

# Palladium-Catalyzed *ortho*-Functionalization of Azoarenes with Aryl Acylperoxides

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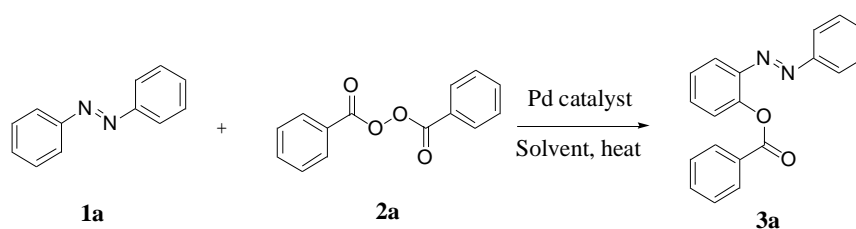
## 1. General experimental information

Unless otherwise noted, reactions were conducted in dry solvents. Purifications of reaction products were carried out by flash chromatography using silica gel (40-63  $\mu\text{m}$ ). Infrared spectra (IR) were recorded on a spectrophotometer and are reported as wavenumber (cm<sup>-1</sup>). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a spectrometer operating at 400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a model spectrometer.

## 2. General procedure for reaction condition screening

### Table S1. General procedure for *ortho*-acyloxylation of azobenzenes:

A 10 mL of reaction tube was charged with azobenzene (**1a**) (0.15 mmol), benzoylperoxide (**2a**) (0.30 mmol), Pd catalyst (10 mol %), and CH<sub>3</sub>CN (2.0 mL). After the reaction was carried out at 60 °C for 24 h, it was cooled to room temperature and concentrated in vacuum, followed by flash chromatography on SiO<sub>2</sub> to provide the corresponding desired product **3a**.<sup>a</sup>



Entry	Pd catalyst	Solvent	Yield (%) <sup>b</sup>
1	PdCl <sub>2</sub>	CH <sub>3</sub> CN	43
2	PdCl <sub>2</sub>	DMSO	NR
3	PdCl <sub>2</sub>	DMF	NR
4	PdCl <sub>2</sub>	THF	14
5	PdCl <sub>2</sub>	Toluene	34
6	PdCl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	26

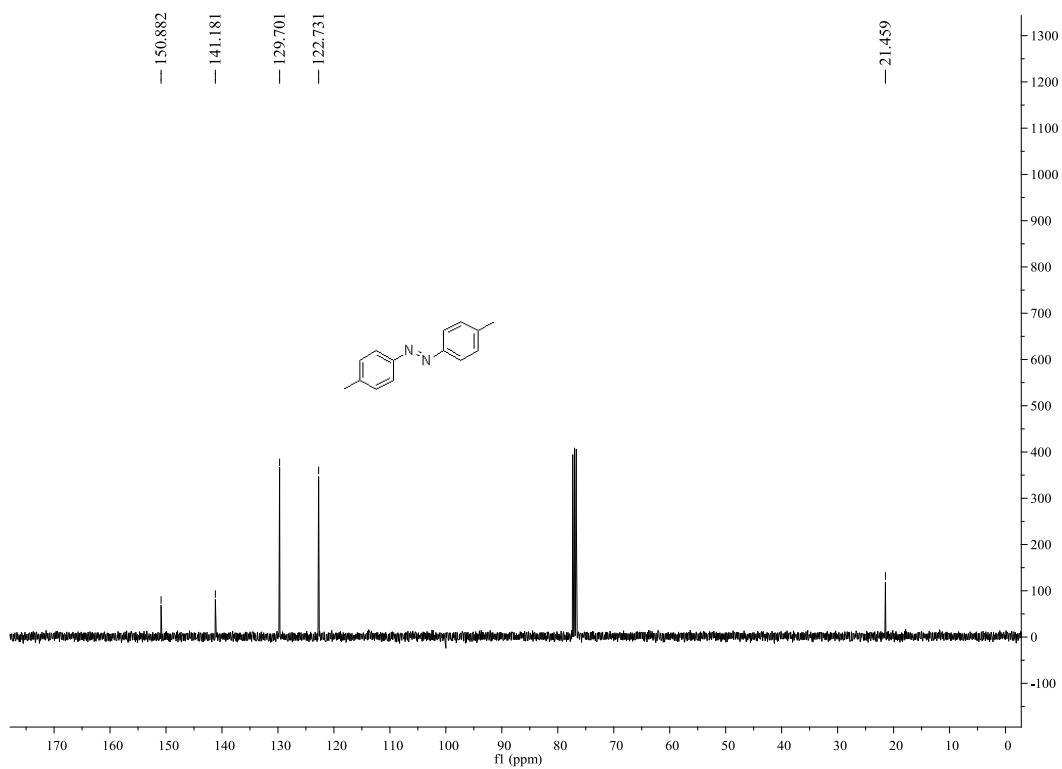
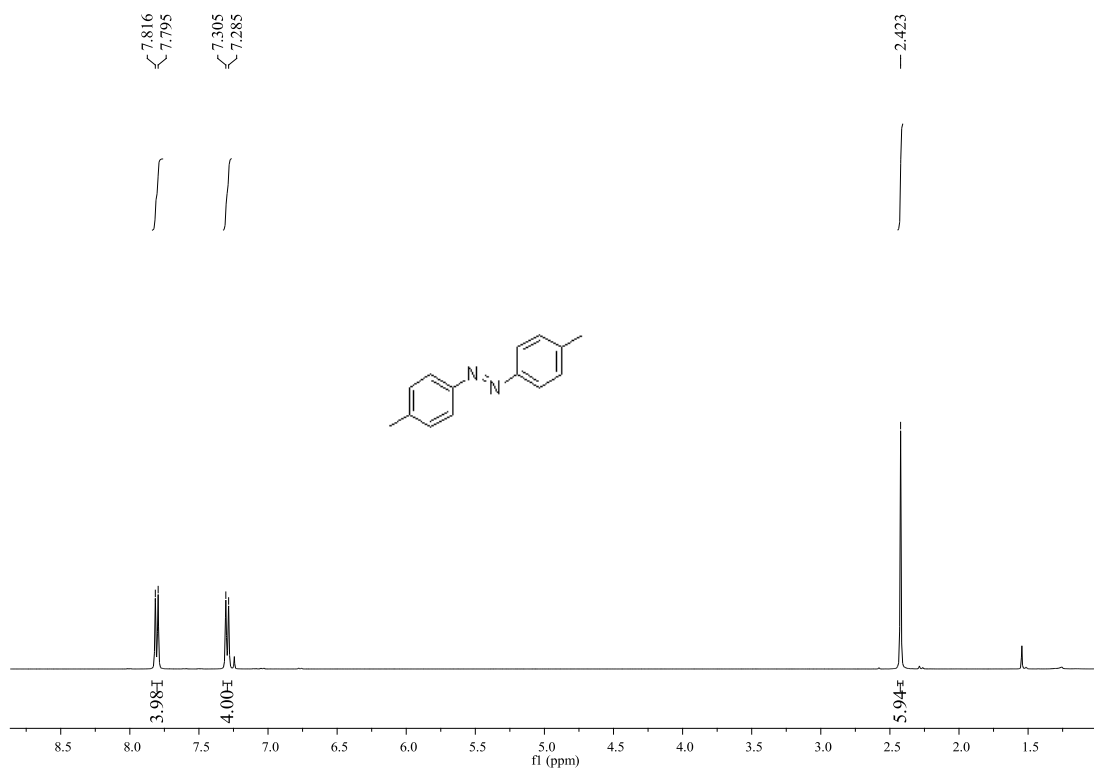


mmol) and benzoyl peroxide (**2a**) (0.30 mmol) with palladium catalyst (10 mol %) in solvent (2.0 mL) at 100 °C for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Reaction temperature:130 °C. <sup>d</sup>Reaction temperature: 90 °C. <sup>e</sup>1 equiv of **2a**.

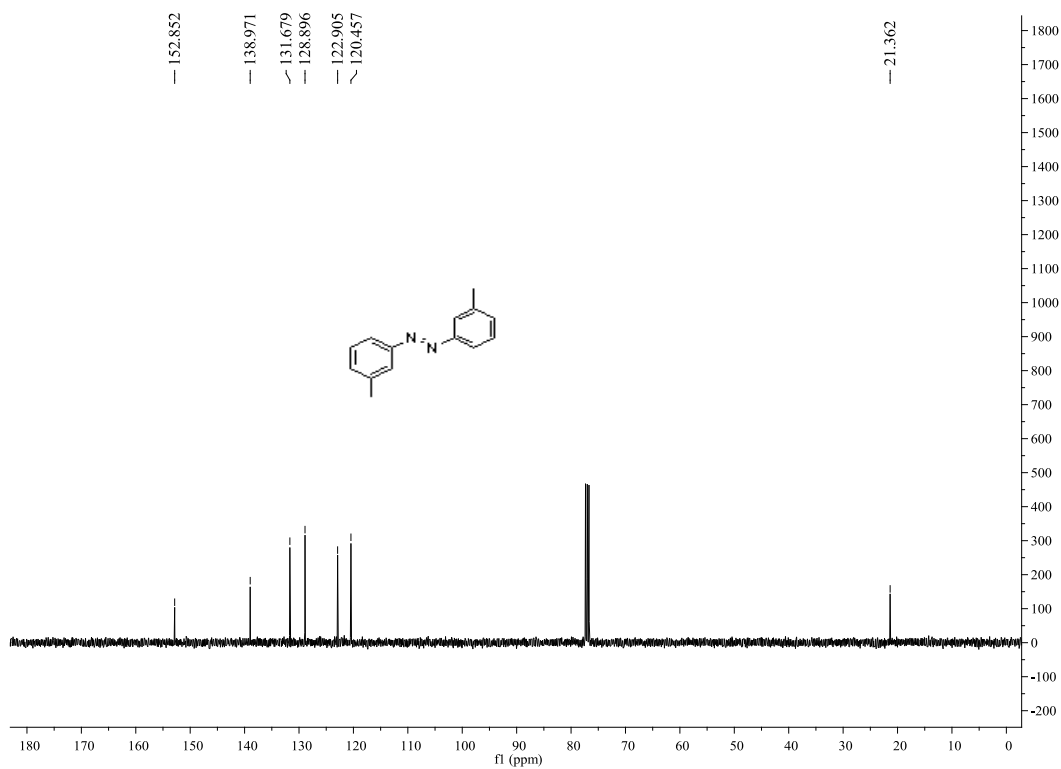
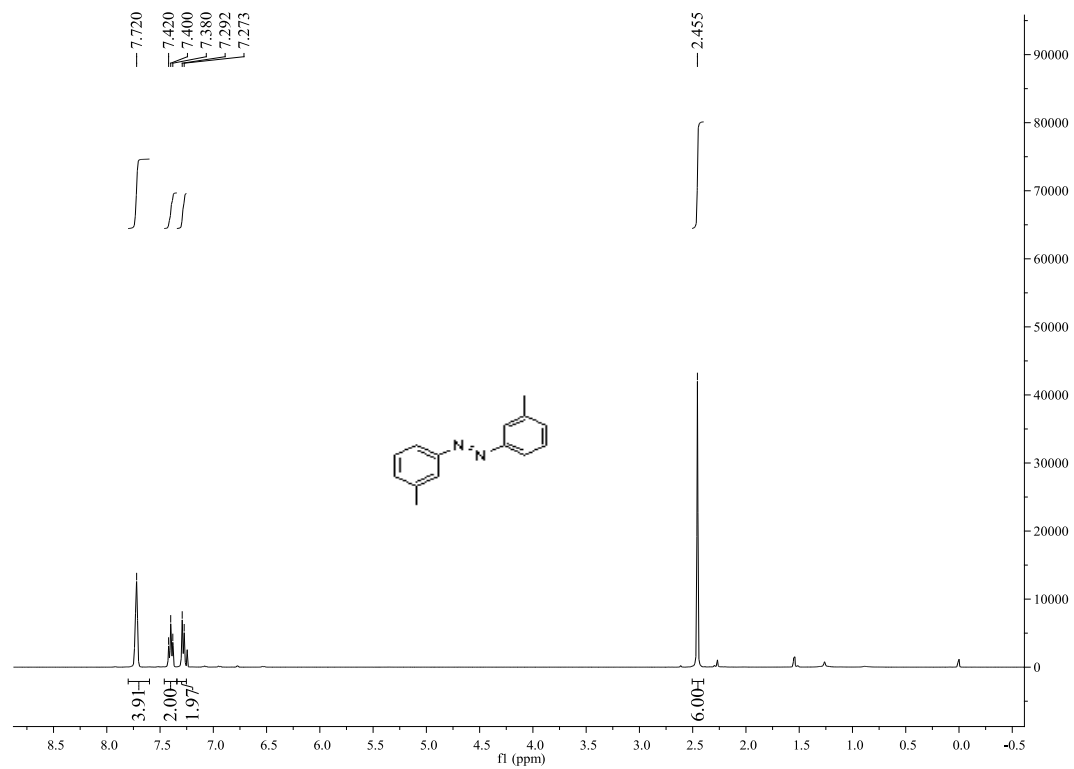
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### 3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectrum for all the isolated products ( $\text{CDCl}_3$ as solvent)

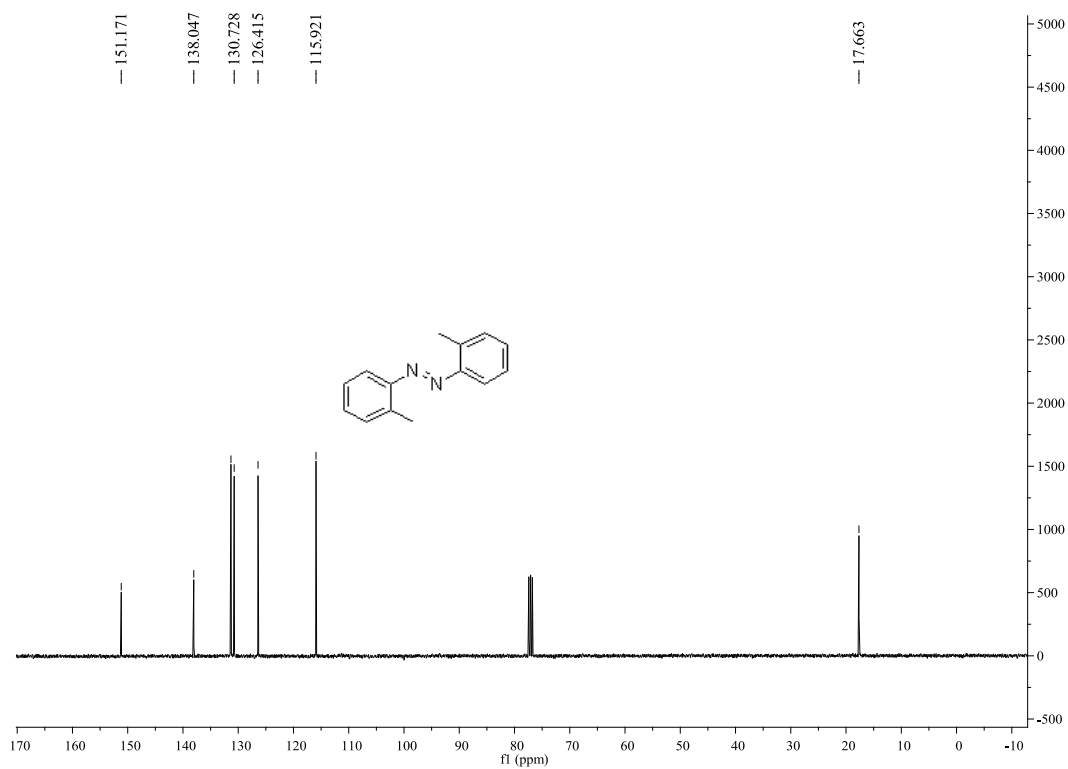
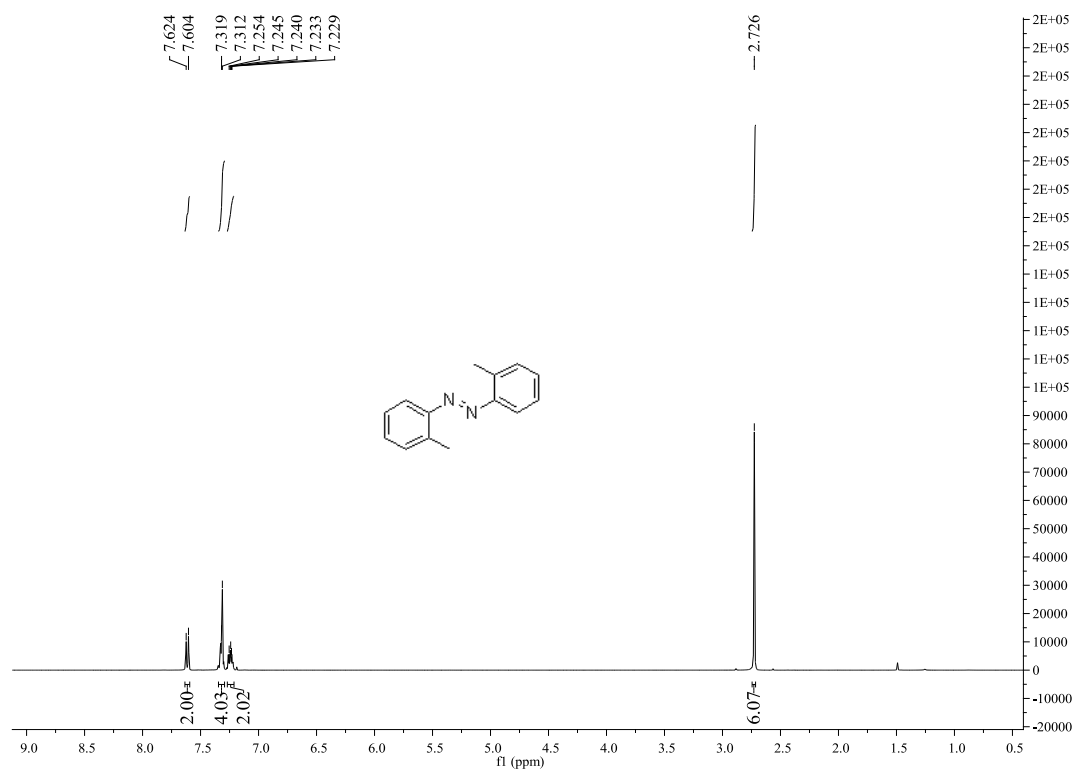
#### 3.1 $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectrum for **1b** ( $\text{CDCl}_3$ as solvent)



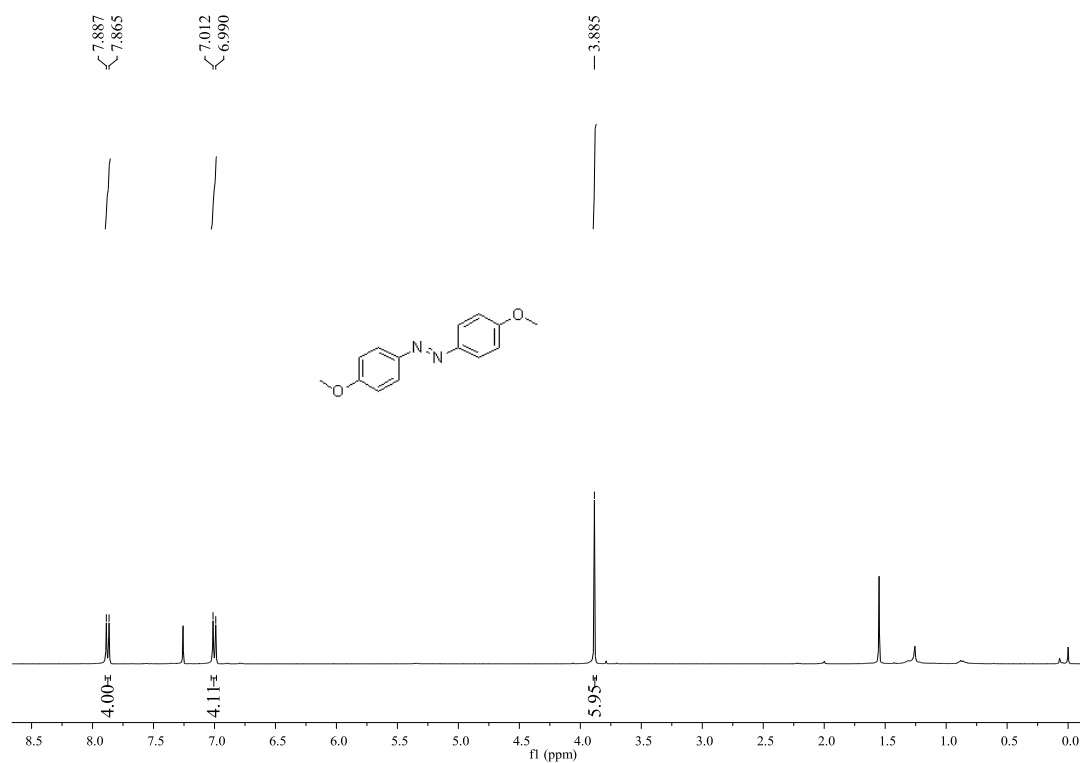
3.2  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1c** ( $\text{CDCl}_3$  as solvent)



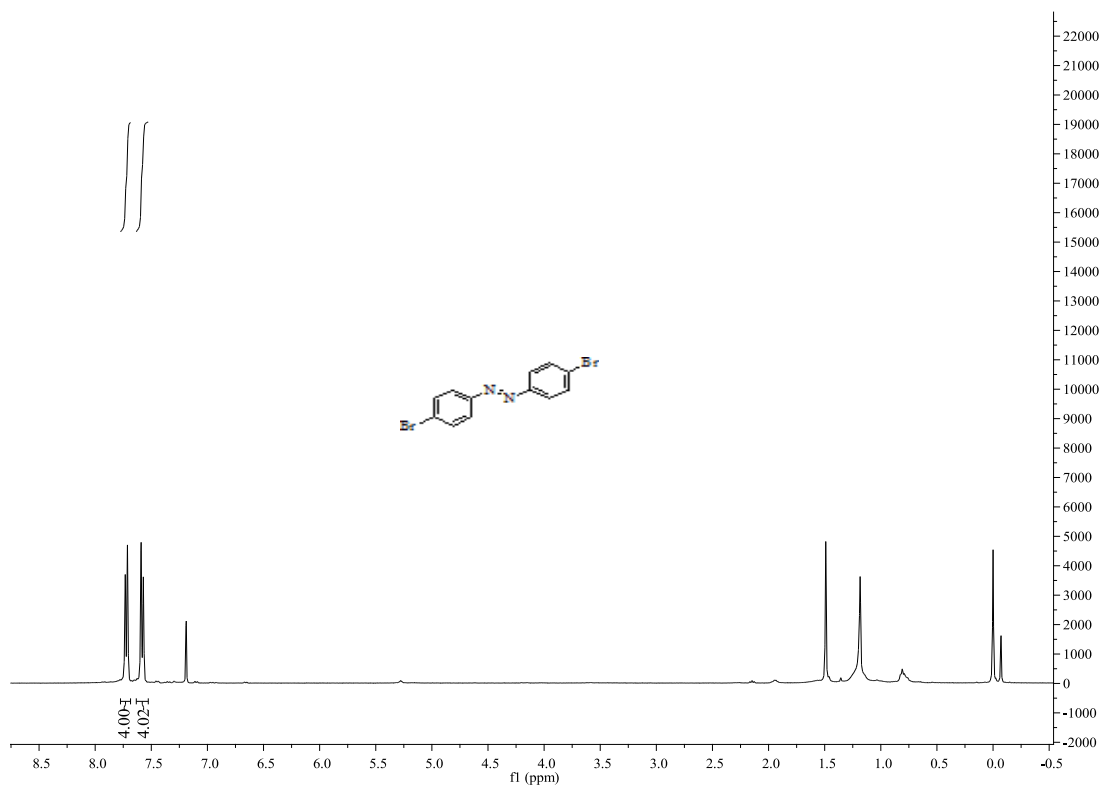
3.3  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1d** ( $\text{CDCl}_3$  as solvent)



3.4  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1e** ( $\text{CDCl}_3$  as solvent)

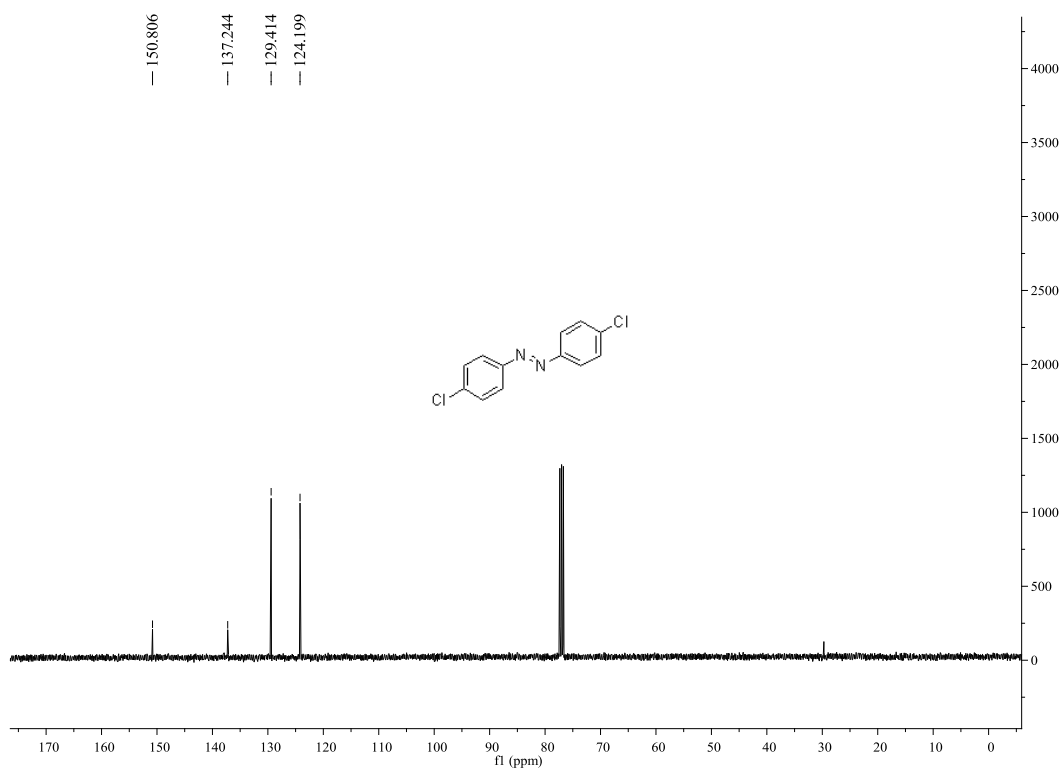
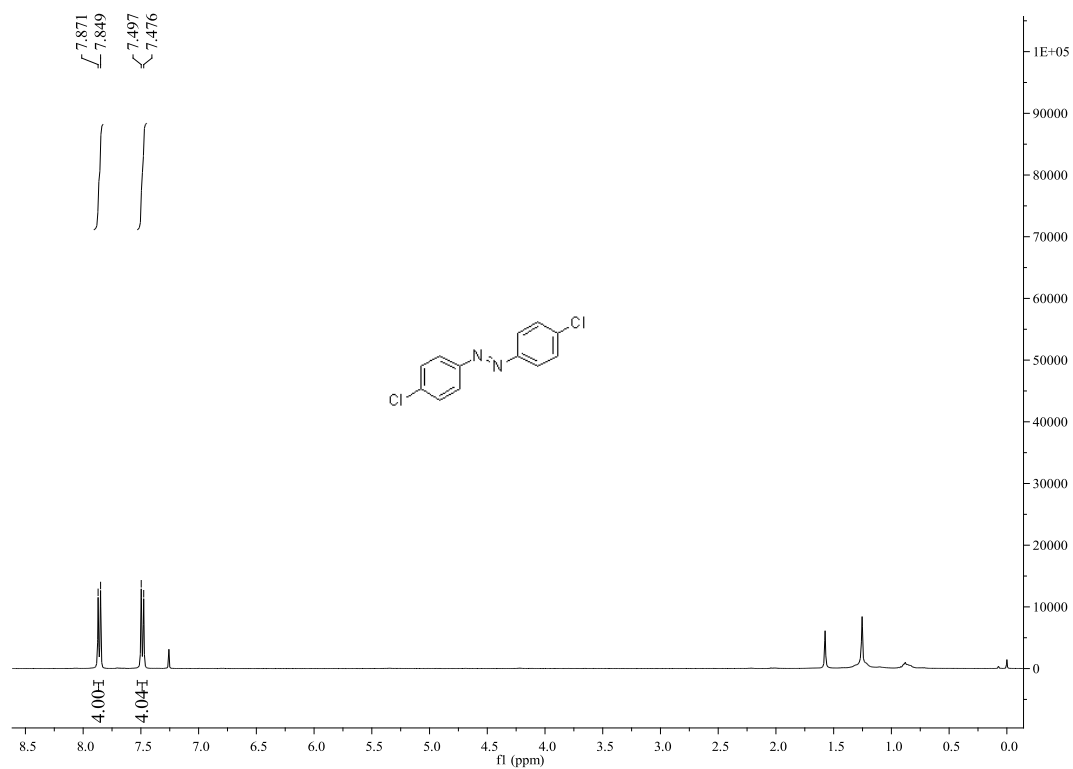


3.5  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1g** ( $\text{CDCl}_3$  as solvent)

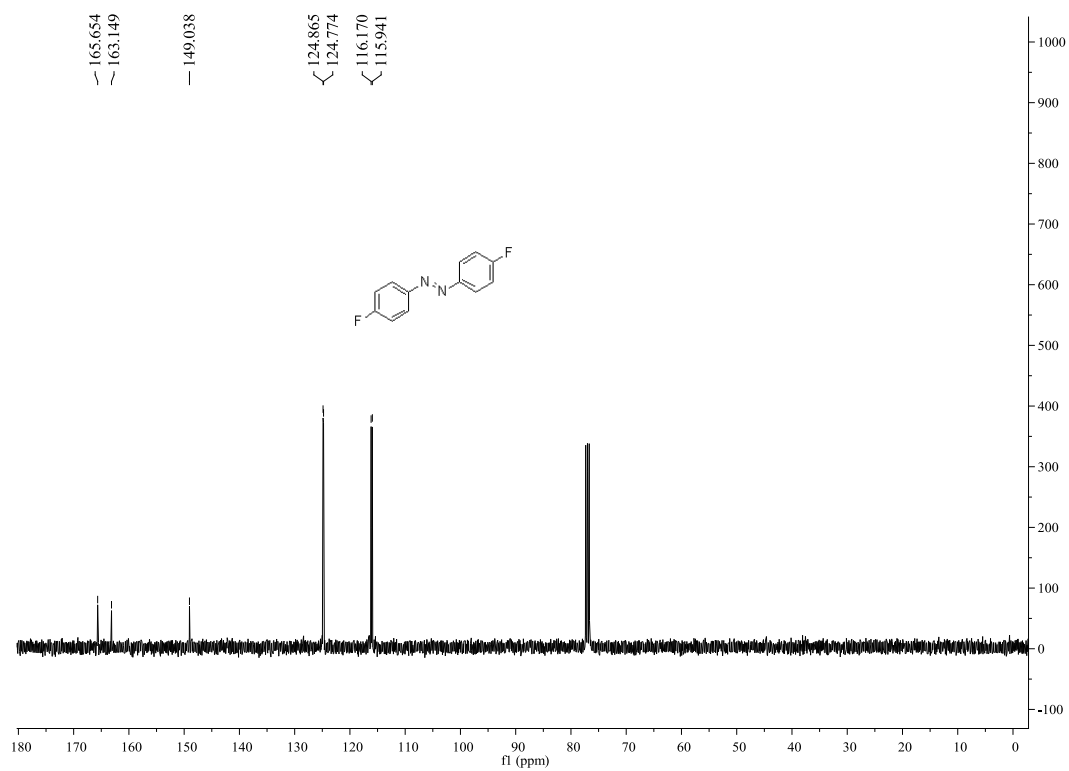
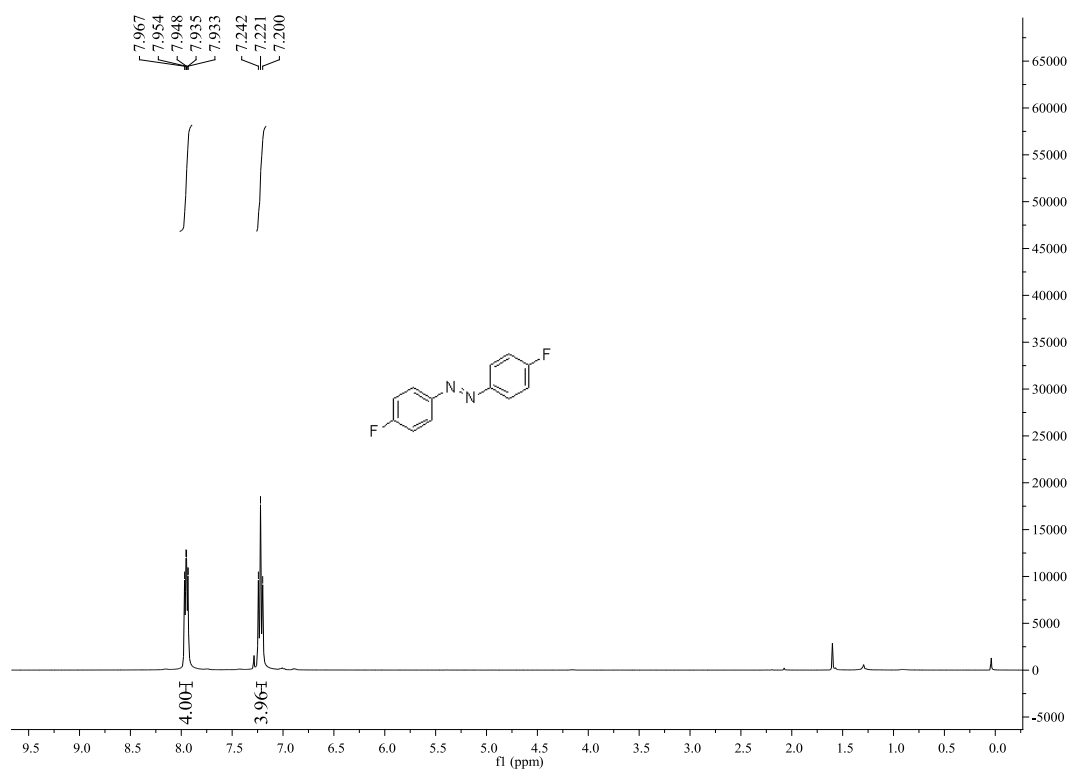




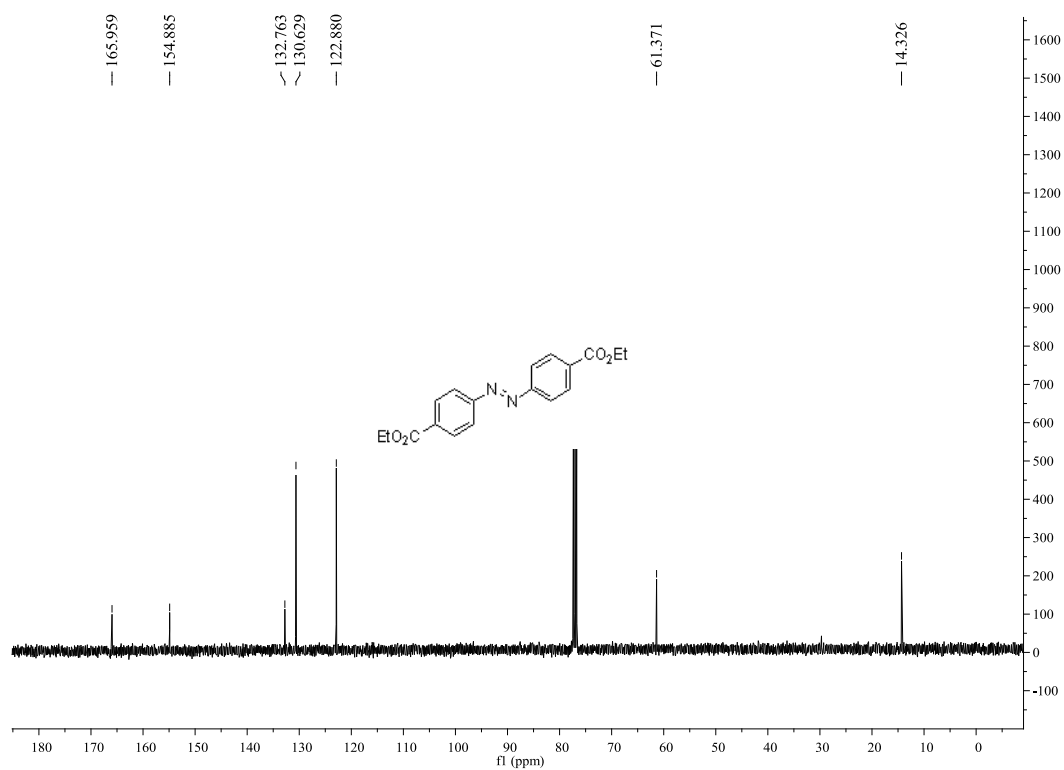
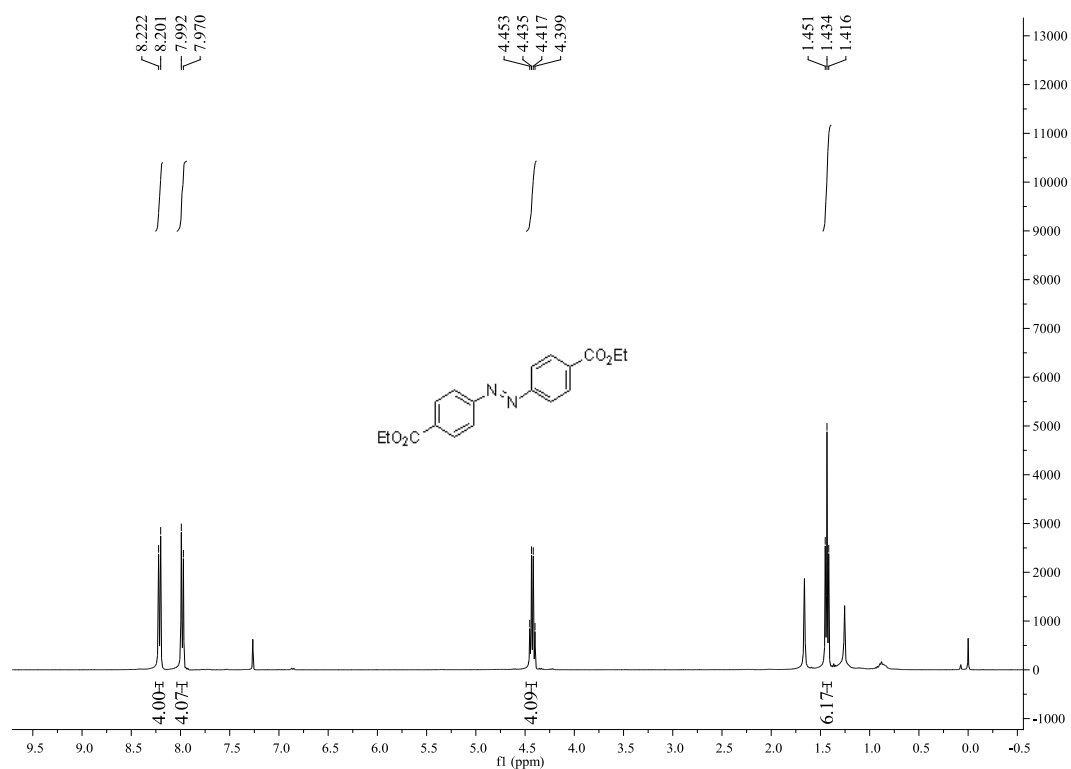
3.6  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1f** ( $\text{CDCl}_3$  as solvent)



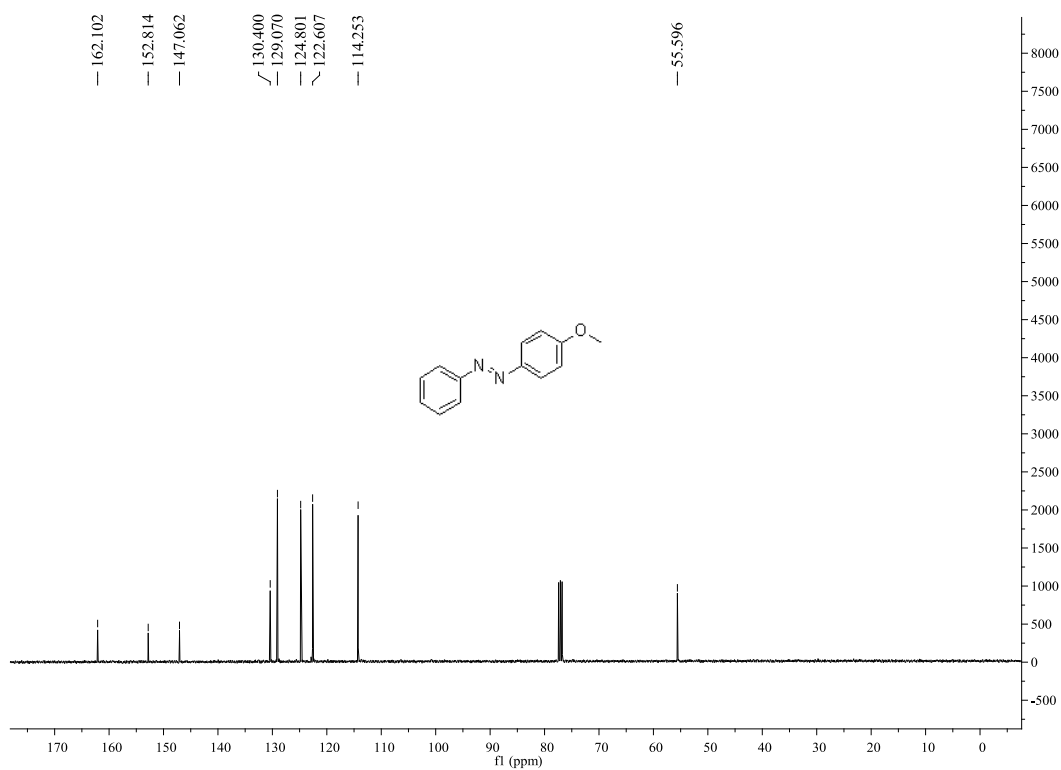
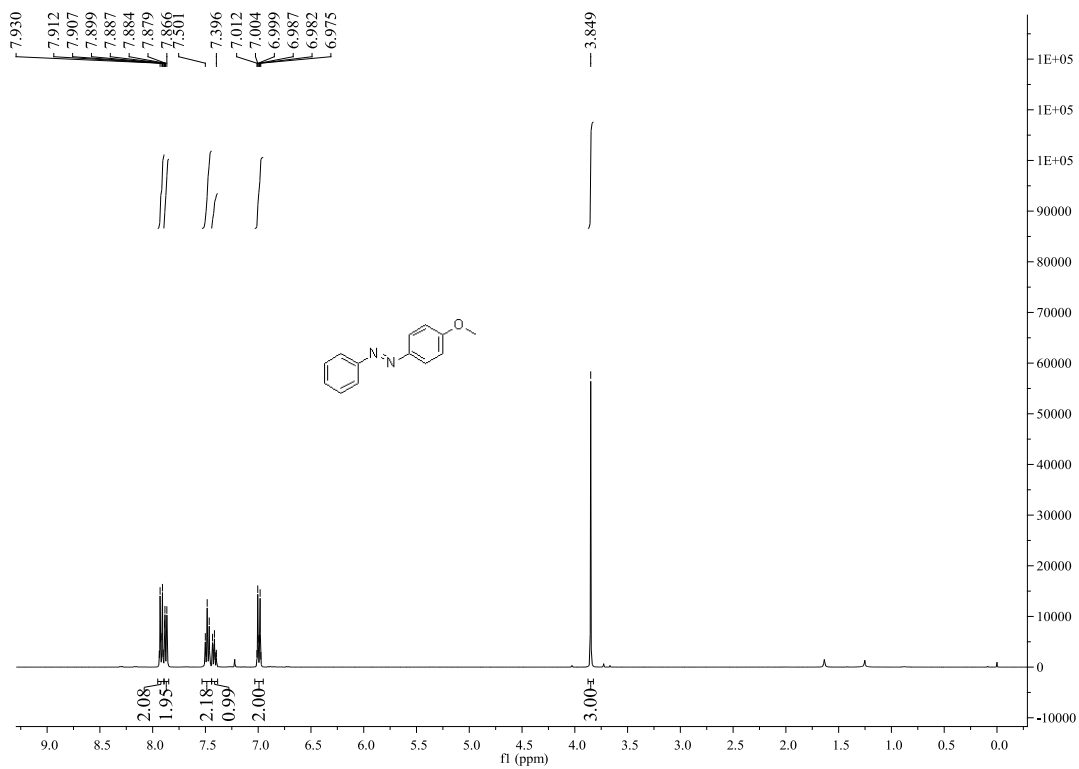
3.7  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1h** ( $\text{CDCl}_3$  as solvent)



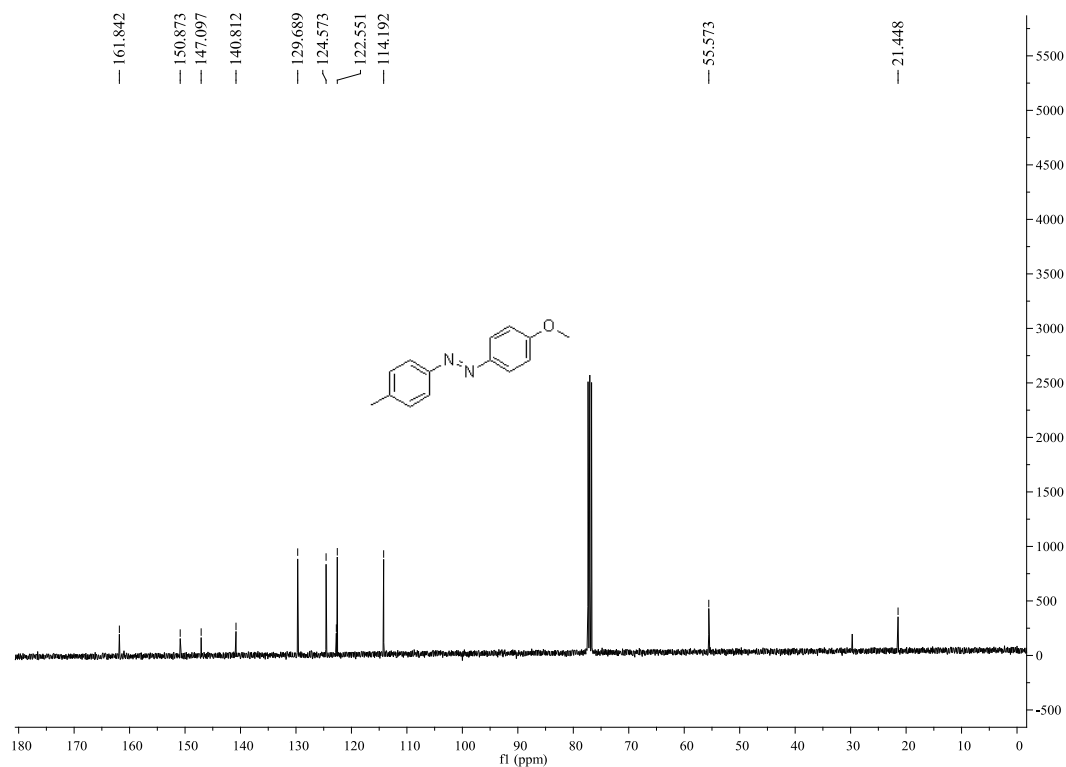
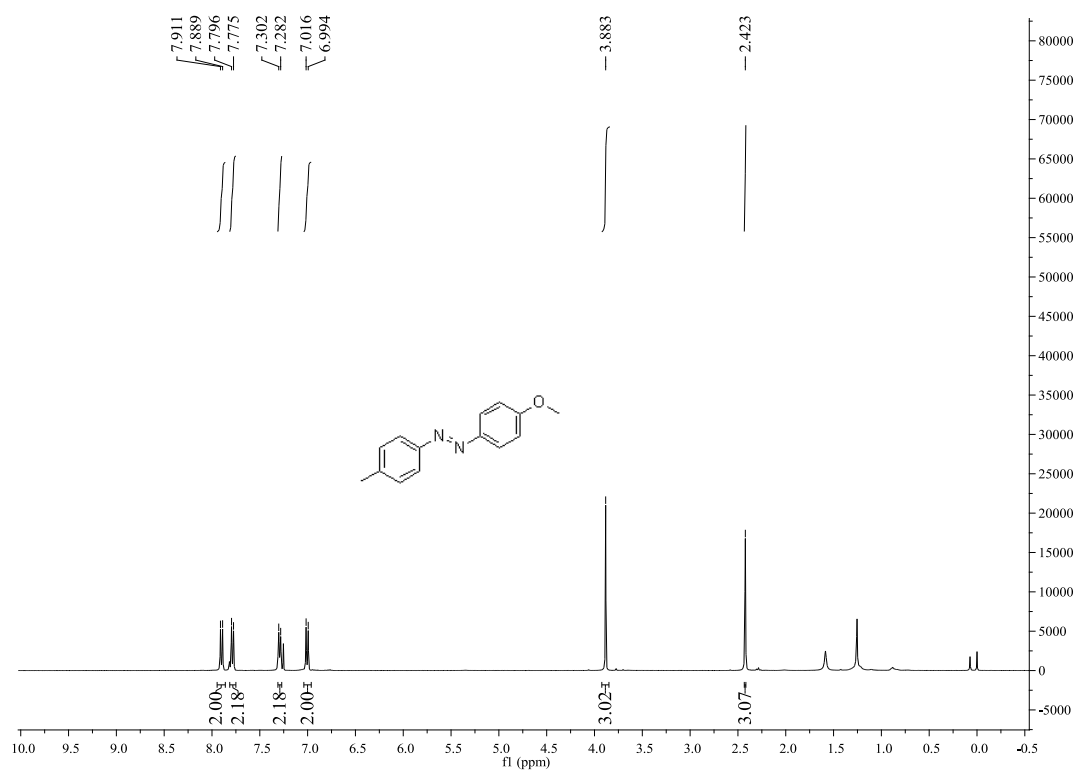
3.8  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1i** ( $\text{CDCl}_3$  as solvent)



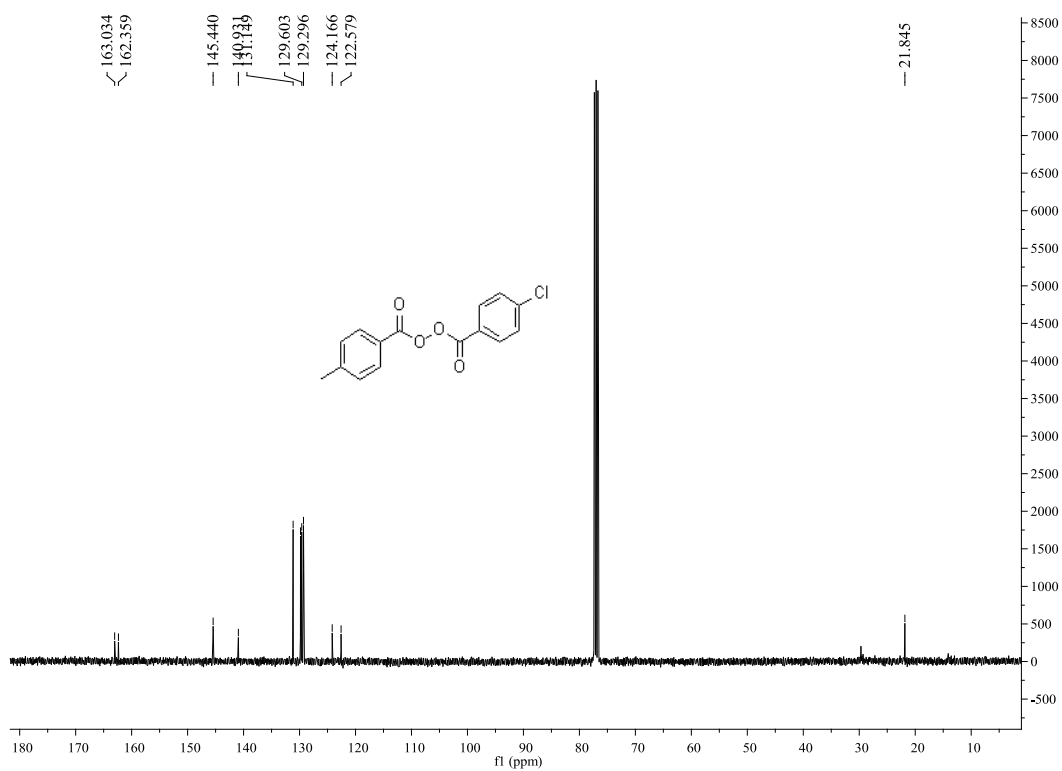
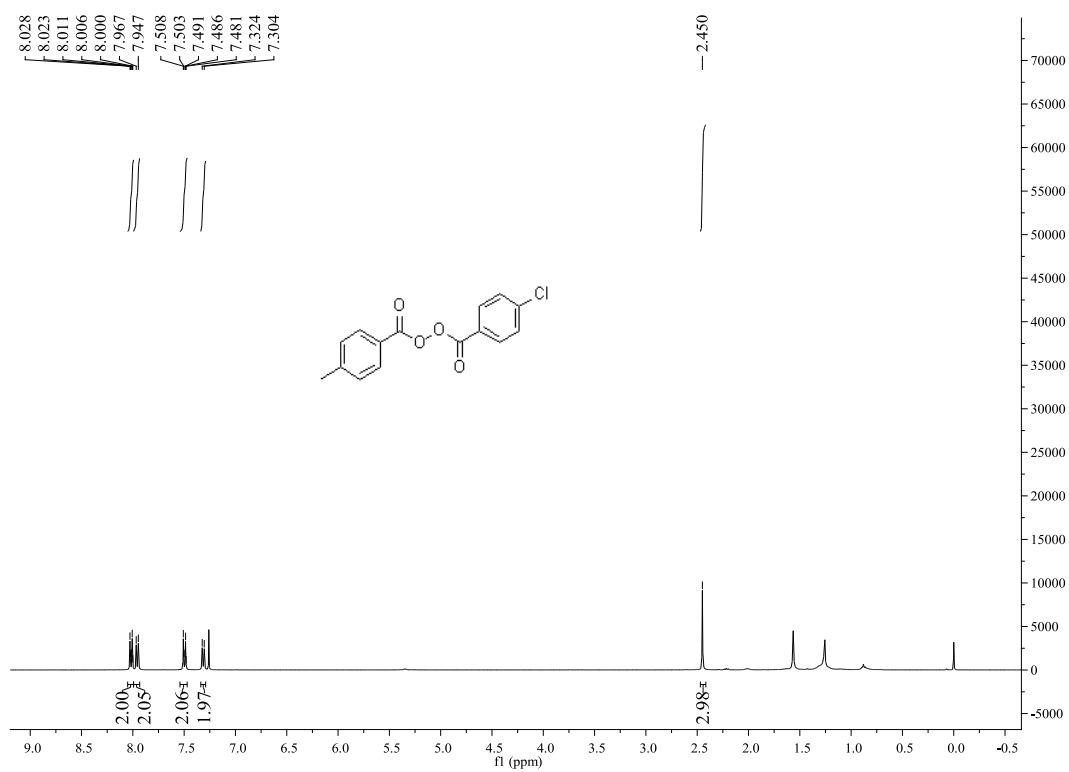
3.9  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1j** ( $\text{CDCl}_3$  as solvent)



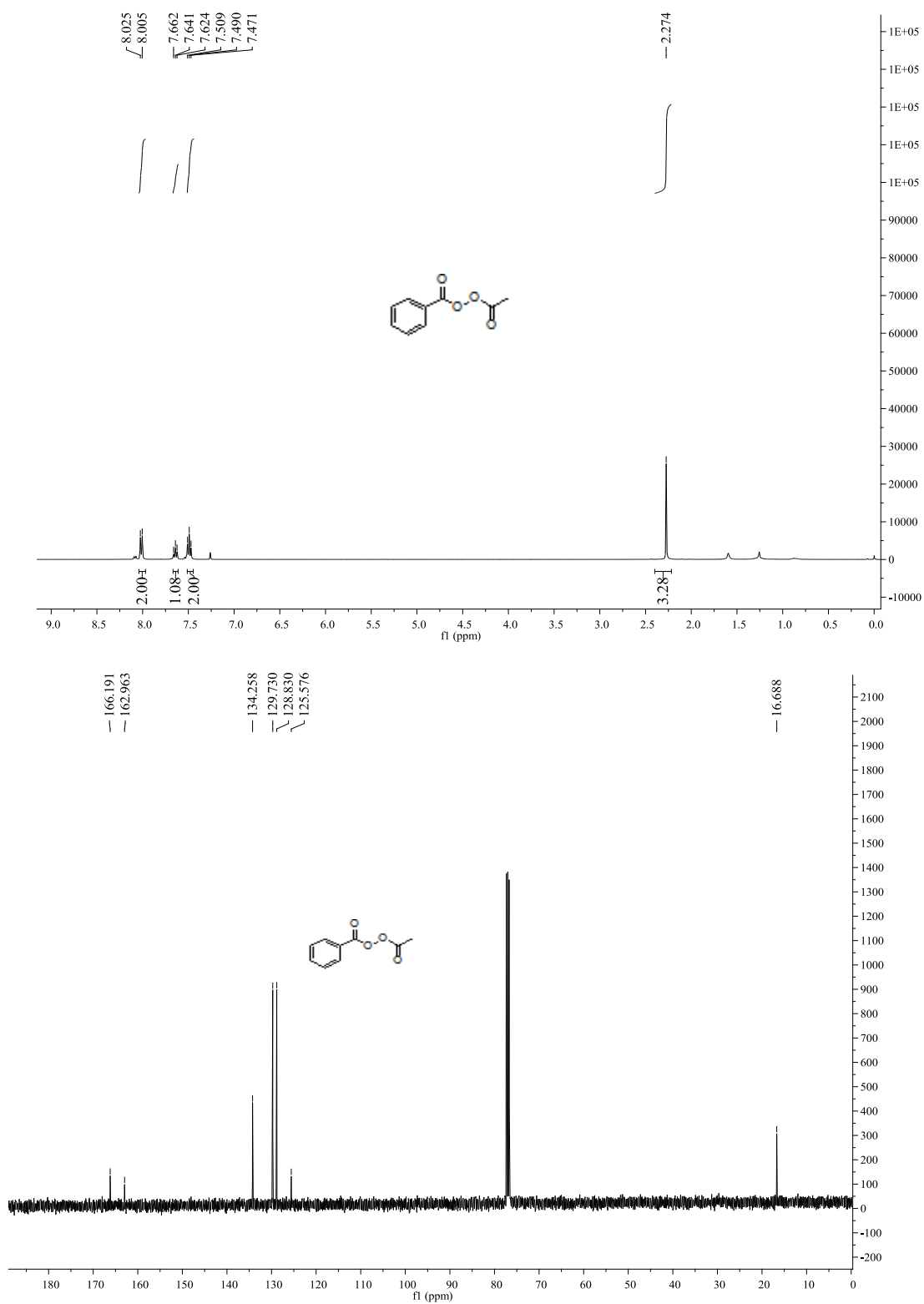
3.10  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **1k** ( $\text{CDCl}_3$  as solvent)



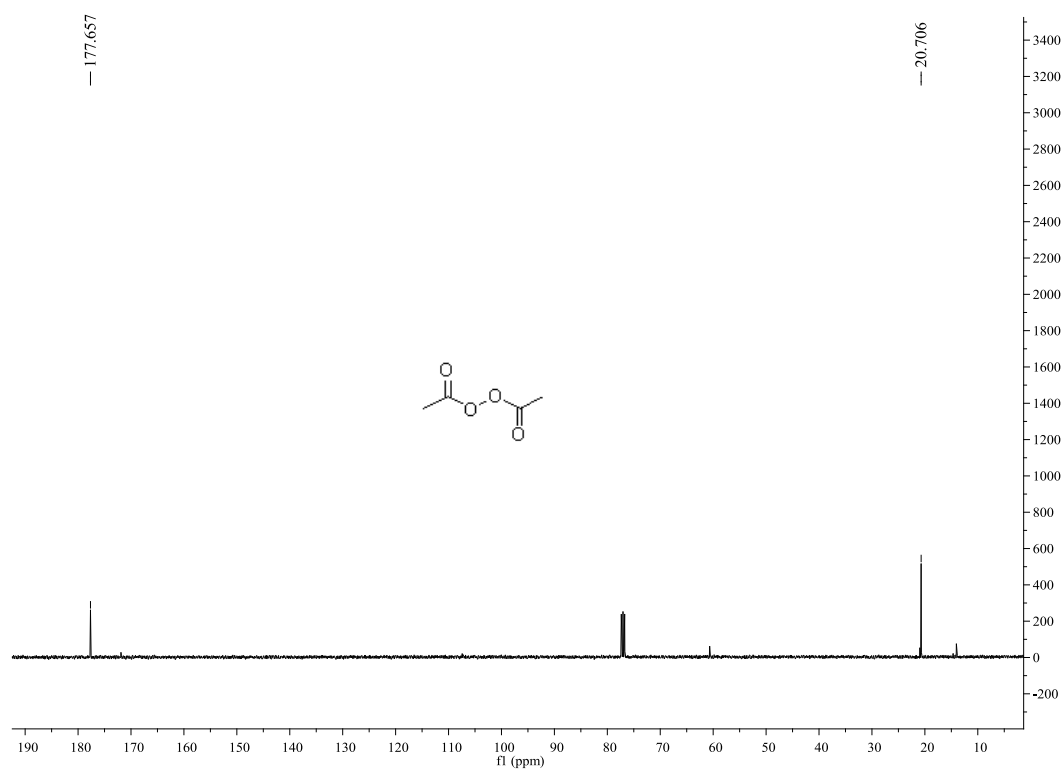
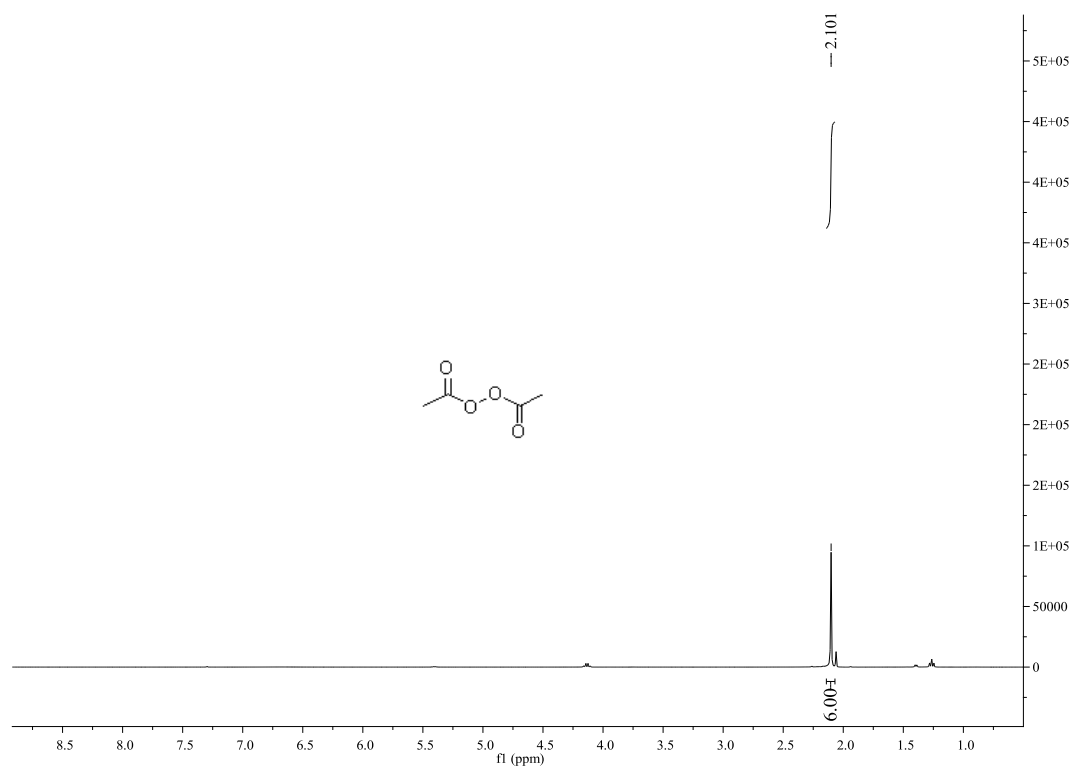
3.11  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **2g** ( $\text{CDCl}_3$  as solvent)



3.12  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **2h** ( $\text{CDCl}_3$  as solvent)

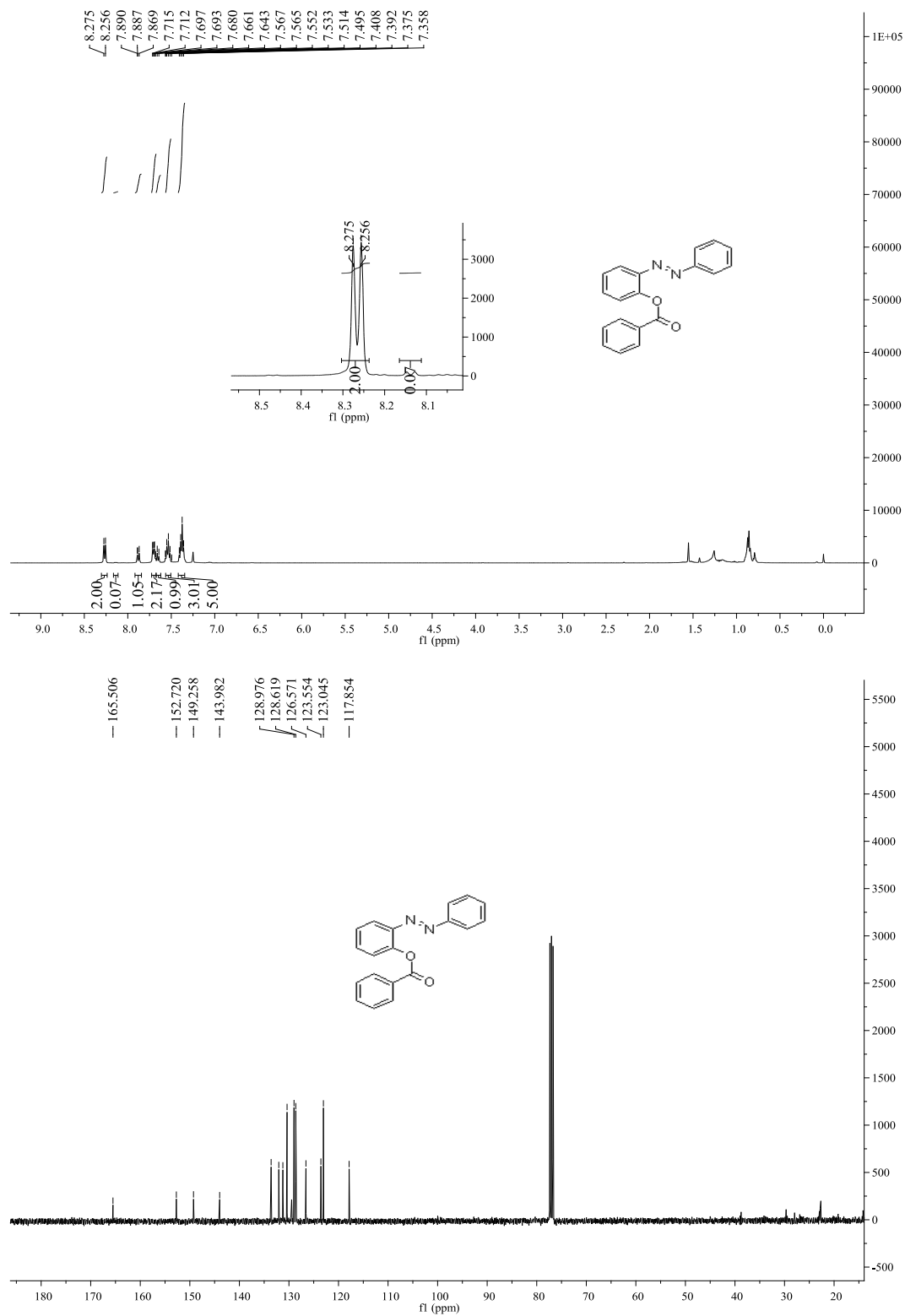


3.13  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **2i** ( $\text{CDCl}_3$  as solvent)

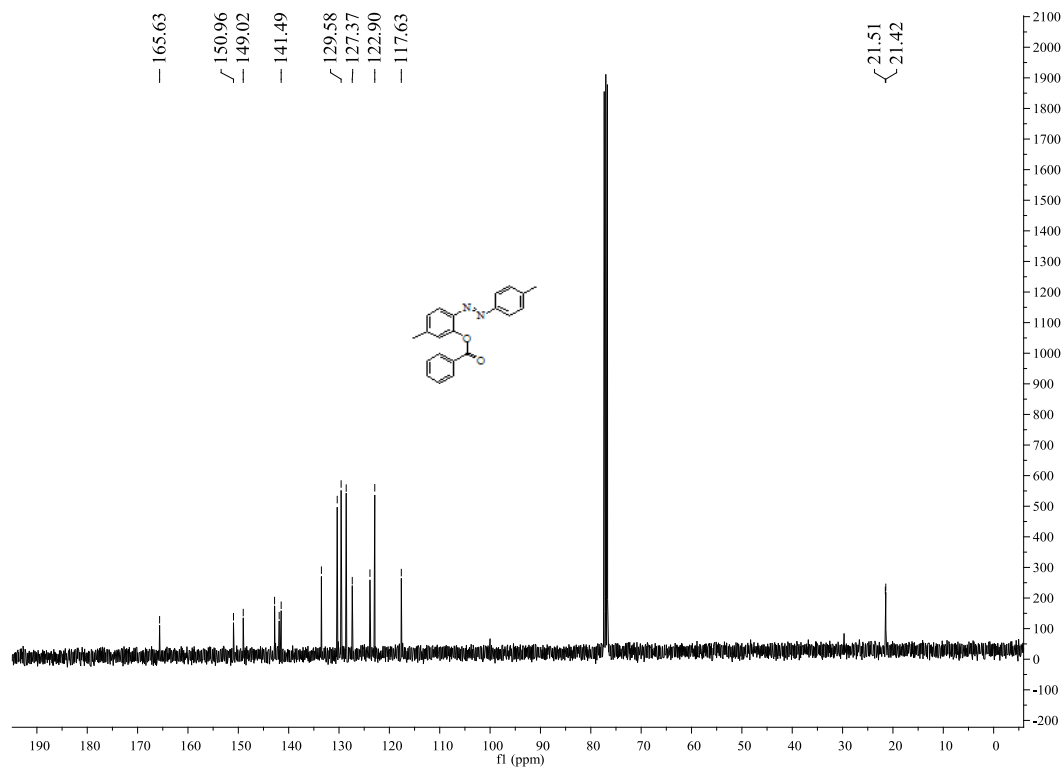
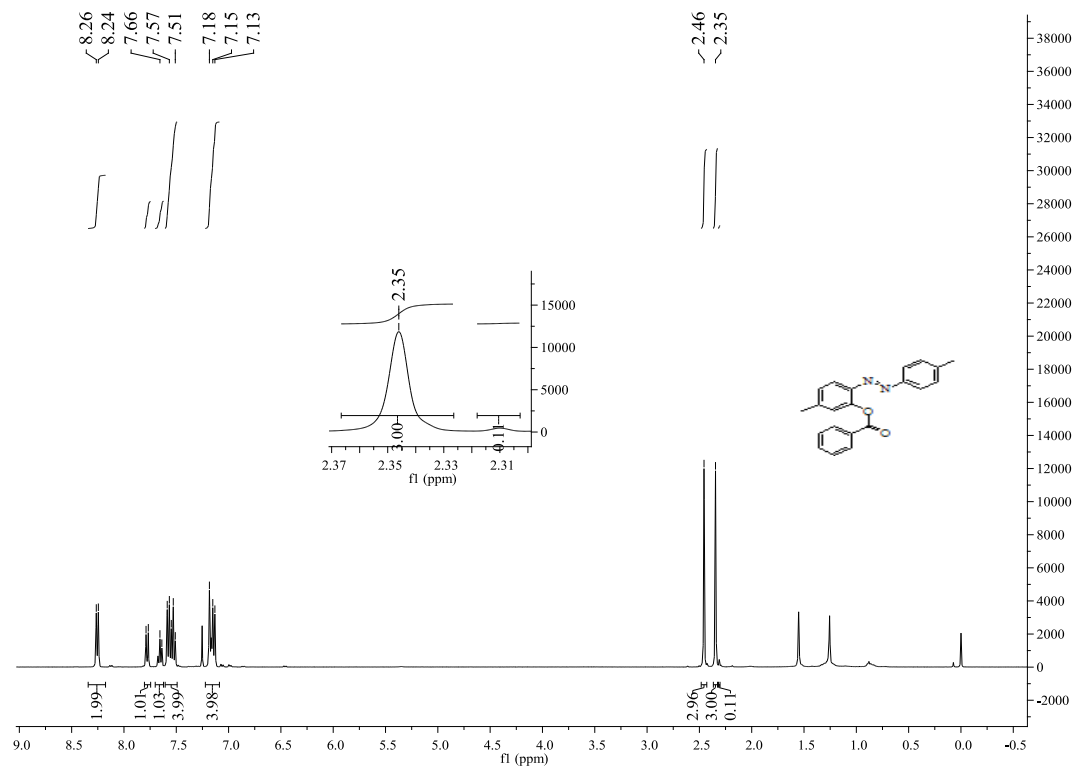




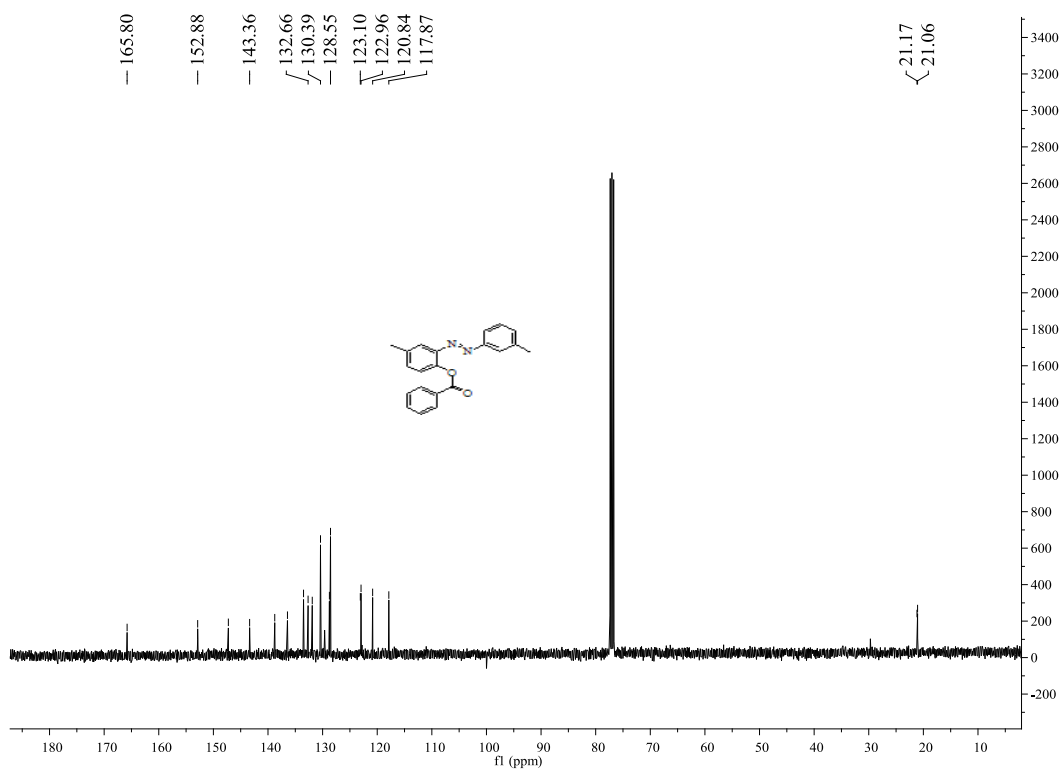
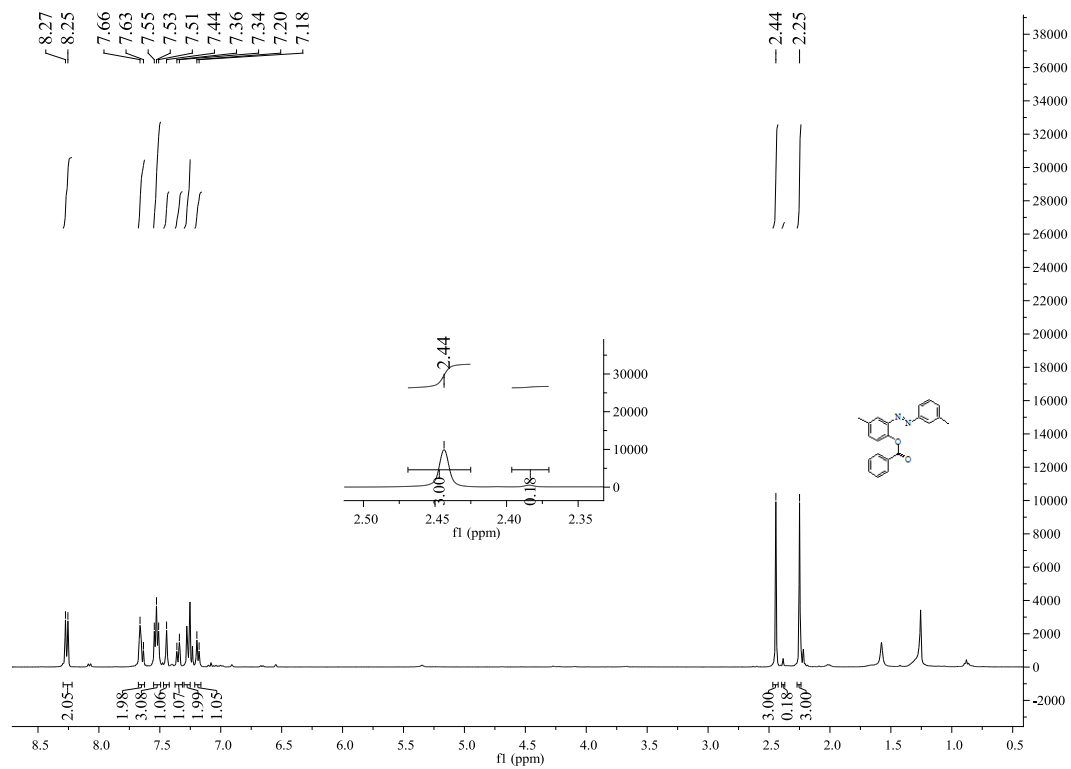
3.14  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3a** ( $\text{CDCl}_3$  as solvent)



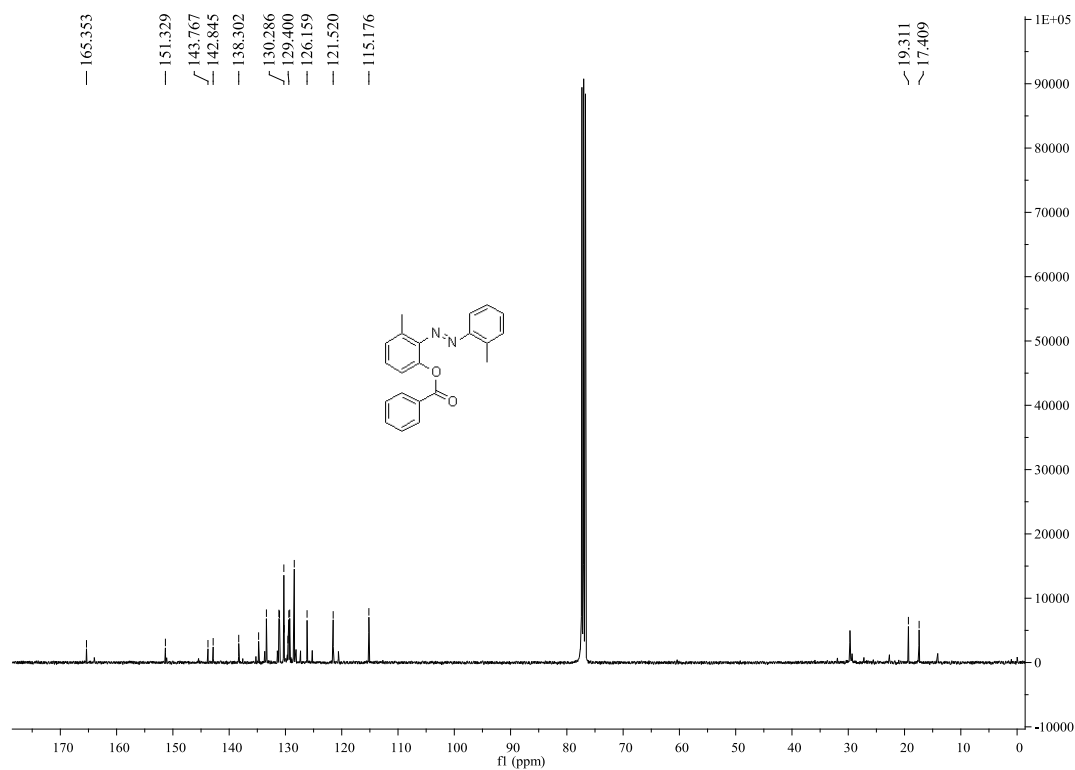
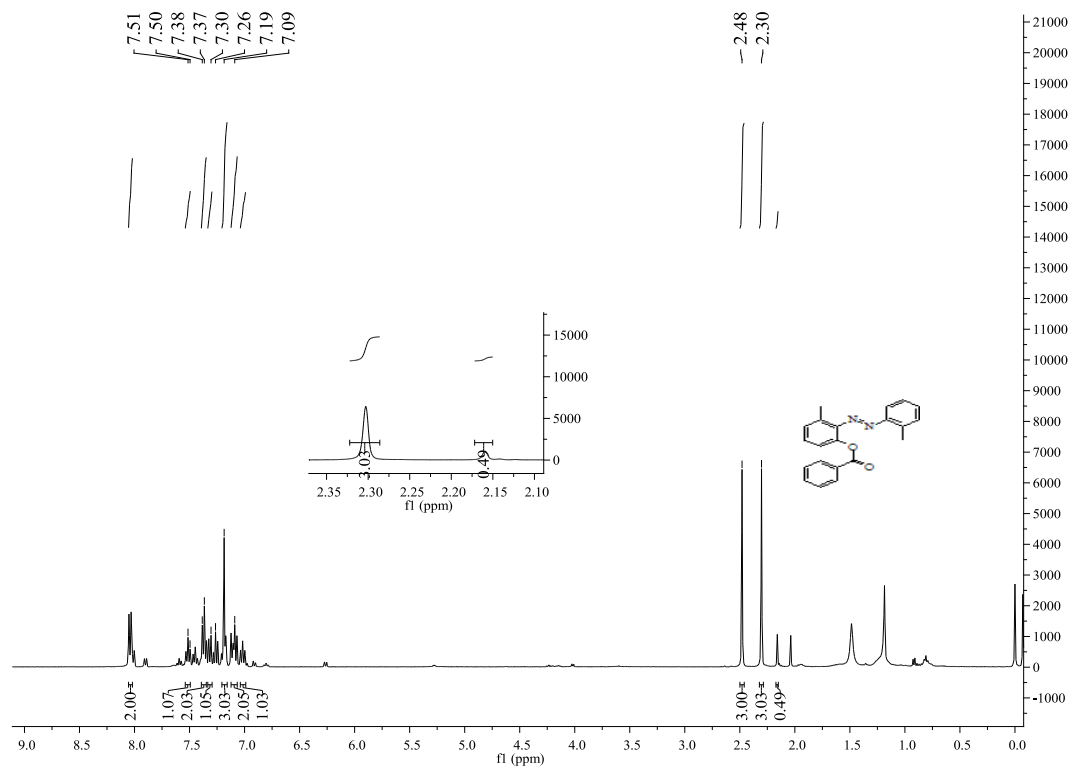
3.15  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3b** ( $\text{CDCl}_3$  as solvent)



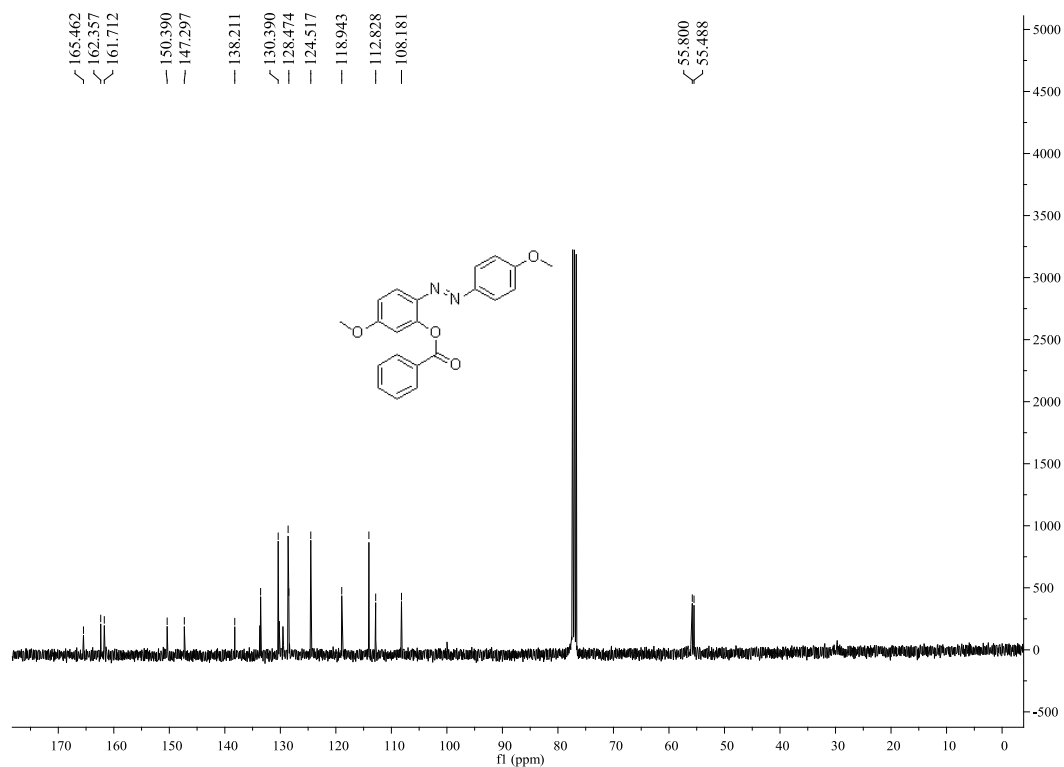
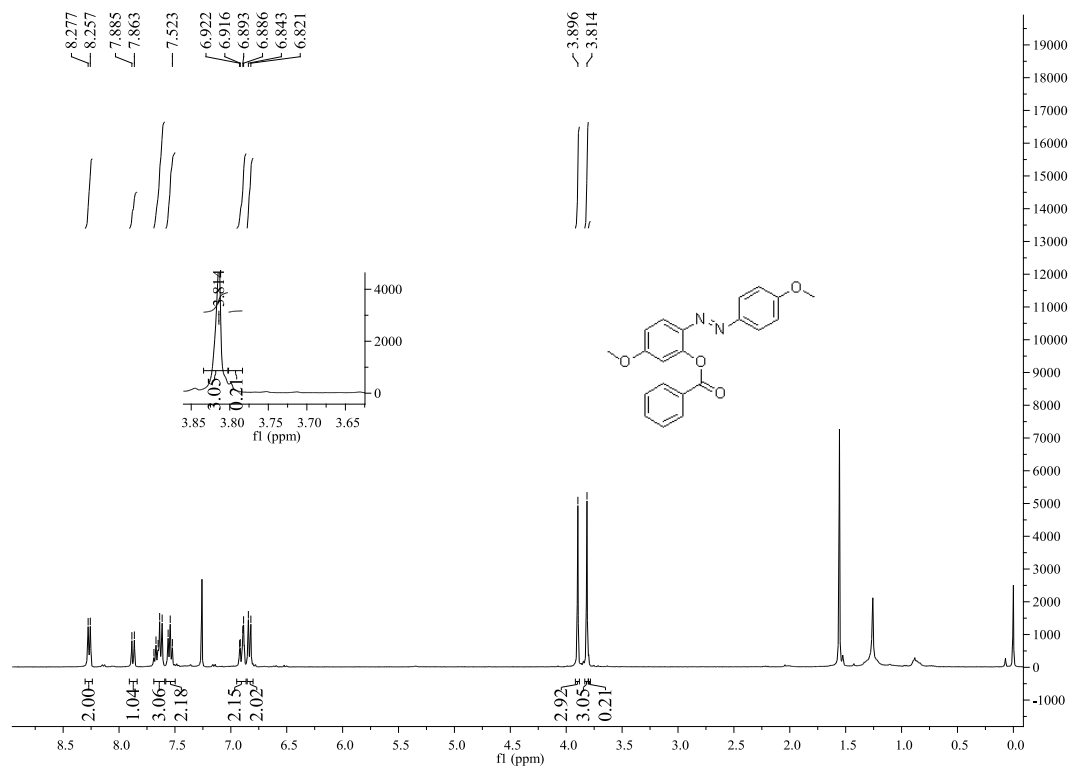
3.16  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3c** ( $\text{CDCl}_3$  as solvent)



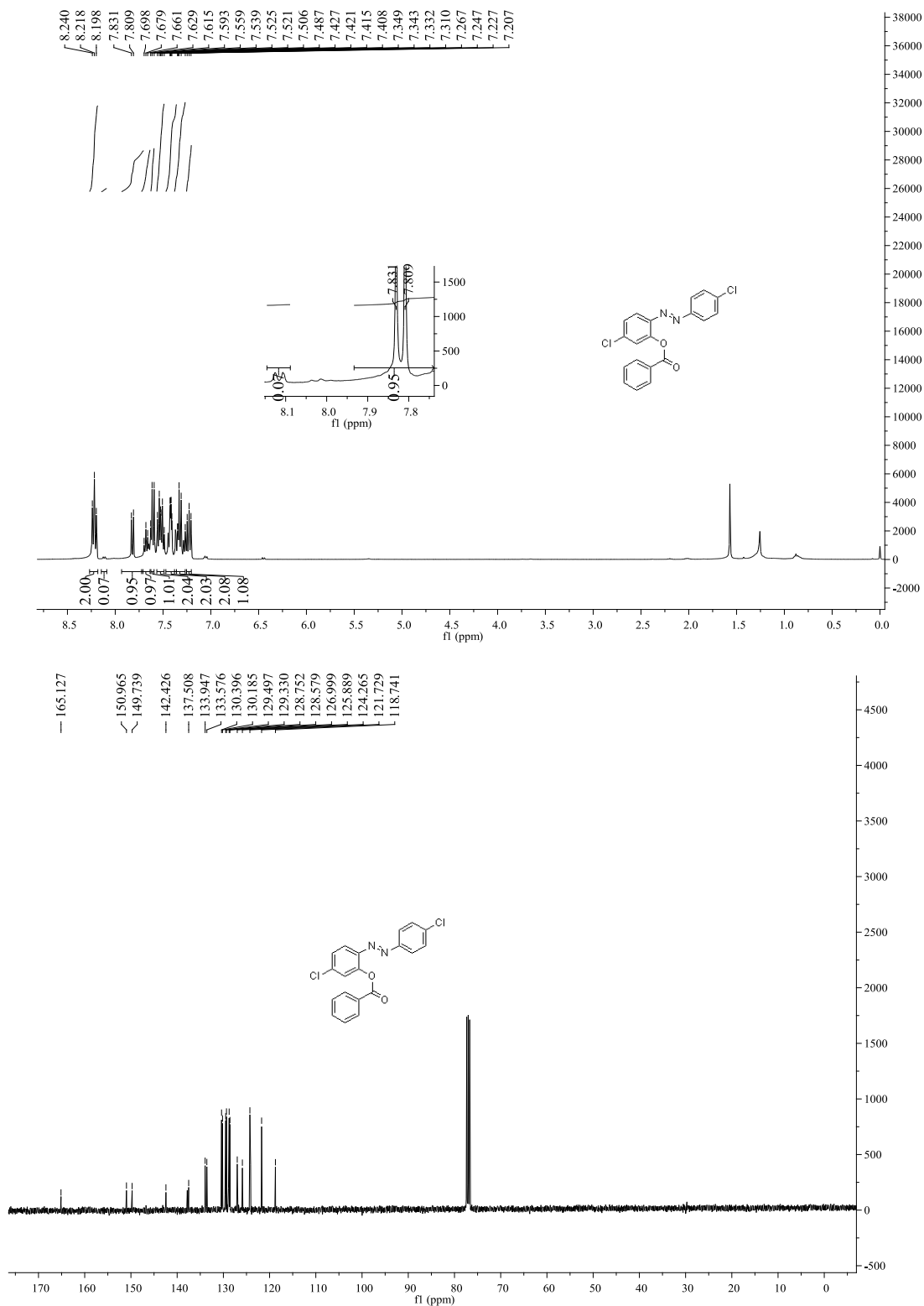
3.17  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3d** ( $\text{CDCl}_3$  as solvent)



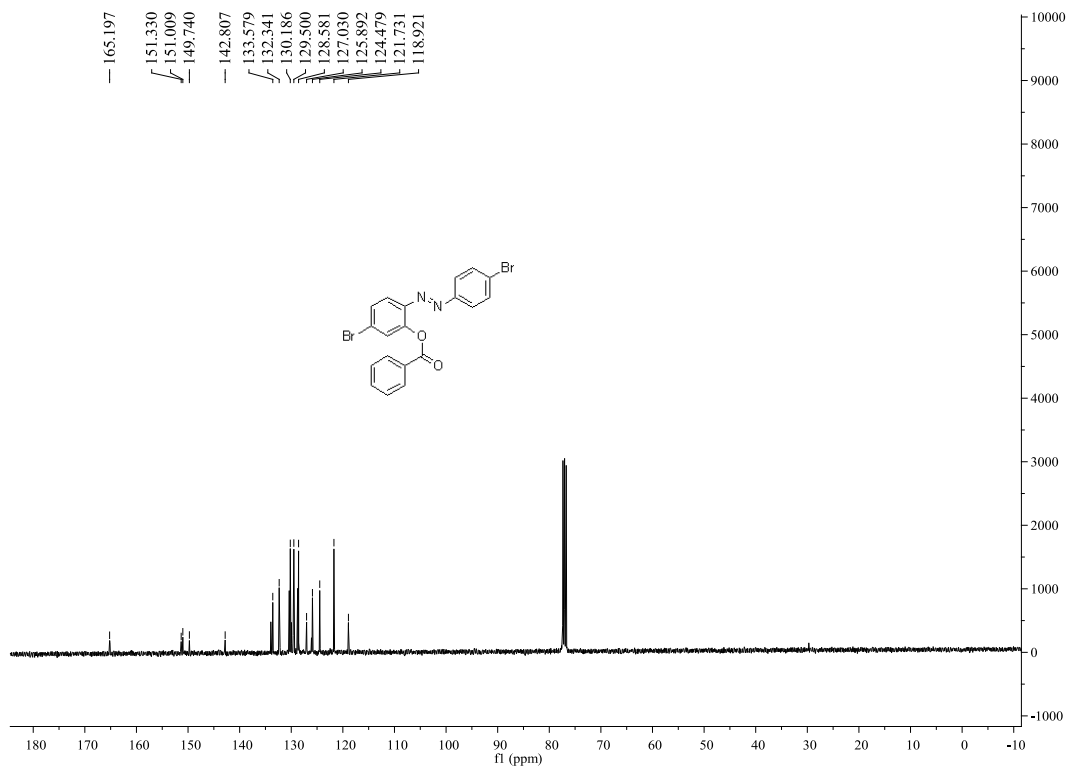
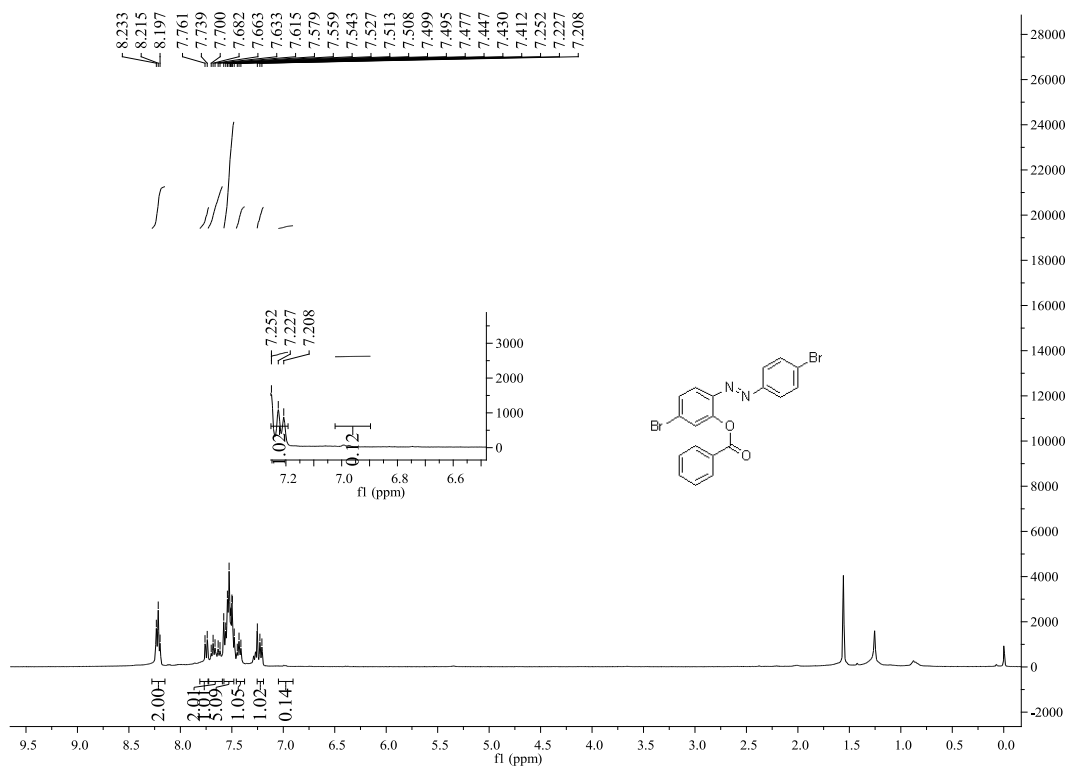
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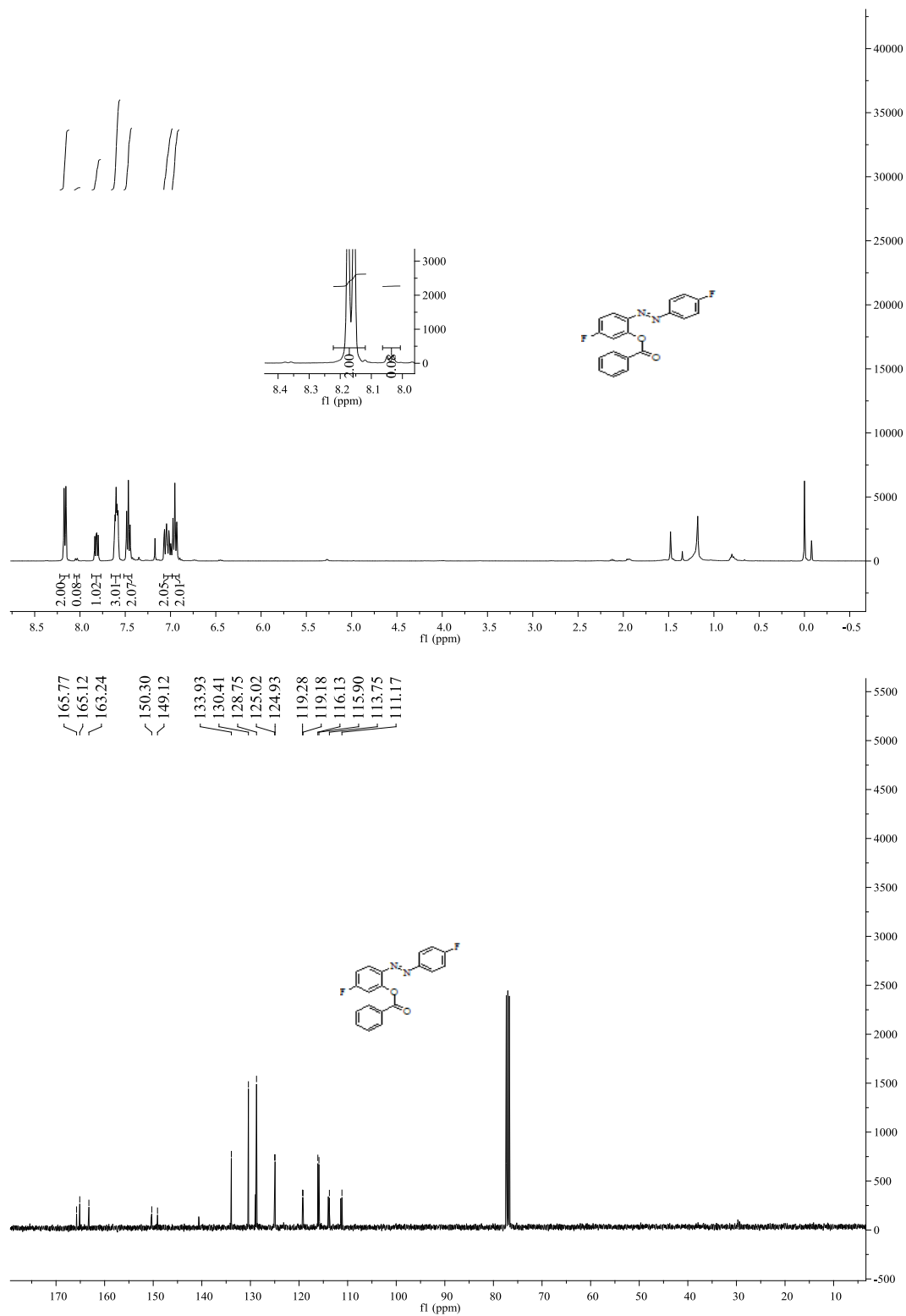
3.19  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3f** ( $\text{CDCl}_3$  as solvent)



3.20  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3g** ( $\text{CDCl}_3$  as solvent)

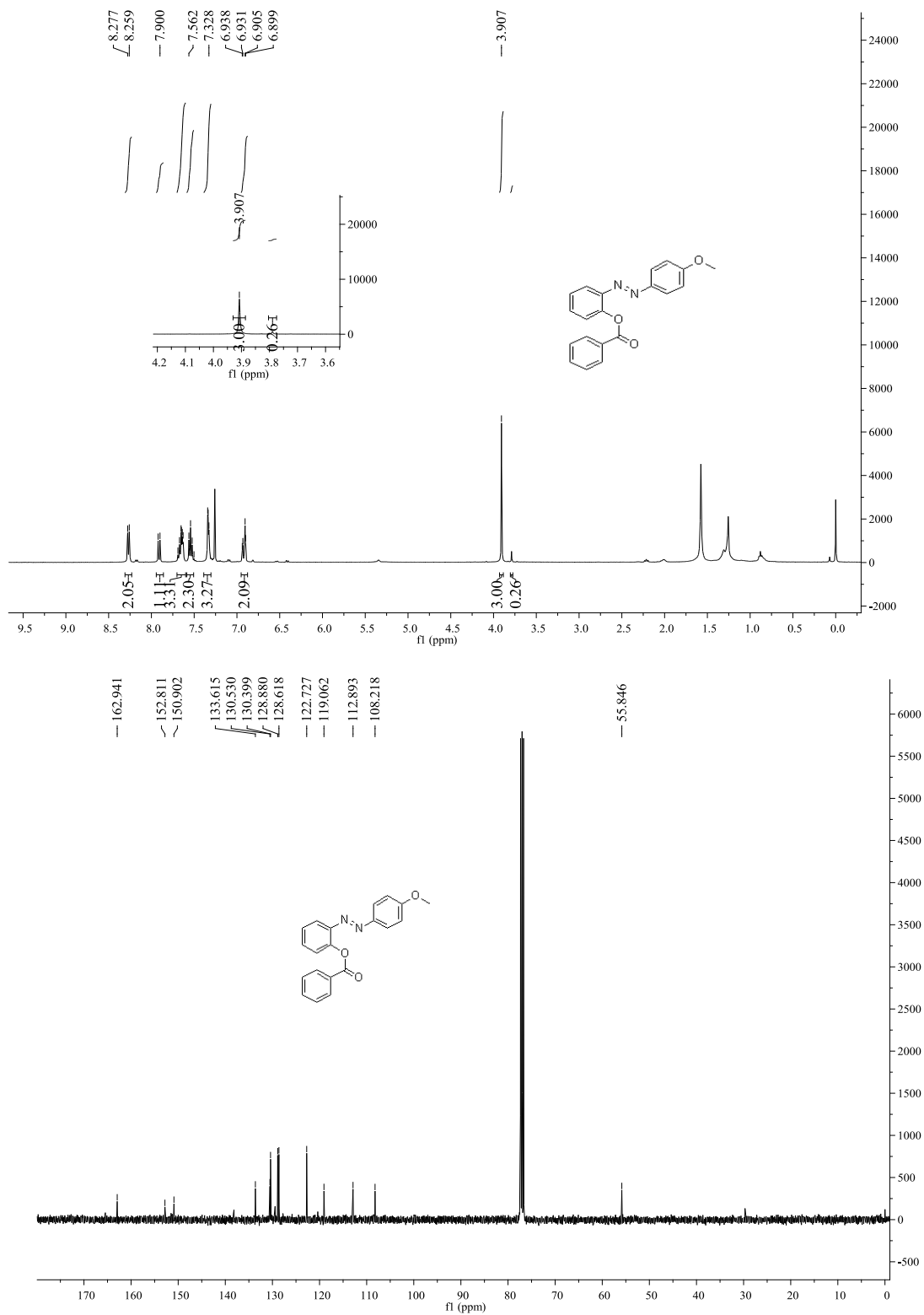


3.21  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3h** ( $\text{CDCl}_3$  as solvent)

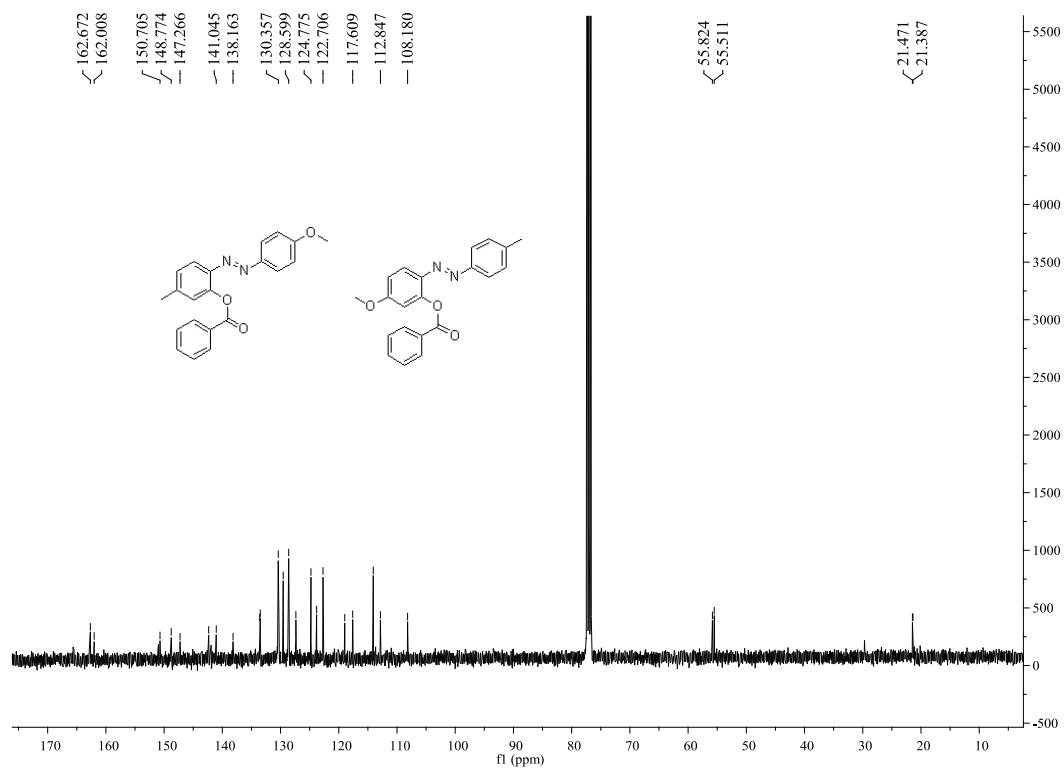
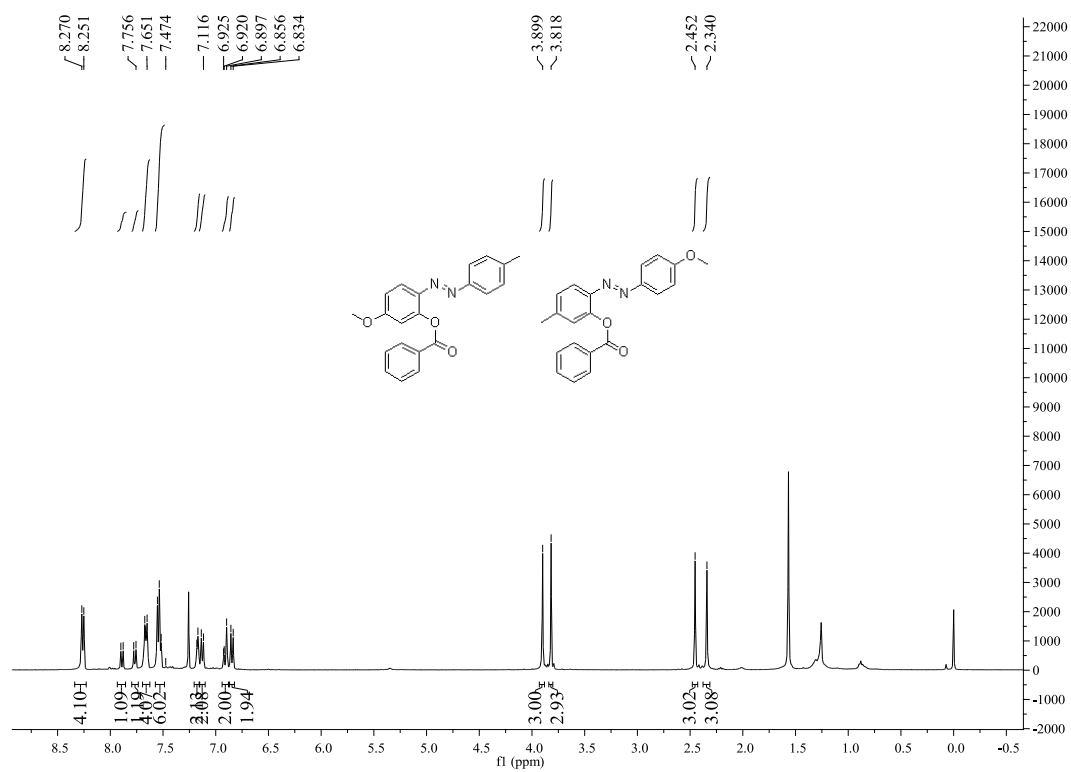




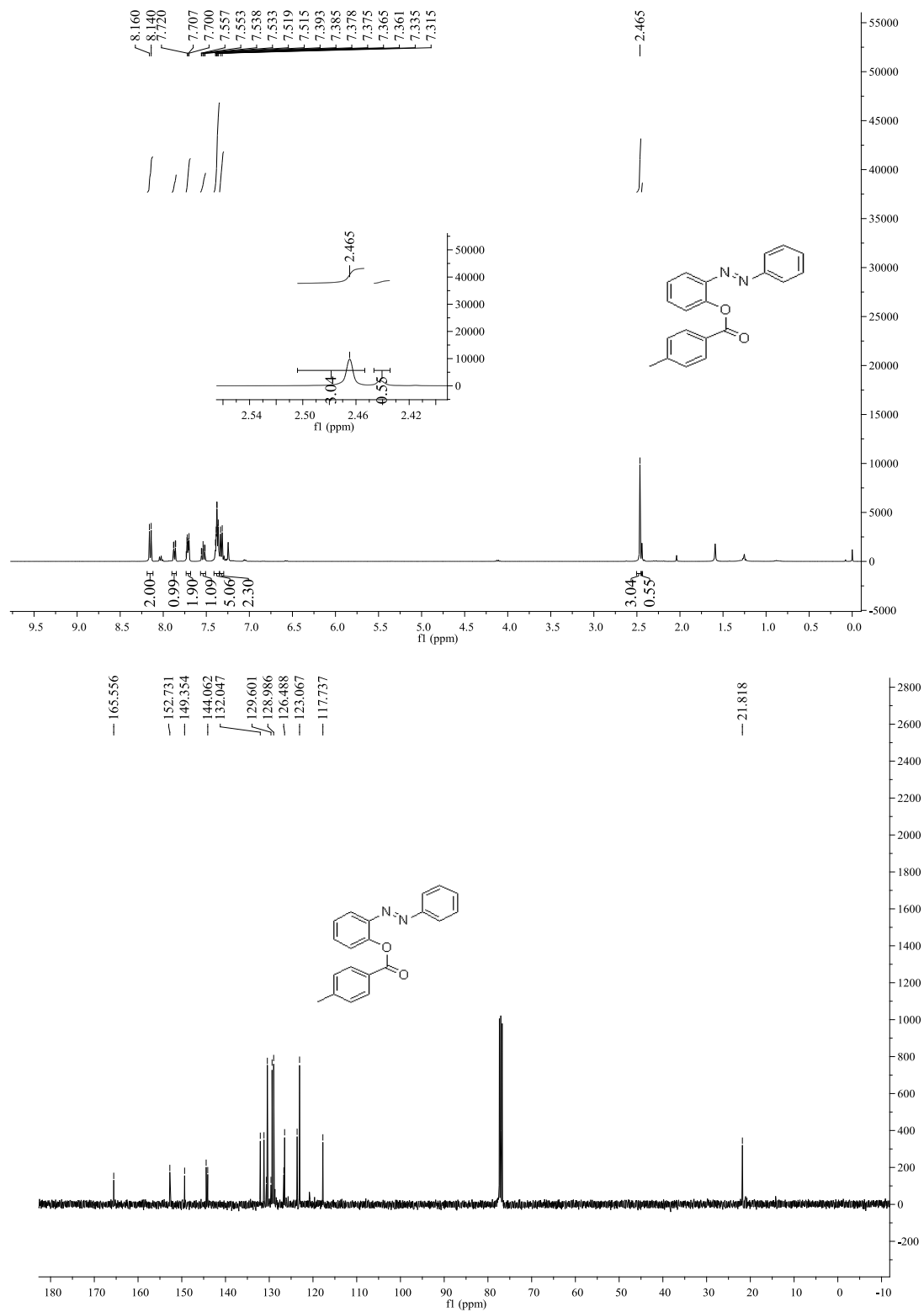
3.22  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3j** ( $\text{CDCl}_3$  as solvent)



3.23  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3k** and **3l** ( $\text{CDCl}_3$  as solvent)

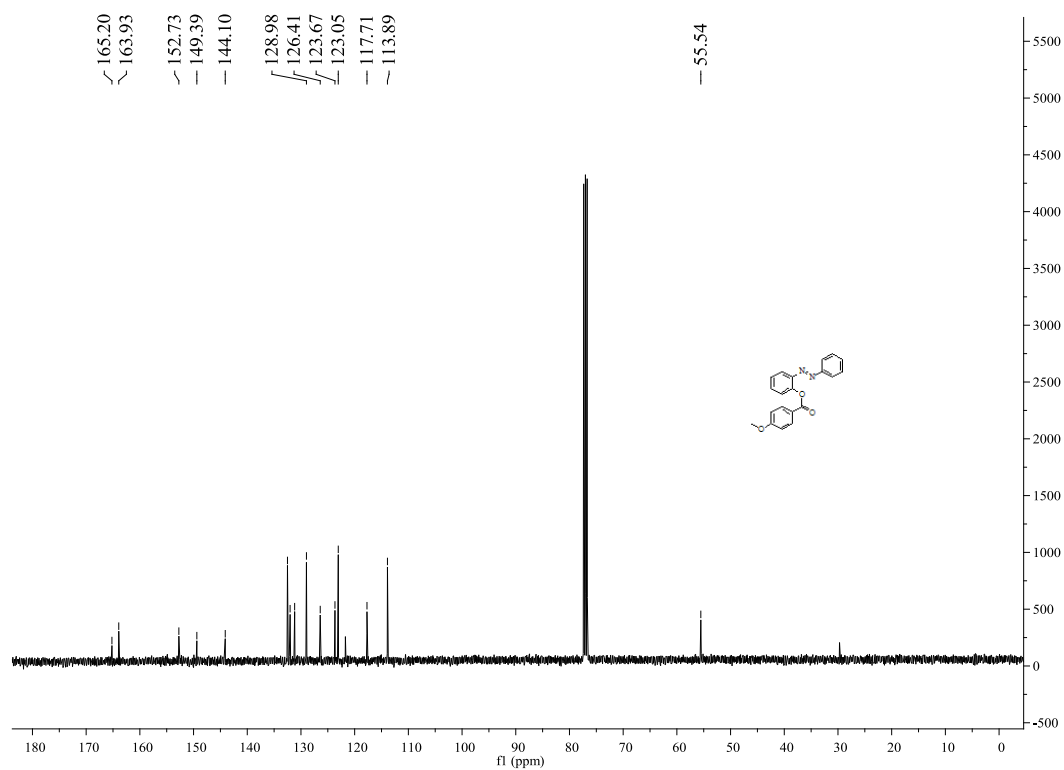
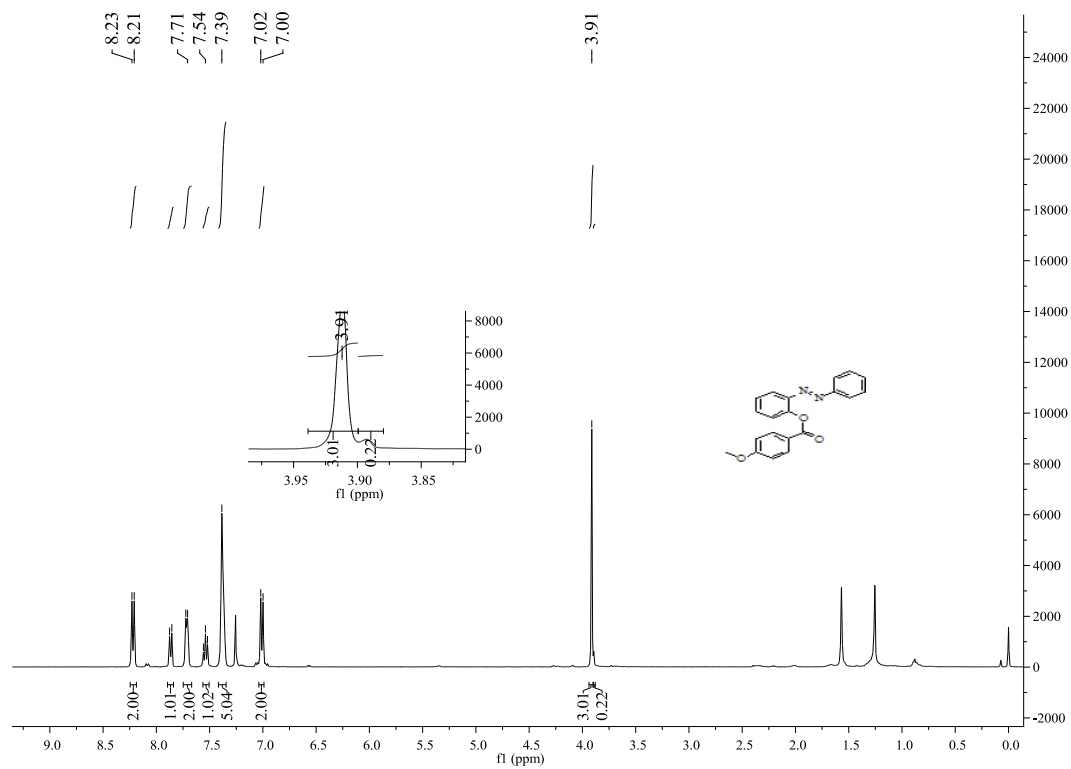


3.24  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3m** ( $\text{CDCl}_3$  as solvent)

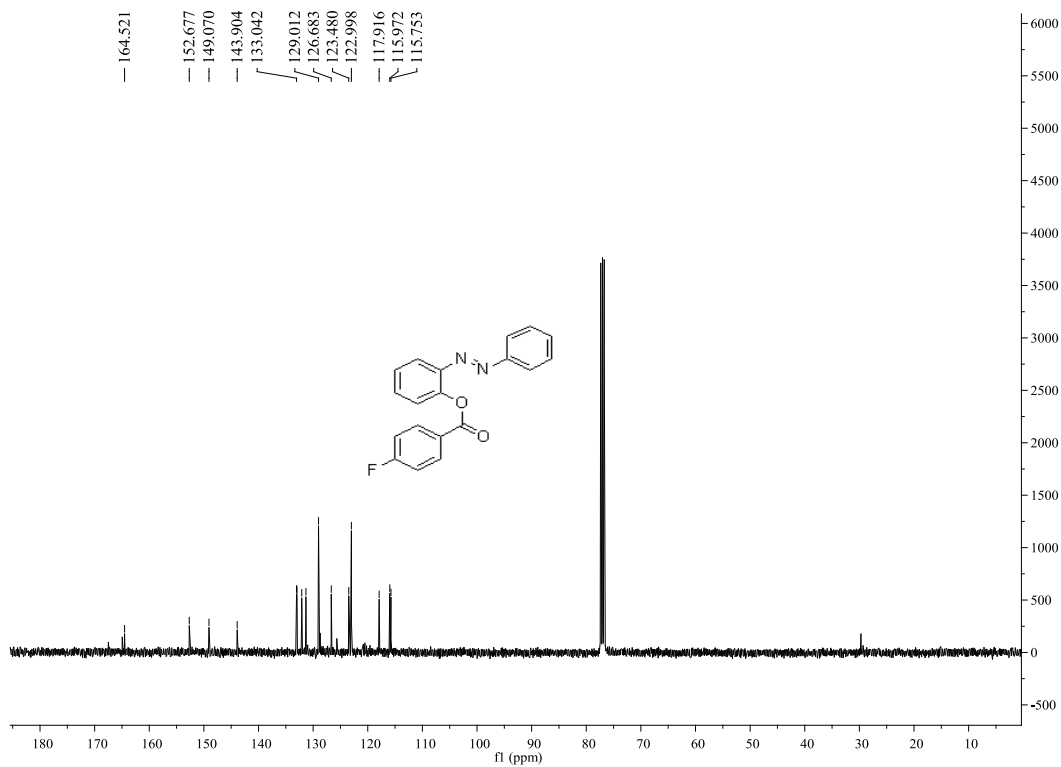
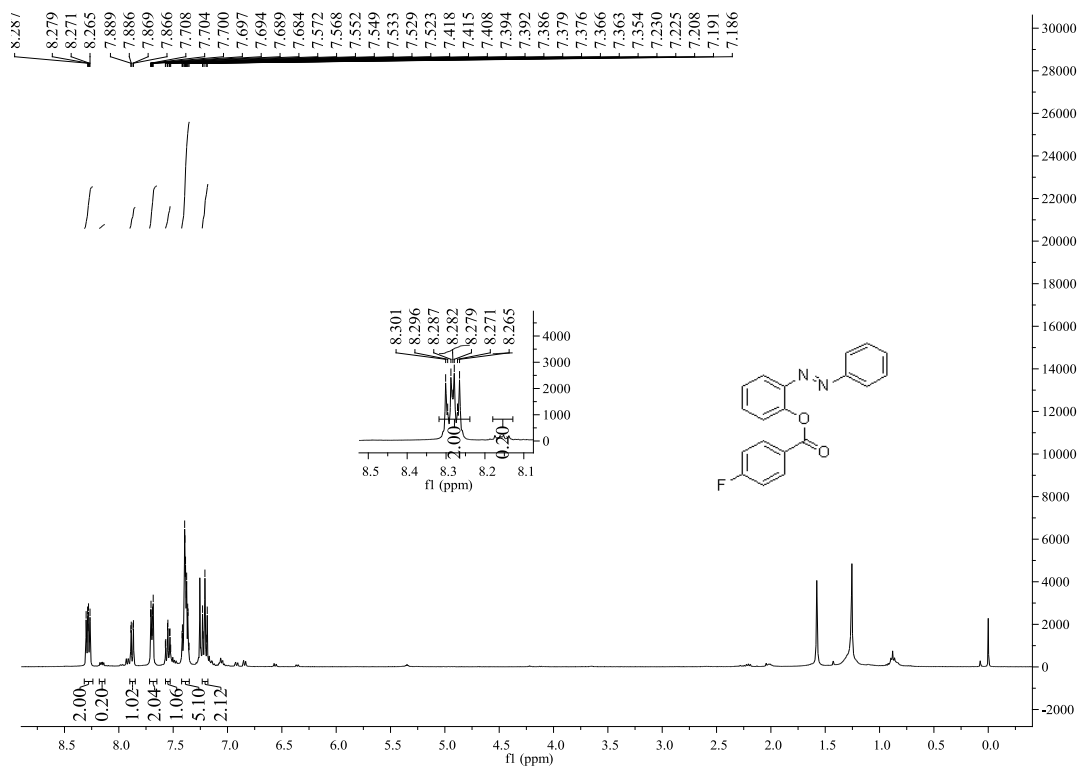




3.26  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3p** ( $\text{CDCl}_3$  as solvent)

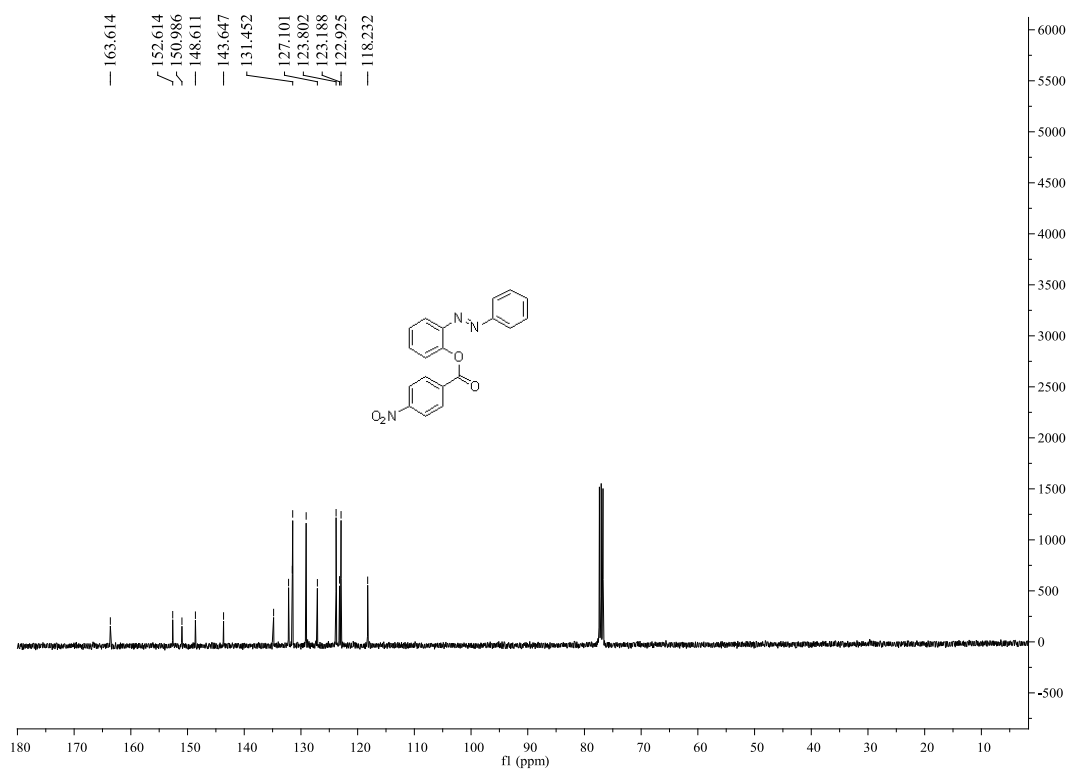
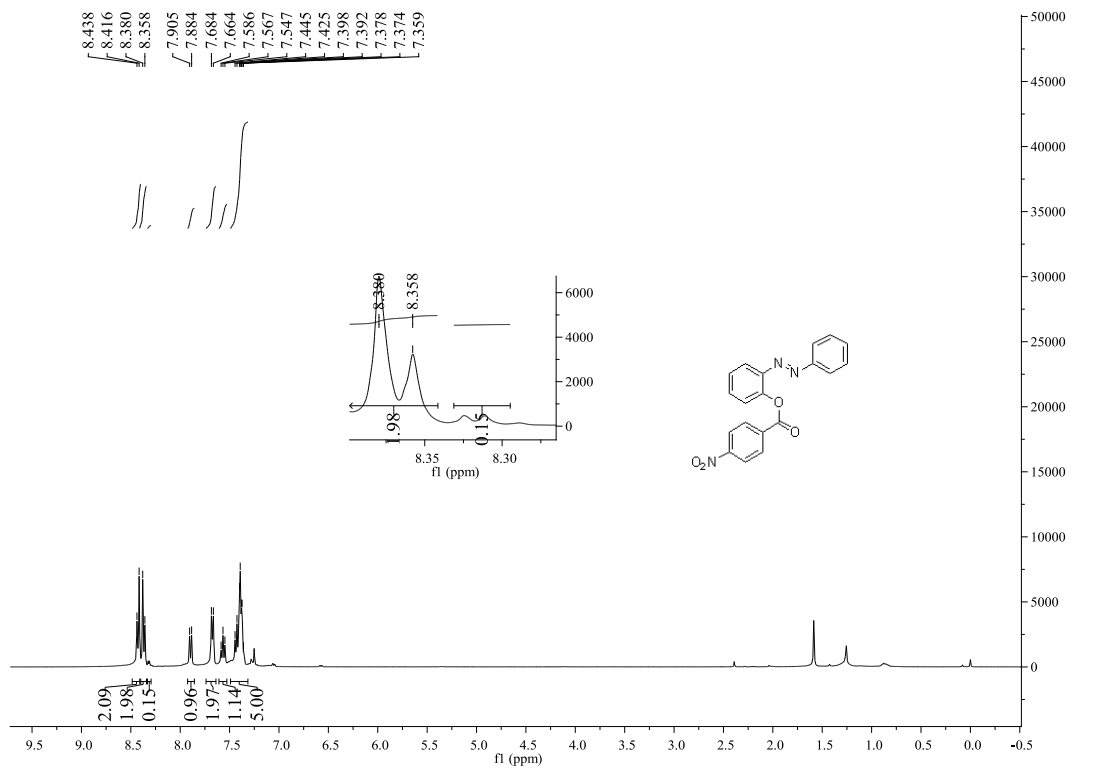


3.27  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3q** ( $\text{CDCl}_3$  as solvent)



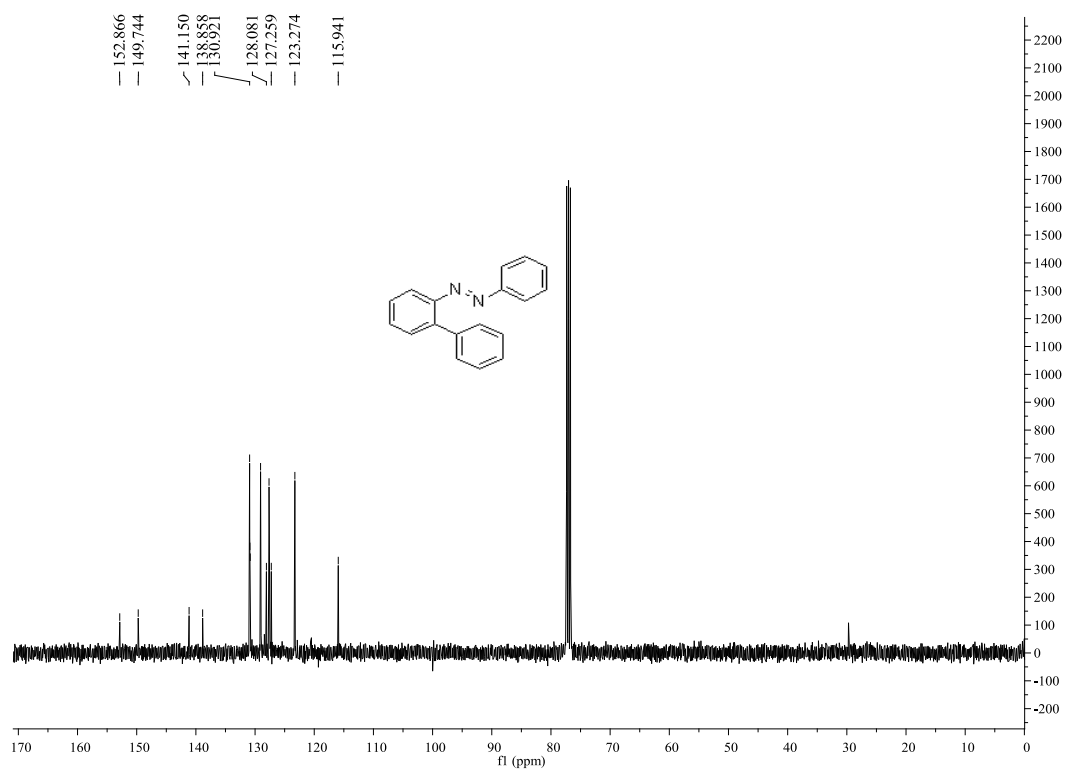
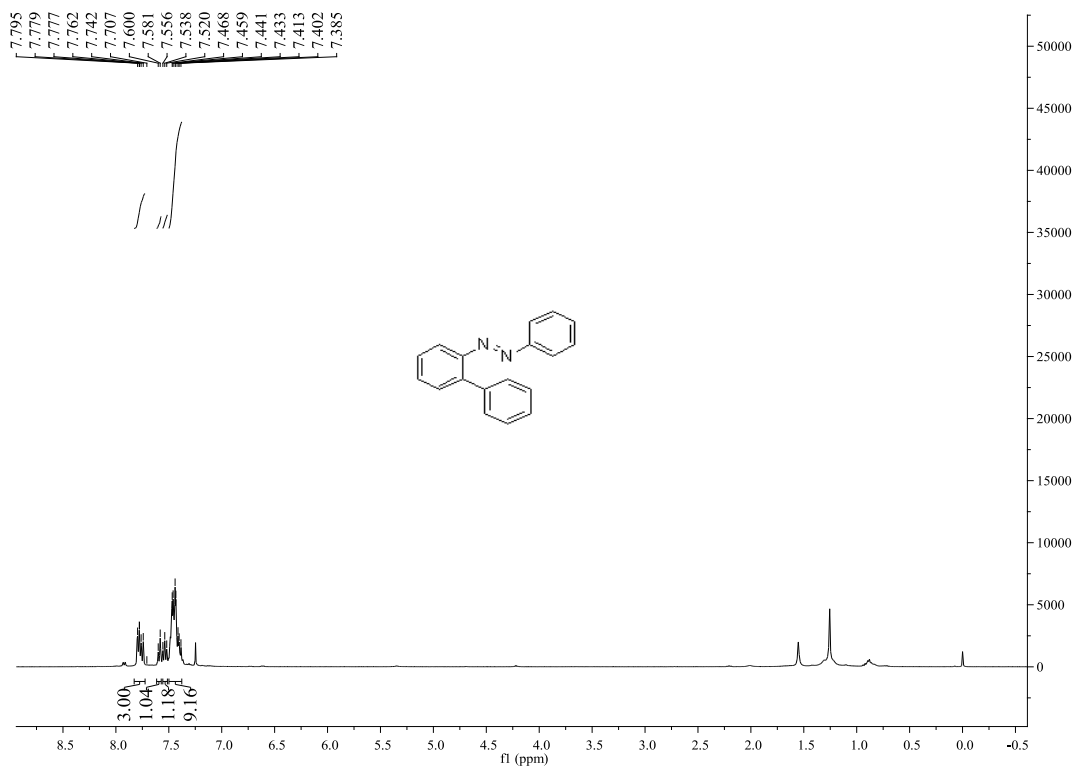


3.20  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **3s** ( $\text{CDCl}_3$  as solvent)

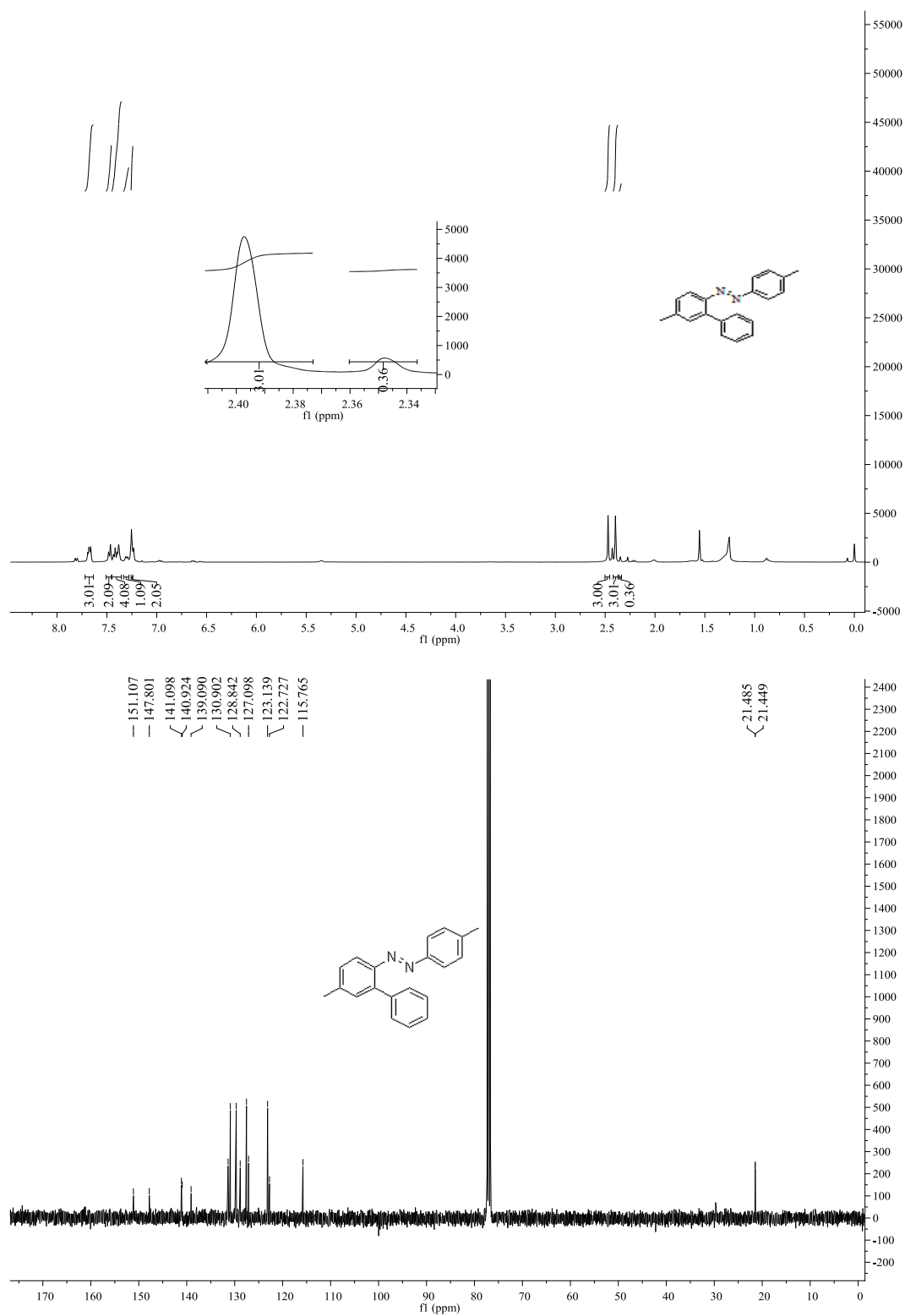




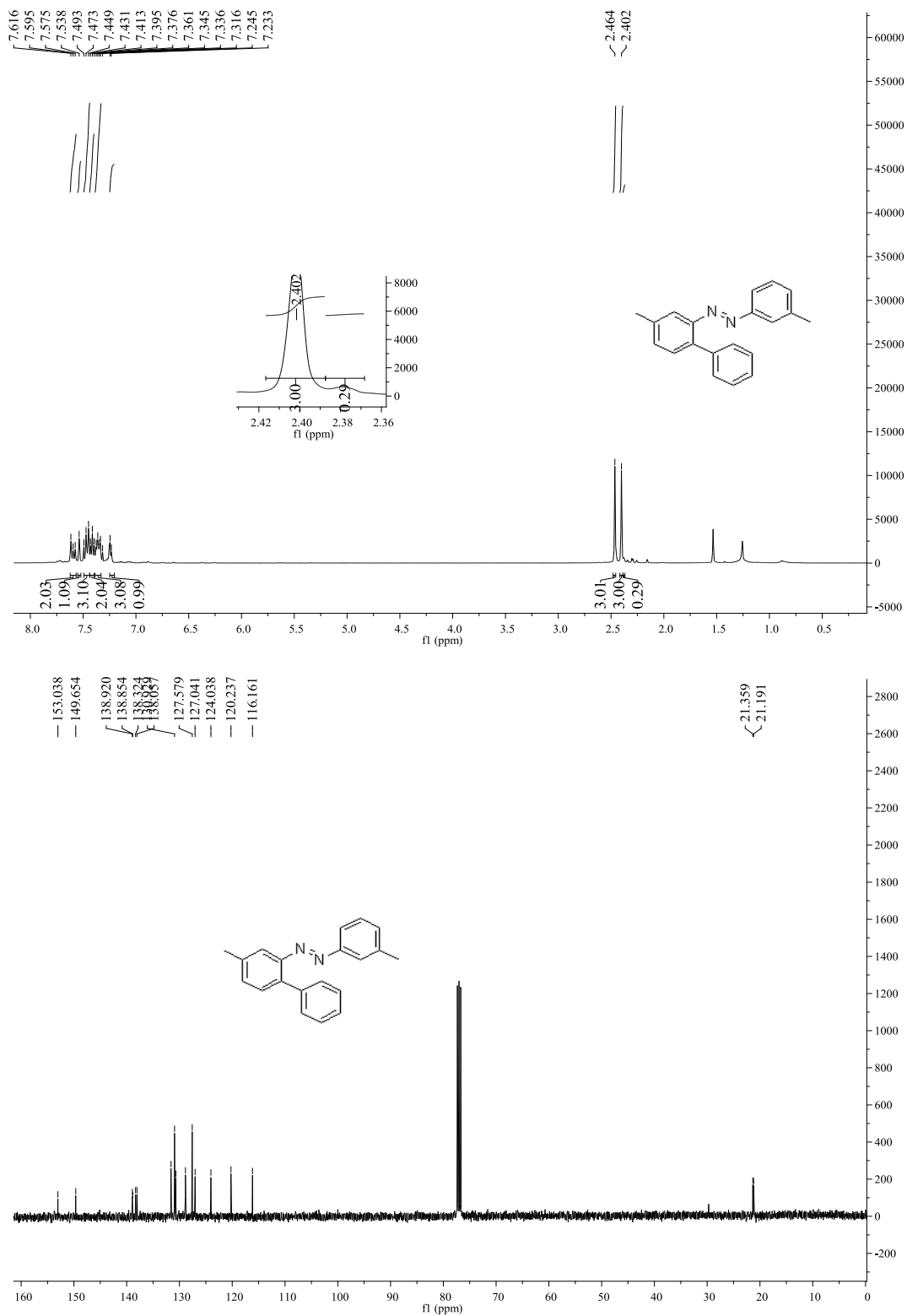
3.30  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4a** ( $\text{CDCl}_3$  as solvent)



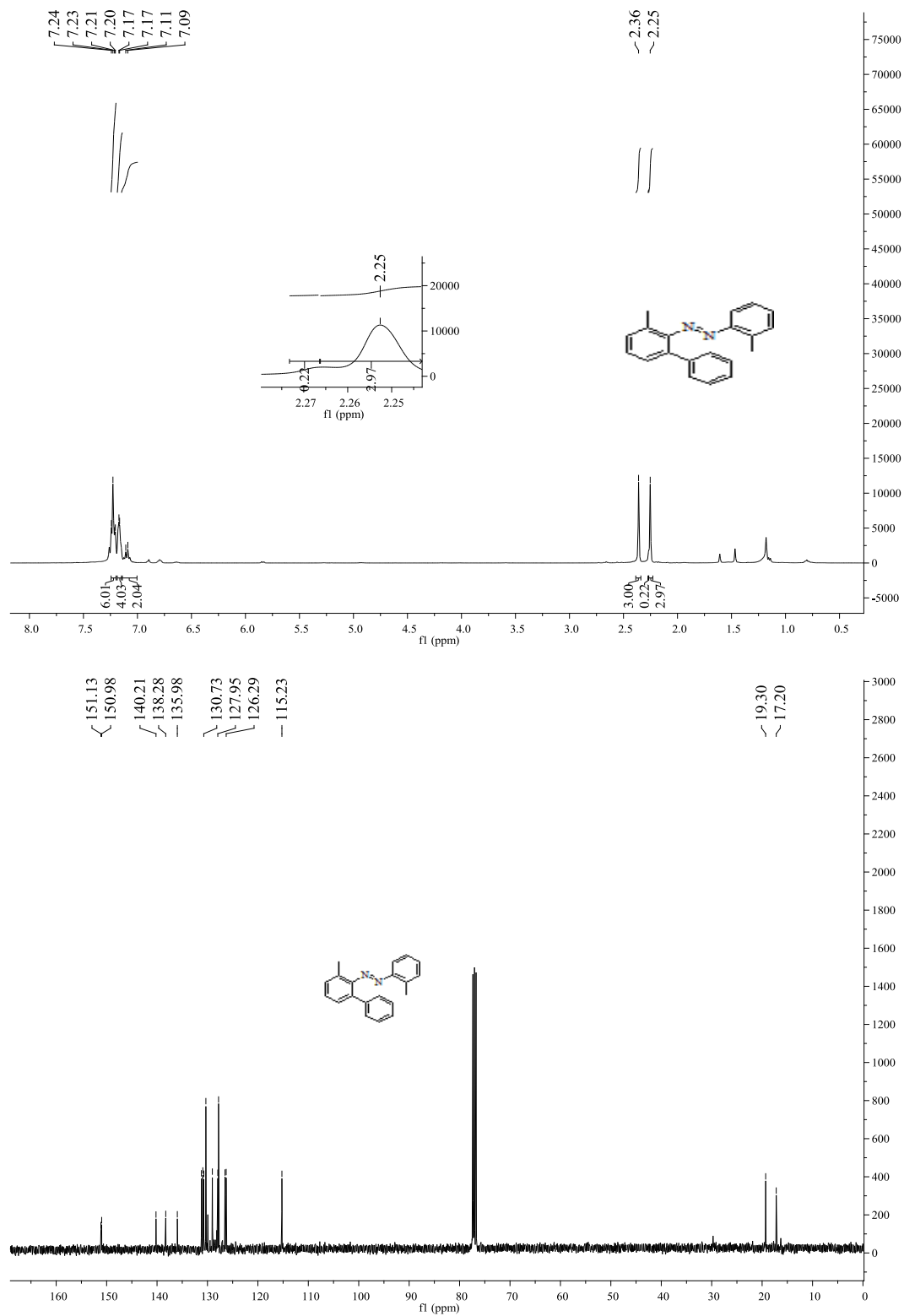
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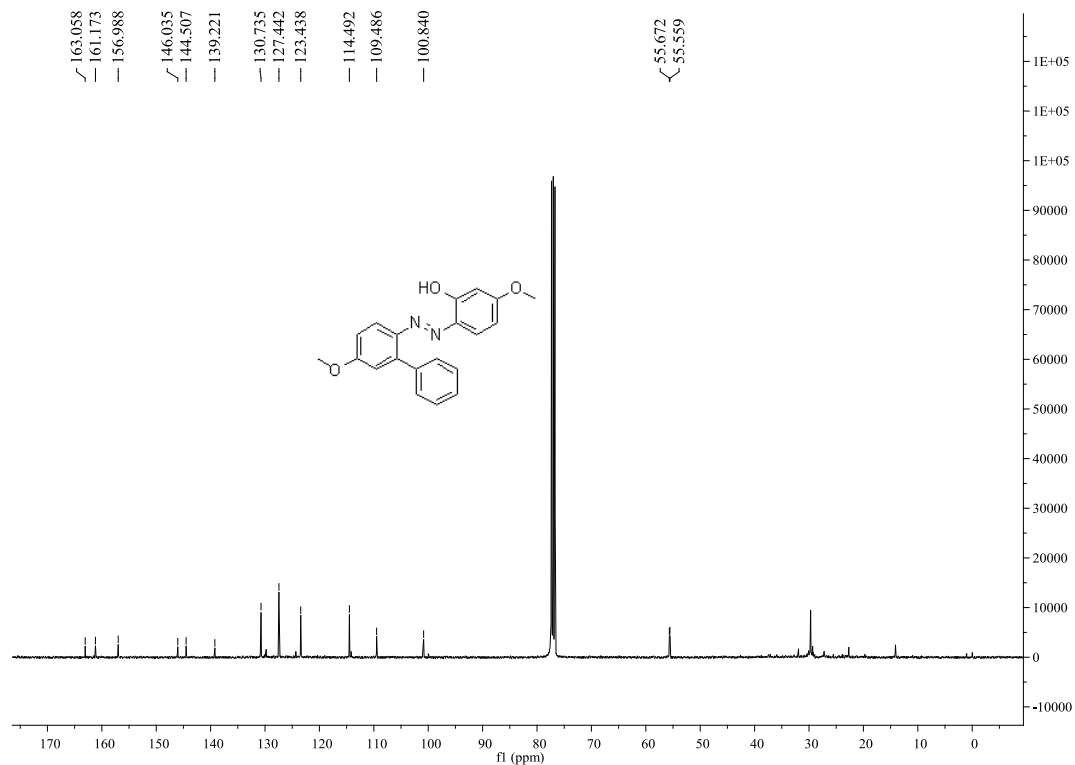
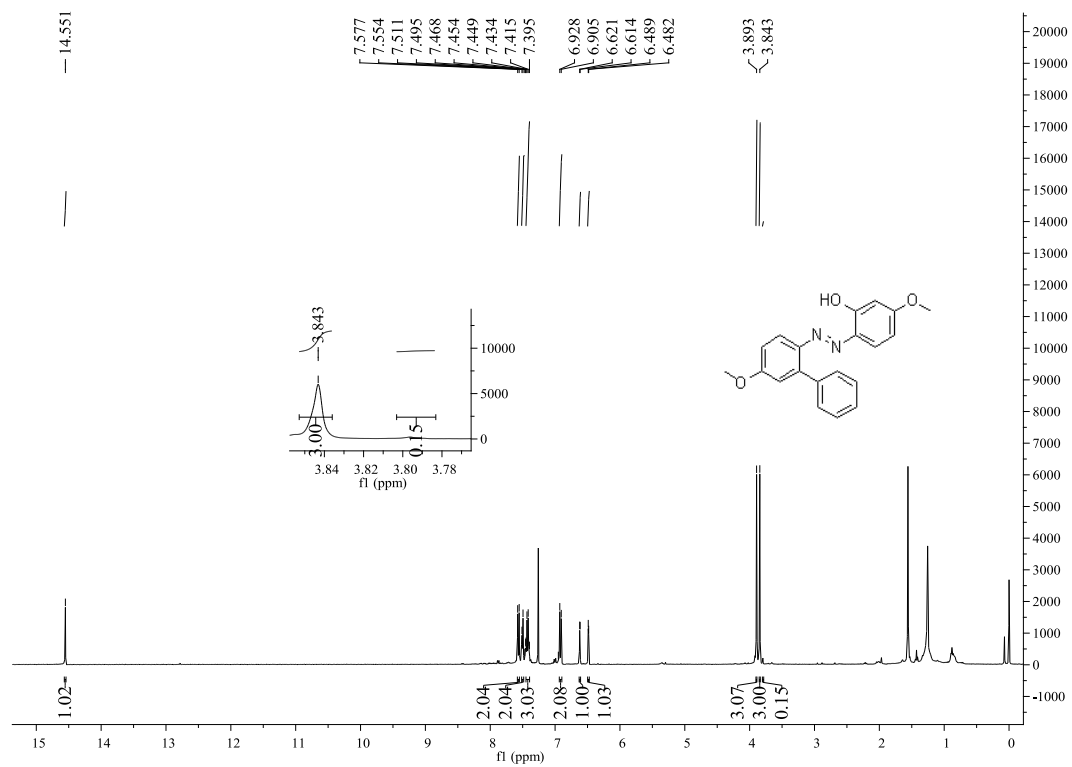
3.32  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4c** ( $\text{CDCl}_3$  as solvent)



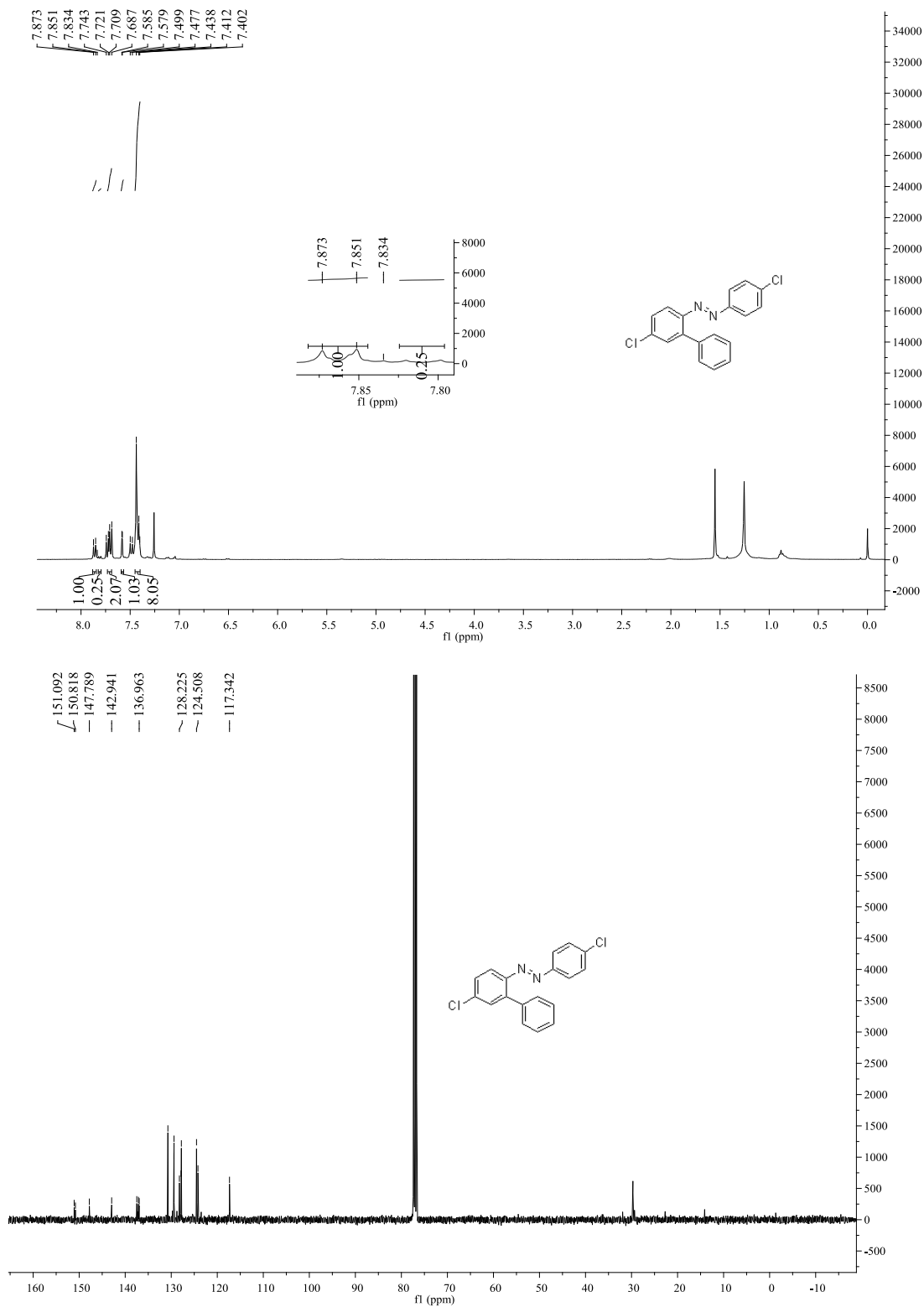
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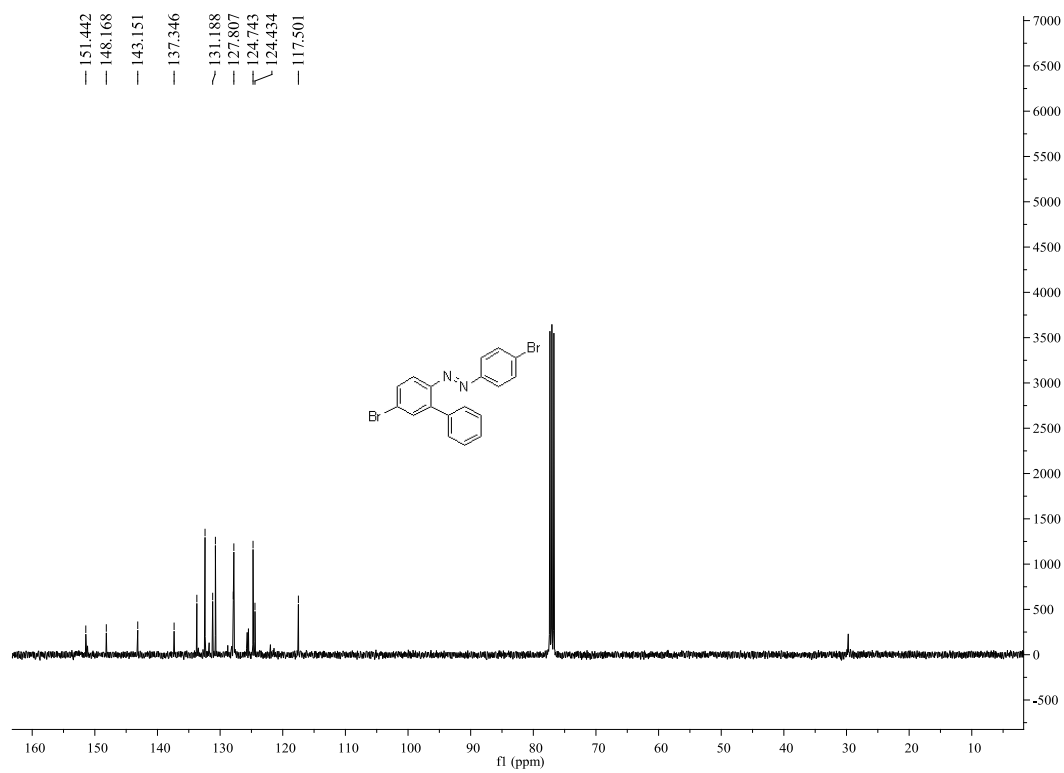
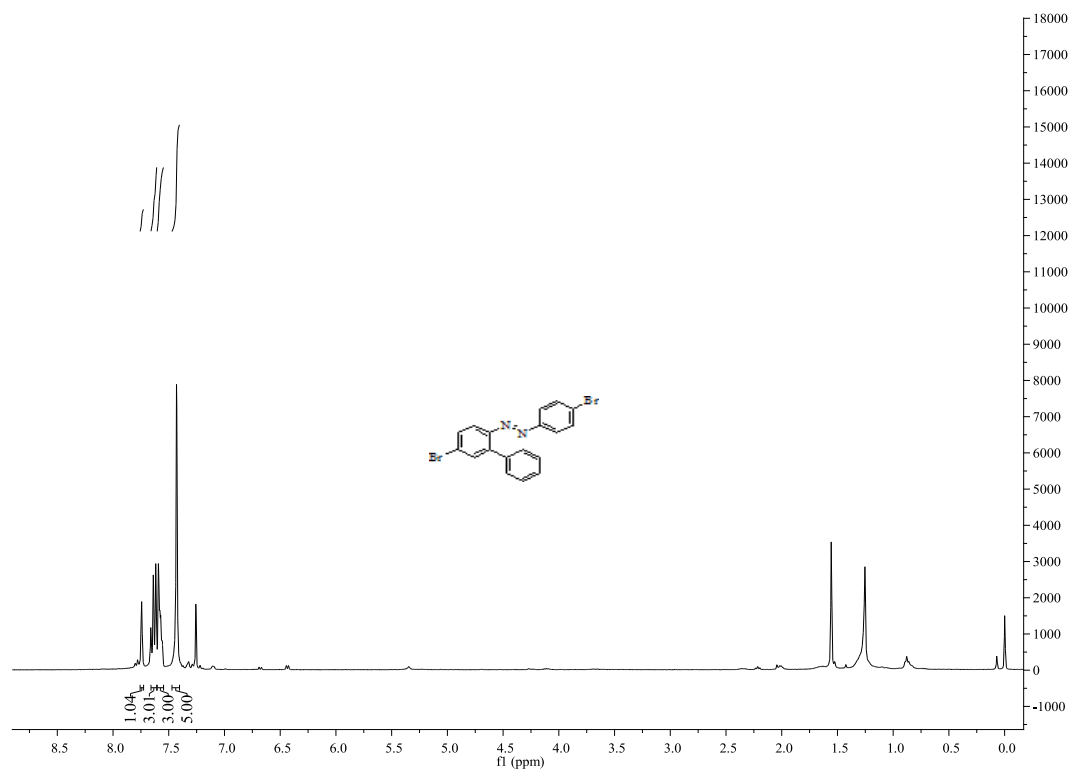
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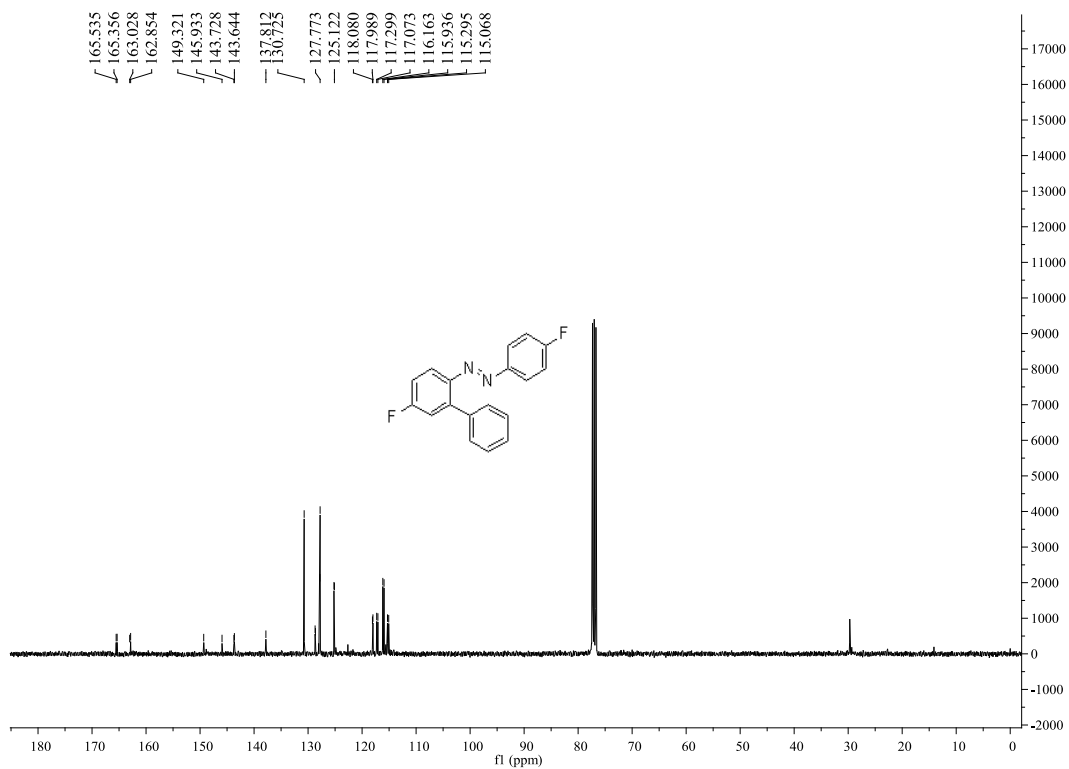
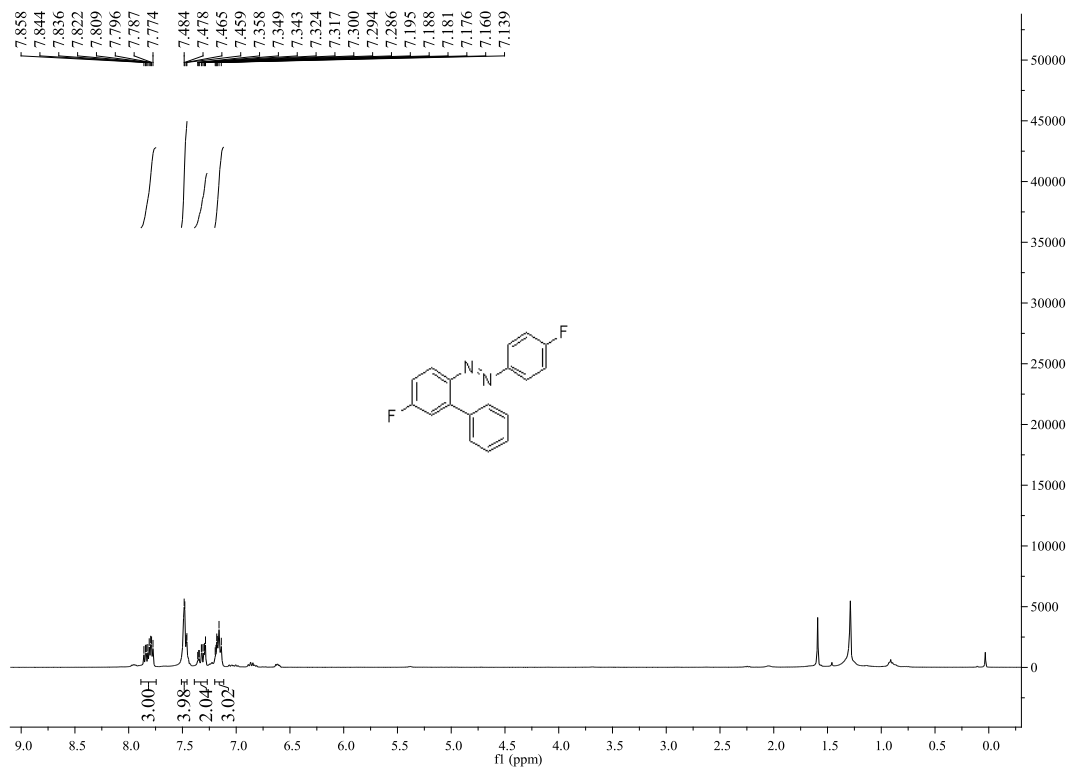
3.35  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4f** ( $\text{CDCl}_3$  as solvent)



3.36  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4g** ( $\text{CDCl}_3$  as solvent)

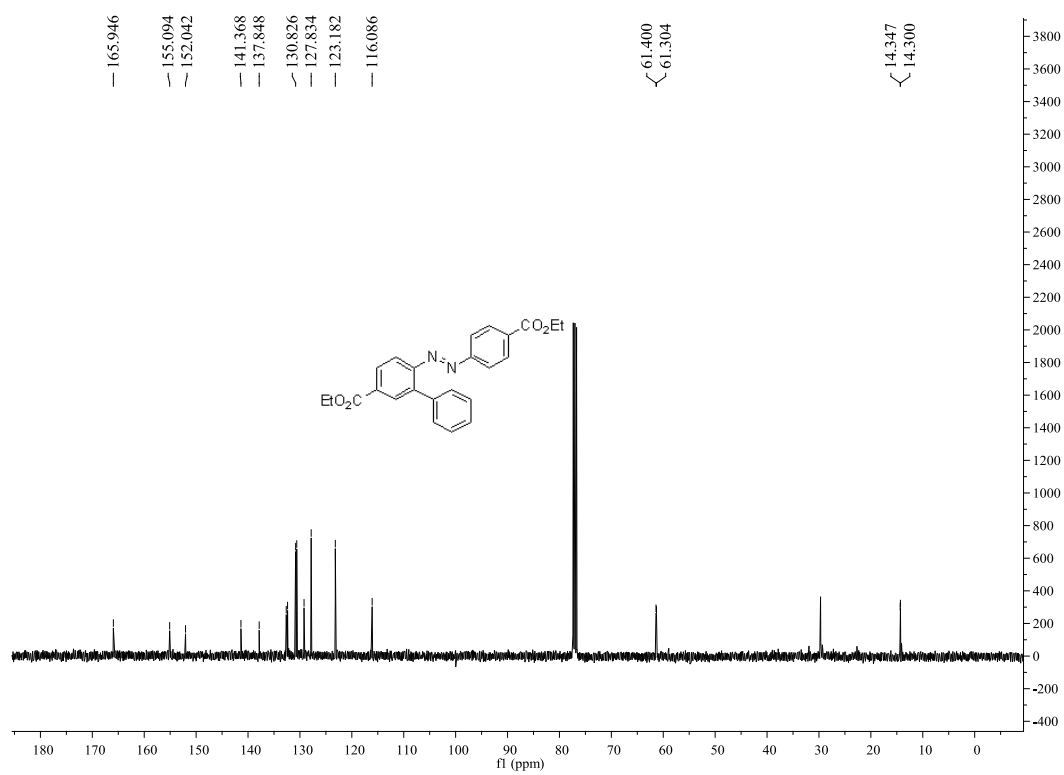
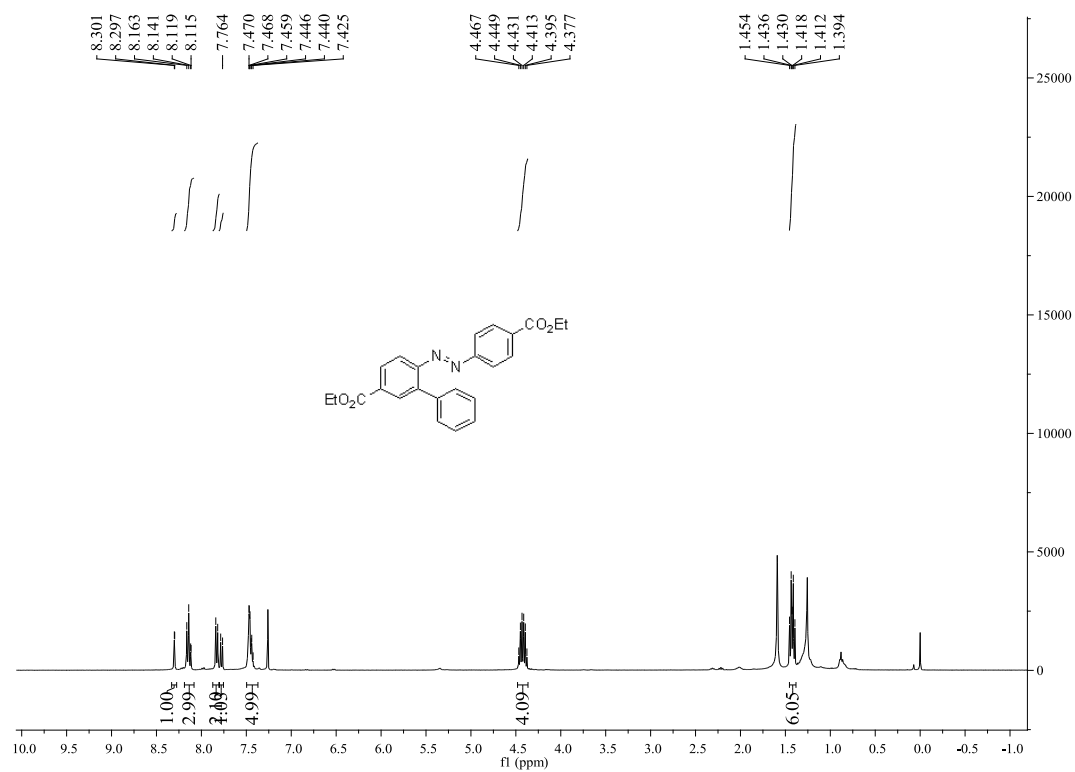


3.37  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4h** ( $\text{CDCl}_3$  as solvent)

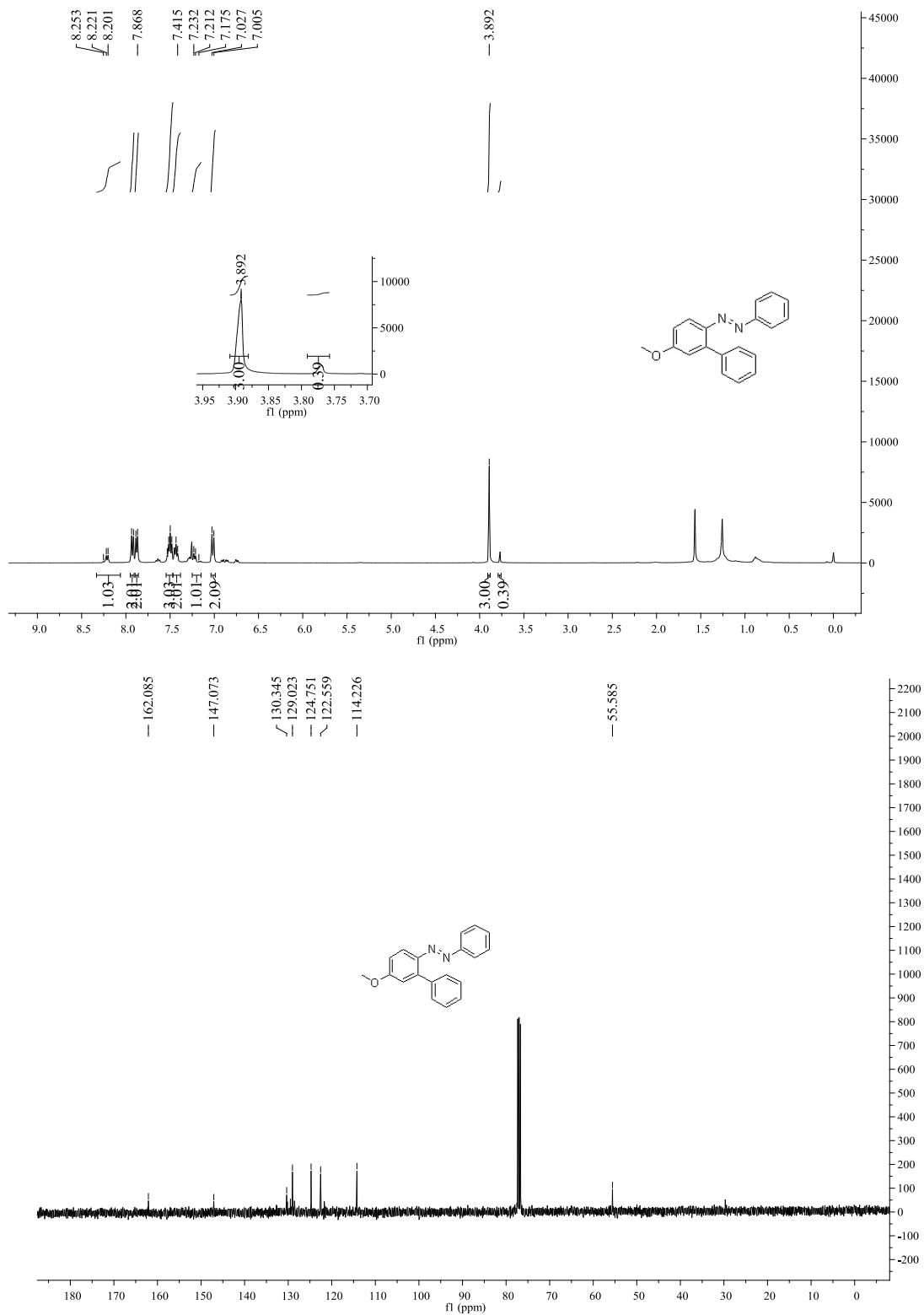




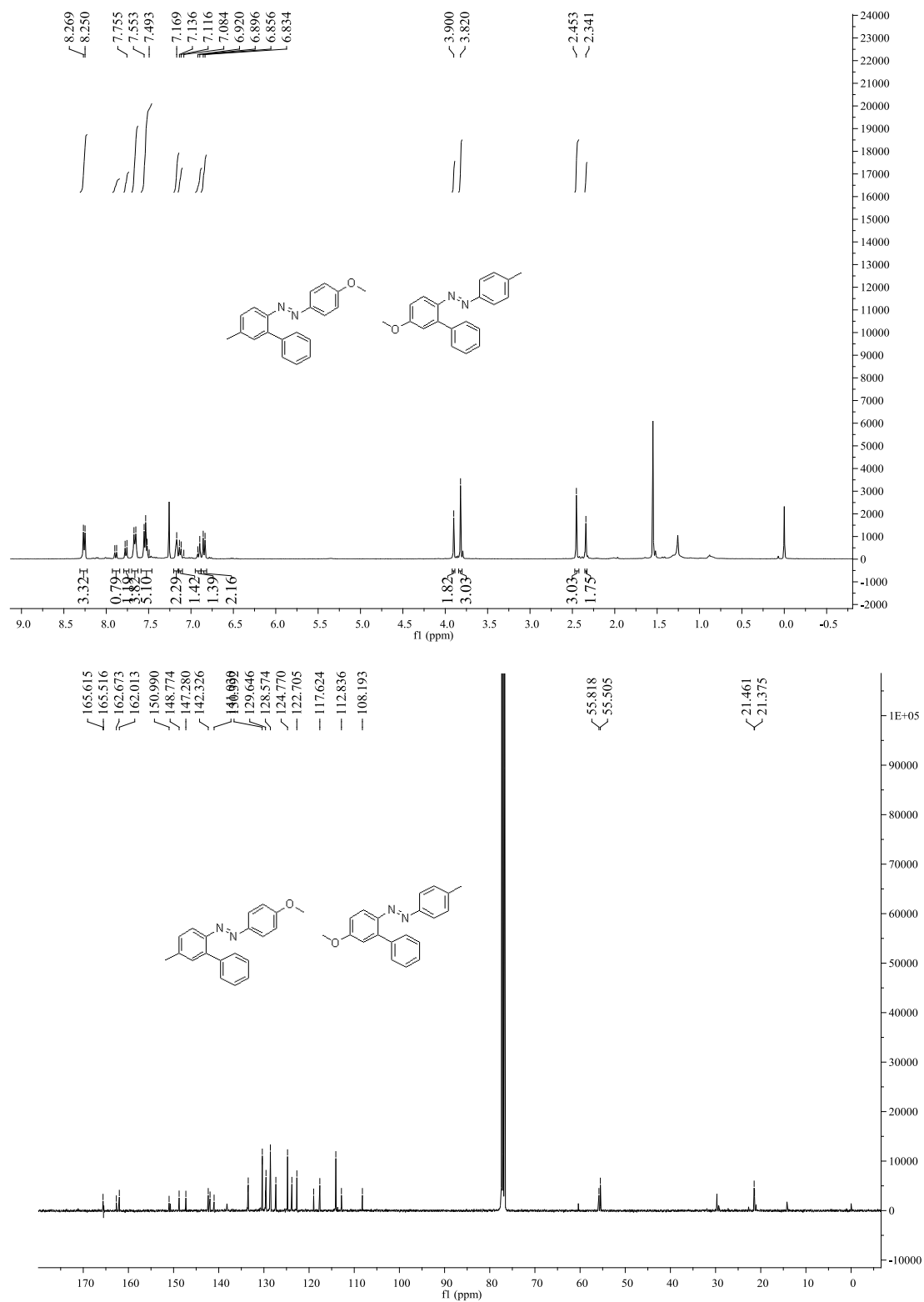
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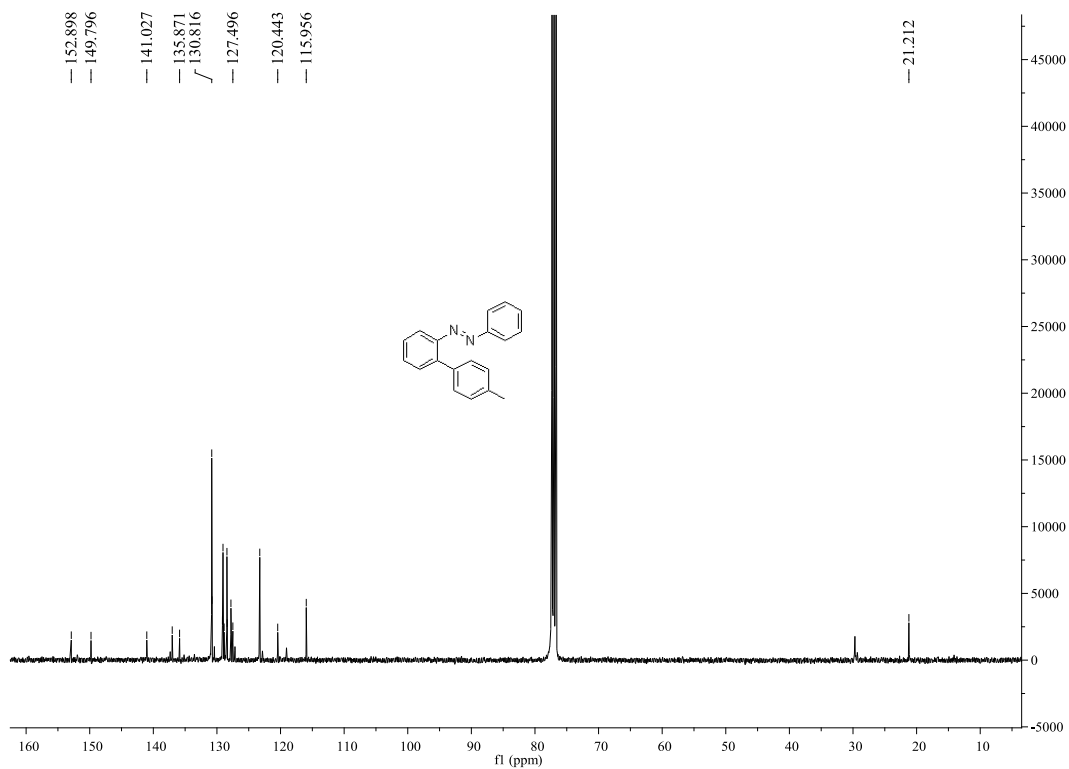
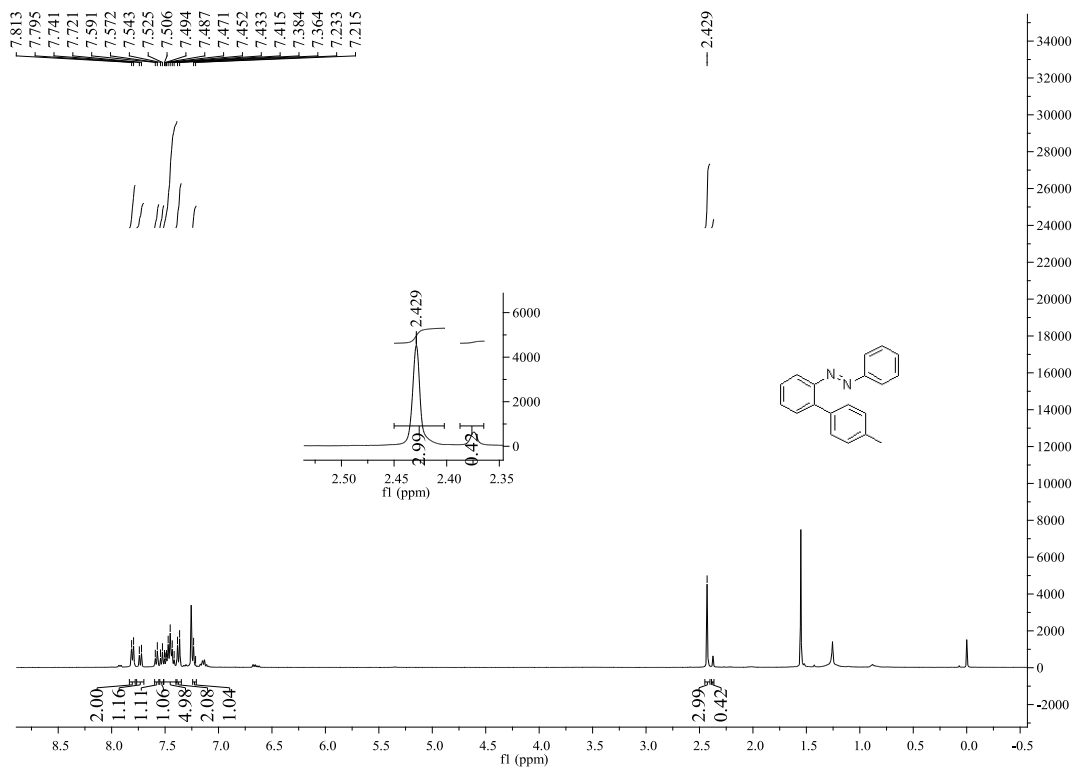
3.39  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4j** ( $\text{CDCl}_3$  as solvent)



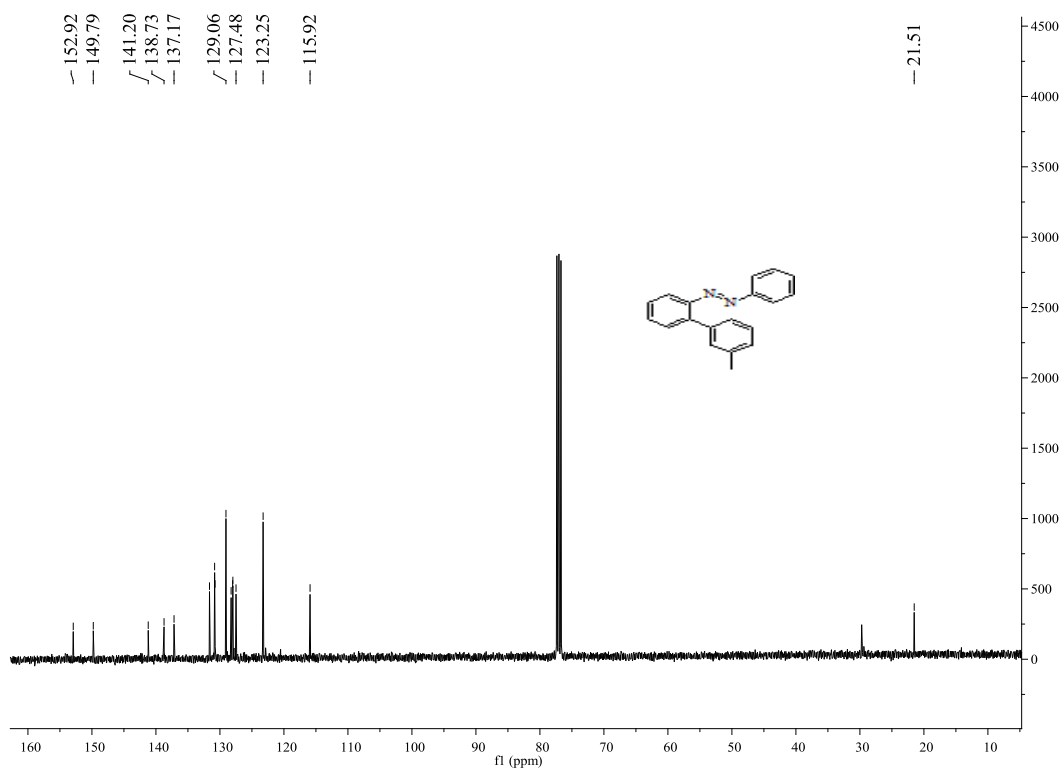
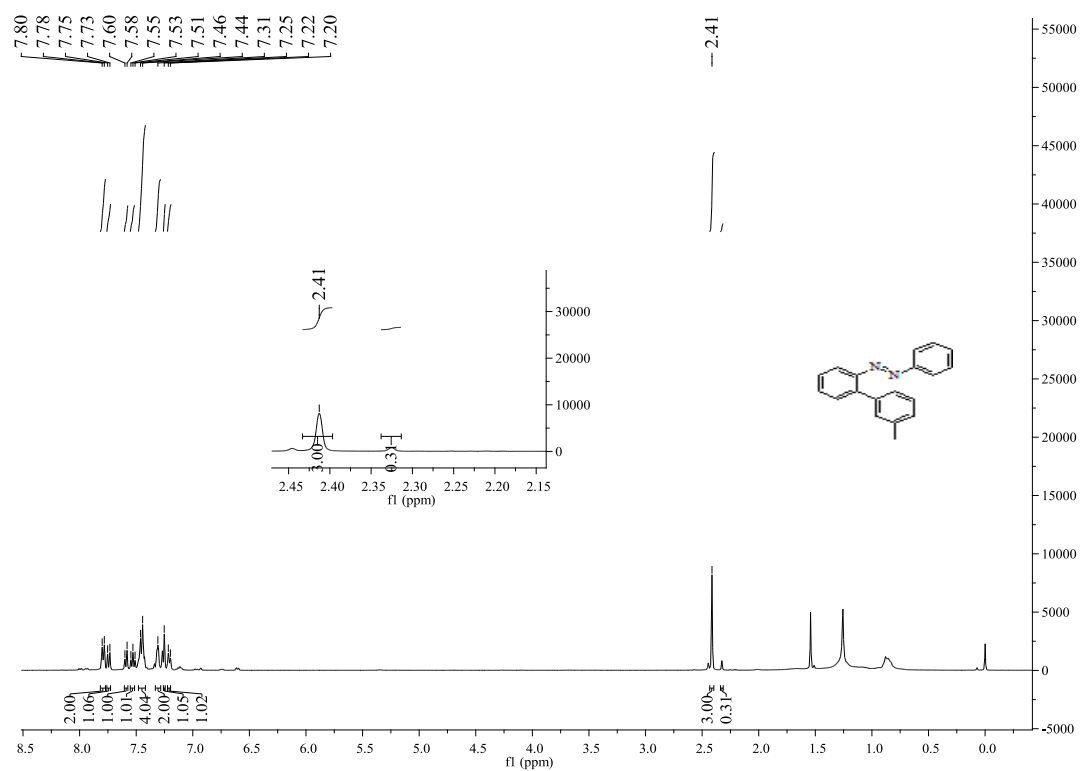
3.40  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4k** and **4l** ( $\text{CDCl}_3$  as solvent)



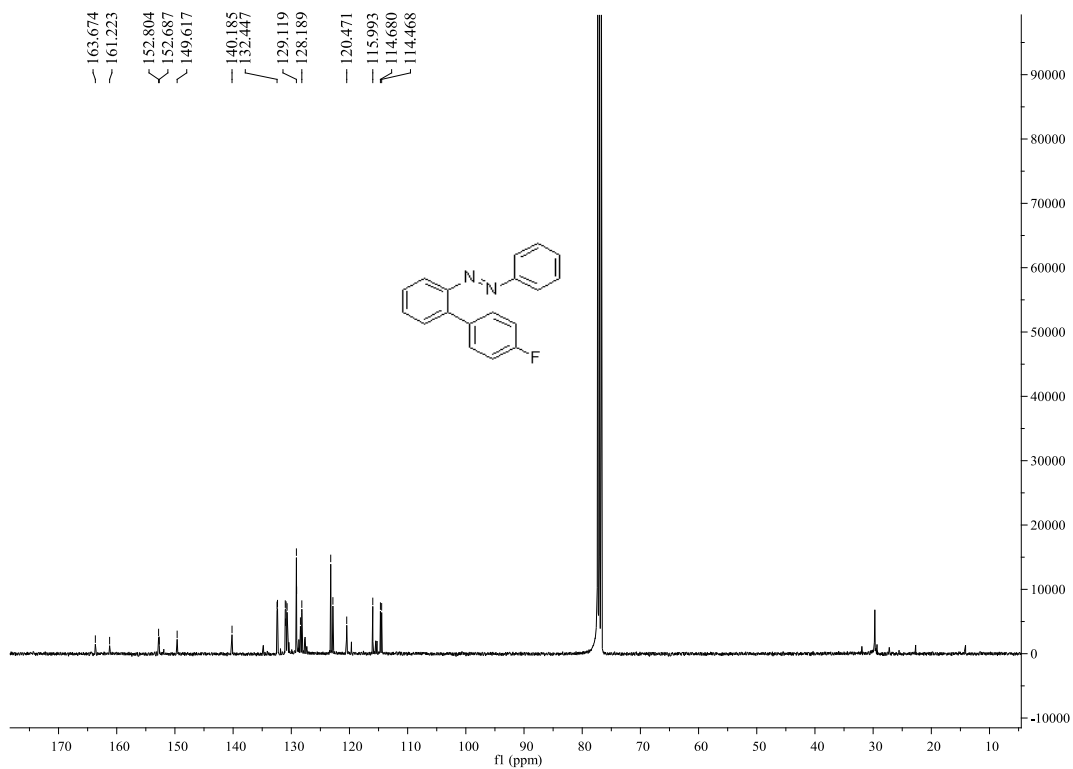
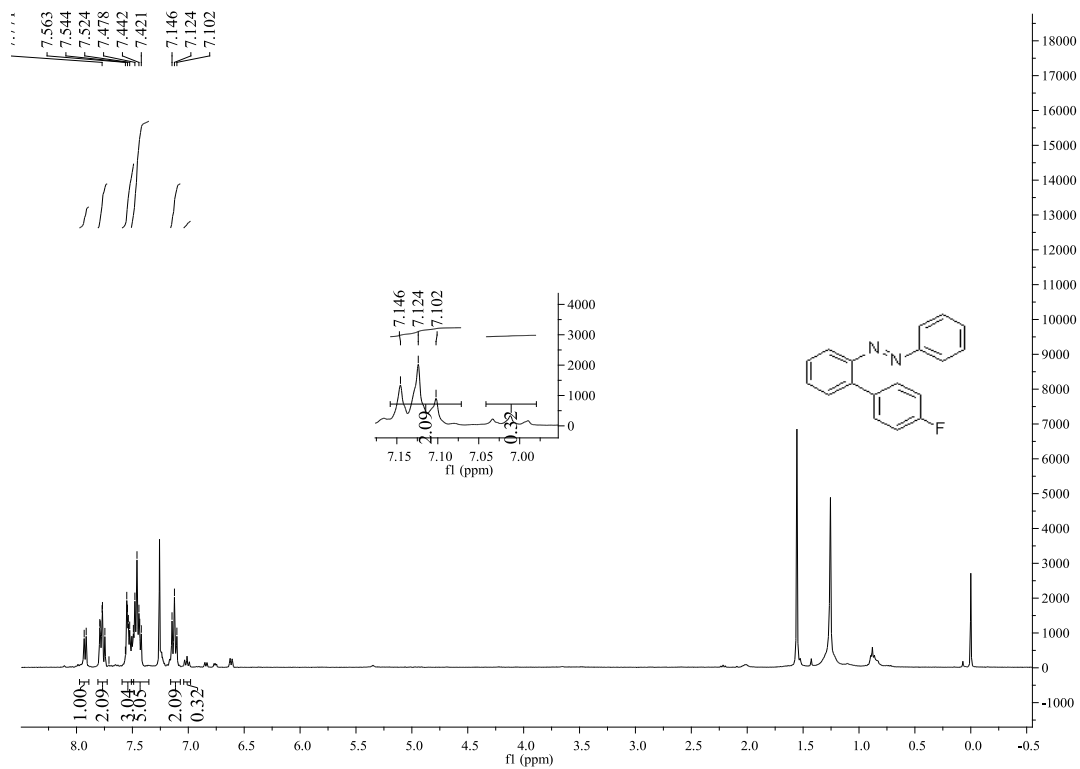
3.41  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4m** ( $\text{CDCl}_3$  as solvent)



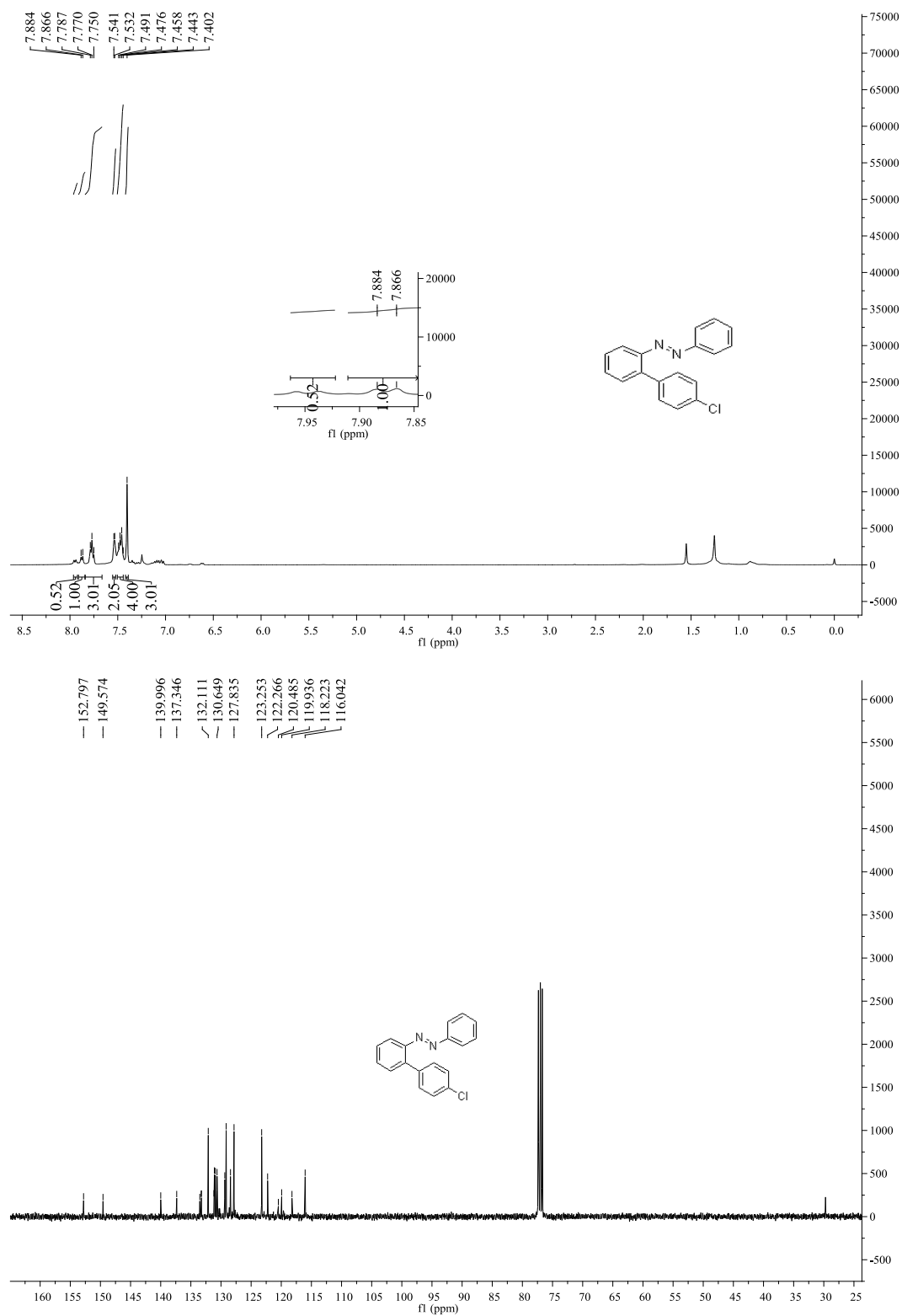
3.42  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4n** ( $\text{CDCl}_3$  as solvent)



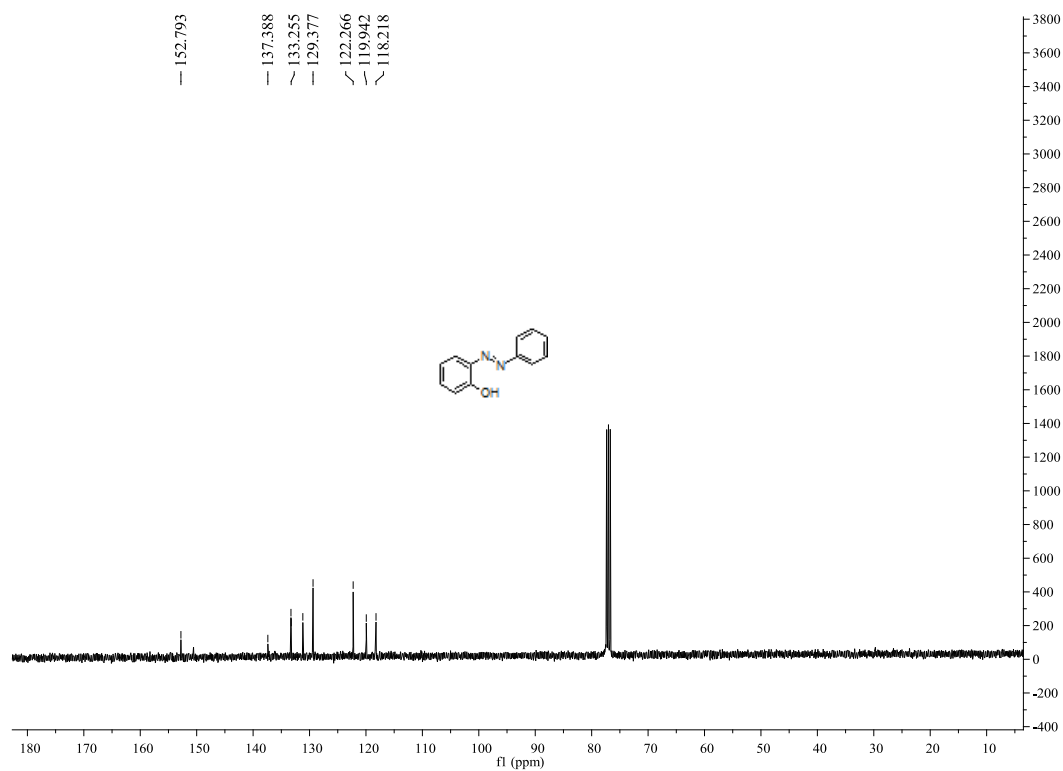
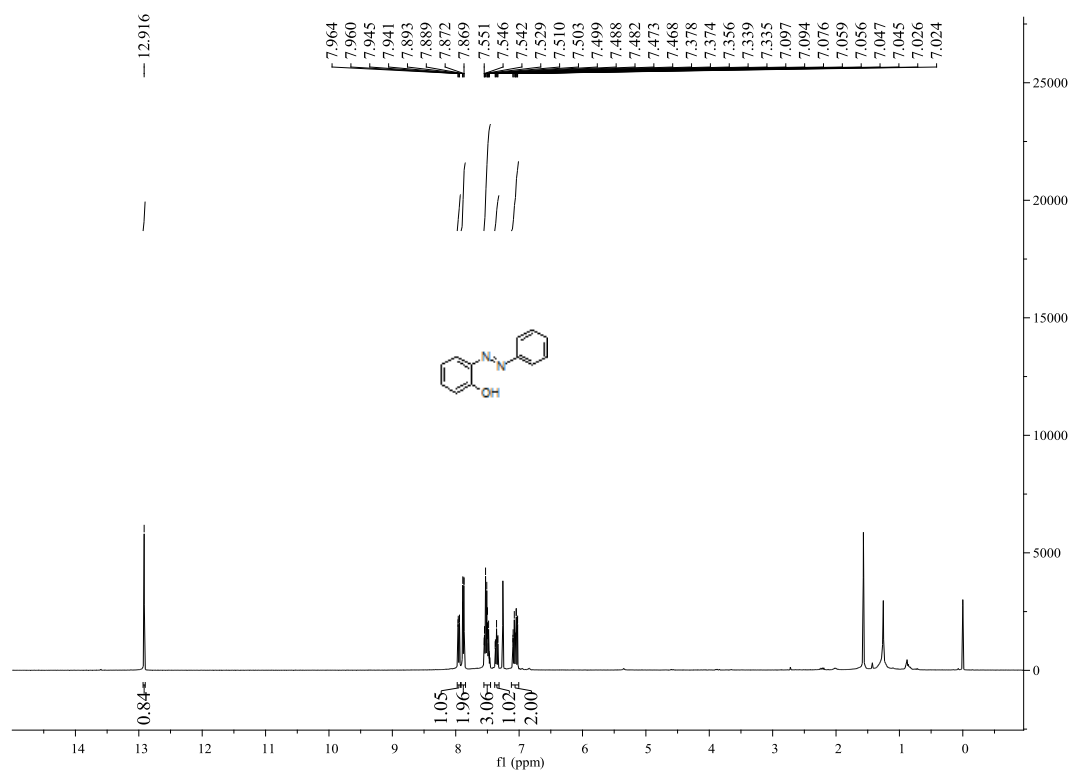
3.43  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4q** ( $\text{CDCl}_3$  as solvent)



3.44  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **4r** ( $\text{CDCl}_3$  as solvent)

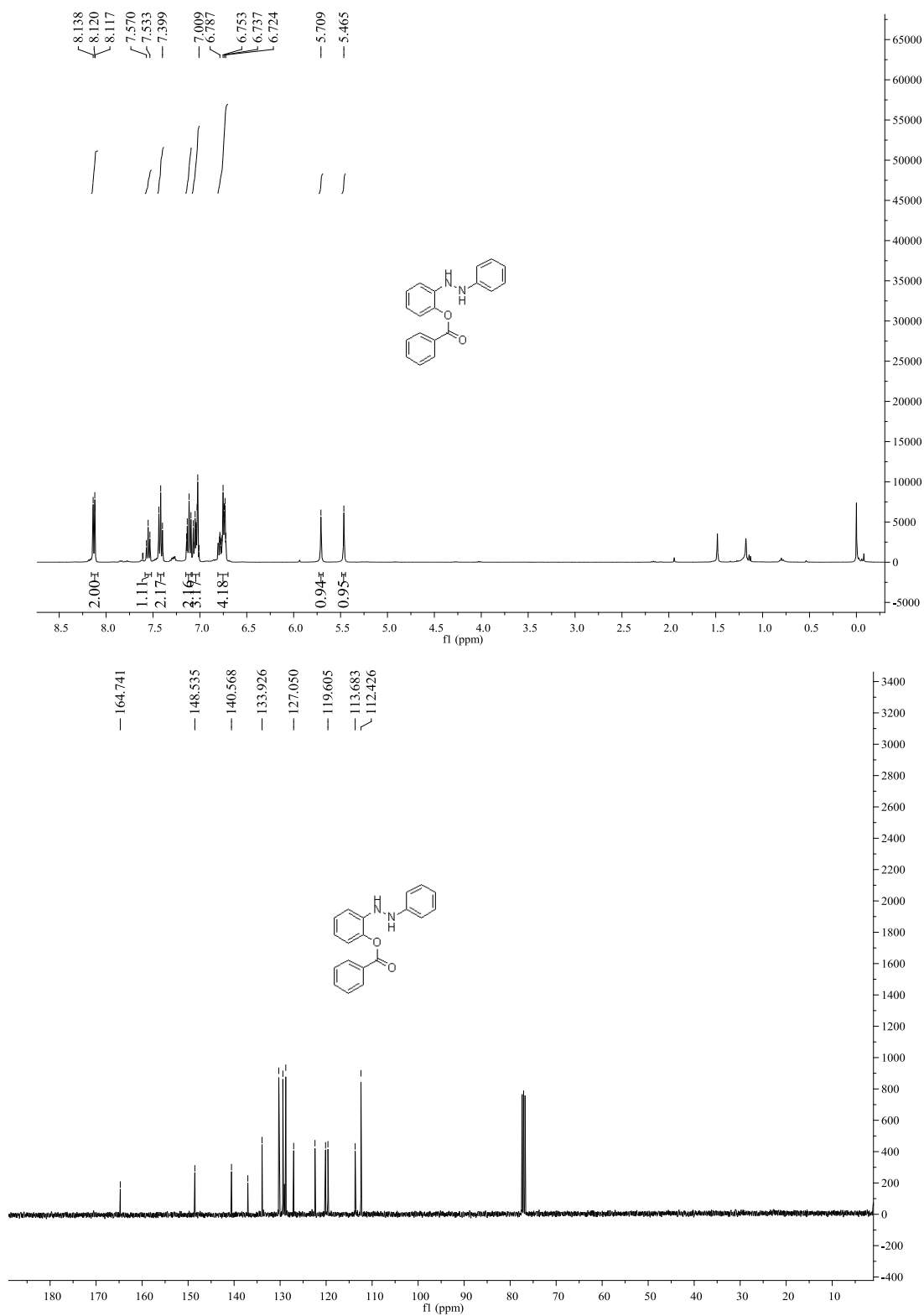


3.45  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **5** ( $\text{CDCl}_3$  as solvent)

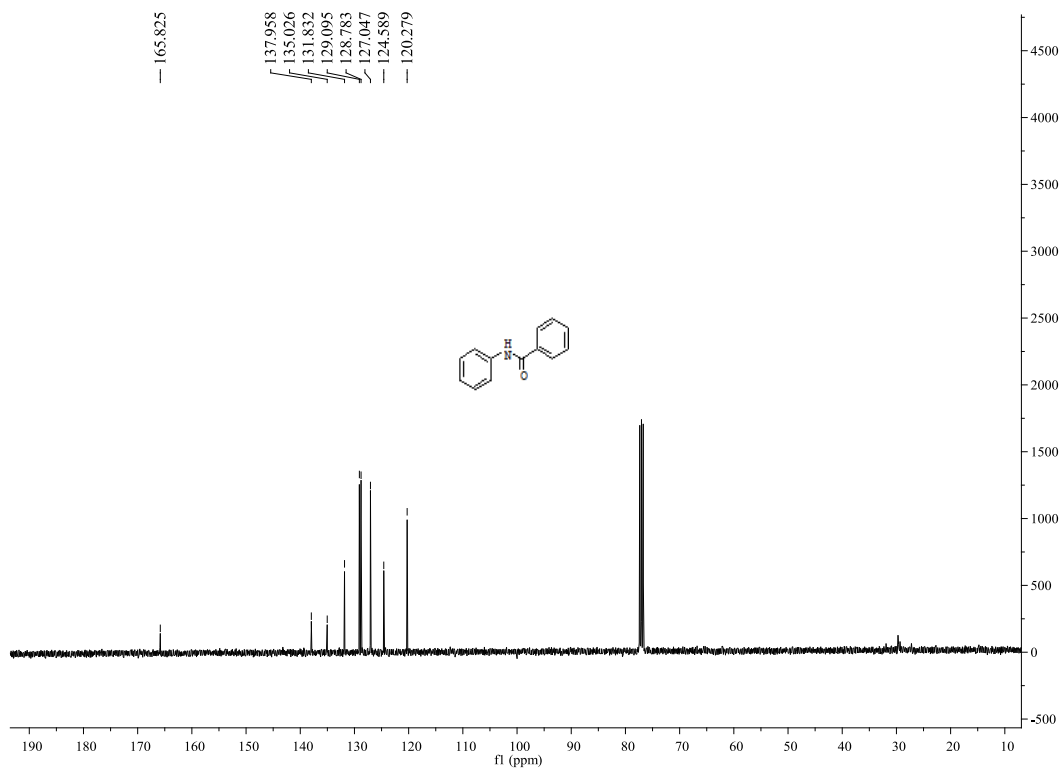
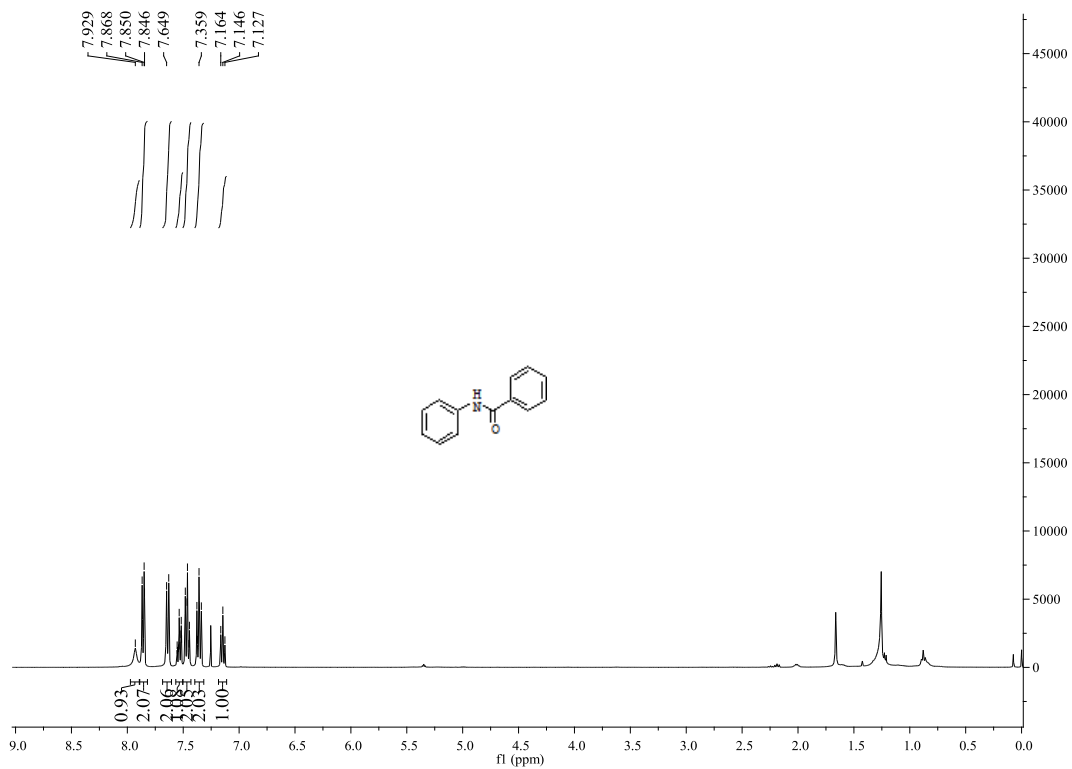




3.46  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **6** ( $\text{CDCl}_3$  as solvent)



3.47  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **7** ( $\text{CDCl}_3$  as solvent)



3.48  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum for **8** (DMSO- $\text{D}_6$  as solvent)

