

## Supporting Information

### **Gold-catalyzed formal (3+2) and (4+2) cycloaddition reactions using propiolates: assembly of 2,3-dihydrofurans and 3,4-dihydropyrans via a multistep cascade process**

*Congdi Zhang<sup>a</sup>, Xiao-Qian Zhang<sup>a</sup>, Yu Nie<sup>a</sup>, Chao Wang<sup>a</sup>, Tianyi Xu<sup>a</sup>, Junjie Zhang<sup>a</sup>, Lu Bai<sup>b</sup>, Chao Feng<sup>b</sup>, Youliang Wang<sup>a\*</sup>*

<sup>a</sup> School of Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, Xi'an Jiaotong University, No.28, West Xianning Road, Xi'an, Shaanxi, 710049, P.R. China. <sup>b</sup> Instrumental Analysis Center, Xi'an Jiaotong University, No.28, West Xianning Road, Xi'an, Shaanxi, 710049, P.R. China

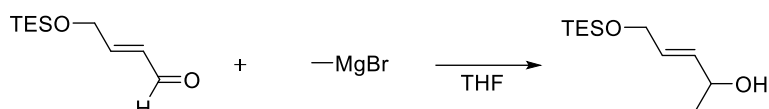
\*Corresponding Author, email: youliangwang@xjtu.edu.cn

<b>Contents</b>	<b>Page number</b>
<b>General</b>	S2
<b>Preparation of the unknown substrates</b>	S3
<b>Reaction condition optimizations</b>	S6
<b>Scope of the diol or protected diol substrates</b>	S8
<b>Scope of the propiolate substrates</b>	S22
<b>Synthetic applications</b>	S35
<b>Spectra</b>	S40

## General

NMR spectra were recorded on a Bruker-400 MHz.  $^1\text{H}$  NMR spectra were recorded at 400 MHz and data are reported as follows: chemical shifts in ppm using residue solvent peak as internal standard ( $\text{CDCl}_3$   $\delta$  7.26 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of nonequivalent resonances), integration.  $^{13}\text{C}$  NMR spectra were recorded at 101 MHz and data are reported as follows: chemical shift in ppm using solvent residue peak as internal indicator ( $\text{CDCl}_3$   $\delta$  77.16 ppm). High resolution mass spectra were performed on a WATERS I-Class VION IMS QToF at the Instrumental Analysis Center of Xi'an Jiaotong University and are given in m/z. GCMS were performed on Agilent 8860 GC/5977B GC/MSD System and are given in m/z. All reactions were carried out in glassware dried overnight in an oven at 110 °C. All reactions were performed under air. Commercial reagents and solvents were used without further purification unless stated otherwise. TLC was performed on pre-coated glass plates visualized either with a UV lamp (254 nm), or using solutions of  $\text{KMnO}_4$ - $\text{K}_2\text{CO}_3$  in water followed by heating. Flash chromatography was performed on silica gel (230-400 mesh).

**(E)-5-((triethylsilyl)oxy)pent-3-en-2-ol (2g)**



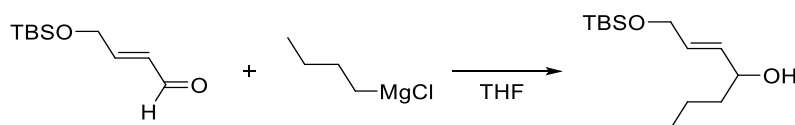
To a solution of the aldehyde (432.3 mg, 2 mmol) in THF (10 mL) was added a solution of methyl magnesium bromide (2 M, 1.5 mL, 3 mmol) at 0 °C. The reaction mixture was stirred for 1h at room temperature. After the reaction was complete as monitored by TLC, it was quenched by saturated aq. NH<sub>4</sub>Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Flash column chromatography (PE/EA=10/1) separation afforded alcohol **2g** (354.5 mg, 1.64 mmol, 82%) as colorless oil.

R<sub>f</sub> 0.21 (Petroleum ether/EtOAc =10/1)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) 5.76 – 5.74 (m, 2H), 4.43 – 4.25 (m, 1H), 4.16 – 4.15 (m, 2H), 1.26 (d, *J* = 6.4 Hz, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 8.2 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 134.5, 129.3, 68.4, 63.0, 23.3, 6.9, 4.6.

**(E)-1-((*t*-butyldimethylsilyl)oxy) oct-2-en-4-ol (2i)**



To a solution of the aldehyde (400.7 mg, 2 mmol) in THF (10 mL) was added a solution of butyl magnesium chloride (2 M, 1.5 mL, 3 mmol) at 0 °C. The reaction mixture was stirred for 1h at room temperature. After the reaction was complete as monitored by TLC, it was quenched by saturated aq. NH<sub>4</sub>Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Flash column chromatography (PE/EA=10/1) separation afforded alcohol **2i** (356.7 mg, 1.38 mmol, 69%) as colorless oil.

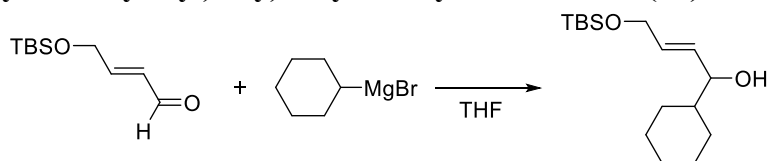
R<sub>f</sub> 0.21 (Petroleum ether/EtOAc =10/1)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 5.73 – 5.70 (m, 2H), 4.17 (d, *J* = 3.5 Hz, 2H), 4.13 – 4.08 (m, 1H), 1.52 (m, 3H), 1.41 – 1.30 (m, 4H), 0.90 (s, 9H), 0.87 (m, 2H), 0.06 (s, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 133.1, 130.2, 72.6, 63.3, 37.0, 27.7, 26.1, 22.7, 18.5, 14.2, -5.1.

HRMS (ESI) *m/z*: [M+K]<sup>+</sup> calcd for C<sub>14</sub>H<sub>30</sub>KO<sub>2</sub>Si 297.1647; found 297.1628.

**(E)-4-((*t*-butyldimethylsilyl) oxy)-1-cyclohexylbut-2-en-1-ol (2k)**



To a solution of the aldehyde (400.7 mg, 2 mmol) in THF (10 mL) was added a solution of cyclohexyl magnesium chloride (2 M, 1.5 mL, 3 mmol) at 0 °C. The reaction mixture was stirred for 1h at room temperature. After the reaction was complete as monitored by TLC, it was quenched by saturated aq. NH<sub>4</sub>Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Flash column chromatography (PE/EA=10/1) separation afforded alcohol **2k** (409.7 mg, 1.44 mmol, 72%) as colorless oil.

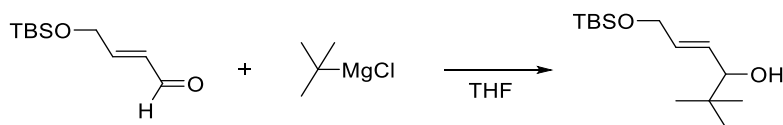
R<sub>f</sub> 0.21 (Petroleum ether/EtOAc =10/1)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 5.73 – 5.63 (m, 2H), 4.19 – 4.11 (m, 2H), 3.88 – 3.79 (m, 1H), 1.86 – 1.80 (m, 1H), 1.76 – 1.69 (m, 2H), 1.67 – 1.62 (m, 2H), 1.43 – 1.34 (m, 1H), 1.22 – 1.03 (m, 3H), 1.03 – 0.94 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 131.7, 131.3, 77.6, 63.5, 43.9, 29.0, 28.8, 26.8, 26.4 (d, *J* = 6.0 Hz), 26.2, 18.7, -4.9.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>33</sub>O<sub>2</sub>Si 285.2244; found 285.2234.

**(E)-6-((*t*-butyldimethylsilyl) oxy)-2,2-dimethylhex-4-en-3-ol (2l)**



To a solution of the aldehyde (400.7 mg, 2 mmol) in THF (10 mL) was added a solution of *t*-butyl magnesium chloride (2 M, 1.5 mL, 3 mmol) at 0 °C. The reaction mixture was stirred for 1h at room temperature. After the reaction was complete as monitored by TLC, it was quenched by saturated aq. NH<sub>4</sub>Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Flash column chromatography (PE/EA=10/1) separation afforded alcohol **2l** (331 mg, 1.28 mmol, 64%) as colorless oil.

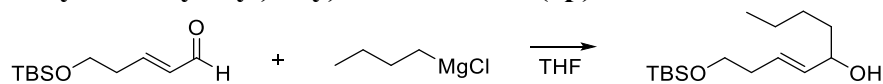
R<sub>f</sub> 0.21 (Petroleum ether/EtOAc =10/1)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 5.81 – 5.70 (m, 2H), 4.19 (dt, *J* = 3.4, 0.8 Hz, 2H), 3.80 – 3.71 (m, 1H), 0.90 (s, 9H), 0.90 (s, 9H), 0.07 (s, 6H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 132.0, 129.7, 80.45, 63.3, 35.0, 26.0, 25.8, 18.5, -5.1.

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>14</sub>H<sub>30</sub>NaO<sub>2</sub>Si 281.1907; found 281.1890.

**(E)-1-((*t*-butyldimethylsilyl) oxy) non-3-en-5-ol (2p)**



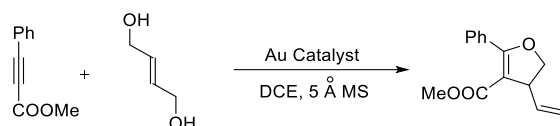
To a solution of the aldehyde (460.1 mg, 2 mmol) in THF (10 mL) was added a solution of methyl magnesium bromide (2 M, 1.5 mL, 3 mmol) at 0 °C. The reaction mixture was stirred for 1h at room temperature. After the reaction was complete as monitored by TLC, it was quenched by saturated aq. NH<sub>4</sub>Cl and extracted with EtOAc. The combined organic phases were dried and concentrated. Flash column chromatography (PE/EA=10/1) separation afforded alcohol **2p** (327 mg, 1.2 mmol, 60%) as colorless oil.

R<sub>f</sub> 0.21 (Petroleum ether/EtOAc =10/1)

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 5.69 – 5.56 (m, 1H), 5.50 (ddt, *J* = 15.4, 6.9, 1.2 Hz, 1H), 4.01 (q, *J* = 6.6 Hz, 1H), 3.62 (t, *J* = 6.7 Hz, 2H), 2.23 (q, *J* = 6.5 Hz, 2H), 1.75 (s, 1H), 1.60 – 1.40 (m, 2H), 1.43 – 1.18 (m, 4H), 0.87 (s, 12H), 0.03 (s, 6H).

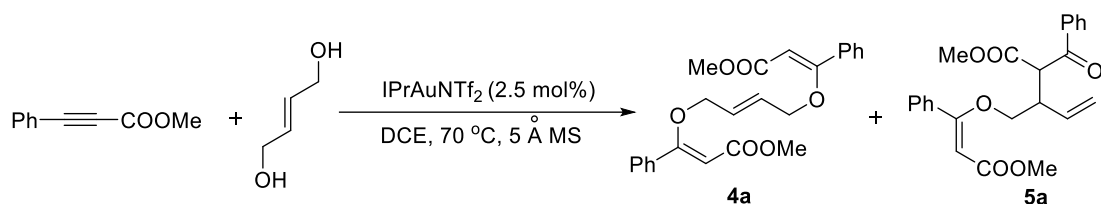
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.3, 128.3, 73.2, 62.9, 37.1, 35.9, 27.7, 26.0, 22.7, 18.4, 14.2, -5.2.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>33</sub>O<sub>2</sub>Si 273.2244; found 273.2265.



Entry	Catalyst (5 mol%)	solvent	condition	x: y	yield
1	JohnPhosAuNTf <sub>2</sub>	DCE	70 °C, 24 h	1:3	49%
2	JohnPhosAuNTf <sub>2</sub>	DCE	90 °C, 3.5 h	1:3	60%
3	JohnPhosAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:3	75%
4	JohnPhosAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:2	70%
5	JohnPhosAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:1	52%
6	JohnPhosAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	2:1	48%
7	JohnPhosAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	3:1	53%
8	BrettPhosAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:2	79%
9	Ph <sub>3</sub> PAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:2	26%
10	IPrAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:2	59%
11	MorDalPhosAuNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:2	46%
12	BrettPhosAuNTf <sub>2</sub>	CH <sub>2</sub> ClCHCl <sub>2</sub>	110 °C, 3.5 h	1:2	58%
13	BrettPhosAuNTf <sub>2</sub>	CHCl <sub>2</sub> CHCl <sub>2</sub>	110 °C, 6 h	1:2	59%
14	BrettPhosAuNTf <sub>2</sub>	PhCl	110 °C, 20 h	1:2	46%
15	BrettPhosAuNTf <sub>2</sub>	PhMe	110 °C, 20 h	1:2	18%
16	BrettPhosAuCl+AgSbF <sub>6</sub>	DCE	110 °C, 3.5 h	1:2	65%
17	BrettPhosAuCl+NaBARF <sub>4</sub>	DCE	110 °C, 7 h	1:2	20%
18	BrettPhosAuCl+AgNTf <sub>2</sub>	DCE	110 °C, 3.5 h	1:2	75%
19	BrettPhosAuNTf <sub>2</sub> (2.5 mol%)	DCE	110 °C, 3.5 h	1:2	79%
20	BrettPhosAuNTf <sub>2</sub> (2.5 mol%)	DCE (0.5 ml)	110 °C, 3.5 h	1:2	69%
21	BrettPhosAuNTf <sub>2</sub> (1 mol%)	DCE (0.5 ml)	110 °C, 10 h	1:2	50%
22	BrettPhosAuNTf <sub>2</sub> (1 mol%)	DCE	110 °C, 10 h	1:2	67%

**Dimethyl 3,3'-(((*E*)-but-2-ene-1,4-diyl)bis(oxy))(2*Z*,2'*Z*)-bis(3-phenylacrylate)  
**(4a) Methyl (*Z*)-2-benzoyl-3-(((3-methoxy-3-oxo-1-phenylprop-1-en-1-yl)oxy)methyl)pent-4-enoate (5a)****



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol) and (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol) was added to a dried vial sequentially. The reaction was stirred at 70 °C after adding anhydrous DCE (4 mL) and IPrAuNTf<sub>2</sub> (4.4 mg, 2.5 mol%). After 6 h, it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get compound **4a** and **5a**.

For compound **4a**:

R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 4/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) 7.46 – 7.35 (m, 10H), 6.09 – 5.96 (m, 2H), 5.26 (s, 2H), 4.62 – 4.46 (m, 4H), 3.58 (s, 6H).

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>24</sub>O<sub>6</sub>Na 431.1464; found 431.1464.

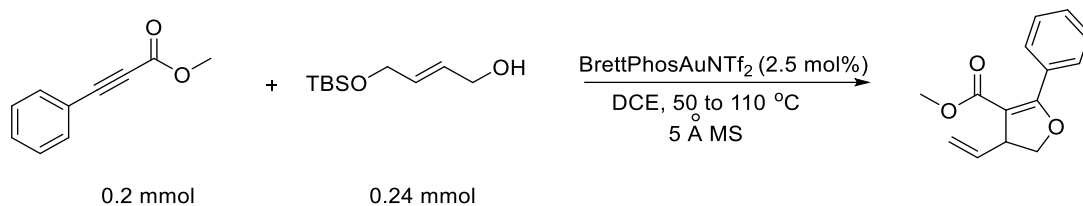
For compound **5a** (dr 2.5/1):

R<sub>f</sub> 0.40 (Petroleum ether/EtOAc = 4/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.27 (m, 8H), 7.22– 7.17 (m, *J* = 7.1 Hz, 2H), 6.03 – 5.90 (m, 1H), 5.26 (d, *J* = 4.1 Hz, 1H), 5.23 – 5.20 (m, 1H), 5.17 (s, 1H), 4.72 (d, *J* = 9.3 Hz, 1H), 4.17 – 4.02 (m, 1H), 4.00 (d, *J* = 4.5 Hz, 2H), 3.63 (s, 3H), 3.53 (s, 3H).

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>24</sub>O<sub>6</sub>Na 431.1464; found 431.1464.

### Methyl 2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (3a)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), ((E)-4-((tert-butyldimethylsilyl)oxy)but-2-en-1-ol (48.5 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred at 50 °C until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (6 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (36.3 mg, 79% yield).

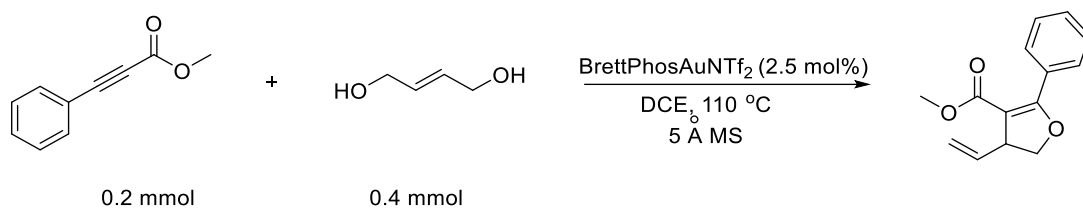
R<sub>f</sub> 0.40 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.71 (m, 2H), 7.49 – 7.33 (m, 3H), 5.97 (ddd, J = 17.1, 10.1, 7.7 Hz, 1H), 5.21 (dt, J = 17.1, 1.2 Hz, 1H), 5.12 (ddd, J = 10.1, 1.4, 0.8 Hz, 1H), 4.62 (t, J = 9.2 Hz, 1H), 4.35 (dd, J = 9.2, 5.1 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.65 (s, 3H).

The titled compound is known. It's <sup>1</sup>H-NMR was in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.



### Methyl 2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (3a)

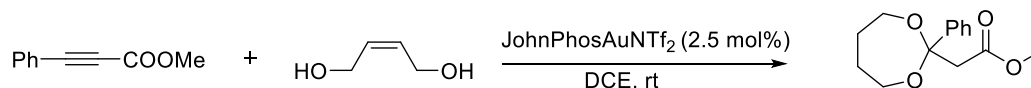


Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (E)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (4 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (35.9 mg, 78% yield).

R<sub>f</sub> 0.40 (Petroleum ether/EtOAc = 20/1).

The titled compound is known. It's <sup>1</sup>H-NMR was in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.

### Methyl 2-(2-phenyl-1,3-dioxepan-2-yl) acetate (3b)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol) and (*Z*)-but-2-ene-1,4-diol (17.6 mg, 0.2 mmol) were added to a dried vial sequentially. The reaction was stirred at room temperature after adding anhydrous DCE (4 mL) and JohnPhosAuNTf<sub>2</sub> (3.9 mg, 2.5 mol%). After 5 h, it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (39.5 mg, 79 % yield).

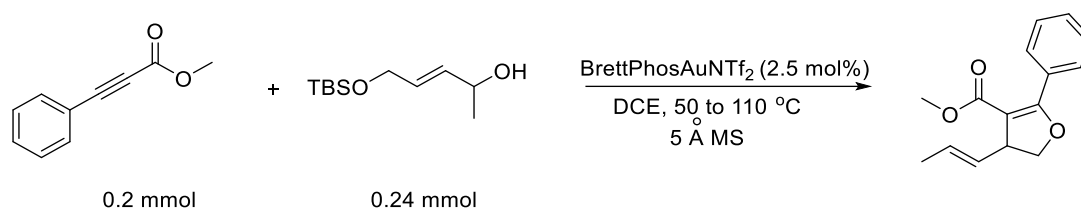
R<sub>f</sub> 0.42 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) 7.56 – 7.46 (m, 2H), 7.39 – 7.26 (m, 3H), 5.66 (t, *J* = 1.7 Hz, 2H), 4.44 – 4.33 (m, 2H), 4.22 – 4.12 (m, 2H), 3.46 (s, 3H), 3.03 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.2, 140.3, 129.3, 128.3, 128.1, 126.6, 103.4, 62.6, 51.6, 44.0.

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>Na 273.1097; found 273.1100.

### Methyl (*E*)-2-phenyl-4-(prop-1-en-1-yl)-4,5-dihydrofuran-3-carboxylate (**3c**)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-5-((*t*-butyldimethylsilyloxy)pent-3-en-2-ol (51.6 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred at 50 °C until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (6 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (31 mg, 64% yield).

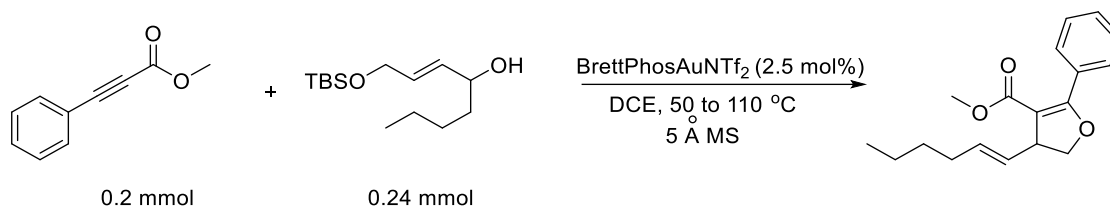
R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.51 – 7.31 (m, 3H), 5.69 – 5.49 (m, 2H), 4.58 (t, *J* = 9.4 Hz, 1H), 4.30 (dd, *J* = 9.1, 5.0 Hz, 1H), 3.98 – 3.88 (m, 1H), 3.65 (s, 3H), 1.71 (d, *J* = 5.5 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.0, 165.8, 131.5, 130.6, 130.1, 129.5, 127.8, 126.5, 106.2, 75.8, 51.0, 46.7, 18.1.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>17</sub>O<sub>3</sub> 245.1172; found 245.1157.

### Methyl (*E*)-4-(hex-1-en-1-yl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3e**)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), ((*E*)-1-((*t*-butyldimethylsilyl)oxy)oct-2-en-4-ol (62.0 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (6 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (38 mg, 66% yield).

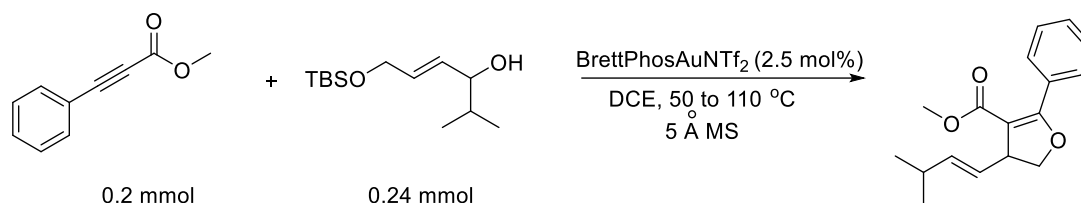
R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.75 (m, 2H), 7.53 – 7.31 (m, 3H), 5.65 – 5.46 (m, 2H), 4.59 (dd, *J* = 9.9, 9.1 Hz, 1H), 4.29 (dd, *J* = 9.1, 5.3 Hz, 1H), 3.96 – 3.91 (m, 1H), 3.64 (s, 3H), 2.09 – 1.99 (m, 2H), 1.49 – 1.22 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.0, 165.8, 132.2, 130.6, 130.3, 130.2, 129.5, 127.8, 106.3, 75.9, 51.0, 46.9, 32.2, 31.6, 22.2, 14.1.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>23</sub>O<sub>3</sub> 287.1642; found 287.1631.

**Methyl (E)-4-(3-methylbut-1-en-1-yl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3f)**



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-6-((*t*-butyldimethylsilyl)oxy)-2-methylhex-4-en-3-ol (58.6 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (6 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (38.4 mg, 70% yield).

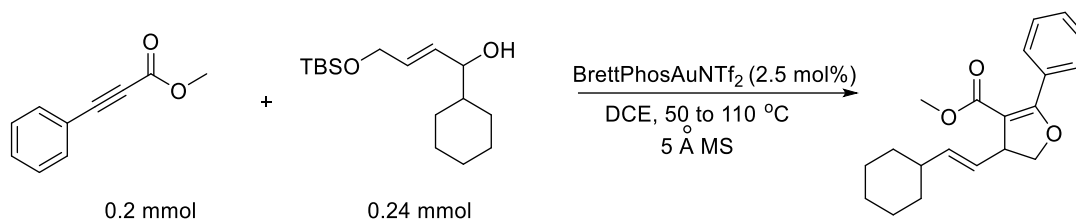
R<sub>f</sub> 0.40 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.71 (m, 2H), 7.47 – 7.31 (m, 3H), 5.55 (ddd, *J* = 15.4, 6.4, 0.6 Hz, 1H), 5.45 (ddd, *J* = 15.3, 7.7, 1.1 Hz, 1H), 4.59 (dd, *J* = 9.9, 9.1 Hz, 1H), 4.28 (dd, *J* = 9.1, 5.4 Hz, 1H), 3.97 – 3.87 (m, 1H), 3.63 (s, 3H), 2.34 – 2.20 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 165.8, 139.2, 130.6, 130.1, 129.4, 127.8, 127.2, 106.3, 75.8, 50.9, 46.9, 31.0, 22.5 (d, *J* = 5.4 Hz).

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub> 273.1485; found 273.1476.

### Methyl (*E*)-4-(2-cyclohexylvinyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (**3g**)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-4-((tert-butyldimethylsilyl)oxy)-1-cyclohexylbut-2-en-1-ol (68.3 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (6 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (43 mg, 69% yield).

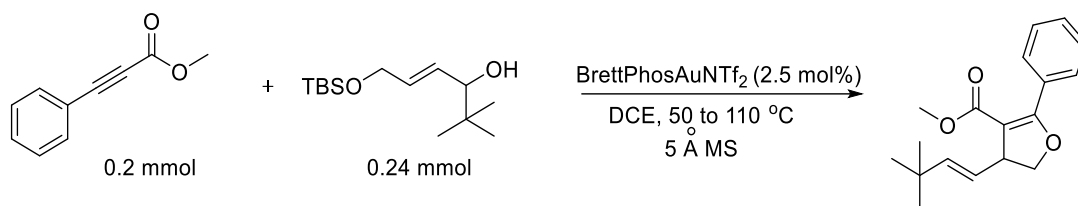
R<sub>f</sub> 0.50 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.75 (m, 2H), 7.43 – 7.35 (m, 3H), 5.79 – 5.21 (m, 2H), 4.59 (dd, *J* = 9.9, 9.1 Hz, 1H), 4.28 (dd, *J* = 9.9, 9.1 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.63 (s, 3H), 2.01 – 1.88 (m, 1H), 1.74 – 1.62 (m, 4H), 1.30 – 1.04 (m, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 165.8, 138.1, 130.5, 130.1, 129.4, 127.8, 127.6, 106.3, 75.8, 50.9, 47.0, 40.6, 33.1, 26.3, 26.1.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>25</sub>O<sub>3</sub> 313.1798; found 313.1793.

**Methyl (E)-4-(3,3-dimethylbut-1-en-1-yl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3h)**



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), ((*E*)-6-((*t*-butyldimethylsilyl)oxy)-2,2-dimethylhex-4-en-3-ol (62.0 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (6 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (42 mg, 74% yield).

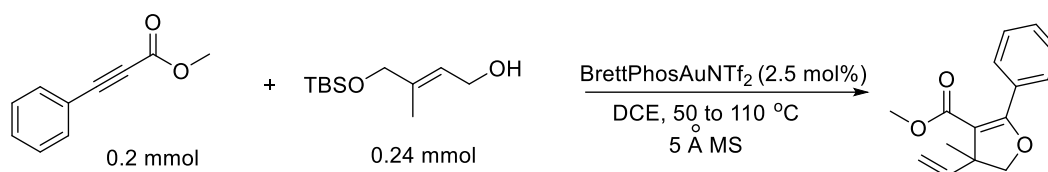
R<sub>f</sub> 0.50 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.77 (m, 2H), 7.50 – 7.31 (m, 3H), 5.61 (d, *J* = 15.6 Hz, 1H), 5.39 (dd, *J* = 15.6, 8.1 Hz, 1H), 4.66 – 4.57 (m, 1H), 4.28 (dd, *J* = 9.1, 5.5 Hz, 1H), 3.96 (m, 1H), 3.64 (s, 3H), 1.01 (s, 9H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 165.8, 143.3, 130.5, 130.1, 129.4, 127.8, 124.8, 106.4, 75.9, 50.8, 47.1, 33.0, 29.6.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>23</sub>O<sub>3</sub> 287.1642; found 287.1629.

### Methyl 4-methyl-2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (3i)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (E)-4-((t-butyltrimethylsilyloxy)methyl)-3-methylbut-2-en-1-ol (51.6 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (2 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (8 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (20 mg, 41% yield).

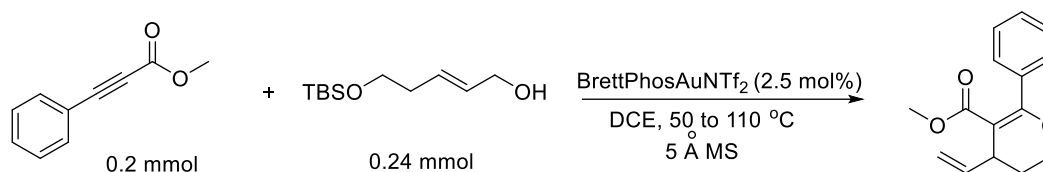
R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.57 (m, 2H), 7.46 – 7.31 (m, 3H), 6.10 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.19 – 5.08 (m, 1H), 4.39 (d, *J* = 8.9 Hz, 1H), 4.19 (d, *J* = 8.8 Hz, 1H), 3.60 (s, 3H), 1.50 (s, 3H).

The titled compound is known. It's <sup>1</sup>H-NMR was in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.



### Methyl 6-phenyl-4-vinyl-3,4-dihydro-2H-pyran-5-carboxylate (6a)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-5-((*t*-butyldimethylsilyl)oxy)pent-2-en-1-ol (51.9 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (4 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (7 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (36.5 mg, 76% yield).

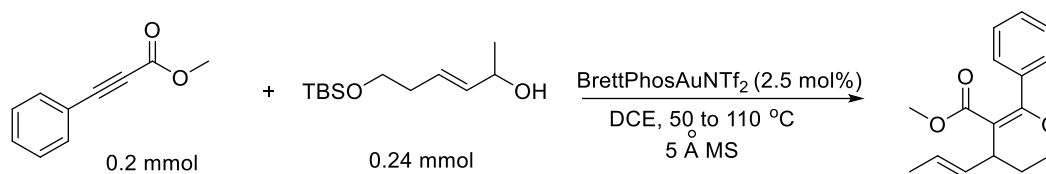
R<sub>f</sub> 0.30 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 5H), 5.88 (ddd, *J* = 17.1, 10.2, 6.0 Hz, 1H), 5.18 – 5.11 (m, 1H), 5.11 – 5.01 (m, 1H), 4.31 (dt, *J* = 10.6, 3.8 Hz, 1H), 4.06 – 3.99 (m, 1H), 3.60 (t, *J* = 5.9 Hz, 1H), 3.44 (s, 3H), 2.08 – 1.94 (m, 1H), 1.87 – 1.77 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.6, 162.8, 140.5, 136.7, 129.3, 128.5, 127.9, 116.3, 105.3, 63.5, 51.3, 35.1, 26.5.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>17</sub>O<sub>3</sub> 255.1172; found 254.1156.

### Methyl (*E*)-6-phenyl-4-(prop-1-en-1-yl)-3,4-dihydro-2H-pyran-5-carboxylate (**6b**)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-6-((*t*-butyldimethylsilyl)oxy)hex-3-en-2-ol (55.3 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (4 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (7 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (43 mg, 82% yield).

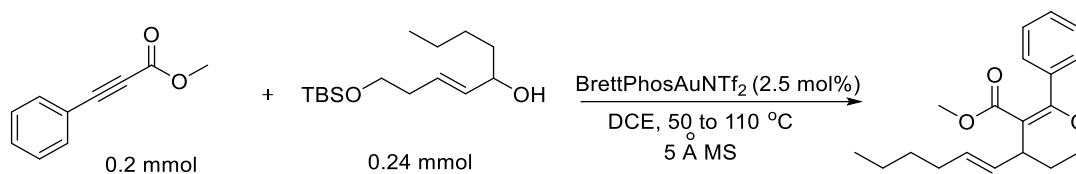
R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 5H), 5.54 – 5.37 (m, 2H), 4.33 – 4.24 (m, 1H), 4.02 (t, *J* = 12.6 Hz, 1H), 3.54 – 3.49 (m, 1H), 3.42 (s, 3H), 2.03 – 1.89 (m, 1H), 1.76 (dq, *J* = 13.8, 6.4 Hz, 1H), 1.67 – 1.65 (m, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.9, 162.0, 136.8, 133.4, 129.3, 128.4, 127.9, 127.0, 106.4, 63.6, 51.3, 34.1, 27.1, 18.1.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>19</sub>O<sub>3</sub> 259.1329; found 259.1317.

### Methyl (*E*)-4-(hex-1-en-1-yl)-6-phenyl-3,4-dihydro-2H-pyran-5-carboxylate (**6c**)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-1-((*t*-butyldimethylsilyl)oxy)non-3-en-5-ol (65.4 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (4 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (7 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (39 mg, 65% yield).

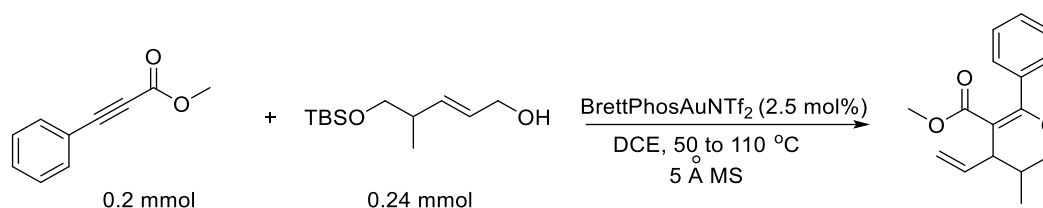
R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.31(m, 5H), 5.48 – 5.41 (m, 2H), 4.33 – 4.26 (m, 1H), 4.06 – 3.99 (m, 1H), 3.53 – 3.51 (m, 1H), 3.43 (s, 3H), 2.07 – 1.91 (m, 3H), 1.81 – 1.73 (m, 1H), 1.38 – 1.20 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.8, 161.8, 136.7, 132.7, 132.1, 129.3, 128.4, 127.9, 106.5, 63.6, 51.2, 34.2, 32.3, 31.7, 27.1, 22.2, 14.1.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>25</sub>O<sub>3</sub> 301.1798; found 301.1781.

### Methyl 3-methyl-6-phenyl-4-vinyl-3,4-dihydro-2H-pyran-5-carboxylate (**6d**)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-5-((*t*-butyldimethylsilyl)oxy)-4-methylpent-2-en-1-ol (55.3 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (9 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 10/1) to get the target product (34 mg, 65% yield, dr 1.4:1).

R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 10/1).

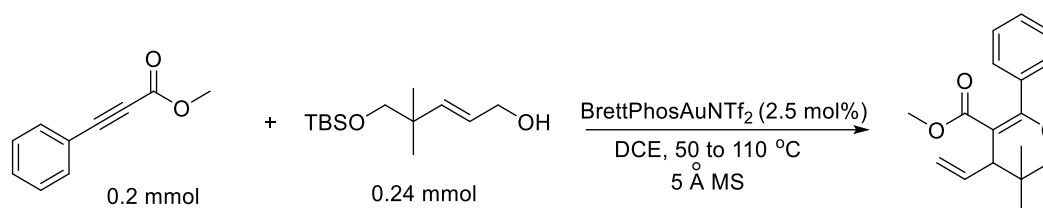
For **6d**, combined peaks for the two diastereomers are reported, and the integration of the methyl group from the methyl ester is set to 3.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 5H), 5.93 – 5.72 (m, 1H), 5.24 – 4.99 (m, 2H), 4.32 – 3.89 (m, 2H), 3.85 – 3.63 (m, 1H), 3.42 (d, *J* = 5.2 Hz, 3H), 1.03 (dd, *J* = 50.2, 7.0 Hz, 3H), 0.93 – 0.77 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.8, 169.4, 162.1, 161.9, 141.0, 136.6, 136.4, 129.3, 129.2, 128.4, 128.4, 128.0, 127.9, 118.5, 116.2, 106.0, 104.1, 68.6, 68.3, 51.2, 42.8, 41.0, 30.5, 30.0, 16.5, 13.5.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>19</sub>O<sub>3</sub> 259.1329; found: *m/z* = 259.1316.

### Methyl 3,3-dimethyl-6-phenyl-4-vinyl-3,4-dihydro-2H-pyran-5-carboxylate (6e)



Methyl 3-phenylpropiolate (32.0 mg, 0.2 mmol), (*E*)-5-((*t*-butyldimethylsilyloxy)-4,4-dimethylpent-2-en-1-ol (58.7 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (3 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (6 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (33 mg, 60% yield).

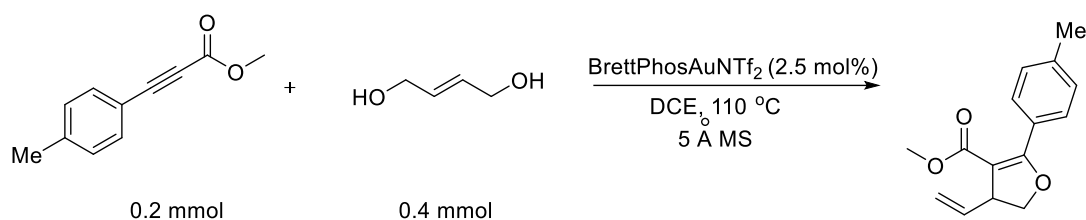
R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 5H), 5.85 – 5.77 (m, 1H), 5.17 – 5.04 (m, 2H), 3.82 (d, *J* = 10.5 Hz, 1H), 3.68 (d, *J* = 10.5 Hz, 1H), 3.42 (s, 3H), 3.10 (d, *J* = 7.4 Hz, 1H), 1.09 (s, 3H), 0.95 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.6, 160.8, 138.3, 136.6, 129.3, 128.4, 128.0, 117.4, 105.5, 72.6, 51.2, 47.2, 30.9, 25.2, 22.5.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub> 273.1485; found 273.1476.

### Methyl 2-(p-tolyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3j)



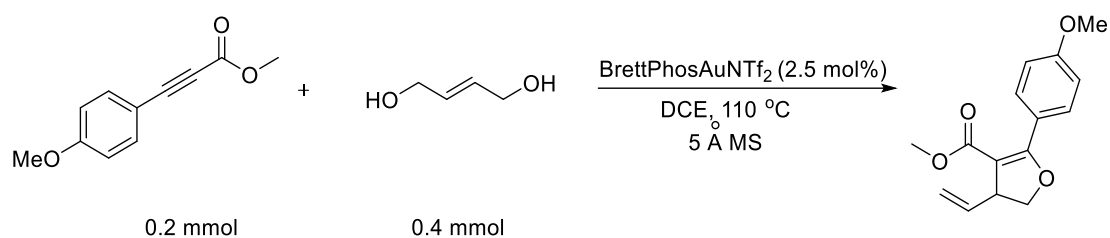
Methyl 3-(p-tolyl)propiolate (32.0 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (3 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 10/1) to get the target product (32 mg, 53% yield).

R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 10/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.02 – 5.85 (m, 1H), 5.19 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.12 – 5.09 (m, 1H), 4.64 – 4.57 (m, 1H), 4.33 (dd, *J* = 9.2, 5.0 Hz, 1H), 4.00 – 3.94 (m, 1H), 3.65 (s, 3H), 2.38 (s, 3H).  
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.7, 165.8, 141.1, 138.8, 129.5, 128.6, 127.1, 115.5, 105.0, 75.1, 51.0, 47.6, 21.7.

The titled compound is known. It's <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.

### Methyl 2-(4-methoxyphenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3k)



Methyl 3-(4-methoxyphenyl)propiolate (38.4 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EAc = 20/1) to get the target product (33.1 mg, 64% yield).

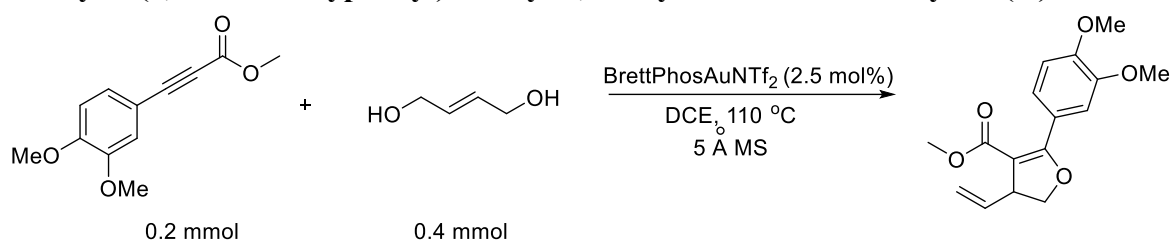
R<sub>f</sub> 0.25 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 9.1 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), δ 6.00 – 5.89 (m, 1H), 5.18 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.12 – 5.08 (m, 1H), 4.57 (dd, *J* = 9.7, 9.2 Hz, 1H), 4.32 (dd, *J* = 9.2, 4.8 Hz, 1H), 3.98 – 3.92 (m, 1H), 3.84 (s, 3H), 3.66 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.4, 165.9, 161.5, 138.9, 131.4, 122.2, 115.4, 113.2, 104.2, 74.9, 55.4, 51.0, 47.6.

The titled compound is known. It's <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.

### Methyl 2-(3,4-dimethoxyphenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (31)



Methyl 3-(3,4-dimethoxyphenyl)propiolate (43.8 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 4/1) to get the target product (32.7 mg, 56% yield).

R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 4/1).

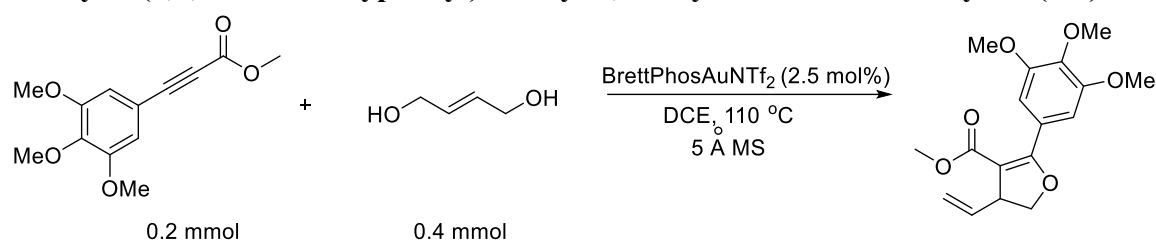
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.46 (m, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.95 (ddd, *J* = 17.0, 10.1, 7.7 Hz, 1H), 5.21 – 5.16 (m, 1H), 5.11 – 5.08 (m, 1H), 4.57 (dd, *J* = 9.8, 9.2 Hz, 1H), 4.32 (dd, *J* = 9.2, 4.8 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.91 (d, *J* = 3.1 Hz, 6H), 3.67 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.9, 165.8, 151.1, 148.1, 138.9, 123.3, 122.2, 115.4, 112.5, 110.1, 104.5, 74.8, 56.0, 56.0, 51.1, 47.8.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>19</sub>O<sub>5</sub> 291.1227; found: *m/z* = 291.1220.



### Methyl 2-(3,4,5-trimethoxyphenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3m)



Methyl 3-(3,4,5-trimethoxyphenyl)propiolate (50.5 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 4/1) to get the target product (43.0 mg, 67% yield).

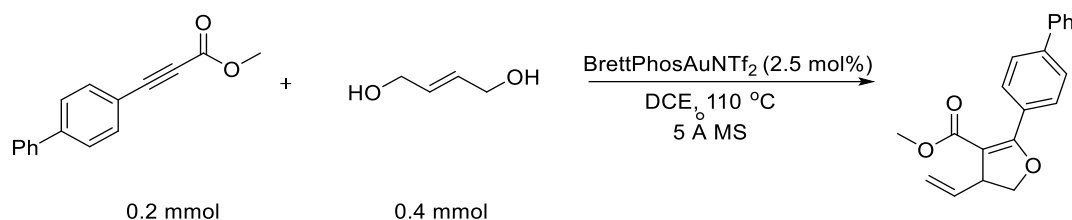
R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 4/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.18 (s, 2H), 5.95 (ddd, *J* = 17.1, 10.1, 7.7 Hz, 1H), 5.19 (dt, *J* = 17.1 Hz, 1H), 5.12 – 5.09 (m, 1H), 4.58 (dd, *J* = 9.7, 9.2 Hz, 1H), 4.33 (dd, *J* = 9.2, 5.0 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.88 (d, *J* = 0.9 Hz, 9H), 3.68 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6, 165.5, 152.5, 140.1, 138.7, 124.8, 115.6, 107.1, 105.4, 74.8, 61.0, 56.3, 51.2, 47.9.

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>20</sub>NaO<sub>3</sub> 343.1152; found 343.1170.

### Methyl 2-([1,1'-biphenyl]-4-yl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3n)



Methyl 3-([1,1'-biphenyl]-4-yl)propiolate (47.2 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (36.5 mg, 60% yield).

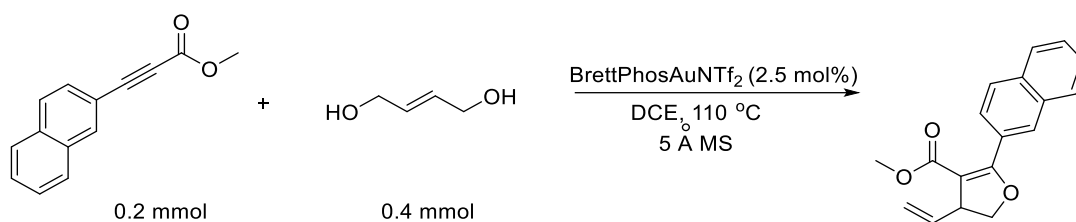
R<sub>f</sub> 0.40 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.87 (m, 2H), 7.65 – 7.62 (m, 4H), 7.48 – 7.44 (m, 2H), 7.40 – 7.36 (m, 1H), 5.99 (ddd, *J* = 17.5, 10.1, 7.6 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 4.64 (t, *J* = 9.5 Hz, 1H), 4.38 (dd, *J* = 9.2, 5.0 Hz, 1H), 4.13 – 3.92 (m, 1H), 3.69 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.2, 165.7, 143.4, 141.0, 140.5, 138.7, 130.0, 129.0, 128.8, 127.9, 127.3, 126.5, 115.6, 105.7, 75.2, 51.1, 47.7.

The titled compound is known. It's <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.

### Methyl 2-(naphthalen-2-yl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3o)



Methyl 3-(naphthalen-2-yl) propiolate (42.0 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 10/1) to get the target product (33.0 mg, 59% yield).

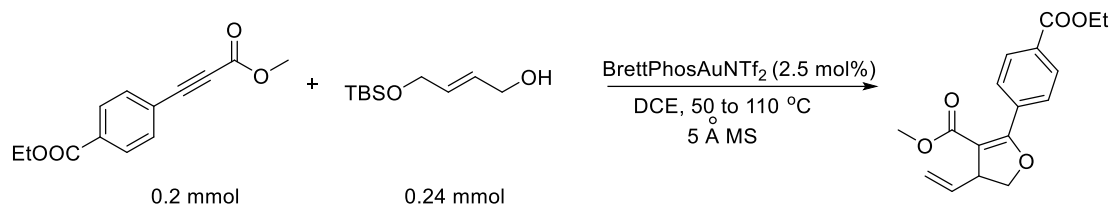
R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 10/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.34 – 8.31 (m, 1H), 7.92 – 7.79 (m, 4H), 7.58 – 7.46 (m, 2H), 6.01 (ddd, *J* = 17.1, 10.1, 7.7 Hz, 1H), 5.24(dt, *J* = 17.2, 1.2 Hz, 1H), 5.15 (ddd, *J* = 10.1, 1.4, 0.8 Hz, 1H), 4.68 (dd, *J* = 9.8, 9.2 Hz, 1H), 4.41 (dd, *J* = 9.2, 5.1 Hz, 1H), 4.13 – 3.91 (m, 1H), 3.67 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.4, 165.7, 138.7, 134.4, 132.6, 130.0, 129.0, 127.8, 127.5, 127.4, 127.3, 126.4, 126.3, 115.7, 106.0, 75.3, 51.1, 47.7.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>17</sub>O<sub>3</sub> 281.1172; found 281.1152.

### Methyl 2-(4-(ethoxycarbonyl)phenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3p)



Ethyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)benzoate (46.4 mg, 0.2 mmol), (*E*)-4-((*t*-butyldimethylsilyl)oxy)but-2-en-1-ol (48.5 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (2 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (8 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (39 mg, 65% yield).

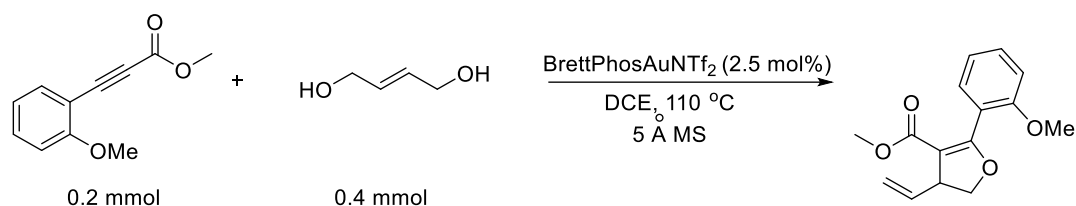
R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 10/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.95 (m, 2H), 7.86 – 7.77 (m, 2H), 5.96 (ddd, *J* = 17.1, 10.1, 7.7 Hz, 1H), 5.21 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.13 (dt, *J* = 10.1, 1.1 Hz, 1H), 4.64 (dd, *J* = 10.0, 9.2 Hz, 1H), 4.46 – 4.31 (m, 2H), 4.06 – 3.96 (m, 1H), 3.65 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.2, 165.3, 165.1, 138.4, 134.2, 132.1, 129.5, 129.0, 116.0, 107.2, 75.5, 61.3, 51.2, 47.4, 14.4.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>19</sub>O<sub>5</sub> 303.1227; found 303.1222.

### Methyl 2-(2-methoxyphenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3q)



Methyl 3-(2-methoxyphenyl)propiolate (38.0 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (7 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 10/1) to get the target product (32 mg, 62% yield).

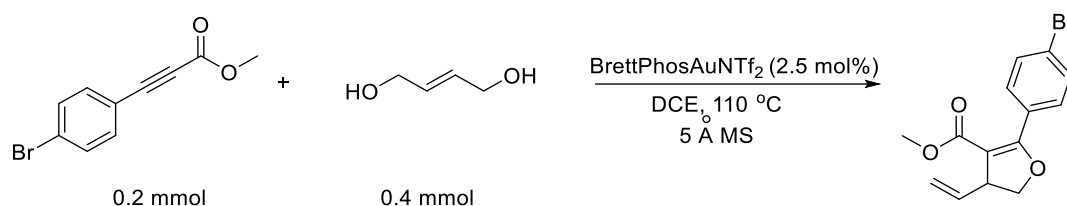
R<sub>f</sub> 0.25 (Petroleum ether/EtOAc = 10/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 2H), 7.04 – 6.88 (m, 2H), 5.97 (ddd, *J* = 17.1, 10.1, 7.6 Hz, 1H), 5.23 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.12 (ddd, *J* = 10.1, 1.4, 0.7 Hz, 1H), 4.64 (dd, *J* = 9.9, 9.1 Hz, 1H), 4.33 (dd, *J* = 9.1, 5.5 Hz, 1H), 4.03 – 3.86 (m, 1H), 3.80 (s, 3H), 3.53 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6, 164.4, 157.4, 138.7, 131.5, 130.7, 120.2, 115.8, 111.1, 108.0, 76.0, 55.9, 50.9, 47.0.

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>16</sub>NaO<sub>4</sub> 283.0941; found 283.0940.

### Methyl 2-(4-bromophenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (**3r**)



Methyl 3-(4-bromophenyl)propiolate (47.8 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EAc = 10/1) to get the target product (34.8 mg, 56% yield).

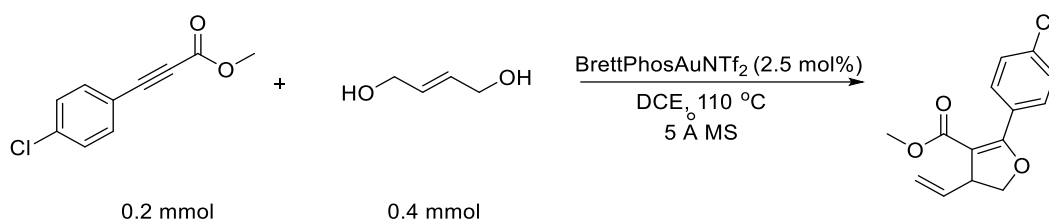
R<sub>f</sub> 0.60 (Petroleum ether/EtOAc = 10/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 5.94 (ddd, *J* = 17.2, 10.2, 7.7 Hz, 1H), 5.19 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.13 – 5.10 (m, 1H), 4.60 (dd, *J* = 9.9, 9.2 Hz, 1H), 4.34 (dd, *J* = 9.2, 5.1 Hz, 1H), 4.01 – 3.95 (m, 1H), 3.66 (s, 3H).

<sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 165.5, 165.2, 138.5, 131.1, 131.1, 128.8, 125.2, 115.8, 106.2, 75.3, 51.2, 47.6.

The titled compound is known. It's <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.

### Methyl 2-(4-chlorophenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3s)



Methyl 3-(4-chlorophenyl)propiolate (38.9 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 10/1) to get the target product (29.6 mg, 56% yield).

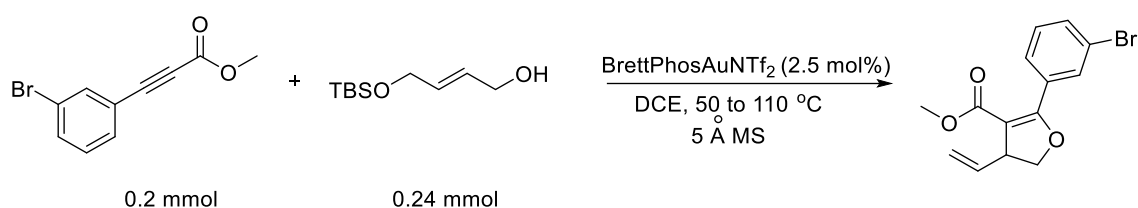
R<sub>f</sub> 0.45 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.73 (m, 2H), 7.38 – 7.34 (m, 2H), 5.94 (ddd, *J* = 17.1, 10.1, 7.7 Hz, 1H), 5.18 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.12 (ddd, *J* = 10.1, 1.3, 0.8 Hz, 1H), 4.61 (dd, *J* = 9.9, 9.2 Hz, 1H), 4.35 (dd, *J* = 9.2, 5.1 Hz, 1H), 4.02 – 3.92 (m, 1H), 3.66 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.5, 165.1, 138.5, 136.7, 131.0, 128.3, 128.1, 115.8, 106.1, 75.3, 51.2, 48.6.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>14</sub>H<sub>14</sub>ClO<sub>3</sub> 265.0626; found 265.0606.

### Methyl 2-(3-bromophenyl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3t)



Methyl 3-(3-bromophenyl)propiolate (47.8 mg, 0.2 mmol), (*E*)-4-((*t*-butyldimethylsilyl)oxy)but-2-en-1-ol (48.5 mg, 0.24 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (2 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (8 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (37.7 mg, 61% yield).

R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 20/1).

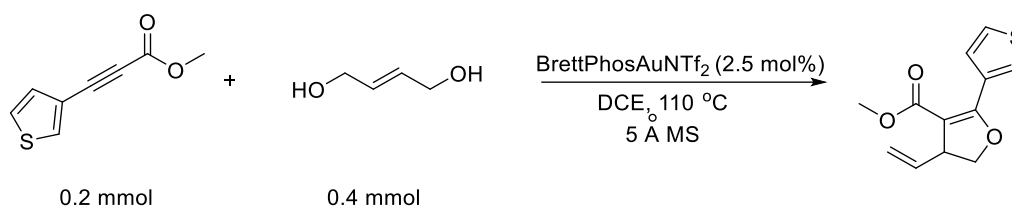
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.92 (t, *J* = 1.8 Hz, 1H), 7.82 – 7.70 (m, 1H), 7.59 – 7.46 (m, 1H), 7.32 – 7.19 (m, 1H), 5.94 (ddd, *J* = 17.1, 10.1, 7.7 Hz, 1H), 5.20 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.12 (dt, *J* = 10.2, 1.2 Hz, 1H), 4.61 (dd, *J* = 9.9, 9.3 Hz, 1H), 4.35 (dd, *J* = 9.3, 5.2 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.66 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.3, 164.5, 138.4, 133.6, 132.4, 131.9, 129.4, 128.3, 121.8, 115.9, 106.7, 75.4, 51.2, 47.6.

HRMS (ESI) *m/z*: [M+K]<sup>+</sup> calcd for C<sub>14</sub>H<sub>13</sub>BrKO<sub>3</sub> 346.9680; found 346.9674.



### Methyl 2-(thiophen-3-yl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3u)



Methyl 3-(thiophen-3-yl)propiolate (33.2mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (4 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 10/1) to get the target product (29.3 mg, 62% yield).

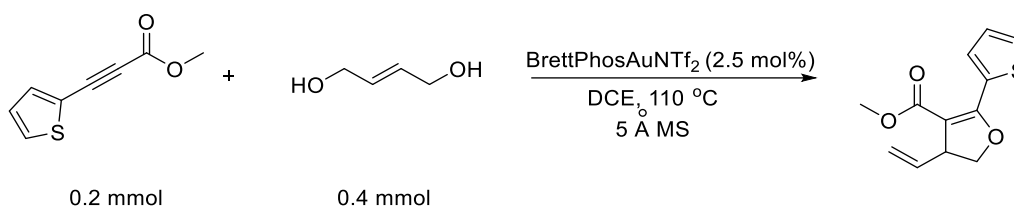
R<sub>f</sub> 0.65 (Petroleum ether/EtOAc = 10/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.40 (dd, *J* = 3.1, 1.2 Hz, 1H), 7.70 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.28 (dd, *J* = 5.1, 3.1 Hz, 1H), 5.99 – 5.86 (m, 1H), 5.16 (dt, *J* = 17.2, 1.2 Hz, 1H), 5.10 – 5.07 (m, 1H), 4.56 (dd, *J* = 9.8, 9.1 Hz, 1H), 4.32 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.96 (m, *J* = 8.7, 4.8 Hz, 1H), 3.72 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.8, 161.0, 138.8, 130.8, 128.5, 124.6, 115.5, 104.5, 74.7, 51.1, 47.5.

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>12</sub>NaO<sub>3</sub>S 259.0399; found 259.0404.

### Methyl 2-(thiophen-2-yl)-4-vinyl-4,5-dihydrofuran-3-carboxylate (3v)



Methyl 3-(thiophen-2-yl) propiolate (33.2 mg, 0.2 mmol), (*E*)-but-2-ene-1,4-diol (35.2 mg, 0.4 mmol), and 5 Å MS (50 mg) were added to a dried vial sequentially. The reaction was stirred at 110 °C after adding anhydrous DCE (4 mL) and BrettPhosAuNTf<sub>2</sub> (5.0 mg, 2.5 mol%), until the complete consumption of the intermediates monitored by TLC (2 h). Then it was concentrated in vacuum and separated on silica gel (PE/EAc = 10/1) to get the target product (30.2 mg, 64% yield).

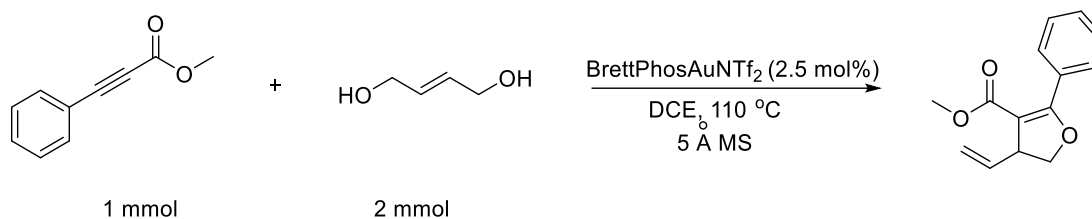
R<sub>f</sub> 0.65 (Petroleum ether/EtOAc = 10/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.51 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.12 – 7.09 (m, 1H), 5.92 (ddd, *J* = 17.1, 10.1, 7.7 Hz, 1H), 5.16 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.08 (ddd, *J* = 10.1, 1.4, 0.8 Hz, 1H), 4.57 (dd, *J* = 9.6, 9.1 Hz, 1H), 4.34 (dd, *J* = 9.1, 4.6 Hz, 1H), 3.99 – 3.94 (m, 1H), 3.75 (s, 3H).

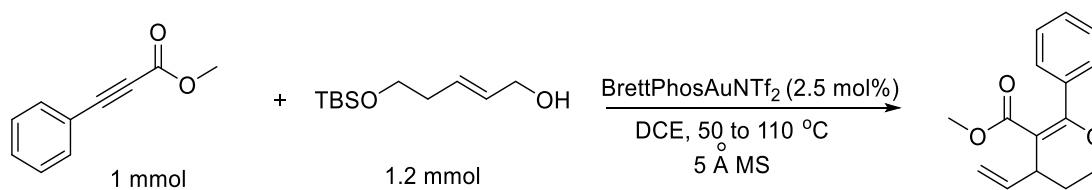
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.7, 159.7, 138.5, 132.7, 131.4, 130.6, 127.3, 115.6, 103.9, 75.0, 51.2, 47.6.

The titled compound is known. It's <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were in accordance with the literature: Juan Wang, Yun-Fan Li, Juan Du, Shuai Huang, Chang-Hua Ding, Henry N. C. Wong, and Xue-Long Hou, Palladium-Catalyzed Asymmetric (3 + 2) Cycloaddition of Vinyl Epoxides with Substituted Propiolates. Enantioselective Formation of 2,3,4-Trisubstituted 2,3-Dihydrofurans. *Org. Lett.* **2022**, *24*, 1561–1565.

**The scale-up reaction of Methyl 2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (3a) and Methyl 6-phenyl-4-vinyl-3,4-dihydro-2H-pyran-5-carboxylate (6a)**

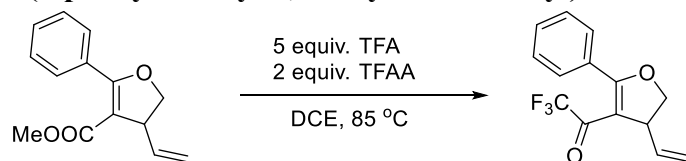


Methyl 3-phenylpropiolate (160.2 mg, 1 mmol), ((E)-4-((tert-butylidimethylsilyl)oxy)but-2-en-1-ol (176.2 mg, 2 mmol), and 5 Å MS (250 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (20 mL) and BrettPhosAuNTf<sub>2</sub> (25.0 mg, 2.5 mol%). The reaction mixture was stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (4 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (170.1 mg, 74% yield).



Methyl 3-phenylpropiolate (160.2 mg, 1 mmol), (E)-5-((t-butylidimethylsilyl)oxy)pent-2-en-1-ol (259.6 mg, 1.2 mmol), and 5 Å MS (250 mg) were added to a dried vial sequentially. The reaction was stirred at 50 °C after adding anhydrous DCE (20 mL) and BrettPhosAuNTf<sub>2</sub> (25.0 mg, 2.5 mol%). The reaction mixture was stirred until complete consumption of the propiolate monitored by TLC (4 h). The reaction was then stirred at 110 °C until the complete consumption of the intermediates monitored by TLC (7 h). Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (161.3 mg, 66% yield).

### 2,2,2-Trifluoro-1-(2-phenyl-4-vinyl-4,5-dihydrofuran-3-yl)ethan-1-one (10)



Methyl 2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (46.0 mg, 0.2 mmol), TFA (74  $\mu$ l, 1 mmol), and TFAA (56  $\mu$ l, 0.4 mmol) were added to a vial sequentially. The reaction was stirred at 85 °C after adding DCE (2 ml). After 2 days, the reaction mixture was poured into aqueous  $K_2CO_3$  and extracted with EA. The combined organic layer was dried with anhydrous  $Na_2SO_4$ . Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (36 mg, 63% yield).

$R_f$  0.35 (Petroleum ether/EtOAc = 20/1).

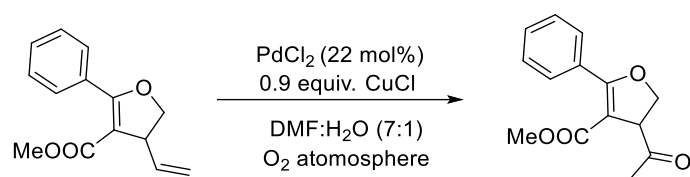
$^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.80 – 7.71 (m, 2H), 7.57 – 7.48 (m, 1H), 7.44 (t,  $J$  = 7.5 Hz, 2H), 6.04 – 5.91 (m, 1H), 5.28 – 5.15 (m, 2H), 4.72 (t,  $J$  = 9.3 Hz, 1H), 4.49 (dd,  $J$  = 9.3, 3.8 Hz, 1H), 4.18 – 4.08 (m, 1H).

$^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  176.6 (q,  $J$  = 35.1 Hz), 174.6, 137.9, 132.3, 129.9, 129.2, 128.1, 116.7, 116.7 (q,  $J$  = 292.8 Hz), 109.5, 77.5, 46.0.

$^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -73.3 (s, 3F).

HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{14}H_{12}F_3O_2$  269.0784; found 269.0784.

### Methyl 4-acetyl-2-phenyl-4,5-dihydrofuran-3-carboxylate (11)



Methyl 2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (46.0 mg, 0.2 mmol), PdCl<sub>2</sub> (7.8 mg, 0.044 mmol), and CuCl (17.6 mg, 0.18 mmol) were added to a vial sequentially. The reaction was stirred at room temperature after adding DMF (3.5 ml) and H<sub>2</sub>O (0.5 mL). The reaction mixture was stirred until complete consumption of starting material was observed by TLC (2 d). Extraction was then carried out with ethyl acetate, and the organic phase was dried. Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (43 mg, 88% yield).

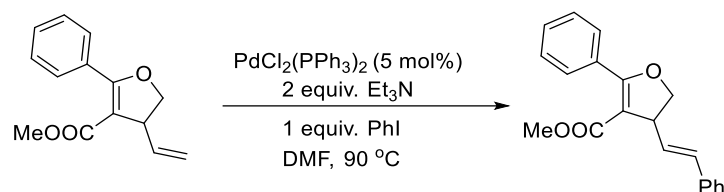
R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.73 (m, 2H), 7.41 (d, *J* = 7.5 Hz, 3H), 4.64 (d, *J* = 8.3 Hz, 2H), 4.26 (t, *J* = 8.3 Hz, 1H), 3.66 (s, 3H), 2.31 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 208.3, 168.7, 165.0, 131.2, 129.6, 129.2, 127.9, 103.2, 72.3, 56.3, 51.4, 28.6.

HRMS (ESI) *m/z*: [M+Na]<sup>+</sup> calcd for C<sub>14</sub>H<sub>14</sub>NaO<sub>4</sub> 269.0784; found 269.0762.

### Methyl (E)-2-phenyl-4-styryl-4,5-dihydrofuran-3-carboxylate (12)



Methyl 2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (46.0 mg, 0.2 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (7 mg, 0.01 mmol), PhI (40.8 mg, 0.2 mmol) and Et<sub>3</sub>N (55.4  $\mu$ l, 0.4 mmol) were added to a vial sequentially. The reaction was stirred at 90 °C after adding DMF (2 ml). The reaction mixture was stirred until complete consumption of starting material was observed by TLC (24 h). The reaction mixture was extracted with EA. Then the organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Then it was concentrated in vacuum and separated on silica gel (PE/EA = 20/1) to get the target product (24 mg, 40% yield).

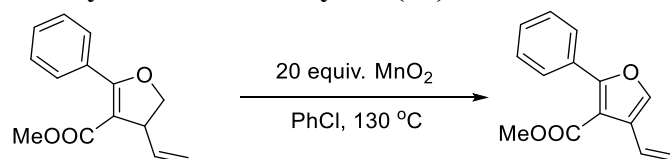
R<sub>f</sub> 0.35 (Petroleum ether/EtOAc = 20/1).

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.88 – 7.74 (m, 2H), 7.50 – 7.35 (m, 5H), 7.39 – 7.27 (m, 2H), 7.27 – 7.19 (m, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.33 (dd, *J* = 15.8, 8.2 Hz, 1H), 4.69 (t, *J* = 9.5 Hz, 1H), 4.44 (dd, *J* = 9.5, 4.9 Hz, 1H), 4.21 – 4.11 (m, 1H), 3.65 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.5, 165.6, 137.2, 130.9, 130.8, 130.2, 129.9, 129.6, 128.7, 127.9, 127.6, 126.5, 105.8, 75.6, 51.2, 47.2.

HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>19</sub>O<sub>3</sub> 307.1329; found 307.1316.

### Methyl 2-phenyl-4-vinylfuran-3-carboxylate (13)



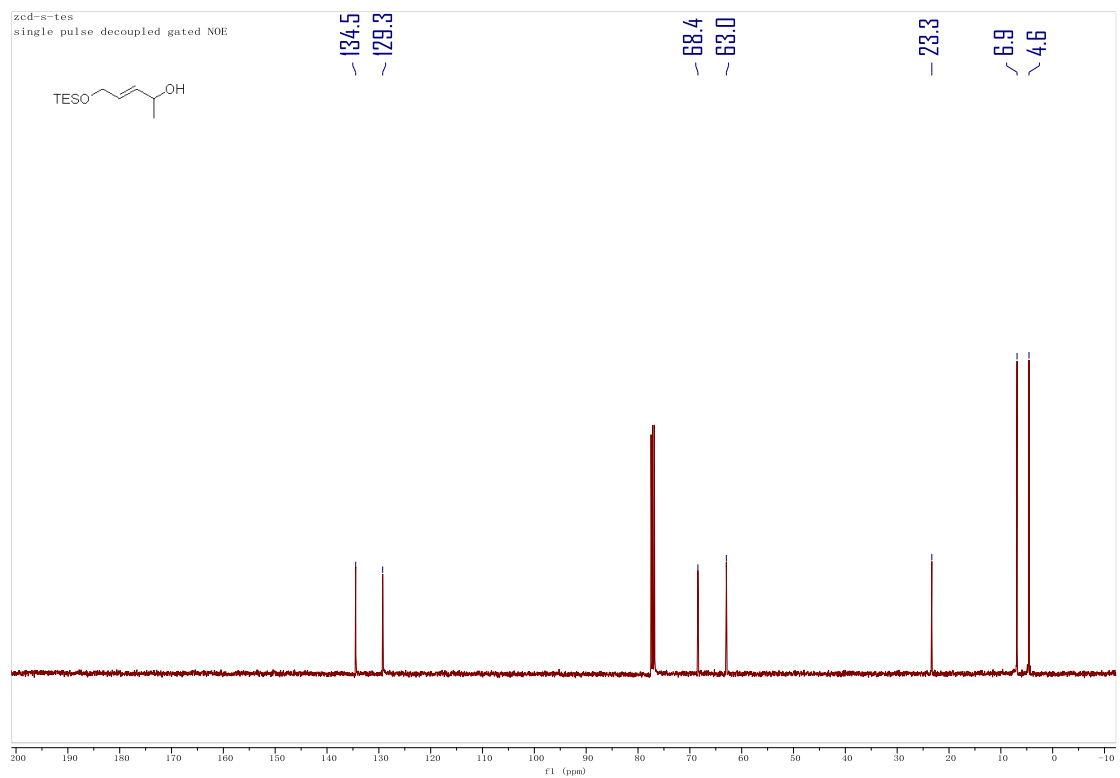
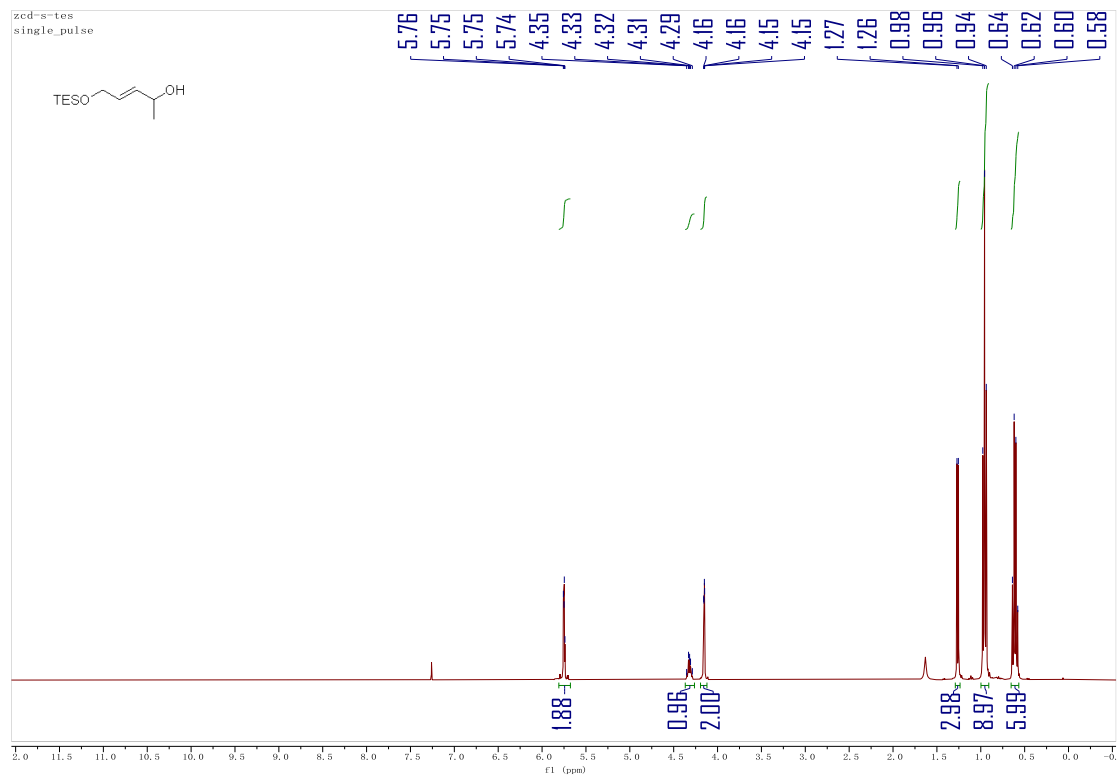
Methyl 2-phenyl-4-vinyl-4,5-dihydrofuran-3-carboxylate (46.0 mg, 0.2 mmol) and  $\text{MnO}_2$  (377.8 mg, 4 mmol) were added to a vial sequentially. The reaction was stirred at  $130\text{ }^\circ\text{C}$  after adding PhCl (2 ml). The reaction mixture was stirred until complete consumption of starting material was observed by TLC (12 h). The mixture was filtered through Celite and washed with EA. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (PE/EA = 20/1) to get the target product (28 mg, 61% yield).

$R_f$  0.62 (Petroleum ether/EtOAc = 20/1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.74 – 7.77 (m, 2H), 7.59 – 7.58 (m, 1H), 7.49 – 7.33 (m, 3H), 6.84 (ddd,  $J = 17.8, 11.0, 0.9$  Hz, 1H), 5.55 (dd,  $J = 17.8, 1.6$  Hz, 1H), 5.25 (dd,  $J = 11.0, 1.6$  Hz, 1H), 3.82 (s, 3H).

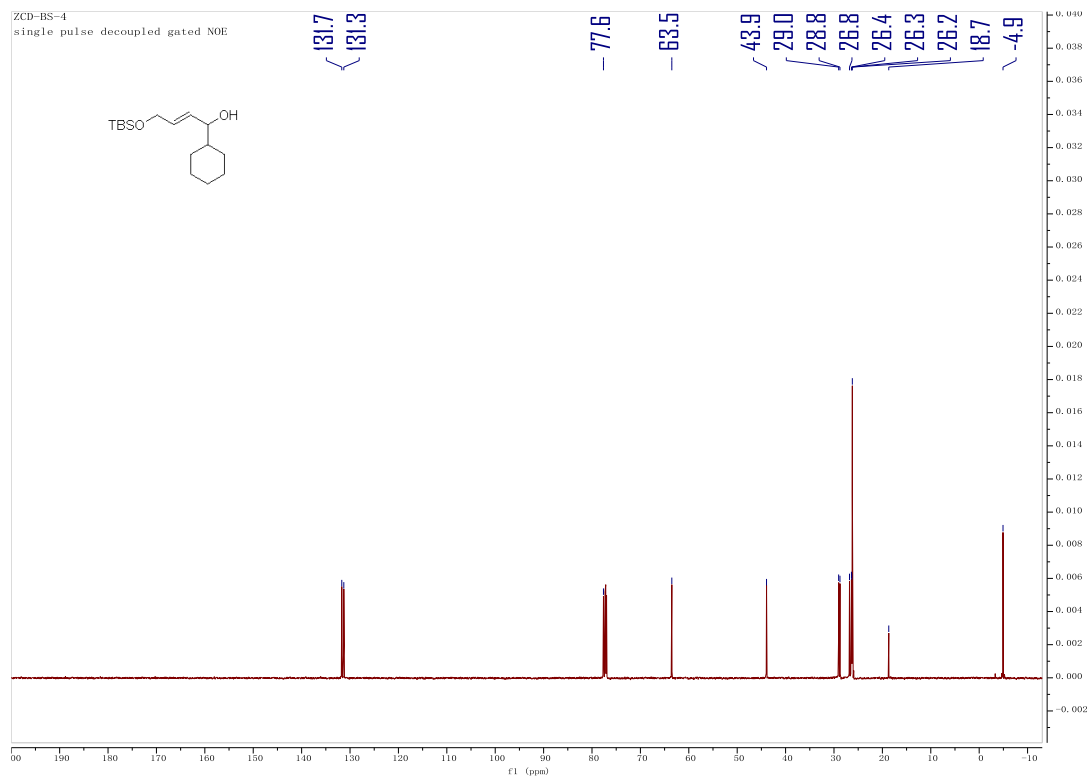
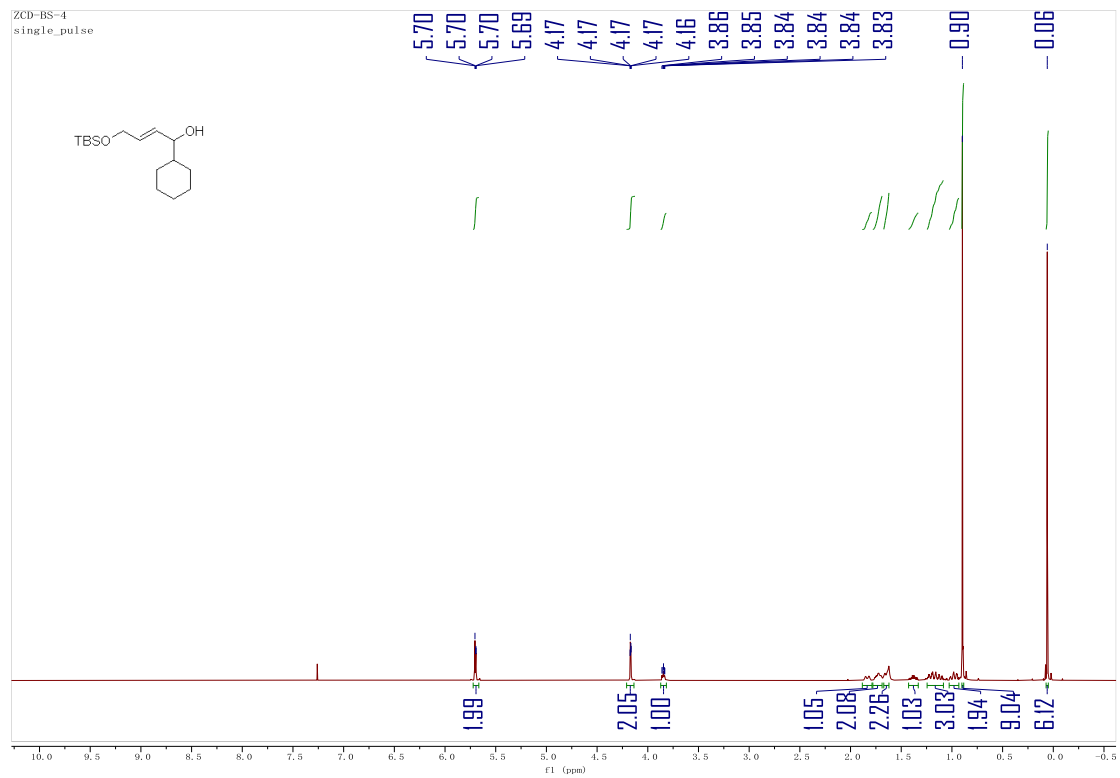
$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 158.2, 138.6, 130.1, 129.4, 128.4, 128.2, 127.0, 126.4, 115.9, 112.5, 51.7.

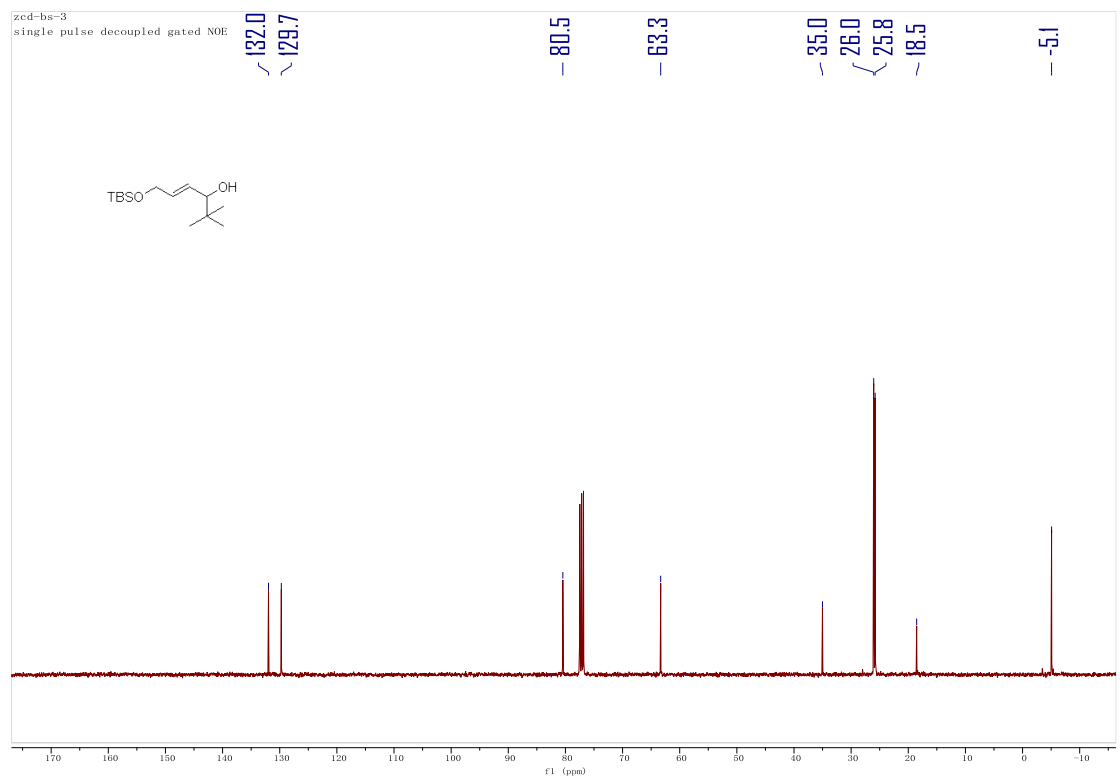
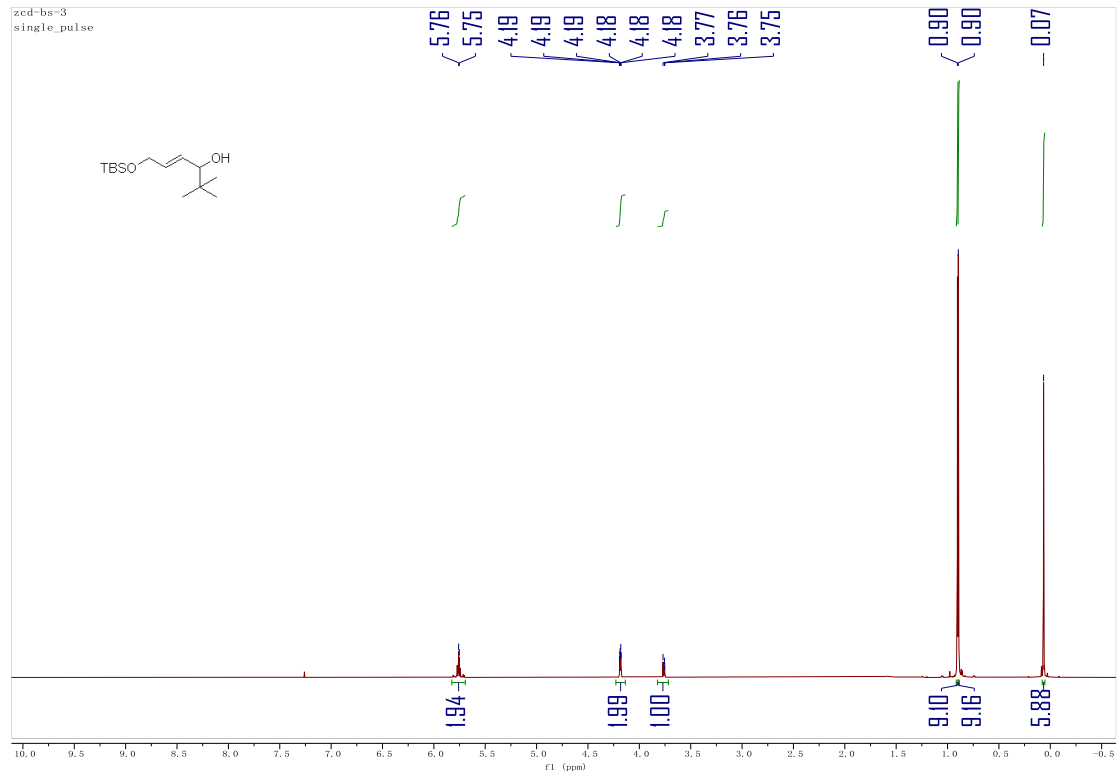
**HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{13}\text{O}_3$  229.0859; found 229.0842.

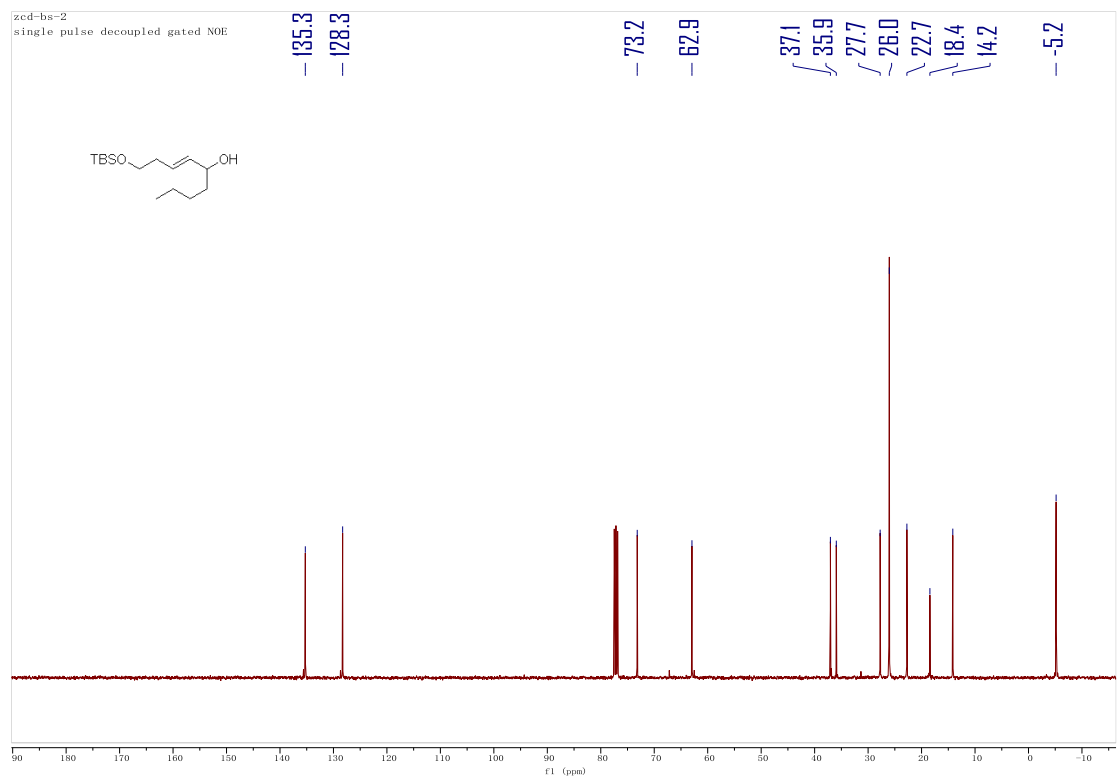
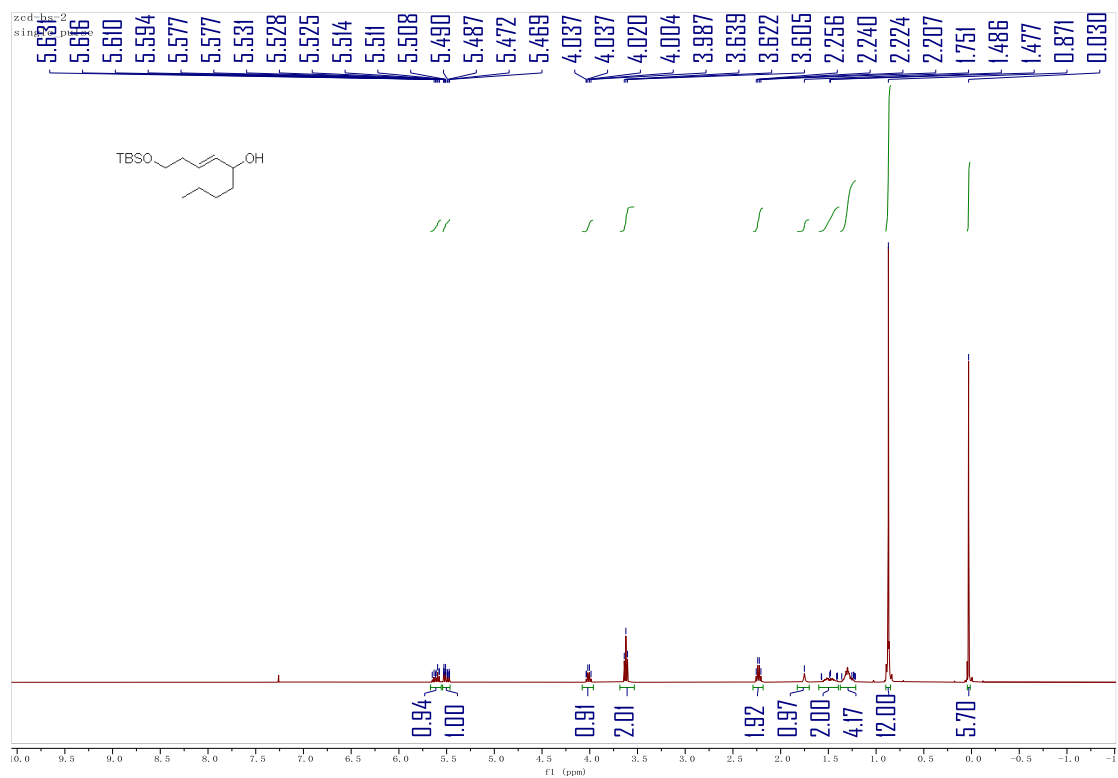


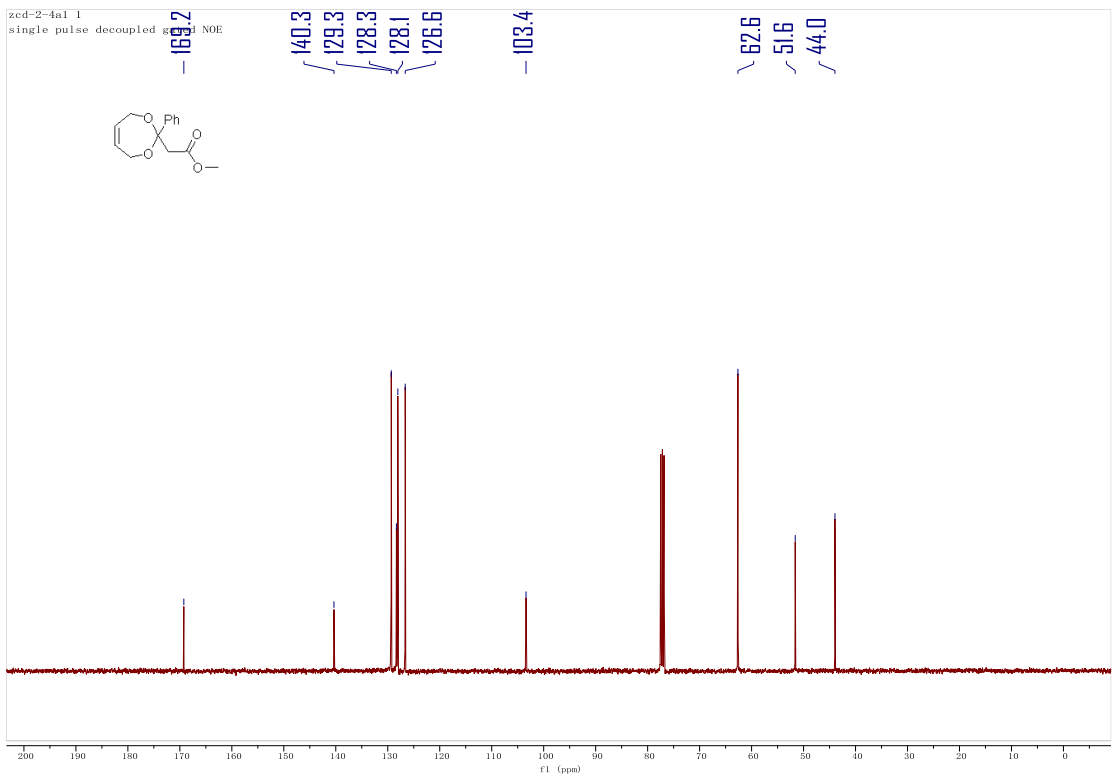
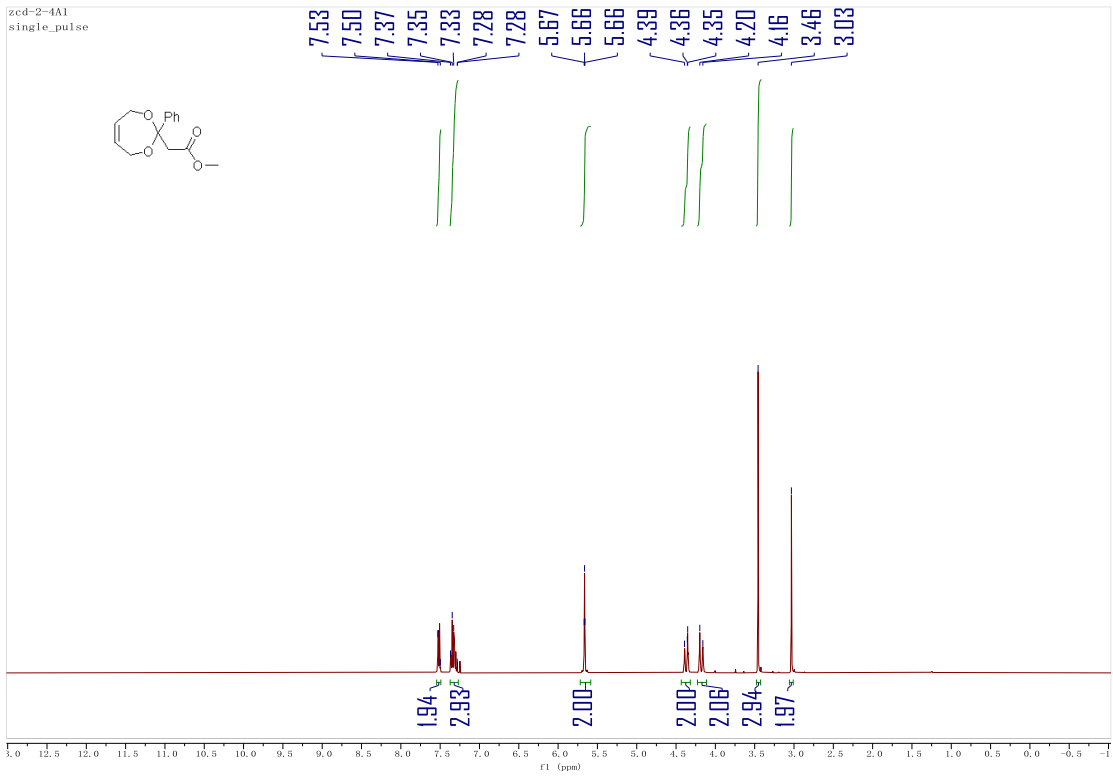




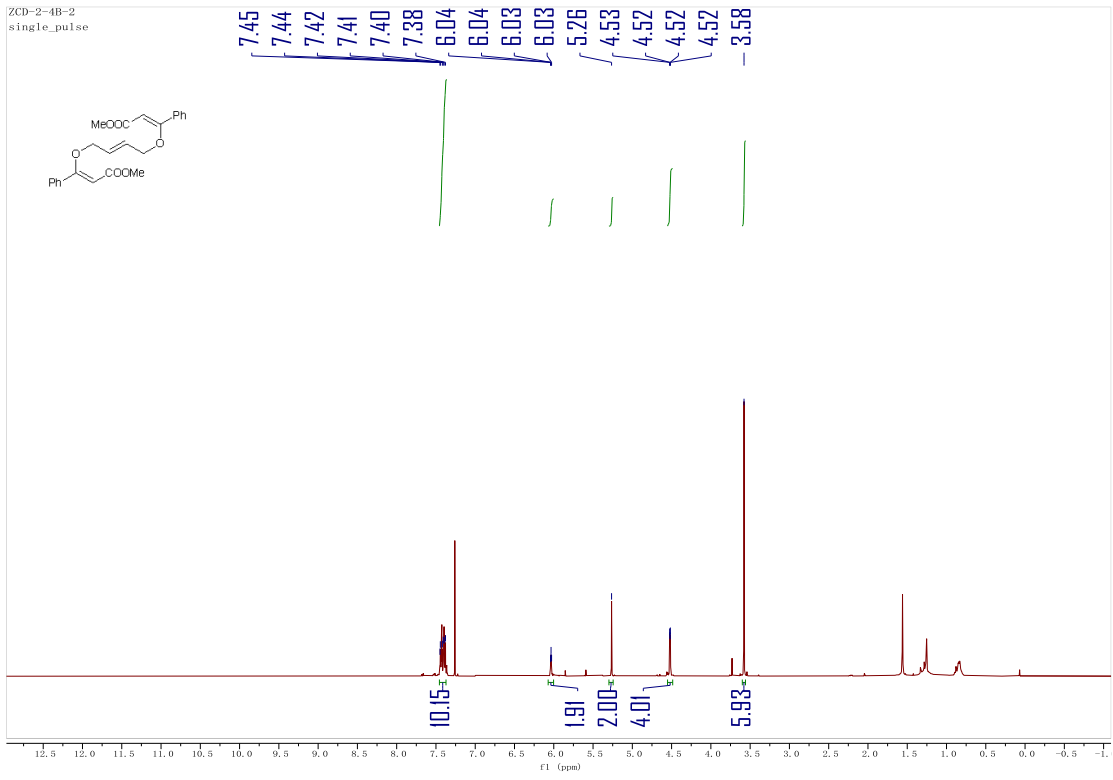




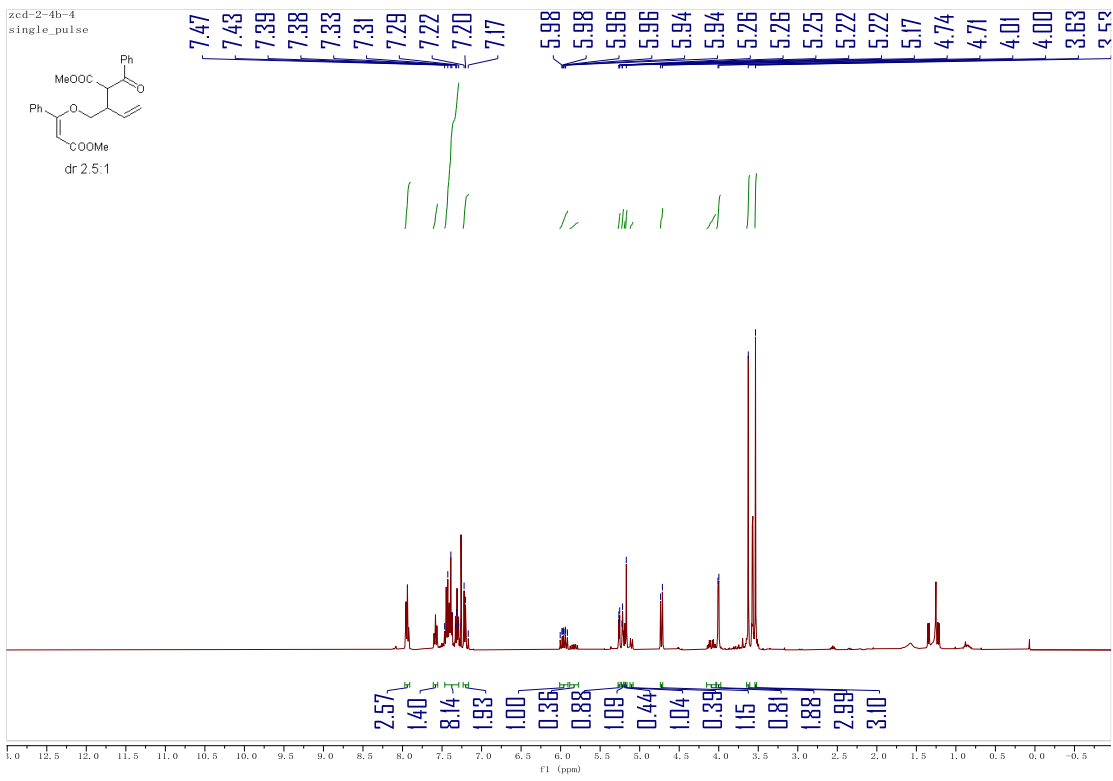


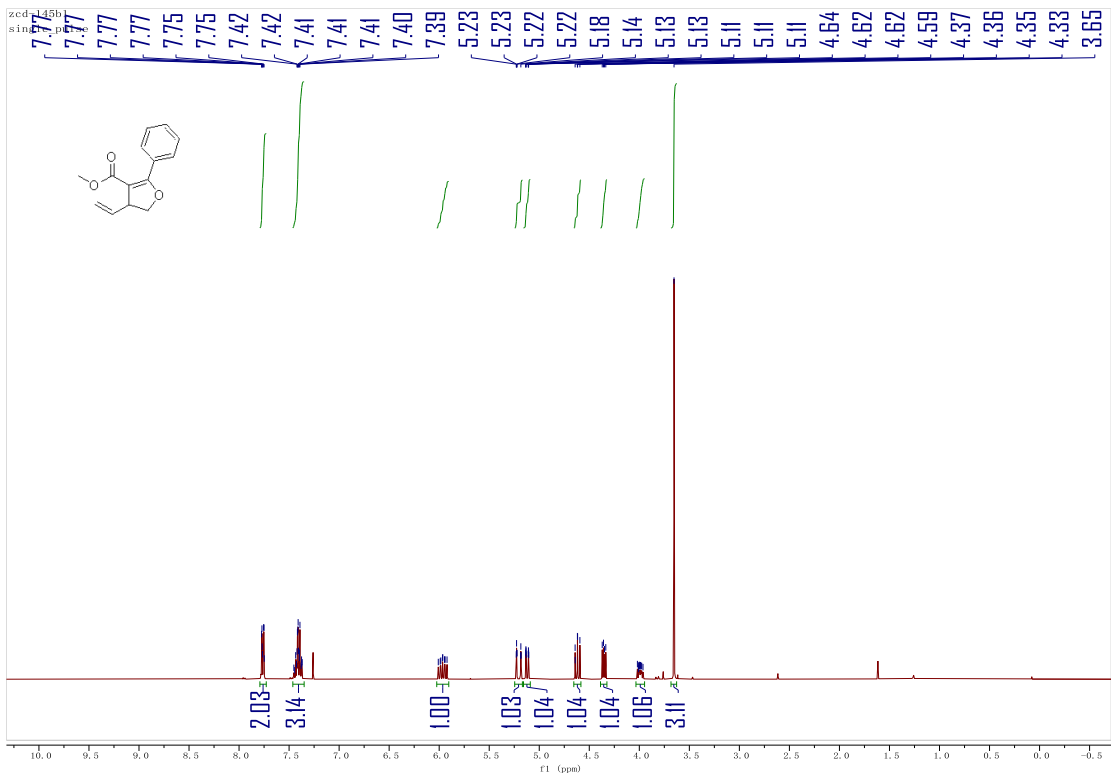
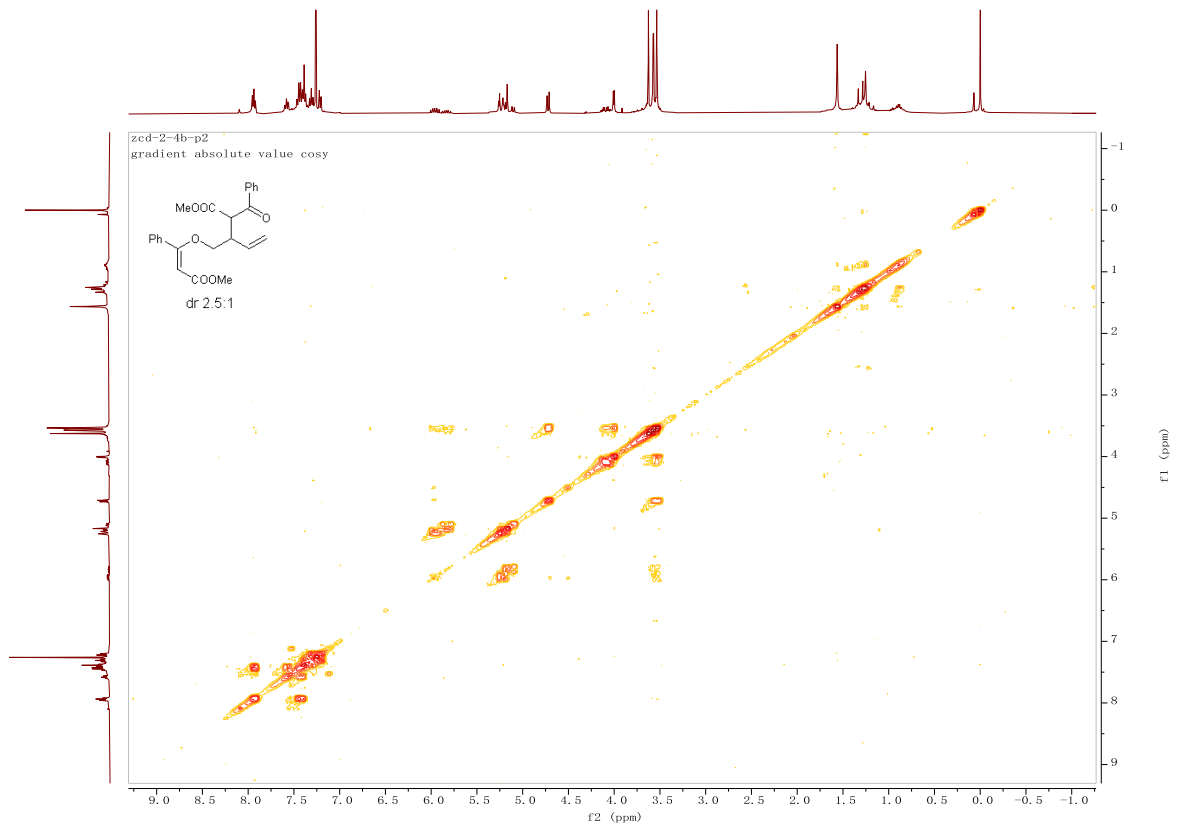


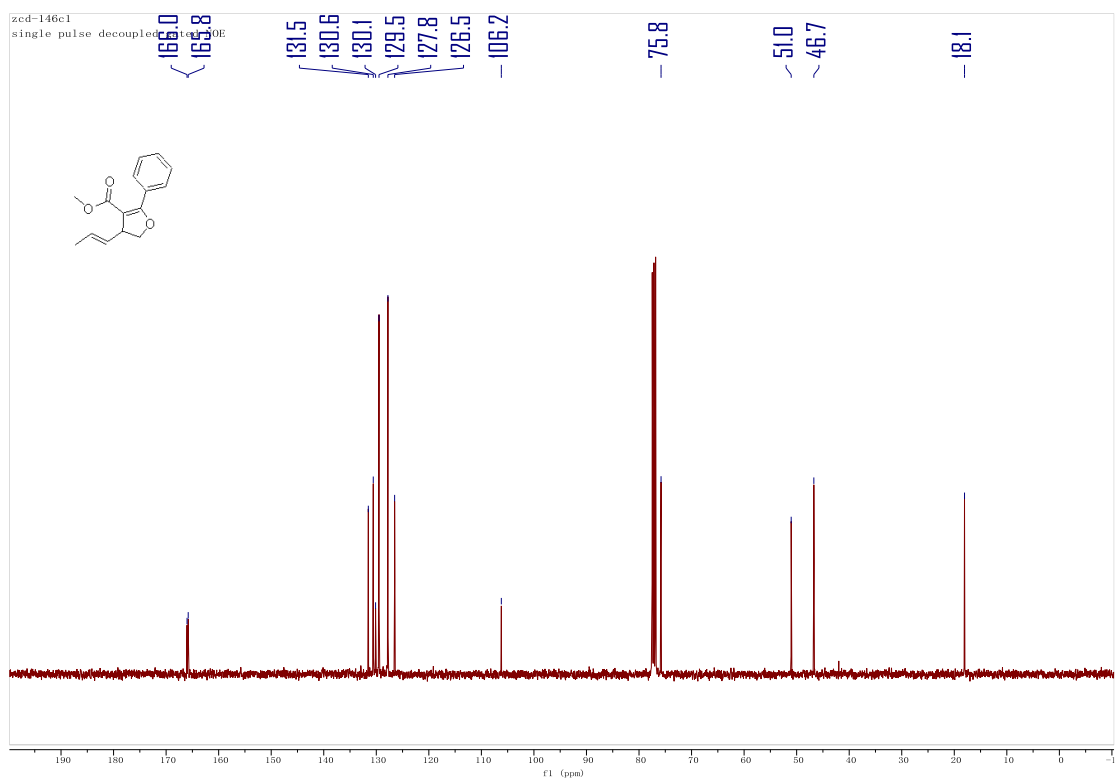
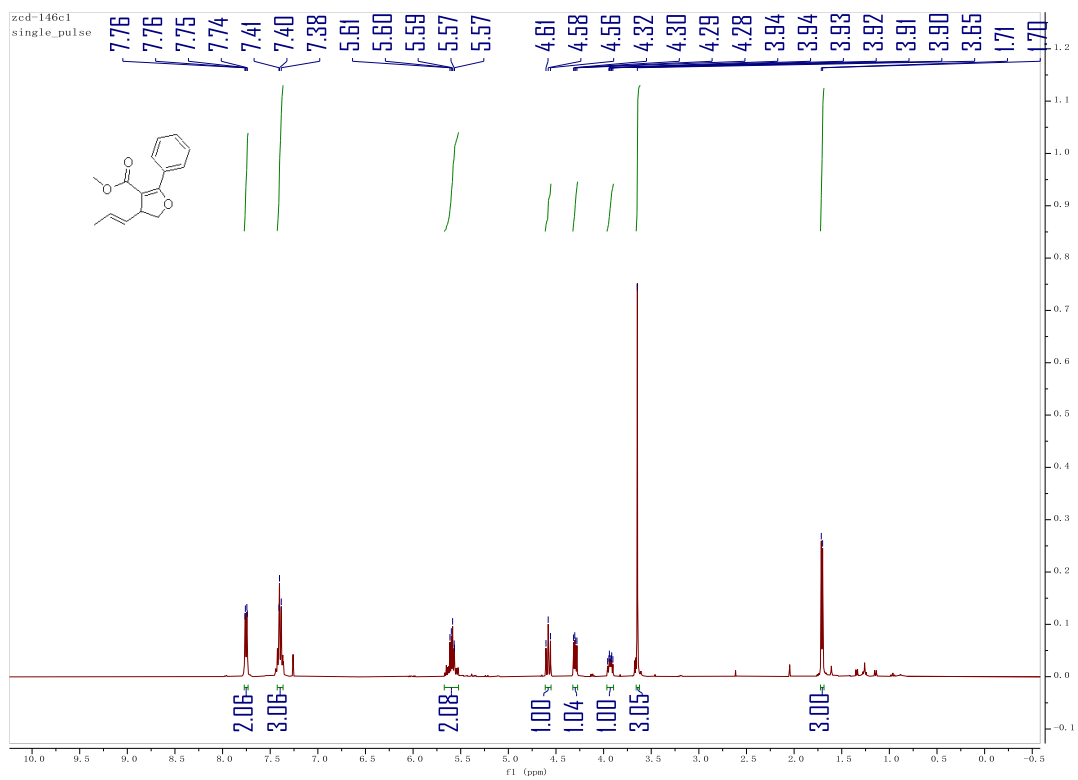
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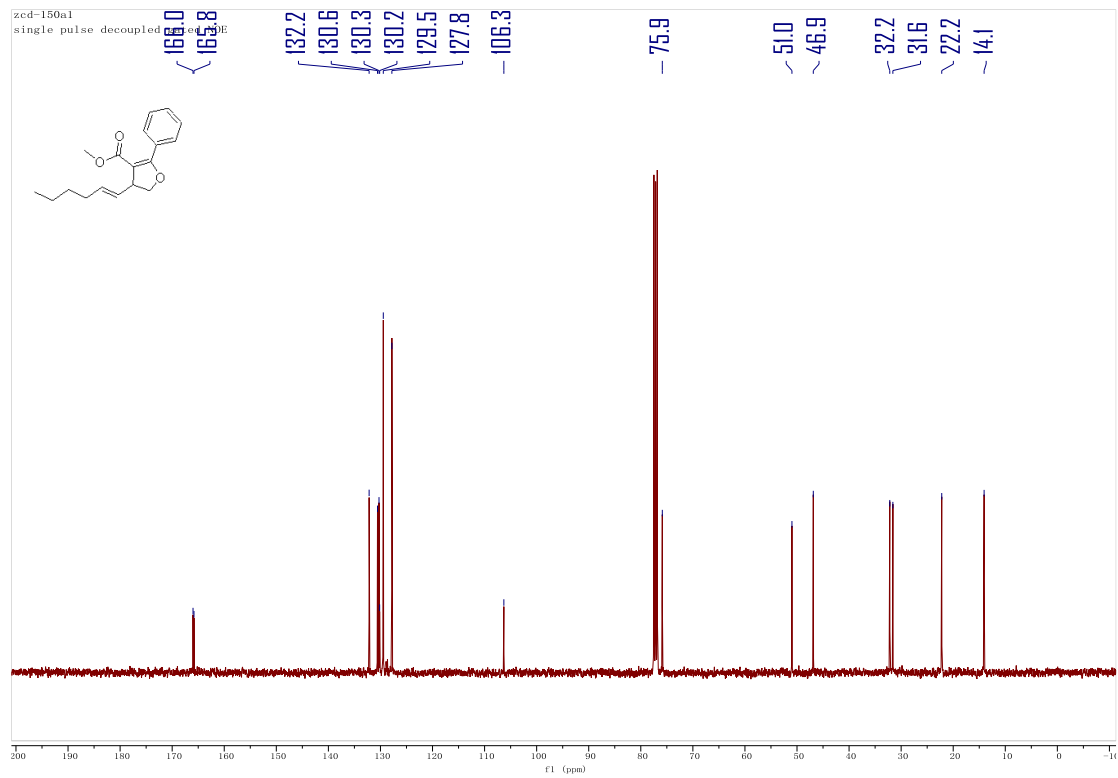
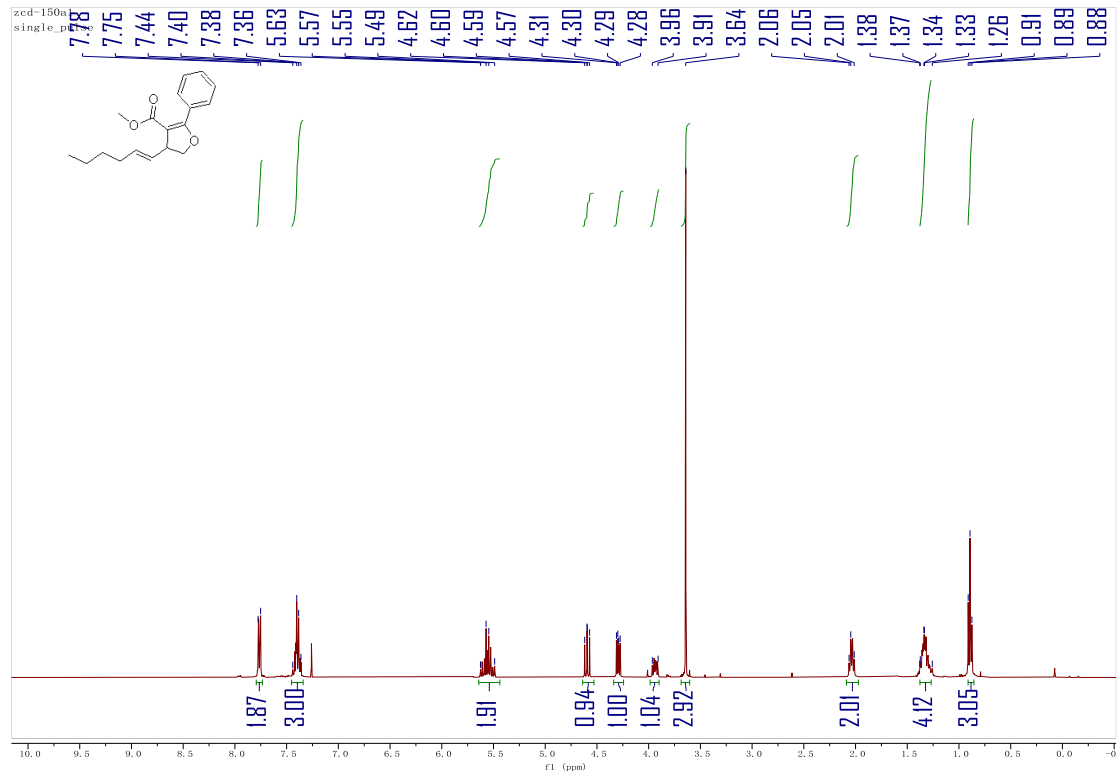
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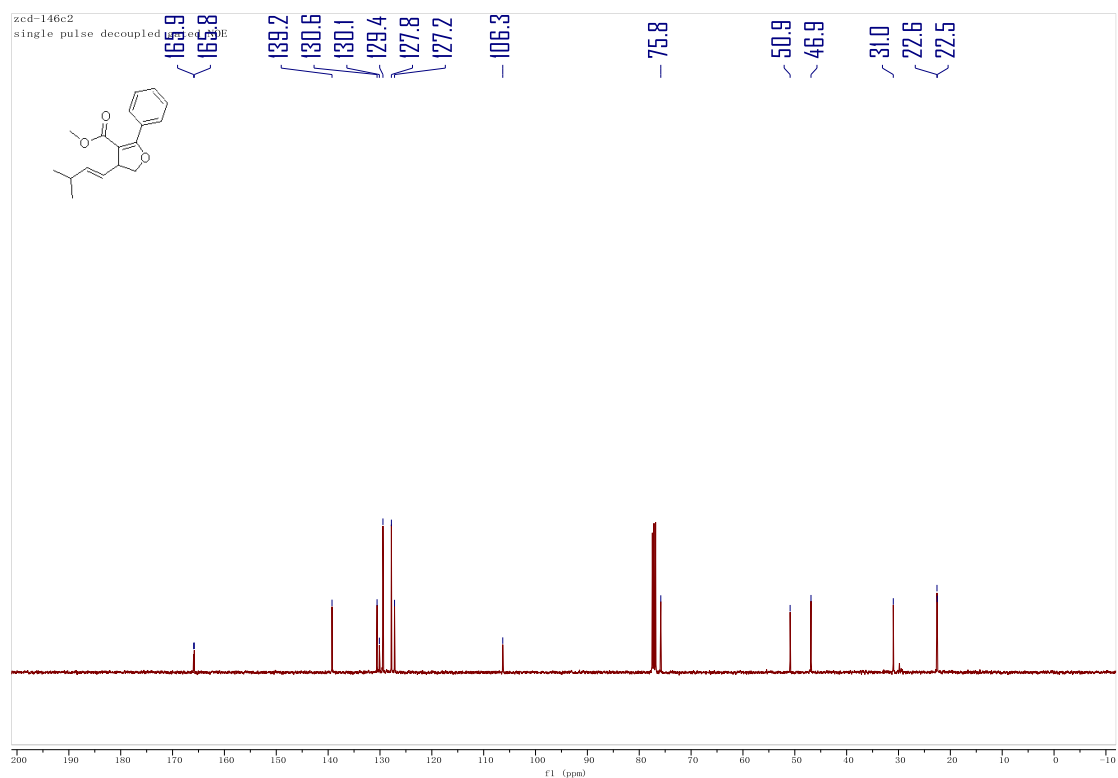
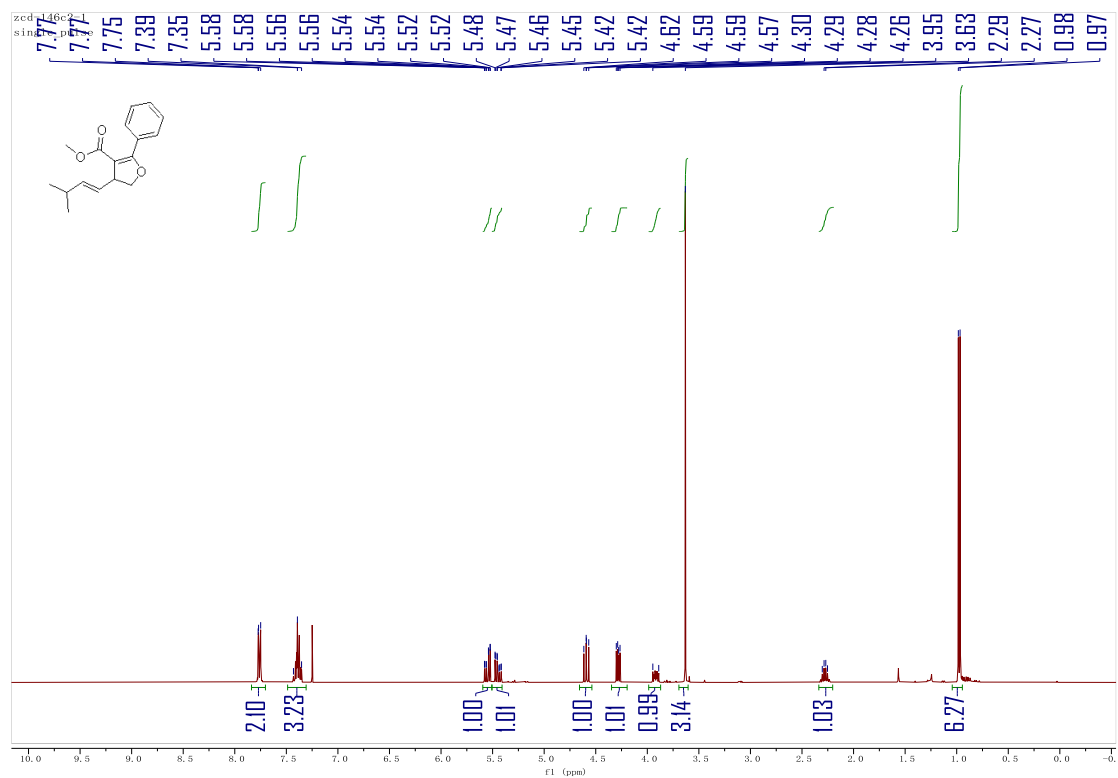


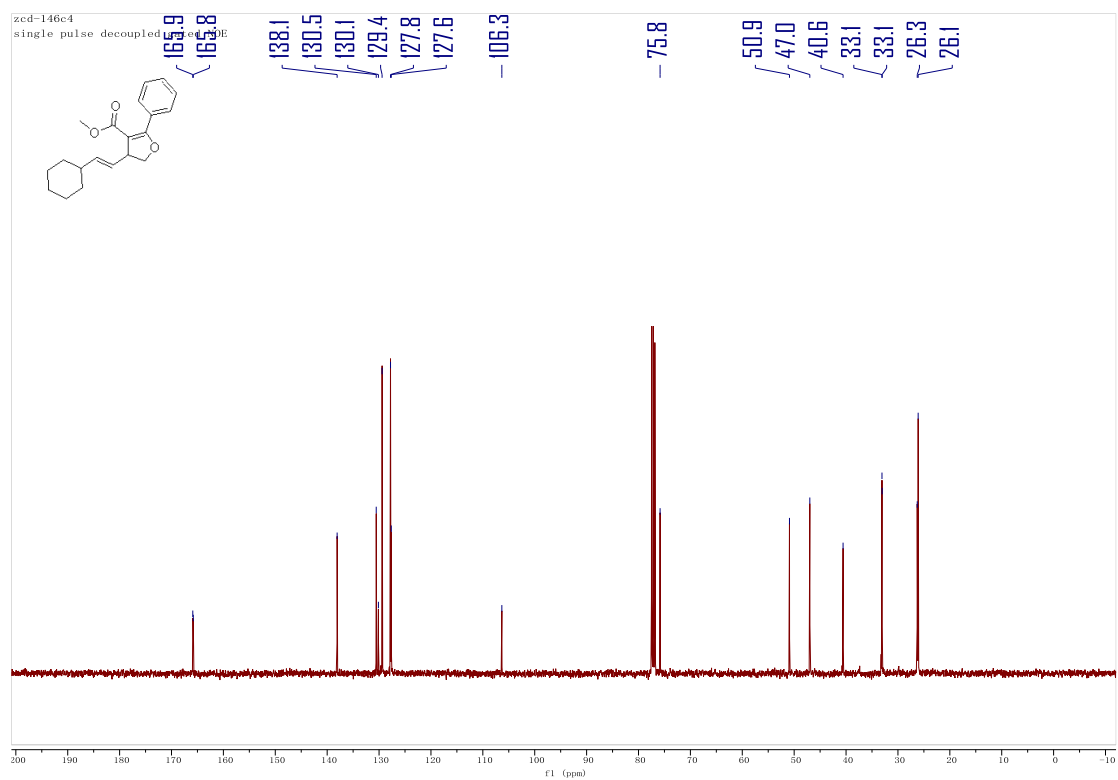
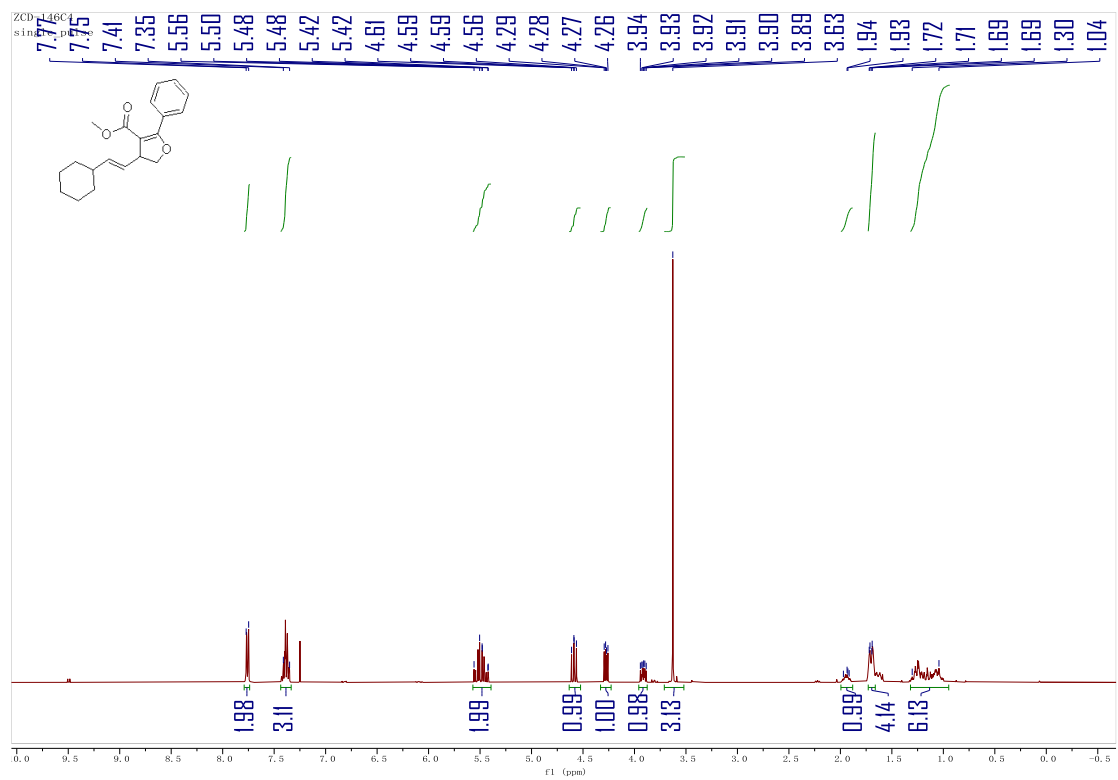


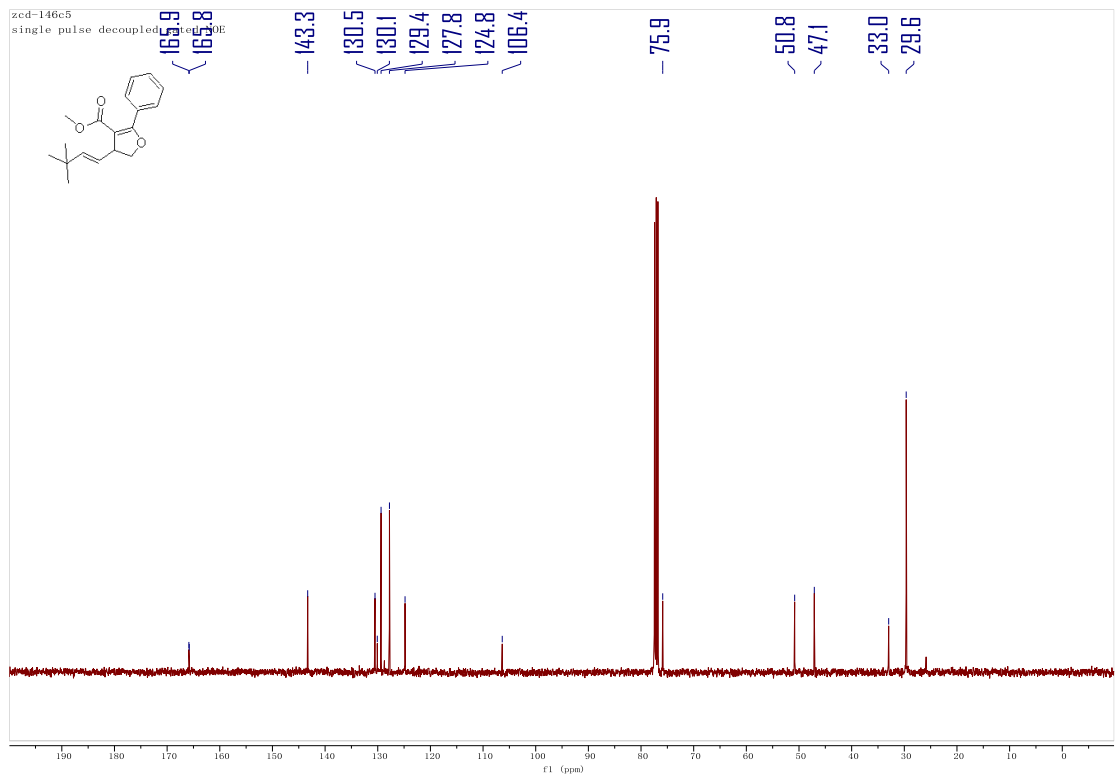
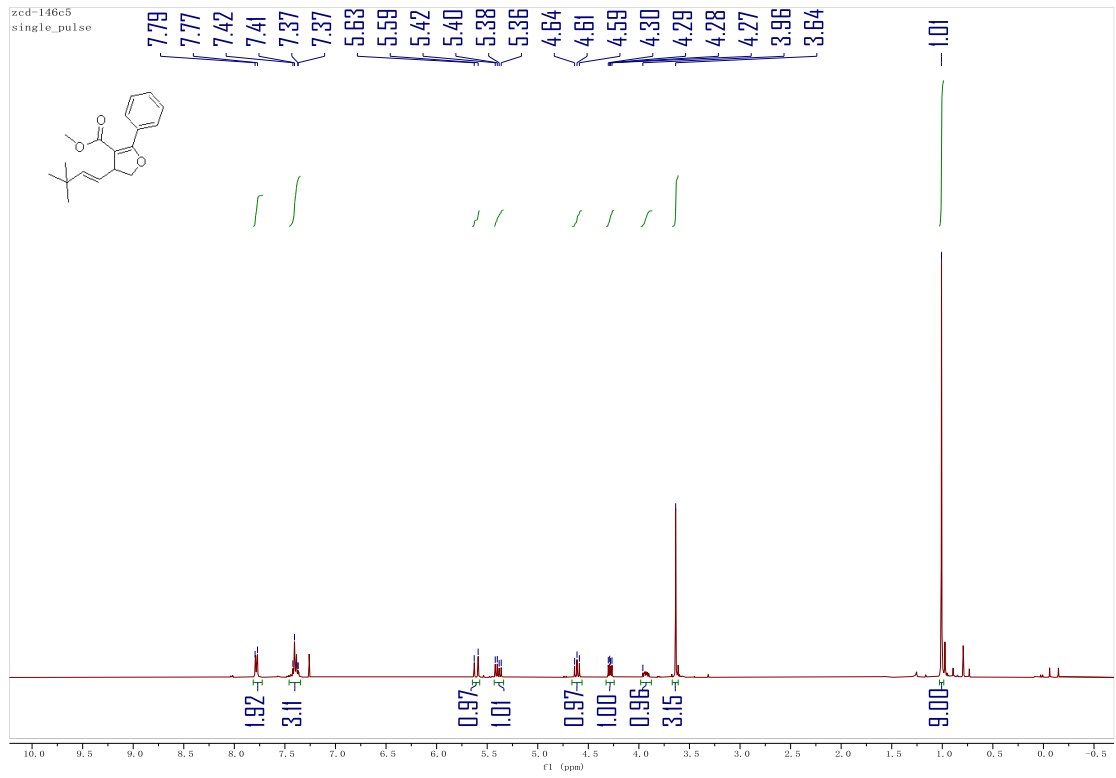


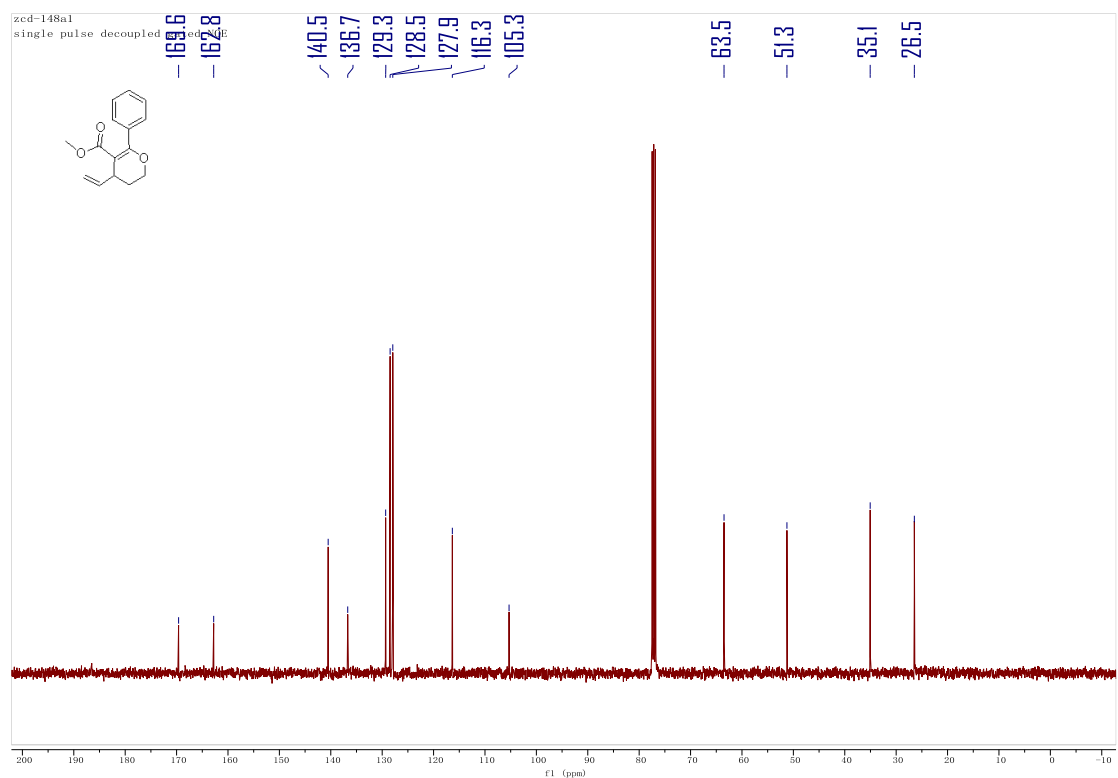
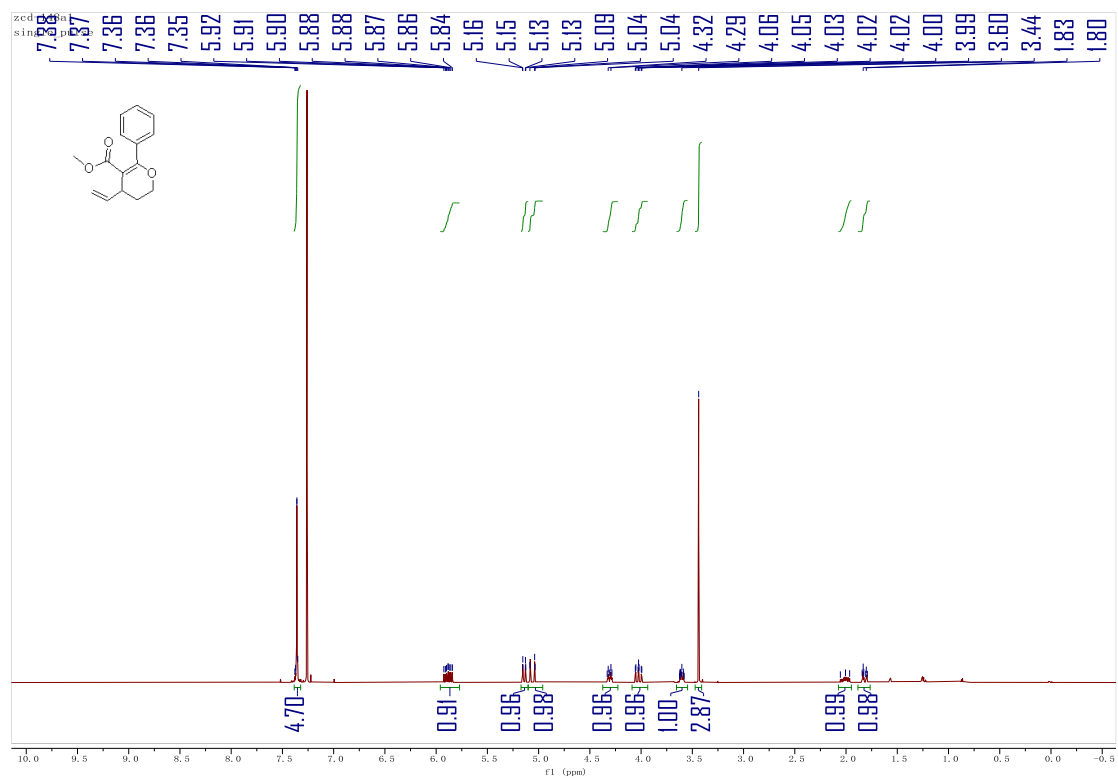


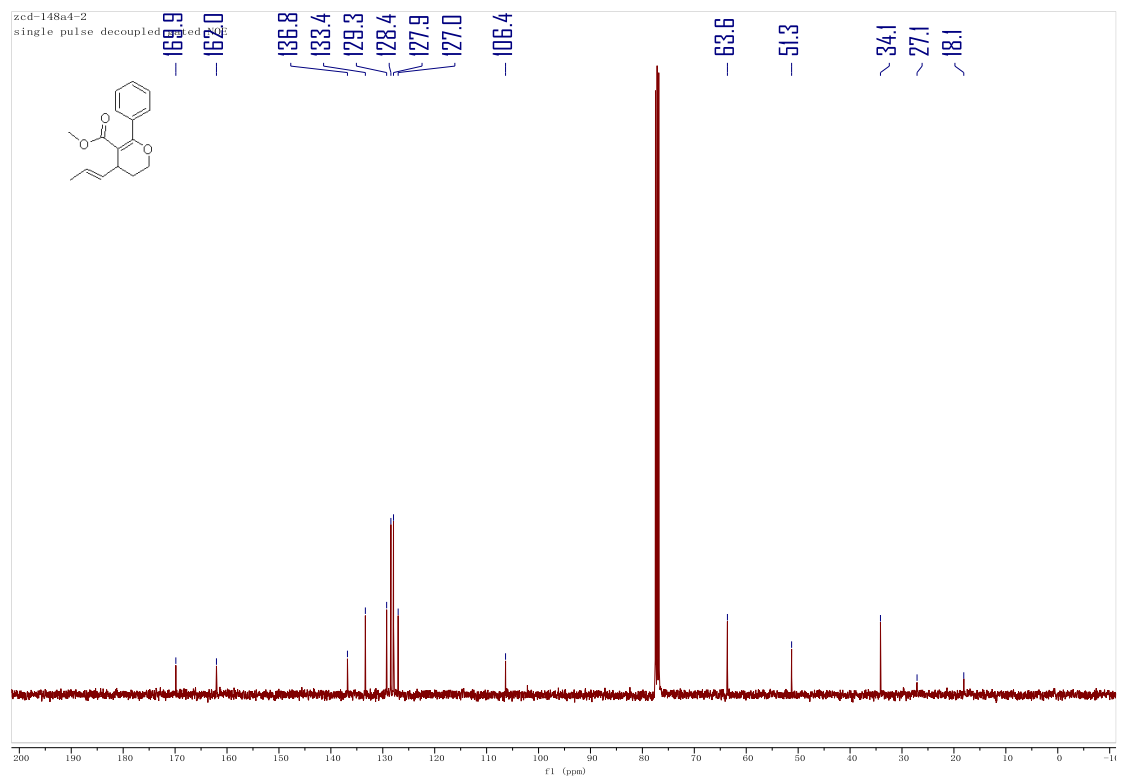
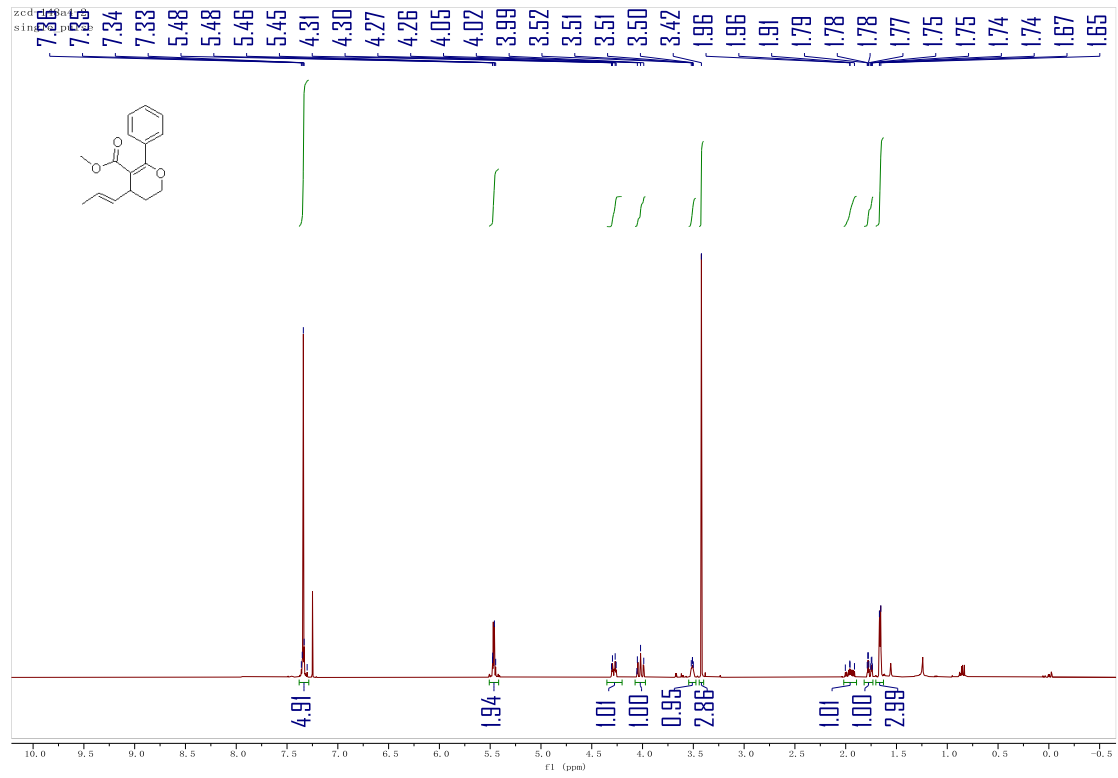


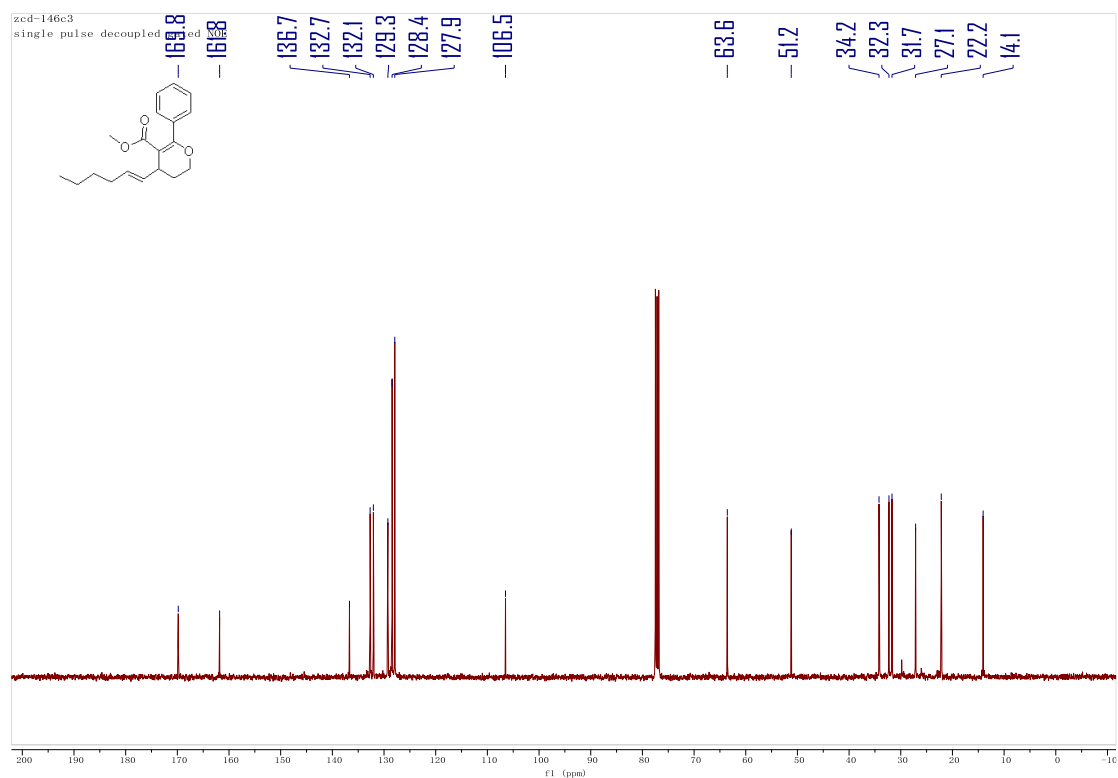
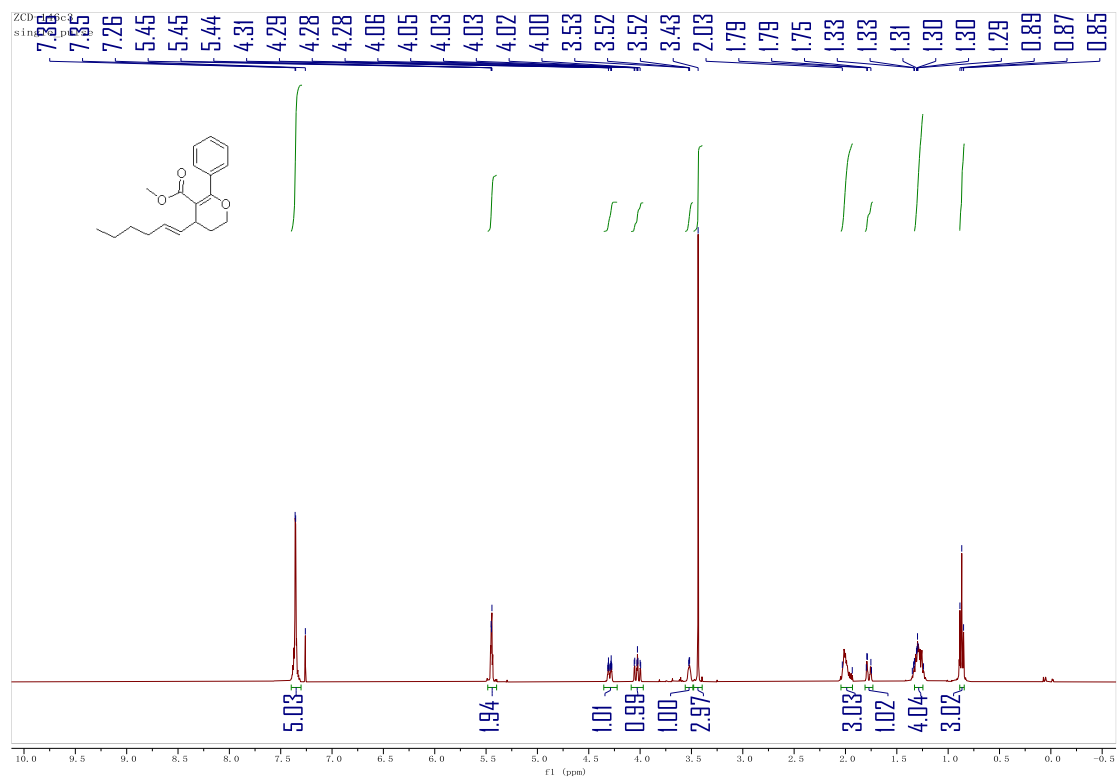


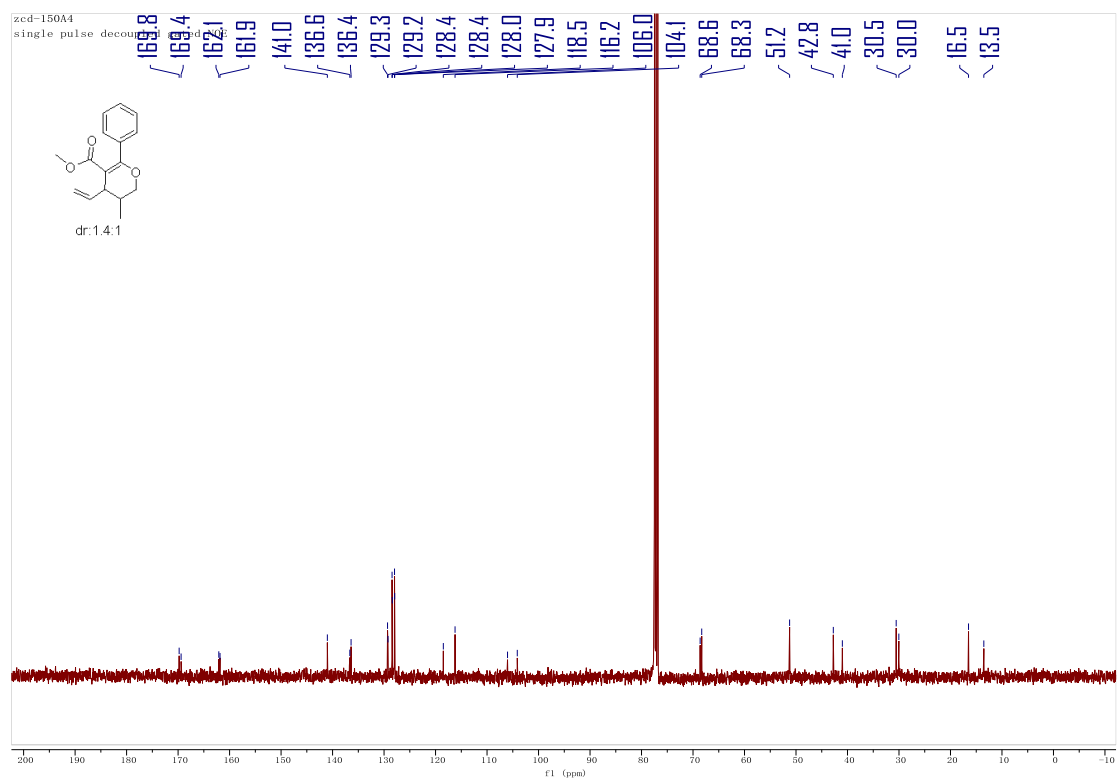
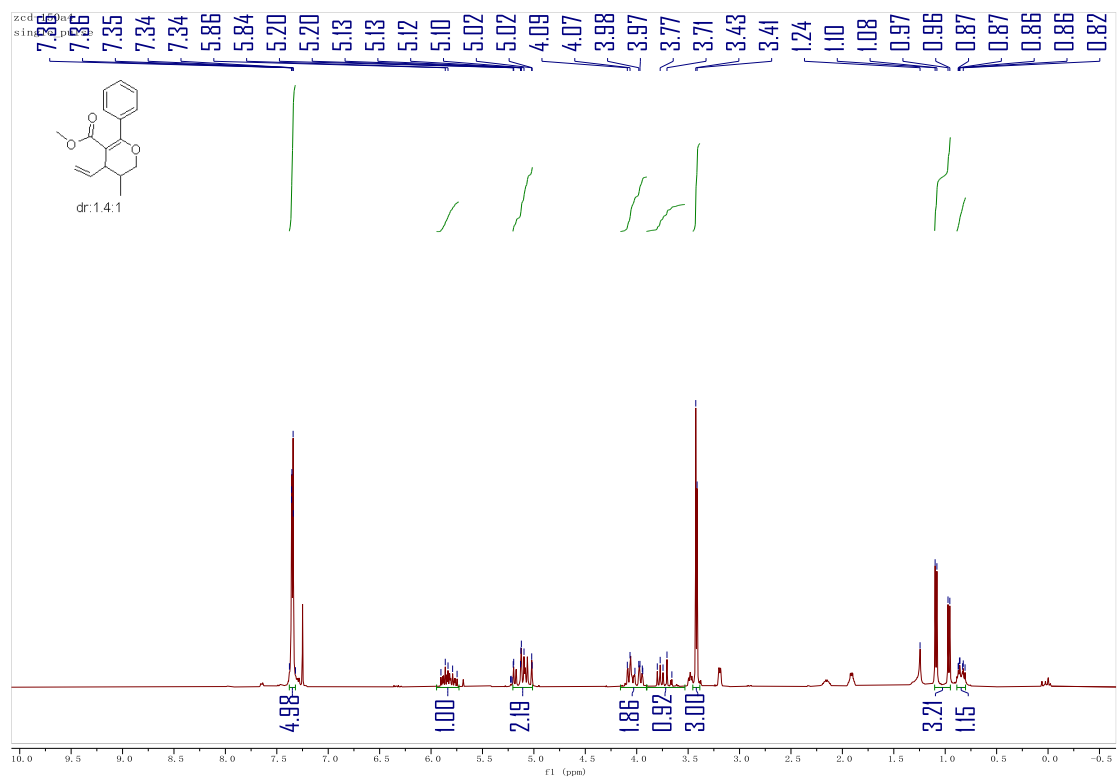




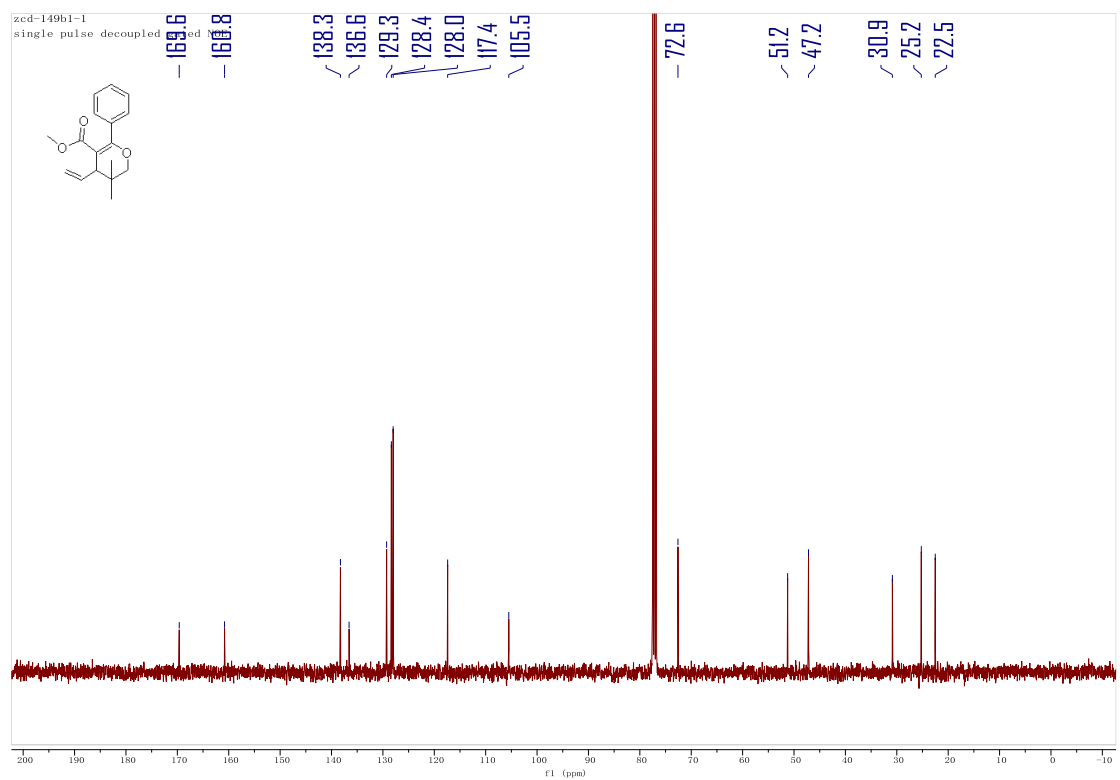
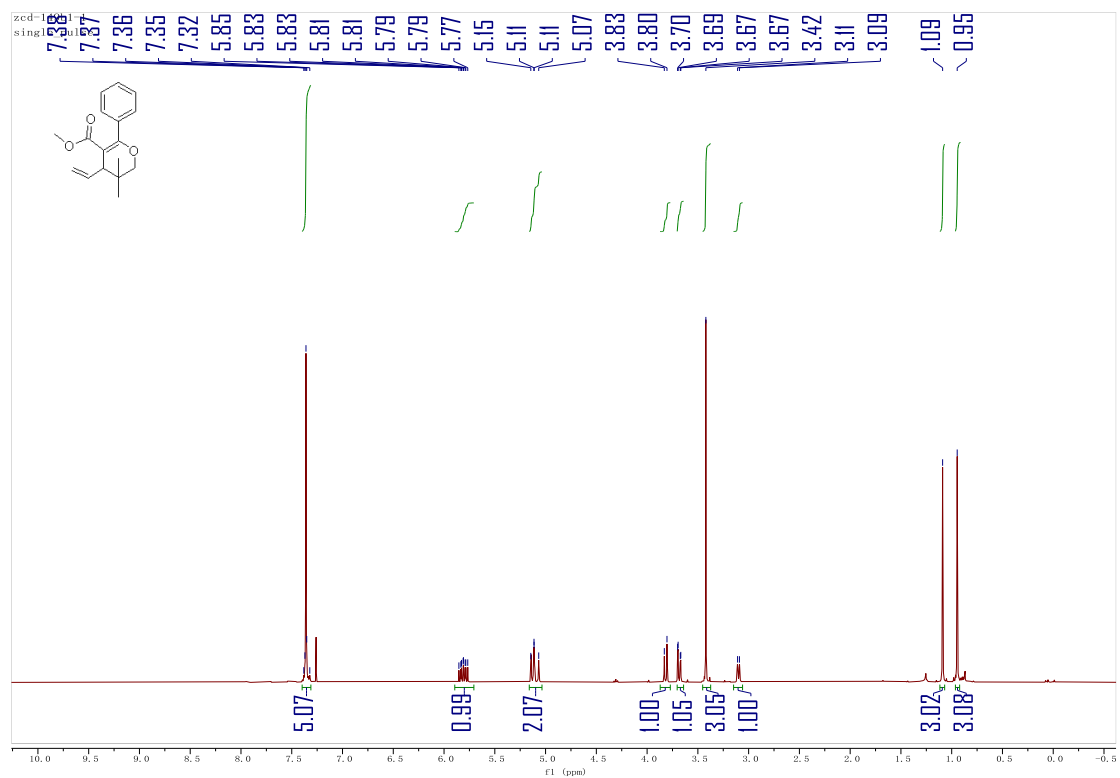


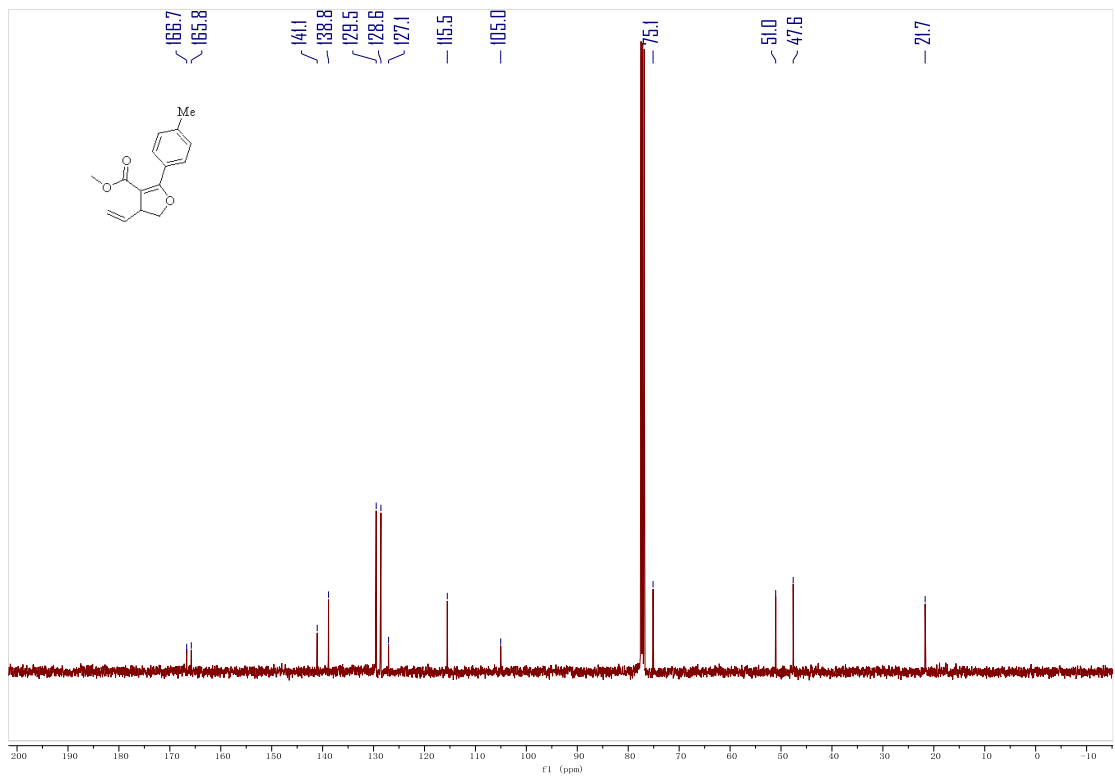
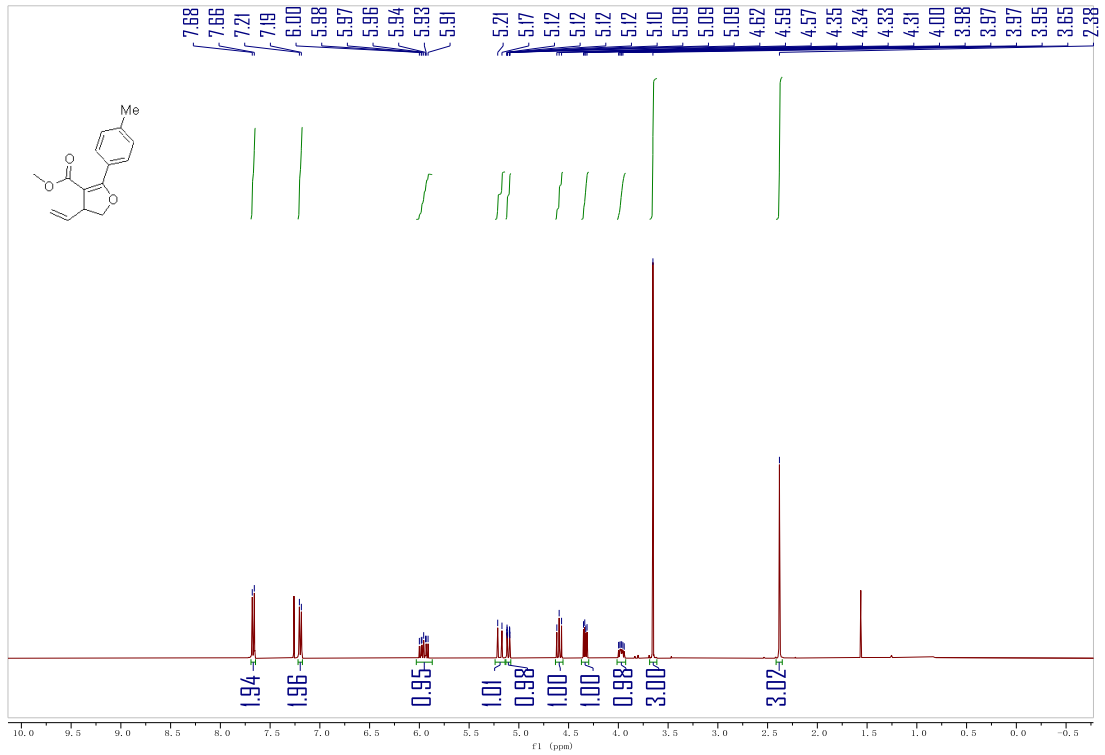


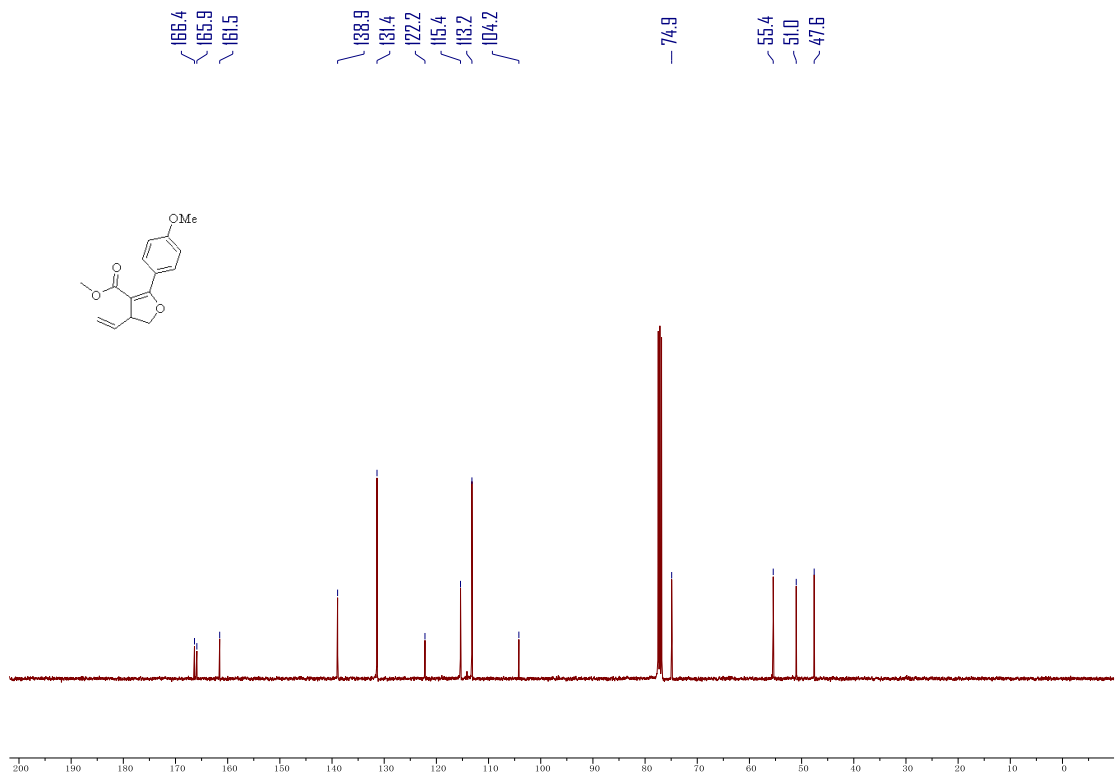
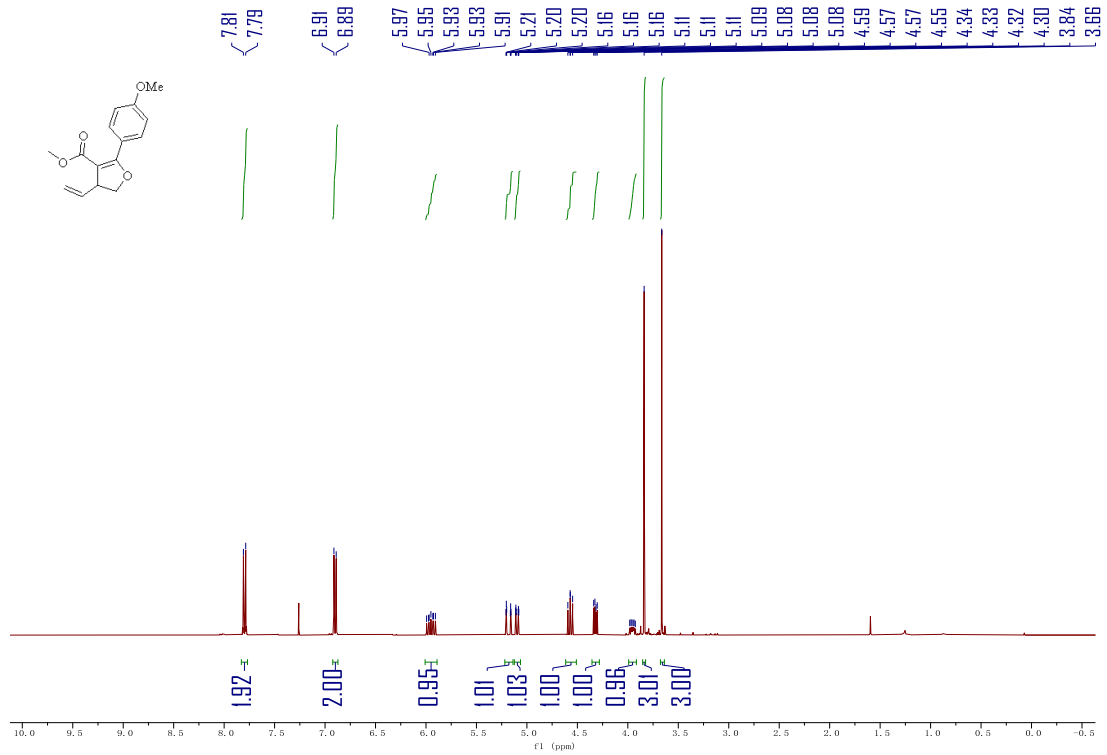


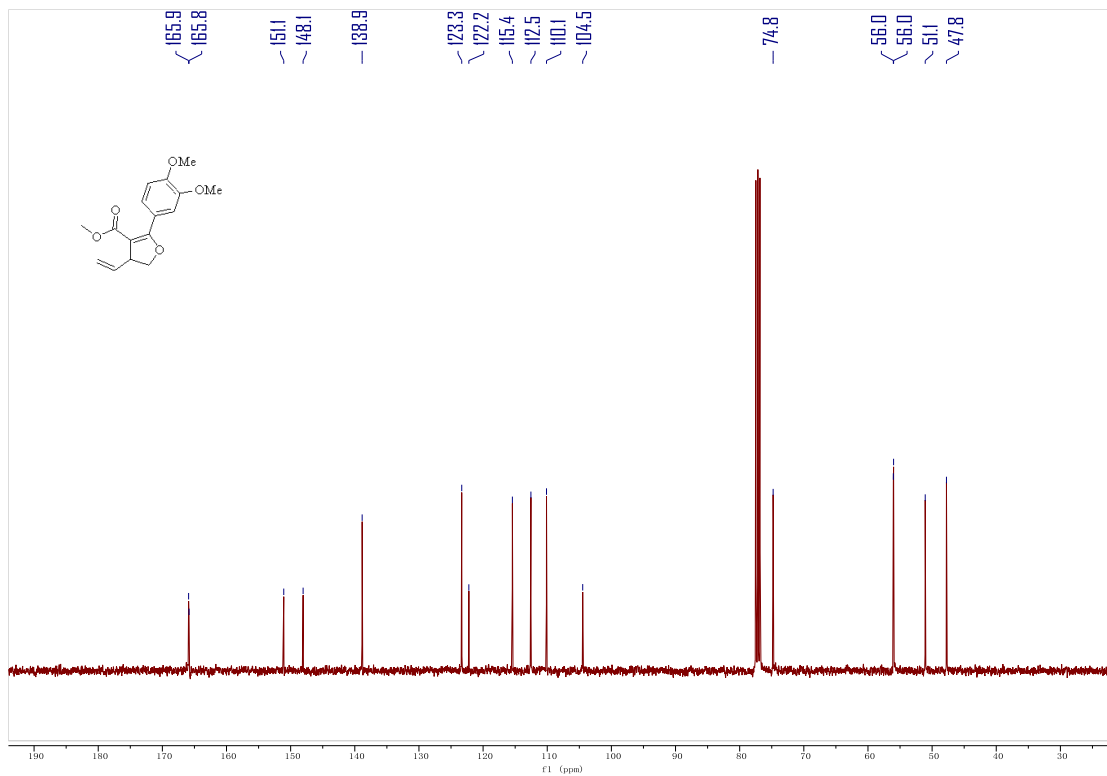
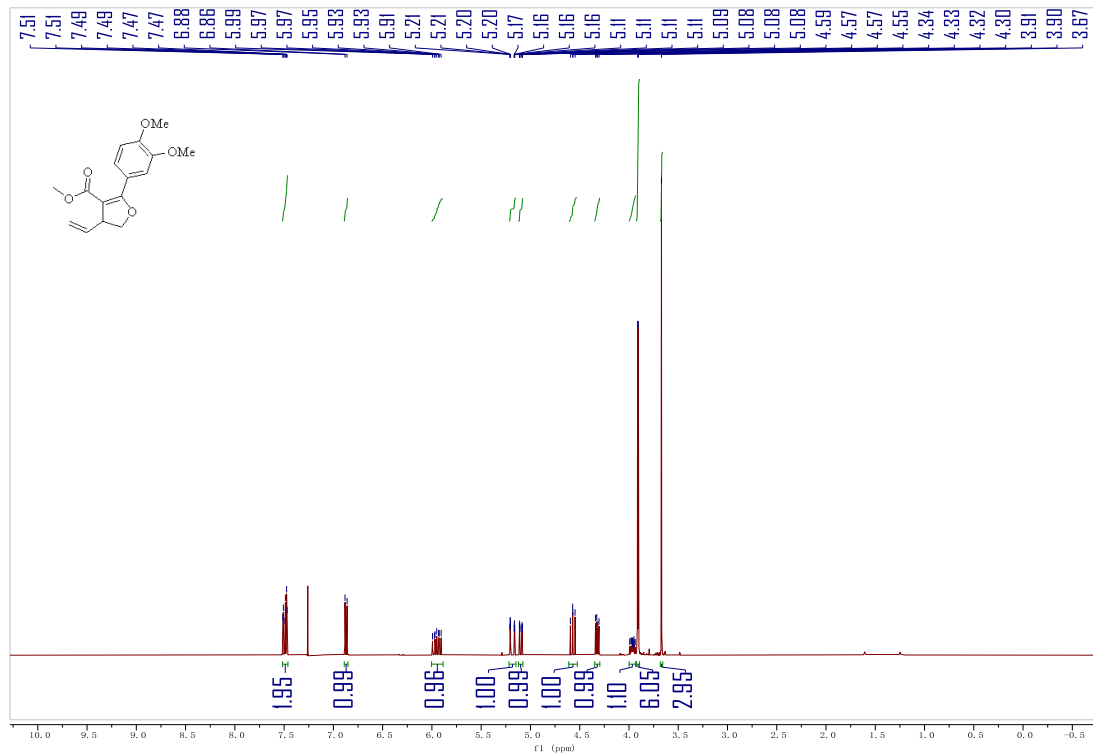


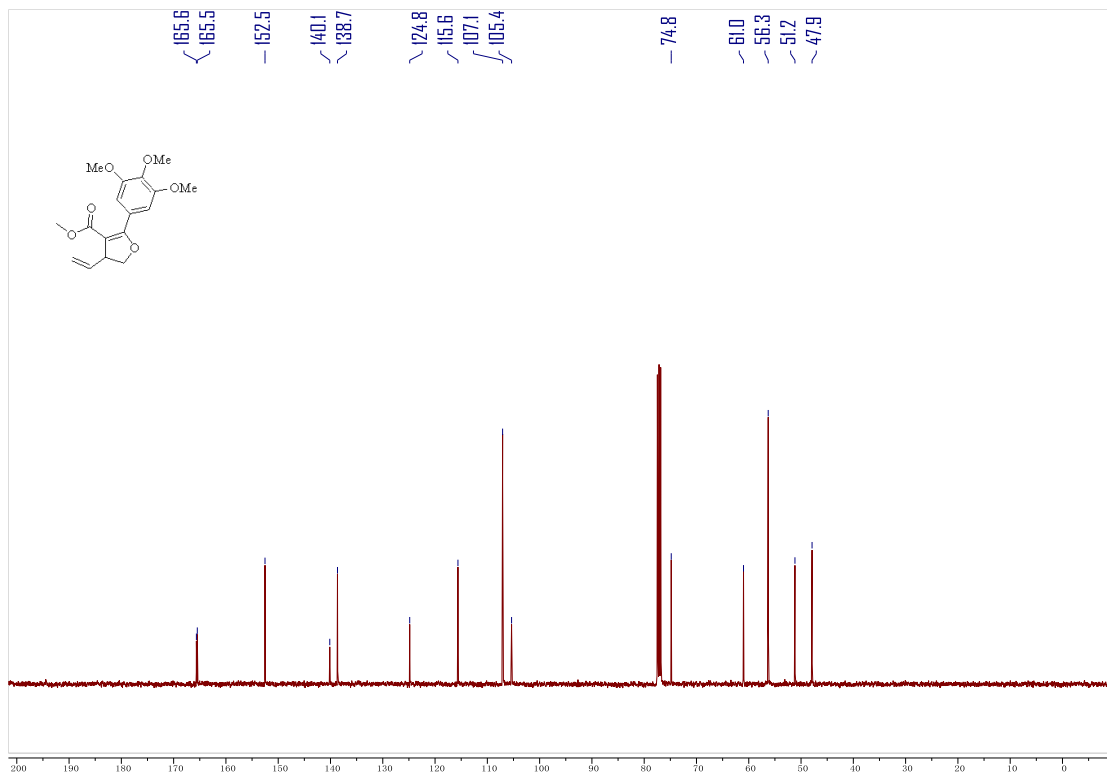
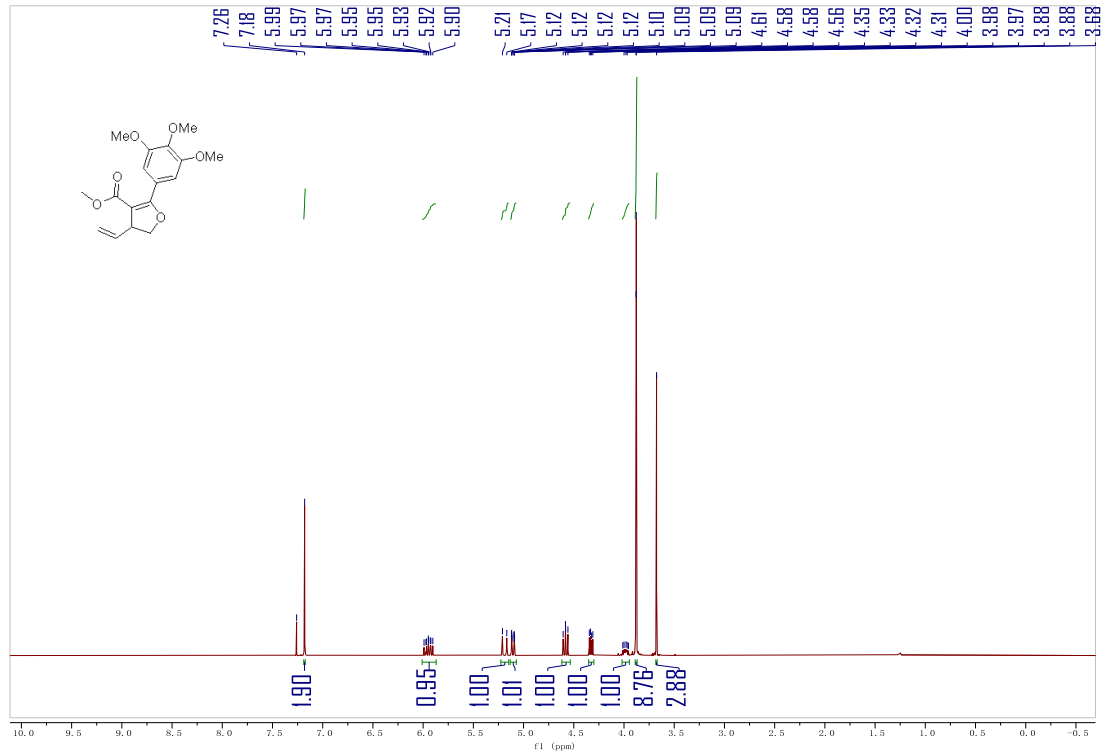


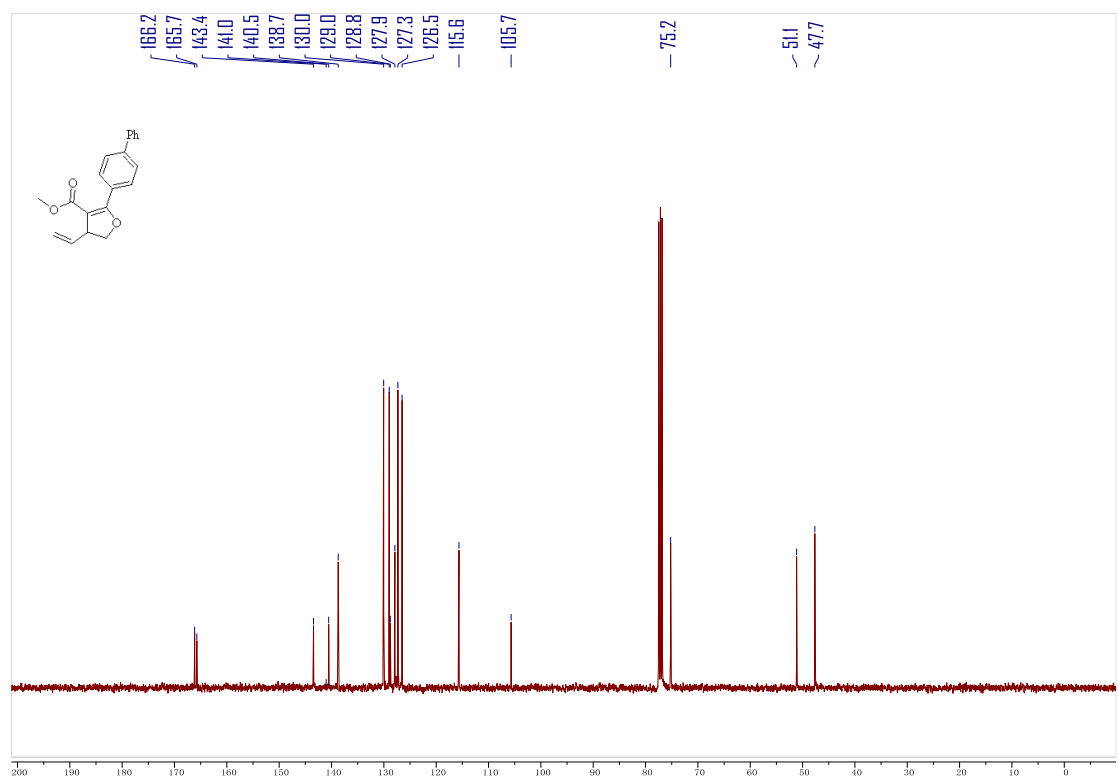
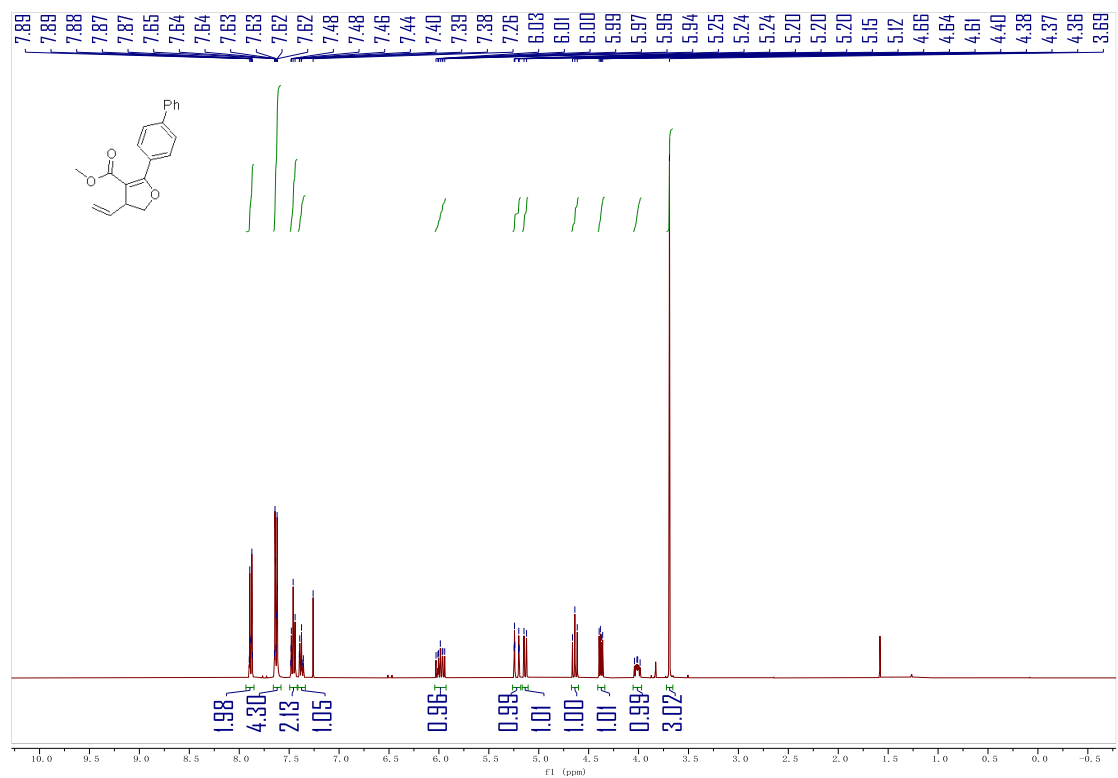


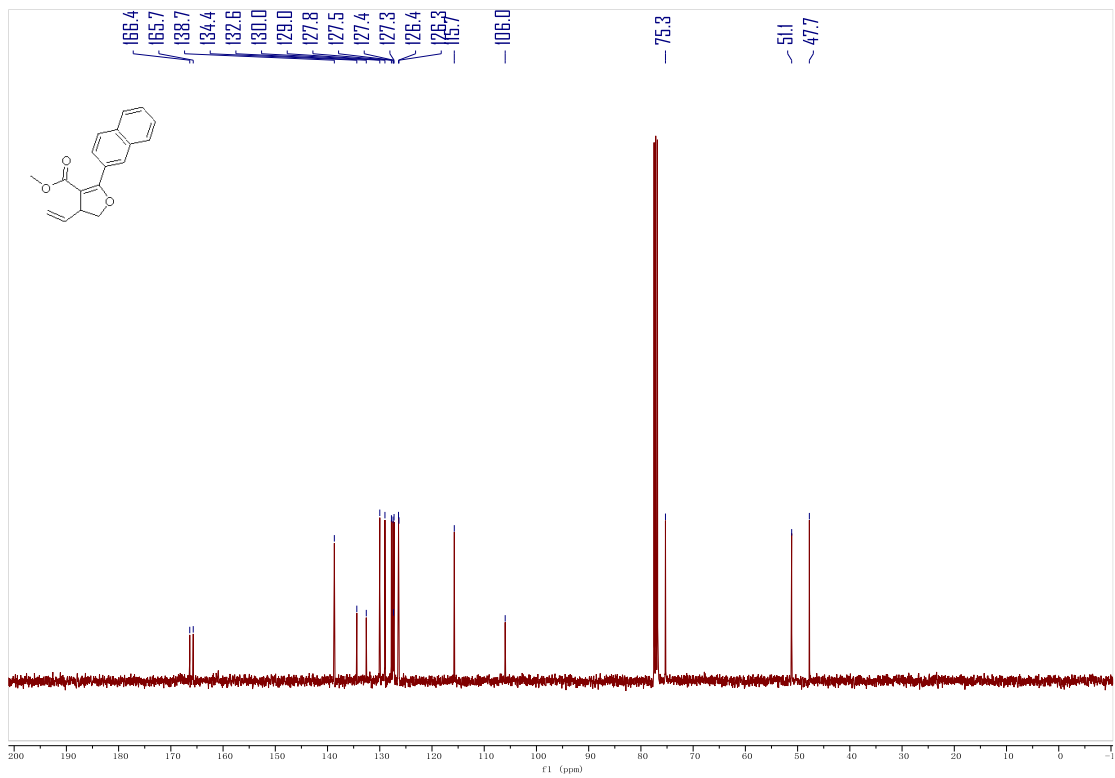
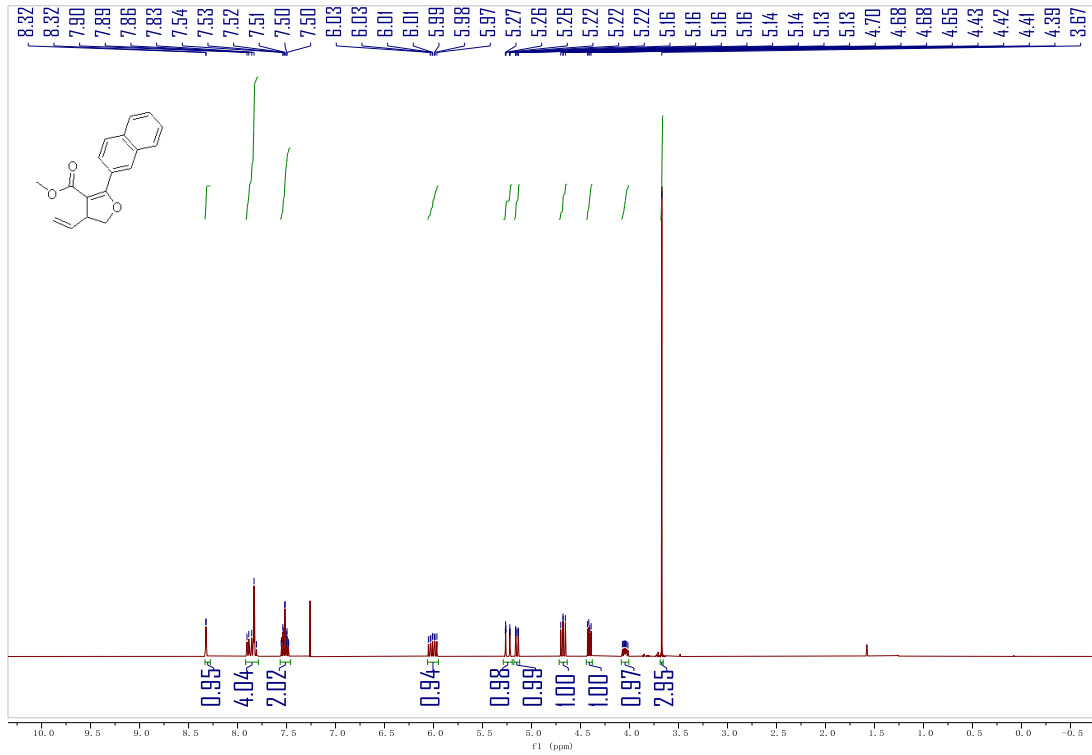


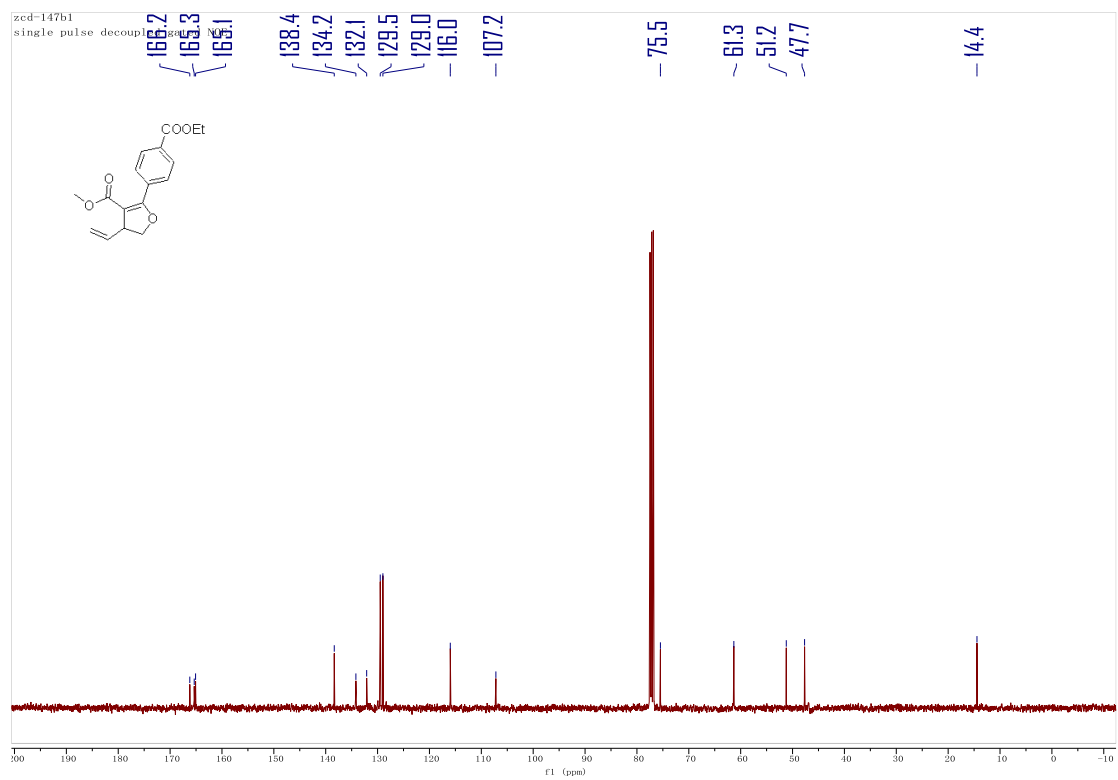
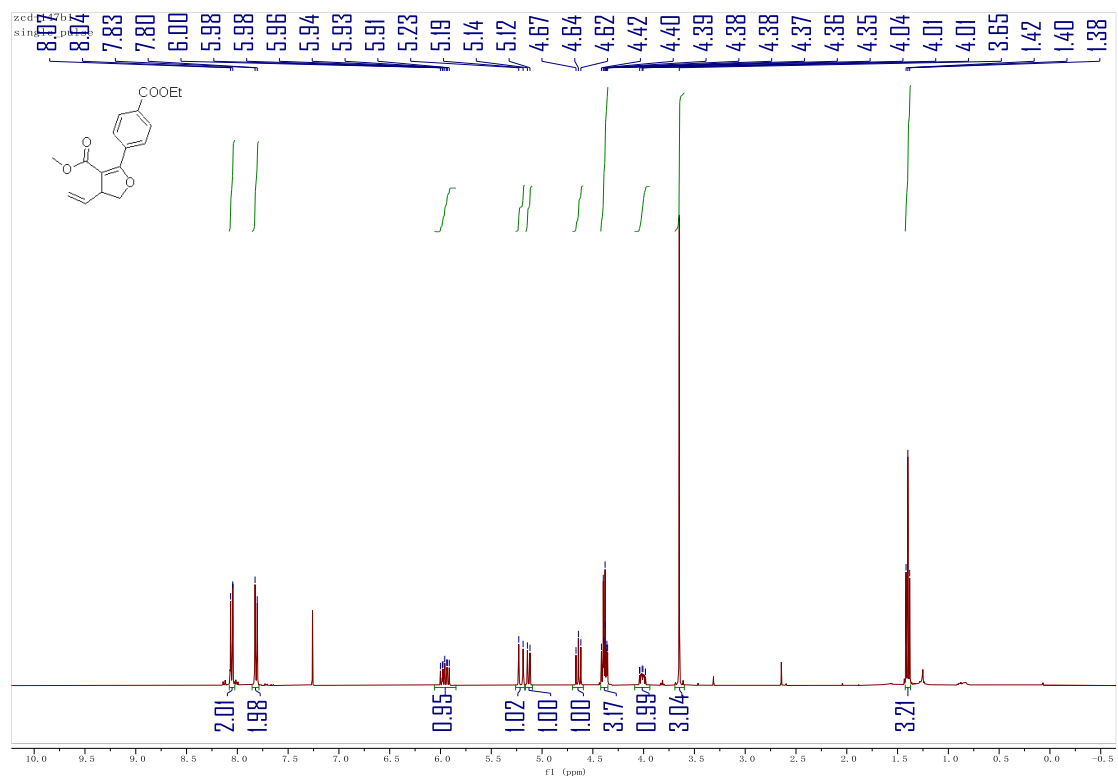




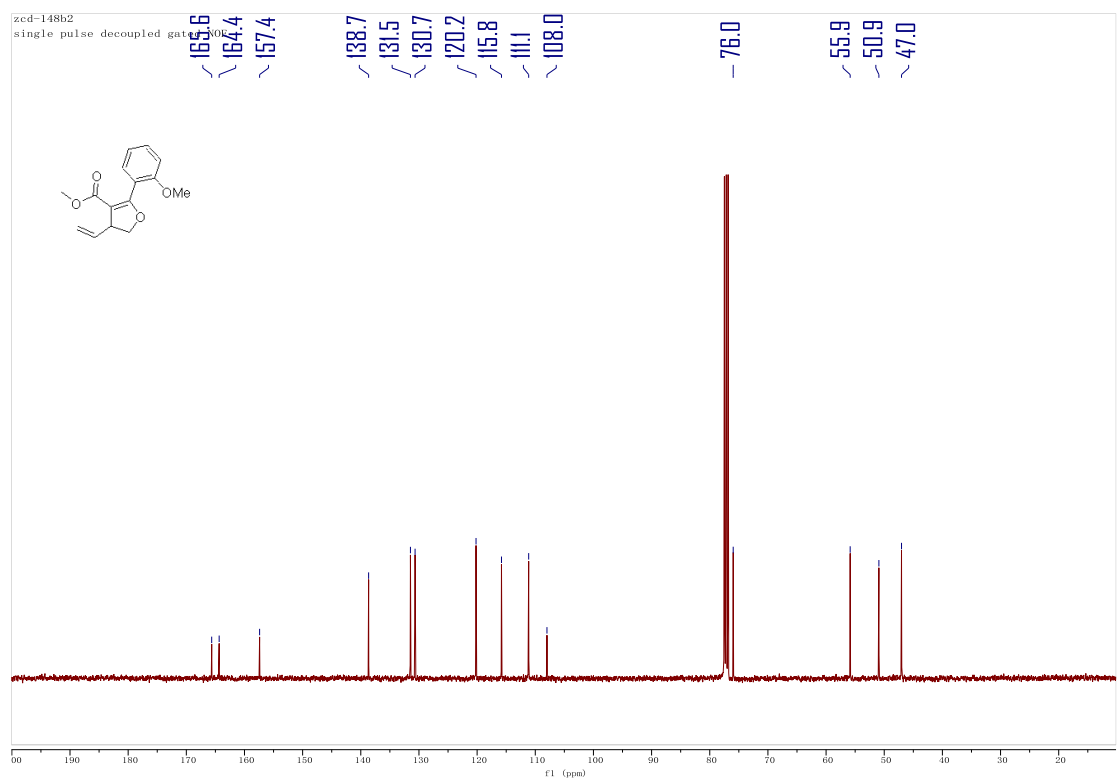
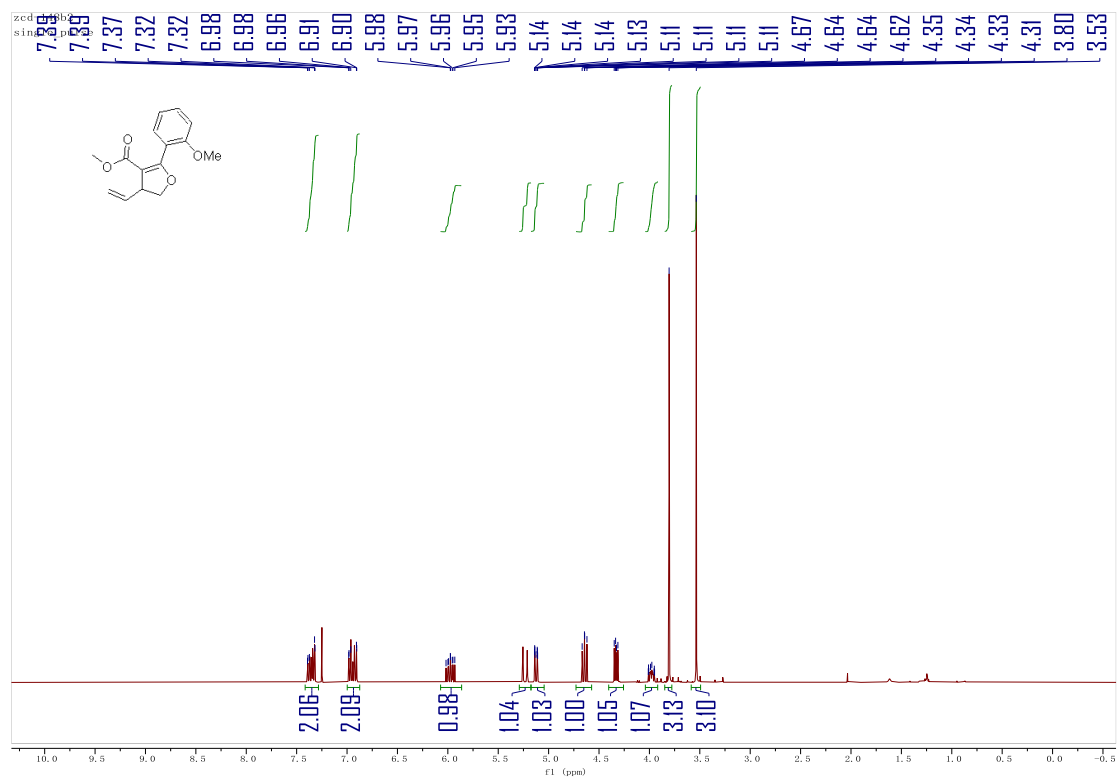


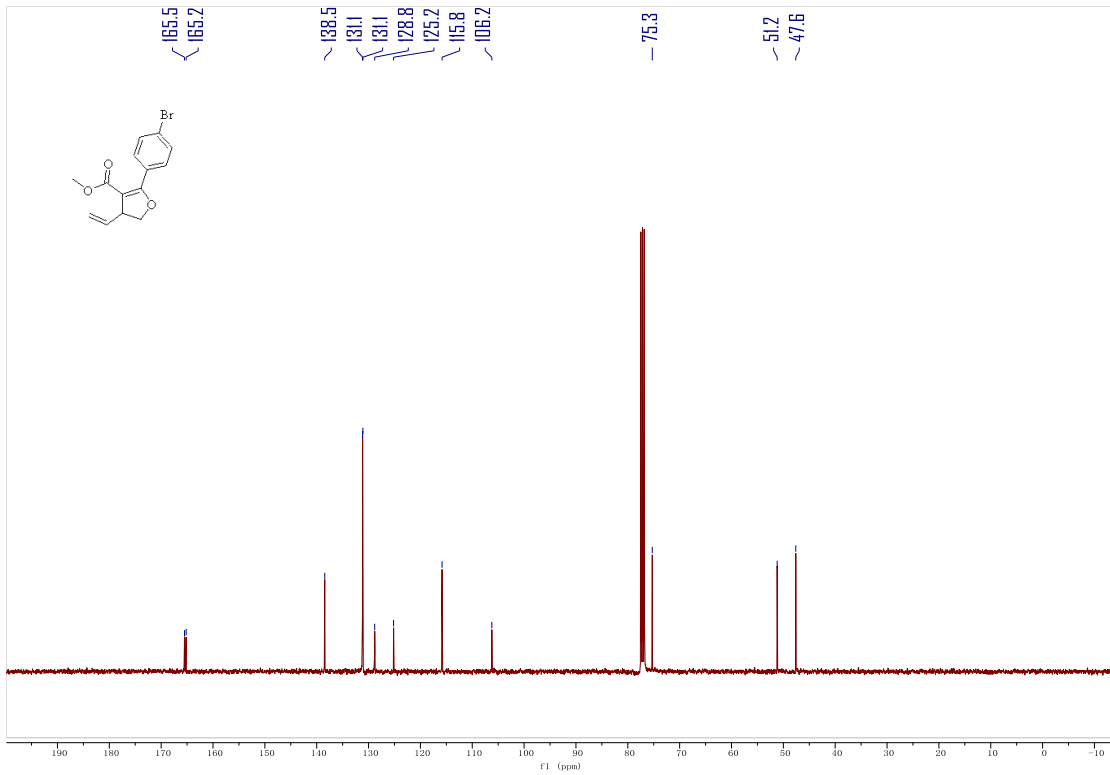
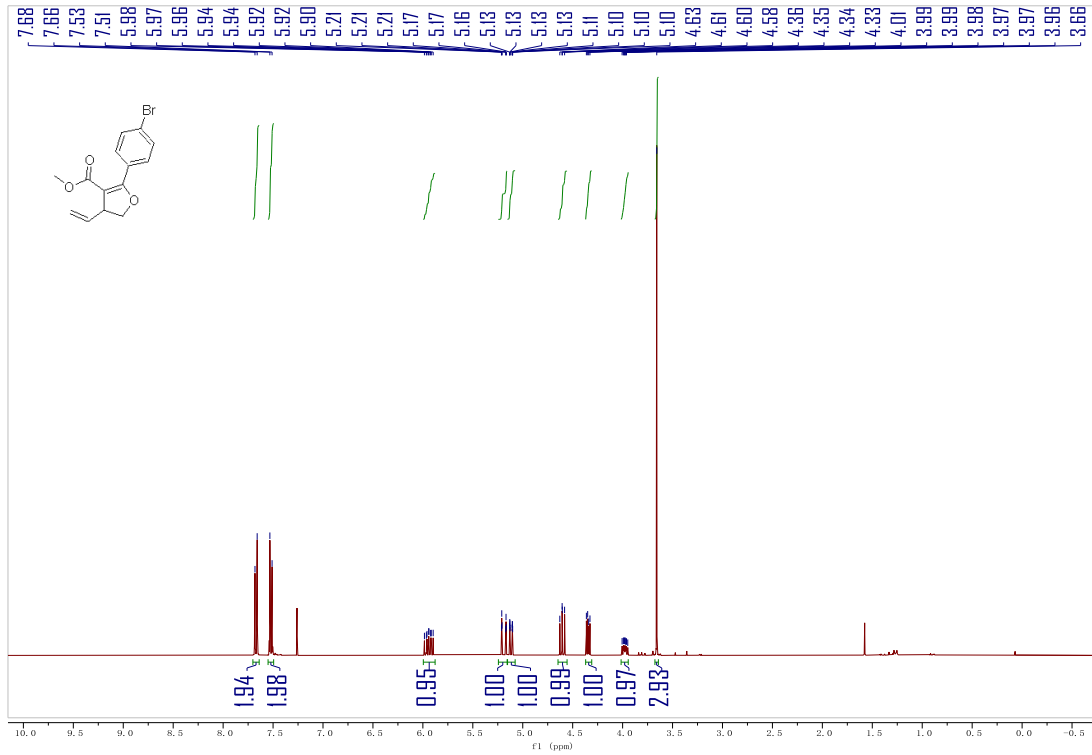


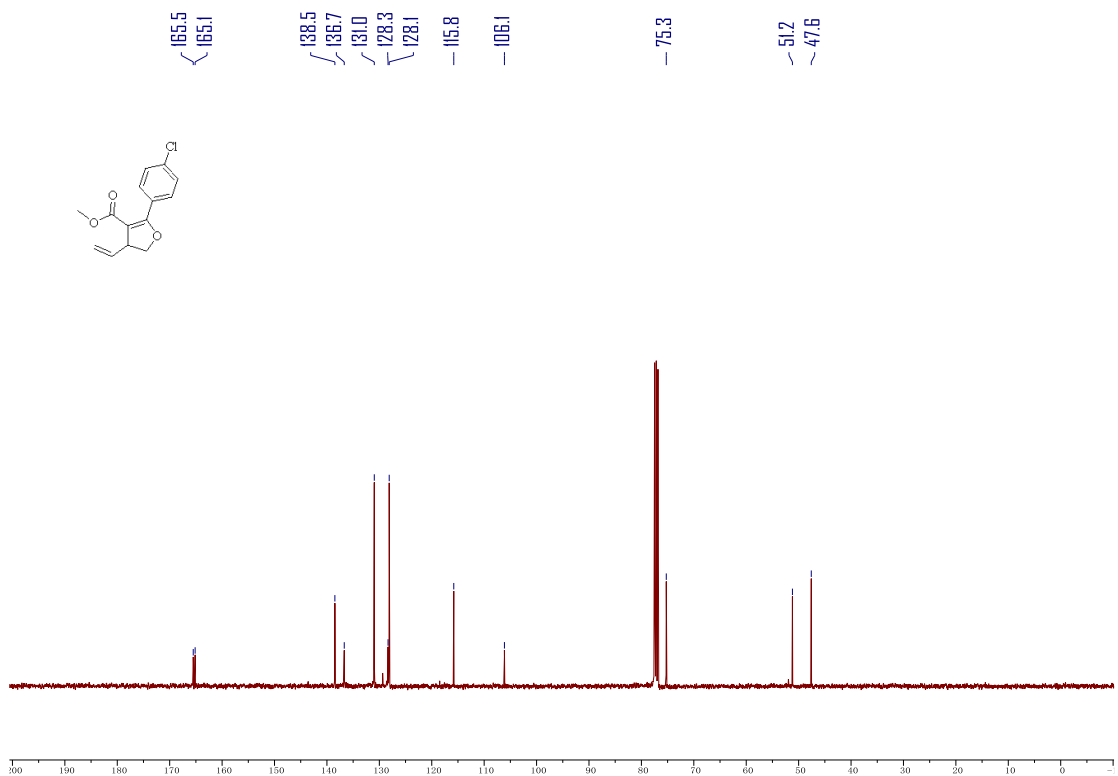
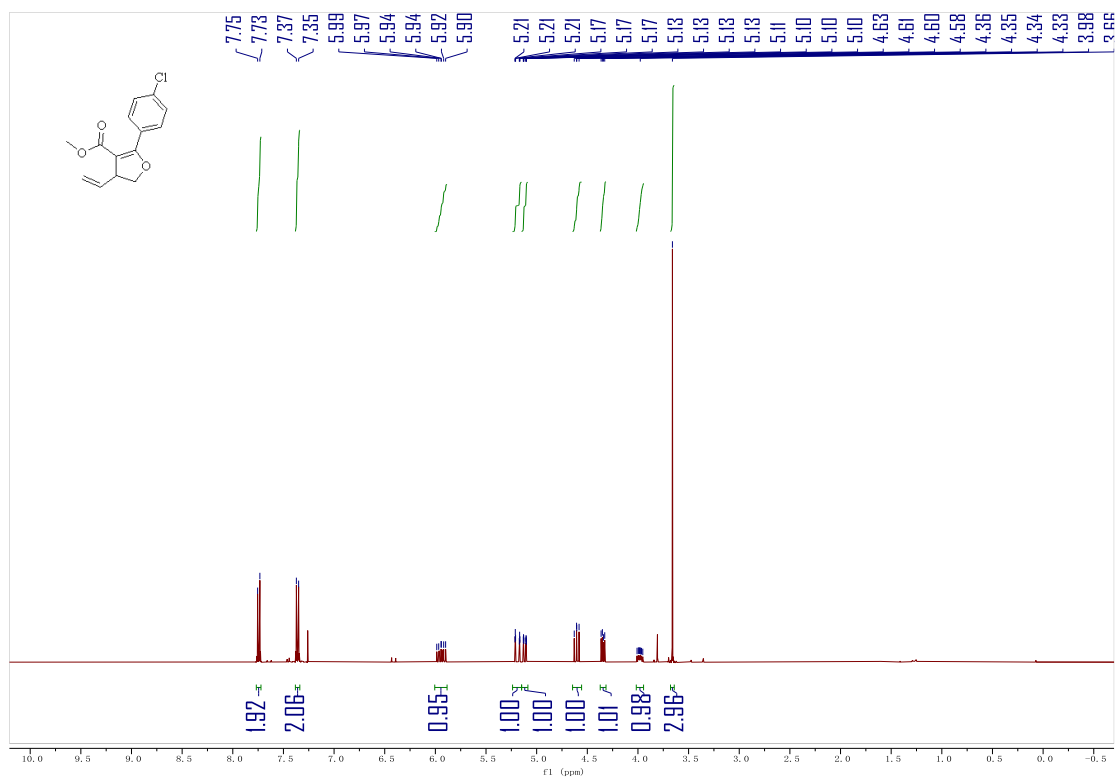


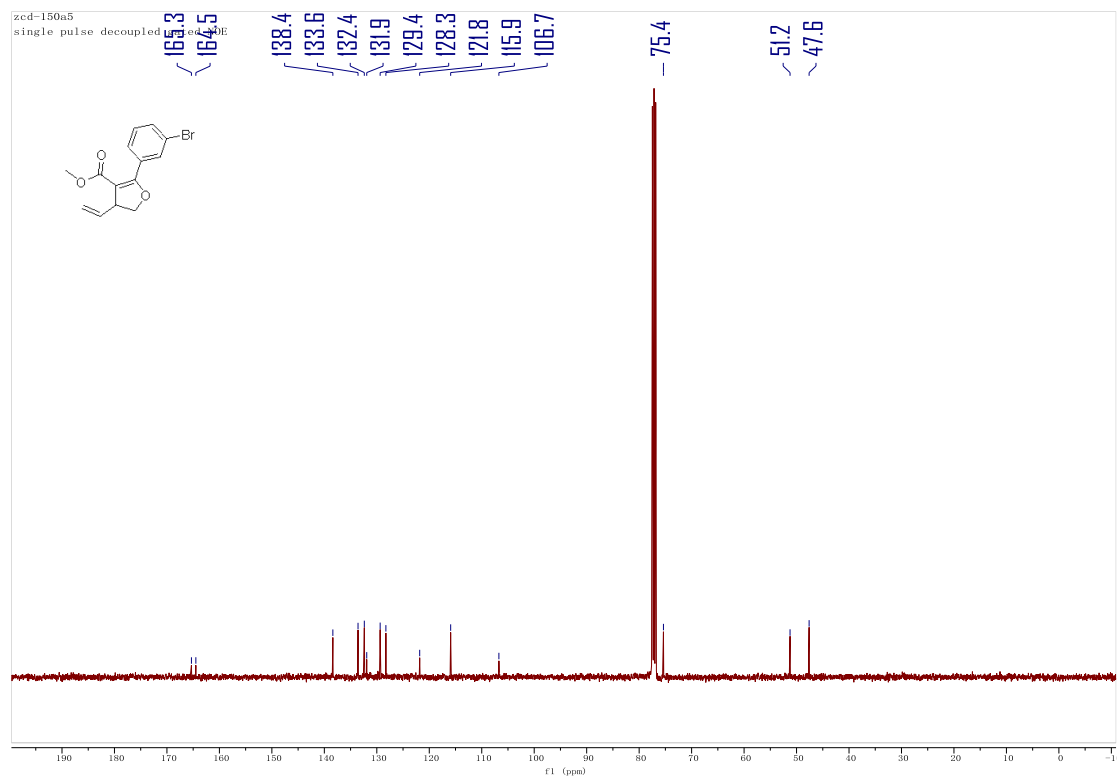


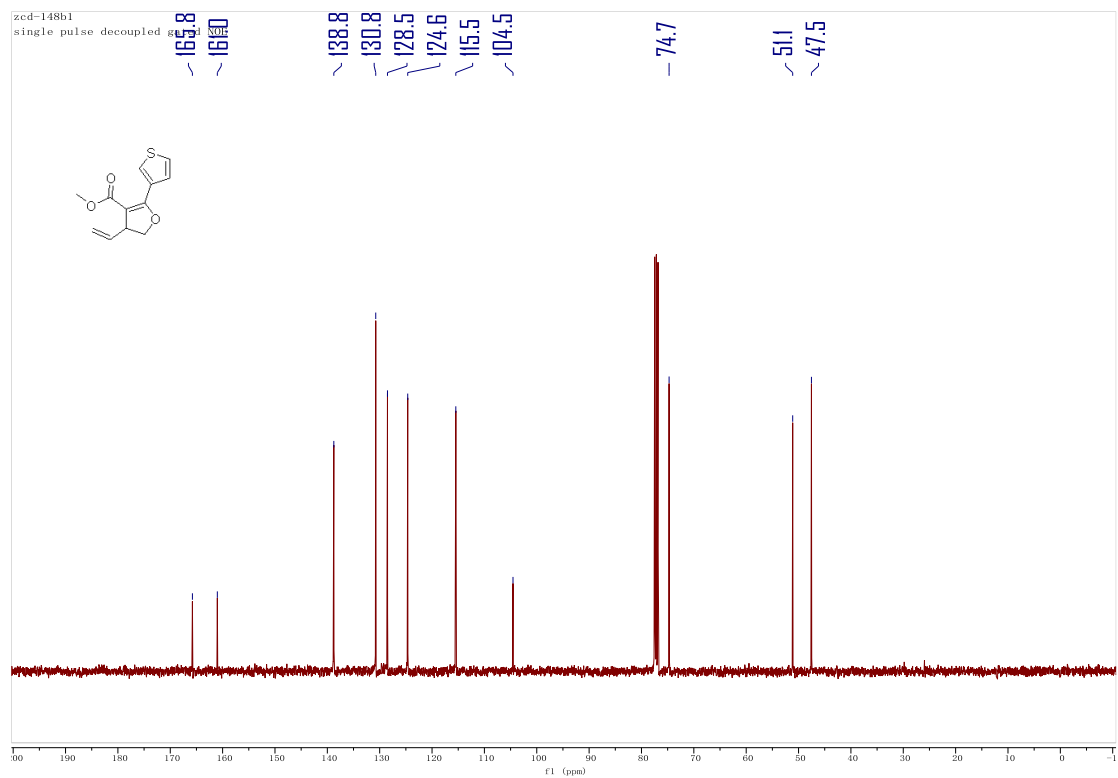
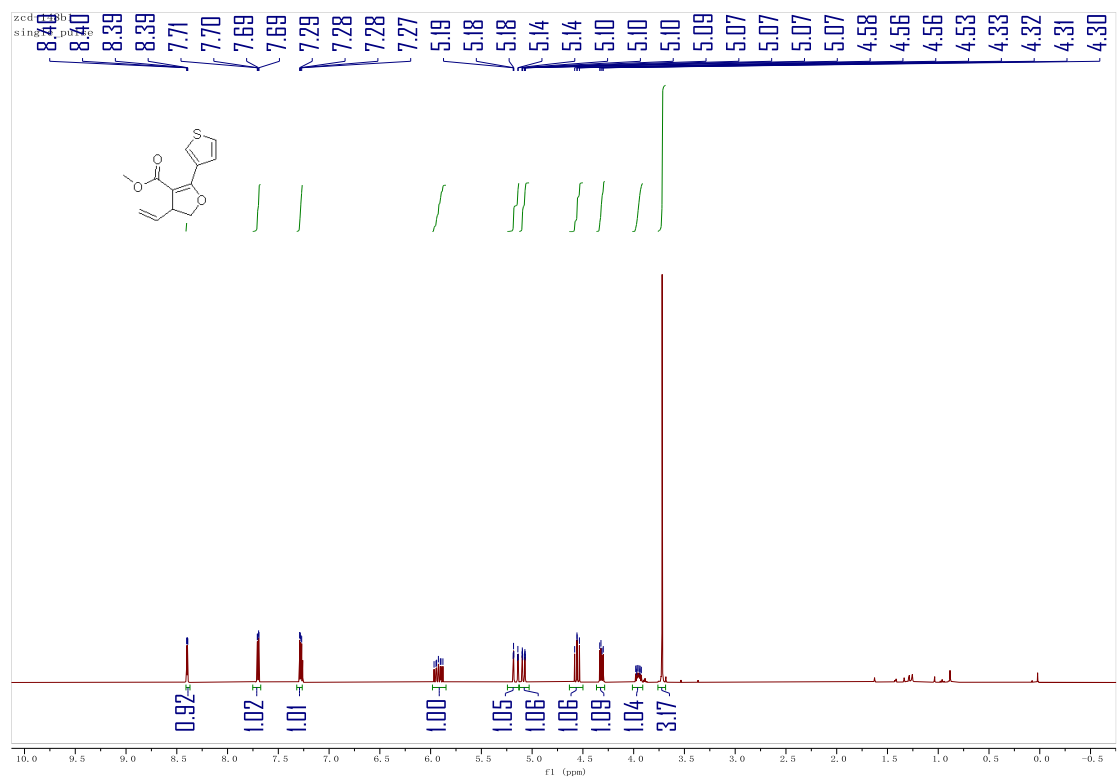


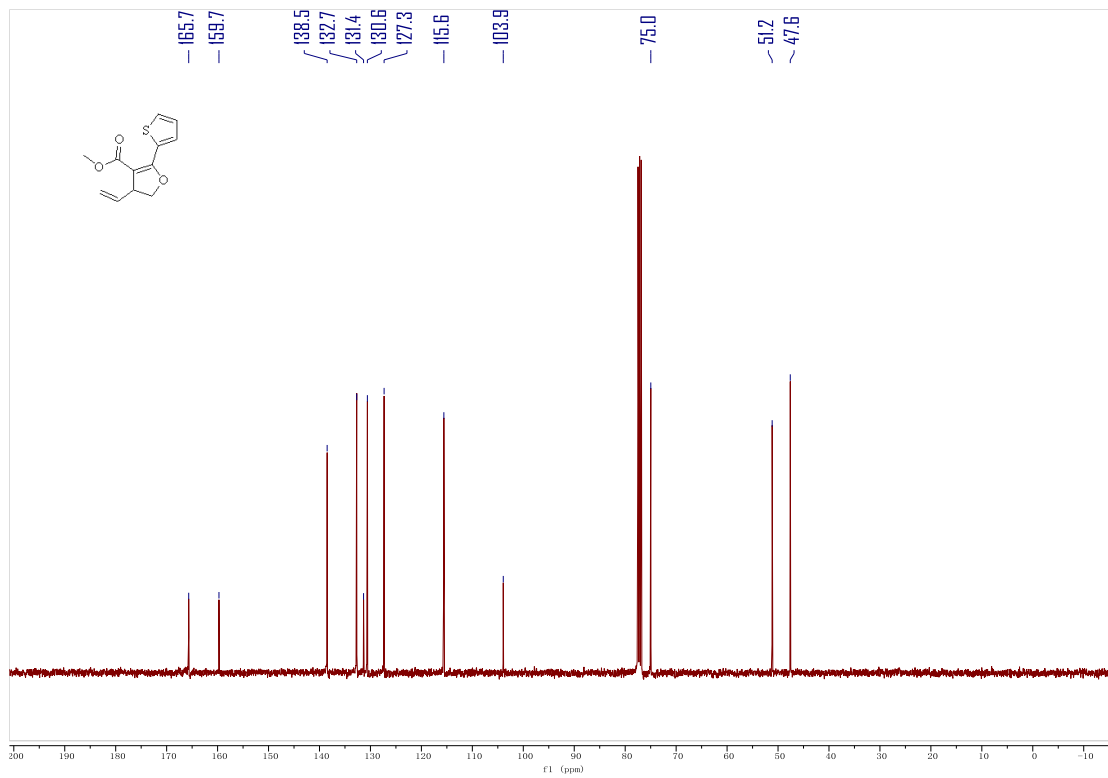
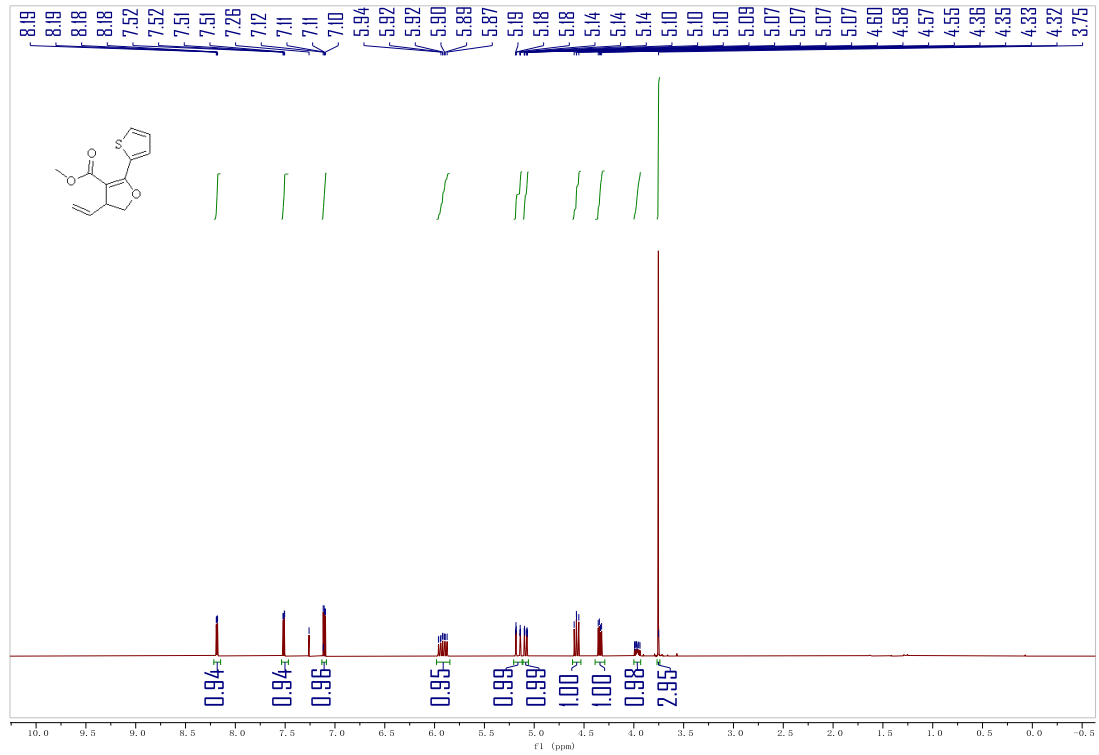


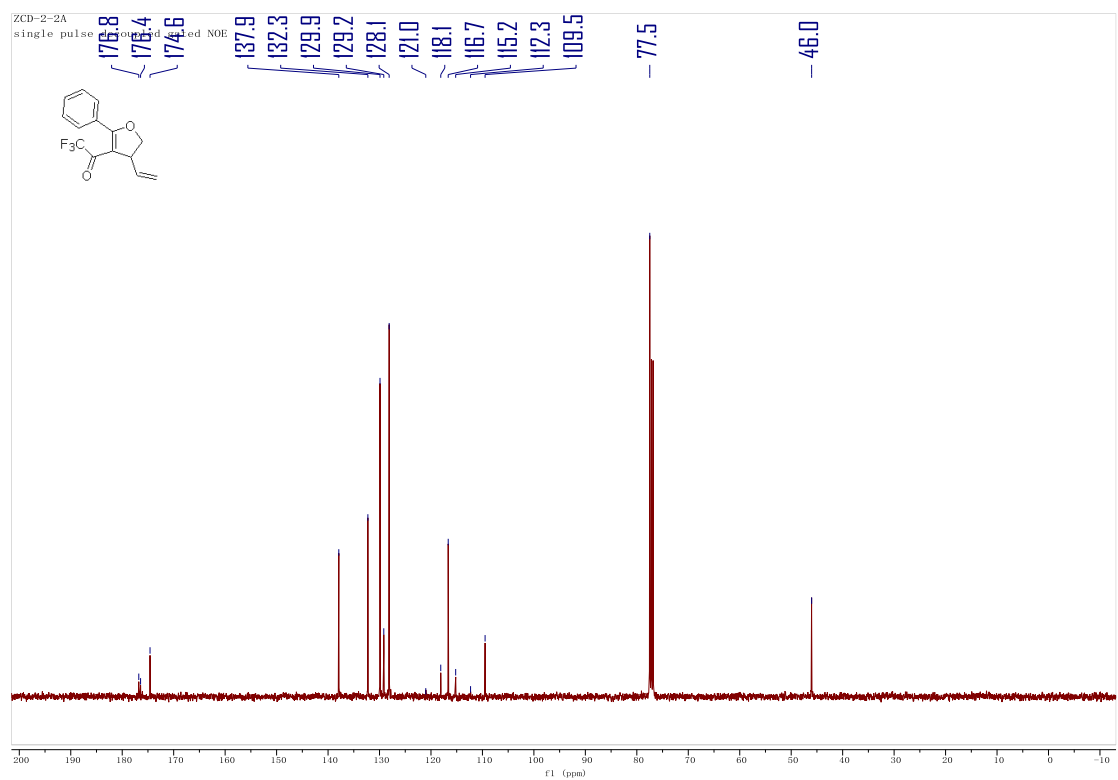
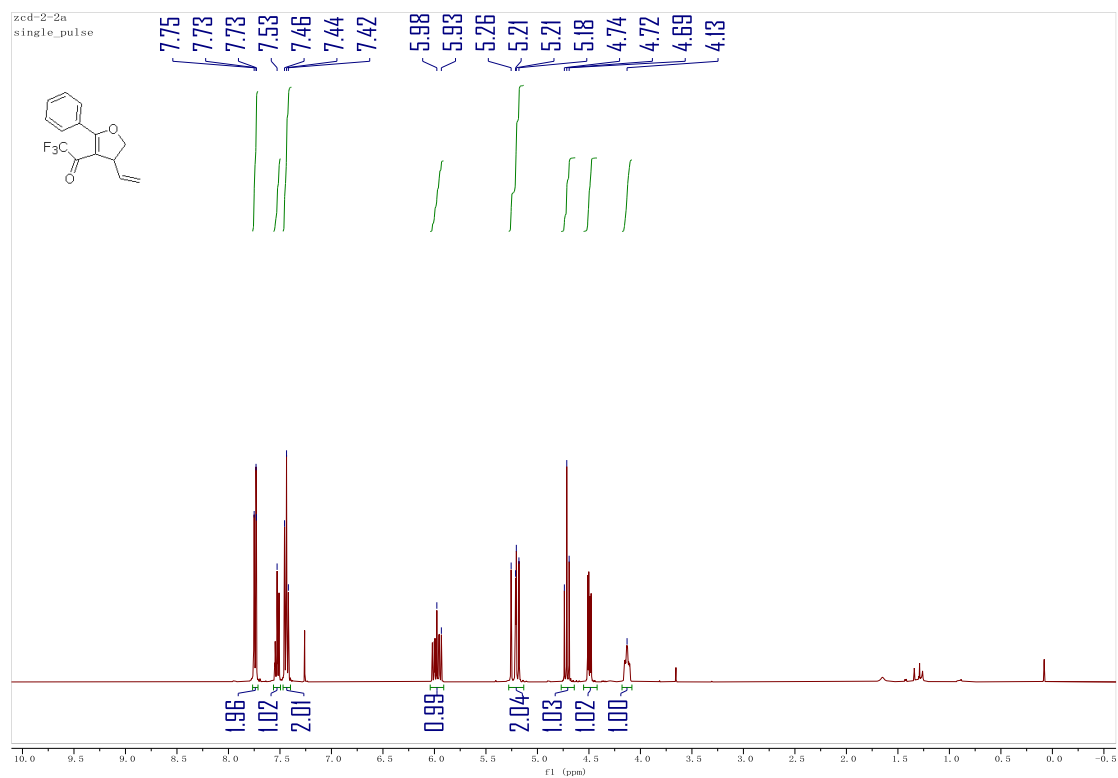




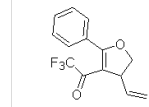








zcd-10 2  
single\_pulse



-- 73.30

