

## Supplementary Information

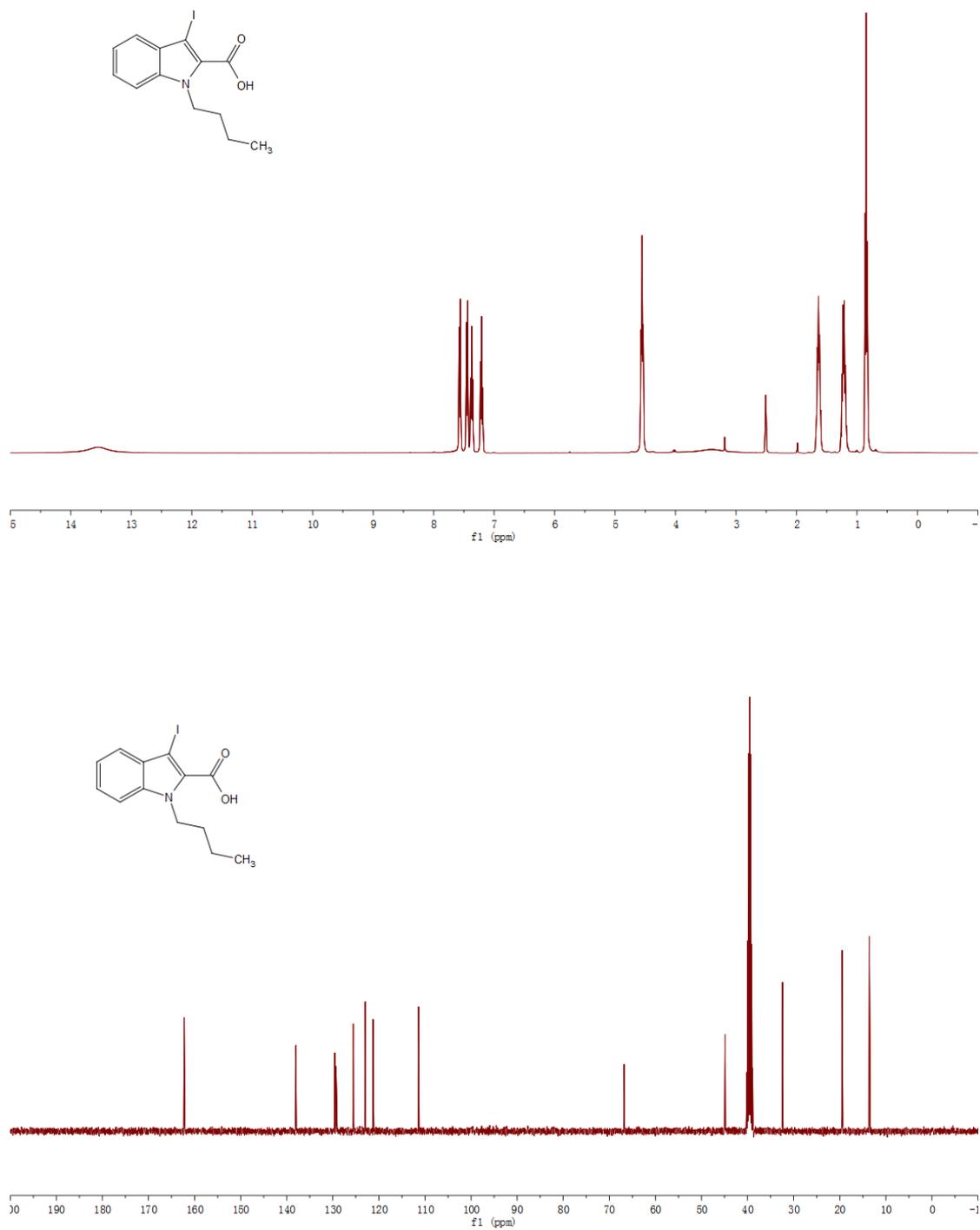
**Copper-Catalyzed Annulation of Heteroaromatic  $\beta$ -Halo- $\alpha,\beta$ -unsaturated Carboxylic Acids with Alkynes for the Synthesis of Indolo[2,3-*c*]pyrane-1-ones and Thieno[2,3-*c*]pyrane-7-ones**

**Da-Wei Gu, and Xun-Xiang Guo\***

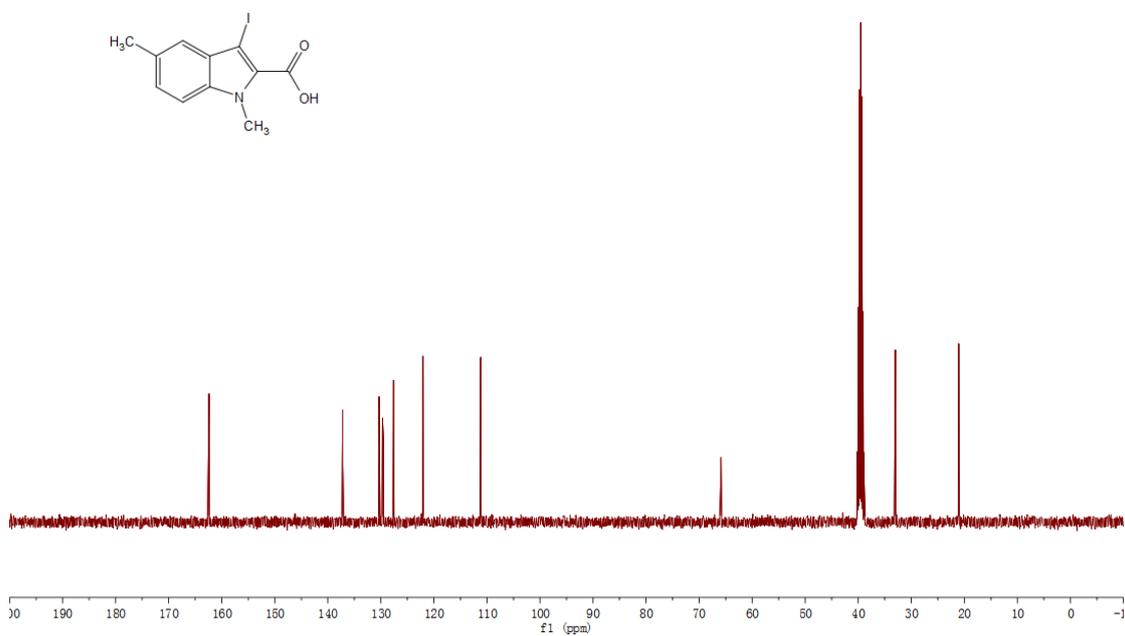
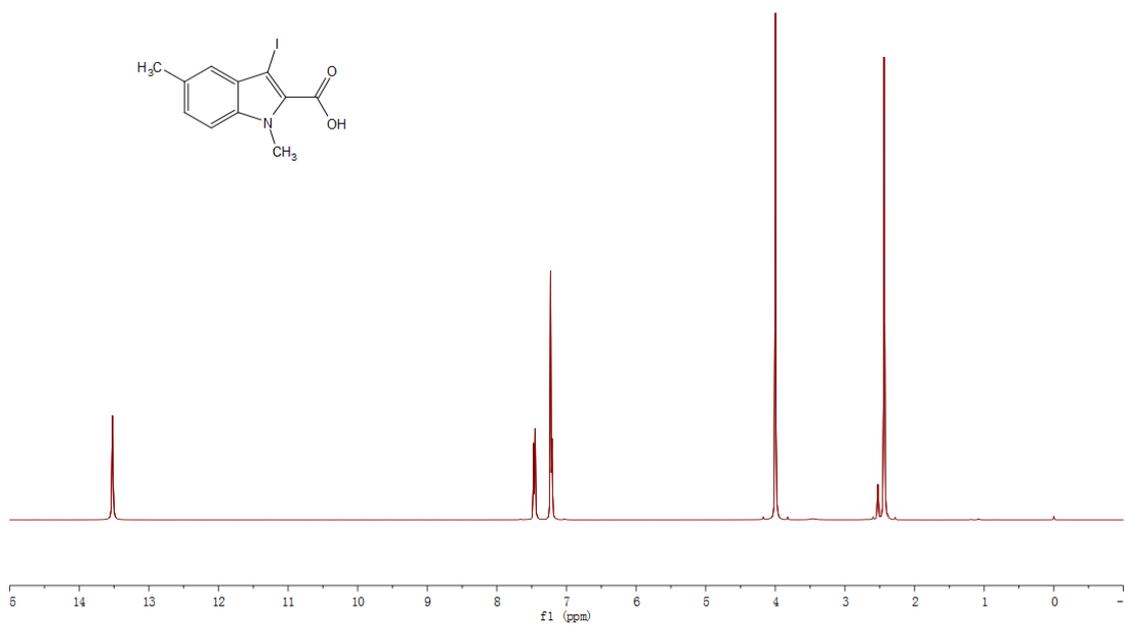
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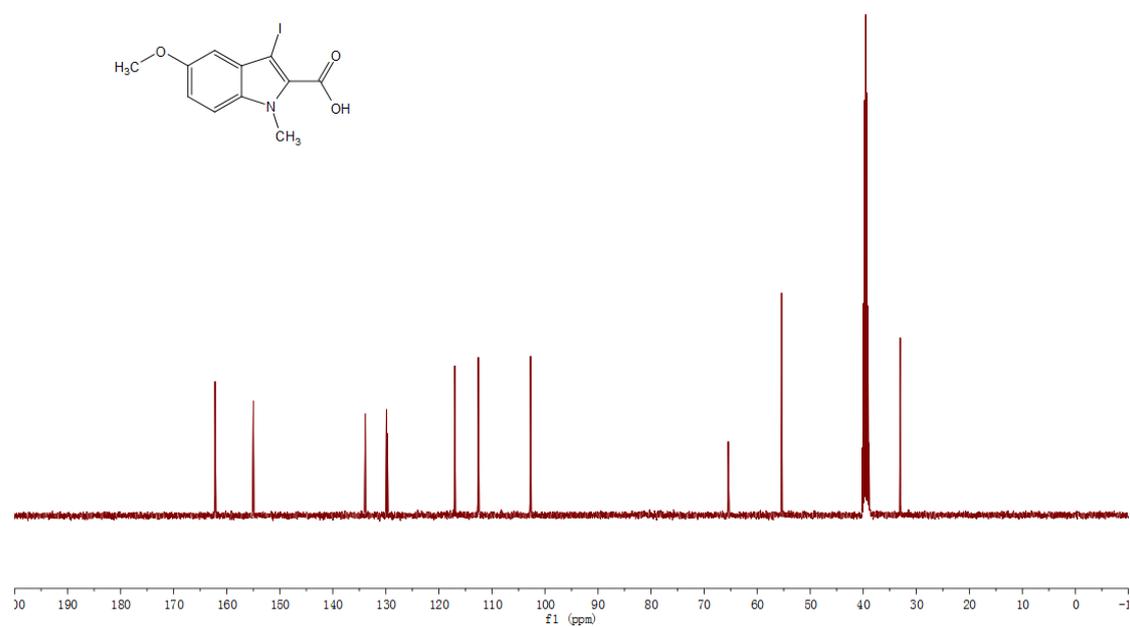
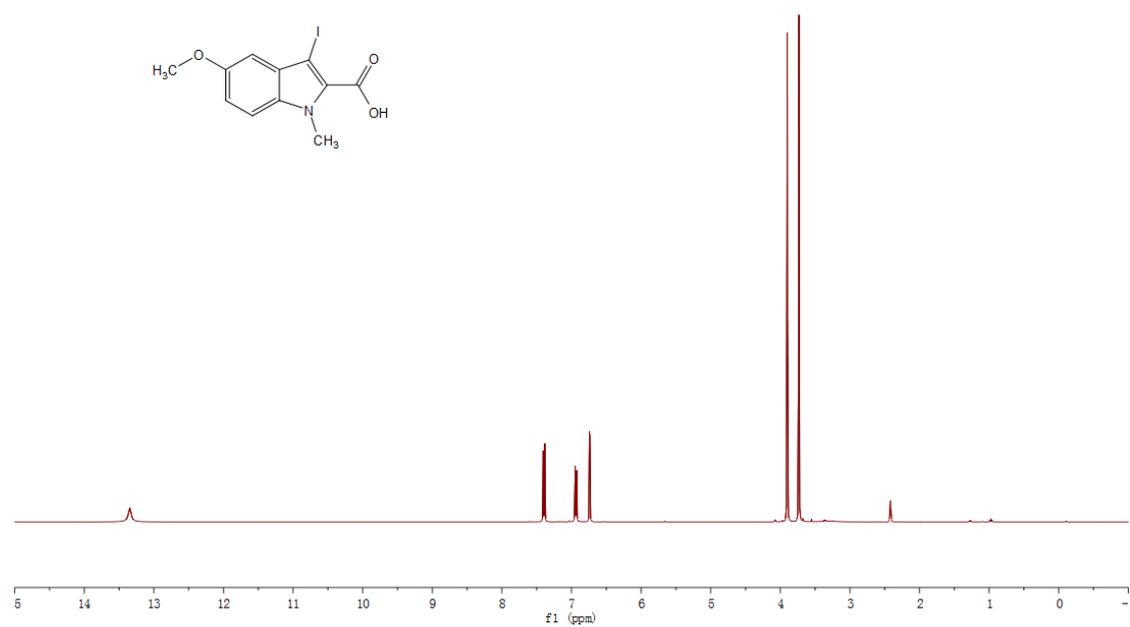
# 1. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Starting Materials 1c-g



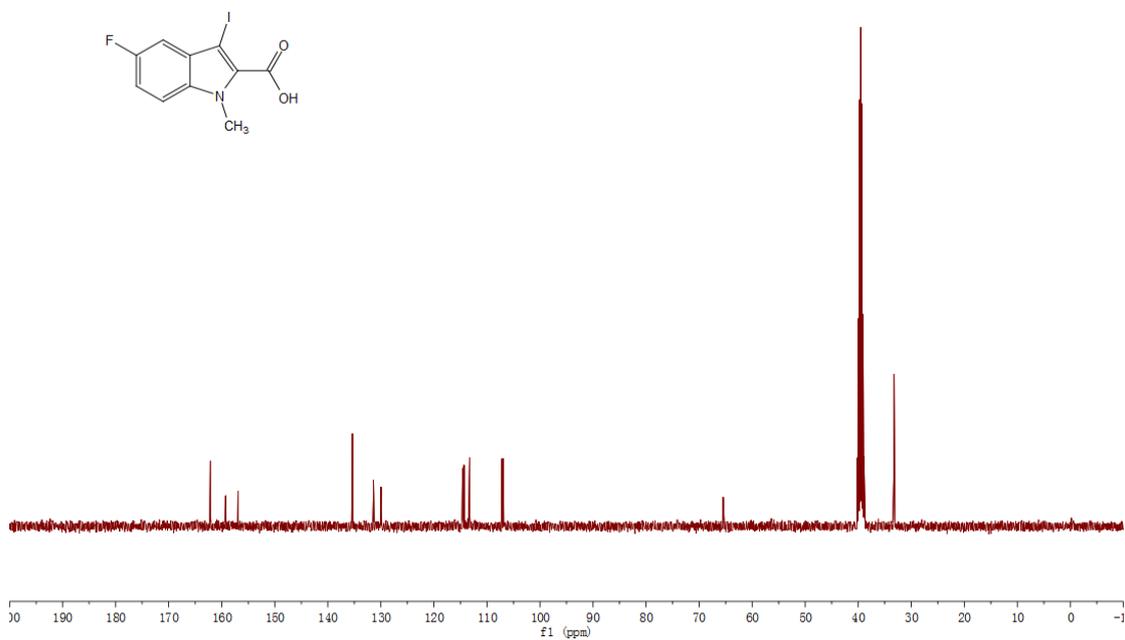
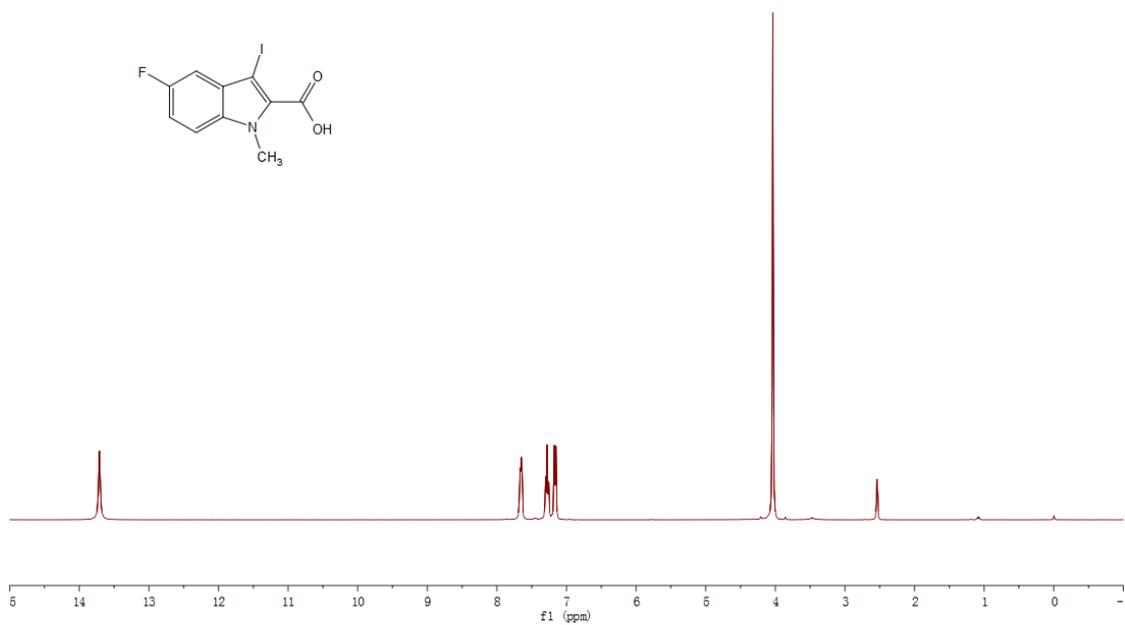
**Figure 1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of starting material **1c** in  $\text{DMSO-d}_6$



**Figure 2.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of starting material **1e** in DMSO- $d_6$

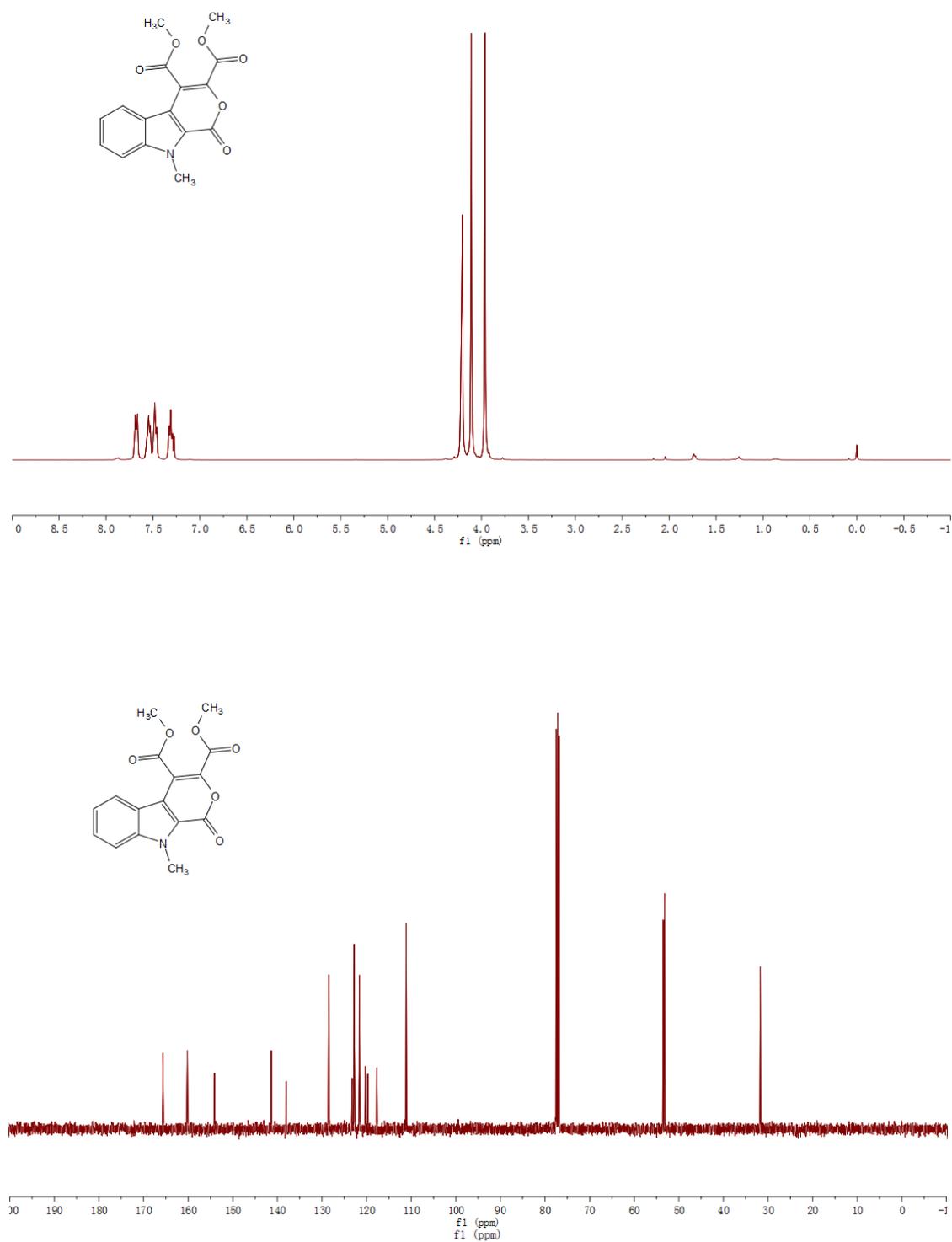


**Figure 3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of starting material **1f** in DMSO- $d_6$

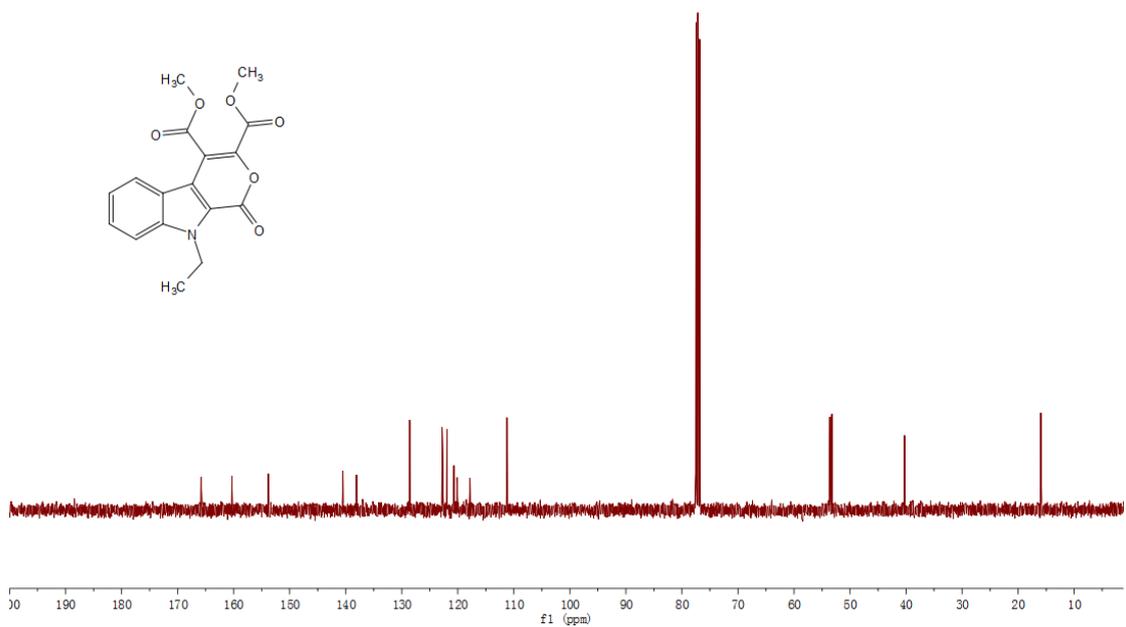
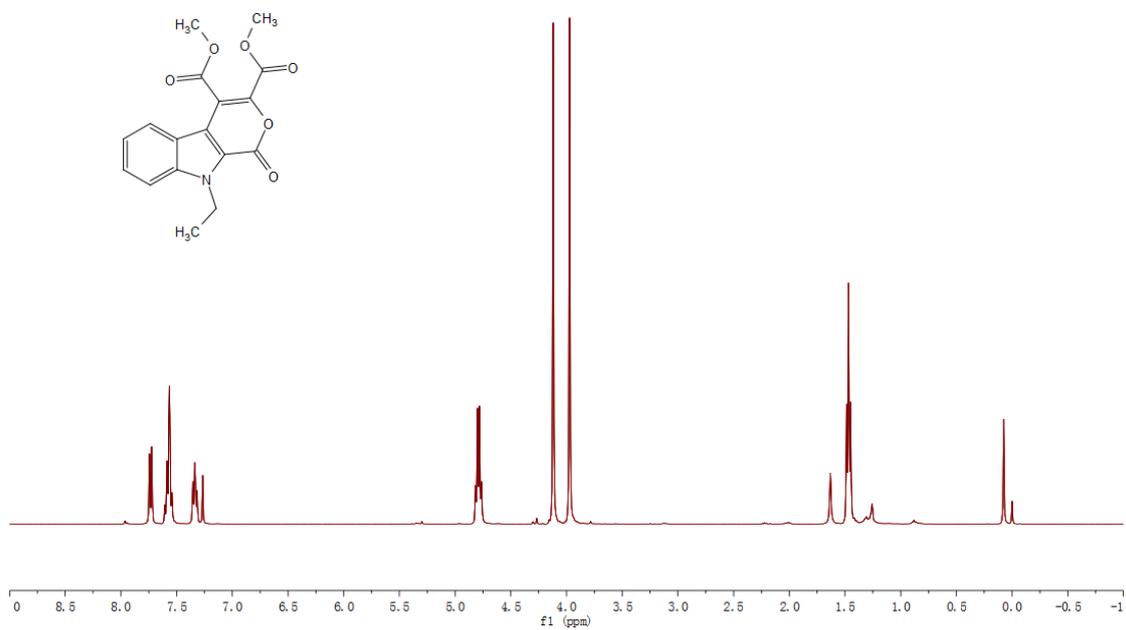


**Figure 4.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of starting material **1g** in  $\text{DMSO-d}_6$

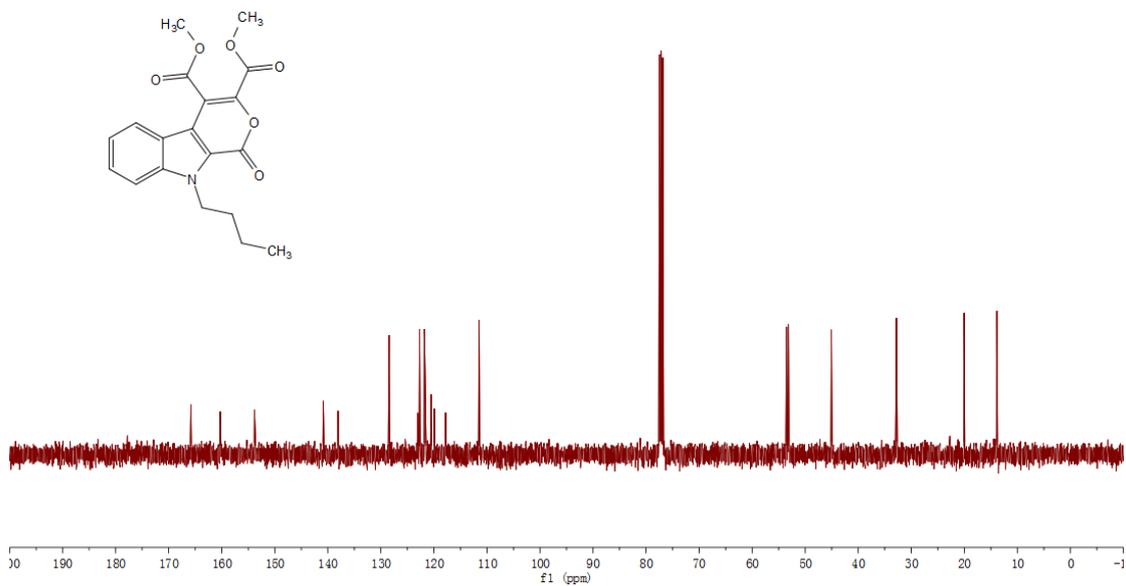
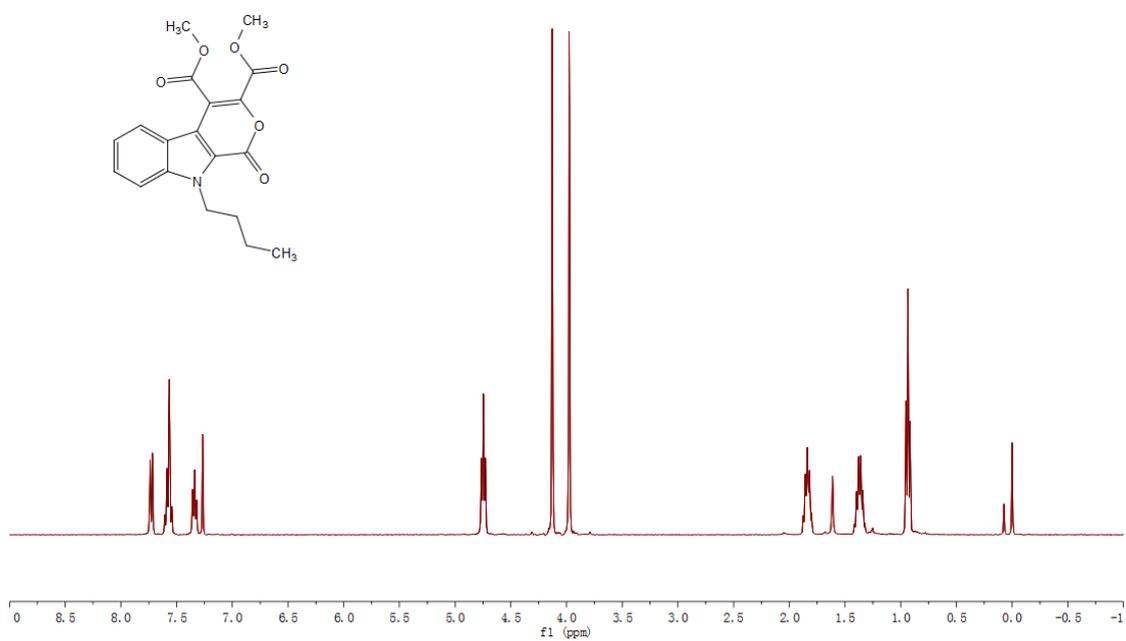
## 2. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compounds 3aa-ia, 3ab-ag



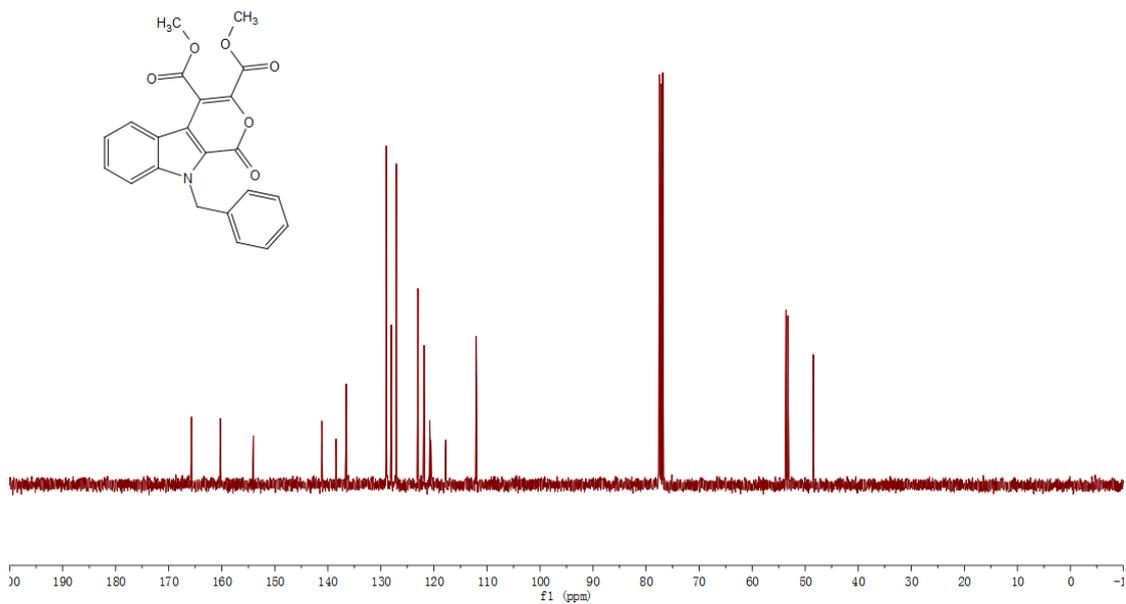
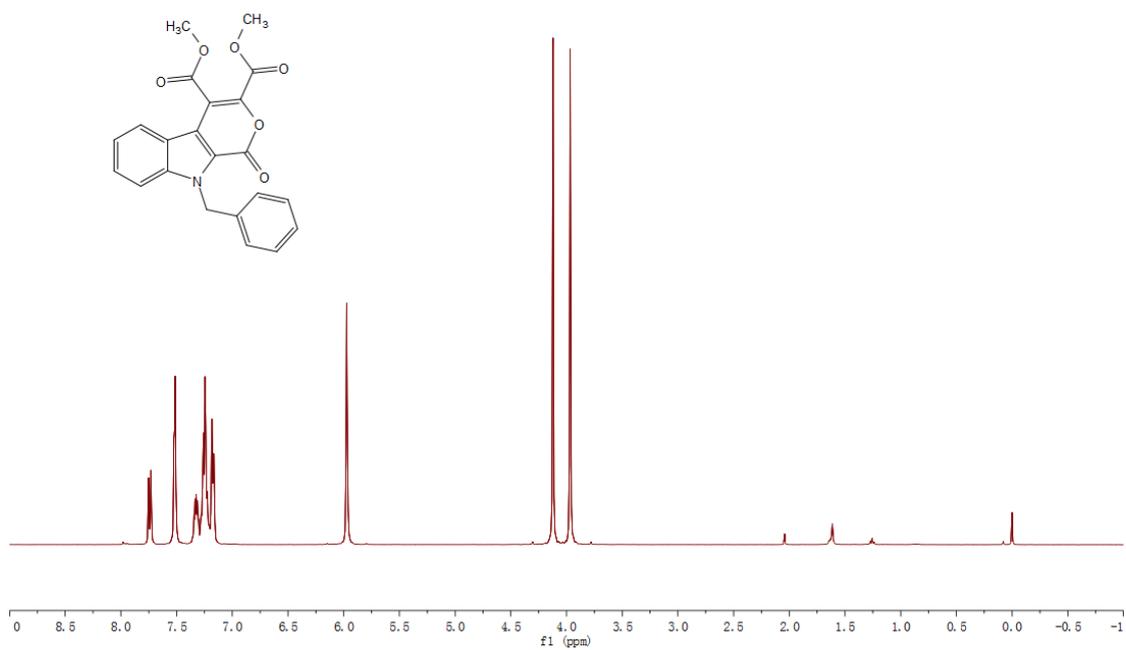
**Figure 5.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3aa** in  $\text{CDCl}_3$



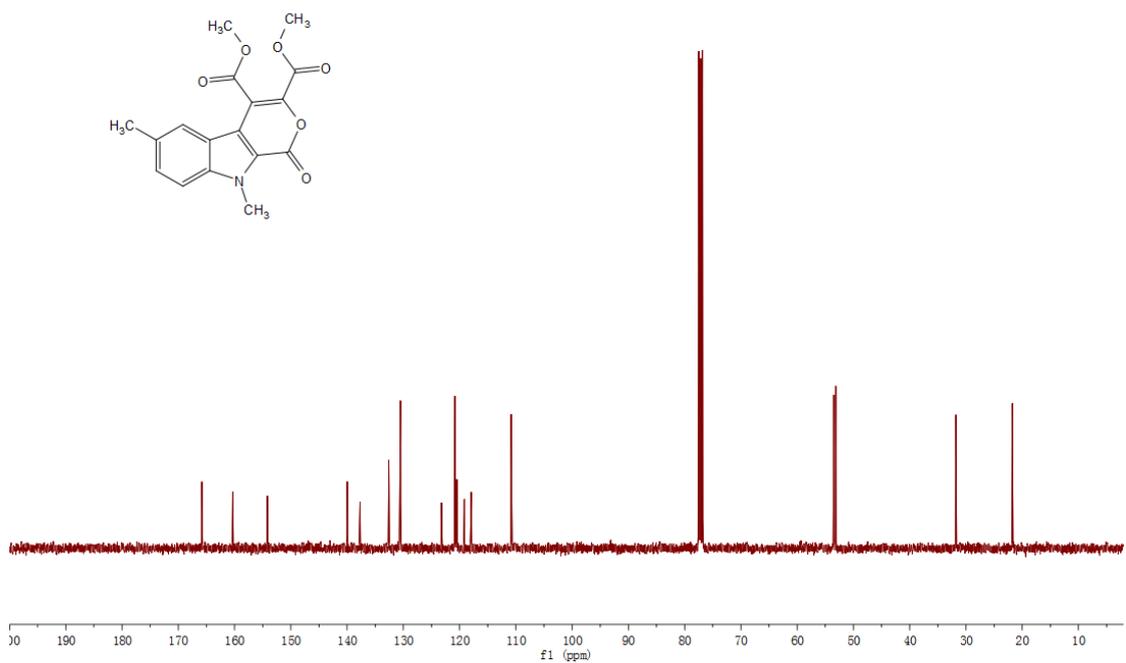
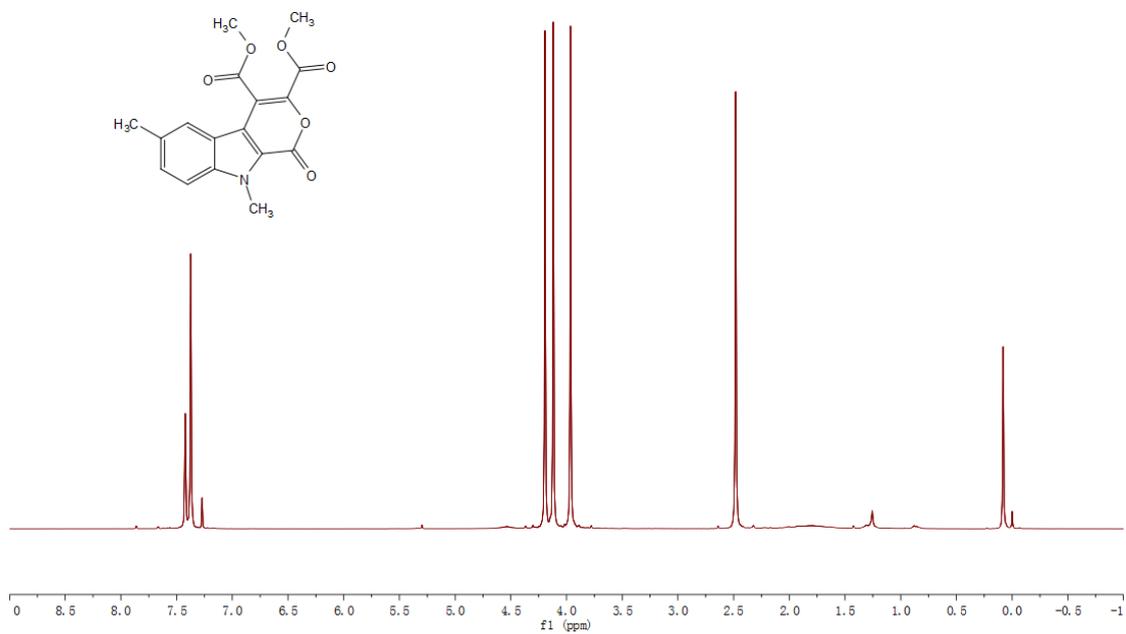
**Figure 6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ba** in  $\text{CDCl}_3$



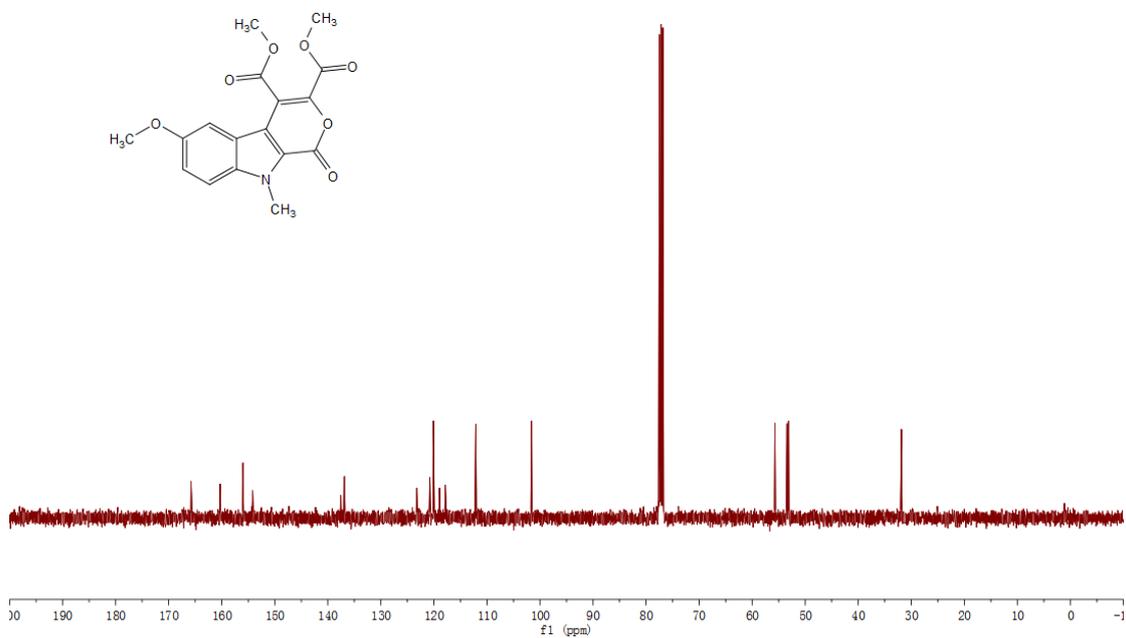
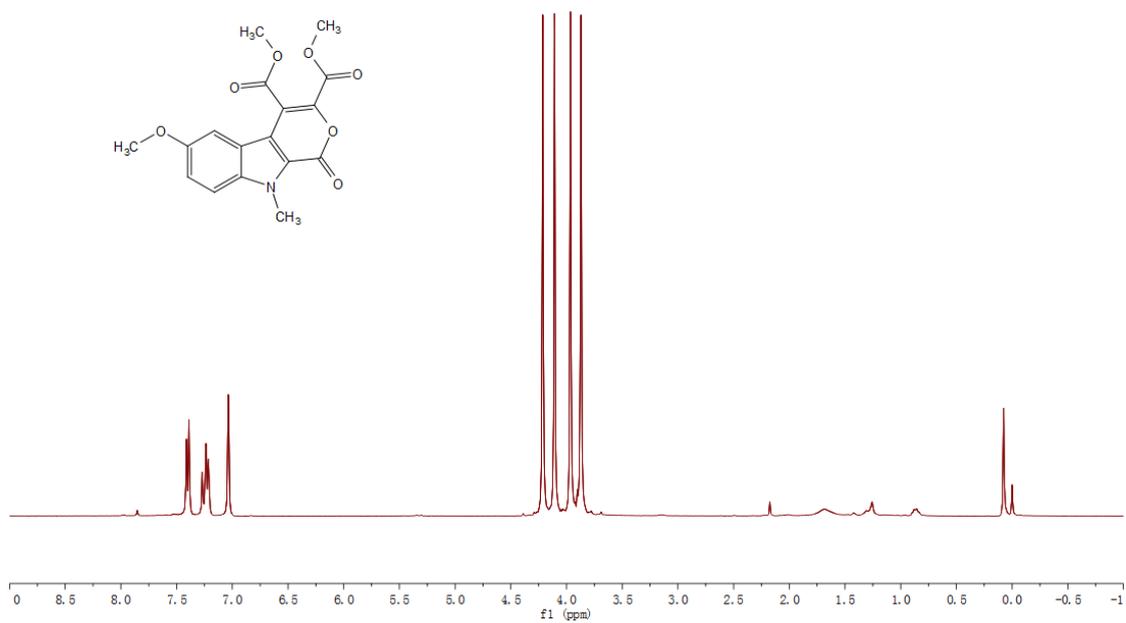
**Figure 7.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ca** in  $\text{CDCl}_3$



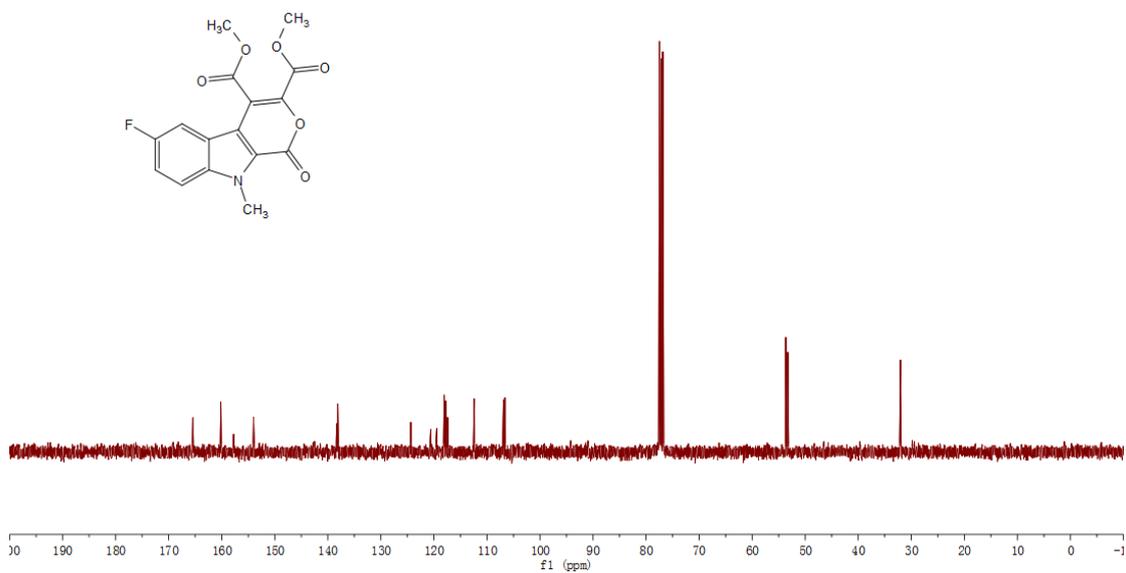
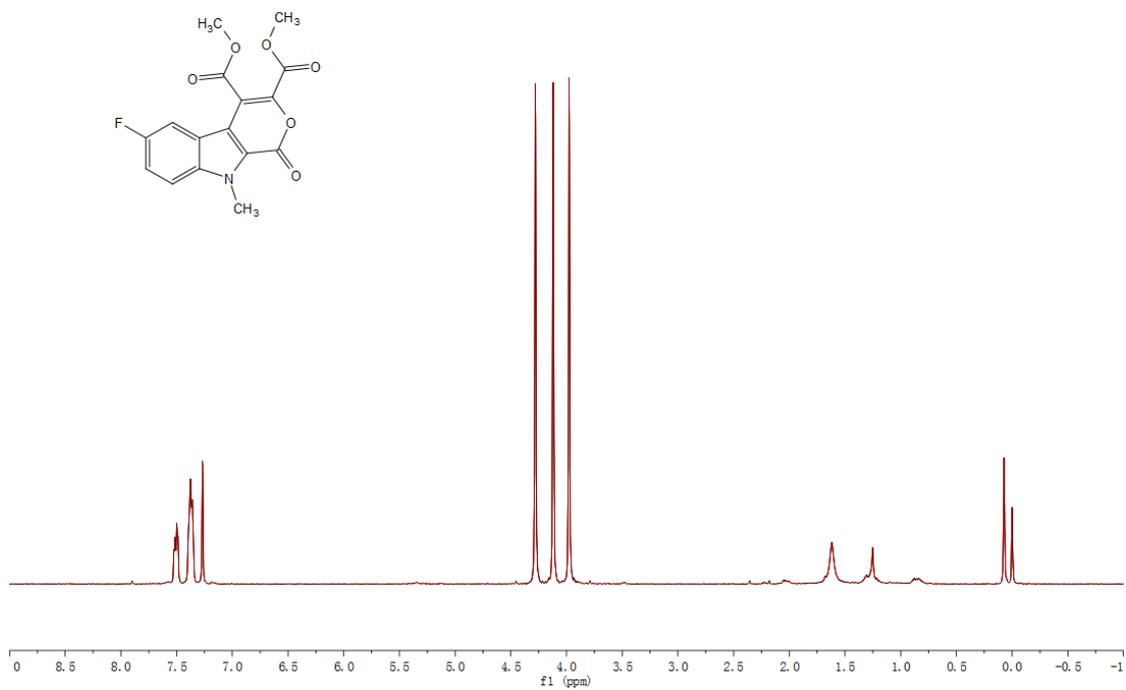
**Figure 8.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3da** in  $\text{CDCl}_3$



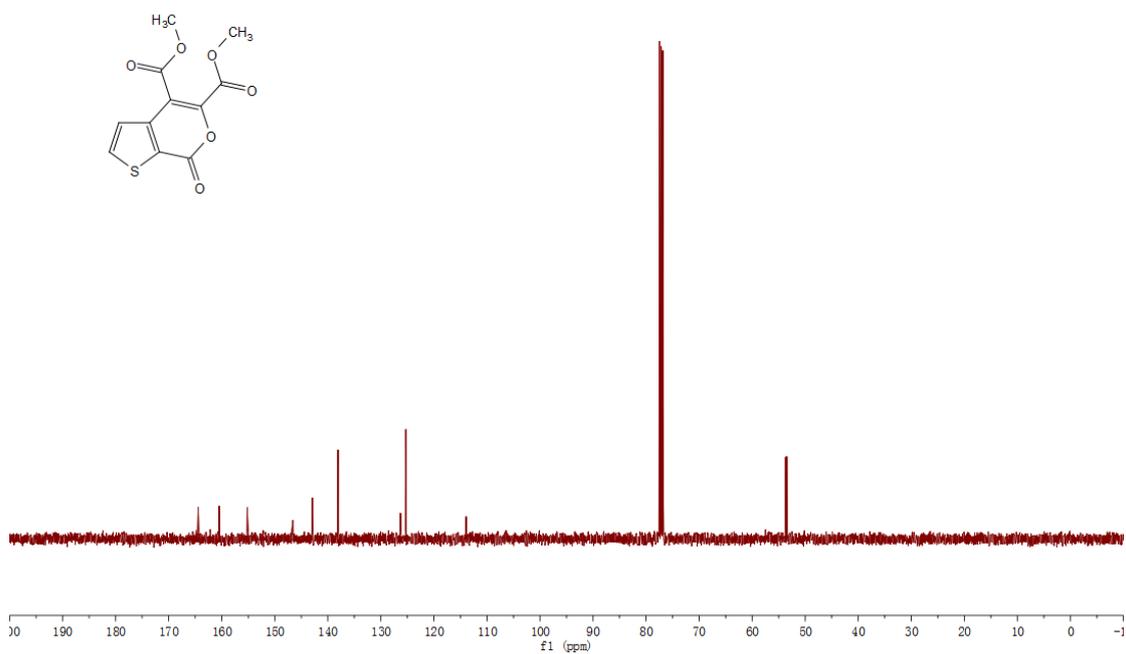
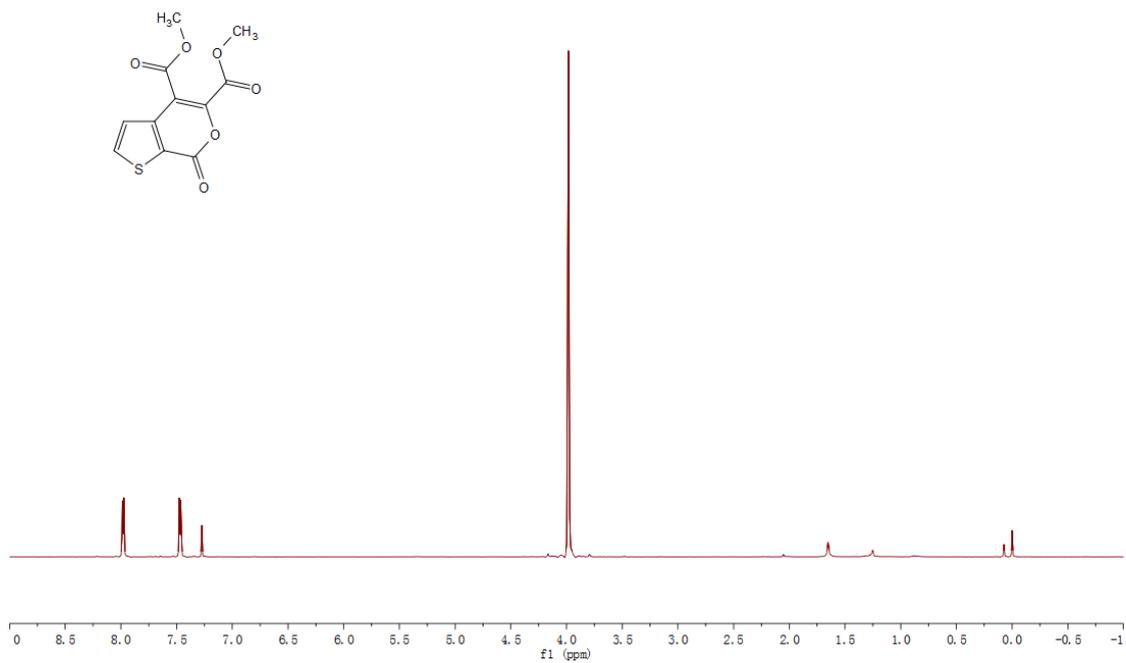
**Figure 9.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 3ea in CDCl<sub>3</sub>



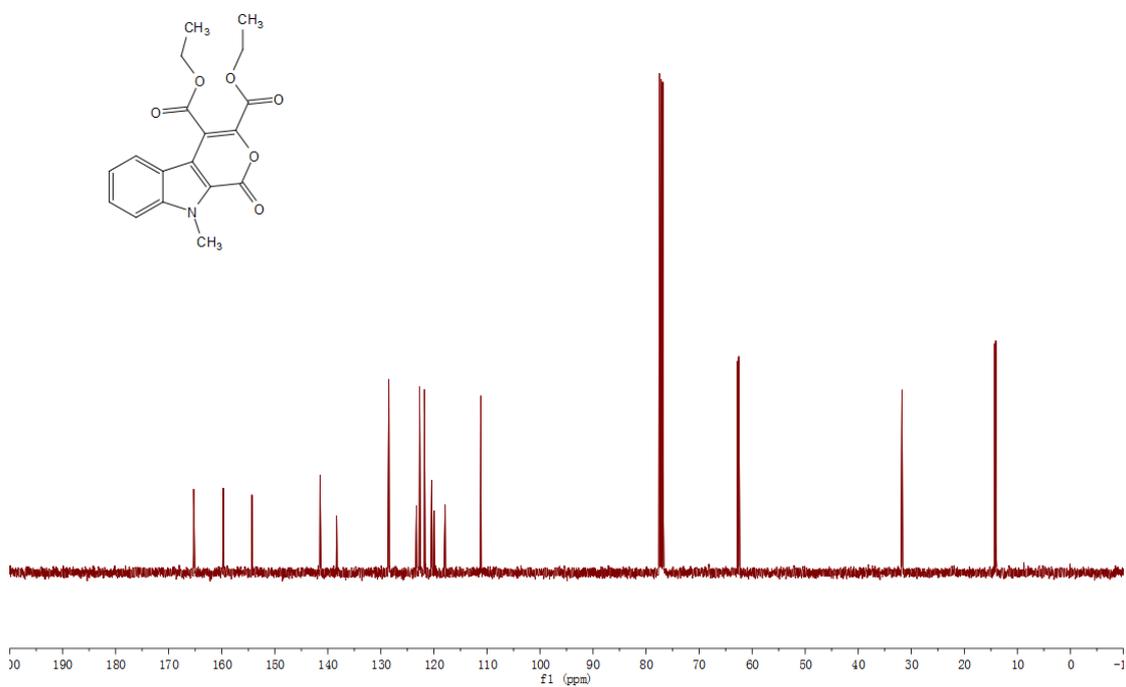
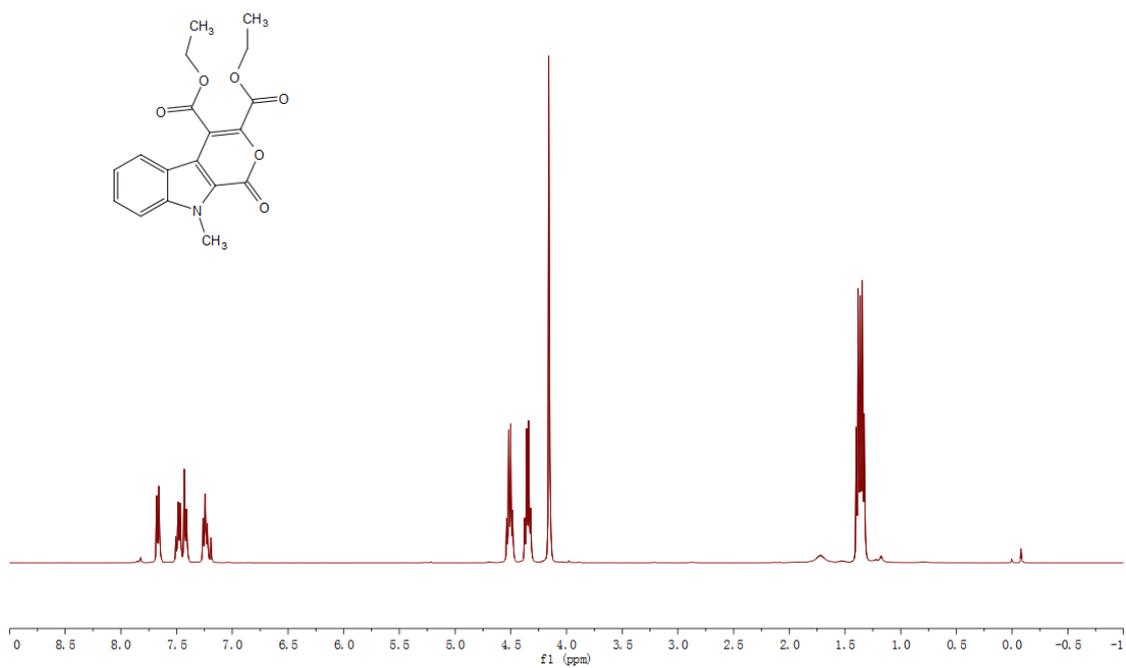
**Figure 10.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 3fa in  $\text{CDCl}_3$



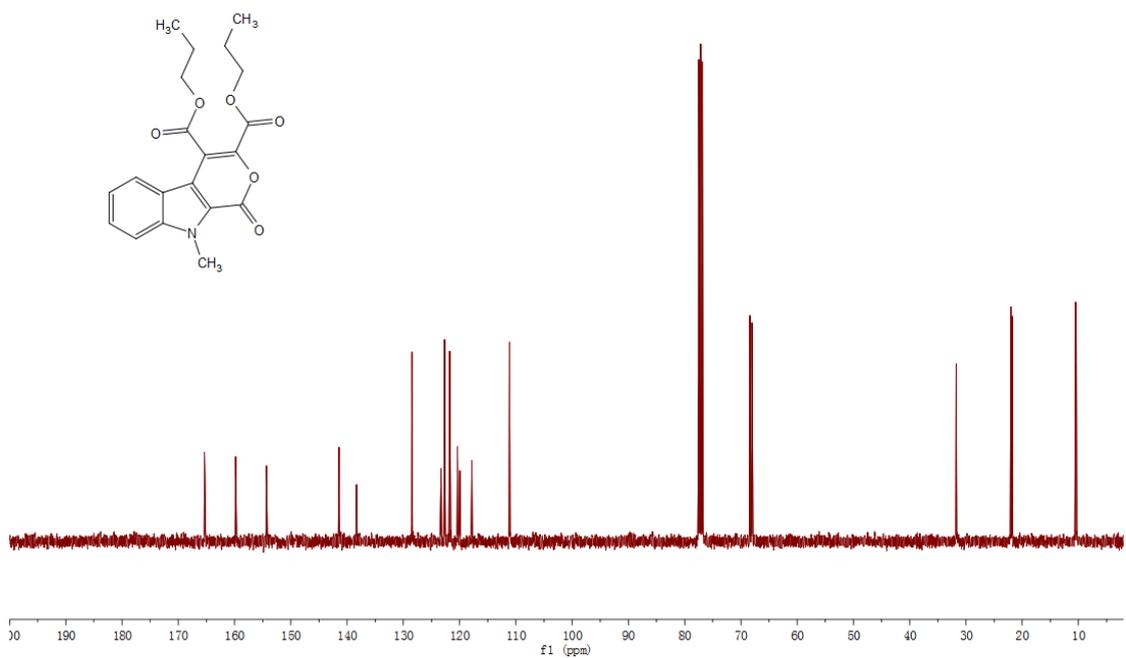
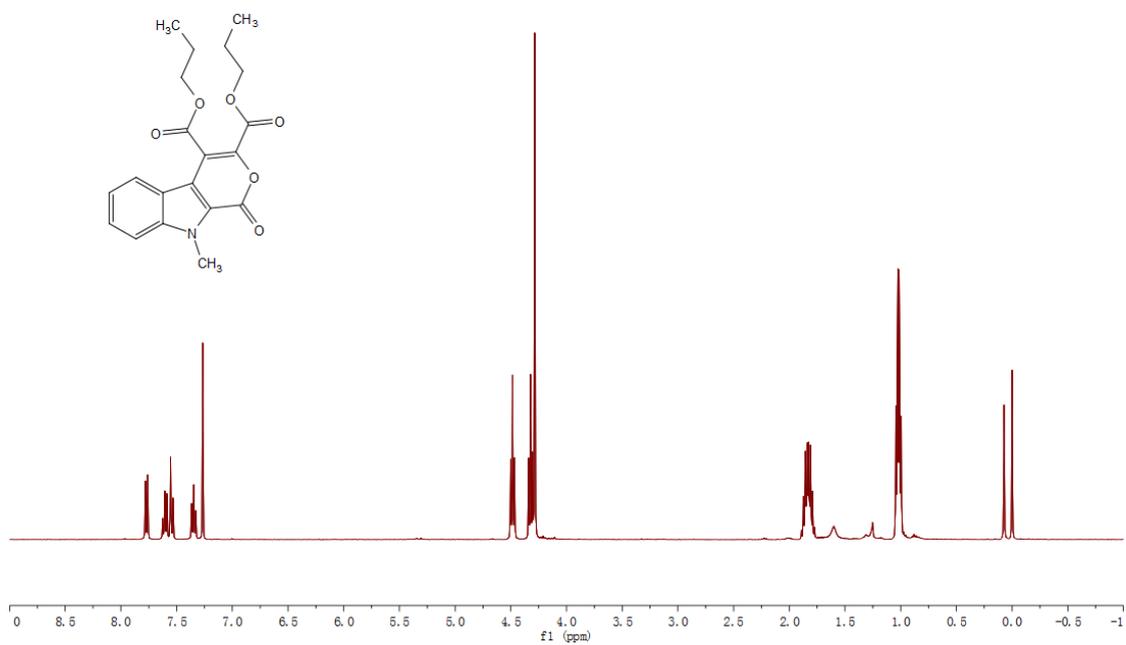
**Figure 11.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ga** in  $\text{CDCl}_3$



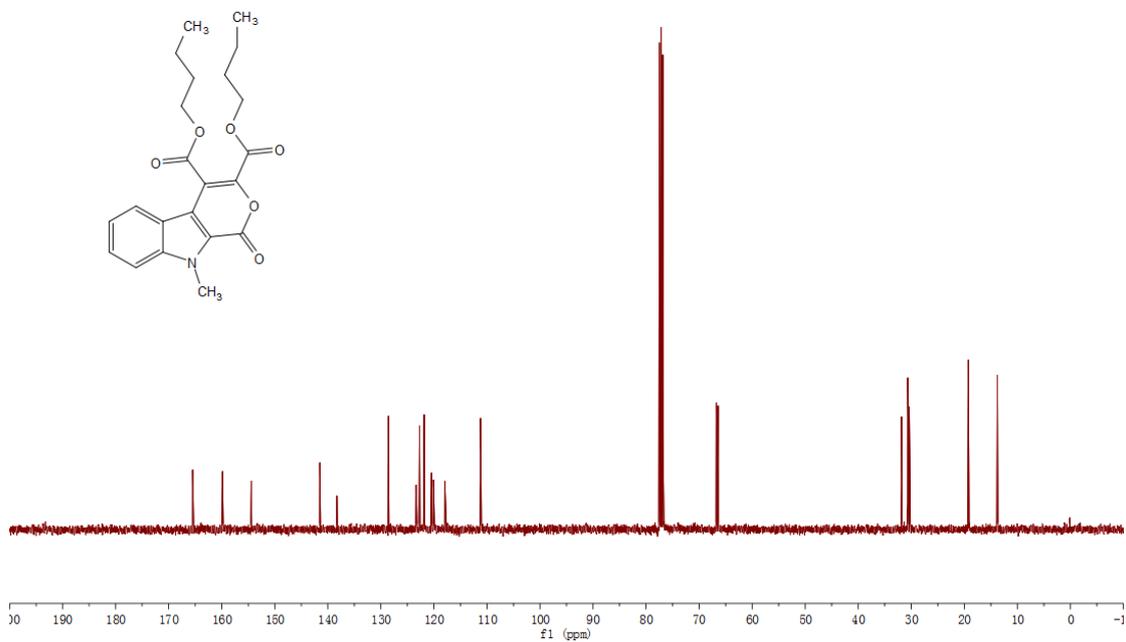
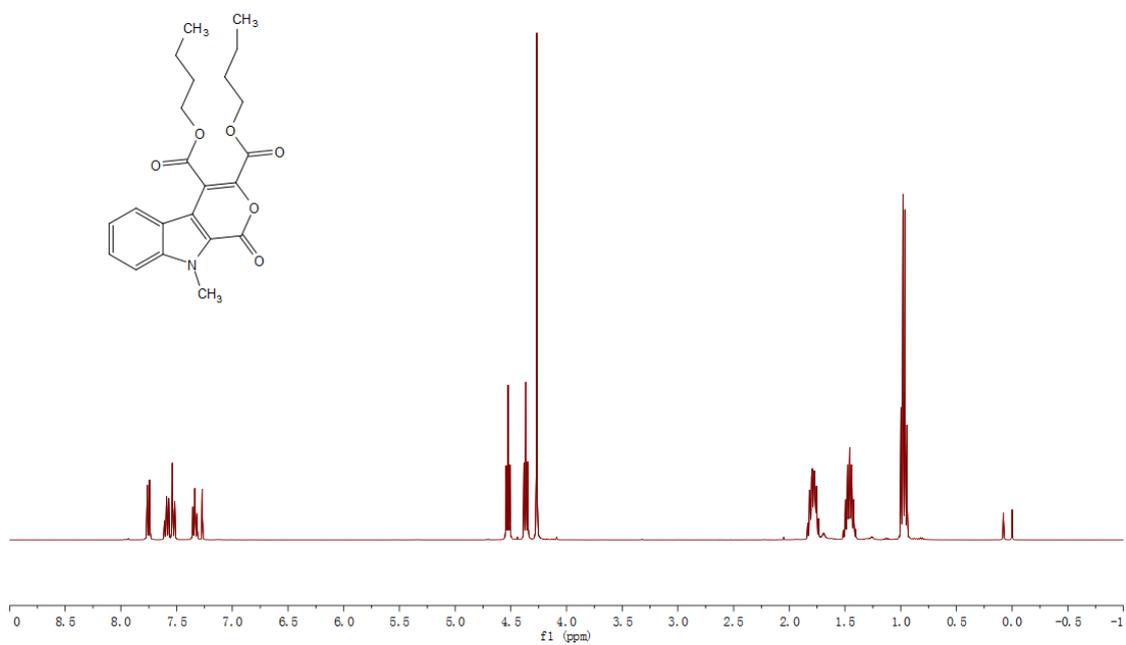
**Figure 12.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound **3ia** in CDCl<sub>3</sub>



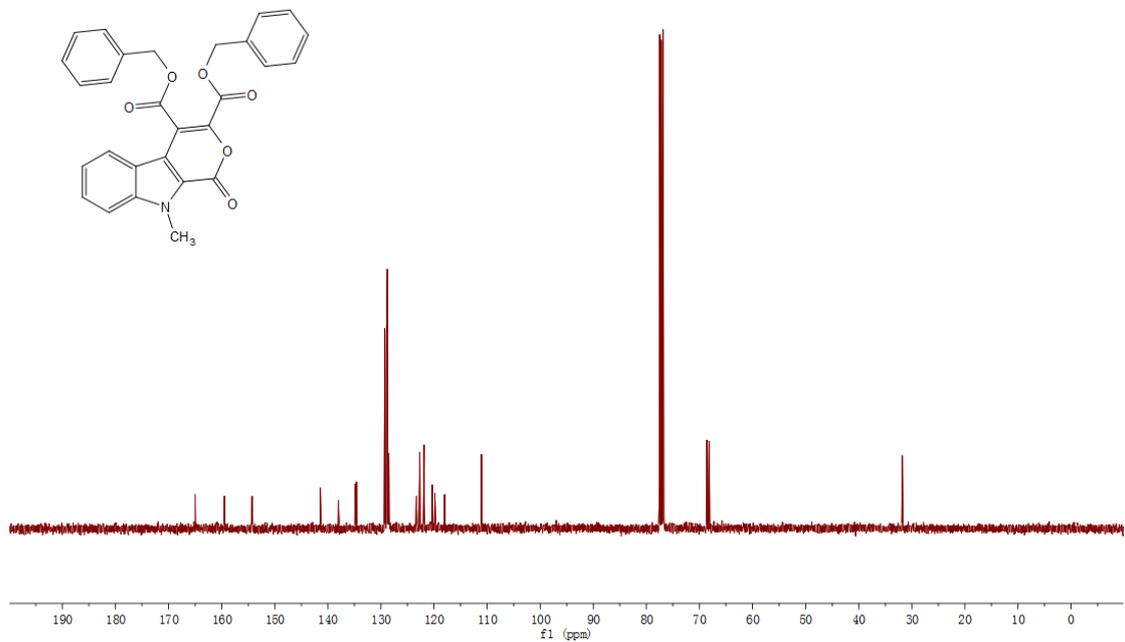
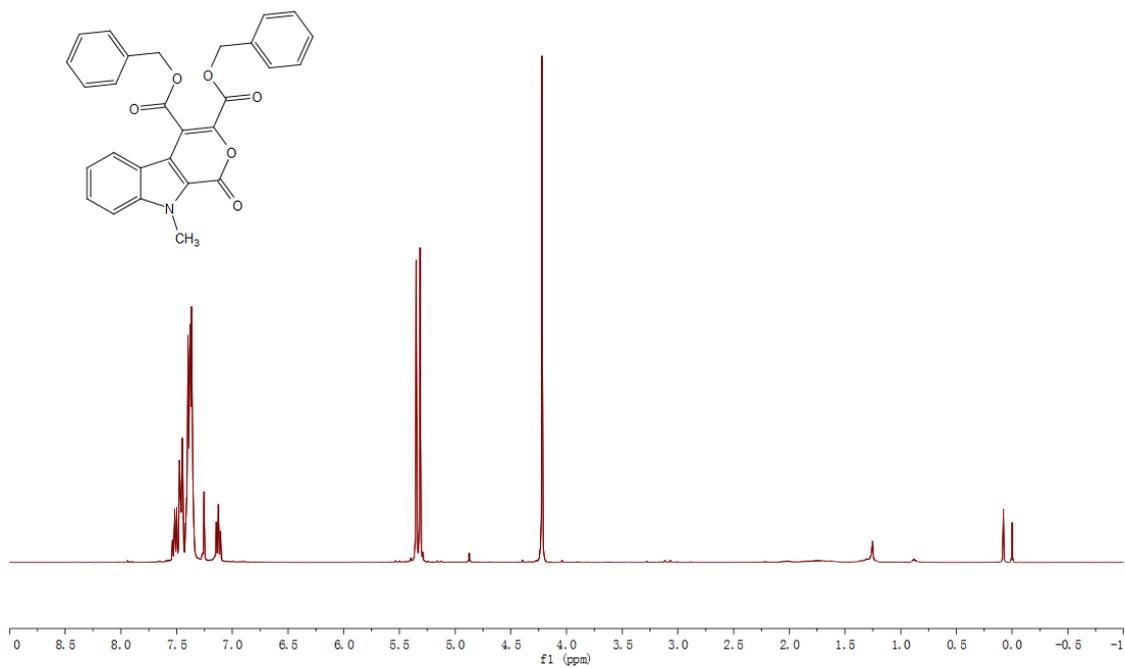
**Figure 13.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ab** in  $\text{CDCl}_3$



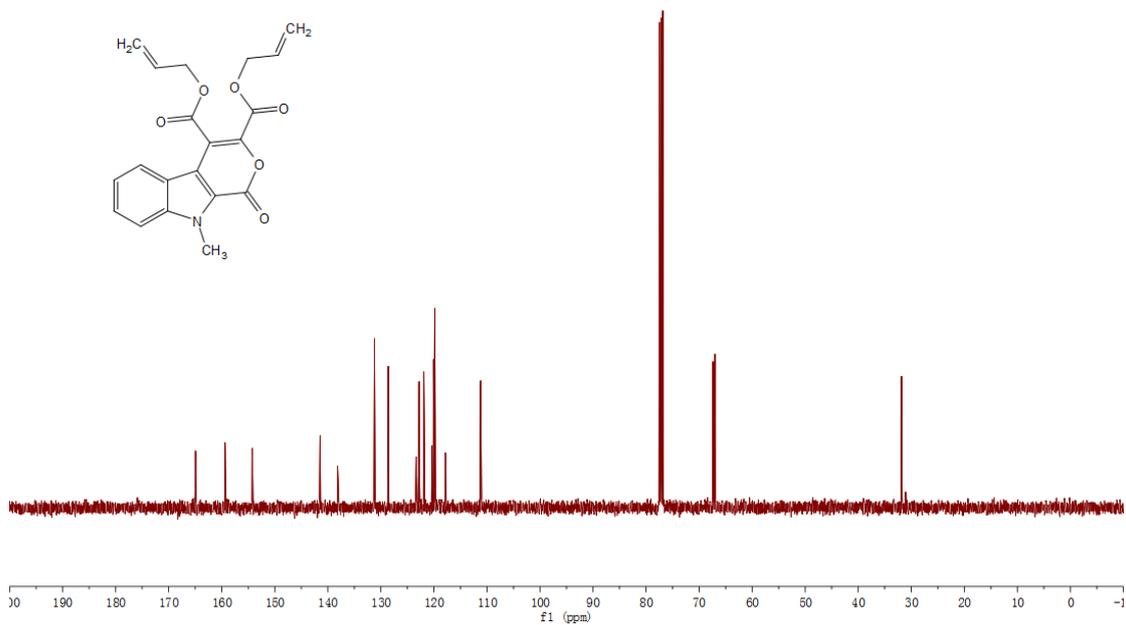
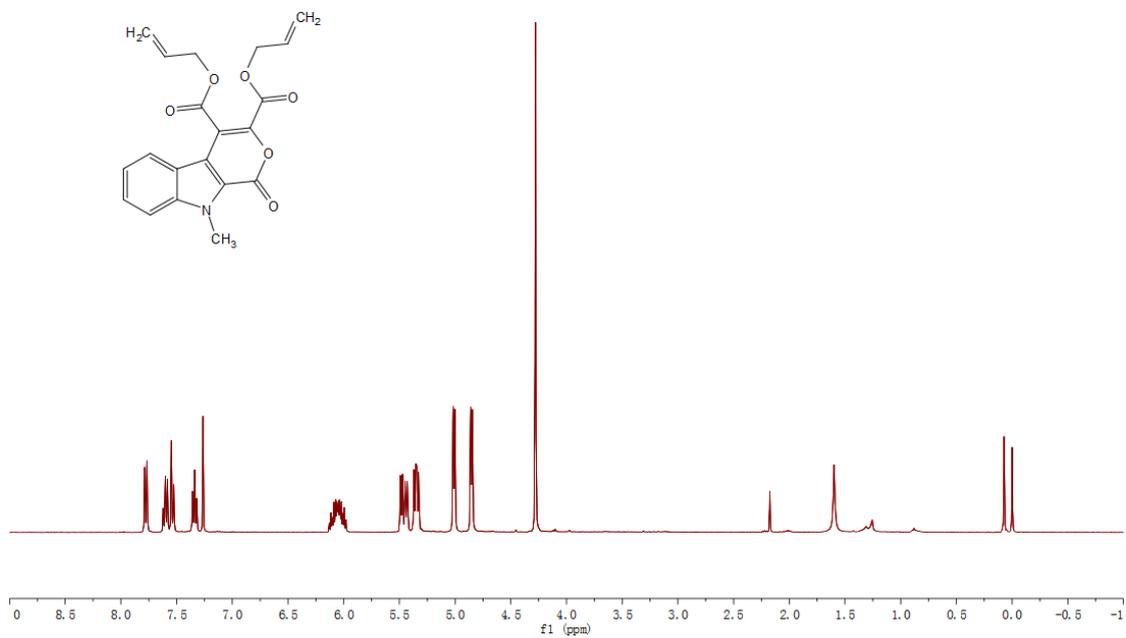
**Figure 14.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ac** in  $\text{CDCl}_3$



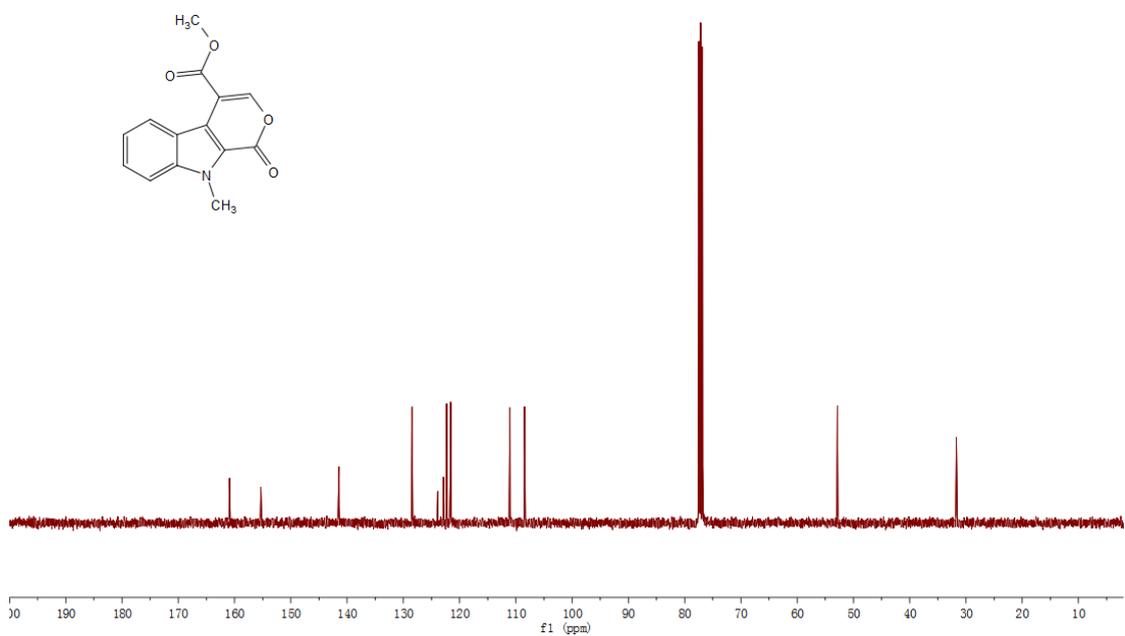
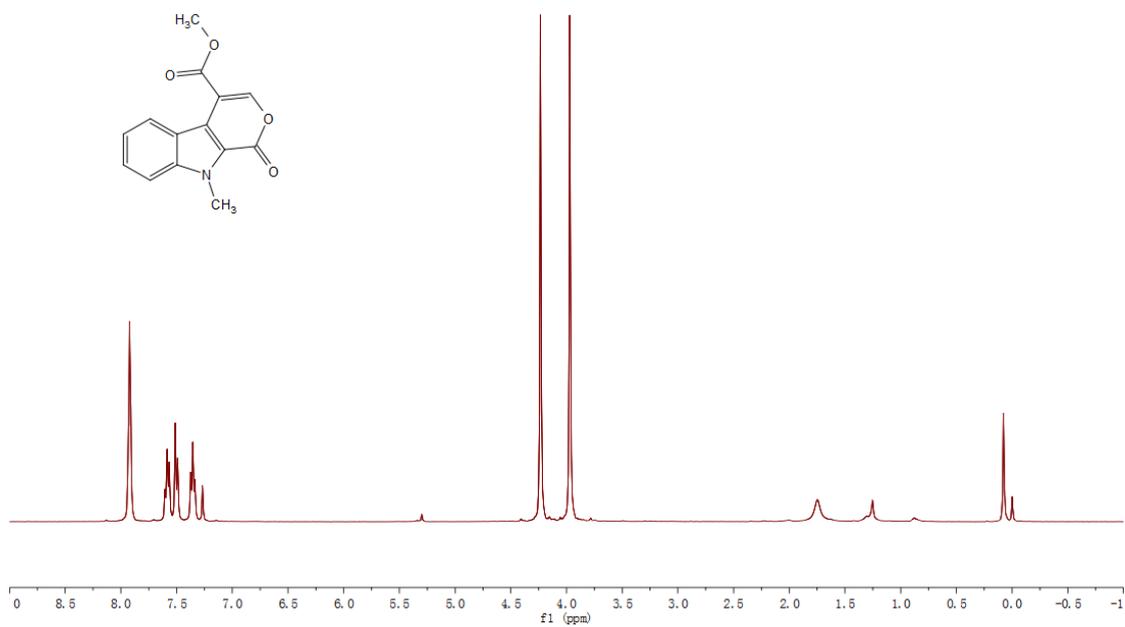
**Figure 15.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ad** in  $\text{CDCl}_3$



**Figure 16.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ae** in  $\text{CDCl}_3$



**Figure 17.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3af** in  $\text{CDCl}_3$



**Figure 18.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **3ag** in  $\text{CDCl}_3$