

Photoredox-Catalyzed Synthesis of 3-Sulfonylated Pyrrolin-2-ones via a Regioselective Tandem Sulfonylation Cyclization of 1,5-Dienes

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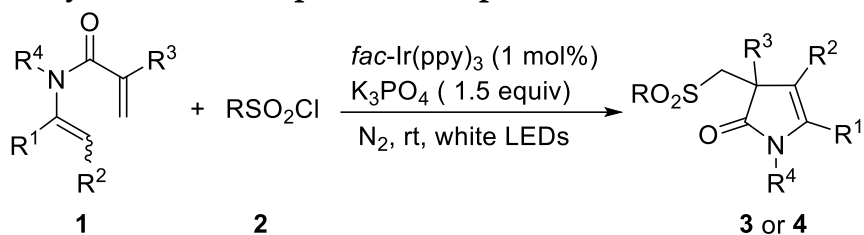
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S1. General information

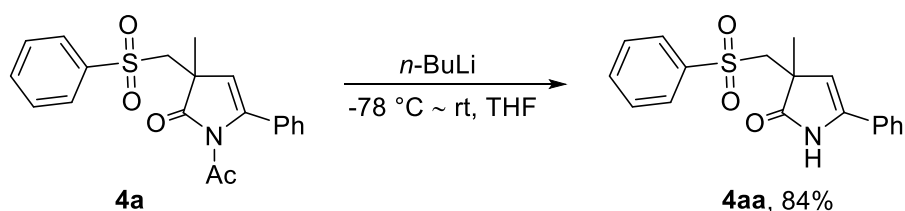
All the reagents purchased from Leyan company were directly used. ¹H-NMR and ¹³C-NMR spectra of the products were recorded on a Bruker FT-NMR 400M or 600M spectrometers. Chemical shifts spectra are given as δ in the units of parts per million (ppm) with reference to tetramethylsilane (TMS). Multiplicities were indicated as follows: d (doublet); s (singlet); t (triplet); q (quartet); m (multiplets) and etc. Coupling constants are reported as a J value in Hz. High resolution mass spectral analysis (HRMS) of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) instrument.

S2. Procedure for the synthesis of compound 3a – 3p, 4a – 4o.



A dry 25-mL Schlenk tube containing a magnetic stirring bar was charged with 1,5-dienes **1** (0.1 mmol), sulfonyl chlorides **2** (0.2 mmol), *fac*-Ir(ppy)₃ (1 mol%), K₃PO₄ (1.5 equiv), and CH₂Cl₂ (1 mL). Then the mixture was irradiated with white LEDs at room temperature under N₂ for 16 h. After finishing, the reaction mixture was concentrated on a rotary evaporator and the residue was directly subjected to flash column chromatography on silica gel with (10-40% EtOAc/Petroleum ether) as eluate to furnish the desired product.

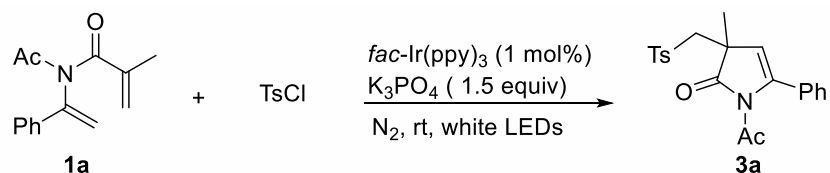
S3. Procedures for the formation of 4aa



n-BuLi (2.5 M, 0.24 mmol) was slowly added to the solution of compound **4a** (0.2 mmol) and THF (8 mL) at -78 °C. After 15 minutes the reaction has risen to room temperature. After completing, 8 mL water was added to quench the reaction. Then, the mixture was extracted with 10 mL dichloromethane for 3 times. The combined dichloromethane were dried over CaCl₂, concentrated in vacuo and purified by flash column chromatography (30% EtOAc/Petroleum ether) to furnish the desired product **4aa** (84% yield).

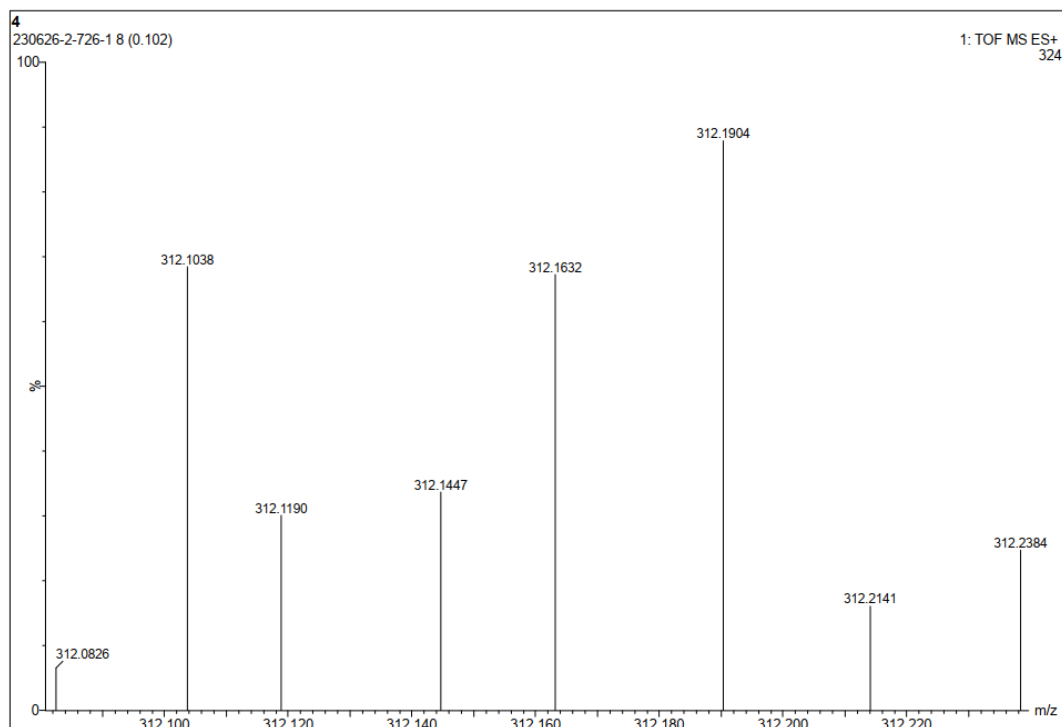
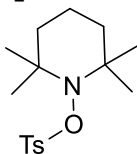
S4. The Transformation with the Light ON/OFF over Time

The reaction mixture was stirred for 60 min with light-off. All of the following yields were analyzed in the identical way after a 60 min light on or off.



Time (h)	0	1	2	3	4	5	6
On/off	off	on	off	on	off	on	off
Yield (%)	0	26	26	46	46	62	62

S5. The radical trapping reaction residue was analyzed by high resolution mass spectrometry (HRMS)



Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

459 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

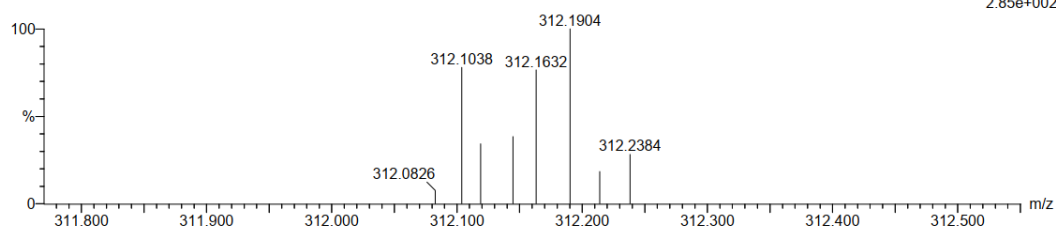
Elements Used:

C: 16-16 H: 4-50 N: 0-200 O: 0-200 S: 1-3

4

230626-2-726-1 8 (0.102)

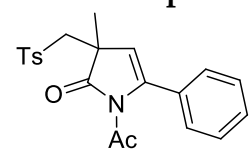
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2.85e+002



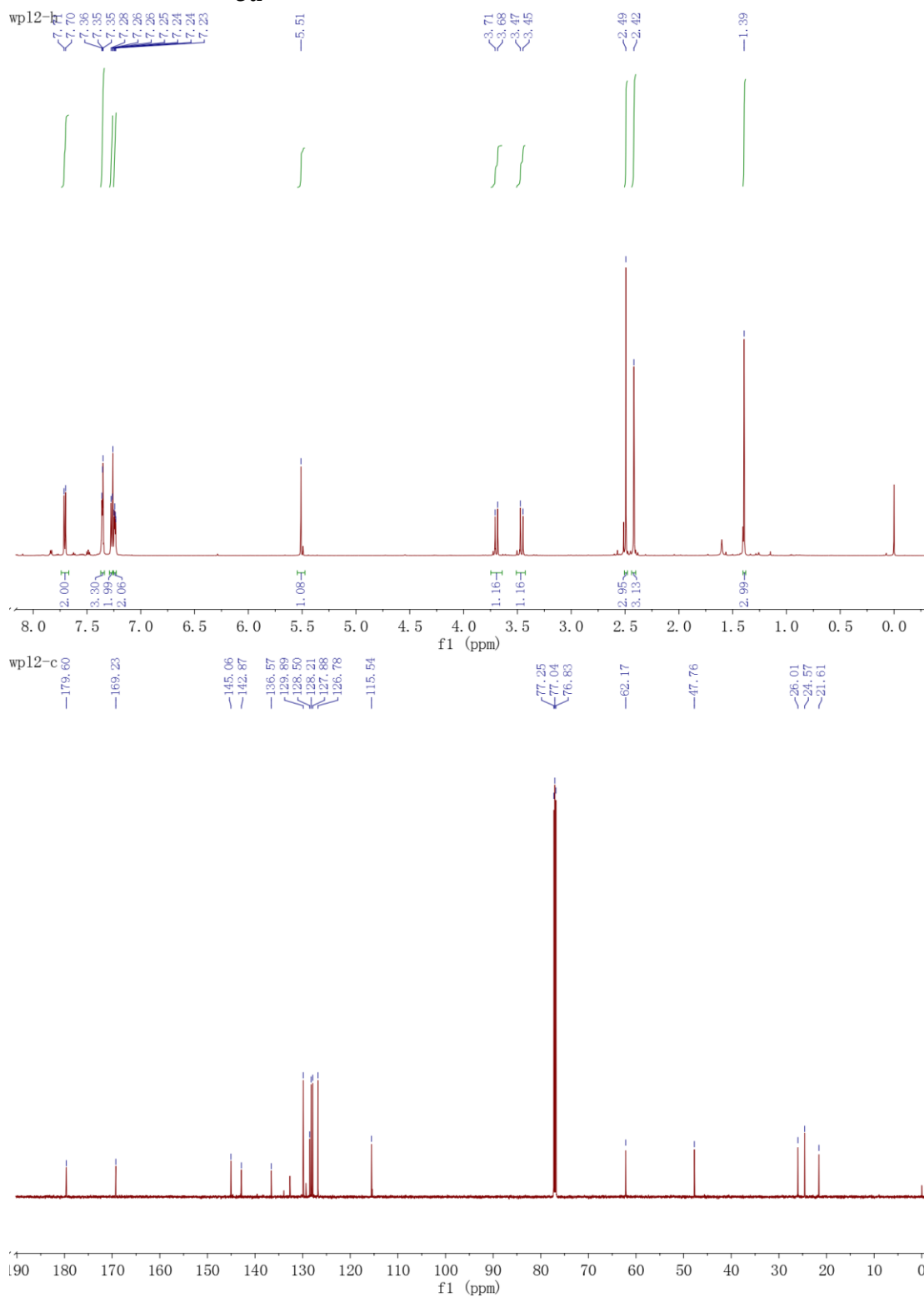
Minimum: -1.5
Maximum: 5.0 10.0 50.0

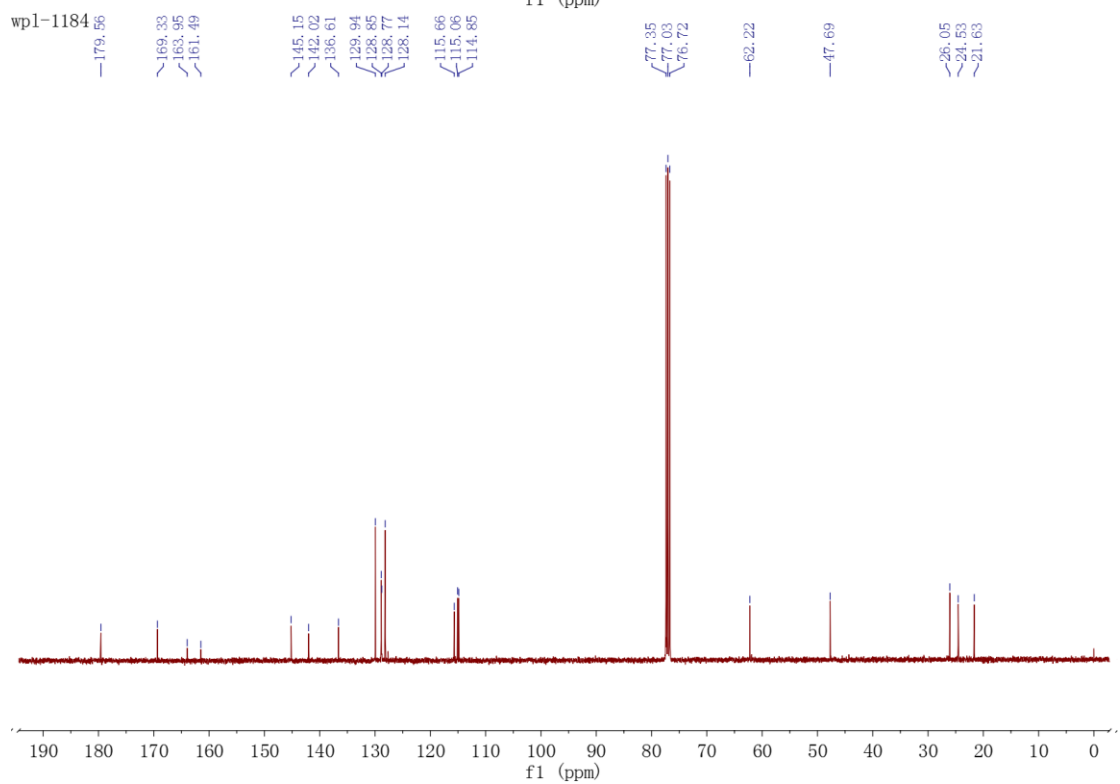
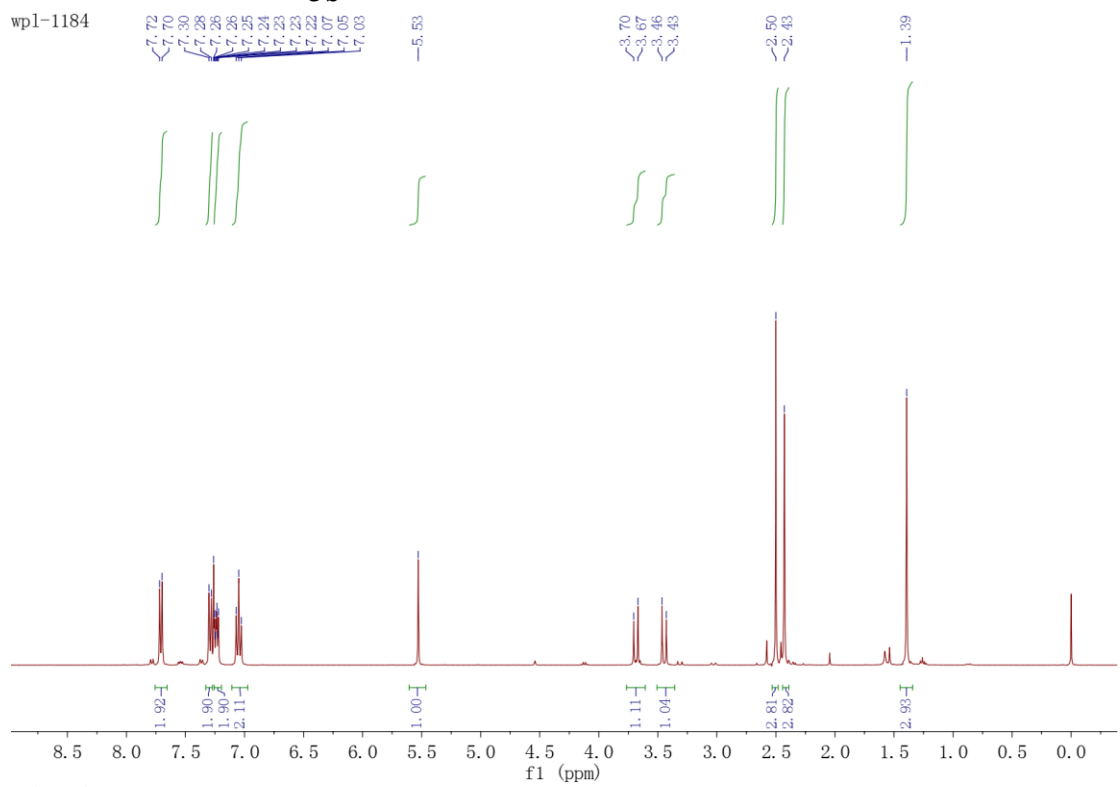
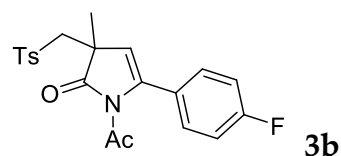
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
312.1632	312.1633	-0.1	-0.3	4.5	47.5	n/a	n/a	C16 H26 N O3 S

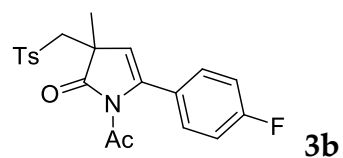
S6. NMR spectra



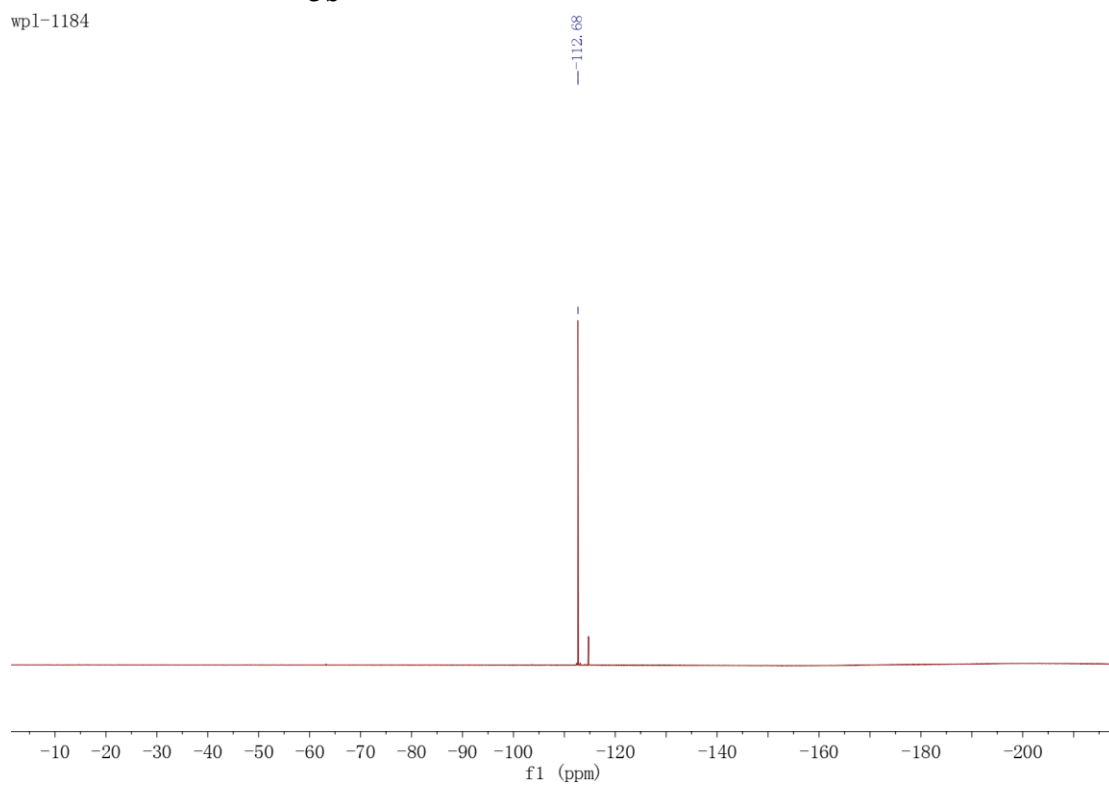
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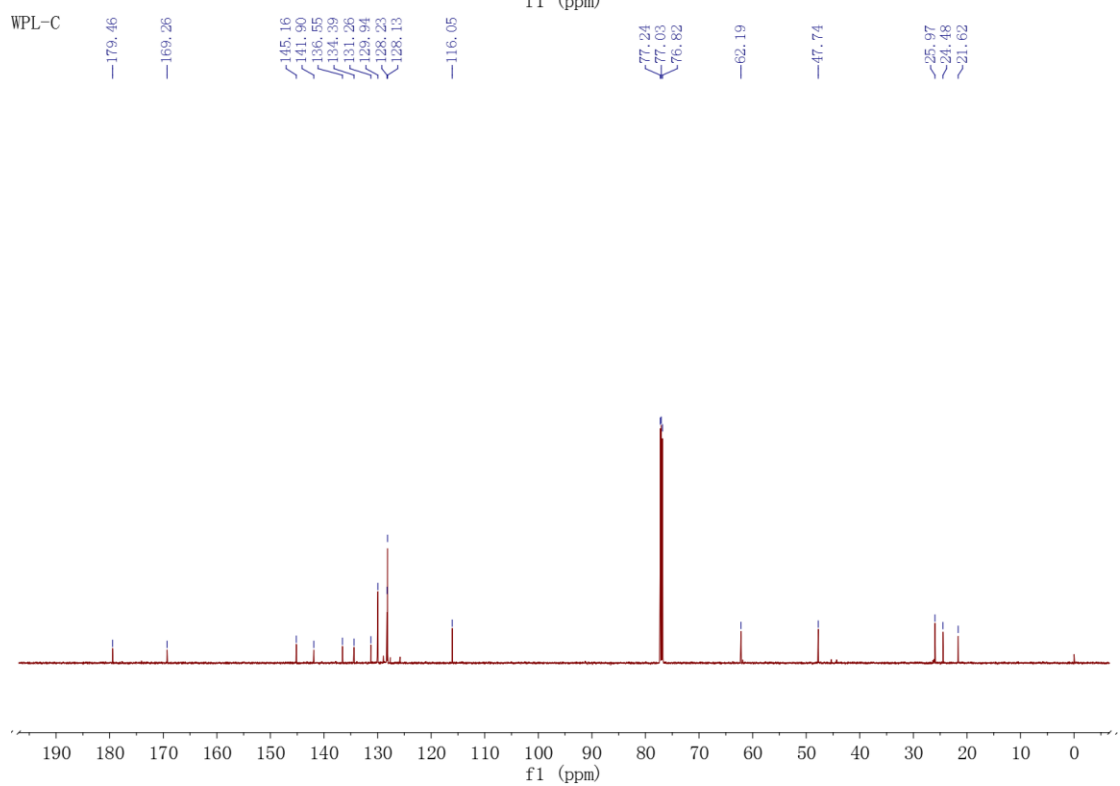
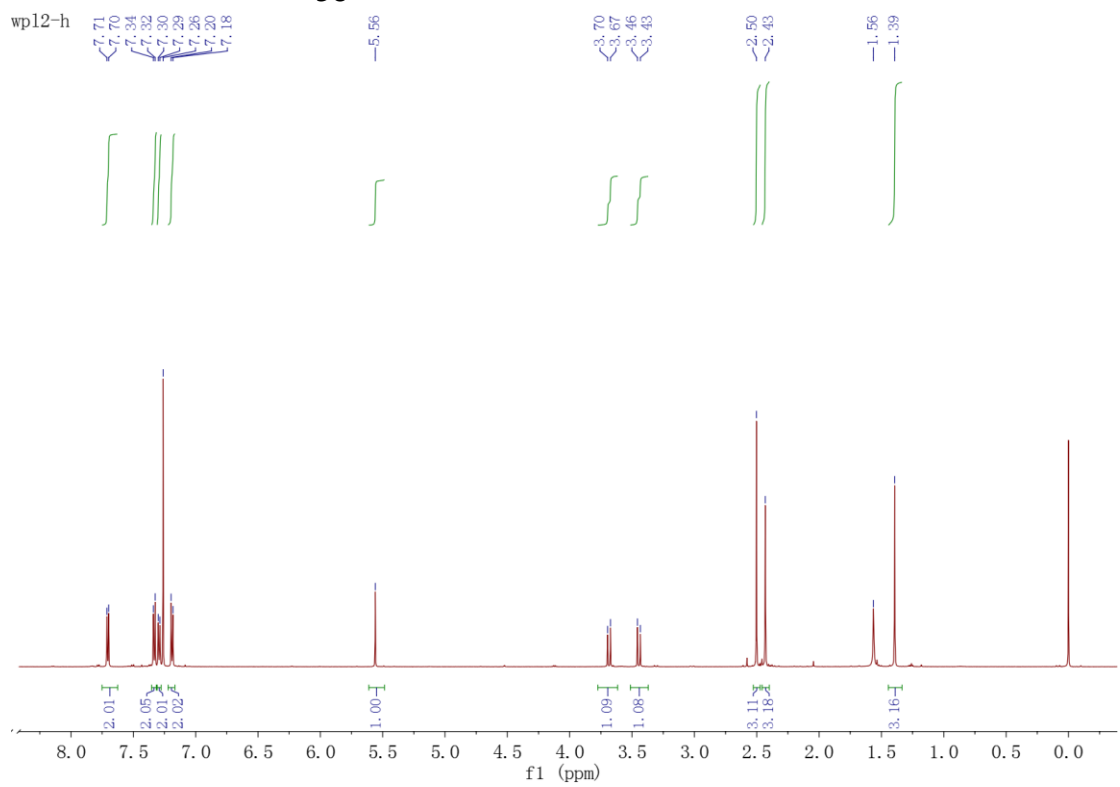
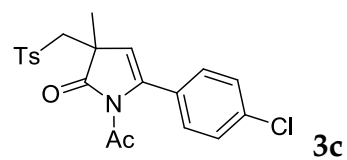


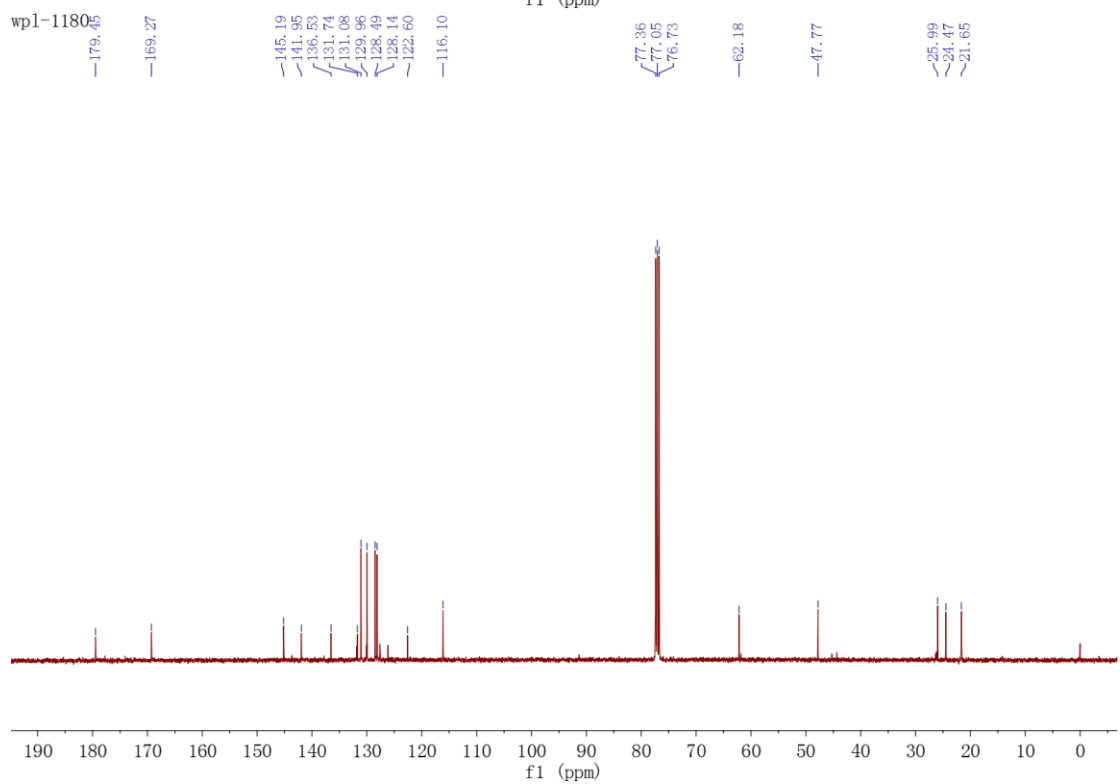
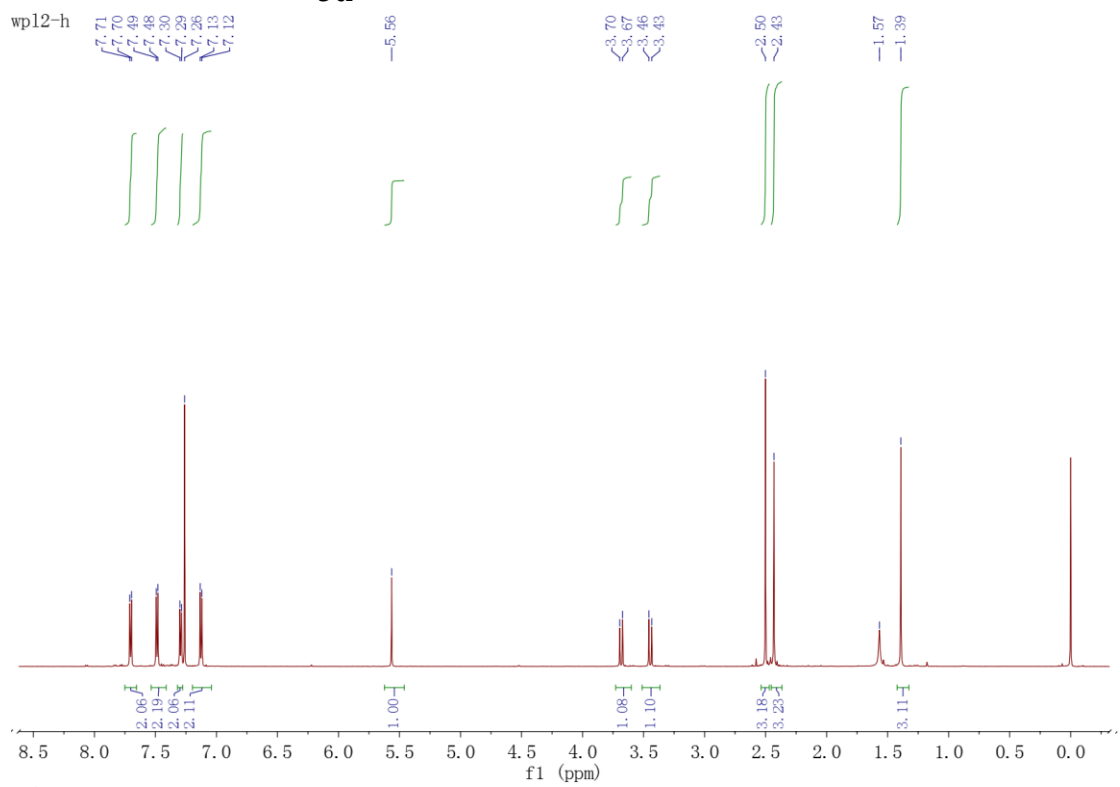
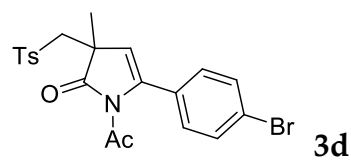


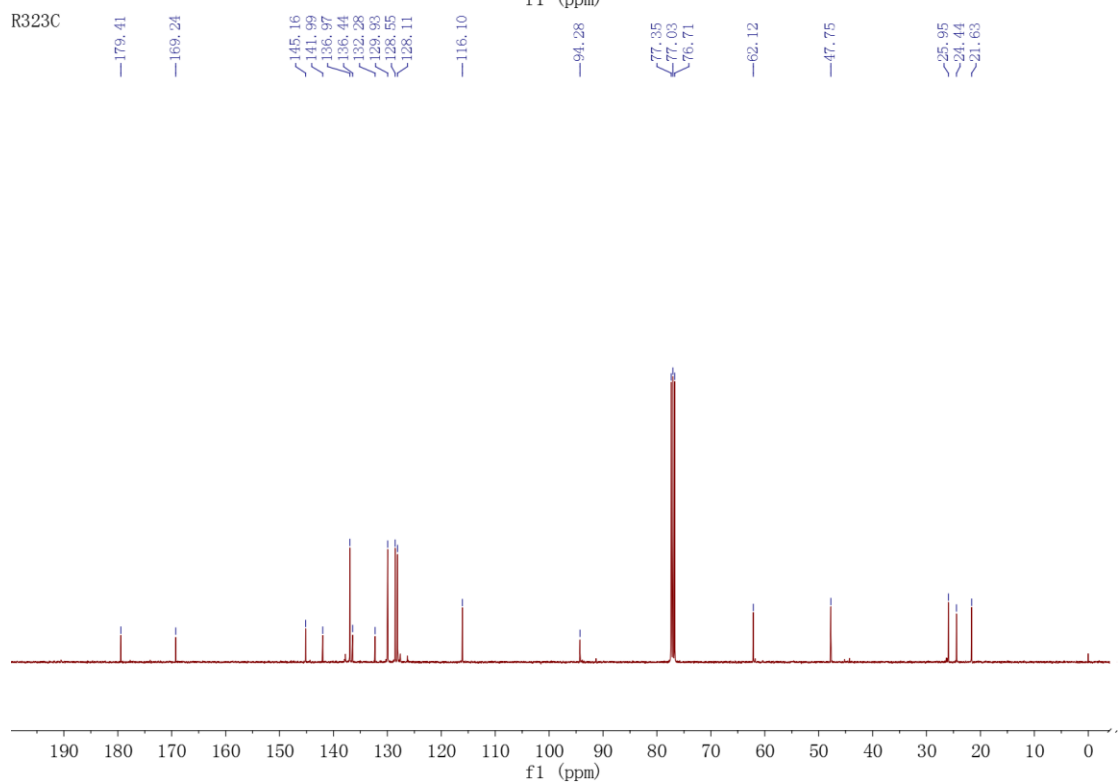
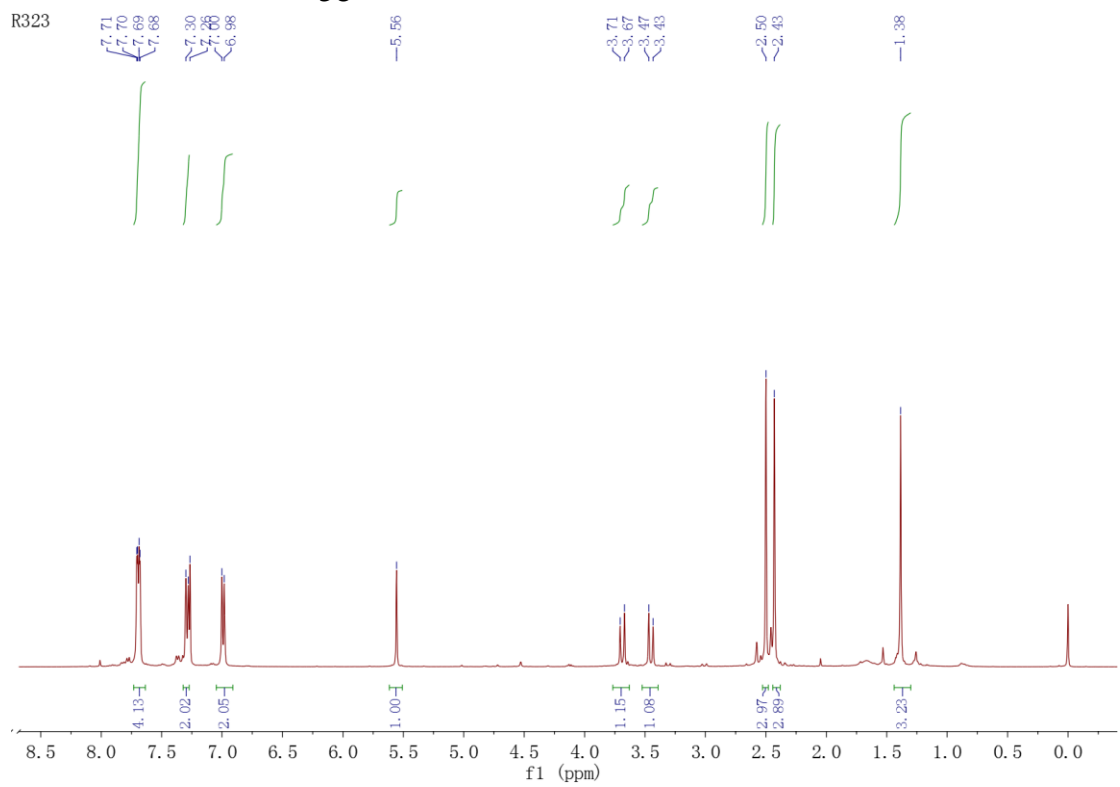
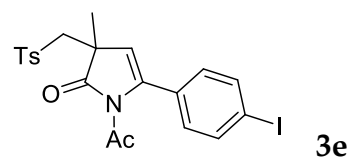


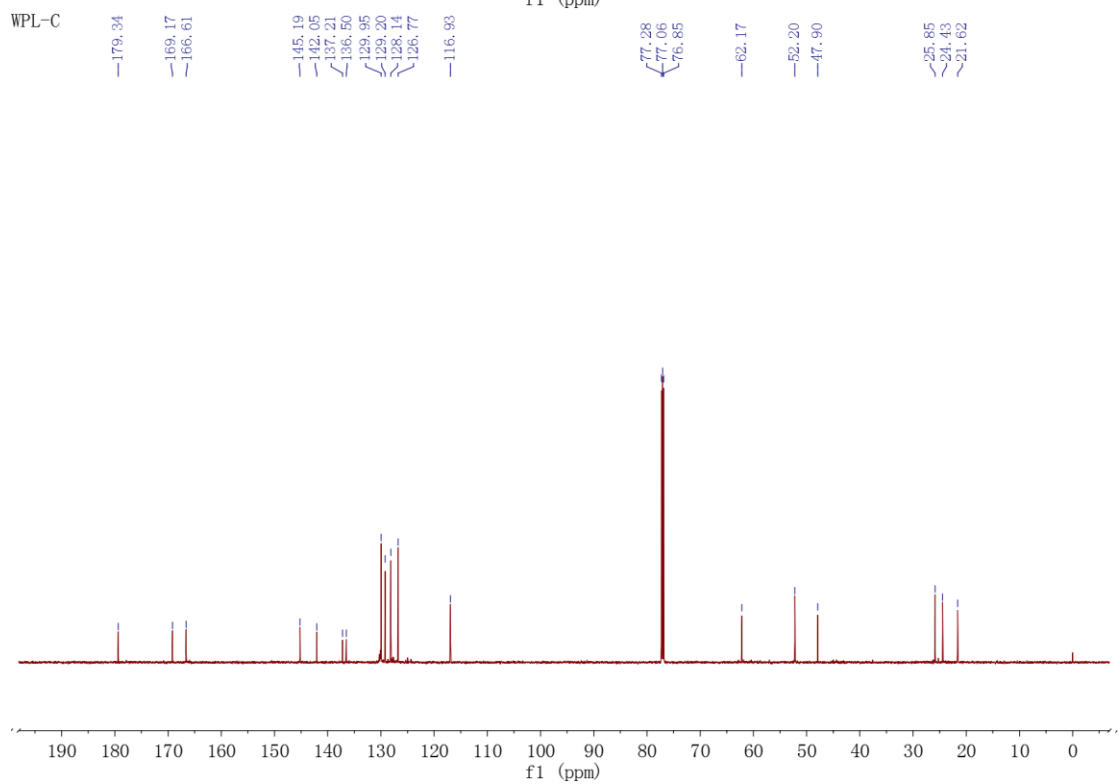
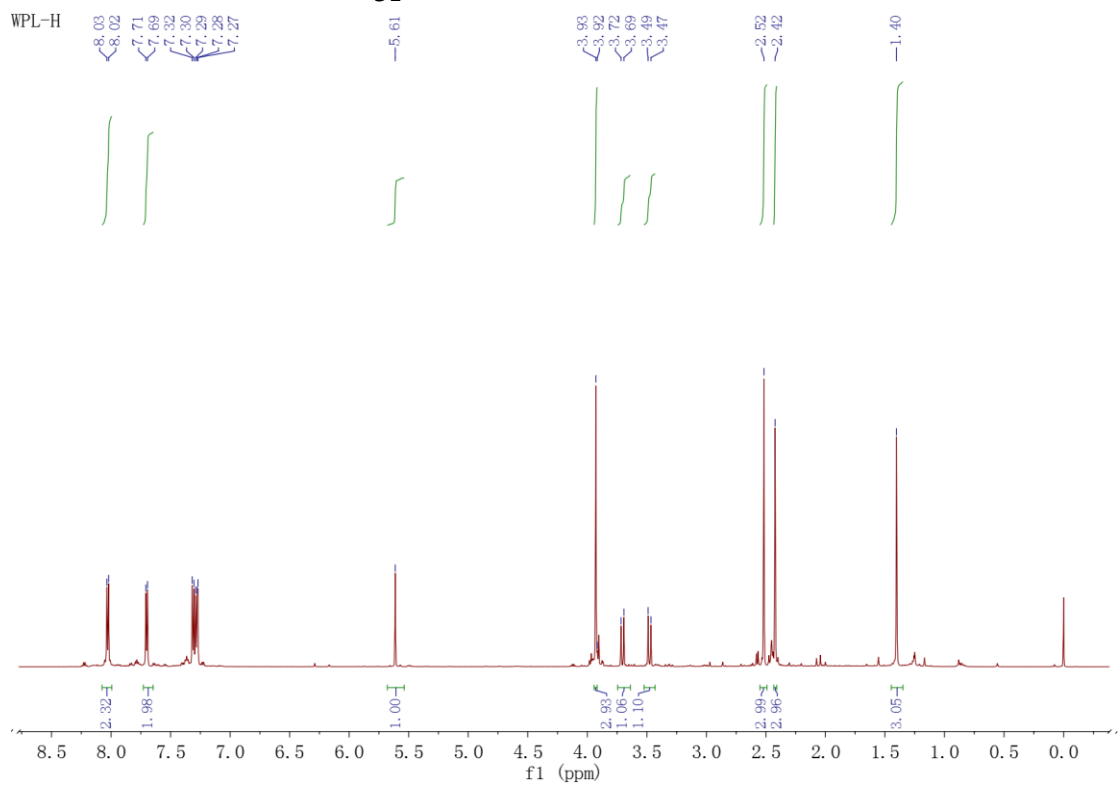
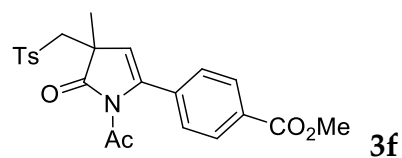
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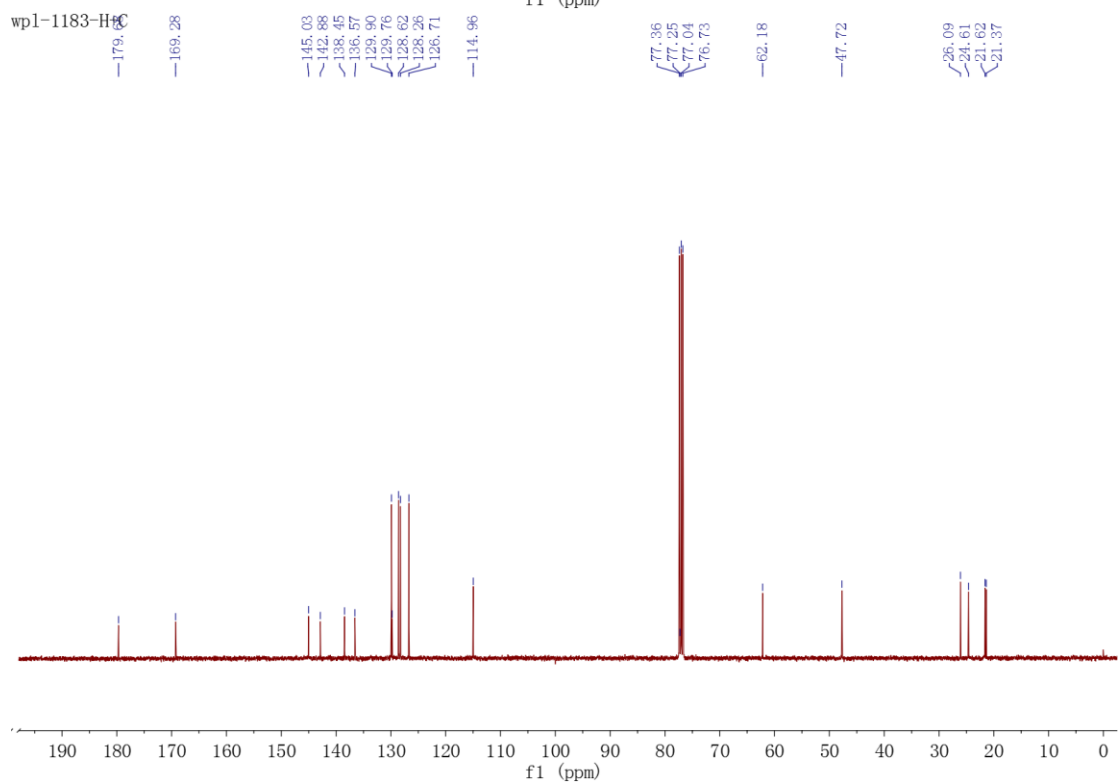
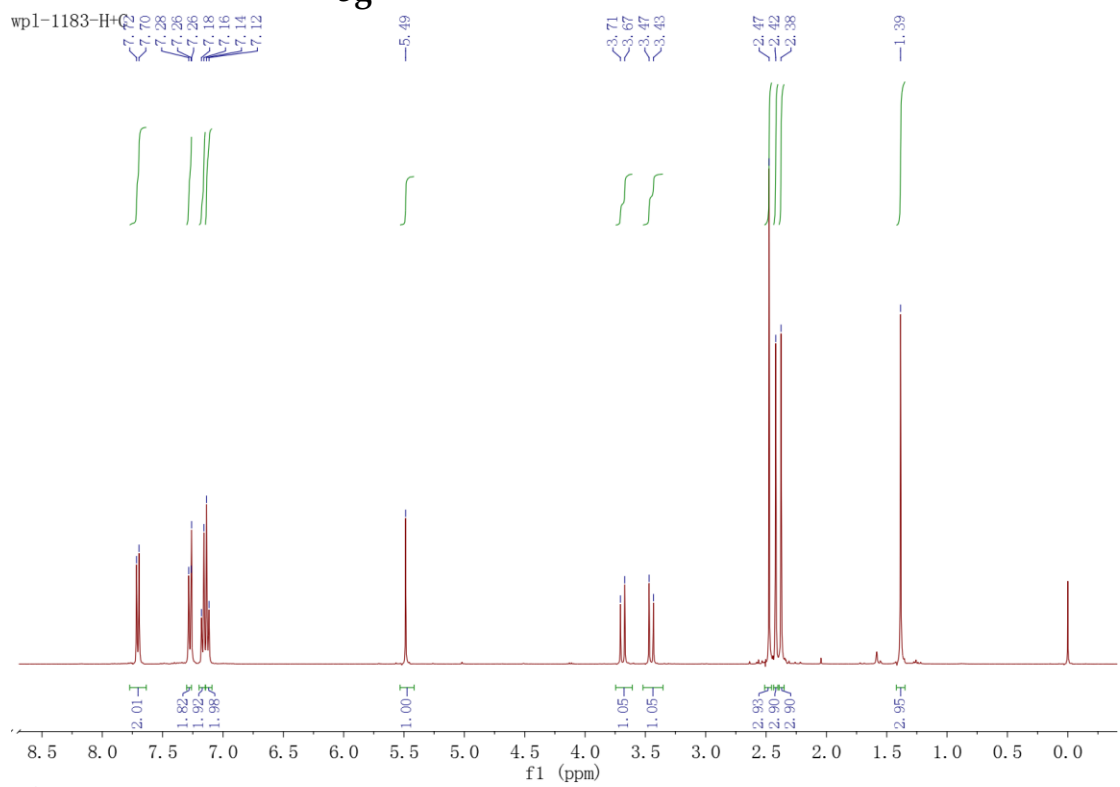
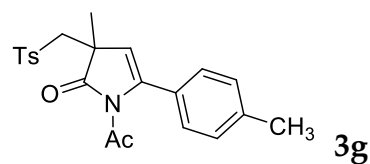


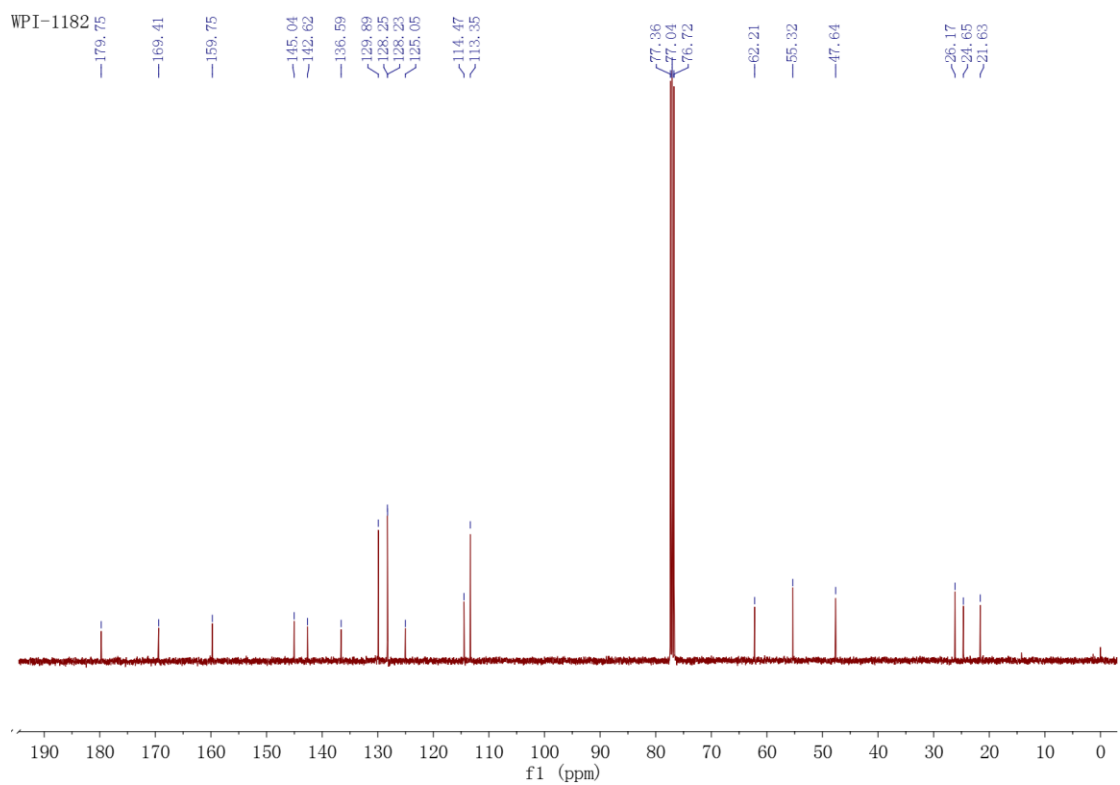
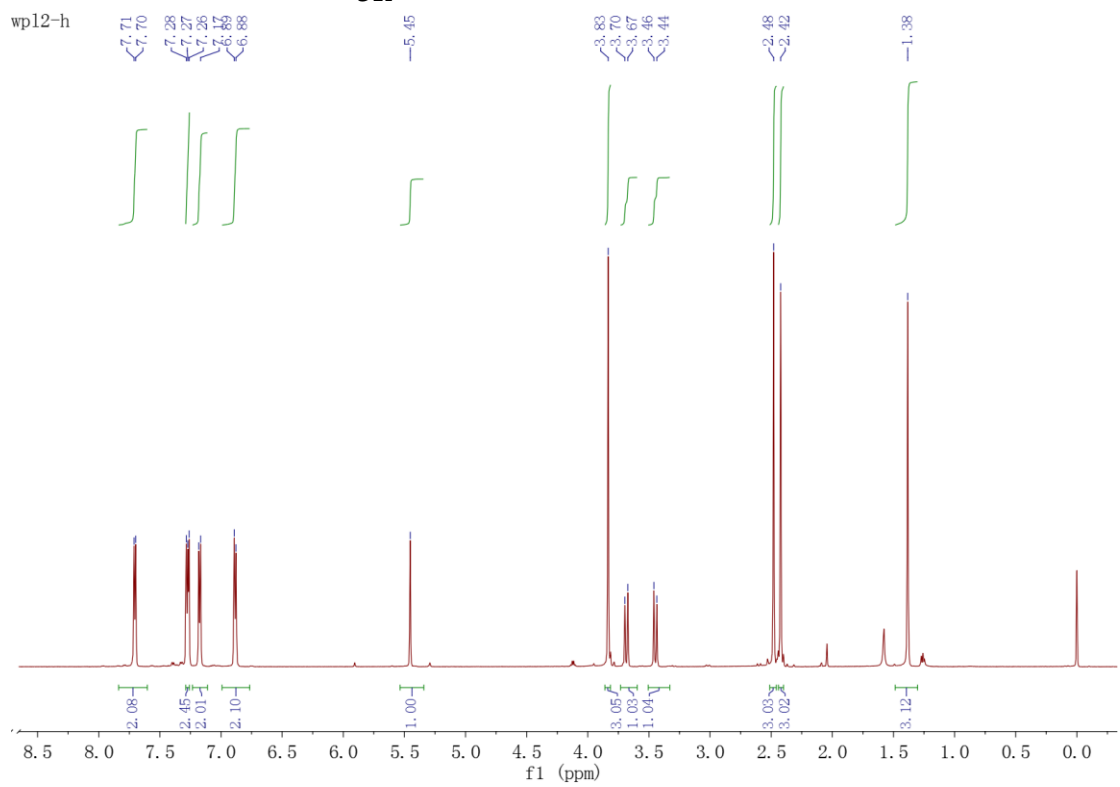
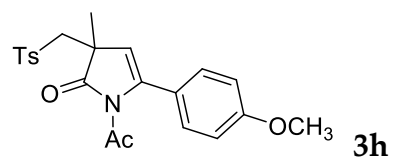


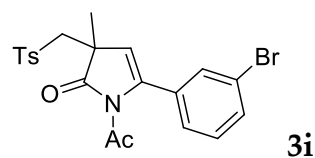




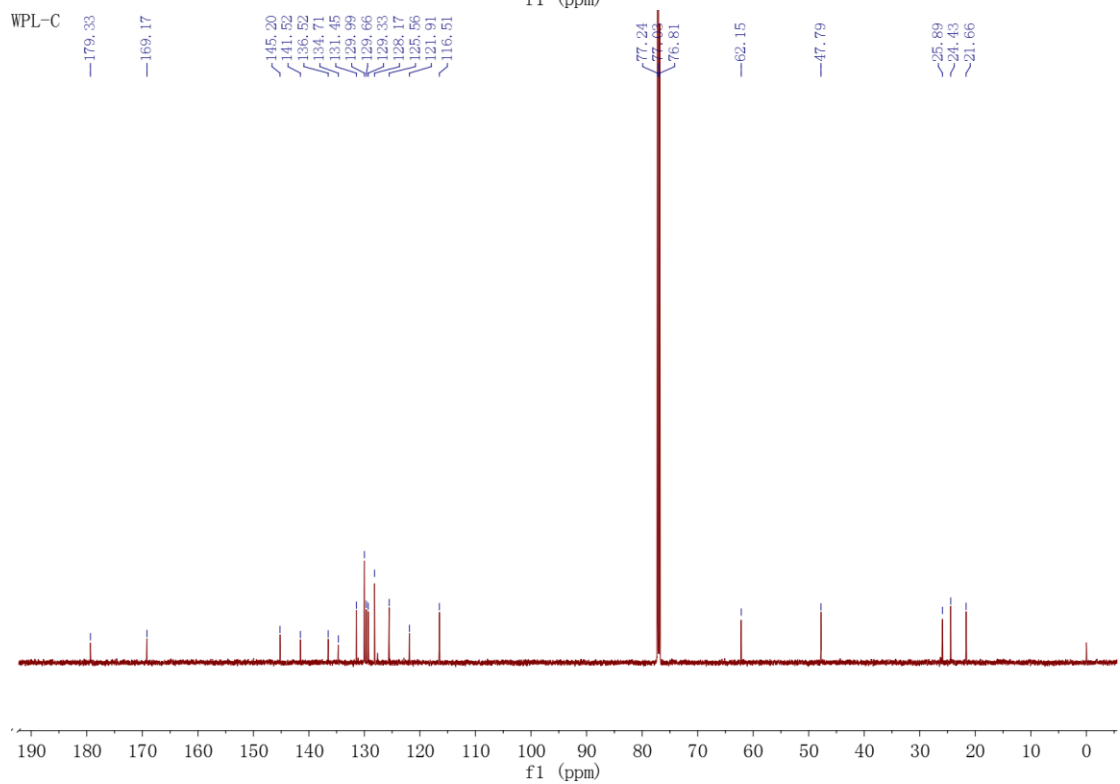
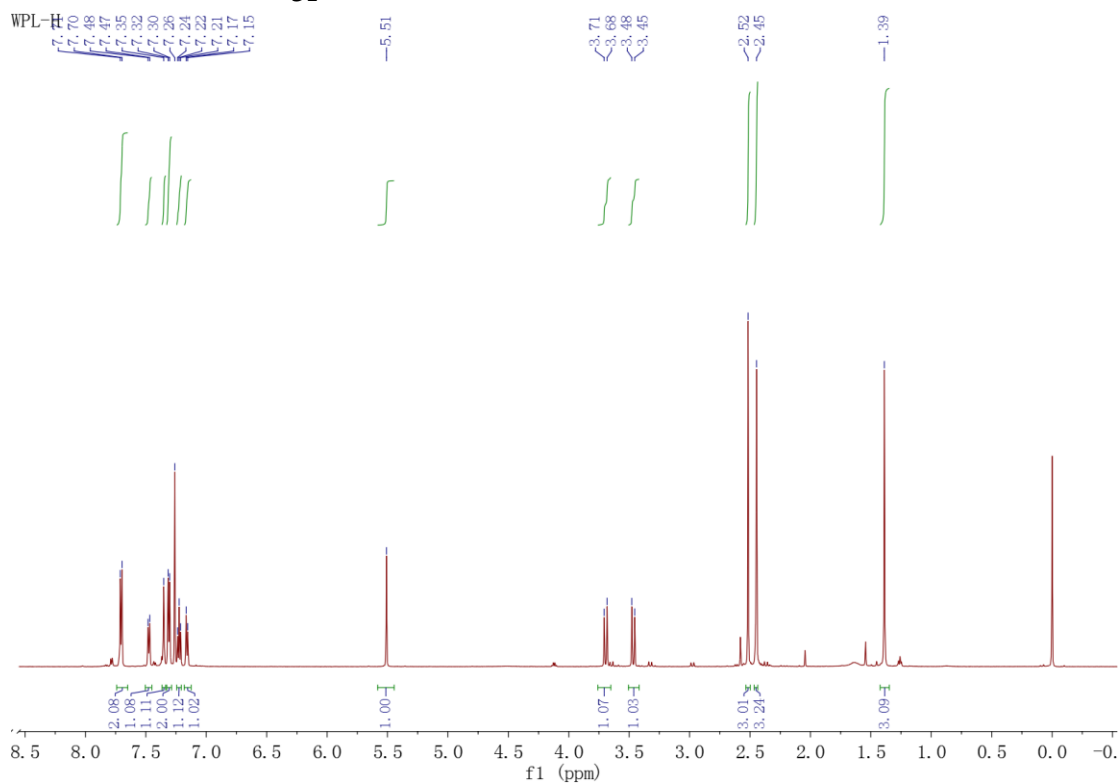


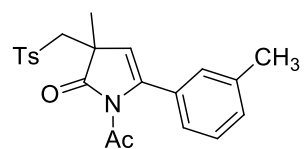




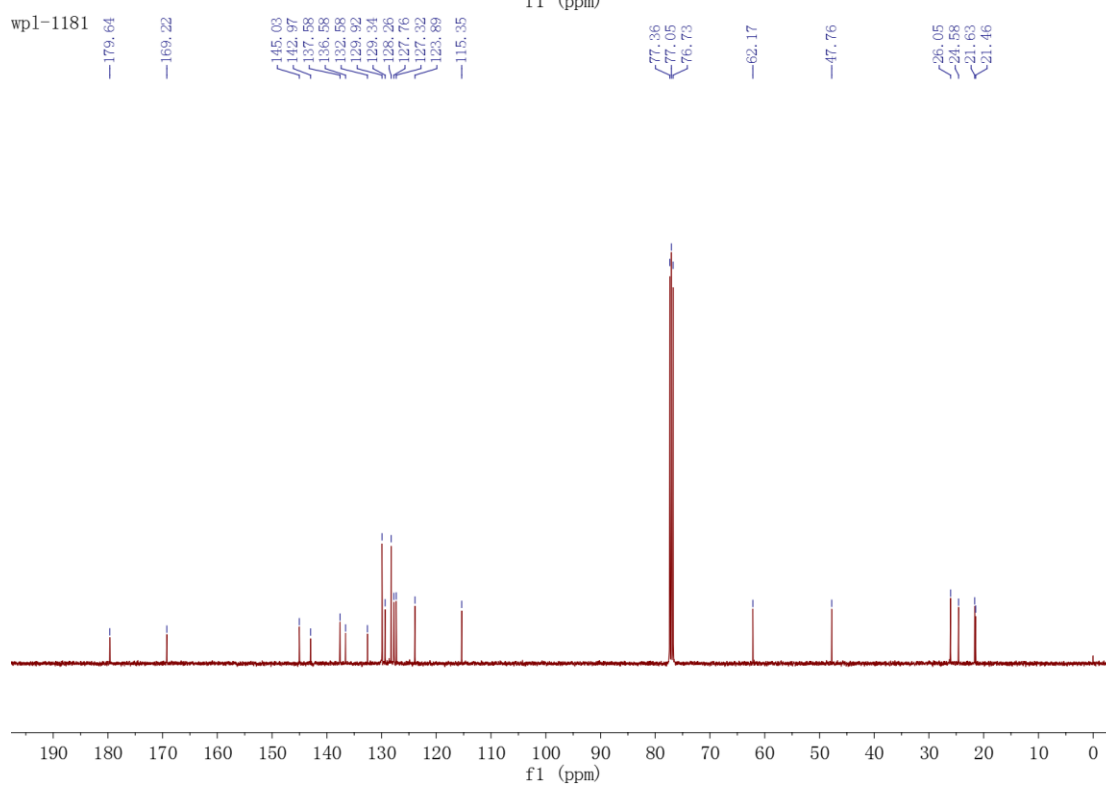
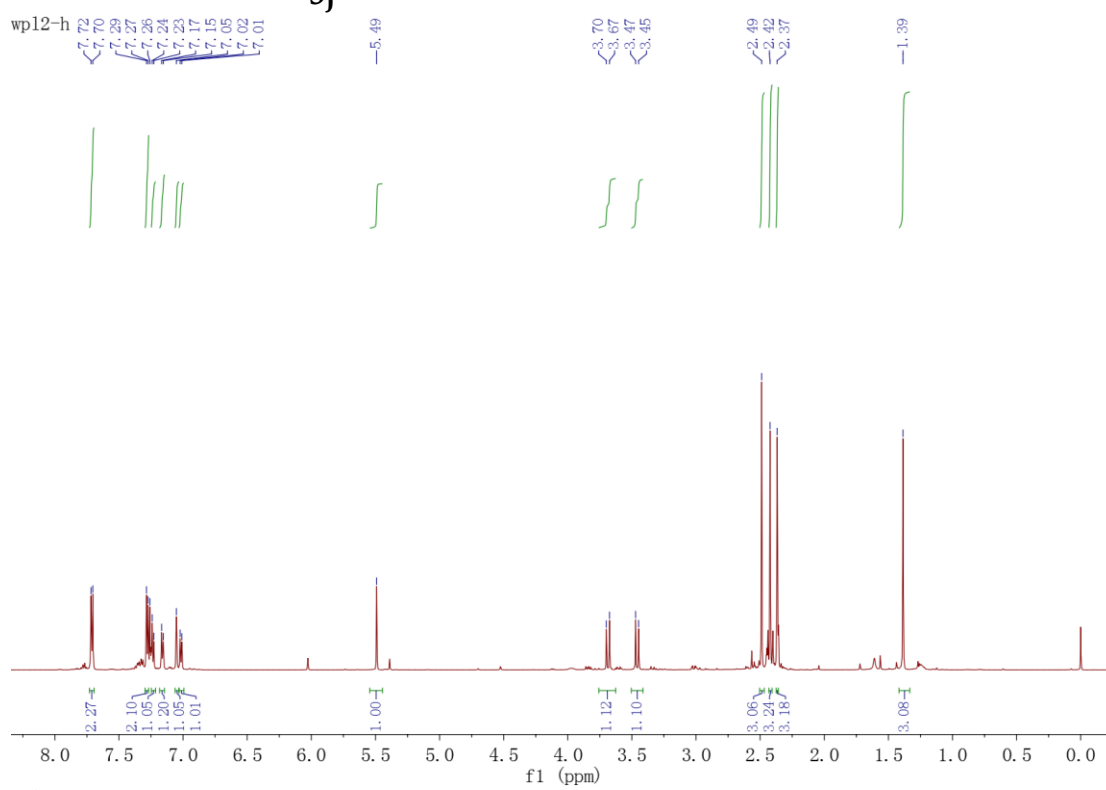


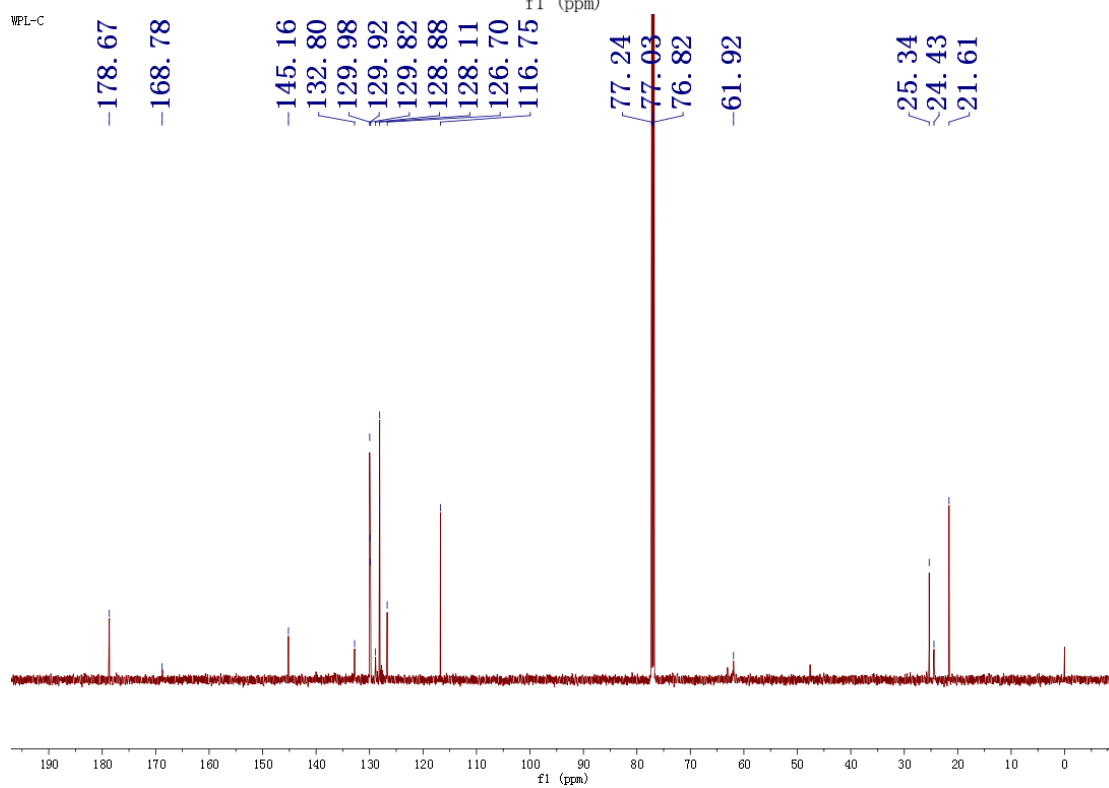
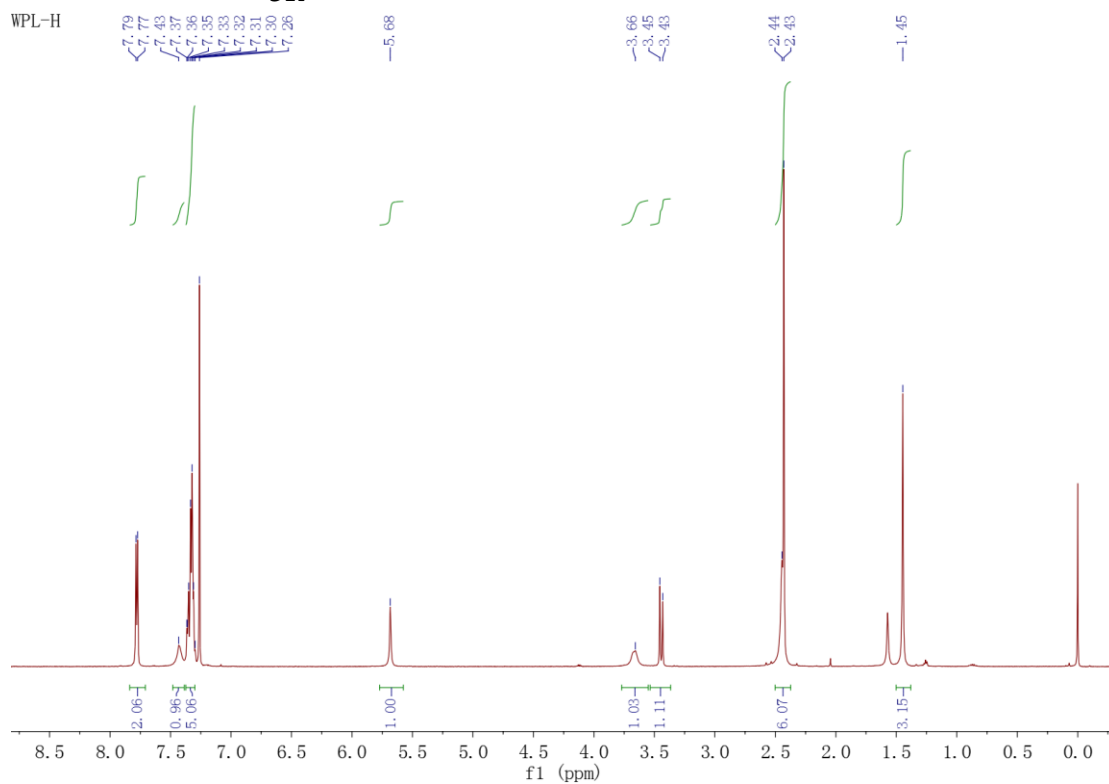
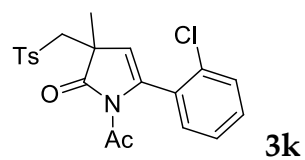
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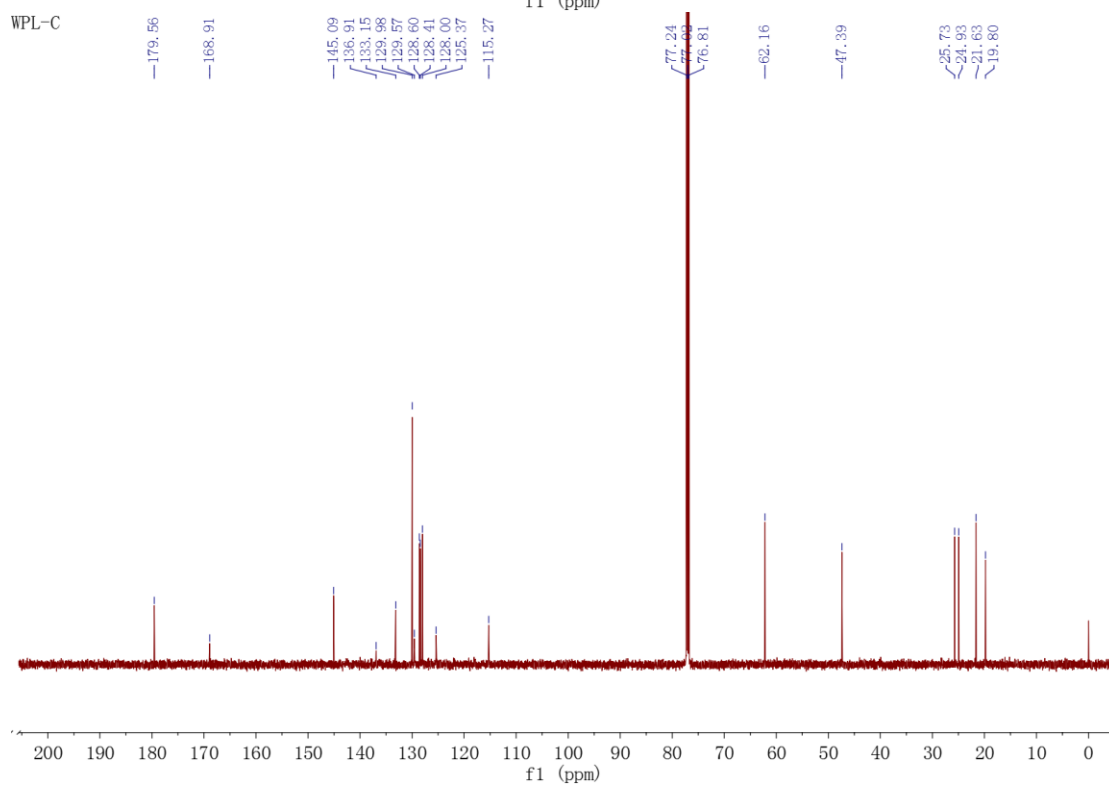
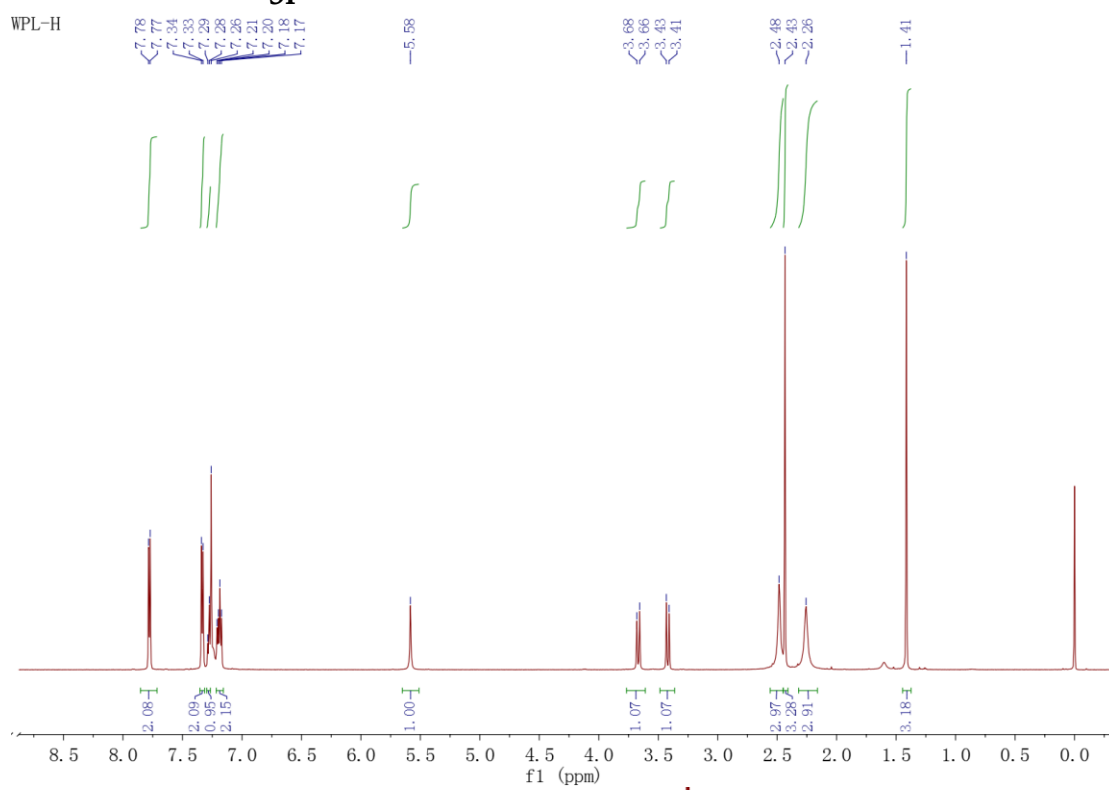
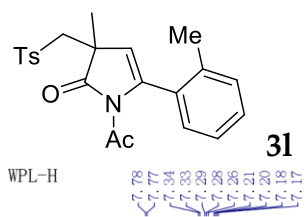


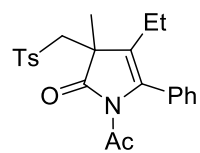


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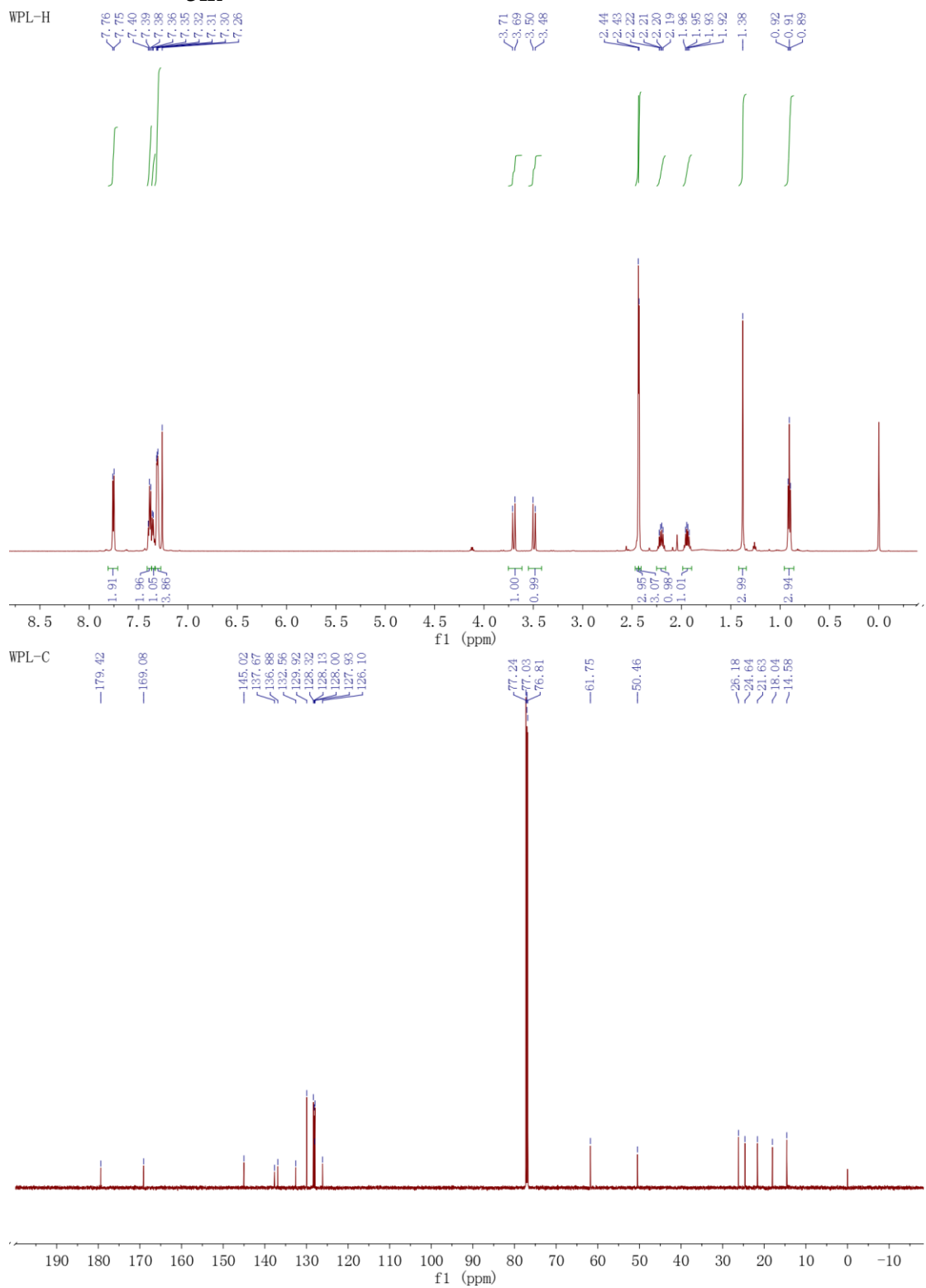


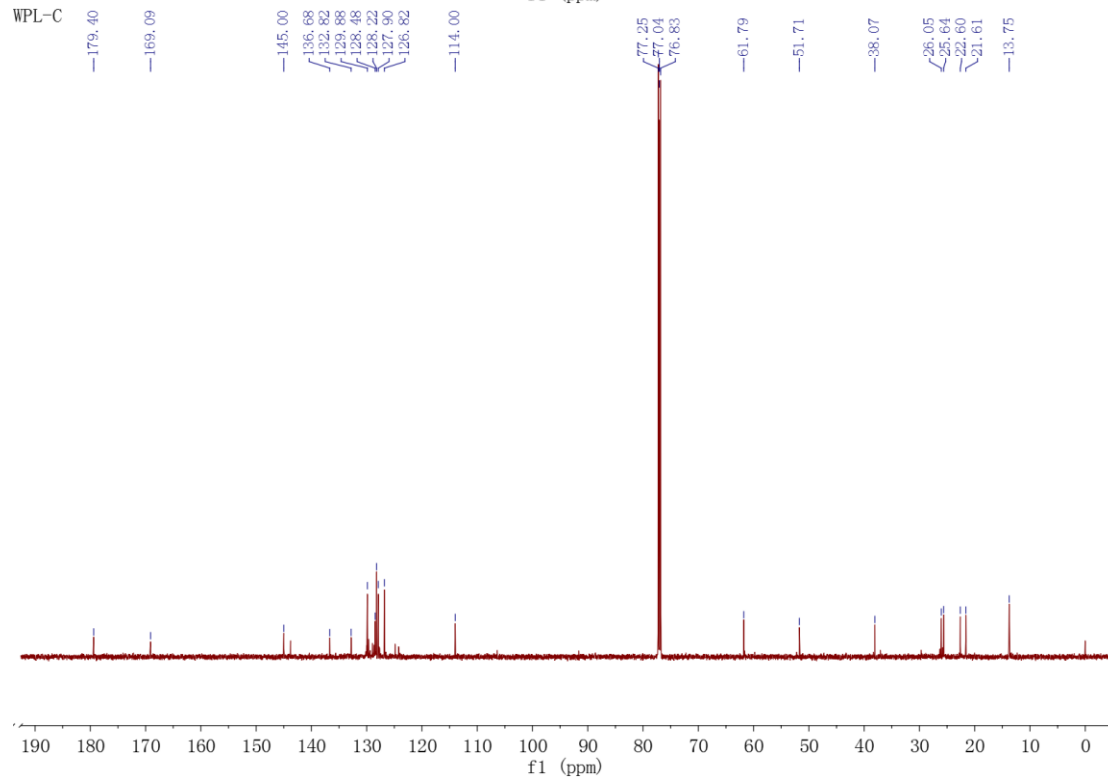
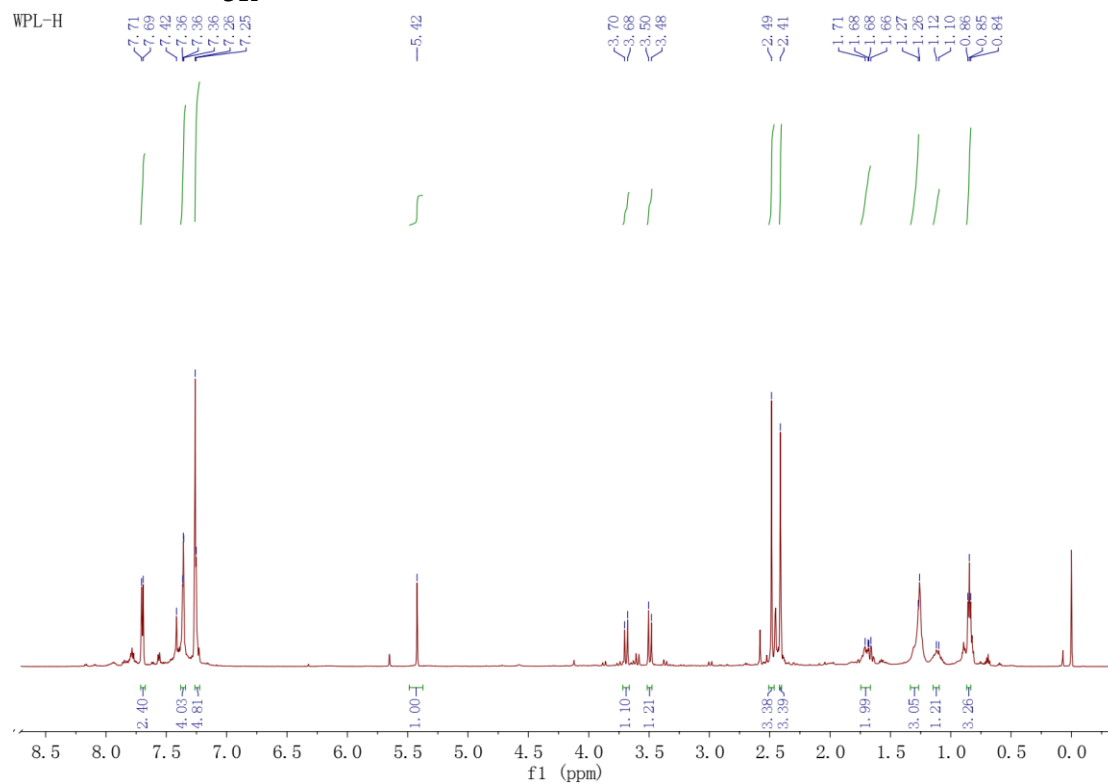
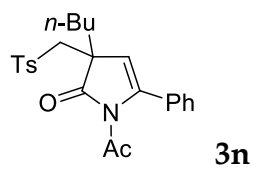


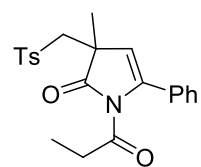




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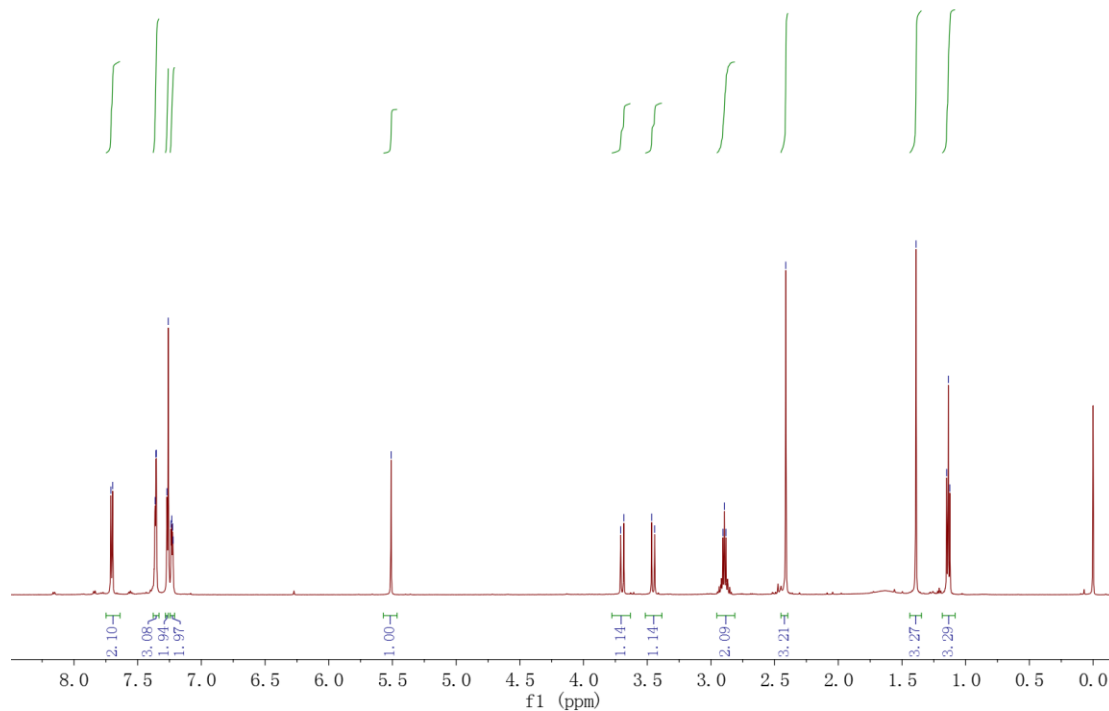




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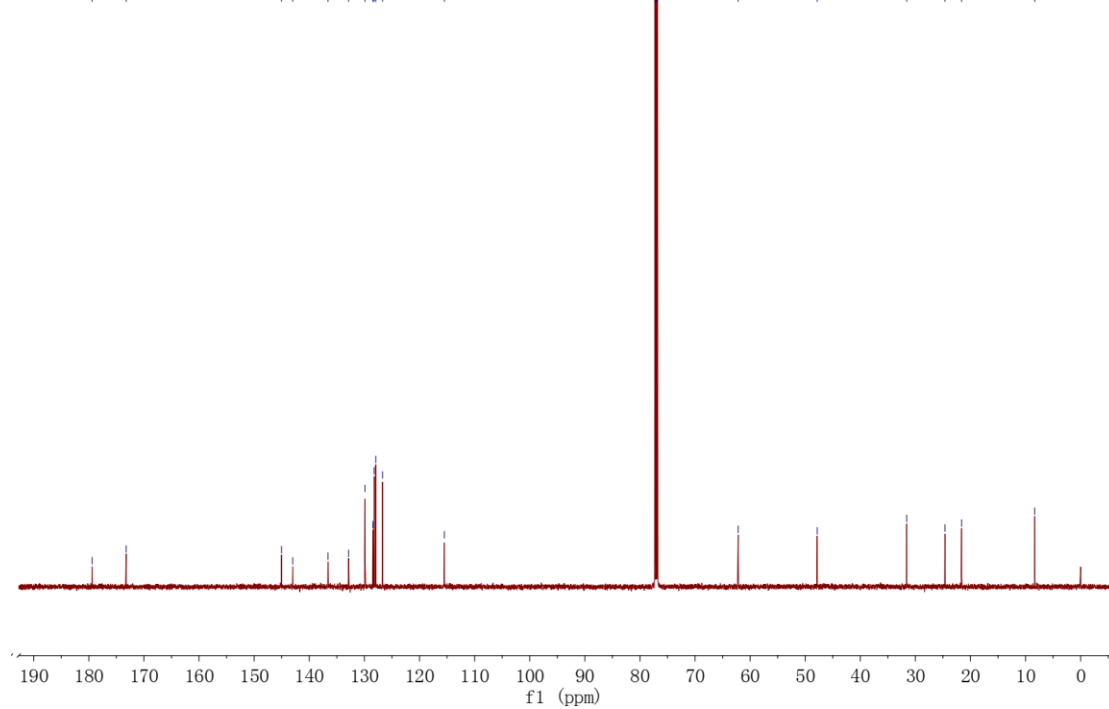
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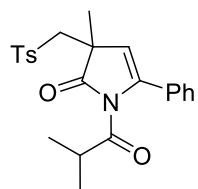
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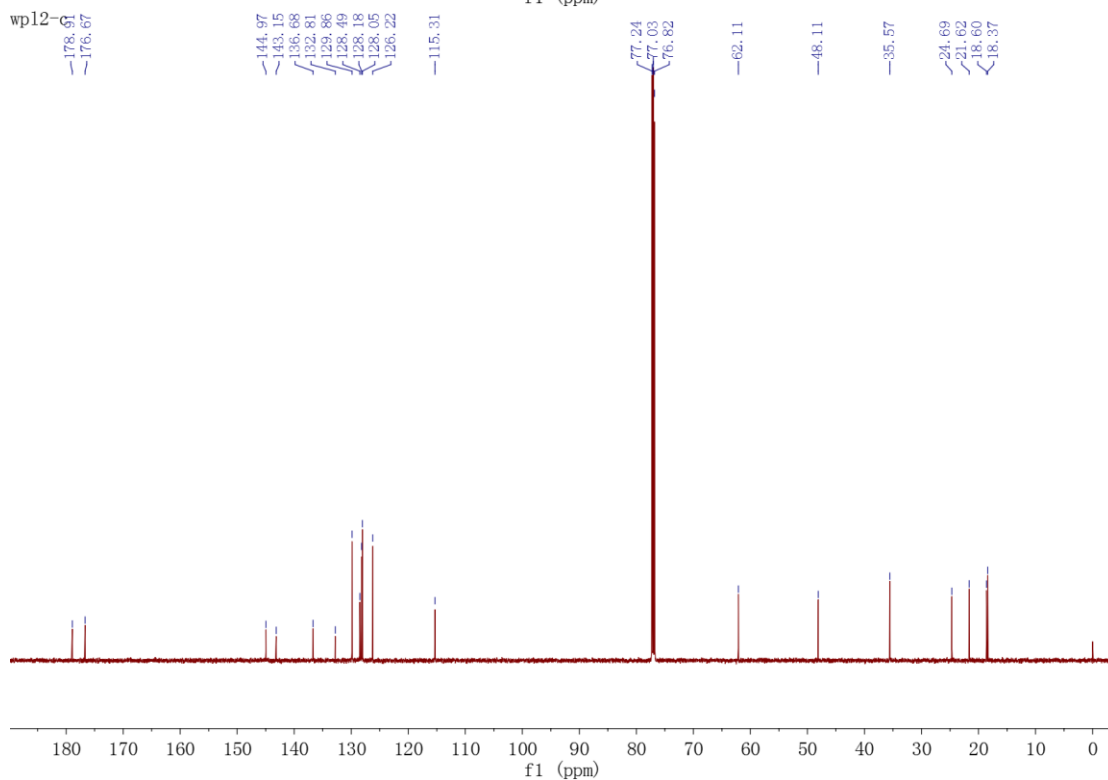
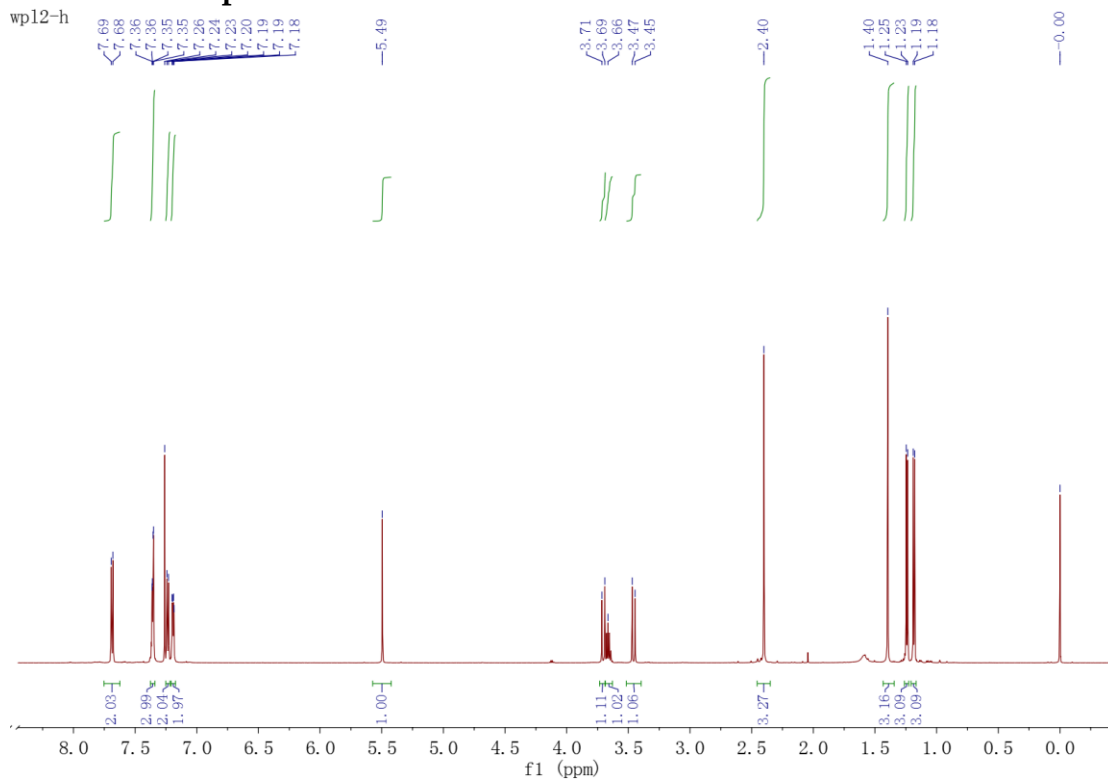
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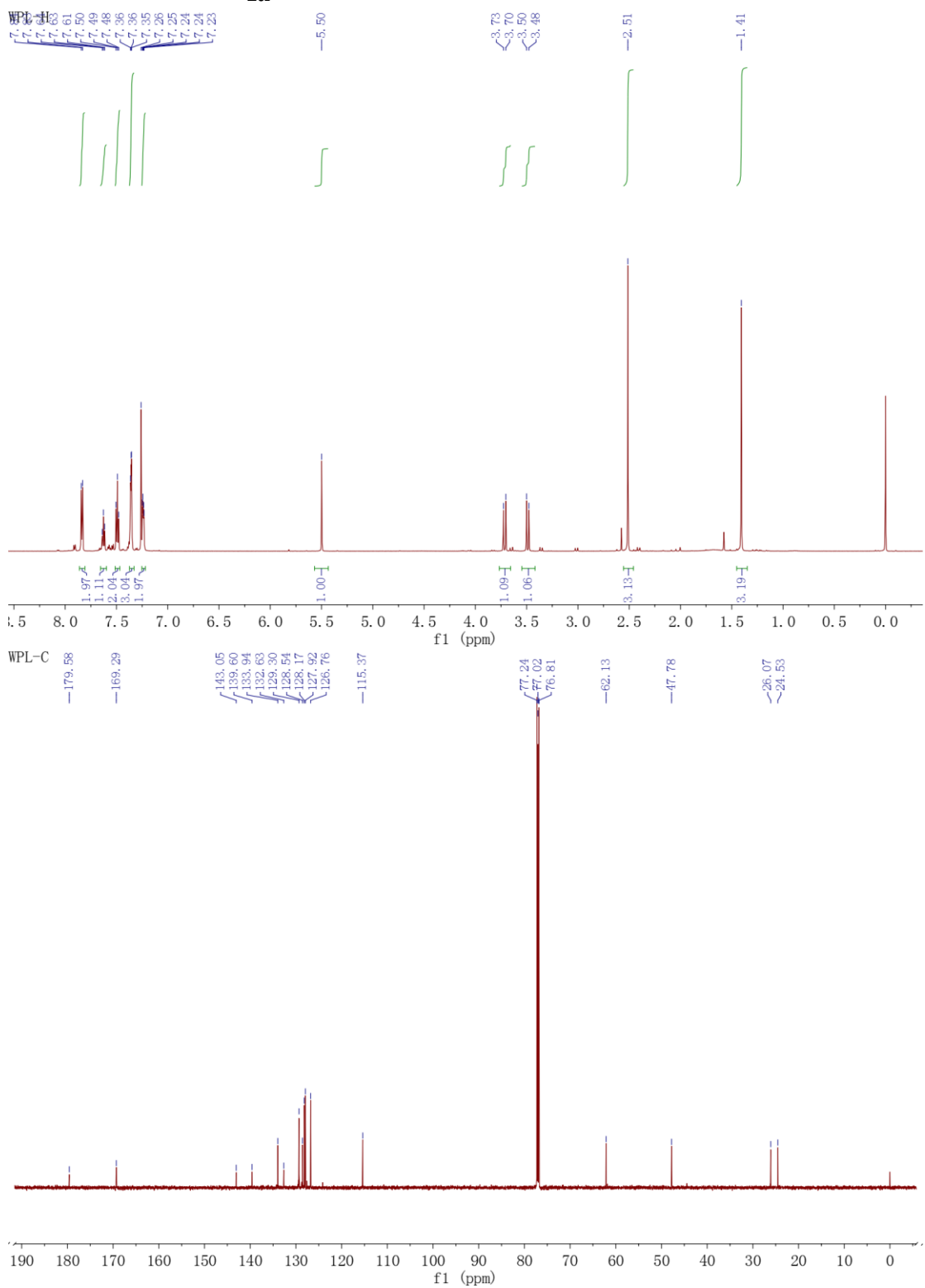
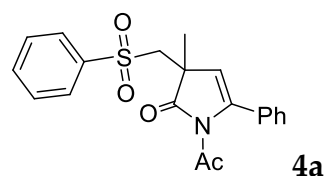
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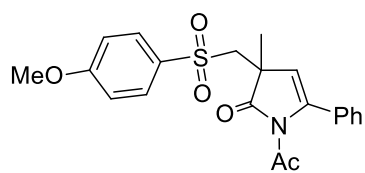




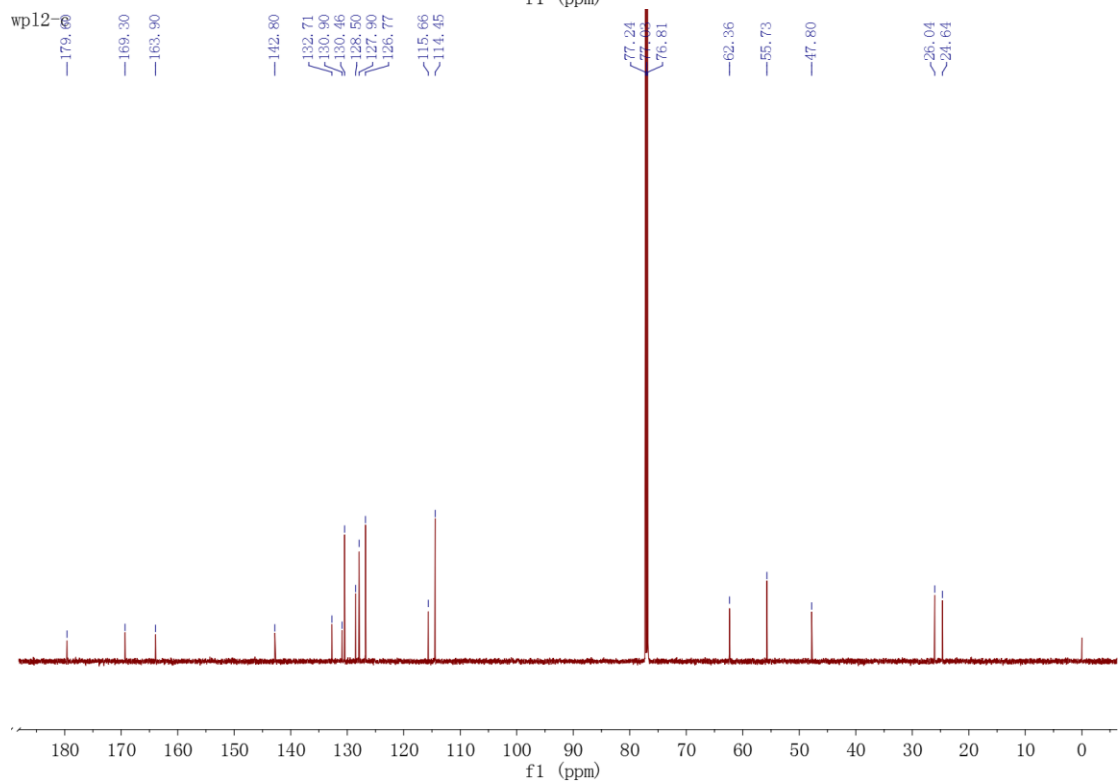
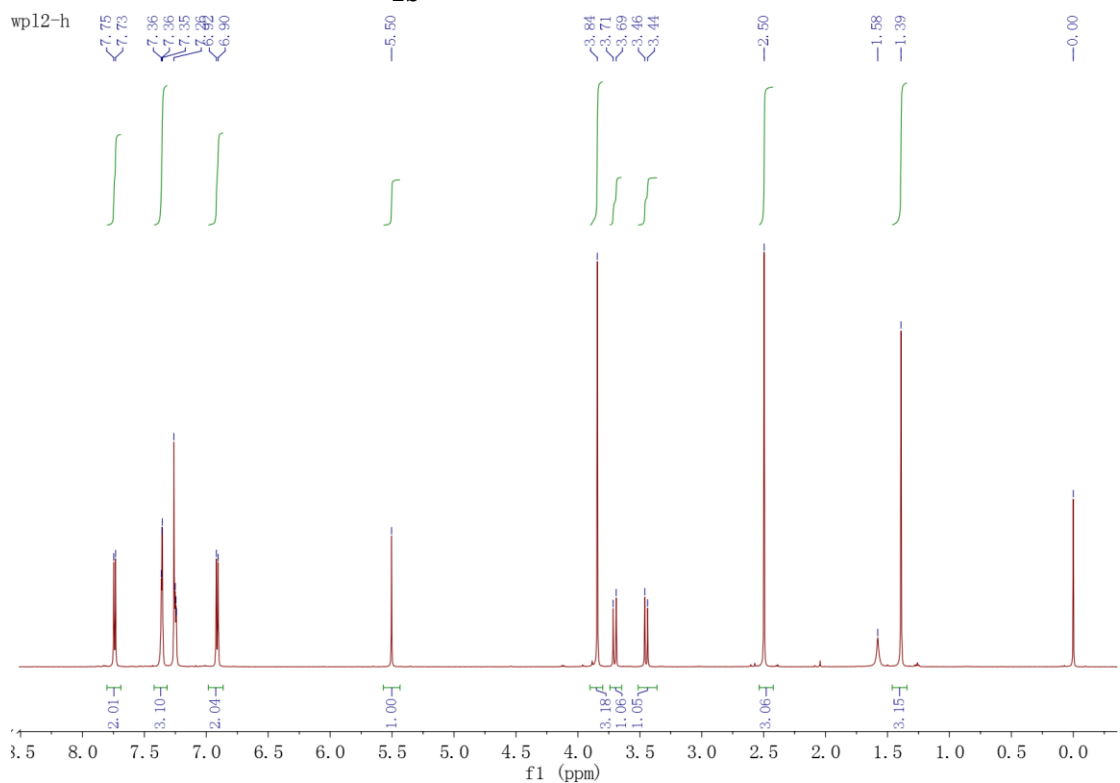
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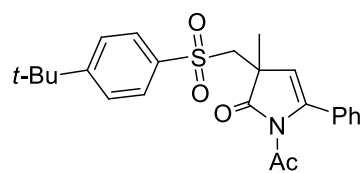




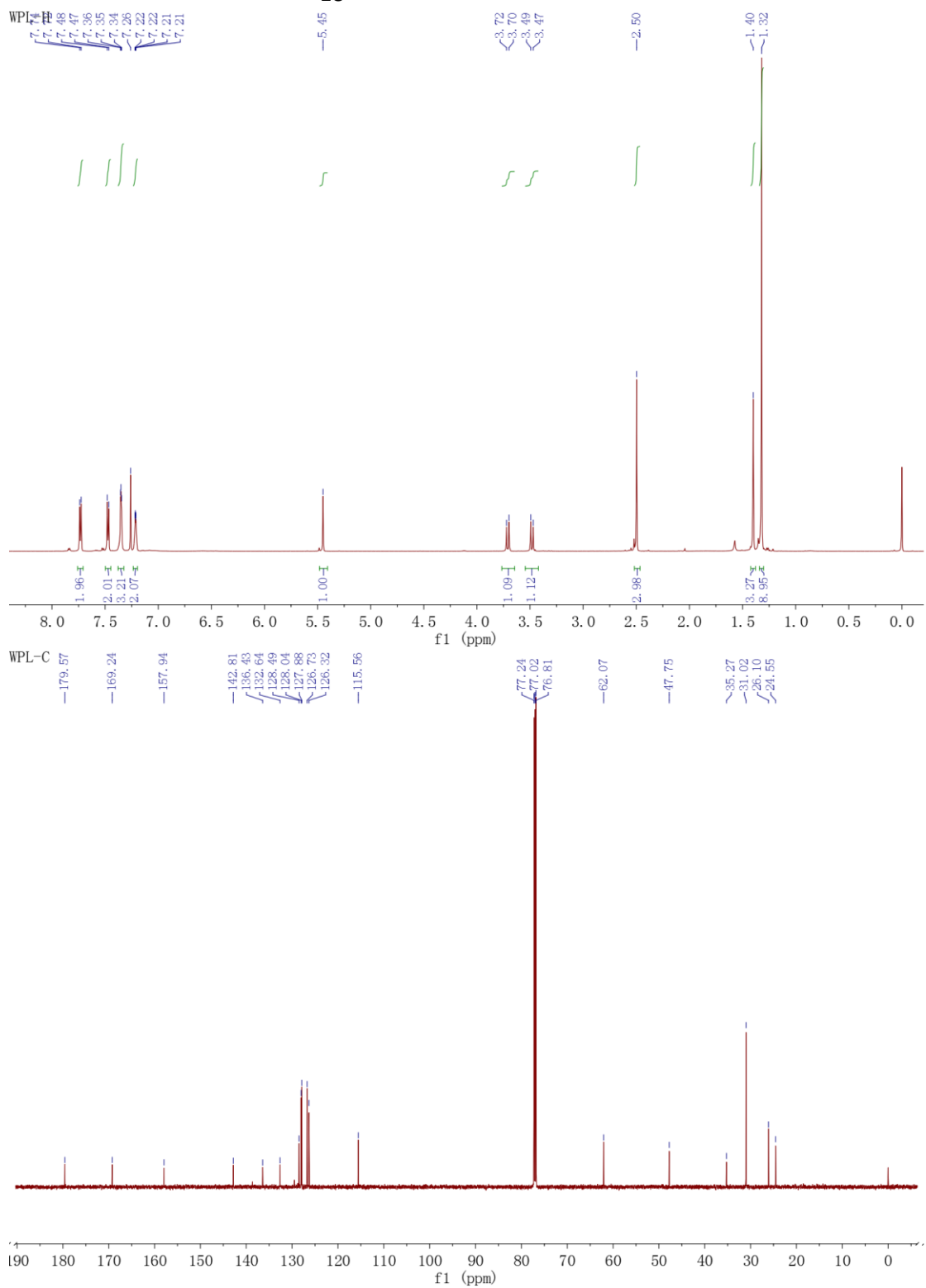


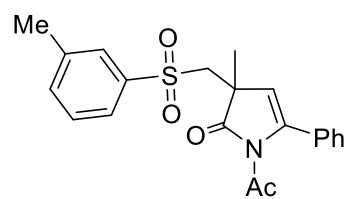
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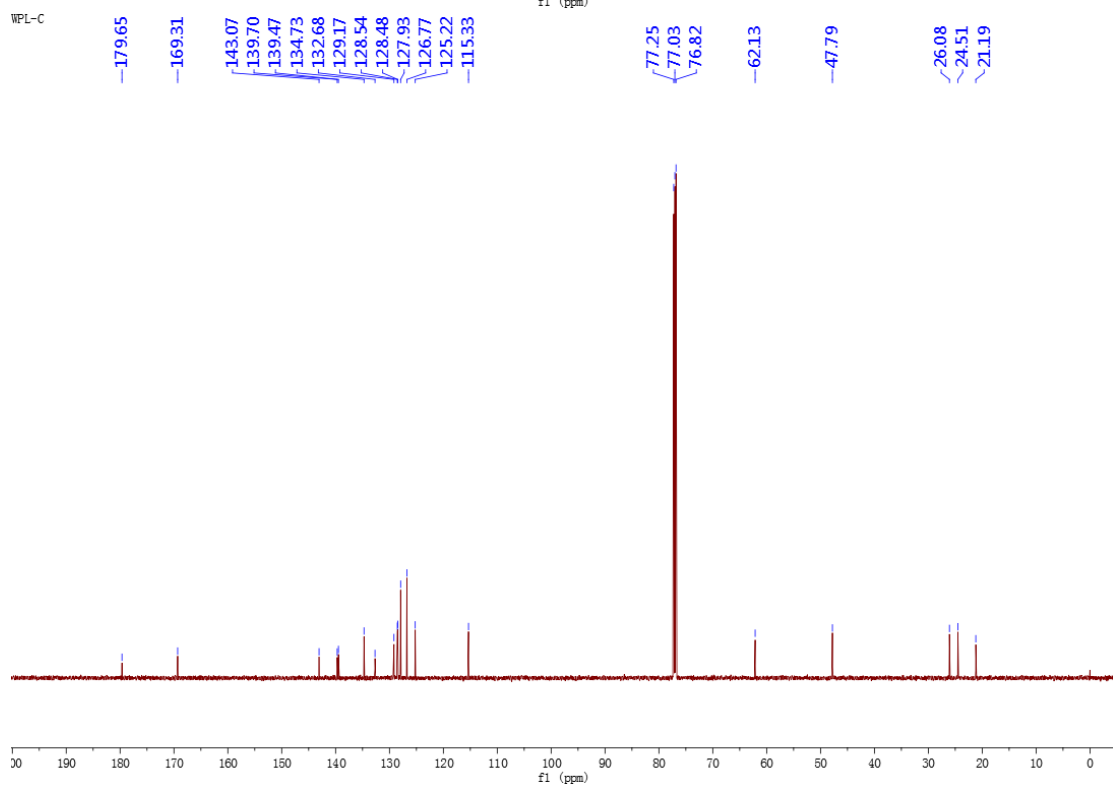
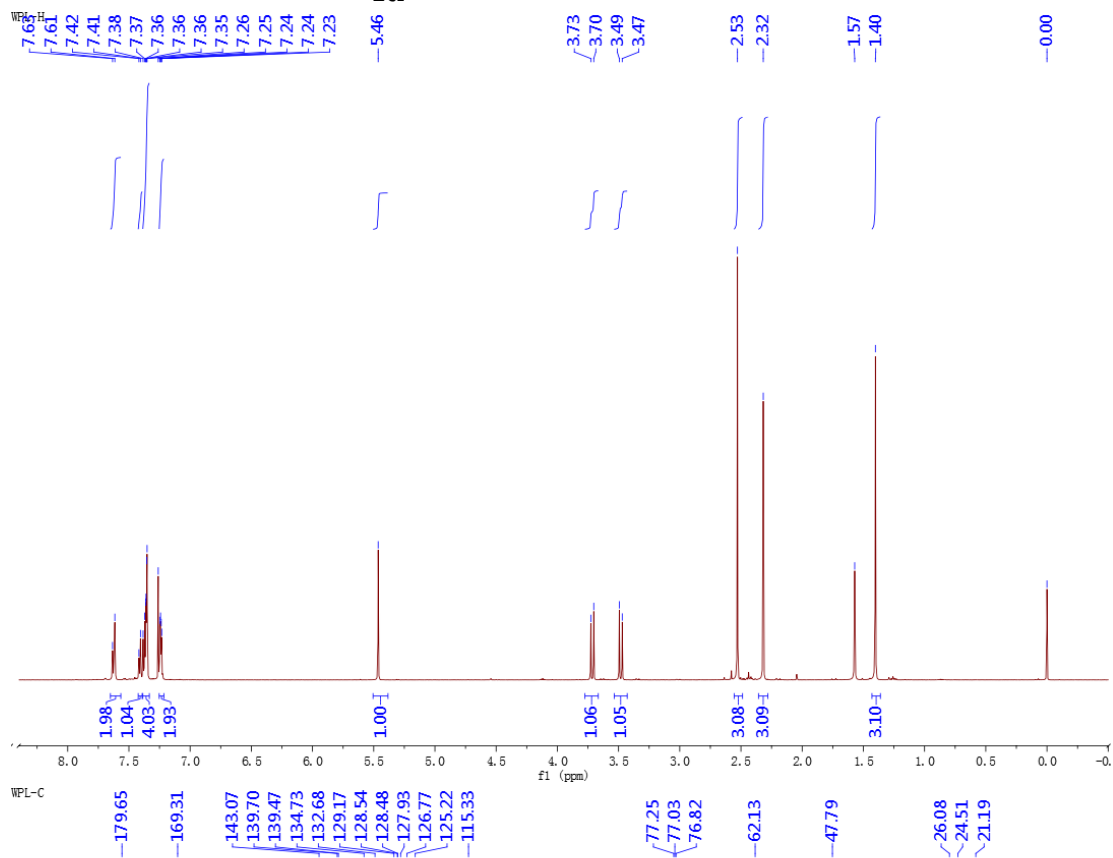


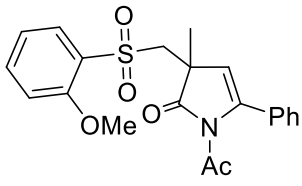
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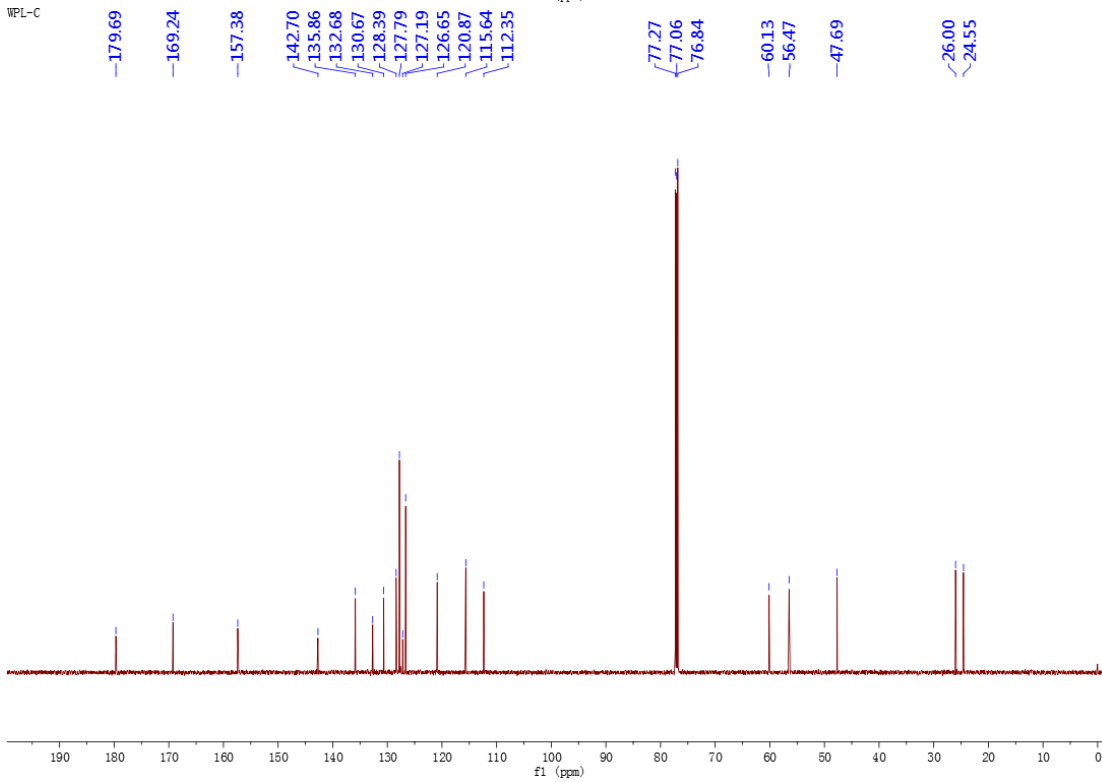
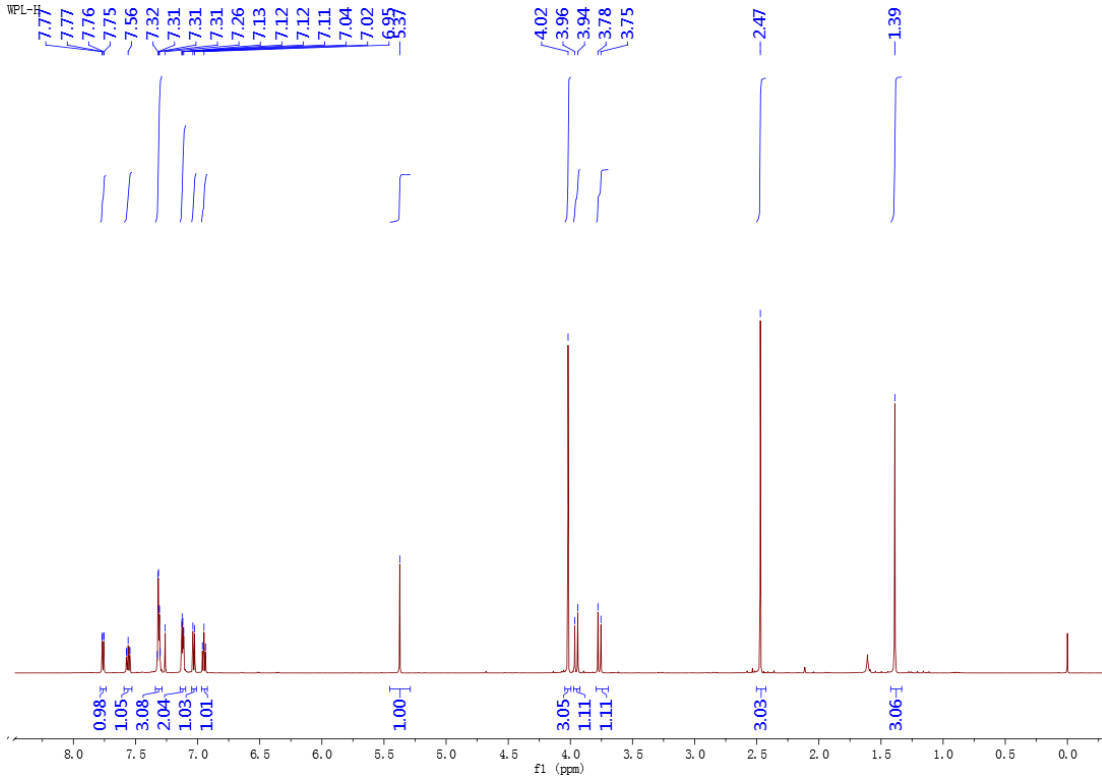


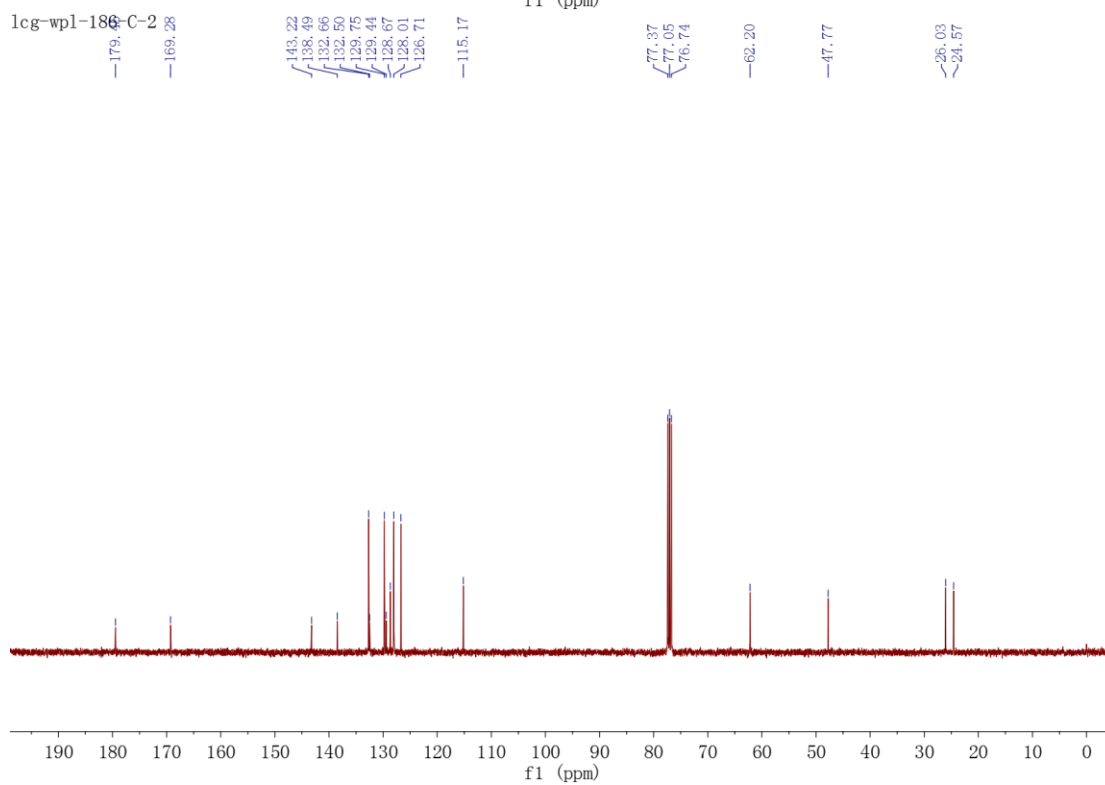
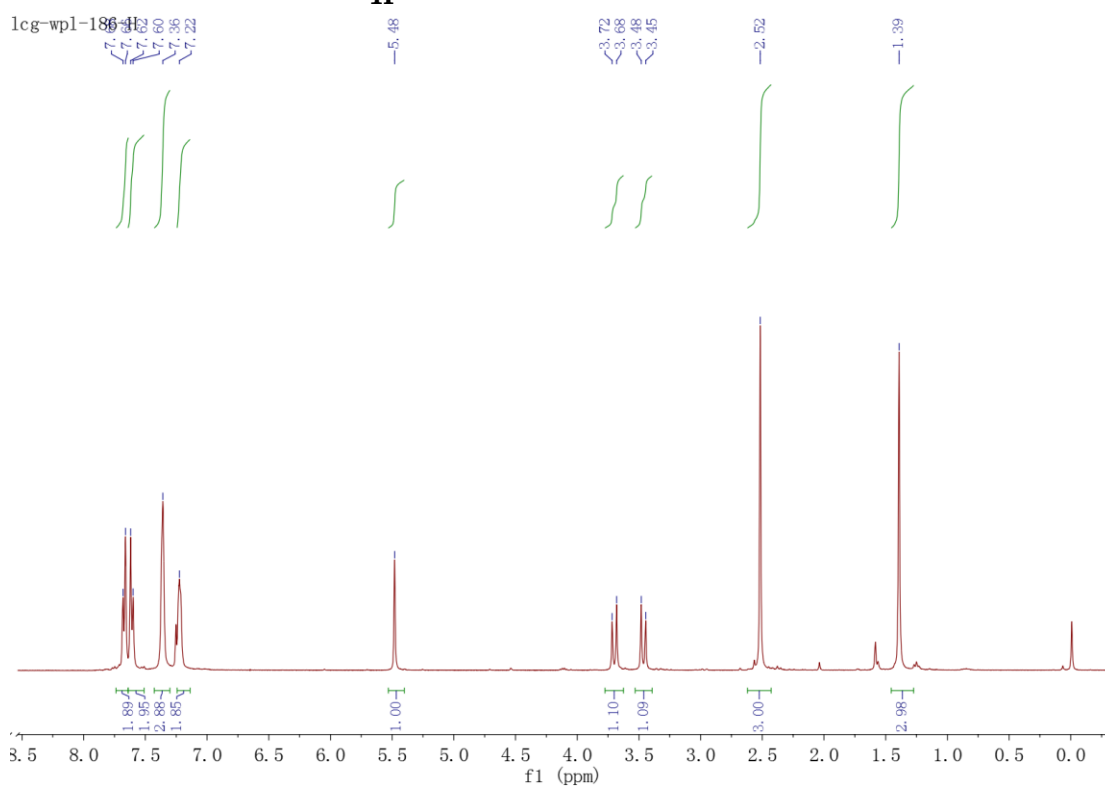
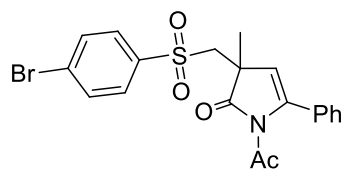
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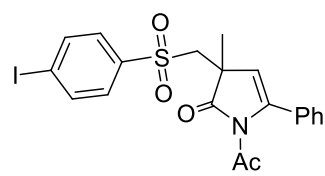




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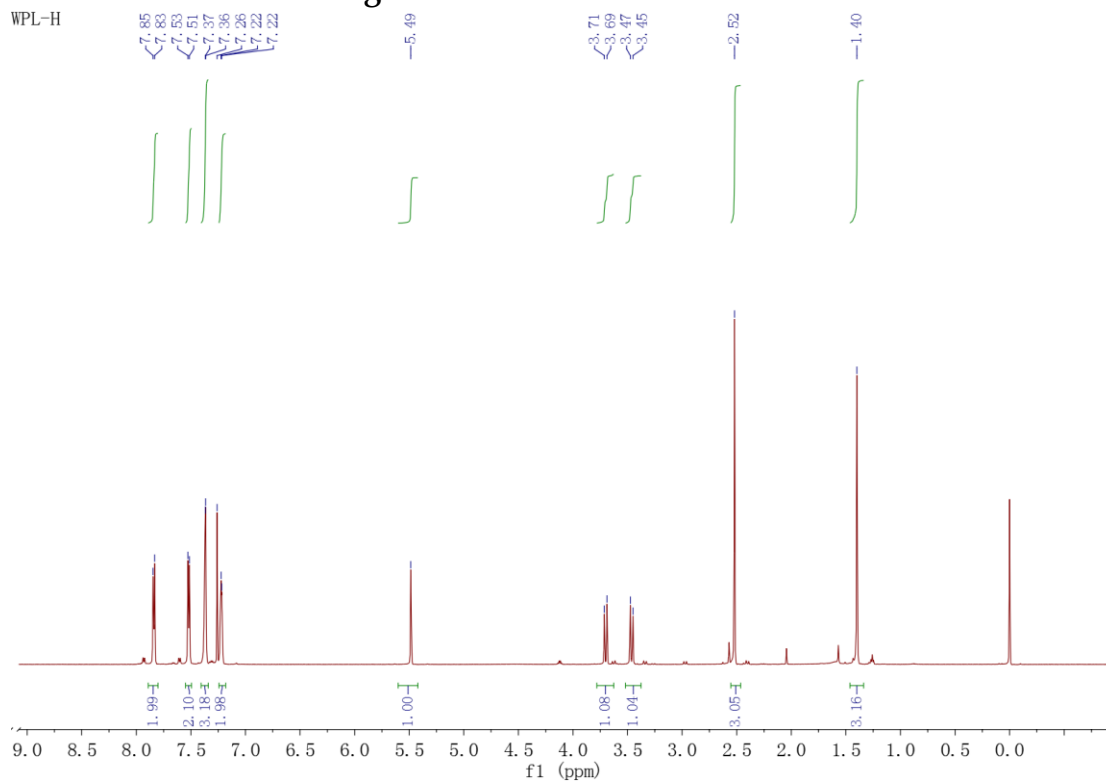




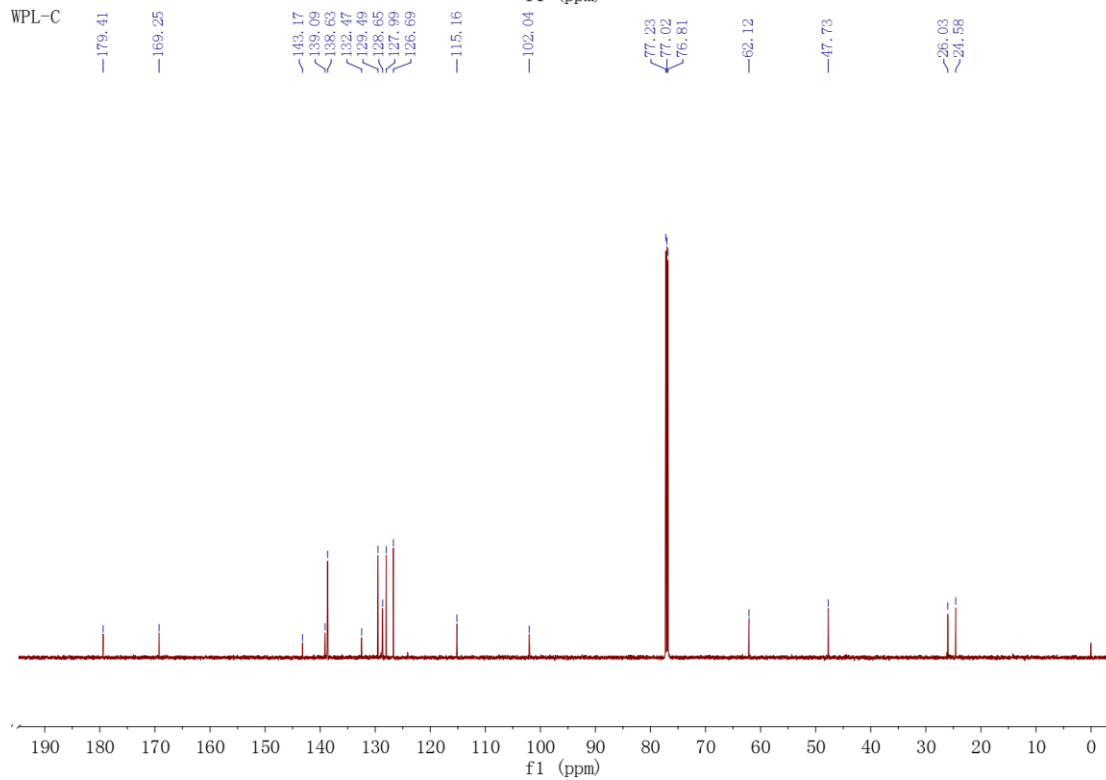


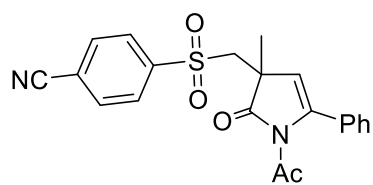
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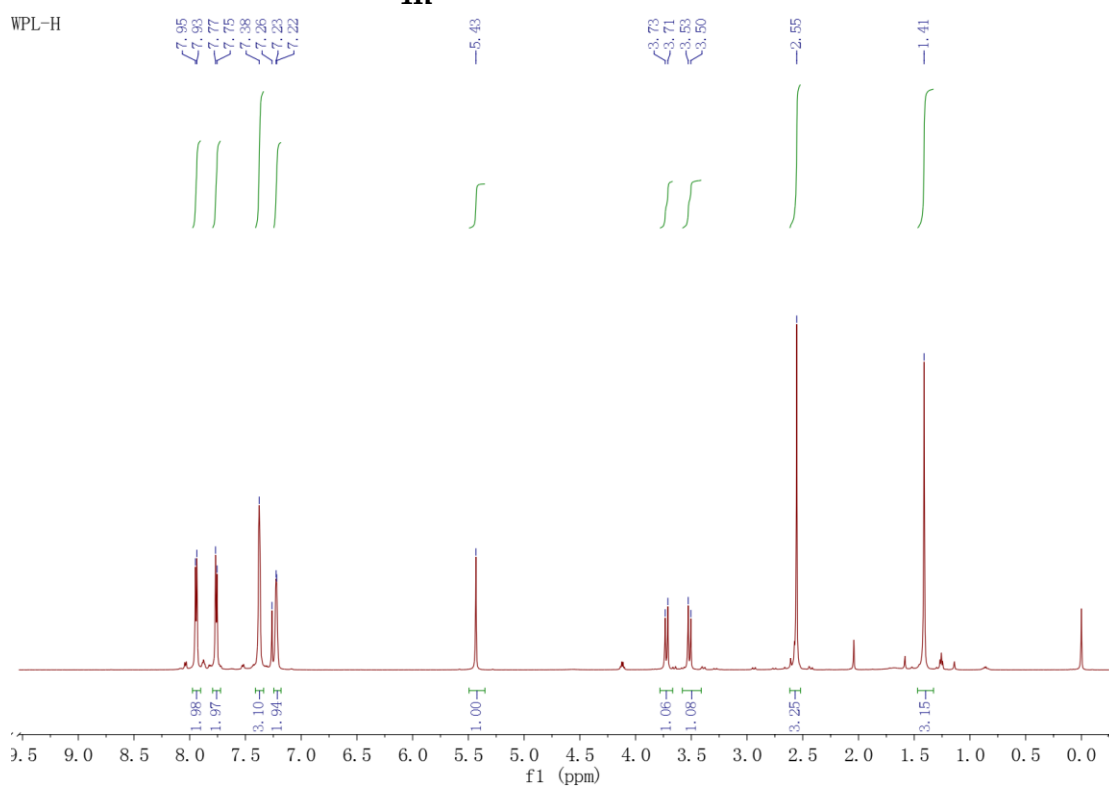
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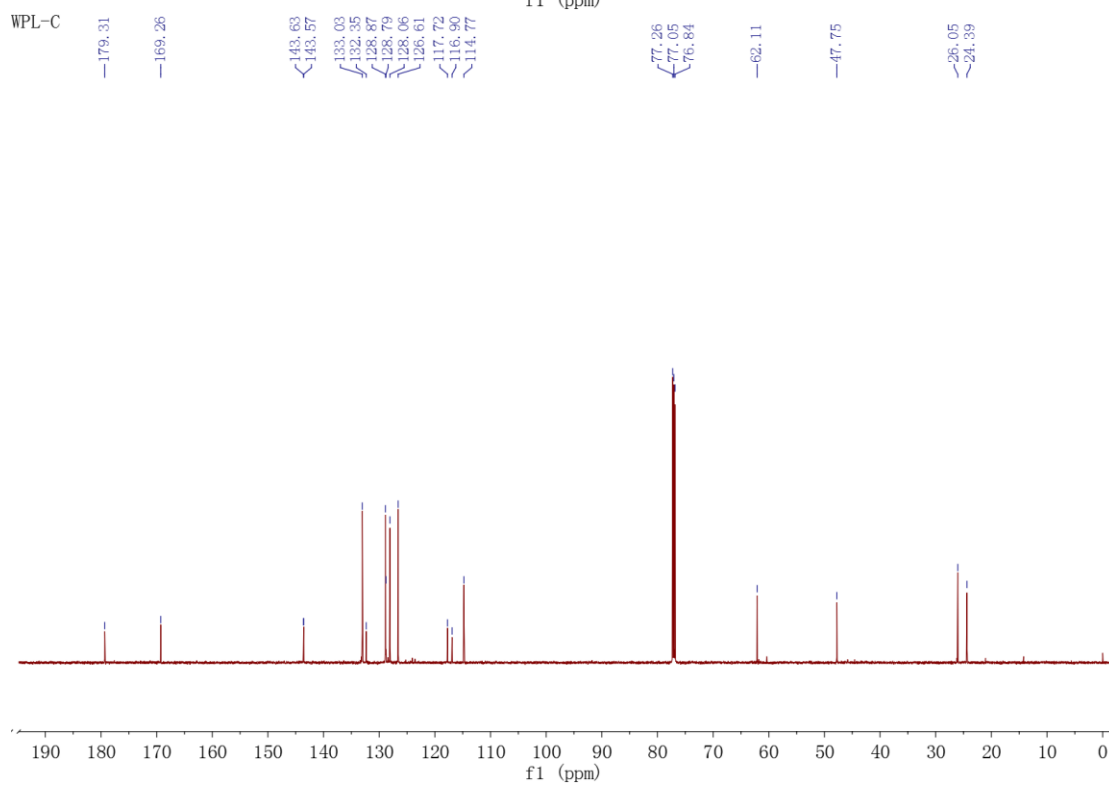


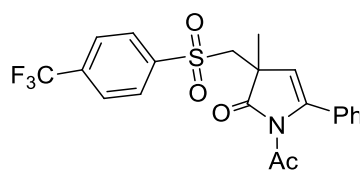
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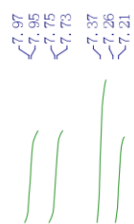
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4i

RD-345

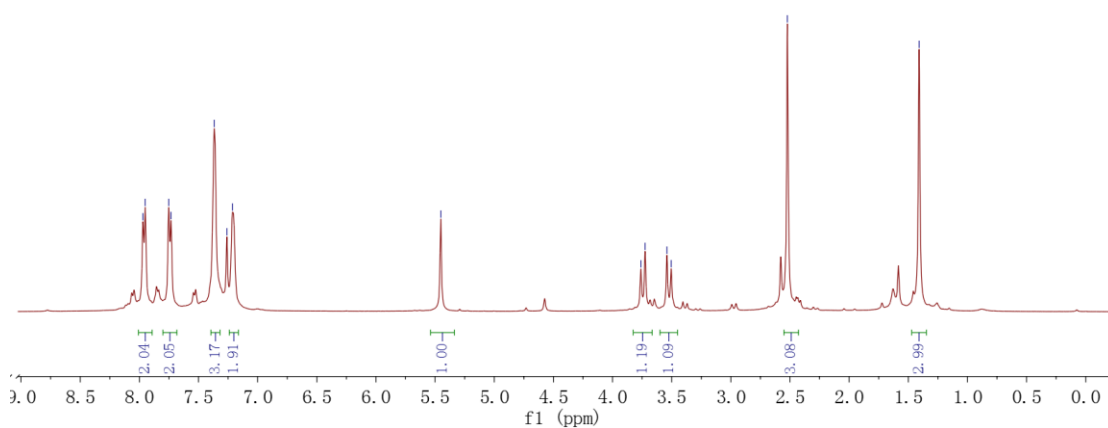


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3.76
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3.54
3.50

2.52

1.41



RD-345C

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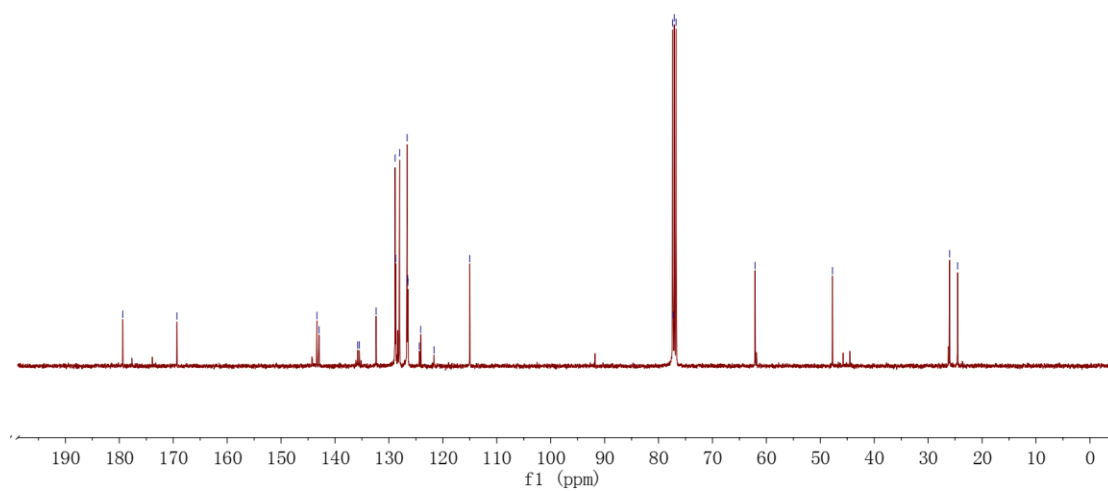
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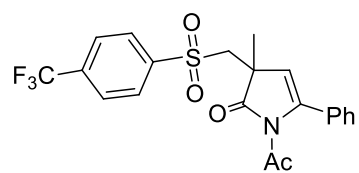
77.38
77.27
77.06
76.75

62.08

47.74

26.03
24.53

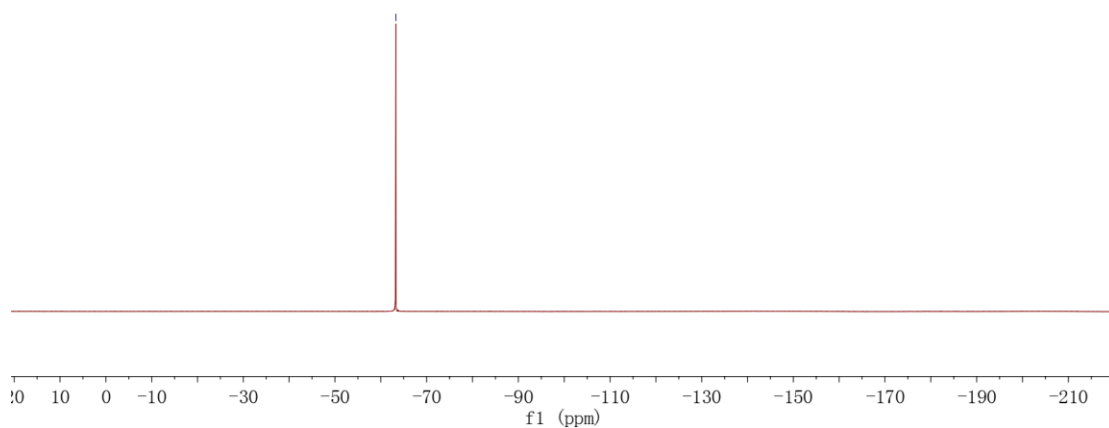


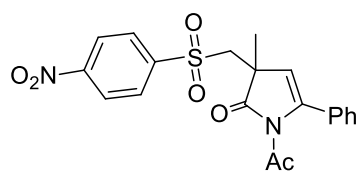


4i

RD-345F

— 63.25





4j

lcg-rd-346-H

8.37, 8.28, 8.02, 8.00

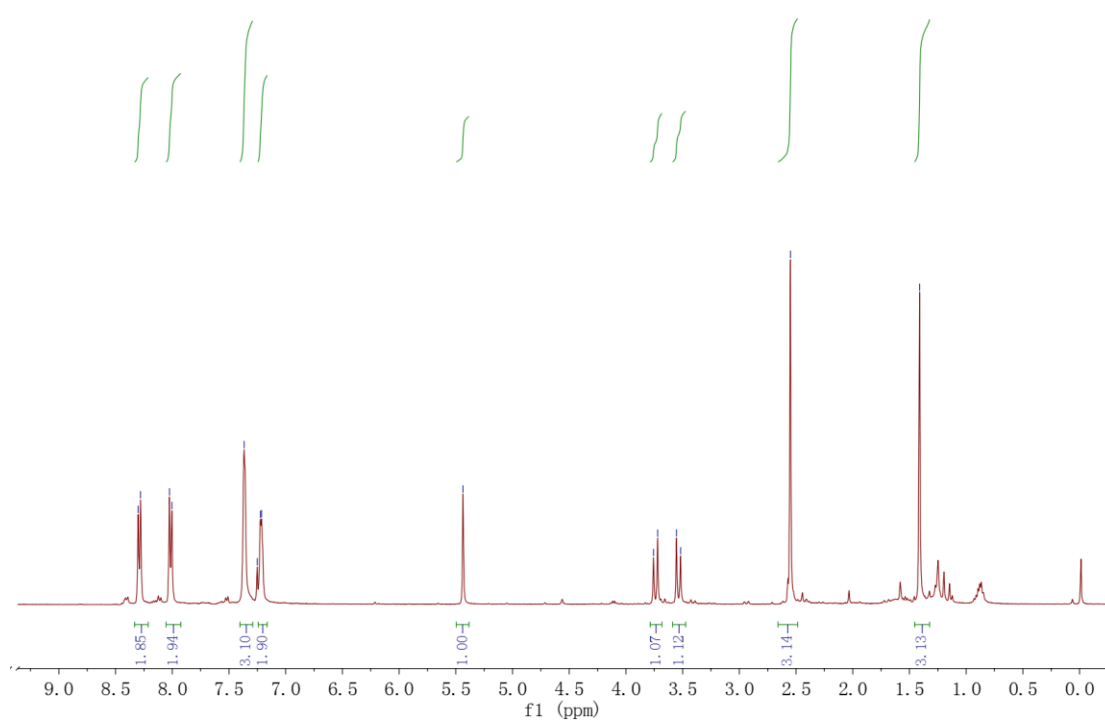
7.37, 7.25, 7.23, 7.21

5.44

3.76, 3.72, 3.55, 3.52

2.55

1.41



lcg-rd-346-C

179.27

169.27

150.85

145.06

143.63

132.28

129.62

128.80

128.06

126.57

124.44

114.68

77.35

77.03

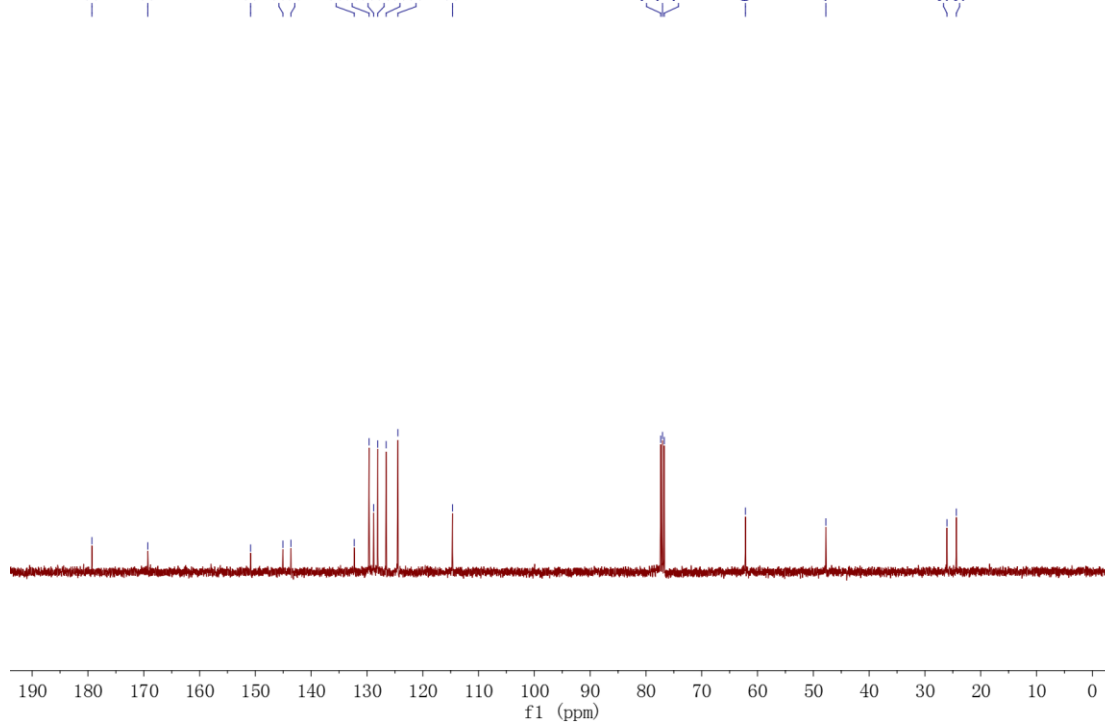
76.71

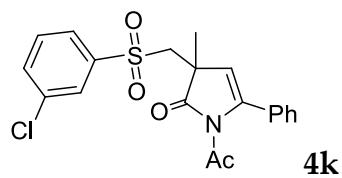
62.16

47.75

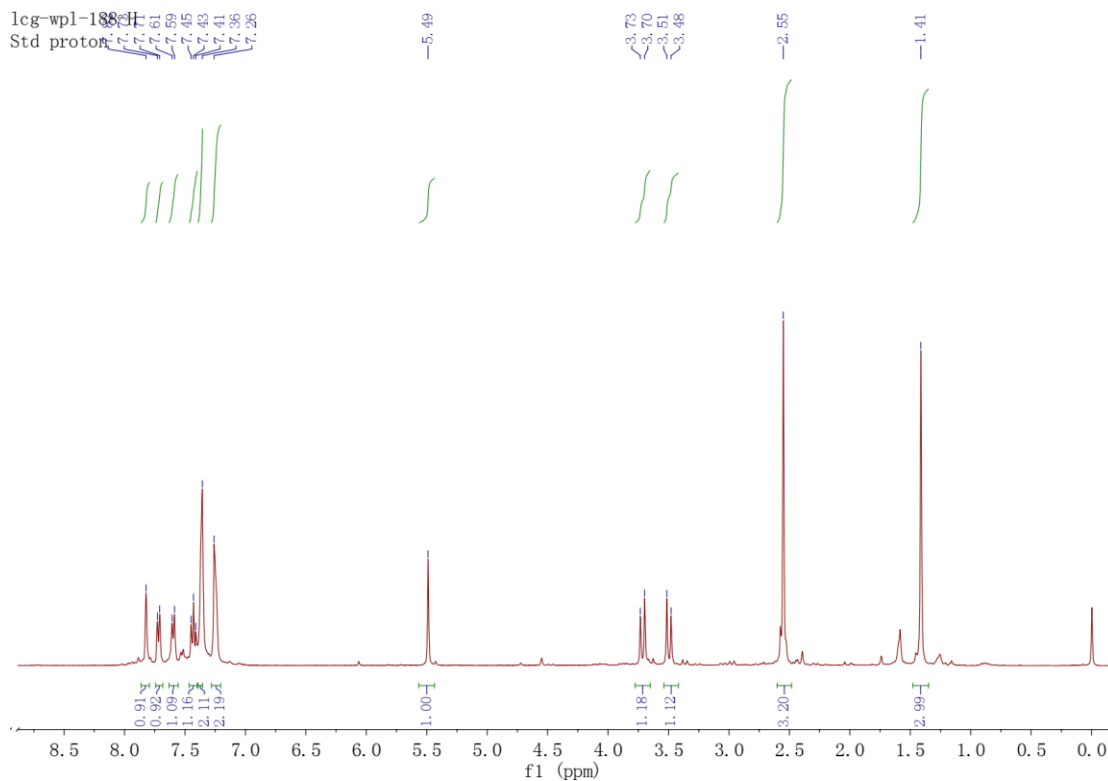
26.05

24.38

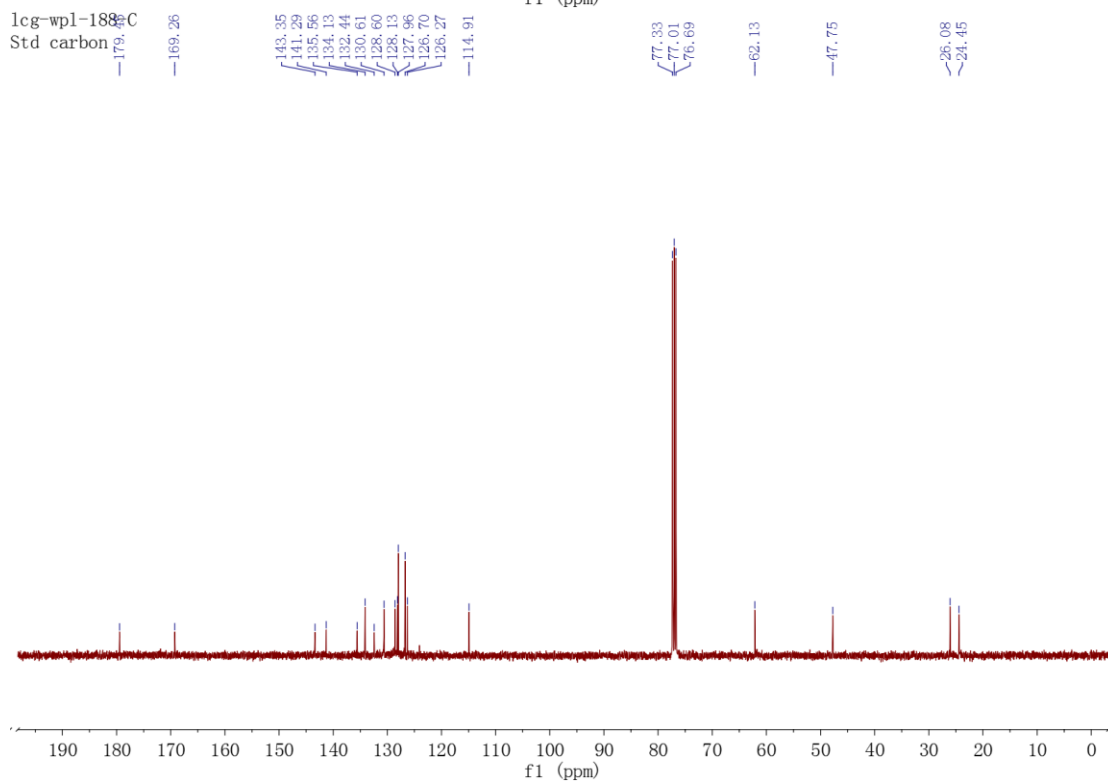


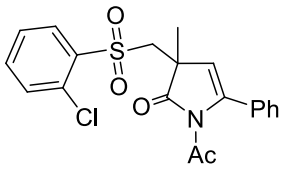


lcg-wpl-188-H
Std proton

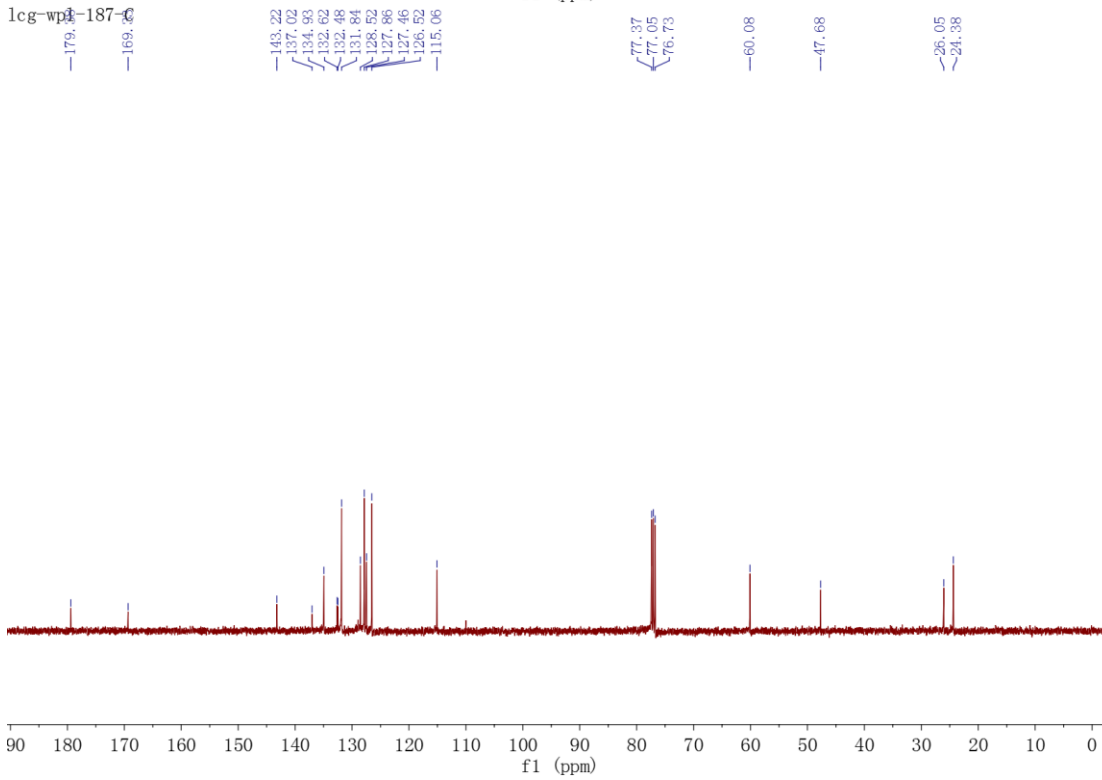
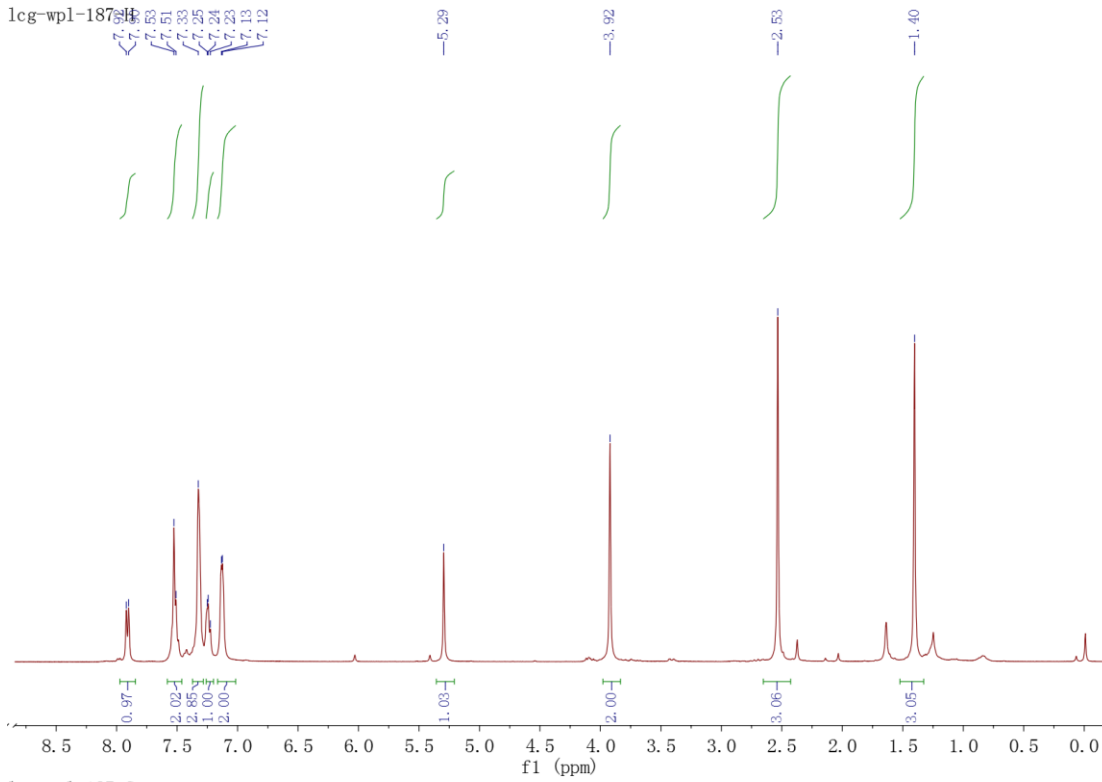


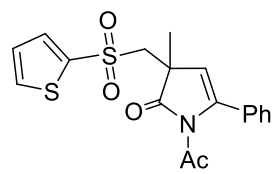
lcg-wpl-188-C
Std carbon



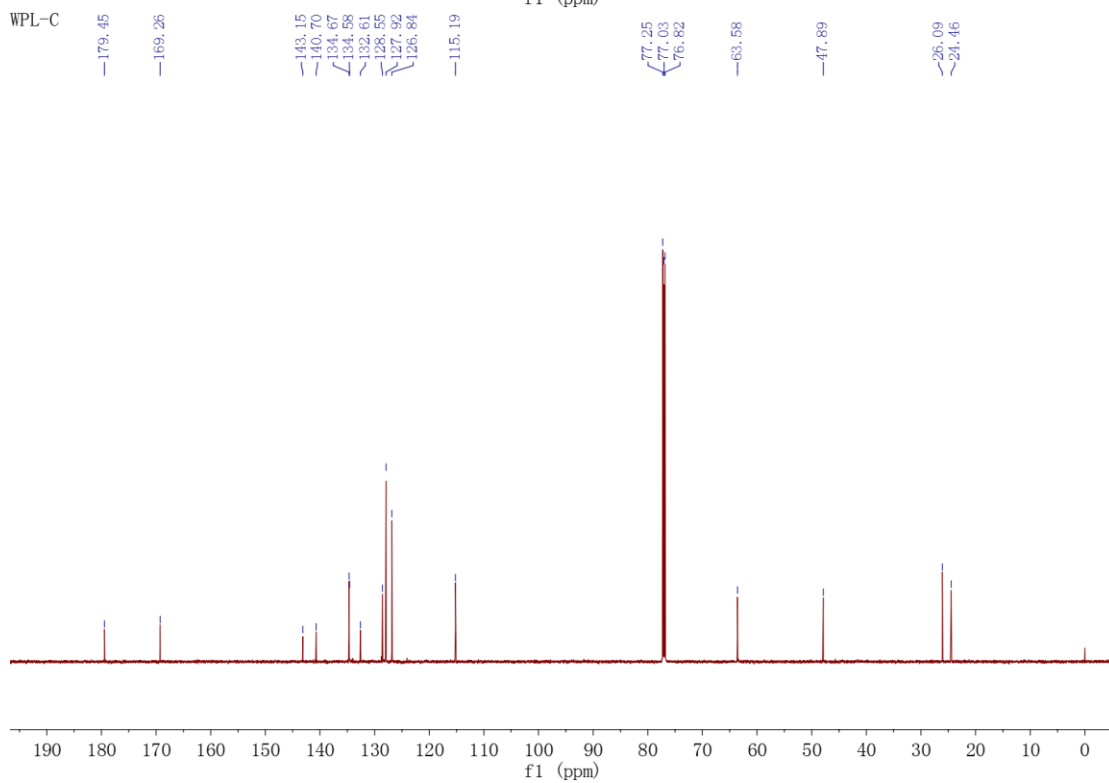
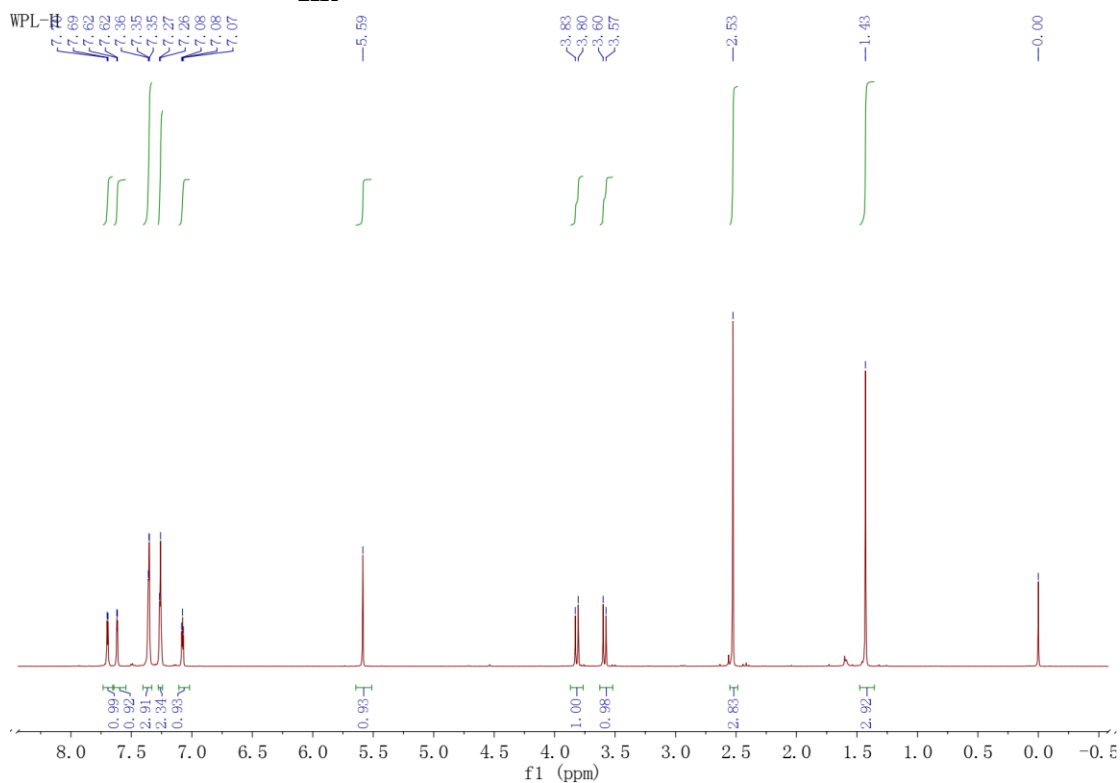


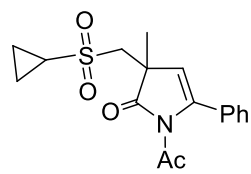
41



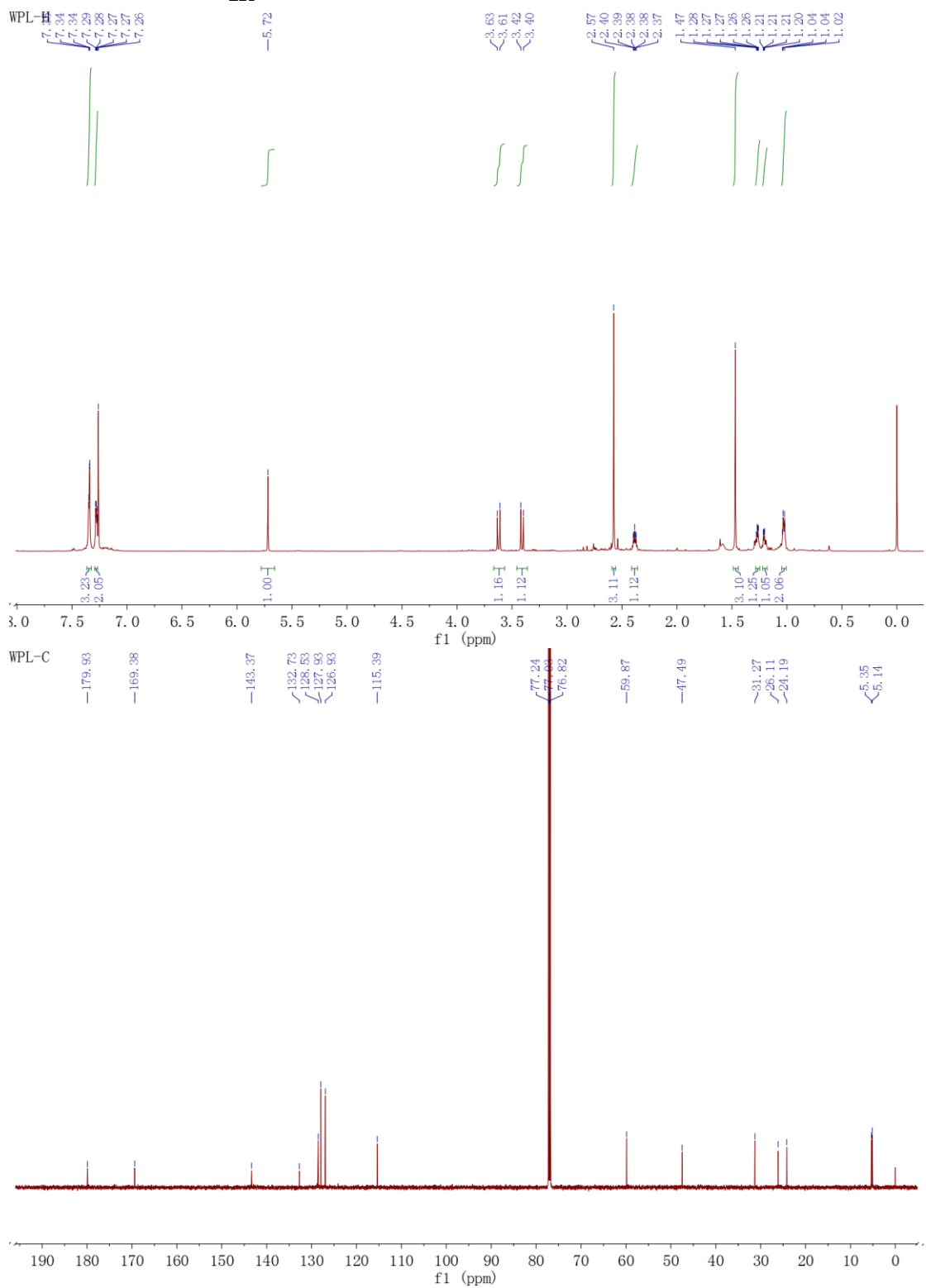


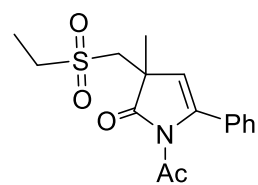
4m



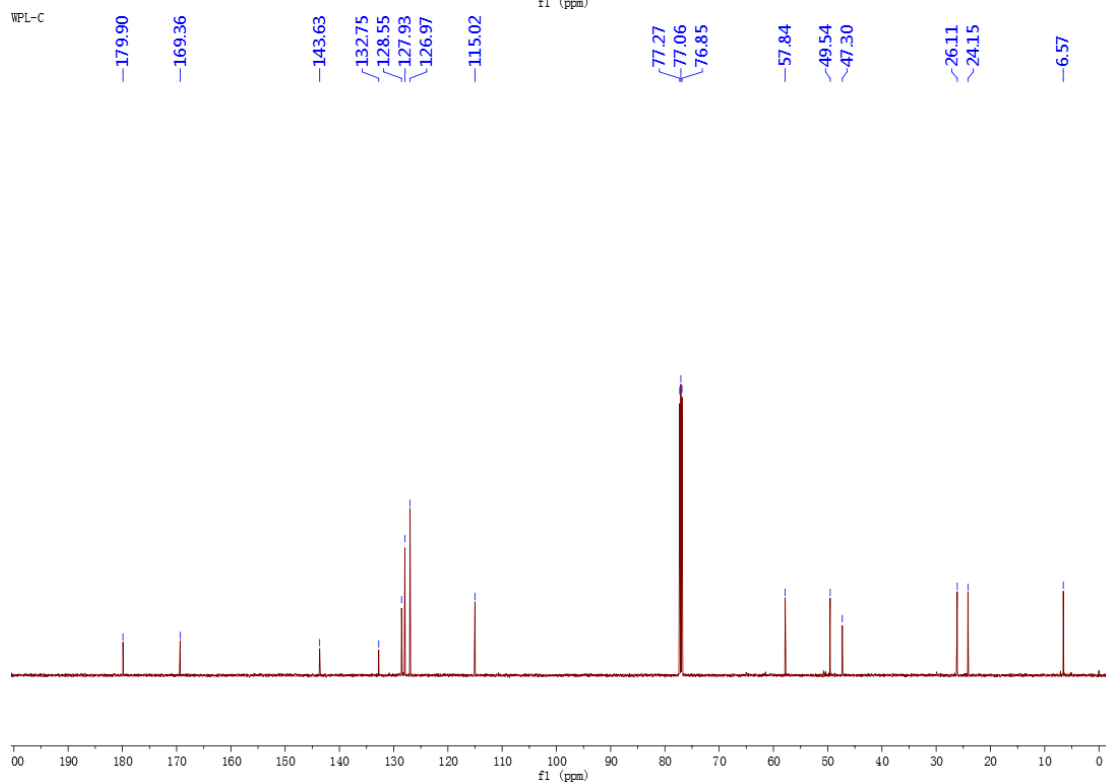
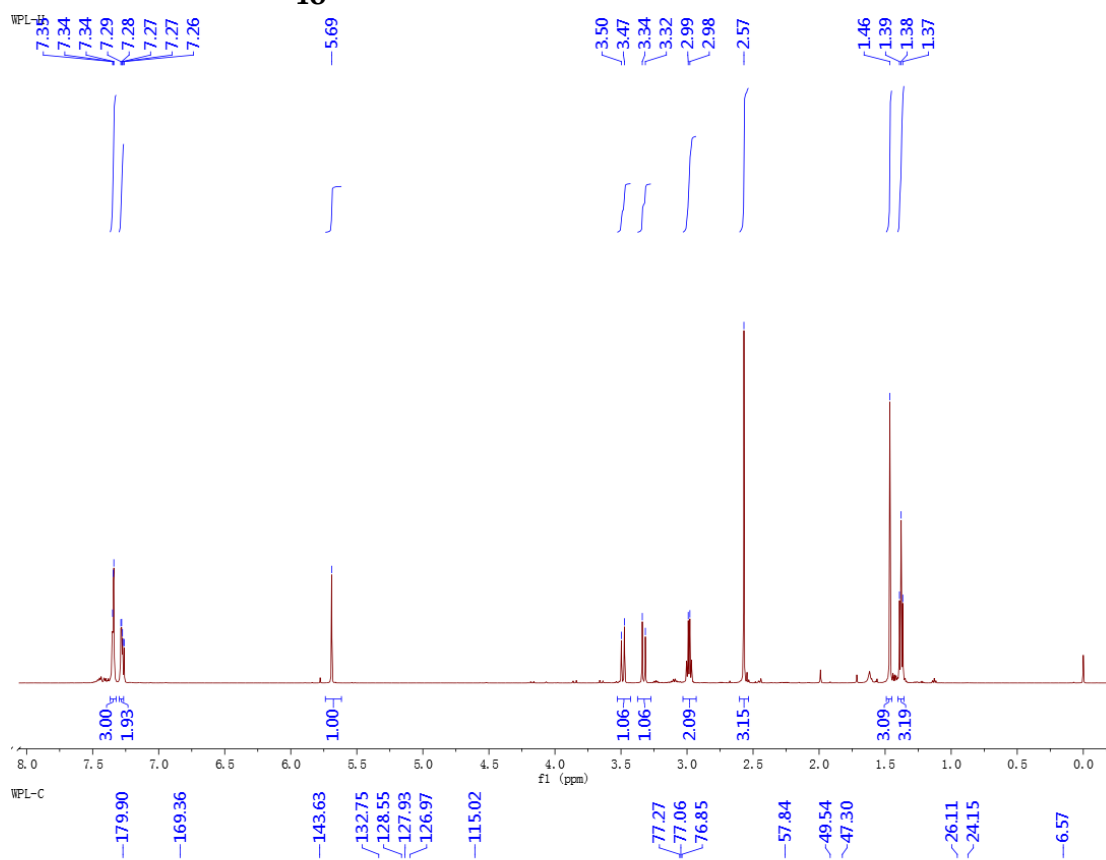


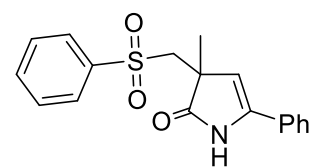
4n



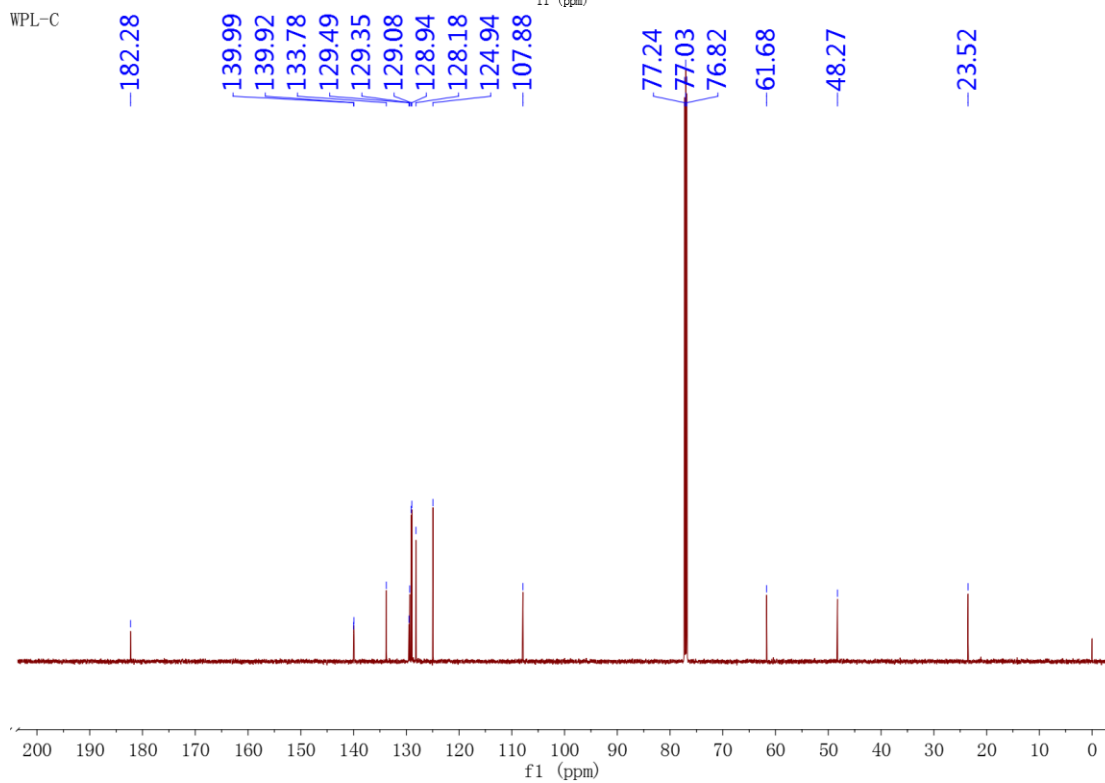
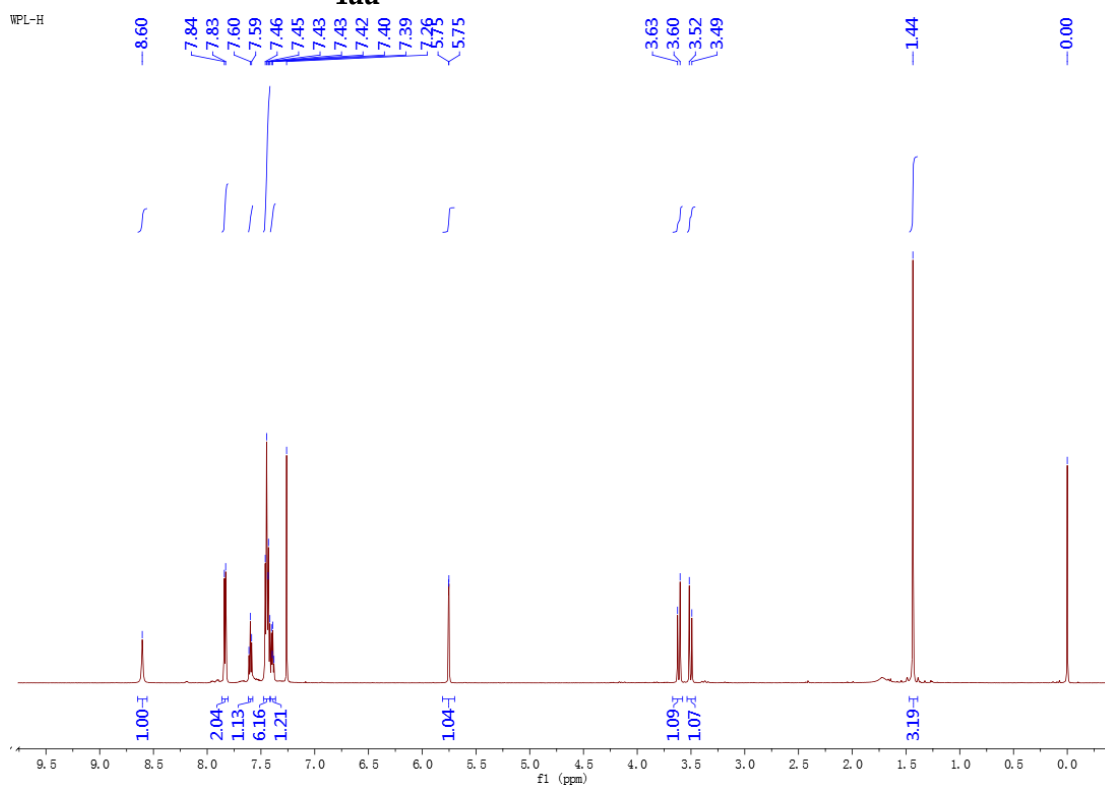


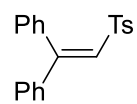
4o



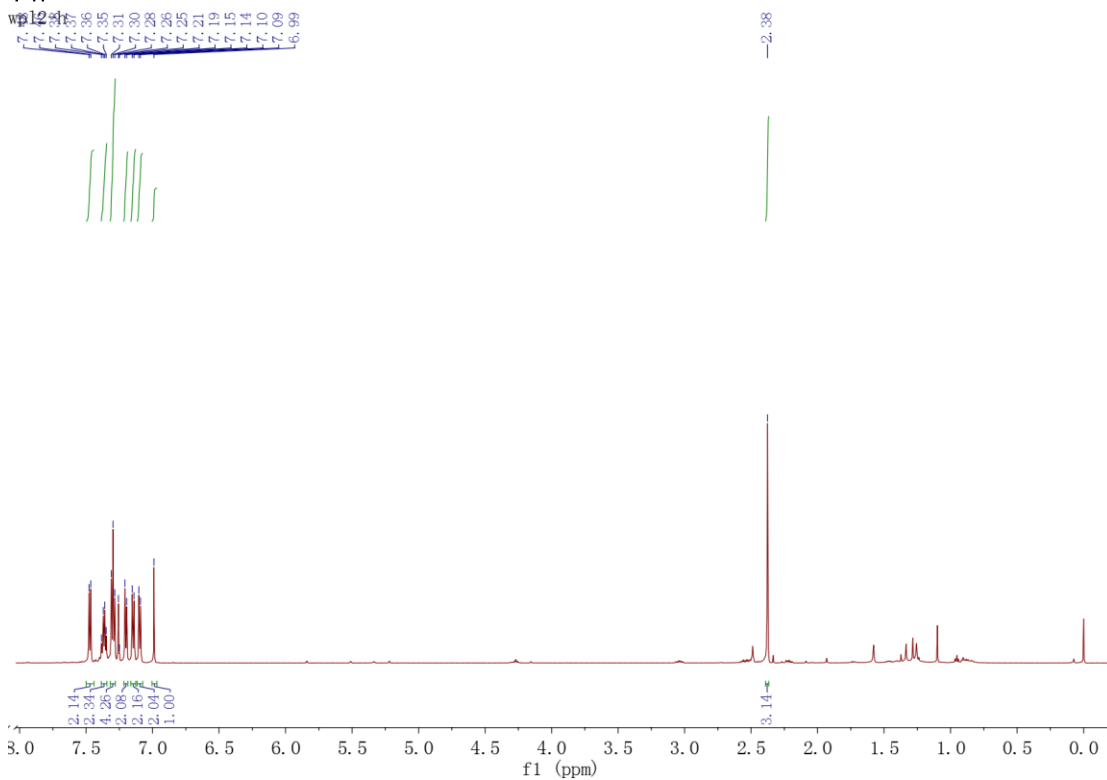


4aa





wp12-c



wp12-c

