

Supplementary information for

**Regio- and stereoselective base-catalyzed assembly of 6-methylene-5-oxaspiro[2.4]heptanones from
alkynyl cyclopropyl ketones**

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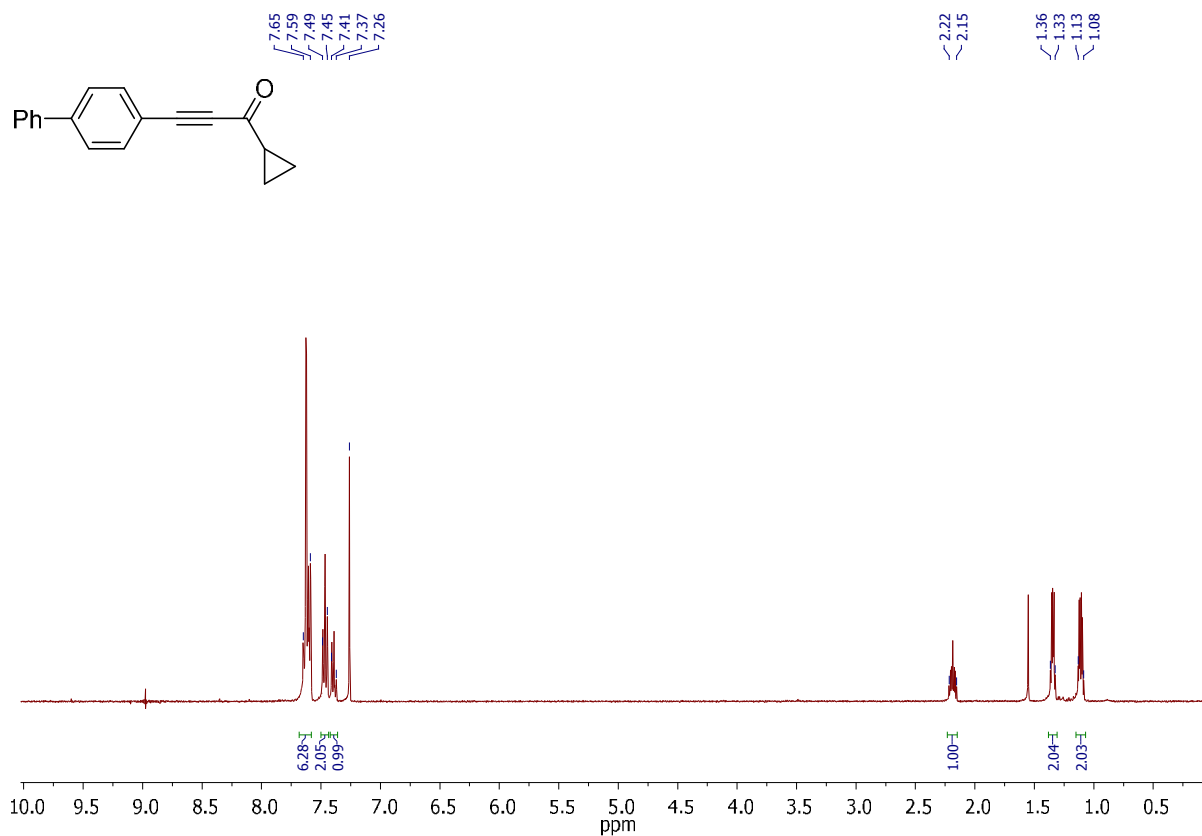
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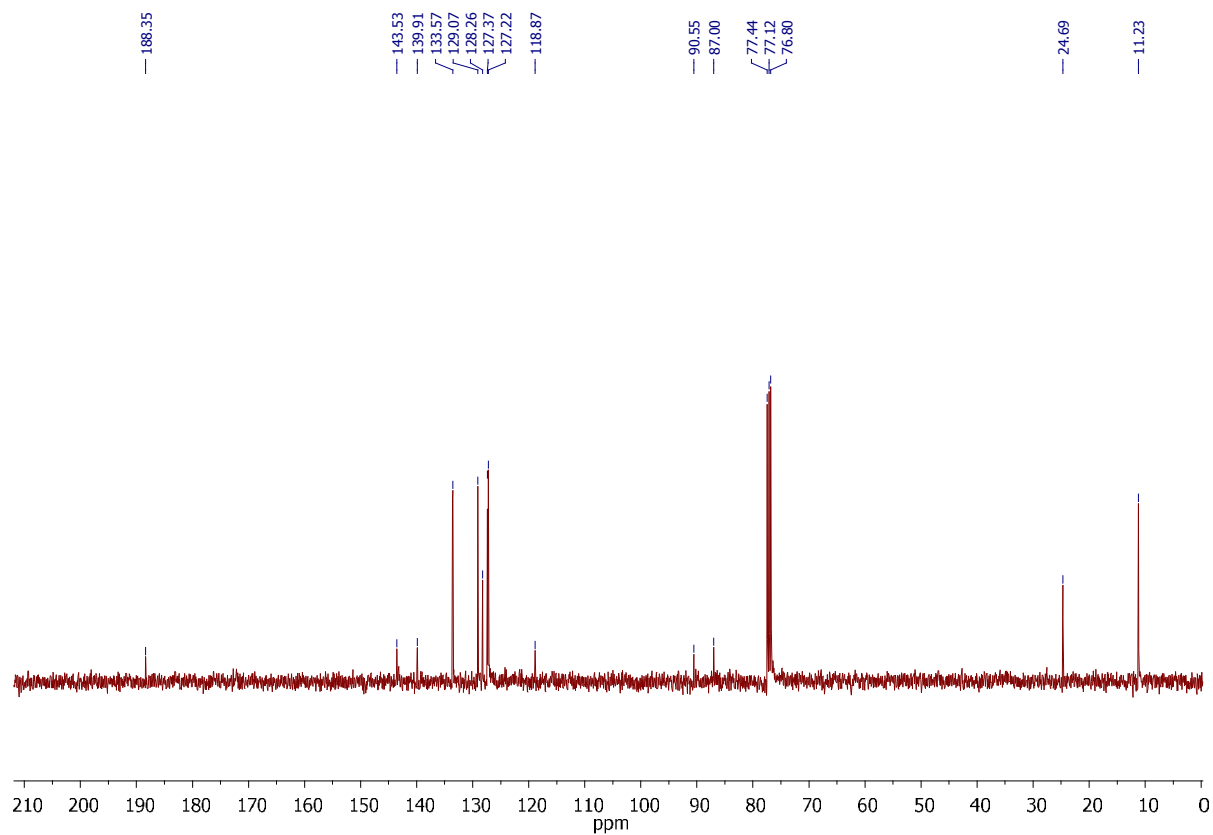
X-Ray diffraction analysis of 2e

The determination of the unit cell and the data collection for (*Z*)-6-(4-bromobenzylidene)-4-((4-bromophenyl)ethynyl)-4-cyclopropyl-5-oxaspiro[2.4]heptan-7-one (**2e**) was performed on a Bruker Venture D8 diffractometer with MoK α radiation ($\lambda = 0.71073$) at 273(2) K using the ω - ϕ scan technique. A specimen of C₂₄H₁₈Br₂O₂, approximate dimensions 0.34 mm x 0.26 mm x 0.24 mm, light, colorless, prism was obtained by evaporation of methanol solution and used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic cell with *P*2₁/*c* space group yielded a total of 19405 reflections to a maximum θ angle of 26.8° (0.79 Å resolution), of which 4568 were independent (completeness = 99.9%, R_{int} = 9.55%, R_{sig}=13.62%) and 20216 were greater than 2 σ (F₂). The final cell constants of **a** = 10.087(3) Å, **b** = 24.117(7) Å, **c** = 10.137(3) Å, β =119.385(8)°, Z=4, volume = 2148.7(11) Å³. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.5685. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.980 and 0.986. The structure was solved and refined using the Bruker SHELXTL Software Package¹ and refined using the OLEX2.² The H atoms were determined by rider method. The final anisotropic full-matrix least-squares refinement on F₂ with 261 variables converged at R₁ = 6.94%, for the observed data and wR₂ = 13.45% for all data. The goodness-of-fit was 1.02. The largest peak in the final difference electron density synthesis was 0.44 e⁻/Å³ and the largest hole was -0.38 e⁻/Å³. On the basis of the final model, the calculated density was 1.540 g/cm³ and F(000), 992 e⁻. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC **2159542**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

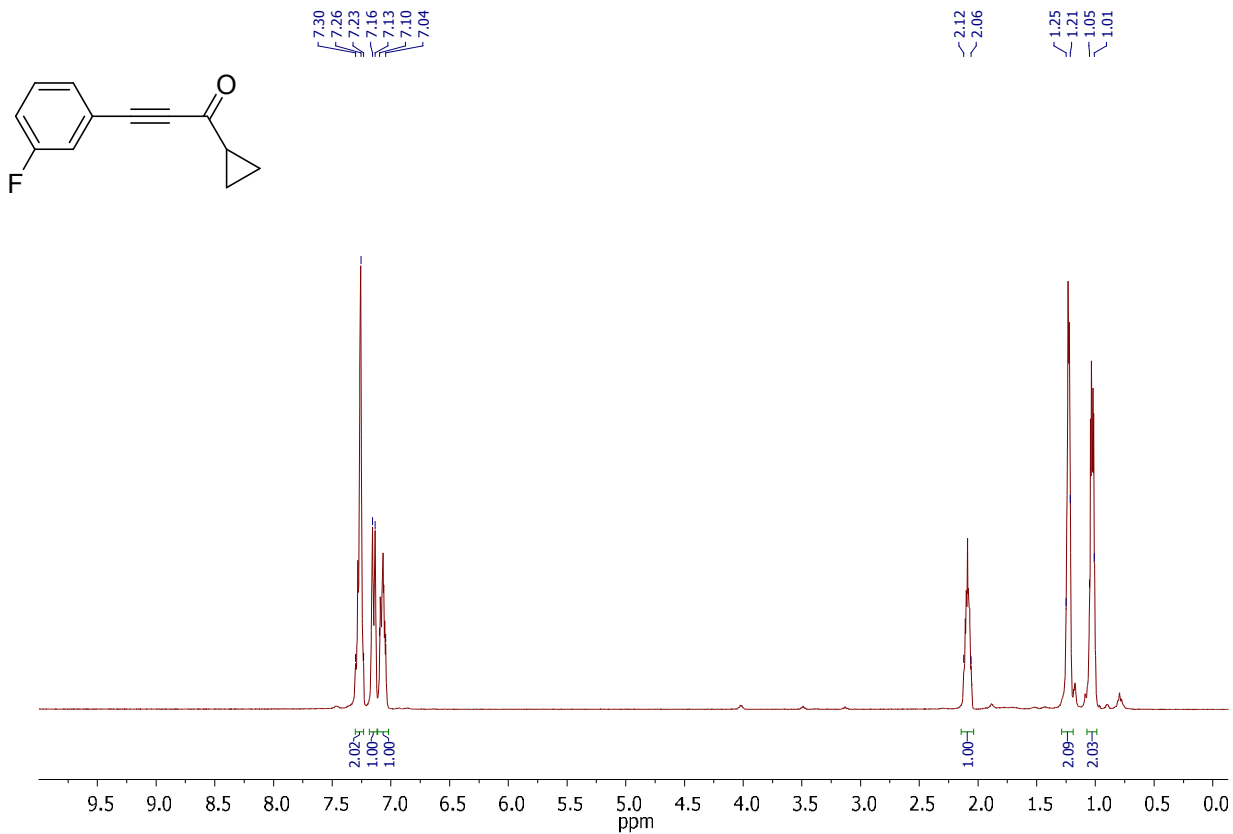
^1H and ^{13}C Spectra of alkynyl cyclopropyl ketones **1**



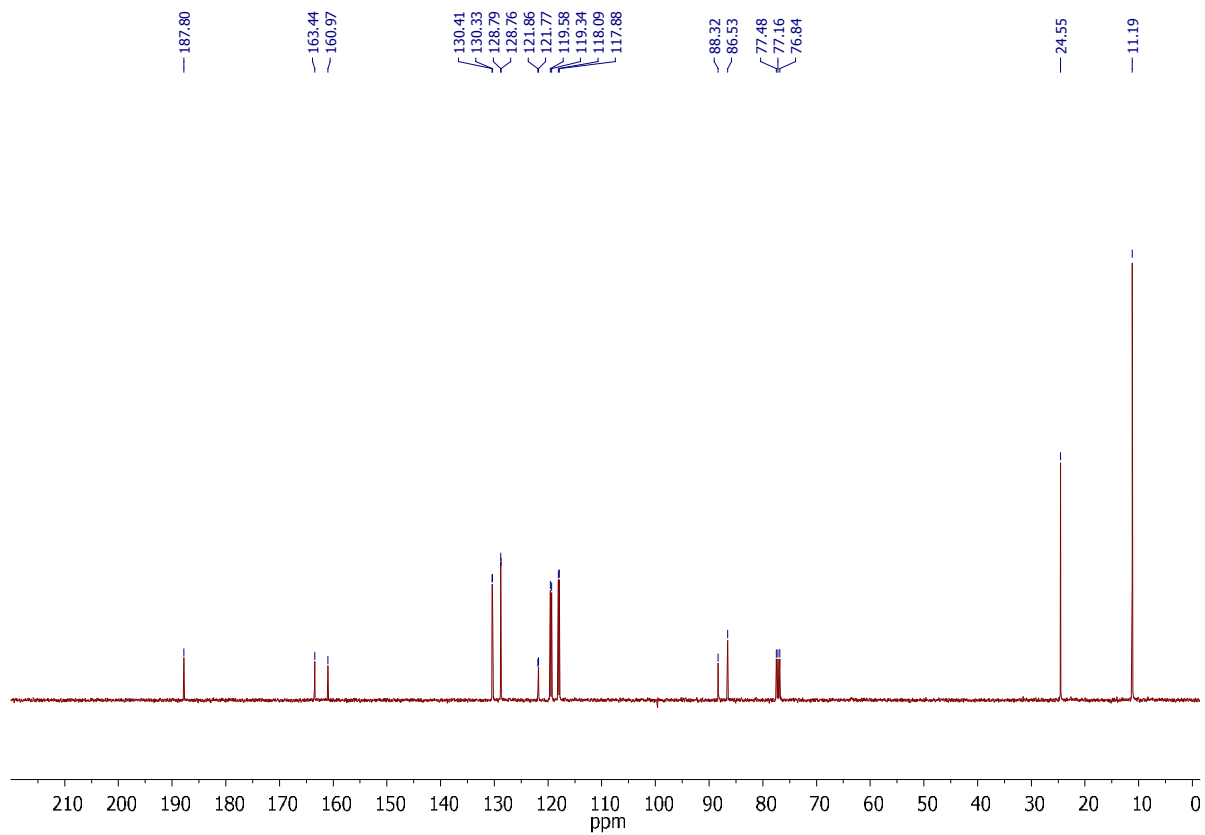
^1H NMR spectrum of **1c** (400.1 MHz, CDCl_3)



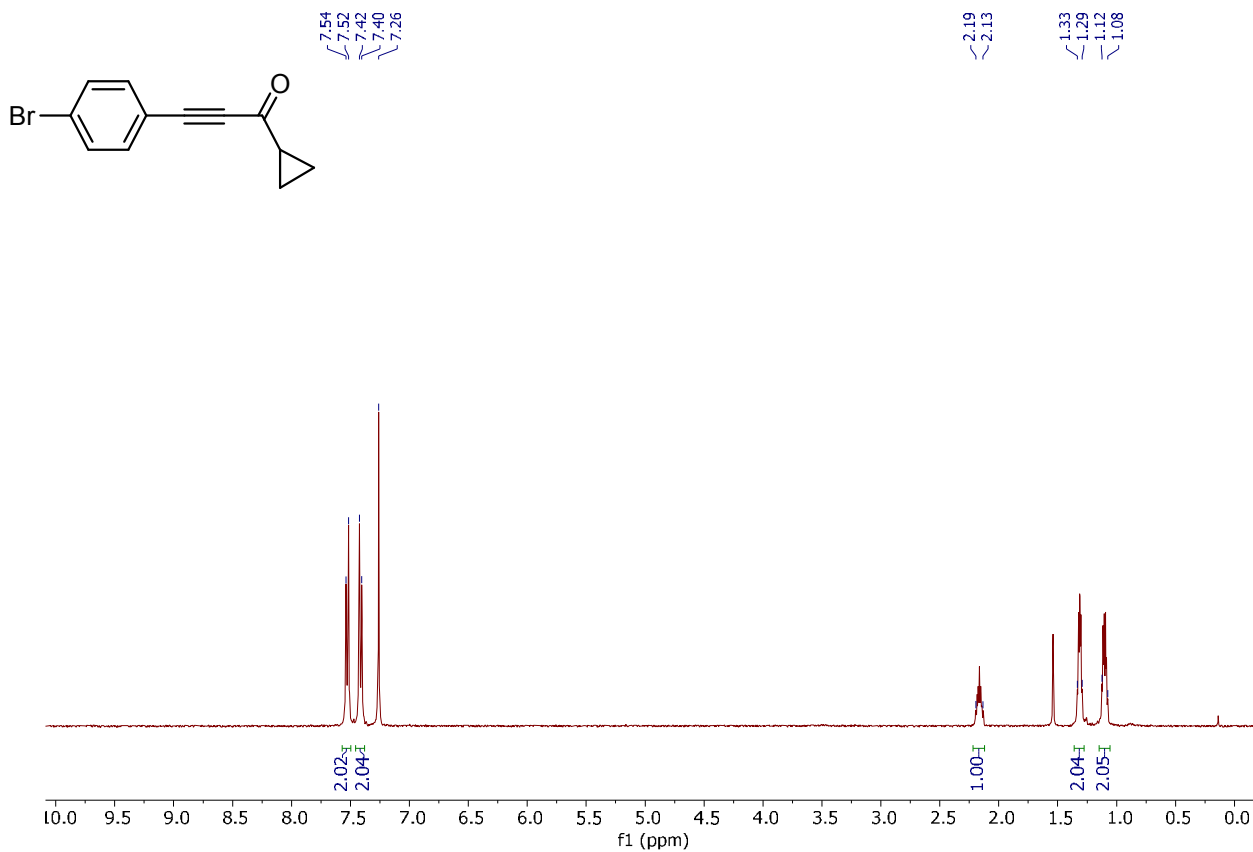
^{13}C NMR spectrum of **1c** (100.6 MHz, CDCl_3)



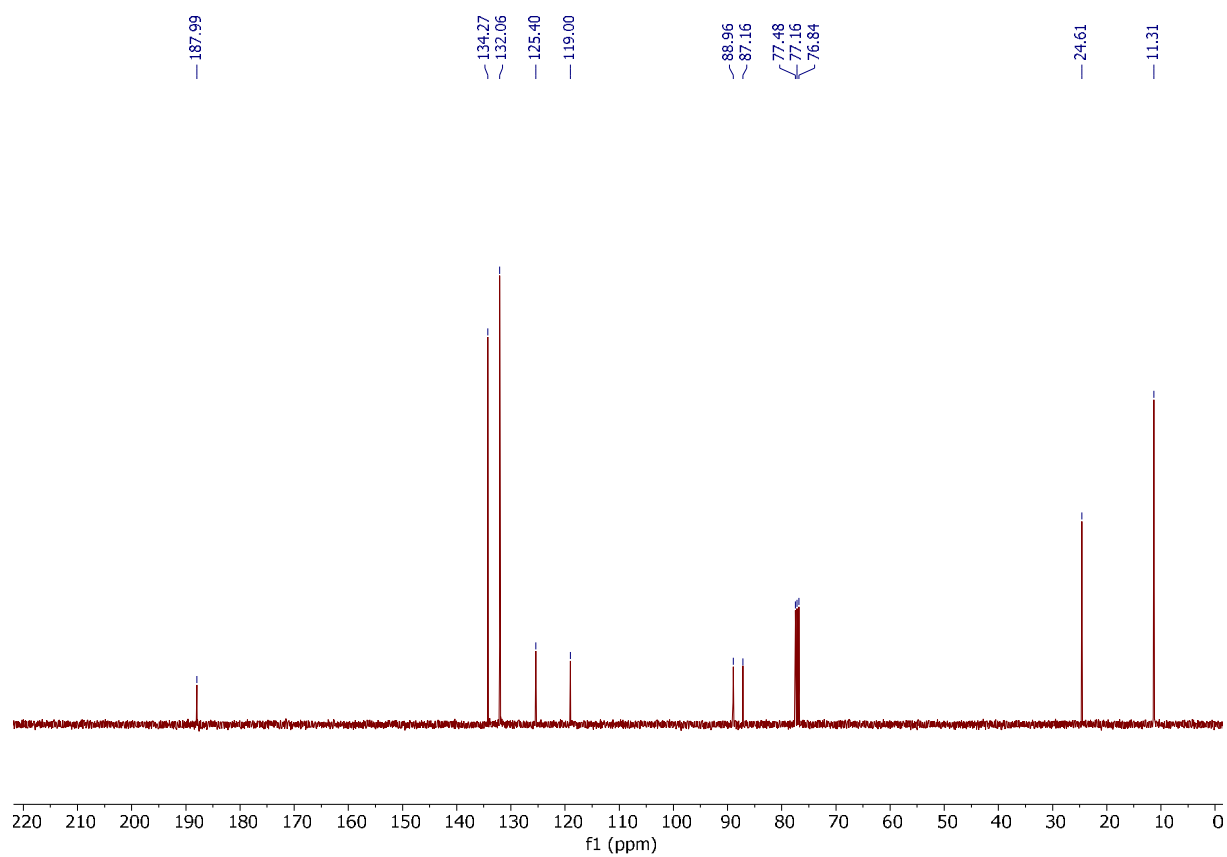
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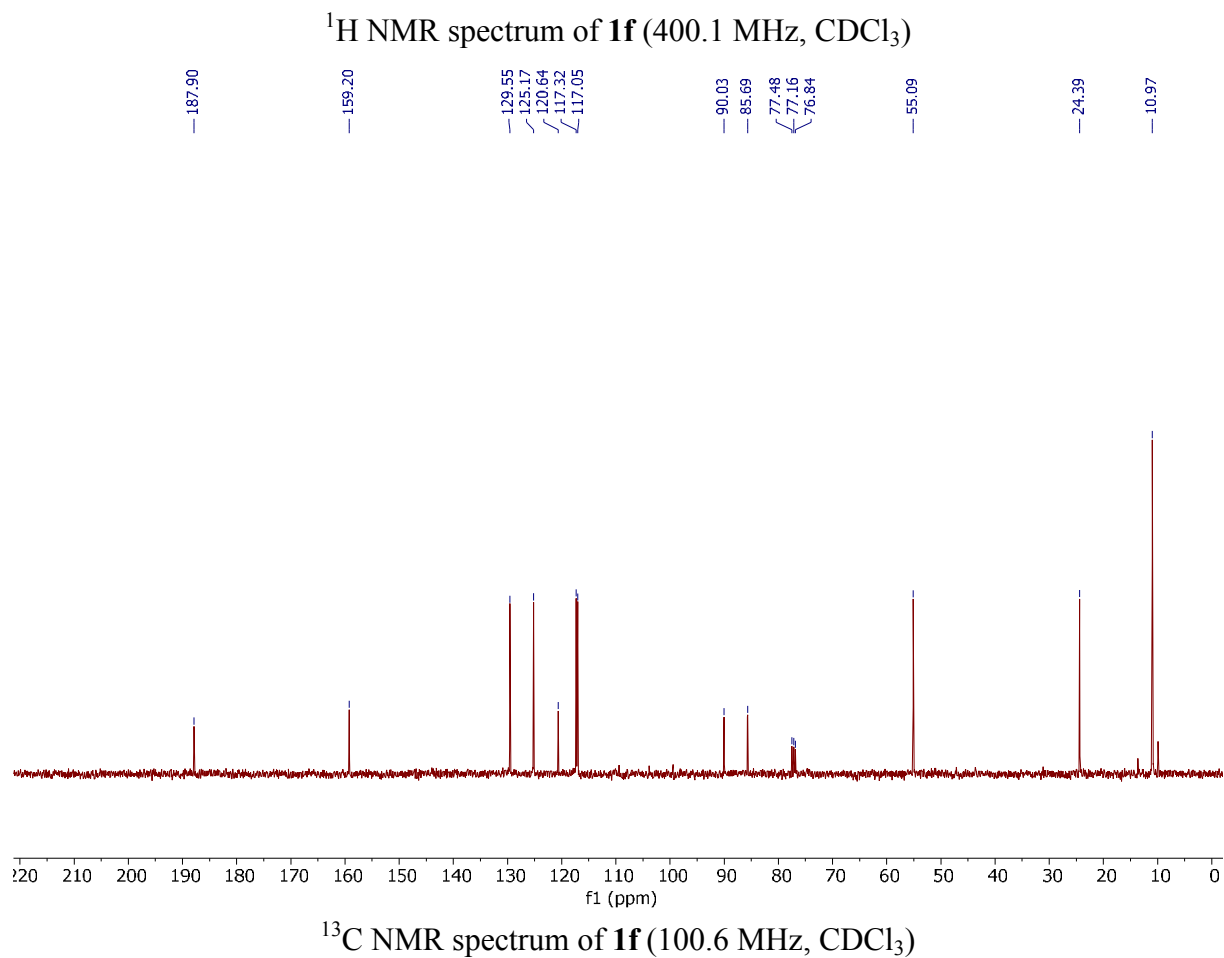
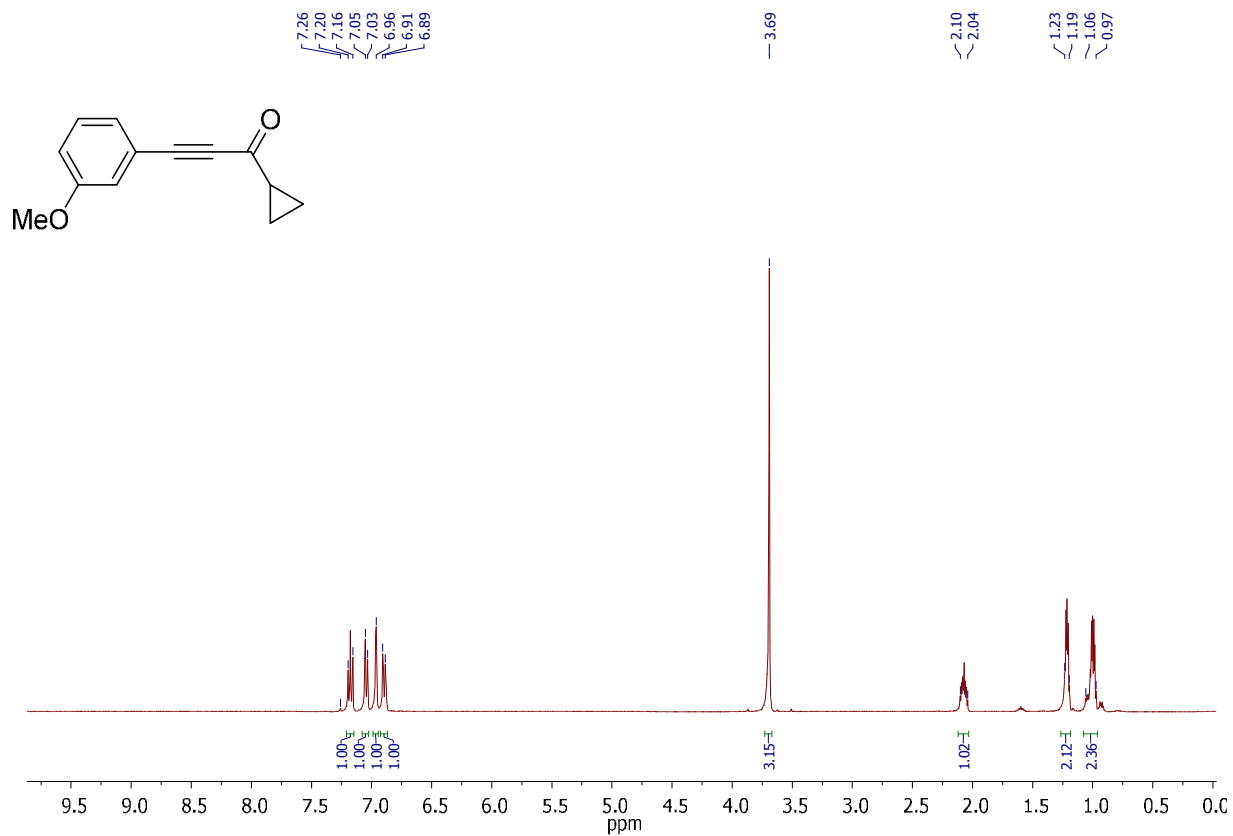
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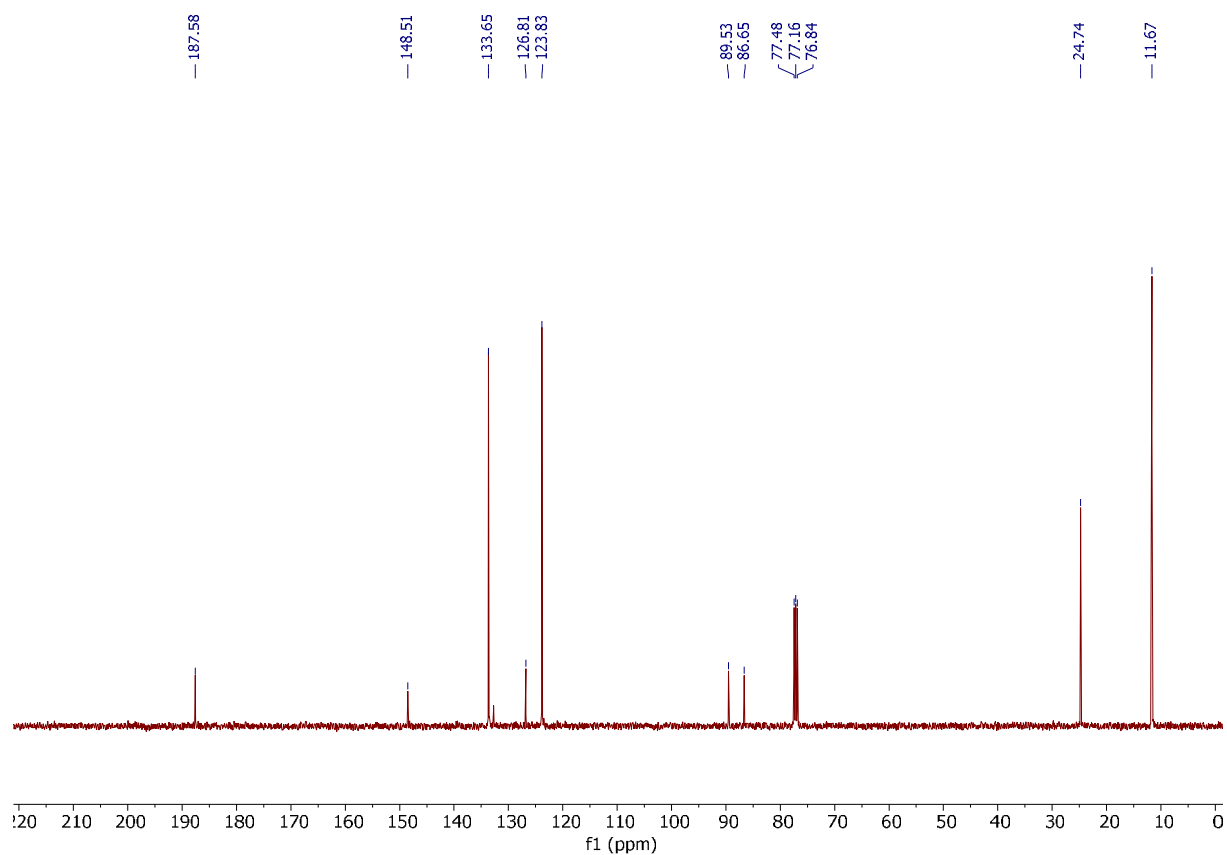
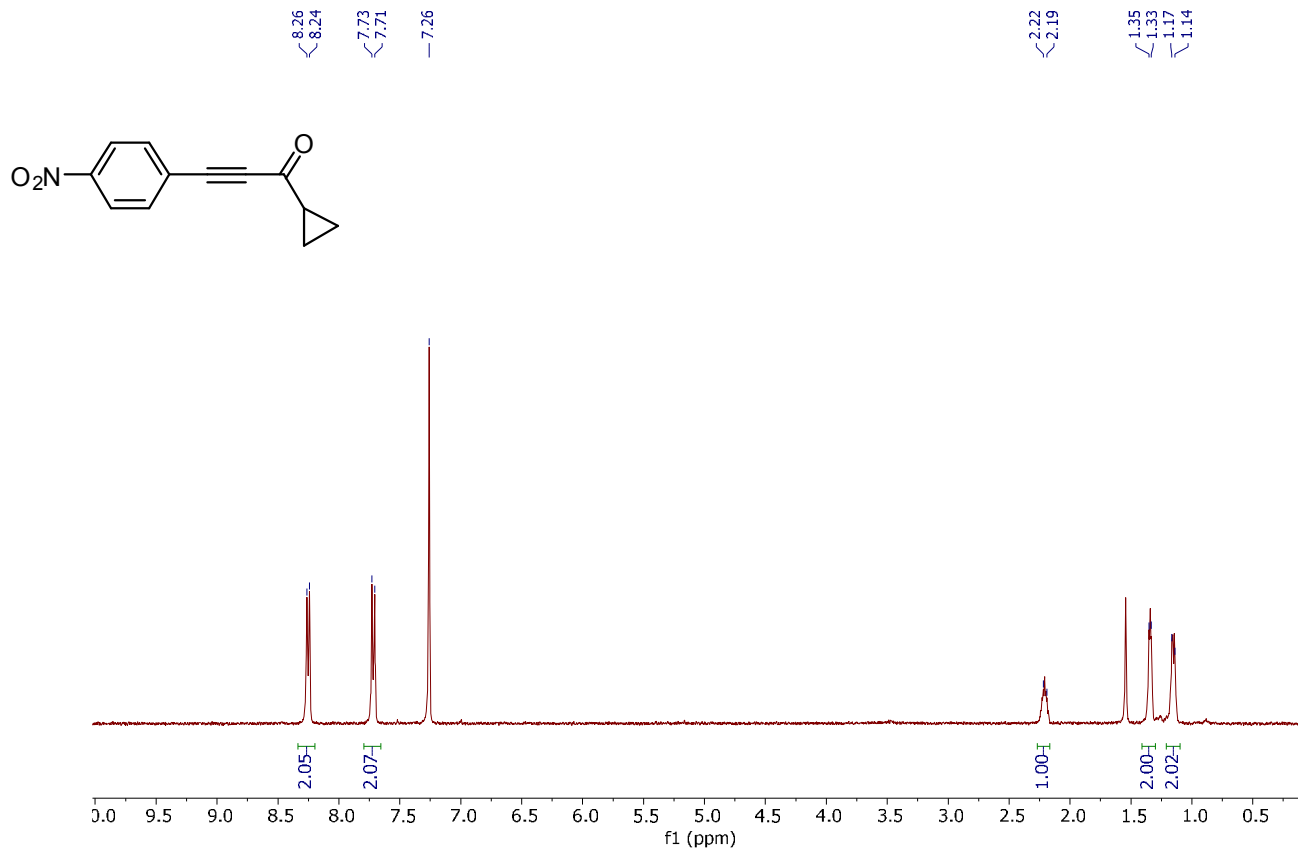


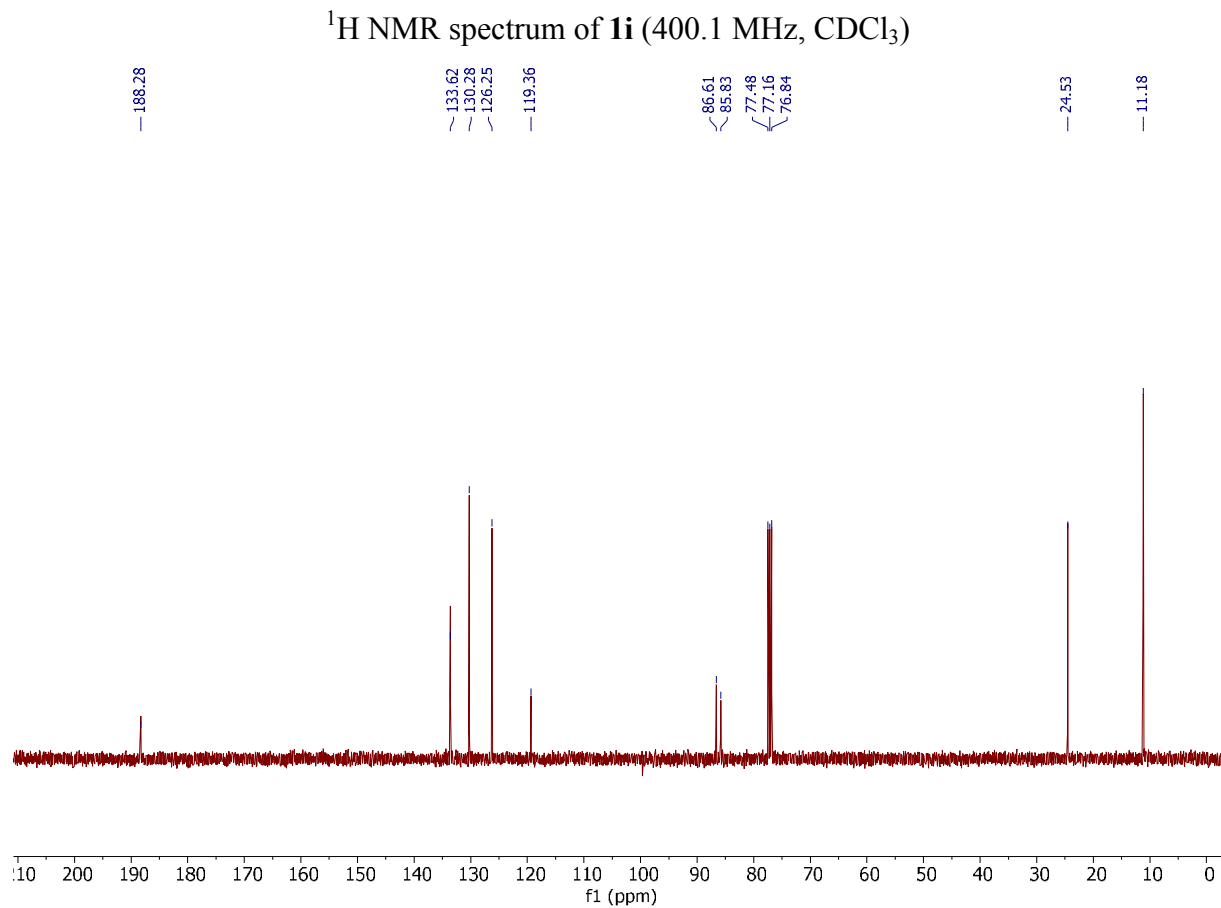
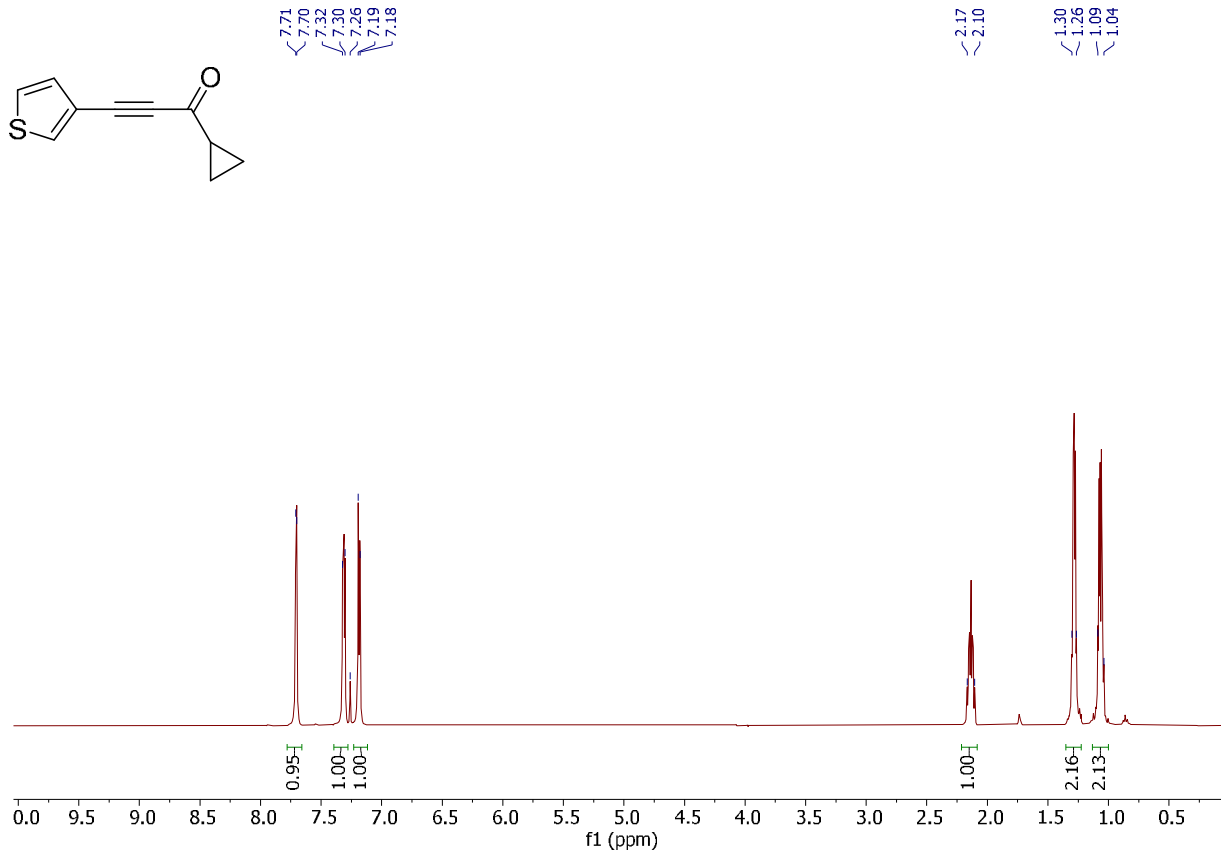
¹H NMR spectrum of **1e** (400.1 MHz, CDCl₃)

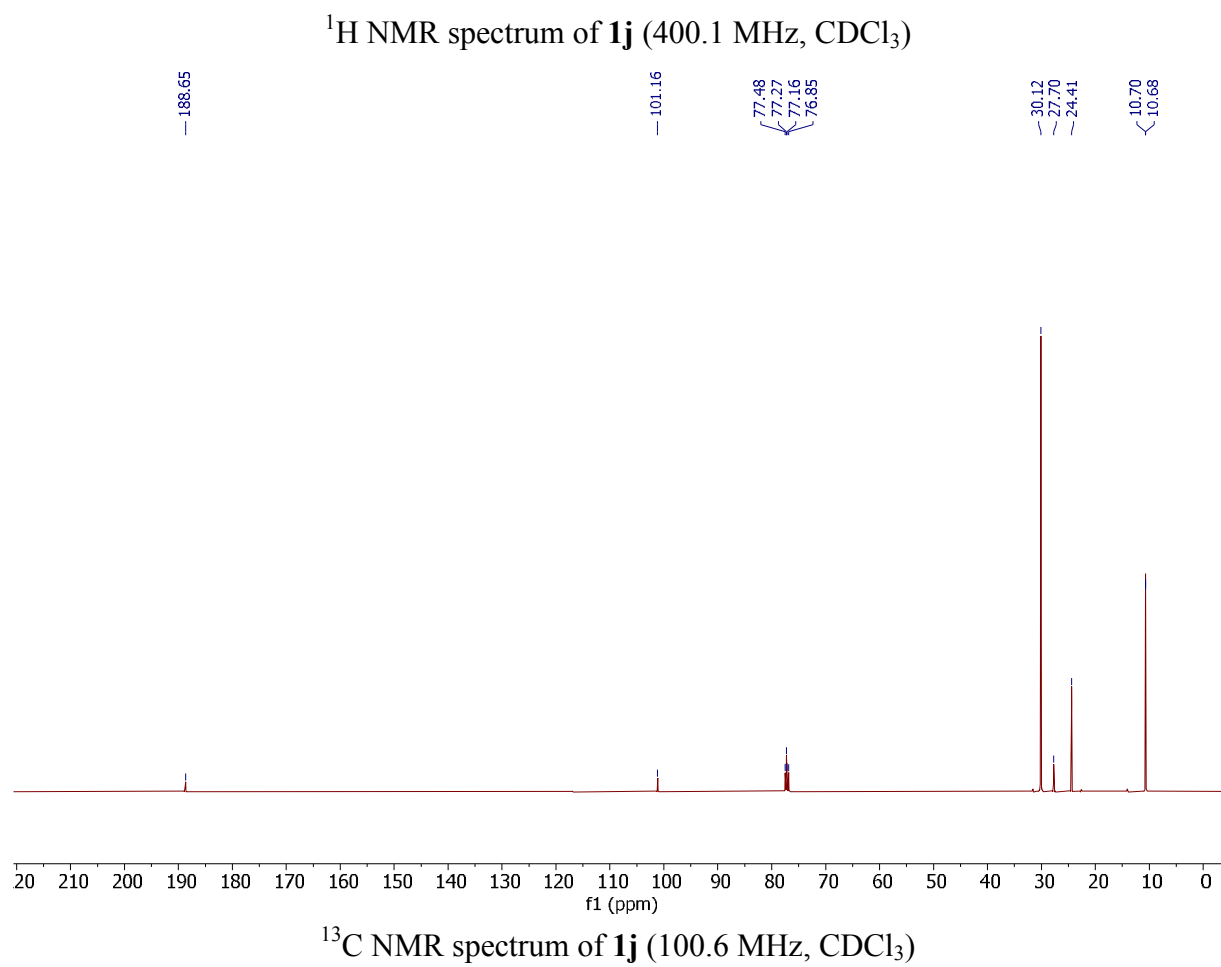
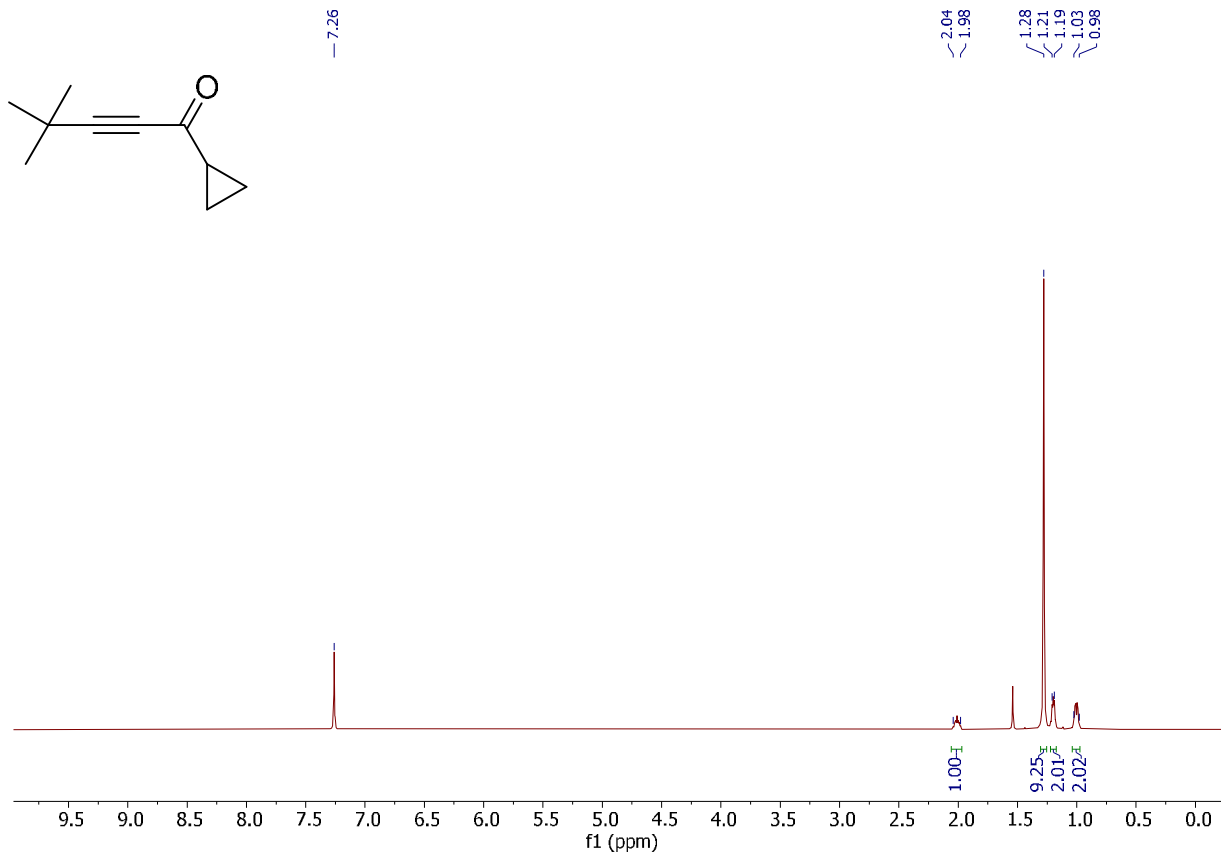


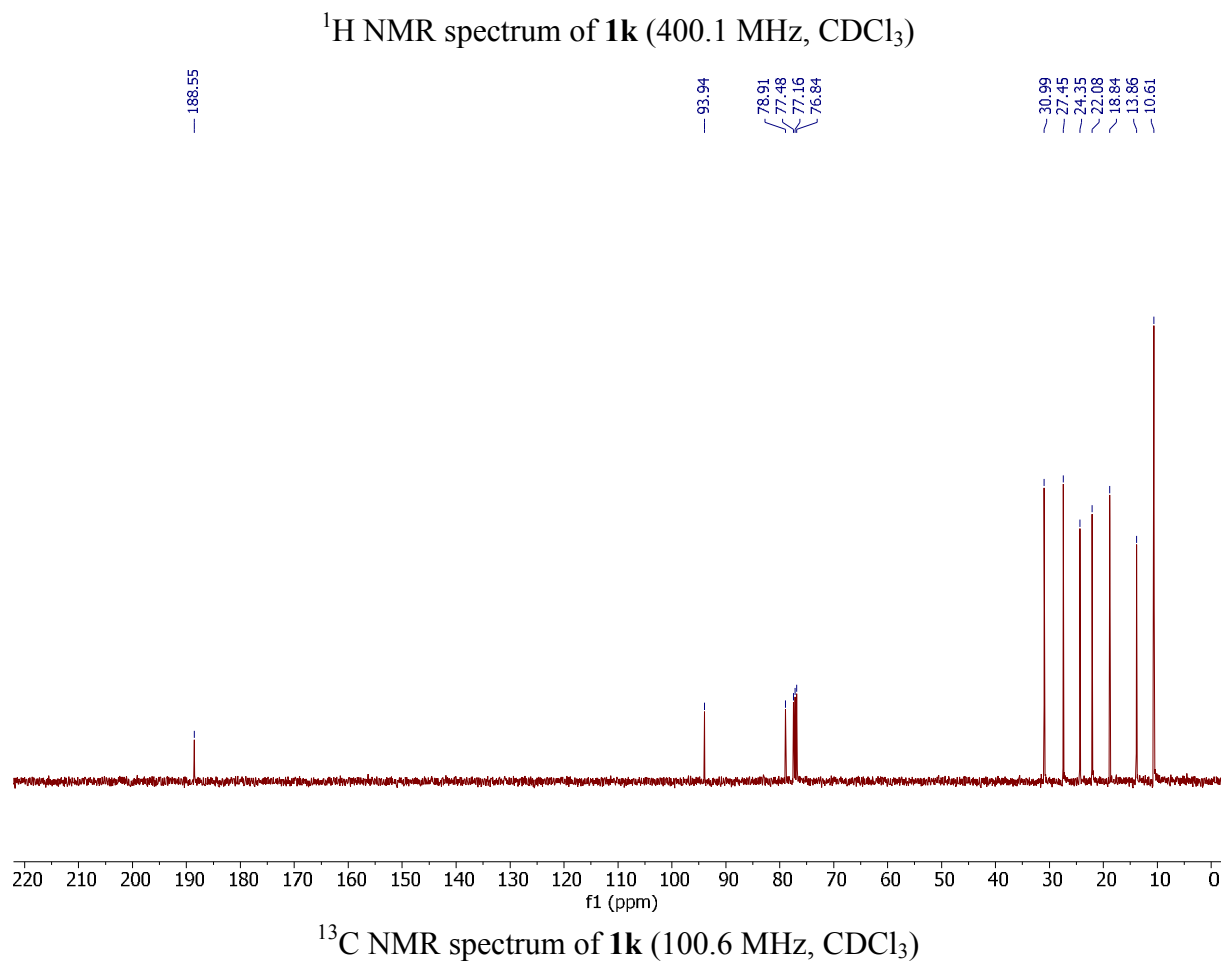
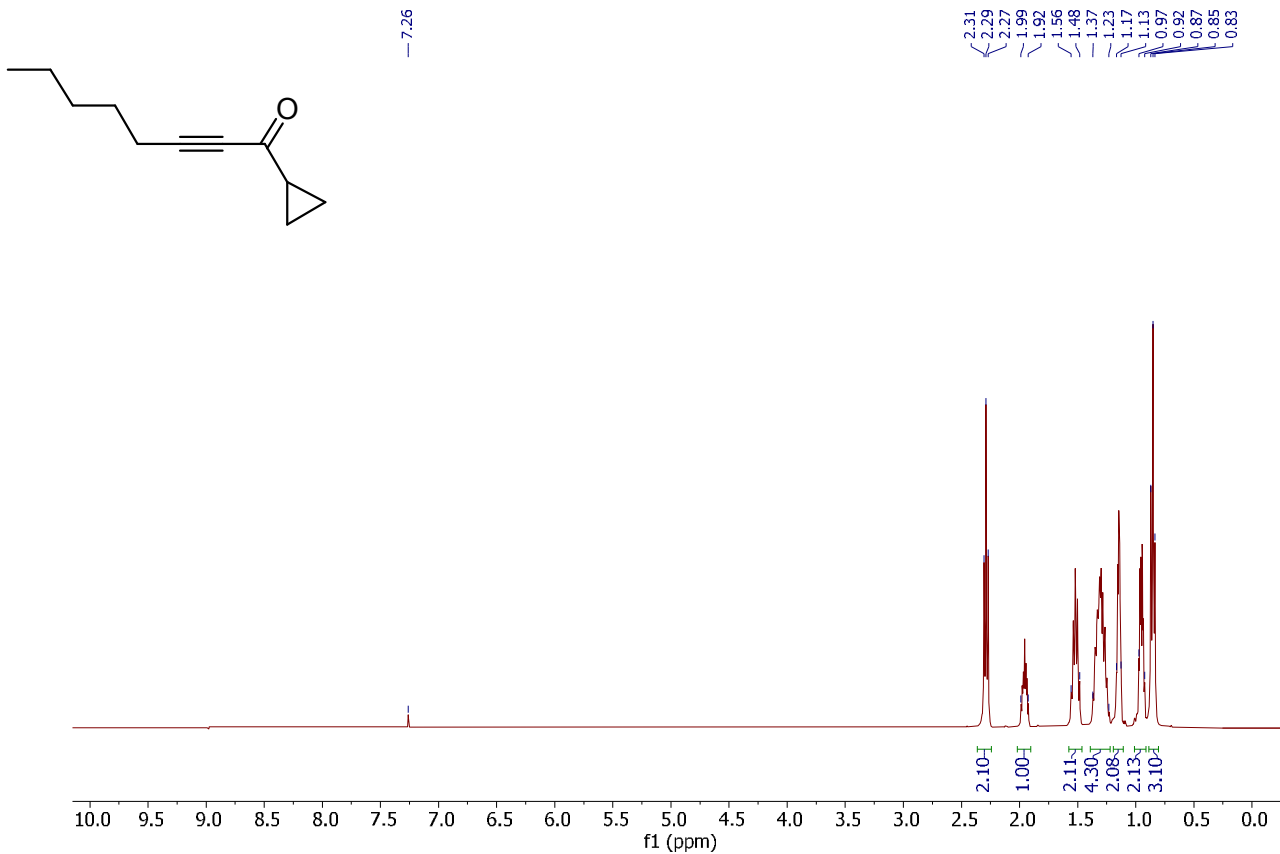
¹³C NMR spectrum of **1e** (100.6 MHz, CDCl₃)

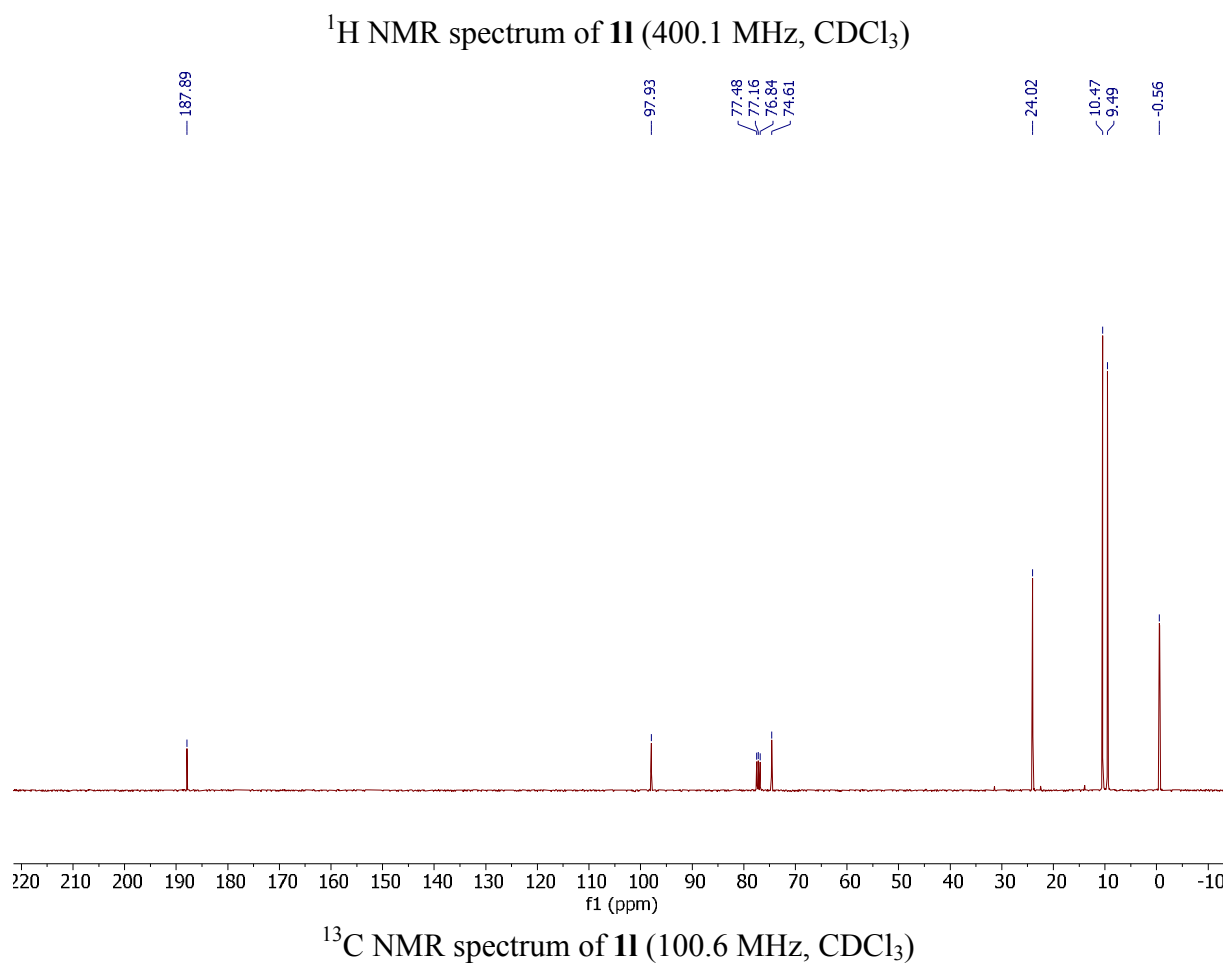
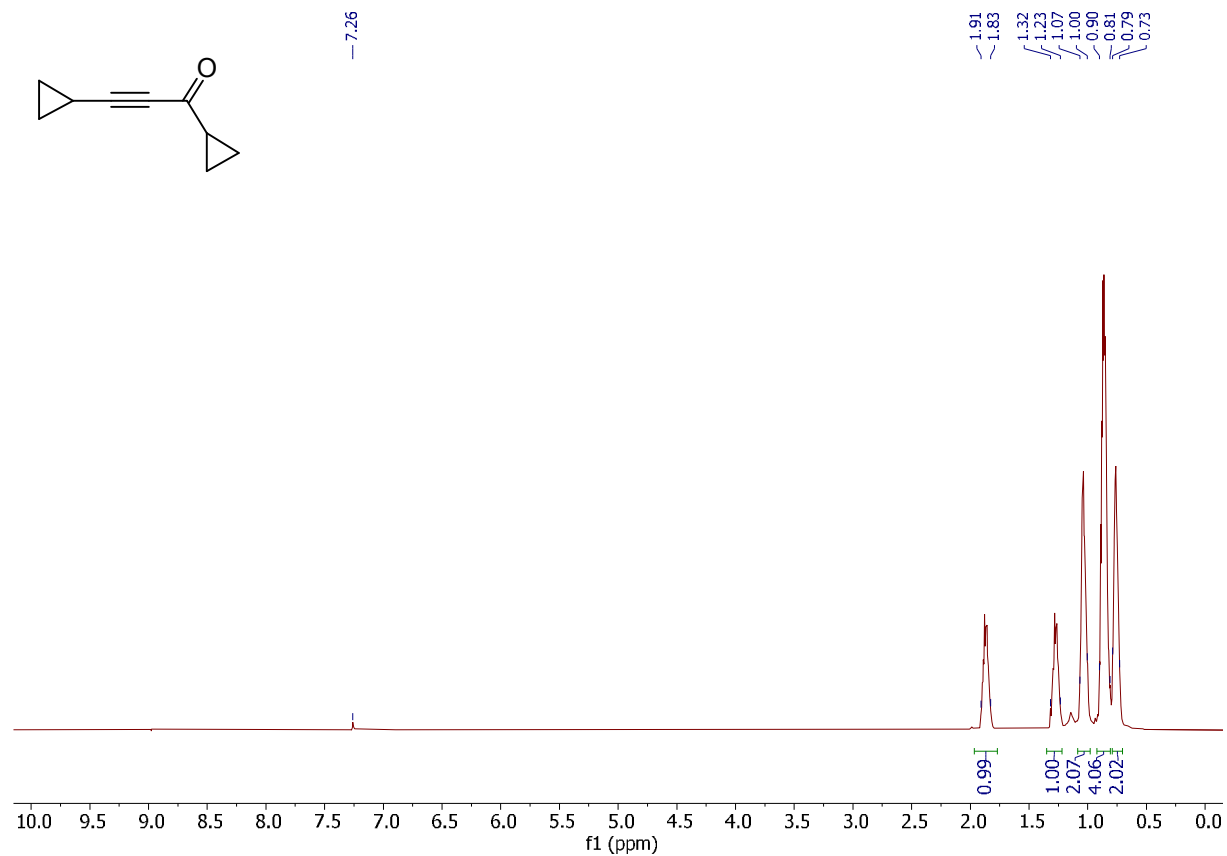


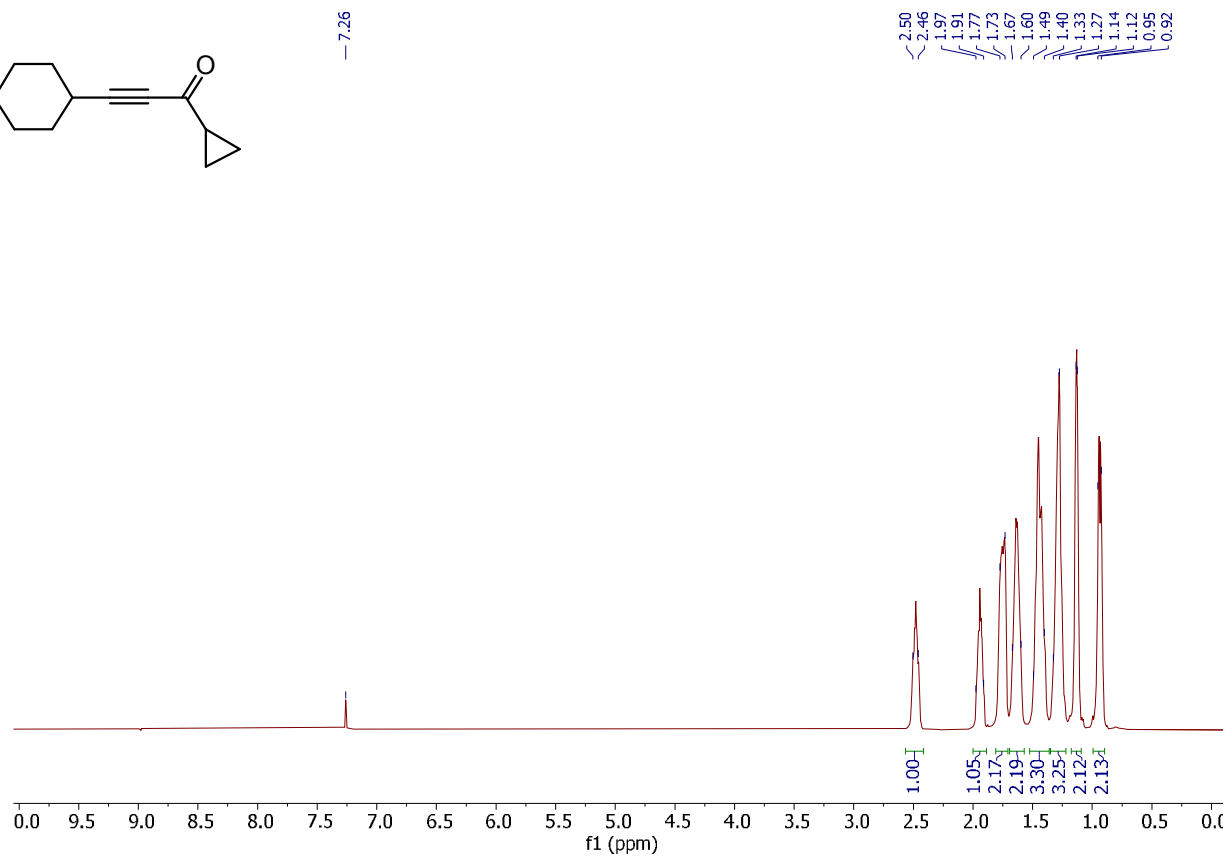
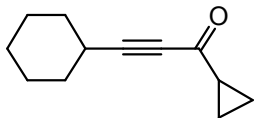




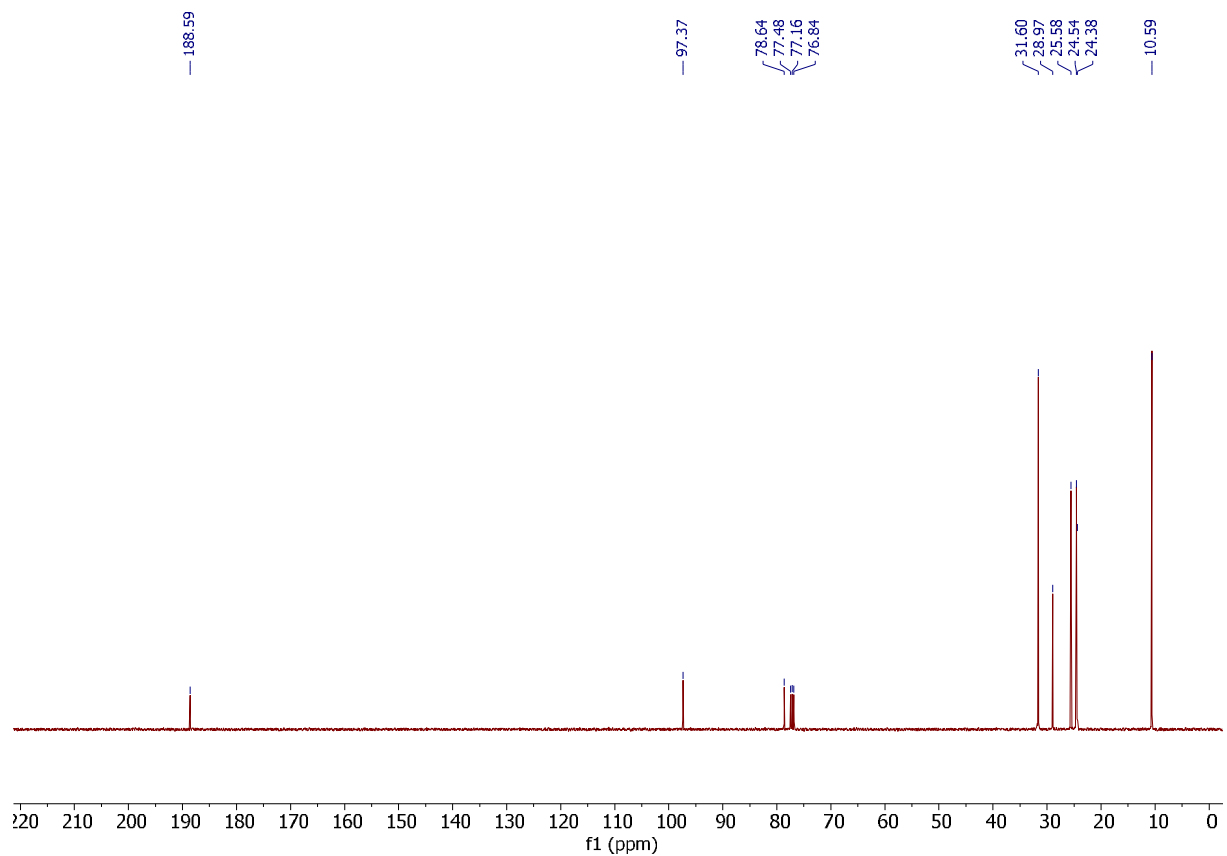






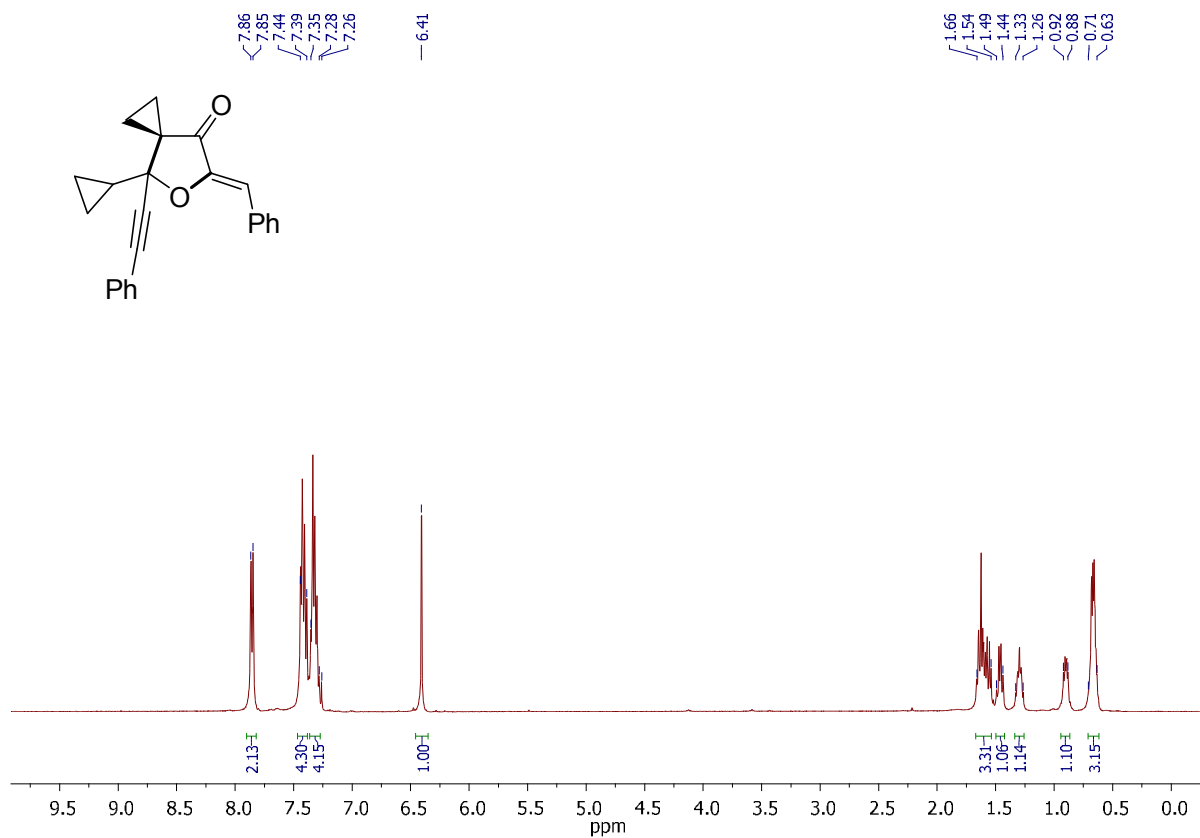


^1H NMR spectrum of **1m** (400.1 MHz, CDCl_3)

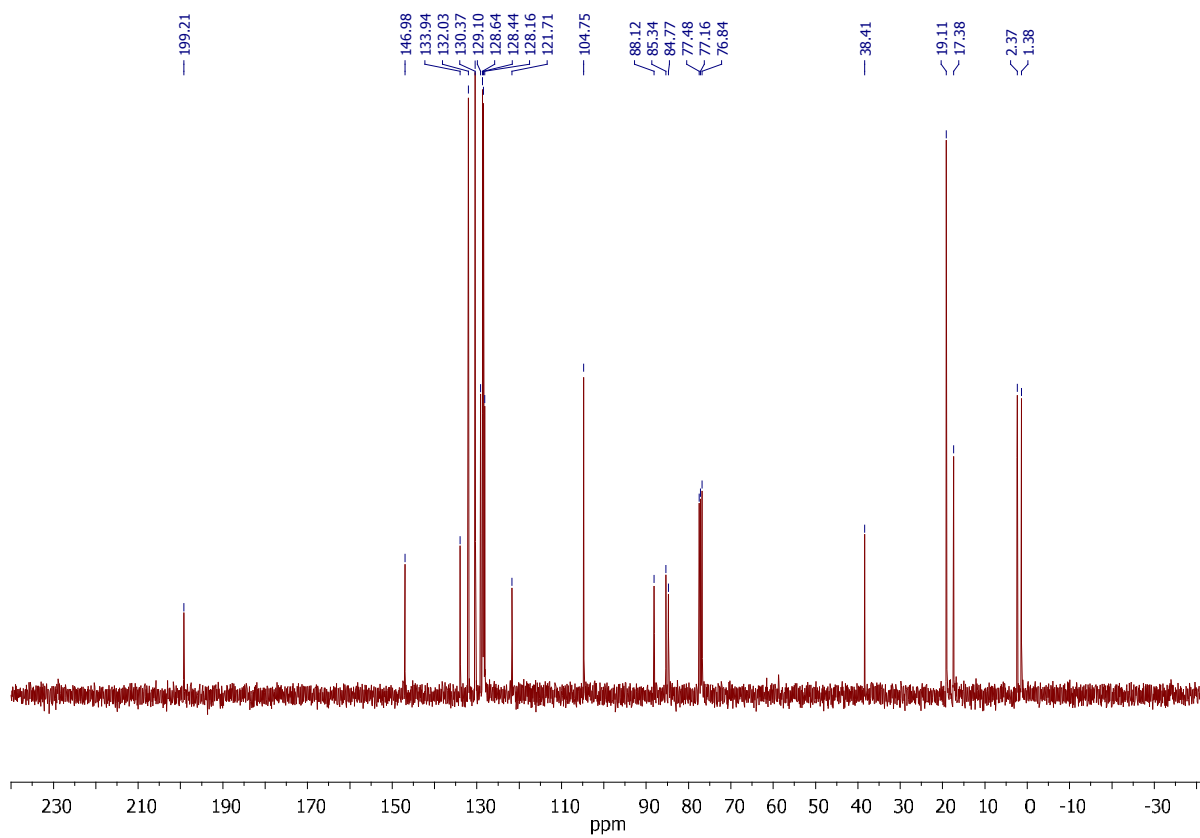


^{13}C NMR spectrum of **1m** (100.6 MHz, CDCl_3)

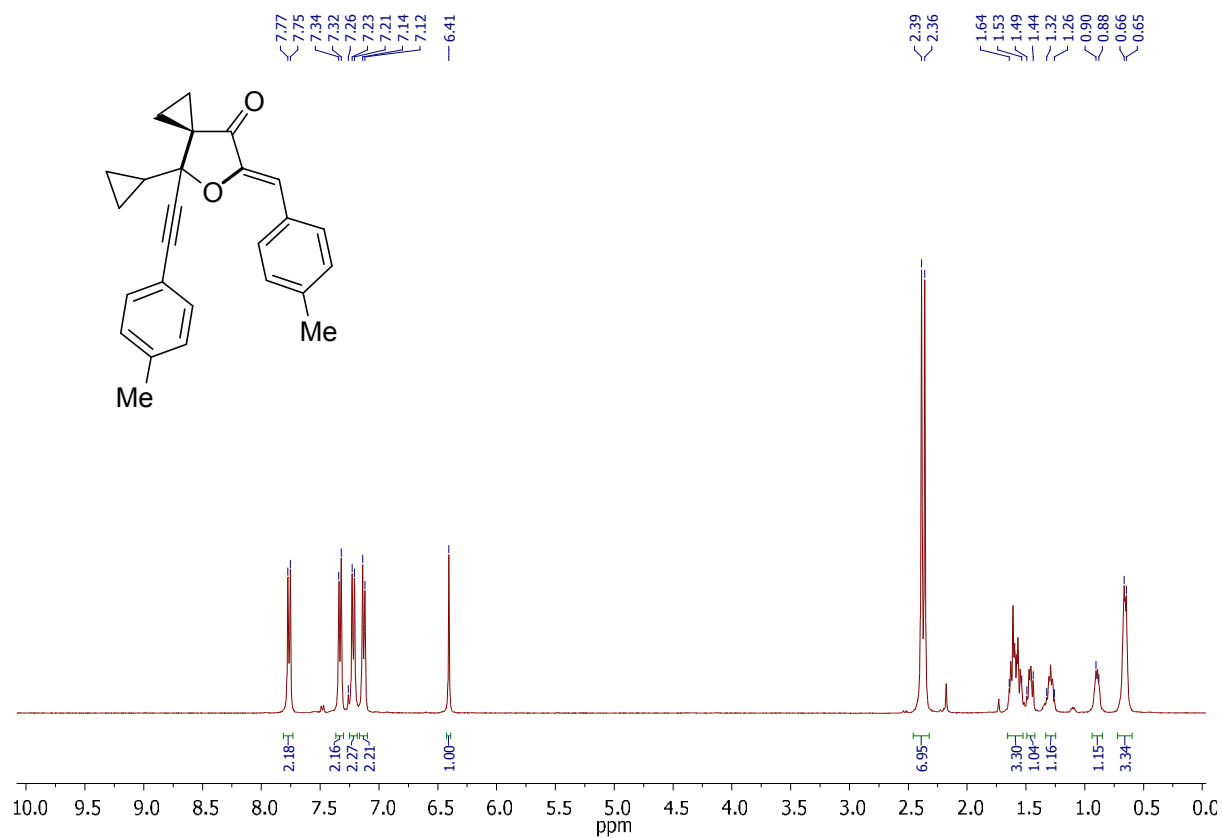
^1H and ^{13}C Spectra of spirocyclopropanes **2** and **4**



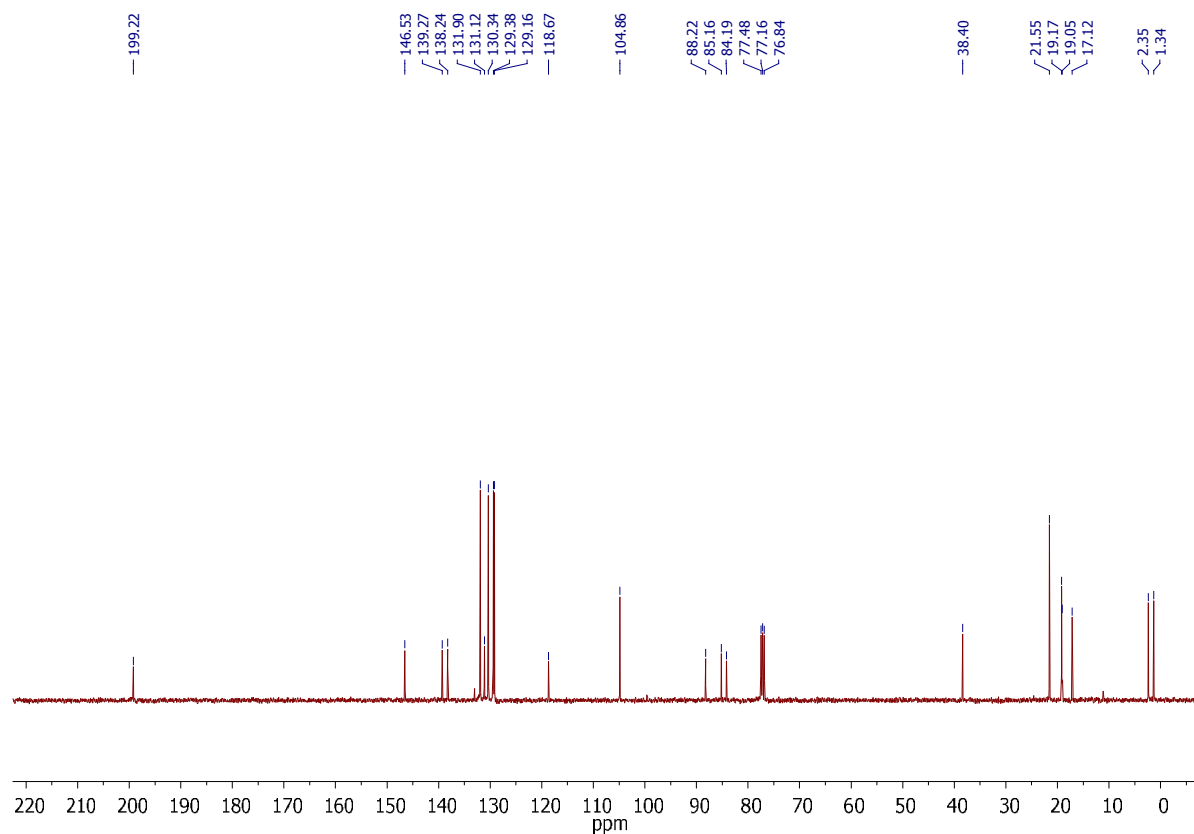
^1H NMR spectrum of **2a** (400.1 MHz, CDCl_3)



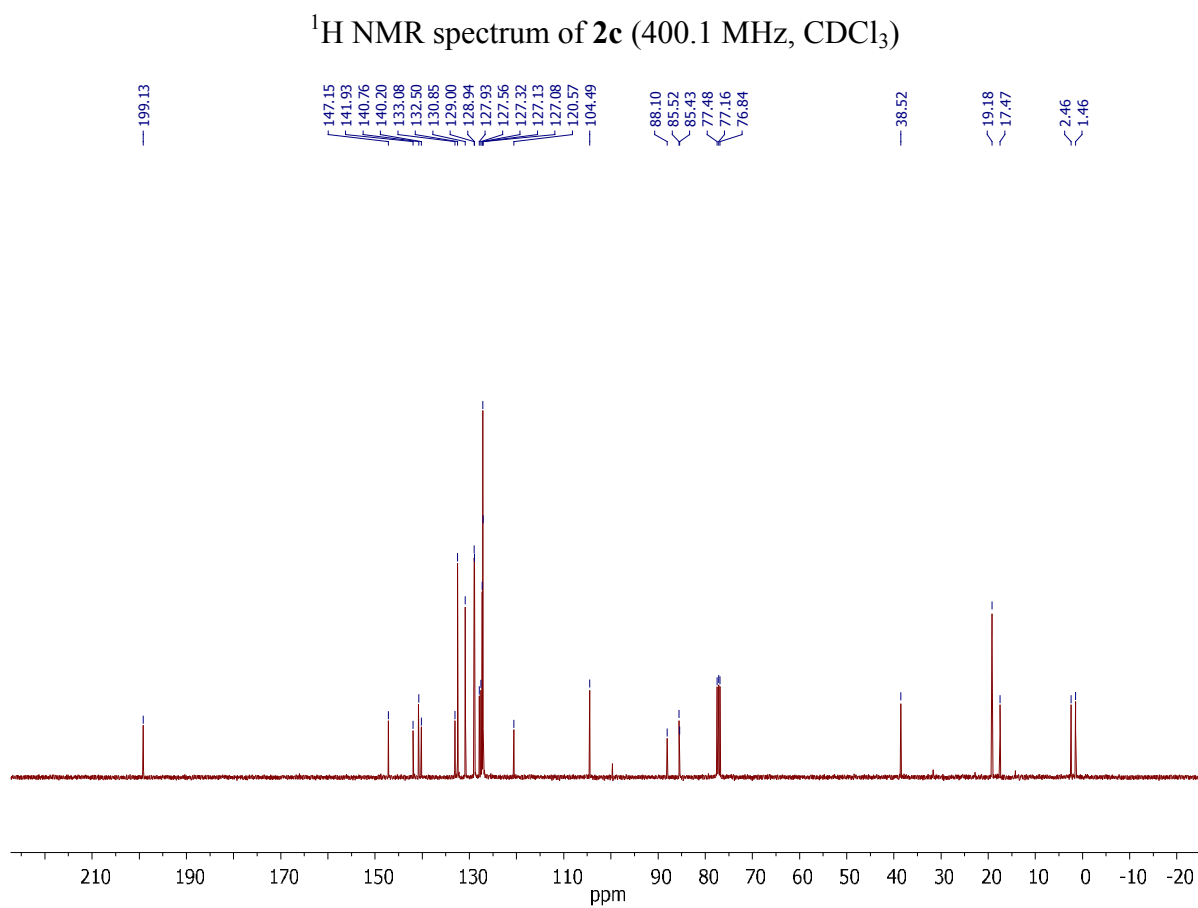
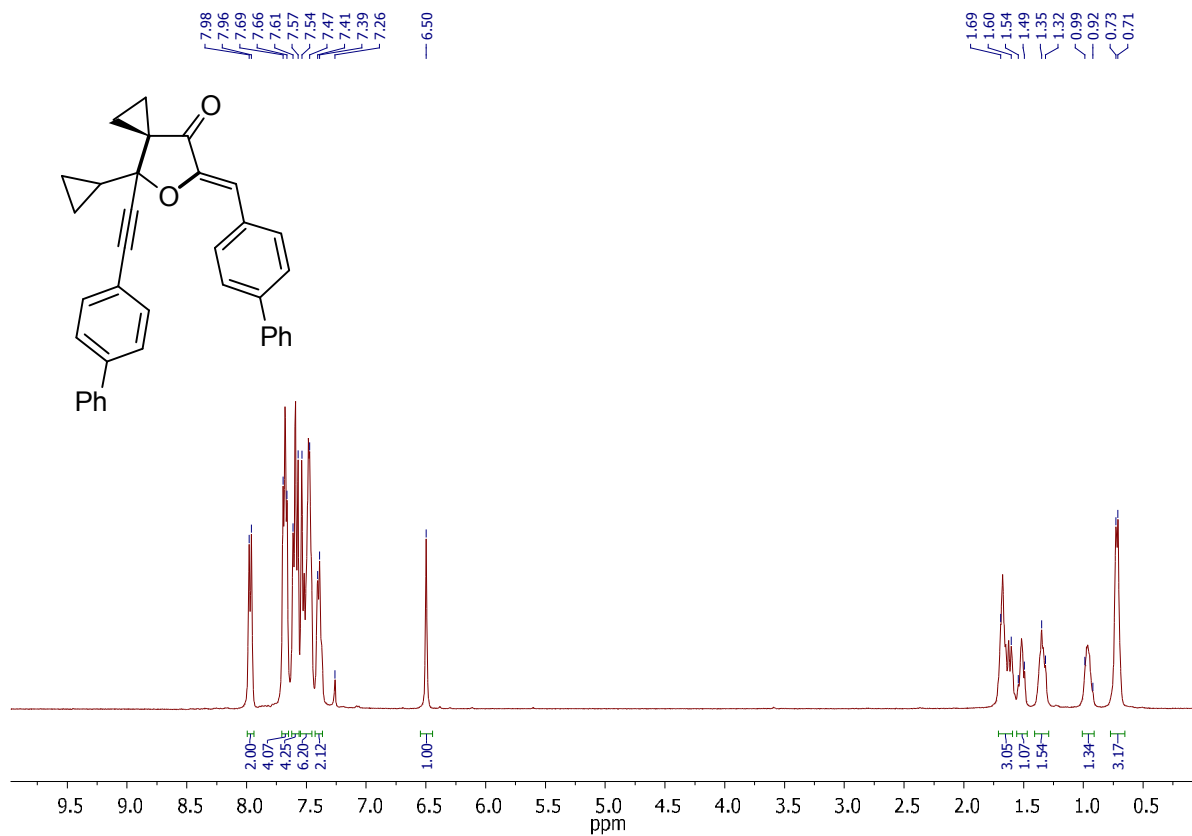
^{13}C NMR spectrum of **2a** (100.6 MHz, CDCl_3)

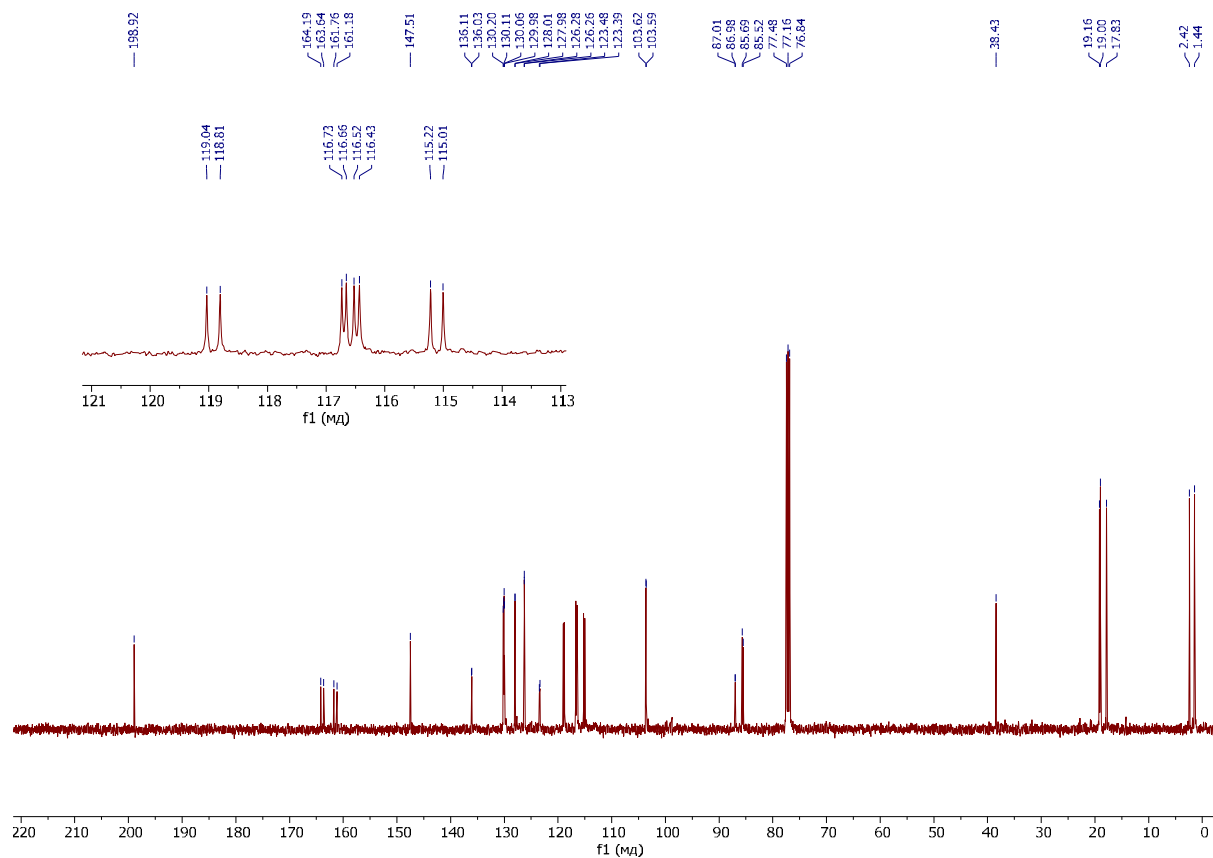
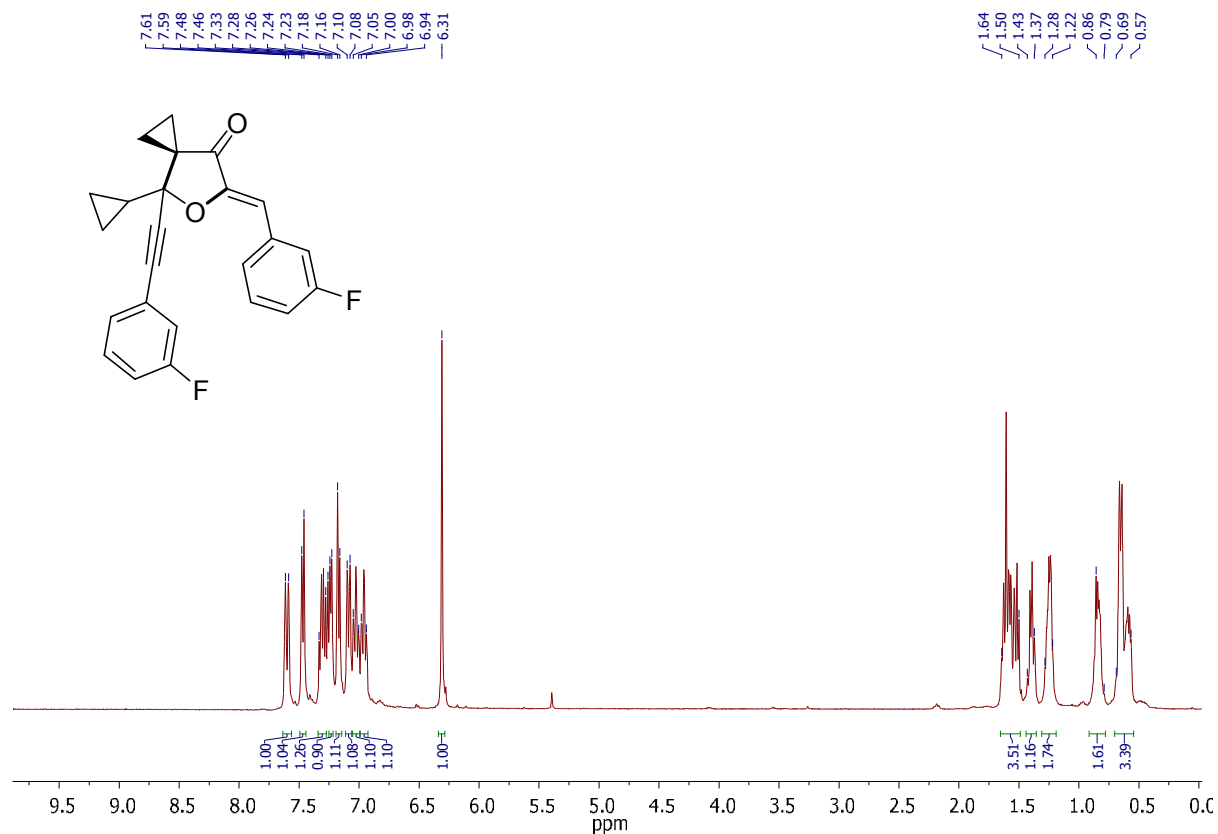


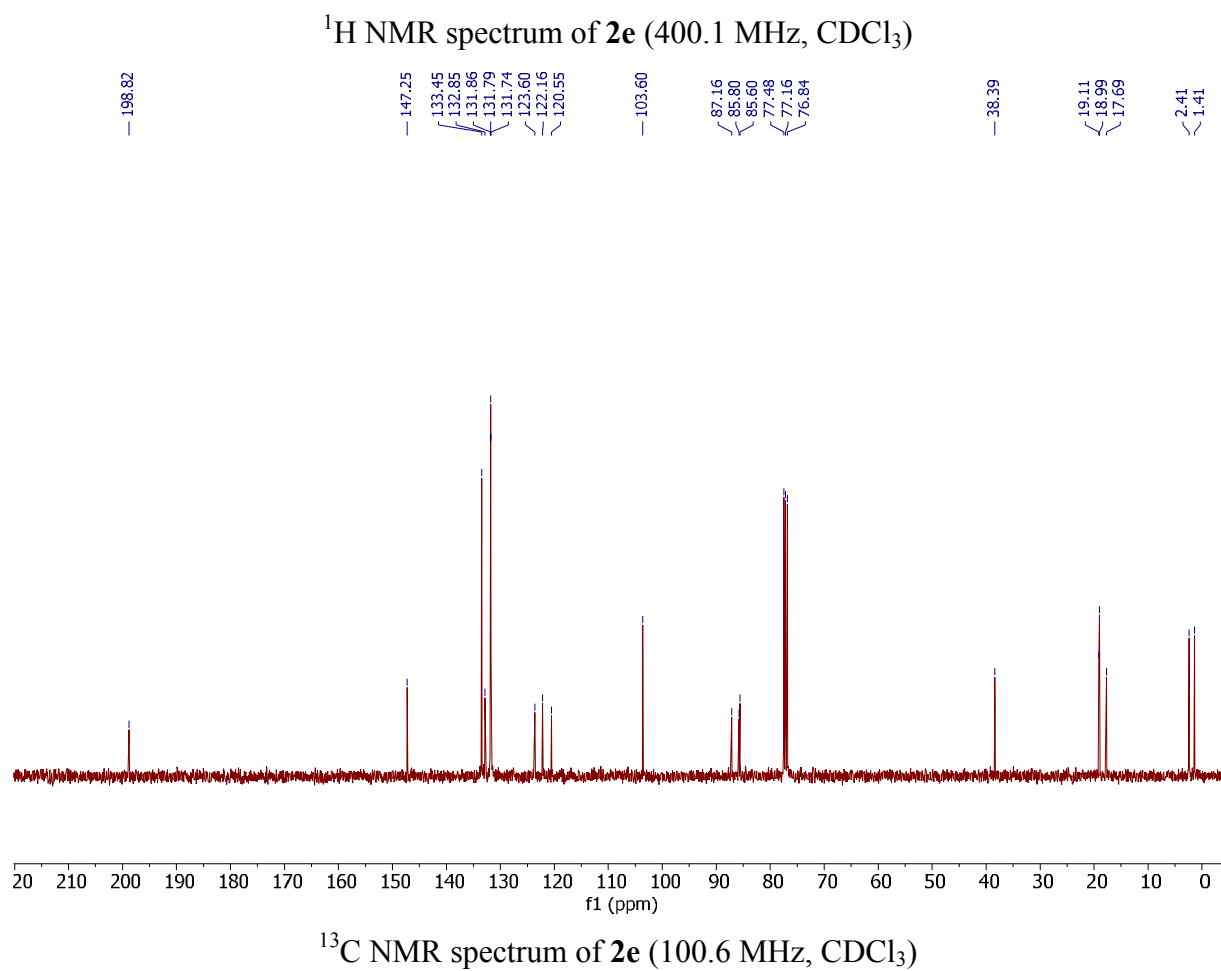
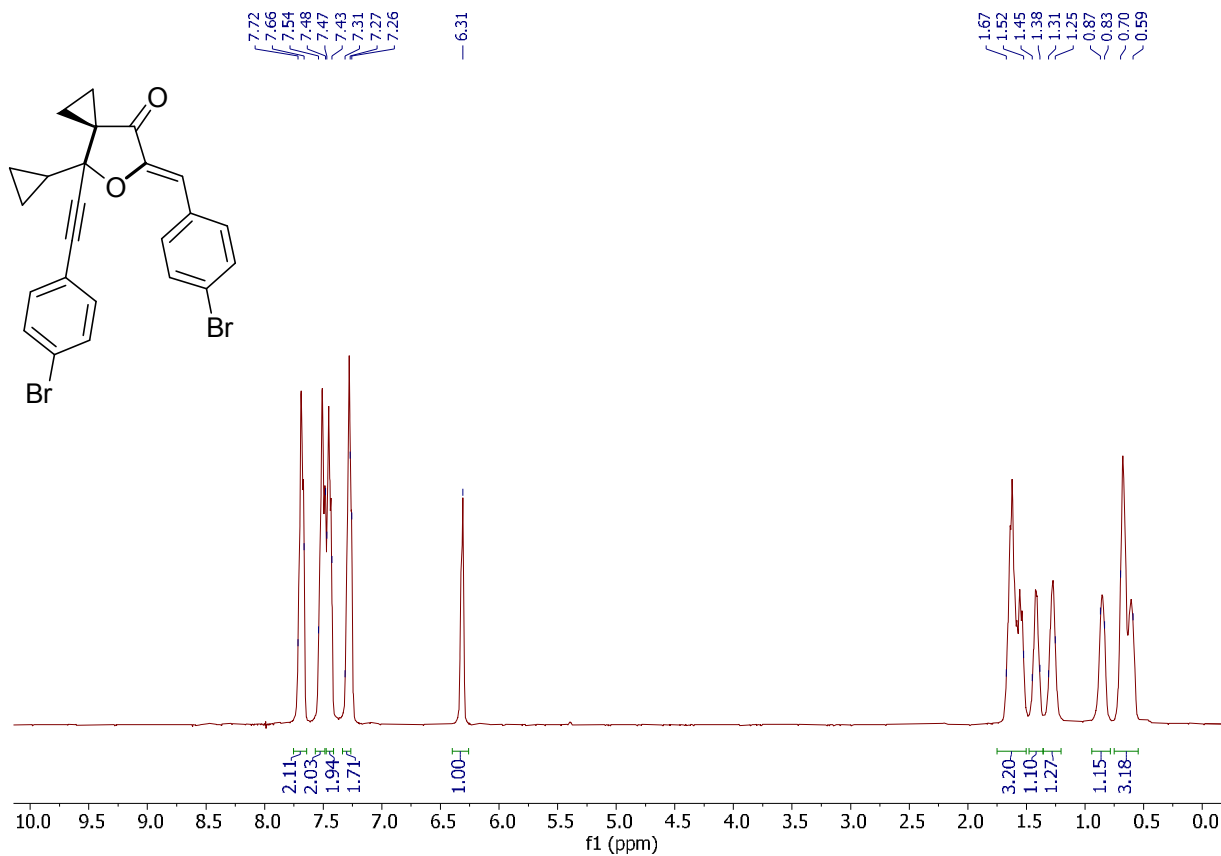
^1H NMR spectrum of **2b** (400.1 MHz, CDCl_3)

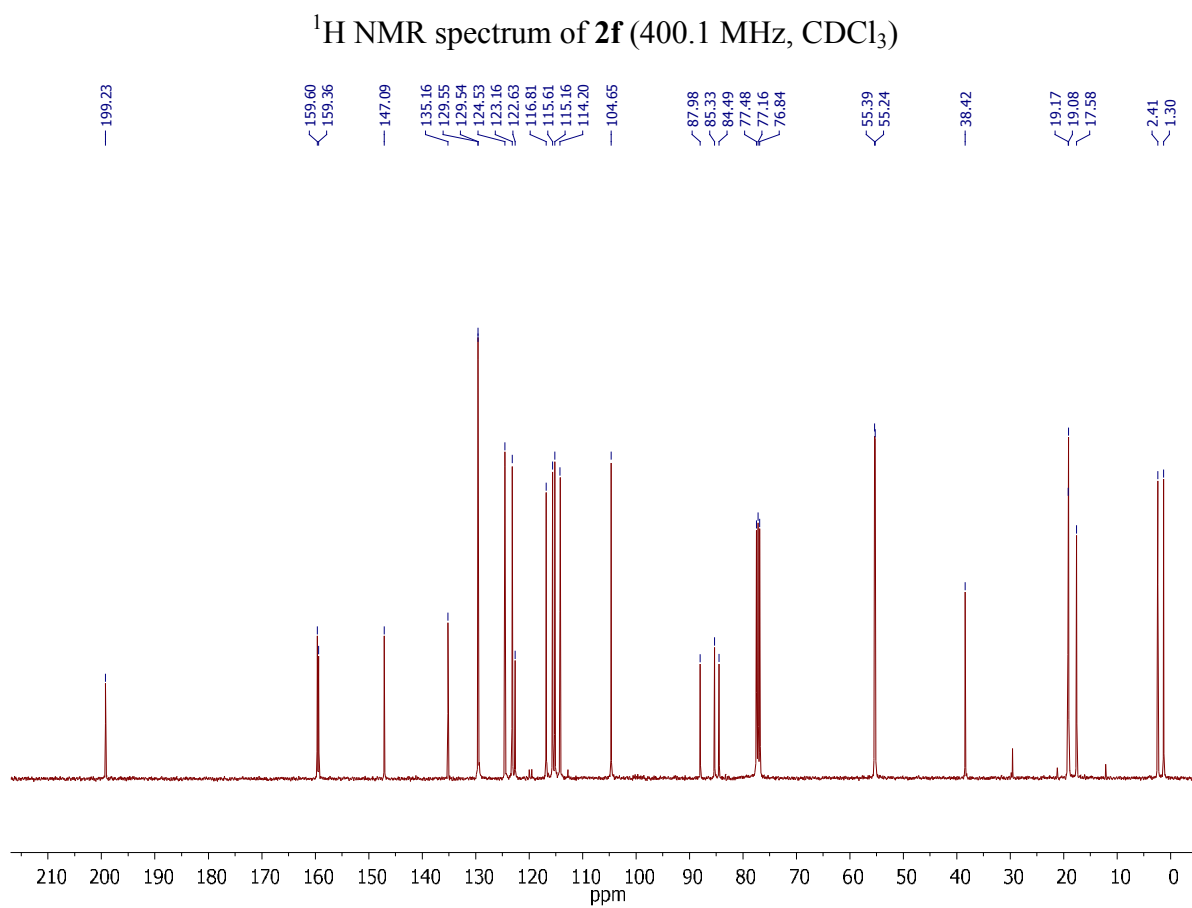
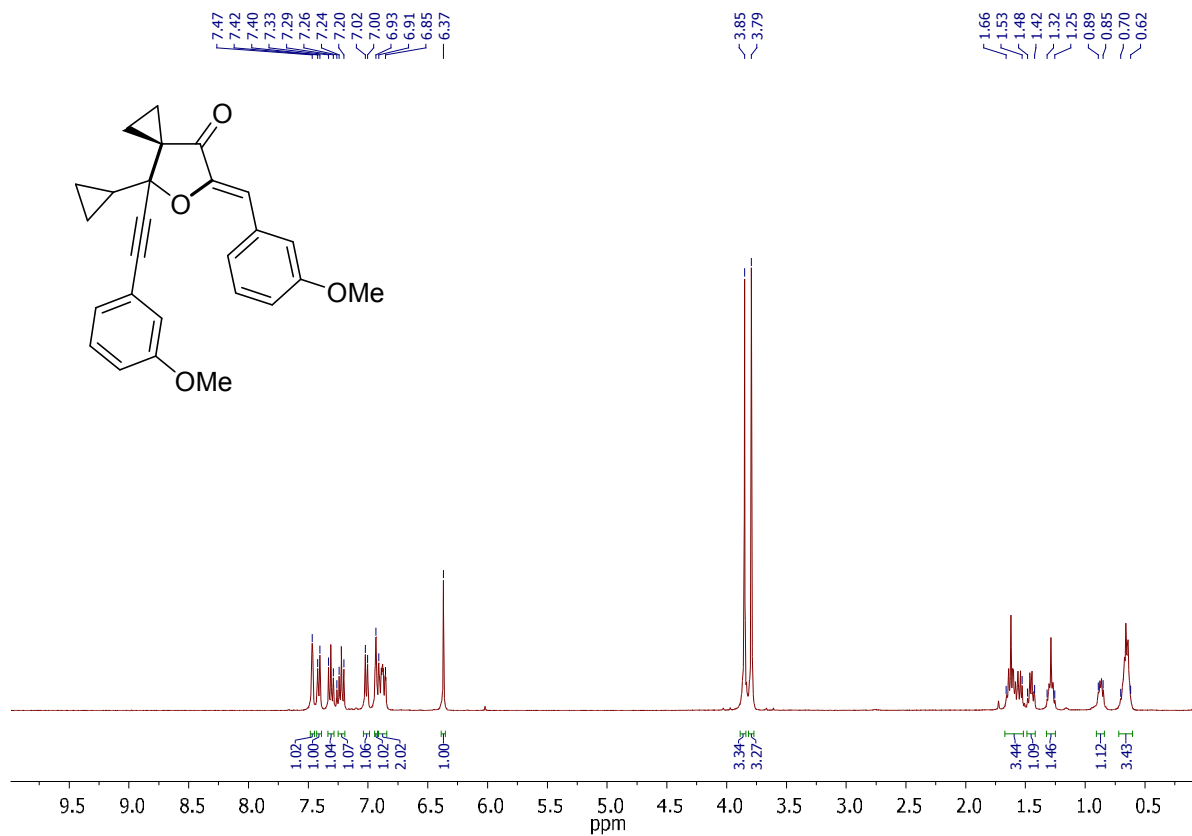


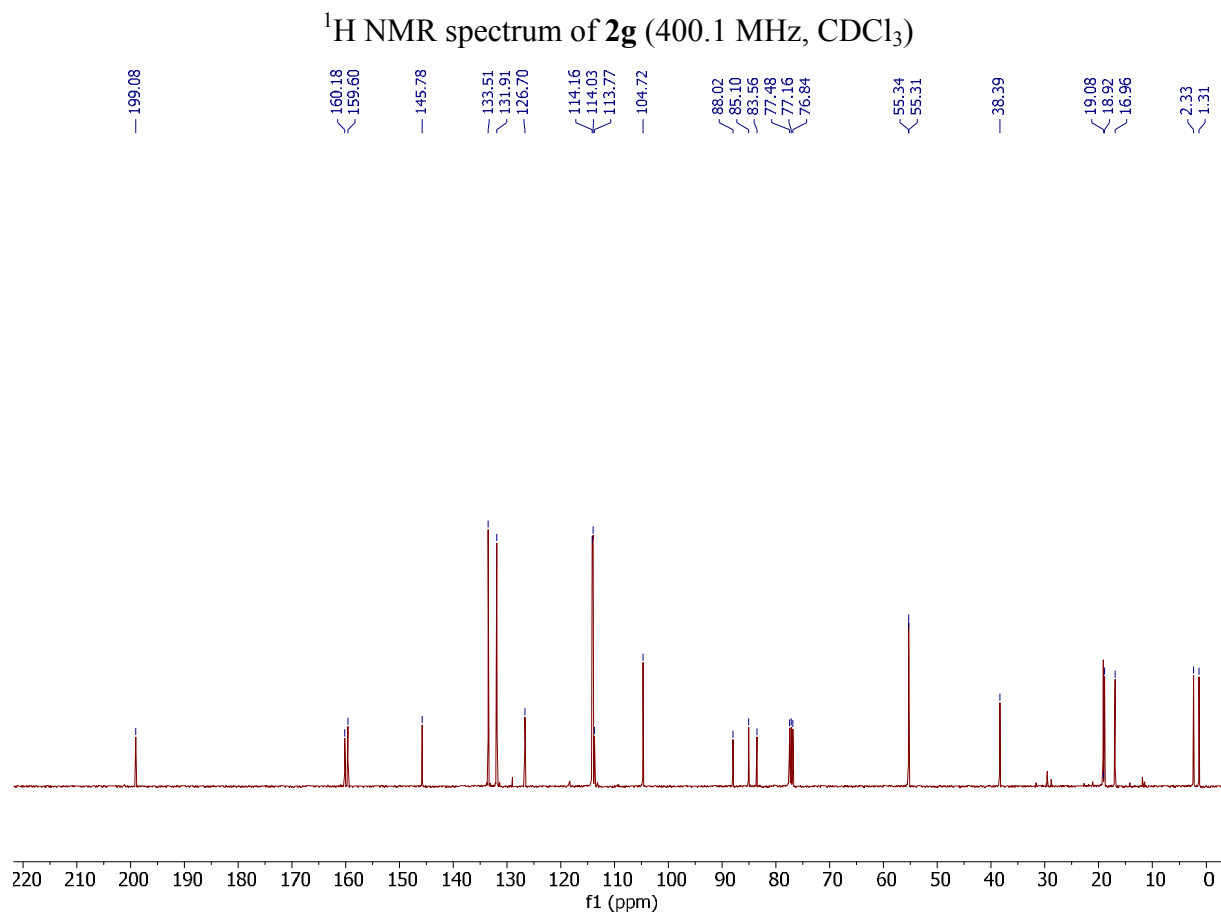
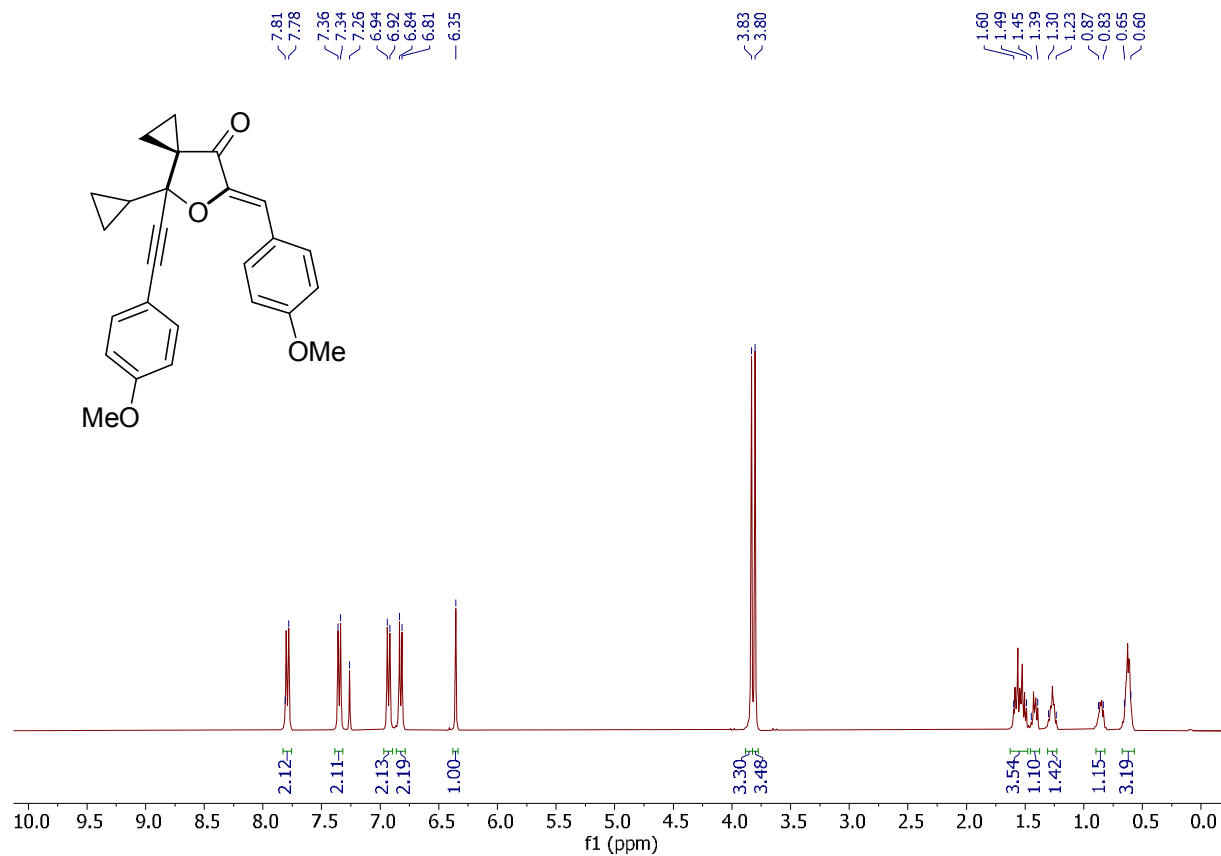
^{13}C NMR spectrum of **2b** (100.6 MHz, CDCl_3)

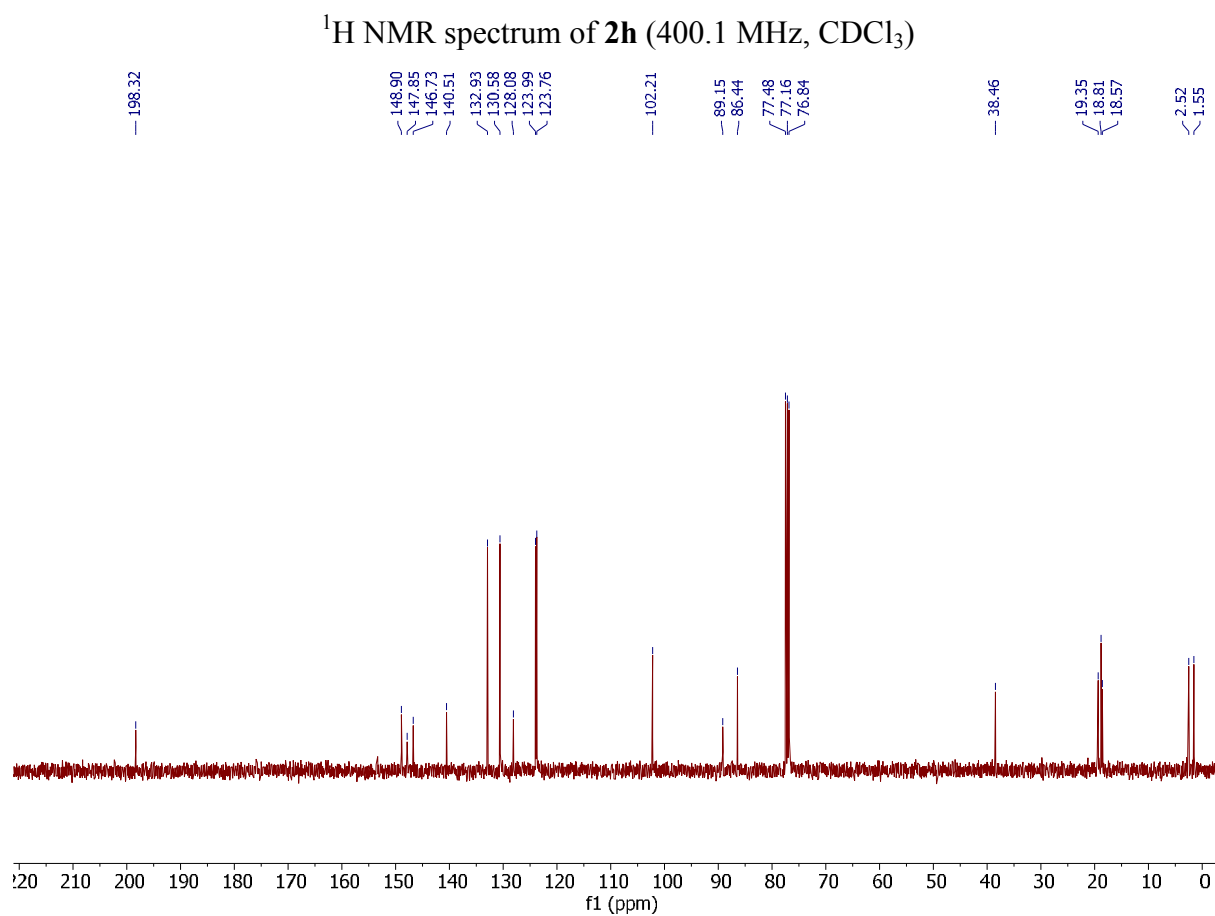
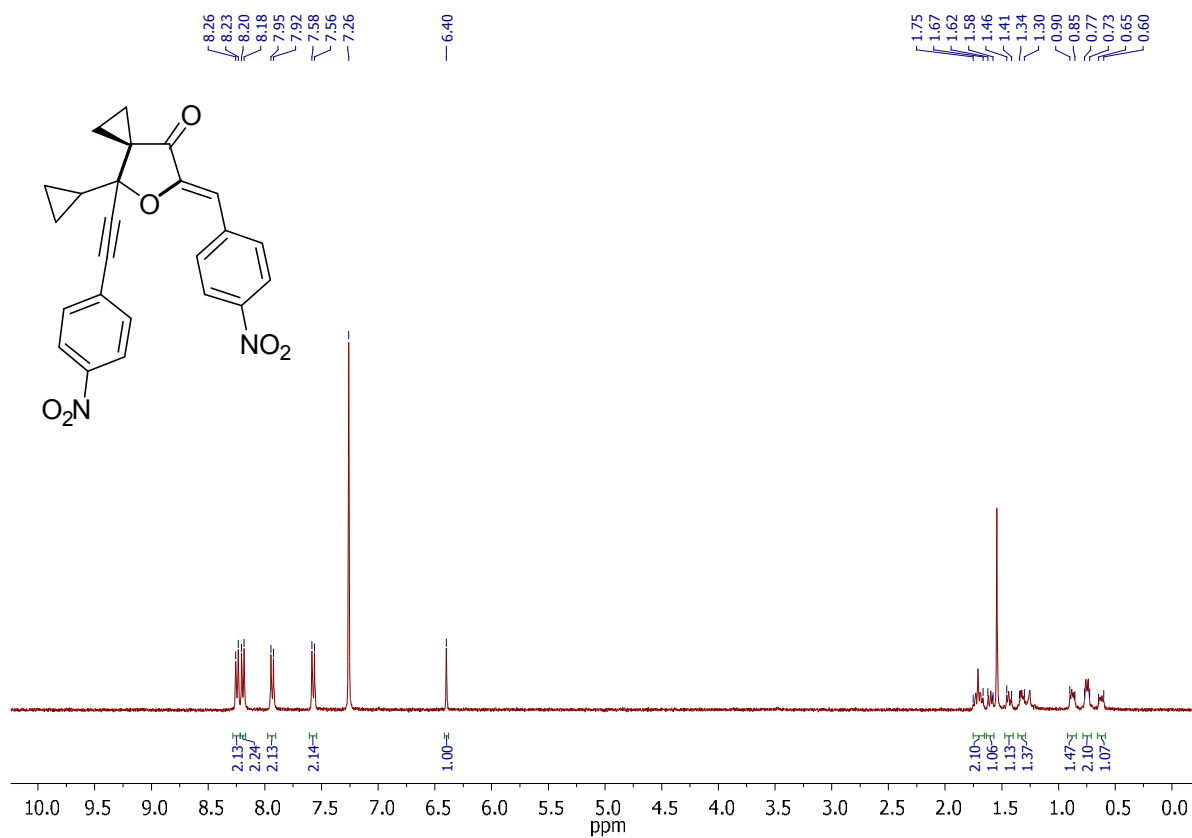


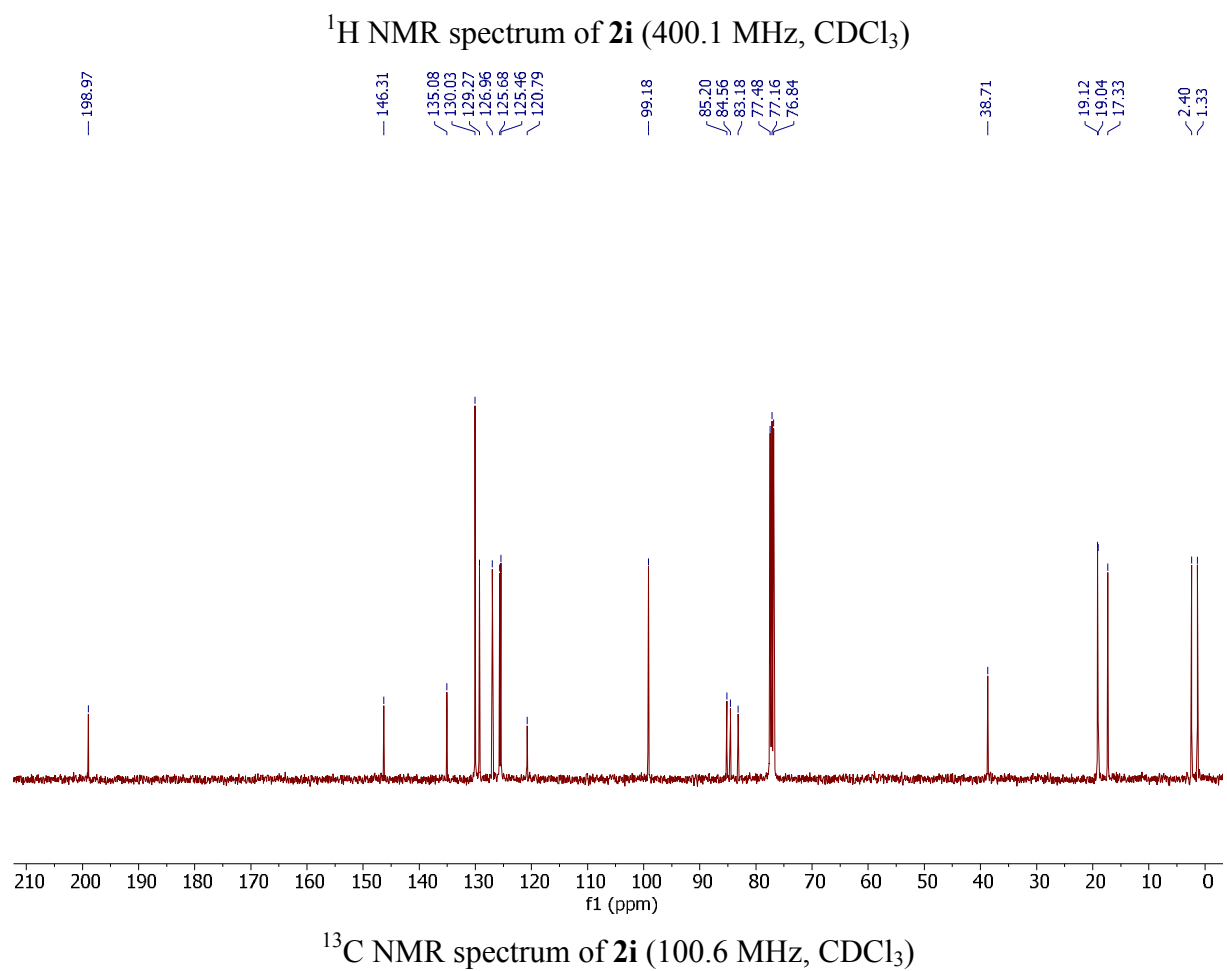
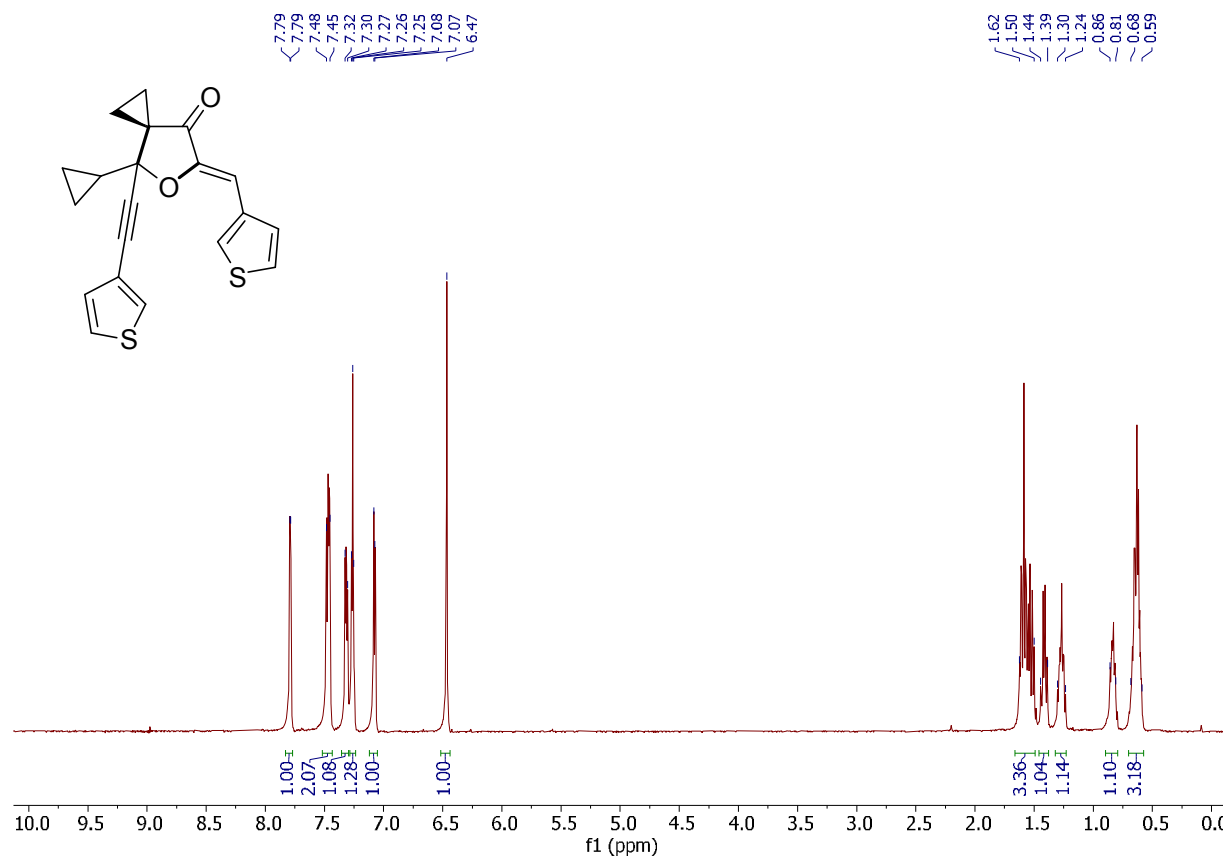


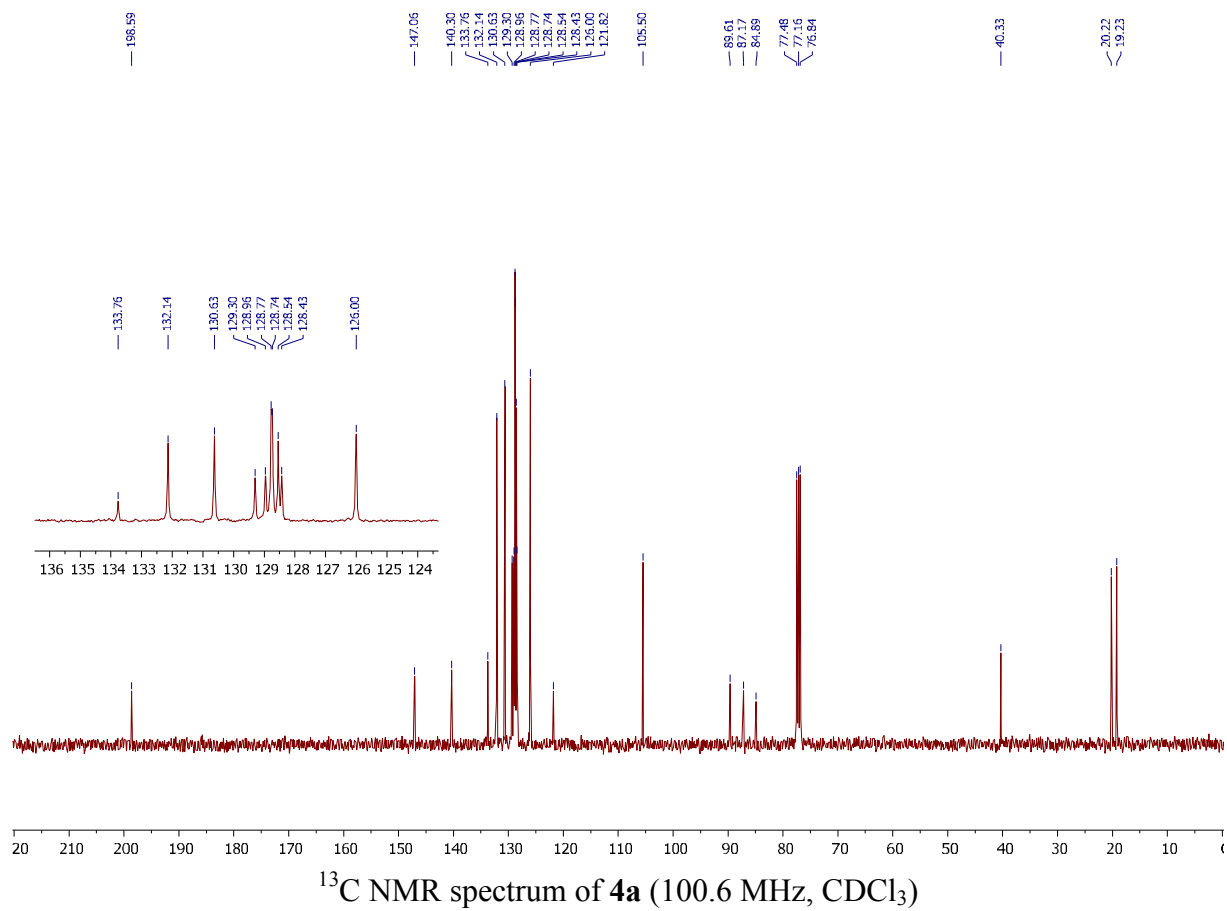
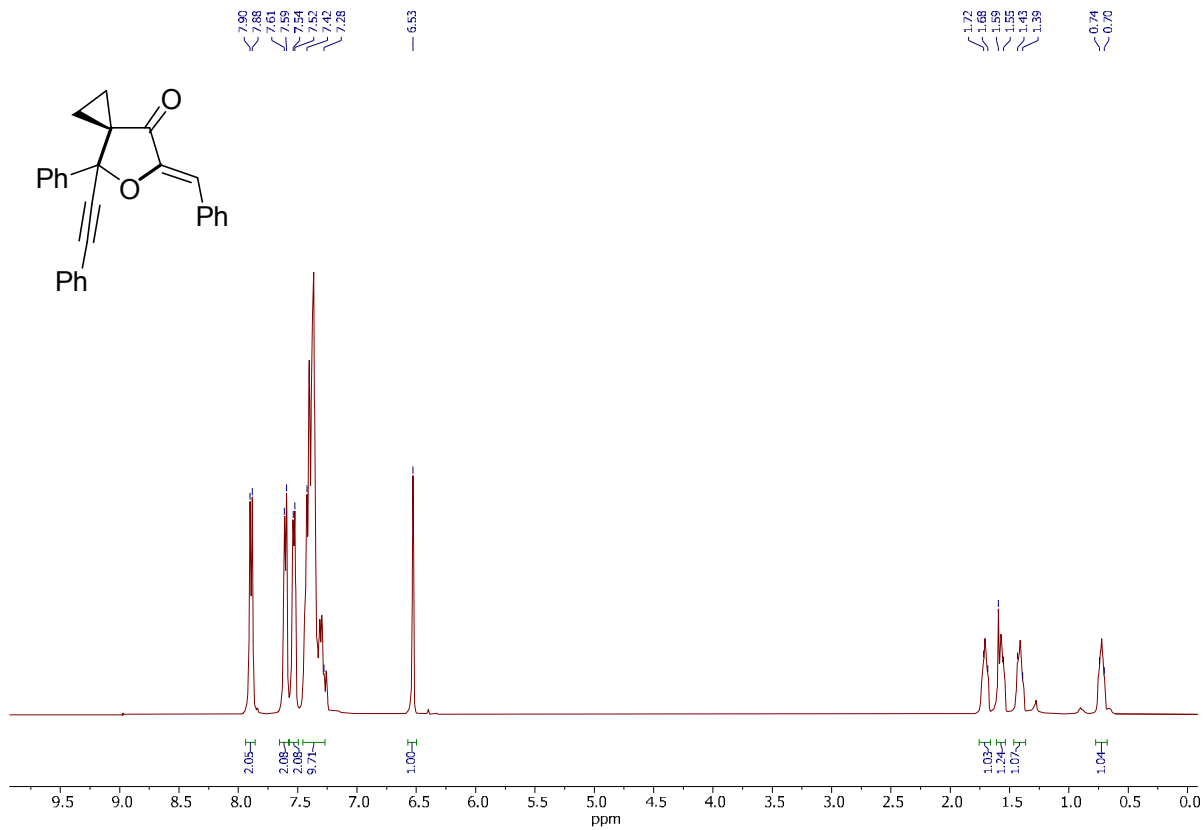


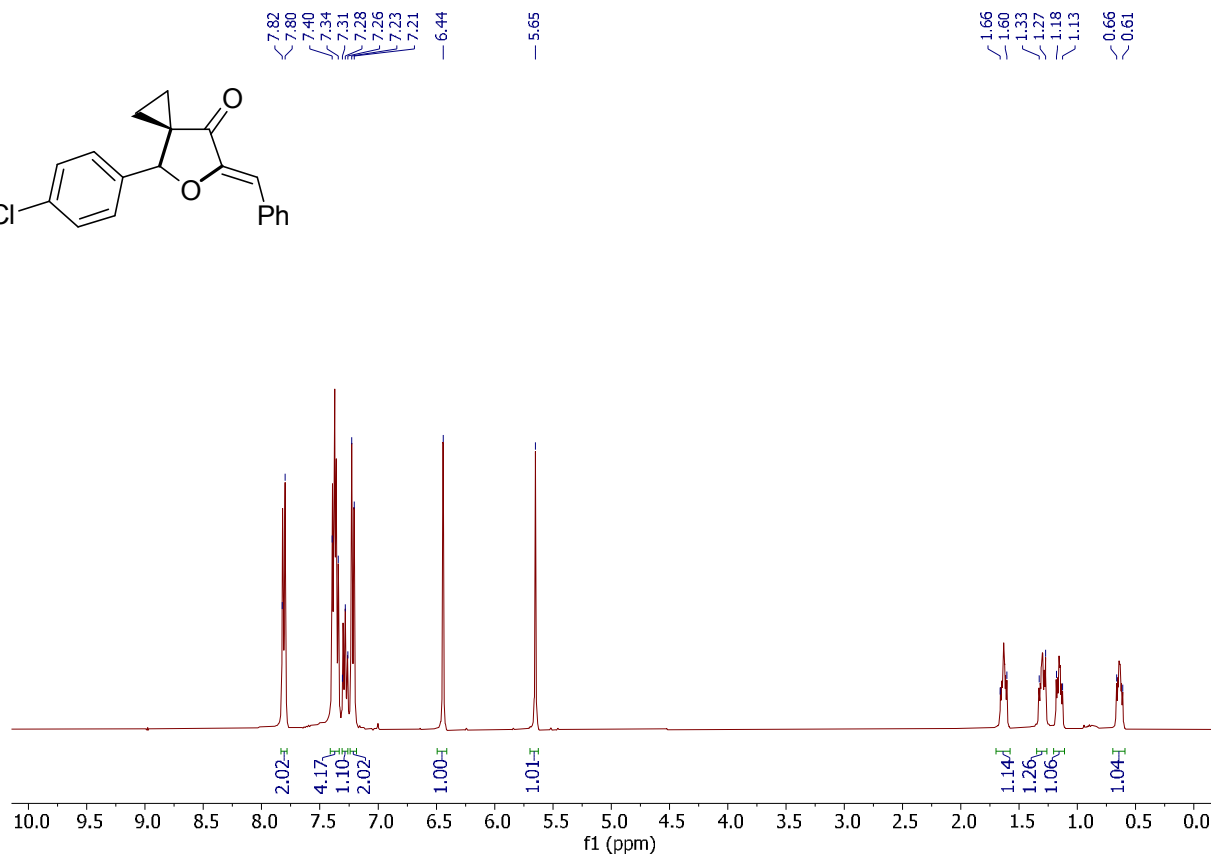
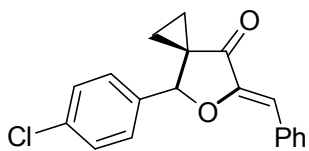




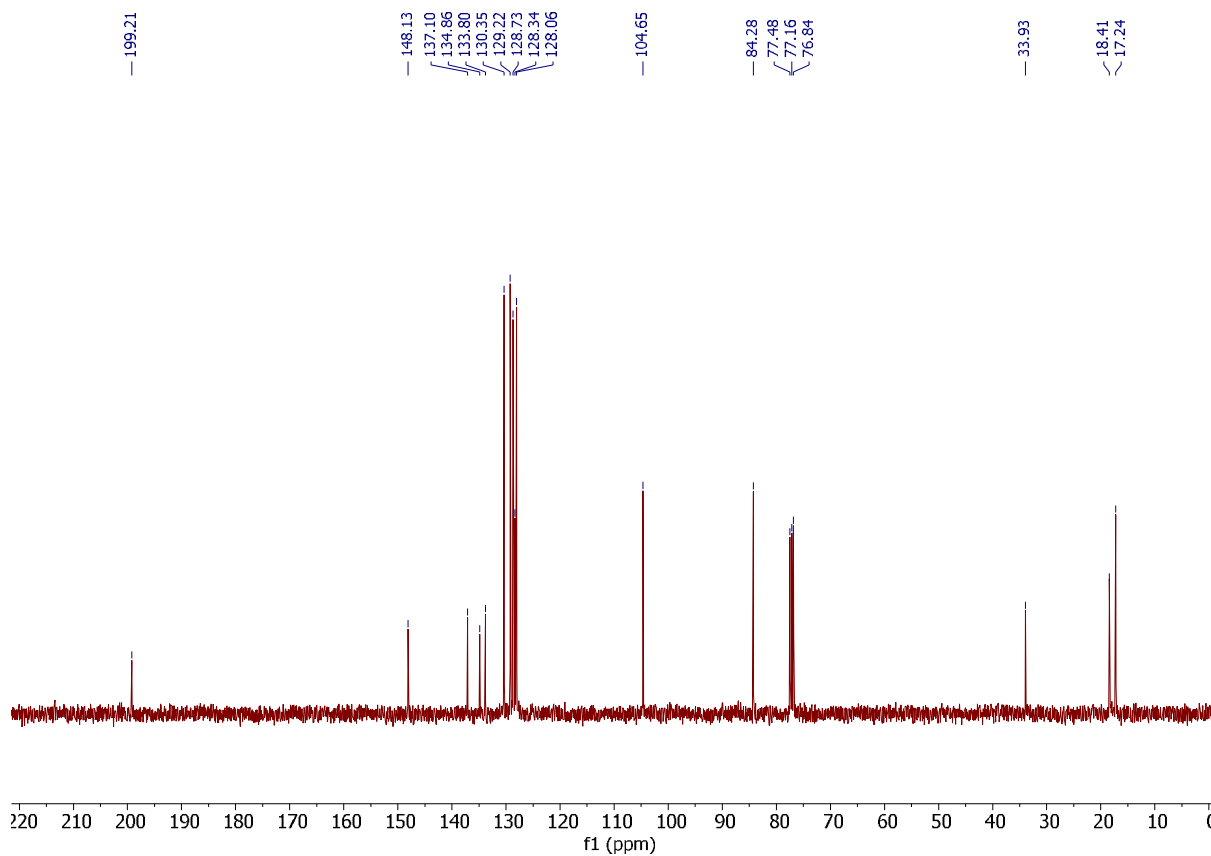




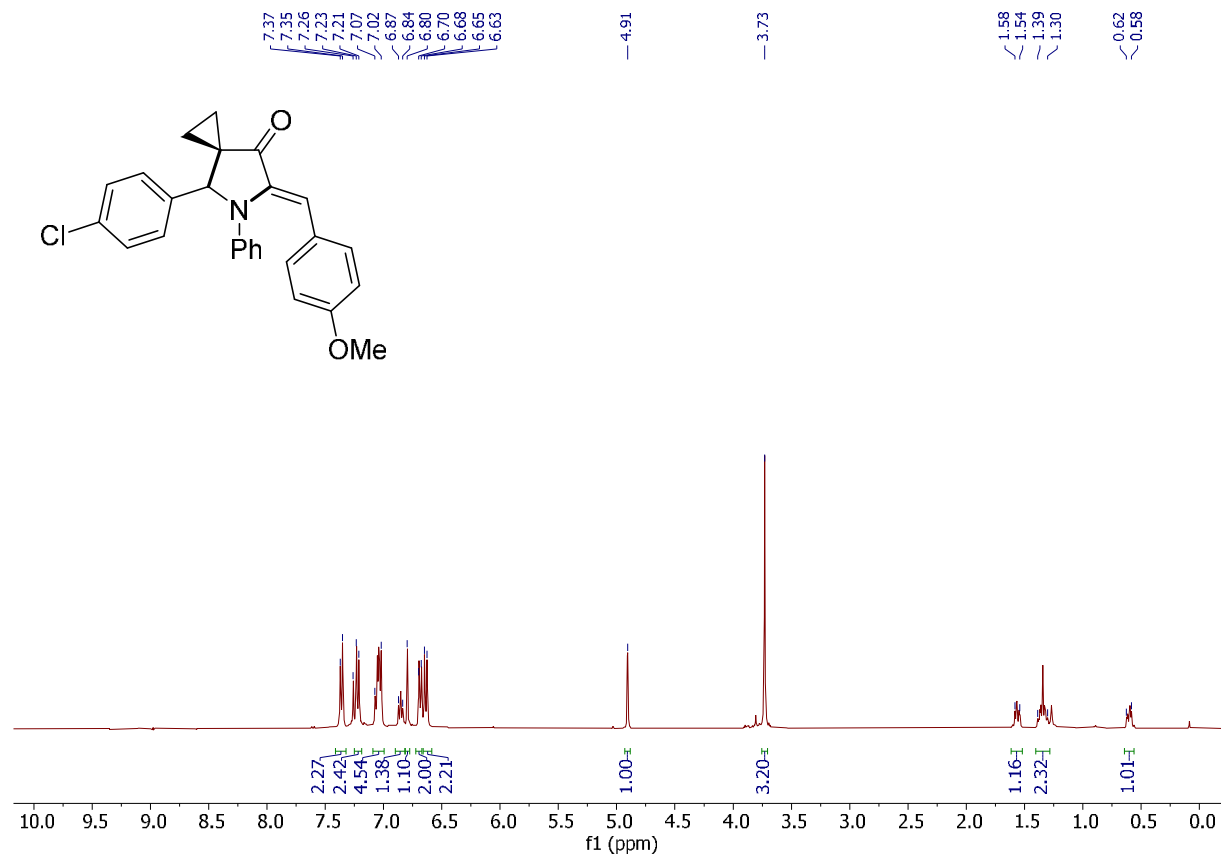




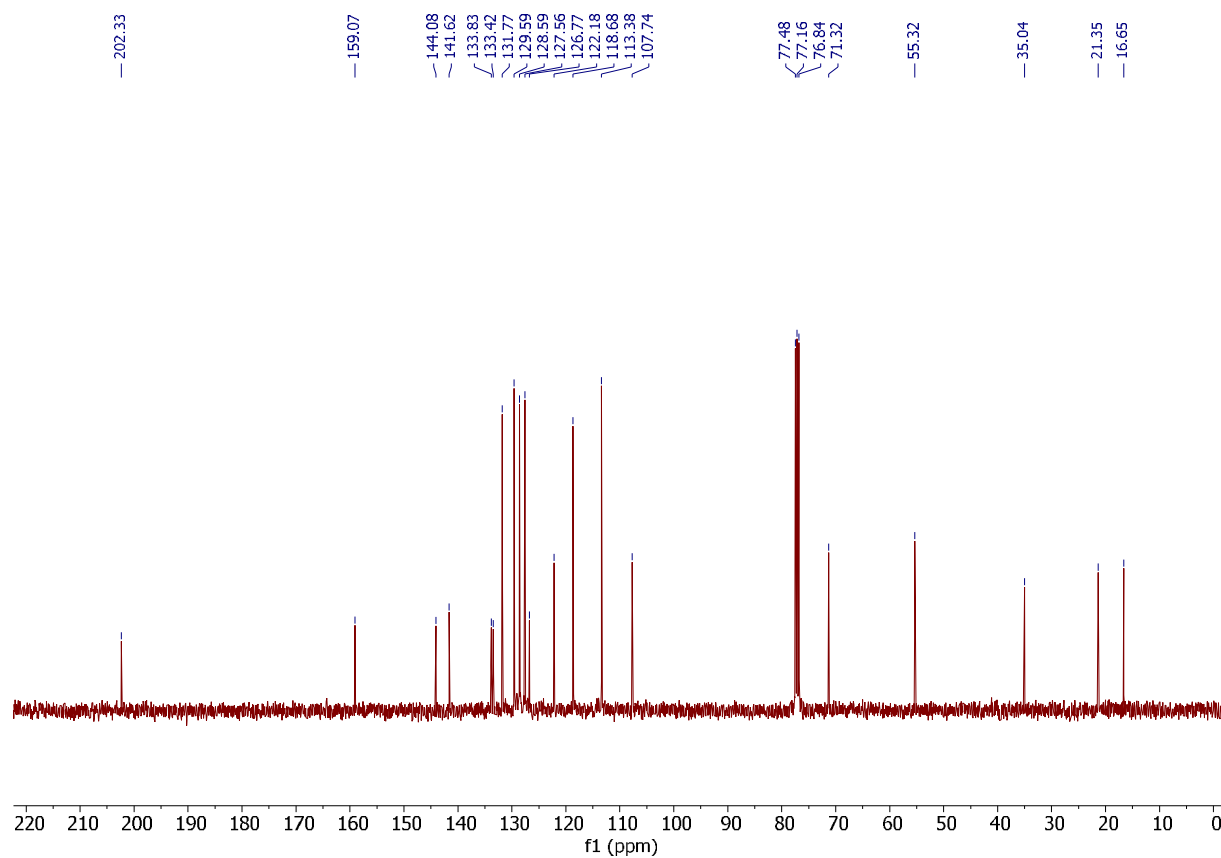
¹H NMR spectrum of **4b** (400.1 MHz, CDCl₃)



¹³C NMR spectrum of **4b** (100.6 MHz, CDCl₃)

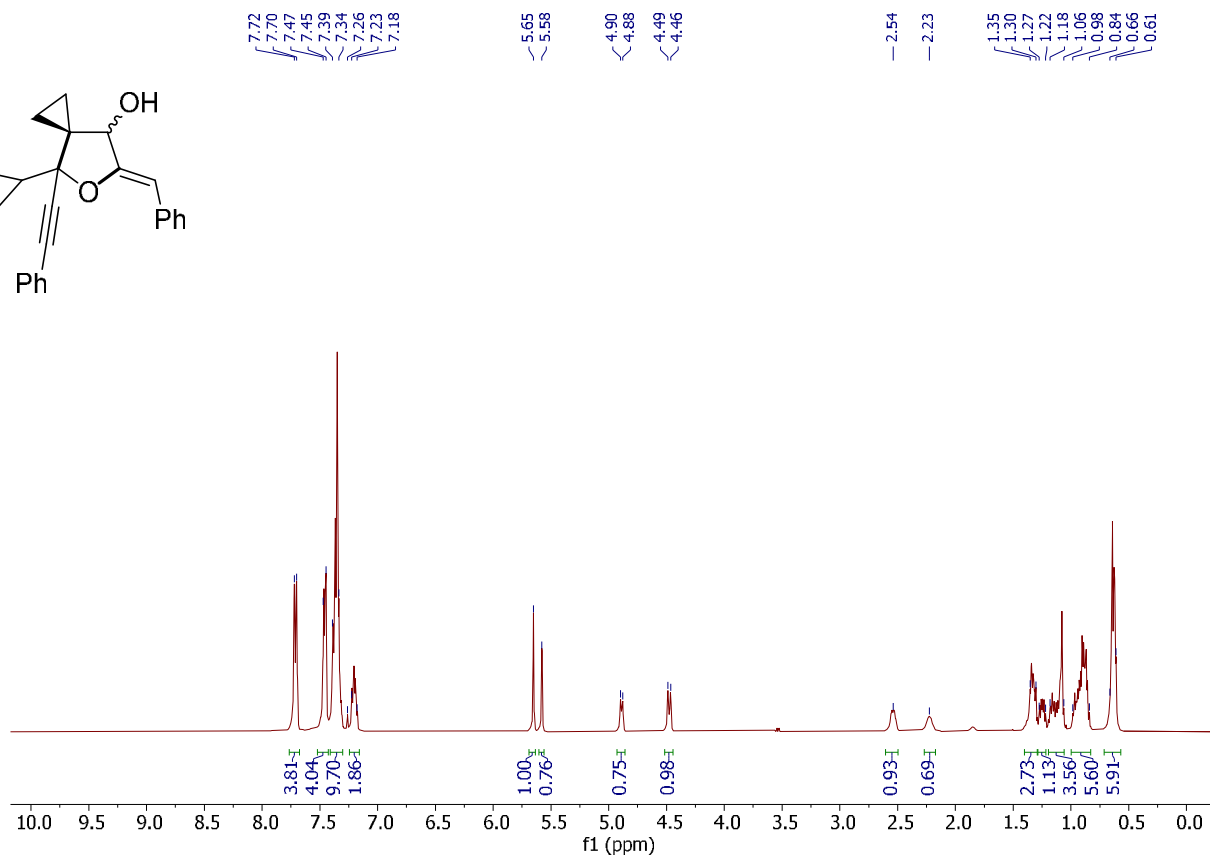
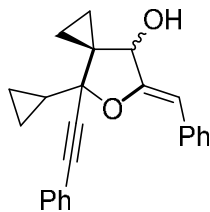


¹H NMR spectrum of **4c** (400.1 MHz, CDCl₃)

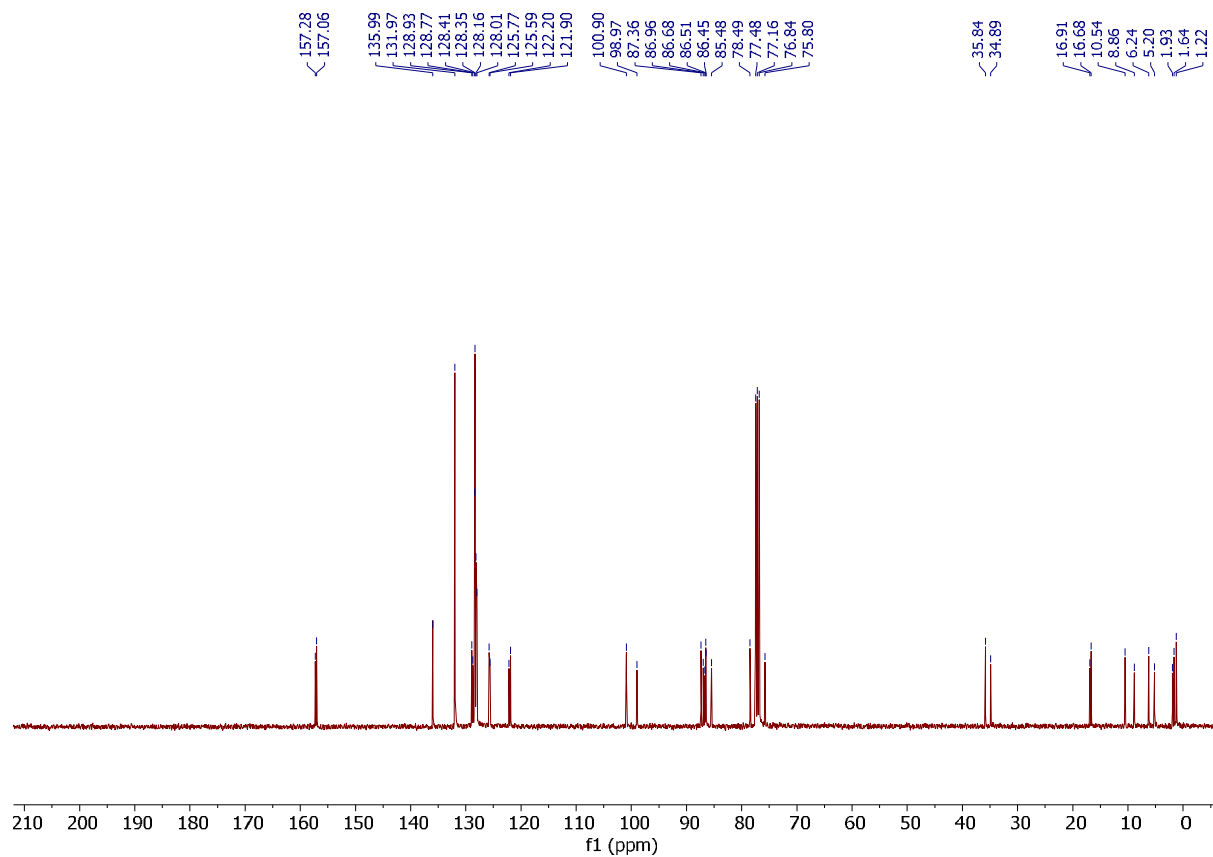


¹³C NMR spectrum of **4c** (100.6 MHz, CDCl₃)

^1H and ^{13}C Spectra for product **5**



^1H NMR spectrum of **5** (400.1 MHz, CDCl_3)



^{13}C NMR spectrum of **5** (100.6 MHz, CDCl_3)

References

- 1 Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3-8.
- 2 Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.