

Supporting information

Discovery of Novel Potential Aphid Repellents: **Geranic Acid Esters**

Containing Substituted Aromatic Rings

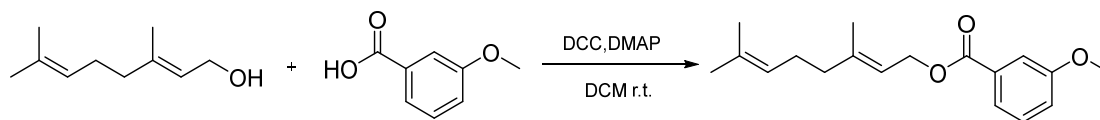
Shixiang Pan , Wenhao Li , Yaoguo Qin , Zhaokai Yang , Yan Liu , Zhuo Shi ,

Cheng Qu , Chen Luo * , and Xinling Yang *

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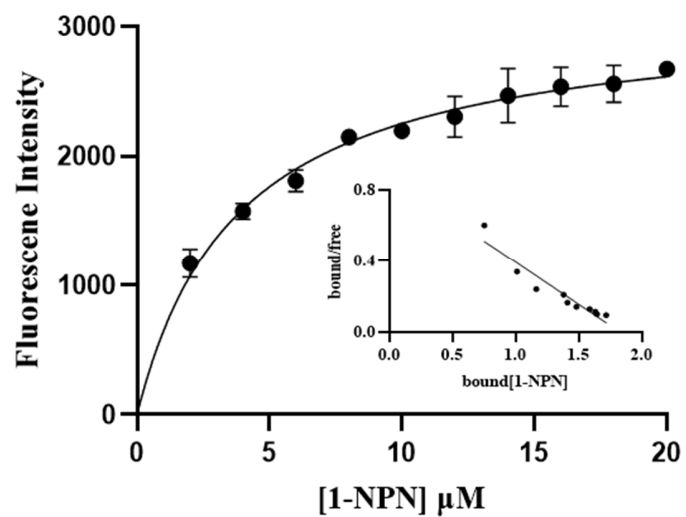
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1. Scheme S1. Synthetic route of CAU13.

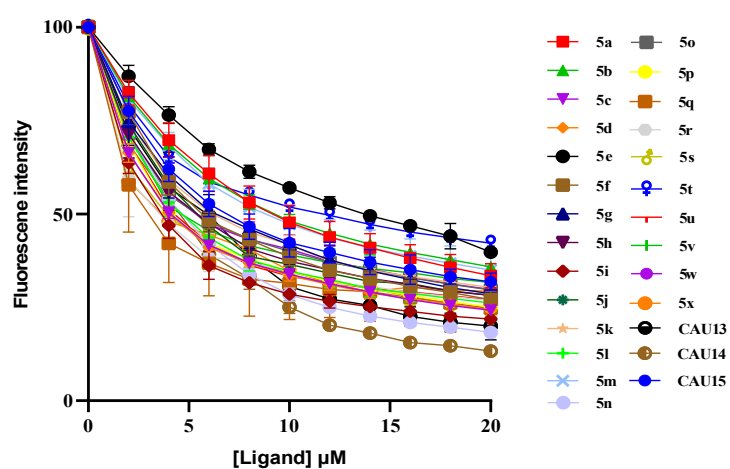


The synthesis of **CAU13** was started by stirring geraniol (5 mmol) with 3-Methoxybenzoic acid (5 mmol) in DCM (30 mL) under ice bath. Then dicyclohexylcarbodiimide (DCC, 6 mmol) and 4-dimethylaminopyridine (DMAP, 0.6 mmol) were added into reaction stirring for 30 minutes. After that removed the ice bath and the mixture was finished by TLC detected after stirring 6 h, washed with saturated aqueous sodium bicarbonate solution for 3 times, extracted with DCM, dried with anhydrous sodium sulfate, and filtered. The organic phase was concentrated under reduced pressure and purified by column chromatography to obtain it as colorless liquid, 90.1% yield. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.57 (t, *J* = 2.0 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 8.2, 2.7 Hz, 1H), 5.47 (tt, *J* = 7.1, 1.4 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.84 (d, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 2.14 – 2.06 (m, 4H), 1.77 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 166.6, 159.6, 142.4, 131.9, 129.3, 123.8, 122.0, 119.3, 114.1, 62.0, 55.4, 39.6, 26.3, 25.7, 17.7, 16.6.

2. **Figure S1.** Binding curves and Scatchard plots (insert) of probe to ApisOBP9

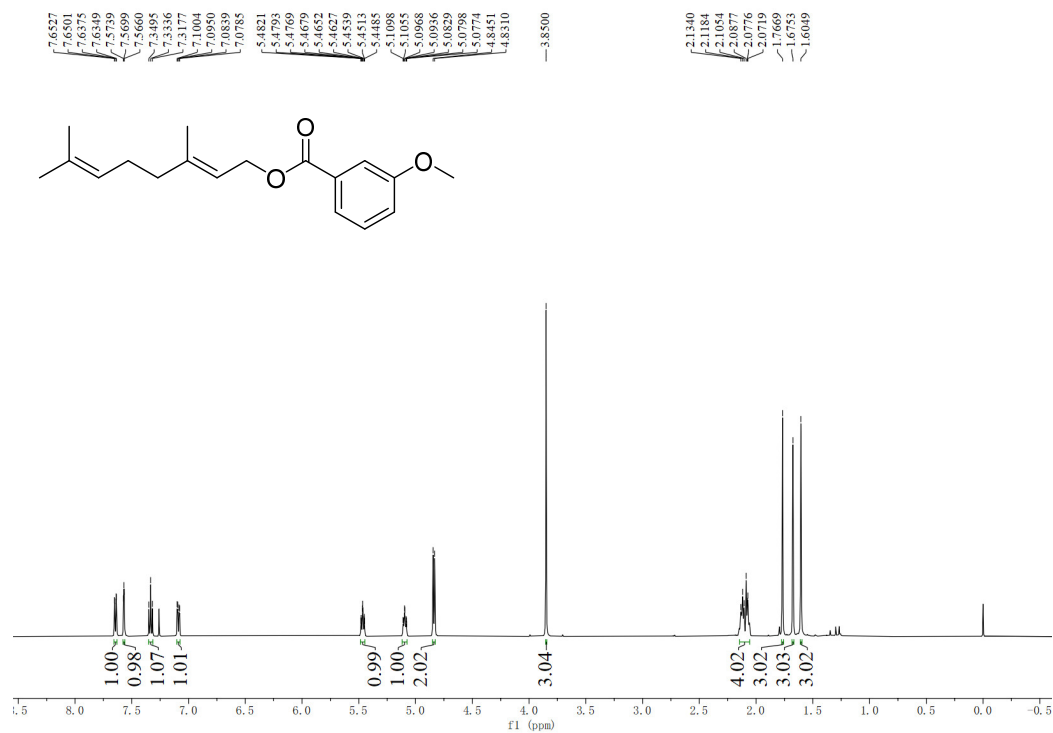


3. **Figure S2.** Competitive binding curves of compounds to ApisOBP9

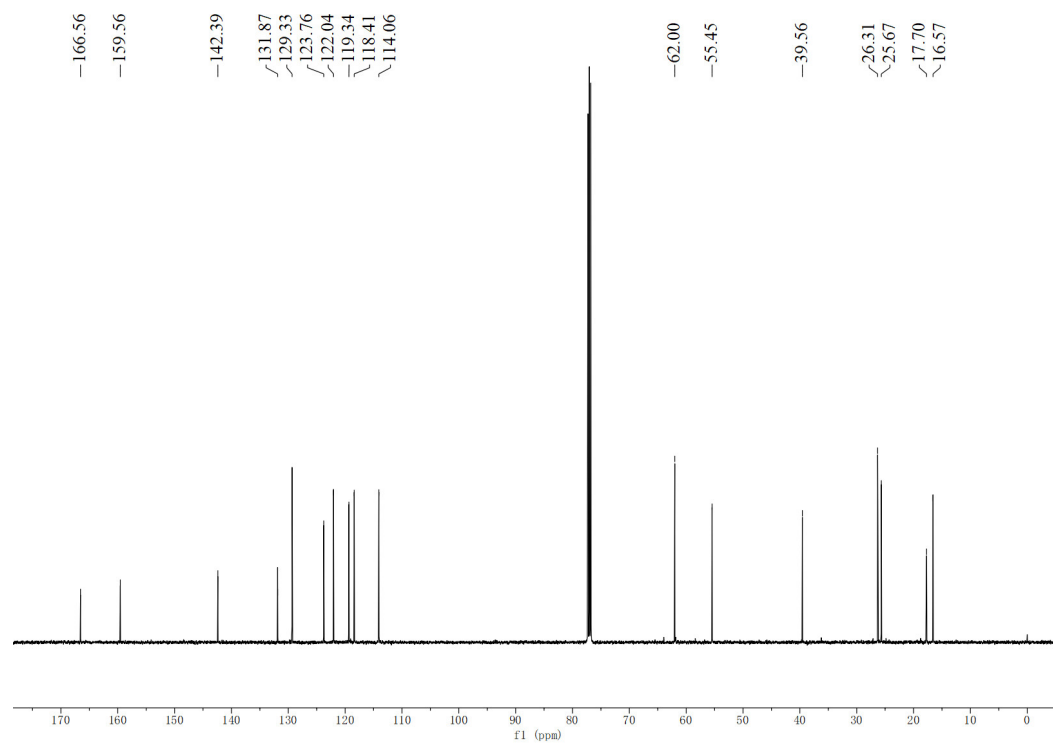


4. ^1H NMR and ^{13}C NMR Spectrums of compounds **CAU13** and **5a-5x**

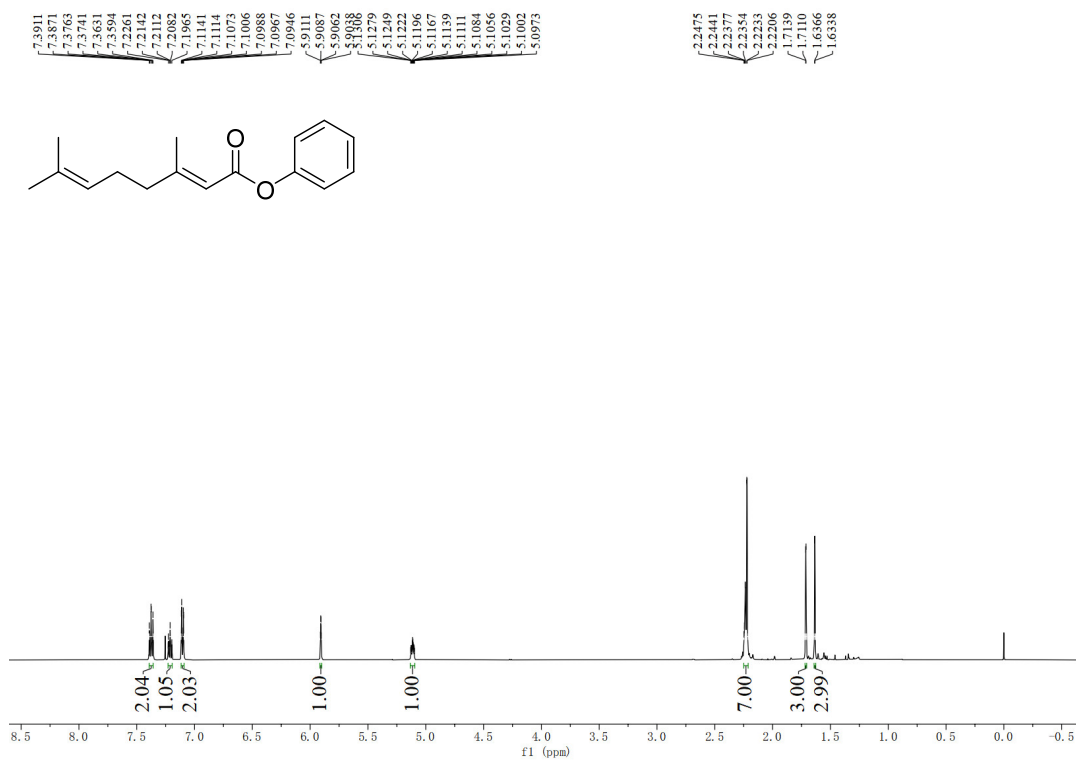
^1H NMR of **CAU13**



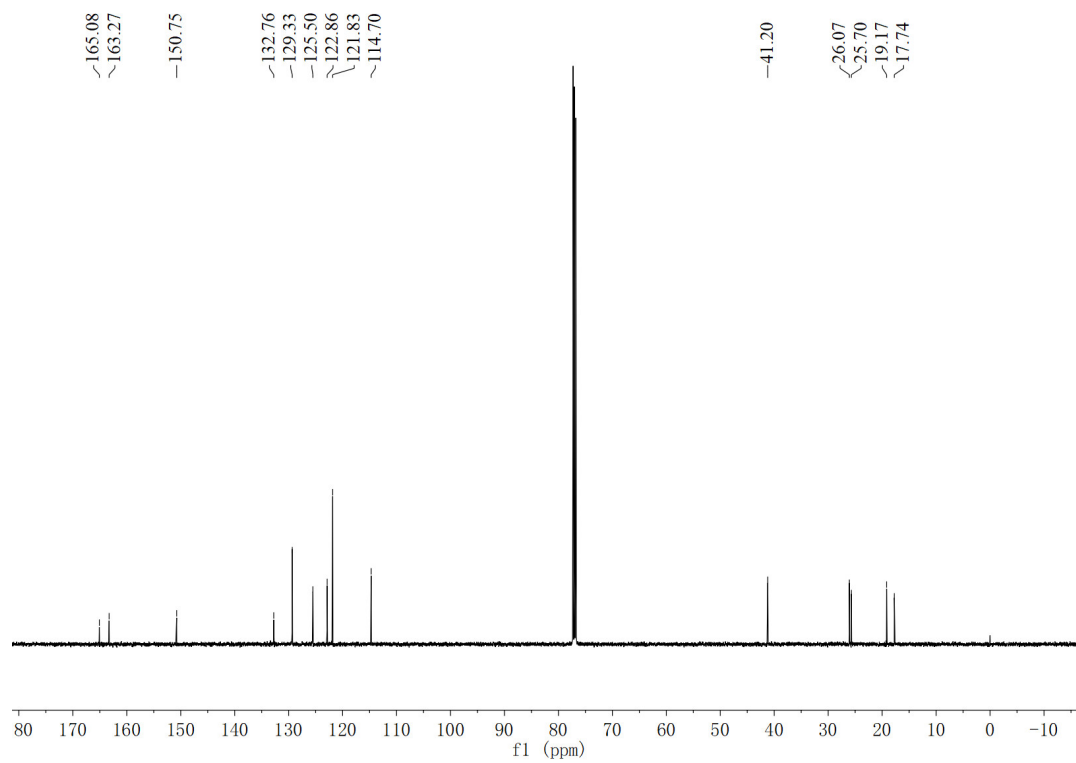
^{13}C NMR of **CAU13**



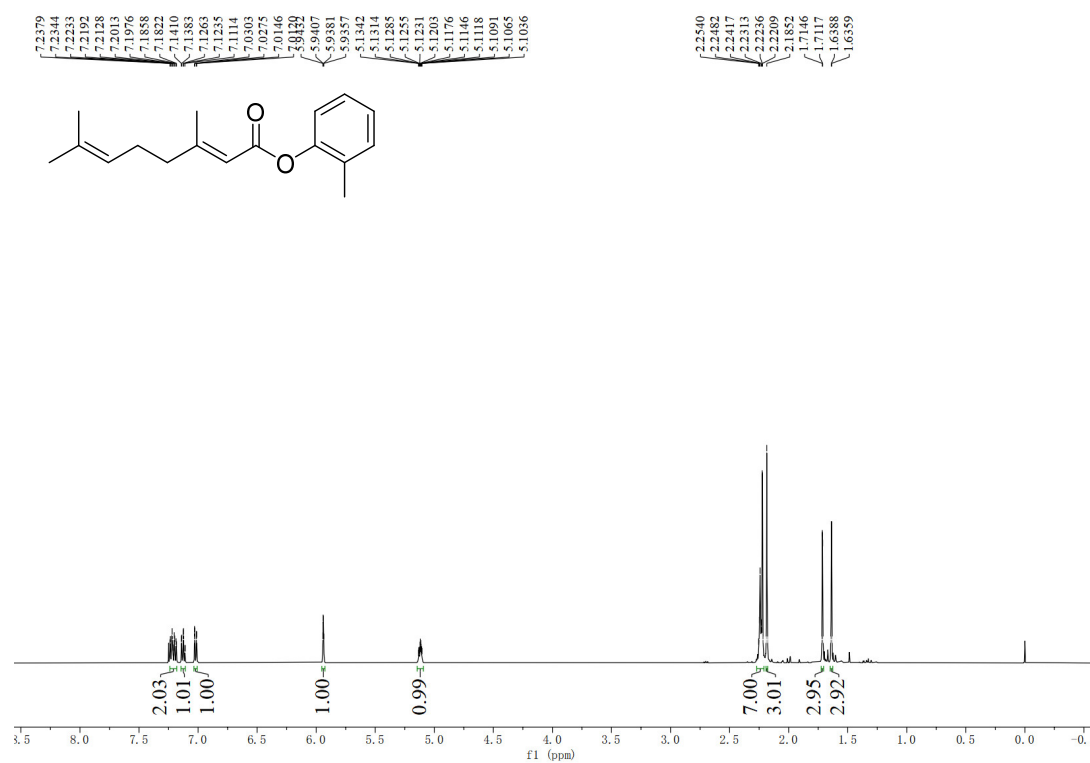
¹H NMR of **5a**



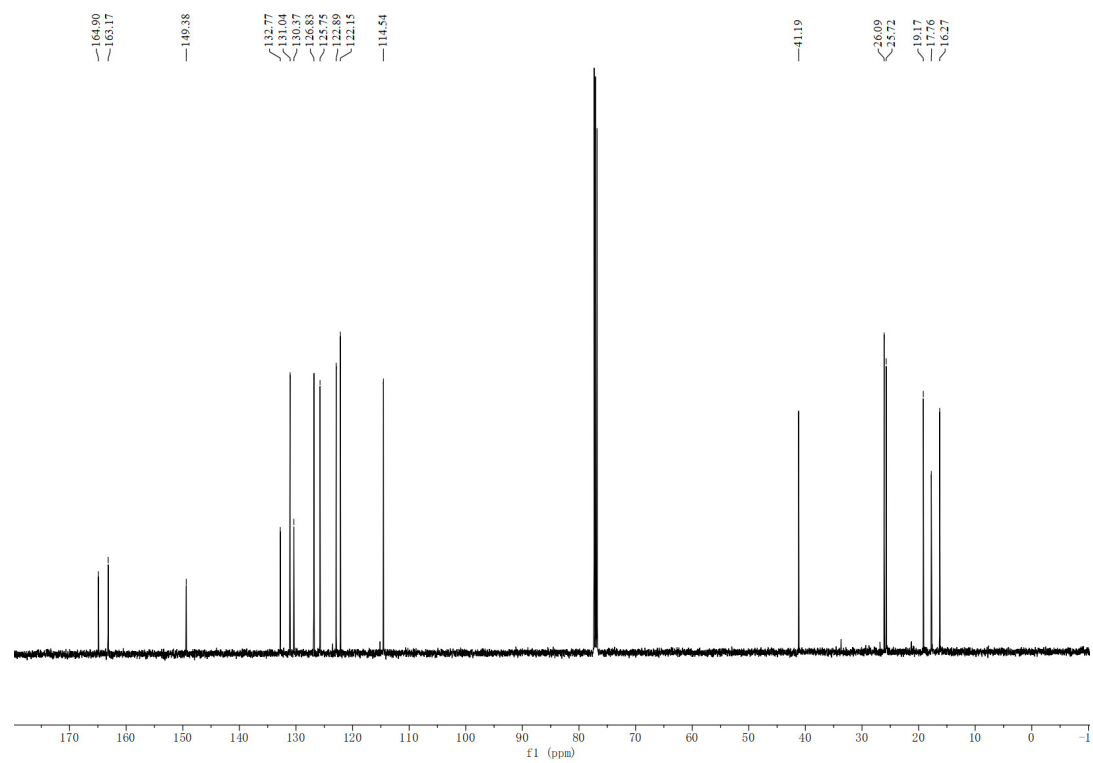
¹³C NMR of **5a**



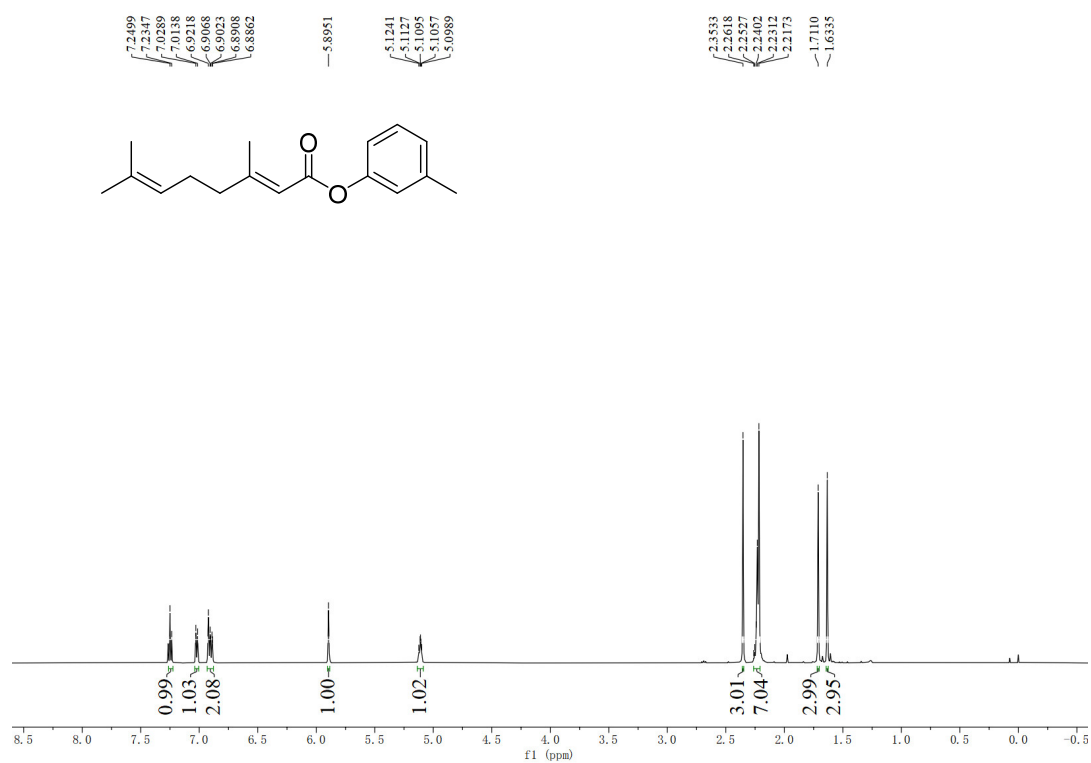
¹H NMR of **5b**



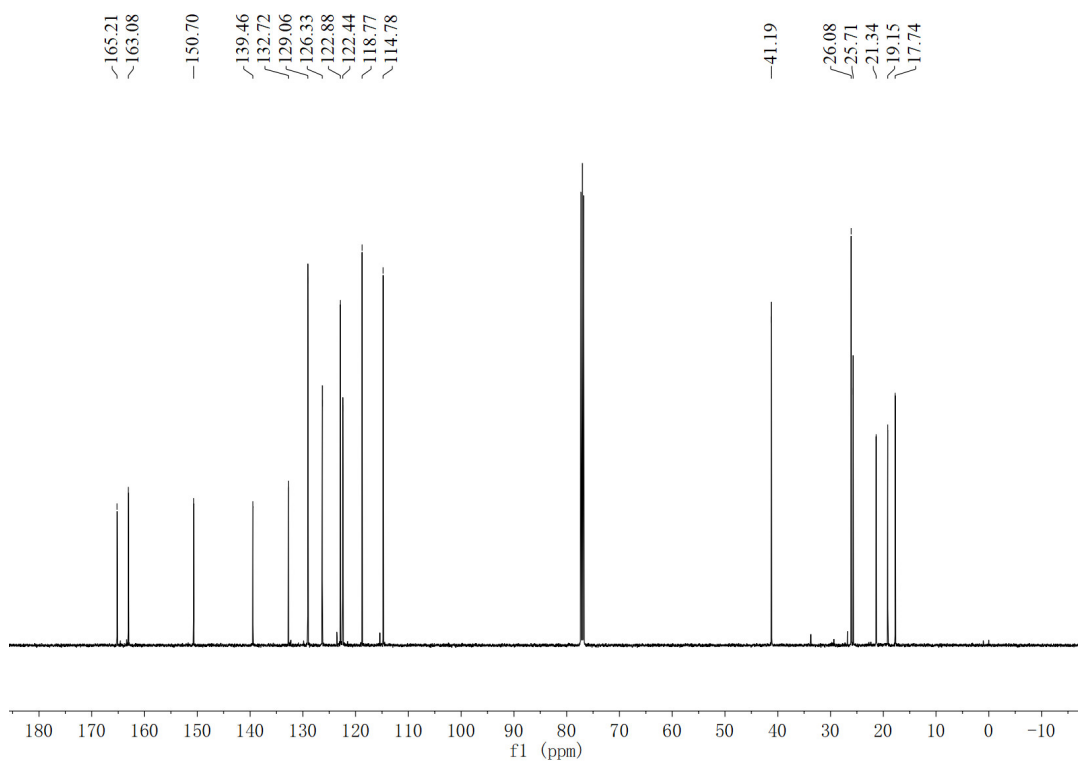
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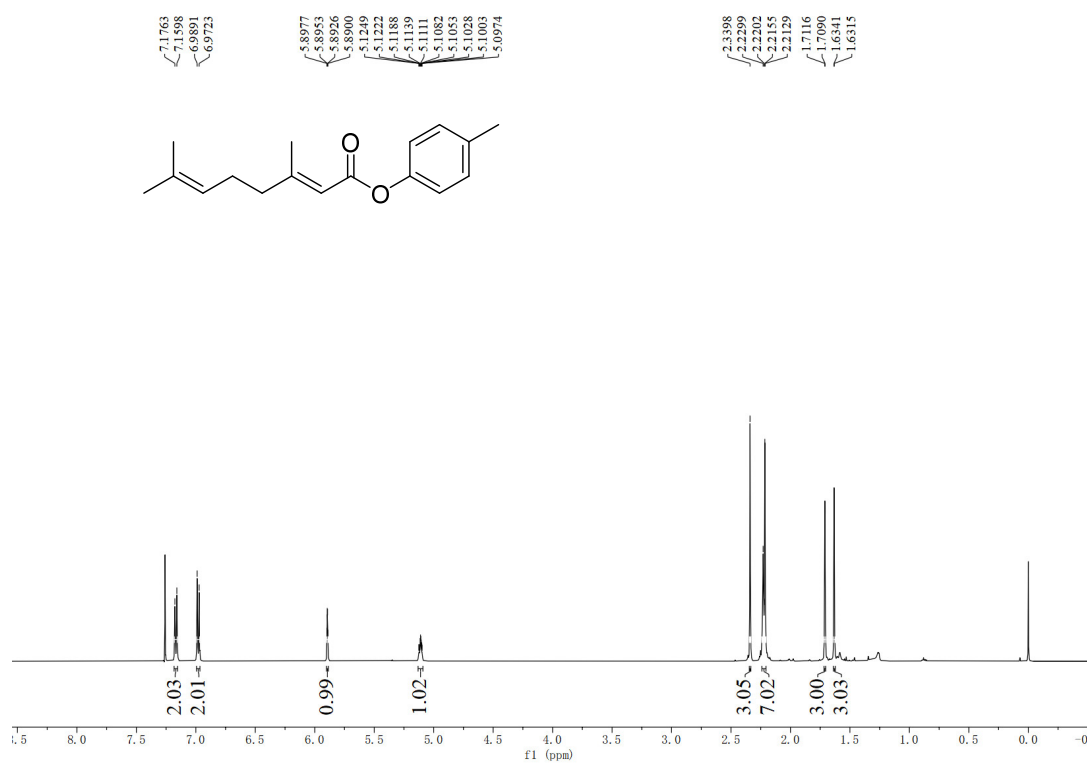
¹H NMR of **5c**



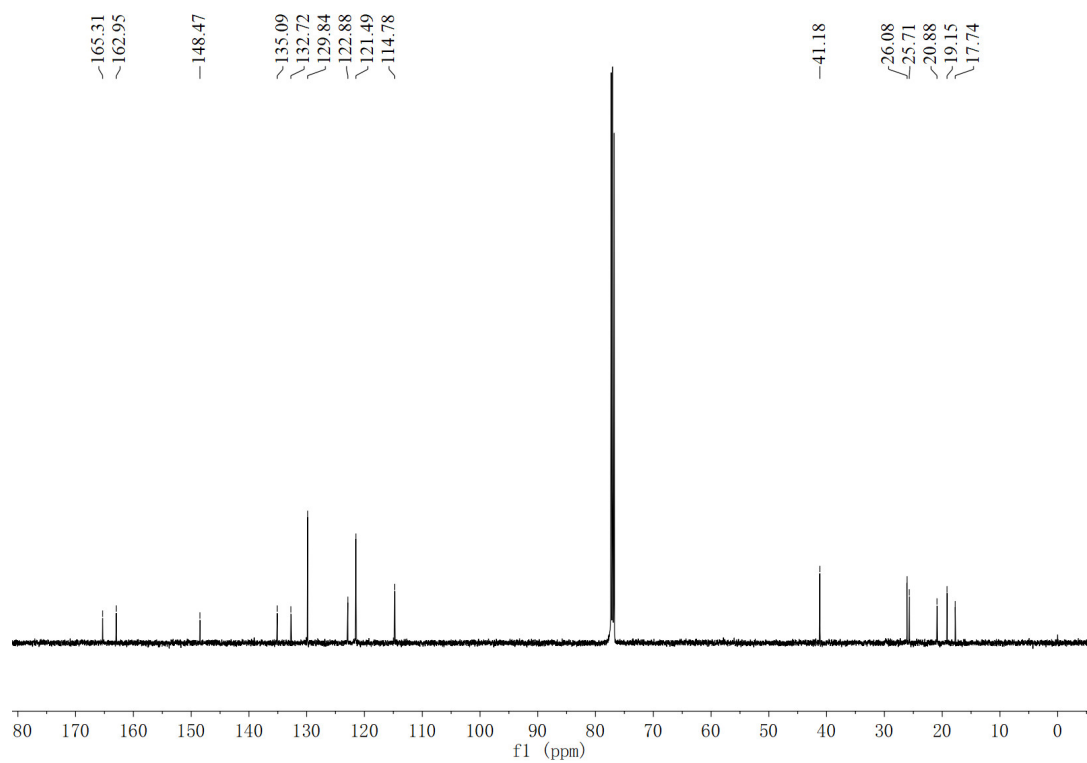
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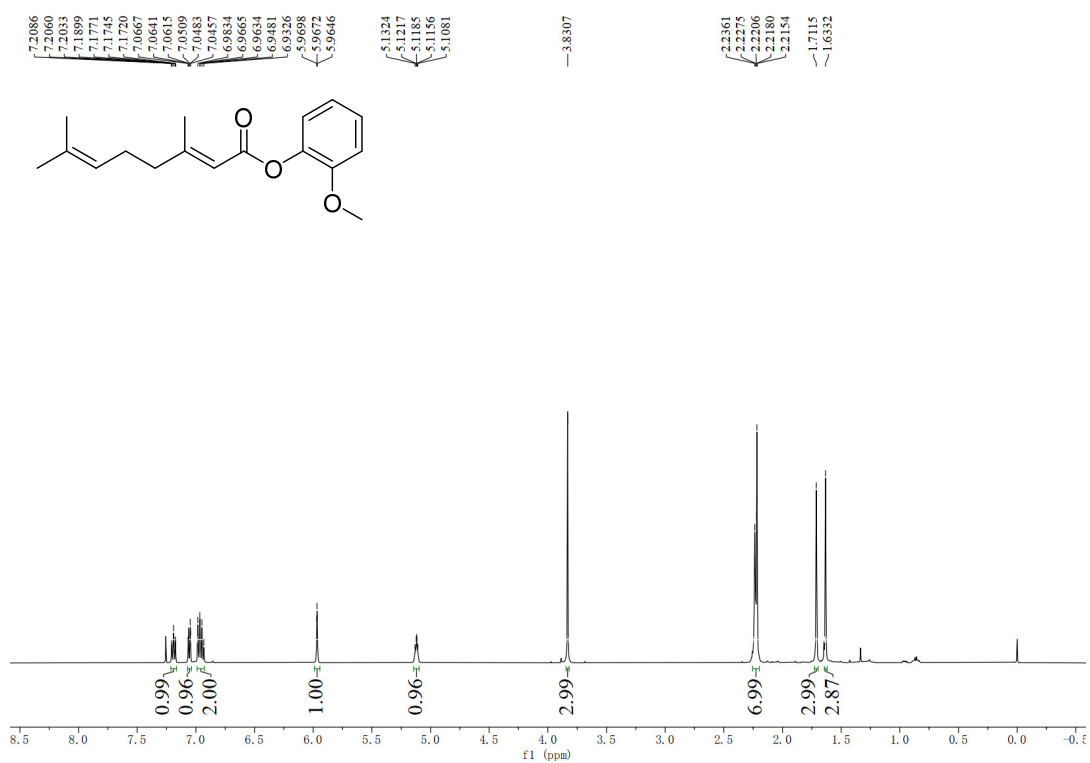
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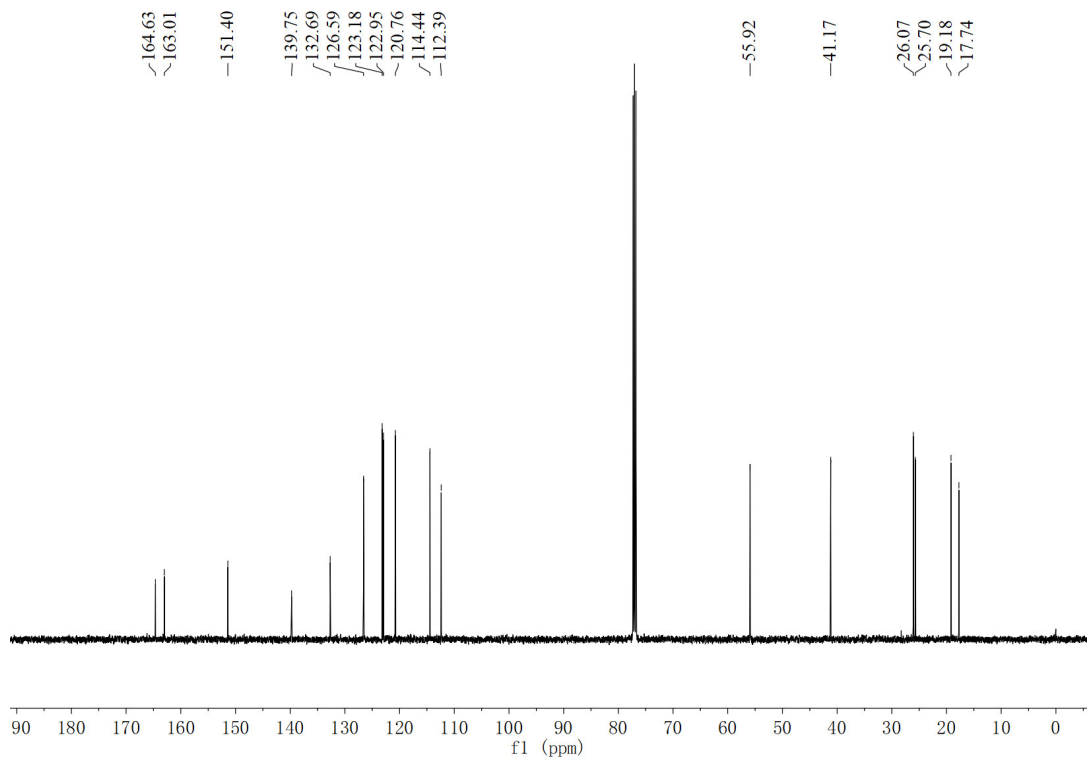
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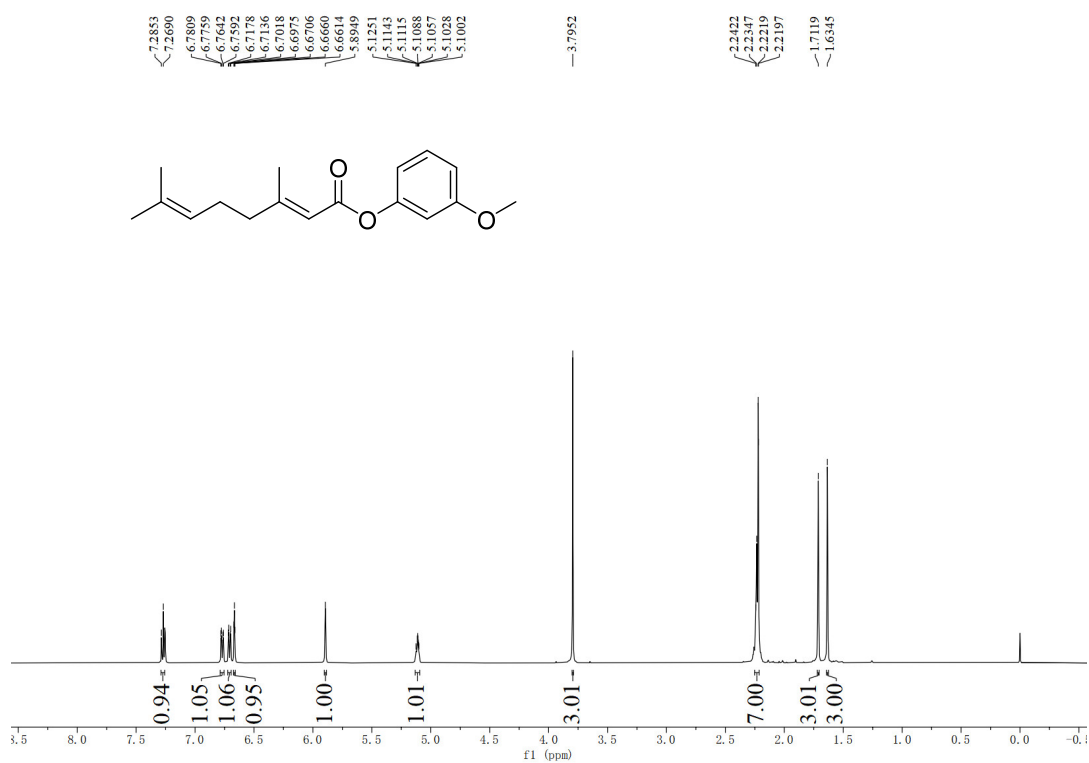
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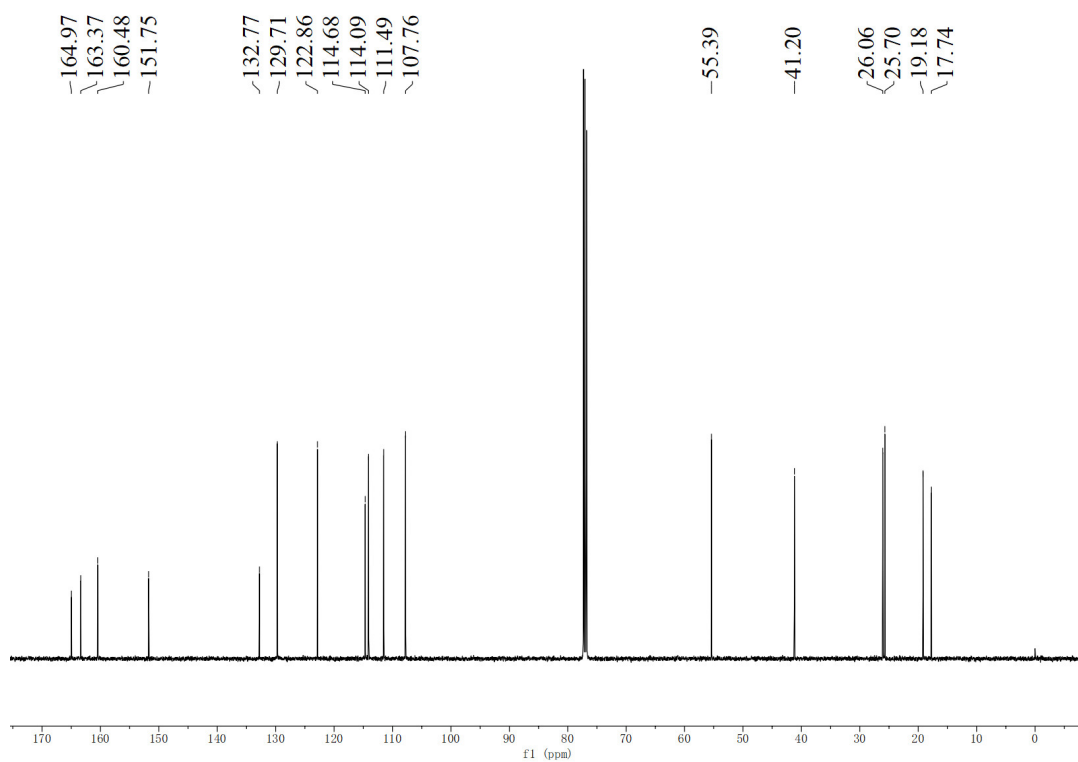
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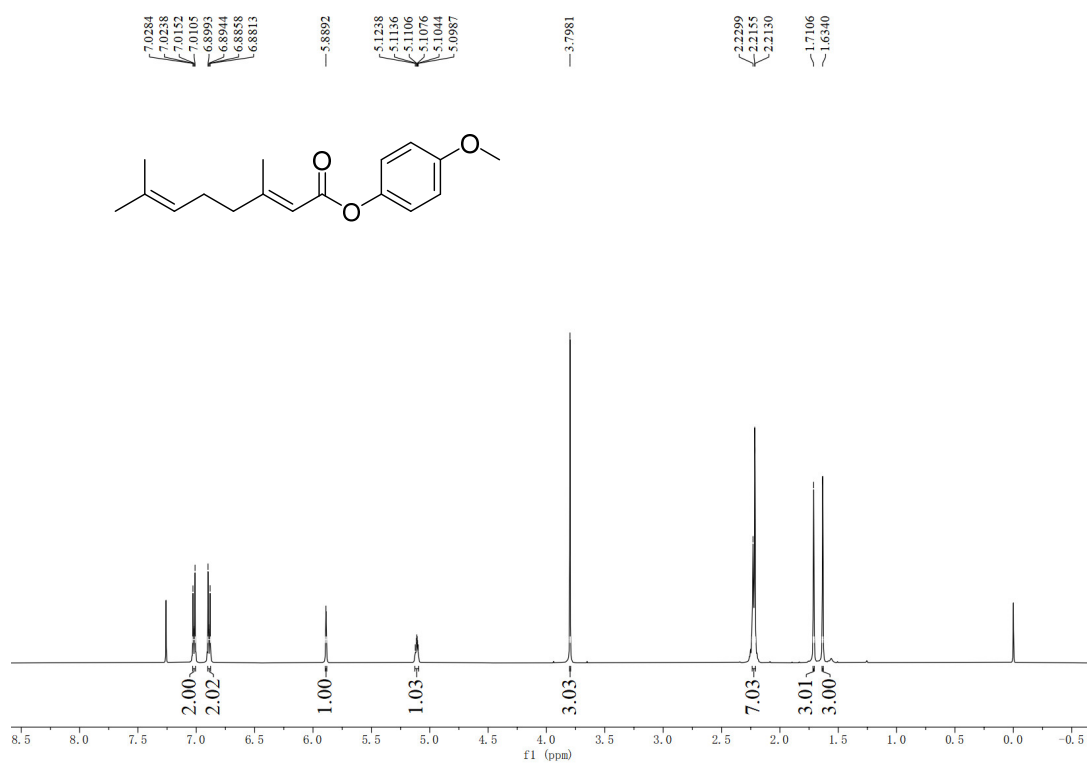
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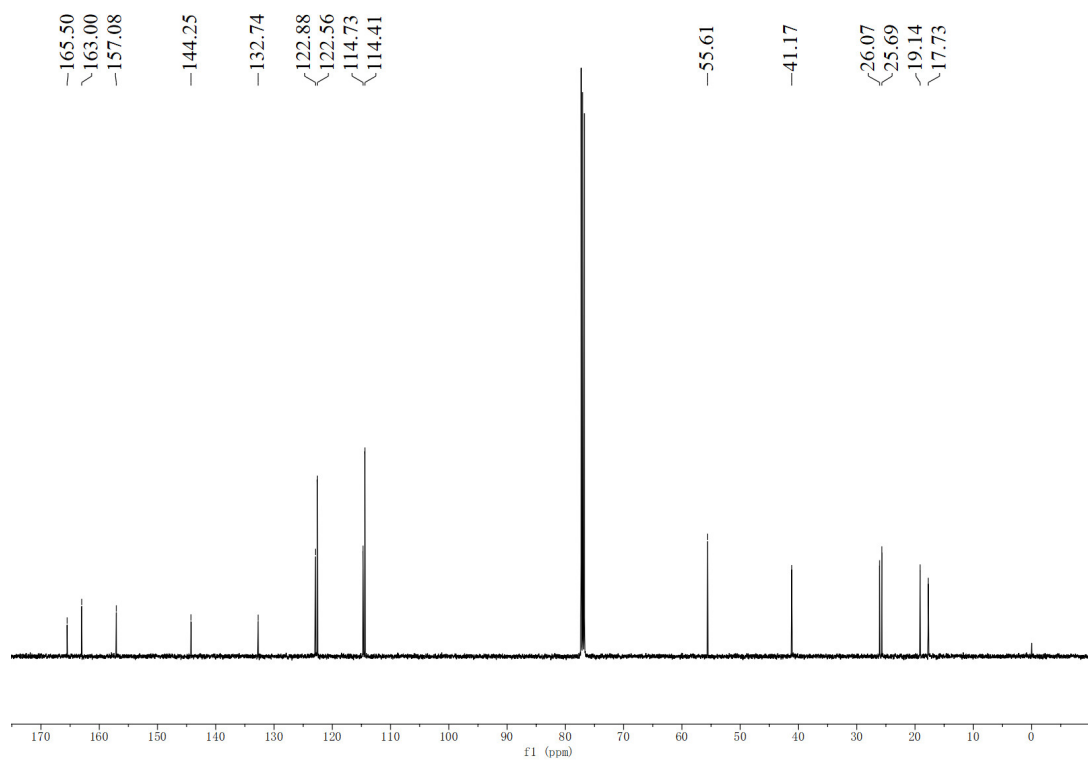
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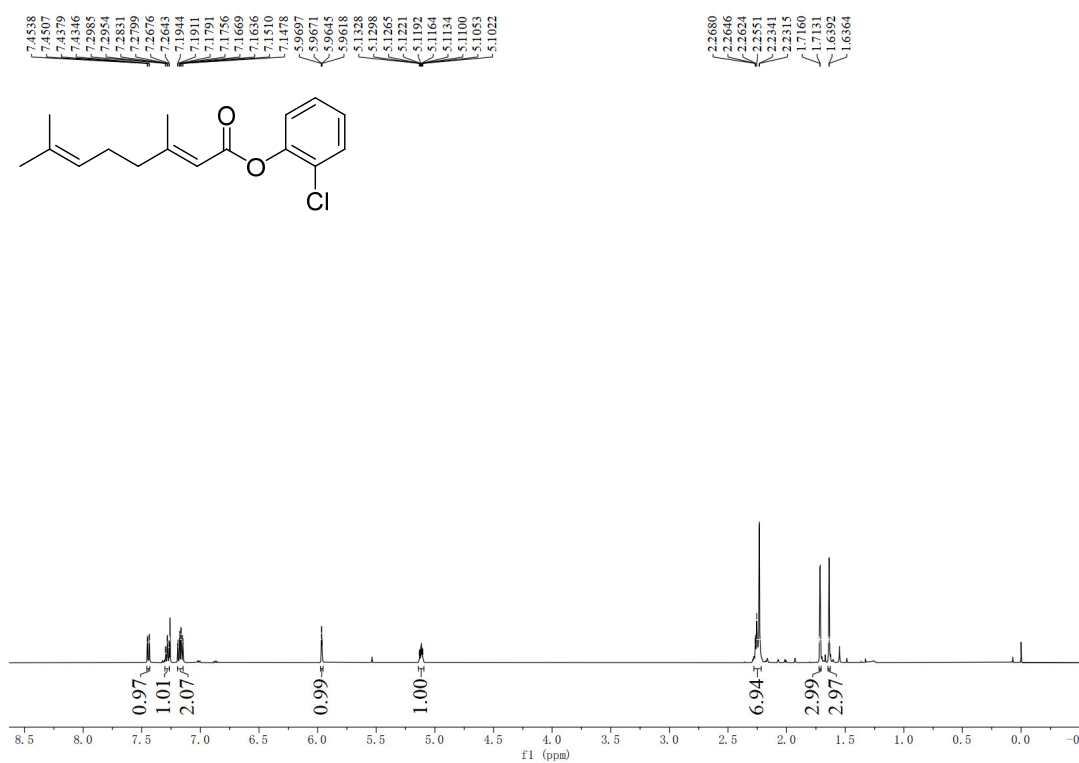
¹H NMR of **5g**



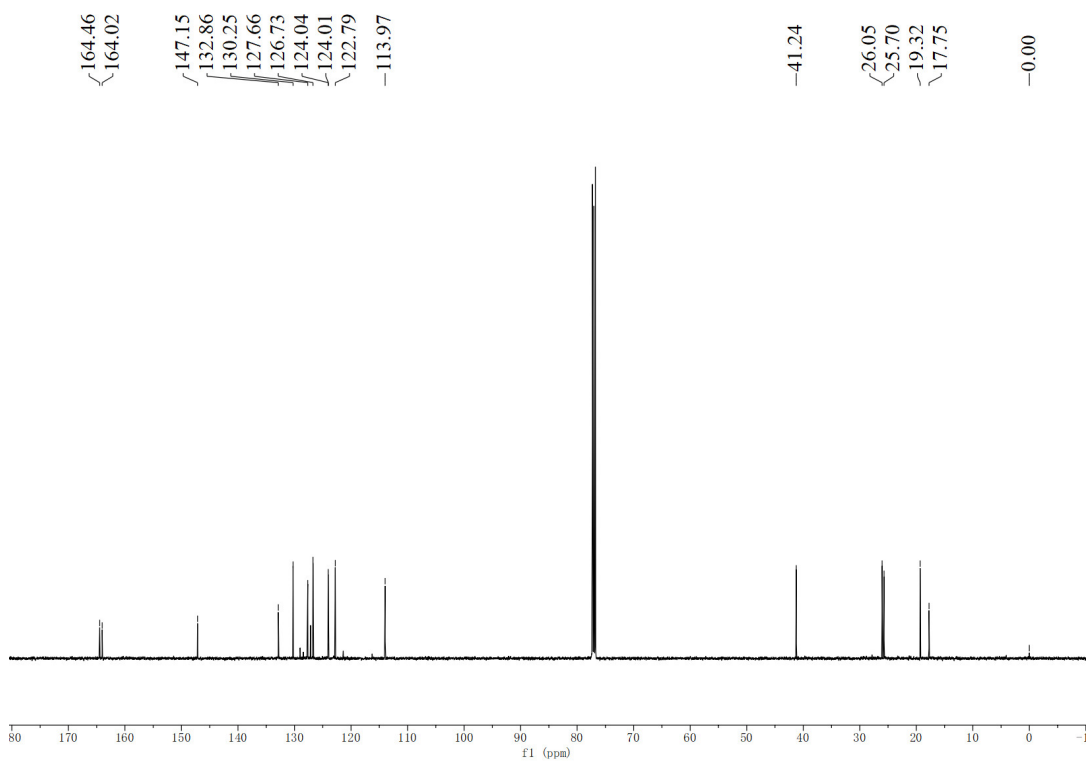
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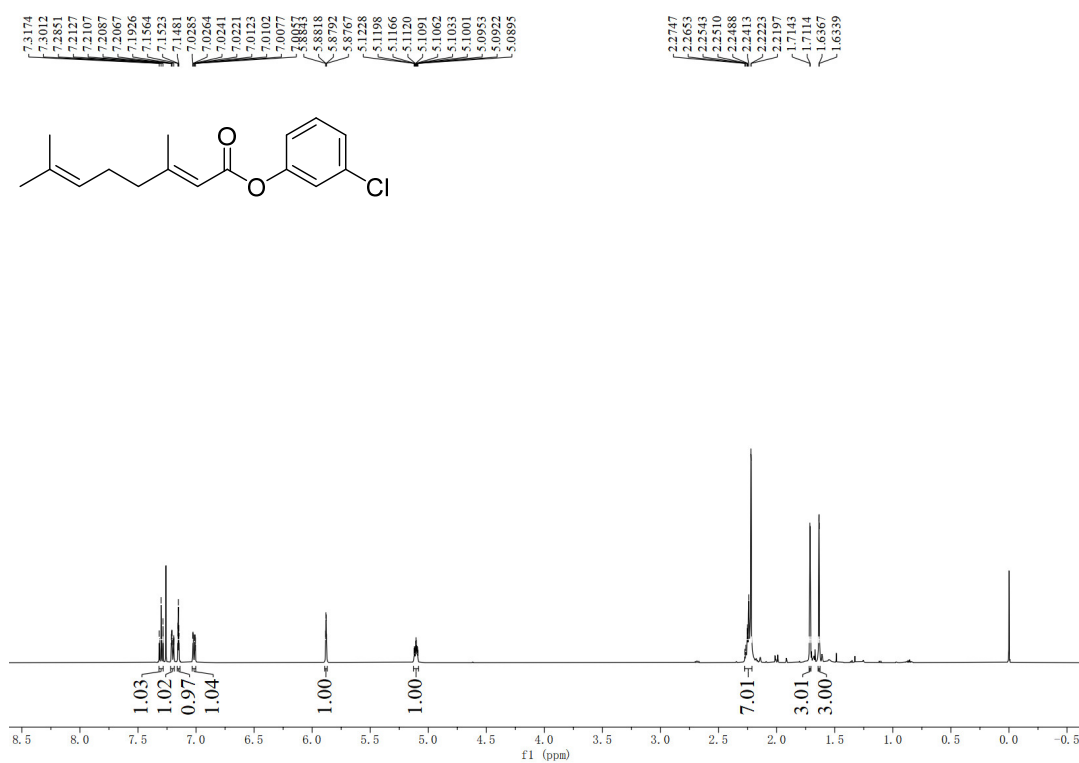
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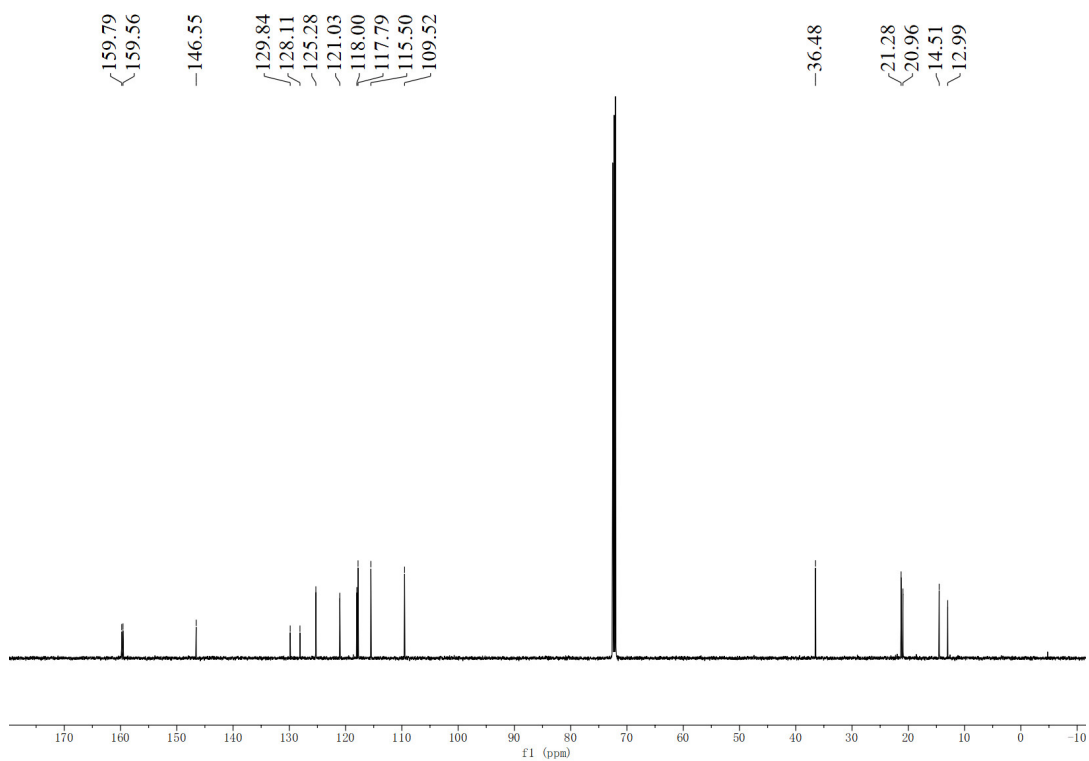
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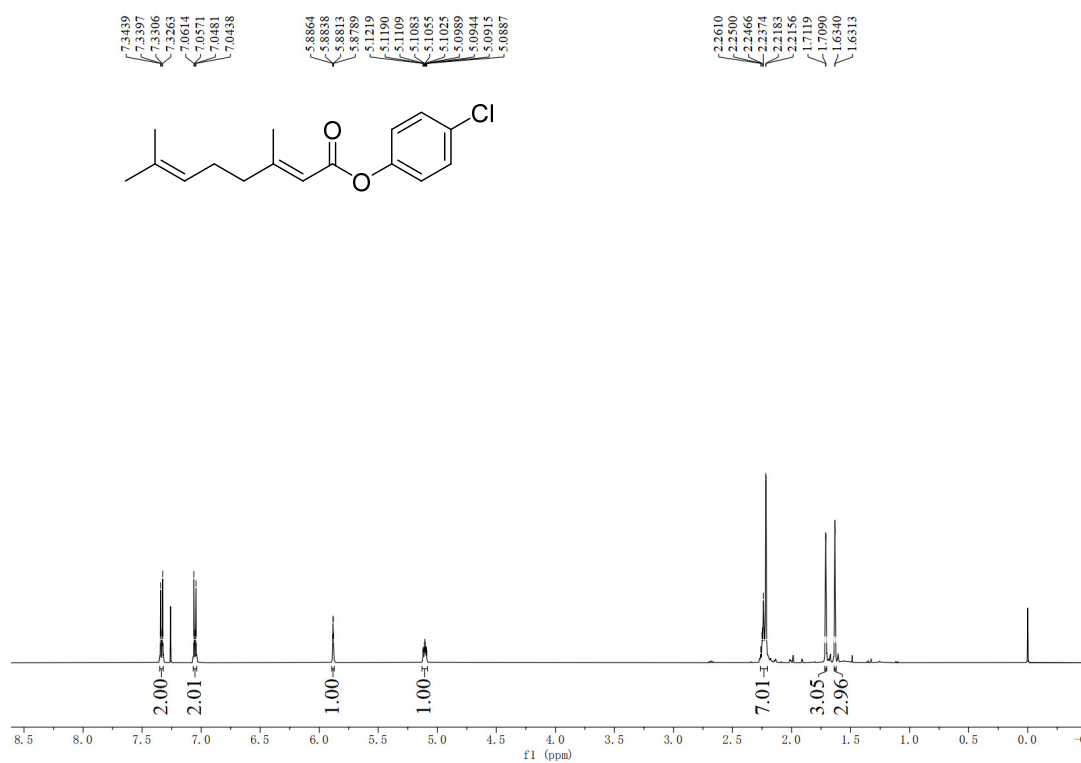
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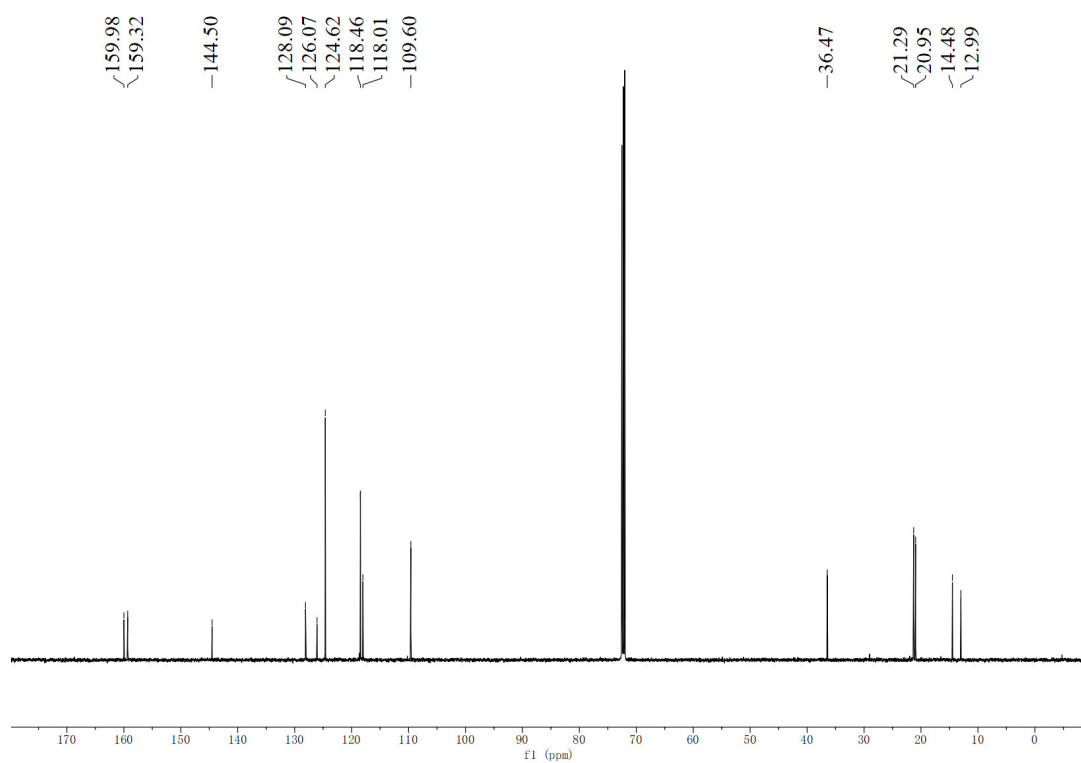
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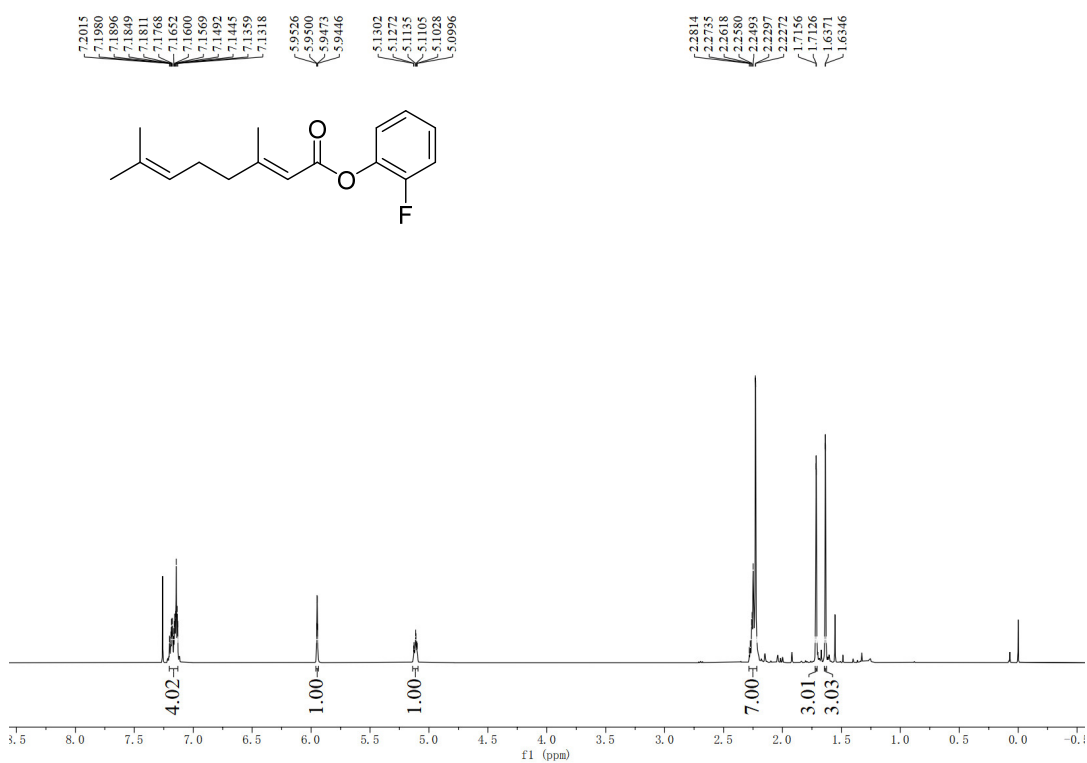
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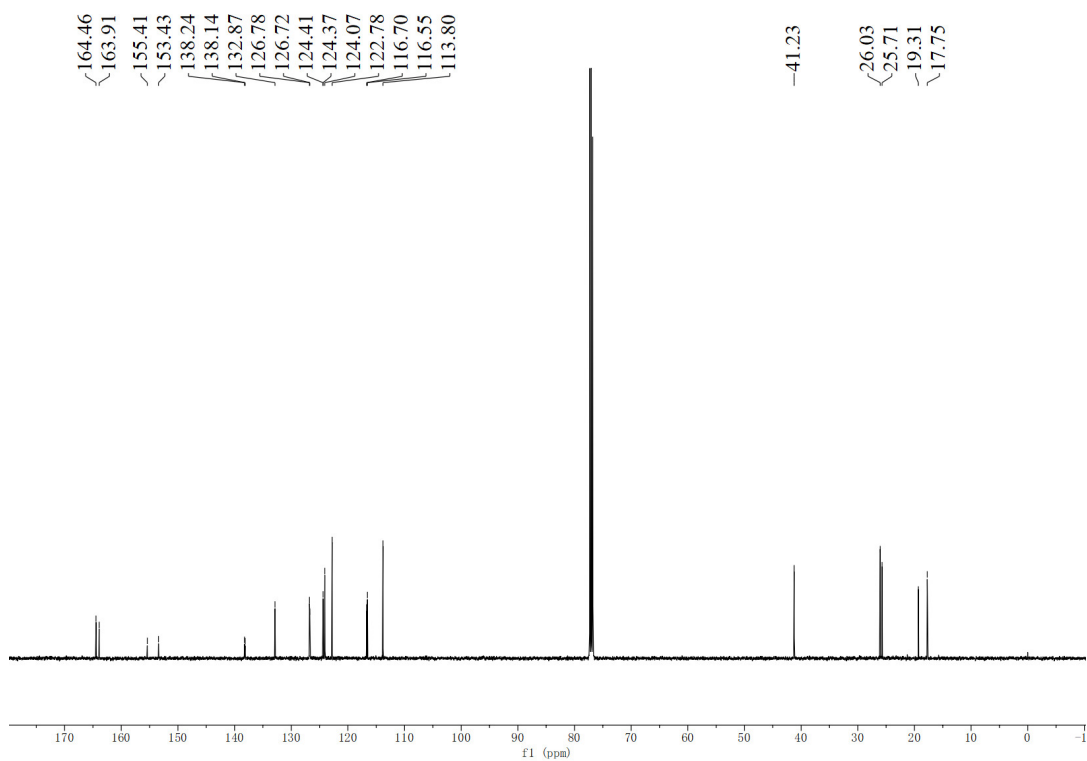
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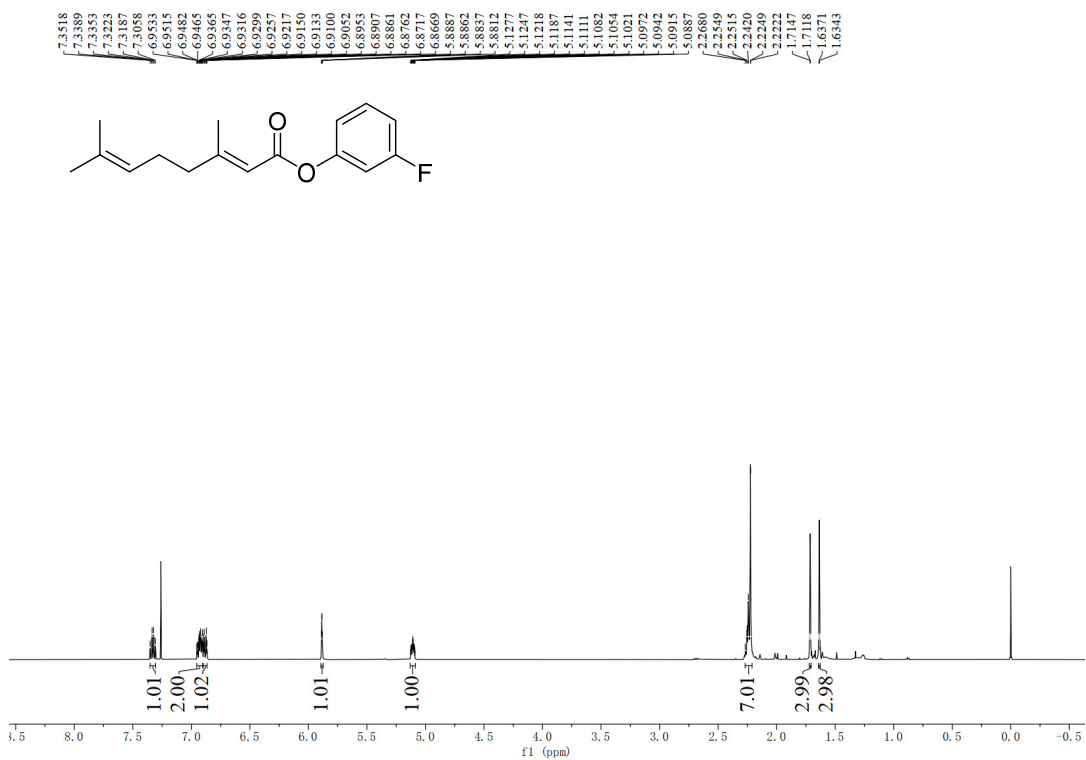
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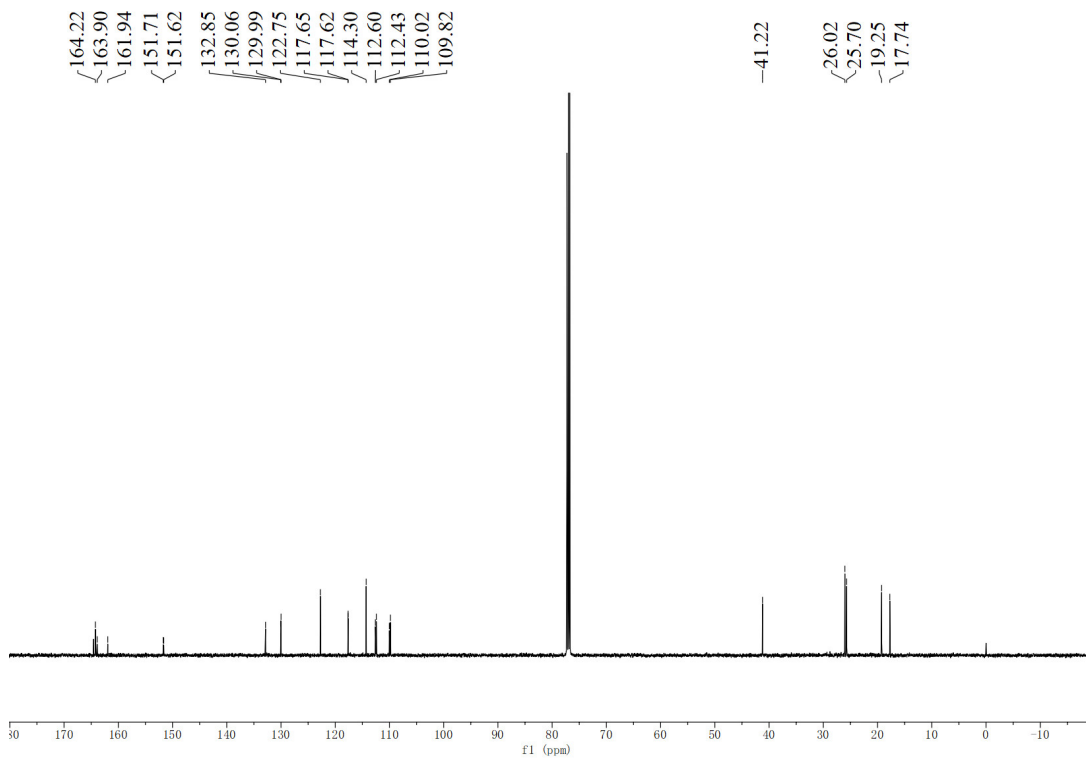
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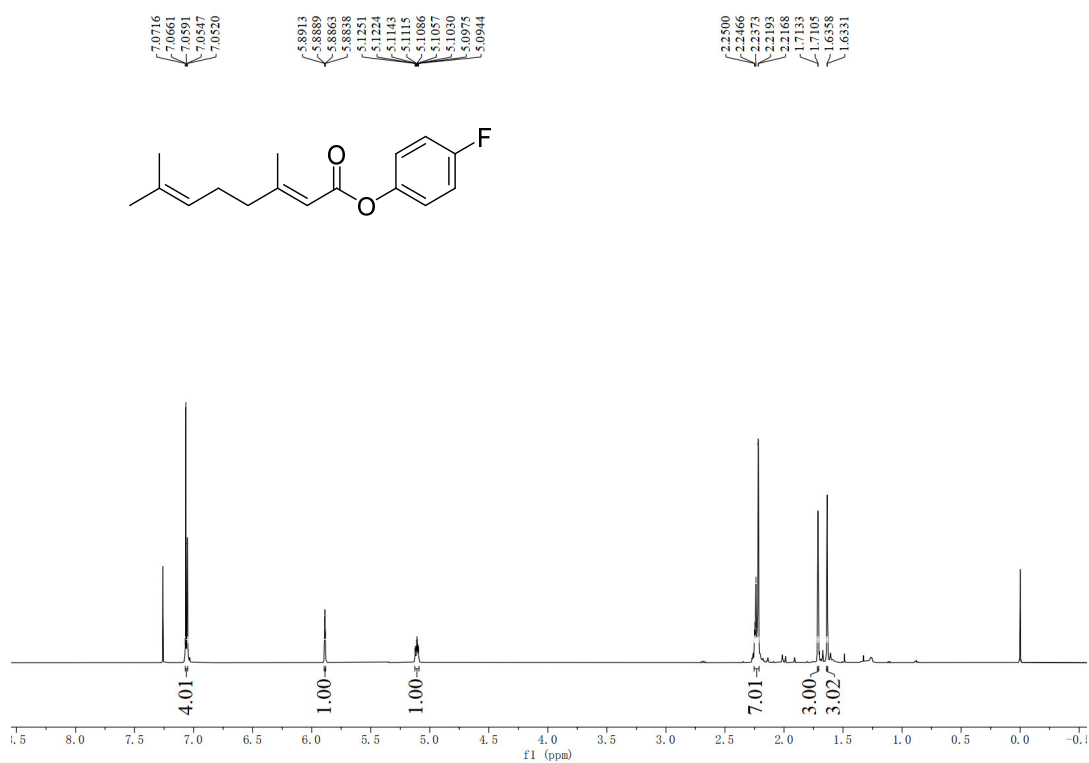
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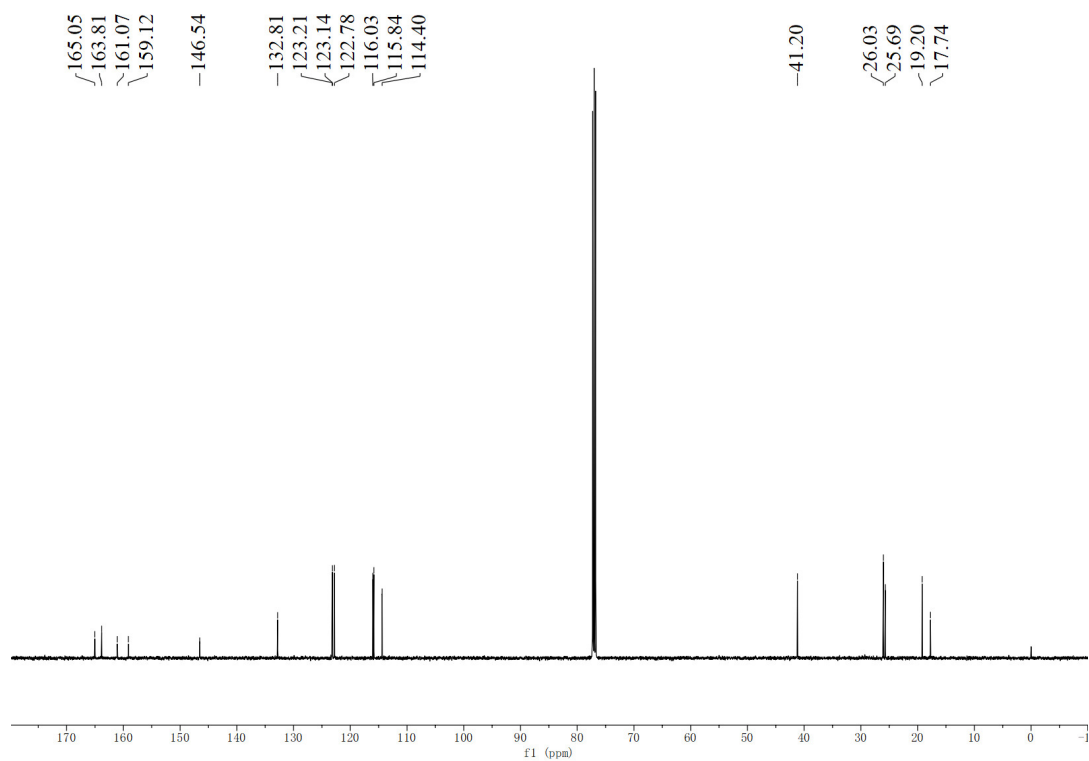
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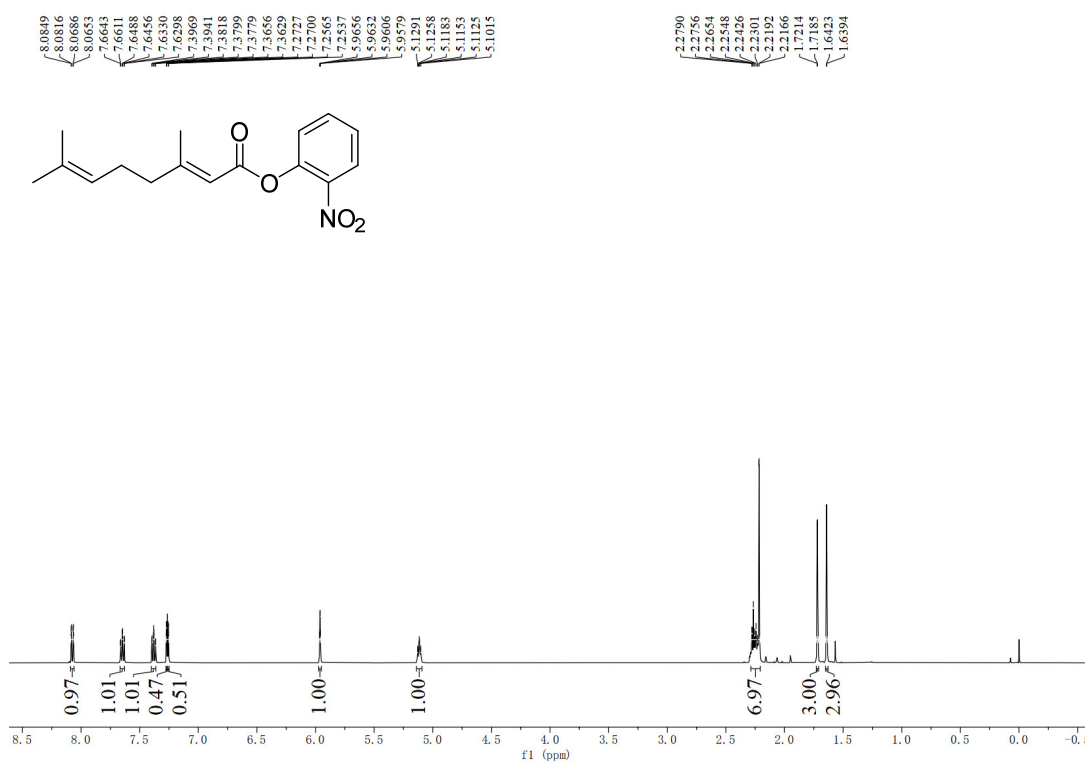
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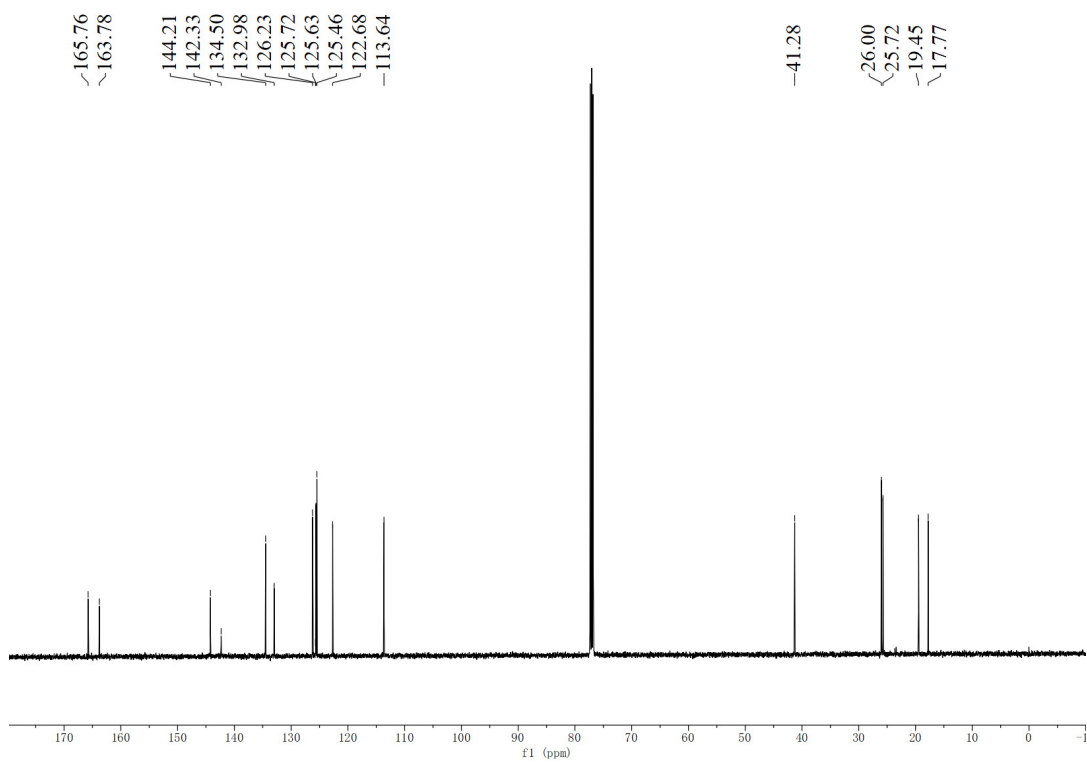
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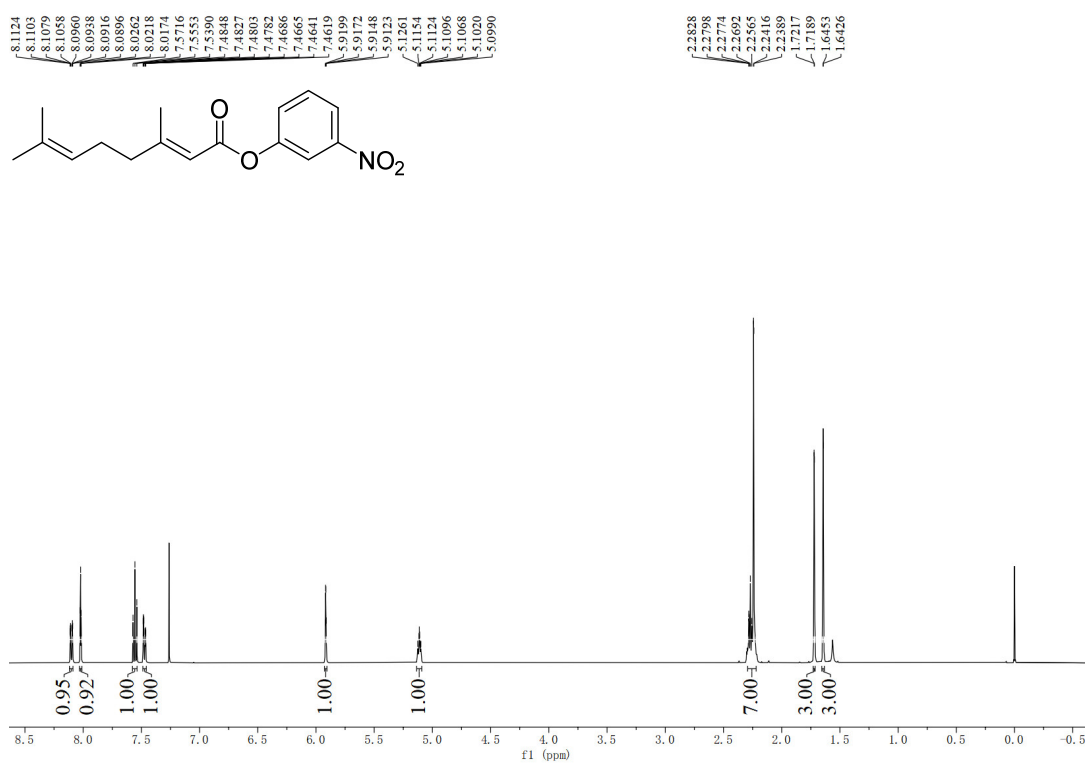
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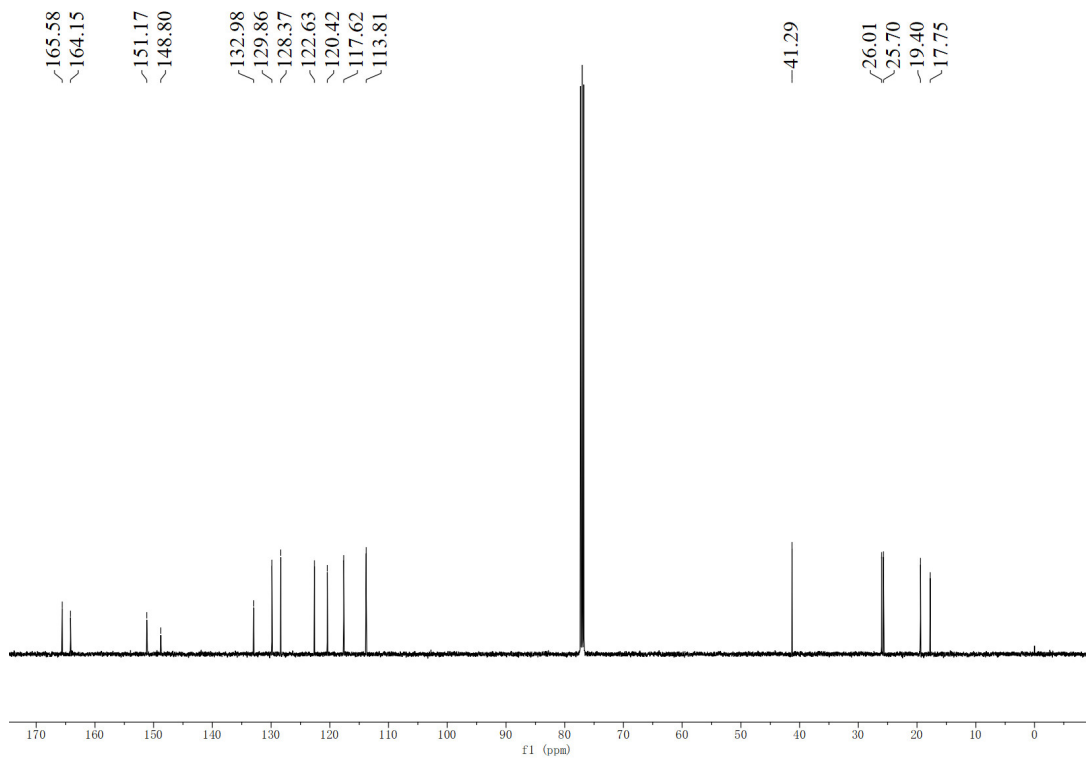
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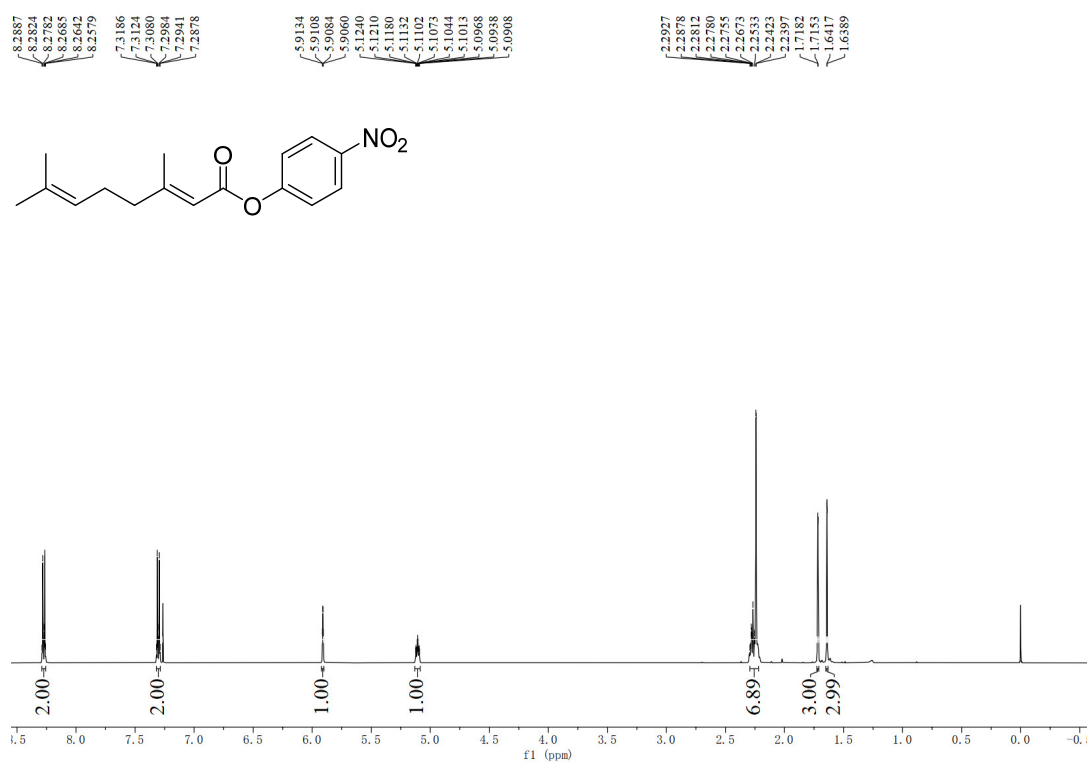
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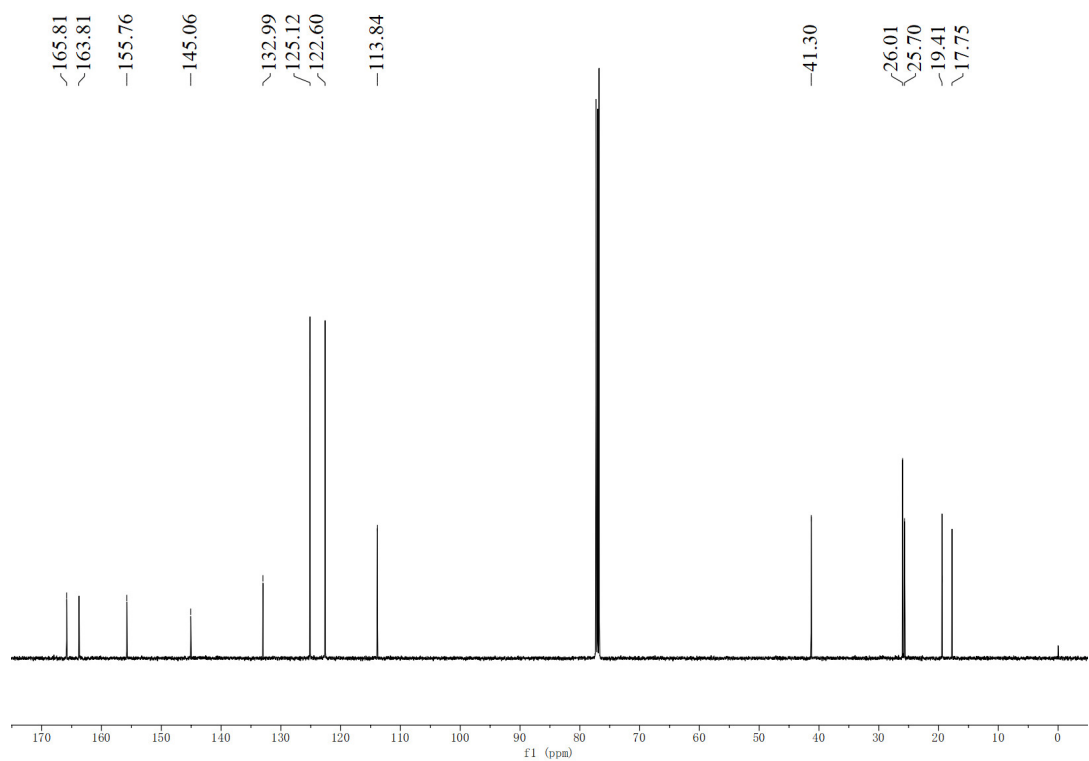
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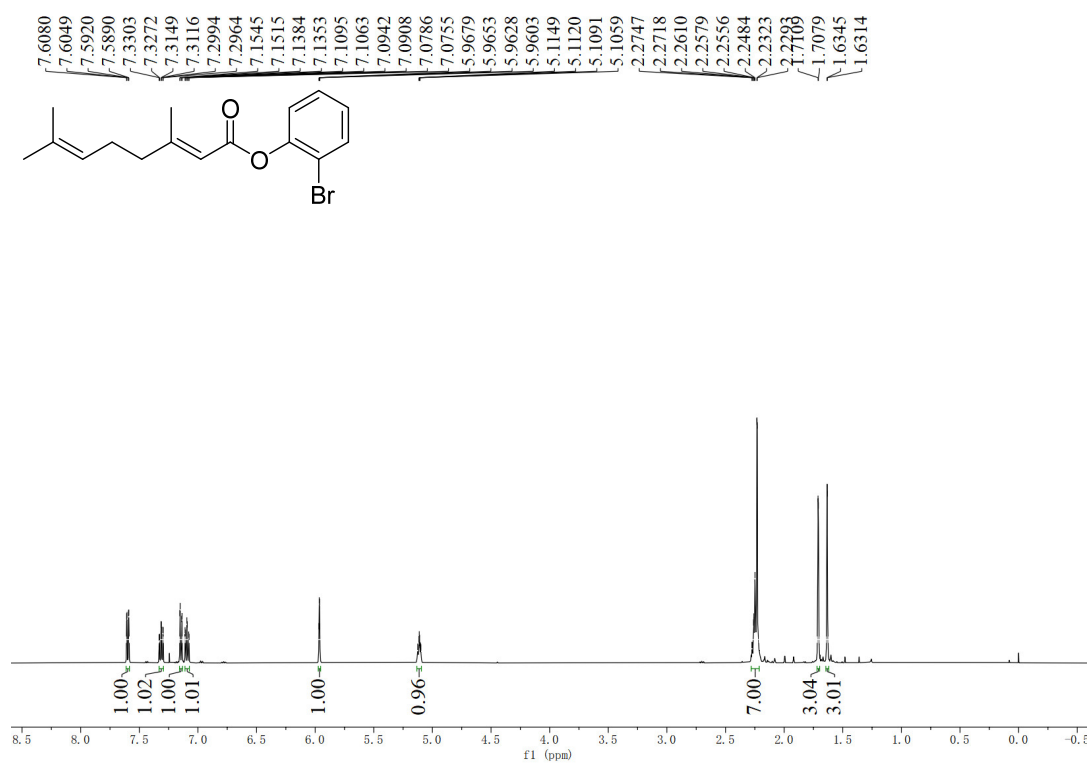
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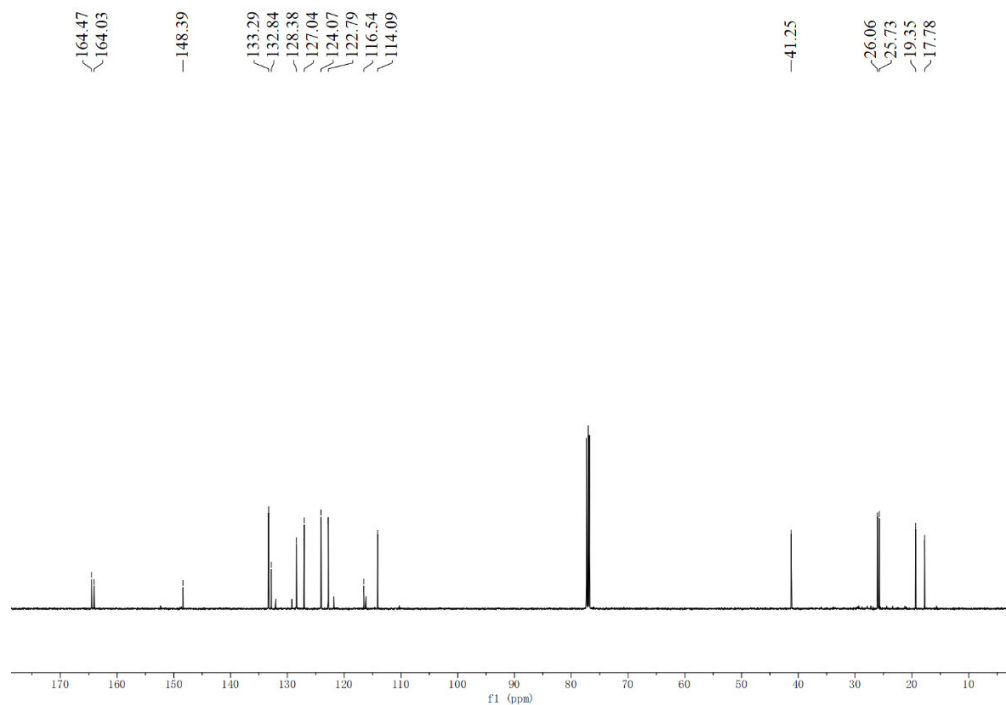
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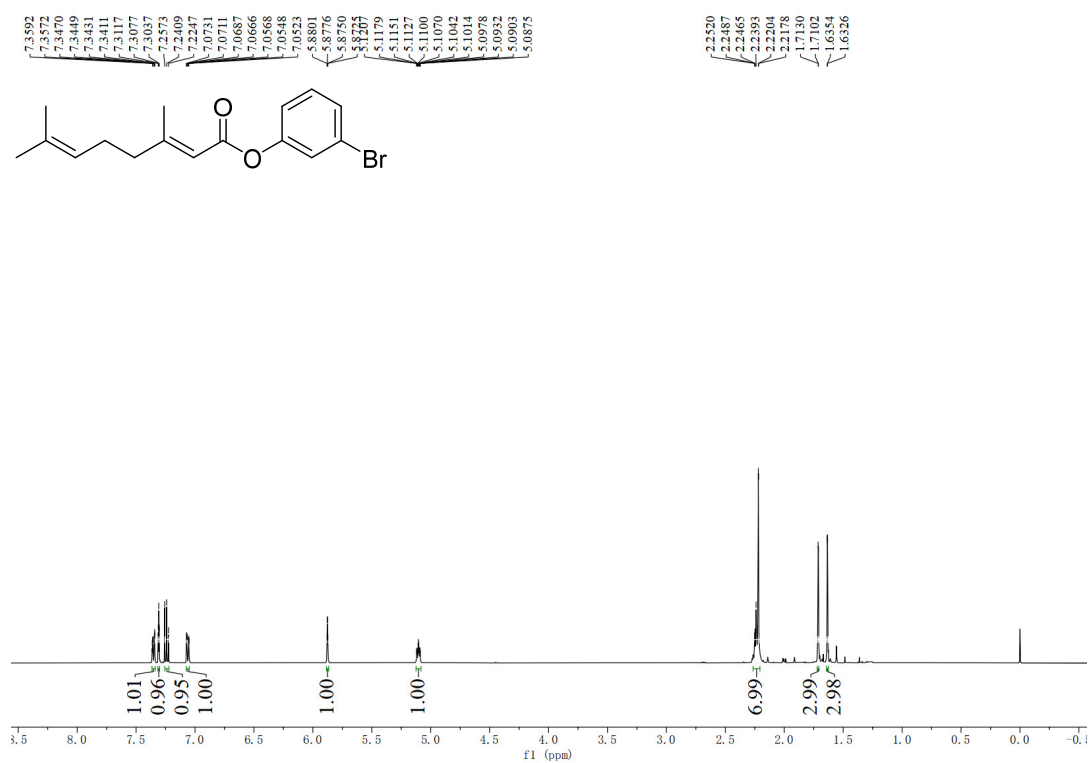
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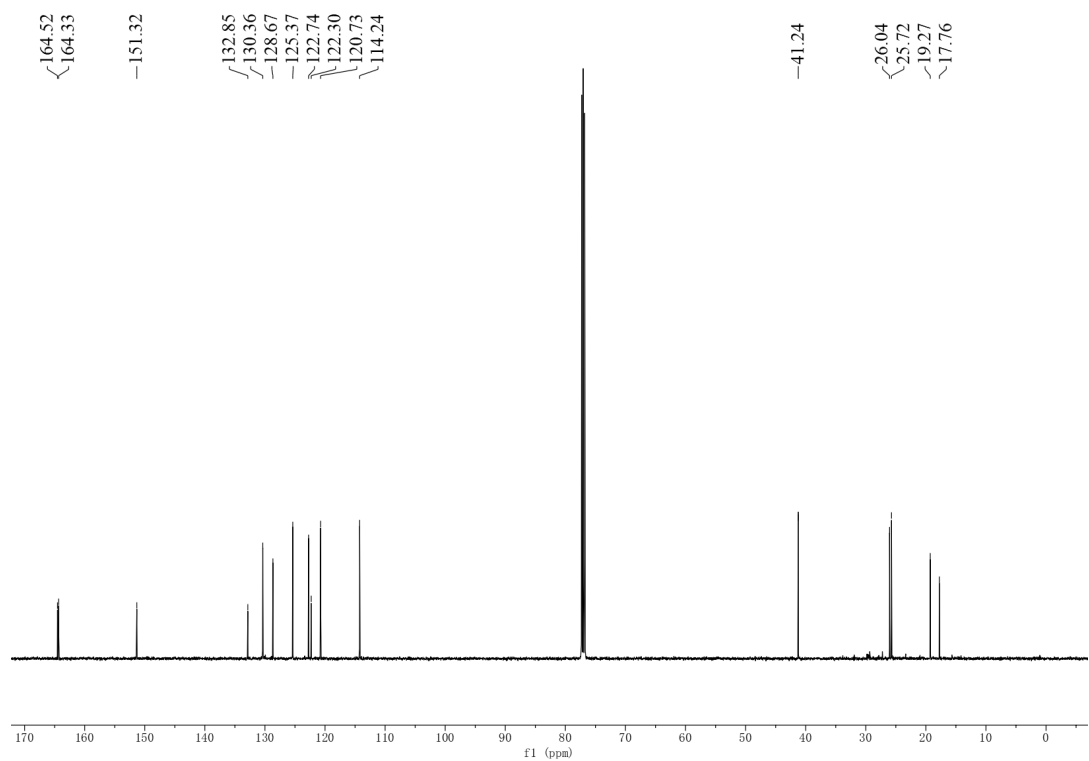
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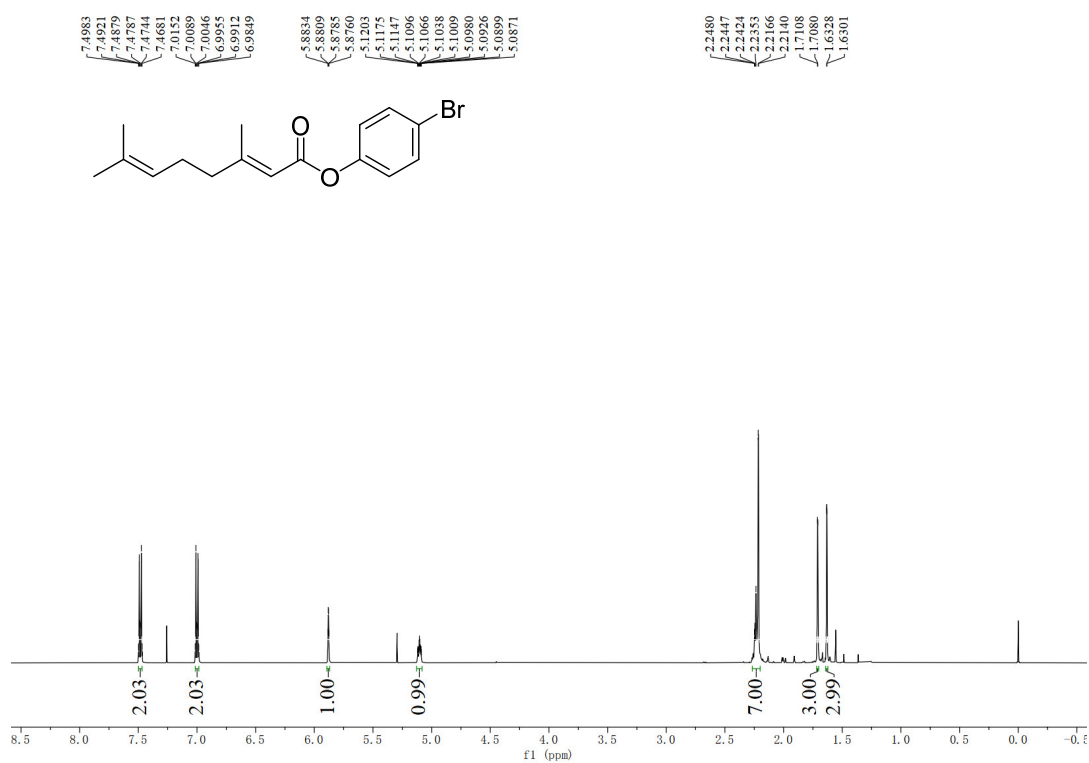
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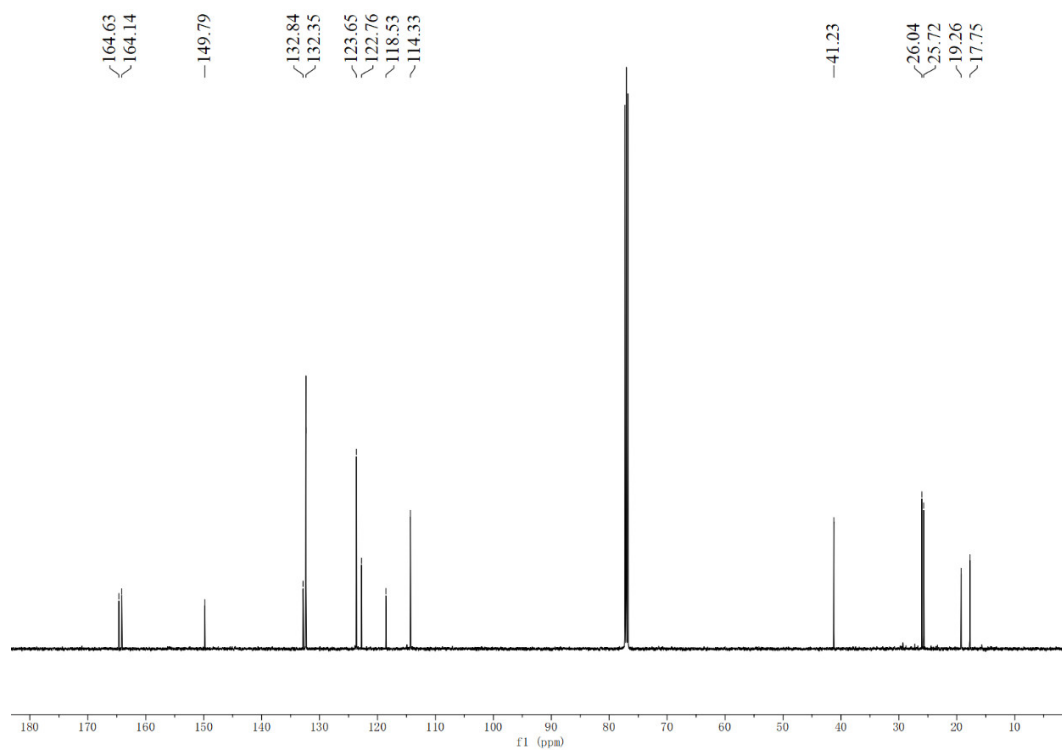
¹³C NMR of **5r**



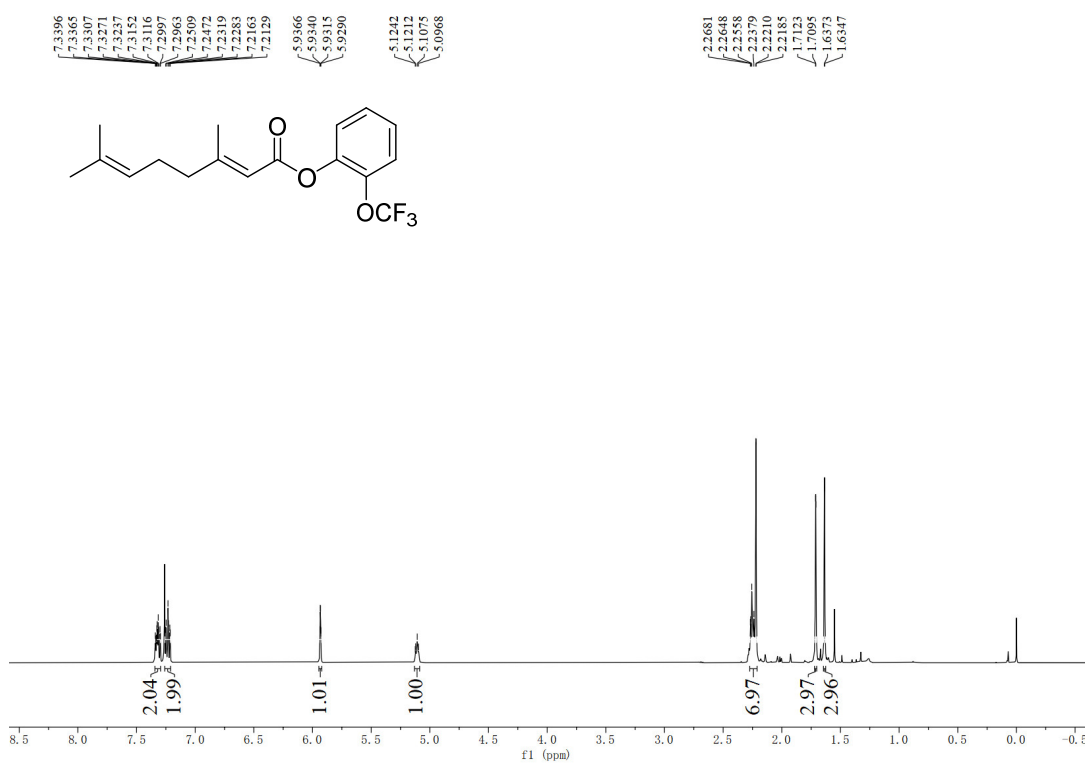
¹H NMR of **5s**



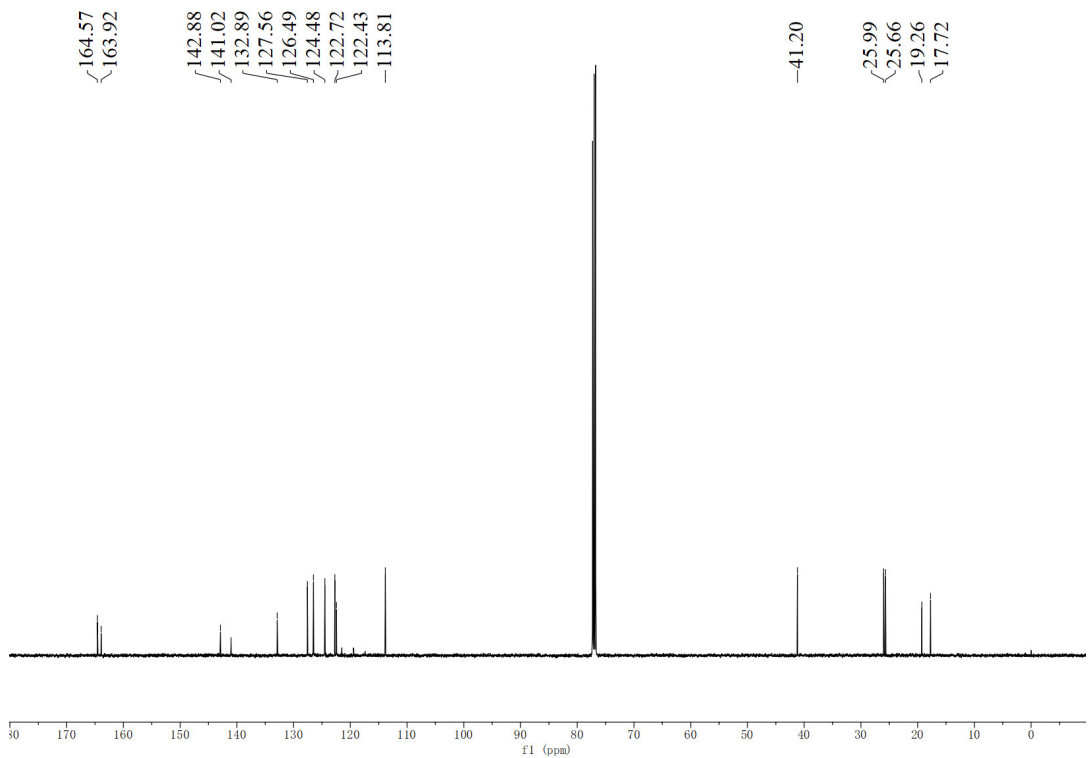
¹³C NMR of **5s**



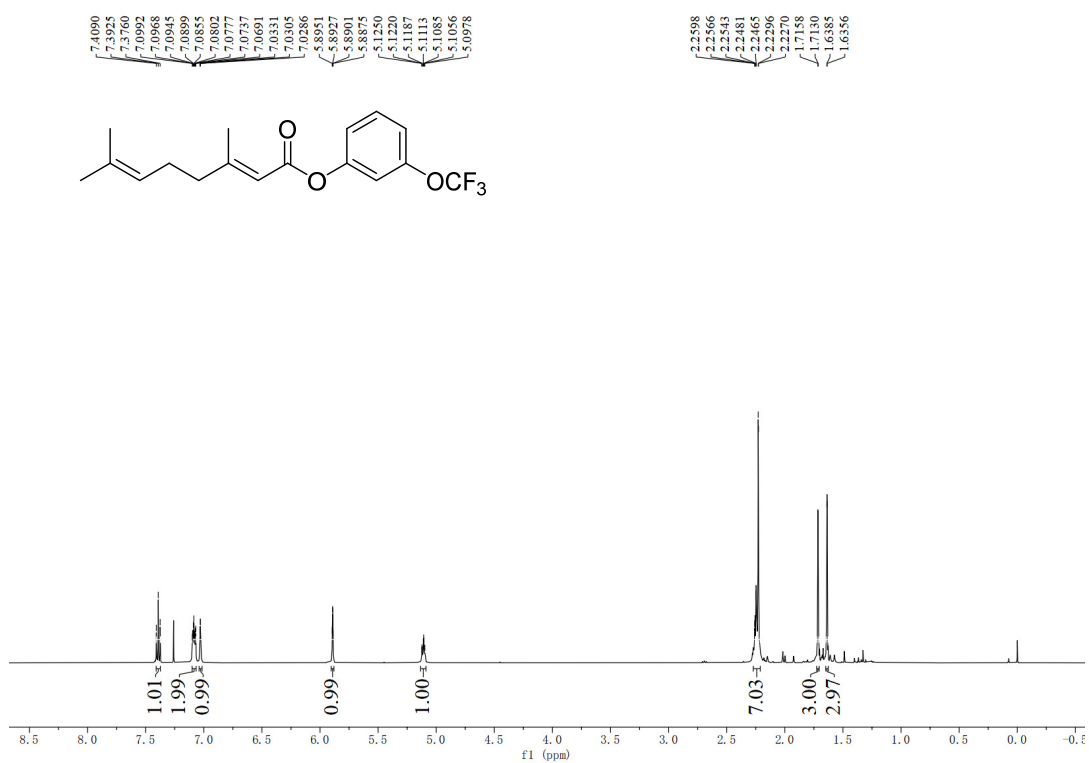
¹H NMR of **5t**



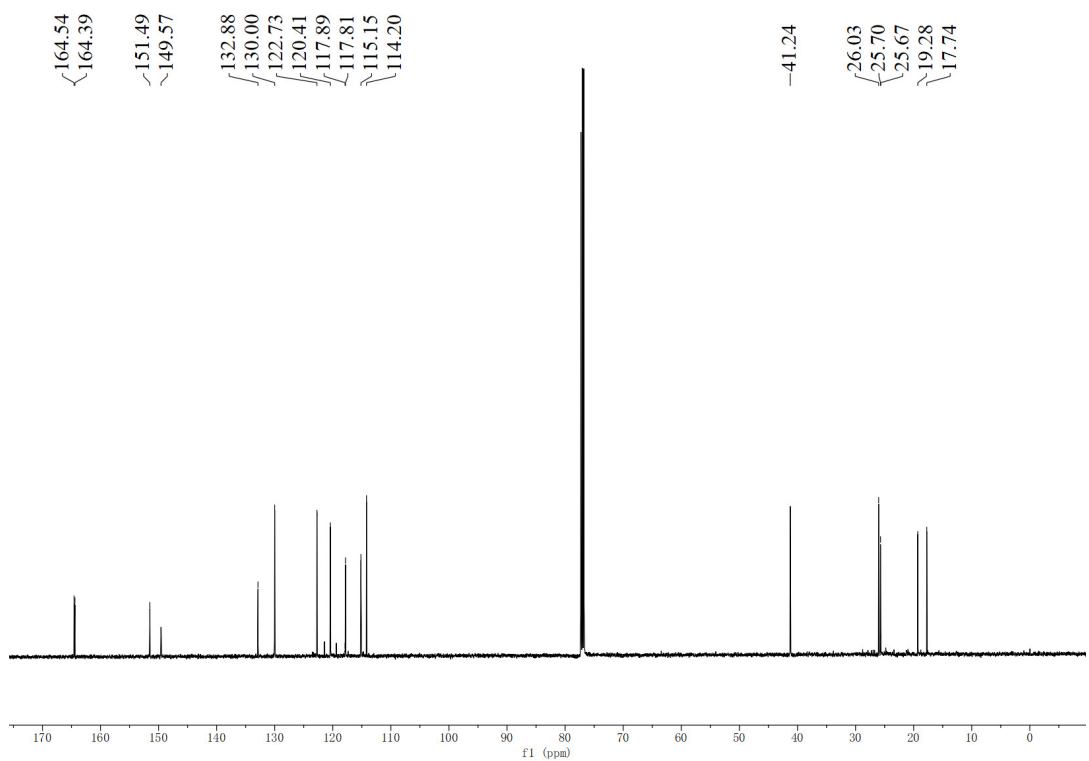
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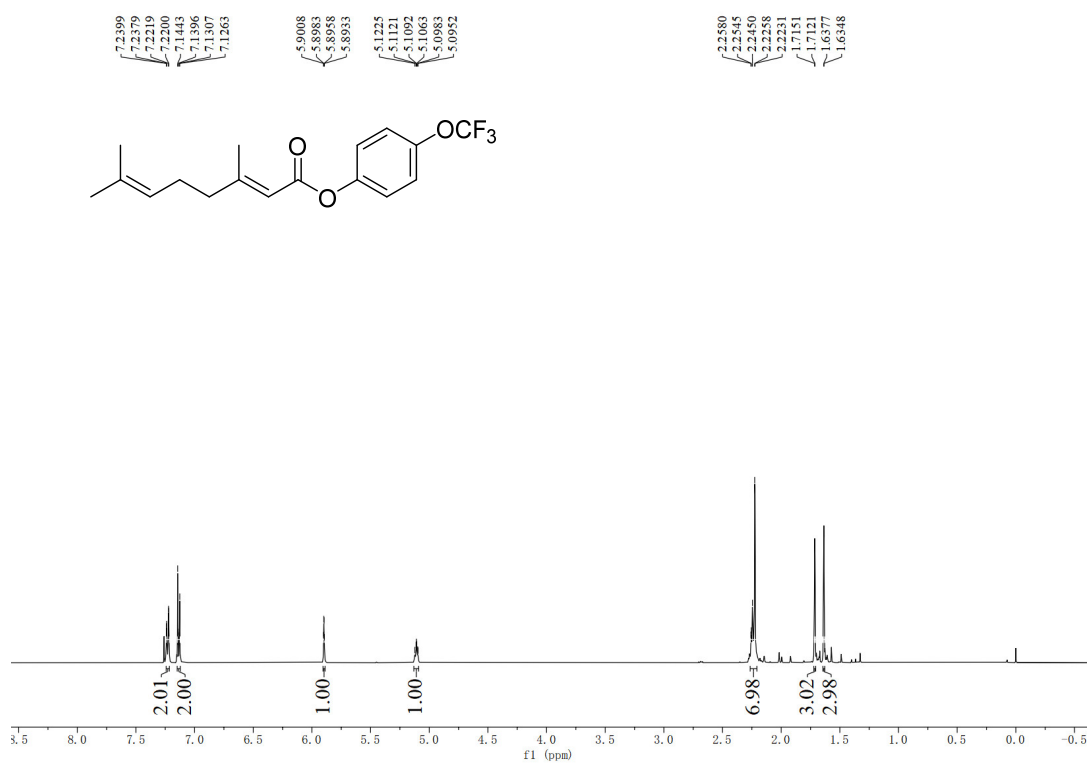
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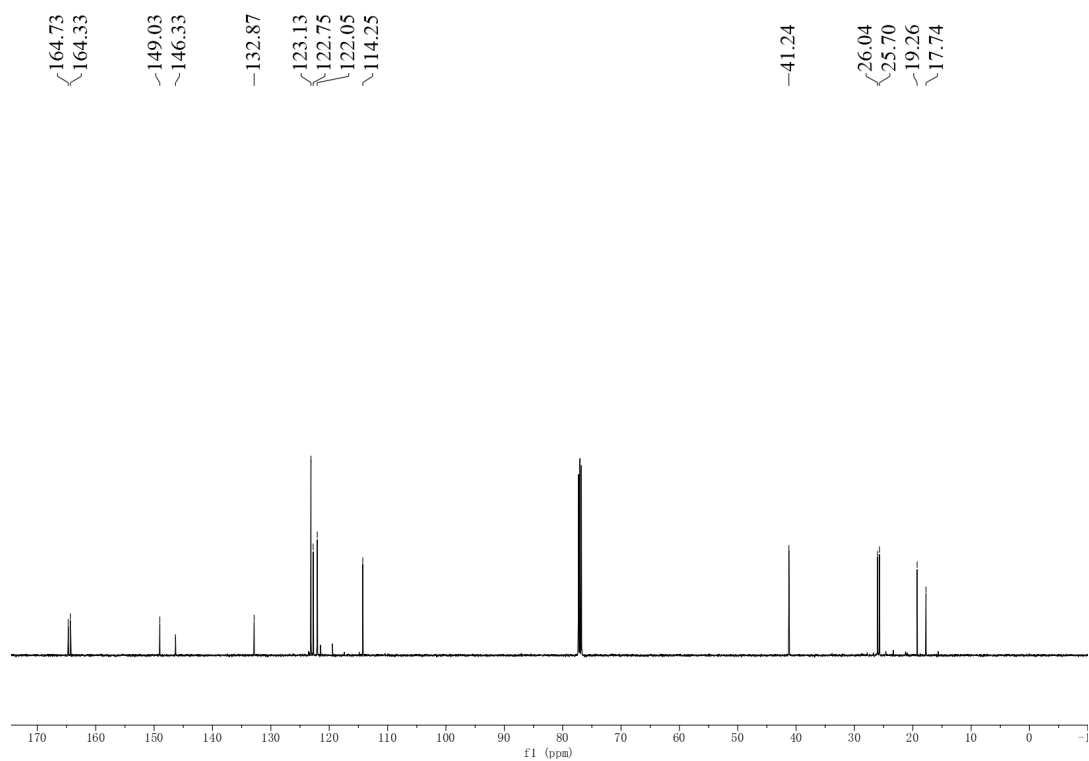
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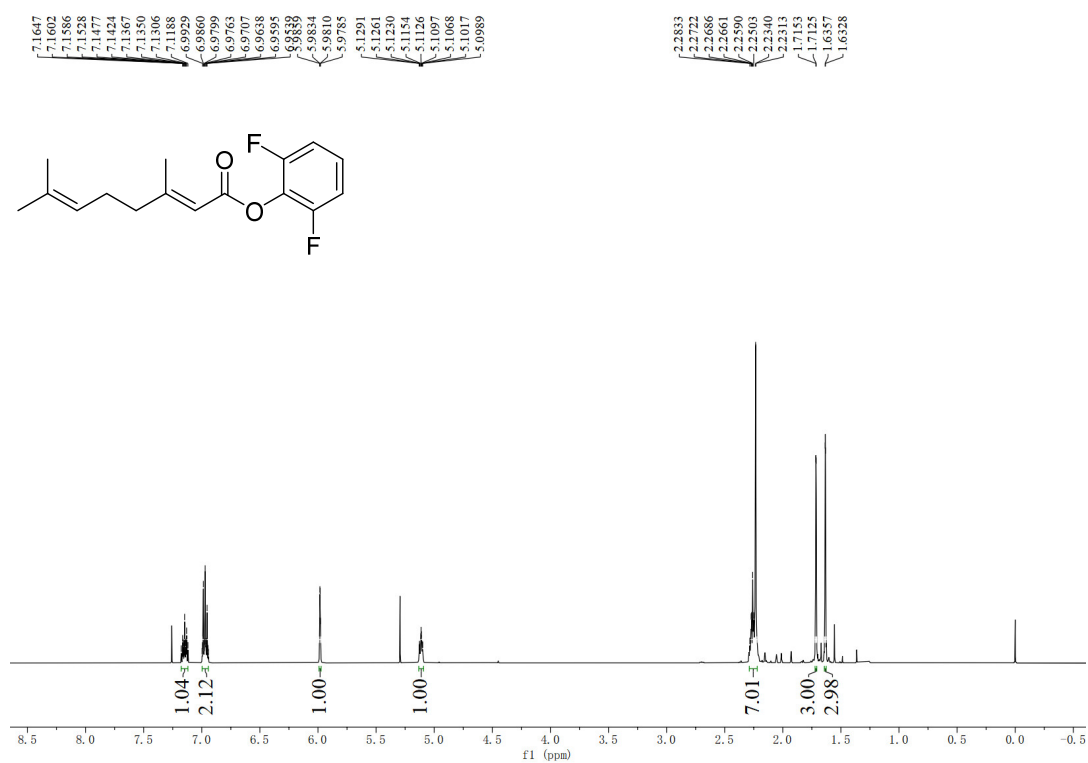
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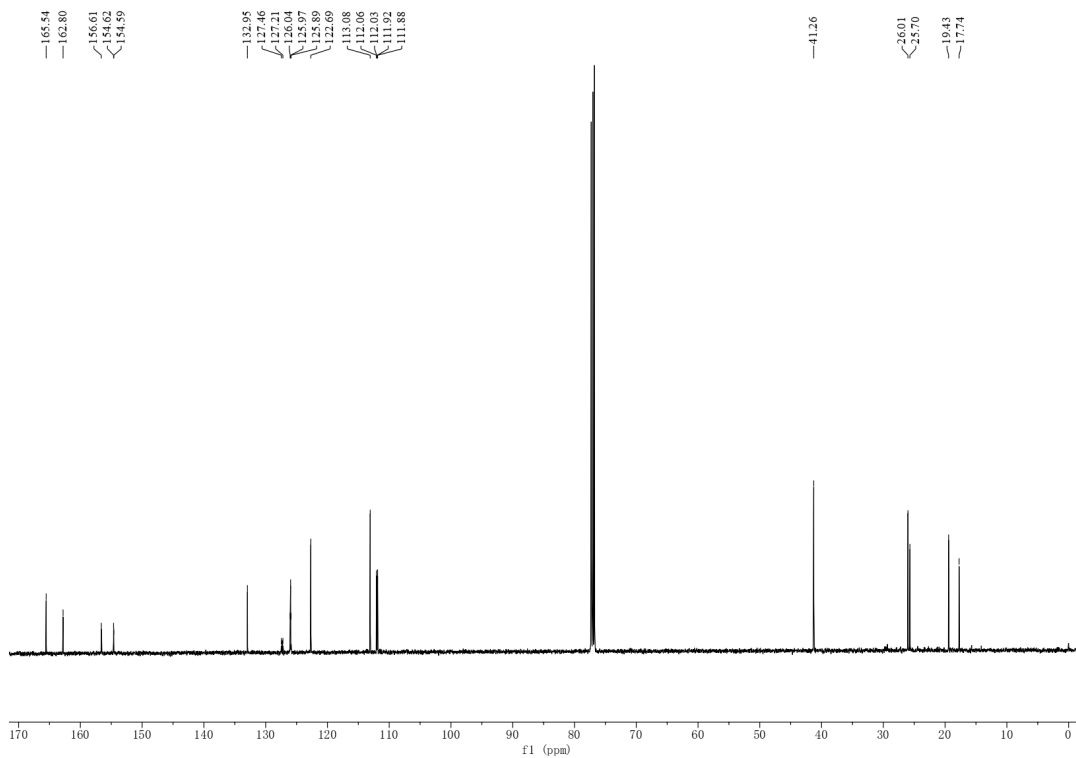
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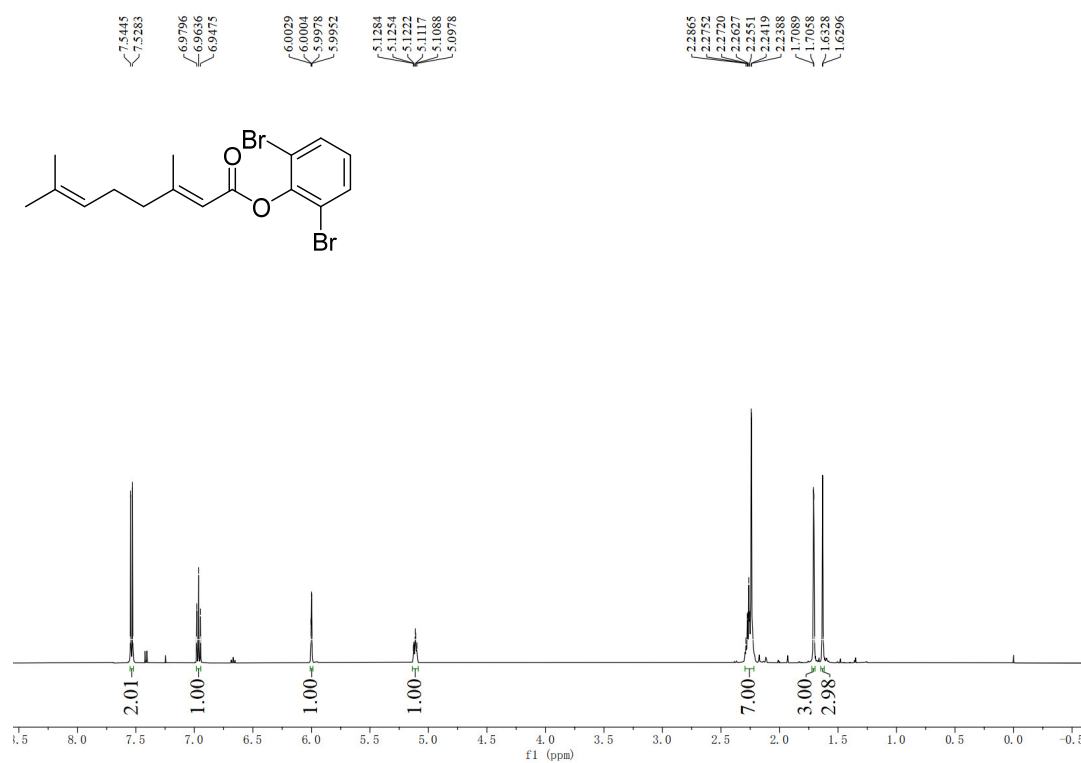
¹H NMR of **5w**



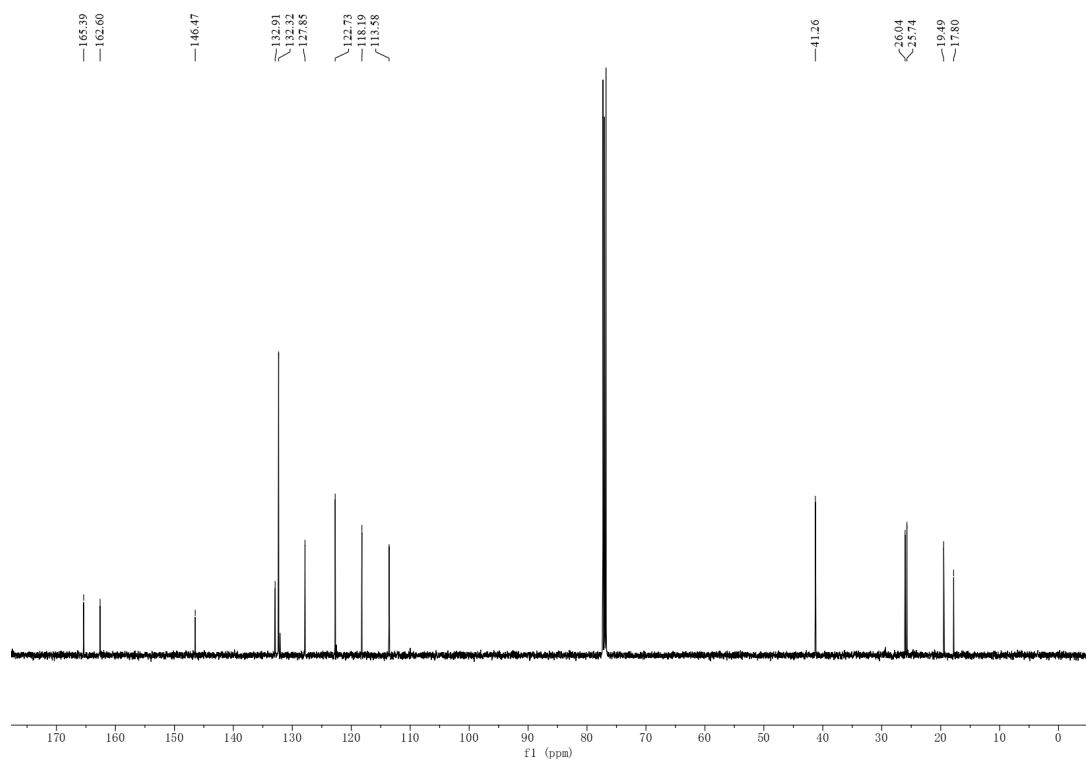
¹³C NMR of **5w**



¹H NMR of **5x**

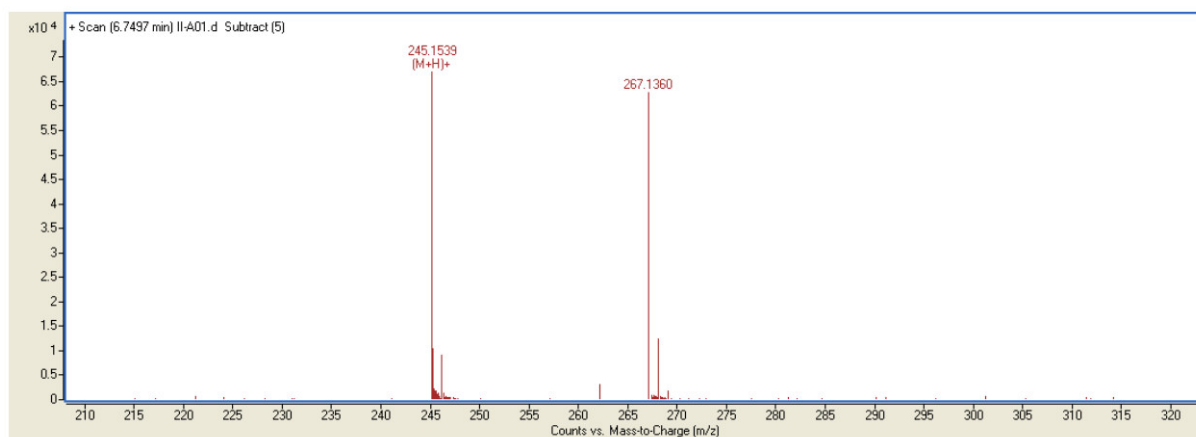


¹³C NMR of **5x**

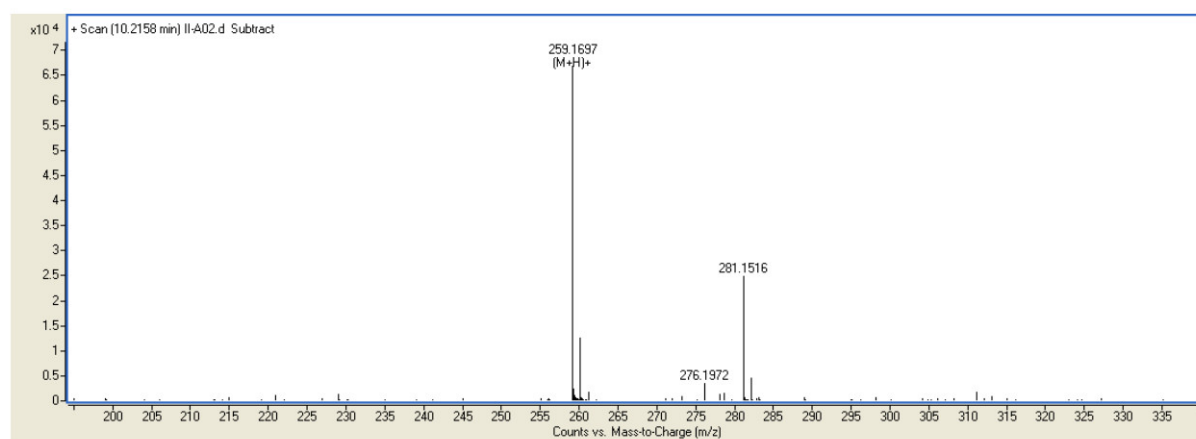


5. HRMS Spectrums of compounds **5a-5x**

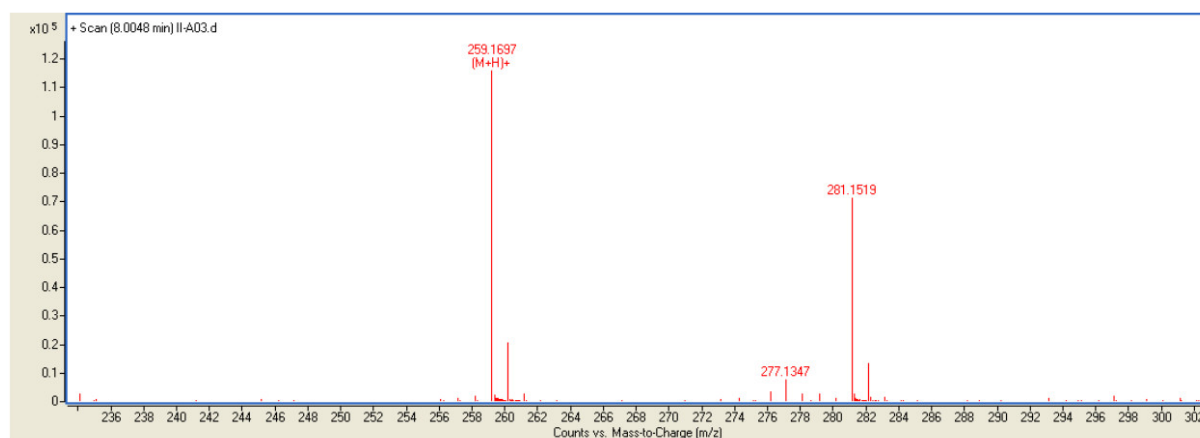
HRMS Spectrum of **5a**



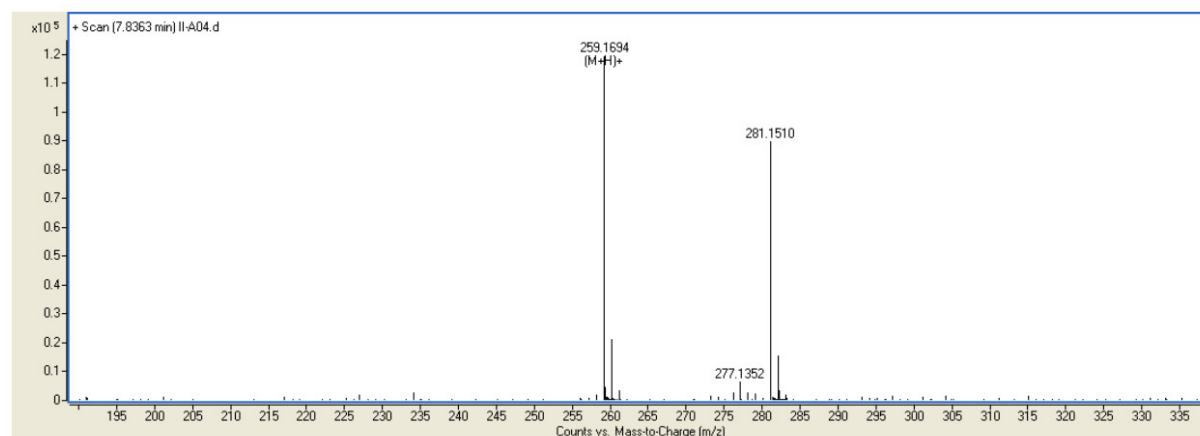
HRMS Spectrum of **5b**



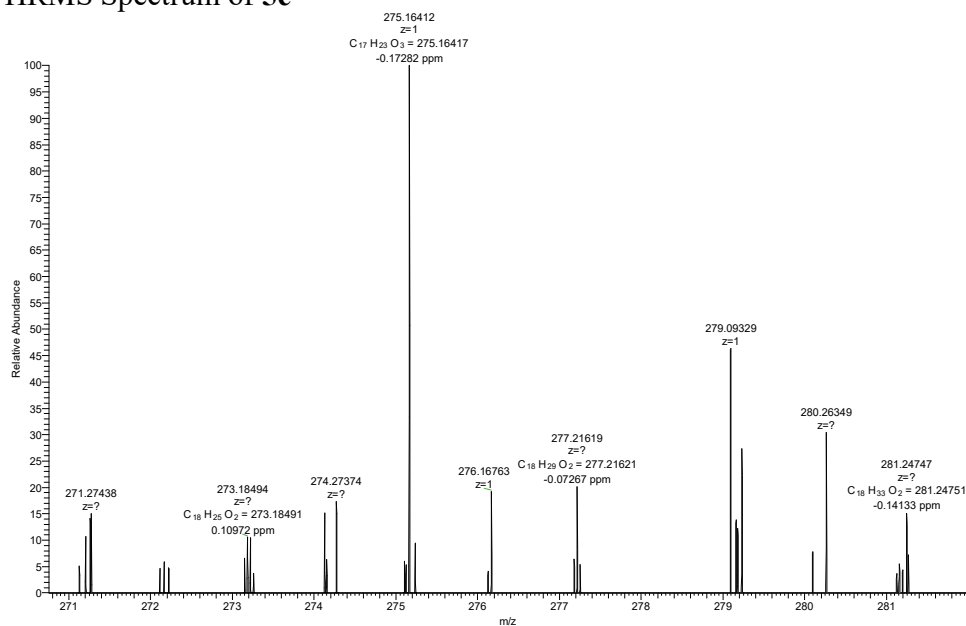
HRMS Spectrum of **5c**



HRMS Spectrum of **5d**

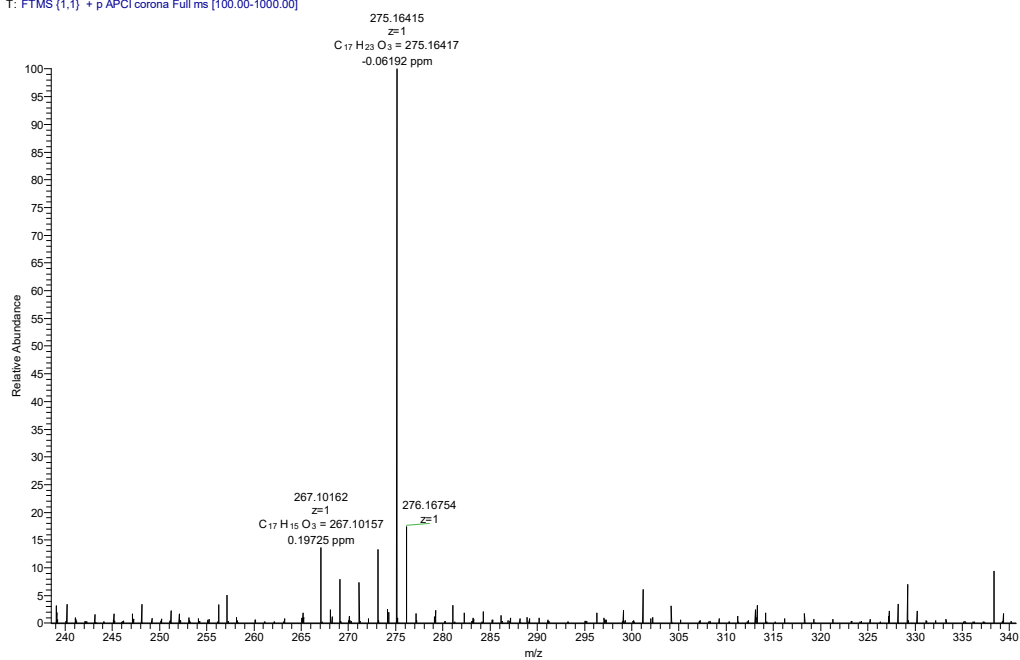


HRMS Spectrum of **5e**



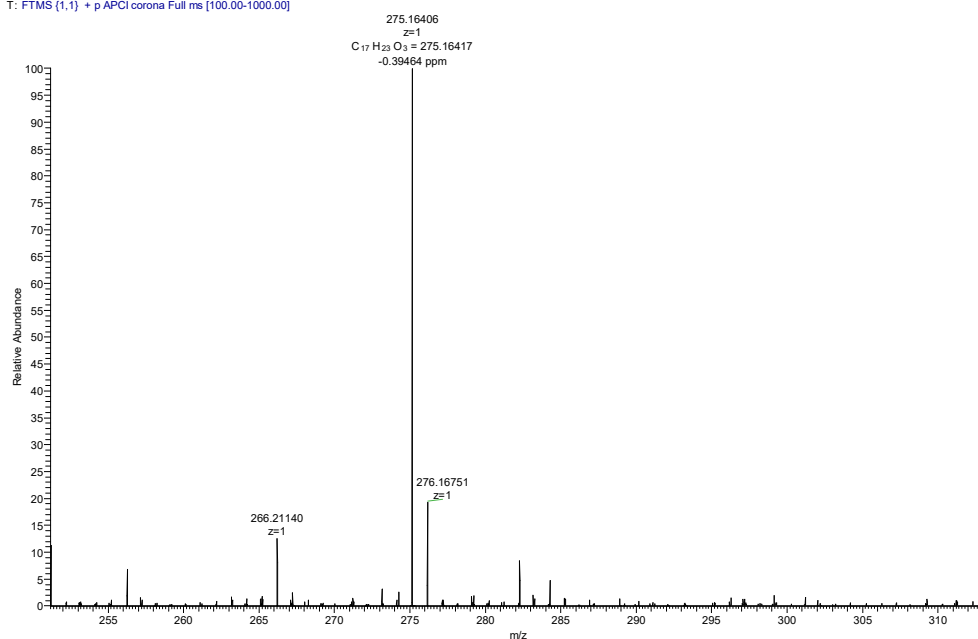
HRMS Spectrum of **5f**

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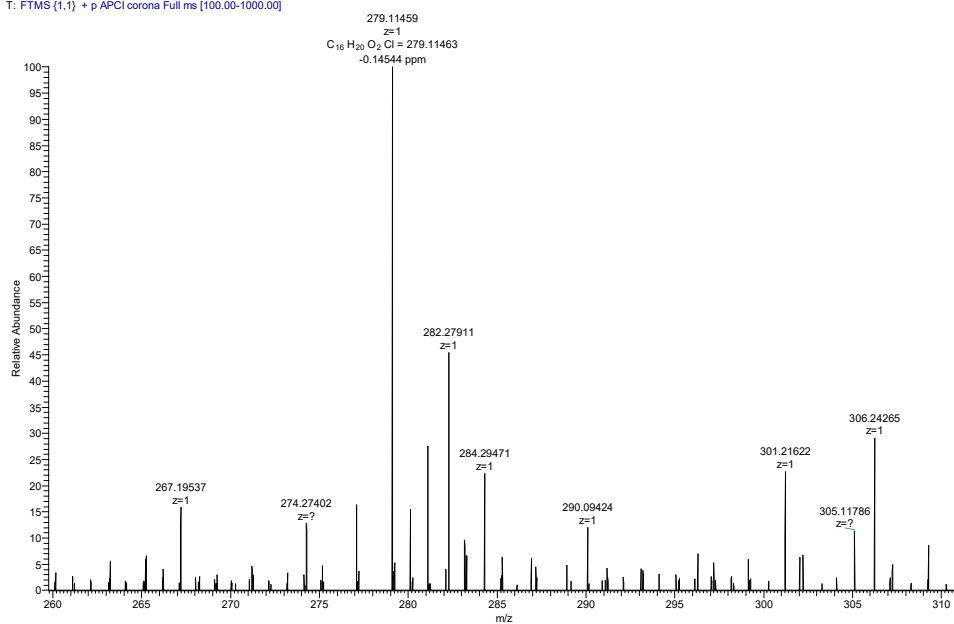
HRMS Spectrum of **5g**

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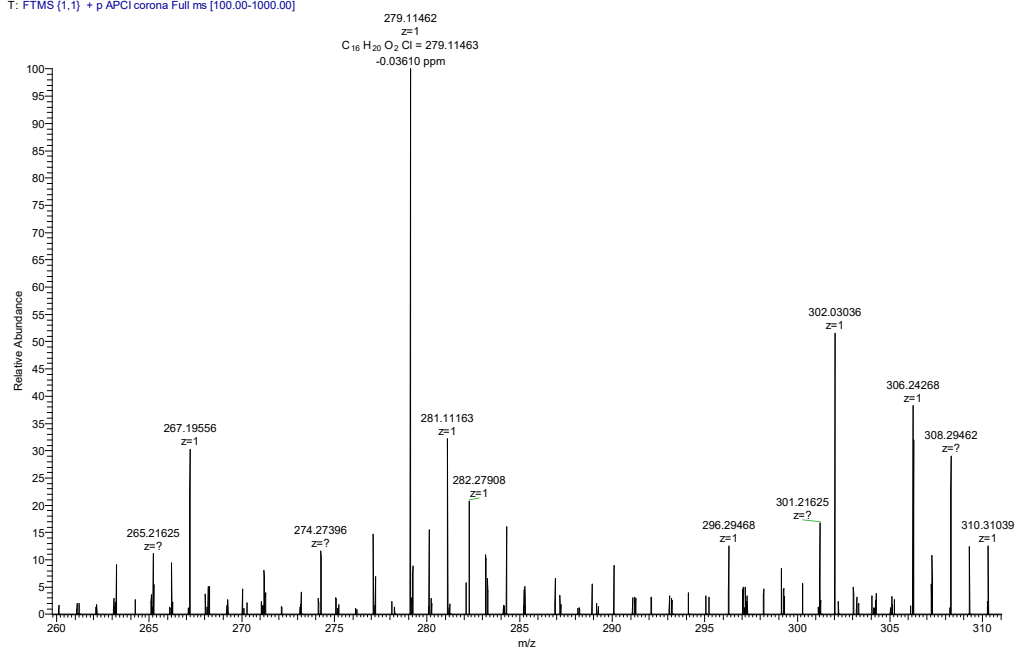
HRMS Spectrum of **5h**

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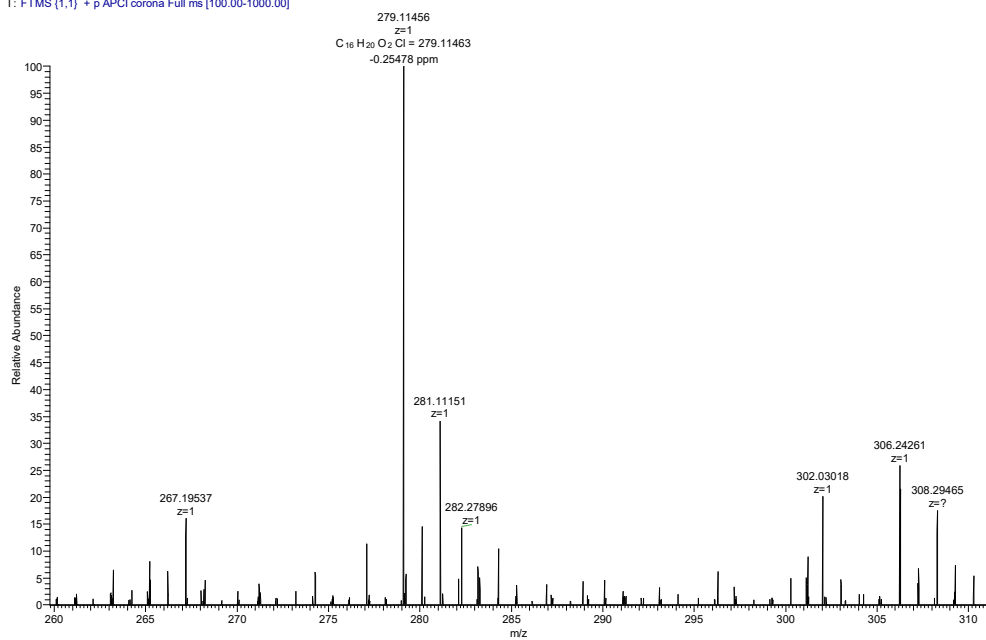
HRMS Spectrum of 5i

LA09 #5 RT: 0.06 AV: 1 NL: 1.74E5
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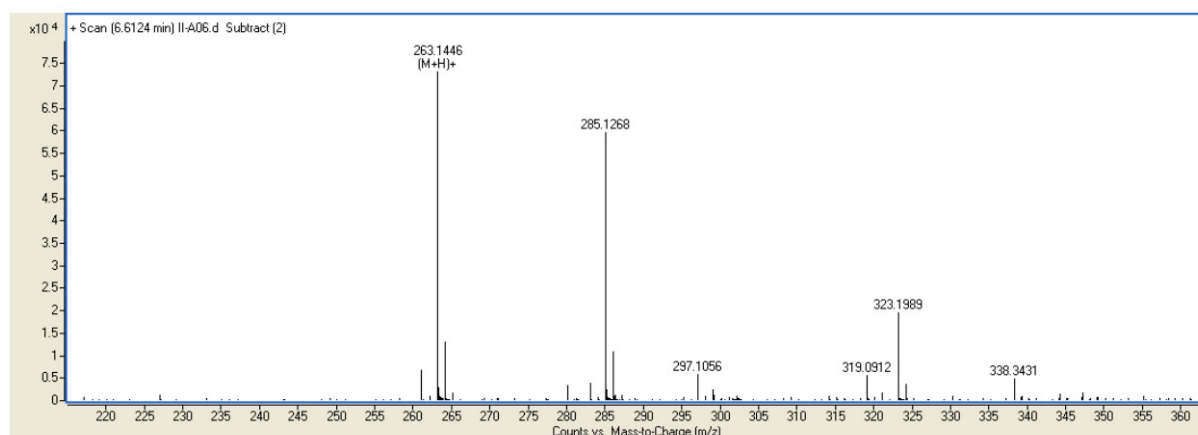


HRMS Spectrum of 5j

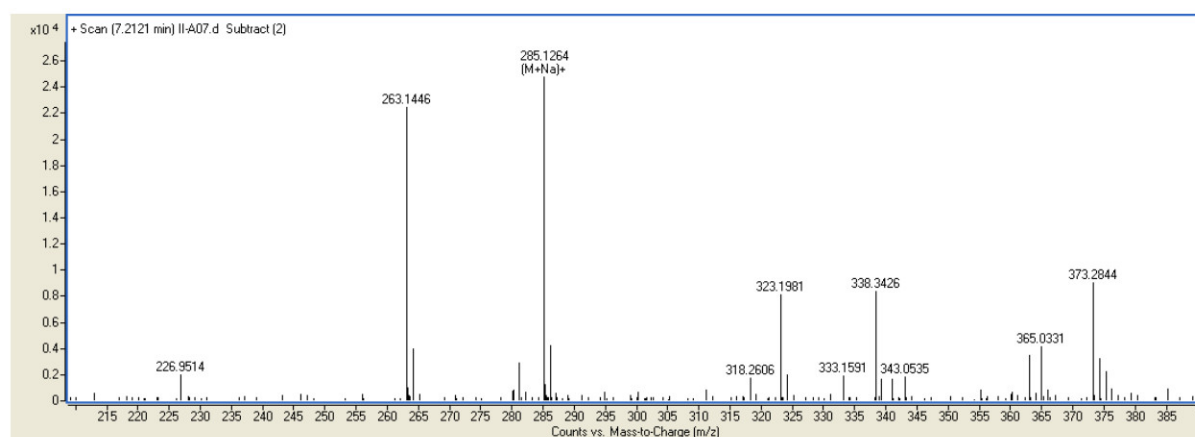
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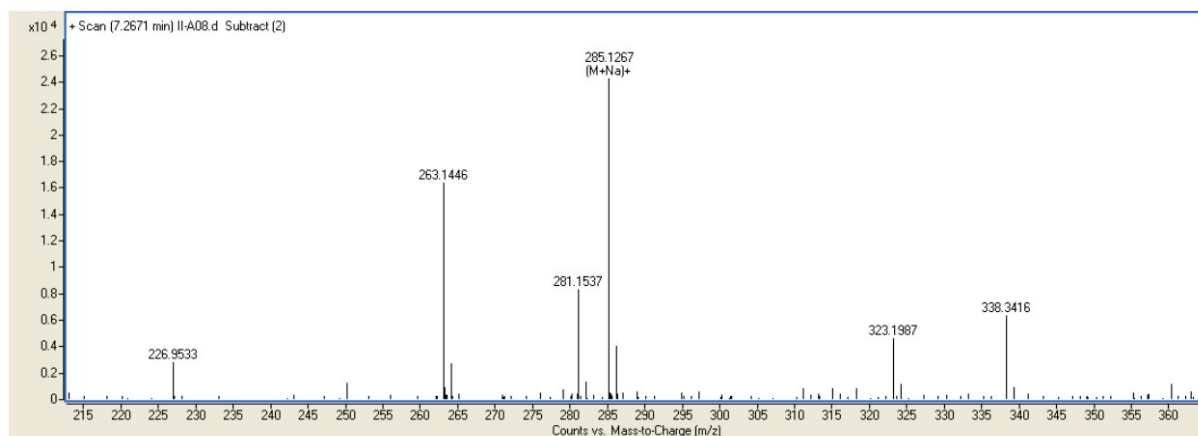
HRMS Spectrum of **5k**



HRMS Spectrum of **5l**

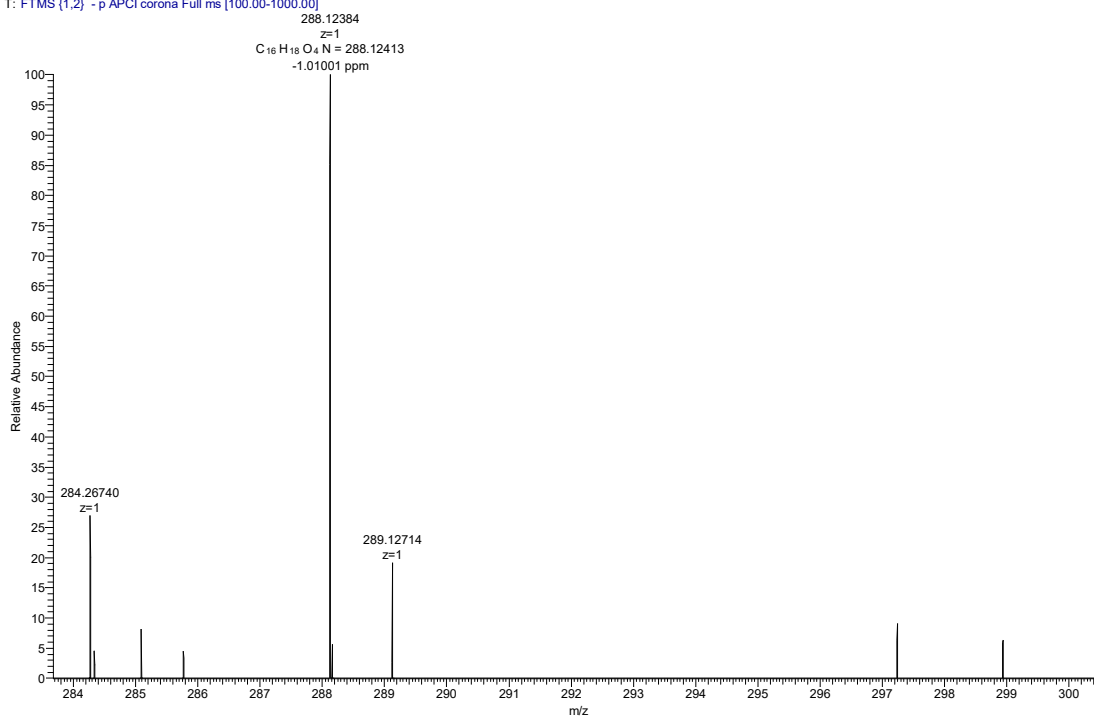


HRMS Spectrum of **5m**



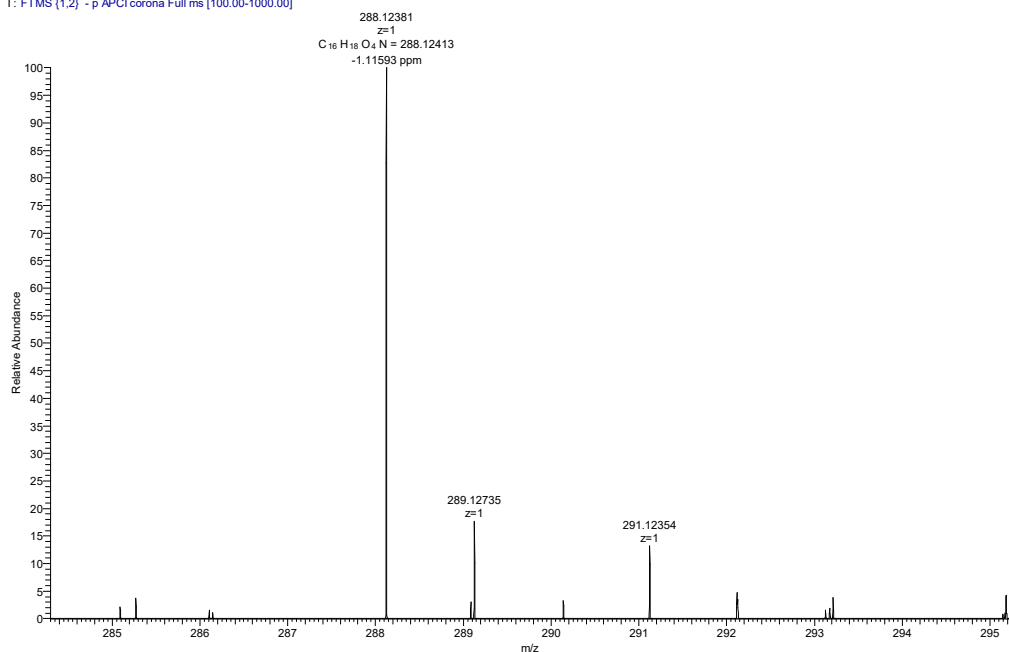
HRMS Spectrum of **5n**

I-A14 #6 RT: 0.07 AV: 1 NL: 6.26E4
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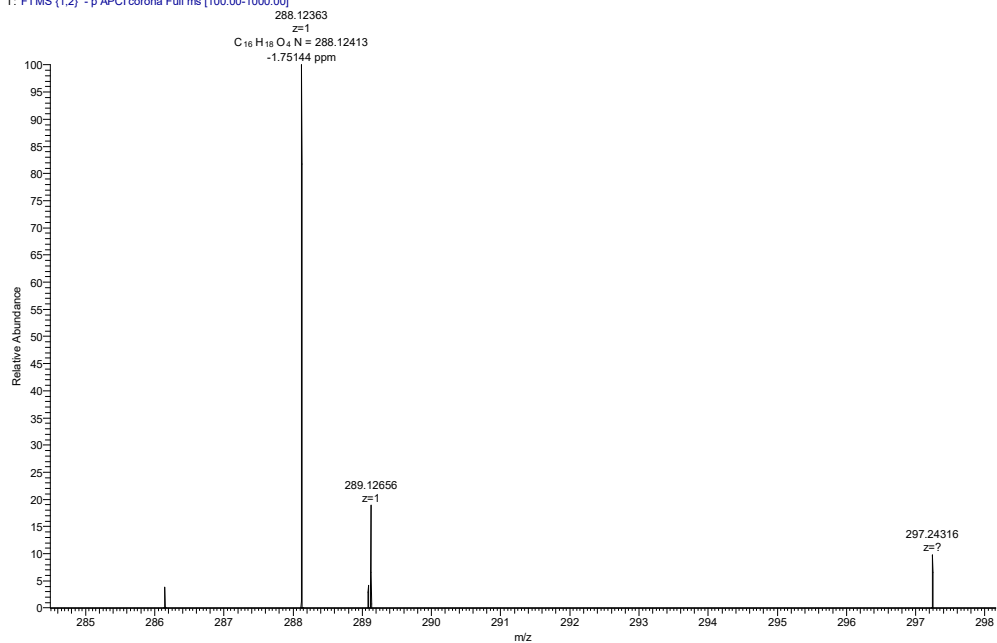
HRMS Spectrum of **5o**

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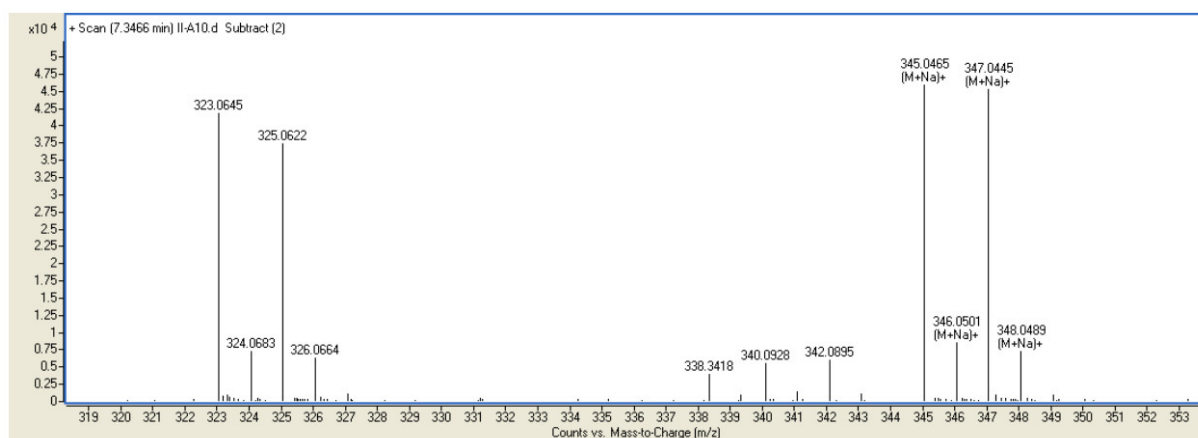


HRMS Spectrum of **5p**

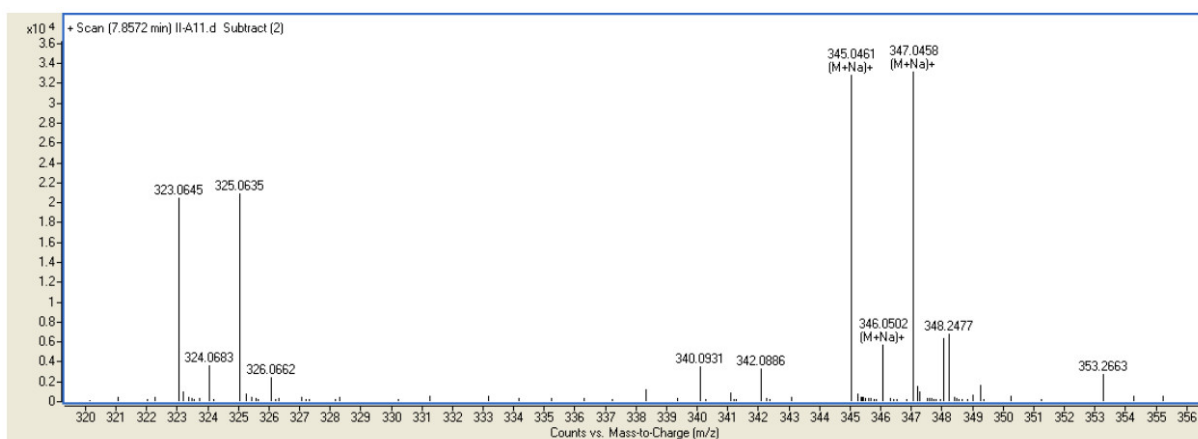
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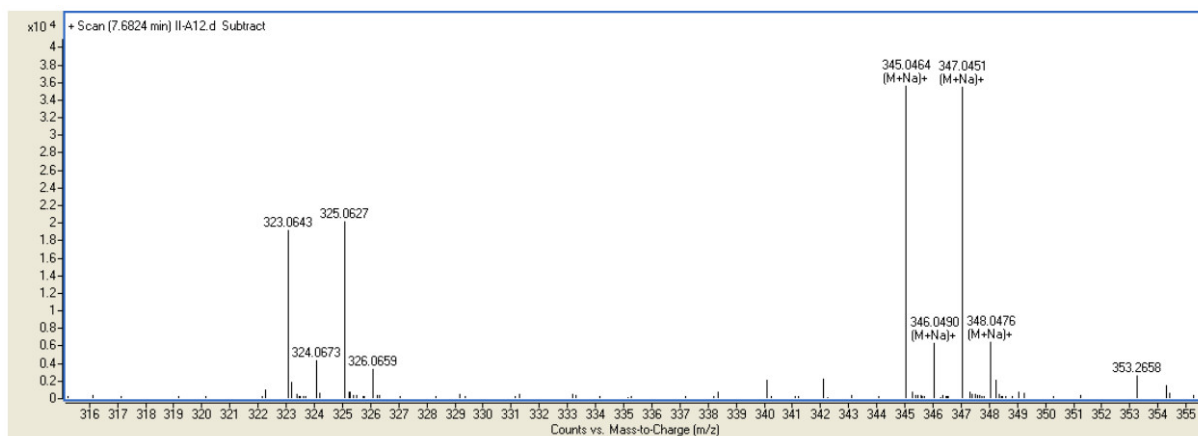
HRMS Spectrum of **5q**



HRMS Spectrum of **5r**

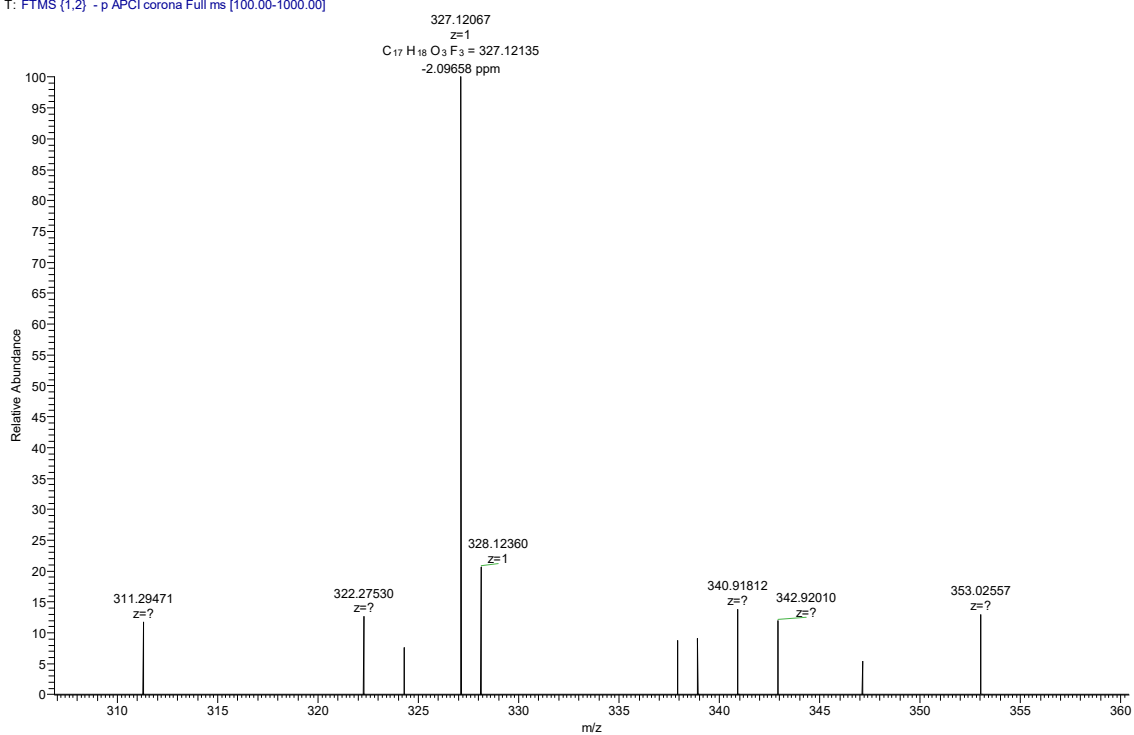


HRMS Spectrum of **5s**



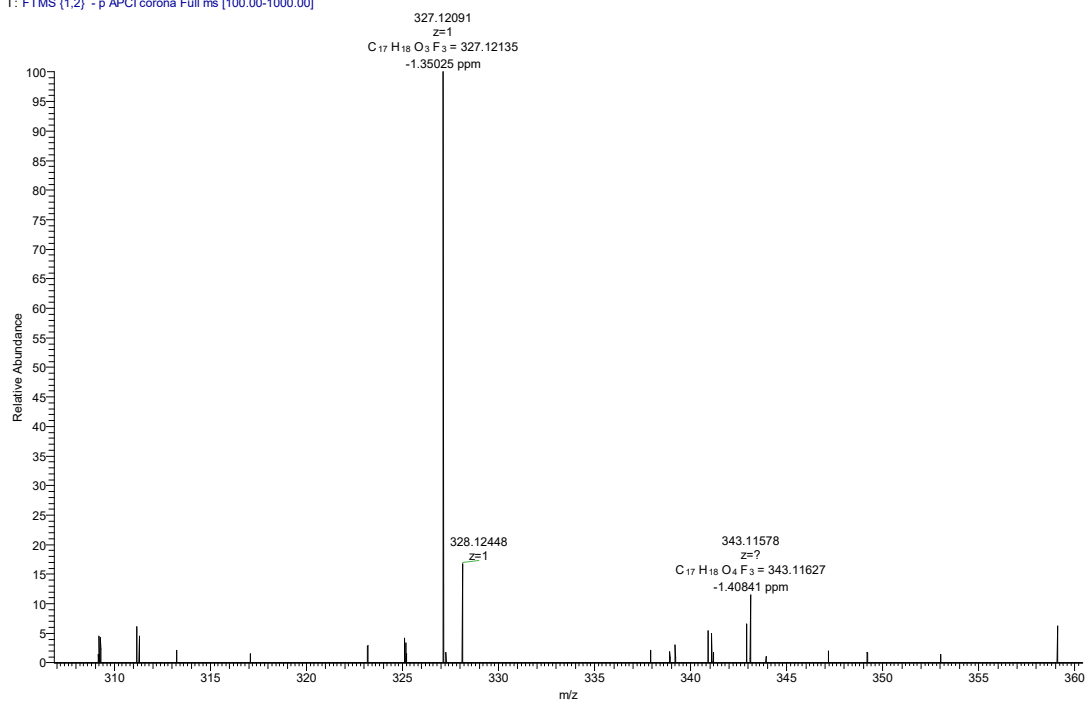
HRMS Spectrum of **5t**

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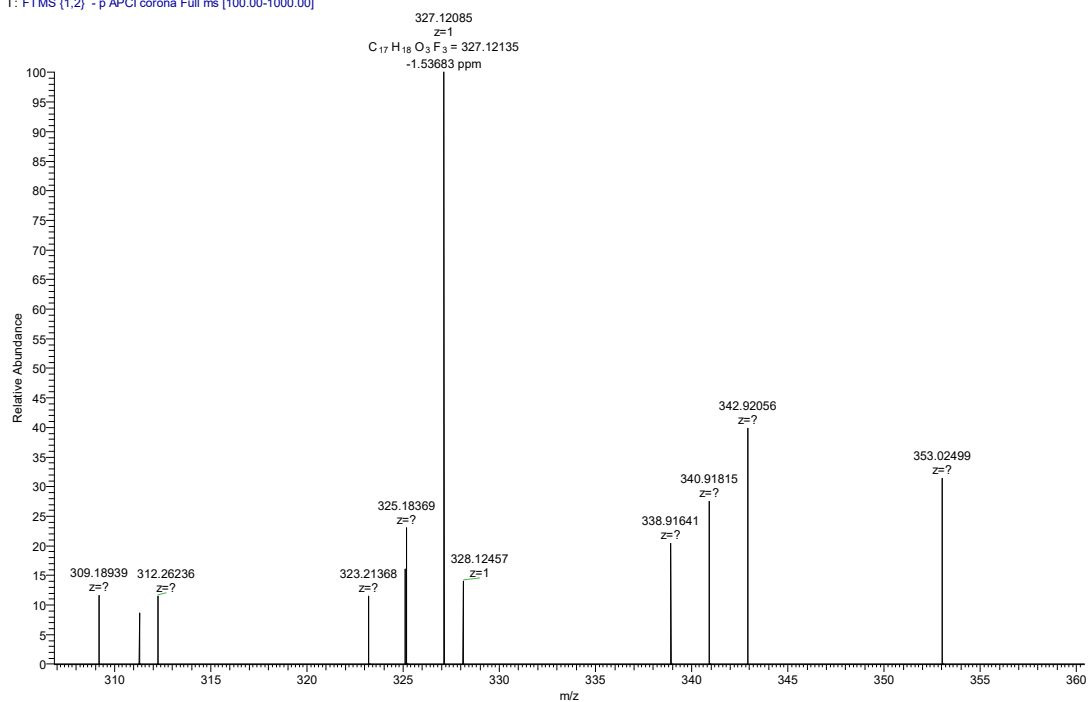
HRMS Spectrum of **5u**

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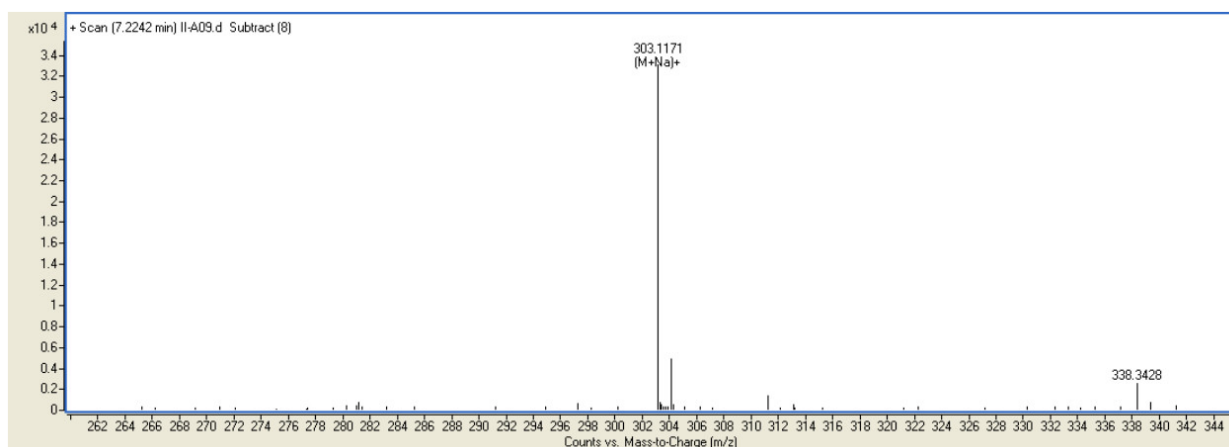


HRMS Spectrum of **5v**

L-A22 #12 RT: 0.14 AV: 1 NL: 1.41E4
T: FTMS (1,2) -p APCI corona Full ms [100.00-1000.00]



HRMS Spectrum of **5w**



HRMS Spectrum of **5x**

