

## Supporting Information

### Catalyst-free synthesis of diversely substituted 6*H*-benzo[*c*]chromenes and 6*H*-benzo[*c*]chromen-6-ones in aqueous media under MWI

Yan He, Xinying Zhang,\* Liangyan Cui, Jianji Wang, and Xuesen Fan\*

*School of Chemistry and Environmental Science, Key Laboratory of Green Chemical Media and Reactions, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, P. R. China*

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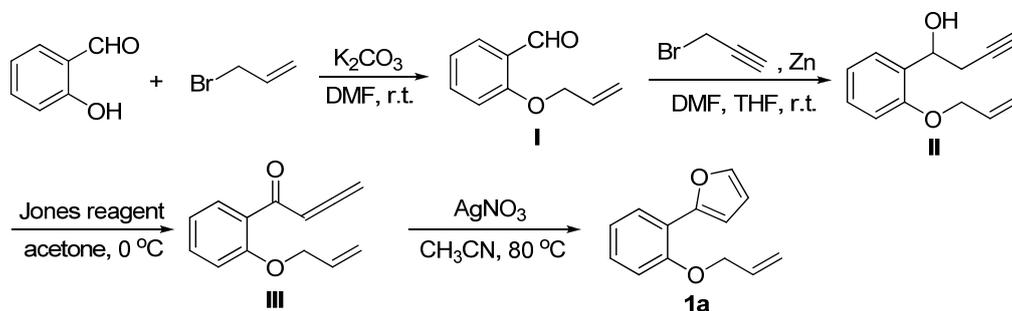
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## Experimental details and spectroscopic data

### 1. General experimental information

The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra were recorded at 400 MHz or 100 MHz, respectively. Chemical shifts were reported in ppm from tetramethylsilane (TMS) as internal standard in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  solutions. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. and coupling constants were given in Hz. High resolution mass spectra (HRMS) were performed on a time-of-flight (microTOF) mass spectrometer. The conversion of starting materials were monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm). MWI promoted reactions were performed in a commercial microwave reactor (XH-200A, Beijing Xianghu Science and Technology Development Co. Ltd, Beijing, China). The temperature of the reaction mixture was measured by an immersed platinum resistance thermometer.

### 2. Experimental procedures for the synthesis of 2-(2-(allyloxy)phenyl)furan (1a)



#### 2.1 Procedure for the preparation of 2-(allyloxy)benzaldehyde (I)

A mixture of 2-hydroxybenzaldehyde (5 mmol), 3-bromoprop-1-ene (7.5 mmol), and  $\text{K}_2\text{CO}_3$  (6 mmol) in DMF (20 mL) was stirred at ambient temperature for 1.5 h. Then, the reaction was quenched with aqueous  $\text{NH}_4\text{Cl}$  and the mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic phases were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/hexane (10%) to give 2-(allyloxy)benzaldehyde (I, 91%).

## 2.2 Procedure for the synthesis of 1-(2-(allyloxy)phenyl)but-3-yn-1-ol (**II**)

To a flask containing 2-(allyloxy)benzaldehyde (**I**, 3 mmol), THF (6 mL), DMF (6 mL) and propargyl bromide (6 mmol) were added activated zinc dust (9 mmol) portion-wise with stirring. The mixture was then stirred at room temperature. Upon completion, it was diluted with saturated aqueous NH<sub>4</sub>Cl (10 mL) and the excess zinc was filtered. The filtrate was concentrated and to the residue was added water. The aqueous phase was extracted with EtOAc (10 mL × 3). The combined organic phases were dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/hexane (10%) to give 1-(2-(allyloxy)phenyl)but-3-yn-1-ol (**II**, 86%).

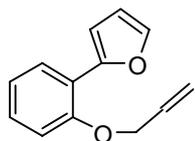
## 2.3 Procedure for the synthesis of 1-(2-(allyloxy)phenyl)buta-2,3-dien-1-one (**III**)

To a solution of 1-(2-(allyloxy)phenyl)but-3-yn-1-ol (**II**, 3 mmol) in acetone (30 mL) cooled to 0 °C was added Jones reagent (3.6 mmol) in a dropwise manner. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was quenched by addition of isopropanol. The mixture was filtered and the filtrate was concentrated under vacuum. The residue were purified by column chromatography on silica gel with EtOAc/hexane (10%) to give 1-(2-(allyloxy)phenyl)buta-2,3-dien-1-one (**III**, 90%).

## 2.4 Procedure for the synthesis of 2-(2-(allyloxy)phenyl)furan (**1a**)

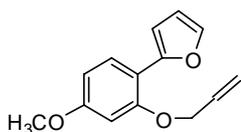
A mixture of 1-(2-(allyloxy)phenyl)buta-2,3-dien-1-one (**III**, 2.2 mmol) and AgNO<sub>3</sub> (0.44 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 80 °C for 1.5 h. Then, the mixture was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography on silica gel with EtOAc/hexane (5%) to give 2-(2-(allyloxy)phenyl)furan (**1a**, 88%).

**1b-1k** were prepared in a similar manner as that for **1a** from the corresponding starting materials.



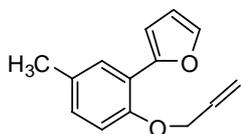
**2-(2-(Allyloxy)phenyl)furan (1a)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.65-4.67 (m, 2H), 5.35-5.52 (m, 2H), 6.14-6.21 (m, 1H), 6.54-6.55 (m, 1H), 6.96 (d,  $J = 8.4$  Hz, 1H), 7.05-7.09 (m, 2H), 7.22-7.27 (m, 1H), 7.51 (d, 1H,  $J = 1.2$  Hz), 7.94 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 69.2, 110.1, 111.8, 112.2, 118.1, 120.1, 120.9, 126.0, 128.0, 133.2, 141.1, 150.3, 154.3. MS:  $m/z$  201  $[\text{MH}]^+$ .



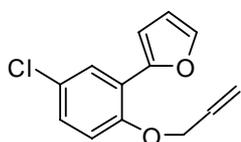
**2-(2-(Allyloxy)-4-methoxyphenyl)furan (1b)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.84 (s, 3H), 4.64 (d,  $J = 5.2$  Hz, 2H), 5.32-5.52 (m, 2H), 6.13-6.20 (m, 1H), 6.51-6.56 (m, 2H), 6.59-6.62 (m, 1H), 6.90-6.91 (m, 1H), 7.47 (s, 1H), 7.82 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.3, 69.3, 99.9, 105.1, 108.0, 111.6, 113.7, 118.1, 126.9, 133.1, 140.4, 150.4, 155.5, 159.8. MS:  $m/z$  231  $(\text{MH})^+$ .



**2-(2-(Allyloxy)-5-methylphenyl)furan (1c)**

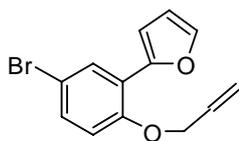
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.37 (s, 3H), 4.64 (d,  $J = 4.8$  Hz, 2H), 5.3-5.50 (m, 2H), 6.13-6.17 (m, 1H), 6.51-6.52 (m, 1H), 6.86 (d,  $J = 8.4$  Hz, 1H), 7.02-7.04 (m, 2H), 7.48 (s, 1H), 7.72 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 20.6, 69.4, 109.9, 111.7, 112.5, 117.8, 119.9, 126.5, 128.3, 130.1, 133.4, 140.9, 150.4, 152.3. MS:  $m/z$  215  $(\text{MH})^+$ .



**2-(2-(Allyloxy)-5-chlorophenyl)furan (1d)**

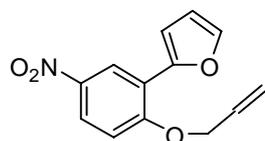
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.62 (d, 2H,  $J = 5.6$  Hz), 5.34-5.48 (m, 2H), 6.09-6.16 (m, 1H), 6.51-6.52 (m, 1H), 6.84 (d,  $J = 8.8$  Hz, 1H), 7.05 (d,  $J = 2.8$  Hz, 1H), 7.15 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 1H), 7.48 (s, 1H), 7.87 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 69.6, 111.0, 111.9, 113.5, 118.4, 121.5, 125.7, 126.1, 127.3, 132.7, 141.6, 148.9, 152.7. MS:  $m/z$  235  $(\text{MH})^+$ .

**2-(2-(Allyloxy)-5-bromophenyl)furan (1e)**



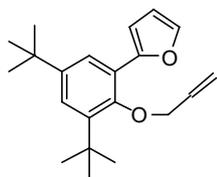
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.61 (d,  $J = 5.2$  Hz, 2H), 5.34-5.48 (m, 2H), 6.09-6.16 (m, 1H), 6.51-6.52 (m, 1H), 6.79 (d,  $J = 8.8$  Hz, 1H), 7.03-7.04 (m, 1H), 7.28 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.0$  Hz, 1H), 7.48 (s, 1H), 8.00 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 69.5, 111.1, 111.9, 113.4, 113.9, 118.4, 122.0, 128.5, 130.2, 132.7, 141.6, 148.8, 153.2. MS:  $m/z$  279 (MH) $^+$ .

**2-(2-(Allyloxy)-5-nitrophenyl)furan (1f)**



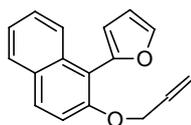
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.74 (d,  $J = 5.2$  Hz, 2H), 5.39-5.50 (m, 2H), 6.09-6.16 (m, 1H), 6.50-6.51 (m, 1H), 6.95 (d,  $J = 9.2$  Hz, 1H), 7.02-7.03 (m, 1H), 7.50 (s, 1H), 8.05 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 2.4$  Hz, 1H), 8.68 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 70.0, 111.7, 111.9, 112.0, 119.4, 120.6, 121.5, 123.3, 131.7, 141.6, 142.2, 147.9, 158.4. MS:  $m/z$  246 (MH) $^+$ .

**2-(3,5-di-tert-Butyl-2-(allyloxy)phenyl)furan (1g)**



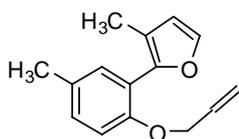
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.44 (s, 9H), 1.54 (s, 9H), 4.29-4.30 (m, 2H), 5.31-5.56 (m, 2H), 6.04-6.12 (m, 1H), 6.54-6.55 (m, 1H), 6.90 (d,  $J = 2.4$  Hz, 1H), 7.43 (s, 1H), 7.54 (s, 1H), 7.69 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 31.0, 31.6, 34.7, 35.5, 72.3, 108.4, 111.7, 116.1, 123.1, 124.0, 124.5, 134.1, 141.3, 142.6, 145.8, 151.6, 152.7. MS:  $m/z$  313 (MH) $^+$ .

**2-(2-(allyloxy)naphthalen-1-yl)furan (1h)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.65-4.66 (m, 2H), 5.22-5.39 (m, 2H), 5.97-6.05 (m, 1H), 6.63-6.66 (m, 2H), 7.31 (d,  $J = 9.2$  Hz, 1H), 7.40 (t,  $J = 7.6$  Hz, 1H), 7.48 (t,  $J = 7.6$  Hz, 1H), 7.67 (s, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 7.87 (d,  $J = 9.2$  Hz, 1H), 7.92 (d,  $J = 8.8$  Hz, 1H).  $^{13}\text{C}$

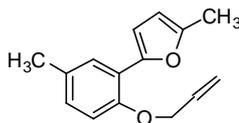
NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 70.4, 110.8, 111.4, 115.3, 115.5, 117.1, 123.9, 125.2, 126.9, 127.9, 129.2, 130.5, 133.3, 133.7, 142.1, 148.8, 154.6. MS:  $m/z$  251 (MH)<sup>+</sup>.



**2-(2-(Allyloxy)-5-methylphenyl)-3-methylfuran (1i)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.19 (s, 3H), 2.43 (s, 3H), 4.60 (d,  $J$  = 4.8 Hz, 2H), 5.31-5.48 (m, 2H), 6.06-6.14 (m, 1H), 6.44 (s, 1H), 6.96 (d,  $J$  = 8.4 Hz,

1H), 7.19 (d,  $J$  = 8.8 Hz, 1H), 7.35-7.36 (m, 1H), 7.53 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 11.5, 20.5, 69.6, 113.2, 114.0, 117.1, 117.7, 121.1, 129.7, 130.0, 131.3, 133.6, 141.3, 147.0, 153.8. MS:  $m/z$  229 (MH)<sup>+</sup>.



**2-(2-(Allyloxy)-5-methylphenyl)-4-methylfuran (1j)**

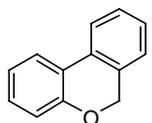
Yellow Liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.43 (s, 3H), 2.47 (s, 3H), 4.66 (d,  $J$  = 5.2 Hz, 2H), 5.37-5.55 (m, 2H), 6.17-6.27 (m, 2H), 6.88 (d,  $J$  = 8.4 Hz,

1H), 6.99 (d,  $J$  = 2.8 Hz, 1H), 7.04 (d,  $J$  = 8.4 Hz, 1H), 7.77 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 13.7, 20.7, 69.4, 107.9, 111.1, 112.4, 117.7, 120.2, 126.1, 127.8, 130.1, 133.6, 148.8, 150.8, 152.2. MS:  $m/z$  229 (MH)<sup>+</sup>.

### 3. Typical procedure for the preparation of 6H-benzo[c]chromene (2a)

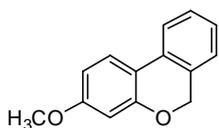
2-(2-(Allyloxy)phenyl)furan (**1a**, 0.5 mmol) was put into a 10 mL reaction vessel equipped with a magnetic stirring bar. To this was added H<sub>2</sub>O (5 mL) and the vessel was sealed and put into the cavity of the microwave synthesis apparatus and irradiated at 300 W at 150 °C for 15 × 20 min at intervals. Between two irradiations, the reaction temperature was allowed to cool to 60 °C. The internal pressure within the vessel was not measured. Upon completion of the reaction, the vessel was cooled to room temperature and extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column

chromatography on silica gel eluenting with ethyl acetate/hexane (5-10%) to give 6*H*-benzo[*c*]chromene (**2a**). **2b-2j** were obtained in a similar manner.



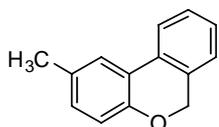
**6*H*-Benzo[*c*]chromene (2a)<sup>1</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.14 (s, 2H), 7.02 (d, 1H, *J* = 8.0 Hz), 7.08 (t, 1H, *J* = 7.6 Hz), 7.17 (d, 1H, *J* = 7.2 Hz), 7.24-7.32 (m, 2H), 7.39 (t, 1H, *J* = 7.6 Hz), 7.72 (d, 1H, *J* = 8.0 Hz), 7.75 (d, 1H, *J* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 68.5, 117.4, 122.0, 122.1, 122.9, 123.3, 124.7, 127.7, 128.4, 129.4, 130.1, 131.4, 154.8. MS: *m/z* 183 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>11</sub>O: 183.0811[M+H], found: 183.0822.



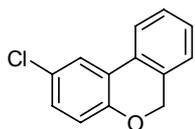
**3-Methoxy-6*H*-Benzo[*c*]chromene (2b)<sup>2</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.83 (s, 3H), 5.12 (s, 2H), 6.57 (d, 1H, *J* = 2.0 Hz), 6.64 (dd, 1H, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2.0 Hz), 7.13 (d, 1H, *J* = 7.2 Hz), 7.23 (t, 1H, *J* = 8.4 Hz), 7.36 (t, 1H, *J* = 8.4 Hz), 7.62 (d, 1H, *J* = 8.4 Hz), 7.65 (d, 1H, *J* = 8.4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 55.4, 68.7, 102.3, 108.8, 115.9, 121.2, 124.2, 124.6, 126.7, 128.4, 130.2, 130.3, 156.0, 160.9. MS: *m/z* 213 (MH)<sup>+</sup>. HRMS calcd for C<sub>14</sub>H<sub>13</sub>O<sub>2</sub>: 213.0916[M+H], found: 213.0913.



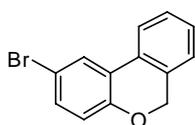
**2-Methyl-6*H*-benzo[*c*]chromene (2c)<sup>2</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.37 (s, 3H), 5.09 (s, 2H), 6.90 (d, 1H, *J* = 8.0 Hz), 7.05 (d, 1H, *J* = 8.0 Hz), 7.15 (d, 1H, *J* = 7.2 Hz), 7.28 (d, 1H, *J* = 7.6 Hz), 7.37 (t, 1H, *J* = 8.0 Hz), 7.54 (s, 1H), 7.70 (d, 1H, *J* = 7.6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 20.9, 68.5, 117.0, 121.9, 122.6, 123.6, 124.6, 127.5, 128.3, 130.0, 130.2, 131.31, 131.6, 152.6. MS: *m/z* 197 (MH)<sup>+</sup>. HRMS calcd for C<sub>14</sub>H<sub>13</sub>O: 197.0967[M+H], found: 197.0968.



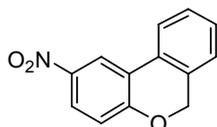
**2-Chloro-6H-benzo[c]chromene (2d)<sup>2</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.11 (s, 3H), 6.93 (d, 1H, *J* = 8.8 Hz), 7.15-7.20 (m, 2H), 7.32 (t, 1H, *J* = 7.2 Hz), 7.39 (t, 1H, *J* = 7.6 Hz), 7.65 (d, 1H, *J* = 7.6 Hz), 7.68 (d, 1H, *J* = 2.4 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 68.5, 118.7, 122.1, 123.1, 124.3, 124.7, 127.1, 128.3, 128.6, 129.1, 131.3, 153.3. MS: *m/z* 217 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>10</sub>ClO: 217.0421[M+H], found: 217.0426.



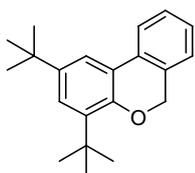
**2-Bromo-6H-benzo[c]chromene (2e)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.11 (s, 3H), 6.88 (d, 1H, *J* = 8.4 Hz), 7.15 (d, 1H, *J* = 7.2 Hz), 7.31-7.33 (m, 2H), 7.39 (t, 1H, *J* = 8.0 Hz), 7.64 (d, 1H, *J* = 7.6 Hz), 7.83 (d, 1H, *J* = 2.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 68.5, 114.5, 119.2, 122.1, 124.7, 124.9, 126.1, 128.3, 128.6, 128.9, 131.2, 132.0, 153.8. MS: *m/z* 261 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>10</sub>BrO: 260.9916[M+H], found: 260.9901.



**2-Nitro-6H-benzo[c]chromene (2f)<sup>3</sup>**

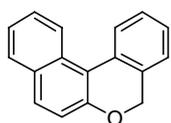
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 5.25 (s, 2H), 7.03 (d, 1H, *J* = 9.2 Hz), 7.18 (d, 1H, *J* = 7.2 Hz), 7.39 (t, 1H, *J* = 7.2 Hz), 7.44 (t, 1H, *J* = 7.2 Hz), 7.76 (d, 1H, *J* = 7.6 Hz), 8.10 (dd, 1H, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz), 8.61 (d, 1H, *J* = 2.8 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 68.8, 118.0, 119.2, 122.4, 123.0, 124.8, 124.9, 127.9, 129.0, 129.1, 130.4, 142.7, 159.8. MS: *m/z* 228 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>10</sub>NO<sub>3</sub>: 228.0661[M+H], found: 228.0668.



**2,4-di-tert-Butyl-6H-benzo[c]chromene (2g)**

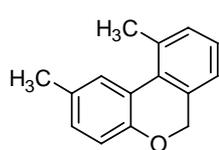
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.38 (s, 9H), 1.44 (s, 9H), 5.05 (s, 2H), 7.18 (d, 1H, *J* = 8.0 Hz), 7.28 (d, 1H, *J* = 7.6 Hz), 7.32 (d, 1H, *J* = 2.0 Hz), 7.38 (t, 1H, *J* = 8.0

Hz), 7.64 (d, 1H,  $J = 2.0$  Hz), 7.73 (d, 1H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 29.8, 31.6, 34.6, 34.8, 67.6, 118.1, 122.4, 123.0, 124.0, 124.3, 127.1, 128.2, 131.3, 132.0, 138.1, 143.7, 151.3. MS:  $m/z$  295 (MH) $^+$ . HRMS calcd for  $\text{C}_{21}\text{H}_{27}\text{O}$ : 295.2063[M+H], found: 295.2075.



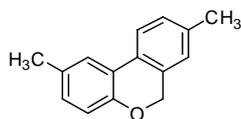
**5H-dibenzo[*c,f*]chromene (2h) $^4$**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.09 (s, 2H), 7.30 (d, 1H,  $J = 8.4$  Hz), 7.31-7.40 (m, 2H), 7.44-7.51 (m, 2H), 7.57-7.61 (m, 1H), 7.79 (d, 1H,  $J = 8.8$  Hz), 7.89 (d, 1H,  $J = 8.0$  Hz), 8.08 (d, 1H,  $J = 8.0$  Hz), 8.60 (d, 1H,  $J = 8.0$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 69.3, 117.7, 118.3, 123.9, 124.8, 125.3, 126.3, 126.9, 127.1, 128.2, 128.9, 130.1, 130.2, 130.3, 130.7, 132.9, 154.2. MS:  $m/z$  233 (MH) $^+$ . HRMS calcd for  $\text{C}_{17}\text{H}_{13}\text{O}$ : 233.0967[M+H], found: 233.0981.



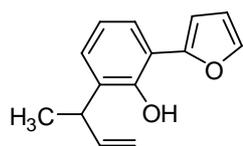
**2,10-Dimethyl-6H-benzo[*c*]chromene (2i)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.41 (s, 3H), 2.68 (s, 3H), 4.96 (s, 2H), 6.99 (d, 1H,  $J = 8.4$  Hz), 7.07 (d, 2H,  $J = 6.8$  Hz), 7.21-7.26 (m, 2H), 7.61 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 21.2, 23.1, 69.8, 116.9, 122.7, 124.3, 127.0, 128.4, 129.2, 129.4, 30.5, 132.1, 134.1, 134.6, 154.3. MS:  $m/z$  211 (MH) $^+$ . HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{O}$ : 211.1124 [M+H], found: 211.1135.



**2,8-Dimethyl-6H-benzo[*c*]chromene (2j)**

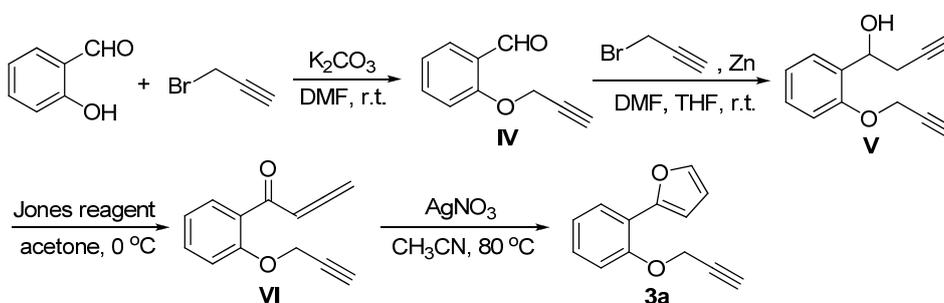
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.18 (s, 3H), 2.38 (s, 3H), 5.07 (s, 2H), 6.91 (d, 1H,  $J = 8.0$  Hz), 6.97 (s, 1H), 7.03 (d, 1H,  $J = 8.0$  Hz), 7.19 (d, 1H,  $J = 8.0$  Hz), 7.53 (s, 1H), 7.60 (d, 1H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 20.9, 21.2, 68.5, 117.0, 121.9, 122.7, 123.4, 125.3, 127.5, 129.0, 129.6, 131.2, 131.6, 137.4, 152.4. MS:  $m/z$  211 (MH) $^+$ . HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{O}$ : 211.1124[M+H], found: 211.1128.



### 2-(But-3-en-2-yl)-6-(furan-2-yl)phenol (I)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.40 (d, 3H,  $J = 6.8$  Hz), 3.92-3.95 (m, 1H), 5.11-5.18 (m, 2H), 6.07-6.14 (m, 1H), 6.53-6.54 (m, 1H), 6.70 (d, 1H,  $J = 3.6$  Hz), 6.92 (t, 1H,  $J = 7.6$  Hz), 7.10-7.12 (m, 1H), 7.18 (s, 1H), 7.42-7.44 (m, 1H), 7.51 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 19.0, 36.5, 106.8, 111.7, 113.6, 116.6, 120.4, 124.4, 127.5, 132.7, 141.1, 142.4, 150.1, 152.8. MS:  $m/z$  215 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{15}\text{O}_2$ : 215.1073[M+H], found: 215.1066.

## 4 Experimental procedures for the synthesis of 2-(2-(prop-2-ynyloxy)phenyl)furan (3a)



### 4.1 Procedure for the preparation of 2-(prop-2-ynyloxy)benzaldehyde (IV)

A mixture of 2-hydroxybenzaldehyde (5 mmol), propargyl bromide (7.5 mmol), and  $\text{K}_2\text{CO}_3$  (6 mmol) in DMF (20 mL) was stirred at ambient temperature for 2 h. The reaction was quenched with aqueous  $\text{NH}_4\text{Cl}$  and the mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic phases were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/hexane (10%) to give 2-(prop-2-ynyloxy)benzaldehyde (IV, 91%).

### 4.2 Procedure for the synthesis of 1-(2-(prop-2-ynyloxy)phenyl)but-3-yn-1-ol (V)

To a flask containing 2-(prop-2-ynyloxy)benzaldehyde (IV, 3 mmol), THF (6 mL), DMF (6 mL) and propargyl bromide (6 mmol) were added activated zinc dust (9 mmol) portion-wise with stirring.

The mixture was then stirred at room temperature. Upon completion, it was diluted with saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL) and the excess zinc was filtered. The filtrate was concentrated and to the residue was added water. The aqueous phase was extracted with EtOAc (10 mL  $\times$  3). The combined organic phases were dried with anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by column chromatography on silica gel with EtOAc/hexane (10%) to give 1-(2-(prop-2-ynyloxy)phenyl)but-3-yn-1-ol (**V**, 89%).

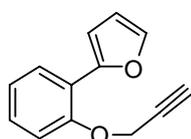
#### 4.3 Procedure for the synthesis of 1-(2-(prop-2-ynyloxy)phenyl)buta-2,3-dien-1-one (**VI**)

To a solution of 1-(2-(prop-2-ynyloxy)phenyl)but-3-yn-1-ol (**V**, 3 mmol) in acetone (30 mL) cooled to 0 °C was added Jones reagent (3.6 mmol) in a dropwise manner. Upon complete consumption of the starting material as monitored by TLC, the reaction mixture was quenched by addition of isopropanol. The mixture was filtered and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel with EtOAc/hexane (10%) to give 1-(2-(prop-2-ynyloxy)phenyl)buta-2,3-dien-1-one (**VI**, 87%).

#### 4.4 Procedure for the synthesis of 2-(2-(prop-2-ynyloxy)phenyl)furan (**3a**)

A mixture of 1-(2-(prop-2-ynyloxy)phenyl)buta-2,3-dien-1-one (**VI**, 2 mmol) and  $\text{AgNO}_3$  (0.4 mmol) in  $\text{CH}_3\text{CN}$  (10 mL) was stirred at 80 °C for 1.5 h. Then, the mixture was cooled to room temperature and concentrated under vacuum. The residue was purified by column chromatography on silica gel with EtOAc/hexane (5%) to give 2-(2-(prop-2-ynyloxy)phenyl)furan (**3a**, 90%).

**3b-3j** were prepared in a similar manner from the corresponding starting materials.

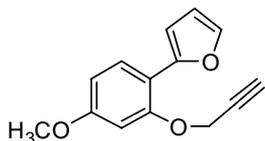


**2-(2-(Prop-2-ynyloxy)phenyl)furan (3a)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.58 (t,  $J$  = 2.4 Hz, 1H), 4.82 (d,  $J$  = 2.4 Hz, 2H),

6.53-6.54 (m, 1H), 7.05-7.12 (m, 3H), 7.24-7.28 (m, 1H), 7.05 (s, 1H), 7.92 (dd,  $J_1 = 7.6$  Hz,  $J_2 = 1.2$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 56.1, 75.7, 78.4, 110.2, 111.8, 112.6, 120.5, 121.7, 126.2, 127.8, 141.2, 149.9, 153.3. MS:  $m/z$  199 (MH) $^+$ .

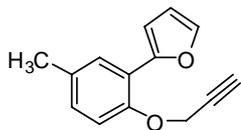
**2-(4-Methoxy-2-(prop-2-ynoxy)phenyl)furan (3b)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.58 (t,  $J = 2.4$  Hz, 1H), 3.82 (s, 3H), 4.77 (d,  $J = 2.0$  Hz, 2H), 6.48-6.49 (m, 1H), 6.60-6.63 (m, 2H), 6.86 (d,  $J = 3.2$  Hz,

1H), 7.43 (s, 1H), 7.78 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.4, 56.2, 75.9, 78.3, 100.1, 105.9, 108.2, 111.6, 113.9, 127.0, 140.5, 150.0, 154.4, 159.6. MS:  $m/z$  229 (MH) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_3$ : 229.0865[M+H], found: 229.0867.

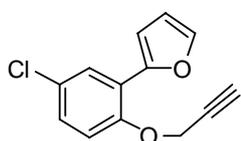
**2-(5-Methyl-2-(prop-2-ynoxy)phenyl)furan (3c)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.39 (s, 3H), 2.57 (t,  $J = 2.4$  Hz, 1H), 4.78 (d,  $J = 2.0$  Hz, 2H), 6.54-6.55 (m, 1H), 6.97 (d,  $J = 8.4$  Hz, 1H), 7.05-7.08 (m, 2H), 7.51 (s, 1H), 7.74 (s,

1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 20.7, 56.3, 75.6, 78.7, 110.1, 111.8, 112.8, 120.3, 126.7, 128.3, 131.0, 141.1, 150.0, 151.3. MS:  $m/z$  213 (MH) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_2$ : 213.0916[M+H], found: 213.0922.

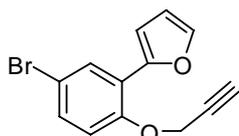
**2-(5-Chloro-2-(prop-2-ynoxy)phenyl)furan (3d)**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.57 (t,  $J = 2.0$  Hz, 1H), 4.77 (d,  $J = 2.0$  Hz, 2H), 6.51-6.52 (m, 1H), 6.96 (d,  $J = 8.8$  Hz, 1H), 7.04 (d,  $J = 3.2$  Hz, 1H), 7.17

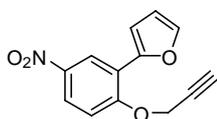
(dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 1H), 7.48 (s, 1H), 7.86 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 56.4, 76.1, 78.0, 111.2, 111.9, 113.8, 121.9, 125.8, 126.9, 127.2, 141.7, 148.6, 151.6. MS:  $m/z$  233 (MH) $^+$ . HRMS calcd for  $\text{C}_{13}\text{H}_{10}\text{ClO}_2$ : 233.0370[M+H], found: 233.0368.

**2-(5-Bromo-2-(prop-2-ynyloxy)phenyl)furan (3e)**



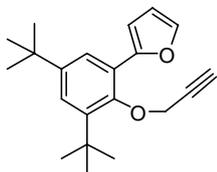
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.58 (t,  $J = 2.4$  Hz, 1H), 4.77 (d,  $J = 2.4$  Hz, 2H), 6.51-6.52 (m, 1H), 6.90 (d,  $J = 8.8$  Hz, 1H), 7.03 (d,  $J = 3.2$  Hz, 1H), 7.31 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 1H), 7.48 (s, 1H), 8.00 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 56.3, 76.2, 77.9, 111.3, 111.9, 114.2, 114.3, 122.3, 128.7, 130.1, 141.8, 148.4, 152.1. MS:  $m/z$  277 (MH) $^+$ . HRMS calcd for  $\text{C}_{13}\text{H}_{10}\text{BrO}_2$ : 276.9865[M+H], found: 276.9851.

**2-(5-Nitro-2-(prop-2-ynyloxy)phenyl)furan (3f)**



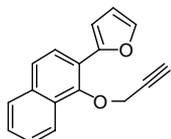
$^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 2.63 (t,  $J = 2.4$  Hz, 1H), 4.94 (d,  $J = 2.4$  Hz, 2H), 6.53-6.54 (m, 1H), 7.07 (d,  $J = 3.2$  Hz, 1H), 7.13 (d,  $J = 8.8$  Hz, 1H), 7.54 (s, 1H), 8.14 (dd,  $J_1 = 9.2$  Hz,  $J_2 = 2.8$  Hz, 1H), 8.76 (d,  $J = 2.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 56.7, 77.3, 112.00, 112.04, 112.2, 121.1, 121.7, 123.2, 142.3, 142.2, 147.6, 157.2. MS:  $m/z$  244 (MH) $^+$ .

**2-(3,5-di-tert-Butyl-2-(prop-2-ynyloxy)phenyl)furan (3g)**

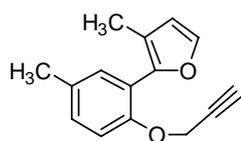


Yellow Liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.45 (s, 9H), 1.60 (s, 9H), 2.55 (t,  $J = 2.0$  Hz, 1H), 4.43 (s, 2H), 6.60-6.61 (m, 1H), 7.03 (d,  $J = 2.8$  Hz, 1H), 7.45 (s, 1H), 7.56 (s, 1H), 7.70 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 31.2, 31.6, 34.7, 35.5, 59.8, 74.9, 79.4, 109.2, 111.9, 123.2, 124.1, 124.4, 141.6, 142.8, 146.5, 151.0, 151.9. MS:  $m/z$  311 (MH) $^+$ .

**2-(3-(Prop-2-ynyloxy)naphthalen-2-yl)furan (3h)**

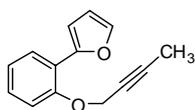


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.52 (s, 1H), 4.77 (s, 2H), 6.66 (s, 1H), 6.70 (d,  $J = 2.8$  Hz, 1H), 7.40-7.51 (m, 3H), 7.69 (s, 1H), 7.84 (d,  $J = 8.0$  Hz, 1H), 7.91 (d,  $J = 9.2$  Hz, 1H), 7.95 (d,  $J = 8.4$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 57.6, 75.8, 78.8, 110.9, 111.7, 115.7, 116.3, 124.4, 125.4, 127.0, 128.0, 129.7, 130.5, 133.6, 142.3, 148.4, 153.6. MS:  $m/z$  249 (MH) $^+$ .



**3-Methyl-2-(5-methyl-2-(prop-2-ynoxy)phenyl)furan (3i)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.18 (s, 3H), 2.41 (s, 3H), 2.54 (t,  $J = 2.0$  Hz, 1H), 4.71 (t,  $J = 2.0$  Hz, 2H), 6.24 (s, 1H), 7.08 (d,  $J = 8.4$  Hz, 1H), 7.20 (d,  $J = 8.4$  Hz, 1H), 7.35 (s, 1H), 7.51 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 11.5, 20.5, 56.4, 75.6, 78.9, 113.7, 114.1, 118.0, 121.4, 129.7, 131.0, 131.3, 141.5, 146.5, 152.6. MS:  $m/z$  227 ( $\text{MH}$ ) $^+$ .

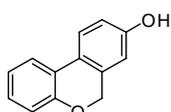


**2-(2-(But-2-ynoxy)phenyl)furan (3j)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.91 (d,  $J = 2.0$  Hz, 3H), 4.81 (t,  $J = 2.0$  Hz, 2H), 6.56-6.58 (m, 1H), 7.11-7.14 (m, 3H), 7.26-7.36 (m, 1H), 7.52 (s, 1H), 7.94-7.97 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.7, 56.7, 74.1, 83.9, 110.2, 111.8, 112.6, 120.4, 121.4, 126.1, 127.9, 141.2, 150.1, 153.6. MS:  $m/z$  213 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_2$ : 213.0916[M+H], found: 213.0918.

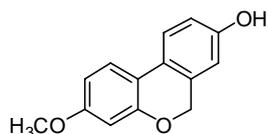
**5. Typical procedure for the preparation of 6H-benzo[c]chromen-8-ol (4a)**

2-(2-(Prop-2-ynoxy)phenyl)furan (**3a**, 0.5 mmol) was put into a 10 mL reaction vessel equipped with a magnetic stirring bar. To this was added  $\text{H}_2\text{O}$  (4 mL) and ethanol (1 mL) and the vessel was sealed and put into the cavity of the microwave synthesis apparatus and irradiated at 300 W at 150 °C for 18  $\times$  20 min at intervals. Between two irradiations, the reaction temperature was allowed to cool to 60 °C. The internal pressure within the tube was not measured. Upon completion of the reaction, the vessel was cooled to room temperature and extracted with ethyl acetate (5 mL  $\times$  3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (10%) to give 6H-benzo[c]chromen-8-ol (**4a**). **4b-4j** were obtained in a similar manner.



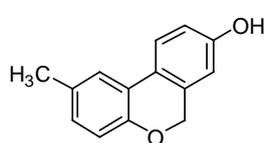
**6H-Benzo[c]chromen-8-ol (4a)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.02 (s, 1H), 5.06 (s, 2H), 6.64 (s, 1H), 6.85 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 2.0$  Hz), 6.97 (d, 1H,  $J = 7.6$  Hz), 7.05 (t, 1H,  $J = 6.8$  Hz), 7.19 (t, 1H,  $J = 6.8$  Hz), 7.58 (d, 1H,  $J = 8.4$  Hz), 7.64 (d, 1H,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 68.2, 111.5, 115.4, 117.2, 122.2, 122.6, 122.9, 123.1, 123.7, 128.4, 133.3, 153.9, 155.3. MS:  $m/z$  199 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{13}\text{H}_{11}\text{O}_2$ : 199.0760 [ $\text{M}+\text{H}$ ], found: 199.0769.



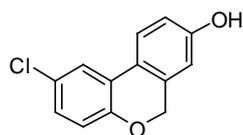
**3-Methoxy-6H-benzo[c]chromen-8-ol (4b)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.81 (s, 3H), 5.04 (s, 2H), 5.11 (s, 1H), 6.55 (d, 1H,  $J = 2.4$  Hz), 6.61-6.64 (m, 2H), 6.81 (dd, 1H,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz), 7.48 (d, 1H,  $J = 8.4$  Hz), 7.54 (d, 1H,  $J = 8.4$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 55.4, 68.5, 102.4, 108.7, 111.5, 115.4, 115.9, 122.8, 123.4, 132.0, 154.6, 155.0, 160.1. MS:  $m/z$  229 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_3$ : 229.0865 [ $\text{M}+\text{H}$ ], found: 229.0861.



**2-Methyl-6H-benzo[c]chromen-8-ol (4c)**

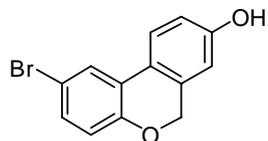
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.35 (s, 3H), 5.02 (s, 2H), 5.04 (s, 1H), 6.63 (s, 1H), 6.84-6.88 (m, 2H), 6.98 (d, 1H,  $J = 8.0$  Hz), 7.45 (s, 1H), 7.57 (d, 1H,  $J = 8.8$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 20.9, 68.4, 111.6, 115.4, 116.9, 122.7, 123.1, 123.6, 129.1, 131.6, 133.3, 151.6, 155.4. MS:  $m/z$  213 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_2$ : 213.0916 [ $\text{M}+\text{H}$ ], found: 213.0929.



**2-Chloro-6H-benzo[c]chromen-8-ol (4d)**

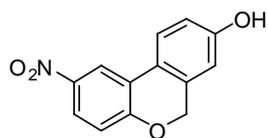
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 5.02 (s, 2H), 5.67 (s, 1H), 6.61 (d, 1H,  $J = 1.6$  Hz), 6.83 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 2.4$  Hz), 6.89 (d, 1H,  $J = 8.8$  Hz), 7.11 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 2.4$  Hz), 7.50 (d, 1H,  $J = 8.4$  Hz), 7.57 (d, 1H,  $J = 2.4$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 68.3,

111.6, 115.6, 118.5, 121.9, 122.5, 123.9, 124.4, 127.2, 128.0, 133.2, 152.3, 155.9. MS:  $m/z$  233 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>10</sub>ClO<sub>2</sub>: 233.0370 [M+H], found: 233.0362.



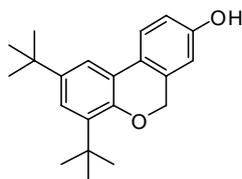
**2-Bromo-6H-benzo[c]chromen-8-ol (4e)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 4.99 (s, 2H), 6.49 (s, 1H), 6.58 (s, 1H), 6.80-6.84 (m, 2H), 7.24 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 1.6$  Hz), 7.45 (d, 1H,  $J = 8.8$  Hz), 7.69 (d, 1H,  $J = 1.6$  Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 68.3, 111.7, 114.7, 115.7, 119.0, 121.6, 123.9, 125.0, 125.4, 130.9, 133.1, 152.7, 156.1. MS:  $m/z$  277 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>10</sub>BrO<sub>2</sub>: 276.9865 [M+H], found: 276.9866.



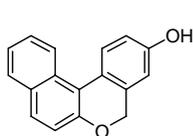
**2-Nitro-6H-benzo[c]chromen-8-ol (4f)**

<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 5.20 (s, 2H), 6.67 (s, 1H), 6.82 (dd, 1H,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz), 7.08 (d, 1H,  $J = 8.8$  Hz), 7.77 (d, 1H,  $J = 8.4$  Hz), 8.00 (dd, 1H,  $J_1 = 8.8$  Hz,  $J_2 = 1.6$  Hz), 8.49 (d, 1H,  $J = 2.0$  Hz), 9.93 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 68.5, 111.9, 116.3, 118.2, 118.3, 118.6, 123.8, 124.0, 124.9, 132.8, 142.7, 159.0, 159.1. MS:  $m/z$  244 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>10</sub>NO<sub>4</sub>: 244.0611 [M+H], found: 244.0621.



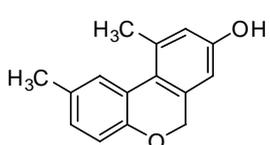
**2,4-Di-tert-butyl-6H-benzo[c]chromen-8-ol (4g)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 1.37 (s, 9H), 1.43 (s, 9H), 4.96-4.98 (m, 2H), 6.66 (s, 1H), 6.84 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 2.0$  Hz), 7.26 (s, 1H), 7.55 (d, 1H,  $J = 2.0$  Hz), 7.61 (d, 1H,  $J = 8.4$  Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 29.9, 31.6, 34.6, 34.8, 67.4, 111.3, 115.2, 117.5, 123.0, 123.1, 124.0, 124.3, 133.8, 138.0, 143.8, 150.4, 154.9. MS:  $m/z$  311 (MH)<sup>+</sup>. HRMS calcd for C<sub>21</sub>H<sub>27</sub>O<sub>2</sub>: 311.2012 [M+H], found: 311.2016.



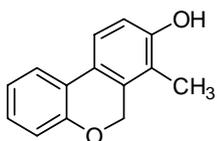
**5H-Dibenzo[*c,f*]chromen-3-ol (4h)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 4.99 (s, 2H), 5.24 (s, 1H), 6.80 (d, 1H,  $J = 2.0$  Hz), 6.92 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 2.0$  Hz), 7.24 (d, 1H,  $J = 8.8$  Hz), 7.41 (t, 1H,  $J = 7.6$  Hz), 7.52 (t, 1H,  $J = 8.0$  Hz), 7.71 (d, 1H,  $J = 8.8$  Hz), 7.85 (d, 1H,  $J = 8.0$  Hz), 7.91 (d, 1H,  $J = 8.4$  Hz), 8.49 (d, 1H,  $J = 8.4$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 69.1, 112.3, 115.0, 117.7, 118.1, 123.2, 123.8, 124.7, 126.6, 127.7, 128.8, 129.1, 130.0, 130.7, 134.9, 153.2, 154.8. MS:  $m/z$  249 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{17}\text{H}_{13}\text{O}_2$ : 249.0916 [ $\text{M}+\text{H}$ ], found: 249.0928.



**2,10-Dimethyl-6H-benzo[*c*]chromen-8-ol (4i)**

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 2.29 (s, 3H), 2.50 (s, 3H), 4.80 (s, 2H), 6.57 (s, 1H), 6.67 (s, 1H), 6.86 (d, 1H,  $J = 8.0$  Hz), 6.94 (d, 1H,  $J = 8.4$  Hz), 7.48 (s, 1H), 9.59 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 21.2, 23.2, 69.4, 110.4, 116.9, 118.9, 120.4, 124.6, 127.7, 128.1, 130.5, 135.8, 136.5, 153.4, 156.8. MS:  $m/z$  227 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_2$ : 227.1073 [ $\text{M}+\text{H}$ ], found: 227.1078.



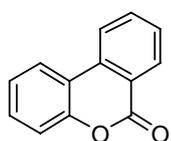
**7-Methyl-6H-benzo[*c*]chromen-8-ol (4j)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 2.19 (s, 3H), 4.99 (s, 1H), 5.16 (s, 2H), 6.79 (d, 1H,  $J = 8.0$  Hz), 6.97 (d, 1H,  $J = 8.0$  Hz), 7.02 (t, 1H,  $J = 8.0$  Hz), 7.18 (t, 1H,  $J = 8.0$  Hz), 7.44 (d, 1H,  $J = 8.4$  Hz), 7.63 (d, 1H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 10.5, 65.7, 114.6, 116.9, 119.3, 120.7, 122.1, 122.7, 123.0, 123.2, 128.3, 131.9, 153.4, 153.5. MS:  $m/z$  213 ( $\text{MH}$ ) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_2$ : 213.0916 [ $\text{M}+\text{H}$ ], found: 213.0921.

**6. Typical procedure for the preparation of 6H-benzo[*c*]chromen-8-ol (5a)**

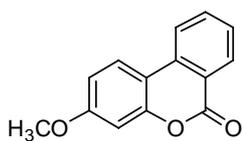
To a round-bottom flask equipped with a condenser containing 6H-benzo[*c*]chromene (**2a**, 0.2 mmol) was added  $\text{H}_2\text{O}_2$  (30%, 1.2 mmol) and ethanol (2 mL). The flask was put into the cavity of

the microwave synthesis apparatus and irradiated at 300 W at 80 °C for 16 × 30 min at intervals. Between two irradiations, the reaction temperature was allowed to cool to 40 °C. Upon completion, it was cooled to room temperature and extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (10-15%) to give 6*H*-benzo[*c*]chromen-6-one (**5a**). **5b-5e** and **5g-5j** were obtained in a similar manner.



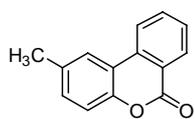
**6*H*-benzo[*c*]chromen-6-one (5a)<sup>5</sup>**

Colorless solid, m.p. 89-90 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.32-7.37 (m, 2H), 7.48 (t, 1H, *J* = 7.2 Hz), 7.58 (t, 1H, *J* = 7.6 Hz), 7.84 (t, 1H, *J* = 7.2 Hz), 8.06 (d, 1H, *J* = 8.0 Hz), 8.12 (d, 1H, *J* = 8.0 Hz), 8.40 (d, 1H, *J* = 8.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 117.8, 118.0, 121.2, 121.7, 122.7, 124.5, 128.9, 130.4, 130.5, 134.7, 134.8, 151.3, 161.2. IR (ν/cm<sup>-1</sup>): 2930, 1721. MS: *m/z* 197 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>: 197.0603 [M+H], found: 197.0608.



**3-Methoxy-6*H*-benzo[*c*]chromen-6-one (5b)<sup>6</sup>**

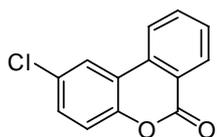
Colorless solid, m.p. 147-149 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.87 (s, 3H), 6.83 (s, 1H), 6.88 (dd, 1H, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 1.2 Hz), 7.48 (s, 1H, *J* = 8.0 Hz), 7.76 (d, 1H, *J* = 8.0 Hz), 7.90 (d, 1H, *J* = 8.8 Hz), 7.96 (d, 1H, *J* = 8.4 Hz), 8.32 (d, 1H, *J* = 8.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 55.6, 101.6, 111.1, 112.4, 119.9, 121.0, 123.7, 127.7, 130.5, 134.8, 135.1, 152.5, 161.4. IR (ν/cm<sup>-1</sup>): 2928, 1725. MS: *m/z* 227 (MH)<sup>+</sup>. HRMS calcd for C<sub>14</sub>H<sub>11</sub>O<sub>3</sub>: 227.0709 [M+H], found: 227.0722.



**2-Methyl-6*H*-benzo[*c*]chromen-6-one (5c)<sup>2</sup>**

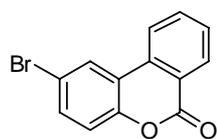
Colorless solid, m.p. 126-127 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.47 (s, 3H), 7.27

(d, 2H,  $J = 6.0$  Hz), 7.58 (t, 1H,  $J = 8.0$  Hz), 7.79-7.86 (m, 2H), 8.12 (d, 1H,  $J = 8.0$  Hz), 8.41 (d, 1H,  $J = 7.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 21.1, 117.4, 117.5, 121.2, 121.5, 122.7, 128.6, 130.5, 131.3, 134.0, 134.6, 134.7, 149.3, 161.3. MS:  $m/z$  211 (MH) $^+$ . HRMS calcd for  $\text{C}_{14}\text{H}_{11}\text{O}_2$ : 211.0760 [M+H], found: 211.0751.



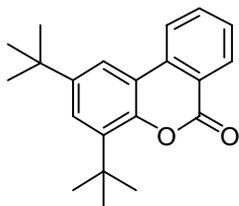
**2-Chloro-6H-benzo[c]chromen-6-one (5d)<sup>2</sup>**

Colorless solid, m.p. 180-181 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.28 (d, 1H,  $J = 8.8$  Hz), 7.40 (dd, 1H,  $J_1 = 8.8$  Hz,  $J_2 = 2.0$  Hz), 7.61 (t, 1H,  $J = 7.6$  Hz), 7.83 (t, 1H,  $J = 7.6$  Hz), 7.97 (d, 1H,  $J = 2.0$  Hz), 8.02 (d, 1H,  $J = 8.0$  Hz), 8.38 (d, 1H,  $J = 8.0$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 119.1, 119.3, 121.2, 121.7, 122.6, 129.6, 130.1, 130.3, 130.7, 133.5, 135.0, 149.6, 160.5. MS:  $m/z$  231 (MH) $^+$ . HRMS calcd for  $\text{C}_{13}\text{H}_8\text{ClO}_2$ : 231.0214 [M+H], found: 231.0221.



**2-Bromo-6H-benzo[c]chromen-6-one (5e)**

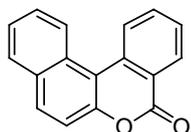
Colorless solid, m.p. 199-200 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.23 (d, 1H,  $J = 8.4$  Hz), 7.55 (dd, 1H,  $J_1 = 8.8$  Hz,  $J_2 = 2.0$  Hz), 7.62 (d, 1H,  $J = 7.6$  Hz), 7.84 (d, 1H,  $J = 7.2$  Hz), 8.03 (d, 1H,  $J = 8.0$  Hz), 8.13 (d, 1H,  $J = 2.0$  Hz), 8.38 (d, 1H,  $J = 8.0$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 117.4, 119.5, 119.8, 121.2, 121.7, 125.6, 129.6, 130.7, 133.2, 133.4, 135.0, 150.1, 160.5. IR ( $\nu/\text{cm}^{-1}$ ): 2924, 1714. MS:  $m/z$  275 (MH) $^+$ . HRMS calcd for  $\text{C}_{13}\text{H}_8\text{BrO}_2$ : 274.9708 [M+H], found: 274.9712.



**2,4-Di-tert-butyl-6H-benzo[c]chromen-6-one (5g)**

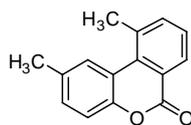
Colorless solid, m.p. 175-176 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.42 (s, 9H), 1.56 (s, 9H), 7.55-7.57 (m, 2H), 7.82 (t, 1H,  $J = 8.0$  Hz), 7.96 (s, 1H), 8.19 (d, 1H,  $J = 8.0$  Hz), 8.41 (d, 1H,  $J = 8.0$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 30.1, 31.5, 34.9, 35.3,

117.0, 117.4, 120.8, 121.8, 125.6, 128.3, 130.2, 134.5, 135.8, 137.9, 146.3, 148.1, 160.8. MS:  $m/z$  309 (MH)<sup>+</sup>. HRMS calcd for C<sub>21</sub>H<sub>25</sub>O<sub>2</sub>: 309.1855 [M+H], found: 309.1858.



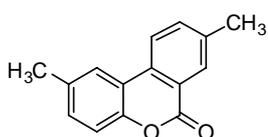
**5H-Dibenzo[*c,f*]chromen-5-one (5h)**

Colorless solid, m.p. 156-157 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.41 (d, 1H,  $J = 9.2$  Hz), 7.51 (t, 1H,  $J = 7.6$  Hz), 7.57-7.64 (m, 2H), 7.82-7.90 (m, 3H), 8.46 (d, 1H,  $J = 7.6$  Hz), 8.56 (d, 1H,  $J = 8.4$  Hz), 8.68 (d, 1H,  $J = 8.4$  Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 112.4, 117.5, 122.2, 124.9, 125.3, 126.3, 127.7, 128.1, 129.3, 129.4, 130.6, 131.4, 131.5, 134.3, 135.3, 150.1, 161.2. MS:  $m/z$  247 (MH)<sup>+</sup>. HRMS calcd for C<sub>17</sub>H<sub>11</sub>O<sub>2</sub>: 247.0760 [M+H], found: 247.0751.



**2,10-Dimethyl-6H-benzo[*c*]chromen-6-one (5i)**

Colorless solid, m.p. 127-128 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.45 (s, 3H), 2.87 (s, 3H), 7.25 (s, 2H), 7.43 (t, 1H,  $J = 7.6$  Hz), 7.61 (d, 1H,  $J = 7.6$  Hz), 8.05 (s, 1H), 8.34 (d, 1H,  $J = 8.0$  Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 21.5, 25.4, 117.5, 119.2, 122.7, 127.2, 128.0, 129.1, 130.3, 133.3, 133.5, 134.9, 138.9, 149.2, 161.8. IR (ν/cm<sup>-1</sup>): 2918, 1712. MS:  $m/z$  225 (MH)<sup>+</sup>. HRMS calcd for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>: 225.0916 [M+H], found: 225.0918.

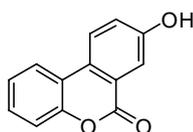


**2,8-Dimethyl-6H-benzo[*c*]chromen-6-one (5j)**

Colorless solid, m.p. 120-121 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 2.42 (s, 3H), 2.45 (s, 3H), 7.18 (s, 2H), 7.56 (d, 1H,  $J = 8.0$  Hz), 7.72 (s, 1H), 7.91 (d, 1H,  $J = 8.4$  Hz), 8.12 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 21.1, 21.2, 117.2, 117.7, 121.0, 121.5, 122.4, 130.2, 130.7, 132.2, 133.9, 135.8, 138.9, 149.0, 161.5. MS:  $m/z$  225 (MH)<sup>+</sup>. HRMS calcd for C<sub>15</sub>H<sub>13</sub>O<sub>2</sub>: 225.0916 [M+H], found: 225.0918.

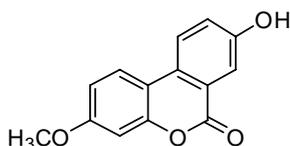
## 7. A typical procedure for the synthesis of 8-hydroxy-6*H*-benzo[*c*]chromen-6-one (6a)

To a round-bottom flask equipped with a condenser containing 6*H*-benzo[*c*]chromen-8-ol (**4a**, 0.2 mmol) was added H<sub>2</sub>O<sub>2</sub> (30%, 1.2 mmol) and ethanol (2 mL). The flask was put into an oil bath and stirred at 80 °C for 24 h. Upon completion, it was cooled to room temperature and extracted with ethyl acetate (5 mL × 3). The combined organic phases were dried, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with ethyl acetate/hexane (10-20%) to give 8-hydroxy-6*H*-benzo[*c*]chromen-6-one (**6a**). **6b-6e**, **6g** and **6h** were obtained in a similar manner.



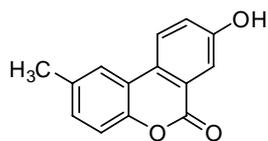
**8-Hydroxy-6*H*-benzo[*c*]chromen-6-one (6a)**

Colorless solid, m.p. 240-241 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.33-7.37 (m, 3H), 7.43-7.47 (m, 1H), 7.56 (d, 1H, *J* = 2.4 Hz), 8.21 (d, 1H, *J* = 8.0 Hz), 8.27 (d, 1H, *J* = 8.8 Hz), 10.41 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 114.2, 117.4, 118.5, 122.3, 124.4, 125.1, 126.4, 129.5, 150.0, 158.7, 160.6. IR (ν/cm<sup>-1</sup>): 3254, 1712. MS: *m/z* 213 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>9</sub>O<sub>3</sub>: 213.0552 [M+H], found: 213.0558.



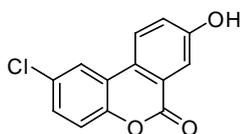
**8-Hydroxy-3-methoxy-6*H*-benzo[*c*]chromen-6-one (6b)**

Pale yellow solid, m.p. 246-247 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 3.83 (s, 3H), 6.94-6.97 (m, 2H), 7.32 (dd, 1H, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz), 7.52 (d, 1H, *J* = 2.4 Hz), 8.12 (d, 1H, *J* = 8.8 Hz), 8.16 (d, 1H, *J* = 8.8 Hz), 10.26 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 56.1, 101.8, 111.5, 112.6, 114.0, 120.9, 124.2, 124.3, 124.6, 127.0, 151.3, 157.7, 160.5, 160.9. IR (ν/cm<sup>-1</sup>): 3258, 1716. MS: *m/z* 243 (MH)<sup>+</sup>. HRMS calcd for C<sub>14</sub>H<sub>11</sub>O<sub>4</sub>: 243.0658 [M+H], found: 243.0662.



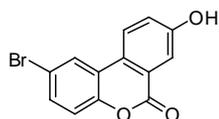
**8-Hydroxy-2-methyl-6H-benzo[c]chromen-6-one (6c)**

Colorless solid, m.p. 247-249 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 2.39 (s, 3H), 7.25 (s, 2H), 7.34 (dd, 1H, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2.4 Hz), 7.55 (d, 1H, *J* = 2.4 Hz), 8.02 (s, 1H), 8.24 (d, 1H, *J* = 8.8 Hz), 10.38 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 21.0, 114.2, 117.2, 118.1, 122.3, 123.0, 124.3, 125.0, 126.4, 130.3, 134.3, 148.1, 158.6, 160.8. MS: *m/z* 227 (MH)<sup>+</sup>. HRMS calcd for C<sub>14</sub>H<sub>11</sub>O<sub>3</sub>: 227.0709[M+H], found: 227.0718.



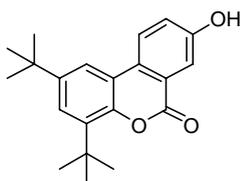
**2-Chloro-8-hydroxy-6H-benzo[c]chromen-6-one (6d)**

Pale yellow solid, m.p. 259-260 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.34 (dd, 1H, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz), 7.39 (d, 1H, *J* = 8.4 Hz), 7.47 (dd, 1H, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.0 Hz), 7.55 (d, 1H, *J* = 2.4 Hz), 8.31-8.34 (m, 2H), 10.52 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 114.3, 119.4, 120.3, 122.5, 122.7, 124.4, 125.2, 125.6, 129.1, 129.4, 148.7, 159.3, 160.3. MS: *m/z* 247 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>8</sub>ClO<sub>3</sub>: 247.0163[M+H], found: 247.0179.



**2-Bromo-8-hydroxy-6H-benzo[c]chromen-6-one (6e)**

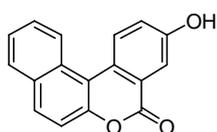
Pale yellow solid, m.p. 248-250 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.34 (dd, 2H, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.8 Hz), 7.56 (d, 1H, *J* = 2.4 Hz), 7.59 (dd, 1H, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.0 Hz), 8.34 (d, 1H, *J* = 8.8 Hz), 8.44 (d, 1H, *J* = 2.0 Hz), 10.52 (s, 1H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 114.3, 117.3, 119.6, 120.7, 122.5, 124.3, 125.1, 125.6, 131.9, 149.1, 159.2, 160.2. IR (ν/cm<sup>-1</sup>): 3273, 1716. MS: *m/z* 291 (MH)<sup>+</sup>. HRMS calcd for C<sub>13</sub>H<sub>8</sub>BrO<sub>3</sub>: 290.9658[M+H], found: 290.9659.



**2,4-Di-tert-butyl-8-hydroxy-6H-benzo[c]chromen-6-one (6g)**

Colorless solid, m.p. 252-253 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 1.33 (s, 9H), 1.45 (s, 9H), 7.36-7.38 (m, 2H), 7.56 (d, 1H, *J* = 2.0 Hz), 8.02 (s, 1H),

8.36 (d, 1H,  $J = 8.8$  Hz), 10.35 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$ : 30.2, 31.7, 35.0, 35.2, 113.7, 117.7, 118.1, 121.7, 123.8, 124.4, 125.4, 127.3, 136.8, 146.5, 146.7, 158.4, 160.2. MS:  $m/z$  325 (MH) $^+$ . HRMS calcd for C<sub>21</sub>H<sub>25</sub>O<sub>3</sub>: 325.1804[M+H], found: 325.1806.

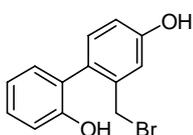


**3-Hydroxy-5H-dibenzo[*c,f*]chromen-5-one (6h)**

Pale yellow solid, m.p. 219-220 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 7.46 (dd, 1H,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz), 7.53-7.61 (m, 2H), 7.68-7.70 (m 2H), 8.02-8.07 (m, 2H), 8.60 (d, 1H,  $J = 8.8$  Hz), 8.76 (d, 1H,  $J = 8.4$  Hz), 10.53 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$ : 112.6, 114.7, 117.7, 123.6, 123.9, 125.4, 125.8, 126.7, 128.3, 129.0, 129.7, 130.7, 131.7, 148.8, 158.0, 160.7. MS:  $m/z$  263 (MH) $^+$ . HRMS calcd for C<sub>17</sub>H<sub>11</sub>O<sub>3</sub>: 263.0709 [M+H], found: 263.0719.

**8. Procedure for the synthesis of 2'-(bromomethyl)biphenyl-2,4'-diol (7)**

To a dried round bottom flask were added 6H-benzo[*c*]chromene-8-ol (**4a**, 0.5 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The flask was purged with nitrogen. BBr<sub>3</sub> (1.2 equiv) were then added dropwise to the mixture. The mixture was allowed to stir at room temperature for 3 h. The reaction was quenched with water, and the resulting mixture was extracted with ethyl acetate. The combined organic phases were dried, filtered and concentrated under reduced pressure. The residue were purified through column chromatography eluenting with ethyl acetate/hexanes (20%) to give 2'-(bromomethyl)biphenyl- 2,4'-diol (**7**) in a yield of 90%.



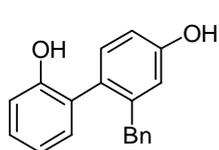
**2'-(Bromomethyl)biphenyl-2,4'-diol (7)**

$^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.22-4.35 (m, 2H), 4.94 (br s, 2H), 6.85 (dd,  $J_1 = 8.4$  Hz, 1H,  $J_2 = 2.4$  Hz), 6.98-7.04 (m, 3H), 7.12 (d, 1H,  $J = 8.4$  Hz), 7.17-7.19 (m, 1H), 7.29-7.33

(m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 31.4, 115.7, 116.4, 117.7, 120.7, 125.6, 128.2, 129.6, 130.9, 132.5, 138.7, 152.7, 155.9. MS:  $m/z$  279 ( $\text{MH}^+$ ). HRMS calcd for  $\text{C}_{13}\text{H}_{12}\text{BrO}_2$ : 279.0021 [ $\text{M}+\text{H}$ ], found: 279.0009.

### 9. Procedure for the synthesis of 2'-benzylbiphenyl-2,4'-diol (**8**)

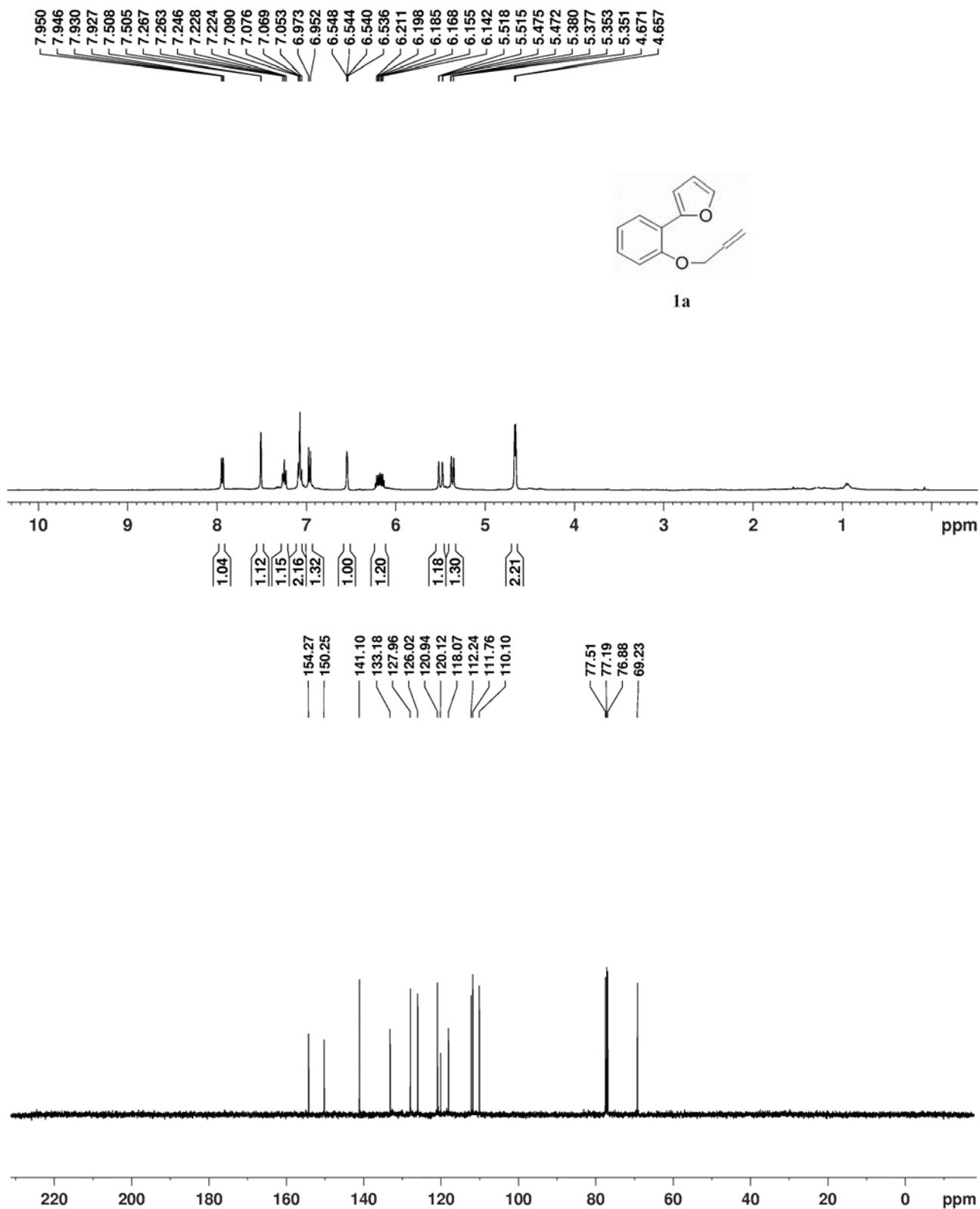
To a dried round bottom flask was added 2'-(bromomethyl)biphenyl-2,4'-diol (**7**, 0.4 mmol) and benzene (5 mL).  $\text{FeCl}_3$  (1 equiv) were then added portion-wise to the mixture. The mixture was allowed to stir at 70 °C for 0.5 h. The reaction was then quenched with water, and the mixture was extracted with ethyl acetate. The organic phases were dried, filtered and concentrated under reduced pressure. The residue were then purified through column chromatography eluting with ethyl acetate/hexanes (20%) to give 2'-benzylbiphenyl-2,4'-diol (**8**) in a yield of 89%.

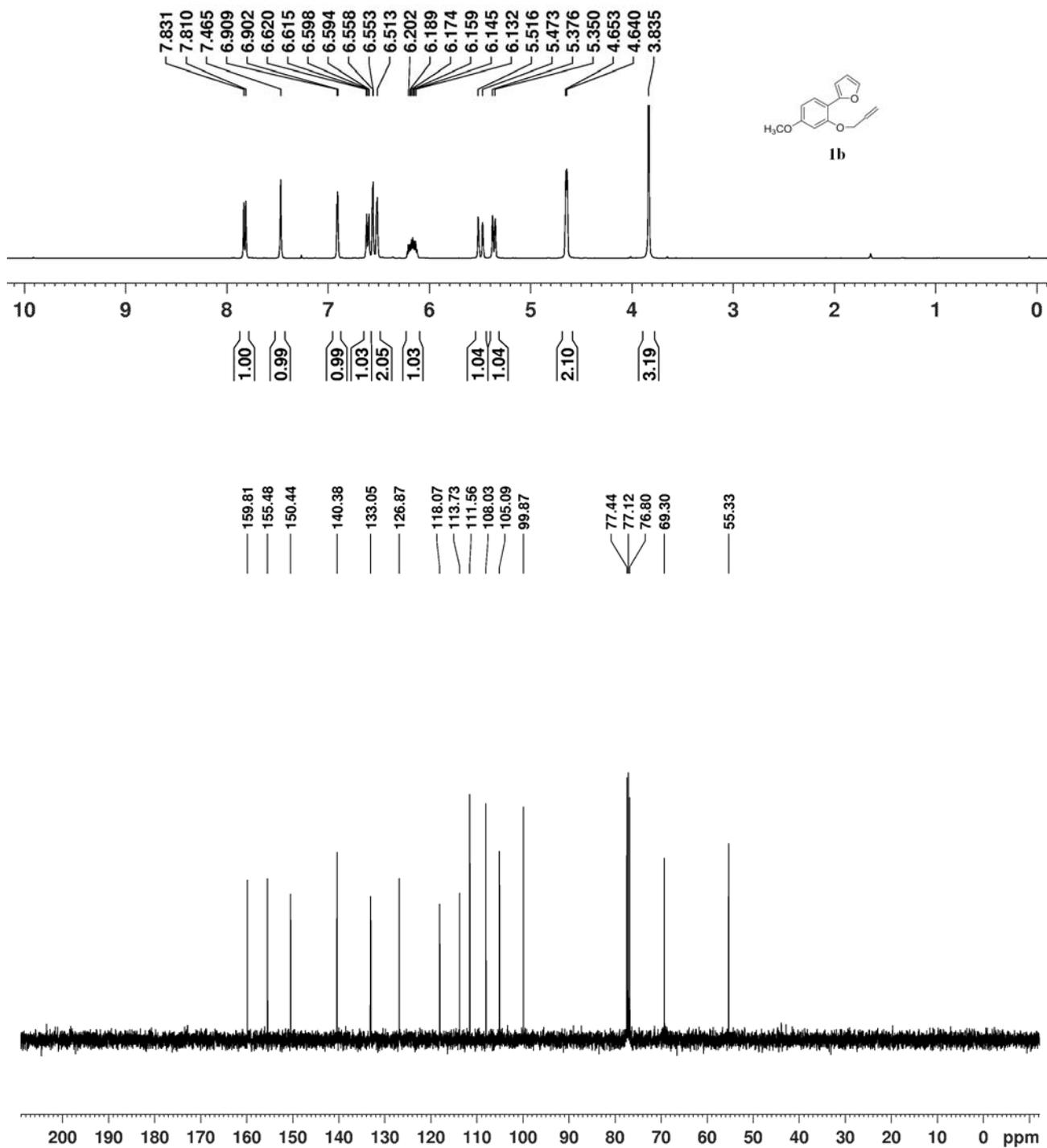


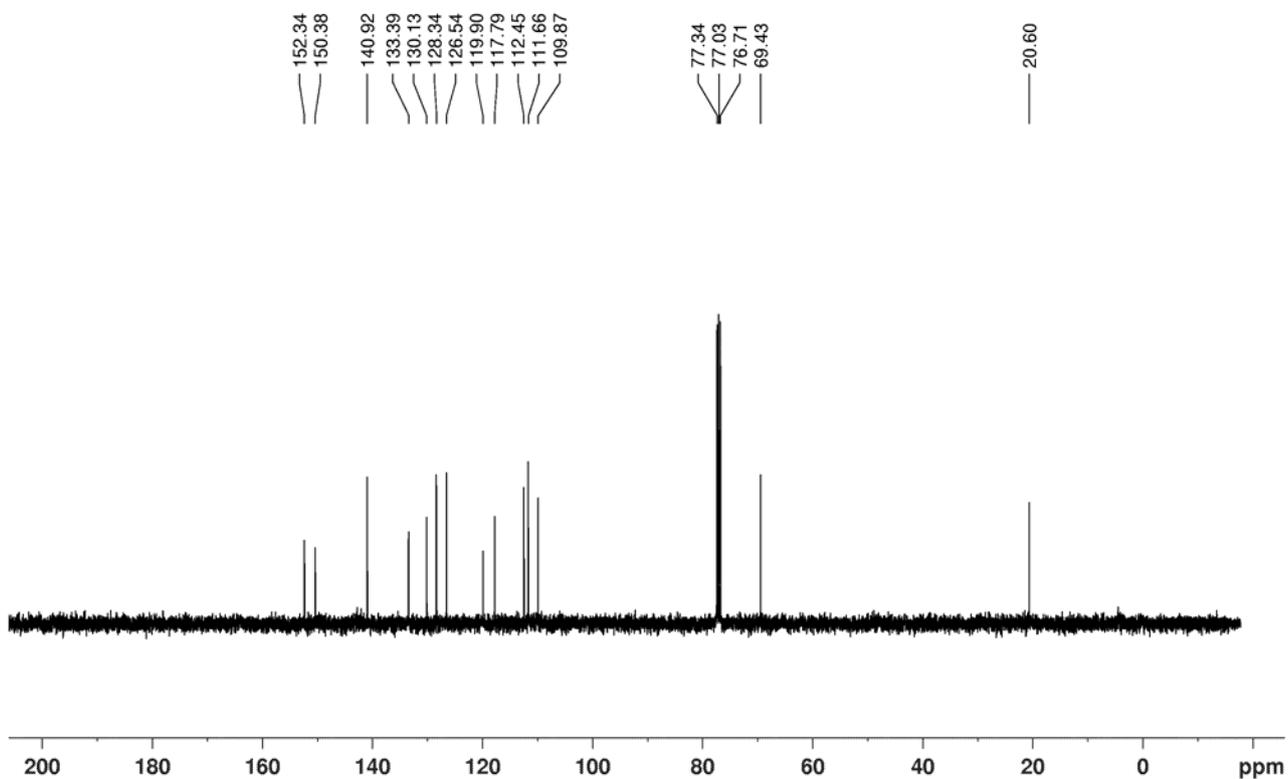
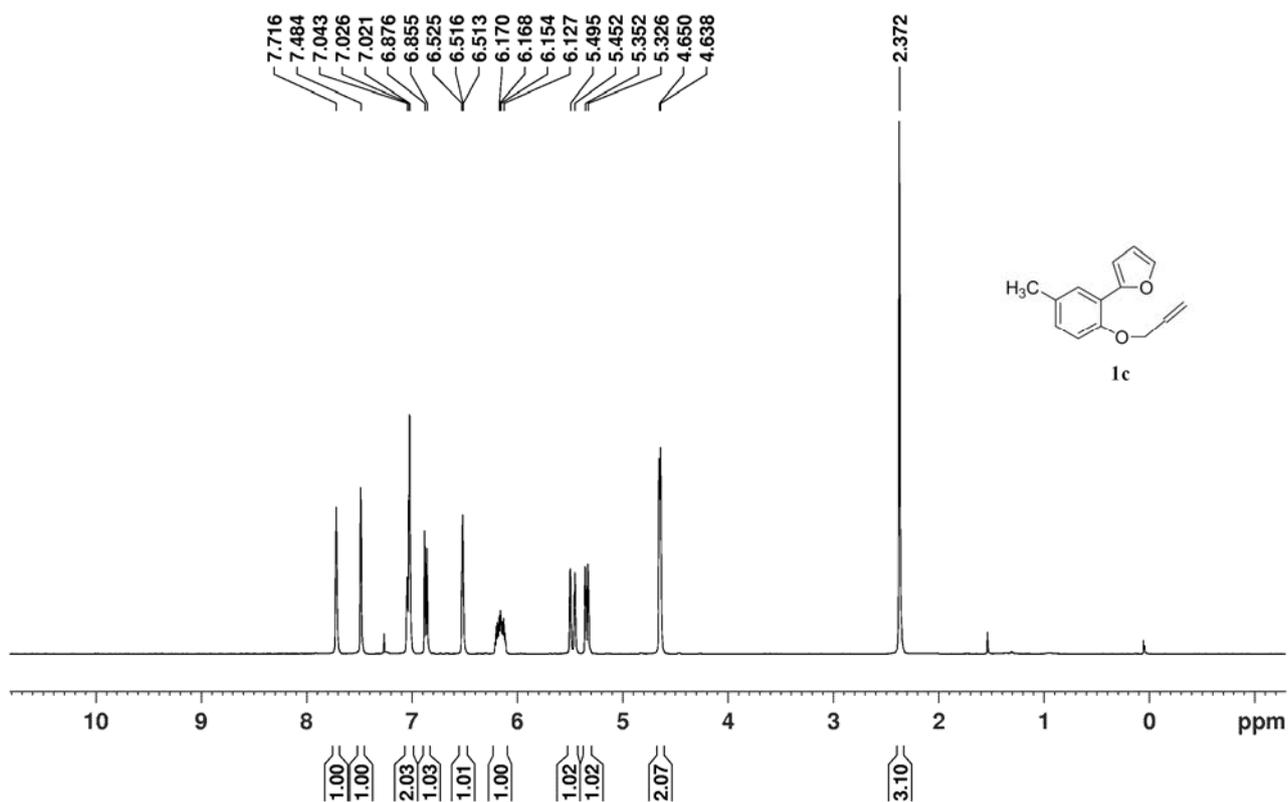
**2'-Benzylbiphenyl-2,4'-diol (8)**

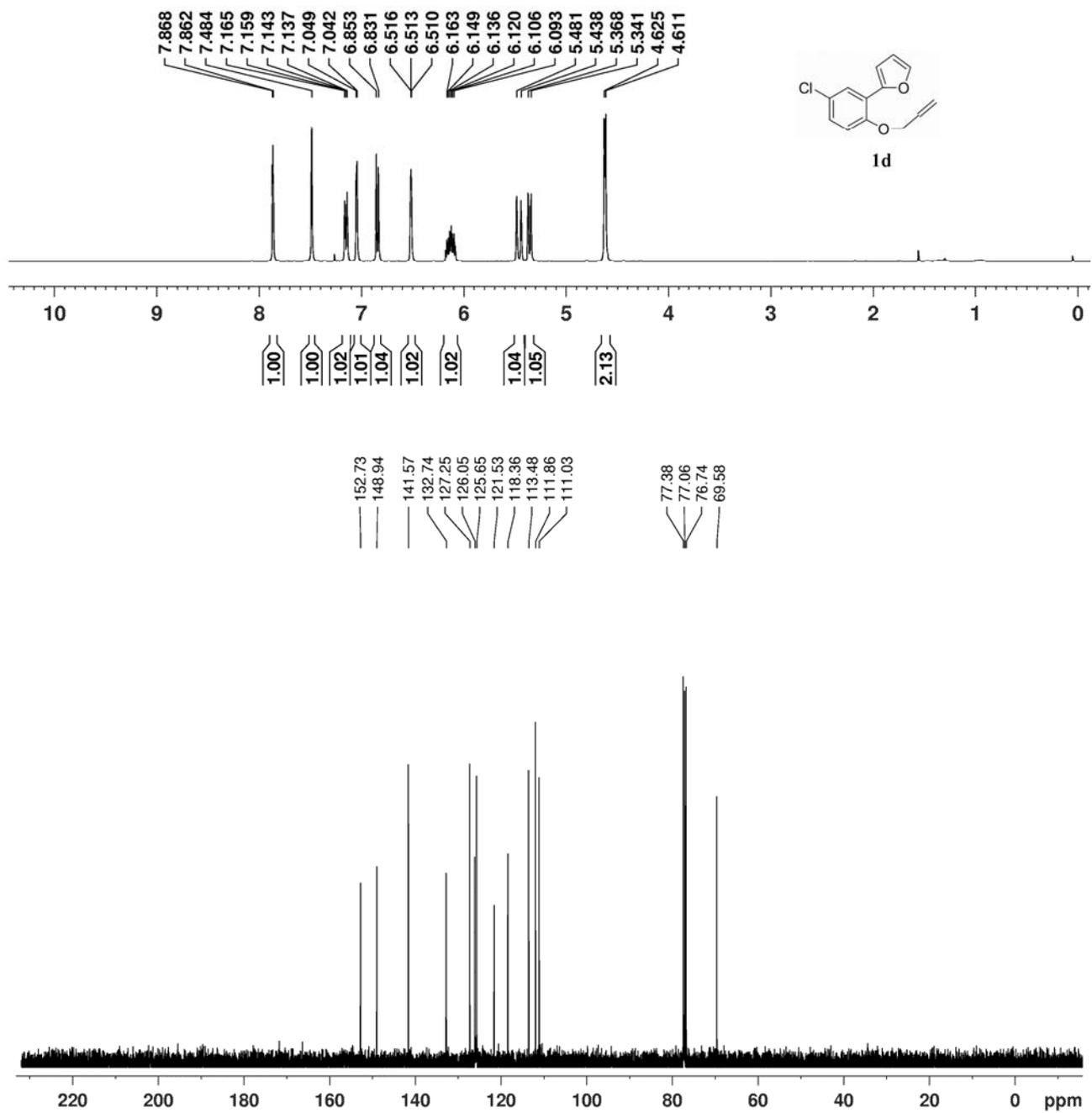
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 3.72-3.81 (m, 2H), 4.75 (s, 1H), 4.94 (s, 1H), 6.73 (d, 1H,  $J = 2.4$  Hz), 6.80 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 2.4$  Hz), 6.94-6.98 (m, 4H), 7.05-7.07 (m, 1H), 7.13-7.28 (m, 5H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 39.1, 113.9, 115.2, 117.2, 120.4, 126.0, 126.9, 127.8, 128.3, 128.9, 129.1, 130.8, 132.1, 140.2, 142.7, 152.9, 155.8. MS:  $m/z$  277 ( $\text{MH}^+$ ). HRMS calcd for  $\text{C}_{19}\text{H}_{17}\text{O}_2$ : 277.1229 [ $\text{M}+\text{H}$ ], found: 277.1233.

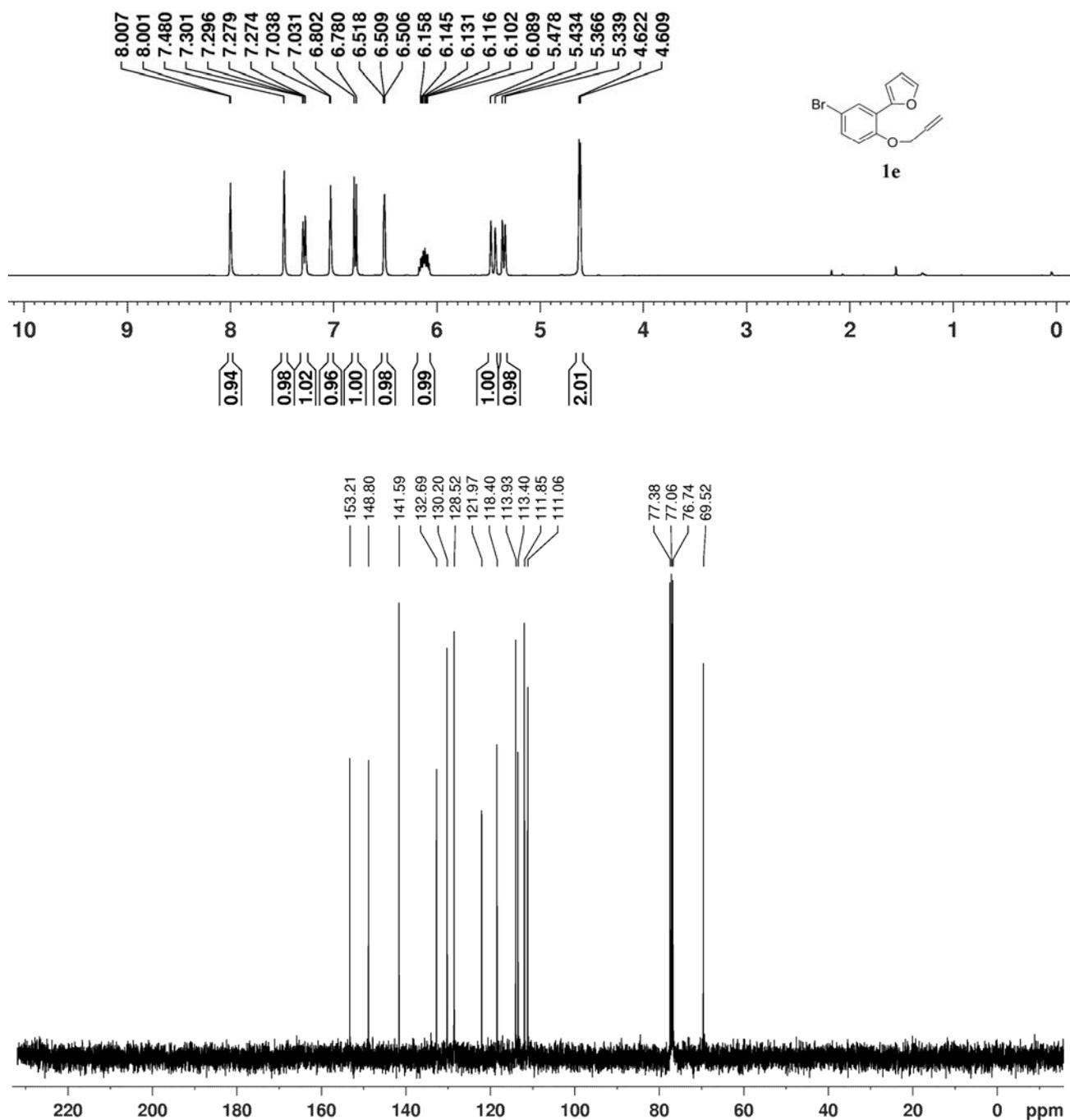
#### 4. Selected copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

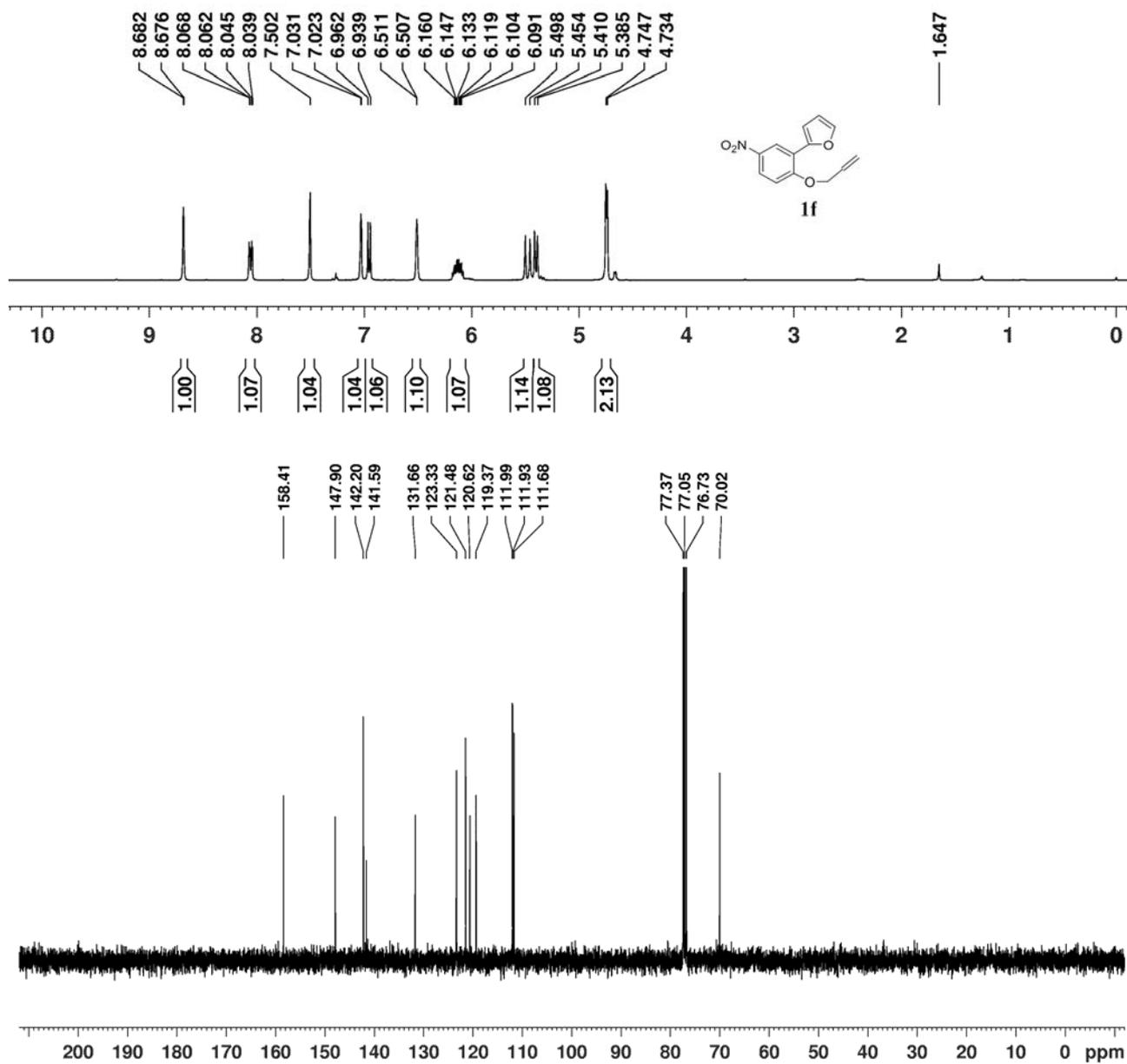


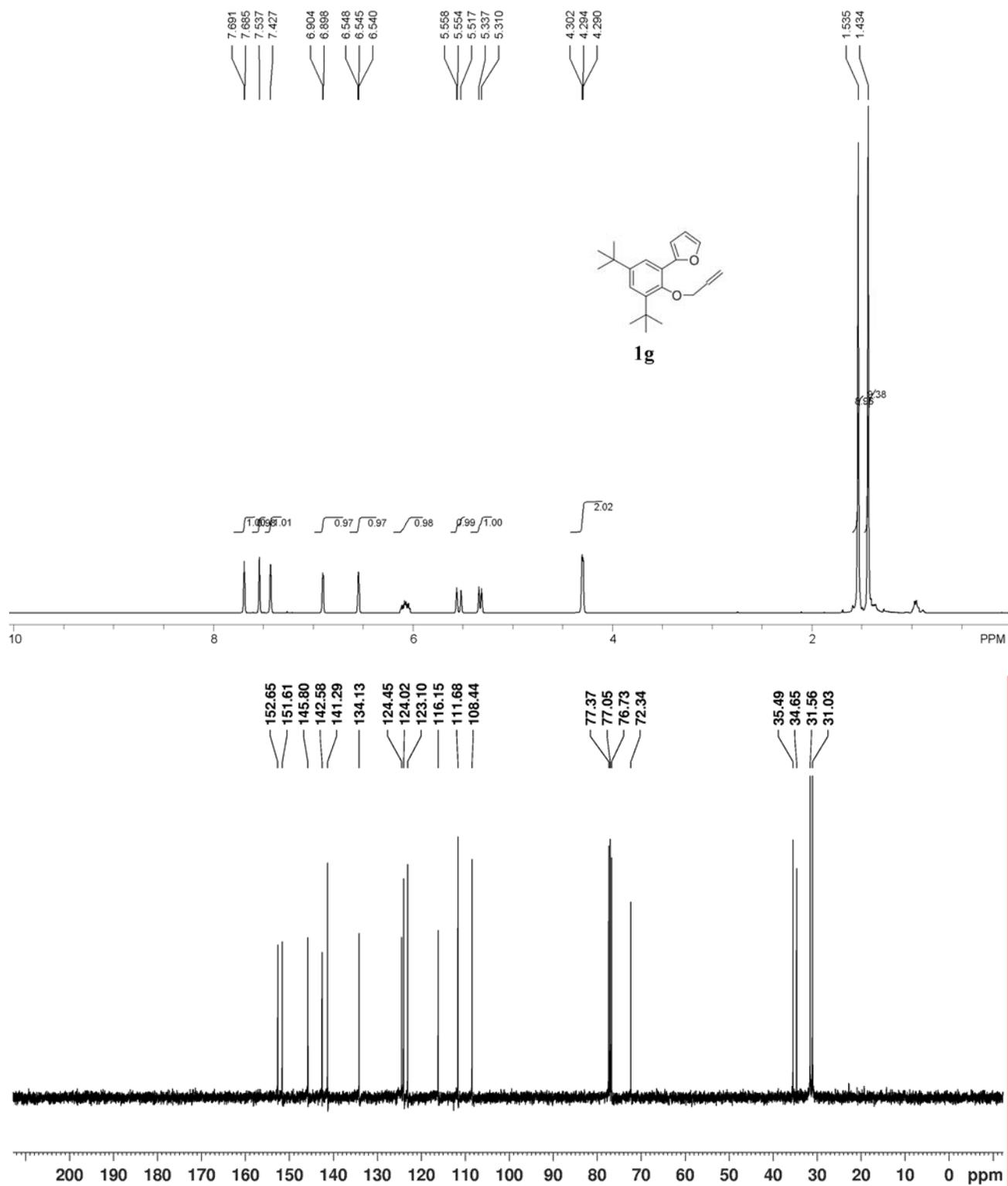


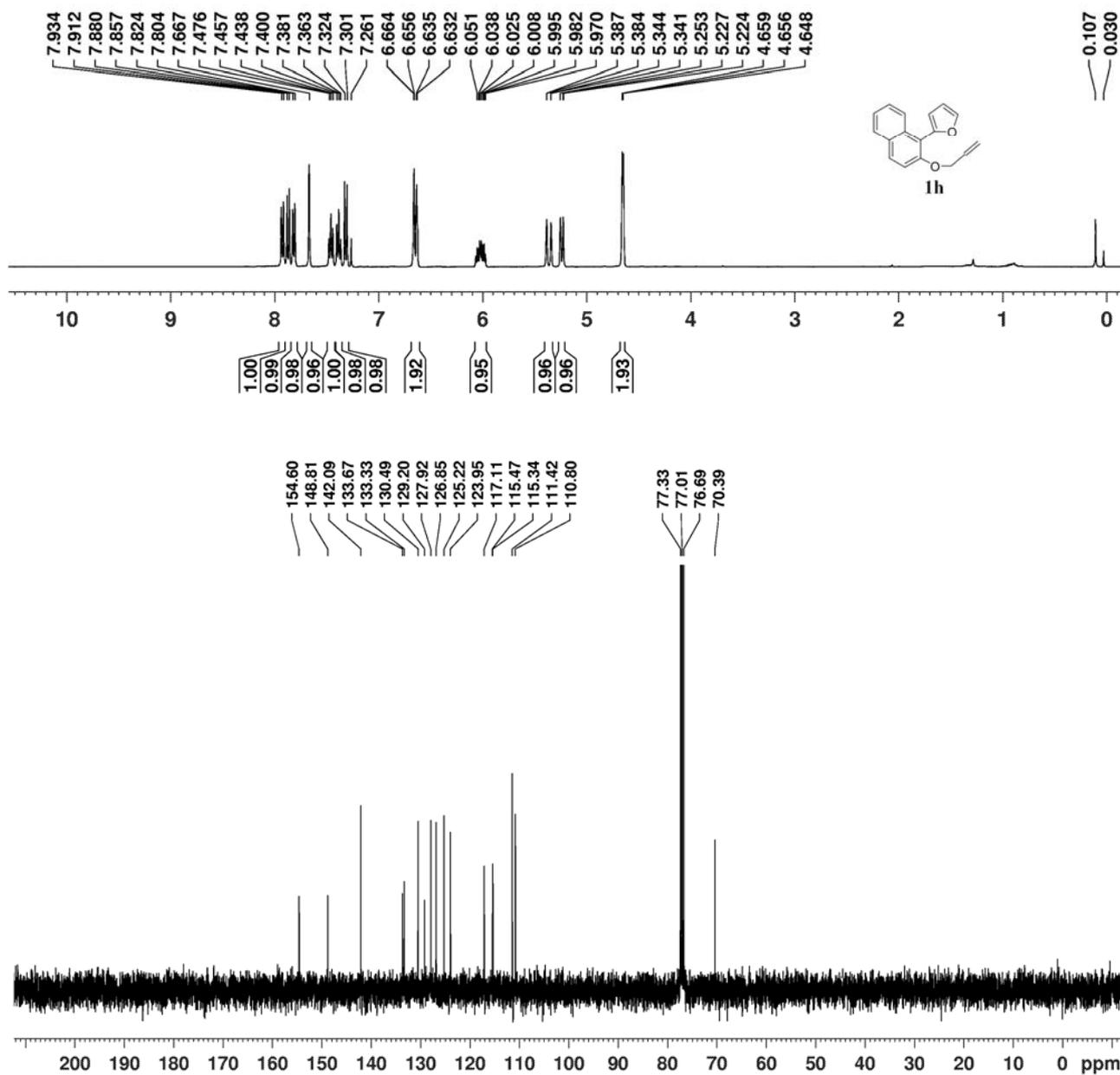


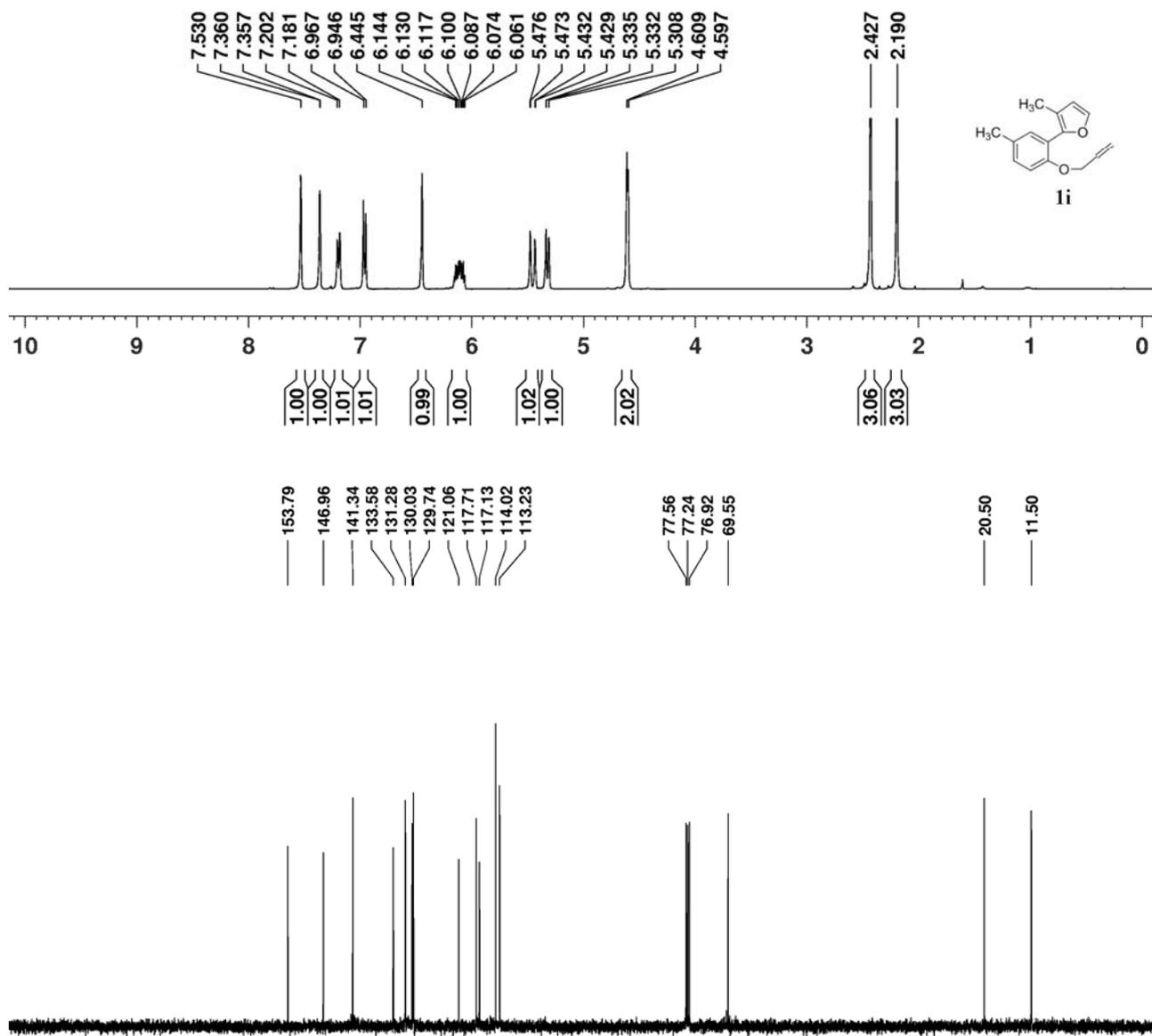


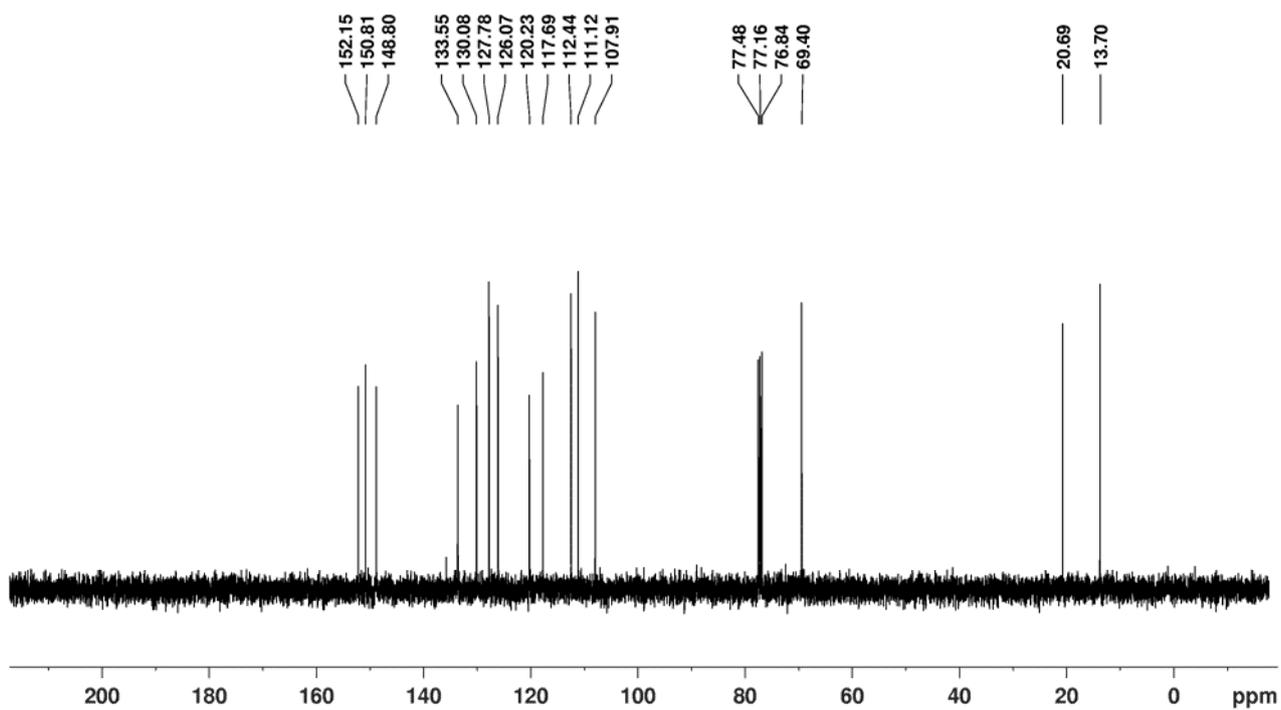
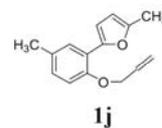
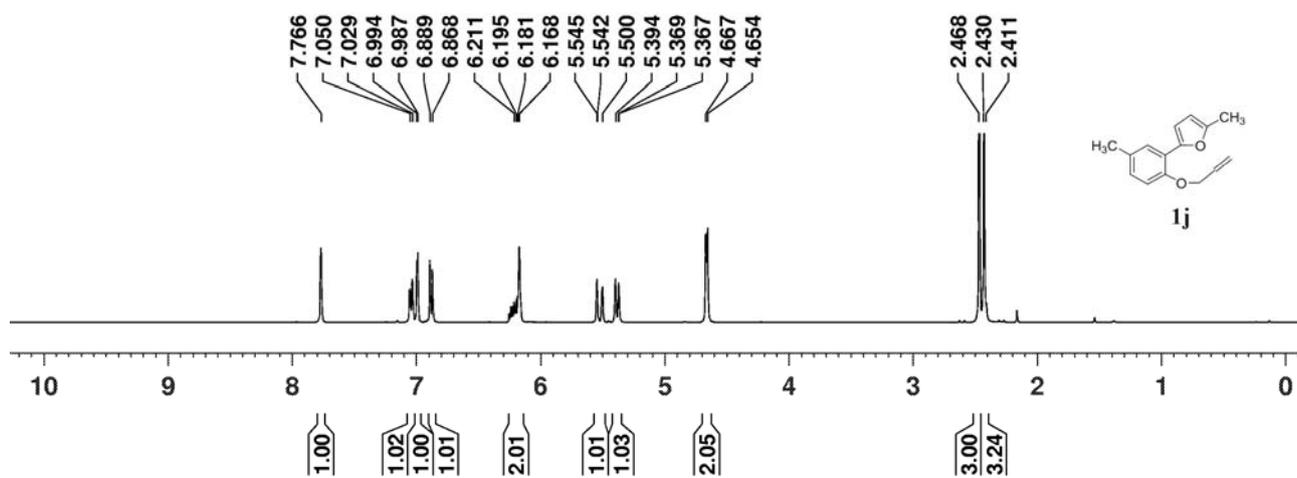


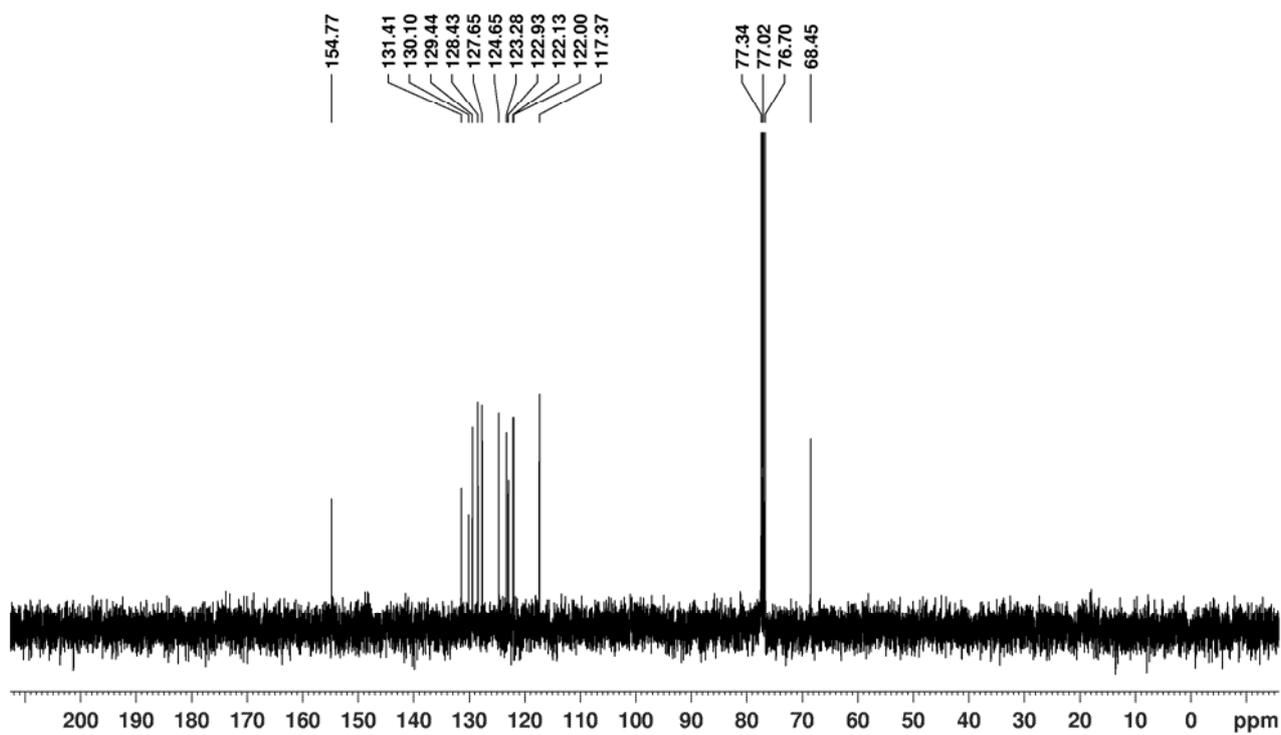
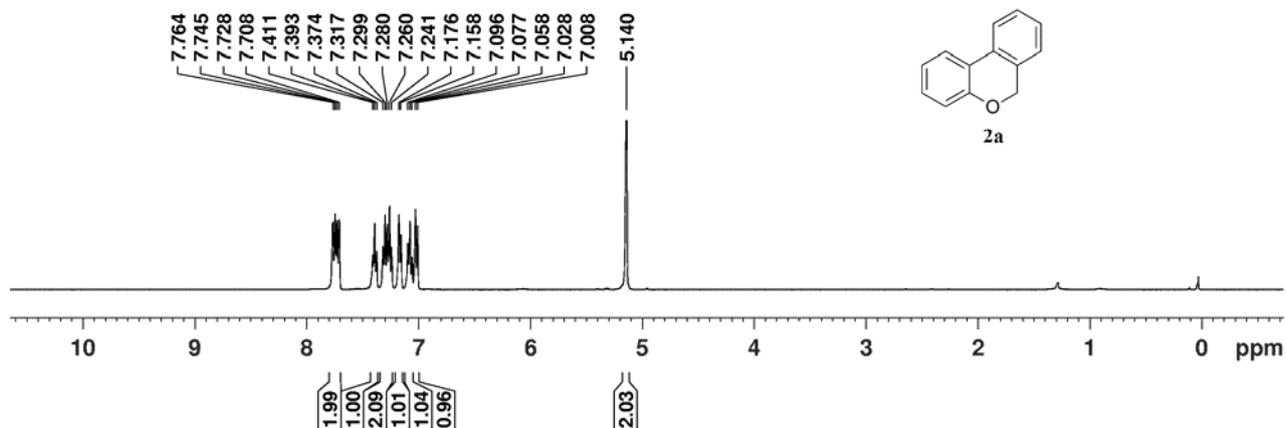


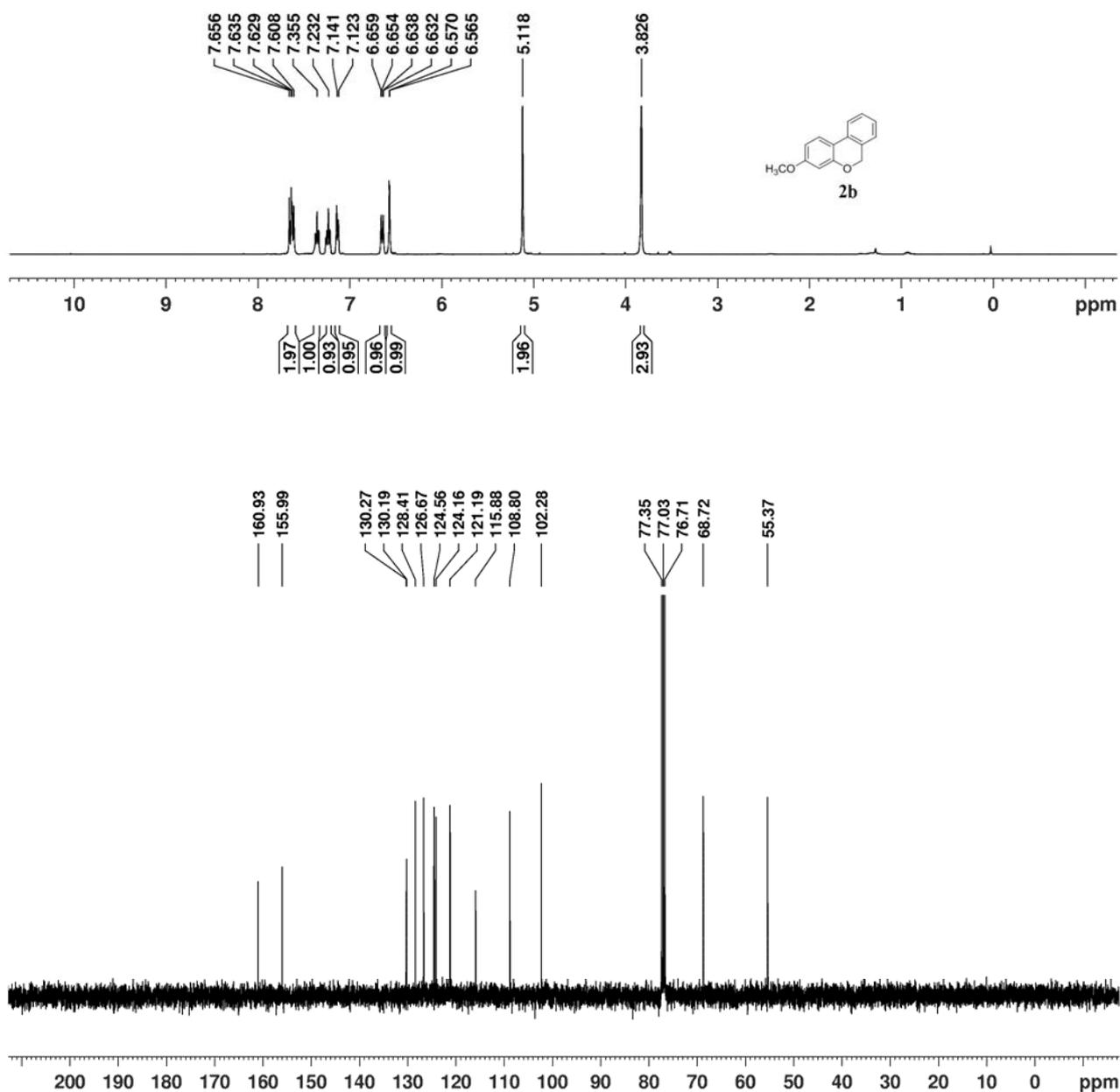


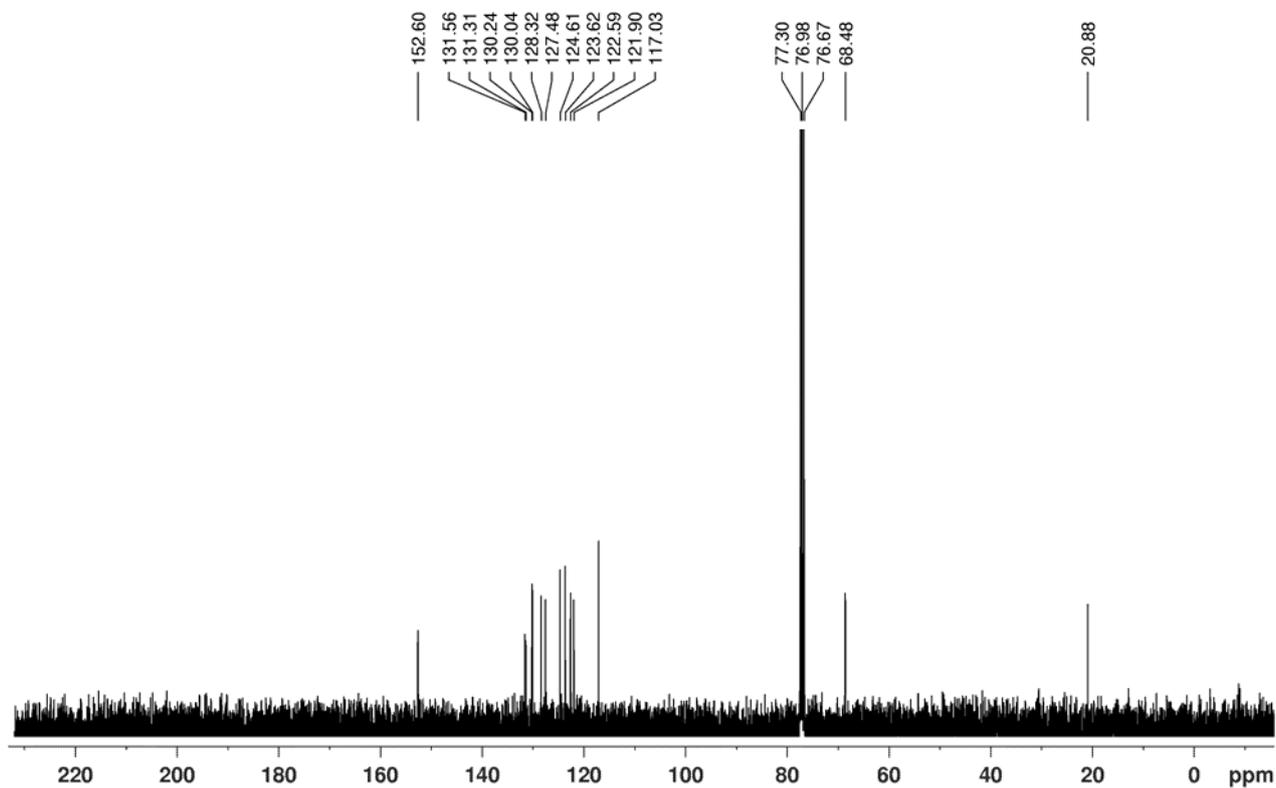
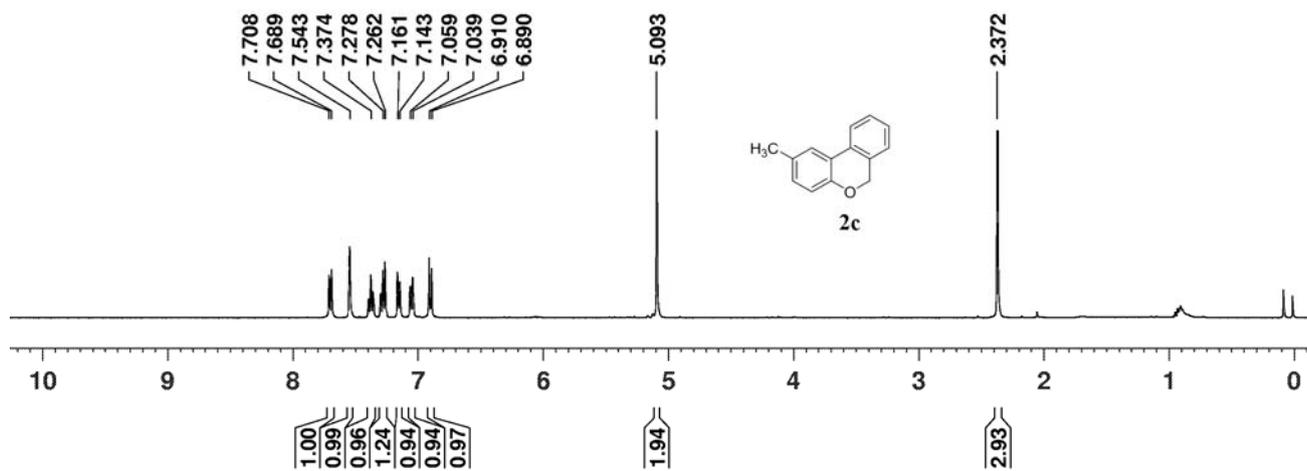


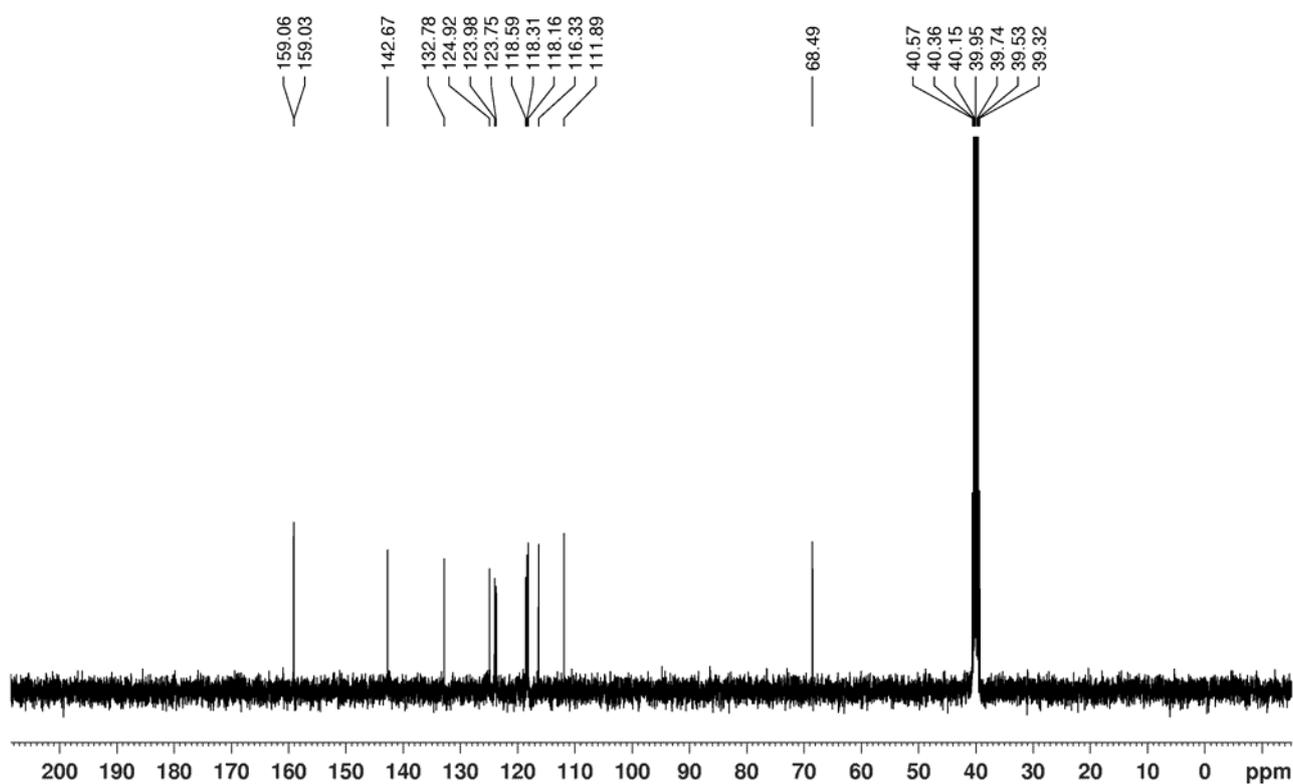
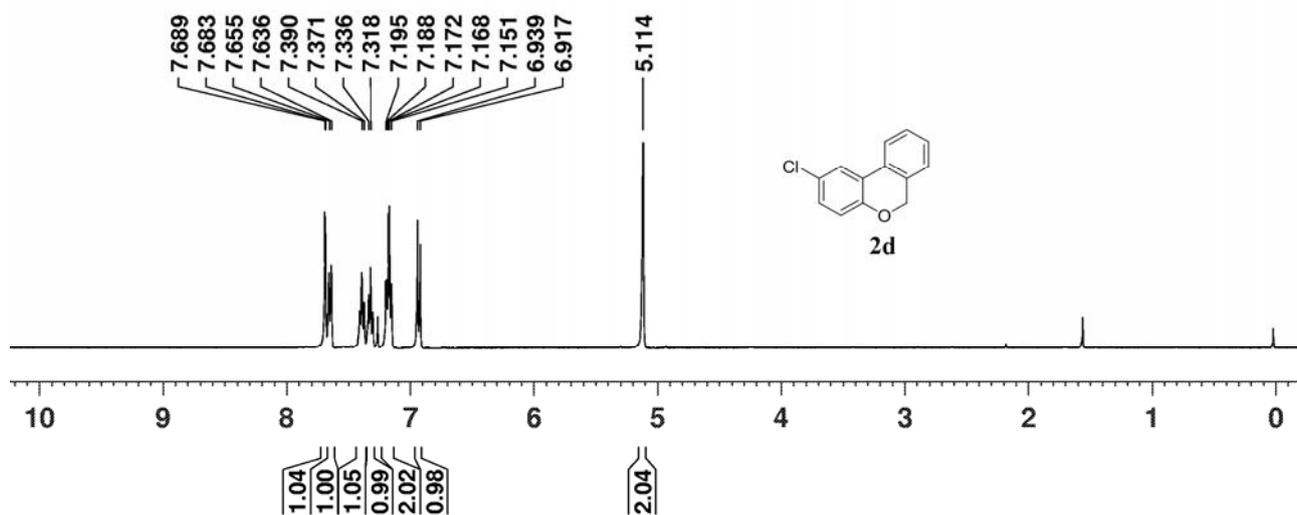


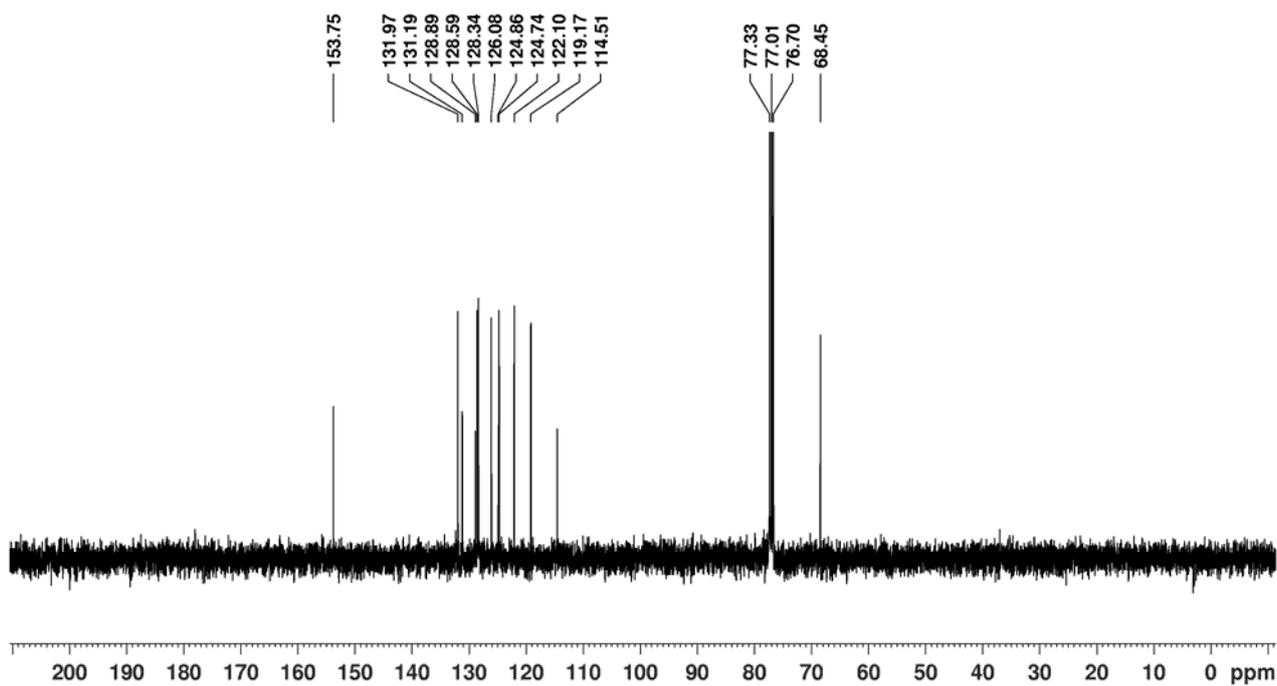
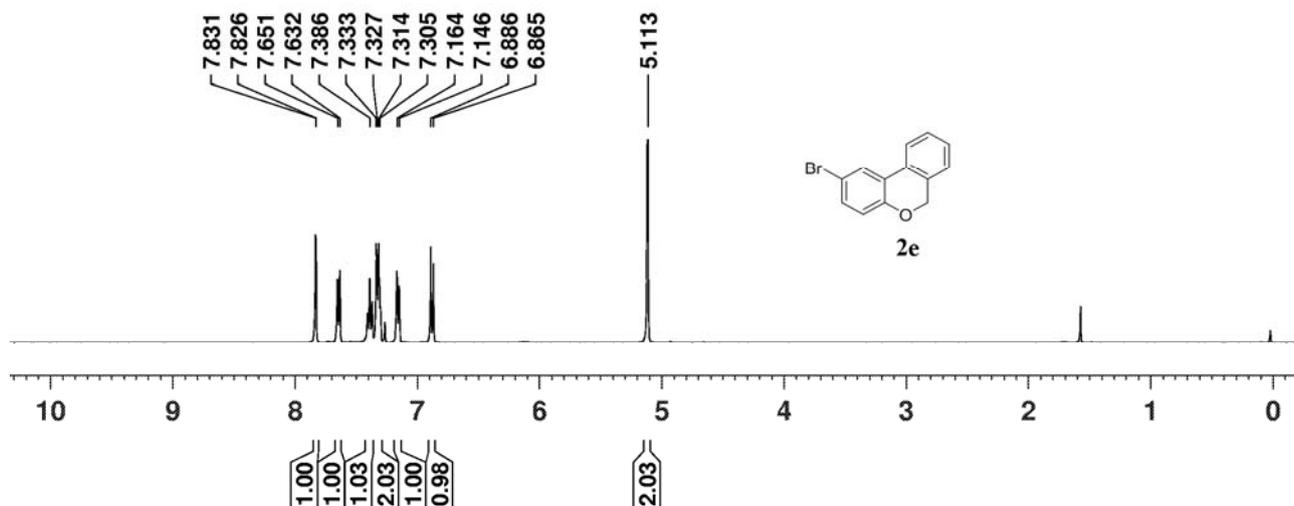


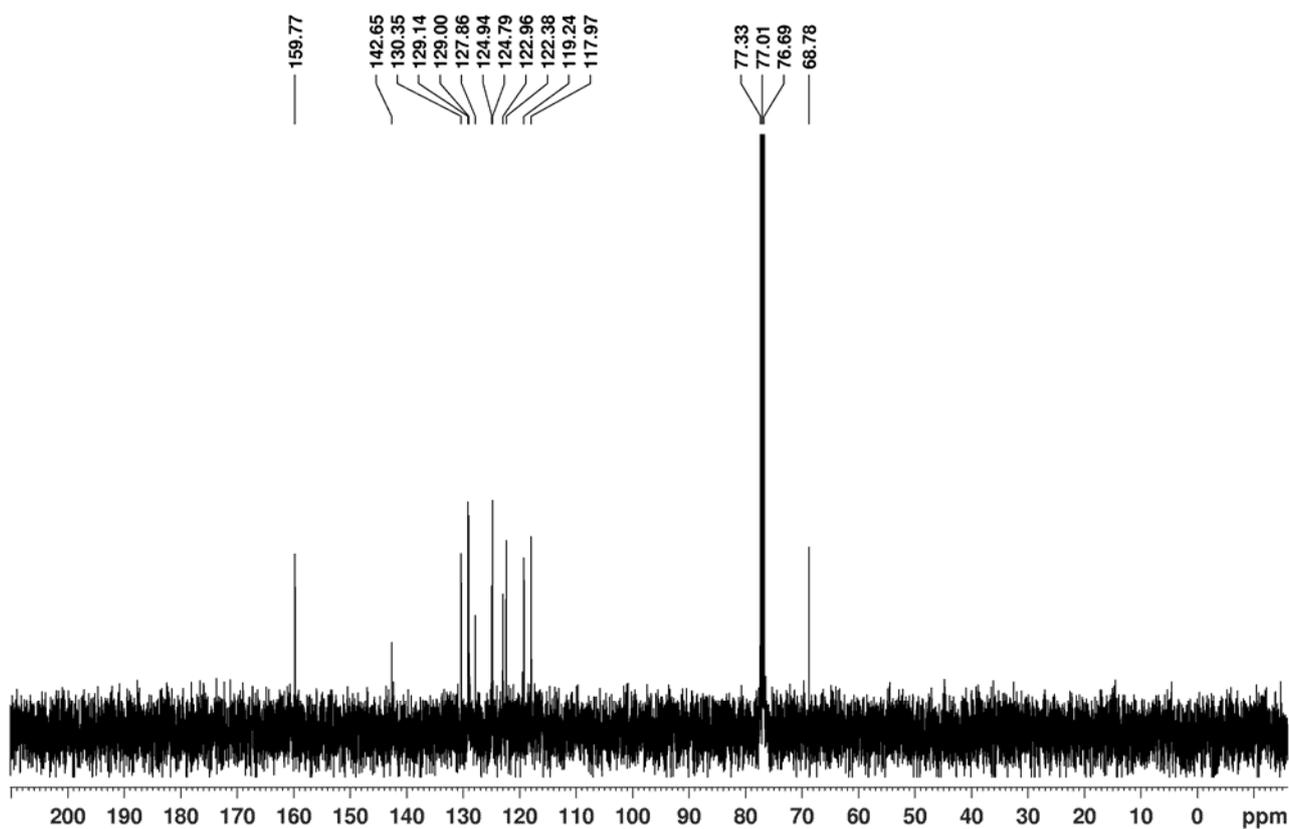
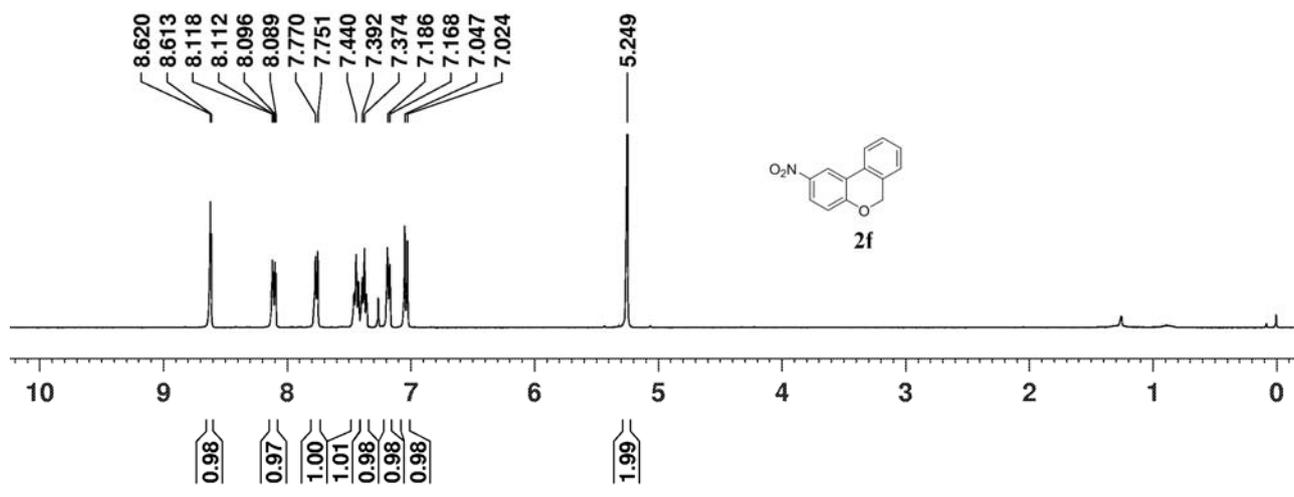


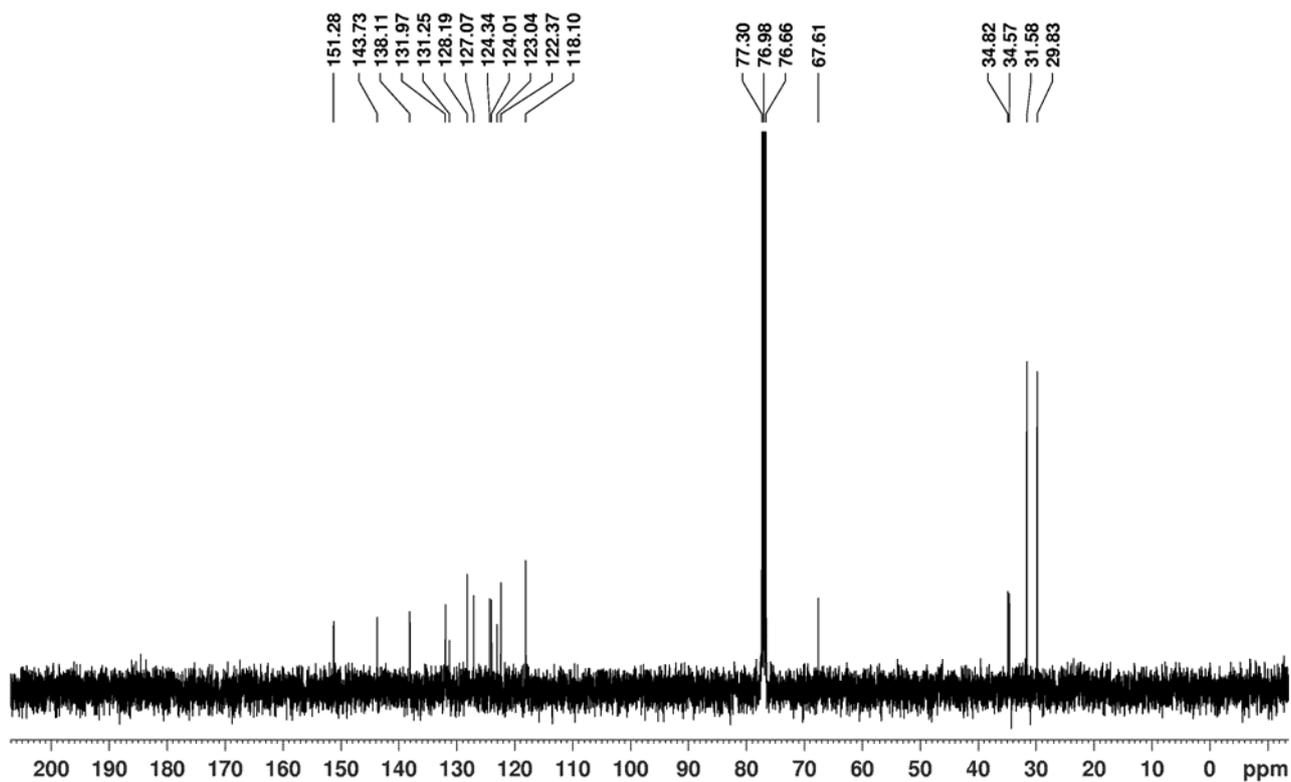
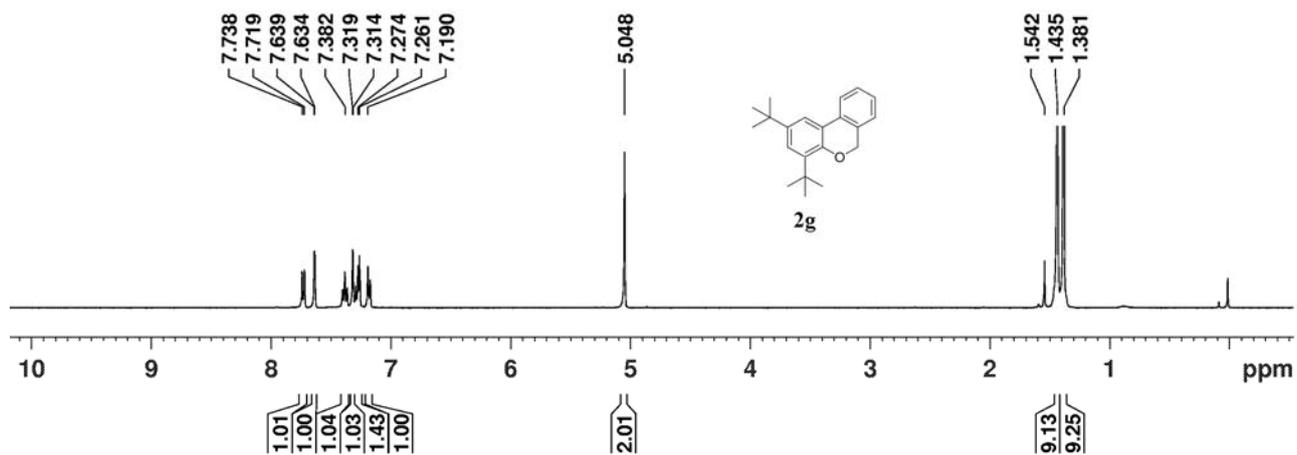


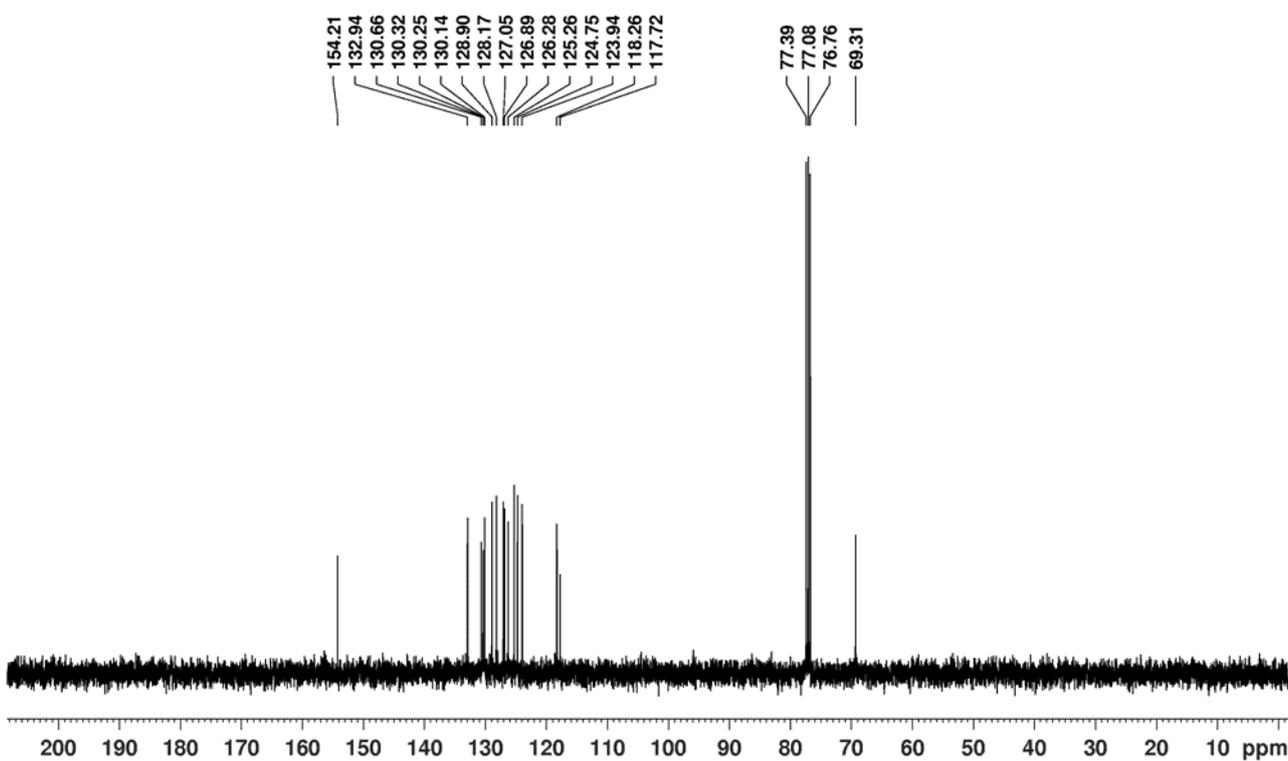
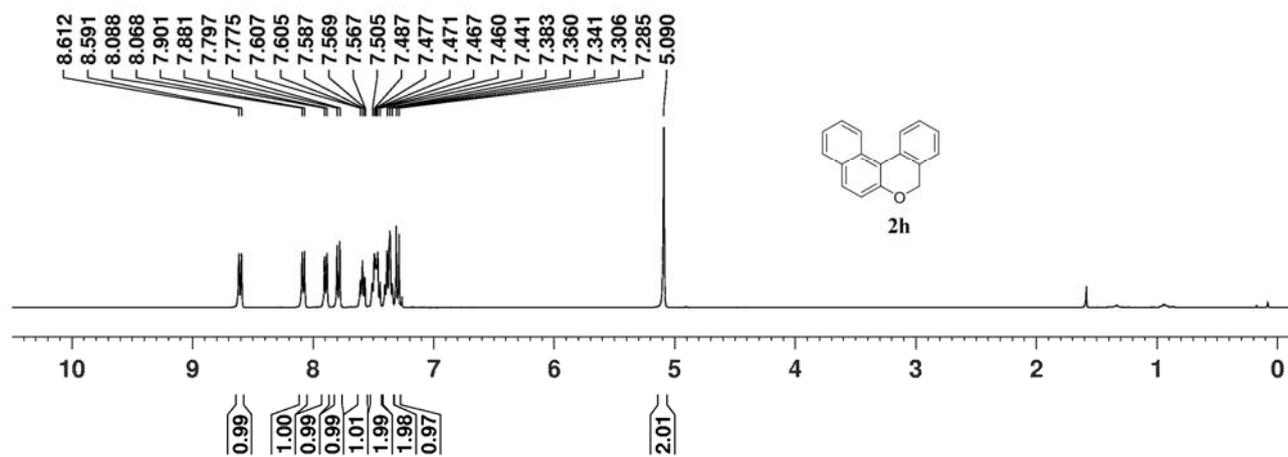


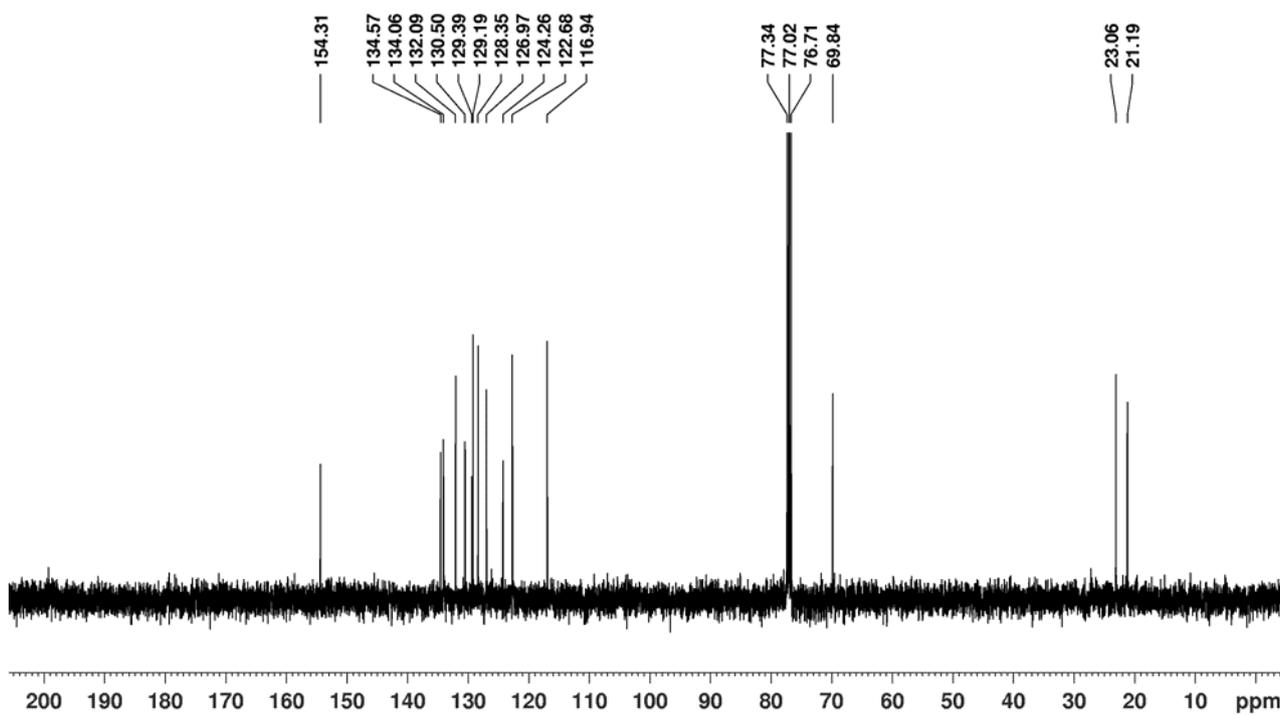
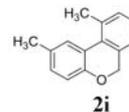
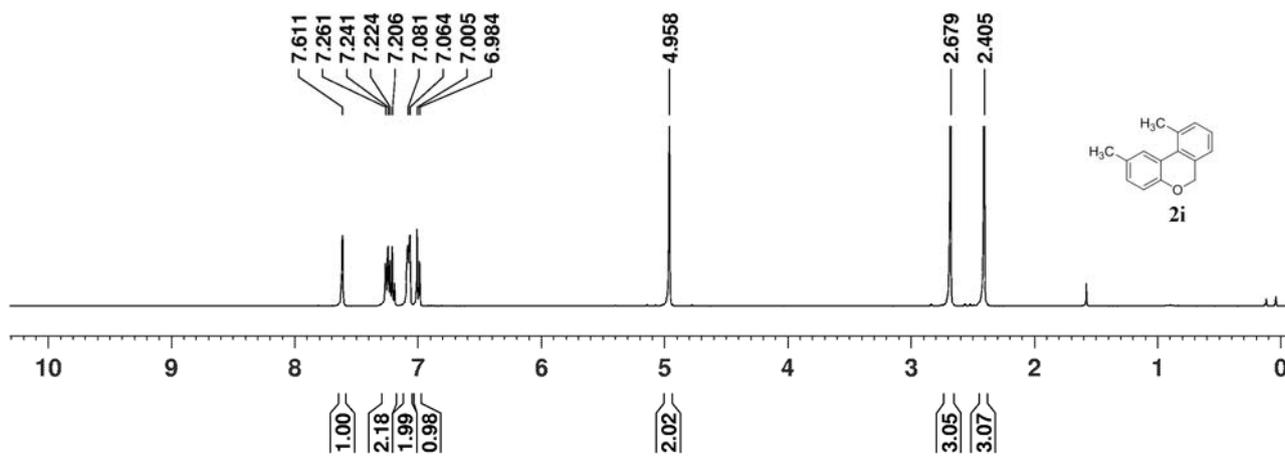


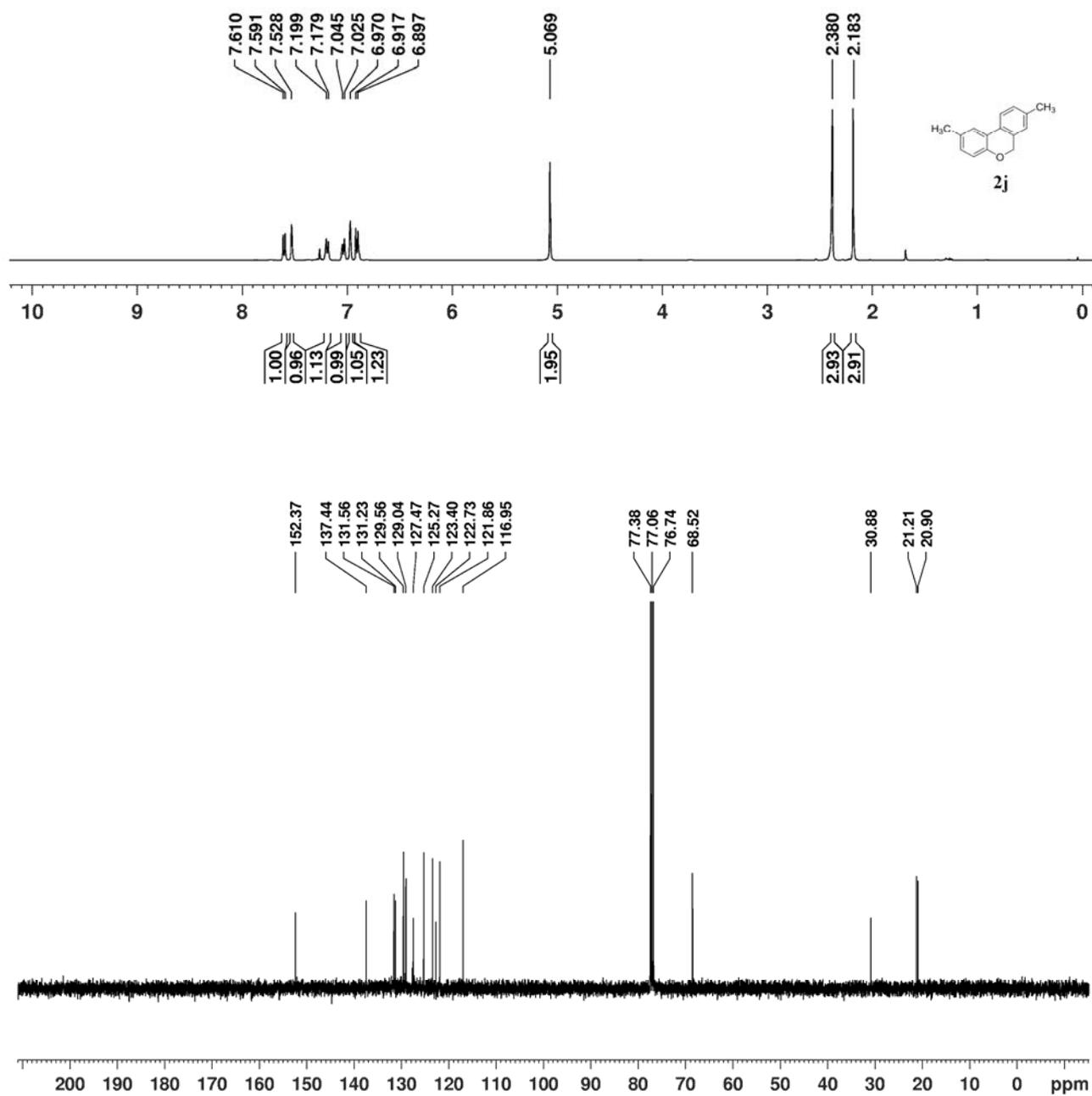


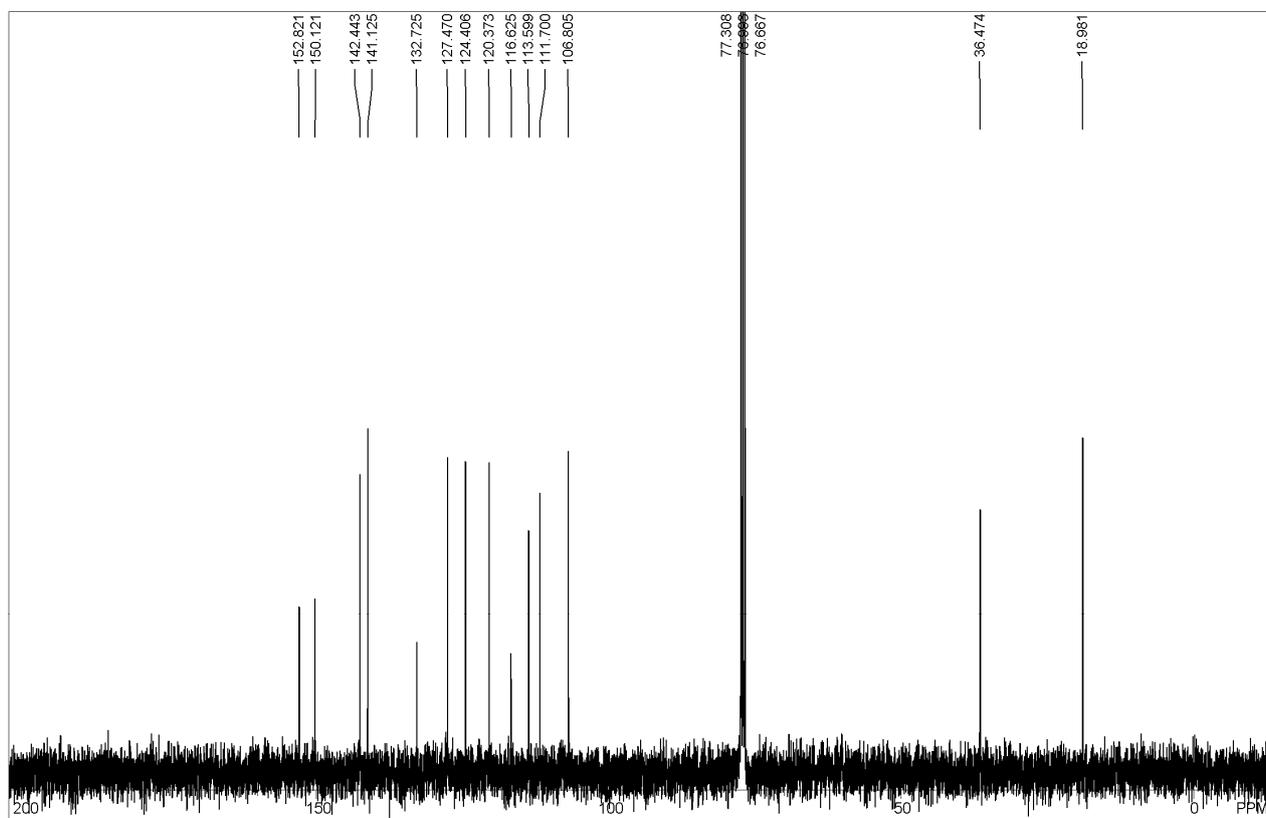
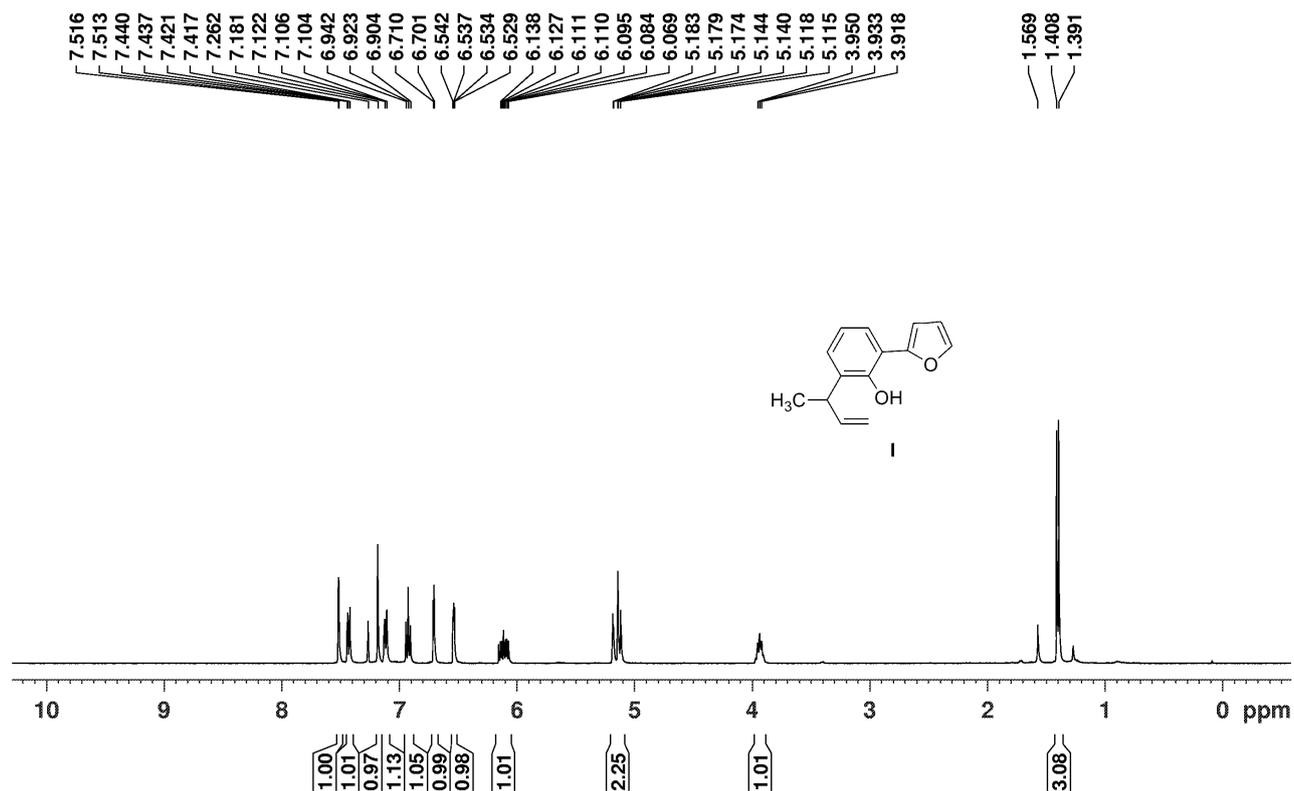


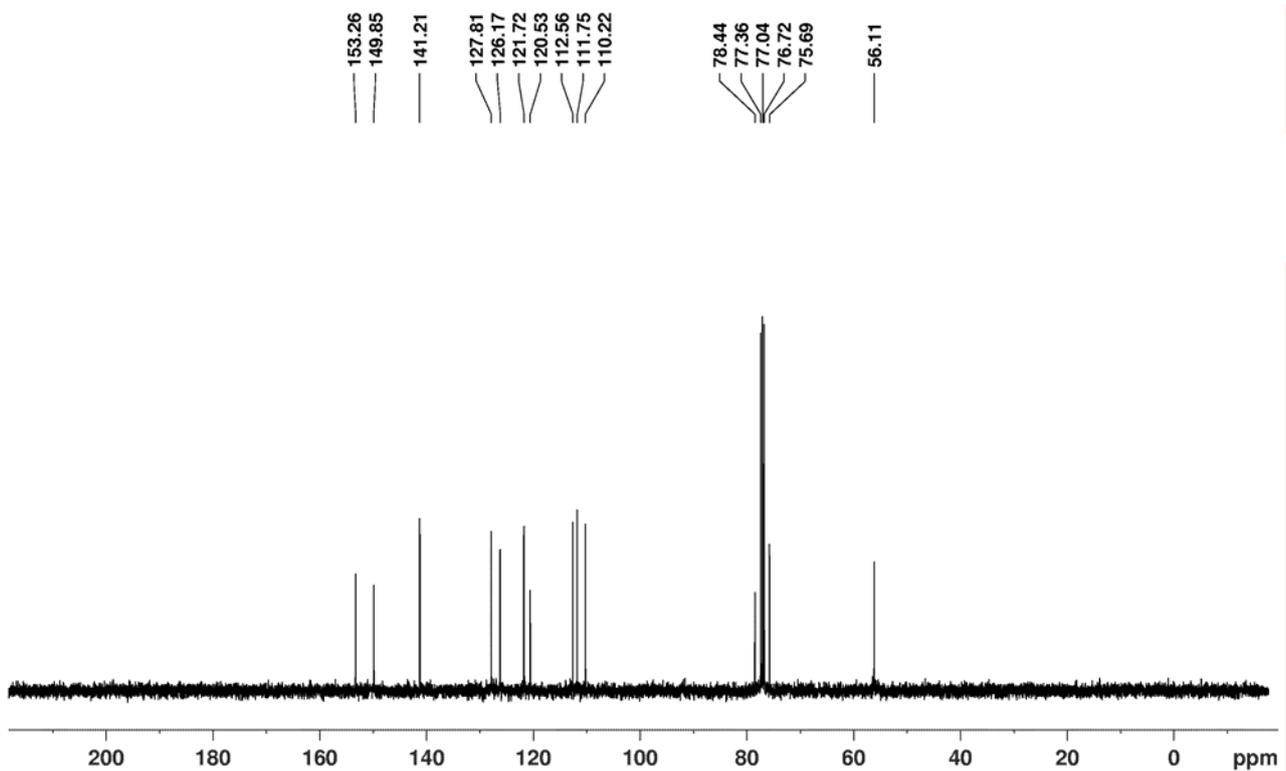
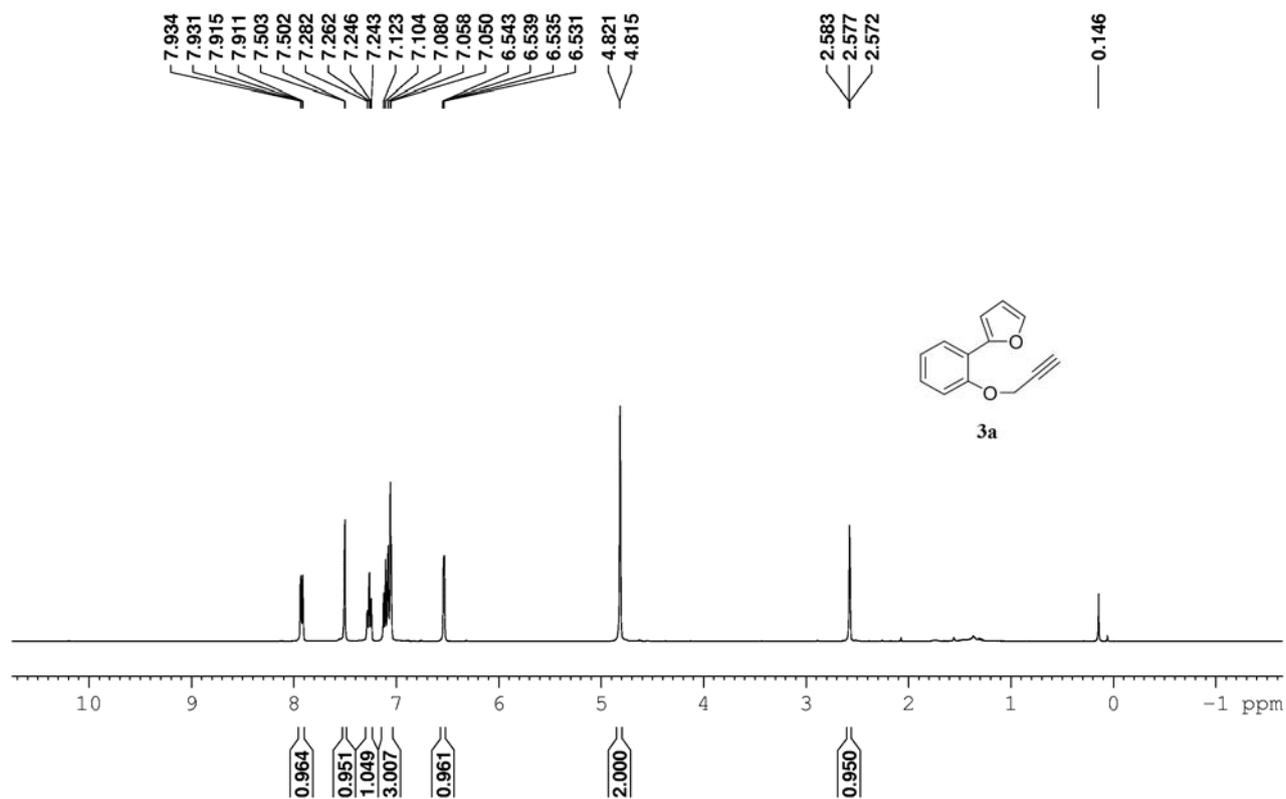


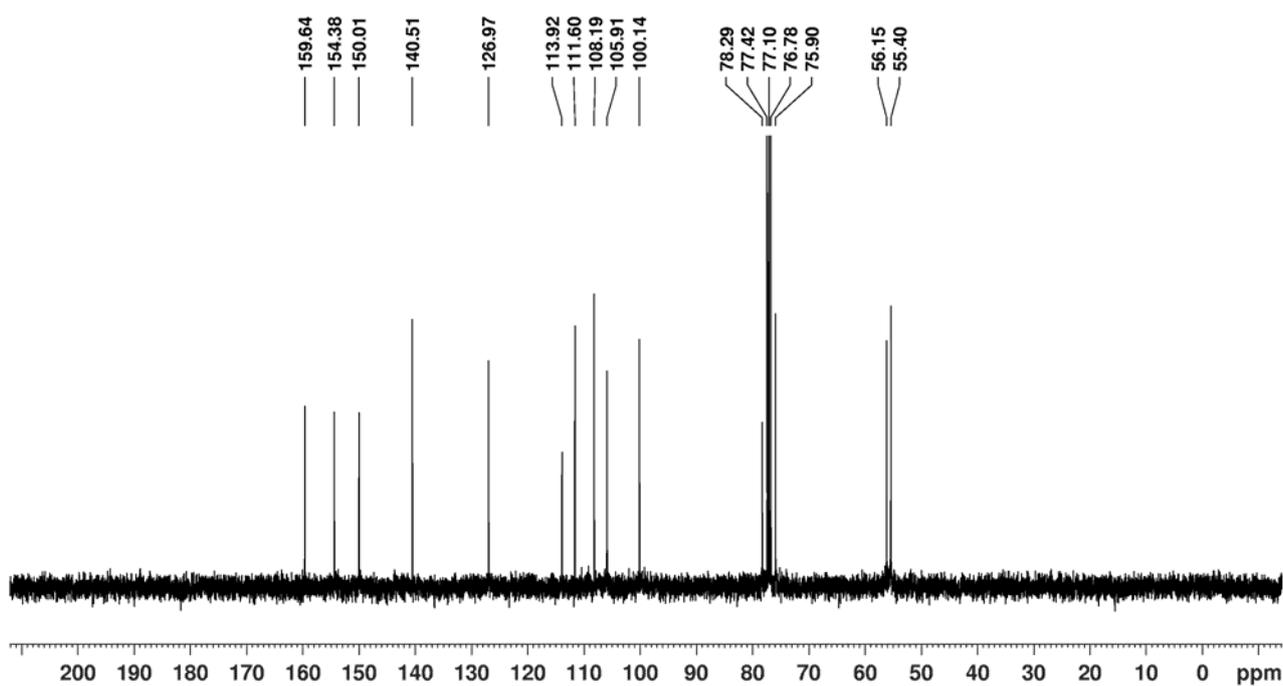
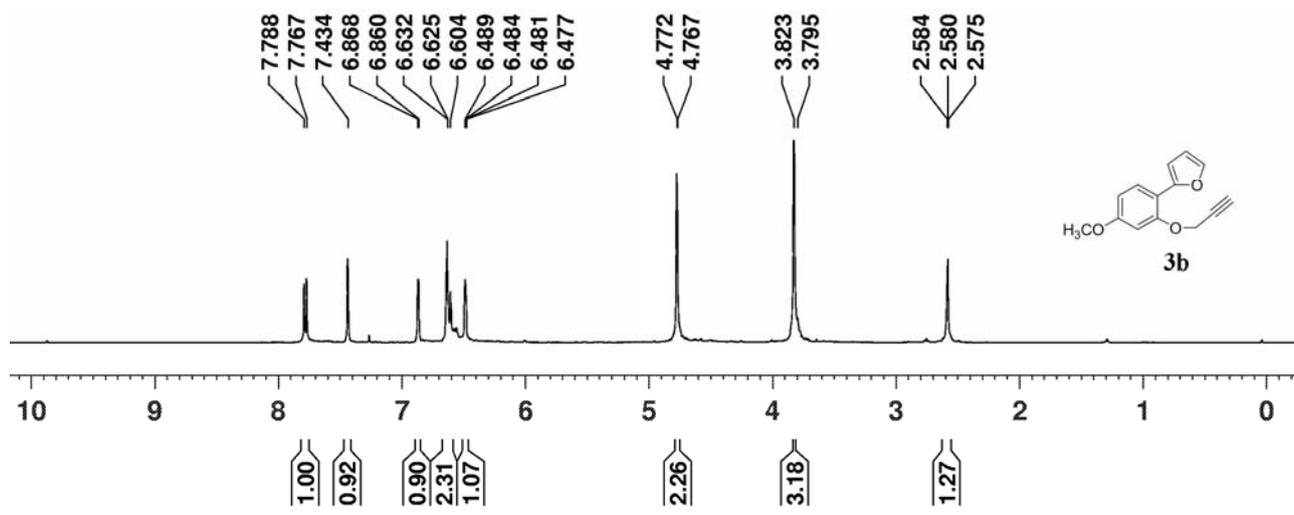


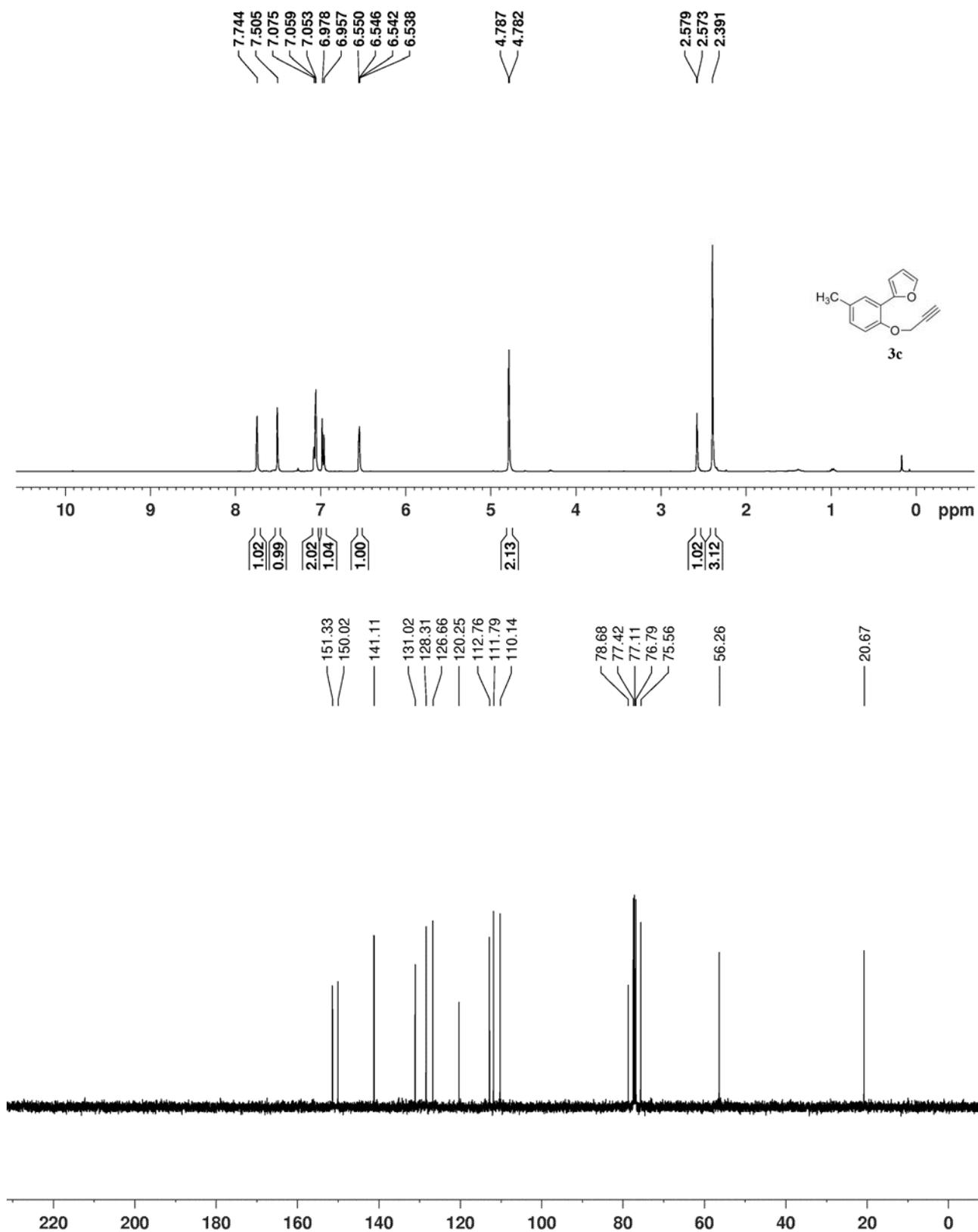


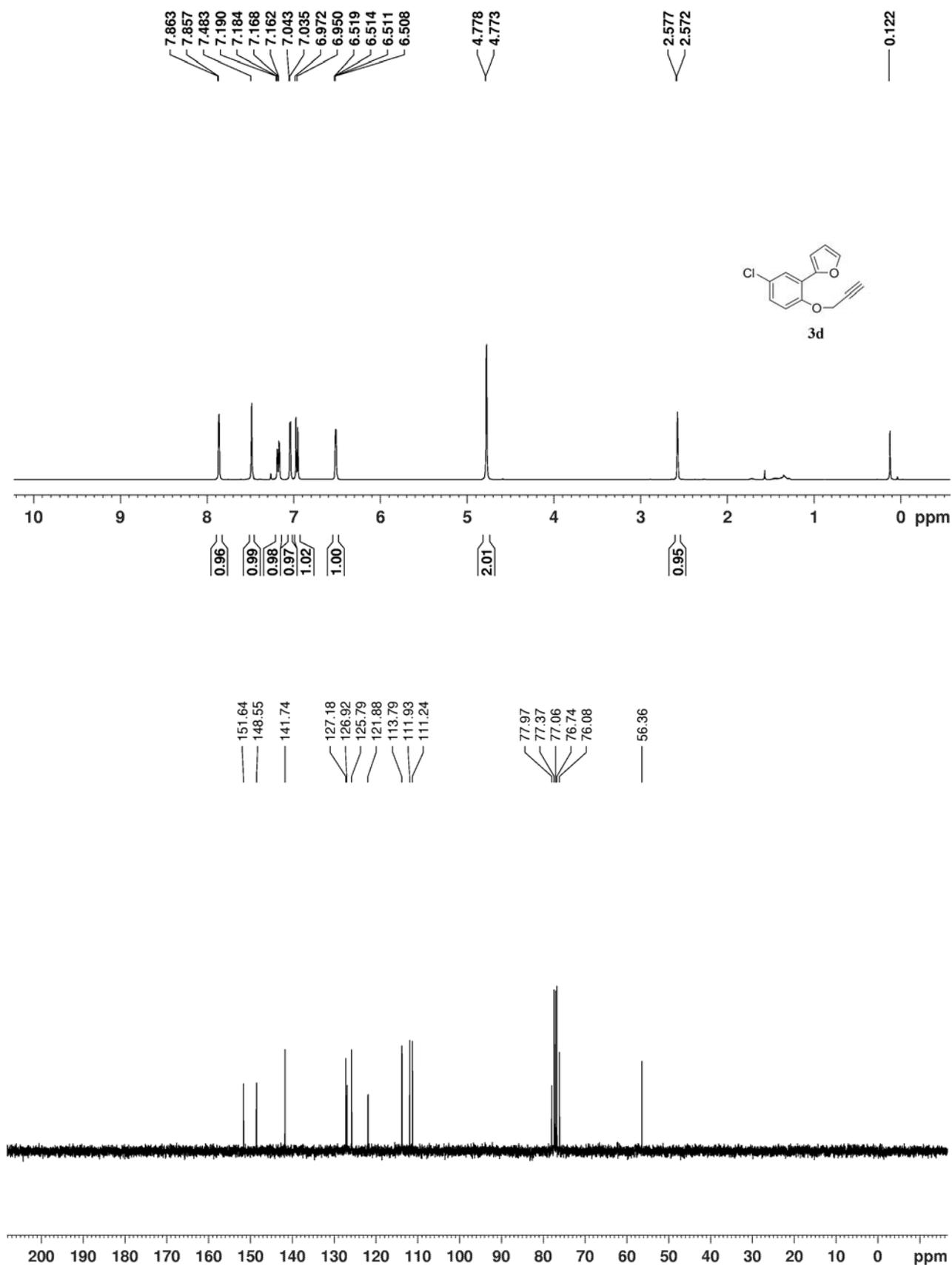


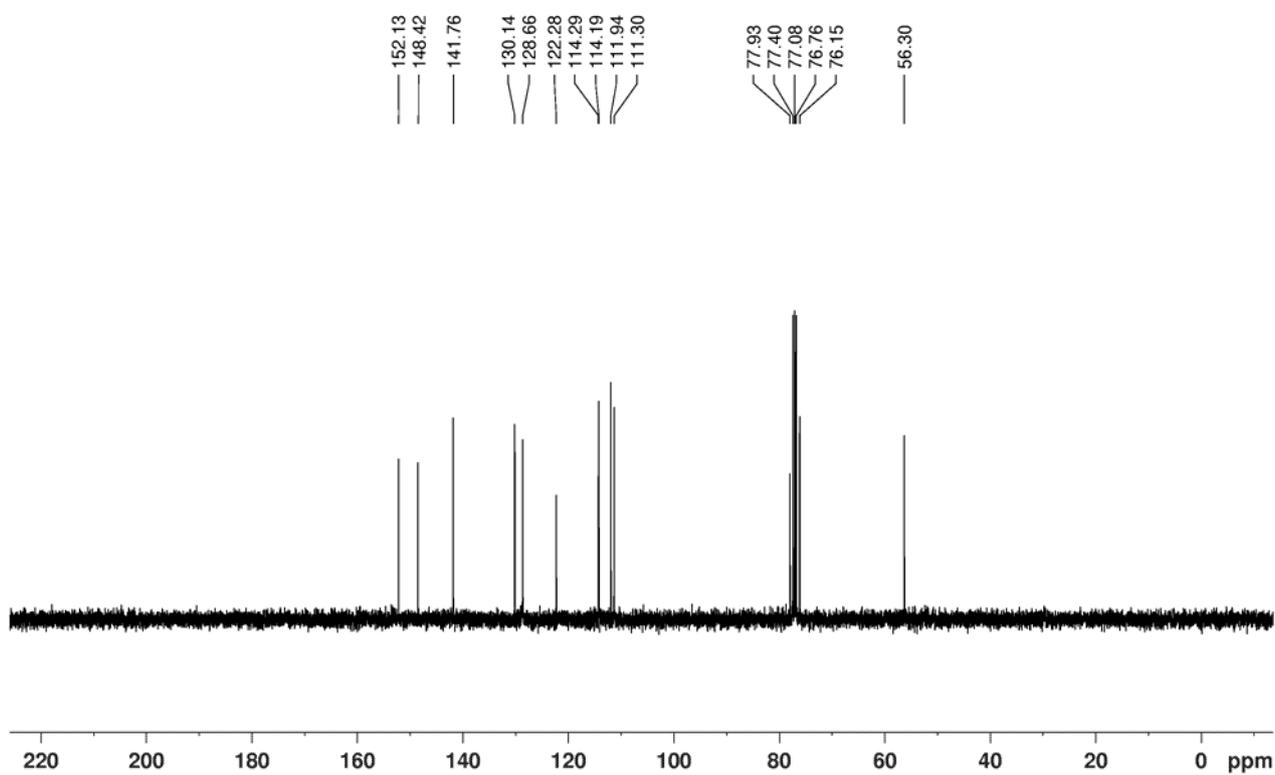
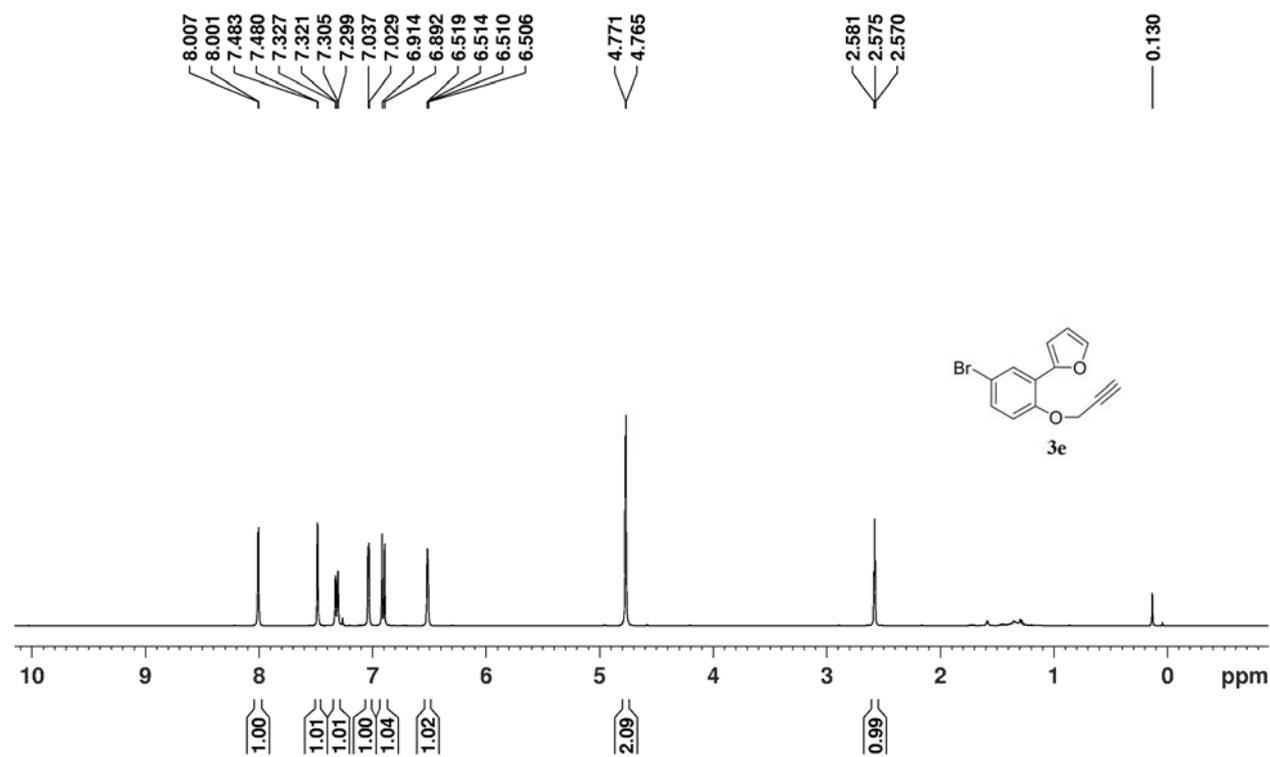


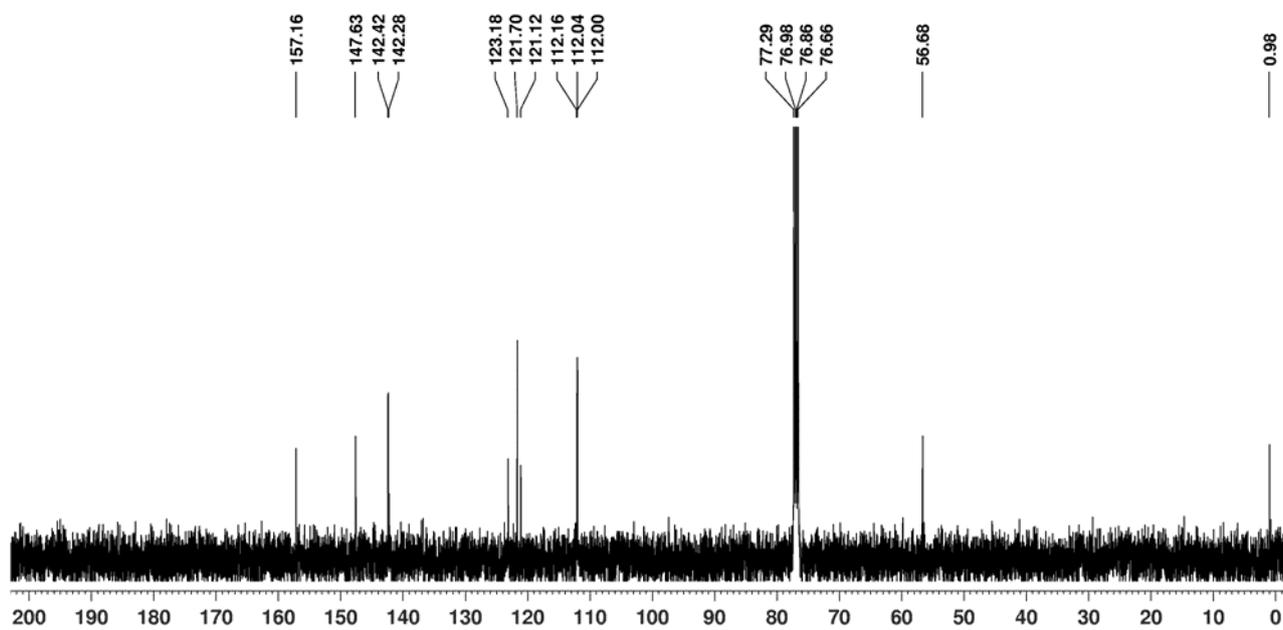
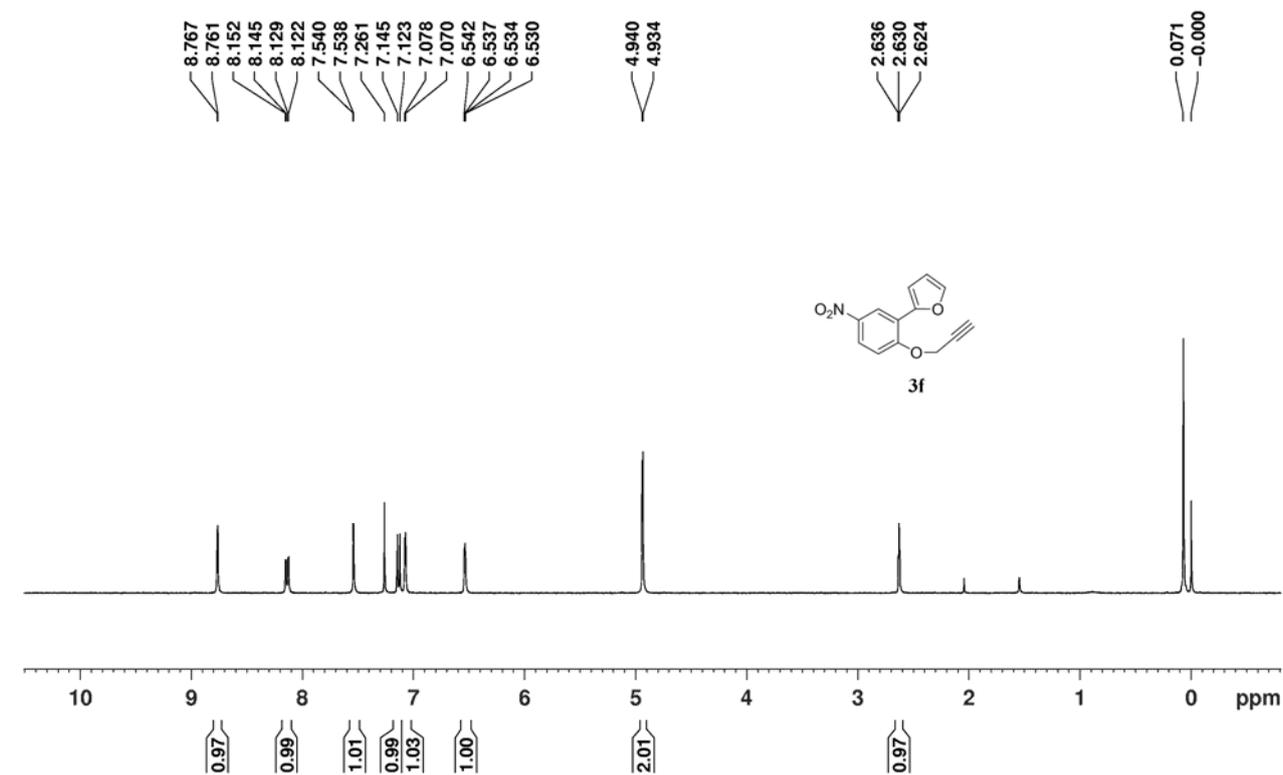


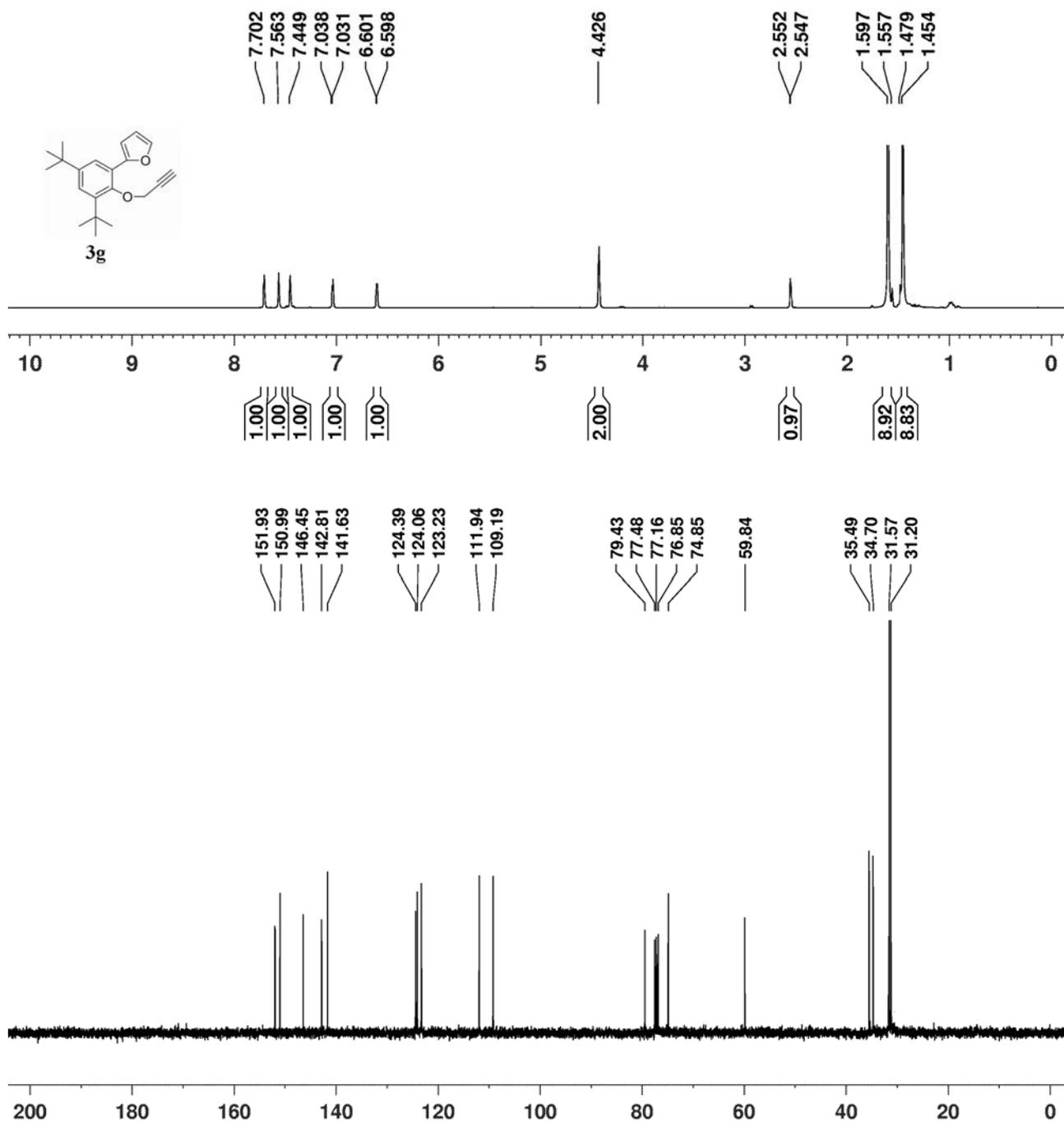


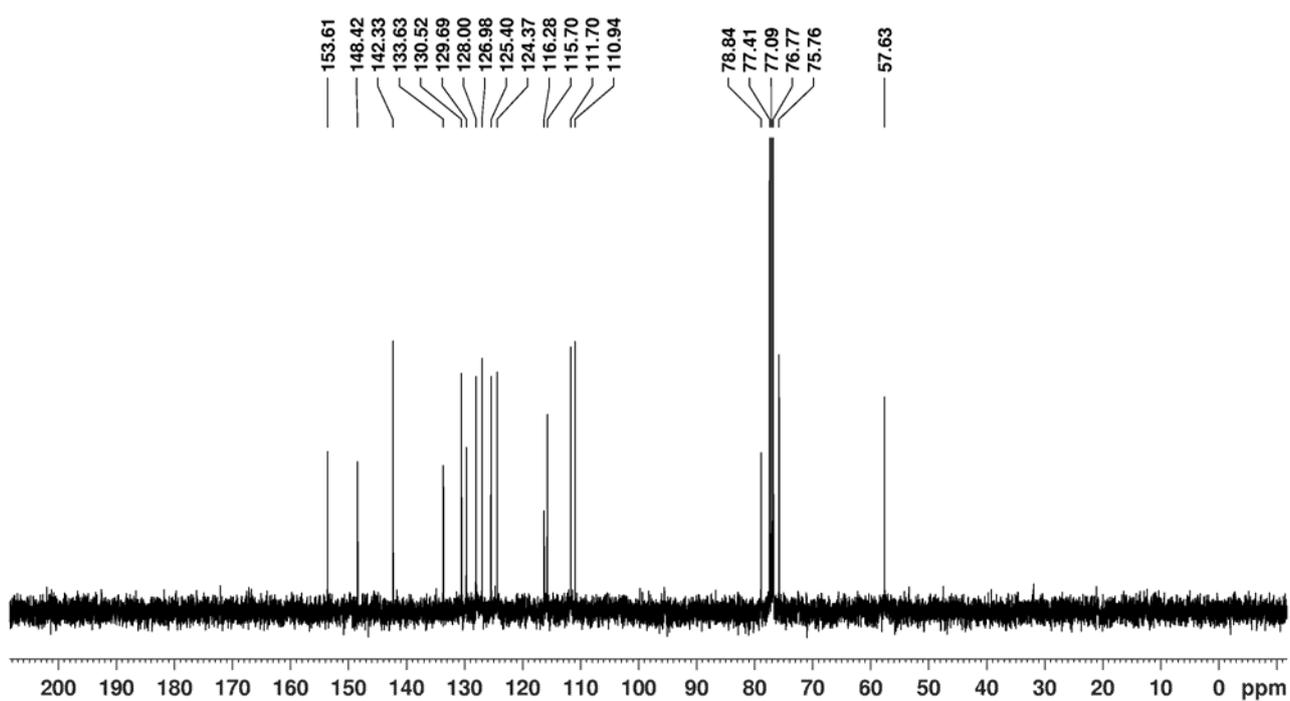
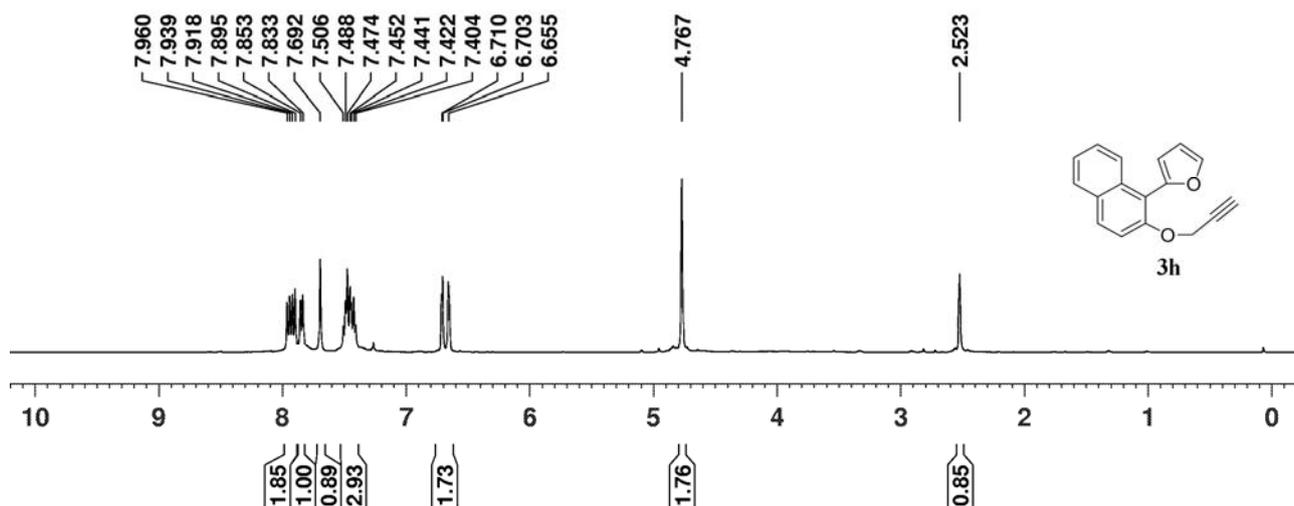


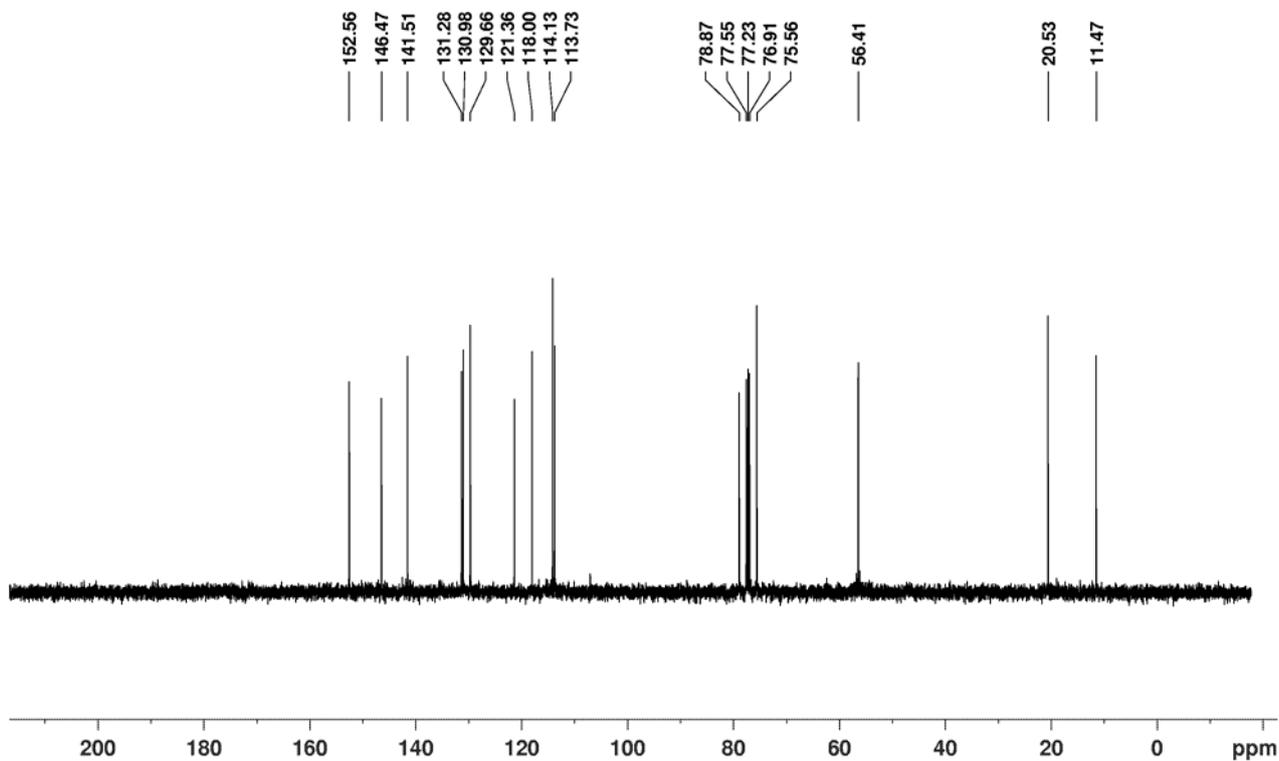
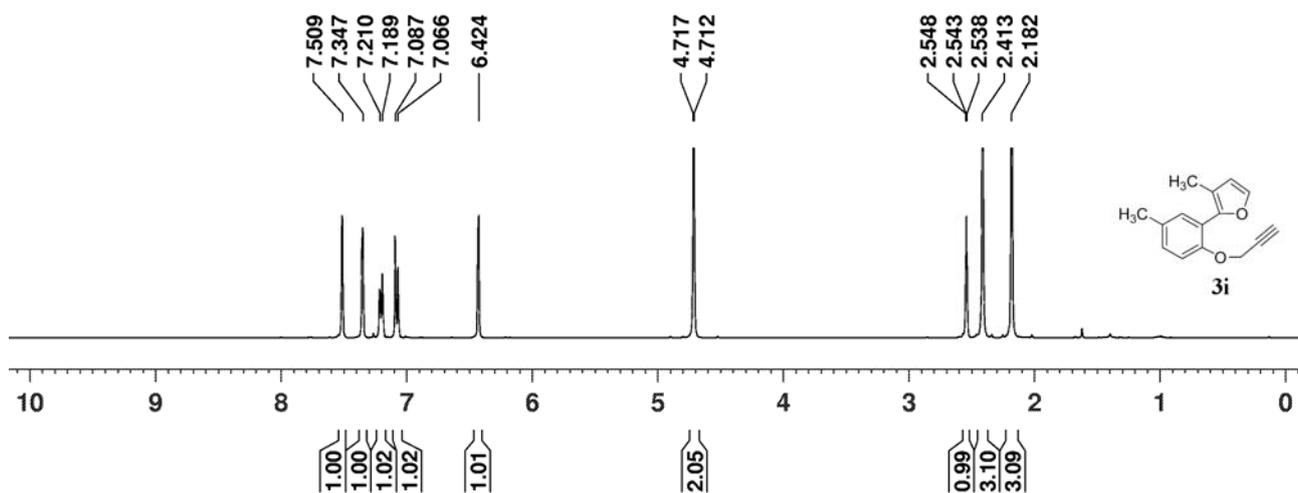


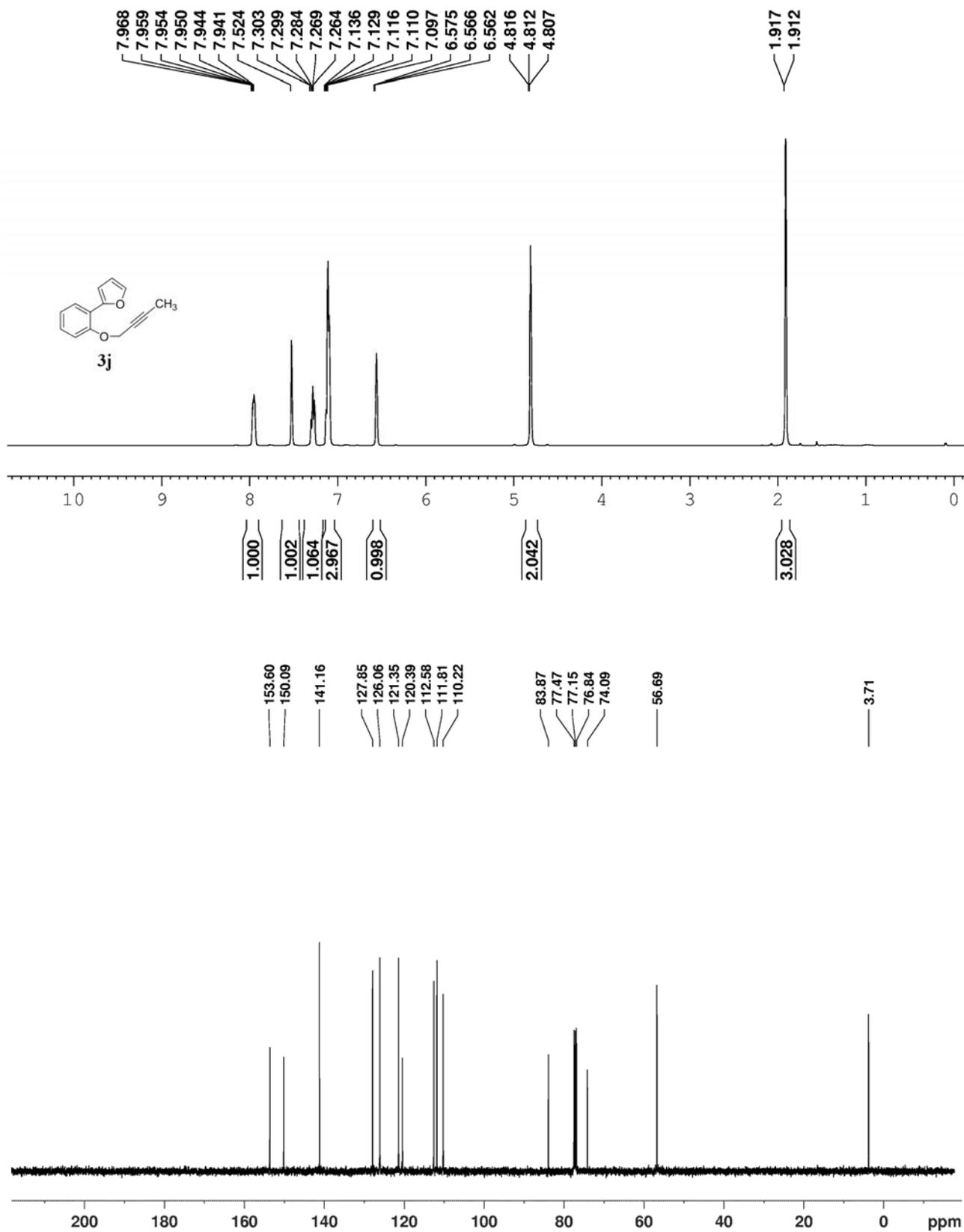


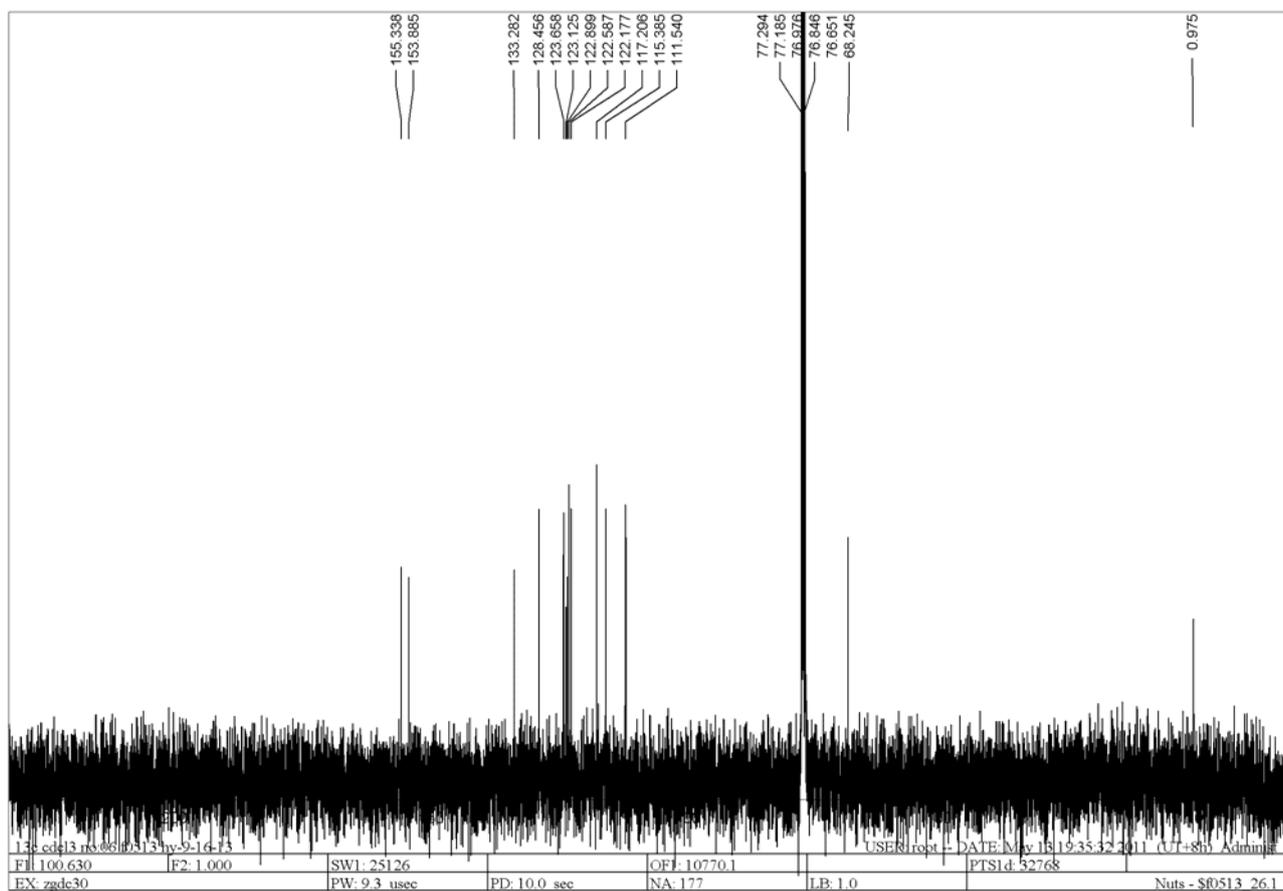
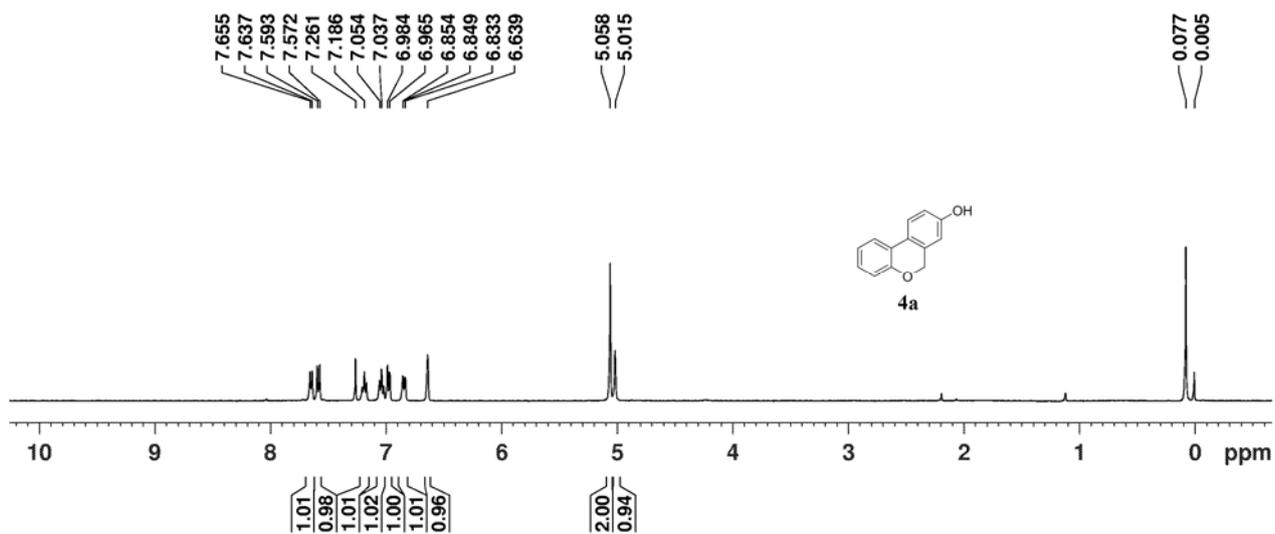


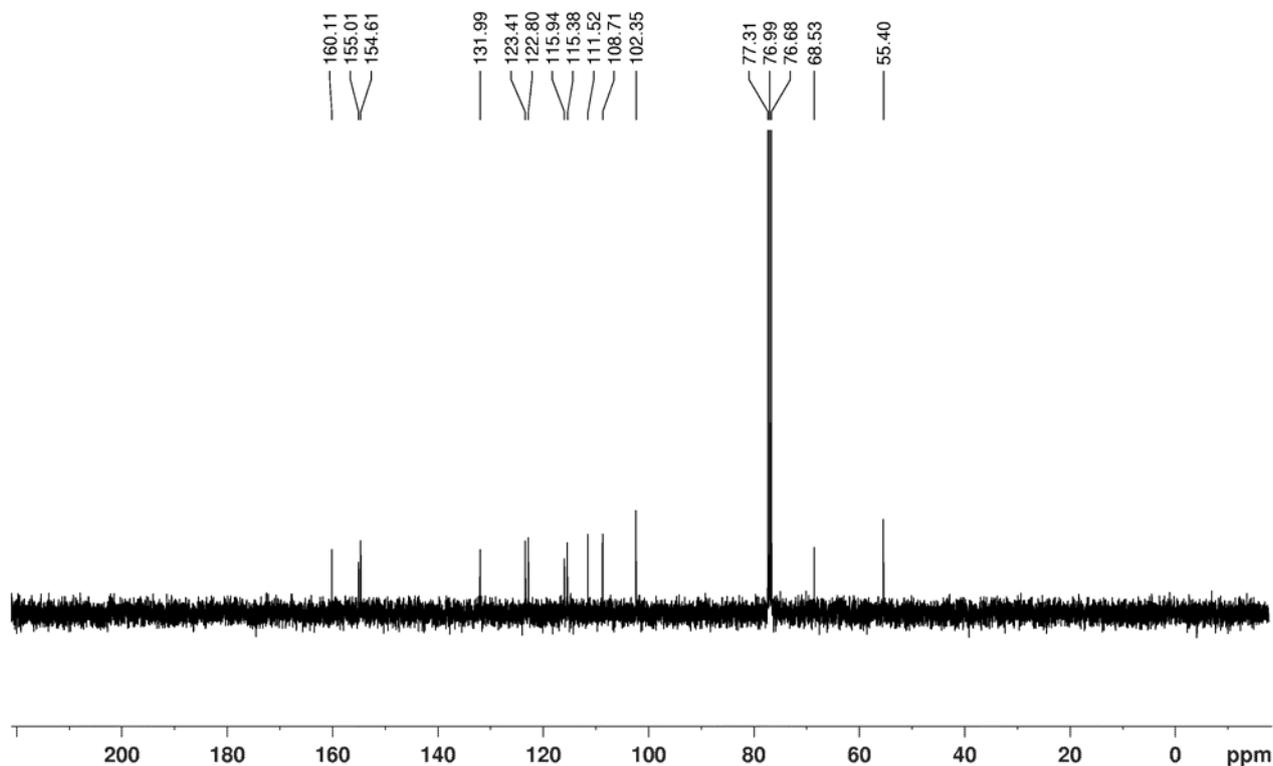
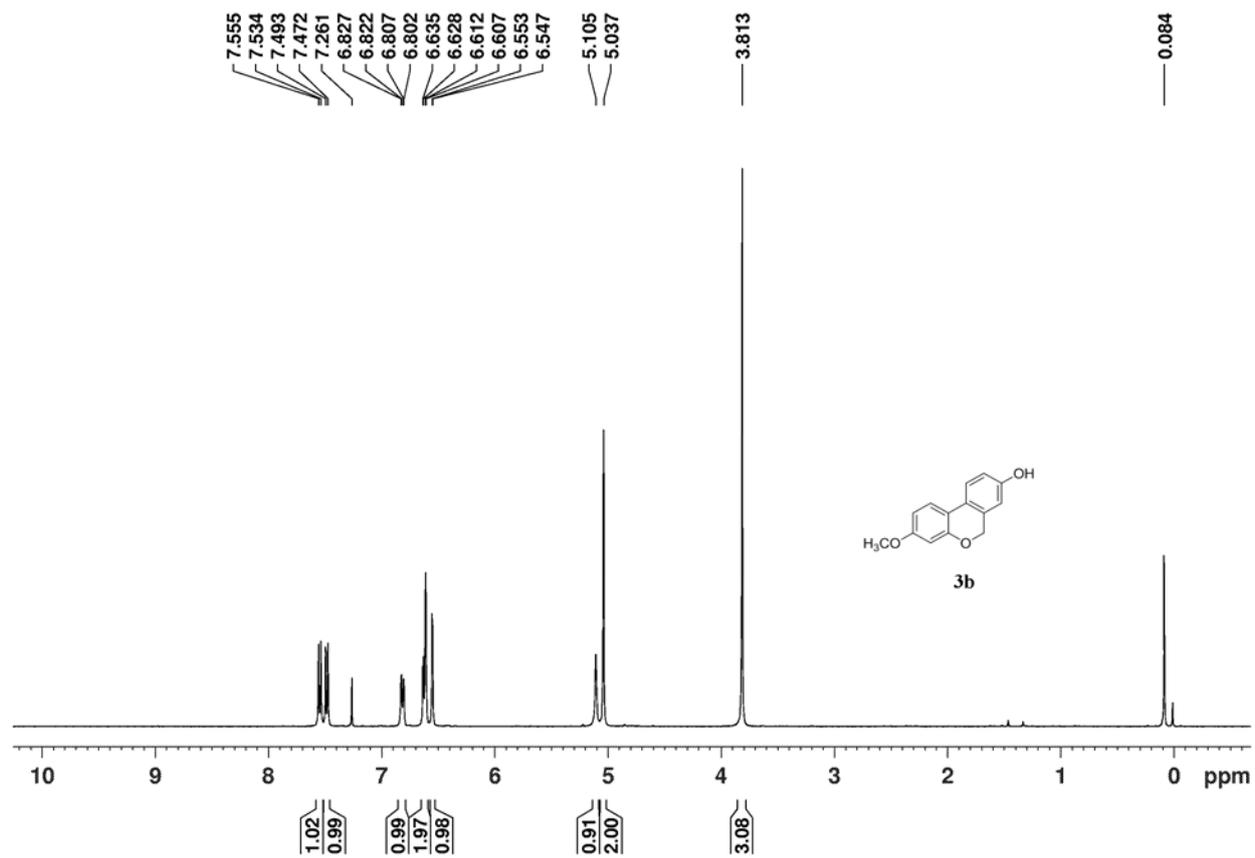


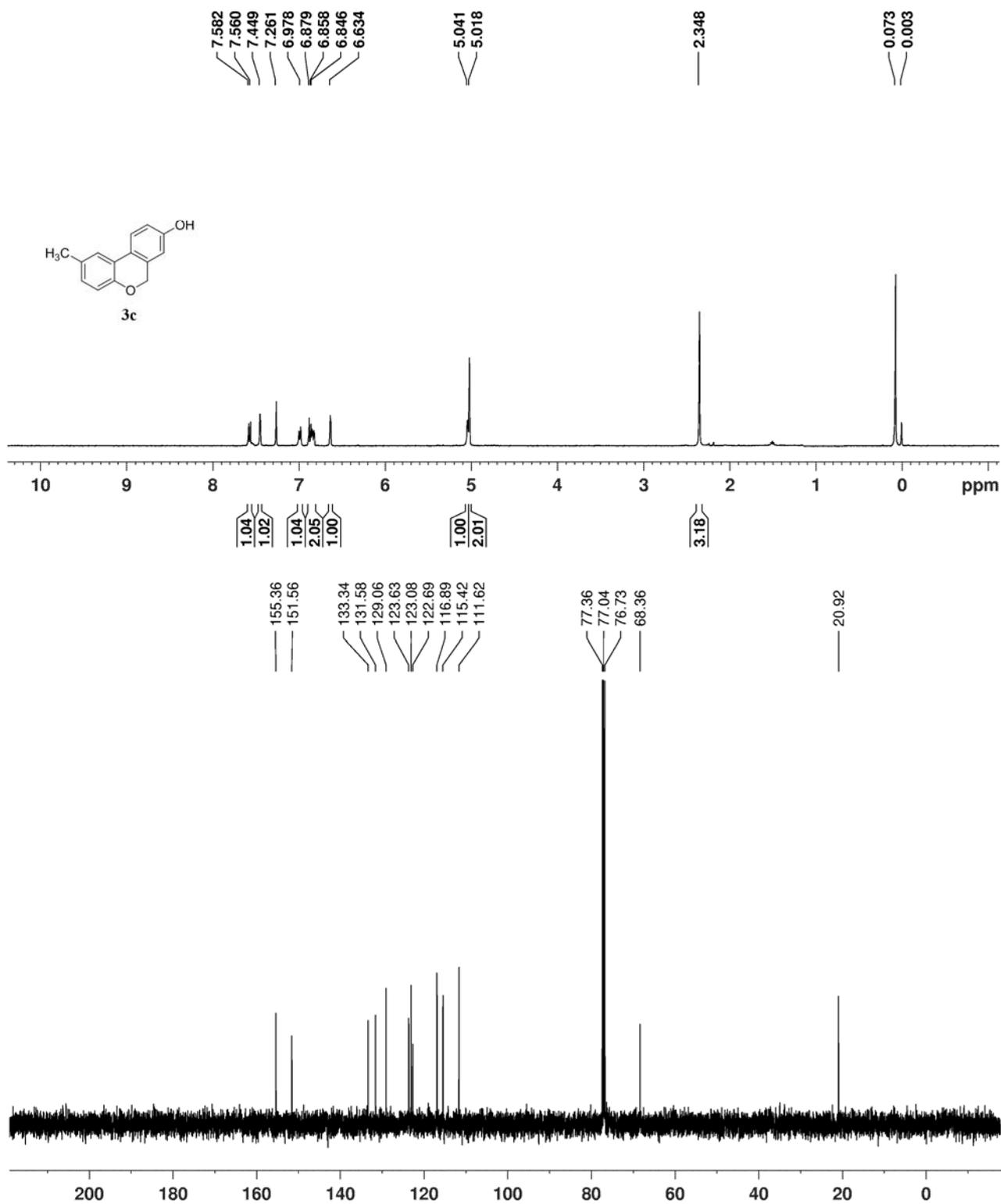


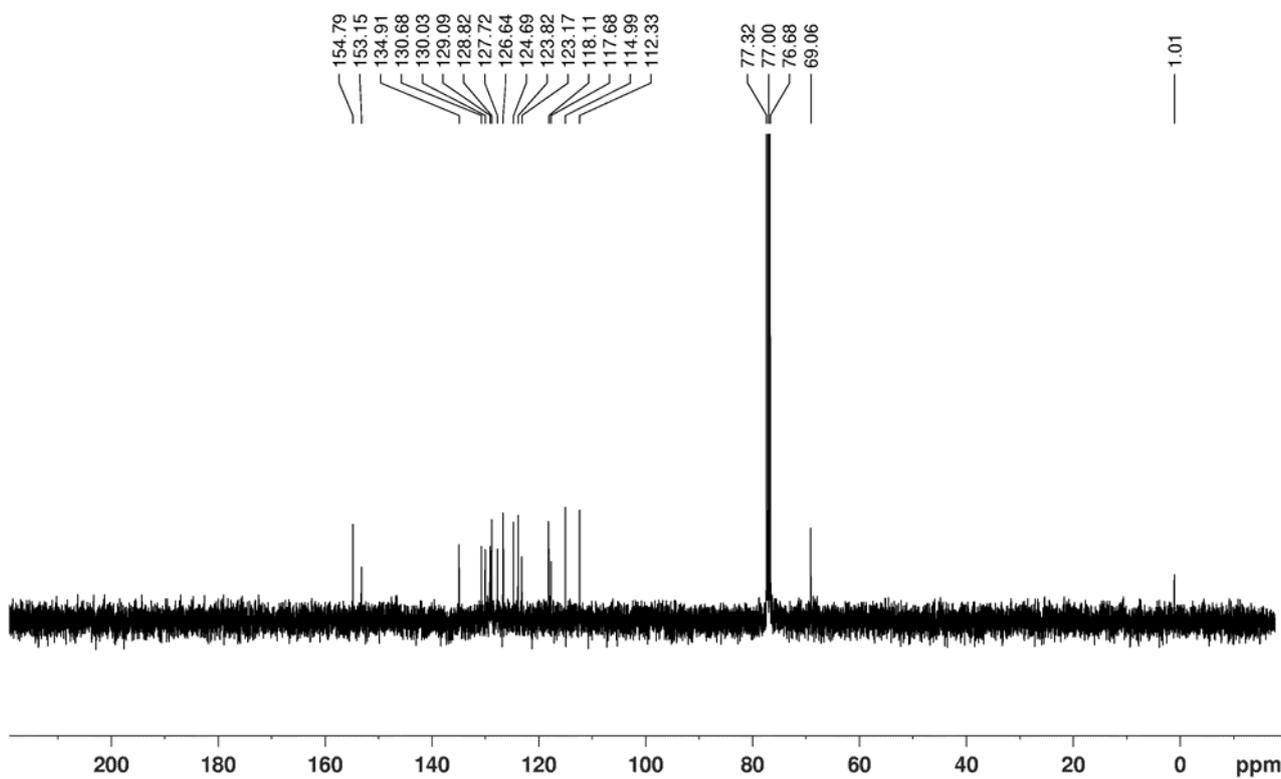
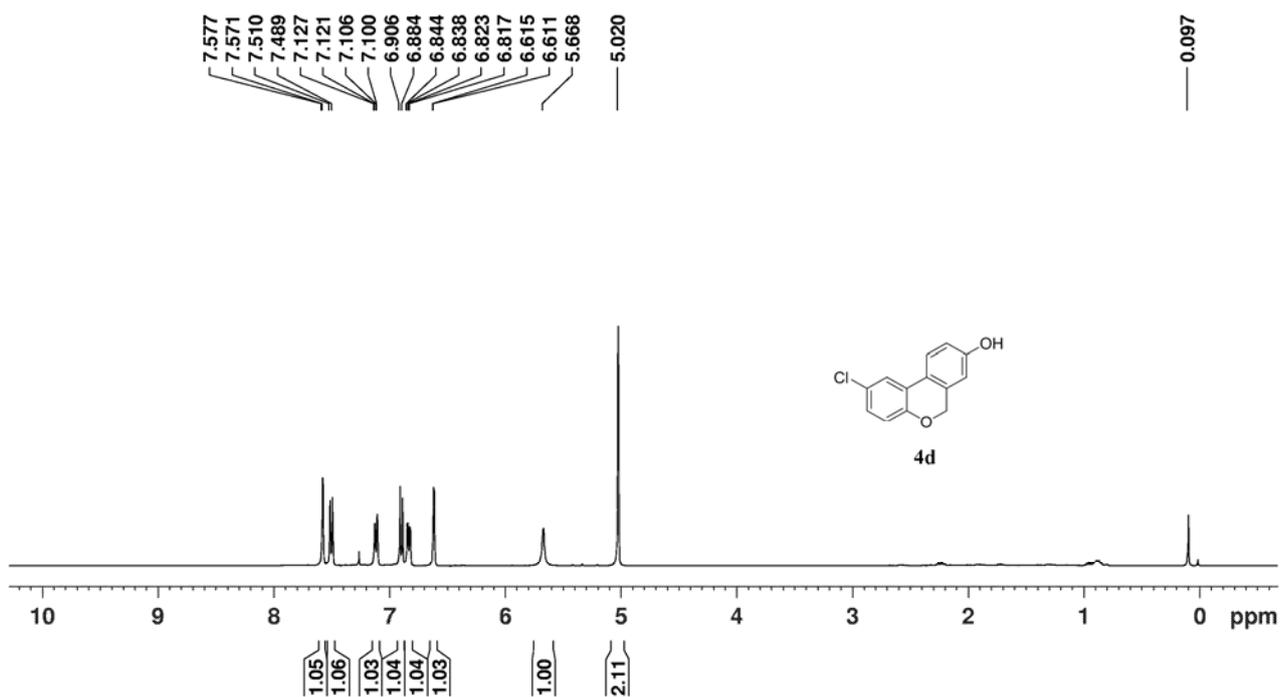


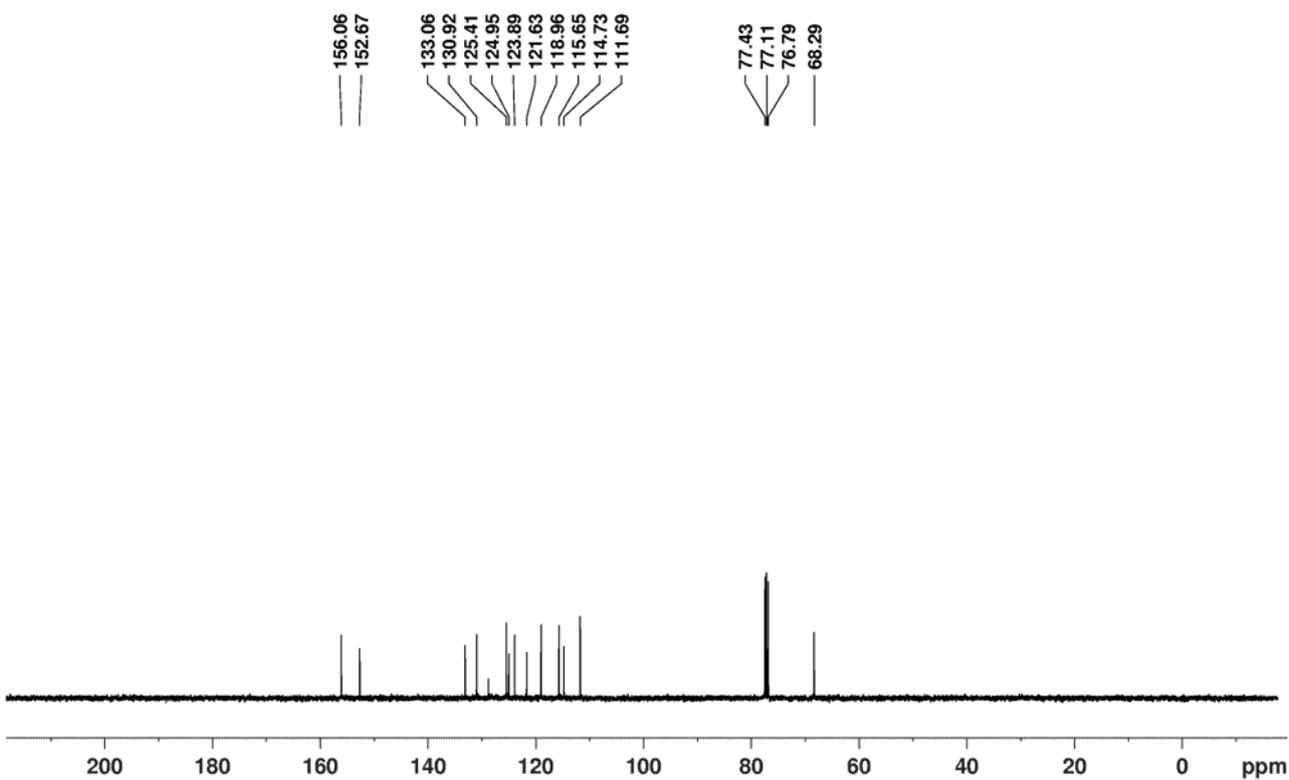
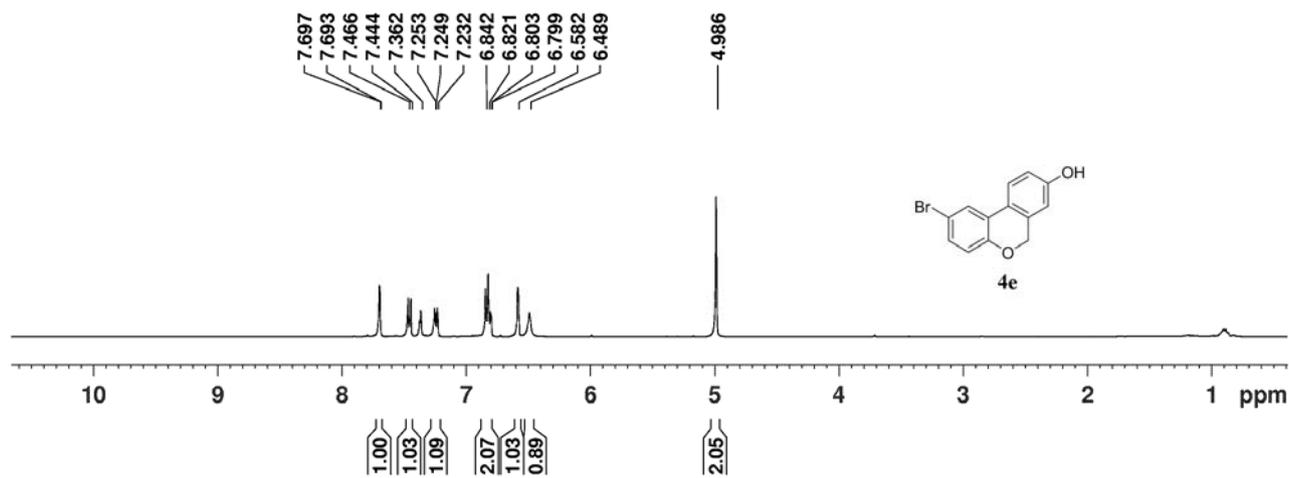


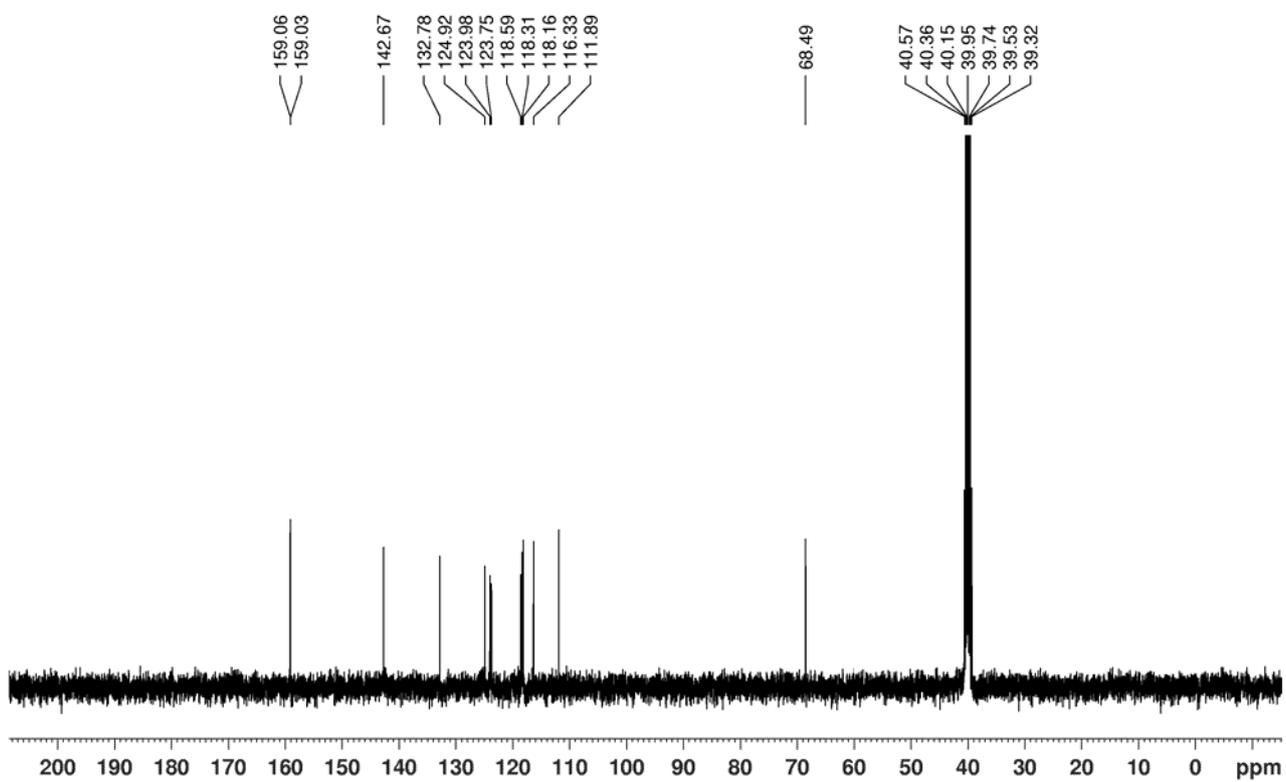
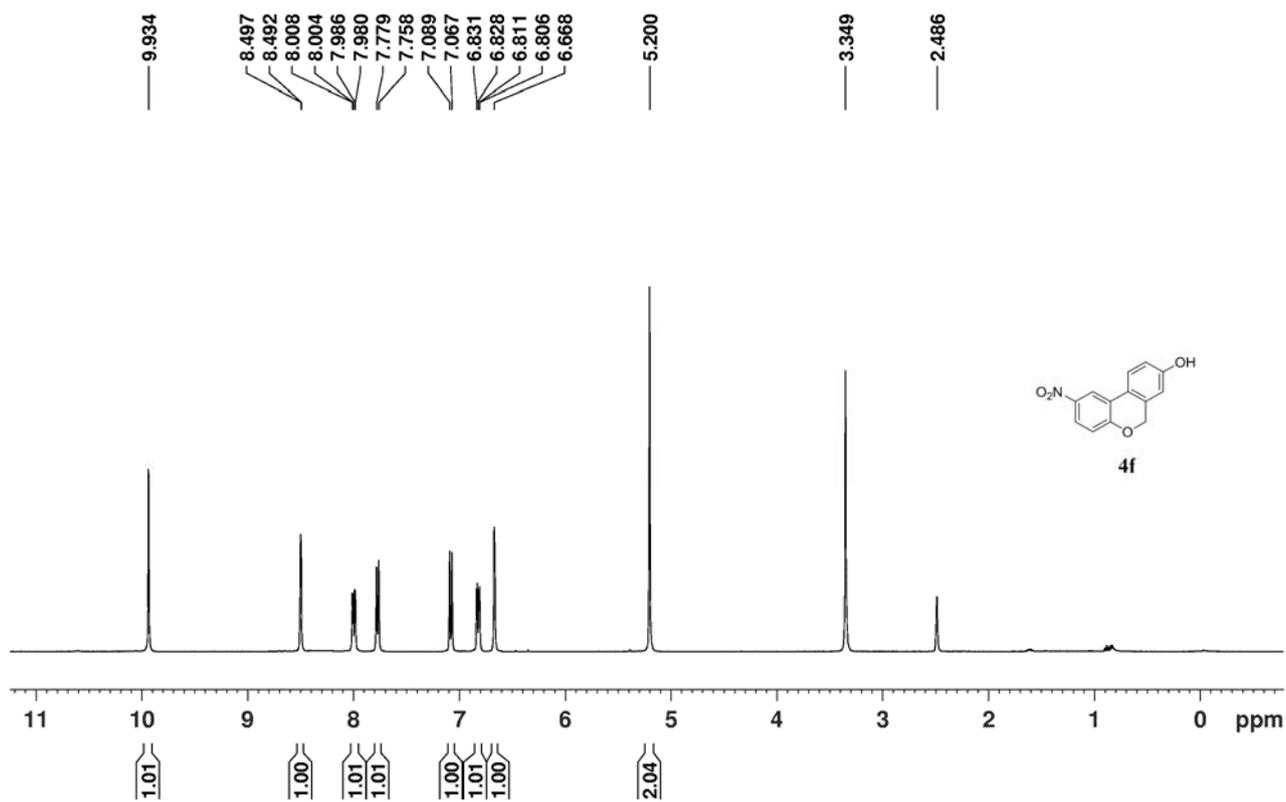


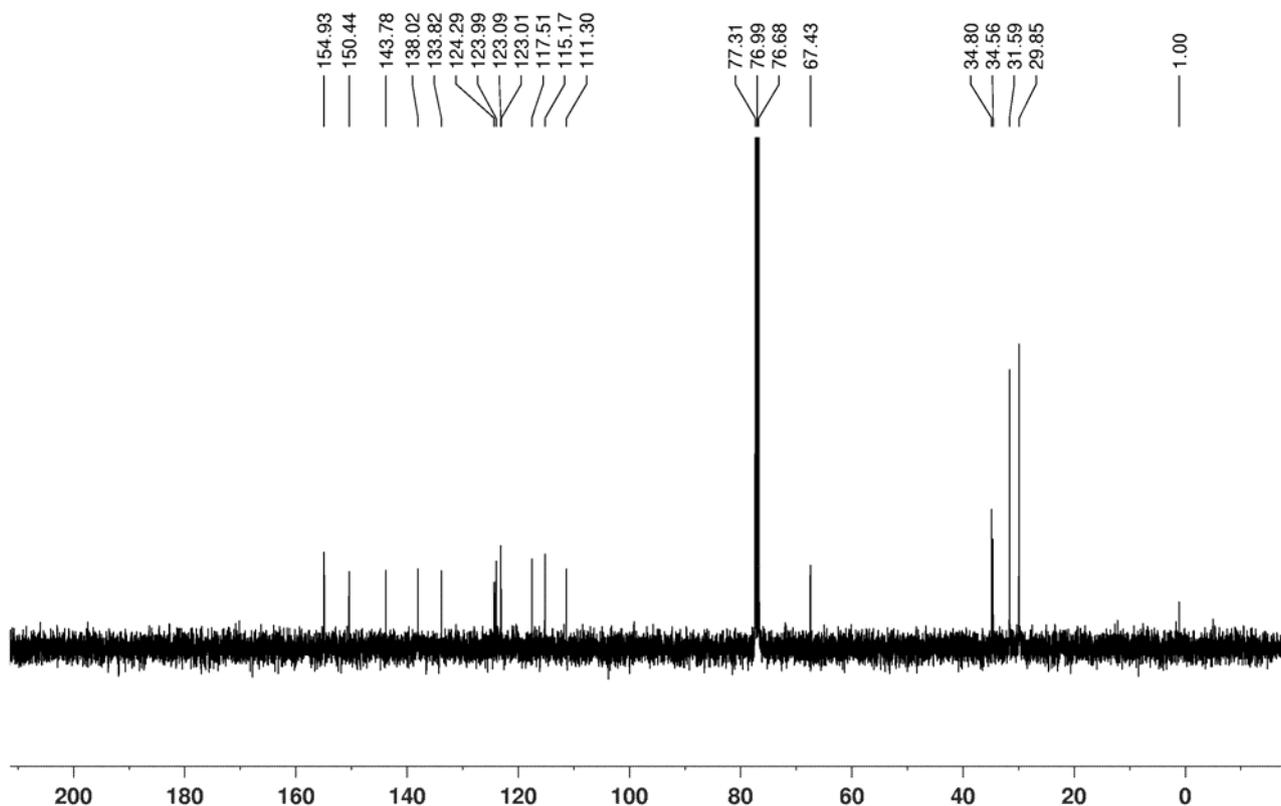
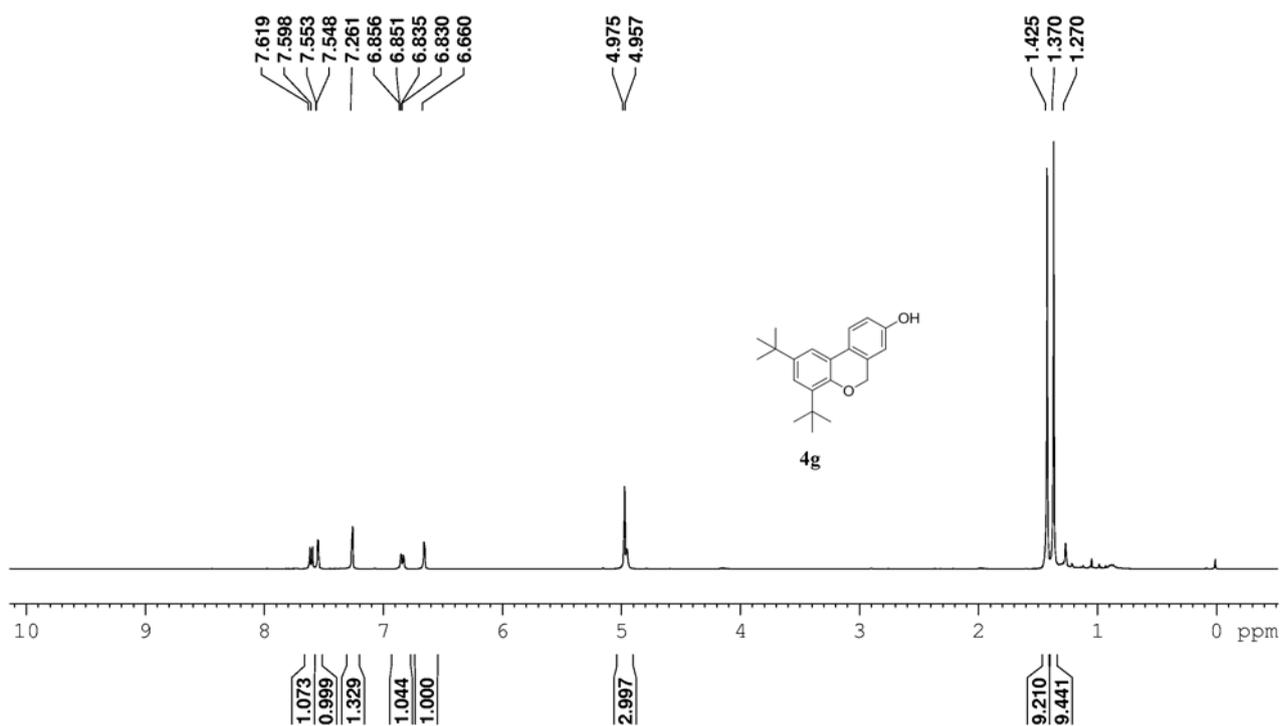


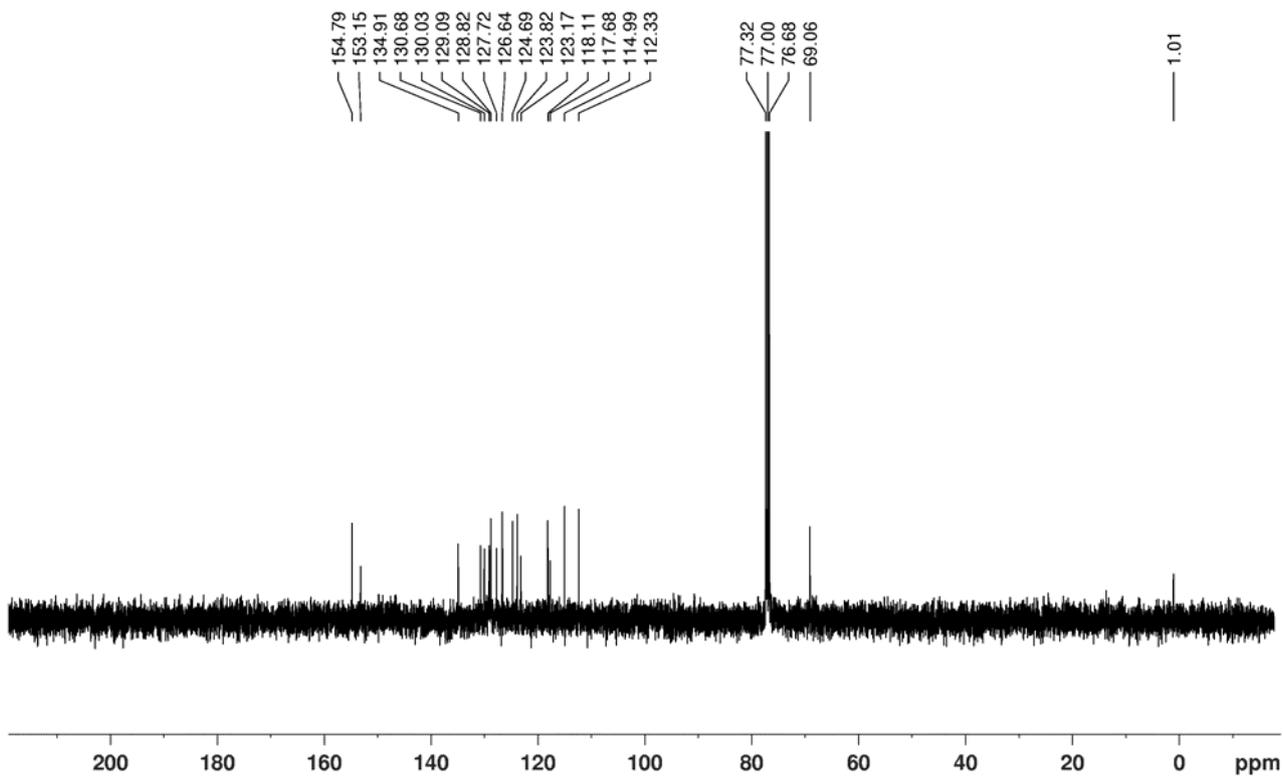
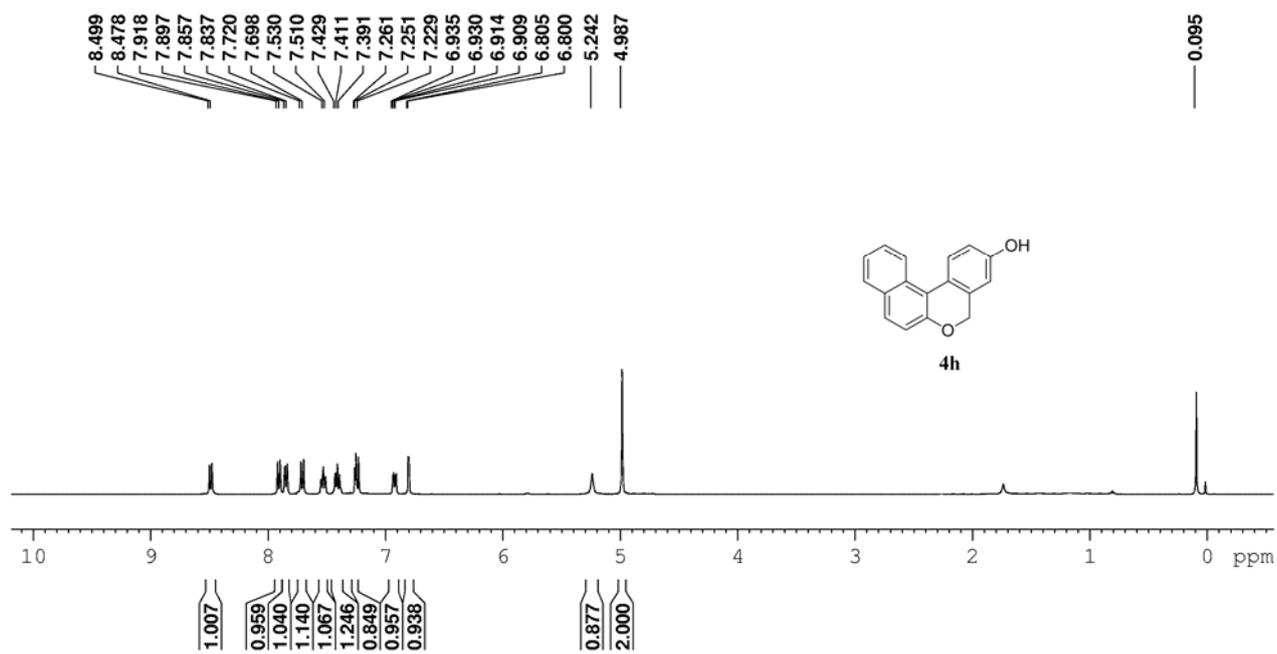


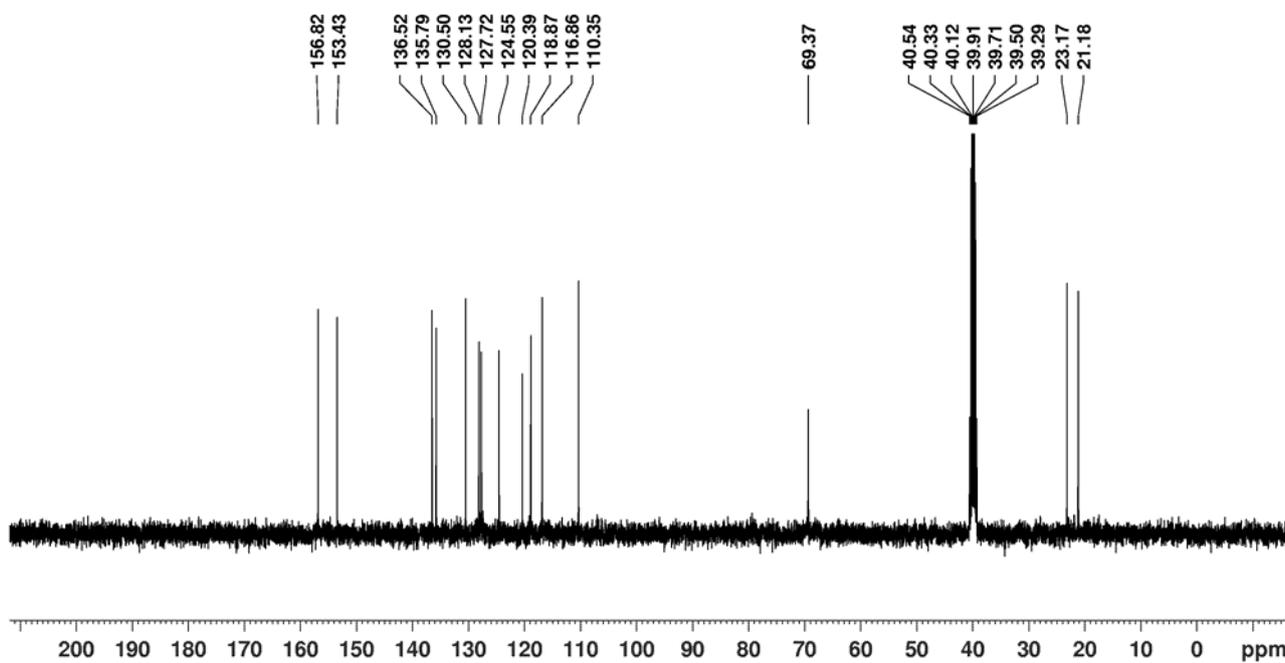
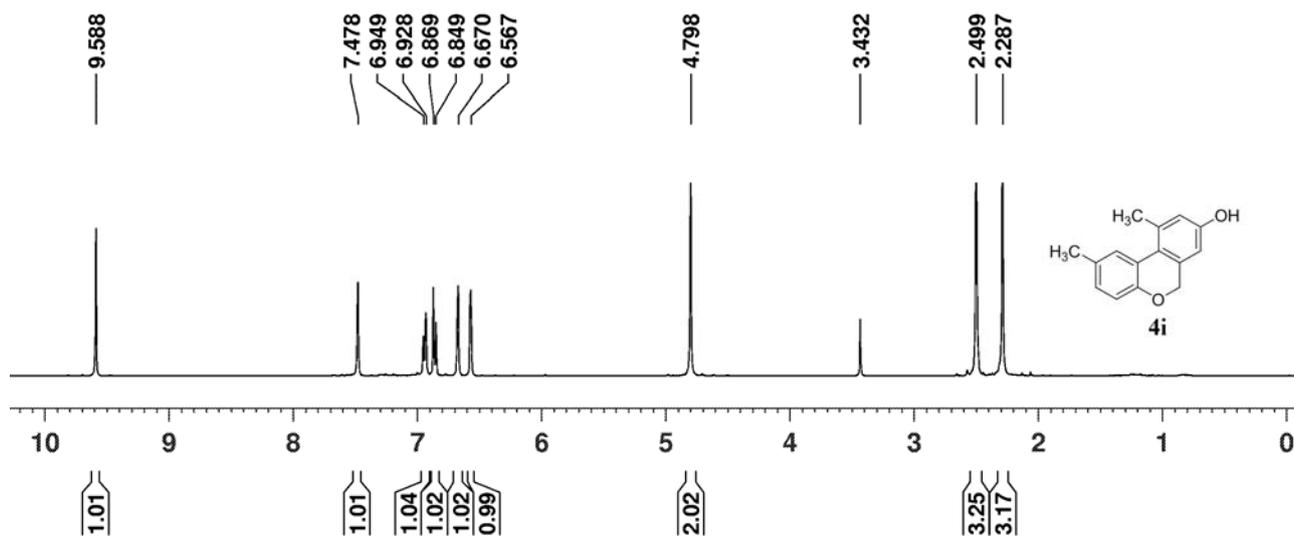


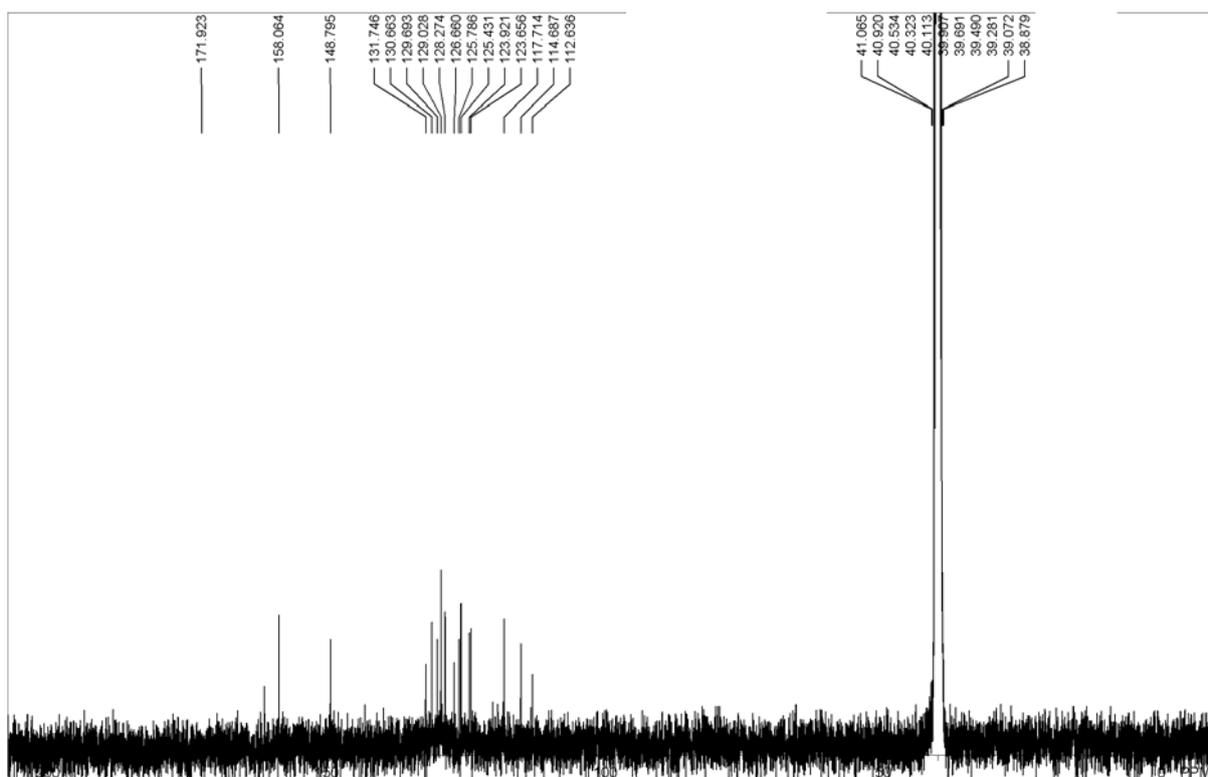
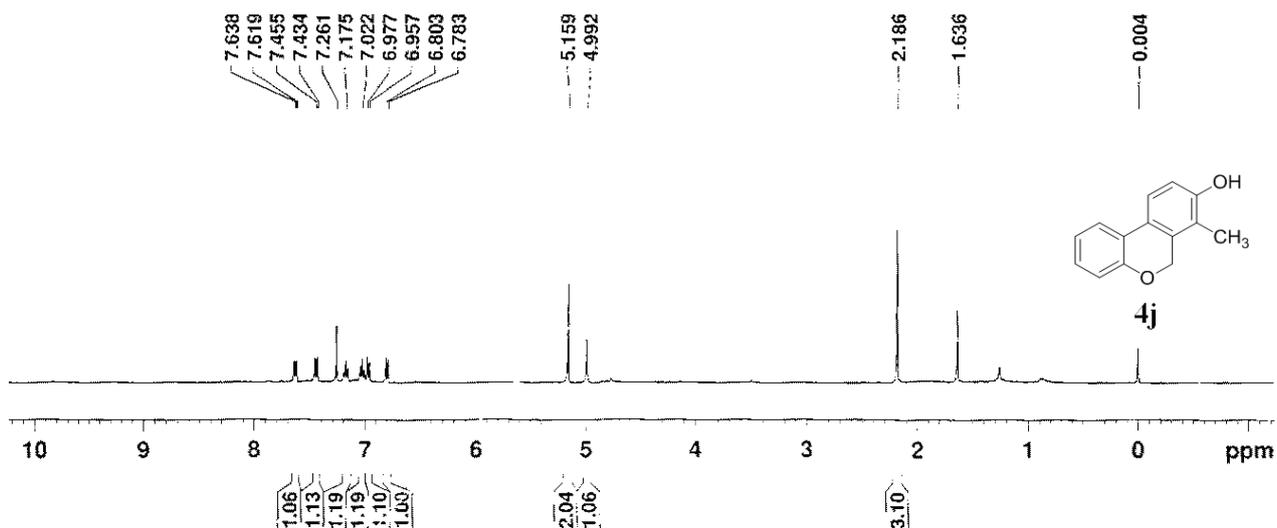


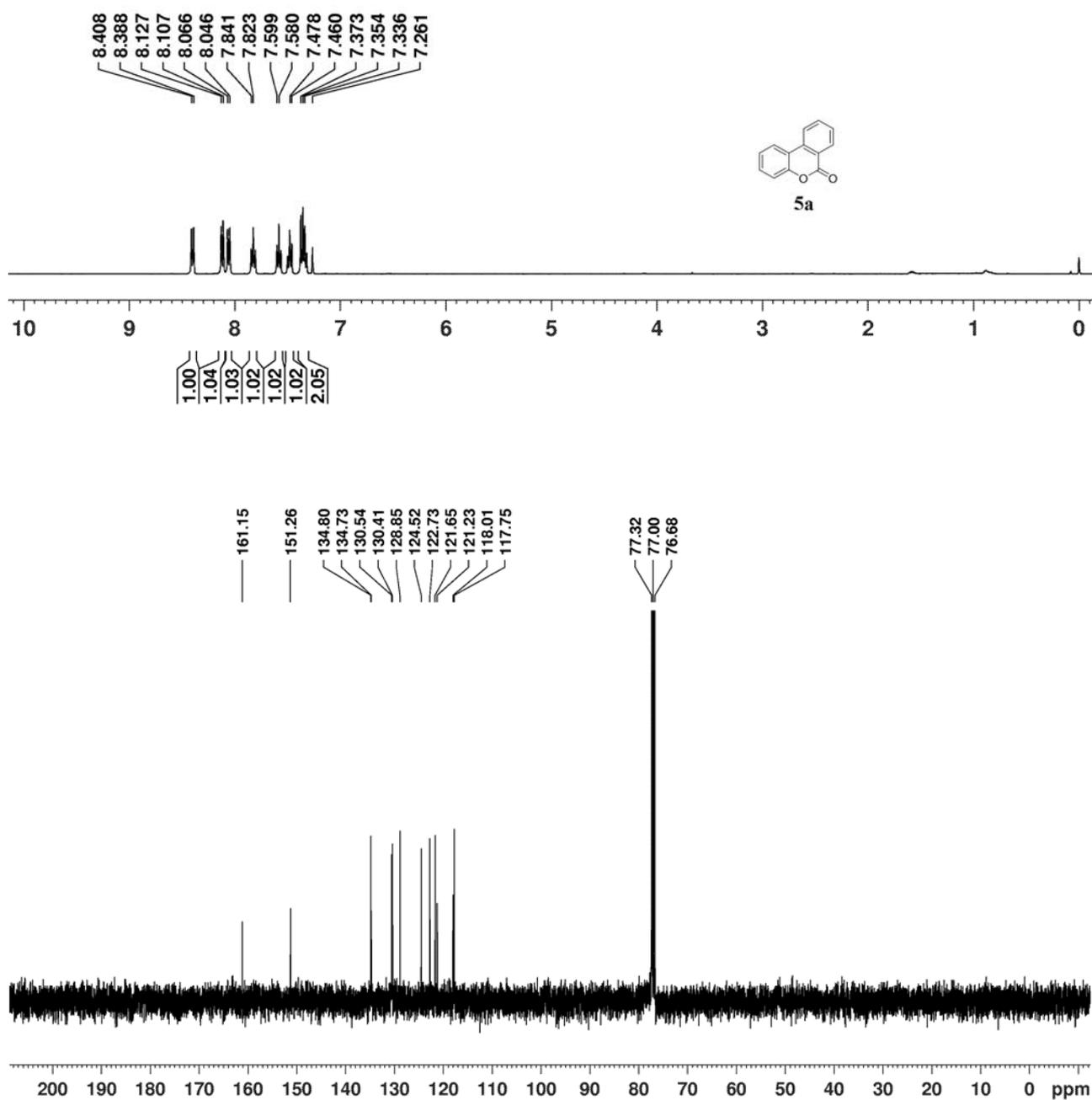


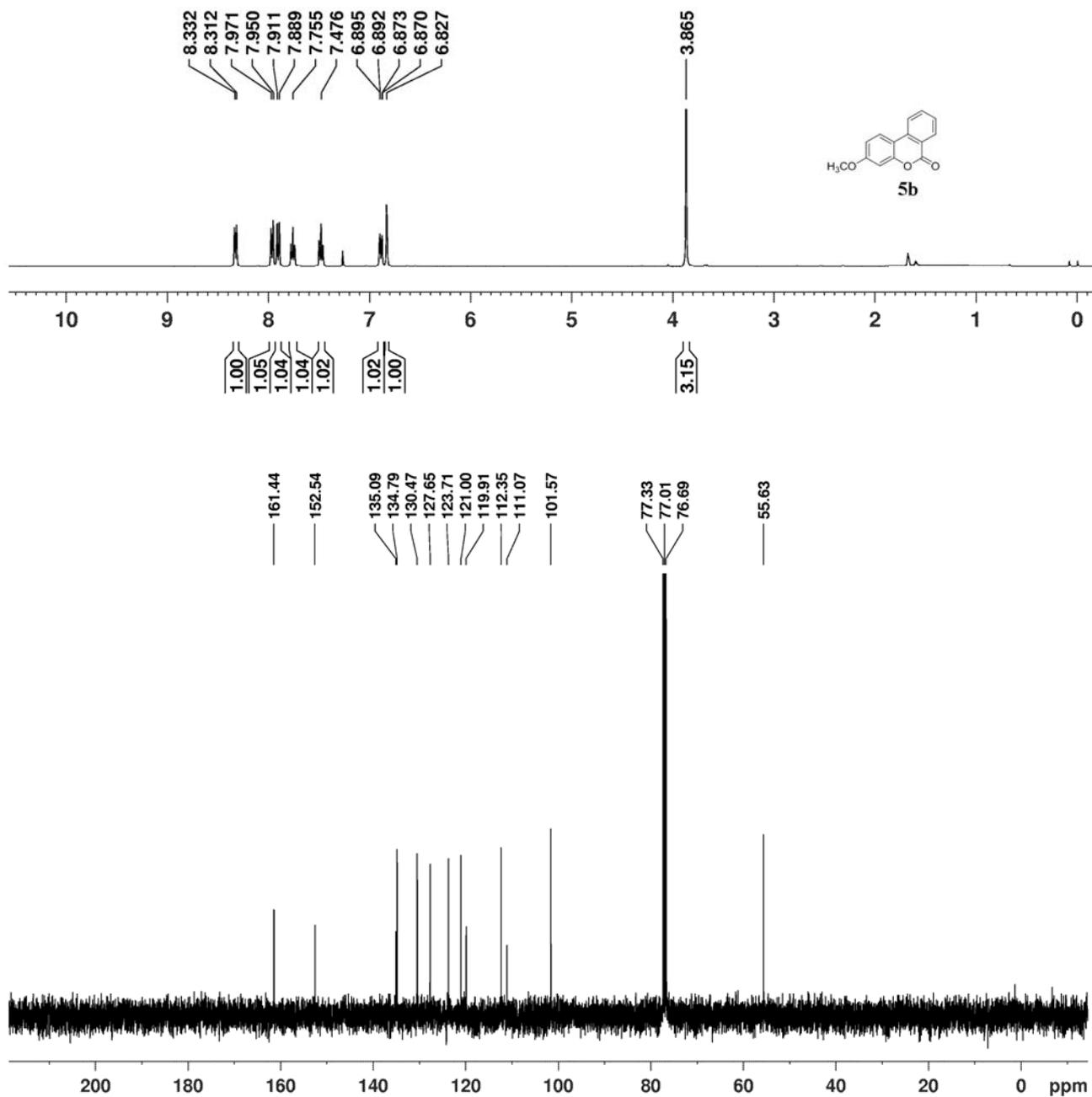


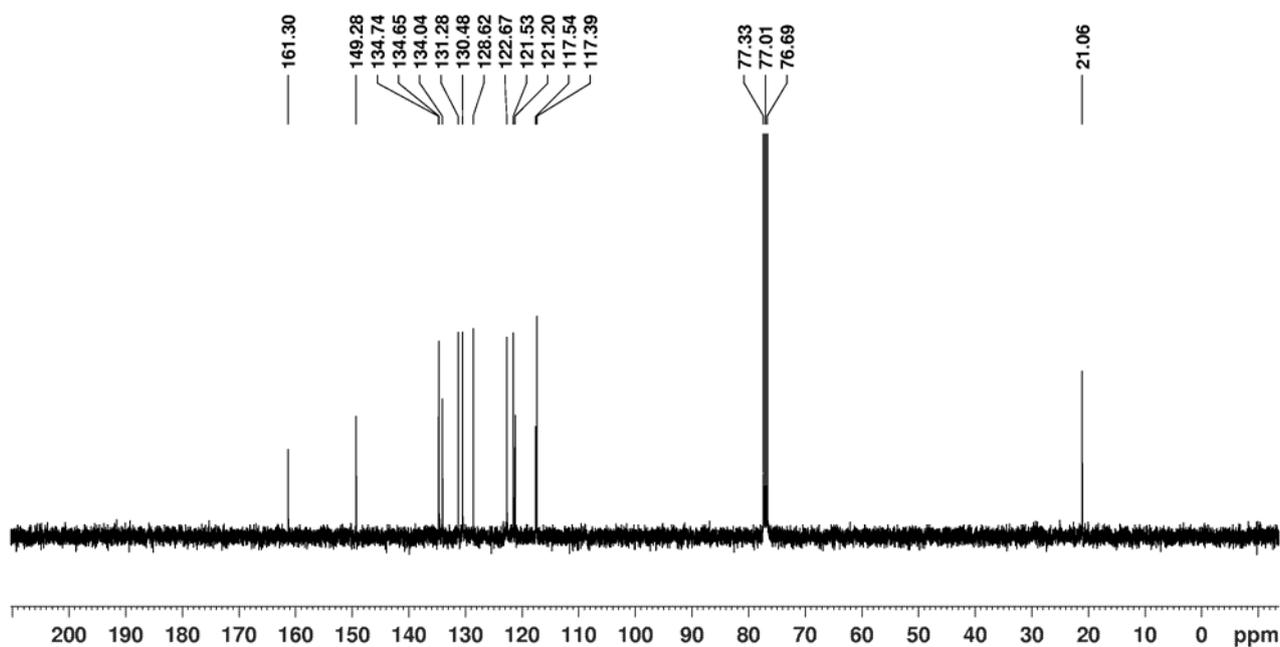
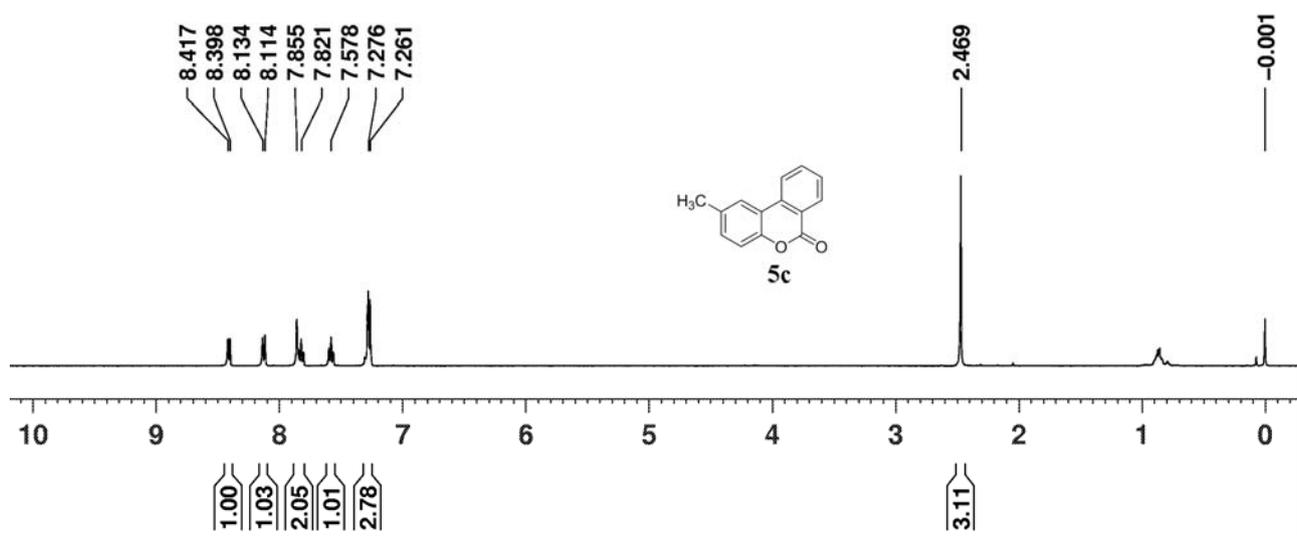


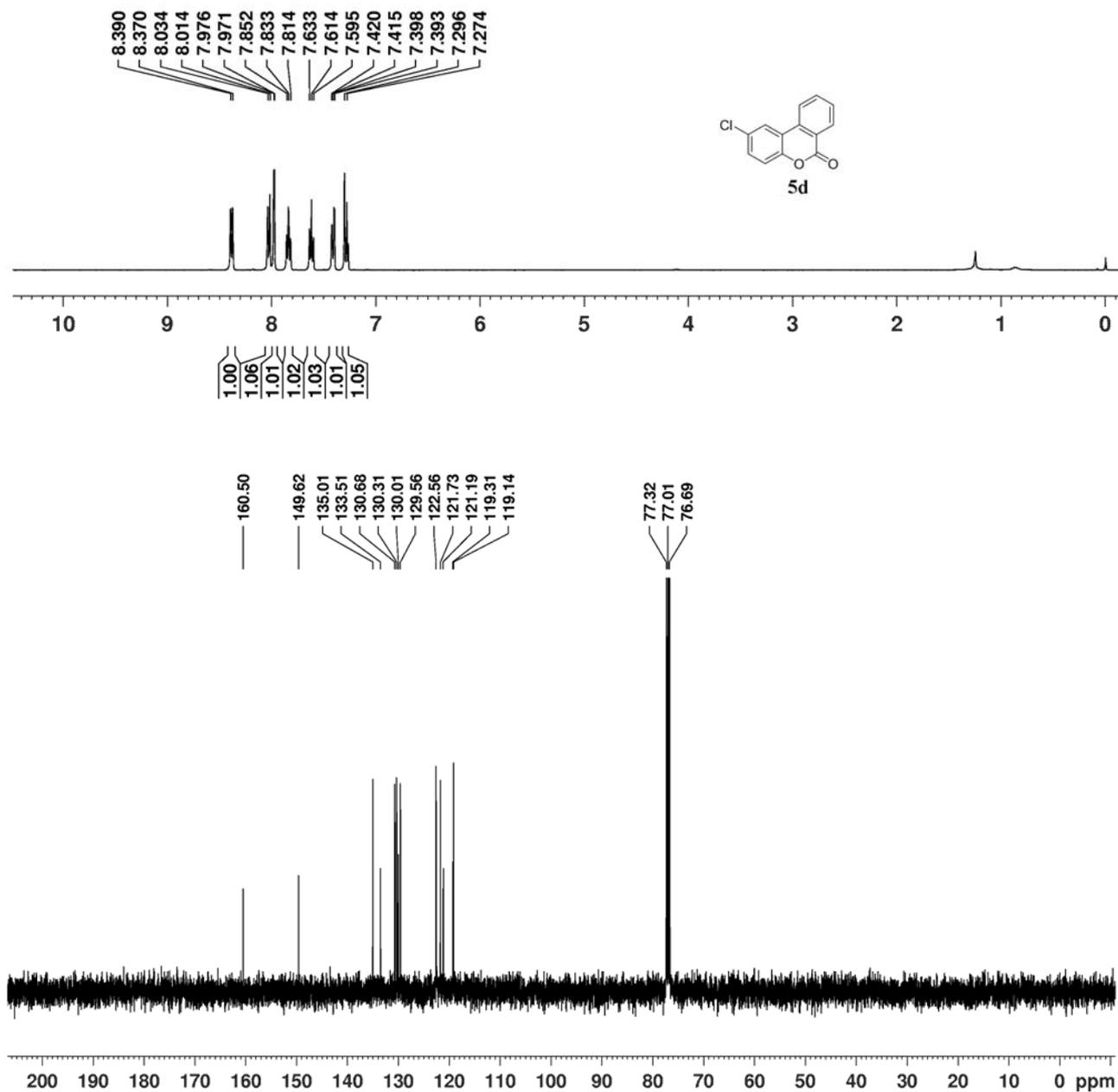


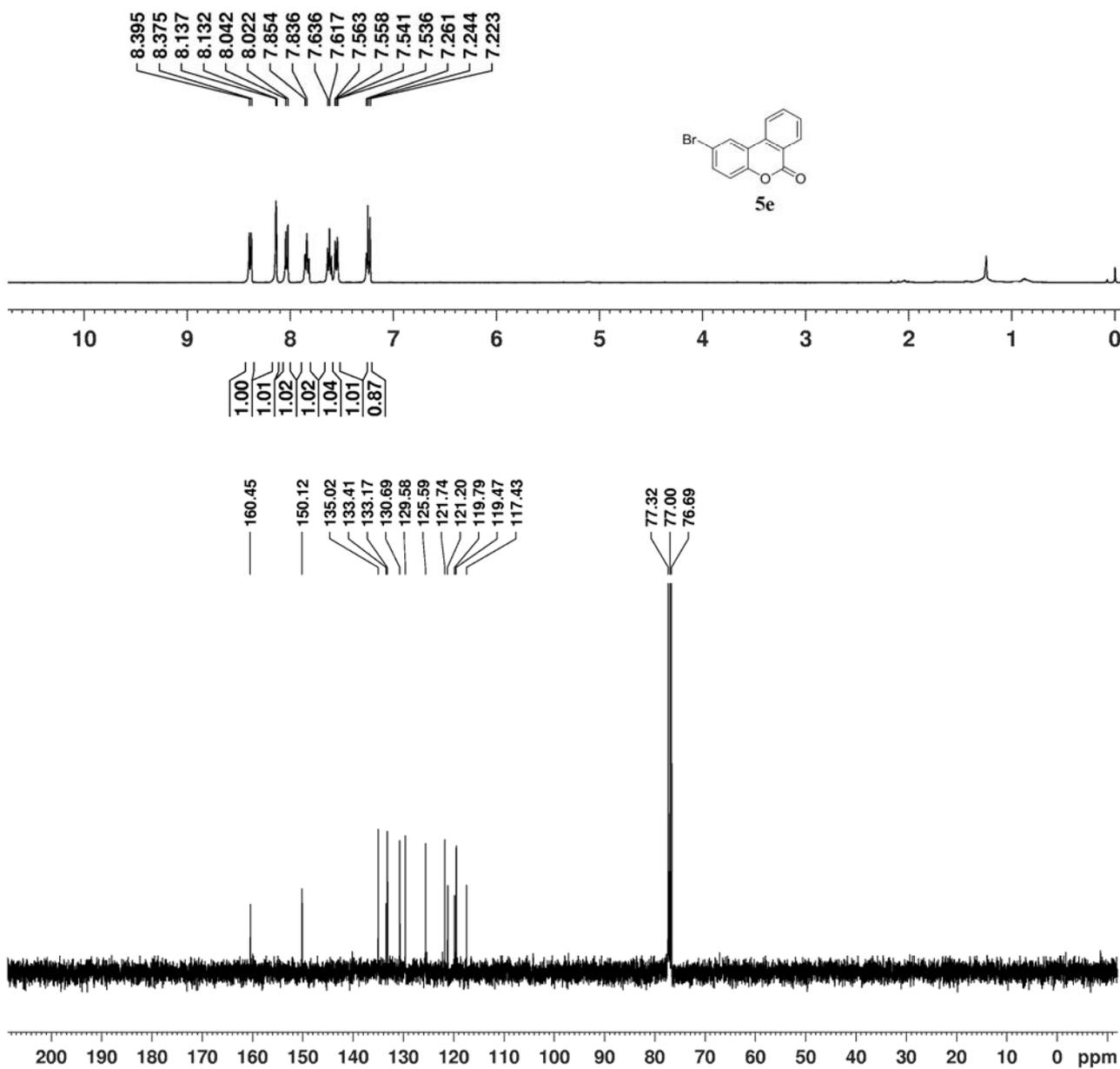


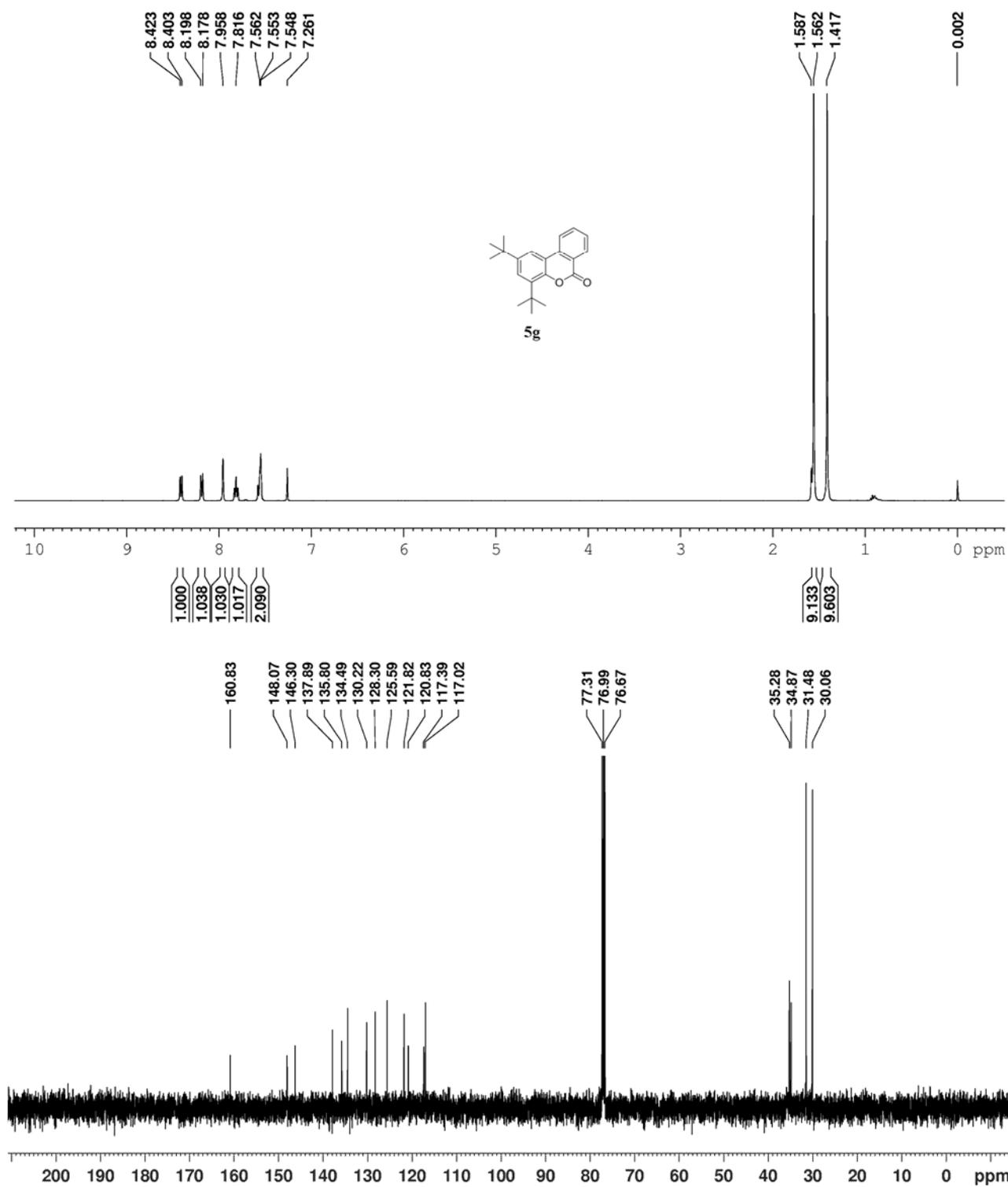


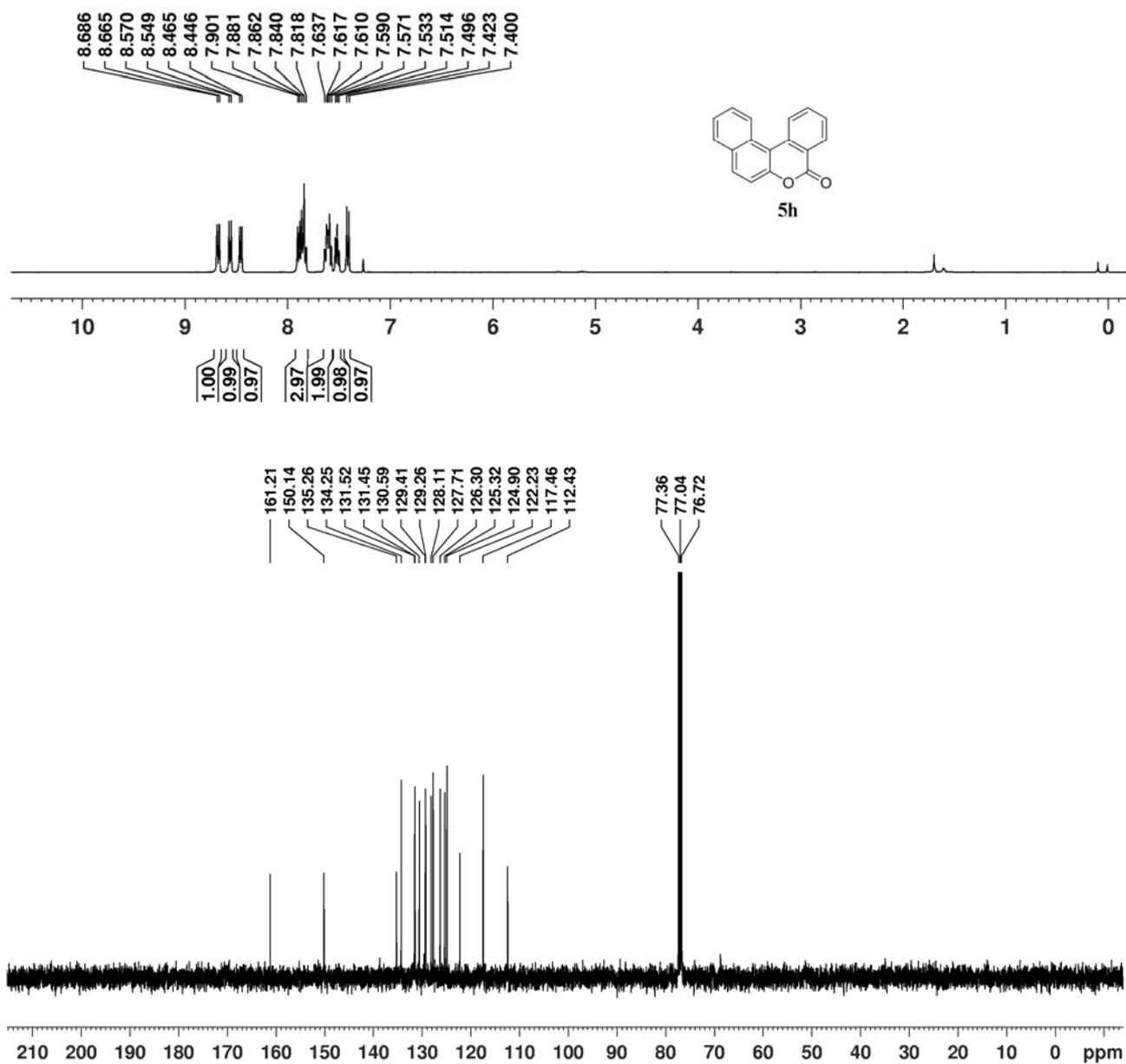


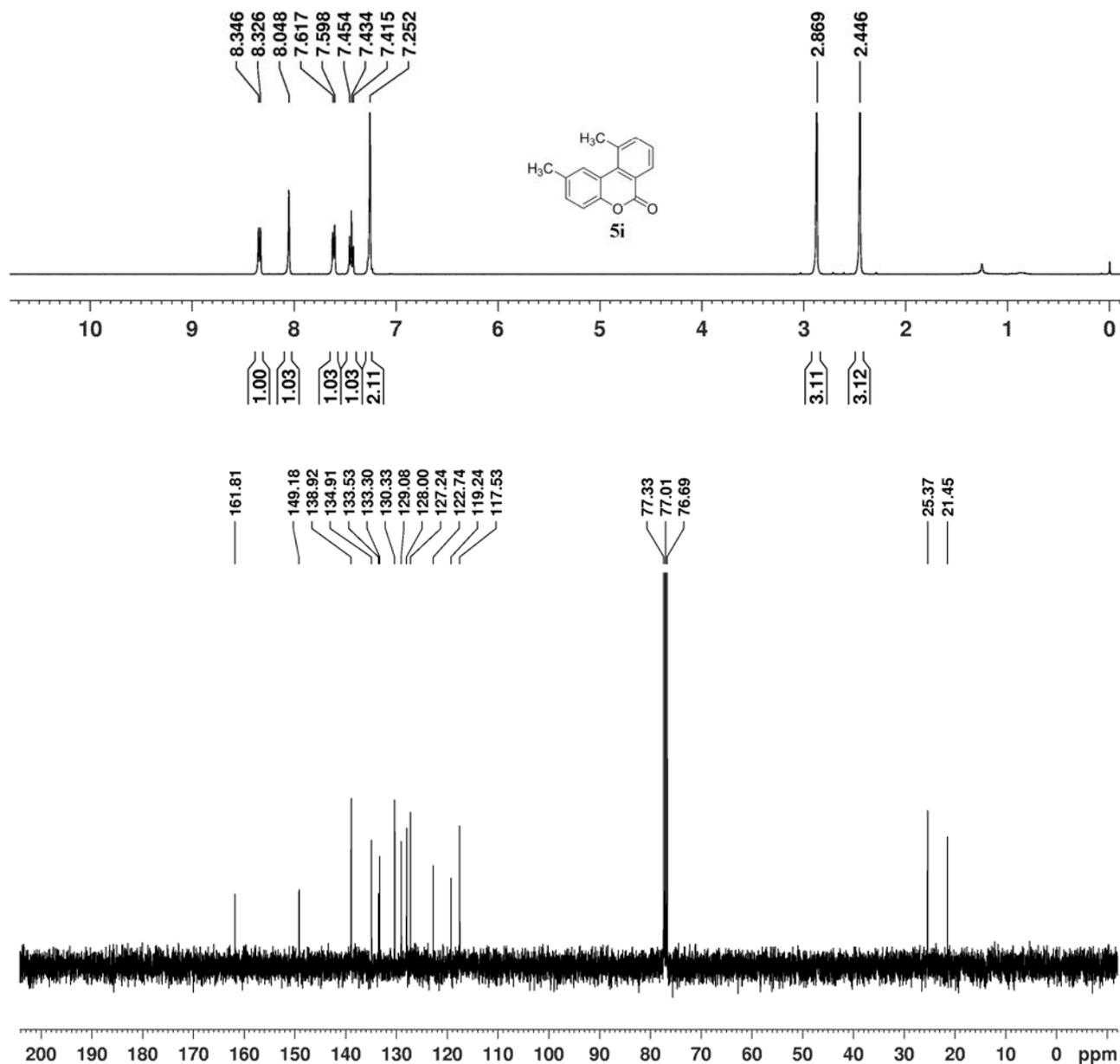


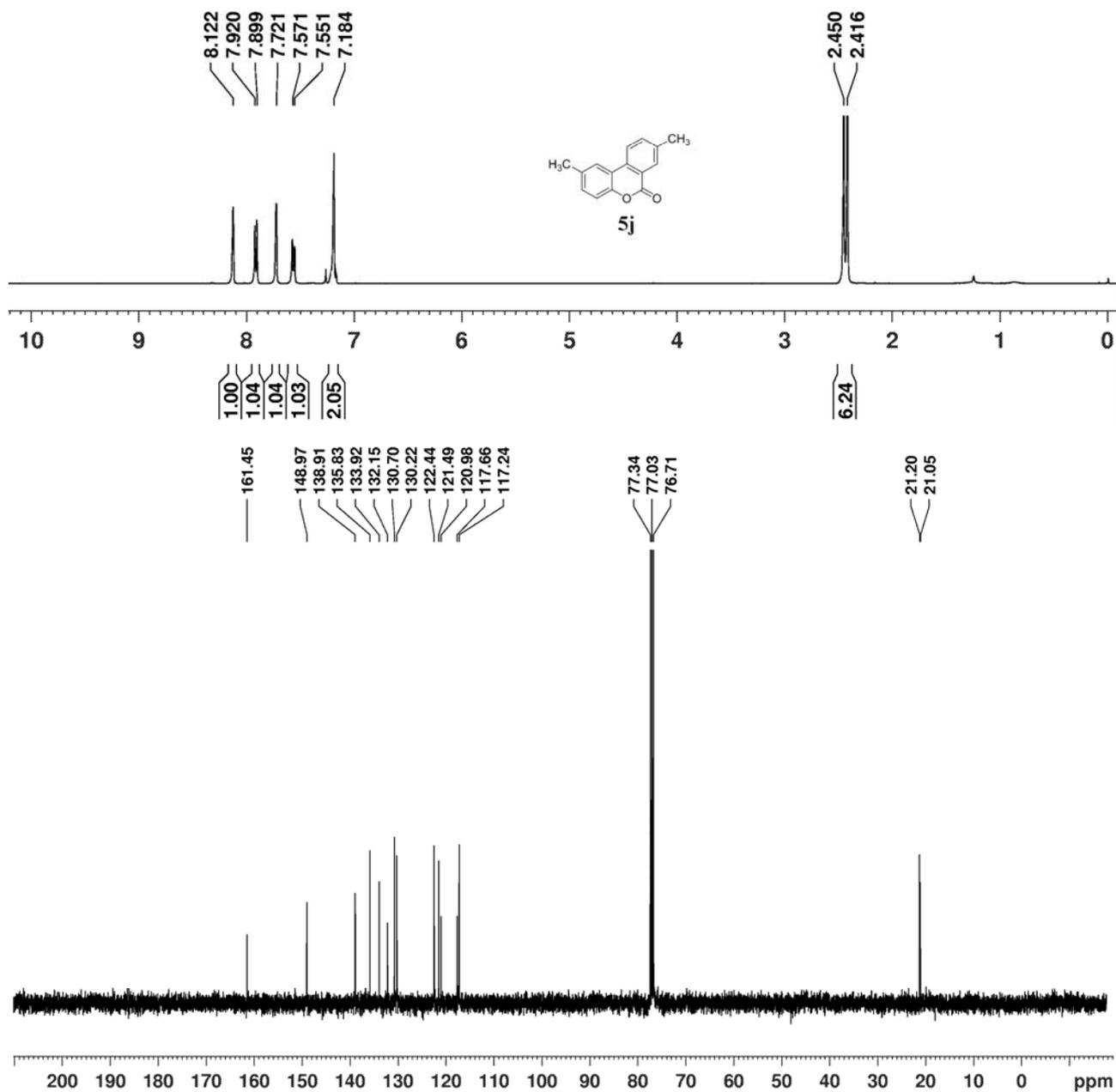


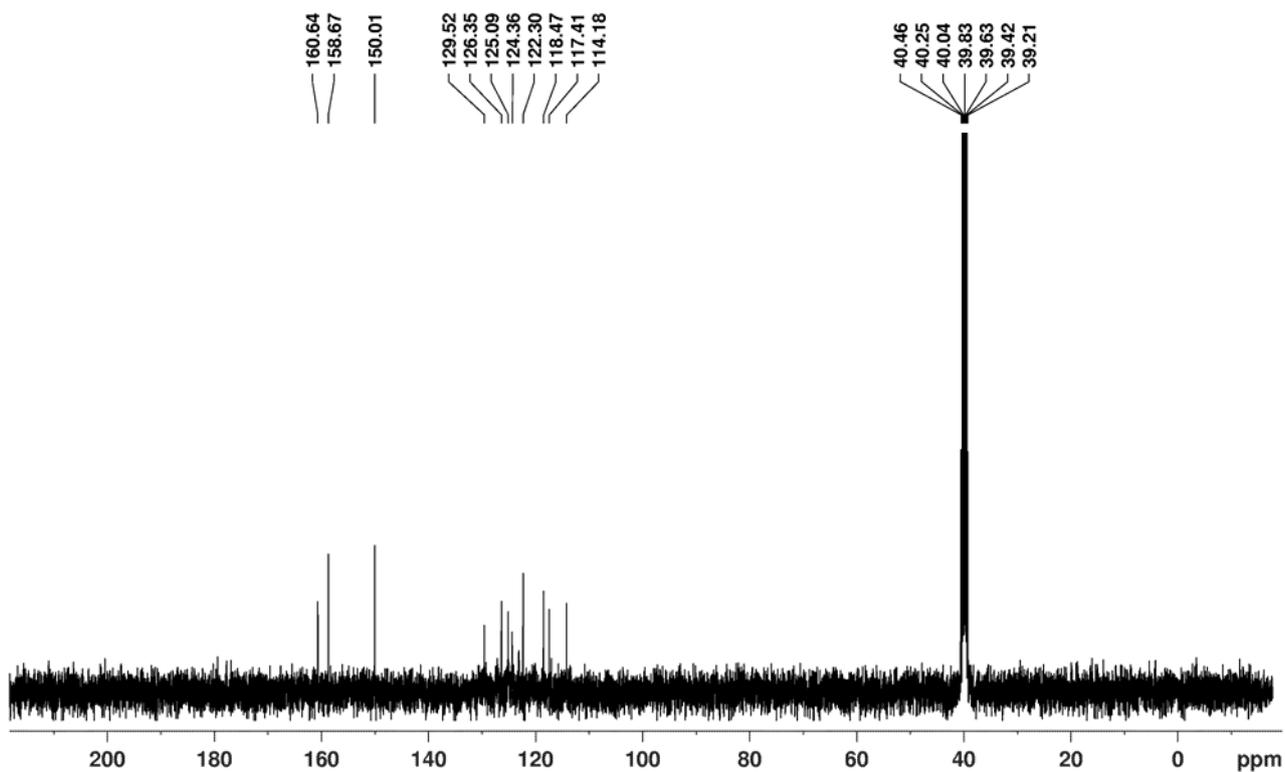
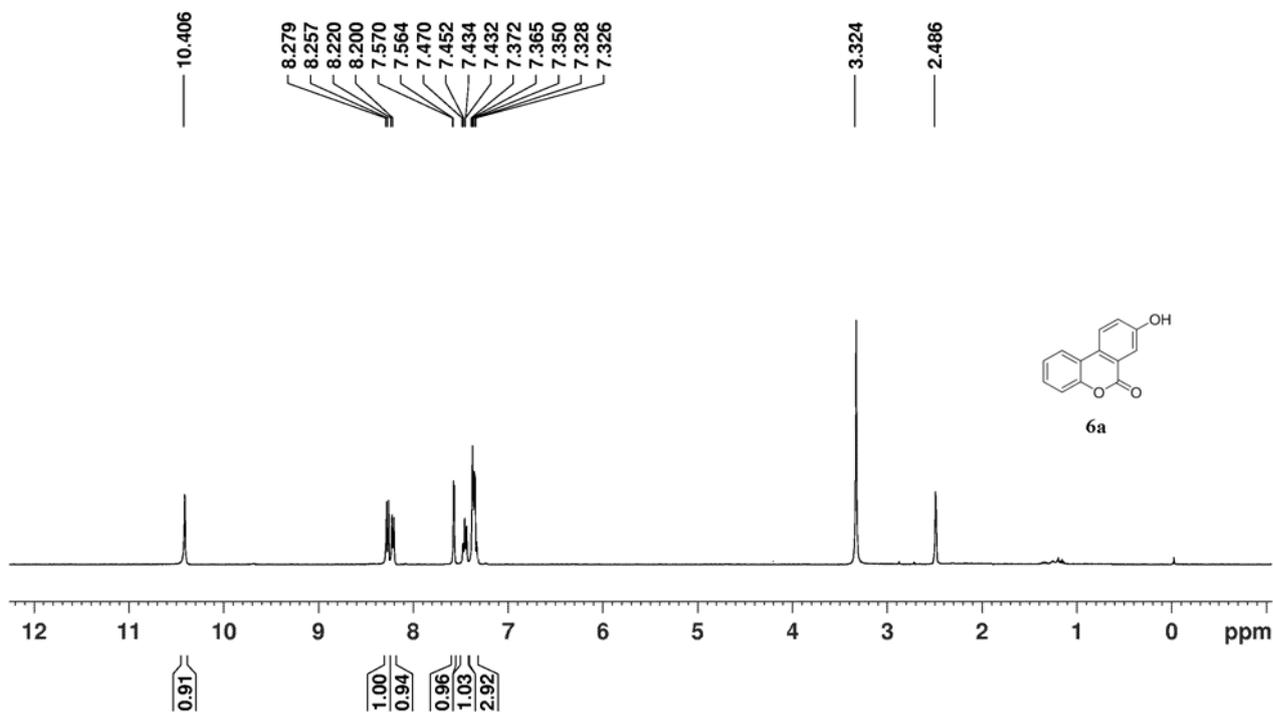


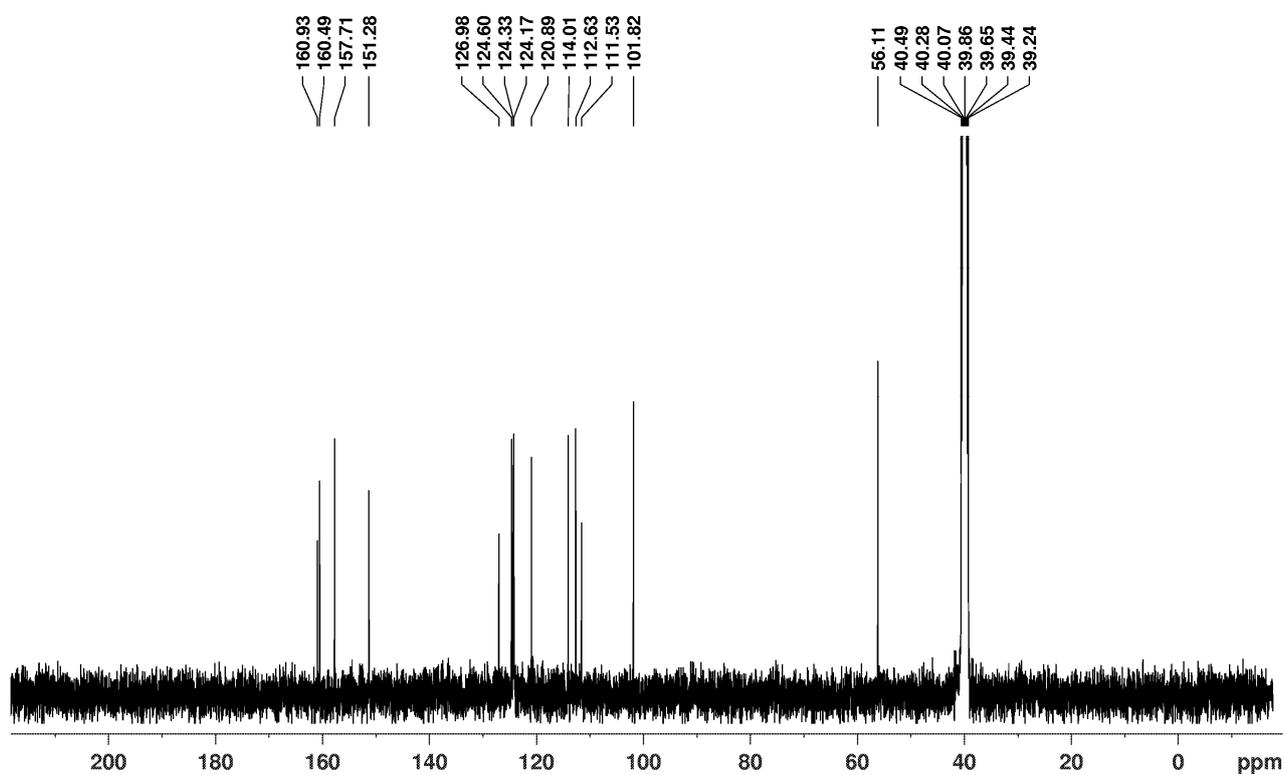
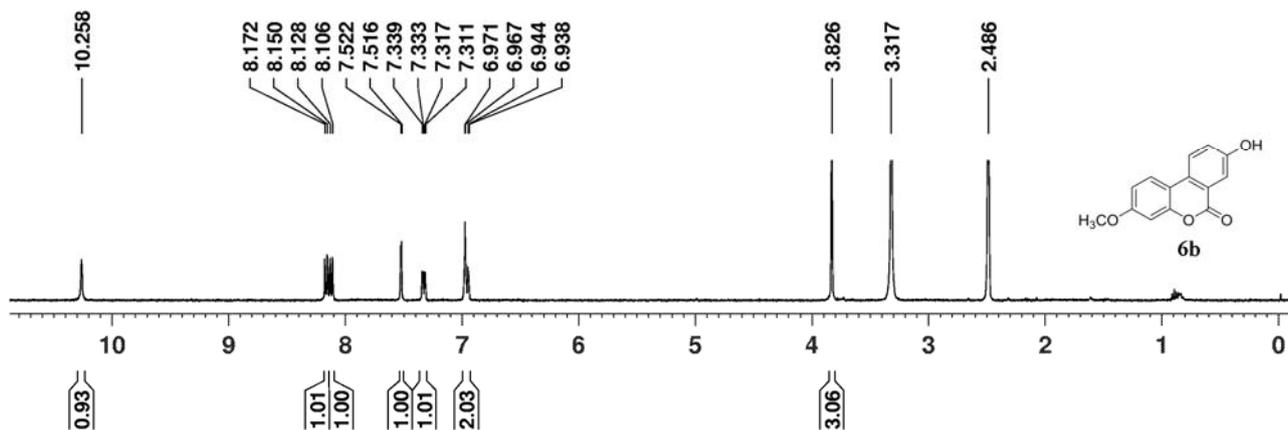


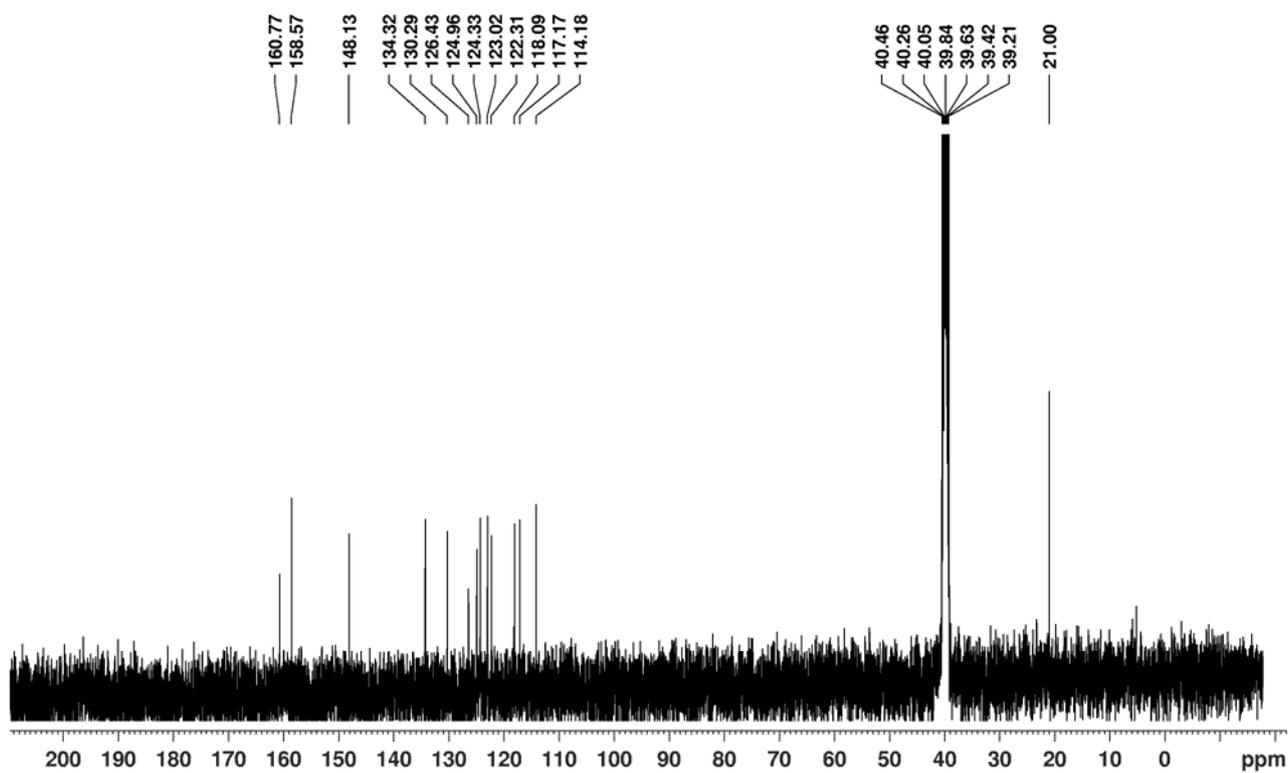
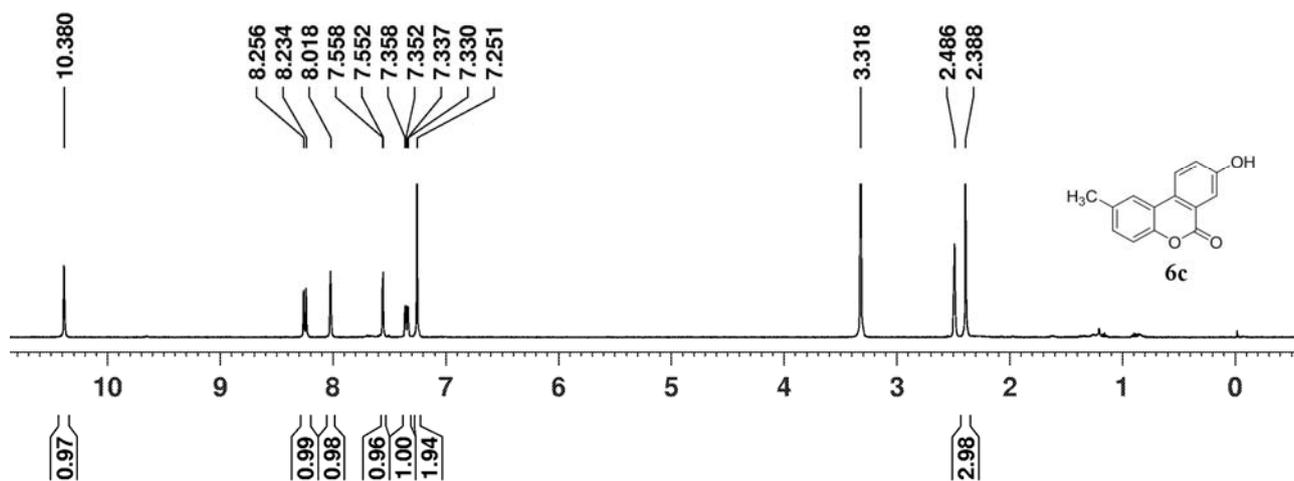


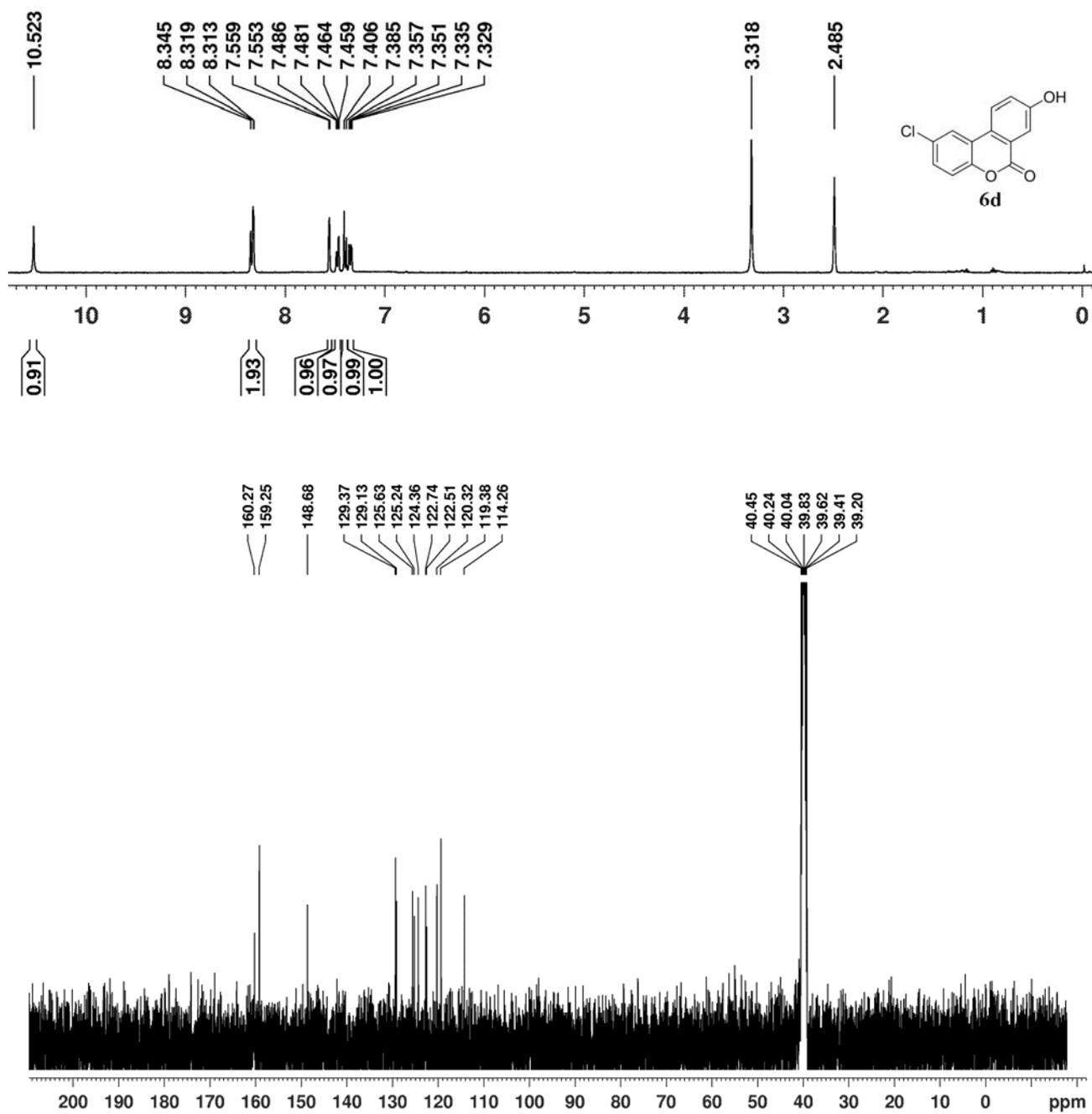


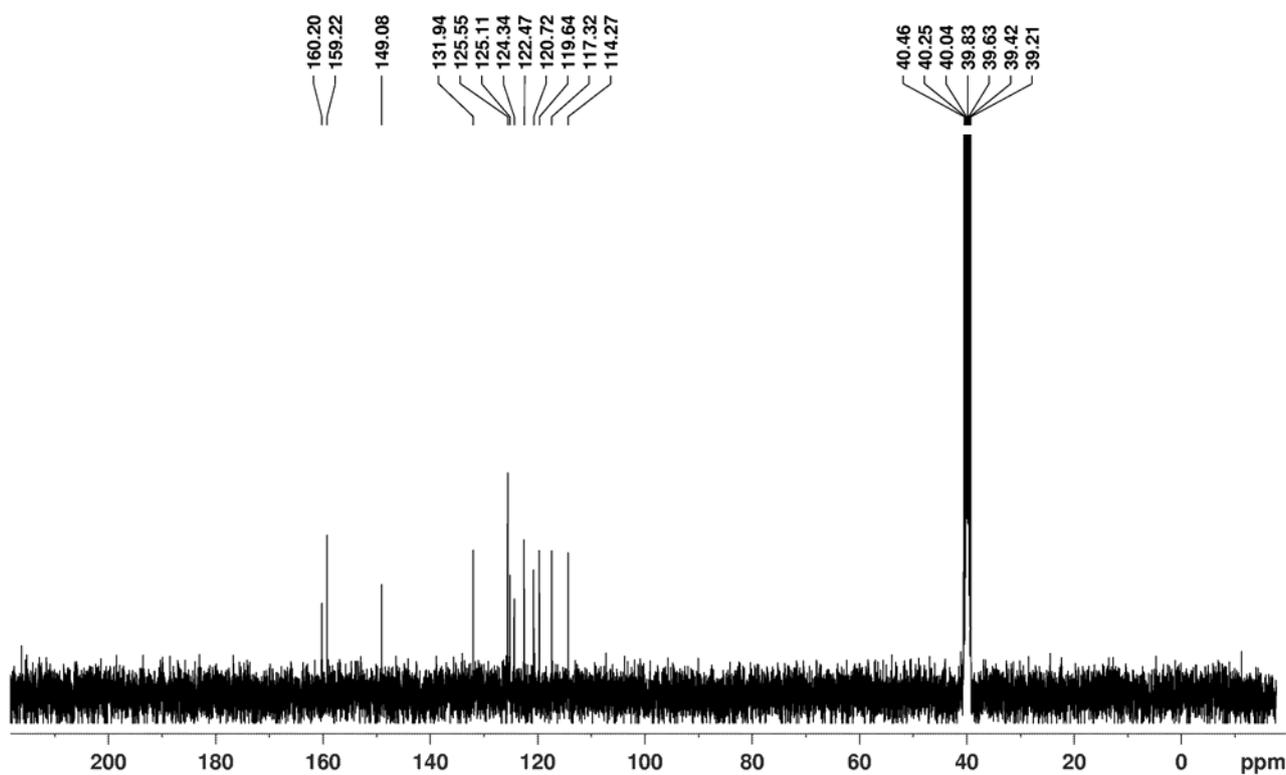
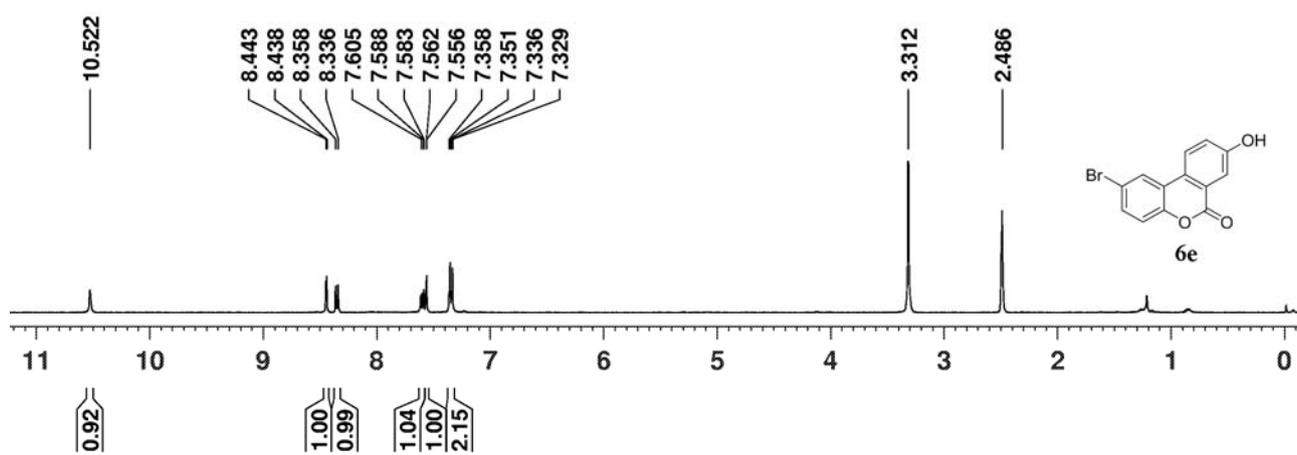


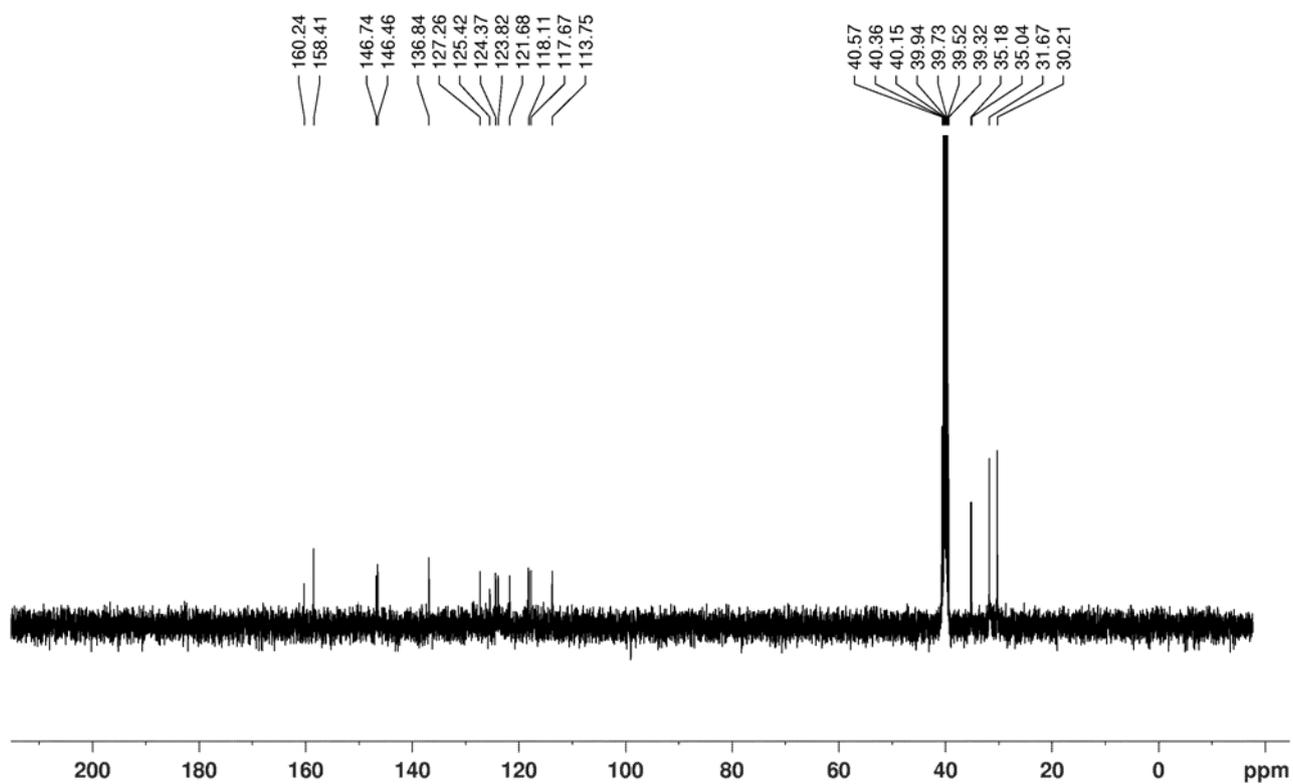
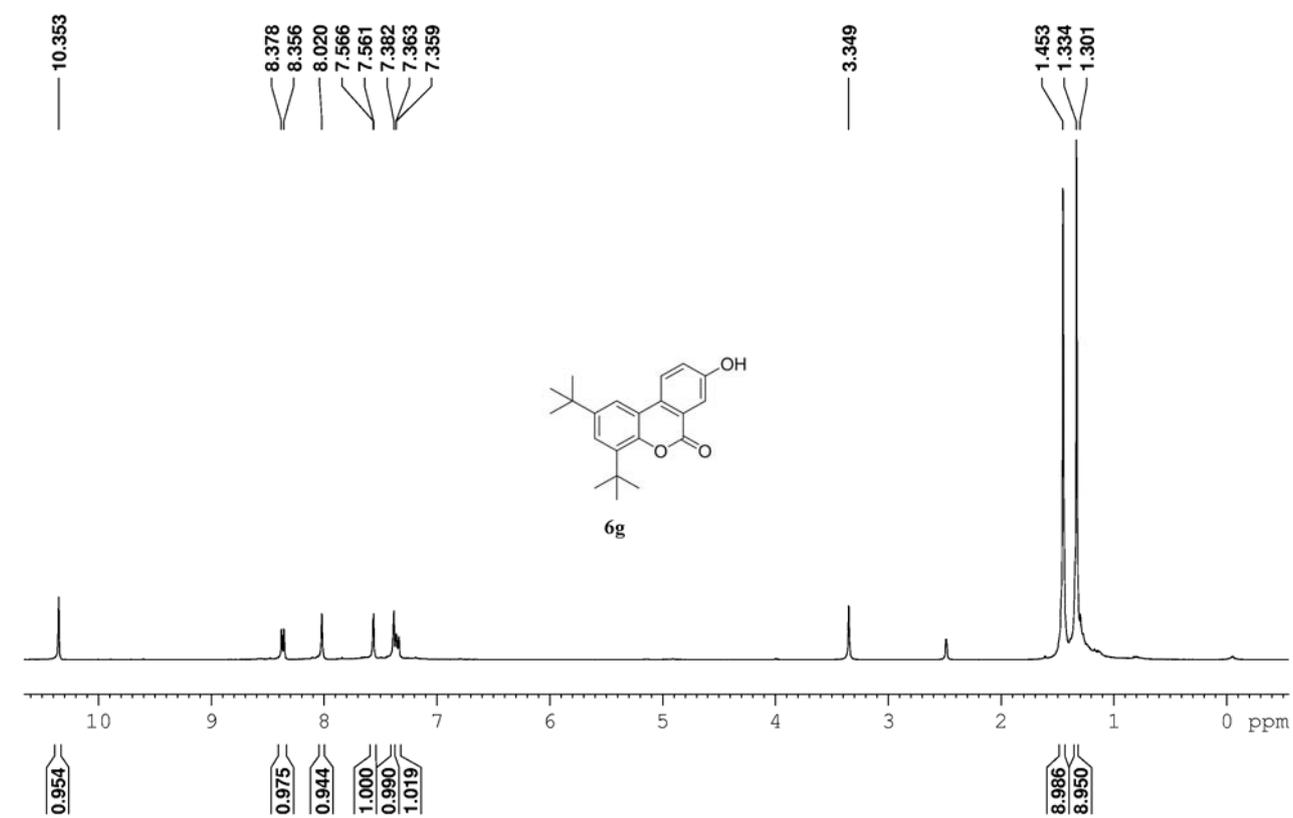


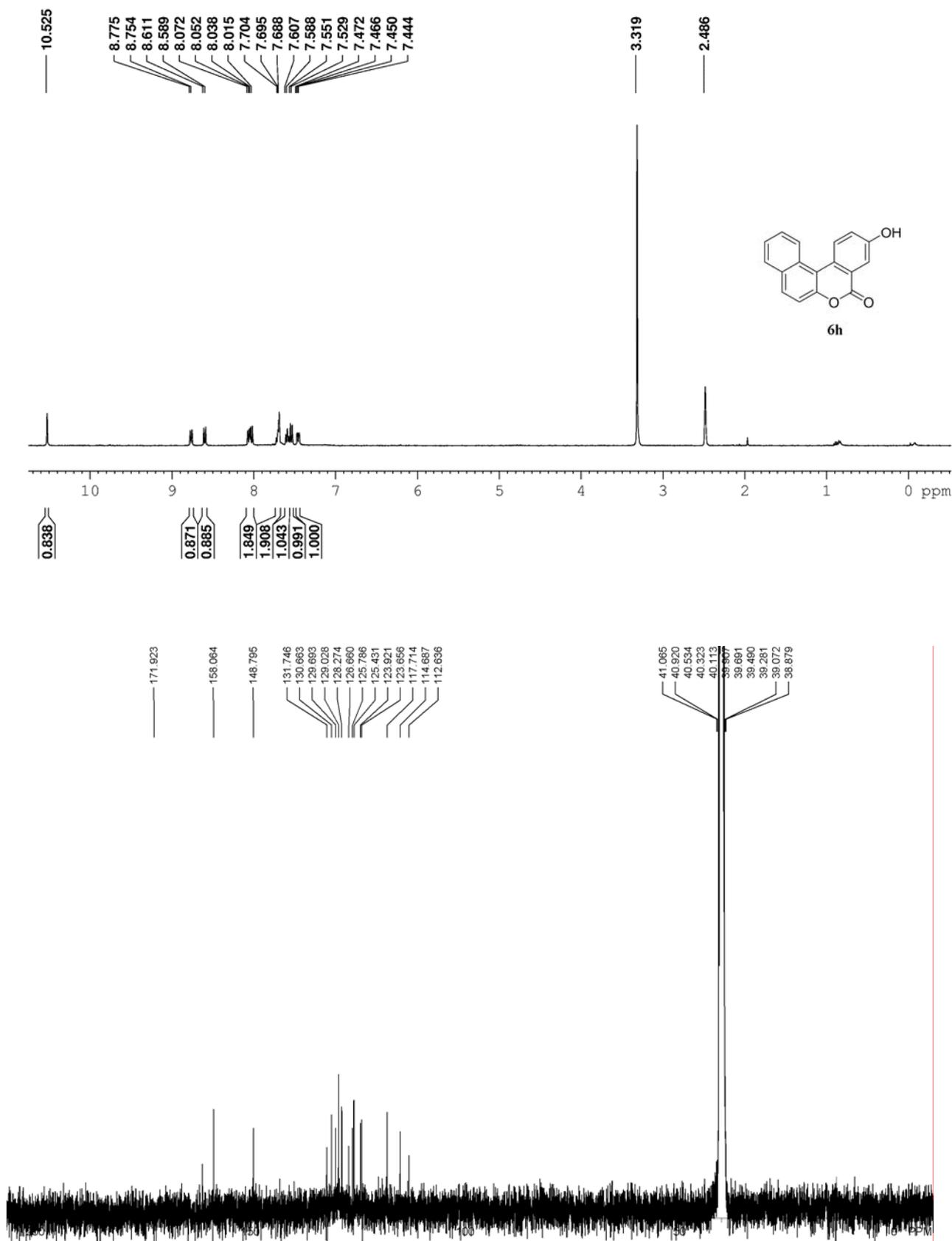


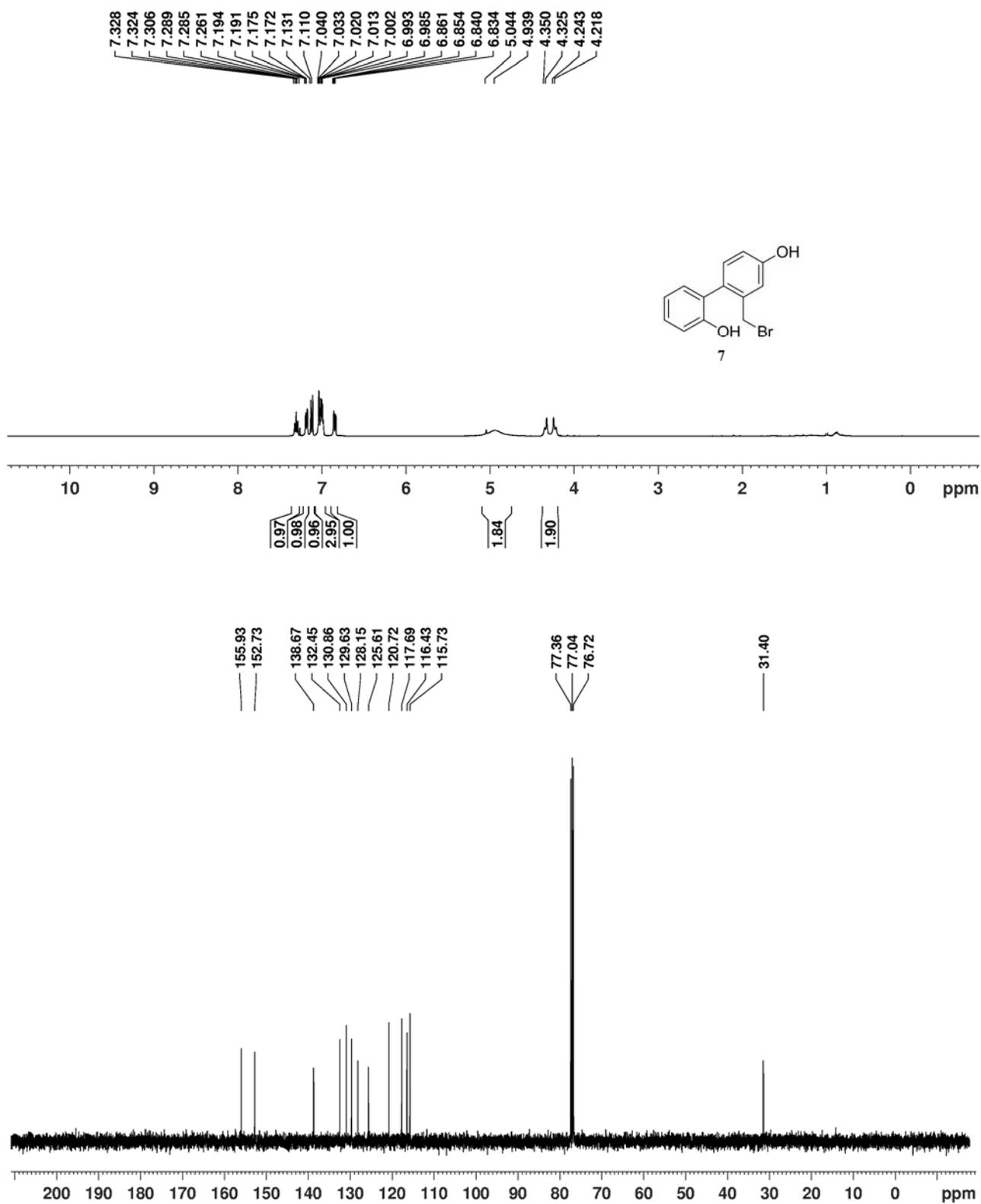


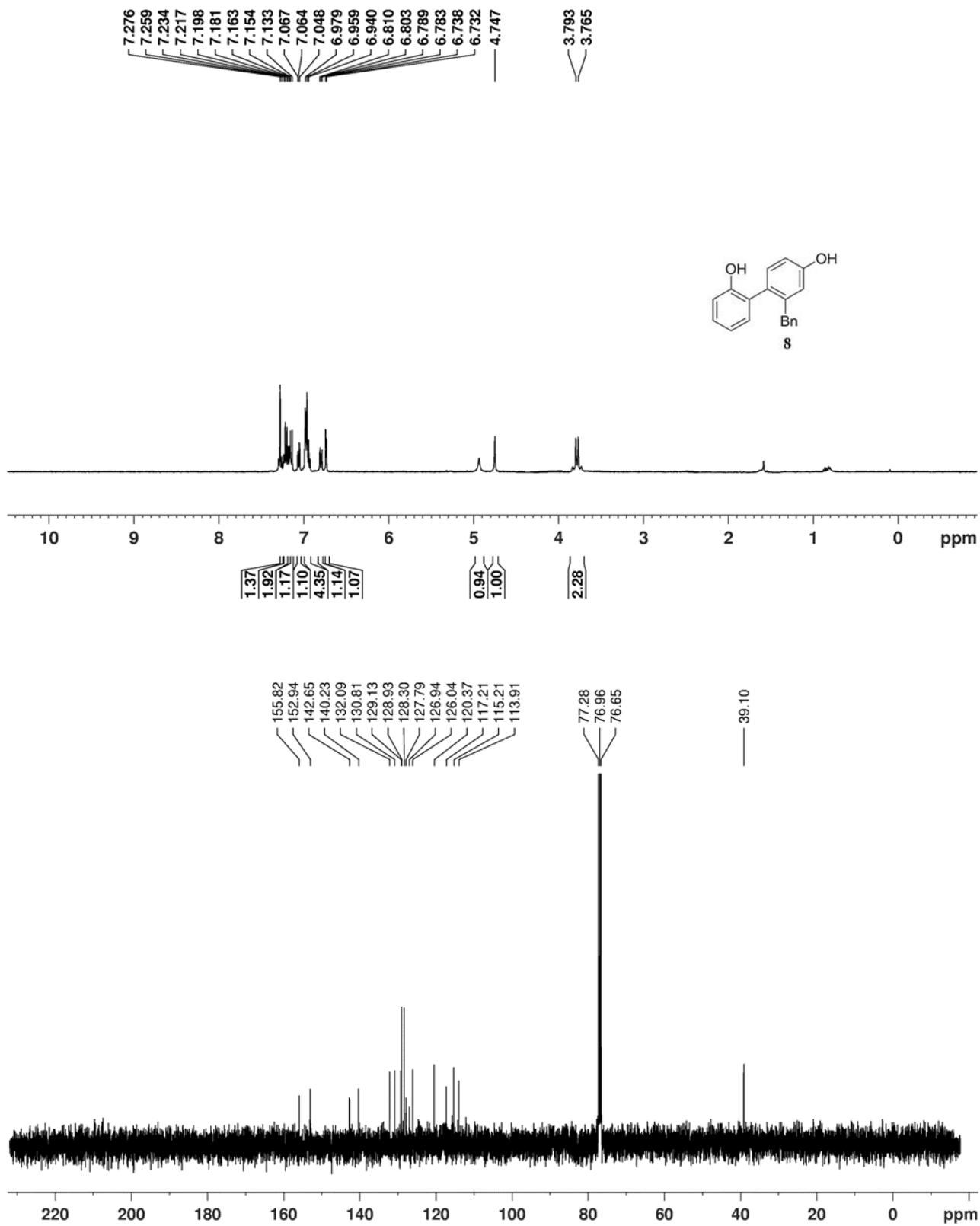












## References

1. D. E. Ames, A. Opalko, *Tetrahedron*, 1984, **40**, 1919.
2. W. R. Bowman, E. Mann and J. Parr, *J. Chem. Soc., Perkin Trans. 1*, 2000, 2991.
3. L.-C. Campeau, P. Thansandote, K. Fagnou, *Org. Lett.*, 2005, **7**, 1857.
4. L.-C. Campeau, M. Parisien, A. Jean, K. Fagnou, *J. Am. Chem. Soc.*, 2006, **128**, 581.
5. K. Vishnumurthy, A. Makriyannis, *J. Comb. Chem.*, 2010, **12**, 664.
6. D. J. Hart, A. Kim, R. Krishnamurthy, G. H. Merriman, A.-M. Waltos, *Tetrahedron*, 1992, **48**, 8179.