

## Supporting Information

### **Ir(III)-Catalyzed Decarbonylative Annulation of Salicylaldehydes with Cyclohexane-1,3-diones**

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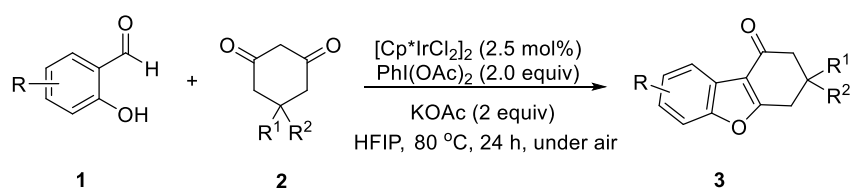
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## 1. General information

Unless otherwise noted, commercially available reagents were used without further purification. All reactions were performed in oven-dried glassware.  $^1\text{H}$  NMR spectra were recorded on Bruker 400 MHz spectrometers and chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ( $\text{CDCl}_3$ ,  $\delta$  7.26 ppm). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Coupling constants were reported as a  $J$  value in Hz.  $^{13}\text{C}$  NMR spectra were recorded at 101 MHz on 400 MHz instruments and chemical data for carbons are reported in parts per million (ppm,  $\delta$  scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ( $\text{CDCl}_3$ :  $\delta$  77.16). Flash chromatography was performed on Lisure science EZ purification system using the Santai technologies silica gel cartridge. Thin layer chromatography (TLC) was performed using Jiangyou TLC silica gel plates HSG F254 and visualized using UV light.

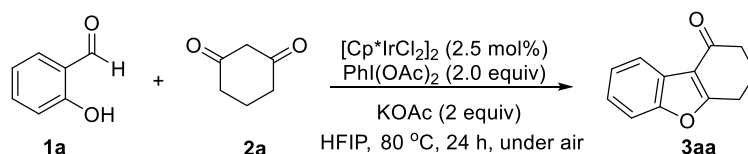
## 2. General procedures for the synthesis of dihydrodibenzofuranones



To an oven-dried sealed tube was added salicylaldehyde **1** (1.0 equiv, 0.2 mmol), 1,3-cyclohexanedione **2** (2.0 equiv, 0.4 mmol),  $[\text{Cp}^*\text{IrCl}_2]_2$  (4 mg, 2.5 mol %),  $\text{PhI(OAc)}_2$  (129 mg, 0.4 mmol), KOAc (39 mg, 0.4 mmol), and HFIP (2.0 mL) under air atmosphere. The reaction mixture was heated at 80 °C on oil bath and stirred for 24 h. Then, the reaction mixture was cooled to room temperature and diluted with  $\text{CH}_2\text{Cl}_2$  (10 mL). The solvents were removed

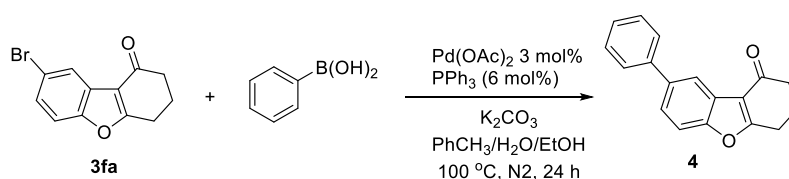
under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EtOAc) to give the desired dihydrodibenzofuranones **3**.

### 3. Gram-scale synthesis of **3aa**



To an oven-dried sealed tube was added salicylaldehyde **1a** (610 mg, 5 mmol), 1,3-cyclohexanedione **2a** (1.12 g, 10 mmol),  $[\text{Cp}^*\text{IrCl}_2]_2$  (100 mg, 2.5 mol %),  $\text{PhI}(\text{OAc})_2$  (3.2 g, 10 mmol),  $\text{KOAc}$  (975 mg, 10 mmol), and HFIP (50 mL) under air atmosphere. The reaction mixture was heated at 80 °C on oil bath and stirred for 24 h. Then, the reaction mixture was cooled to room temperature and diluted with  $\text{CH}_2\text{Cl}_2$  (50 mL). The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EtOAc) to give the desired dihydrodibenzofuranones **3aa** (65%, 605 mg).

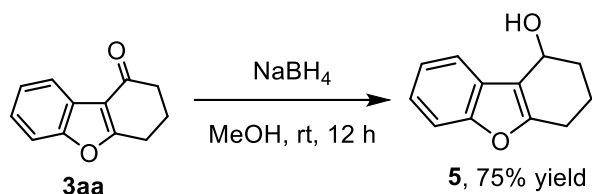
### 4. Synthetic application



To an oven-dried sealed tube was added **3fa** (1.0 equiv, 26.4 mg, 0.1 mmol), benzeneboronic acid (2.0 equiv, 24.4 mg, 0.2 mmol),  $\text{Pd}(\text{OAc})_2$  (0.7 mg, 3 mol%),  $\text{PPh}_3$  (1.6 mg, 6 mol%),  $\text{K}_2\text{CO}_3$  (42 mg, 0.3 mmol), and  $\text{PhCH}_3$  (0.5 mL),  $\text{H}_2\text{O}$  (0.1 mL) and  $\text{EtOH}$  (0.5 mL) under  $\text{N}_2$  atmosphere. The reaction mixture was heated at 100 °C on oil bath and stirred for 24 h. Then, the reaction

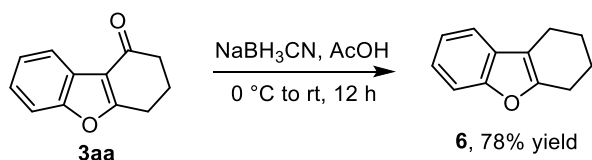
mixture was cooled to room temperature and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EtOAc) to give the desired coupling product **4** (62%, 16.3 mg).

**8-Phenyl-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (4):** 72% yield, white solid. m.p. 132-133 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.61-7.58 (m, 2H), 7.54-7.50 (m, 2H), 7.44-7.38 (m, 1H), 3.13 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 6.4 Hz, 2H), 2.40-2.35 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 194.1, 170.8, 153.6, 140.5, 137.6, 128.2, 127.0, 126.5, 123.9, 123.7, 119.7, 116.1, 110.6, 37.3, 23.3, 21.9. HRMS (ESI): Calcd for C<sub>18</sub>H<sub>15</sub>O<sub>2</sub><sup>+</sup> (M+Na)<sup>+</sup> 263.1067, found 263.1057.



To an oven-dried sealed tube was added **3a** (1.0 equiv, 0.1 mmol), NaBH<sub>4</sub> (3.0 equiv, 0.3 mmol), and MeOH (1 mL) under air atmosphere. The reaction mixture was stirred for 12 h at room temperature. Then, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EtOAc) to give the desired coupling product **5** in 75% yield.

**1,2,3,4-Tetrahydrodibenzo[b,d]furan-1-ol (6) :** white solid. m.p. 92-93 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 – 7.60 (m, 1H), 7.46 – 7.42(m, 1H), 7.33 – 7.23 (m, 2H), 5.06 (s, 1H), 3.08 – 2.61 (m, 2H), 2.31– 2.15 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.1, 154.5, 127.2, 123.6, 122.7, 119.1, 115.6, 111.0, 63.4, 32.6, 23.4, 18.8. HRMS (ESI): Calcd for C<sub>12</sub>H<sub>12</sub>NaO<sub>2</sub><sup>+</sup> (M+Na)<sup>+</sup> 211.0729, found 211.0736.



To an oven-dried sealed tube was added **3aa** (1.0 equiv, 0.1 mmol), NaBH<sub>3</sub>CN (2.0 equiv, 0.2 mmol) and HOAc (1 mL) at 0 °C under air atmosphere. Then, the reaction mixture was stirred at room temperature for 12 h. After the reaction was complete, the reaction mixture was diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The organic solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EtOAc) to give the desired coupling product **6** in 78% yield.

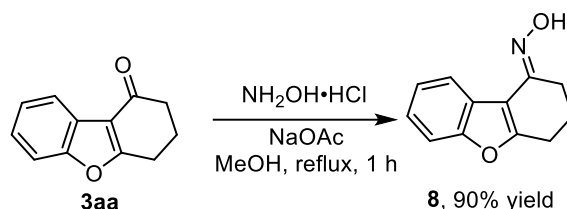
**1,2,3,4-Tetrahydrodibenzo[b,d]furan (6):** colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.43 (m, 2H), 7.30 – 7.20 (m, 2H), 2.80 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 6.0 Hz, 2H), 2.03 – 1.97 (m, 2H), 1.93 – 1.88 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.3, 154.1, 128.9, 123.0, 122.1, 118.4, 112.9, 110.8, 23.5, 23.0, 22.7, 20.5. HRMS (ESI): Calcd for C<sub>12</sub>H<sub>13</sub>O<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 173.0916, found 173.0920.



To an oven-dried sealed tube was added **3aa** (1.0 equiv, 0.1 mmol), I<sub>2</sub> (3.0 equiv, 0.3 mmol), and DMSO (1 mL) under N<sub>2</sub> atmosphere. The reaction mixture was heated at 120 °C on oil bath and stirred for 24 h. Then, the reaction mixture was cooled to room temperature, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EtOAc) to give the desired coupling product **7** in 44% yield.

**2-Iodo-3,4-dihydrodibenzo[b,d]furan-1(2H)-one (7) :** white solid. m.p. 190-191 °C <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 7.96 (d, *J* = 6.8 Hz, 1H), 7.74 (d,

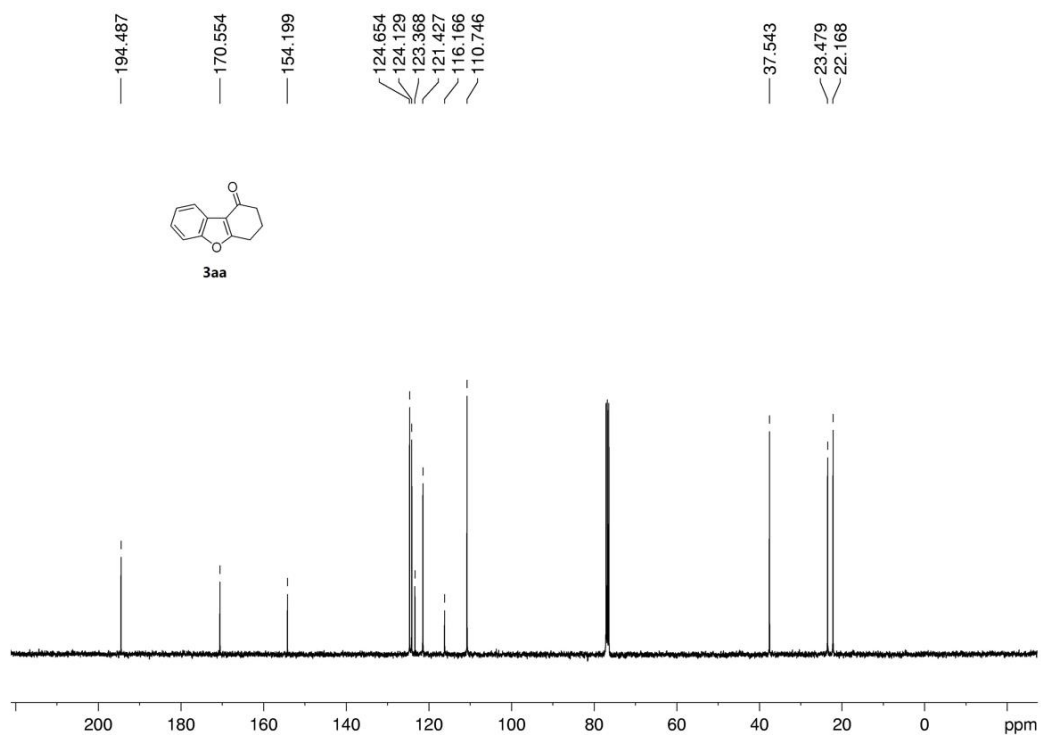
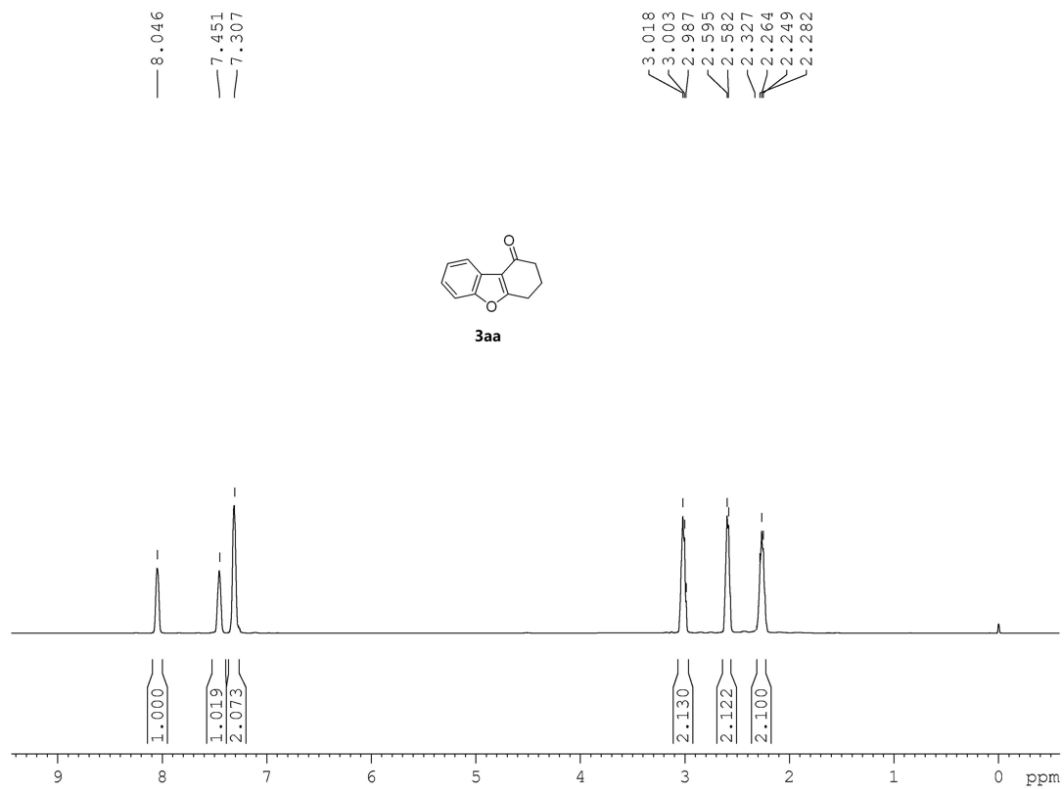
$J = 6.8$  Hz, 1H), 7.46 – 7.39 (m, 2H), 5.10-5.06 (m, 1H), 2.74 – 2.59 (m, 2H), 2.45 – 2.37 (m, 1H), 2.15 – 2.07 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  194.8, 171.4, 154.6, 126.2, 125.2, 123.4, 121.7, 115.5, 112.31, 62.2, 35.8, 32.5. HRMS (ESI): Calcd for  $\text{C}_{12}\text{H}_{10}\text{O}_2^+$  (M+H) $^+$  312.9720, found 312.9707.



To an oven-dried sealed tube was added **3aa** (1.0 equiv, 0.1 mmol), NaOAc (2.0 equiv, 0.2 mmol),  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (2.0 equiv, 0.2 mmol), and MeOH (2 mL) under  $\text{N}_2$  atmosphere. The reaction mixture was heated at 80 °C on oil bath and stirred for 1 h. Then, the reaction mixture was cooled to room temperature, diluted with water and extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL). The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EtOAc) to give the desired coupling product **8** in 90% yield.

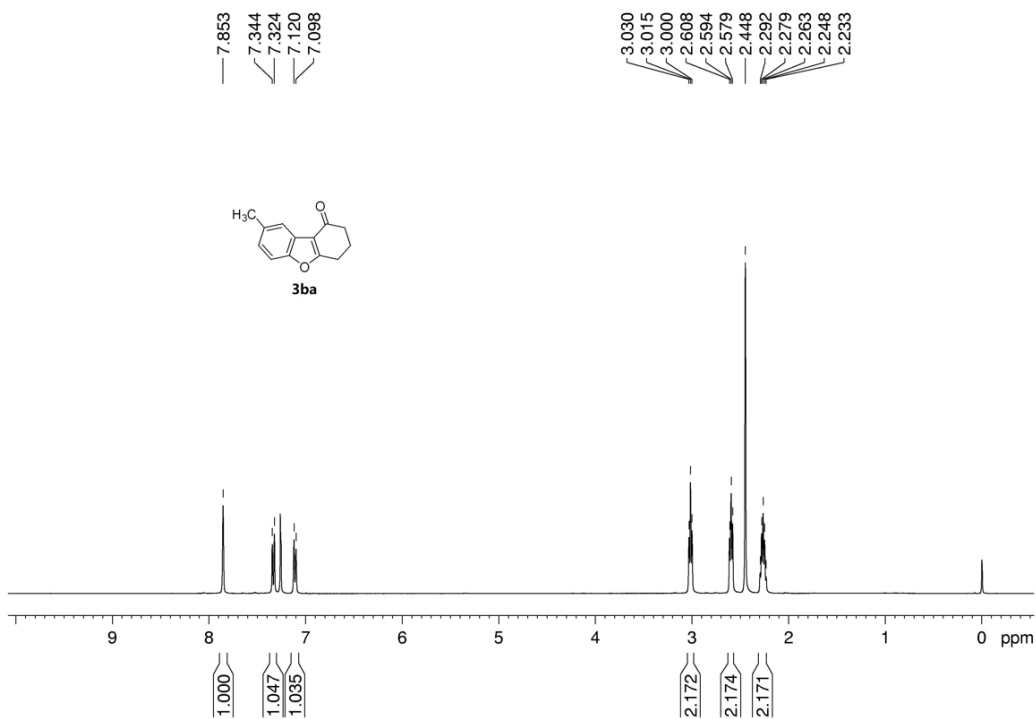
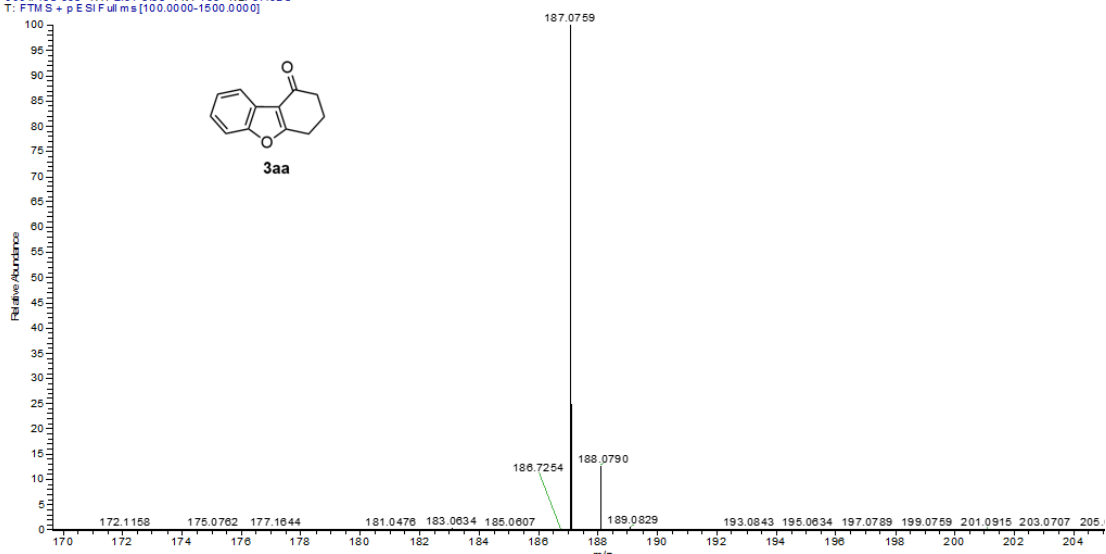
**(Z)-3,4-Dihydrodibenzo[b,d]furan-1(2H)-one oxime (8)** : white solid. m.p. 215-216 °C  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.11 (s, 1H), 8.13 – 7.92 (m, 1H), 7.71 – 7.48 (m, 1H), 7.35 – 7.33 (m, 2H), 3.07 – 2.67 (m, 4H), 2.31 – 1.98 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.9, 154.7, 153.6, 124.4, 124.3, 123.7, 121.8, 111.2, 111.0, 23.50, 22.3, 21.5. HRMS (ESI): Calcd for  $\text{C}_{12}\text{H}_{12}\text{NO}_2^+$  (M+H) $^+$  202.0863, found 202.0866.

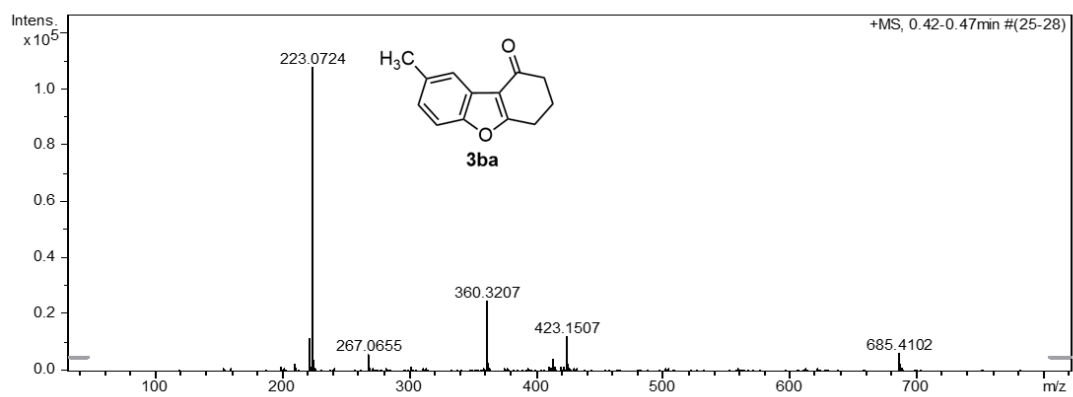
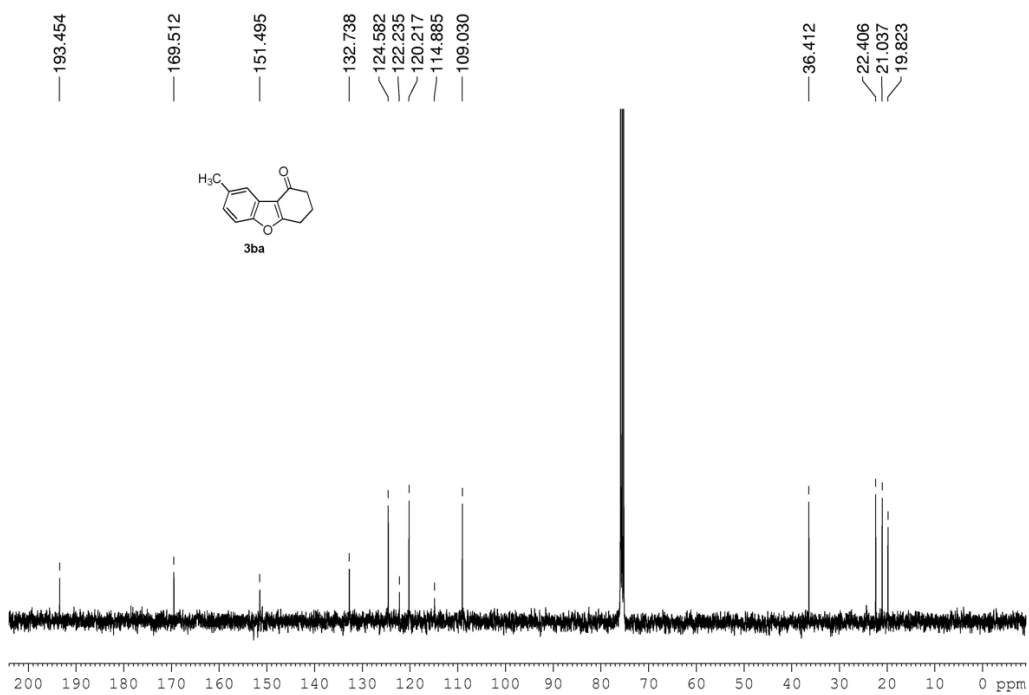
## 5. NMR and HRMS spectra

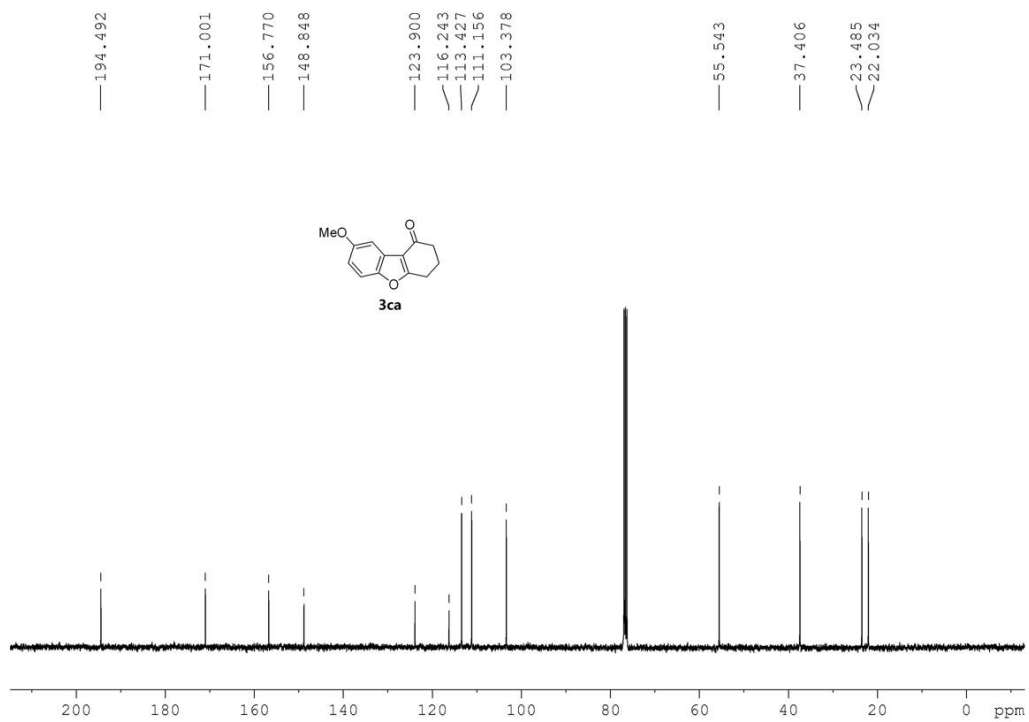
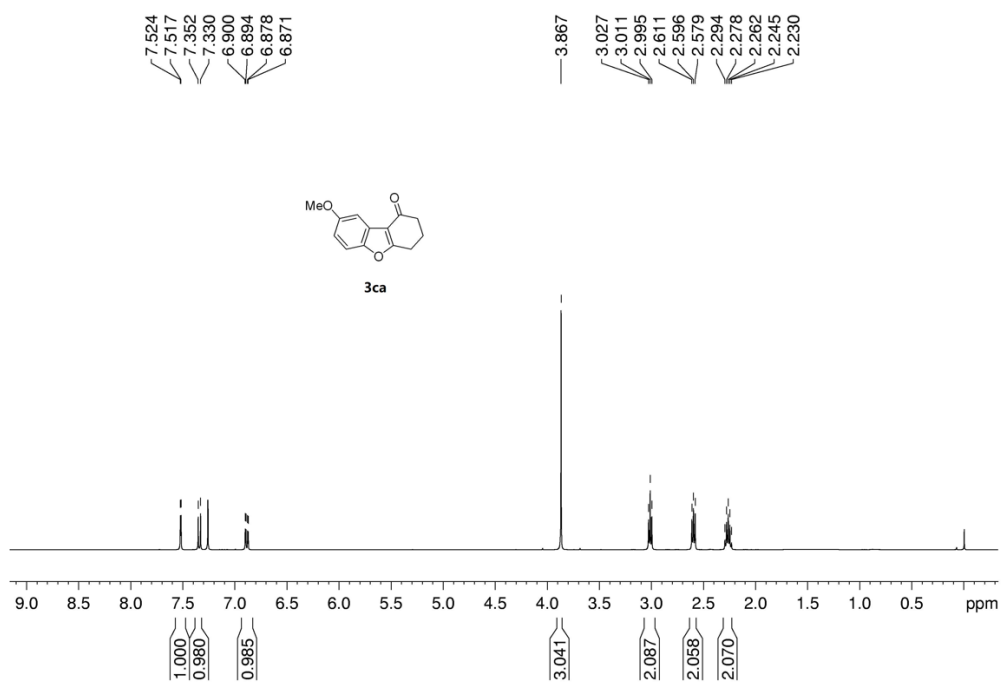


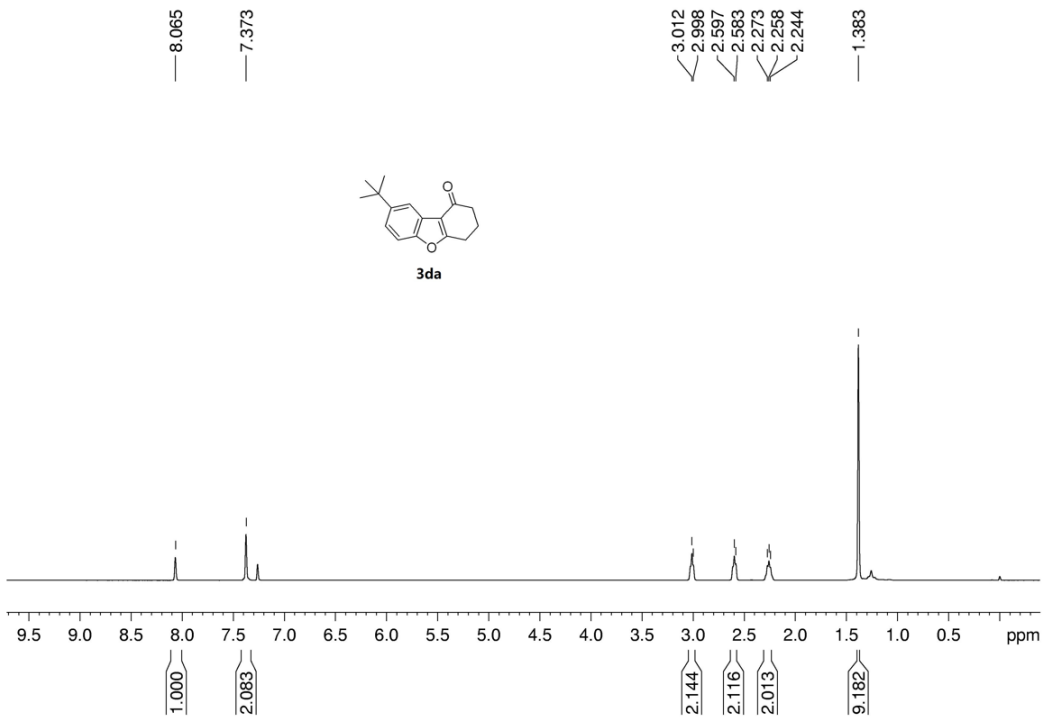
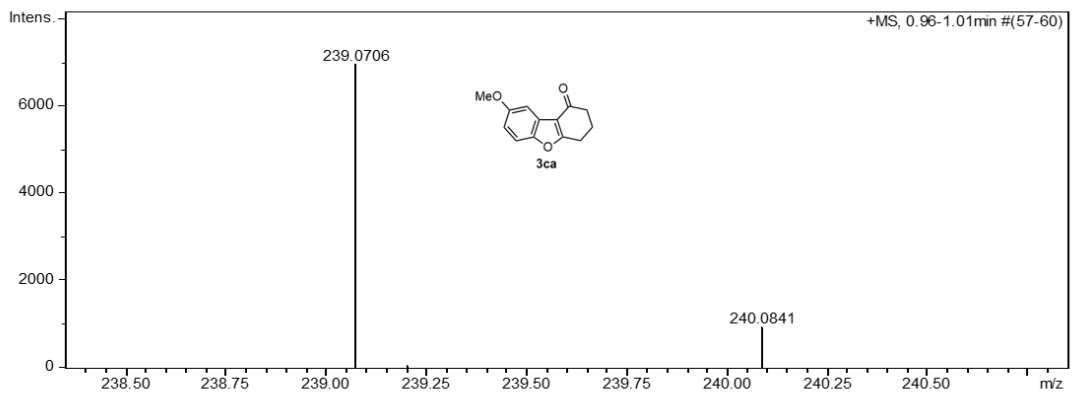


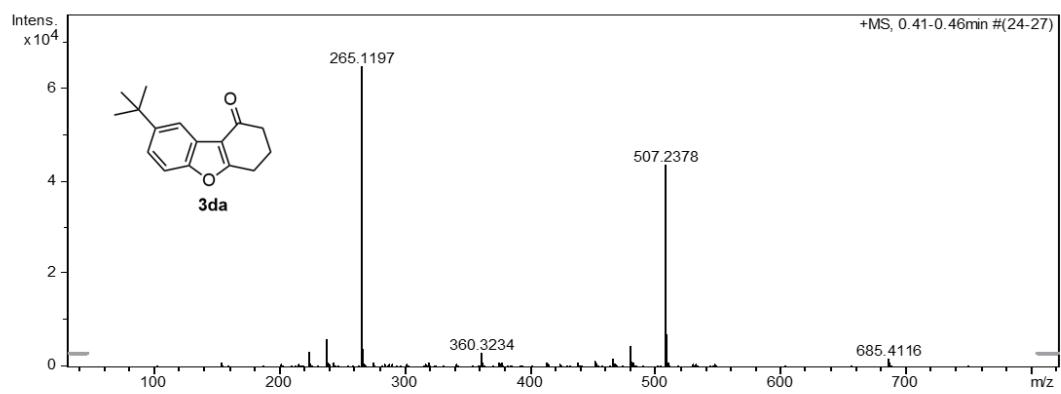
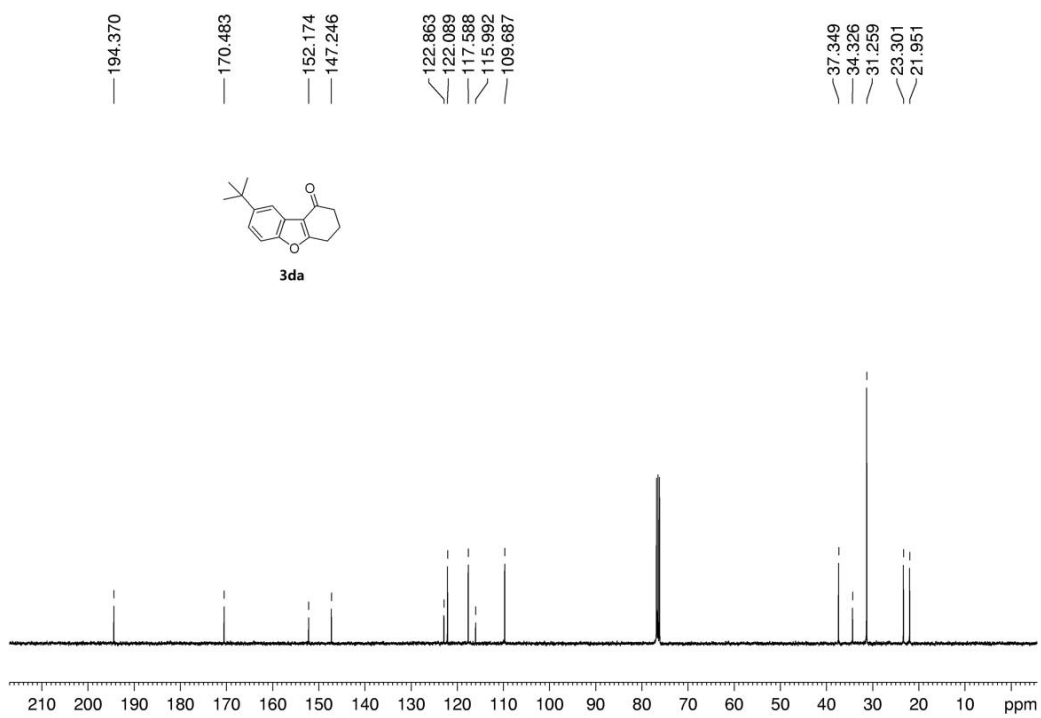
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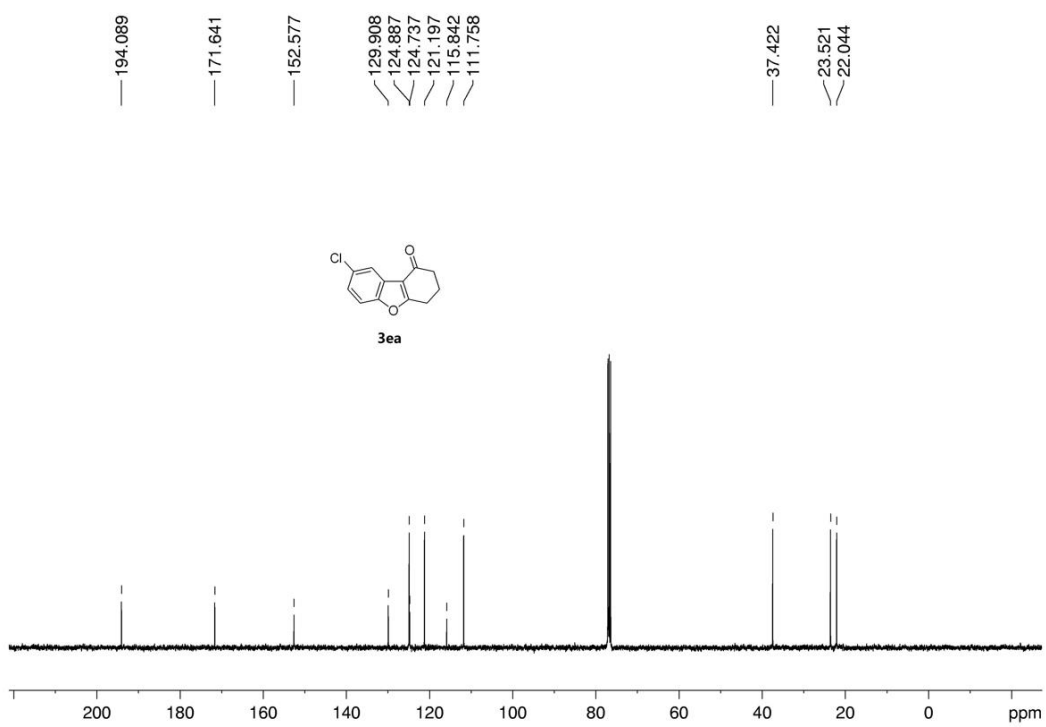
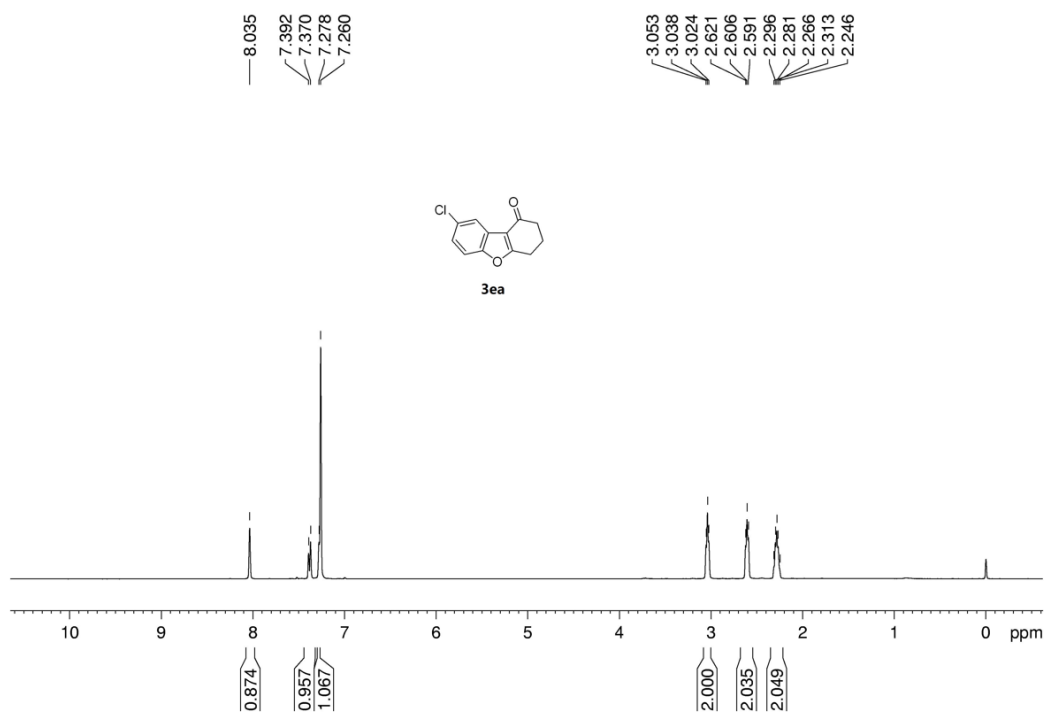


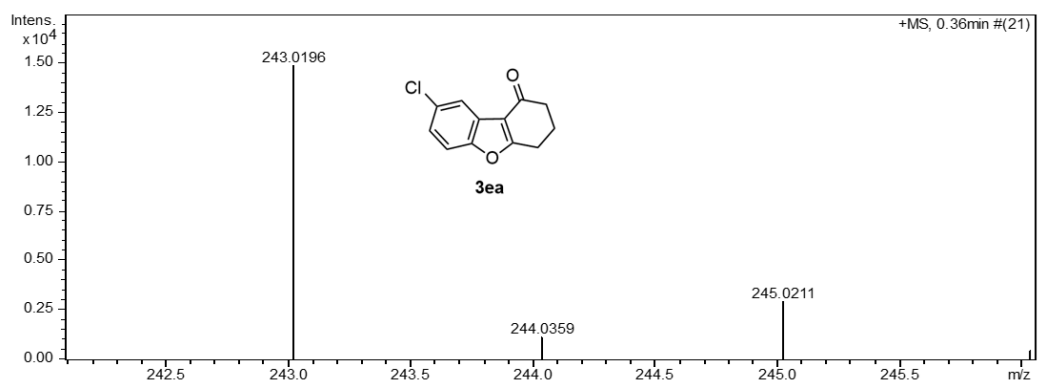






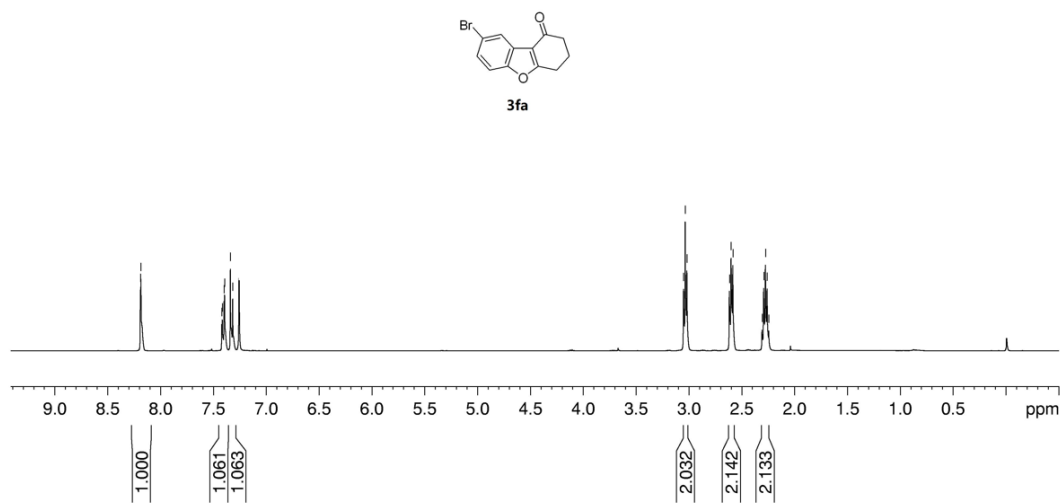




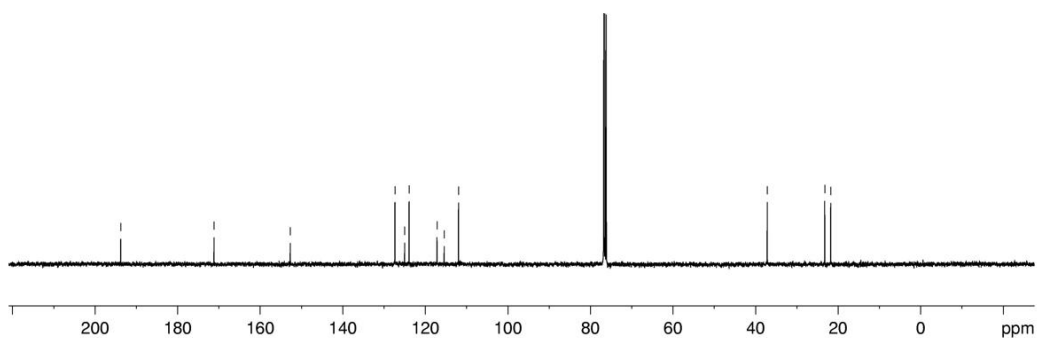
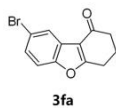


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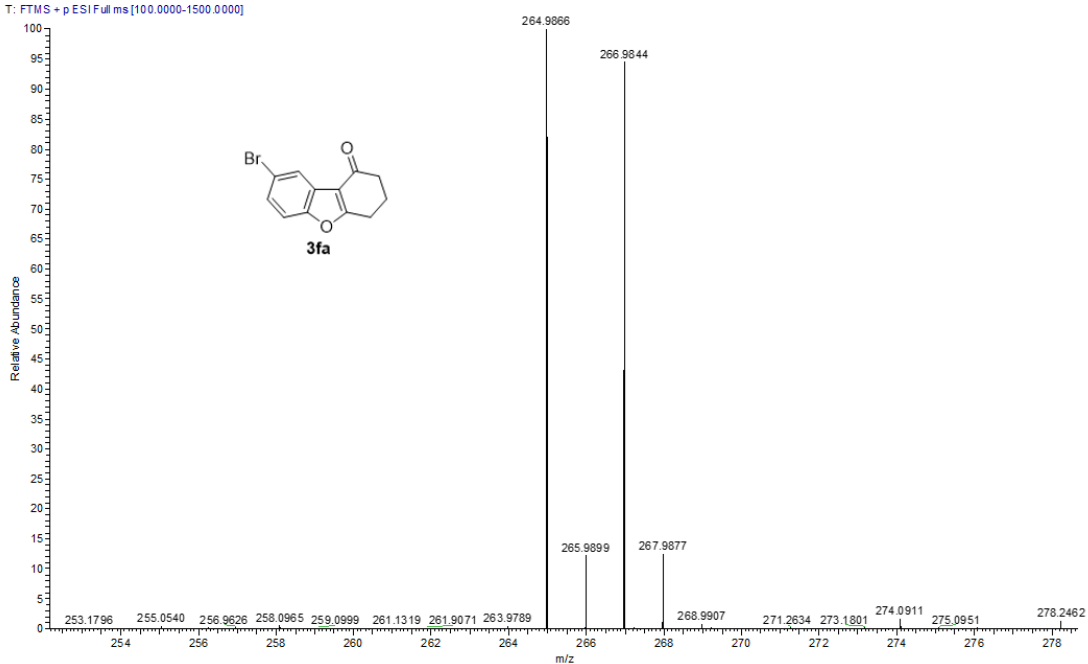
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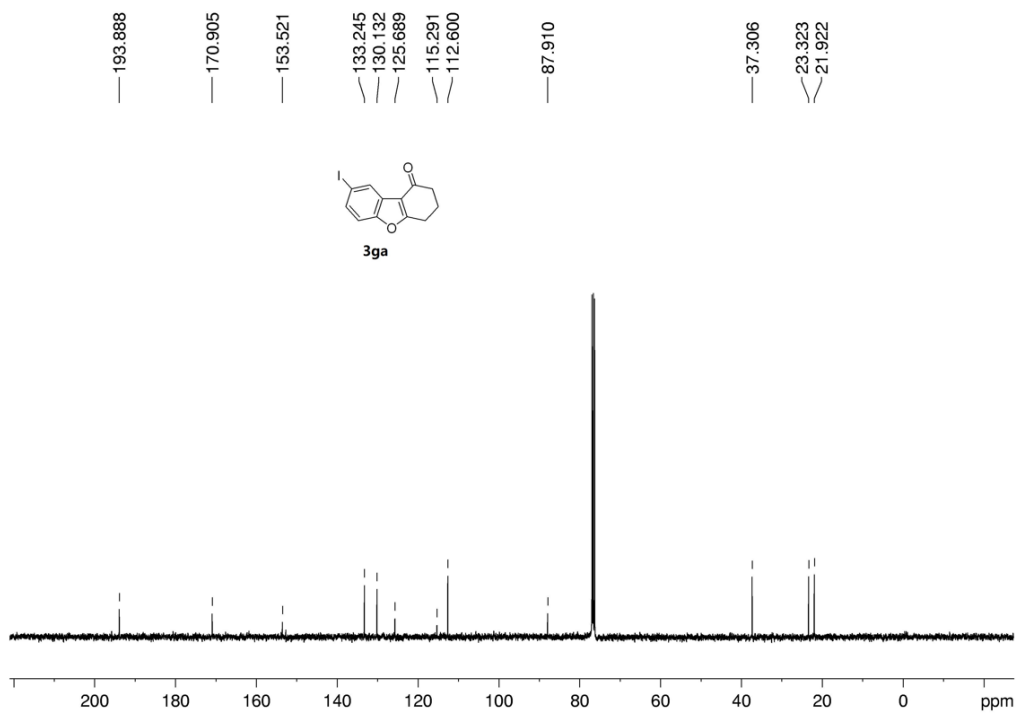
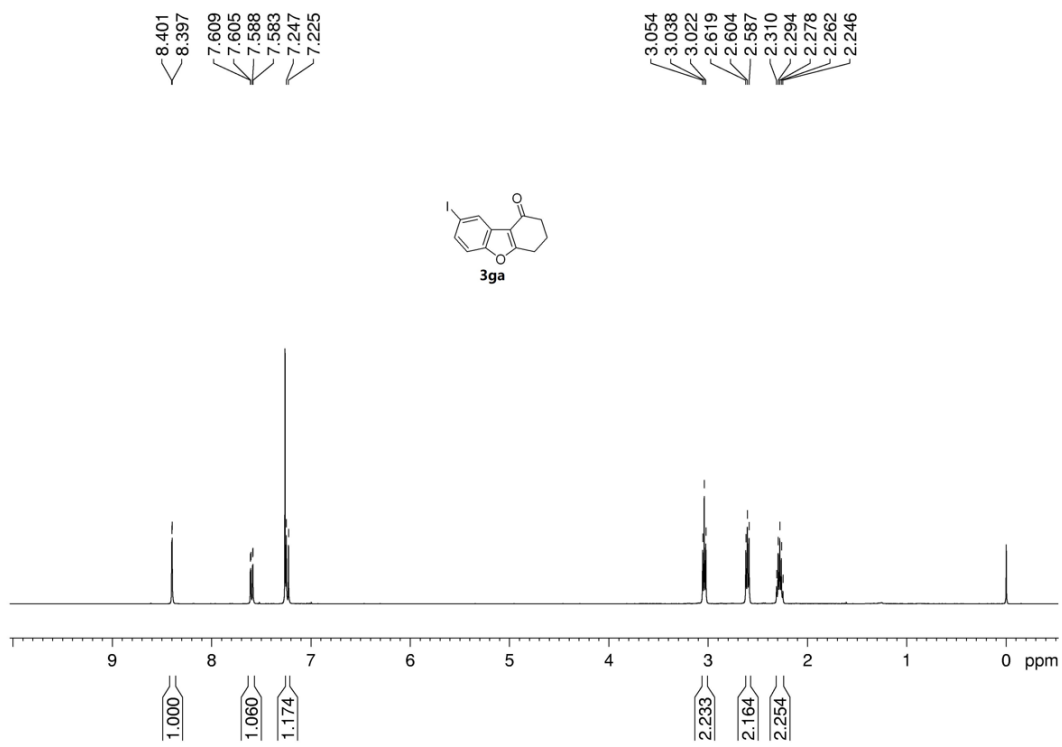
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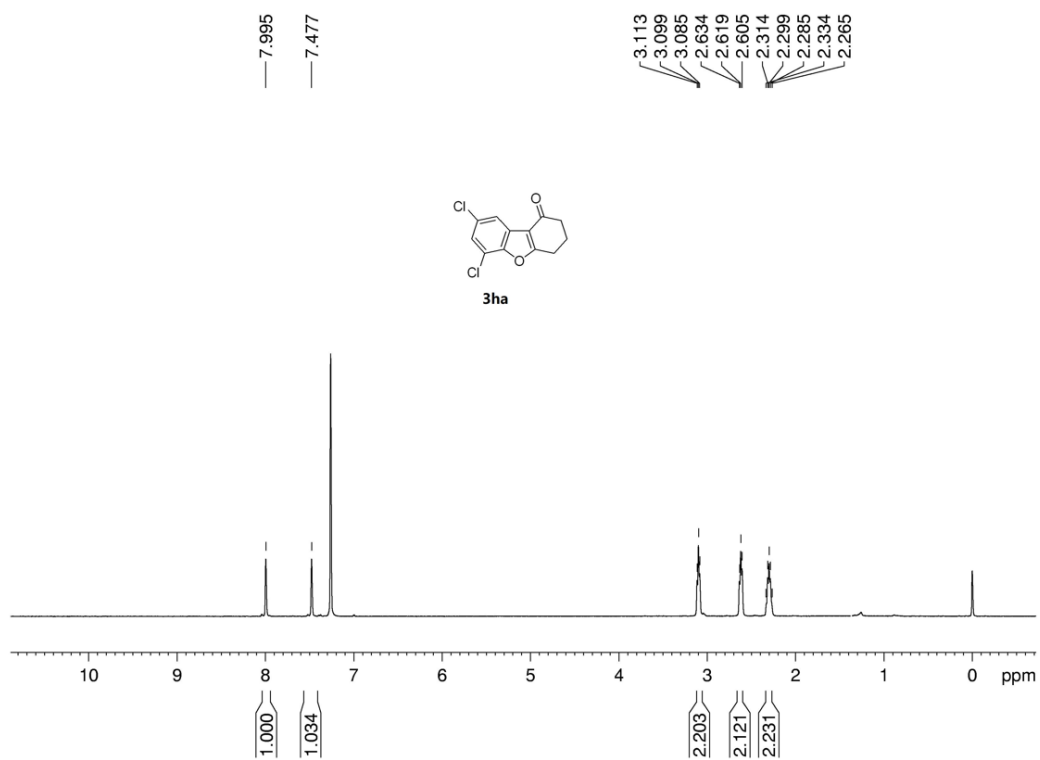
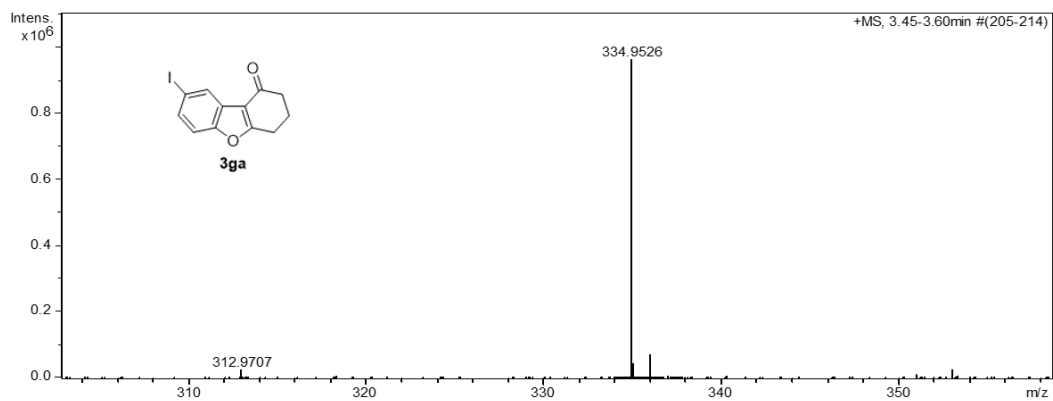


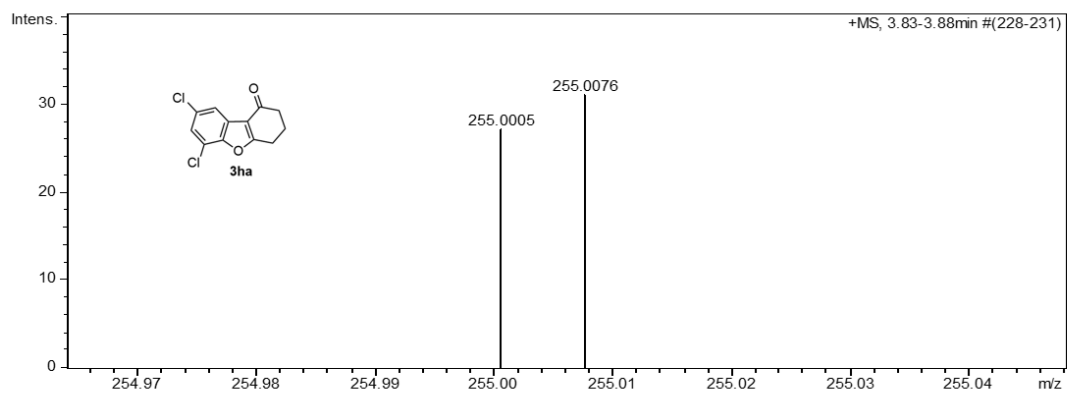
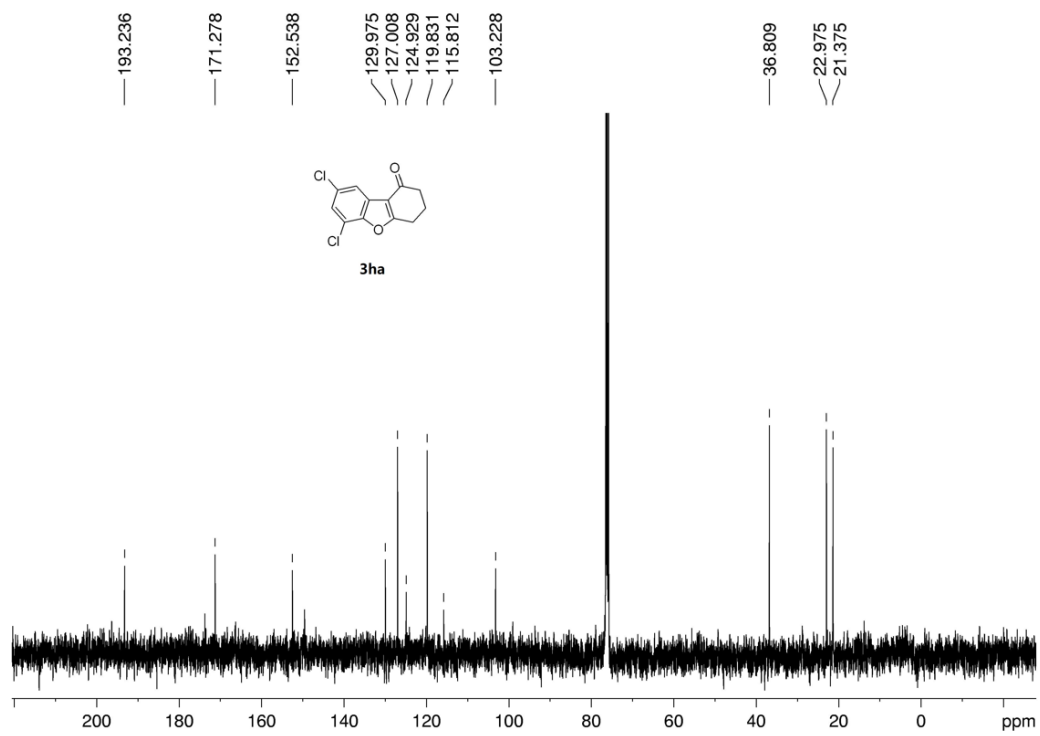
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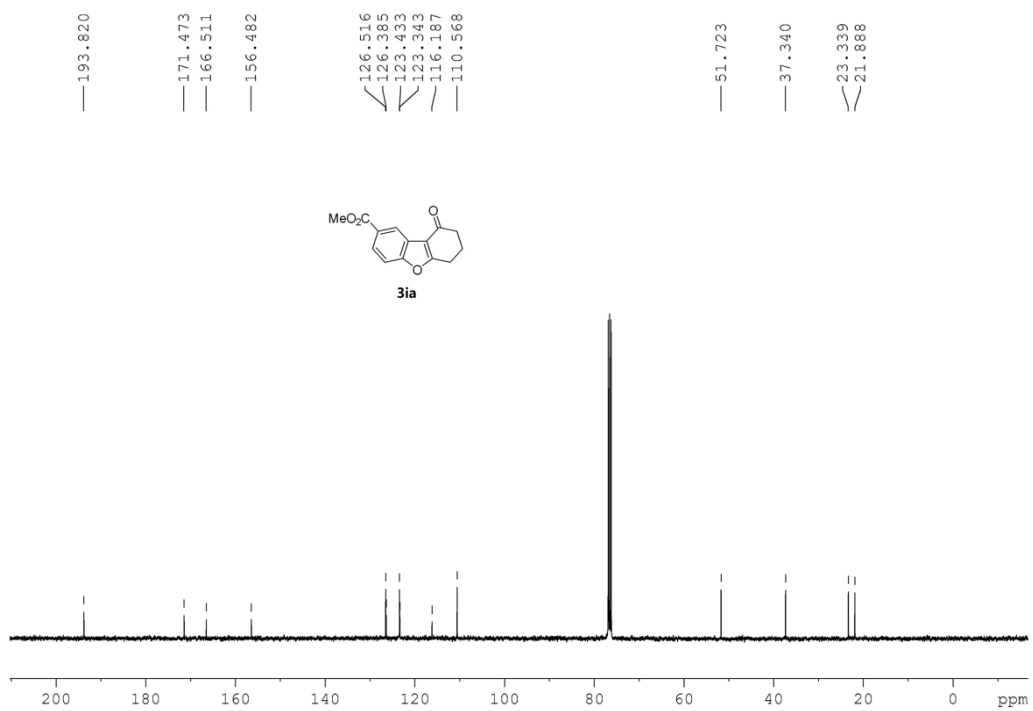
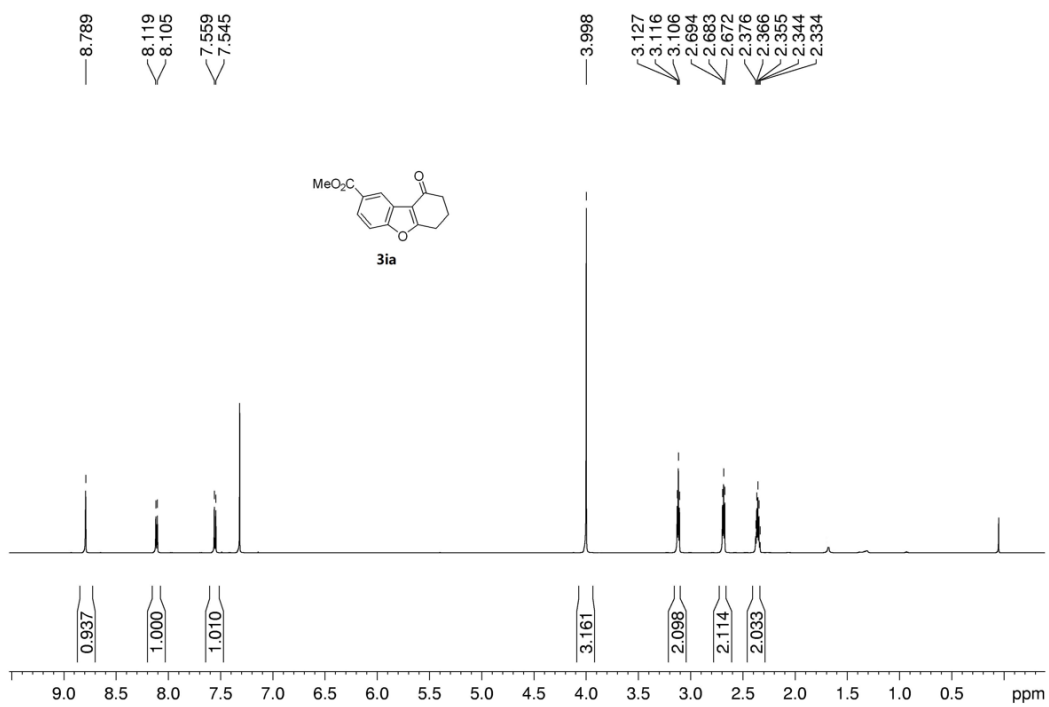


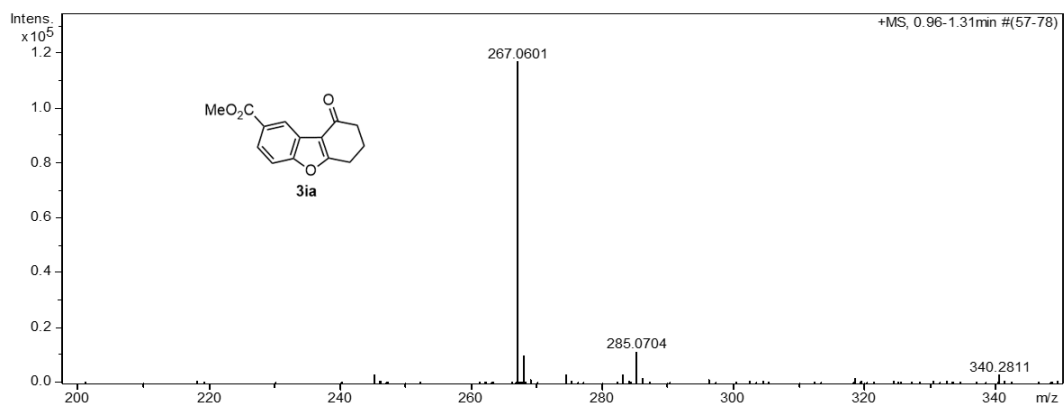












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7.562

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2.642

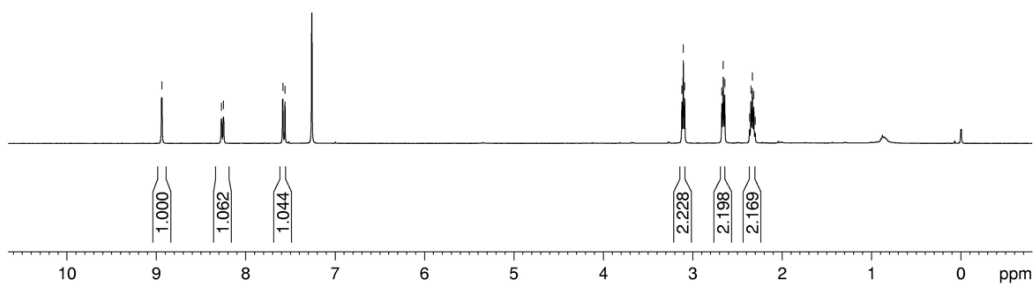
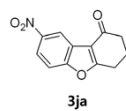
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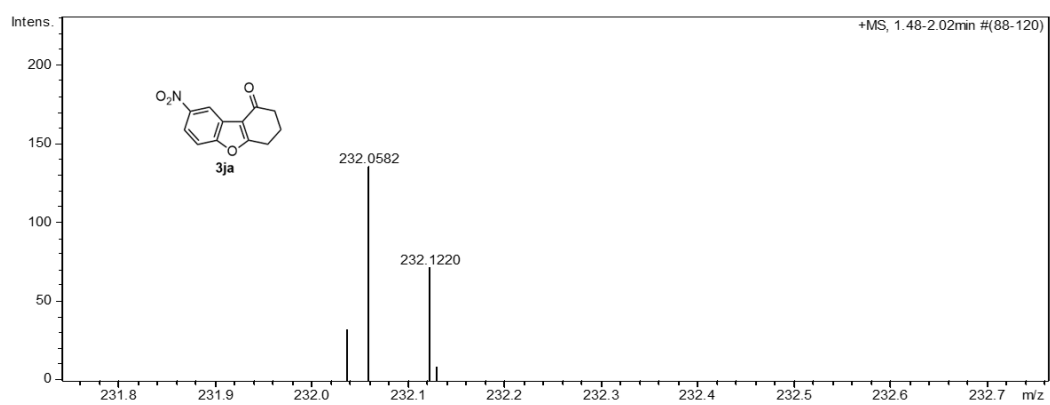
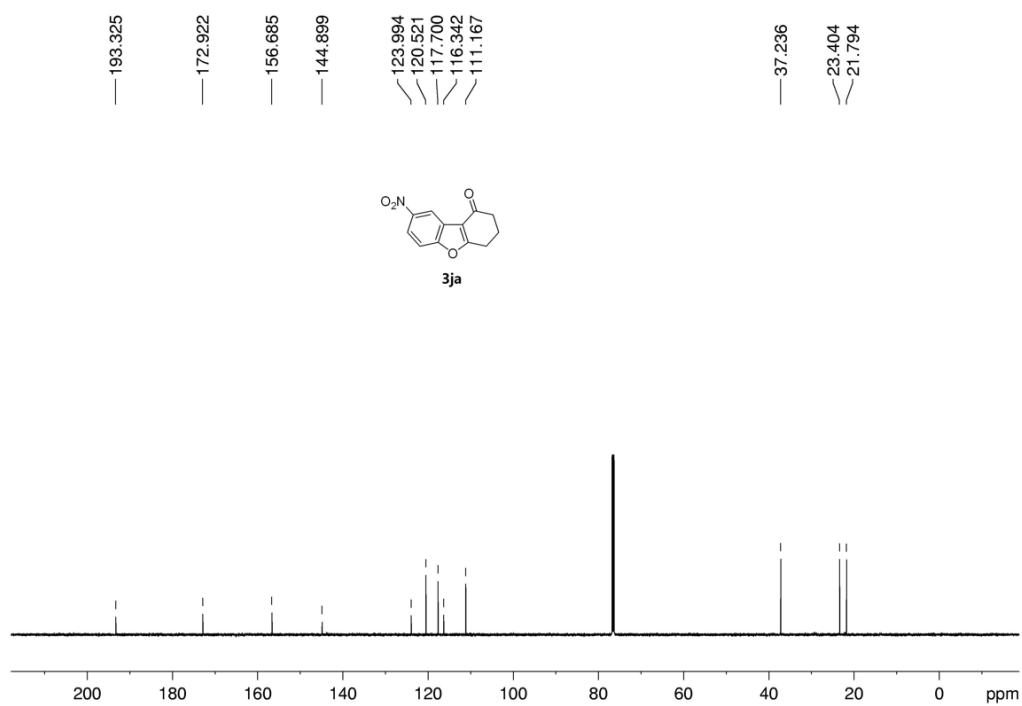
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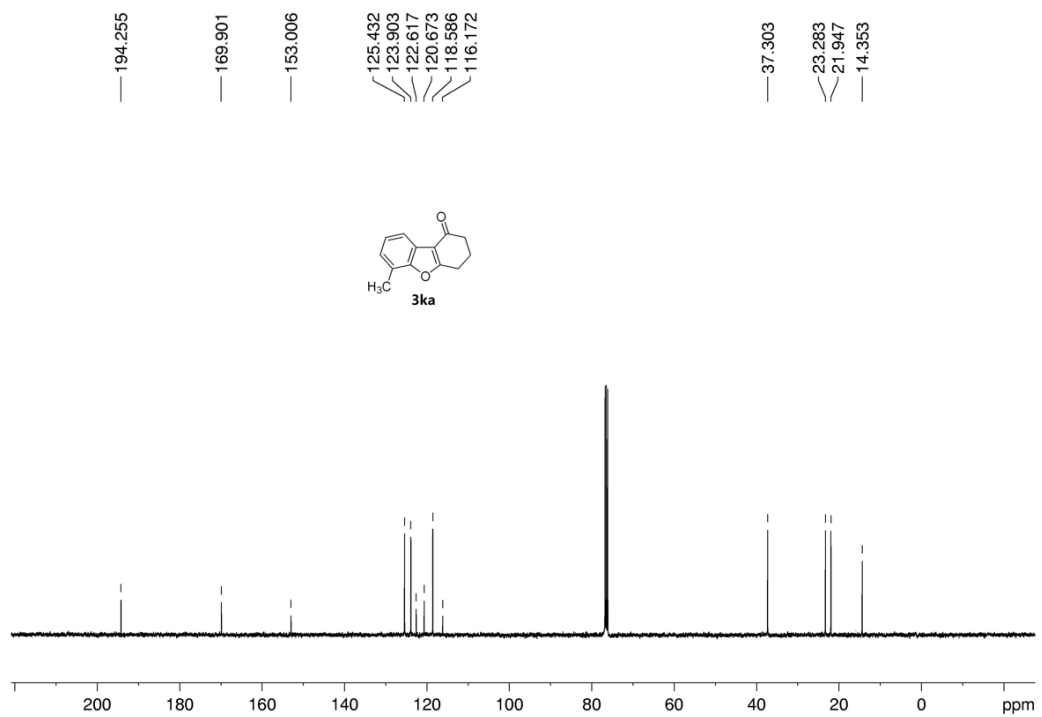
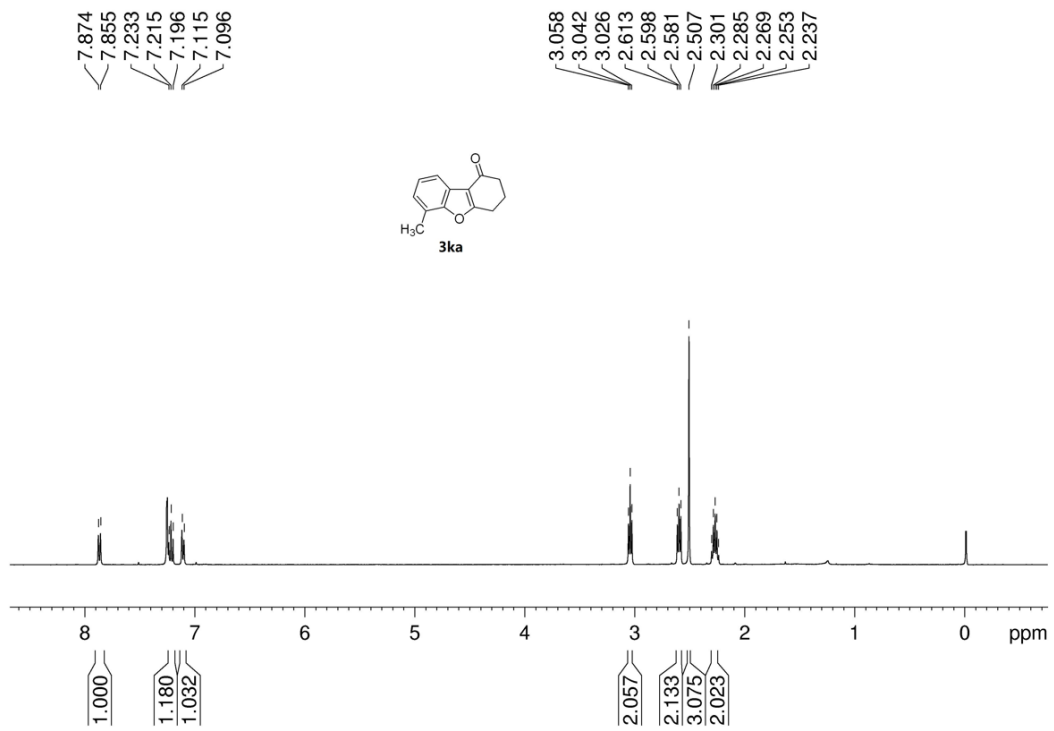
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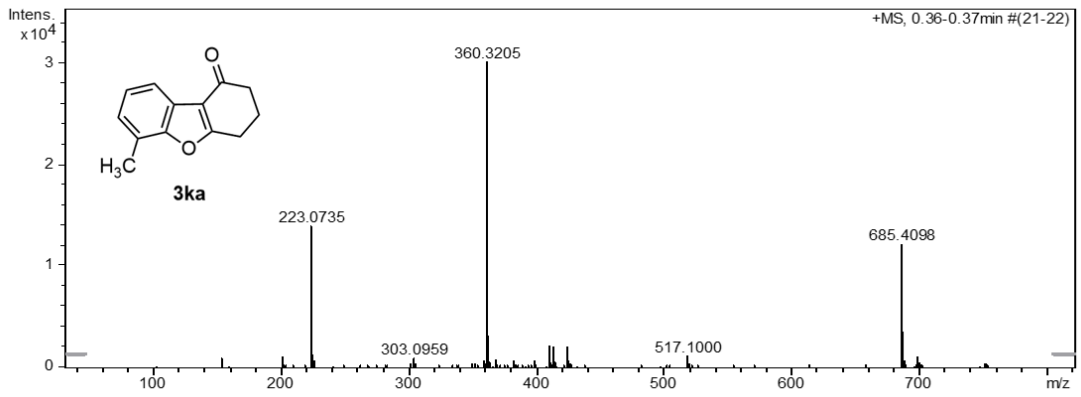
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2.301



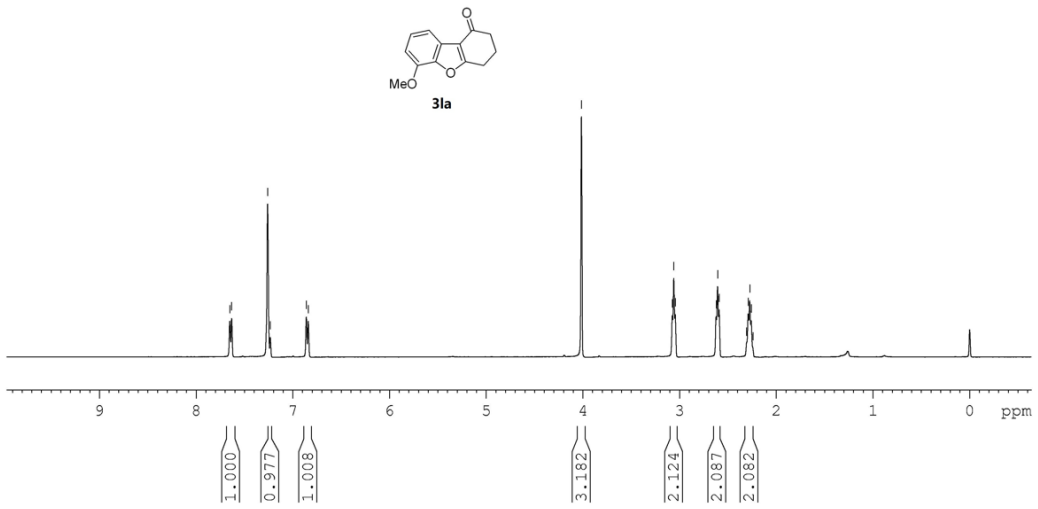






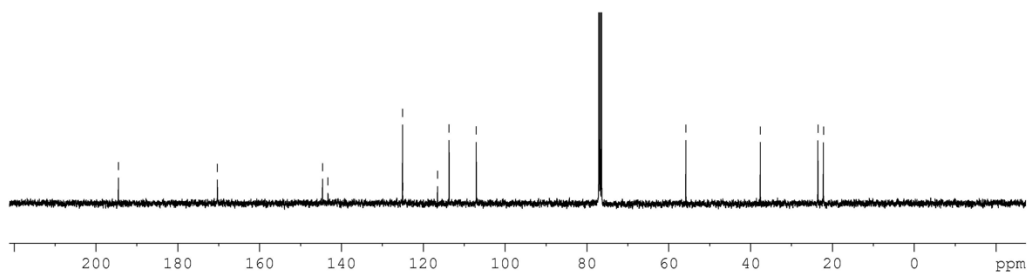
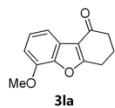
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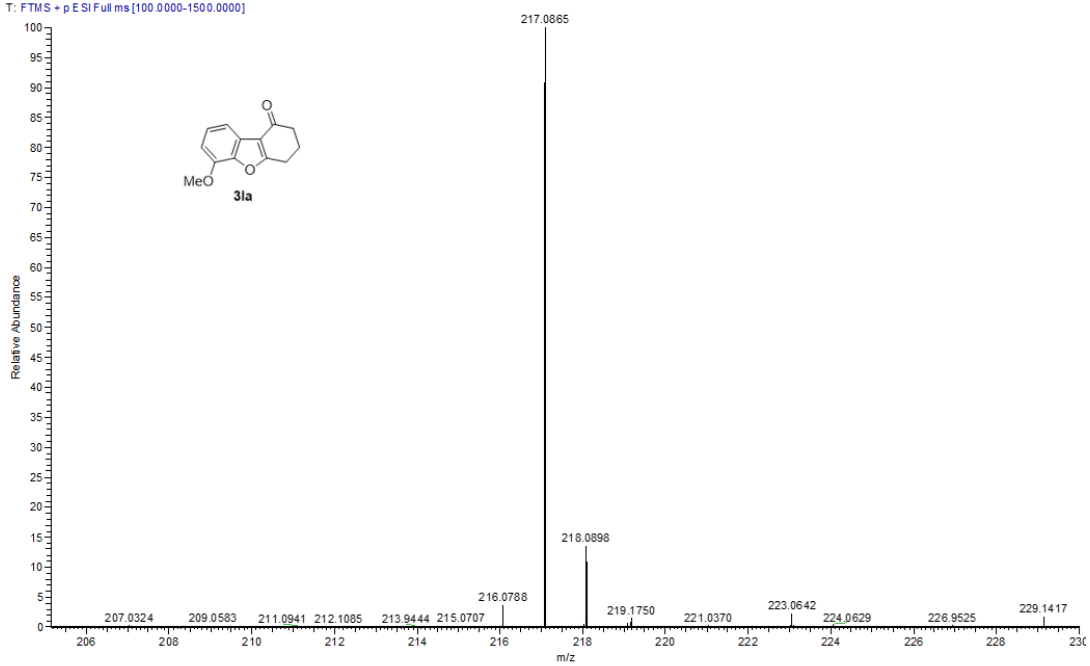


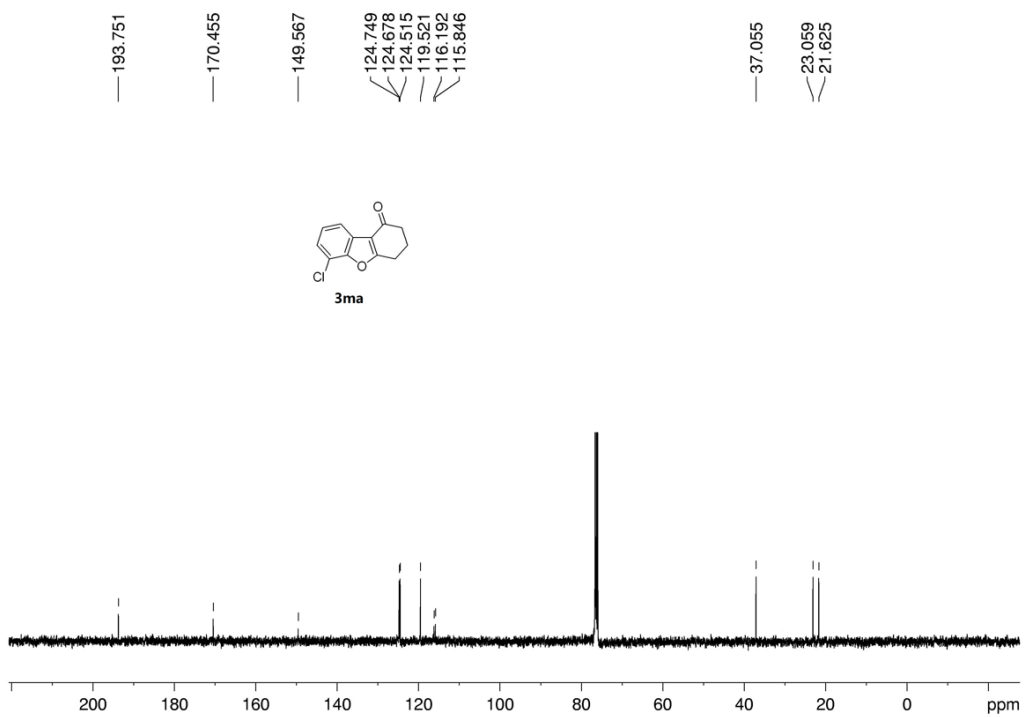
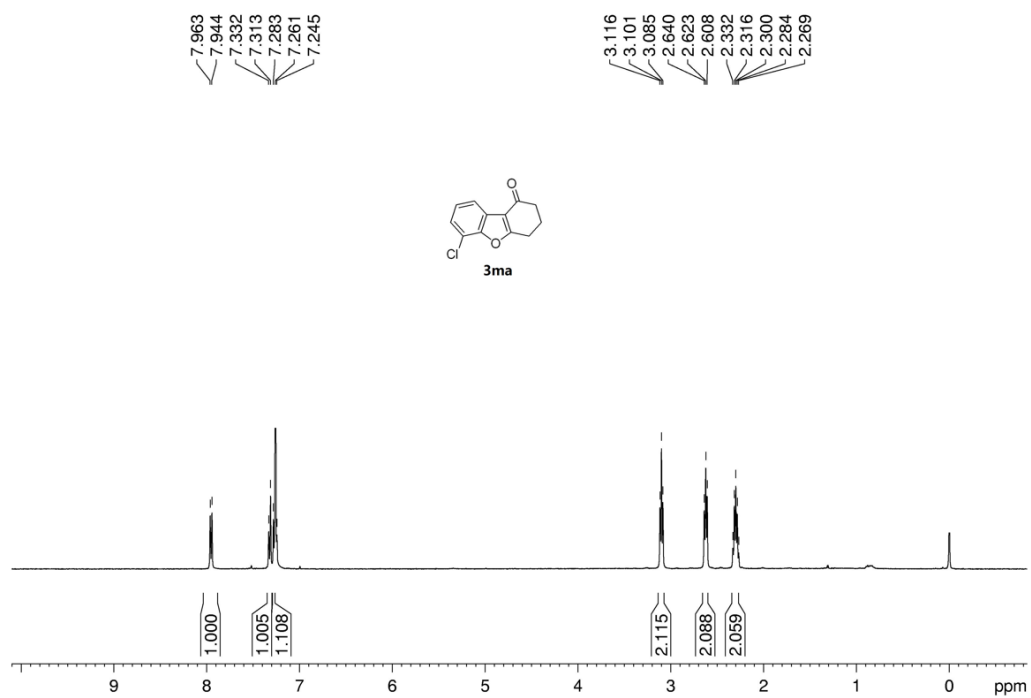


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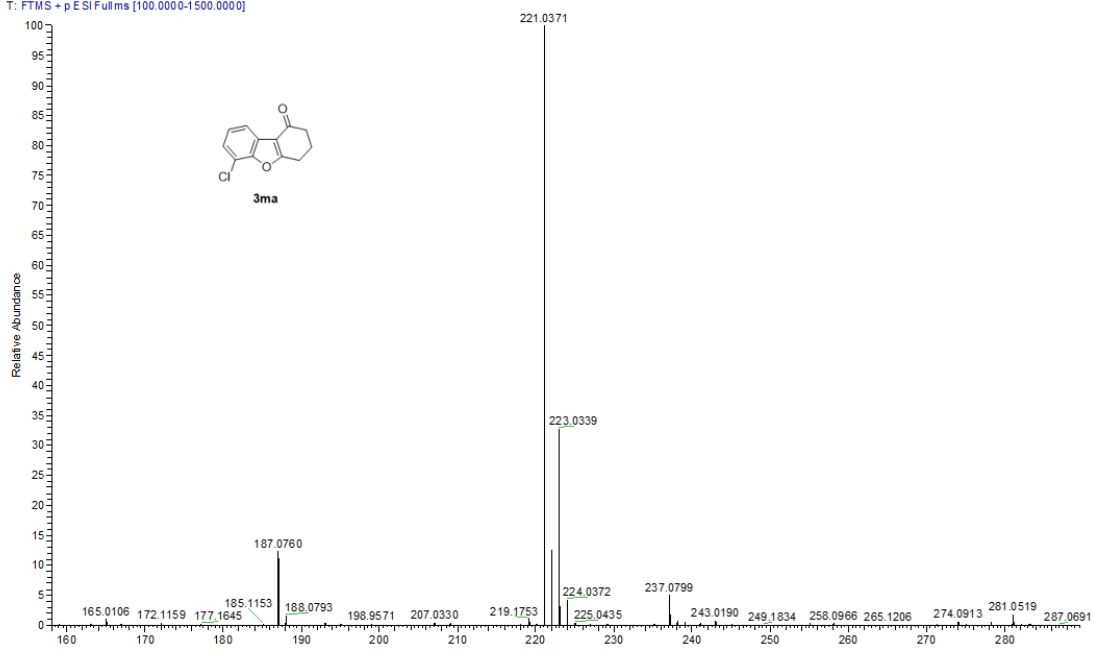


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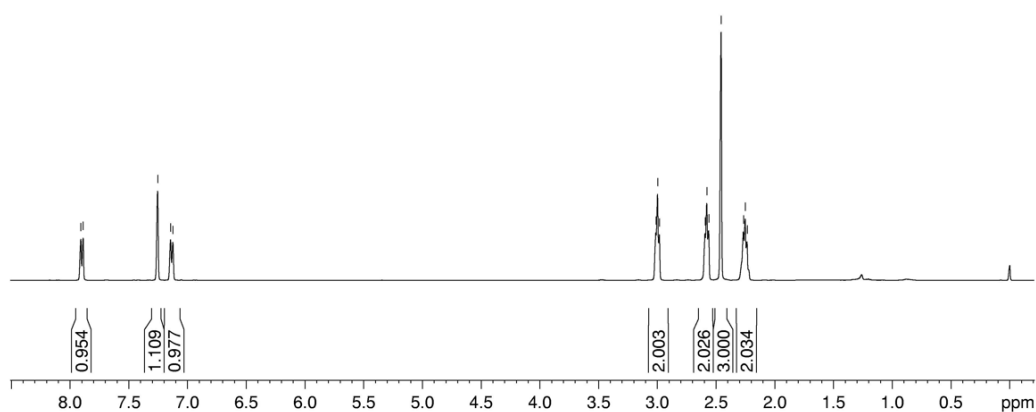
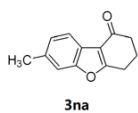
471 #614-698 RT: 3.50-3.97 AV: 85 NL: 1.08E8  
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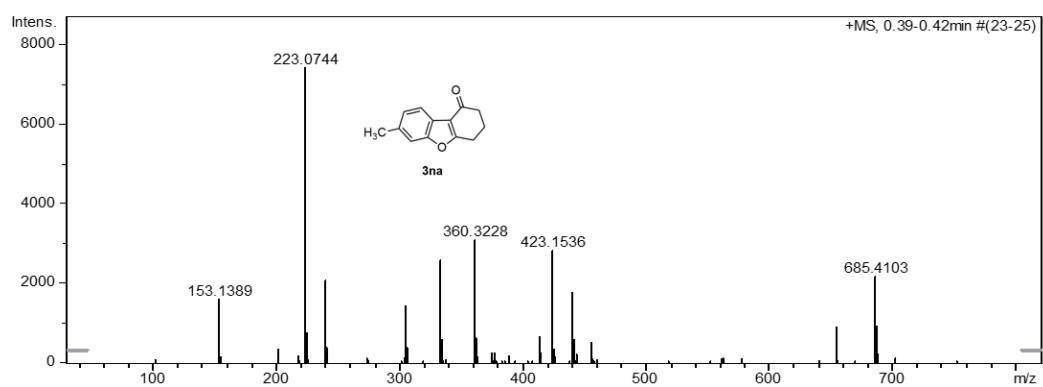
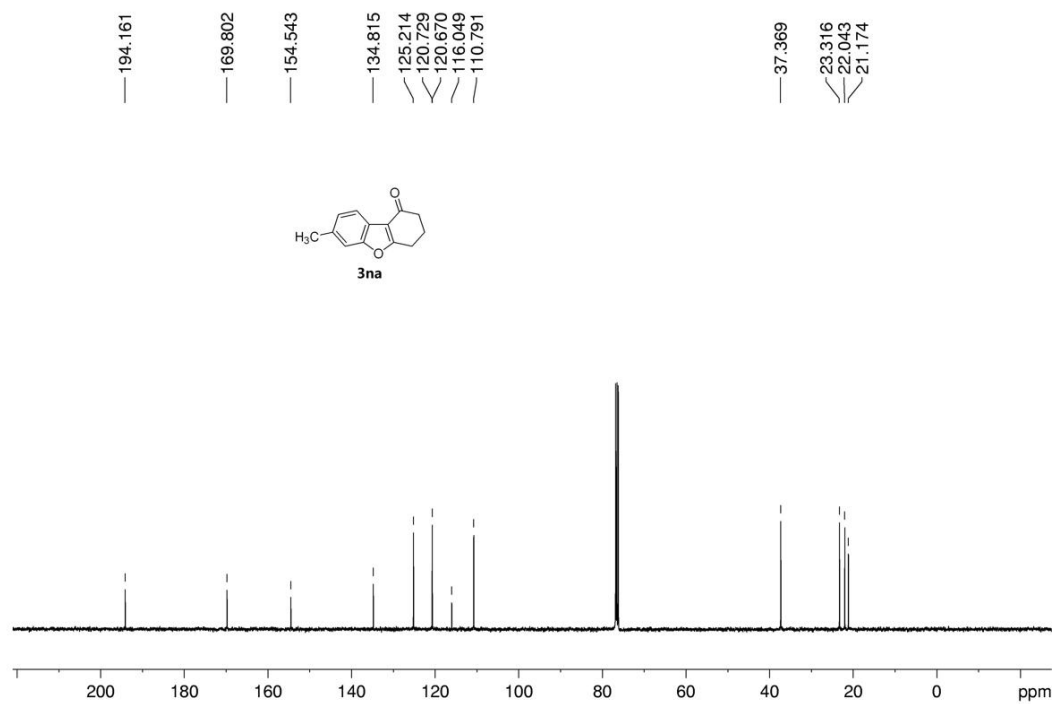


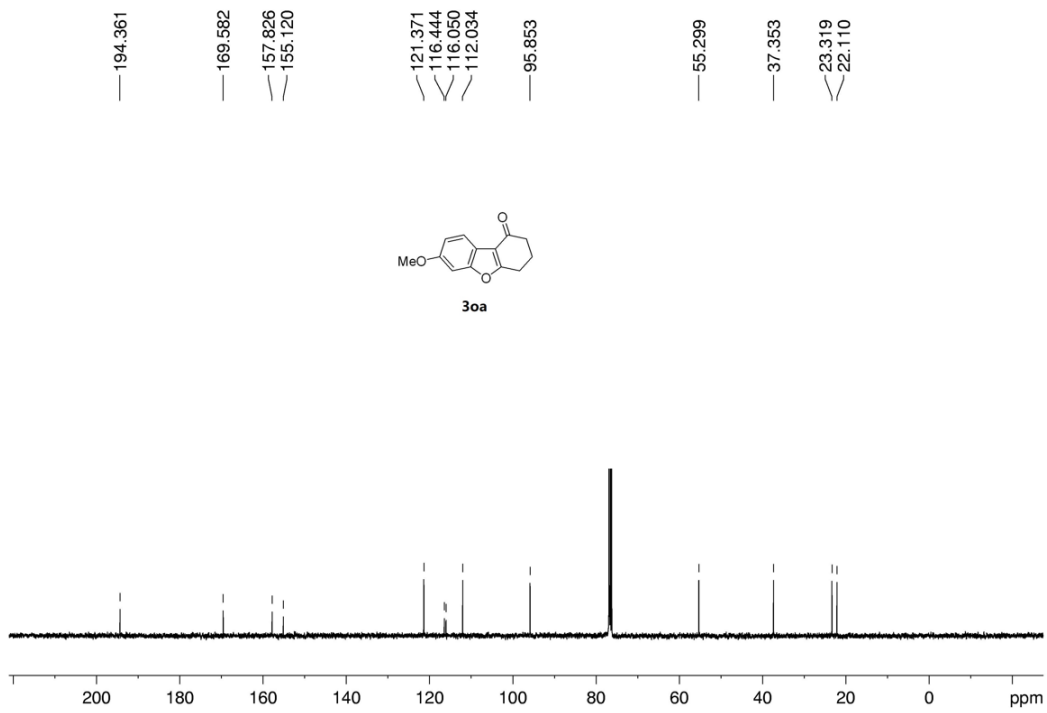
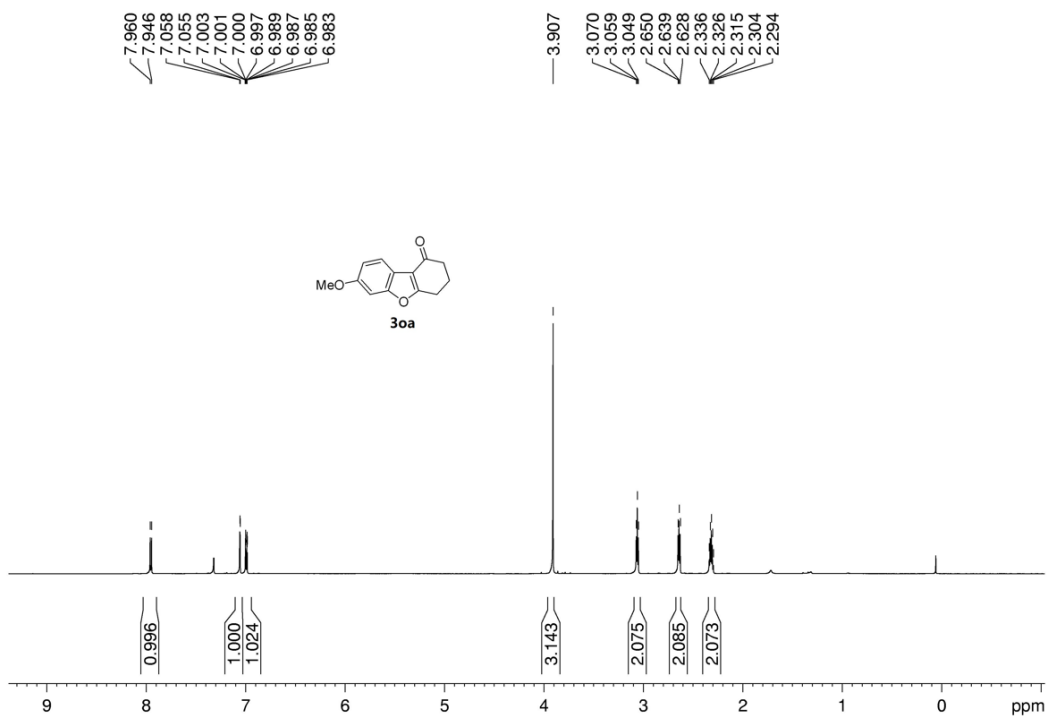
7.908  
7.888

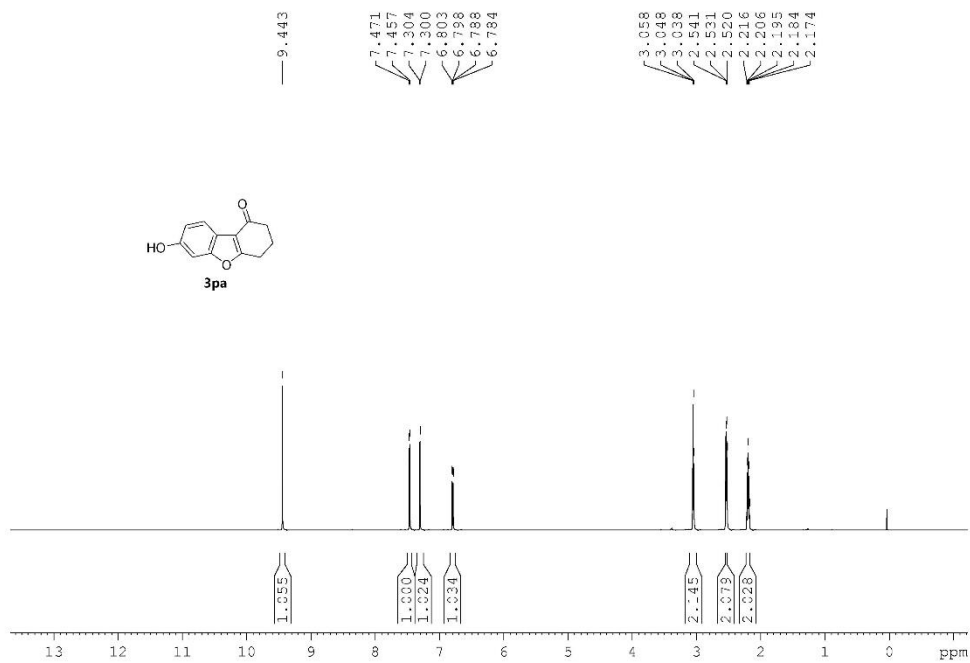
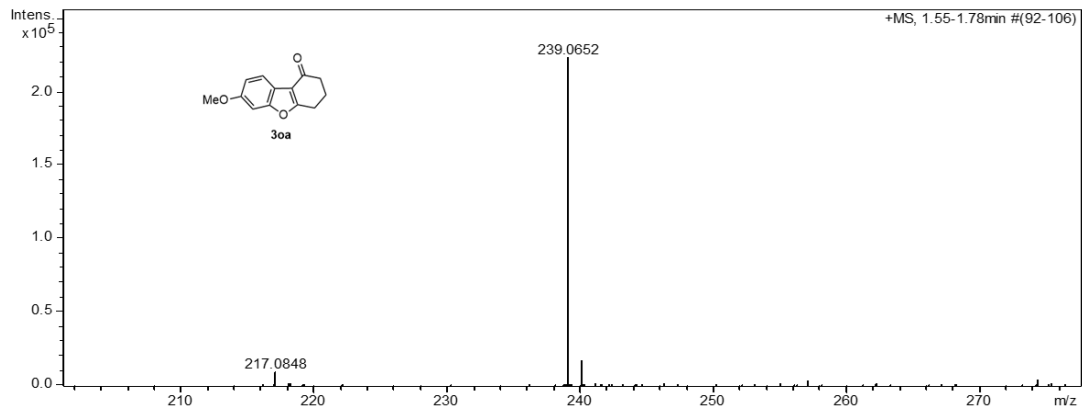
7.254  
7.144  
7.124

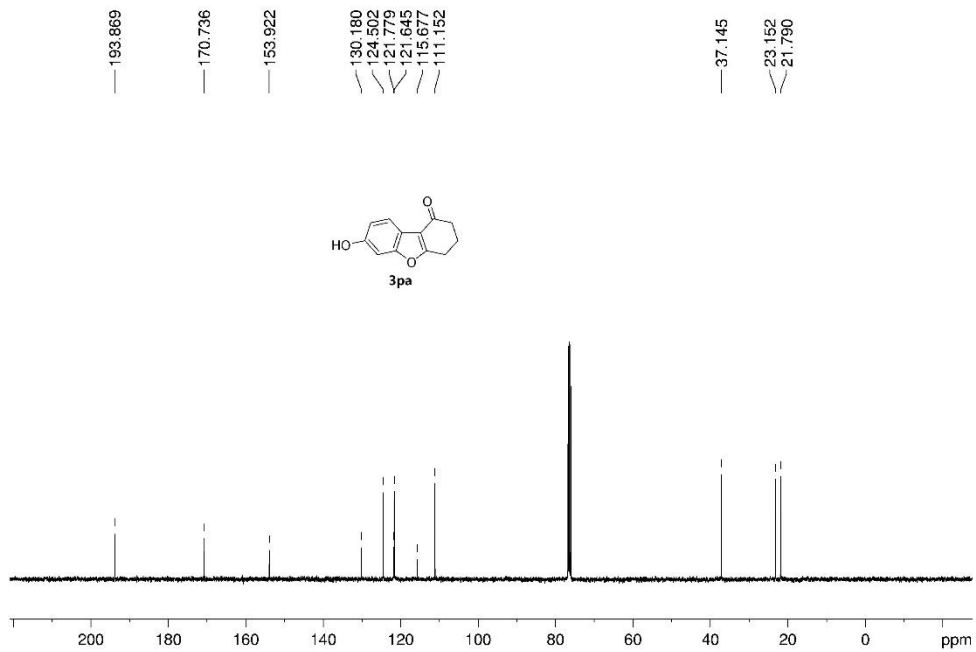
3.012  
2.997  
2.982  
2.593  
2.578  
2.562  
2.456  
2.266  
2.251  
2.235



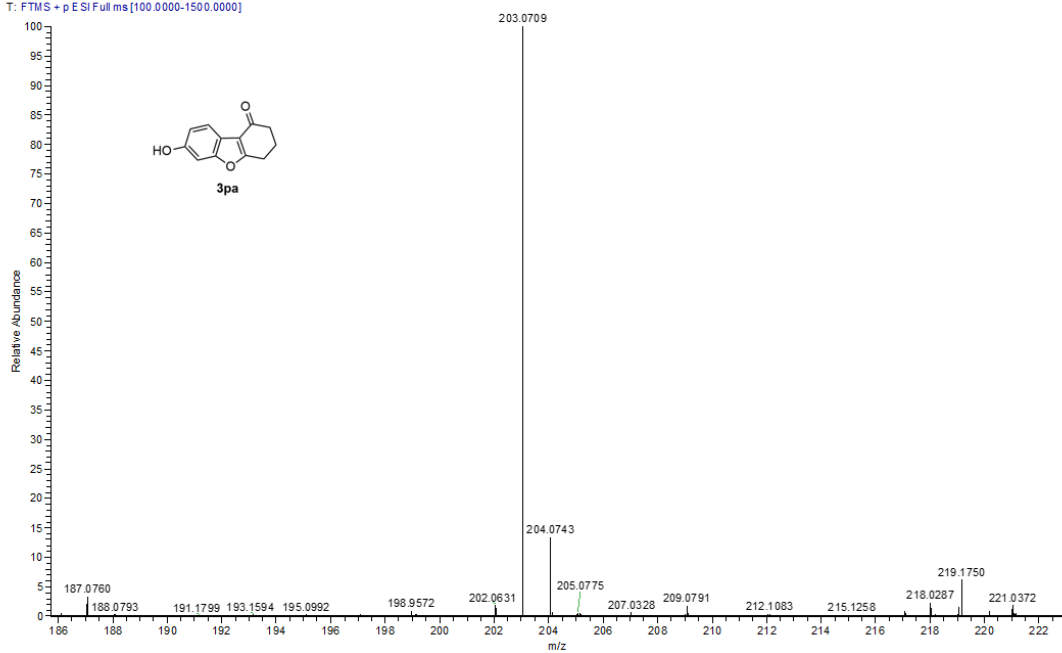


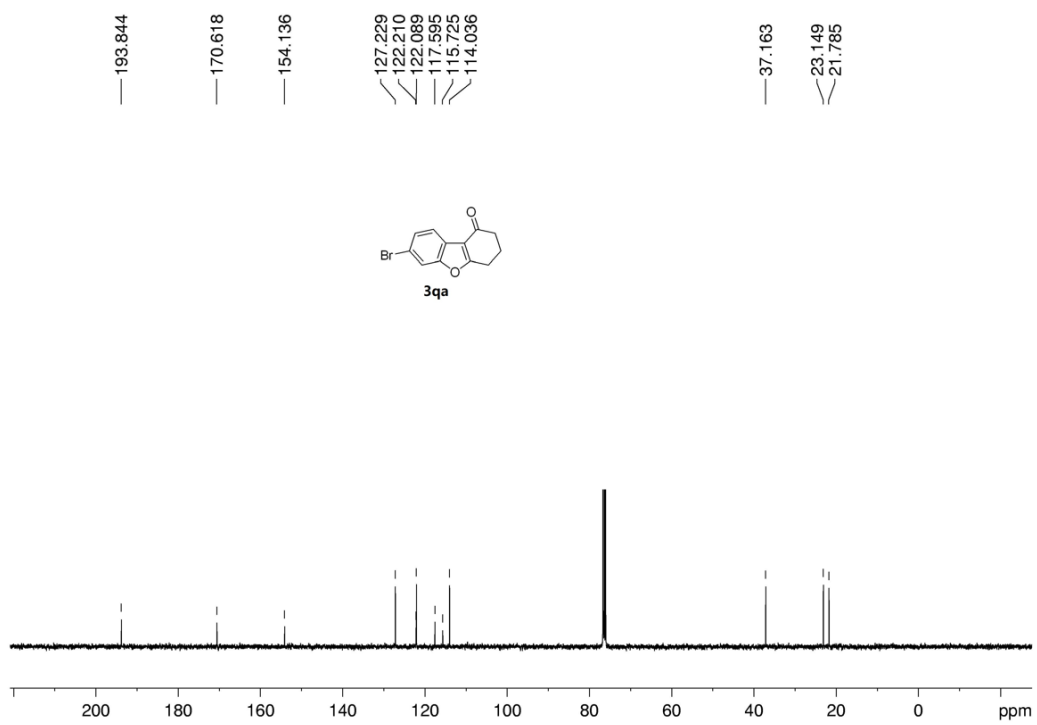
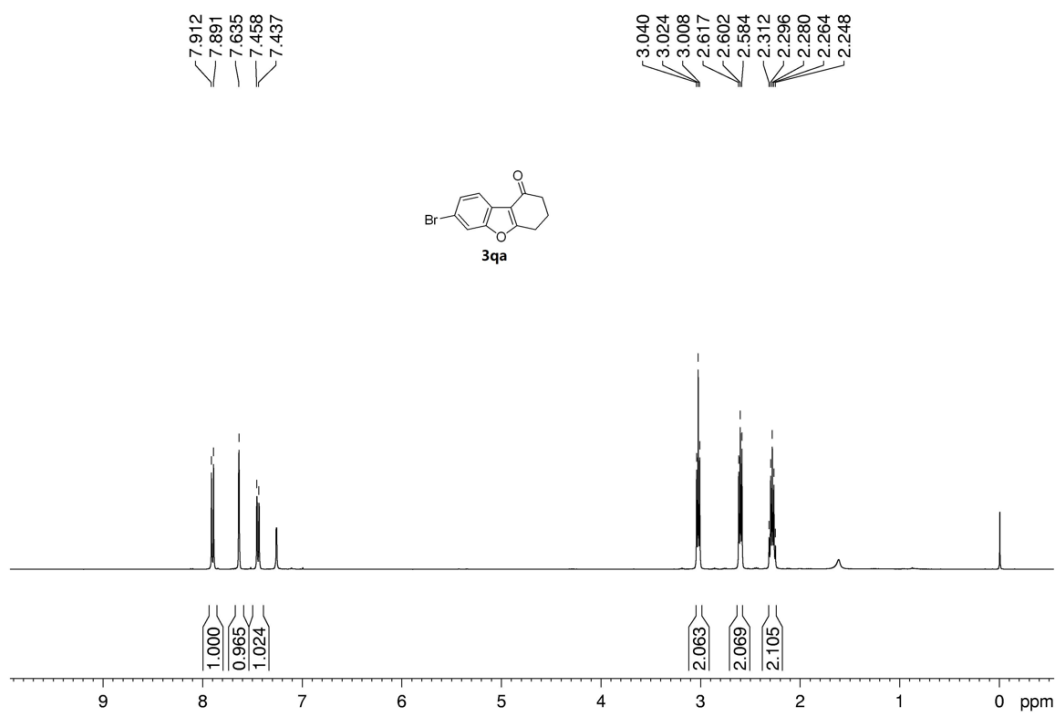






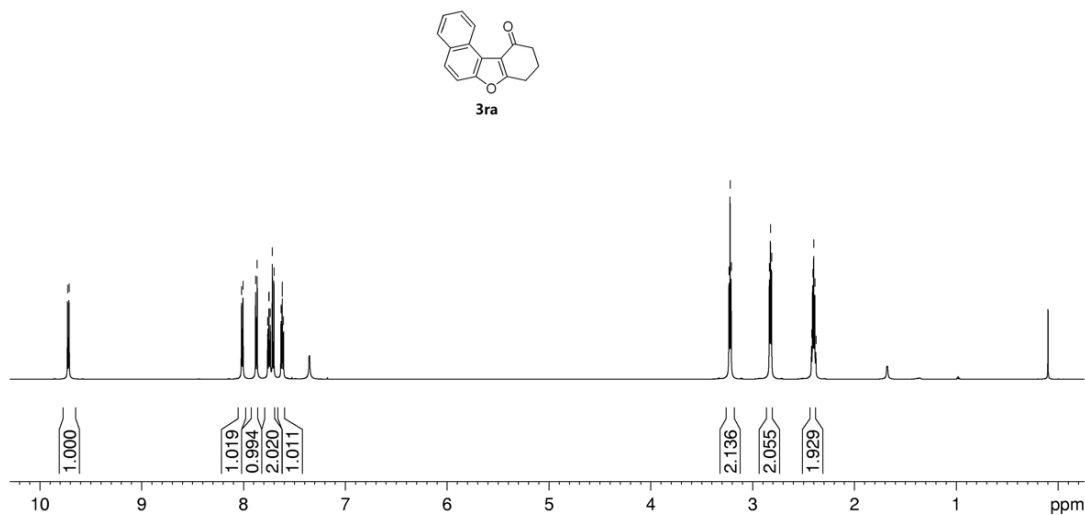
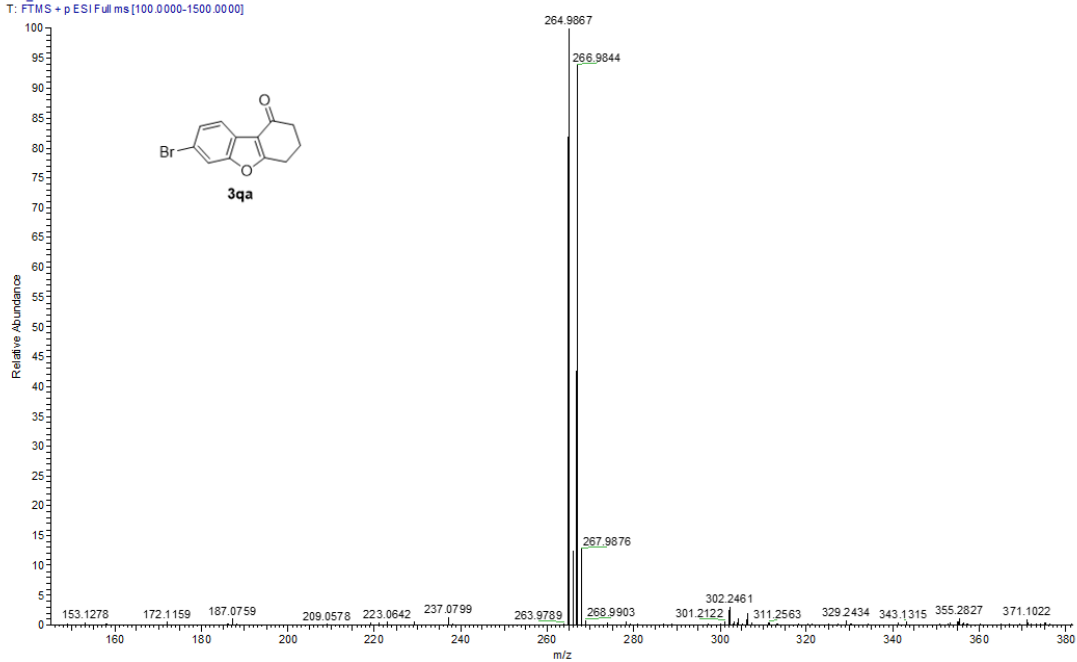
483\_230321201654 #411 RT: 2.31 AV: 1 NL: 1.91E7  
T: FTMS - p ESI Full ms [100.0000-1500.0000]

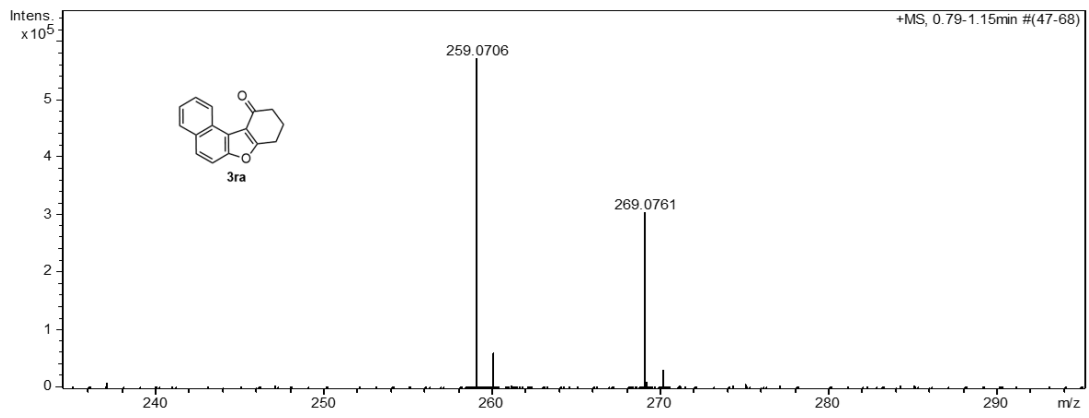
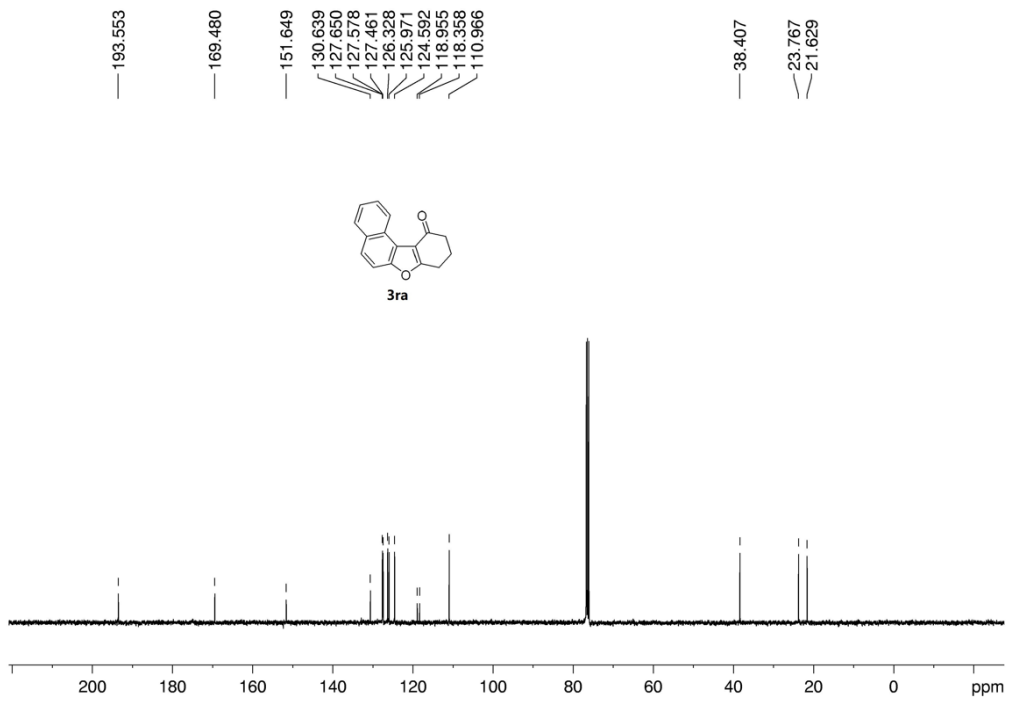


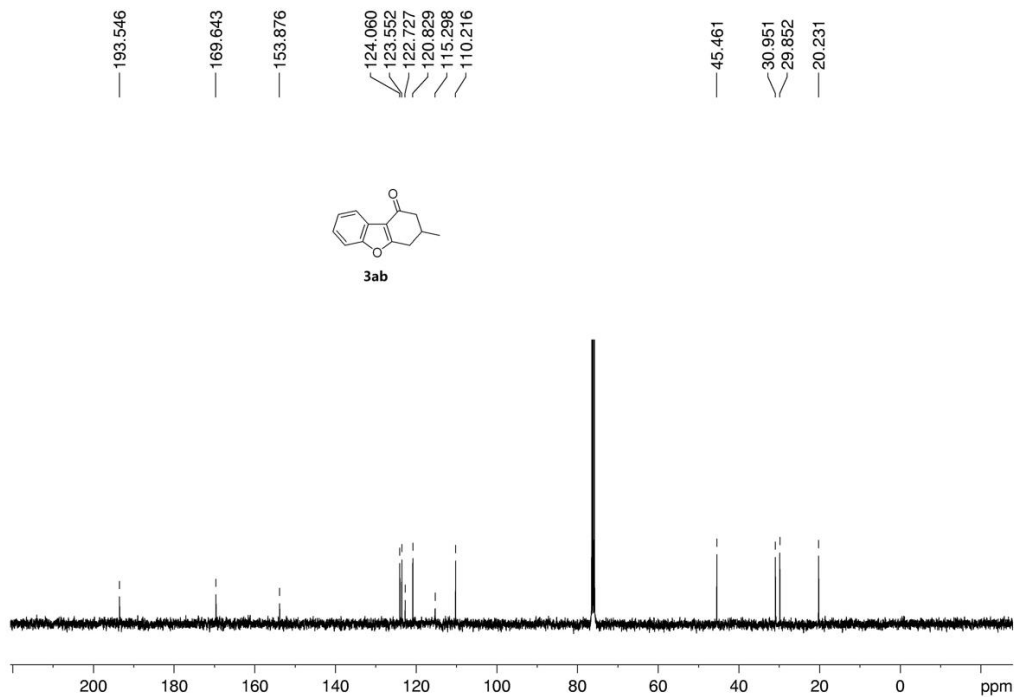
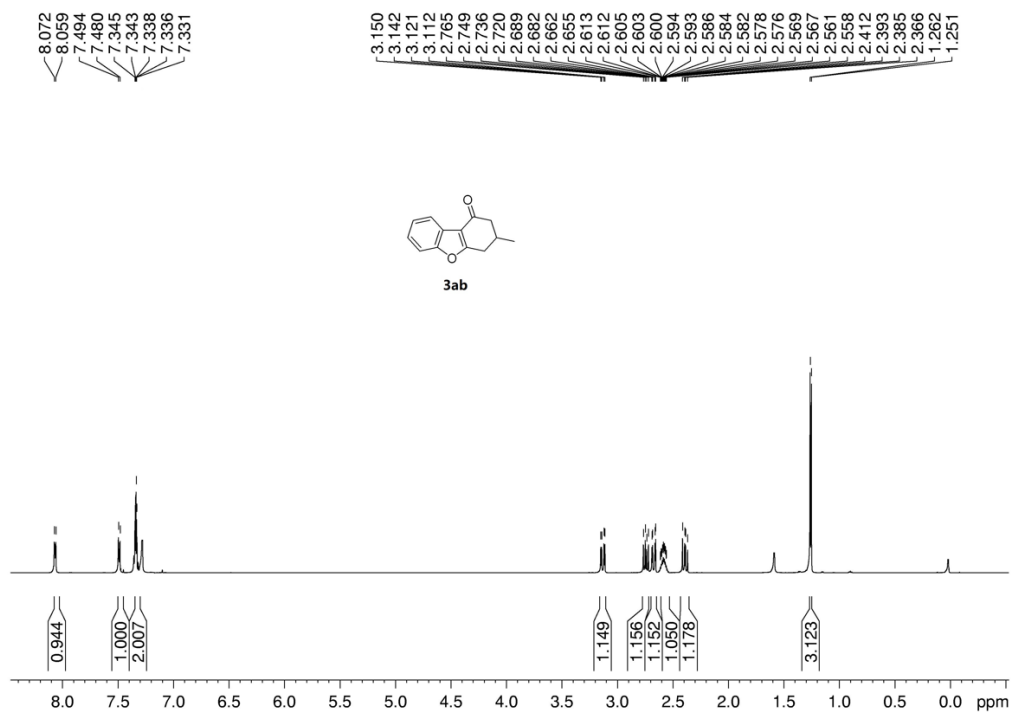


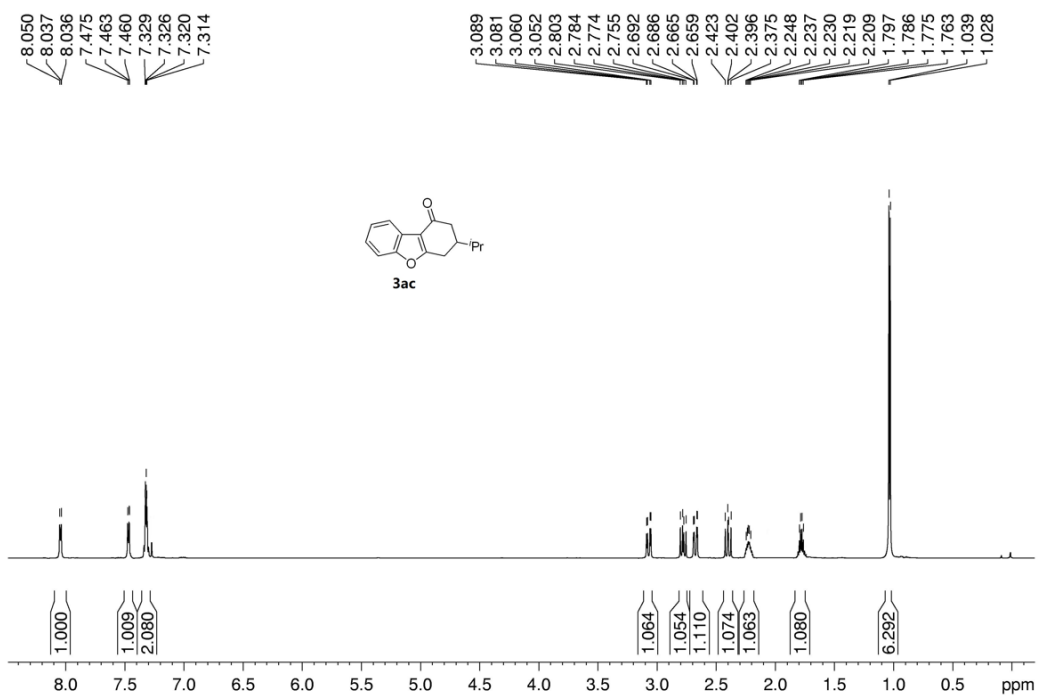
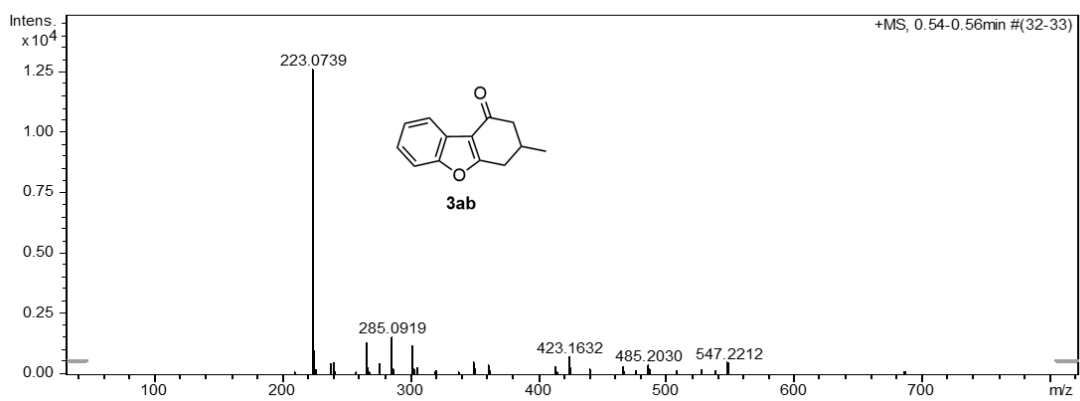


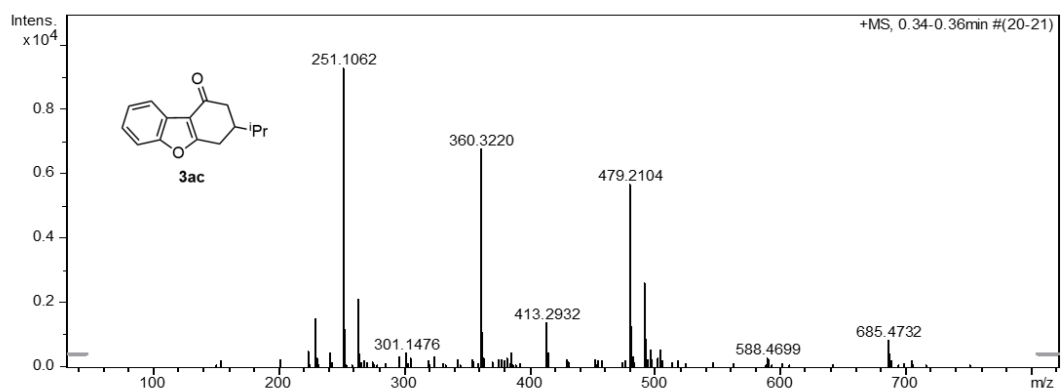
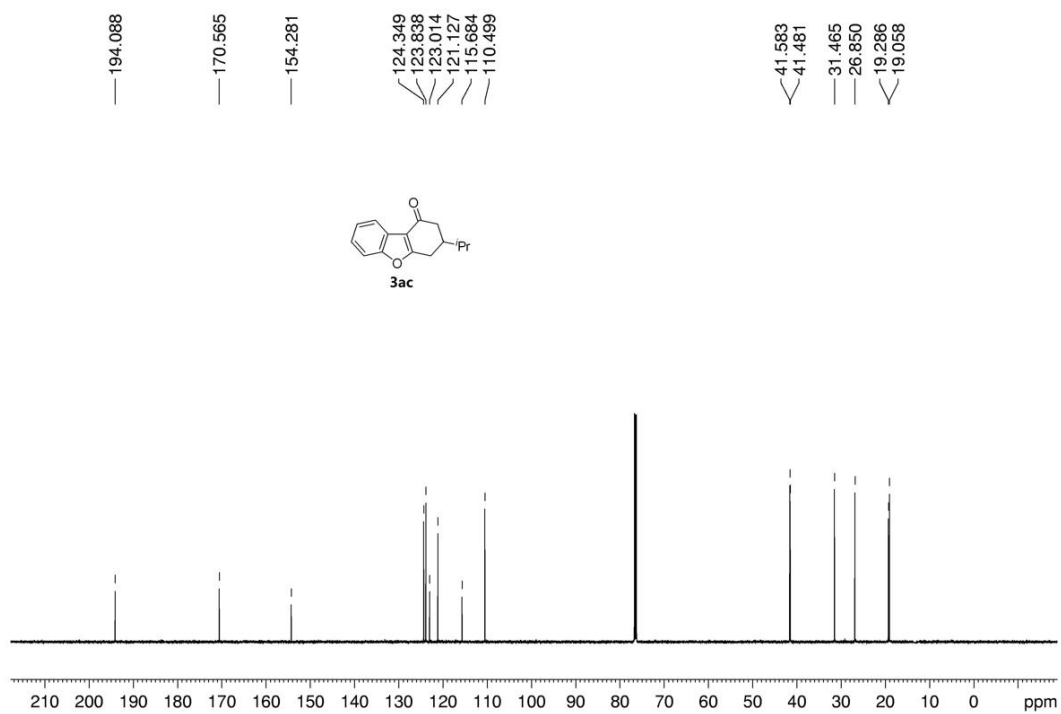
472\_230321200723#463 RT: 2.58 AV: 1 NL: 2.36E8  
T: FTMS + p ESI Full ms [100.0000-1500.0000]

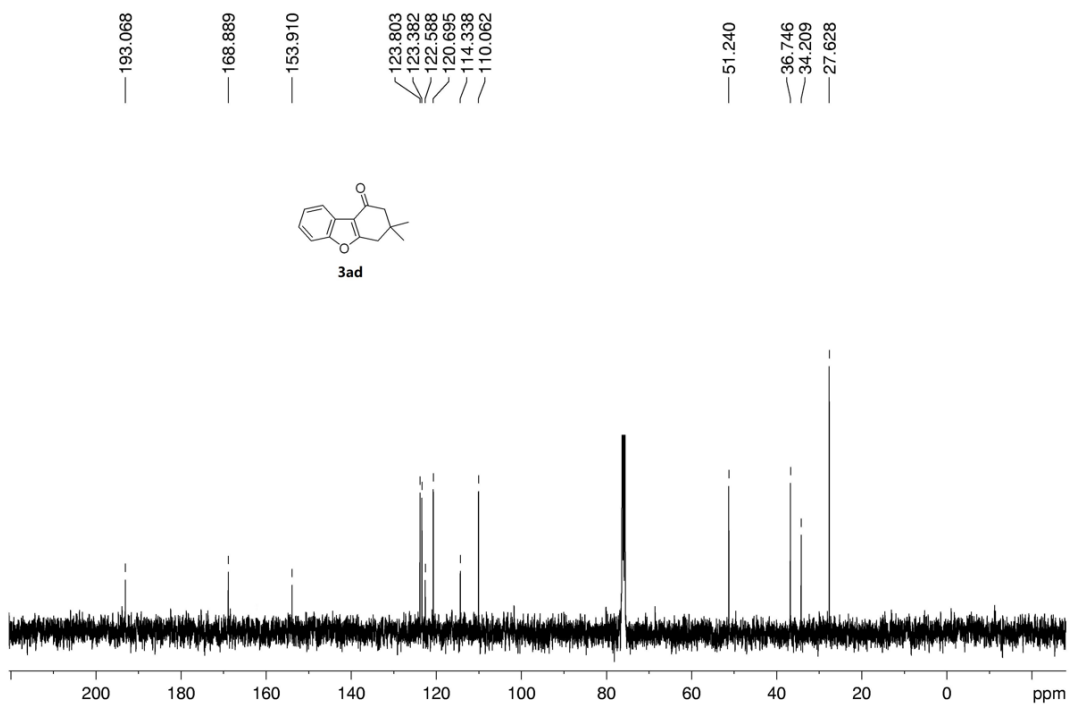
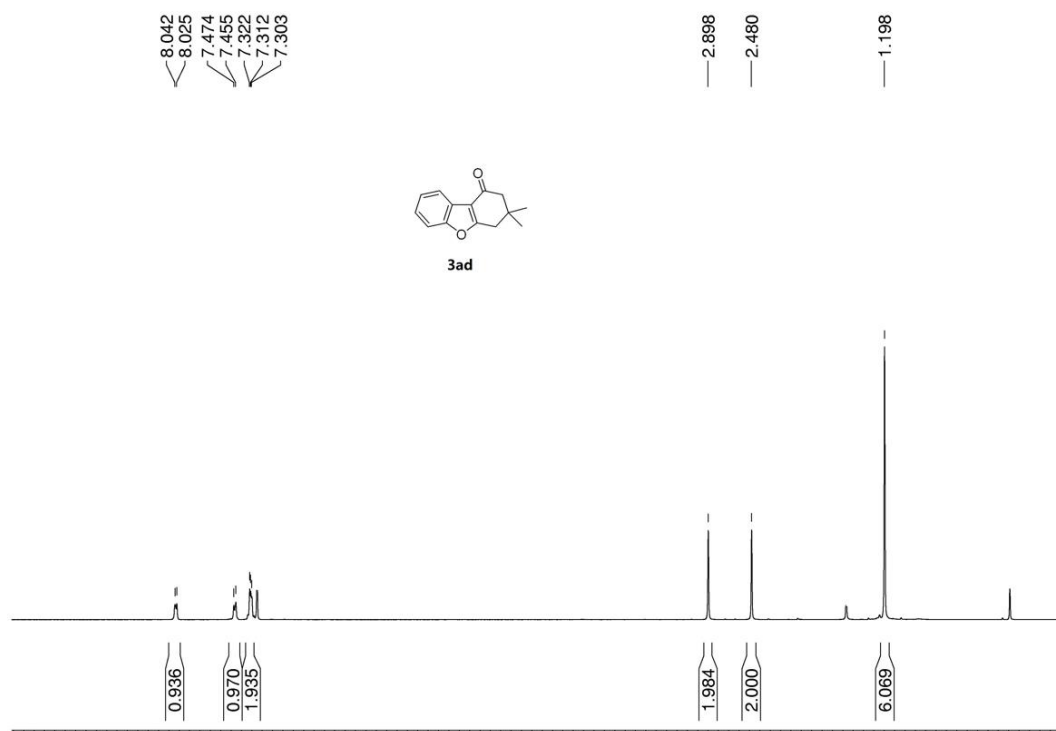


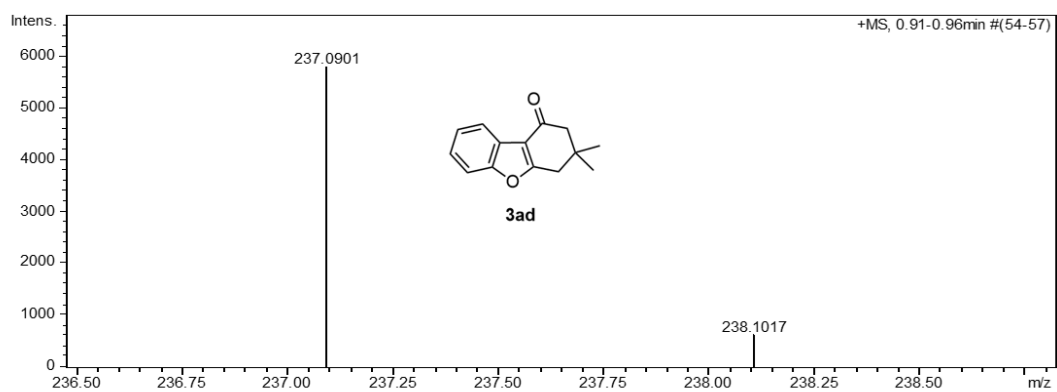






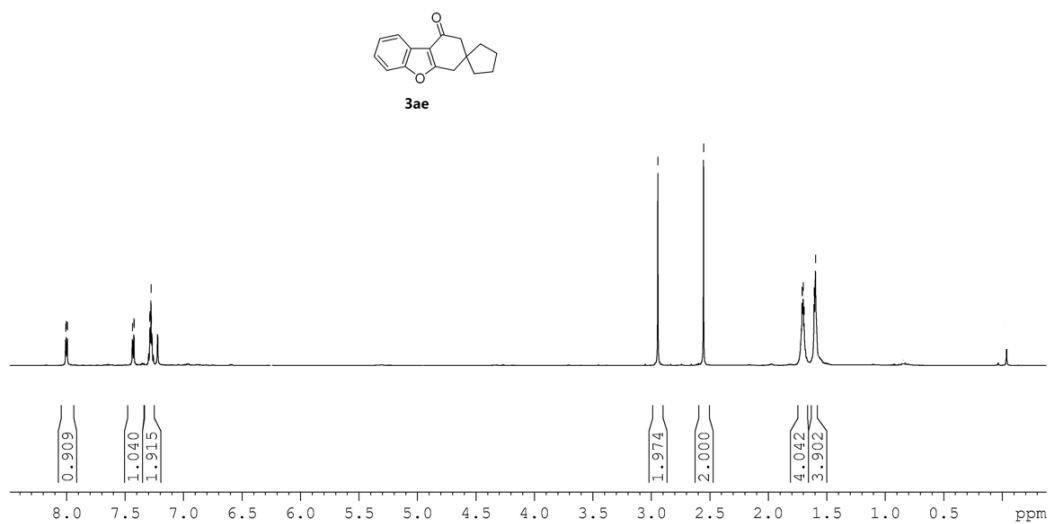


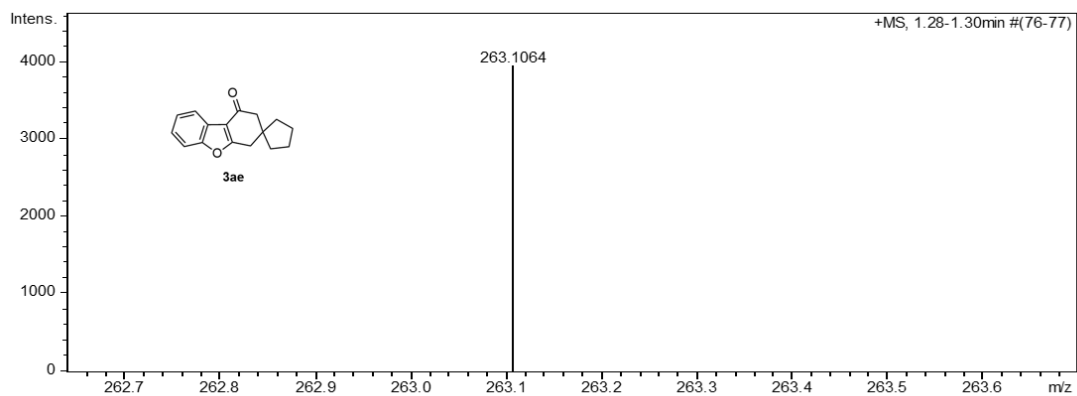
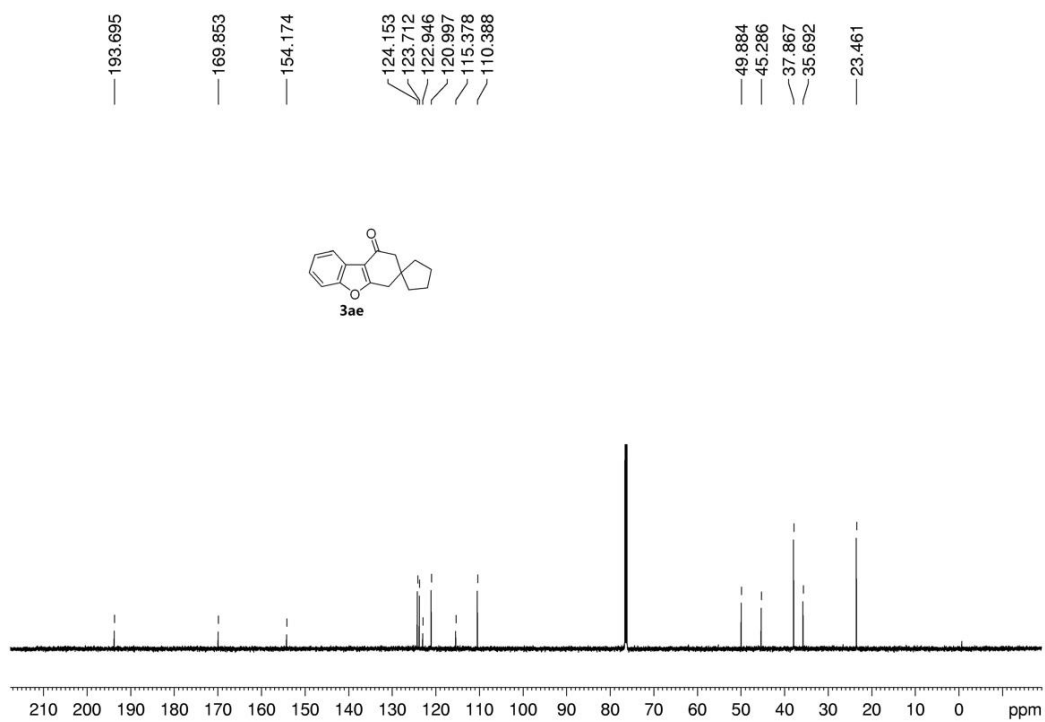




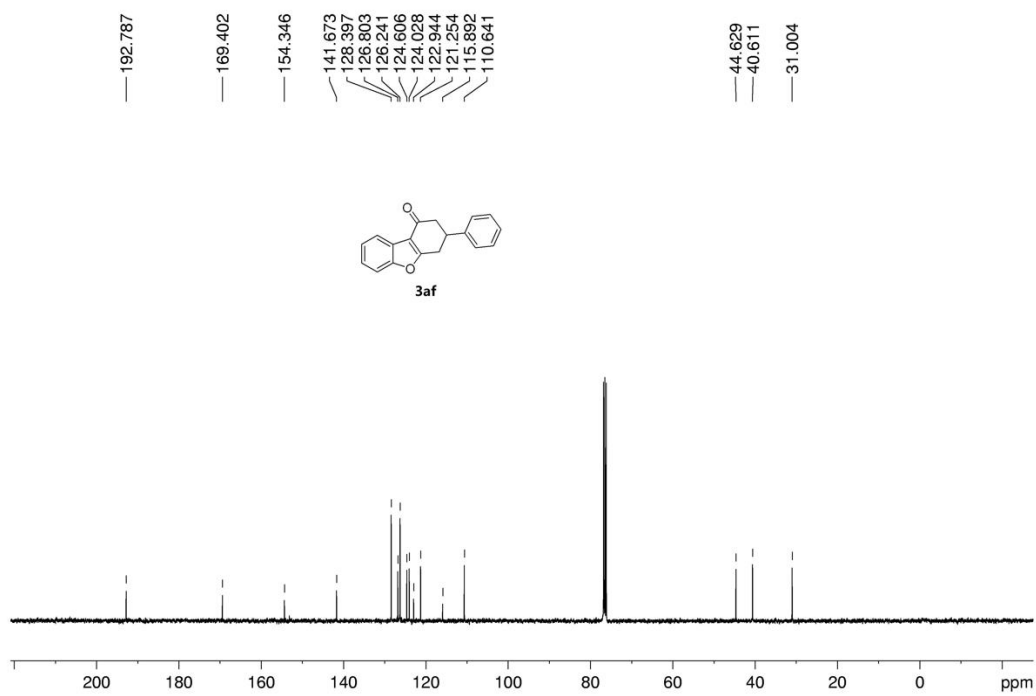
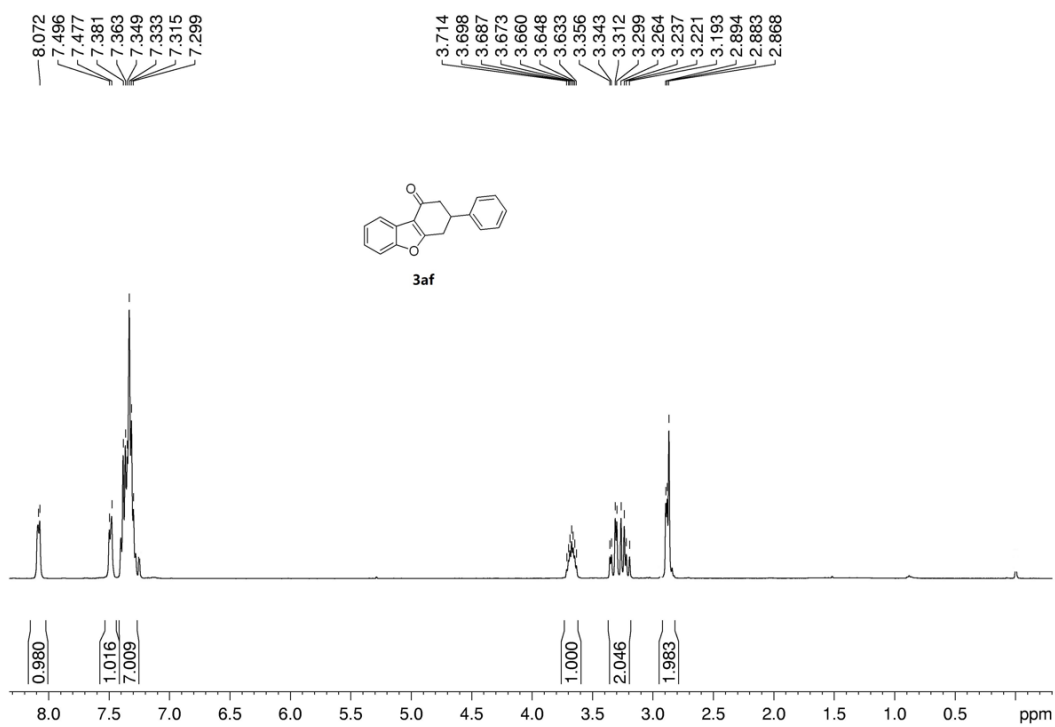
8.007  
8.003  
7.992  
7.436  
7.425  
7.421  
7.289  
7.287  
7.284  
7.279  
7.275

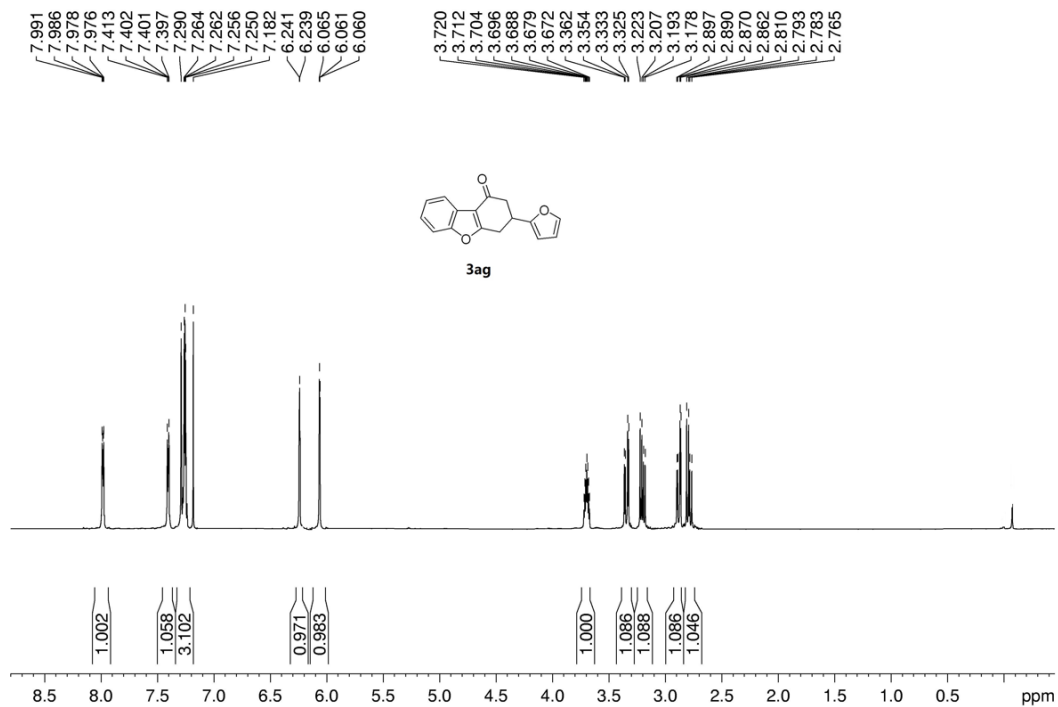
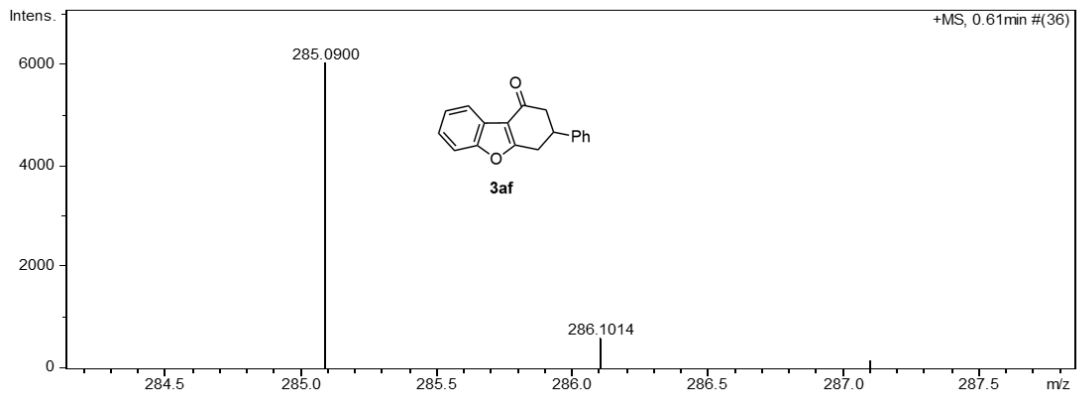
2.944  
2.553  
1.710  
1.708  
1.702  
1.694  
1.607  
1.605  
1.603  
1.596



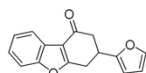




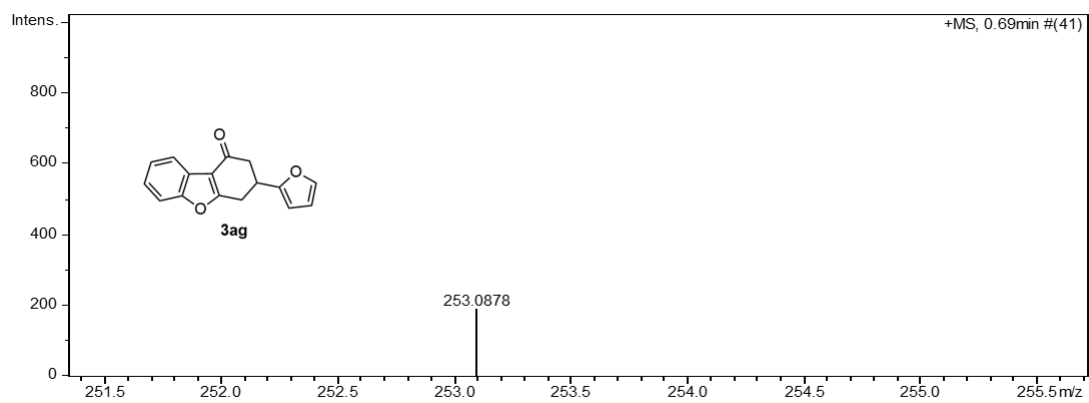
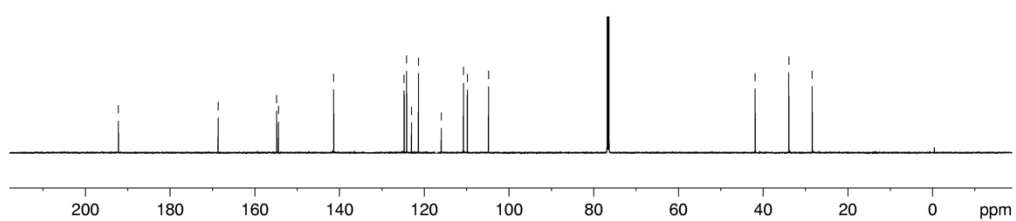


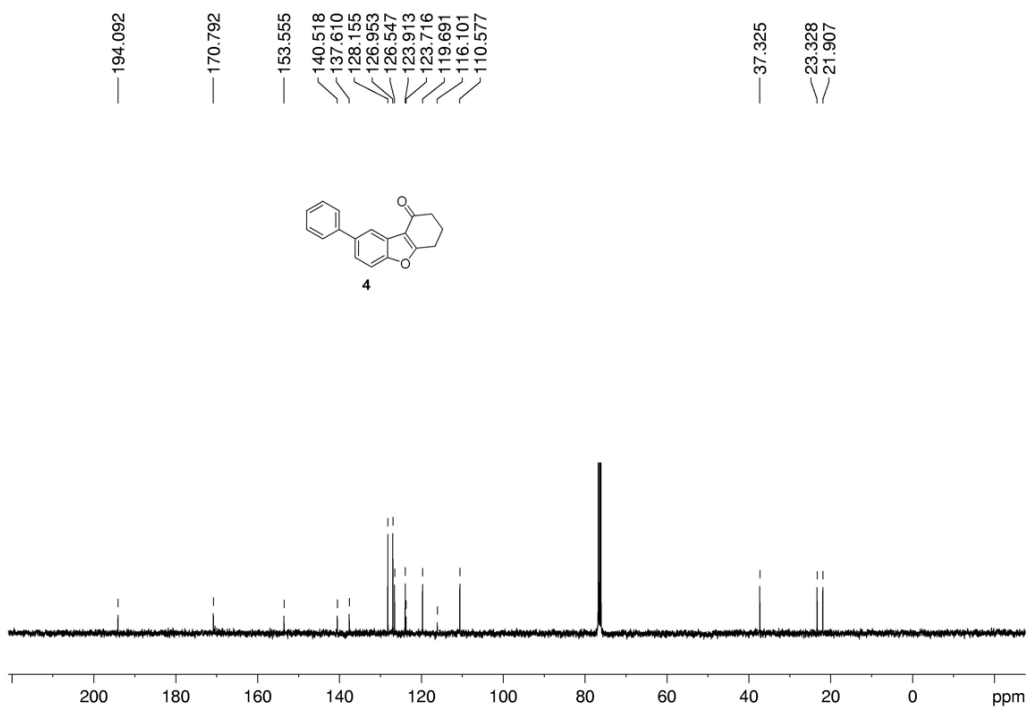
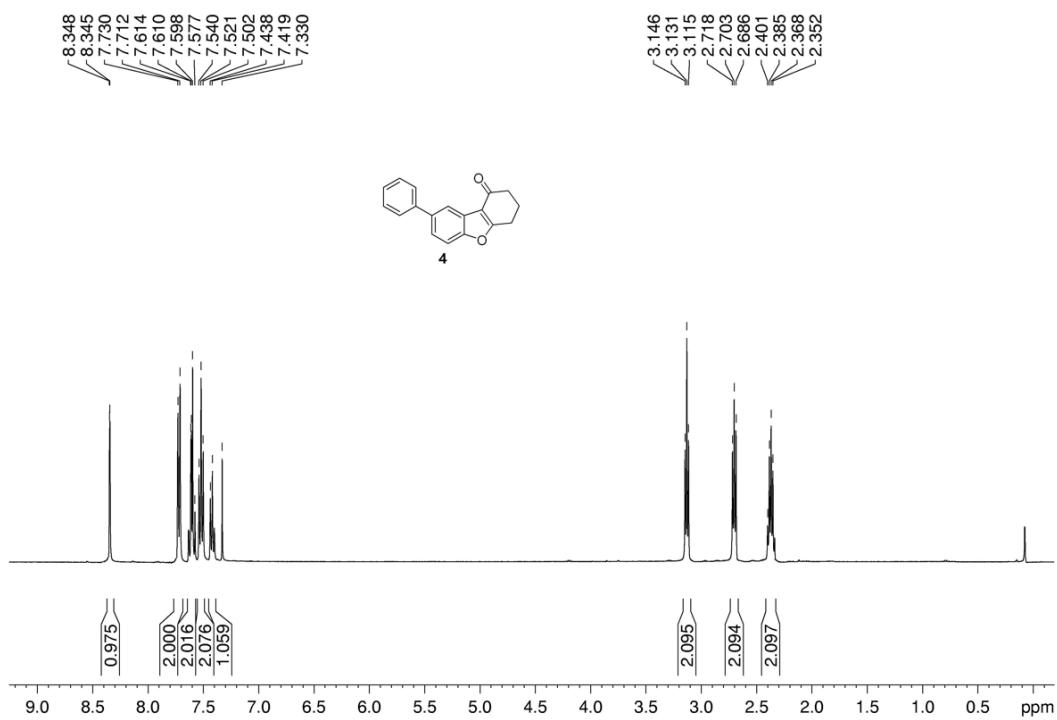


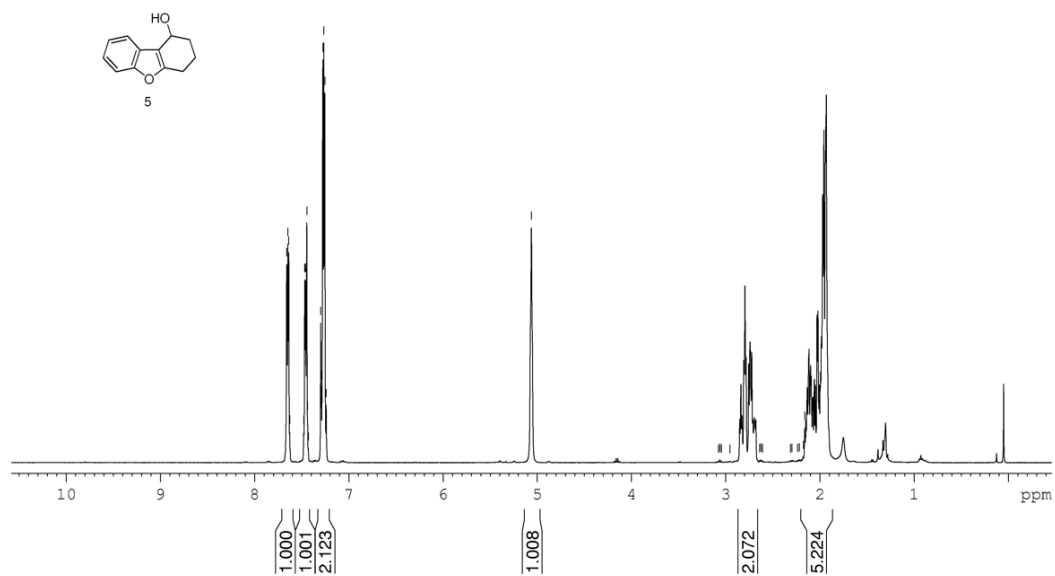
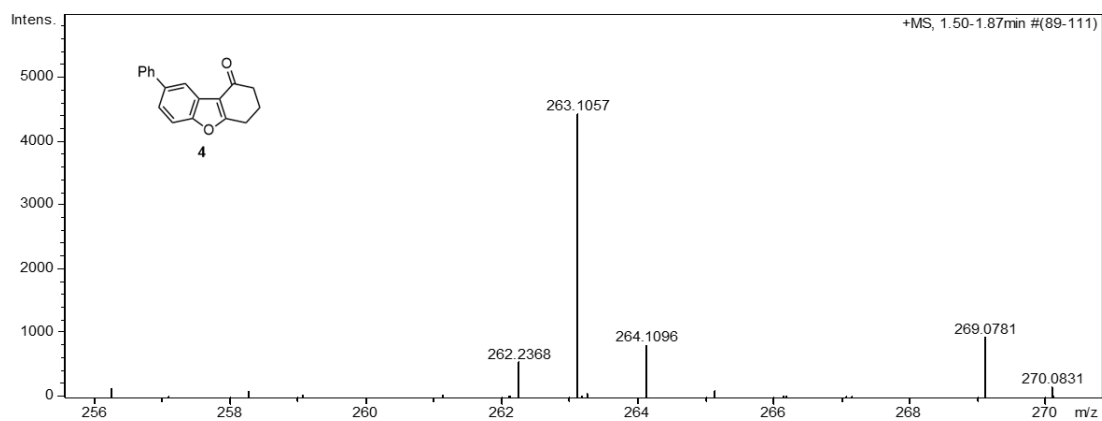
192.222  
 168.679  
 154.840  
 154.436  
 141.394  
 124.757  
 124.167  
 123.040  
 121.395  
 116.007  
 110.757  
 109.841  
 104.846  
 41.889  
 33.919  
 28.427

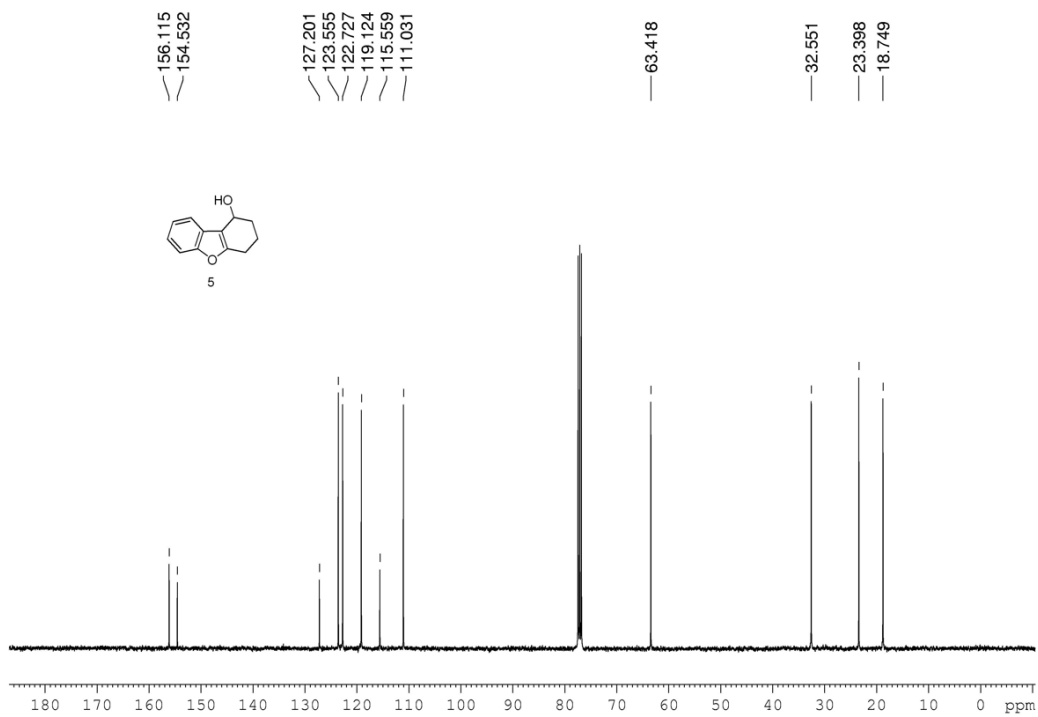


**3ag**

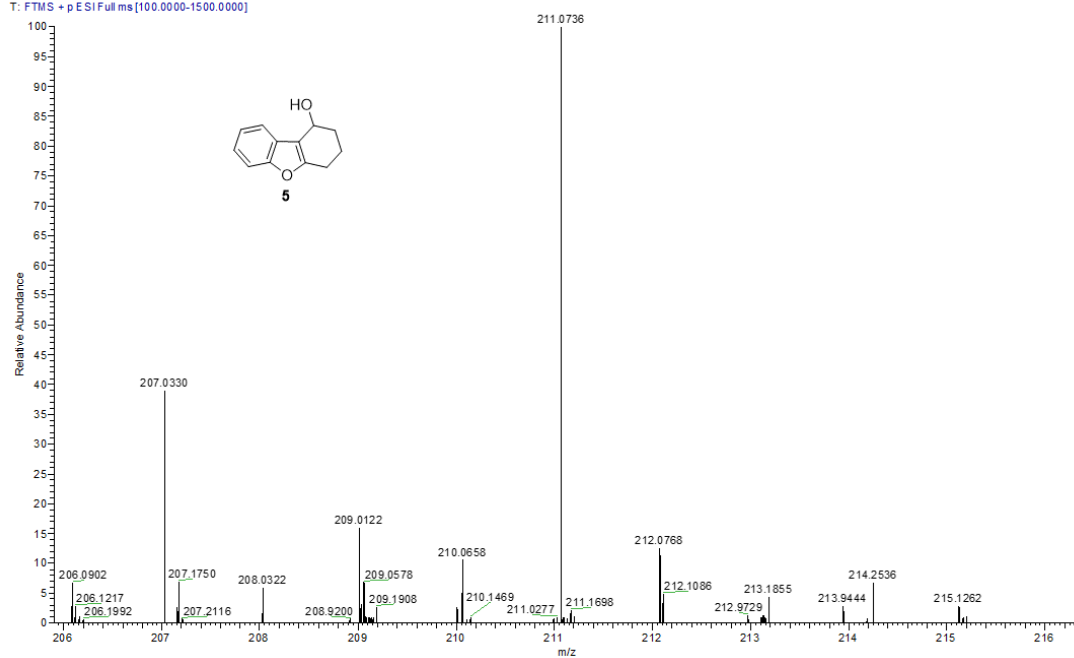


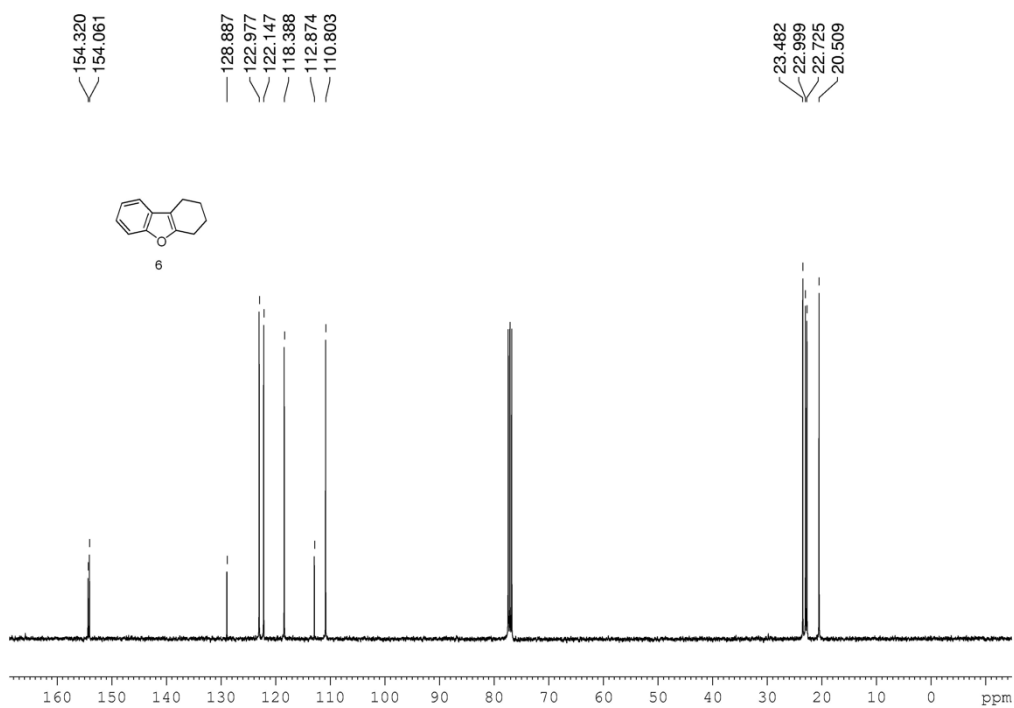
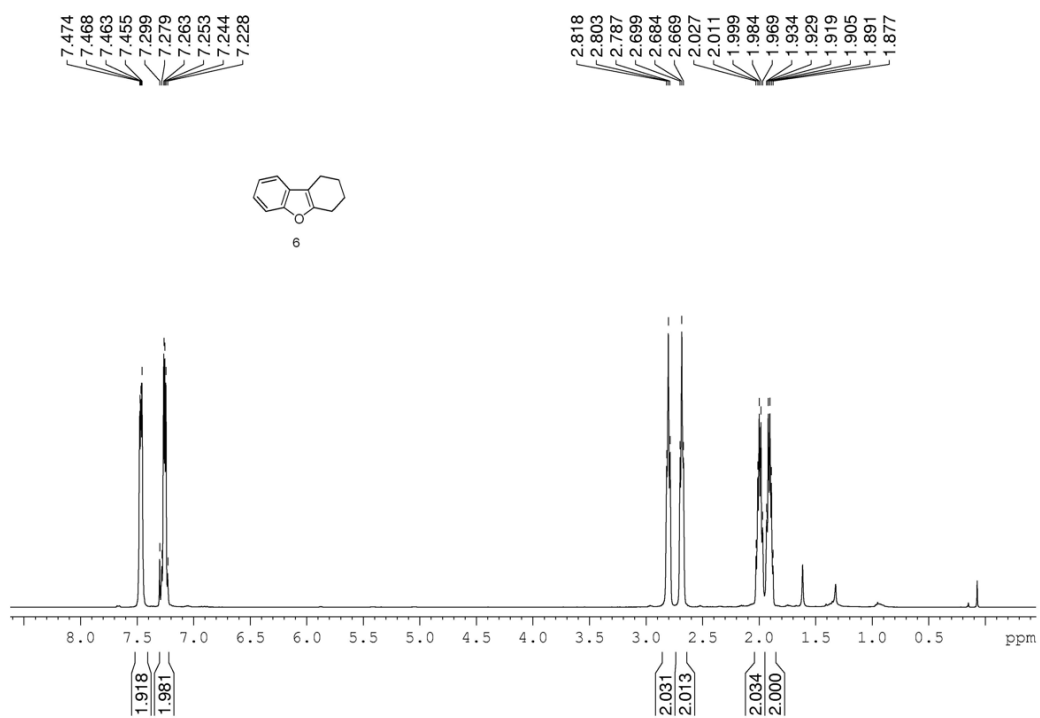




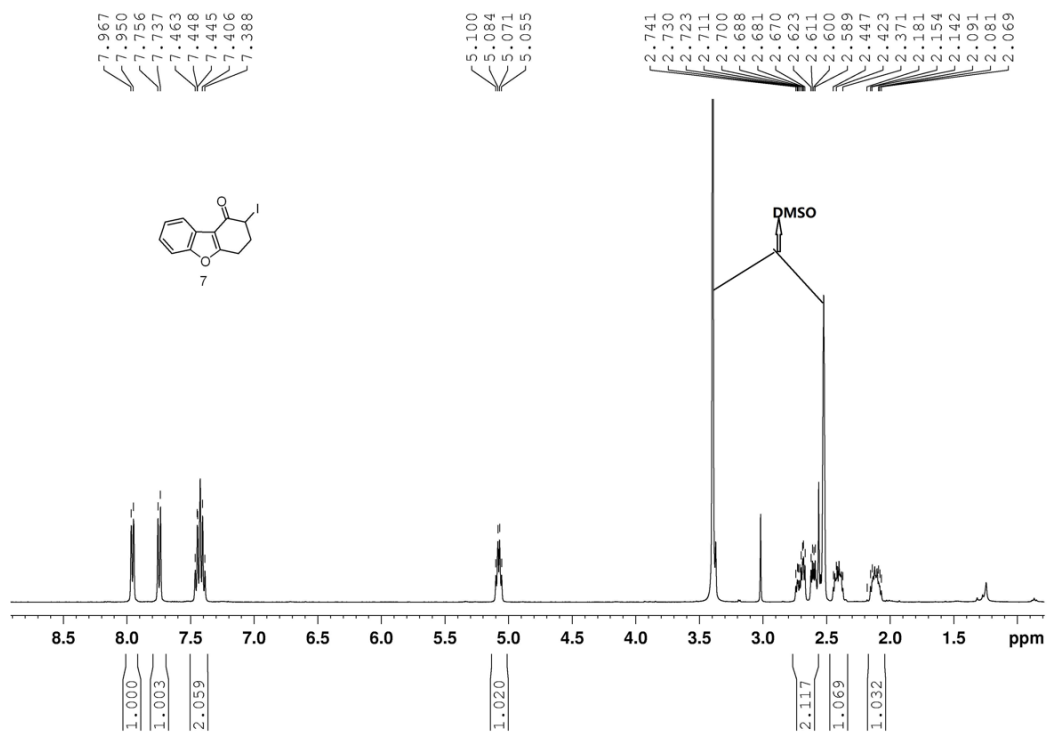
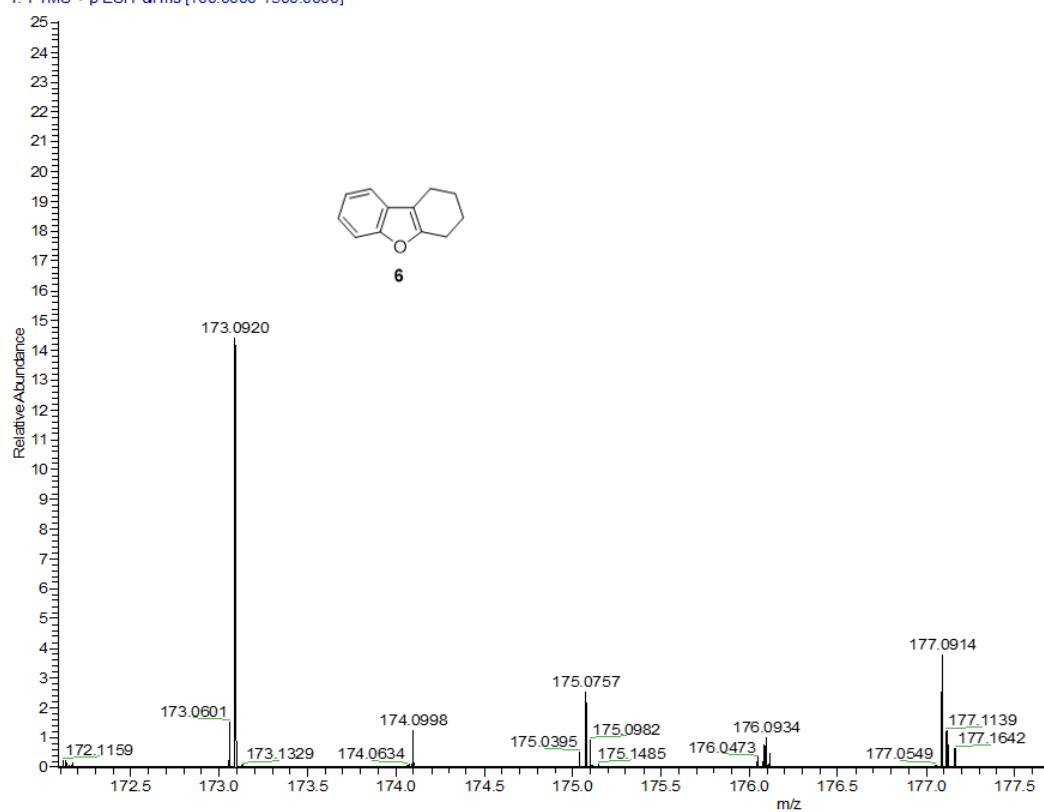


98#580 RT: 3.38 AV: 1 NL: 941E5  
T: FTMS → pESI Full ms [100.0000-1500.0000]

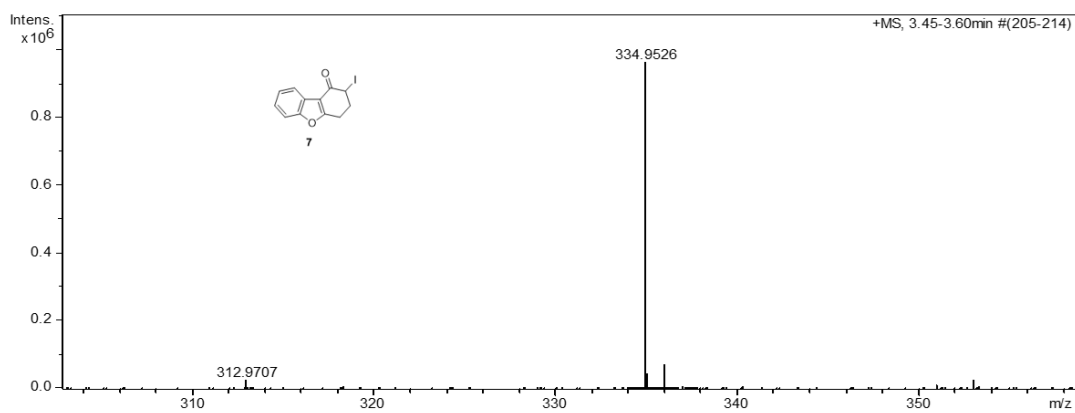
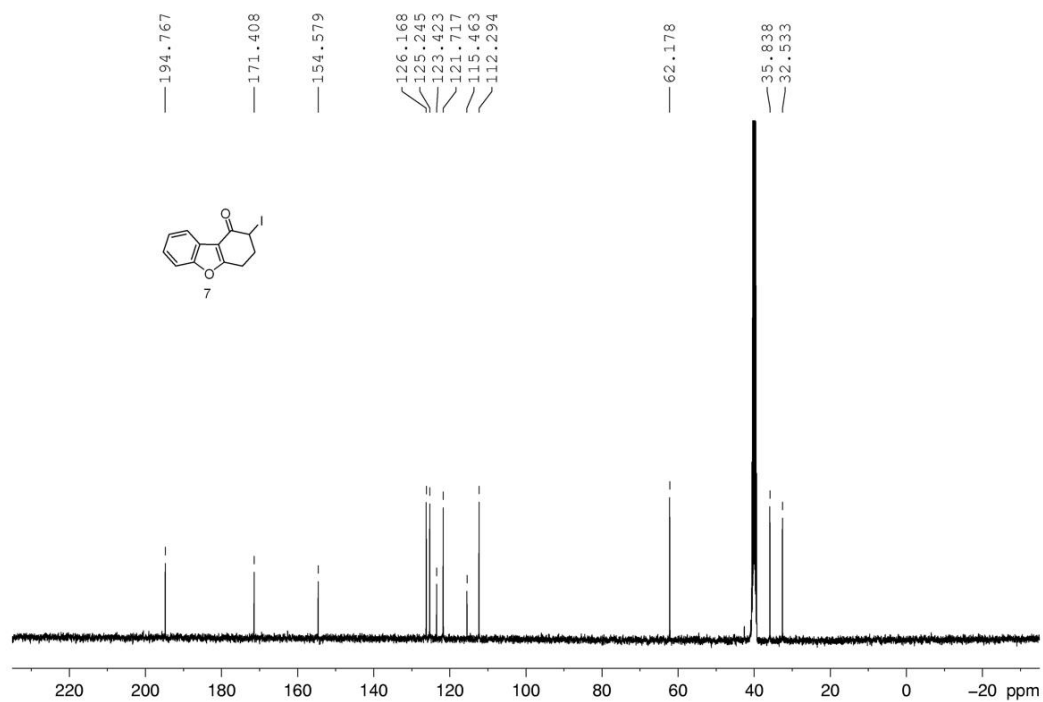


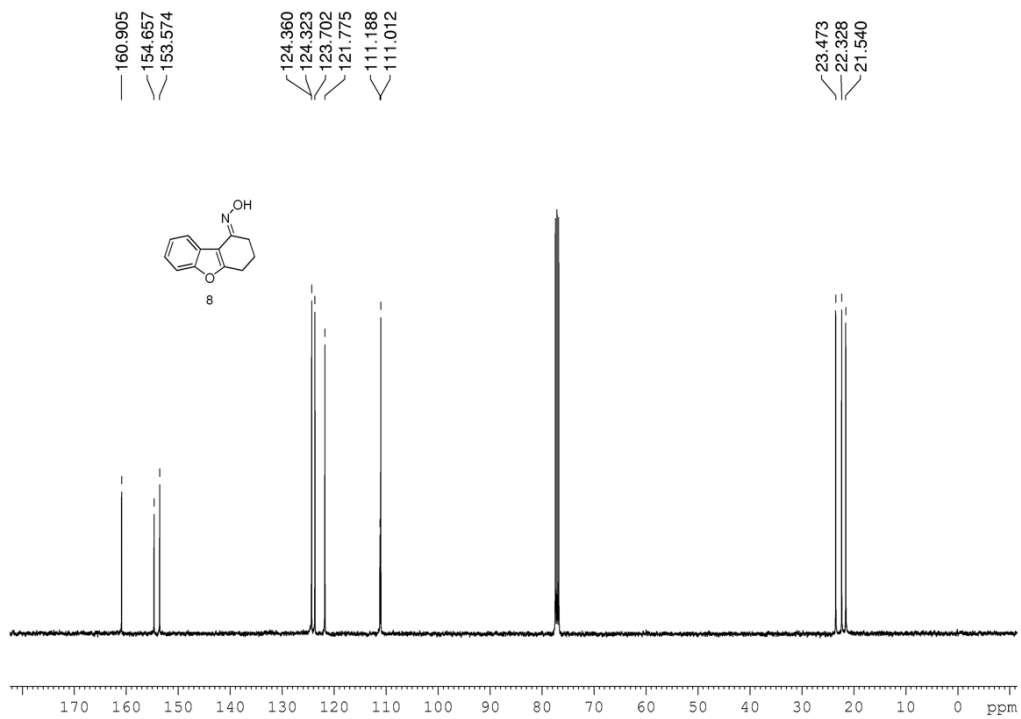
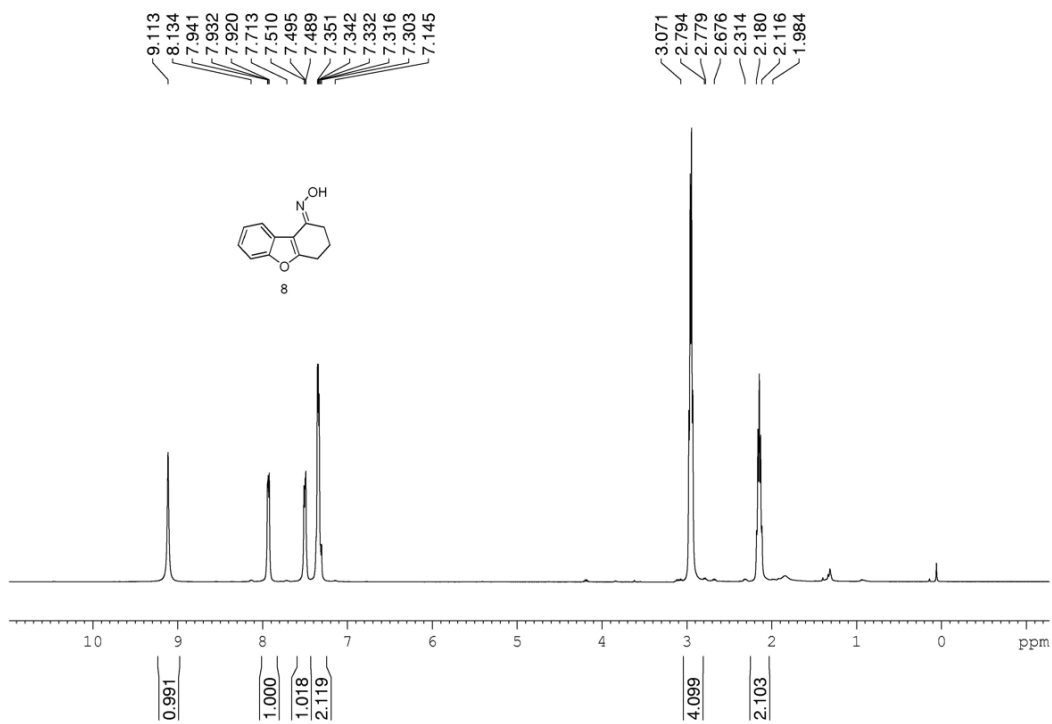


11\_230322130743 #153 RT: 1.16 AV: 1 NL: 5.10E6  
T: FTMS + p ESI Full ms [100.0000-1500.0000]









6 #733 RT: 4.33 AV: 1 NL: 7.14E7  
T: FTMS + pE SIFullms [100.0000-1500.0000]

