

Supporting Information

Relay Rh(II)/Pd(0) Dual Catalysis: Synthesis of α -Quaternary β -Keto-Esters via [1,2]- Sigmatropic Rearrangement/Allylic Alkylation Cascade of α -Diazo Tertiary Alcohols

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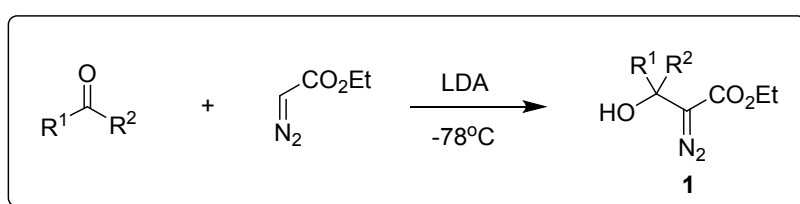
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1. General Remarks

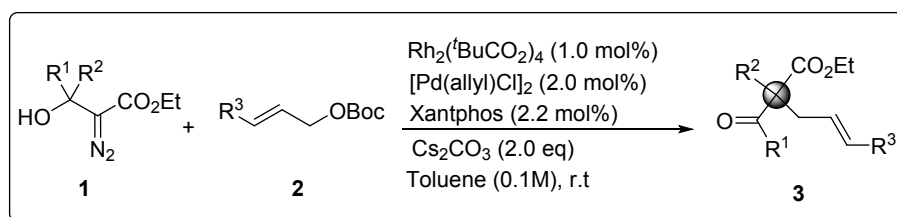
For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90 °C) are used. ^1H NMR spectra were recorded at 500 MHz in CDCl_3 and ^{13}C NMR spectra were recorded at 125 MHz in CDCl_3 using TMS as internal standard. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^1H NMR and ^{13}C NMR spectra were provided. Toluene was dried over sodium. Commercially available reagents and solvents were used without further purification. The $\text{Rh}_2(\text{tBuCO}_2)_4$,¹ and allyl tert-butyl carbonates **2**² were prepared according to the literature procedures.

2. General procedure for the synthesis of α -diazo tertiary alcohols **1**³.



To a stirring solution of LDA [prepared by the addition of $n\text{-BuLi}$ (3.2 mmol) in hexane to a -78°C solution of diisopropylamine (4.0 mmol) in THF (5.0 mL)] was added a cooled (-78°C) solution of α -diazo ethyl acetate (3.0 mmol) in dry THF (5.0 mL) at -78°C in 15 min. After 10 min from the end of the addition, a solution of ketones (2.0 mmol) in THF (10 mL) was then added in 10 min at -78°C . After 15 min a cooled (-78°C) solution of AcOH (0.3 mL) in THF (20 mL) was added in 5 min. The reaction mixture was taken into H_2O and extracted with EtOAc. The combined organic extracts were washed with saturated aqueous NaHCO_3 solution and brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography to afford the pure α -diazo tertiary alcohols **1** by using a mixture of petroleum ether/ethyl acetate as eluent (40:1, v:v).

3. General procedure for the synthesis of α -quaternary allylated β -ketoesters **3**.



In an oven-dried 10 mL Schlenk flask equipped with a stir bar, $[\text{PdCl}(\text{allyl})]_2$ (1.5 mg, 4.0×10^{-3} mmol, 2.0 mol %), Xantphos (2.6 mg, 4.4×10^{-3} mmol, 2.2 mol %), $\text{Rh}_2(\text{tBuCO}_2)_4$ (1.2 mg, 2.0×10^{-3} mmol, 1.0 mol %), and Cs_2CO_3 (130.3mg, 0.4 mmol, 2.0 equiv) were stirred in anhydrous toluene (0.5 mL) at room temperature for 5 min under an argon atmosphere. Then, a solution of α -diazo tertiary alcohols **1** (0.24 mmol, 1.2 equiv) and allyl tert-butyl carbonates **2** (0.20 mmol, 1.0 equiv) in anhydrous toluene (1.5 mL) was introduced by syringe. The mixture was stirred at room temperature.

When the reaction was considered complete (determined by TLC analysis), the product **3** was directly isolated by chromatography on silica-gel.

4. Optimization of the asymmetric relay Rh(II)/Pd(0) dual-catalyzed reaction conditions

In an oven-dried 10 mL Schlenk flask equipped with a stir bar, [PdCl(allyl)]₂ (0.8 mg, 2.0x10⁻³ mmol, 2.0 mol %), chiral Ligand (2.2x10⁻³ mmol, 2.2 mol %), Rh₂L₄ (1.0x10⁻³ mmol, 1.0 mol %), and Cs₂CO₃ (65.2mg, 0.2 mmol, 2.0 equiv) were stirred in anhydrous toluene (0.3 mL) at room temperature for 20 min under an argon atmosphere. Then, a solution of α-diazo tertiary alcohols **1a** (0.12 mmol, 1.2 equiv) and allyl tert-butyl carbonate **2a** (0.10 mmol, 1.0 equiv) in anhydrous toluene (0.7 mL) was introduced by syringe. The mixture was stirred at room temperature. As determined by TLC analysis, the product **3aa** was directly isolated by chromatography on silica-gel (eluent: petroleum ether/ethyl acetate = 60:1). The enantiomeric excess was determined by chiral HPLC analysis. (Chiral ND column, flow 0.5 ml/min, n-hexane/i-PrOH = 9/1, 254 nm) t = 7.9 min (major), 8.8 min (minor).

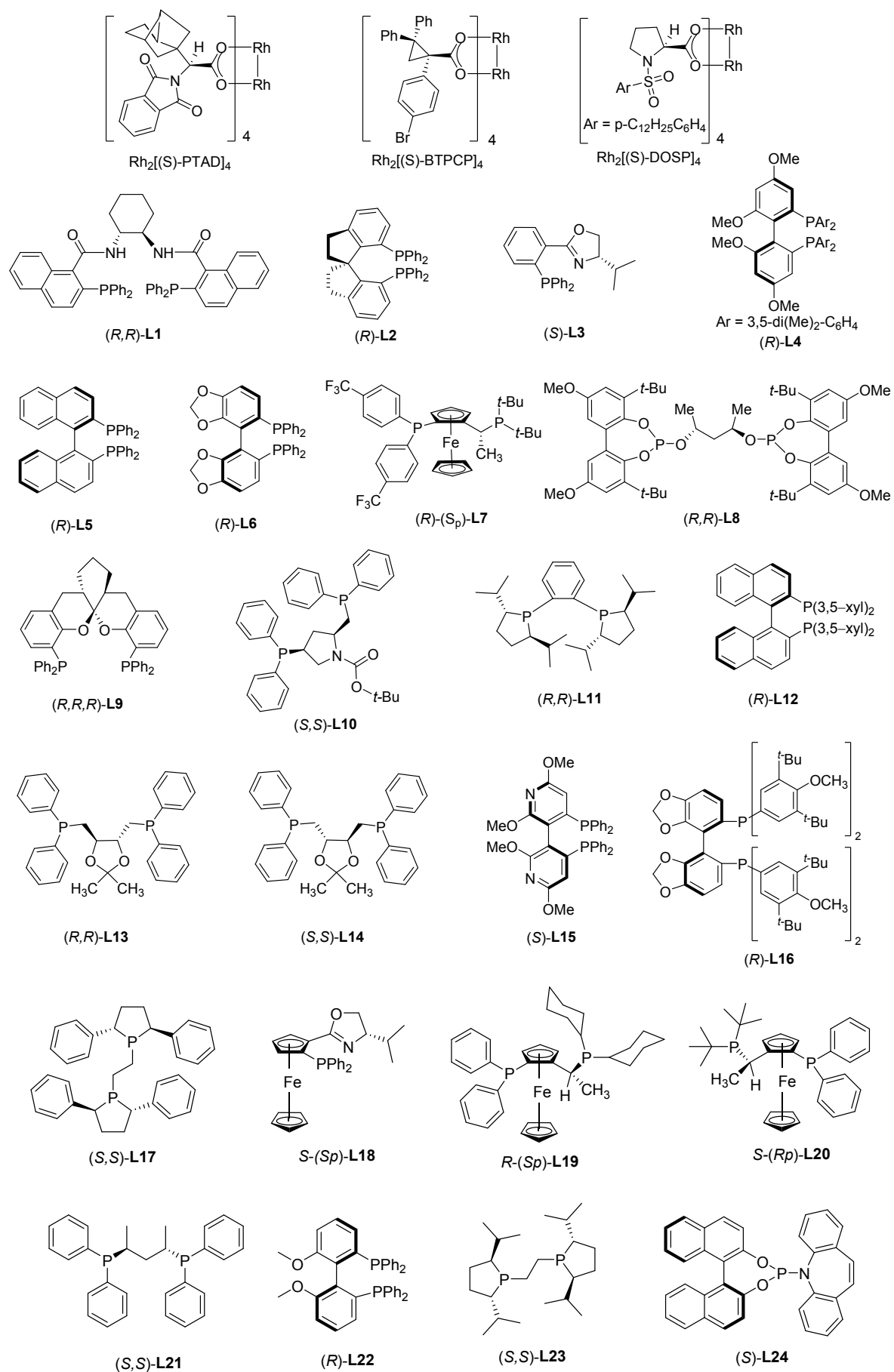
Table S-1. Condition screening of asymmetric relay Rh(II)/Pd(0) dual catalysis ^a

Reaction scheme: **1a** (1.2 equiv) + **2a** → **3aa**. Conditions: Rh₂L₄ (1 mol%), [Pd(allyl)Cl]₂ (2 mol%), Ligand (2.2 mol%), Cs₂CO₃ (2 eq), Toluene (0.1M), T.

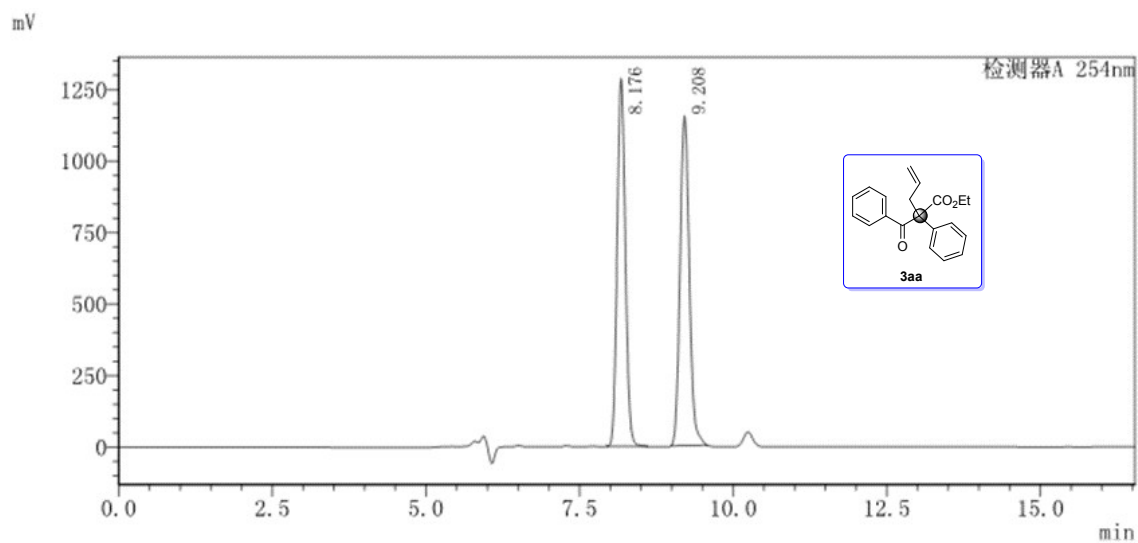
Entry	Rh ₂ L ₄	Ligand	T(°C)	t(h)	Yield(%) ^b	ee% ^c
1	Rh ₂ [(S)-PTAD] ₄	Xantphos	r.t	1	89	0
2	Rh ₂ [(S)-DOSP] ₄	Xantphos	r.t	2	84	0
3	Rh ₂ [(S)-BTPCP] ₄	Xantphos	r.t	2	83	0
4	Rh ₂ (^t BuCO ₂) ₄	L1	r.t	1	72	0
5	Rh ₂ (^t BuCO ₂) ₄	L2	r.t	1	80	0
6	Rh ₂ (^t BuCO ₂) ₄	L3	r.t	1	86	0
7	Rh ₂ (^t BuCO ₂) ₄	L4	r.t	1	79	6
8	Rh ₂ (^t BuCO ₂) ₄	L5	r.t	8	80	0
9	Rh ₂ (^t BuCO ₂) ₄	L6	r.t	2	99	0
10	Rh ₂ (^t BuCO ₂) ₄	L7	r.t	3	35	16
11	Rh ₂ (^t BuCO ₂) ₄	L8	r.t	2	57	39
12	Rh ₂ (^t BuCO ₂) ₄	L9	r.t	1	66	7
13	Rh ₂ (^t BuCO ₂) ₄	L10	r.t	1	79	0
14	Rh ₂ (^t BuCO ₂) ₄	L11	r.t	1	79	0

15	Rh ₂ (^t BuCO ₂) ₄	L12	r.t	1	79	6
16	Rh ₂ (^t BuCO ₂) ₄	L13	r.t	1	81	0
17	Rh ₂ (^t BuCO ₂) ₄	L14	r.t	1	82	0
18	Rh ₂ (^t BuCO ₂) ₄	L15	r.t	2	87	0
19	Rh ₂ (^t BuCO ₂) ₄	L16	r.t	4	85	0
20	Rh ₂ (^t BuCO ₂) ₄	L17	r.t	1	95	19
21	Rh ₂ (^t BuCO ₂) ₄	L18	r.t	1	93	23
22	Rh ₂ (^t BuCO ₂) ₄	L19	r.t	1	93	0
23	Rh ₂ (^t BuCO ₂) ₄	L20	r.t	1	94	29
24	Rh ₂ (^t BuCO ₂) ₄	L21	r.t	1	88	6
25	Rh ₂ (^t BuCO ₂) ₄	L22	r.t	1	90	0
26	Rh ₂ (^t BuCO ₂) ₄	L23	r.t	4	74	0
27	Rh ₂ (^t BuCO ₂) ₄	L24	r.t	4	87	7
28	Rh ₂ (^t BuCO ₂) ₄	L8	0	4	63	52
29	Rh₂(^tBuCO₂)₄	L8	-10	8	59	53
30	Rh ₂ (^t BuCO ₂) ₄	L8	-20	8	46	53

^a Reaction conditions: **1a** (0.12 mmol, 1.2 equiv), **2a** (0.1 mmol, 1.0 equiv), Rh₂L₄ (1.0 mol %), [Pd(allyl)Cl]₂ (2.0 mol %), and **L** (2.2 mol %) in toluene (1.0 ml); ^b The yields in parentheses are isolated yield; ^c Determined by chiral HPLC analysis.



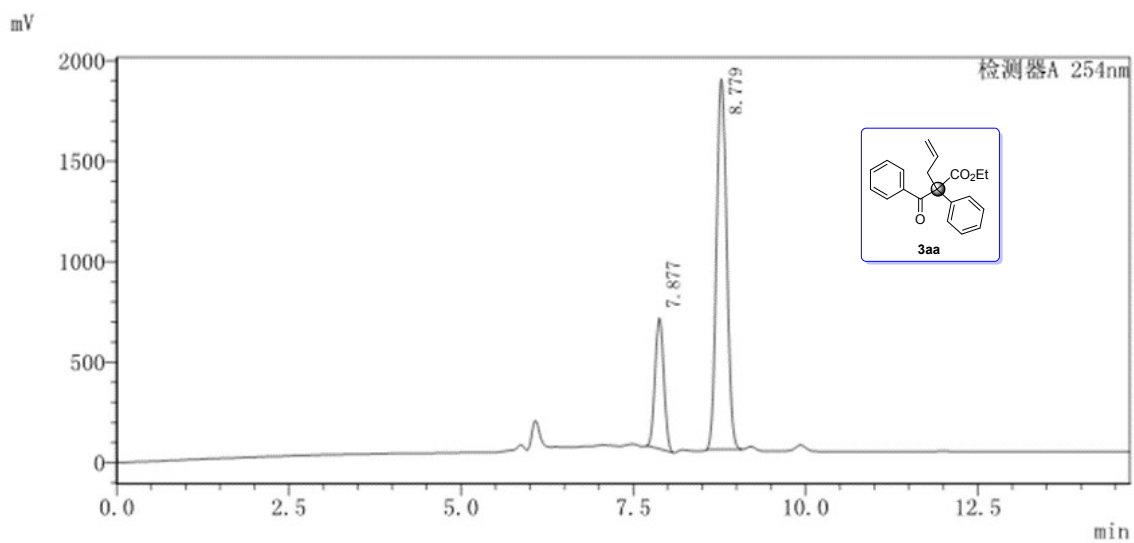
Chiral HPLC chromatograms:



<峰表>

检测器A 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.176	11875113	1286003	49.538		M	
2	9.208	12096403	1151986	50.462		M	
总计		23971515	2437989				



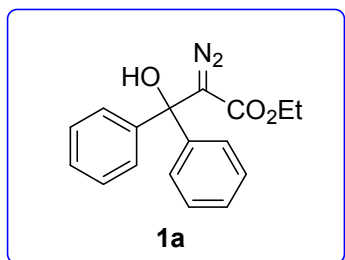
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检测器A 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.877	5757214	652527	23.336		M	
2	8.779	18913488	1843550	76.664		M	
总计		24670702	2496077				

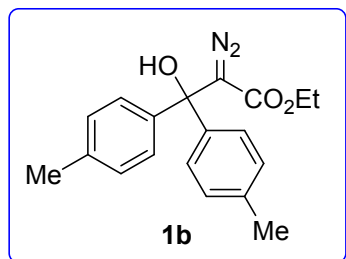
5. Characterization data for all compounds

Ethyl 2-diazo-3-hydroxy-3,3-diphenylpropanoate 1a³. ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.33 (m, 4H),



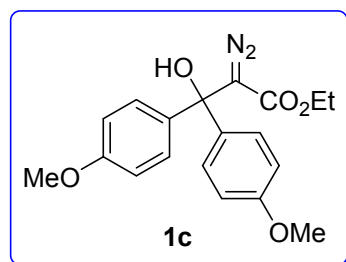
7.28-7.24 (m, 4H), 7.23-7.19 (m, 2H), 4.91 (brs, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.3 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 167.3, 143.5, 128.4, 128.2, 126.9, 79.0, 61.3, 14.4 ppm.

Ethyl 2-diazo-3-hydroxy-3,3-di-p-tolylpropanoate 1b⁴. ¹H NMR (500 MHz, CDCl₃) δ 7.22-7.20 (m, 4H),



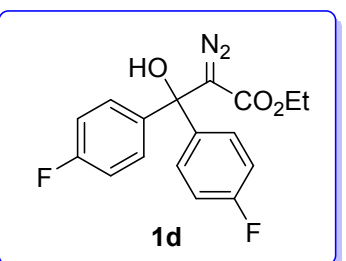
7.06-7.04 (m, 4H), 4.81(brs, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 167.4, 140.8, 137.8, 129.0, 126.7, 78.76, 61.2, 21.1, 14.4 ppm.

Ethyl 2-diazo-3-hydroxy-3,3-bis(4-methoxyphenyl)propanoate 1c⁴. ¹H NMR (500 MHz, CDCl₃) δ 7.25-



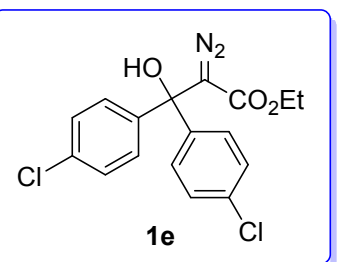
7.22 (m, 4H), 6.80-6.76 (m, 4H), 4.82 (brs, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.17 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 167.4, 159.3, 135.9, 128.2, 113.5, 78.4, 61.2, 55.3, 14.4 ppm.

Ethyl 2-diazo-3,3-bis(4-fluorophenyl)-3-hydroxypropanoate 1d⁴. ¹H NMR (500 MHz, CDCl₃) δ 7.39-



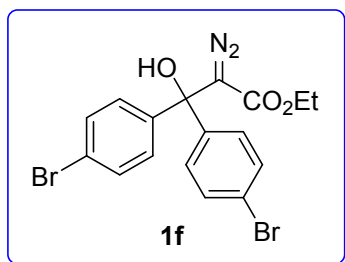
7.36 (m, 4H), 7.04-7.01 (m, 4H), 5.01 (brs, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 167.1, 162.5 (d, *J*_{CF} = 246.2 Hz), 139.2 (d, *J*_{CF} = 3.1 Hz), 128.7 (d, *J*_{CF} = 8.2 Hz), 115.3 (d, *J*_{CF} = 21.4 Hz), 78.2, 61.5, 14.4 ppm.

Ethyl 3,3-bis(4-chlorophenyl)-2-diazo-3-hydroxypropanoate 1e⁴. ¹H NMR (500 MHz, CDCl₃) δ 7.35-



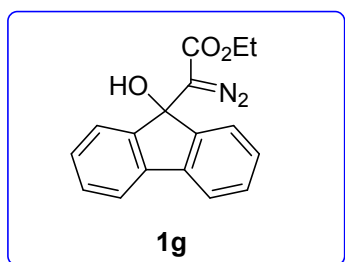
7.30 (m, 8H), 4.99 (brs, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 167.1, 141.7, 134.4, 128.7, 128.2, 78.2, 61.6, 14.4 ppm.

Ethyl 3, 3-bis(4-bromophenyl)-2-diazo-3-hydroxypropanoate 1f. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.41-7.38



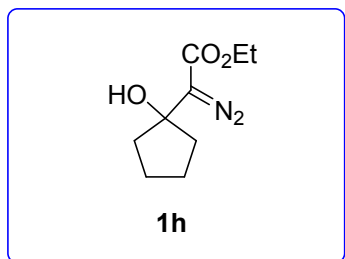
(m, 4H), 7.21-7.19 (m, 4H), 4.91 (brs, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 1.20 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 167.0, 142.1, 131.7, 128.5, 122.6, 78.3, 61.6, 14.4 ppm.

Ethyl 2-diazo-2-(9-hydroxy-9H-fluoren-9-yl) acetate 1g⁴. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz,



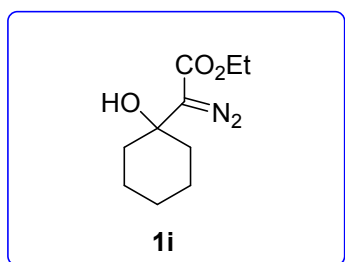
2H), 7.52 (d, $J = 7.5$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.22 (t, $J = 7.5$ Hz, 2H), 4.96 (brs, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 168.1, 146.4, 139.3, 129.9, 128.5, 124.3, 120.3, 78.6, 61.3, 14.4 ppm.

Ethyl 2-diazo-2-(1-hydroxycyclopentyl) acetate 1h⁵. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.25 (q, $J = 7.1$ Hz, 2H),



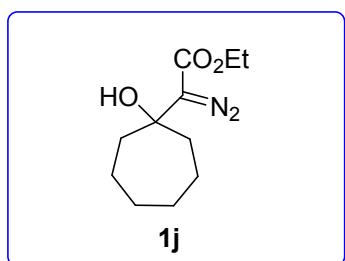
3.28 (brs, 1H), 2.09-2.04 (m, 2H), 1.95-1.86 (m, 2H), 1.83-1.77 (m, 2H), 1.75-1.67 (m, 2H), 1.29 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 167.3, 78.6, 60.8, 39.4, 23.0, 14.4 ppm.

Ethyl 2-diazo-2-(1-hydroxycyclohexyl) acetate 1i⁵⁻⁶. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.24 (q, $J = 7.2$ Hz, 2H),



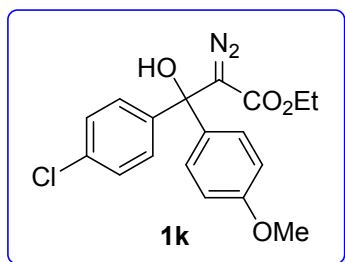
3.49 (brs, 1H), 1.92-1.87 (m, 2H), 1.78-1.69 (m, 4H), 1.57-1.52 (m, 1H), 1.49-1.41 (m, 2H), 1.37-1.32 (m, 1H), 1.29 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 167.2, 70.2, 60.7, 36.4, 25.3, 22.0, 14.4 ppm.

Ethyl 2-diazo-2-(1-hydroxycycloheptyl) acetate 1j⁷. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.24 (q, $J = 7.1$ Hz, 2H),



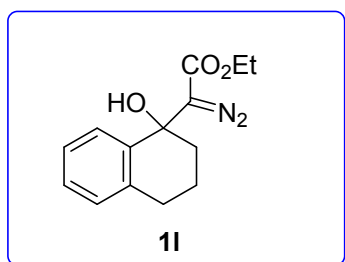
3.75 (brs, 1H), 2.06-2.02 (m, 2H), 1.93-1.88 (m, 2H), 1.75-1.62 (m, 4H), 1.58-1.51 (m, 2H), 1.45-1.39 (m, 2H), 1.29 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 167.6, 74.0, 60.8, 40.2, 29.1, 21.9, 14.4 ppm.

Ethyl 3-(4-chlorophenyl)-2-diazo-3-hydroxy-3-(4-methoxyphenyl) propanoate 1k. $^1\text{H NMR}$ (500 MHz,



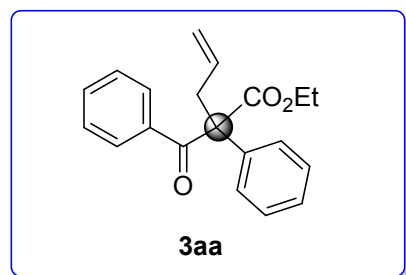
CDCl_3) δ 7.38-7.36 (m, 2H), 7.32-7.26 (m, 4H), 6.86-6.84 (m, 2H), 4.94 (brs, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 167.2, 159.5, 142.7, 134.9, 134.0, 128.5, 128.3, 128.1, 113.8, 78.3, 61.4, 55.3, 14.4 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{ClN}_2\text{O}_4\text{Na}^+$ [$\text{M}+\text{Na}^+$]: 383.0769, found 383.0767.

Ethyl 2-diazo-2-(1-hydroxy-1, 2, 3, 4-tetrahydronaphthalen-1-yl) acetate 1l. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ



7.67-7.65 (m, 1H), 7.25-7.20 (m, 2H), 7.11-7.09 (m, 1H), 4.36 (brs, 1H), 4.31-4.20 (m, 2H), 2.87-2.75 (m, 2H), 2.53-2.48 (m, 1H), 2.10-2.04 (m, 1H), 2.02-1.95 (m, 1H), 1.82-1.73 (m, 1H), 1.28 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 167.1, 137.4, 136.6, 129.1, 128.5, 127.5, 126.7, 72.7, 61.0, 37.7, 29.1, 20.3, 14.4 ppm.

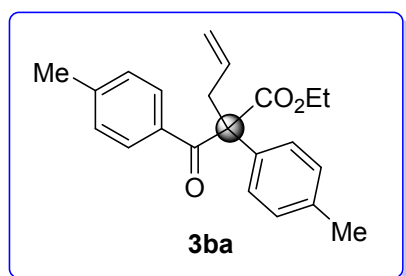
Ethyl 2-benzoyl-2-phenylpent-4-enoate 3aa. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.71 (d, $J = 7.0$ Hz, 2H),



7.62 (d, $J = 7.3$ Hz, 2H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 2H), 7.27-7.23 (m, 3H), 5.74-5.66 (m, 1H), 5.00 (d, $J = 10.3$ Hz, 1H), 4.95 (d, $J = 17.0$ Hz, 1H), 4.11-4.02 (m, 2H), 3.14 (dd, $J = 14.0, 7.8$ Hz, 1H), 2.94 (dd, $J = 14.0, 7.0$ Hz, 1H), 0.96 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 195.1, 170.8, 138.0, 135.9, 133.1, 132.4, 129.5, 128.5, 128.2, 127.9,

127.4, 118.7, 65.4, 61.2, 44.2, 13.7 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{20}\text{H}_{21}\text{O}_3^+$ [$\text{M}+\text{H}^+$]: 309.1485, found 309.1489.

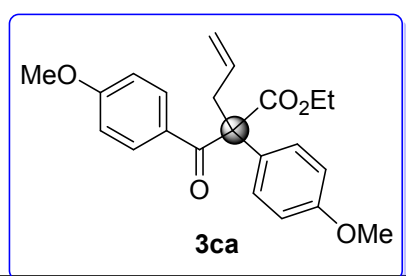
Ethyl 2-(4-methylbenzoyl)-2-(p-tolyl)pent-4-enoate 3ba. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.56-7.54



(m, 2H), 7.42-7.39 (m, 2H), 7.03-6.97 (m, 4H), 5.65-5.58 (m, 1H), 4.92-4.85 (m, 2H), 3.99-3.98 (m, 2H), 3.04 (dd, $J = 13.4, 6.0$ Hz, 1H), 2.83 (dd, $J = 14.0, 6.8$ Hz, 1H), 2.21 (s, 6H), 0.92 (t, $J = 7.5$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 194.8, 171.0, 143.1, 136.9, 135.2, 133.3, 129.7, 129.1, 128.8, 127.8, 118.4, 65.1, 61.1, 44.2, 21.5, 21.0, 13.8 ppm; **HRMS** (ESI) m/z

calcd for $\text{C}_{22}\text{H}_{25}\text{O}_3^+$ [$\text{M}+\text{H}^+$]: 337.1798, found 337.1800.

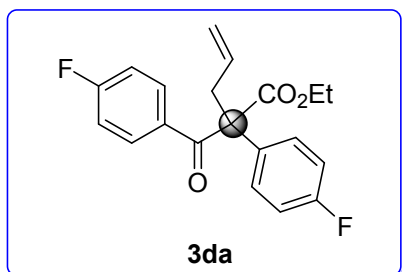
Ethyl 2-(4-methoxybenzoyl)-2-(4-methoxyphenyl)pent-4-enoate 3ca. $^1\text{H NMR}$ (500 MHz, CDCl_3)



δ 7.73-7.70 (m, 2H), 7.53-7.50 (m, 2H), 6.85-6.82 (m, 2H), 6.75-6.73 (m, 2H), 5.72-5.64 (m, 1H), 5.00-4.97 (m, 1H), 4.95-4.91 (m, 1H), 4.08 (q, $J = 7.2$ Hz, 2H), 3.77 (d, $J = 1.8$ Hz, 6H), 3.10 (dd, $J = 14.0, 7.8$ Hz, 1H), 2.90 (dd, $J = 14.0, 6.9$ Hz, 1H), 1.01

(t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 193.8, 171.2, 162.8, 158.5, 133.3, 131.9, 130.4, 129.2, 128.7, 118.4, 113.7, 113.3, 64.7, 61.1, 55.3, 55.1, 44.2, 13.8 ppm; HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{25}\text{O}_5^+$ [$\text{M}+\text{H}^+$]: 369.1697, found 369.1699.

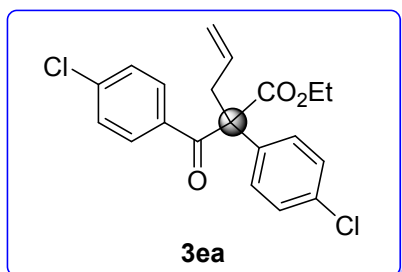
Ethyl 2-(4-fluorobenzoyl)-2-(4-fluorophenyl)pent-4-enoate 3da. ^1H NMR (500 MHz, CDCl_3) δ



7.64 (d, $J = 7.6$ Hz, 2H), 7.53 (d, $J = 7.6$ Hz, 2H), 7.30-7.25 (m, 4H), 5.68-5.59 (m, 1H), 5.02 (d, $J = 10.2$ Hz, 1H), 4.94 (d, $J = 17.0$ Hz, 1H), 4.11-4.07 (m, 2H), 3.11 (dd, $J = 14.1, 7.6$ Hz, 1H), 2.86 (dd, $J = 14.1, 7.1$ Hz, 1H), 1.02 (t, $J = 6.7$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 193.4, 170.3, 139.2, 136.2, 133.7, 133.6, 132.3, 130.9, 129.3, 128.8, 128.6, 119.3, 64.8, 61.6, 44.1,

13.8 ppm. HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{F}_2\text{O}_3^+$ [$\text{M}+\text{H}^+$] 345.1297, found 345.1297.

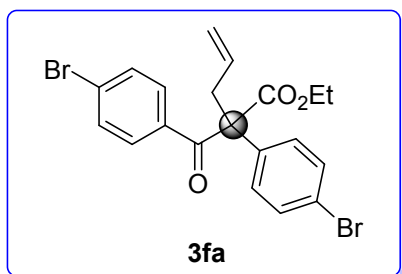
Ethyl 2-(4-chlorobenzoyl)-2-(4-chlorophenyl)pent-4-enoate 3ea. ^1H NMR (500 MHz, CDCl_3) δ



7.65-7.62 (m, 2H), 7.54-7.51 (m, 2H), 7.31-7.24 (m, 4H), 5.68-5.59 (m, 1H), 5.03-5.01 (m, 1H), 4.96-4.92 (m, 1H), 4.13-4.04 (m, 2H), 3.11 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.86 (dd, $J = 14.0, 7.1$ Hz, 1H), 1.02 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 193.4, 170.3, 139.2, 136.2, 133.8, 133.6, 132.4, 130.9, 129.3, 128.8, 128.6, 119.3, 64.9, 61.6, 44.1, 13.8 ppm; HRMS

(ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{O}_3^+$ [$\text{M}+\text{H}^+$]: 377.0706, found 377.0708.

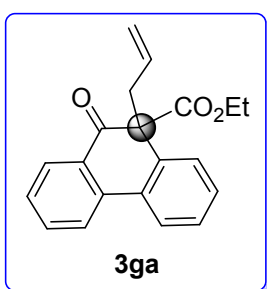
Ethyl 2-(4-bromobenzoyl)-2-(4-bromophenyl)pent-4-enoate 3fa. ^1H NMR (500 MHz, CDCl_3) δ



7.57-7.54 (m, 2H), 7.47-7.41 (m, 6H), 5.67-5.59 (m, 1H), 5.03-5.01 (m, 1H), 4.96-4.92 (m, 1H), 4.13-4.04 (m, 2H), 3.10 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.85 (dd, $J = 14.0, 7.1$ Hz, 1H), 1.02 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 193.5, 170.3, 136.7, 134.1, 132.3, 131.7, 131.6, 131.0, 129.6, 128.0, 121.9, 119.3, 64.9, 61.6, 44.0, 13.8 ppm; HRMS (ESI) m/z calcd for

$\text{C}_{20}\text{H}_{19}\text{Br}_2\text{O}_3^+$ [$\text{M}+\text{H}^+$]: 464.9696, found 464.9691.

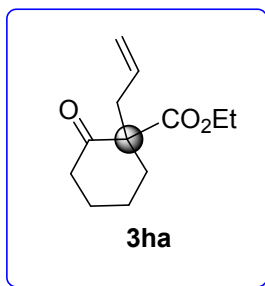
Ethyl 9-allyl-10-oxo-9,10-dihydrophenanthrene-9-carboxylate 3ga. ^1H NMR (500 MHz, CDCl_3) δ



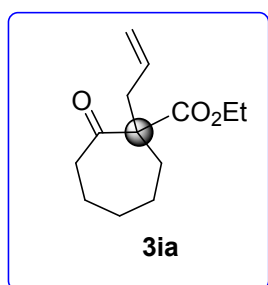
8.13 (dd, $J = 7.9, 1.5$ Hz, 1H), 8.07-8.05 (m, 2H), 7.71-7.68 (m, 1H), 7.45-7.36 (m, 3H), 7.29-7.26 (m, 1H), 5.36-5.28 (m, 1H), 4.80 (dd, $J = 16.7, 1.7$ Hz, 1H), 4.73 (dd, $J = 10.1, 1.8$ Hz, 1H), 4.18-4.07 (m, 2H), 3.17 (dd, $J = 13.9, 7.5$ Hz, 1H), 2.95 (dd, $J = 14.0, 7.3$ Hz, 1H), 1.08 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 196.1, 171.1, 137.3, 136.7, 134.9, 131.5, 129.8, 129.2, 129.1, 128.4, 128.1, 127.8, 127.7, 123.7, 123.2, 119.0, 62.8, 61.7, 44.4, 13.8 ppm; HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3^+$ [$\text{M}+\text{H}^+$]:

307.1329, found 307.1330.

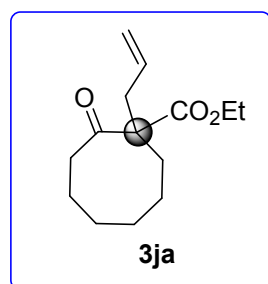
Ethyl 1-allyl-2-oxocyclohexane-1-carboxylate 3ha. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.79-5.70 (m, 1H), 5.05-5.04 (m, 1H), 5.03-5.02 (m, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.61 (dd, $J = 14.0, 7.1$ Hz, 1H), 2.50 (q, $J = 3.3$ Hz, 1H), 2.47-2.44 (m, 2H), 2.34 (dd, $J = 14.0, 7.9$ Hz, 1H), 2.04-1.98 (m, 1H), 1.78-1.75 (m, 1H), 1.74-1.59 (m, 2H), 1.50-1.44 (m, 1H), 1.25 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 207.5, 171.5, 133.3, 118.2, 61.2, 60.9, 41.1, 39.3, 35.8, 27.5, 22.5, 14.2 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{12}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 211.1329, found 211.1330.



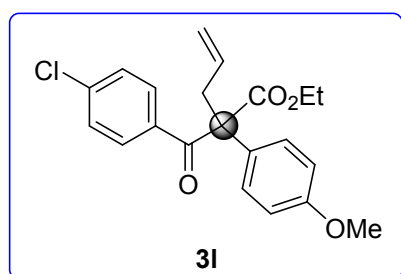
Ethyl 1-allyl-2-oxocycloheptane-1-carboxylate 3ia. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.77-5.69 (m, 1H), 5.08-5.05 (m, 2H), 4.17 (q, $J = 7.2$ Hz, 2H), 2.74 (dd, $J = 13.7, 6.3$ Hz, 1H), 2.68-2.63 (m, 1H), 2.48-2.43 (m, 1H), 2.34 (dd, $J = 13.6, 7.7$ Hz, 1H), 2.13-2.09 (m, 1H), 1.82-1.74 (m, 2H), 1.73-1.68 (m, 1H), 1.65-1.63 (m, 1H), 1.62-1.57 (m, 2H), 1.46-1.38 (m, 1H), 1.25 (t, $J = 7.0$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 209.1, 172.0, 133.6, 118.6, 62.8, 61.2, 42.1, 39.7, 32.1, 29.9, 25.5, 24.6, 14.1 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{13}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 225.1485, found 225.1487.



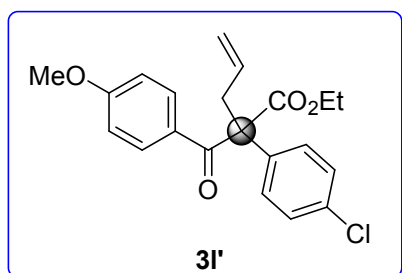
Ethyl 1-allyl-2-oxocyclooctane-1-carboxylate 3ja. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.75-5.67 (m, 1H), 5.10-5.04 (m, 2H), 4.15 (q, $J = 7.2$ Hz, 2H), 2.84 (dd, $J = 14.3, 7.1$ Hz, 1H), 2.72 (td, $J = 12.1, 3.6$ Hz, 1H), 2.51-2.45 (m, 1H), 2.35 (dd, $J = 14.5, 8.5$ Hz, 1H), 2.29-2.24 (m, 1H), 2.03-1.98 (m, 1H), 1.89-1.82 (m, 1H), 1.80-1.70 (m, 2H), 1.68-1.56 (m, 2H), 1.54-1.45 (m, 1H), 1.39-1.31 (m, 1H), 1.23 (t, $J = 7.1$ Hz, 3H), 1.04-0.96 (m, 1H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 212.0, 171.3, 133.7, 118.2, 62.5, 61.3, 38.6, 35.5, 29.2, 28.3, 25.6, 24.3, 23.0, 14.1 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{14}\text{H}_{23}\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 239.1642, found 239.1645.



Ethyl 2-(4-chlorobenzoyl)-2-(4-methoxyphenyl)pent-4-enoate 3l. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.667.64 (m, 2H), 7.51-7.48 (m, 2H), 7.25-7.22 (m, 2H), 6.86-6.83 (m, 2H), 5.72-5.63 (m, 1H), 5.01-4.99 (m, 1H), 4.97-4.93 (m, 1H), 4.11-4.05 (m, 2H), 3.78 (s, 3H), 3.09 (dd, $J = 14.1, 7.7$ Hz, 1H), 2.89 (dd, $J = 14.0, 6.9$ Hz, 1H), 1.02 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 194.0, 170.7, 158.7, 138.8, 134.2, 133.0, 131.0, 129.6, 129.1, 128.5, 118.7, 113.9, 64.9, 61.3, 55.2, 44.1, 13.8 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{ClO}_4^+$ $[\text{M}+\text{H}^+]$: 373.1201, found 373.1203.



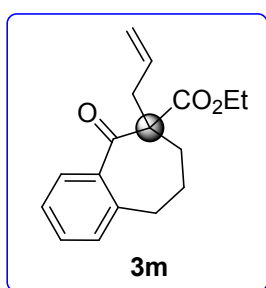
Ethyl 2-(4-chlorophenyl)-2-(4-methoxybenzoyl)pent-4-enoate 3l'. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ



7.71-7.68 (m, 2H), 7.56-7.54 (m, 2H), 7.29-7.27 (m, 2H), 6.77-6.74 (m, 2H), 5.68-5.59 (m, 1H), 5.01-4.99 (m, 1H), 4.95-4.91 (m, 1H), 4.11-4.06 (m, 2H), 3.79 (s, 3H), 3.12 (dd, $J = 14.0, 7.6$ Hz, 1H), 2.86 (dd, $J = 14.0, 6.9$ Hz, 1H), 1.01 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 193.1, 170.8, 163.0, 136.9, 133.2, 132.7, 131.9, 129.5, 128.5, 128.2, 119.0, 113.5, 64.7,

61.4, 55.4, 44.1, 13.8 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{ClO}_4^+$ $[\text{M}+\text{H}]^+$ 373.1201, found 373.1200.

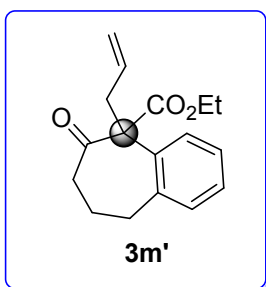
Ethyl 6-allyl-5-oxo-6, 7, 8, 9-tetrahydro-5H-benzo [7] annulene-6-carboxylate 3m. $^1\text{H NMR}$ (500



MHz, CDCl_3) δ 7.43 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.34 (td, $J = 7.5, 1.6$ Hz, 1H), 7.26-7.23 (m, 1H), 7.11 (dd, $J = 7.7, 1.1$ Hz, 1H), 5.76-5.67 (m, 1H), 5.11-5.05 (m, 2H), 4.07-3.97 (m, 2H), 3.03-2.97 (m, 1H), 2.82-2.77 (m, 1H), 2.75-2.65 (m, 2H), 2.42-2.37 (m, 1H), 2.10-2.02 (m, 1H), 1.88-1.75 (m, 2H), 1.04 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 204.4, 171.8, 140.3, 138.9, 133.0, 131.0, 129.2, 129.0, 126.3, 118.8, 62.0, 61.1, 41.5, 33.3, 32.5, 24.1, 13.8 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{17}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 273.1485, found 273.1488.

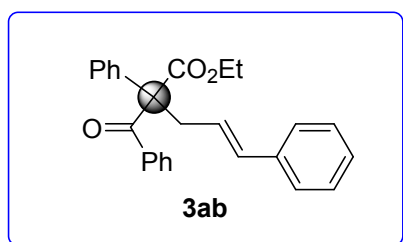
$\text{C}_{17}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 273.1485, found 273.1488.

Ethyl 5-allyl-6-oxo-6, 7, 8, 9-tetrahydro-5H-benzo [7] annulene-5-carboxylate 3m'. $^1\text{H NMR}$



(500 MHz, CDCl_3) δ 7.25-7.24 (m, 2H), 7.19-7.15 (m, 2H), 5.71-5.63 (m, 1H), 4.93-4.90 (m, 2H), 4.23-4.12 (m, 2H), 3.04 (dd, $J = 14.2, 6.8$ Hz, 1H), 2.96-2.92 (m, 2H), 2.92-2.88 (m, 1H), 2.78-2.72 (m, 1H), 2.52-2.47 (m, 1H), 2.10-1.98 (m, 2H), 1.20 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 209.4, 170.6, 139.1, 136.6, 133.6, 130.6, 128.1, 128.0, 126.9, 118.4, 69.8, 61.8, 39.2, 38.8, 31.8, 26.6, 13.9 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{17}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 273.1485, found 273.1487.

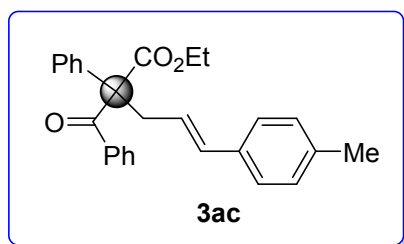
Ethyl (E)-2-benzoyl-2,5-diphenylpent-4-enoate 3ab. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.73-7.71 (m,



2H), 7.64-7.62 (m, 2H), 7.41-7.38 (m, 1H), 7.34-7.31 (m, 2H), 7.28-7.23 (m, 7H), 7.19-7.16 (m, 1H), 6.25 (d, $J = 15.8$ Hz, 1H), 6.13-6.07 (m, 1H), 4.10-4.01 (m, 2H), 3.31 (dd, $J = 14.0, 7.5$ Hz, 1H), 3.03 (dd, $J = 13.9, 7.4$ Hz, 1H), 0.95 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 195.2, 170.8, 138.1, 137.4, 135.9, 133.6, 132.4, 129.5, 128.5, 128.4, 128.1, 127.9, 127.4,

127.2, 126.2, 124.9, 66.0, 61.3, 43.6, 13.7 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{26}\text{H}_{25}\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 385.1799, found 385.1803.

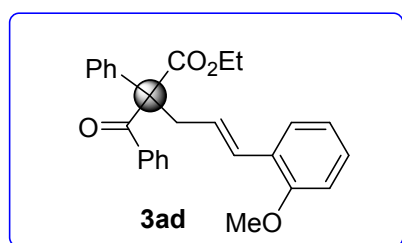
Ethyl (*E*)-2-benzoyl-2-phenyl-5-(*p*-tolyl)pent-4-enoate 3ac. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.71 (d,



$J = 7.8$ Hz, 2H), 7.63-7.61 (m, 2H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 2H), 7.27-7.23 (m, 3H), 7.13 (d, $J = 7.9$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 2H), 6.21 (d, $J = 15.8$ Hz, 1H), 6.08-6.02 (m, 1H), 4.09-4.00 (m, 2H), 3.30 (dd, $J = 13.9, 7.4$ Hz, 1H), 3.01 (dd, $J = 13.9, 7.4$ Hz, 1H), 2.30 (s, 3H), 0.94 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 195.3, 170.8, 138.2,

137.0, 136.0, 134.6, 133.5, 132.4, 129.6, 129.1, 128.5, 128.1, 127.9, 127.4, 126.1, 123.8, 66.0, 61.3, 43.6, 21.2, 13.7 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{O}_3^+$ [$\text{M}+\text{H}^+$]: 399.1955, found 399.1957.

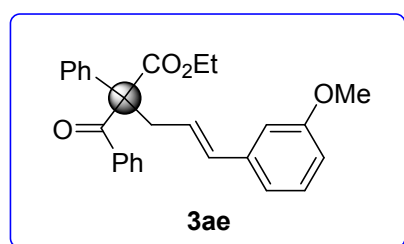
Ethyl (*E*)-2-benzoyl-5-(2-methoxyphenyl)-2-phenylpent-4-enoate 3ad. $^1\text{H NMR}$ (500 MHz,



CDCl_3) δ 7.73-7.71 (m, 2H), 7.65-7.63 (m, 2H), 7.41-7.37 (m, 1H), 7.33-7.29 (m, 3H), 7.27-7.23 (m, 3H), 7.18-7.15 (m, 1H), 6.88-6.85 (m, 1H), 6.81-6.79 (m, 1H), 6.62 (d, $J = 16.0$ Hz, 1H), 6.10-6.04 (m, 1H), 4.08-4.02 (m, 2H), 3.77 (s, 3H), 3.34 (dd, $J = 13.8, 7.8$ Hz, 1H), 3.05 (dd, $J = 13.8, 7.2$ Hz, 1H), 0.97 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 195.3,

170.8, 156.4, 138.2, 136.0, 132.4, 129.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.3, 126.8, 126.6, 125.4, 120.6, 110.8, 66.1, 61.3, 55.4, 43.9, 13.7 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{O}_4^+$ [$\text{M}+\text{H}^+$]: 415.1904, found 415.1909.

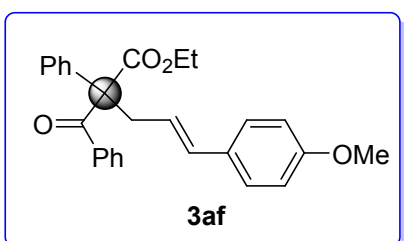
Ethyl (*E*)-2-benzoyl-5-(3-methoxyphenyl)-2-phenylpent-4-enoate 3ae. $^1\text{H NMR}$ (500 MHz,



CDCl_3) δ 7.72-7.71 (m, 2H), 7.63-7.61 (m, 2H), 7.41-7.38 (m, 1H), 7.33-7.30 (m, 2H), 7.28-7.25 (m, 3H), 7.18-7.15 (m, 1H), 6.84-6.83 (m, 1H), 6.77-6.73 (m, 2H), 6.22 (d, $J = 15.8$ Hz, 1H), 6.13-6.07 (m, 1H), 4.10-4.01 (m, 2H), 3.78 (s, 3H), 3.30 (dd, $J = 14.0, 7.4$ Hz, 1H), 3.03 (dd, $J = 14.0, 7.4$ Hz, 1H), 0.95 (t, $J = 7.1$ Hz, 3H) ppm; $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 195.2, 170.7,

159.7, 138.8, 138.1, 136.0, 133.5, 132.4, 129.6, 129.4, 128.5, 128.1, 127.9, 127.4, 125.3, 118.9, 112.7, 111.7, 66.0, 61.3, 55.2, 43.5, 13.7 ppm; **HRMS** (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{O}_4^+$ [$\text{M}+\text{H}^+$]: 415.1904, found 415.1908.

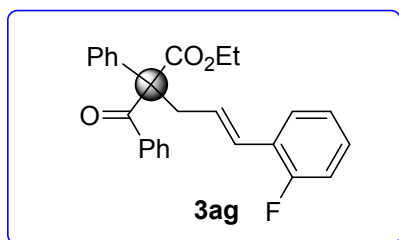
Ethyl (*E*)-2-benzoyl-5-(4-methoxyphenyl)-2-phenylpent-4-enoate 3af. $^1\text{H NMR}$ (500 MHz,



CDCl_3) δ 7.72-7.70 (m, 2H), 7.63-7.61 (m, 2H), 7.39 (t, $J = 7.4$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.27-7.23 (m, 3H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.5$ Hz, 2H), 6.19 (d, $J = 15.8$ Hz, 1H), 5.99-5.93 (m, 1H), 4.07-4.02 (m, 2H), 3.77 (s, 3H), 3.29 (dd, $J = 14.0, 7.5$ Hz, 1H), 3.01 (dd, $J = 13.9, 6.9$ Hz, 1H), 0.94 (t, $J =$

7.1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.3, 170.8, 159.0, 138.2, 136.0, 133.0, 132.4, 130.3, 129.5, 128.5, 128.1, 127.9, 127.4, 127.3, 122.6, 113.9, 66.1, 61.2, 55.3, 43.6, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{27}\text{H}_{27}\text{O}_4^+$ [$\text{M}+\text{H}^+$]: 415.1904, found 415.1906.

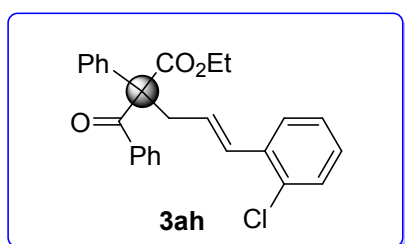
Ethyl (*E*)-2-benzoyl-5-(2-fluorophenyl)-2-phenylpent-4-enoate 3ag. ^1H NMR (500 MHz, CDCl_3) δ



7.65-7.64 (m, 2H), 7.57-7.55 (m, 2H), 7.34-7.30 (m, 1H), 7.27-7.23 (m, 3H), 7.20-7.17 (m, 3H), 7.10-7.05 (m, 1H), 6.97-6.94 (m, 1H), 6.91-6.87 (m, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 6.13-6.07 (m, 1H), 3.99 (q, $J = 7.1$ Hz, 2H), 3.25 (dd, $J = 13.9, 7.8$ Hz, 1H), 2.99 (dd, $J = 13.8, 7.2$ Hz, 1H), 0.89 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.2, 170.7, 160.9,

159.0, 138.1, 135.9, 132.5, 129.6, 128.51 (d, $J_{\text{CF}} = 15.3$ Hz), 128.2, 127.9, 127.6 (d, $J_{\text{CF}} = 3.4$ Hz), 127.5, 127.3 (d, $J_{\text{CF}} = 3.7$ Hz), 125.9 (d, $J_{\text{CF}} = 3.4$ Hz), 125.1 (d, $J_{\text{CF}} = 12.2$ Hz), 124.0 (d, $J_{\text{CF}} = 3.0$ Hz), 115.5 (d, $J_{\text{CF}} = 21.9$ Hz), 65.9, 61.4, 43.9, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{FO}_3^+$ [$\text{M}+\text{H}^+$]: 403.1704, found 403.1708.

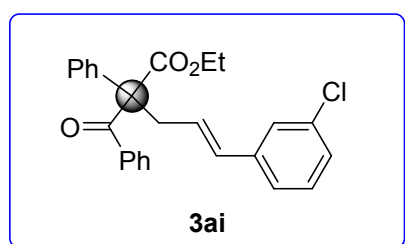
Ethyl (*E*)-2-benzoyl-5-(2-chlorophenyl)-2-phenylpent-4-enoate 3ah. ^1H NMR (500 MHz, CDCl_3)



δ 7.74-7.72 (m, 2H), 7.65-7.64 (m, 2H), 7.41-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.28-7.24 (m, 4H), 7.16-7.19 (m, 2H), 6.66 (d, $J = 15.8$ Hz, 1H), 6.12-6.06 (m, 1H), 4.12-4.03 (m, 2H), 3.35 (dd, $J = 14.0, 7.9$ Hz, 1H), 3.10 (dd, $J = 14.0, 7.3$ Hz, 1H), 0.96 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.1, 170.7,

138.0, 135.9, 135.5, 132.7, 132.5, 129.9, 129.6, 129.5, 128.6, 128.3, 128.2, 127.9, 127.9, 127.5, 127.0, 126.8, 65.9, 61.4, 43.6, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{ClO}_3^+$ [$\text{M}+\text{H}^+$]: 419.1409, found 419.1409.

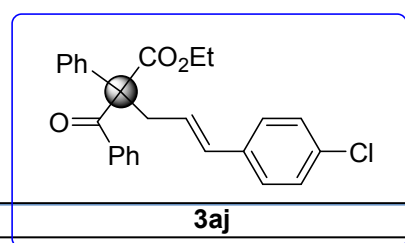
Ethyl (*E*)-2-benzoyl-5-(3-chlorophenyl)-2-phenylpent-4-enoate 3ai. ^1H NMR (500 MHz, CDCl_3) δ



7.72-7.70 (m, 2H), 7.62-7.60 (m, 2H), 7.41-7.38 (m, 1H), 7.34-7.31 (m, 2H), 7.28-7.25 (m, 3H), 7.21-7.08 (m, 4H), 6.18 (d, $J = 16.0$ Hz, 1H), 6.15-6.10 (m, 1H), 4.11-4.01 (m, 2H), 3.29 (dd, $J = 14.1, 6.9$ Hz, 1H), 3.04 (dd, $J = 14.1, 6.9$ Hz, 1H), 0.95 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.1, 170.7,

139.2, 138.0, 135.9, 134.4, 132.5, 132.3, 129.7, 129.6, 128.6, 128.2, 127.9, 127.5, 127.2, 126.7, 126.1, 124.4, 65.9, 61.3, 43.5, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{ClO}_3^+$ [$\text{M}+\text{H}^+$]: 419.1409, found 419.1410.

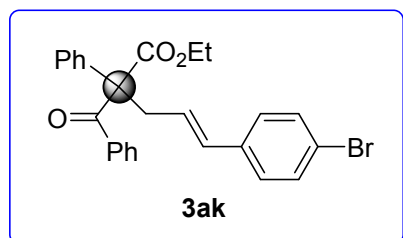
Ethyl (*E*)-2-benzoyl-5-(4-chlorophenyl)-2-phenylpent-4-enoate 3aj. ^1H NMR (500 MHz, CDCl_3) δ



7.72-7.70 (m, 2H), 7.62-7.61 (m, 2H), 7.41-7.38 (m, 1H), 7.34-7.30 (m, 2H), 7.28-7.24 (m, 3H), 7.22-7.20 (m, 2H), 7.16-7.14 (m, 2H), 6.19 (d, $J = 15.8$ Hz, 1H), 6.12-6.06 (m, 1H), 4.10-4.00

(m, 2H), 3.29 (dd, $J = 14.0, 7.3$ Hz, 1H), 3.03 (dd, $J = 14.0, 7.4$ Hz, 1H), 0.94 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.1, 170.7, 138.1, 135.9, 135.8, 132.8, 132.5, 132.4, 129.5, 128.6, 128.5, 128.2, 127.9, 127.5, 127.4, 125.8, 65.9, 61.3, 43.5, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{ClO}_3^+$ [$\text{M}+\text{H}^+$]: 419.1409, found 419.1410.

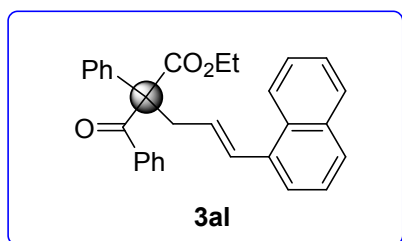
Ethyl (*E*)-2-benzoyl-5-(4-bromophenyl)-2-phenylpent-4-enoate 3ak. ^1H NMR (500 MHz, CDCl_3)



δ 7.73-7.70 (m, 2H), 7.64-7.60 (m, 2H), 7.40-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.23 (m, 5H), 7.16-7.07 (m, 1H), 6.21 (dd, $J = 40.1, 15.8$ Hz, 1H), 6.14-6.08 (m, 1H), 4.09-4.00 (m, 2H), 3.34-3.26 (m, 1H), 3.06-3.01 (m, 1H), 0.94 (t, $J = 8.9$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.2, 170.8, 138.2, 137.4, 136.0, 133.7, 132.4, 131.6, 129.6, 128.4, 128.1, 127.9,

127.7, 127.4, 126.2, 124.9, 65.99, 61.28, 43.59, 13.73 ppm; HRMS (ESI) m/z calcd for $\text{C}_{26}\text{H}_{24}\text{BrO}_3^+$ [$\text{M}+\text{H}^+$]: 463.0903, found 463.0901.

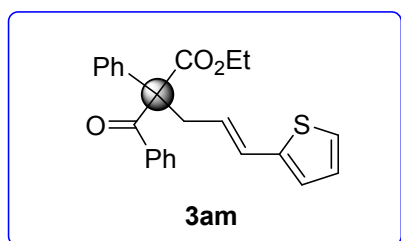
Ethyl (*E*)-2-benzoyl-5-(naphthalen-1-yl)-2-phenylpent-4-enoate 3al. ^1H NMR (500 MHz, CDCl_3)



δ 7.82-7.79 (m, 2H), 7.76-7.71 (m, 3H), 7.67-7.66 (m, 2H), 7.45-7.42 (m, 3H), 7.40-7.37 (m, 2H), 7.35-7.32 (m, 2H), 7.29-7.25 (m, 3H), 6.93 (d, $J = 15.5$ Hz, 1H), 6.16-6.09 (m, 1H), 4.16-4.02 (m, 2H), 3.42 (dd, $J = 13.8, 7.4$ Hz, 1H), 3.19 (dd, $J = 13.8, 7.6$ Hz, 1H), 0.94 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.3, 170.9, 138.2, 135.9, 135.2, 133.5, 132.5, 131.4,

131.1, 129.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.6, 127.4, 125.8, 125.7, 125.6, 124.0, 123.9, 66.0, 61.4, 43.9, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{30}\text{H}_{27}\text{O}_3^+$ [$\text{M}+\text{H}^+$]: 435.1955, found 435.1956.

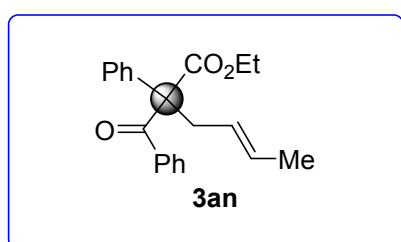
Ethyl (*E*)-2-benzoyl-2-phenyl-5-(thiophen-2-yl)pent-4-enoate 3am. ^1H NMR (500 MHz, CDCl_3) δ



7.72-7.70 (m, 2H), 7.61-7.60 (m, 2H), 7.41-7.38 (m, 1H), 7.33-7.30 (m, 2H), 7.28-7.24 (m, 3H), 7.07 (d, $J = 5.1$ Hz, 1H), 6.90-6.88 (m, 1H), 6.80 (d, $J = 3.6$ Hz, 1H), 6.37 (d, $J = 15.6$ Hz, 1H), 5.98-5.92 (m, 1H), 4.10-4.01 (m, 2H), 3.28 (dd, $J = 13.9, 7.6$ Hz, 1H), 2.97 (dd, $J = 13.9, 7.7$ Hz, 1H), 0.95 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 195.1, 170.7, 142.4,

138.1, 135.9, 132.5, 129.6, 128.6, 128.1, 127.9, 127.5, 127.2, 126.7, 124.9, 124.7, 123.8, 65.9, 61.3, 43.6, 13.7 ppm; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{23}\text{O}_3\text{S}^+$ [$\text{M}+\text{H}^+$]: 391.1363, found 391.1368.

Ethyl (*E*)-2-benzoyl-2-phenylhex-4-enoate 3an. ^1H NMR (500 MHz, CDCl_3) δ 7.70-7.69 (m, 2H),



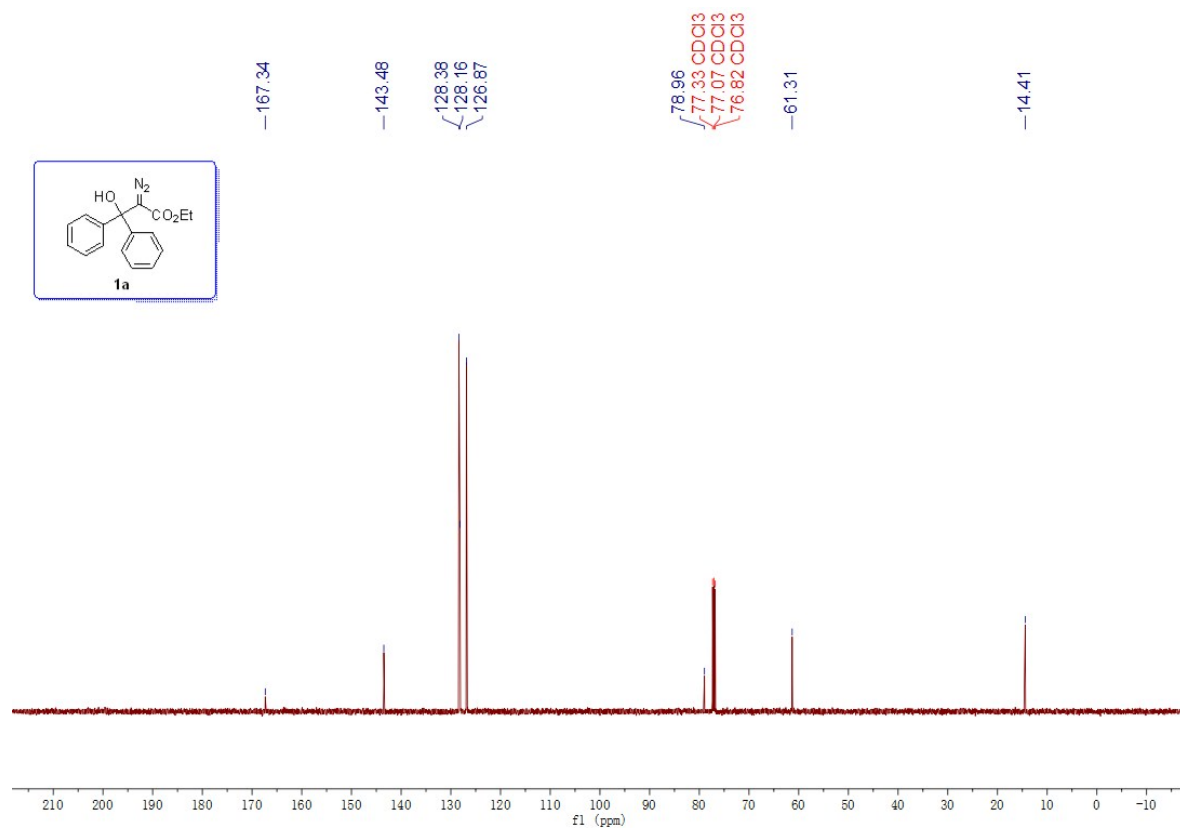
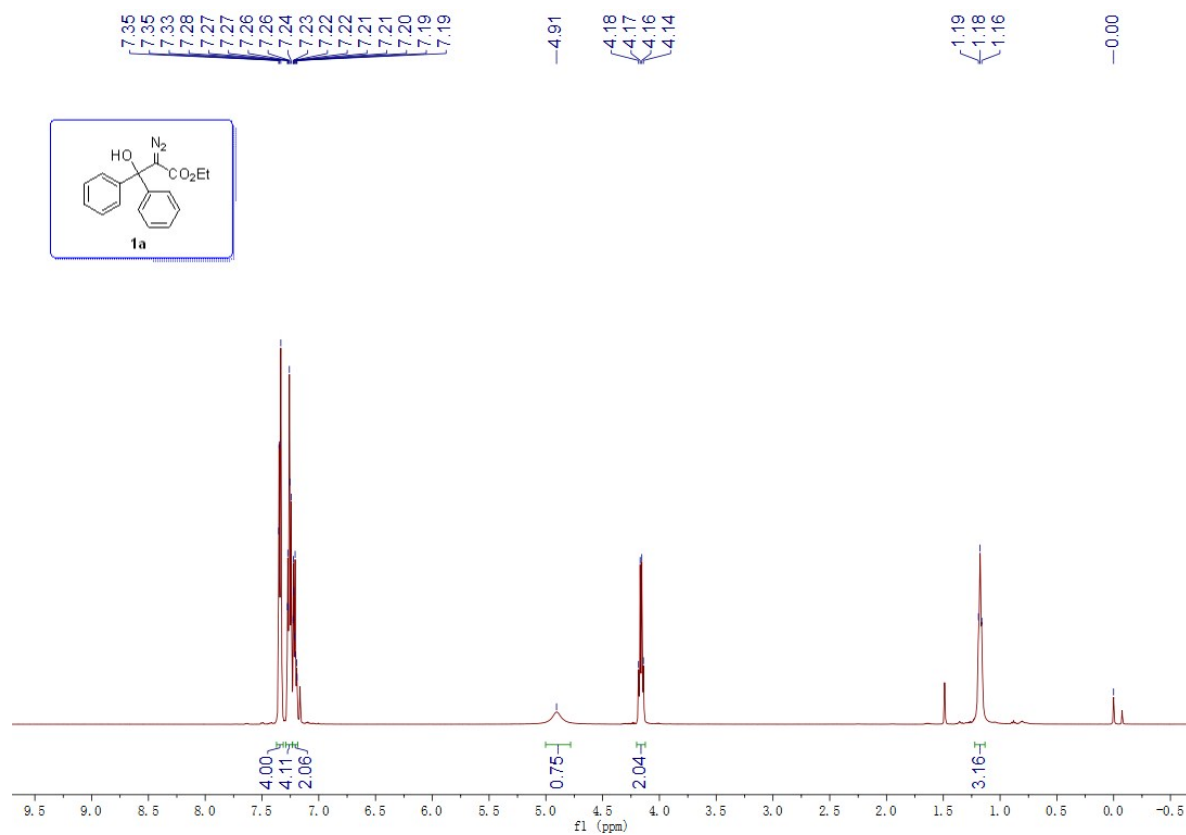
7.60-7.59 (m, 2H), 7.39-7.36 (m, 1H), 7.32-7.29 (m, 2H), 7.36-7.23 (m, 3H), 5.34-5.33 (m, 2H), 4.05 (q, $J = 7.1$ Hz, 2H), 3.09 (dd, $J = 14.8, 4.0$ Hz, 1H), 2.83 (dd, $J = 15.0, 3.9$ Hz, 1H), 1.57 (d, $J = 3.1$ Hz, 3H), 0.96 (t, $J = 7.1$ Hz, 3H) ppm; ^{13}C NMR

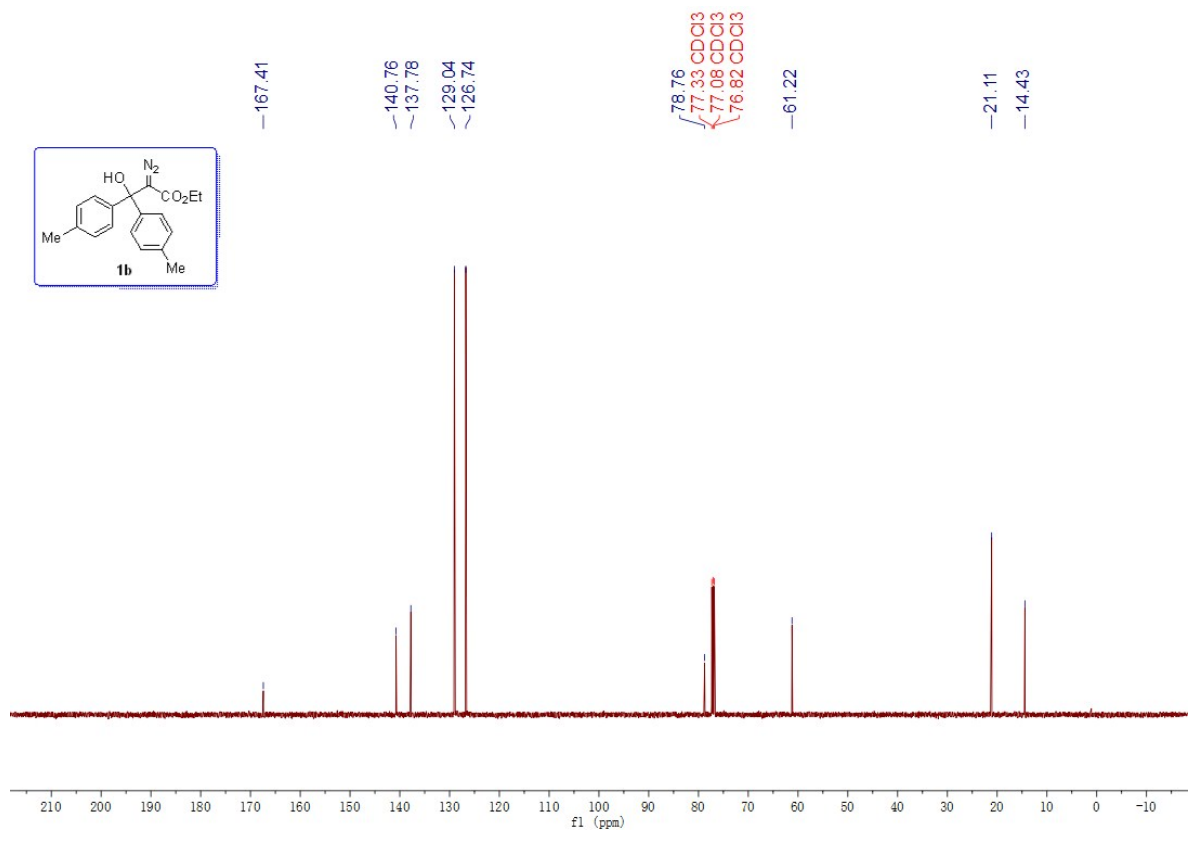
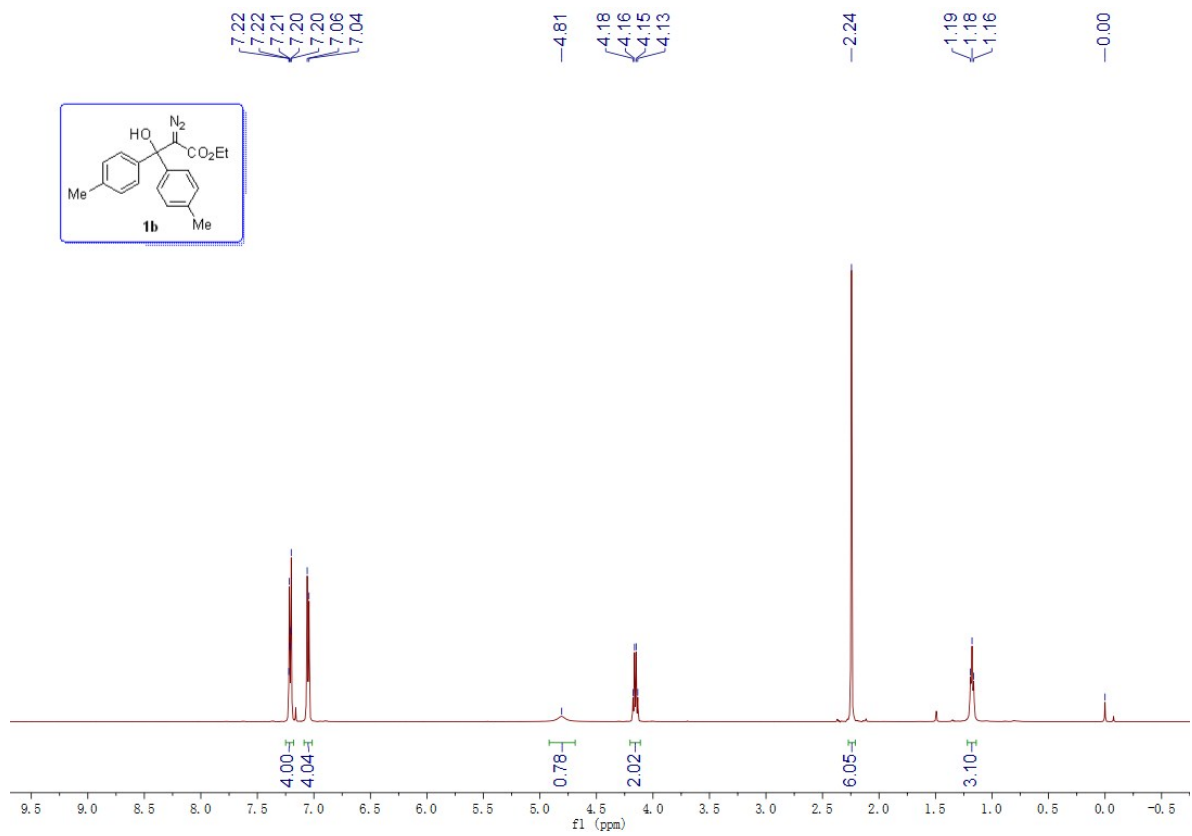
(126 MHz, CDCl₃) δ 195.4, 170.9, 138.2, 136.0, 132.4, 132.3, 129.5, 128.4, 128.1, 128.0, 127.2, 125.3, 65.7, 61.1, 43.1, 18.0, 13.7 ppm; HRMS (ESI) m/z calcd for C₂₁H₂₃O₃⁺ [M+H⁺]: 323.1642, found 323.1644.

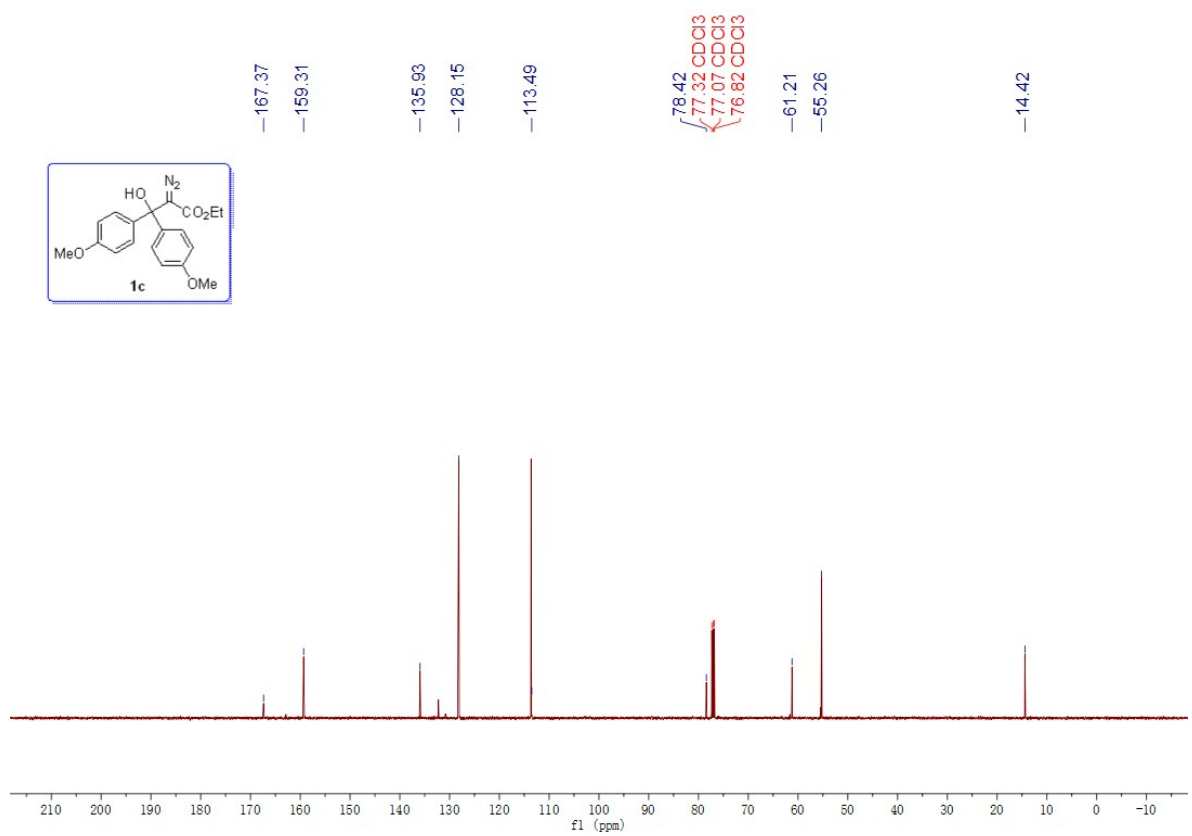
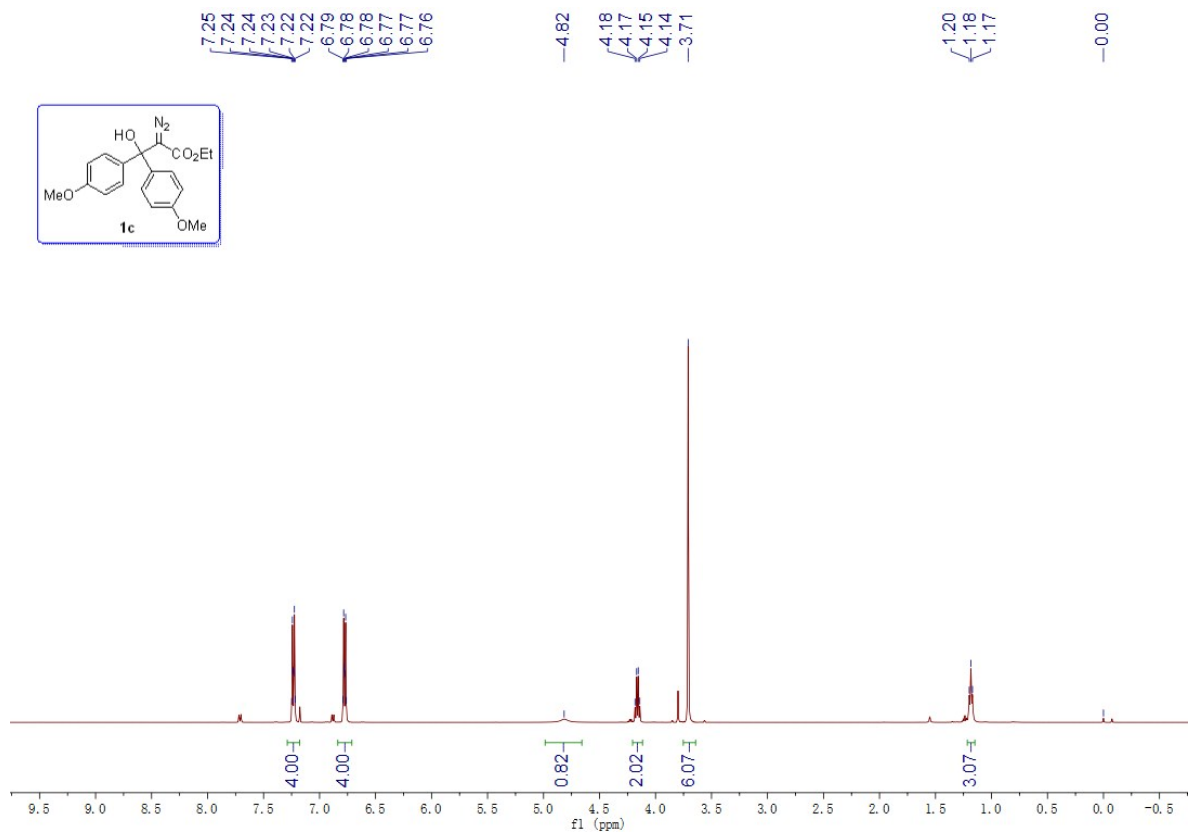
6. Reference:

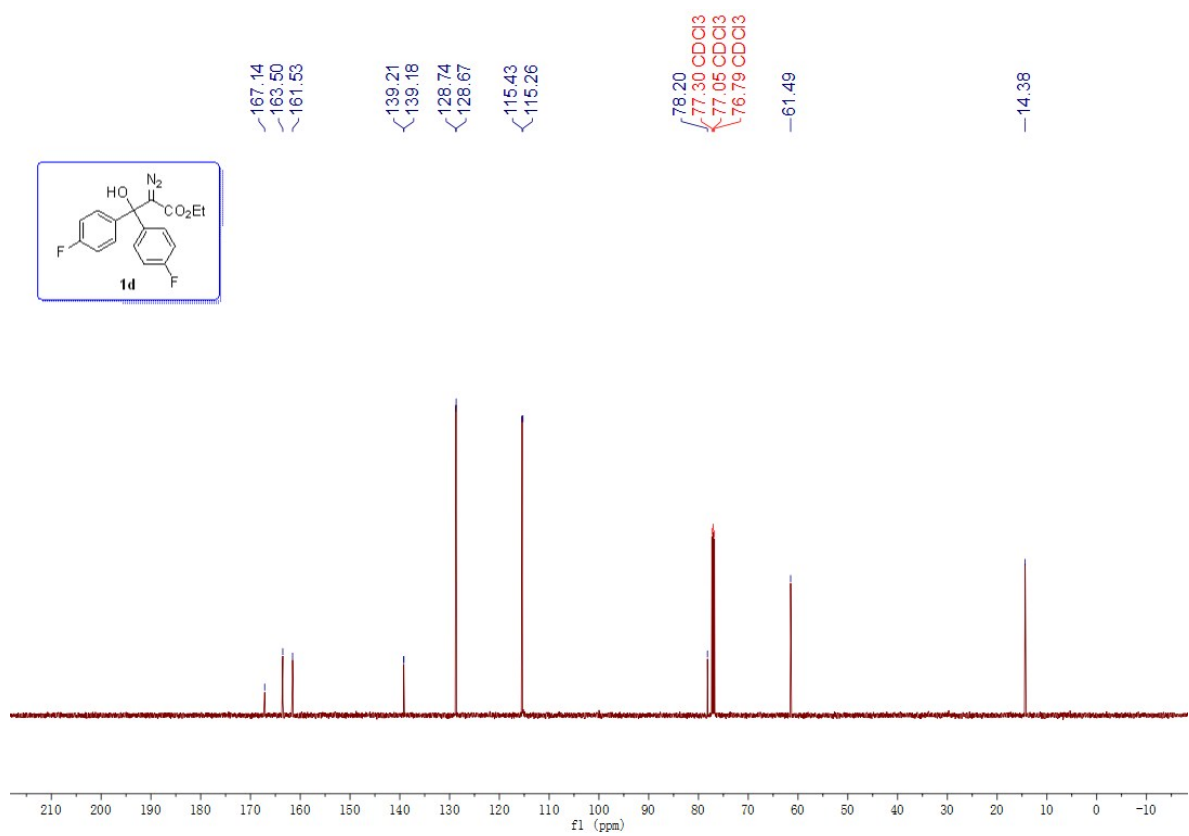
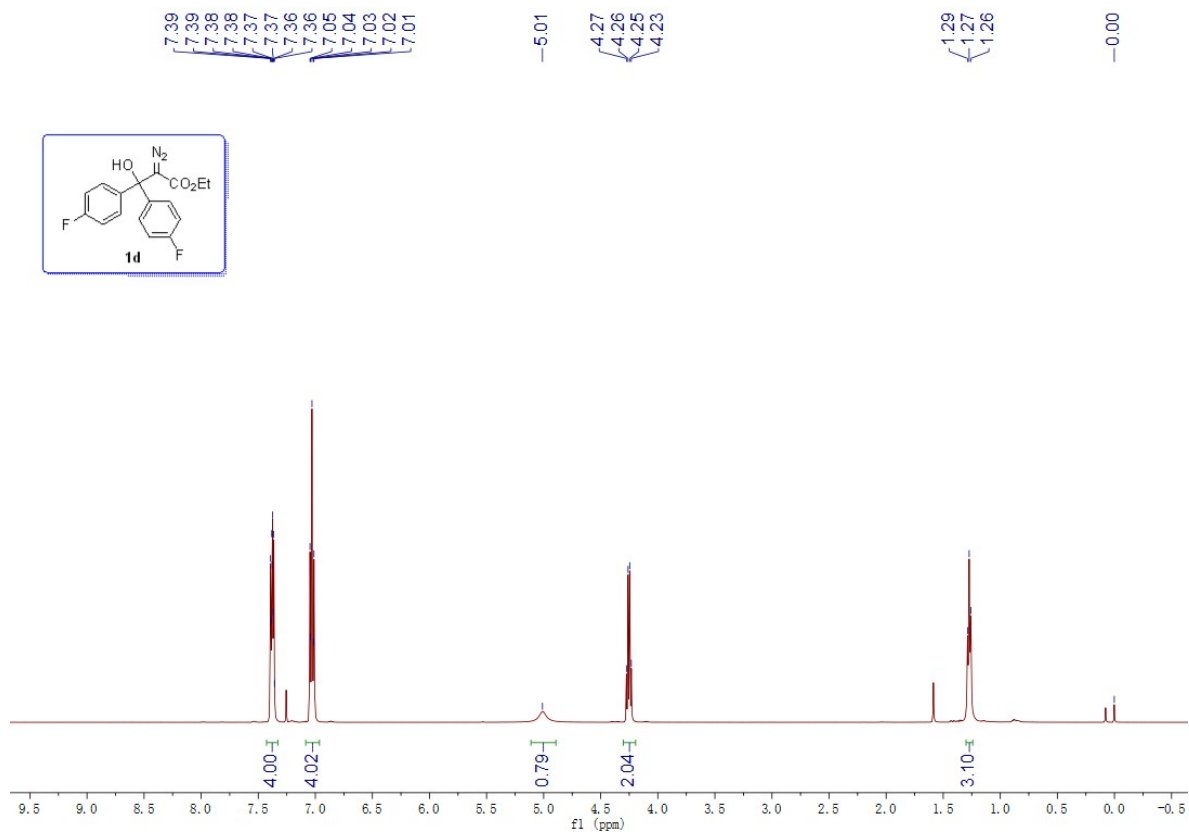
1. P. Müller, Y. Allenbach and Robert, E. *Tetrahedron Asymmetry*, 2003, **14**, 779-785.
2. (a) T. H. West, D. S. B. Daniels, A. M. Z. Slawin and A. D. Smith, *J. Am. Chem. Soc.*, 2014, **136**, 4476-4479; (b) Z.-S. Chen, X.-H. Duan, P.-X. Zhou, S. Ali, J.-Y. Luo and Y.-M. Liang, *Angew. Chem. Int. Ed.*, 2012, **51**, 1370-1374; (c) Z.-S. Chen, L.-Z. Huang, H. J. Jeon, Z. Xuan and S.G. Lee, *ACS Catal.*, 2016, **6**, 4914-4919.
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7. W. F. Shi, M. Ma, J. Wang, *Chin. Chem. Lett.*, 2004, **15**, 911-914.

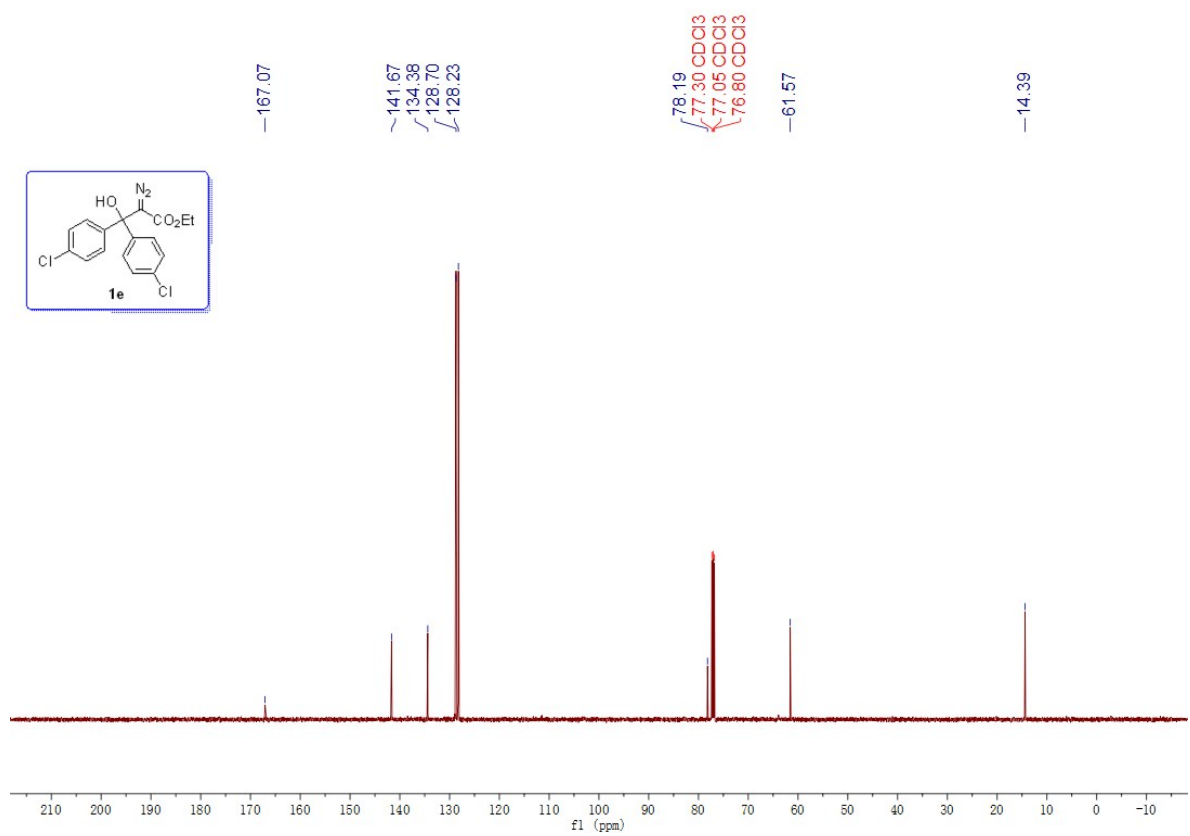
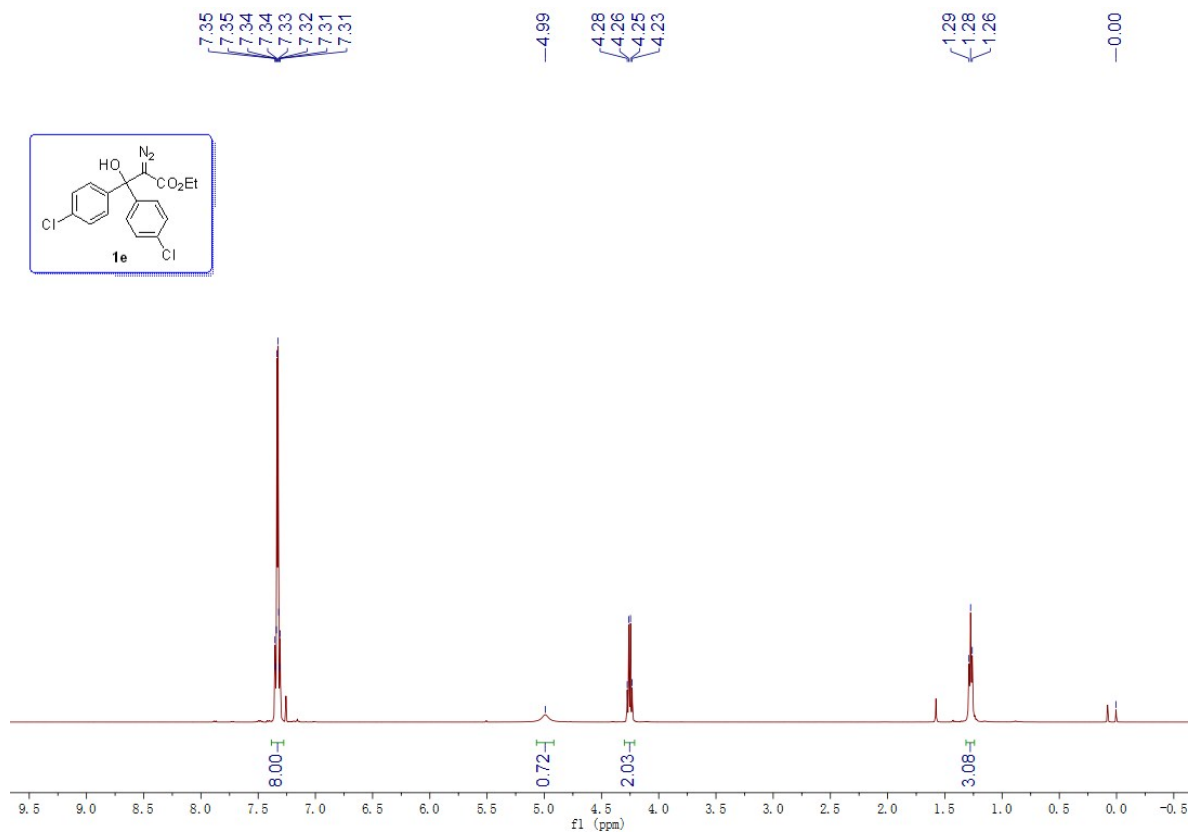
7. ¹H and ¹³C NMR Spectra for All Compounds :

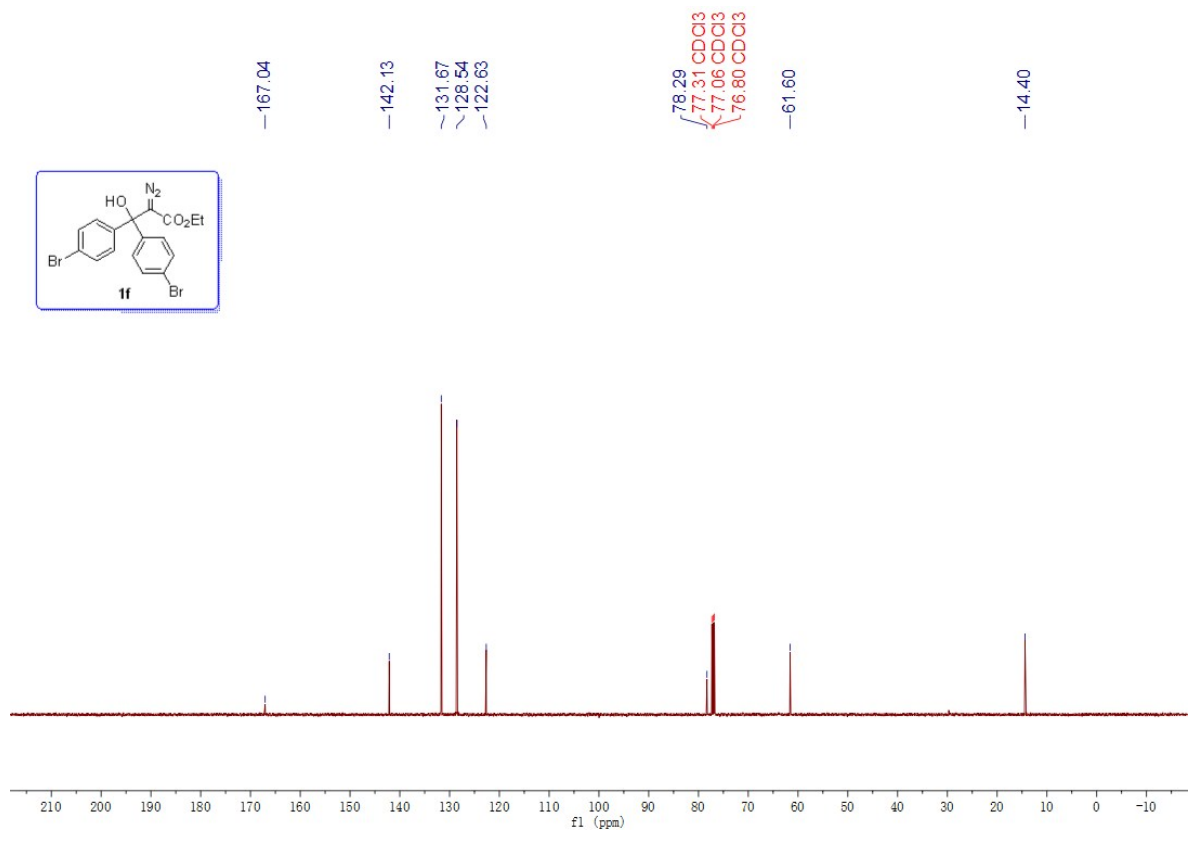
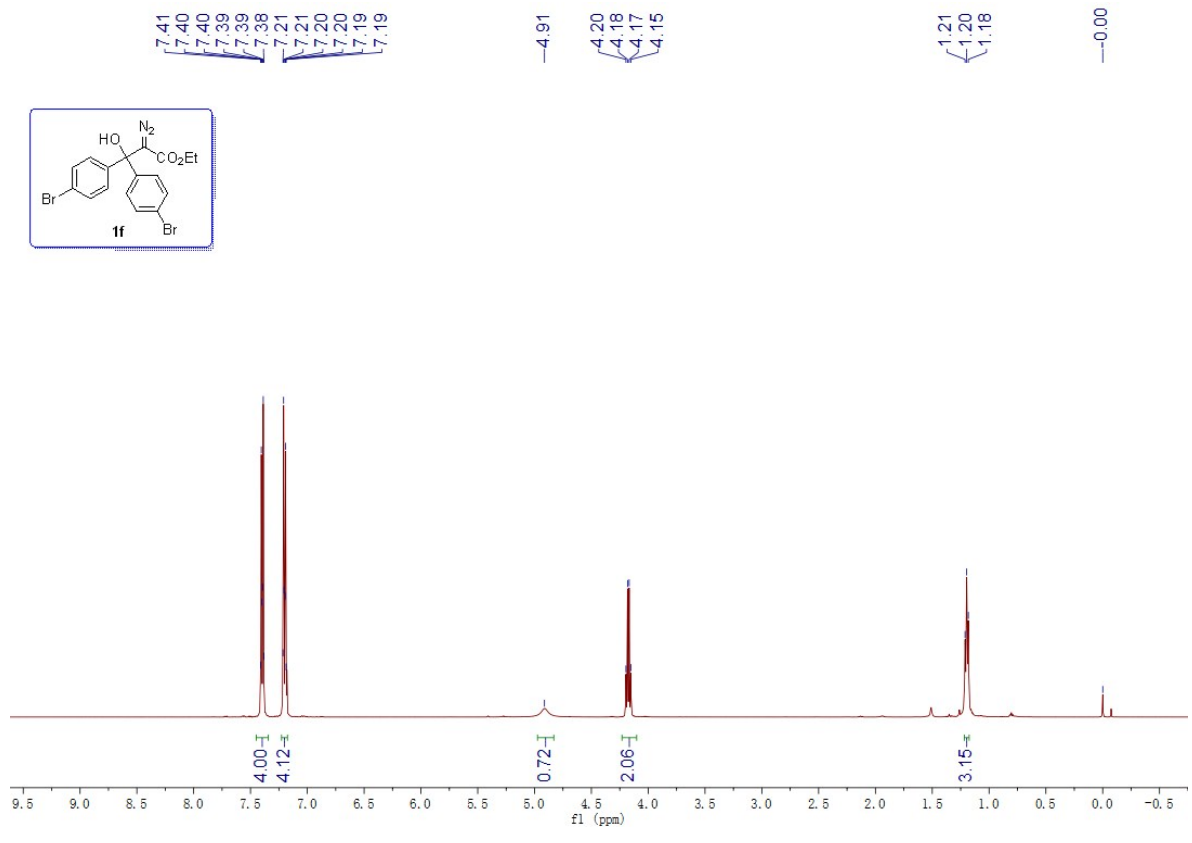


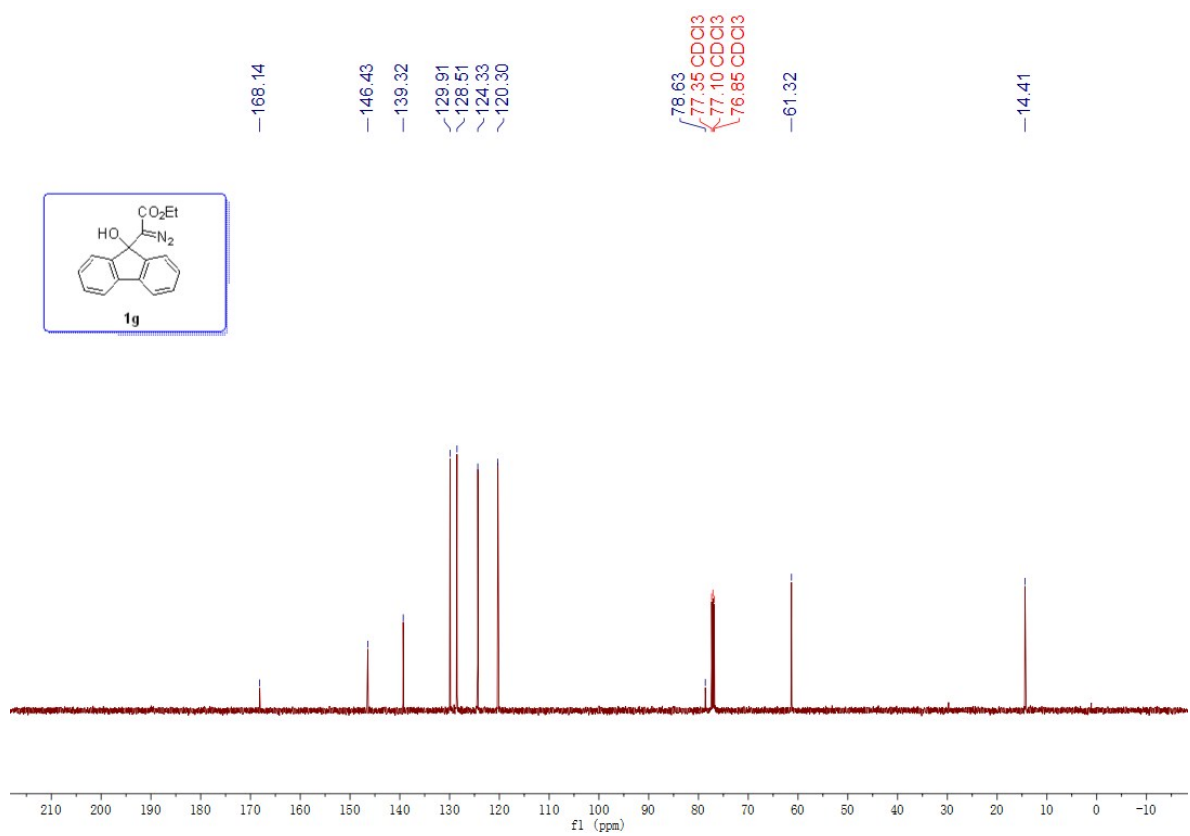
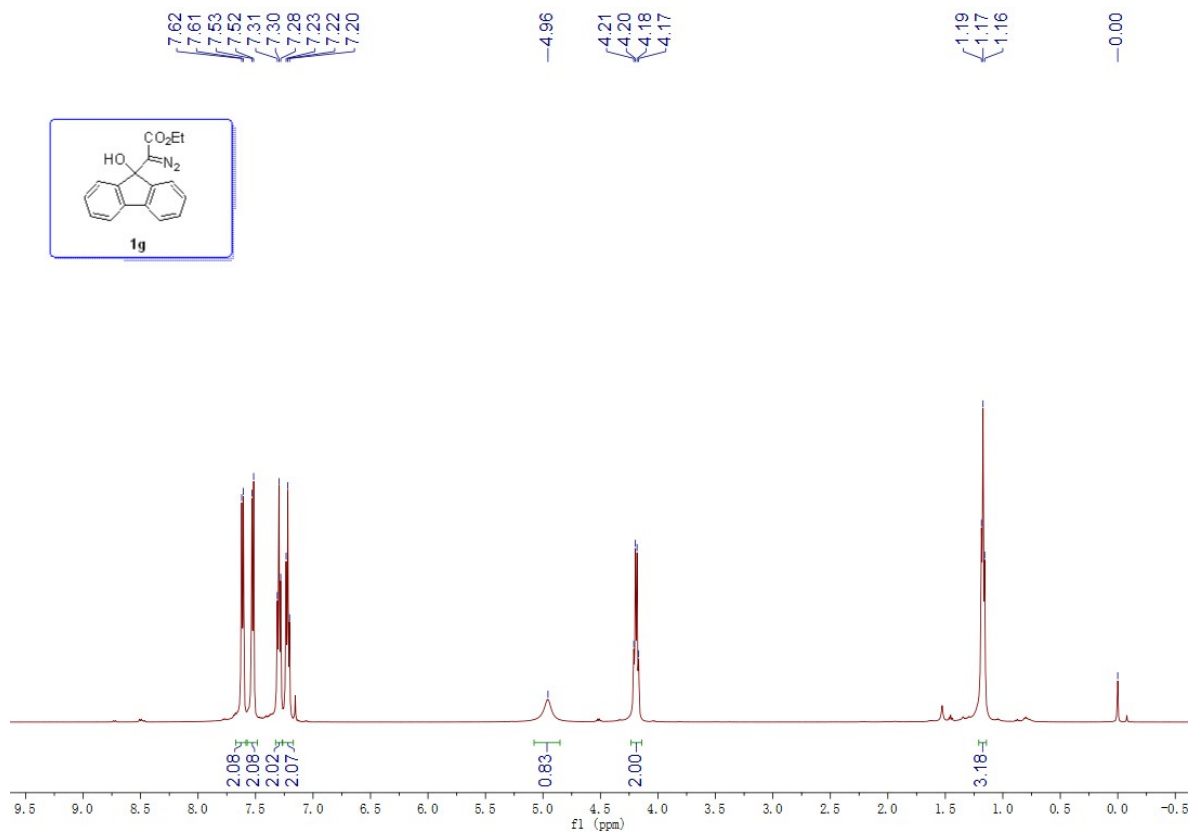


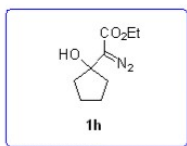
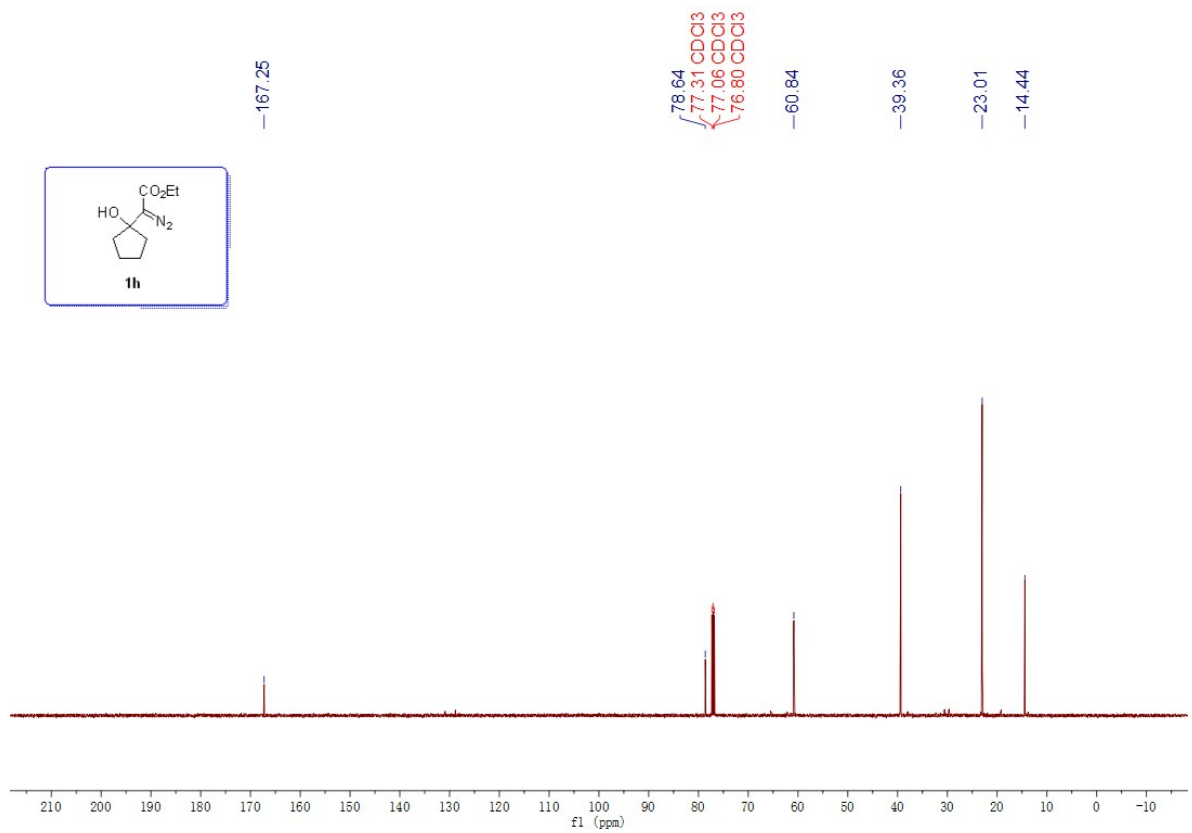
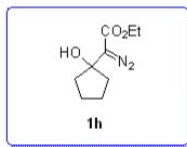
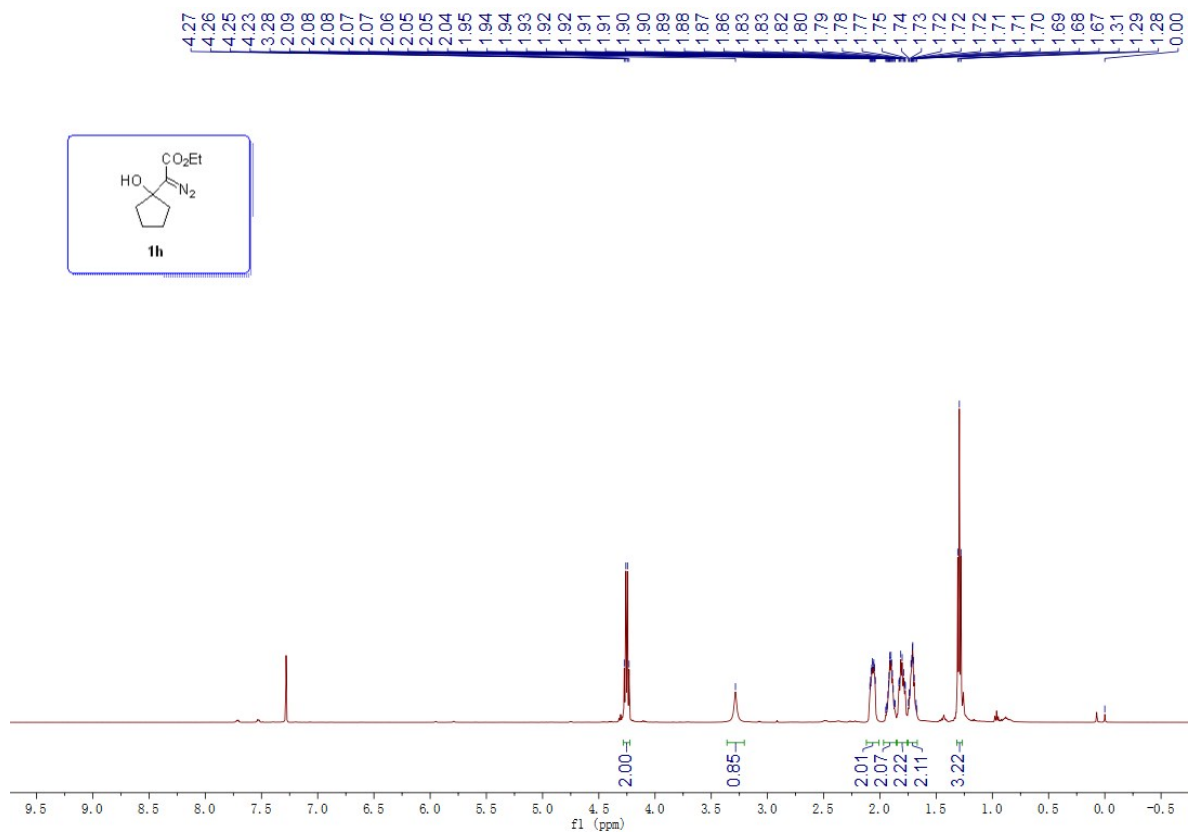


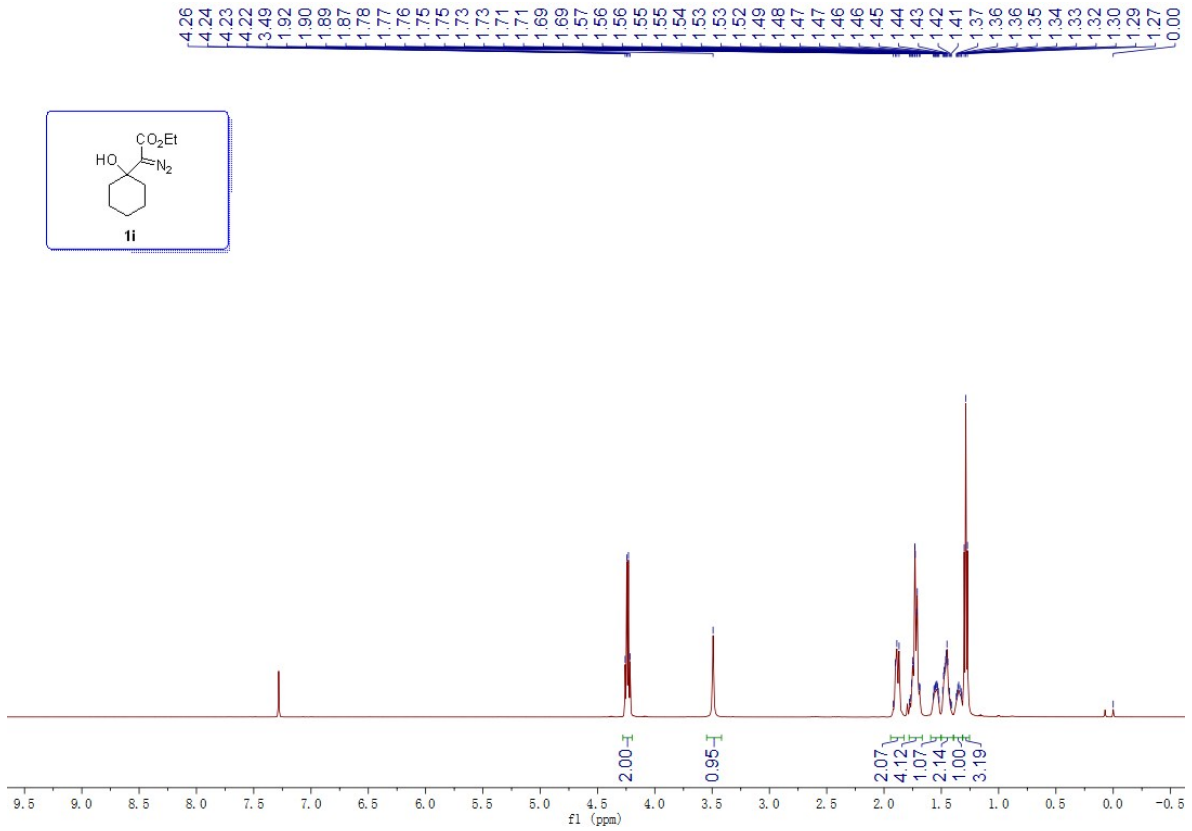
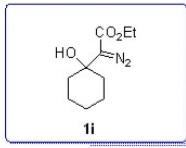












-167.22

77.31 CDCl3
77.06 CDCl3
76.80 CDCl3
70.19

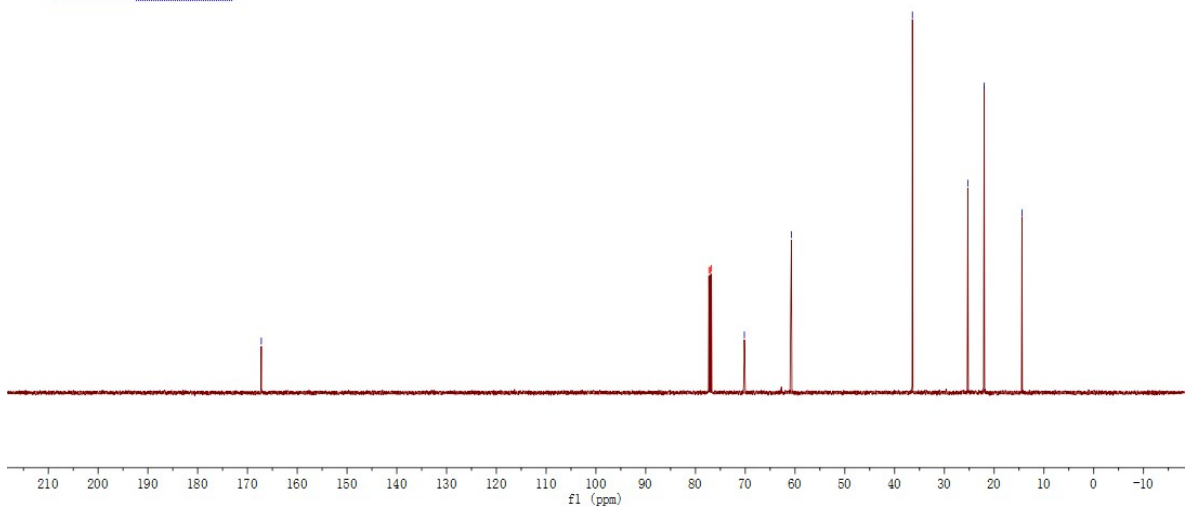
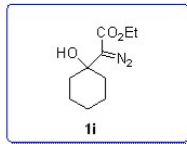
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-36.43

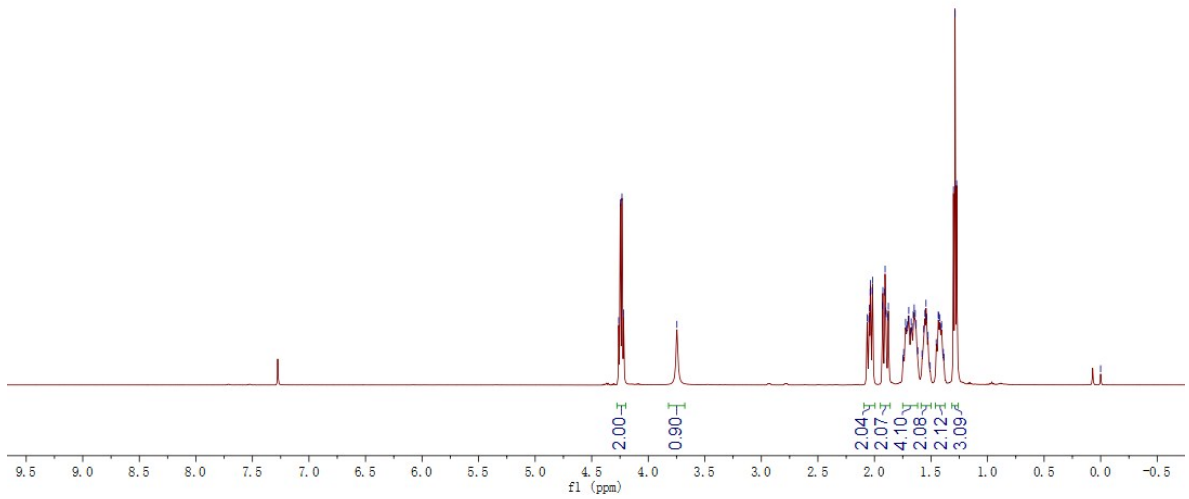
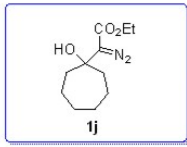
25.29

22.01

14.42



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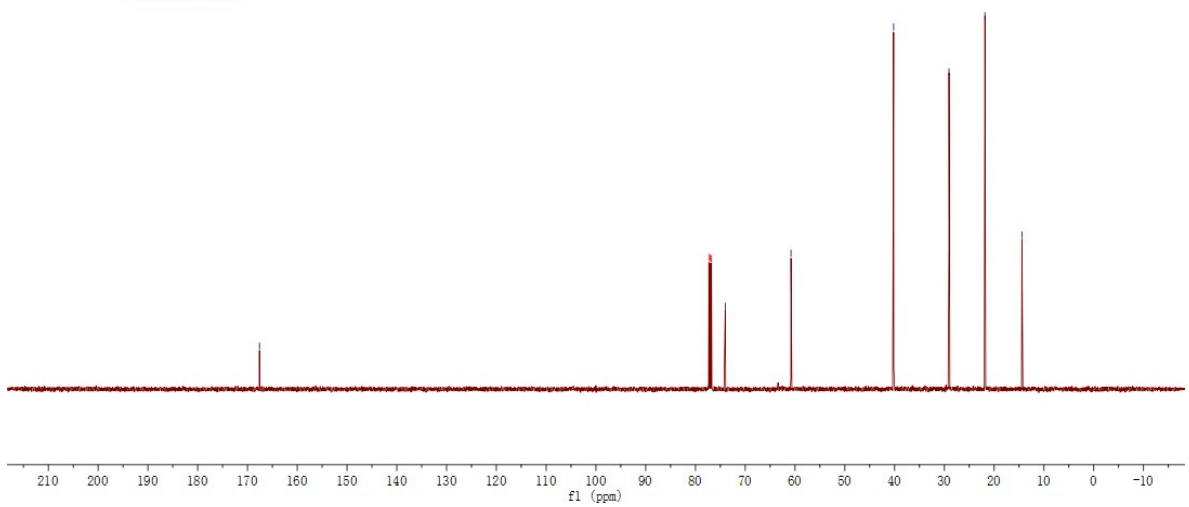
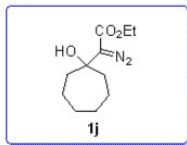
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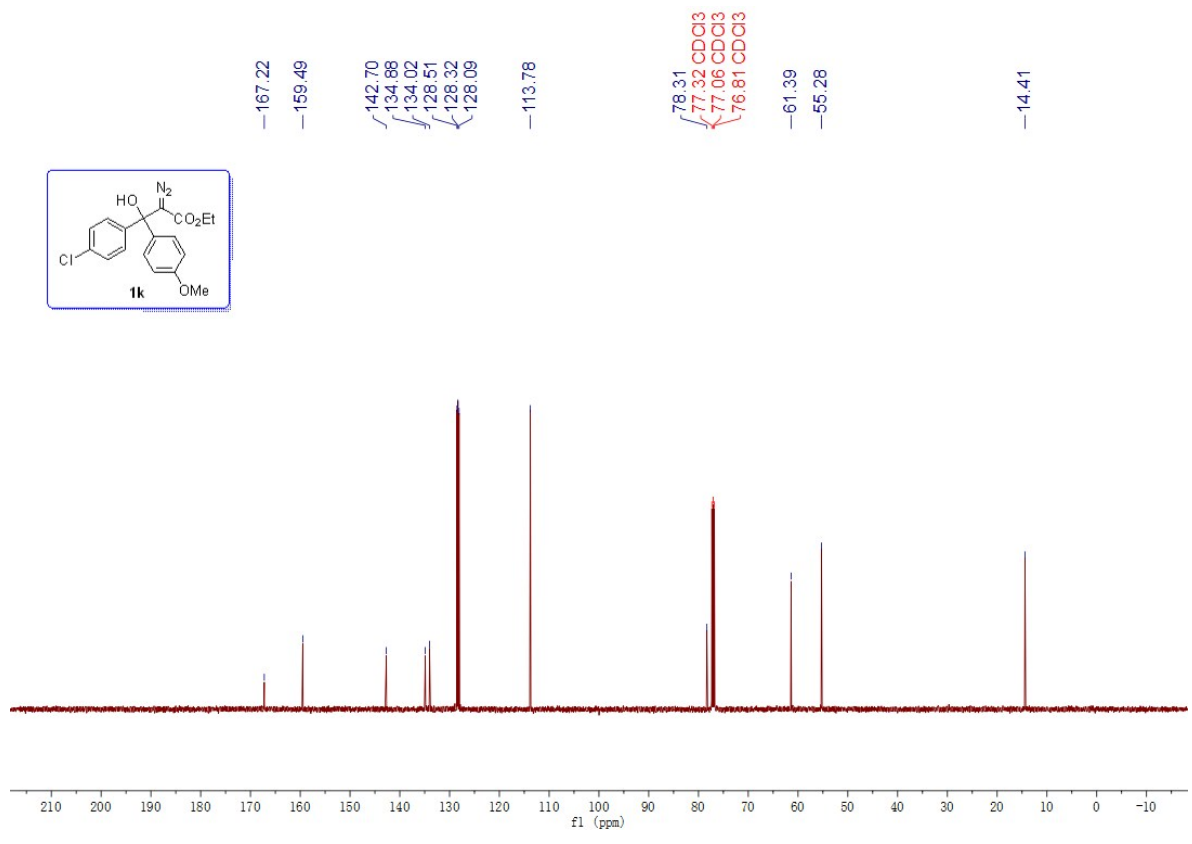
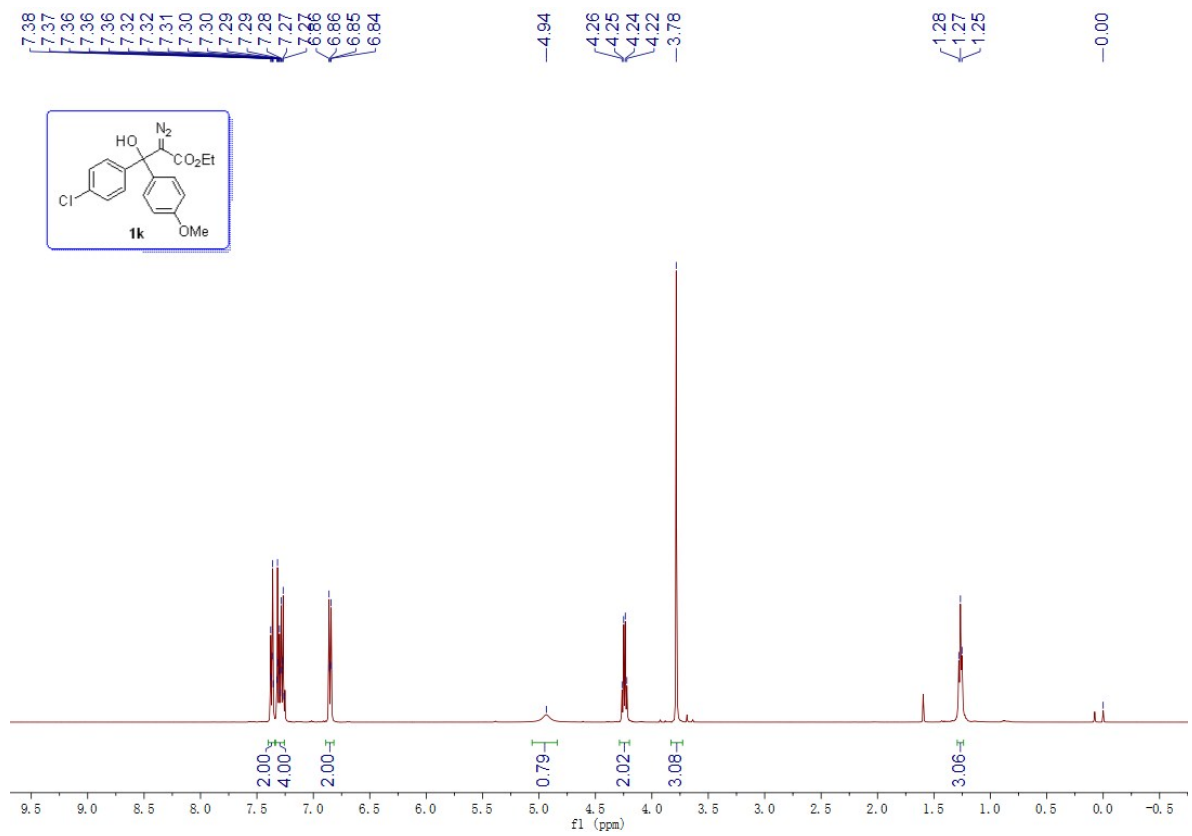
77.30 CDCl3
77.05 CDCl3
76.79 CDCl3
74.03

-60.82

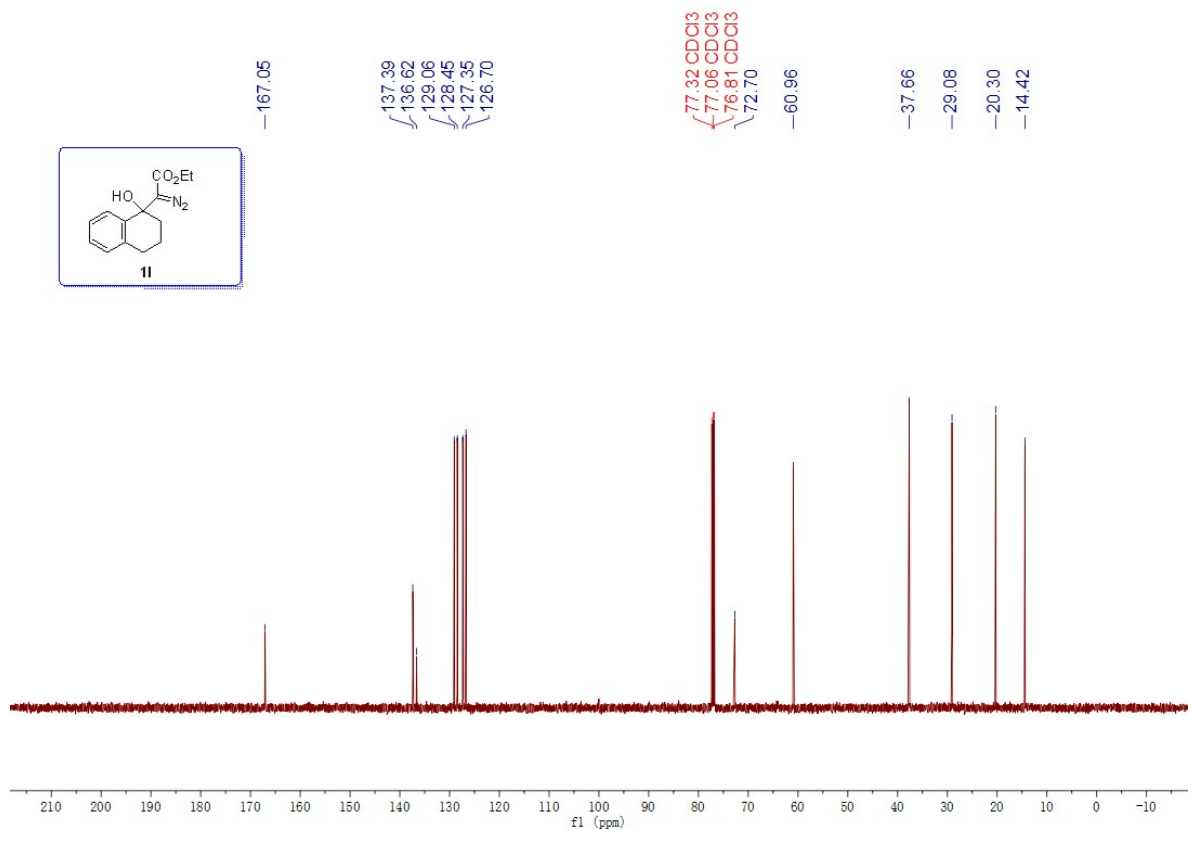
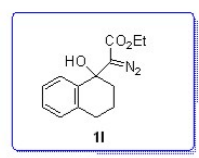
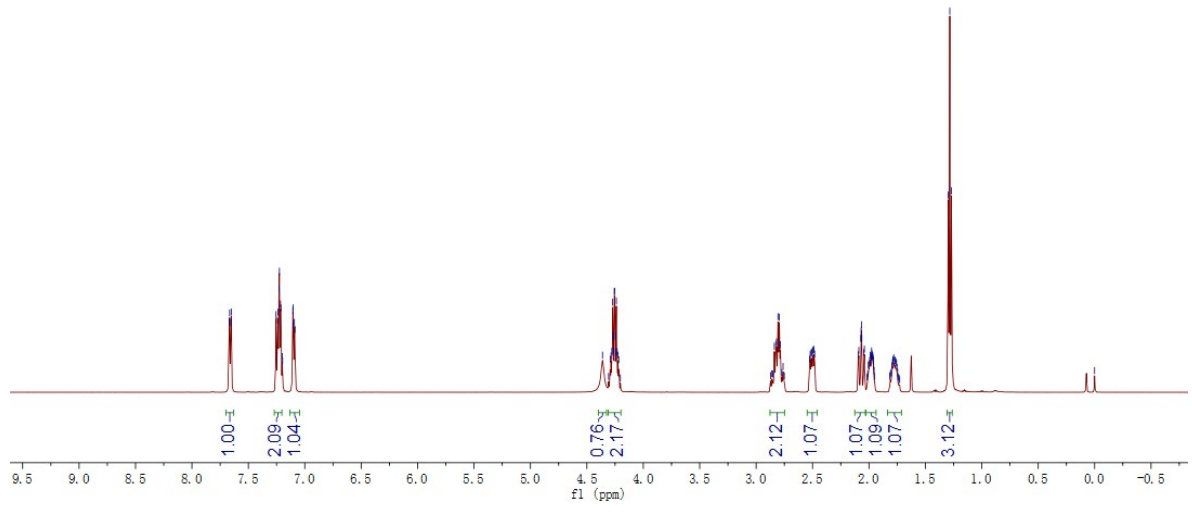
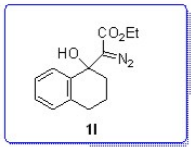
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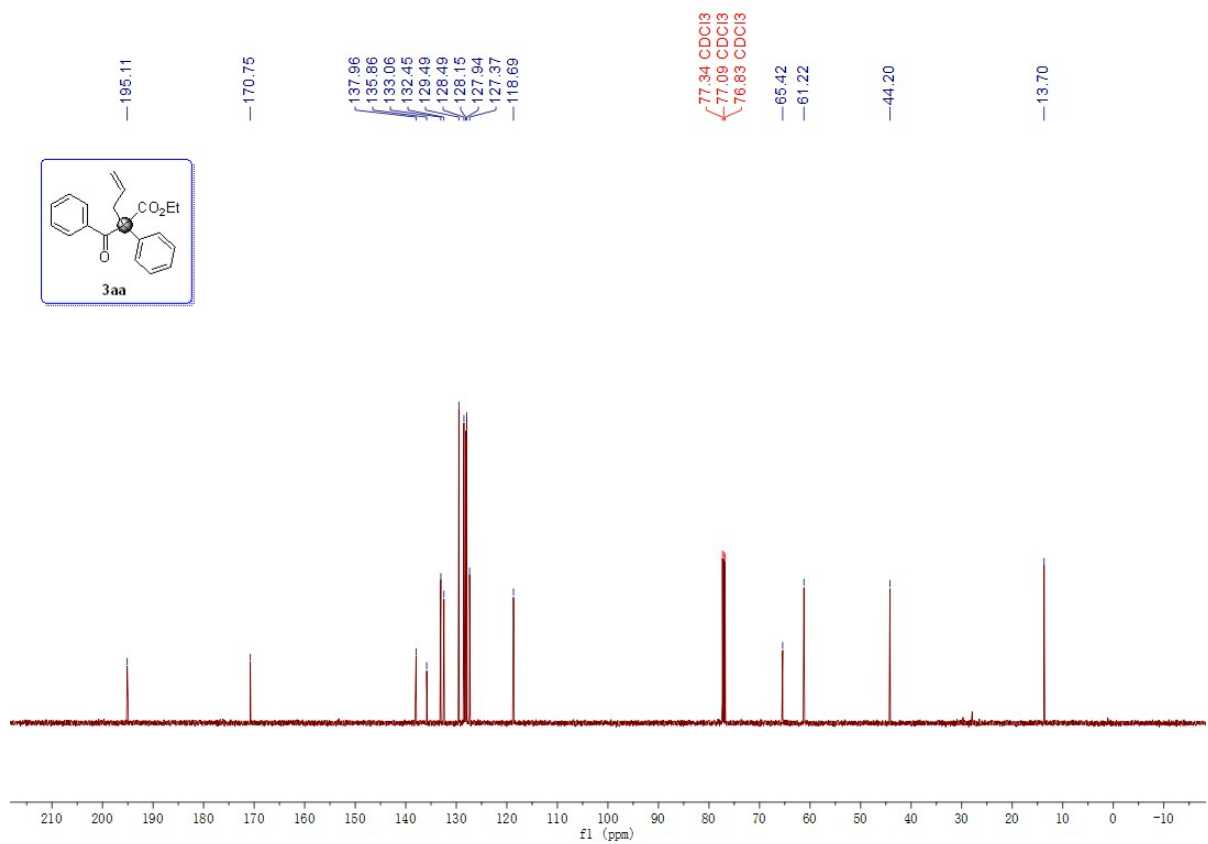
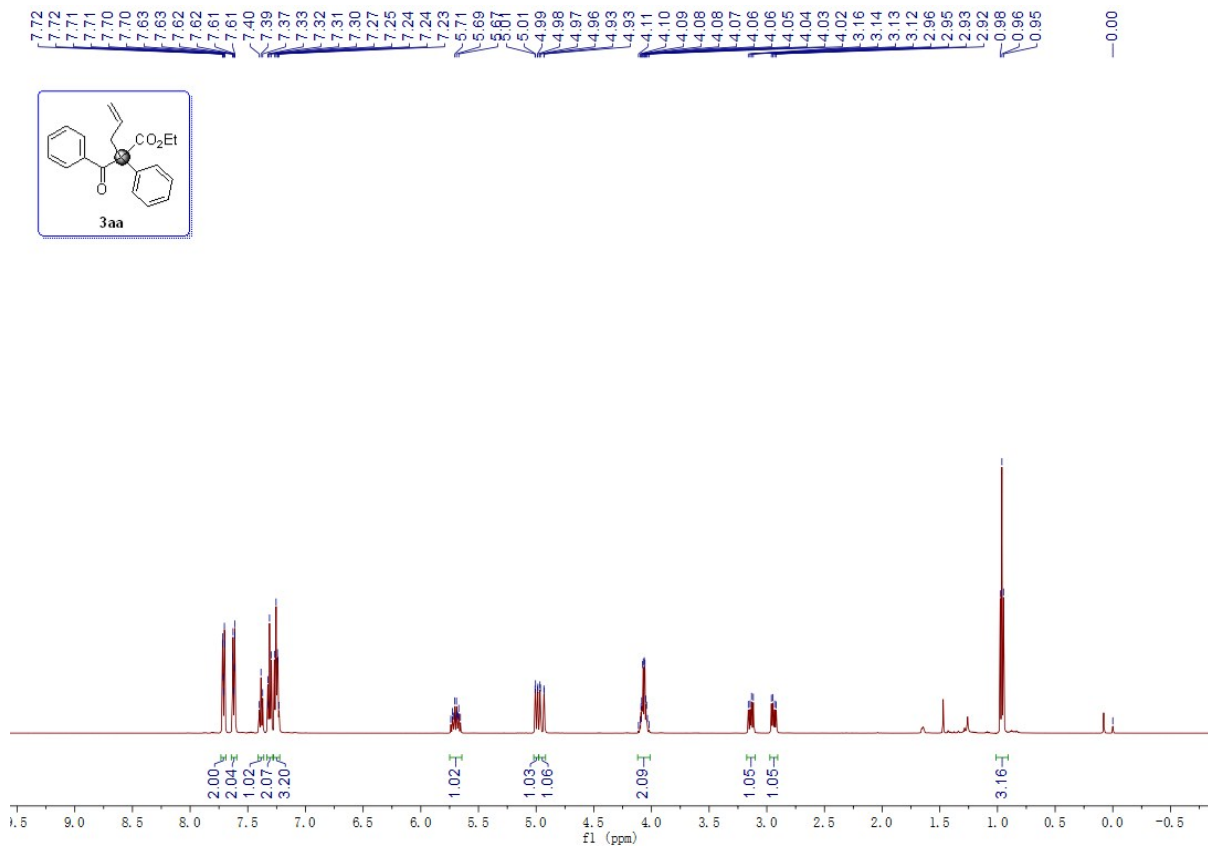
29.08
21.86
14.42

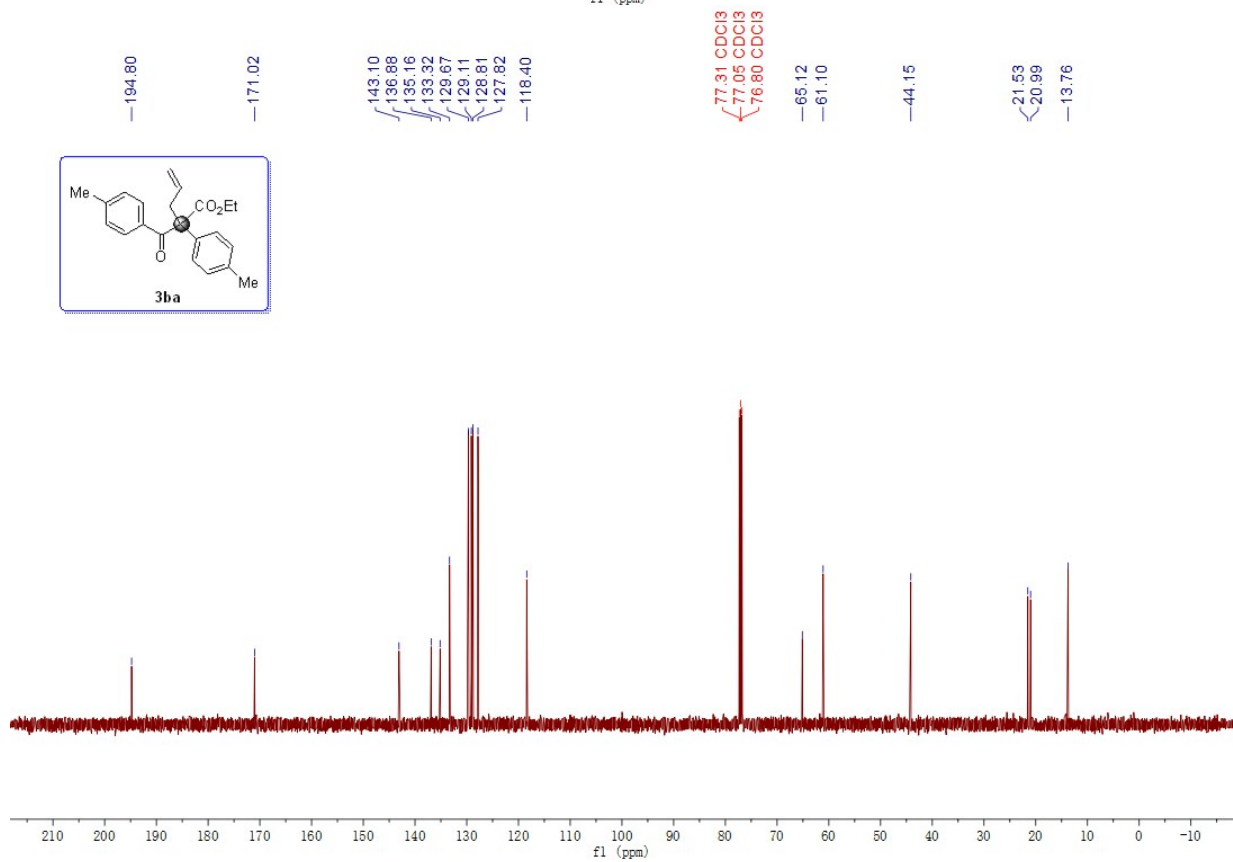
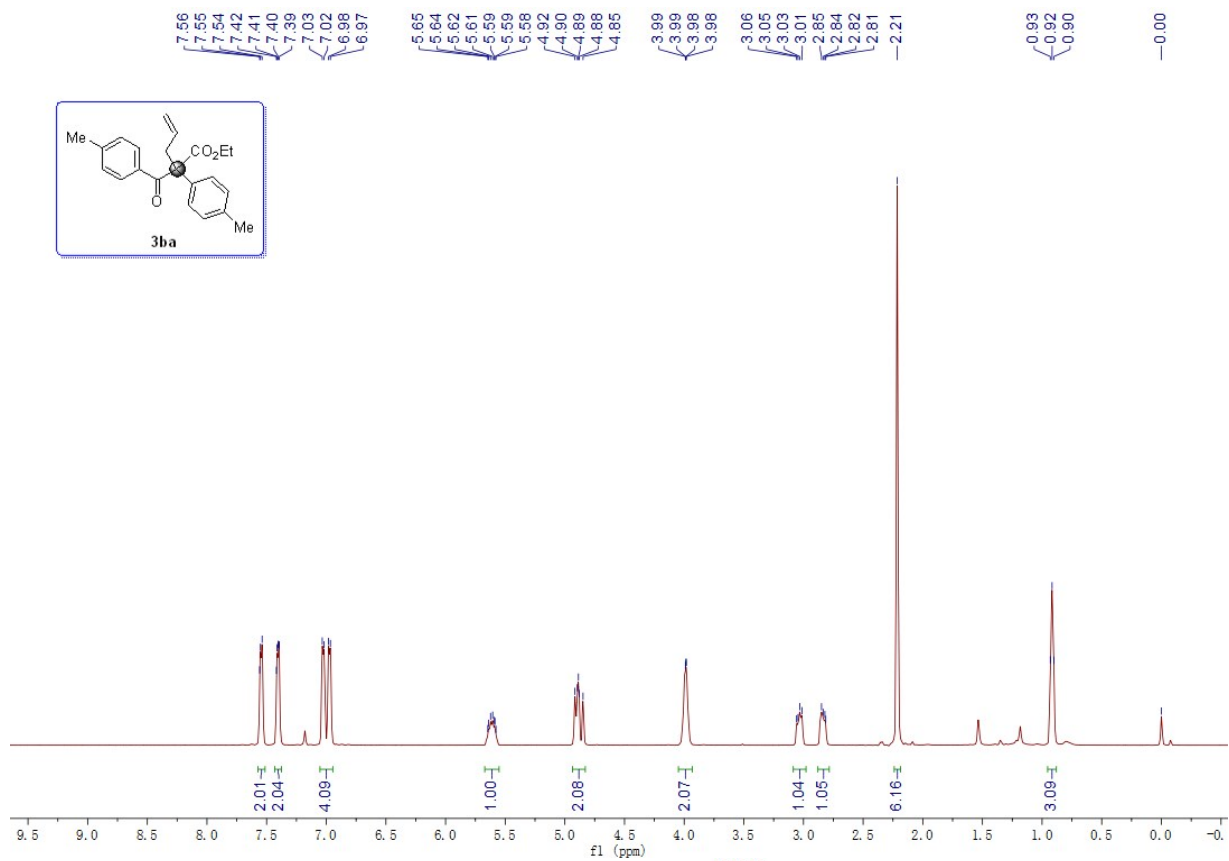


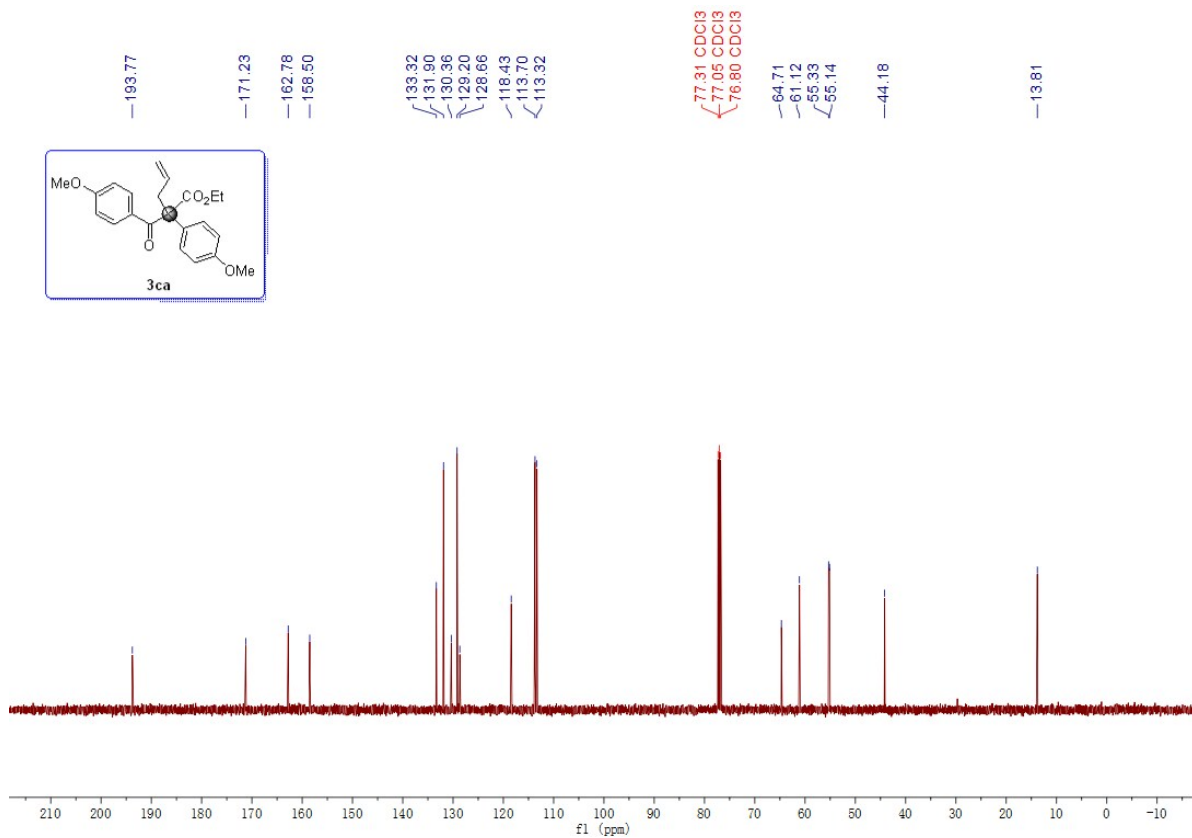
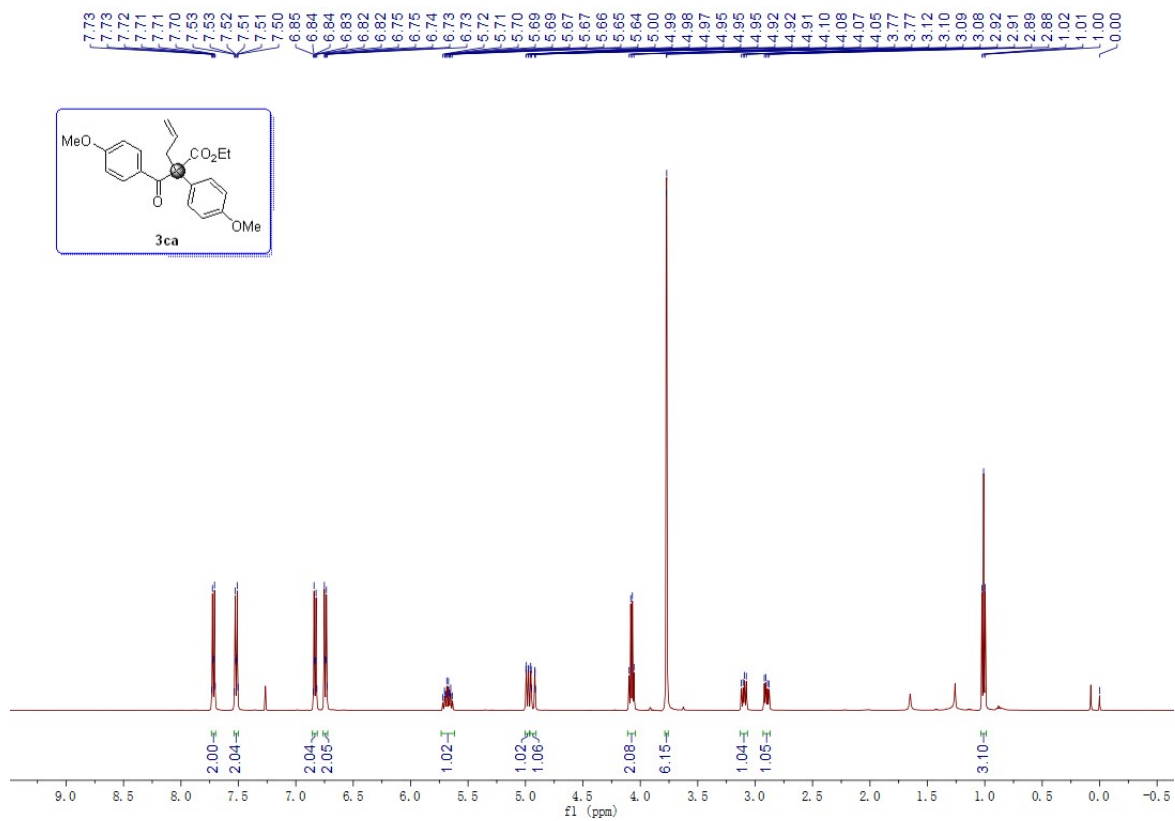


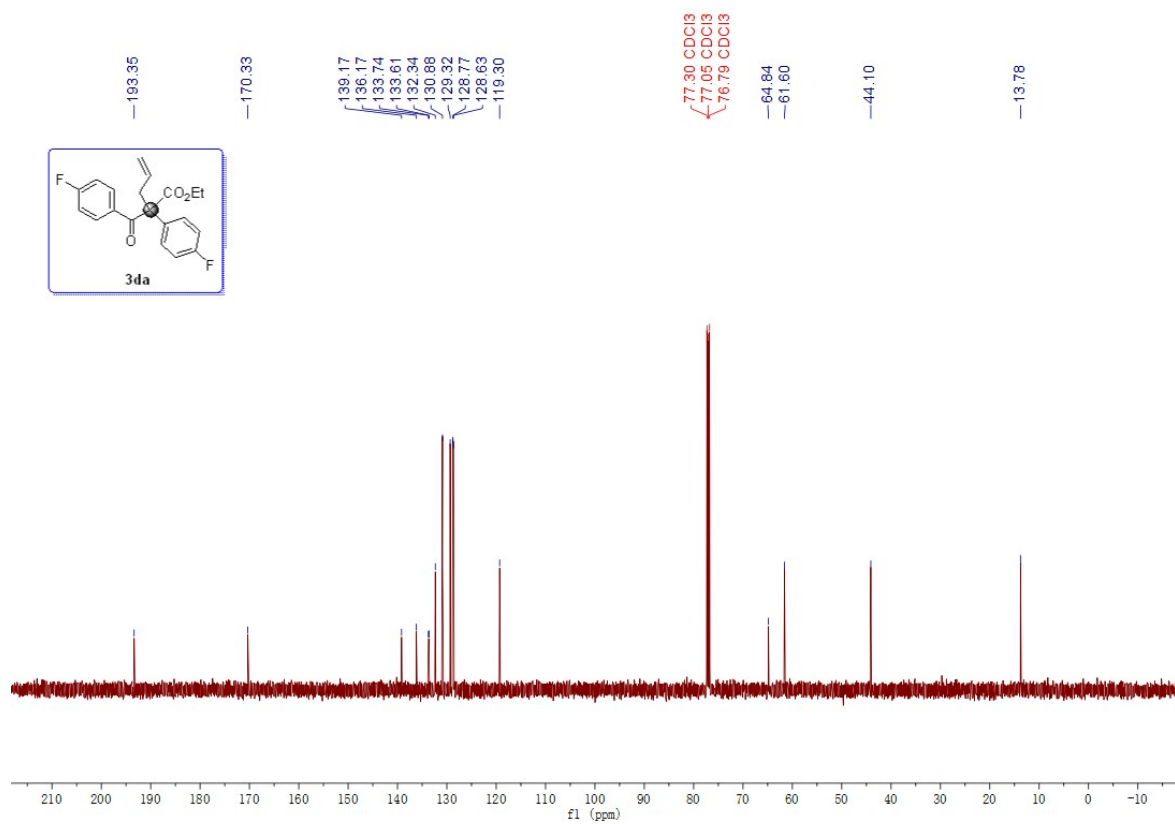
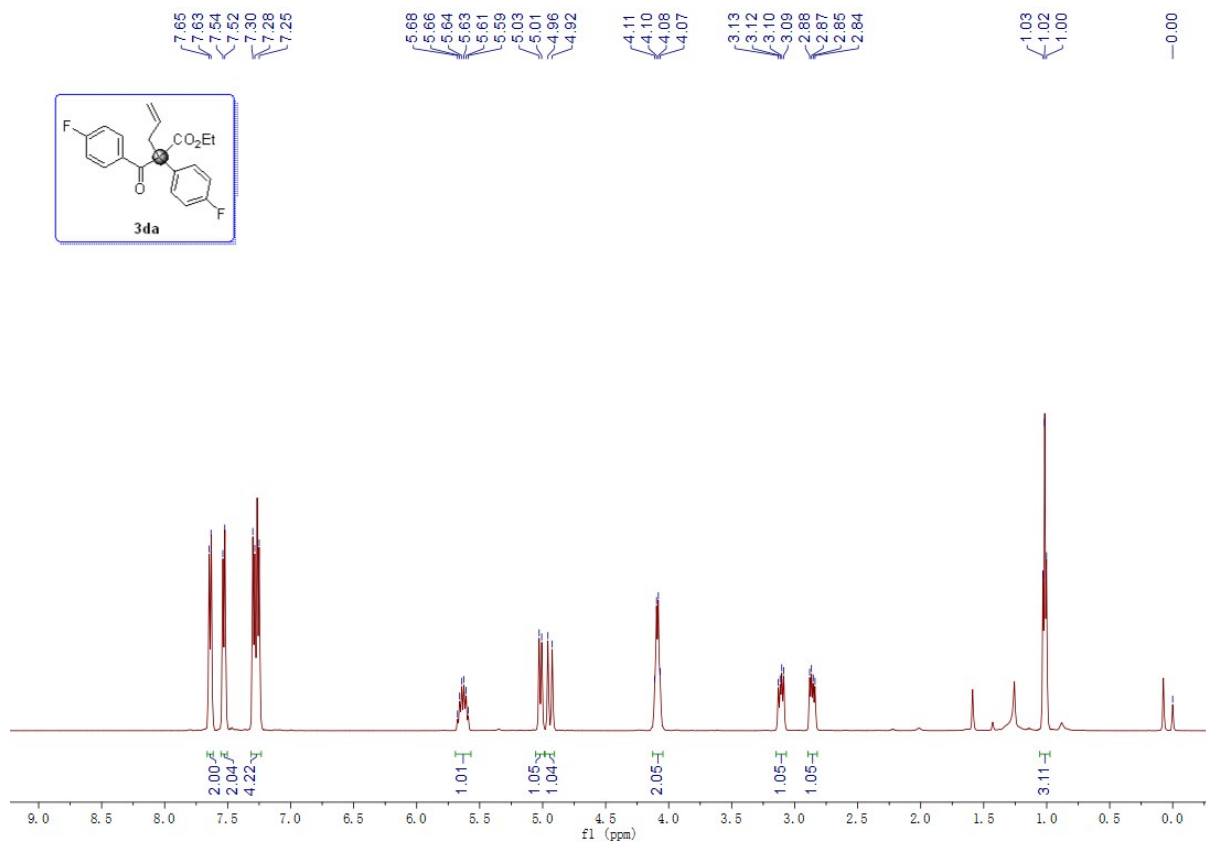
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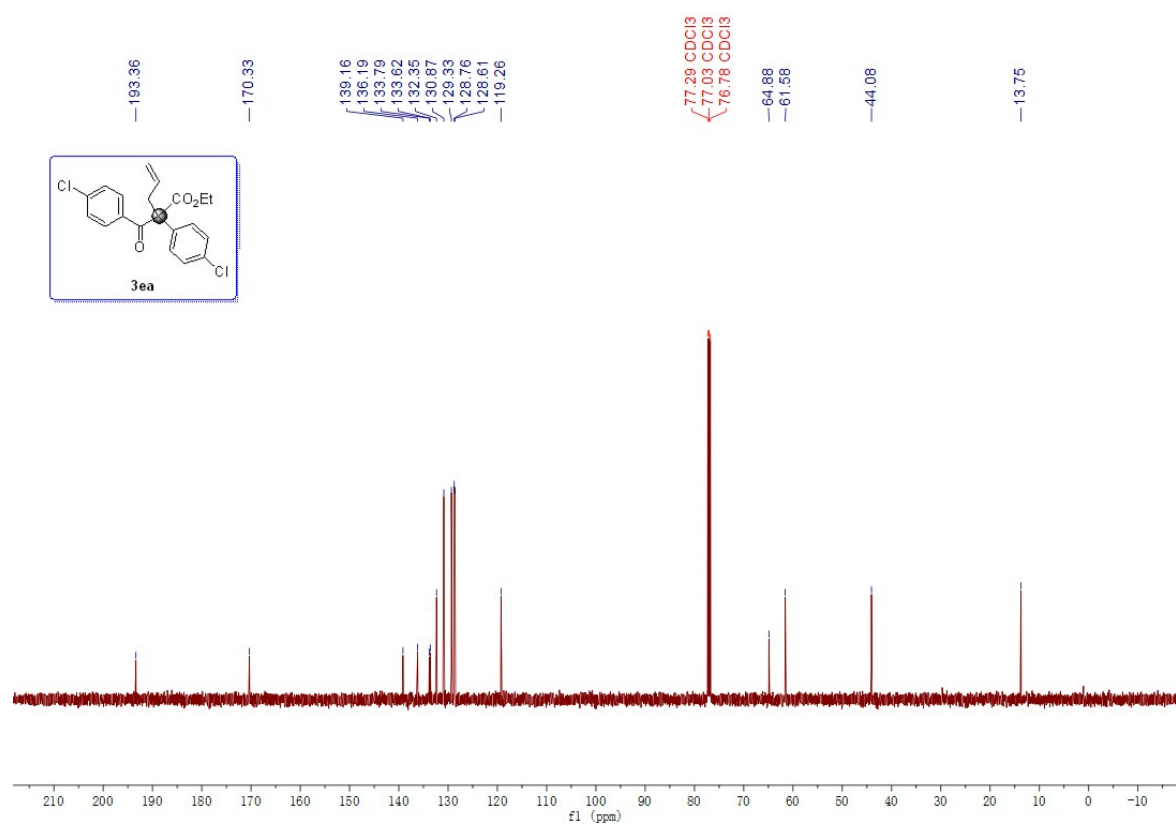
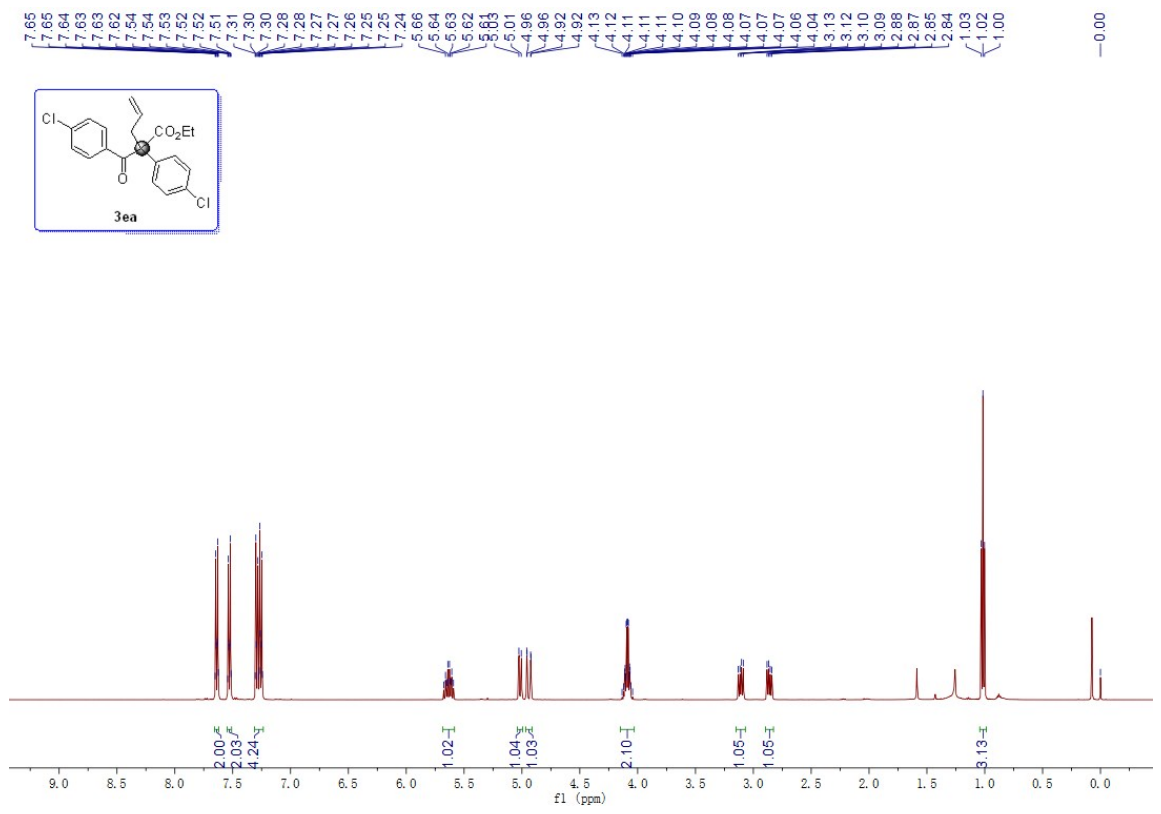


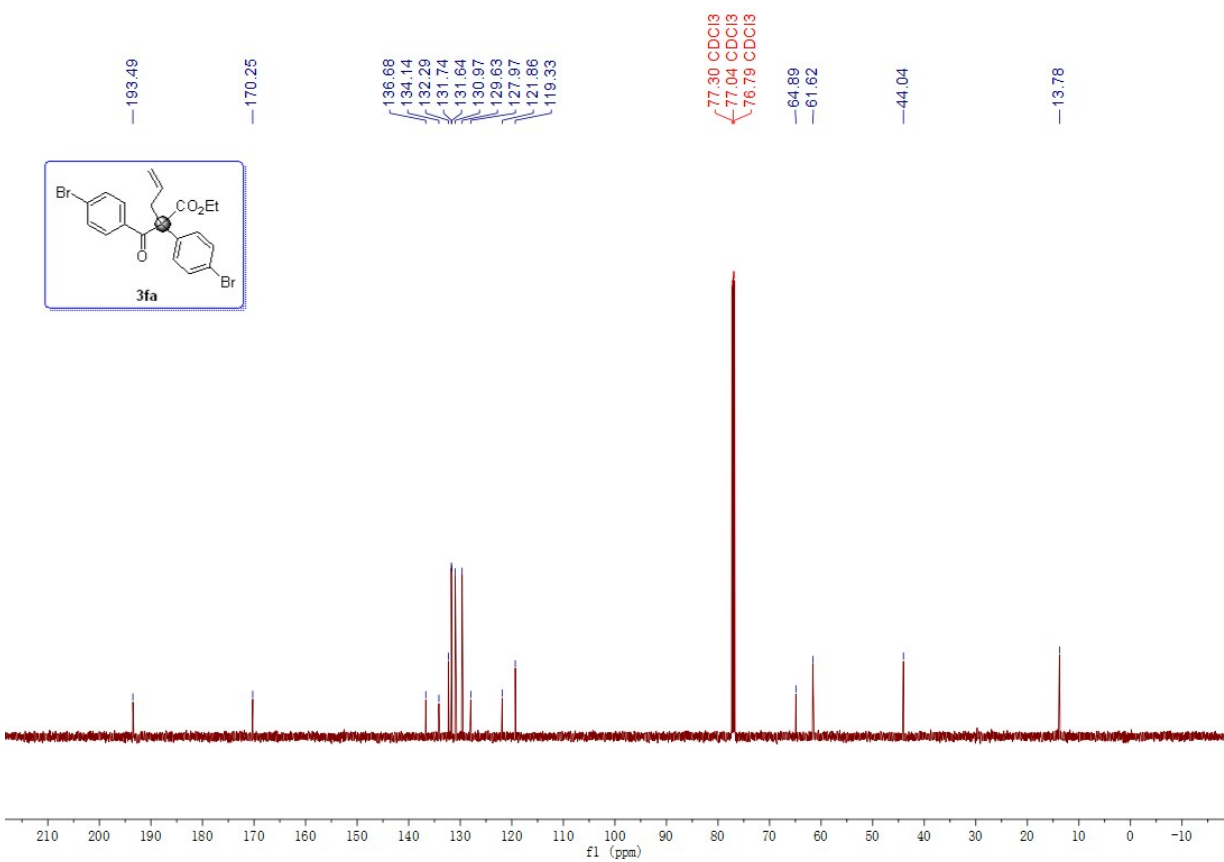
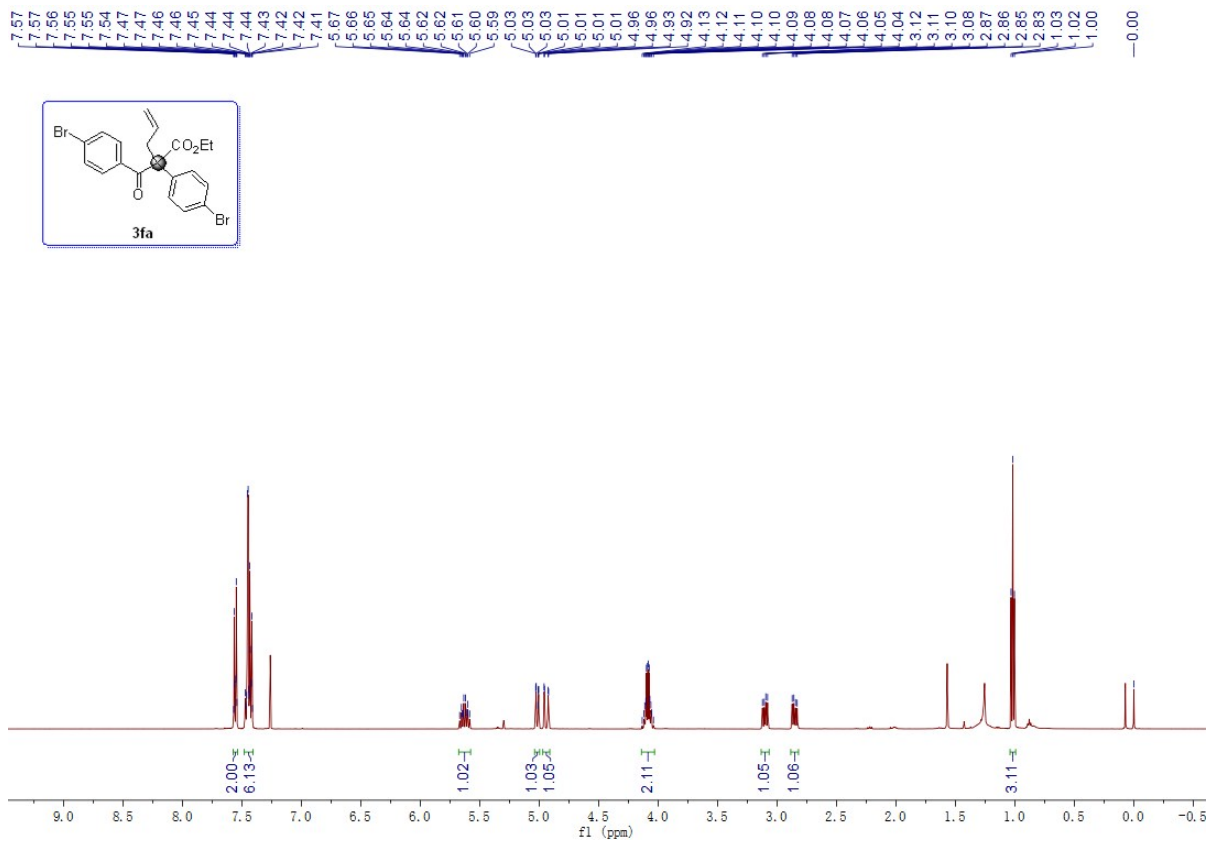


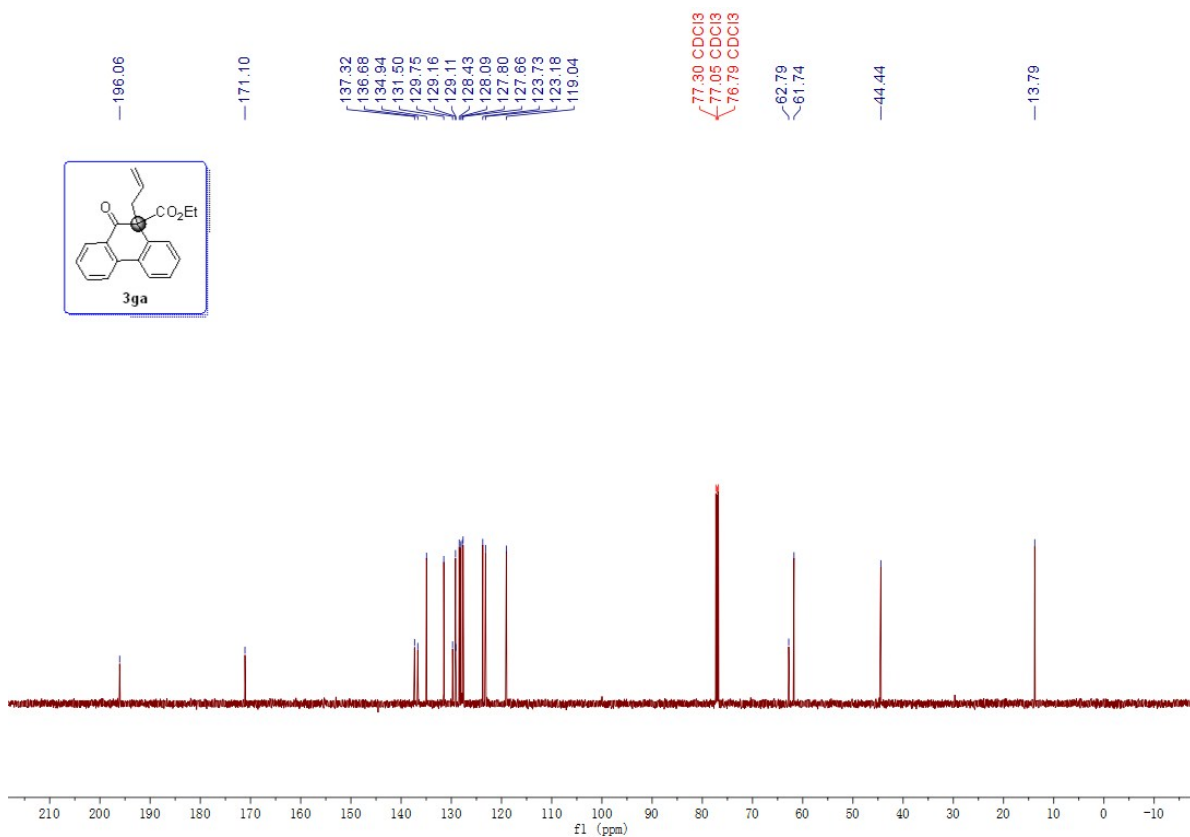
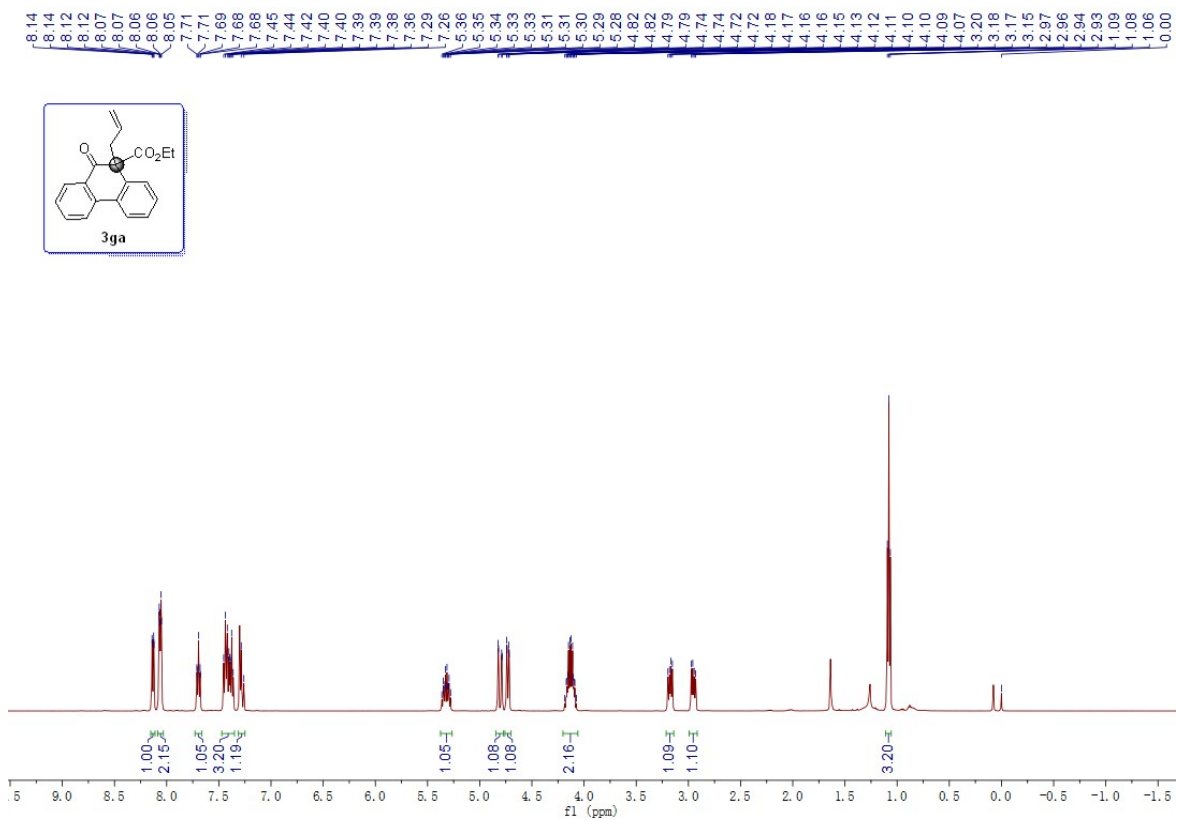




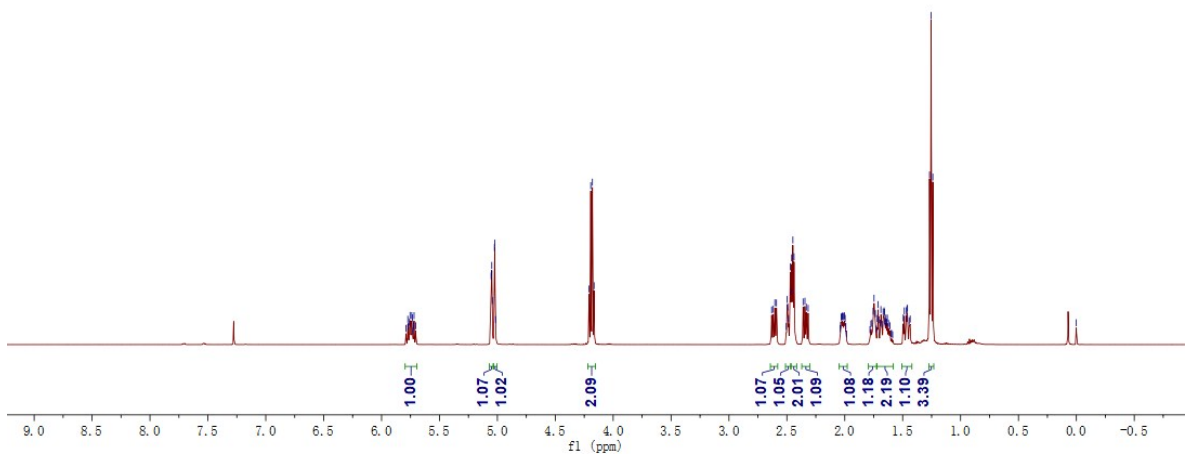
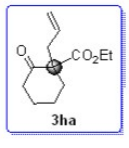




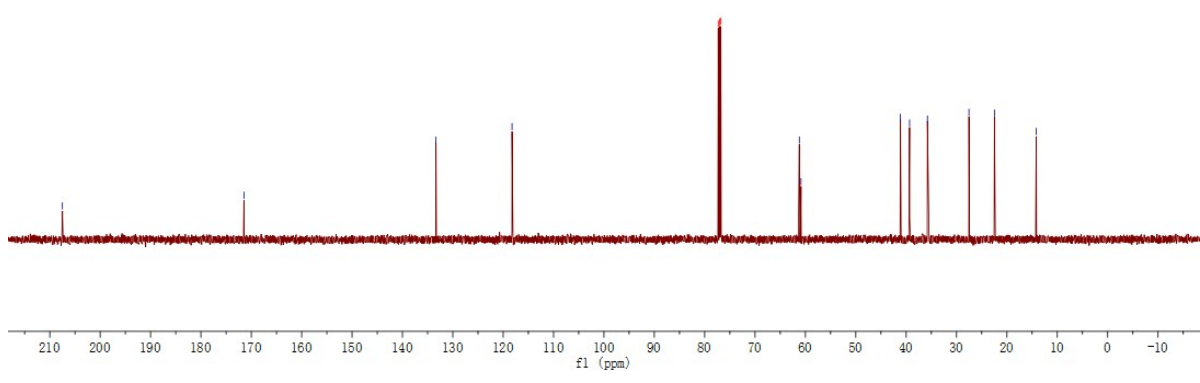
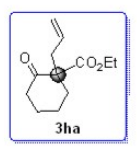


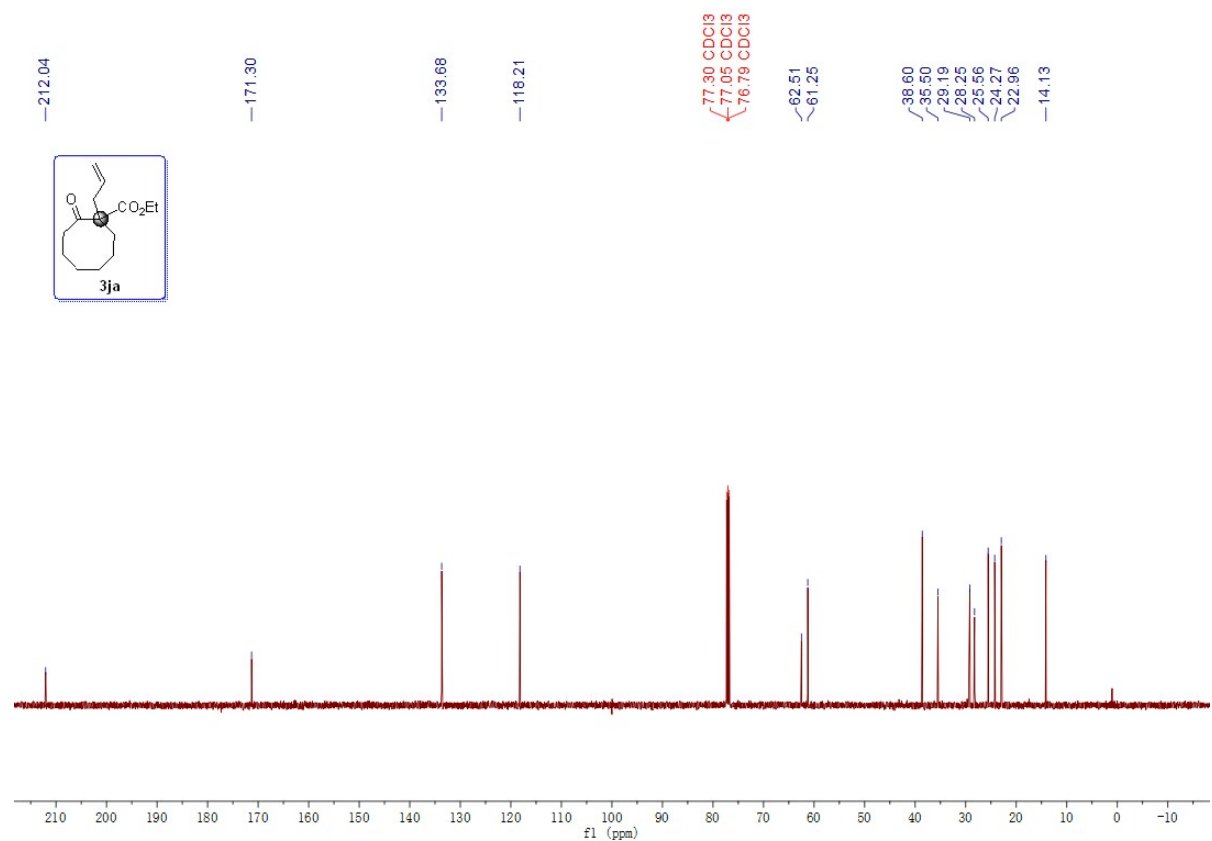
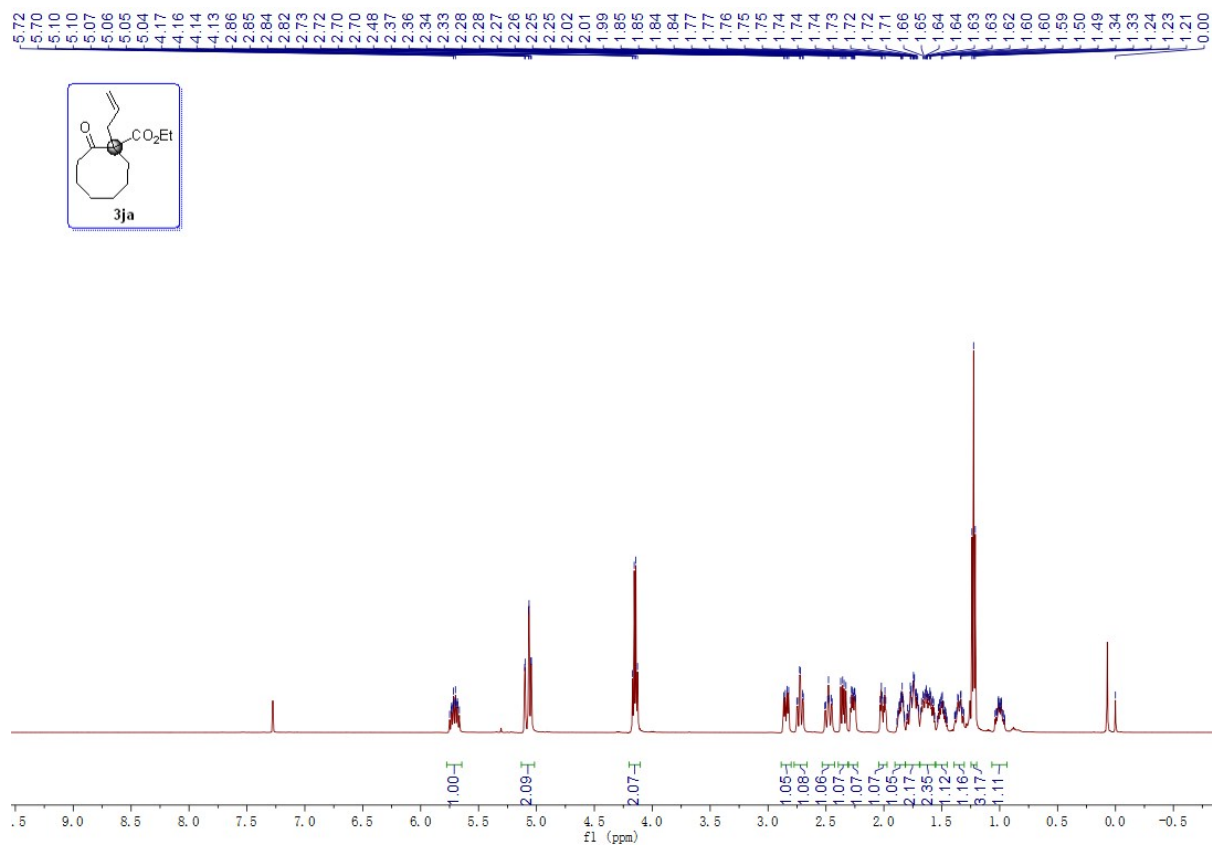


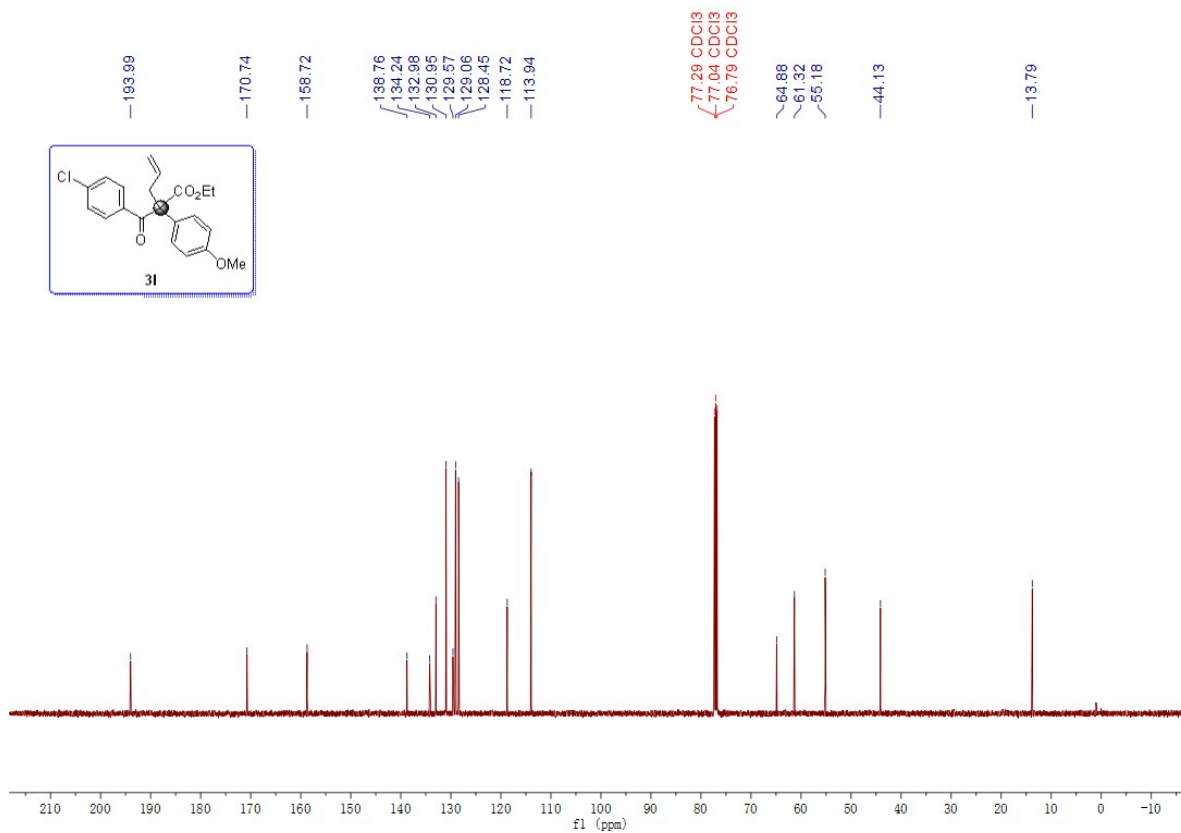
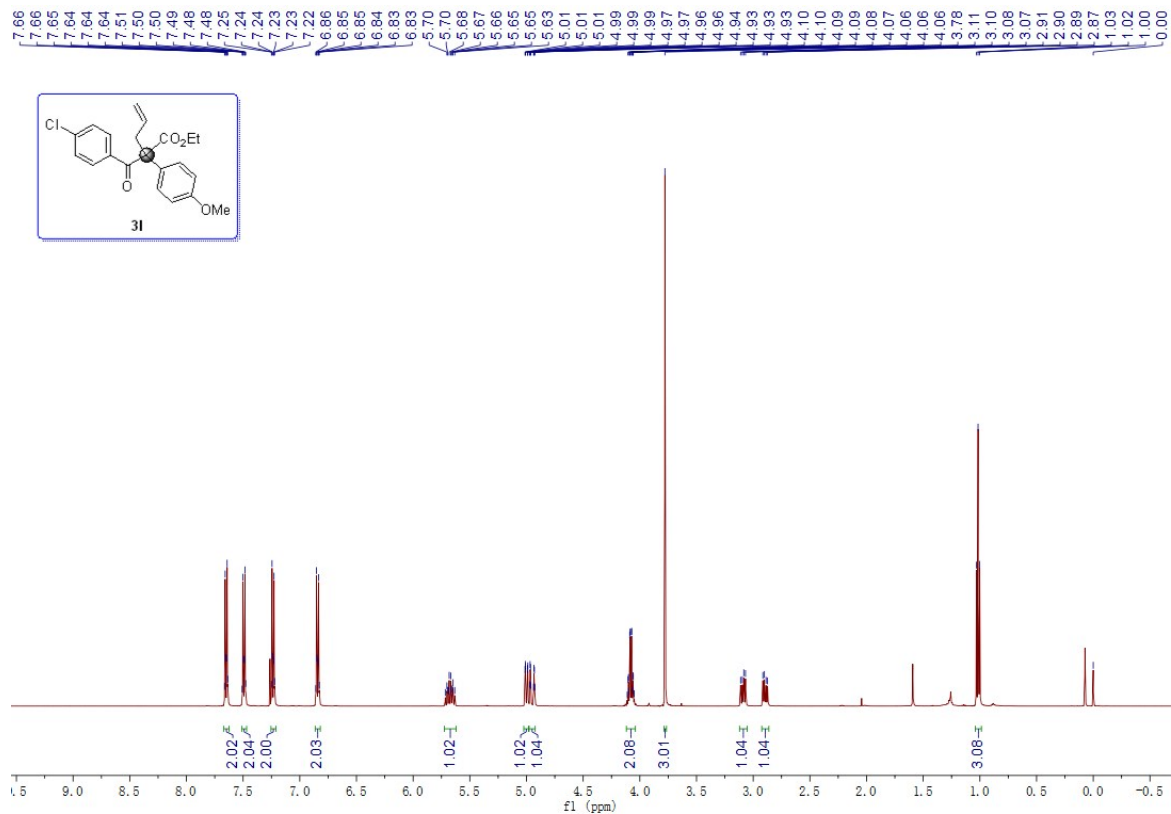
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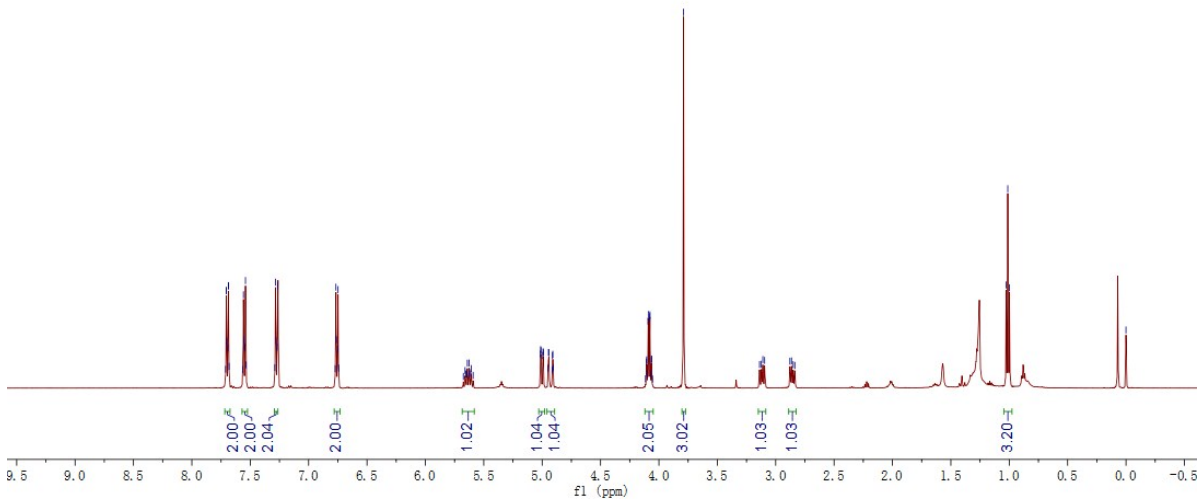
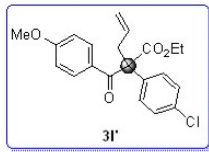
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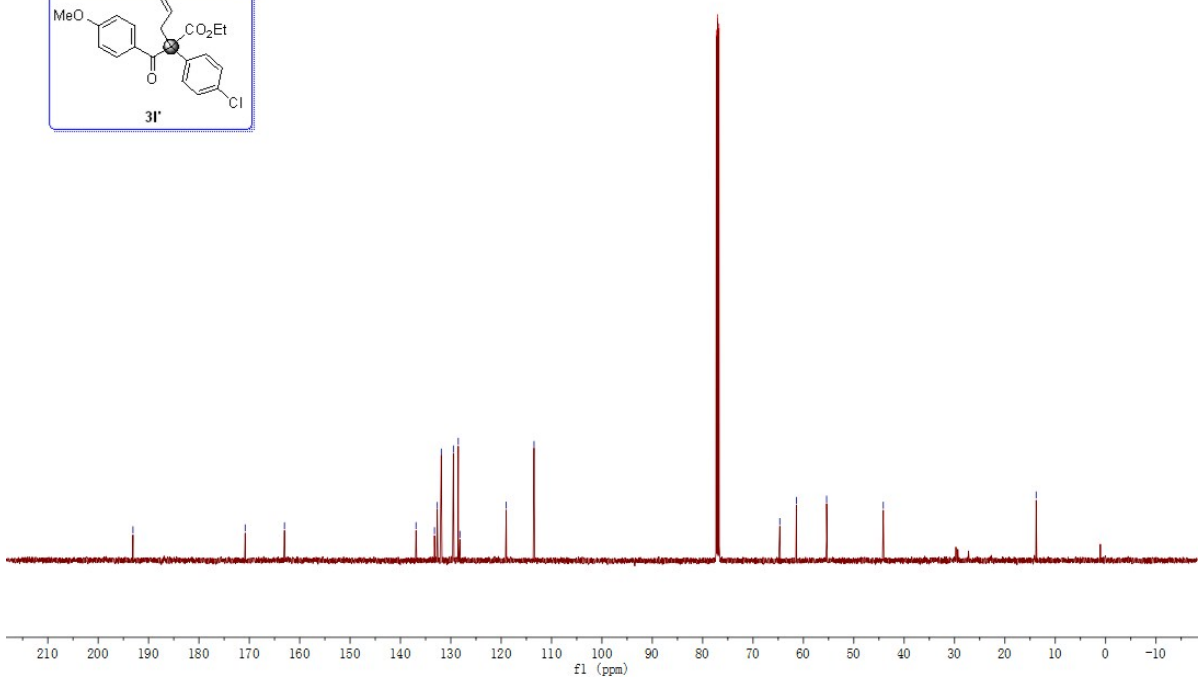
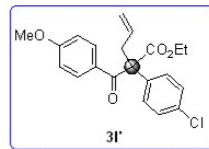


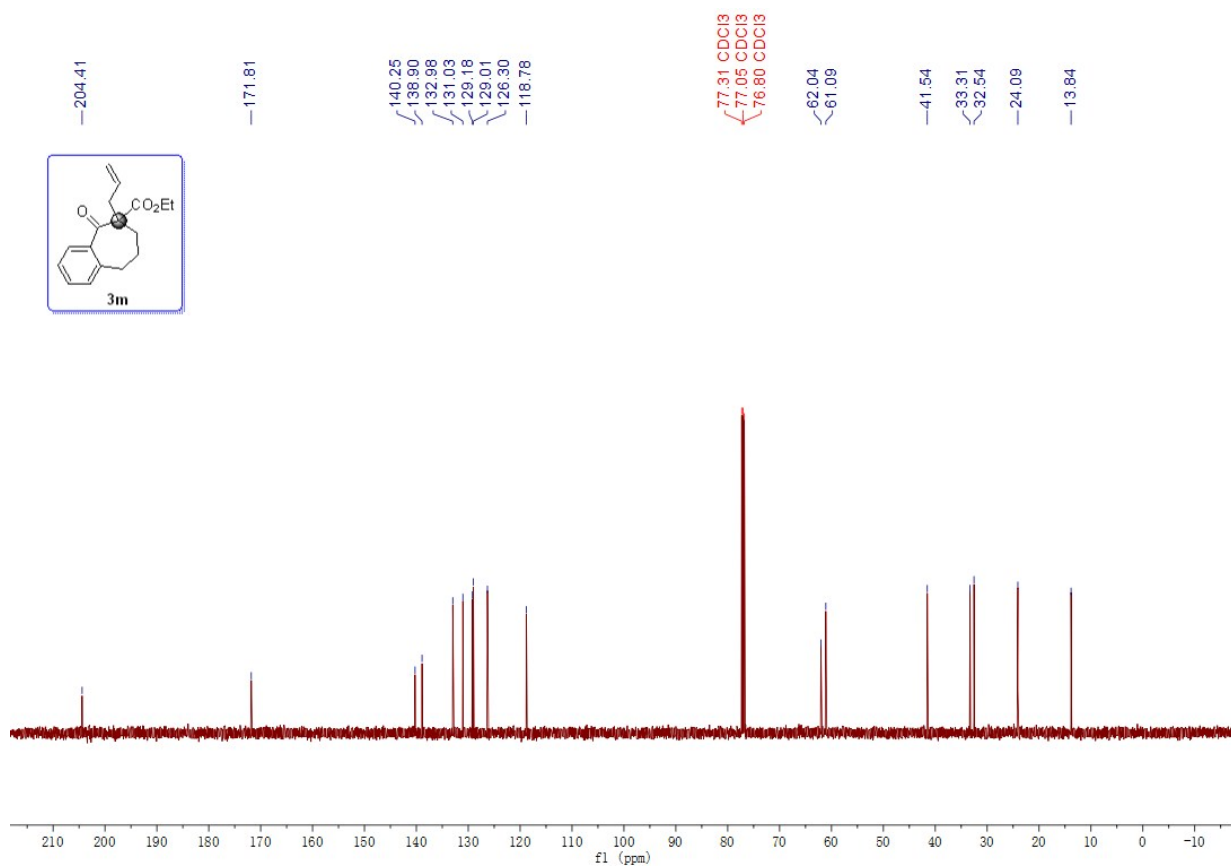
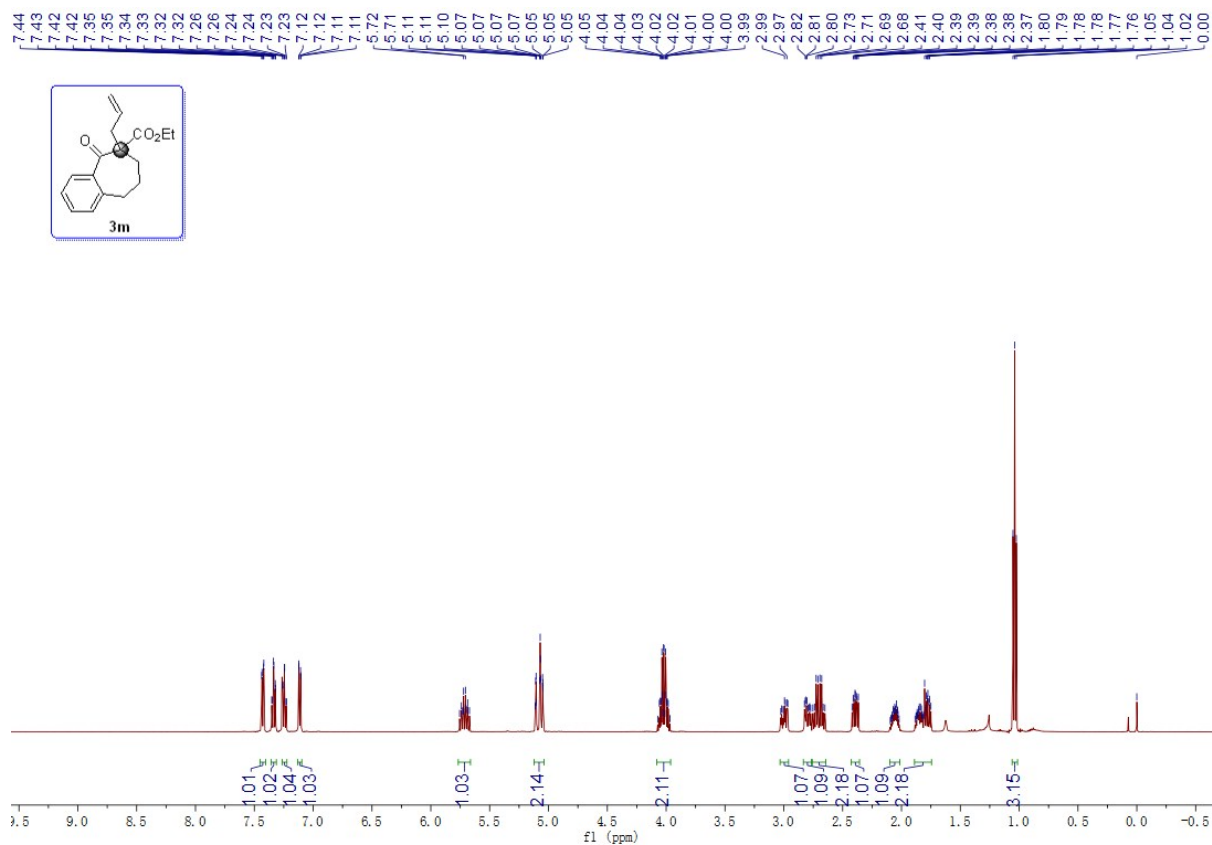


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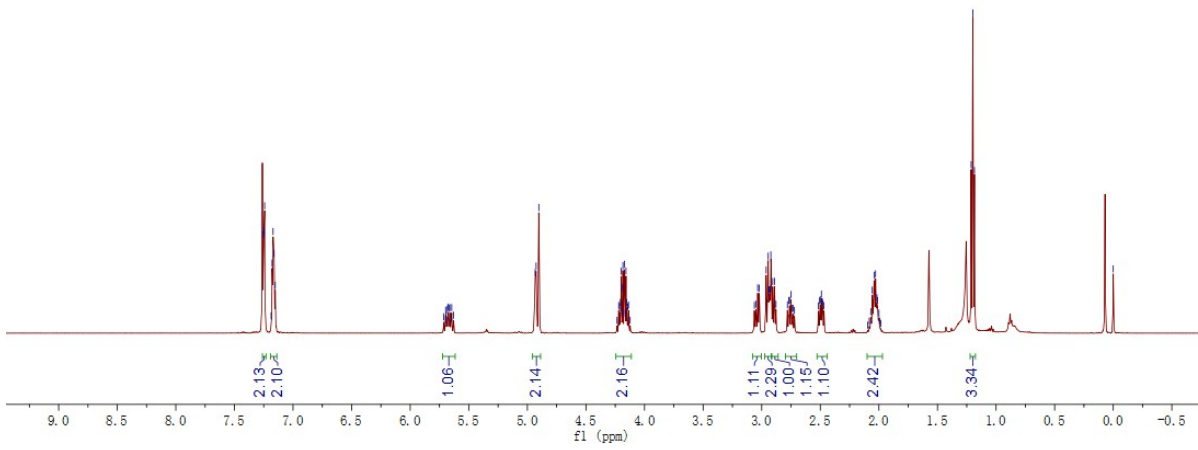
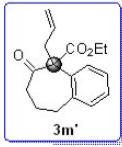


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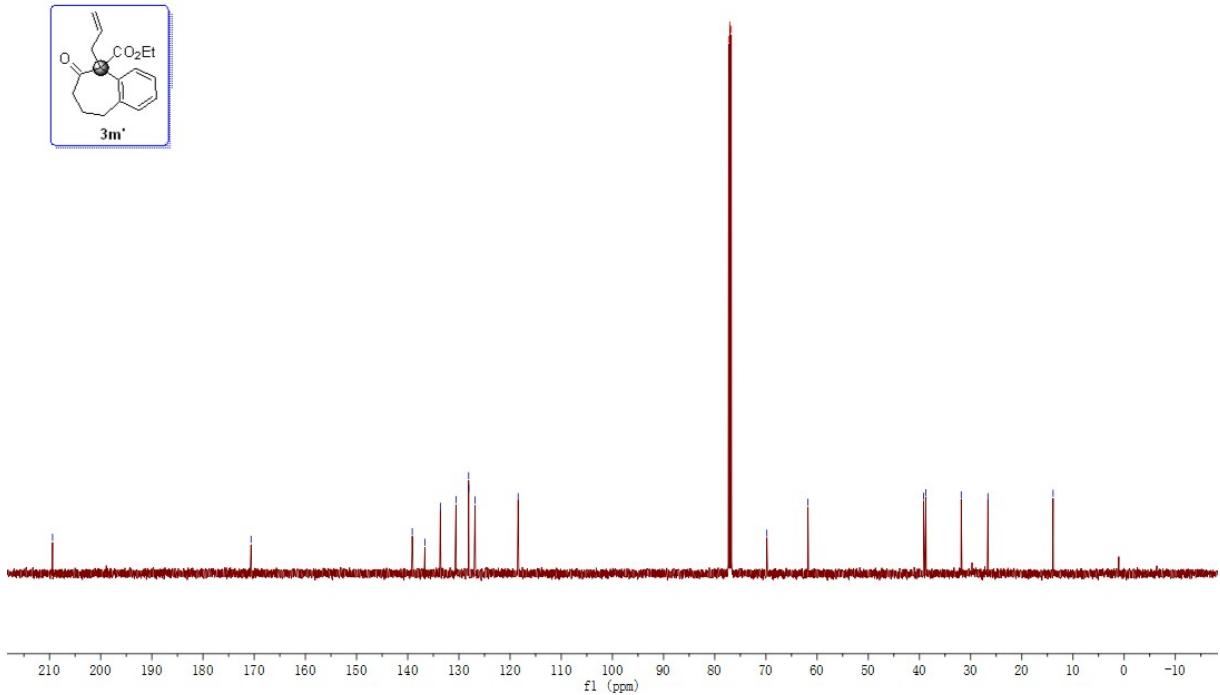
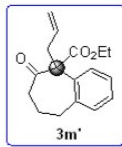
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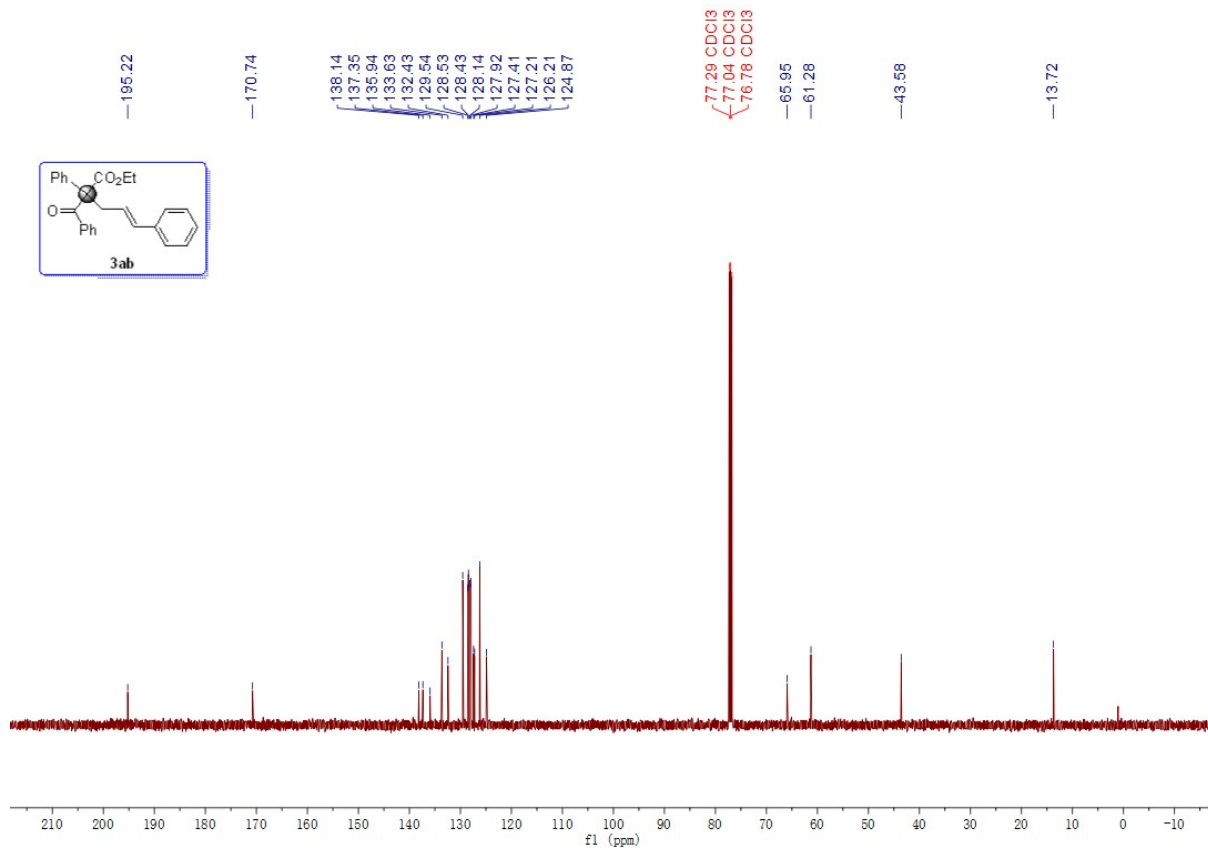
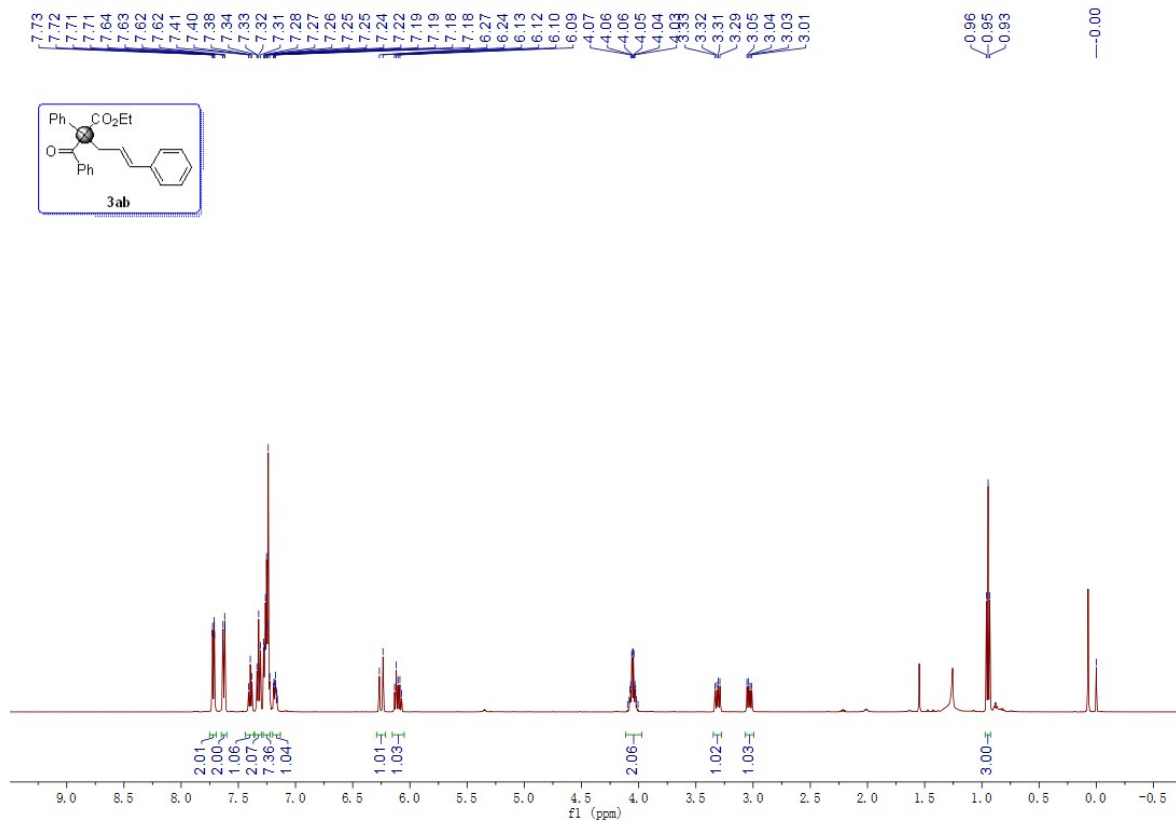
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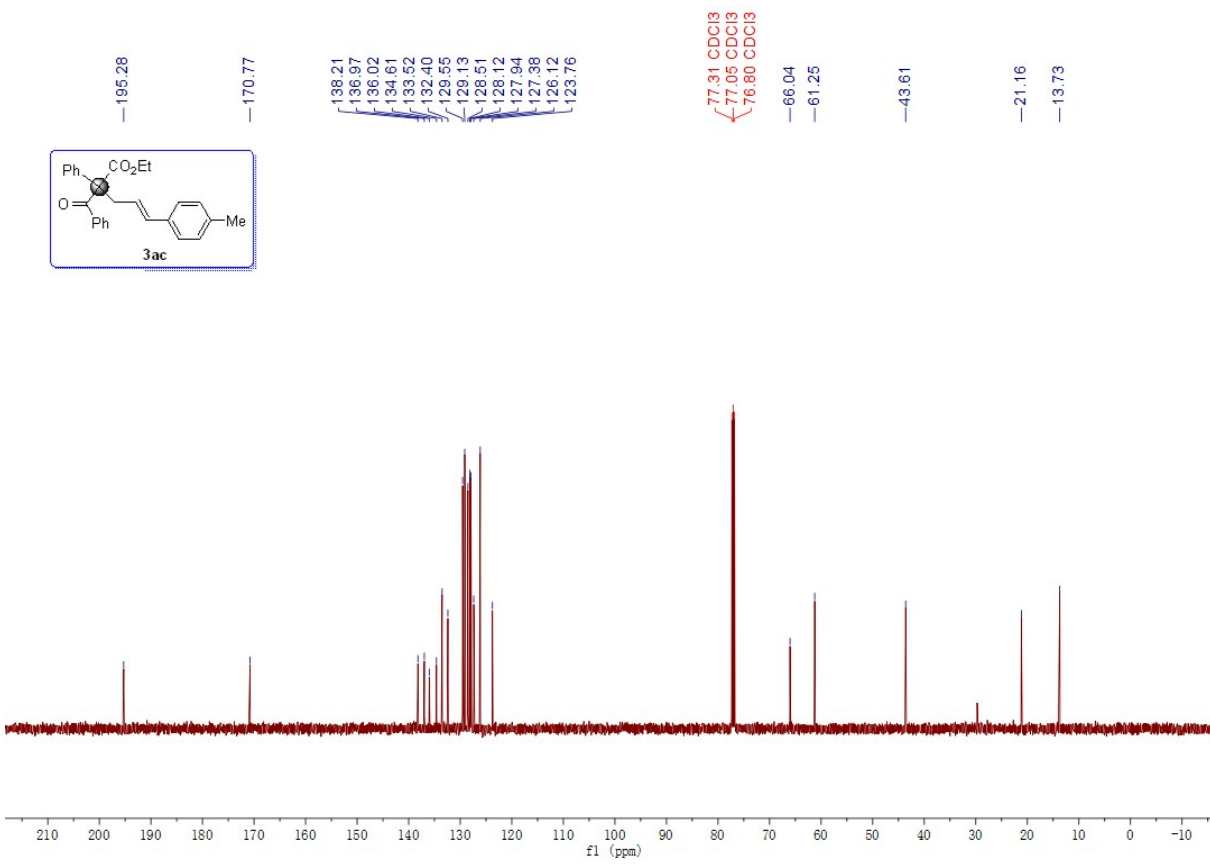
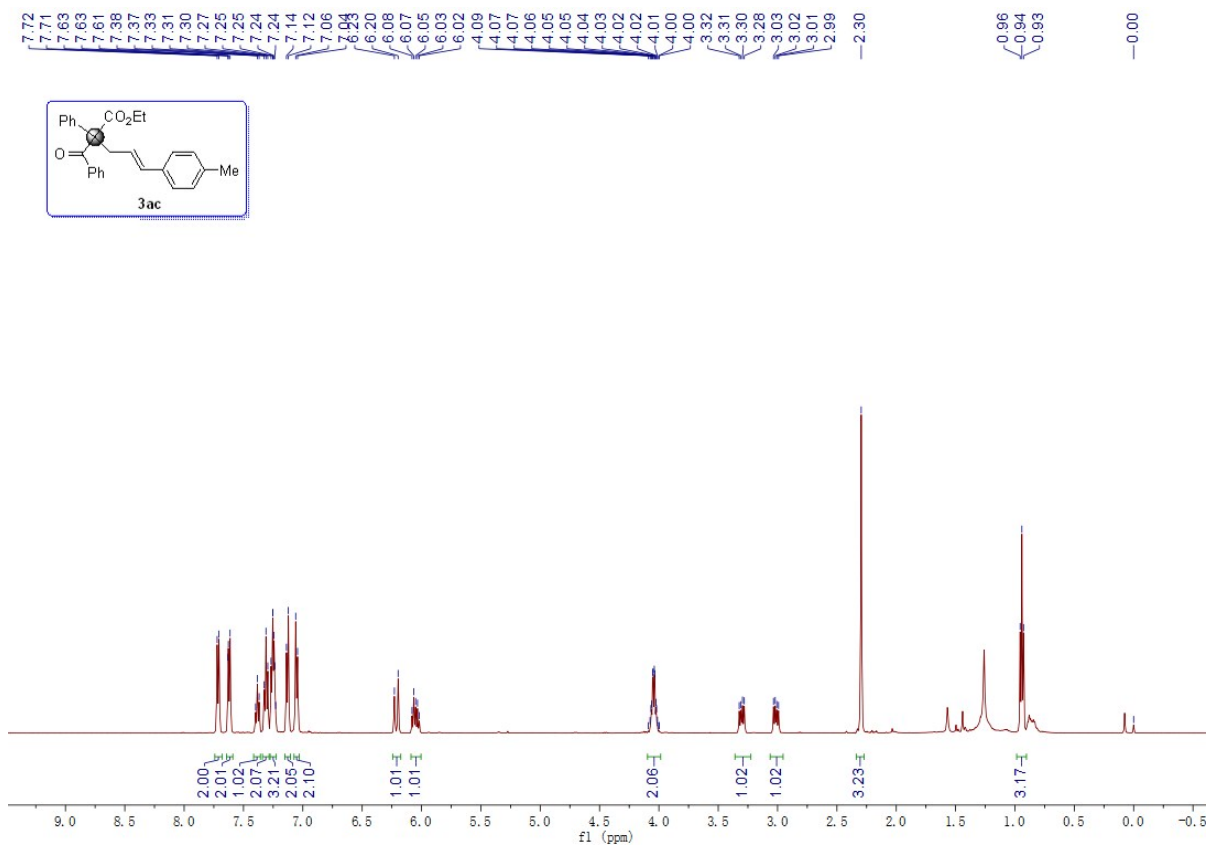
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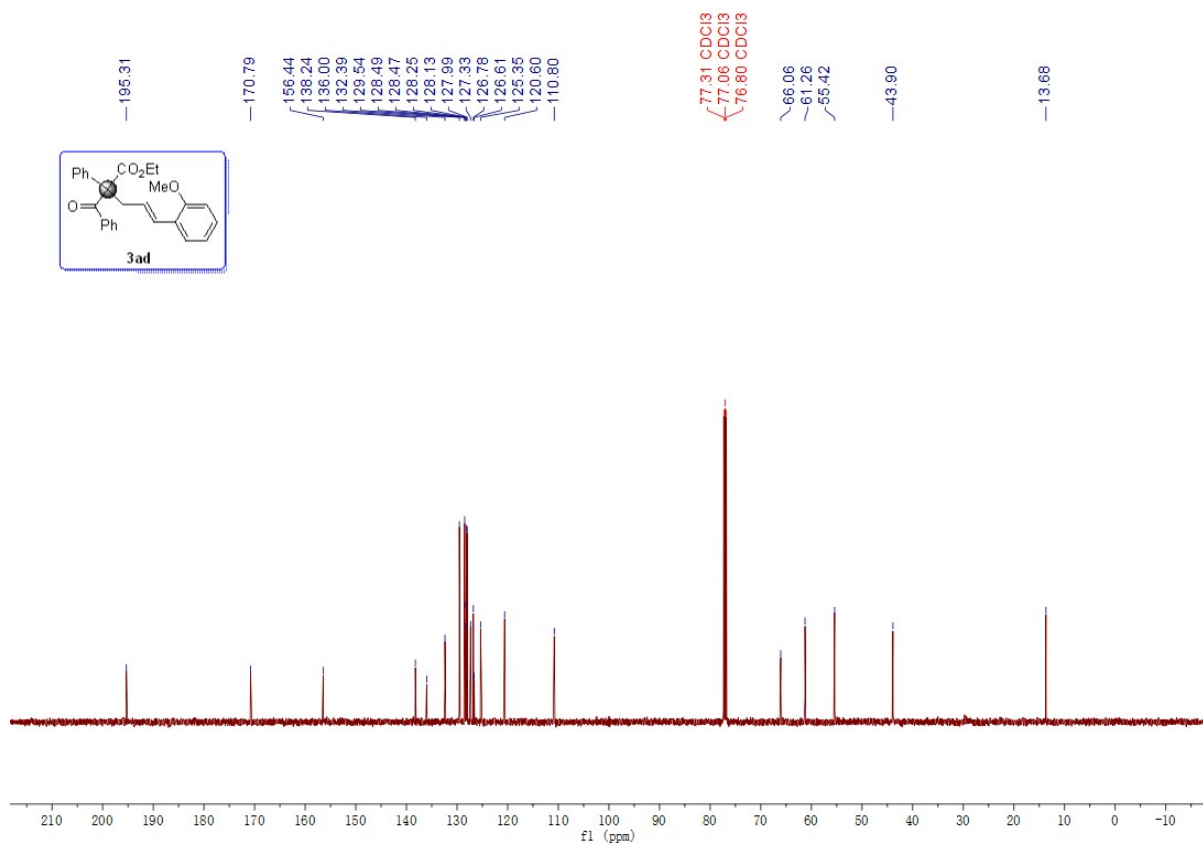
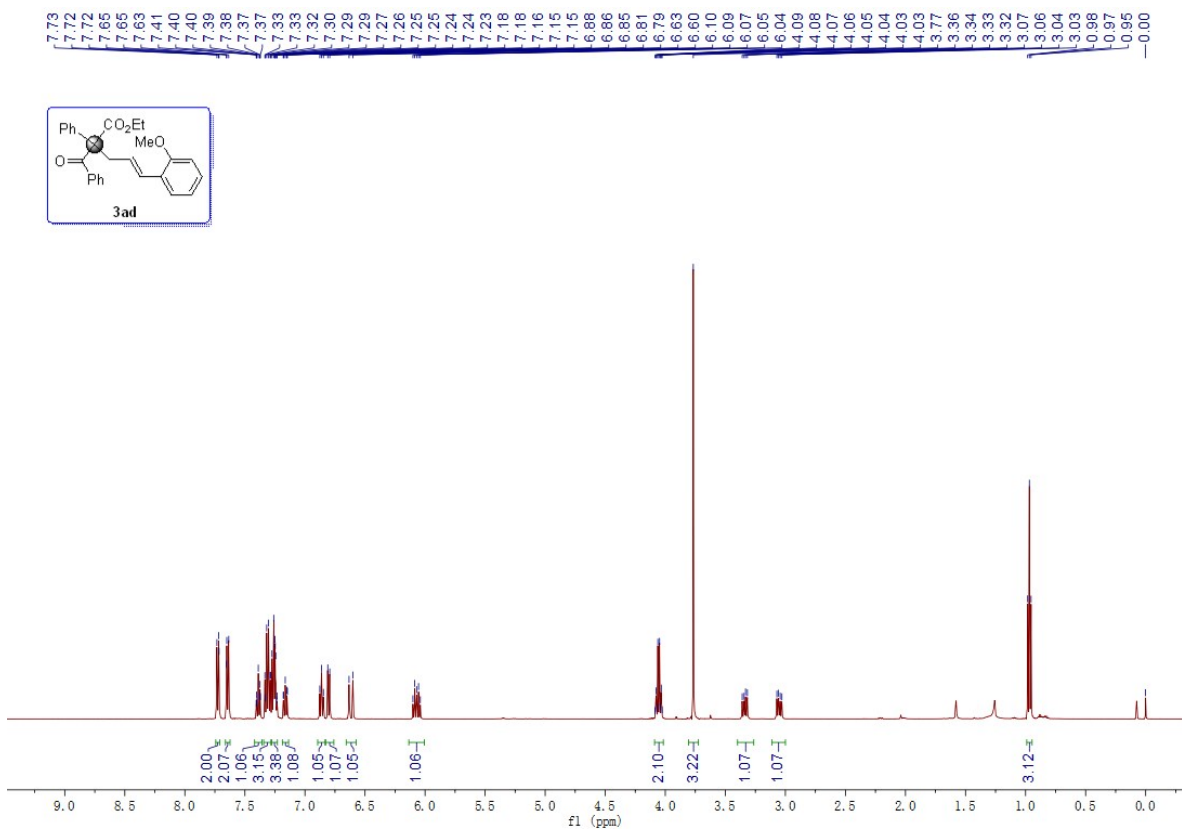
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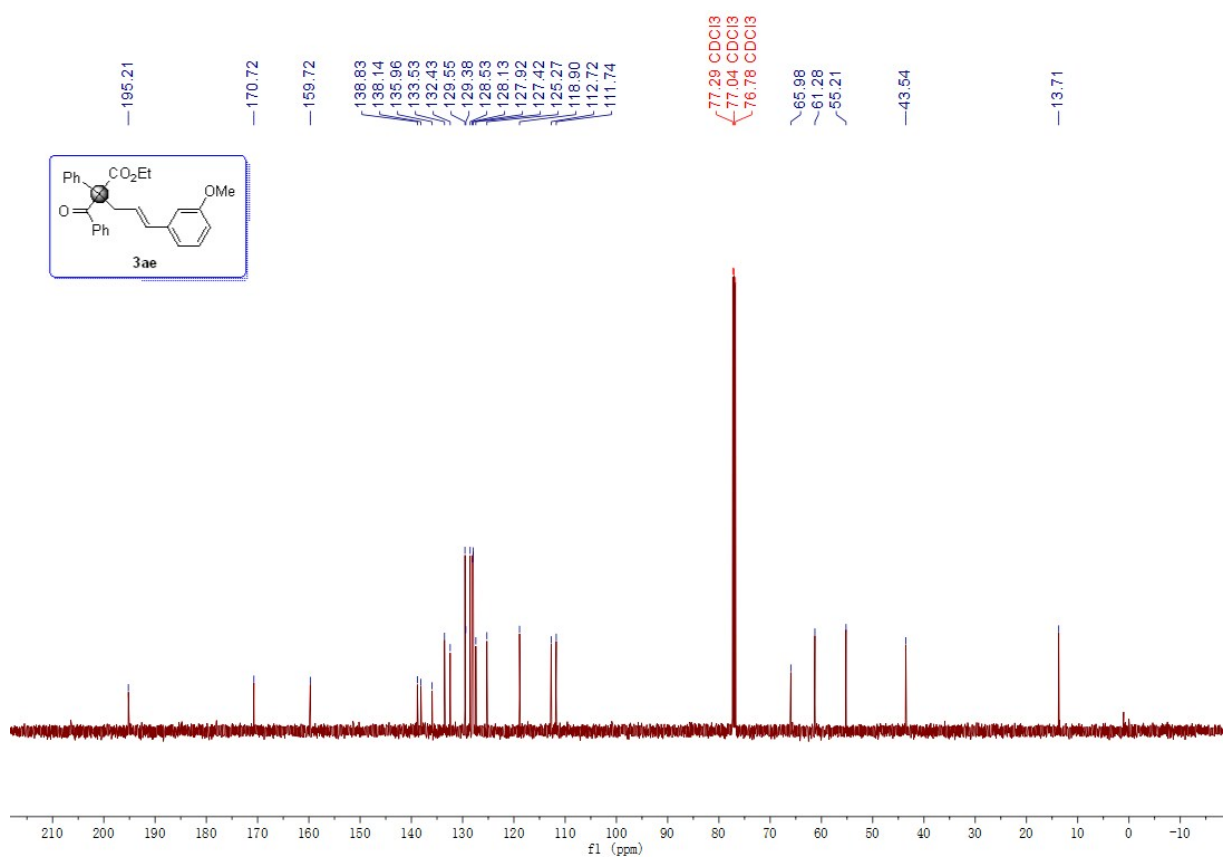
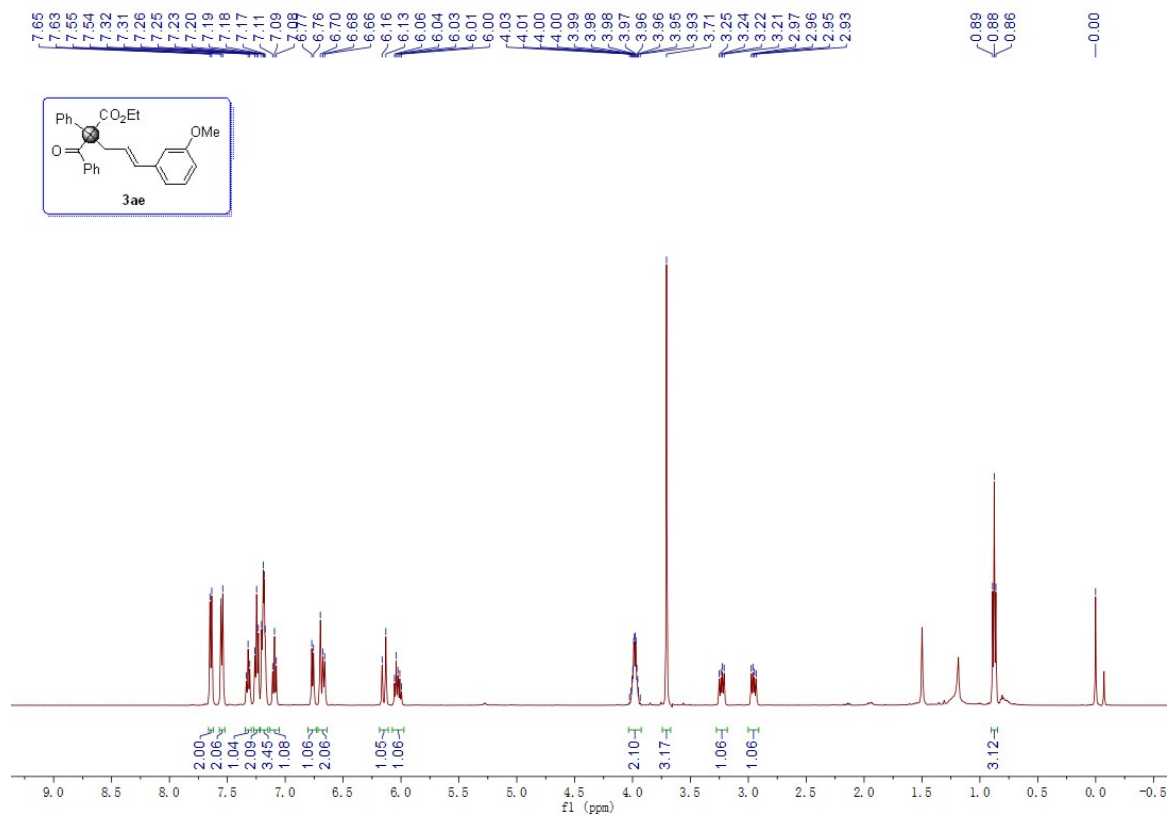
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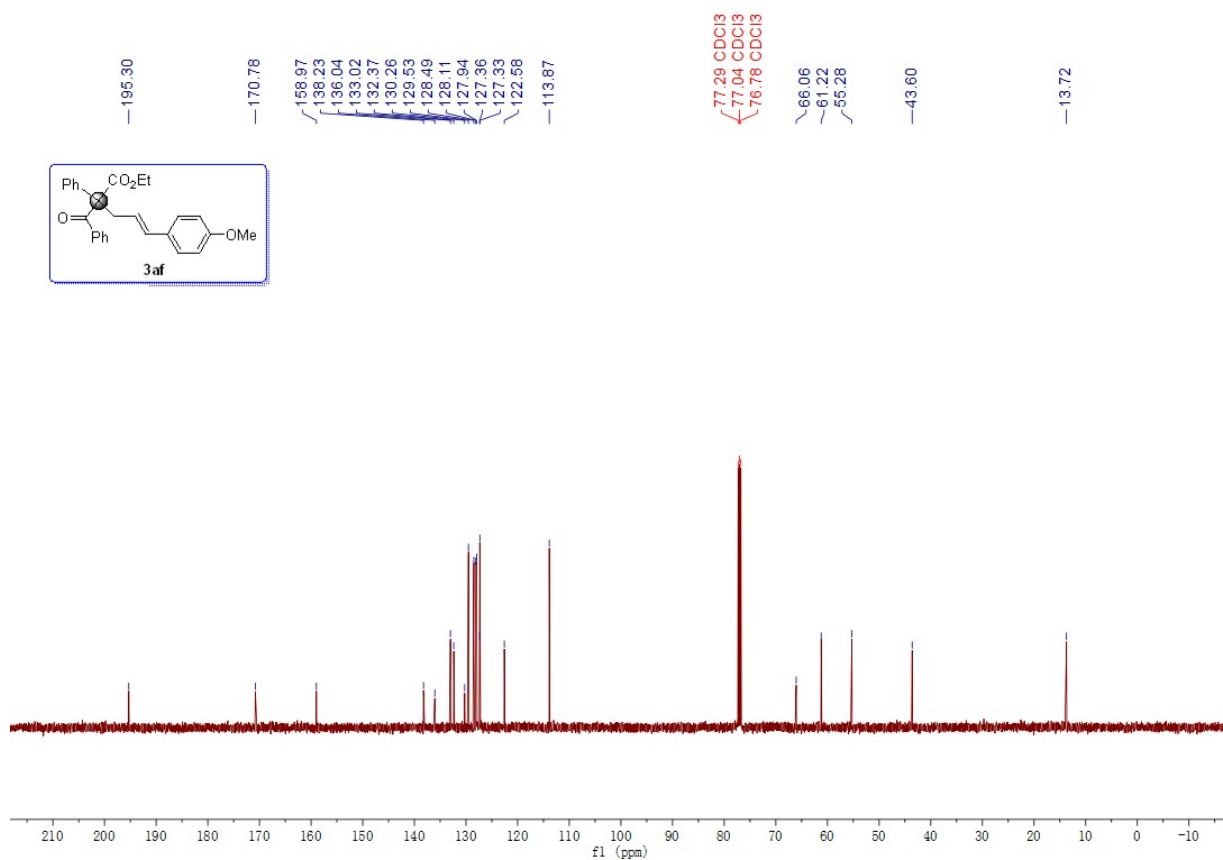
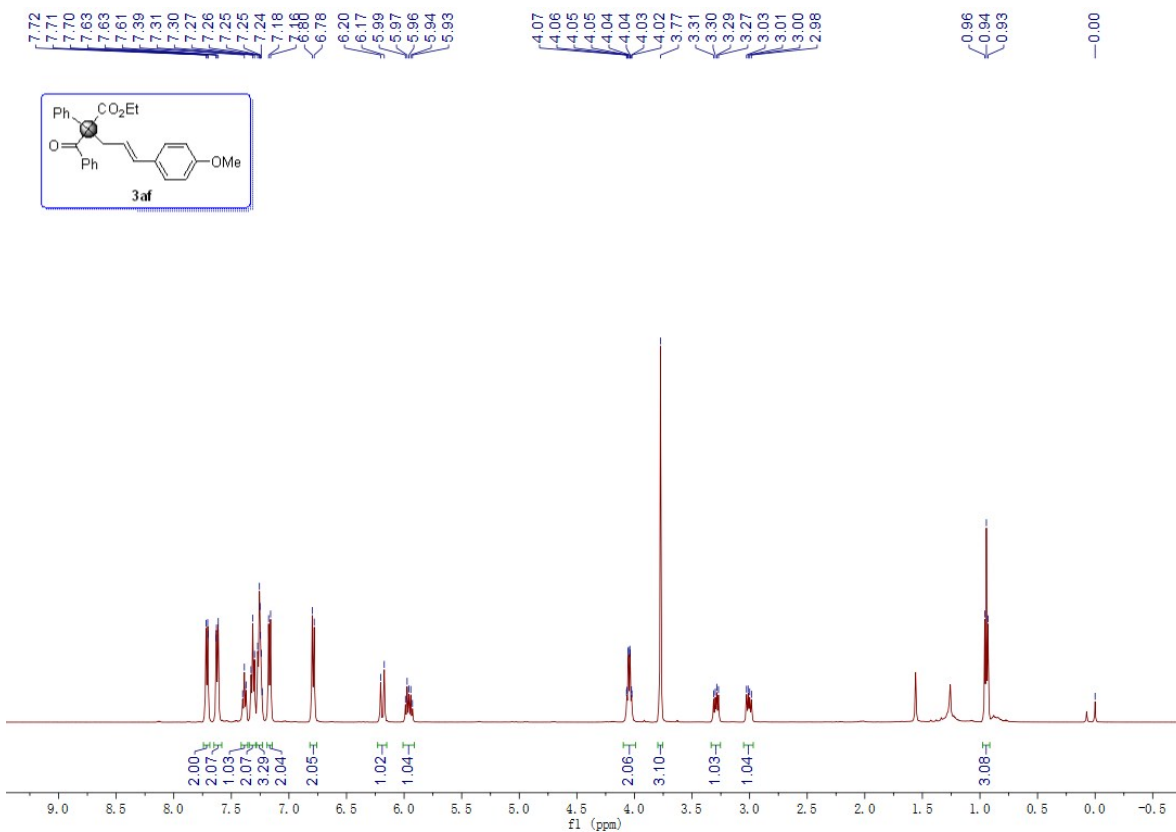




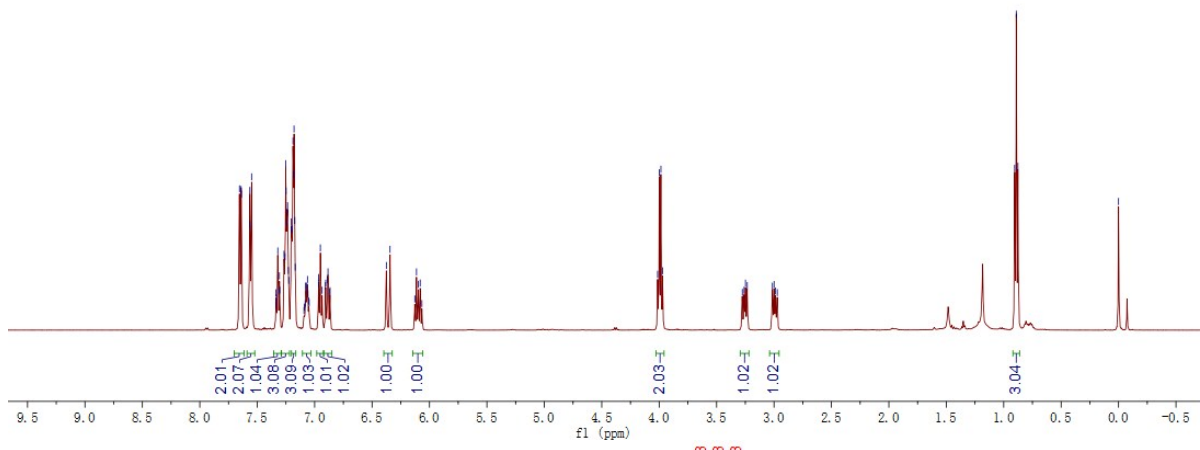
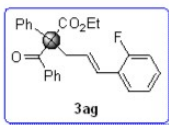




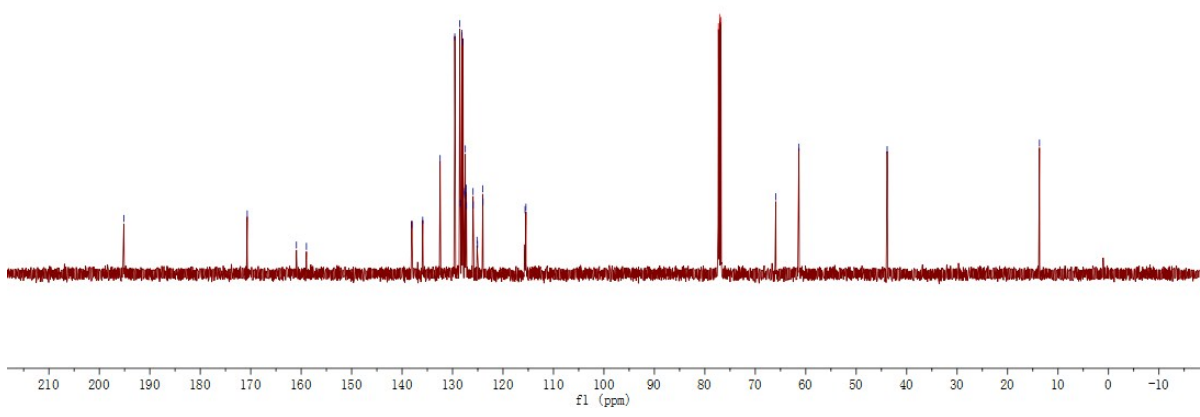
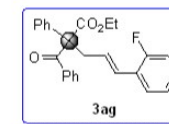




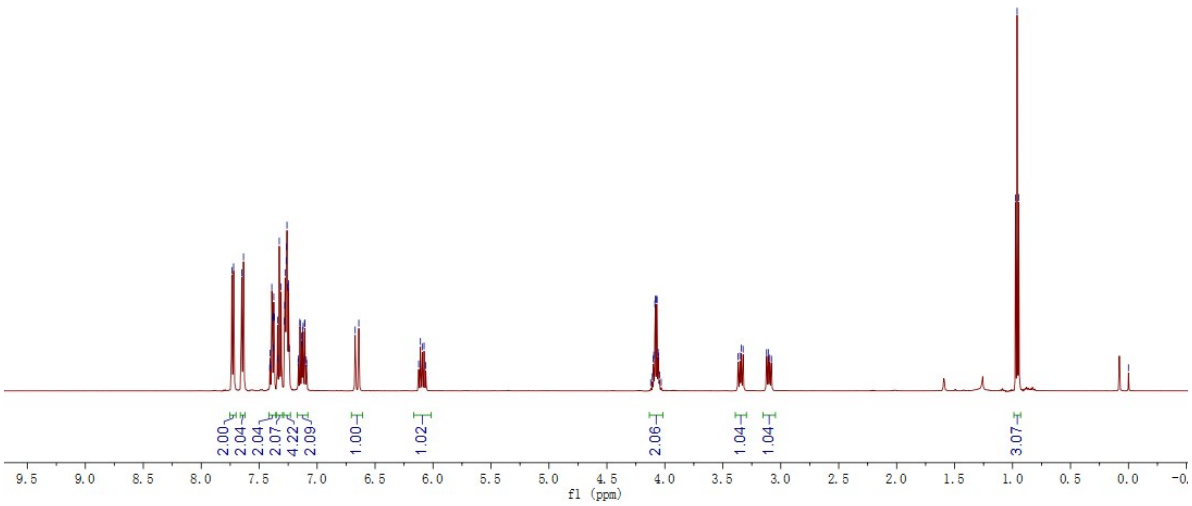
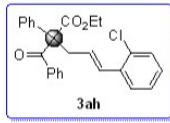
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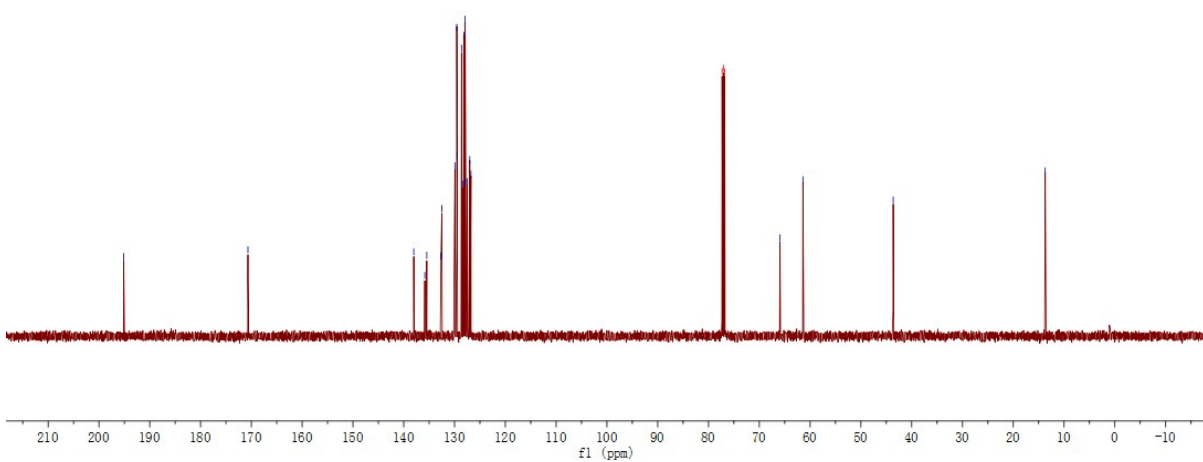
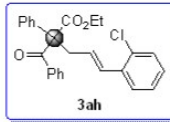
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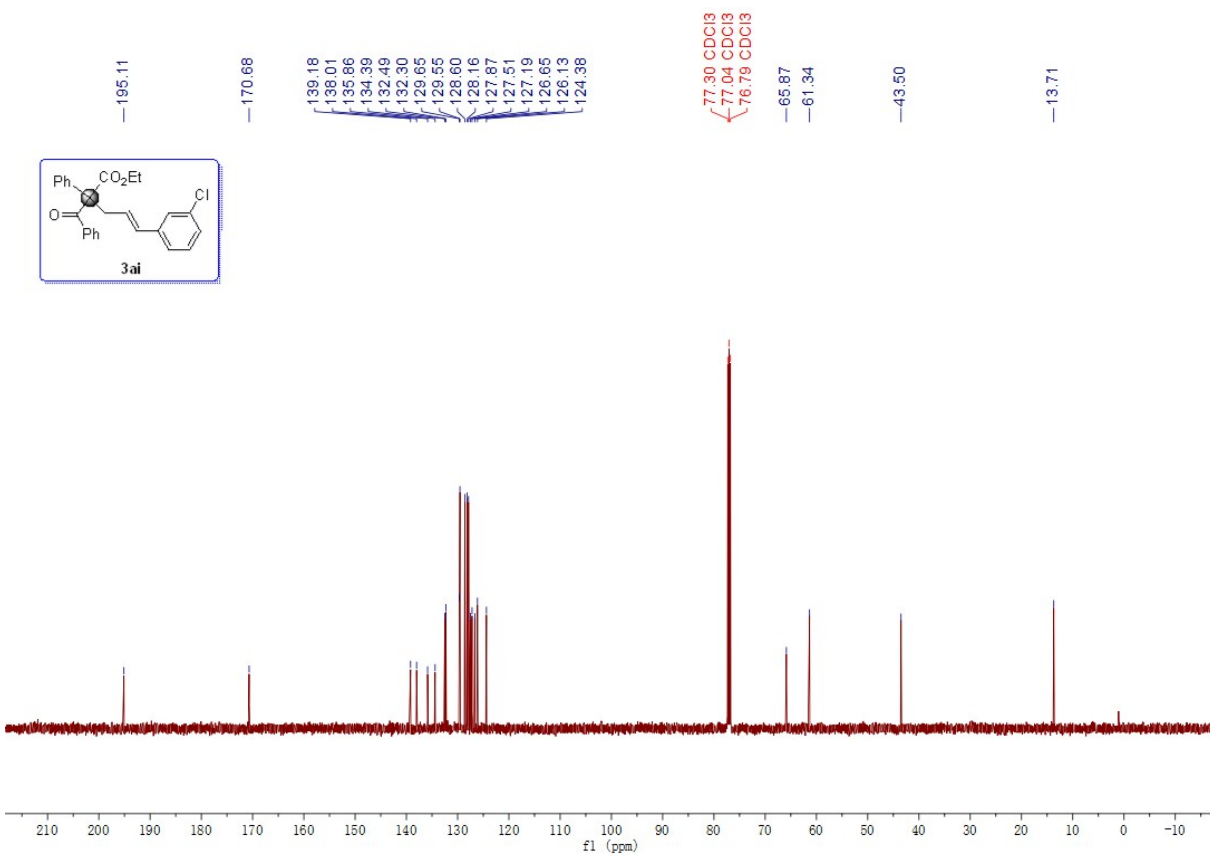
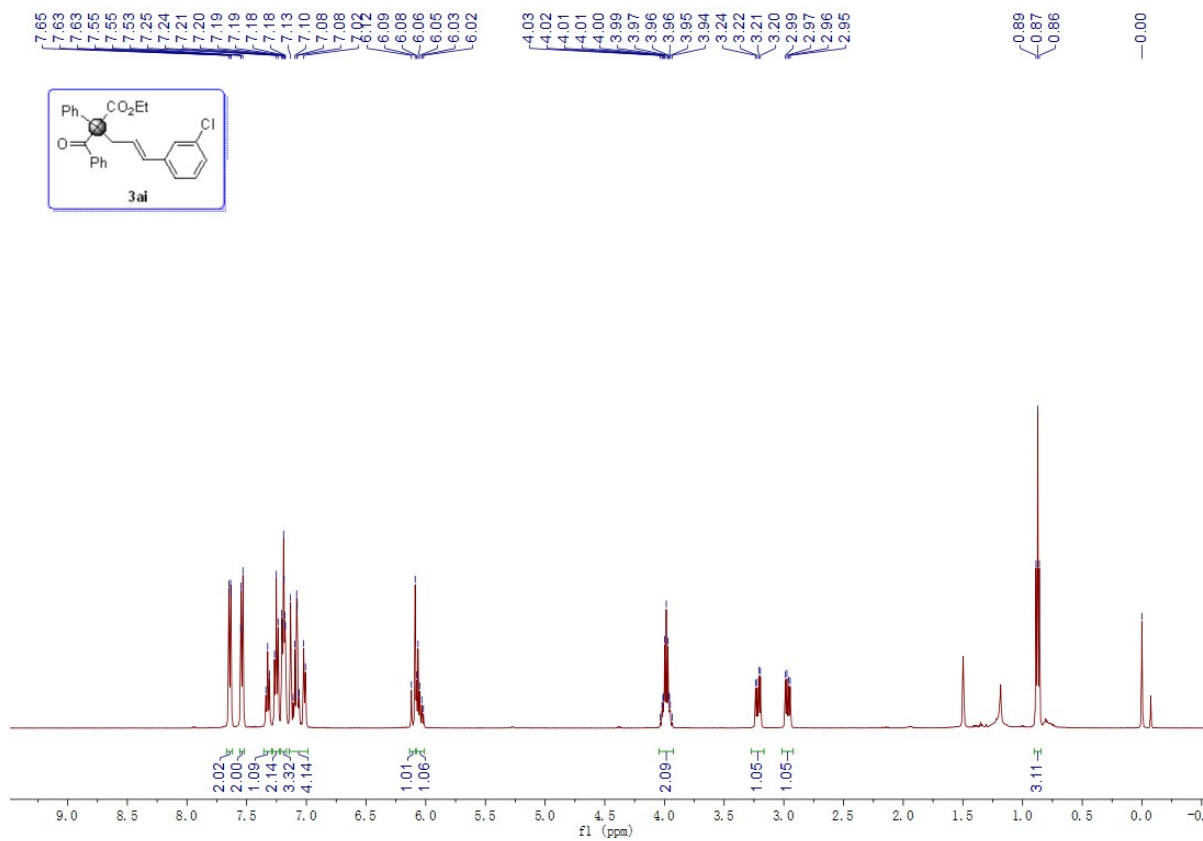


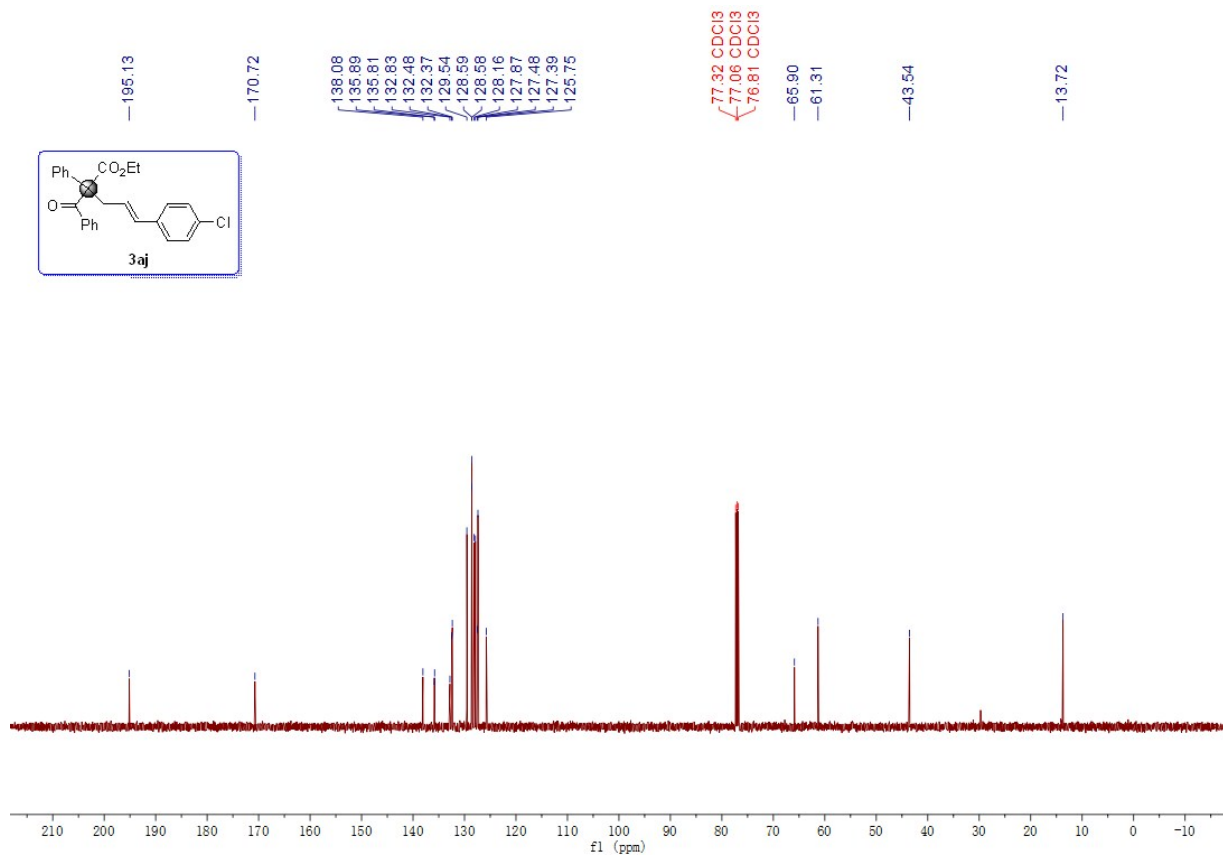
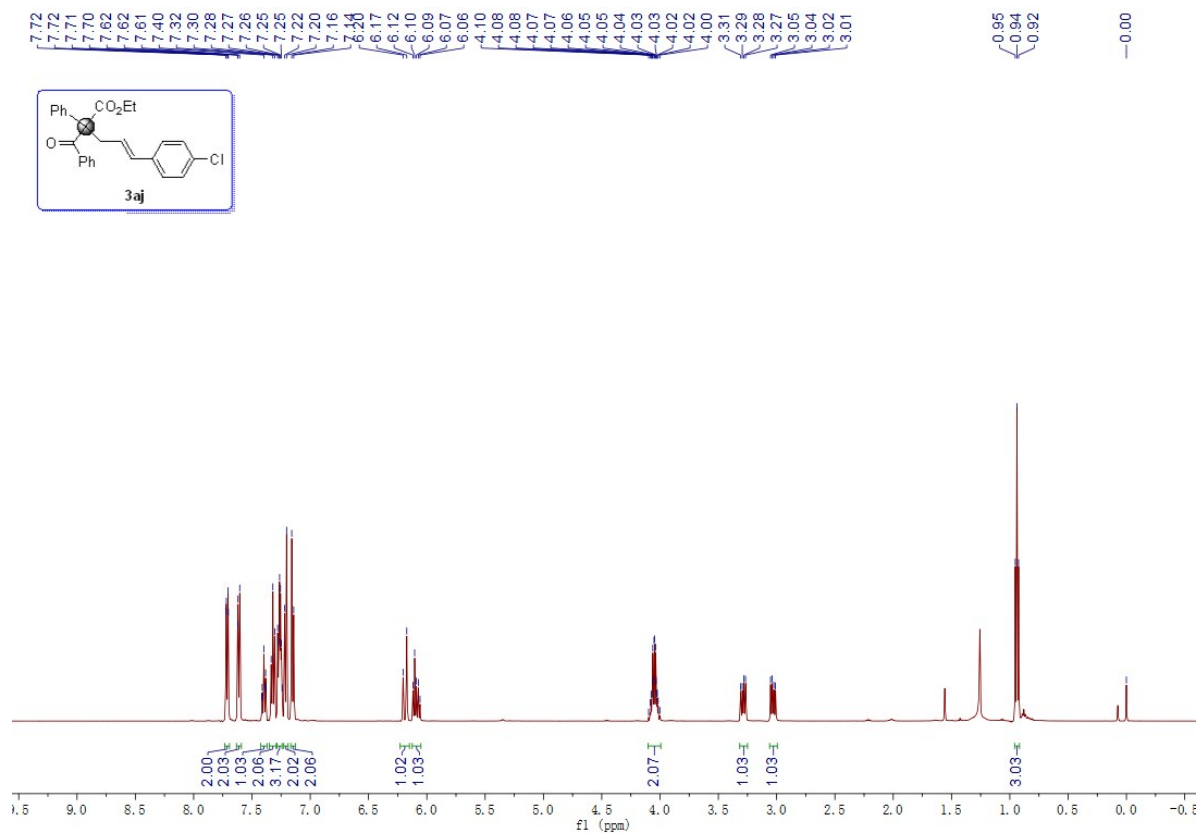
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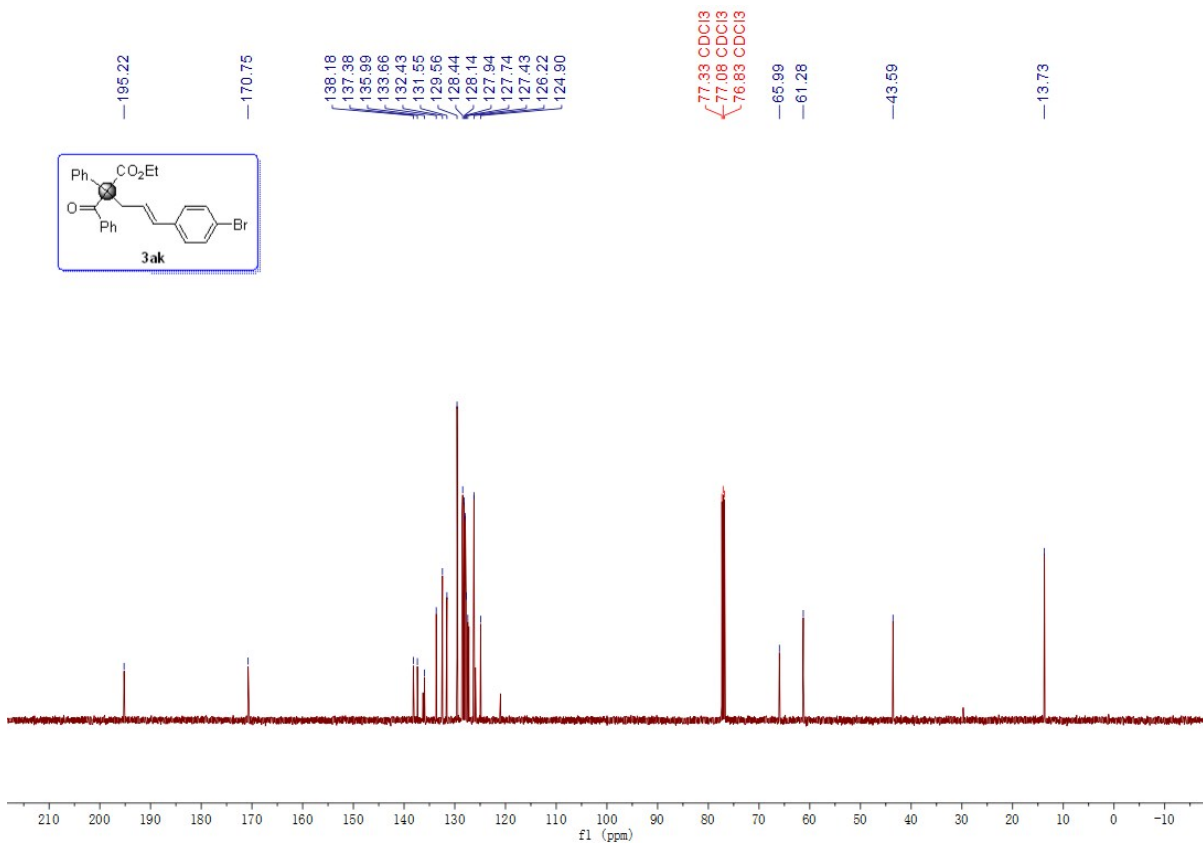
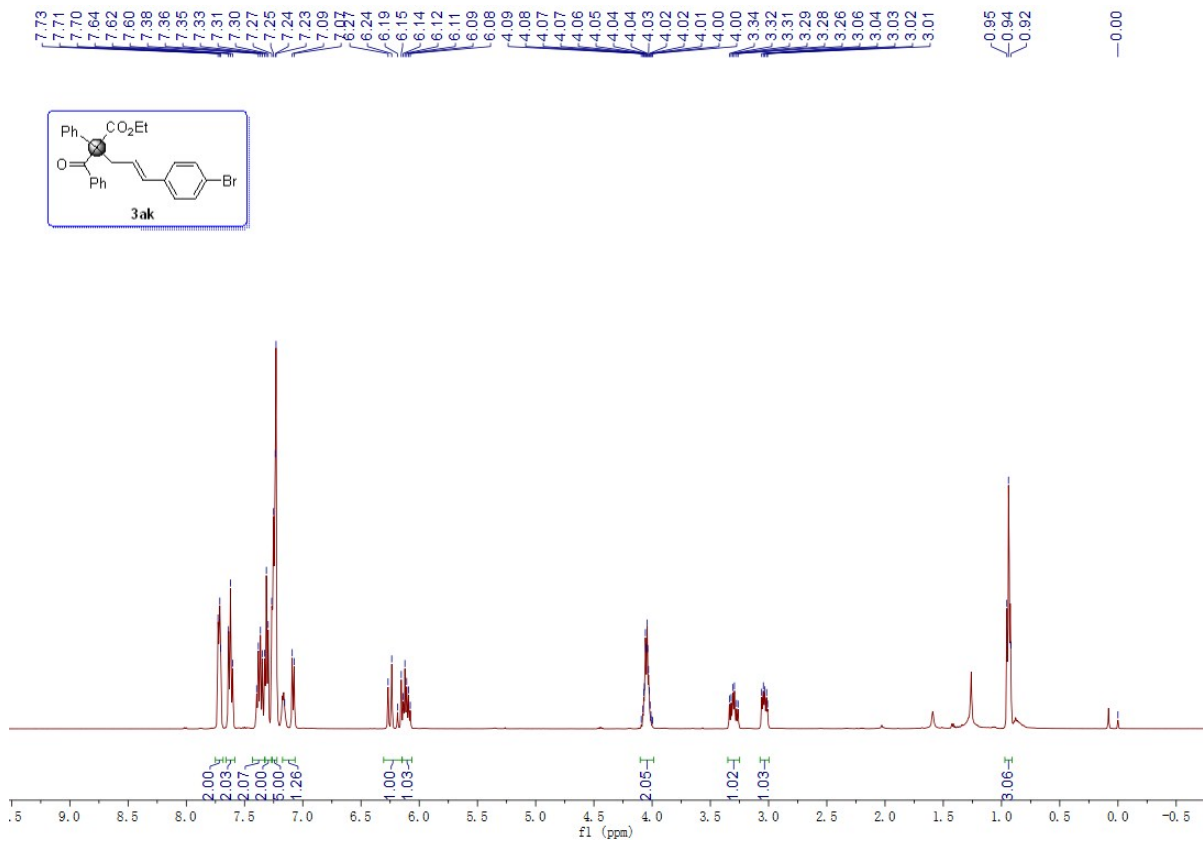


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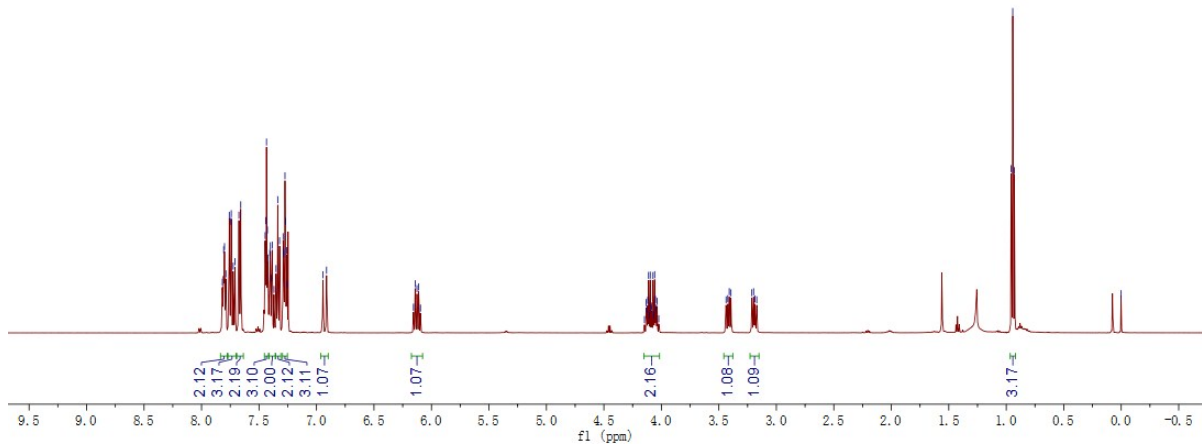
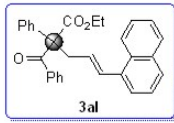








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