

**Unexpected Cycloisomerization of Nonclassical
Carbocations Intermediates in Gold(I)-Catalyzed *homo*-
Rautenstrauch Cyclization**

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Table of Contents

| | | |
|-----|---|----|
| I. | Absolute configuration of compound 16 and compound 21 by ECD measurement..... | S2 |
| II. | Copies of spectra for new compounds..... | S4 |

Absolute configuration of compound **16** and compound **21** by ECD measurement

The absolute configuration of compound **16** (90% ee) and compound **21** (47% ee) was determined by means of a theoretical simulation of their electronic circular dichroism spectra (ECD).

The calculated spectrum (a constant width of 0.3 eV for all transitions) of compound **16** reproduces well the experimentally recorded spectrum. Specifically, it could be concluded from Figure 1 that calculated signals, positions as well as intensities of the bands ((*1S,2S*)-type) match well with the experiment ECD spectrum of compound **16** (90% ee). This means that the absolute configuration of excessive enantiomer in compound **16** (90% ee) is (*1S,2S*)-2-methyl-2-(1-methylethenyl)cyclopropanecarboxylic acid. Similarly, in Figure 2, from TD-DFT calculations (a constant width of 0.3 eV for all transitions) for *R* type compound **21**, it could be concluded that the absolute configuration of excessive enantiomer in compound **21** (47% ee) is (*S*)-2,4-dimethyl-4-(1-methylethenyl)cyclohex-2-enone.

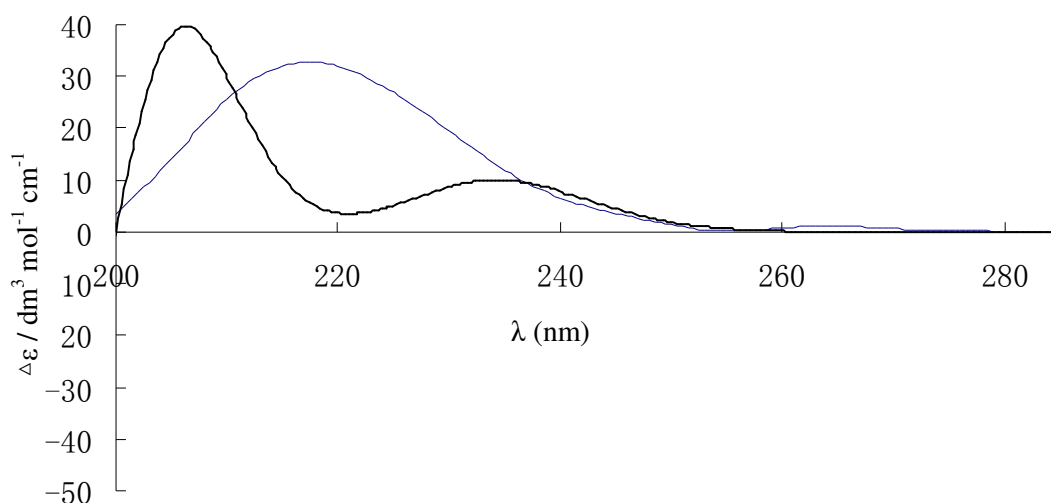


Figure 1. Experimental ECD spectrum of compound **16** (90% ee) and theoretical ECD spectra of (*1S,2S*)-**16**. Experimental spectrum (90% ee, in methanol, *c* = 0.5 mM) was shown in dashed line, theoretical for (*1S,2S*)-**16** in full line. Calculated spectra were shifted to lower energy by 0.564 eV.

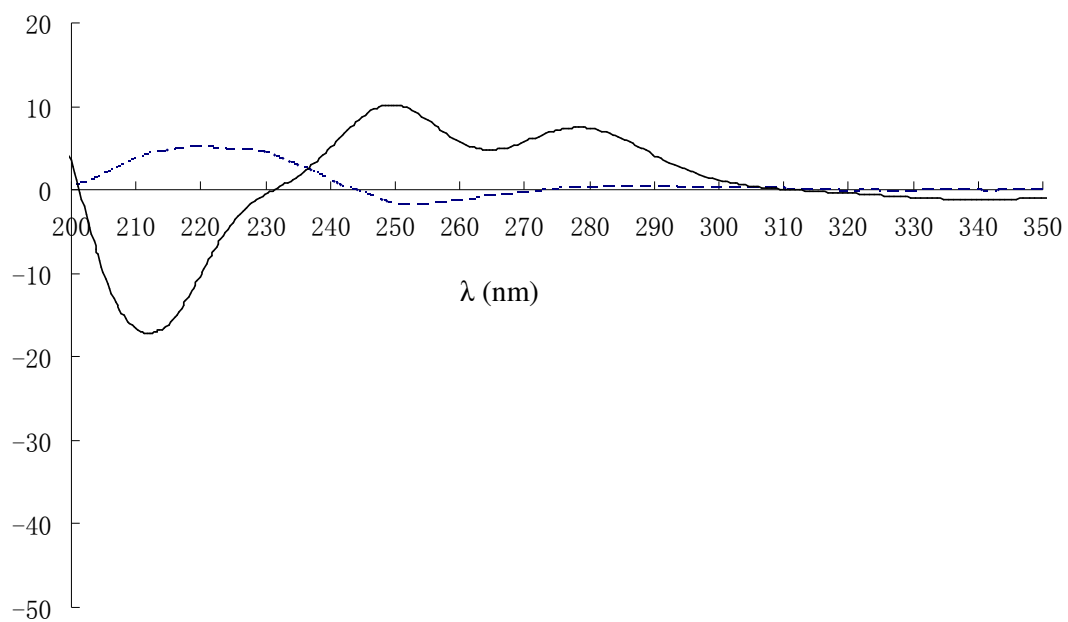
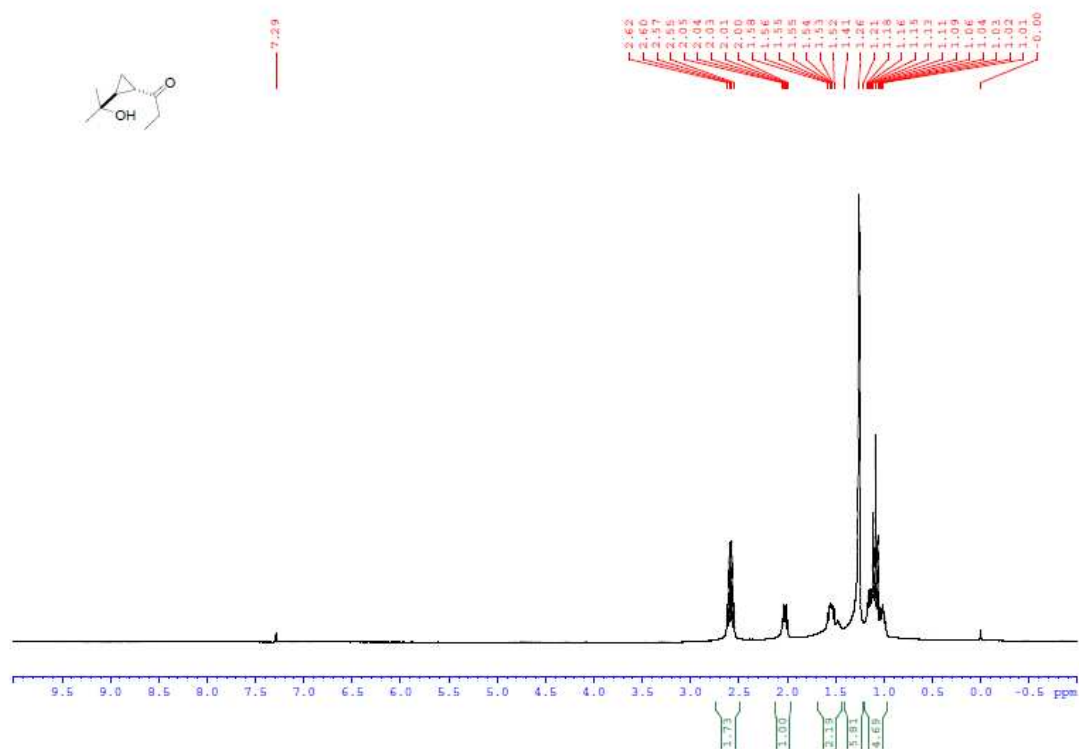
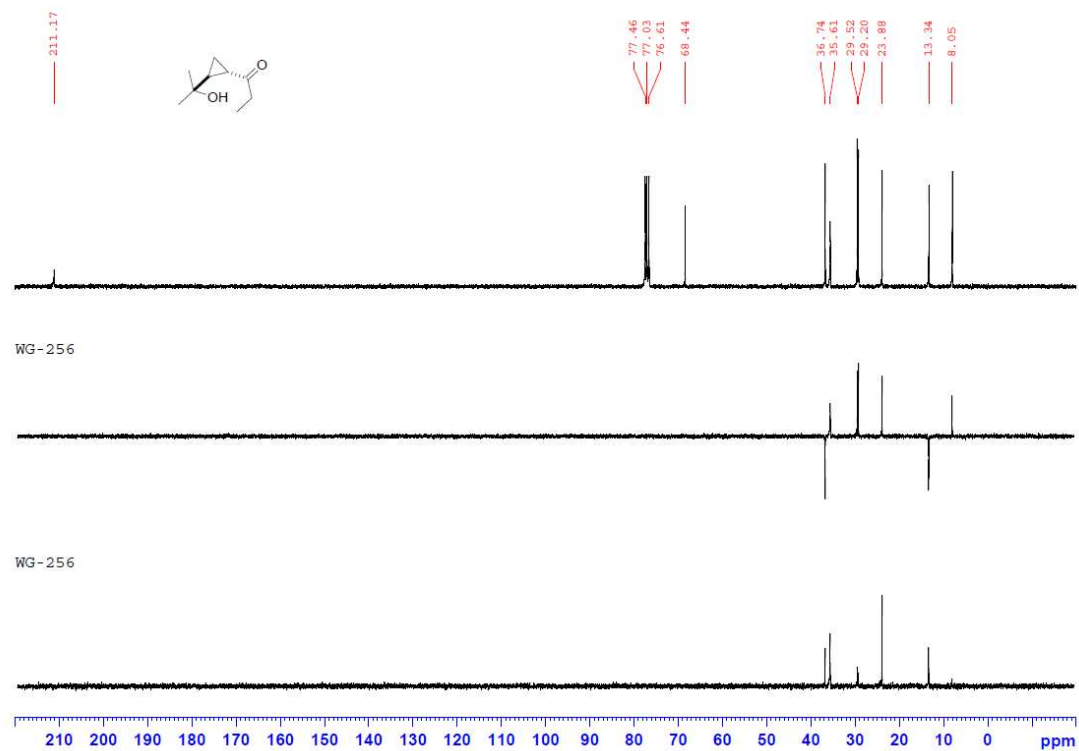
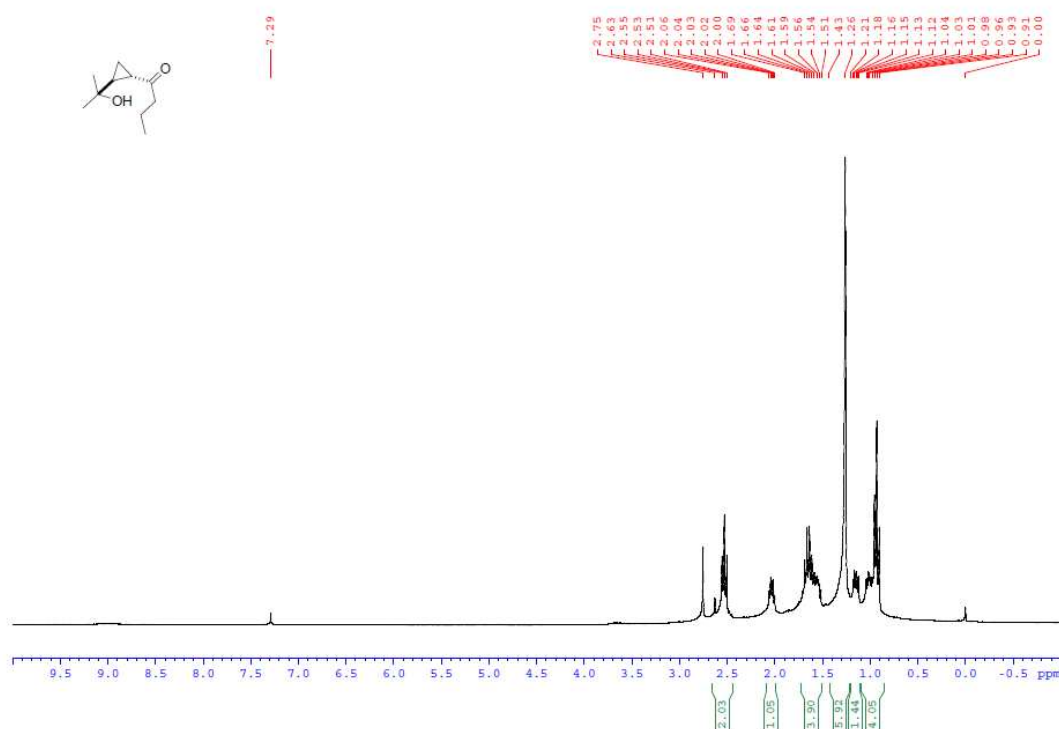
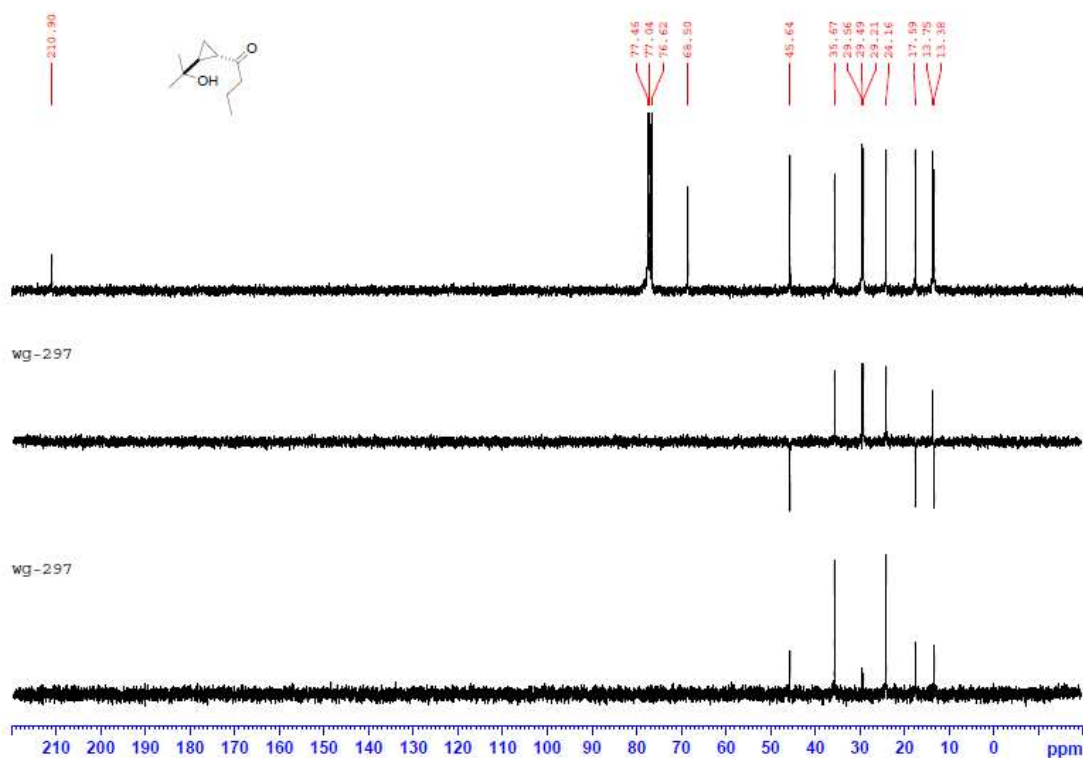
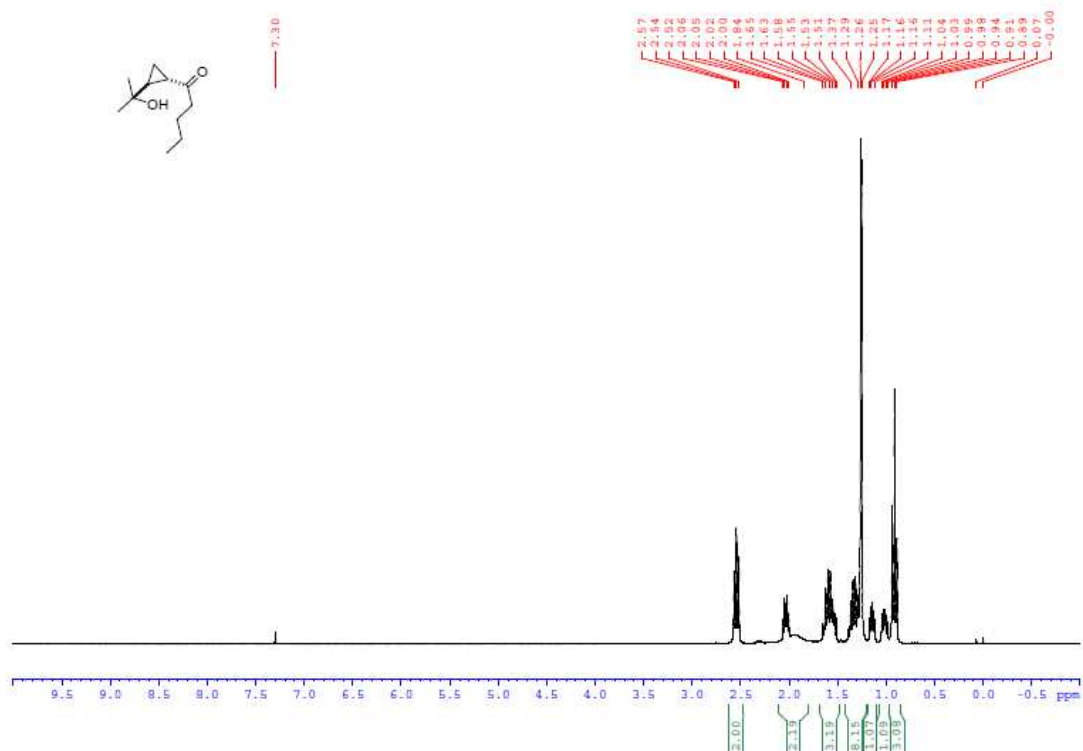
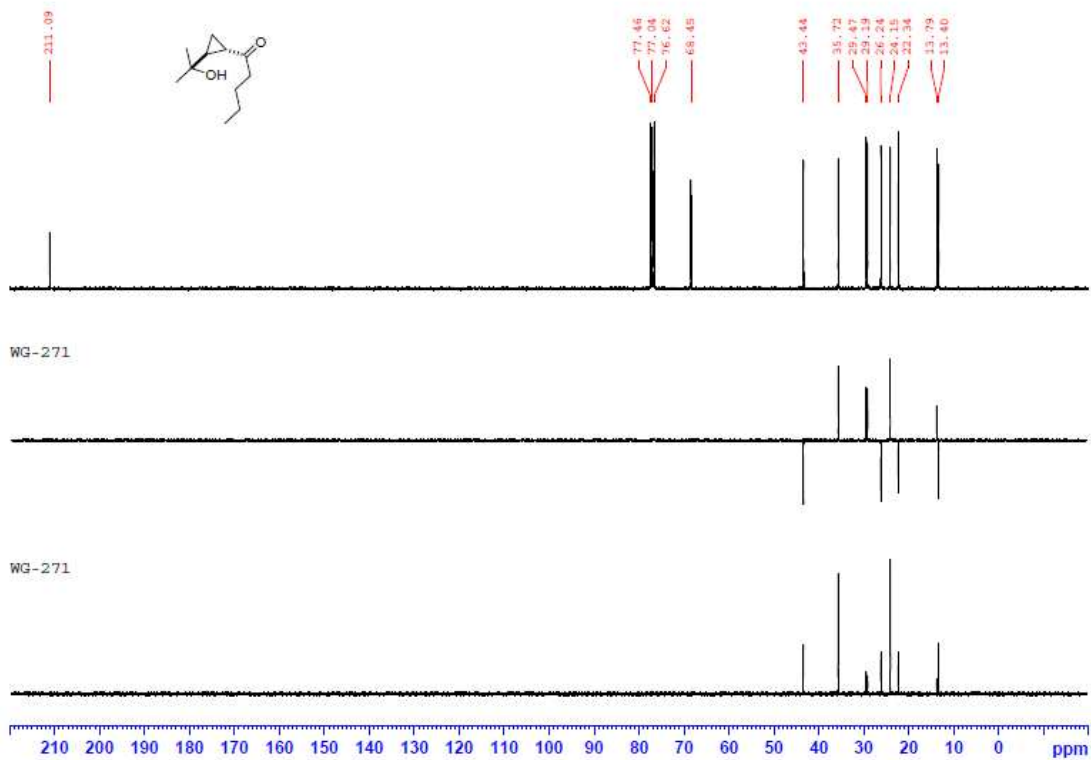


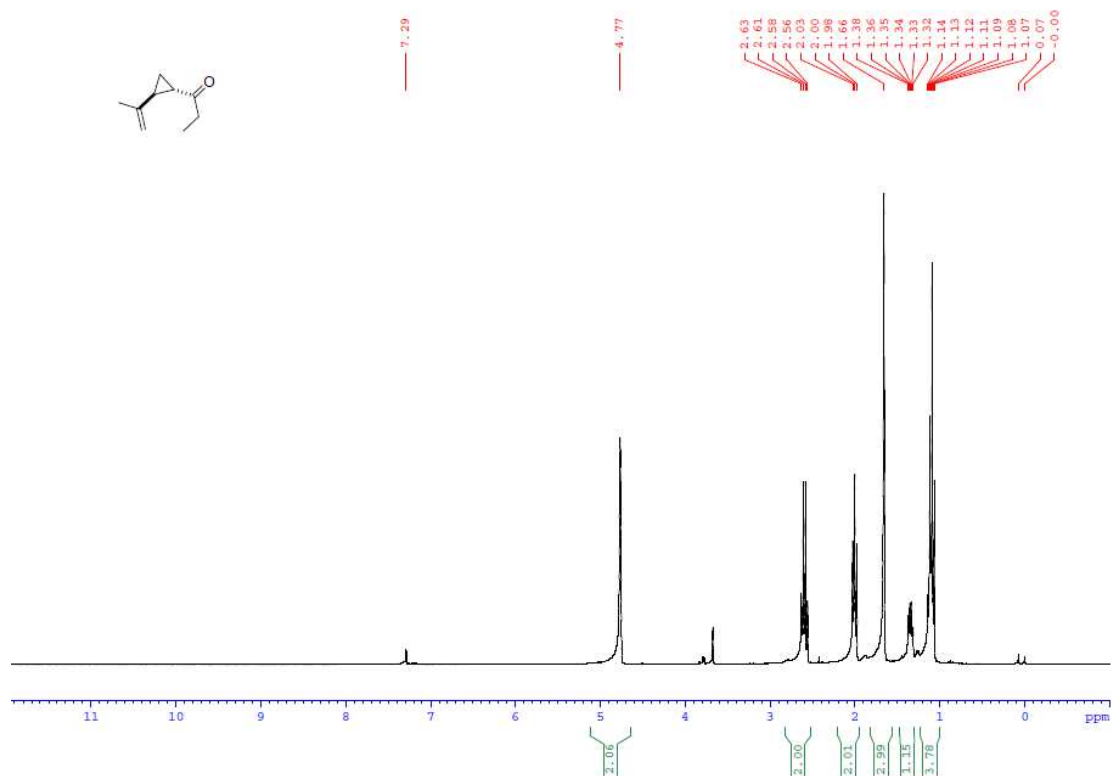
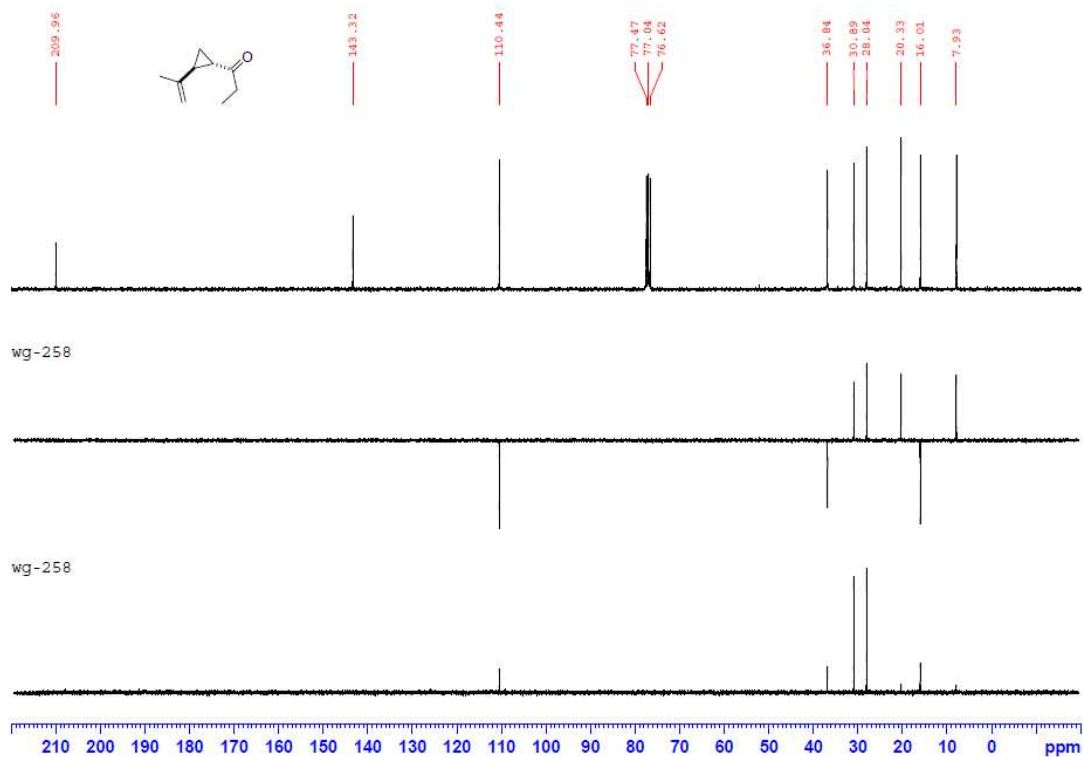
Figure 2. Experimental ECD spectrum of compound **21** (47% ee) and theoretical ECD spectra of (*R*)-**21**. Experimental spectrum (in methanol, $c = 0.025$ M) was shown in dashed line, theoretical spectrum for (*R*)-**21** in full line. Calculated spectra were shifted to lower energy by 0.326 eV.

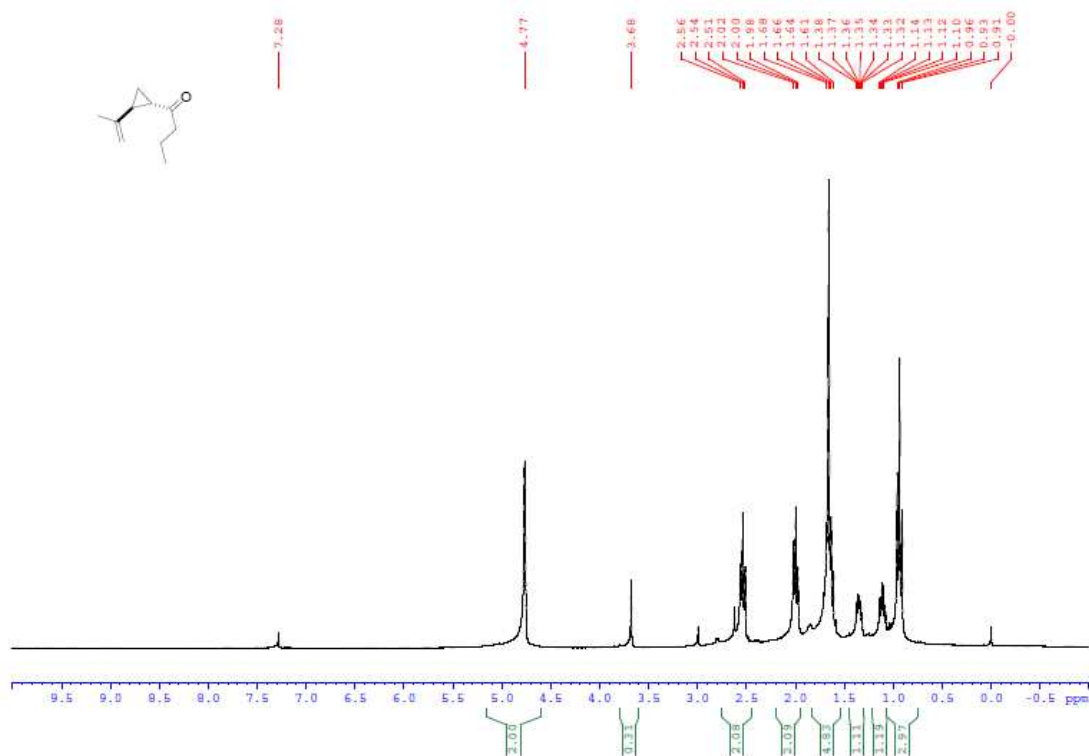
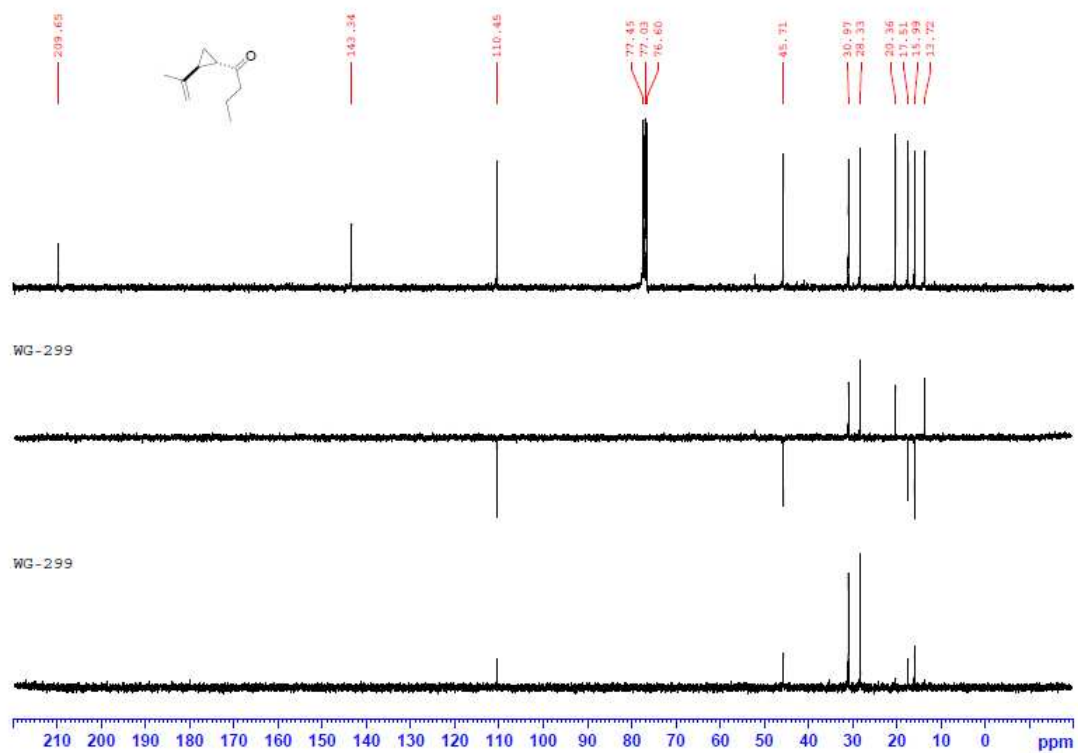
Copies of spectra for new compounds

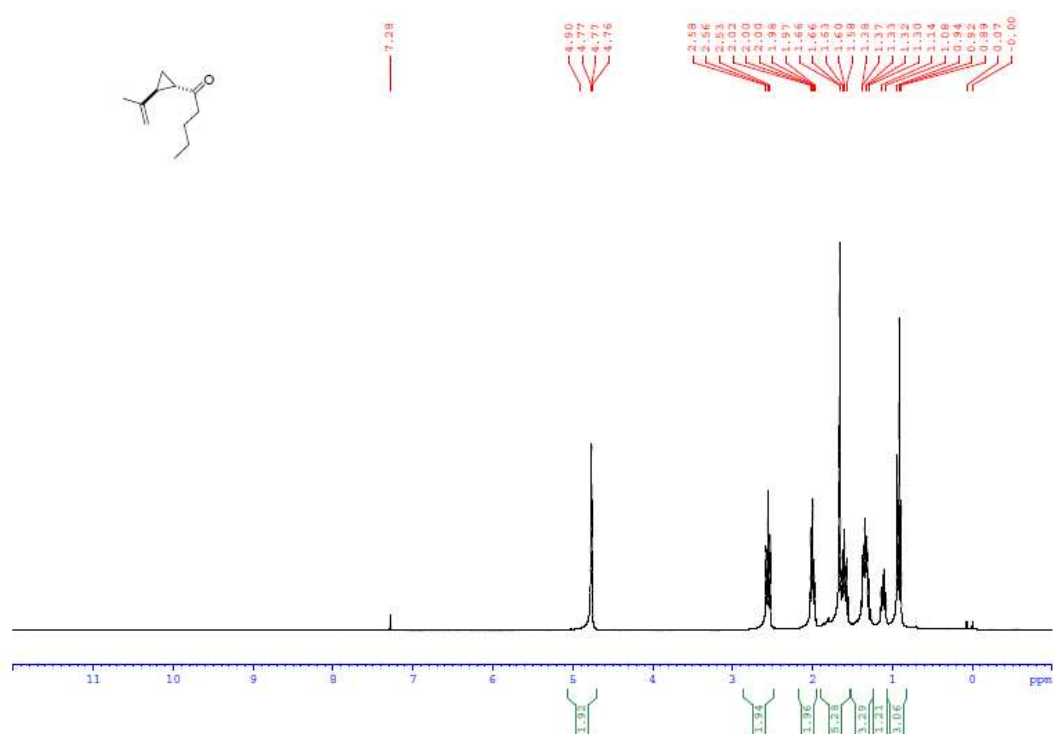
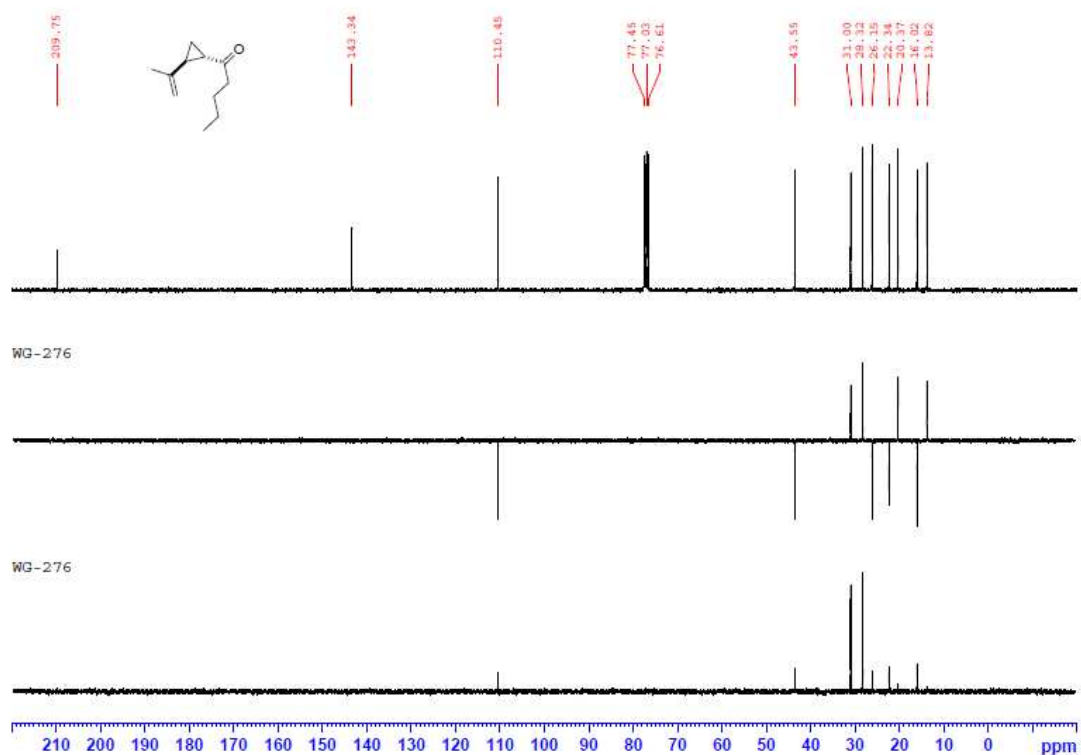
 ^1H NMR spectrum of 12b ^{13}C NMR spectrum of 12b

^1H NMR spectrum of 12c **^{13}C NMR spectrum of 12c**

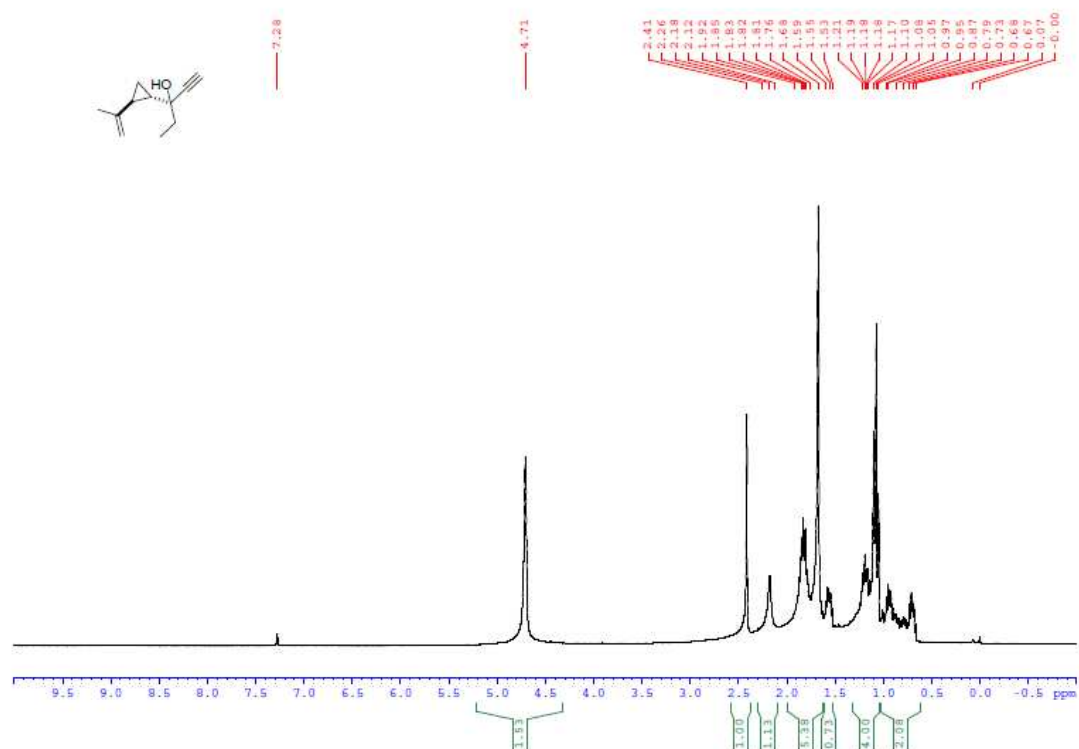
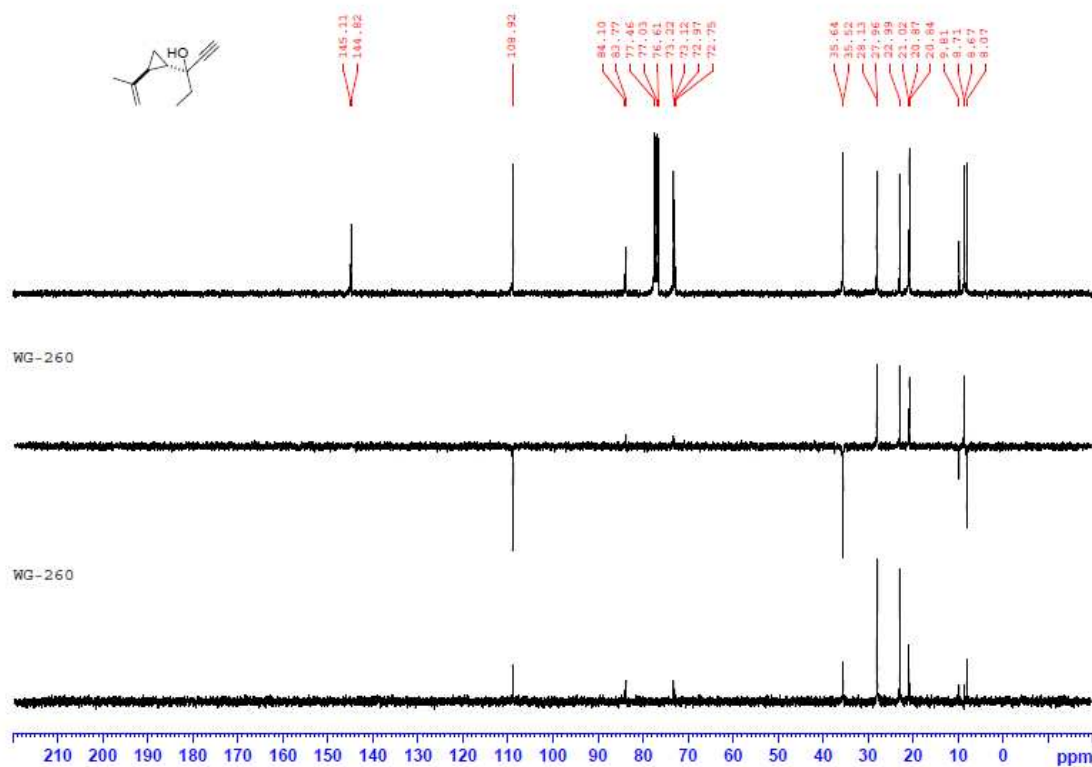
^1H NMR spectrum of 12d **^{13}C NMR spectrum of 12d**

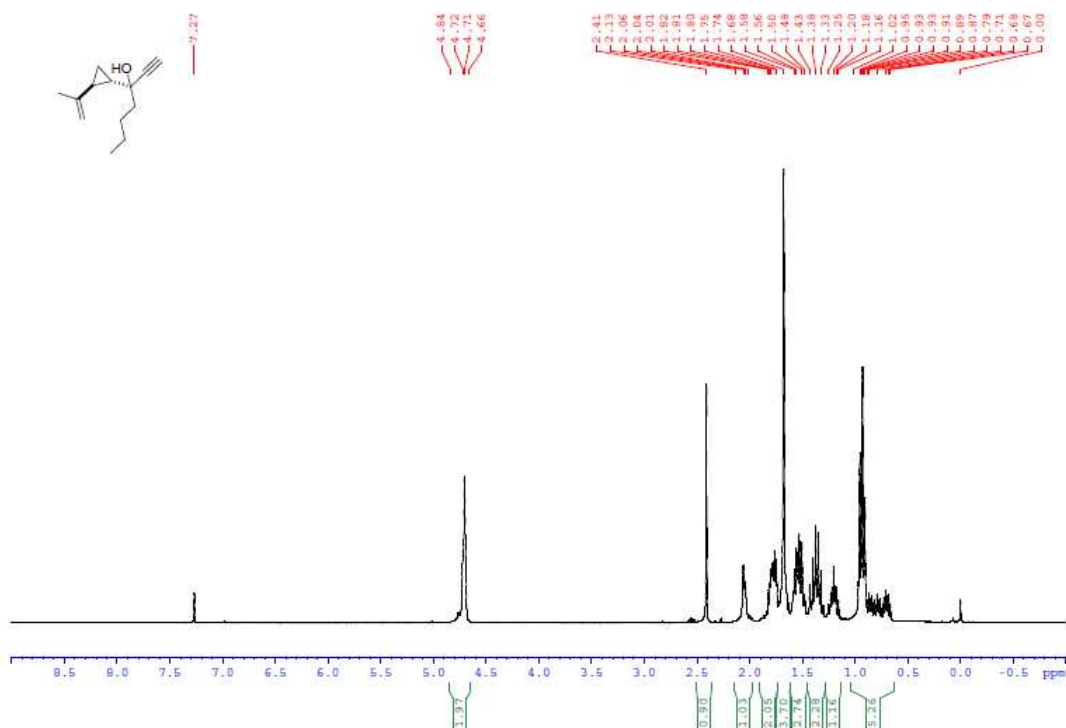
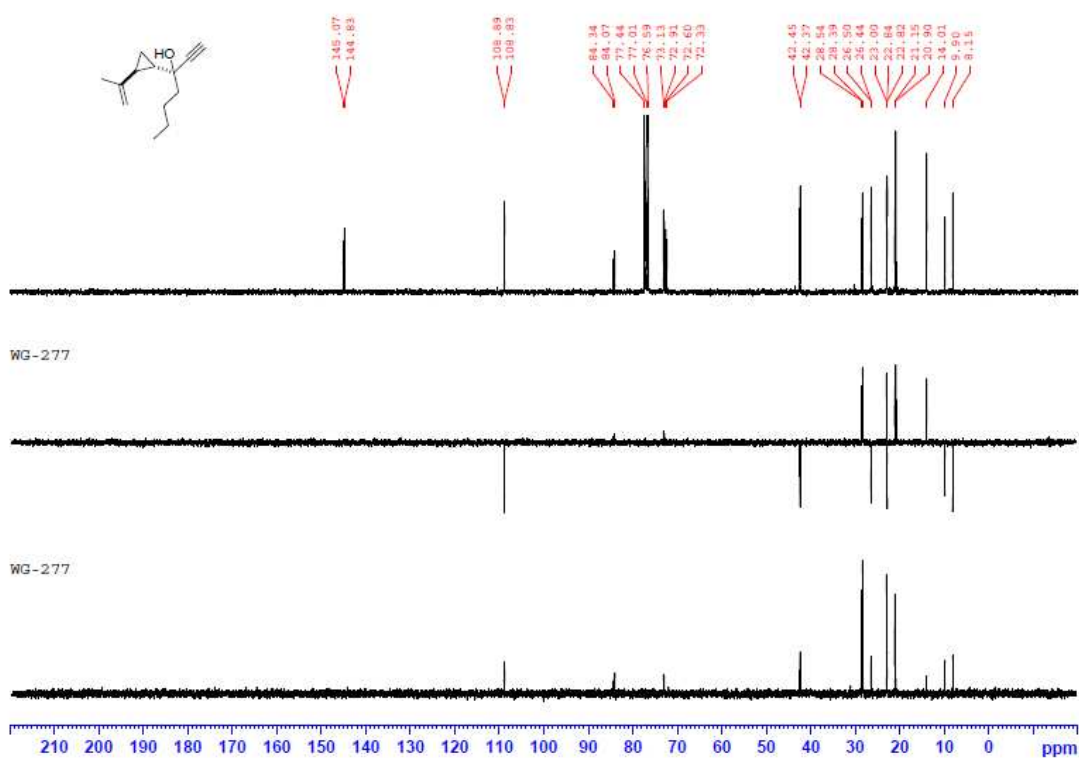
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^1H NMR spectrum of 13c **^{13}C NMR spectrum of 13c**

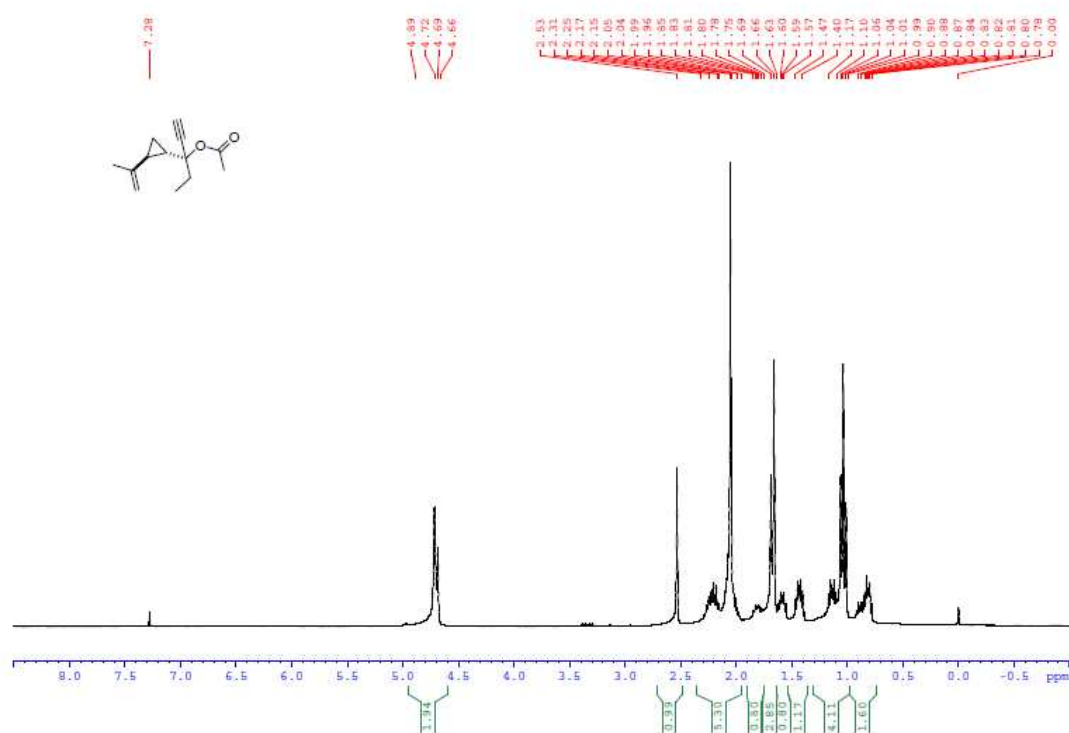
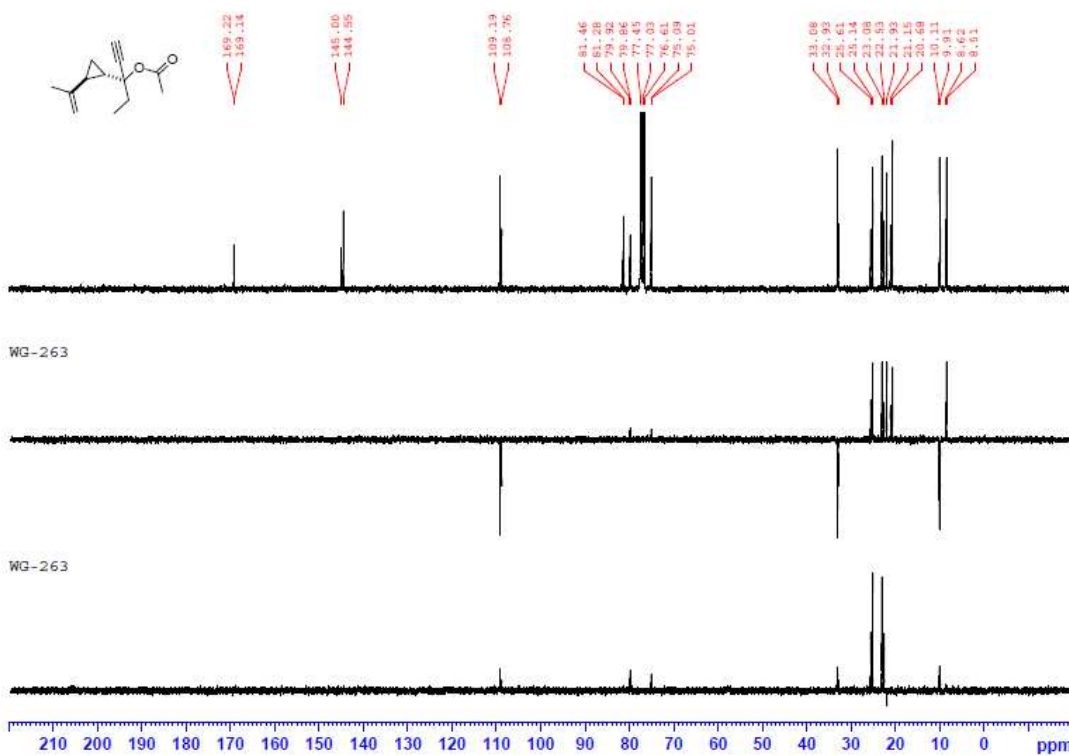
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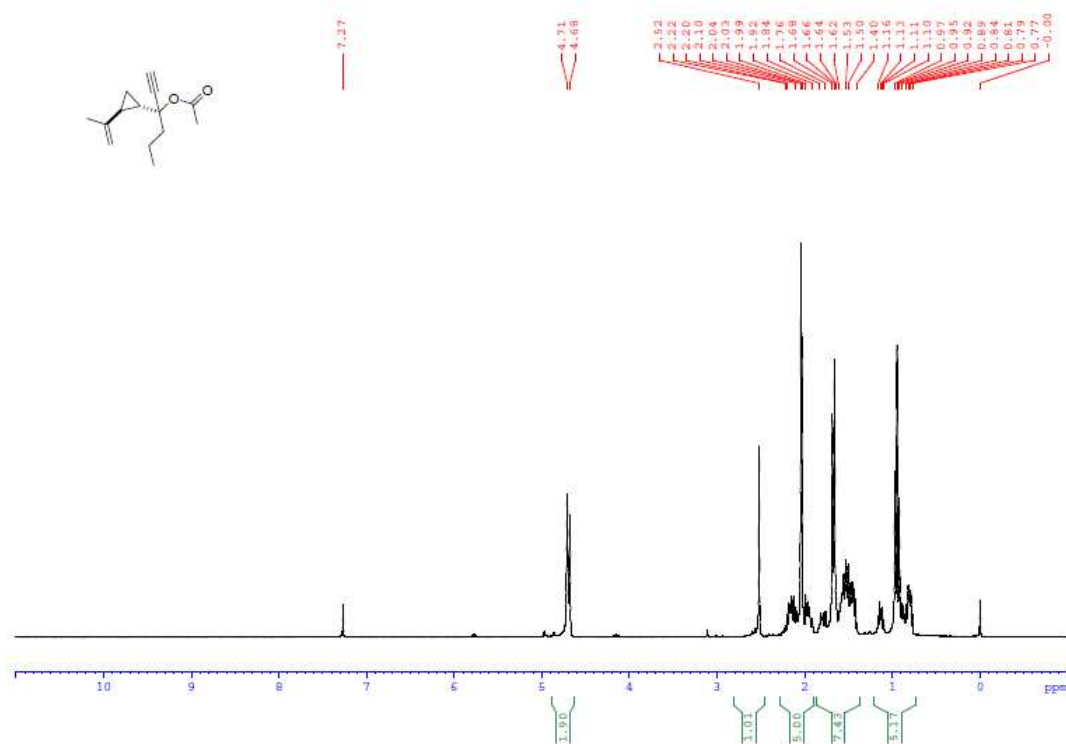
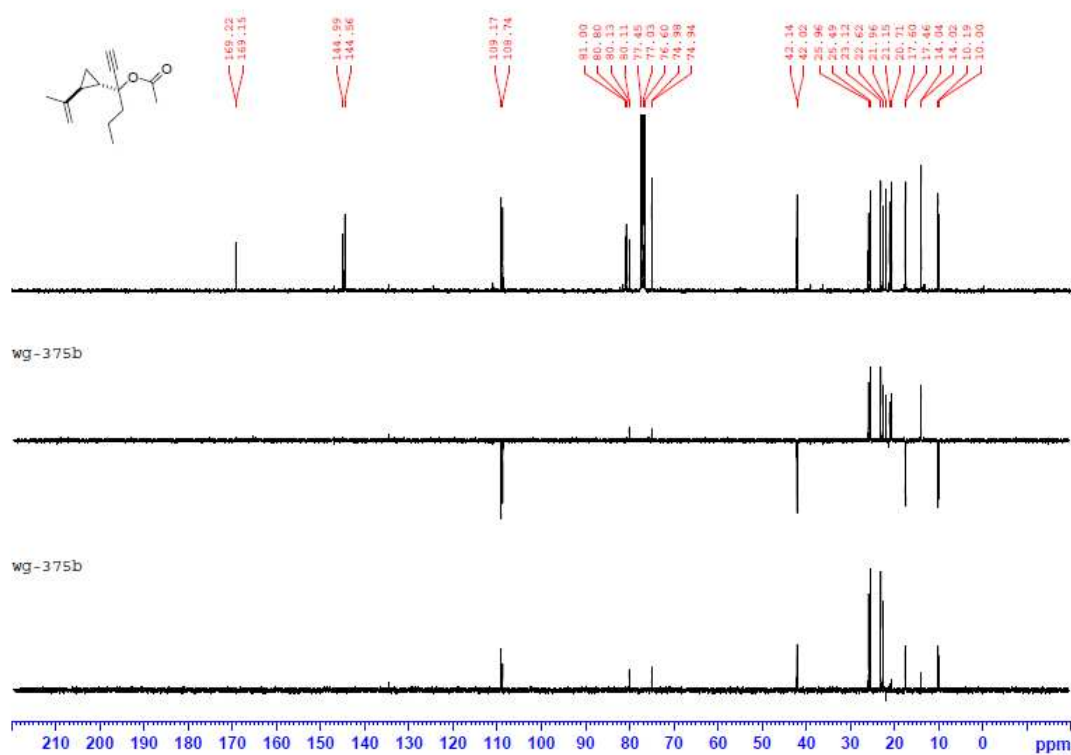


^1H NMR spectrum of 14b **^{13}C NMR spectrum of 14b**

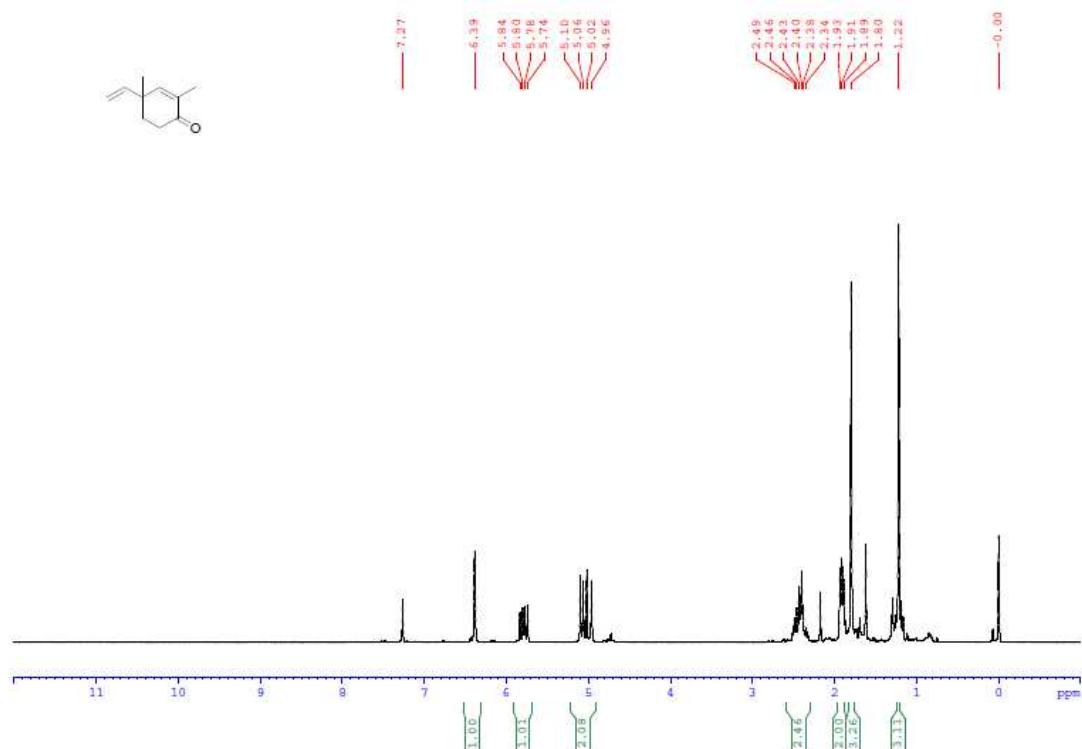
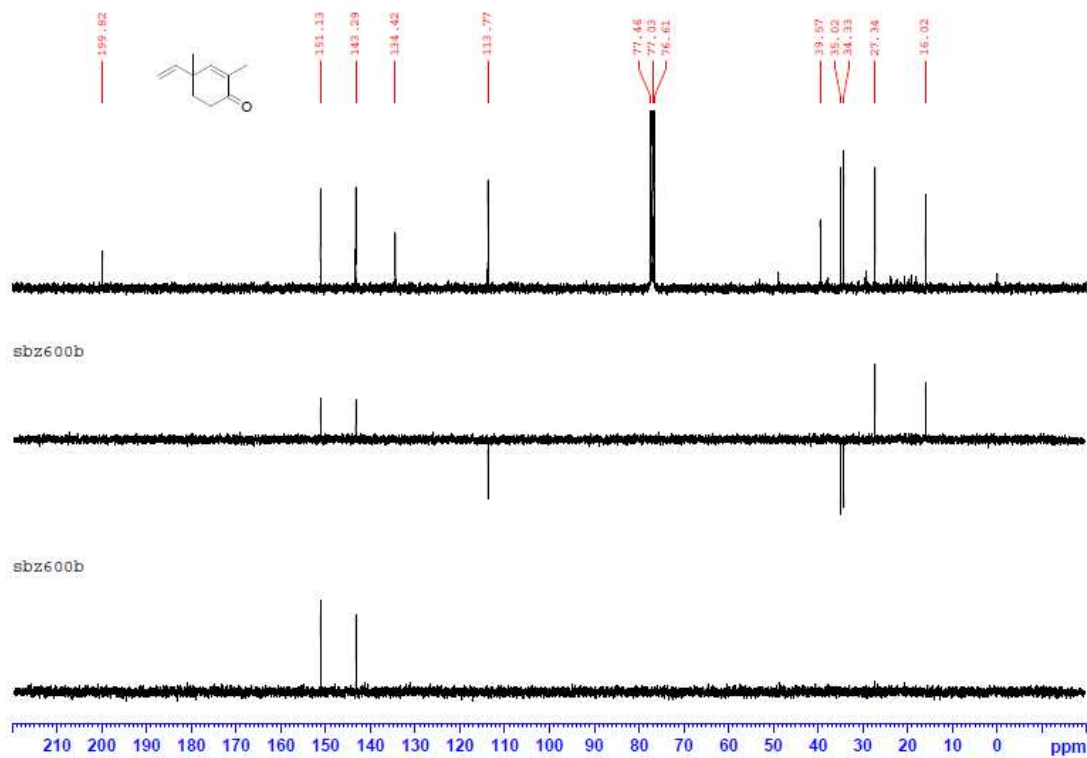
^1H NMR spectrum of 14d **^{13}C NMR spectrum of 14d**

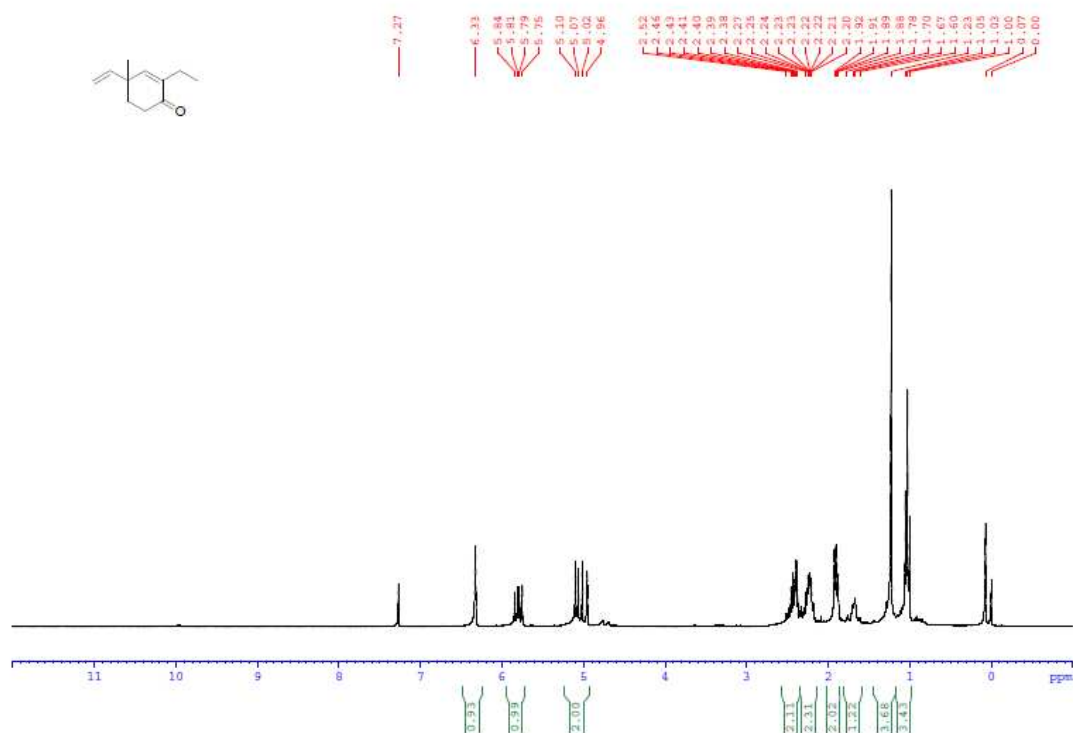
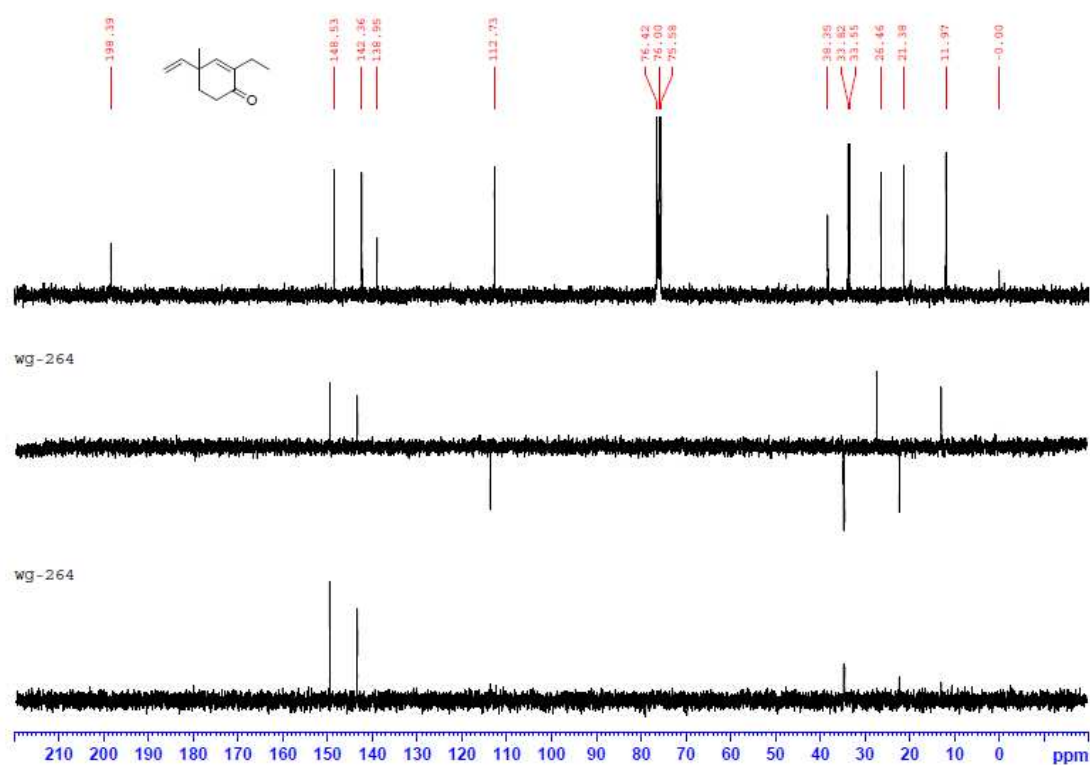


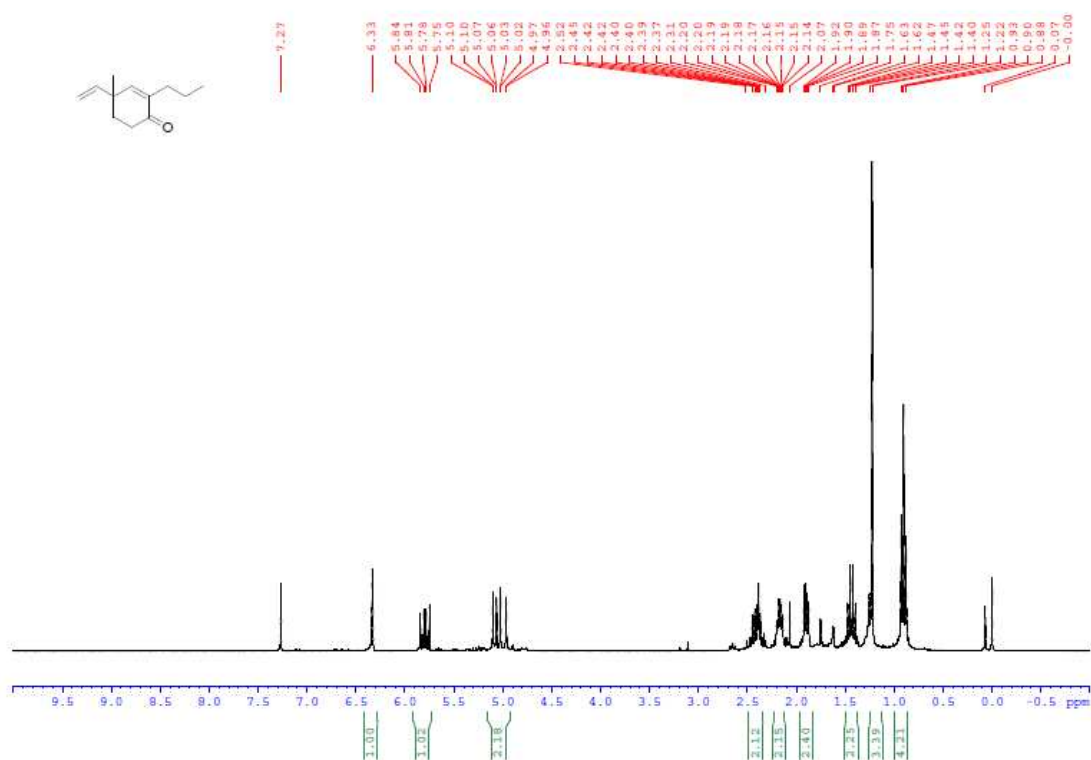
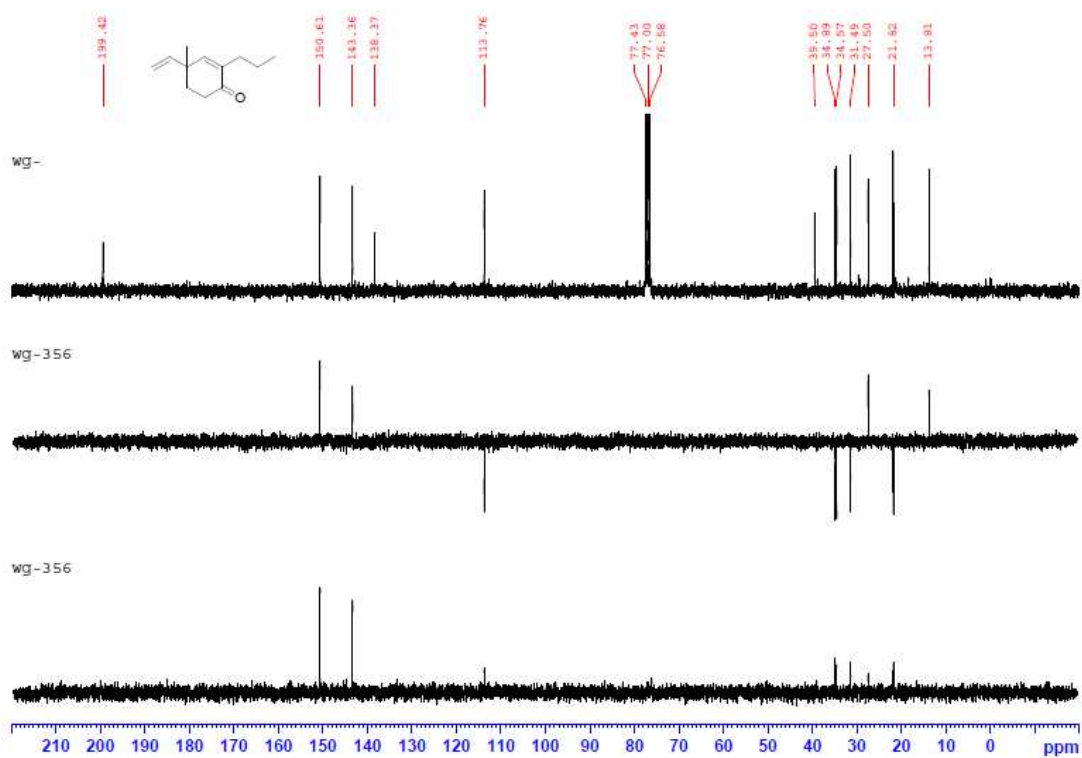
¹H NMR spectrum of 1b¹³C NMR spectrum of 1b

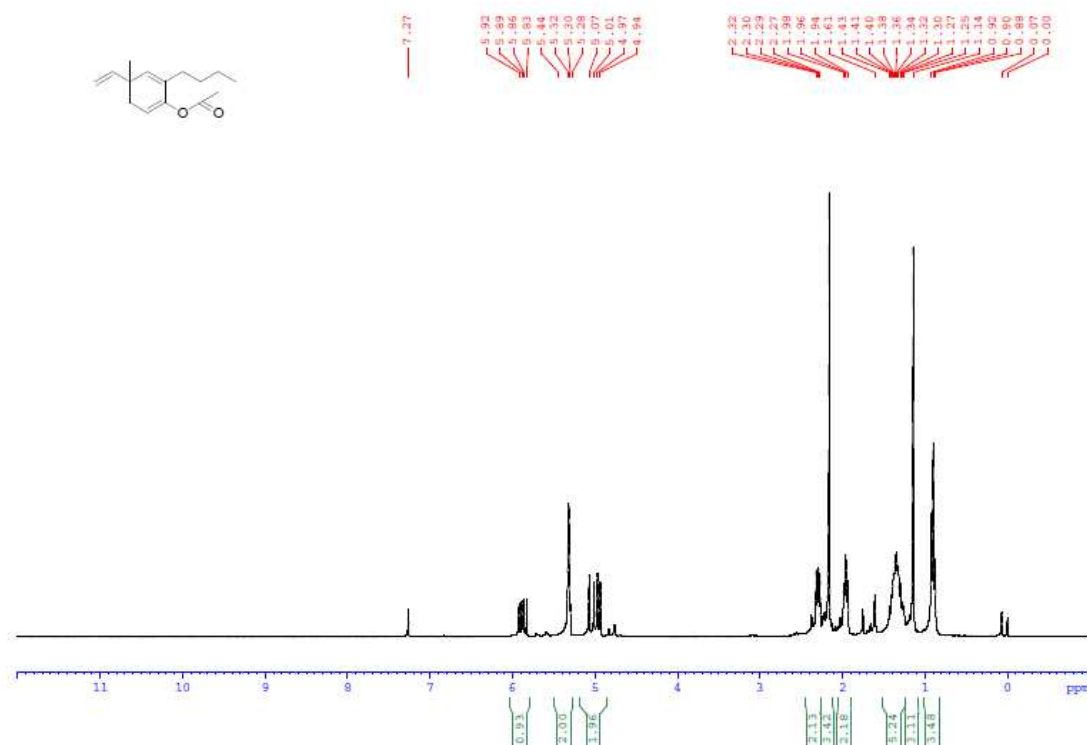
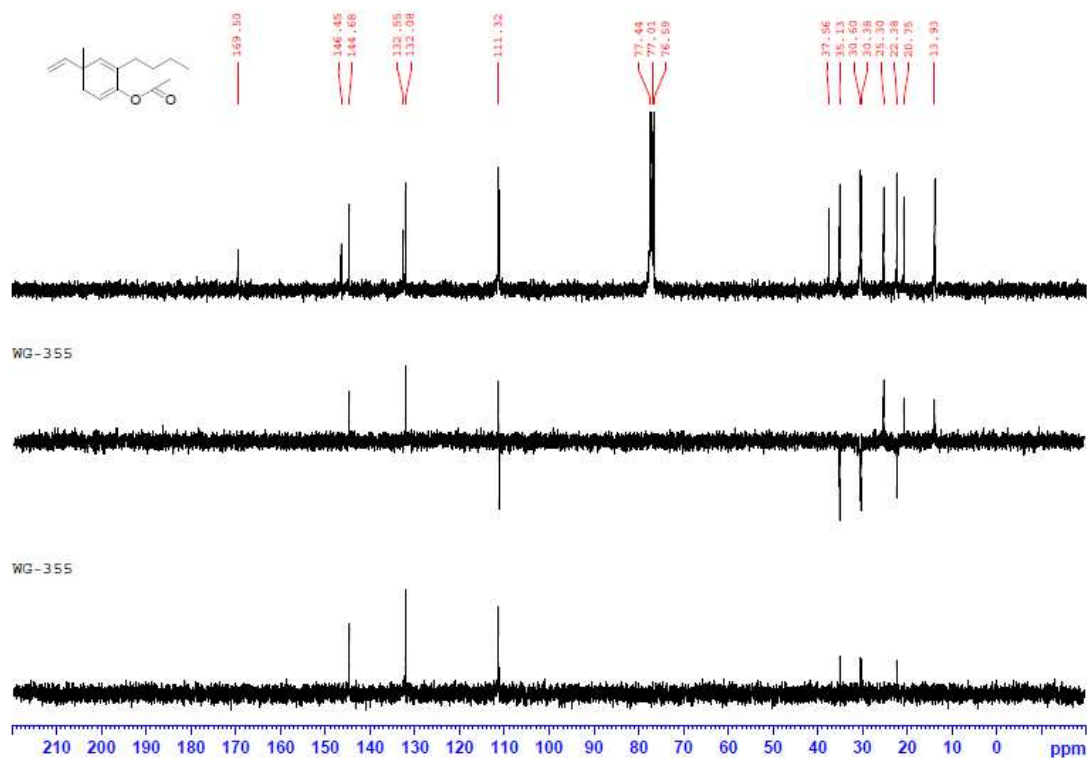
¹H NMR spectrum of 1c**¹³C NMR spectrum of 1c**

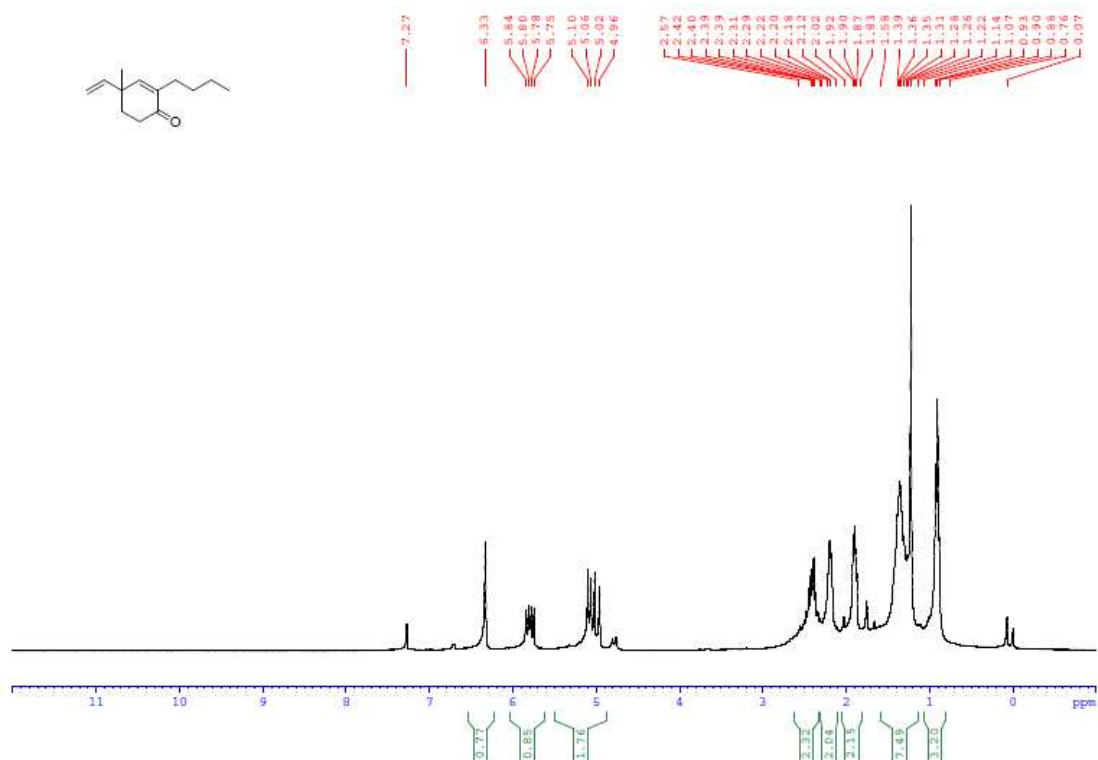
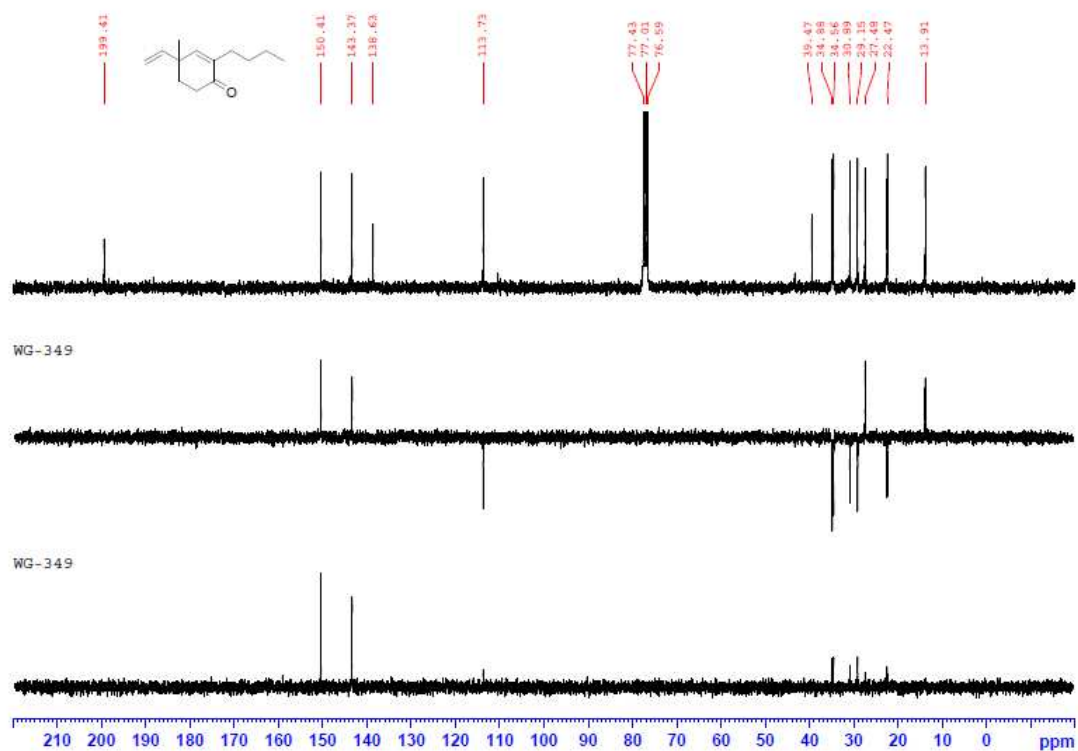


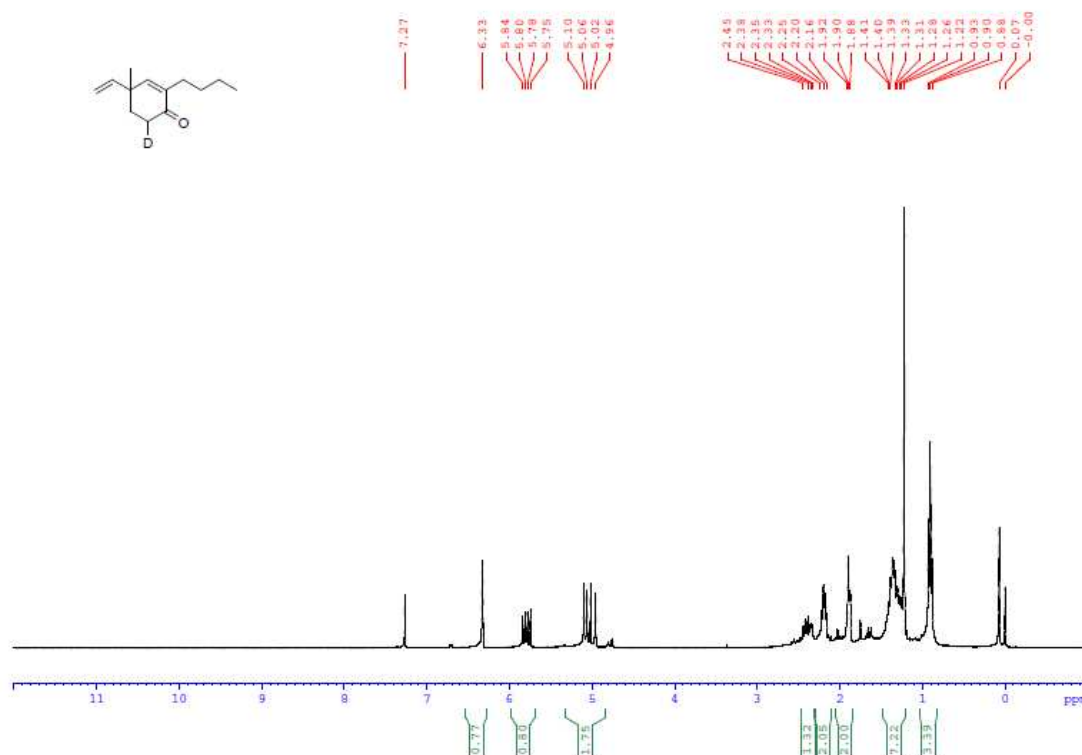
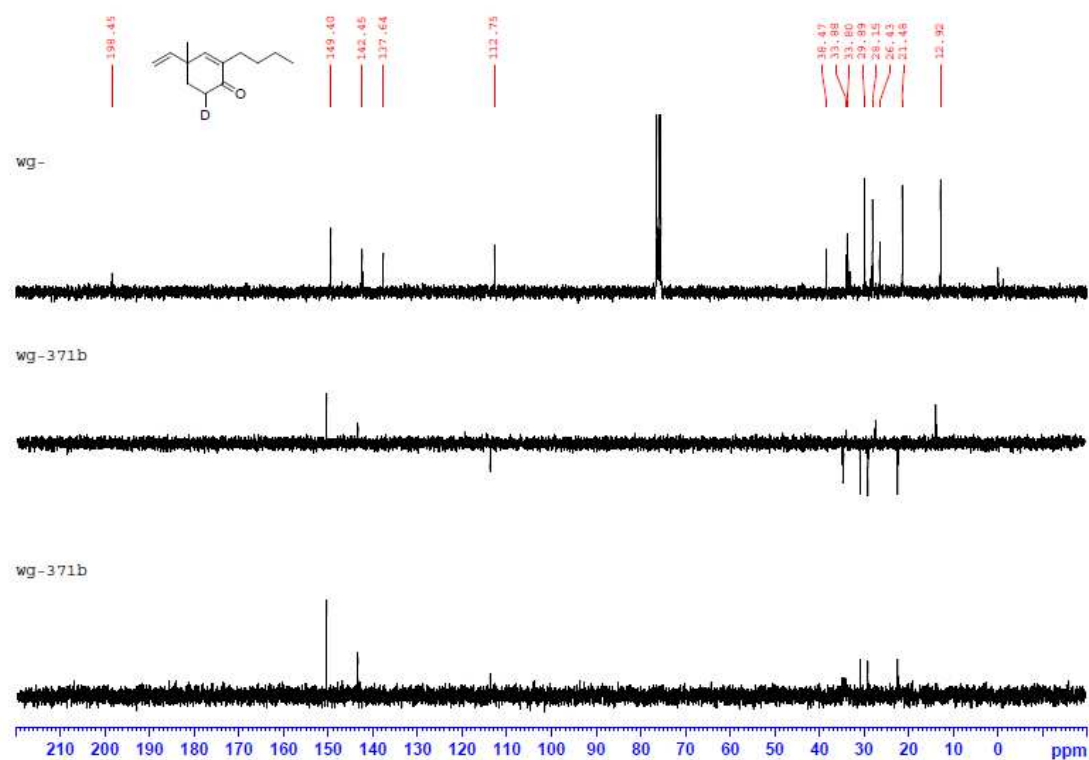
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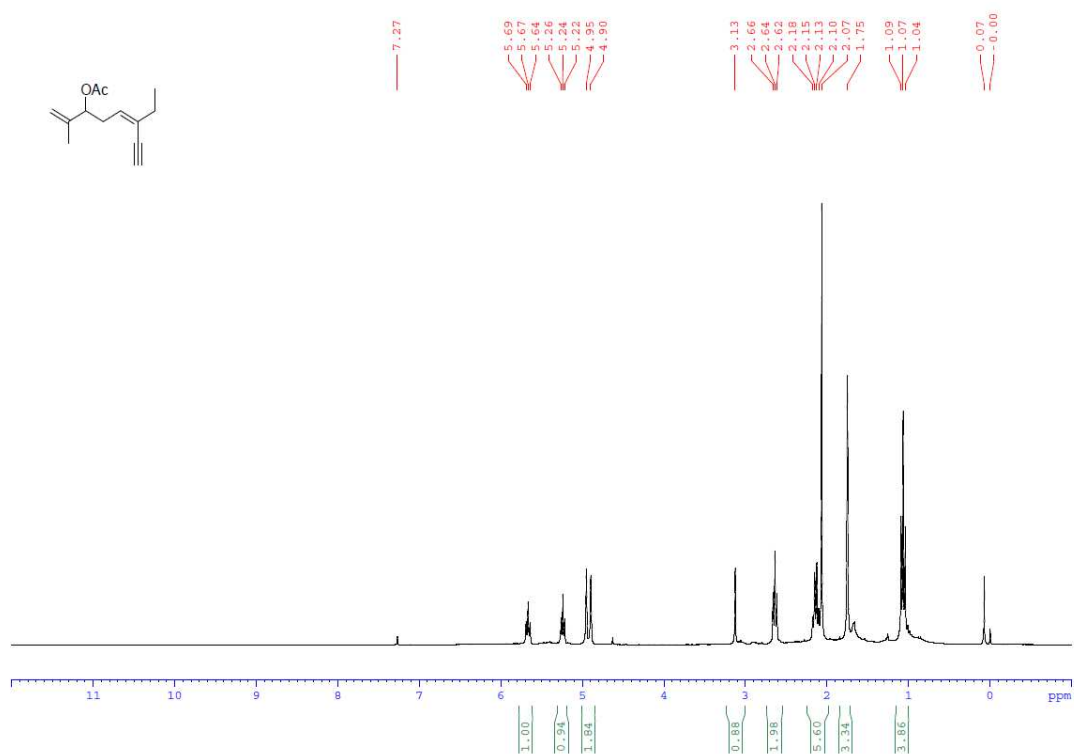
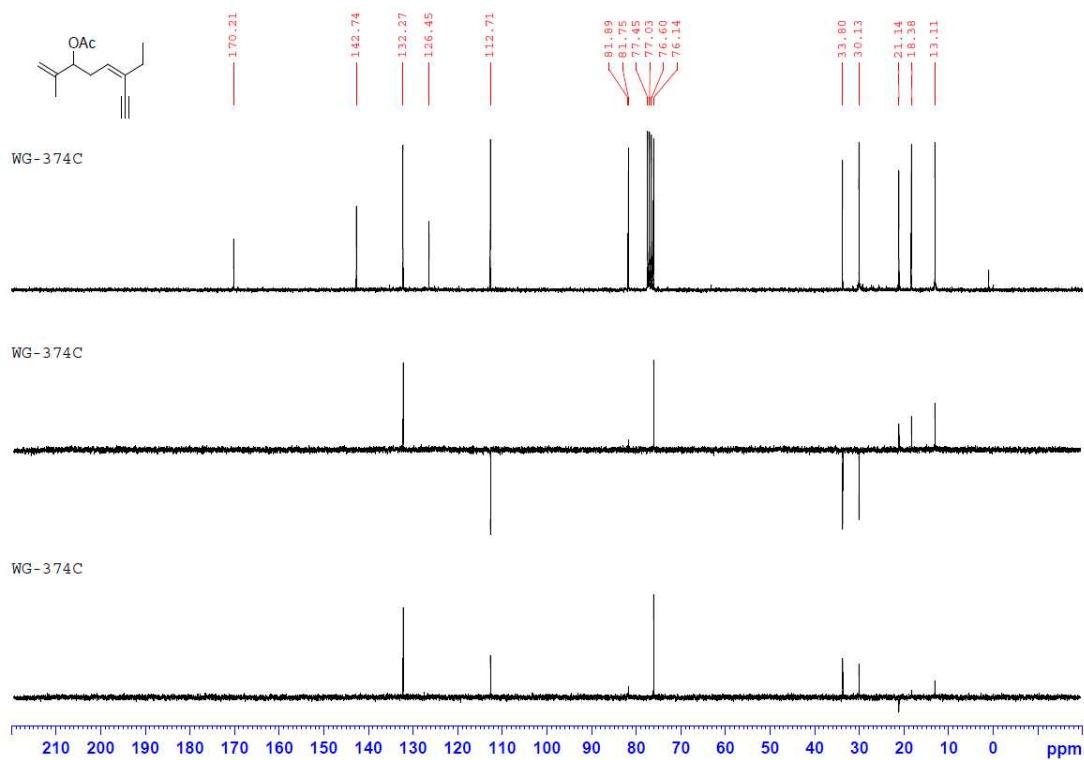
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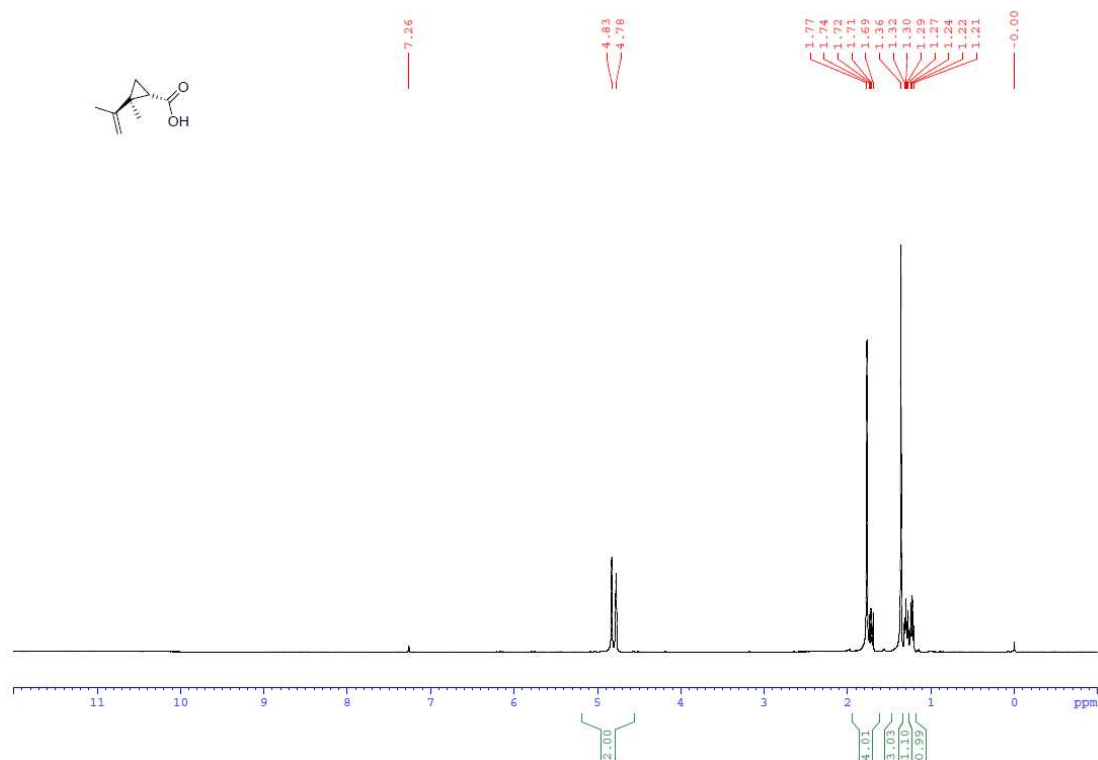
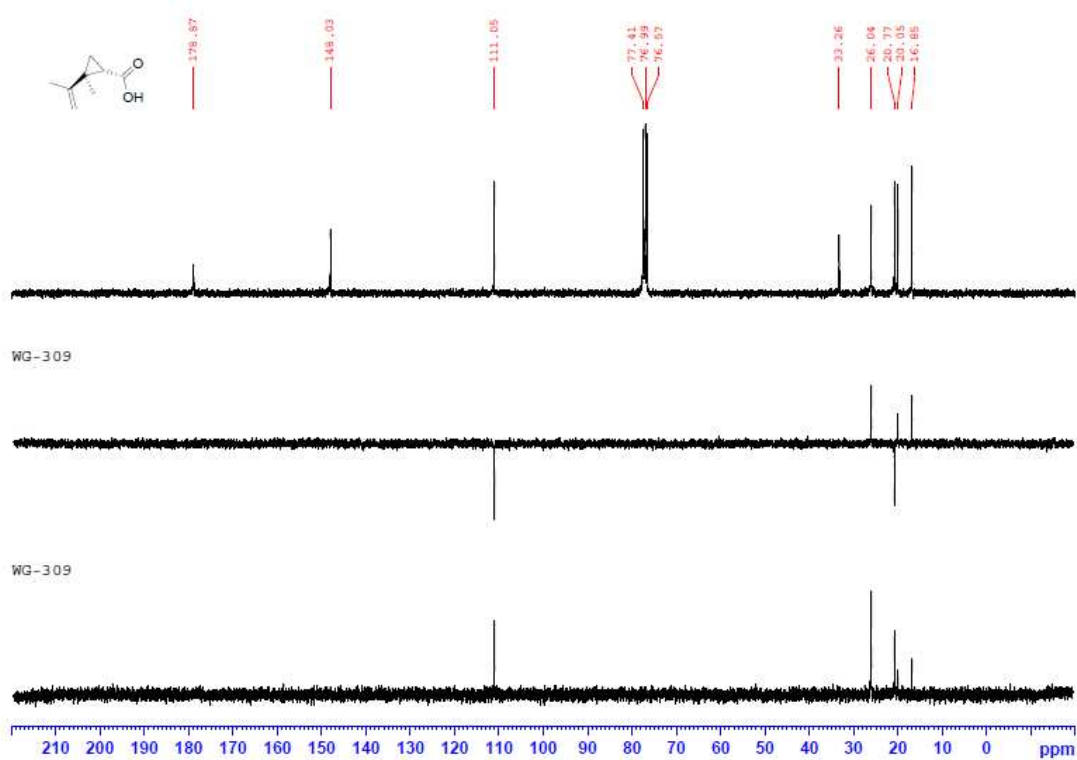
¹H NMR spectrum of 6c**¹³C NMR spectrum of 6c**

¹H NMR spectrum of 6d'**¹³C NMR spectrum of 6d'**

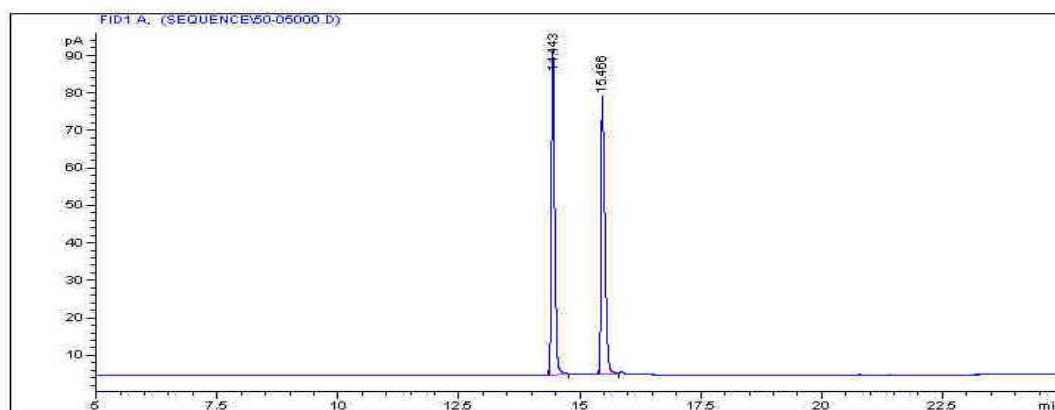
¹H NMR spectrum of 6d**¹³C NMR spectrum of 6d**

^1H NMR spectrum of 6e **^{13}C NMR spectrum of 6e**

^1H NMR spectrum of 6f **^{13}C NMR spectrum of 6f**

^1H NMR spectrum of 16 **^{13}C NMR spectrum of 16**

Chiral GC spectrum of rac-16



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Area Percent Report
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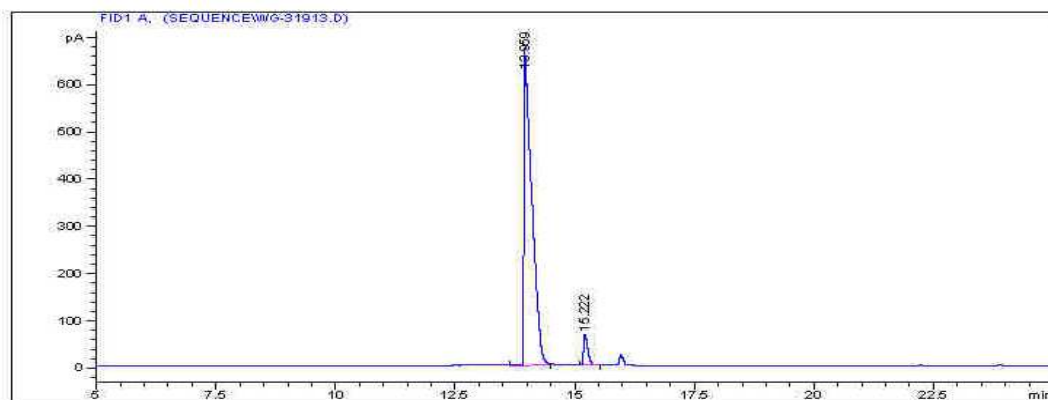
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Results obtained with enhanced integrator!

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*** End of Report ***

Chiral GC spectrum of (1S,2S)-16 (90 % ee)



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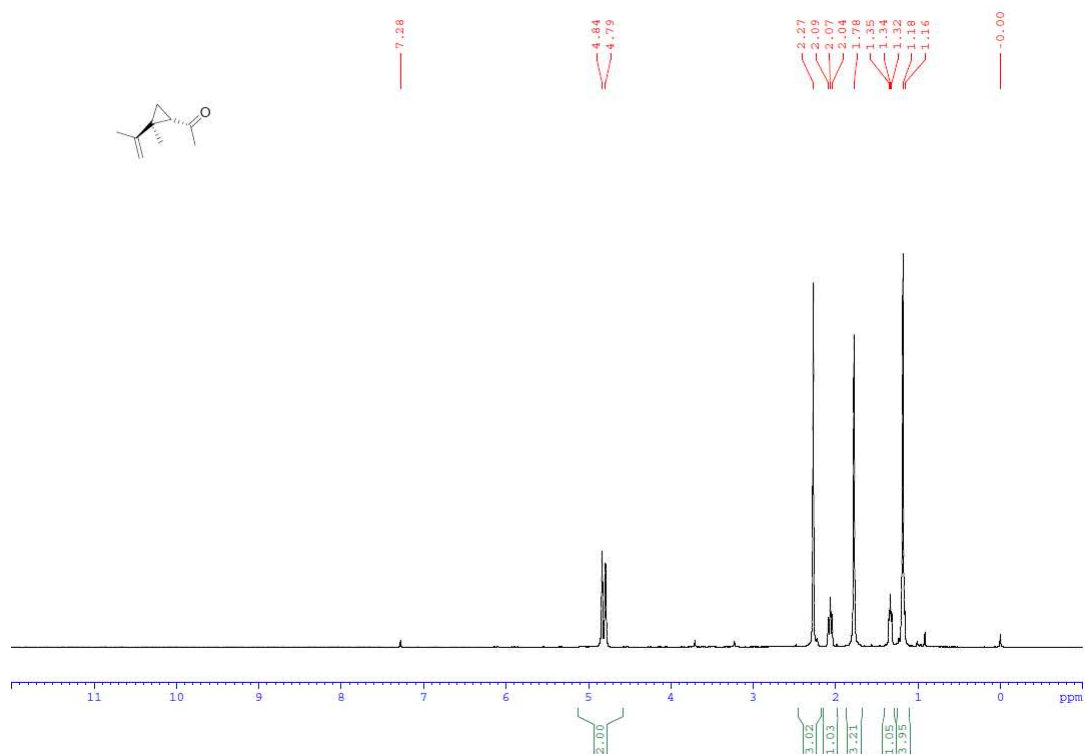
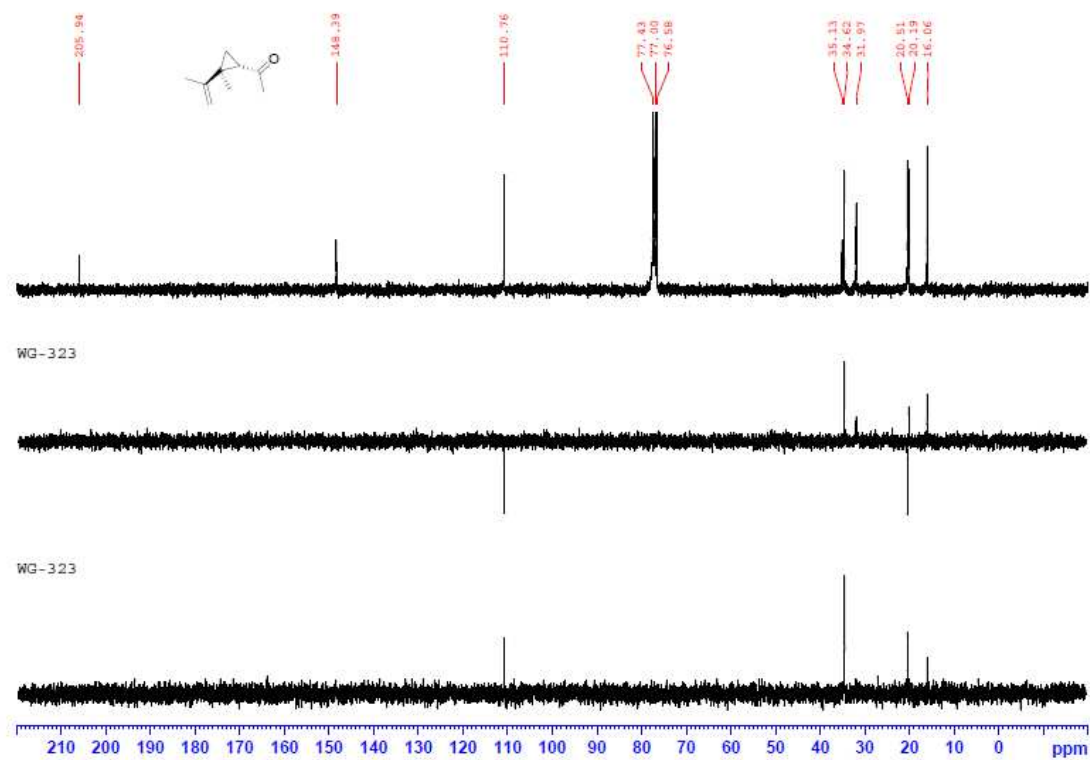
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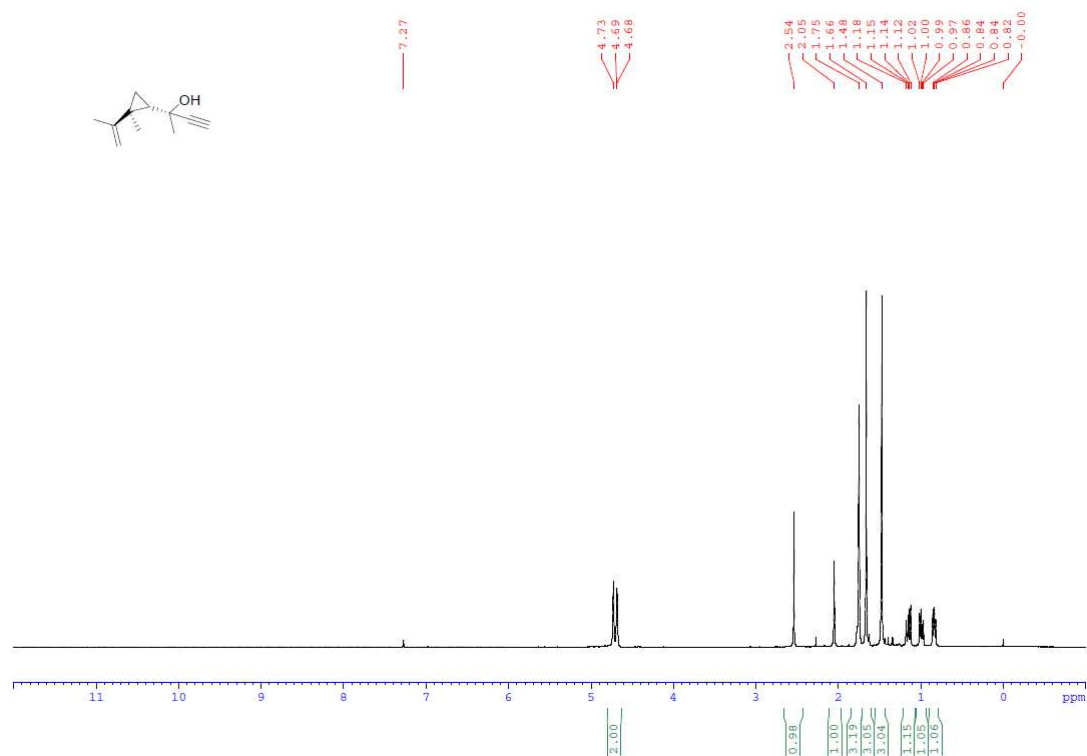
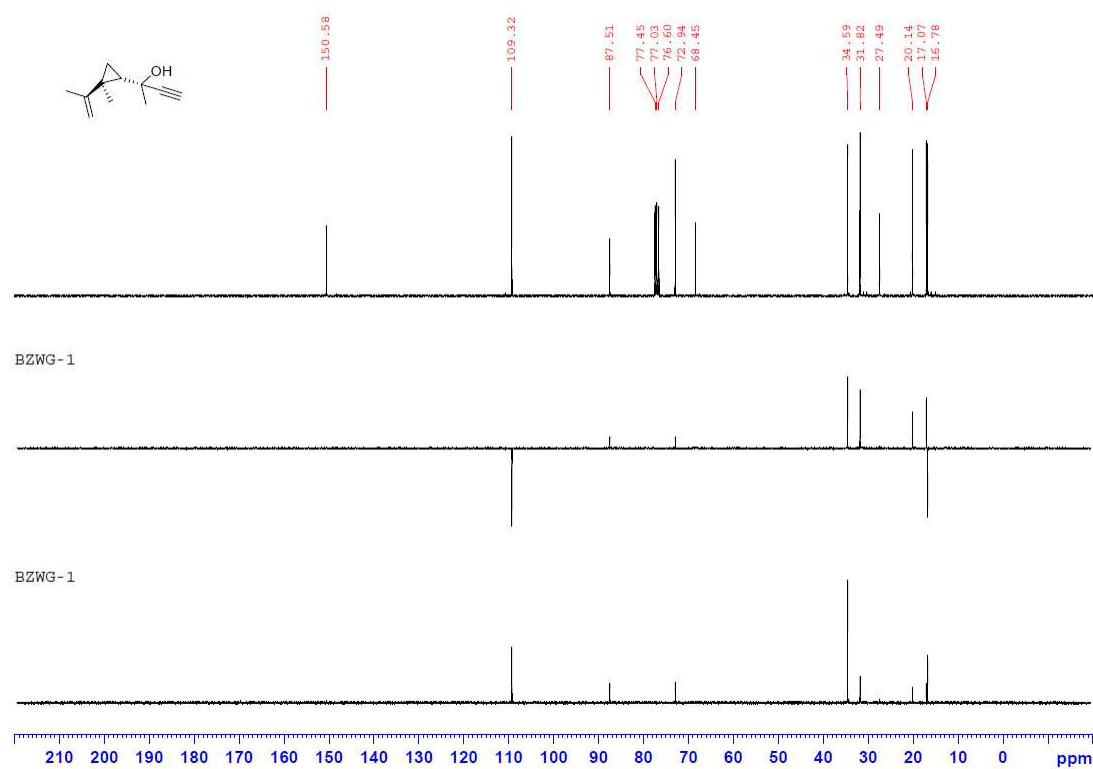
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Results obtained with enhanced integrator!

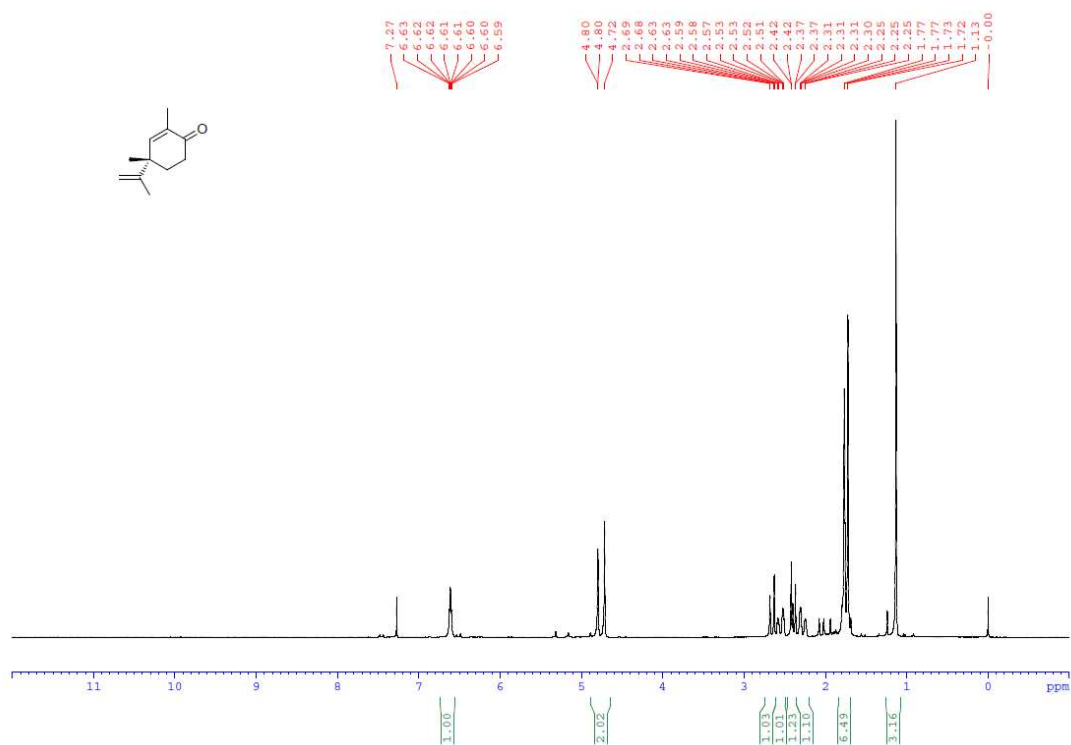
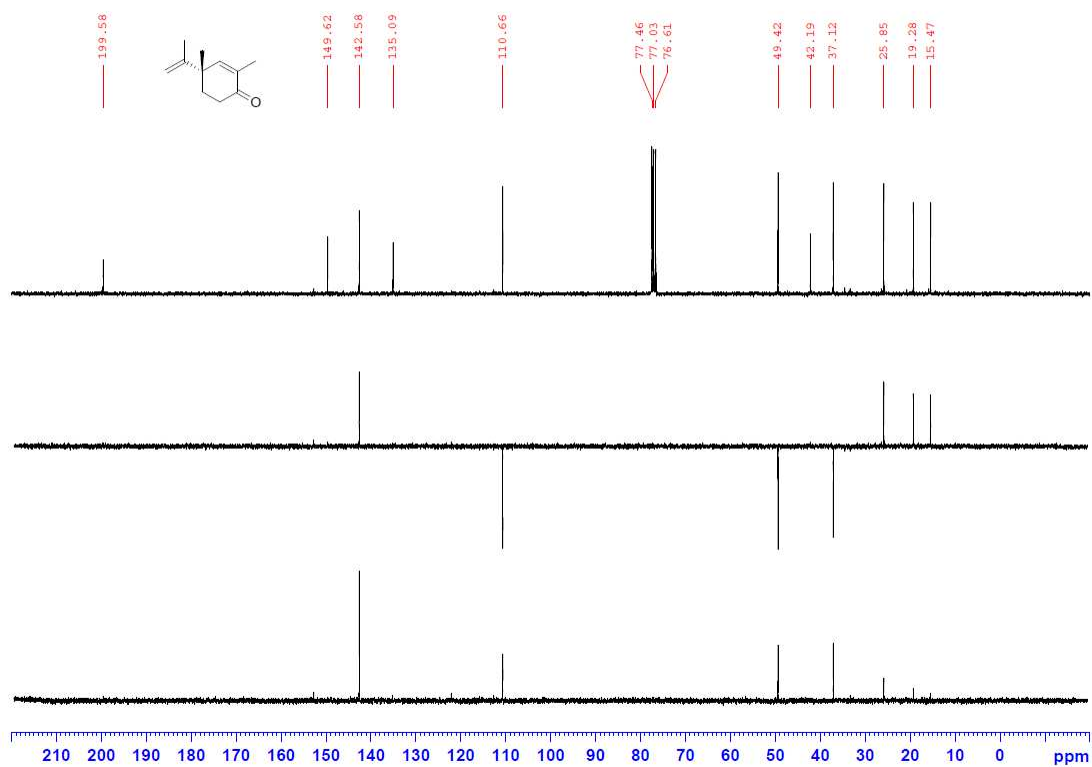
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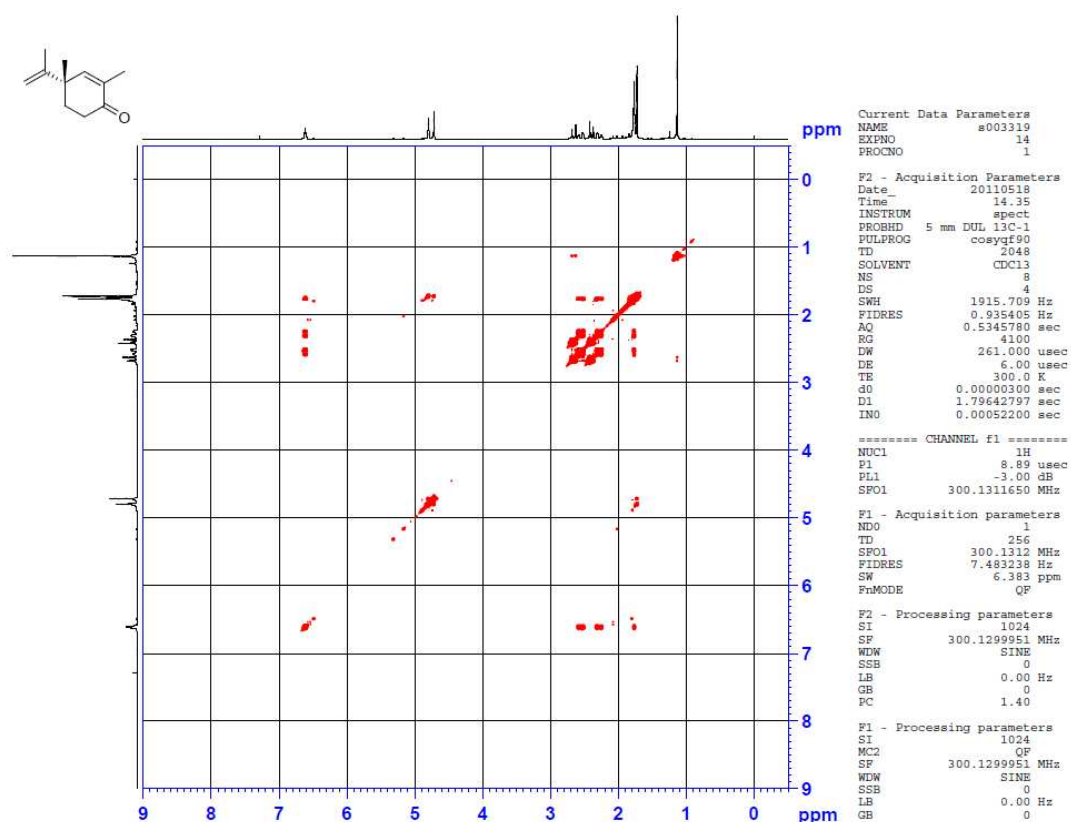
¹H NMR spectrum of 18**¹³C NMR spectrum of 18**

^1H NMR spectrum of 19 **^{13}C NMR spectrum of 19**

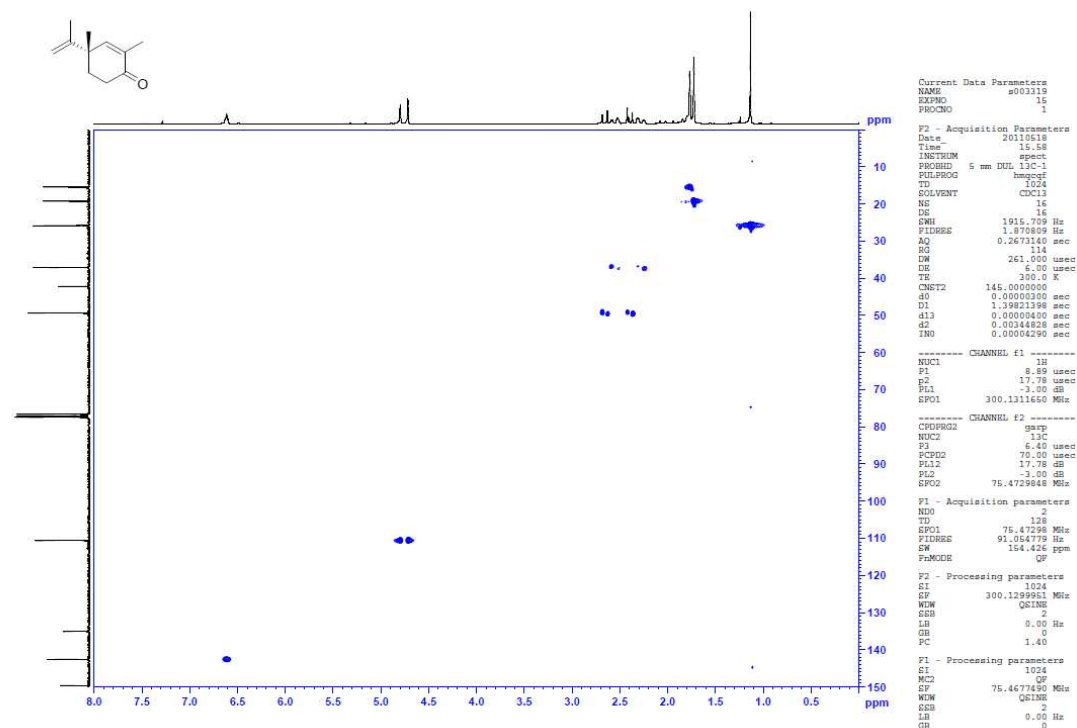


¹H NMR spectrum of 21**¹³C NMR spectrum of 21**

COSY spectrum of 21



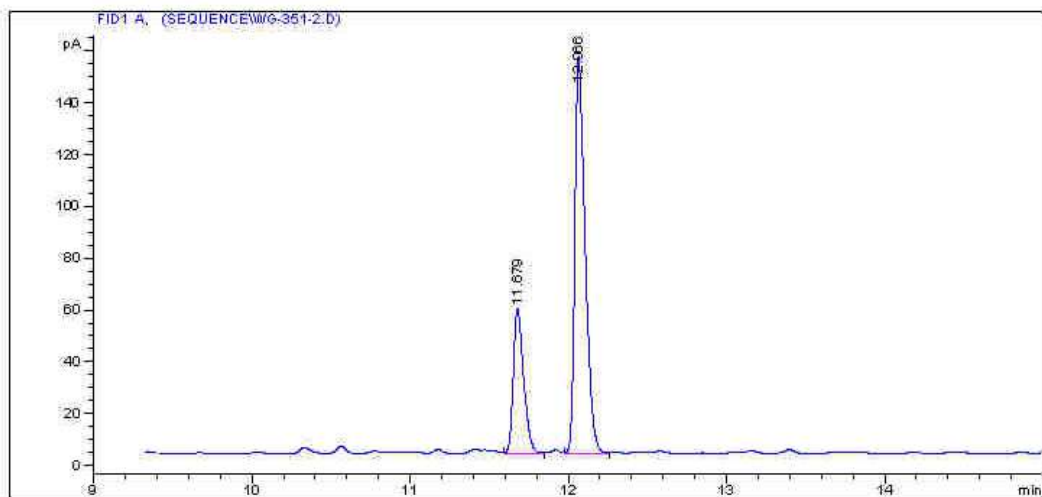
HMQC spectrum of 21



Chiral GC spectrum of 21 (47% ee)

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Area Percent Report

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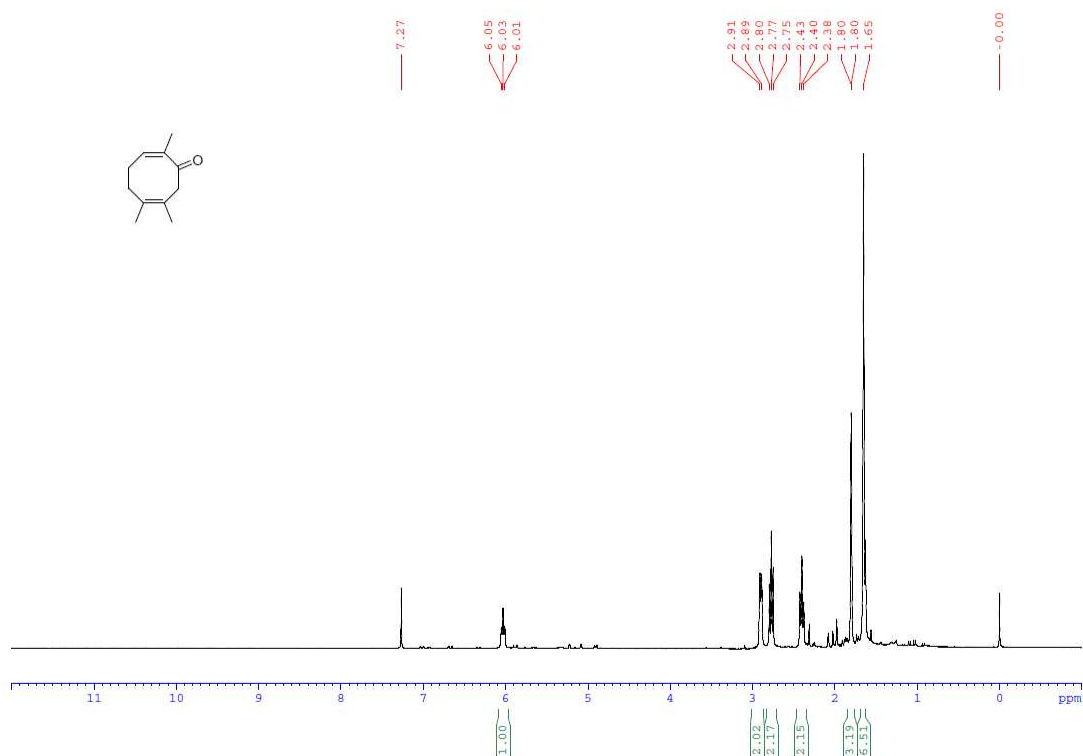
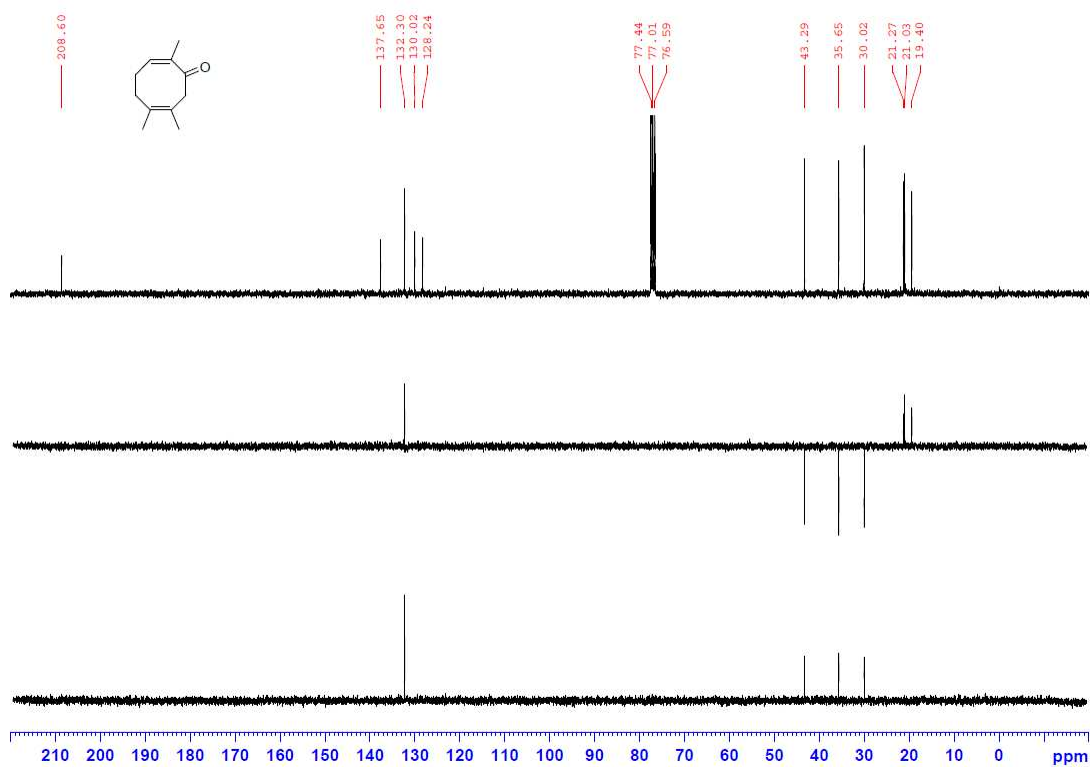
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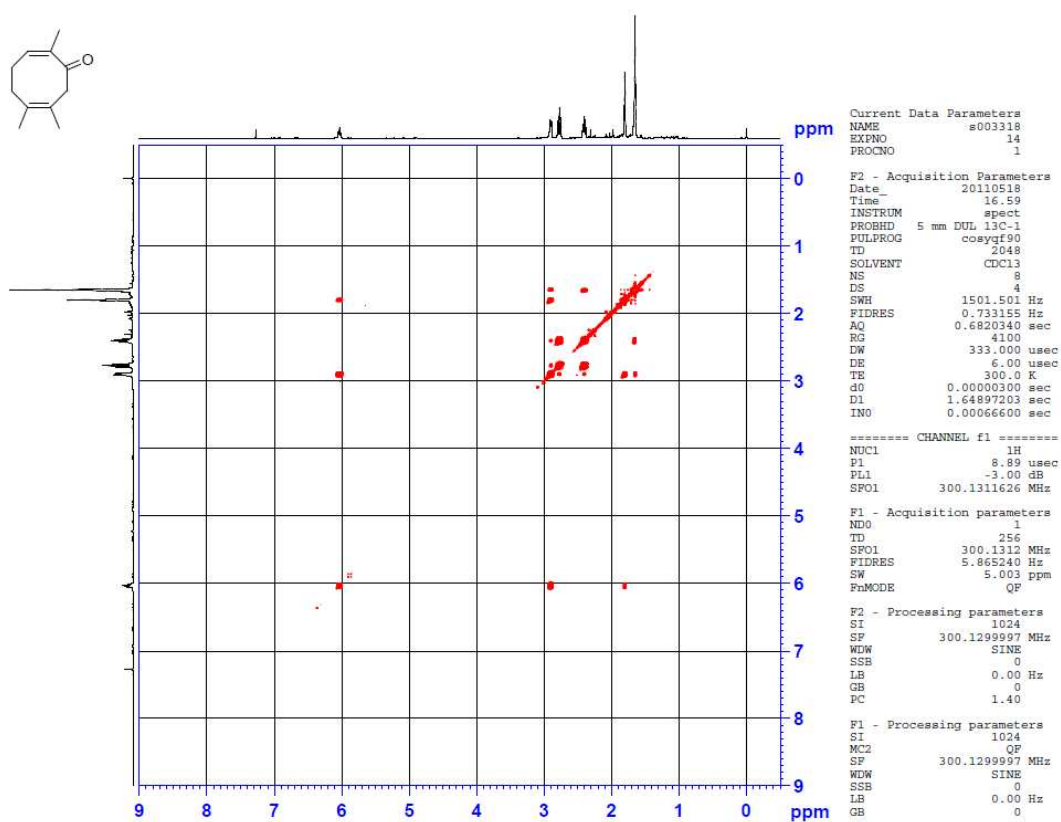
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Results obtained with enhanced integrator!

*** End of Report ***

^1H NMR spectrum of 22 **^{13}C NMR spectrum of 22**

COSY spectrum of 22



HMQC spectrum of 22

