

Supporting Information  
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## Supporting Information

### Synthesis and Reactivity of Aziridines with Internal Dipolarophiles: an Approach to 1,4-Dihydrochromeno[4,3-*b*]pyrroles and 3-Methylenechromano[4,3-*b*]pyrroles

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## Experimental Details

Microwave reactions were carried out in a microwave reactor CEM Focused Synthesis System Discover S-Class. Flash column chromatography was performed with silica gel 60 as the stationary phase.

### General procedures for the microwave-induced thermolysis of the aziridines

*Method A:* A solution of the appropriated aziridine in toluene (1 mL) was irradiated in the microwave reactor for 15 min with the temperature set to 150 °C. After cooling to room temperature, the solvent was removed under reduced pressure and the crude product was purified by preparative thin layer chromatography [ethyl acetate/hexane (1:4)].

*Method B:* A solution of potassium *tert*-butoxide (0.5 equiv.) in *tert*-butyl alcohol (1 mL) was added to a solution of aziridine in *tert*-butyl alcohol (1 mL). The resulting mixture was irradiated in the microwave reactor for 20 min with the temperature set to 80 °C. After cooling to room temperature, water was added to the reaction mixture and the aqueous layer was extracted with diethyl ether. The organic layer was washed with saturated aqueous NH<sub>4</sub>Cl solution, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent removed in vacuum. The crude product was purified by flash chromatography [ethyl acetate/hexane (1:5)].

### 2-Benzoyl-1-benzyl-1,4-dihydrochromeno[4,3-*b*]pyrrole (23)

Prepared by *method A* from aziridine **11a** (100 mg, 0.27 mmol). Purification by preparative thin layer chromatography [ethyl acetate/hexane (1:4)] afforded compound **23** (29 mg, 29%).

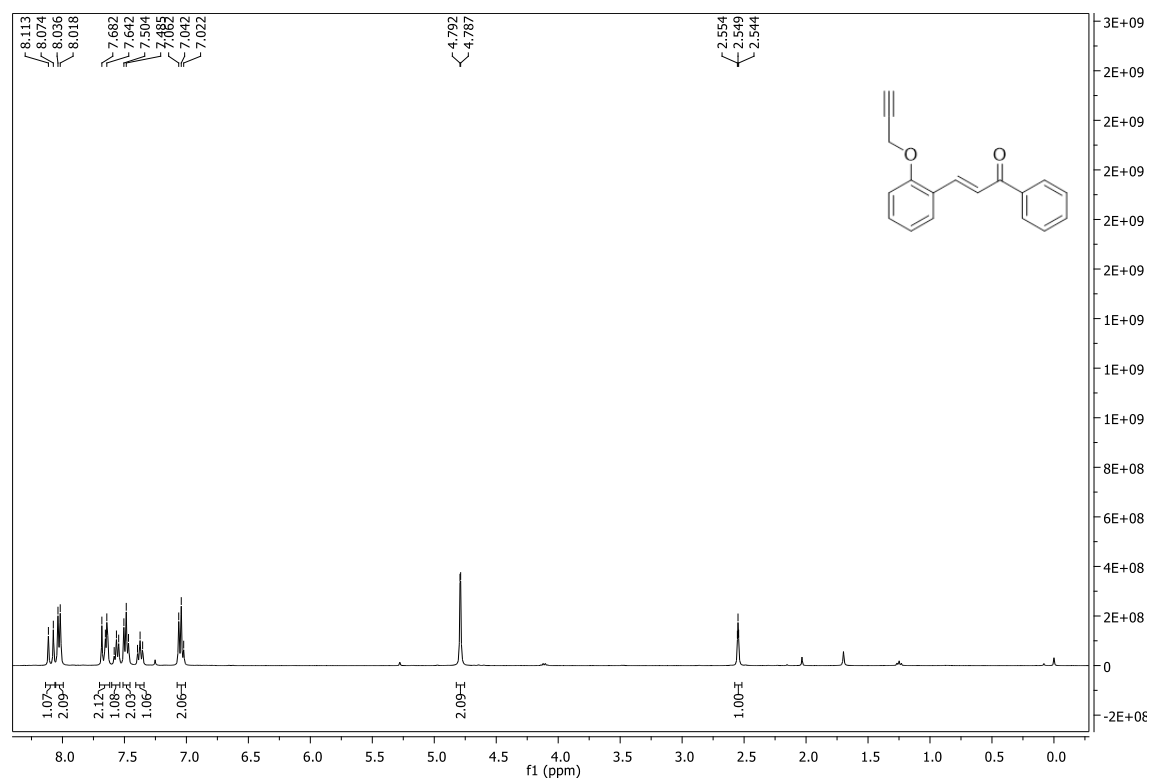
Prepared by *method B* from aziridine **11a** (100 mg, 0.27 mmol) and potassium *tert*-butoxide (16 mg, 0.14 mmol). Purification by flash chromatography [ethyl acetate/hexane (1:5)] afforded compound **23** (26 mg, 26%).

### 2-Benzoyl-1-benzyl-3-methylenechromano[4,3-*b*]pyrrole (24), 2-benzoyl-1-benzyl-3-methyl-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole (25) and 2-benzoyl-1-benzyl-3-methyl-1,4-dihydrochromeno[4,3-*b*]pyrrole (26)

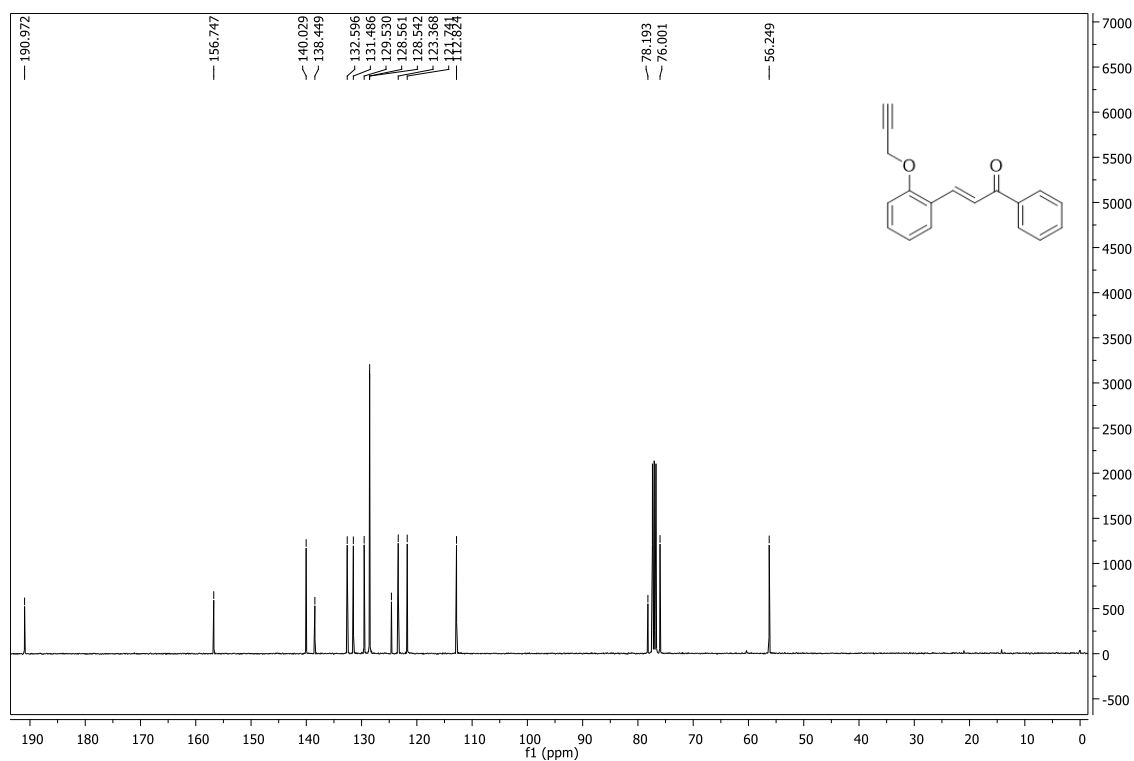
Prepared by *method A* from aziridine **13a** (130 mg, 0.34 mmol). Purification by preparative thin layer chromatography [ethyl acetate/hexane (1:4)] afforded, in order of elution,

compound **24** (<4%) as an orange oil and a 43:57 mixture of the compounds **25** and **26** (18 mg, 18%).

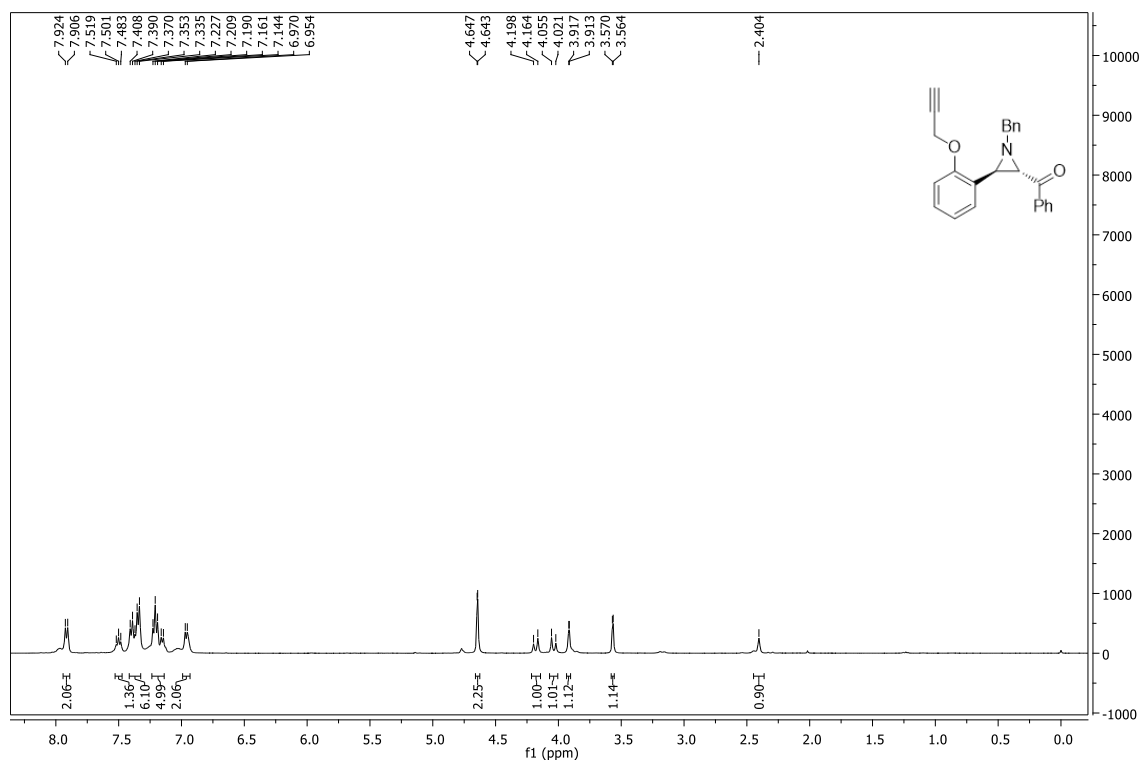
**1.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of all new compounds and NOESY spectra of selected compounds**



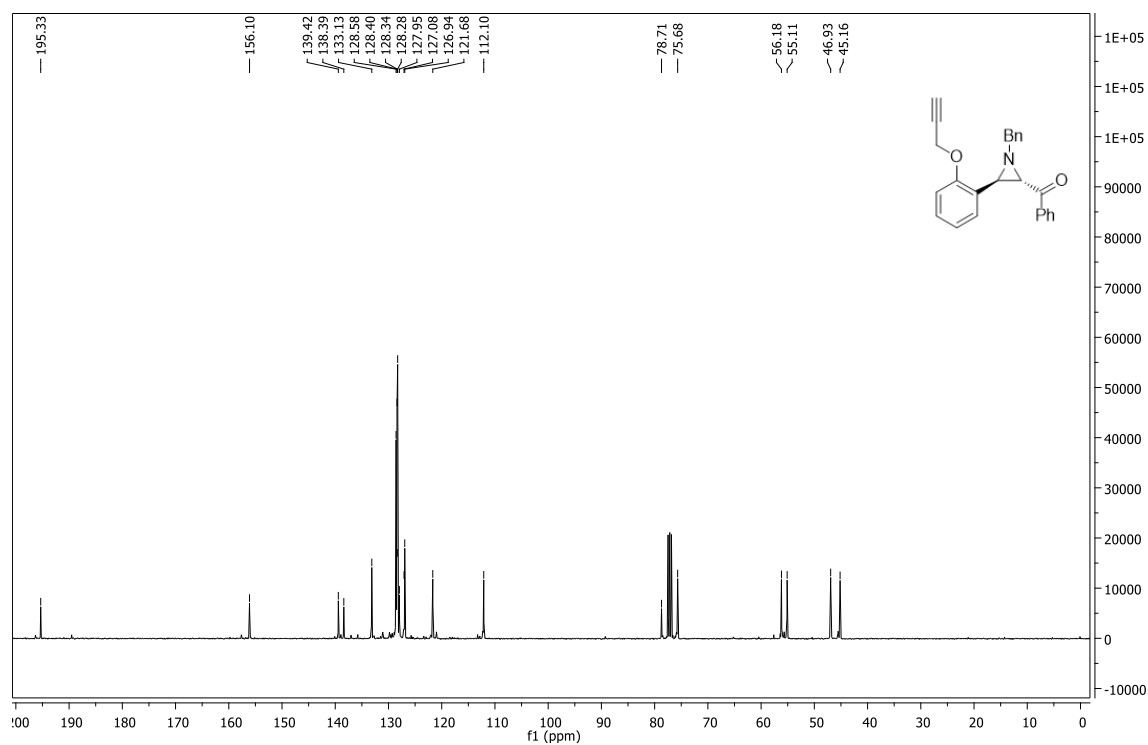
**Figure S1.**  $^1\text{H}$  NMR spectrum of compound **10**.



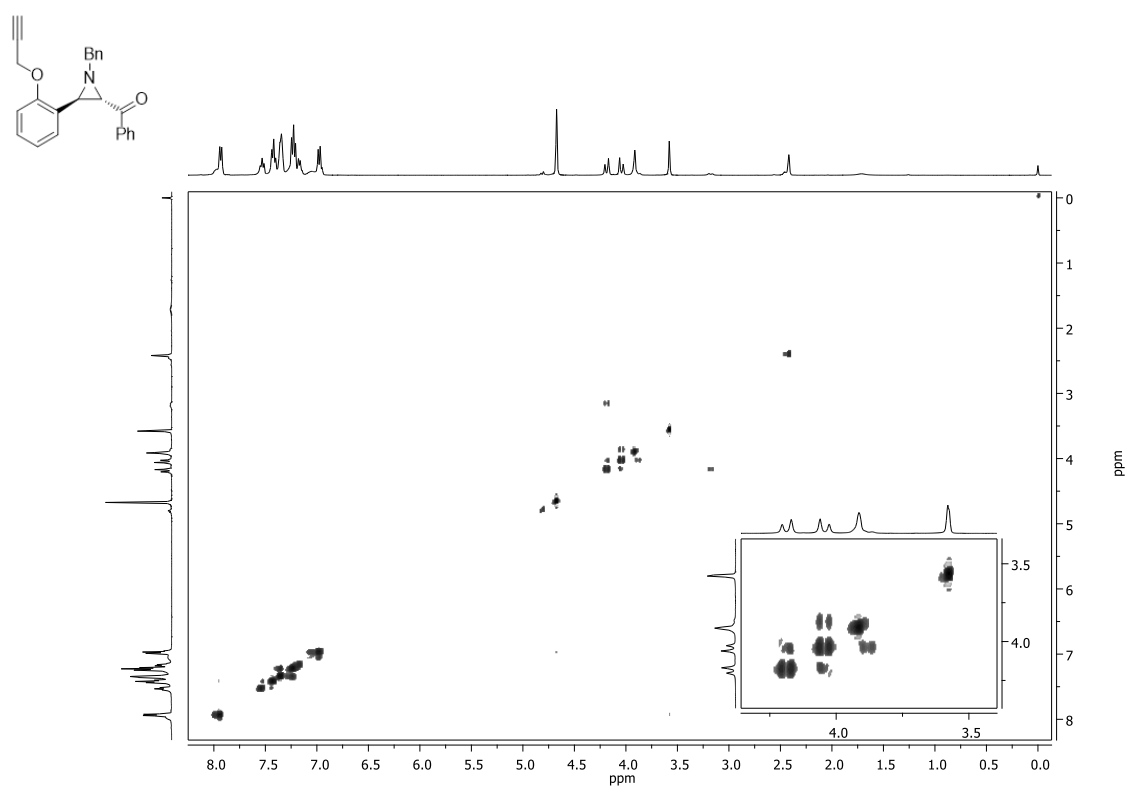
**Figure S2.** <sup>13</sup>C NMR spectrum of compound 10.



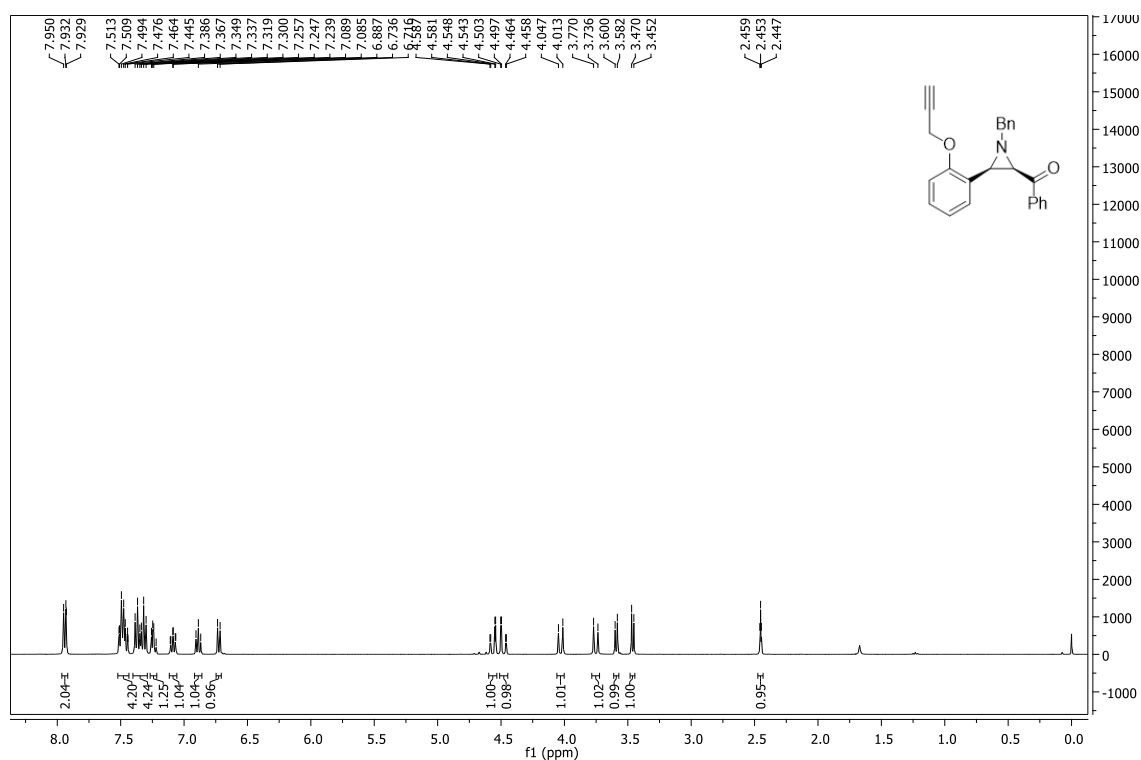
**Figure S3.** <sup>1</sup>H NMR spectrum of compound 11a.



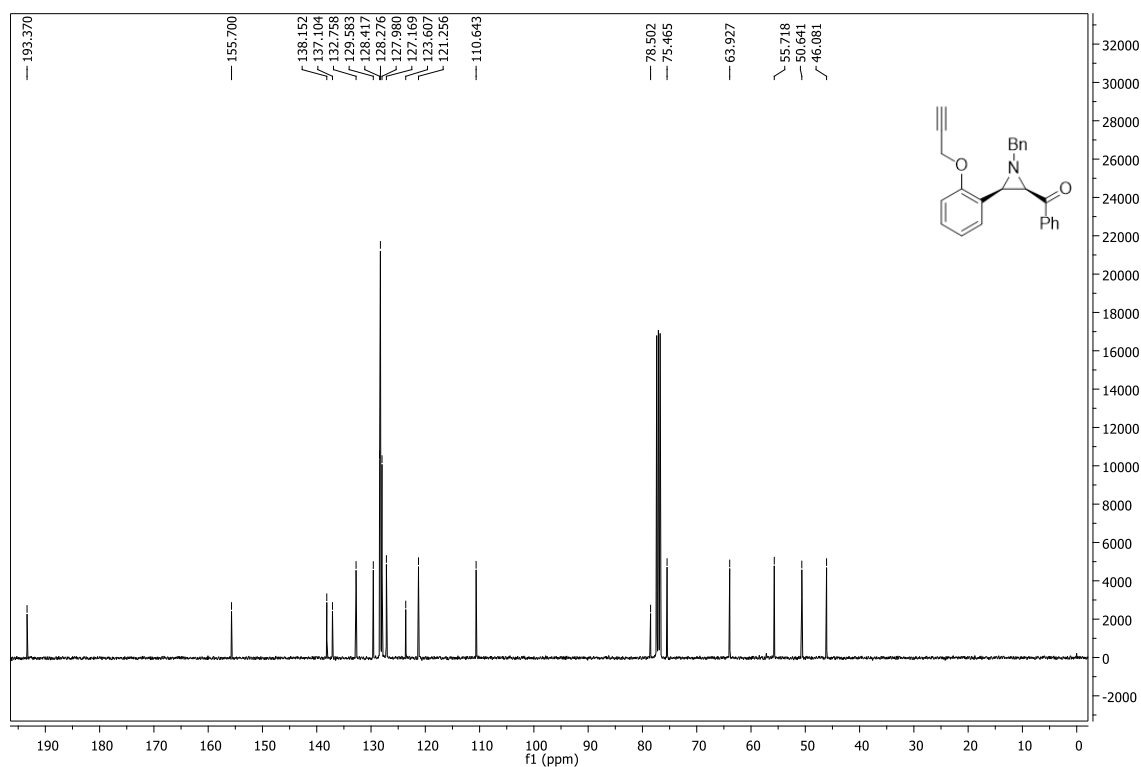
**Figure S4.** <sup>13</sup>C NMR spectrum of compound **11a**.



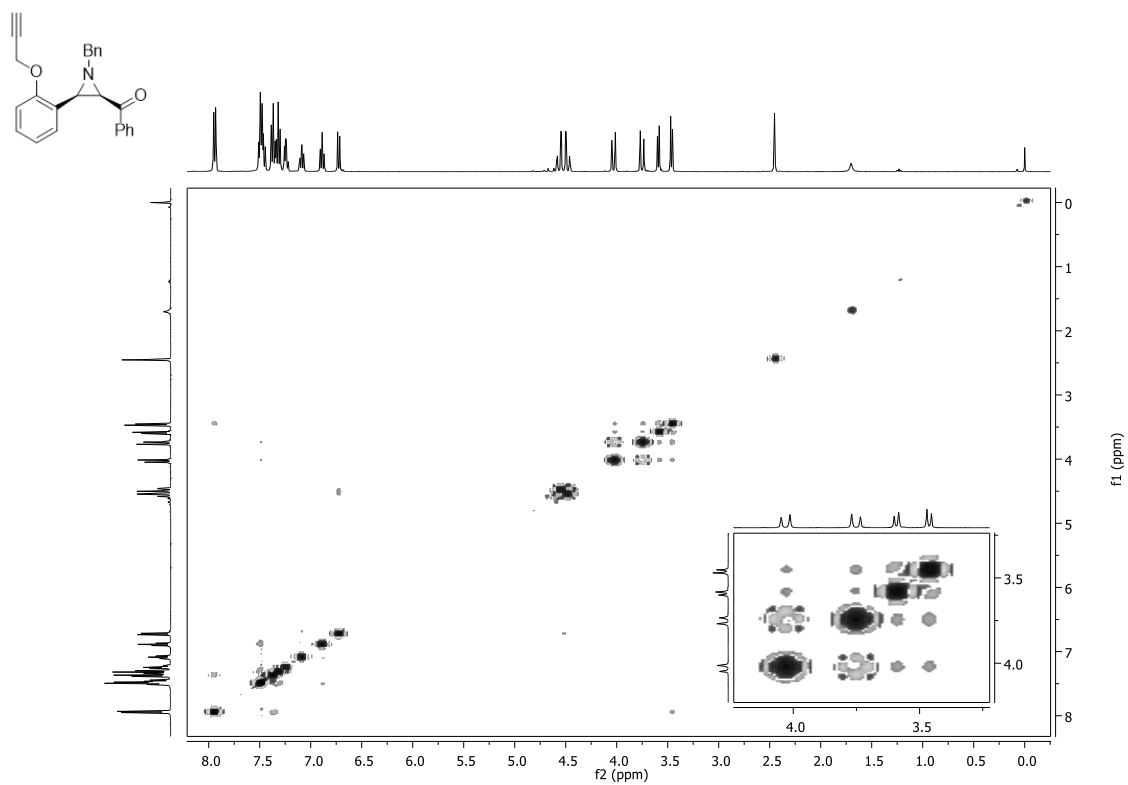
**Figure S5.** NOESY spectrum of compound **11a**.



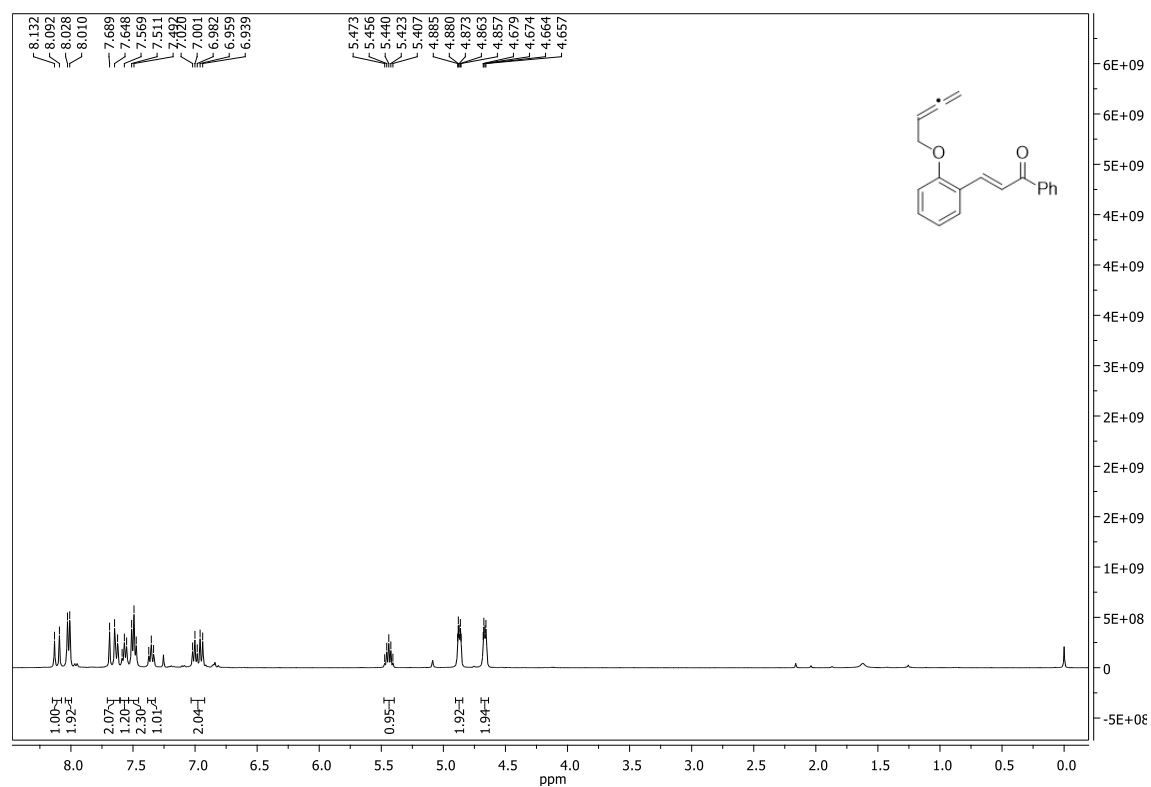
**Figure S6.** <sup>1</sup>H NMR spectrum of compound 11b.



**Figure S7.** <sup>13</sup>C NMR spectrum of compound 11b.

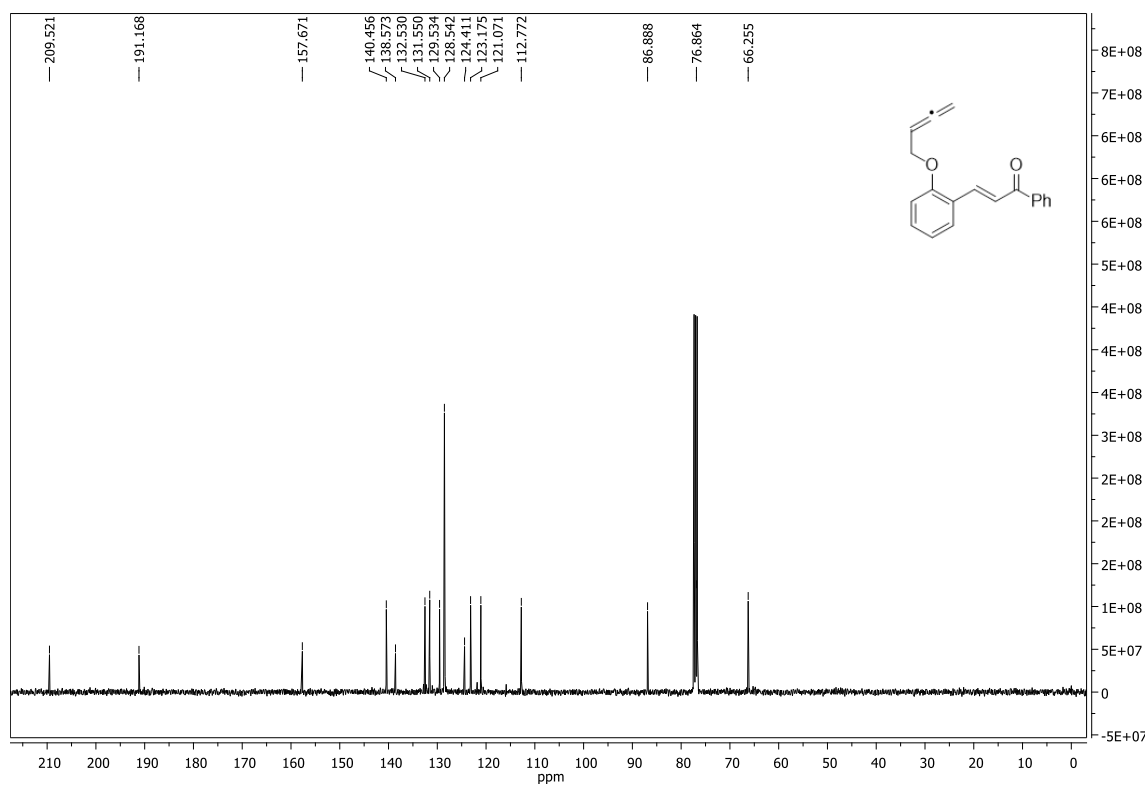


**Figure S8.** NOESY spectrum of compound **11b**.

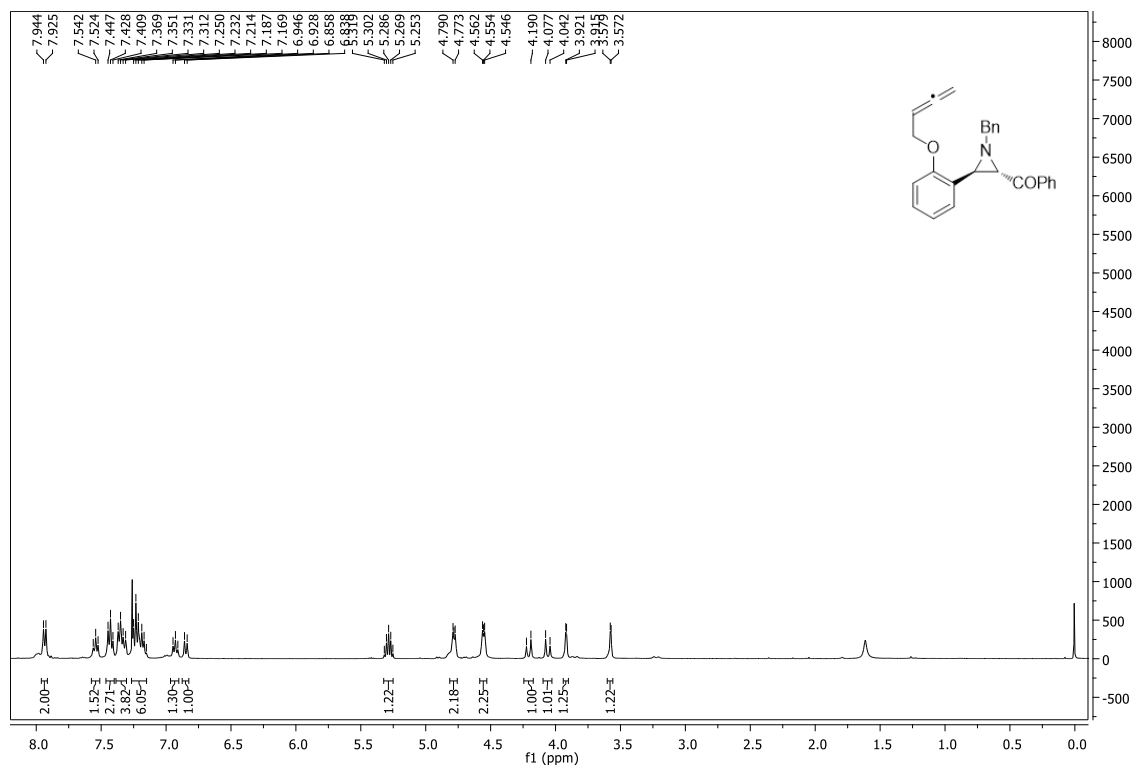


**Figure S9.**  $^1\text{H}$  NMR spectrum of compound **12**.

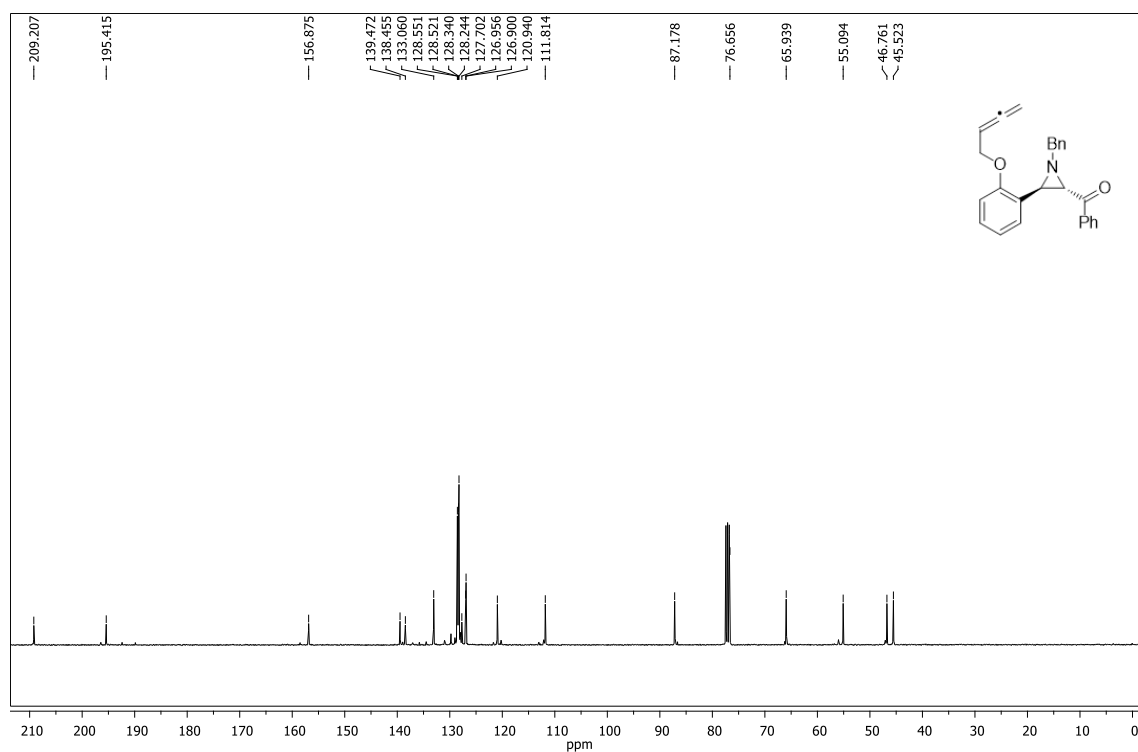




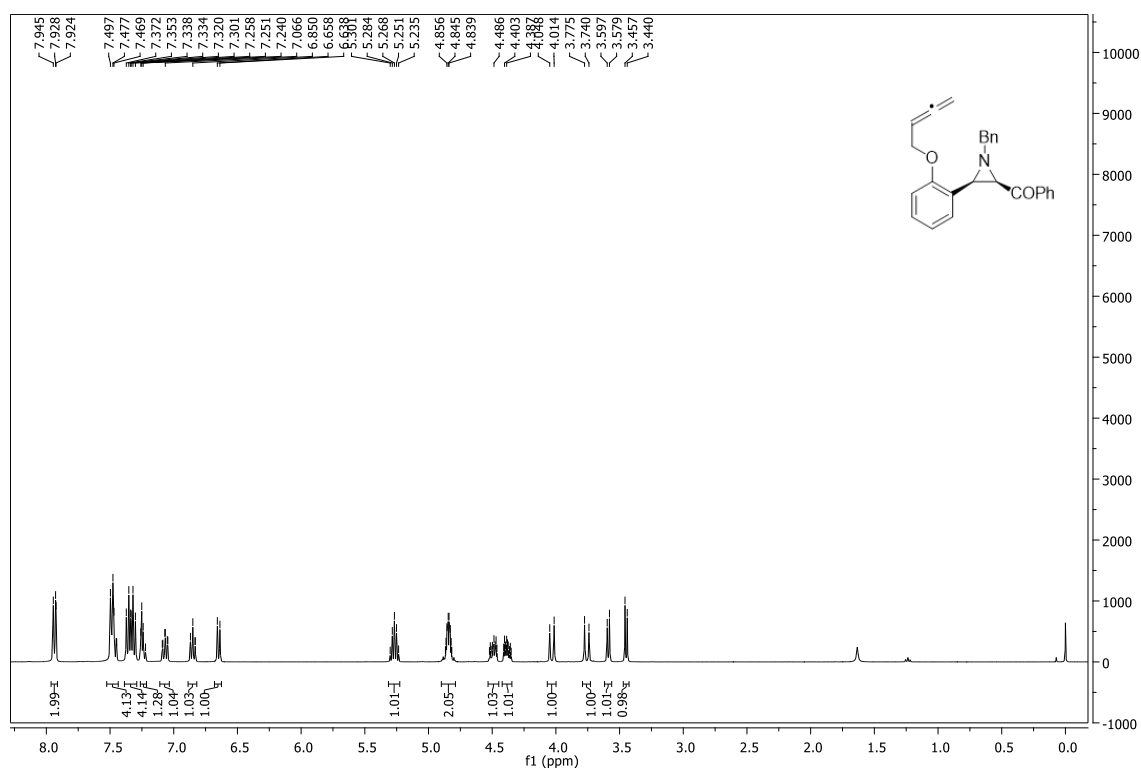
**Figure S10.** <sup>13</sup>C NMR spectrum of compound **12**.



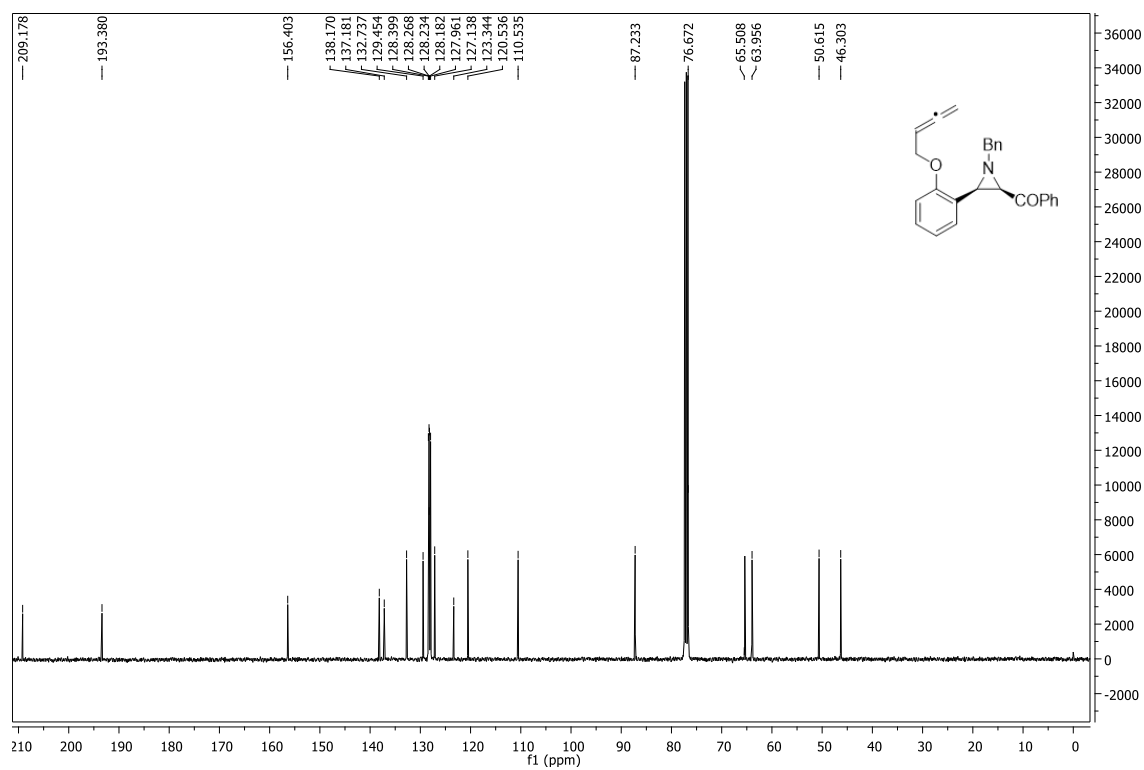
**Figure S11.** <sup>1</sup>H NMR spectrum of compound **13a**.



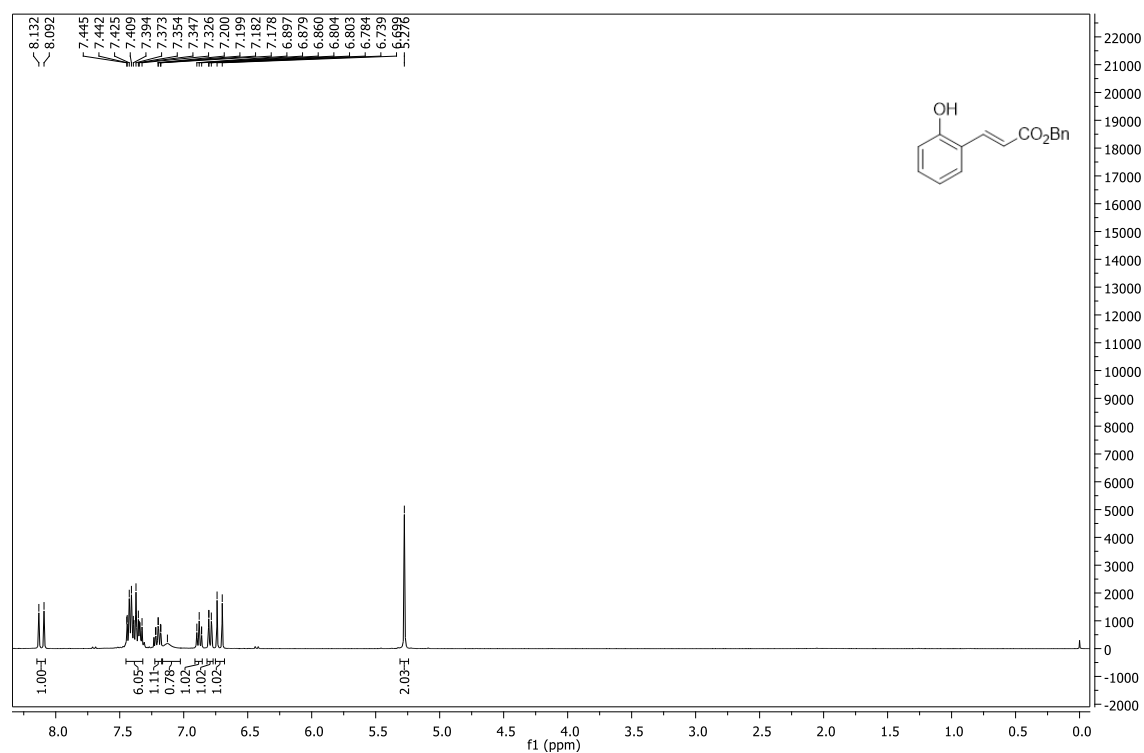
**Figure S12.** <sup>13</sup>C NMR spectrum of compound **13a**.



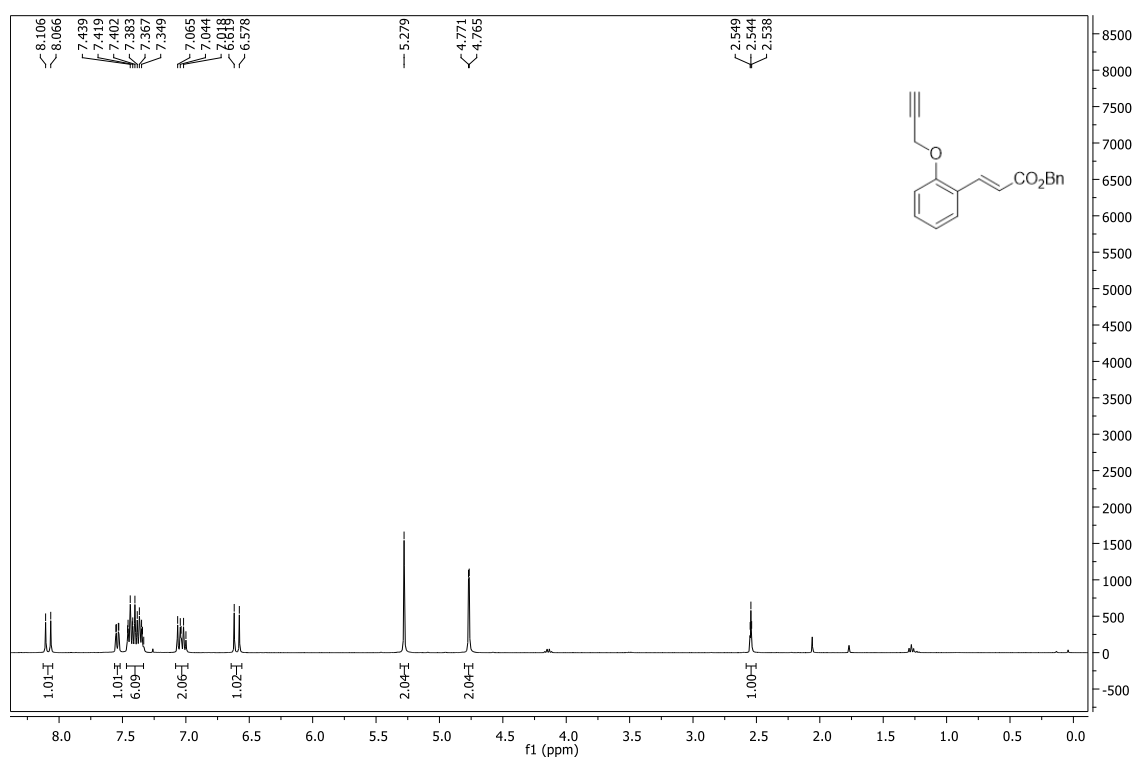
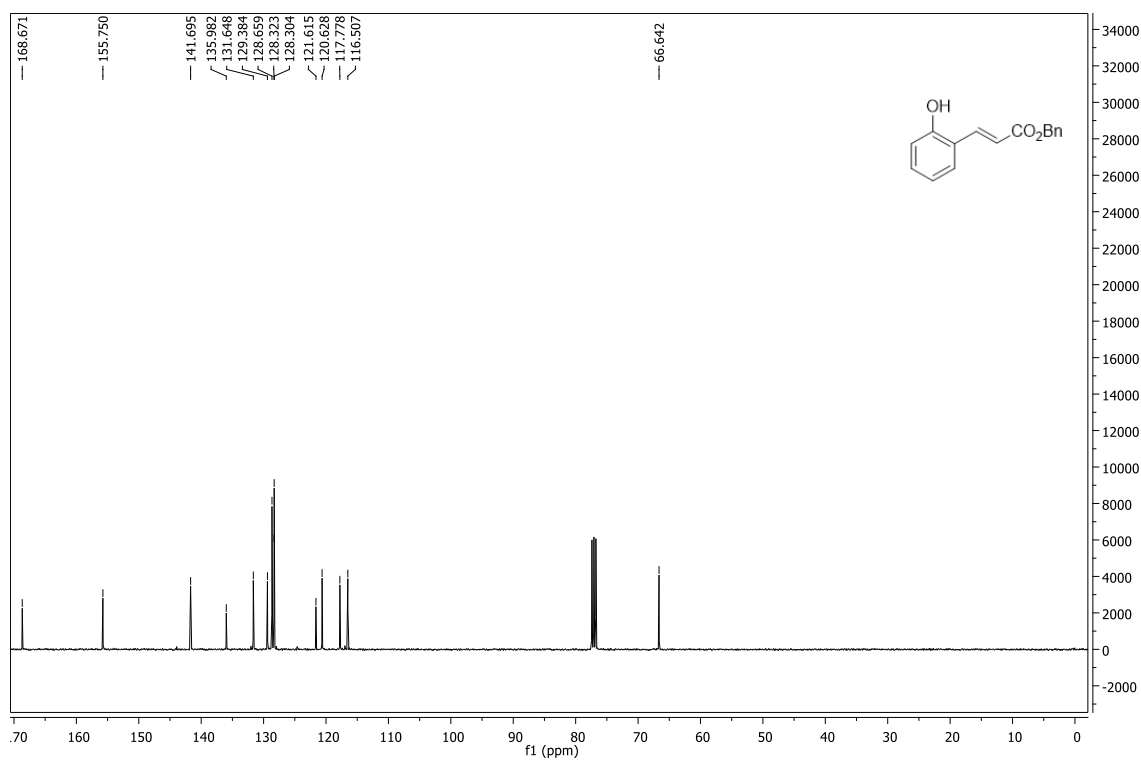
**Figure S13.** <sup>1</sup>H NMR spectrum of compound **13b**.

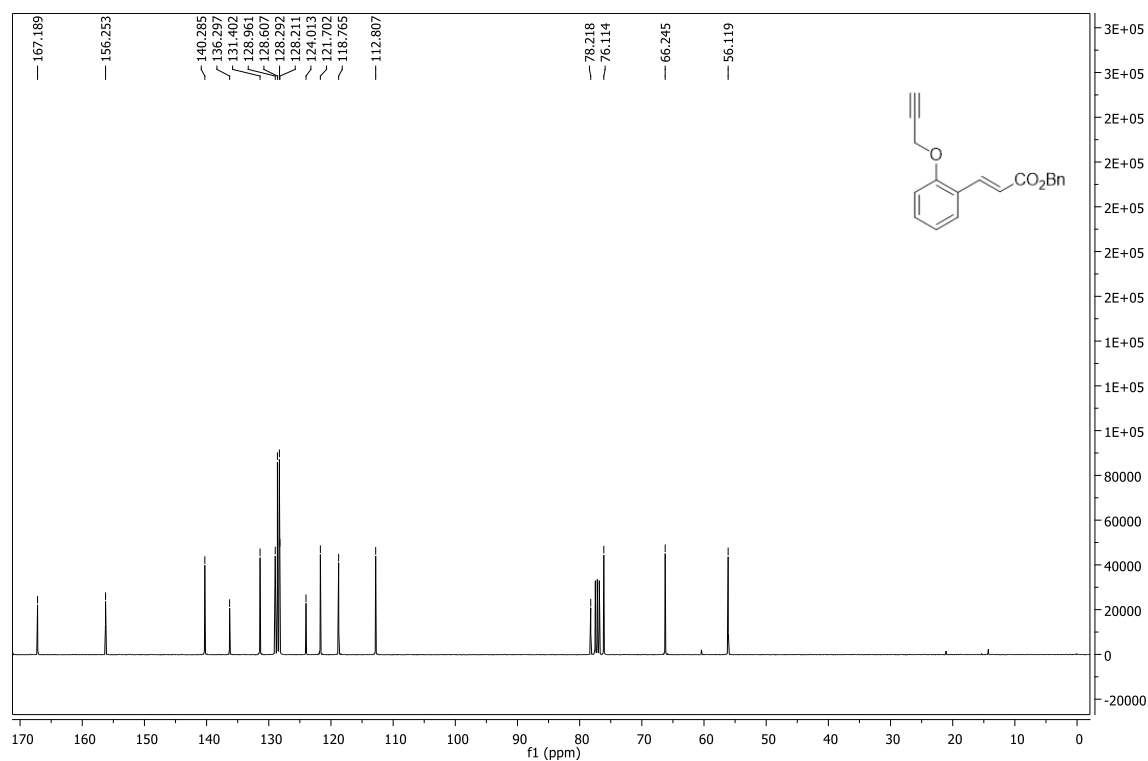


**Figure S14.** <sup>13</sup>C NMR spectrum of compound **13b**.

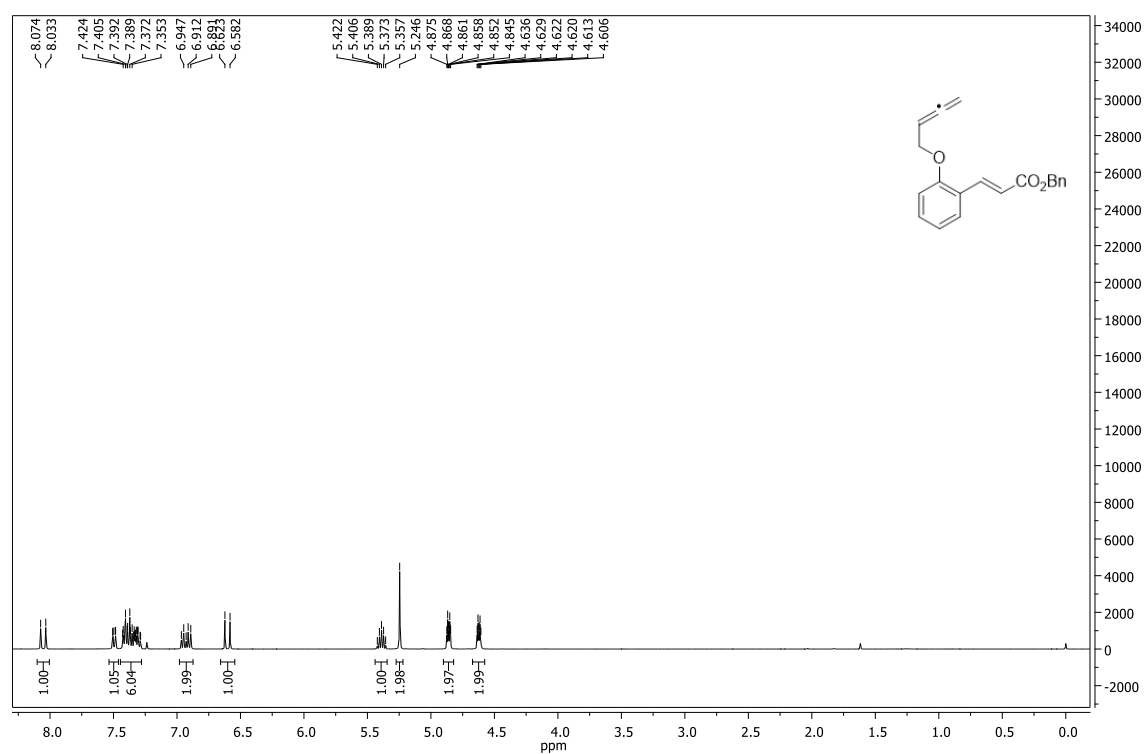


**Figure S15.** <sup>1</sup>H NMR spectrum of compound **16**.

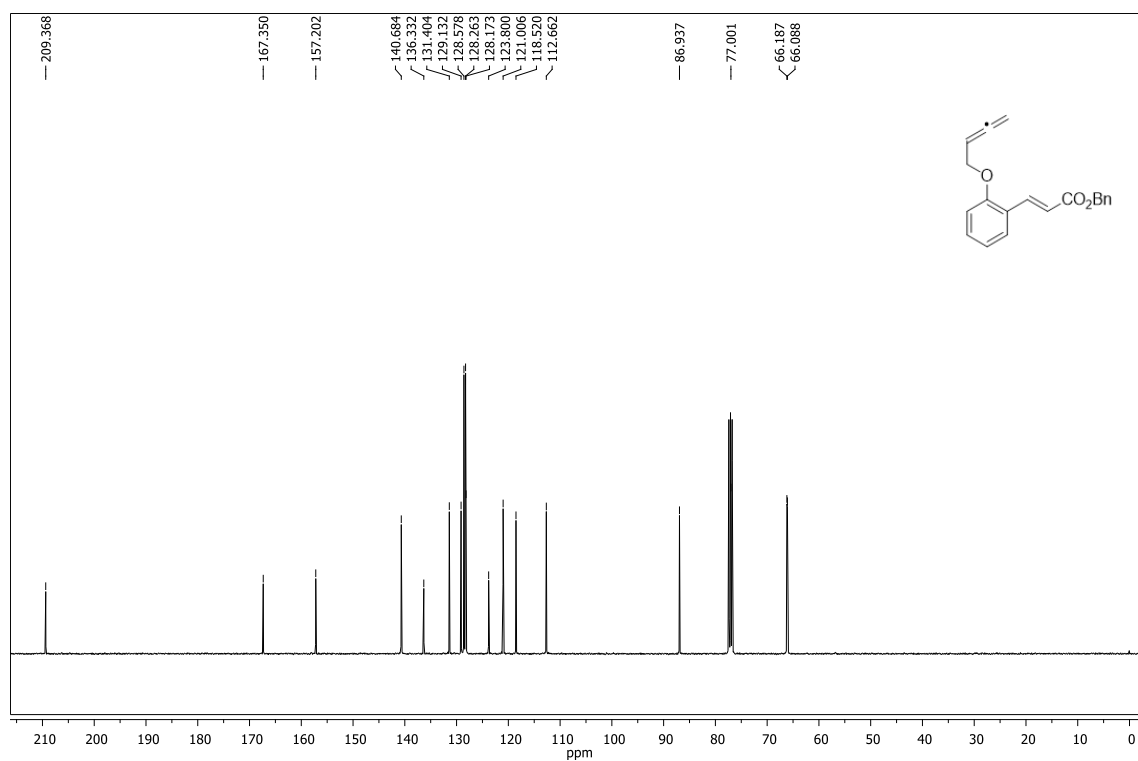




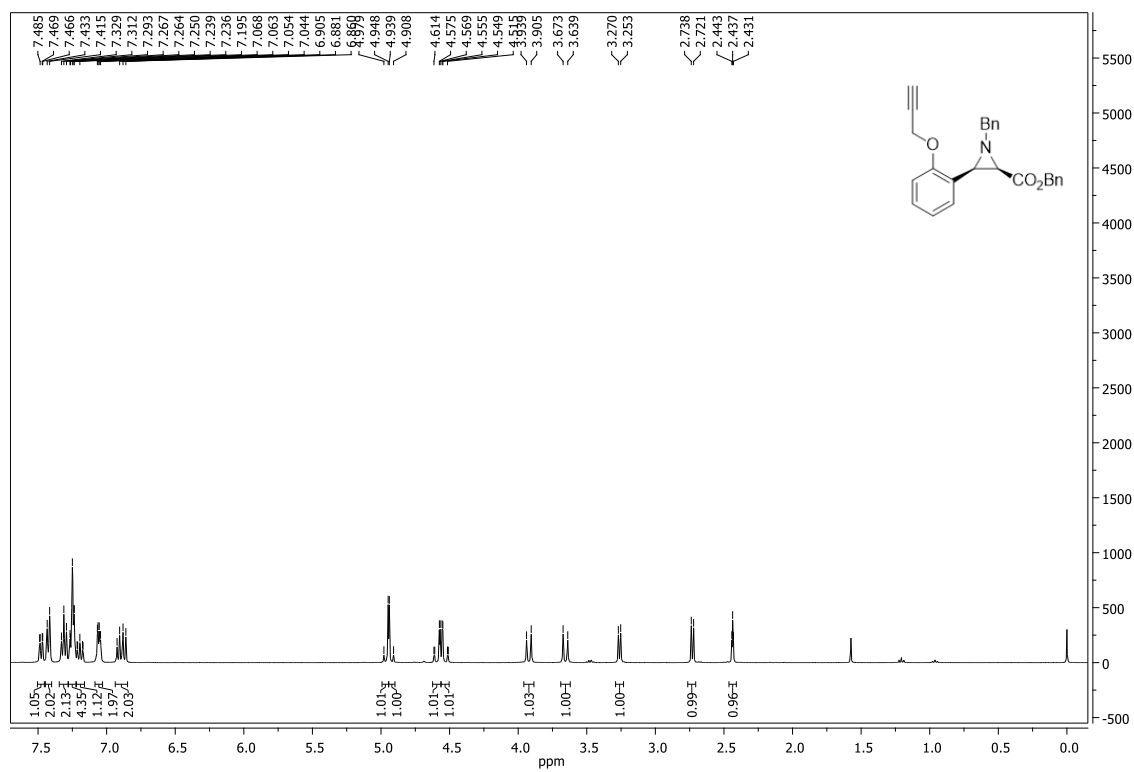
**Figure S18.** <sup>13</sup>C NMR spectrum of compound 17.



**Figure S19.** <sup>1</sup>H NMR spectrum of compound 18.



**Figure S20.** <sup>13</sup>C NMR spectrum of compound **18**.



**Figure S21.** <sup>1</sup>H NMR spectrum of compound **19**.

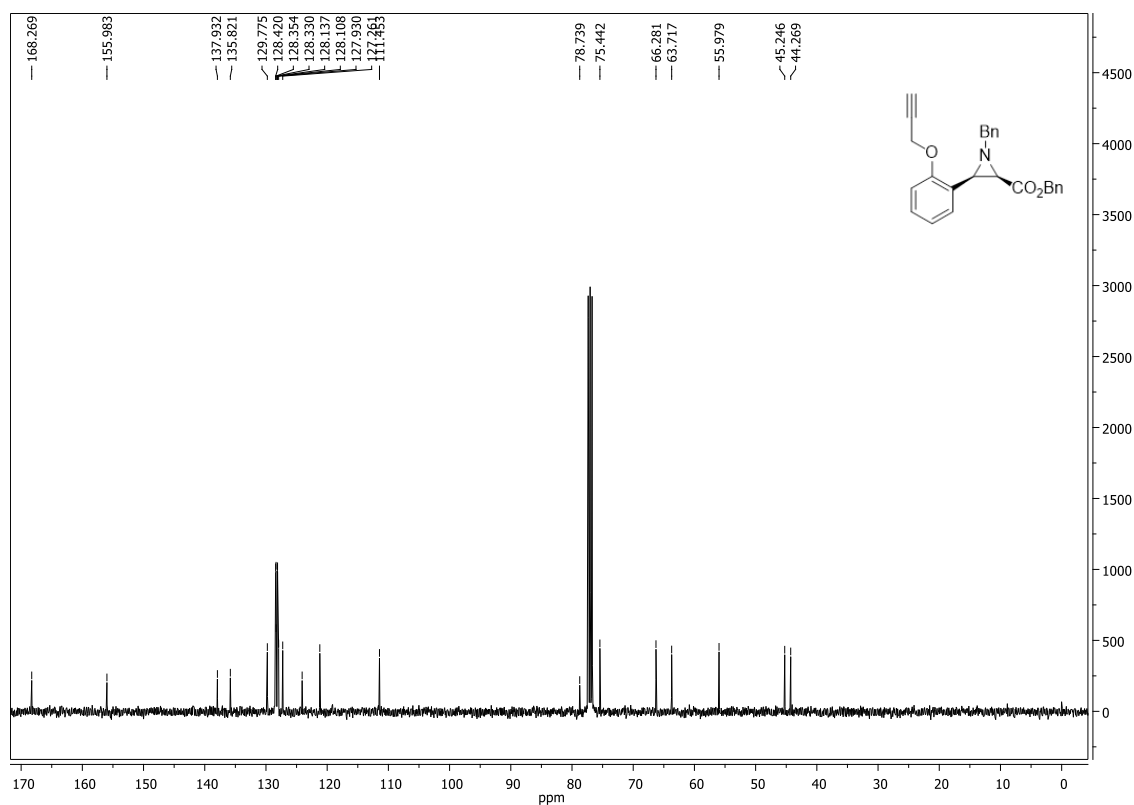


Figure S22. <sup>13</sup>C NMR spectrum of compound 19.

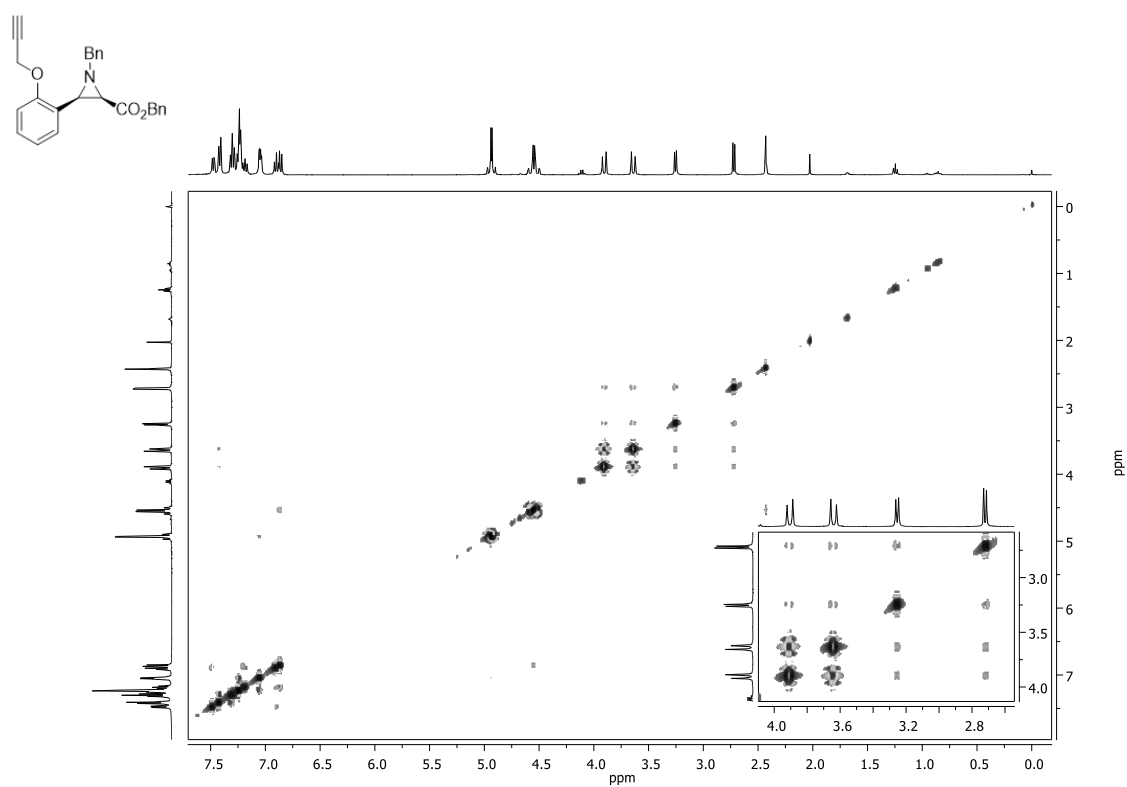


Figure S23. NOESY spectrum of compound 19.

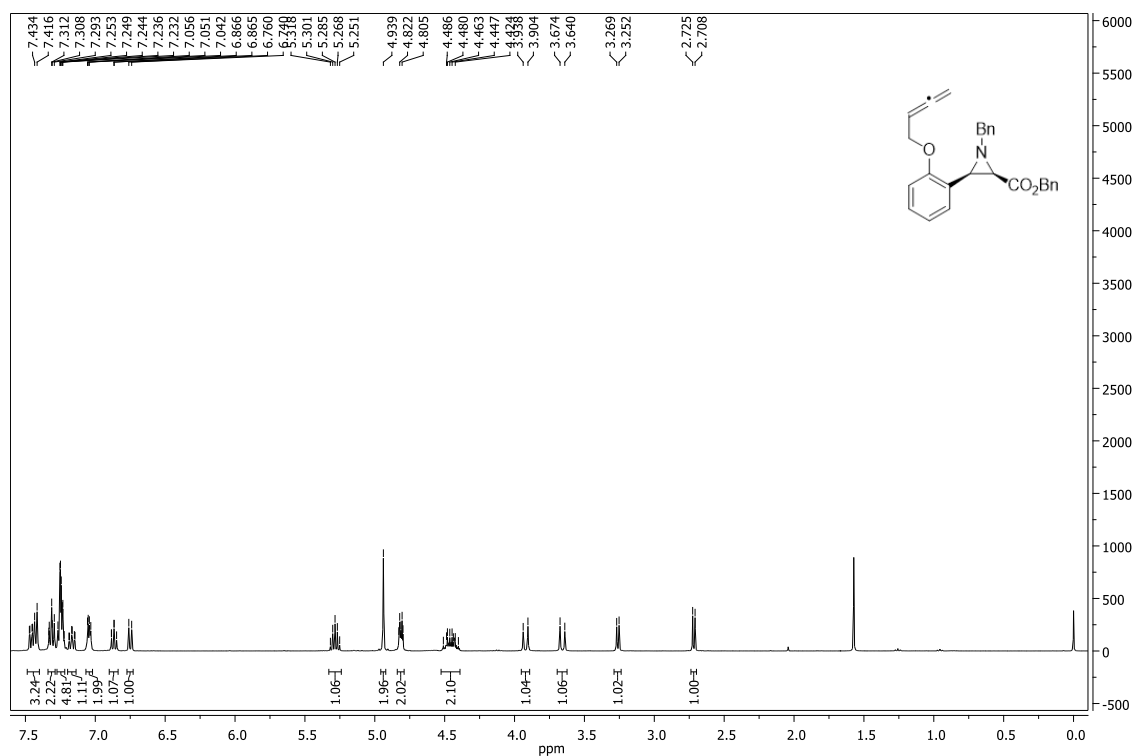


Figure S24.  $^1\text{H}$  NMR spectrum of compound 20.

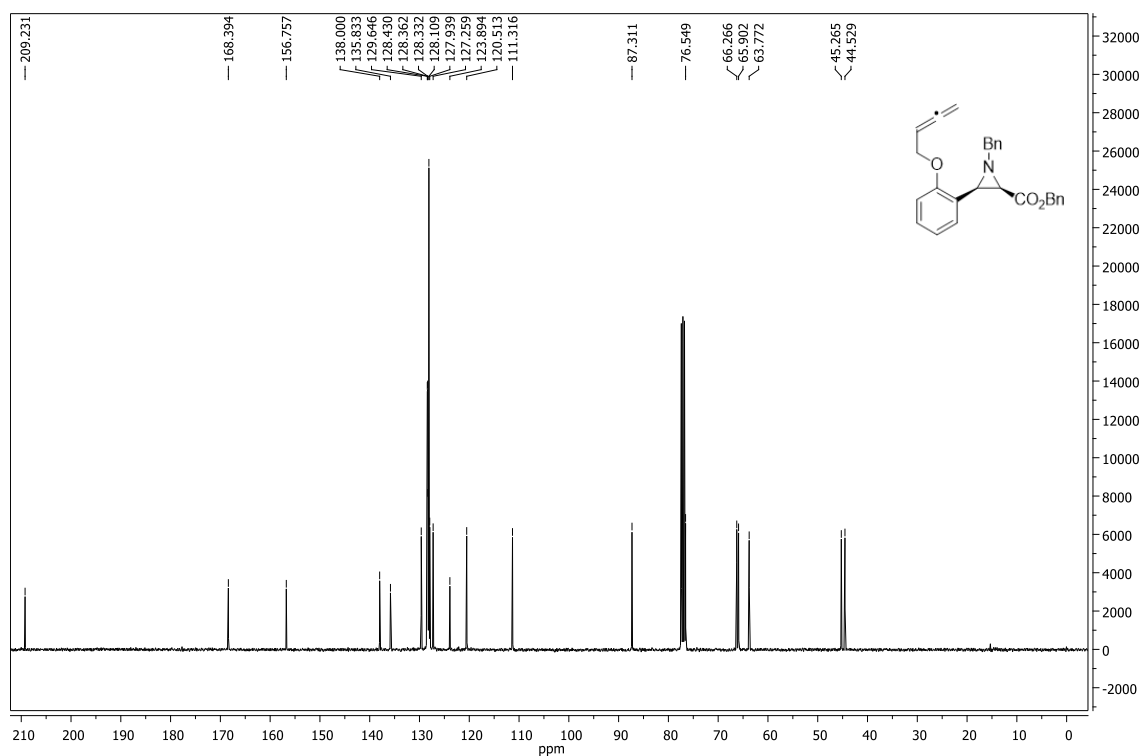
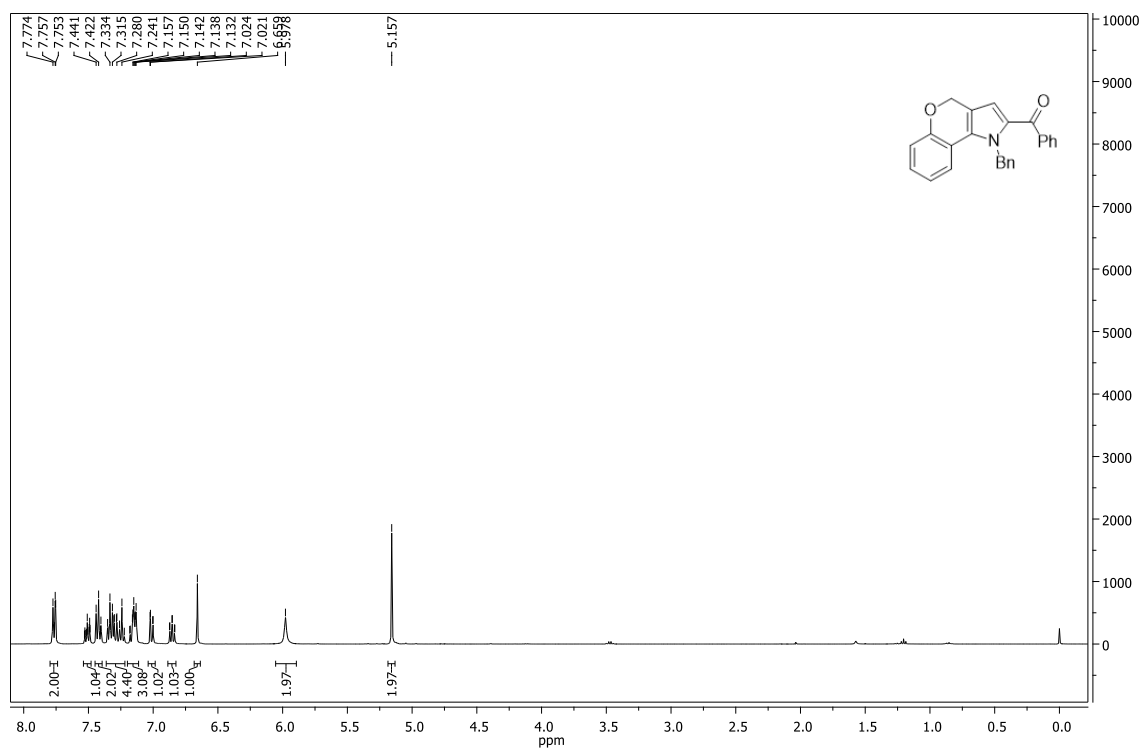
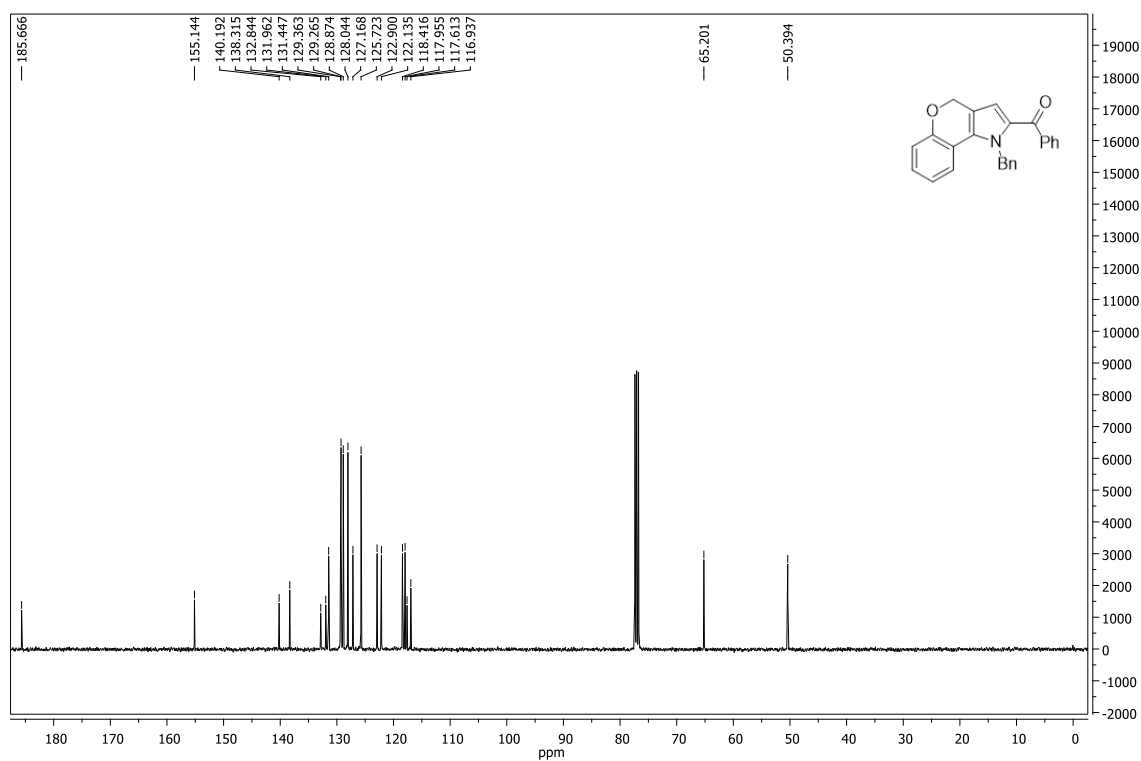


Figure S25.  $^{13}\text{C}$  NMR spectrum of compound 20.





**Figure S26.** <sup>1</sup>H NMR spectrum of compound **23**.



**Figure S27.** <sup>13</sup>C NMR spectrum of compound **23**.

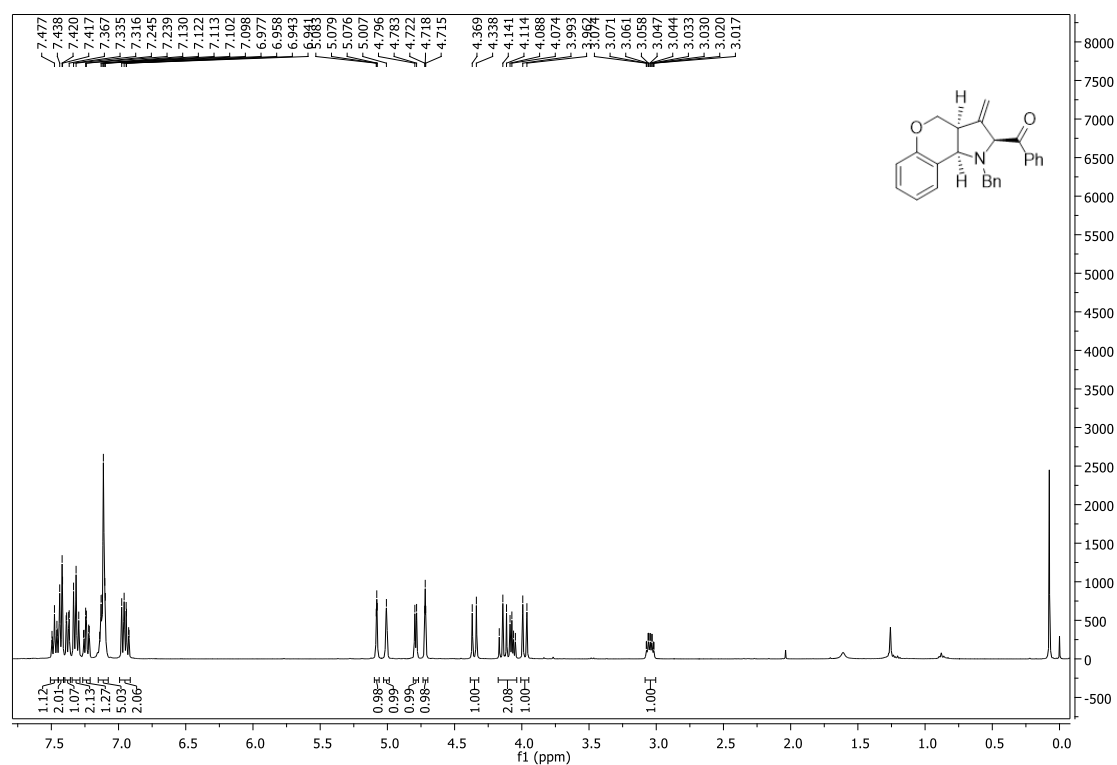


Figure S28.  $^1\text{H}$  NMR spectrum of compound 24.

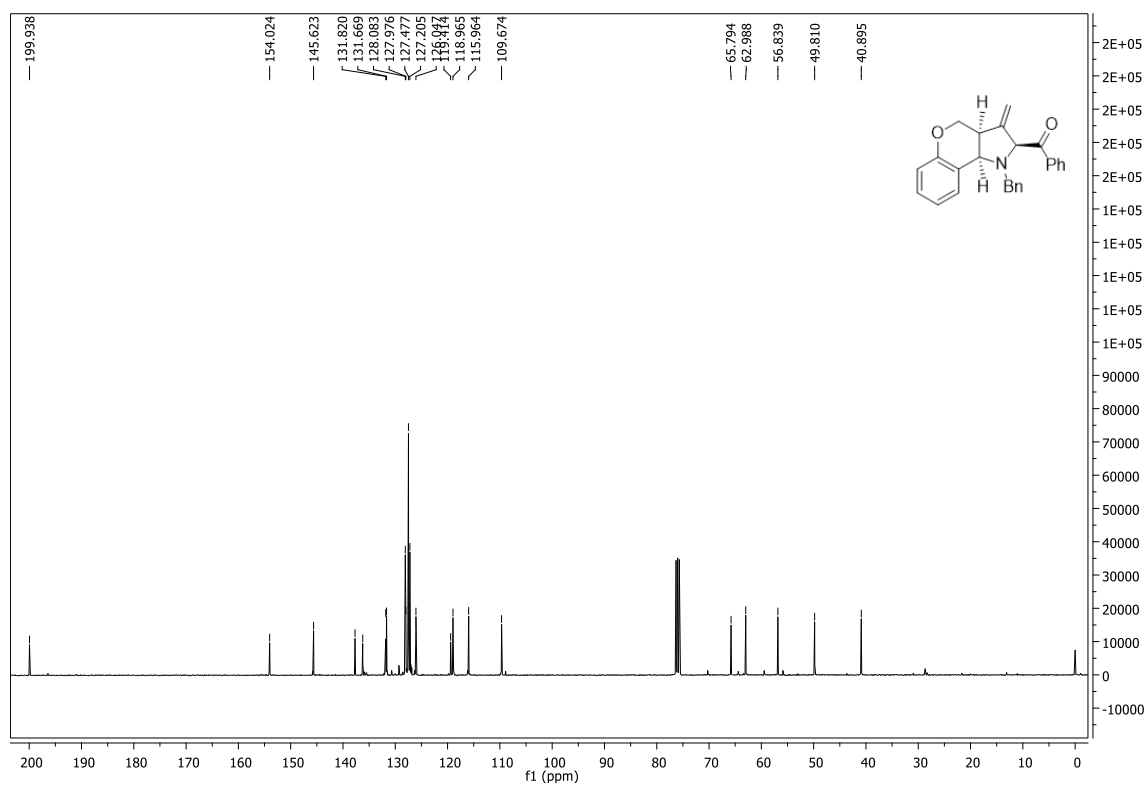


Figure S29.  $^{13}\text{C}$  NMR spectrum of compound 24.

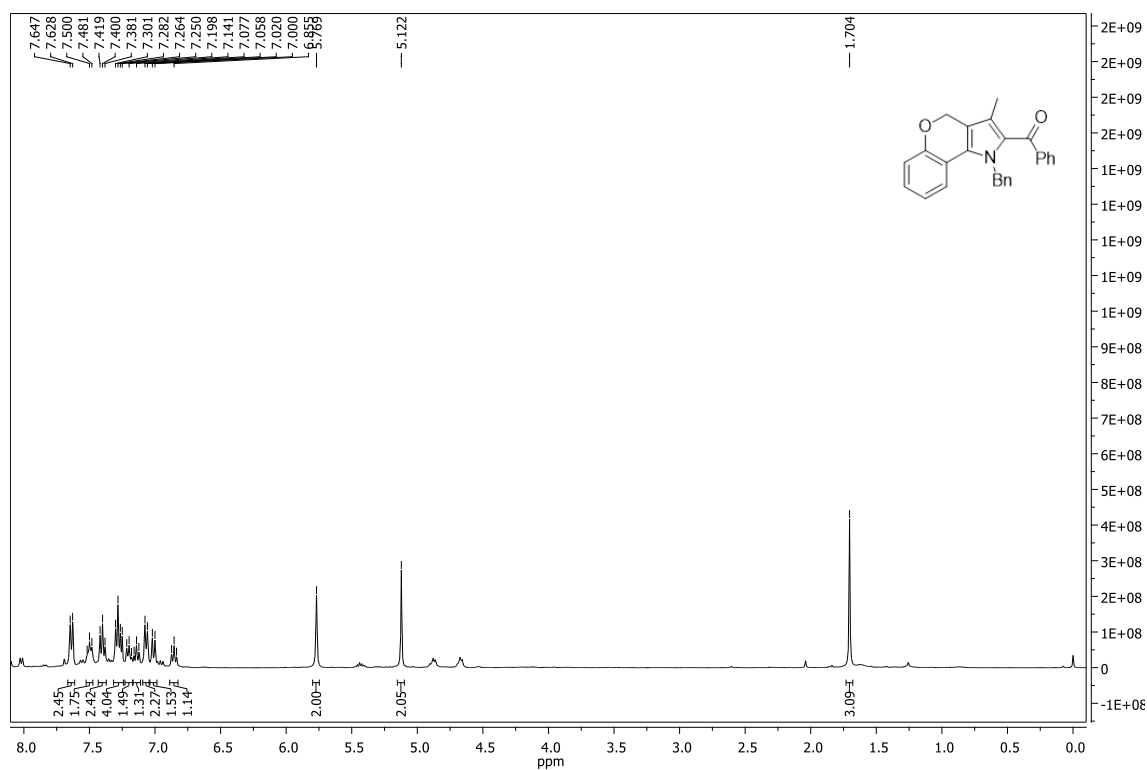


Figure S30. <sup>1</sup>H NMR spectrum of compound 26.

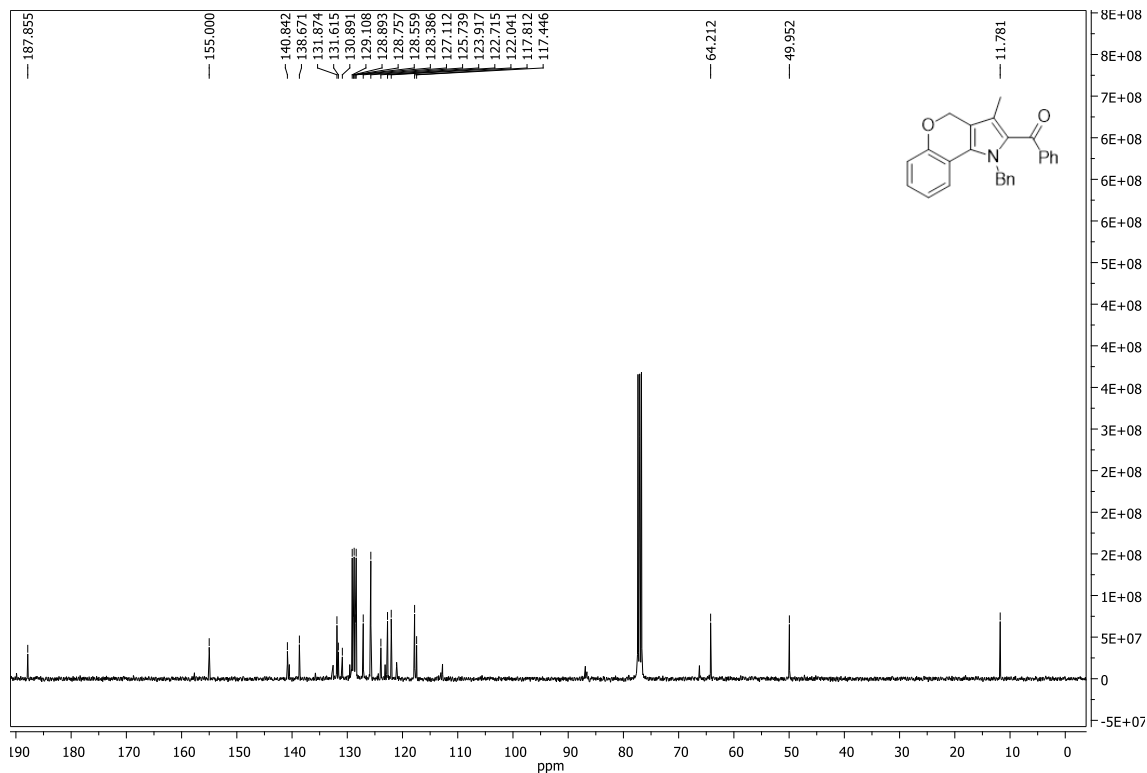


Figure S31. <sup>13</sup>C NMR spectrum of compound 26.

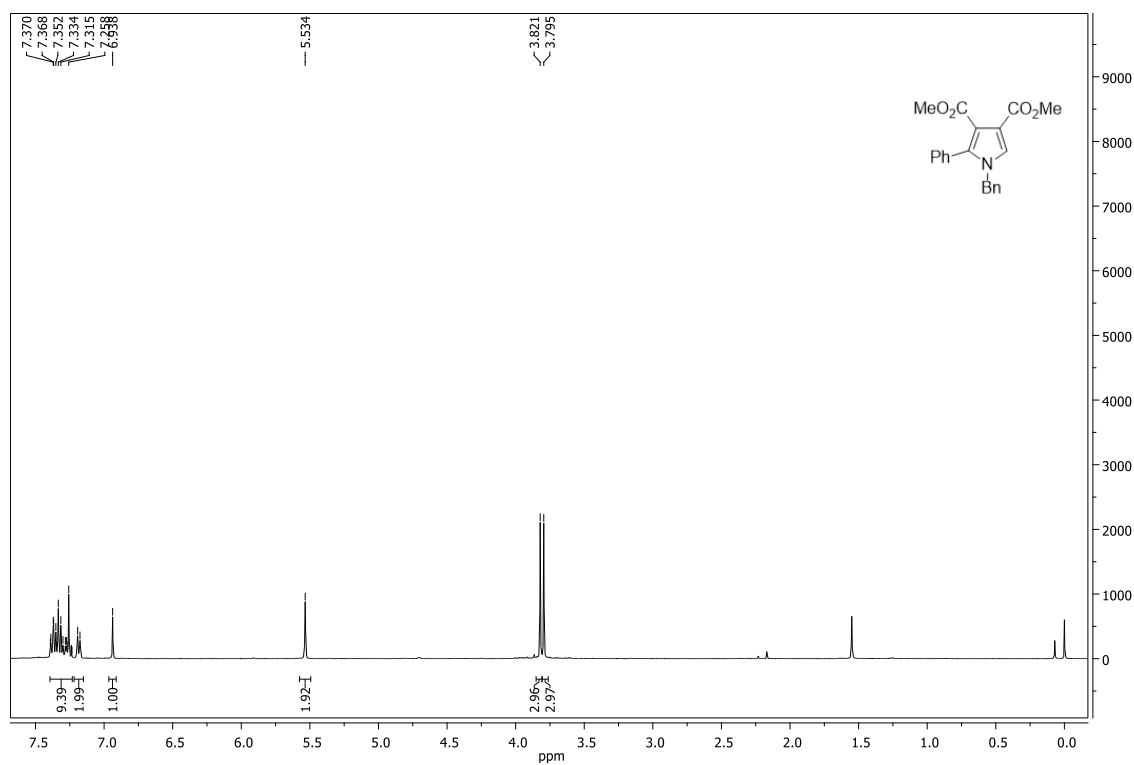


Figure S32. <sup>1</sup>H NMR spectrum of compound 27.

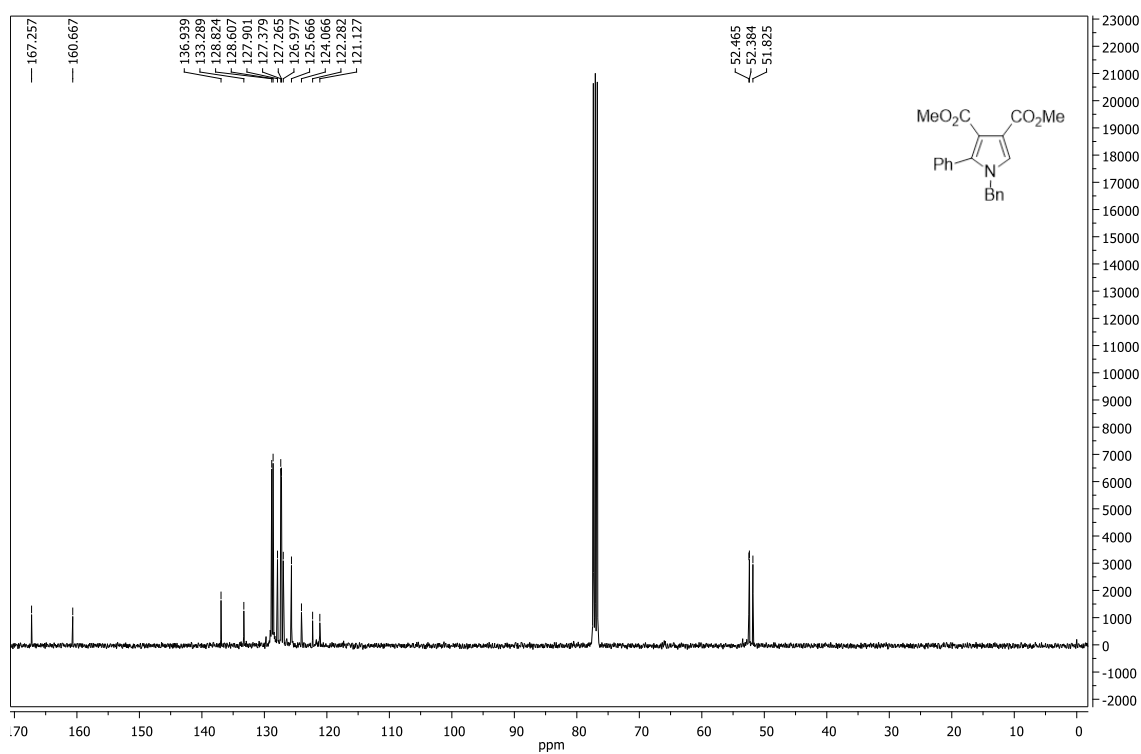
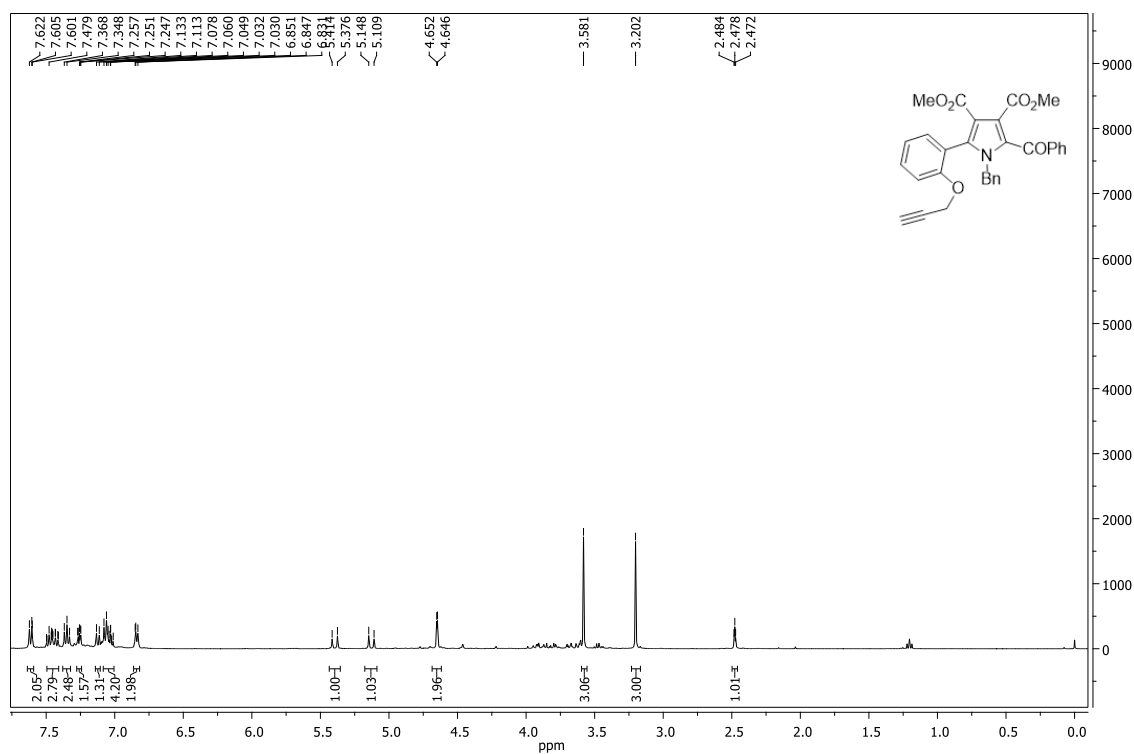
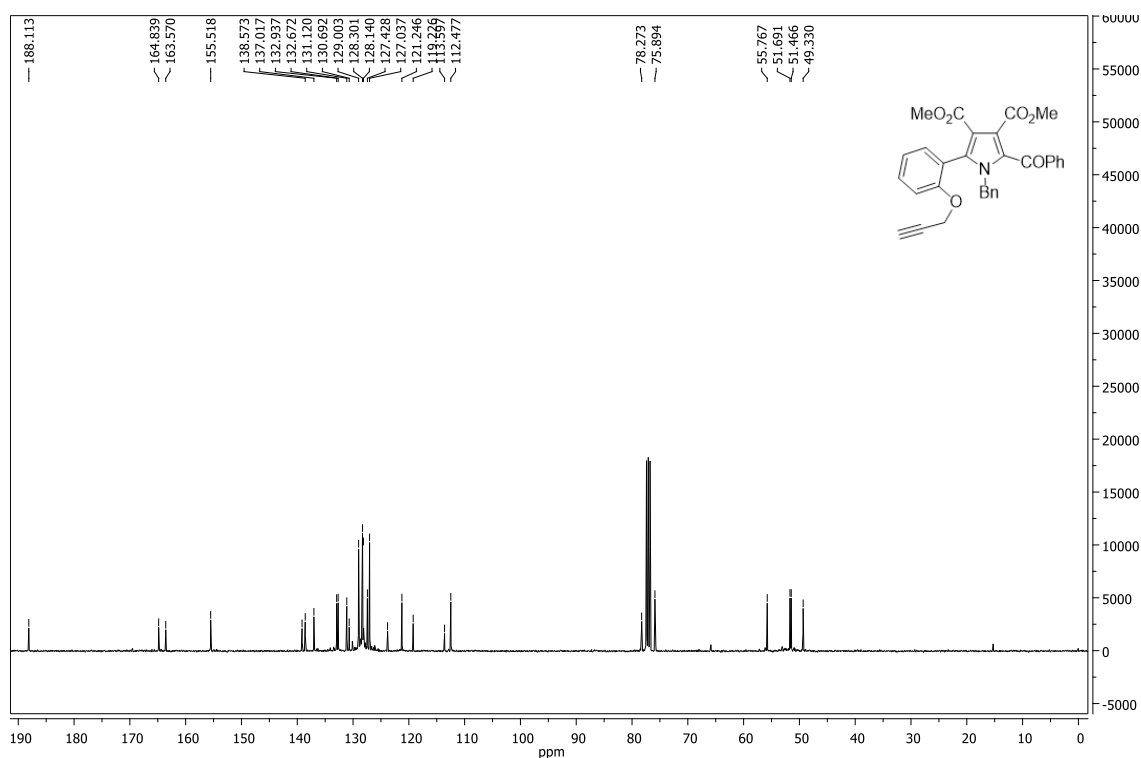


Figure S33. <sup>13</sup>C NMR spectrum of compound 27.



**Figure S34.** <sup>1</sup>H NMR spectrum of compound **28a**.



**Figure S35.** <sup>13</sup>C NMR spectrum of compound **28a**.

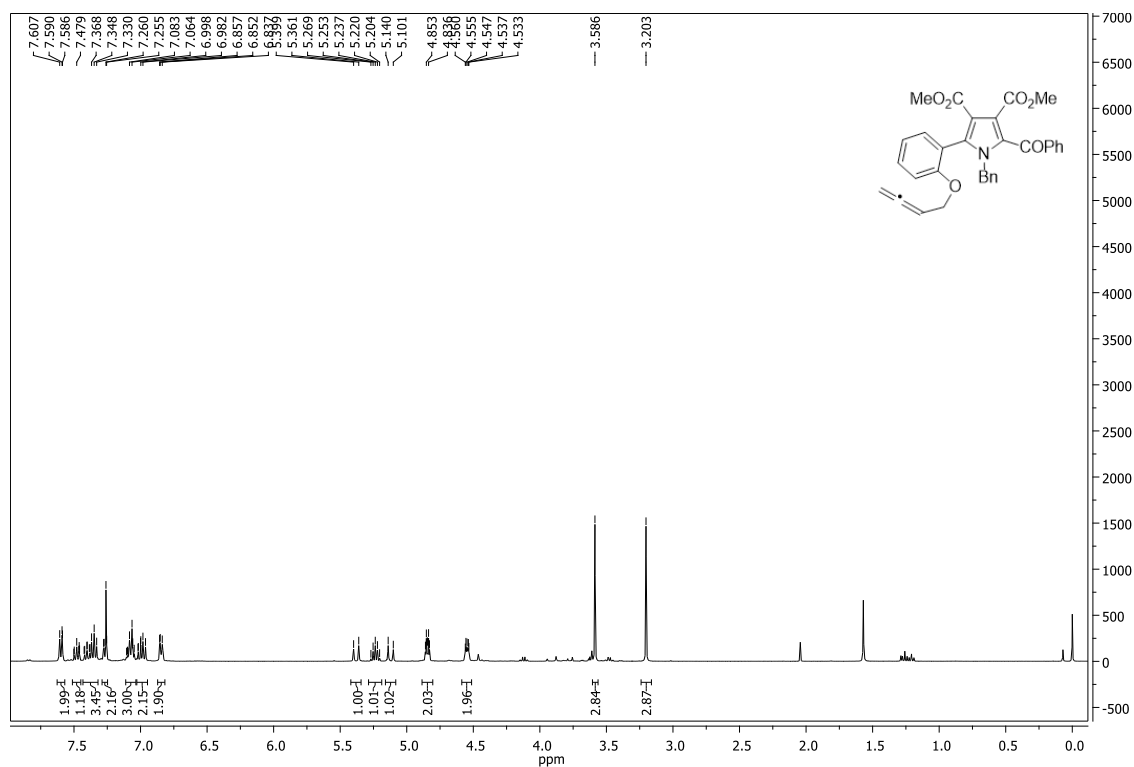


Figure S36. <sup>1</sup>H NMR spectrum of compound **28b**.

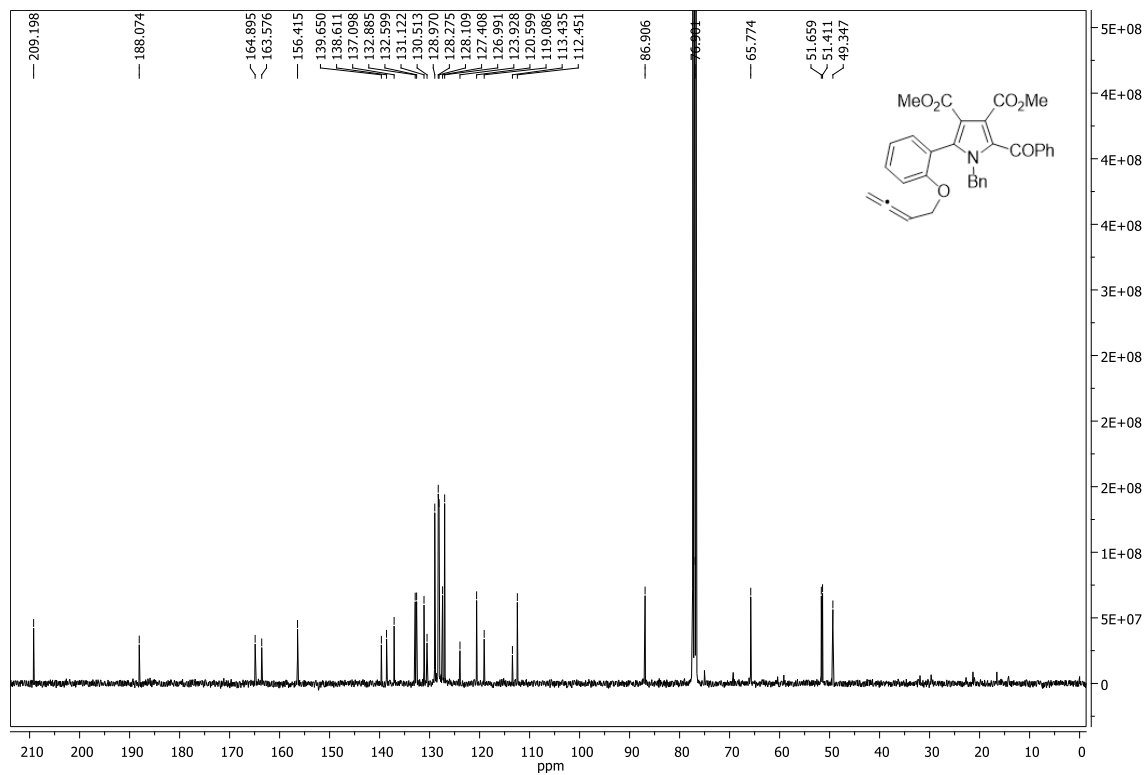
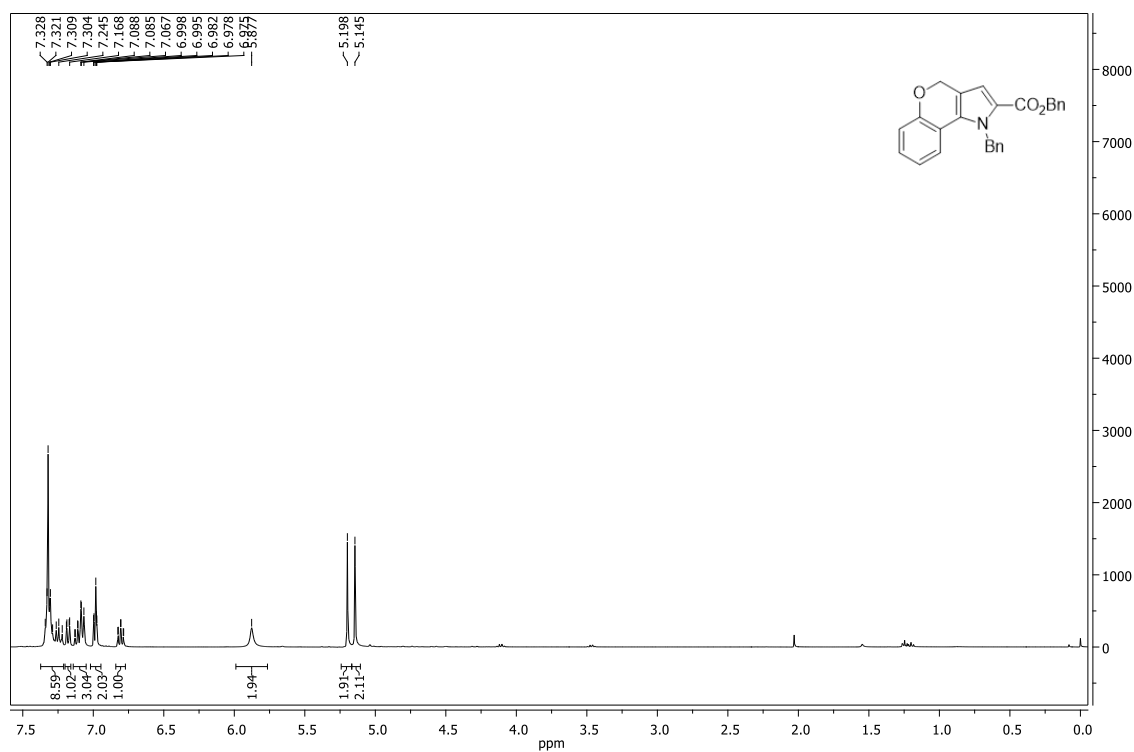
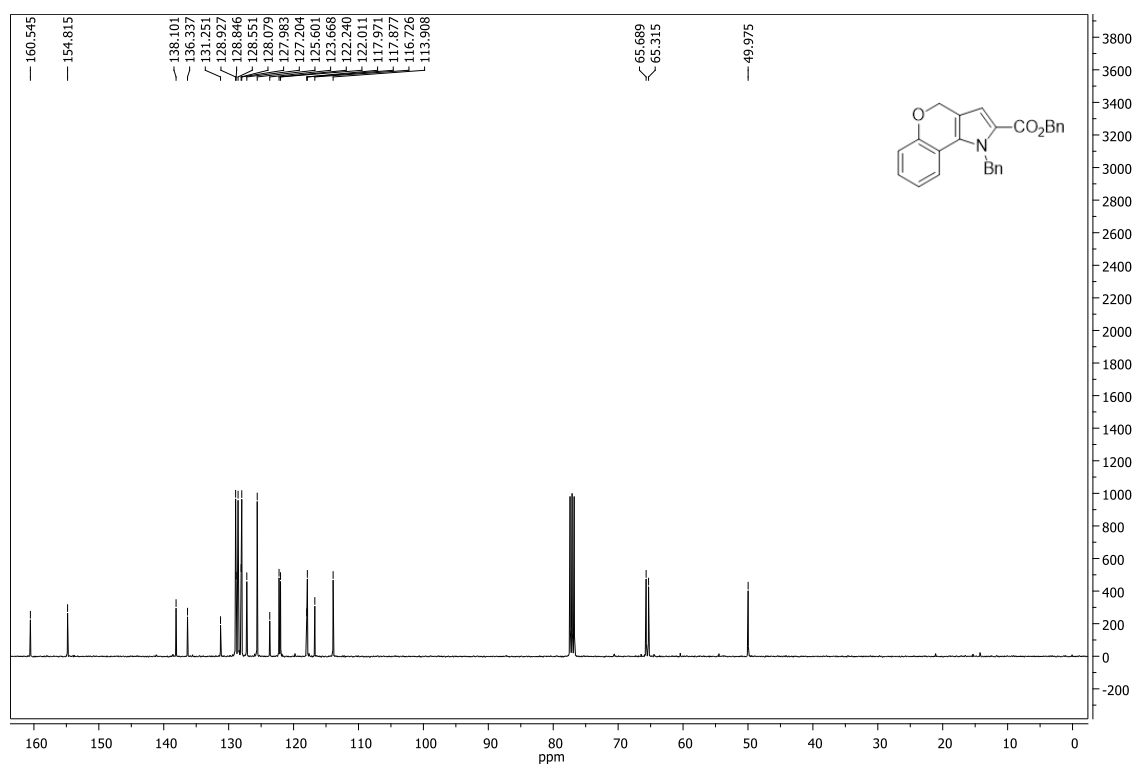


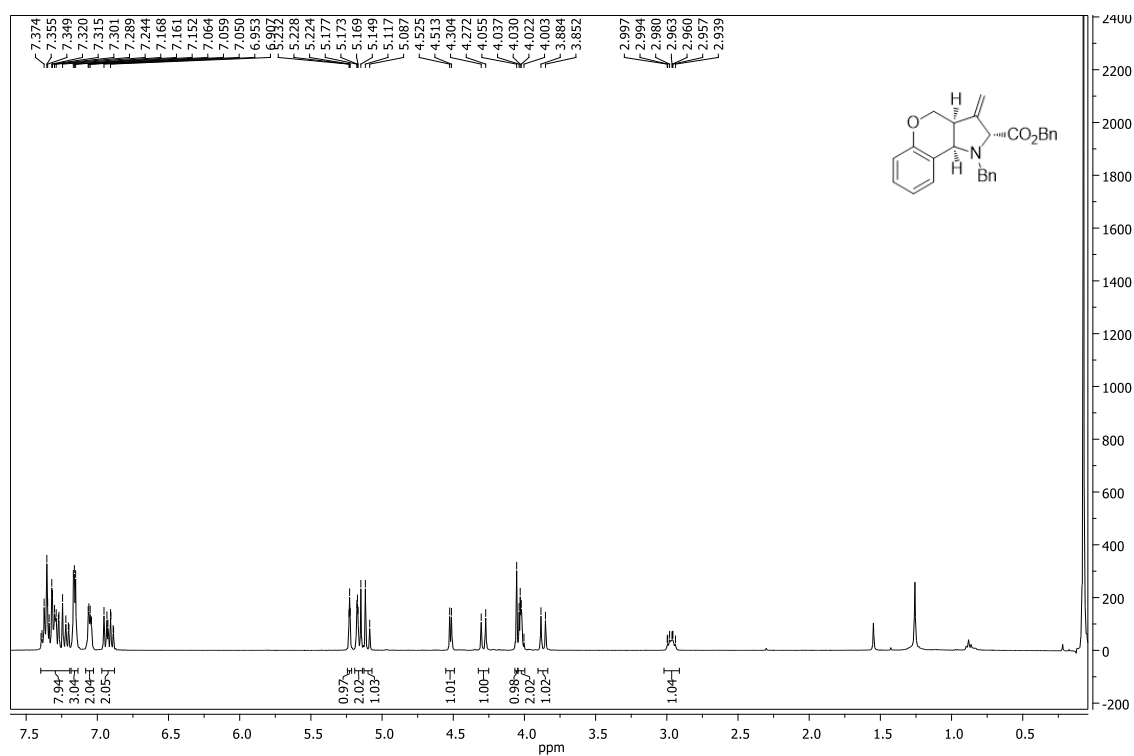
Figure S37. <sup>13</sup>C NMR spectrum of compound **28b**.



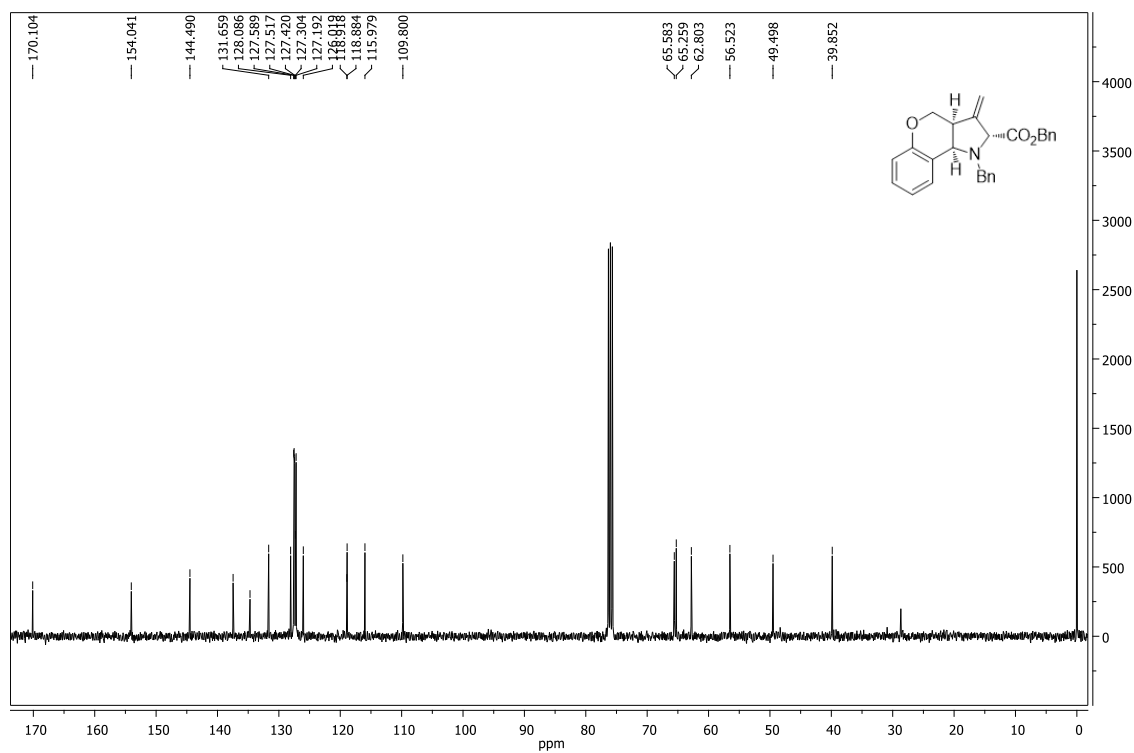
**Figure S38.** <sup>1</sup>H NMR spectrum of compound **30**.



**Figure S39.** <sup>13</sup>C NMR spectrum of compound **30**.



**Figure S40.** <sup>1</sup>H NMR spectrum of compound **31**.



**Figure S41.** <sup>13</sup>C NMR spectrum of compound **31**.