

## Supporting Information

### A Free Radical Nitration of Olefins with $\text{NaNO}_2/\text{I}_2\text{O}_5$

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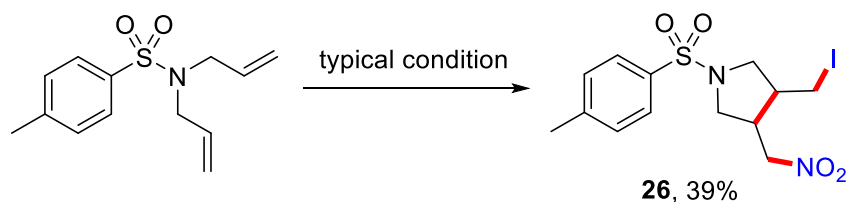
#### General Information

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker advance III 400 spectrometer in  $\text{CDCl}_3$  with TMS as internal standard. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. All products were identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, HRMS. The starting materials were purchased from Aldrich, Acros Organics, Adamas, J&K Chemicals or TCI and used without further purification.

## Typical procedure

A mixture of olefin (1 equiv., 0.2 mmol),  $\text{NaNO}_2$  (6 equiv., 1.2 mmol),  $\text{I}_2\text{O}_5$  (5 equiv., 1.0 mmol) and  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (19/1, 4.0 ml) was stirred in a sealed tube at room temperature for 15 hours. After the reaction finished, saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (5 mL) was added into the mixture, then it was abstracted by  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL). The organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , the filtrate was evaporated under vacuum and purified by column chromatography to afford the desired product.

## Mechanistic studies

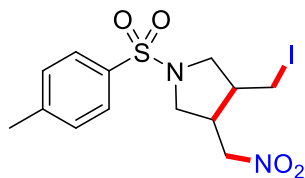


## Reaction procedure:

A mixture of *N,N*-diallyl-4-methylbenzenesulfonamide (1 equiv., 0.2 mmol),  $\text{NaNO}_2$  (6 equiv., 1.2 mmol),  $\text{I}_2\text{O}_5$  (5 equiv., 1.0 mmol) and  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (19/1, 4.0 ml) was stirred in a sealed tube at room temperature for 15h. After the reaction finished, saturated aqueous solution of  $\text{Na}_2\text{S}_2\text{O}_3$  (5 mL) was added into the mixture, then it was abstracted by  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5$  mL). The organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$ , the filtrate was evaporated under vacuum and a white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).

## 3-(iodomethyl)-4-(nitromethyl)-1-tosylpyrrolidine (**26**)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), 39% yield. m.p.: 72-75 °C.



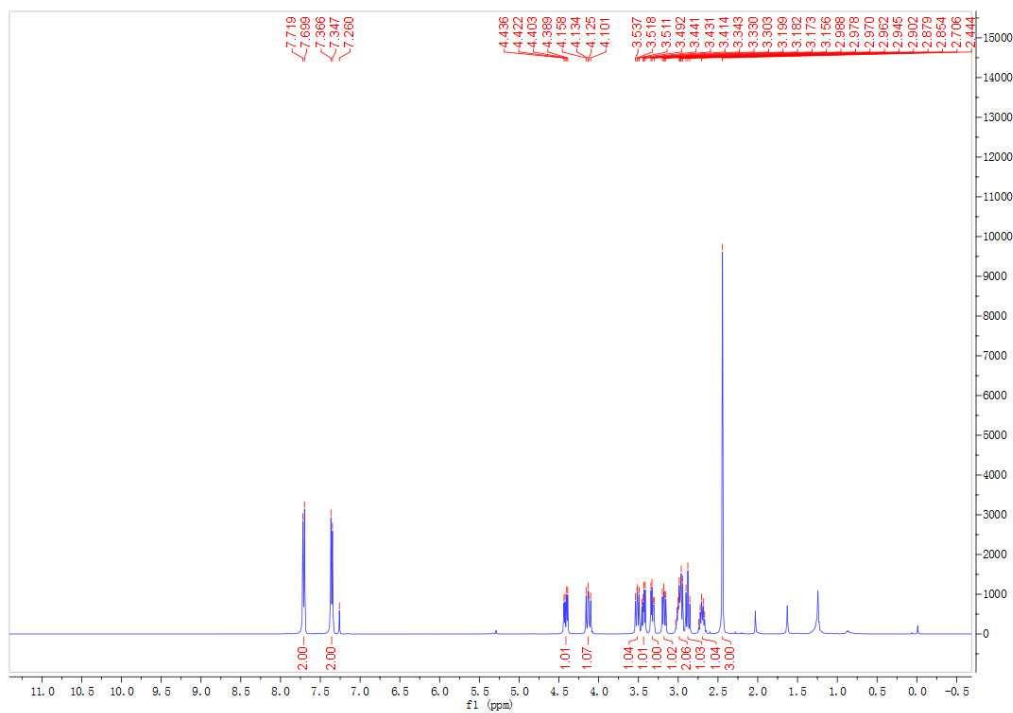
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J = 8.0$  Hz, 2H), 7.36 (d,  $J = 7.6$  Hz, 2H), 4.41 (dd,  $J = 13.2, 5.6$  Hz, 1H), 4.13 (dd,  $J = 13.2, 9.6$  Hz, 1H), 3.51 (dd,  $J = 10.4, 7.6$  Hz, 1H), 3.44 (dd,  $J = 10.4, 6.4$  Hz, 1H), 3.32 (dd,  $J = 10.8, 5.2$  Hz, 1H), 3.18 (dd,  $J =$

10.4, 6.8 Hz, 1H), 3.03 - 2.95 (m, 2H), 2.88 (t, J = 9.2 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.44 (s, 3H).

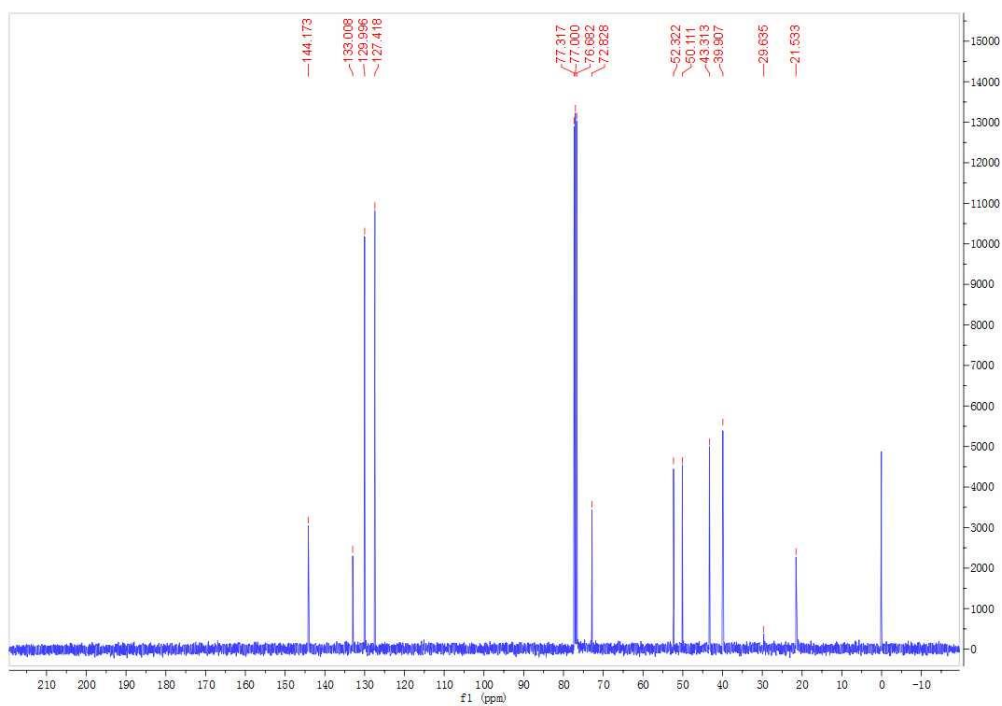
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 144.2, 133.0, 130.0, 127.4, 72.8, 52.3, 50.1, 43.3, 39.9, 29.6, 21.5.

**HRMS (ESI, m/z):** Calculated for C<sub>13</sub>H<sub>17</sub>IN<sub>2</sub>O<sub>4</sub>S [M+H]<sup>+</sup> 425.0038, found 425.0026.

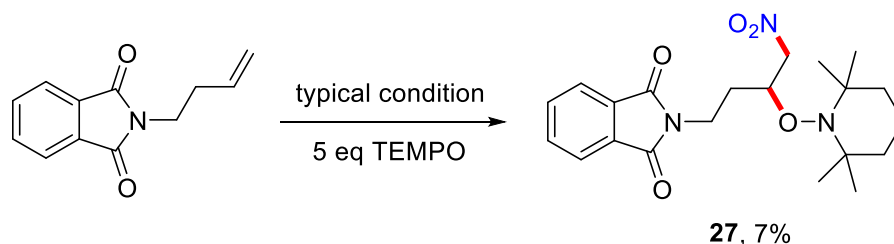
### <sup>1</sup>H NMR



### <sup>13</sup>C NMR

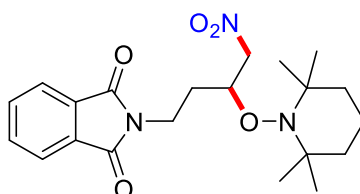


**General procedure for trapping radical :** A mixture of 2-(pent-4-en-1-yl)isoindoline-1,3-dione (0.1 mmol), NaNO<sub>2</sub> (0.6 mmol), I<sub>2</sub>O<sub>5</sub> (0.5 mmol), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (0.5 mmol) and CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O (19/1, 4 mL) was stirred in a sealed tube at room temperature for 15h. After the reaction finished, saturated aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL) was added into the mixture, then it was abstracted by CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL). The organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, the filtrate was evaporated under vacuum and a white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1).



**2-(4-nitro-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butyl)isoindoline-1,3-dione**

**(27)**

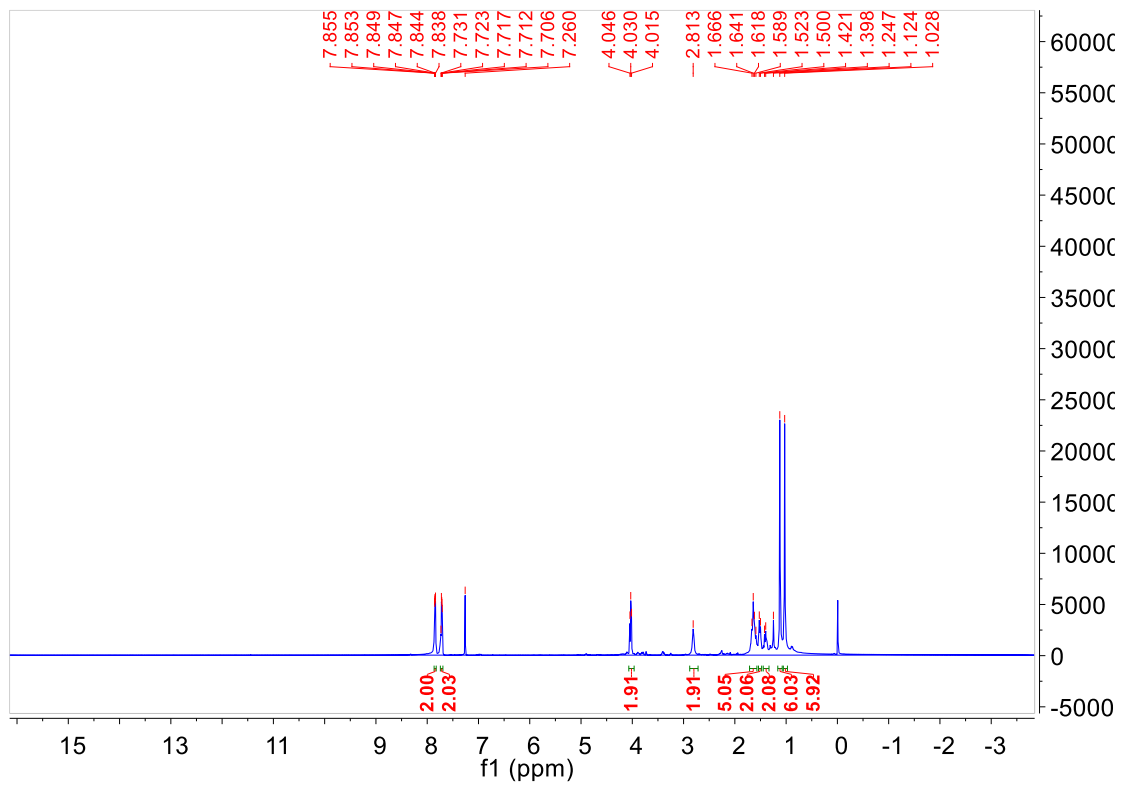


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 – 7.82 (m, 2H), 7.71 (dd, *J* = 5.3, 3.1 Hz, 2H), 4.10 – 3.95 (m, 2H), 2.81 (s, 2H), 1.63 (d, *J* = 11.5 Hz, 5H), 1.51 (d, *J* = 11.4 Hz, 2H), 1.41 (dd, *J* = 21.0, 9.6 Hz, 2H), 1.12 (s, 6H), 1.03 (s, 6H).

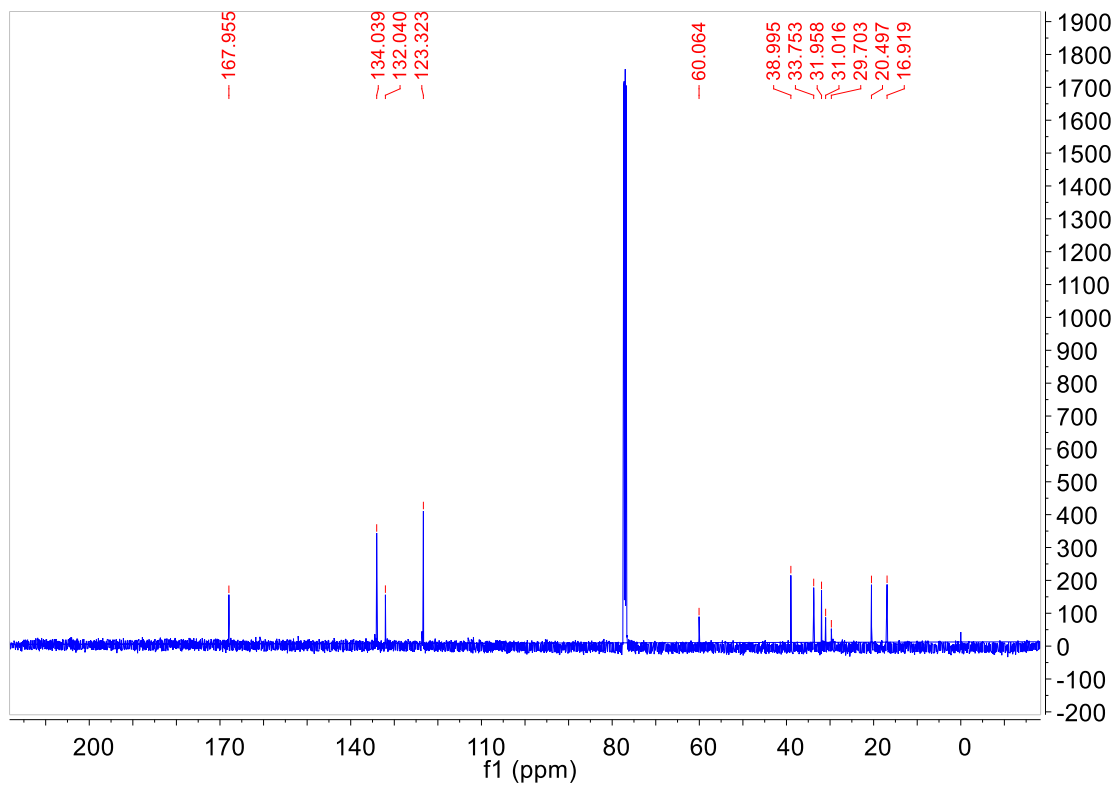
<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.0, 134.0, 132.0, 123.3, 60.1, 39.0, 33.8, 32.0, 31.0, 29.7, 20.5, 16.9.

HRMS (ESI, *m/z*): Calculated for C<sub>21</sub>H<sub>29</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 404.2180, found 404.2185.

<sup>1</sup>H NMR



**<sup>13</sup>C NMR**



### Physical data and references for the following products

All known compounds are determined by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

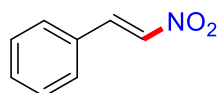
### References:

1. Tian, Y.; Liu, Z.-Q. *Green Chem.* **2017**, *19*, 5230.
2. Tian, Y.; Sun, C.; Tan R. X.; Liu, Z.-Q. *Green Chem.* **2018**, *20*, 588.
3. Li, Z.; Xiao, Y.; Liu, Z.-Q. *Chem. Commun.* **2015**, *51*, 9969.
4. Terad, A.; Kim, H.-D.; Cho, Y.-S.; Cook, C.-H. *Chem. Lett.* **1986**, 1747.
5. Shechter, H.; Gardikes, J. J.; Pagano A. H. *J. Am. Chem. Soc.*, **1959**, *81*, 5420.
6. Maity, S.; Naveen, T.; Sharma, U.; Maiti, D. *Org. Lett.*, **2013**, *15*, 3384.

### Physical data for the following products:

#### 1. (*E*)-(2-nitrovinyl)benzene (1)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 80%. m. p.: 55-58 °C



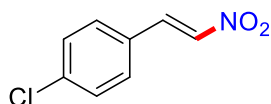
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01 (d,  $J = 13.6$  Hz, 1H), 7.60 – 7.54 (m, 3H), 7.50-7.43 (m, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.0, 137.1, 132.1, 130.1, 129.4, 129.1.

MS (EI):  $m/z$ (%): 51 (37), 78 (100), 91 (53), 102 (60), 132 (19), 149 (46).

#### 2. (*E*)-1-chloro-4-(2-nitrovinyl)benzene(2)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 76%. m. p.: 112-116 °C



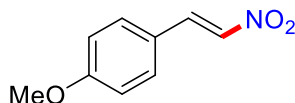
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J = 14.0$  Hz, 1H), 7.56 (d,  $J = 13.6$ Hz, 1H), 7.50 – 7.47 (m, 2H), 7.44 – 7.41 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  138.3, 137.7, 137.4, 130.2, 129.8, 128.5.

MS(EI):  $m/z$ (%): 101 (100), 102 (94), 125 (63), 136 (97), 148 (38), 183 (59).

### 3. (*E*)-1-methoxy-4-(2-nitrovinyl)benzene (3)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 82%. m. p.: 86-88 °C



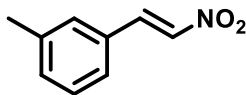
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (d,  $J = 13.6$  Hz, 1H), 7.52 – 7.47 (m, 3H), 6.96 – 6.93 (m, 2H), 3.86 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.9, 139.0, 135.0, 131.1, 122.5, 114.9, 55.5.

MS(ED):  $m/z$ (%): 117 (19), 118 (15), 132 (100), 133 (15), 134 (4), 162 (7), 179 (69).

### 4. (*E*)-1-methyl-3-(2-nitrovinyl)benzene

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 75%. m. p.: 48-49 °C.



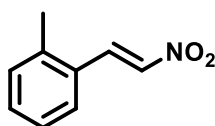
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.98 (d,  $J = 13.6$  Hz, 1H), 7.58 (d,  $J = 14.0$  Hz, 1H), 7.33 (dd,  $J = 14.0, 6.0$  Hz, 4H), 2.40 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.3, 139.2, 136.8, 133.0, 129.9, 129.7, 129.2, 126.4, 21.3.

MS(ED): (ESI,  $m/z$ ): 91(58), 115(100), 116(41), 163(90).

### 5. (*E*)-1-methyl-2-(2-nitrovinyl)benzene

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 75%. m. p.: 65-66 °C



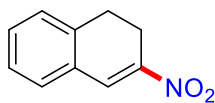
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.31 (d,  $J = 13.6$  Hz, 1H), 7.53 – 7.49 (m, 2H), 7.39 (t,  $J = 7.6$  Hz, 1H), 7.27 (dd,  $J = 12.8, 7.2$  Hz, 2H), 2.49 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.2, 137.5, 136.8, 131.9, 131.3, 128.8, 127.3, 126.7, 19.9.

MS(ED): (ESI,  $m/z$ ): 115 (100), 116 (50), 118 (12), 133 (5), 146 (9), 163 (43).

### 6. 3-nitro-1,2-dihydronaphthalene (4)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 83%.



$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85 (s, 1H), 7.37 – 7.22 (m, 4H), 3.08 – 2.96 (m,

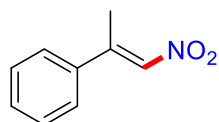
4H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 147.9, 136.4, 131.6, 131.2, 130.2, 130.1, 127.9, 127.3, 27.9, 22.4.

**HRMS (ESI, m/z):** Calculated for C<sub>10</sub>H<sub>9</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 176.0706, found: 176.0708.

### 7. (E)-(1-nitroprop-1-en-2-yl)benzene (5)

A yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 75%. m. p.: 44-46 °C

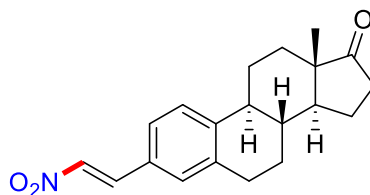


**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.45 (d, *J* = 3.8 Hz, 5H), 7.31 (d, *J* = 1.3 Hz, 1H), 2.65 (d, *J* = 1.4 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 149.9, 138.3, 136.4, 130.3, 129.0, 126.8, 18.6.

### 8. (8R,9S,13S,14S)-13-methyl-3-((E)-2-nitrovinyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (6)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). Yield: 72%. m. p.: 124-125 °C

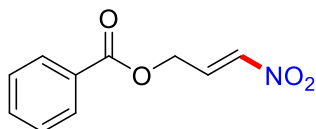


**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.28 – 7.21 (m, 2H), 7.16 (s, 1H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 10.9 Hz, 1H), 2.93 (dd, *J* = 8.8, 4.0 Hz, 2H), 2.52 (dd, *J* = 19.0, 8.8 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.30 (s, 1H), 2.15 (dd, *J* = 18.8, 9.1 Hz, 1H), 2.05 (ddd, *J* = 16.9, 10.6, 4.6 Hz, 2H), 1.97 (d, *J* = 2.6 Hz, 1H), 1.63 – 1.46 (m, 6H), 0.92 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 220.4, 144.8, 139.1, 137.8, 136.4, 129.9, 127.6, 126.5, 50.4, 47.9, 44.7, 37.8, 35.8, 31.5, 29.2, 26.2, 25.5, 21.6, 13.8.

### 9. (E)-3-nitroallyl benzoate (7)

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 60/1). Yield: 77%.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.07 – 8.05 (m, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.39 (dt, *J* = 13.2, 4.4 Hz, 1H), 7.26 – 7.20 (m, 1H), 5.11 (dd, *J* = 4.4, 2.0 Hz, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 165.5, 140.2, 135.6, 133.8, 129.7, 128.8, 128.6,

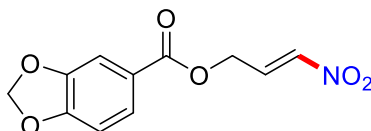


59.8.

**HRMS (ESI, m/z):** Calculated for C<sub>10</sub>H<sub>9</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 208.0604, found 208.0599.

**10. (E)-3-nitroallyl benzo[d][1,3]dioxole-5-carboxylate (7)**

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). Yield: 79%.



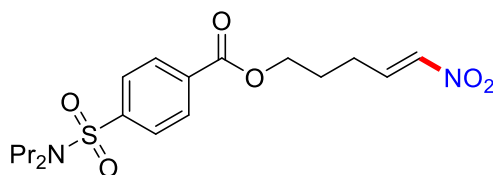
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.66 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.45 (d, *J* = 1.6 Hz, 1H), 7.36 (dt, *J* = 8.4, 4.0 Hz, 1H), 7.20 (t, *J* = 13.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 2H), 5.06 (dd, *J* = 4.0, 2.0 Hz, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 164.7, 152.3, 147.9, 140.1, 135.8, 125.7, 122.6, 109.4, 108.2, 102.0, 59.7.

**HRMS (ESI, m/z):** Calculated for C<sub>11</sub>H<sub>9</sub>N<sub>1</sub>O<sub>6</sub> [M+Na]<sup>+</sup> 274.0322, found 274.0318.

**11. (E)-5-nitropent-4-en-1-yl 4-(*N,N*-dipropylsulfamoyl)benzoate (9)**

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 82%.



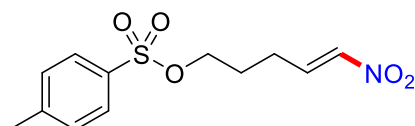
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.03 (d, *J* = 13.6 Hz, 1H), 4.41 (t, *J* = 6.4 Hz, 2H), 3.10 – 3.07 (m, 4H), 2.46 (q, *J* = 7.2 Hz, 2H), 2.06 – 1.99 (m, 2H), 1.53 (dd, *J* = 15.2, 7.6 Hz, 4H), 0.86 (t, *J* = 7.2 Hz, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 165.0, 144.4, 141.0, 140.0, 133.0, 130.1, 127.0, 64.2, 49.9, 26.9, 25.3, 21.9, 11.1.

**HRMS (ESI, m/z):** Calculated for C<sub>18</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>S [M+H]<sup>+</sup> 399.1584, found 399.1580.

**12. (E)-5-nitropent-4-en-1-yl 4-methylbenzenesulfonate (10)**

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 80%.



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.14 – 7.07 (m, 1H), 6.84 (d, *J* = 13.2 Hz, 1H), 4.04 (t, *J* = 6.0 Hz, 2H), 2.45 (s, 3H), 2.33 (td, *J* = 8.0, 0.8 Hz, 2H), 1.89 – 1.83 (m, 2H).

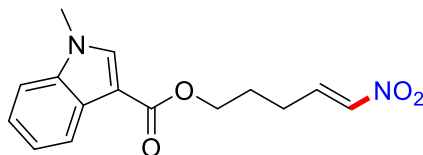
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 145.2, 140.3, 140.2, 132.4, 129.9, 127.8, 68.6, 26.8,

24.3, 21.6.

**HRMS (ESI, m/z):** Calculated for C<sub>12</sub>H<sub>15</sub>NO<sub>5</sub>S [M+Na]<sup>+</sup>: 322.0720, found 322.0721.

**13. (E)-5-nitropent-4-en-1-yl 1-methyl-1H-indole-3-carboxylate (11)**

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 85%.



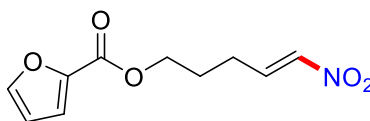
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 8.13 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.78 (s, 1H), 7.37 – 7.27 (m, 4H), 7.04 (d, *J* = 13.6 Hz, 1H), 4.39 (t, *J* = 6.0 Hz, 2H), 3.84 (s, 3H), 2.51 – 2.45 (m, 2H), 2.06 – 1.99 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 164.7, 141.7, 139.9, 137.2, 135.3, 126.5, 122.9, 122.0, 121.4, 109.9, 106.5, 62.4, 33.4, 27.3, 25.6.

**HRMS (ESI, m/z):** Calculated for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> [M+Na]<sup>+</sup>: 311.1002, found 311.1004.

**14. (E)-5-nitropent-4-en-1-yl furan-2-carboxylate (12)**

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 76%.



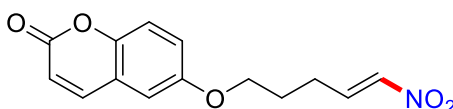
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.59 (d, *J* = 0.8 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.03 (d, *J* = 13.2 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.6 Hz, 1H), 4.36 (t, *J* = 6.4 Hz, 2H), 2.44 (qd, *J* = 7.2, 1.2 Hz, 2H), 2.02 – 1.95 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 158.4, 146.5, 144.2, 141.3, 140.0, 118.2, 111.9, 63.6, 26.9, 25.3.

**HRMS (ESI, m/z):** Calculated for C<sub>10</sub>H<sub>11</sub>NO<sub>5</sub> [M+NH<sub>4</sub>]<sup>+</sup>: 243.0975, found 243.0974.

**15. (E)-6-((5-nitropent-4-en-1-yl)oxy)-2H-chromen-2-one (13)**

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). Yield: 74%.



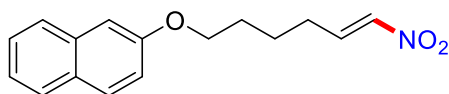
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.63 (d, *J* = 9.6 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.03 (d, *J* = 13.2 Hz, 1H), 6.82 – 6.77 (m, 2H), 6.24 (d, *J* = 9.6 Hz, 1H), 4.06 (t, *J* = 6.0 Hz, 2H), 2.51 (td, *J* = 8.4, 1.2 Hz, 2H), 2.08 – 2.01 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 161.6, 161.1, 155.7, 143.4, 141.4, 139.9, 128.9, 113.2, 112.7, 112.7, 101.2, 67.0, 27.2, 25.2.

**HRMS (ESI, m/z):** Calculated for C<sub>14</sub>H<sub>13</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 276.0866, found 276.0856.

### 16. (*E*)-2-((6-nitrohex-5-en-1-yl)oxy)naphthalene (14)

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 87%.



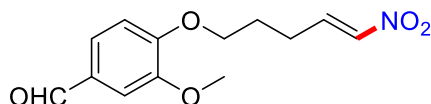
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (dd,  $J = 17.2, 8.4$  Hz, 3H), 7.45 (dd,  $J = 14, 6.8$  Hz, 1H), 7.32 (dt,  $J = 14.8, 7.2$  Hz, 2H), 7.15 (dd,  $J = 11.6, 2.4$  Hz, 2H), 7.02 (d,  $J = 13.6$  Hz, 1H), 4.10 (t,  $J = 6.0$  Hz, 2H), 2.40 – 2.34 (m, 2H), 1.94 – 1.87 (m, 2H), 1.80 – 1.72 (m, 2H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.7, 142.1, 139.8, 134.5, 129.4, 128.9, 127.6, 126.6, 126.4, 123.6, 118.8, 106.5, 67.1, 28.6, 28.1, 24.5.

**HRMS (ESI,  $m/z$ ):** Calculated for  $\text{C}_{16}\text{H}_{17}\text{NO}_3$  [ $\text{M}+\text{NH}_4$ ] $^+$  289.1547, found 289.1546.

### 17. (*E*)-3-methoxy-4-((5-nitropent-4-en-1-yl)oxy)benzaldehyde (15)

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). Yield: 85%.



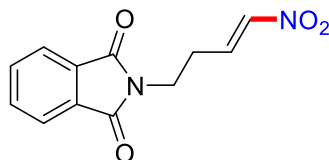
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.84 (s, 1H), 7.43 – 7.34 (m, 3H), 7.03 (d,  $J = 13.6$  Hz, 1H), 6.94 (d,  $J = 8.0$  Hz, 1H), 4.14 (t,  $J = 6.0$  Hz, 2H), 3.91 (s, 3H), 2.55 – 2.49 (m, 2H), 2.10 (dt,  $J = 13.2, 7.2$  Hz, 2H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 153.4, 149.8, 141.6, 140.0, 130.2, 126.5, 111.4, 109.2, 67.7, 55.8, 27.1, 25.4.

**HRMS (ESI,  $m/z$ ):** Calculated for  $\text{C}_{13}\text{H}_{15}\text{NO}_5$  [ $\text{M}+\text{Na}$ ] $^+$  288.0842, found: 288.0836.

### 18. (*E*)-2-(4-nitrobut-3-en-1-yl)isoindoline-1,3-dione (16)

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 75%. m. p.: 81-84 °C



$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (dt,  $J = 5.2, 2.8$  Hz, 2H), 7.76 – 7.73 (m, 2H), 7.27 – 7.20 (m, 1H), 7.02 (d,  $J = 13.6$  Hz, 1H), 3.90 (t,  $J = 6.8$  Hz, 2H), 2.69 (qd,  $J = 7.2, 1.6$  Hz, 2H).

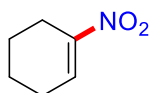
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.0, 141.0, 137.9, 134.3, 131.8, 123.5, 35.8, 27.7.

**HRMS (ESI,  $m/z$ ):** Calculated for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_4$  [ $\text{M}+\text{Na}$ ] $^+$  269.0530, found 269.0535.

### 19. 1-nitrocyclohex-1-ene (17)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl

acetate = 100/1). Yield: 78%.



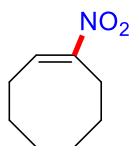
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.32 (t, *J* = 4.0 Hz, 1H), 2.57 (td, *J* = 6.0, 1.6 Hz, 2H), 2.33 (dt, *J* = 6.0, 3.6 Hz, 2H), 1.79 – 1.73 (m, 2H), 1.65 – 1.59 (m, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 149.6, 134.4, 24.8, 23.8, 21.7, 20.6.

**MS (EI): *m/z*(%):** 77 (18), 79 (83), 81 (100), 97 (15), 127 (4).

## 20. (*E*)-1-nitrocyclooct-1-ene (18)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 81%.



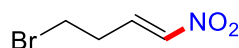
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.29 (dd, *J* = 17.6, 8.8 Hz, 1H), 2.74 – 2.71 (m, 2H), 2.34 – 2.28 (m, 2H), 1.70 – 1.68 (m, 4H), 1.50 – 1.48 (m, 4H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 152.2, 136.4, 29.0, 28.2, 26.6, 26.3, 25.6, 24.7.

**MS(EI): *m/z*(%):** 107 (9), 109 (21), 110 (3), 138 (4), 155 (2).

## 21. (*E*)-4-bromo-1-nitrobut-1-ene (19)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 40/1). Yield: 76%.



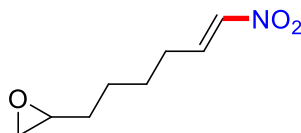
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.23 (dd, *J* = 14.0, 6.8 Hz, 1H), 7.07 (d, *J* = 13.2 Hz, 1H), 3.51 (t, *J* = 6.4 Hz, 2H), 2.87 (td, *J* = 7.2, 1.2 Hz, 2H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 141.1, 138.3, 31.2, 28.8.

**HRMS (ESI, *m/z*):** Calculated for C<sub>4</sub>H<sub>6</sub>BrNO<sub>2</sub> [M+H]<sup>+</sup> 179.9655, found 179.9653.

## 22. (*E*)-2-(6-nitrohex-5-en-1-yl)oxirane (20)

A yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 100/1). Yield: 68%.



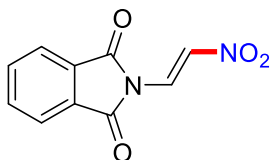
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.29– 7.22 (m, 1H), 6.98 (d, *J* = 13.2 Hz, 1H), 2.90 (dd, *J* = 3.6, 2.4 Hz, 1H), 2.75 (t, *J* = 4.8 Hz, 1H), 2.46 (dd, *J* = 4.8, 2.8 Hz, 1H), 2.29 (dd, *J* = 14.0, 6.8 Hz, 2H), 1.65 – 1.46 (m, 6H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):** δ 142.2, 139.7, 51.9, 46.9, 32.0, 28.3, 27.4, 25.6.

**HRMS (ESI, *m/z*):** Calculated for C<sub>8</sub>H<sub>13</sub>NO<sub>3</sub> [M+Na]<sup>+</sup> 194.0788, found 194.0781.

**23. (E)-2-(2-nitrovinyl)isoindoline-1,3-dione (21)**

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). Yield: 85%. m.p.: 98-99 °C.



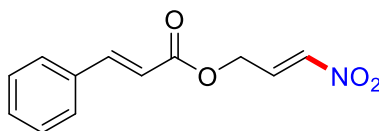
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.41 (dd, *J* = 33.2, 12.8 Hz, 2H), 8.02 (dd, *J* = 5.2, 2.8 Hz, 2H), 7.90 (dd, *J* = 5.6, 3.2 Hz, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.4, 135.8, 131.3, 130.3, 127.7, 124.8.

MS(EI): *m/z*(%): 147 (15), 149 (12), 160 (61), 172 (100), 218 (2).

**24. (E)-3-nitroallyl cinnamate (22)**

A light-yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1). Yield: 79%.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.56 – 7.55 (m, 2H), 7.43 – 7.41 (m, 3H), 7.35 (dt, *J* = 13.6, 4.4 Hz, 1H), 7.20 (d, *J* = 13.2 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 5.00 – 4.99 (m, 2H).

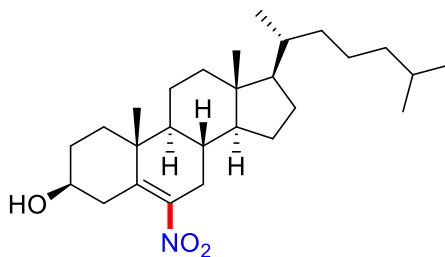
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.8, 146.7, 140.1, 135.7, 133.8, 130.9, 129.0, 128.3, 116.3, 59.4.

HRMS (ESI, *m/z*): Calculated for C<sub>12</sub>H<sub>11</sub>NO<sub>4</sub> [M+Na]<sup>+</sup> 256.0580, found 256.0583.

**25.**

**(8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-6-nitro-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-ol (23)**

A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 4/1). Yield: 65%. m.p.: 168-169 °C.



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.61 (s, 1H), 2.75 (dd, *J* = 13.8, 2.5 Hz, 1H), 2.56 – 2.46 (m, 1H), 2.16 – 2.08 (m, 2H), 2.06 – 2.02 (m, 1H), 1.99 – 1.95 (m, 1H), 1.91 – 1.83 (m, 2H), 1.73 (s, 1H), 1.64 – 1.44 (m, 7H), 1.39 – 1.24 (m, 6H), 1.19 (dd, *J* = 15.7, 3.6 Hz, 2H), 1.13 – 1.08 (m, 6H),

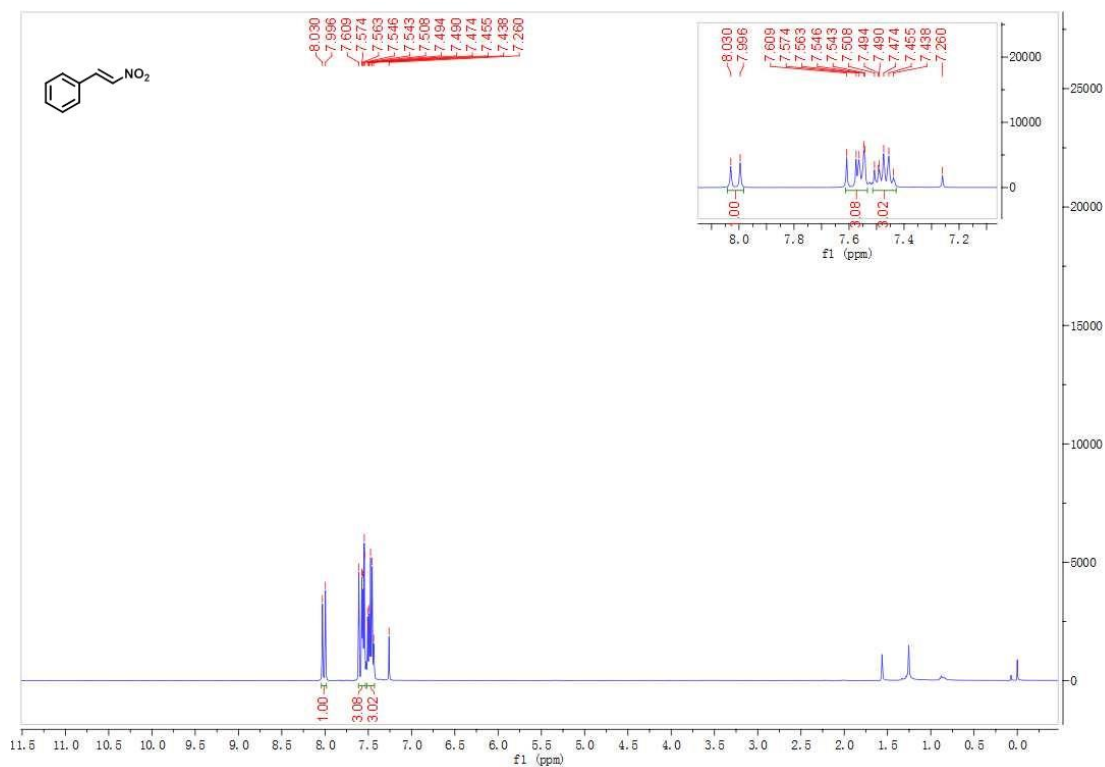
0.99 (dd,  $J = 11.8, 6.7$  Hz, 2H), 0.91 (d,  $J = 6.5$  Hz, 3H), 0.86 (dd,  $J = 6.6, 2.3$  Hz, 6H), 0.68 (s, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  146.2, 138.3, 70.2, 56.1, 56.0, 49.0, 42.3, 39.4, 39.3, 37.8, 36.6, 36.1, 35.7, 35.1, 33.3, 31.6, 30.5, 28.1, 28.0, 24.1, 23.8, 22.8, 22.5, 21.0, 19.6, 18.7, 11.8.

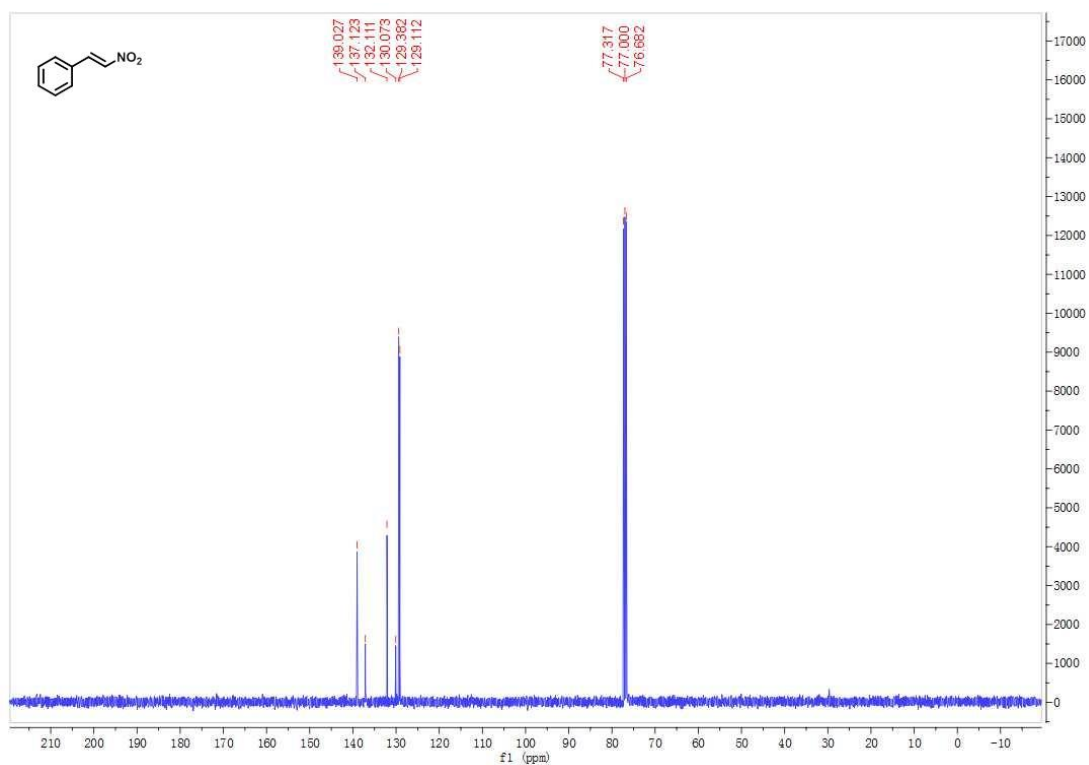
**HRMS (ESI,  $m/z$ ):** Calculated for  $\text{C}_{27}\text{H}_{46}\text{NO}_3$   $[\text{M}+\text{H}]^+$  432.3472, found: 432.3470.

# Copies of the $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra

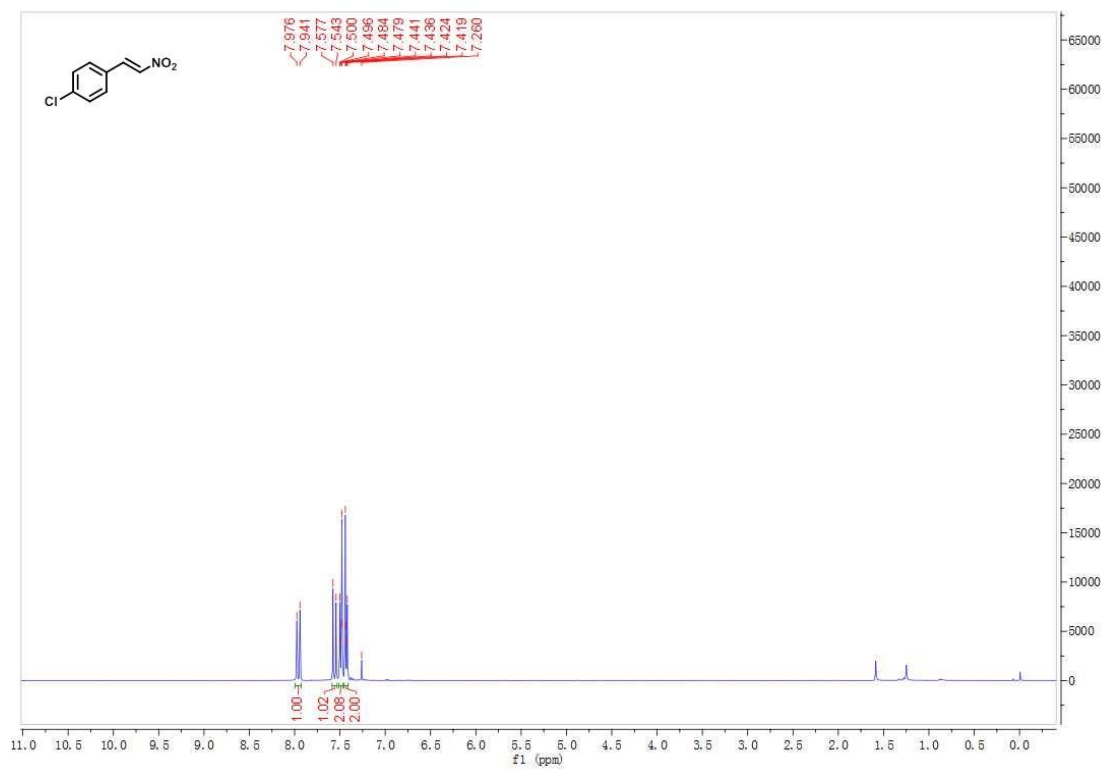
## 1. $^1\text{H}$ NMR



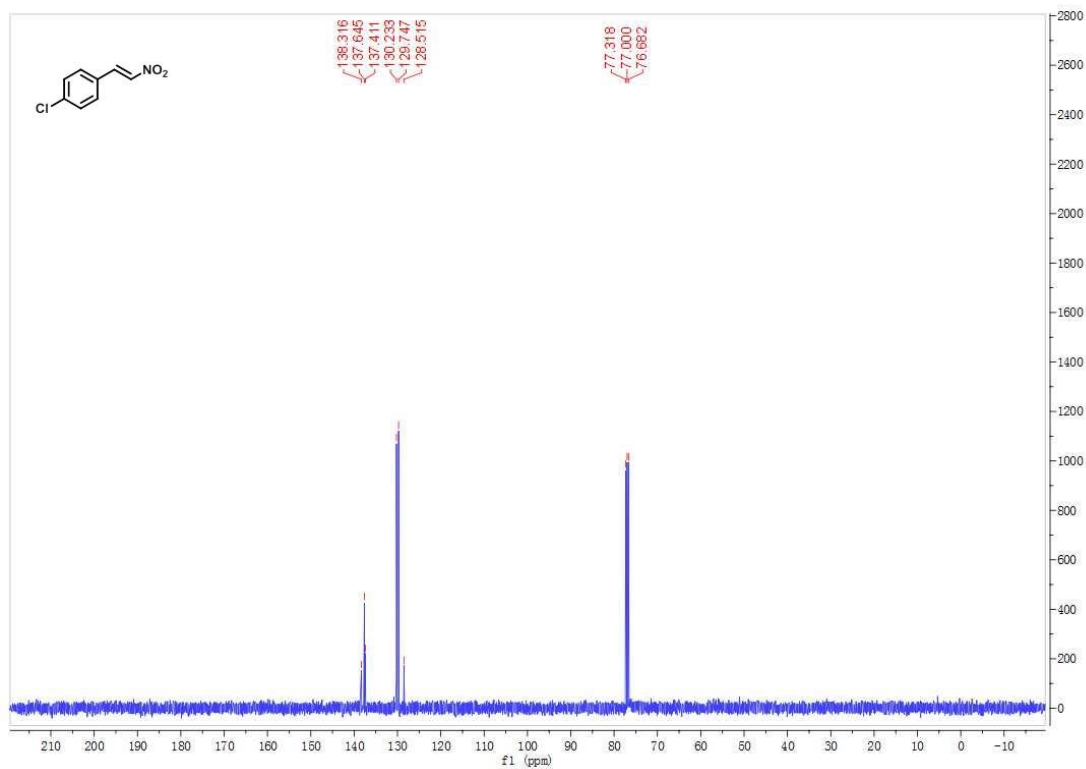
## 1. $^{13}\text{C}$ NMR



## 2. <sup>1</sup>H NMR

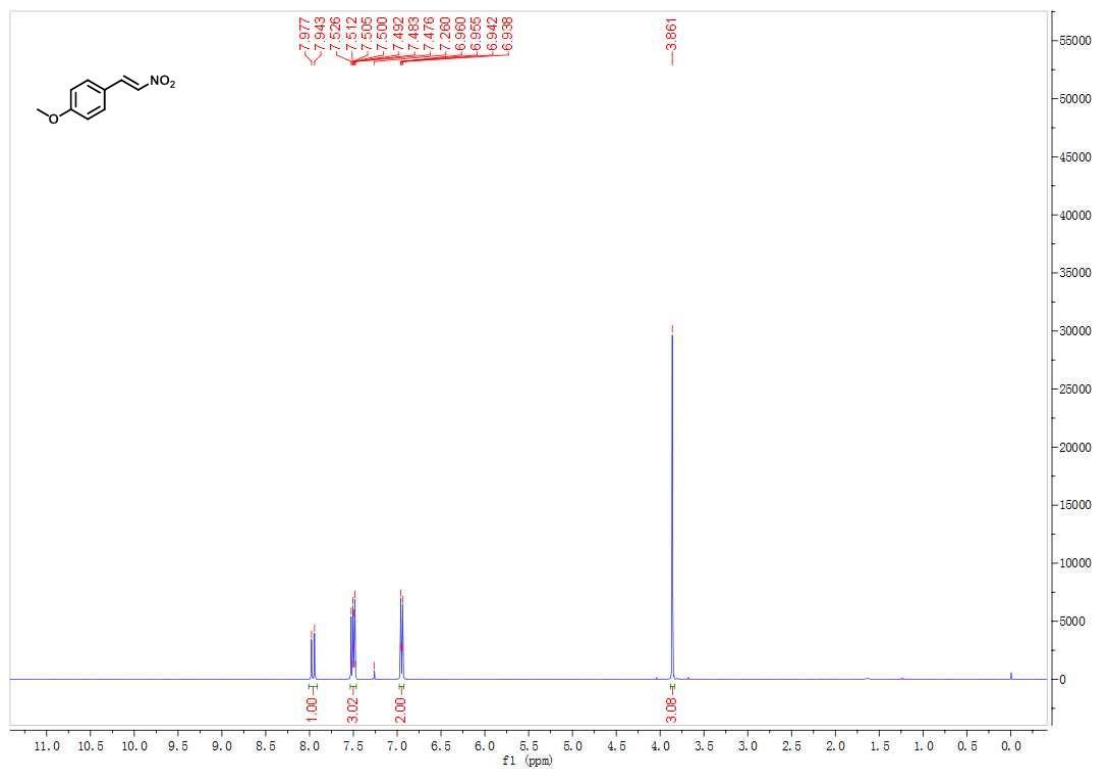


## 2. <sup>13</sup>C NMR

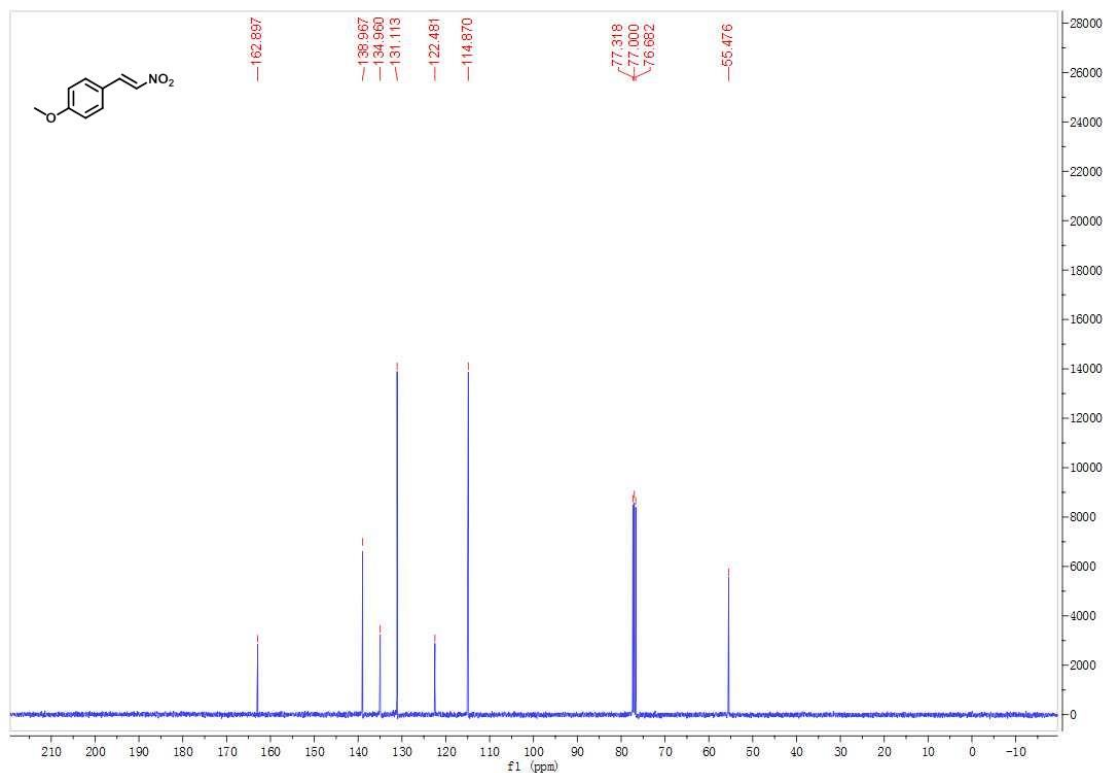




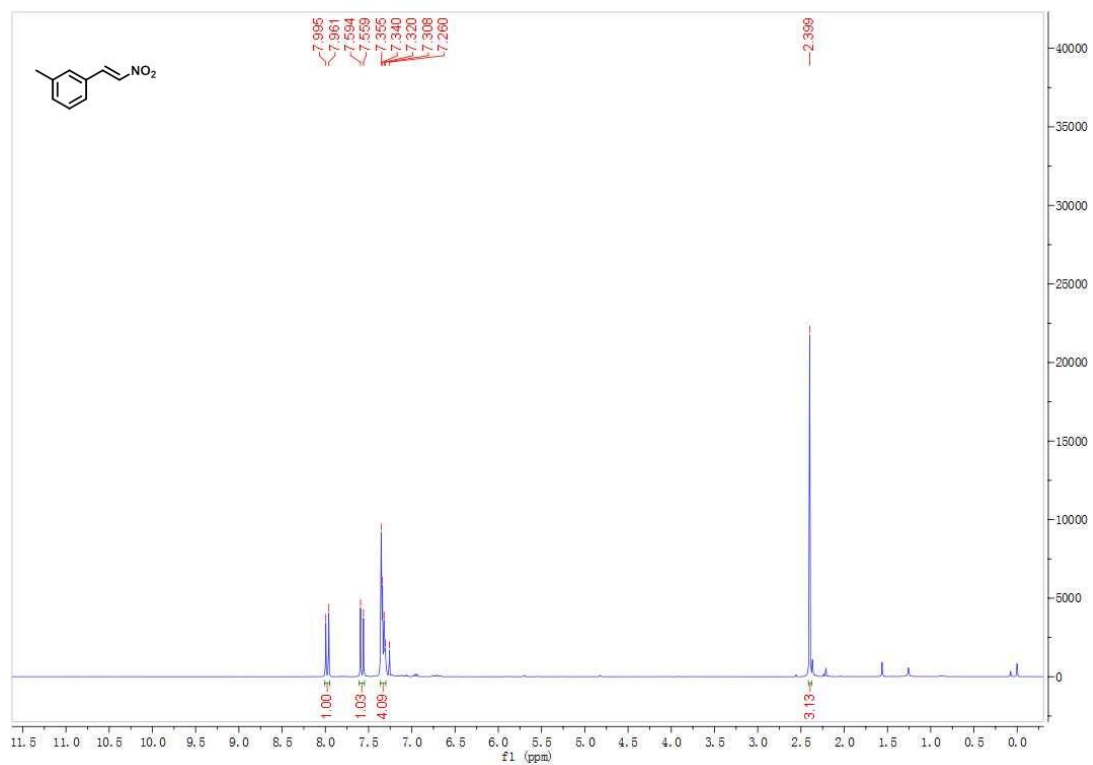
### 3. <sup>1</sup>H NMR



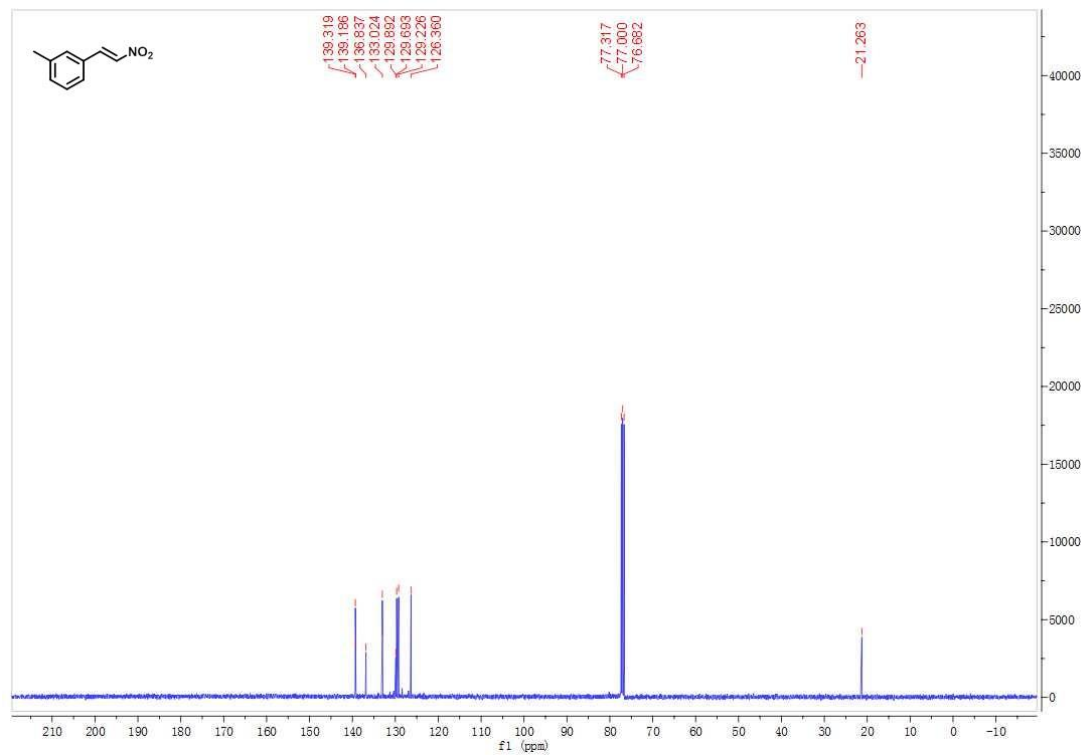
### 3. <sup>13</sup>C NMR



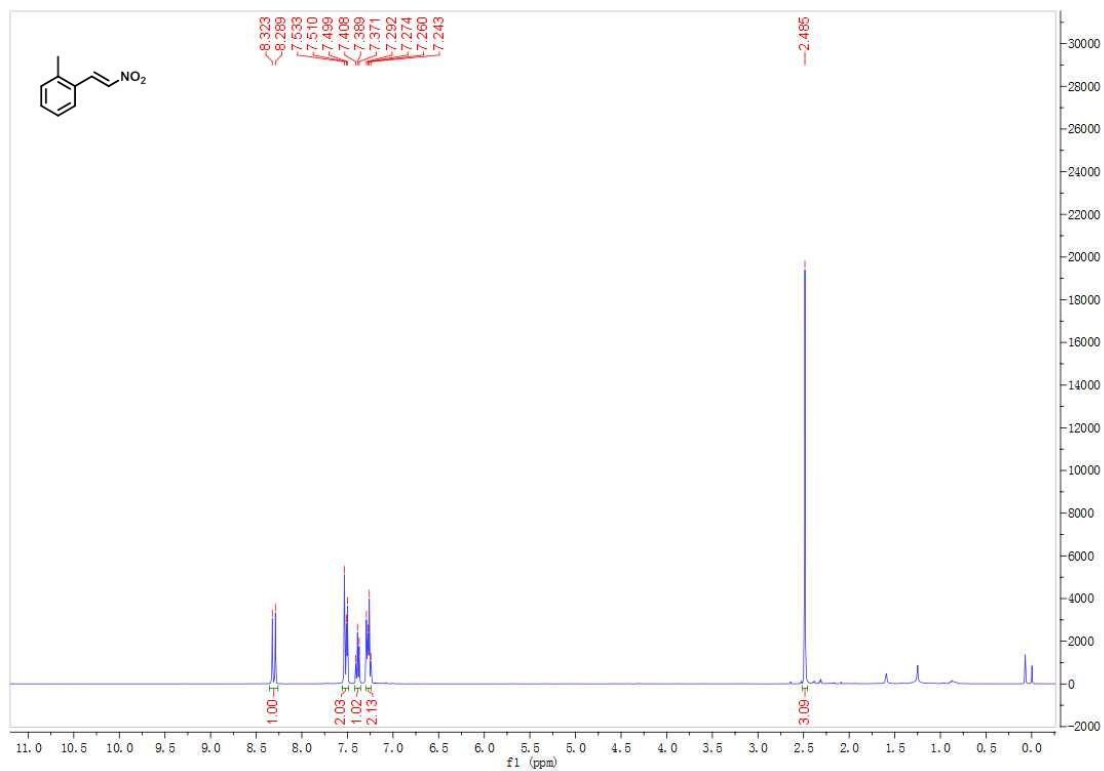
#### 4. <sup>1</sup>H NMR



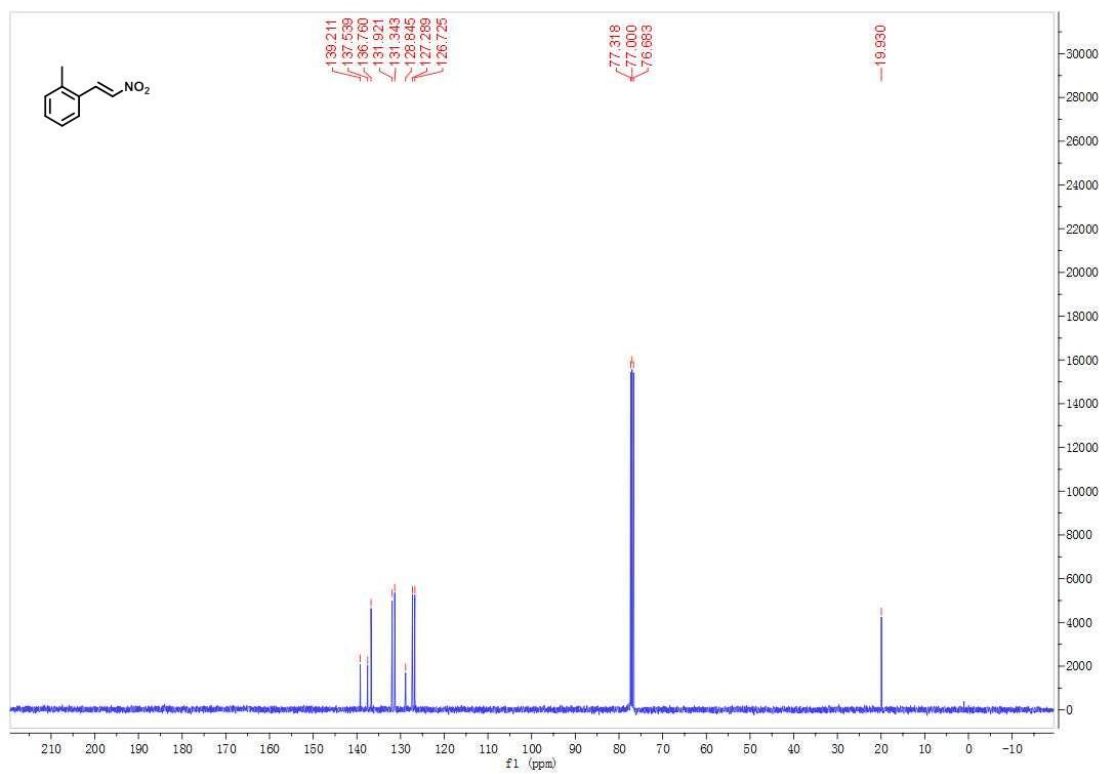
#### 4. <sup>13</sup>C NMR



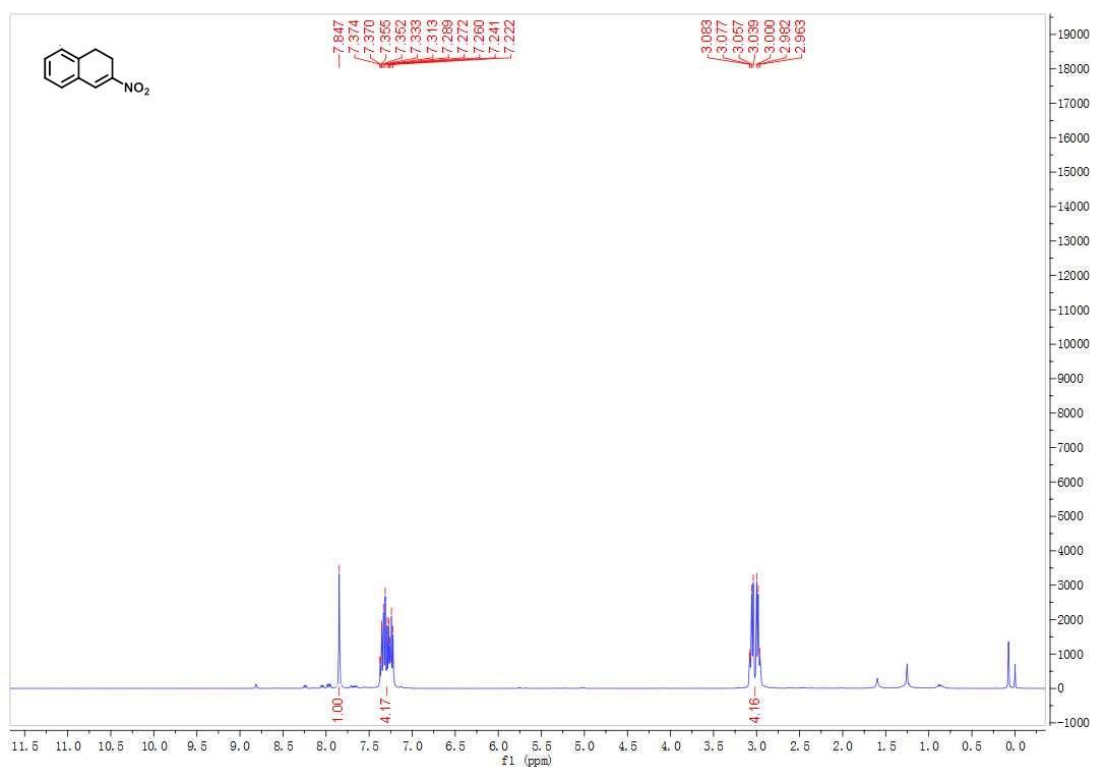
## 5. <sup>1</sup>H NMR



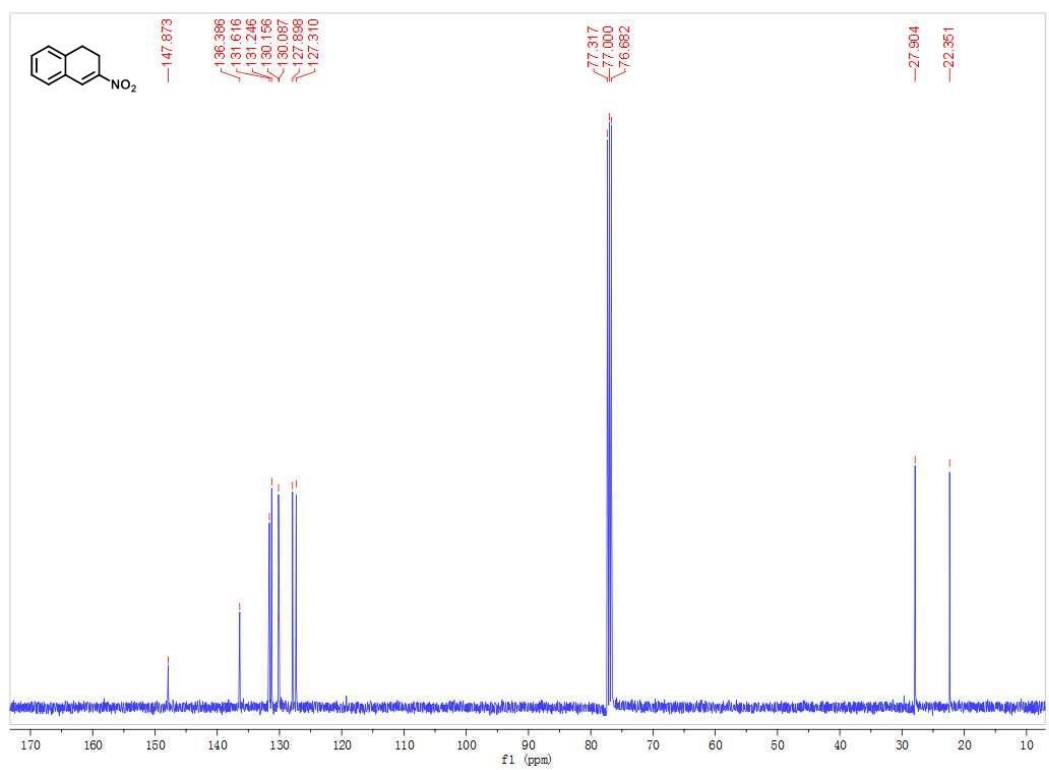
## 5. <sup>13</sup>C NMR



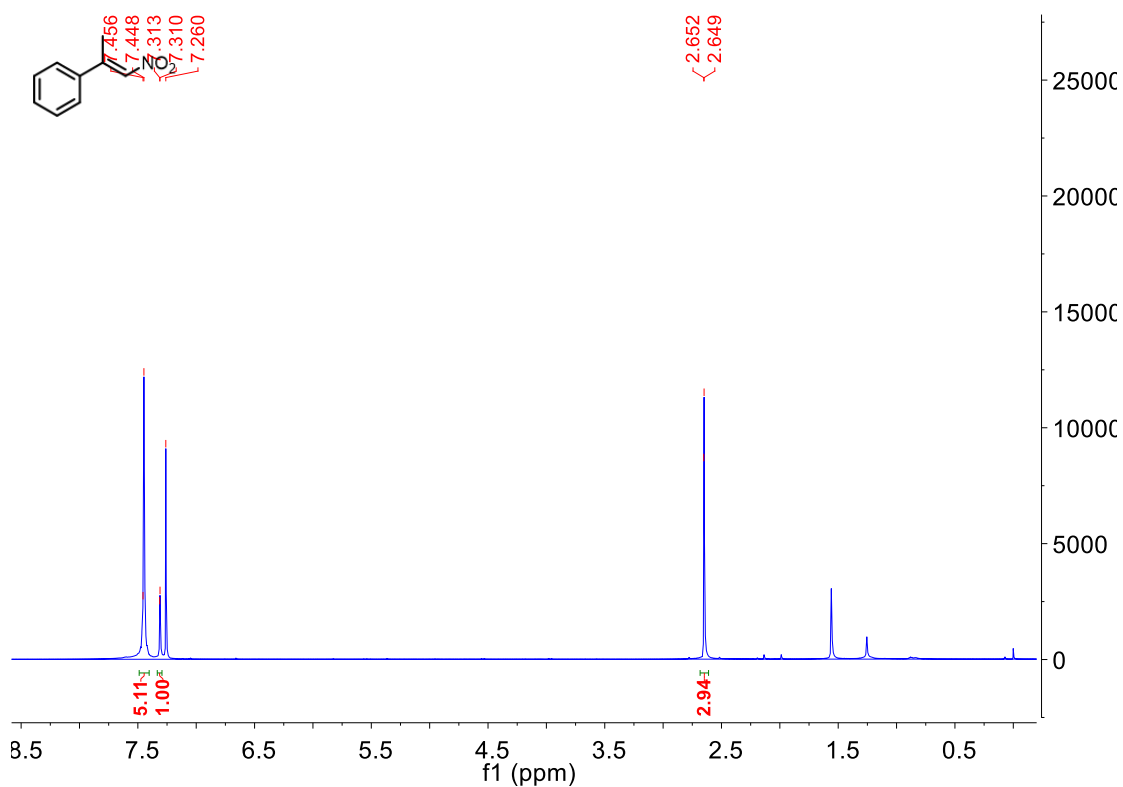
## 6. <sup>1</sup>H NMR



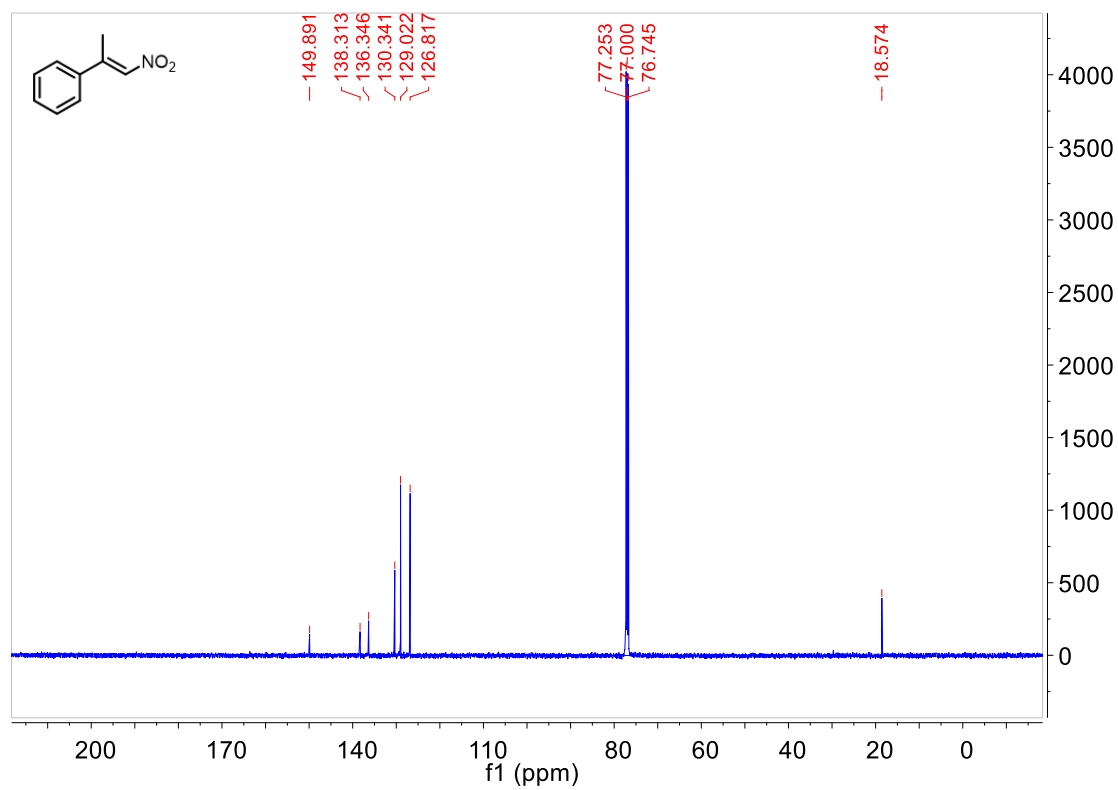
## 6. <sup>13</sup>C NMR



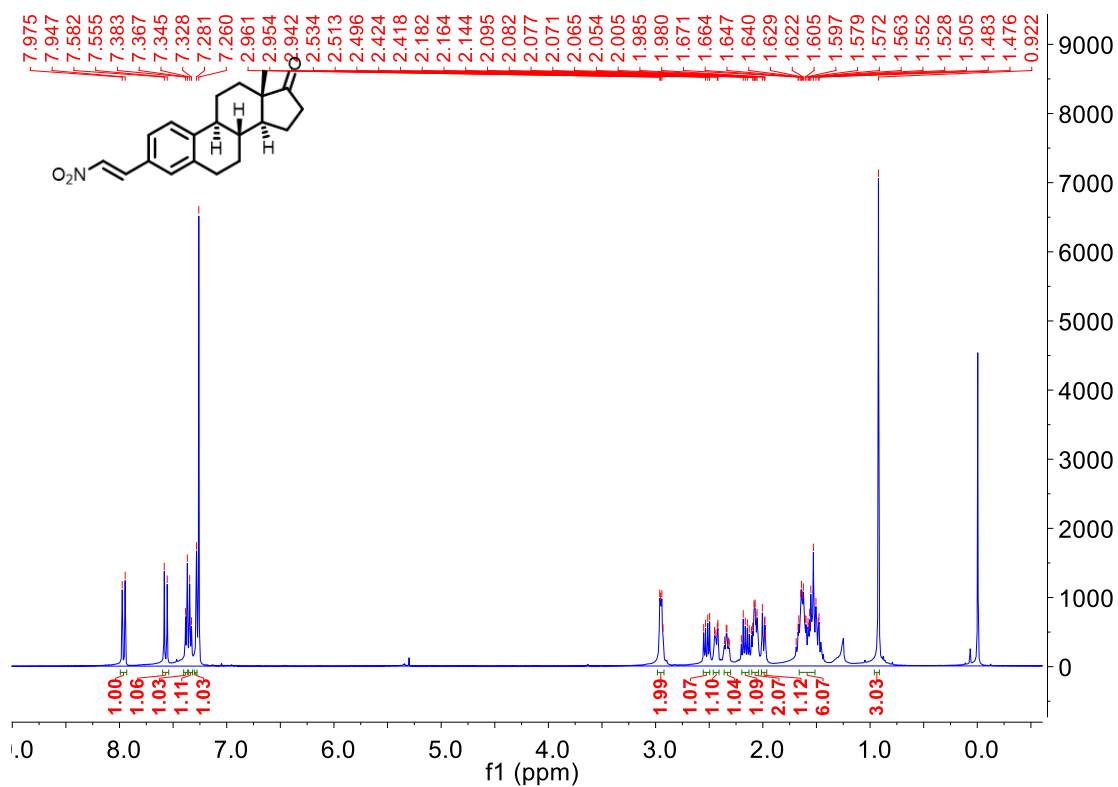
## 7. <sup>1</sup>H NMR



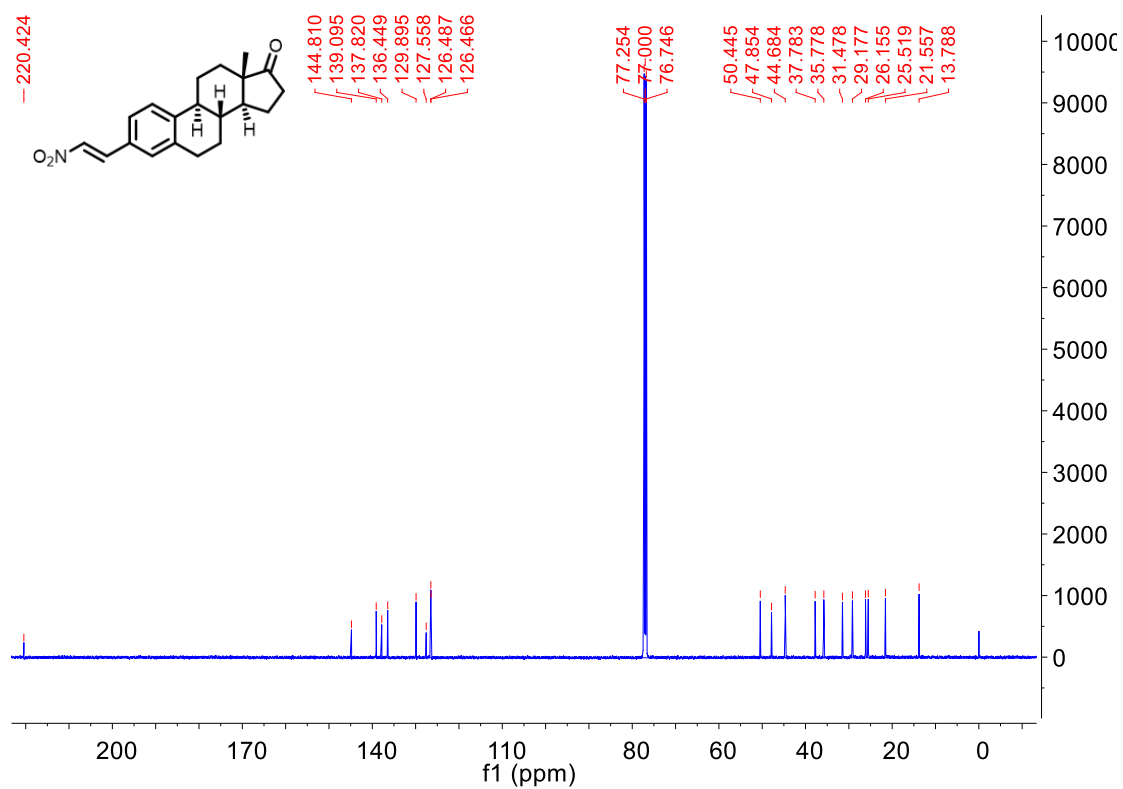
## 7. <sup>13</sup>C NMR



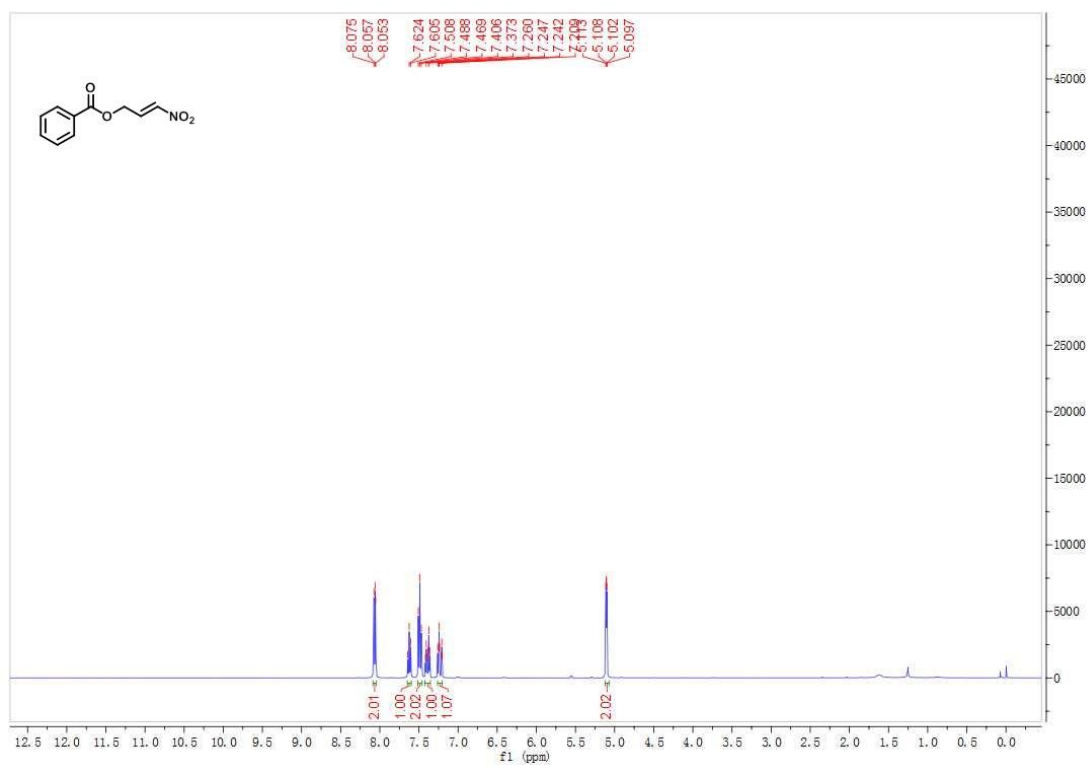
## 8. <sup>1</sup>H NMR



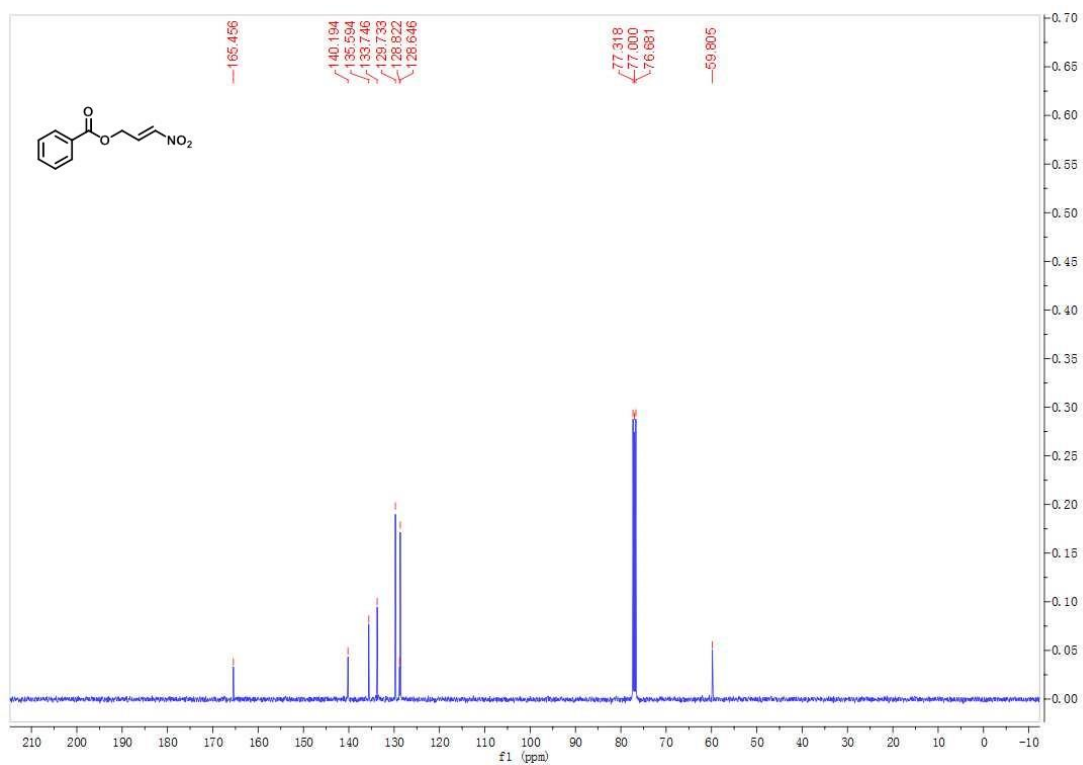
## 8. <sup>13</sup>C NMR



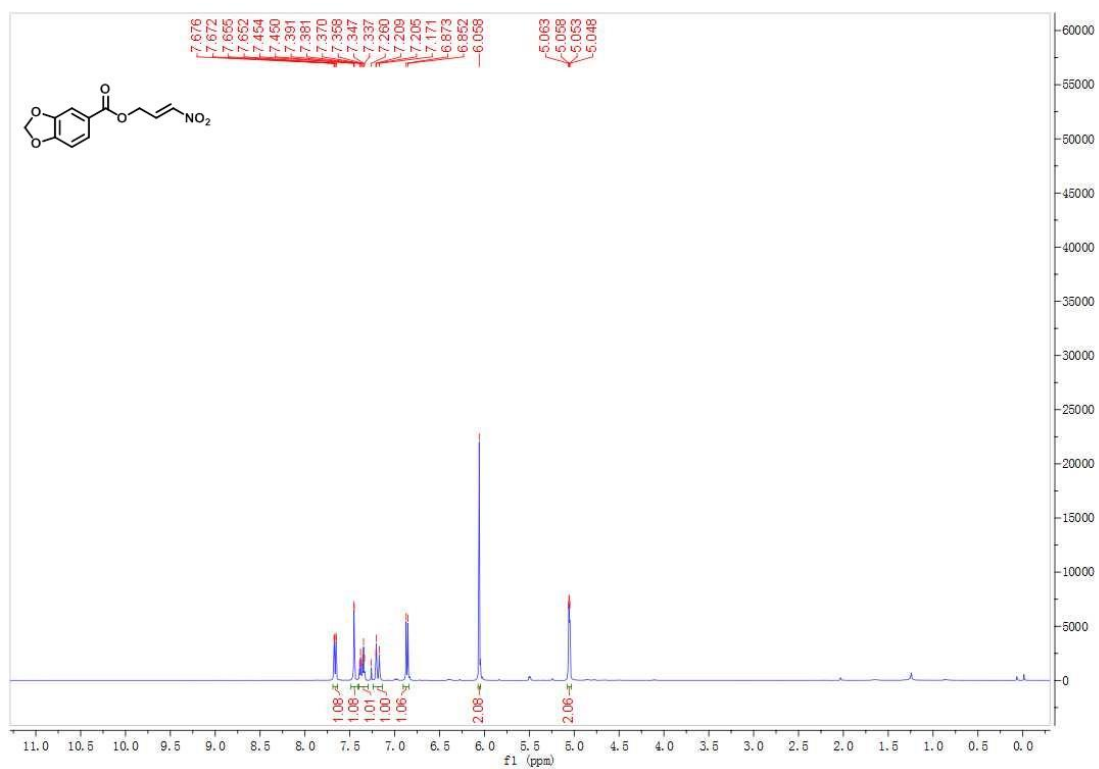
## 9. <sup>1</sup>H NMR



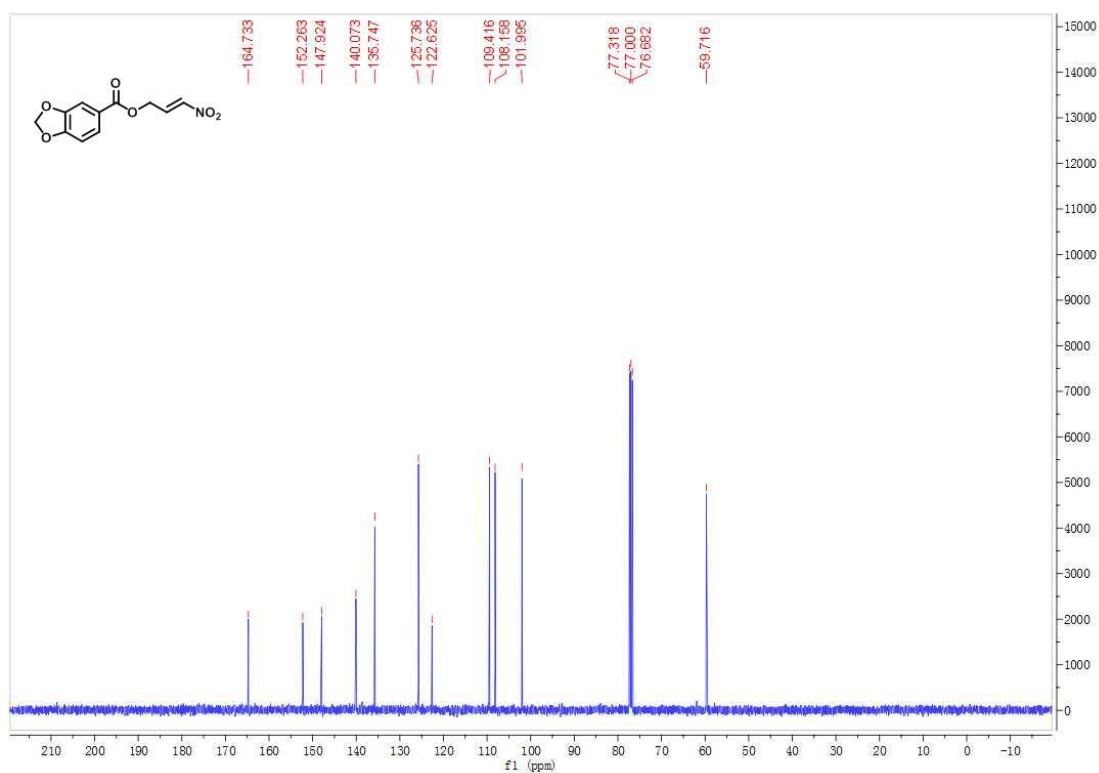
## 9. <sup>13</sup>C NMR



## 10. <sup>1</sup>H NMR

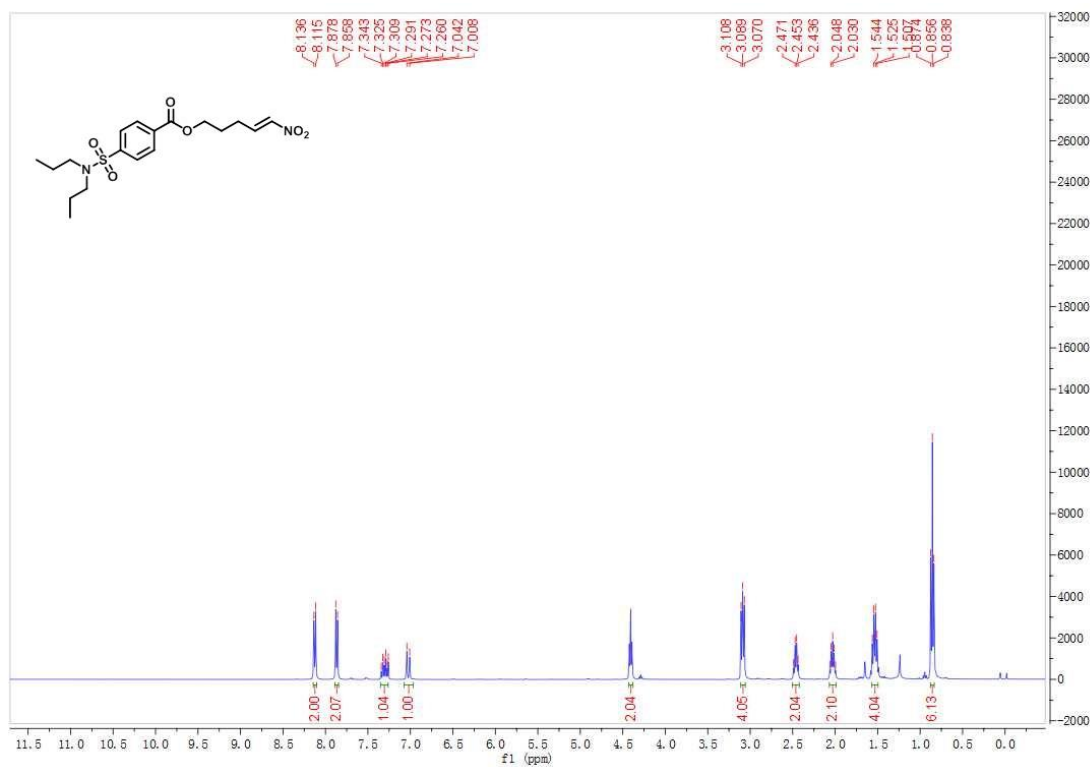


## 10. <sup>13</sup>C NMR

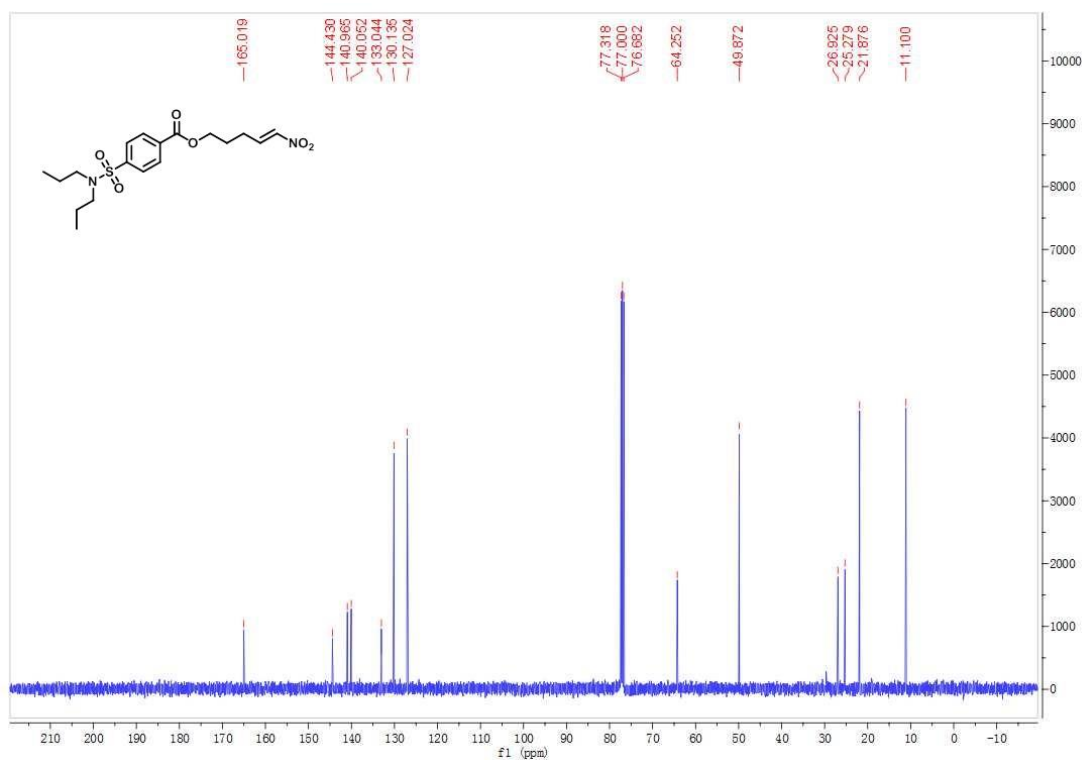




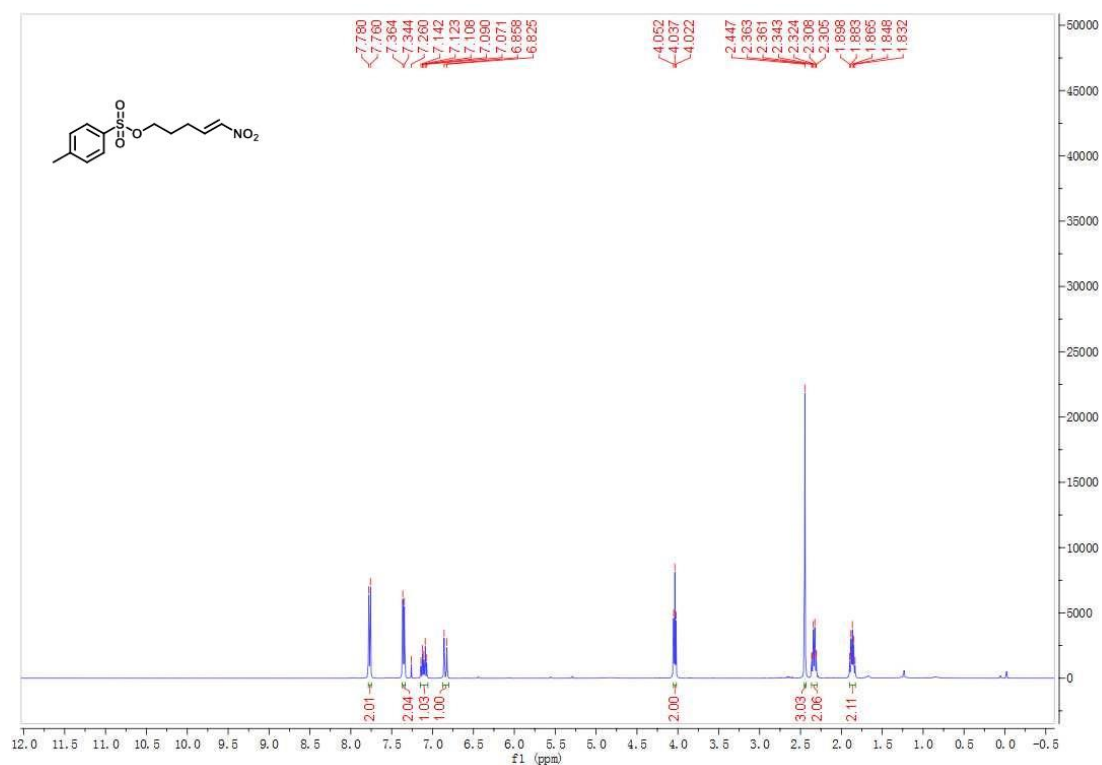
## 11. <sup>1</sup>H NMR



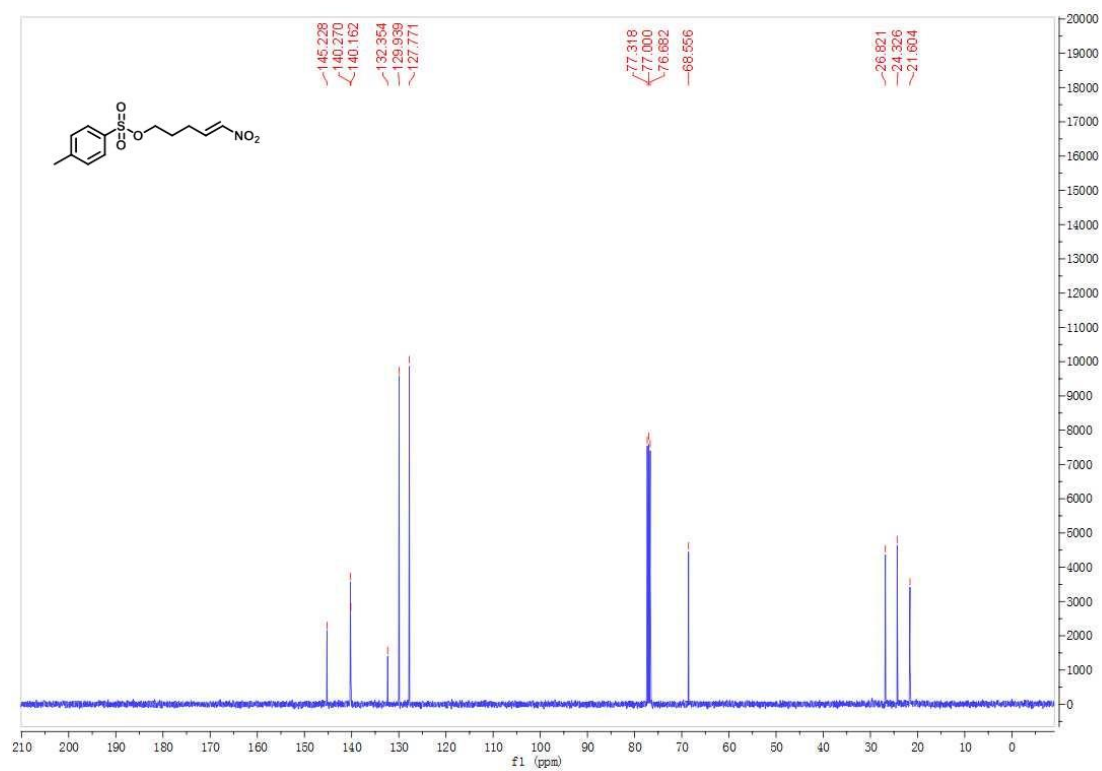
## 11. <sup>13</sup>C NMR



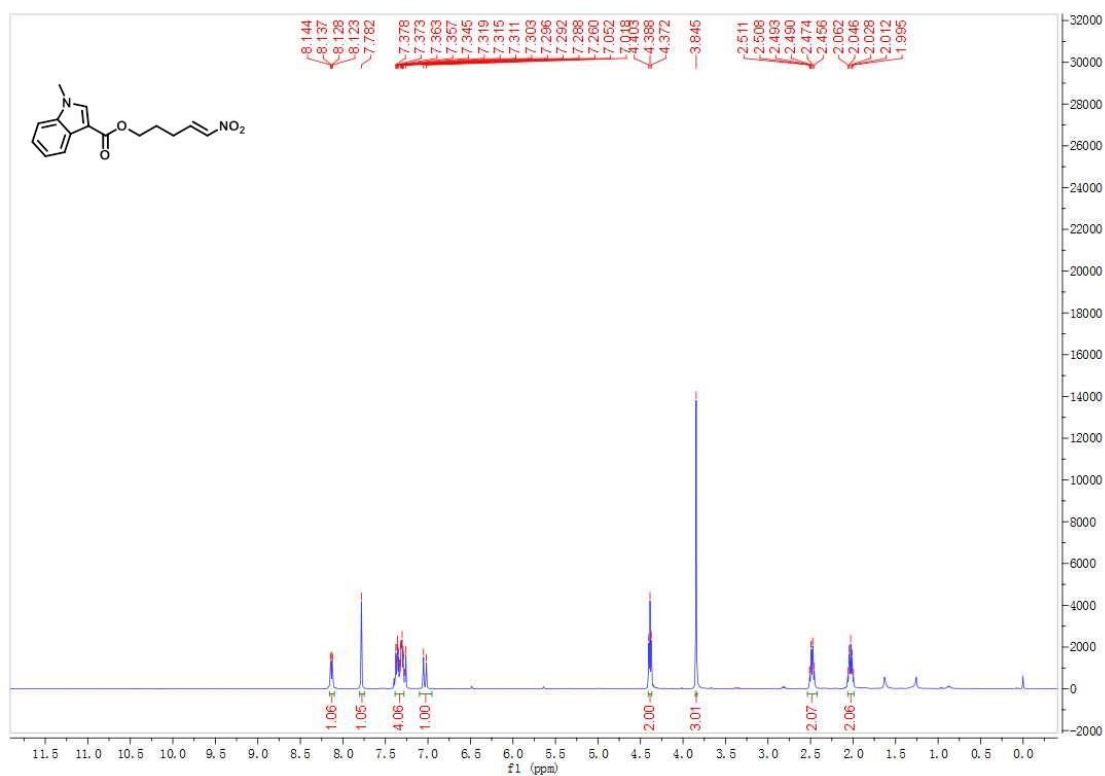
## 12. <sup>1</sup>H NMR



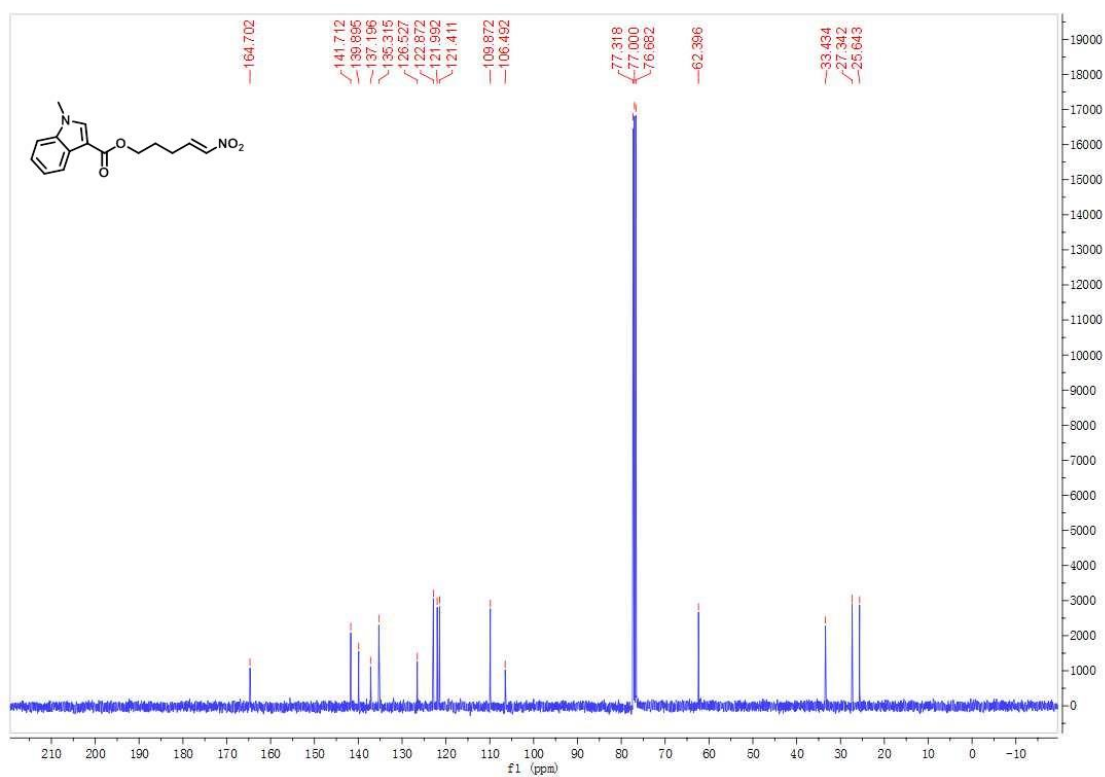
## 12. <sup>13</sup>C NMR



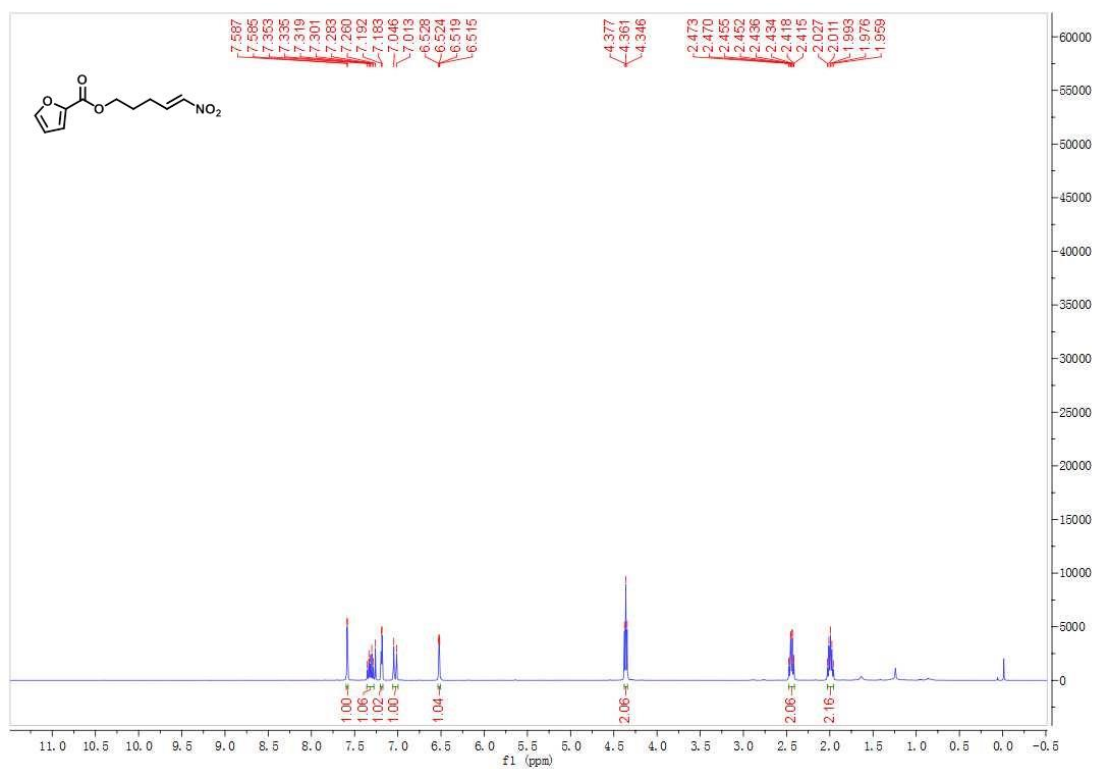
### 13. <sup>1</sup>H NMR



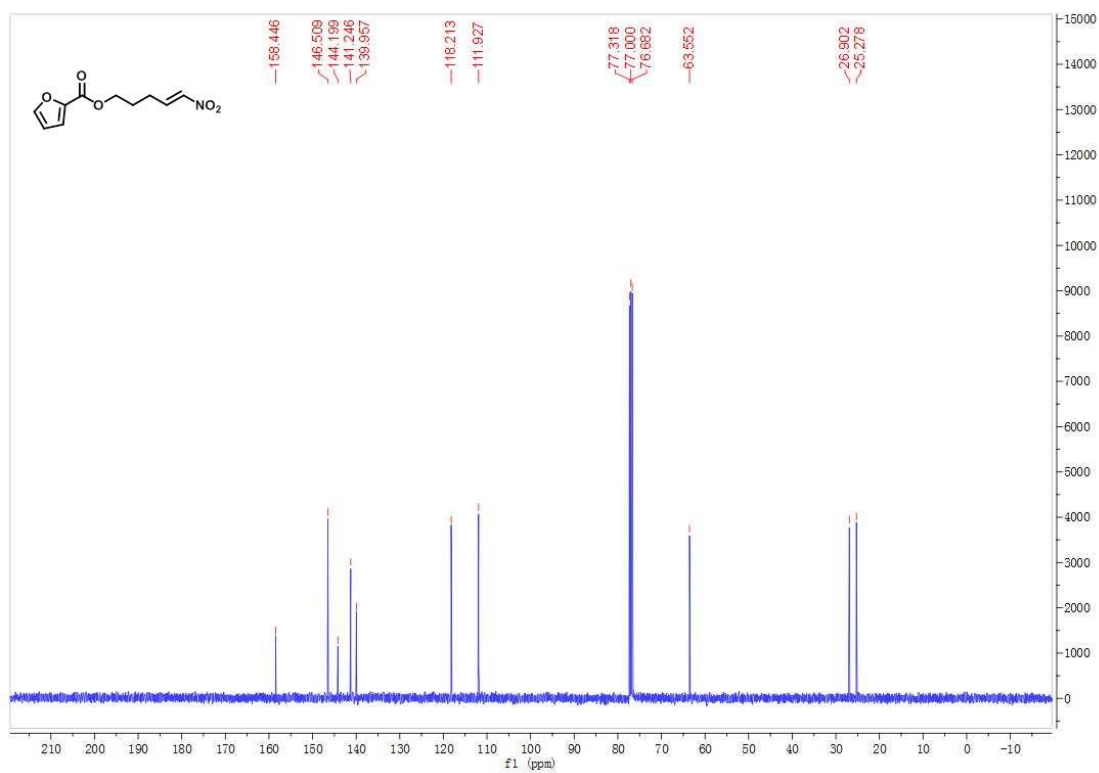
### 13. <sup>13</sup>C NMR



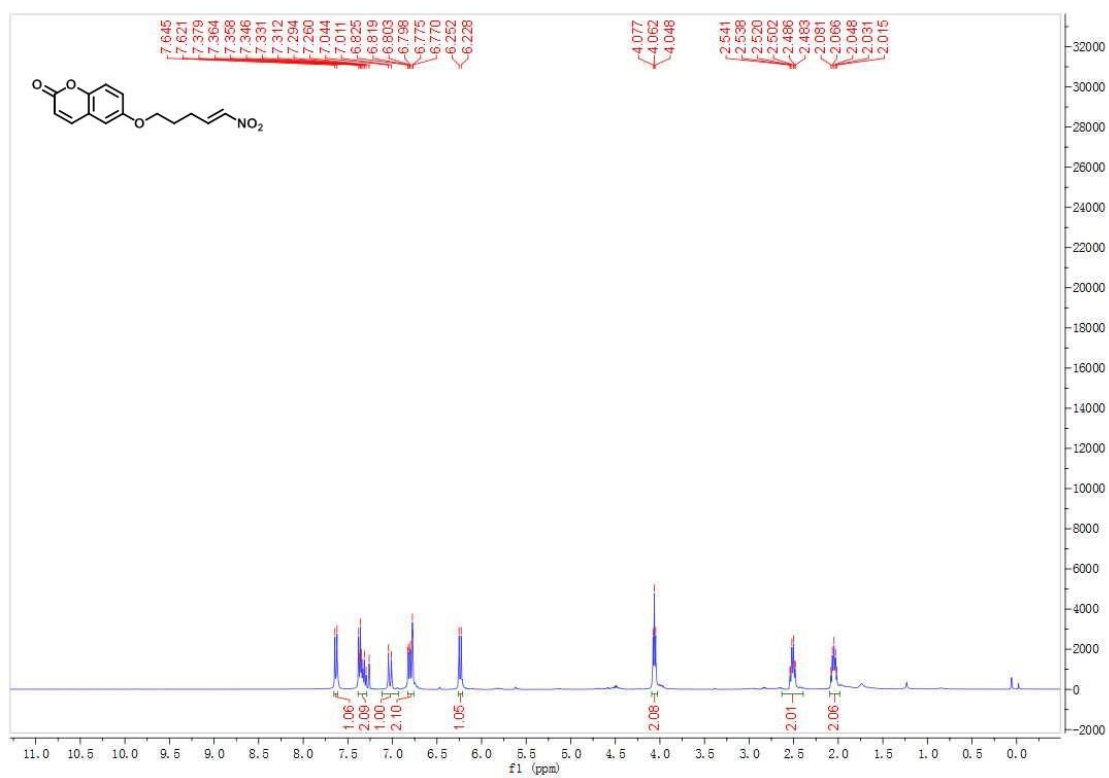
## 14. <sup>1</sup>H NMR



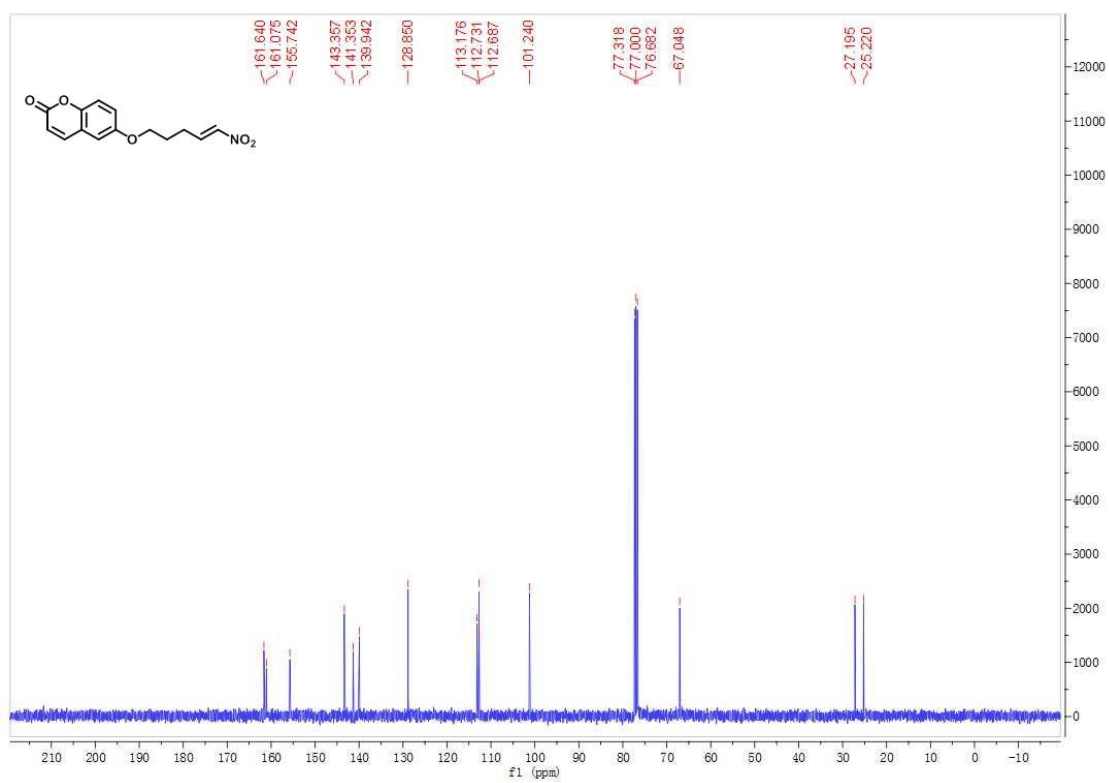
## 14. <sup>13</sup>C NMR



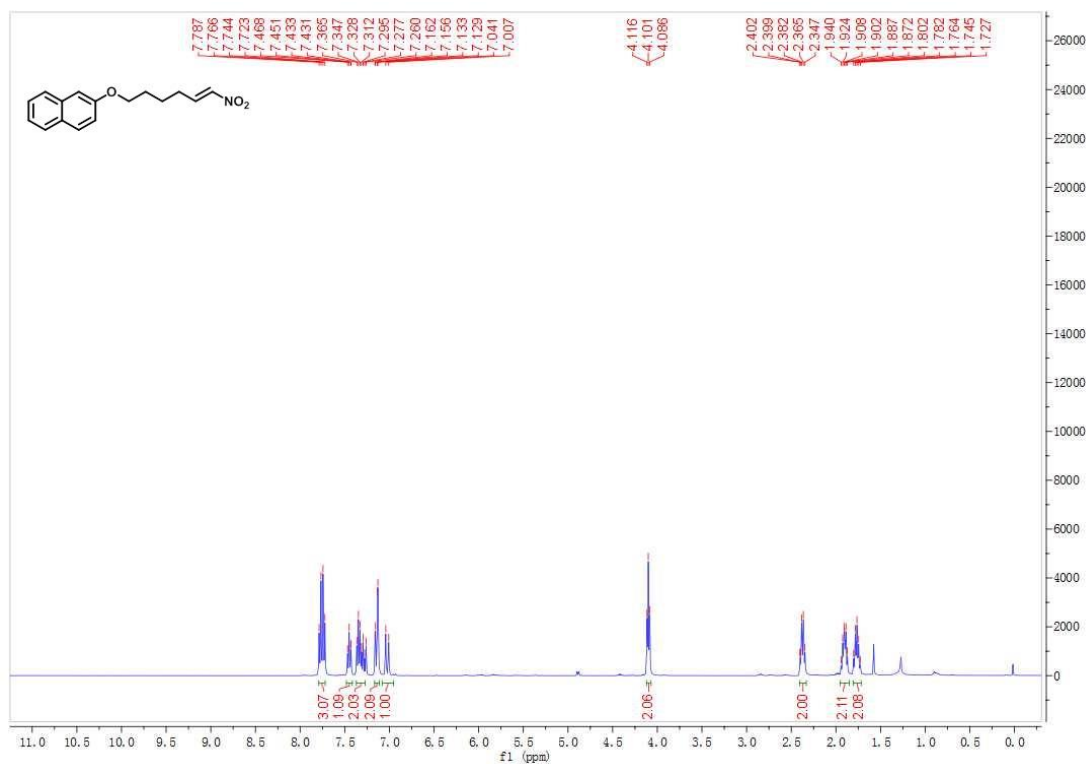
## 15. <sup>1</sup>H NMR



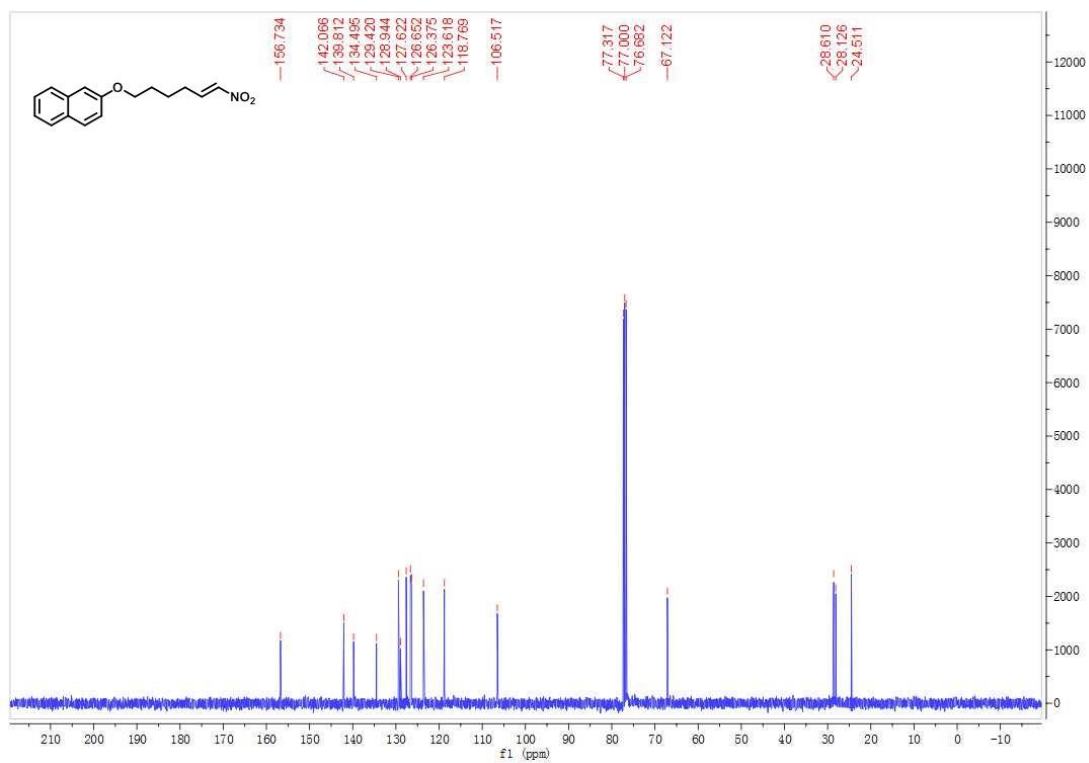
## 15. <sup>13</sup>C NMR



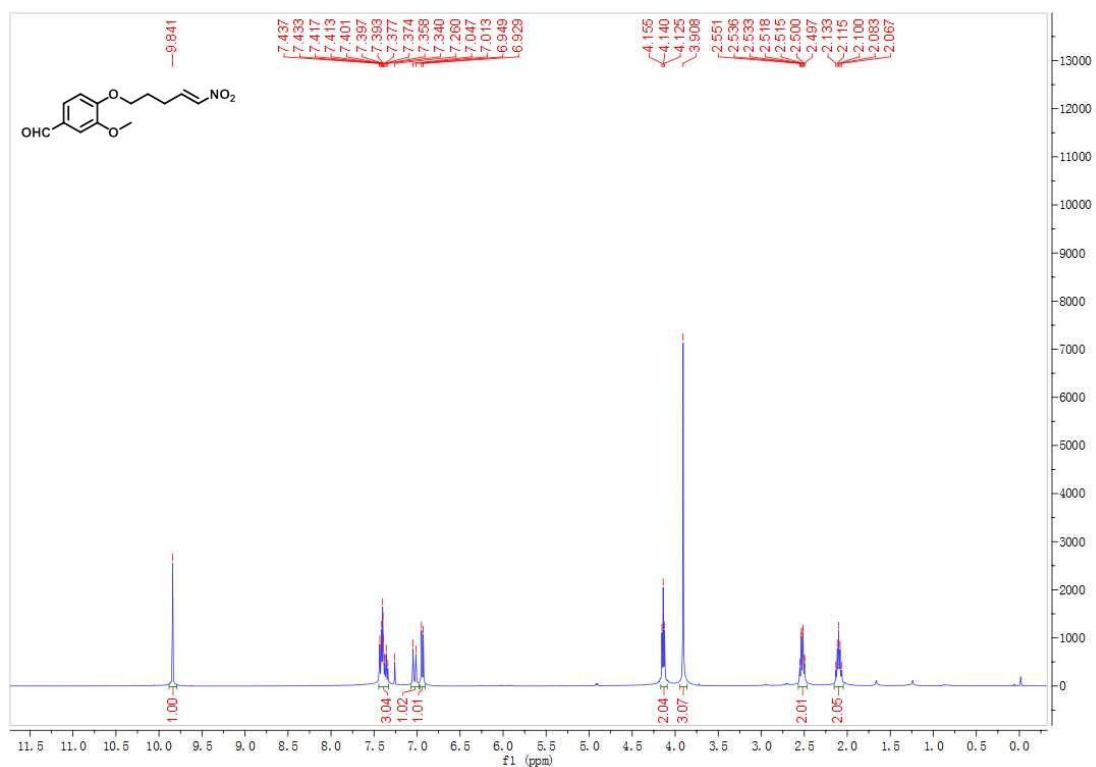
## 16. <sup>1</sup>H NMR



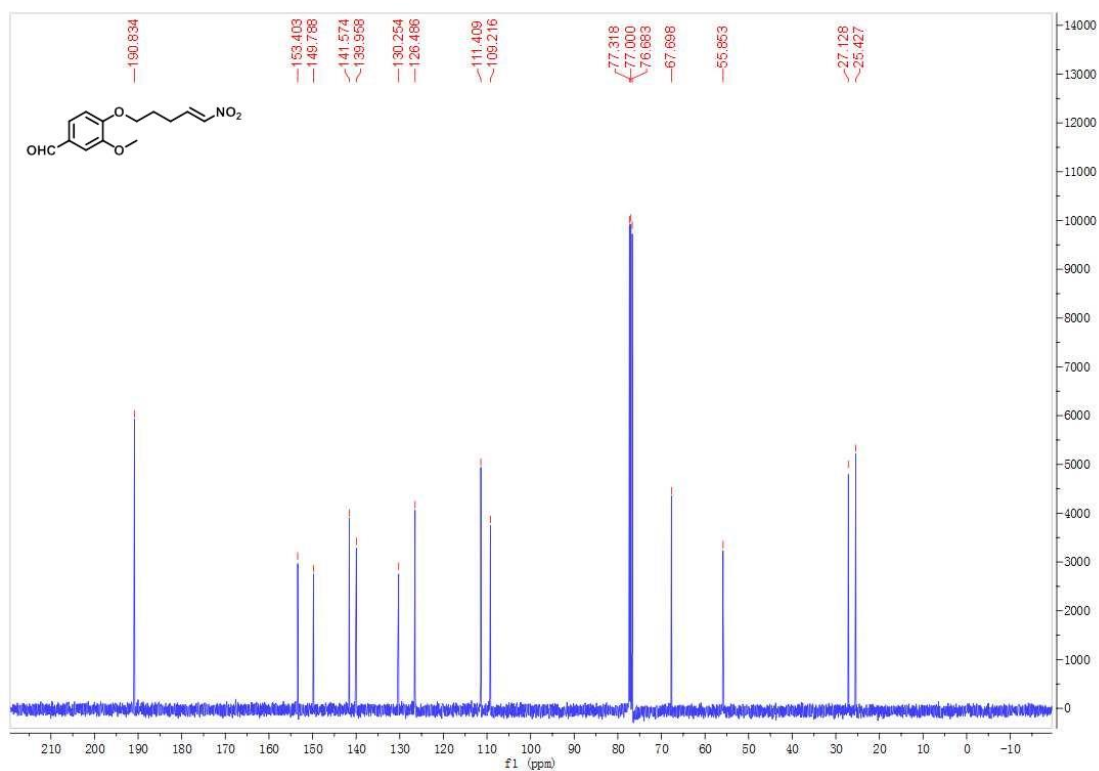
## 16. <sup>13</sup>C NMR



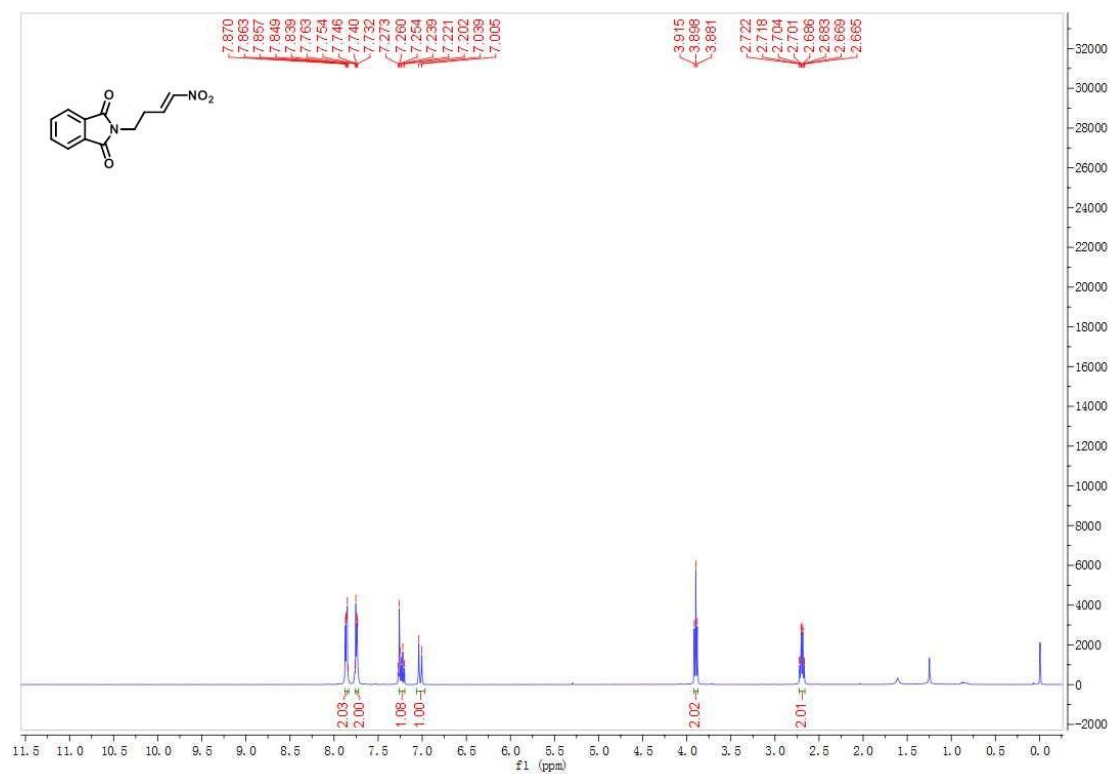
## 17. <sup>1</sup>H NMR



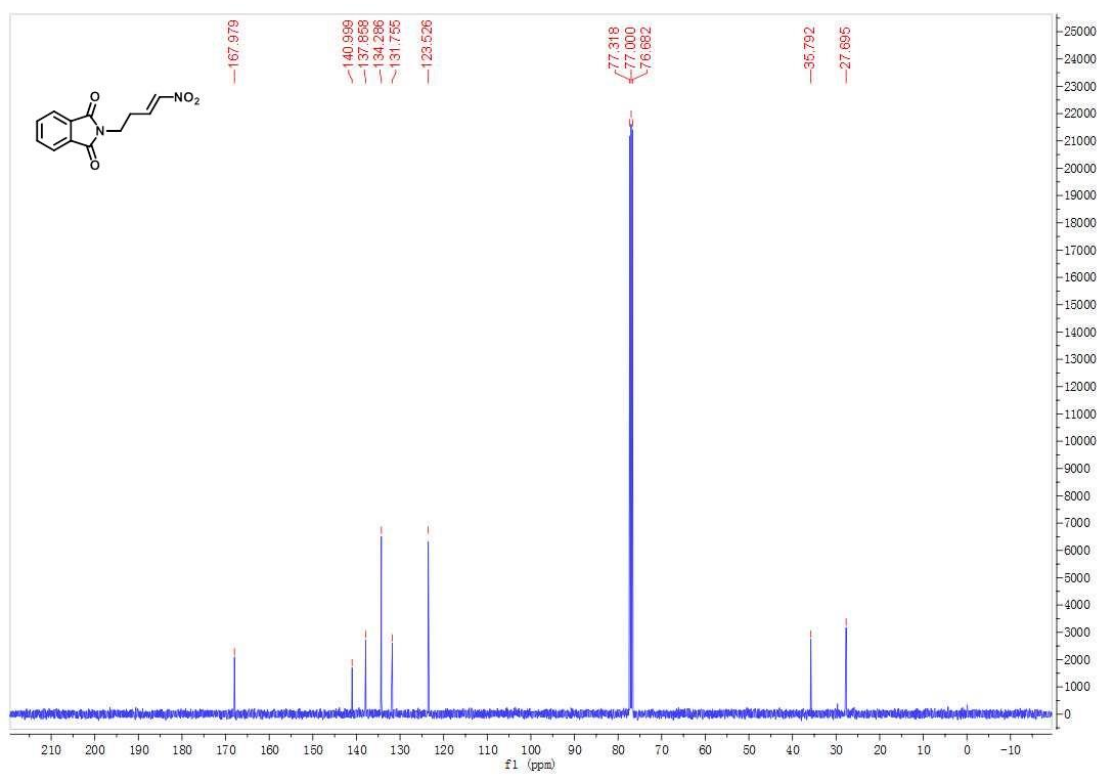
## 17. <sup>13</sup>C NMR



## 18. <sup>1</sup>H NMR

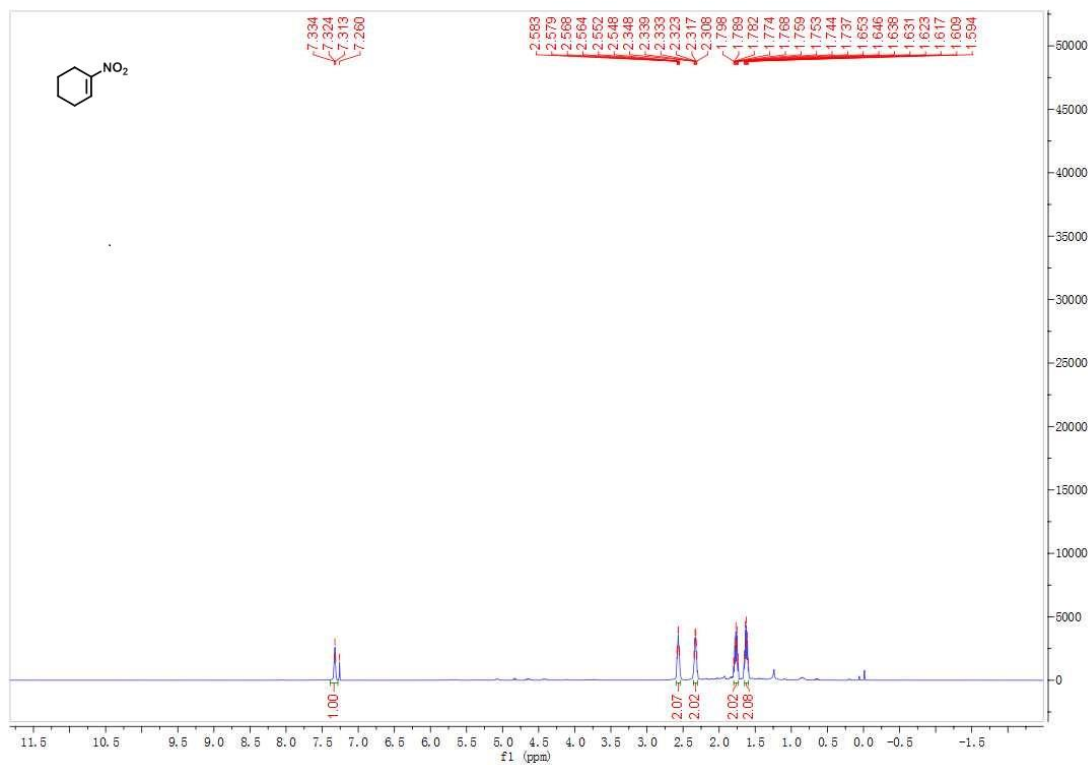


## 18. <sup>13</sup>C NMR

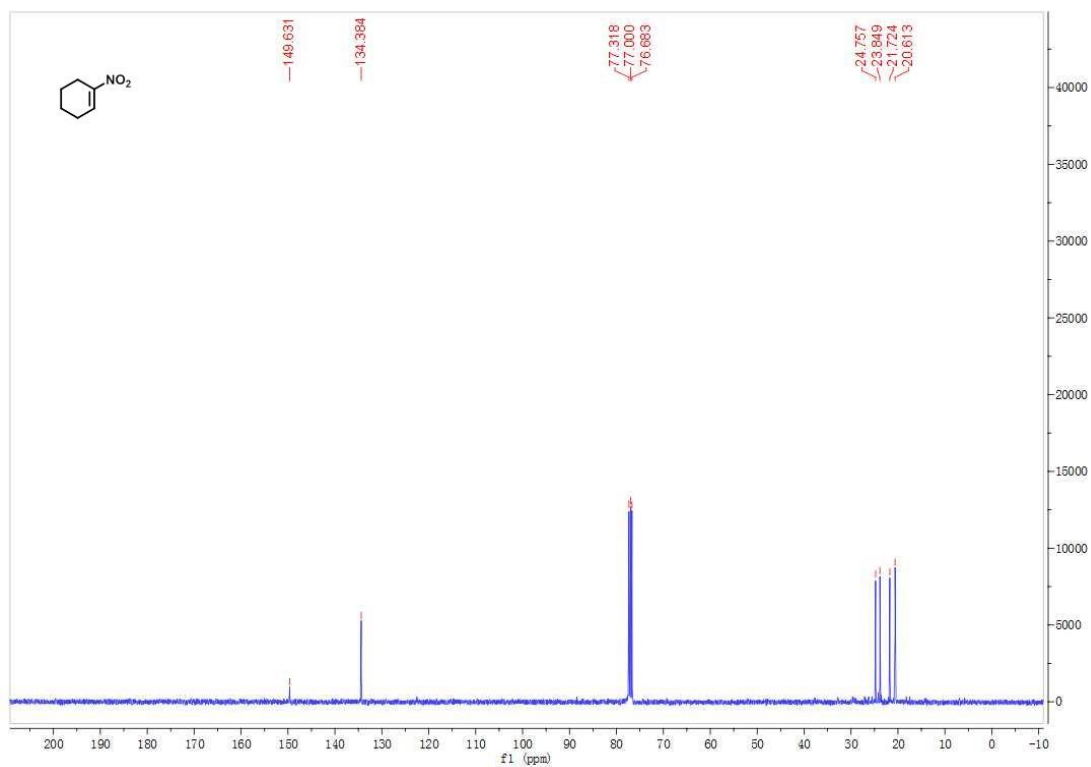




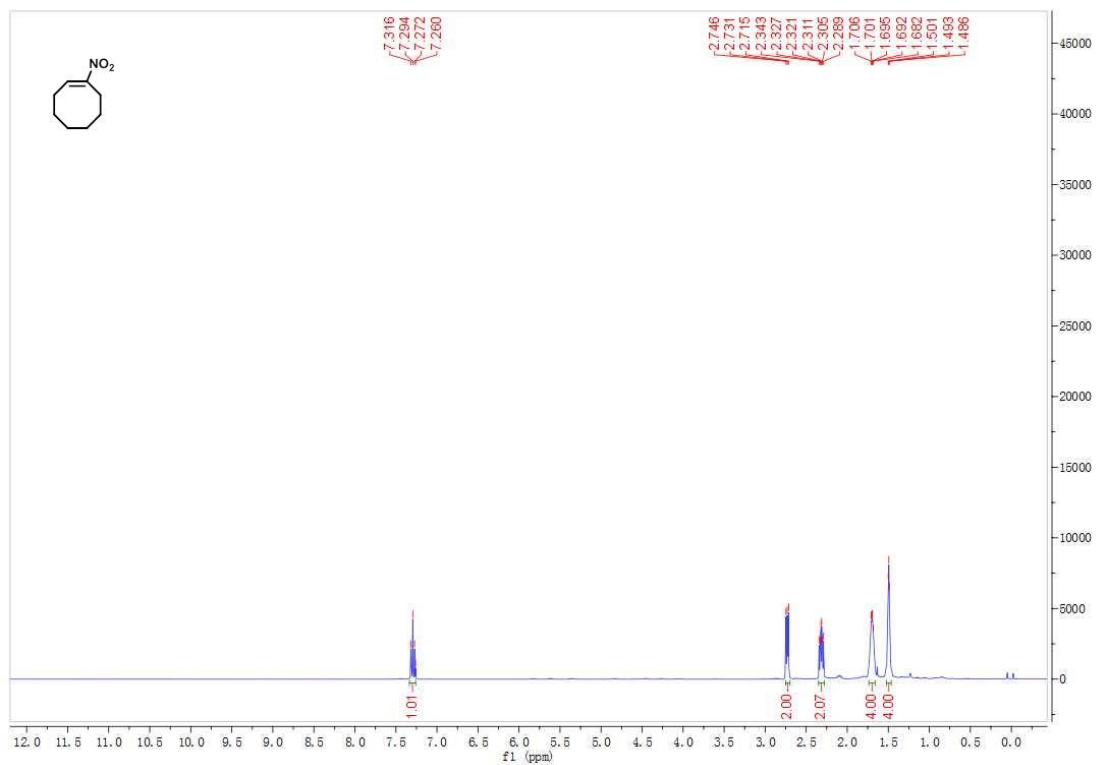
## 19. <sup>1</sup>H NMR



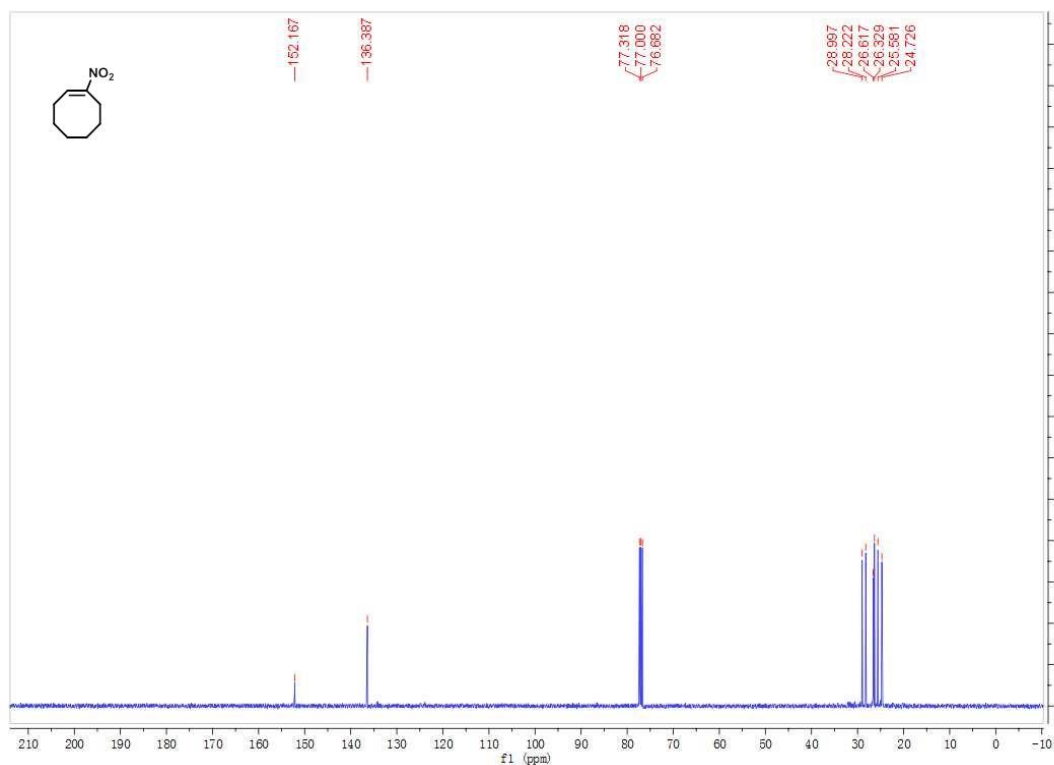
## 19. <sup>13</sup>C NMR



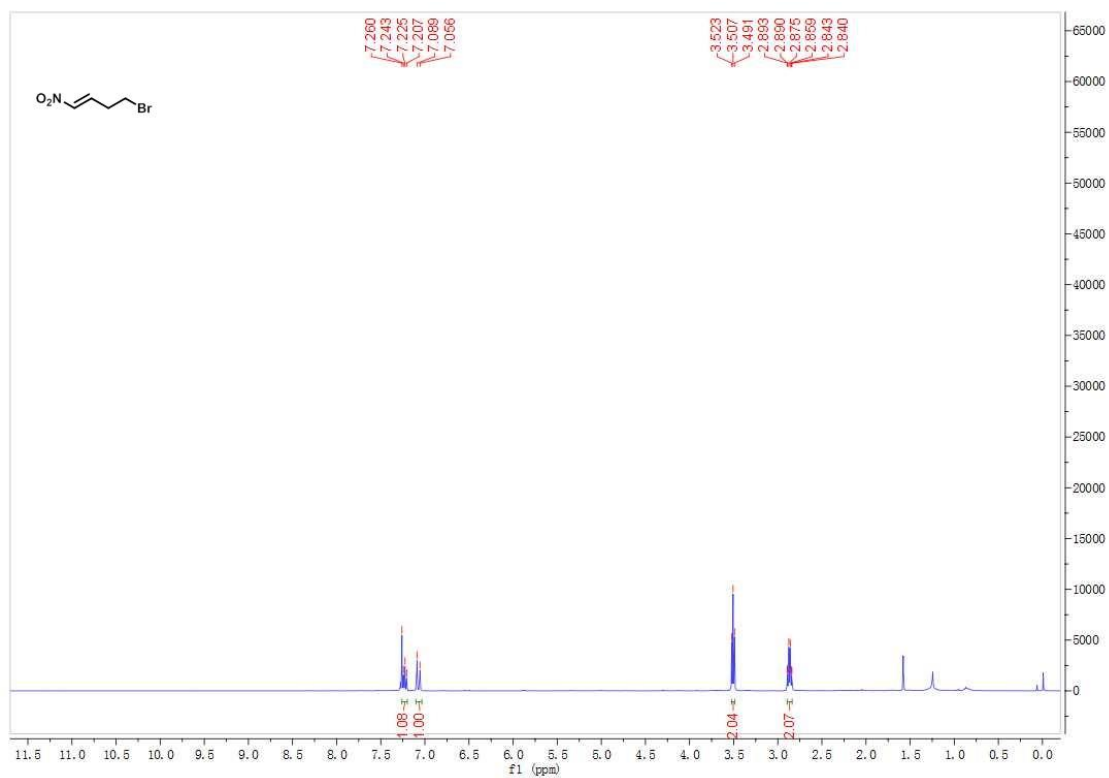
## 20. <sup>1</sup>H NMR



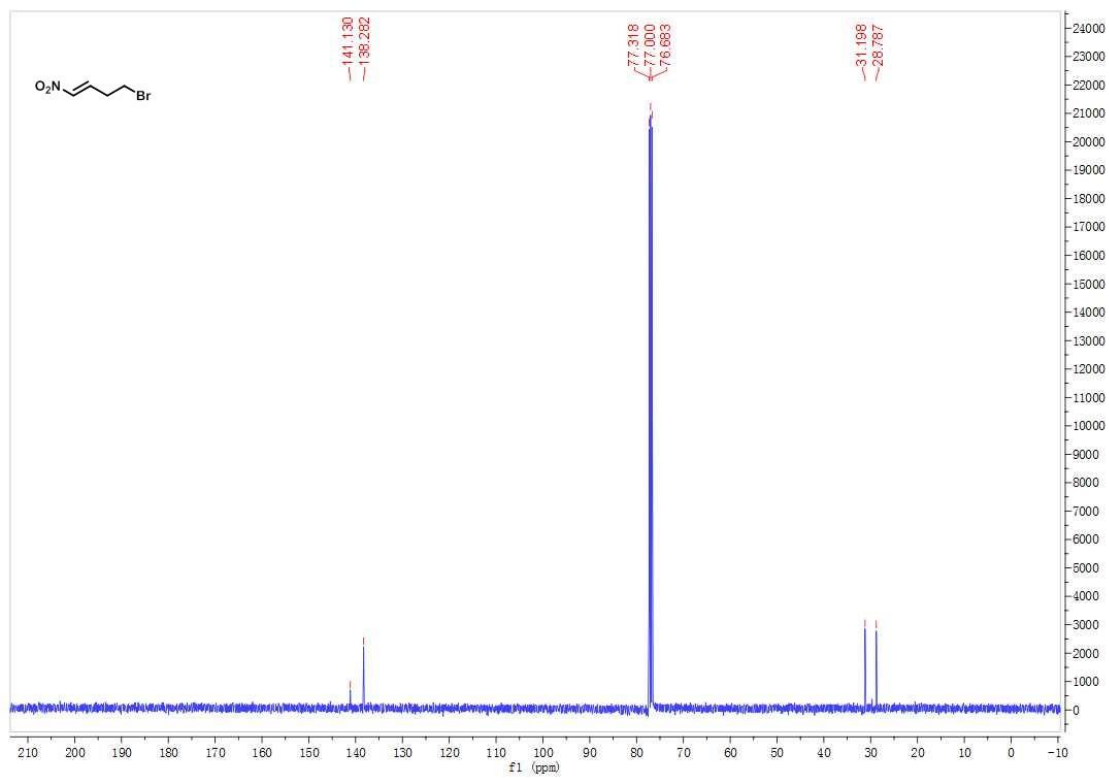
## 20. <sup>13</sup>C NMR



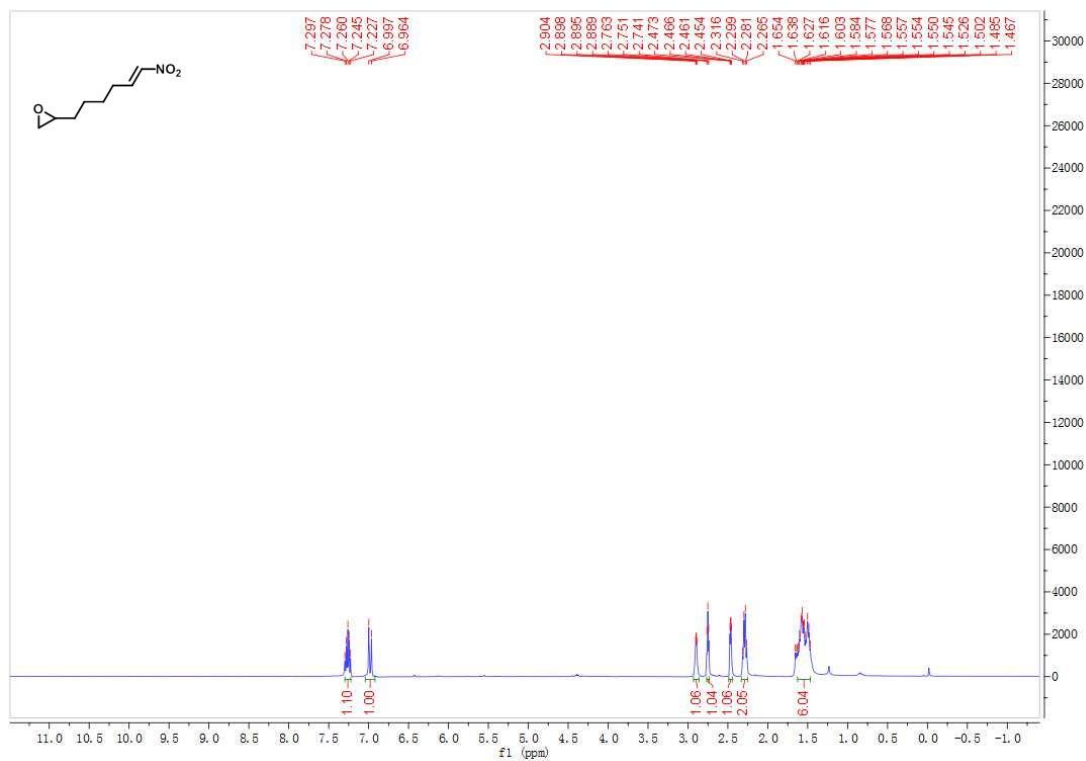
## 21. $^1\text{H}$ NMR



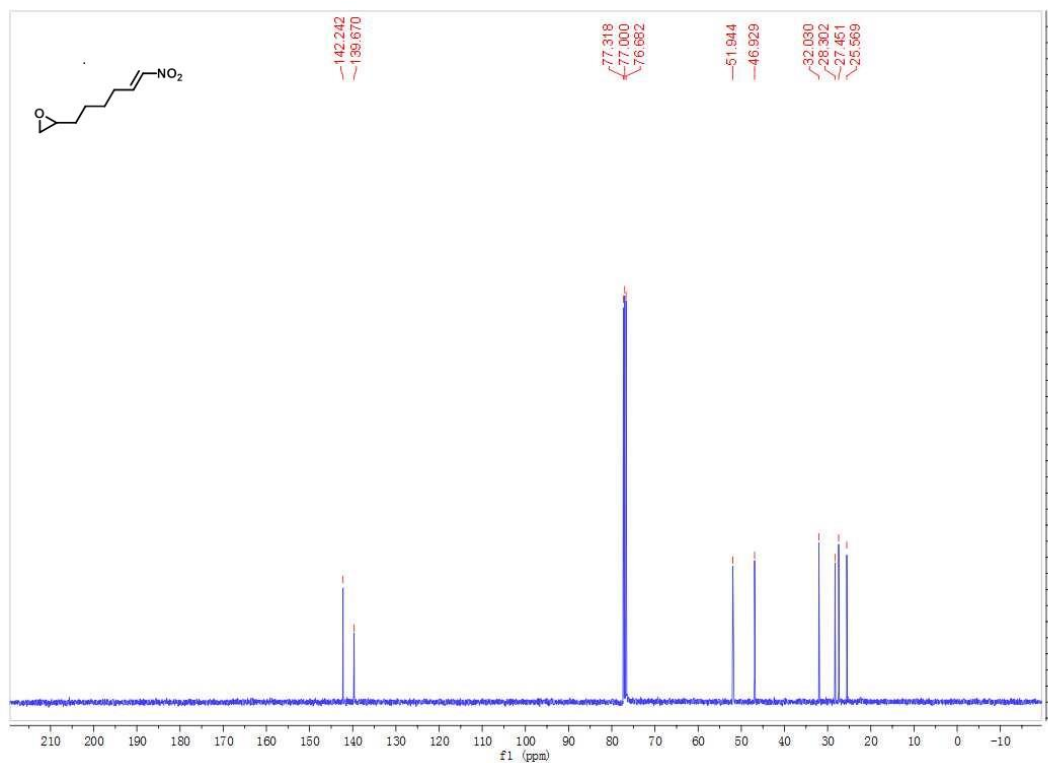
## 21. $^{13}\text{C}$ NMR



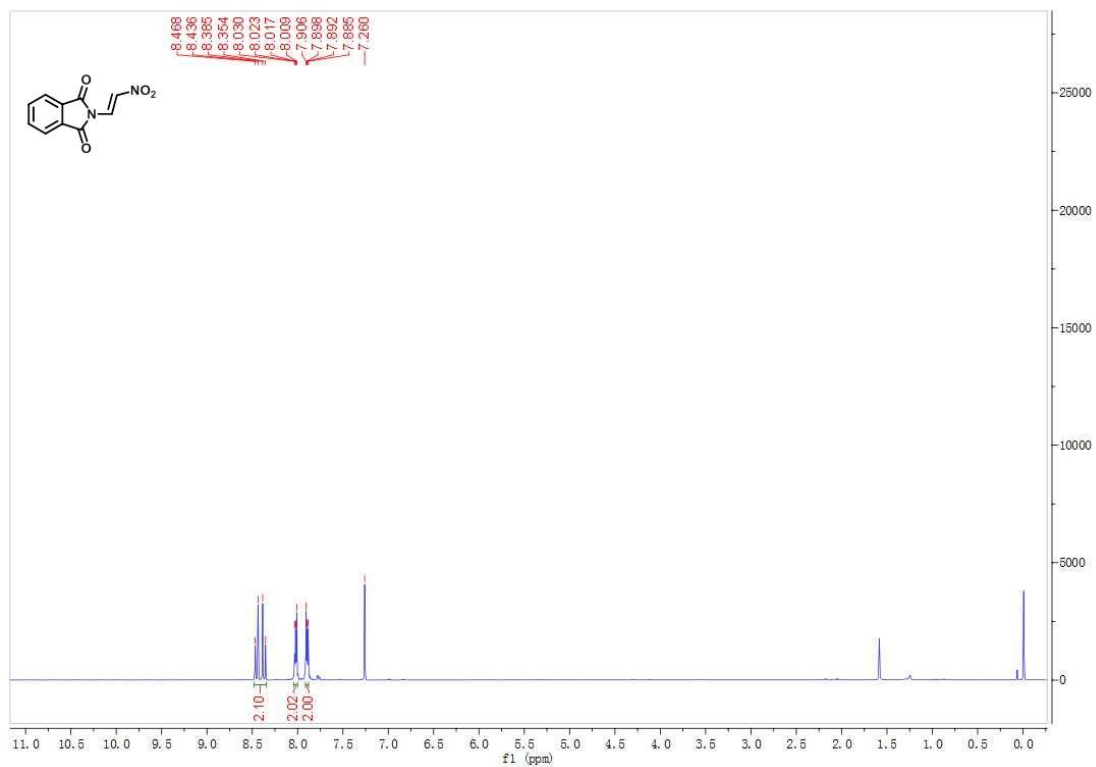
## 22. <sup>1</sup>H NMR



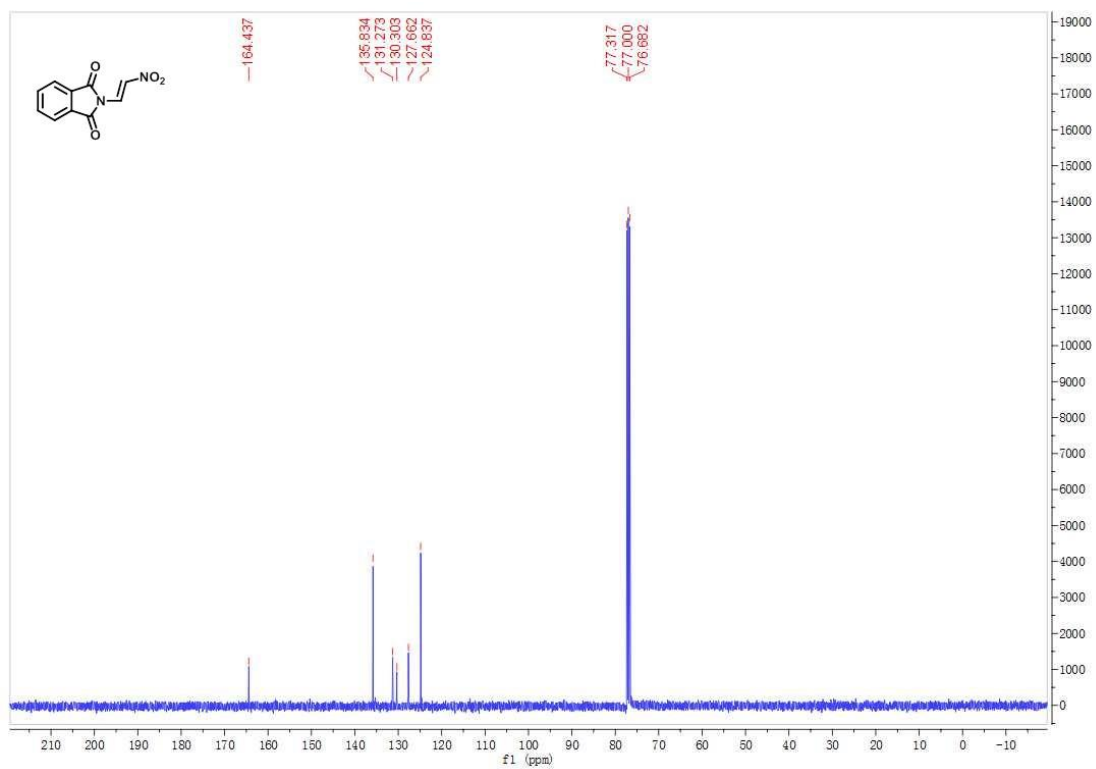
## 22. <sup>13</sup>C NMR



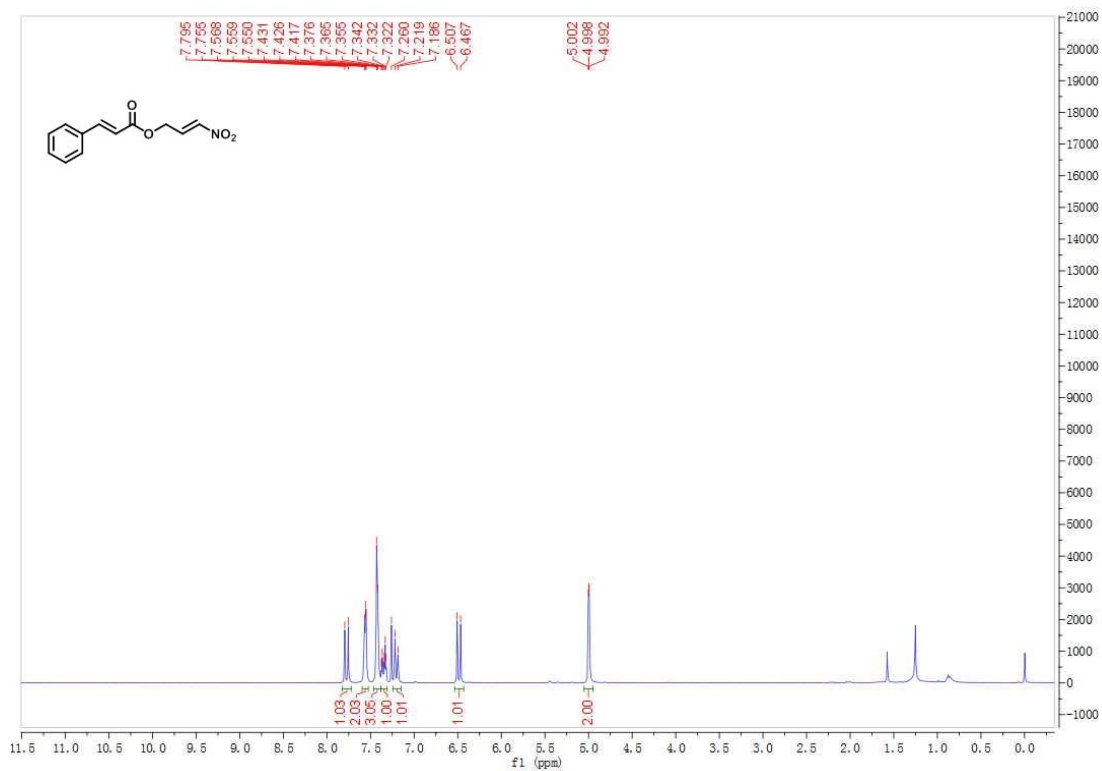
## 23. <sup>1</sup>H NMR



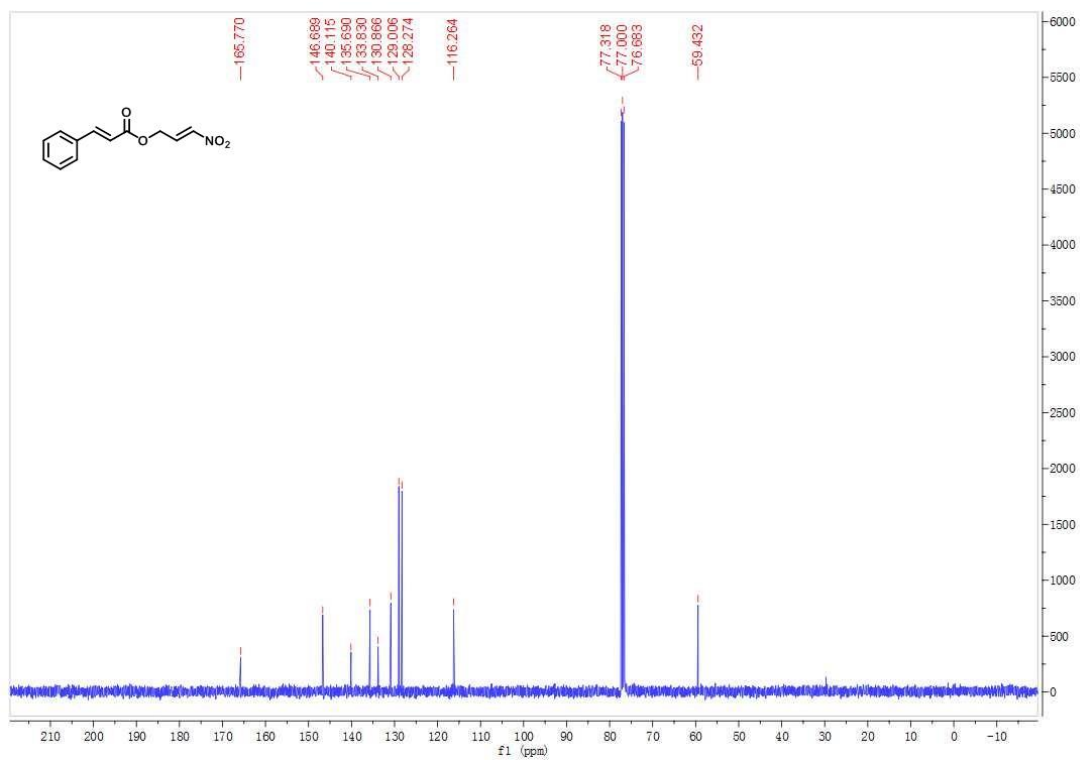
## 23. <sup>13</sup>C NMR



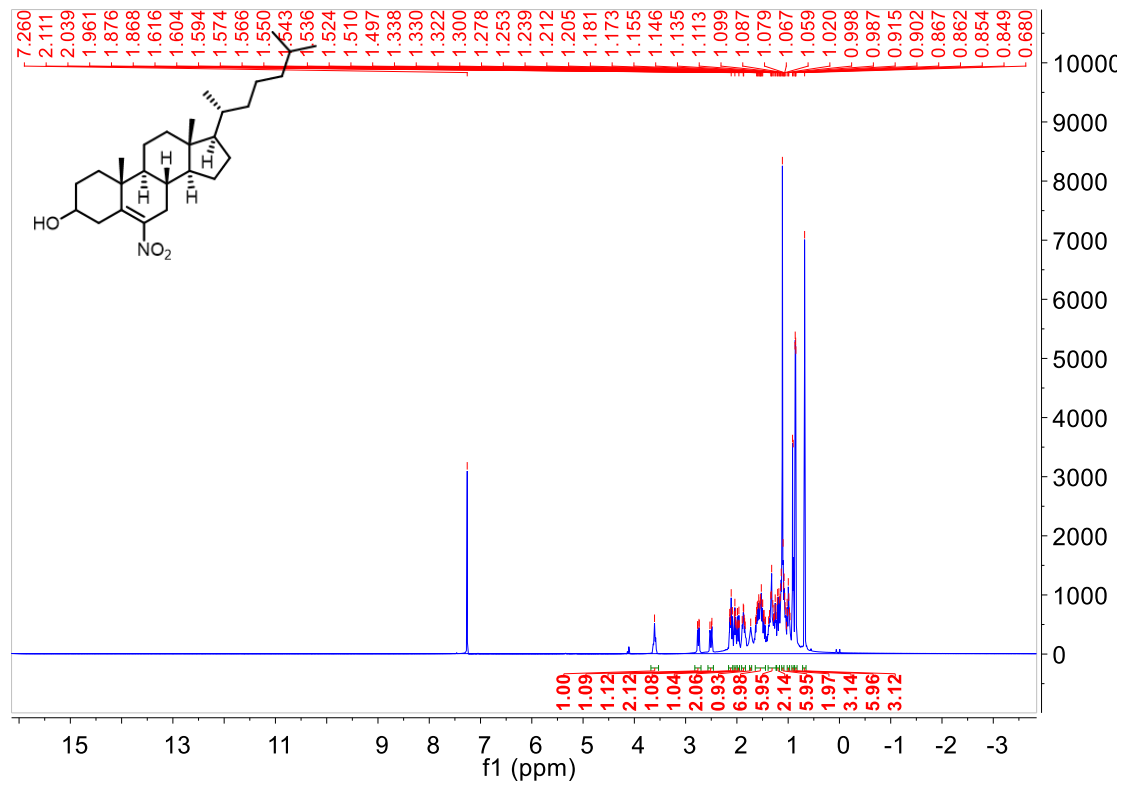
## 24. <sup>1</sup>H NMR



## 24. <sup>13</sup>C NMR



## 25. <sup>1</sup>H NMR



## 25. <sup>13</sup>C NMR

