

Supporting Information for

Diastereoselective [4+1] Cycloaddition of Alkenyl Propargyl Acetates with CO

Catalyzed by $[\text{RhCl}(\text{CO})_2]_2$

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I. Analytical Instruments:

High resolution mass spectra were obtained by EI [70-VSE(C)] or ESI (Q-ToF) analysis and the [M] or [MH⁺] was observed.

II. General Data:

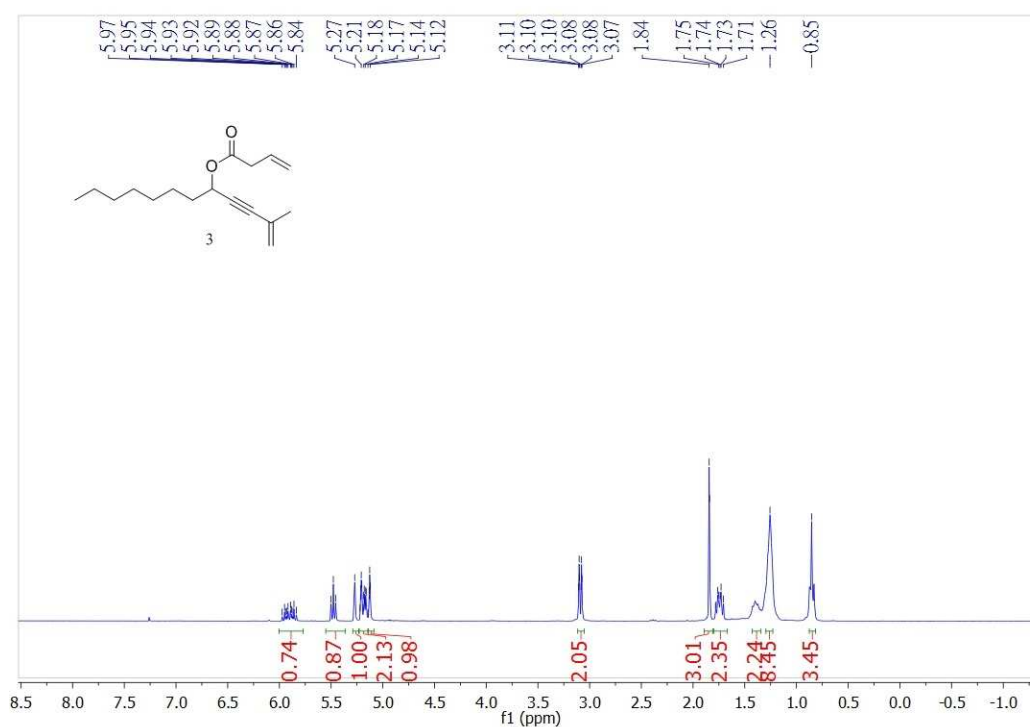
All commercial chemicals were used as received unless otherwise noted.

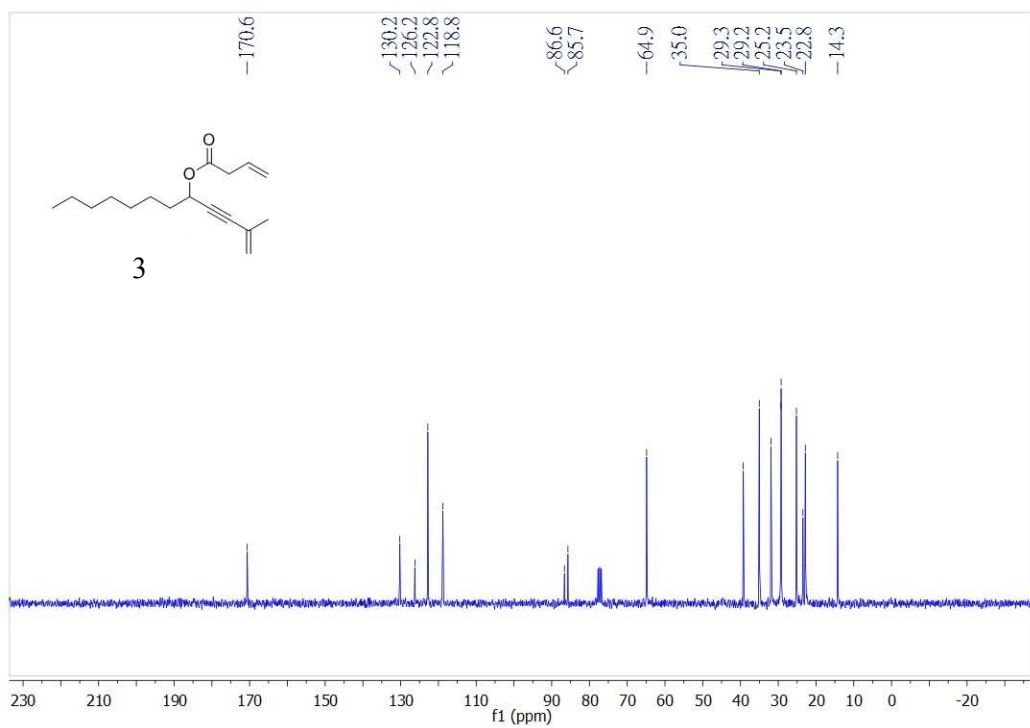
[RhCl(CO)₂]₂ was purchased and stored in a dry nitrogen atmosphere.

THF was distilled over sodium and benzophenone under nitrogen atmosphere. to prepare alkenyl propargylic acetate according to the general method used.

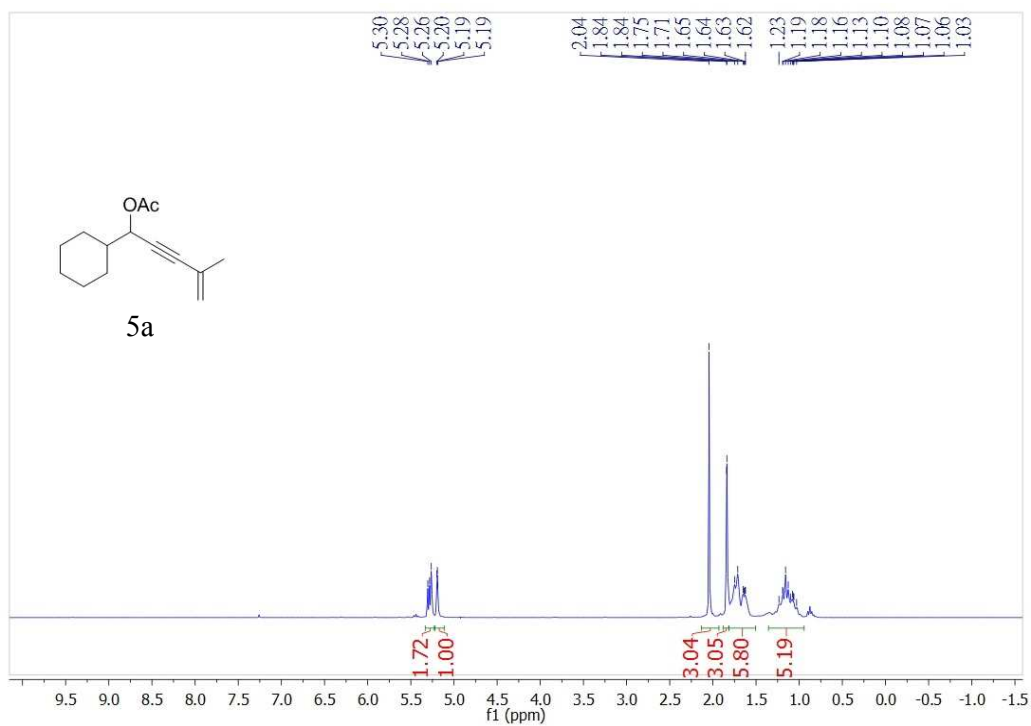
III. ¹H NMR, ¹³C, and 2D NMR Spectra

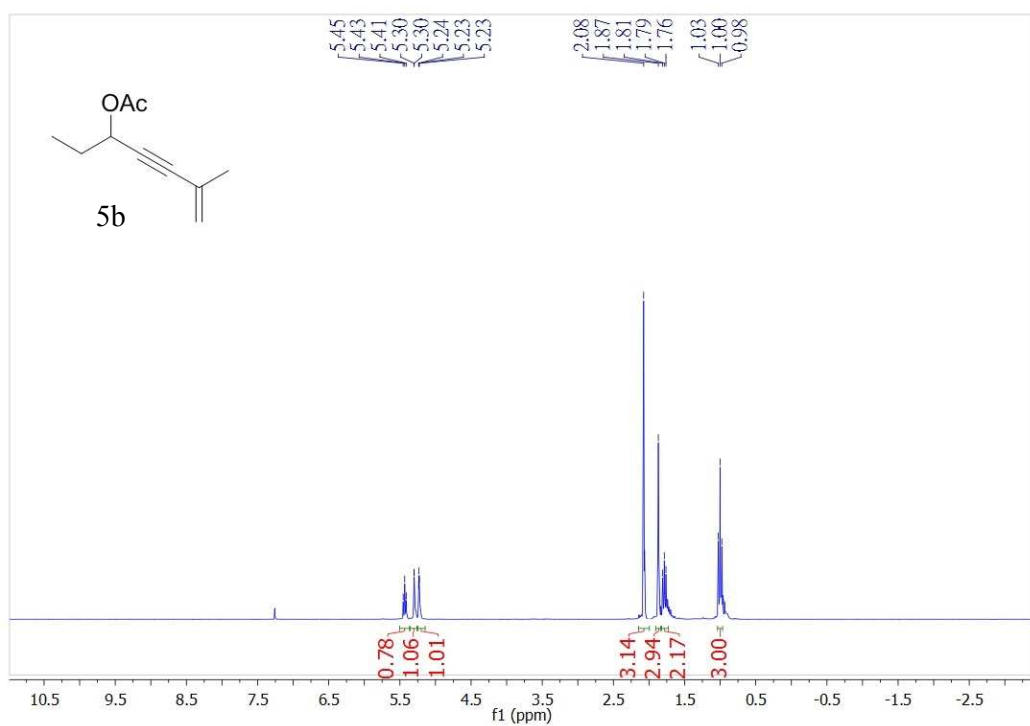
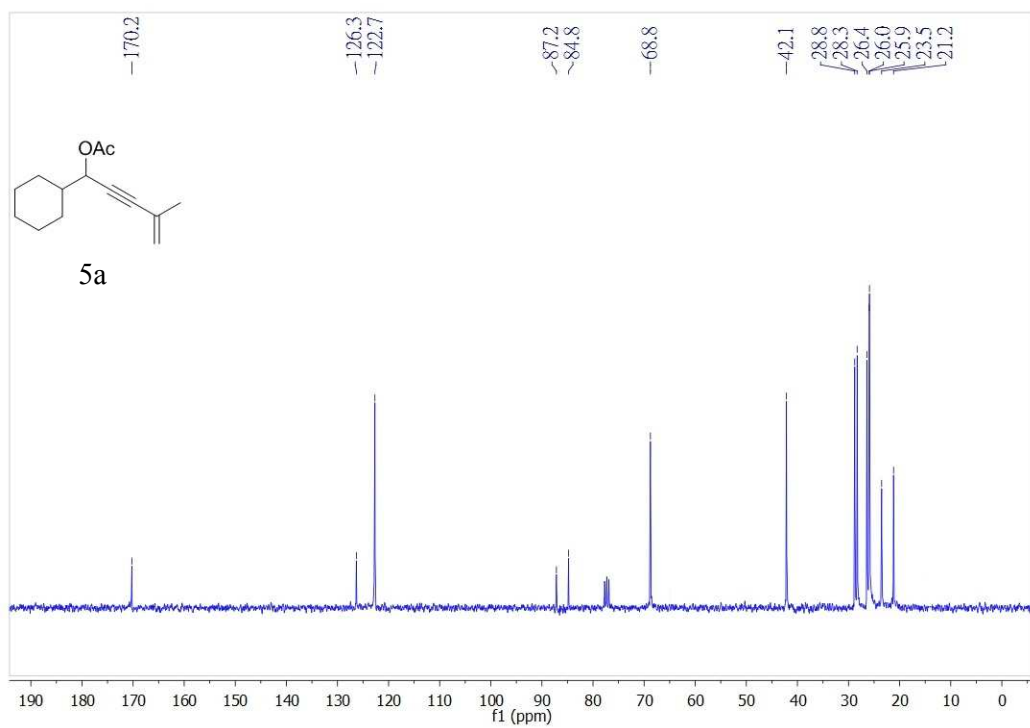
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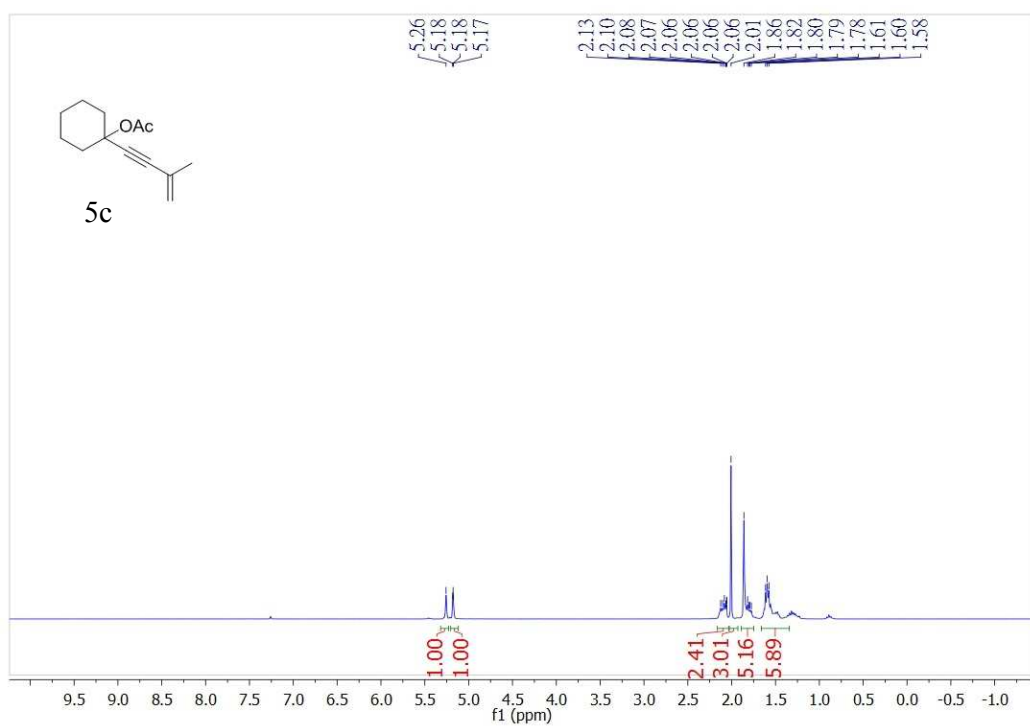
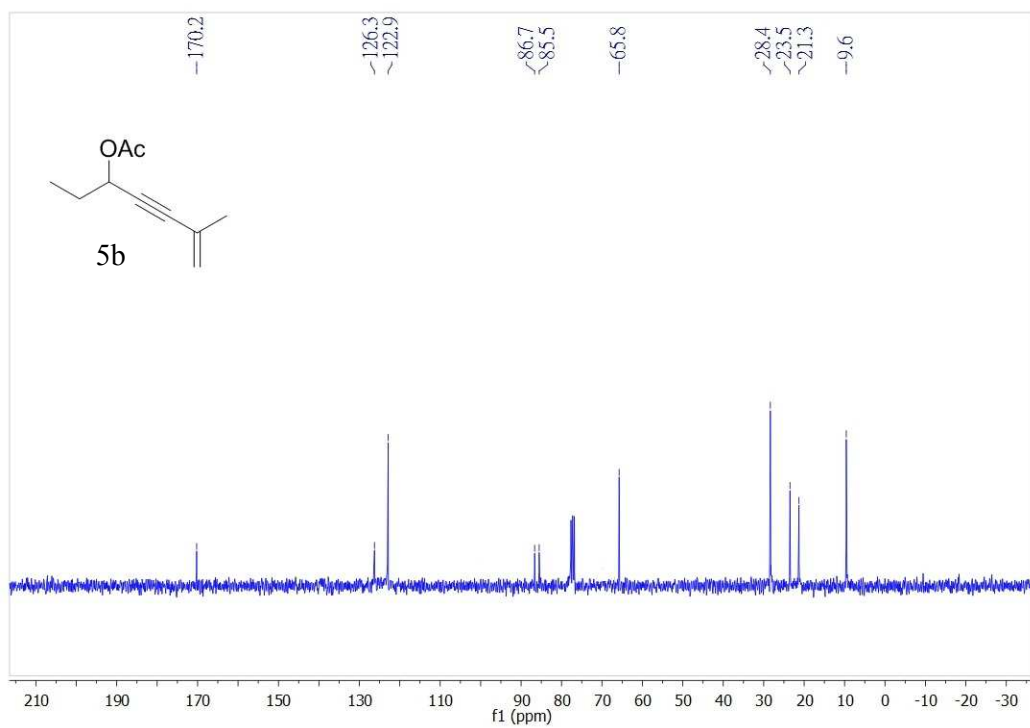


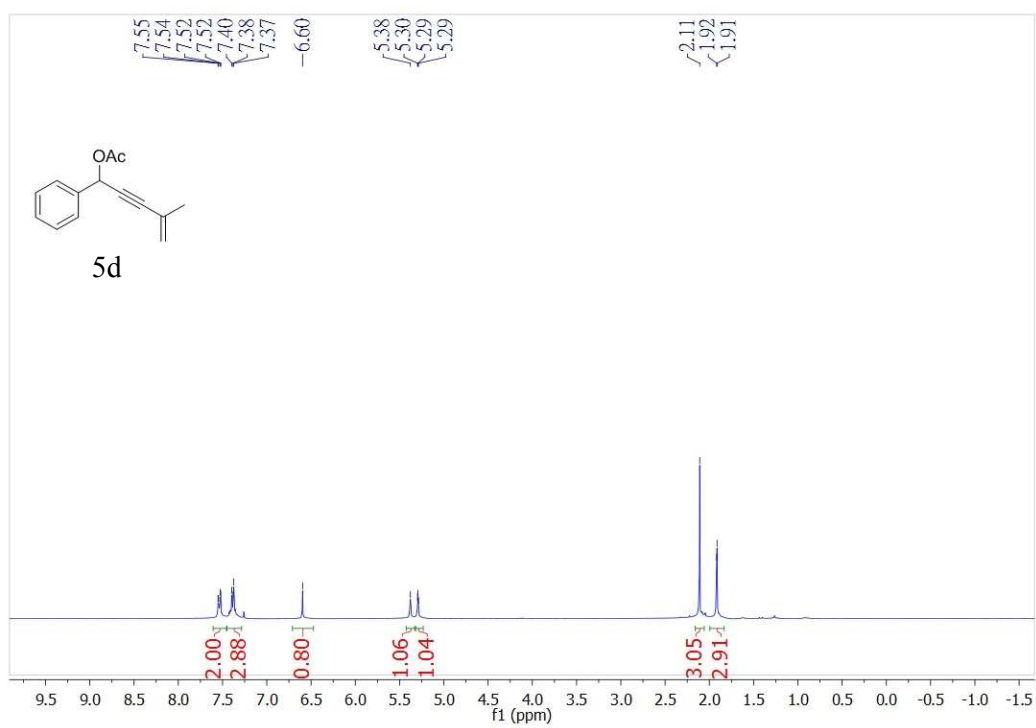
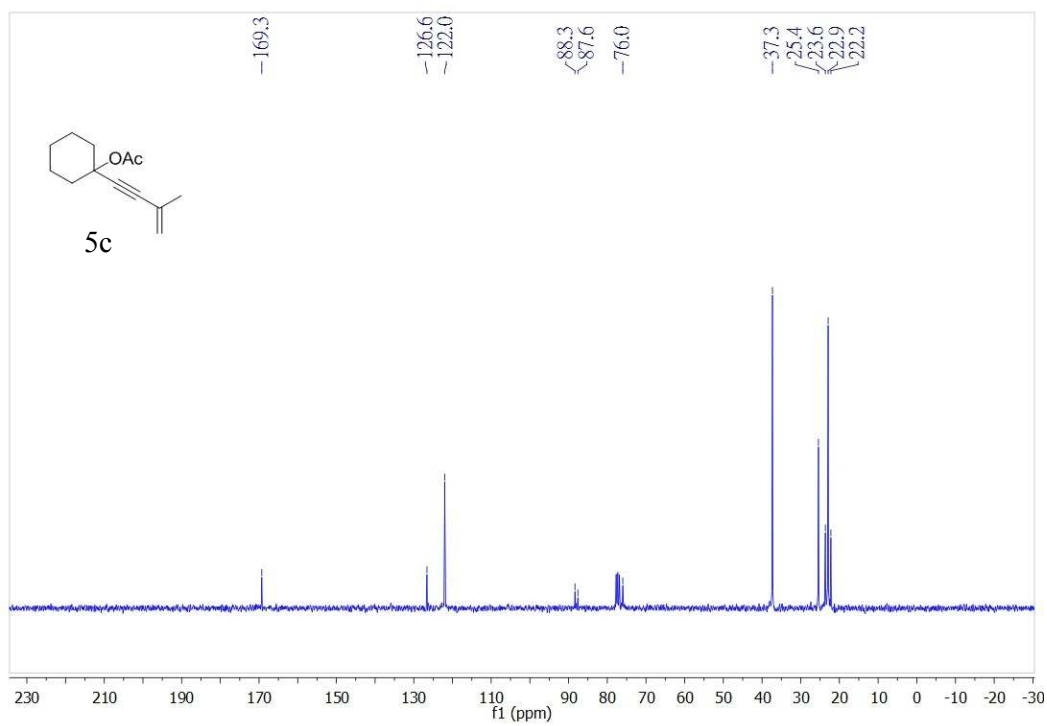


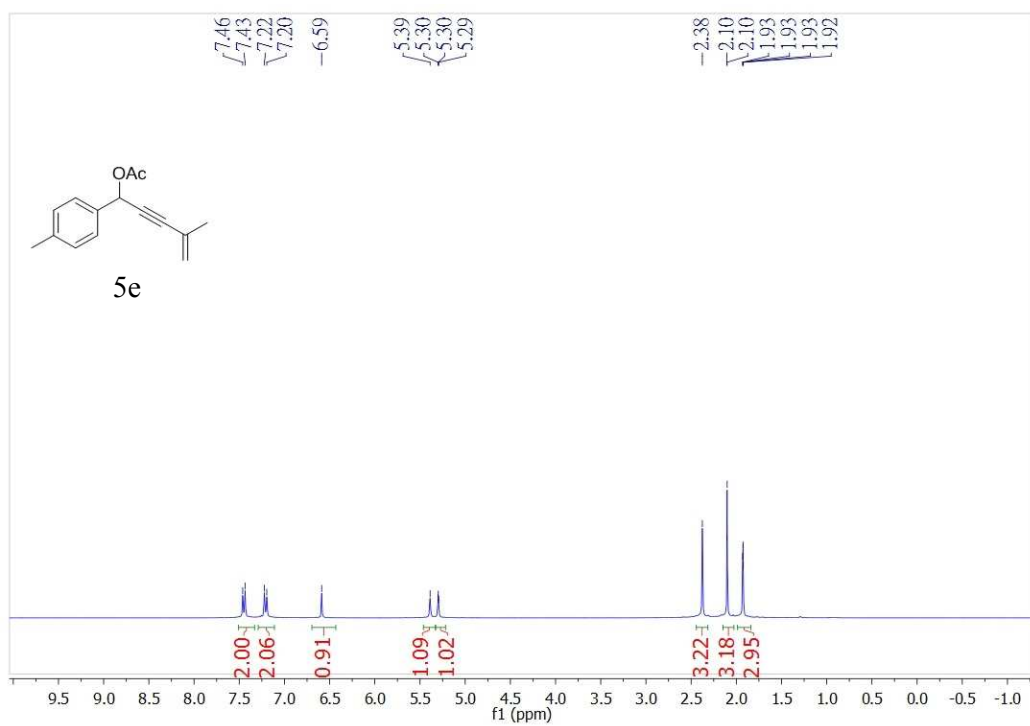
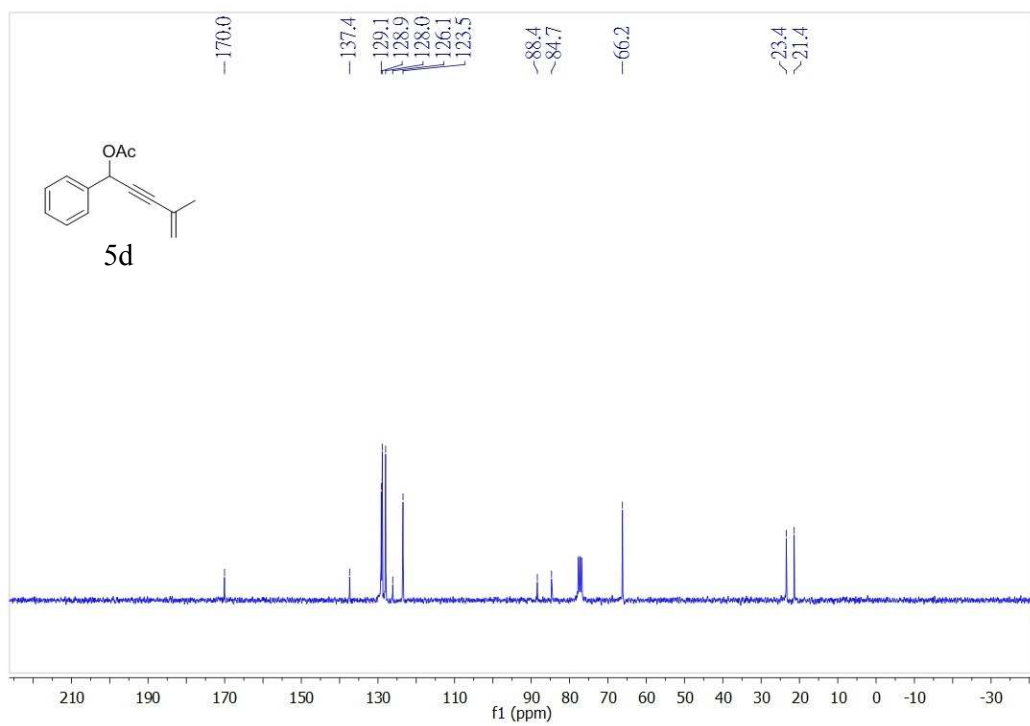
3. Alkenyl Propargylic Acetates **5**

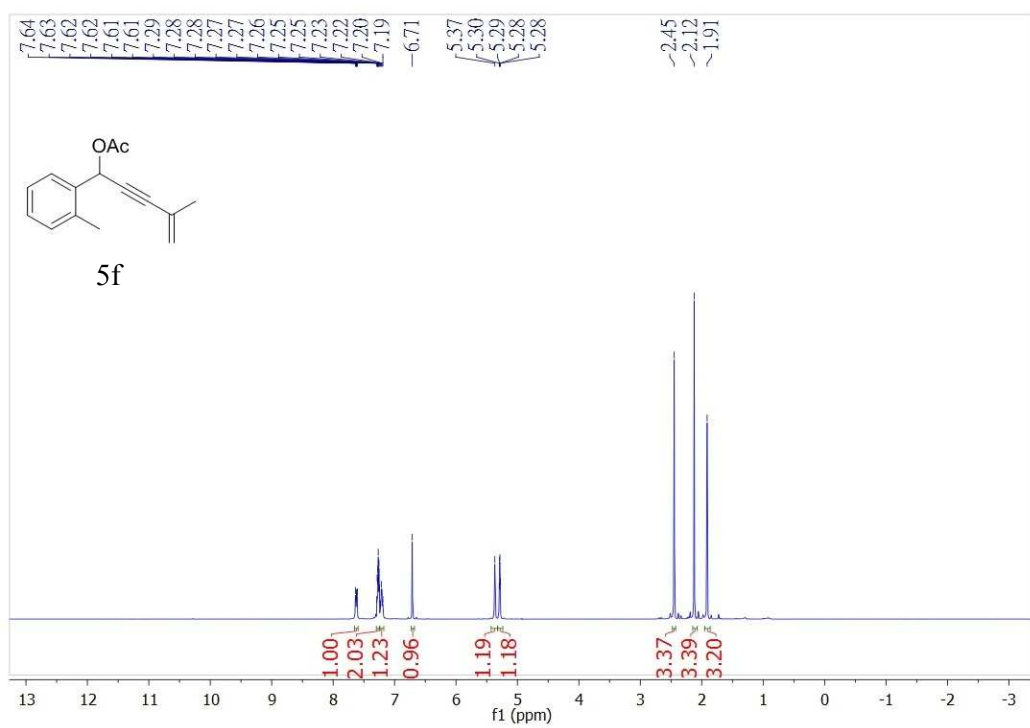
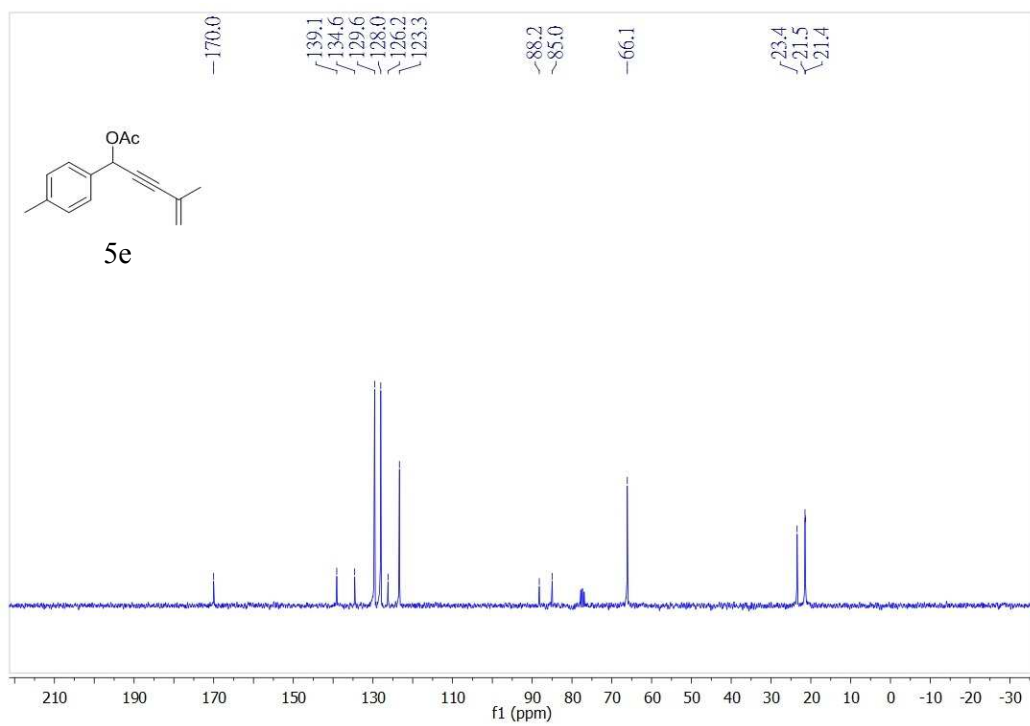


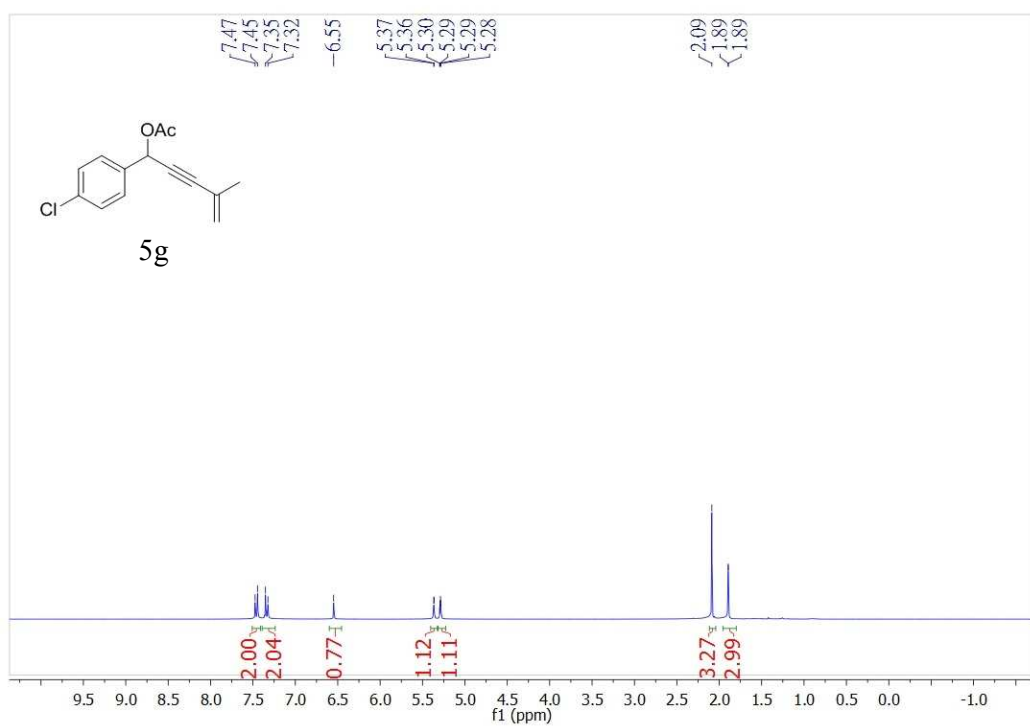
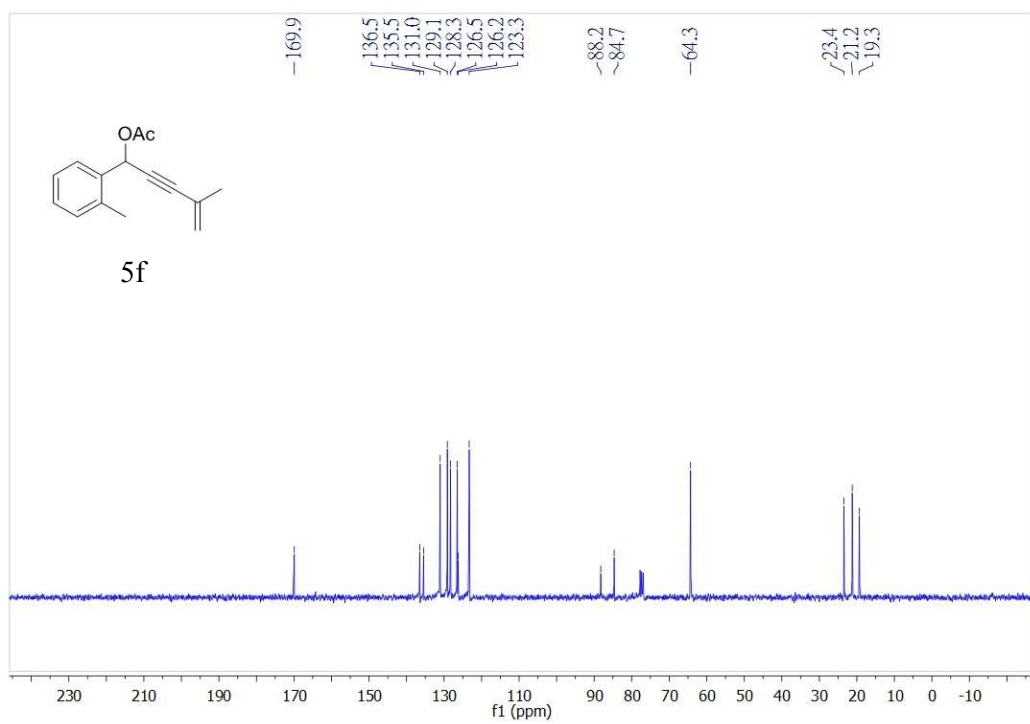


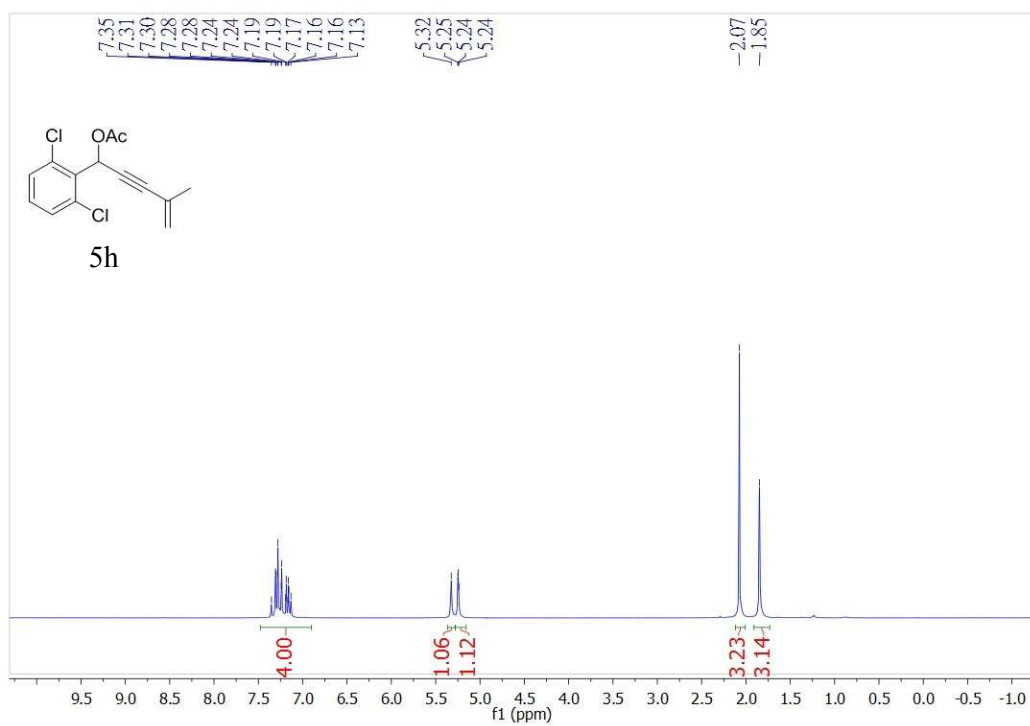
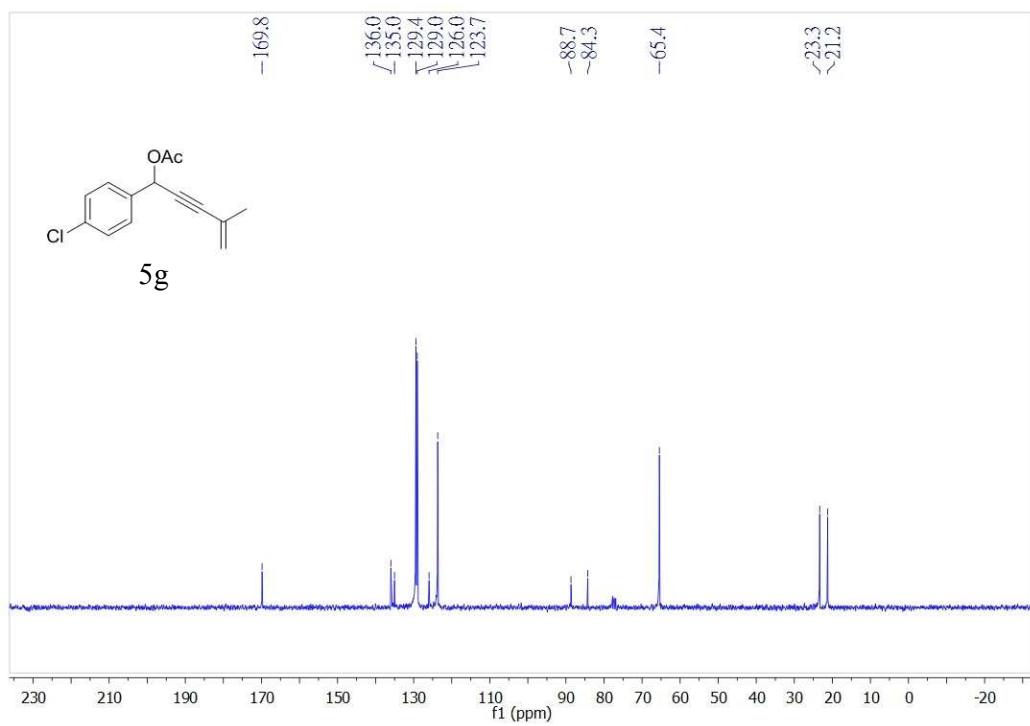


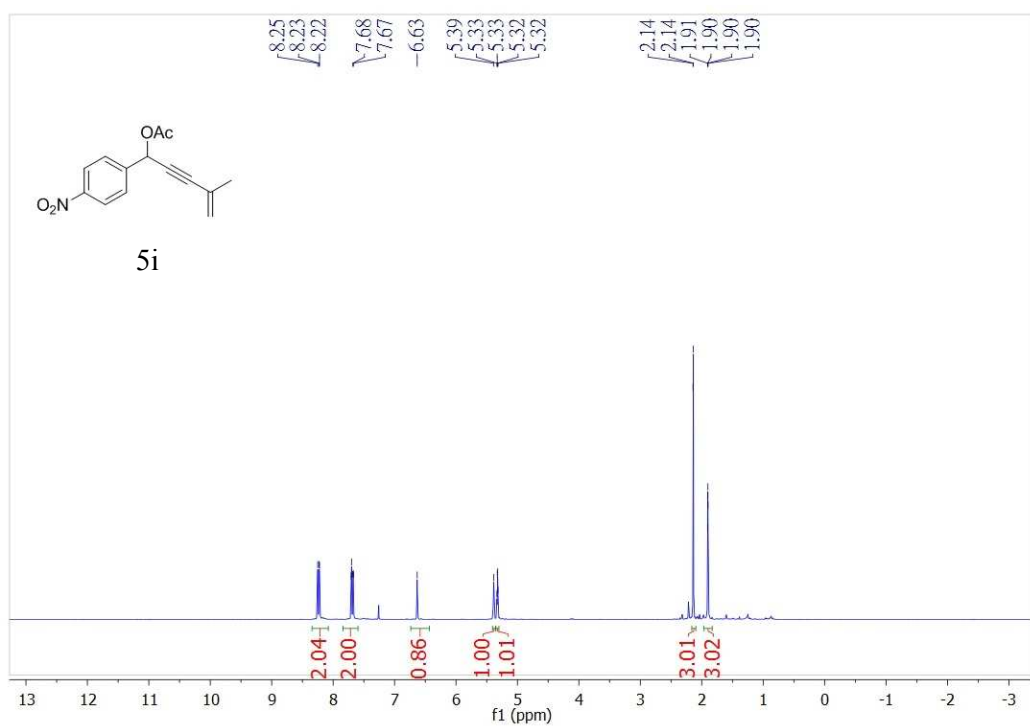
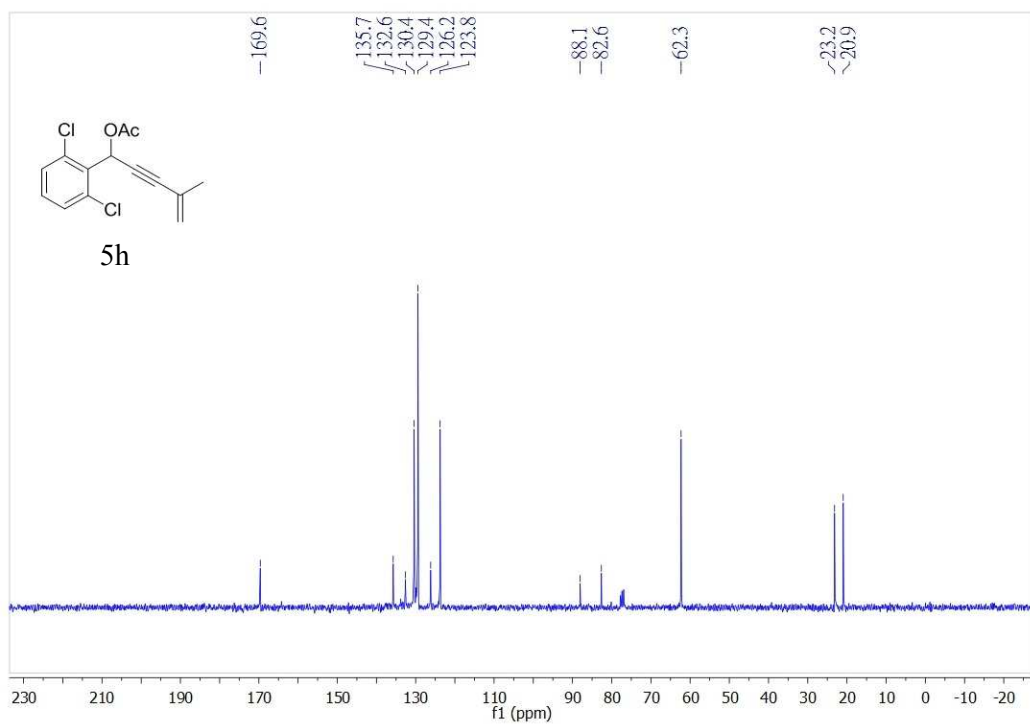


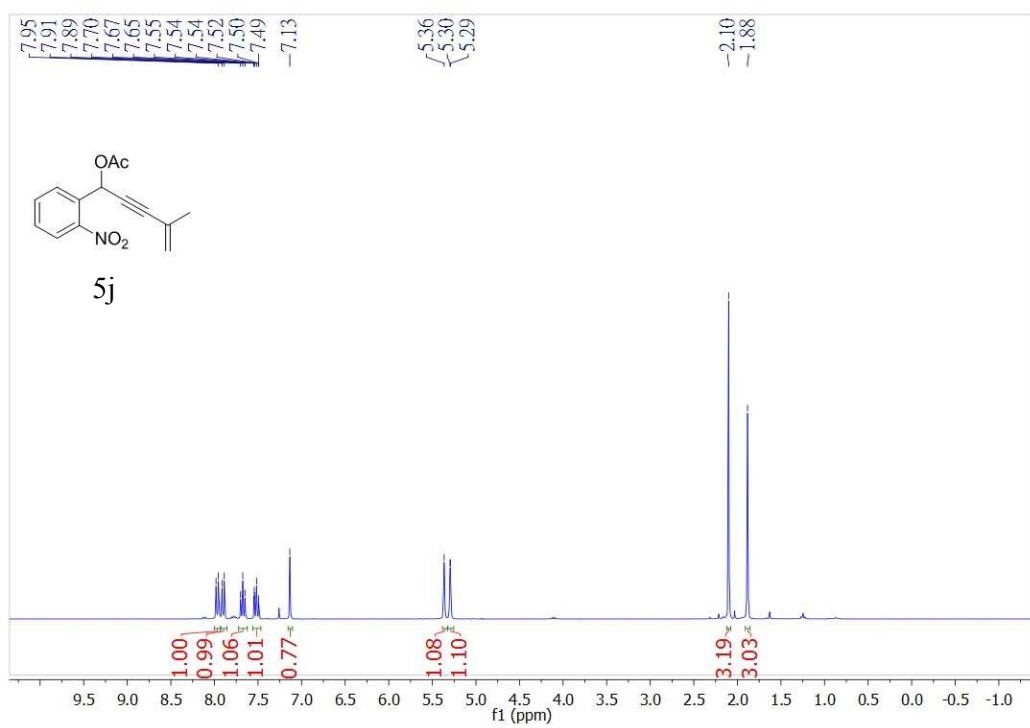
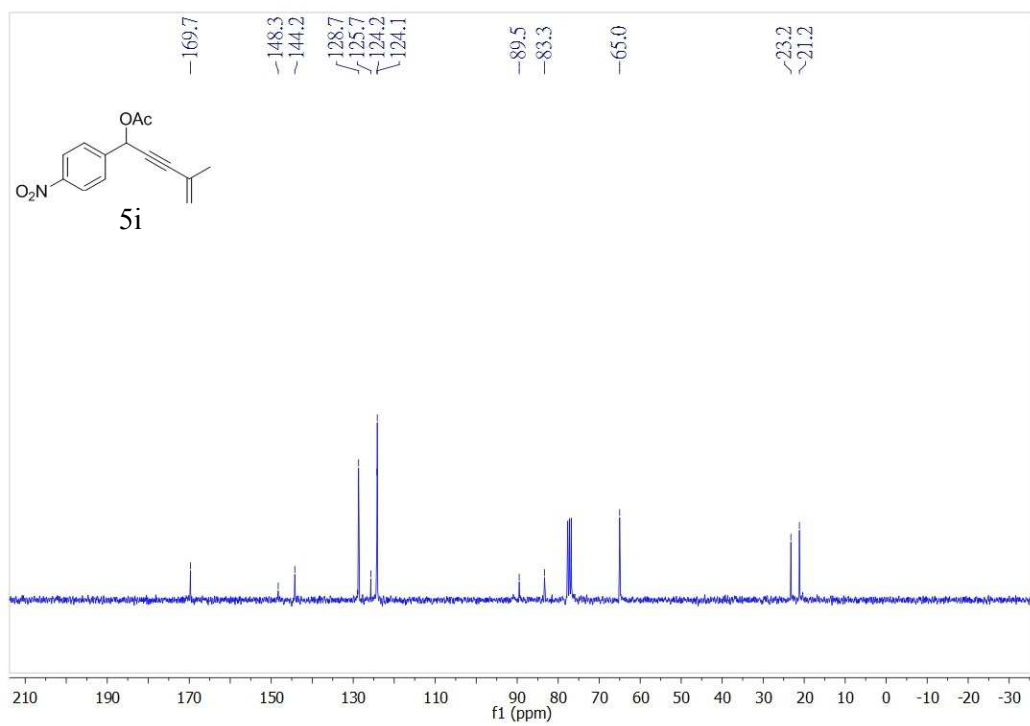


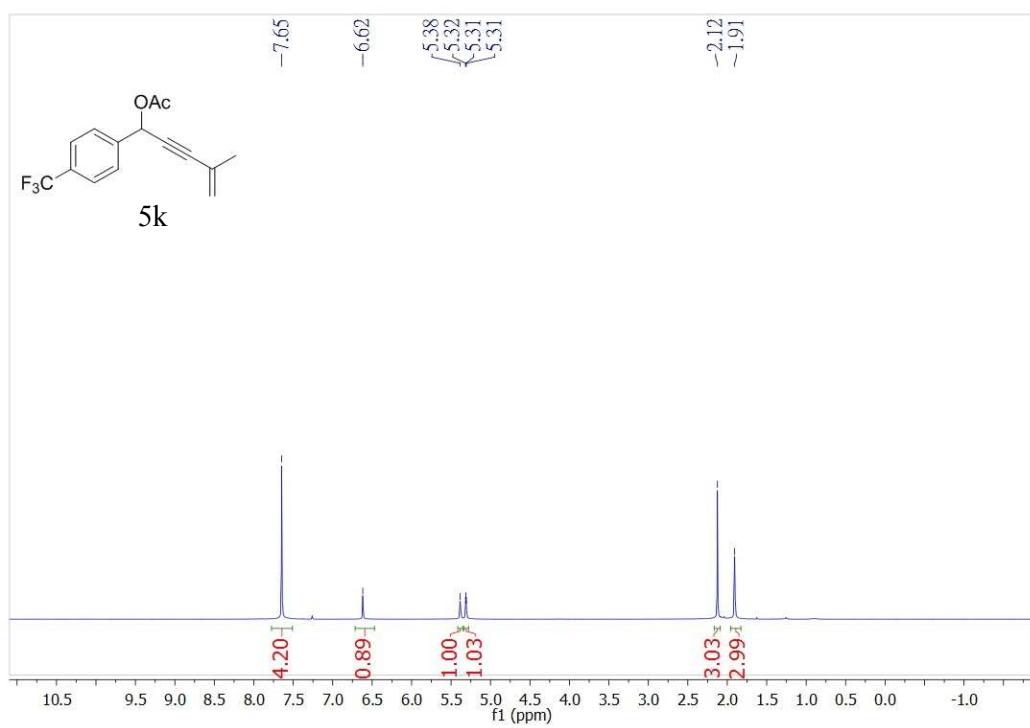
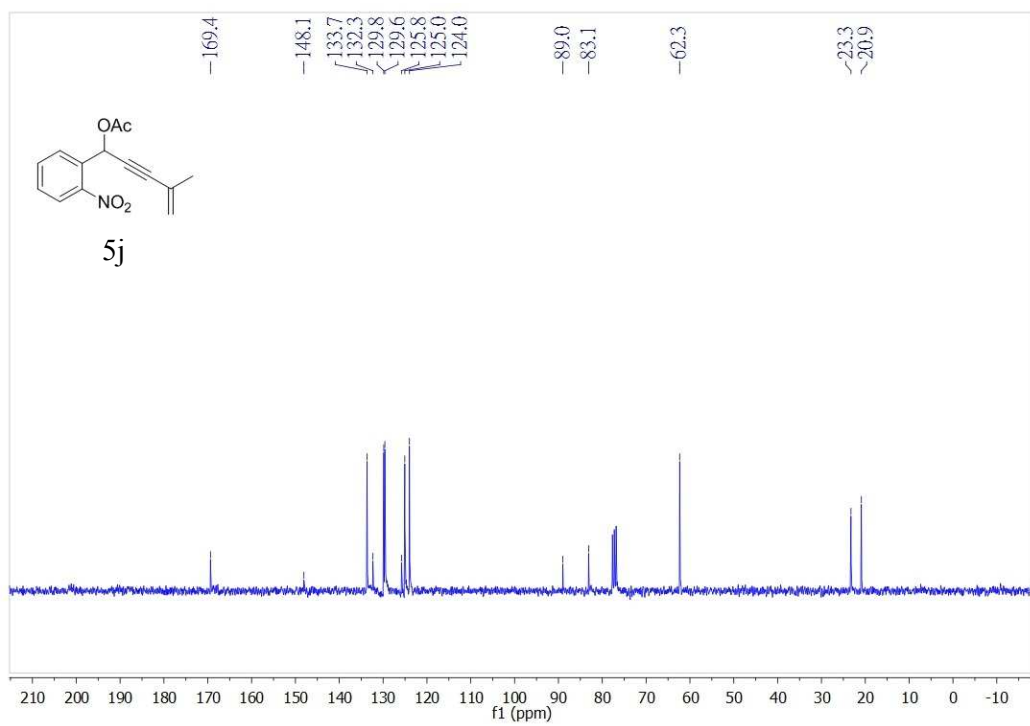


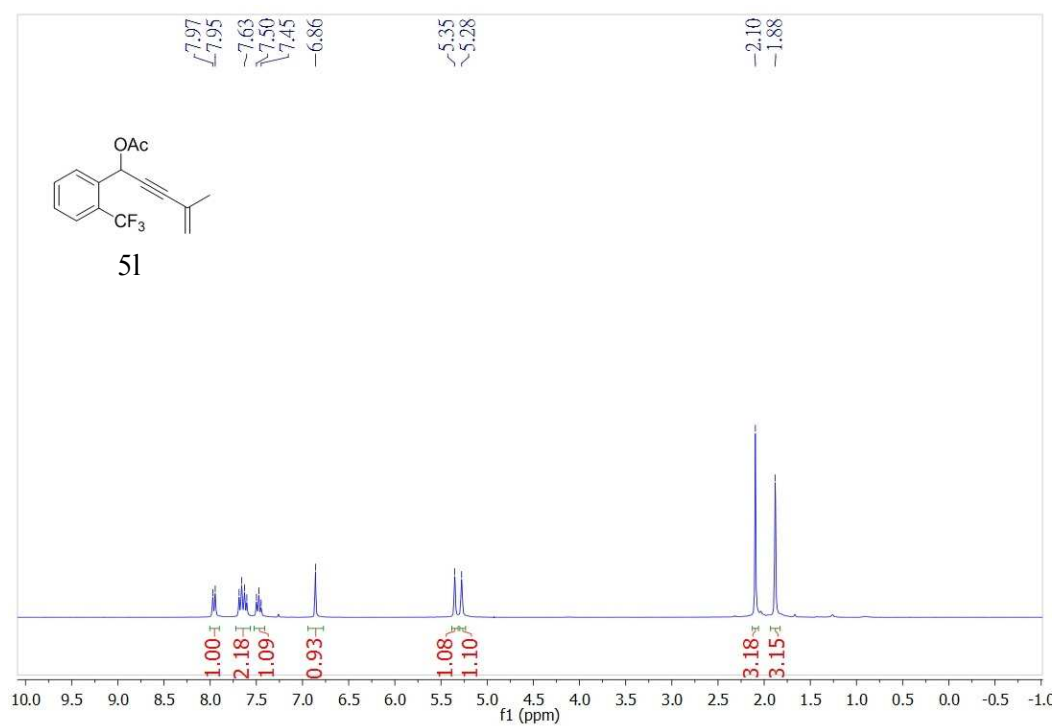
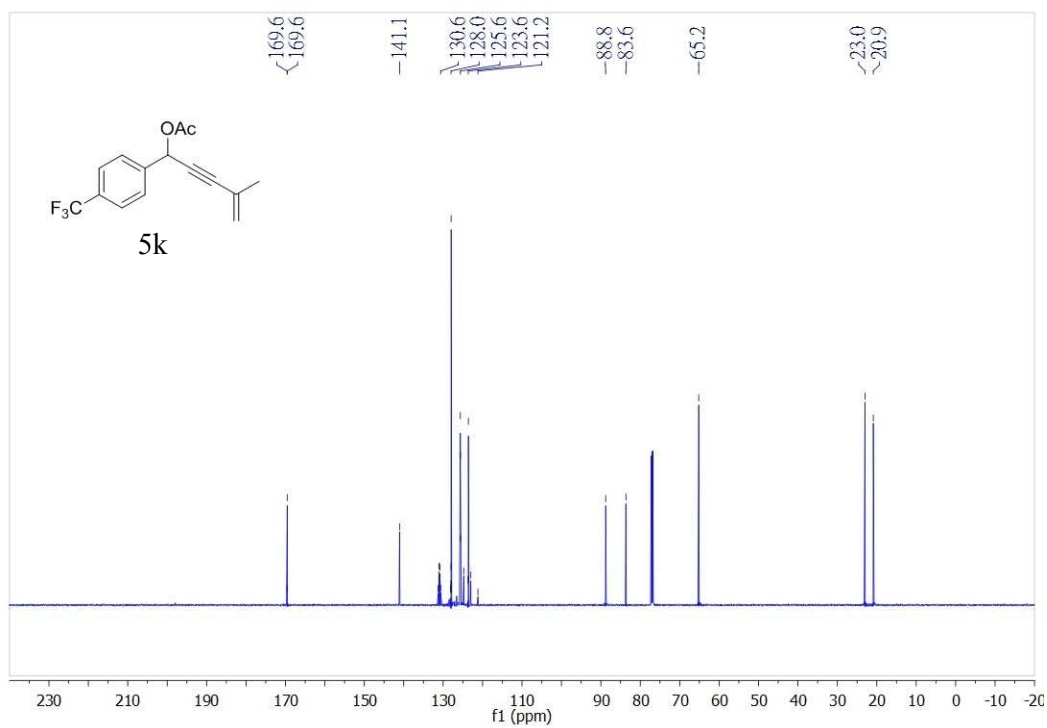


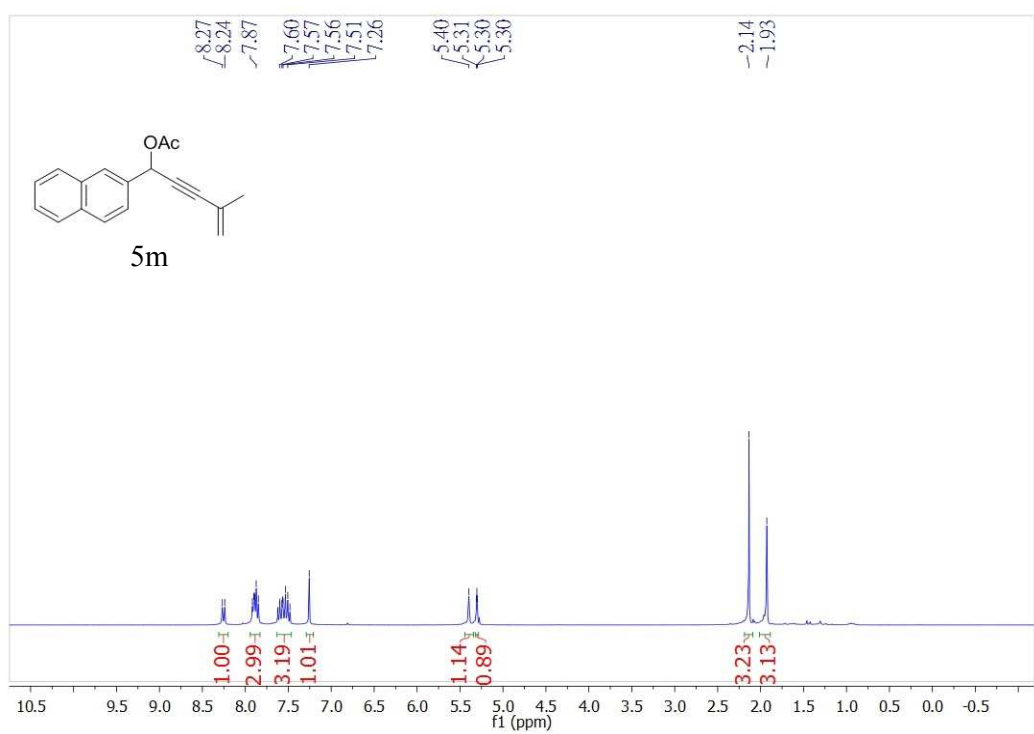
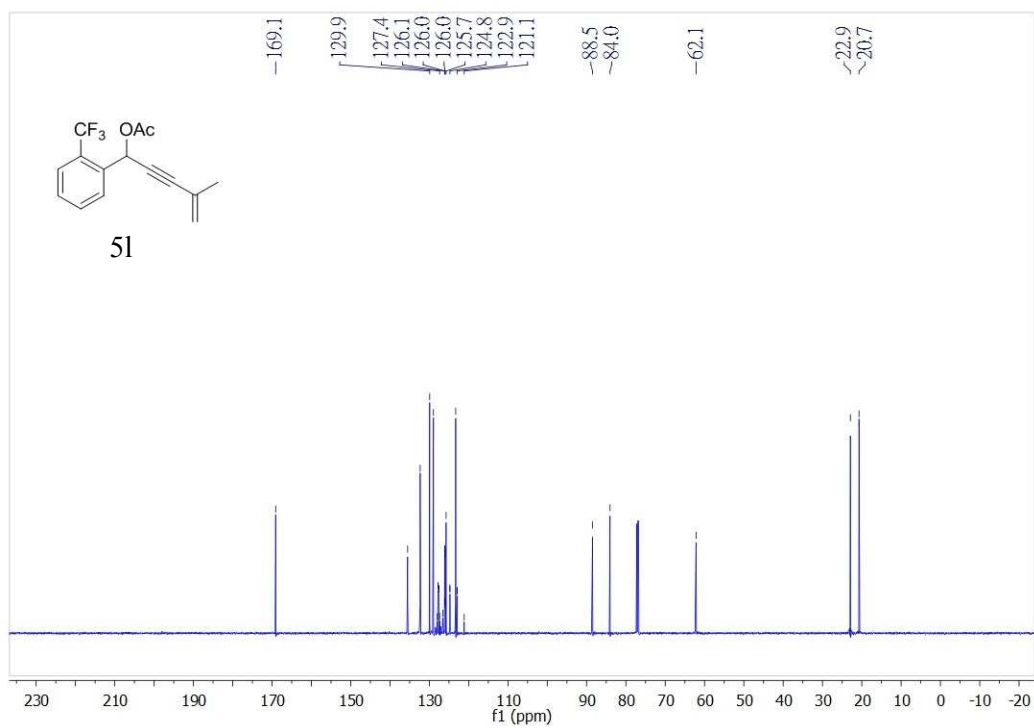


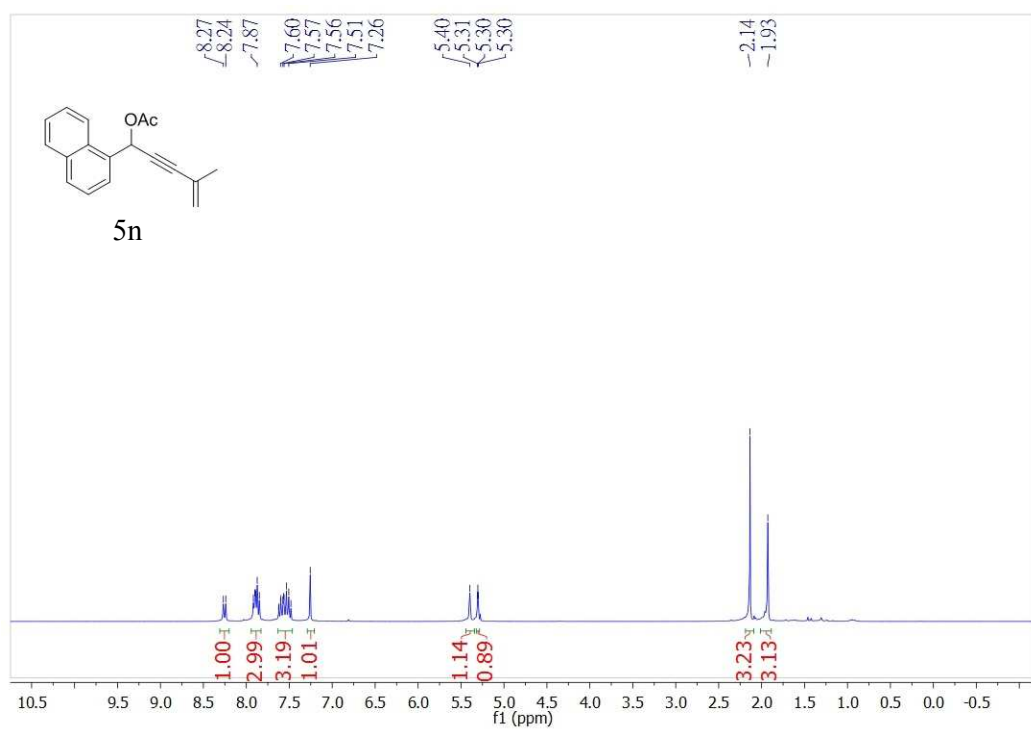
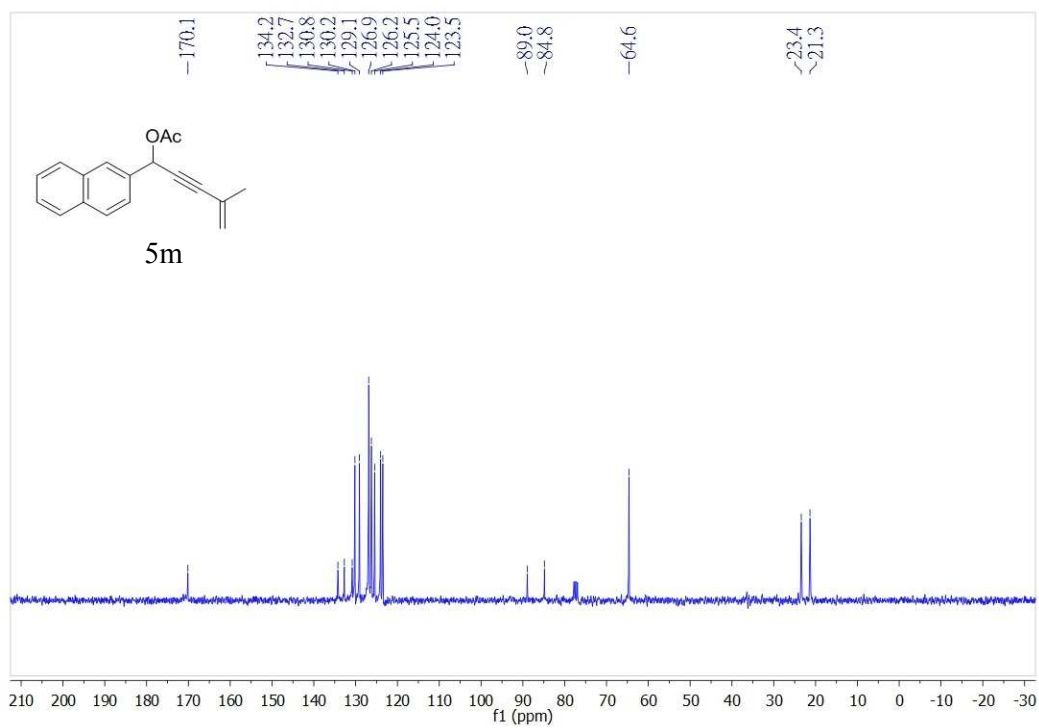


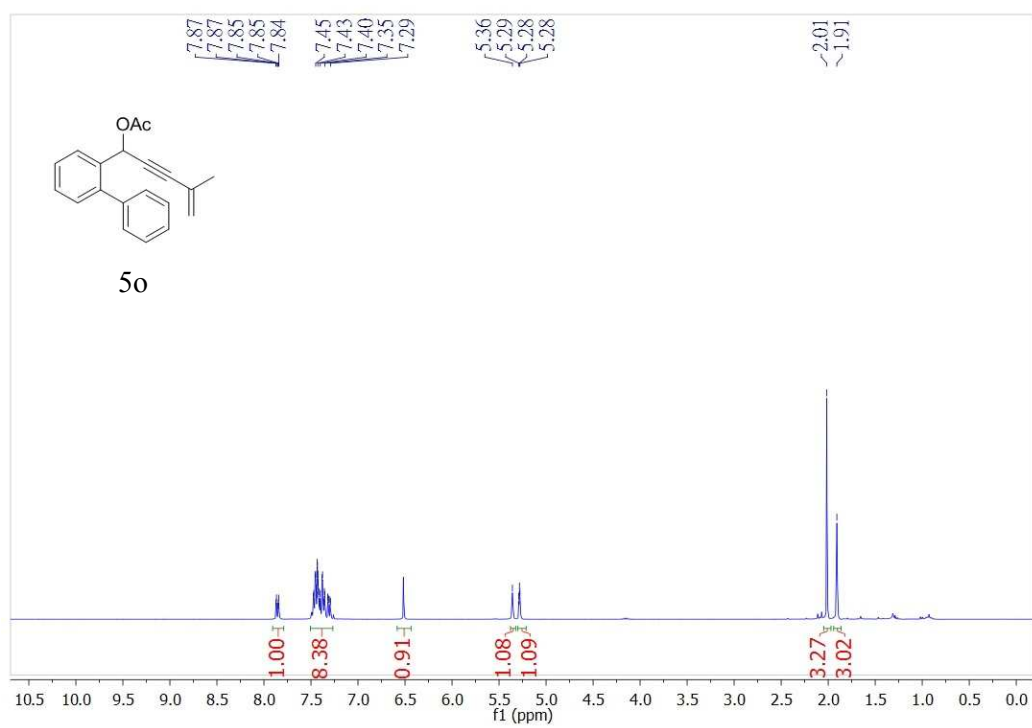
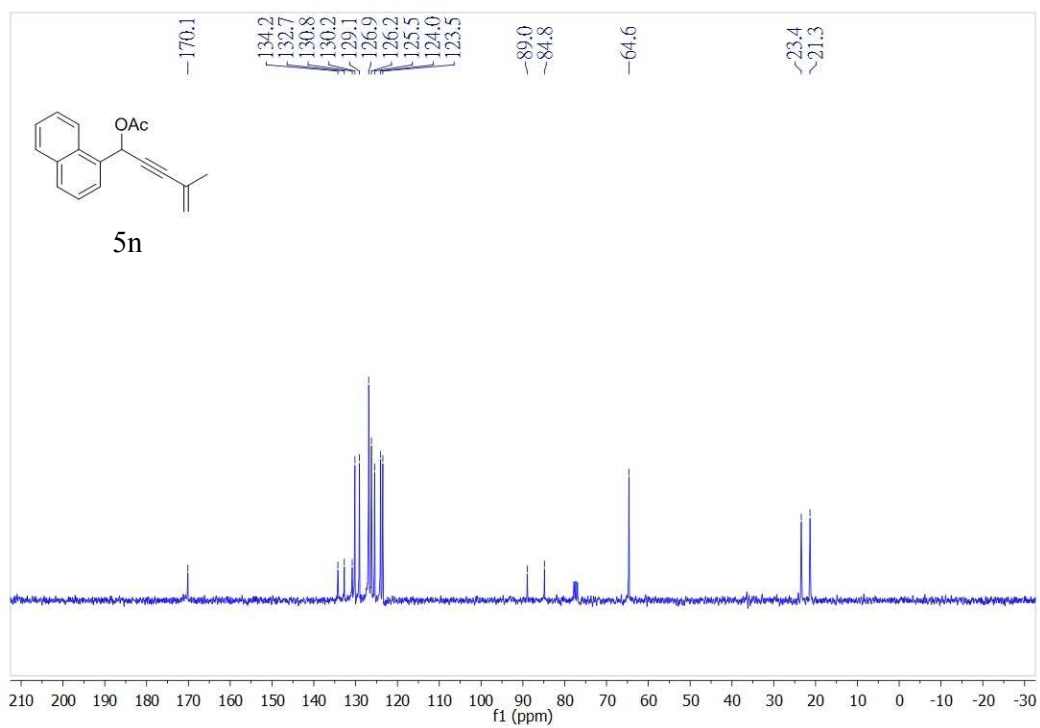


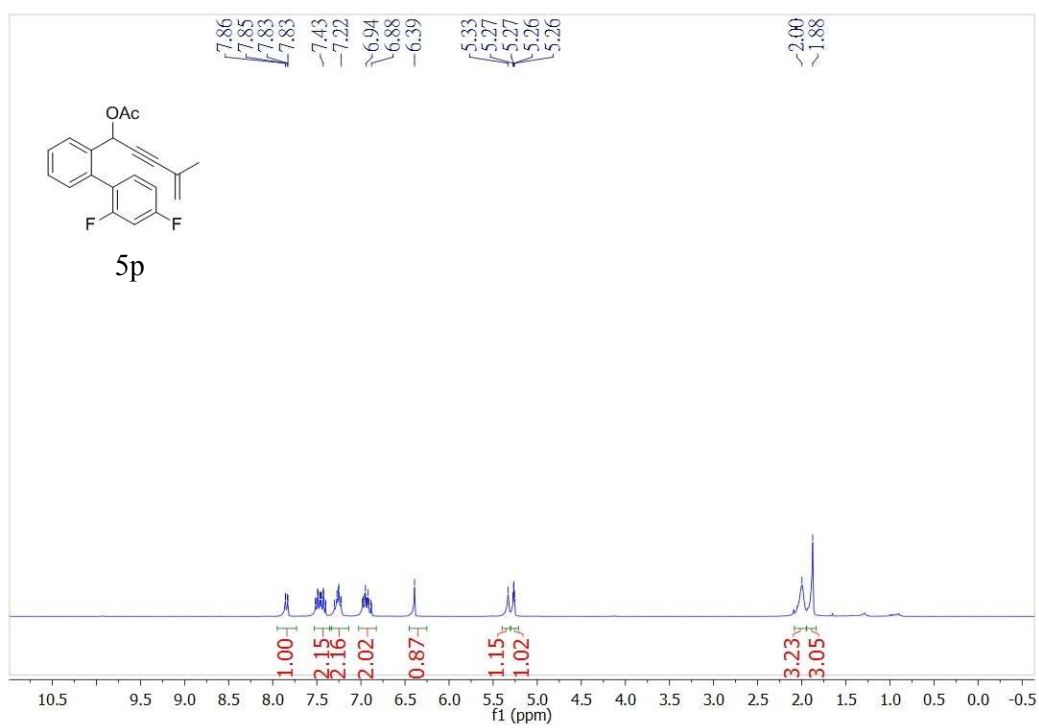
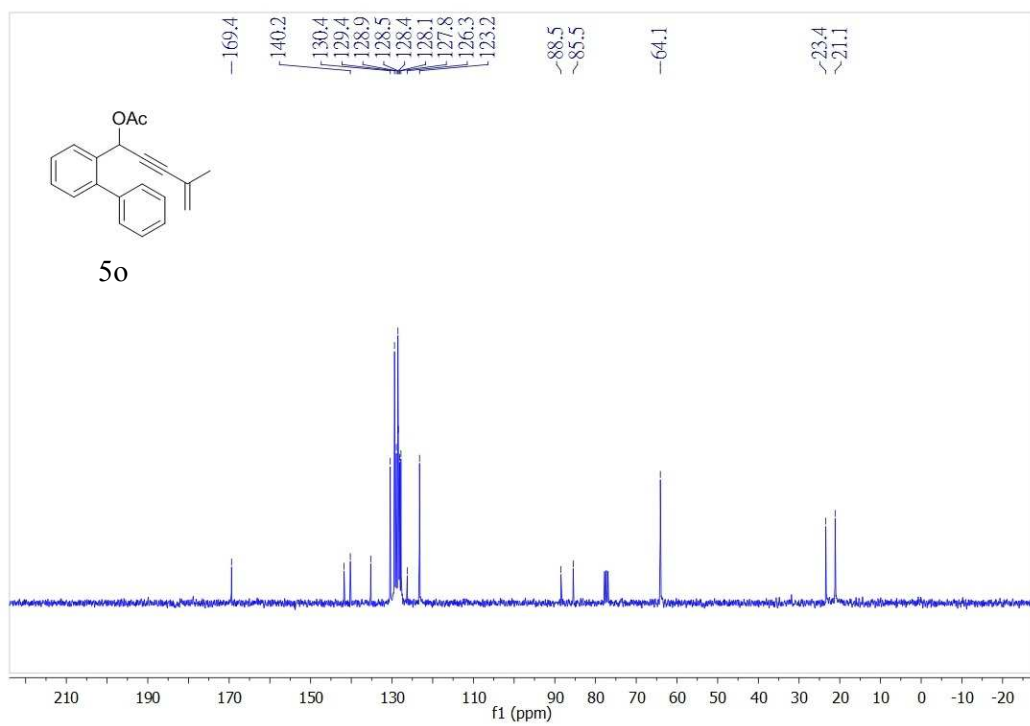


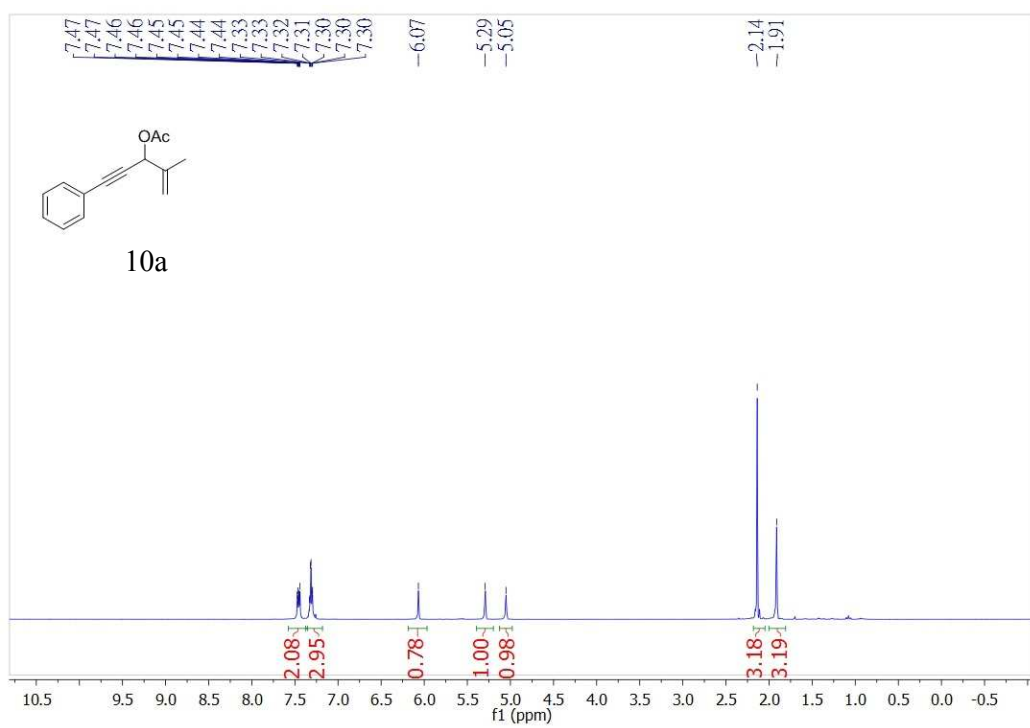
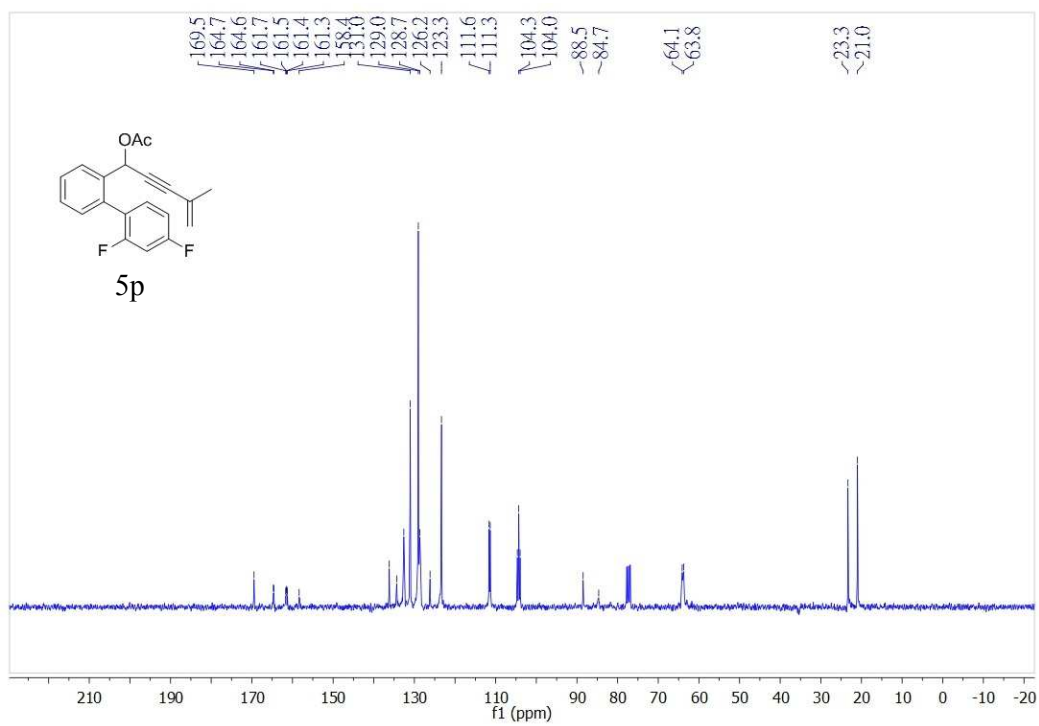


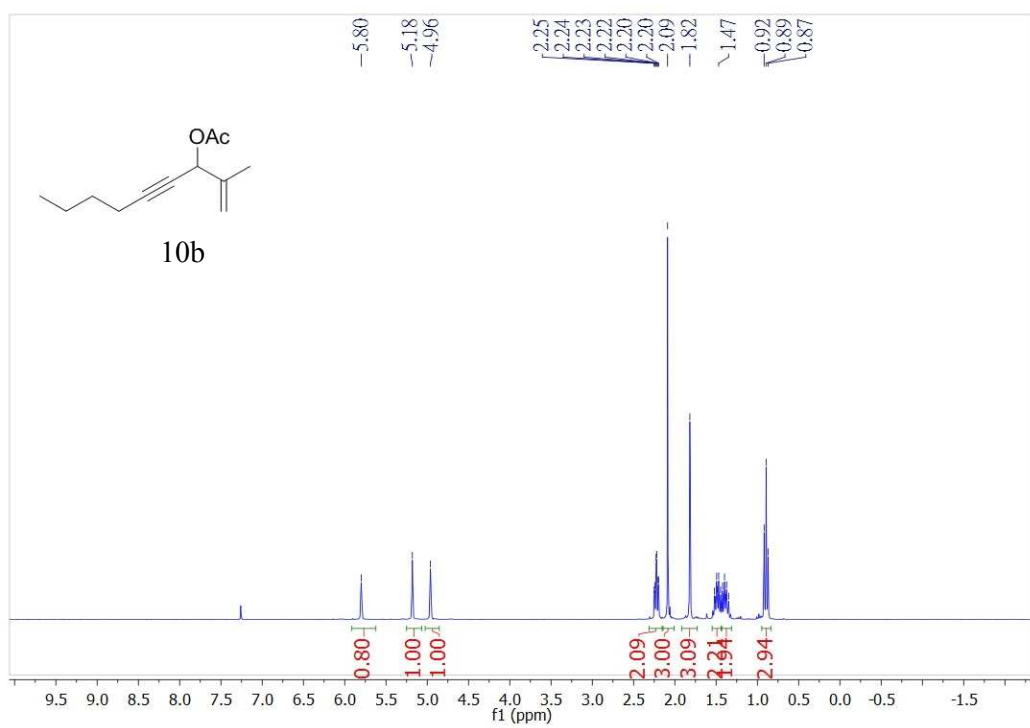
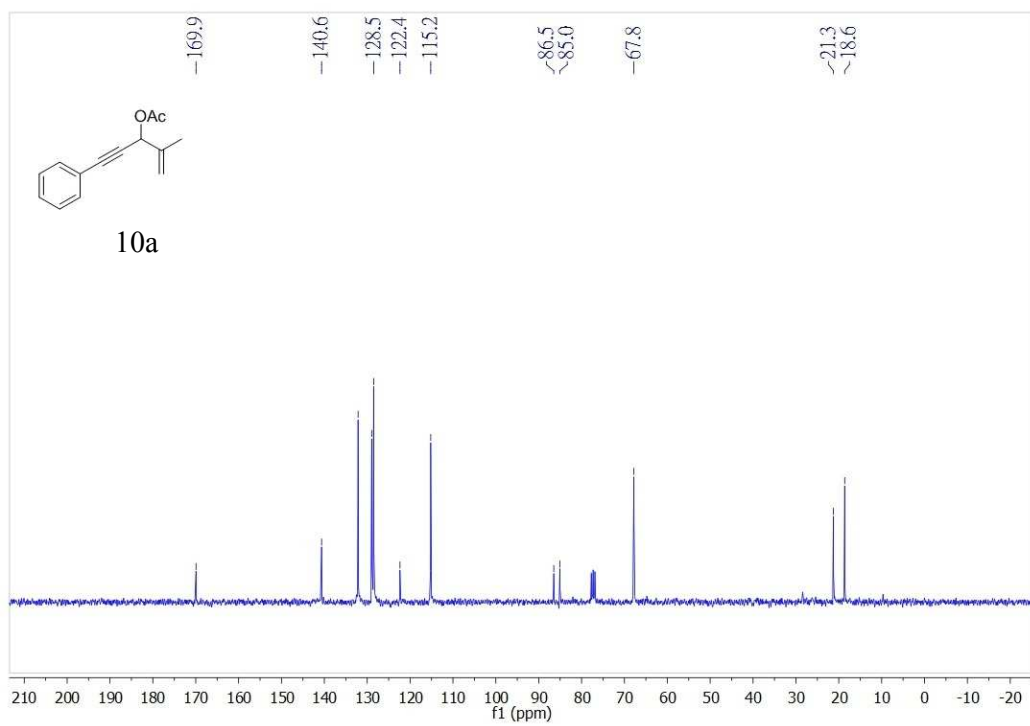


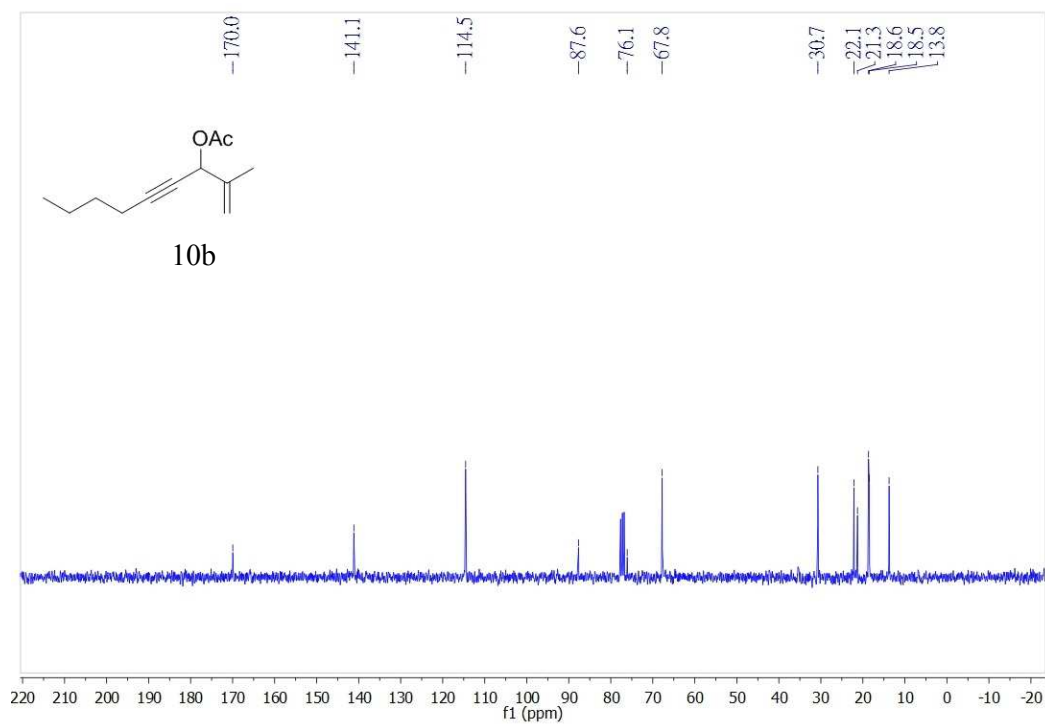




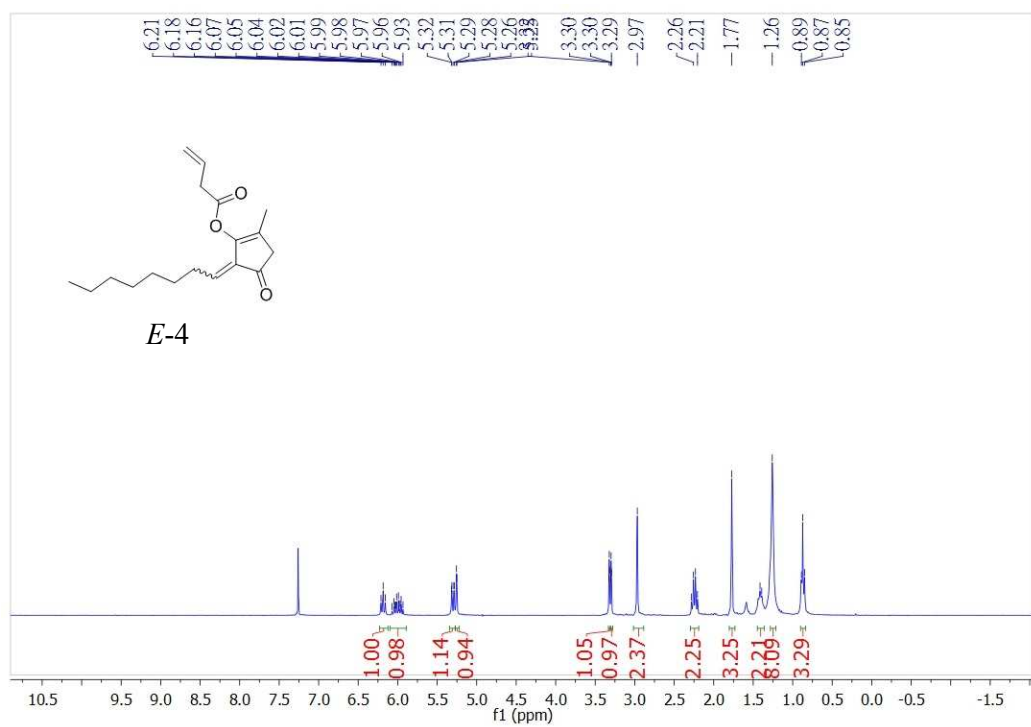


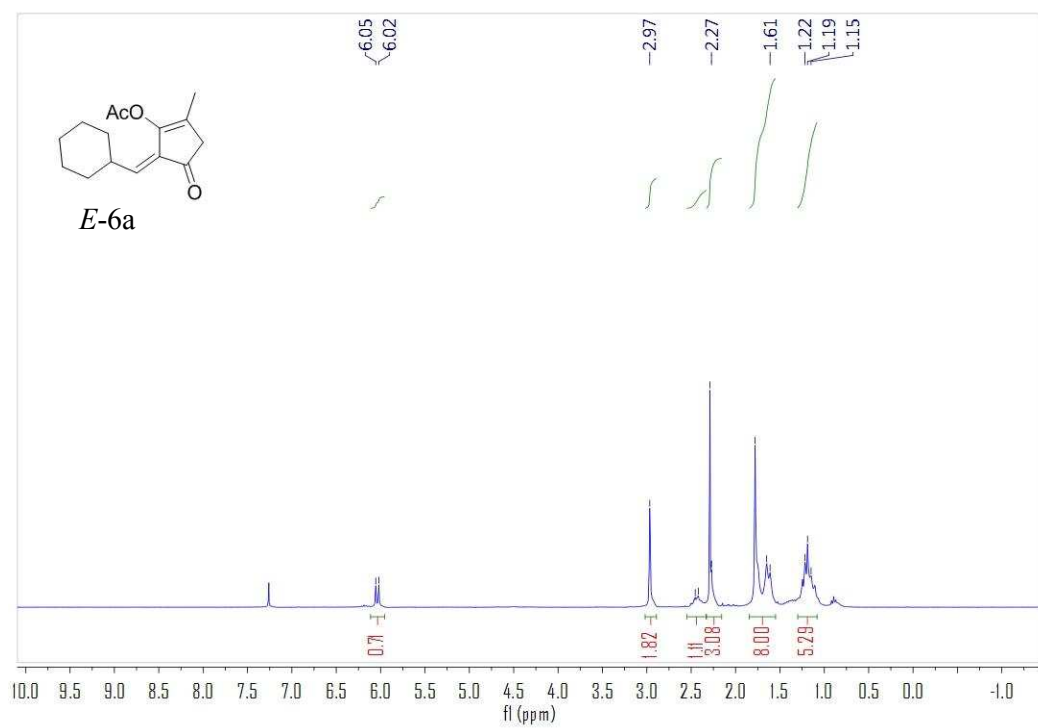
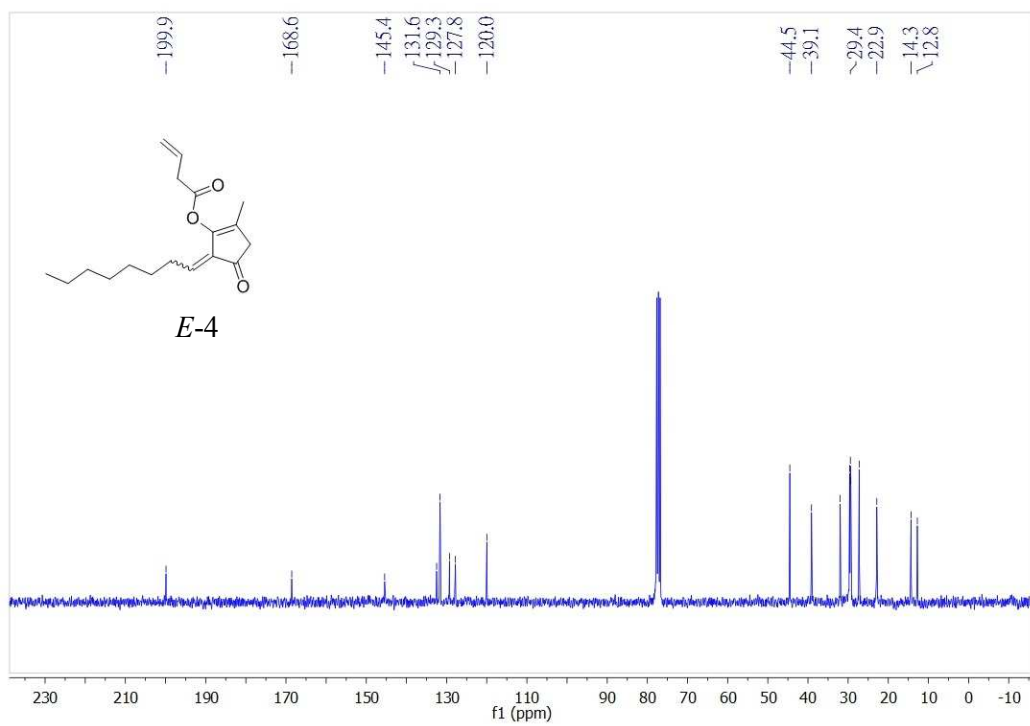


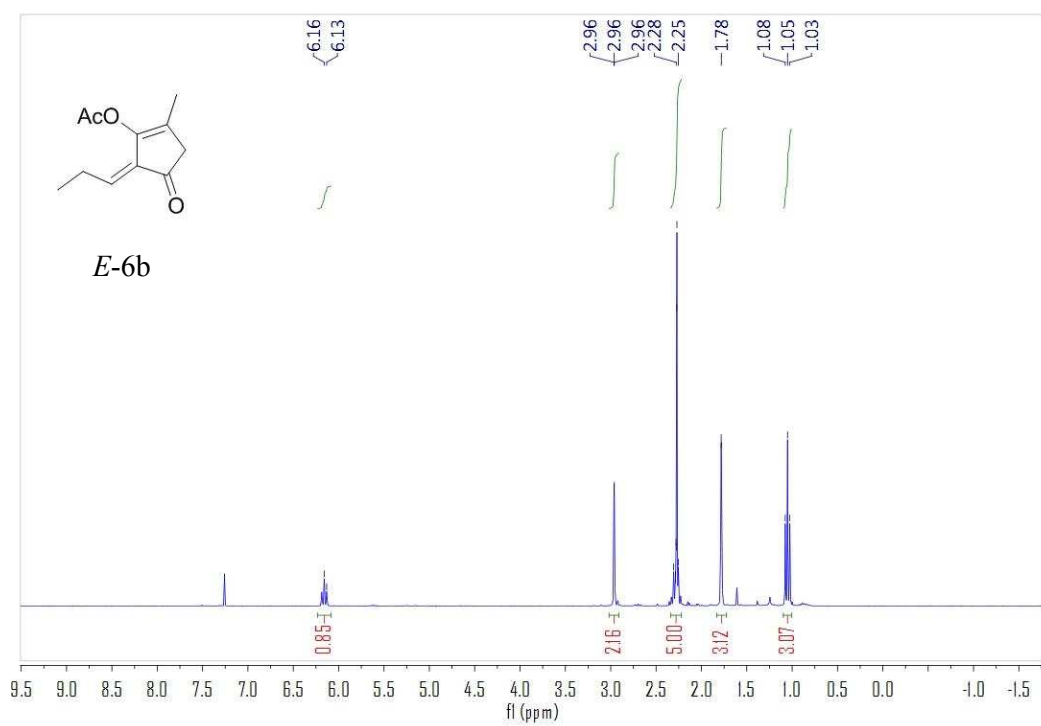
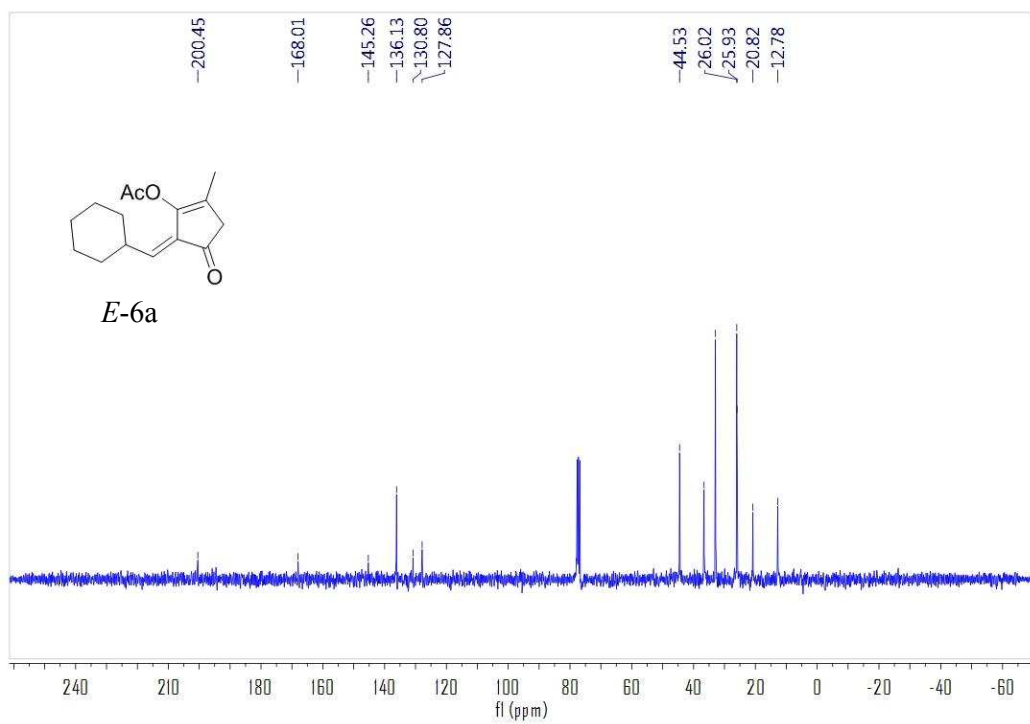


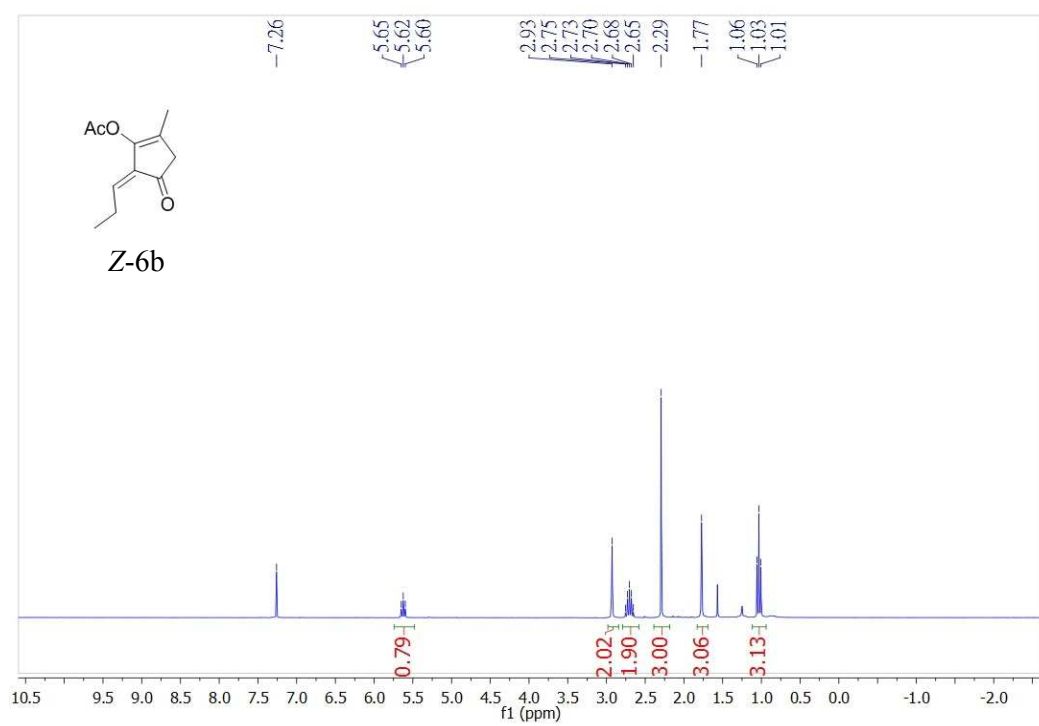
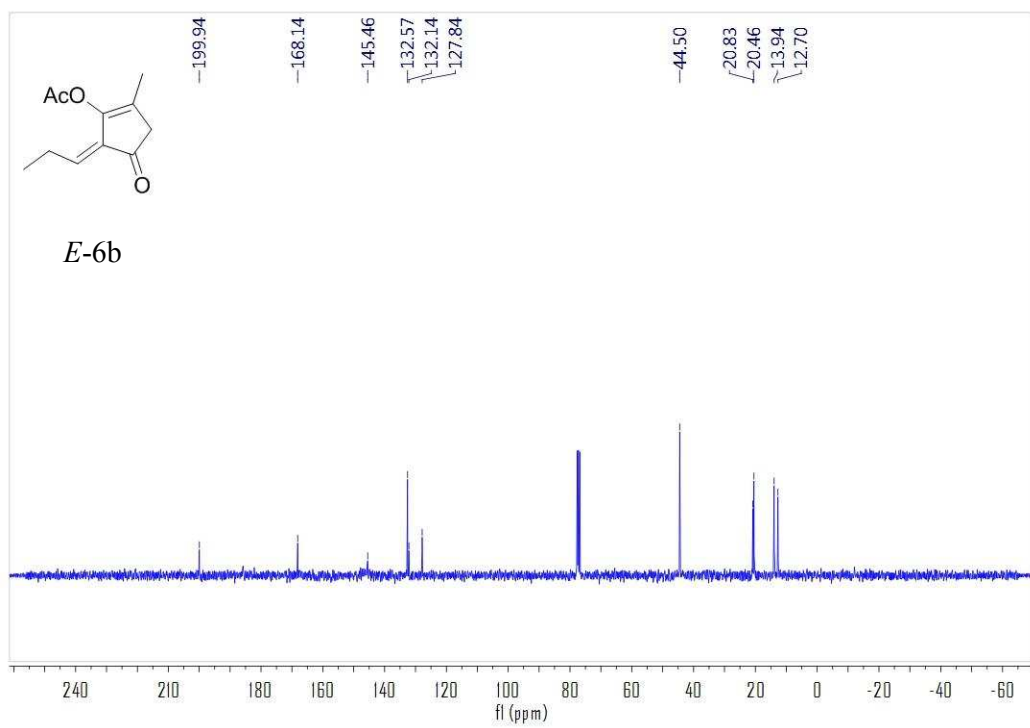


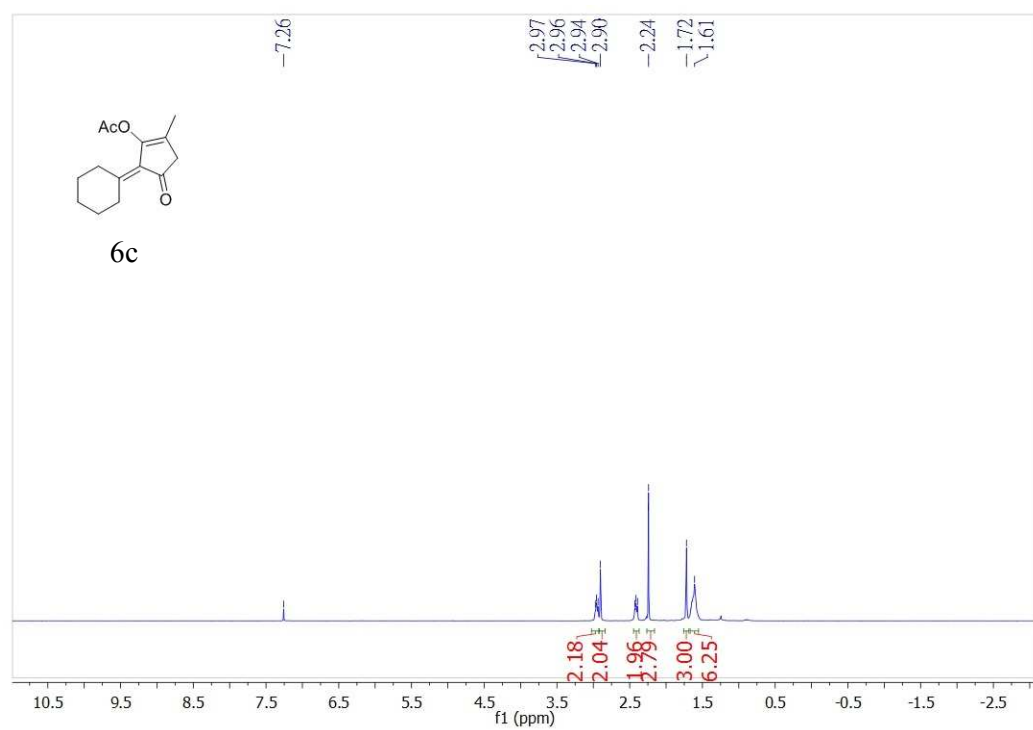
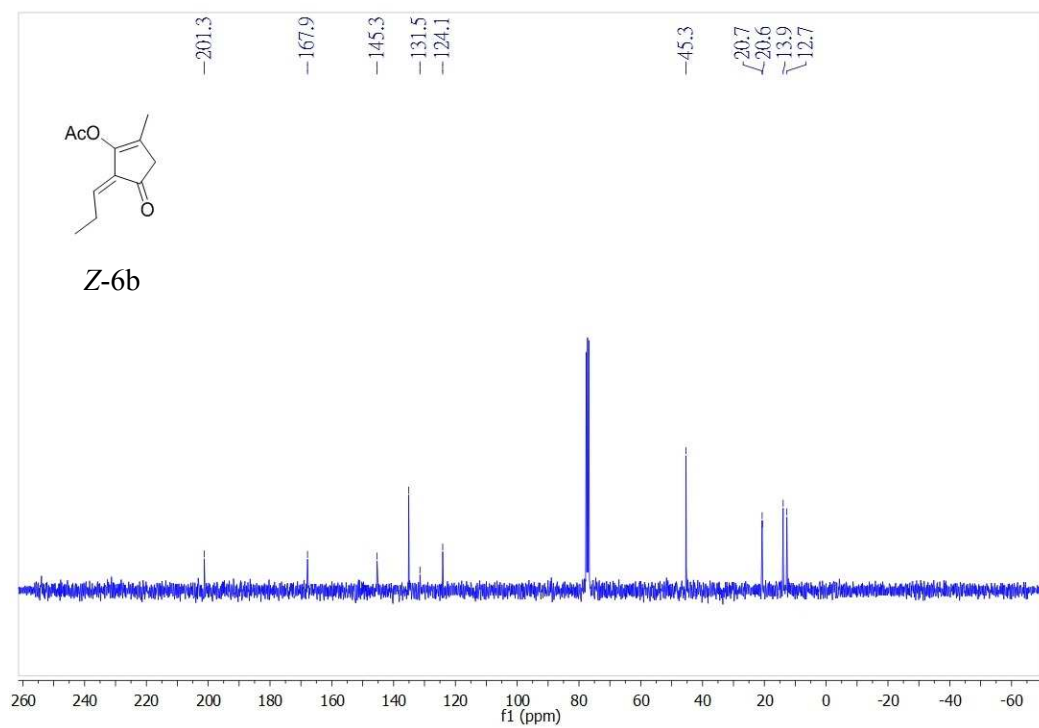
4. [4+1] cycloaddition products **4** & **6** & **11**

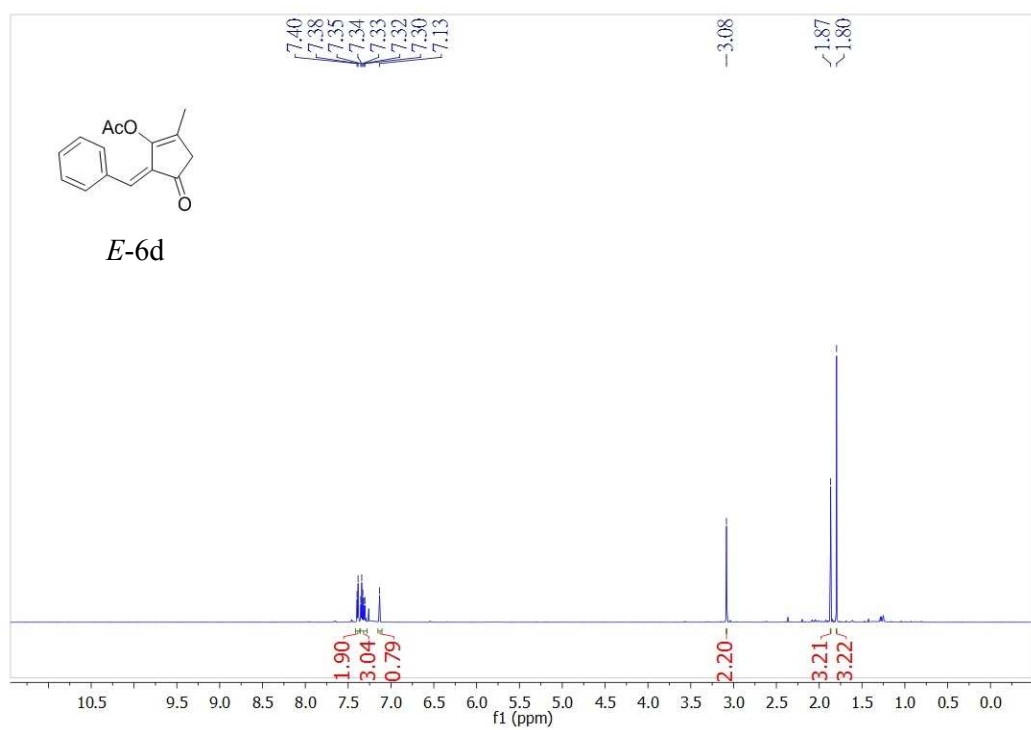
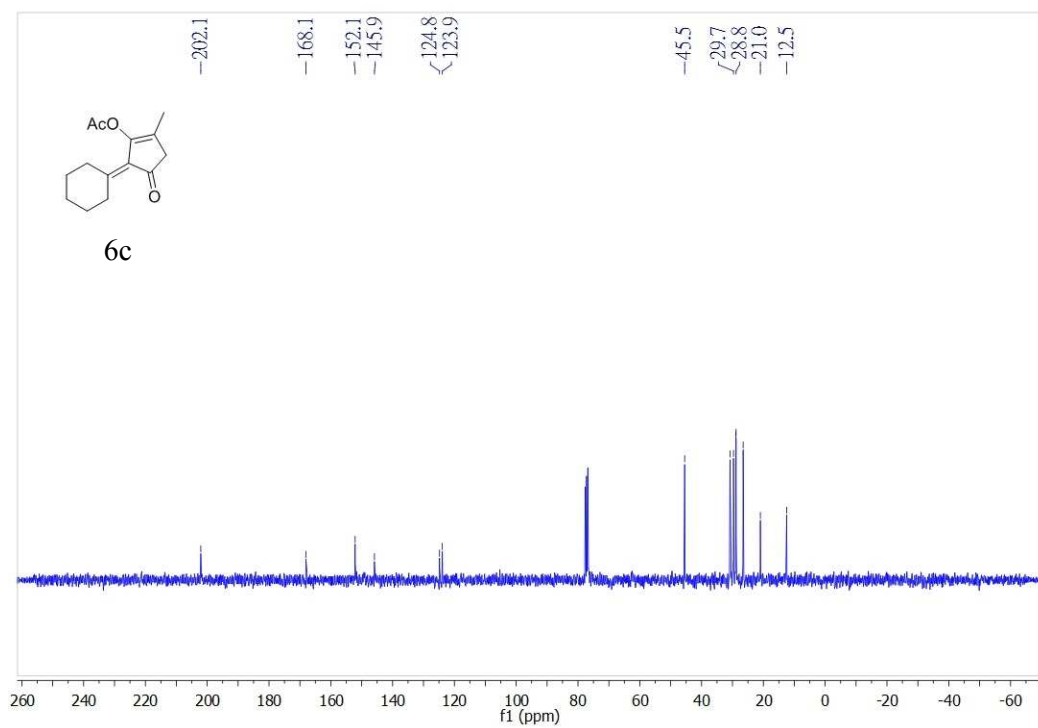


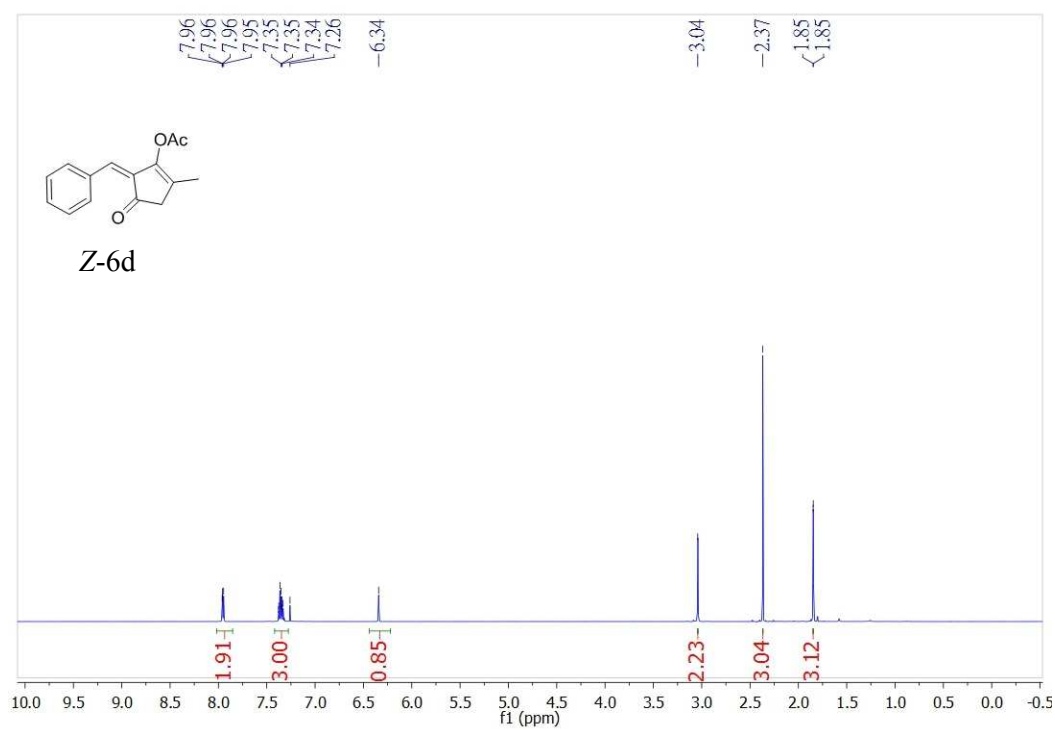
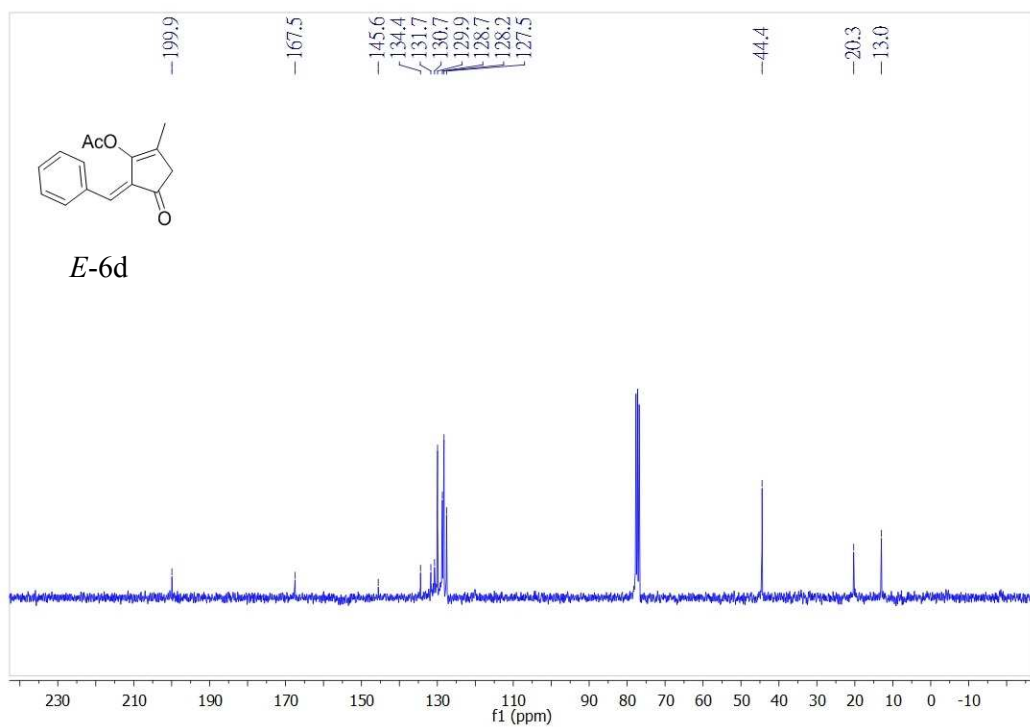


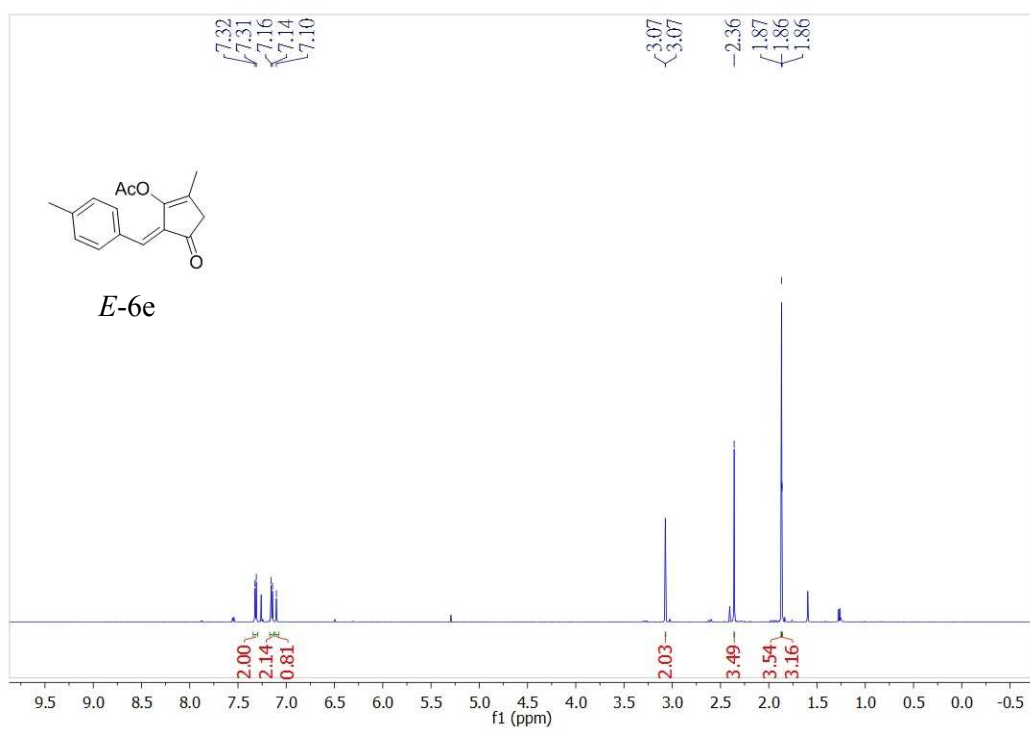
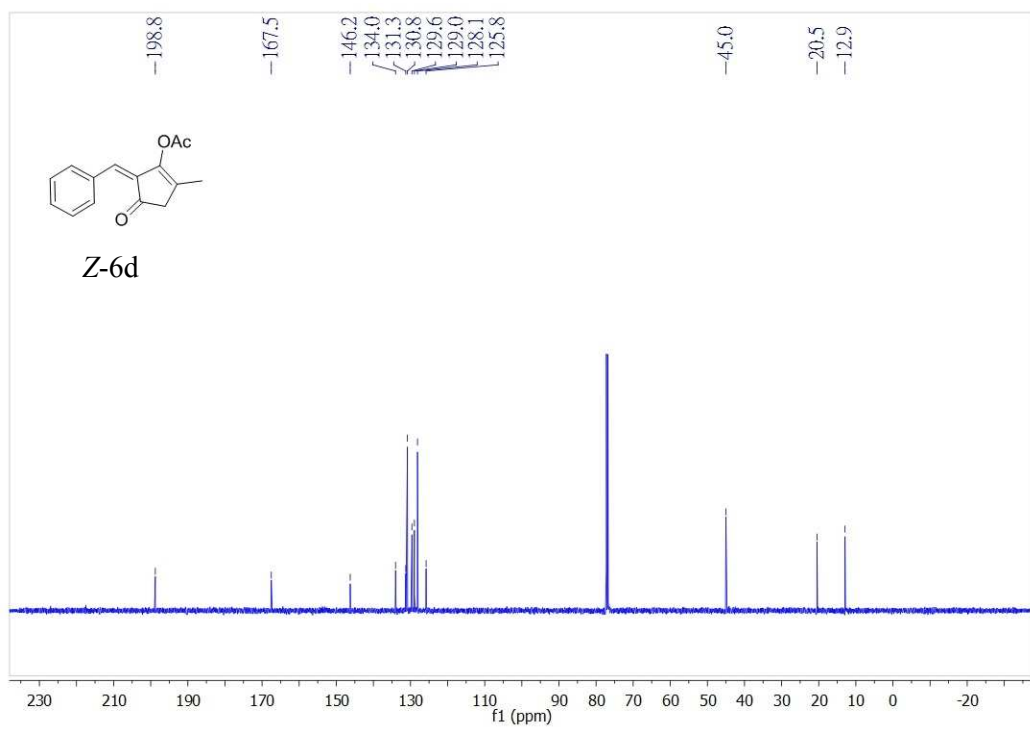


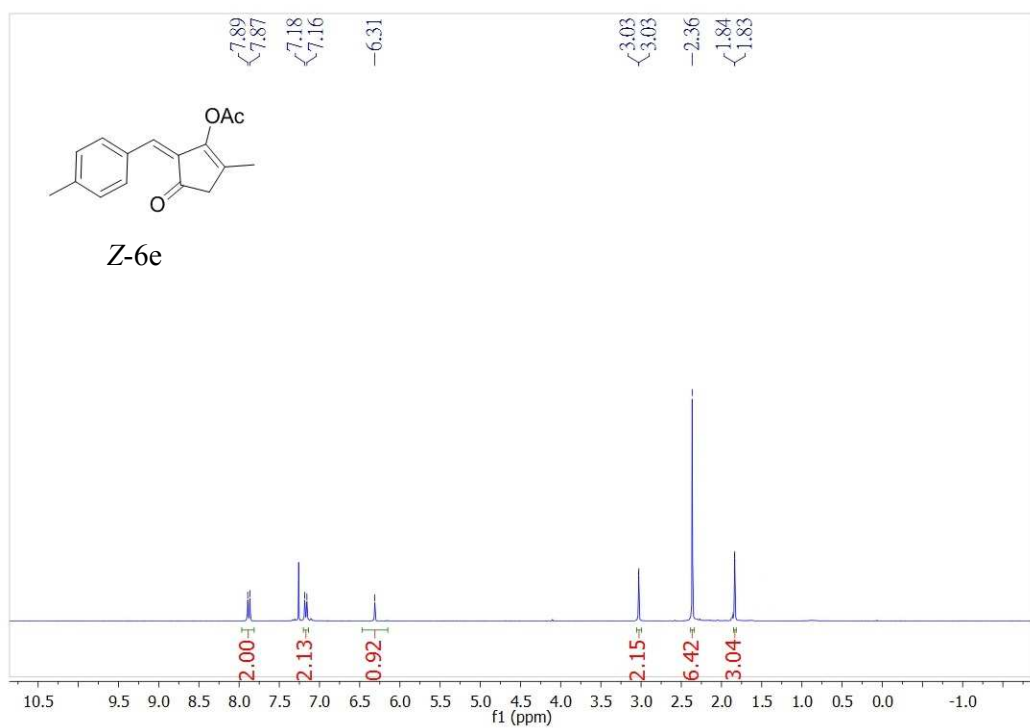
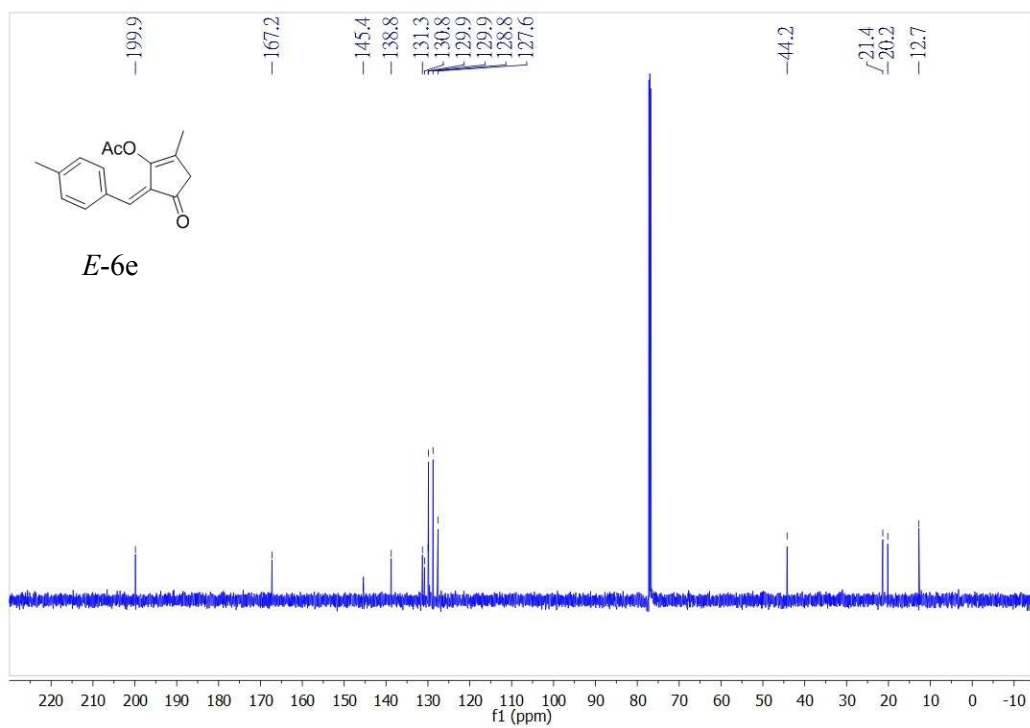


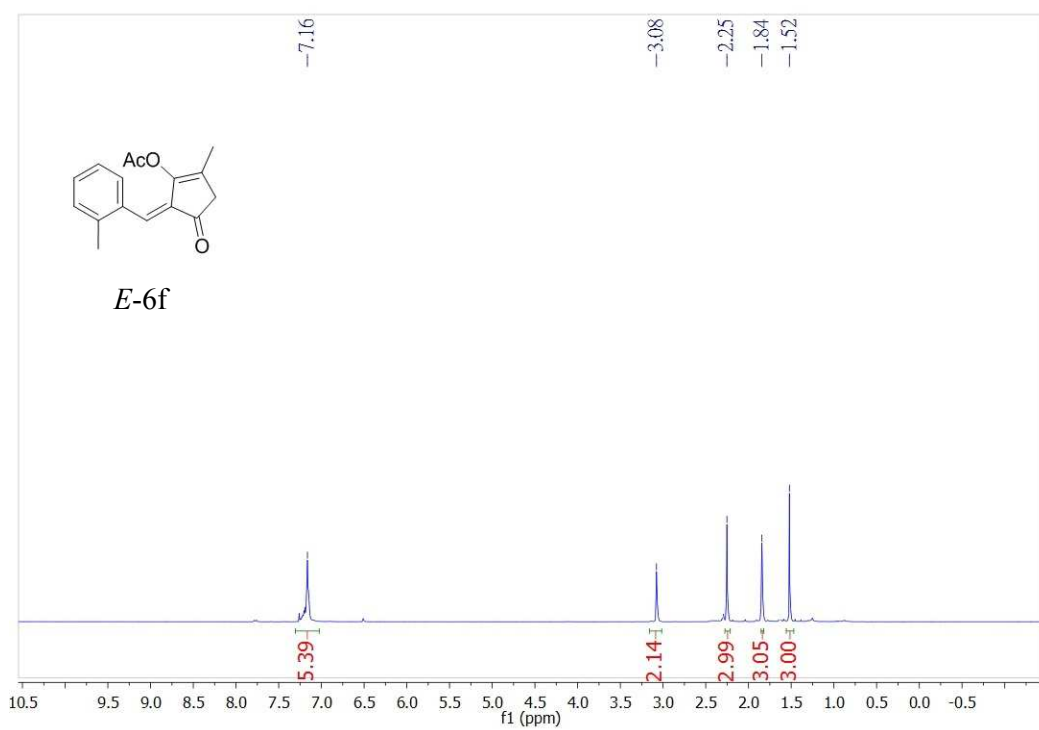
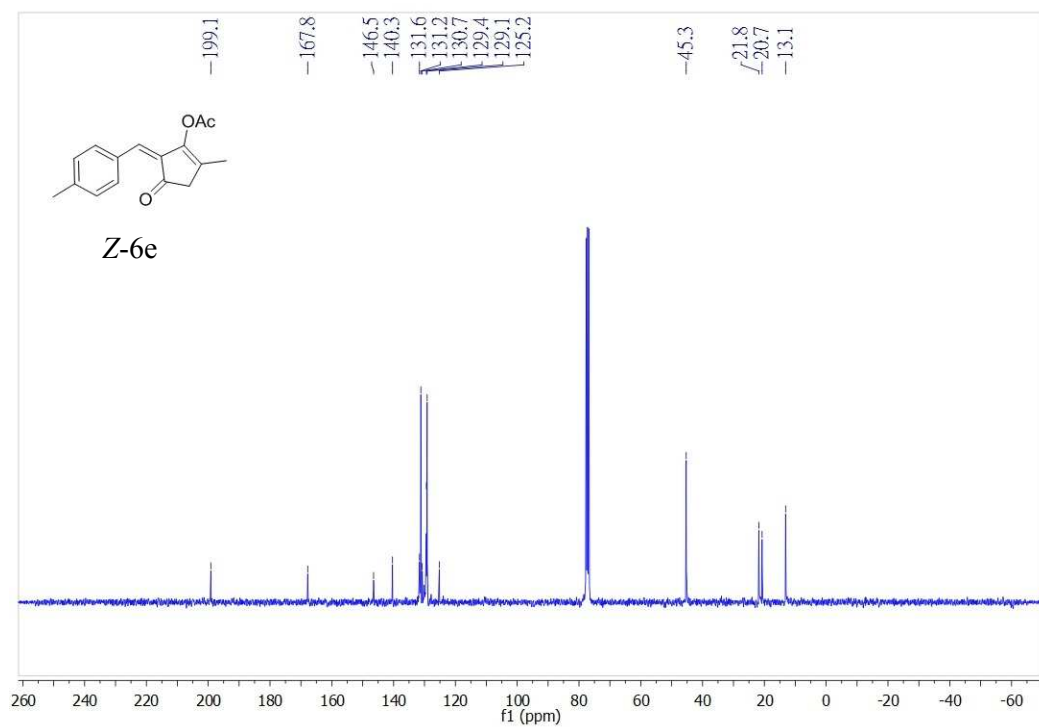


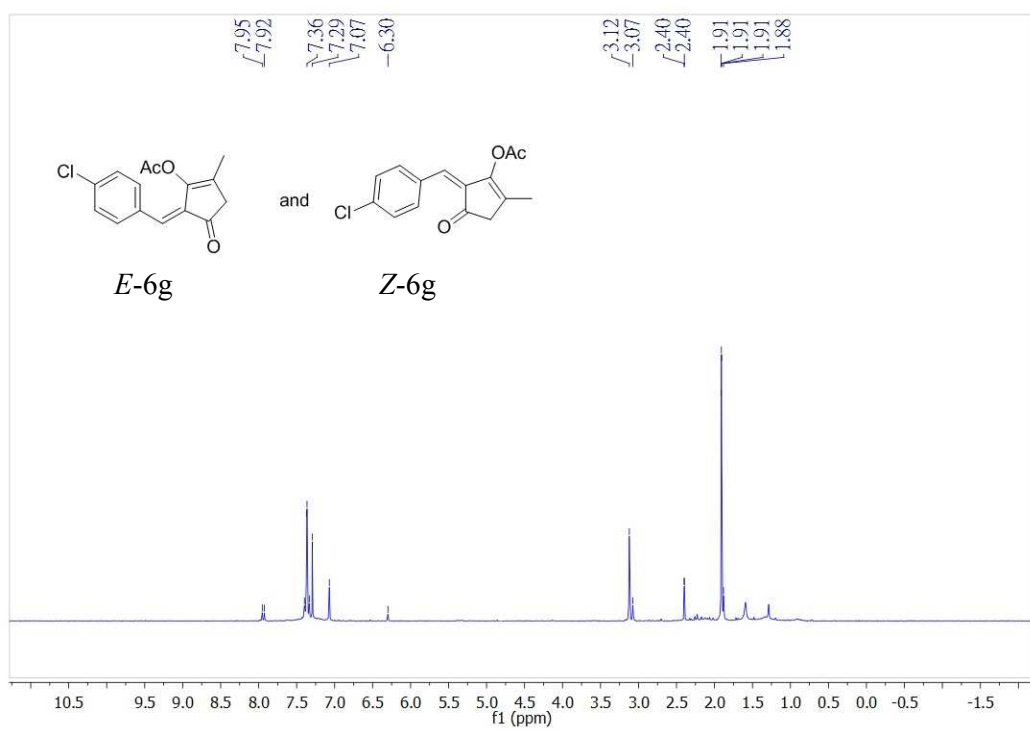
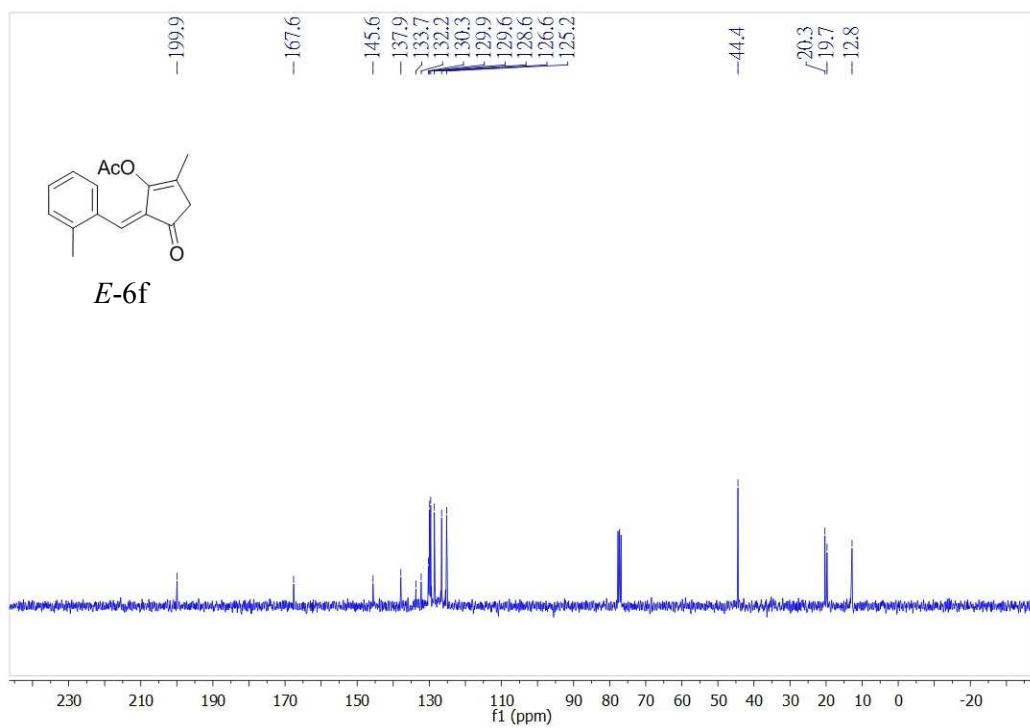


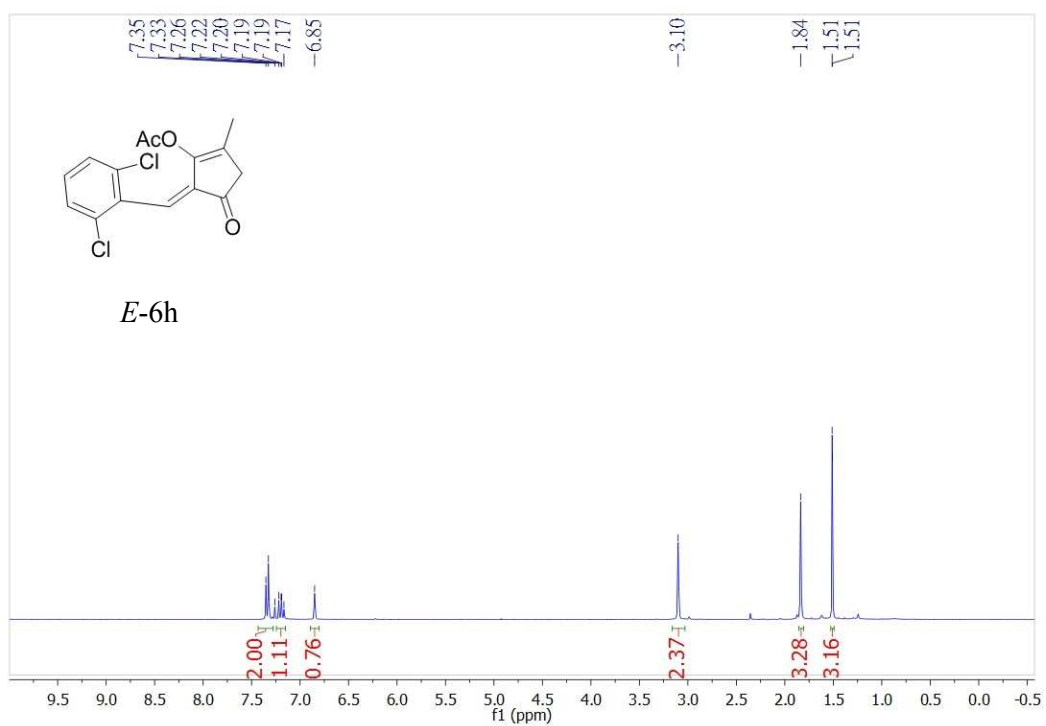
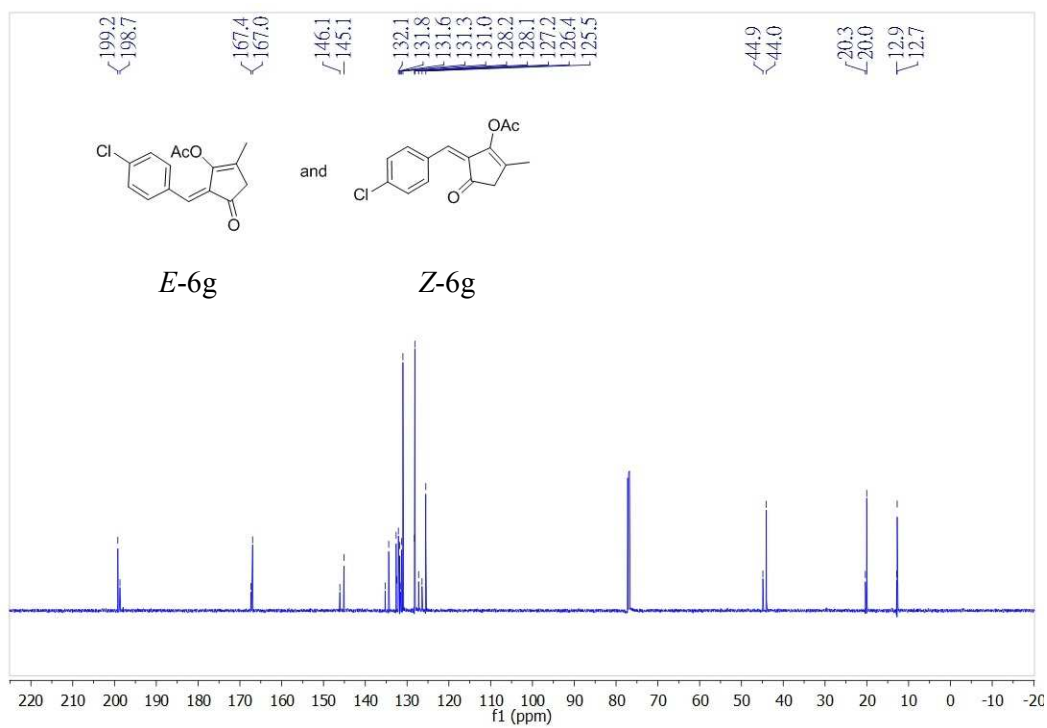


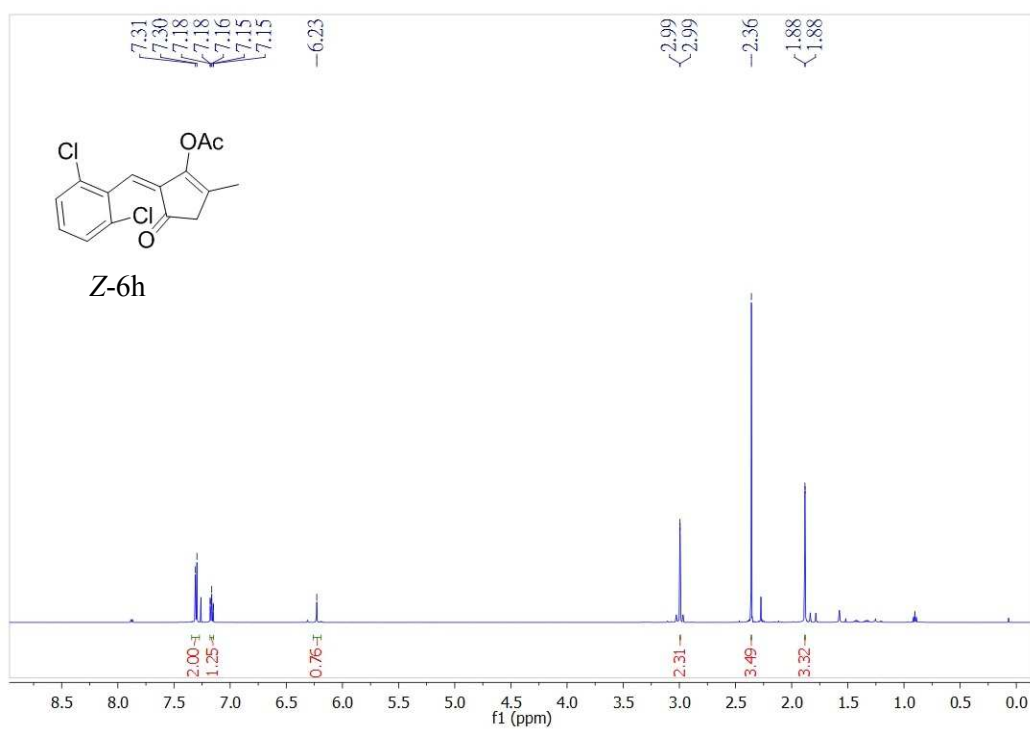
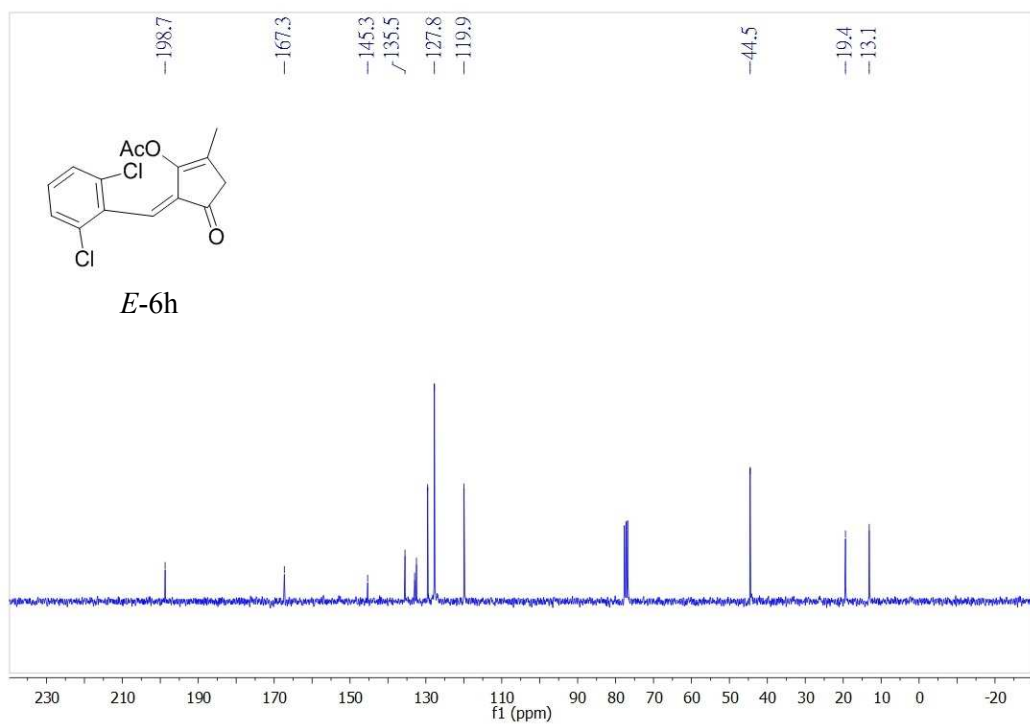


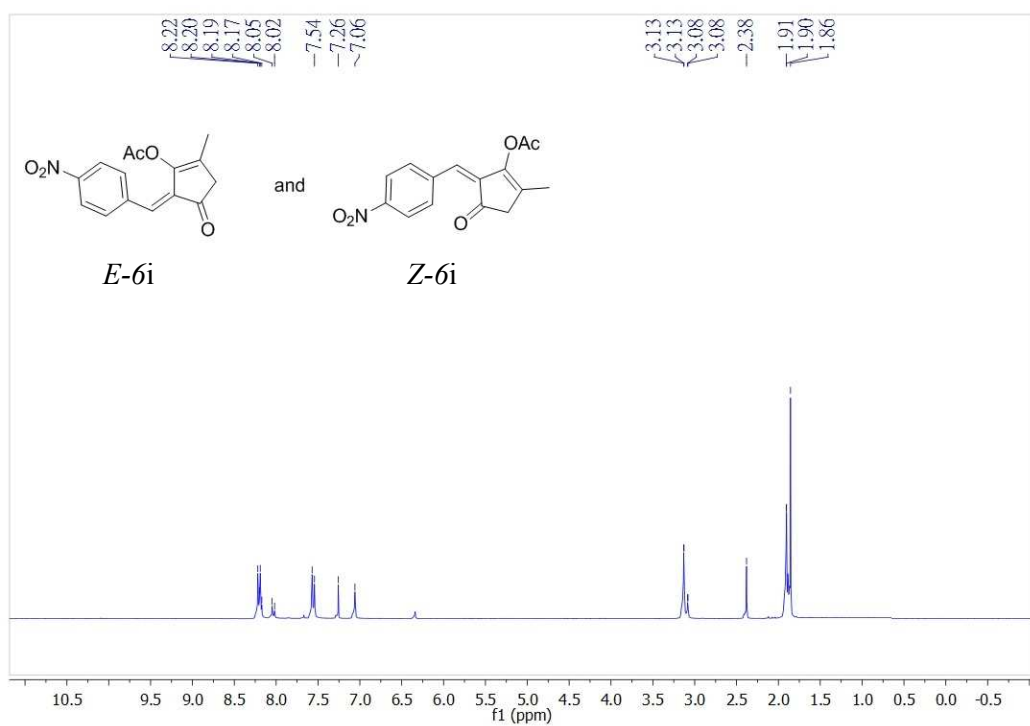
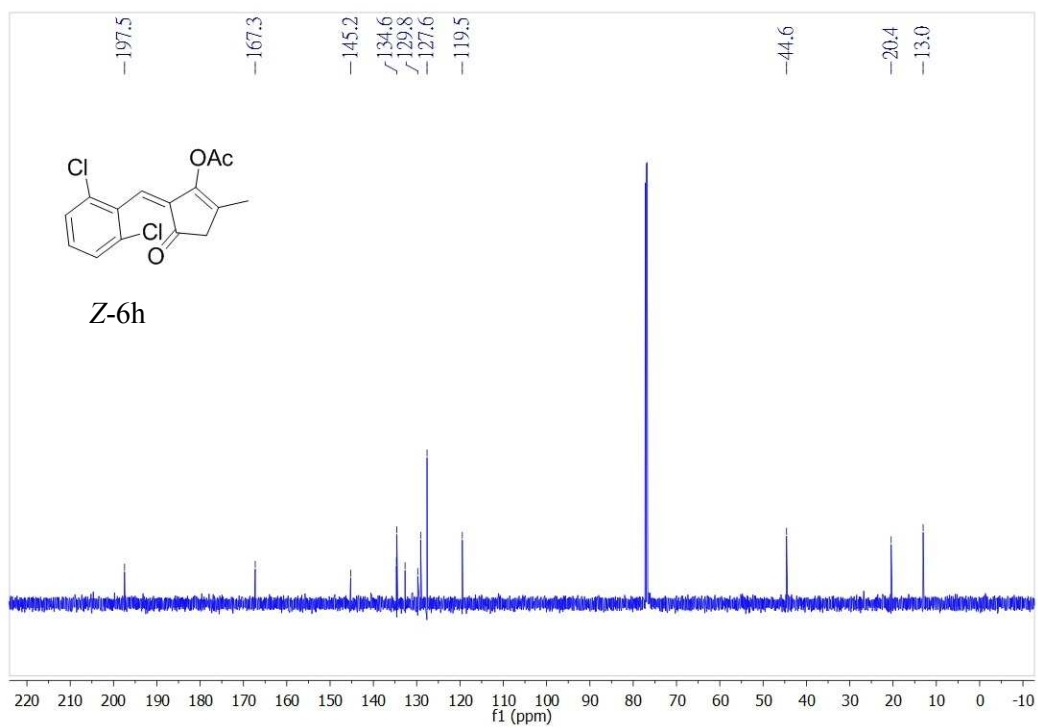


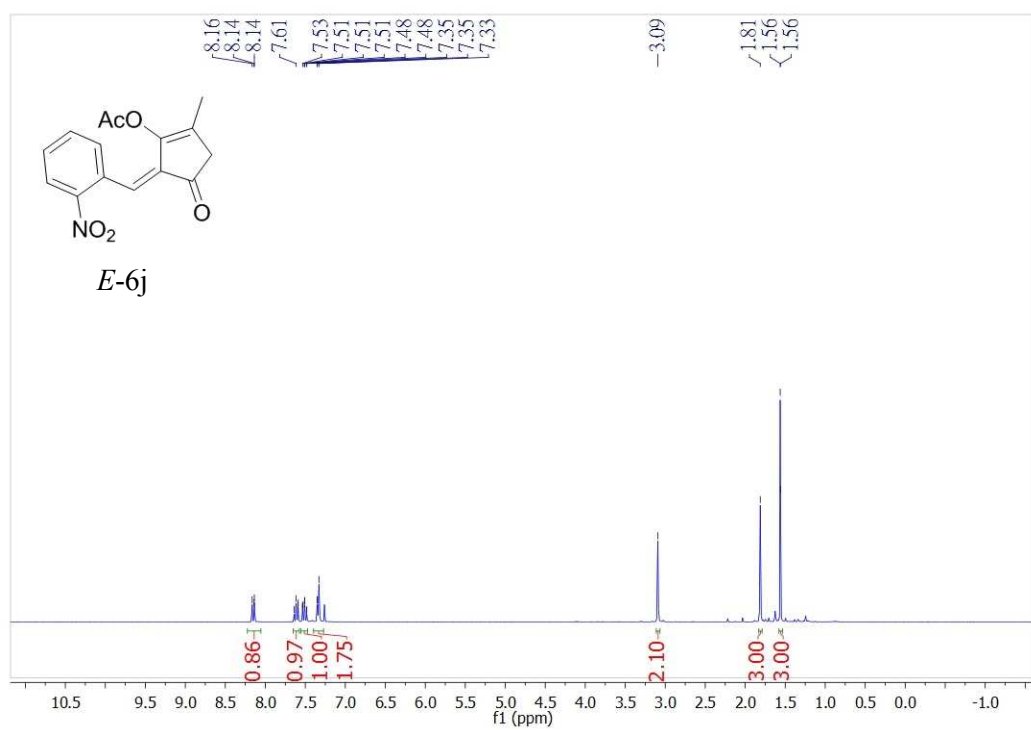
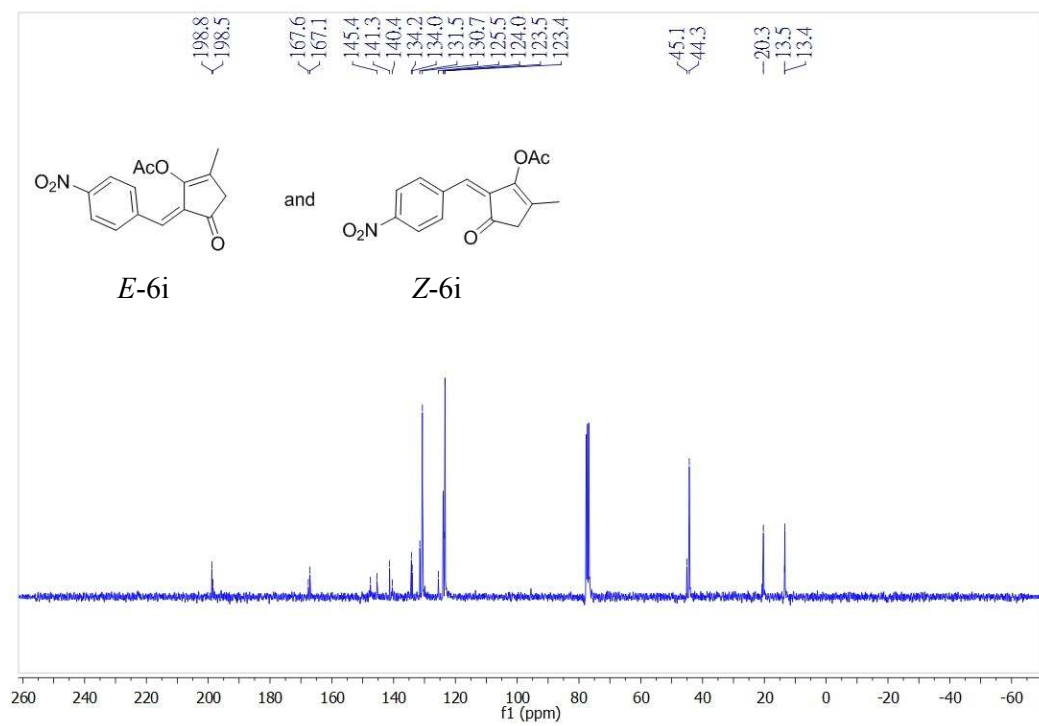


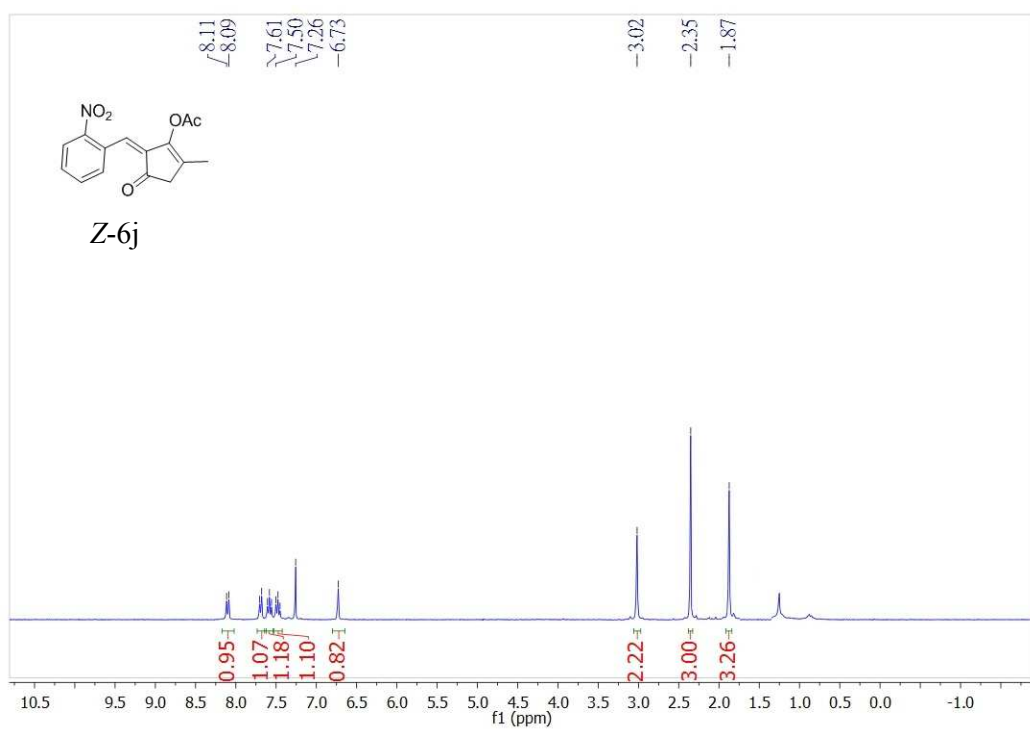
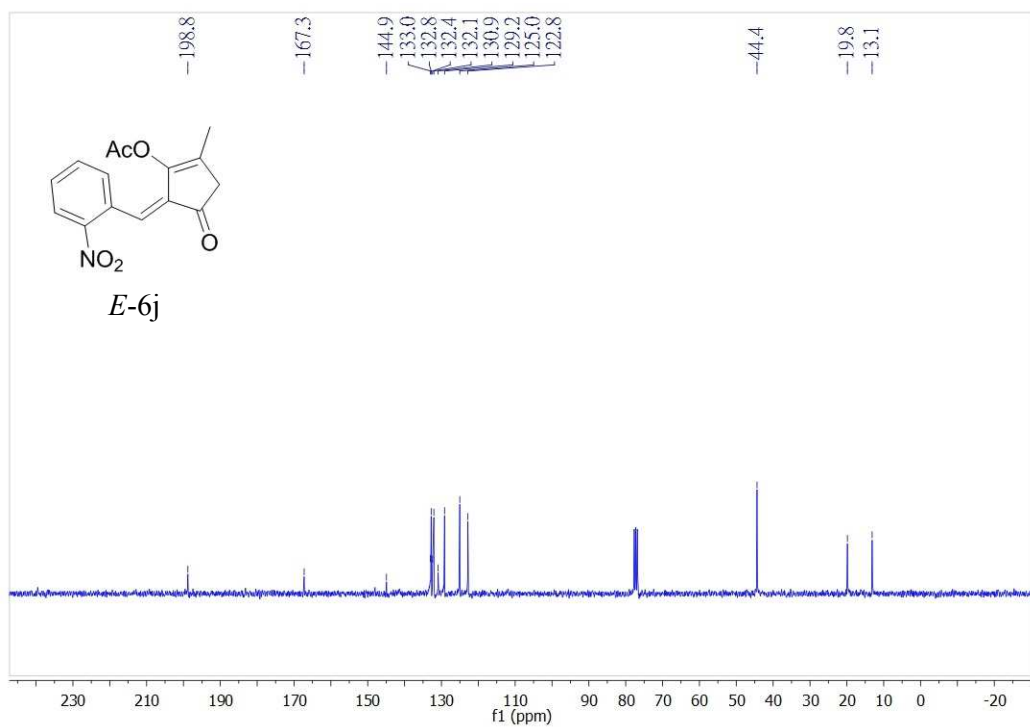


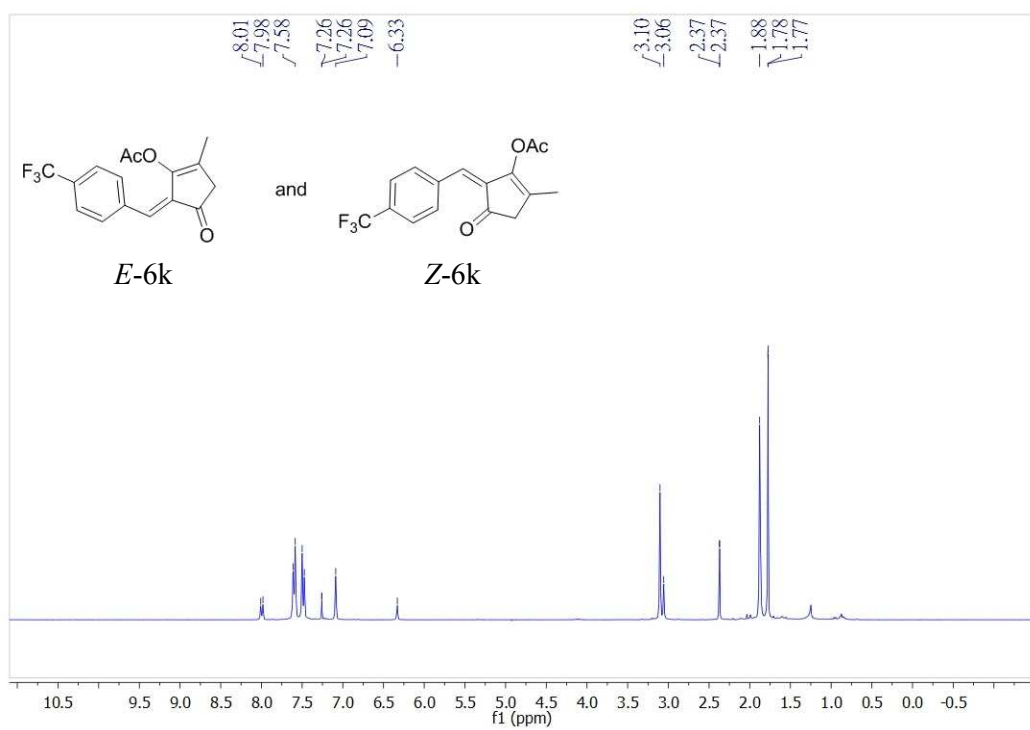
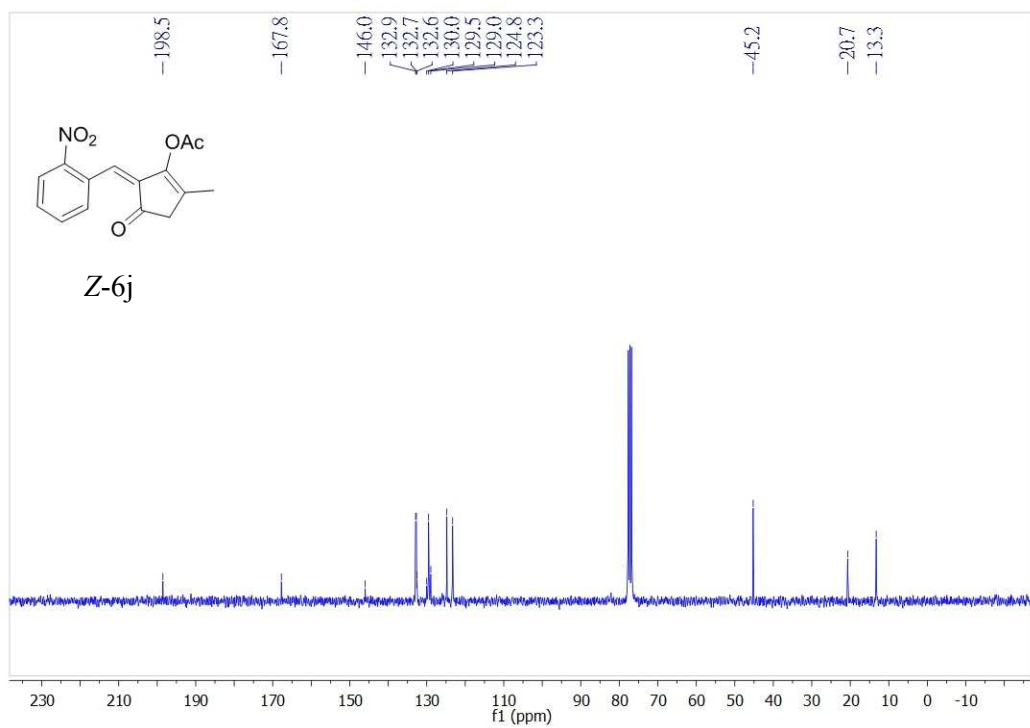


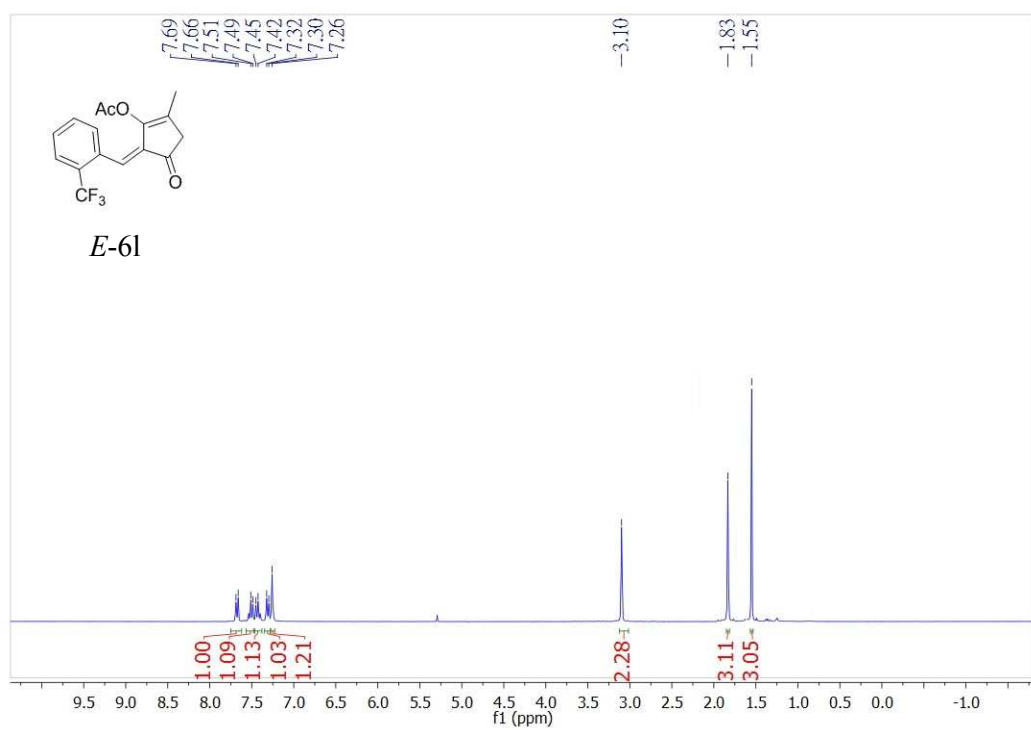
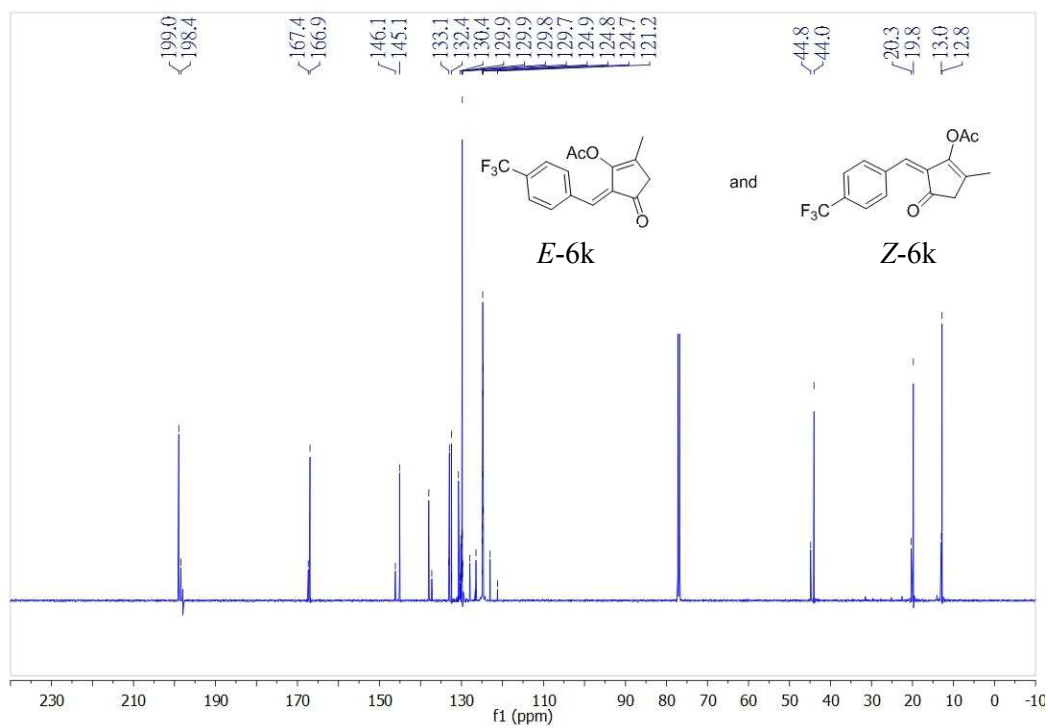


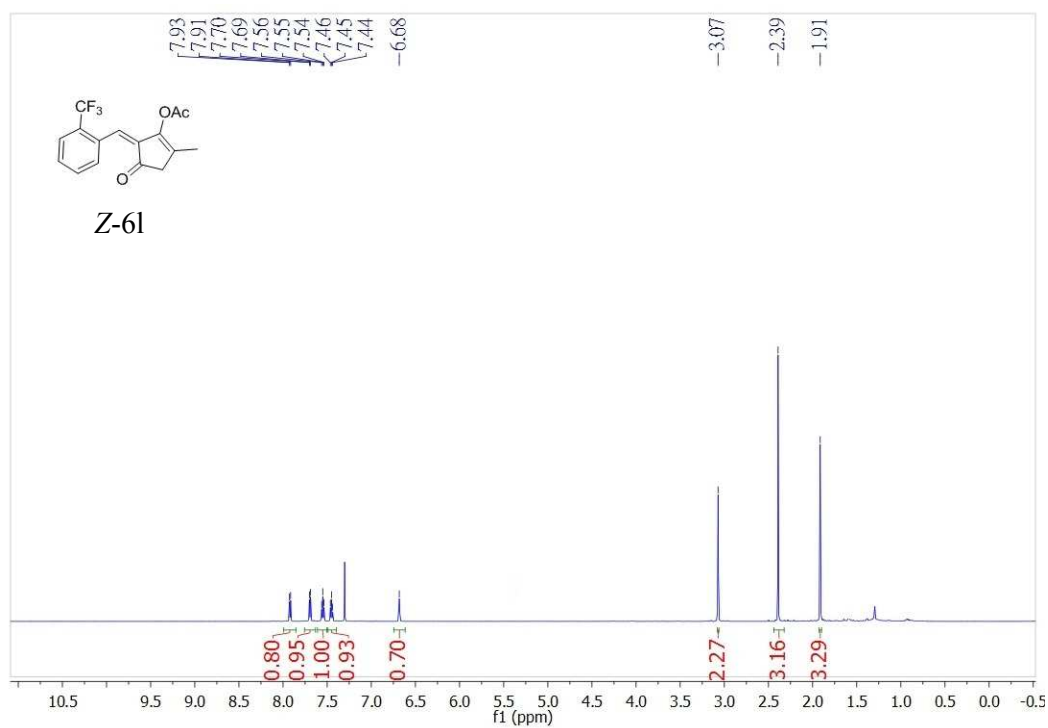
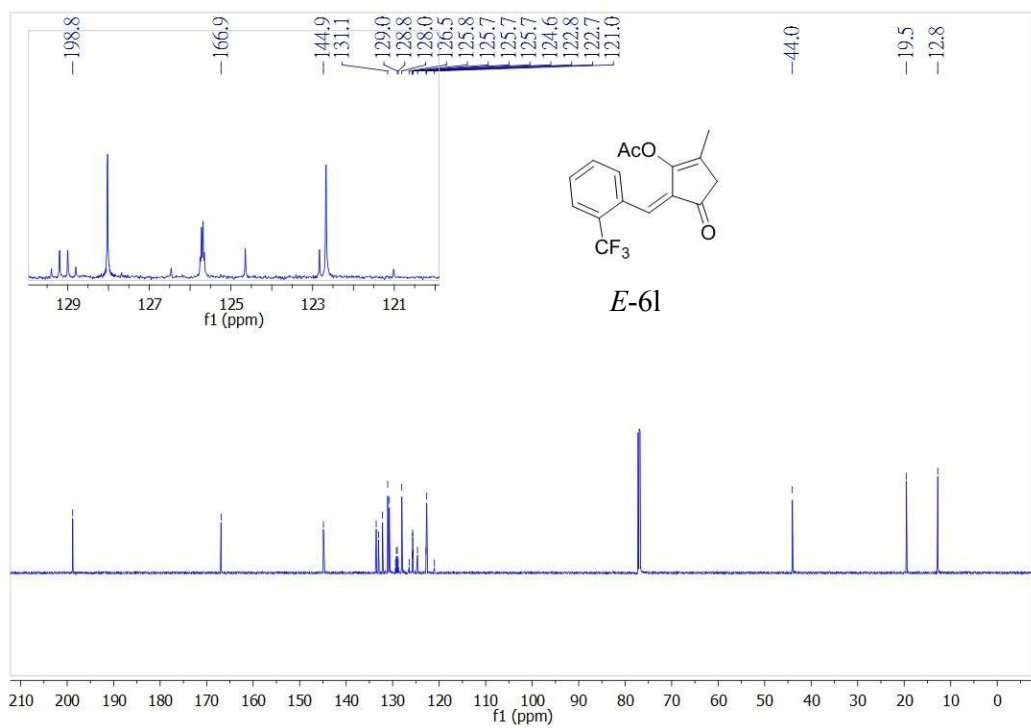


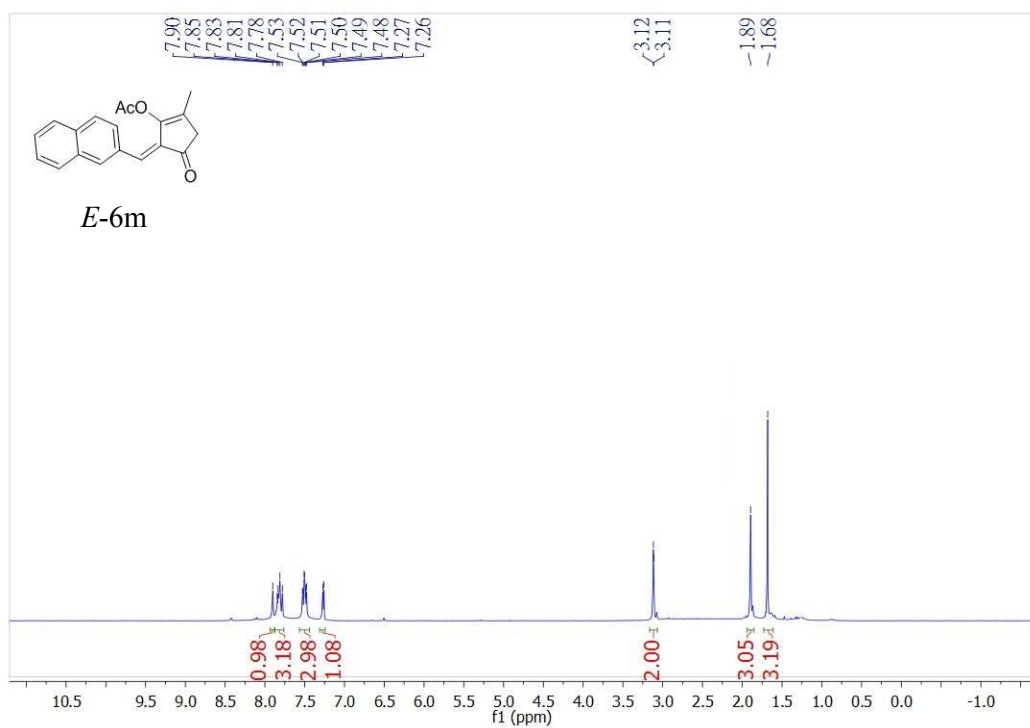
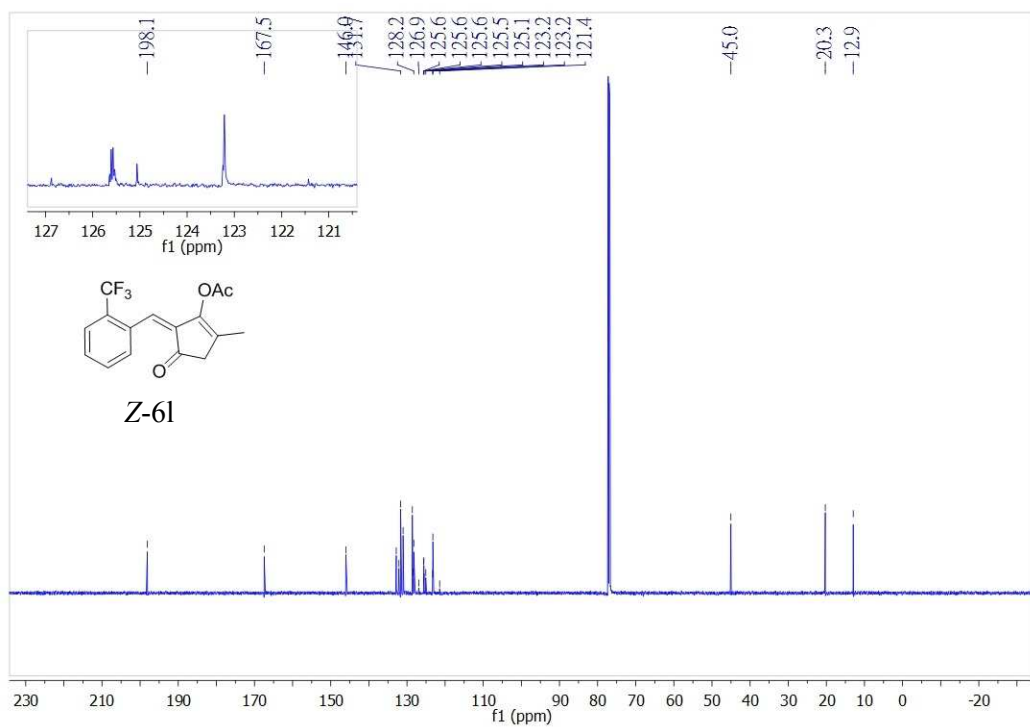


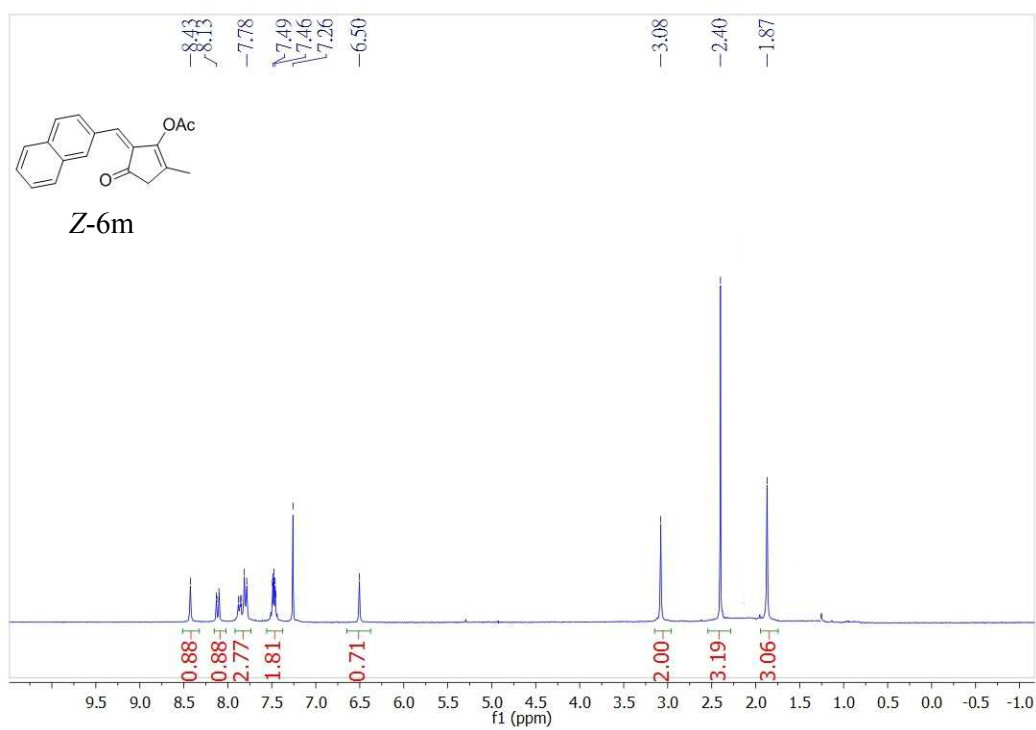
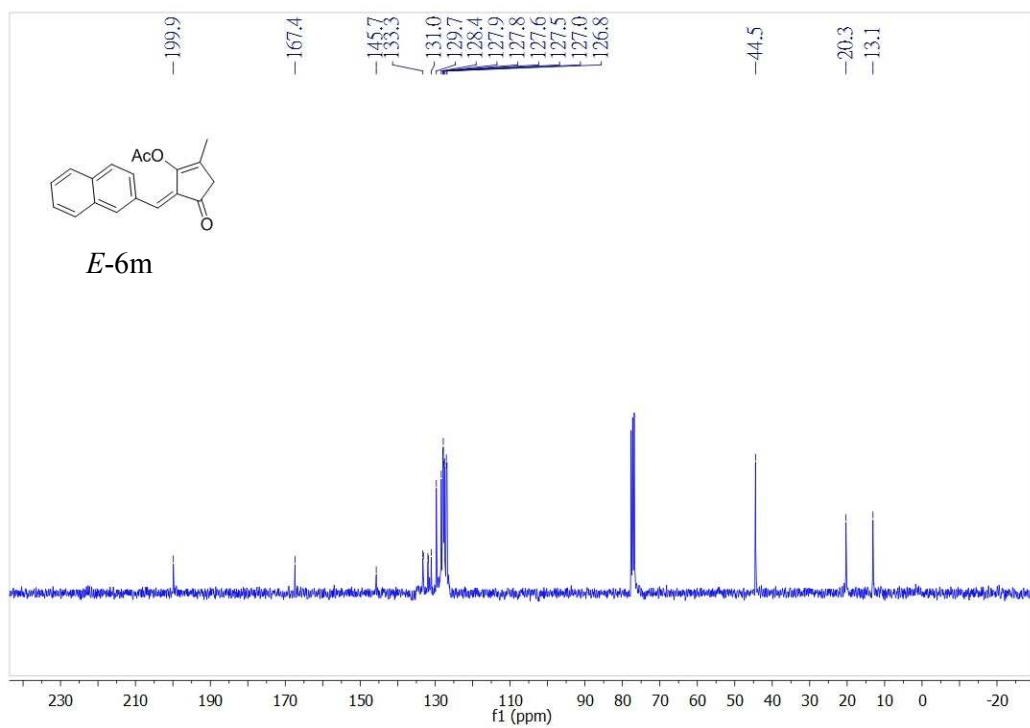


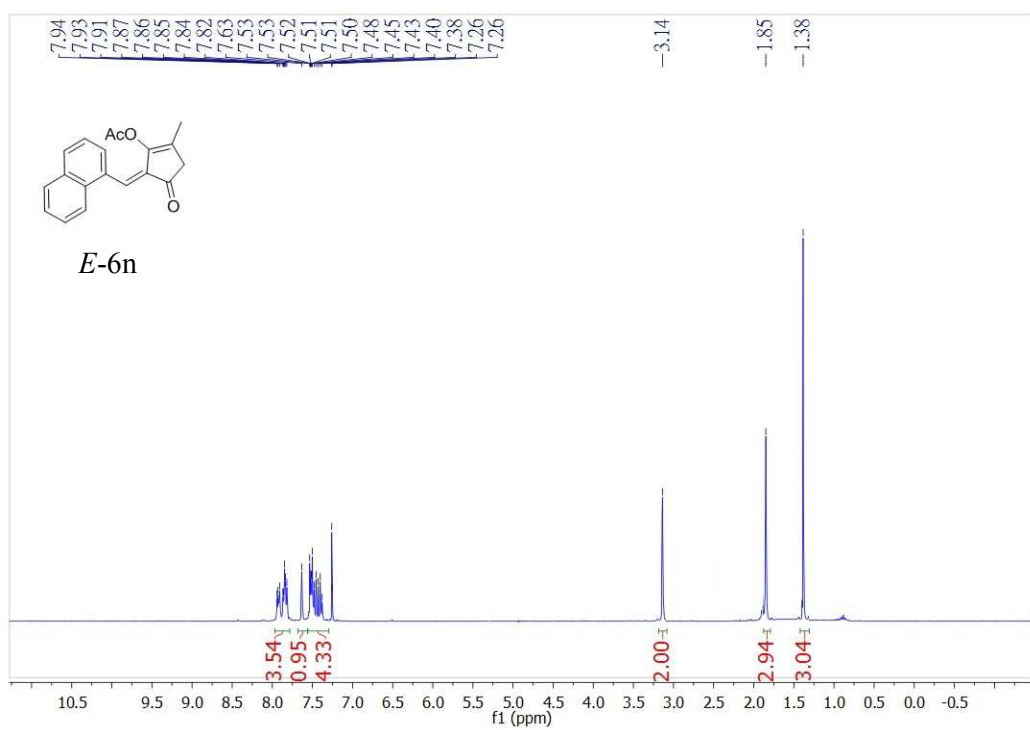
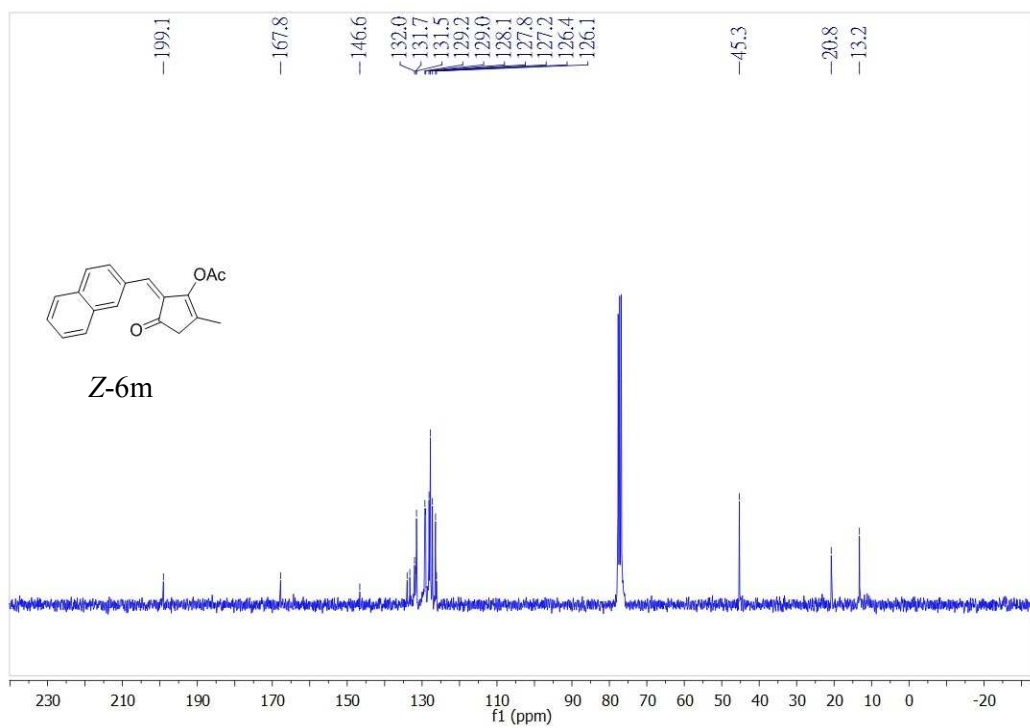


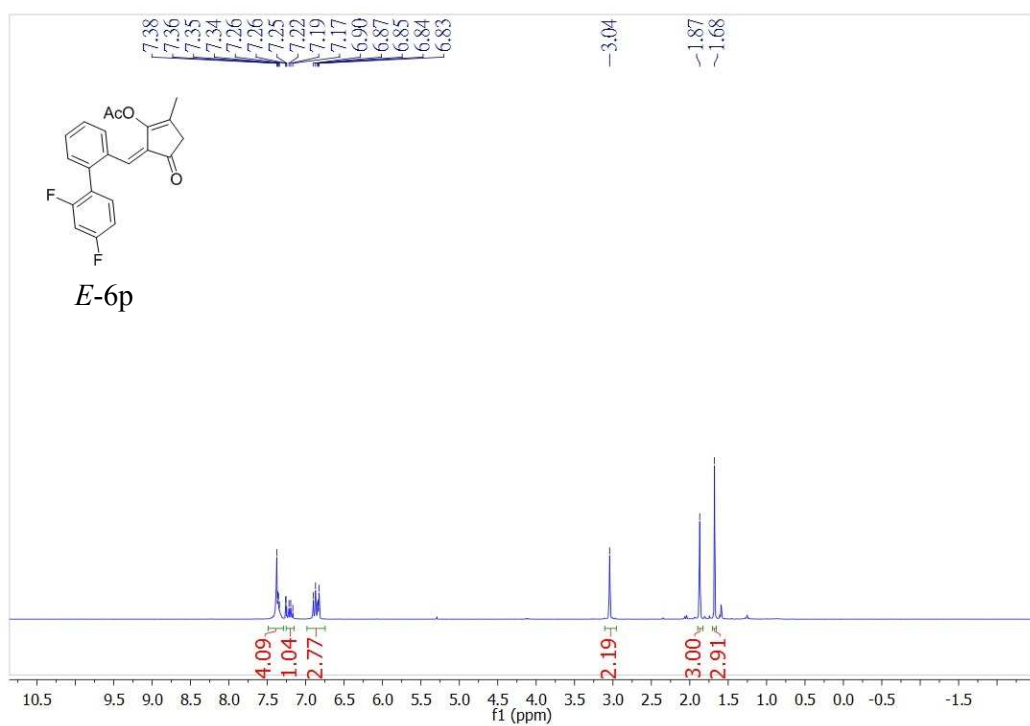
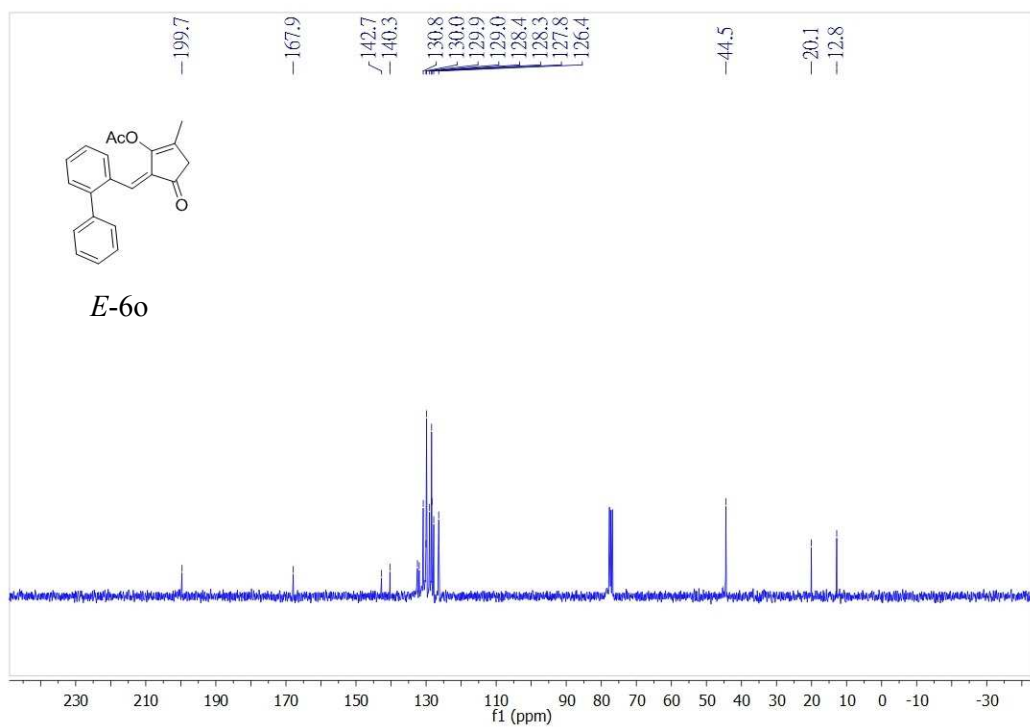


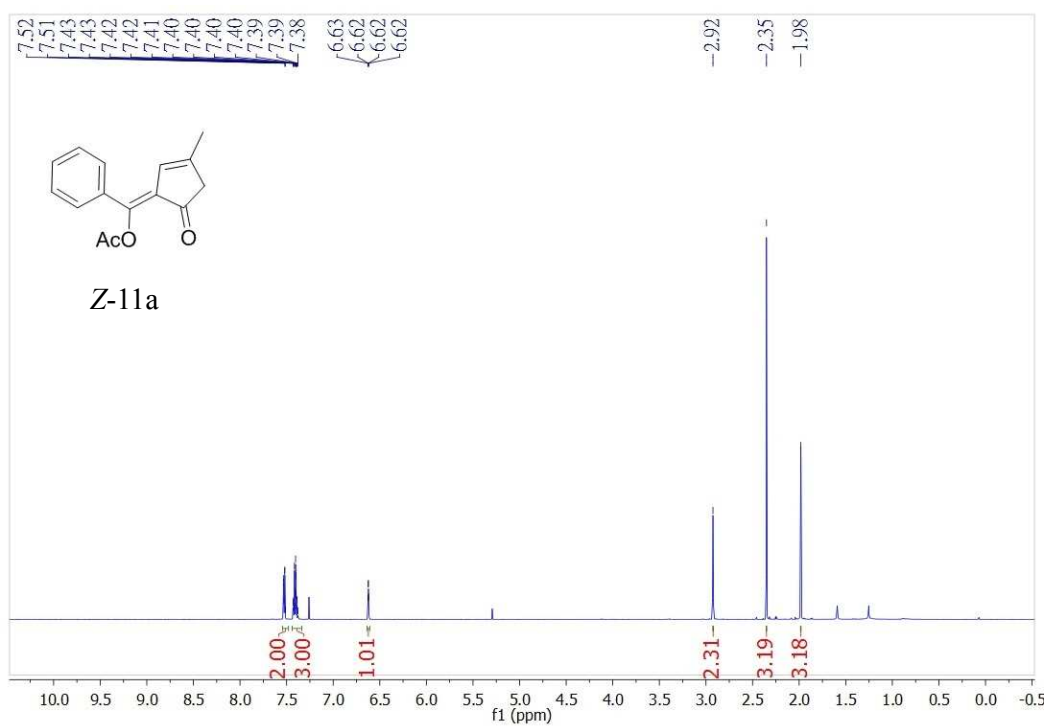
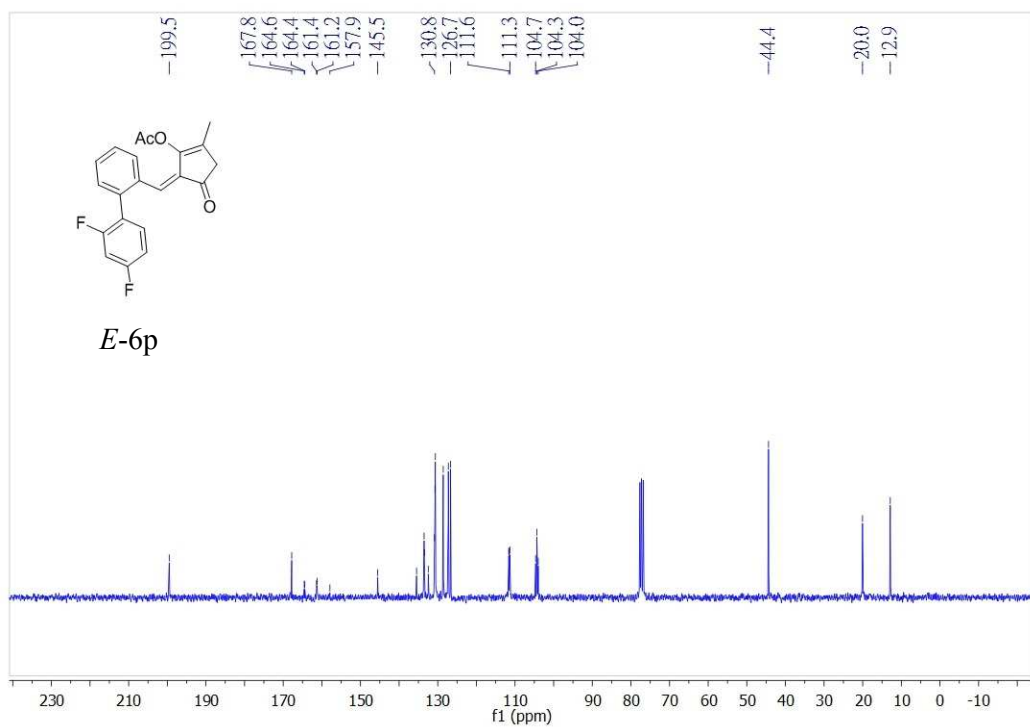


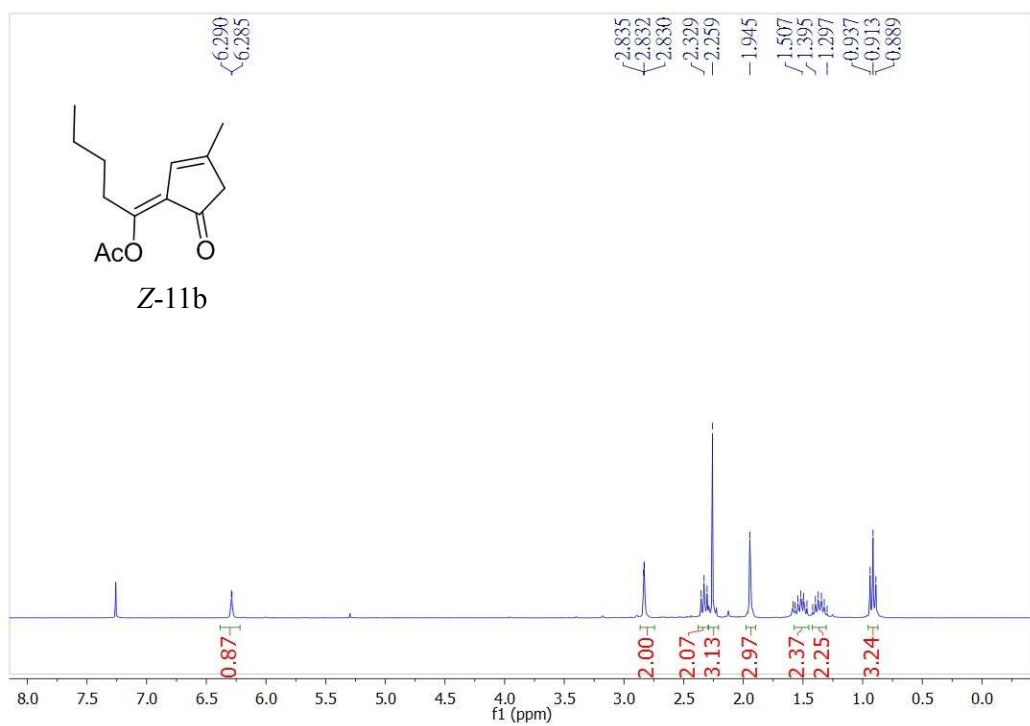
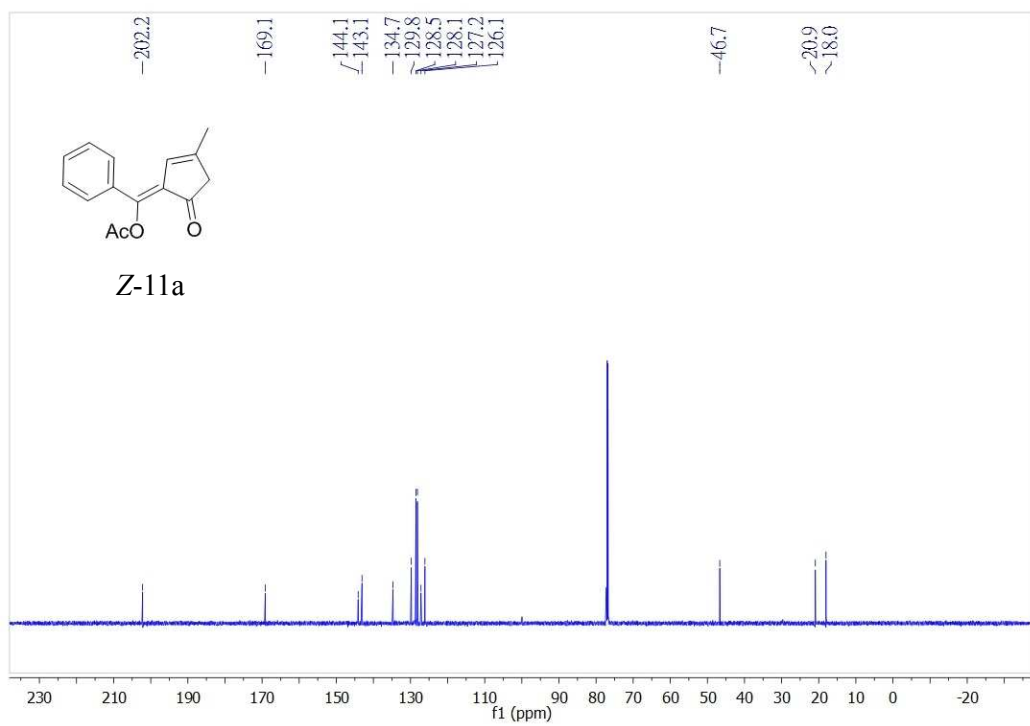


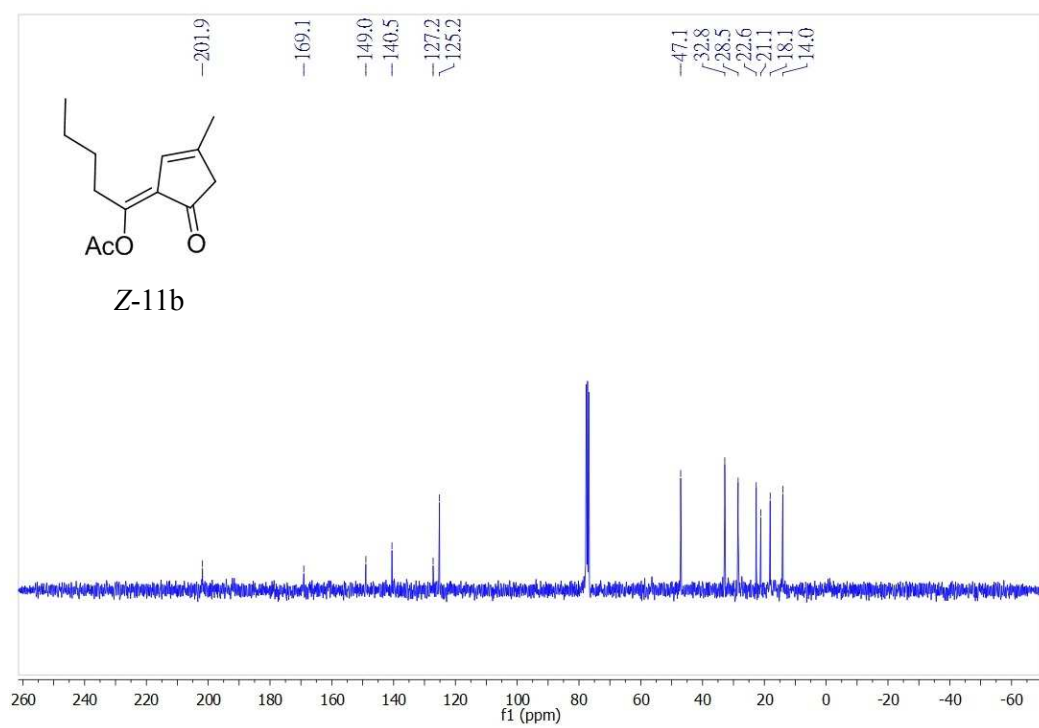






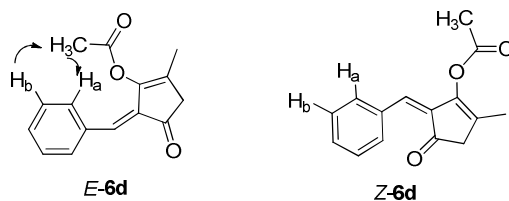




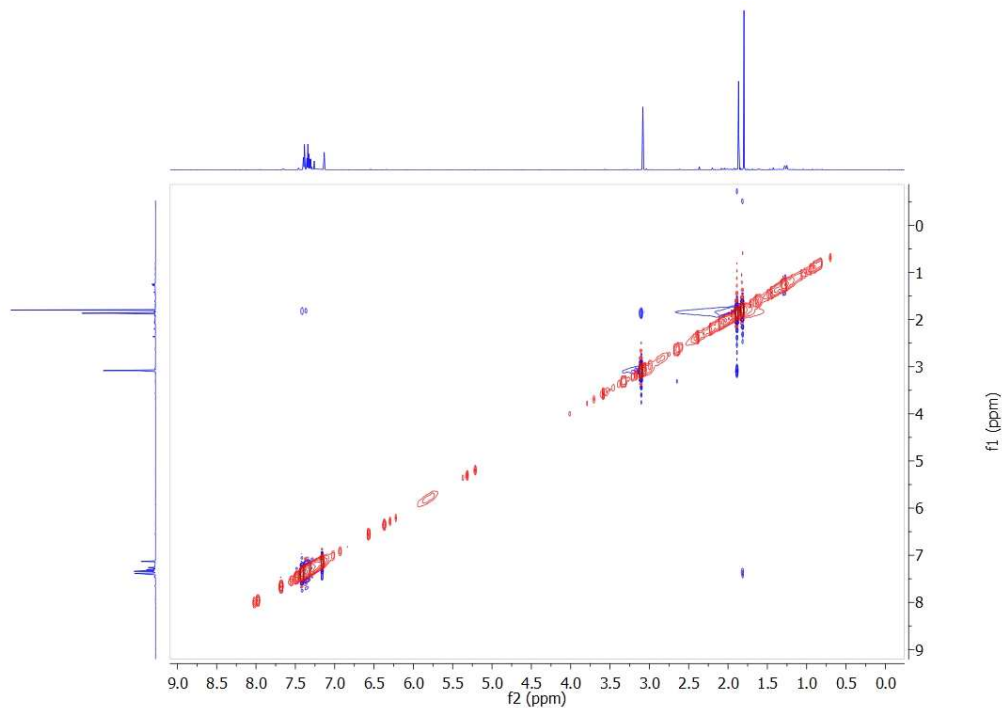


4. NOESY 2D NMR Spectra of *E*-6d (a) and *Z*-6d (b).

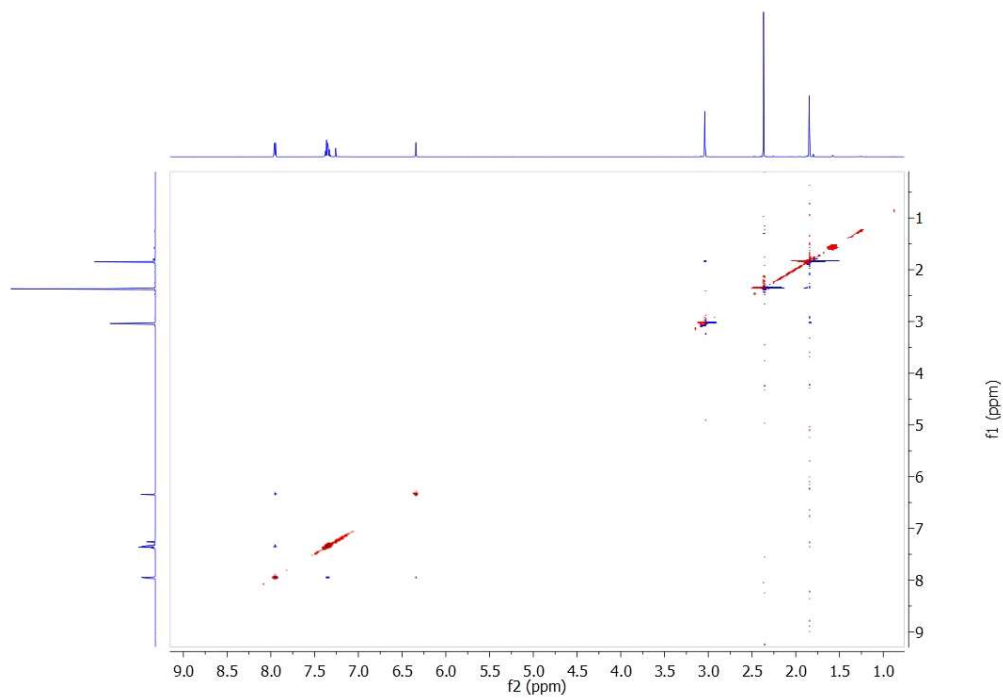
Following two figures (a) and (b) give the NOESY spectra of *E*- and *Z*-6d respectively which allow the determination of their stereochemistry. As shown in (a), NOE effects were observed for *E*-6d between the aromatic protons H_a and H_b at δ 7.35 and the AcO proton signal at δ 1.80. In contrast, (b) shows no NOE effect between the aromatic protons and the AcO protons for *Z*-6d.



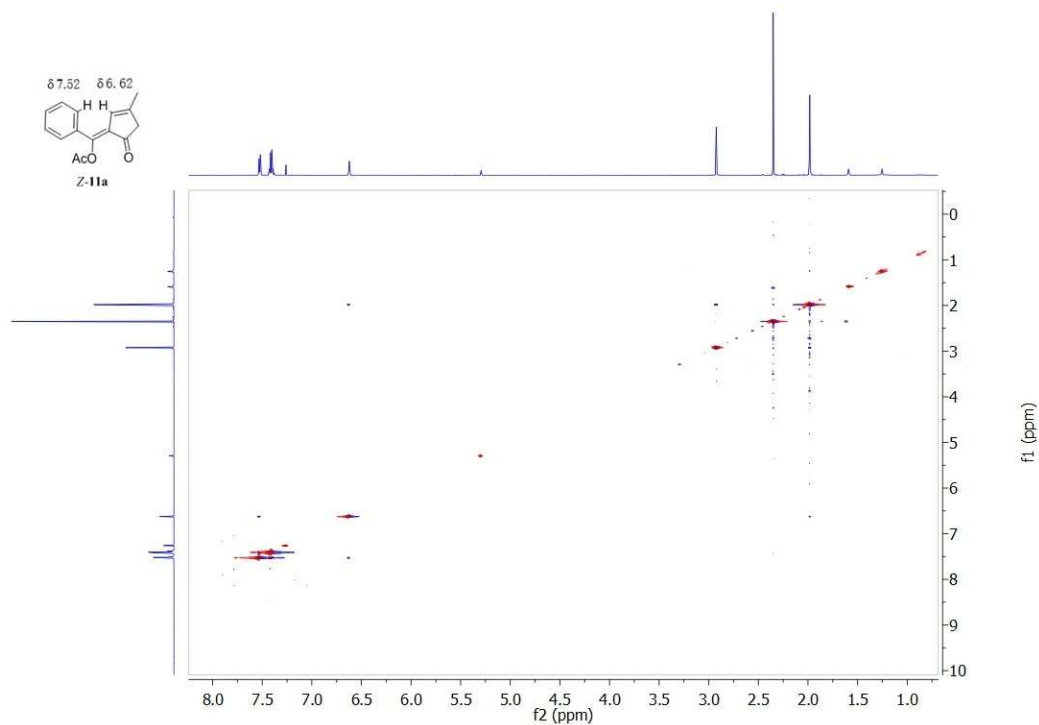
(a)



(b)



5. NOESY 2D Spectra NMR for cycloaddition products **Z-11a**



As shown in the figure, NOE effect was observed for **Z-11a** between the aromatic protons at δ 7.52 and vinyl proton at 6.62 on the cyclopentenone ring.

6. NMR spectra used to determine the *E-Z* ratio

