

## Supporting Information

### Regioselective, Copper(I)-Catalyzed, Tandem Sulfonylation-Cyclization of 1,5-Dienes with Sulfonyl Chlorides

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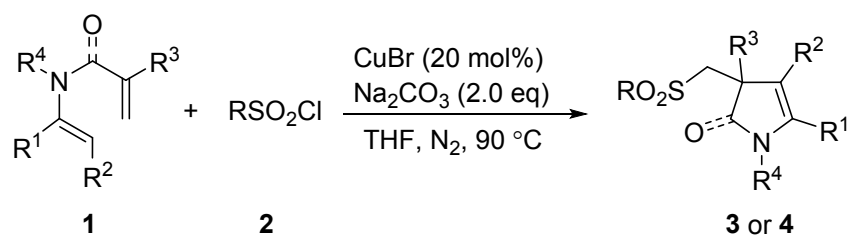
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## 1. General information

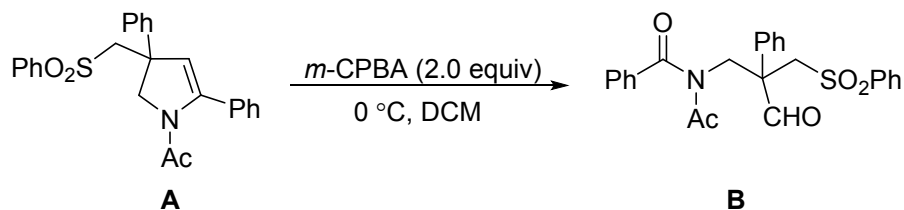
Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification.  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded at 25 °C on Bruker Advance 600M or 400M NMR spectrometers ( $\text{CDCl}_3$ , DMSO as solvent). Chemical shifts for  $^1\text{H}$  NMR spectra are reported as  $\delta$  in units of parts per million (ppm) downfield from  $\text{SiMe}_4$  ( $\delta$  0.0) and relative to the signal of  $\text{SiMe}_4$  ( $\delta$  0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and *etc.* Coupling constants are reported as a  $J$  value in Hz.  $^{13}\text{C}$  NMR spectra are reported as  $\delta$  in units of parts per million (ppm) downfield from  $\text{SiMe}_4$  ( $\delta$  0.0) and relative to the signal of chloroform-d ( $\delta$  77.00 triplet). High resolution mass spectral analysis (HRMS) was performed on WaterXEVOG2 Q-TOF (Waters Corporation). Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system.

## 2. Procedure for the synthesis of compound 3a – 3q, 4a – 4l, A.



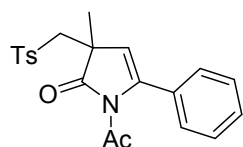
A dry 25-mL Schlenk tube containing a magnetic stirring bar was charged with 1,5-diene (0.1 mmol), sulfonyl chlorides (0.2 mmol), CuBr (20 mol%), Na<sub>2</sub>CO<sub>3</sub> (2.0 equiv), THF (1ml), Then the mixture was charged with N<sub>2</sub> and heated at 90 °C oil bath. After finishing, the reaction mixture was concentrated on a rotary evaporator and the residue was directly subjected to flash column chromatography on silica gel with (10-30% EtOAc/Petroleum ether) as eluate to furnish the desired product.

## 3. Procedures for the formation of B.



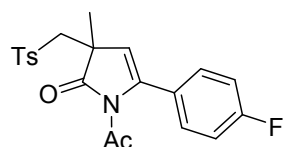
(0.4 mmol) *m*-CPBA was added to the mixture of **A** (0.2 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (8 ml) at 0 °C. After the reaction finished as indicated by TLC, the reaction mixture was diluted with water and extracted with 10 ml dichloromethane for 3 times. The combined organic layers were washed with water, saturated brine, dried over CaCl<sub>2</sub>, concentrated in vacuo and purified by chromatography on silica gel with (30% EtOAc/Petroleum ether) as eluate to furnish the desired product **B** (62% yield).

### 1-acetyl-3-methyl-5-phenyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3a)



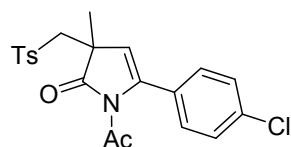
White solid; mp 104.5-105.2 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.34 (m, 3H), 7.28 (s, 2H), 7.24 (dd, *J* = 6.5, 2.9 Hz, 2H), 5.51 (s, 1H), 3.70 (d, *J* = 14.4 Hz, 1H), 3.46 (d, *J* = 14.4 Hz, 1H), 2.49 (s, 3H), 2.42 (s, 3H), 1.39 (s, 4H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.62, 169.23, 145.06, 142.90, 136.63, 132.71, 129.90, 128.51, 128.23, 127.89, 126.81, 115.56, 62.19, 47.78, 26.00, 24.57, 21.61. HRMS (ESI, *m/z*): Calcd. For C<sub>21</sub>H<sub>21</sub>NSO<sub>4</sub>Na [M+Na]<sup>+</sup> 406.1083, found: 406.1085.

### 1-acetyl-5-(4-fluorophenyl)-3-methyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3b)



Yellow solid; mp 113.1-114 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.05 (t, *J* = 8.7 Hz, 2H), 5.53 (s, 1H), 3.69 (d, *J* = 14.3 Hz, 1H), 3.45 (d, *J* = 14.3 Hz, 1H), 2.50 (s, 3H), 2.43 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.55, 169.33, 162.72 (*J* = 252 Hz), 145.15, 142.00, 136.57, 129.93, 128.82, 128.77, 128.14, 115.65, 115.02, 114.88, 62.20, 47.67, 26.05, 24.53, 21.62. <sup>19</sup>F NMR (565 MHz, CDCl<sub>3</sub>) δ -112.71. HRMS (ESI, *m/z*): Calcd. For C<sub>21</sub>H<sub>20</sub>NSO<sub>4</sub>FNa [M+Na]<sup>+</sup> 424.0989, found: 424.0991.

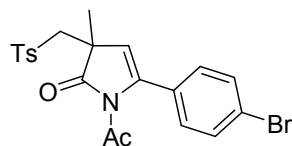
### 1-acetyl-5-(4-chlorophenyl)-3-methyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3c)



White solid; mp 104.3-105.2 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 5.56 (s, 1H), 3.69 (d, *J* = 14.3 Hz, 1H), 3.45 (d, *J* = 14.3 Hz, 1H), 2.50 (s, 3H), 2.43 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.46, 169.27, 145.17, 141.89, 136.52, 134.39, 131.25, 129.94, 128.22, 128.13, 116.05, 62.18, 47.74, 25.99, 24.48, 21.63.

HRMS (ESI, m/z): Calcd. For C<sub>21</sub>H<sub>20</sub>NSO<sub>4</sub>ClNa [M+Na]<sup>+</sup> 440.0694, found: 440.0695.

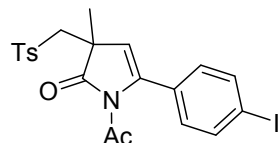
**1-acetyl-5-(4-bromophenyl)-3-methyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3d)**



White solid; mp 80.2-81.3 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 5.56 (s, 1H), 3.69 (d, *J* = 14.3 Hz, 1H), 3.45 (d, *J* = 14.3 Hz, 1H), 2.50 (s, 3H), 2.43 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.44, 169.25, 145.17, 141.94, 136.51, 131.72, 131.07, 129.95, 128.48, 128.13, 122.60, 116.08, 62.17, 47.76, 25.97, 24.46, 21.63.

HRMS (ESI, m/z): Calcd. For C<sub>21</sub>H<sub>20</sub>NSO<sub>4</sub>BrNa [M+Na]<sup>+</sup> 484.0189, found: 484.0190.

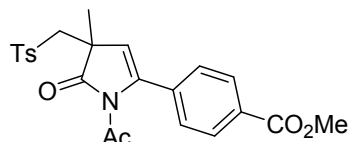
**1-acetyl-5-(4-iodophenyl)-3-methyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3e)**



White solid; mp 123-124 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.69 (dd, *J* = 8.1, 5.9 Hz, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 5.56 (s, 1H), 3.68 (d, *J* = 14.3 Hz, 1H), 3.45 (d, *J* = 14.3 Hz, 1H), 2.50 (s, 3H), 2.43 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.42, 169.24, 145.16, 142.03, 136.99, 136.49, 132.30, 129.94, 128.57, 128.13, 116.10, 94.29, 62.15, 47.77, 25.95, 24.45, 21.63.

HRMS (ESI, m/z): Calcd. For C<sub>21</sub>H<sub>20</sub>NSO<sub>4</sub>INa [M+Na]<sup>+</sup> 532.0050, found: 532.0052.

**Methyl-4-(1-acetyl-4-methyl-5-oxo-4-(tosylmethyl)-4,5-dihydro-1H-pyrrol-2-yl)benzoate (3f)**

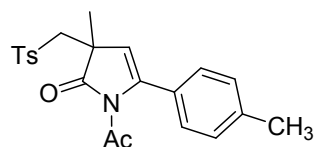


White solid; mp 65.7-66.5 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.62 (s, 1H), 3.70 (d, *J* = 14.4 Hz, 1H), 3.47 (d, *J* = 14.4 Hz, 1H), 2.52 (s, 3H), 2.43 (s, 3H),

1.41 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.34, 169.16, 166.61, 145.20, 142.06, 137.19, 136.48, 129.96, 129.21, 128.15, 126.76, 116.90, 62.17, 52.21, 47.90, 25.86, 24.45, 21.63.

HRMS (ESI, m/z): Calcd. For C<sub>23</sub>H<sub>23</sub>NSO<sub>6</sub>INa [M+Na]<sup>+</sup> 464.1138, found: 464.1140.

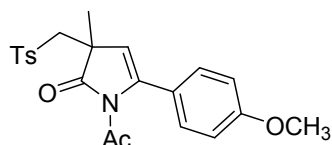
### 1-acetyl-3-methyl-5-p-tolyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3g)



White solid; mp 111.7-112.5 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.14 – 7.11 (m, 2H), 5.49 (s, 1H), 3.69 (d, *J* = 14.4 Hz, 1H), 3.45 (d, *J* = 14.4 Hz, 1H), 2.47 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.66, 169.27, 145.02, 142.85, 138.44, 136.53, 129.89, 129.74, 128.60, 128.25, 126.68, 114.95, 62.15, 47.70, 26.08, 24.60, 21.61, 21.35.

HRMS (ESI, m/z): Calcd. For C<sub>22</sub>H<sub>23</sub>NSO<sub>4</sub>Na [M+Na]<sup>+</sup> 420.1240, found: 420.1245.

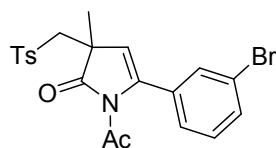
### 1-acetyl-5-(4-methoxyphenyl)-3-methyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3h)



White solid; mp 146.3-147.2 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.45 (s, 1H), 3.69 (d, *J* = 14.4 Hz, 1H), 3.45 (d, *J* = 14.4 Hz, 1H), 1.38 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.73, 169.39, 159.73, 145.02, 142.59, 136.57, 129.87, 128.23, 128.20, 125.03, 114.45, 113.32, 62.19, 55.30, 47.62, 26.16, 24.63, 21.61.

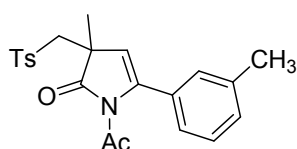
HRMS (ESI, m/z): Calcd. For C<sub>22</sub>H<sub>23</sub>NSO<sub>5</sub>Na [M+Na]<sup>+</sup> 436.1189, found: 436.1190.

### 1-acetyl-5-(3-bromophenyl)-3-methyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3i)



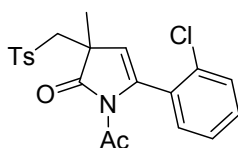
White solid; mp 149.7-150.3 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.48 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.35 (t, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.18 – 7.14 (m, 1H), 5.51 (s, 1H), 3.70 (d, *J* = 14.4 Hz, 1H), 3.47 (d, *J* = 14.4 Hz, 1H), 2.52 (s, 3H), 2.45 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.33, 169.17, 145.20, 141.50, 136.49, 134.70, 131.44, 129.99, 129.64, 129.33, 128.17, 125.54, 121.90, 116.51, 62.14, 47.78, 25.90, 24.43, 21.66.  
HRMS (ESI, m/z): Calcd. For C<sub>21</sub>H<sub>20</sub>NSO<sub>4</sub>BrNa [M+Na]<sup>+</sup> 484.0189, found: 484.0190.

### 1-acetyl-3-methyl-5-m-tolyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3j)



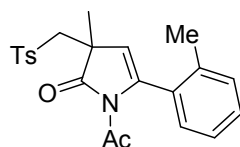
White solid; mp 134.1-135 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 5.49 (s, 1H), 3.69 (d, *J* = 14.4 Hz, 1H), 3.46 (d, *J* = 14.4 Hz, 1H), 2.49 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.63, 169.21, 145.01, 142.96, 137.56, 136.57, 132.56, 129.90, 129.33, 128.24, 127.75, 127.30, 123.88, 115.34, 62.15, 47.74, 26.03, 24.56, 21.62, 21.44.  
HRMS (ESI, m/z): Calcd. For C<sub>22</sub>H<sub>23</sub>NSO<sub>4</sub>Na [M+Na]<sup>+</sup> 420.1240, found: 420.1245.

### 1-acetyl-5-(2-chlorophenyl)-3-methyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3k)



White solid; mp 113.5-114.2 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.39 (m, 1H), 7.39 – 7.29 (m, 5H), 5.68 (s, 1H), 3.66 (s, 1H), 3.45 (d, *J* = 14.2 Hz, 1H), 2.48 – 2.40 (m, 6H), 1.44 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 178.67, 168.78, 145.16, 132.80, 129.98, 129.92, 129.82, 128.88, 128.11, 126.70, 116.75, 61.92, 25.34, 24.43, 21.61.  
HRMS (ESI, m/z): Calcd. For C<sub>21</sub>H<sub>20</sub>NSO<sub>4</sub>ClNa [M+Na]<sup>+</sup> 440.0694, found: 440.0695.

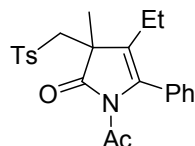
### 1-acetyl-3-methyl-5-o-tolyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3l)



White solid; mp 137.5-138.1 °C;  $^1\text{H}$  NMR (600 MHz, DMSO)  $\delta$  7.74 (d,  $J = 8.1$  Hz, 2H), 7.44 (d,  $J = 8.1$  Hz, 2H), 7.25 (t,  $J = 7.5$  Hz, 1H), 7.17 (dd,  $J = 11.5, 7.5$  Hz, 2H), 7.11 (d,  $J = 7.1$  Hz, 1H), 5.41 (s, 1H), 3.97 (d,  $J = 14.5$  Hz, 1H), 3.71 (d,  $J = 14.5$  Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 2.16 (s, 3H), 1.33 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, DMSO)  $\delta$  179.67, 168.79, 145.08, 133.97, 130.37, 129.79, 128.53, 127.98, 125.66, 116.56, 61.04, 47.53, 25.77, 24.50, 21.53, 19.85.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{21}\text{H}_{20}\text{NSO}_4\text{ClNa}$   $[\text{M}+\text{Na}]^+$  440.0694, found: 440.0695.

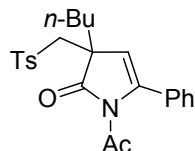
### 1-acetyl-4-ethyl-3-methyl-5-phenyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3m)



White solid; mp 160.6-161.0 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.2$  Hz, 2H), 7.35 (ddd,  $J = 19.0, 8.8, 6.3$  Hz, 7H), 3.70 (d,  $J = 14.3$  Hz, 1H), 3.49 (d,  $J = 14.3$  Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.19 (dd,  $J = 9.0, 6.1$  Hz, 1H), 1.95 (dt,  $J = 15.0, 7.5$  Hz, 1H), 1.38 (s, 3H), 0.90 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.43, 169.09, 145.03, 137.67, 136.89, 132.57, 130.05, 129.93, 128.33, 128.14, 128.01, 127.94, 127.70, 126.12, 124.87, 61.76, 50.47, 26.20, 24.64, 21.65, 18.05, 14.59.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{23}\text{H}_{25}\text{NSO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  434.1397, found: 434.1399.

### 1-acetyl-3-butyl-5-phenyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3n)



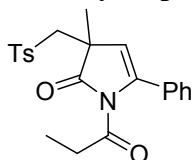
Amorphous solid;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  7.71 (d,  $J = 8.2$  Hz, 2H), 7.41 (dd,  $J = 11.7, 5.1$  Hz, 5H), 7.17 (dd,  $J = 7.1, 2.4$  Hz, 2H), 5.34 (s, 1H), 4.11 (d,  $J = 14.8$  Hz, 1H), 3.74 (d,  $J = 14.8$  Hz, 1H), 2.48 (s, 3H), 2.45 (s, 3H), 1.70 (ddd,  $J = 25.2, 12.6, 6.1$  Hz, 2H), 1.23 (dd,  $J = 8.2, 5.2$  Hz, 3H), 1.10 – 0.99 (m, 1H), 0.84 (t,  $J = 7.0$  Hz,



3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  179.57, 169.14, 144.95, 142.74, 137.26, 133.18, 130.20, 128.48, 128.22, 128.21, 126.71, 115.13, 60.97, 51.91, 37.19, 26.08, 25.36, 22.55, 21.53, 14.10.

HRMS (ESI, m/z): Calcd. For  $\text{C}_{24}\text{H}_{27}\text{NSO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  448.1553, found: 448.1557.

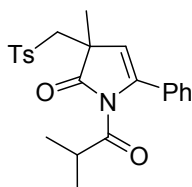
### 3-methyl-5-phenyl-1-propionyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3o)



White solid; mp 147.3-144.5 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 8.0$  Hz, 2H), 7.38 – 7.34 (m, 3H), 7.29 – 7.25 (m, 3H), 7.24 – 7.21 (m, 2H), 5.50 (s, 1H), 3.70 (d,  $J = 14.4$  Hz, 1H), 3.46 (d,  $J = 14.4$  Hz, 1H), 2.96 – 2.81 (m, 2H), 2.41 (s, 3H), 1.39 (s, 3H), 1.14 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.42, 173.21, 145.02, 142.99, 136.57, 132.85, 129.86, 128.46, 128.21, 127.91, 126.68, 115.48, 62.14, 47.81, 31.57, 24.62, 21.61, 8.32.

HRMS (ESI, m/z): Calcd. For  $\text{C}_{22}\text{H}_{23}\text{NSO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  420.1240, found: 420.1241.

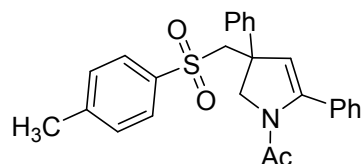
### 1-isobutyryl-3-methyl-5-phenyl-3-(tosylmethyl)-1H-pyrrol-2(3H)-one (3p)



White solid; mp 125.2-126 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 8.3$  Hz, 2H), 7.36 (dd,  $J = 5.0, 1.9$  Hz, 3H), 7.24 (d,  $J = 8.0$  Hz, 2H), 7.21 – 7.16 (m, 2H), 5.50 (s, 1H), 3.70 (d,  $J = 14.4$  Hz, 1H), 3.69 – 3.63 (m, 1H), 3.46 (d,  $J = 14.4$  Hz, 1H), 2.40 (s, 3H), 1.40 (s, 3H), 1.24 (d,  $J = 6.9$  Hz, 3H), 1.18 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  178.90, 176.66, 144.97, 143.14, 136.65, 132.79, 129.85, 128.49, 128.17, 128.05, 126.20, 115.30, 62.09, 48.10, 35.57, 24.69, 21.63, 18.60, 18.36.

HRMS (ESI, m/z): Calcd. For  $\text{C}_{23}\text{H}_{25}\text{NSO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  434.1397, found: 434.1397.

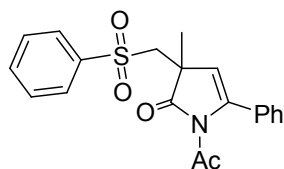
### 1-(3,5-diphenyl-3-(tosylmethyl)-2,3-dihydro-1H-pyrrol-1-yl)ethan-1-one (3q)



White solid; mp 40-42 °C;  $^1\text{H}$  NMR (600 MHz, DMSO)  $\delta$  7.54 (d,  $J$  = 8.0 Hz, 2H), 7.48 – 7.12 (m, 12H), 5.78 (s, 1H), 4.59 (d,  $J$  = 11.6 Hz, 1H), 4.15 (s, 1H), 4.08 (d,  $J$  = 14.8 Hz, 1H), 4.06 – 3.99 (m, 1H), 2.35 (s, 3H), 1.76 (b, 3H).  $^{13}\text{C}$  NMR (151 MHz, DMSO)  $\delta$  168.25, 144.27, 143.46, 138.29, 133.42, 129.99, 128.81, 127.94, 127.22, 126.95, 118.85, 63.82, 61.99, 60.23, 50.53, 24.53, 21.48.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{26}\text{H}_{25}\text{ClNO}_3\text{SH}$   $[\text{M}+\text{H}]^+$  432.1633, found: 432.1624.

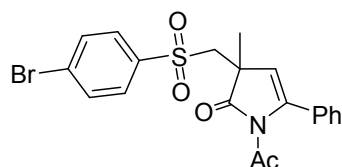
#### 1-acetyl-3-methyl-5-phenyl-3-(phenylsulfonylmethyl)-1H-pyrrol-2(3H)-one (4a)



White solid; mp 76-78 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.80 (m, 2H), 7.63 (t,  $J$  = 7.5 Hz, 1H), 7.49 (t,  $J$  = 7.9 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.24 (dd,  $J$  = 6.6, 3.0 Hz, 2H), 5.49 (s, 1H), 3.72 (d,  $J$  = 14.4 Hz, 1H), 3.49 (d,  $J$  = 14.4 Hz, 1H), 2.51 (s, 3H), 1.40 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.60, 169.32, 143.04, 139.57, 133.98, 132.64, 129.32, 128.56, 128.18, 127.94, 126.76, 115.40, 62.13, 47.79, 26.10, 24.55.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{20}\text{H}_{19}\text{NO}_4\text{SNa}$   $[\text{M}+\text{Na}]^+$  392.0927, found: 392.0935.

#### 1-acetyl-3-((4-bromophenylsulfonyl)methyl)-3-methyl-5-phenyl-1H-pyrrol-2(3H)-one (4b)

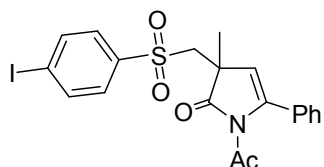


White solid; mp 155.4-156.2 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J$  = 8.6 Hz, 2H), 7.62 (d,  $J$  = 8.6 Hz, 2H), 7.38 – 7.35 (m, 3H), 7.23 (dd,  $J$  = 6.5, 2.9 Hz, 2H), 5.49 (s, 1H), 3.71 (d,  $J$  = 14.4 Hz, 1H), 3.47 (d,  $J$  = 14.4 Hz, 1H), 2.52 (s, 3H), 1.40 (s, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.42, 169.26, 143.19, 138.45, 132.64, 132.47, 129.72, 129.41, 128.65, 127.98, 126.68, 115.14, 62.17, 47.74, 26.02, 24.55.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{20}\text{H}_{18}\text{NO}_4\text{SBrNa}$   $[\text{M}+\text{Na}]^+$  470.0032, found: 470.0035.

**1-acetyl-3-((4-iodophenylsulfonyl)methyl)-3-methyl-5-phenyl-1H-pyrrol-2(3H)-one (4c)**

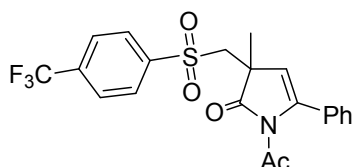


White solid; mp 149.1-150 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.5$  Hz, 2H), 7.52 (d,  $J = 8.5$  Hz, 2H), 7.40 – 7.34 (m, 3H), 7.22 (dd,  $J = 6.6, 2.9$  Hz, 2H), 5.49 (s, 1H), 3.70 (d,  $J = 14.4$  Hz, 1H), 3.46 (d,  $J = 14.4$  Hz, 1H), 2.52 (s, 3H), 1.40 (s, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.40, 169.25, 143.16, 139.07, 138.62, 132.45, 129.49, 128.65, 127.99, 126.68, 115.15, 102.05, 77.23, 77.02, 76.81, 62.11, 47.73, 26.03, 24.58.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{20}\text{H}_{18}\text{NO}_4\text{SiNa}$   $[\text{M}+\text{Na}]^+$  517.9893, found: 517.9898.

**1-acetyl-3-methyl-5-phenyl-3-((4-(trifluoromethyl)phenylsulfonyl)methyl)-1H-pyrrol-2(3H)-one (4d)**

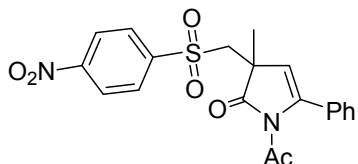


White solid; mp 124.1-125.2 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.2$  Hz, 2H), 7.75 (d,  $J = 8.2$  Hz, 2H), 7.43 – 7.31 (m, 3H), 7.21 (dd,  $J = 6.4, 2.7$  Hz, 2H), 5.47 (s, 1H), 3.74 (d,  $J = 14.4$  Hz, 1H), 3.52 (d,  $J = 14.4$  Hz, 1H), 2.52 (s, 3H), 1.42 (s, 3H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.34, 169.27, 143.39, 142.99, 132.37, 128.86, 128.75, 128.03, 126.64, 126.51, 126.49, 114.96, 62.12, 47.74, 26.03, 24.54.  $^{19}\text{F}$  NMR (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.29.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{21}\text{H}_{18}\text{NF}_3\text{O}_4\text{SNa}$   $[\text{M}+\text{Na}]^+$  460.0801, found: 460.0805.

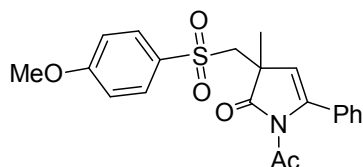
**1-acetyl-3-methyl-3-((4-nitrophenylsulfonyl)methyl)-5-phenyl-1H-pyrrol-2(3H)-one (4e)**



Yellow solid; mp 69.3-70 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 7.40 – 7.36 (m, 3H), 7.25 – 7.21 (m, 2H), 5.45 (s, 1H), 3.75 (d, *J* = 14.4 Hz, 1H), 3.54 (d, *J* = 14.4 Hz, 1H), 2.56 (s, 3H), 1.43 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.31, 169.28, 150.89, 145.10, 143.68, 132.30, 129.64, 128.83, 128.09, 126.60, 124.47, 114.68, 62.21, 47.77, 26.07, 24.41.

HRMS (ESI, *m/z*): Calcd. For C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>SNa [M+Na]<sup>+</sup> 437.0778, found: 517.9898.

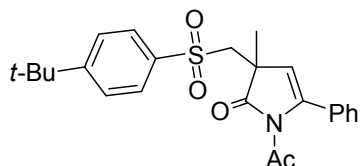
**1-acetyl-3-((4-methoxyphenylsulfonyl)methyl)-3-methyl-5-phenyl-1H-pyrrol-2(3H)-one (4f)**



White solid; mp 125.1-125.8 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.9 Hz, 2H), 7.36 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.26 – 7.22 (m, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.50 (s, 1H), 3.84 (s, 3H), 3.70 (d, *J* = 14.4 Hz, 1H), 3.45 (d, *J* = 14.4 Hz, 1H), 2.50 (s, 3H), 1.39 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.59, 169.29, 163.89, 142.77, 132.70, 130.86, 130.45, 128.48, 127.89, 126.75, 115.66, 114.44, 62.33, 55.72, 47.79, 26.04, 24.64.

HRMS (ESI, *m/z*): Calcd. For C<sub>21</sub>H<sub>21</sub>NO<sub>5</sub>SNa [M+Na]<sup>+</sup> 422.1033, found: 422.1038.

**1-acetyl-3-((4-tert-butylphenylsulfonyl)methyl)-3-methyl-5-phenyl-1H-pyrrol-2(3H)-one (4g)**

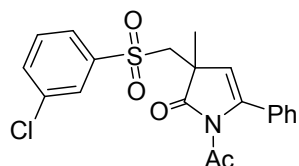


White solid; mp 146.1-147 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.33 (m, 3H), 7.21 (dd, *J* = 6.4, 2.8 Hz, 2H), 5.45 (s, 1H), 3.71 (d, *J* = 14.4 Hz, 1H), 3.48 (d, *J* = 14.5 Hz, 1H), 2.50 (s, 3H), 1.40 (s, 3H),

1.32 (s, 9H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.59, 169.24, 157.95, 142.85, 136.50, 132.67, 128.49, 128.04, 127.88, 126.75, 126.33, 115.57, 62.10, 47.76, 35.28, 31.03, 26.08, 24.54.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{24}\text{H}_{27}\text{NSO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  448.1553, found: 448.1556.

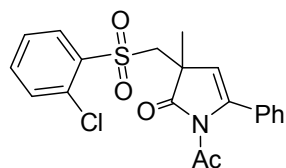
**1-acetyl-3-((3-chlorophenylsulfonyl)methyl)-3-methyl-5-phenyl-1H-pyrrol-2(3H)-one (4h)**



White solid; mp 125.1-125.6 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (s, 1H), 7.72 (d,  $J = 7.8$  Hz, 1H), 7.60 (d,  $J = 8.0$  Hz, 1H), 7.43 (t,  $J = 7.9$  Hz, 1H), 7.39 – 7.34 (m, 3H), 7.26 – 7.21 (m, 2H), 5.50 (s, 1H), 3.71 (d,  $J = 14.4$  Hz, 1H), 3.50 (d,  $J = 14.4$  Hz, 1H), 2.55 (s, 3H), 1.42 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.48, 169.27, 143.40, 141.35, 135.60, 134.15, 132.48, 130.64, 128.63, 128.16, 127.99, 126.74, 126.29, 114.93, 62.17, 47.77, 26.09, 24.47.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{20}\text{H}_{18}\text{NCISO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  426.0537, found: 426.0540.

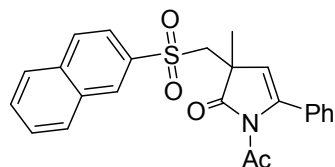
**1-acetyl-3-((2-chlorophenylsulfonyl)methyl)-3-methyl-5-phenyl-1H-pyrrol-2(3H)-one (4i)**



White solid; mp 120.6-121.2 °C;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (dd,  $J = 7.9, 0.9$  Hz, 1H), 7.57 – 7.50 (m, 2H), 7.37 – 7.30 (m, 3H), 7.27 (d,  $J = 1.5$  Hz, 1H), 7.26 – 7.24 (m, 1H), 7.14 (dd,  $J = 6.4, 3.0$  Hz, 2H), 5.31 (s, 1H), 3.93 (s, 2H), 2.54 (s, 3H), 1.42 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  179.41, 169.33, 143.29, 137.17, 134.92, 132.69, 132.56, 131.87, 128.54, 127.88, 127.48, 126.59, 115.09, 60.16, 47.71, 26.02, 24.38.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{20}\text{H}_{18}\text{NCISO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  426.0537, found: 426.0540.

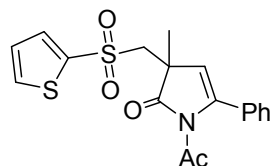
**1-acetyl-3-methyl-3-((naphthalen-2-ylsulfonyl)methyl)-5-phenyl-1H-pyrrol-2(3H)-one (4j)**



White solid; mp 181.2-181.9 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.35 (d, *J* = 1.3 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.69 – 7.63 (m, 1H), 7.62 – 7.55 (m, 1H), 7.37 – 7.29 (m, 3H), 7.21 – 7.15 (m, 2H), 5.44 (s, 1H), 3.81 (d, *J* = 14.5 Hz, 1H), 3.56 (d, *J* = 14.6 Hz, 1H), 2.43 (s, 3H), 1.40 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.55, 169.29, 143.12, 136.24, 135.32, 132.61, 131.93, 130.28, 129.66, 129.54, 128.53, 127.92, 127.90, 127.76, 126.72, 122.58, 115.27, 62.10, 47.86, 25.92, 24.59.

HRMS (ESI, *m/z*): Calcd. For C<sub>24</sub>H<sub>21</sub>NSO<sub>4</sub>Na[M+Na]<sup>+</sup> 442.1083, found: 442.1086.

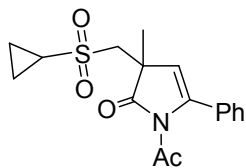
**1-acetyl-3-methyl-5-phenyl-3-((thiophen-2-ylsulfonyl)methyl)-1H-pyrrol-2(3H)-one (4k)**



White solid; mp 95.9-96.6 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.70 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.62 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.36 (dd, *J* = 5.0, 1.7 Hz, 3H), 7.26 (dd, *J* = 5.7, 3.9 Hz, 3H), 7.08 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.59 (s, 1H), 3.82 (d, *J* = 14.4 Hz, 1H), 3.59 (d, *J* = 14.4 Hz, 1H), 2.53 (s, 3H), 1.43 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 179.45, 169.27, 143.14, 140.68, 134.68, 134.59, 132.60, 128.56, 127.92, 126.83, 115.19, 63.57, 47.89, 26.10, 24.46.

HRMS (ESI, *m/z*): Calcd. For C<sub>18</sub>H<sub>17</sub>NS<sub>2</sub>O<sub>4</sub>Na[M+Na]<sup>+</sup> 398.0491, found: 398.0495.

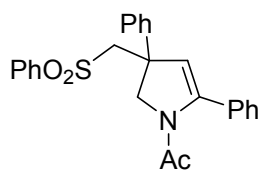
**1-acetyl-3-(cyclopropylsulfonylmethyl)-3-methyl-5-phenyl-1H-pyrrol-2(3H)-one (4l)**



Amorphous solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.31 (m, 3H), 7.30 – 7.27 (m, 2H), 5.72 (s, 1H), 3.62 (d,  $J = 14.0$  Hz, 1H), 3.41 (d,  $J = 14.0$  Hz, 1H), 2.57 (s, 3H), 2.41 – 2.34 (m, 1H), 1.46 (s, 3H), 1.27 (dd,  $J = 9.5, 4.0$  Hz, 1H), 1.20 (dd,  $J = 4.6, 2.3$  Hz, 1H), 1.02 (dd,  $J = 6.3, 3.5$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  179.95, 169.40, 143.36, 132.75, 128.53, 127.94, 126.93, 115.42, 59.88, 47.50, 31.27, 26.13, 24.20, 5.37, 5.15.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{17}\text{H}_{19}\text{NSO}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  356.0927, found: 356.0930.

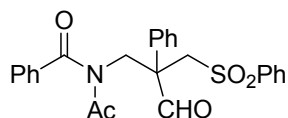
**1-(3,5-diphenyl-3-(phenylsulfonylmethyl)-2,3-dihydro-1H-pyrrol-1-yl)ethanone (3a)**



White solid; mp 44-46 °C;  $^1\text{H}$  NMR (600 MHz, DMSO)  $\delta$  7.72 – 7.56 (m, 3H), 7.47 (t,  $J = 7.8$  Hz, 2H), 7.26 (ddd,  $J = 32.1, 22.9, 10.4$  Hz, 10H), 5.82 (s, 1H), 4.59 (d,  $J = 11.6$  Hz, 1H), 4.19 (d,  $J = 11.6$  Hz, 1H), 4.13 (d,  $J = 15.0$  Hz, 1H), 4.09 (d,  $J = 15.0$  Hz, 1H), 1.77 (b, 3H).  $^{13}\text{C}$  NMR (151 MHz, DMSO)  $\delta$  167.95, 144.41, 143.32, 141.22, 133.72, 133.46, 129.53, 128.81, 127.84, 127.32, 126.97, 118.60, 63.84, 62.00, 50.40, 39.68, 24.49.

HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{25}\text{H}_{23}\text{NO}_3\text{SH}$   $[\text{M}+\text{H}]^+$  418.1477, found: 418.1472.

***N*-acetyl-*N*-(2-formyl-2-phenyl-3-(phenylsulfonyl)propyl)benzamide (B)**



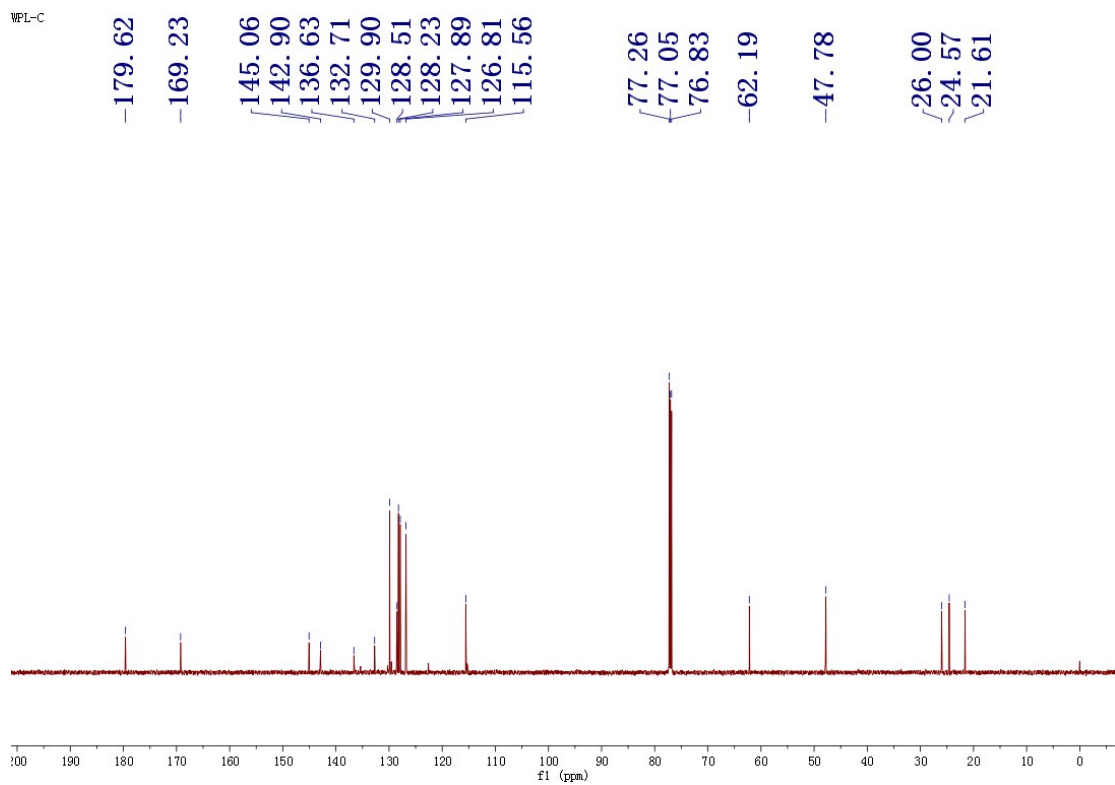
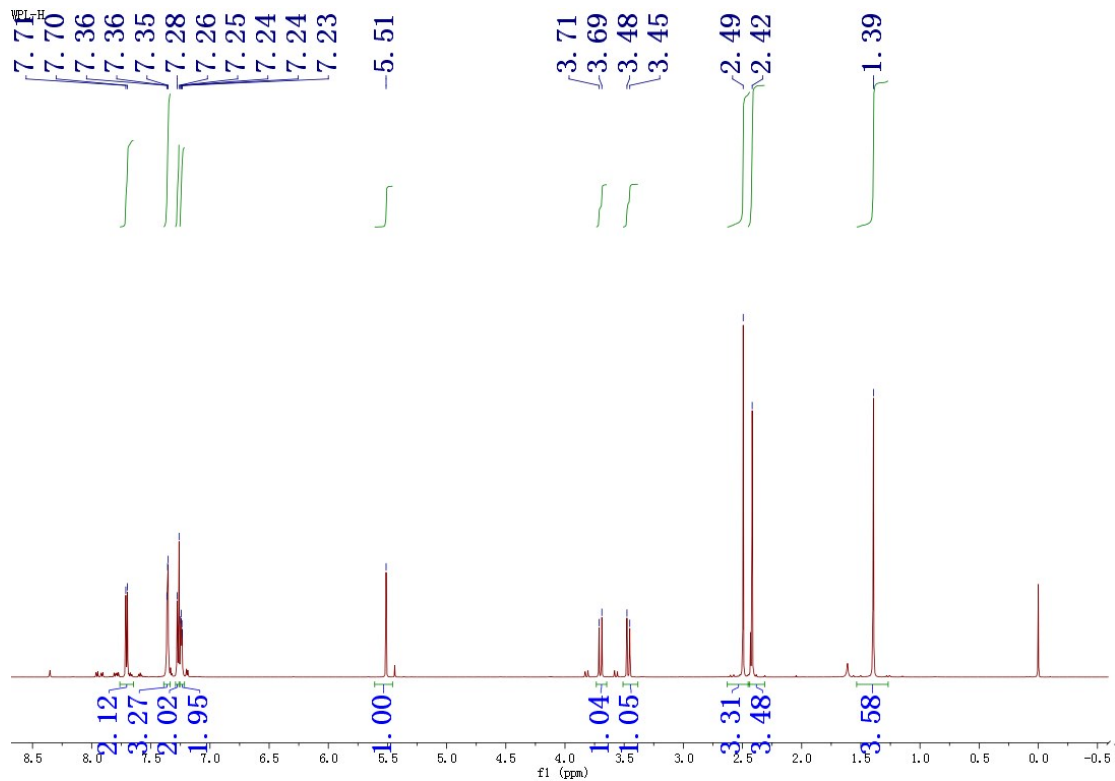
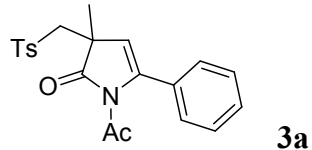
Amorphous solid;  $^1\text{H}$  NMR (600 MHz, DMSO)  $\delta$  9.81 (s, 1H), 7.66-7.58 (m, 2H), 7.56 (d,  $J = 7.6$  Hz, 2H), 7.47 (dd,  $J = 17.0, 8.0$  Hz, 4H), 7.43 (d,  $J = 7.4$  Hz, 2H), 7.25 - 7.07 (m, 5H), 4.51 (d,  $J = 14.3$  Hz, 1H), 4.43 (d,  $J = 14.3$  Hz, 1H), 4.37 (d,  $J =$

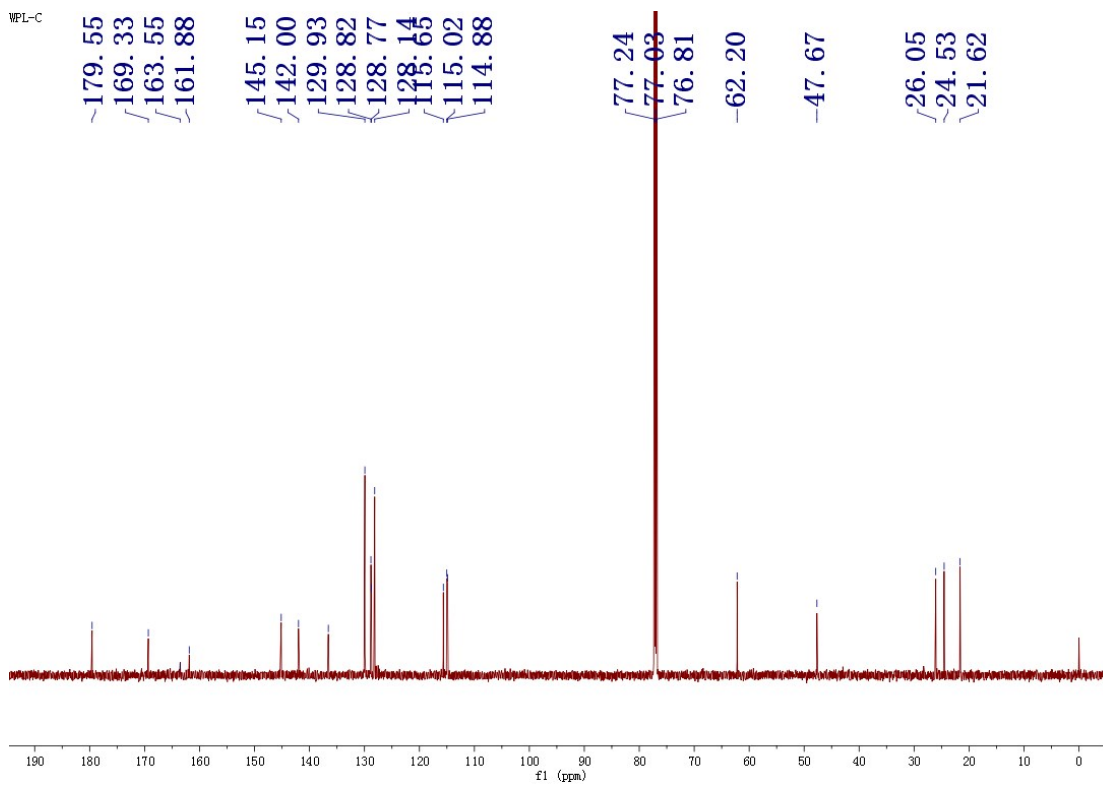
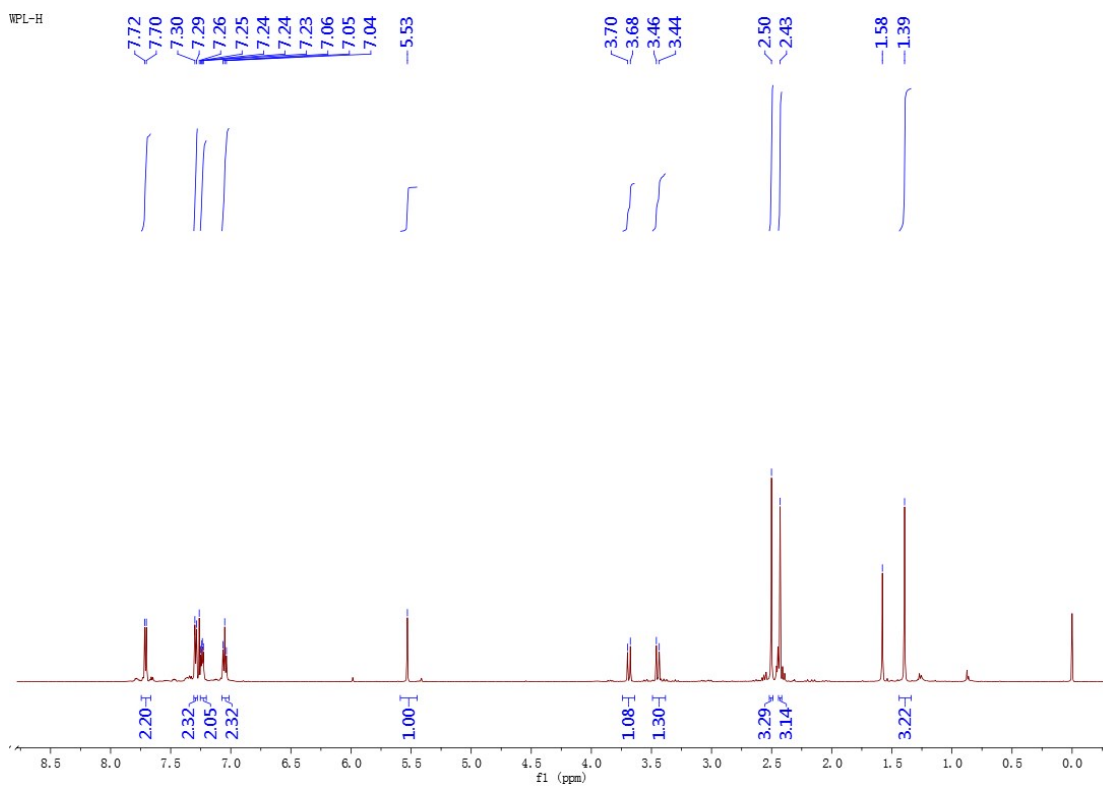
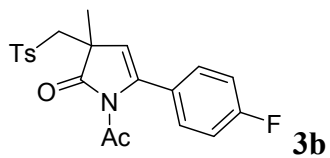
15.0 Hz, 1H), 4.17 (d,  $J = 15.0$  Hz, 1H), 1.74 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz, DMSO)  $\delta$  198.36, 174.29, 173.23, 141.05, 135.15, 134.11, 133.94, 133.40, 129.56, 129.39, 129.17, 128.78, 128.38, 127.62, 58.94, 56.82, 49.56, 25.97.

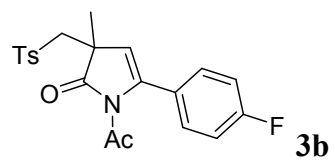
HRMS (ESI,  $m/z$ ): Calcd. For  $\text{C}_{25}\text{H}_{23}\text{NO}_5\text{SNa}$   $[\text{M}+\text{Na}]^+$  472.1189, found: 472.1184.



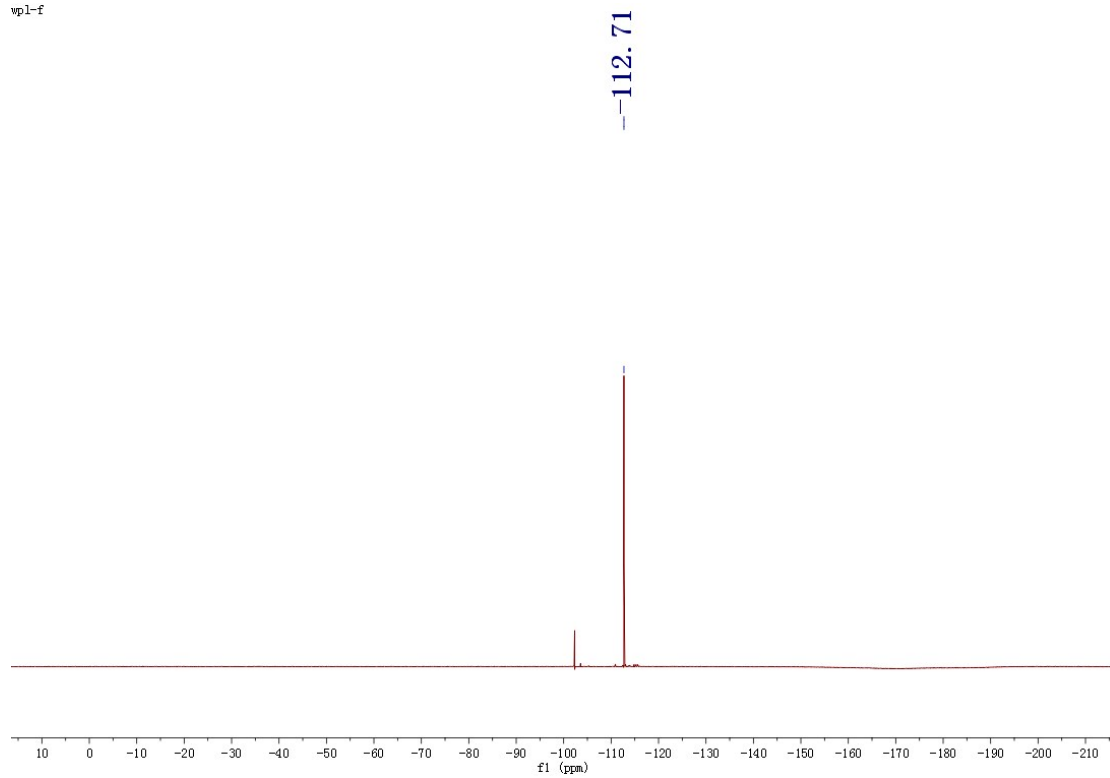
# NMR spectra

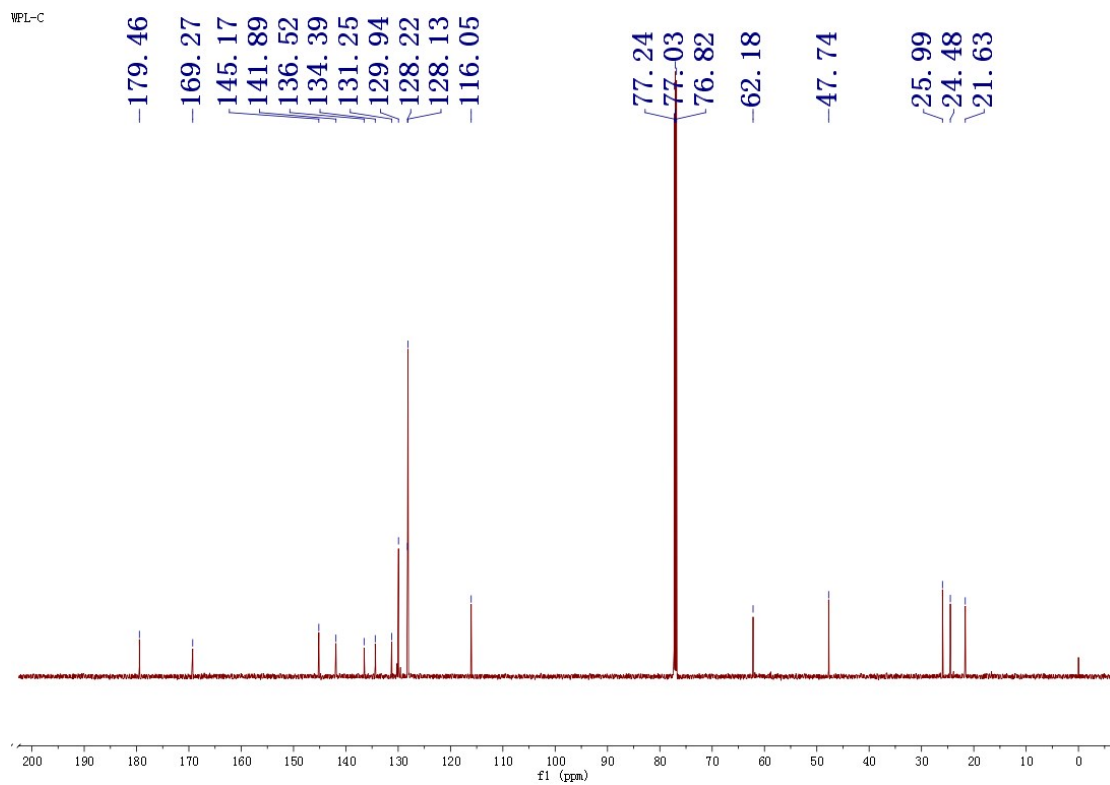
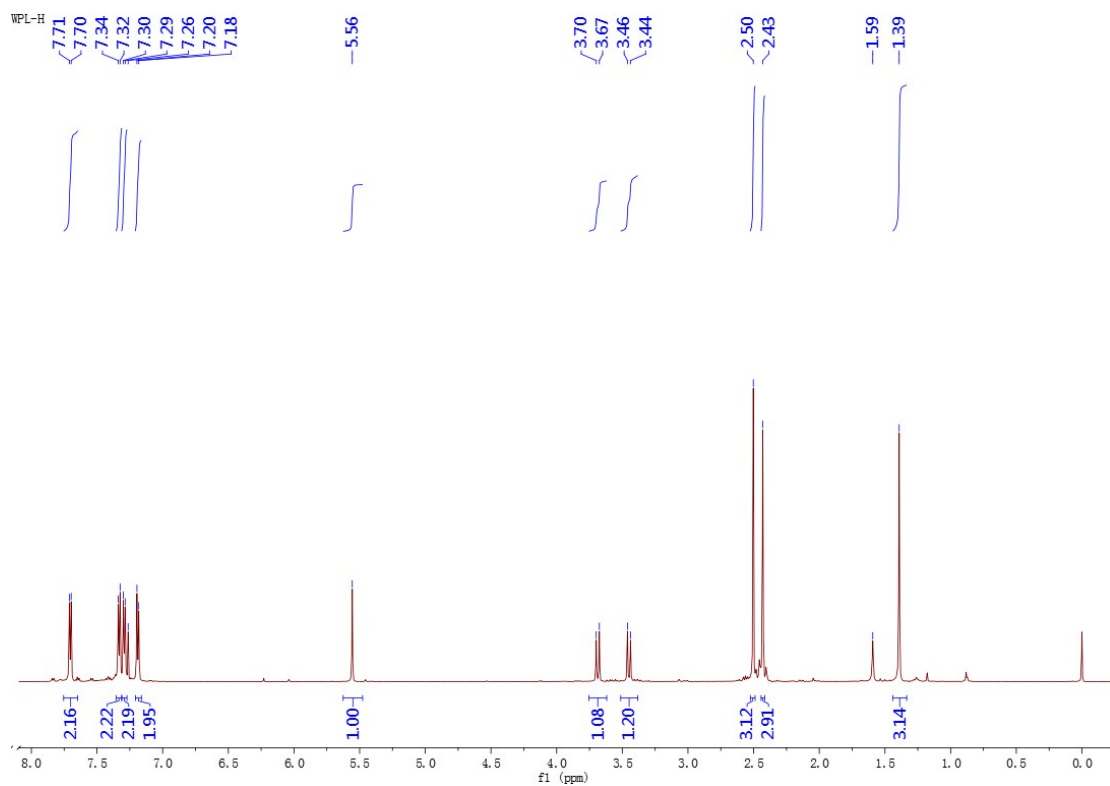
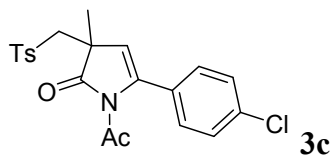


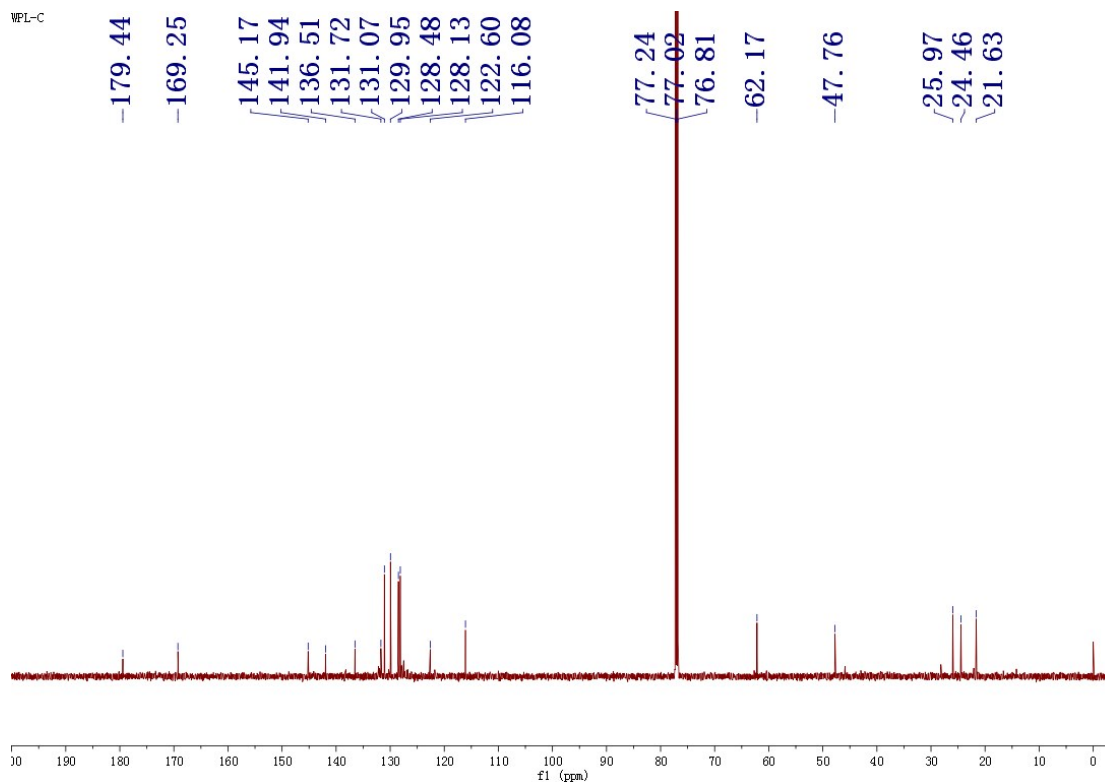
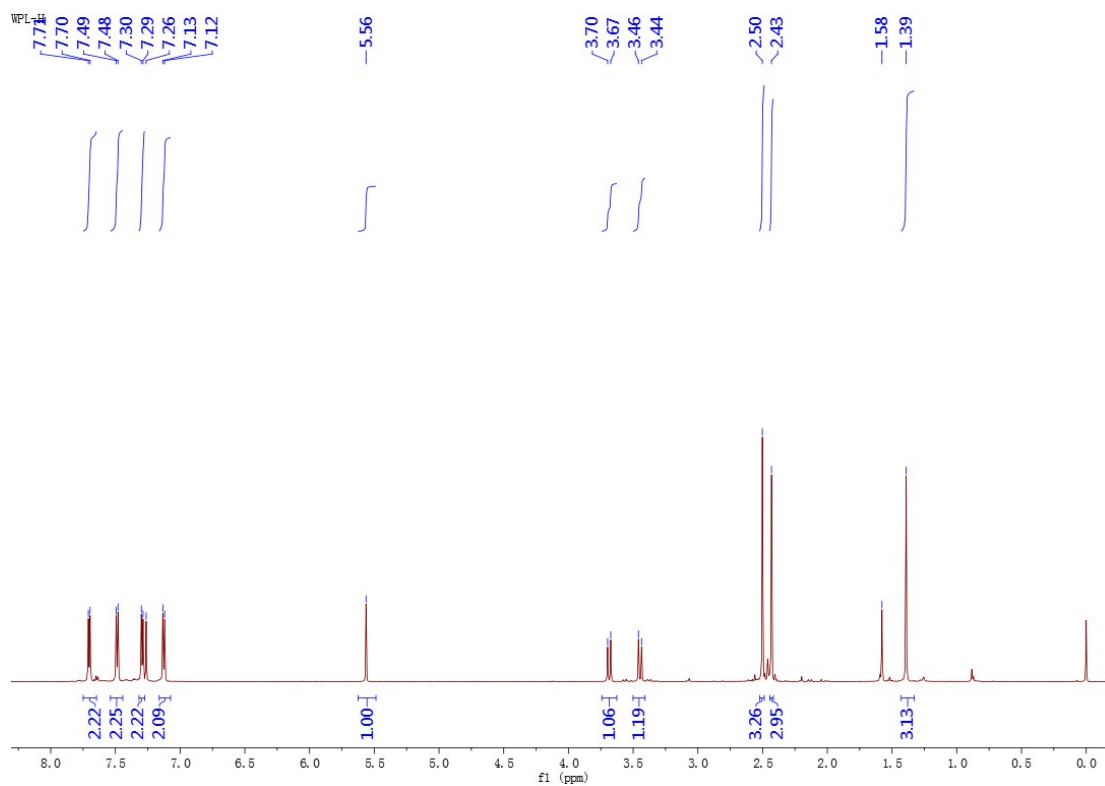
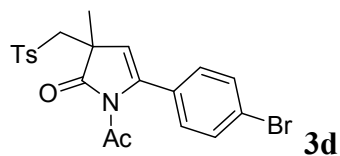


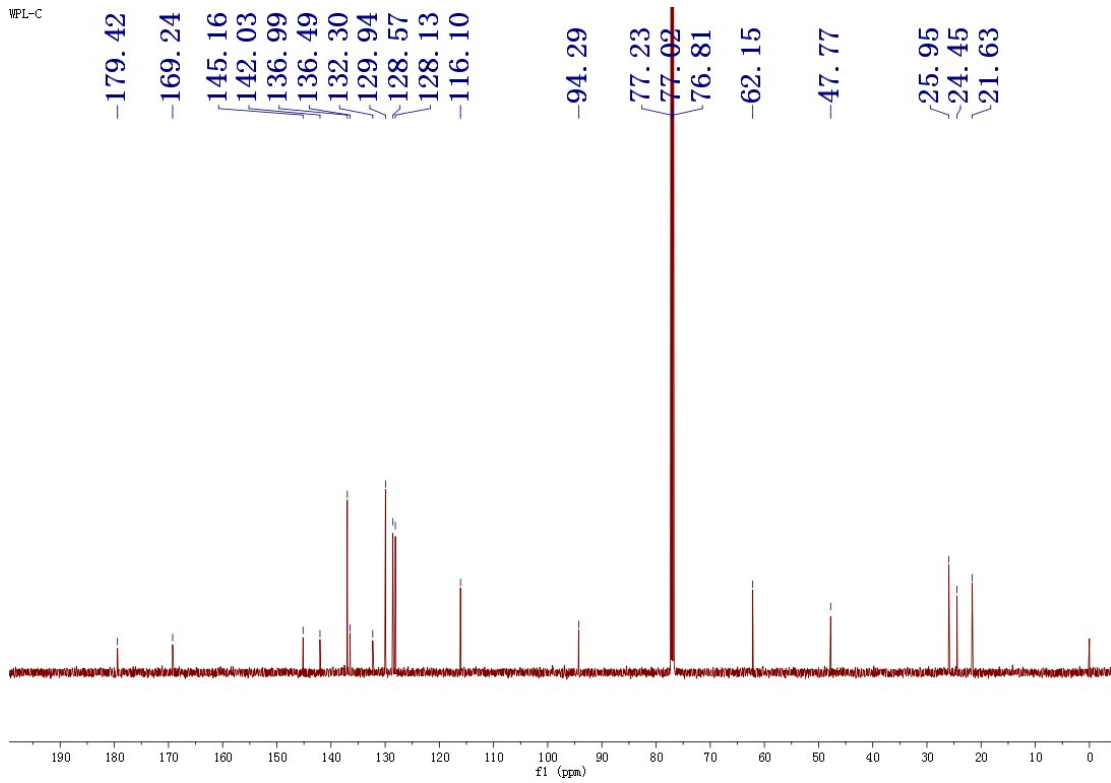
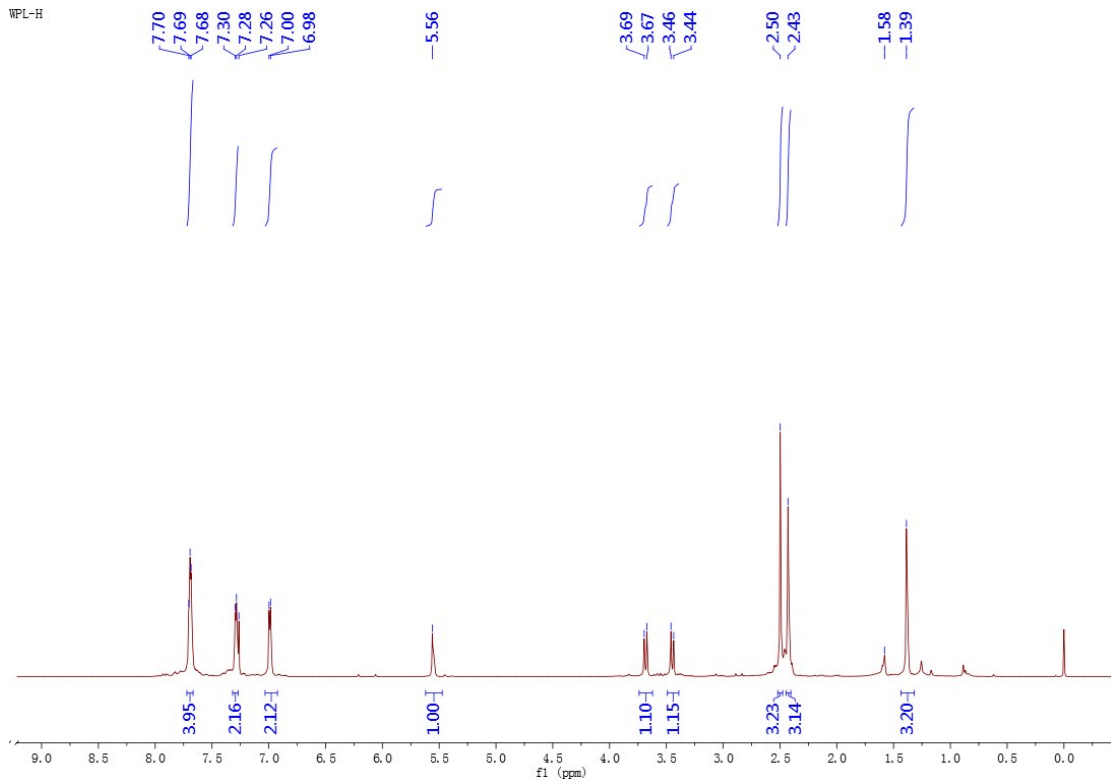
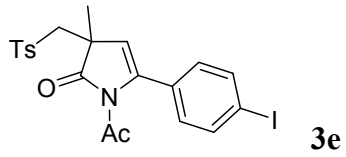


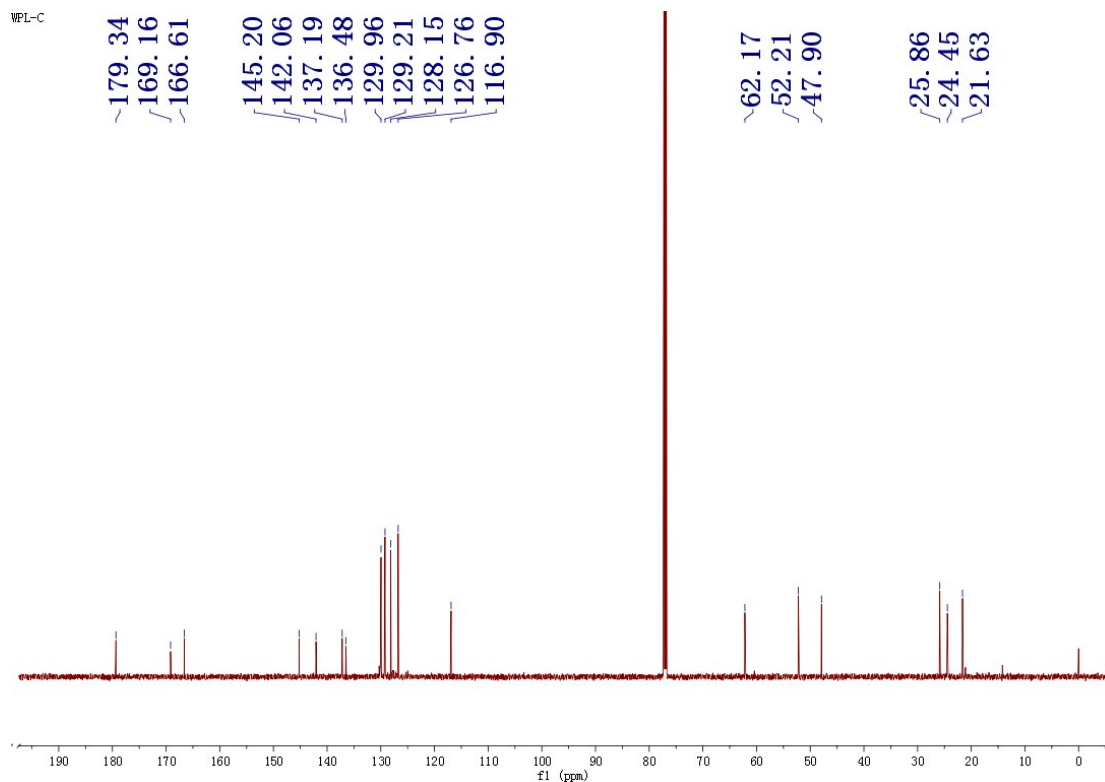
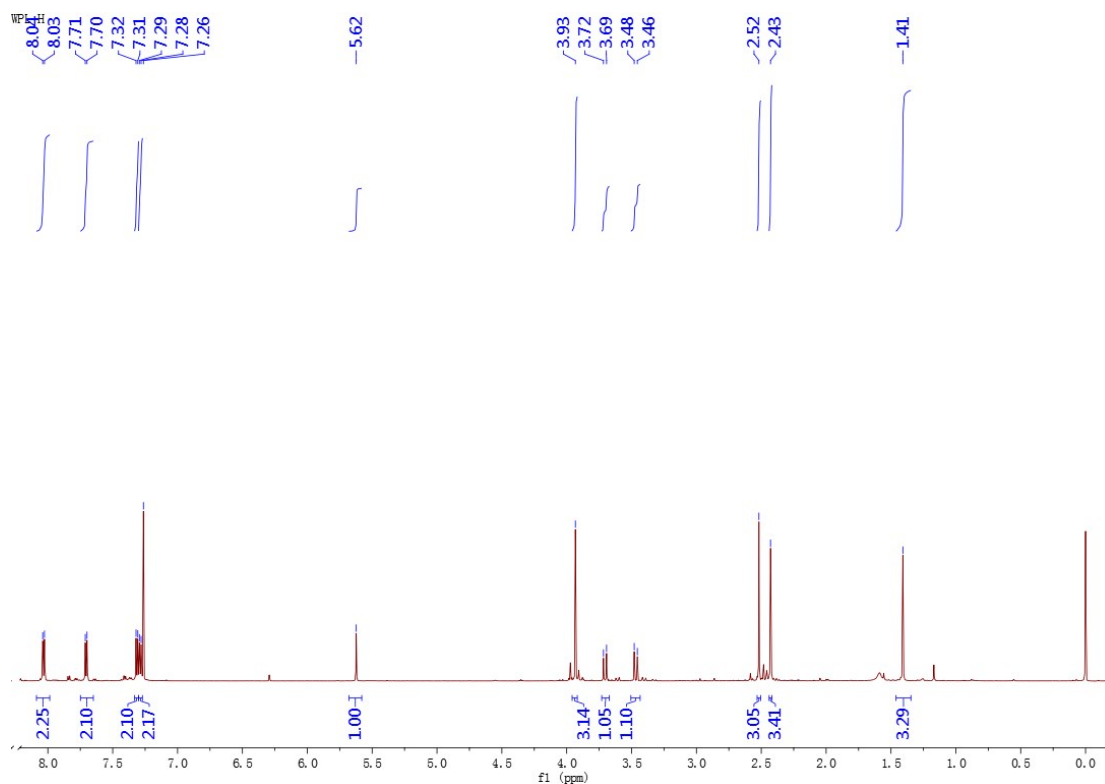
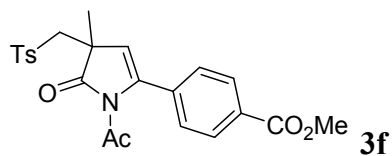
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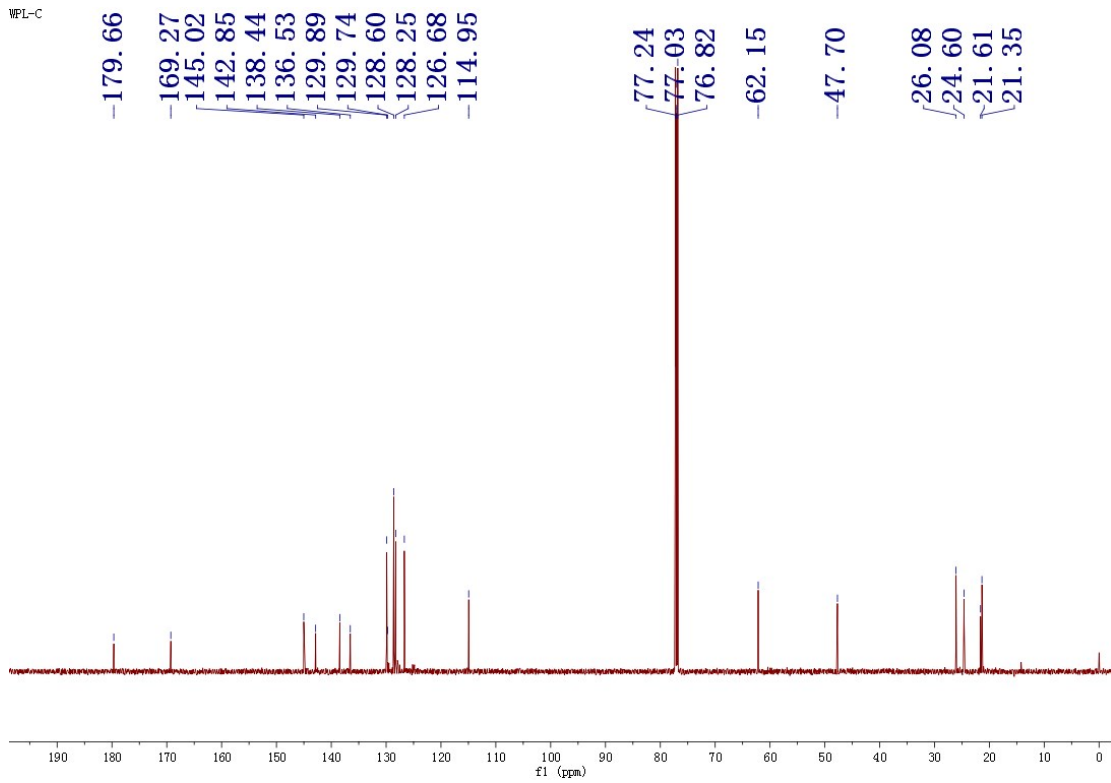
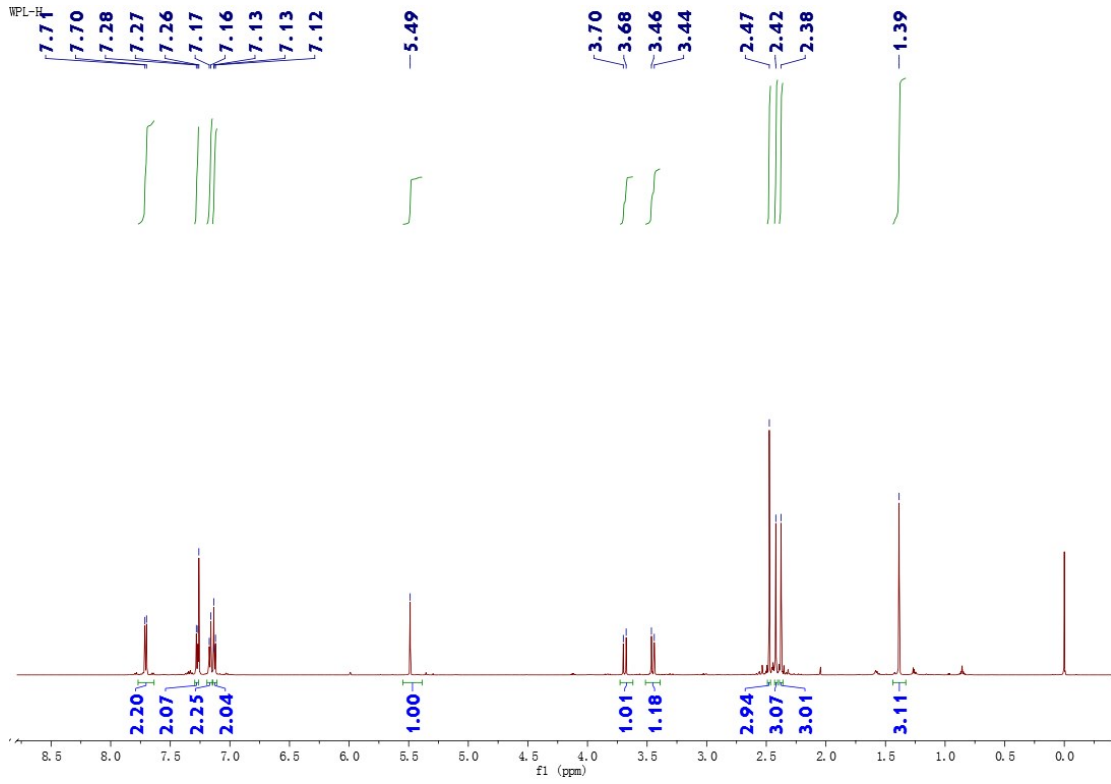
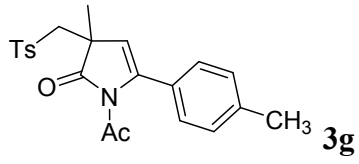




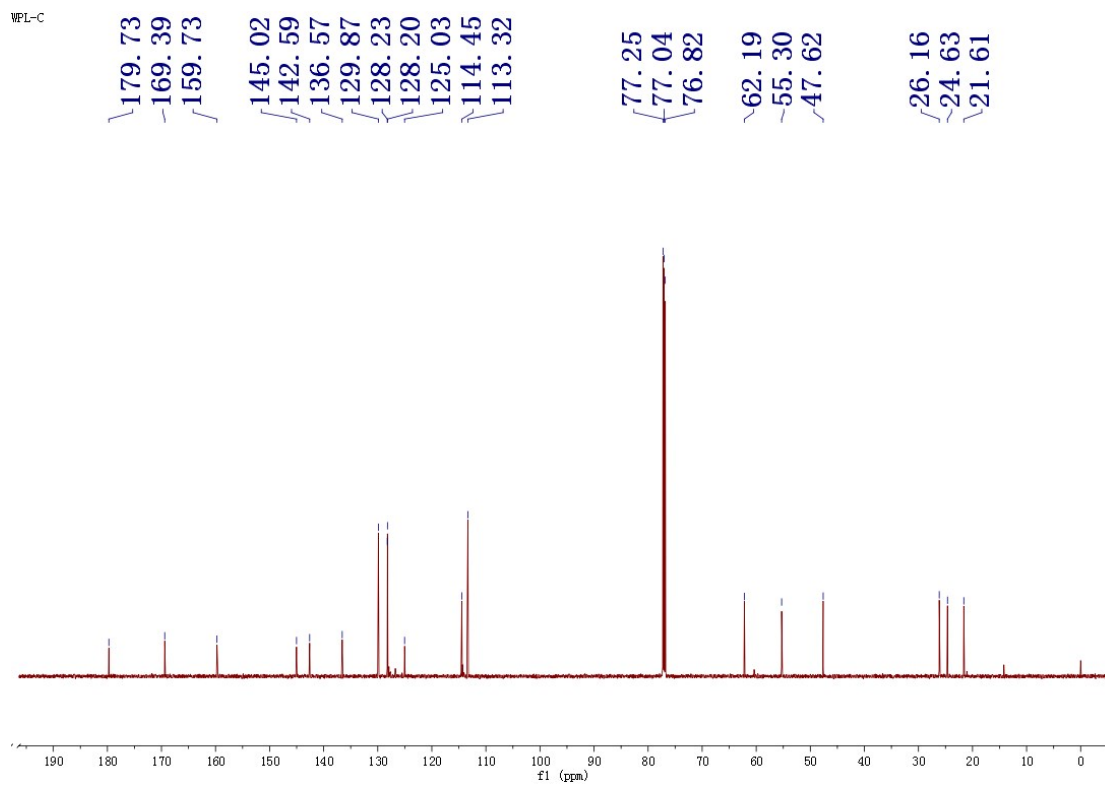
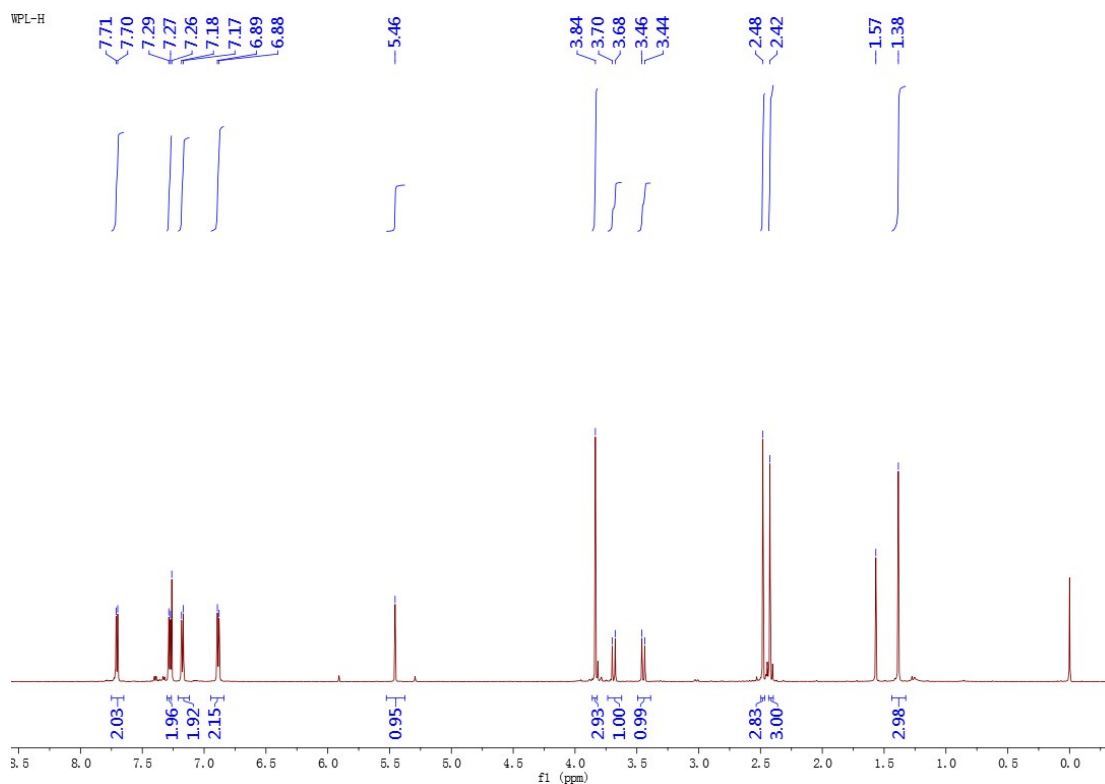
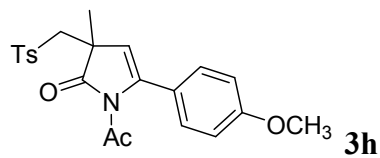


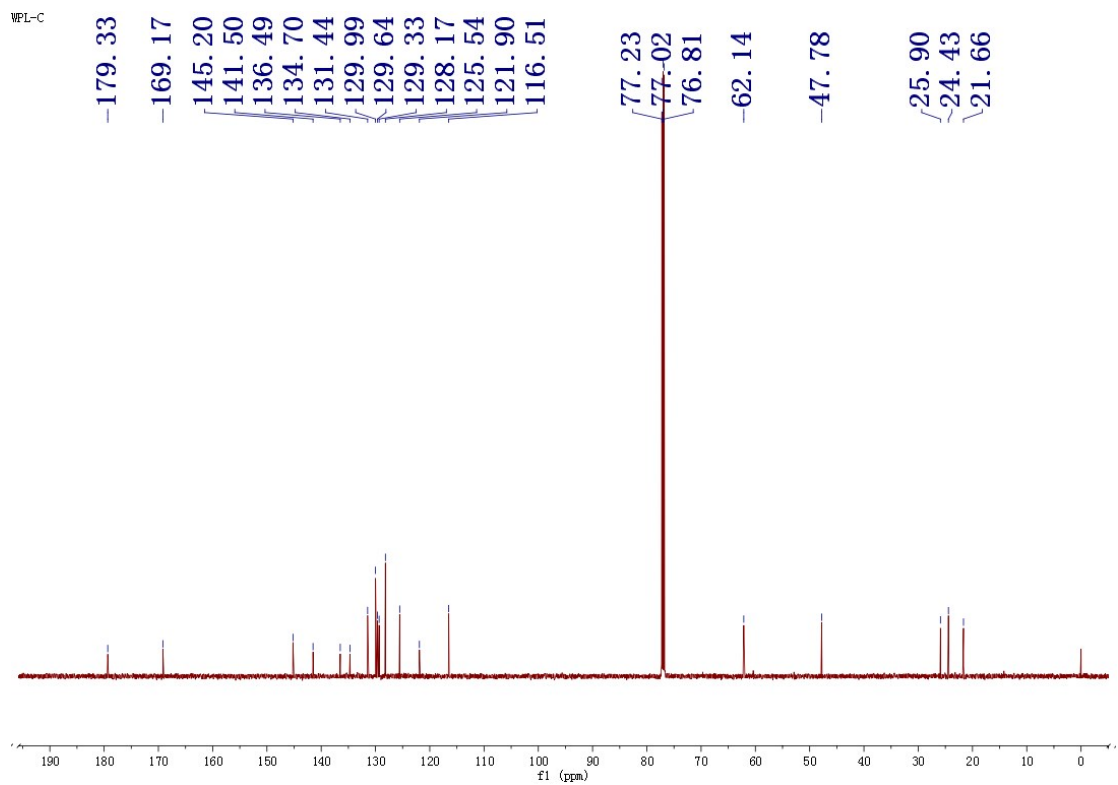
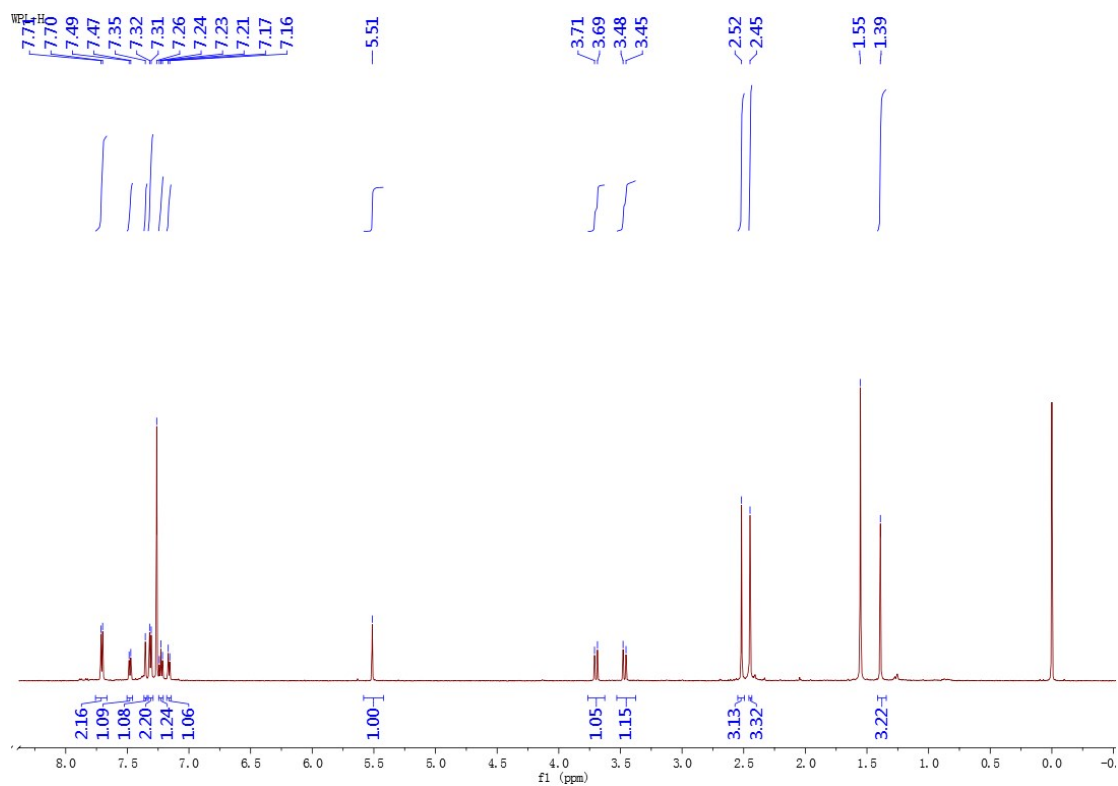
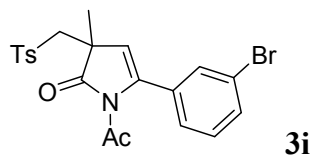


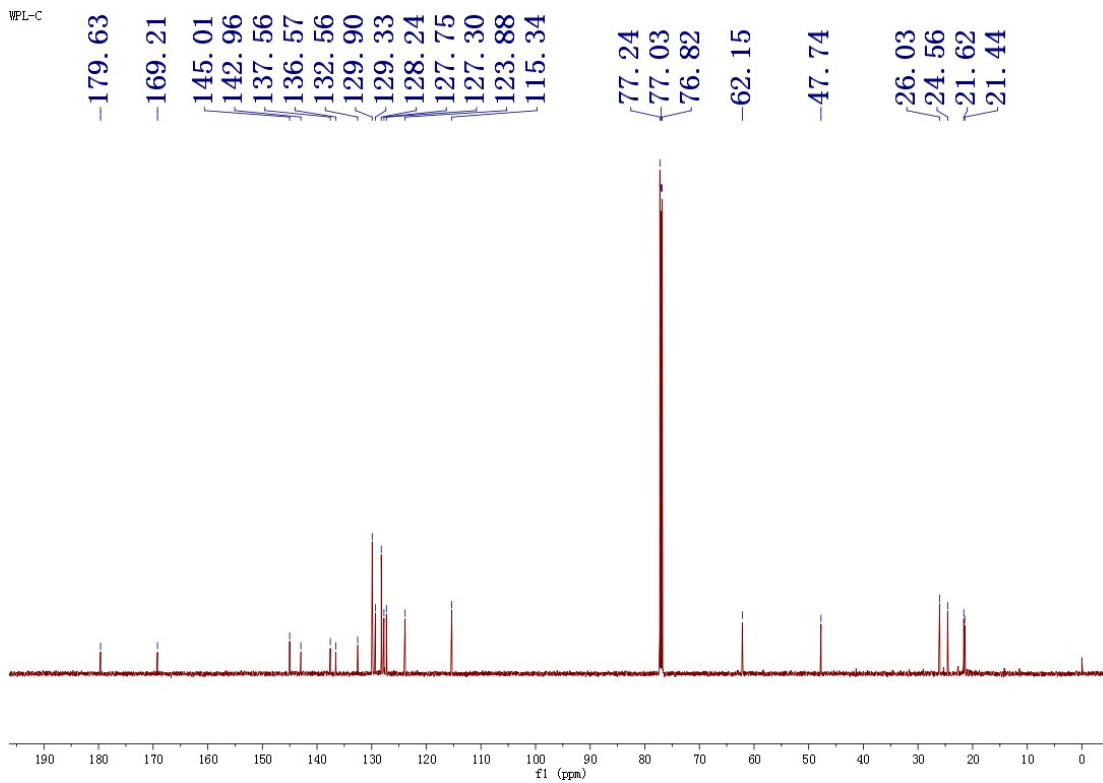
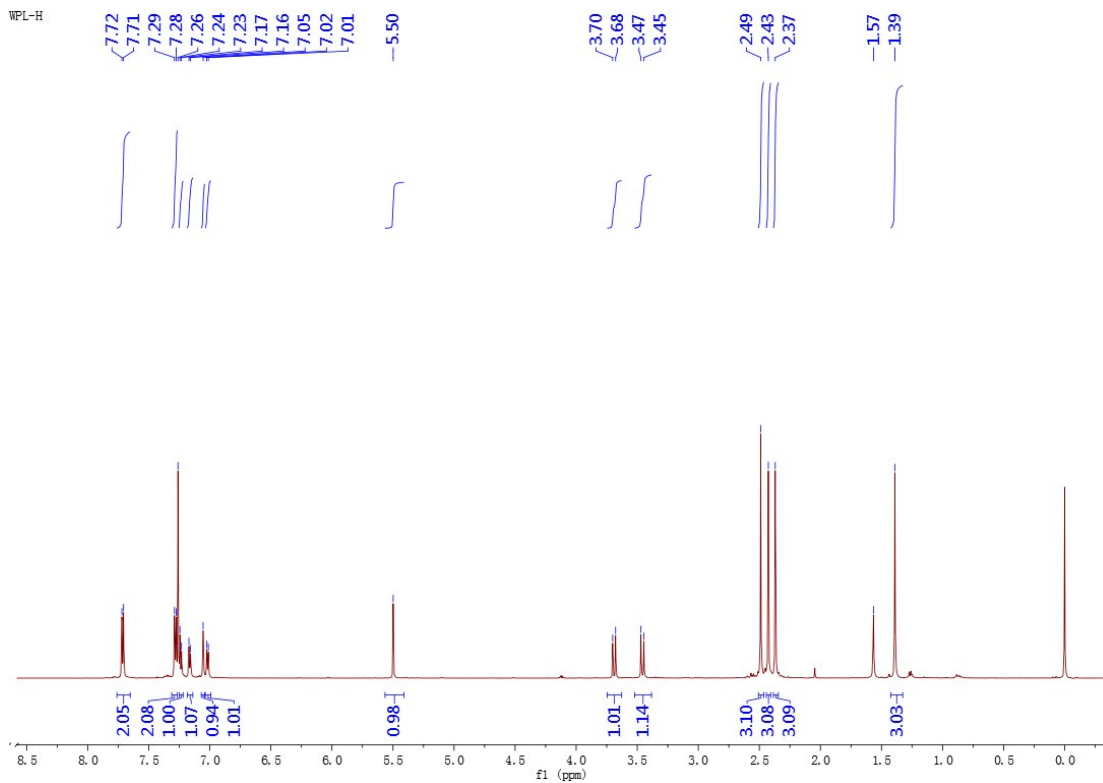
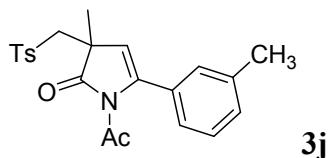


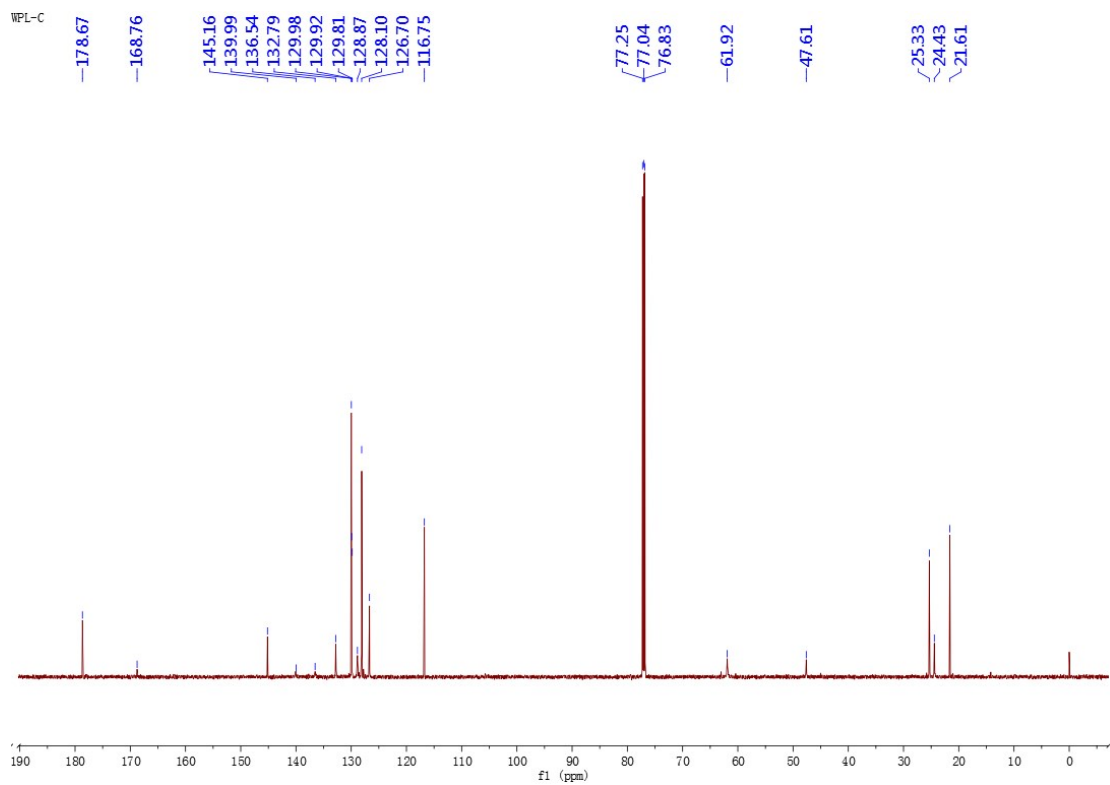
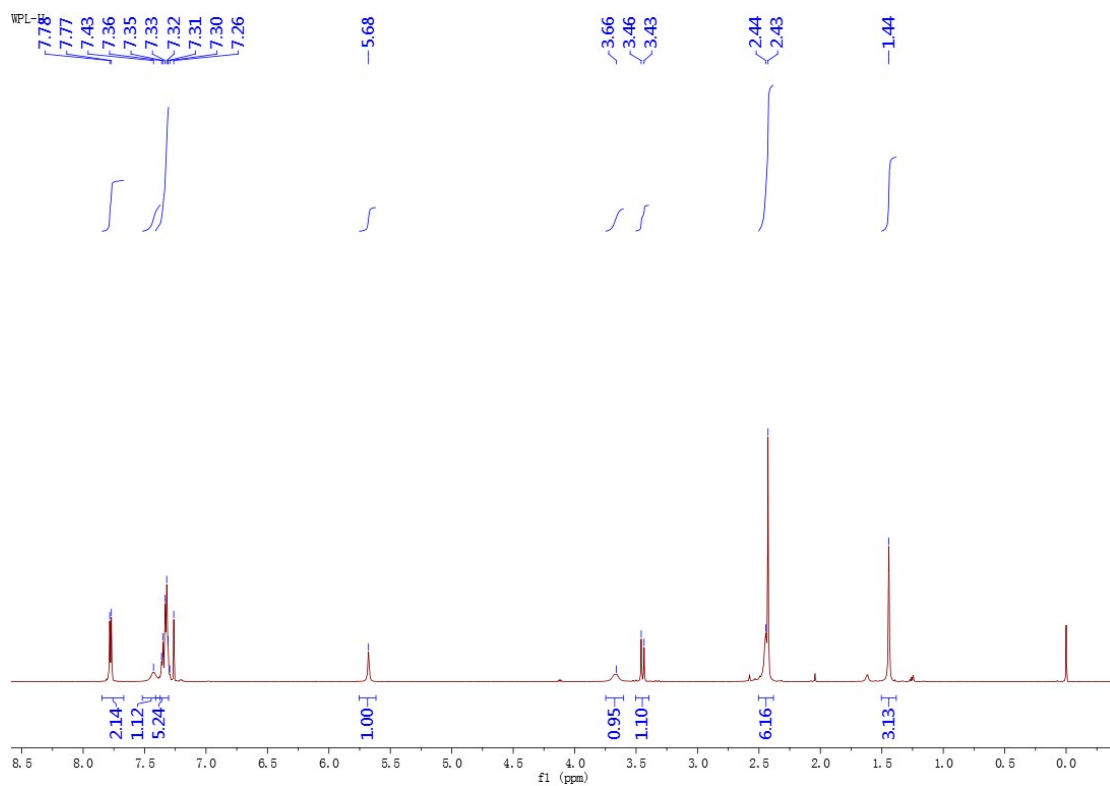
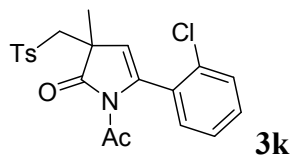


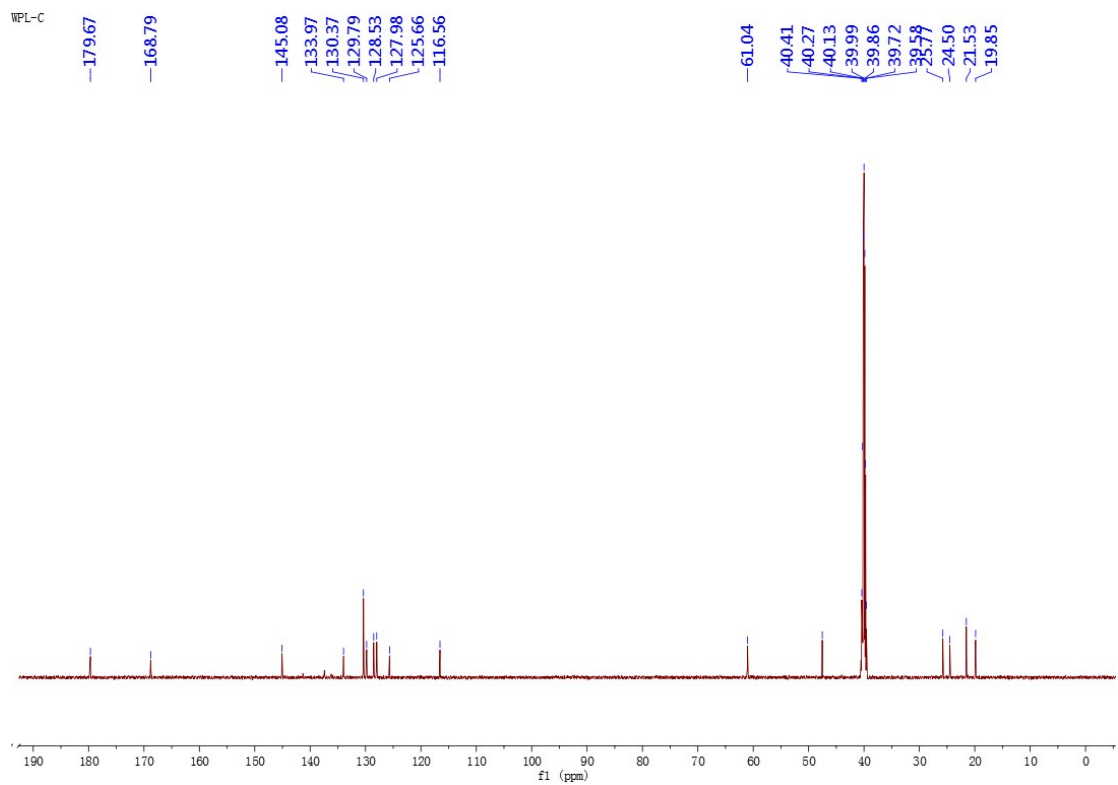
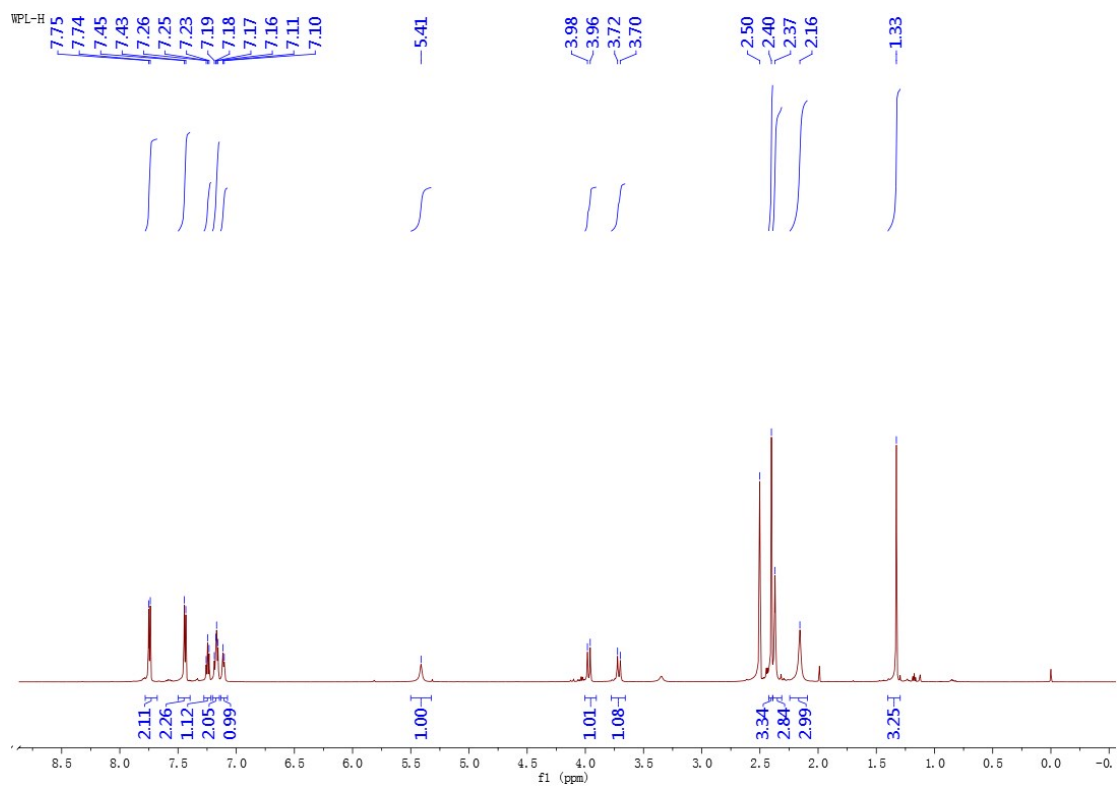
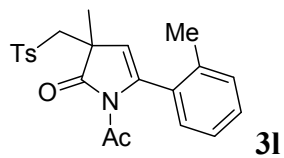


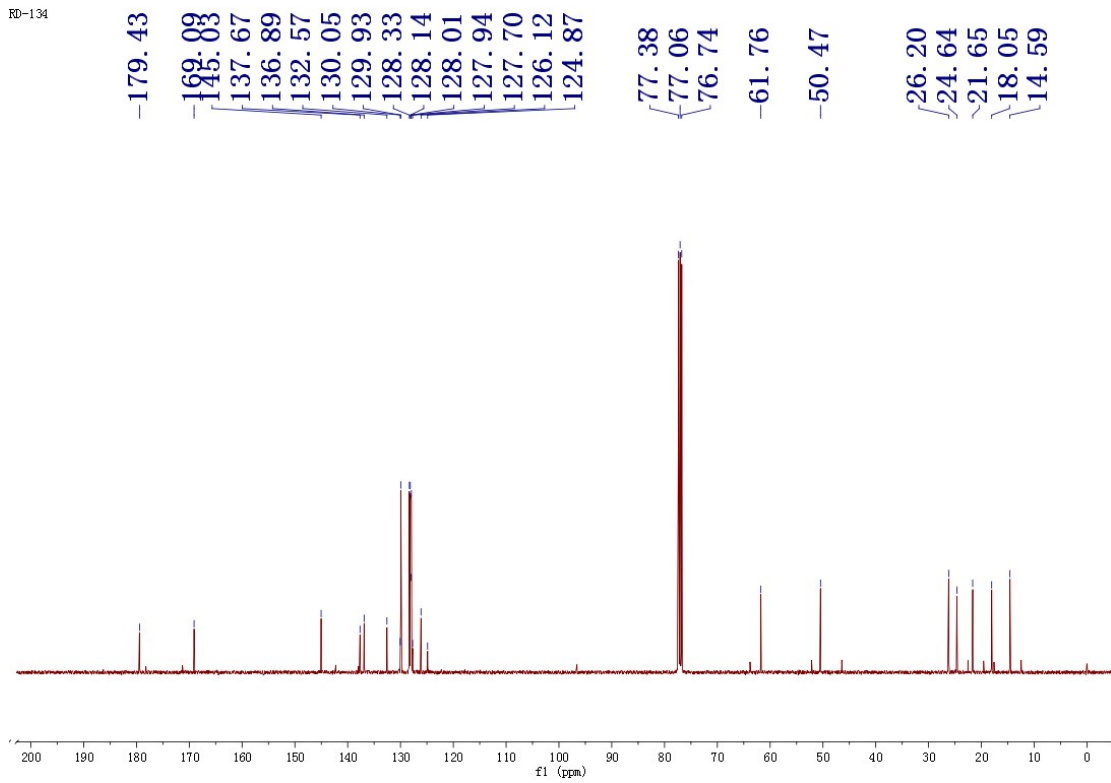
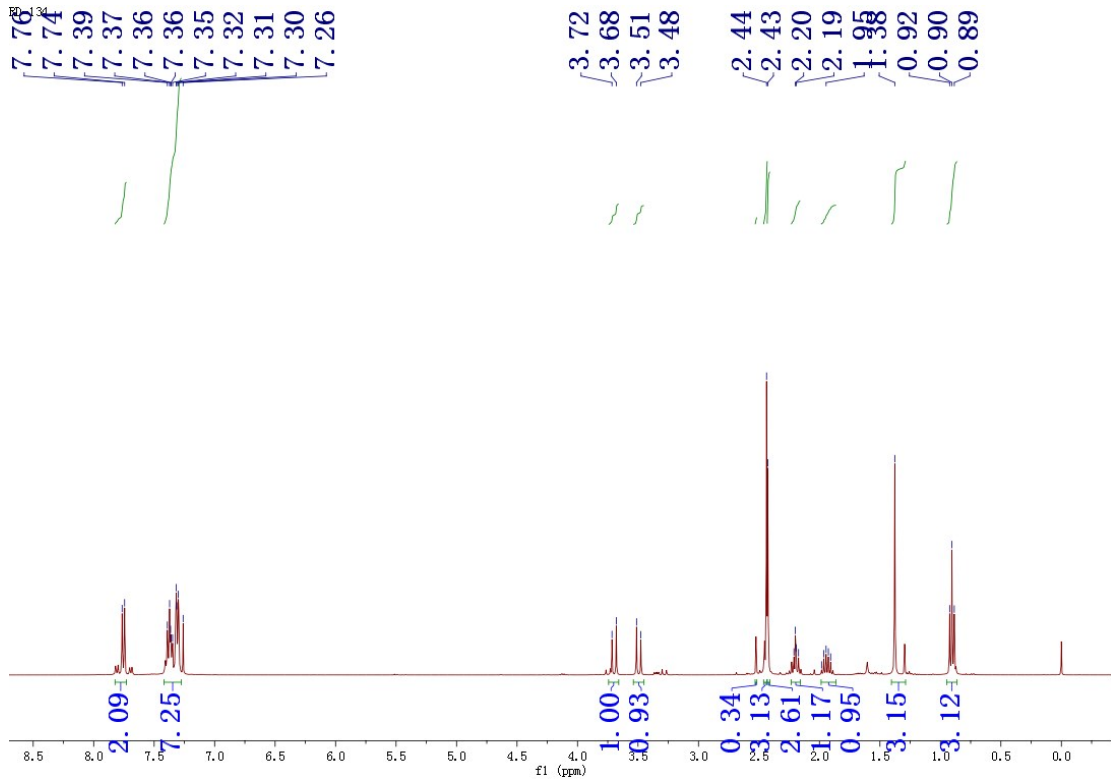
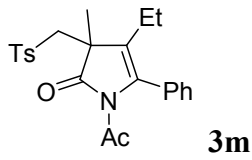


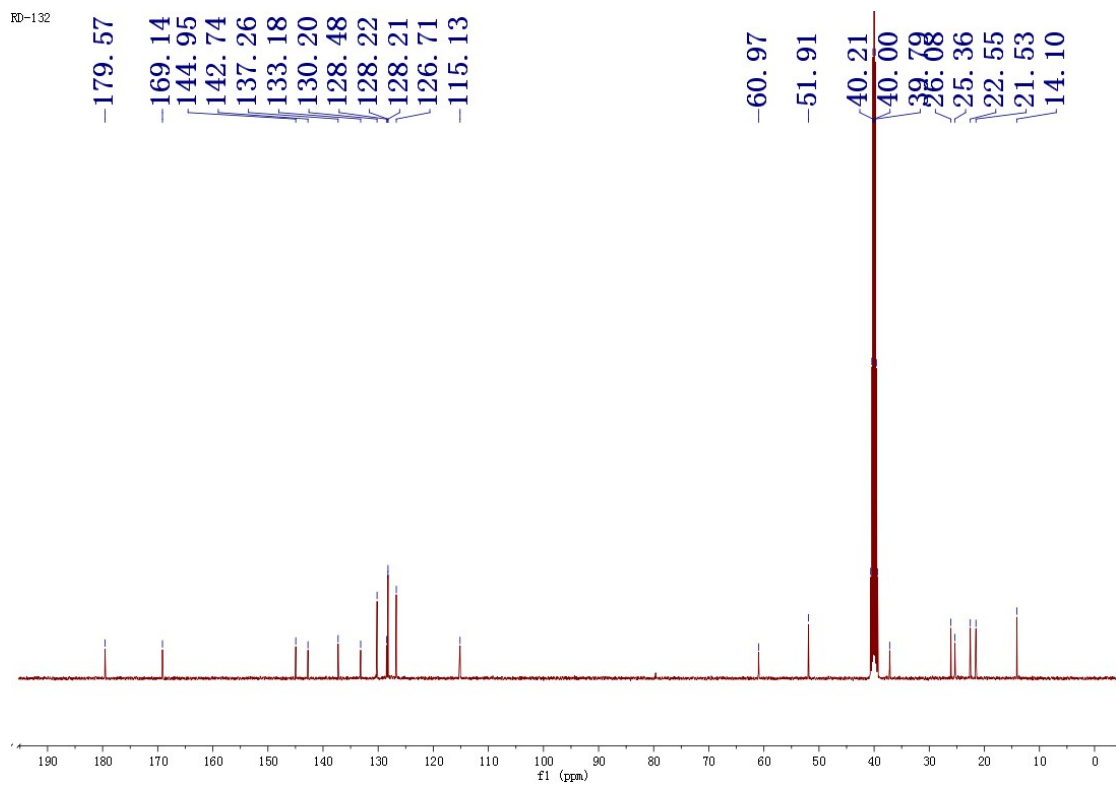
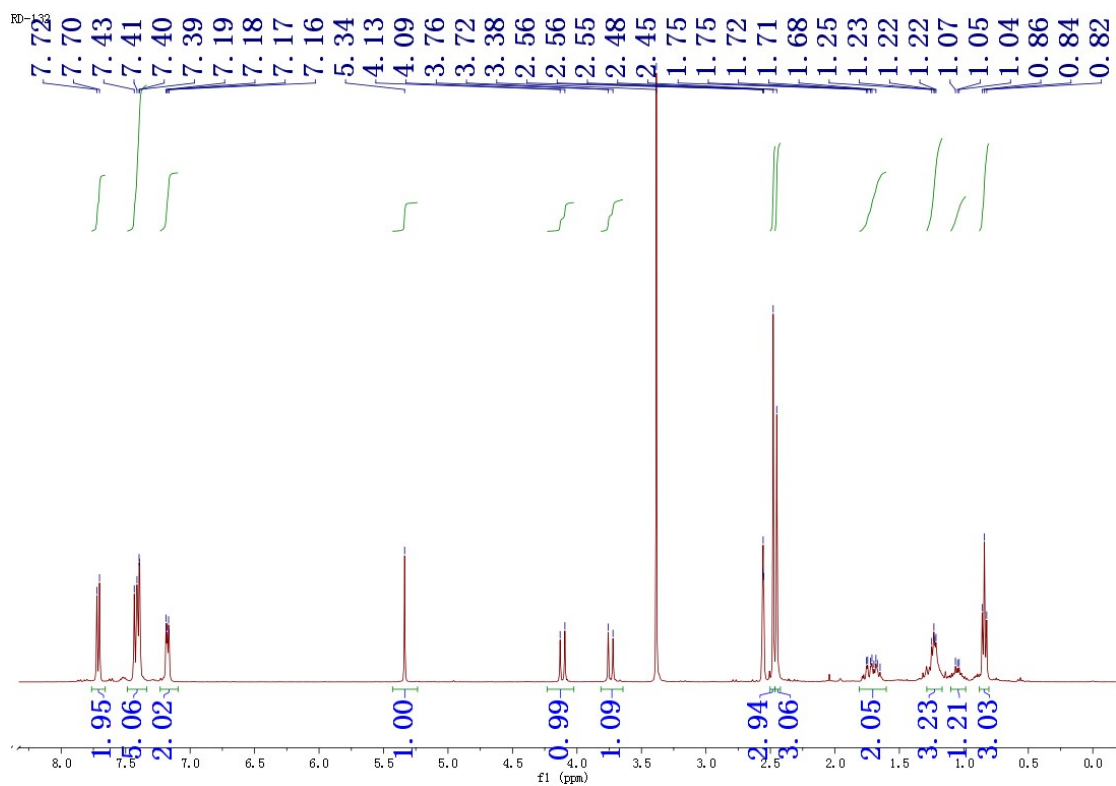
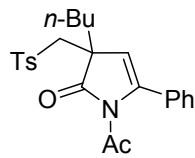


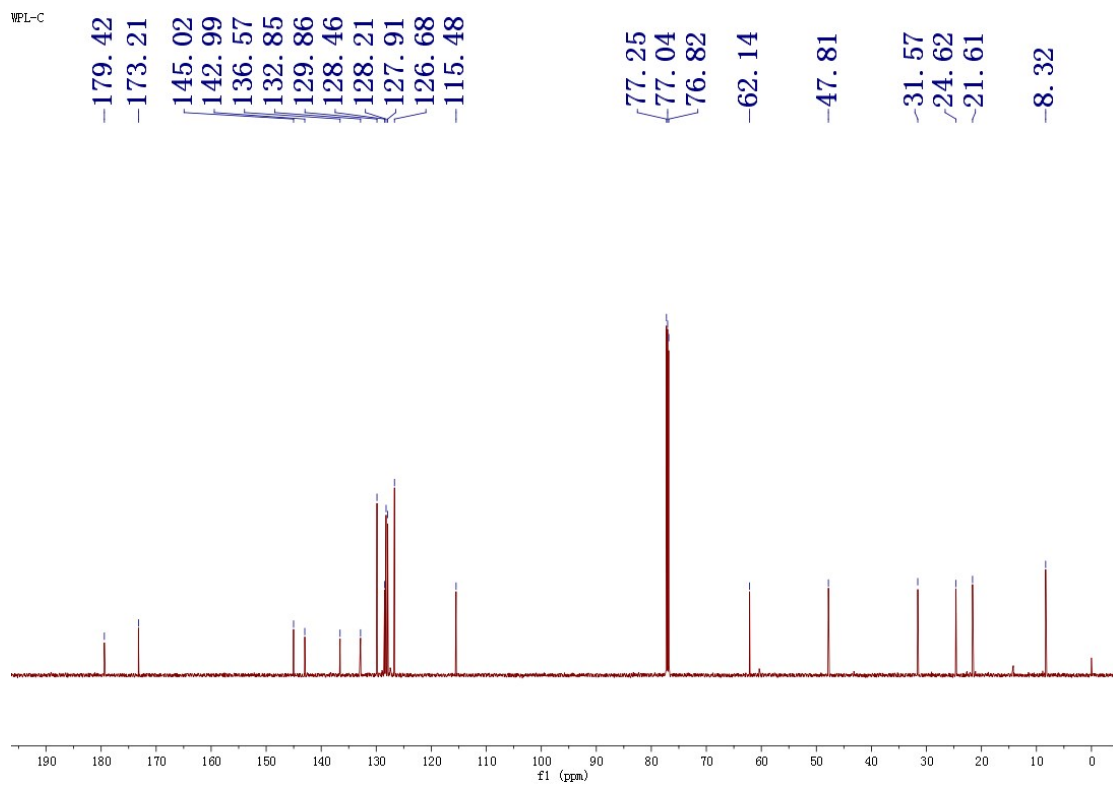
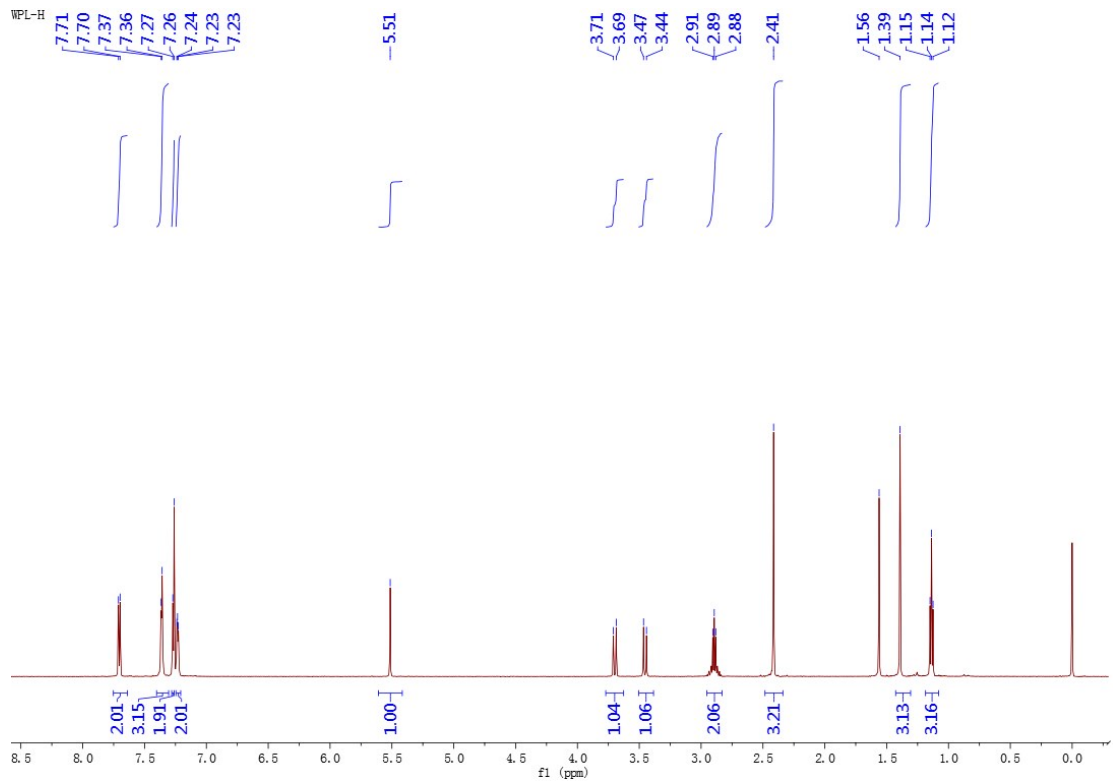
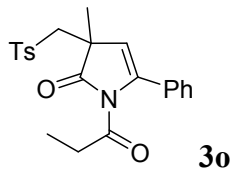




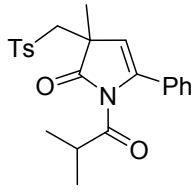




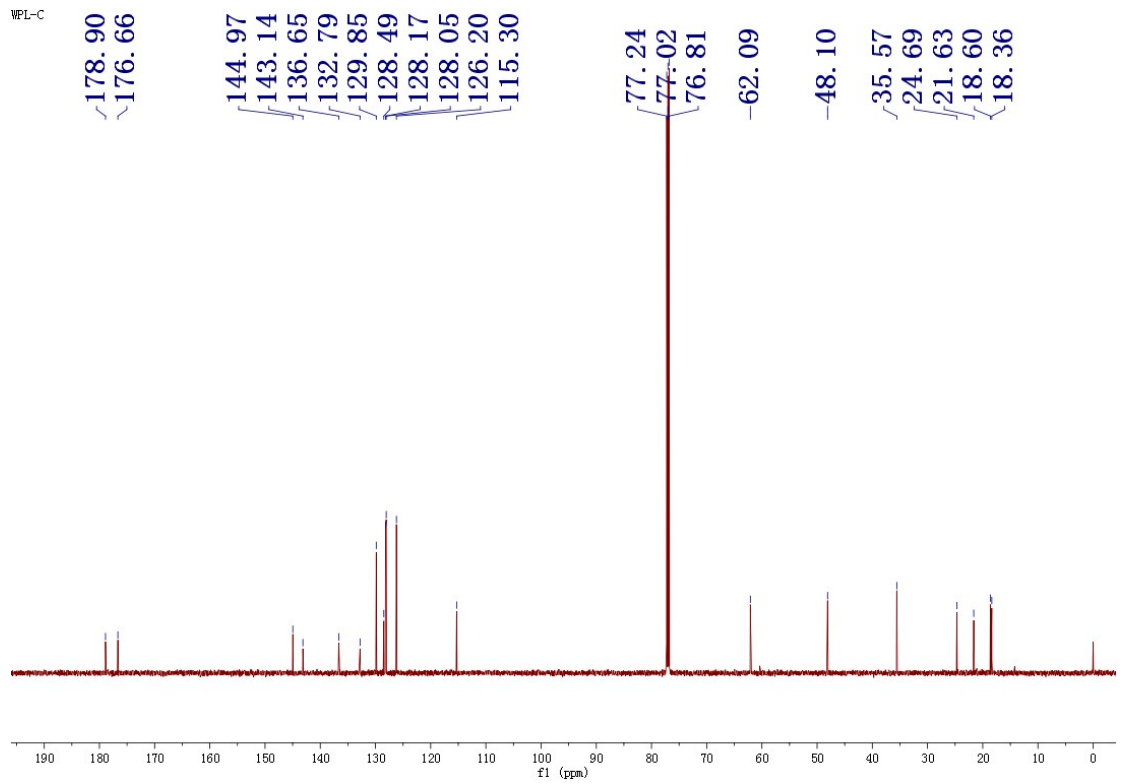
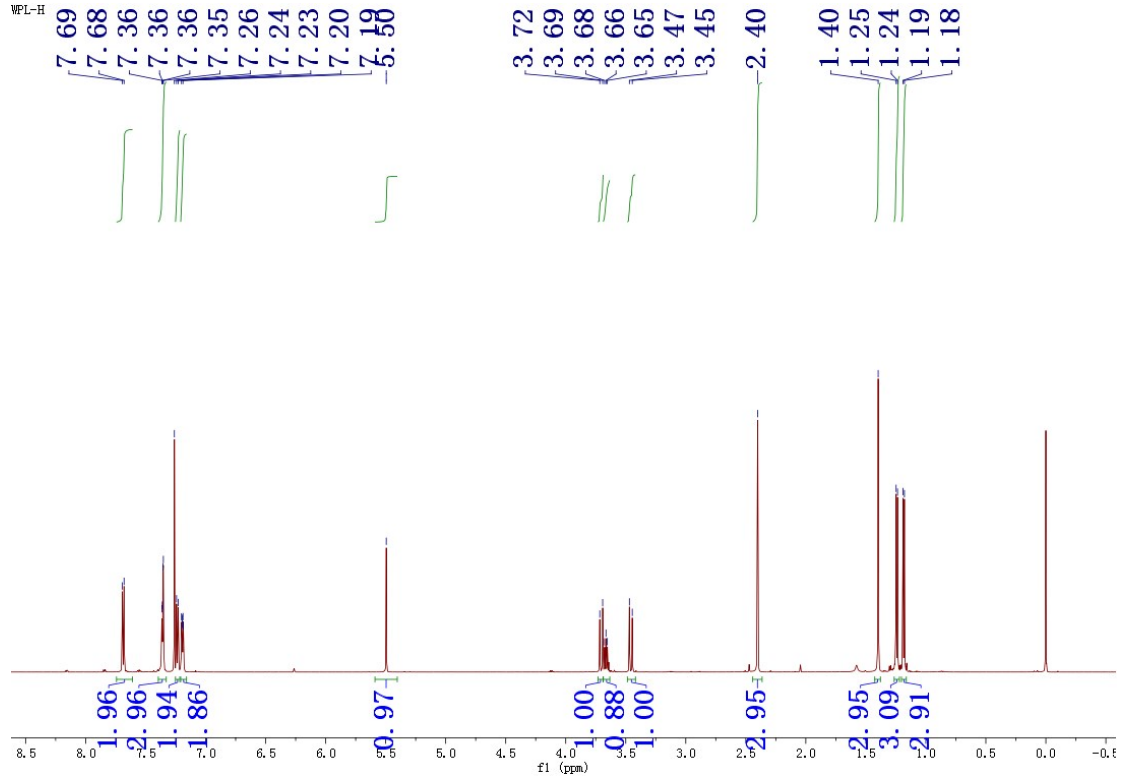


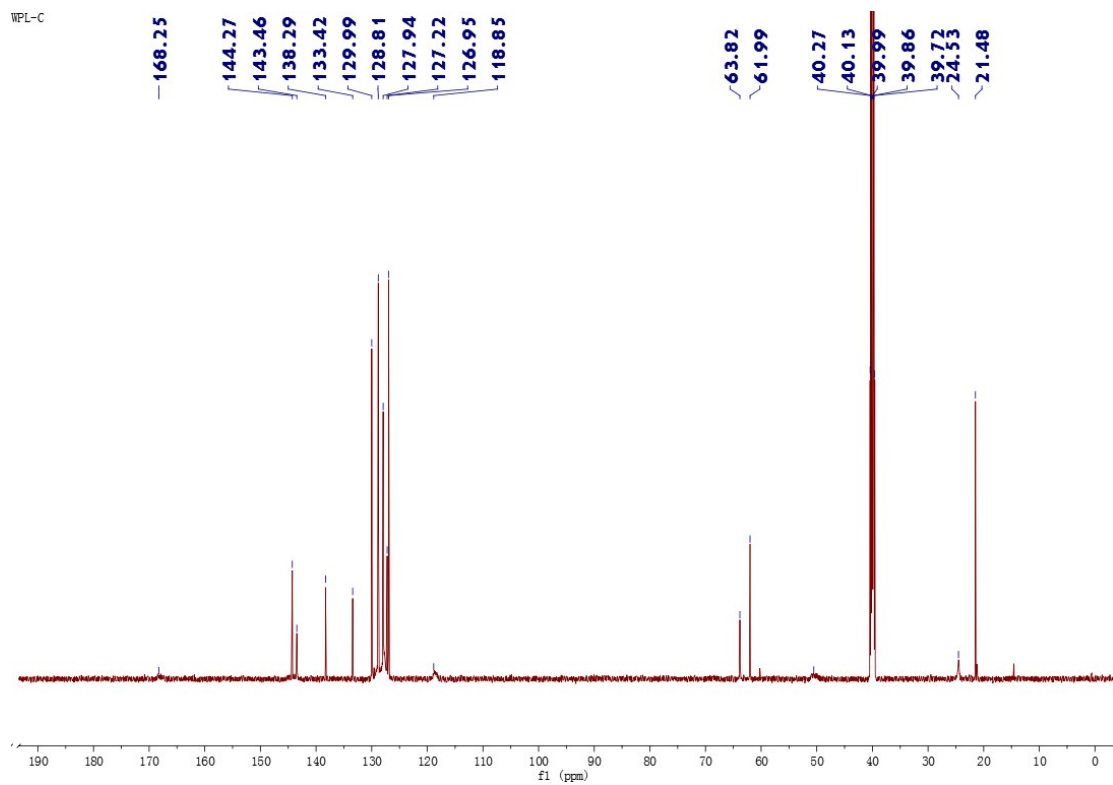
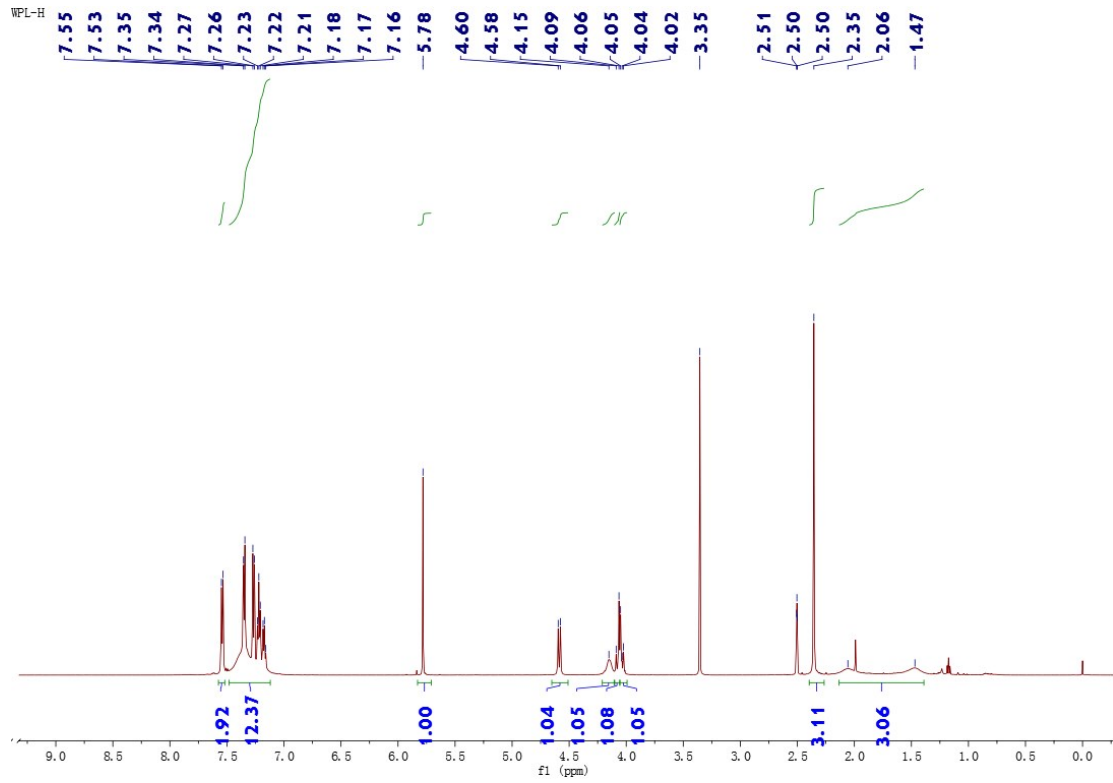
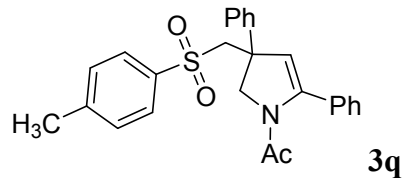


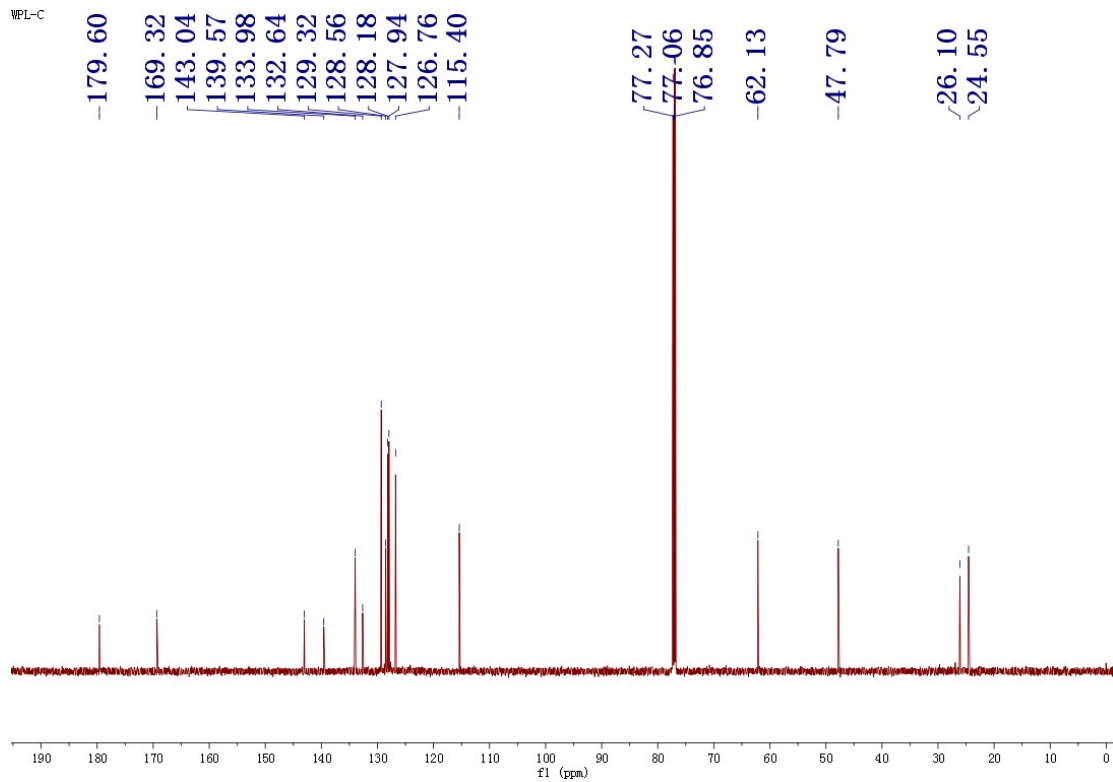
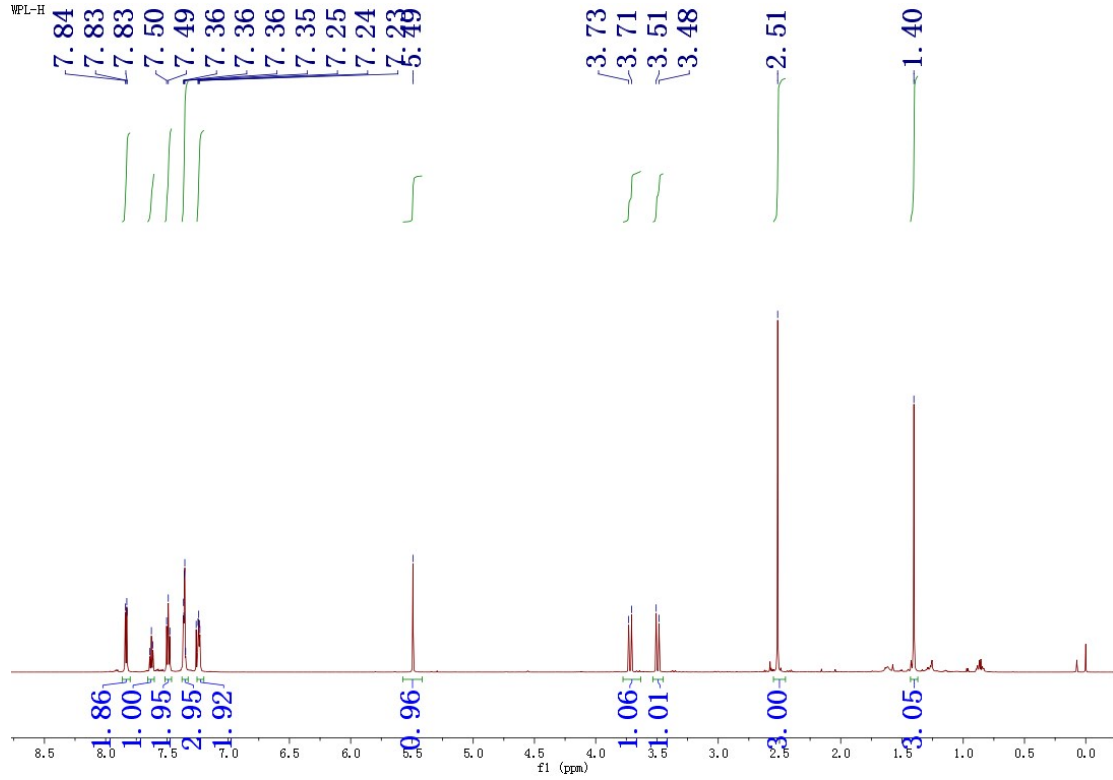
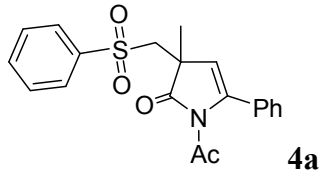


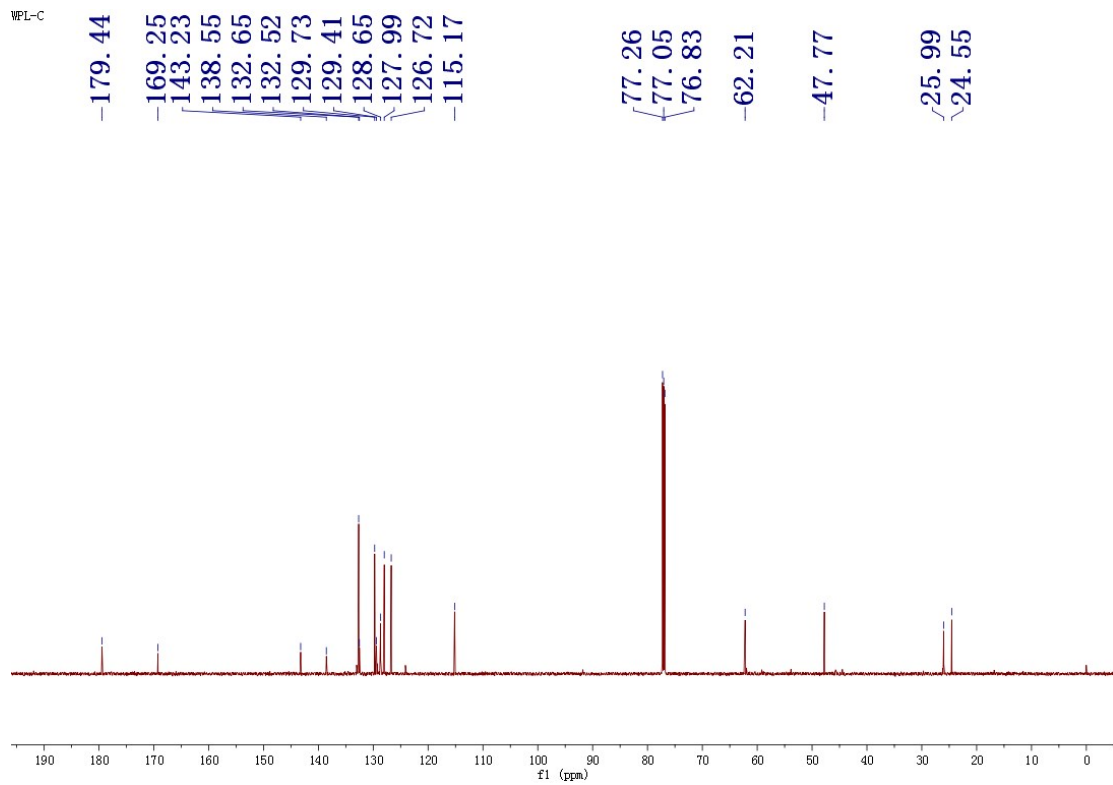
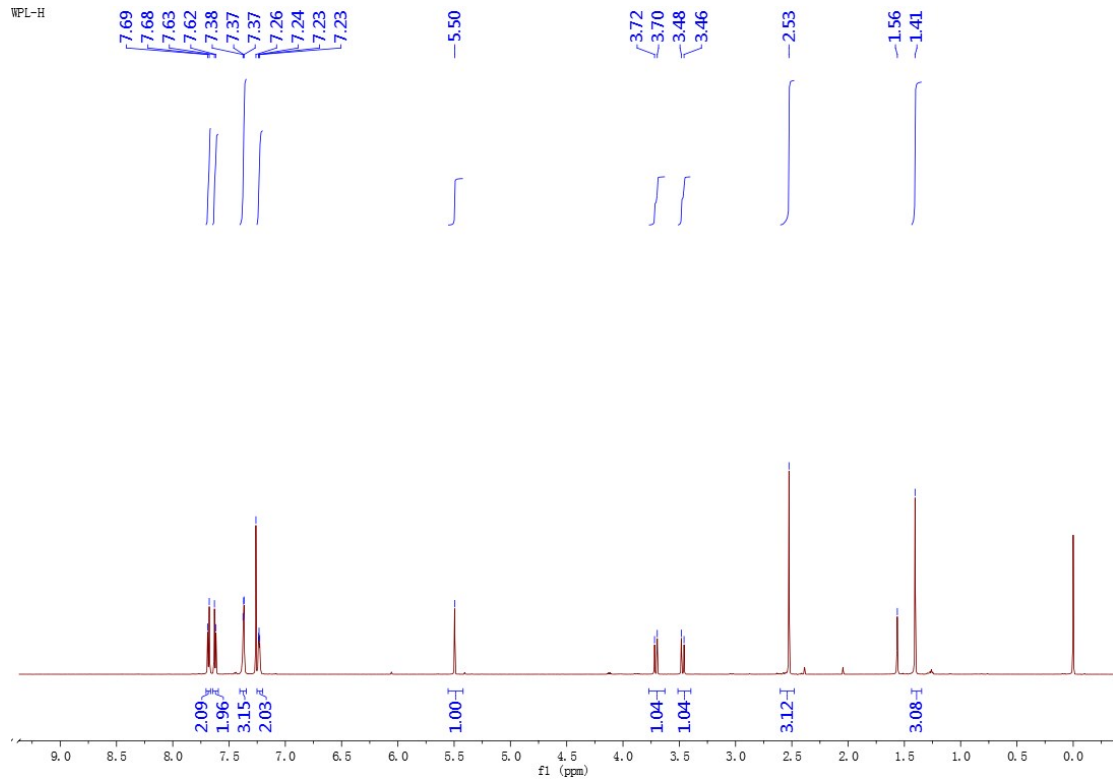
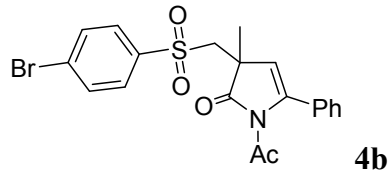


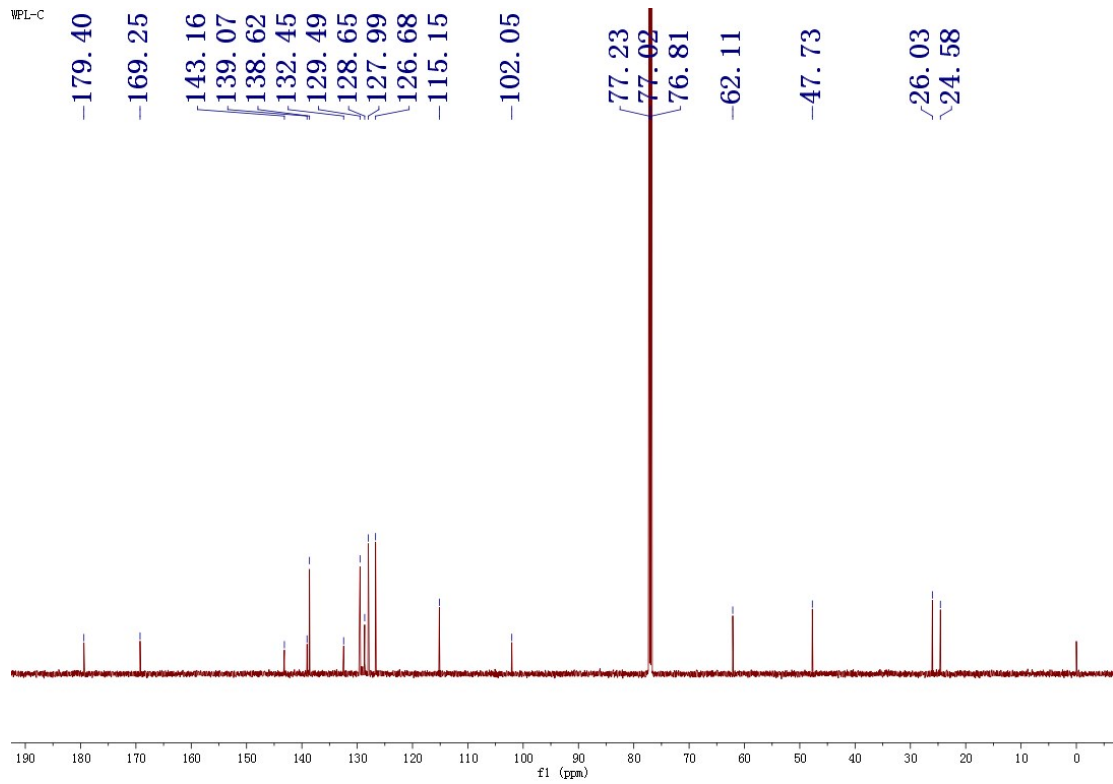
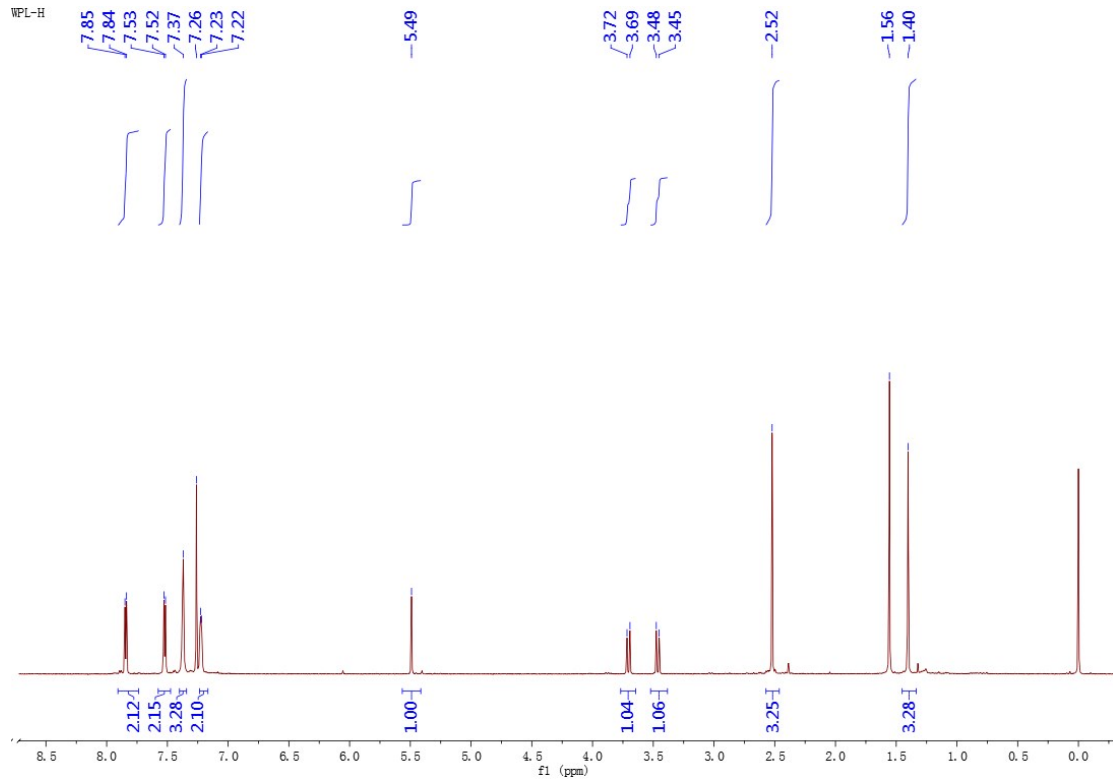
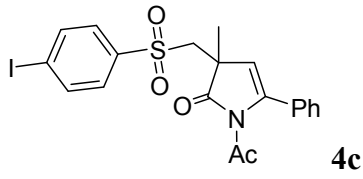
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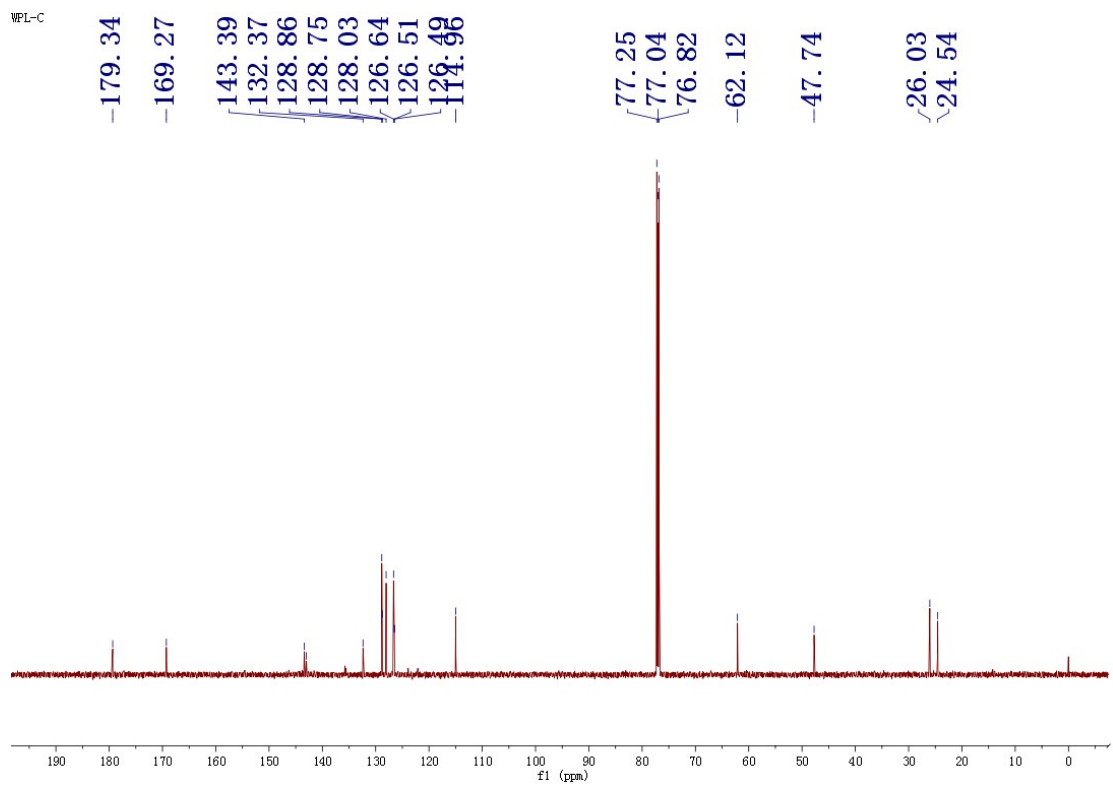
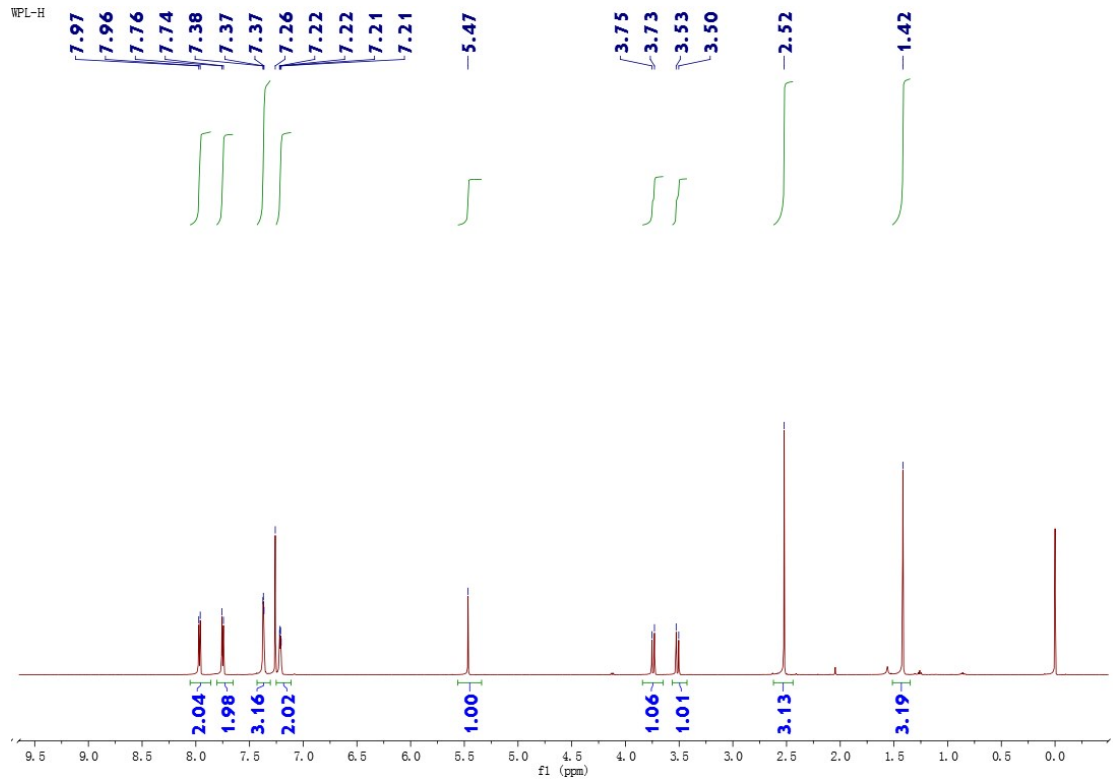
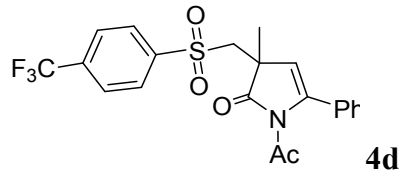


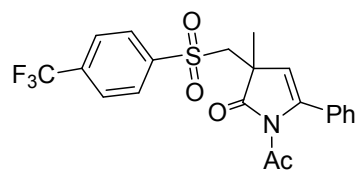








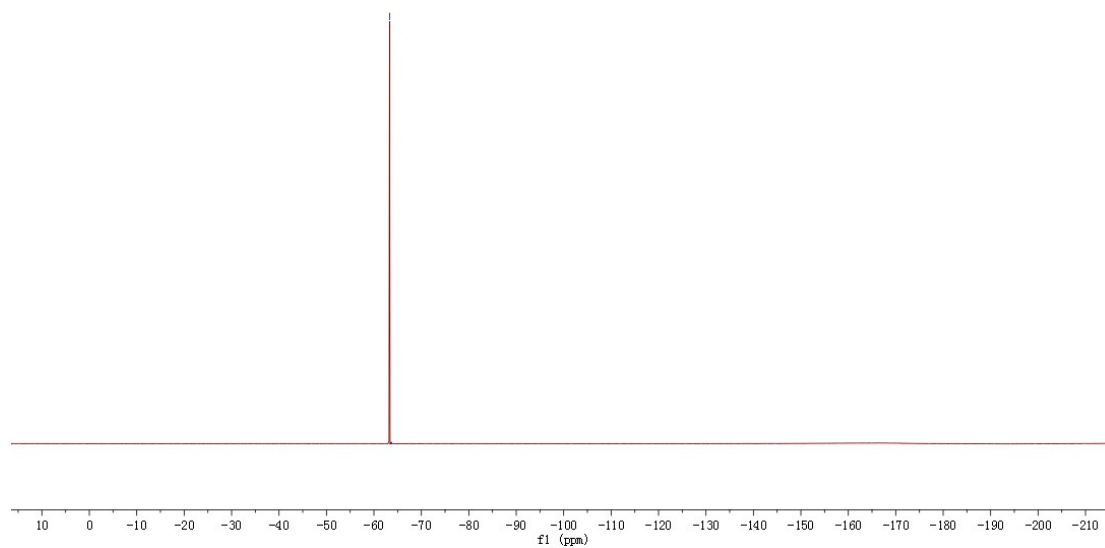


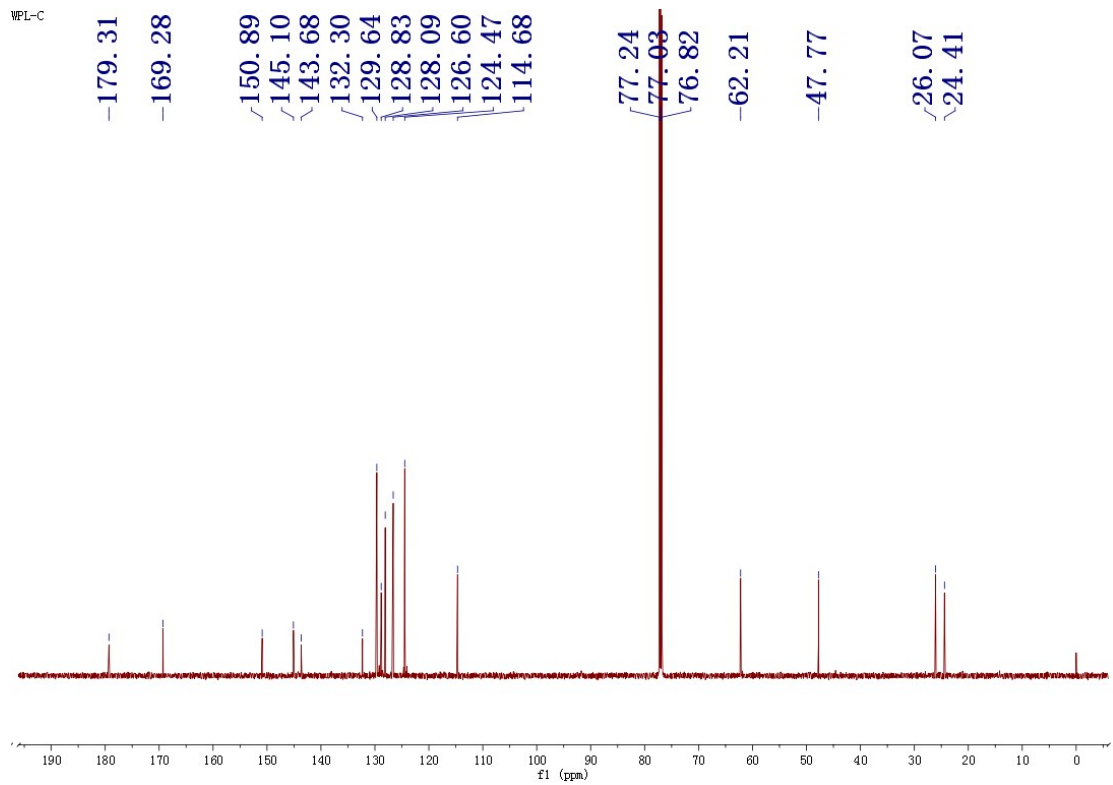
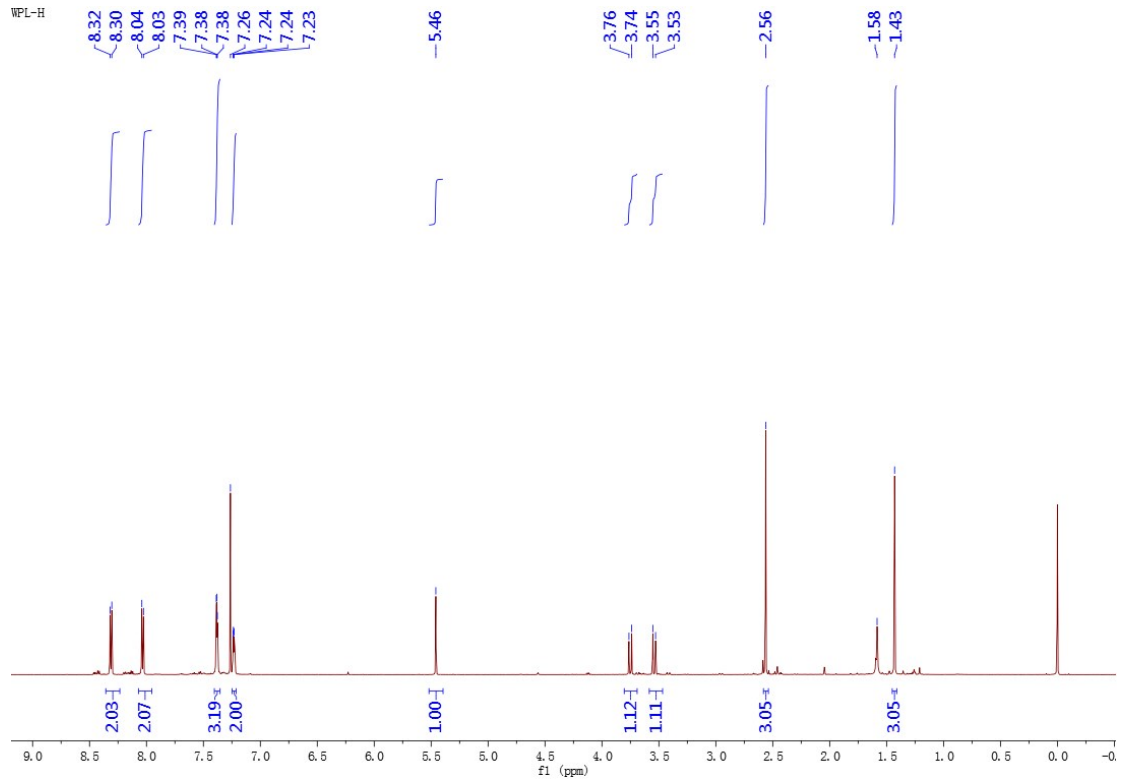
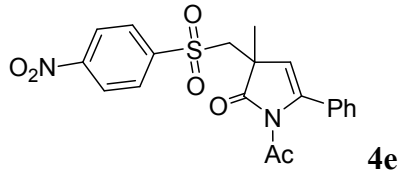


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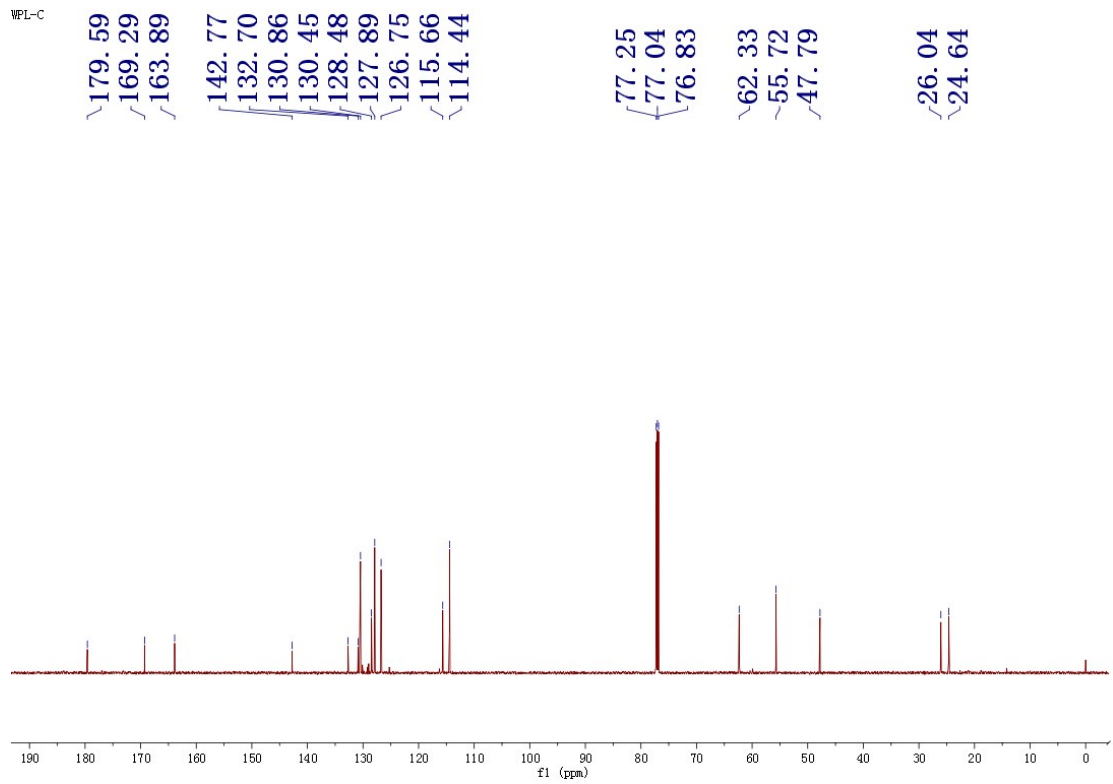
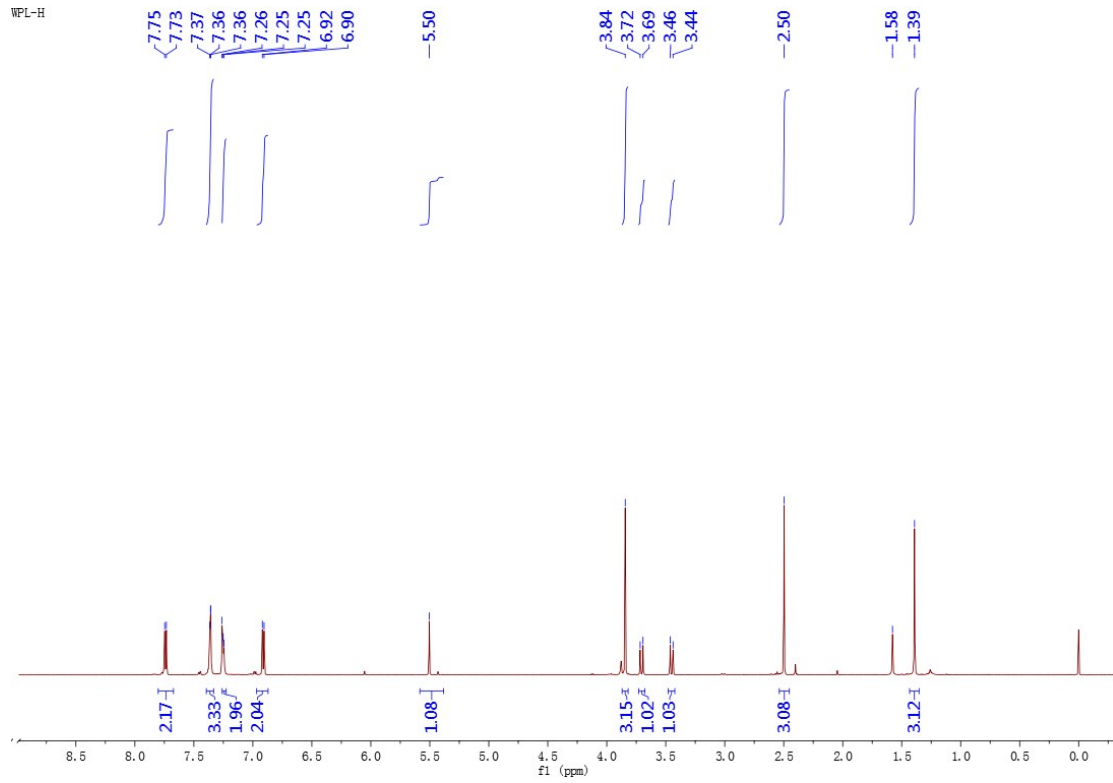
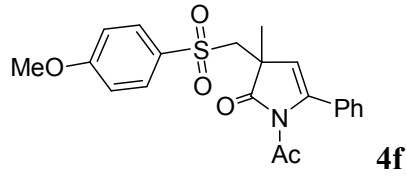
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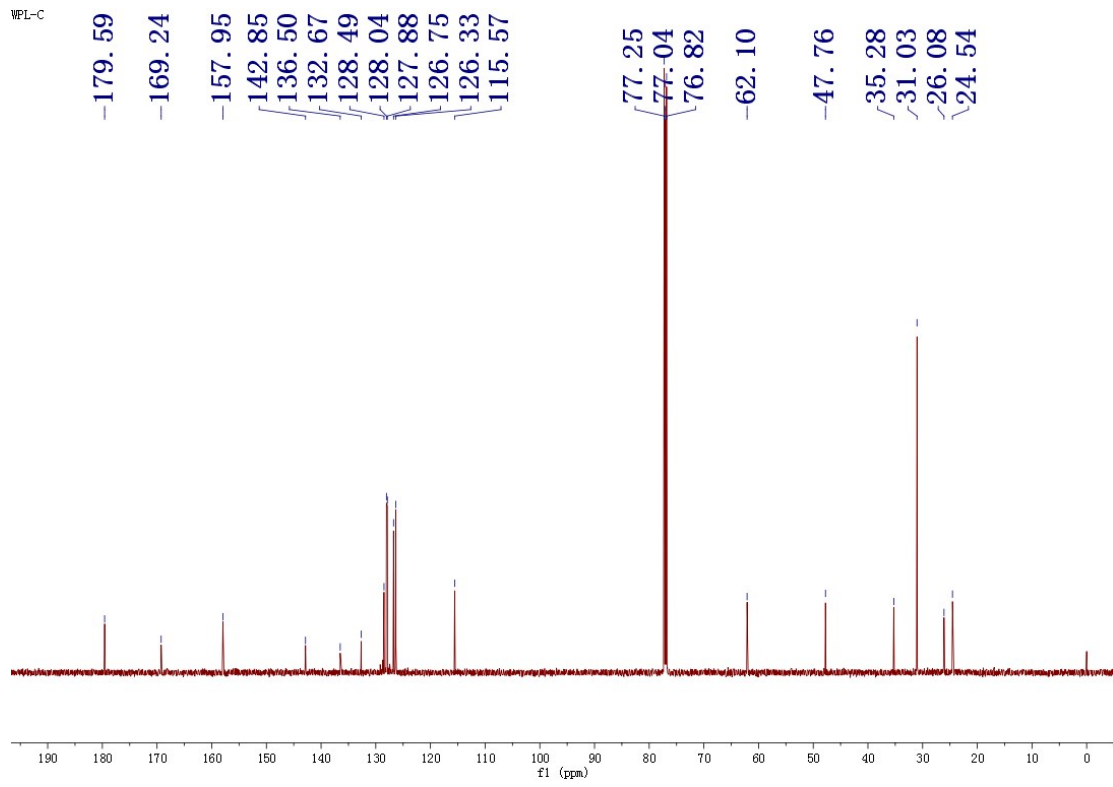
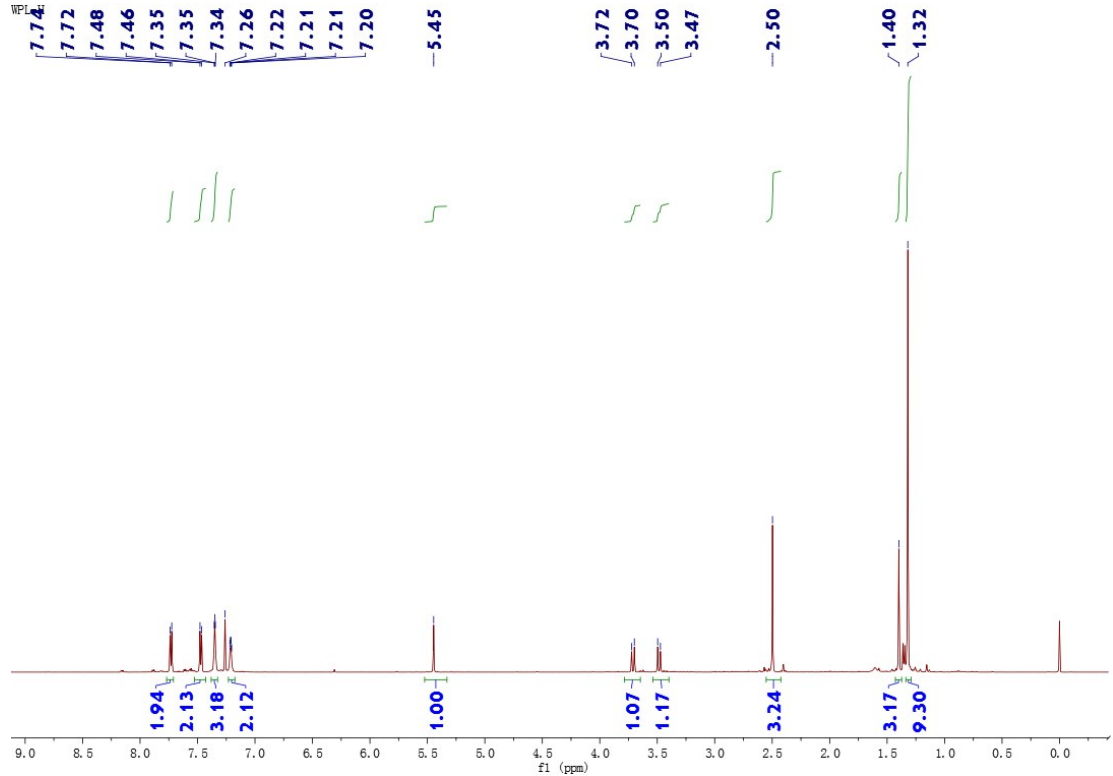
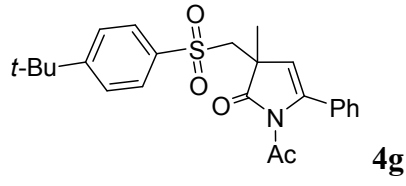
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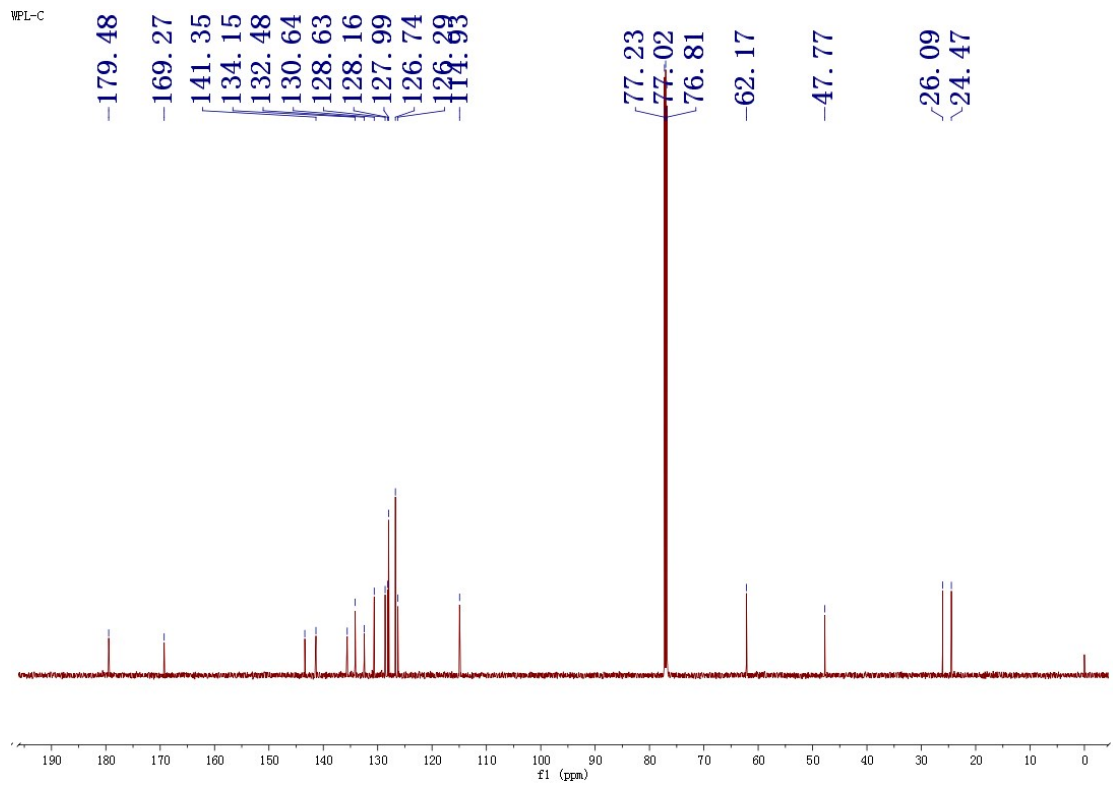
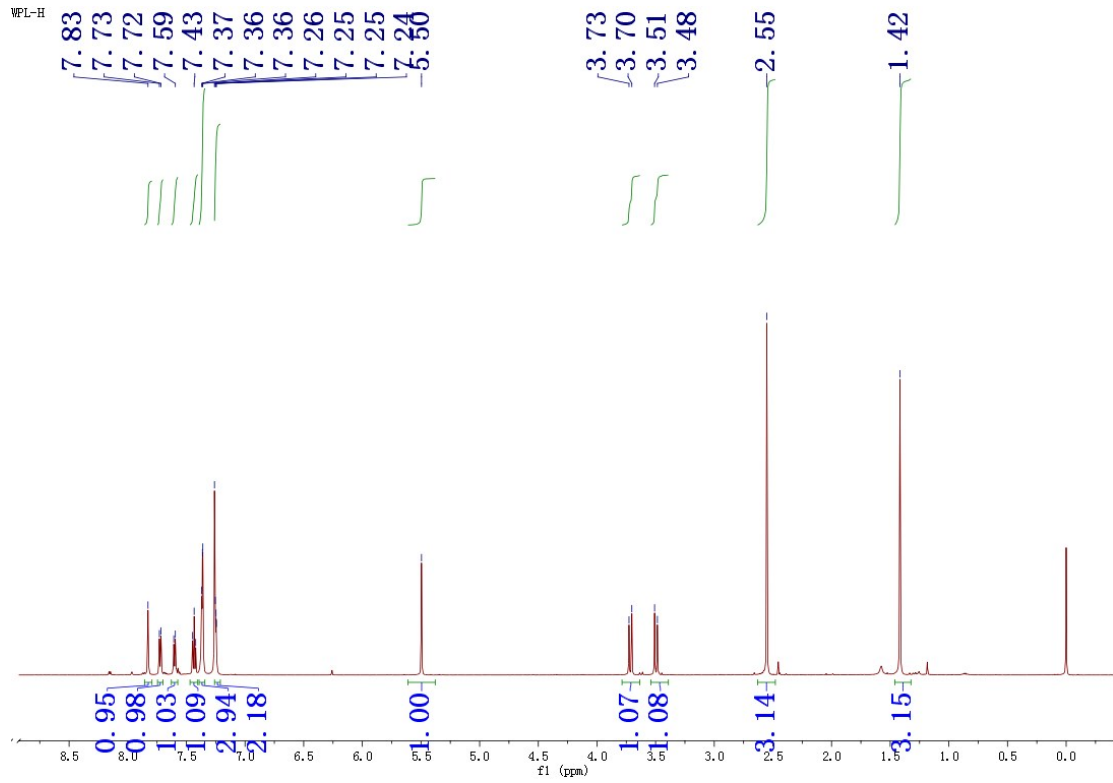
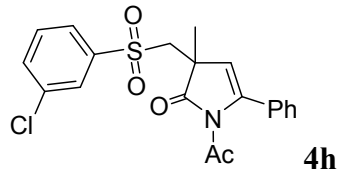


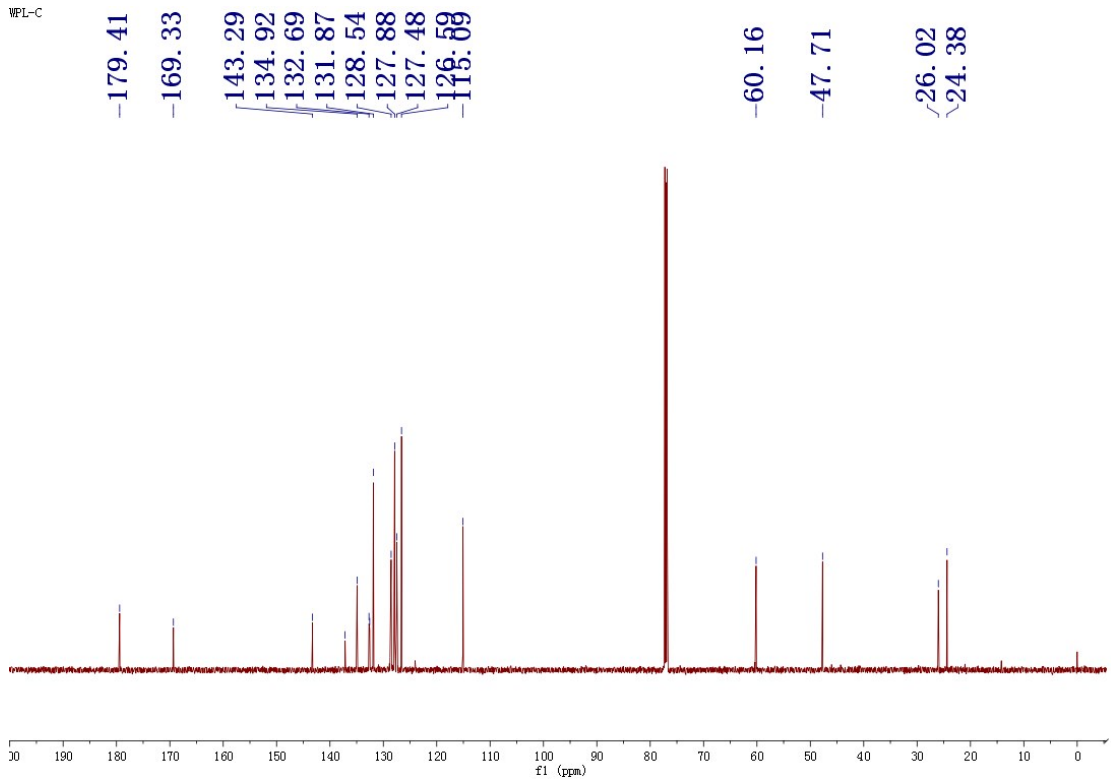
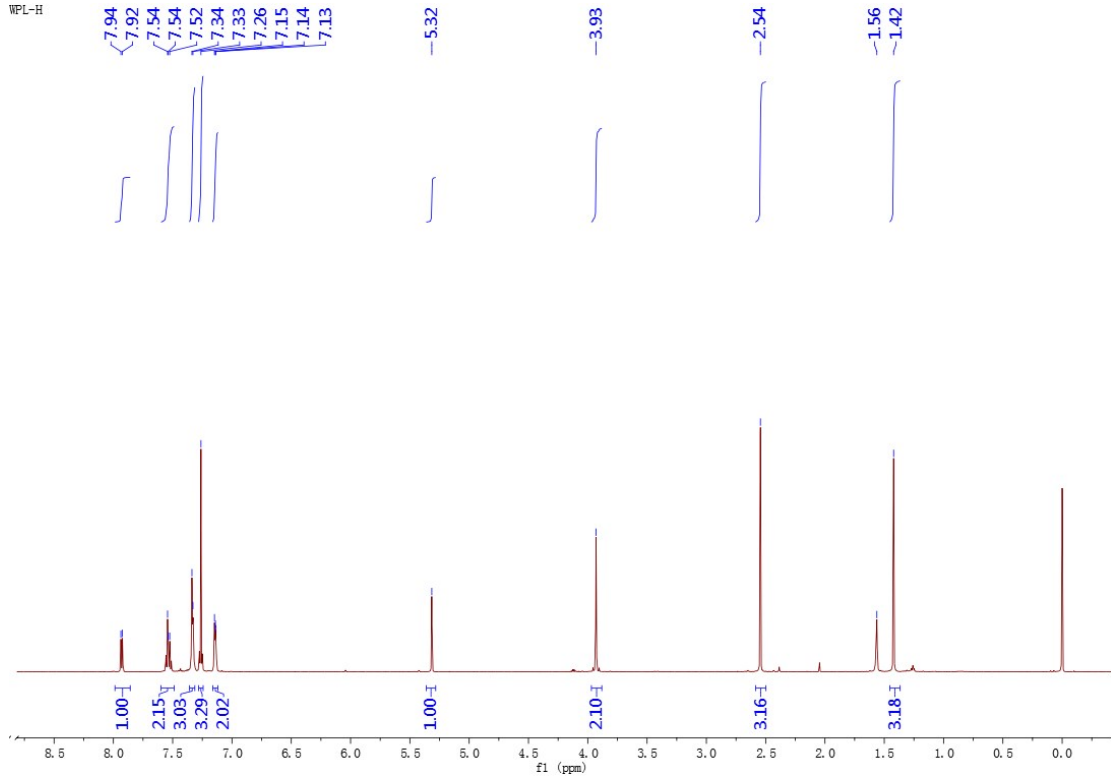
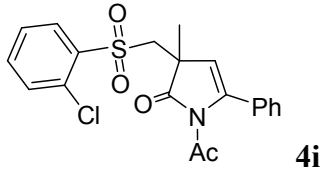


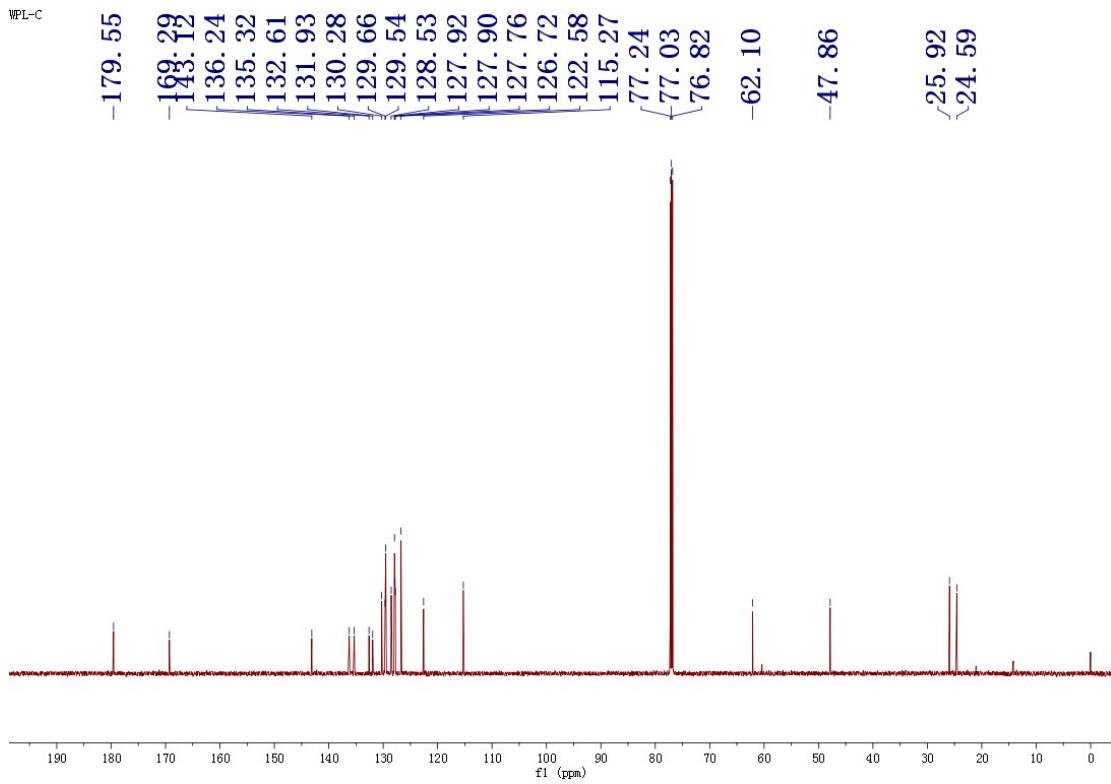
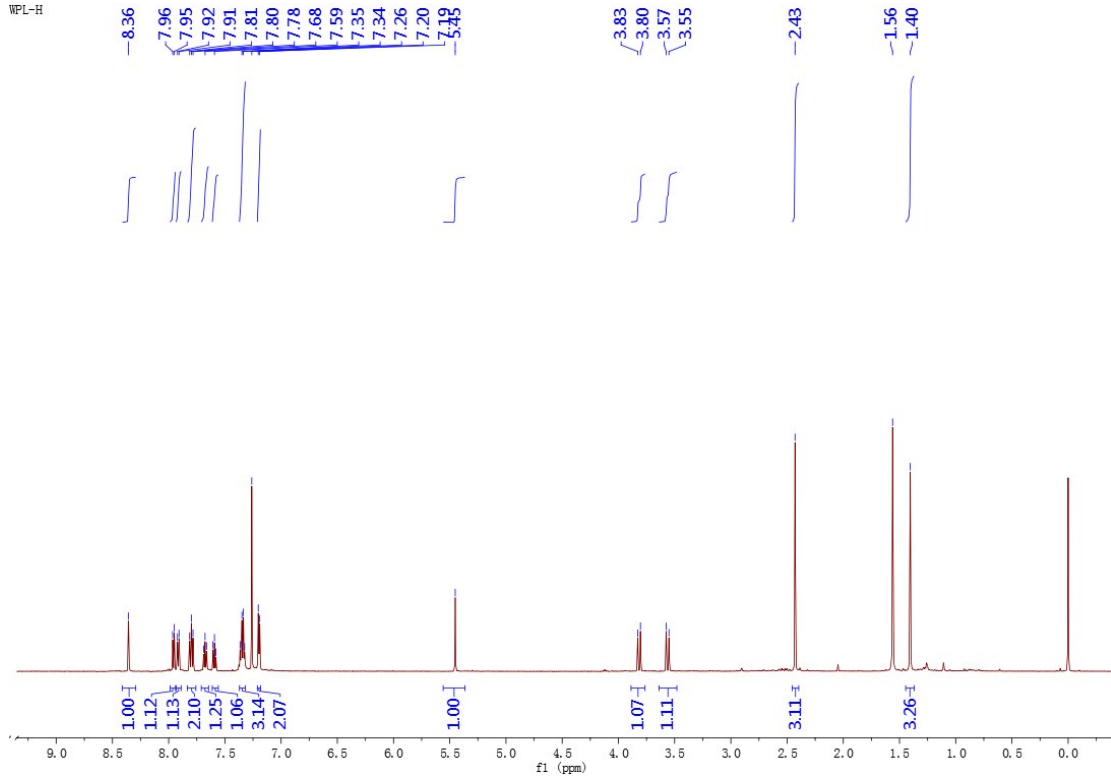
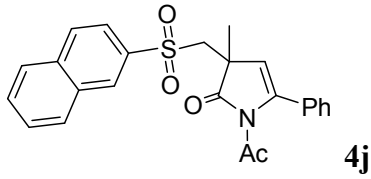


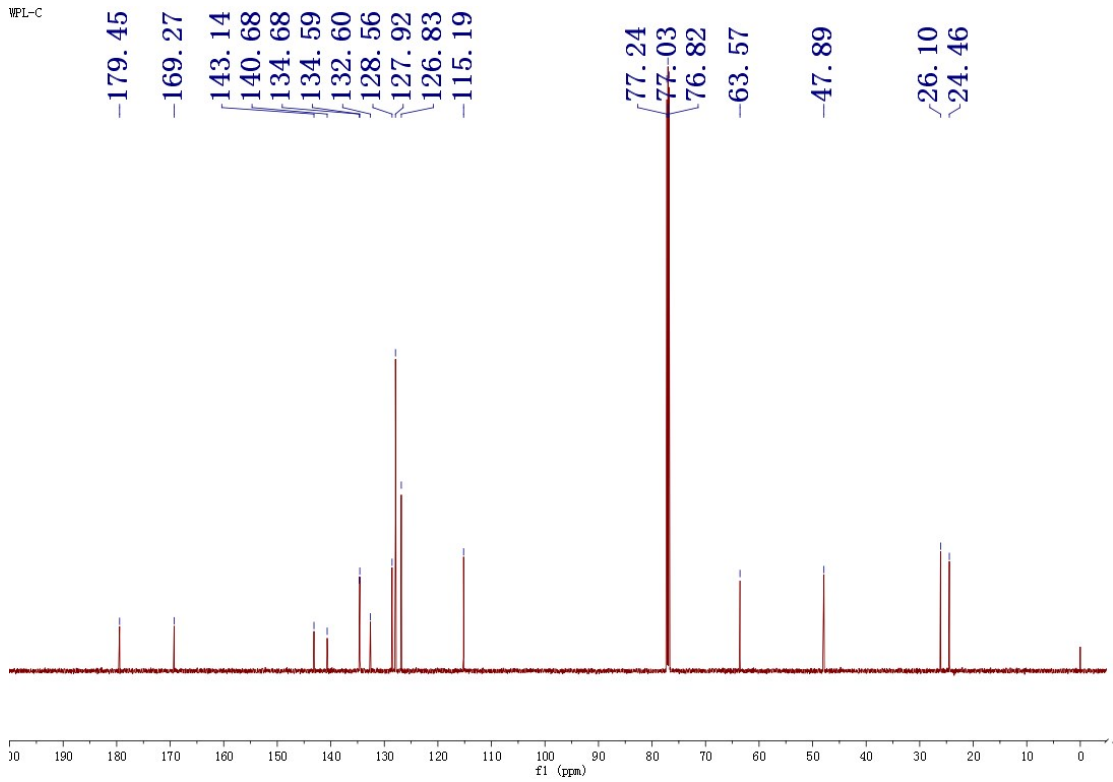
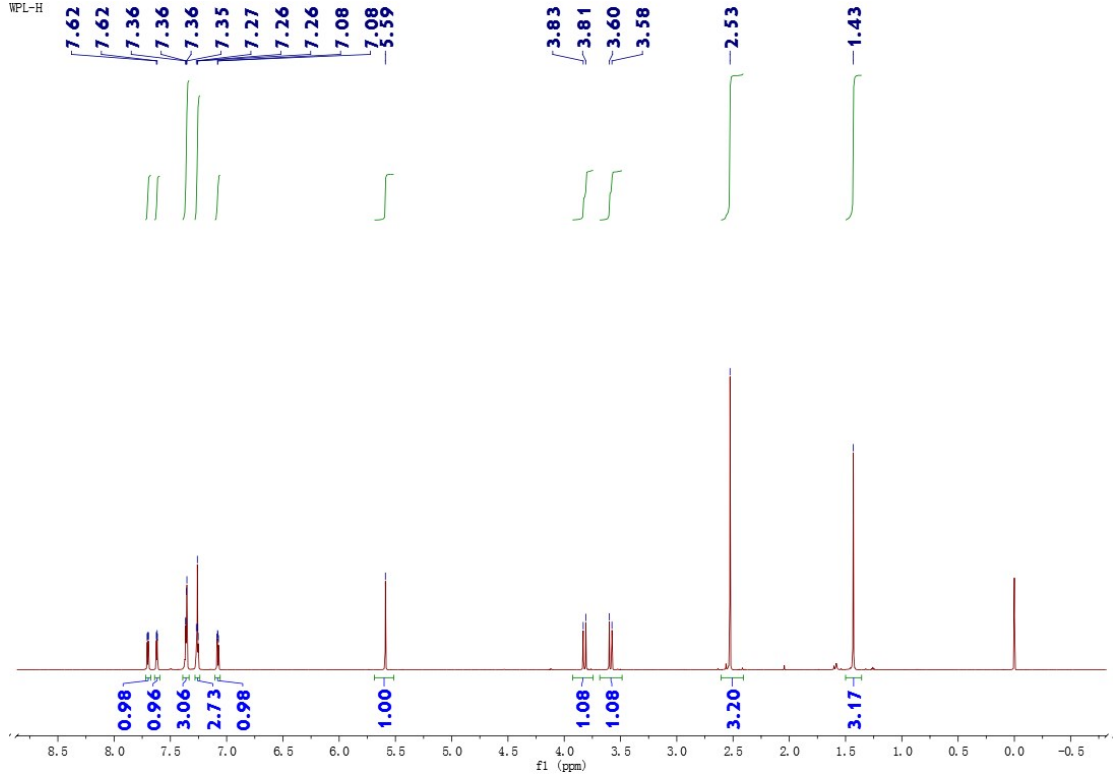
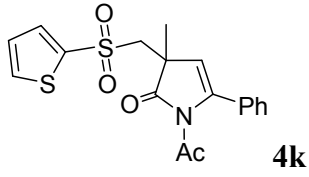


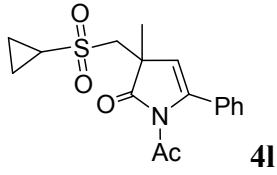




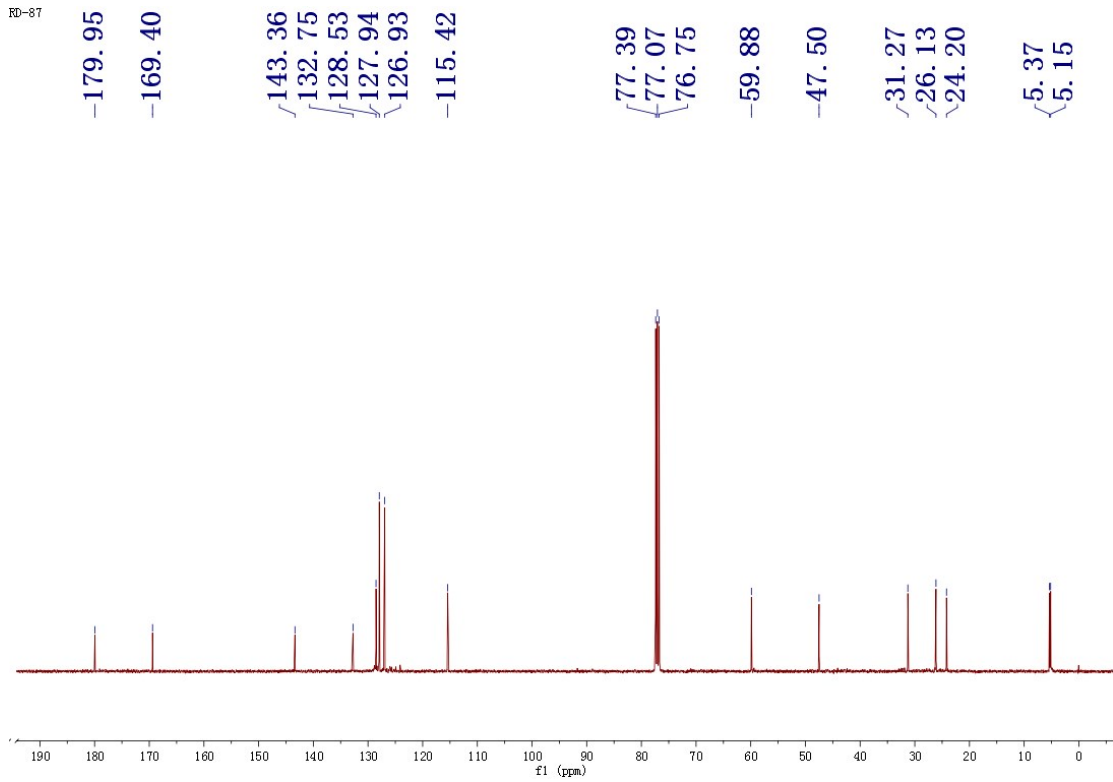
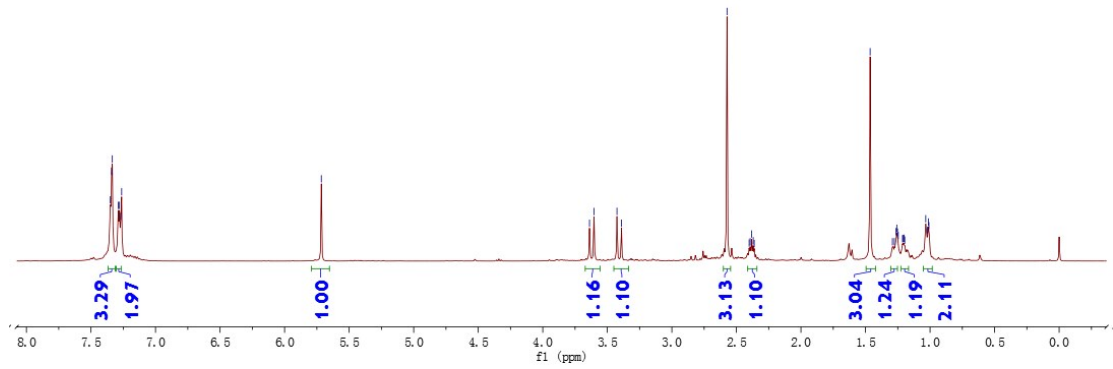
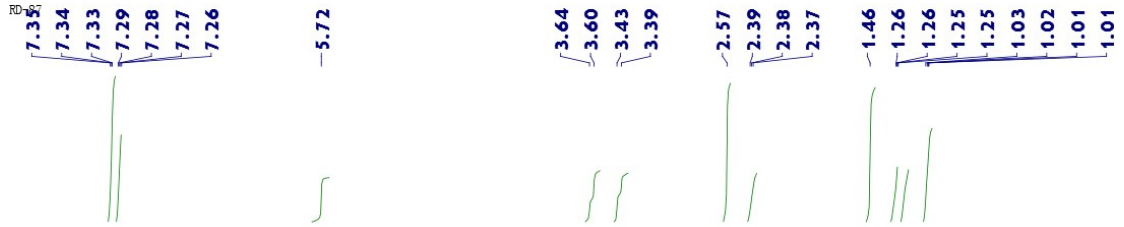


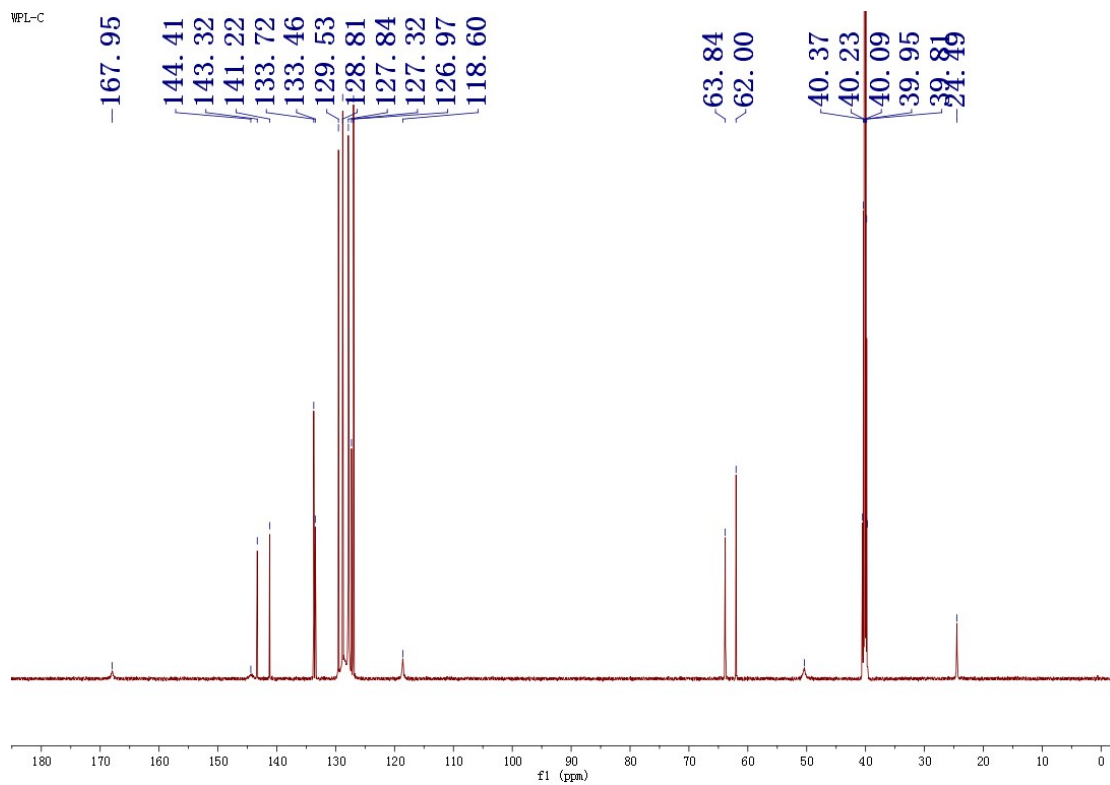
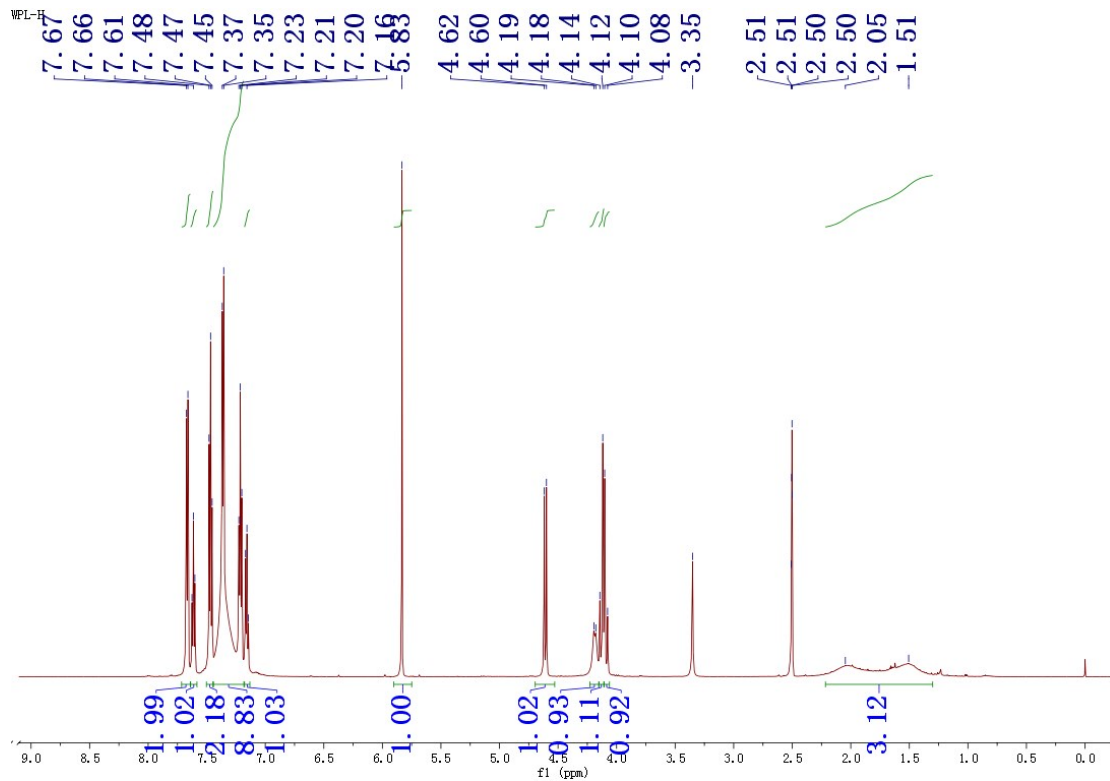
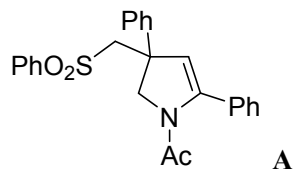




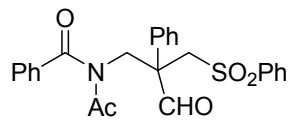


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**B**

