

## Supporting Information

# Regiospecific and Site-Selective C–H Alkylation of Phenols with Vinyldiazo Compounds Catalyzed by In(III)

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## 1. General Information:

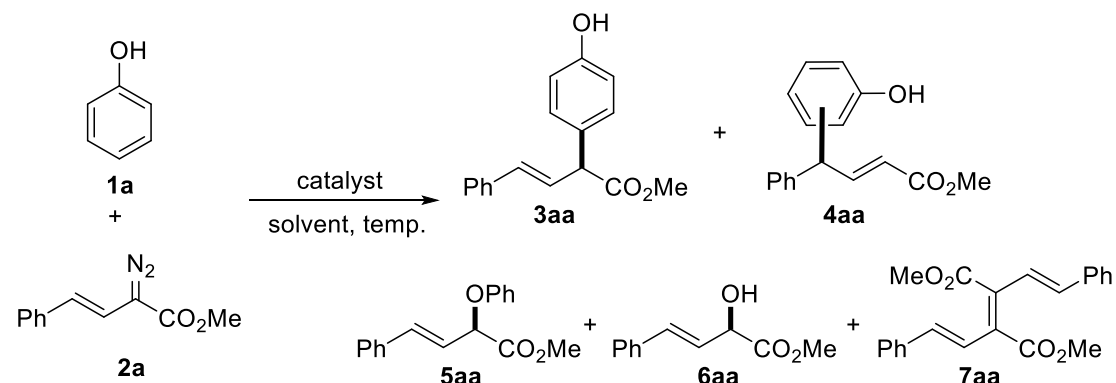
Unless otherwise noted, all reactions were carried out in standard Schlenk techniques with magnetic stirring bar under air. Materials obtained from commercial suppliers were used directly without further purification.  $^1\text{H}$  NMR spectra were recorded on a BRUKER 500 (500 MHz) spectrometer in  $\text{CDCl}_3$ . Chemical shifts are reported in ppm with tetramethylsilane (TMS: 0 ppm) with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration.  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER 500 (125 MHz) spectrometer in  $\text{CDCl}_3$  with complete proton decoupling. Chemical shifts are reported in ppm with the deuterium solvent as the internal standard (e.g.  $\text{CDCl}_3$ : 77.0 ppm).

Anhydrous tetrahydrofuran (THF), toluene, 1,4-Dioxane and diethyl ether ( $\text{Et}_2\text{O}$ ) were distilled from sodium and benzophenone to use; Anhydrous dichloromethane (DCM) and 1,2-dichloroethane (DCE) were distilled from  $\text{CaH}_2$ . Unless otherwise noted, analytical grade solvents and commercially available reagents were used directly.

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate.

## 2. Optimization of Conditions

**Table S1:** Optimization of reaction conditions<sup>[a]</sup>

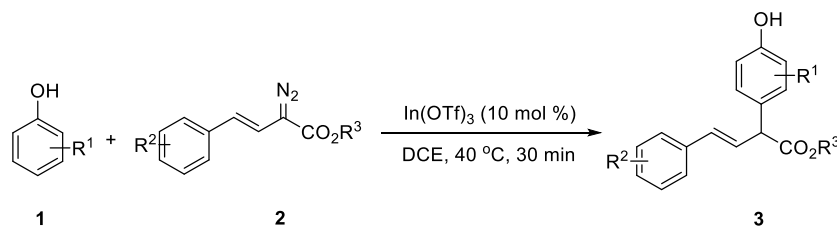


Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%) <sup>[b]</sup>
					3/4/5/6/7
1	Sc(OTf) <sub>3</sub>	DCM	25	12	0/0/0/0/0
2	Mn(OTf) <sub>3</sub>	DCM	25	12	0/0/0/0/0
3	Rh <sub>2</sub> (OAc) <sub>4</sub>	DCM	25	0.5	trace/0/33/0/42
4	[Ir(COD)Cl] <sub>2</sub>	DCM	25	0.5	trace/0/0/0/41
5	Cu(OTf) <sub>2</sub>	DCM	25	0.5	22(19)/0/23/0/30
6	Pd(OAc) <sub>2</sub>	DCM	25	12	0/0/0/0/0
7	Yb(OTf) <sub>3</sub>	DCM	25	12	0/0/0/0/0
8	AgSbF <sub>6</sub>	DCM	25	0.5	13/0/24/0/29
9	AgNTf <sub>2</sub>	DCM	25	0.5	15/0/17/0/26
10	AgOTf	DCM	25	0.5	23(18)/0/21/0/37
11	AuCl <sub>3</sub>	DCM	25	12	0/0/0/0/0
12	Hg(OTf) <sub>2</sub>	DCM	25	0.5	45/0/22/0/27
13	Fe(OTf) <sub>2</sub>	DCM	25	12	0/0/0/0/0
14	Fe(OTf) <sub>3</sub>	DCM	25	0.5	43/0/27/0/25
15 <sup>[c]</sup>	LPAuCl/AgSbF <sub>6</sub>	DCM	25	0.5	21/0/0/0/40
16 <sup>[c]</sup> [d]	LPAuCl/AgSbF <sub>6</sub>	DCM	25	0.5	17/0/0/0/32
17	(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> B	DCM	25	0.5	0/0/11/(15)/25
18	In(OTf) <sub>3</sub>	DCM	25	0.5	(56)/0/0/0/42
19	InF <sub>3</sub>	DCM	25	24	0/0/0/0/0
20	InCl <sub>3</sub>	DCM	25	24	0/0/0/0/0
21	InBr <sub>3</sub>	DCM	25	0.5	32/0/0/0/24
22	InI <sub>3</sub>	DCM	25	0.5	30/0/0/0/27
23	In <sub>2</sub> O <sub>3</sub>	DCM	25	24	0/0/0/0/0
24	(AcO) <sub>3</sub> In	DCM	25	24	0/0/0/0/0
25 <sup>[e]</sup>	In(OTf) <sub>3</sub>	DCM	25	0.5	75/0/0/0/21
26 <sup>[e]</sup>	In(OTf) <sub>3</sub>	THF	25	16	0/0/0/0/0
27 <sup>[e]</sup>	In(OTf) <sub>3</sub>	Et <sub>2</sub> O	25	16	0/0/0/0/0

28 <sup>[e]</sup>	In(OTf) <sub>3</sub>	1,4-Dioxane	25	16	0/0/0/0
29 <sup>[e]</sup>	In(OTf) <sub>3</sub>	MeCN	25	0.5	56/0/0/36
30 <sup>[e]</sup>	In(OTf) <sub>3</sub>	Toluene	25	0.5	40/0/0/32
31 <sup>[e]</sup>	In(OTf) <sub>3</sub>	CHCl <sub>3</sub>	25	0.5	36/0/0/39
32 <sup>[e]</sup>	In(OTf) <sub>3</sub>	Chlorobenzene	25	0.5	42/0/0/35
33 <sup>[e]</sup>	In(OTf) <sub>3</sub>	DCE	25	0.5	83/0/0/13
34 <sup>[e]</sup>	In(OTf) <sub>3</sub>	DCM	40	0.5	84/0/0/15
35 <sup>[e]</sup>	In(OTf) <sub>3</sub>	DCE	40	0.5	99/0/0/11
36 <sup>[e]</sup>	In(OTf) <sub>3</sub>	DCE	50	0.5	76/0/0/22
37 <sup>[e]</sup>	In(OTf) <sub>3</sub>	DCE	60	0.5	74/0/0/25
38 <sup>[e] [f]</sup>	In(OTf) <sub>3</sub>	DCE	25	0.5	45/0/0/10
39 <sup>[e] [g]</sup>	In(OTf) <sub>3</sub>	DCE	25	0.5	85/0/0/32
40 <sup>[e] [h]</sup>	In(OTf) <sub>3</sub>	DCE	25	0.5	trace/0/0/0
41 <sup>[e] [i]</sup>	In(OTf) <sub>3</sub>	DCE	25	0.5	38/0/0/14
42 <sup>[e] [j]</sup>	In(OTf) <sub>3</sub>	DCE	25	0.5	80/0/0/19

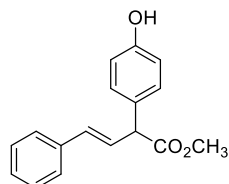
[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.20 mmol) catalyst (10 mol %), solvent (2 mL). [b] Yields were determined by <sup>1</sup>H-NMR using CH<sub>2</sub>Br<sub>2</sub> as internal standard, The numbers in parentheses are isolated yield. [c] L = (2, 4'-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>3</sub>P. [d] **1a** (0.15 mmol), **2a** (0.10 mmol) catalyst (5 mol %), solvent (1 mL). [e] **1a** (0.10 mmol), catalyst (10 mol %), solvent (1 mL), solution of **2a** (0.20 mmol) in 1 mL of solvent was introduced into the reaction mixture by a syringe in 10 min and then being stirred for another 30 min. [f] **1a** (0.10 mmol), **2a** (0.10 mmol) catalyst (10 mol %), solvent (2 mL). [g] **1a** (0.10 mmol), **2a** (0.30 mmol) catalyst (10 mol %), solvent (2 mL). [h] **1a** (0.10 mmol), **2a** (0.20 mmol) catalyst (1 mol %), solvent (2 mL). [i] **1a** (0.10 mmol), **2a** (0.20 mmol) catalyst (5 mol %), solvent (2 mL). [j] **1a** (0.10 mmol), **2a** (0.20 mmol) catalyst (20 mol %), solvent (2 mL). Tf = trifluoromethanesulfonyl.

### 3. General Procedure for the C-H Functionalization:



In a dried Schlenk tube, a solution of In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol, 10 mol %), phenol (28.2 mg, 0.30 mmol) in DCE (1 mL) was stirred at 40 °C. Then a solution of methyl (E)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol) in 2 mL of DCE was introduced into the reaction mixture by a syringe in 15 mins. The resulting mixture was continually stirred at room temperature for 30 min and **2a** was consumed completely determined by TLC analysis. The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the desired product.

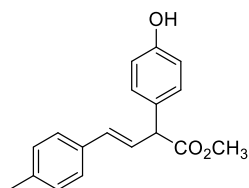
#### 1) Synthesis of methyl (E)-2-(4-hydroxyphenyl)-4-phenylbut-3-enoate (**3aa**).



Phenol **1a** (28.2 mg, 0.30 mmol), methyl (E)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3aa** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 79.7 mg; 99% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.33 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.16 (m, 3H), 6.90 – 6.73 (m, 2H), 6.55 (dd, *J* = 15.9, 8.1 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 5.29 (s, 1H), 4.42 (d, *J* = 8.1 Hz, 1H), 3.73 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.4, 155.0, 136.6, 132.3, 130.3, 129.2, 128.5, 127.7, 127.2, 126.4, 115.7, 54.1, 52.3; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>16</sub>NaO<sub>3</sub> 291.0992, found 291.0995.

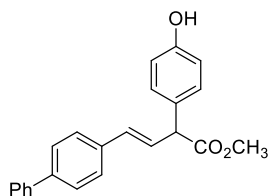
## 2) Synthesis of methyl (*E*)-2-(4-hydroxyphenyl)-4-(*p*-tolyl)but-3-enoate (**3ab**).



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-(*p*-tolyl)but-3-enoate **2b** (130 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ab** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 83.9 mg; 99% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.13 – 7.08 (m, 4H), 7.08 – 7.04 (m, 2H), 6.78 – 6.69 (m, 2H), 6.68 – 6.53 (m, 1H), 6.10 (d, *J* = 10.8 Hz, 1H), 5.90 (d, *J* = 12.0 Hz, 1H), 5.22 (s, 1H), 3.73 (s, 3H), 2.31 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.8, 154.2, 150.9, 140.1, 136.2, 135.1, 129.4, 129.3, 128.1, 118.2, 115.4, 51.3, 46.9, 21.0; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>18</sub>NaO<sub>3</sub> 305.1148, found 305.1155.

## 3) Synthesis of methyl (*E*)-4-([1,1'-biphenyl]-4-yl)-2-(4-hydroxyphenyl)but-3-enoate (**3ac**).

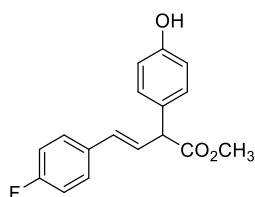


The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.3 mmol), methyl (*E*)-4-([1,1'-biphenyl]-4-yl)-2-diazobut-3-enoate **2c** (167 mg, 0.6 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ac** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 93.0 mg; 90% yield; White solid; m.p. = 130.2 – 131.2 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.50 (m, 4H), 7.46 – 7.39 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.78

(dd,  $J = 15.6, 1.3$  Hz, 1H), 5.34 (s, 1H), 4.84 (d,  $J = 7.3$  Hz, 1H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 154.7, 150.6, 140.7, 140.7, 139.8, 133.4, 129.8, 128.9, 128.7, 127.4, 127.3, 127.0, 122.2, 115.6, 52.3, 51.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{23}\text{H}_{20}\text{NaO}_3$  367.1305, found 367.1301.

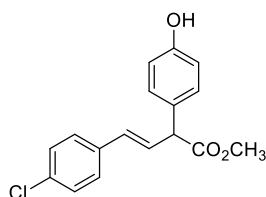
#### 4) Synthesis of methyl (*E*)-4-(4-fluorophenyl)-2-(4-hydroxyphenyl)but-3-enoate (**3ad**).



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-(4-fluorophenyl)but-3-enoate **2d** (132 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ad** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 85.0 mg; 99% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.29 (m, 2H), 7.20 (d,  $J = 8.6$  Hz, 2H), 7.09 – 6.92 (m, 2H), 6.89 – 6.74 (m, 2H), 6.52 – 6.34 (m, 2H), 5.38 (s, 1H), 4.40 (d,  $J = 7.6$  Hz, 1H), 3.73 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 163.3, 161.3, 155.1, 132.79, 132.76, 131.1, 130.2, 129.2, 128.0, 127.9, 126.98, 126.96, 115.7, 115.5, 115.3, 54.0, 52.4;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.29; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{17}\text{H}_{15}\text{FNaO}_3$  309.0897, found 309.0903.

#### 5) Synthesis of methyl (*E*)-4-(4-chlorophenyl)-2-(4-hydroxyphenyl)but-3-enoate (**3ae**).

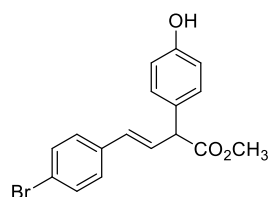


The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl

(*E*)-4-(4-chlorophenyl)-2-diazobut-3-enoate **2e** (142 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ae** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 86.3 mg; 95% yield; White solid; m.p. = 120.5 – 121.3 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.23 (m, 4H), 7.21 – 7.13 (m, 2H), 6.87 – 6.73 (m, 2H), 6.52 (dd, *J* = 15.9, 8.2 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 5.39 (s, 1H), 4.40 (d, *J* = 8.1 Hz, 1H), 3.73 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.3, 155.1, 135.1, 133.3, 131.1, 130.0, 129.2, 128.7, 127.9, 127.6, 115.7, 54.0, 52.4; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>15</sub>ClNaO<sub>3</sub> 325.0602, found 325.0604.

#### 6) Synthesis of methyl (*E*)-4-(4-bromophenyl)-2-(4-hydroxyphenyl)but-3-enoate (**3af**).

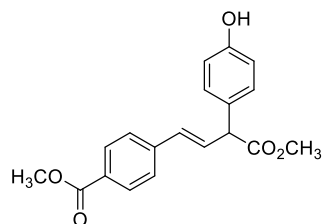


The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-4-(4-bromophenyl)-2-diazobut-3-enoate **2f** (169 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3af** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 99.0 mg; 95% yield; White solid; m.p. = 140.5 – 141.5 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.21 (dd, *J* = 15.4, 8.5 Hz, 4H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.54 (dd, *J* = 15.9, 8.2 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 5.35 (s, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 3.72 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.1, 155.1, 135.6, 131.6, 131.1, 130.0, 129.2, 128.1, 128.0, 121.4, 115.7, 54.0, 52.4; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>15</sub>BrNaO<sub>3</sub> 369.0097, found 369.0094.



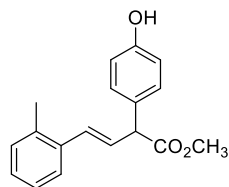
**7) Synthesis of methyl (*E*)-4-(3-(4-hydroxyphenyl)-4-methoxy-4-oxobut-1-en-1-yl)benzoate (**3ag**).**



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-4-(3-diazo-4-methoxy-4-oxobut-1-en-1-yl)benzoate **2g** (156 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ag** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 78.3 mg; 80% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, *J* = 15.7, 6.8 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.18 – 7.09 (m, 1H), 7.04 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.94 – 6.85 (m, 1H), 6.78 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.72 (dd, *J* = 15.7, 1.6 Hz, 1H), 5.65 (s, 1H), 5.26 (d, *J* = 6.7 Hz, 1H), 3.89 (s, 3H), 3.73 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.06, 167.04, 153.2, 149.1, 146.4, 129.8, 129.6, 128.6, 128.6, 128.5, 127.3, 122.8, 120.9, 115.8, 52.1, 51.7, 46.9; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>18</sub>NaO<sub>5</sub> 345.1046, found 349.1055.

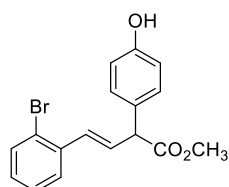
**8) Synthesis of methyl (*E*)-2-(4-hydroxyphenyl)-4-(*o*-tolyl)but-3-enoate (**3ah**).**



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-(*o*-tolyl)but-3-enoate **2h** (130 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ah** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 77.1 mg; 91% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.39 (m, 1H), 7.22 (d,  $J = 8.6$  Hz, 2H), 7.19 – 7.07 (m, 3H), 6.84 – 6.77 (m, 2H), 6.68 (d,  $J = 15.7$  Hz, 1H), 6.44 (dd,  $J = 15.7, 8.4$  Hz, 1H), 5.42 (s, 1H), 5.29 (s, 1H), 4.46 (d,  $J = 8.3$  Hz, 1H), 3.74 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.5, 155.0, 135.7, 135.4, 130.4, 130.2, 130.2, 129.2, 128.5, 127.6, 126.0, 125.7, 115.6, 54.3, 52.3, 19.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{18}\text{NaO}_3$  305.1148, found 305.1153.

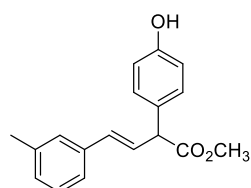
**9) Synthesis of methyl (*E*)-4-(2-bromophenyl)-2-(4-hydroxyphenyl)but-3-enoate (**3ai**).**



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-4-(2-bromophenyl)-2-diazobut-3-enoate **2i** (169 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ai** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 85.4 mg; 82% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 – 7.44 (m, 2H), 7.30 – 7.18 (m, 3H), 7.14 – 7.05 (m, 1H), 6.89 – 6.75 (m, 3H), 6.50 (dd,  $J = 15.8, 8.4$  Hz, 1H), 5.18 (s, 1H), 4.47 (d,  $J = 8.4$  Hz, 1H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 155.1, 136.5, 132.9, 131.0, 130.2, 130.1, 129.2, 128.9, 127.4, 127.1, 123.6, 115.7, 54.1, 52.4; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{17}\text{H}_{15}\text{BrNaO}_3$  369.0097, found 369.0098.

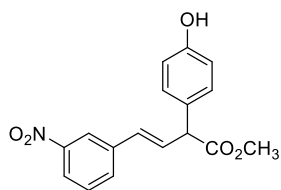
**10) Synthesis of methyl (*E*)-2-(4-hydroxyphenyl)-4-(*m*-tolyl)but-3-enoate (**3aj**).**



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-(*m*-tolyl)but-3-enoate **2j** (130 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min, **3aj** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 83.9 mg; 99% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.24–7.14 (m, 5H), 7.05 (d, *J* = 6.7 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.54 (dd, *J* = 15.8, 8.2 Hz, 1H), 6.43 (d, *J* = 15.9 Hz, 1H), 5.50 (s, 1H), 4.42 (d, *J* = 8.1 Hz, 1H), 3.74 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.5, 155.1, 138.1, 136.5, 132.4, 130.2, 129.2, 128.5, 128.4, 127.1, 126.9, 123.6, 115.6, 54.1, 52.4, 21.3; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>18</sub>NaO<sub>3</sub> 305.1148, found 305.1151.

#### 11) Synthesis of methyl (*E*)-2-(4-hydroxyphenyl)-4-(3-nitrophenyl)but-3-enoate (**3ak**).

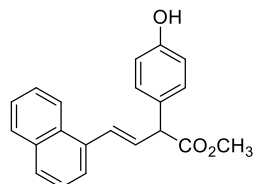


The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-(3-nitrophenyl)but-3-enoate **2k** (148 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ak** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 47.0 mg; 50% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.23 (s, 1H), 8.10 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.27–7.18 (m, 2H), 7.09 (s, 1H), 6.96 (t, *J* = 7.8 Hz, 2H), 6.79 (dd, *J* = 15.9, 7.6 Hz, 1H), 6.56 (d, *J* = 15.9 Hz, 1H), 4.69 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 174.5, 154.2, 148.5, 138.3, 132.3, 130.7, 130.0, 129.4, 128.4, 123.4, 122.4, 121.2, 117.7, 53.0, 51.6; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>15</sub>NNaO<sub>5</sub> 336.0842, found 336.0851.

## 12) Synthesis of methyl (*E*)-2-(4-hydroxyphenyl)-4-(naphthalen-1-yl)but-3-enoate

### (3al).

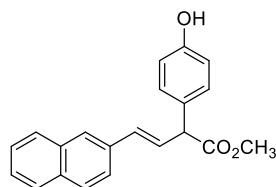


The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-(naphthalen-1-yl)but-3-enoate **2l** (151 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3al** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 67.8 mg; 71% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.15 – 8.09 (m, 1H), 7.91 – 7.84 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 10.4 Hz, 1H), 6.85 – 6.69 (m, 3H), 5.99 (d, *J* = 11.3 Hz, 1H), 5.25 (s, 1H), 3.76 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 166.7, 154.3, 151.2, 139.1, 135.2, 134.1, 131.8, 129.3, 128.7, 127.5, 126.2, 125.6, 125.4, 125.3, 124.3, 118.5, 115.5, 51.4, 43.7; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>18</sub>NaO<sub>3</sub> 341.1148, found 341.1156.

## 13) Synthesis of methyl (*E*)-2-(4-hydroxyphenyl)-4-(naphthalen-2-yl)but-3-enoate

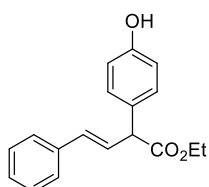
### (3am).



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-(naphthalen-2-yl)but-3-enoate **2m** (151 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3am** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 83.1 mg; 87% yield; White solid; m.p. = 140.2 – 141.2 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (t, *J* = 7.5 Hz, 3H), 7.70 (s, 1H), 7.59 (d, *J* = 8.6 Hz, 1H), 7.49 – 7.35 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.67 (dd, *J* = 15.8, 7.8 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 5.46 (s, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 3.74 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.5, 155.1, 134.1, 133.5, 133.0, 132.4, 130.2, 129.2, 128.2, 127.9, 127.6, 127.6, 126.4, 126.2, 125.9, 123.6, 115.7, 54.2, 52.4; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>18</sub>NaO<sub>3</sub> 341.1148, found 341.1151.

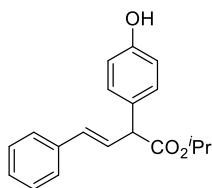
#### 14) Synthesis of ethyl (*E*)-2-(4-hydroxyphenyl)-4-phenylbut-3-enoate (**3an**).



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), ethyl (*E*)-2-diazo-4-phenylbut-3-enoate **2n** (130 mg, 0.6 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3an** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 68.6 mg; 81% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 3H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.55 (dd, *J* = 15.9, 8.1 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 5.01 (s, 1H), 4.39 (d, *J* = 8.0 Hz, 1H), 4.27 – 4.01 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.8, 154.9, 136.7, 132.1, 130.6, 129.2, 128.5, 127.6, 127.5, 126.4, 115.6, 61.2, 54.2, 14.1; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>18</sub>H<sub>18</sub>NaO<sub>3</sub> 305.1148, found 305.1152.

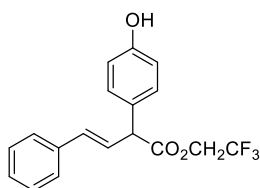
#### 15) Synthesis of isopropyl (*E*)-2-(4-hydroxyphenyl)-4-phenylbut-3-enoate (**3ao**).



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), isopropyl (*E*)-2-diazo-4-phenylbut-3-enoate **2o** (138 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ao** was obtained after purification by flash chromatography (PE/EA = 15:1)

(PE/EA = 15:1) 88.0 mg; 99% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.19 (m, 3H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.54 (dd, *J* = 15.9, 8.0 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 5.10 – 5.00 (m, 1H), 4.97 (s, 1H), 4.36 (d, *J* = 8.0 Hz, 1H), 1.23 (dd, *J* = 22.8, 6.3 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.4, 154.9, 136.8, 132.1, 130.7, 129.2, 128.5, 127.60, 127.59, 126.4, 115.6, 68.6, 54.4, 21.74, 21.66; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>20</sub>NaO<sub>3</sub> 319.1305, found 319.1315.

#### 16) Synthesis of 2,2,2-trifluoroethyl (*E*)-2-(4-hydroxyphenyl)-4-phenylbut-3-enoate (**3ap**).

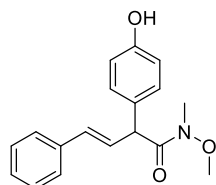


The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), 2,2,2-trifluoroethyl (*E*)-2-diazo-4-phenylbut-3-enoate **2p** (154 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min, **3ap** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 85.8 mg; 85% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.20 (m, 3H), 6.87 – 6.69 (m, 2H), 6.58 – 6.40 (m, 2H), 4.98 (s, 1H), 4.62 – 4.31 (m, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ

171.1, 155.2, 136.4, 133.0, 129.4, 129.3, 128.6, 127.9, 126.5, 126.1, 115.8, 60.8, 60.5, 53.5.  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -73.64; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NaO}_3$  359.0865, found 359.0865.

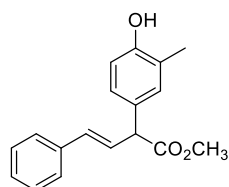
**17) Synthesis of (*E*)-2-(4-hydroxyphenyl)-*N*-methoxy-*N*-methyl-4-phenylbut-3-enamide (**3aq**).**



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), (*E*)-2-diazo-*N*-methoxy-*N*-methyl-4-phenylbut-3-enamide **2q** (139 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3aq** was obtained after purification by flash chromatography (PE/EA = 4:1).

(PE/EA = 4:1) 79.4 mg; 89% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 7.5$  Hz, 2H), 7.30 – 7.15 (m, 5H), 6.77 (d,  $J = 8.4$  Hz, 2H), 6.61 (dd,  $J = 15.9, 8.3$  Hz, 1H), 6.42 (d,  $J = 15.9$  Hz, 1H), 6.27 (s, 1H), 4.90 (s, 1H), 3.54 (s, 3H), 3.21 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 155.2, 136.9, 131.6, 130.6, 129.3, 128.7, 128.4, 127.4, 126.4, 125.5, 115.7, 61.5, 50.2, 32.3, 30.3; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{19}\text{NNaO}_3$  320.1257, found 320.1258.

**19) Synthesis of methyl (*E*)-2-(4-hydroxy-3-methylphenyl)-4-phenylbut-3-enoate (**3ba**).**

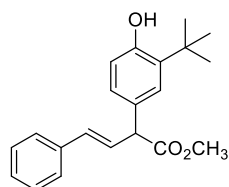


The procedure is similar with that of **3aa**: o-cresol **1b** (32.4 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ba** was obtained after purification by flash

chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 83.9 mg; 99% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.38 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.21 (m, 1H), 7.13 (d,  $J = 1.9$  Hz, 1H), 7.08 (dd,  $J = 8.2, 2.2$  Hz, 1H), 6.76 (d,  $J = 8.2$  Hz, 1H), 6.58 (dd,  $J = 15.9, 8.2$  Hz, 1H), 6.48 (d,  $J = 15.9$  Hz, 1H), 4.98 (s, 1H), 4.41 (d,  $J = 8.2$  Hz, 1H), 3.75 (s, 3H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 153.2, 136.7, 132.1, 130.5, 130.3, 128.5, 127.6, 127.4, 126.5, 126.4, 124.2, 115.2, 54.1, 52.3, 15.8; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{18}\text{NaO}_3$  305.1148, found 305.1157.

## 20) Synthesis of methyl (*E*)-2-(3-(tert-butyl)-4-hydroxyphenyl)-4-phenylbut-3-enoate (**3ca**).



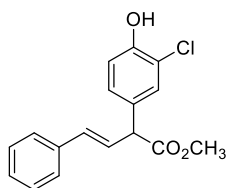
The procedure is similar with that of **3aa**: 2-(tert-butyl)phenol **1c** (45.1 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ca** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 82.7 mg; 85% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.36 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 2H), 7.07 (dd,  $J = 8.1, 2.2$  Hz, 1H), 6.64 (d,  $J = 8.1$  Hz, 1H), 6.55 (dd,  $J = 15.8, 8.2$  Hz, 1H), 6.46 (d,  $J = 15.9$  Hz, 1H), 4.93 (s, 1H), 4.40 (d,  $J = 8.2$  Hz, 1H), 3.73 (s, 3H), 1.40 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.4, 153.7, 136.8, 136.4, 132.0, 129.9, 128.6, 128.5, 127.6, 126.9, 126.4, 126.2, 116.8, 54.5, 52.2, 34.6, 29.5; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{21}\text{H}_{24}\text{NaO}_3$  347.1618, found 347.1613.

## 21) Synthesis of methyl (*E*)-2-(3-chloro-4-hydroxyphenyl)-4-phenylbut-3-enoate



**(3da).**

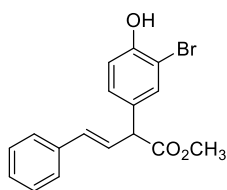


The procedure is similar with that of **3aa**: 2-chlorophenol **1d** (38.6 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3da** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 74.5 mg; 82% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.55 – 6.43 (m, 2H), 5.59 (s, 1H), 4.39 (d, *J* = 7.1 Hz, 1H), 3.74 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.6, 150.7, 136.4, 132.8, 131.4, 128.6, 128.4, 128.1, 127.9, 126.5, 126.5, 120.1, 116.4, 53.8, 52.4; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>15</sub>ClNaO<sub>3</sub> 325.0602, found 325.0608.

**22) Synthesis of methyl (*E*)-2-(3-bromo-4-hydroxyphenyl)-4-phenylbut-3-enoate**

**(3ea).**

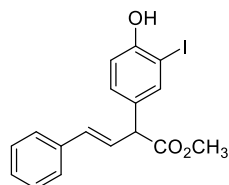


The procedure is similar with that of **3aa**: 2-bromophenol **1e** (84.4 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ea** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 74.5 mg; 81% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 2.1 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.18 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.55 – 6.42 (m, 1H), 5.59 (s, 1H), 4.39 (d, *J* = 7.1 Hz, 1H),

3.73 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 151.7, 136.4, 132.8, 131.8, 131.4, 128.8, 128.6, 127.9, 126.5, 126.5, 116.3, 110.4, 53.7, 52.4; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{17}\text{H}_{15}\text{BrNaO}_3$  369.0097, found 369.0097.

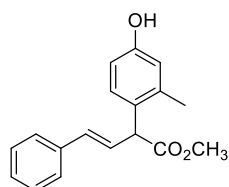
**23) Synthesis of methyl (*E*)-2-(4-hydroxy-3-iodophenyl)-4-phenylbut-3-enoate (3fa).**



The procedure is similar with that of **3aa**: 2-iodophenol **1f** (66.0 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3fa** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 104.1 mg; 88% yield; Brown oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 2.1$  Hz, 1H), 7.42 – 7.35 (m, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.27 – 7.19 (m, 2H), 6.96 (d,  $J = 8.4$  Hz, 1H), 6.59 – 6.29 (m, 2H), 5.43 (s, 1H), 4.37 (d,  $J = 7.2$  Hz, 1H), 3.73 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.7, 154.3, 137.5, 136.4, 132.8, 132.3, 129.9, 128.6, 127.9, 126.6, 126.5, 115.2, 85.9, 53.5, 52.5; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{17}\text{H}_{15}\text{INaO}_3$  416.9958, found 416.9944.

**24) Synthesis of methyl (*E*)-2-(4-hydroxy-2-methylphenyl)-4-phenylbut-3-enoate (3ga).**

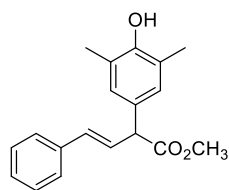


The procedure is similar with that of **3aa**: *m*-cresol **1g** (32.4 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ga** was obtained after purification by flash

chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 61.0 mg; 72% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 7.4$  Hz, 2H), 7.29 (t,  $J = 7.6$  Hz, 2H), 7.21 (dd,  $J = 17.5, 8.3$  Hz, 2H), 6.70 – 6.63 (m, 2H), 6.54 (dd,  $J = 15.9, 7.6$  Hz, 1H), 6.37 (d,  $J = 15.9$  Hz, 1H), 5.20 (s, 1H), 4.62 (d,  $J = 7.6$  Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 154.7, 137.7, 136.7, 132.0, 129.2, 128.8, 128.5, 127.6, 127.0, 126.4, 117.5, 113.3, 52.3, 50.3, 19.7; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{18}\text{NaO}_3$  305.1148, found 305.1148.

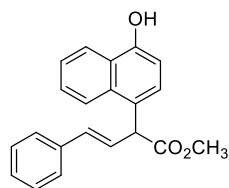
#### 25) Synthesis of methyl (*E*)-2-(4-hydroxy-3,5-dimethylphenyl)-4-phenylbut-3-enoate (**3ha**).



The procedure is similar with that of **3aa**: 2,6-dimethylphenol **1h** (36.7 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol),  $\text{In}(\text{OTf})_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ha** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 77.3 mg; 87% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 7.3$  Hz, 2H), 7.29 (t,  $J = 7.6$  Hz, 2H), 7.22 (t,  $J = 7.3$  Hz, 1H), 6.96 (s, 2H), 6.55 (dd,  $J = 15.9, 8.3$  Hz, 1H), 6.45 (d,  $J = 15.9$  Hz, 1H), 4.65 (s, 1H), 4.34 (d,  $J = 8.3$  Hz, 1H), 3.72 (s, 3H), 2.23 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.3, 151.6, 136.8, 132.0, 129.8, 128.5, 128.0, 127.6, 127.5, 126.4, 123.4, 54.2, 52.3, 16.0; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{20}\text{NaO}_3$  319.1305, found 319.1304.

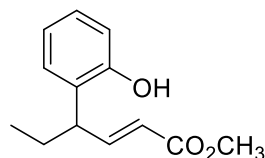
#### 26) Synthesis of methyl (*E*)-2-(4-hydroxynaphthalen-1-yl)-4-phenylbut-3-enoate (**3ia**).



The procedure is similar with that of **3aa**: naphthalen-1-ol **1i** (43.3 mg, 0.30 mmol), methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (121 mg, 0.60 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **3ia** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 86.0 mg; 90% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.76 (dd, *J* = 15.9, 7.5 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.12 (s, 1H), 5.15 (d, *J* = 7.5 Hz, 1H), 3.75 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 174.1, 151.5, 136.7, 132.8, 132.4, 128.5, 127.6, 127.0, 126.7, 126.44, 126.36, 126.34, 125.00, 124.97, 123.1, 122.7, 108.2, 52.5, 50.7; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>21</sub>H<sub>18</sub>NaO<sub>3</sub> 341.1148, found 341.1156.

#### 27) Synthesis of methyl (*E*)-4-(2-hydroxyphenyl)hex-2-enoate (**4ar**).

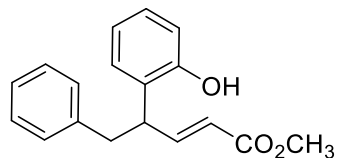


The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-hex-3-enoate **2r** (92.5 mg, 0.6 mmol), In(OTf)<sub>3</sub> (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **4ar** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 49.6 mg; 75% yield; Yellow oil; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21 – 7.06 (m, 3H), 6.90 – 6.93 (m, 1H), 6.78 (dd, *J* = 7.9, 1.2 Hz, 1H), 5.87 (dd, *J* = 15.7, 1.3 Hz, 1H), 5.59 (s, 1H), 3.72 – 3.76 (m, 4H), 1.83 – 1.89 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 167.7, 153.5, 152.1, 128.4, 128.2, 127.6,

120.9, 120.3, 115.7, 51.6, 43.5, 26.5, 12.2; HRMS (ESI-TOF)  $m/z$ :  $[M+Na]^+$  calculated for  $C_{13}H_{16}NaO_3$  243.0992, found 243.1003.

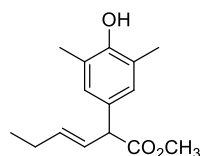
### 28) Synthesis of methyl (*E*)-4-(2-hydroxyphenyl)-5-phenylpent-2-enoate (**4as**).



The procedure is similar with that of **3aa**: phenol **1a** (28.2 mg, 0.30 mmol), methyl (*E*)-2-diazo-5-phenylpent-3-enoate **2s** (130 mg, 0.60 mmol),  $In(OTf)_3$  (16.9 mg, 0.030 mmol), DCE, 40 °C, 30 min. **4as** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 65.2 mg; 77% yield; Yellow oil;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.28 – 7.19 (m, 3H), 7.18 – 7.00 (m, 5H), 6.88 – 6.85 (m, 1H), 6.72 (dd,  $J = 7.9, 1.2$  Hz, 1H), 5.75 (dd,  $J = 15.7, 1.3$  Hz, 1H), 5.50 (s, 1H), 4.13 – 4.08 (m, 1H), 3.69 (s, 3H), 3.29 – 2.99 (m, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  167.5, 153.3, 150.9, 139.4, 129.1, 128.7, 128.2, 127.9, 127.9, 126.2, 120.9, 120.8, 115.8, 51.6, 44.1, 40.0; HRMS (ESI-TOF)  $m/z$ :  $[M+Na]^+$  calculated for  $C_{18}H_{18}NaO_3$  305.1148, found 305.1155.

### 29) Synthesis of (*E*)-methyl 2-(4-hydroxy-3,5-dimethylphenyl)hex-3-enoate (**4hr**).

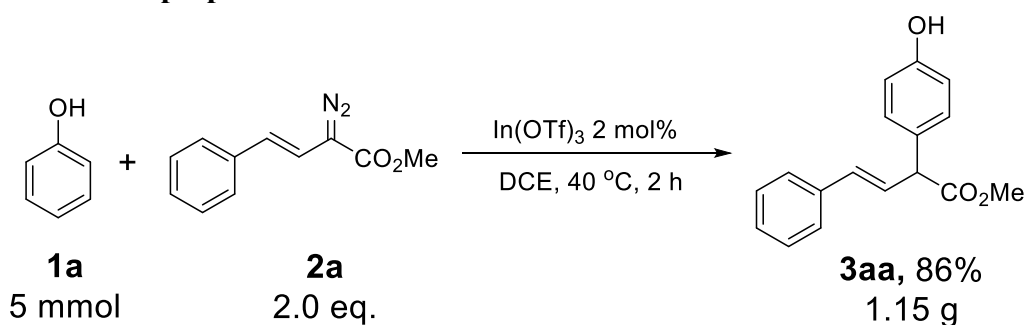


The procedure is similar with that of **3aa**: 2,6-dimethylphenol **1h** (36.7 mg, 0.3 mmol), methyl (*E*)-2-diazohex-3-enoate **2r** (92.5 mg, 0.6 mmol),  $In(OTf)_3$  (16.9 mg, 0.03 mmol), DCE, 40 °C, 30 min, **4hr** was obtained after purification by flash chromatography (PE/EA = 15:1).

(PE/EA = 15:1) 8.2 mg; 11% yield; Yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.04 (dd,  $J = 15.6, 8.0$  Hz, 1H), 6.76 (s, 2H), 5.77 (dd,  $J = 15.6, 1.2$  Hz, 1H), 4.61 (s, 1H), 3.71 (s, 3H), 3.15 (q,  $J = 7.6$  Hz, 1H), 2.22 (s, 6H), 1.80 – 1.69 (m, 2H), 0.87 (t,  $J = 7.3$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 152.8, 150.9, 133.6, 127.8, 123.2, 119.8, 51.5, 49.6, 27.9, 16.0, 12.2; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{15}\text{H}_{20}\text{NaO}_3$  271.1305, found 271.1308.

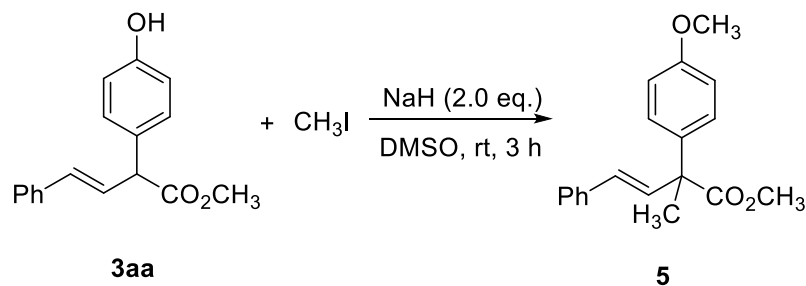
## 4. Gram Scale Preparation of 3aa and Synthetic Application

### 1) Gram scale preparation of 3aa



In a dried Schlenk tube, a solution of  $\text{In}(\text{OTf})_3$  (56.2 mg, 0.10 mmol, 2.0 mol %), phenol (0.471 g, 5.0 mmol) in DCE (10 mL) was stirred at 40 °C. Then a solution of methyl (*E*)-2-diazo-4-phenylbut-3-enoate **2a** (2.02 g, 10.0 mmol) in 20 mL of DCE was introduced into the reaction mixture by a syringe in 1 h. The resulting mixture was continually stirred at room temperature for 1 h and **2a** was consumed completely determined by TLC analysis. The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 15:1) to afford **3aa** (1.15 g, 86%).

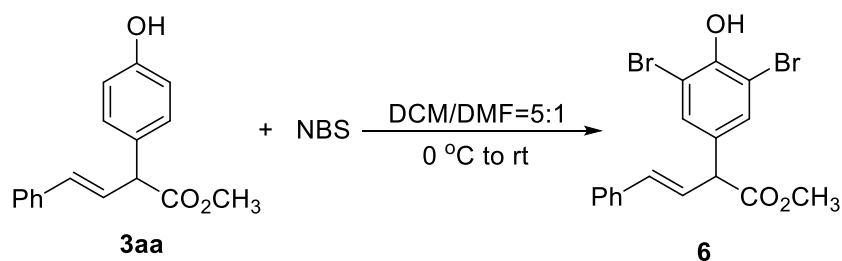
### 2) Methyl (*E*)-2-(4-methoxyphenyl)-2-methyl-4-phenylbut-3-enoate (**5**).



In a dried flask, **3aa** (268 mg, 1.0 mmol) and DMSO (10 mL) were added at 0 °C. Then NaH (80.0 mg, 2.0 mmol) was added, the reaction was warmed to room temperature and stirred for 30 minutes. Then CH<sub>3</sub>I (284 mg, 2.0 mmol) was introduced into the reaction mixture by a syringe. The resulting mixture was continually stirred for 3 hours. Finally, H<sub>2</sub>O was added to the mixture, and extracted with DCM. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After being filtrated through celite and concentrated, The residue was purified by silica chromatography (PE/EA = 60:1) to get desired product **5** (267 mg, 90%) as a yellow oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.20 (m, 4H), 6.90 – 6.82 (m, 2H), 6.76 (d, *J* = 16.3 Hz, 1H), 6.43 (d, *J* = 16.3 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 1.73 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 175.4, 158.4, 137.0, 135.9, 133.1, 129.7, 128.6, 127.61, 127.57, 126.5, 113.8, 55.2, 52.7, 52.4, 24.3; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>19</sub>H<sub>20</sub>NaO<sub>3</sub> 319.1305, found 319.1315.

### 3) Methyl (*E*)-2-(3,5-dibromo-4-hydroxyphenyl)-4-phenylbut-3-enoate (**6**).<sup>1</sup>

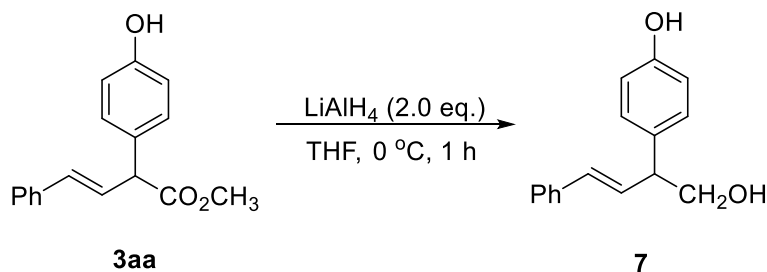


To a solution of **3aa** (107 mg, 0.40 mmol) in DCM (10 mL) and DMF (2 mL) was added NBS (214 mg, 1.2 mmol) at 0 °C and then the reaction was warmed to room temperature and stirred for 5 minutes. The reaction was quenched with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

solution and extracted with ethyl acetate. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by silica chromatography (PE/EA = 20:1 to 10:1) to get desired product **6** (145 mg, 85%) as a white solid (m.p. = 124.0 – 125.0 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (s, 2H), 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 6.53 – 6.36 (m, 2H), 5.90 (s, 1H), 4.36 (d, *J* = 6.3 Hz, 1H), 3.75 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.1, 148.8, 136.2, 133.3, 132.7, 131.5, 128.6, 128.0, 126.5, 125.8, 110.0, 53.3, 52.6; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>14</sub>Br<sub>2</sub>NaO<sub>3</sub> 446.9202, found 446.9202.

#### 4) (*E*)-4-(1-Hydroxy-4-phenylbut-3-en-2-yl)phenol (**7**).<sup>2</sup>

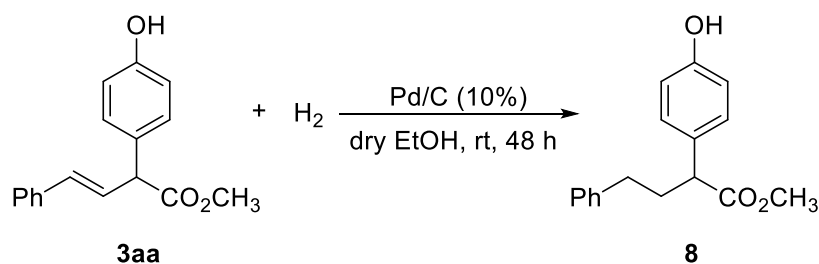


To a solution of **3aa** (268 mg, 1.0 mmol) in THF (20 mL) was added LiAlH<sub>4</sub> (75.9 mg, 2.0 mmol) at 0 °C and stirred for 1h. The reaction was quenched with NaHCO<sub>3</sub> solution and extracted with ethyl acetate. The combined organic layer was concentrated and dried with Na<sub>2</sub>SO<sub>4</sub>. The residue was purified by silica chromatography (PE/EA = 2:1) to get desired product **7** (237.9 mg, 99%) as a white solid (m.p. = 127.2 – 128.2 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.34 (dd, *J* = 15.9, 7.8 Hz, 1H), 3.88 (d, *J* = 7.1 Hz, 2H), 3.64 (q, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.7, 137.0, 132.5, 131.9, 129.8, 129.1, 128.5, 127.5, 126.2, 115.7, 66.4, 50.8; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>16</sub>H<sub>16</sub>NaO<sub>2</sub> 263.1043, found 263.1049.

#### 5) Methyl 2-(4-hydroxyphenyl)-4-phenylbutanoate (**8**)

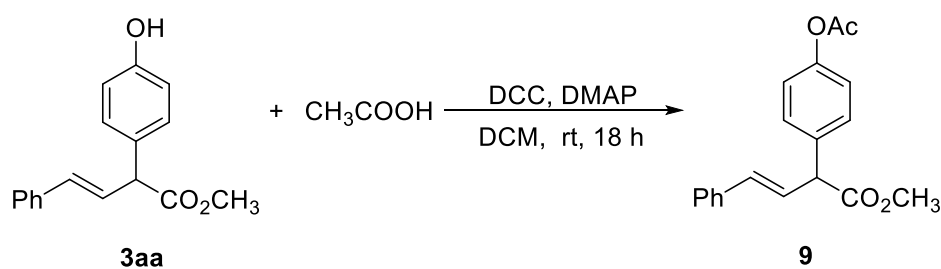




To a mixture of Pd/C (10.7 mg, 10% w/w Pd on carbon) in dry EtOH (4.0 mL) was added **3aa** (107 mg, 0.40 mmol) under argon atmosphere. Then, the reaction flask was evacuated and refilled with hydrogen through a balloon. The resulting reaction mixture was stirred under the hydrogen atmosphere at room temperature for 48 h. After completion, the reaction mixture was filtered and rinsed with DCM. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford **8** as a colorless oil (107 mg, 99%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.23 (m, 2H), 7.21 – 7.11 (m, 5H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.76 (s, 1H), 3.65 (s, 3H), 3.50 (t, *J* = 7.7 Hz, 1H), 2.61 – 2.48 (m, 2H), 2.45 – 2.30 (m, 1H), 2.14 – 2.01 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 175.1, 155.1, 141.2, 130.5, 129.2, 128.4, 128.4, 126.0, 115.6, 52.1, 49.9, 34.8, 33.4; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>17</sub>H<sub>18</sub>NaO<sub>3</sub> 293.1148, found 293.1161.

#### 6) Methyl (*E*)-2-(4-acetoxyphenyl)-4-phenylbut-3-enoate (**9**)

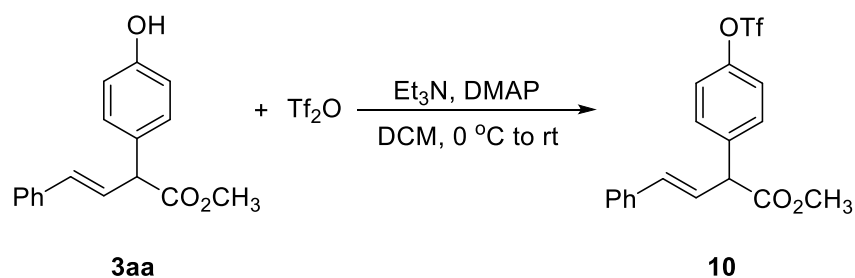


The mixture of compound **3aa** (268 mg, 1.0 mmol), CH<sub>3</sub>COOH (72.1 mg, 1.2 mmol), DCC (227 mg, 1.1 mmol) and DMAP (24.4 mg, 0.20 mmol) in DCM was stirred at room temperature for 18 hours. After being filtrated through celite and concentrated, the residue was purified by column chromatography to get a yellow oil **9** (289 mg, 93%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.35 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.25 –

7.20 (m, 1H), 7.09 – 7.05 (m, 2H), 6.55 (dd,  $J = 15.9, 7.9$  Hz, 1H), 6.48 (d,  $J = 15.9$  Hz, 1H), 4.47 (d,  $J = 7.9$  Hz, 1H), 3.73 (s, 4H), 2.29 (s, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.6, 169.4, 149.9, 136.5, 135.7, 132.7, 129.0, 128.5, 127.8, 126.8, 126.5, 121.8, 54.3, 52.4, 21.1; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{19}\text{H}_{18}\text{NaO}_4$  333.1097, found 333.1105.

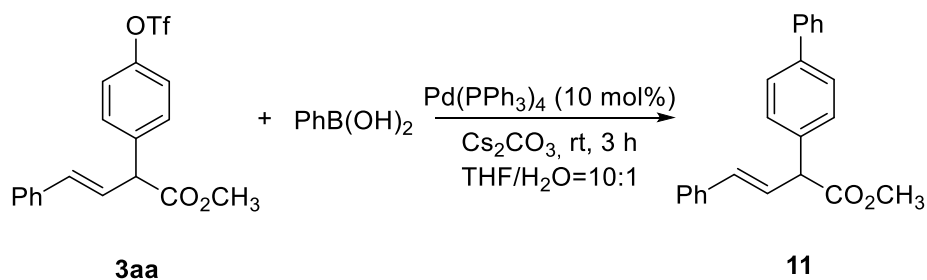
**7) Methyl (*E*)-4-phenyl-2-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)but-3-enoate (10).<sup>3</sup>**



To a solution of **3aa** (403 mg, 1.5 mmol),  $\text{Et}_3\text{N}$  (233 mg, 2.3 mmol) and DMAP (18.3 mg, 0.15 mmol) in DCM was added  $\text{Tf}_2\text{O}$  (649 mg, 2.3 mmol) dropwise at  $0\text{ }^\circ\text{C}$ , the reaction was then allowed warmed to room temperature and stirred for another 15 minutes. The reaction was quenched with aqueous saturated  $\text{NaHCO}_3$  and extracted with ethyl acetate. The combined organic layer was dried and concentrated under reduced pressure after filtration. The residue was purified by silica chromatography (PE/EA = 10:1) to give the desired product **10** (589 mg, 98%) as a yellow oil.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.43 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.28 – 7.22 (m, 3H), 6.57 – 6.44 (m, 2H), 4.51 (d,  $J = 6.8$  Hz, 1H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.1, 148.8, 138.7, 136.2, 133.3, 129.9, 128.6, 128.0, 126.5, 126.0, 122.5, 121.6, 120.0, 117.4, 114.9, 54.2, 52.5;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -72.85; HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  calculated for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NaO}_5\text{S}$  423.0484, found 423.0494.

**8) Methyl (*E*)-2-([1,1'-biphenyl]-4-yl)-4-phenylbut-3-enoate (11).<sup>4</sup>**



The mixture of compound **10** (120 mg, 0.30 mmol), Ph(OH)<sub>2</sub> (54.9 mg, 0.45 mmol), Cs<sub>2</sub>CO<sub>3</sub> (489 mg, 1.5 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (35.0 mg, 0.030 mmol) in THF/H<sub>2</sub>O (11 mL, 10:1) was stirred at room temperature for 3 hours. Then the reaction was extracted with ethyl acetate. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure after filtration. The residue was purified by silica chromatography (PE/EA = 10:1) to give the desired product **11** (82.8 mg, 84%) as a white solid (m.p. = 78.5 – 79.5 °C).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.55 (m, 4H), 7.46 – 7.38 (m, 6H), 7.36 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 6.61 (dd, *J* = 15.9, 8.2 Hz, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 4.53 (d, *J* = 8.2 Hz, 1H), 3.75 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.9, 140.7, 140.4, 137.3, 136.6, 132.6, 128.8, 128.5, 128.4, 127.7, 127.5, 127.3, 127.1, 127.0, 126.5, 54.6, 52.4; HRMS (ESI-TOF) *m/z*: [M+Na]<sup>+</sup> calculated for C<sub>23</sub>H<sub>20</sub>NaO<sub>2</sub> 351.1356, found 351.1359.

## 5. X-Ray Crystal Data

### 1) Crystal Structure Information of **3ae**

0.1 mL of DCM was added to a 10 mL oven-dried glass sample bottle with 10 mg pure **3ae** to dissolve the sample, then 8 mL n-hexane was slowly added to the solution, sealed with perforated paper, and then the solvent was slowly dried at room temperature to obtain crystals. Single crystal X-ray diffraction data were collected on Bruker Smart Apex II CCD diffractometer. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC): 2067260

Compound Name: methyl (*E*)-4-(4-chlorophenyl)-2-(4-hydroxyphenyl)but-3-enoate

Formula: C<sub>17</sub>H<sub>15</sub>ClO<sub>3</sub>

Unit Cell Parameters: a 11.0617(2) b 8.39460(10) c 32.7088(5)

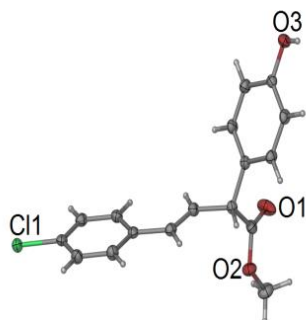


Table S2: crystal data for compounds **3ae**

Compound	<b>3ae</b>
Empirical formula	C <sub>17</sub> H <sub>15</sub> ClO <sub>3</sub>
Formula weight	302.75
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	11.0617(2)
b/Å	8.39460(10)
c/Å	32.7088(5)
α/°	90
β/°	95.1310(10)
γ/°	90
Volume/Å <sup>3</sup>	3025.12(8)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.329
μ/mm <sup>-1</sup>	2.298

F(000)	1264.0
Crystal size/mm <sup>3</sup>	0.32 × 0.22 × 0.16
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.238 to 149.526
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 7, -40 ≤ l ≤ 40
Reflections collected	33273
Independent reflections	6116 [R <sub>int</sub> = 0.0622, R <sub>sigma</sub> = 0.0460]
Data/restraints/parameters	6116/0/389
Goodness-of-fit on F <sup>2</sup>	1.033
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0406, wR <sub>2</sub> = 0.0990
Final R indexes [all data]	R <sub>1</sub> = 0.0479, wR <sub>2</sub> = 0.1028
Largest diff. peak/hole / e Å <sup>-3</sup>	0.20/-0.36

## 2) Crystal Structure Information of 7

0.1 mL of DCM was added to a 10 mL oven-dried glass sample bottle with 10 mg pure **7** to dissolve the sample, then 8 mL n-hexane was slowly added to the solution, sealed with perforated paper, and then the solvent was slowly dried at room temperature to obtain crystals. Single crystal X-ray diffraction data were collected on Bruker Smart Apex II CCD diffractometer. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC): 2067276

Compound Name: (*E*)-4-(1-hydroxy-4-phenylbut-3-en-2-yl)phenol (**7**)

Formula: C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>

Unit Cell Parameters: a 16.80664(11) b 12.67126(8) c 6.02846(5)

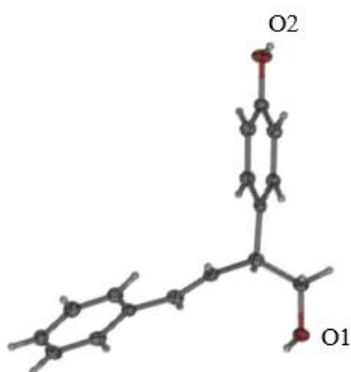


Table S3: crystal data for compounds **7**

Compound	<b>7</b>
Empirical formula	C <sub>16</sub> H <sub>16</sub> O <sub>2</sub>
Formula weight	240.30
Temperature/K	100.1(4)
Crystal system	orthorhombic
Space group	Pna2 <sub>1</sub>
a/Å	16.80664(11)
b/Å	12.67126(8)
c/Å	6.02846(5)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1283.829(16)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.243
μ/mm <sup>-1</sup>	0.641
F(000)	512.0
Crystal size/mm <sup>3</sup>	0.38 × 0.36 × 0.28
Radiation	CuKα (λ = 1.54184)

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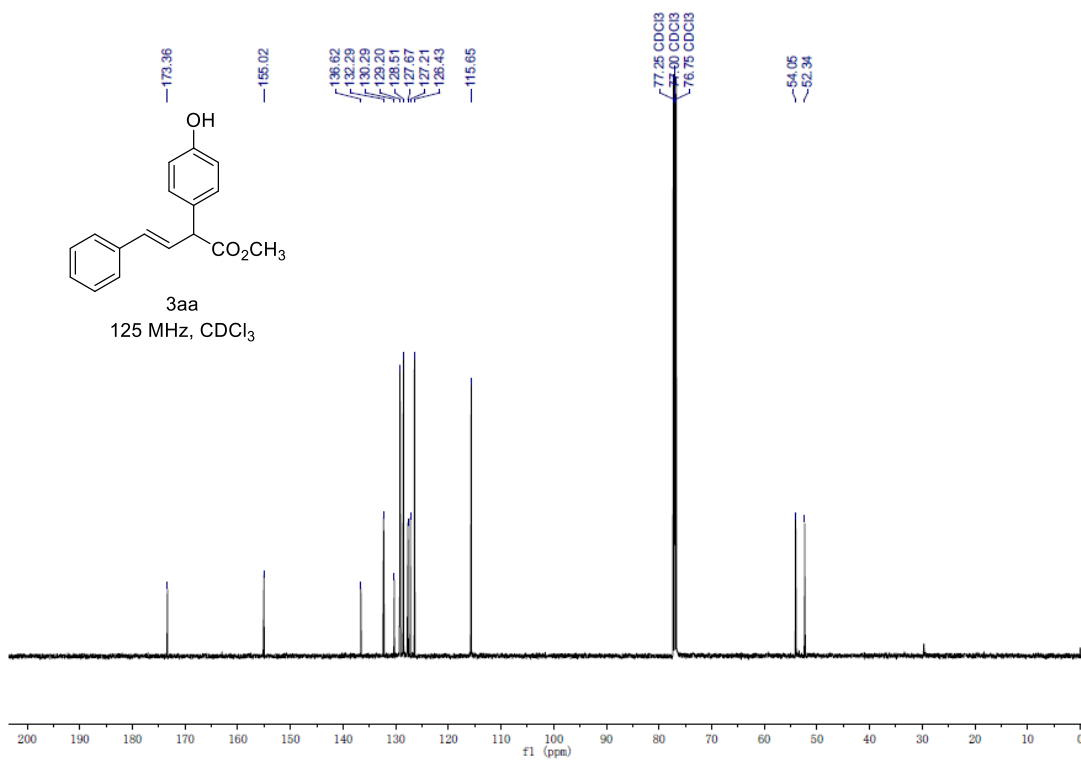
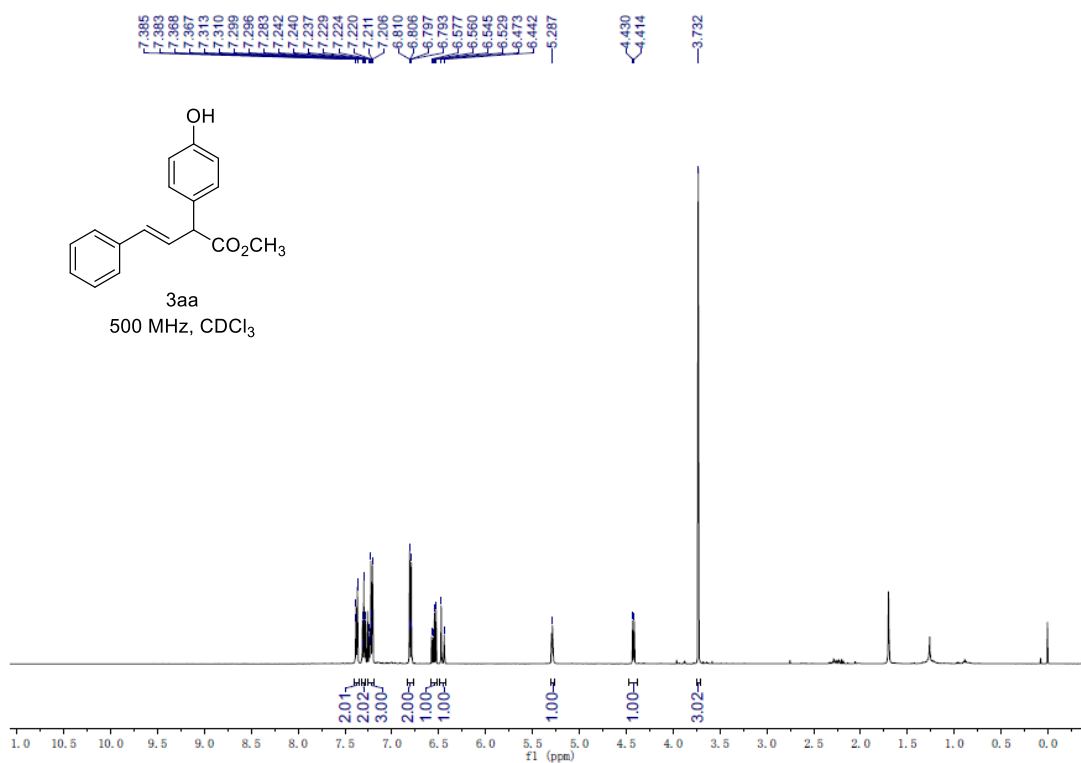
2 $\theta$ range for data collection/ $^{\circ}$	10.528 to 134.1
Index ranges	$-20 \leq h \leq 20, -15 \leq k \leq 15, -7 \leq l \leq 7$
Reflections collected	26347
Independent reflections	2180 [ $R_{\text{int}} = 0.0298, R_{\text{sigma}} = 0.0123$ ]
Data/restraints/parameters	2180/1/166
Goodness-of-fit on $F^2$	1.060
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0228, wR_2 = 0.0564$
Final R indexes [all data]	$R_1 = 0.0229, wR_2 = 0.0564$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.16/-0.10

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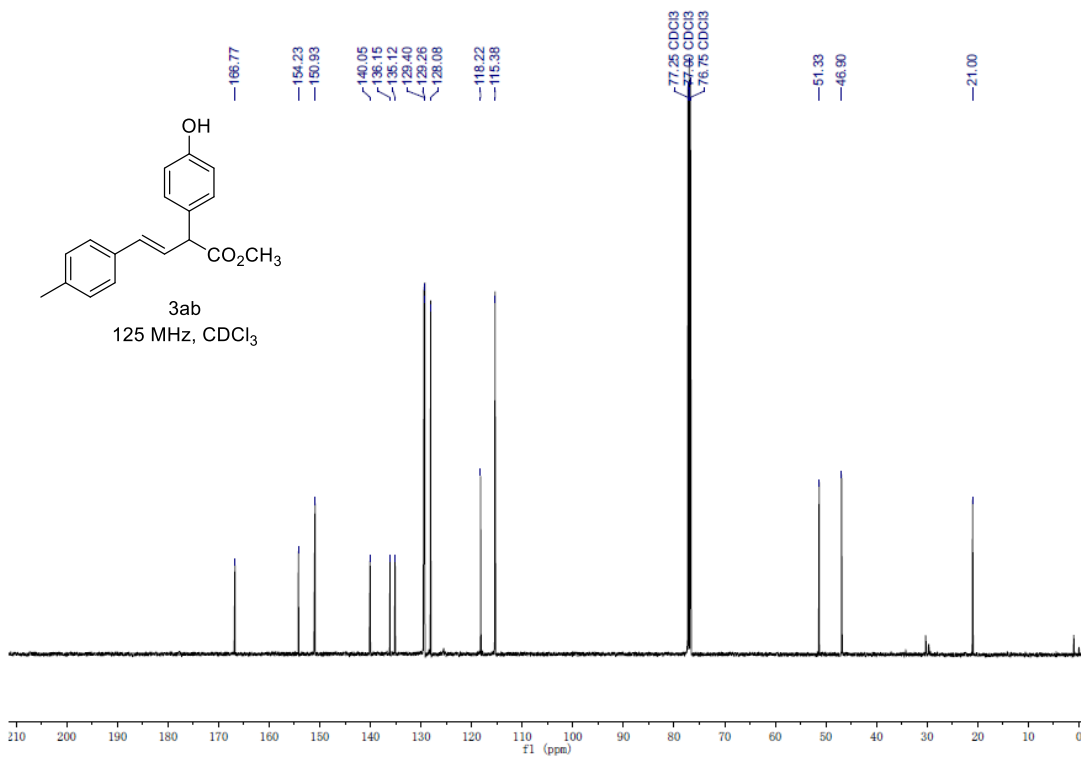
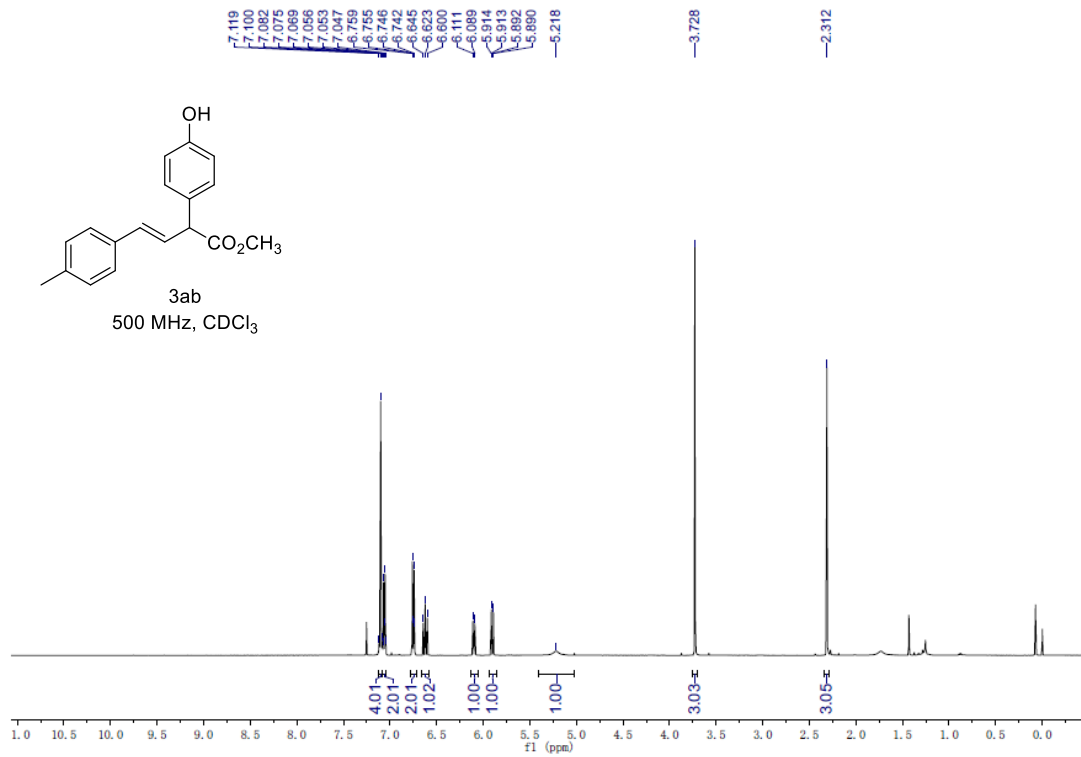
## 6. References

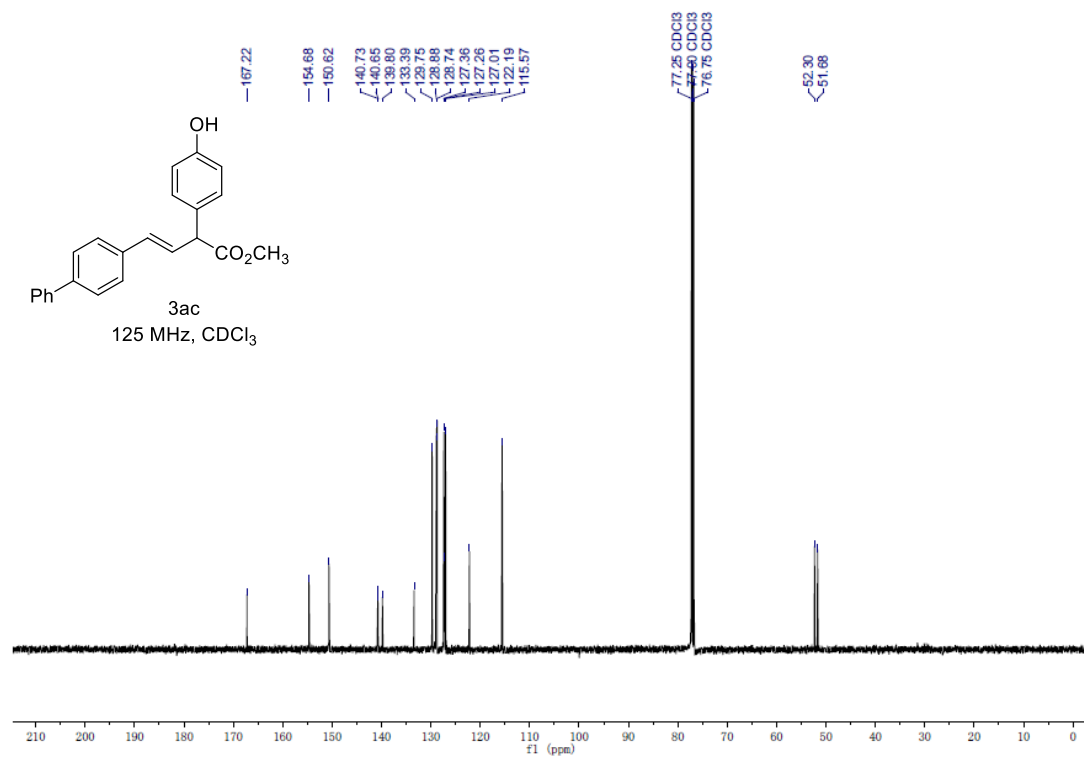
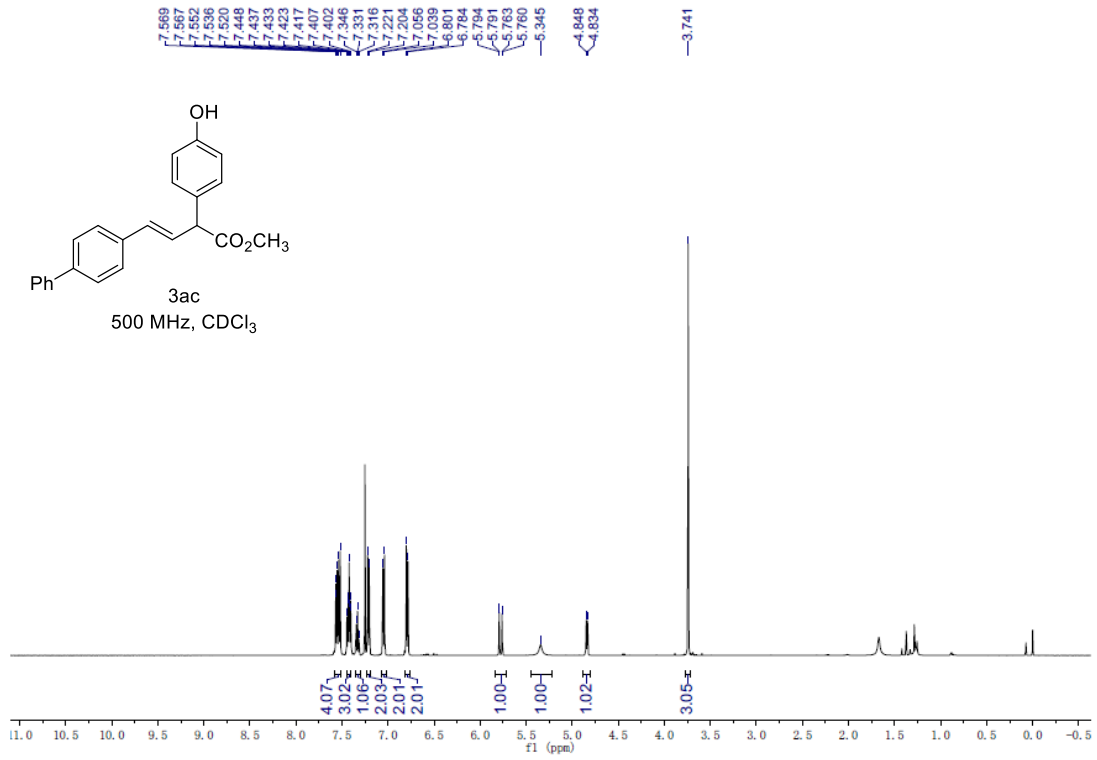
- (1) Zhao, J.-L.; Fan, X.; Shi, J.-G. *J. Nat. Prod.* **2004**, *67*, 1032.
- (2) Kuznetsov, A.; Gevorgyan, V. *Org. Lett.* **2012**, *14*, 914.
- (3) Yu, Z.-Z.; Ma, B.; Liu, L.; Zhang, J. *J. Am. Chem. Soc.* **2014**, *136*, 6904.
- (4) Kovina, I. M.; Tsukervanik, I. P. *Uzbekskii Khimicheskii Zhurnal* **1964**, *8*, 33.

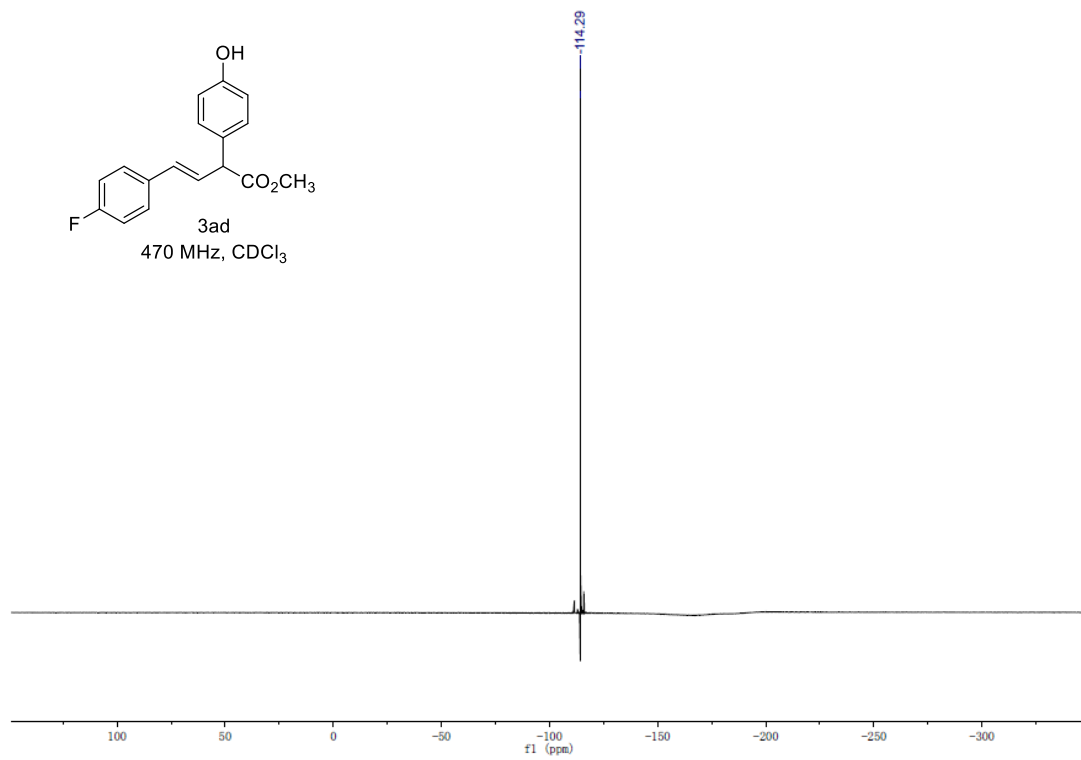
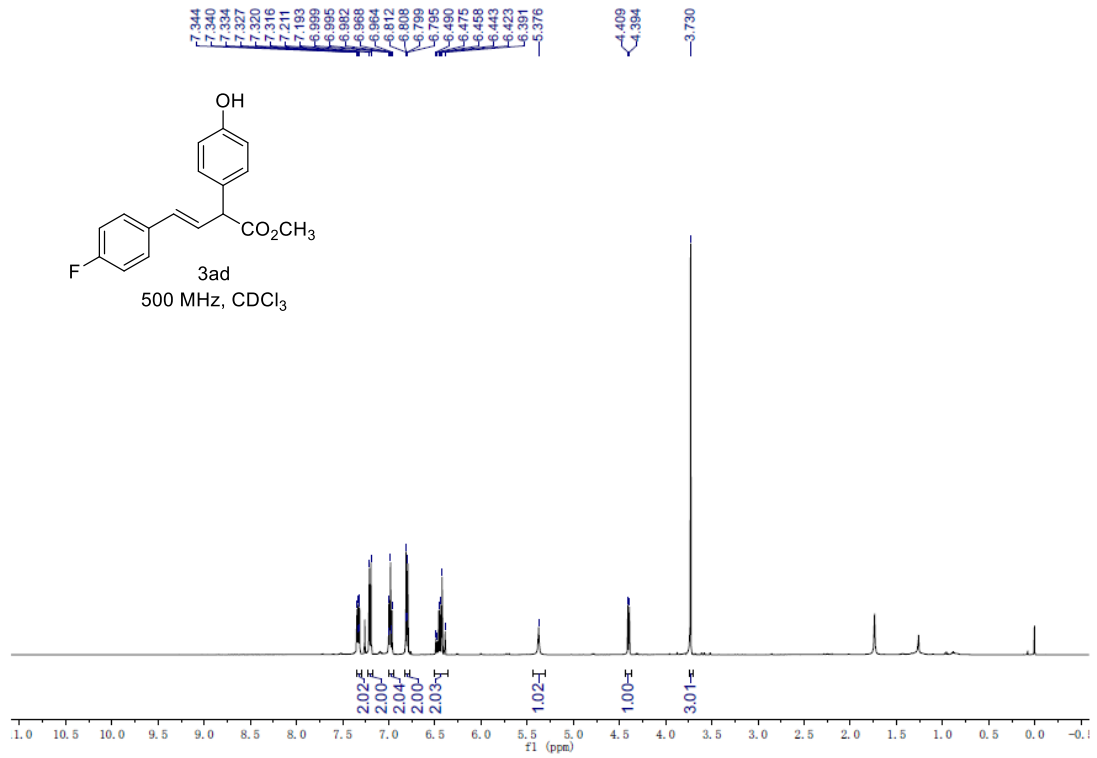
## 7. NMR Spectra of New Compounds

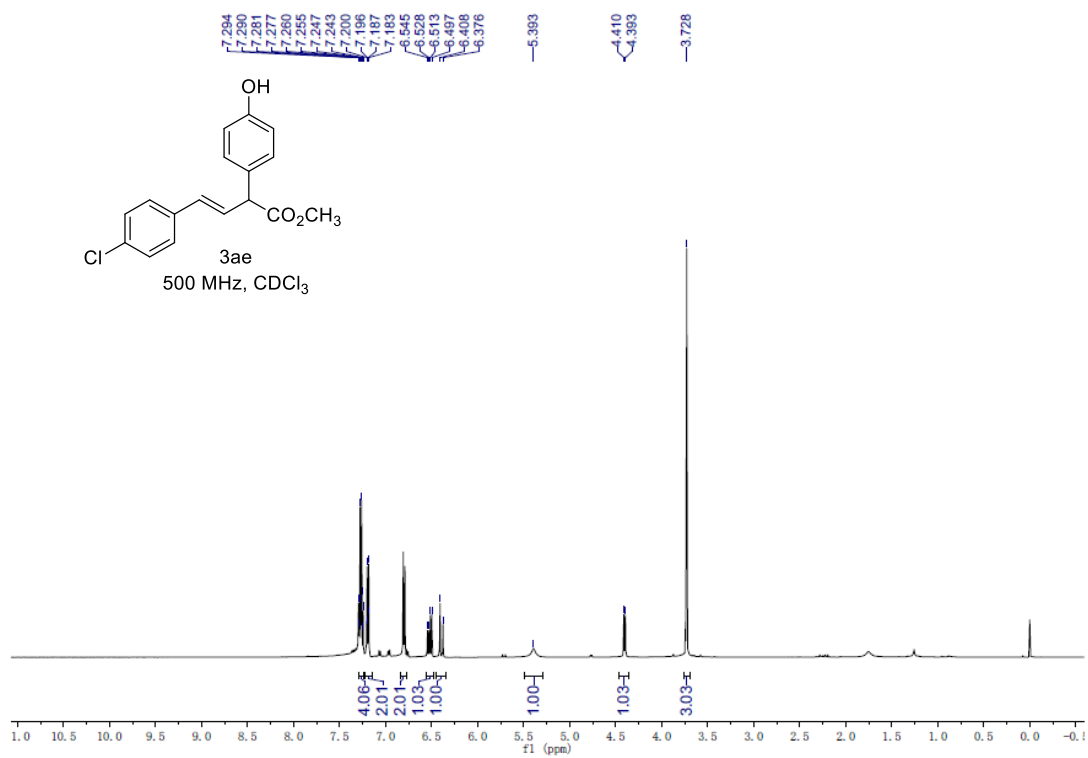
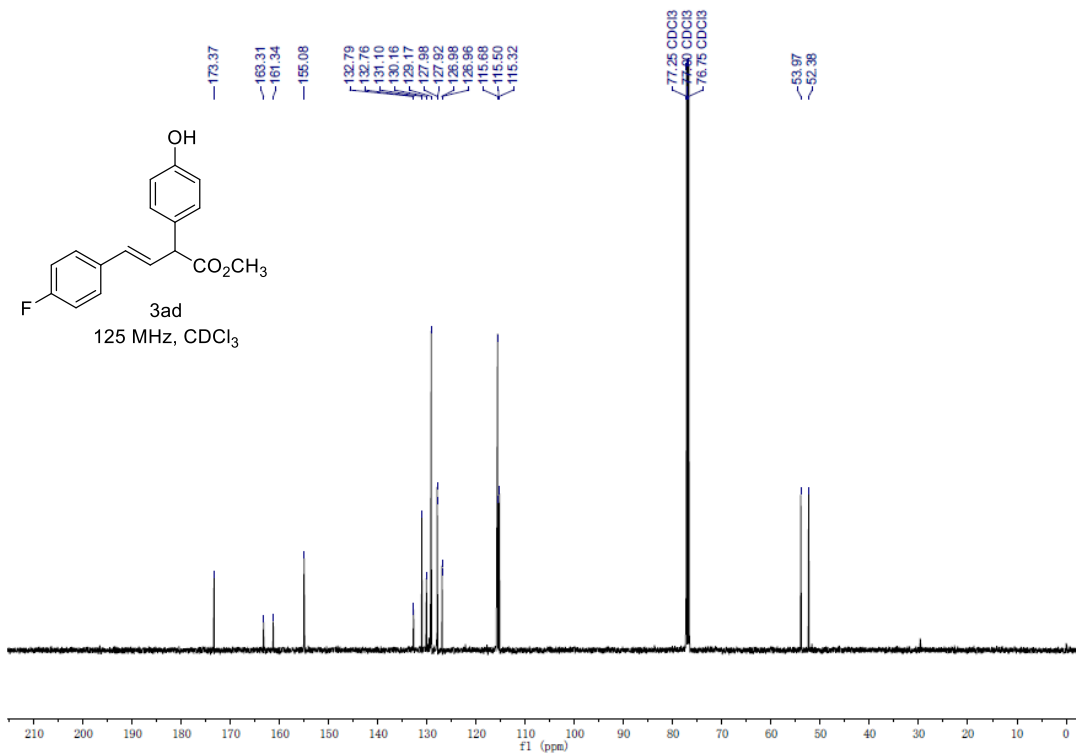


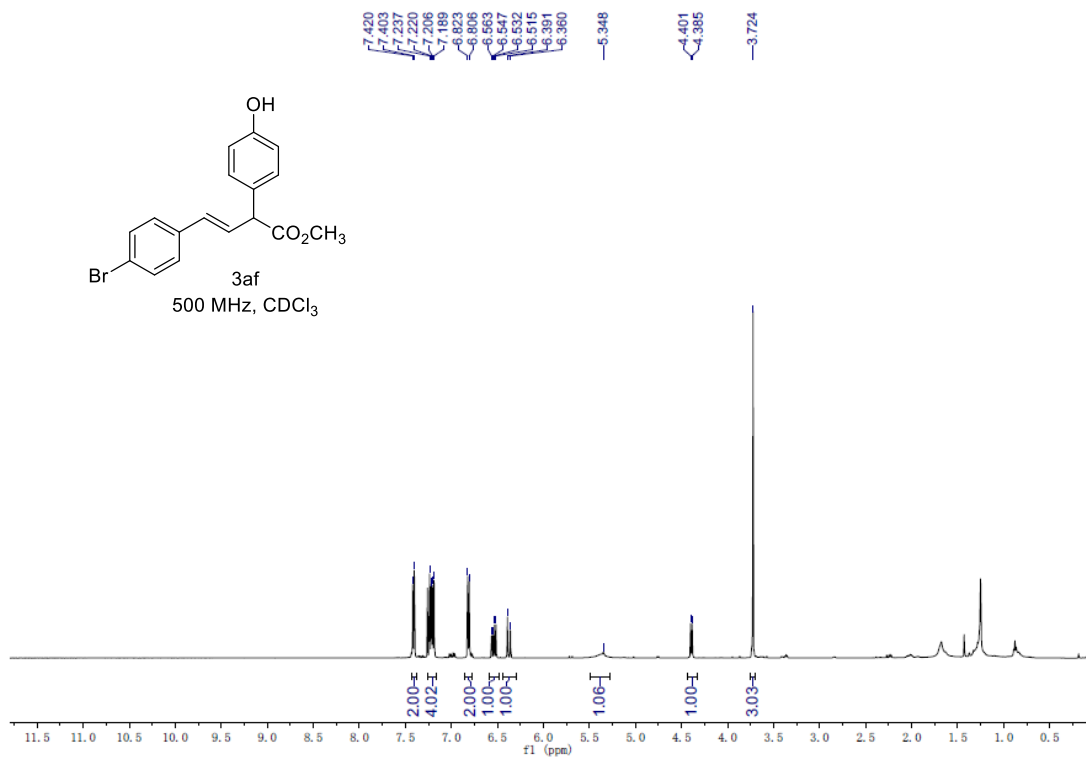
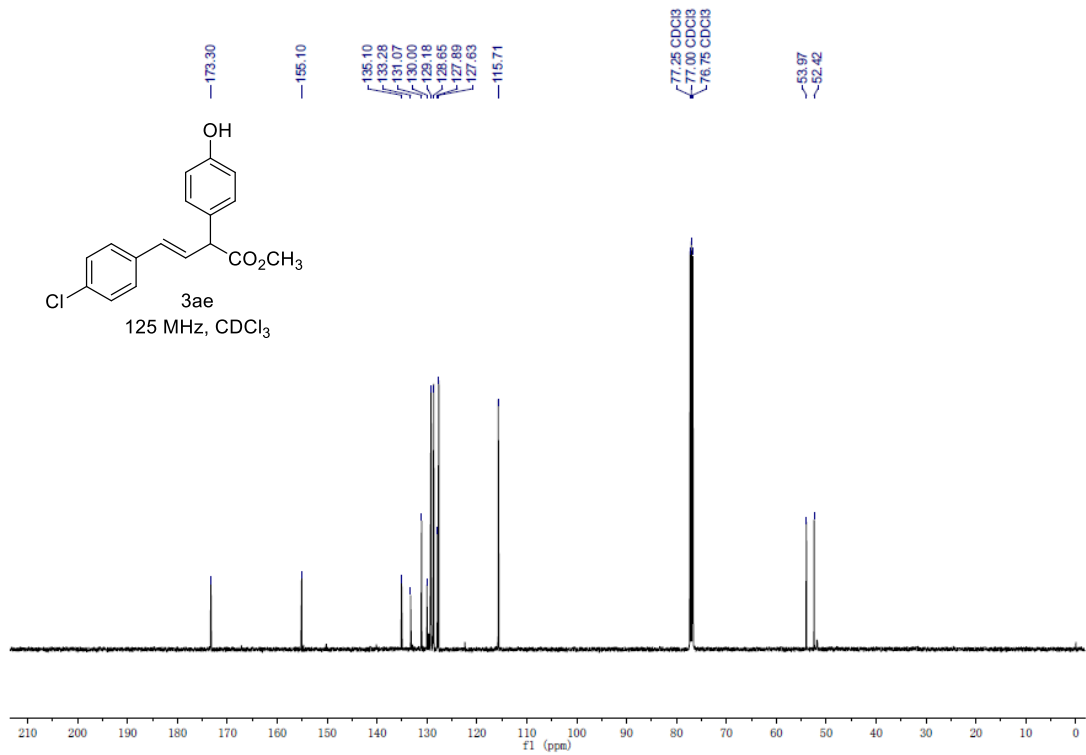


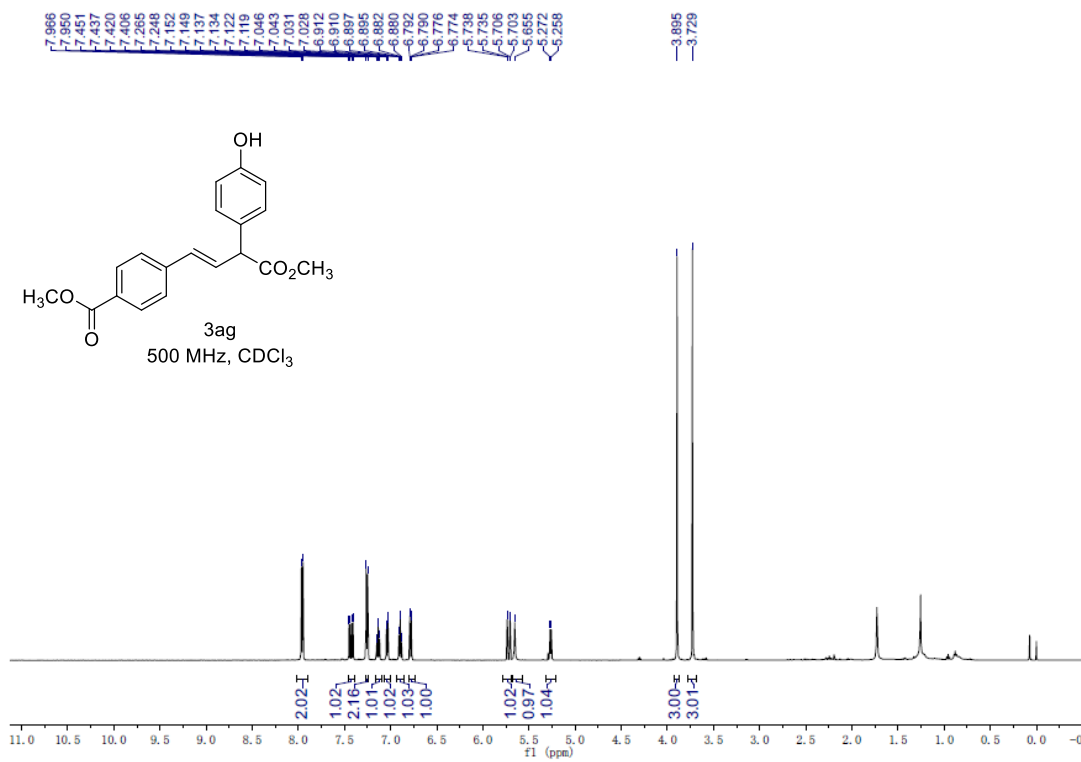
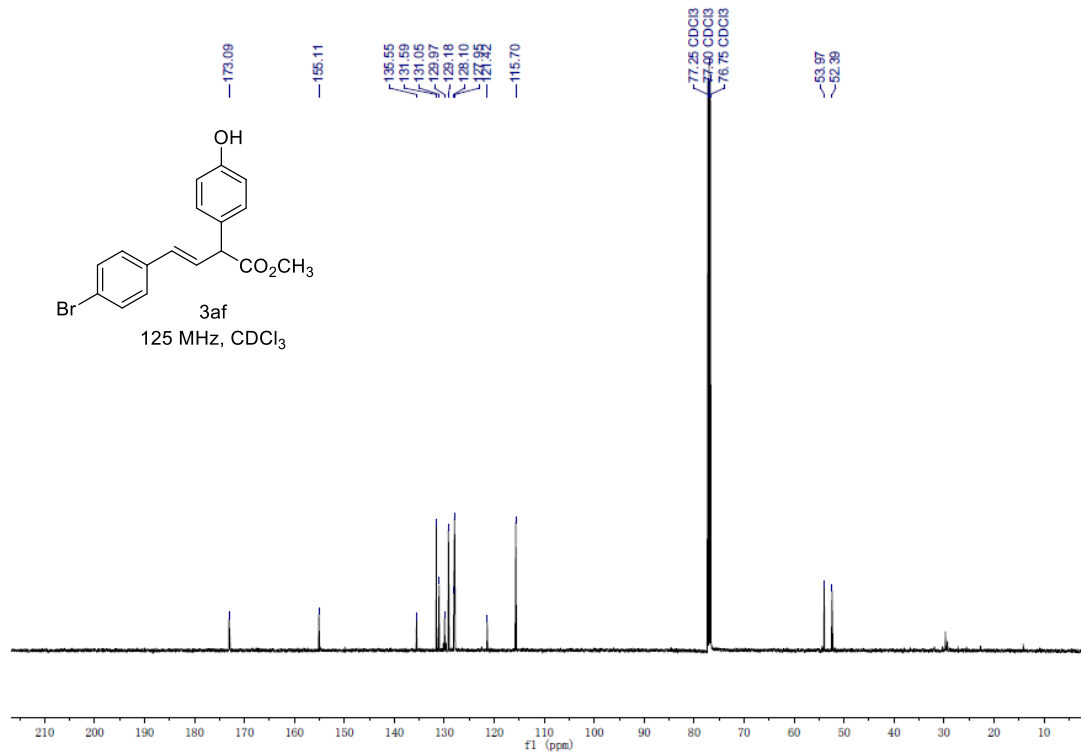


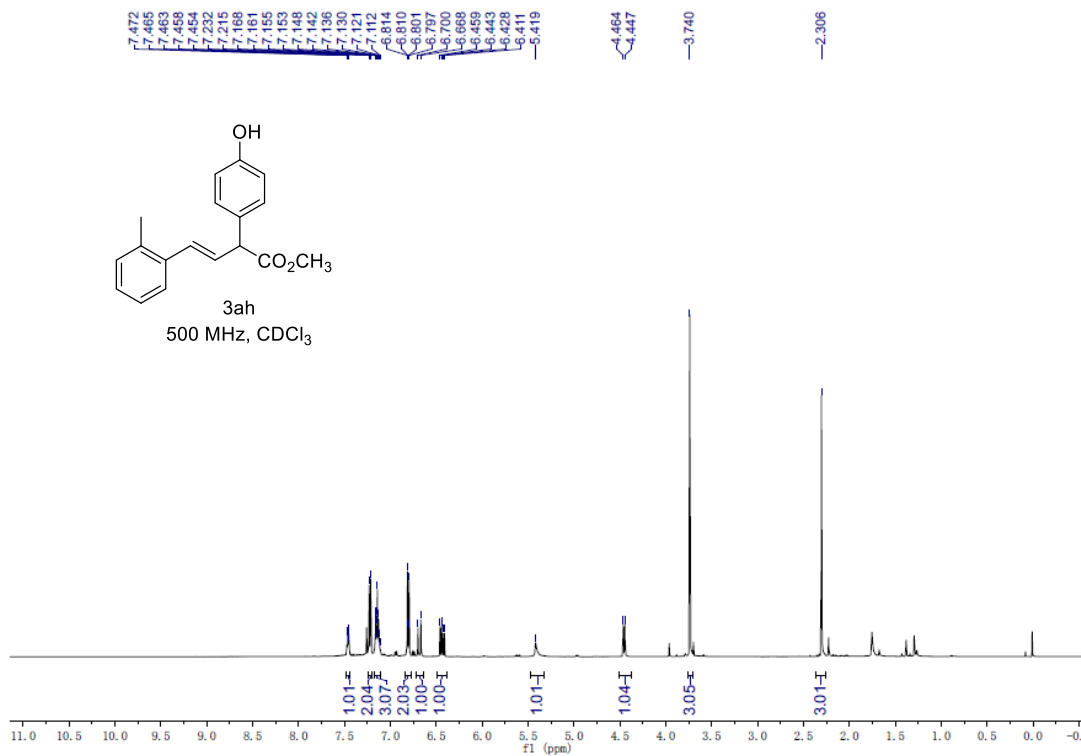
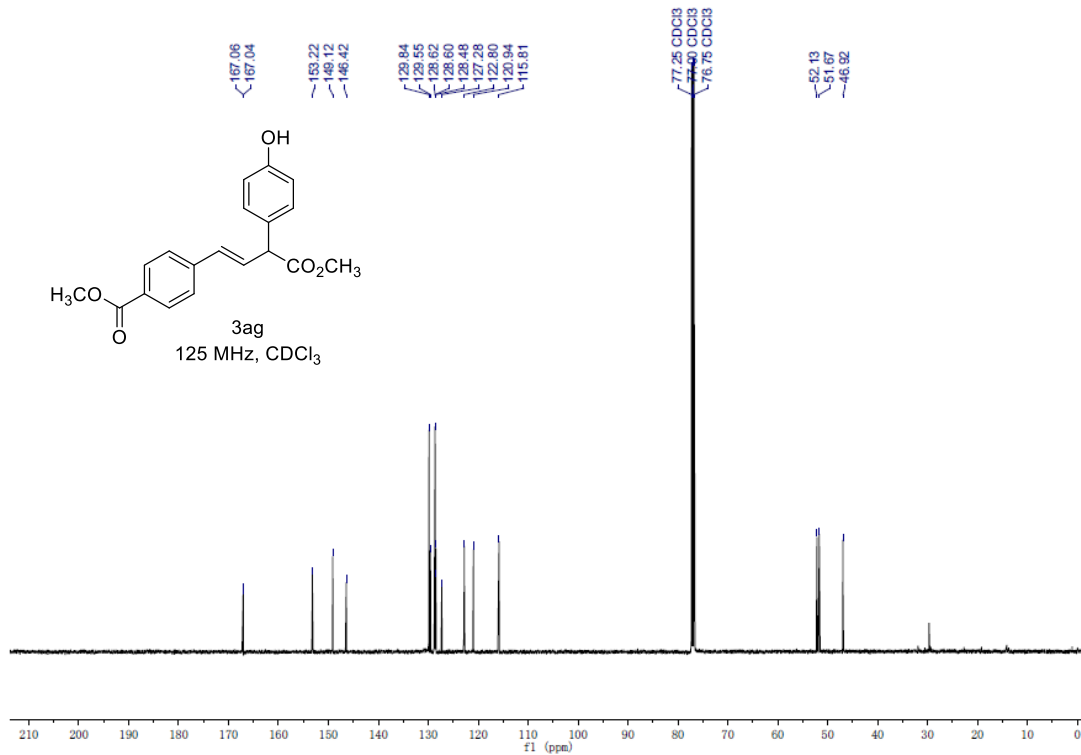


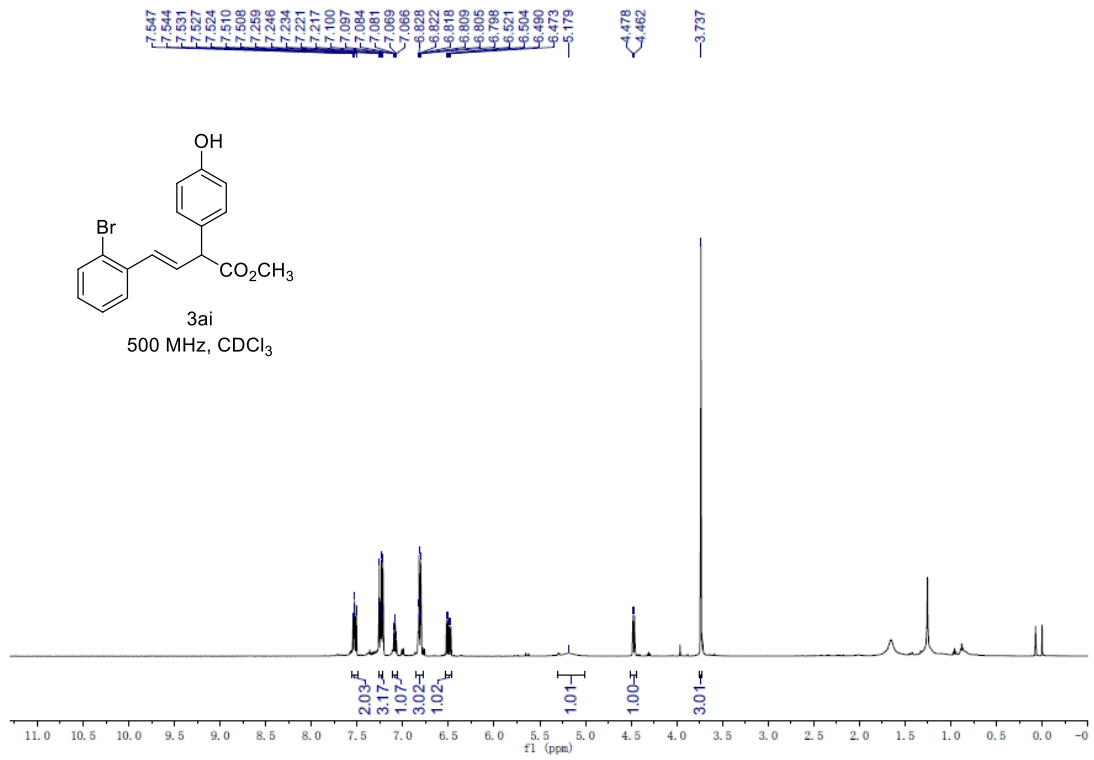
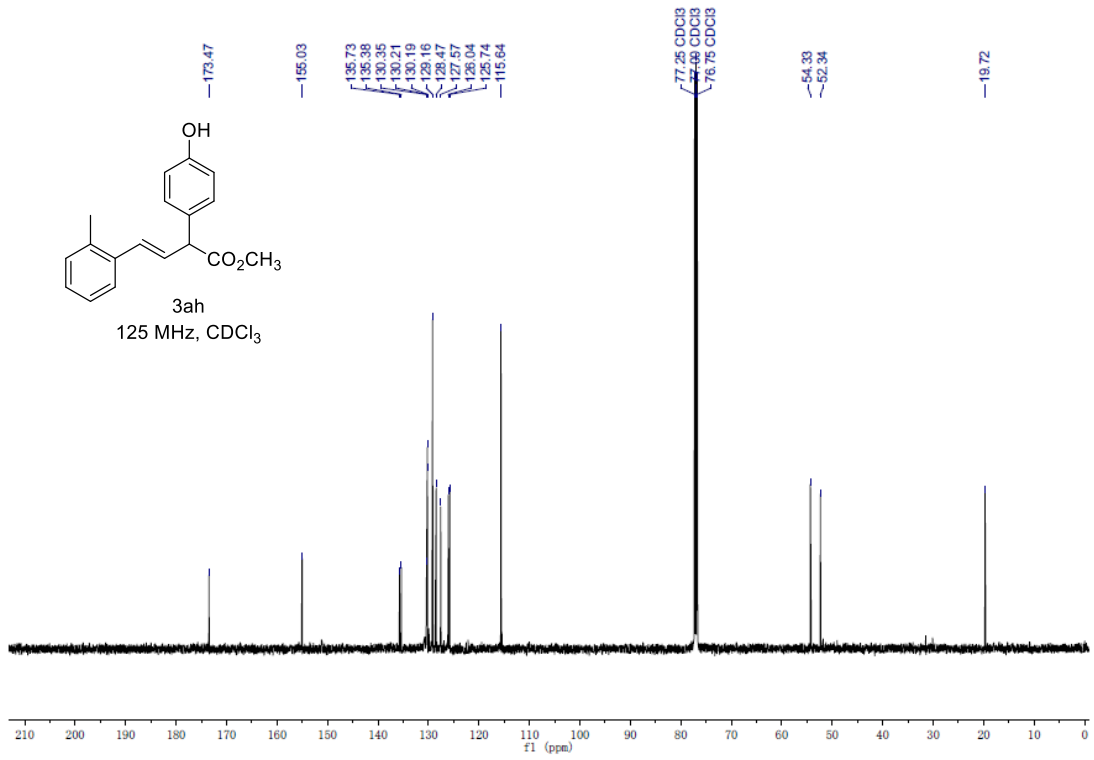




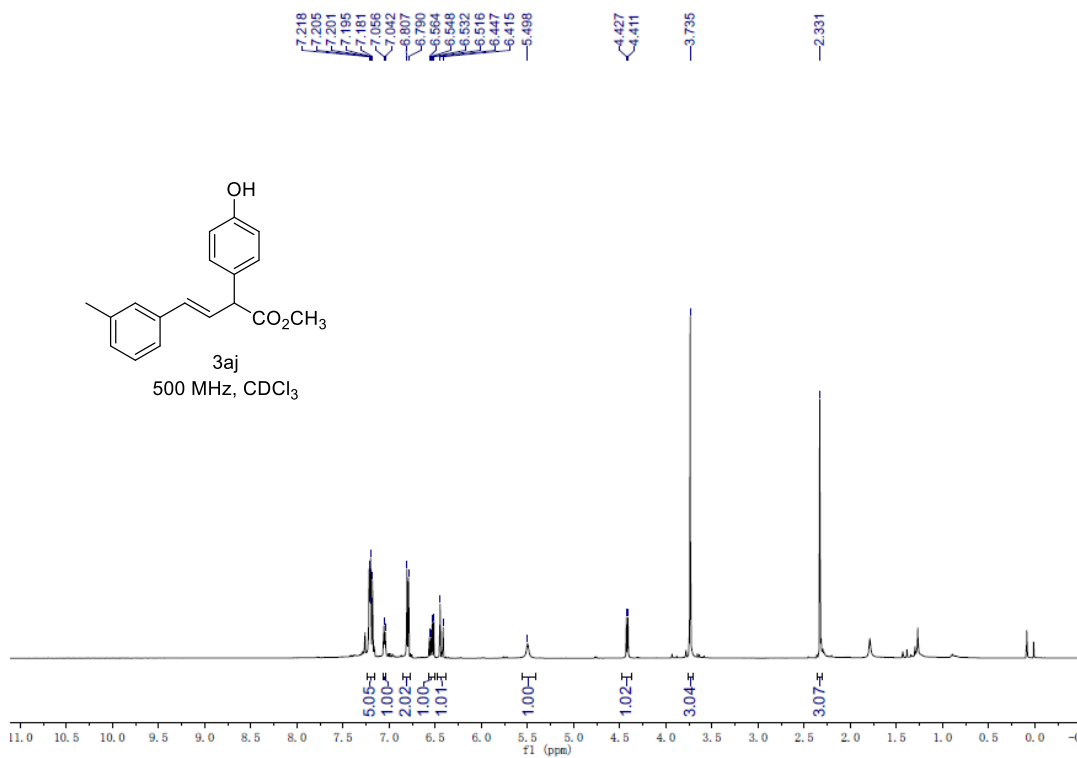
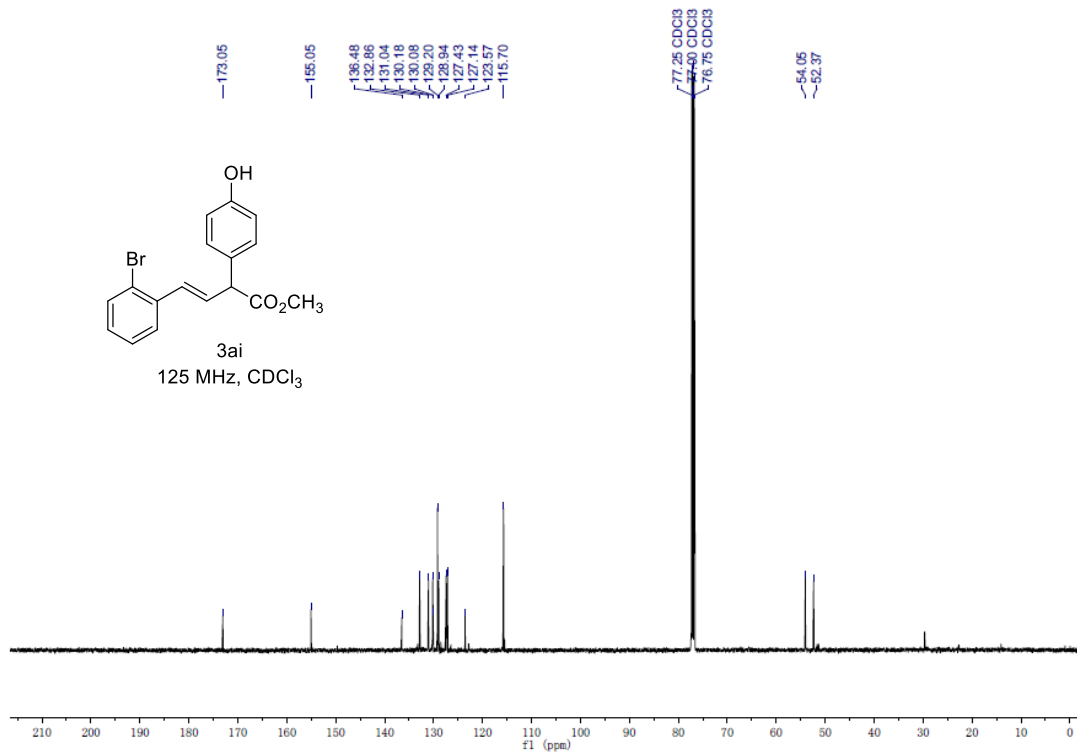


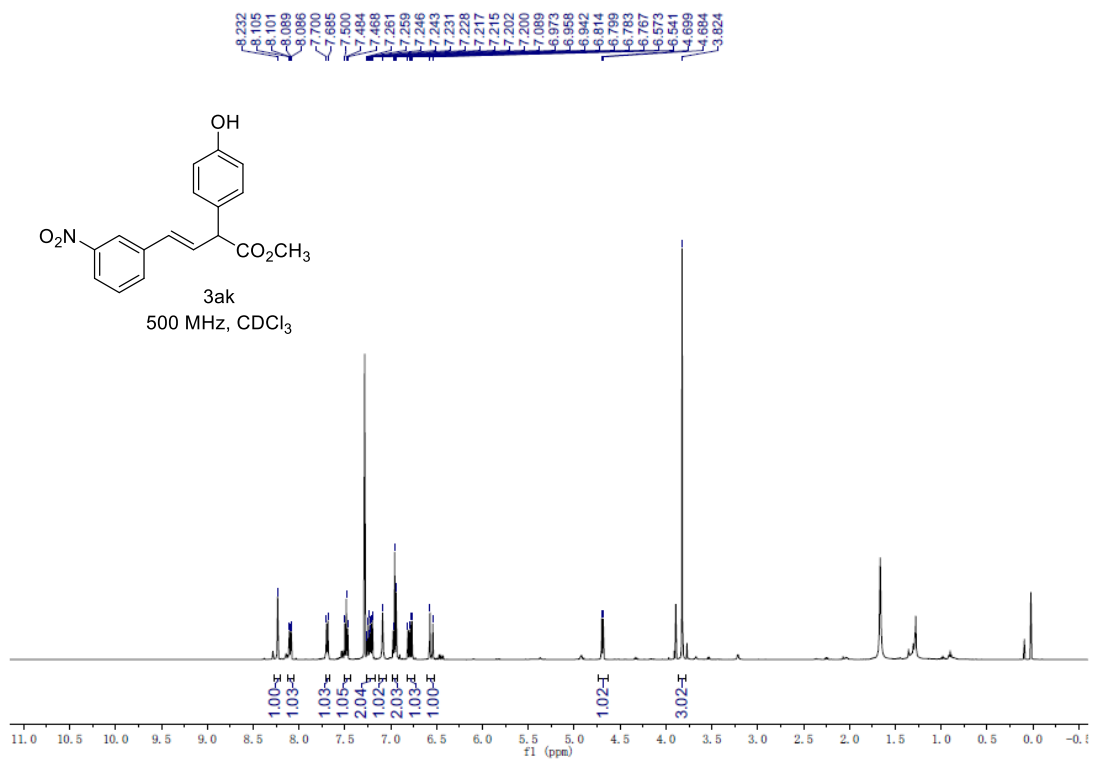
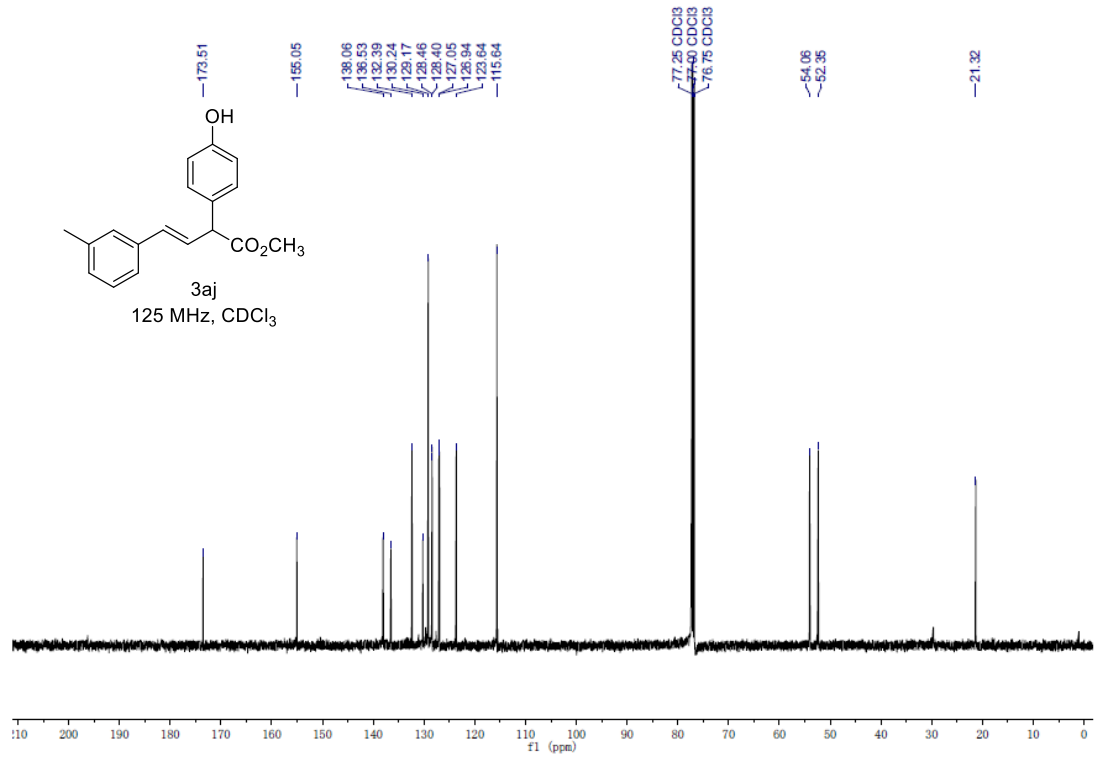


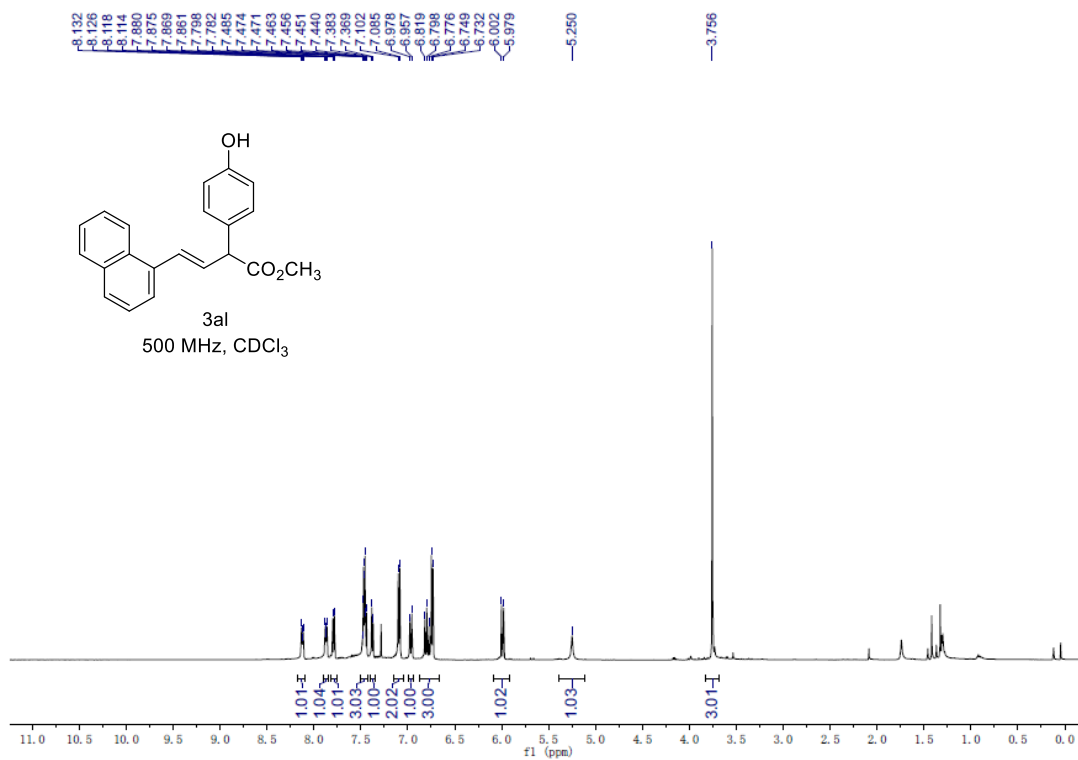
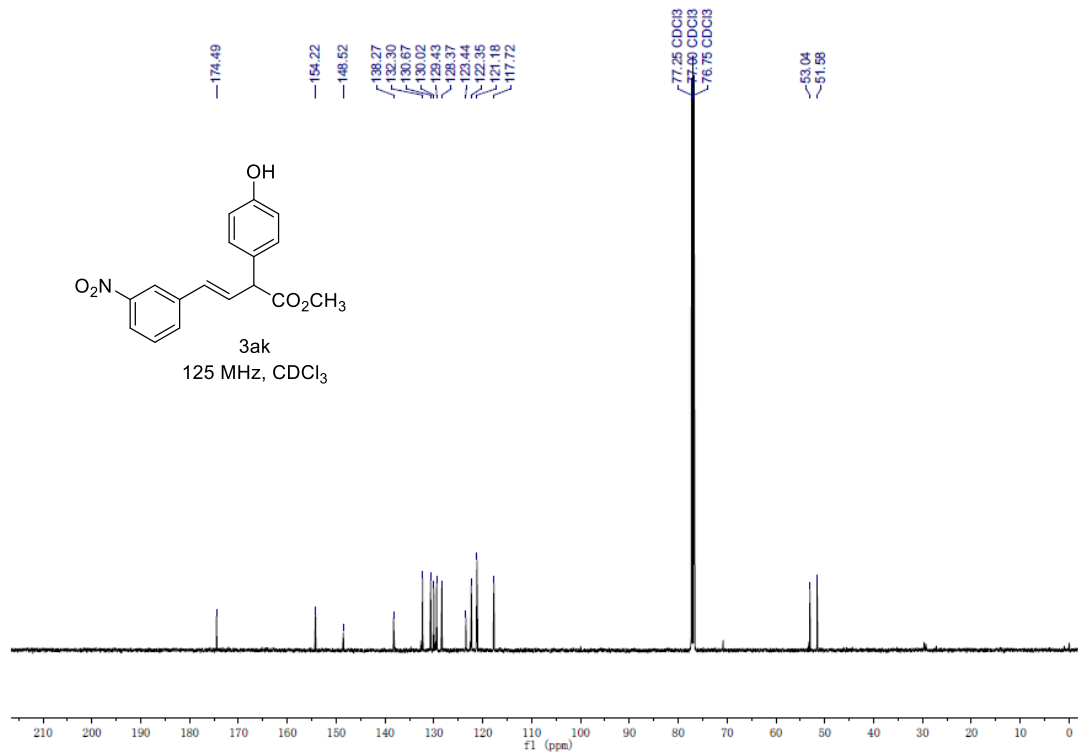




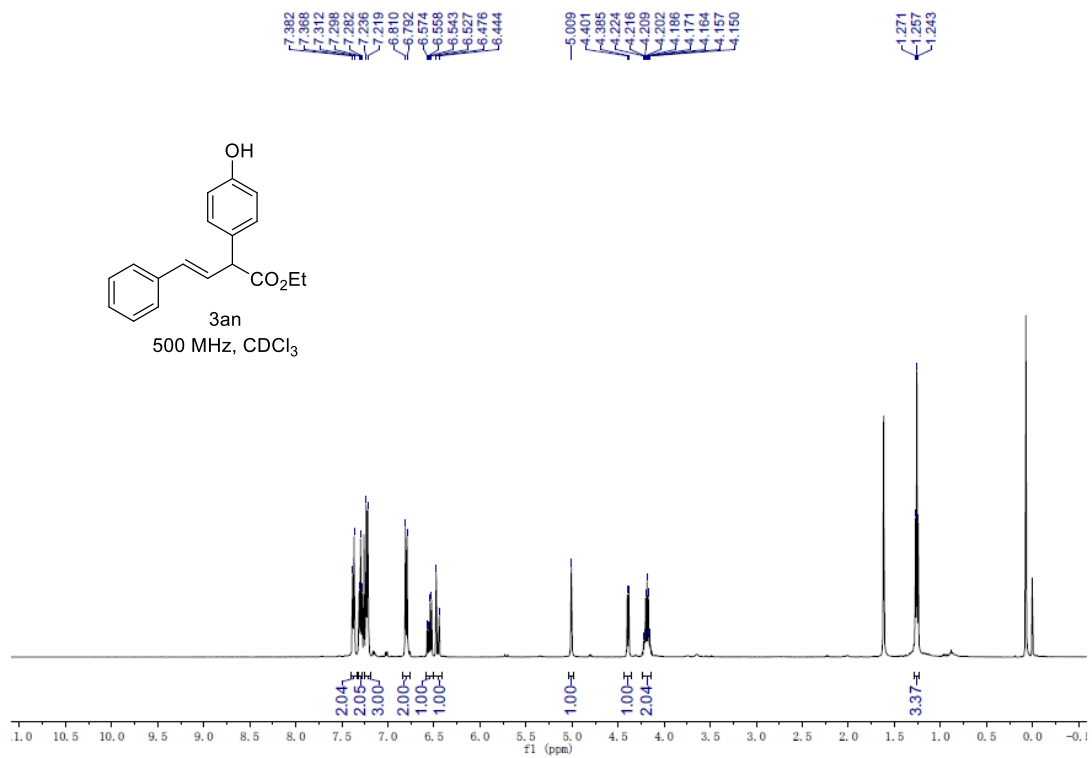
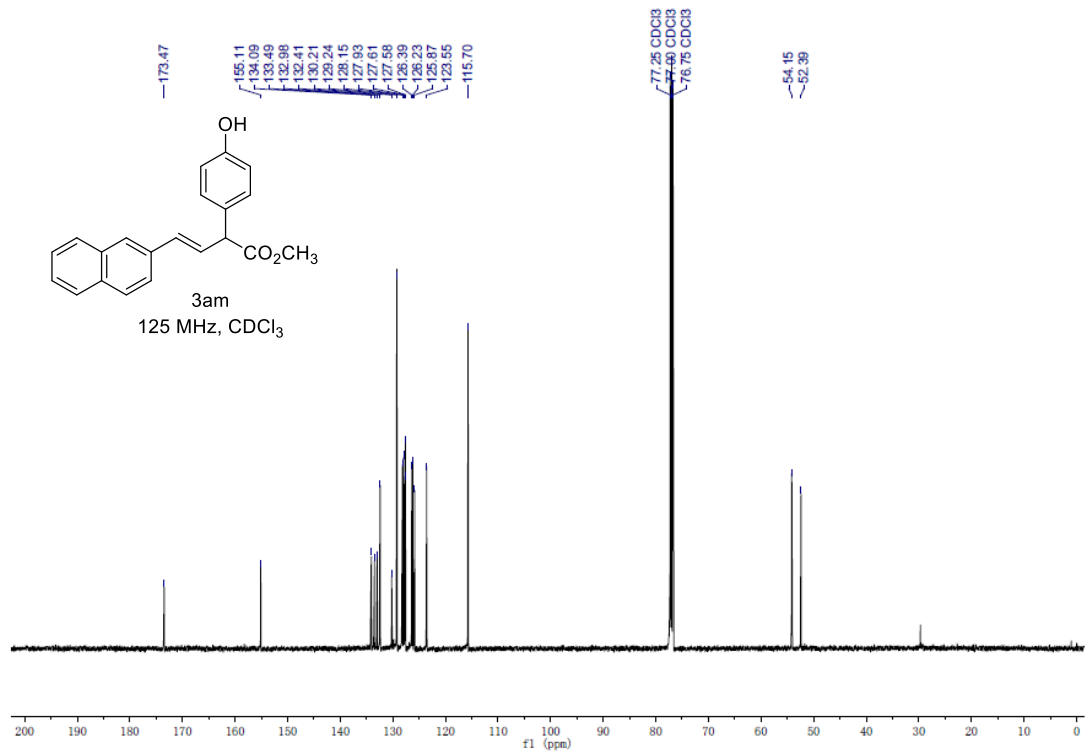


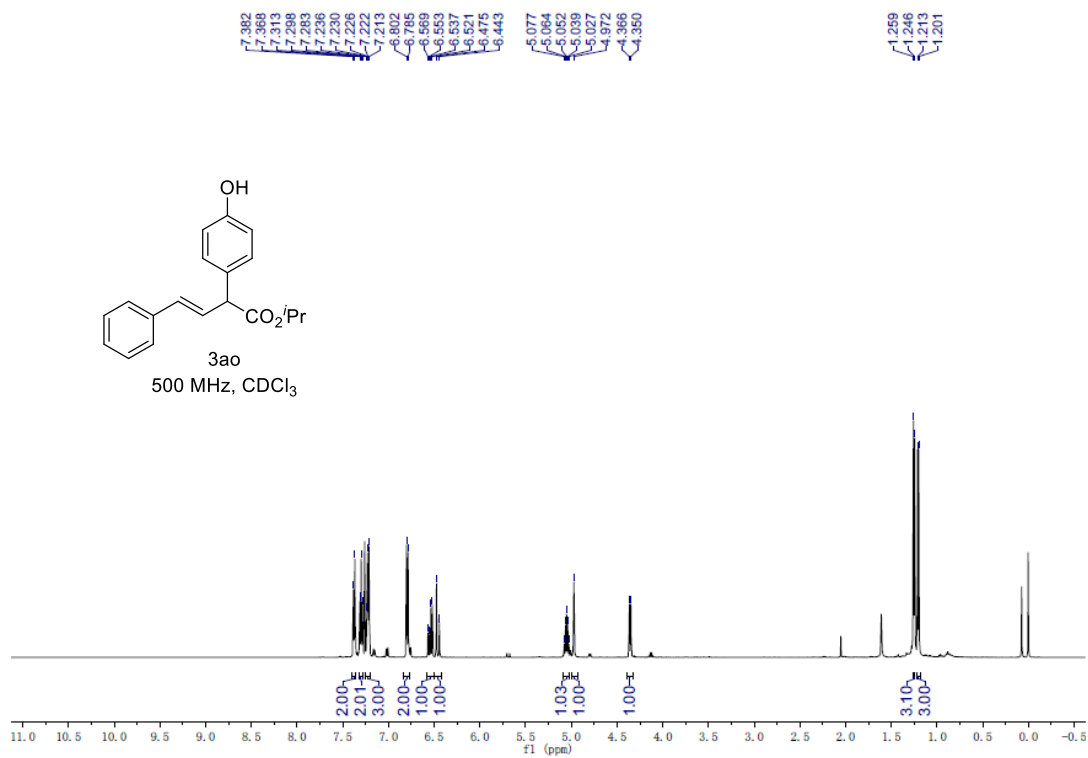
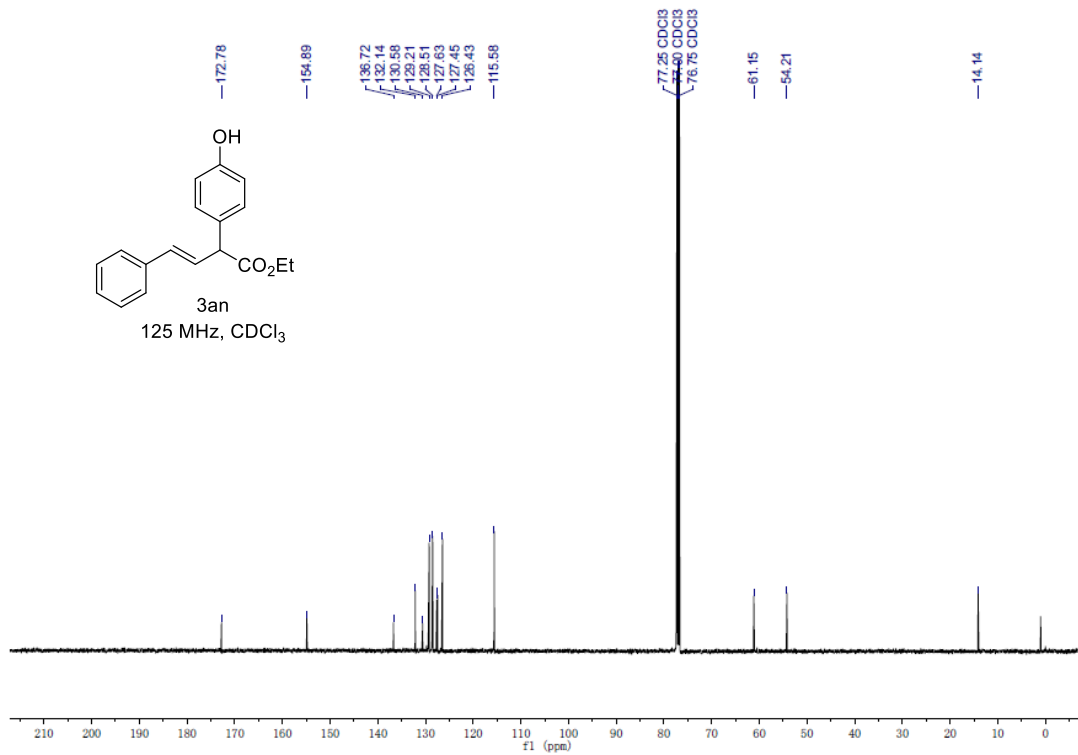


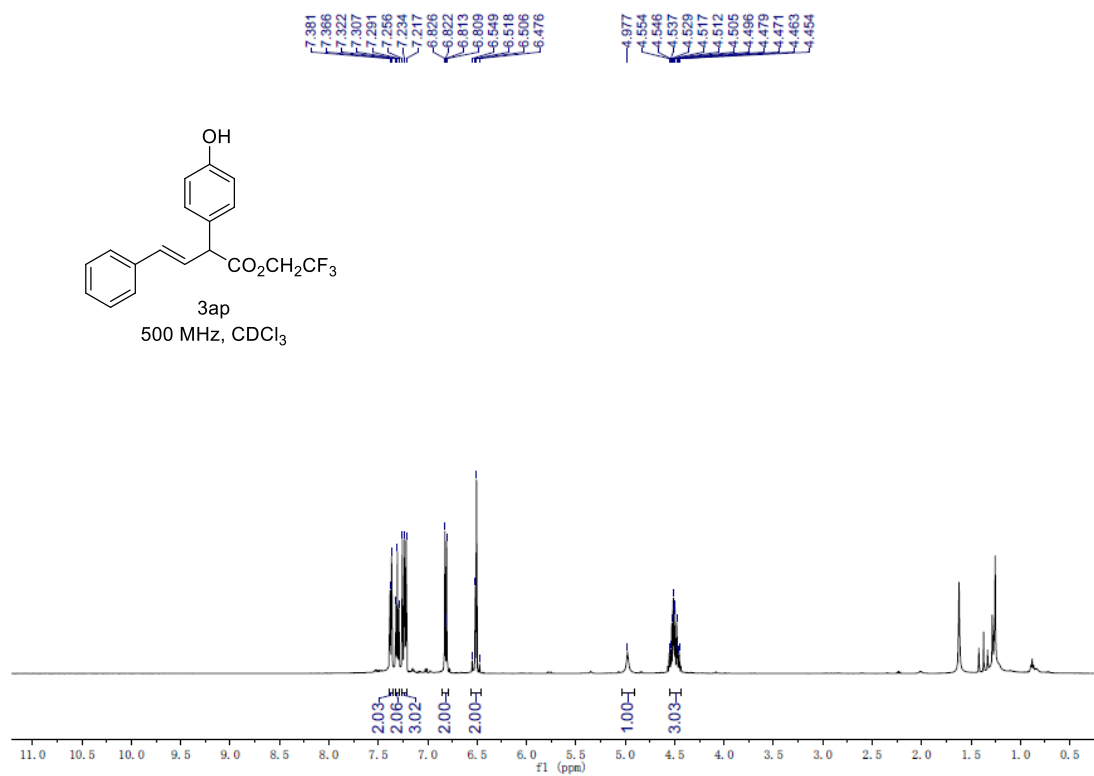
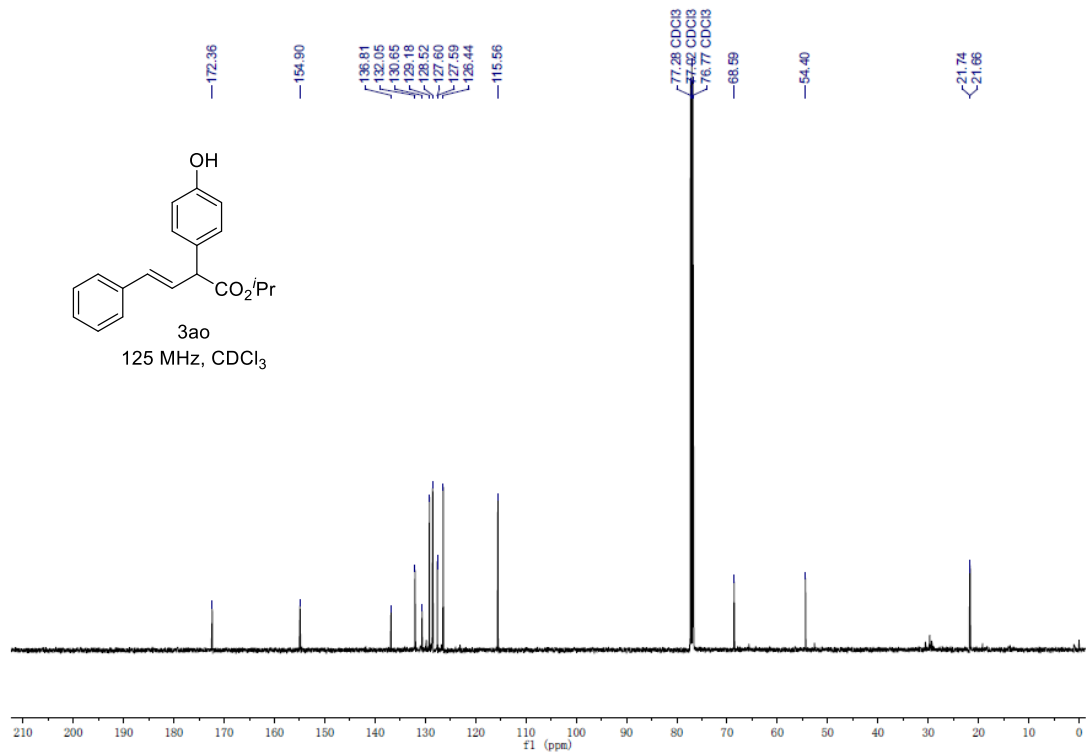


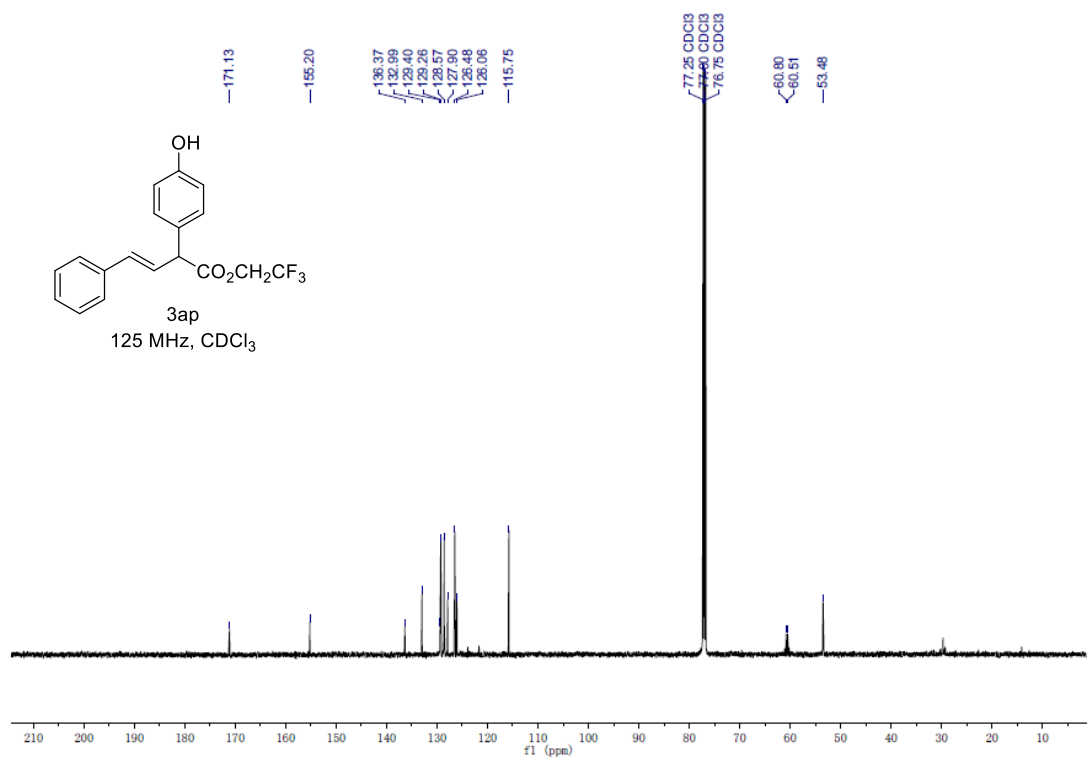
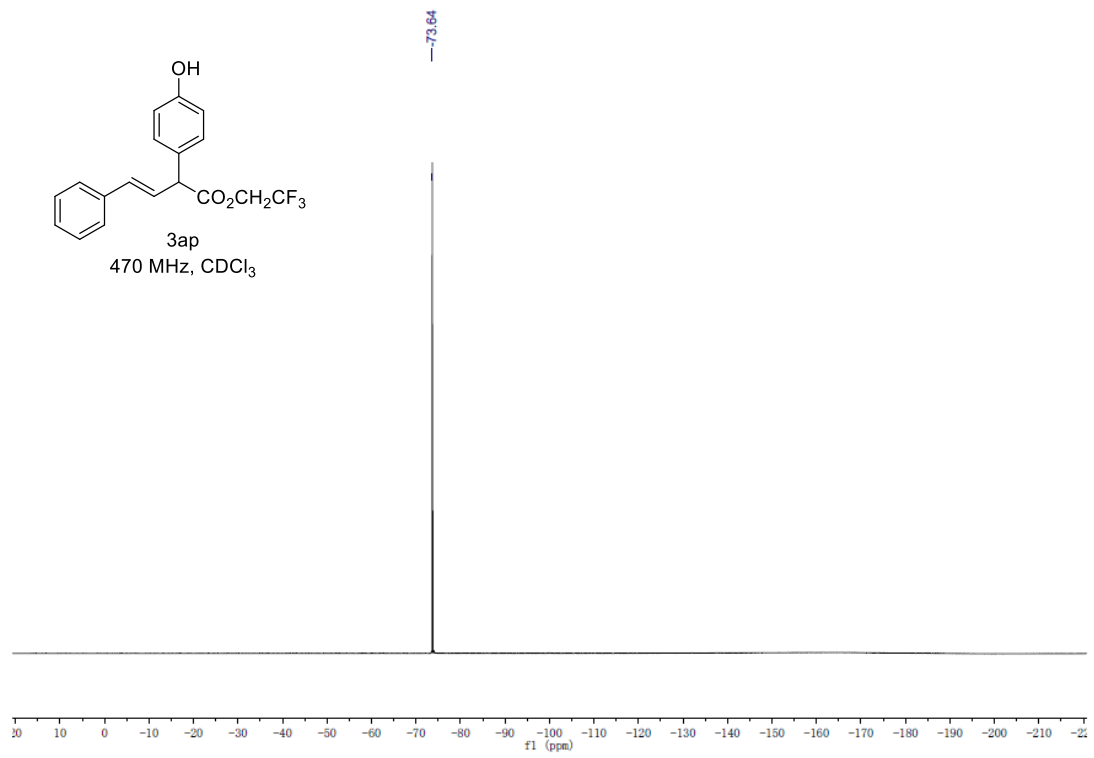




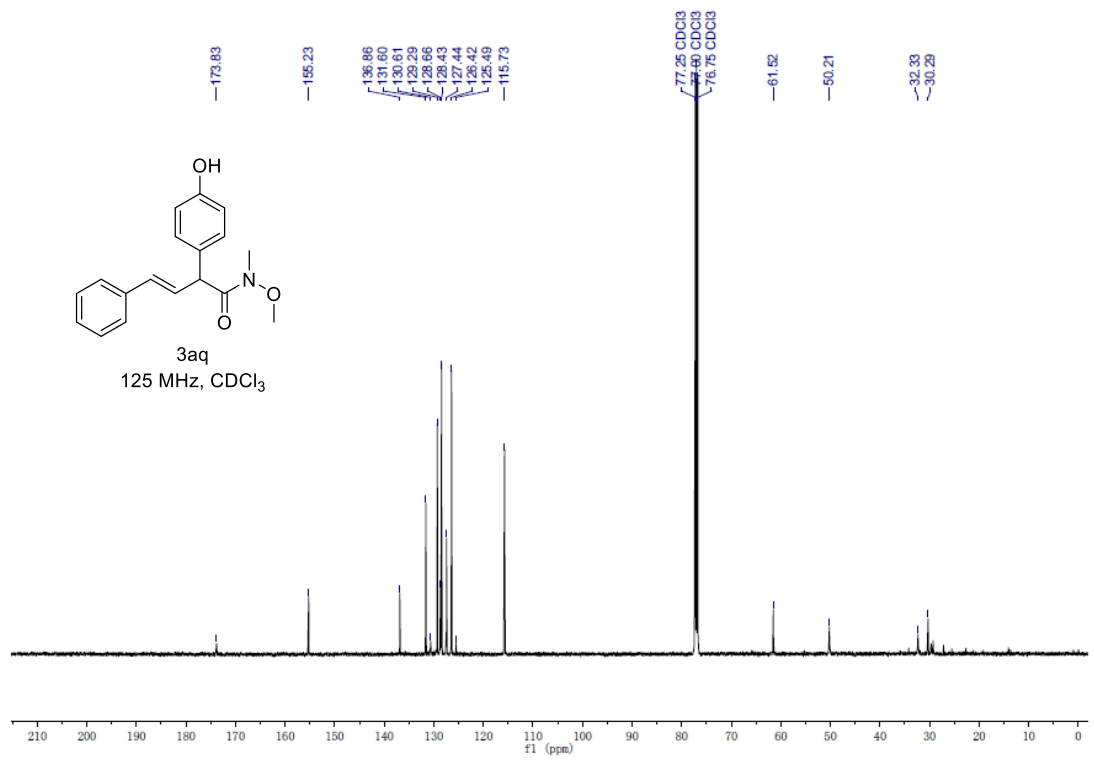
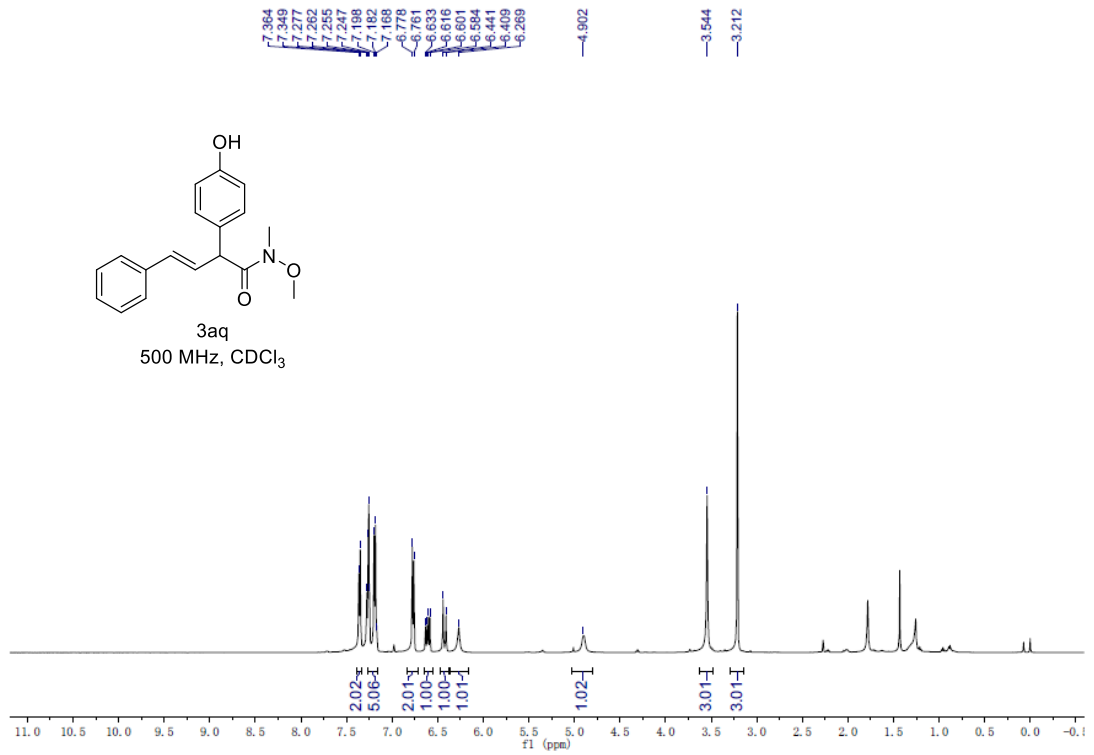




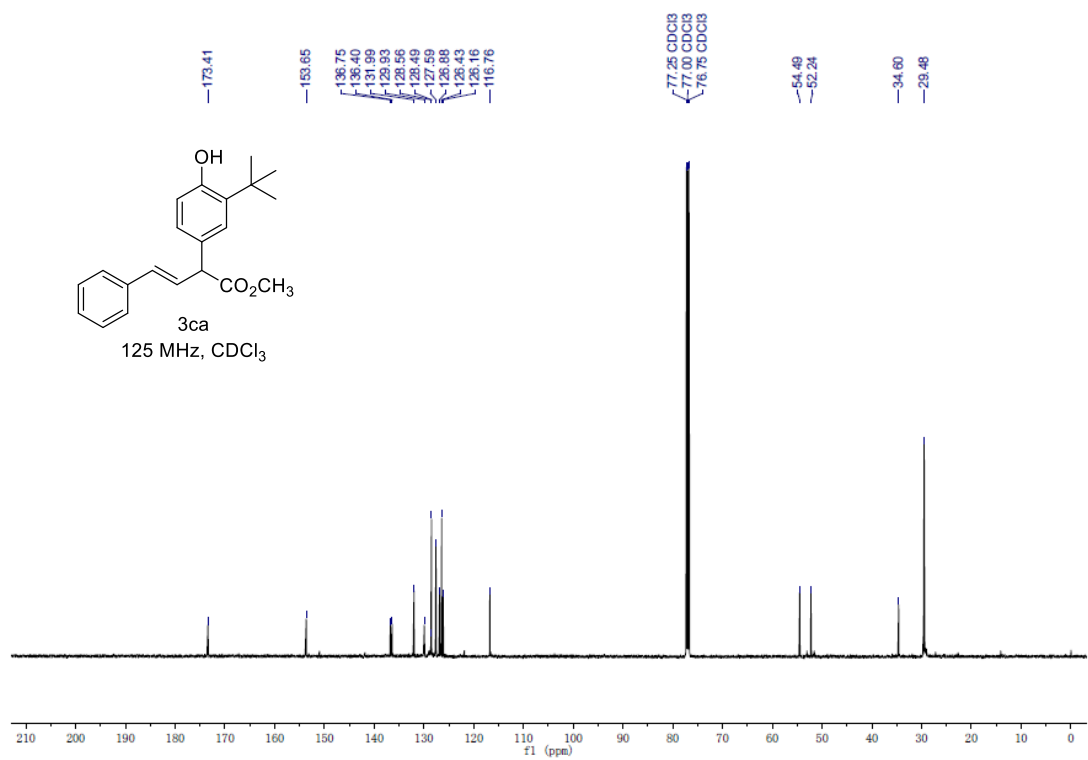
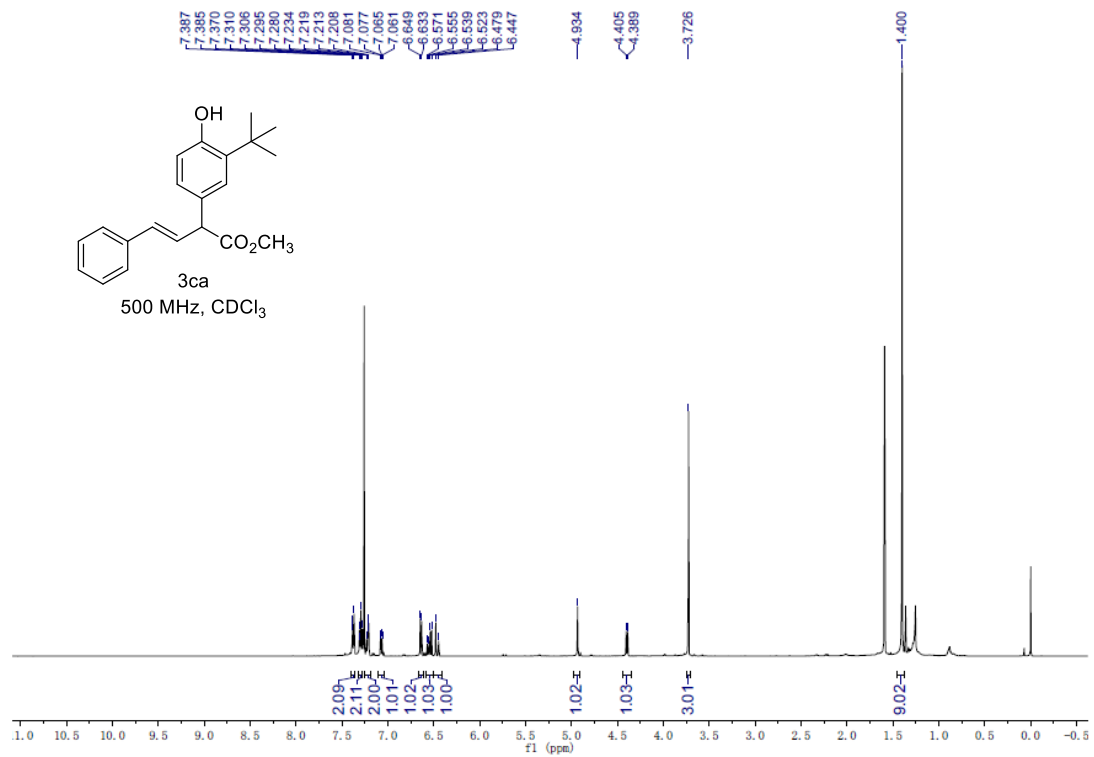


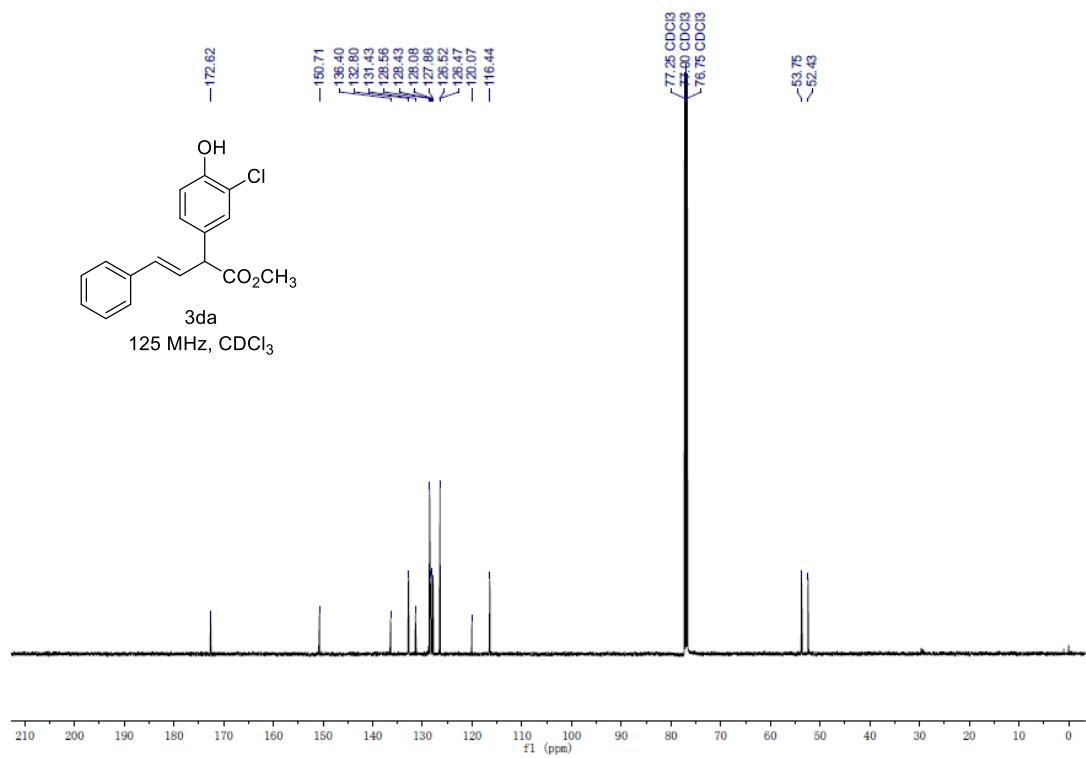
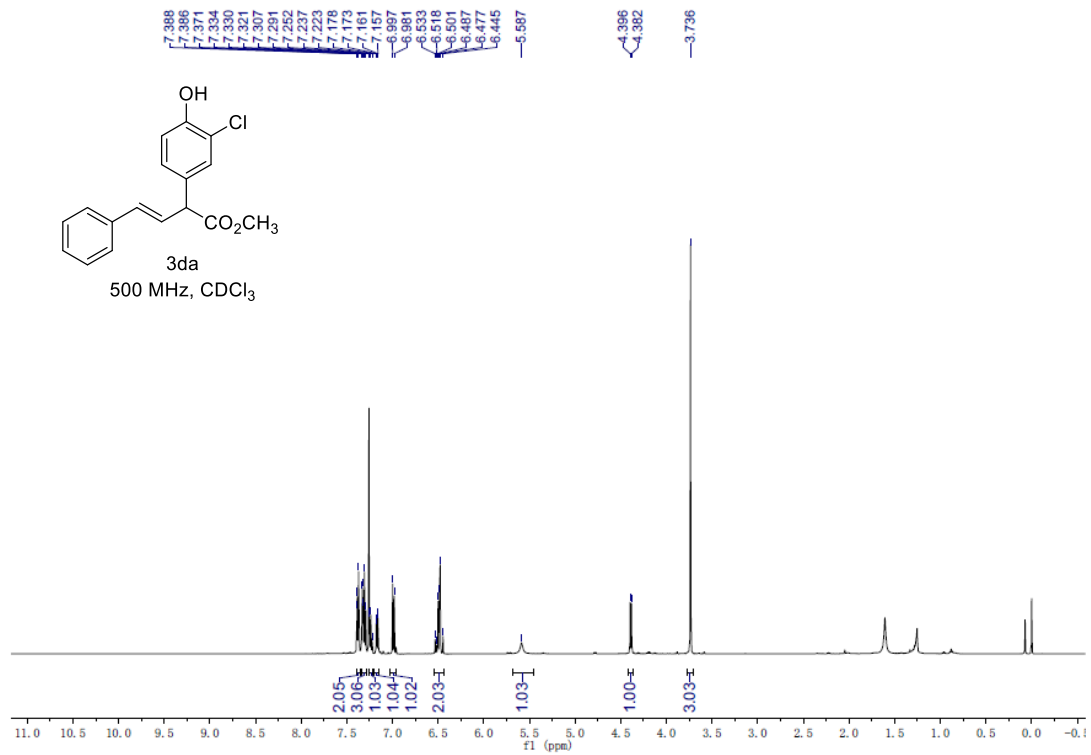


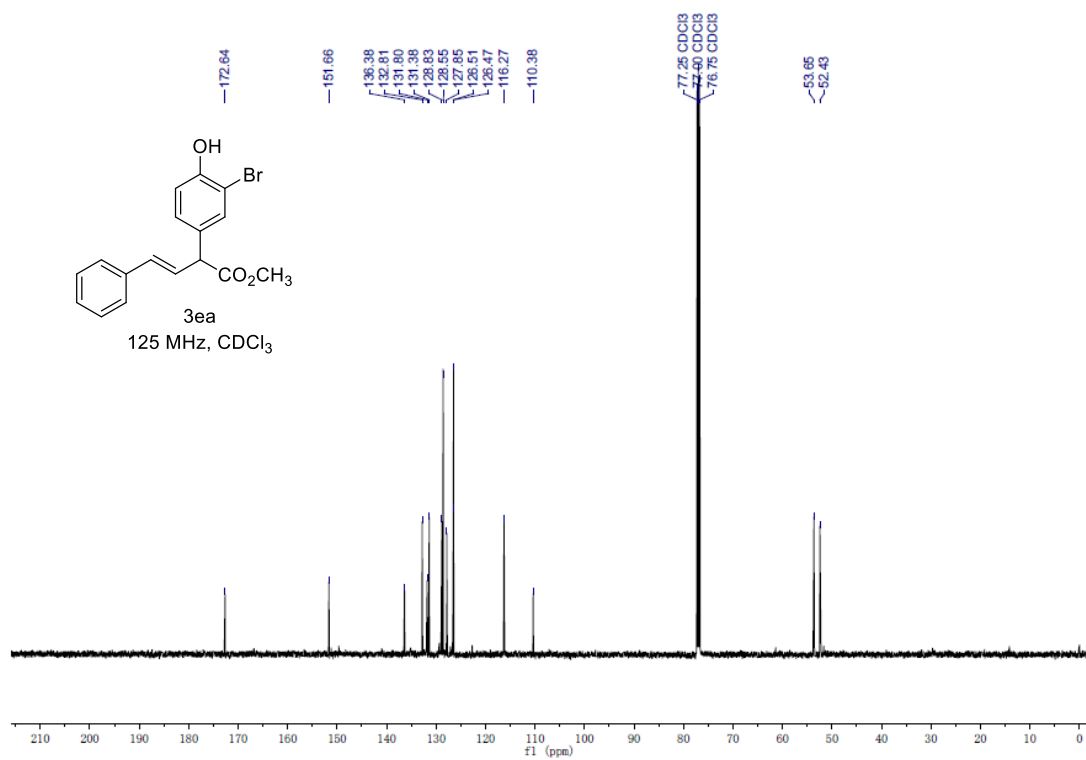
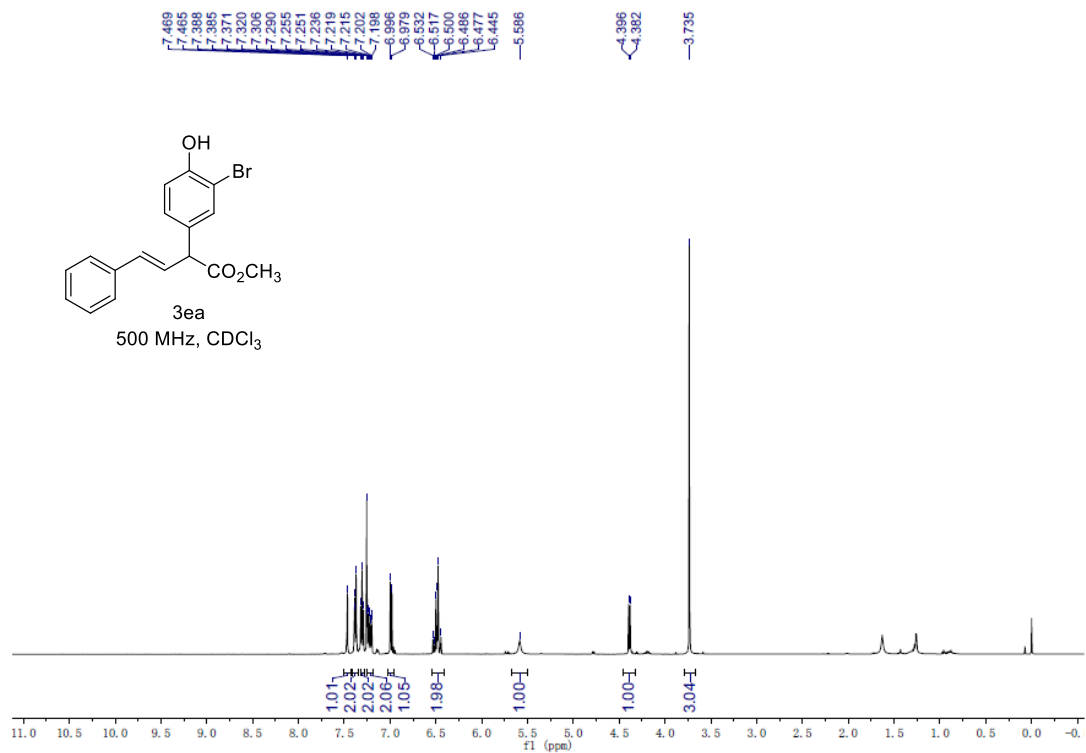


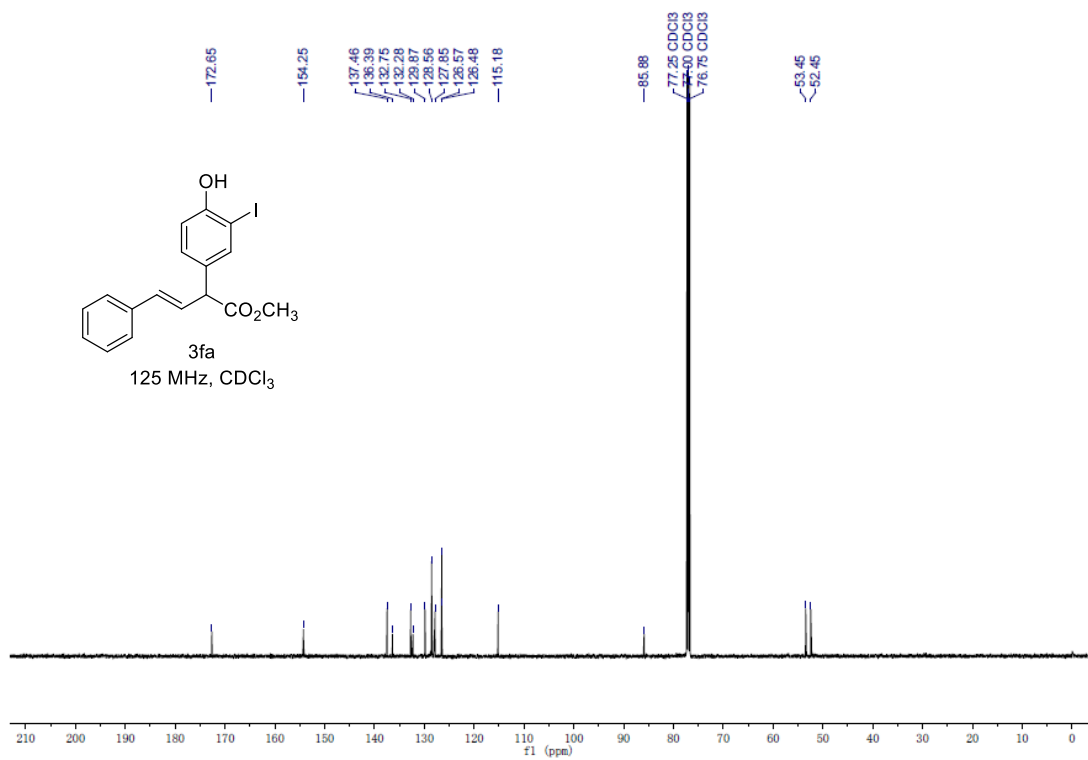
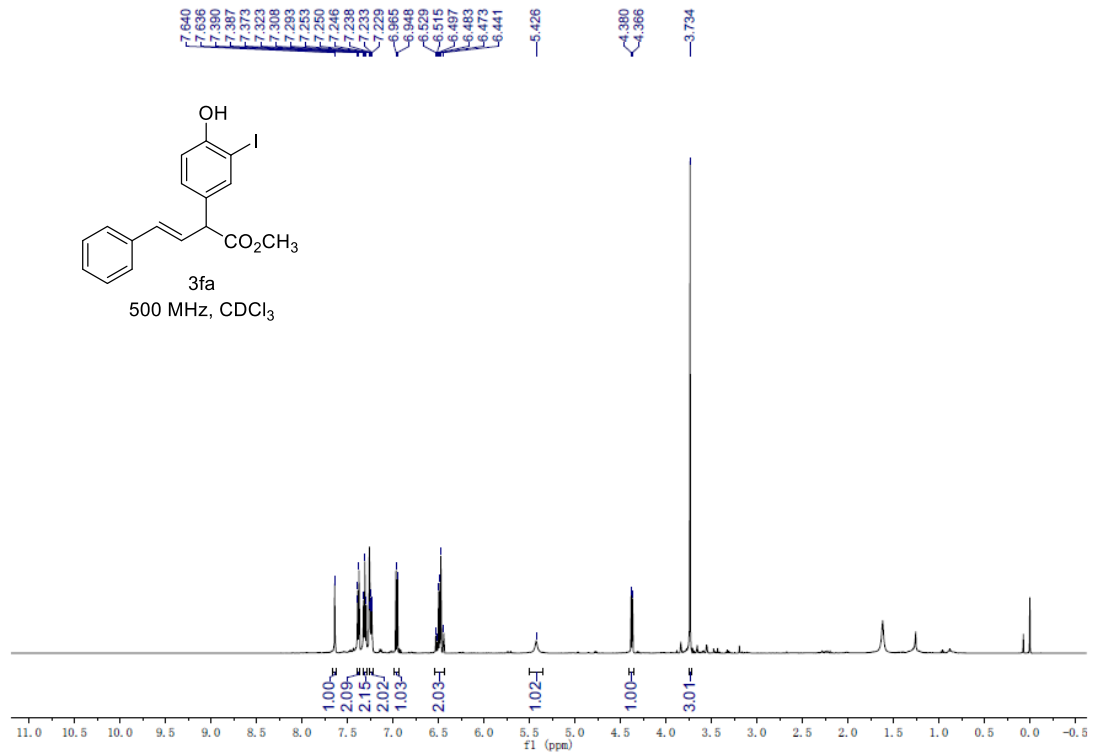


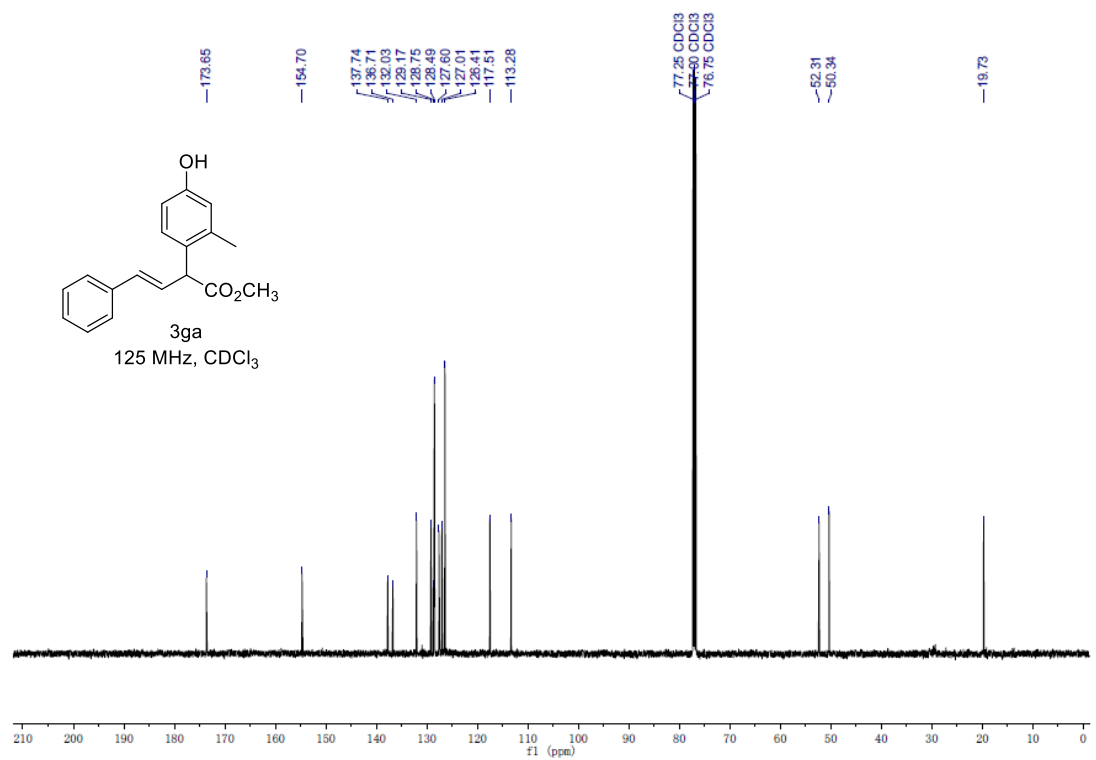
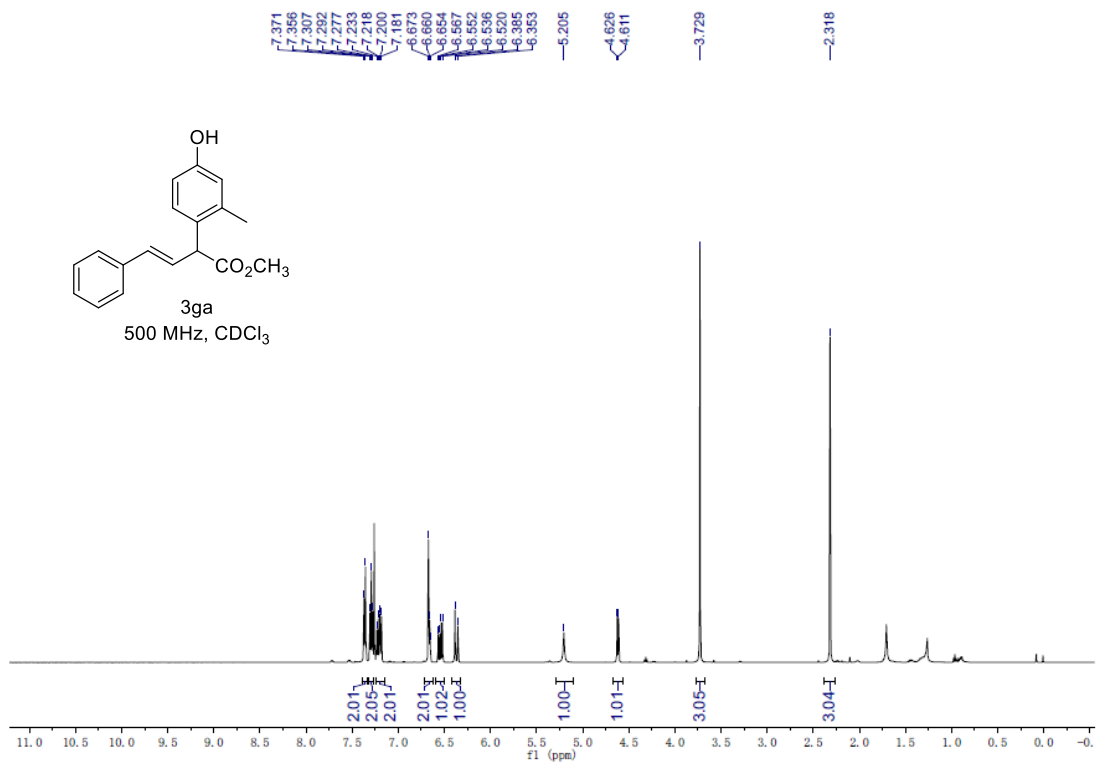


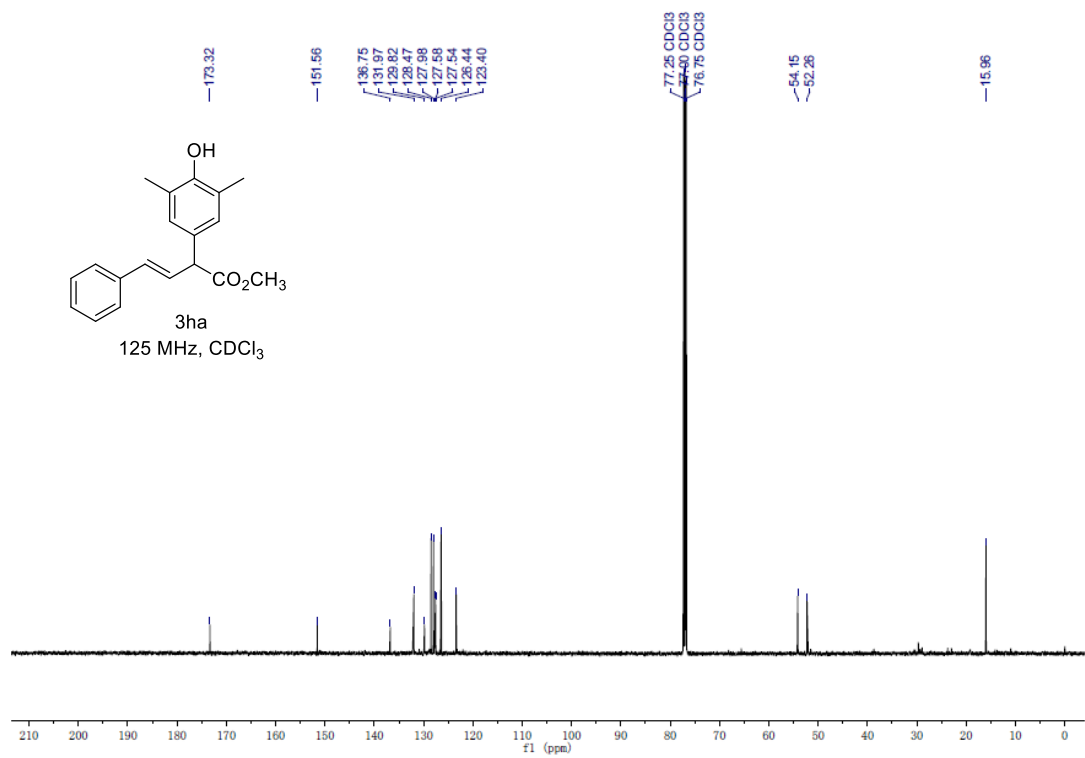
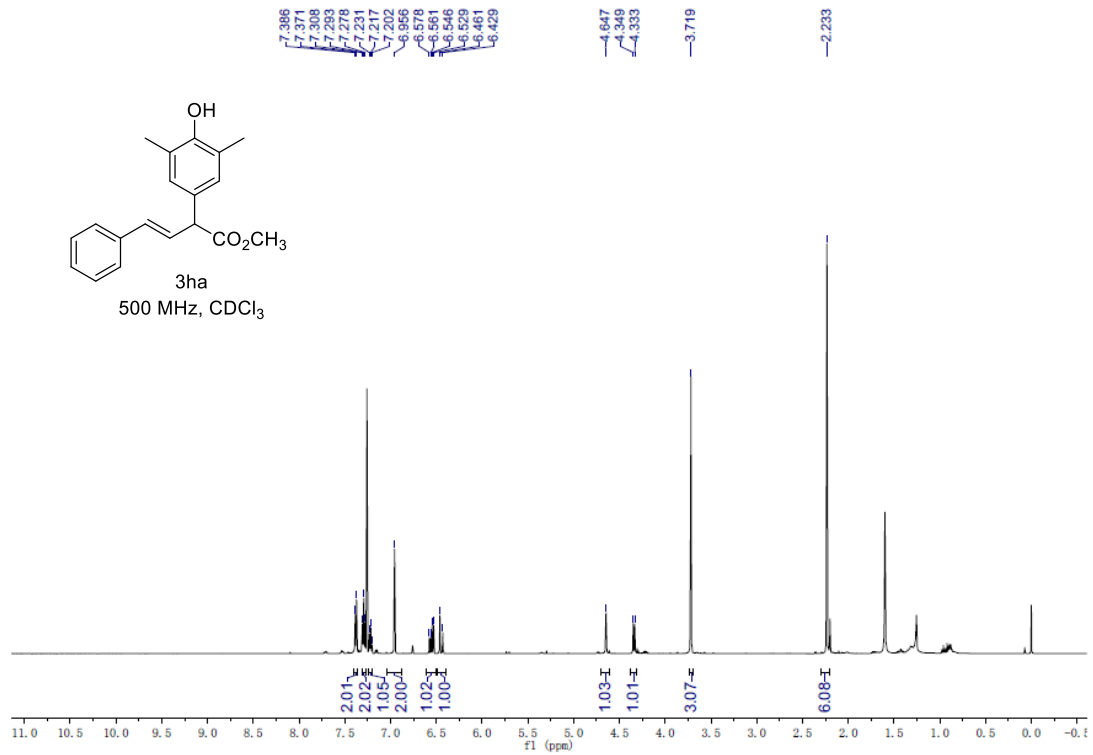




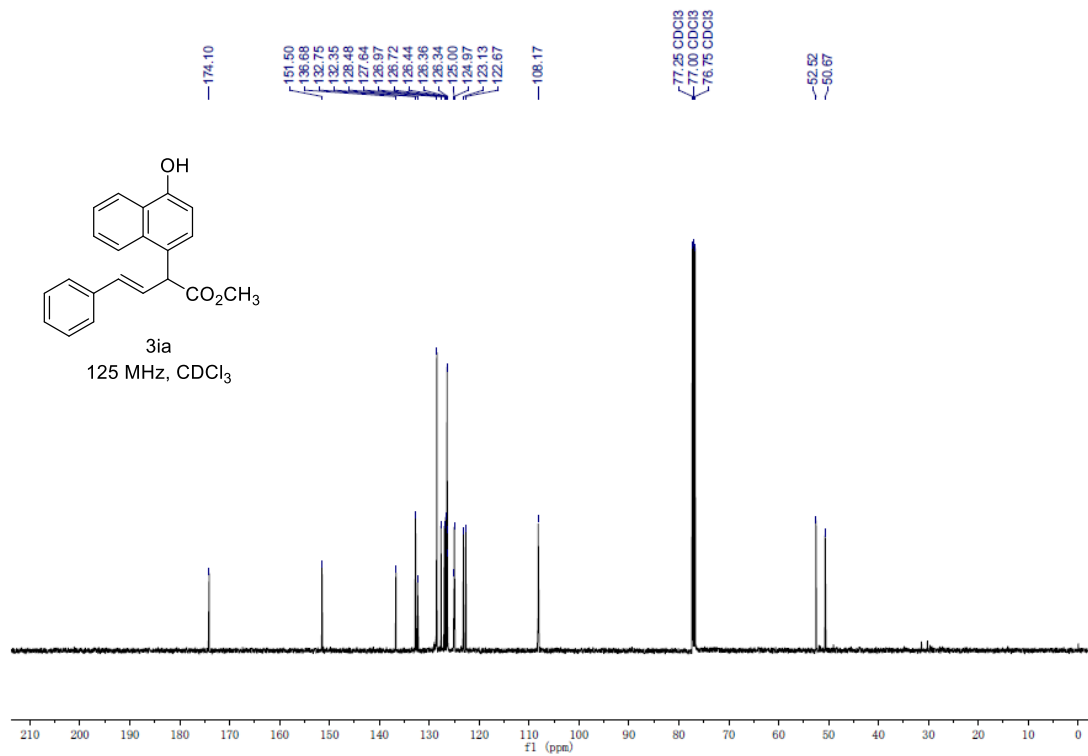
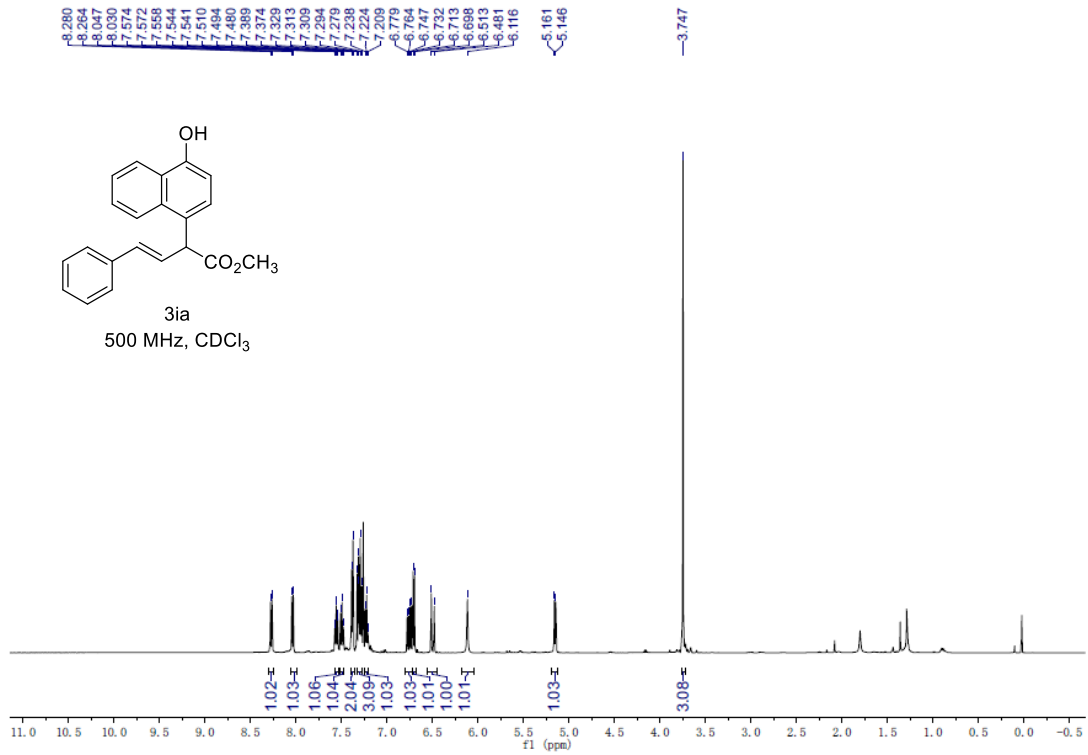


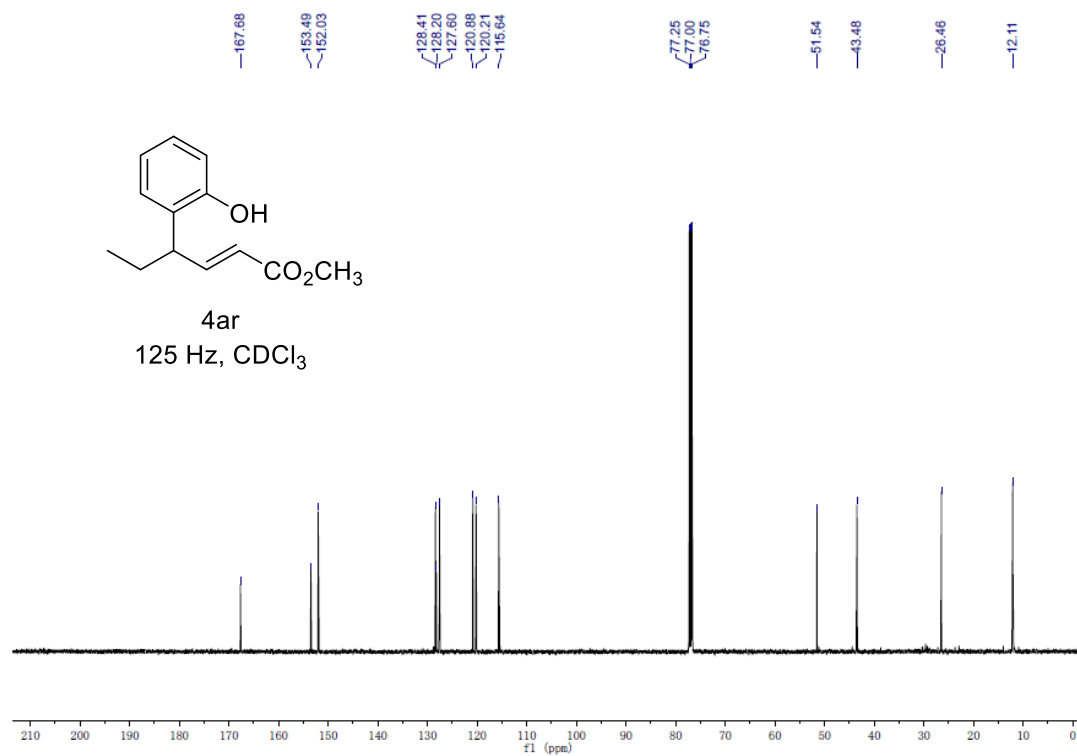
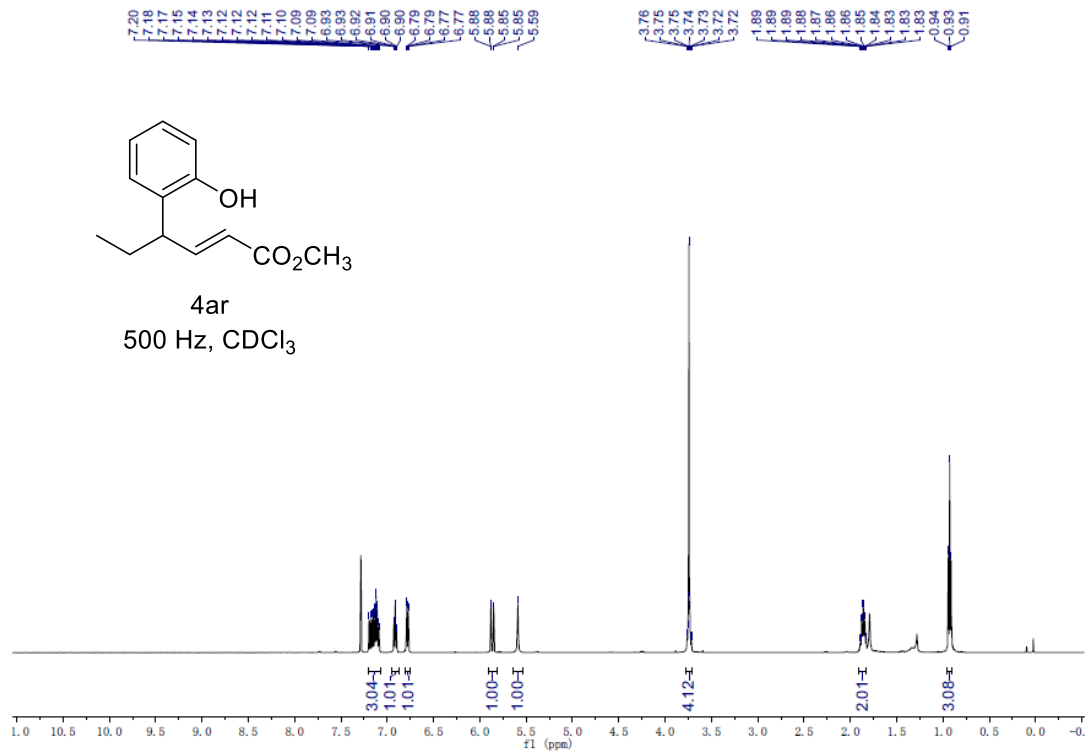


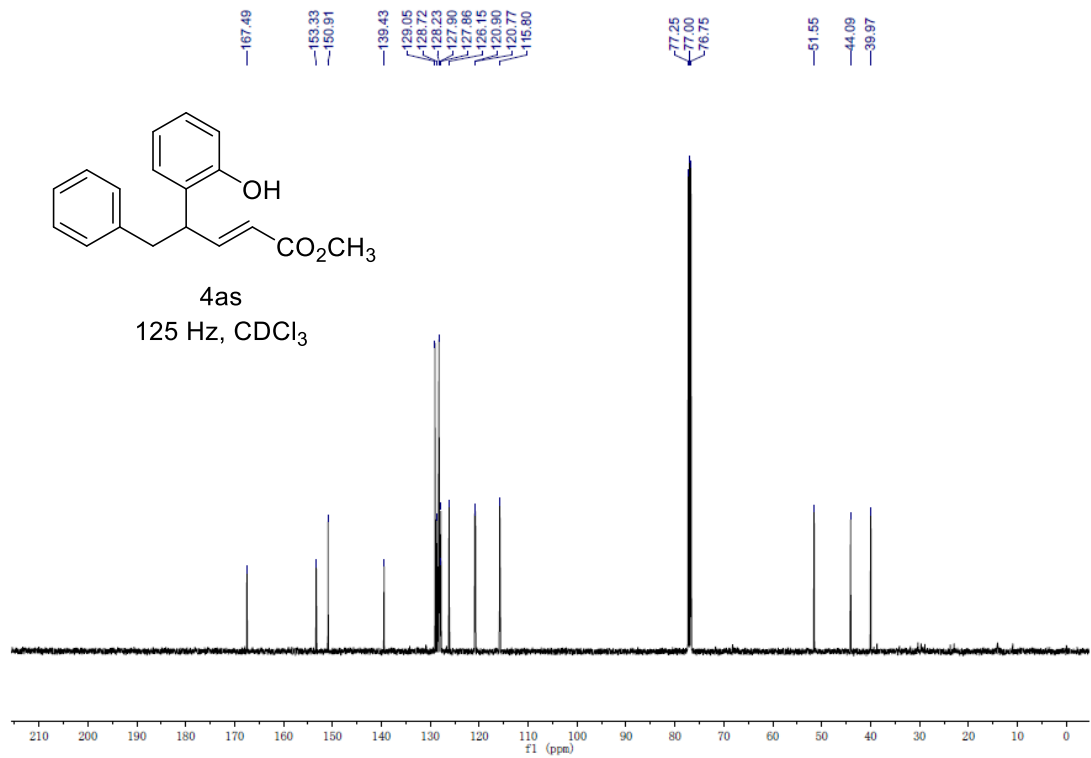
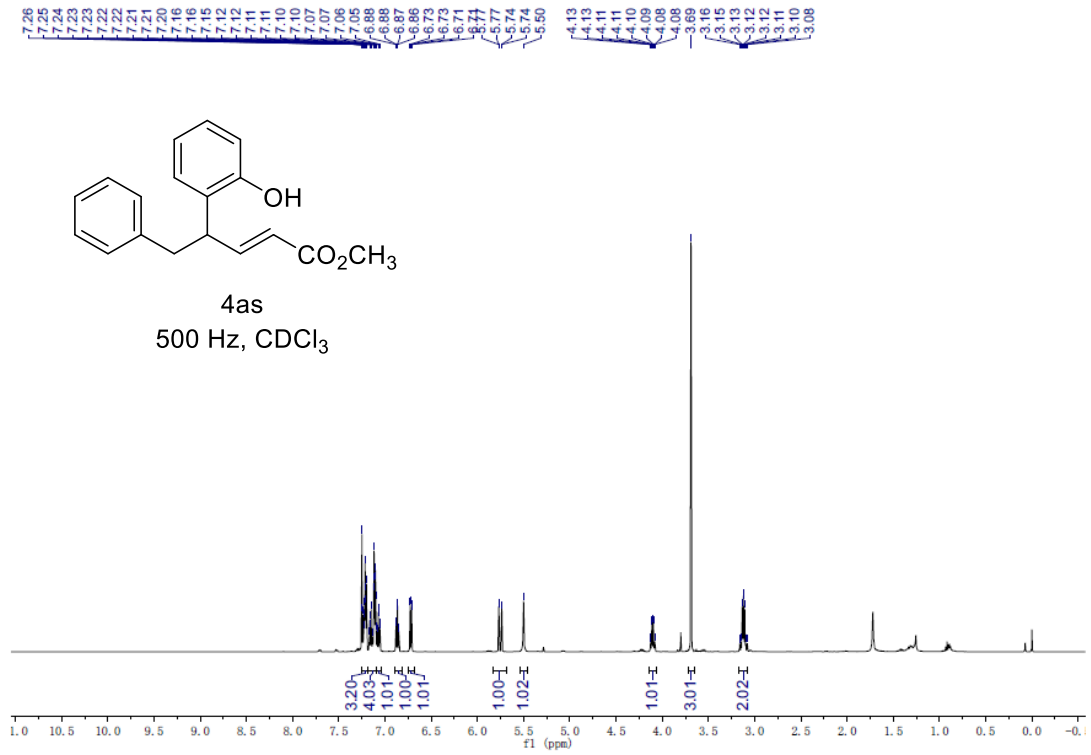




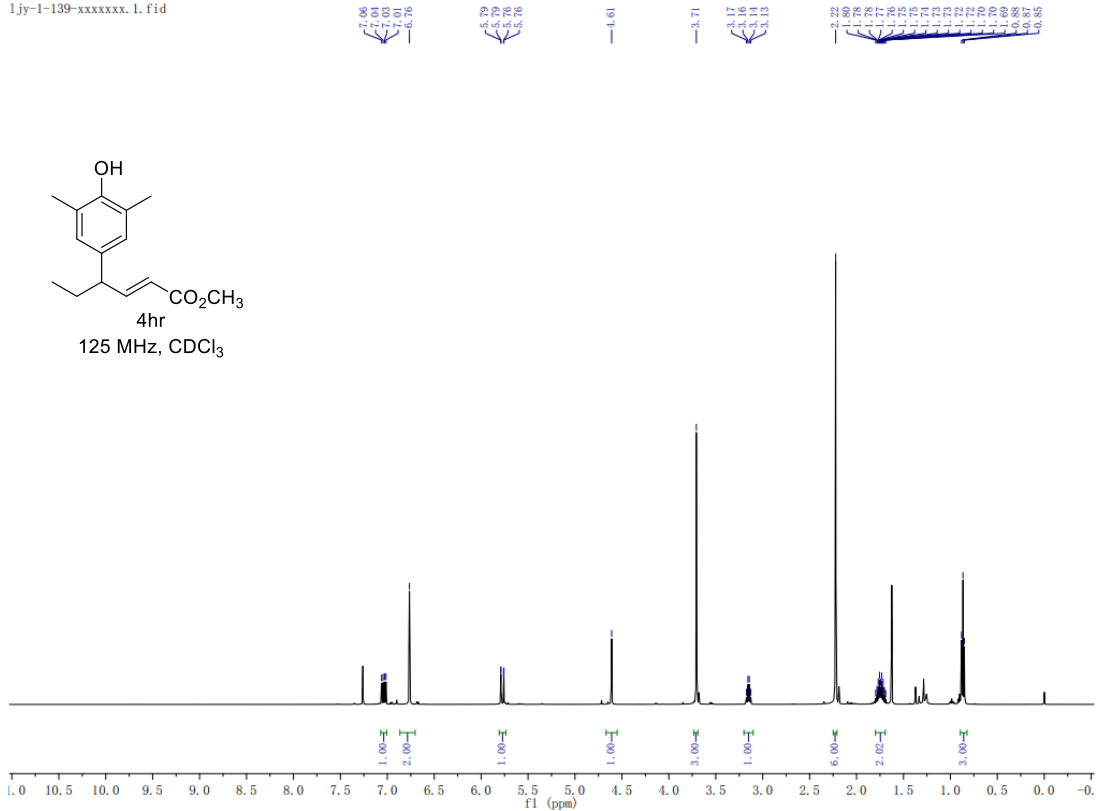








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