

# Electronic Supplementary Information

## Modular Construction of $\alpha$ -Furanyl Ketones *via* Semi-pinacol

### Rearrangement-Mediated Ring Expansion

Yang Chen,<sup>a</sup> Shifa Zhu<sup>\*,a,b</sup>

<sup>a</sup>Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, P. R. China;

<sup>b</sup>Guangdong Youmei Institute of Intelligent Biomanufacturing, Foshan 528225, PR China

*E-mail: zhusf@scut.edu.cn*

### Table of contents

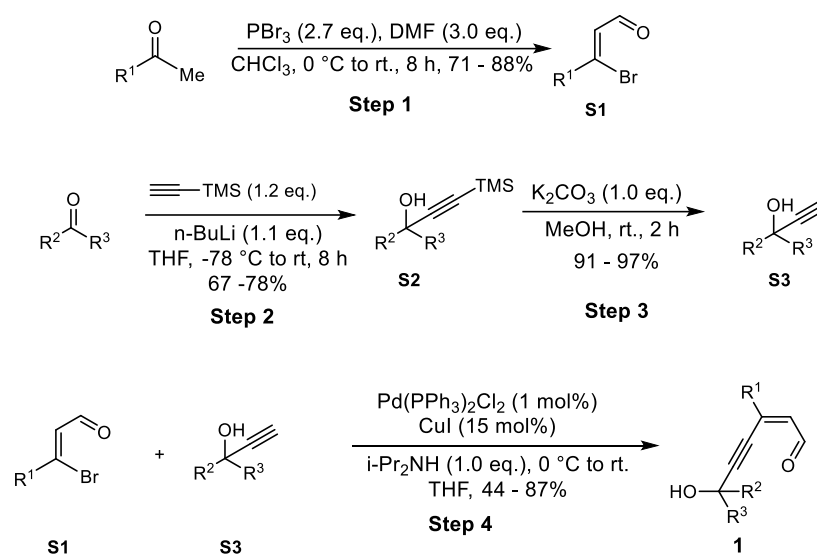
I. General information.....	2
II. General Experimental Procedure.....	2
1. General procedure for preparation of enynals <b>1</b> .....	2
2. Optimization of the reaction conditions for Synthesis of <b>2a</b> .....	11
3. General procedure for the synthesis of <b>2a-2z</b> .....	11
4. Derivatization of product <b>2m</b> .....	20
III. General X-ray Procedures.....	22
1. Crystallography information for <b>2w</b> .....	22
IV. Copies of NMR spectra.....	29

## I. General information

All reactions were conducted under dry N<sub>2</sub> atmosphere in schlenk tube. Catalysts were commercial available. Commercially obtained reagents were used without purification. Reaction starting materials were prepared as depicted in the literature. <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on the Bruker AVANCE 400 (400 MHz for <sup>1</sup>H; 101 MHz for <sup>13</sup>C; 376 MHz for <sup>19</sup>F) and Bruker AVANCE 500 (500 MHz for <sup>1</sup>H; 126 MHz for <sup>13</sup>C; 471 MHz for <sup>19</sup>F), <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using ESI and DART mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

## II. General Experimental Procedure

### 1. General procedure for preparation of enynals.<sup>[1]</sup>



#### General procedure for preparation of bromo aldehyde (S1).

To a mixture of DMF (3.0 eq) and chloroform (0.5 M) was added PBr<sub>3</sub> (2.7 eq.) dropwise at 0 °C, and the mixture was stirred for 60 min. before the addition of ketone (1.0 eq.). The resulting solution was stirred for 8 h at room temperature before it was poured into 300 ml water, neutralized with solid NaHCO<sub>3</sub>, and extracted with dichloromethane. The extract was washed with a saturated NaCl solution, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography (silica gel, petroleum ether/ ethyl acetate = 20:1) gave **S1** with 71 - 88% yield.

#### General procedure for preparation of propargylic alcohol (S2).

Trimethylsilylacetylene (1.2 eq.) was dissolved into THF (0.5 M), and the solution was cooled to -

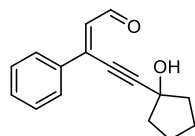
78 °C. To this solution, n-Butyllithium (1.1 eq., 2.5M in hexane) was added. After being stirred for 20 minutes at -78 °C, ketone (1.0 eq.) was added. The resulting mixture was allowed to warm up to room temperature for 8 h, and then the reaction was quenched by saturated NH<sub>4</sub>Cl (aq.), and extracted three times with ether. The combined organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed under a reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the desired **S2** (67 - 78%) as an orange oil.

#### General procedure for preparation of propargylic alcohol (**S3**).

In a 25 mL one-neck round bottom flask equipped with magnetic stir bar was placed **S4** (1.0 eq.) and MeOH (1.0 M). To this stirring mixture was added K<sub>2</sub>CO<sub>3</sub> (1.0 eq.) and the solution was stirred for 30 min, when TLC indicated the reaction was complete. Water (20 mL) was added and the solution was extracted (3 × 25 mL, CH<sub>2</sub>Cl<sub>2</sub>), dried (MgSO<sub>4</sub>) and concentrated under vacuum. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1) to yield **S5** (91 - 97%) as an orange oil.

#### General procedure for preparation of aryl-enynals (**1**).

The bromo aldehyde (1.2 eq.) and propargylic alcohol (1.0 eq.) were placed in a clean and anhydrous round-bottom flask equipped with a stir bar, then anhydrous THF and <sup>t</sup>Pr<sub>2</sub>NH (1.0 eq.) were added under a nitrogen atmosphere, and the flask was cooled to 0 °C. Subsequently, CuI (15 mol%) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (1 mol%) were placed in the reaction flask; then after 20 min at 0 °C. Reaction progress was monitored by thin-layer chromatography (TLC) analysis. After complete consumption of the bromo aldehyde, the reaction was quenched with saturated NH<sub>4</sub>Cl and extracted with ethyl acetate (EtOAc). The combined organic layer was washed with brine, dried (MgSO<sub>4</sub>), and concentrated. The crude material was typically purified by flash chromatography using a petroleum ether/ethyl acetate = 5:1 mixture as eluent to yield the enynals **1** (44 - 91%).



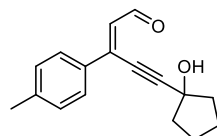
#### (Z)-5-(1-hydroxycyclopentyl)-3-phenylpent-2-en-4-ynal (**1a**)

Yield: 56%, yellow oil, R<sub>f</sub> = 0.34 (petroleum ether/AcOEt = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.22 (d, J = 8.0 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.42 – 7.34 (m, 3H), 6.70 (d, J = 8.0 Hz, 1H), 3.59 (brs, 1H), 2.16 – 2.06 (m, 4H), 1.96 – 1.87 (m, 2H), 1.85 – 1.73 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 193.7, 193.7, 142.7, 135.4, 131.1, 130.8, 128.8, 127.2, 107.2, 77.8, 74.7, 42.4, 23.6.

HRMS (ESI) ([M+H]<sup>+</sup>) Calcd. for [C<sub>16</sub>H<sub>17</sub>O<sub>2</sub>]<sup>+</sup>: 241.1223, Found. 241.1218.



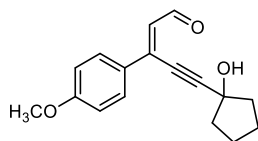
#### (Z)-5-(1-hydroxycyclopentyl)-3-(p-tolyl)pent-2-en-4-ynal (**1b**)

Yield: 55%, yellow oil, R<sub>f</sub> = 0.33 (petroleum ether/AcOEt = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.22 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.9 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.1 Hz, 1H), 2.37 (s, 3H), 2.11 (t, J = 6.5 Hz, 4H), 1.97 – 1.88 (m, 2H), 1.85 – 1.75 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.7, 142.7, 141.8, 132.6, 130.0, 129.6, 127.2, 106.8, 77.9, 77.5, 42.4, 23.6, 21.4.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{17}\text{H}_{19}\text{O}_2]^+$ : 255.1380, Found. 255.1382.



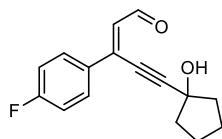
**(Z)-5-(1-hydroxycyclopentyl)-3-(4-methoxyphenyl)pent-2-en-4-ynal (1c)**

Yield: 67%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 5:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.20 (d,  $J = 8.0$  Hz, 1H), 7.75 – 7.70 (m, 2H), 6.97 – 6.89 (m, 2H), 6.67 (d,  $J = 8.0$  Hz, 1H), 3.85 (s, 3H), 2.40 (brs, 1H), 2.14 – 2.08 (m, 4H), 1.97 – 1.88 (m, 2H), 1.88 – 1.77 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.4, 162.2, 141.9, 129.1, 128.9, 127.8, 114.3, 106.1, 78.1, 74.9, 55.5, 42.5, 23.6, 23.5.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{17}\text{H}_{19}\text{O}_3]^+$ : 271.1329, Found. 271.1331.



**(Z)-3-(4-fluorophenyl)-5-(1-hydroxycyclopentyl)pent-2-en-4-ynal (1d)**

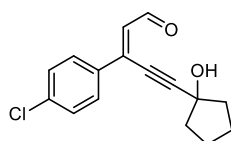
Yield: 68%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 3:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.21 (d,  $J = 7.8$  Hz, 1H), 7.84 – 7.64 (m, 2H), 7.11 (t,  $J = 8.4$  Hz, 2H), 6.67 (d,  $J = 7.9$  Hz, 1H), 2.64 (brs, 1H), 2.11 (t,  $J = 6.4$  Hz, 4H), 1.92 (qd,  $J = 10.5, 8.9, 5.2$  Hz, 2H), 1.82 (qd,  $J = 8.4, 6.8, 3.8$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.2, 164.5 (d,  $J = 253.1$  Hz), 141.2, 131.5 (d,  $J = 3.3$  Hz), 130.7, 129.2 (d,  $J = 8.8$  Hz), 116.0 (d,  $J = 22.0$  Hz), 106.9, 77.8, 74.9, 42.5, 23.6.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.4.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{FO}_2]^+$ : 259.1129, Found. 259.1125.



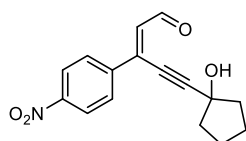
**(Z)-3-(4-chlorophenyl)-5-(1-hydroxycyclopentyl)pent-2-en-4-ynal (1e)**

Yield: 67%, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 5:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.21 (d,  $J = 7.9$  Hz, 1H), 7.70 – 7.64 (m, 2H), 7.46 – 7.33 (m, 2H), 6.69 (d,  $J = 7.9$  Hz, 1H), 2.63 (brs, 1H), 2.17 – 2.06 (m, 4H), 1.99 – 1.87 (m, 2H), 1.87 – 1.77 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.2, 141.0, 137.3, 133.9, 131.1, 129.1, 128.4, 107.0, 77.6, 74.9, 42.5, 23.6.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{ClO}_2]^+$ : 275.0833, Found. 275.0836.



**(Z)-5-(1-hydroxycyclopentyl)-3-(4-nitrophenyl)pent-2-en-4-ynal (1f)**

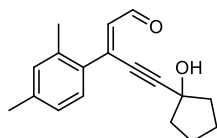


Yield: 45%, yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.26 (d,  $J = 7.7$  Hz, 1H), 8.28 (d,  $J = 8.4$  Hz, 2H), 7.91 (d,  $J = 8.1$  Hz, 2H), 6.79 (d,  $J = 7.7$  Hz, 1H), 2.40 (brs, 1H), 2.12 (t,  $J = 6.4$  Hz, 4H), 2.00 – 1.89 (m, 2H), 1.89 – 1.72 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.9, 149.0, 141.5, 139.7, 133.2, 128.1, 124.0, 108.0, 77.1, 74.8, 42.5, 23.6.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{NO}_4]^+$ : 286.1074, Found. 286.1073.



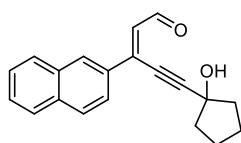
**(E)-3-(2,4-dimethylphenyl)-5-(1-hydroxycyclopentyl)pent-2-en-4-ynal (1g)**

Yield: 48%, yellow oil,  $R_f = 0.37$  (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.42 (d,  $J = 8.2$  Hz, 1H), 7.11 (d,  $J = 8.1$  Hz, 2H), 7.05 (d,  $J = 7.8$  Hz, 1H), 6.45 (d,  $J = 8.2$  Hz, 1H), 2.37 (d,  $J = 2.9$  Hz, 6H), 2.00 (t,  $J = 6.3$  Hz, 4H), 1.93 – 1.83 (m, 2H), 1.80 – 1.71 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.5, 144.4, 139.4, 135.8, 135.2, 131.6, 131.4, 129.9, 126.5, 105.8, 82.7, 74.9, 42.3, 23.5, 21.2, 19.8.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{18}\text{H}_{21}\text{O}_2]^+$ : 269.1536, Found. 269.1533.



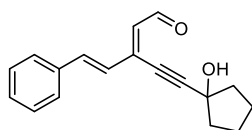
**(Z)-5-(1-hydroxycyclopentyl)-3-(naphthalen-2-yl)pent-2-en-4-ynal (1h)**

Yield: 56%, yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.29 (d,  $J = 7.9$  Hz, 1H), 8.28 (d,  $J = 1.9$  Hz, 1H), 7.92 – 7.87 (m, 1H), 7.87 – 7.80 (m, 2H), 7.74 (dd,  $J = 8.7, 1.9$  Hz, 1H), 7.59 – 7.49 (m, 2H), 6.86 (d,  $J = 7.9$  Hz, 1H), 2.41 (brs, 1H), 2.24 – 2.08 (m, 4H), 2.03 – 1.89 (m, 2H), 1.88 – 1.78 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.4, 142.2, 134.5, 132.9, 132.7, 131.2, 129.1, 128.7, 128.4, 127.8, 127.7, 126.9, 123.2, 106.5, 78.1, 75.0, 42.6, 42.4, 23.6.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{20}\text{H}_{19}\text{O}_2]^+$ : 291.1380, Found. 291.1381.



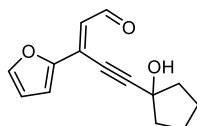
**(2Z,4E)-3-((1-hydroxycyclopentyl)ethynyl)-5-phenylpenta-2,4-dienal (1i)**

Yield: 78%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.16 (d,  $J = 8.3$  Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 (brs, 1H), 7.38 (d,  $J = 3.3$  Hz, 1H), 7.37 – 7.32 (m, 2H), 6.84 (d,  $J = 15.6$  Hz, 1H), 6.27 (d,  $J = 8.2$  Hz, 1H), 2.20 – 2.03 (m, 4H), 1.99 – 1.87 (m, 2H), 1.85 – 1.76 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.3, 141.0, 139.8, 135.4, 133.4, 129.7, 128.9, 127.8, 127.2, 106.1, 75.7, 74.7, 42.5, 23.6.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{18}\text{H}_{19}\text{O}_2]^+$ : 267.1380, Found. 267.1384.



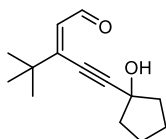
**(E)-3-(furan-2-yl)-5-(1-hydroxycyclopentyl)pent-2-en-4-ynal (1j)**

Yield: 56%, yellow oil,  $R_f = 0.34$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.09 (d,  $J = 8.3$  Hz, 1H), 7.51 (d,  $J = 1.7$  Hz, 1H), 6.96 (d,  $J = 3.5$  Hz, 1H), 6.65 (d,  $J = 8.3$  Hz, 1H), 6.51 (dd,  $J = 3.5, 1.8$  Hz, 1H), 3.27 (brs, 1H), 2.08 (td,  $J = 7.0, 6.2, 2.1$  Hz, 4H), 1.97 – 1.87 (m, 2H), 1.85 – 1.74 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.8, 151.0, 145.9, 130.6, 126.6, 116.0, 112.9, 103.9, 75.5, 74.6, 42.4, 23.5.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{14}\text{H}_{15}\text{O}_3]^+$ : 231.1016, Found. 231.1017.



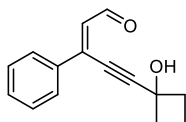
**(Z)-3-(tert-butyl)-5-(1-hydroxycyclopentyl)pent-2-en-4-ynal (1k)**

Yield: 67%, yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.37 (d,  $J = 8.0$  Hz, 1H), 8.32 (s, 1H), 8.02 (d,  $J = 7.9$  Hz, 2H), 7.88 – 7.72 (m, 4H), 7.54 (m, 7H), 7.38 (d,  $J = 6.9$  Hz, 3H), 6.95 (d,  $J = 7.9$  Hz, 1H), 4.08 (brs, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.7, 156.8, 130.4, 106.7, 77.9, 74.6, 42.3, 37.6, 28.6, 23.4.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{14}\text{H}_{21}\text{O}_2]^+$ : 221.1536, Found. 221.1539.



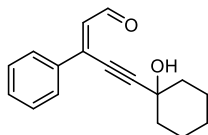
**(Z)-5-(1-hydroxycyclobutyl)-3-phenylpent-2-en-4-ynal (1l)**

Yield: 52%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.34 – 10.18 (m, 1H), 7.86 – 7.65 (m, 2H), 7.50 – 7.35 (m, 3H), 6.84 – 6.49 (m, 1H), 3.96 (brs, 1H), 2.63 – 2.52 (m, 2H), 2.50 – 2.39 (m, 2H), 1.99 – 1.85 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.6, 142.7, 135.3, 131.2, 131.0, 128.9, 127.2, 106.6, 78.1, 68.1, 38.5, 13.2.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{15}\text{H}_{14}\text{NaO}_2]^+$ : 249.0886, Found. 249.0889.



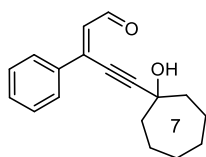
**(Z)-5-(1-hydroxycyclohexyl)-3-phenylpent-2-en-4-ynal (1m)**

Yield: 67%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.28 (d,  $J = 8.0$  Hz, 1H), 7.77 (d,  $J = 6.8$  Hz, 2H), 7.50 – 7.39 (m, 3H), 6.76 (d,  $J = 8.0$  Hz, 1H), 3.05 (brs, 1H), 2.14 – 1.99 (m, 2H), 1.87 – 1.70 (m, 4H), 1.67 – 1.50 (m, 3H), 1.45 – 1.21 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.3, 142.5, 135.5, 131.2, 131.2, 128.9, 127.2, 106.7, 78.9, 69.3, 39.7, 25.1, 23.3.

**HRMS (ESI)** ( $[M+Na]^+$ ) Calcd. for  $[C_{17}H_{18}NaO_2]^+$ : 277.1199, Found. 277.1202.



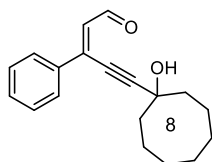
**(Z)-5-(1-hydroxycycloheptyl)-3-phenylpent-2-en-4-ynal (1n)**

Yield: 44%, yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 3:1).

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  10.25 (d,  $J = 8.0$  Hz, 1H), 7.75 (d,  $J = 7.3$  Hz, 2H), 7.47 – 7.36 (m, 3H), 6.74 (d,  $J = 8.0$  Hz, 1H), 3.34 (brs, 1H), 2.18 (dd,  $J = 14.2, 8.2$  Hz, 2H), 2.01 (dd,  $J = 13.8, 9.2$  Hz, 2H), 1.82 – 1.68 (m, 2H), 1.68 – 1.44 (m, 6H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  193.5, 142.7, 135.5, 131.2, 131.1, 128.8, 127.2, 108.1, 78.0, 72.3, 42.8, 28.1, 22.2.

**HRMS (ESI)** ( $[M+H]^+$ ) Calcd. for  $[C_{18}H_{21}O_2]^+$ : 269.1536, Found. 269.1539.



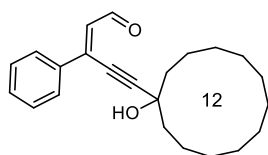
**(Z)-5-(1-hydroxycyclooctyl)-3-phenylpent-2-en-4-ynal (1o)**

Yield: 88%, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 3:1).

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  10.22 (d,  $J = 8.0$  Hz, 1H), 7.73 (d,  $J = 7.2$  Hz, 2H), 7.47 – 7.30 (m, 3H), 6.71 (d,  $J = 8.0$  Hz, 1H), 3.00 (brs, 1H), 2.08 (t,  $J = 9.0$  Hz, 4H), 1.77 – 1.56 (m, 8H), 1.55 – 1.41 (m, 2H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  193.5, 142.6, 135.5, 131.1, 131.1, 128.8, 127.2, 107.8, 77.9, 72.0, 37.9, 27.9, 24.4, 22.1.

**HRMS (ESI)** ( $[M+H]^+$ ) Calcd. for  $[C_{19}H_{23}O_2]^+$ : 283.1693, Found. 283.1695.



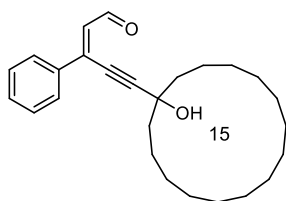
**(Z)-5-(1-hydroxycyclododecyl)-3-phenylpent-2-en-4-ynal (1p)**

Yield: 56%, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 5:1).

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  10.26 (d,  $J = 7.9$  Hz, 1H), 7.76 (d,  $J = 7.1$  Hz, 2H), 7.51 – 7.36 (m, 3H), 6.75 (d,  $J = 7.9$  Hz, 1H), 2.82 (s, 1H), 2.01 (td,  $J = 13.3, 4.4$  Hz, 2H), 1.91 – 1.77 (m, 2H), 1.58 (d,  $J = 10.3$  Hz, 2H), 1.51 – 1.25 (m, 16H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  193.4, 142.5, 135.5, 131.1, 128.9, 127.2, 107.4, 78.2, 71.5, 35.7, 26.0, 25.9, 22.5, 22.2, 19.7.

**HRMS (ESI)** ( $[M+H]^+$ ) Calcd. for  $[C_{23}H_{31}O_2]^+$ : 339.2319, Found. 339.2319.



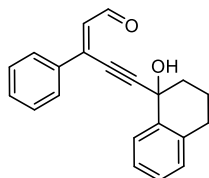
**(Z)-5-(1-hydroxycyclopentadecyl)-3-phenylpent-2-en-4-ynal (1q)**

Yield: 56%, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.26 – 10.18 (m, 1H), 7.77 – 7.65 (m, 2H), 7.43 – 7.32 (m, 3H), 6.74 – 6.67 (m, 1H), 3.64 (brs, 1H), 1.95 – 1.78 (m,  $J = 6.1$  Hz, 4H), 1.55 – 1.21 (m, 20H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.5, 142.6, 135.4, 131.1, 130.9, 128.8, 127.2, 107.8, 78.1, 77.6, 71.4, 39.3, 27.5, 26.9, 26.7, 26.7, 26.4, 22.2.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{26}\text{H}_{36}\text{NaO}_2]^+$ : 403.2608, Found. 403.2605.



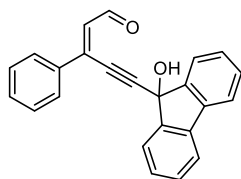
**(Z)-5-(1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)-3-phenylpent-2-en-4-ynal (1r)**

Yield: 59%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.18 (d,  $J = 7.9$  Hz, 1H), 7.77 (d,  $J = 6.9$  Hz, 1H), 7.70 (d,  $J = 7.3$  Hz, 2H), 7.47 – 7.32 (m, 3H), 7.27 – 7.19 (m, 2H), 7.10 (d,  $J = 6.8$  Hz, 1H), 6.70 (d,  $J = 7.9$  Hz, 1H), 3.29 (brs, 1H), 2.94 – 2.68 (m, 2H), 2.31 (t,  $J = 6.2$  Hz, 2H), 2.14 – 2.00 (m, 1H), 2.00 – 1.86 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.4, 142.3, 138.3, 136.2, 135.4, 131.4, 131.2, 129.4, 128.9, 128.5, 127.8, 127.2, 126.8, 106.9, 79.1, 68.5, 38.8, 29.2, 19.3.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{21}\text{H}_{19}\text{O}_2]^+$ : 303.1380, Found. 303.1383.



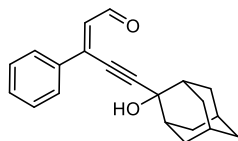
**(Z)-5-(9-hydroxy-9H-fluoren-9-yl)-3-phenylpent-2-en-4-ynal (1s)**

Yield: 50%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.97 (d,  $J = 8.0$  Hz, 1H), 7.69 (d,  $J = 7.3$  Hz, 2H), 7.57 (d,  $J = 7.3$  Hz, 2H), 7.51 (d,  $J = 7.3$  Hz, 2H), 7.34 – 7.20 (m, 7H), 6.56 (d,  $J = 8.0$  Hz, 1H), 4.35 (brs, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.6, 146.5, 142.2, 139.2, 135.1, 131.8, 131.3, 130.1, 128.9, 128.8, 127.3, 124.4, 120.5, 103.1, 77.3, 75.2.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{24}\text{H}_{17}\text{O}_2]^+$ : 337.1223, Found. 337.1224.



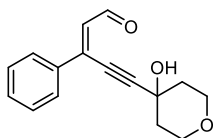
**(Z)-5-((1r,3r,5r,7r)-2-hydroxyadamantan-2-yl)-3-phenylpent-2-en-4-ynal (1t)**

Yield: 56%, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 2:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.00 (d,  $J = 240.6, 8.1$  Hz, 1H), 7.79 (dd,  $J = 7.8, 1.9$  Hz, 2H), 7.53 – 7.40 (m, 3H), 6.77 (d, 1H), 2.27 (dd,  $J = 13.1, 3.1$  Hz, 2H), 2.19 – 2.12 (m, 4H), 2.00 – 1.82 (m, 4H), 1.80 – 1.70 (m, 3H), 1.69 – 1.62 (m, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.2, 142.4, 135.6, 131.3, 131.1, 128.9, 127.2, 107.4, 79.7, 73.4, 38.7, 37.4, 35.6, 31.5, 26.8, 26.7.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{21}\text{H}_{22}\text{NaO}_2]^+$ : 329.1512, Found. 329.1514.



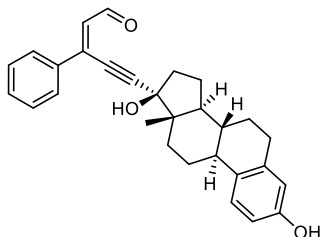
**(Z)-5-(4-hydroxytetrahydro-2H-pyran-4-yl)-3-phenylpent-2-en-4-ynal (1u)**

Yield: 58%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.26 (d,  $J = 7.9$  Hz, 1H), 7.74 (dd,  $J = 7.8, 1.7$  Hz, 2H), 7.51 – 7.38 (m, 3H), 6.77 (d,  $J = 7.9$  Hz, 1H), 3.97 (dt,  $J = 11.8, 4.9$  Hz, 2H), 3.71 (ddd,  $J = 11.7, 8.5, 3.0$  Hz, 3H), 3.31 (s, 1H), 2.11 (dt,  $J = 13.3, 3.9$  Hz, 2H), 1.97 (dd,  $J = 8.8, 4.0$  Hz, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.9, 141.9, 135.3, 131.6, 131.3, 129.0, 127.1, 105.0, 79.3, 77.3, 66.3, 64.6, 39.6.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{17}\text{O}_3]^+$ : 257.1172, Found. 257.1178.



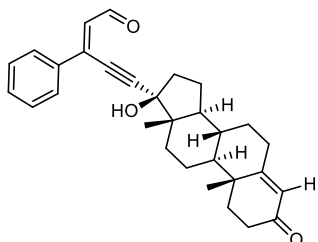
**(Z)-5-((8R,9S,13S,14S)-3,17-dihydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)-3-phenylpent-2-en-4-ynal (1v)**

Yield: 78%, yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 1:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.31 (d,  $J = 8.0$  Hz, 1H), 7.80 (d,  $J = 7.3$  Hz, 2H), 7.45 (dq,  $J = 14.1, 7.0$  Hz, 3H), 7.12 (d,  $J = 8.5$  Hz, 1H), 7.02 (s, 1H), 6.81 (d,  $J = 8.0$  Hz, 1H), 6.71 (d,  $J = 8.3$  Hz, 1H), 6.64 (s, 1H), 3.78 (s, 1H), 2.81 (d,  $J = 6.4$  Hz, 2H), 2.52 (td,  $J = 9.3, 4.7$  Hz, 1H), 2.39 – 2.31 (m, 1H), 2.29 – 2.14 (m, 2H), 1.90 (dq,  $J = 13.0, 7.0, 5.7$  Hz, 4H), 1.83 – 1.73 (m, 1H), 1.59 – 1.43 (m, 3H), 1.36 (ddt,  $J = 20.0, 13.3, 7.4$  Hz, 1H), 1.00 (s, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  194.0, 153.9, 143.3, 138.0, 135.5, 131.9, 131.4, 130.9, 129.0, 127.3, 126.5, 115.5, 113.0, 107.3, 81.1, 80.9, 77.4, 50.5, 48.2, 43.7, 39.5, 39.3, 33.4, 29.6, 27.4, 26.4, 25.9, 23.1, 13.1.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{29}\text{H}_{31}\text{O}_3]^+$ : 427.2268, Found. 427.2272.

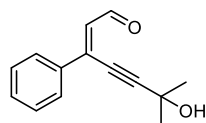


**(Z)-5-((8R,9S,10R,13S,14S,17R)-17-hydroxy-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-3-phenylpent-2-en-4-ynal (1w)**

Yield: 62%, yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.21 (d,  $J = 8.1$  Hz, 1H), 7.71 (d,  $J = 7.4$  Hz, 2H), 7.45 – 7.31 (m, 3H), 6.69 (d,  $J = 7.8$  Hz, 1H), 5.70 (s, 1H), 4.12 (brs, 1H), 2.48 – 2.08 (m, 7H), 2.01 – 1.92 (m, 1H), 1.88 – 1.71 (m, 3H), 1.68 – 1.53 (m, 4H), 1.53 – 1.33 (m, 3H), 1.14 (s, 3H), 0.95 (s, 3H), 0.93 – 0.77 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 193.3, 171.5, 142.5, 135.5, 131.2, 131.0, 128.8, 127.2, 123.8, 107.1, 80.7, 80.2, 53.6, 50.8, 47.6, 39.2, 38.6, 36.2, 35.6, 33.8, 33.1, 32.7, 31.5, 23.3, 20.7, 17.4, 12.9.  
HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{30}\text{H}_{34}\text{NaO}_3]^+$ : 465.2400, Found. 465.2402.



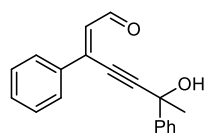
**(Z)-6-hydroxy-6-methyl-3-phenylhept-2-en-4-ynal (1x)**

Yield: 78%, yellow oil,  $R_f = 0.37$  (petroleum ether/AcOEt = 3:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.15 (d,  $J = 8.0$  Hz, 1H), 7.64 (dd,  $J = 8.0, 1.7$  Hz, 2H), 7.34 – 7.27 (m, 3H), 6.63 (d,  $J = 8.0$  Hz, 1H), 4.40 (brs, 1H), 1.62 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.8, 142.7, 135.2, 131.2, 130.8, 128.8, 127.2, 107.9, 76.6, 65.4, 31.1.

HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{14}\text{H}_{14}\text{NaO}_2]^+$ : 237.0886, Found. 237.0887.



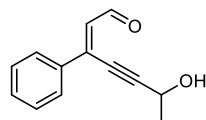
**(Z)-6-hydroxy-3,6-diphenylhept-2-en-4-ynal (1y)**

Yield: 64%, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 3:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.25 (d,  $J = 8.0$  Hz, 1H), 7.77 (d,  $J = 7.3$  Hz, 2H), 7.51 (d,  $J = 8.2$  Hz, 2H), 7.48 – 7.40 (m, 3H), 6.95 (d,  $J = 8.2$  Hz, 2H), 6.77 (d,  $J = 8.0$  Hz, 1H), 5.74 (s, 1H), 3.94 – 3.46 (m, 4H), 3.37 (s, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.3, 160.0, 142.1, 135.2, 132.2, 131.7, 131.2, 128.9, 128.1, 127.2, 114.3, 102.5, 80.8, 77.3, 64.7, 55.4.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{19}\text{H}_{17}\text{O}_2]^+$ : 277.1223, Found. 277.1224.



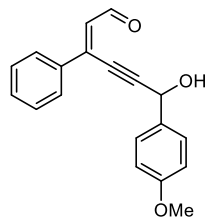
**(Z)-6-hydroxy-3-phenylhept-2-en-4-ynal (1z)**

Yield: 56%, yellow oil,  $R_f = 0.37$  (petroleum ether/AcOEt = 3:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.23 (d,  $J = 8.0$  Hz, 1H), 7.74 (d,  $J = 8.1$  Hz, 2H), 7.48 – 7.36 (m, 3H), 6.73 (d,  $J = 8.0$  Hz, 1H), 4.86 (q,  $J = 6.7$  Hz, 1H), 3.69 (brs, 1H), 1.61 (d,  $J = 6.7$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.7, 142.5, 135.2, 131.2, 131.2, 128.9, 127.2, 104.8, 78.5, 58.6, 24.0.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{13}\text{H}_{13}\text{O}_2]^+$ : 201.0910, Found. 201.0910.



**(Z)-6-hydroxy-6-(4-methoxyphenyl)-3-phenylhex-2-en-4-ynal (1aa)**

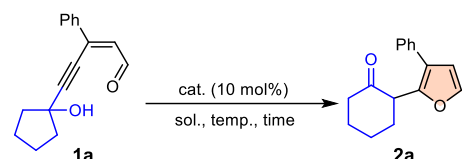
Yield: 89%, yellow oil,  $R_f = 0.37$  (petroleum ether/AcOEt = 3:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.25 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.40 (m, 3H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.74 (s, 1H), 3.94 – 3.46 (m, 4H), 3.37 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 193.3, 160.0, 142.1, 135.2, 132.2, 131.7, 131.2, 128.9, 128.1, 127.2, 114.3, 102.5, 80.8, 77.3, 64.7, 55.4.

HRMS (ESI) ([M+Na]<sup>+</sup>) Calcd. for [C<sub>19</sub>H<sub>16</sub>NaO<sub>3</sub>]<sup>+</sup>: 315.0992, Found. 315.0995

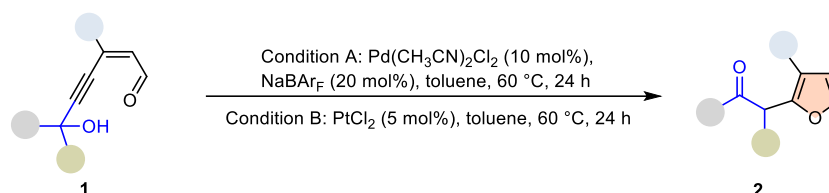
## 2. Optimization of the reaction conditions for Synthesis of 2a<sup>a</sup>



Entry	Cat.	T.	Sol.	Time/h	2a
1	Pd(PhCN) <sub>2</sub> Cl <sub>2</sub>	rt	Toluene	36	trace
2	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	rt	Toluene	36	trace
3	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	60 °C	Toluene	36	50%
4 <sup>b</sup>	<b>Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub></b>	<b>60 °C</b>	<b>Toluene</b>	<b>6</b>	<b>79%</b>
5 <sup>c</sup>	<b>PtCl<sub>2</sub></b>	<b>60 °C</b>	Toluene	<b>6</b>	<b>63%</b>
6 <sup>b</sup>	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	80 °C	Toluene	6	47%
7 <sup>b</sup>	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	60 °C	THF	24	40%
8 <sup>b</sup>	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	60 °C	DCE	24	16%
9 <sup>d</sup>	Rh <sub>2</sub> (OAc) <sub>4</sub>	60 °C	Toluene	24	20%

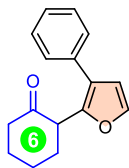
<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), and 10 mol% cat. in solvent (2 mL) under N<sub>2</sub>. The yield was determined by <sup>1</sup>H NMR analysis using CH<sub>3</sub>NO<sub>2</sub> as an internal standard; <sup>b</sup>NaBAR<sub>F</sub> (20 mol%) was used as additive. <sup>c</sup>PtCl<sub>2</sub> (5 mol%) was used. <sup>d</sup>Rh<sub>2</sub>(OAc)<sub>4</sub> (2 mol%) was used.

## 3. General procedure for the synthesis of 2a-2z.



**Condition A:** under nitrogen atmosphere, to a solution of enynals **1** (0.2 mmol) in dry toluene (0.025 M), Pd(CH<sub>3</sub>CN)<sub>2</sub>Cl<sub>2</sub> (0.1 eq., 5.2 mg) and NaBAR<sub>F</sub> (0.2 eq., 35 mg) were added. The reaction mixture was then heated to a temperature of 60 °C and stirred for 24 hours. After the reaction was completed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The bifuran product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) to yield **2**.

**Condition B:** under nitrogen atmosphere, to a solution of enynals **1** (0.2 mmol) in dry toluene (0.025 M), PtCl<sub>2</sub> (0.05 eq., 2.7 mg) were added. The reaction mixture was then heated to a temperature of 60 °C and stirred for 24 hours. After the reaction was completed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The bifuran product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) to yield **2**.



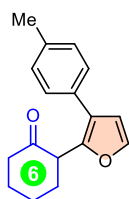
### 2-(3-phenylfuran-2-yl)cyclohexan-1-one (2a)

Condition A, Yield: 79% (38 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 7.26 – 7.20 (m, 1H), 6.44 (d,  $J = 1.9$  Hz, 1H), 3.54 (t,  $J = 9.8$  Hz, 1H), 2.42 – 2.20 (m, 4H), 2.19 – 2.08 (m, 1H), 1.91 – 1.73 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  216.6, 147.3, 141.4, 133.6, 128.7, 128.0, 127.1, 124.6, 111.6, 47.5, 38.2, 29.5, 21.1.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{NaO}_2]^+$ : 263.1043, Found. 263.1048.



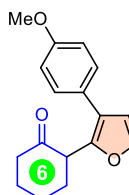
### 2-(3-(p-tolyl)furan-2-yl)cyclohexan-1-one (2b)

Condition A, Yield: 72% (36 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 1.7$  Hz, 1H), 7.24 – 7.18 (m, 4H), 6.52 (d,  $J = 1.9$  Hz, 1H), 3.85 (q, 1H), 2.63 (dt,  $J = 14.1, 4.5$  Hz, 1H), 2.44 (dd,  $J = 12.9, 6.0$  Hz, 1H), 2.40 (s, 3H), 2.29 – 2.18 (m, 2H), 2.16 – 2.00 (m, 2H), 1.96 – 1.81 (m, 1H), 1.80 – 1.69 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.8, 147.6, 141.4, 136.6, 130.9, 129.3, 128.0, 123.3, 111.7, 49.6, 42.0, 32.2, 27.2, 24.8, 21.1.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{17}\text{H}_{19}\text{O}_2]^+$ : 255.1380, Found. 255.1383.



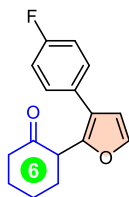
### 2-(3-(4-methoxyphenyl)furan-2-yl)cyclohexan-1-one (2c)

Condition A, Yield: 78% (42 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (d,  $J = 1.9$  Hz, 1H), 7.26 – 7.20 (m, 2H), 6.97 – 6.91 (m, 2H), 6.50 (d,  $J = 1.9$  Hz, 1H), 3.85 (s, 3H), 2.62 (dt, 1H), 2.43 (td,  $J = 13.7, 13.0, 5.7$  Hz, 1H), 2.27 – 2.17 (m, 2H), 2.15 – 2.00 (m, 2H), 1.95 – 1.81 (m, 1H), 1.80 – 1.68 (m, 1H), 1.68 – 1.57 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.9, 158.7, 147.4, 141.4, 129.2, 126.2, 123.0, 114.1, 111.7, 49.6, 41.9, 32.2, 27.2, 24.8.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{17}\text{H}_{19}\text{O}_3]^+$ : 271.1329, Found. 271.1327.





### 2-(3-(4-fluorophenyl)furan-2-yl)cyclohexan-1-one (2d)

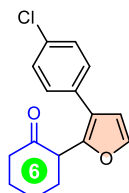
Condition A, Yield: 44% (23 mg), yellow oil,  $R_f = 0.33$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 1.9$  Hz, 1H), 7.31 – 7.24 (m, 2H), 7.13 – 7.04 (m, 2H), 6.49 (d,  $J = 1.9$  Hz, 1H), 3.79 (dd,  $J = 10.9, 6.3$  Hz, 1H), 2.63 (dtd,  $J = 14.2, 4.4, 1.5$  Hz, 1H), 2.48 – 2.37 (m, 1H), 2.29 – 2.18 (m, 2H), 2.16 – 1.99 (m, 2H), 1.96 – 1.81 (m, 1H), 1.81 – 1.66 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.6, 162.0 (d,  $J = 245.9$  Hz), 147.8, 141.5, 129.8 (d,  $J = 3.3$  Hz), 129.7 (d,  $J = 8.0$  Hz), 122.6, 115.5 (d,  $J = 21.5$  Hz), 111.6, 77.4, 77.1, 76.7, 49.6, 41.9, 32.1, 27.1, 24.7.

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.6.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{FO}_2]^+$ : 259.1129, Found. 259.1127.



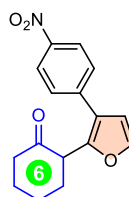
### 2-(3-(4-chlorophenyl)furan-2-yl)cyclohexan-1-one (2e)

Condition A, Yield: 56% (31 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 1.9$  Hz, 1H), 7.40 – 7.34 (m, 2H), 7.26 – 7.20 (m, 2H), 6.50 (d,  $J = 1.9$  Hz, 1H), 3.79 (dd,  $J = 10.9, 6.4$  Hz, 1H), 2.63 (dtd,  $J = 14.3, 4.4, 1.4$  Hz, 1H), 2.48 – 2.36 (m, 1H), 2.29 – 2.17 (m, 2H), 2.16 – 2.01 (m, 2H), 1.94 – 1.82 (m, 1H), 1.80 – 1.61 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.6, 148.0, 141.7, 132.8, 132.3, 129.3, 128.8, 122.5, 111.4, 49.6, 41.9, 32.1, 27.1, 24.7.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{ClO}_2]^+$ : 275.0833, Found. 275.0829.



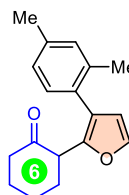
### 2-(3-(4-nitrophenyl)furan-2-yl)cyclohexan-1-one (2f)

Condition A, Yield: 37% (21 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J = 8.4$  Hz, 2H), 7.50 (d,  $J = 1.9$  Hz, 1H), 7.46 (d,  $J = 8.3$  Hz, 2H), 6.58 (d,  $J = 1.9$  Hz, 1H), 3.82 (q,  $J = 10.7, 6.6$  Hz, 1H), 2.73 – 2.58 (m, 1H), 2.45 (td,  $J = 13.7, 13.1, 5.7$  Hz, 1H), 2.26 (td,  $J = 10.3, 9.9, 3.6$  Hz, 2H), 2.19 – 2.03 (m, 2H), 1.98 – 1.83 (m, 1H), 1.83 – 1.69 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.8, 147.6, 141.4, 136.6, 130.9, 129.3, 128.0, 123.3, 111.7, 49.6, 42.0, 32.2, 27.2, 24.8, 21.1.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{15}\text{NNaO}_4]^+$ : 308.0893, Found. 308.0898.



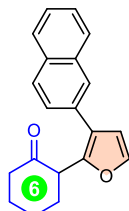
### 2-(3-(2,4-dimethylphenyl)furan-2-yl)cyclohexan-1-one (2g)

Condition A, Yield: 75% (38 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.45 (d, *J* = 1.9 Hz, 1H), 7.09 (s, 1H), 7.01 (s, 2H), 6.38 (d, *J* = 1.8 Hz, 1H), 3.56 (t, 1H), 2.55 (dtd, *J* = 14.0, 4.2, 1.4 Hz, 1H), 2.37 (s, 3H), 2.34 – 2.27 (m, 1H), 2.21 (s, 3H), 2.16 (td, *J* = 9.6, 8.8, 3.9 Hz, 2H), 2.10 – 2.02 (m, 1H), 2.02 – 1.93 (m, 1H), 1.89 – 1.76 (m, 1H), 1.74 – 1.63 (m, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 208.6, 148.2, 141.0, 137.2, 137.0, 130.9, 130.2, 130.1, 126.4, 122.4, 112.7, 49.4, 42.0, 32.3, 27.2, 24.8, 21.1, 20.2.

**HRMS (ESI) ([M+H]<sup>+</sup>)** Calcd. for [C<sub>18</sub>H<sub>21</sub>O<sub>2</sub>]<sup>+</sup>: 269.1536, Found. 269.1538.



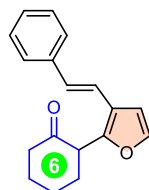
### 2-(3-(naphthalen-2-yl)furan-2-yl)cyclohexan-1-one (2h)

Condition A, Yield: 61% (35 mg), yellow oil, *R*<sub>f</sub> = 0.35 (petroleum ether/AcOEt = 10:1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.90 – 7.83 (m, 3H), 7.75 (s, 1H), 7.51 (q, *J* = 4.1, 3.3 Hz, 3H), 7.45 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.64 (d, *J* = 1.9 Hz, 1H), 3.93 (dd, *J* = 11.0, 6.3 Hz, 1H), 2.66 (dt, *J* = 14.2, 4.5 Hz, 1H), 2.44 (td, *J* = 13.6, 13.1, 5.8 Hz, 1H), 2.33 – 2.18 (m, 2H), 2.18 – 2.00 (m, 2H), 1.97 – 1.81 (m, 1H), 1.80 – 1.67 (m, 1H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 208.8, 148.2, 141.7, 133.5, 132.3, 131.3, 128.2, 127.9, 127.7, 126.6, 126.6, 126.3, 125.8, 123.5, 111.8, 49.8, 42.0, 32.2, 27.2, 24.8.

**HRMS (ESI) ([M+H]<sup>+</sup>)** Calcd. for [C<sub>20</sub>H<sub>19</sub>O<sub>2</sub>]<sup>+</sup>: 291.1380, Found. 291.1385.



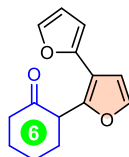
### (E)-2-(3-styrylfuran-2-yl)cyclohexan-1-one (2i)

Condition A, Yield: 66% (35 mg), yellow oil, *R*<sub>f</sub> = 0.35 (petroleum ether/AcOEt = 10:1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.50 – 7.45 (m, 2H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.22 (m, 1H), 6.89 – 6.75 (m, 2H), 6.67 (d, *J* = 2.0 Hz, 1H), 3.91 (t, *J* = 8.3 Hz, 1H), 2.69 – 2.58 (m, 1H), 2.53 – 2.42 (m, 1H), 2.31 – 2.21 (m, 2H), 2.18 – 2.03 (m, 2H), 1.97 – 1.76 (m, 2H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 207.9, 149.5, 142.1, 137.6, 128.6, 128.3, 127.3, 126.2, 120.8, 118.3, 108.0, 49.3, 41.8, 32.2, 27.3, 24.7.

**HRMS (ESI) ([M+H]<sup>+</sup>)** Calcd. for [C<sub>18</sub>H<sub>19</sub>O<sub>2</sub>]<sup>+</sup>: 267.1380, Found. 267.1380.



### 2-[(2,3'-bifuran)-2'-yl]cyclohexan-1-one (2j)

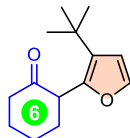
Condition B, Yield: 61% (28 mg), yellow oil, *R*<sub>f</sub> = 0.35 (petroleum ether/AcOEt = 10:1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.39 (d, *J* = 2.1 Hz, 2H), 6.57 (d, *J* = 1.9 Hz, 1H), 6.42 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.30 (d, *J* = 3.3 Hz, 1H), 4.21 (dd, *J* = 11.2, 6.3 Hz, 1H), 2.61 (dt, *J* = 14.5, 4.4 Hz, 1H), 2.49

(td,  $J = 13.5, 12.8, 5.8$  Hz, 1H), 2.32 – 2.22 (m, 2H), 2.15 (dd,  $J = 11.7, 5.0$  Hz, 1H), 2.06 (dd,  $J = 11.3, 5.0$  Hz, 1H), 1.95 – 1.76 (m, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  207.9, 148.5, 147.9, 141.8, 141.2, 114.2, 111.1, 109.2, 105.7, 50.4, 42.0, 31.9, 27.3, 24.9.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{14}\text{H}_{15}\text{O}_3]^+$ : 231.1016, Found. 231.1012.



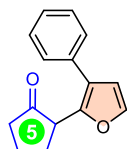
### 2-(3-(tert-butyl)furan-2-yl)cyclohexan-1-one (2k)

Condition A, Yield: 57% (25 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (d,  $J = 1.3$  Hz, 1H), 6.52 (t,  $J = 1.2$  Hz, 1H), 3.79 – 3.65 (m, 1H), 1.99 – 1.77 (m, 4H), 1.77 – 1.62 (m, 4H), 1.38 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.6, 147.8, 144.1, 142.9, 112.9, 47.8, 31.3, 29.4, 29.3, 26.2.

HRMS (ESI) ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{14}\text{H}_{20}\text{NaO}_2]^+$ : 243.1356, Found. 243.1358.



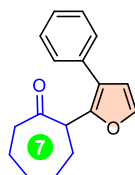
### 2-(3-phenylfuran-2-yl)cyclopentan-1-one (2l)

Condition A, Yield: 63% (28 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 7.26 – 7.20 (m, 1H), 6.44 (d,  $J = 1.9$  Hz, 1H), 3.54 (t,  $J = 9.8$  Hz, 1H), 2.42 – 2.20 (m, 4H), 2.19 – 2.08 (m, 1H), 1.91 – 1.73 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  216.6, 147.3, 141.4, 133.6, 128.7, 128.0, 127.1, 124.6, 111.6, 47.5, 38.2, 29.5, 21.1.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{15}\text{H}_{15}\text{O}_2]^+$ : 227.1067, Found. 227.1068.



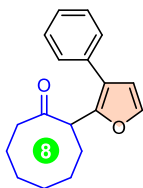
### 2-(3-phenylfuran-2-yl)cycloheptan-1-one (2m)

Condition B, Yield: 62% (31 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 6.9$  Hz, 2H), 7.46 – 7.40 (m, 3H), 7.36 – 7.30 (m, 1H), 6.52 (d,  $J = 1.8$  Hz, 1H), 3.97 (dd,  $J = 10.3, 4.8$  Hz, 1H), 2.92 (td,  $J = 12.4, 3.0$  Hz, 1H), 2.66 – 2.55 (m, 1H), 2.23 – 1.88 (m, 5H), 1.72 – 1.47 (m, 2H), 1.44 – 1.27 (m, 1H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  212.0, 149.0, 141.3, 133.5, 128.6, 128.2, 126.9, 122.7, 111.7, 51.4, 42.8, 30.4, 29.9, 28.1, 25.7.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{17}\text{H}_{19}\text{O}_2]^+$ : 255.1380, Found. 255.1383.



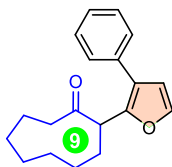
### 2-(3-phenylfuran-2-yl)cyclooctan-1-one (2n)

Condition B, Yield: 70% (37 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 7.5$  Hz, 2H), 7.37 – 7.29 (m, 3H), 7.22 (t,  $J = 7.3$  Hz, 1H), 6.41 (d,  $J = 1.8$  Hz, 1H), 3.85 (dd,  $J = 11.8, 3.0$  Hz, 1H), 2.86 (td,  $J = 12.2, 3.8$  Hz, 1H), 2.48 (dtd,  $J = 15.3, 11.7, 3.7$  Hz, 1H), 2.26 (ddd,  $J = 12.6, 6.3, 3.6$  Hz, 1H), 1.94 – 1.79 (m, 2H), 1.78 – 1.71 (m, 1H), 1.70 – 1.61 (m, 2H), 1.59 – 1.51 (m, 1H), 1.49 – 1.35 (m, 2H), 1.31 – 1.15 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  214.5, 148.0, 141.6, 133.4, 128.6, 128.3, 127.0, 122.8, 111.8, 50.9, 39.8, 29.2, 28.1, 26.8, 26.3, 24.7.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{18}\text{H}_{21}\text{O}_2]^+$ : 269.1536, Found. 269.1538.



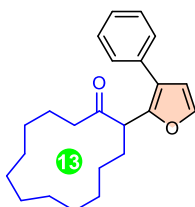
### 2-(3-phenylfuran-2-yl)cyclononan-1-one (2o)

Condition A, Yield: 53% (30 mg), yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.4$  Hz, 2H), 7.57 (s, 1H), 7.47 – 7.35 (m, 3H), 6.66 (s, 1H), 3.41 (td,  $J = 9.1, 4.1$  Hz, 1H), 1.94 – 1.81 (m, 2H), 1.80 – 1.66 (m, 4H), 1.64 – 1.48 (m, 8H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 146.4, 144.1, 133.7, 132.3, 129.3, 128.4, 128.1, 115.0, 46.0, 28.8, 26.5, 26.5, 25.6.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{19}\text{H}_{23}\text{O}_2]^+$ : 283.1693, Found. 283.1691.



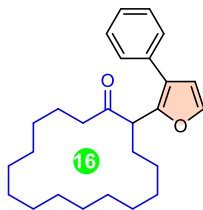
### 2-(3-phenylfuran-2-yl)cyclotridecan-1-one (2p)

Condition A, Yield: 58% (39 mg), yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 5.4$  Hz, 3H), 7.36 – 7.25 (m, 3H), 6.48 (s, 1H), 4.00 (d,  $J = 10.6$  Hz, 1H), 2.44 (dd,  $J = 14.7, 10.2$  Hz, 1H), 2.30 (tt,  $J = 20.0, 15.9, 6.0$  Hz, 2H), 1.72 – 1.47 (m, 4H), 1.41 – 1.31 (m, 4H), 1.32 – 1.17 (m, 11H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.3, 147.8, 141.8, 133.4, 128.7, 128.1, 127.0, 123.1, 111.8, 50.8, 39.7, 29.7, 29.4, 26.7, 26.1, 25.9, 25.7, 25.2, 24.8, 24.5, 23.0.

HRMS (ESI) ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{23}\text{H}_{31}\text{O}_2]^+$ : 339.2319, Found. 339.2316.



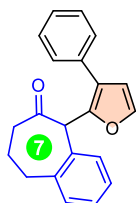
### 2-(3-phenylfuran-2-yl)cyclohexadecan-1-one (2q)

Condition B, Yield: 62% (47 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.38 (m, 3H), 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 6.50 (d,  $J = 1.9$  Hz, 1H), 3.96 (dd,  $J = 9.0, 5.8$  Hz, 1H), 2.45 (ddd,  $J = 16.5, 7.6, 6.1$  Hz, 1H), 2.37 – 2.16 (m, 2H), 1.76 (dq,  $J = 12.9, 6.6$  Hz, 1H), 1.56 (ddt,  $J = 26.9, 13.6, 7.2$  Hz, 2H), 1.28 (q,  $J = 7.5, 6.4$  Hz, 22H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.9, 147.5, 141.7, 133.5, 128.7, 128.1, 127.0, 123.6, 111.8, 50.8, 39.8, 29.5, 27.6, 27.3, 27.1, 27.0, 26.5, 26.5, 26.5, 26.4, 26.4, 23.0.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{26}\text{H}_{37}\text{O}_2]^+$ : 381.2788, Found. 381.2786.



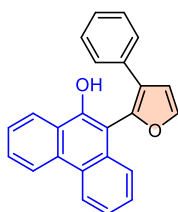
### 5-(3-phenylfuran-2-yl)-5,7,8,9-tetrahydro-6H-benzo[7]annulen-6-one (2r)

Condition B, Yield: 62% (37 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 7.2$  Hz, 2H), 7.63 (s, 1H), 7.40 (q,  $J = 9.5, 8.4$  Hz, 3H), 7.21 – 7.07 (m, 3H), 7.00 (d,  $J = 7.6$  Hz, 1H), 6.75 (s, 1H), 4.83 (t,  $J = 6.5$  Hz, 1H), 2.97 – 2.74 (m, 2H), 2.16 (q,  $J = 6.5, 6.0$  Hz, 2H), 2.08 – 1.90 (m, 1H), 1.89 – 1.70 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6, 146.6, 144.6, 138.1, 134.5, 134.4, 131.8, 129.5, 129.3, 128.5, 128.1, 126.5, 125.8, 115.2, 47.8, 29.3, 26.9, 20.5.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{21}\text{H}_{19}\text{O}_2]^+$ : 303.1380, Found. 303.1377.



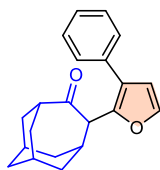
### 10-(3-phenylfuran-2-yl)phenanthren-9-ol (2s)

Condition B, Yield: 71% (48 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (dd,  $J = 18.8, 8.4$  Hz, 2H), 8.34 (d,  $J = 7.8$  Hz, 1H), 7.78 – 7.68 (m, 2H), 7.62 (t,  $J = 7.6$  Hz, 1H), 7.53 – 7.42 (m, 3H), 7.32 (dd,  $J = 6.5, 3.4$  Hz, 2H), 7.14 (d,  $J = 5.3$  Hz, 3H), 6.93 (d,  $J = 1.9$  Hz, 1H), 5.91 (s, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2, 144.6, 142.7, 132.1, 132.1, 131.7, 128.9, 128.2, 127.5, 127.4, 126.7, 126.7, 125.2, 124.8, 124.5, 123.8, 122.7, 122.6, 111.3, 107.0.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{24}\text{H}_{17}\text{O}_2]^+$ : 337.1223, Found. 337.1229.



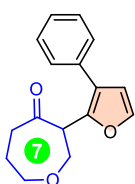
**5-(3-phenylfuran-2-yl)tricyclo[4.3.1.13,8]undecan-4-one (2t)**

Condition B (80 °C), Yield: 62% (38 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 6.9$  Hz, 2H), 7.52 (d,  $J = 1.7$  Hz, 1H), 7.47 – 7.36 (m, 3H), 6.62 (d,  $J = 1.7$  Hz, 1H), 3.42 (s, 1H), 2.30 (q,  $J = 3.0$  Hz, 2H), 2.17 (dd,  $J = 12.9, 3.0$  Hz, 2H), 1.95 (p,  $J = 3.2$  Hz, 1H), 1.91 – 1.80 (m, 5H), 1.76 (d,  $J = 13.4$  Hz, 2H), 1.60 (d,  $J = 12.5$  Hz, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.7, 147.1, 143.5, 133.0, 132.5, 129.2, 128.3, 128.2, 114.8, 52.8, 38.9, 37.6, 33.0, 29.9, 28.0, 27.4.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{21}\text{H}_{23}\text{O}_2]^+$ : 307.1693, Found. 307.1694.



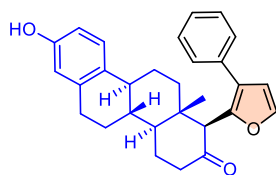
**3-(3-phenylfuran-2-yl)oxepan-4-one (2u)**

Condition B, Yield: 62% (32 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.29 (m, 5H), 7.24 (q,  $J = 4.5$  Hz, 1H), 6.43 (d,  $J = 1.9$  Hz, 1H), 4.06 (tt,  $J = 10.1, 3.4$  Hz, 2H), 3.97 (ddd,  $J = 12.8, 5.5, 4.0$  Hz, 1H), 3.62 (ddd,  $J = 12.6, 9.8, 2.6$  Hz, 1H), 3.51 (ddd,  $J = 12.4, 9.9, 1.8$  Hz, 1H), 3.02 (ddd,  $J = 14.2, 9.9, 3.9$  Hz, 1H), 2.63 (ddd,  $J = 14.8, 5.5, 2.6$  Hz, 1H), 2.34 (dtd,  $J = 15.5, 10.2, 2.5$  Hz, 1H), 2.06 – 1.92 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.7, 148.0, 141.7, 133.4, 128.7, 128.2, 127.1, 123.2, 111.8, 71.2, 66.5, 50.2, 46.5, 31.4.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{NaO}_3]^+$ : 279.0992, Found. 279.0991.



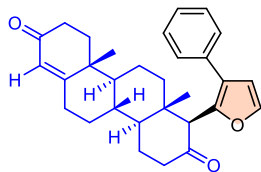
**(4aS,4bS,10bS,12aS)-8-hydroxy-12a-methyl-1-(3-phenylfuran-2-yl)-3,4,4a,4b,5,6,10b,11,12,12a-decahydrochrysen-2(1H)-one (2v)**

Condition B, Yield: 48% (41 mg), yellow oil,  $R_f = 0.31$  (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 1.8$  Hz, 1H), 7.29 (d,  $J = 7.4$  Hz, 1H), 7.20 (d,  $J = 7.2$  Hz, 1H), 7.14 (d,  $J = 6.5$  Hz, 3H), 6.96 (d,  $J = 8.4$  Hz, 1H), 6.49 (dd,  $J = 8.4, 2.7$  Hz, 1H), 6.44 (d,  $J = 2.7$  Hz, 1H), 6.39 (d,  $J = 1.8$  Hz, 1H), 4.65 (s, 1H), 3.65 (s, 1H), 2.70 (dd,  $J = 8.4, 4.4$  Hz, 2H), 2.52 – 2.45 (m, 1H), 2.31 (dd,  $J = 14.7, 12.0$  Hz, 1H), 2.15 (td,  $J = 11.5, 7.7$  Hz, 2H), 2.07 – 1.95 (m, 2H), 1.56 – 1.47 (m, 3H), 1.31 – 1.21 (m, 2H), 1.15 (s, 1H), 1.13 – 1.08 (m, 1H), 1.05 (s, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.2, 153.6, 153.5, 146.0, 141.8, 138.0, 134.3, 132.3, 128.8, 128.7, 128.5, 126.9, 126.4, 126.2, 126.0, 124.9, 115.3, 115.0, 112.9, 111.5, 61.0, 49.9, 43.2, 42.9, 40.8, 39.5, 38.8, 29.8, 26.5, 26.1, 25.5, 15.7.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{29}\text{H}_{31}\text{O}_3]^+$ : 427.2268, Found. 427.2272.



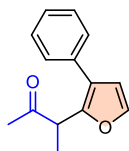
**(4a*S*,4b*S*,10a*R*,10b*S*,12a*S*)-10a,12a-dimethyl-1-(3-phenylfuran-2-yl)-1,3,4,4a,4b,5,6,9,10,10a,10b,11,12,12a-tetradecahydrochrysene-2,8-dione (2w)**

Condition B, Yield: 77% (68 mg), white solid, m.p. = 172 - 174 °C,  $R_f$  = 0.35 (petroleum ether/AcOEt = 3:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.21 (d,  $J$  = 8.1 Hz, 1H), 7.71 (d,  $J$  = 7.3 Hz, 2H), 7.45 – 7.32 (m, 3H), 6.69 (d,  $J$  = 7.8 Hz, 1H), 5.70 (s, 1H), 4.12 (s, 1H), 2.47 – 2.28 (m, 4H), 2.26 – 2.08 (m, 2H), 1.96 (dd,  $J$  = 17.5, 6.7 Hz, 1H), 1.79 (dd,  $J$  = 21.4, 8.6 Hz, 3H), 1.63 (td,  $J$  = 17.8, 15.6, 8.3 Hz, 4H), 1.54 – 1.33 (m, 3H), 1.14 (s, 3H), 1.02 – 0.83 (m, 5H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.8, 193.3, 171.5, 142.5, 135.5, 131.2, 131.0, 128.8, 127.2, 123.8, 107.1, 80.7, 80.2, 77.5, 53.6, 50.8, 47.6, 39.2, 38.6, 36.2, 35.6, 33.8, 33.1, 32.7, 31.5, 23.3, 20.7, 17.4, 12.9.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{30}\text{H}_{34}\text{NaO}_3]^+$ : 465.2400, Found. 465.2403.



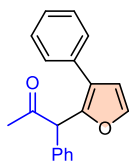
**3-(3-phenylfuran-2-yl)butan-2-one (2x)**

Condition B, Yield: 65% (28 mg), yellow oil,  $R_f$  = 0.35 (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.38 (m, 5H), 7.37 – 7.31 (m, 1H), 6.57 (d,  $J$  = 1.9 Hz, 1H), 3.99 (q,  $J$  = 7.1 Hz, 1H), 2.04 (s, 3H), 1.50 (d,  $J$  = 7.1 Hz, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  206.6, 141.8, 133.3, 128.8, 127.9, 127.1, 123.3, 111.9, 45.8, 27.9, 14.7.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{14}\text{H}_{15}\text{O}_2]^+$ : 215.1067, Found. 215.1069.



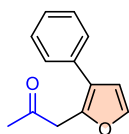
**1-phenyl-1-(3-phenylfuran-2-yl)propan-2-one (2y)**

Condition B, Yield: 63% (35 mg), yellow oil,  $R_f$  = 0.35 (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J$  = 1.9 Hz, 1H), 7.38 (dt,  $J$  = 13.8, 7.5 Hz, 4H), 7.31 (td,  $J$  = 7.3, 2.5 Hz, 6H), 6.57 (d,  $J$  = 1.8 Hz, 1H), 5.15 (s, 1H), 2.12 (s, 3H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  204.0, 146.3, 142.3, 136.7, 133.2, 129.0, 128.8, 128.1, 127.5, 127.3, 124.6, 112.0, 57.6, 28.7.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{19}\text{H}_{17}\text{O}_2]^+$ : 277.1223, Found. 277.1216.



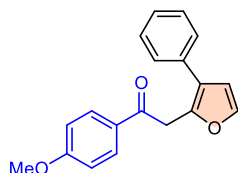
**1-(3-phenylfuran-2-yl)propan-2-one (2z)**

Condition B, Yield: 37% (15 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.40 (m, 3H), 7.39 – 7.31 (m, 3H), 6.60 (d,  $J = 1.9$  Hz, 1H), 3.85 (s, 2H), 2.20 (s, 3H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  204.5, 144.1, 141.9, 133.2, 128.8, 127.7, 127.1, 124.1, 111.7, 77.3, 77.0, 76.7, 42.3, 29.4.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{13}\text{H}_{13}\text{O}_2]^+$ : 201.0910, Found. 201.0916.



### 1-(4-methoxyphenyl)-2-(3-phenylfuran-2-yl)ethan-1-one (2aa)

Condition B, Yield: 69% (40 mg), yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

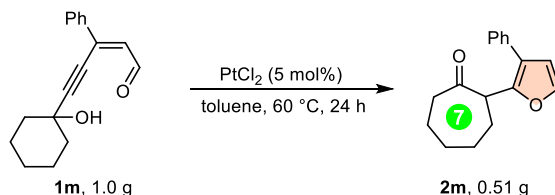
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.34 (m, 2H), 7.34 – 7.28 (m, 3H), 7.26 – 7.20 (m, 1H), 6.44 (d,  $J = 1.9$  Hz, 1H), 3.54 (t,  $J = 9.8$  Hz, 1H), 2.42 – 2.20 (m, 4H), 2.19 – 2.08 (m, 1H), 1.91 – 1.73 (m, 1H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  216.6, 147.3, 141.4, 133.6, 128.7, 128.0, 127.1, 124.6, 111.6, 47.5, 38.2, 29.5, 21.1.

**HRMS (ESI)** ( $[\text{M}+\text{Na}]^+$ ) Calcd. for  $[\text{C}_{16}\text{H}_{16}\text{NaO}_2]^+$ : 263.1043, Found. 263.1048.

## 4. Derivatization of product 2m

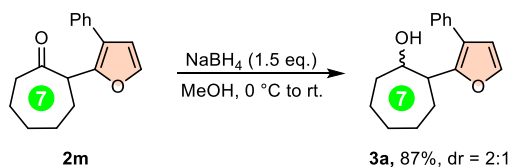
### 4.1 The gram-scale synthesis of product 2m



### The general procedure for the gram-scale synthesis of product 2m:

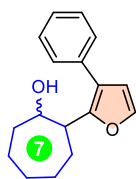
Under nitrogen atmosphere, to a solution of enynals **1m** (3.9 mmol, 1.0 g) in dry toluene (0.025 M),  $\text{PtCl}_2$  (0.05 eq., 52 mg) were added. The reaction mixture was then heated to a temperature of 60 °C and stirred for 24 hours. After the reaction was completed, the reaction mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The bifuran product was purified by flash column chromatography (silica gel, petroleum ether/AcOEt = 10:1) to yield **2m**.

### 4.2 Derivatization of product 2m.



To a solution of **2m** (50.8 mg, 0.2 mmol) in MeOH (2 mL),  $\text{NaBH}_4$  (11.3 mg, 0.3 mmol) was added at 0 °C. The mixture was stirred at 0 °C to room temperature for 4 h. Then  $\text{H}_2\text{O}$  (1 mL) was added. The organic layer was extracted with ethyl acetate and washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/5, v/v) to afford the product.





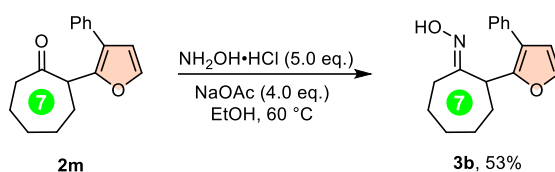
### 2-(3-phenylfuran-2-yl)cycloheptan-1-ol (**3a**)

Yield: 87%, dr = 2:1, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 5:1).

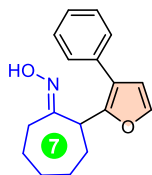
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 7.2$  Hz, 1H), 7.42 (ddt,  $J = 12.1, 8.6, 4.7$  Hz, 5H), 7.33 (dq,  $J = 7.0, 3.0, 2.3$  Hz, 1H), 6.53 (d,  $J = 1.9$  Hz, 1H), 4.21 (dt,  $J = 6.4, 3.1$  Hz, 1H), 3.28 (dt,  $J = 10.8, 3.0$  Hz, 1H), 2.24 (dtd,  $J = 14.5, 10.7, 3.5$  Hz, 1H), 2.12 – 1.94 (m, 1H), 1.91 – 1.45 (m, 7H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.5, 153.5, 140.9, 134.0, 128.7, 128.6, 128.2, 128.1, 126.7, 120.7, 111.7, 111.6, 75.2, 73.3, 46.3, 42.4, 35.6, 35.1, 30.1, 28.1, 27.6, 27.0, 26.7, 26.3, 22.7, 22.3.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{17}\text{H}_{21}\text{O}_2]^+$ : 257.1536, Found. 257.1536.



To a solution of **2m** (50.8 mg, 0.2 mmol) in EtOH (2 mL), hydroxylamine hydrochloride (68.0 mg, 1.0 mmol) and sodium acetate (65.6 mg, 0.8 mmol) were added. The mixture was stirred at 60 °C for 8 h. Then  $\text{H}_2\text{O}$  (1 mL) was added. The organic layer was extracted with ethyl acetate and washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20, v/v) to afford the product.



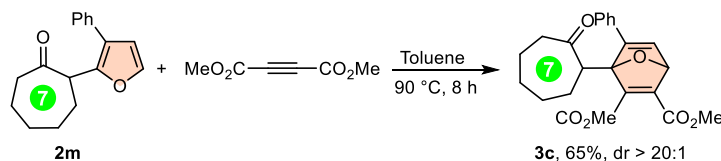
### (E)-2-(3-phenylfuran-2-yl)cycloheptan-1-one oxime (**3b**)

Yield: 53%, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 20:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 7.48 – 7.37 (m, 5H), 7.34 – 7.27 (m, 1H), 6.50 (d,  $J = 1.8$  Hz, 1H), 4.00 (dd,  $J = 9.9, 6.1$  Hz, 1H), 2.99 (ddd,  $J = 14.0, 6.7, 2.7$  Hz, 1H), 2.47 (ddd,  $J = 14.3, 11.8, 2.7$  Hz, 1H), 2.13 – 2.00 (m, 2H), 1.96 – 1.83 (m, 3H), 1.67 – 1.52 (m, 1H), 1.50 – 1.38 (m, 1H), 1.38 – 1.27 (m, 1H).

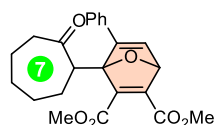
$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 151.1, 141.0, 133.8, 128.6, 128.3, 126.7, 121.3, 111.6, 42.0, 31.7, 30.8, 27.0, 26.6, 25.6.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{17}\text{H}_{20}\text{NO}_2]^+$ : 270.1489, Found. 270.1486.



To a 10-mL oven-dried round-bottom flask with a magnetic stirring bar, **2m** (50.8 mg, 0.2 mmol), dimethyl acetylenedicarboxylate (142.1 mg, 1.0 mmol, 5.0 equiv.), and toluene (2.0 mL) were added in sequence under  $\text{N}_2$  atmosphere. Then the reaction mixture was stirred at 90 °C for 8 h. When the reaction

was completed (monitored by TLC), the crude reaction mixture was purified by flash column chromatography on silica gel (petroleum ether: EtOAc = 10:1) to give 51.5 mg of pure product **3c** as yellow oil, 65% yield.



### 3c

Yield: 65%, dr > 20:1, yellow oil,  $R_f = 0.35$  (petroleum ether/AcOEt = 10:1).

**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.38 (d,  $J = 7.1$  Hz, 2H), 7.31 (t,  $J = 7.6$  Hz, 2H), 7.23 (t,  $J = 7.5$  Hz, 1H), 6.95 (d,  $J = 2.2$  Hz, 1H), 5.73 (d,  $J = 2.2$  Hz, 1H), 4.10 (dd,  $J = 10.2, 2.8$  Hz, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 2.23 – 2.15 (m, 1H), 2.00 – 1.83 (m, 5H), 1.79 – 1.70 (m, 1H), 1.67 – 1.55 (m, 2H), 1.55 – 1.41 (m, 1H).

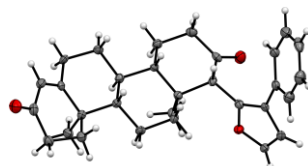
**$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  210.1, 165.2, 163.1, 159.7, 154.4, 153.4, 136.7, 134.5, 128.5, 127.8, 126.0, 99.6, 83.4, 52.5, 52.3, 48.2, 43.5, 29.1, 28.7, 28.5, 23.8.

**HRMS (ESI)** ( $[\text{M}+\text{H}]^+$ ) Calcd. for  $[\text{C}_{23}\text{H}_{25}\text{O}_6]^+$ : 397.1646, Found. 397.1641.

## III. General X-ray Procedures

Experimental Procedure Single crystals of **2w** was recrystallized by DCM/MeOH solvent system. A suitable crystal was selected and measured on a Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.0(2) K during data collection.

### 1. Crystallography information for **2w**.



Ellipsoid drawing of the crystal structure of **2w**. The crystal of **2w** was obtained by slow evaporation of DCM/MeOH solution at rt.

**Table 1 Crystal data and structure refinement for **2w**.**

CCDC	1989586
Identification code	C36
Empirical formula	$\text{C}_{30}\text{H}_{34}\text{O}_3$
Formula weight	442.57
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
$a/\text{\AA}$	7.2131(4)
$b/\text{\AA}$	14.0281(7)
$c/\text{\AA}$	11.7885(7)
$\alpha/^\circ$	90

$\beta/^\circ$	93.280(5)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	1190.88(11)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.234
$\mu/\text{mm}^{-1}$	0.078
F(000)	476.0
Crystal size/ $\text{mm}^3$	$0.13 \times 0.12 \times 0.11$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	4.518 to 50
Index ranges	$-8 \leq h \leq 8, -16 \leq k \leq 14, -13 \leq l \leq 13$
Reflections collected	7053
Independent reflections	3627 [ $R_{\text{int}} = 0.0541, R_{\text{sigma}} = 0.0795$ ]
Data/restraints/parameters	3627/1/300
Goodness-of-fit on $F^2$	1.004
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0447, wR_2 = 0.0901$
Final R indexes [all data]	$R_1 = 0.0535, wR_2 = 0.0965$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.18/-0.22
Flack parameter	0.0(10)

**Table 2 Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 2w.  $U_{\text{eq}}$  is defined as 1/3 of of the trace of the orthogonalised  $U_{ij}$  tensor.**

Atom	x	y	z	U(eq)
O3	8785(3)	6262.2(16)	268(2)	20.8(6)
O1	7519(4)	928.9(19)	7014(2)	32.8(7)
O2	4482(4)	6252.9(18)	-564(2)	30.2(7)
C13	6739(5)	4720(2)	1482(3)	15.5(8)
C18	6002(5)	5754(2)	1201(3)	16.6(8)
C19	7428(5)	6491(2)	1013(3)	17.5(8)
C17	4494(5)	5710(2)	246(3)	18.7(8)
C12	8194(5)	4784(2)	2469(3)	18.9(8)
C22	7759(5)	7380(2)	1439(3)	16.8(8)
C20	9959(5)	7023(2)	250(3)	20.9(9)
C14	5072(5)	4126(2)	1862(3)	14.0(8)
C28	4710(5)	7936(2)	2127(3)	21.0(9)
C9	5642(5)	3139(2)	2352(3)	16.9(8)
C4	7827(5)	2229(2)	3813(3)	17.3(8)
C23	6643(5)	7932(2)	2217(3)	19.6(9)
C1	7638(5)	1266(3)	6064(3)	22.7(9)

C3	9242(5)	2411(2)	4814(3)	21.9(9)
C11	8841(5)	3811(2)	2887(3)	19.7(8)
C16	2964(5)	5013(3)	407(3)	21.2(9)
C5	6110(5)	1740(2)	4222(3)	17.7(8)
C15	3590(5)	4040(3)	889(3)	19.4(8)
C6	6039(5)	1360(2)	5263(3)	22.0(9)
C29	8707(5)	1576(3)	2934(3)	23.1(9)
C7	4473(5)	1684(2)	3382(3)	20.7(9)
C21	9412(5)	7712(3)	944(3)	20.9(9)
C00Q	7575(5)	4278(2)	435(3)	20.8(9)
C8	3965(5)	2644(2)	2827(3)	21.1(9)
C10	7211(5)	3215(2)	3282(3)	16.9(8)
C27	3703(6)	8487(3)	2837(3)	27.2(10)
C2	9475(5)	1572(3)	5636(3)	22.3(9)
C26	4589(6)	9051(3)	3663(3)	31.6(11)
C24	7511(6)	8510(3)	3055(4)	27.7(10)
C25	6511(6)	9056(3)	3780(4)	32.2(10)

**Table 3 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 2w. The Anisotropic displacement factor exponent takes the form:  $-2\pi^2[\text{h}^2\text{a}^*2\text{U}_{11}+2\text{hka}^*\text{b}^*\text{U}_{12}+\dots]$ .**

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
O3	18.1(14)	18.5(13)	26.5(14)	0.1(11)	7.4(12)	0.2(12)
O1	35.6(17)	37.9(16)	25.0(16)	12.5(13)	2.9(13)	2.2(14)
O2	29.9(17)	31.2(15)	28.6(15)	11.4(14)	-5.3(13)	-4.2(13)
C13	15(2)	15.2(18)	17(2)	-0.7(16)	1.9(15)	0.5(15)
C18	20(2)	15.4(18)	15.2(18)	2.5(16)	5.4(15)	-0.8(17)
C19	19(2)	17.0(19)	16.9(19)	2.1(16)	3.3(15)	3.1(16)
C17	19(2)	16.6(18)	20(2)	-1.3(17)	0.5(16)	6.9(17)
C12	20(2)	14.7(18)	22(2)	2.3(16)	1.5(16)	-3.0(16)
C22	15(2)	13.8(18)	21(2)	4.5(16)	0.5(16)	1.4(15)
C20	15(2)	20.2(18)	28(2)	8.6(17)	5.5(17)	0.1(17)
C14	12.1(18)	13.5(16)	16.3(19)	-2.5(16)	-0.6(15)	-0.9(16)
C28	20(2)	18.5(19)	25(2)	0.5(17)	-1.2(17)	0.9(17)
C9	17(2)	15.5(18)	19(2)	-2.4(16)	1.6(16)	-1.0(15)
C4	16(2)	15.3(18)	21(2)	3.3(16)	1.6(16)	-1.1(16)
C23	23(2)	13.1(18)	23(2)	2.4(17)	0.3(17)	1.5(16)
C1	29(2)	15.4(18)	24(2)	1.7(18)	3.0(17)	0.4(18)
C3	21(2)	23(2)	22(2)	5.5(17)	0.7(17)	1.3(17)

C11	15(2)	20.2(19)	23(2)	2.8(17)	-3.4(16)	-2.9(16)
C16	18(2)	25(2)	21(2)	0.6(17)	-2.3(16)	0.9(17)
C5	17(2)	9.6(17)	27(2)	-1.3(16)	2.6(16)	0.7(15)
C15	17(2)	20.6(19)	20(2)	1.8(18)	-1.4(15)	-2.8(17)
C6	19(2)	17.9(18)	30(2)	2.5(18)	7.2(17)	-2.2(17)
C29	19(2)	23.1(19)	27(2)	5.2(18)	3.9(17)	3.5(17)
C7	16(2)	17.7(18)	29(2)	5.8(17)	0.5(16)	-6.1(16)
C21	18(2)	17.3(19)	27(2)	6.0(18)	-1.7(16)	-1.5(17)
C00Q	22(2)	17.3(19)	23(2)	-0.3(16)	4.5(17)	-2.2(16)
C8	15(2)	21.3(19)	27(2)	5.0(17)	-1.5(16)	-1.0(16)
C10	15(2)	15.2(17)	20(2)	1.2(16)	2.7(16)	-1.2(16)
C27	24(2)	25(2)	33(3)	4.2(19)	4.8(19)	2.5(19)
C2	23(2)	20.8(19)	23(2)	3.2(17)	-2.5(17)	2.9(17)
C26	46(3)	19(2)	31(2)	2(2)	17(2)	9(2)
C24	25(2)	22(2)	36(3)	-3.8(19)	0.1(19)	-2.6(19)
C25	37(3)	23(2)	36(3)	-7(2)	0(2)	-5(2)

**Table 4 Bond Lengths for 2w.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C19	1.389(4)	C28	C27	1.376(5)
O3	C20	1.364(4)	C9	C8	1.529(5)
O1	C1	1.224(4)	C9	C10	1.534(5)
O2	C17	1.221(4)	C4	C3	1.537(5)
C13	C18	1.573(5)	C4	C5	1.518(5)
C13	C12	1.524(5)	C4	C29	1.546(5)
C13	C14	1.551(5)	C4	C10	1.572(5)
C13	C00Q	1.535(4)	C23	C24	1.398(5)
C18	C19	1.483(5)	C1	C6	1.454(5)
C18	C17	1.522(5)	C1	C2	1.507(5)
C19	C22	1.361(5)	C3	C2	1.526(5)
C17	C16	1.495(5)	C11	C10	1.536(4)
C12	C11	1.516(5)	C16	C15	1.536(5)
C22	C23	1.475(5)	C5	C6	1.342(5)
C22	C21	1.435(5)	C5	C7	1.499(5)
C20	C21	1.340(5)	C7	C8	1.532(5)
C14	C9	1.547(5)	C27	C26	1.383(6)
C14	C15	1.527(5)	C26	C25	1.386(6)
C28	C23	1.392(5)	C24	C25	1.380(5)

**Table 5 Bond Angles for 2w.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C20	O3	C19	106.9(3)	C5	C4	C3	110.4(3)
C12	C13	C18	108.4(3)	C5	C4	C29	108.6(3)
C12	C13	C14	108.8(3)	C5	C4	C10	107.9(3)
C12	C13	C00Q	110.6(3)	C29	C4	C10	111.8(3)
C14	C13	C18	107.4(3)	C28	C23	C22	122.3(3)
C00Q	C13	C18	110.3(3)	C28	C23	C24	117.2(3)
C00Q	C13	C14	111.2(3)	C24	C23	C22	120.4(3)
C19	C18	C13	116.4(3)	O1	C1	C6	122.3(3)
C19	C18	C17	113.0(3)	O1	C1	C2	121.7(4)
C17	C18	C13	109.7(3)	C6	C1	C2	115.9(3)
O3	C19	C18	116.9(3)	C2	C3	C4	113.8(3)
C22	C19	O3	109.3(3)	C12	C11	C10	111.2(3)
C22	C19	C18	133.8(3)	C17	C16	C15	115.1(3)
O2	C17	C18	121.7(3)	C6	C5	C4	123.0(4)
O2	C17	C16	122.4(4)	C6	C5	C7	120.9(3)
C16	C17	C18	115.8(3)	C7	C5	C4	116.1(3)
C11	C12	C13	112.4(3)	C14	C15	C16	112.7(3)
C19	C22	C23	128.4(3)	C5	C6	C1	124.0(3)
C19	C22	C21	106.3(3)	C5	C7	C8	113.3(3)
C21	C22	C23	125.3(3)	C20	C21	C22	107.1(3)
C21	C20	O3	110.5(3)	C7	C8	C9	112.4(3)
C9	C14	C13	113.3(3)	C9	C10	C4	113.8(3)
C15	C14	C13	110.3(3)	C9	C10	C11	111.5(3)
C15	C14	C9	111.7(3)	C11	C10	C4	113.3(3)
C27	C28	C23	121.1(4)	C28	C27	C26	120.7(4)
C8	C9	C14	110.2(3)	C1	C2	C3	111.4(3)
C8	C9	C10	109.7(3)	C27	C26	C25	119.5(4)
C10	C9	C14	112.0(3)	C25	C24	C23	122.0(4)
C3	C4	C29	109.5(3)	C24	C25	C26	119.4(4)
C3	C4	C10	108.6(3)				

**Table 6 Hydrogen Atom Coordinates ( $\text{\AA} \times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for 2w.**

Atom	x	y	z	U(eq)
H18	5377.22	5961.89	1874.71	20

H12A	9254.17	5141.76	2229.22	23
H12B	7676.13	5128.53	3090.38	23
H20	10994.77	7059.2	-183.19	25
H14	4516.55	4482.36	2471.52	17
H28	4088.85	7560.12	1578.31	25
H9	6081.64	2747.31	1733.31	20
H3A	10436.61	2555.94	4517.87	26
H3B	8851.16	2965.6	5230.24	26
H11A	9761.12	3887.19	3513.12	24
H11B	9421.41	3477.33	2279.85	24
H16A	2294.7	4911.13	-319.86	25
H16B	2102.53	5292.71	914.97	25
H15A	2522.21	3706.82	1159.2	23
H15B	4078.39	3661.12	285.32	23
H6	4896.18	1144.29	5486.5	26
H29A	9817.17	1868.58	2685.04	35
H29B	7842.29	1484.32	2293.46	35
H29C	9009.01	970.98	3276.3	35
H7A	3411.02	1446.68	3764.93	25
H7B	4743.98	1230.2	2793.15	25
H21	9993.82	8296.31	1079.38	25
H00A	6829.07	4448.43	-234.59	31
H00B	7603.07	3597.05	512.56	31
H00C	8815.55	4512.58	373.54	31
H8A	3437.11	3055.61	3385.66	25
H8B	3026.91	2542.17	2216.66	25
H10	6695.9	3578.41	3900.55	20
H27	2413.09	8479.51	2759.65	33
H2A	10031	1040.86	5253.29	27
H2B	10306.9	1753.91	6274.75	27
H26	3899.56	9424.17	4136.81	38
H24	8801.42	8527.52	3127.21	33
H25	7122.38	9423.69	4340.81	39

### Crystal structure determination of [2w]

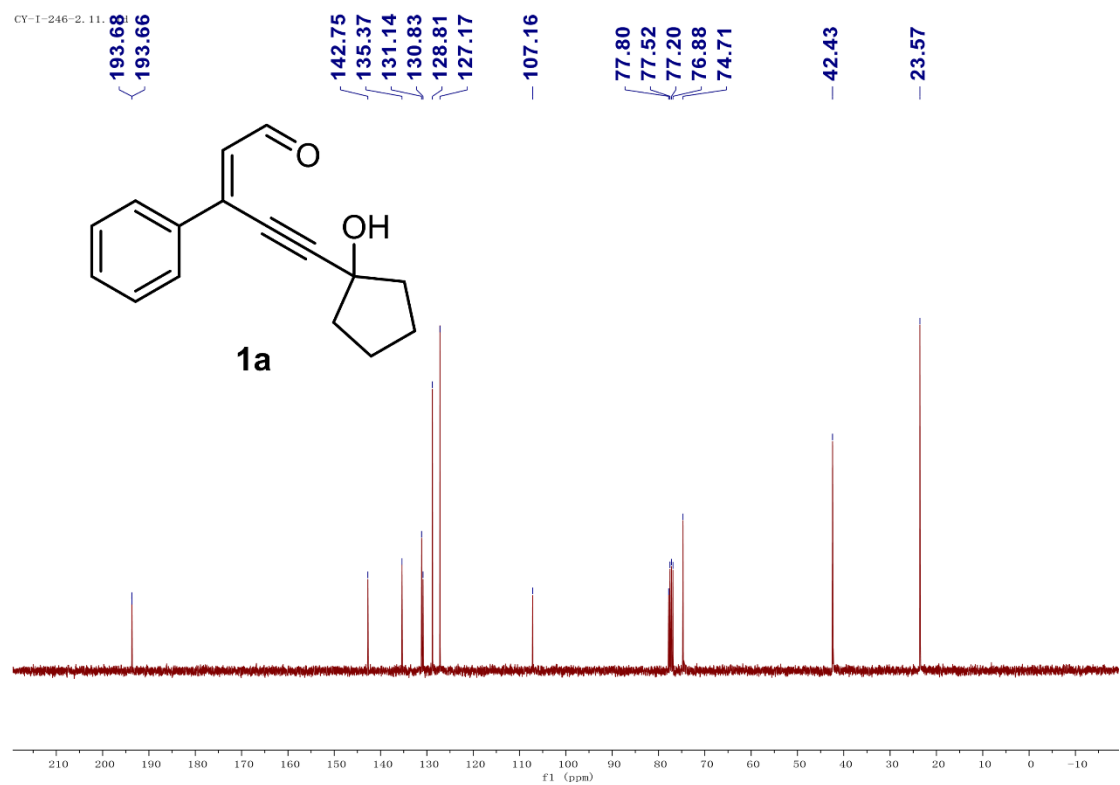
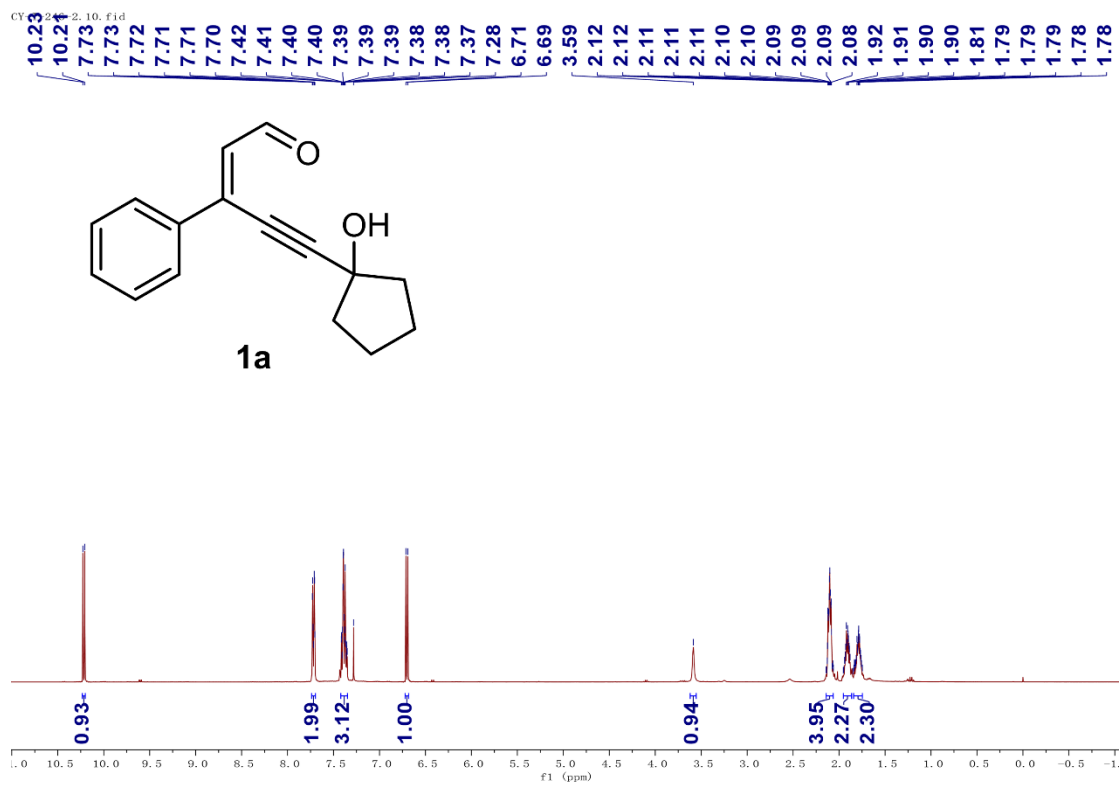
**Crystal Data** for  $C_{30}H_{34}O_3$  ( $M = 442.57$  g/mol): monoclinic, space group  $P2_1$  (no. 4),  $a = 7.2131(4)$  Å,  $b = 14.0281(7)$  Å,  $c = 11.7885(7)$  Å,  $\beta = 93.280(5)$ ,  $V = 1190.88(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 100.00(10)$  K,  $\mu(\text{MoK}\alpha) = 0.078$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.234$  g/cm<sup>3</sup>, 7053 reflections measured ( $4.518^\circ \leq 2\theta \leq 50^\circ$ ), 3627 unique ( $R_{\text{int}} = 0.0541$ ,  $R_{\text{sigma}} = 0.0795$ ) which were used in all calculations. The final  $R_1$  was 0.0447 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0965 (all data).

### References:

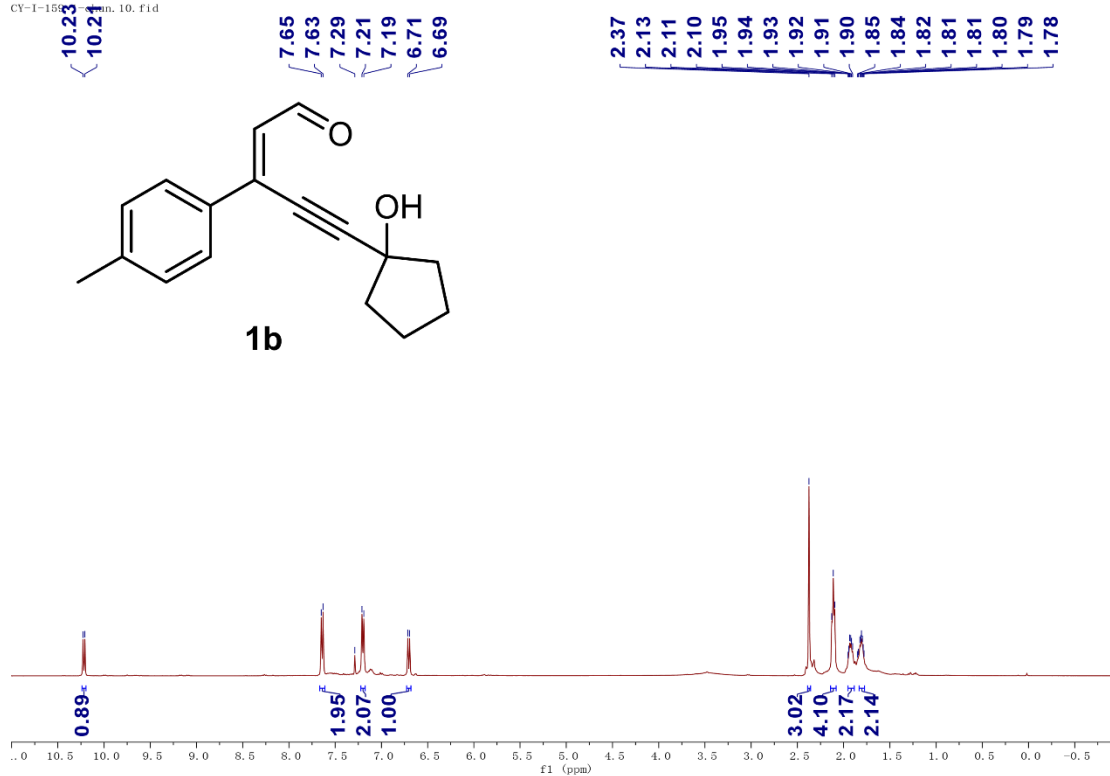
[1] (a) Tang, J. M.; Bhunia, S.; Abu Sohel, S. M.; Lin, M. Y.; Liao, H. Y.; Datta, S.; Das, A.; Liu, R. S. The skeletal rearrangement of gold- and platinum-catalyzed cycloisomerization of cis-4,6-dien-1-yn-3-ols: pinacol rearrangement and formation of bicyclo[4.1.0]heptenone and reorganized styrene derivatives. *J. Am. Chem. Soc.* **2007**, *129*, 15677-15683; (b) Le Foulher, V.; Chen, Y.; Gandon, V.; Bizet, V.; Salomé, C.; Fessard, T.; Liu, F.; Houk, K. N.; Blanchard, N. Activating Pyrimidines by Pre-distortion for the General Synthesis of 7-Aza-indazoles from 2-Hydrazonylpyrimidines via Intramolecular Diels–Alder Reactions. *J. Am. Chem. Soc.* **2019**, *141*, 15901-15909; (c) Hsu, Y. C.; Hsieh, S. A.; Li, P. H.; Liu, R. S. Gold-catalyzed N,O-functionalization of 1,4-diyne-3-ols with N-hydroxyanilines to form highly functionalized pyrrole derivatives. *Chem. Commun.* **2018**, *54*, 2114-2117; (d) Watson, I. D. G.; Ritter, S.; Toste, F. D. Asymmetric Synthesis of Medium-Sized Rings by Intramolecular Au(I)-Catalyzed Cyclopropanation. *J. Am. Chem. Soc.* **2009**, *131*, 2056-2057; (e) Tharra, P.; Baire, B. Mild Approach to 2-Acyfurans via Intercepted Meyer–Schuster Rearrangement of 6-Hydroxyhex-2-en-4-ynals. *J. Org. Chem.* **2015**, *80*, 8314-8328.



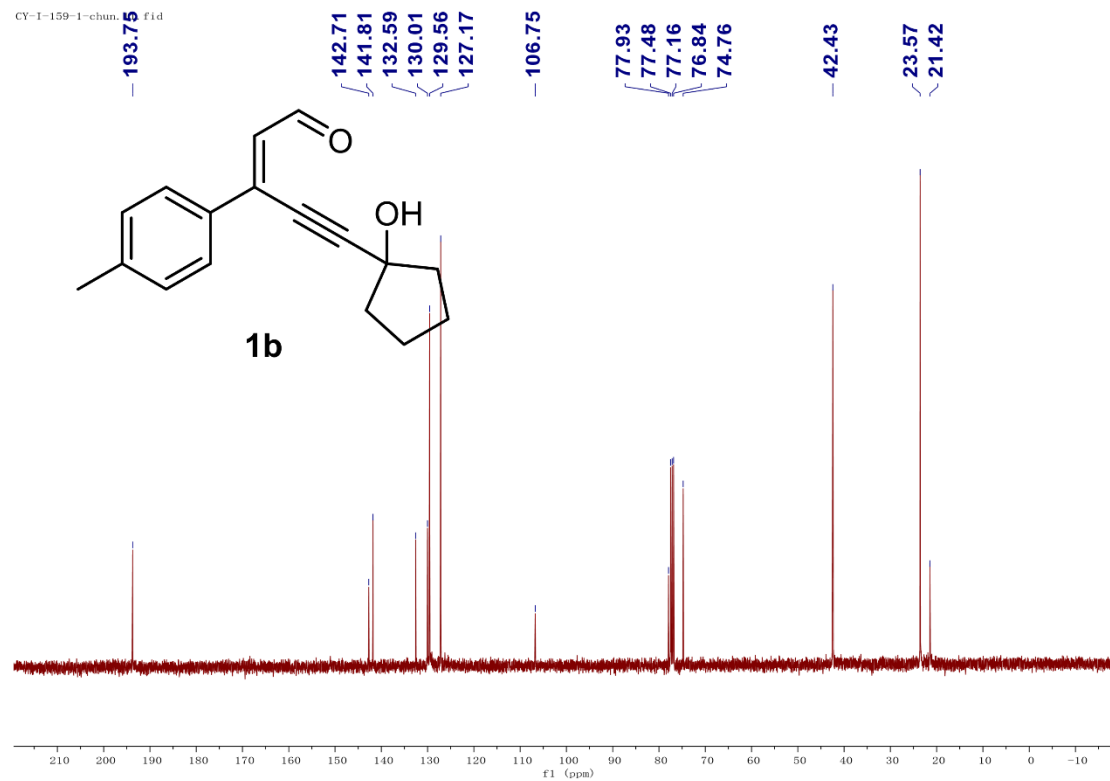
## IV. Copies of NMR spectra

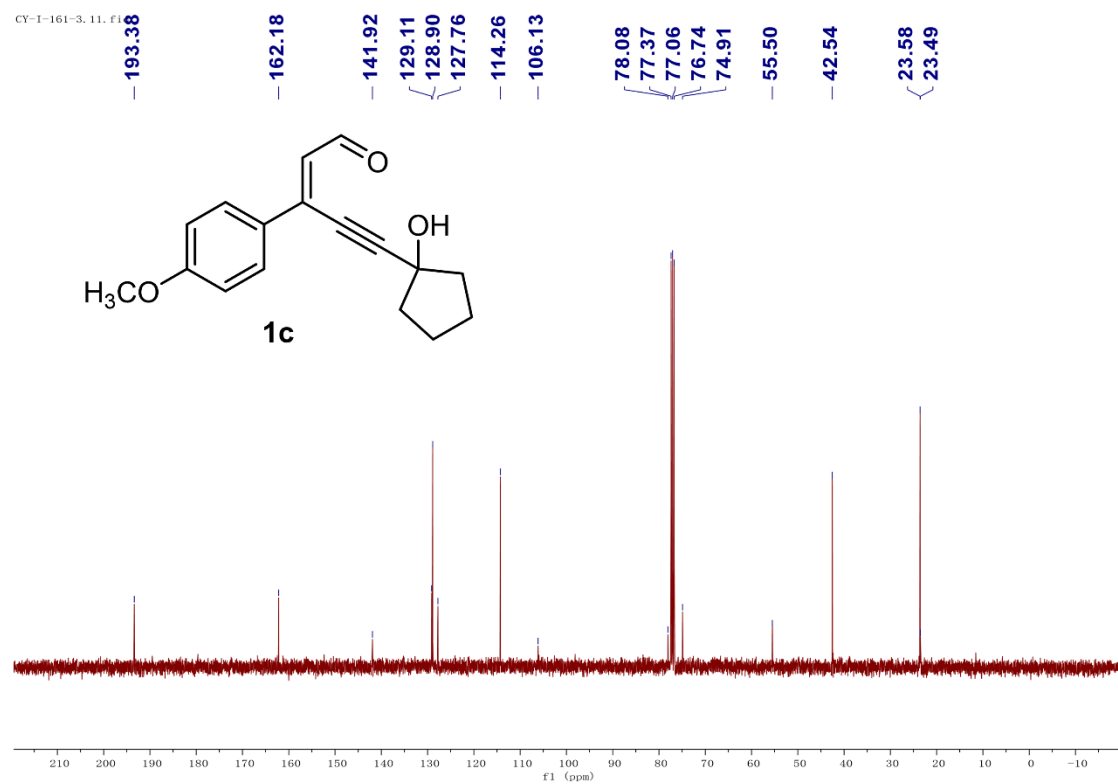
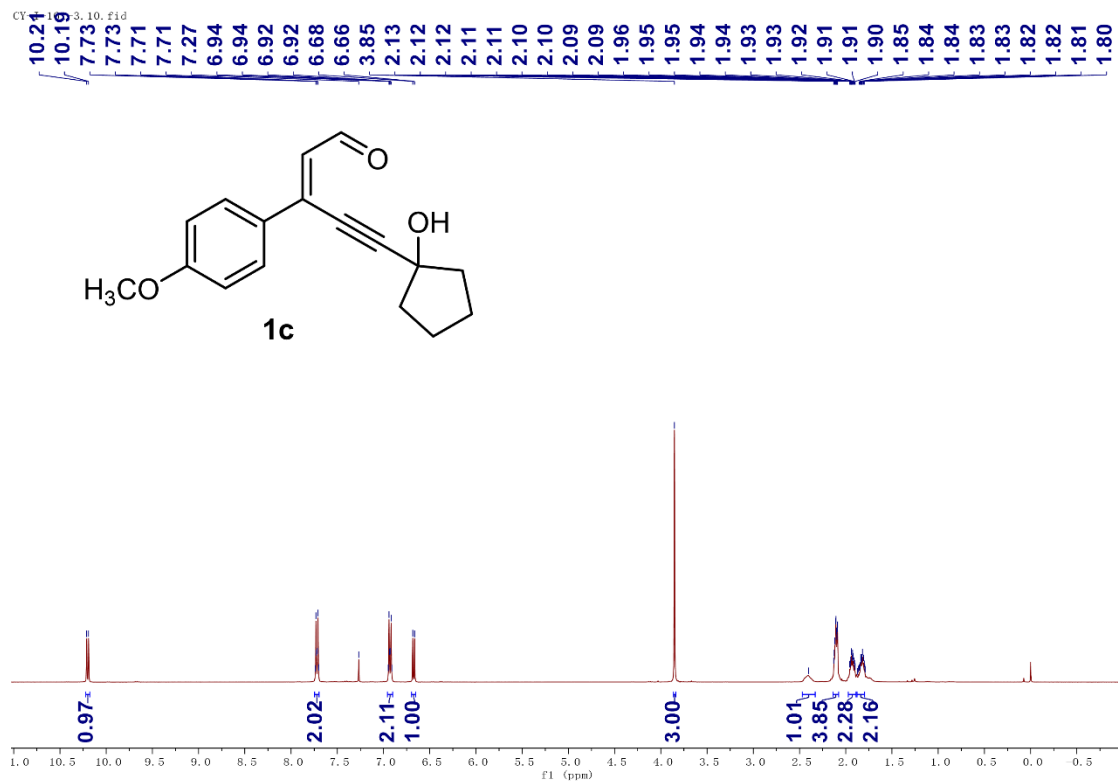


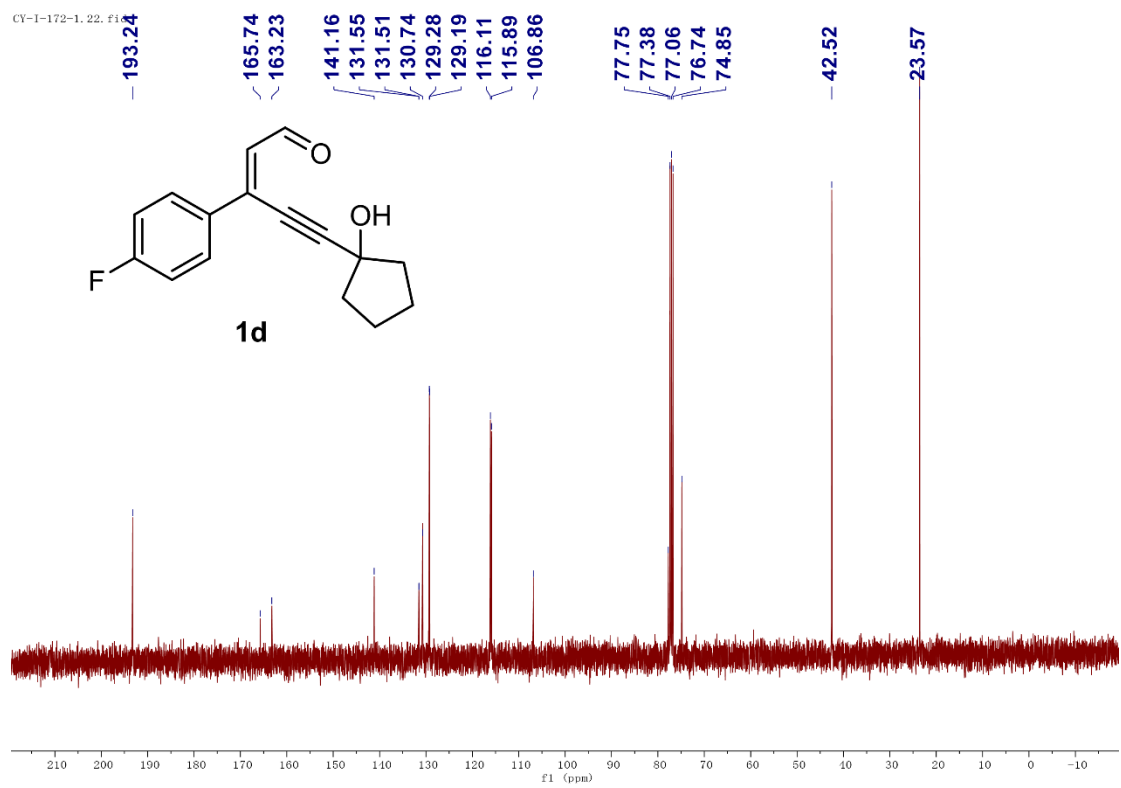
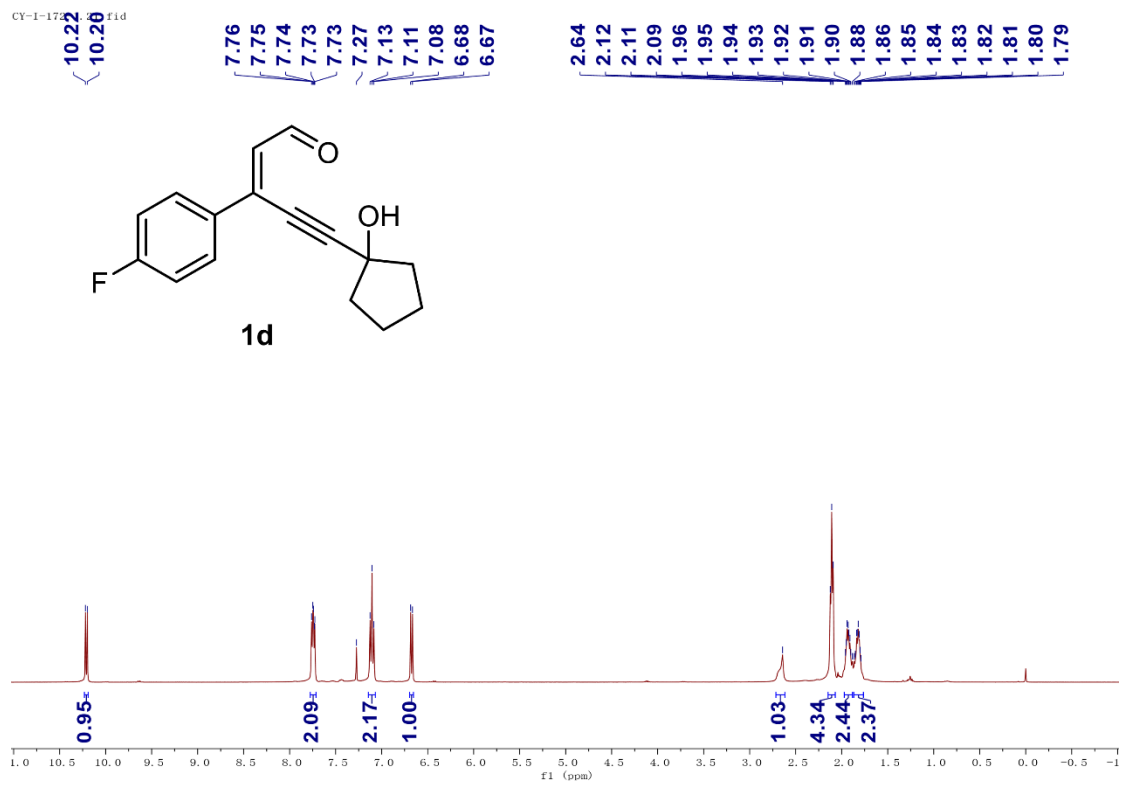
CY-I-159-1-10.fid



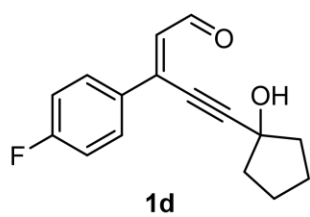
CY-I-159-1-10.fid



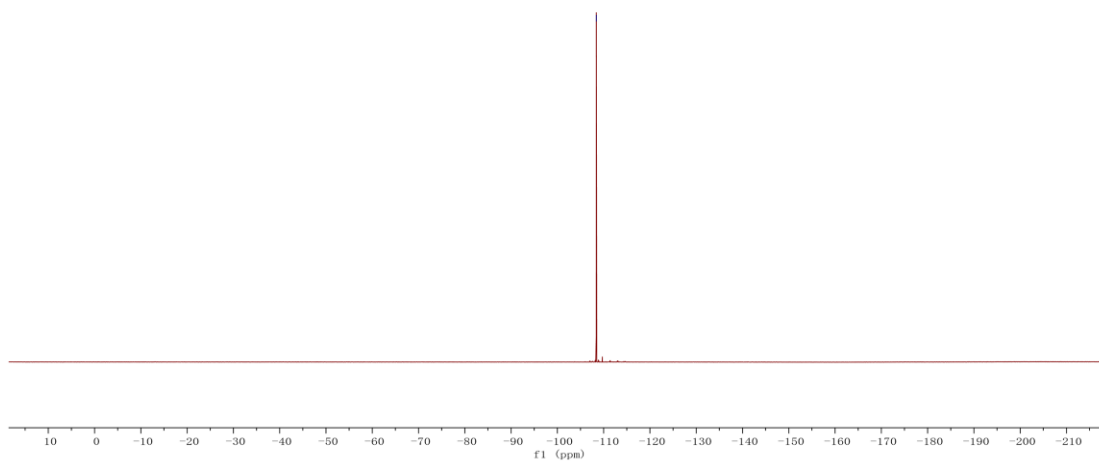


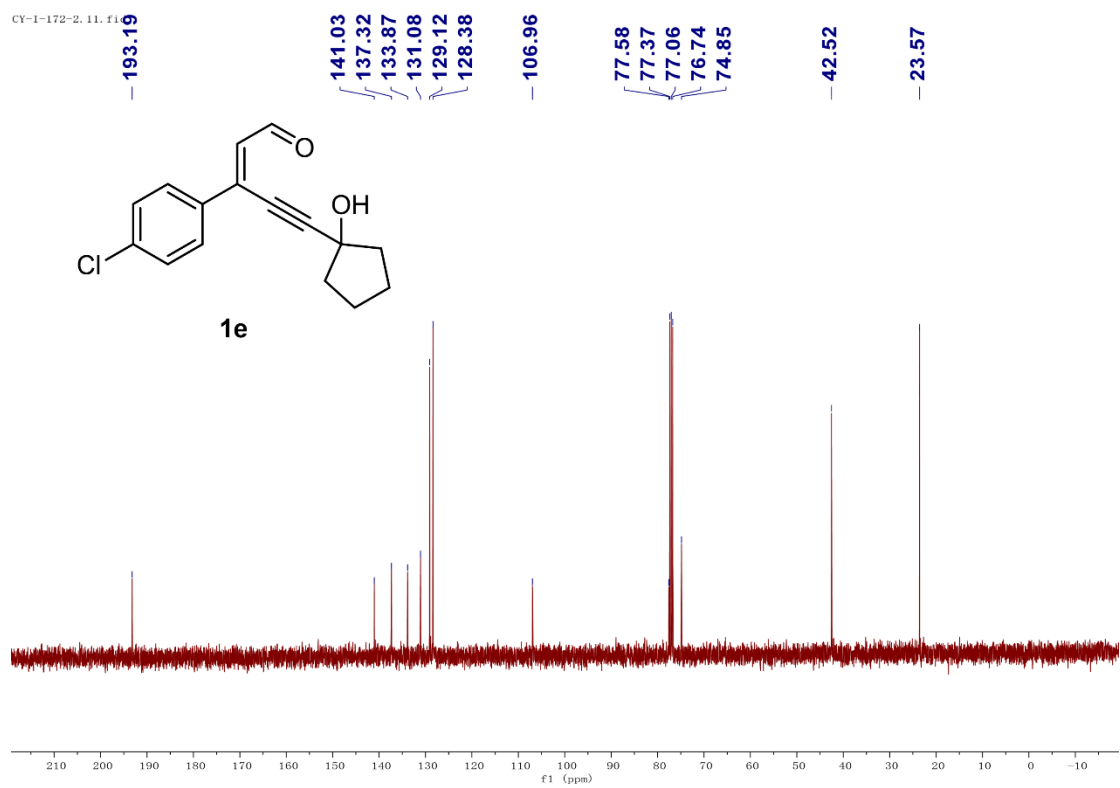
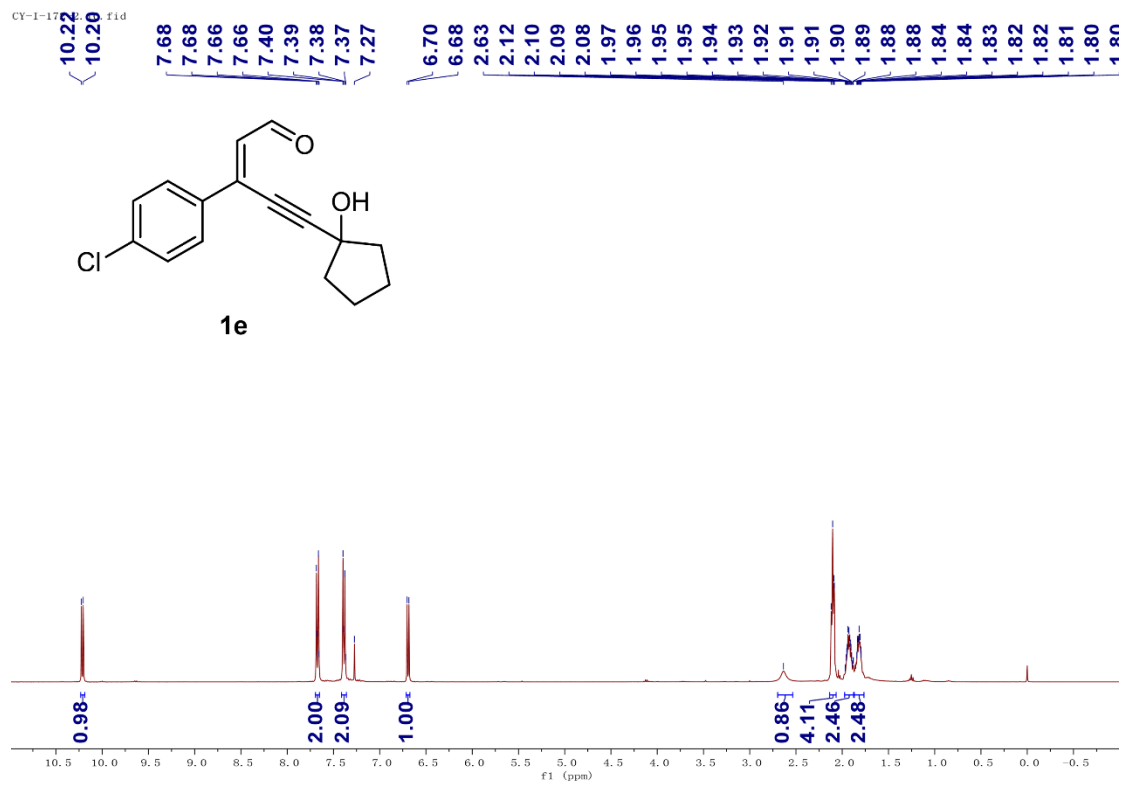


CY-I-172-1-F.10.fid  
F19CPD

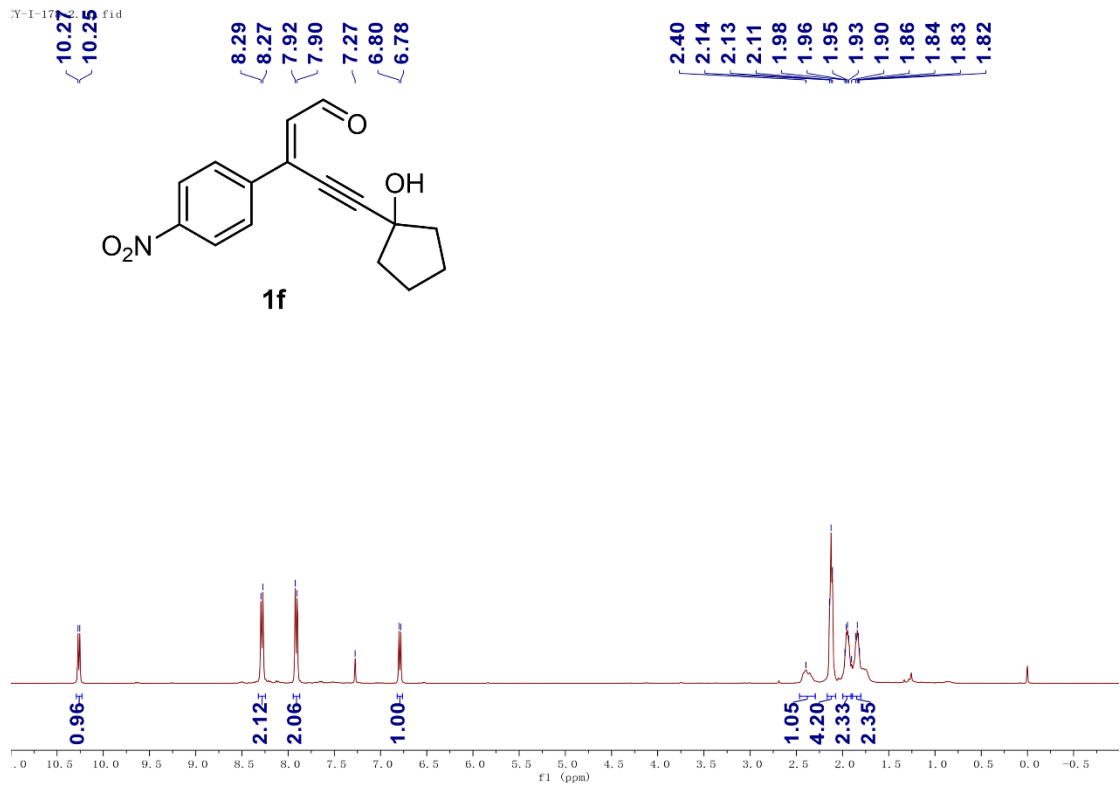


-108.42

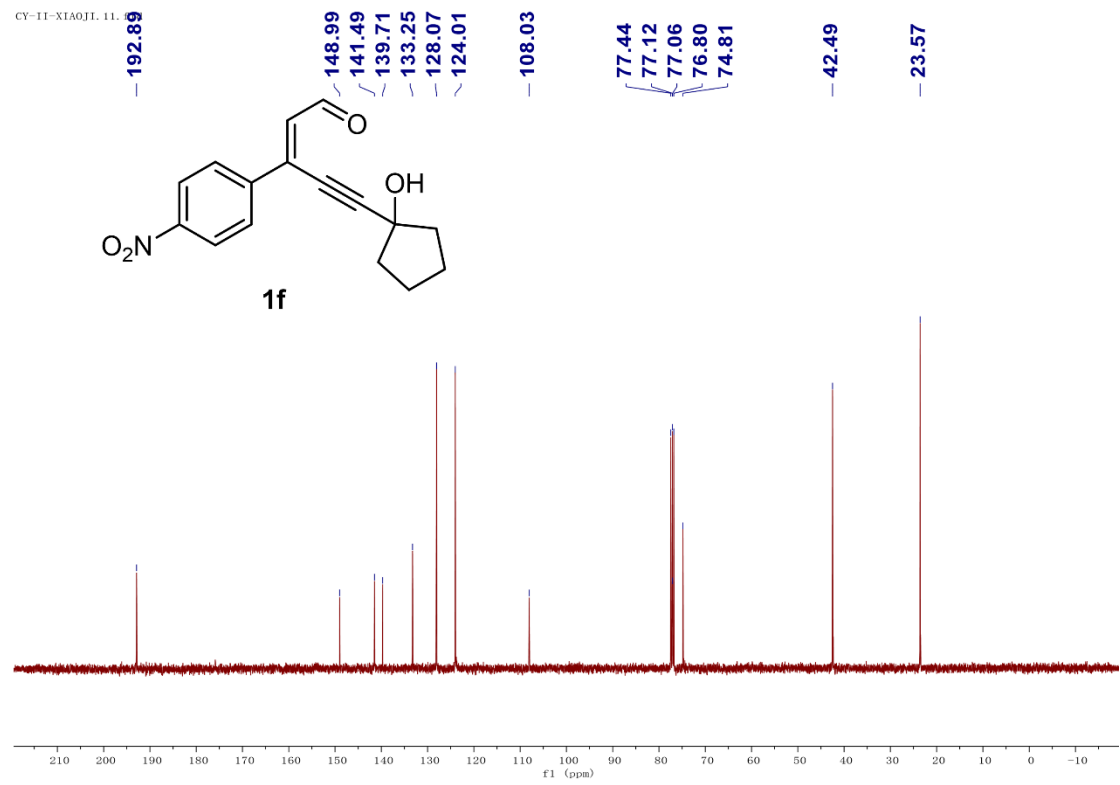




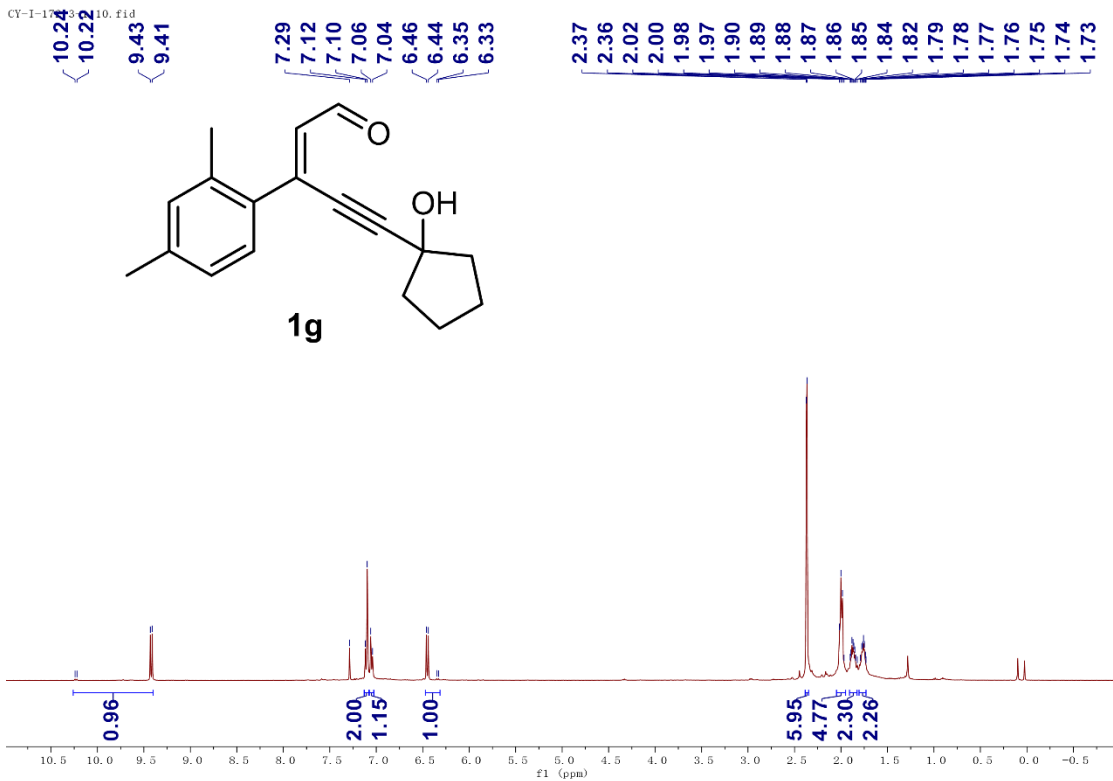
Y-I-177.fid



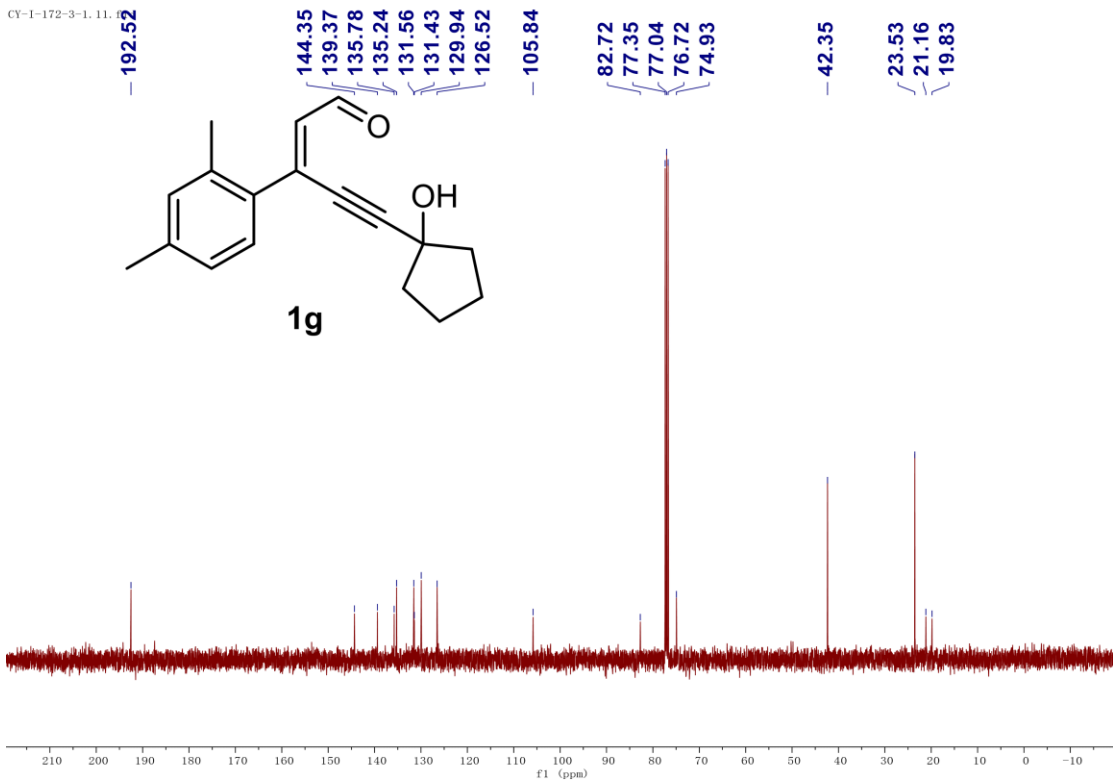
CY-11-XIA011.11.



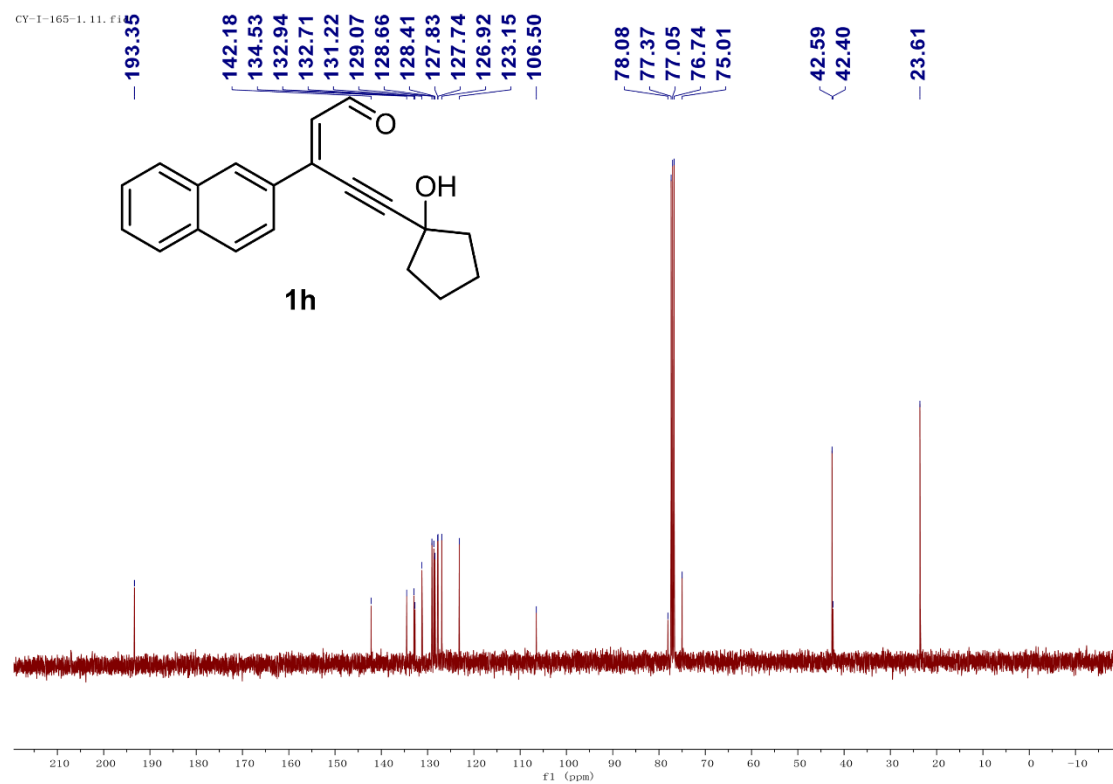
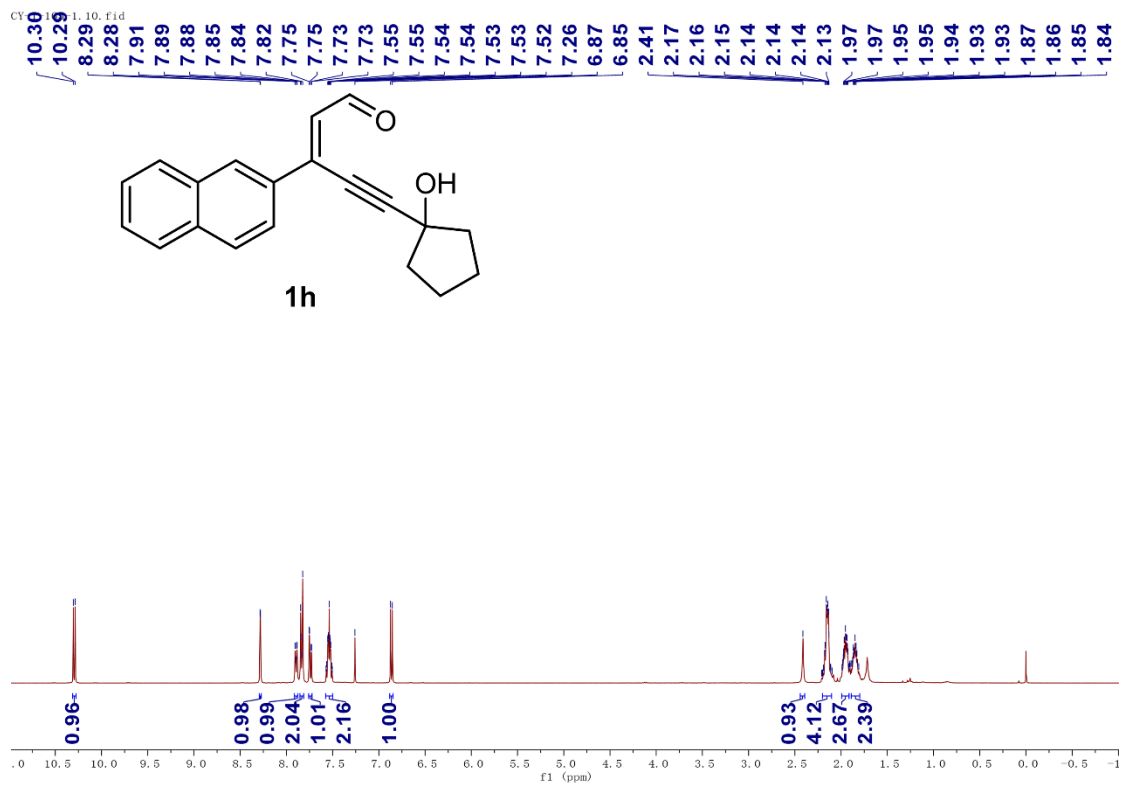
CY-I-172-3-1.10.fid



CY-I-172-3-1.11.

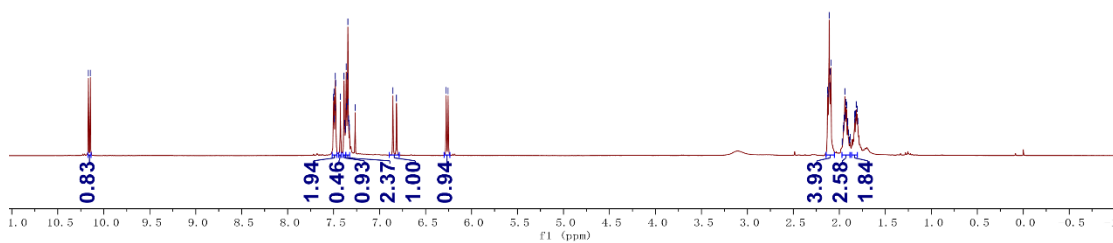
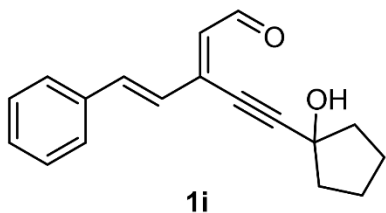






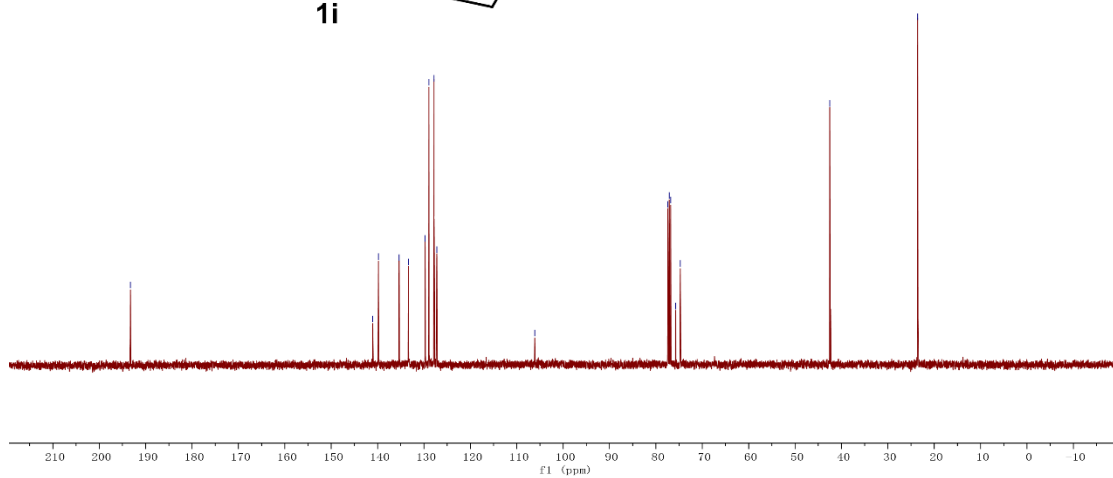
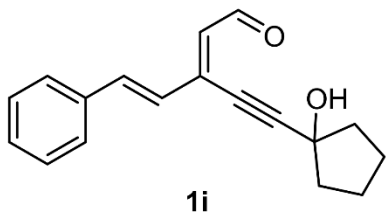
CY-I-165-2.11.fid

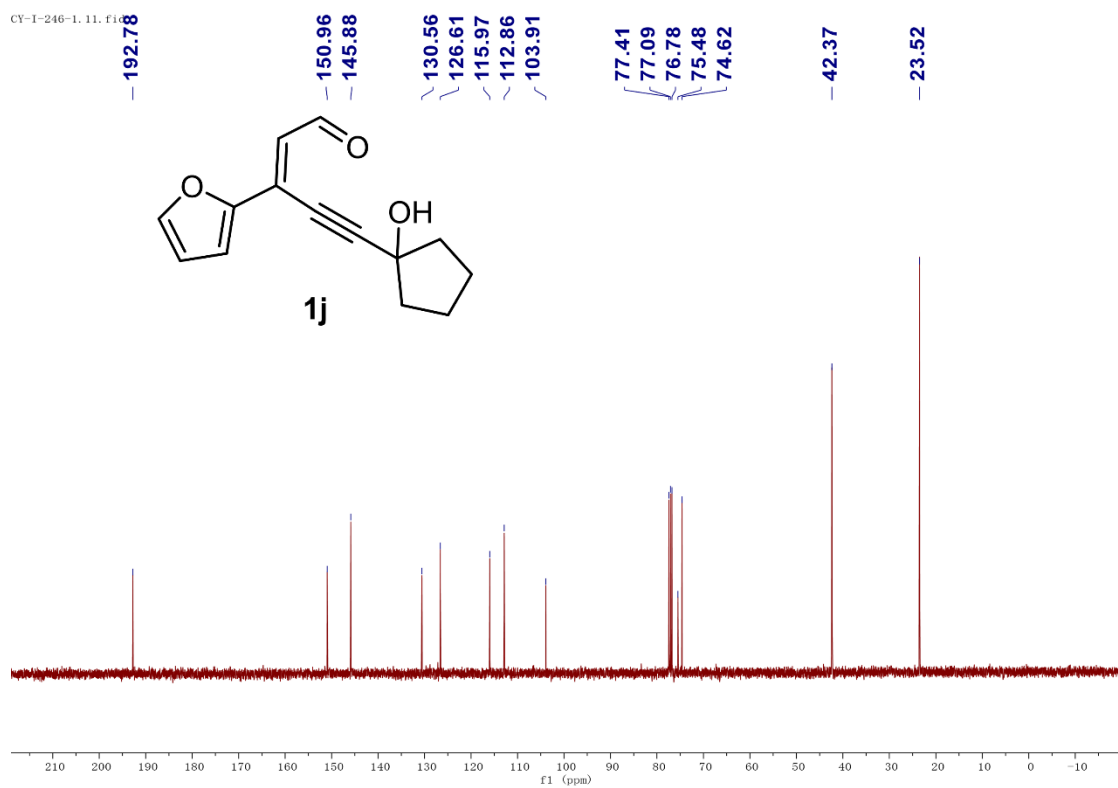
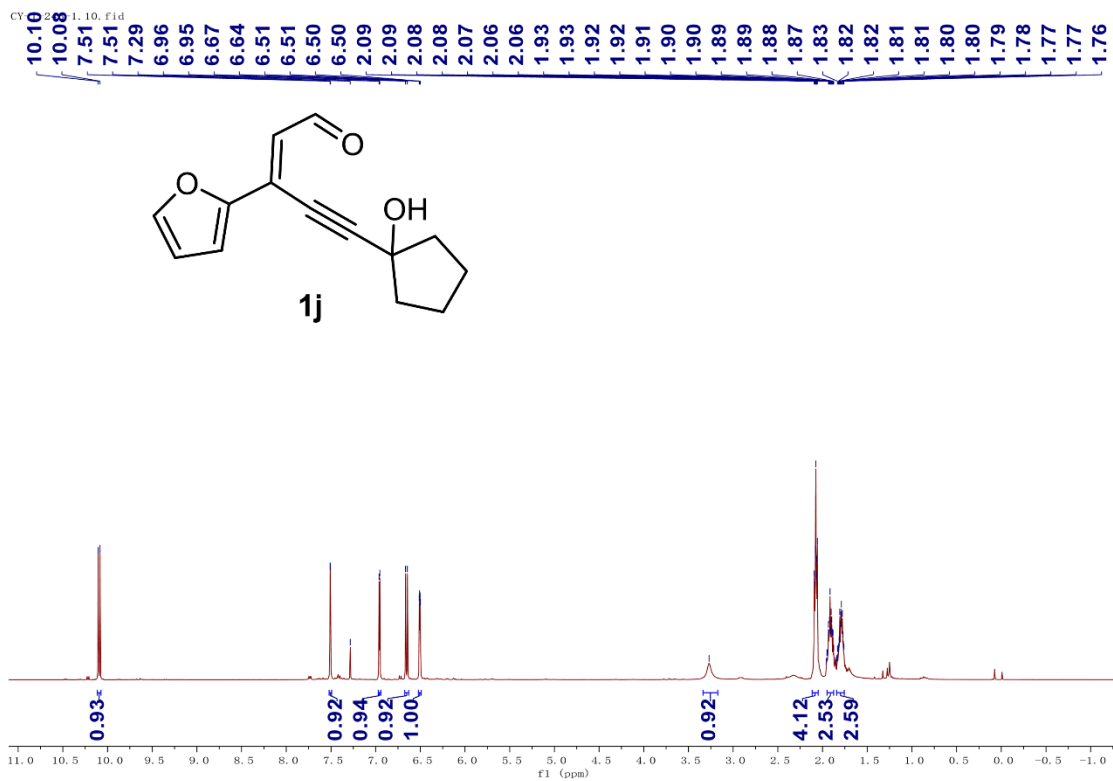
10.17  
10.15  
7.50  
7.49  
7.49  
7.48  
7.48  
7.43  
7.39  
7.38  
7.36  
7.36  
7.35  
7.35  
7.34  
7.34  
7.33  
7.27  
6.86  
6.82  
6.28  
6.25  
2.13  
2.12  
2.11  
2.10  
2.10  
2.09  
1.95  
1.95  
1.94  
1.93  
1.93  
1.92  
1.91  
1.91  
1.83  
1.83  
1.82  
1.82  
1.81  
1.80

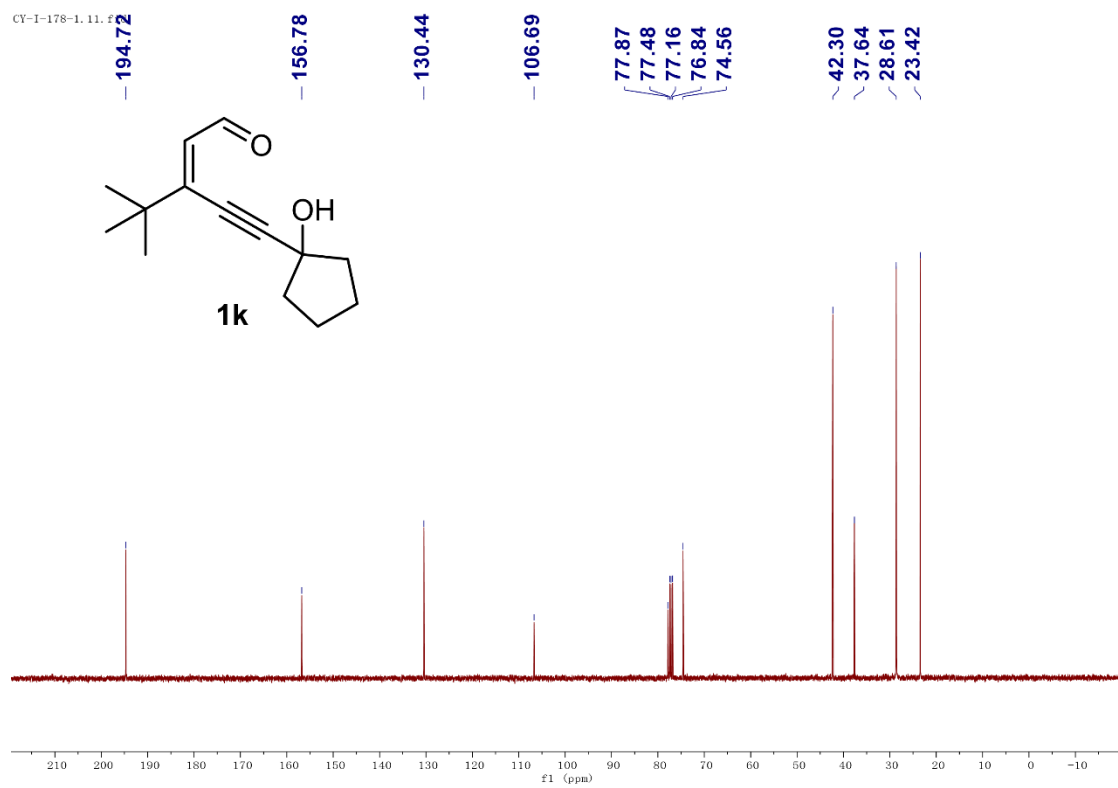
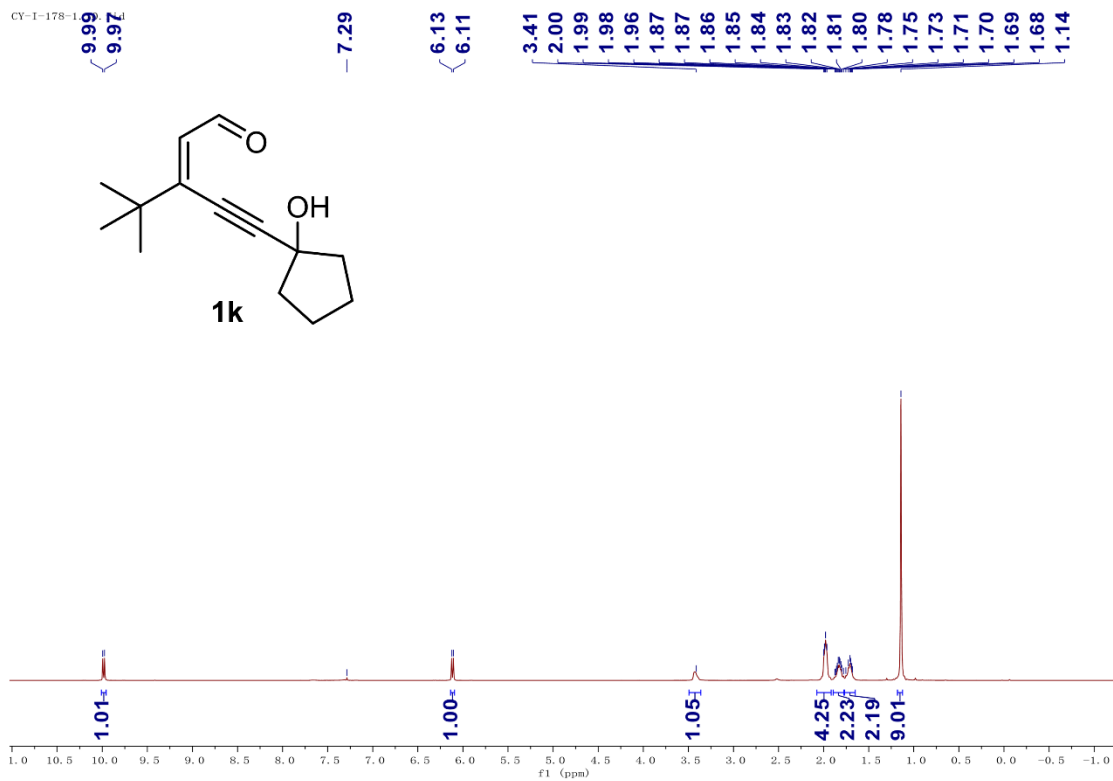


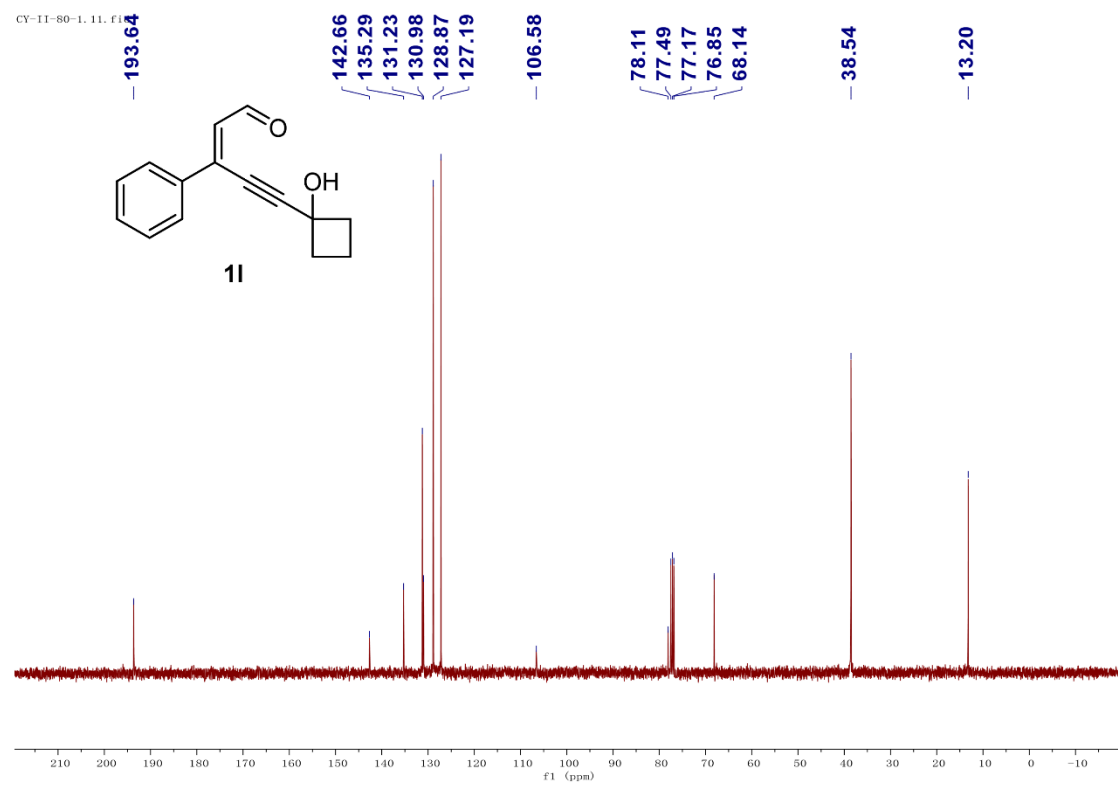
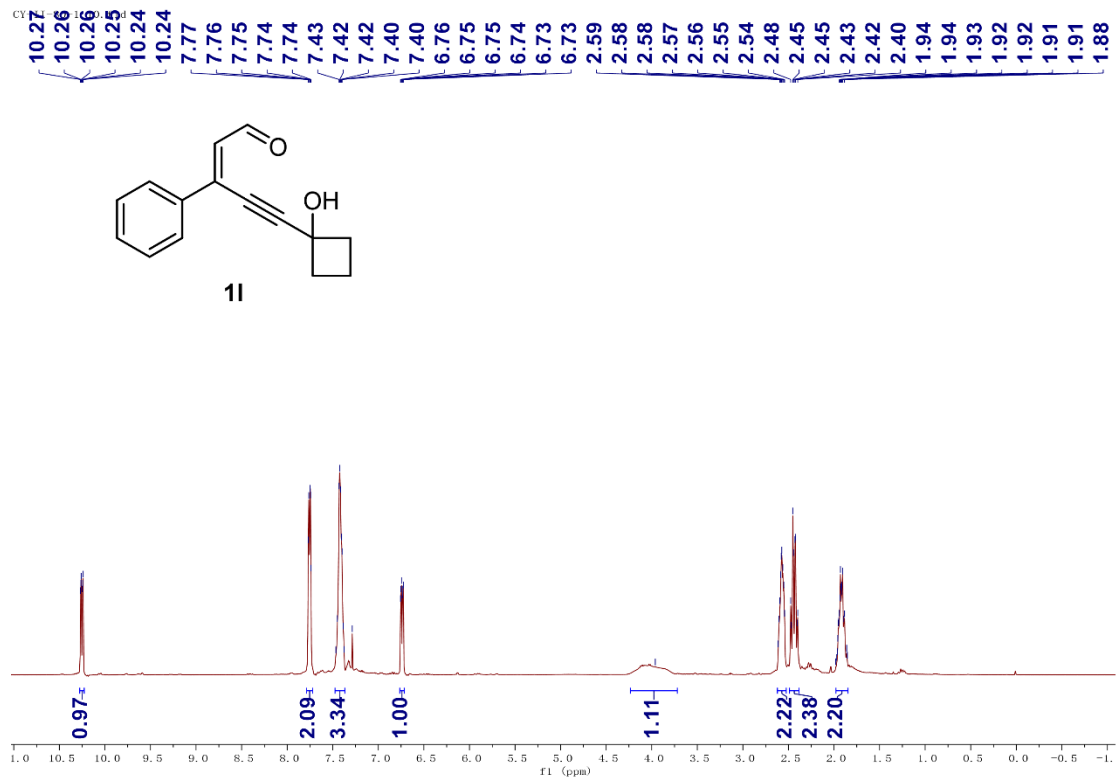
CY-I-165-2.11.fid

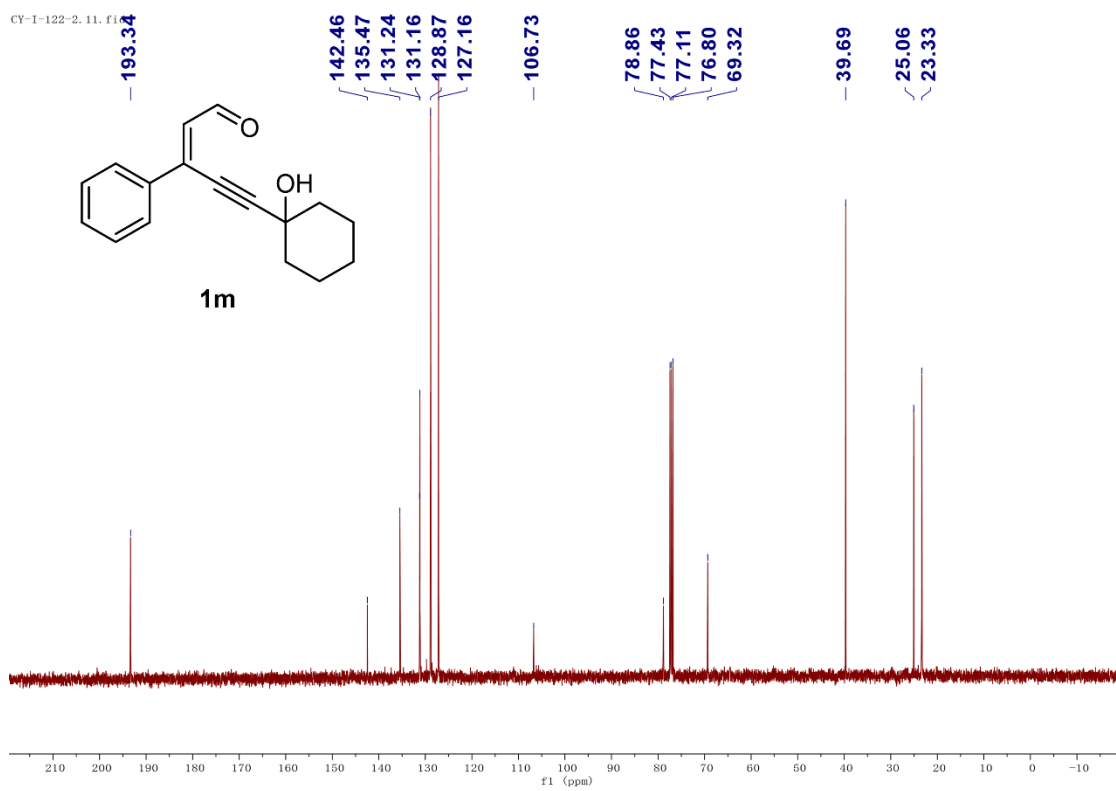
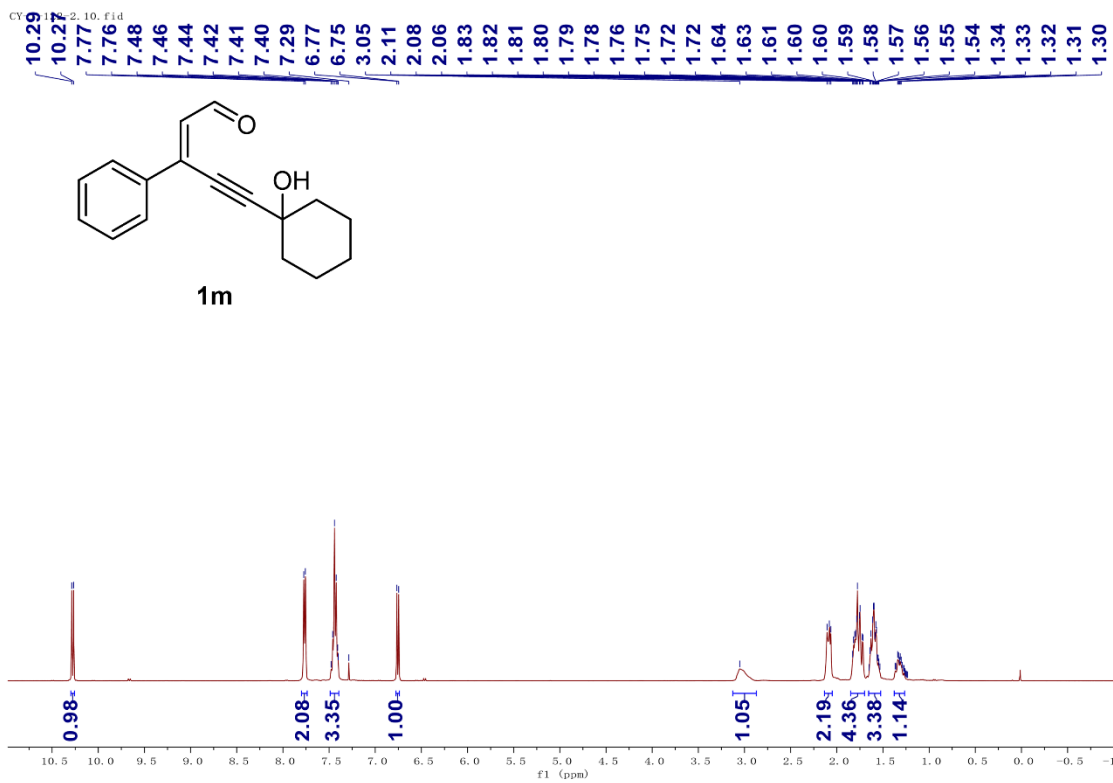
193.29  
141.04  
139.82  
135.35  
133.36  
129.73  
128.93  
127.82  
127.22  
106.11  
77.44  
77.12  
76.81  
75.75  
74.74  
42.51  
23.57

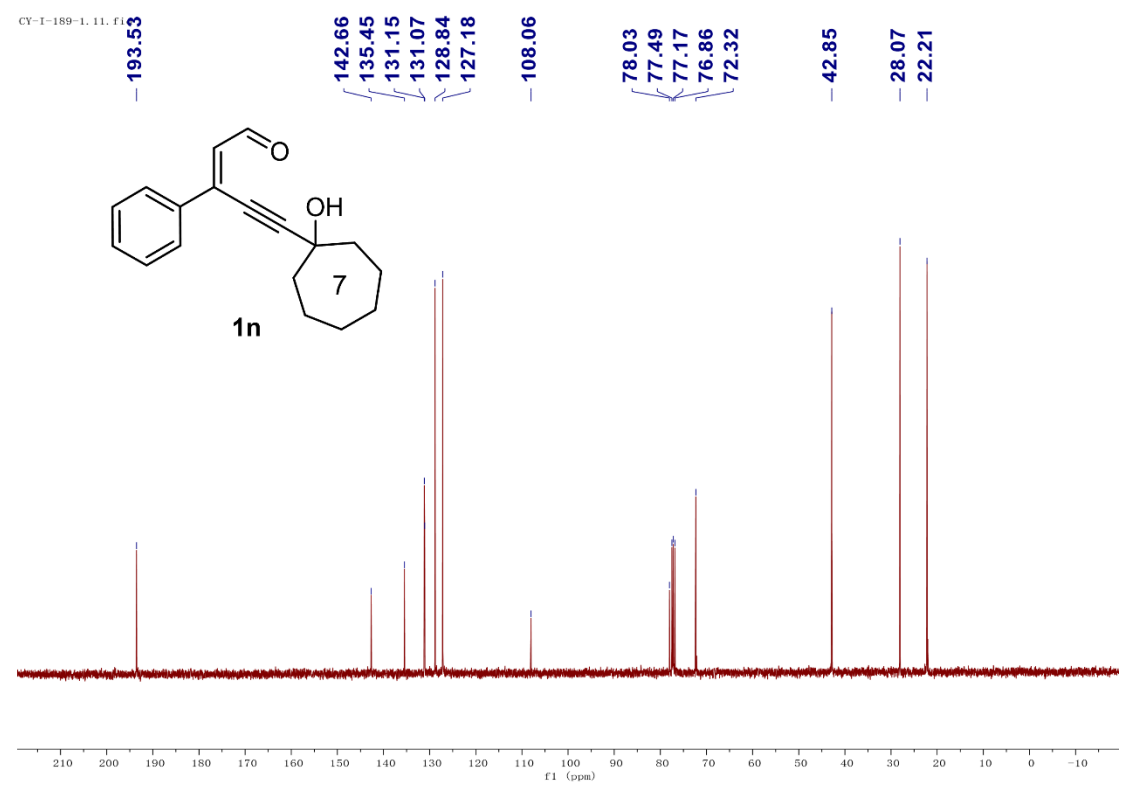
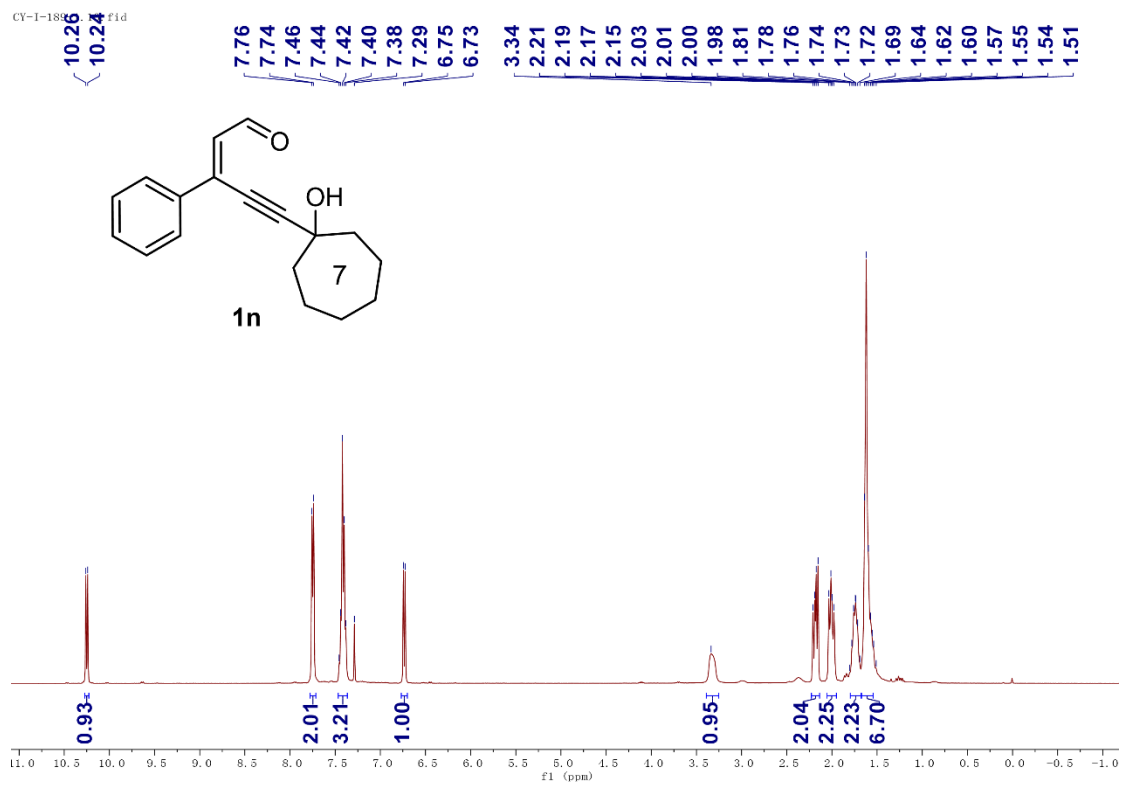










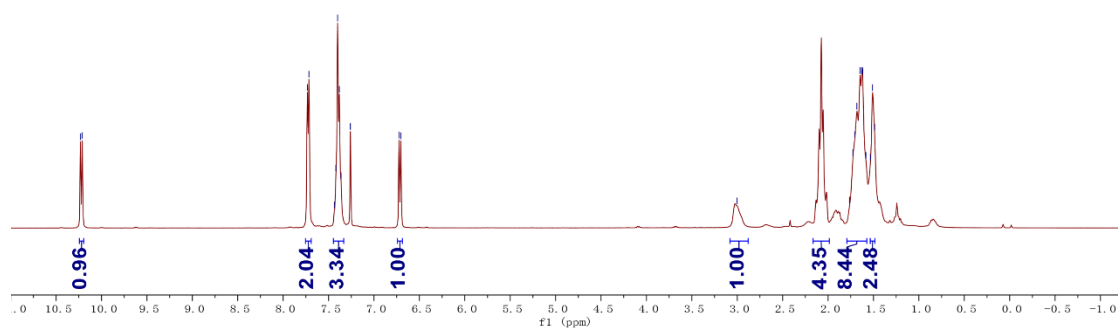
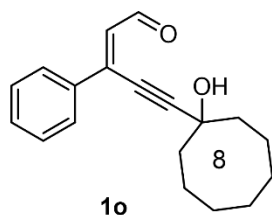


CY-I-188-2-1.10.fid

10.23  
10.21

7.73  
7.72  
7.44  
7.42  
7.40  
7.38  
7.36  
7.26  
6.72  
6.70

3.00  
1.76  
1.73  
1.71  
1.68  
1.65  
1.63  
1.62  
1.58  
1.53  
1.51  
1.49



CY-I-189-2-1.11.

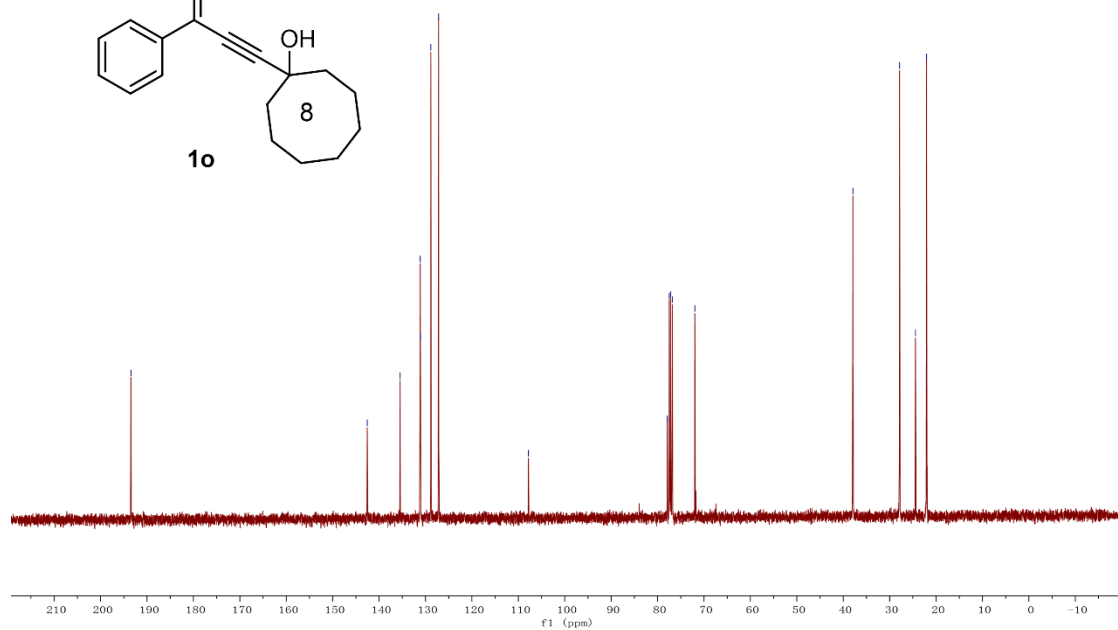
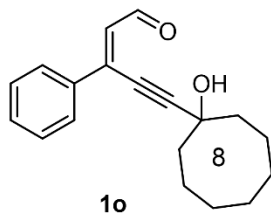
193.46

142.56  
135.47  
131.14  
131.10  
128.85  
127.17

107.82

77.90  
77.47  
77.16  
76.84  
71.97

37.92  
27.86  
24.43  
22.06



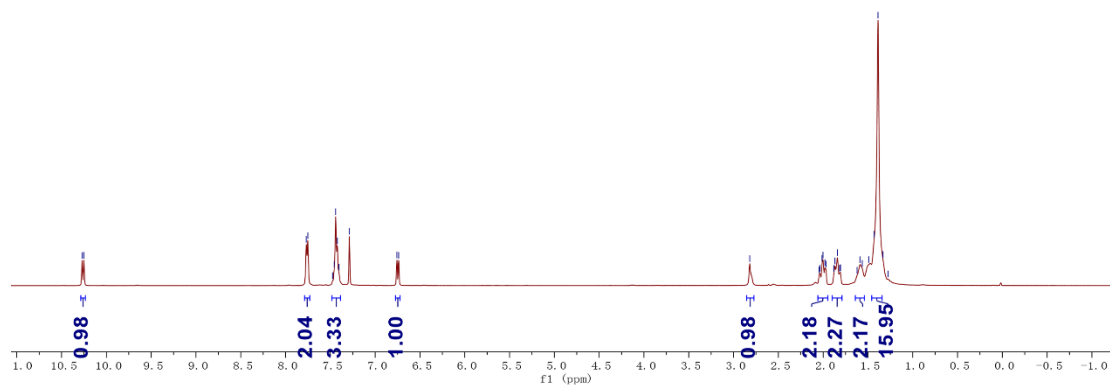
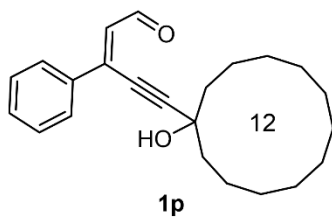


CY-I-194-1.11.f1.d

10.27  
10.25

7.77  
7.75  
7.48  
7.46  
7.44  
7.42  
7.40  
7.29  
6.76  
6.74

2.82  
2.01  
2.00  
1.98  
1.97  
1.87  
1.84  
1.82  
1.81  
1.59  
1.56  
1.49  
1.43  
1.39  
1.33



CY-I-194-1.11.f1

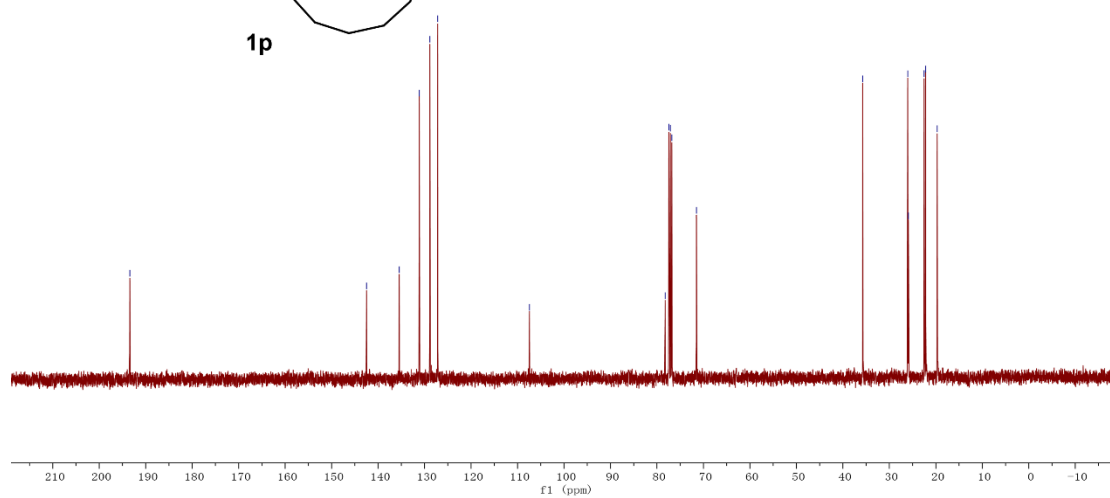
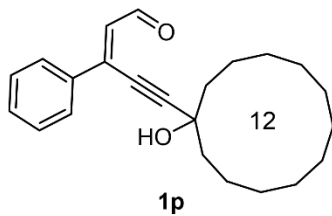
193.42

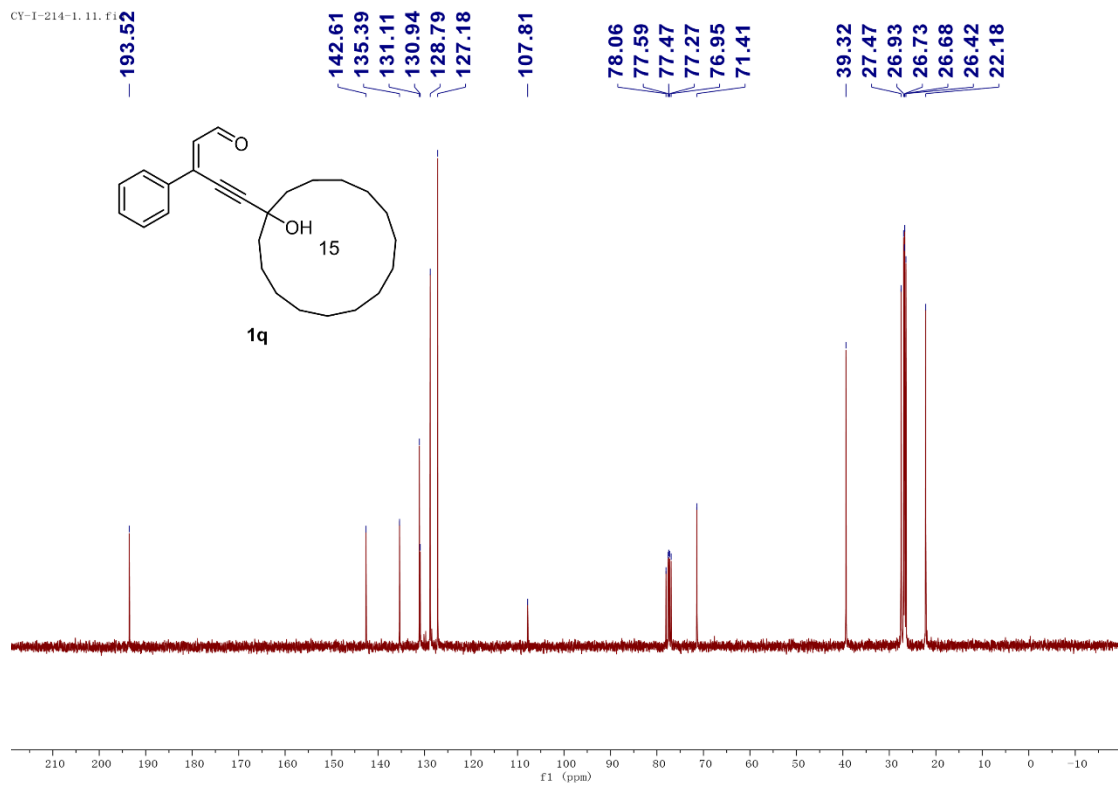
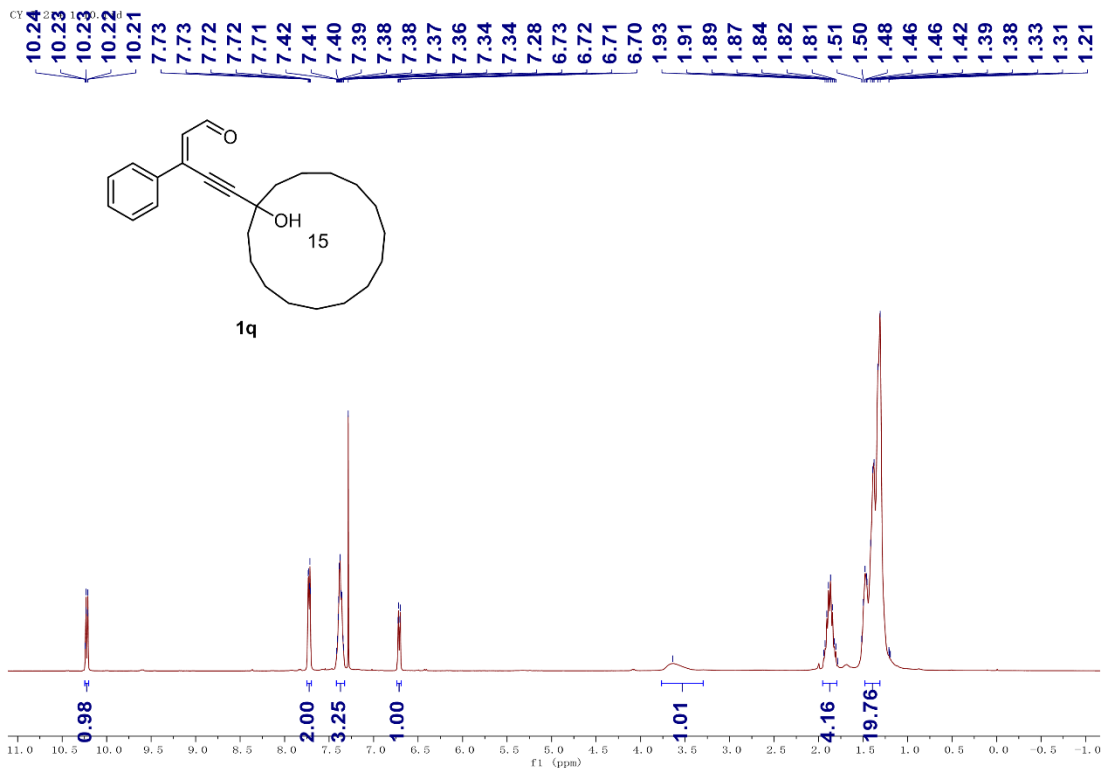
142.48  
135.45  
131.13  
128.86  
127.17

107.43

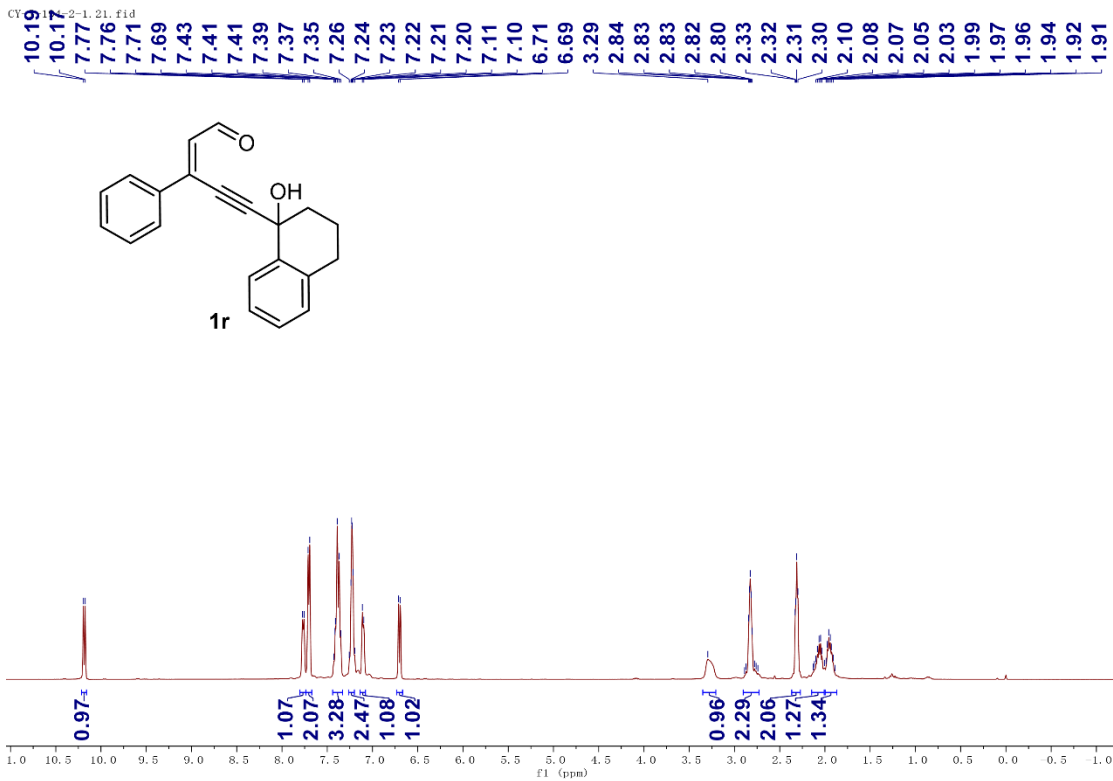
78.24  
77.44  
77.12  
76.80  
71.50

35.73  
26.04  
25.89  
22.52  
22.18  
19.70

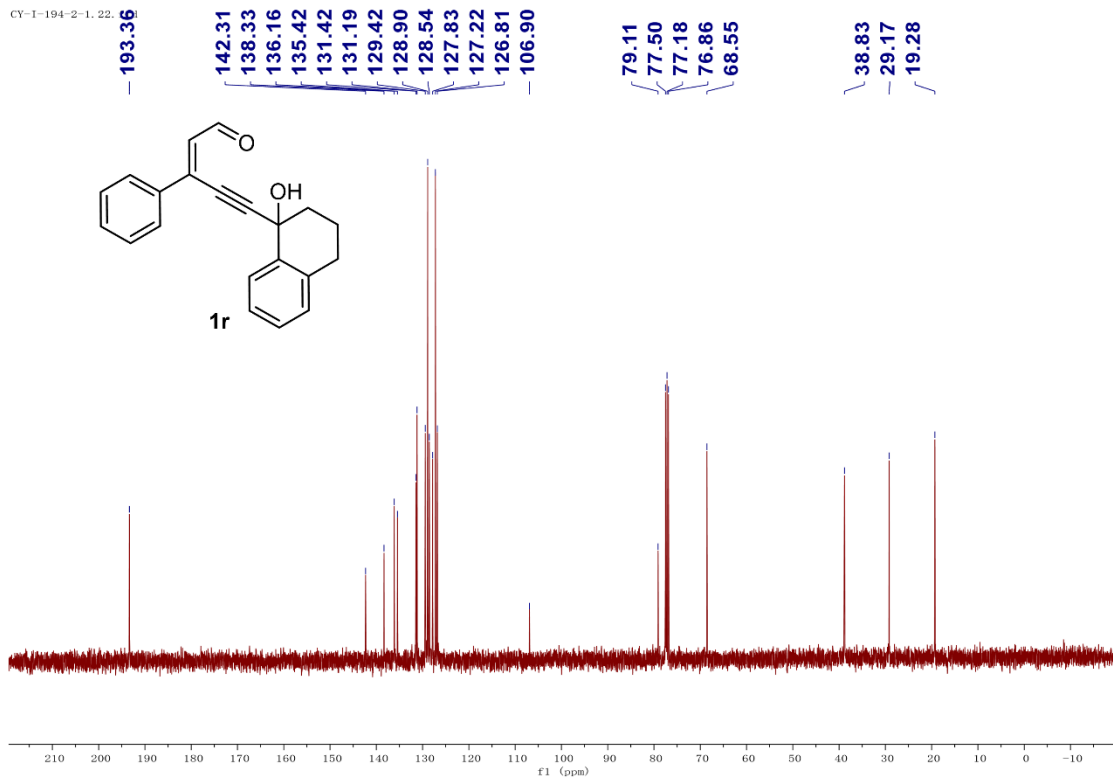




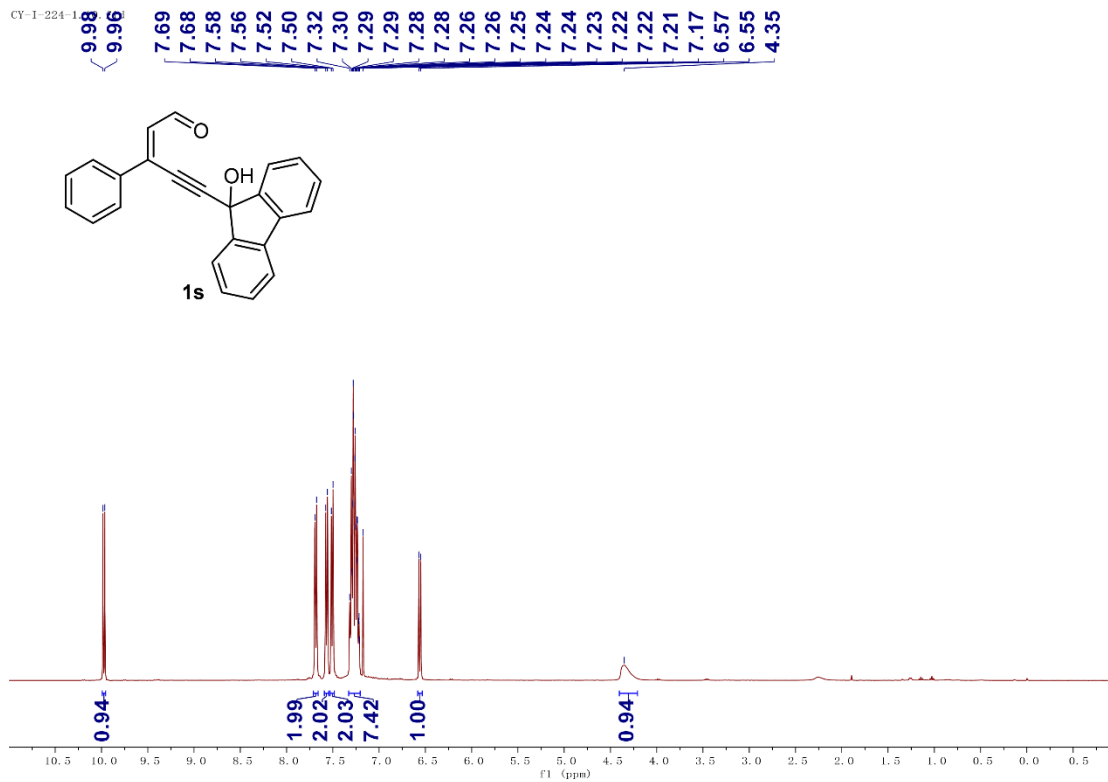
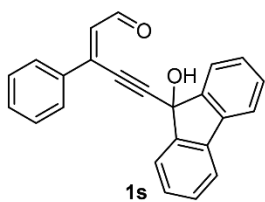
CY-I-194-2-1.21.fid



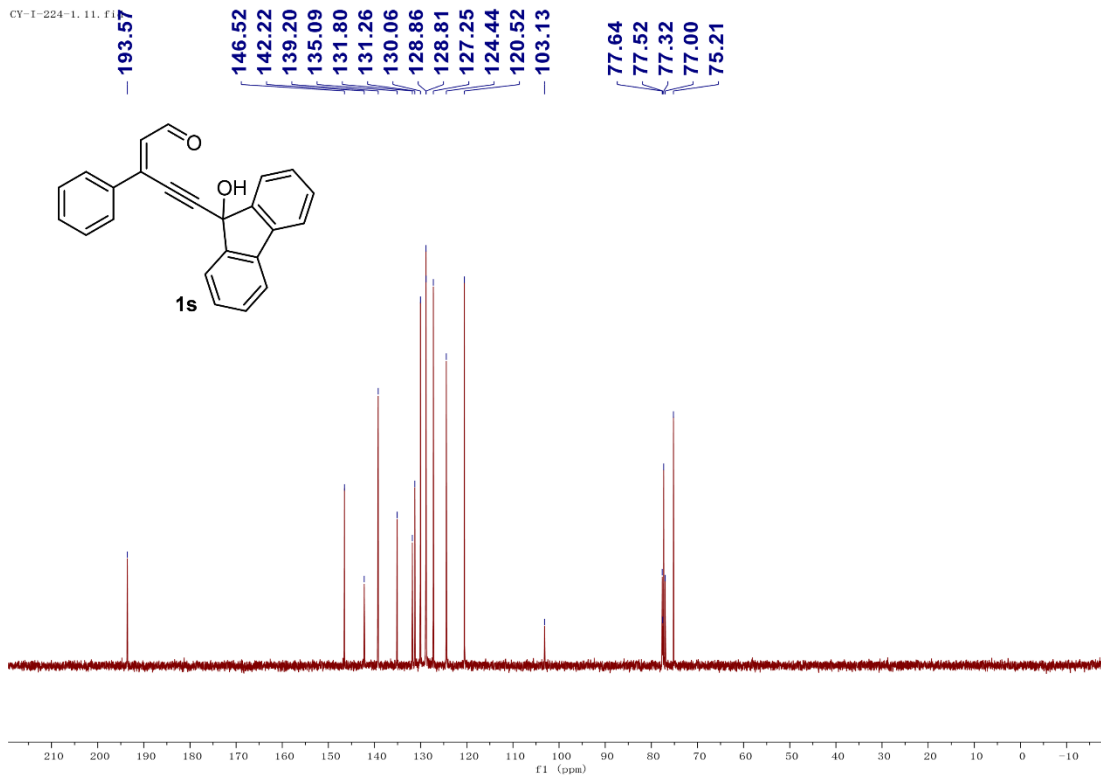
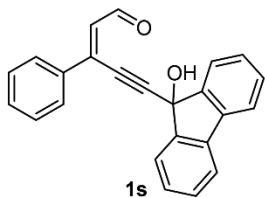
CY-I-194-2-1.22.



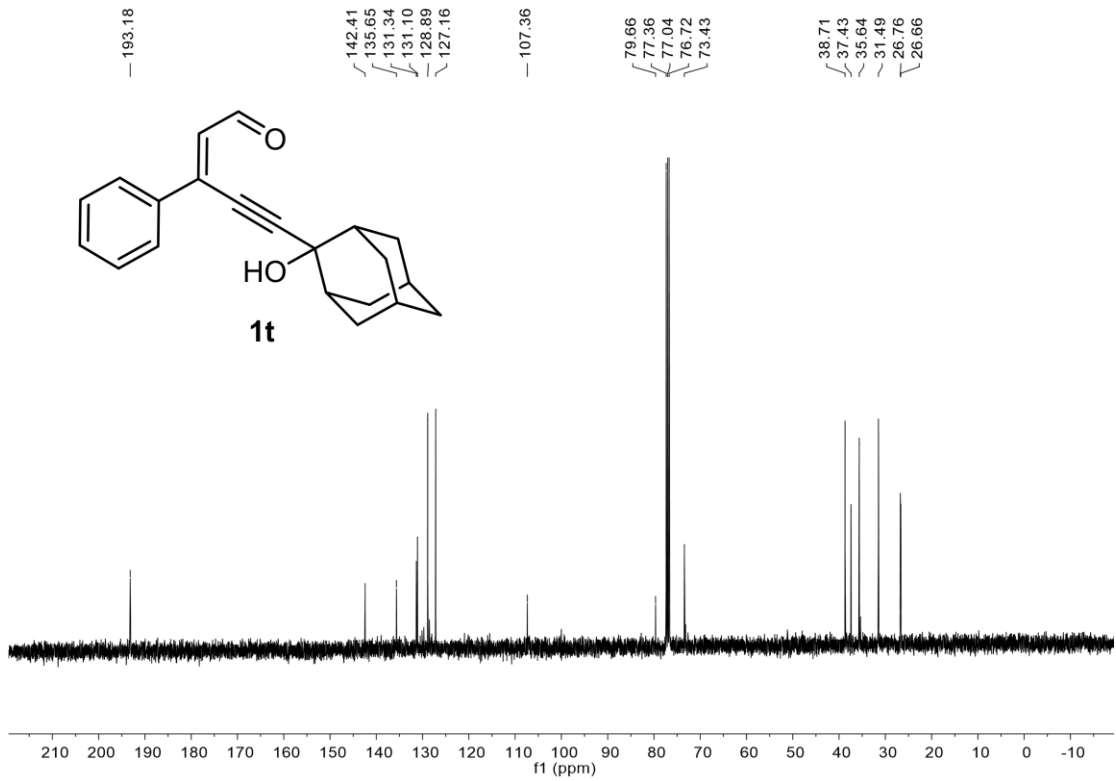
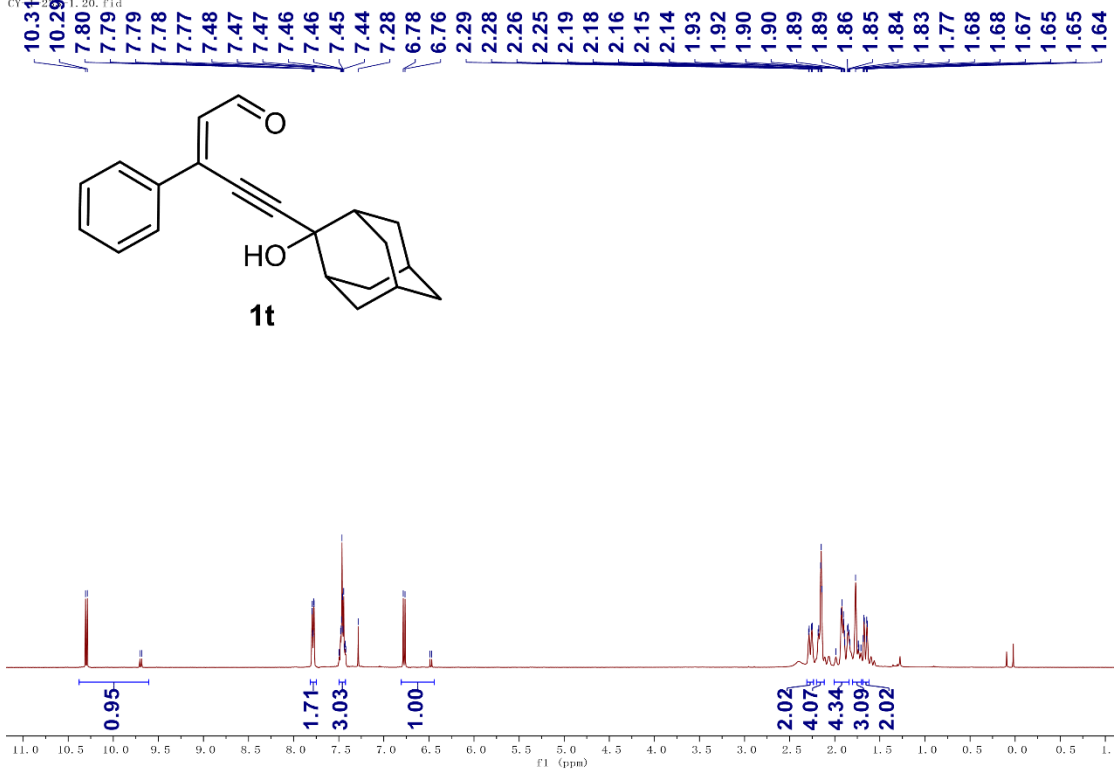
CY-I-224-1



CY-I-224-1. 11. f1

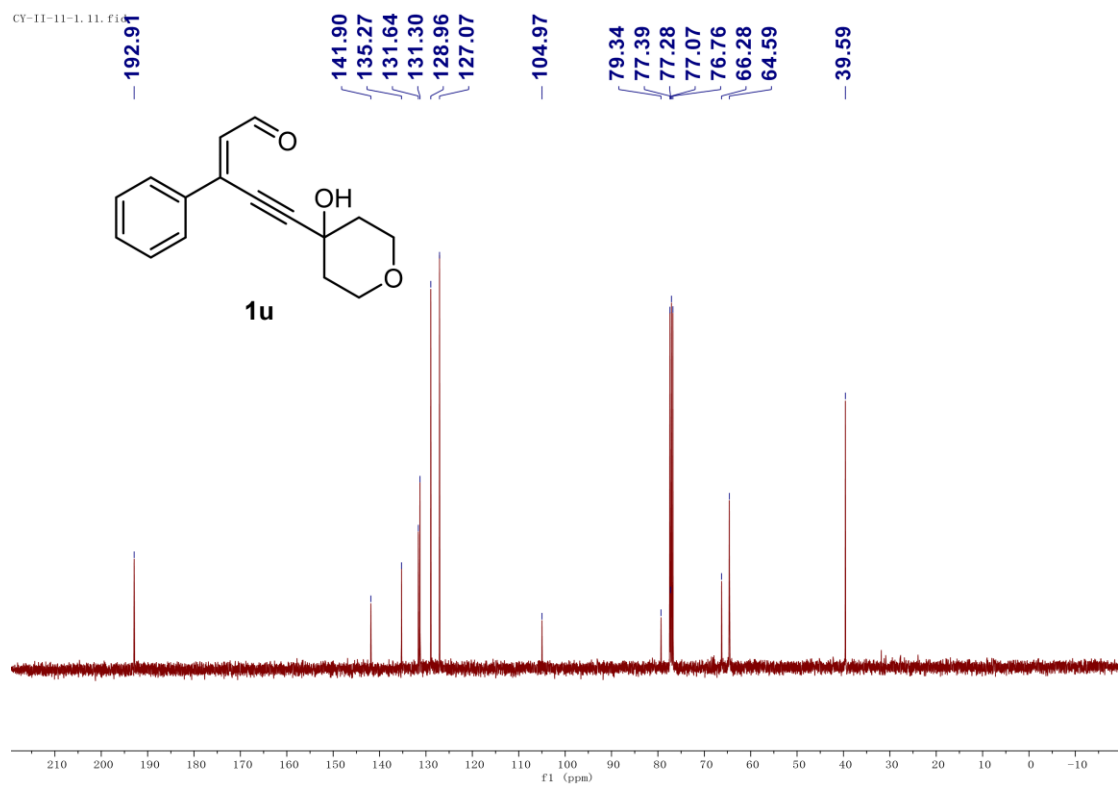
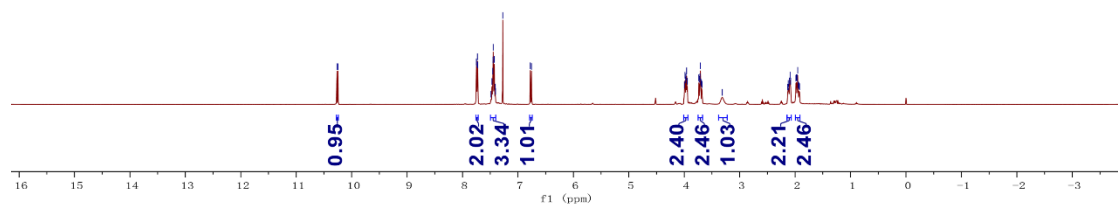
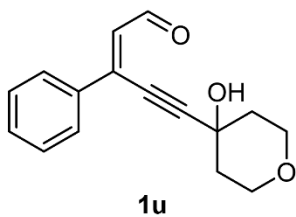


CY 2011.20.fid



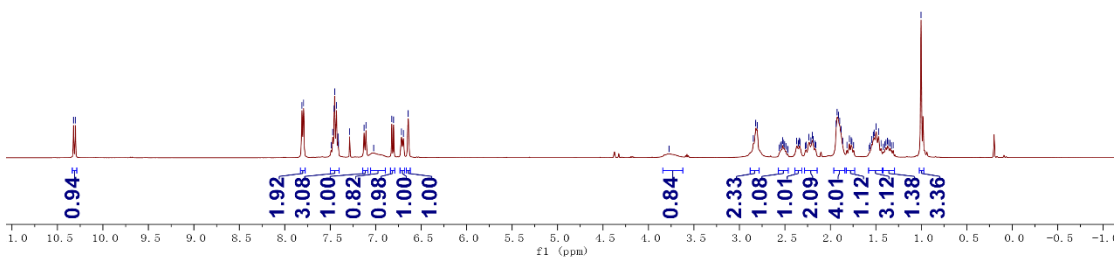
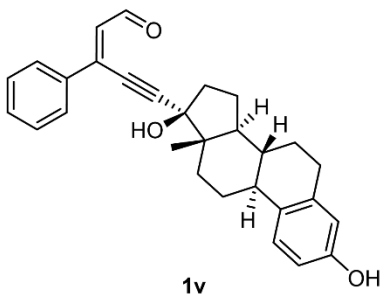
CY-11-11-1.10.f1d

10.27  
10.25  
7.75  
7.75  
7.73  
7.73  
7.47  
7.45  
7.45  
7.45  
7.43  
7.41  
7.40  
7.27  
6.78  
6.76  
4.00  
3.99  
3.97  
3.97  
3.96  
3.94  
3.74  
3.73  
3.72  
3.71  
3.70  
3.69  
3.68  
3.31  
2.13  
2.12  
2.11  
2.10  
2.09  
2.08  
1.99  
1.98  
1.96  
1.95  
1.94  
1.93  
1.92



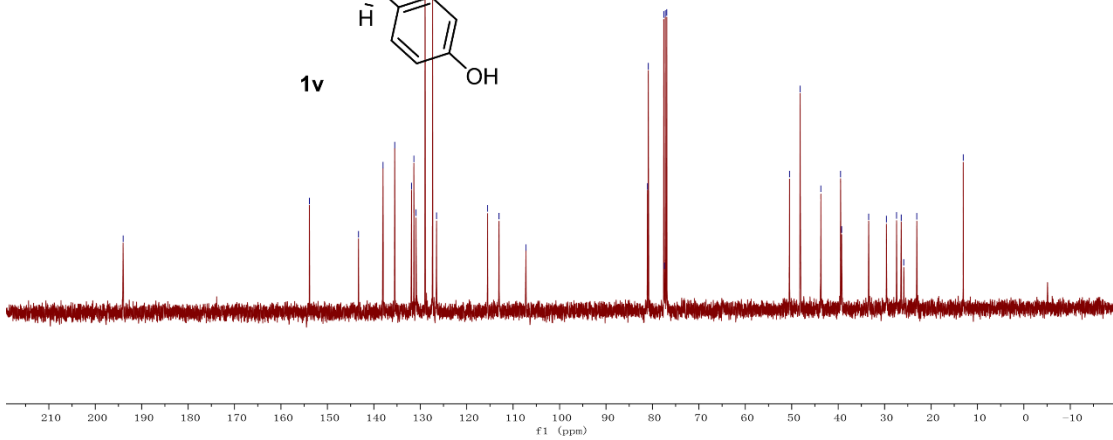
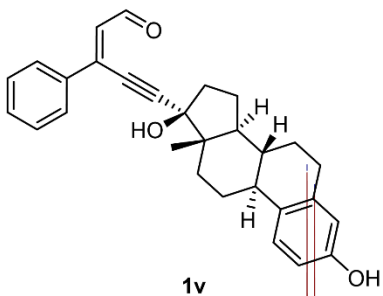
CY-1-257-1.41.fid

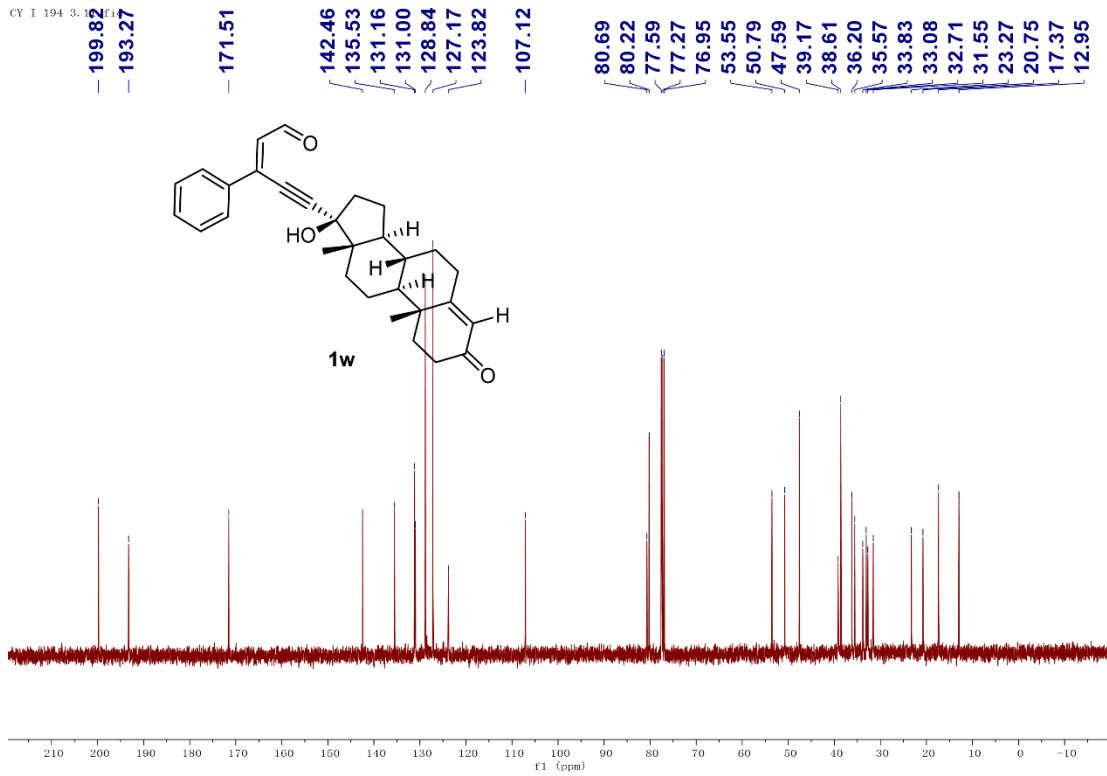
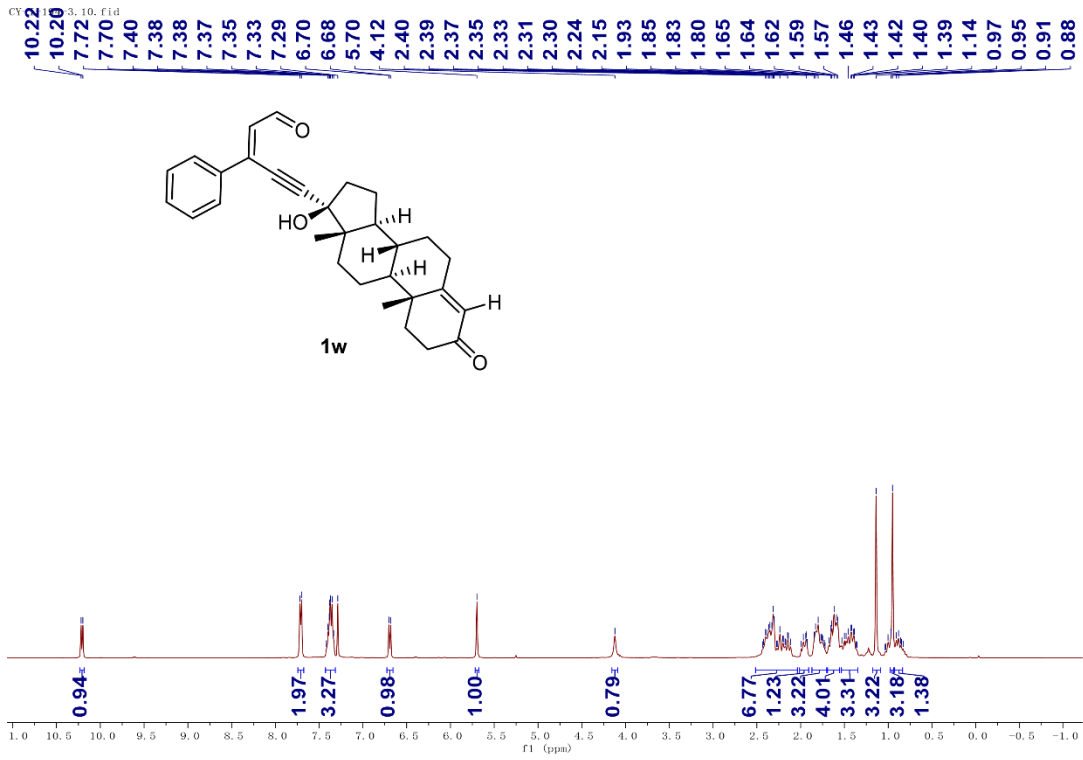
10.32	10.30	7.81	7.79	7.47	7.46	7.45	7.43	7.42	7.29	7.13	7.11	6.82	6.80	6.72	6.70	6.64	2.85	2.82	2.80	2.52	2.37	2.34	2.24	2.21	2.20	2.19	1.94	1.92	1.91	1.90	1.88	1.86	1.79	1.77	1.76	1.55	1.53	1.52	1.50	1.47	1.37	1.00
-------	-------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------



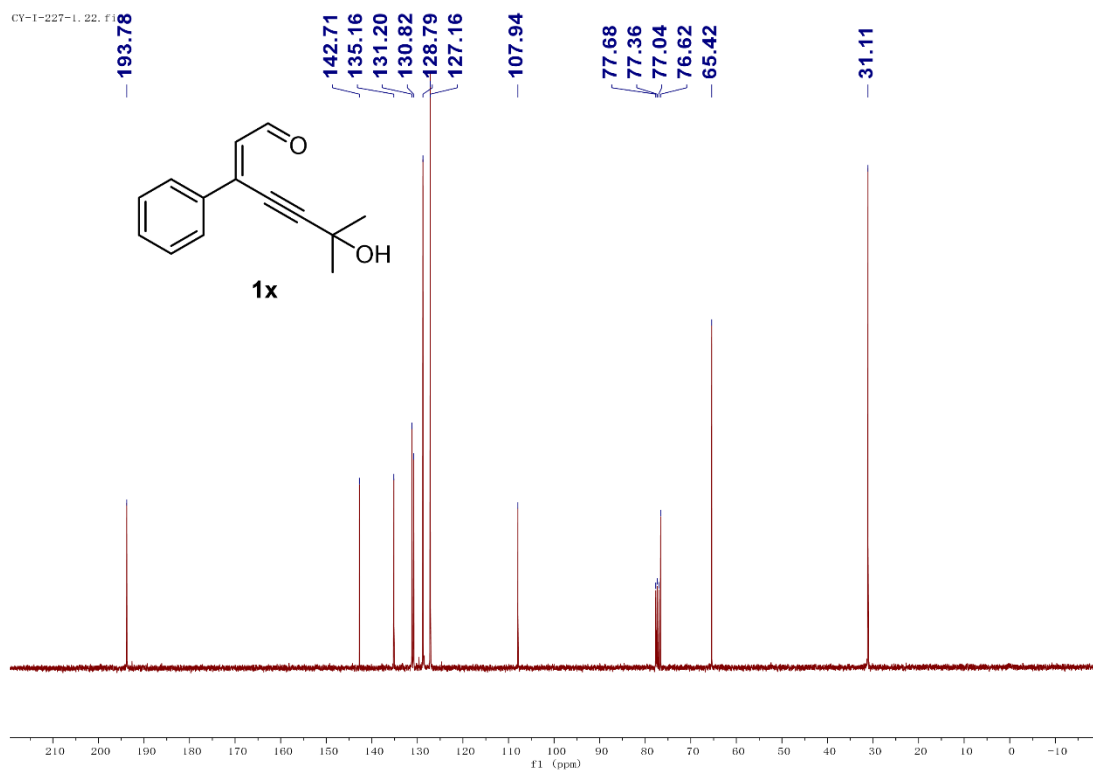
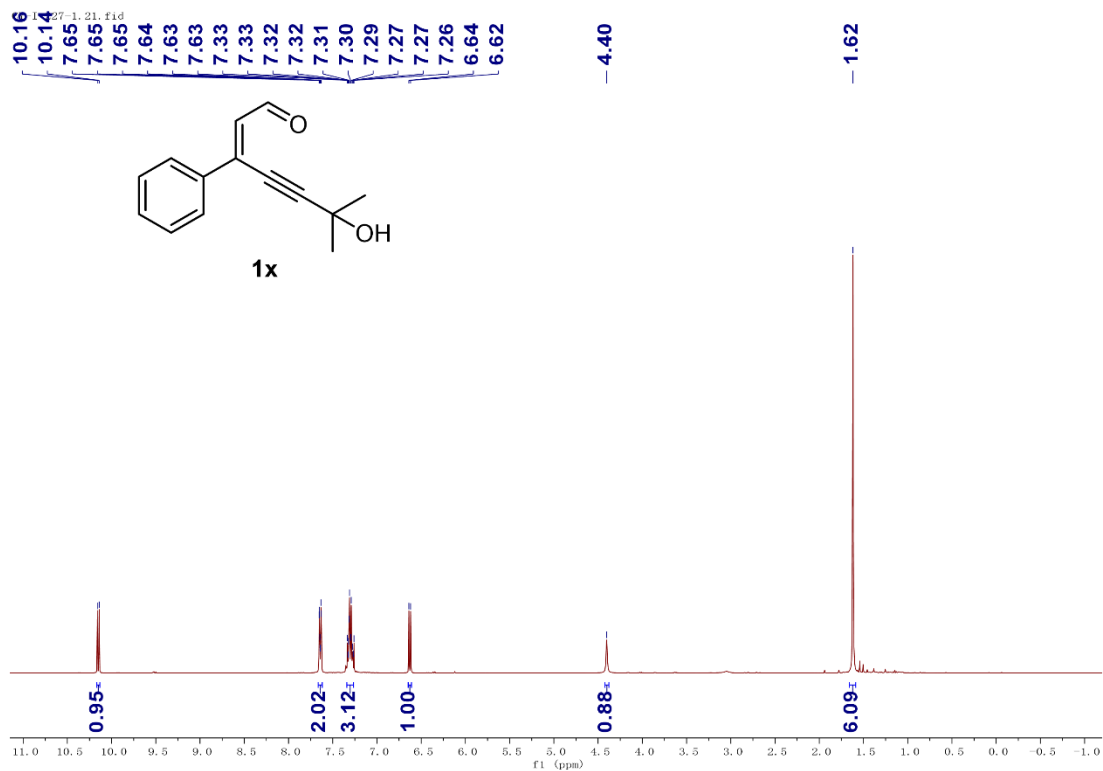
CY-1-257-1.42.fid

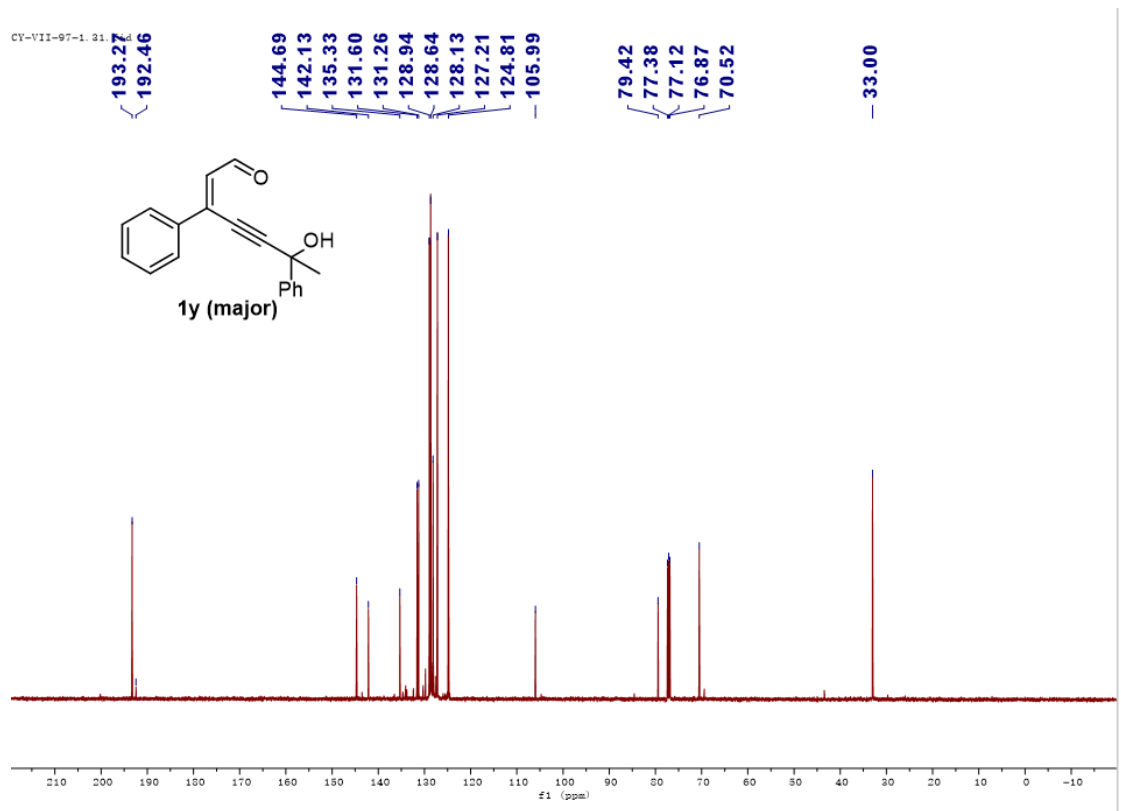
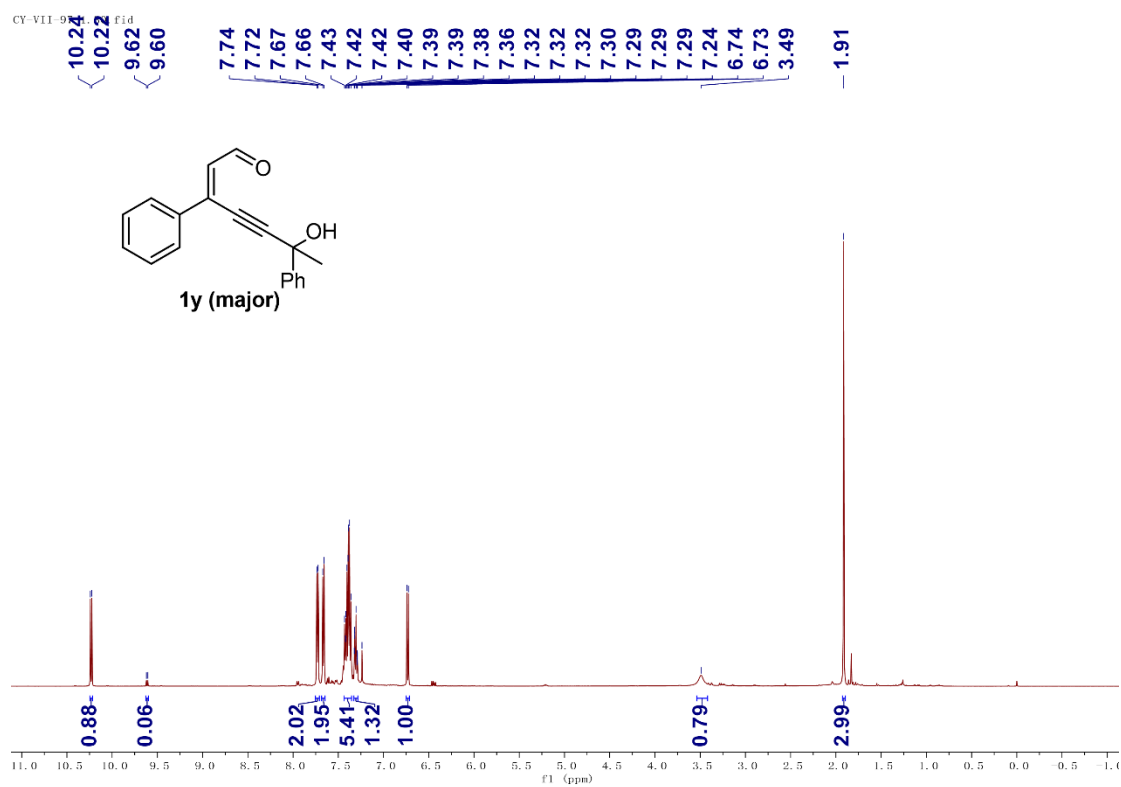
194.00	153.86	143.30	138.01	135.50	131.88	131.38	130.92	128.96	127.34	126.50	115.53	113.04	107.27	81.05	80.90	77.54	77.42	77.22	76.90	50.47	48.17	43.74	39.48	39.26	33.43	29.60	27.42	26.43	25.88	23.07	13.06
--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------



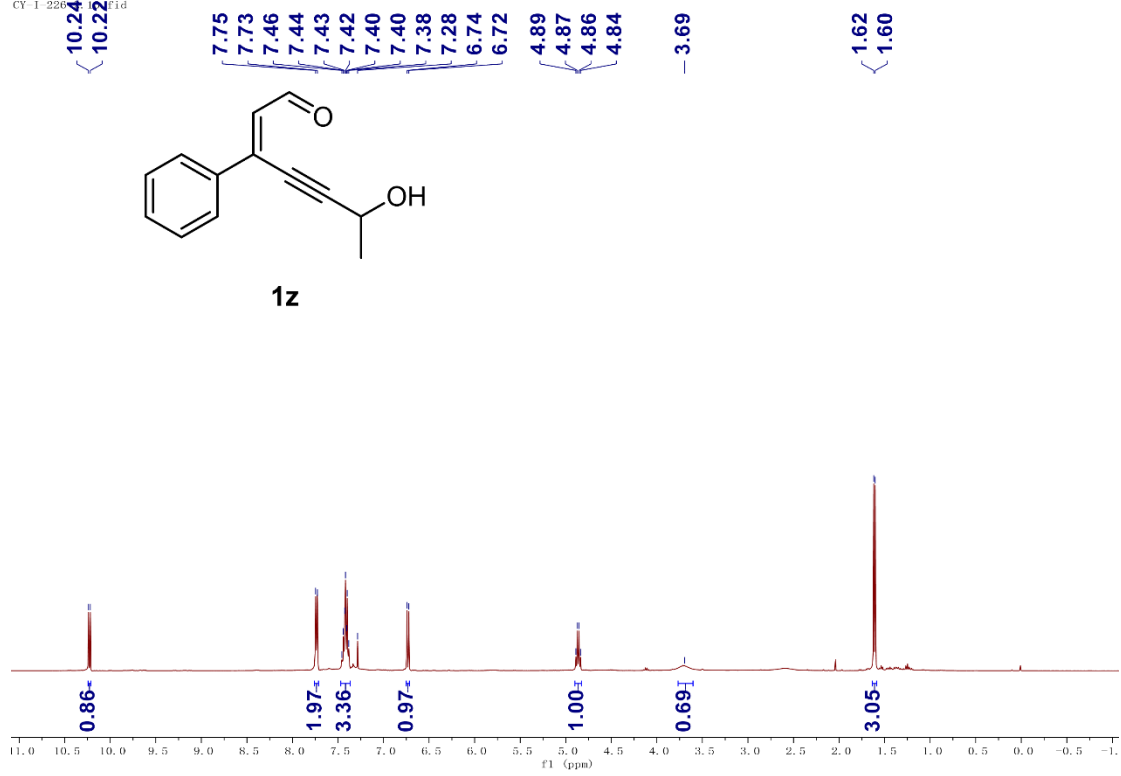




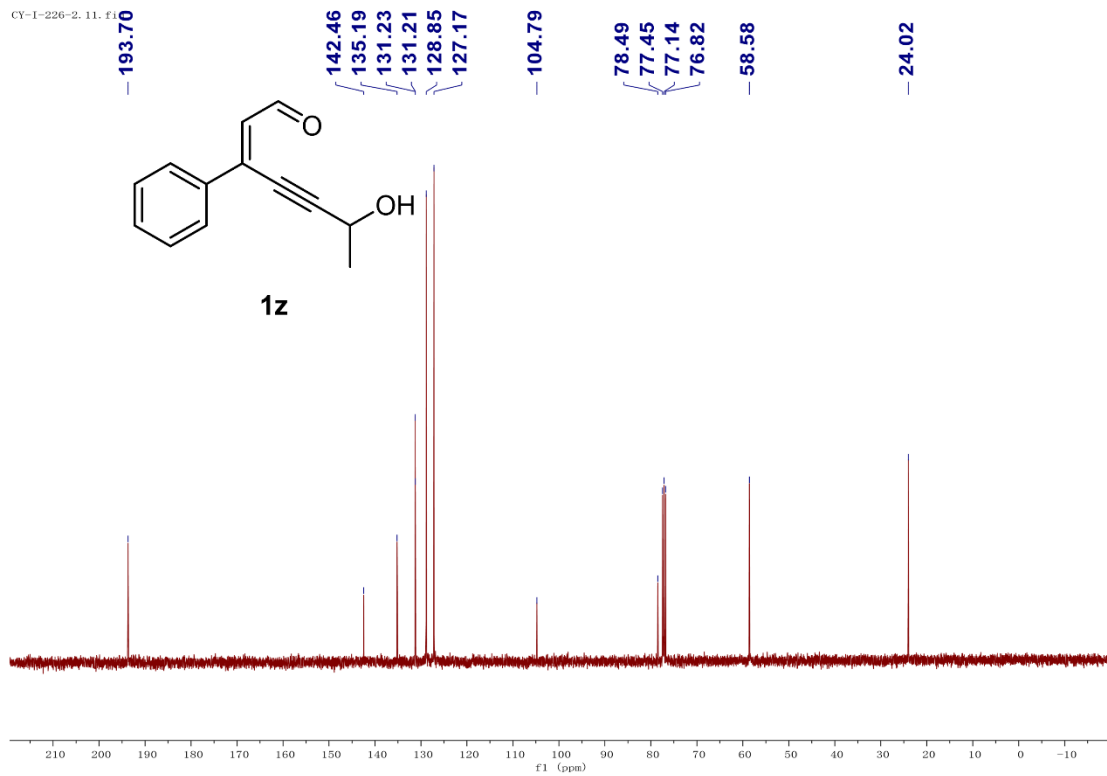


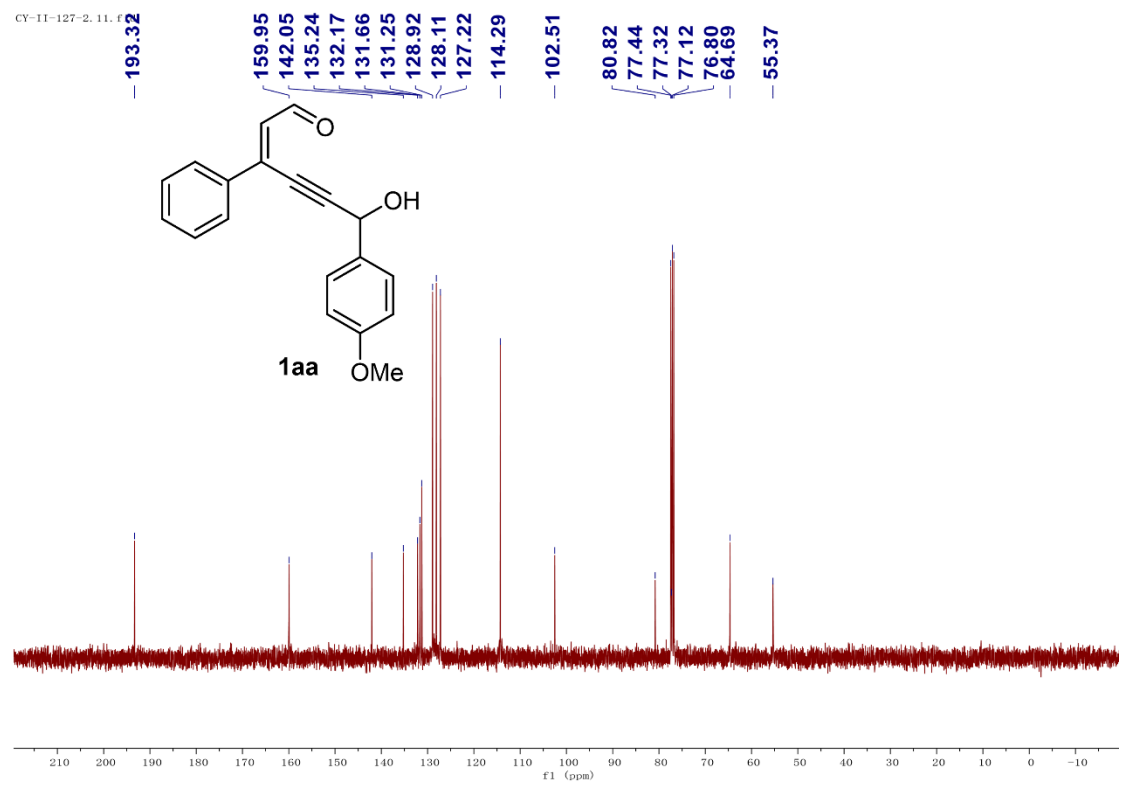
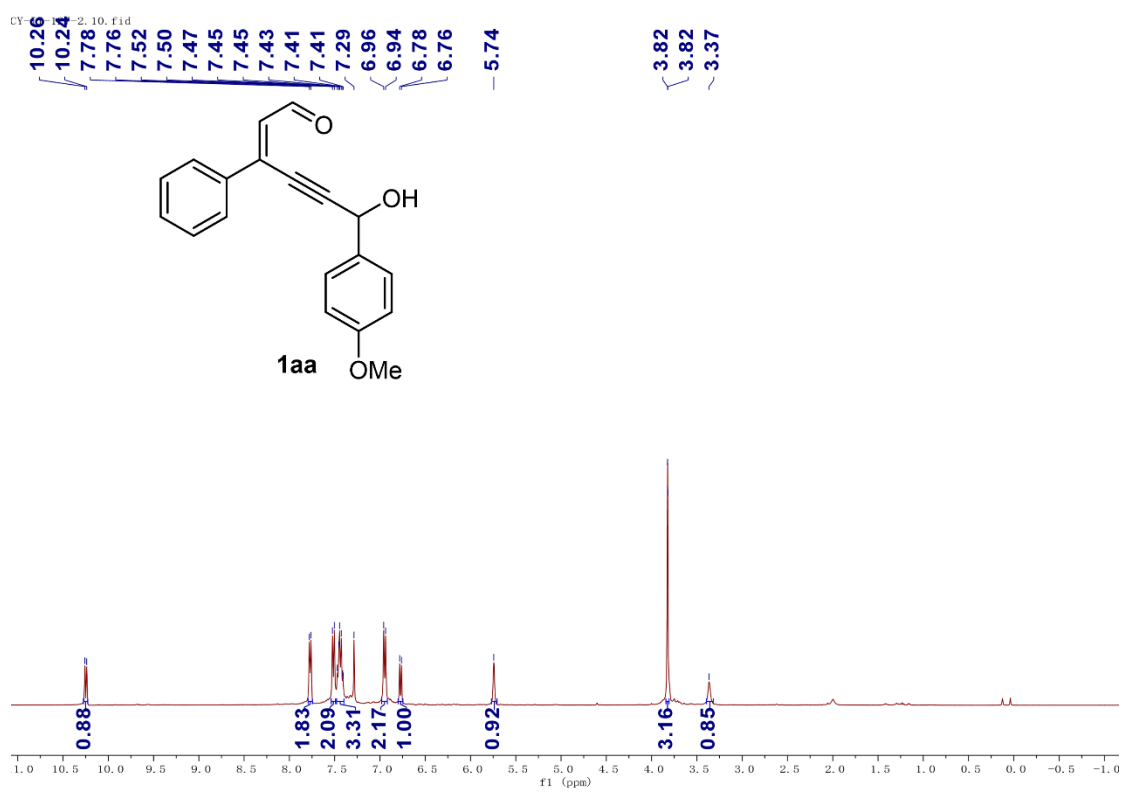


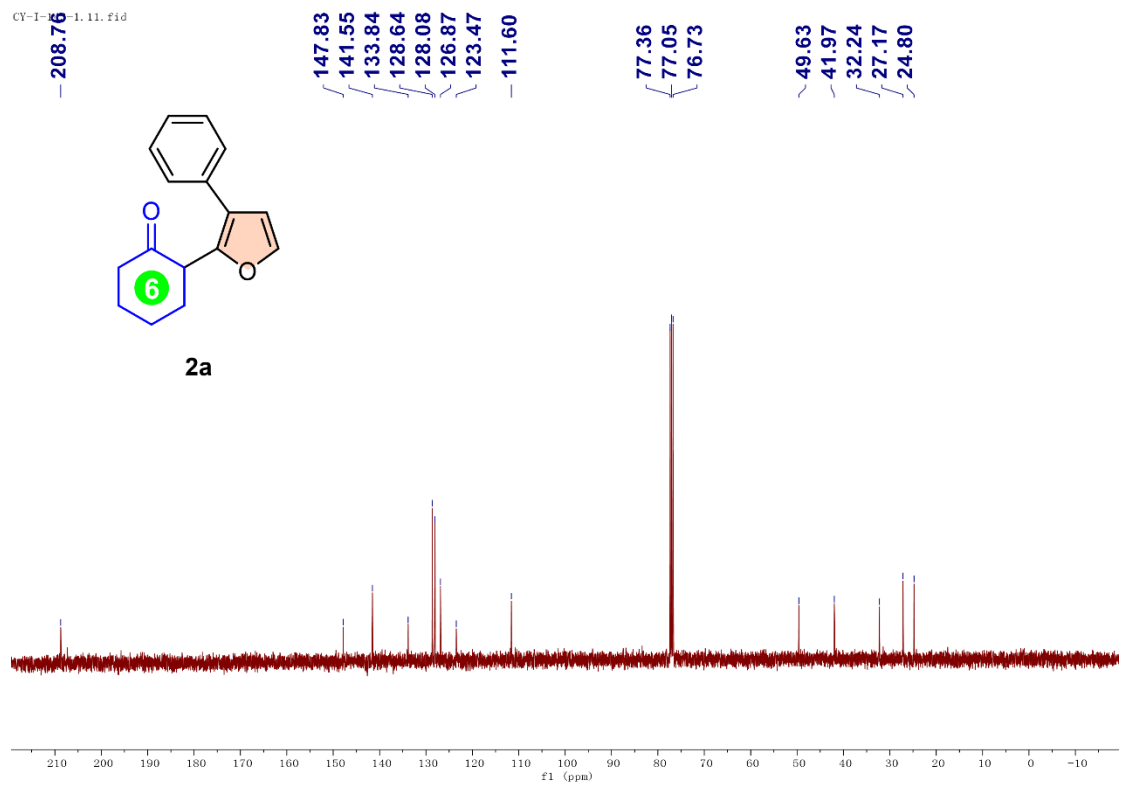
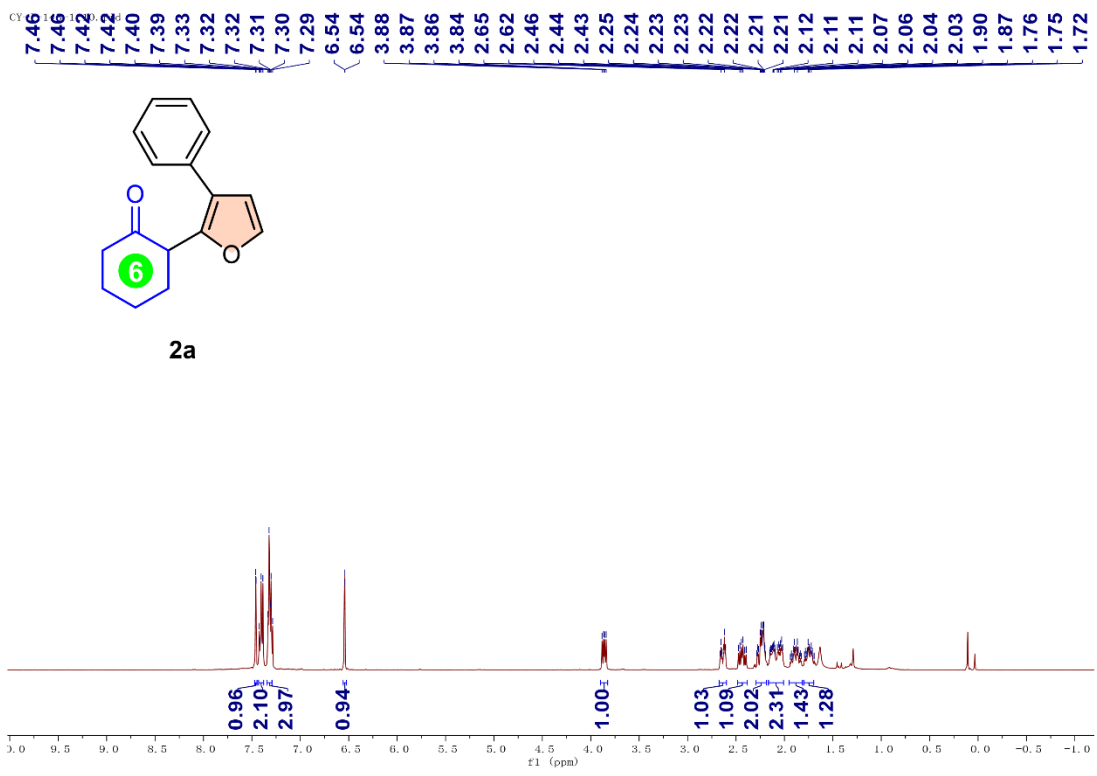
CY-I-226.F1d

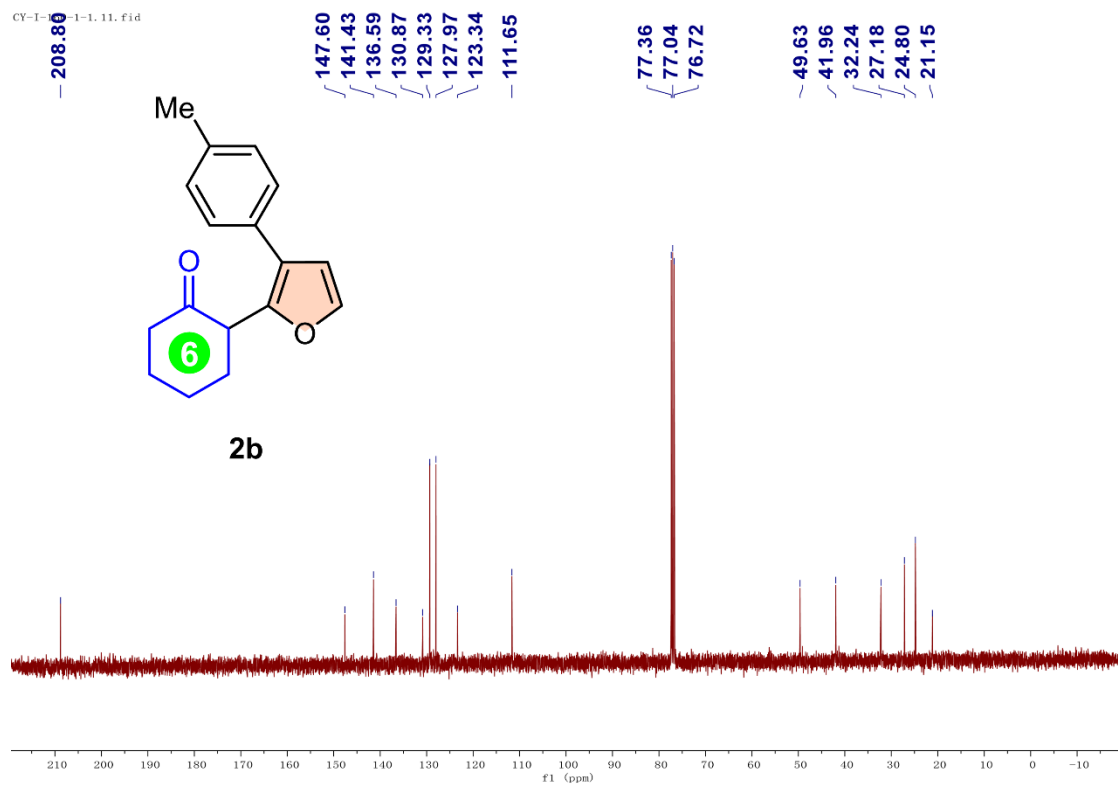
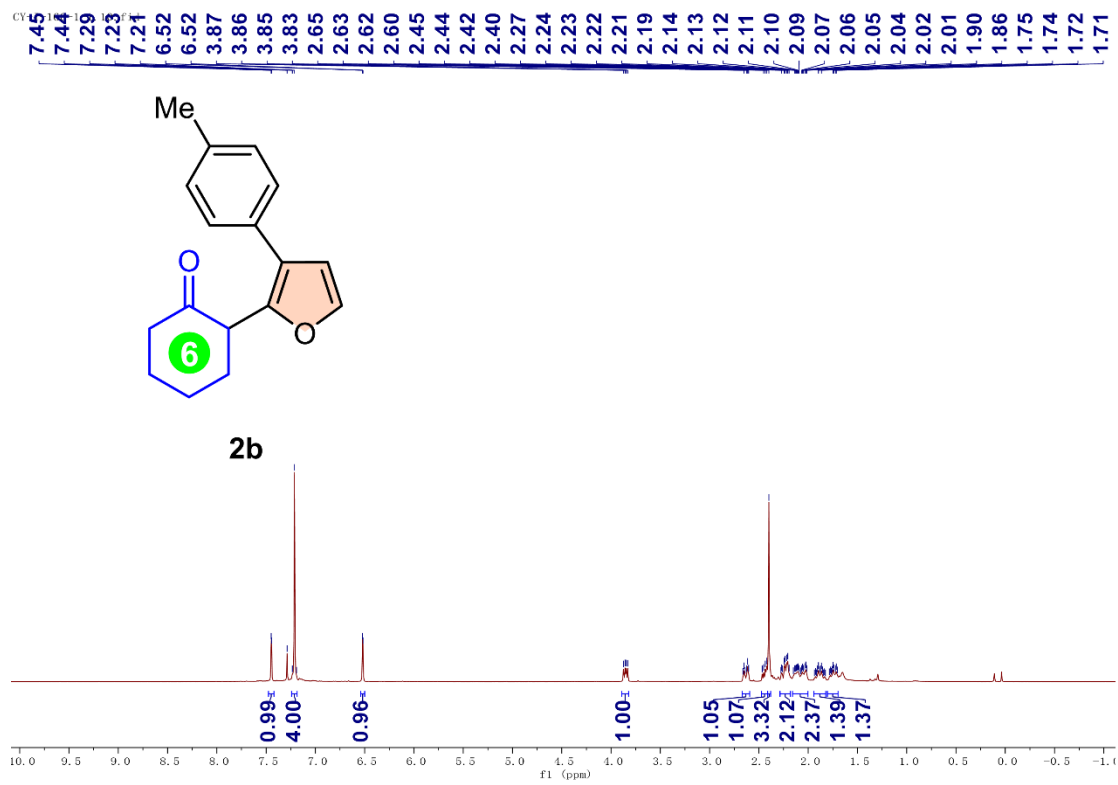


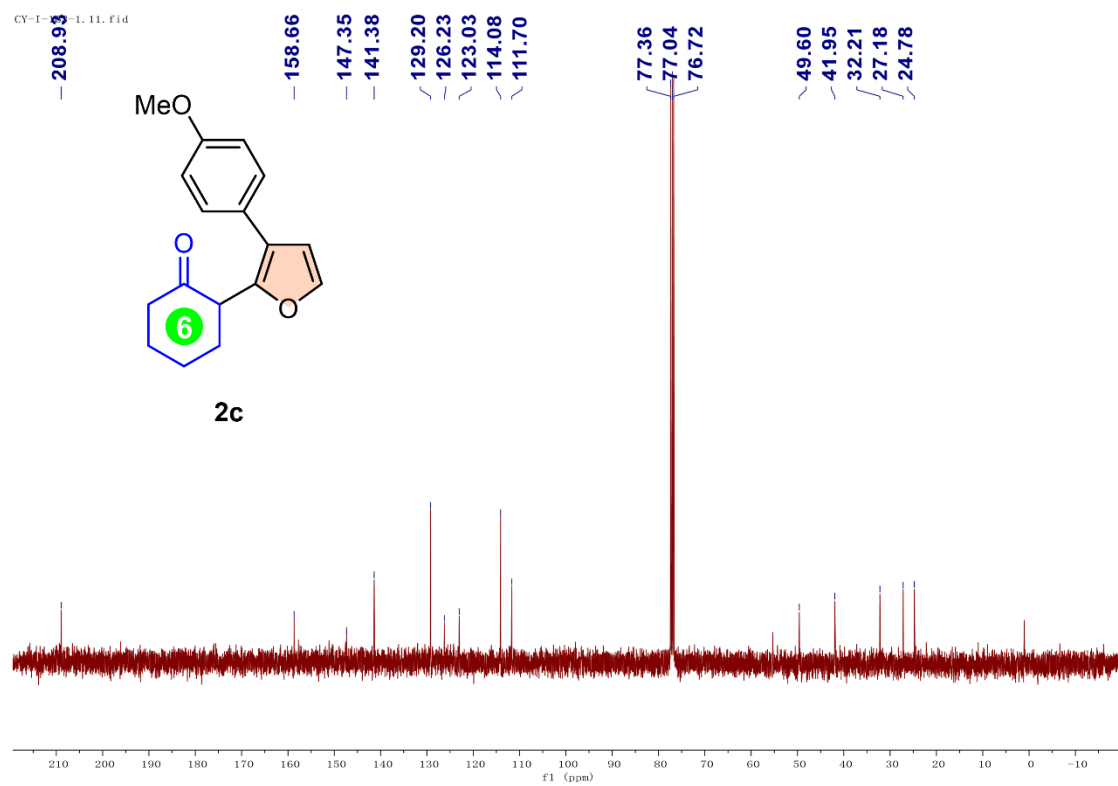
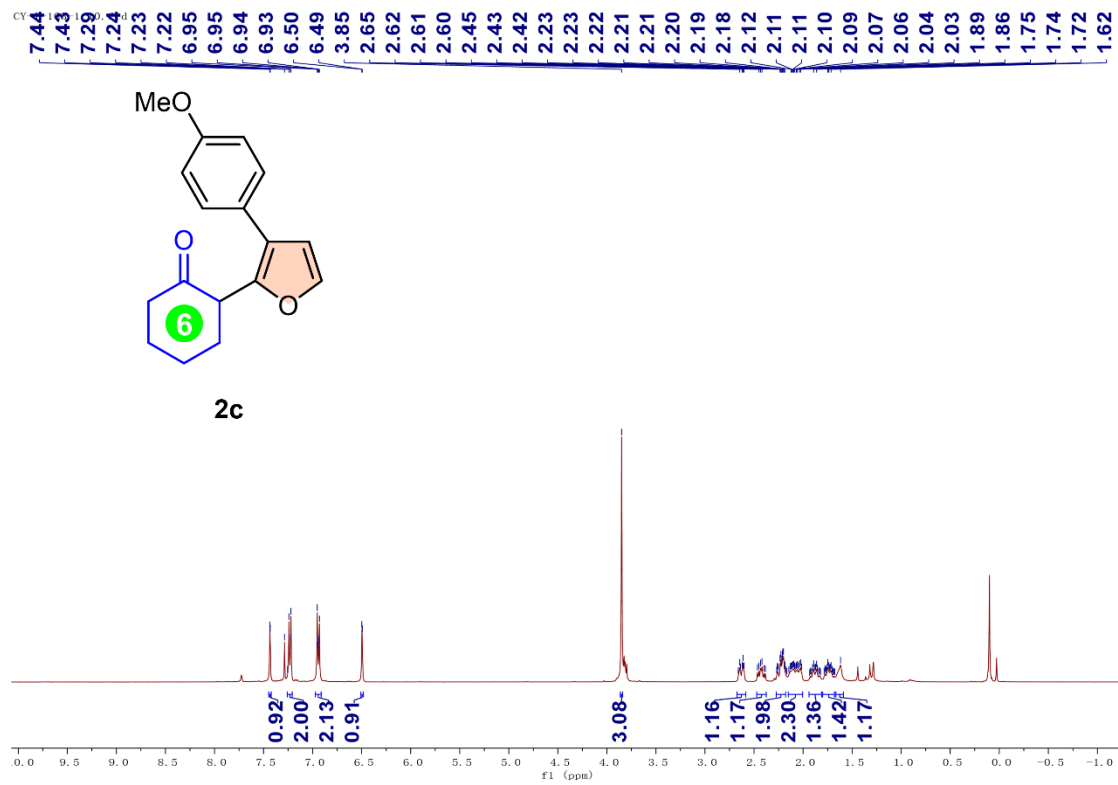
CY-I-226-2.11.F1

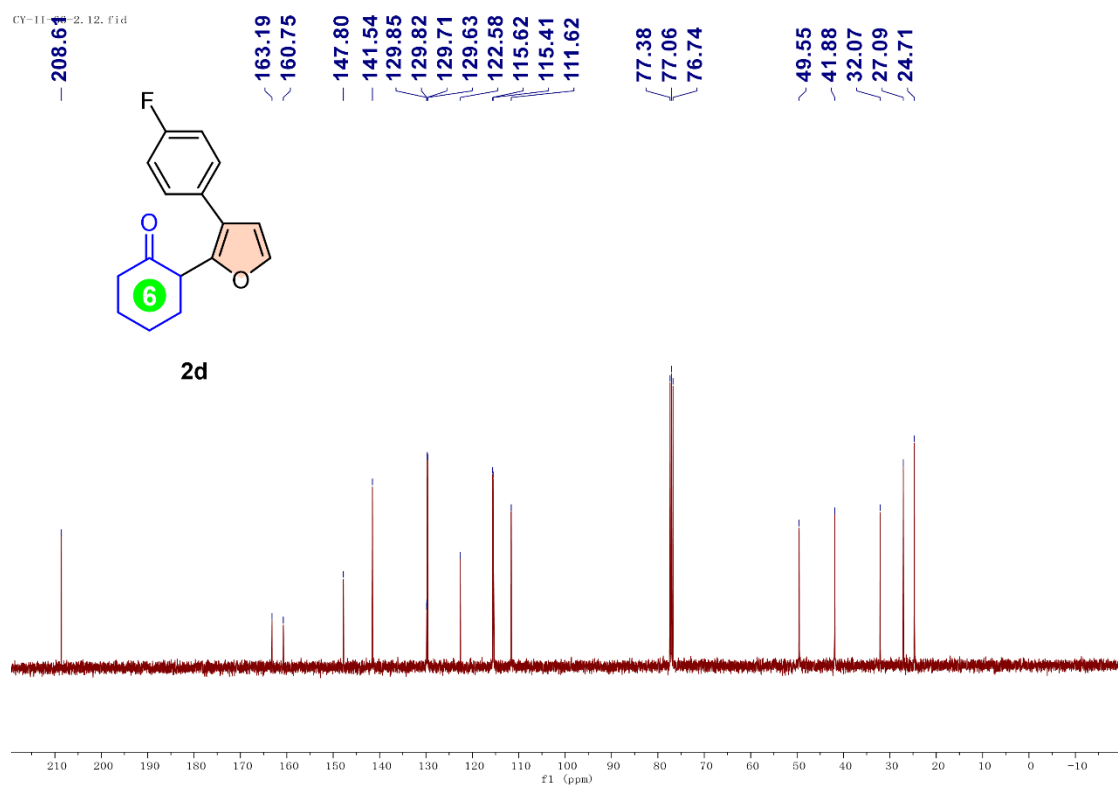
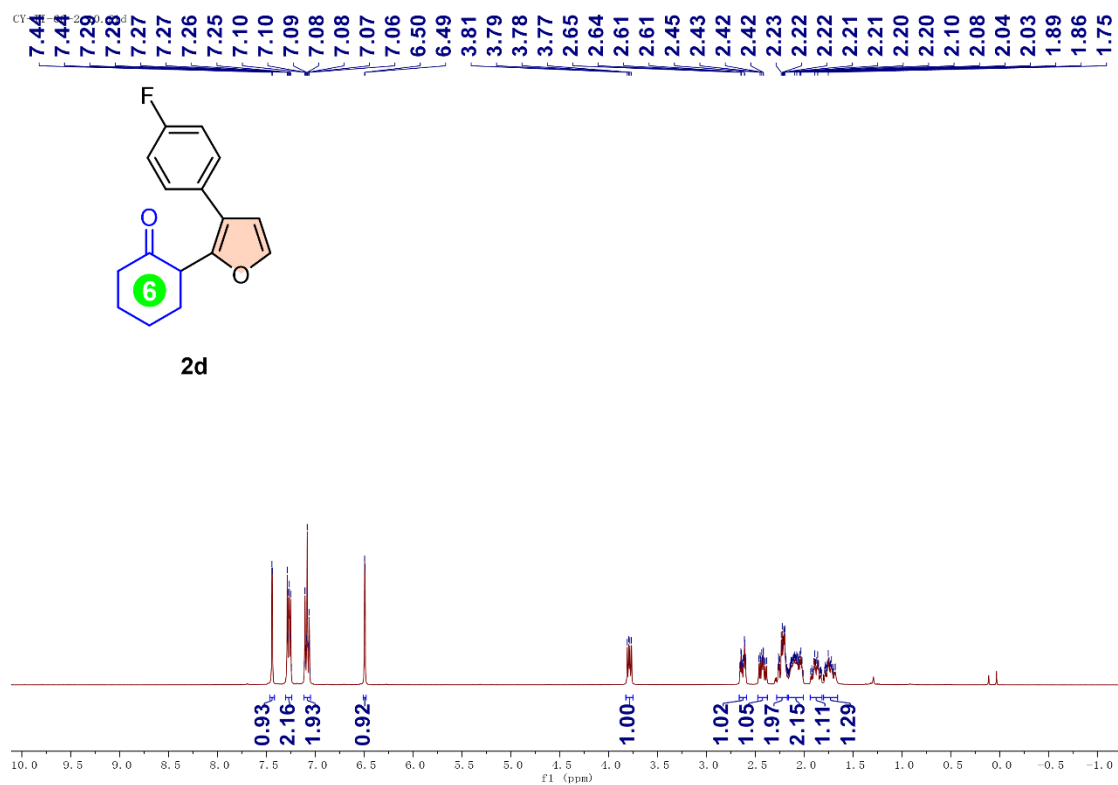






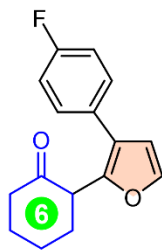




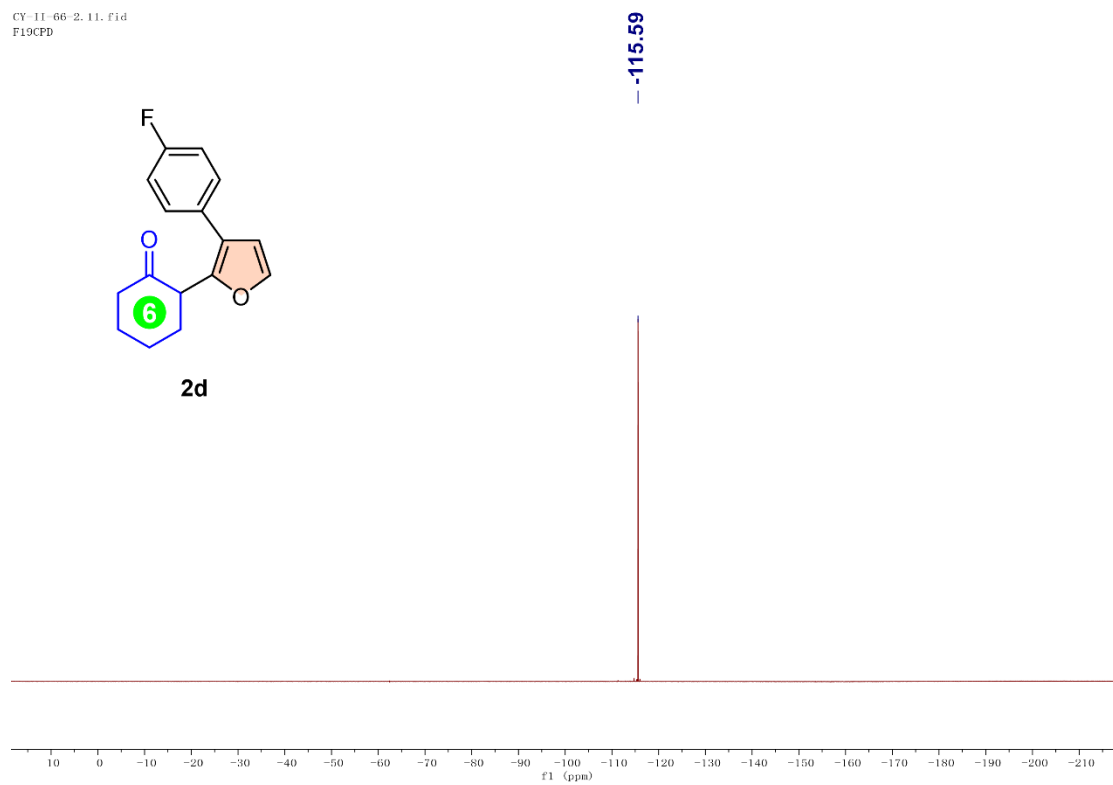


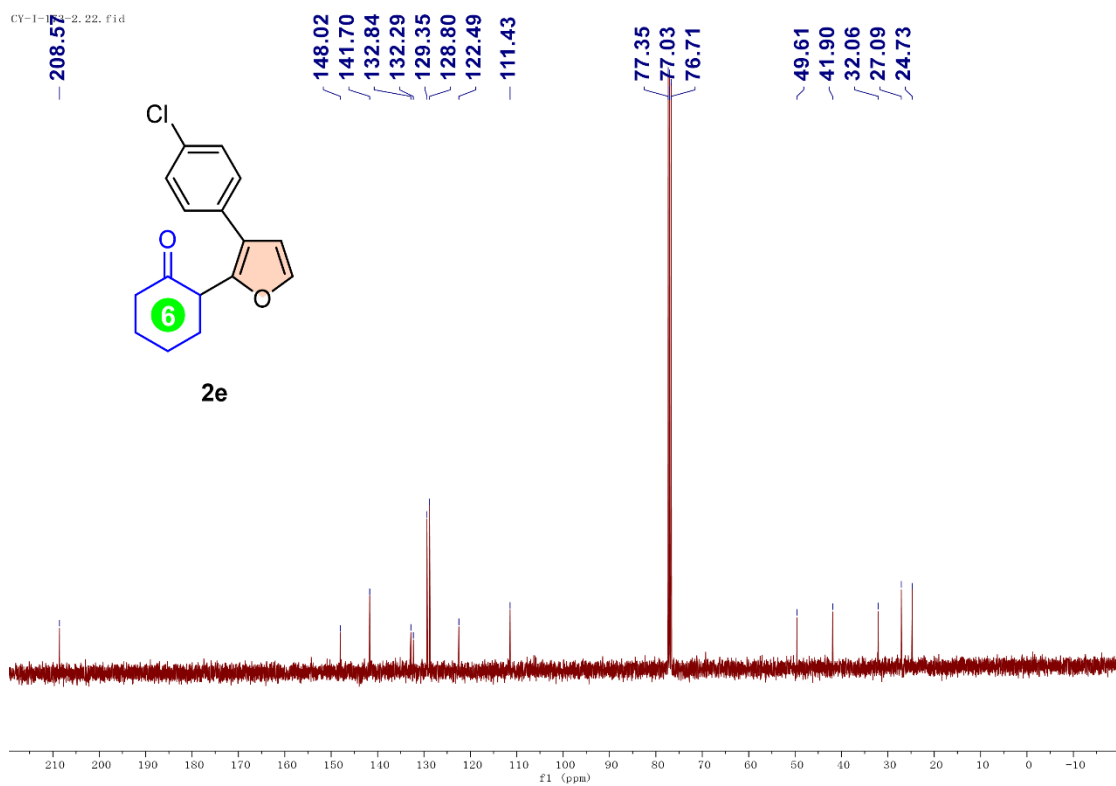
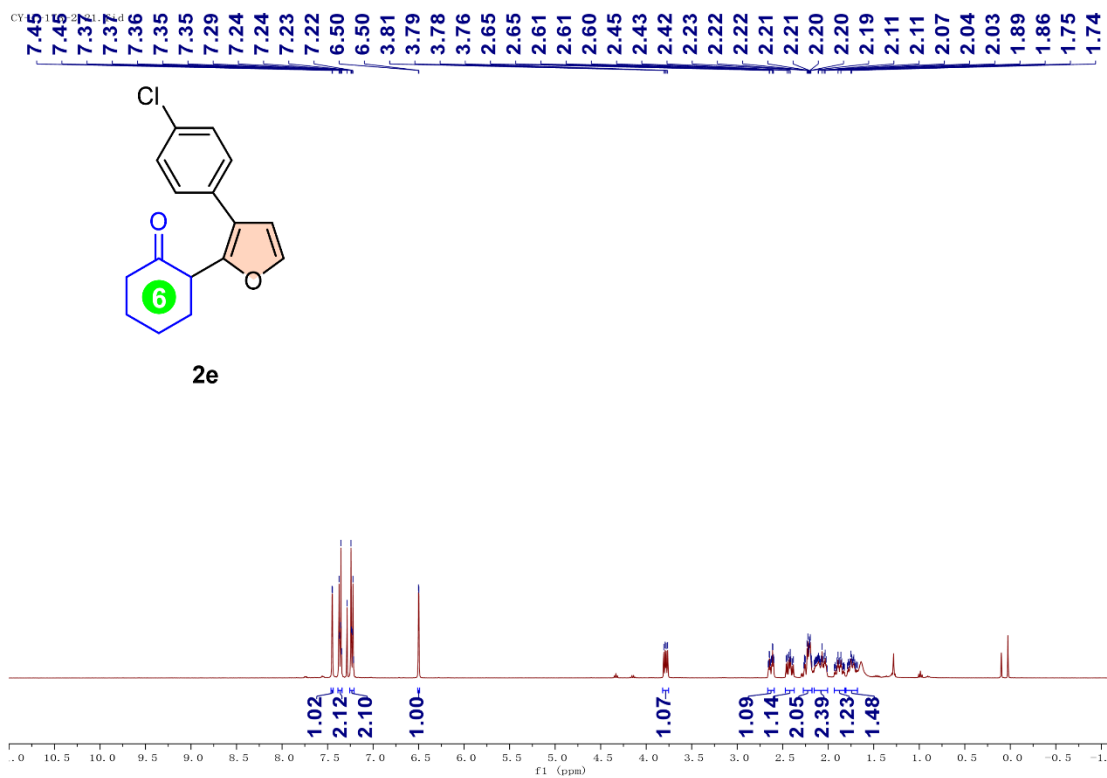


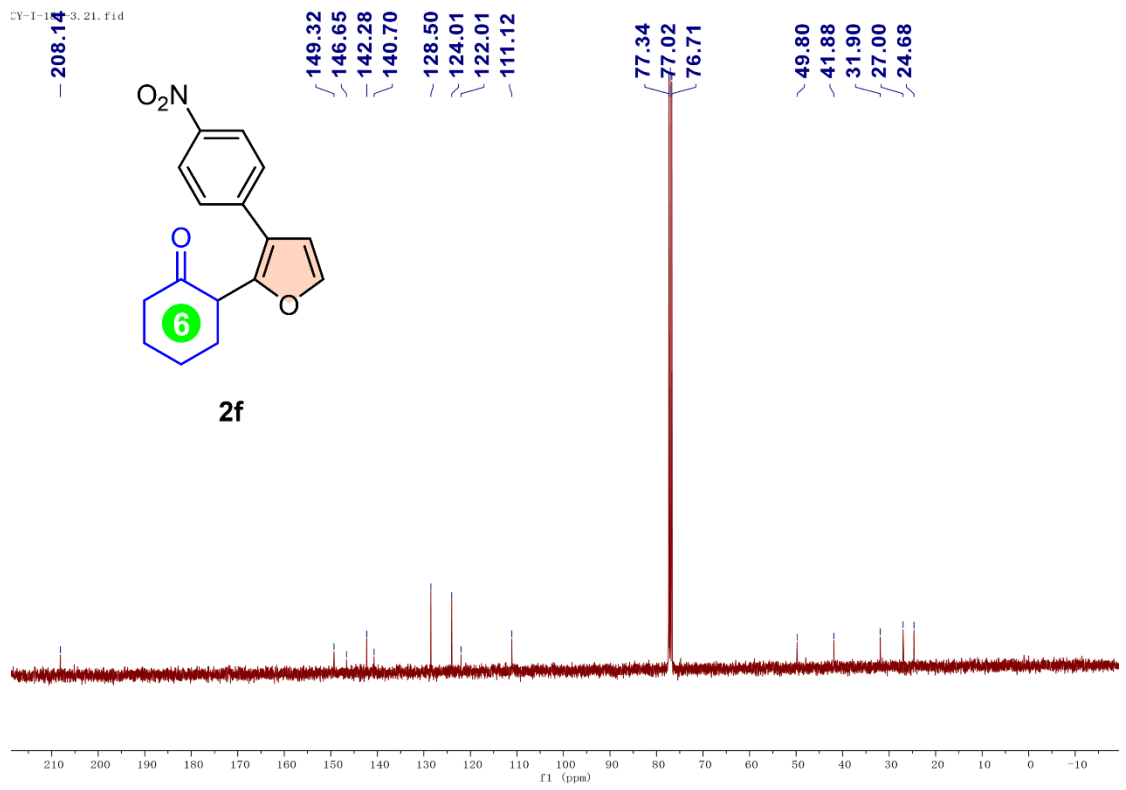
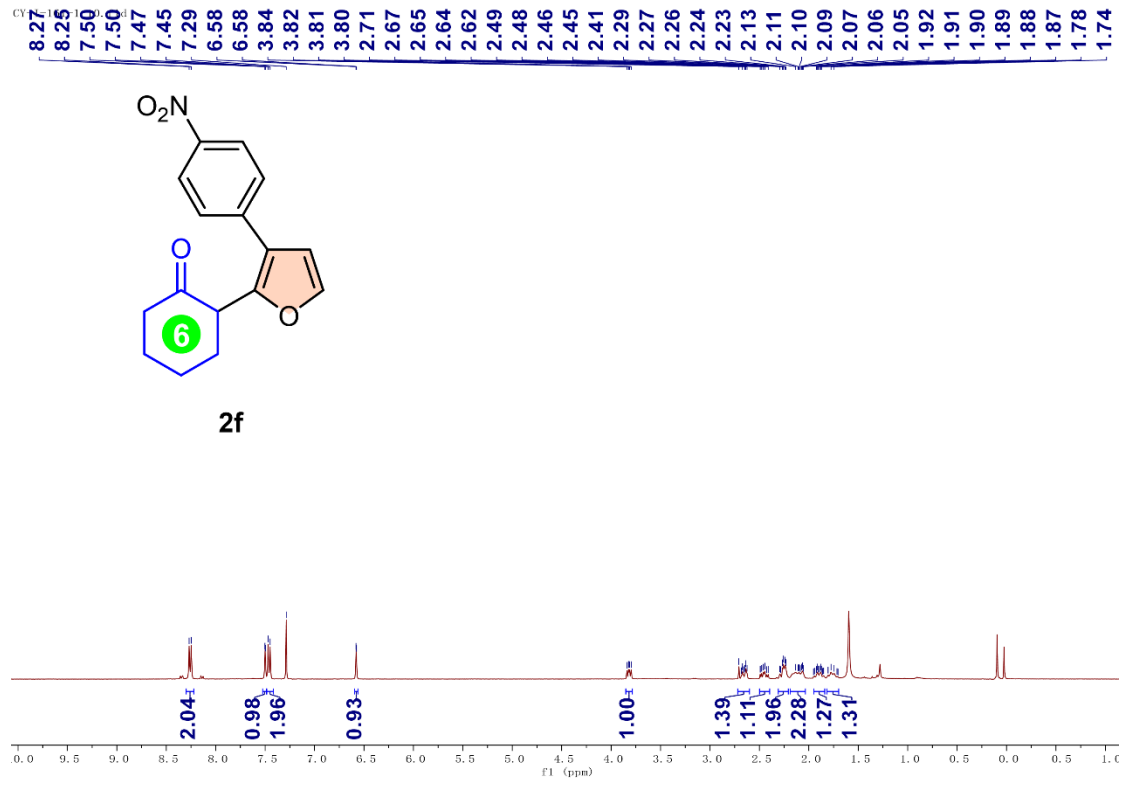
CY-11-66-2.11.fid  
F19CPD

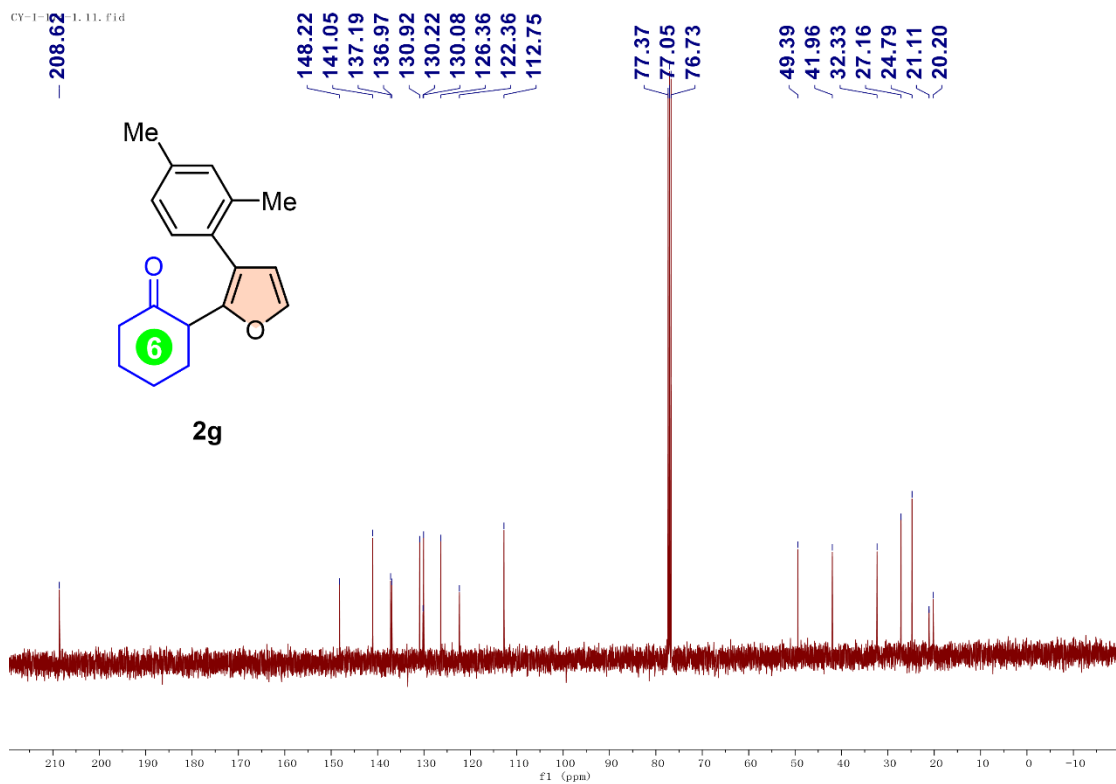
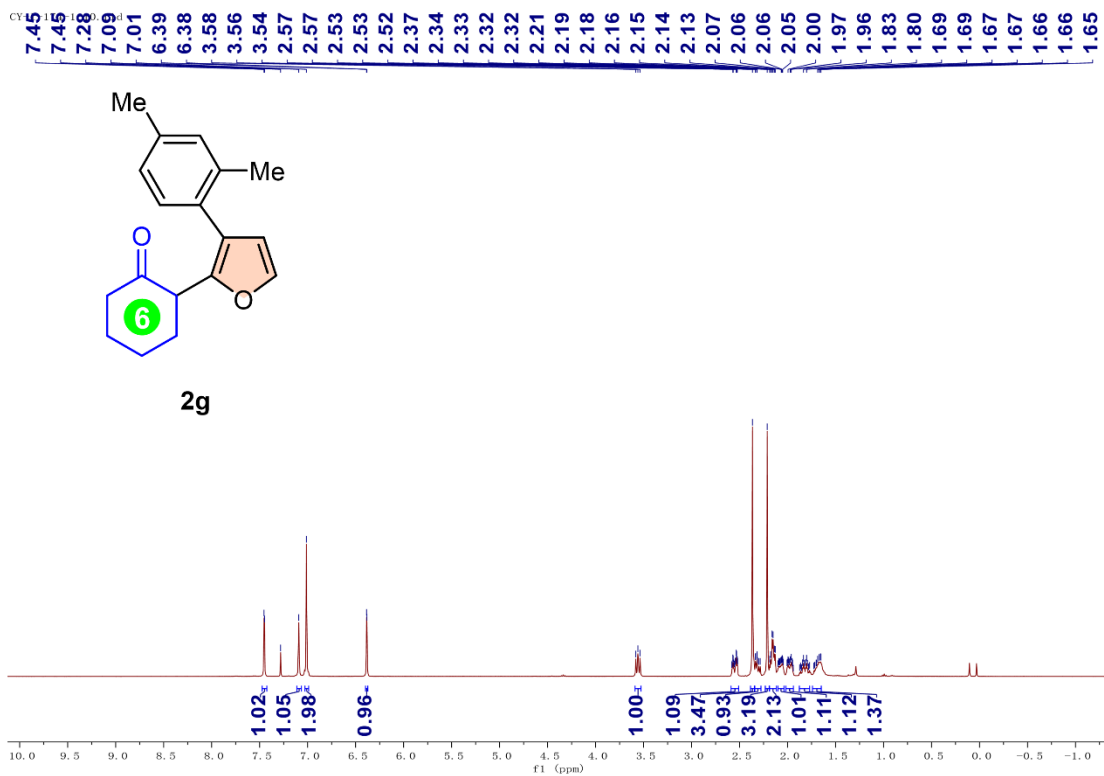


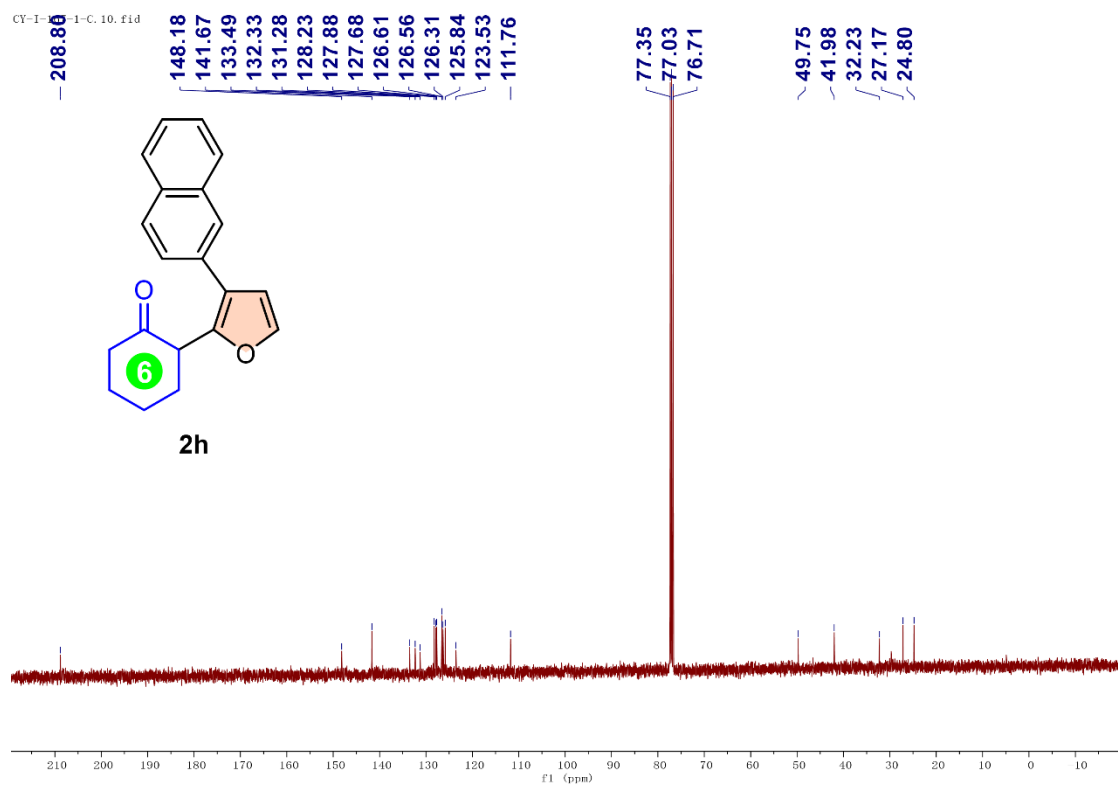
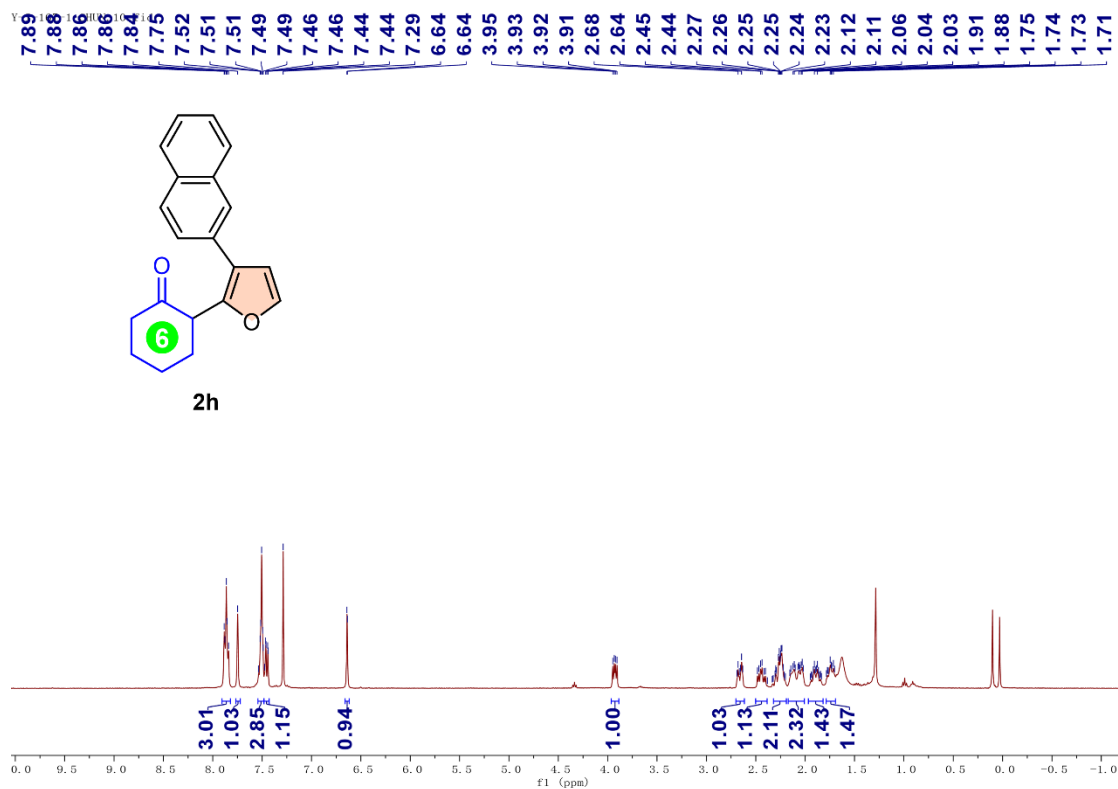
**2d**



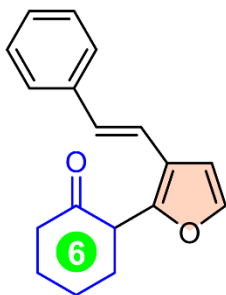




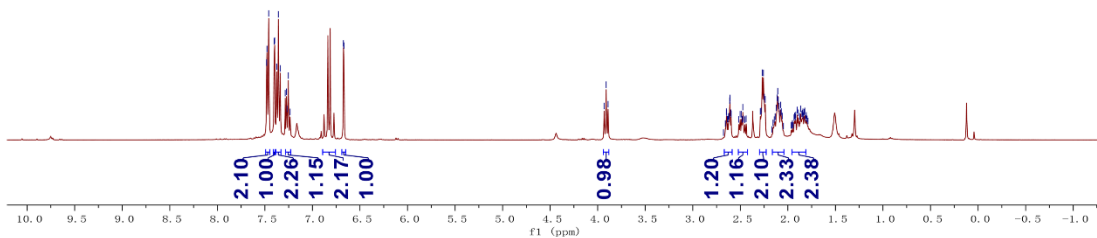




7.48  
7.48  
7.46  
7.40  
7.40  
7.38  
7.36  
7.34  
7.29  
7.27  
7.27  
7.25  
7.24  
6.67  
6.67  
3.93  
3.91  
3.89  
2.65  
2.61  
2.61  
2.60  
2.47  
2.29  
2.28  
2.27  
2.26  
2.25  
2.24  
2.12  
2.11  
2.11  
2.10  
2.09  
2.08  
2.08  
2.07  
1.90  
1.89  
1.87  
1.84  
1.83  
1.82



2i



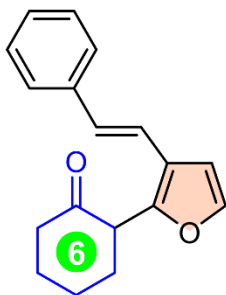
CY-1-11.11.fid

207.91

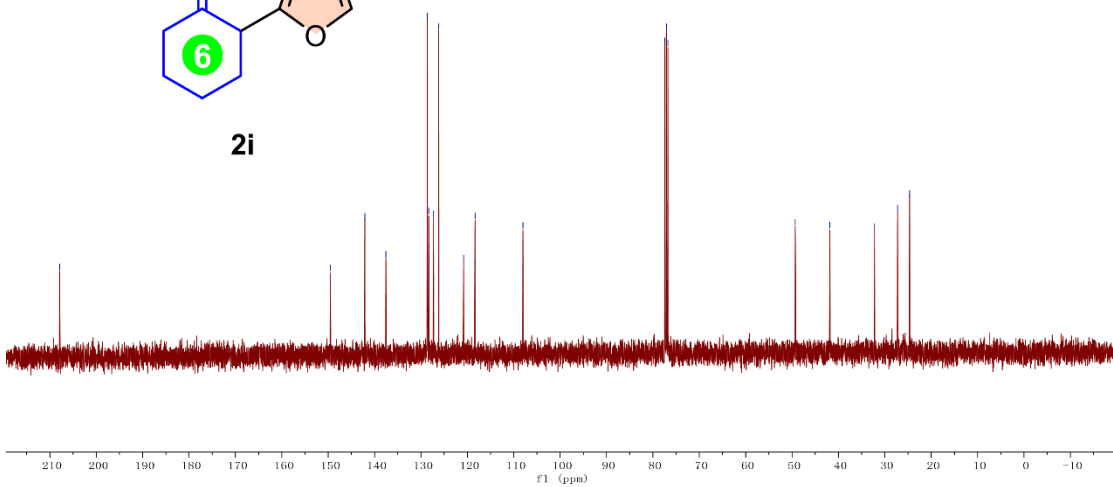
149.50  
142.10  
137.57  
128.62  
128.33  
127.28  
126.17  
120.81  
118.35  
108.02

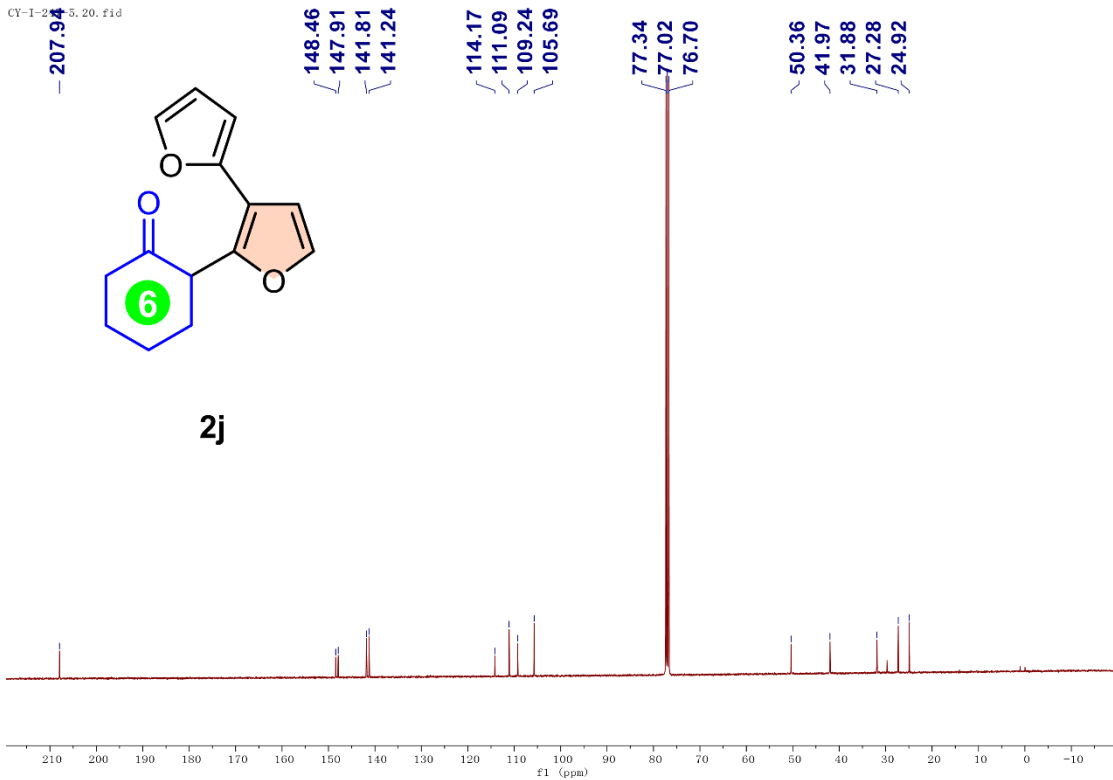
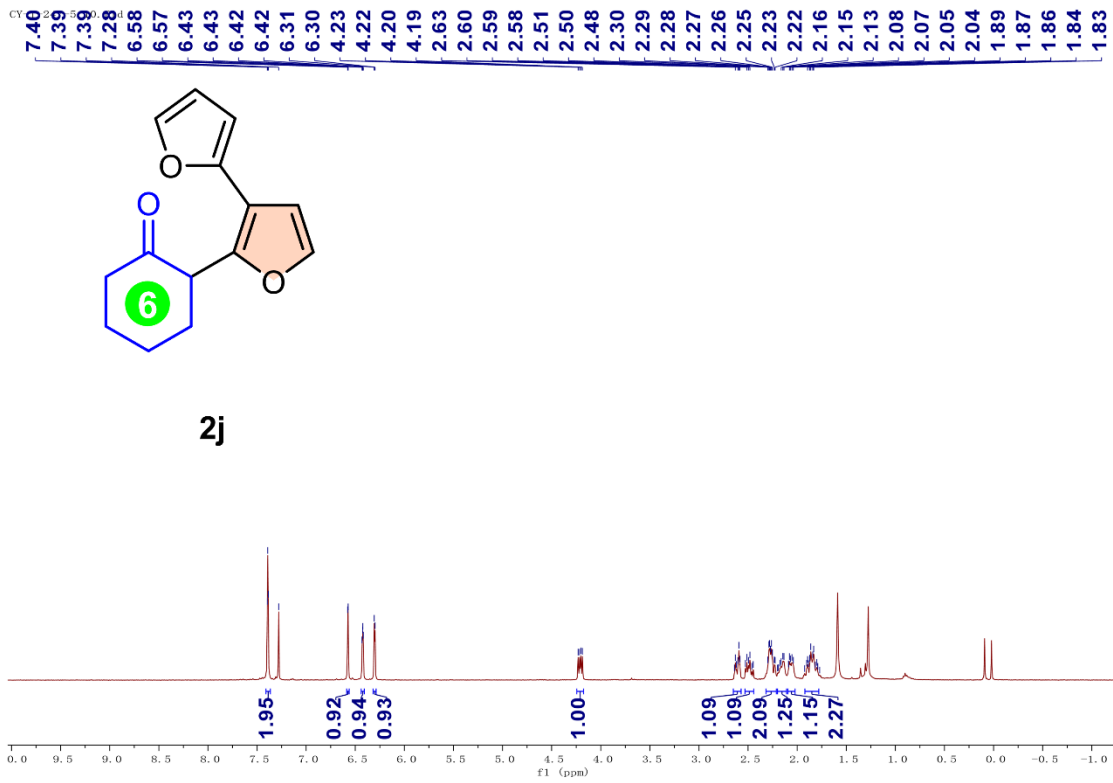
77.41  
77.09  
76.77

49.31  
41.84  
32.20  
27.27  
24.66

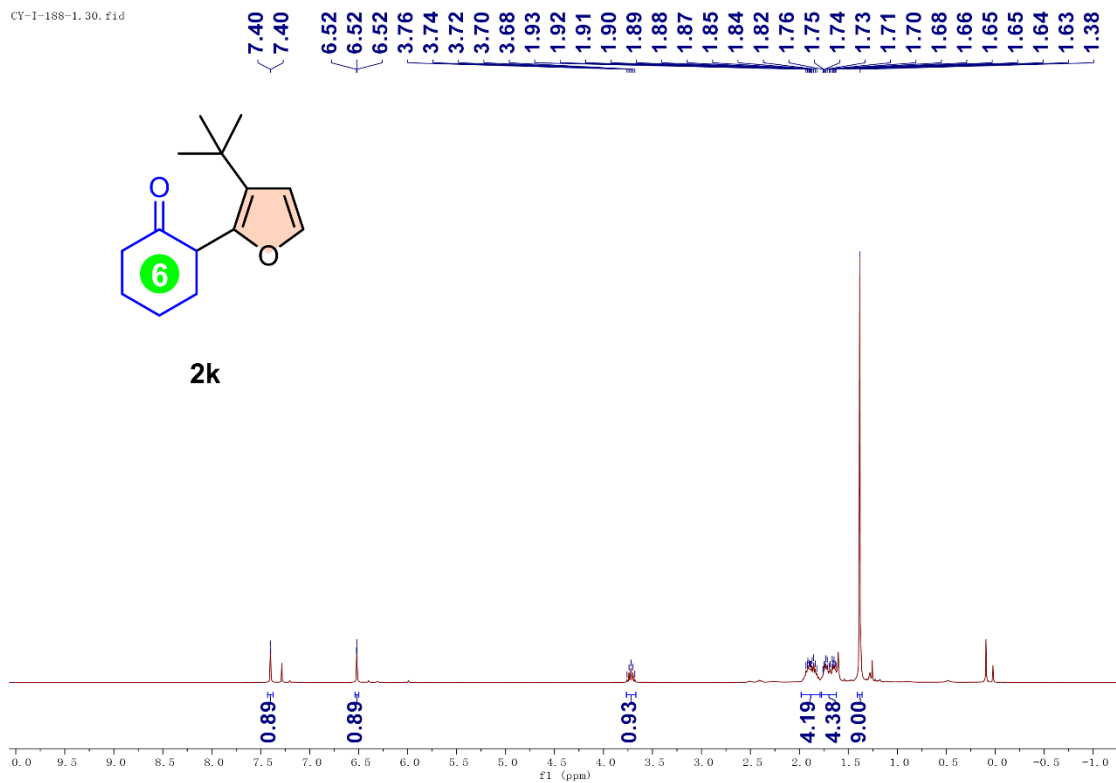


2i

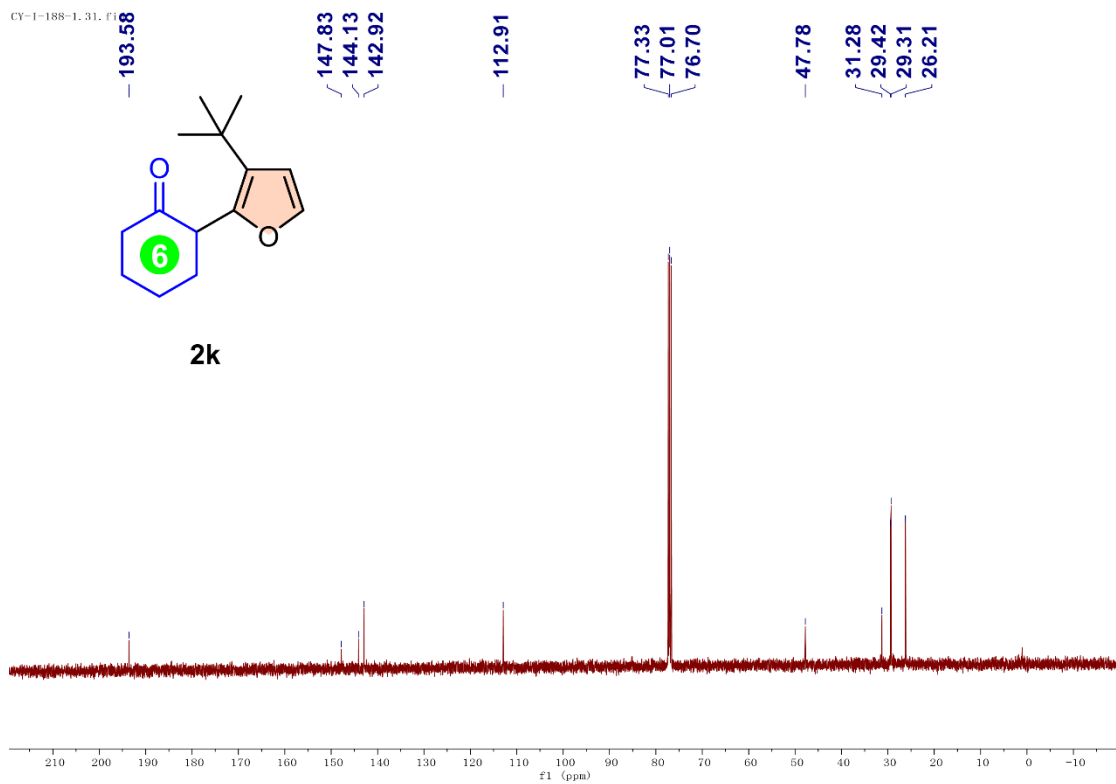




CY-I-188-1.30.fid

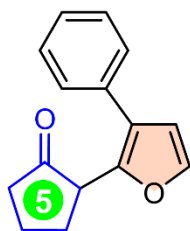


CY-I-188-1.31.fid

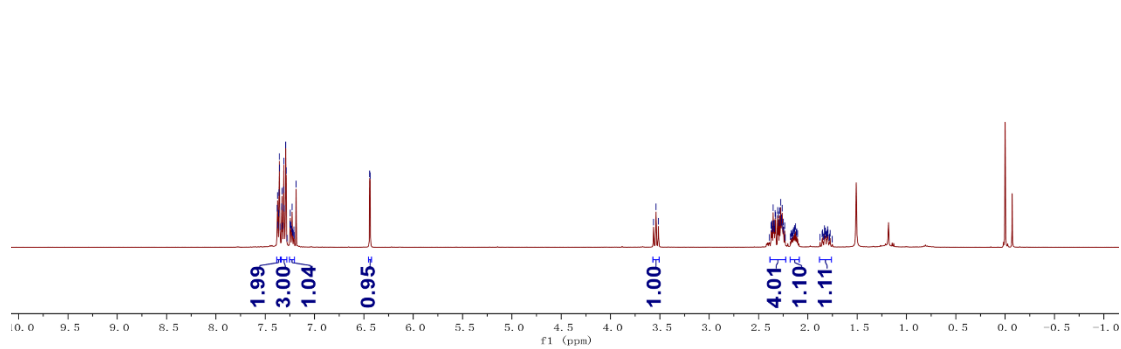




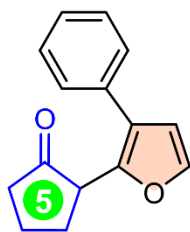
7.38  
7.38  
7.37  
7.36  
7.36  
7.35  
7.33  
7.33  
7.32  
7.31  
7.31  
7.29  
7.29  
7.25  
7.24  
7.23  
7.19  
6.44  
6.44  
3.56  
3.54  
3.51  
2.37  
2.36  
2.35  
2.35  
2.34  
2.33  
2.33  
2.31  
2.30  
2.29  
2.29  
2.28  
2.27  
2.26  
2.25  
2.25



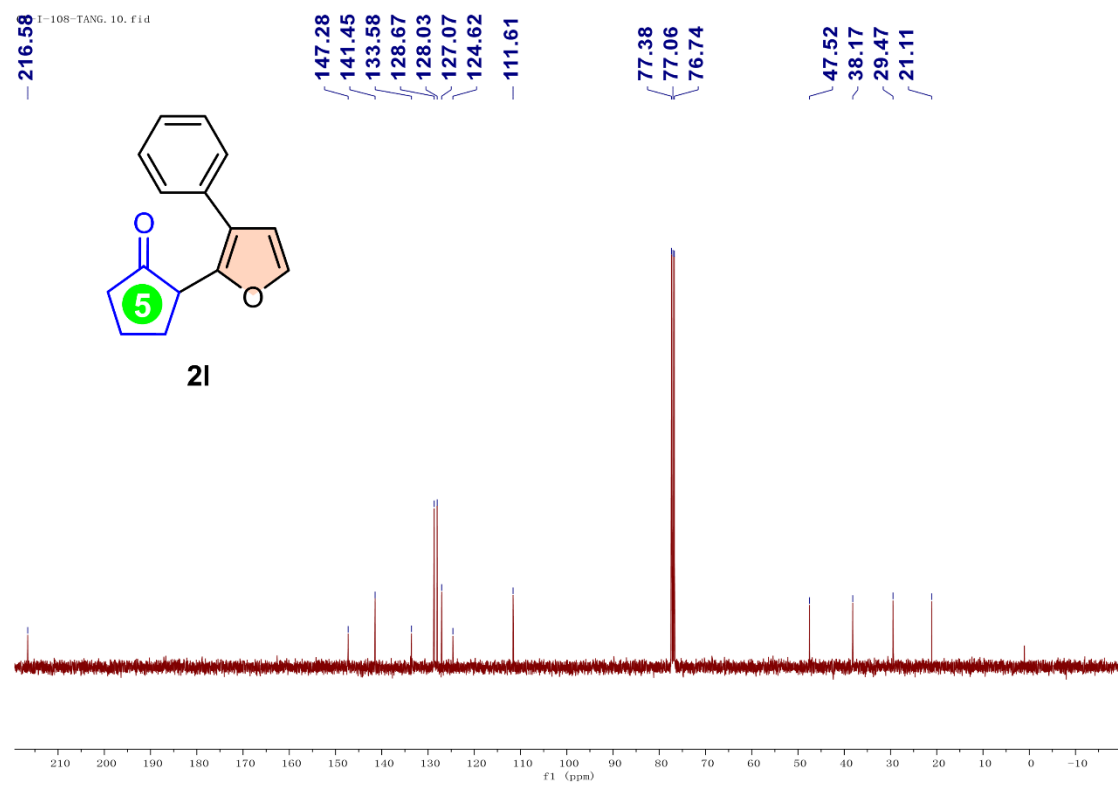
2I



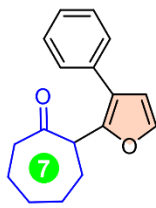
216.58  
1-108-TANG\_10.fid



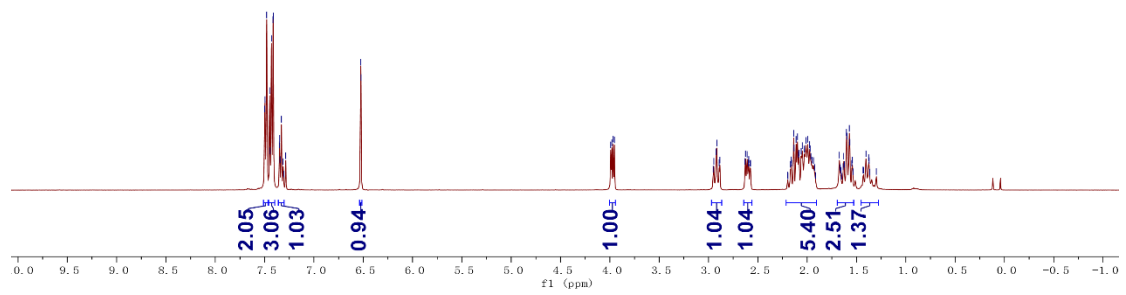
2I



7.50  
 7.50  
 7.48  
 7.45  
 7.44  
 7.43  
 7.41  
 7.41  
 7.35  
 7.35  
 7.33  
 7.29  
 6.53  
 6.52  
 3.99  
 3.98  
 3.97  
 3.95  
 2.92  
 2.92  
 2.62  
 2.61  
 2.14  
 2.13  
 2.11  
 2.10  
 2.09  
 2.08  
 2.06  
 2.05  
 2.03  
 2.01  
 1.99  
 1.98  
 1.97  
 1.96  
 1.67  
 1.63  
 1.60  
 1.60  
 1.57  
 1.57  
 1.40

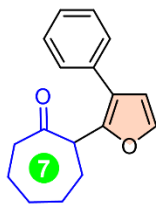


2m

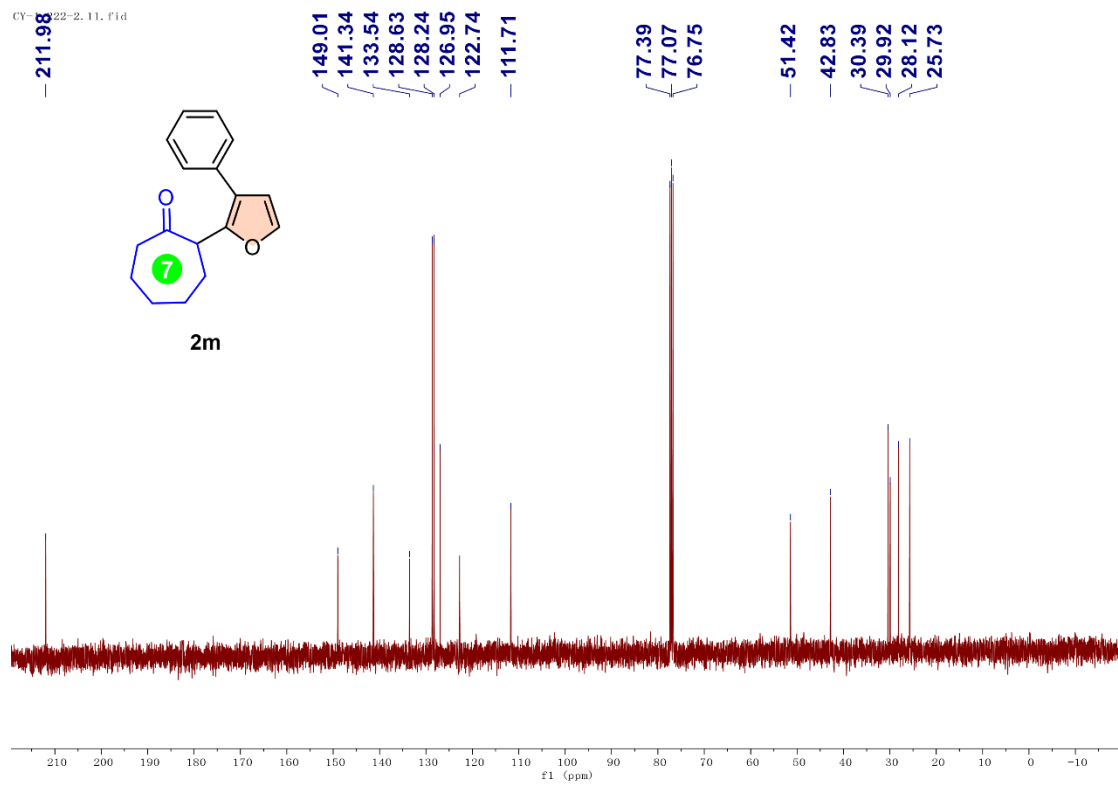


22-2.11.fid

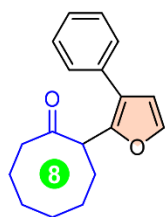
211.98



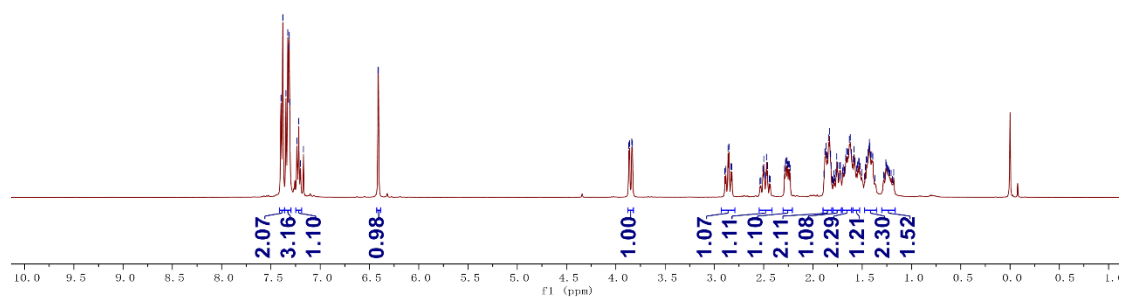
2m



7.40  
 7.38  
 7.35  
 7.33  
 7.32  
 7.31  
 7.31  
 7.24  
 7.22  
 7.17  
 6.41  
 6.41  
 3.87  
 3.86  
 3.84  
 3.83  
 2.86  
 2.85  
 2.50  
 2.47  
 1.88  
 1.87  
 1.86  
 1.85  
 1.84  
 1.83  
 1.82  
 1.76  
 1.67  
 1.66  
 1.64  
 1.63  
 1.62  
 1.61  
 1.59  
 1.58  
 1.44  
 1.43  
 1.43  
 1.42  
 1.42  
 1.40  
 1.39

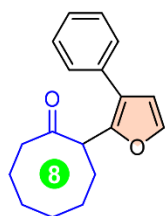


2n

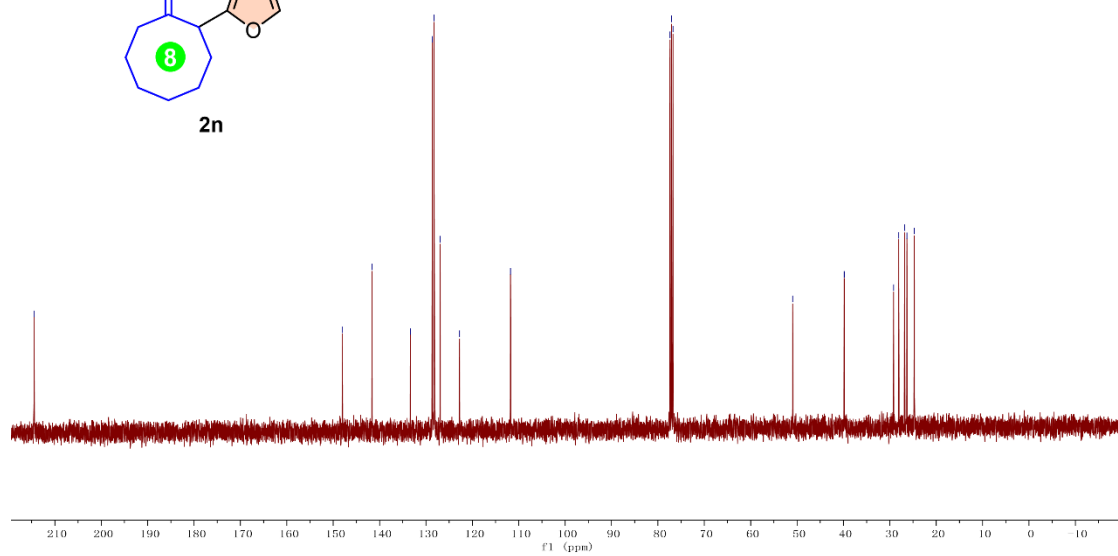


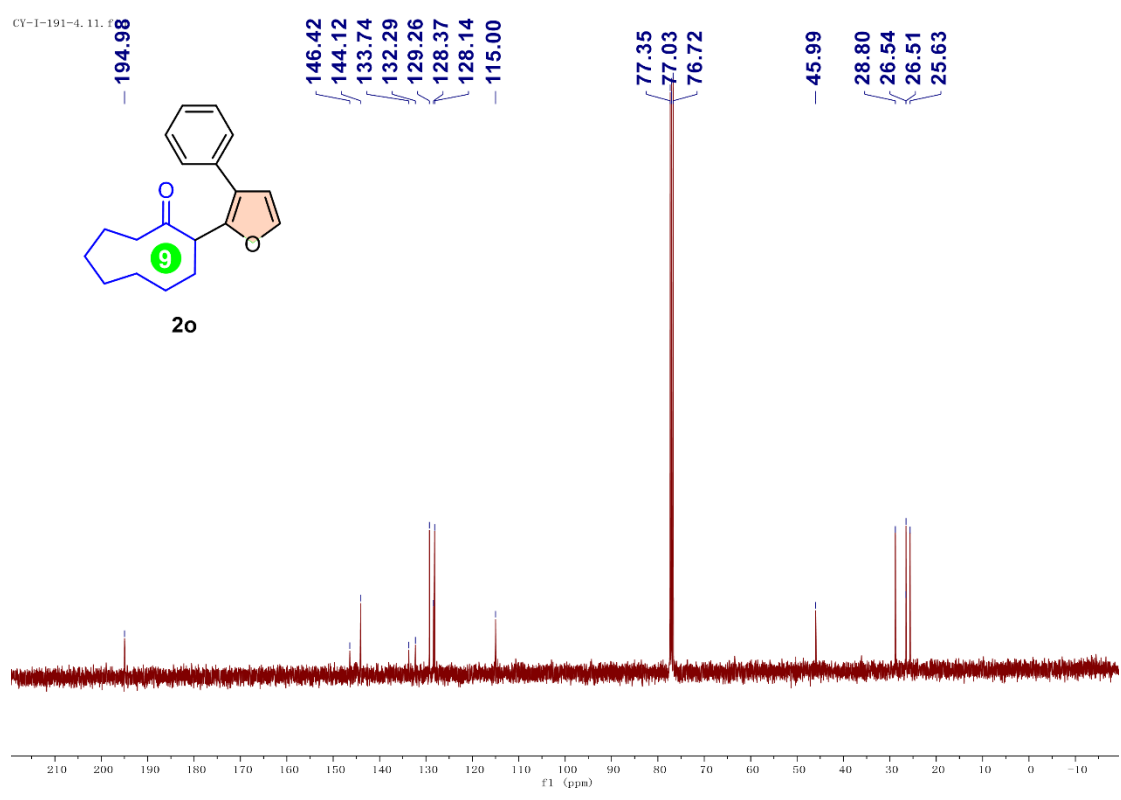
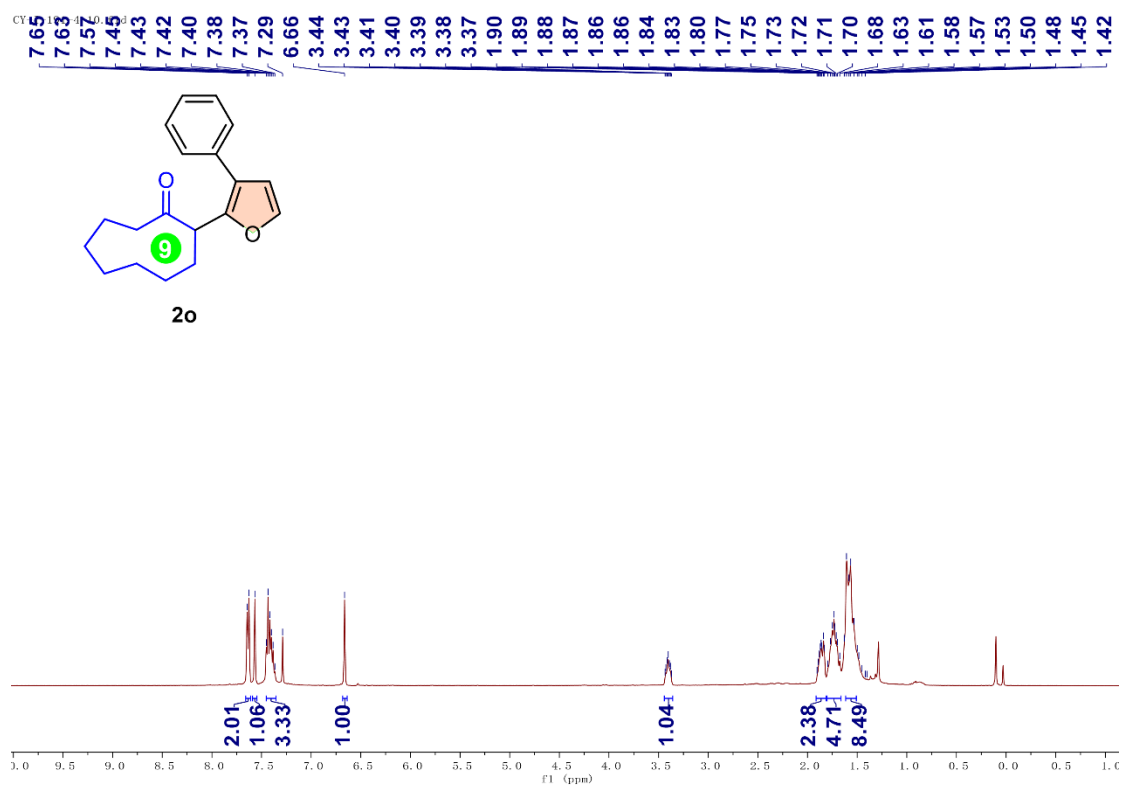
CW-228-1.11.fid

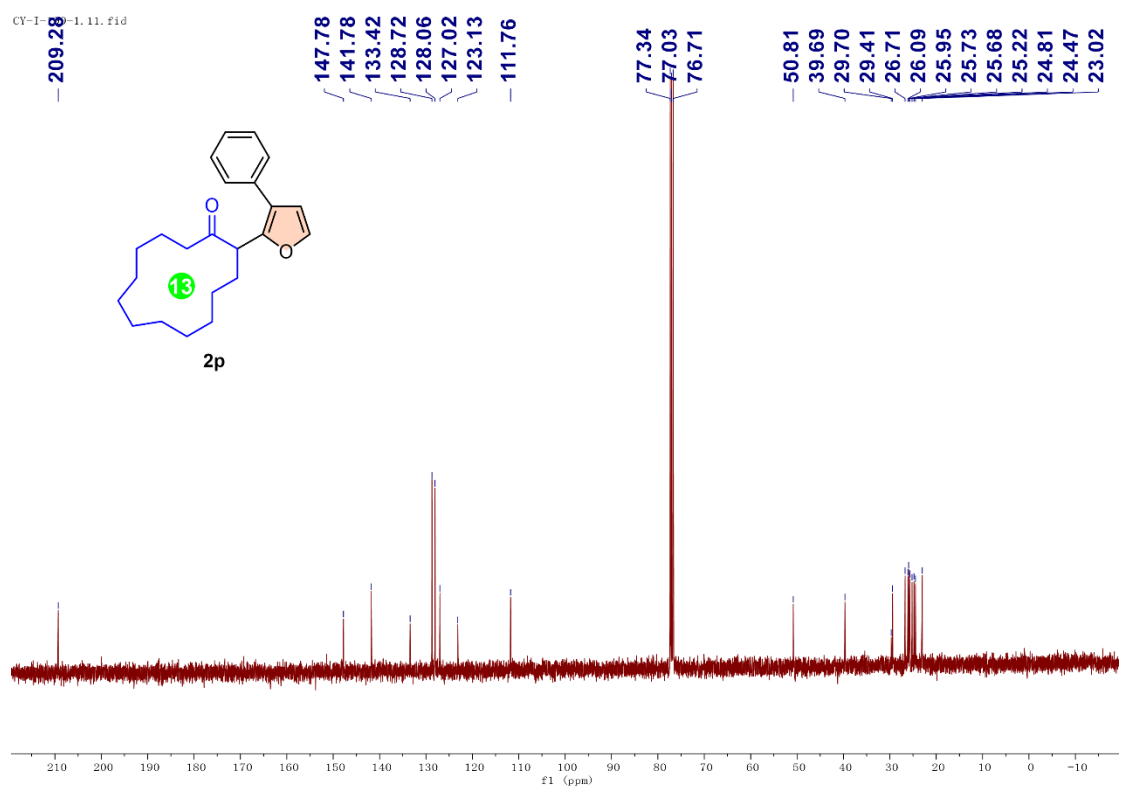
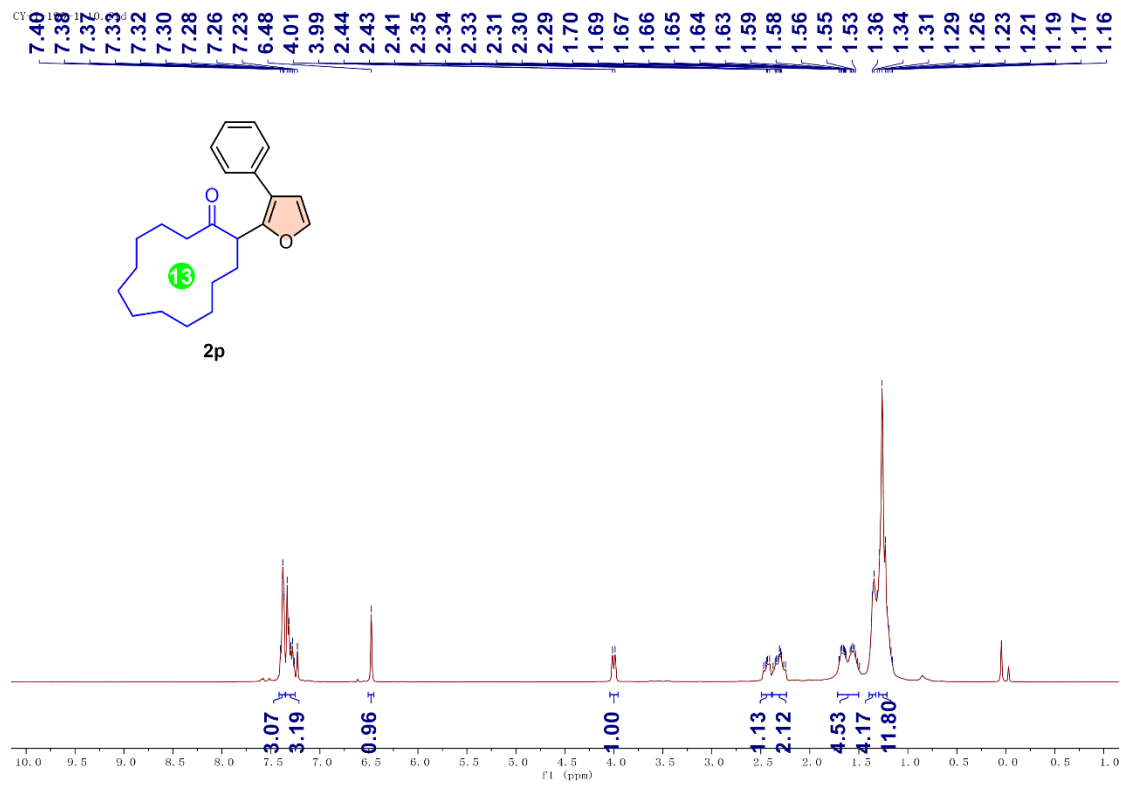
214.51  
 147.99  
 141.63  
 133.38  
 128.65  
 128.29  
 126.96  
 122.77  
 111.78  
 77.39  
 77.07  
 76.75  
 50.94  
 39.84  
 29.19  
 28.08  
 26.83  
 26.32  
 24.72

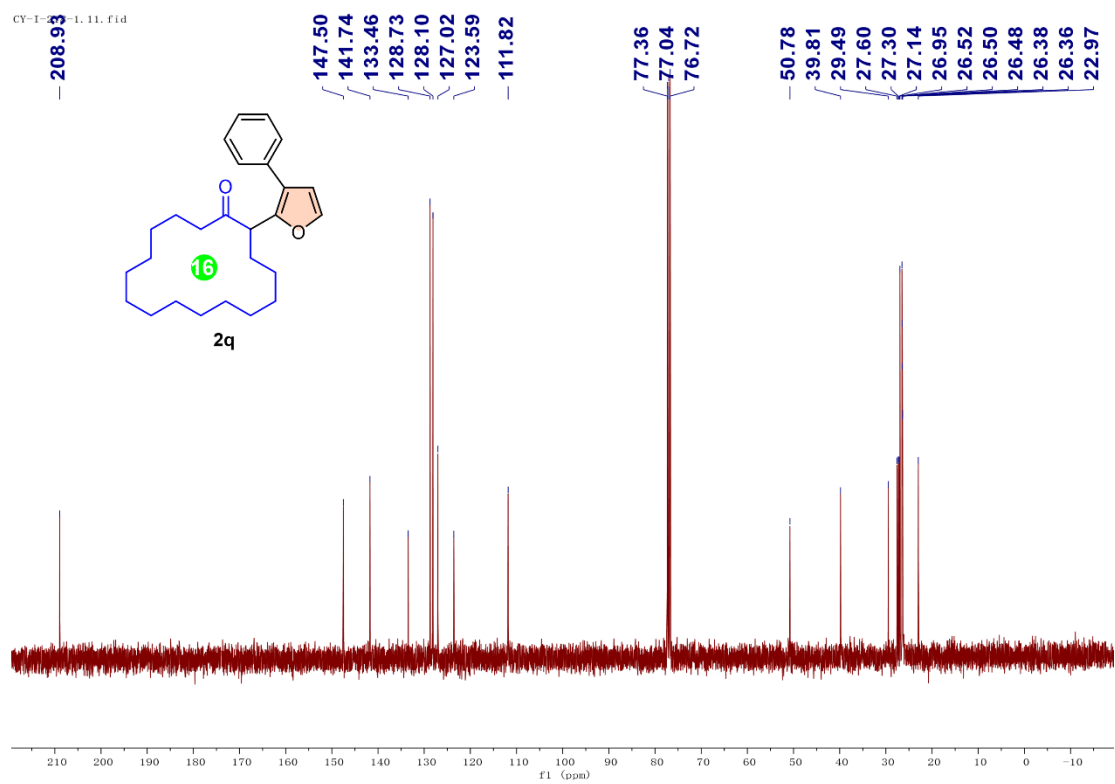
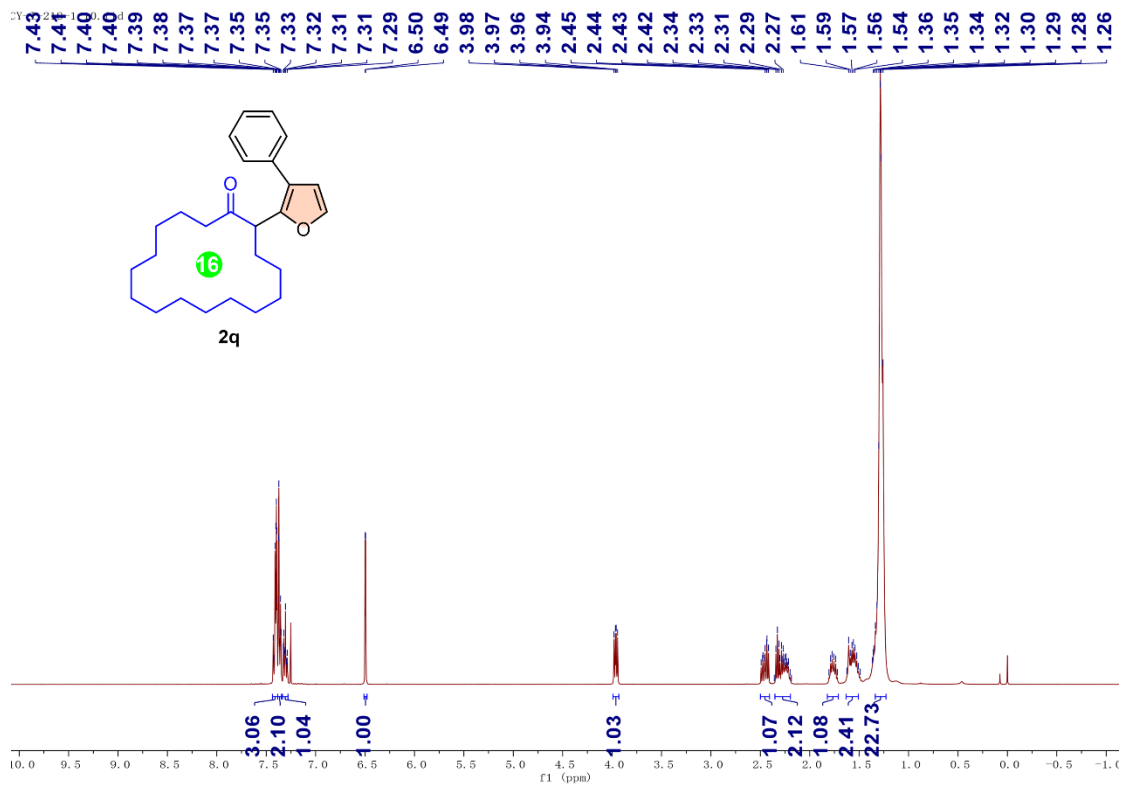


2n

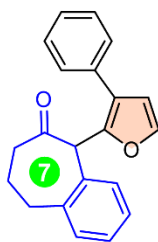




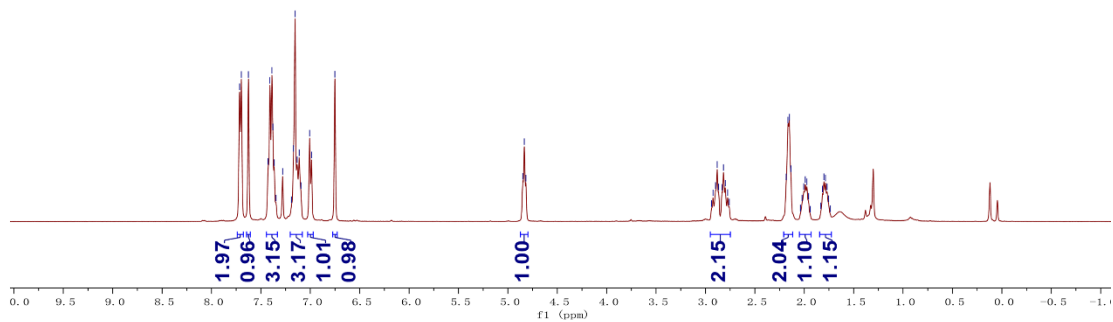




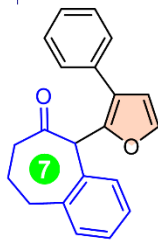
7.72  
7.76  
7.63  
7.43  
7.41  
7.39  
7.38  
7.36  
7.35  
7.28  
7.17  
7.15  
7.13  
7.11  
7.09  
7.01  
6.99  
6.75  
4.85  
4.83  
4.82  
2.92  
2.90  
2.88  
2.87  
2.83  
2.82  
2.80  
2.78  
2.18  
2.17  
2.15  
2.14  
2.02  
2.01  
1.99  
1.97  
1.96  
1.82  
1.80  
1.79  
1.77  
1.75



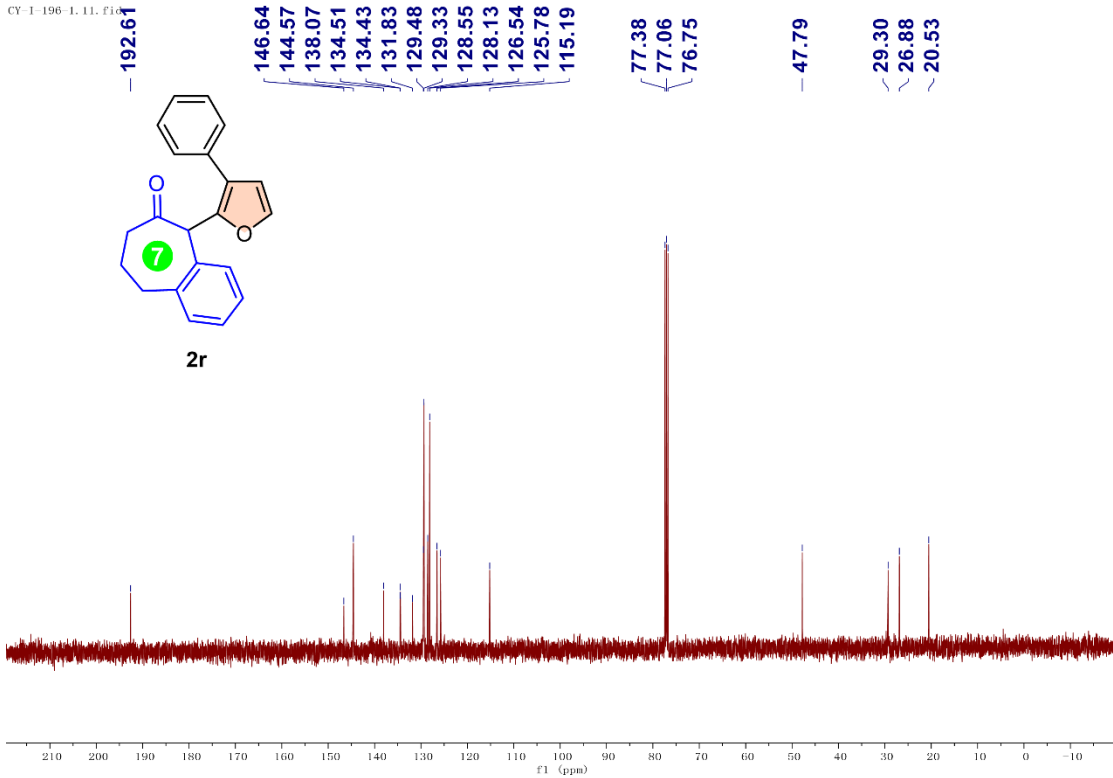
2r



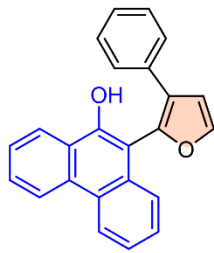
CY-1-196-1.11.f10



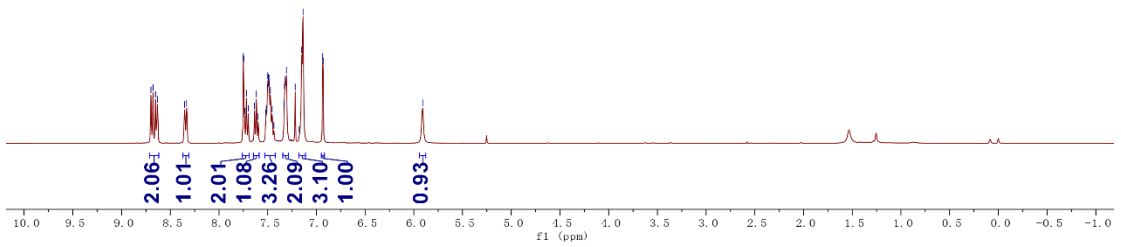
2r



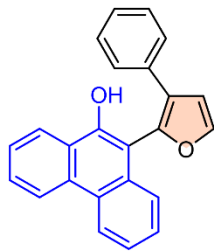
CY-1-226  
 8.70  
 8.66  
 8.65  
 8.63  
 8.35  
 8.33  
 7.75  
 7.75  
 7.74  
 7.72  
 7.70  
 7.64  
 7.62  
 7.60  
 7.52  
 7.51  
 7.50  
 7.50  
 7.49  
 7.49  
 7.48  
 7.47  
 7.45  
 7.44  
 7.33  
 7.33  
 7.32  
 7.31  
 7.22  
 7.18  
 7.15  
 7.14  
 6.94  
 6.93  
 5.91



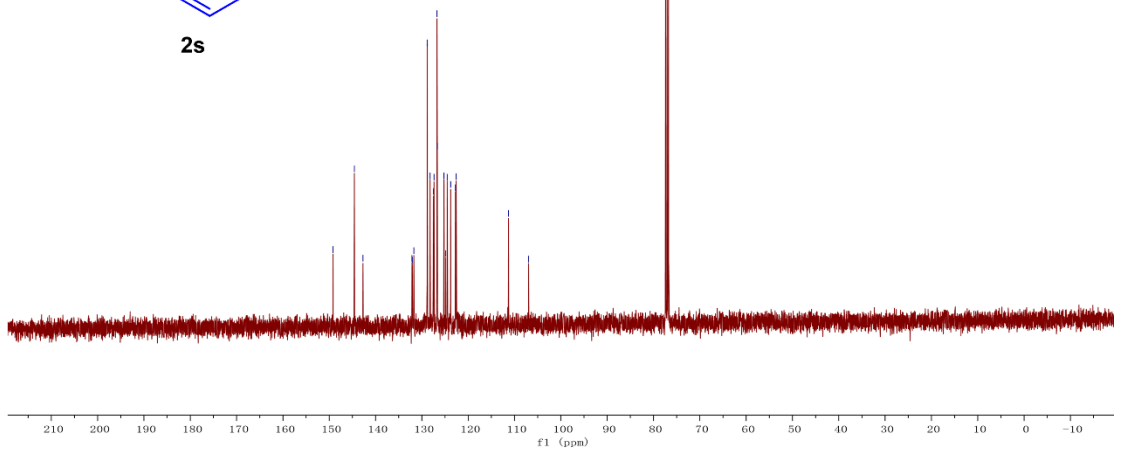
2s



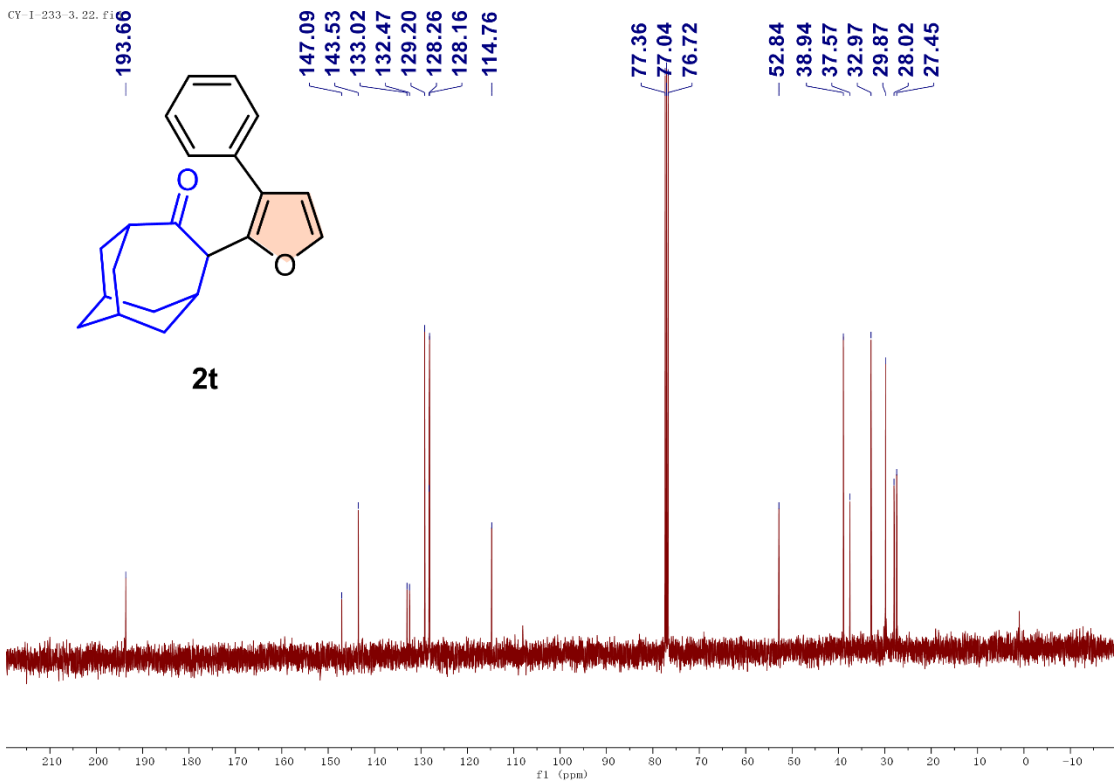
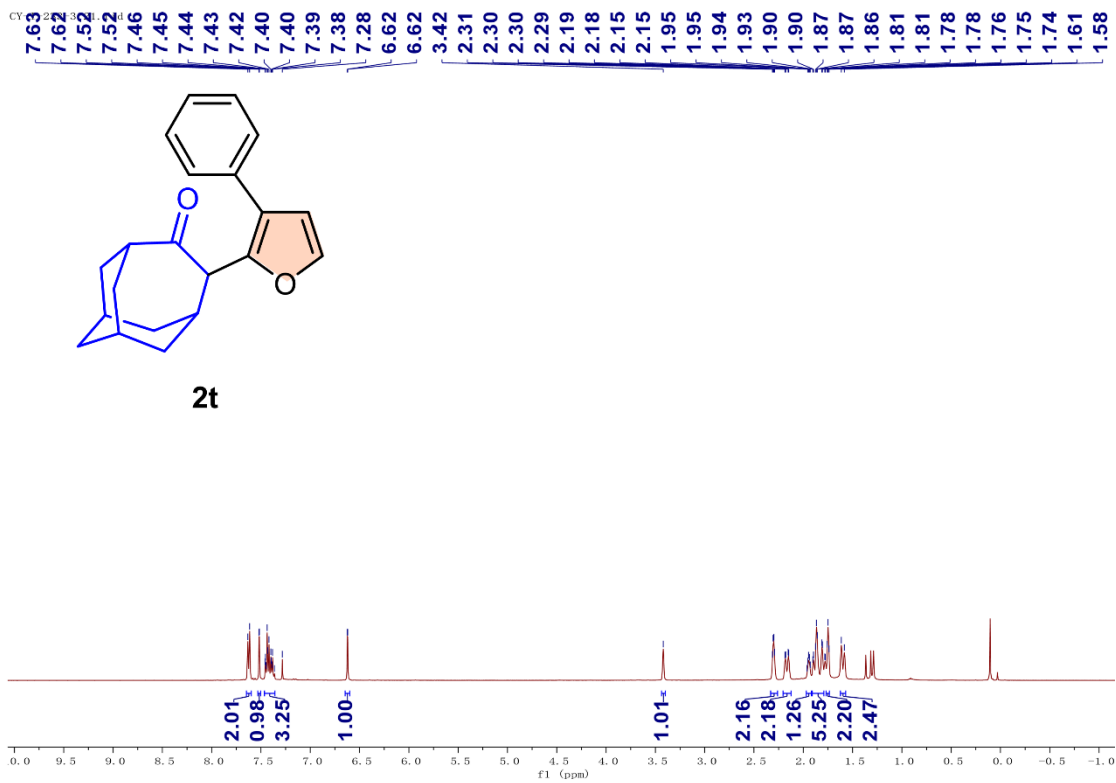
CY-1-226  
 149.18  
 144.57  
 142.72  
 132.15  
 132.07  
 131.74  
 128.86  
 128.22  
 127.50  
 127.38  
 126.73  
 126.66  
 125.22  
 124.84  
 124.53  
 123.79  
 122.74  
 122.61  
 111.30  
 106.98  
 77.39  
 77.07  
 76.75

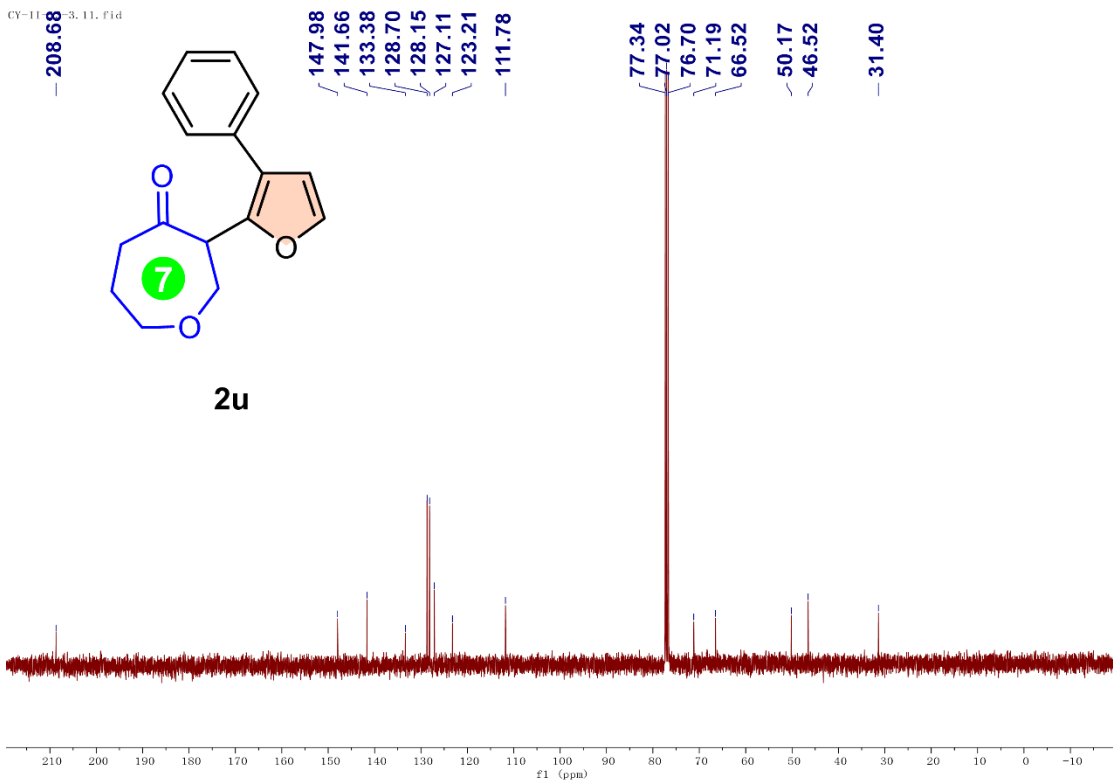
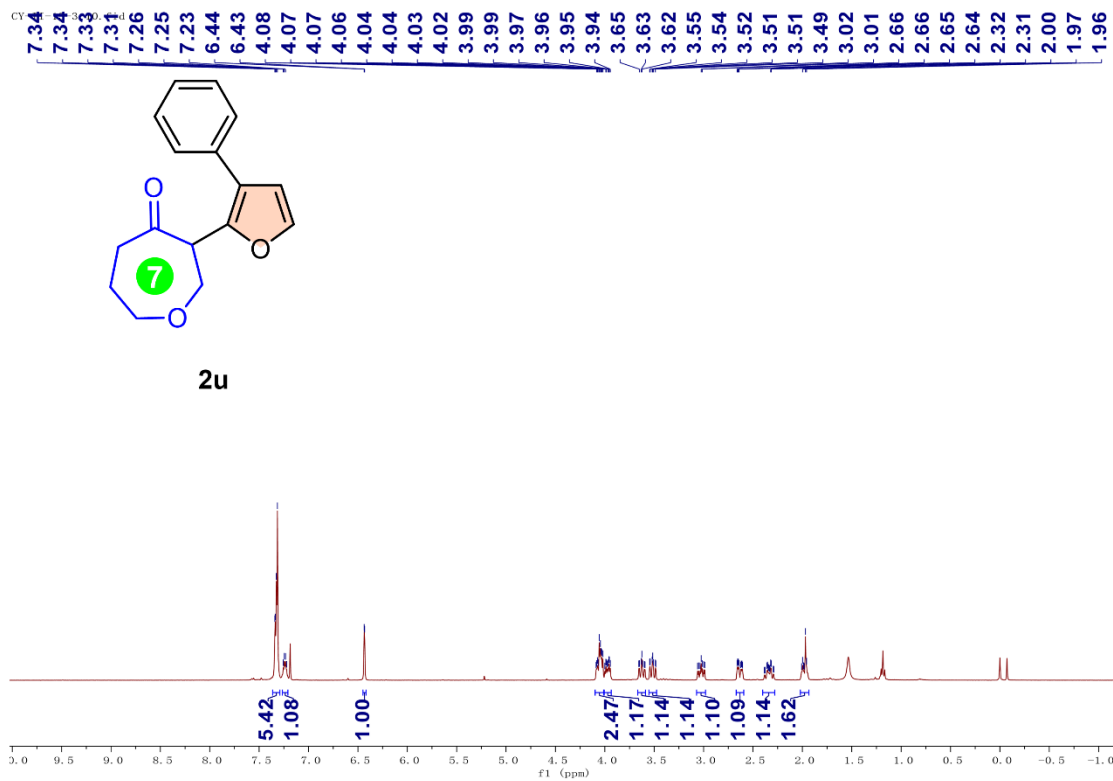


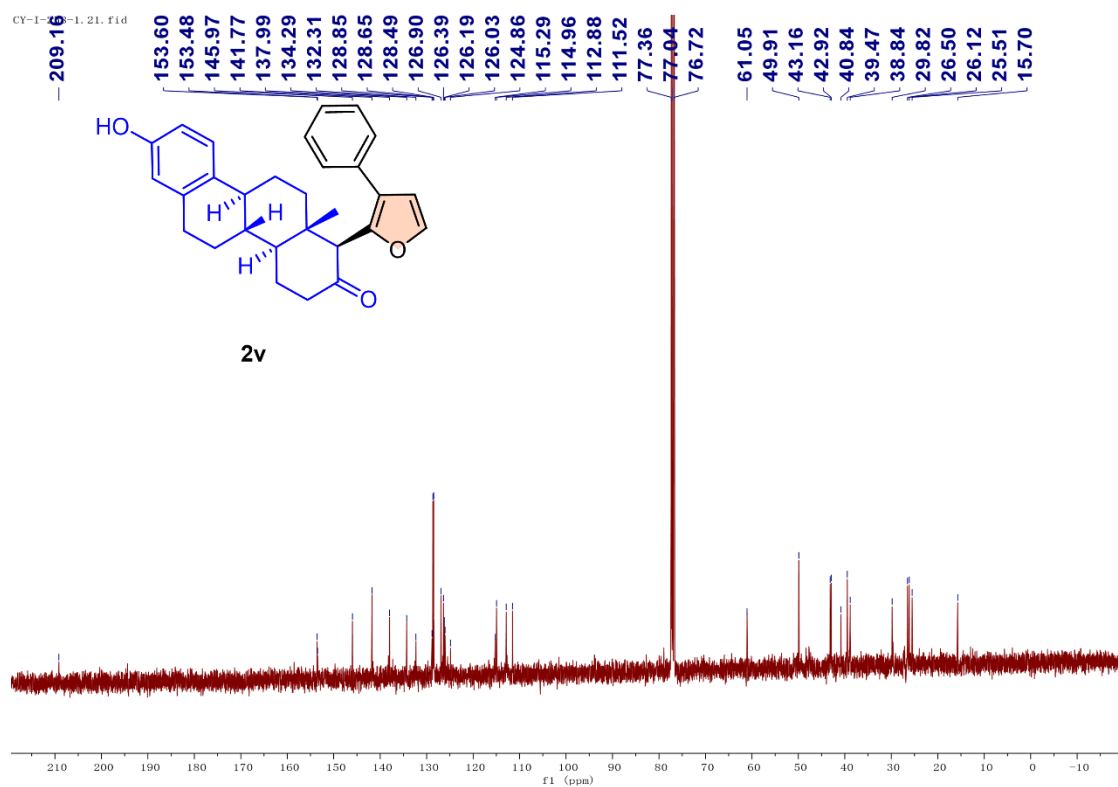
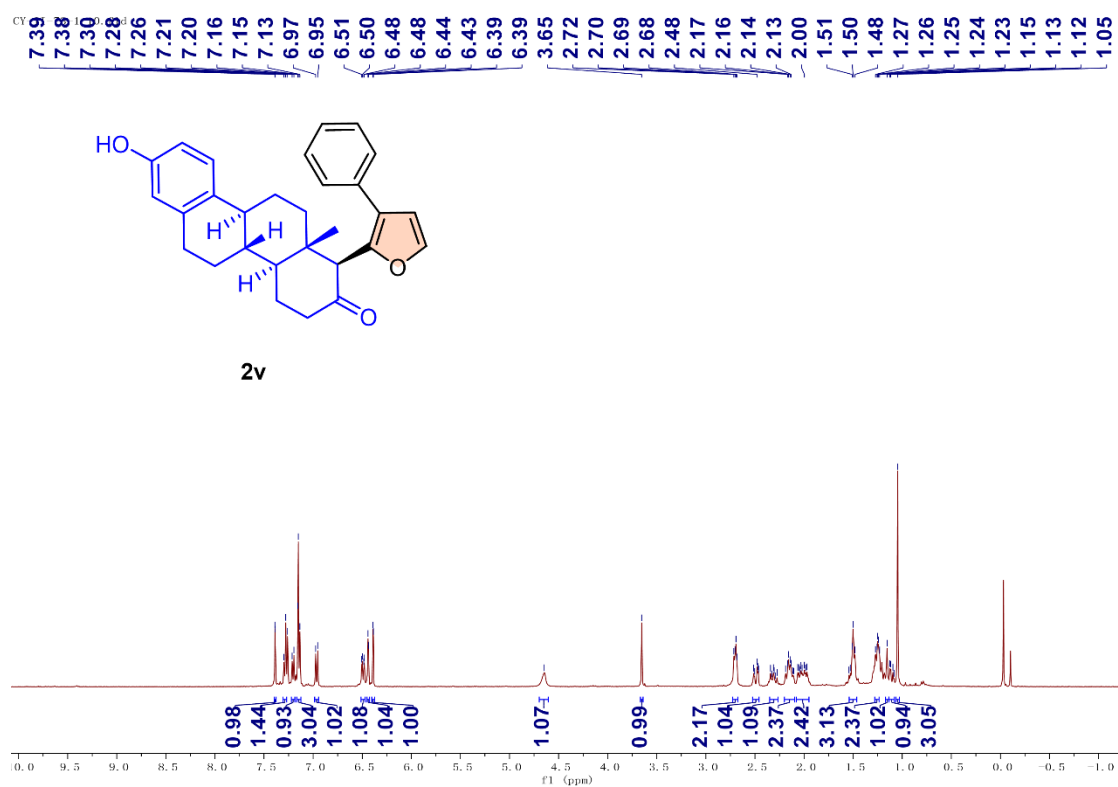
2s

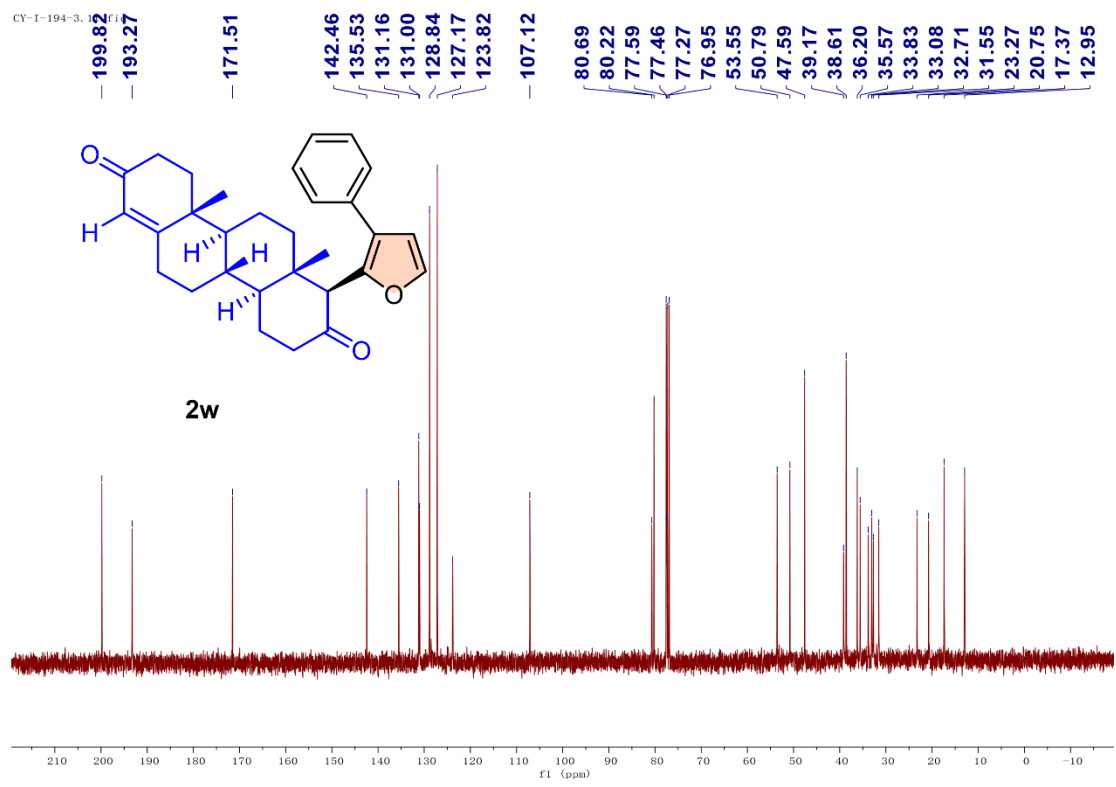
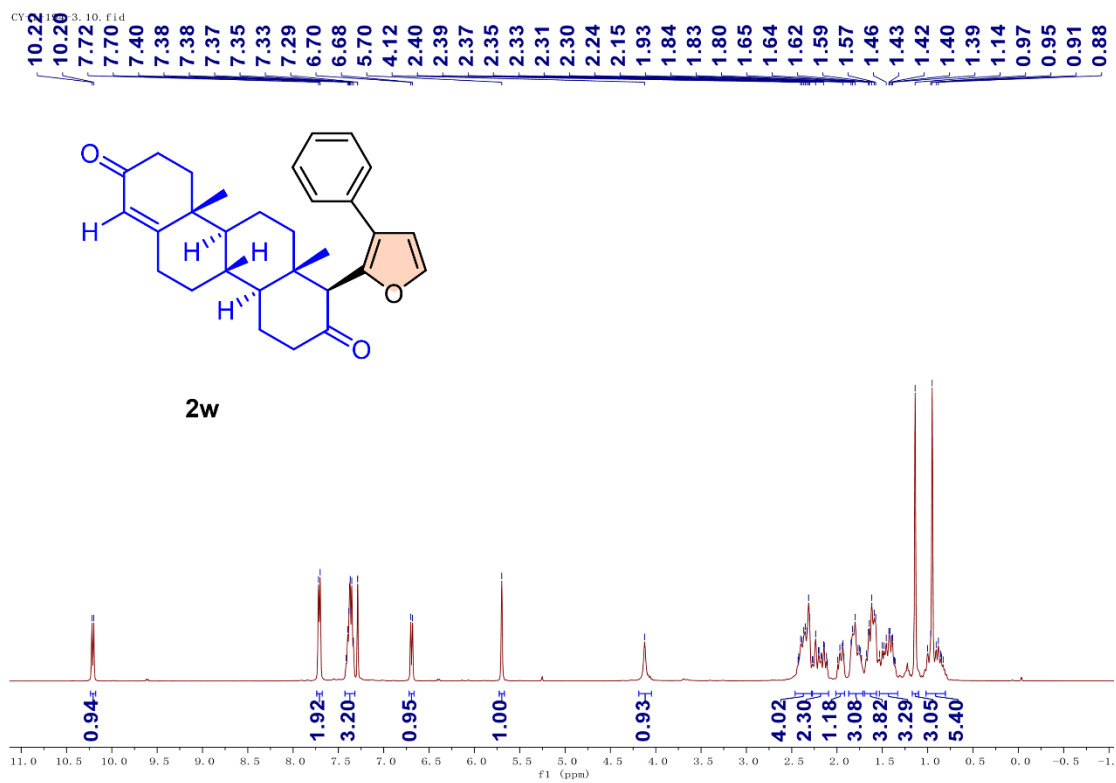


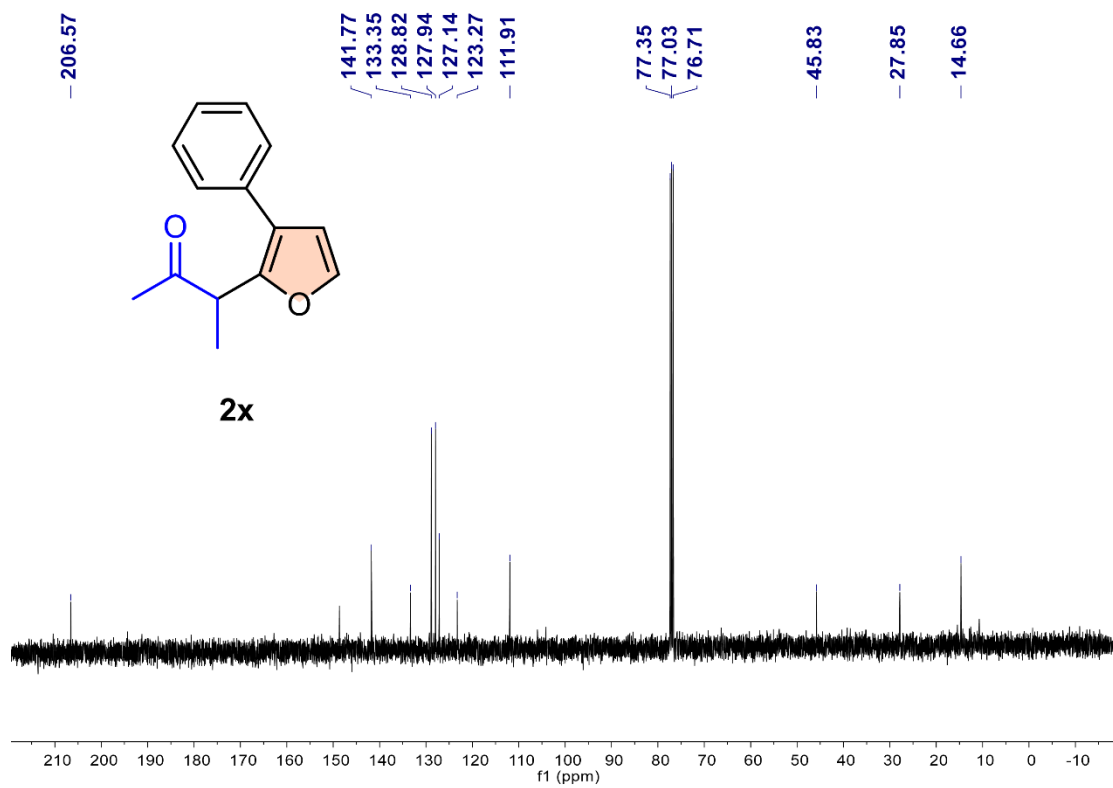
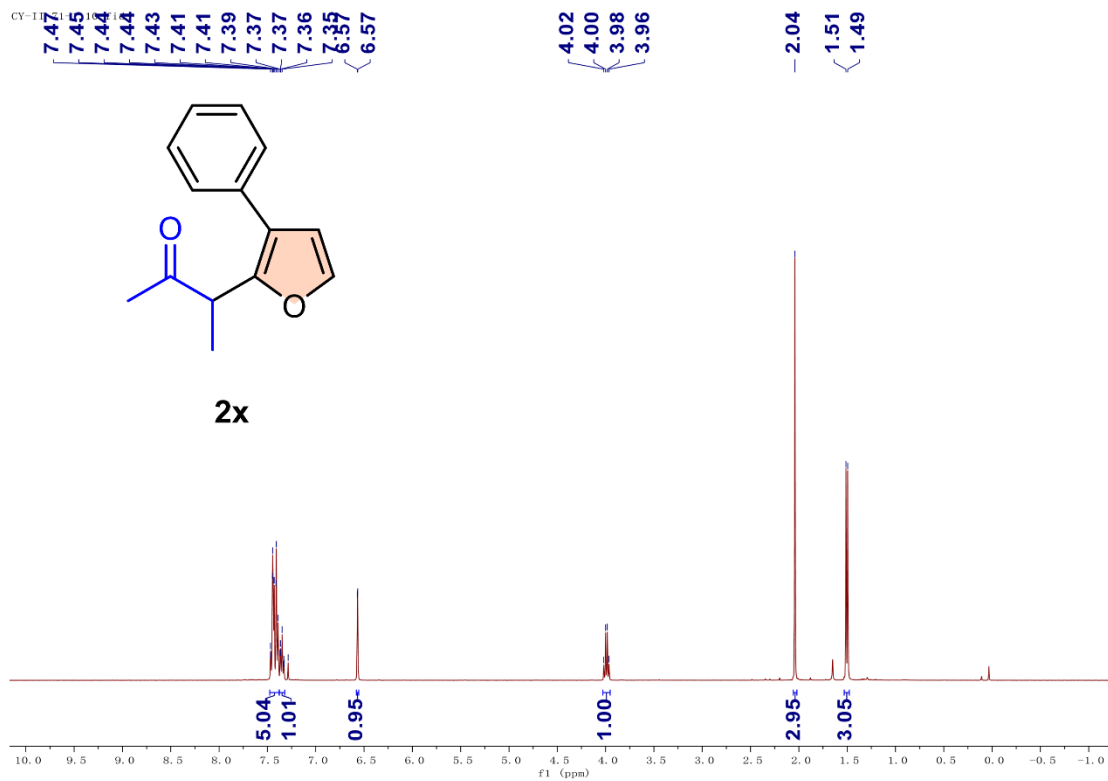


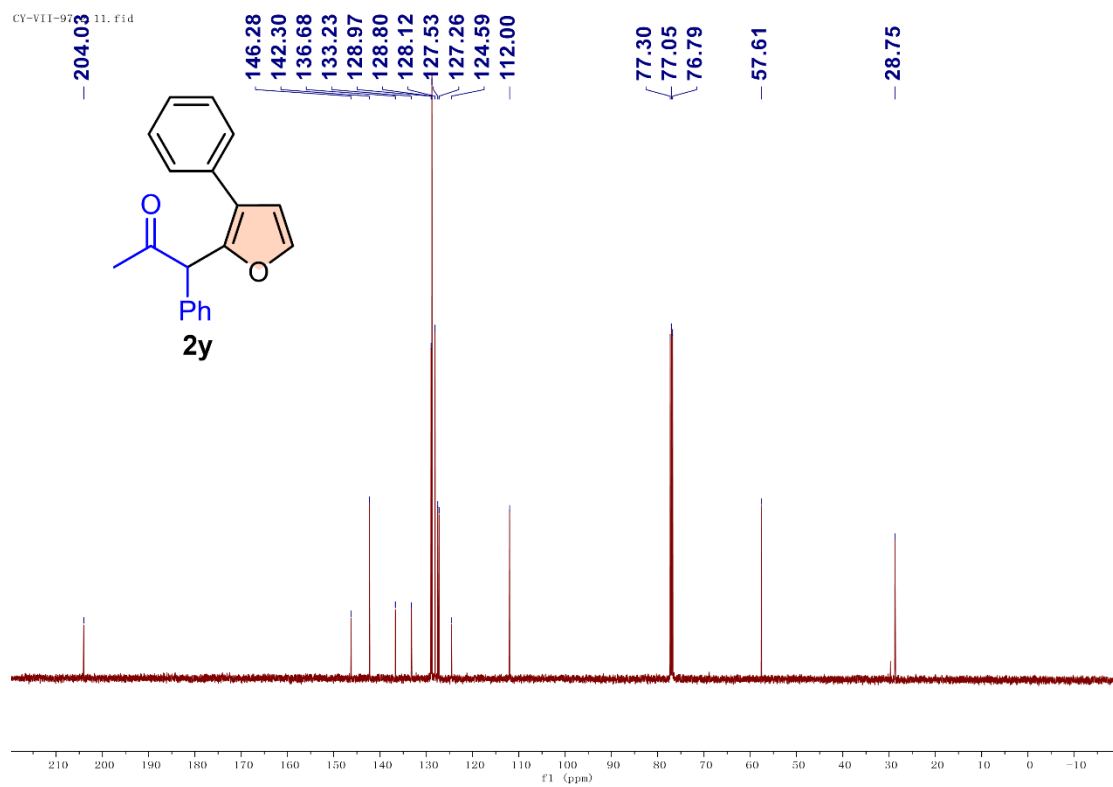
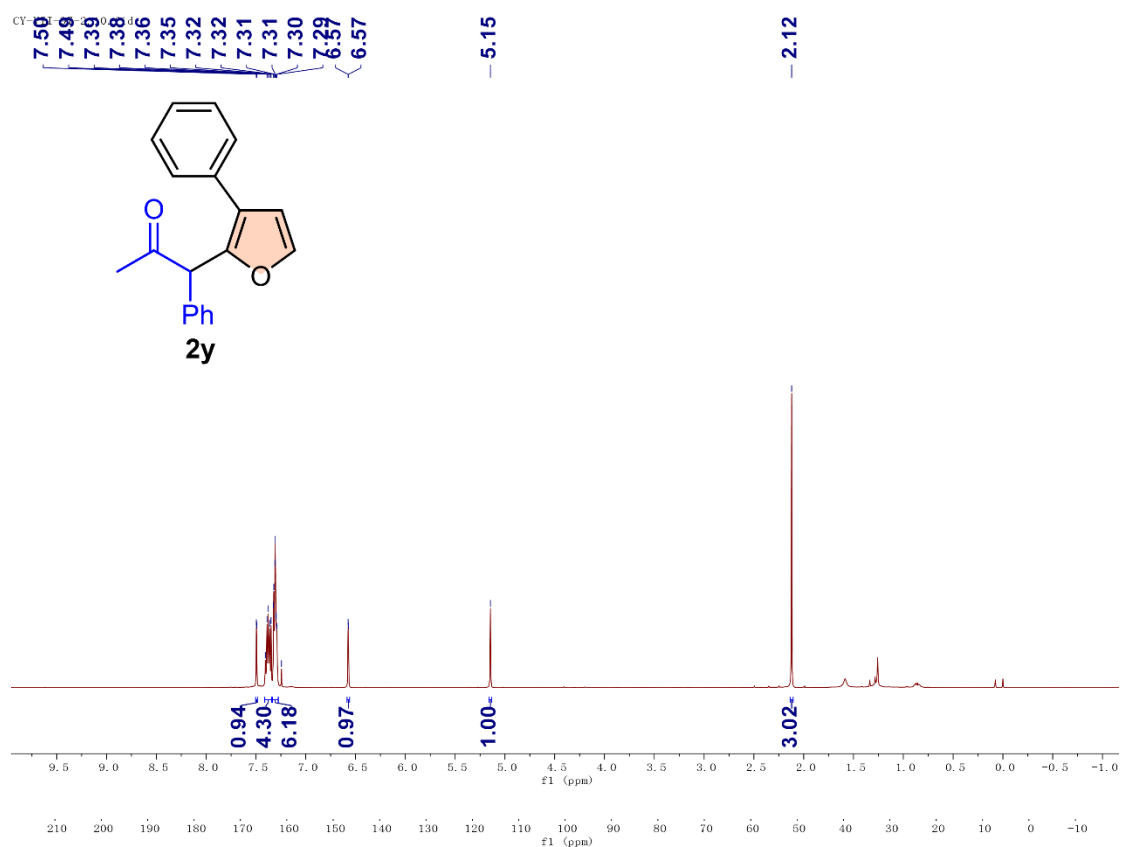


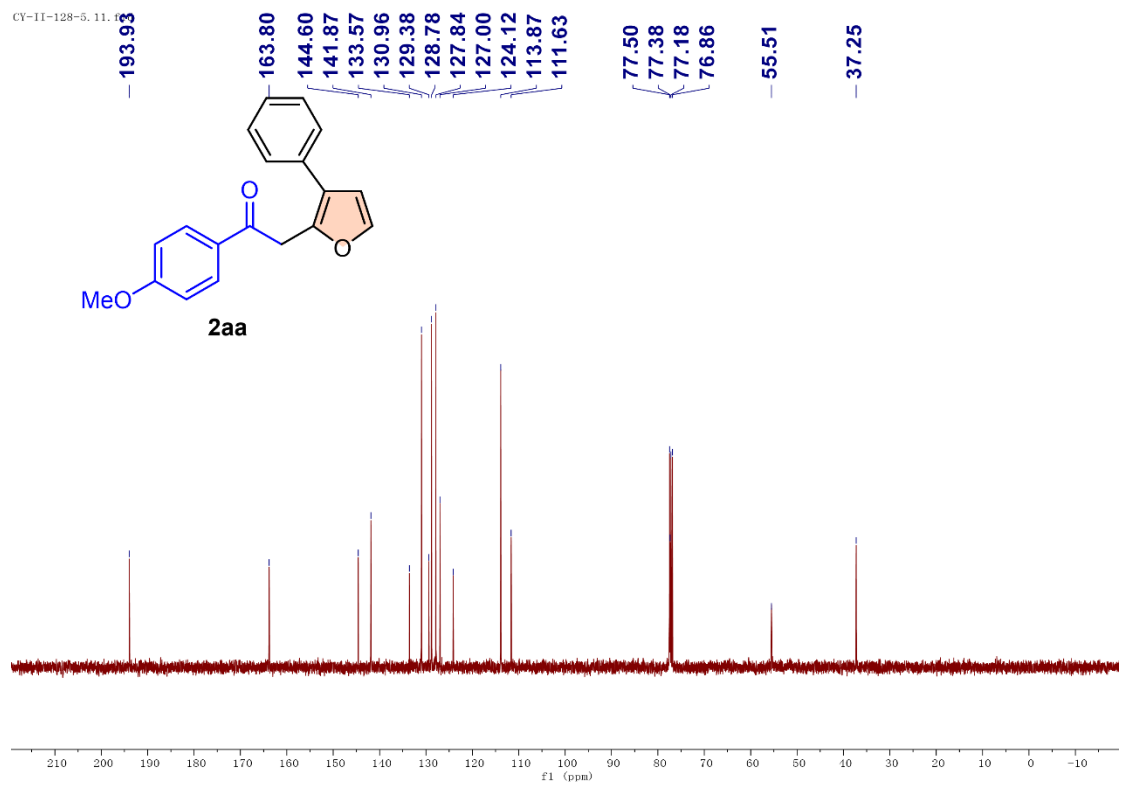
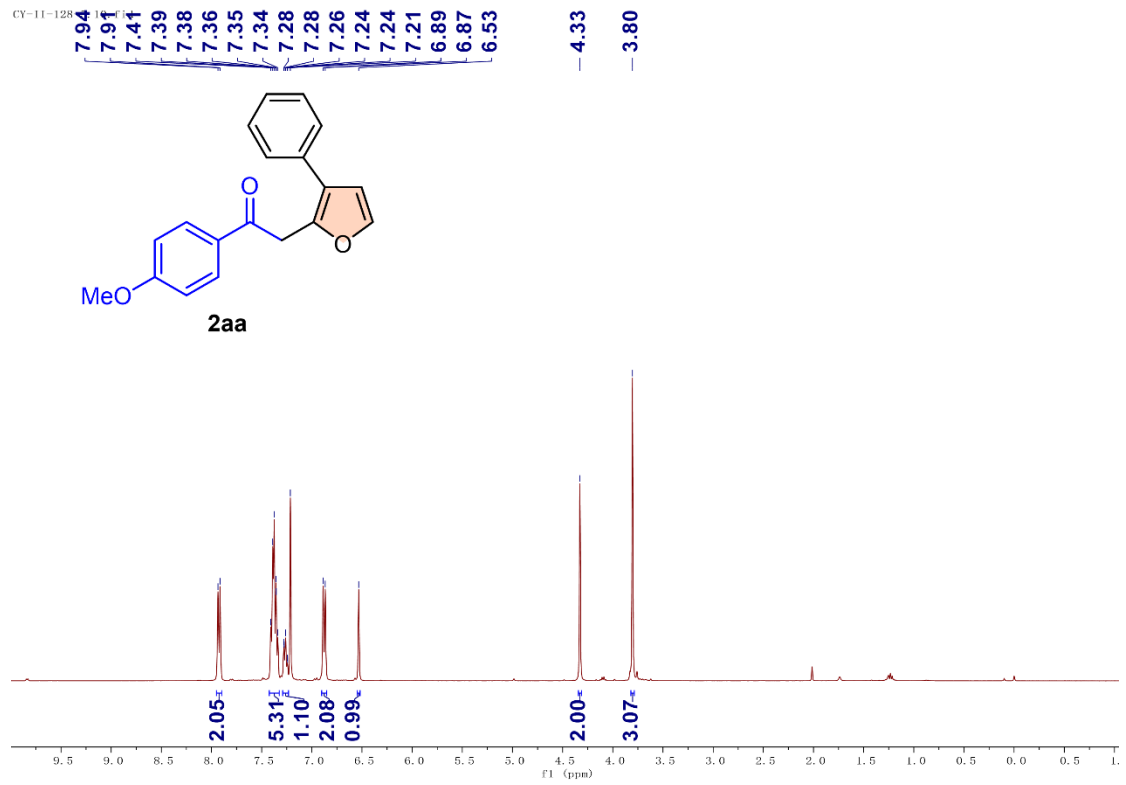




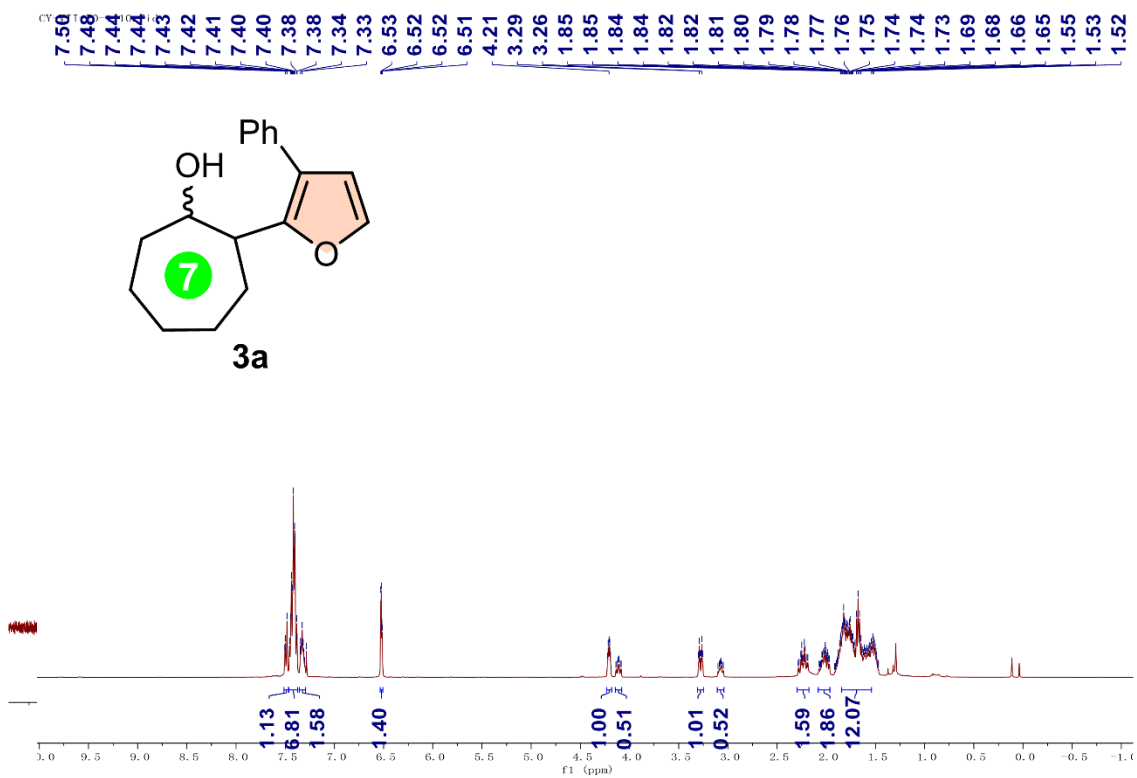








CY-V



CY-VII-70-1.11.F1d

