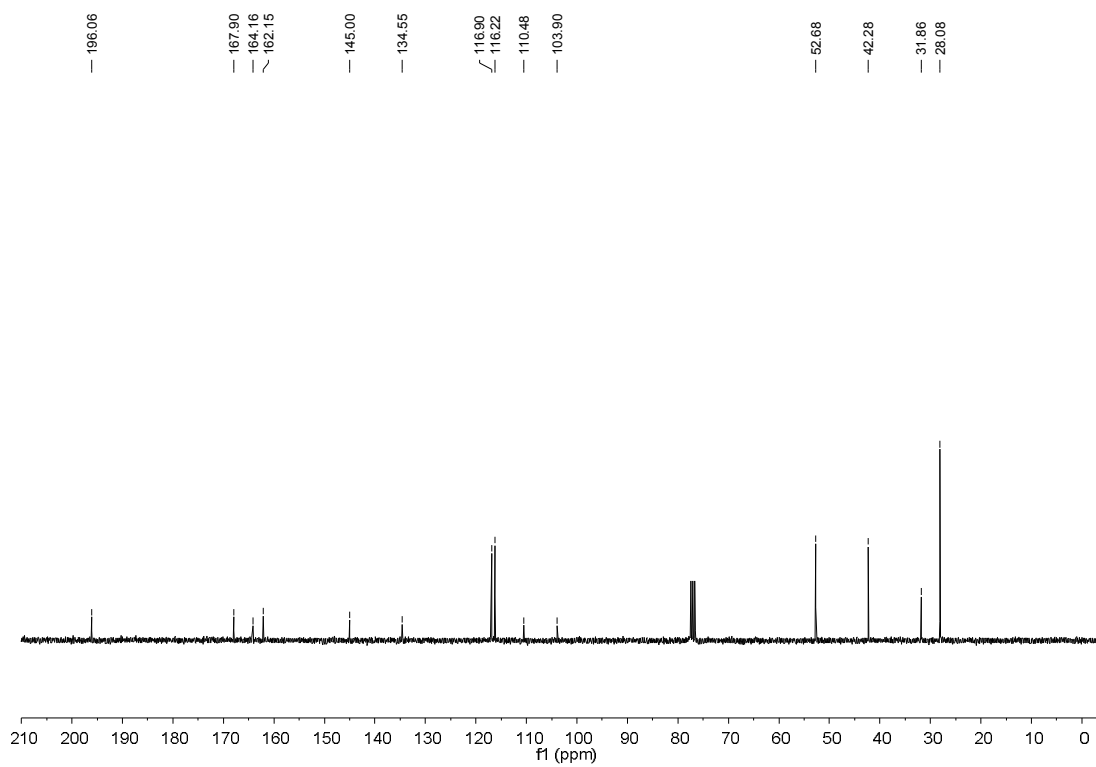
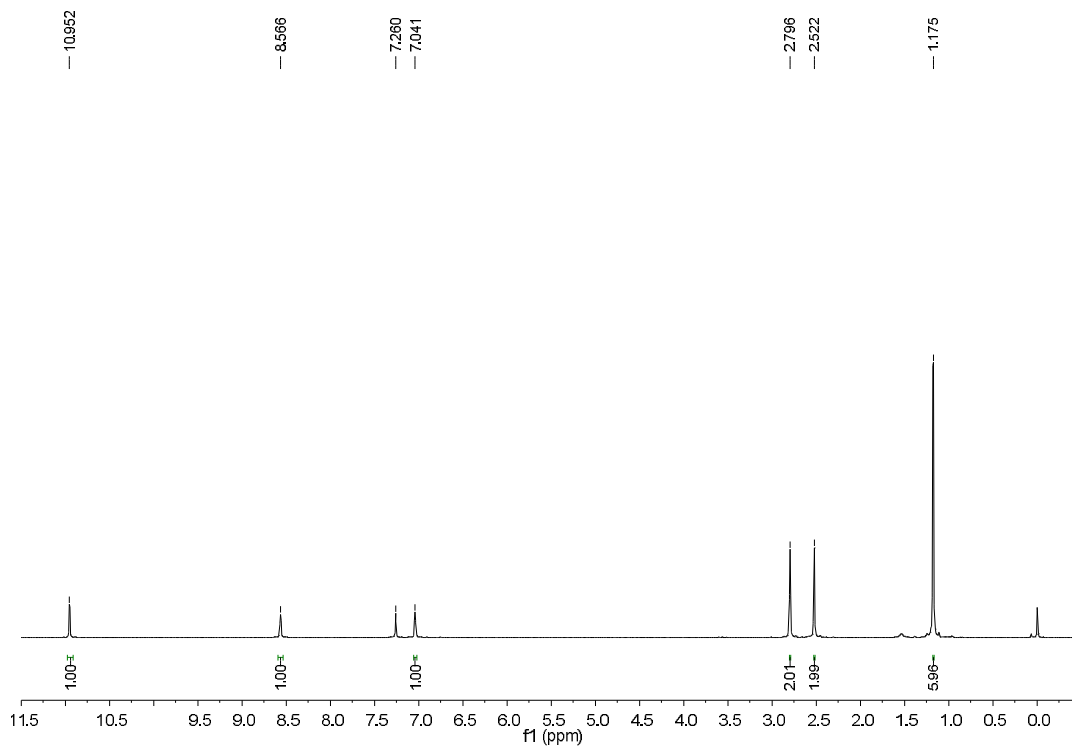
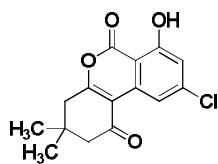
^1H NMR and ^{13}C NMR Spectra of Compound 4aa



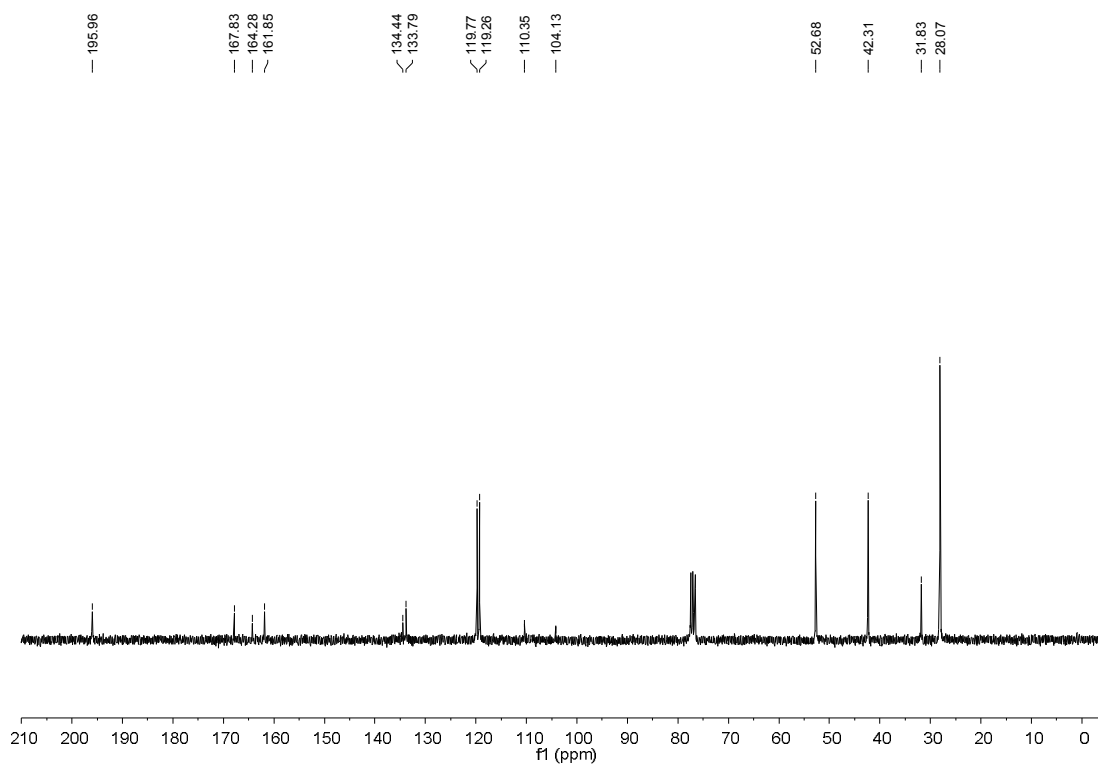
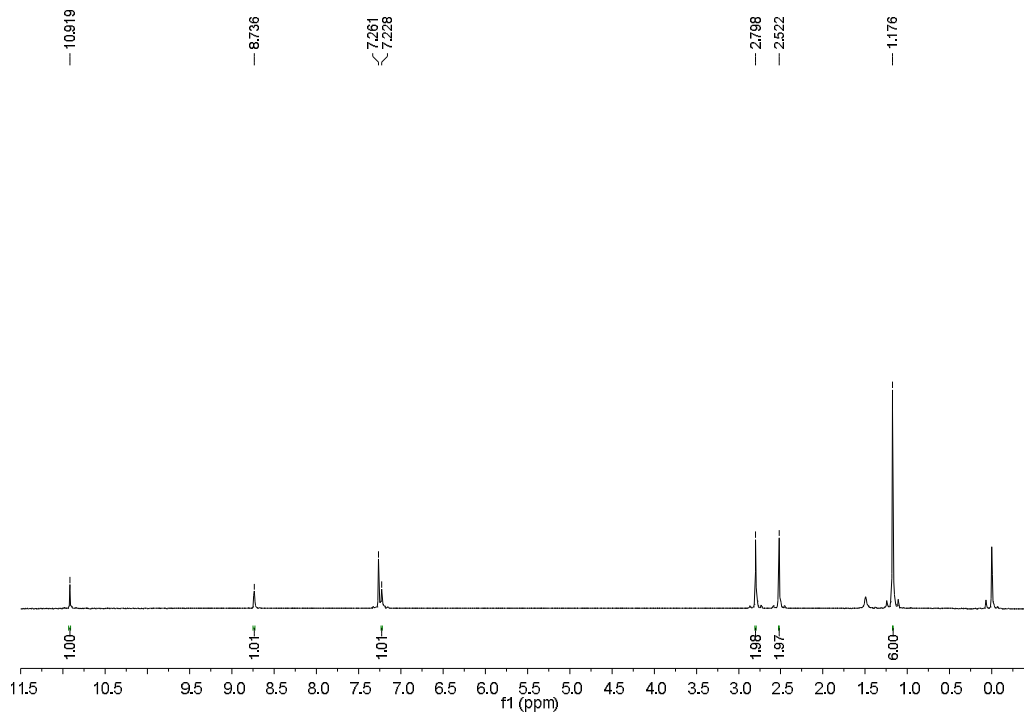
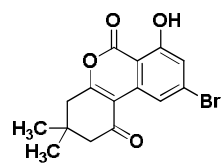
^1H NMR and ^{13}C NMR Spectra of Compound 4ab



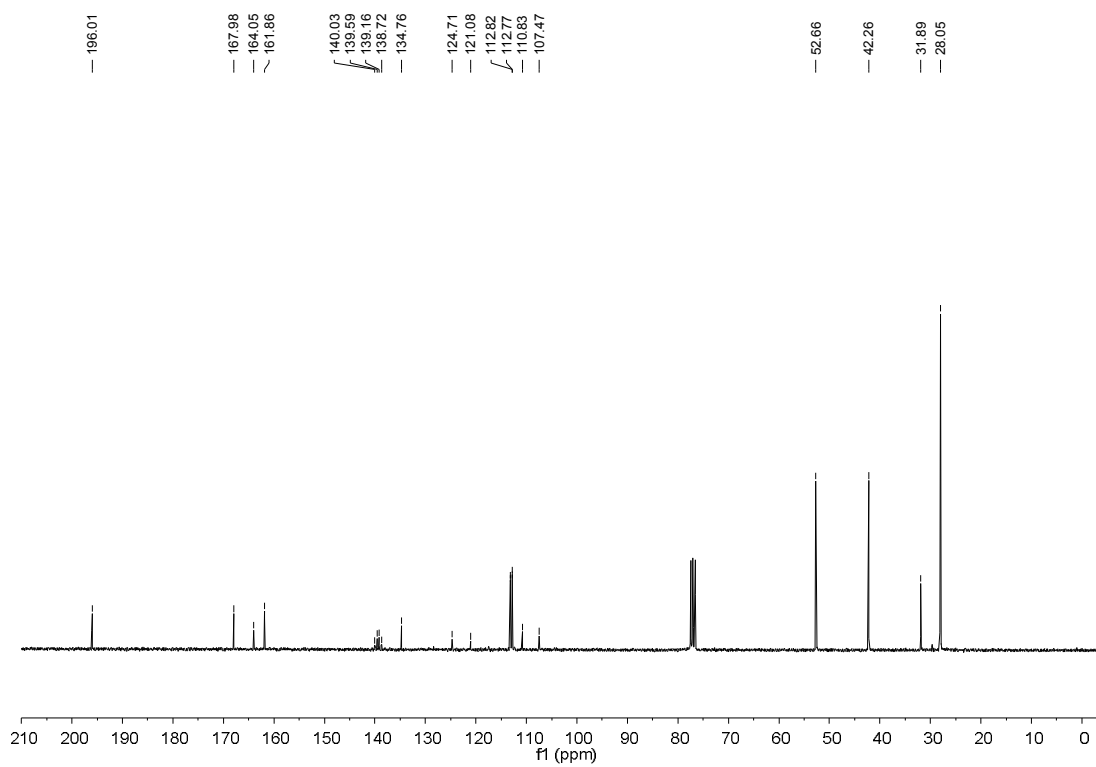
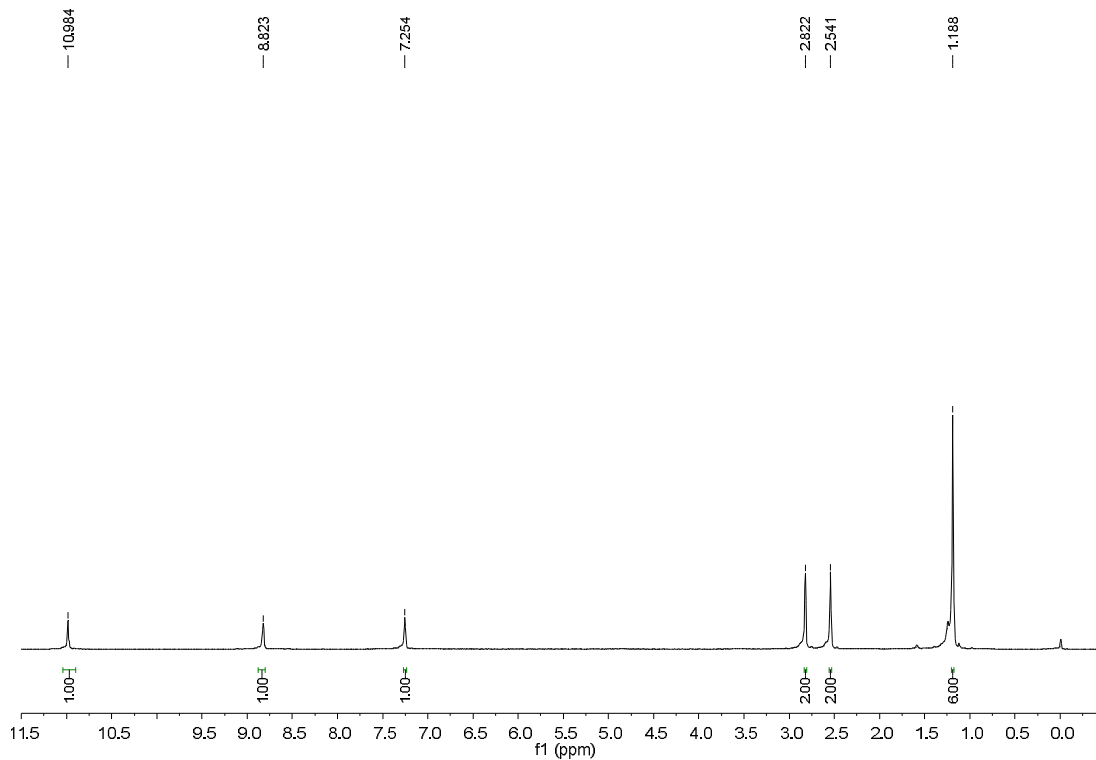
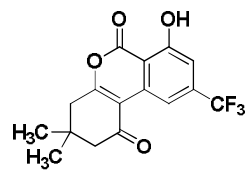
^1H NMR and ^{13}C NMR Spectra of Compound 4ac



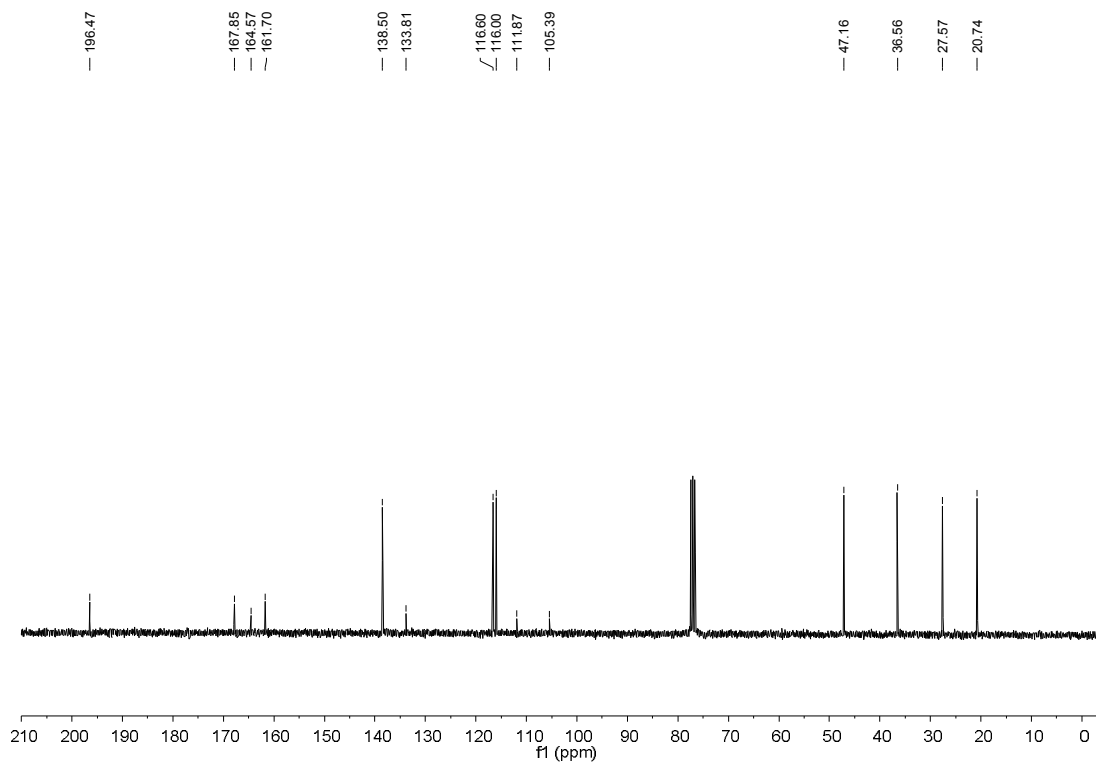
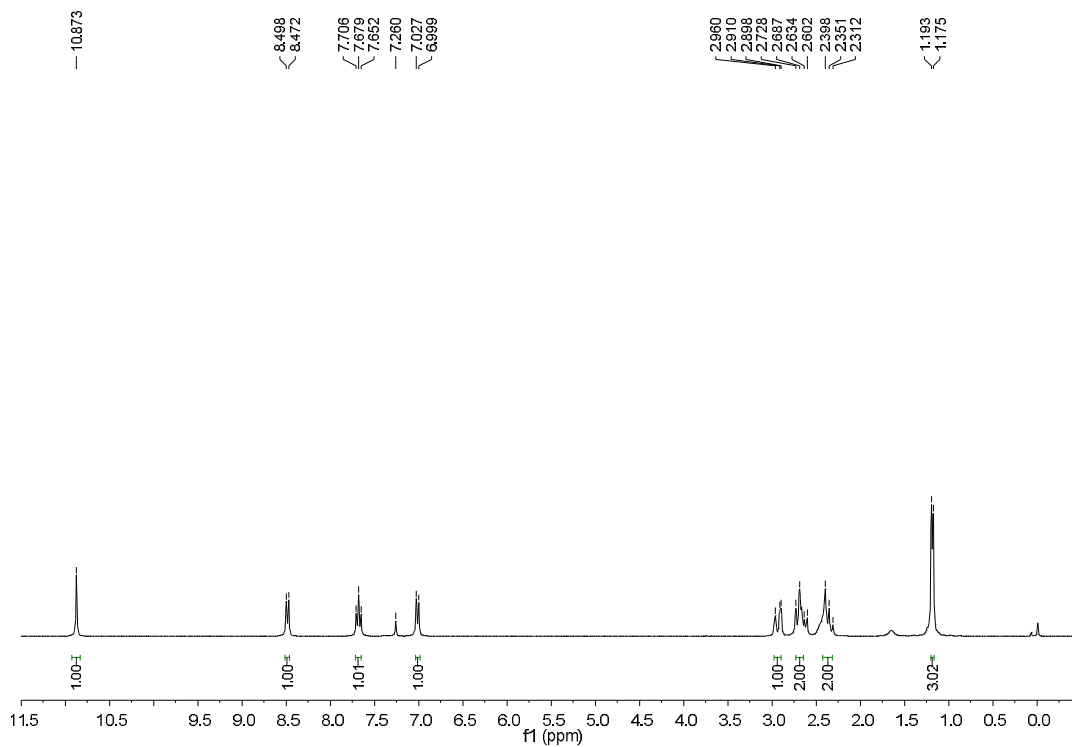
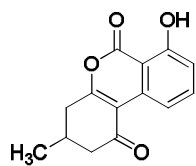
^1H NMR and ^{13}C NMR Spectra of Compound 4ad



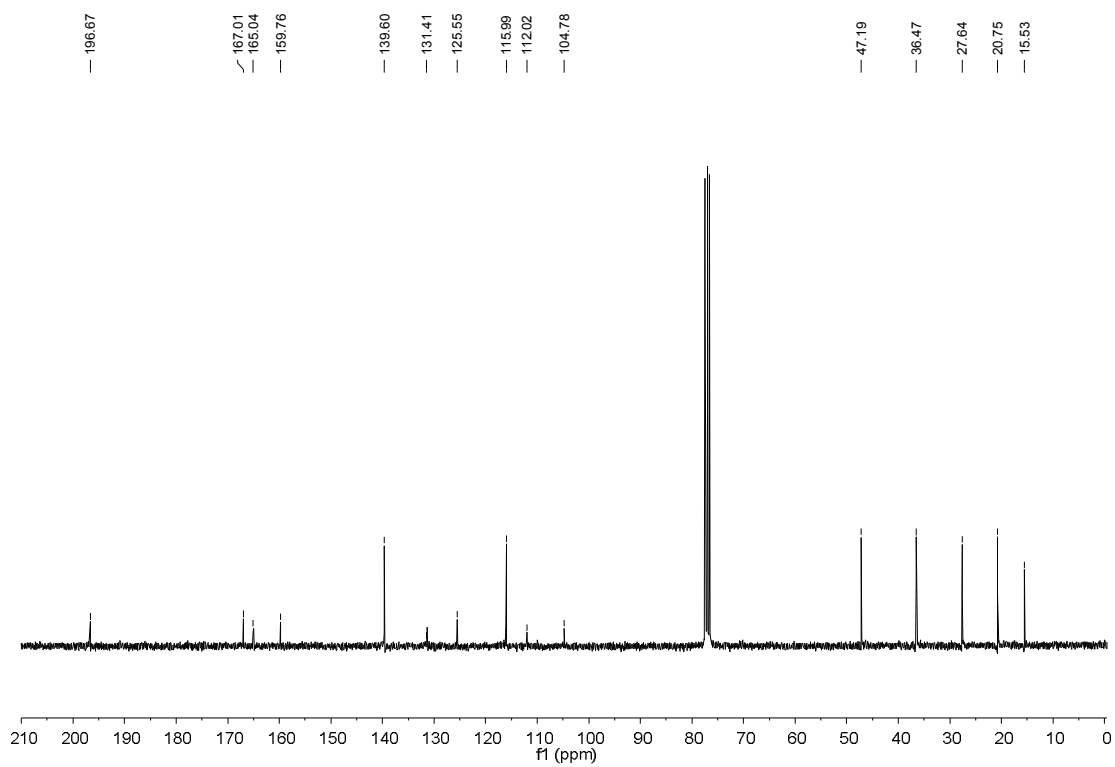
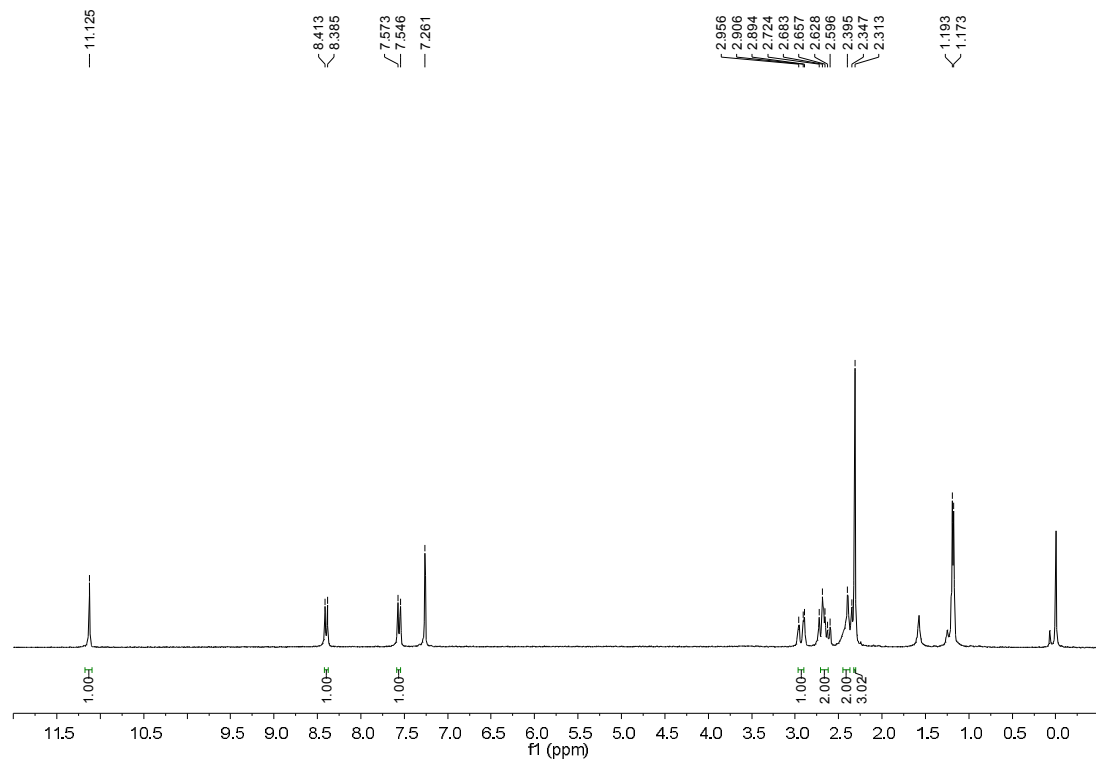
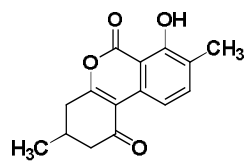
¹H NMR and ¹³C NMR Spectra of Compound 4ae



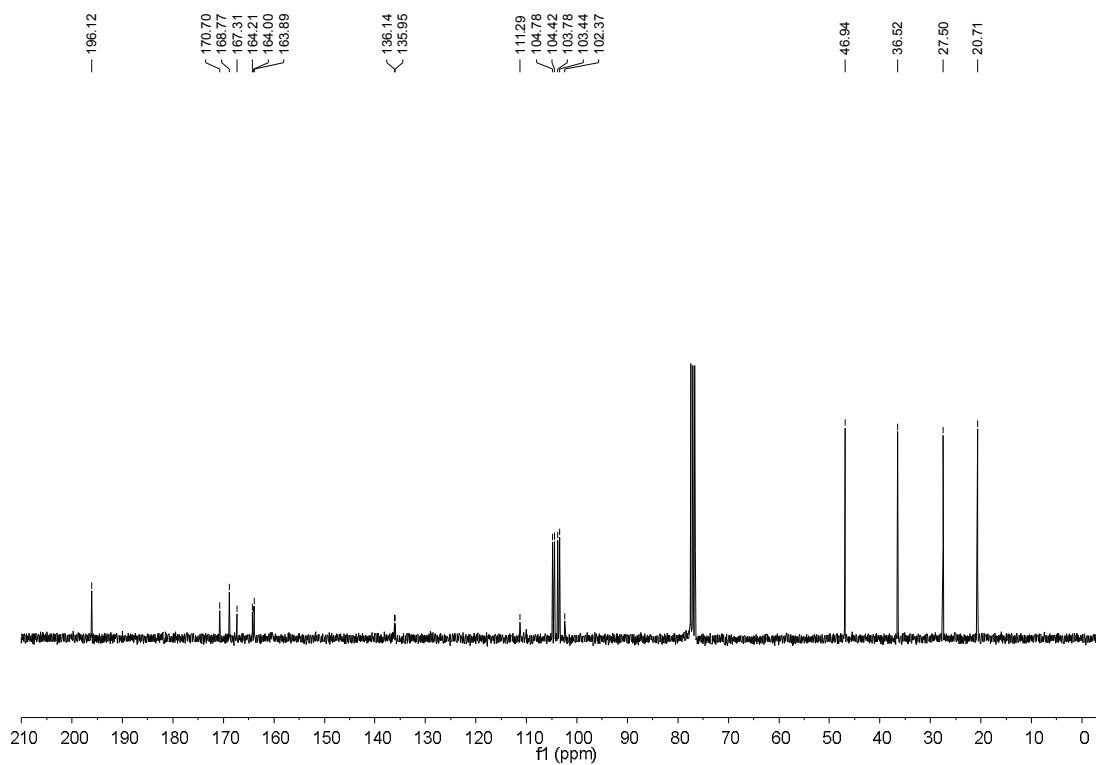
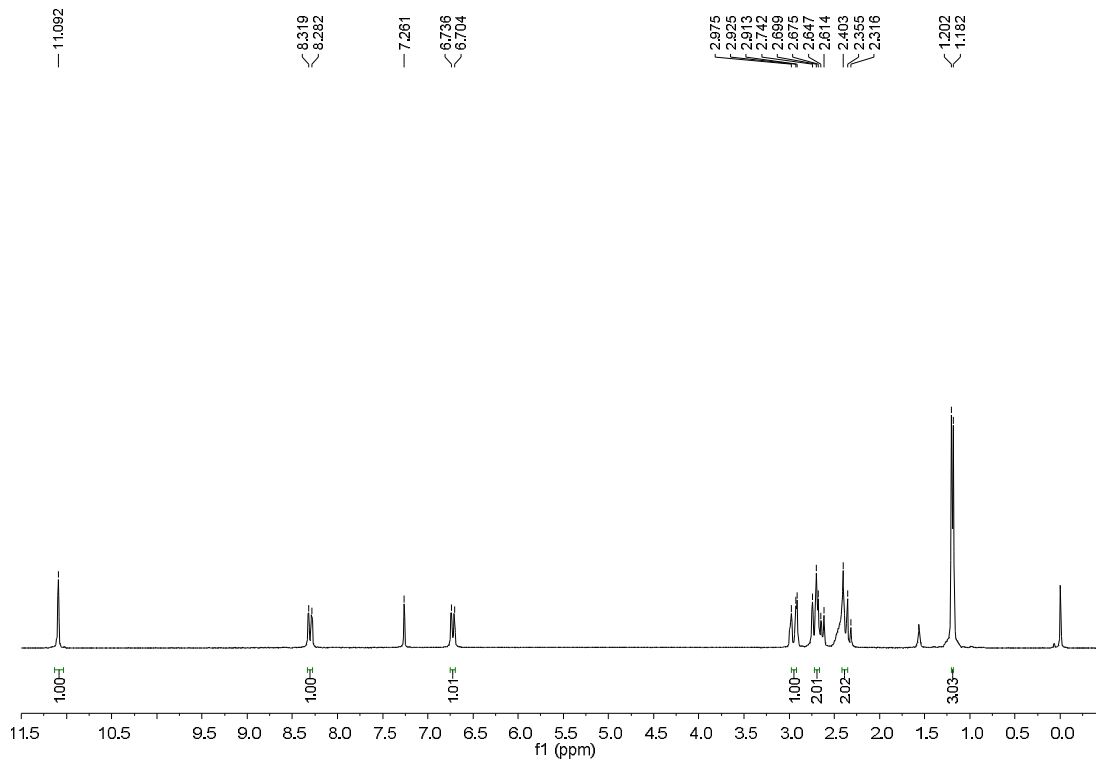
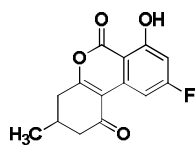
^1H NMR and ^{13}C NMR Spectra of Compound 4ba



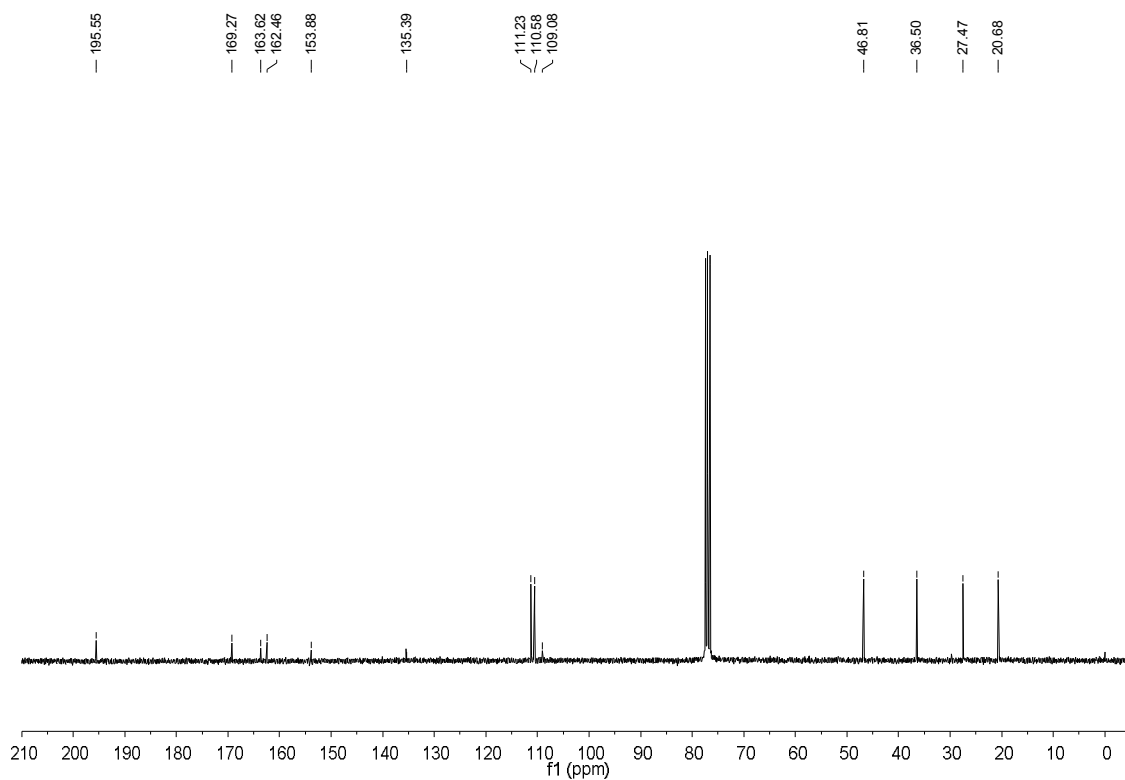
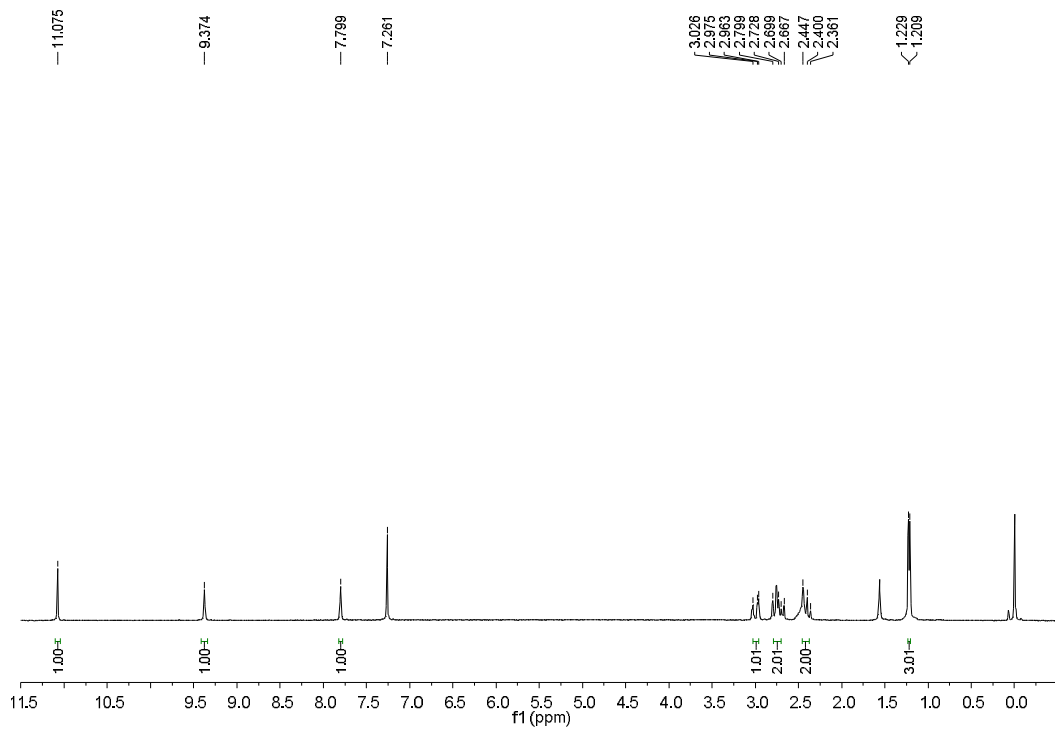
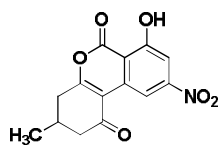
¹H NMR and ¹³C NMR Spectra of Compound 4bb



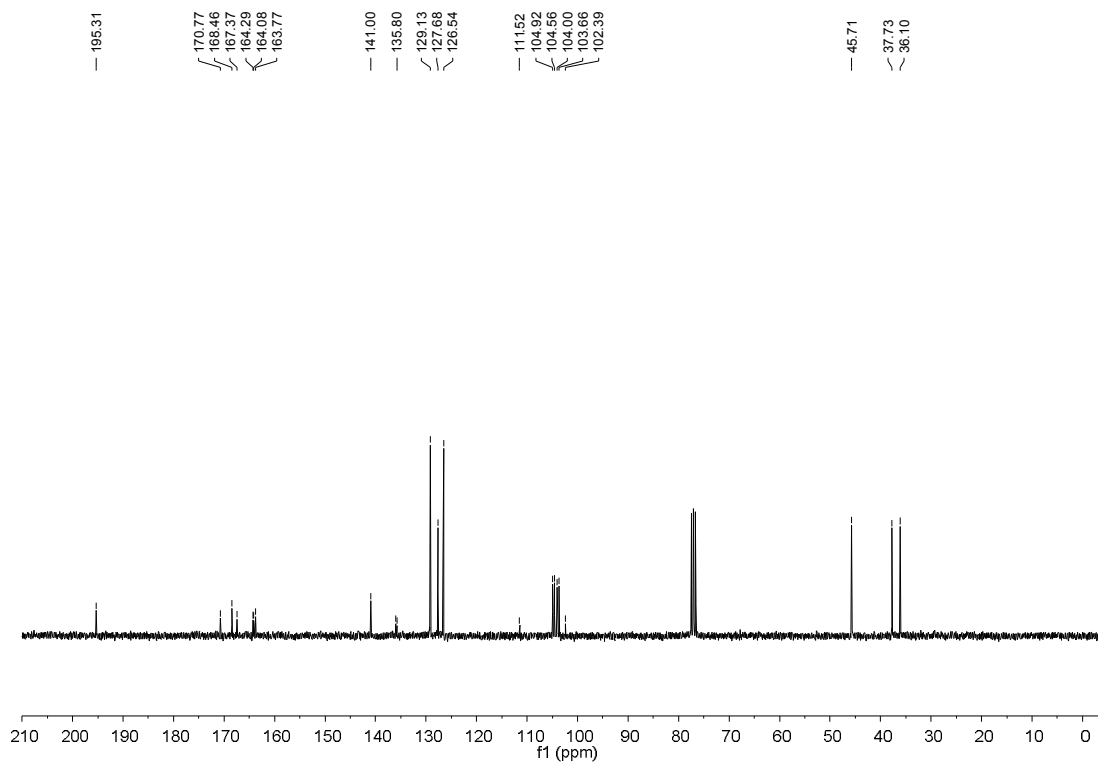
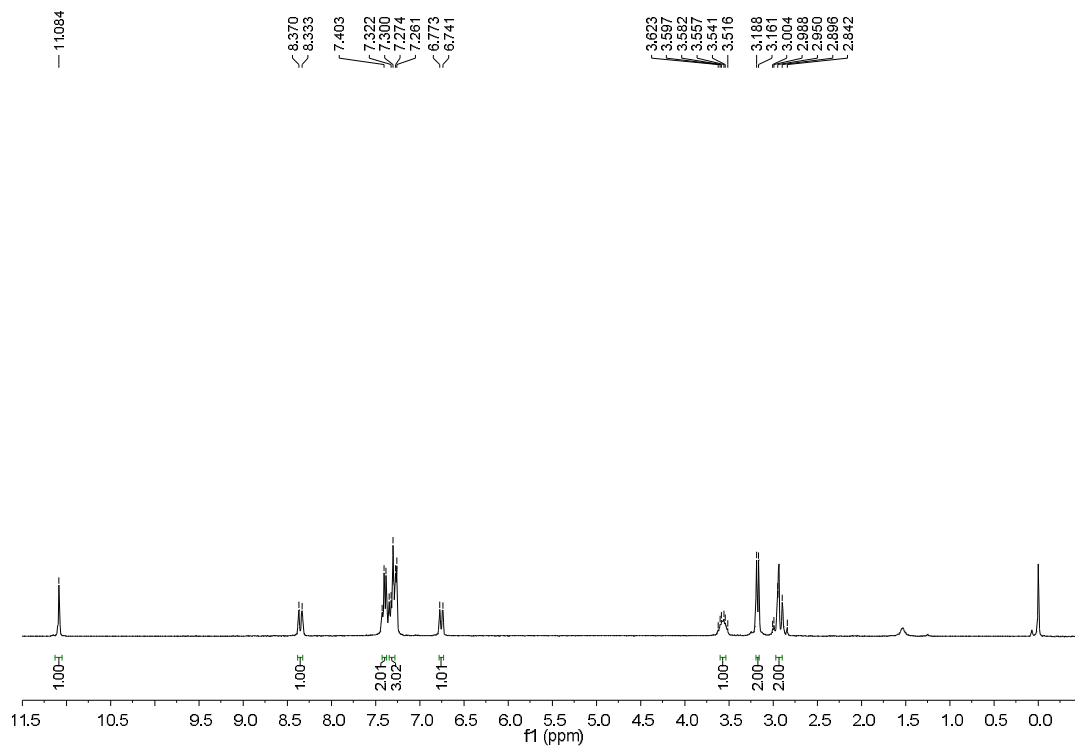
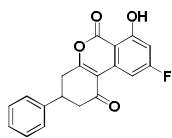
^1H NMR and ^{13}C NMR Spectra of Compound 4bc



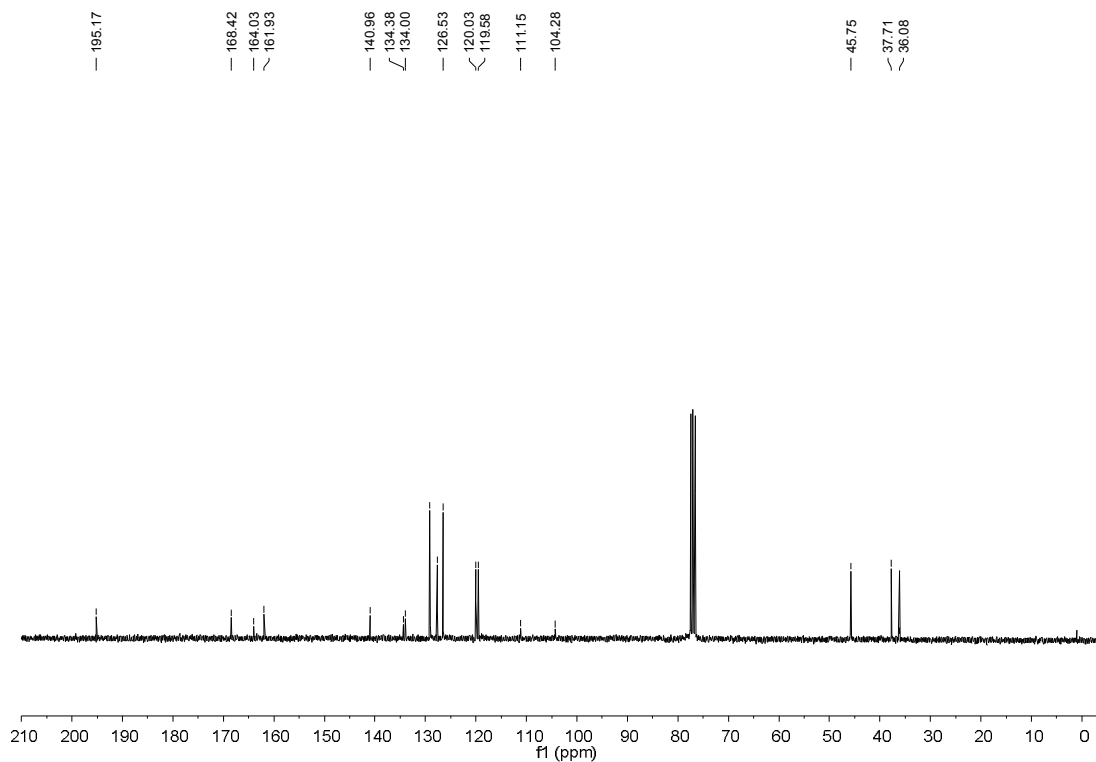
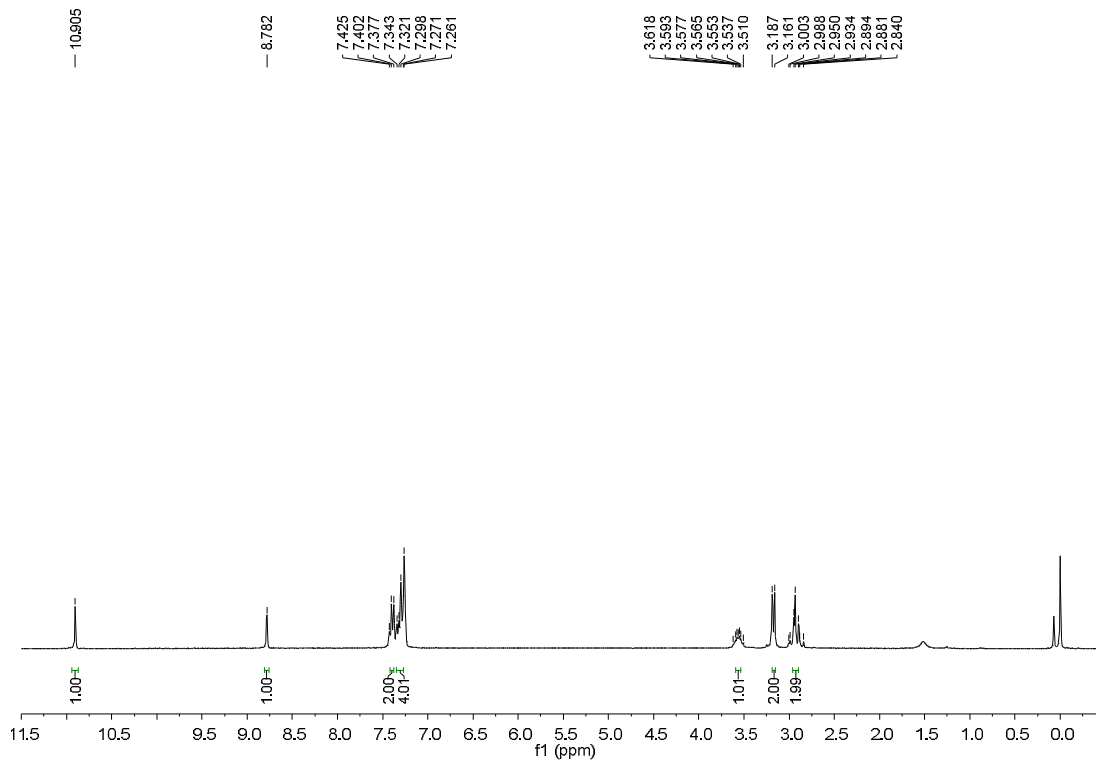
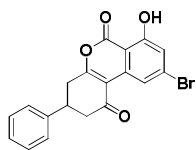
¹H NMR and ¹³C NMR Spectra of Compound 4bd



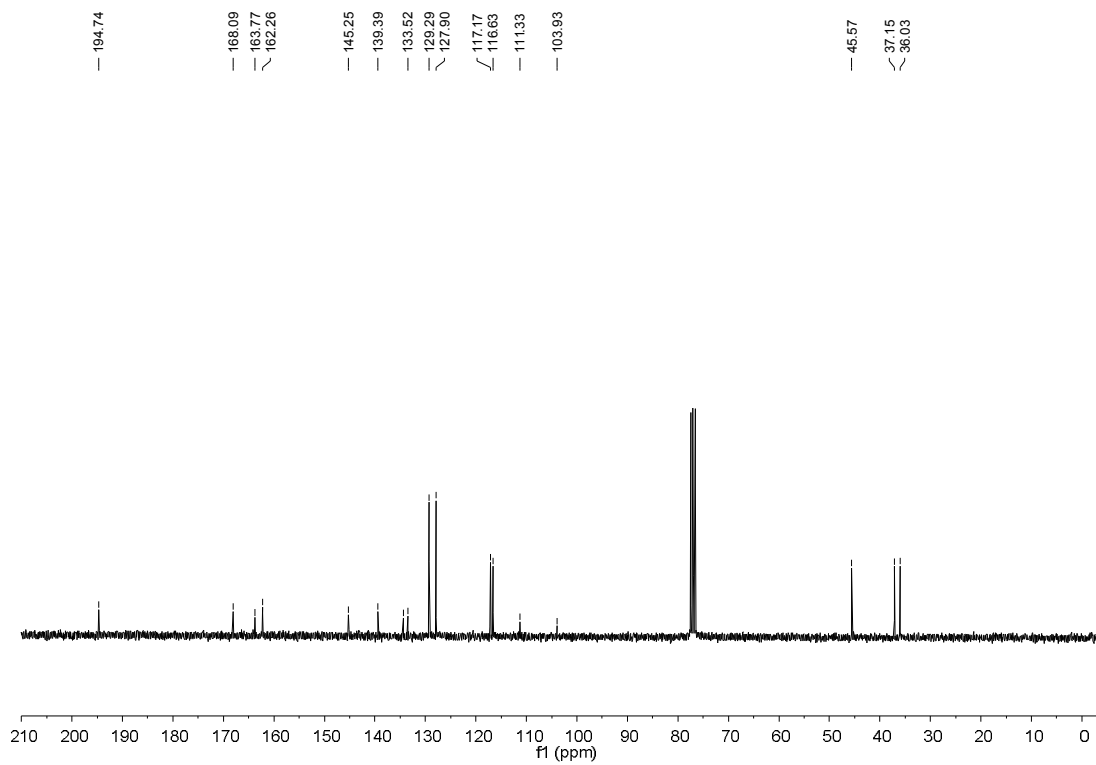
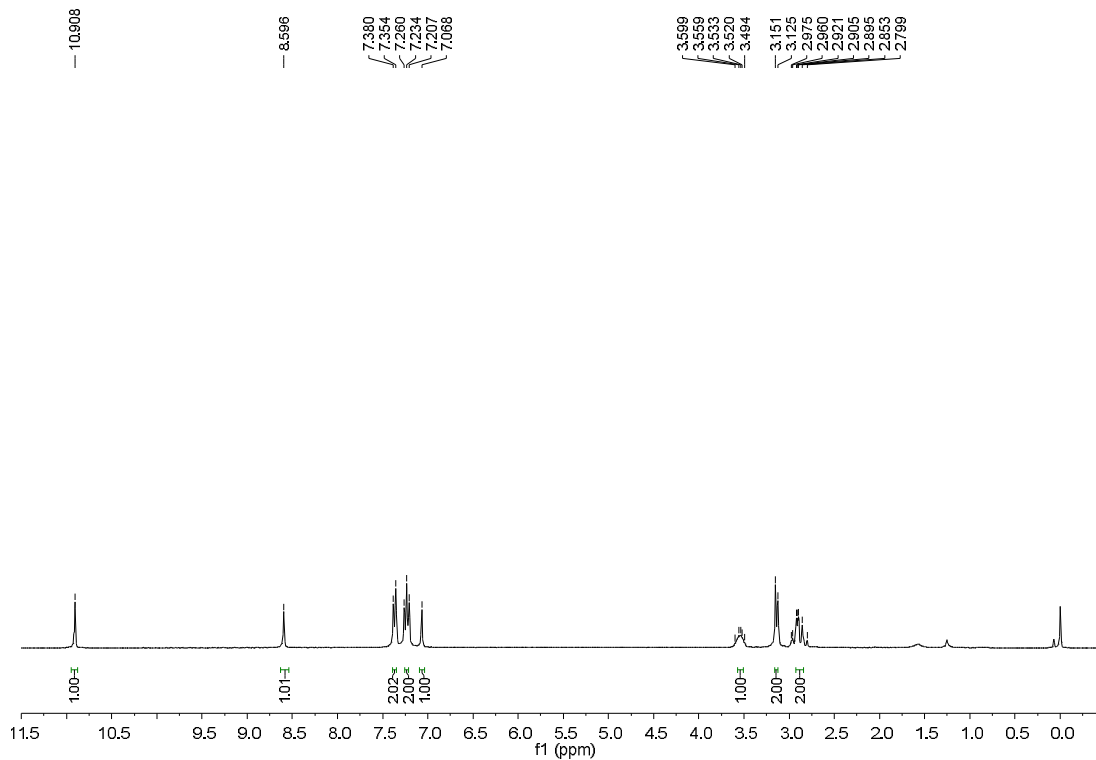
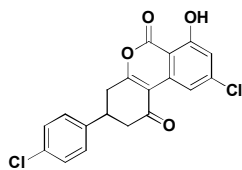
¹H NMR and ¹³C NMR Spectra of Compound 4ca



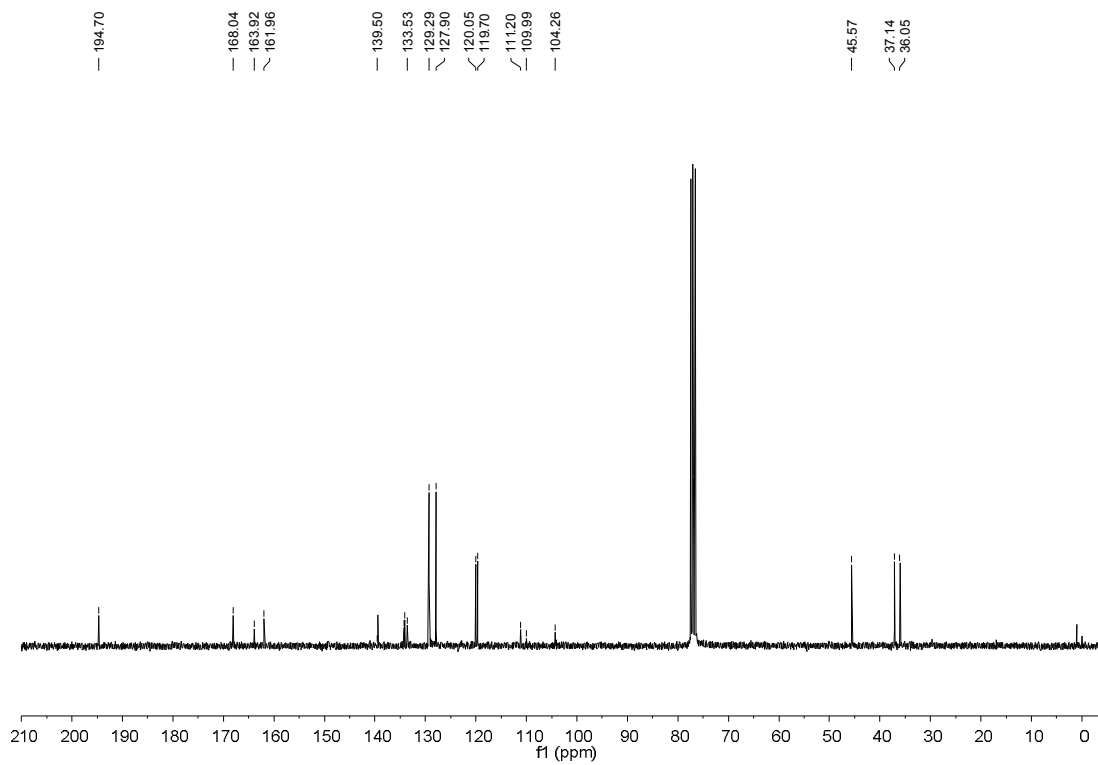
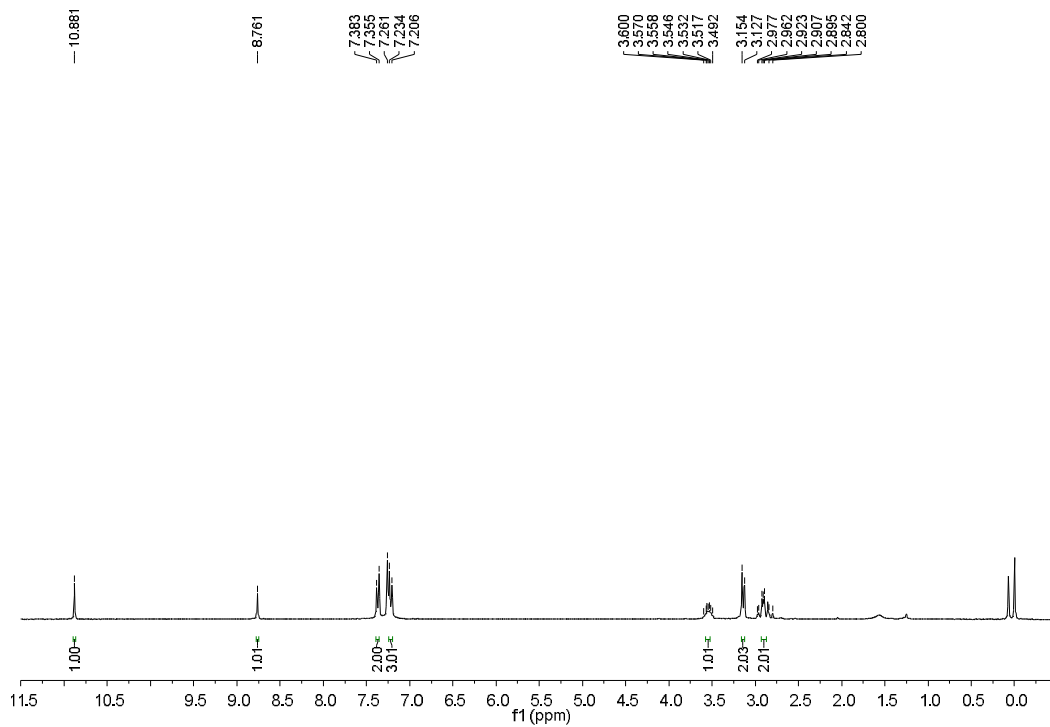
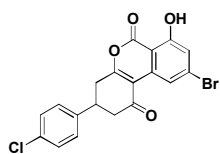
^1H NMR and ^{13}C NMR Spectra of Compound 4cb



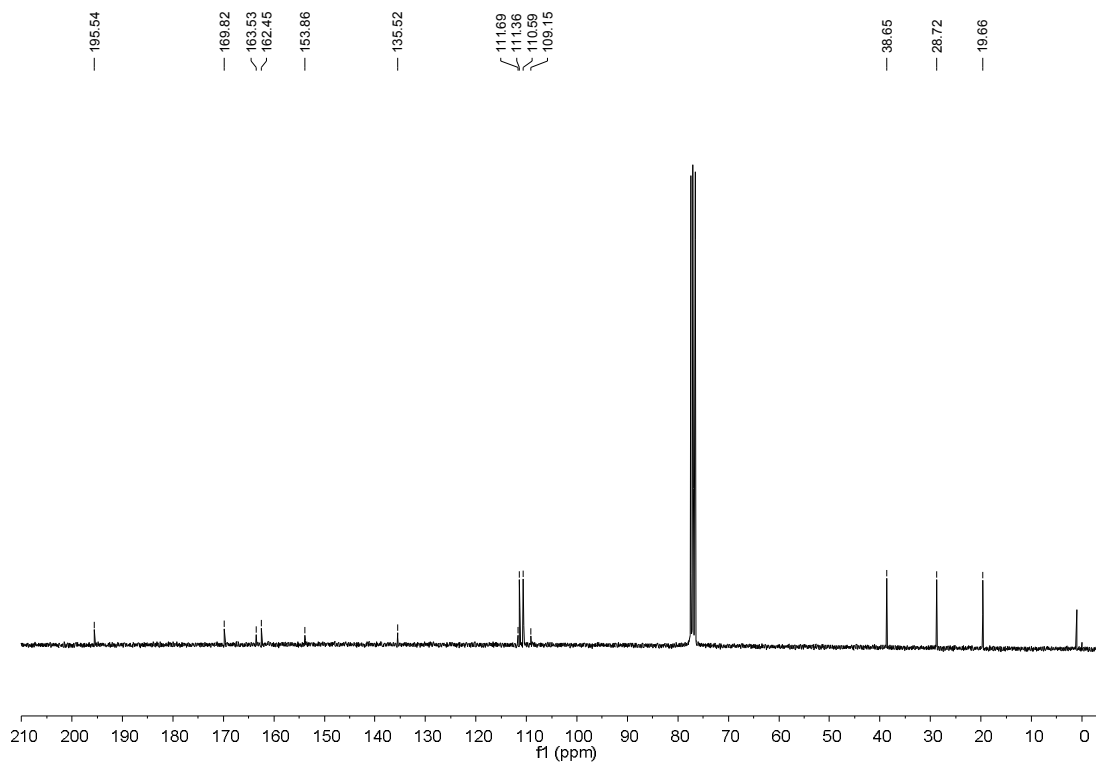
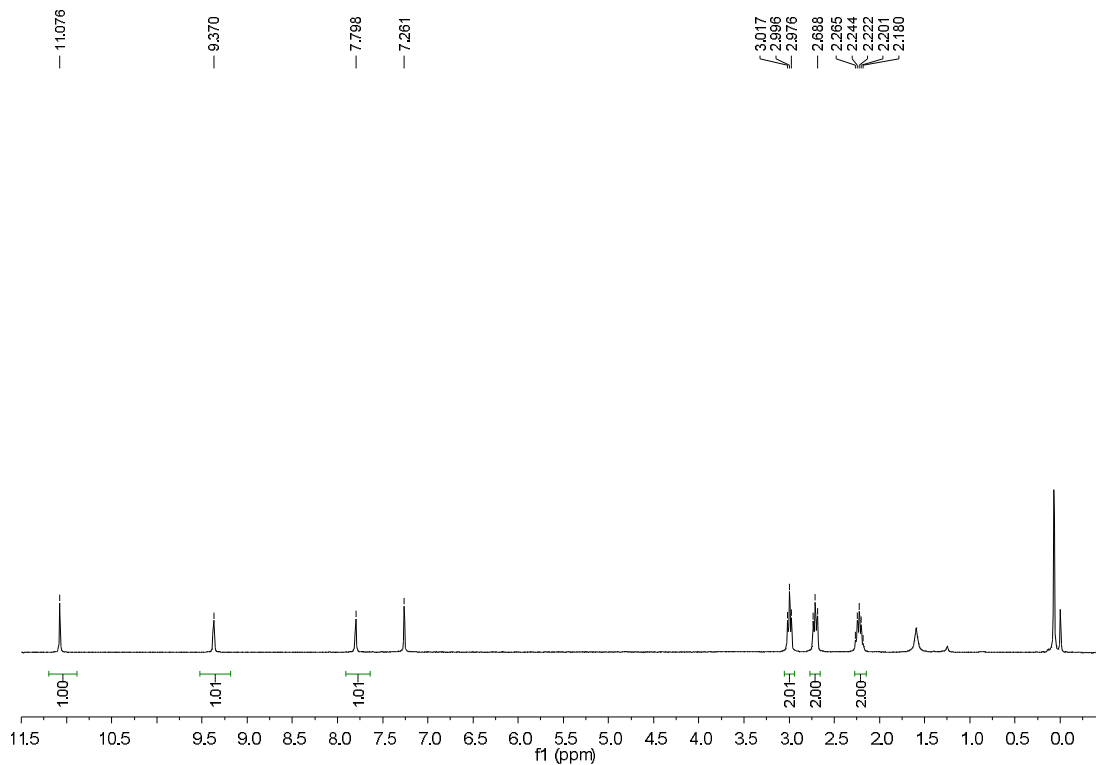
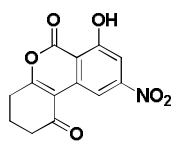
^1H NMR and ^{13}C NMR Spectra of Compound 4da



¹H NMR and ¹³C NMR Spectra of Compound 4db



^1H NMR and ^{13}C NMR Spectra of Compound 4ea



X-Ray Crystallography structures of Compounds **3aa** and **4ab**

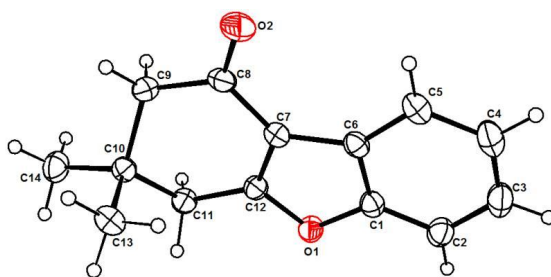


Figure S1. X-ray crystal structure of **3aa**

Crystal data for **3aa**: $C_{14}H_{14}O_2$, $M_r = 214.26$, Monoclinic, $a = 9.4379(9) \text{ \AA}$, $b = 12.1544(11) \text{ \AA}$, $c = 9.8277(9) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 96.810(10)^\circ$, $\gamma = 90^\circ$, $V = 1119.28(18) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $P2(1)/n$, $Z = 8$, 8285 reflections collected, 2061 unique ($R_{\text{int}} = 0.0269$) which were used in all calculation. The ellipsoid contour probability level in the caption of 30 %.

Crystallographic data for compound **3aa** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC-1554775**.

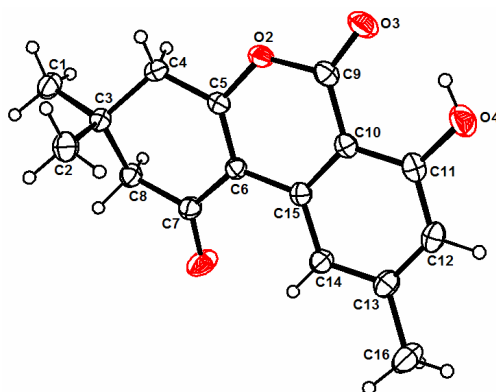
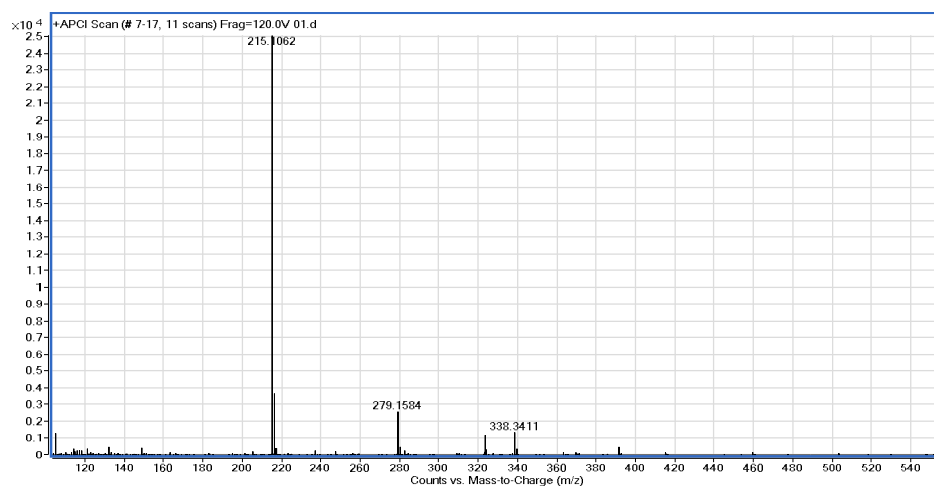


Figure S2. X-ray crystal structure of **4ab**

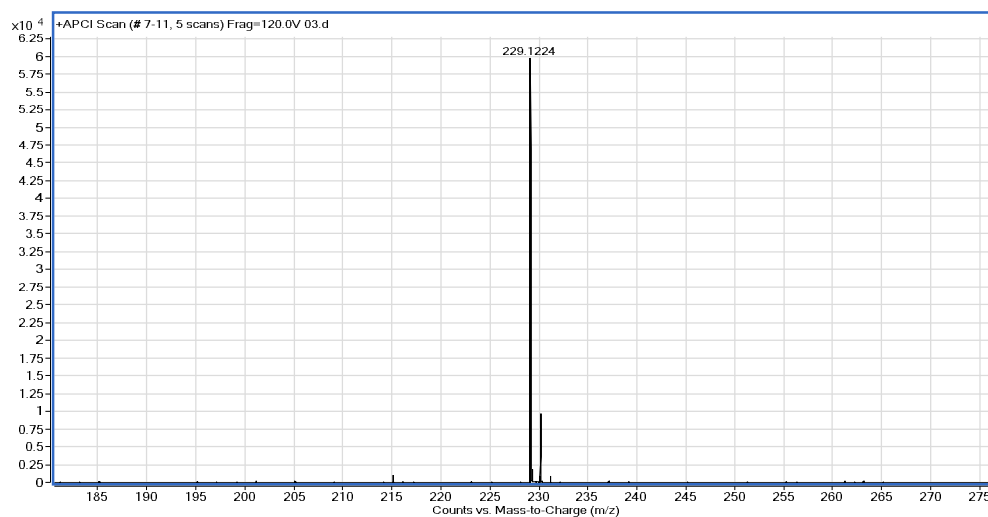
Crystal data for **4ab**: $C_{16}H_{16}O_4$, $M_r = 272.29$, Monoclinic, $a = 8.8746(6) \text{ \AA}$, $b = 15.3282(11) \text{ \AA}$, $c = 10.0135(7) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 95.182(2)^\circ$, $\gamma = 90^\circ$, $V = 1356.59(16) \text{ \AA}^3$, $T = 293(2) \text{ K}$, space group $P2(1)/c$, $Z = 4$, 23206 reflections collected, 2484 unique ($R_{\text{int}} = 0.0390$) which were used in all calculation. The ellipsoid contour probability level in the caption of 30%.

Crystallographic data for compound **4ab** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC- 1555510**.

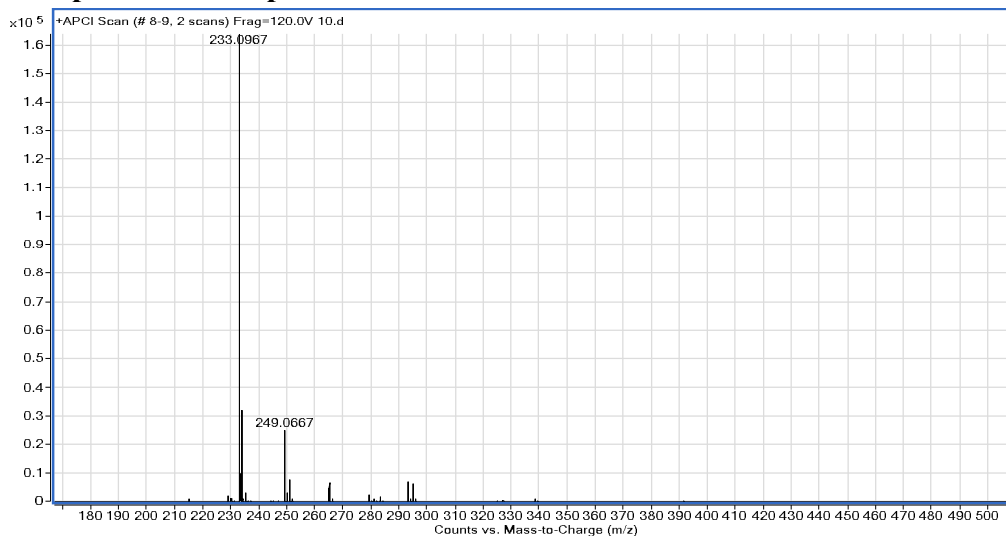
HRMS Spectra of Compound 3aa



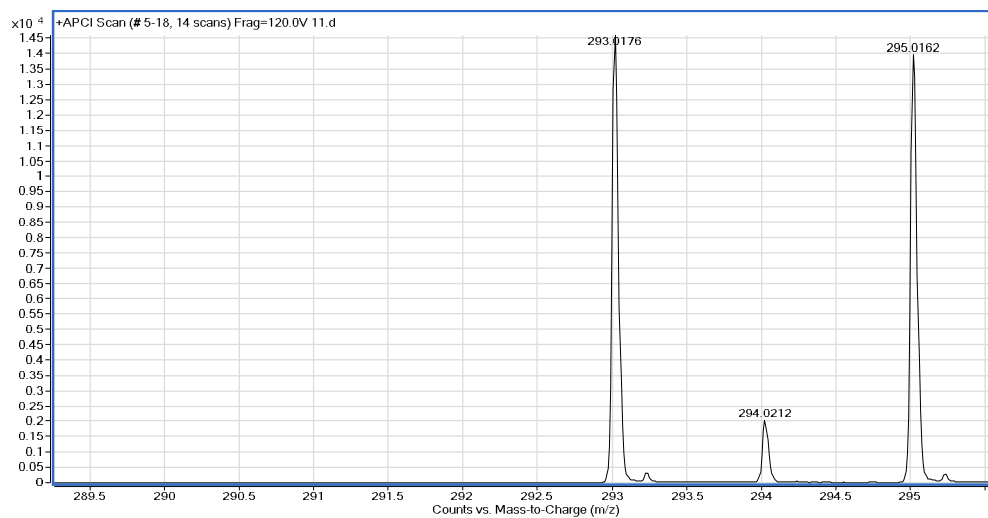
HRMS Spectra of Compound 3ab



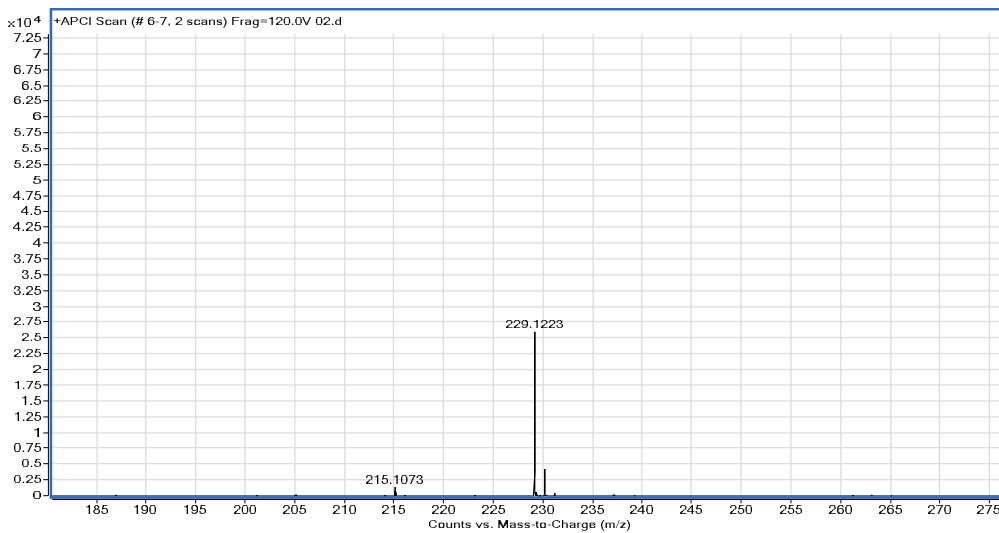
HRMS Spectra of Compound 3ac



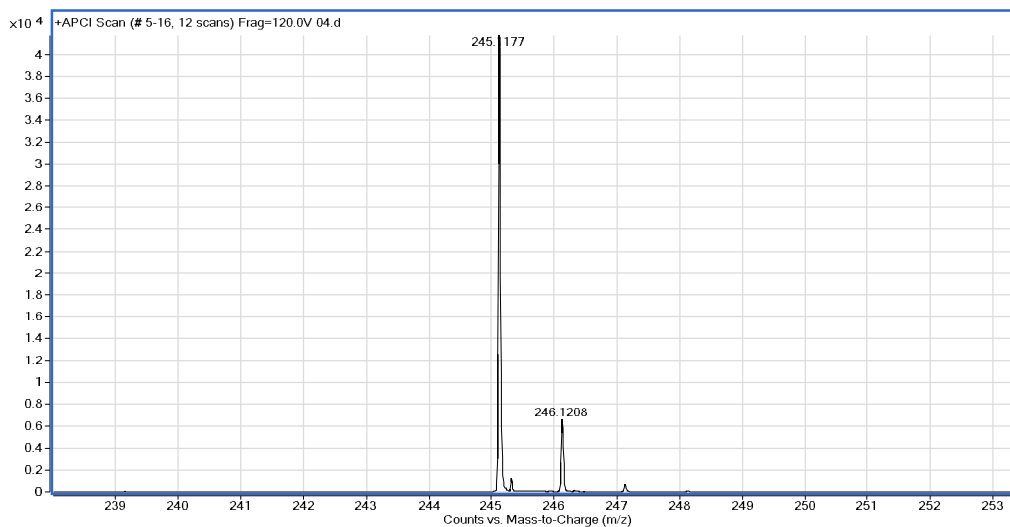
HRMS Spectra of Compound 3ad



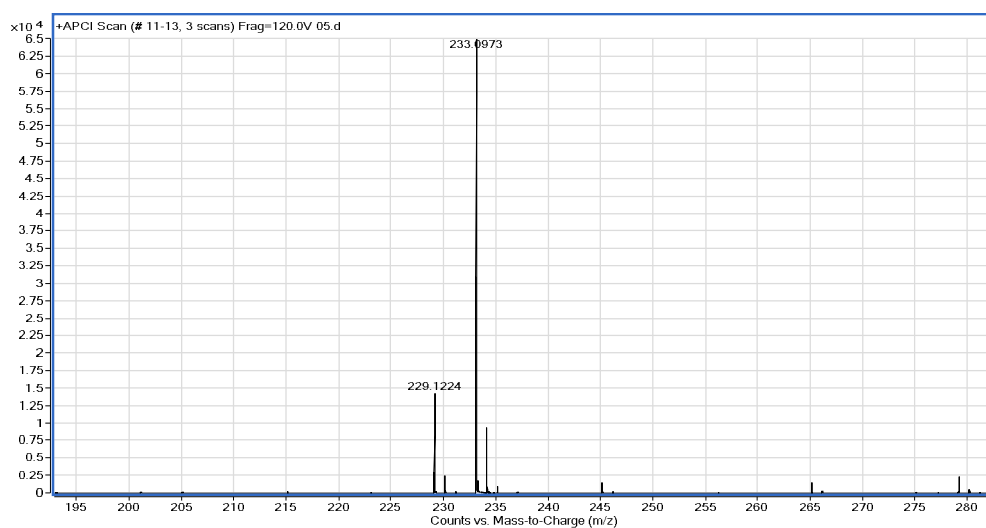
HRMS Spectra of Compound 3ae



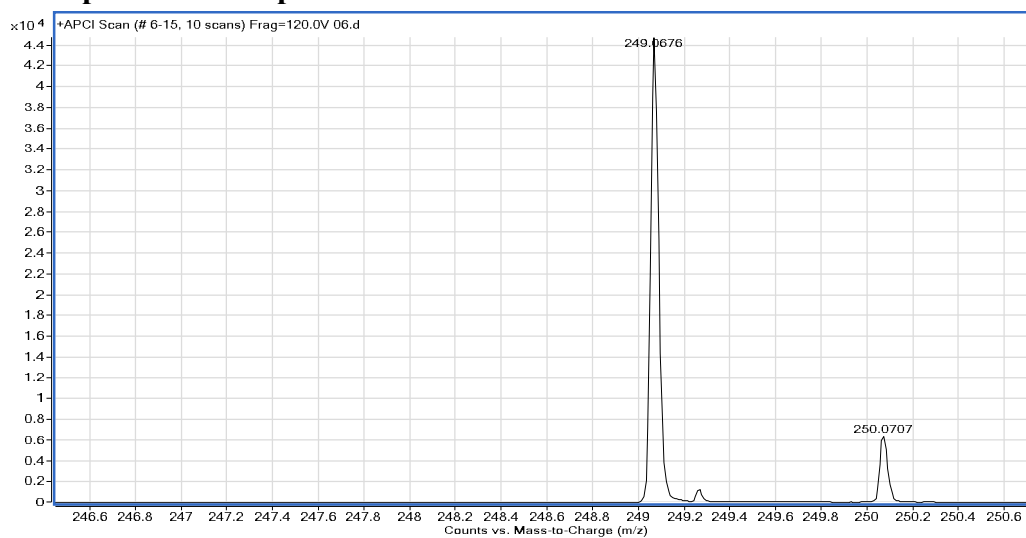
HRMS Spectra of Compound 3af



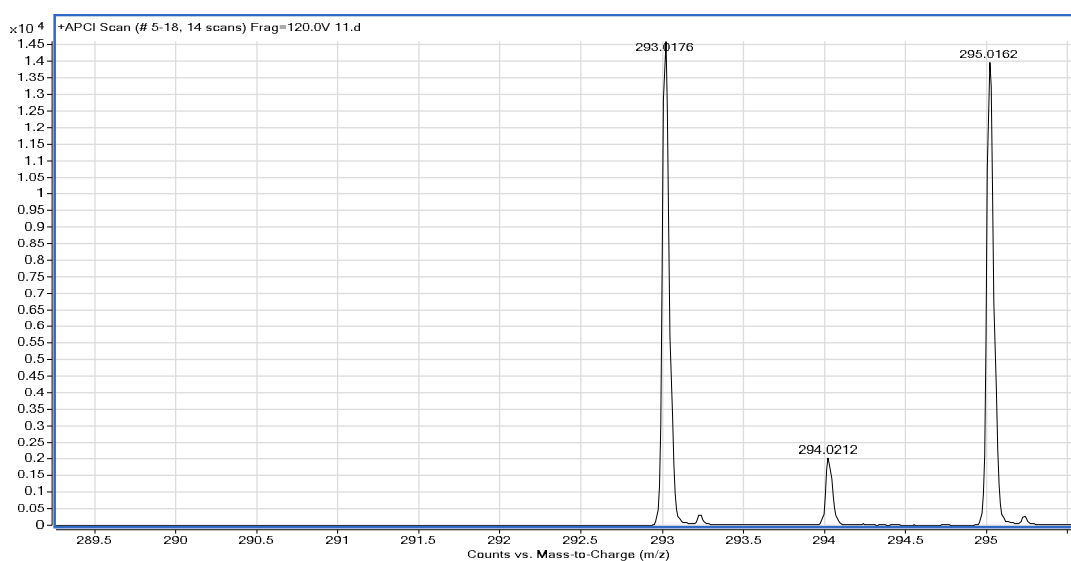
HRMS Spectra of Compound 3ag



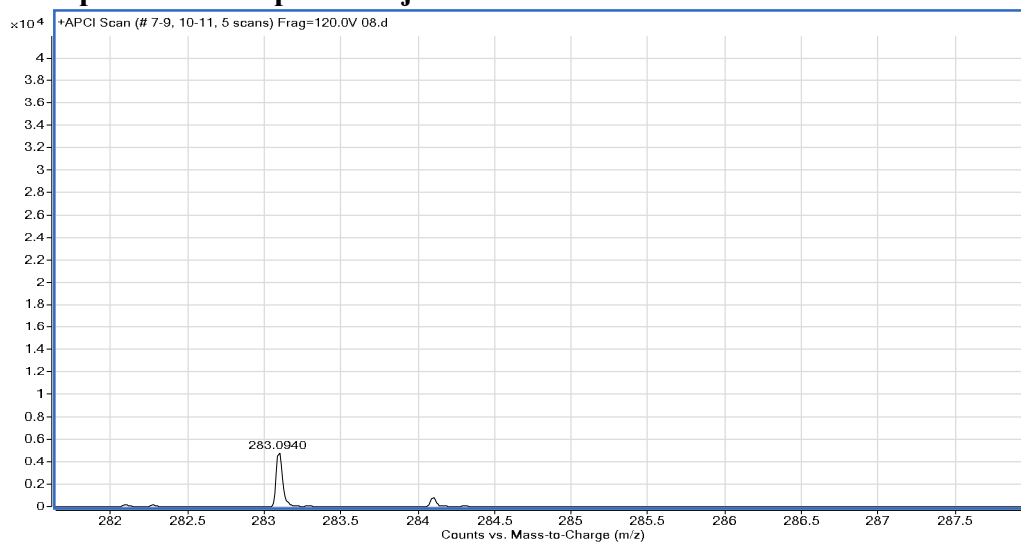
HRMS Spectra of Compound 3ah



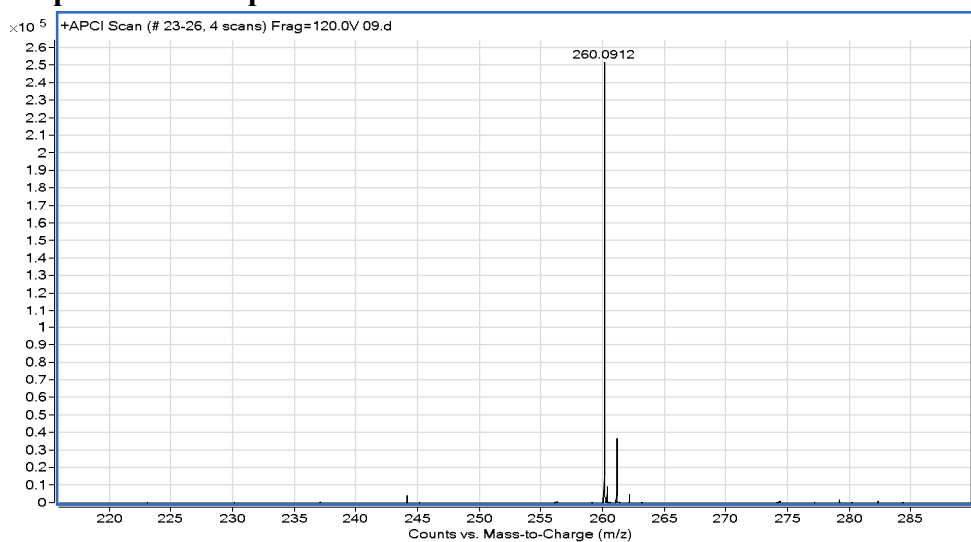
HRMS Spectra of Compound 3ai



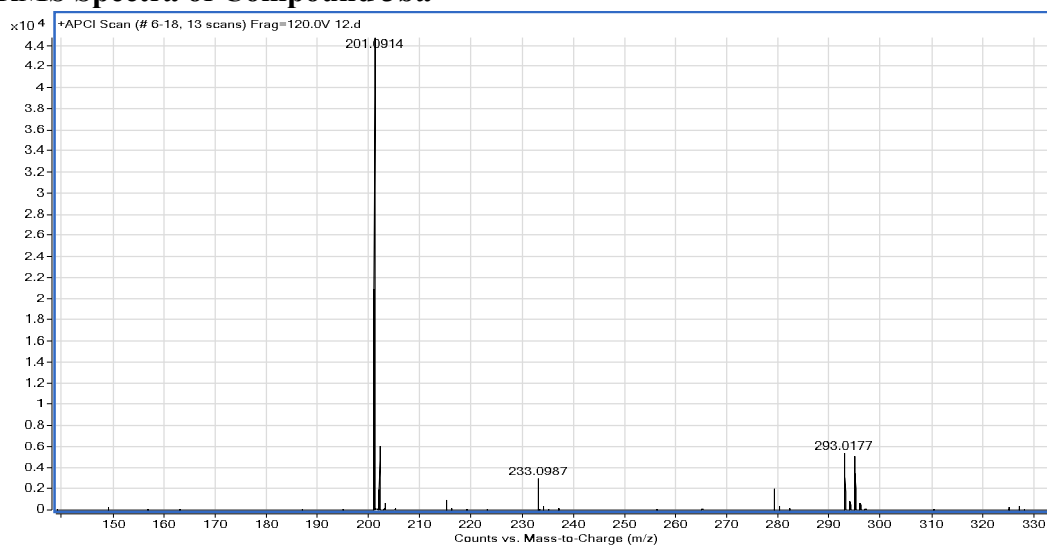
HRMS Spectra of Compound 3aj



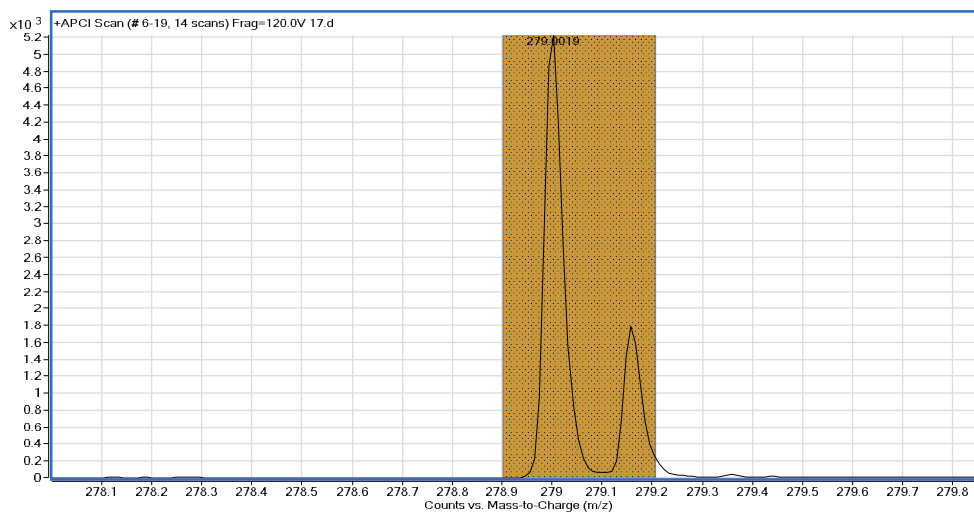
HRMS Spectra of Compound 3ak



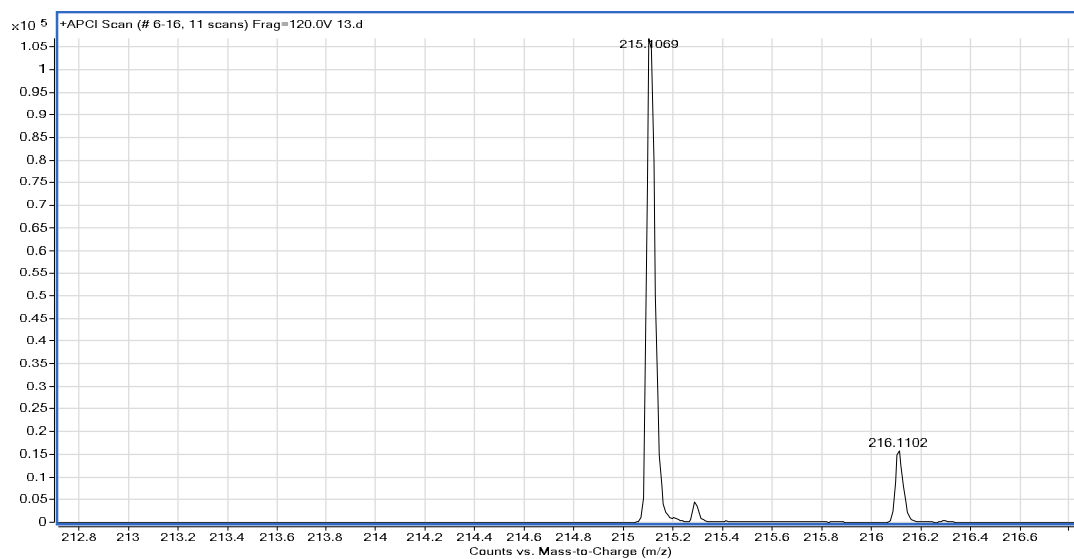
HRMS Spectra of Compound 3ba



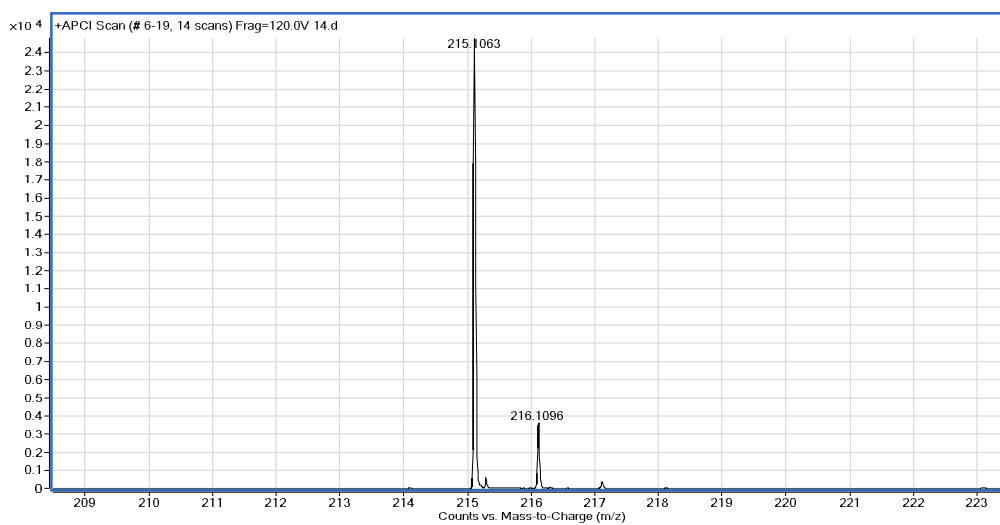
HRMS Spectra of Compound 3bb



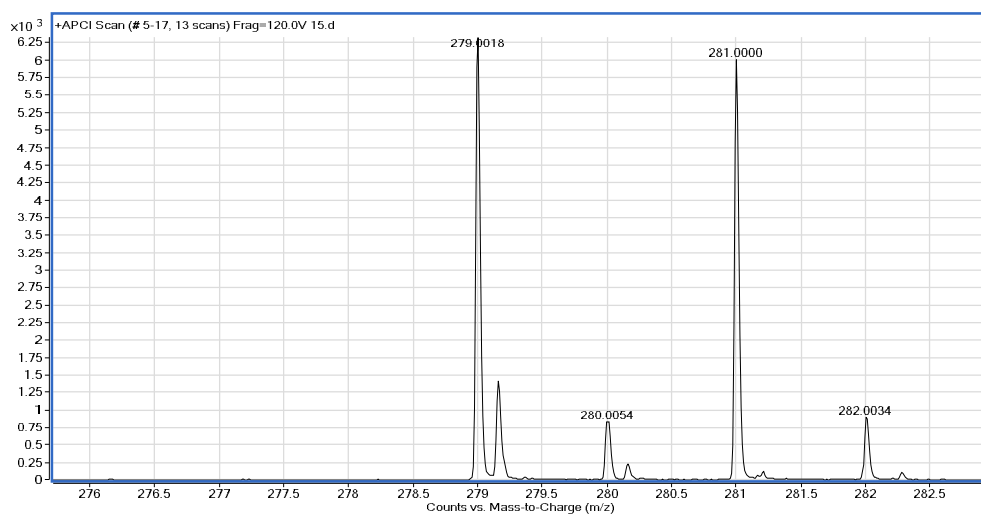
HRMS Spectra of Compound 3bc



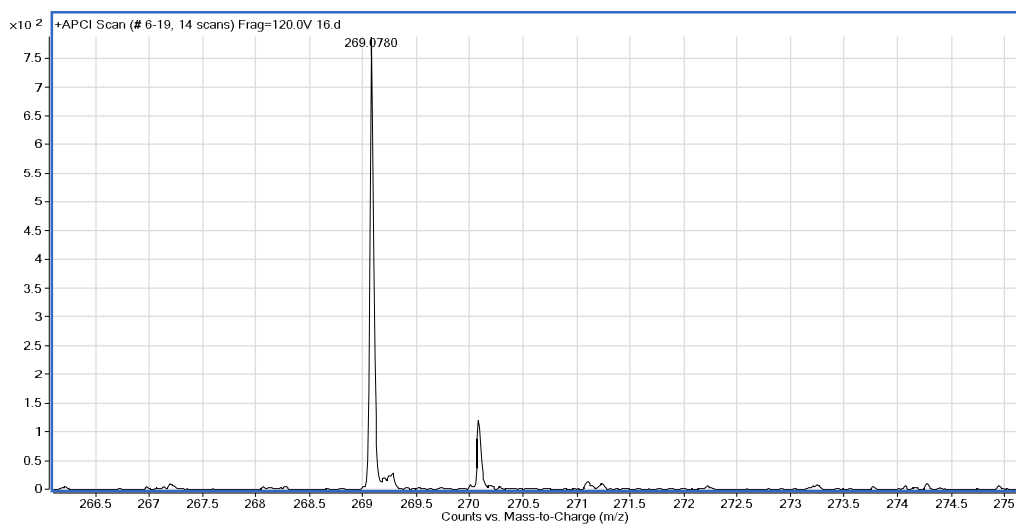
HRMS Spectra of Compound 3bd



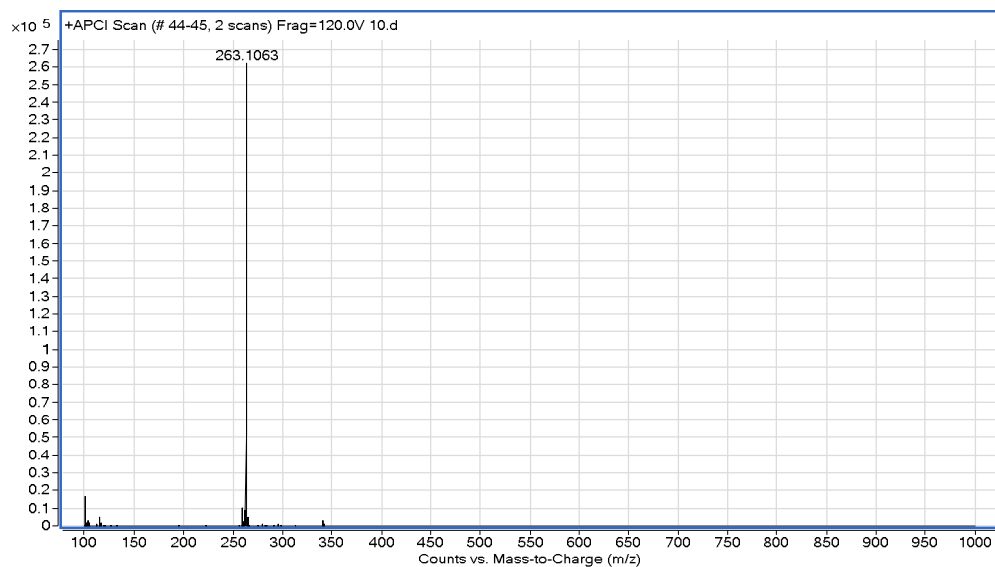
HRMS Spectra of Compound 3be



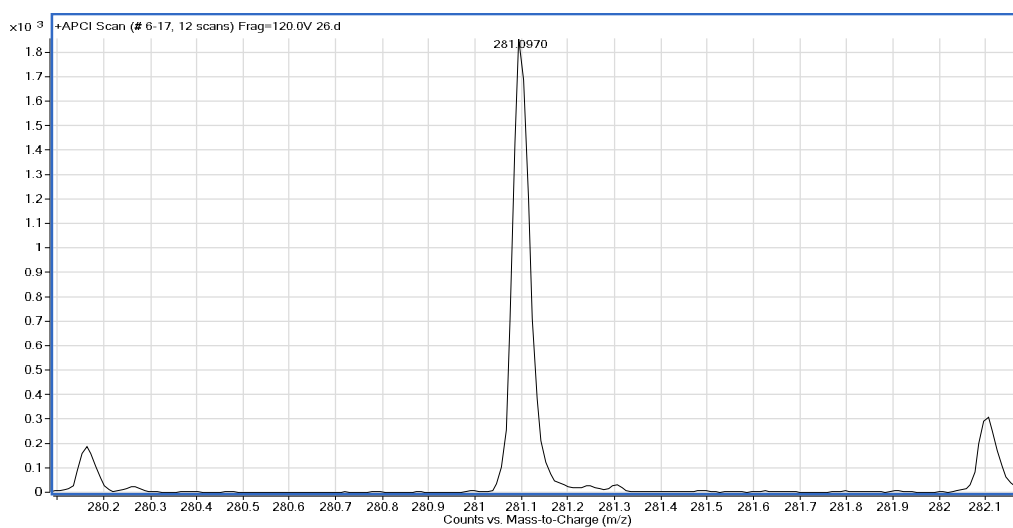
HRMS Spectra of Compound 3bf



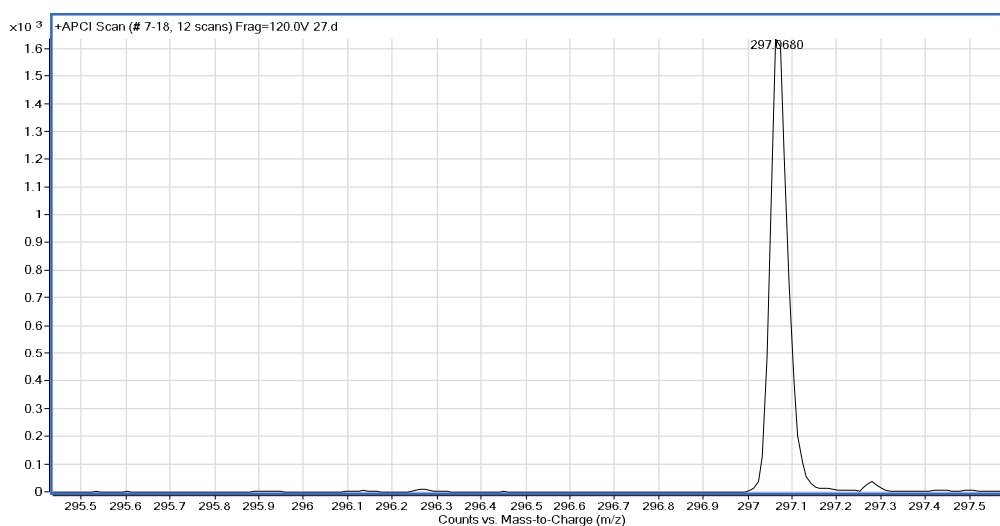
HRMS Spectra of Compound 3ca



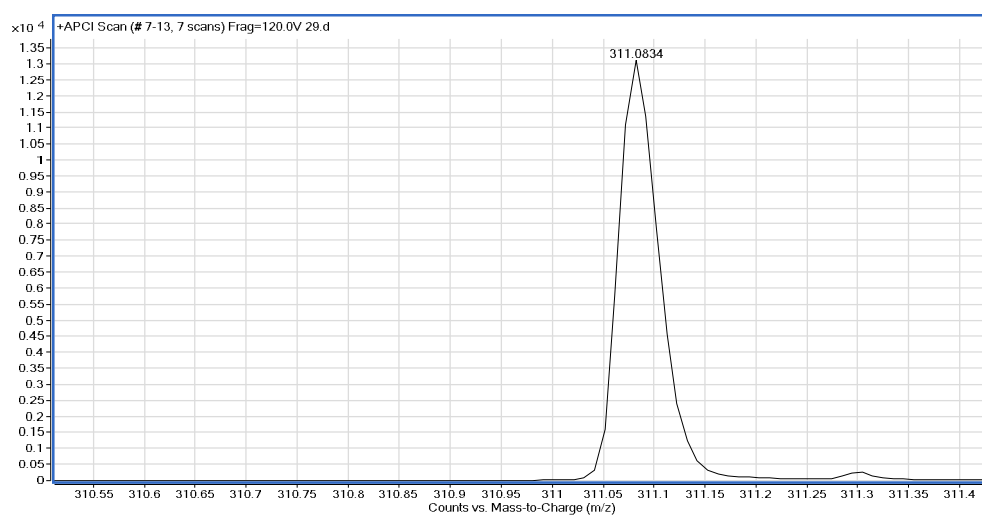
HRMS Spectra of Compound 3cb



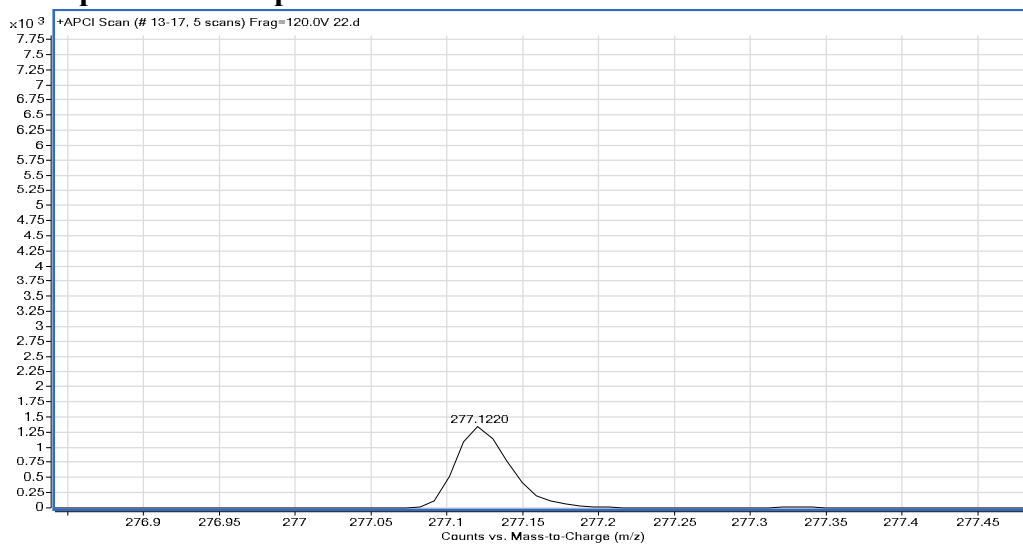
HRMS Spectra of Compound 3cc



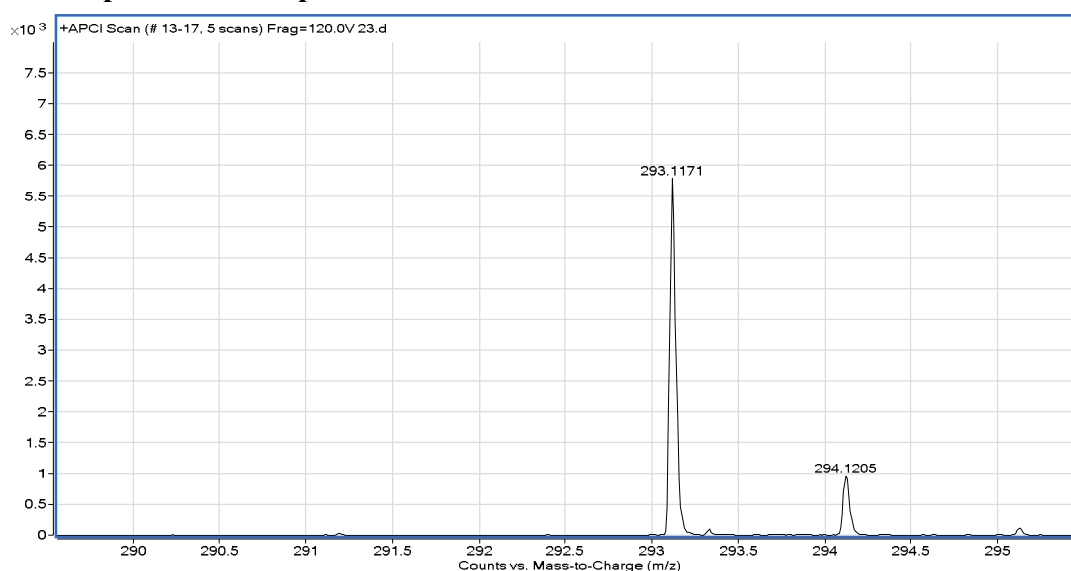
HRMS Spectra of Compound 3cd



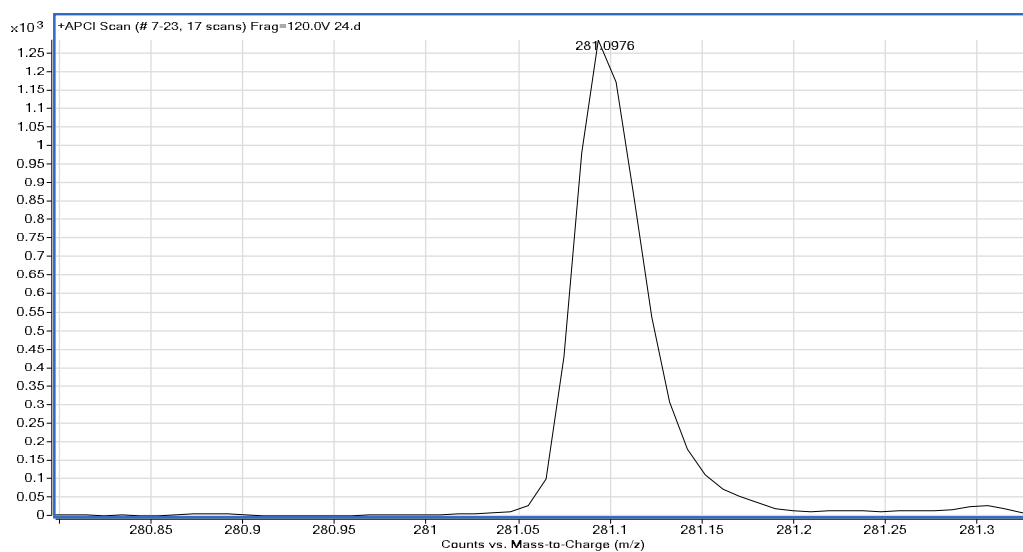
HRMS Spectra of Compound 3ce



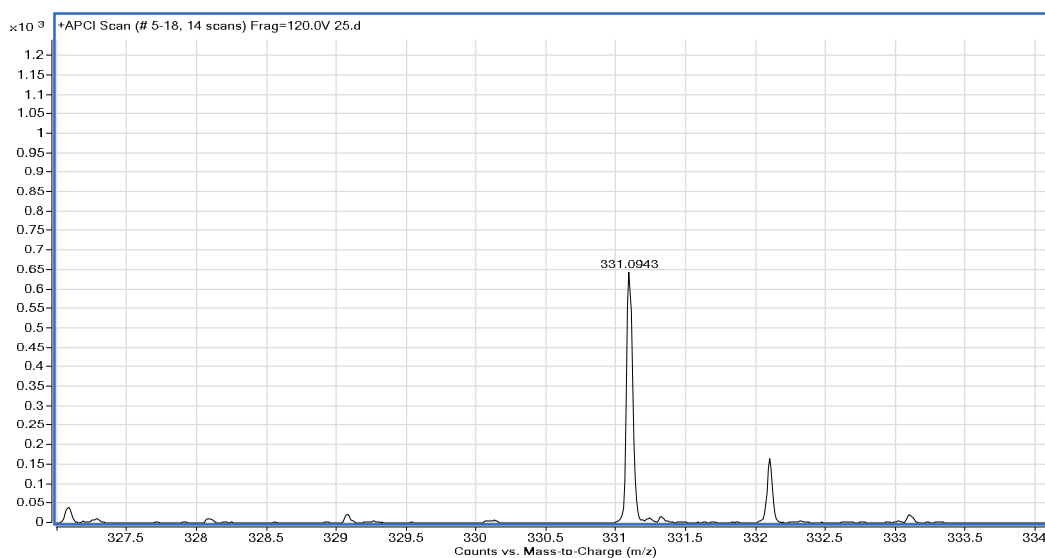
HRMS Spectra of Compound 3cf



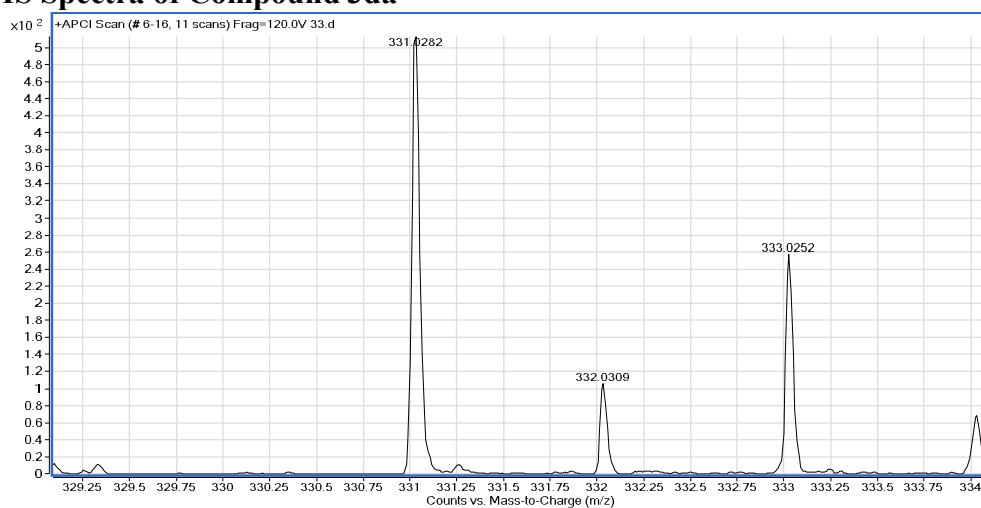
HRMS Spectra of Compound 3cg



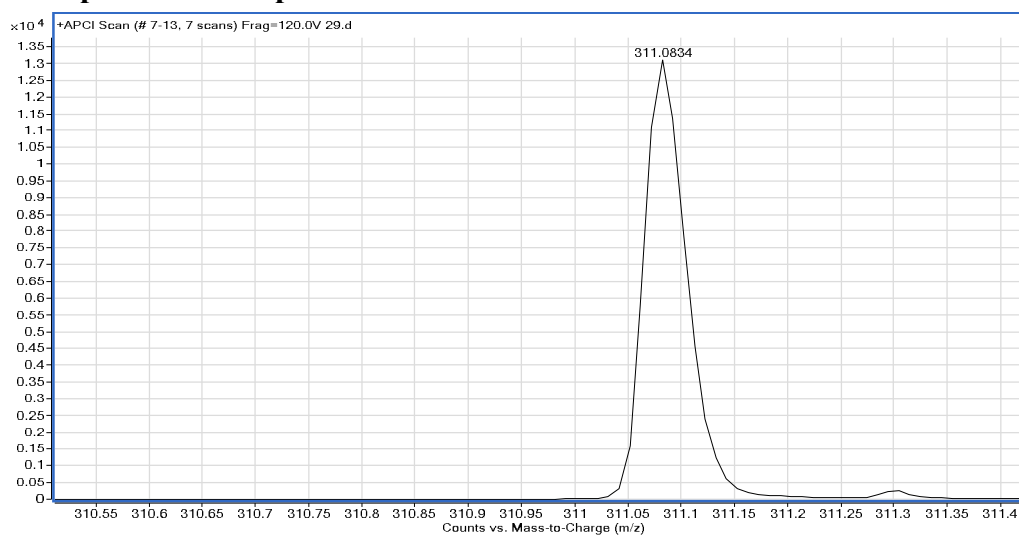
HRMS Spectra of Compound 3cf



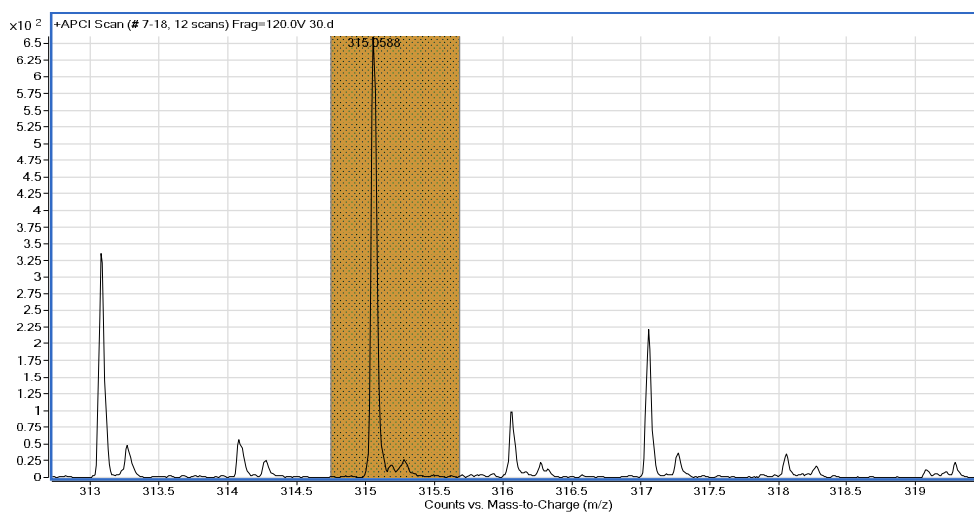
HRMS Spectra of Compound 3da



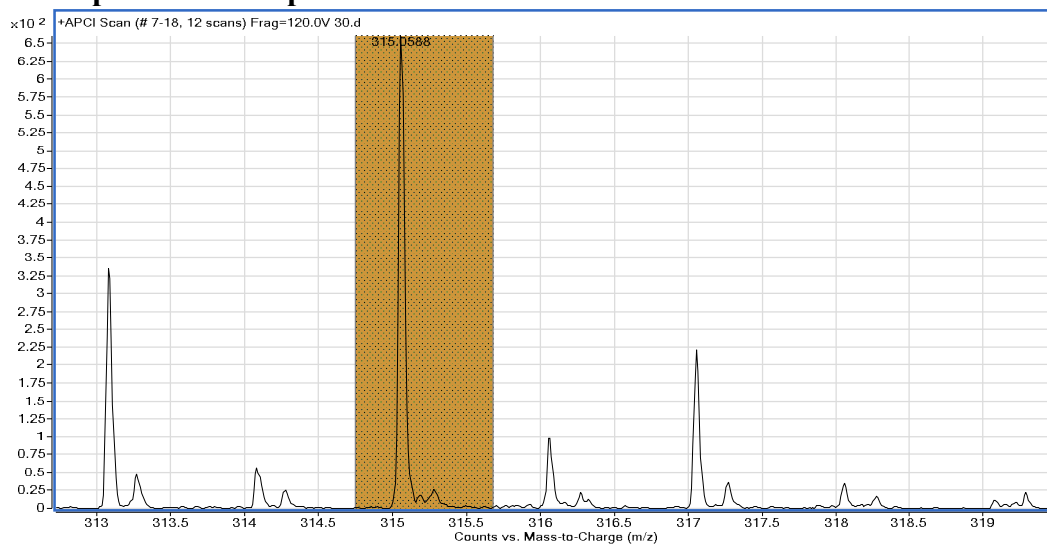
HRMS Spectra of Compound 3db



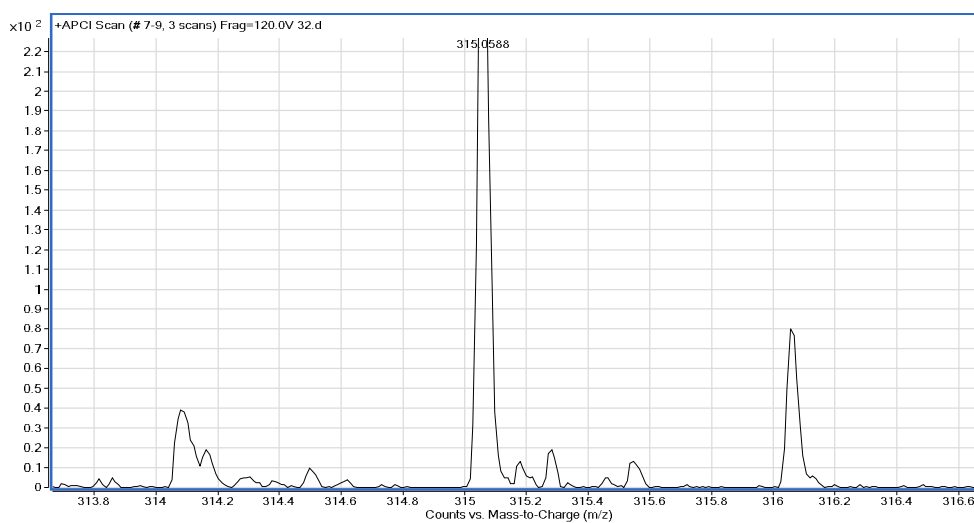
HRMS Spectra of Compound 3dc



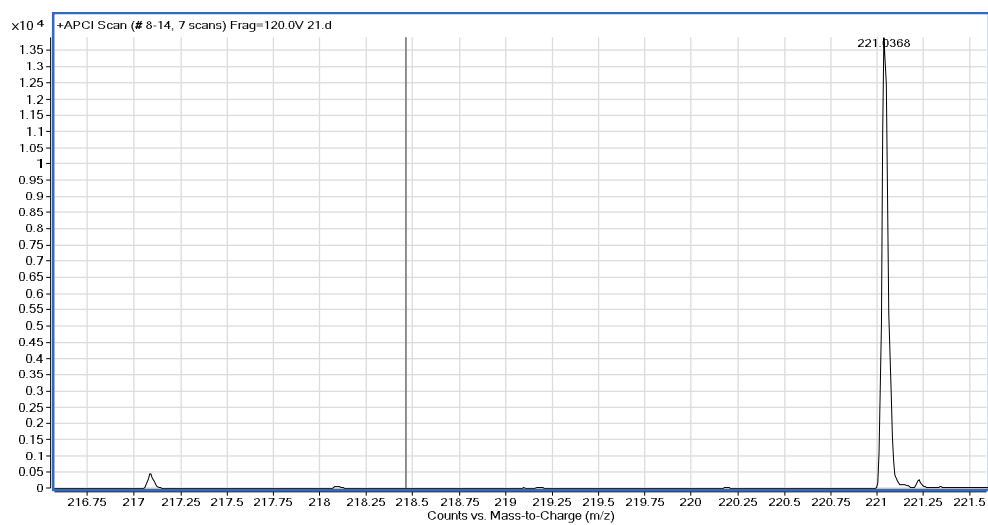
HRMS Spectra of Compound 3dd



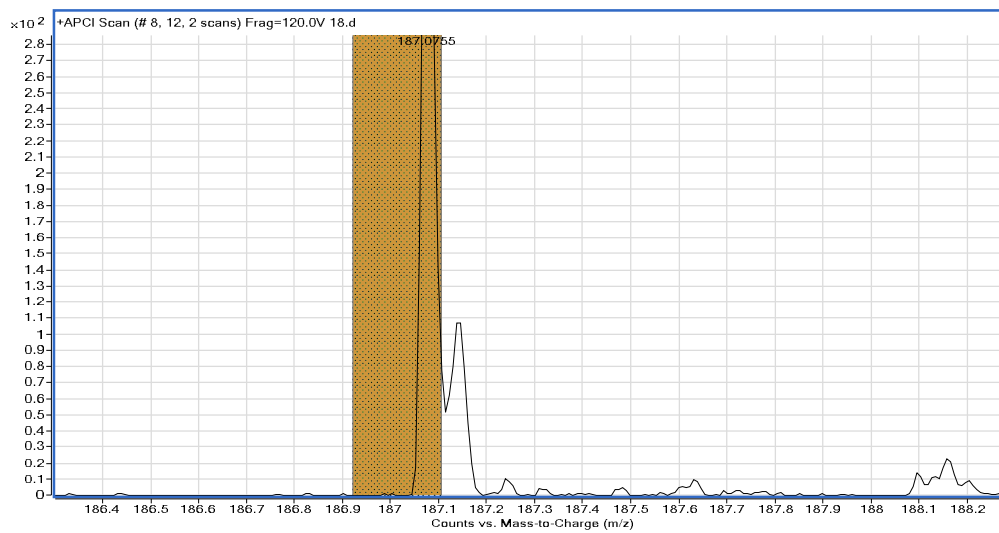
HRMS Spectra of Compound 3de



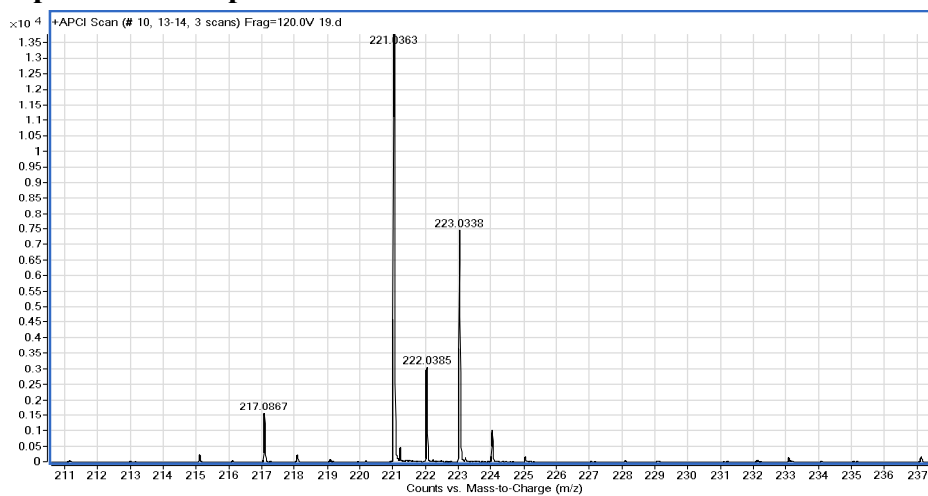
HRMS Spectra of Compound 3ea



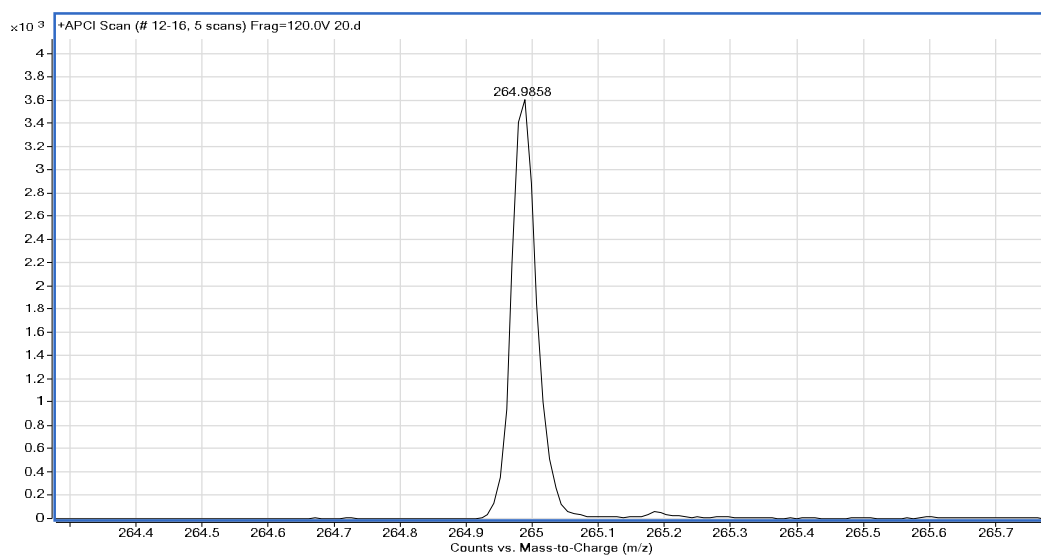
HRMS Spectra of Compound 3eb



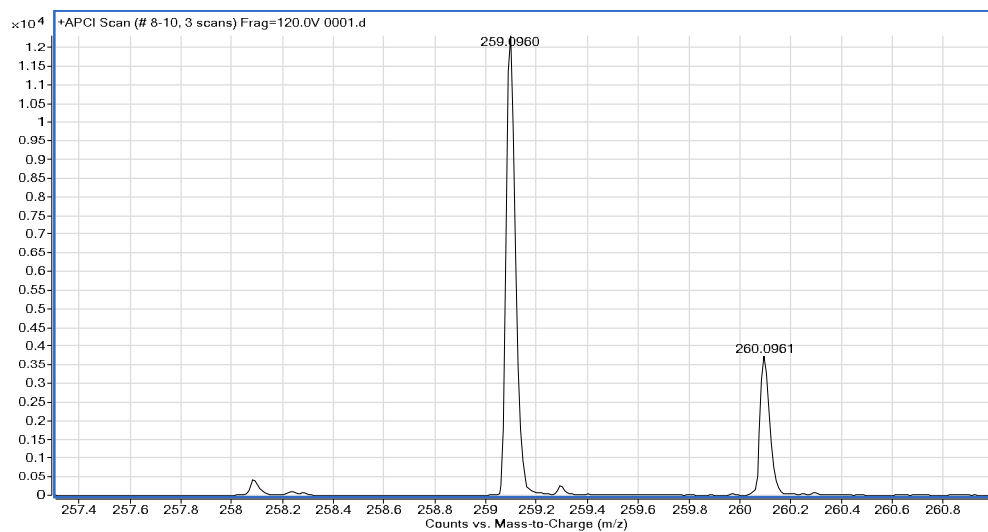
HRMS Spectra of Compound 3ec



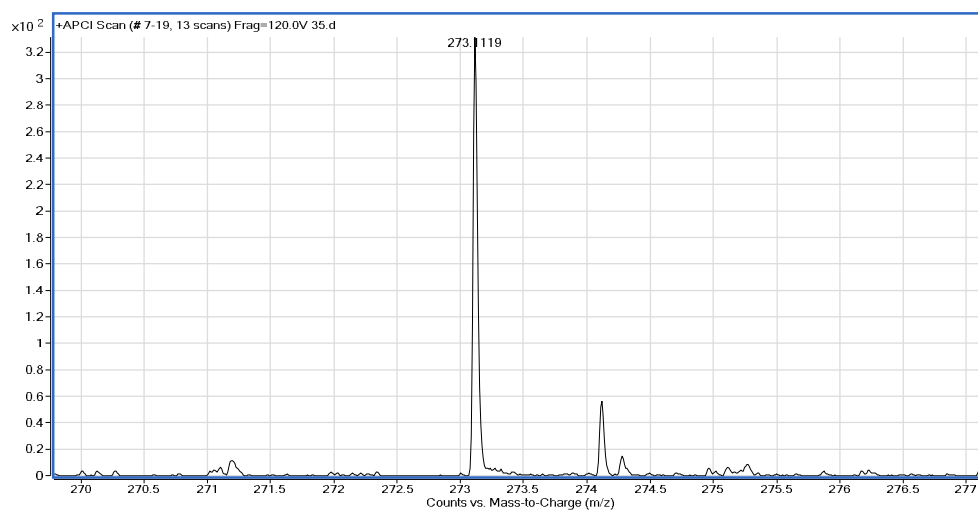
HRMS Spectra of Compound 3ed



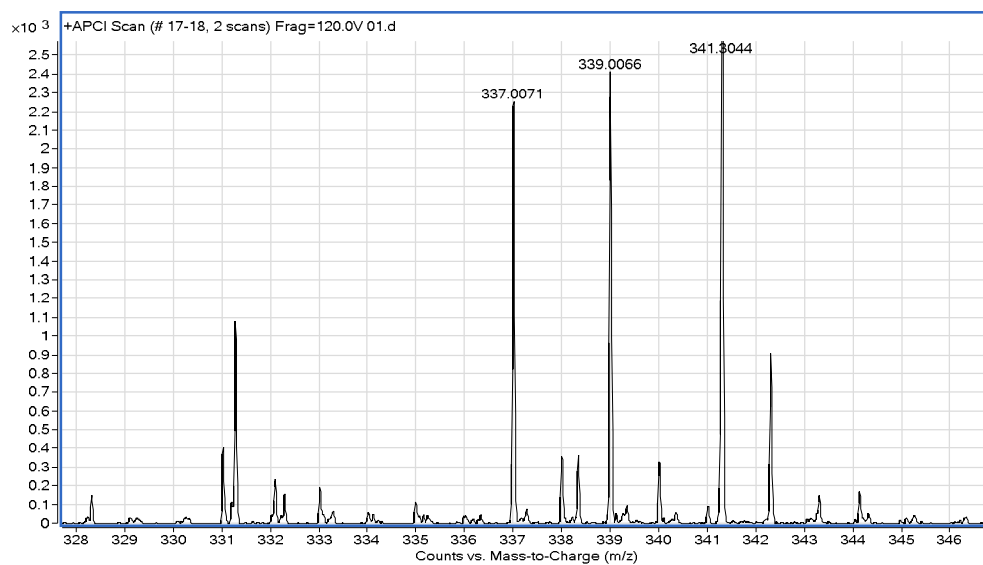
HRMS Spectra of Compound 4aa



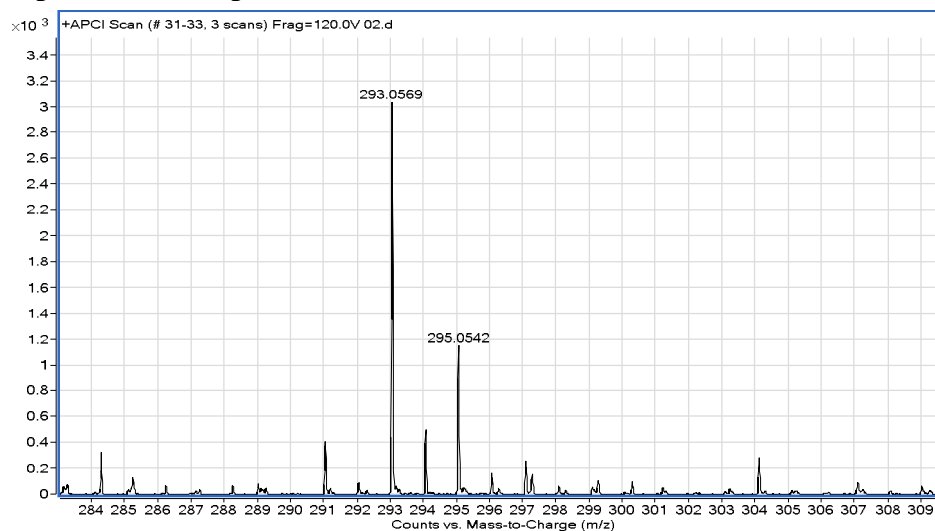
HRMS Spectra of Compound 4ab



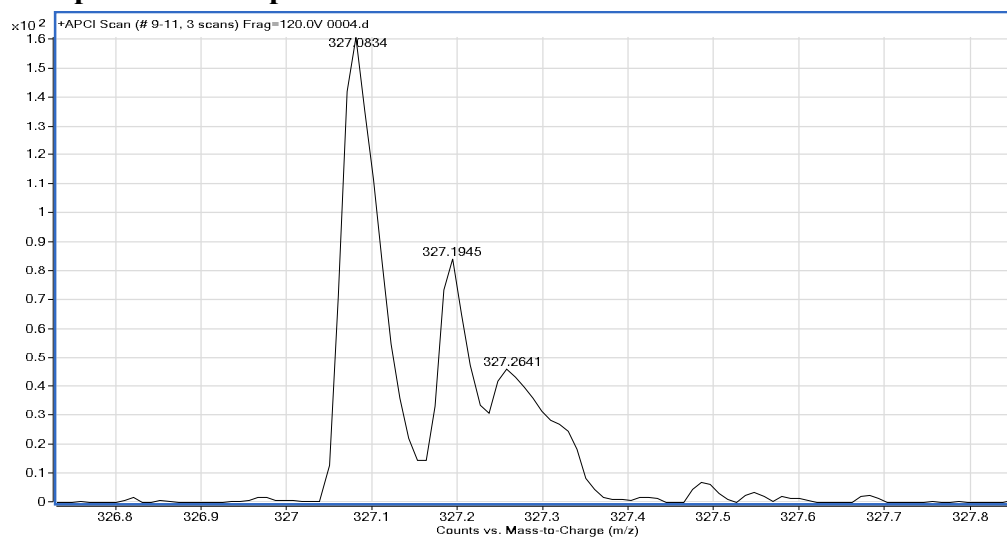
HRMS Spectra of Compound 4ac



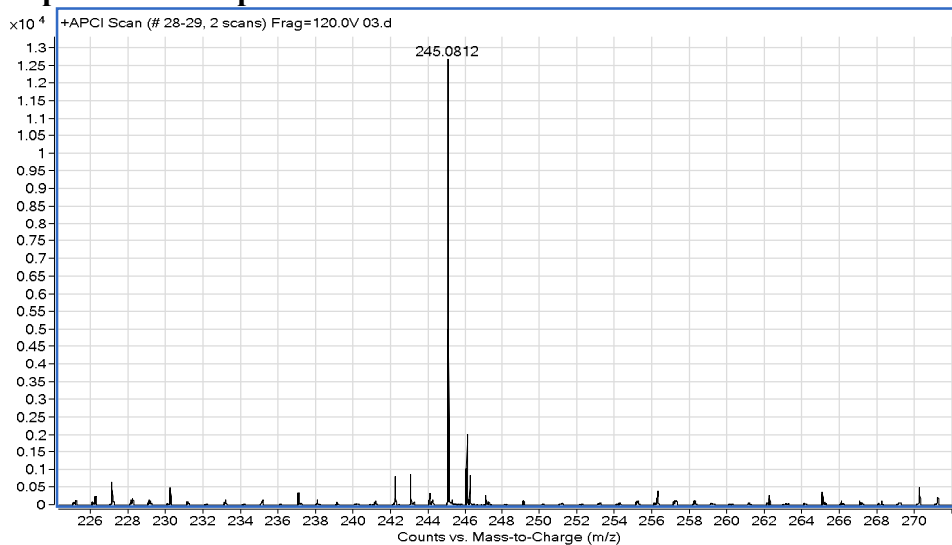
HRMS Spectra of Compound 4ad



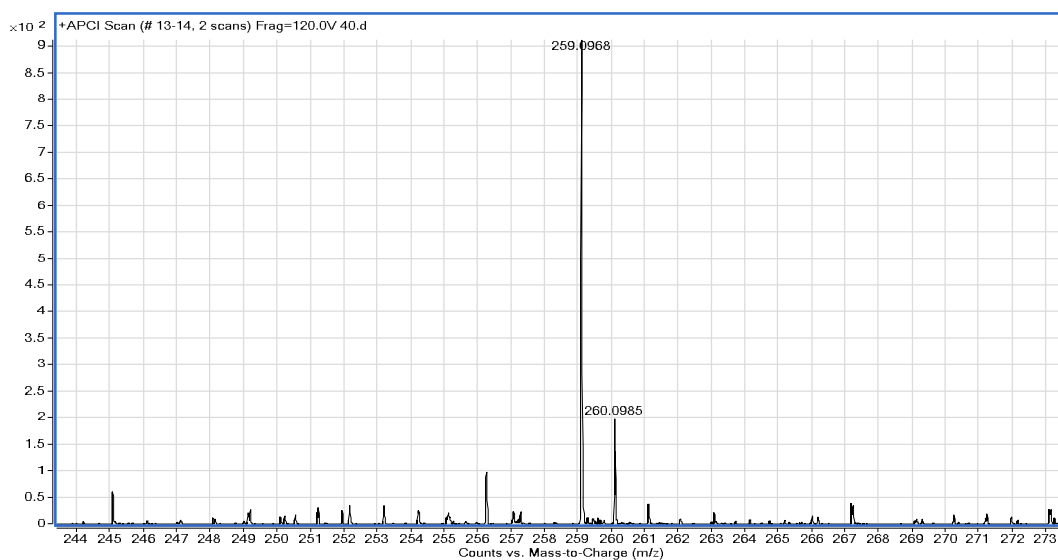
HRMS Spectra of Compound 4ae



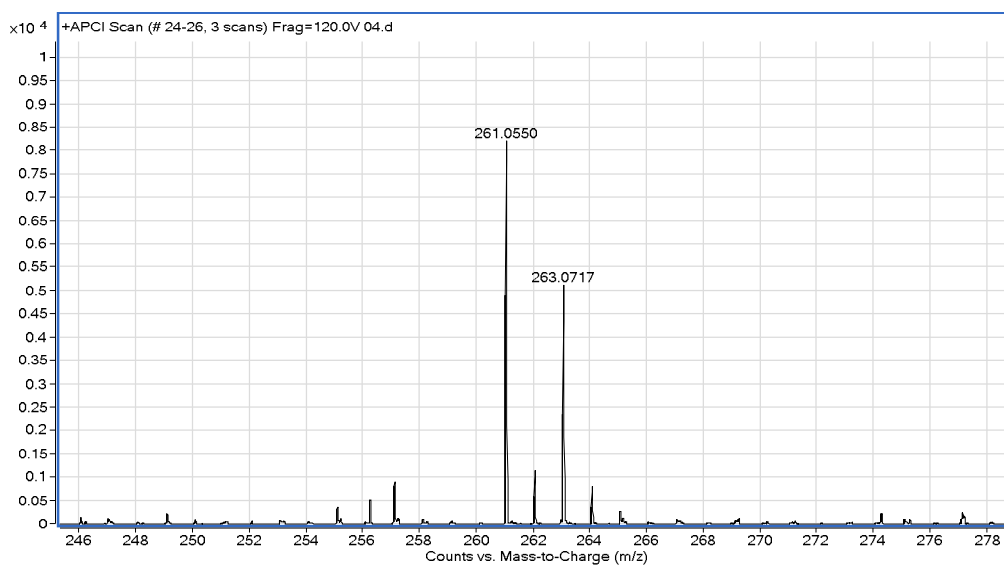
HRMS Spectra of Compound 4ba



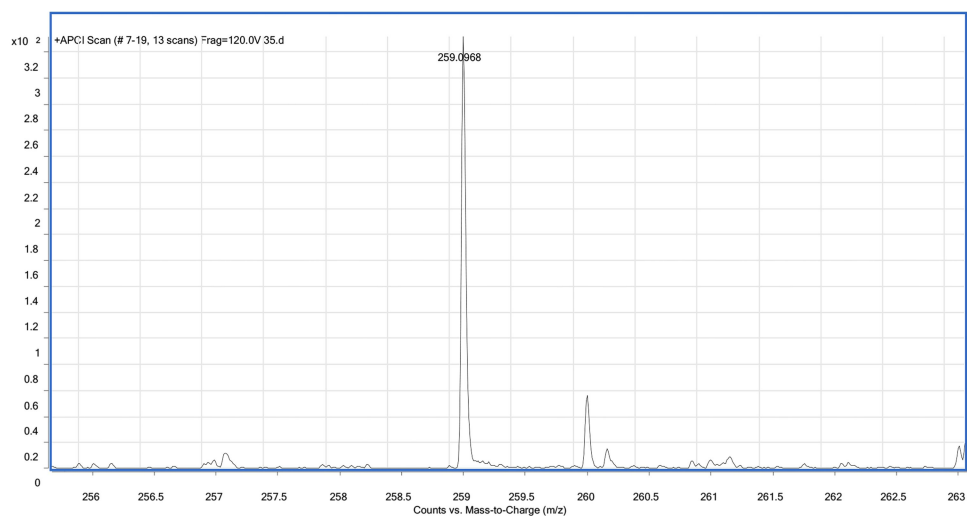
HRMS Spectra of Compound 4bb



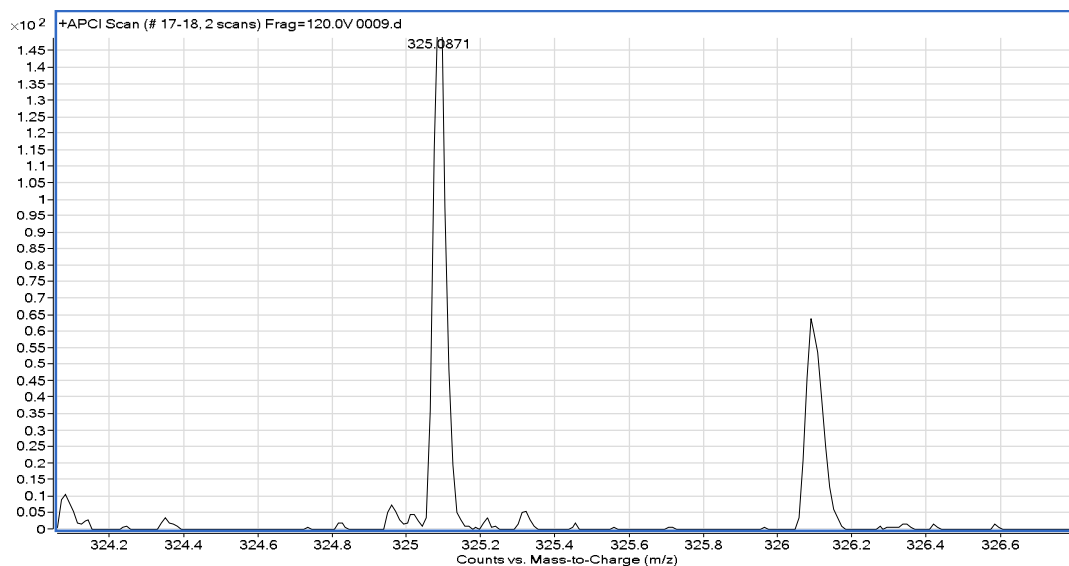
HRMS Spectra of Compound 4bc



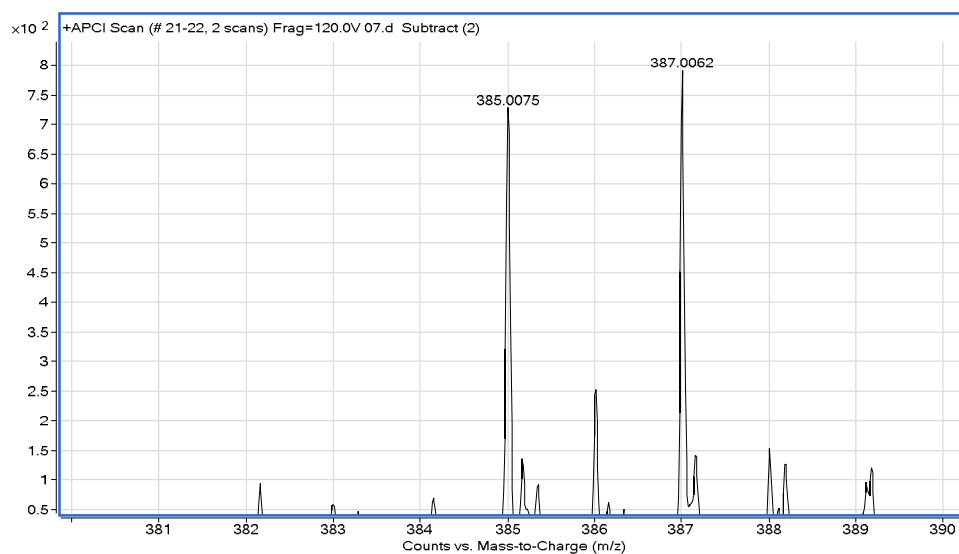
HRMS Spectra of Compound 4bd



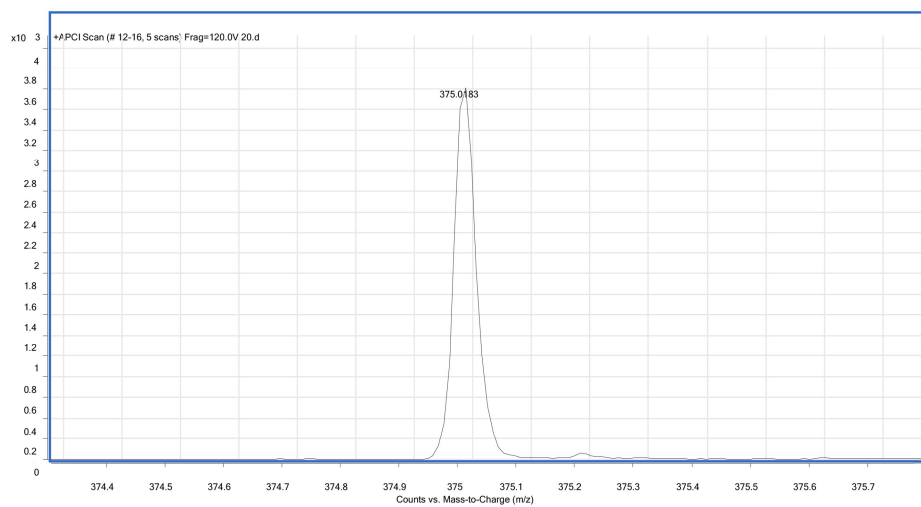
HRMS Spectra of Compound 4ca



HRMS Spectra of Compound 4cb



HRMS Spectra of Compound 4da



HRMS Spectra of Compound 4db

