

## Electronic Supplementary Information

### **Enantioselective aerobic oxidative cross-dehydrogenative coupling of glycine derivatives with ketones and aldehydes via cooperative photoredox catalysis and organocatalysis**

Xiaorong Yang, Zhixiang Xie, Ying Li, and Yuan Zhang\*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, 222 Tianshui South Road, Lanzhou 730000, P. R. China.

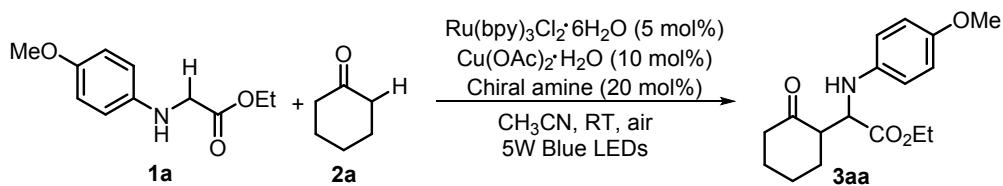
\*E-mail: zhangyuan@lzu.edu.cn.

#### **Table of Contents**

1. Optimization of Reaction Conditions	S2
2. X-ray Crystal Structure for Compound <b>3ae</b>	S7
3. UV/Vis Absorption Spectra	S8
4. Experiment Information and Product Data	S8
5. Transformations of the Products	S26
6. Synthesis of Compound <b>4b</b>	S27
7. References	S28
8. Copies of $^1\text{H}$ , $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR Spectra	S29
9. HPLC Spectra of Products	S69

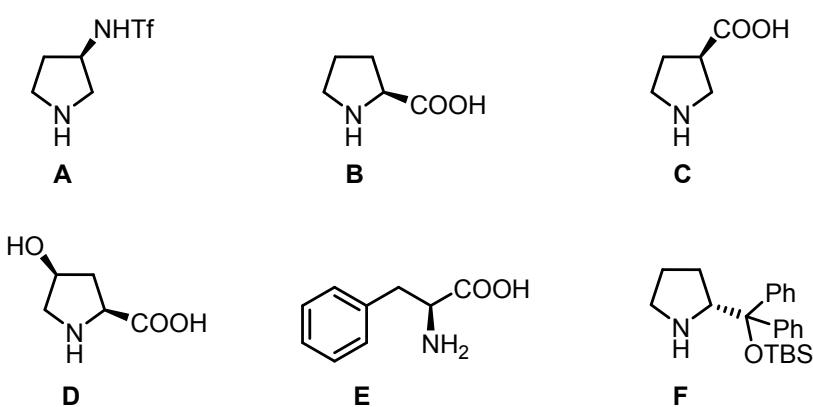
## 1. Optimization of Reaction Conditions

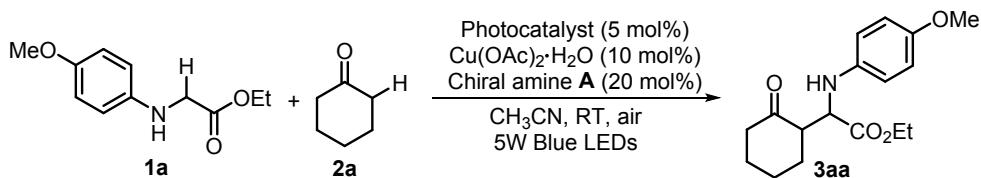
**Table S1** Screening of Chiral Amine<sup>a</sup>



Entry	Amine	Yield (%) <sup>b</sup>	dr (anti/syn) <sup>c</sup>	ee (%) <sup>c</sup>
1	<b>A</b>	76	97/3	96
2	<b>B</b>	ND	-	-
3	<b>C</b>	57	98/2	88
4	<b>D</b>	ND	-	-
5	<b>E</b>	ND	-	-
6	<b>F</b>	Trace	-	-

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), photocatalyst (5 mol %), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (10 mol%), CH<sub>3</sub>CN (2 mL), 5 W blue LED light irradiation under air for 2 h, then chiral amine catalyst (20 mol%) and **2a** (0.5 mmol) were added. <sup>b</sup>Isolated yields. <sup>c</sup>The dr and ee values of product was determined by chiral-phase HPLC analysis.

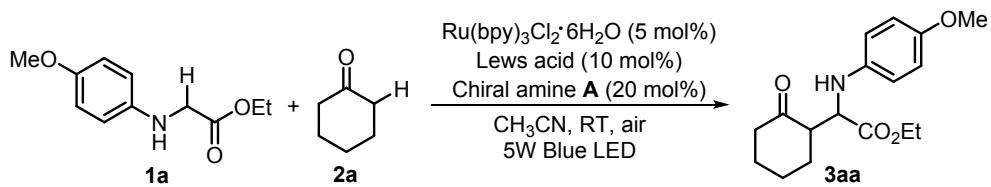


**Table S2** Screening of Photocatalysts<sup>a</sup>

Entry	Photocatalyst	Yield (%) <sup>b</sup>	dr (anti/syn) <sup>c</sup>	ee (%) <sup>c</sup>
1	Eosin Y	Trace	-	-
2	Eosin B	ND	-	-
3	Rose bengal	Trace	-	-
4 <sup>e</sup>	Rhodamine 6G	78	97/3	95
5	Ru(bpy) <sub>3</sub> Cl <sub>2</sub> ·6H <sub>2</sub> O	76	97/3	96
6	Acr <sup>+</sup> -Mes ClO <sub>4</sub> <sup>-</sup>	NR	-	-
7	Ir(ppy) <sub>3</sub>	52	97/3	79
8	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	55	88/12	81
9	-	NR	-	-

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), photocatalyst (5 mol %), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (10 mol%), CH<sub>3</sub>CN (2 mL), 5 W blue LED light irradiation under air for 2 h, then chiral amine catalyst **A** (20 mol%) and **2a** (0.5 mmol) were added. <sup>b</sup>Isolated yields. <sup>c</sup>The dr and ee values of product was determined by chiral-phase HPLC analysis.<sup>e</sup>5 W blue LED light irradiation under air for 8 h.

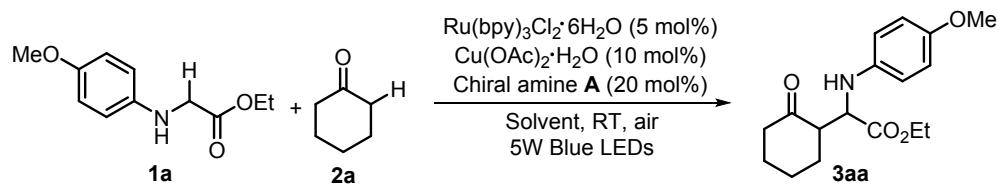
**Table S3** Screening of Lewis Acids<sup>a</sup>



Entry	Additive	Yield (%) <sup>b</sup>	dr (anti/syn) <sup>c</sup>	ee (%) <sup>c</sup>
1	$\text{Zn}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	ND	-	-
2	$\text{Zn}(\text{OAc})_2$	ND	-	-
3	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	76	97/3	96
4	$\text{Cu}(\text{OTf})_2$	63	98/2	86
5	$\text{CuCl}$	59	97/3	91
6	$\text{CuI}$	63	97/3	92
7	$\text{CuSO}_4$	68	97/3	92
8	$\text{Mg}(\text{ClO}_4)_2$	ND	-	-
9	-	ND	-	-

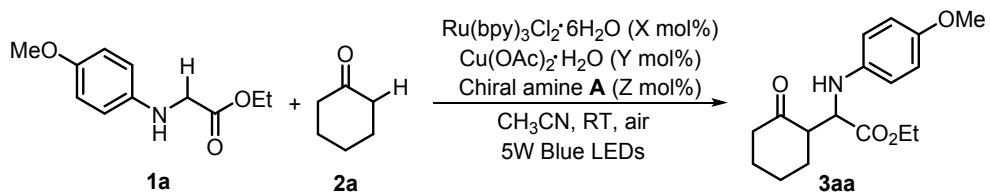
<sup>a</sup>Reaction conditions: **1a** (0.1 mmol),  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (5 mol %), additive (10 mol%),  $\text{CH}_3\text{CN}$  (2 mL), 5 W blue LED light irradiation under air for 2 h, then chiral amine catalyst **A** (20 mol%) and **2a** (0.5 mmol) were added. <sup>b</sup>Isolated yields. <sup>c</sup>The dr and ee values of product was determined by chiral-phase HPLC analysis.

**Table S4** Screening of Solvents<sup>a</sup>



Entry	Solvent	Yield (%) <sup>b</sup>	dr (anti/syn) <sup>c</sup>	ee (%) <sup>c</sup>
1	DCM	59	99/1	83
2	DCE	80	95/5	78
3	DMF	38	91/9	93
4	DMSO	65	97/3	94
5	Toluene	Trace	-	-
6	CH <sub>3</sub> CN	76	97/3	96
7	CHCl <sub>3</sub>	44	94/6	81

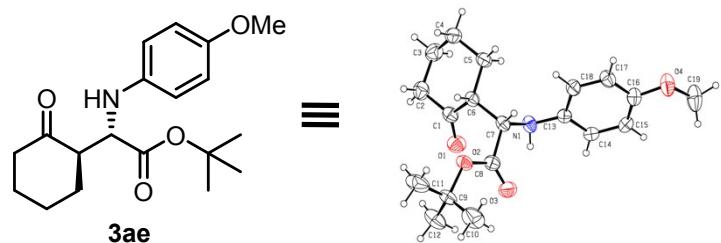
<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (5 mol %), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (10 mol%), solvent (2 mL), 5 W blue LED light irradiation under air for 2 h, then chiral amine catalyst **A** (20 mol%) and **2a** (0.5 mmol) were added. <sup>b</sup>Isolated yields. <sup>c</sup>The dr and ee values of product was determined by chiral-phase HPLC analysis.

**Table S5** Screening of Catalyst Loading<sup>a</sup>

Entry	X (mol %)	Y (mol %)	Z (mol %)	Yield (%) <sup>b</sup>	dr (anti/syn) <sup>c</sup>	ee (%) <sup>c</sup>
1	5	10	20	76	97/3	96
2	3	10	20	78	97/3	96
3	2	10	20	80	97/3	96
4	2	5	20	80	97/3	97
5	2	5	10	47	95/5	94
6 <sup>d</sup>	2	5	20	81	98/2	97
7 <sup>e</sup>	2	5	20	NR	-	-
8 <sup>f</sup>	2	5	20	NR	-	-

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (X mol %), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (Y mol%), CH<sub>3</sub>CN (2 mL), 5 W blue LED light irradiation under air for 2 h, then chiral amine catalyst **A** (Z mol%) and **2a** (0.5 mmol) were added. <sup>b</sup>Isolated yields. <sup>c</sup>The dr and ee values of product were determined by chiral-phase HPLC analysis. <sup>d</sup>1.5 mL CH<sub>3</sub>CN was used. <sup>e</sup>Under Ar atmosphere. <sup>f</sup>In dark.

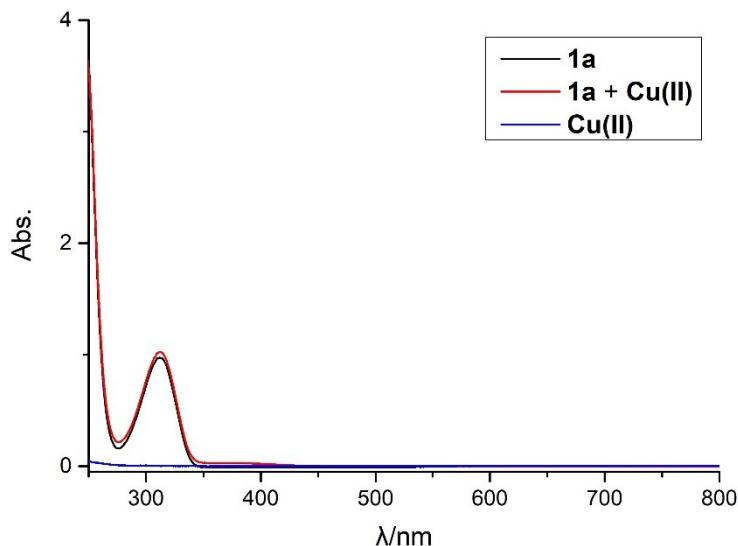
## 2. X-ray Crystal Structure for Compound 3ae



Empirical formula	C <sub>19</sub> H <sub>27</sub> NO <sub>4</sub>
Formula weight	333.41
Temperature/K	293.09(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/Å	8.6070(2)
b/Å	12.3679(4)
c/Å	17.9028(6)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1905.77(10)
Z	4
ρ <sub>calc</sub> g/cm <sup>3</sup>	1.162
μ/mm <sup>-1</sup>	0.654
F(000)	720.0
Crystal size/mm <sup>3</sup>	0.18 × 0.15 × 0.12
Radiation	CuKα ( $\lambda = 1.54184$ )
2Θ range for data collection/°	9.882 to 133.166
Index ranges	-10 ≤ h ≤ 8, -14 ≤ k ≤ 14, -21 ≤ l ≤ 19
Reflections collected	5850
Independent reflections	3234 [R <sub>int</sub> = 0.0174, R <sub>sigma</sub> = 0.0292]
Data/restraints/parameters	3234/0/225
Goodness-of-fit on F <sup>2</sup>	1.117
Final R indexes [I>=2σ (I)]	R <sub>1</sub> = 0.0403, wR <sub>2</sub> = 0.1027
Final R indexes [all data]	R <sub>1</sub> = 0.0456, wR <sub>2</sub> = 0.1078
Largest diff. peak/hole / e Å <sup>-3</sup>	0.12/-0.20
Flack parameter	-0.08(14)

### 3. UV/Vis Absorption Spectra

The UV/Vis absorption spectra were recorded in 1 cm path quartz cuvettes by using a Varian Cary-300 Conc UV/Vis spectrometer, respectively.



**Fig. S1** UV-vis spectra of **1a** (black), **1a** with Cu( II ) ion (red), and Cu( II ) salts (blue) in CH<sub>3</sub>CN. The concentration of **1a** is  $4.0 \times 10^{-4}$  M, and the concentration of Cu( II ) ion is  $2.0 \times 10^{-5}$  M. The Cu( II ) ion used here refers to Cu(OAc)<sub>2</sub>·H<sub>2</sub>O.

### 4. Experiment Information and Product Data

#### 4.1 General Information.

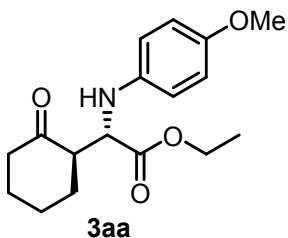
Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. *N*-arylglycine derivatives<sup>2,6</sup> were prepared according to literature procedures. Unless otherwise indicated, all experiments were carried out under air atmosphere. Irradiation of photochemical reactions was carried out using a 5 W blue LED bulb. The silica gel (200–300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Liquid <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QToF).

#### 4.2 General Procedure for the Visible-Light-Induced Enantioselective Aerobic Oxidative Cross-Dehydrogenative Coupling of Glycine Derivatives with Aldehydes or Ketones.

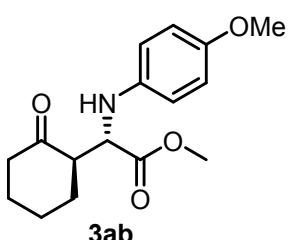
To a solution of *N*-arylglycine derivatives **1** (0.2 mmol, 1 eq) and Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (2 mol%) in dry CH<sub>3</sub>CN (3 mL) was added Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.01 mmol, 5 mol%). The mixed

solution was irradiated with a 5 W blue LED bulb under air atmosphere at room temperature. After full conversion of *N*-arylglycine derivatives as monitored by TLC, ketone (5 eq) or aldehyde (3 eq) and chiral amine catalyst **A** (20 or 10 mol%) were added, then the mixture was stirred in dark overnight. The solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with petroleum ether/EtOAc = 4:1 as eluent) to afford the product.

#### 4.3 Characterization of the Products

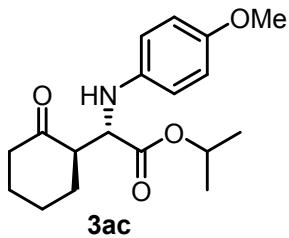


**Ethyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.<sup>1</sup>** The product was obtained in 81% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.76 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 4.48 – 4.05 (m, 3H), 3.99 (d, *J* = 4.1 Hz, 1H), 3.73 (s, 3H), 3.15 – 3.05 (m, 1H), 2.46 – 2.28 (m, 2H), 2.15 – 2.01 (m, 2H), 1.97 – 1.86 (m, 2H), 1.77 – 1.62 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 210.9, 173.0, 152.7, 142.1, 115.6, 114.7, 61.1, 59.0, 55.6, 53.5, 41.8, 30.5, 26.8, 24.5, 14.1. [α]<sub>D</sub><sup>18.2</sup> +30 (c 0.5, CHCl<sub>3</sub>). The enantiomeric excess (97% *ee*) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/i-PrOH = 90:10, flow rate: 0.5 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* major enantiomer) = 26.9 min; t<sub>R</sub> (*anti* minor enantiomer) = 36.6 min.

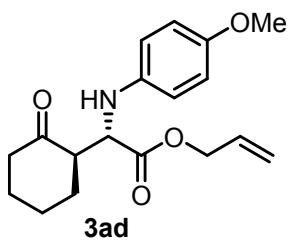


**Methyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.<sup>2</sup>** The product was obtained in 78% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.76 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 4.30 (brs, 1H), 4.00 (d, *J* = 4.0 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.17 – 3.08 (m, 1H), 2.46 – 2.39 (m, 1H), 2.37 – 2.29 (m, 1H), 2.14 – 2.02 (m, 2H), 1.99 – 1.88 (m, 2H), 1.77 – 1.63 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 211.0, 173.6, 152.7, 142.0, 115.4, 114.7, 58.8, 55.6, 53.6, 52.2, 41.8, 30.5, 26.8, 24.5. [α]<sub>D</sub><sup>20.3</sup> +26 (c 0.5, CHCl<sub>3</sub>). The enantiomeric excess (96% *ee*) was determined by HPLC with a Daicel Chiraldpak AS-H column

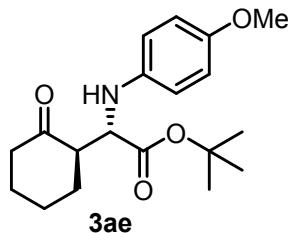
(hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min,  $\lambda_{\max}$  240 nm):  $t_R$  (*anti* major enantiomer) = 36.9 min;  $t_R$  (*anti* minor enantiomer) = 51.8 min.



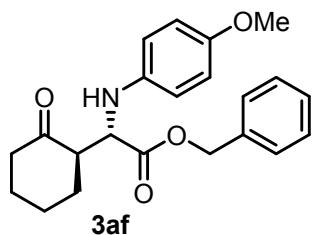
**Isopropyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.<sup>1</sup>** The product was obtained in 79% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.76 (d,  $J$  = 8.9 Hz, 2H), 6.63 (d,  $J$  = 8.9 Hz, 2H), 5.04 – 4.94 (m, 1H), 4.24 (brs, 1H), 3.96 (d,  $J$  = 4.1 Hz, 1H), 3.73 (s, 3H), 3.11 – 3.06 (m, 1H), 2.45 – 2.28 (m, 2H), 2.13 – 2.03 (m, 2H), 1.96 – 1.87 (m, 2H), 1.78 – 1.63 (m, 2H), 1.22 (d,  $J$  = 6.2 Hz, 3H), 1.14 (d,  $J$  = 6.2 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  210.8, 172.4, 152.6, 142.2, 115.6, 114.6, 68.7, 59.1, 55.6, 53.5, 41.7, 30.4, 26.8, 24.4, 21.7, 21.6.  $[\alpha]_D^{13.5} +33$  (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (97% ee) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min,  $\lambda_{\max}$  254 nm):  $t_R$  (*anti* major enantiomer) = 21.1 min;  $t_R$  (*anti* minor enantiomer) = 32.8 min.



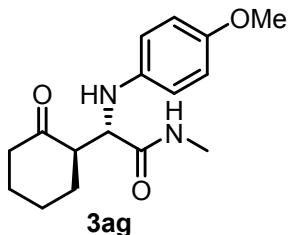
**Allyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.<sup>1</sup>** The product was obtained in 79% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.76 (d,  $J$  = 8.9 Hz, 2H), 6.64 (d,  $J$  = 8.9 Hz, 2H), 5.90 – 5.80 (m, 1H), 5.26 – 5.17 (m, 2H), 4.54 – 4.63 (m, 2H), 4.28 (brs, 1H), 4.01 (d,  $J$  = 3.8 Hz, 1H), 3.73 (s, 3H), 3.17 – 3.11 (m, 1H), 2.45 – 2.28 (m, 2H), 2.15 – 2.03 (m, 2H), 1.97 – 1.88 (m, 2H), 1.78 – 1.62 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  211.0, 172.7, 152.7, 142.0, 131.7, 118.2, 115.5, 114.7, 65.7, 58.9, 55.6, 53.5, 41.8, 30.5, 26.8, 24.5.  $[\alpha]_D^{14.6} +25$  (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (97% ee) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min,  $\lambda_{\max}$  254 nm):  $t_R$  (*anti* major enantiomer) = 32.5 min;  $t_R$  (*anti* minor enantiomer) = 48.0 min.



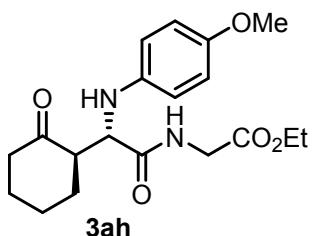
**Tert-butyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.**<sup>1</sup> The product was obtained in 80% yield. White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.76 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 4.20 (brs, 1H), 3.92 (d, *J* = 4.2 Hz, 1H), 3.73 (s, 3H), 3.08 – 2.99 (m, 1H), 2.46 – 2.27 (m, 2H), 2.13 – 2.01 (m, 2H), 1.96 – 1.85 (m, 2H), 1.78 – 1.64 (m, 2H), 1.39 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 210.9, 172.0, 152.5, 142.3, 115.4, 114.6, 81.5, 59.4, 55.6, 53.4, 41.7, 30.3, 27.9, 26.8, 24.4. [α]<sub>D</sub><sup>14.6</sup> +24 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (96% *ee*) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* major enantiomer) = 12.5 min; t<sub>R</sub> (*anti* minor enantiomer) = 20.4 min.



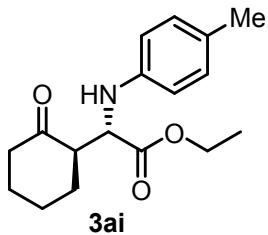
**Benzyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.** The product was obtained in 76% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.28 (m, 3H), 7.25 – 7.20 (m, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 5.16 – 5.07 (m, 2H), 4.30 (brs, 1H), 4.04 (d, *J* = 3.9 Hz, 1H), 3.73 (s, 3H), 3.17 – 3.07 (m, 1H), 2.44 – 2.39 (m, 1H), 2.34 – 2.24 (m, 1H), 2.13 – 1.98 (m, 2H), 1.94 – 1.84 (m, 2H), 1.75 – 1.58 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 211.0, 172.9, 152.7, 142.0, 135.5, 128.4, 128.1, 127.9, 115.6, 114.7, 66.8, 59.0, 55.6, 53.4, 41.7, 30.5, 26.8, 24.5. HRMS (ESI): calcd for C<sub>22</sub>H<sub>25</sub>NO<sub>4</sub>Na (M+Na<sup>+</sup>) 390.1676, found 390.1684. [α]<sub>D</sub><sup>14.5</sup> +23 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (96% *ee*) was determined by HPLC with a Daicel Chiraldpak AD-H column (hexane/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* minor enantiomer) = 29.2 min; t<sub>R</sub> (*anti* major enantiomer) = 43.3 min.



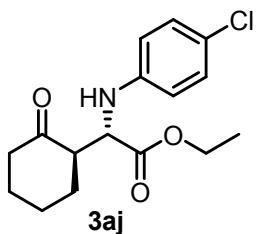
**(S)-2-((4-methoxyphenyl)amino)-N-methyl-2-((R)-2-oxocyclohexyl)acetamide.** The product was obtained in 48% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.98 (brs, 1H), 6.77 (d,  $J$  = 8.9 Hz, 2H), 6.55 (d,  $J$  = 8.9 Hz, 2H), 4.40 (brs, 1H), 3.92 (d,  $J$  = 2.4 Hz, 1H), 3.74 (s, 3H), 3.41 – 3.31 (m, 1H), 2.80 (d,  $J$  = 4.9 Hz, 3H), 2.44 – 2.34 (m, 2H), 2.11 – 2.02 (m, 2H), 1.91 – 1.84 (m, 1H), 1.72 – 1.58 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.6, 172.8, 152.5, 141.2, 115.0, 114.3, 59.1, 55.7, 53.2, 42.4, 31.4, 27.6, 26.1, 25.0. HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_3\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 313.1523, found 313.1516.  $[\alpha]_D^{20.5} +88$  (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (76% ee) was determined by HPLC with a Daicel Chiraldapak IC column (hexane/*i*-PrOH = 80:20, flow rate: 1.0 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* major enantiomer) = 24.6 min;  $t_R$  (*anti* minor enantiomer) = 28.6 min.



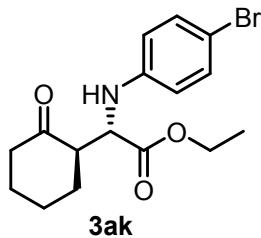
**Ethyl ((S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocyclohexyl)acetyl)glycinate.** The product was obtained in 34% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (brs, 1H), 6.77 (d,  $J$  = 8.9 Hz, 2H), 6.59 (d,  $J$  = 8.9 Hz, 2H), 4.42 (brs, 1H), 4.18 (q,  $J$  = 7.1 Hz, 2H), 4.13 – 4.07 (m, 2H), 3.92 (dd,  $J$  = 18.1, 5.2 Hz, 1H), 3.74 (s, 3H), 3.33 – 3.24 (m, 1H), 2.46 – 2.35 (m, 2H), 2.10 – 2.04 (m, 2H), 1.92 – 1.85 (m, 1H), 1.71 – 1.62 (m, 3H), 1.26 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  213.5, 172.6, 169.5, 152.6, 141.0, 115.0, 114.6, 61.3, 58.7, 55.7, 53.2, 42.3, 41.3, 30.7, 27.5, 24.9, 14.1. HRMS (ESI): calcd for  $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_5\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 385.1734, found 385.1729.  $[\alpha]_D^{20.6} +75$  (c 0.4,  $\text{CHCl}_3$ ). The enantiomeric excess (91% ee) was determined by HPLC with a Daicel Chiraldapak IC column (hexane/*i*-PrOH = 80:20, flow rate: 1.0 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* minor enantiomer) = 55.7 min;  $t_R$  (*anti* major enantiomer) = 64.4 min.



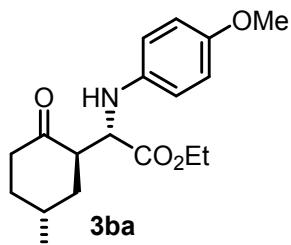
**Ethyl (S)-2-((R)-2-oxocyclohexyl)-2-(*p*-tolylamino)acetate.** The product was obtained in 63% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.99 (d,  $J = 8.2$  Hz, 2H), 6.59 (d,  $J = 8.2$  Hz, 2H), 4.35 (brs, 1H), 4.21 – 4.11 (m, 2H), 4.09 (d,  $J = 3.9$  Hz, 1H), 3.17 – 3.12 (m, 1H), 2.47 – 2.42 (m, 1H), 2.38 – 2.30 (m, 1H), 2.24 (s, 3H), 2.18 – 2.01 (m, 2H), 1.99 – 1.83 (m, 2H), 1.79 – 1.63 (m, 2H), 1.23 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  210.9, 172.9, 145.7, 129.7, 127.5, 114.0, 61.2, 58.0, 53.6, 41.8, 30.4, 26.8, 24.5, 20.3, 14.1. HRMS (ESI): calcd for  $\text{C}_{17}\text{H}_{23}\text{NO}_3\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 312.1570, found 312.1562.  $[\alpha]_D^{18.3} +36$  (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (96% ee) was determined by HPLC with a Daicel Chiraldapak IC column (hexane/*i*-PrOH = 93:7, flow rate: 1.0 mL/min,  $\lambda_{\max}$  245 nm):  $t_R$  (*anti* minor enantiomer) = 16.7 min;  $t_R$  (*anti* major enantiomer) = 19.9 min.



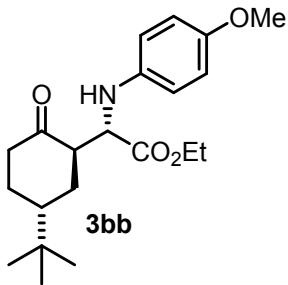
**Ethyl (S)-2-((4-chlorophenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.** The product was obtained in 30% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11 (d,  $J = 8.8$  Hz, 2H), 6.57 (d,  $J = 8.8$  Hz, 2H), 4.53 (brs, 1H), 4.20 – 4.12 (m, 2H), 4.03 (d,  $J = 3.2$  Hz, 1H), 3.22 – 3.12 (m, 1H), 2.47 – 2.30 (m, 2H), 2.16 – 2.04 (m, 2H), 2.00 – 1.92 (m, 1H), 1.89 – 1.79 (m, 1H), 1.78 – 1.62 (m, 2H), 1.22 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.1, 172.4, 146.6, 129.1, 122.9, 114.9, 61.4, 57.7, 53.5, 41.9, 30.6, 26.9, 24.6, 14.1. HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{20}\text{ClNO}_3\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 332.1024, found 332.1018.  $[\alpha]_D^{18.4} +45$  (c 0.2,  $\text{CHCl}_3$ ). The enantiomeric excess (93% ee) was determined by HPLC with a Daicel Chiraldapak IC column (hexane/*i*-PrOH = 97:3, flow rate: 1.0 mL/min,  $\lambda_{\max}$  254 nm):  $t_R$  (*anti* minor enantiomer) = 18.1 min;  $t_R$  (*anti* major enantiomer) = 23.9 min.



**Ethyl (S)-2-((4-bromophenyl)amino)-2-((R)-2-oxocyclohexyl)acetate.** The product was obtained in 29% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 8.9$  Hz, 2H), 6.53 (d,  $J = 8.9$  Hz, 2H), 4.54 (brs, 1H), 4.21 – 4.11 (m, 2H), 4.03 (d,  $J = 2.9$  Hz, 1H), 3.22 – 3.13 (m, 1H), 2.48 – 2.30 (m, 2H), 2.15 – 2.04 (m, 2H), 1.96 – 1.93 (m, 1H), 1.88 – 1.79 (m, 1H), 1.78 – 1.62 (m, 2H), 1.22 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.1, 172.4, 147.1, 131.9, 115.3, 109.9, 61.4, 57.5, 53.4, 41.9, 30.6, 26.9, 24.6, 14.1. HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{20}\text{BrNO}_3\text{Na} (\text{M}+\text{Na}^+)$  376.0519, found 376.0512.  $[\alpha]_D^{18.2} +30$  (c 0.2,  $\text{CHCl}_3$ ). The enantiomeric excess (90% ee) was determined by HPLC with a Daicel Chiraldapak IC column (hexane/*i*-PrOH = 97:3, flow rate: 1.0 mL/min,  $\lambda_{\text{max}}$  254 nm):  $t_R$  (*anti* minor enantiomer) = 19.3 min;  $t_R$  (*anti* major enantiomer) = 26.9 min.

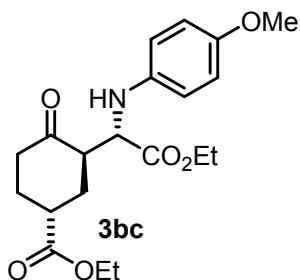


**Ethyl (S)-2-((4-methoxyphenyl)amino)-2-((1*R*,5*R*)-5-methyl-2-oxocyclohexyl)acetate.<sup>3</sup>** The product was obtained in 67% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.76 (d,  $J = 8.9$  Hz, 2H), 6.62 (d,  $J = 9.0$  Hz, 2H), 4.25 – 3.95 (m, 4H), 3.73 (s, 3H), 3.05 – 3.00 (m, 1H), 2.46 – 2.32 (m, 2H), 2.28 – 2.15 (m, 1H), 2.10 – 1.93 (m, 2H), 1.78 – 1.59 (m, 2H), 1.22 (t,  $J = 7.1$  Hz, 3H), 1.14 (d,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.4, 172.8, 152.9, 141.4, 115.5, 114.8, 61.2, 59.0, 55.7, 50.4, 37.8, 36.3, 33.3, 26.8, 19.4, 14.1.  $[\alpha]_D^{17.8} +18$  (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (97% ee) was determined by HPLC with a Daicel Chiraldapak AS-H column (hexane/*i*-PrOH = 96:4, flow rate: 0.7 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* major enantiomer) = 27.7 min;  $t_R$  (*anti* minor enantiomer) = 69.6 min.

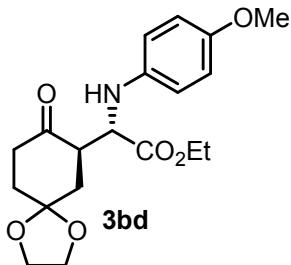


**Ethyl (S)-2-((1R,5R)-5-(tert-butyl)-2-oxocyclohexyl)-2-((4-methoxyphenyl)amino)acetate.**

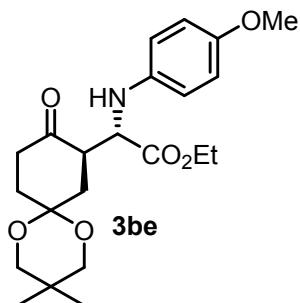
The product was obtained in 73% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.75 (d,  $J = 8.8$  Hz, 2H), 6.62 (d,  $J = 8.9$  Hz, 2H), 4.33 (d,  $J = 9.4$  Hz, 1H), 4.21 – 4.10 (m, 2H), 3.97 (brs, 1H), 3.73 (s, 3H), 2.82 – 2.78 (m, 1H), 2.46 – 2.34 (m, 2H), 2.10 – 1.96 (m, 2H), 1.79 – 1.64 (m, 2H), 1.56 – 1.45 (m, 1H), 1.22 (t,  $J = 7.1$  Hz, 3H), 0.93 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.9, 172.6, 153.0, 140.6, 115.5, 114.7, 61.2, 58.5, 55.6, 51.6, 41.9, 38.7, 32.5, 28.7, 27.3, 26.7, 14.2. HRMS (ESI): calcd for  $\text{C}_{21}\text{H}_{31}\text{NO}_4\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 384.2145, found 384.2161.  $[\alpha]_D^{19.5} +28$  (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (97% ee) was determined by HPLC with a Daicel Chiralpak IC column (hexane/*i*-PrOH = 95:5, flow rate: 0.8 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* major enantiomer) = 41.8 min;  $t_R$  (*anti* minor enantiomer) = 122.4 min.



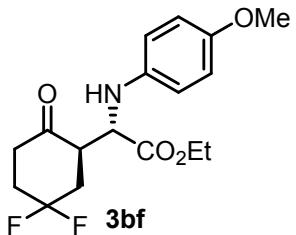
**Ethyl (1R,3R)-3-((S)-2-ethoxy-1-((4-methoxyphenyl)amino)-2-oxoethyl)-4-oxocyclohexane-1-carboxylate.** The product was obtained in 62% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.76 (d,  $J = 8.9$  Hz, 2H), 6.64 (d,  $J = 8.9$  Hz, 2H), 4.24 (q,  $J = 7.1$  Hz, 2H), 4.21 – 4.02 (m, 3H), 3.94 (d,  $J = 4.2$  Hz, 1H), 3.73 (s, 3H), 3.42 – 3.29 (m, 1H), 2.98 – 2.89 (m, 1H), 2.55 – 2.44 (m, 2H), 2.41 – 2.33 (m, 2H), 2.24 – 2.16 (m, 1H), 1.98 – 1.92 (m, 1H), 1.31 (t,  $J = 7.1$  Hz, 3H), 1.21 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  210.1, 173.9, 172.6, 152.8, 142.0, 115.7, 114.7, 61.2, 60.9, 59.0, 55.6, 50.2, 38.4, 38.1, 31.0, 27.6, 14.2, 14.1. HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{27}\text{NO}_6\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 400.1731, found 400.1745.  $[\alpha]_D^{19.8} +2$  (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (97% ee) was determined by HPLC with a Daicel Chiralpak IC column (hexane/*i*-PrOH = 93:7, flow rate: 1.0 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* major enantiomer) = 64.3 min;  $t_R$  (*anti* minor enantiomer) = 101.6 min.



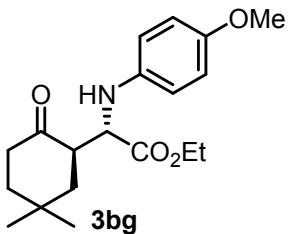
**Ethyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-8-oxo-1,4-dioxaspiro[4.5]decan-7-yl)acetate.**<sup>1</sup> The product was obtained in 84% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.75 (d, *J* = 8.9 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 4.25 – 4.10 (m, 3H), 4.08 – 4.00 (m, 4H), 3.92 (d, *J* = 3.5 Hz, 1H), 3.73 (s, 3H), 3.51 – 3.45 (m, 1H), 2.73 – 2.62 (m, 1H), 2.43 – 2.37 (m, 1H), 2.29 (t, *J* = 13.1 Hz, 1H), 2.14 – 1.96 (m, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 209.5, 172.6, 152.9, 142.1, 115.8, 114.7, 107.4, 64.8, 64.6, 61.2, 58.9, 55.6, 50.0, 37.9, 37.6, 33.8, 14.0. [α]<sub>D</sub><sup>19.1</sup> +15 (c 0.4, CHCl<sub>3</sub>). The enantiomeric excess (96% *ee*) was determined by HPLC with a Daicel Chiralpak IC column (hexane/*i*-PrOH = 88:12, flow rate: 1.0 mL/min, λ<sub>max</sub> 240 nm): t<sub>R</sub> (*anti* minor enantiomer) = 28.2 min; t<sub>R</sub> (*anti* major enantiomer) = 35.1 min.



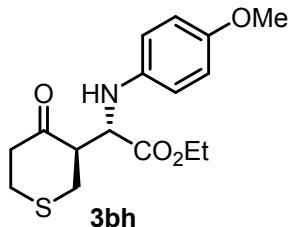
**Ethyl (S)-2-((R)-3,3-dimethyl-9-oxo-1,5-dioxaspiro[5.5]undecan-8-yl)-2-((4-methoxyphenyl)amino)acetate.** The product was obtained in 77% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.76 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 4.47 – 4.00 (m, 3H), 3.94 (d, *J* = 2.8 Hz, 1H), 3.73 (s, 3H), 3.58 (s, 2H), 3.55 (d, *J* = 3.2 Hz, 2H), 3.41 – 3.35 (m, 1H), 2.67 – 2.47 (m, 3H), 2.41 – 2.27 (m, 1H), 2.08 (t, *J* = 13.3 Hz, 1H), 1.80 – 1.71 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.05 (s, 3H), 0.98 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 209.9, 172.7, 152.9, 142.1, 115.8, 114.7, 96.5, 70.7, 70.4, 61.3, 59.0, 55.6, 48.8, 36.8, 35.4, 30.4, 30.2, 22.6, 22.5, 14.1. HRMS (ESI): calcd for C<sub>22</sub>H<sub>31</sub>NO<sub>6</sub>Na (M+Na<sup>+</sup>) 428.2044, found 428.2057. [α]<sub>D</sub><sup>19.3</sup> +12 (c 0.5, CHCl<sub>3</sub>). The enantiomeric excess (95% *ee*) was determined by HPLC with a Daicel Chiralpak IC column (hexane/*i*-PrOH = 88:12, flow rate: 1.0 mL/min, λ<sub>max</sub> 240 nm): t<sub>R</sub> (*anti* minor enantiomer) = 21.1 min; t<sub>R</sub> (*anti* major enantiomer) = 26.5 min.



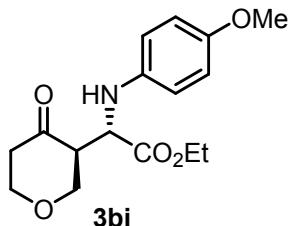
**Ethyl (S)-2-((R)-5,5-difluoro-2-oxocyclohexyl)-2-((4-methoxyphenyl)amino)acetate.** The product was obtained in 56% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.78 (d,  $J = 8.9$  Hz, 2H), 6.64 (d,  $J = 8.9$  Hz, 2H), 4.28 – 4.09 (m, 3H), 3.87 (brs, 1H), 3.75 (s, 3H), 3.62 – 3.45 (m, 1H), 2.74 – 2.64 (m, 1H), 2.60 – 2.37 (m, 4H), 2.27 – 2.11 (m, 1H), 1.23 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  207.0, 172.1, 153.2, 141.8, 116.39 (d,  $J = 4.9$  Hz), 116.1, 114.8, 61.6, 58.9, 55.6, 48.74 (d,  $J = 9.8$  Hz), 36.43 (t,  $J = 10.0$  Hz), 36.28 (d,  $J = 51.0$  Hz), 32.56 (t,  $J = 26.0$  Hz), 14.1.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -94.7 (d,  $J = 242.9$  Hz), -100.8 (d,  $J = 242.5$  Hz). HRMS (ESI): calcd for  $\text{C}_{17}\text{H}_{21}\text{F}_2\text{NO}_4\text{Na} (\text{M}+\text{Na}^+)$  364.1331, found 364.1347.  $[\alpha]_D^{18.7} +12.5$  (c 0.4,  $\text{CHCl}_3$ ). The enantiomeric excess (85% ee) was determined by HPLC with a Daicel Chiralpak IC column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* minor enantiomer) = 26.5 min;  $t_R$  (*anti* major enantiomer) = 36.0 min.



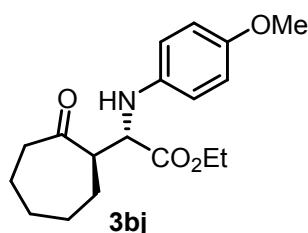
**Ethyl (S)-2-((R)-5,5-dimethyl-2-oxocyclohexyl)-2-((4-methoxyphenyl)amino)acetate.<sup>3</sup>** The product was obtained in 59% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.77 (d,  $J = 9.0$  Hz, 2H), 6.64 (d,  $J = 9.0$  Hz, 2H), 4.25 (brs, 1H), 4.19 – 4.11 (m, 2H), 3.87 (d,  $J = 3.4$  Hz, 1H), 3.74 (s, 3H), 3.31 – 3.26 (m, 1H), 2.53 – 2.44 (m, 1H), 2.32 – 2.26 (m, 1H), 1.95 (t,  $J = 13.2$  Hz, 1H), 1.81 – 1.74 (m, 1H), 1.74 – 1.69 (m, 1H), 1.68 – 1.63 (m, 1H), 1.25 (s, 3H), 1.22 (t,  $J = 7.1$  Hz, 3H), 1.05 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  211.5, 173.1, 152.8, 142.4, 115.7, 114.7, 61.2, 59.4, 55.7, 49.6, 42.9, 38.8, 38.0, 31.5, 30.7, 24.6, 14.1.  $[\alpha]_D^{18.2} +26$  (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (77% ee) was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* major enantiomer) = 17.6 min;  $t_R$  (*anti* minor enantiomer) = 18.9 min.



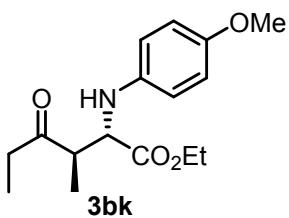
**Ethyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-4-oxotetrahydro-2H-thiopyran-3-yl)acetate.<sup>1</sup>** The product was obtained in 76% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.24 (d, *J* = 4.9 Hz, 1H), 4.21 – 4.09 (m, 3H), 3.74 (s, 3H), 3.38 (dt, *J* = 9.7, 4.7 Hz, 1H), 3.15 (dd, *J* = 13.6, 10.1 Hz, 1H), 3.01 – 2.87 (m, 3H), 2.80 – 2.68 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 208.0, 172.1, 153.1, 141.3, 115.8, 114.7, 61.4, 58.9, 55.6, 55.2, 43.7, 32.7, 29.8, 14.1. [α]<sub>D</sub><sup>13.7</sup> +49 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (97% *ee*) was determined by HPLC with a Daicel Chiraldak OZ-H column (hexane/*i*-PrOH = 97:3, flow rate: 1.0 mL/min, λ<sub>max</sub> 235 nm): t<sub>R</sub> (*anti* minor enantiomer) = 34.1 min; t<sub>R</sub> (*anti* major enantiomer) = 40.3 min.



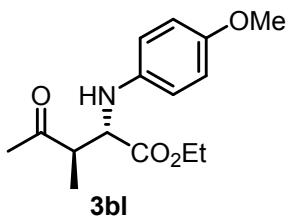
**Ethyl (S)-2-((4-methoxyphenyl)amino)-2-((S)-4-oxotetrahydro-2H-pyran-3-yl)acetate.<sup>1</sup>** The product was obtained in 75% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 4.25 – 4.07 (m, 6H), 3.91 (dd, *J* = 11.2, 9.1 Hz, 1H), 3.83 – 3.77 (m, 1H), 3.73 (s, 3H), 3.27 – 3.22 (m, 1H), 2.64 – 2.57 (m, 1H), 2.48 (dt, *J* = 14.8, 3.8 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.2, 172.1, 153.1, 141.2, 115.8, 114.7, 70.0, 67.8, 61.5, 56.4, 55.6, 53.8, 42.0, 14.1. [α]<sub>D</sub><sup>14.0</sup> +11 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (96% *ee*) was determined by HPLC with a Daicel Chiraldak IC-3 column (hexane/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, λ<sub>max</sub> 240 nm): t<sub>R</sub> (*anti* minor enantiomer) = 32.9 min; t<sub>R</sub> (*anti* major enantiomer) = 36.4 min.



**Ethyl (S)-2-((4-methoxyphenyl)amino)-2-((R)-2-oxocycloheptyl)acetate.<sup>4</sup>** The product was obtained in 65% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 4.42 – 4.24 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.05 – 3.00 (m, 1H), 2.60 – 2.48 (m, 2H), 2.05 – 1.87 (m, 4H), 1.63 – 1.48 (m, 2H), 1.38 – 1.31 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 214.2, 172.5, 152.6, 140.9, 115.1, 114.8, 61.3, 60.6, 55.6, 54.3, 43.8, 29.9, 29.0, 27.1, 24.2, 14.1. [α]<sub>D</sub><sup>14.1</sup> +32 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (97% *ee*) was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/i-PrOH = 90:10, flow rate: 1.0 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* major enantiomer) = 12.1 min; t<sub>R</sub> (*anti* minor enantiomer) = 25.8 min.

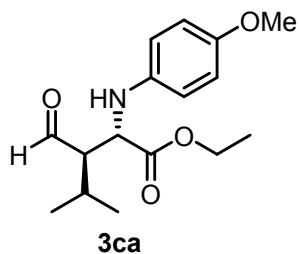


**Ethyl (2S,3R)-2-((4-methoxyphenyl)amino)-3-methyl-4-oxohexanoate.<sup>1</sup>** The product was obtained in 59% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.25 – 4.07 (m, 4H), 3.74 (s, 3H), 3.07 – 3.00 (m, 1H), 2.55 (q, *J* = 7.2 Hz, 2H), 1.26 – 1.21 (m, 3H), 1.20 – 1.16 (m, 3H), 1.07 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 212.2, 172.7, 153.1, 140.8, 115.8, 114.8, 61.2, 60.8, 55.7, 48.4, 34.9, 14.1, 13.4, 7.5. [α]<sub>D</sub><sup>12.7</sup> -30 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (96% *ee*) was determined by HPLC with a Daicel Chiralpak AD-H column (hexane/i-PrOH = 96:4, flow rate: 0.5 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* minor enantiomer) = 33.6 min; t<sub>R</sub> (*anti* major enantiomer) = 38.3 min.

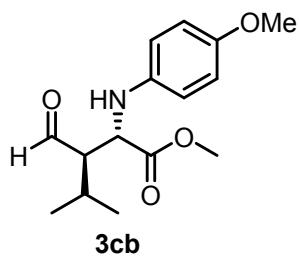


**Ethyl (2S,3R)-2-((4-methoxyphenyl)amino)-3-methyl-4-oxopentanoate.<sup>1</sup>** The product was obtained in 35% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.22 – 4.11 (m, 4H), 3.74 (s, 3H), 3.05 – 2.98 (m, 1H), 2.23 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.19 (d, *J* = 7.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 209.5, 172.5, 153.0, 140.7, 115.7, 114.8, 61.3, 60.5, 55.6, 49.4, 28.6, 14.1, 13.00. [α]<sub>D</sub><sup>18.6</sup> -23.3 (c 0.3, CHCl<sub>3</sub>). The enantiomeric excess (96% *ee*) was determined by HPLC with a Daicel Chiralpak

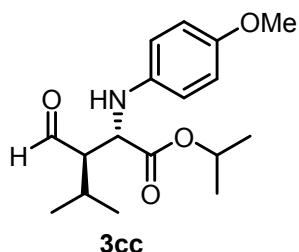
AS-H column (hexane/*i*-PrOH = 96:4, flow rate: 1.0 mL/min,  $\lambda_{\max}$  240 nm):  $t_R$  (*anti* major enantiomer) = 20.7 min;  $t_R$  (*anti* minor enantiomer) = 38.2 min.



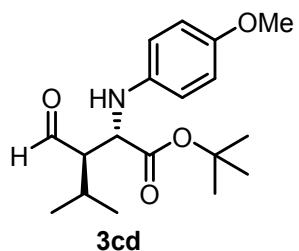
**Ethyl (2*S*,3*R*)-3-formyl-2-((4-methoxyphenyl)amino)-4-methylpentanoate.<sup>5</sup>** The product was obtained in 78% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.74 (d,  $J$  = 3.4 Hz, 1H), 6.77 (d,  $J$  = 8.9 Hz, 2H), 6.66 (d,  $J$  = 8.9 Hz, 2H), 4.36 (d,  $J$  = 7.7 Hz, 1H), 4.15 (q,  $J$  = 7.1 Hz, 2H), 3.99 (brs, 1H), 3.73 (s, 3H), 2.62 – 2.57 (m, 1H), 2.18 – 2.03 (m, 1H), 1.20 (t,  $J$  = 7.1 Hz, 3H), 1.12 (d,  $J$  = 6.9 Hz, 3H), 1.07 (d,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.2, 172.8, 153.2, 140.4, 115.8, 114.7, 61.3, 59.5, 57.2, 55.6, 27.5, 21.2, 19.1, 14.1.  $[\alpha]_D^{13.8}$  -31 (c 0.1,  $\text{CHCl}_3$ ). The enantiomeric excess (94% *ee*) was determined by HPLC with a Daicel Chiraldak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min,  $\lambda_{\max}$  240 nm):  $t_R$  (*anti* major enantiomer) = 17.4 min;  $t_R$  (*anti* minor enantiomer) = 32.8 min.



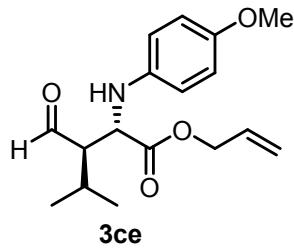
**Methyl (2*S*,3*R*)-3-formyl-2-((4-methoxyphenyl)amino)-4-methylpentanoate.** The product was obtained in 73% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.75 (d,  $J$  = 3.3 Hz, 1H), 6.78 (d,  $J$  = 8.9 Hz, 2H), 6.66 (d,  $J$  = 8.9 Hz, 2H), 4.38 (d,  $J$  = 7.5 Hz, 1H), 4.04 (brs, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 2.65 – 2.58 (m, 1H), 2.16 – 2.04 (m, 1H), 1.13 (d,  $J$  = 6.9 Hz, 3H), 1.08 (d,  $J$  = 6.9 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.2, 173.4, 153.2, 140.4, 115.7, 114.8, 59.6, 57.0, 55.6, 52.3, 27.5, 21.2, 19.2. HRMS (ESI): calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_4\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 302.1363, found 302.1361.  $[\alpha]_D^{19.9}$  -54 (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (93% *ee*) was determined by HPLC with a Daicel Chiraldak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min,  $\lambda_{\max}$  240 nm):  $t_R$  (*anti* major enantiomer) = 24.8 min;  $t_R$  (*anti* minor enantiomer) = 41.5 min.



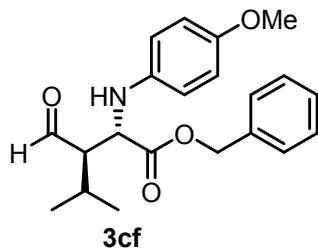
**Isopropyl (2S,3R)-3-formyl-2-((4-methoxyphenyl)amino)-4-methylpentanoate.<sup>5</sup>** The product was obtained in 80% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.73 (d, *J* = 3.6 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 5.05 – 4.96 (m, 1H), 4.33 (d, *J* = 7.9 Hz, 1H), 3.91 (brs, 1H), 3.74 (s, 3H), 2.59 – 2.54 (m, 1H), 2.15 – 2.03 (m, 1H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.2, 172.2, 153.2, 140.4, 115.9, 114.6, 69.0, 59.5, 57.3, 55.6, 27.5, 21.7, 21.6, 21.2, 19.0. [α]<sub>D</sub><sup>13.1</sup> -21 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (90% *ee*) was determined by HPLC with a Daicel Chiraldak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* major enantiomer) = 14.8 min; t<sub>R</sub> (*anti* minor enantiomer) = 35.9 min.



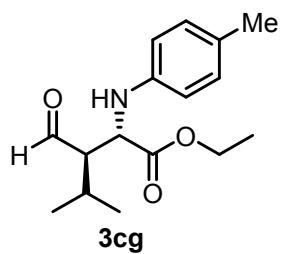
**Tert-butyl (2S,3R)-3-formyl-2-((4-methoxyphenyl)amino)-4-methylpentanoate.<sup>4</sup>** The product was obtained in 82% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.73 (d, *J* = 3.7 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 4.27 (d, *J* = 8.0 Hz, 1H), 3.91 (brs, 1H), 3.74 (s, 3H), 2.55 – 2.50 (m, 1H), 2.16 – 2.07 (m, 1H), 1.38 (s, 9H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.4, 171.8, 153.0, 140.5, 115.8, 114.6, 82.1, 59.5, 57.8, 55.5, 27.8, 27.5, 21.2, 19.0. [α]<sub>D</sub><sup>14.5</sup> -47 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (90% *ee*) was determined by HPLC with a Daicel Chiraldak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* major enantiomer) = 12.2 min; t<sub>R</sub> (*anti* minor enantiomer) = 31.1 min.



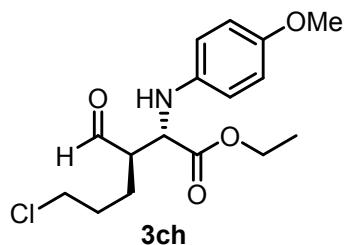
**Allyl (2S,3R)-3-formyl-2-((4-methoxyphenyl)amino)-4-methylpentanoate.<sup>4</sup>** The product was obtained in 81% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.75 (d, *J* = 3.2 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.87 – 5.78 (m, 1H), 5.26 – 5.19 (m, 2H), 4.59 (d, *J* = 5.6 Hz, 2H), 4.40 (d, *J* = 7.4 Hz, 1H), 4.00 (brs, 1H), 3.74 (s, 3H), 2.65 – 2.61 (m, 1H), 2.15 – 2.05 (m, 1H), 1.13 (d, *J* = 6.9 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.2, 172.5, 153.2, 140.3, 131.3, 118.8, 115.7, 114.7, 65.8, 59.5, 57.0, 55.6, 27.5, 21.2, 19.1. [α]<sub>D</sub><sup>12.9</sup> -27 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (91% ee) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/*i*-PrOH = 90:10, flow rate: 0.5 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* major enantiomer) = 19.5 min; t<sub>R</sub> (*anti* minor enantiomer) = 38.3 min.



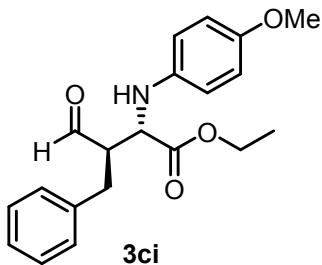
**Benzyl (2S,3R)-3-formyl-2-((4-methoxyphenyl)amino)-4-methylpentanoate.** The product was obtained in 80% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.73 (d, *J* = 3.4 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.25 – 7.19 (m, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 5.13 (s, 2H), 4.44 (d, *J* = 7.4 Hz, 1H), 4.00 (brs, 1H), 3.76 (s, 3H), 2.65 – 2.60 (m, 1H), 2.10 – 2.00 (m, 1H), 1.11 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.2, 172.7, 153.2, 140.3, 135.1, 128.5, 128.3, 128.2, 115.8, 114.7, 67.0, 59.4, 57.1, 55.6, 27.5, 21.2, 19.0. HRMS (ESI): calcd for C<sub>21</sub>H<sub>25</sub>NO<sub>4</sub>Na (M+Na<sup>+</sup>) 378.1676, found 378.1685. [α]<sub>D</sub><sup>14.4</sup> -36 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (94% ee) was determined by HPLC with a Daicel Chiraldpak AD-H column (hexane/*i*-PrOH = 90:10, flow rate: 1.0 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* minor enantiomer) = 14.0 min; t<sub>R</sub> (*anti* major enantiomer) = 20.8 min.



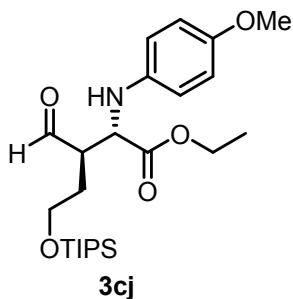
**Ethyl (2S,3R)-3-formyl-4-methyl-2-(p-tolylamino)pentanoate.** The product was obtained in 65% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.76 (d, *J* = 3.3 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 4.43 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.11 (brs, 1H), 2.66 – 2.62 (m, 1H), 2.25 (s, 3H), 2.17 – 2.08 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.3, 172.7, 144.1, 129.8, 128.4, 114.2, 61.4, 59.5, 56.3, 27.5, 21.2, 20.4, 19.3, 14.1. HRMS (ESI): calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>3</sub>Na (M+Na<sup>+</sup>) 300.1570, found 300.1562. [α]<sub>D</sub><sup>18.4</sup> -36 (c 0.5, CHCl<sub>3</sub>). The enantiomeric excess (93% ee) was determined by HPLC with a Daicel Chiraldapak IC column (hexane/i-PrOH = 96:4, flow rate: 1.0 mL/min, λ<sub>max</sub> 240 nm): t<sub>R</sub> (*anti* major enantiomer) = 13.8 min; t<sub>R</sub> (*anti* minor enantiomer) = 14.8 min.



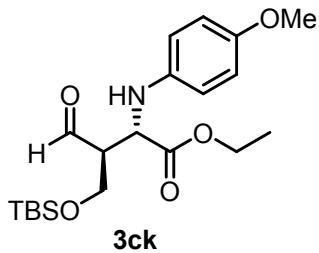
**Ethyl (2S,3R)-6-chloro-3-formyl-2-((4-methoxyphenyl)amino)hexanoate.** The product was obtained in 70% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.69 (d, *J* = 2.0 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 4.31 (d, *J* = 6.1 Hz, 1H), 4.23 – 4.15 (m, 2H), 4.09 (brs, 1H), 3.74 (s, 3H), 3.48 – 3.57 (m, 2H), 2.82 – 2.74 (m, 1H), 1.95 – 1.85 (m, 2H), 1.84 – 1.74 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.4, 171.8, 153.2, 140.0, 115.7, 114.8, 61.7, 58.0, 55.6, 53.1, 44.3, 30.0, 22.7, 14.1. HRMS-ESI calcd for C<sub>16</sub>H<sub>22</sub>ClNO<sub>4</sub>Na (M + Na)<sup>+</sup> 350.1133, found 350.1130. [α]<sub>D</sub><sup>13.2</sup> +12 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (95% ee) was determined by HPLC with a Daicel Chiraldapak AD-H column (hexane/i-PrOH = 90:10, flow rate: 1.0 mL/min, λ<sub>max</sub> 230 nm): t<sub>R</sub> (*anti* minor enantiomer) = 15.5 min; t<sub>R</sub> (*anti* major enantiomer) = 20.5 min.



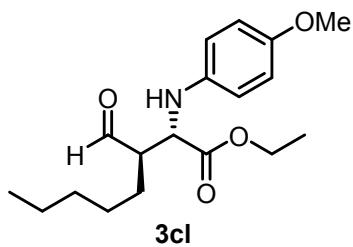
**Ethyl (2S,3R)-3-benzyl-2-((4-methoxyphenyl)amino)-4-oxobutanoate.<sup>4</sup>** The product was obtained in 60% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.73 (d, *J* = 1.2 Hz, 1H), 7.30 – 7.17 (m, 5H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 4.22 – 4.05 (m, 4H), 3.73 (s, 3H), 3.33 – 3.25 (m, 1H), 3.13 (dd, *J* = 14.0, 7.1 Hz, 1H), 2.93 (dd, *J* = 14.0, 7.8 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.8, 172.2, 153.0, 140.5, 137.8, 129.1, 128.7, 126.8, 115.6, 114.7, 61.6, 57.3, 55.6, 55.2, 31.7, 14.1. [α]<sub>D</sub><sup>18.4</sup> -14 (c 0.5, CHCl<sub>3</sub>). The enantiomeric excess (95% ee) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/*i*-PrOH = 98:2, flow rate: 1.0 mL/min, λ<sub>max</sub> 240 nm): t<sub>R</sub> (*anti* major enantiomer) = 50.5 min; t<sub>R</sub> (*anti* minor enantiomer) = 60.2 min.



**Ethyl (2S,3R)-3-formyl-2-((4-methoxyphenyl)amino)-5-((triisopropylsilyloxy)pentanoate.** The product was obtained in 70% yield. Pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.74 (d, *J* = 1.8 Hz, 1H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 4.34 (brs, 1H), 4.22 – 4.13 (m, 3H), 3.85 – 3.76 (m, 2H), 3.74 (s, 3H), 3.10 – 3.01 (m, 1H), 2.08 – 1.97 (m, 1H), 1.86 – 1.79 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.08 – 1.02 (m, 21H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.4, 172.0, 152.9, 140.4, 115.4, 114.8, 61.5, 60.9, 57.8, 55.6, 51.0, 29.0, 17.9, 14.1, 11.8. HRMS (ESI): calcd for C<sub>24</sub>H<sub>41</sub>NO<sub>5</sub>SiNa (M+Na<sup>+</sup>) 474.2646, found 474.2655. [α]<sub>D</sub><sup>14.3</sup> -11 (c 0.1, CHCl<sub>3</sub>). The enantiomeric excess (90% ee) was determined by HPLC with a Daicel Chiraldpak AD-H column (hexane/*i*-PrOH = 99:1, flow rate: 0.5 mL/min, λ<sub>max</sub> 254 nm): t<sub>R</sub> (*anti* minor enantiomer) = 34.5 min; t<sub>R</sub> (*anti* major enantiomer) = 50.6 min.



**Ethyl (2S,3S)-4-((tert-butyldimethylsilyl)oxy)-3-formyl-2-((4-methoxyphenyl)amino)butanoate.** The product was obtained in 58% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77 (d,  $J = 1.3$  Hz, 1H), 6.78 (d,  $J = 8.9$  Hz, 2H), 6.69 (d,  $J = 8.9$  Hz, 2H), 4.50 (d,  $J = 5.6$  Hz, 1H), 4.22 – 4.14 (m, 3H), 4.04 (dd,  $J = 10.4, 5.3$  Hz, 1H), 3.95 (dd,  $J = 10.4, 6.6$  Hz, 1H), 3.75 (s, 3H), 3.01 (q,  $J = 5.3$  Hz, 1H), 1.24 (t,  $J = 7.1$  Hz, 3H), 0.92 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.4, 172.3, 153.1, 140.8, 115.7, 114.7, 61.5, 59.6, 56.14, 56.09, 55.6, 25.8, 18.2, 14.1, -5.62, -5.65. HRMS (ESI): calcd for  $\text{C}_{20}\text{H}_{33}\text{NO}_5\text{SiNa}$  ( $M+\text{Na}^+$ ) 418.2020, found 418.2029.  $[\alpha]_D^{14.2} +6$  (c 0.1,  $\text{CHCl}_3$ ). The enantiomeric excess (94% ee) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/*i*-PrOH = 95:5, flow rate: 0.5 mL/min,  $\lambda_{\text{max}}$  230 nm):  $t_R$  (*anti* major enantiomer) = 14.5 min;  $t_R$  (*anti* minor enantiomer) = 20.5 min.



**Ethyl (2S,3R)-3-formyl-2-((4-methoxyphenyl)amino)octanoate.<sup>5</sup>** The product was obtained in 81% yield. Pale yellow liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.65 (d,  $J = 2.4$  Hz, 1H), 6.77 (d,  $J = 8.8$  Hz, 2H), 6.65 (d,  $J = 8.9$  Hz, 2H), 4.27 – 4.26 (m, 1H), 4.17 (qd,  $J = 7.1, 1.8$  Hz, 2H), 4.05 (brs, 1H), 3.74 (s, 3H), 2.78 – 2.72 (m, 1H), 1.76 – 1.68 (m, 1H), 1.59 – 1.52 (m, 1H), 1.36 – 1.25 (m, 6H), 1.22 (t,  $J = 7.1$  Hz, 3H), 0.87 (t,  $J = 5.9$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  202.2, 172.2, 153.1, 140.3, 115.6, 114.8, 61.4, 58.1, 55.6, 53.9, 31.6, 26.9, 25.6, 22.3, 14.1, 13.9.  $[\alpha]_D^{13.4} -9$  (c 0.1,  $\text{CHCl}_3$ ). The enantiomeric excess (97% ee) was determined by HPLC with a Daicel Chiraldpak AS-H column (hexane/*i*-PrOH = 99:1, flow rate: 1.0 mL/min,  $\lambda_{\text{max}}$  254 nm):  $t_R$  (*anti* major enantiomer) = 26.4 min;  $t_R$  (*anti* minor enantiomer) = 29.9 min.

## 5. Transformations of the Products

### 5.1 Synthesis of compound 5.

To a solution of *tert*-butyl (4-methoxyphenyl) glycinate (47.4 mg, 0.2 mmol, 1 eq), Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (3.0 mg, 2 mol%) in dry CH<sub>3</sub>CN (3 mL) was added Cu(OAc)·H<sub>2</sub>O (2.0 mg, 0.01 mmol, 5 mol%). The mixed solution was irradiated with a 5 W blue LED bulb under air atmosphere at room temperature. After full conversion of the *tert*-butyl (4-methoxyphenyl)glycinate as monitored by TLC, iso-valeraldehyde (51.7 mg, 0.6 mmol, 3 eq) and catalyst A (4.4 mg, 0.02 mmol, 10 mol %) were added, and the mixture was stirred in dark overnight. Then acetic acid (13.7 μL, 0.24 mmol, 1.2 eq) and NaBH<sub>4</sub> (9.1 mg, 0.24 mmol, 1.2 eq) were added at 0 °C. The resulting mixture was vigorously stirred at 0 °C for 0.5 h, then quenched by sodium bicarbonate solution. The reaction mixture was extracted with ethyl acetate, the combined organic layers were washed with H<sub>2</sub>O and brine, respectively, and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (with petroleum ether/EtOAc = 4:1 as eluent) to afford compound 5 (52.3 mg, 81% yield). Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.77 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 4.01 (d, *J* = 7.0 Hz, 1H), 3.84 (d, *J* = 4.8 Hz, 2H), 3.74 (s, 3H), 1.98 – 1.83 (m, 1H), 1.80 – 1.71 (m, 1H), 1.38 (s, 9H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.4, 153.3, 140.9, 116.6, 114.6, 81.6, 62.5, 62.0, 55.6, 48.6, 27.9, 26.7, 21.4, 18.6. HRMS (ESI): calcd for C<sub>18</sub>H<sub>29</sub>NO<sub>4</sub>Na (M+Na<sup>+</sup>) 346.1989, found 346.1986. [α]<sub>D</sub><sup>20.1</sup> -64 (c 0.5, CHCl<sub>3</sub>). The enantiomeric excess (96% ee) was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 95:5, flow rate: 0.8 mL/min, λ<sub>max</sub> 240 nm): t<sub>R</sub> (*anti* major enantiomer) = 10.2 min; t<sub>R</sub> (*anti* minor enantiomer) = 13.9 min.

### 5.2 Synthesis of compound 6.

The solution of Ceric Ammonium Nitrate (CAN, 225 mg, 0.41 mmol, 2.5 eq) in distilled water (2.0 mL) was added slowly to the stirred solution of compound 5 (52.3 mg, 0.16 mmol) in CH<sub>3</sub>CN/H<sub>2</sub>O (3/1, 4.0 mL) at 0 °C. The reaction mixture was further stirred at 0 °C for about 1 h, till the reaction completed as monitored by TLC. The reaction was then quenched by adding the saturated Na<sub>2</sub>SO<sub>3</sub> solution and extracted with ethyl acetate. The combined organic layer was extracted with 0.1M HCl. The combined aqueous layer was neutralized by NaHCO<sub>3</sub> (pH = 7) and extracted with ethyl acetate. The combined organic layer was washed with brine solution, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure, compound 6 (25.4 mg, 73% yield) was afforded without further purification. Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.84 – 3.72 (m, 2H), 3.66 (d, *J* = 5.9 Hz, 1H), 3.02 (brs, 3H), 1.92 – 1.80 (m, 1H), 1.64 – 1.53

(m, 1H), 1.46 (s, 9H), 1.01 (d,  $J$  = 6.8 Hz, 3H), 0.95 (d,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 81.5, 62.5, 57.7, 48.7, 28.0, 26.2, 21.2, 19.0. HRMS (ESI): calcd for  $\text{C}_{11}\text{H}_{23}\text{NO}_3\text{H}$  ( $\text{M}+\text{H}^+$ ) 218.1751, found 218.1747.  $[\alpha]_D^{20.2} +26$  (c 0.5,  $\text{CHCl}_3$ ).

### 5.3 Synthesis of compound 7.

The solution of **3ca** (40 mg, 0.136 mmol, 1 eq) in EtOH (0.7 mL) was added dropwise to the stirred solution of  $\text{NaBH}_4$  (5.7 mg, 0.15 mmol, 1.1 eq) in EtOH (0.3 mL) under argon atmosphere at 0 °C. The resulting mixture was further stirred at 0 °C for about 1 h, till the reaction completed as monitored by TLC. The reaction was subsequently quenched with saturated  $\text{NaHCO}_3$  solution and extracted with ethyl acetate. The combined organic extracts were washed with brine once, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuum after filtration. The residue was purified by silica gel column chromatography (with petroleum ether/EtOAc = 4:1 as eluent) to afford compound **7** (24 mg, 71% yield). Colorless liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.82 (d,  $J$  = 8.9 Hz, 2H), 6.65 (d,  $J$  = 8.9 Hz, 2H), 4.43 – 4.30 (m, 2H), 4.16 – 3.98 (m, 2H), 3.77 (s, 3H), 2.79 – 2.75 (m, 1H), 2.00 – 1.92 (m, 1H), 0.95 (d,  $J$  = 7.0 Hz, 3H), 0.83 (d,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.7, 152.9, 141.1, 115.0, 114.2, 67.0, 56.2, 55.7, 45.2, 25.0, 21.1, 17.4. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{Na}$  ( $\text{M}+\text{Na}^+$ ) 272.1257, found 272.1254.  $[\alpha]_D^{18.3} +94$  (c 0.5,  $\text{CHCl}_3$ ). The enantiomeric excess (94% ee) was determined by HPLC with a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 80:20, flow rate: 0.5 mL/min,  $\lambda_{\text{max}}$  240 nm):  $t_R$  (*anti* minor enantiomer) = 34.8 min;  $t_R$  (*anti* major enantiomer) = 51.7 min.

## 6. Synthesis of Compound 4b.

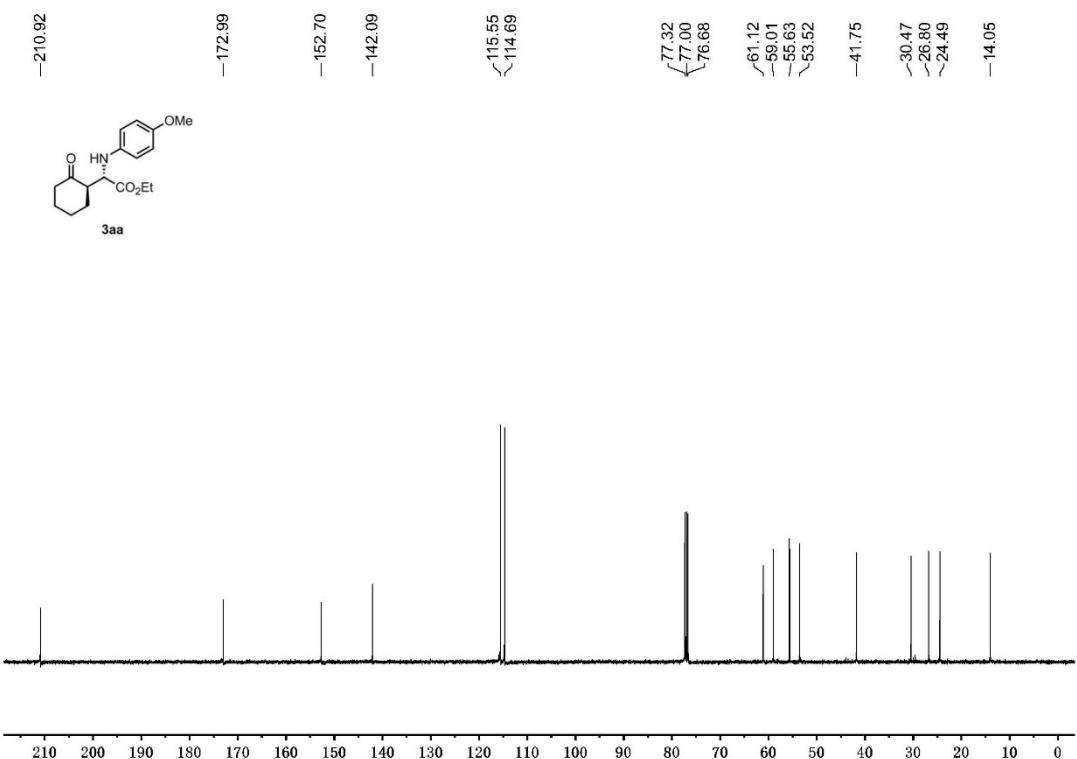
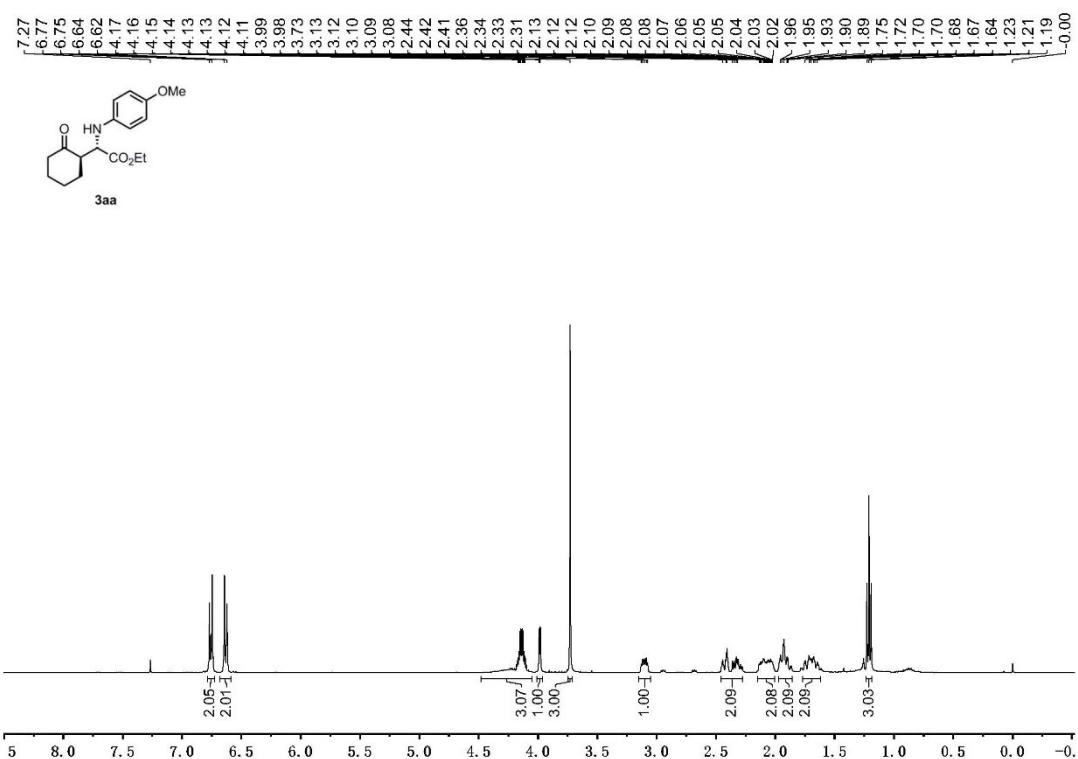
The solution of **1a** (41.8 mg, 0.2 mmol) and  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (3 mg, 2 mol%) in dry  $\text{CH}_3\text{CN}$  (3 mL) was irradiated with a 5 W blue LED bulb under air atmosphere at room temperature. After full conversion of **1a** as monitored by TLC, the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with petroleum ether/EtOAc = 4/1 as eluent) to afford the product **4b** (32 mg, 71% yield).

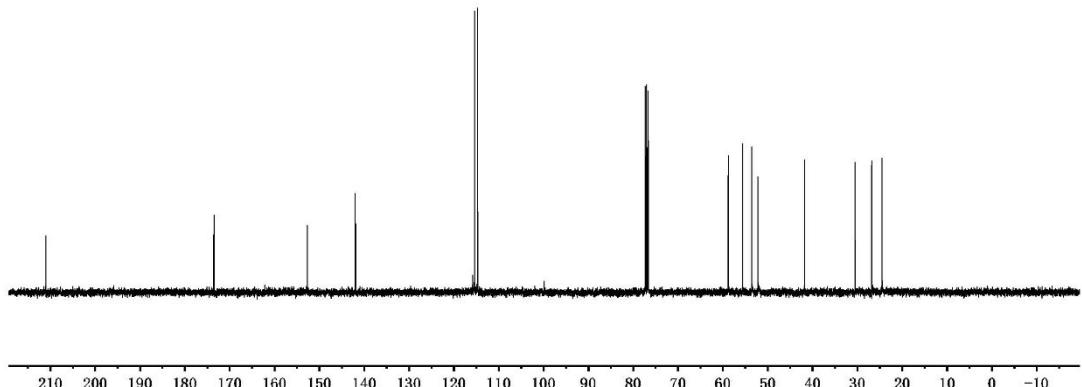
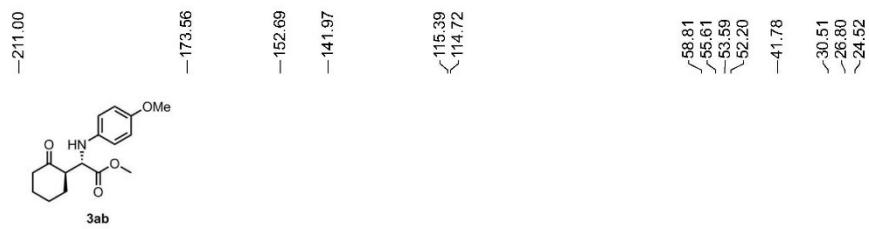
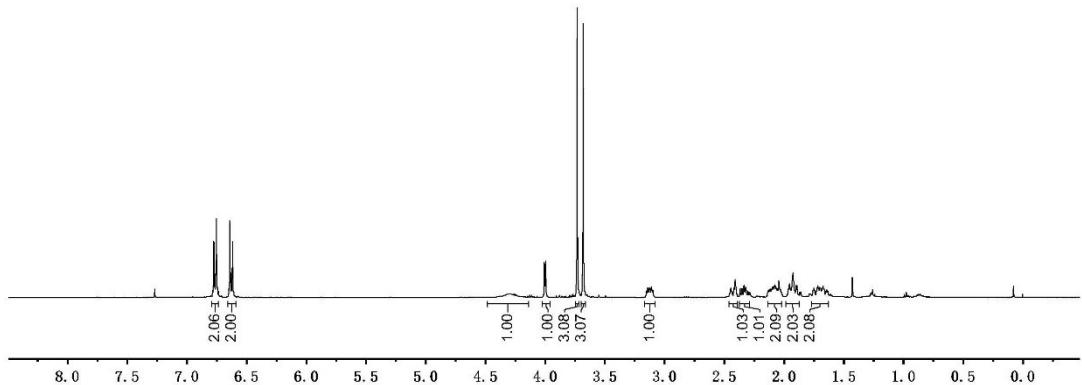
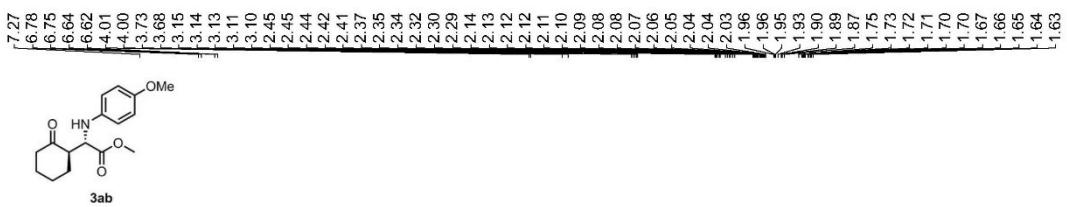
**Ethyl 2-((4-methoxyphenyl)amino)-2-oxoacetate.**<sup>7</sup> White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (brs, 1H), 7.57 (d,  $J$  = 9.0 Hz, 2H), 6.90 (d,  $J$  = 9.0 Hz, 2H), 4.41 (q,  $J$  = 7.1 Hz, 2H), 3.81 (s, 3H), 1.42 (t,  $J$  = 7.2 Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1, 157.1, 153.6, 129.5, 121.3, 114.3, 63.6, 55.4, 14.0. HRMS (ESI): calcd for  $\text{C}_{11}\text{H}_{14}\text{NO}_4$  ( $\text{M}+\text{H}^+$ ) 224.0917, found 224.0918.

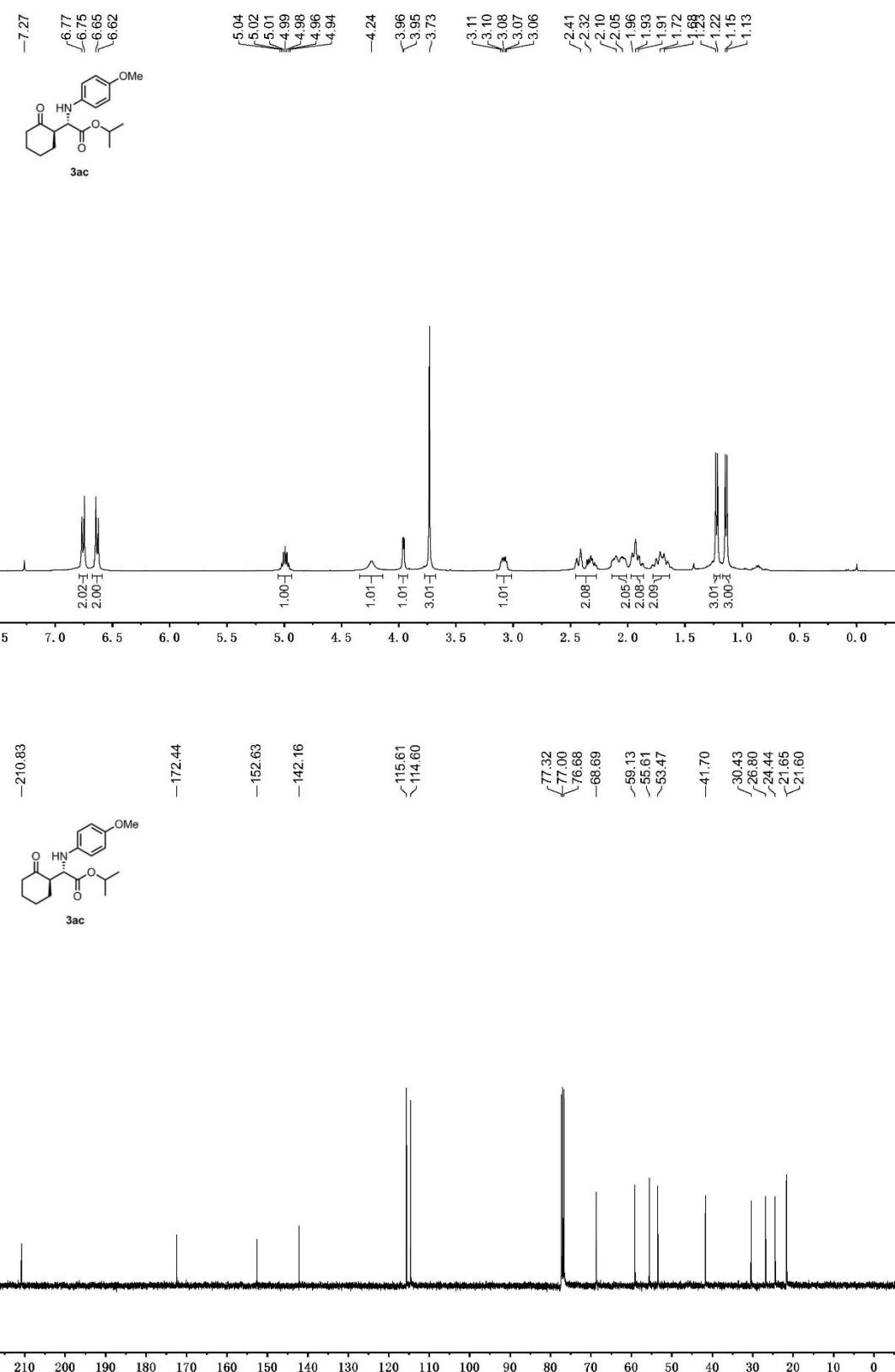
## 7. References

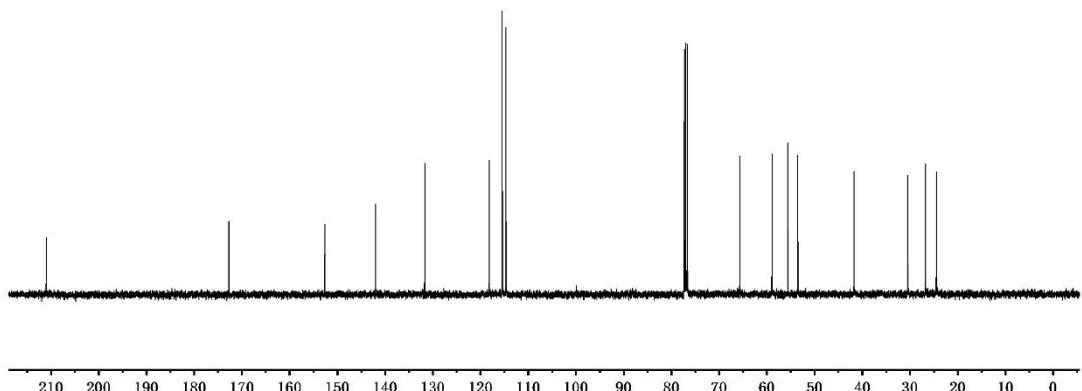
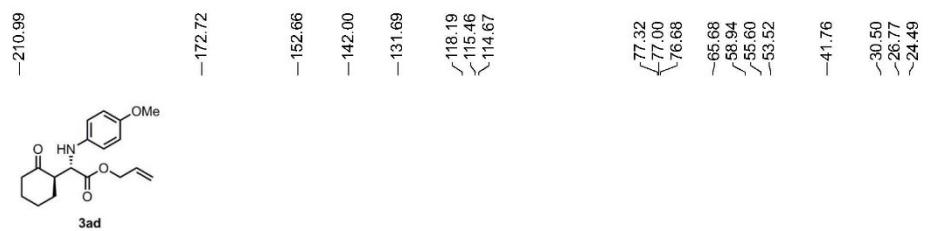
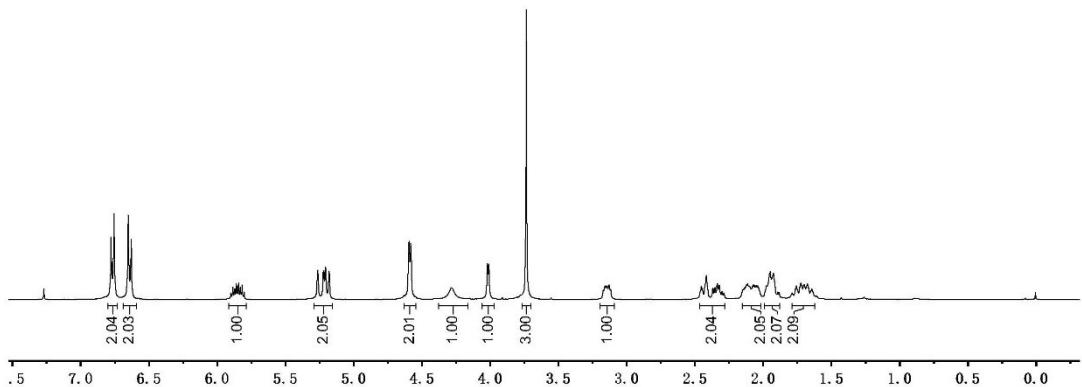
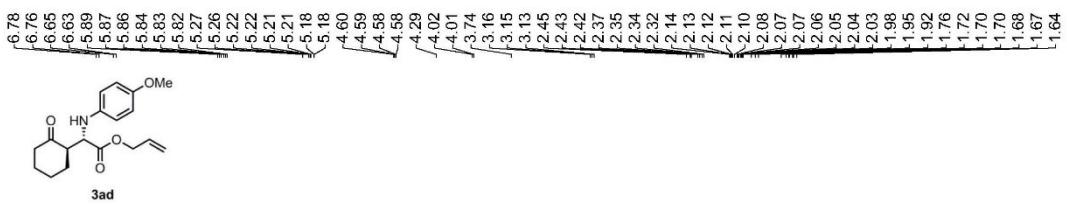
1. H. Zhang, M. Mifsud, F. Tanaka and C. F. Barbas, III, *J. Am. Chem. Soc.*, 2006, **128**, 9630-9631.
2. J. Xie and Z.-Z. Huang, *Angew. Chem., Int. Ed.*, 2010, **49**, 10181-10185.
3. R. Martín-Rapún, S. Sayalero and M. A. Pericàs, *Green Chem.*, 2013, **15**, 3295-3301.
4. H. Zhang, S. Mitsumori, N. Utsumi, M. Imai, N. Garcia-Delgado, M. Mifsud, K. Albertshofer, P. H.-Y. Cheong, K. N. Houk, F. Tanaka and C. F. Barbas, III, *J. Am. Chem. Soc.*, 2008, **130**, 875-886.
5. S. Mitsumori, H. Zhang, P. H. Y. Cheong, K. N. Houk, F. Tanaka and C. F. Barbas, *J. Am. Chem. Soc.*, 2006, **128**, 1040-1041.
6. L. Zhao, O. Basle and C.-J. Li, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 4106-4111.
7. C. Huo, Y. Yuan, M. Wu, X. Jia, X. Wang, F. Chen and J. Tang, *Angew. Chem., Int. Ed.*, 2014, **53**, 13544-13547.

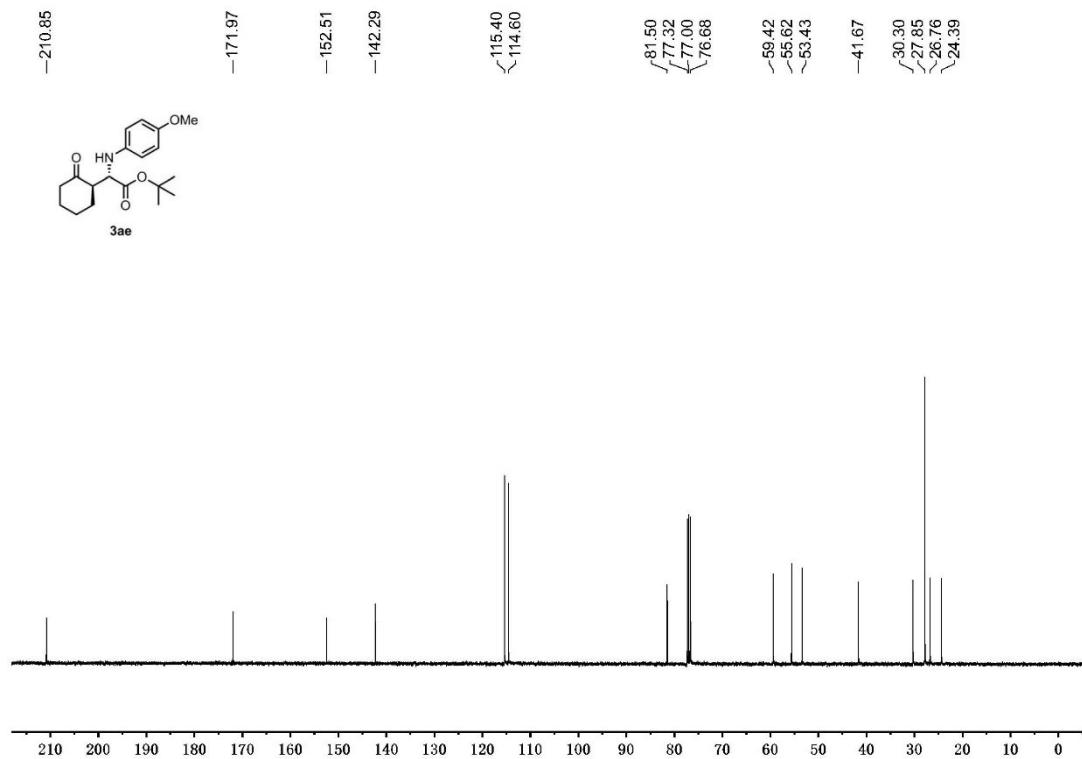
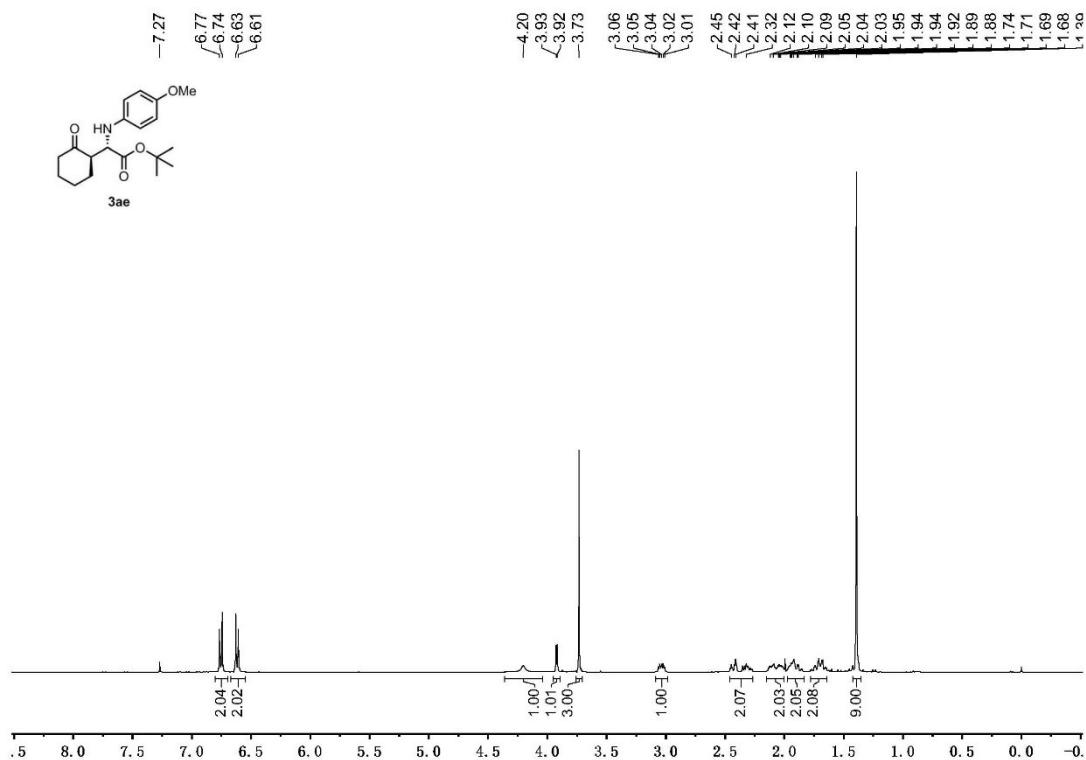
## 8. Copies of $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra

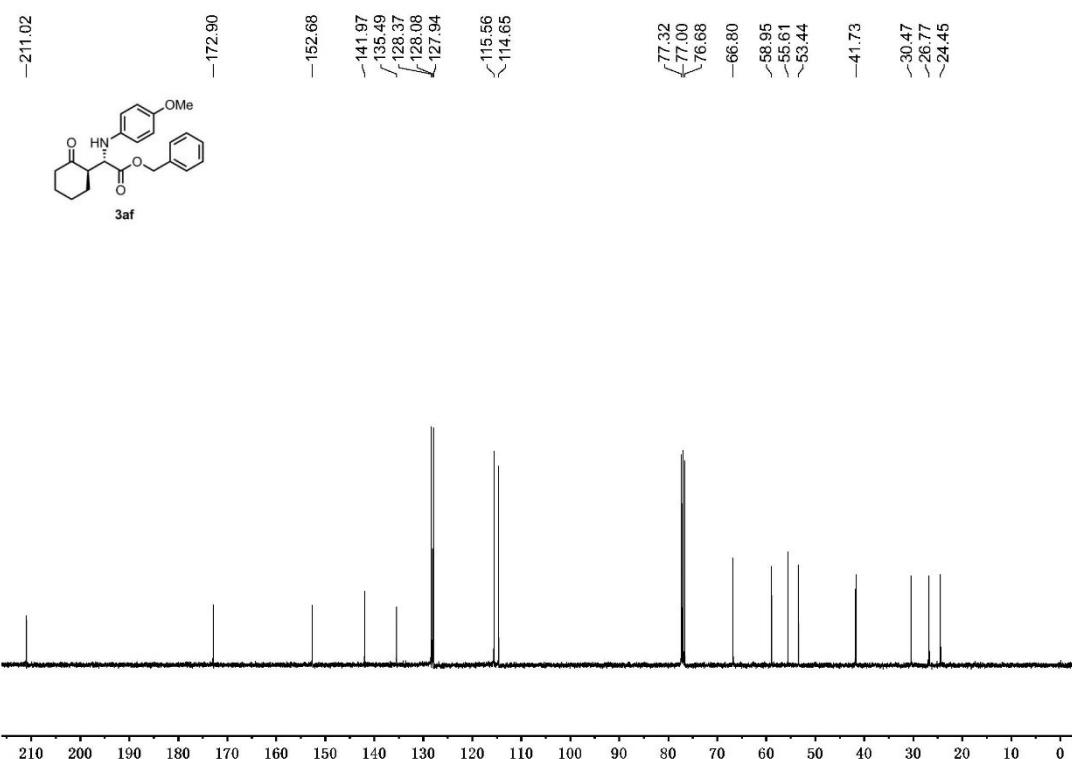
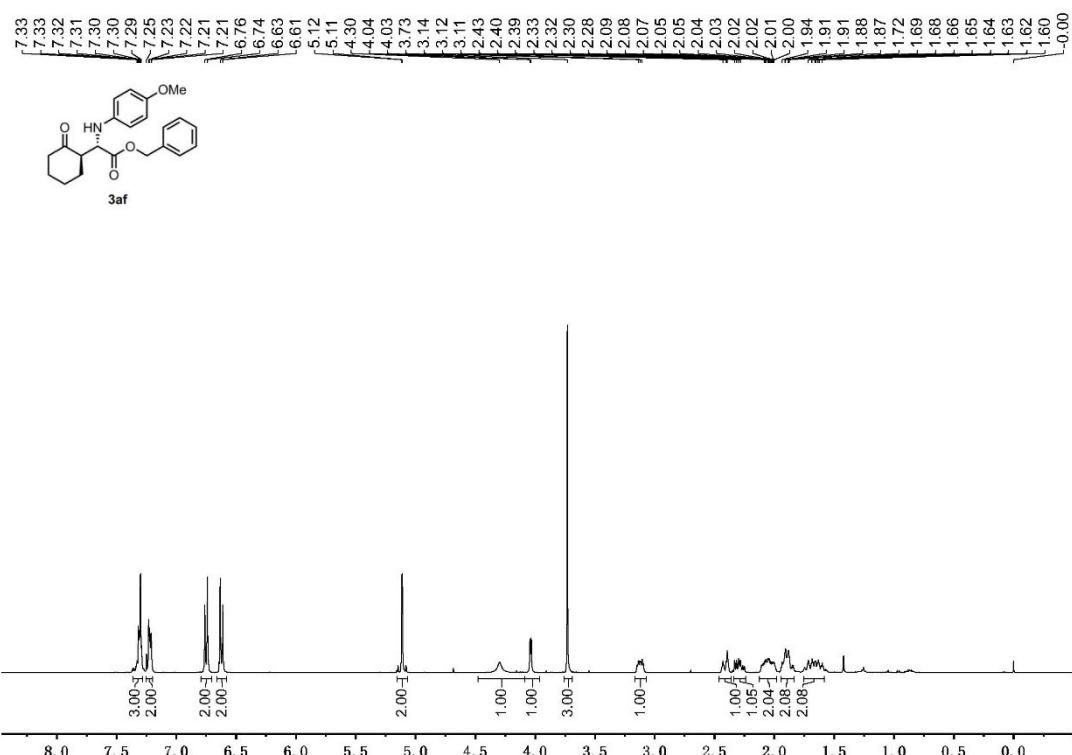


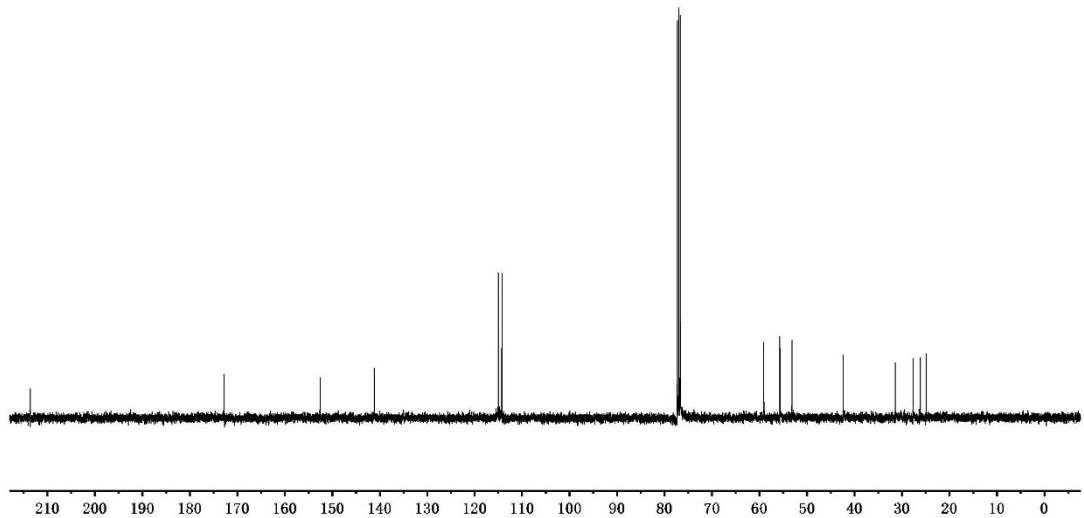
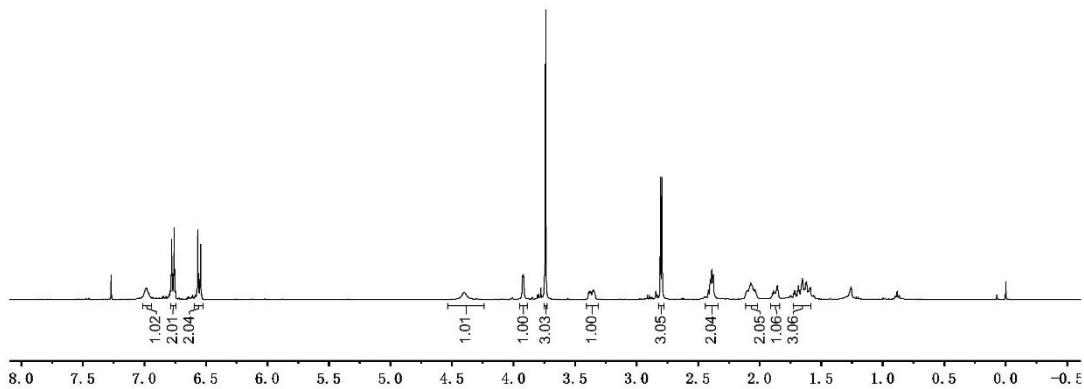
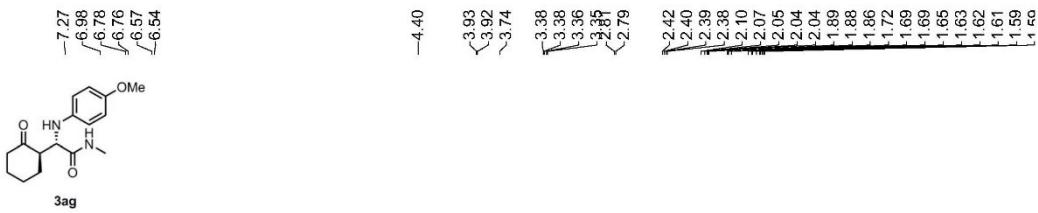


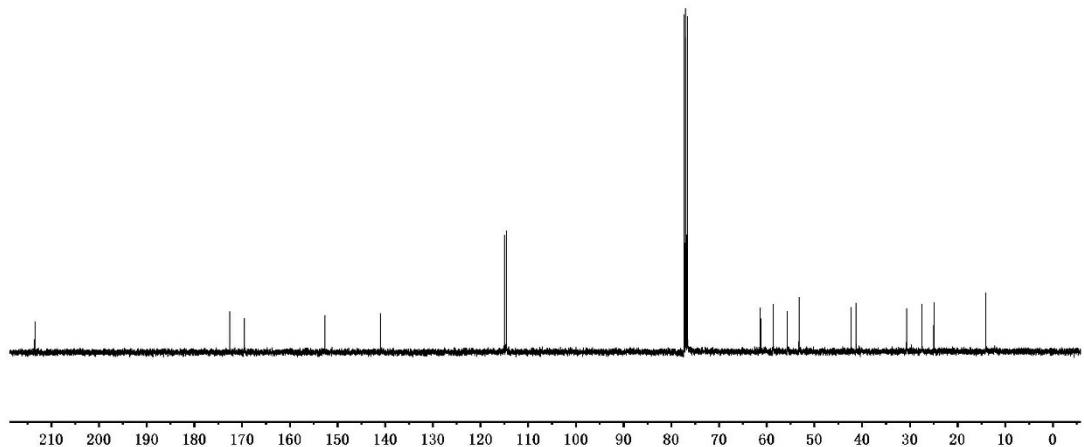
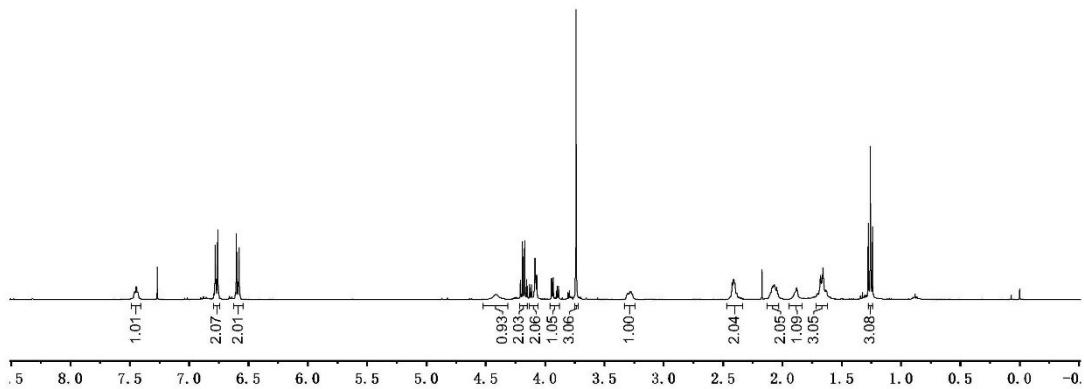
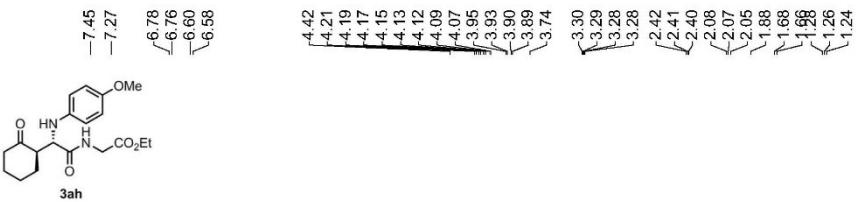


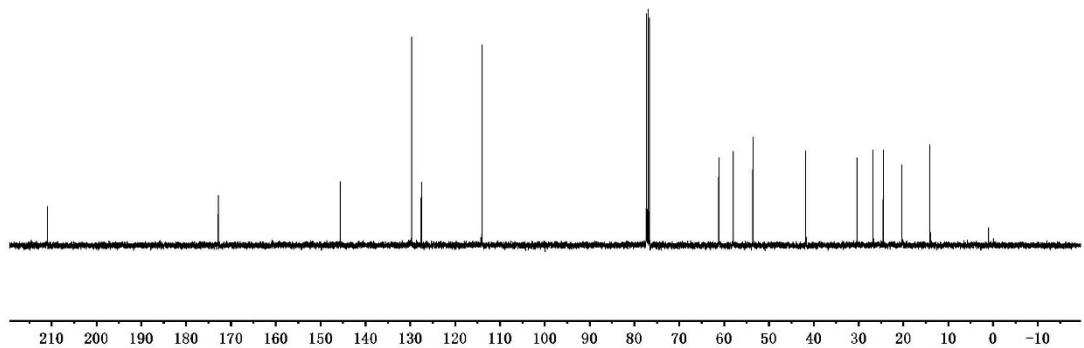
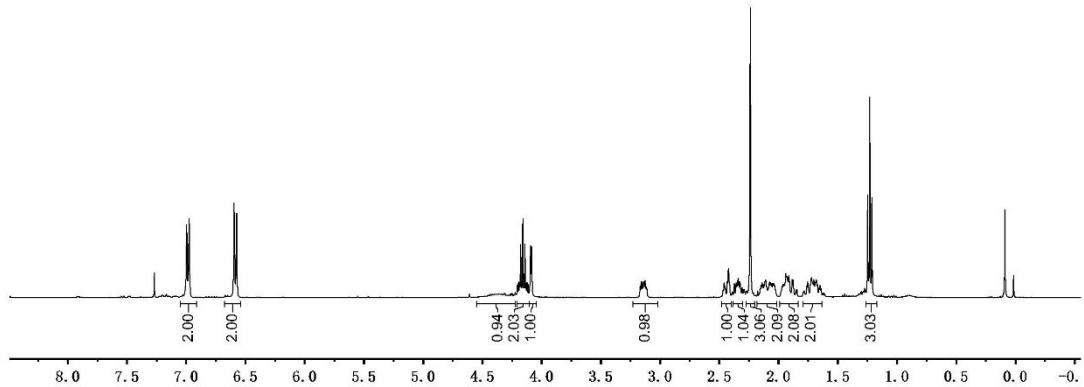
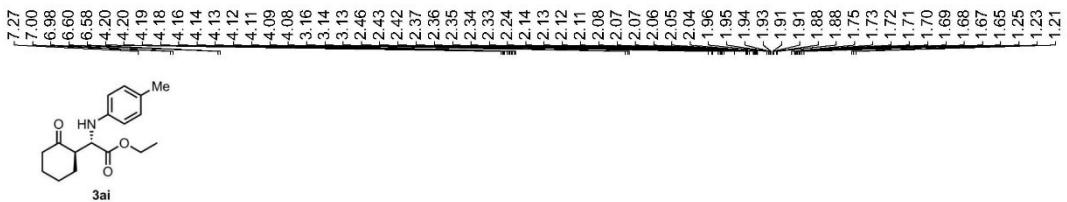


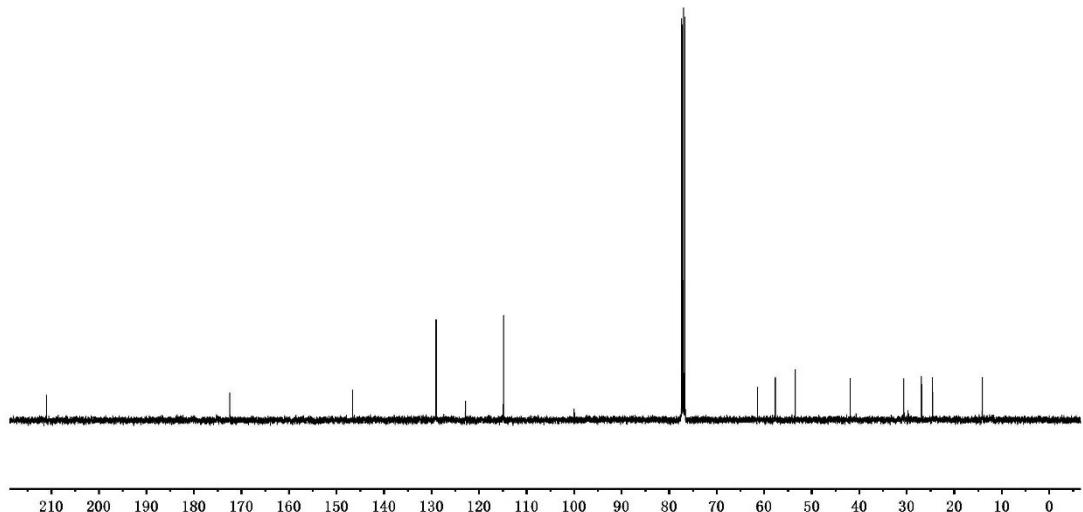
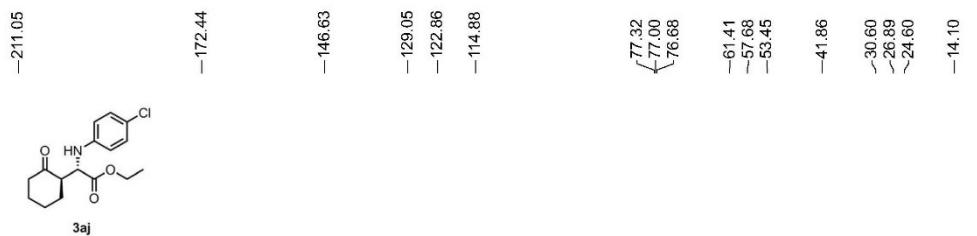
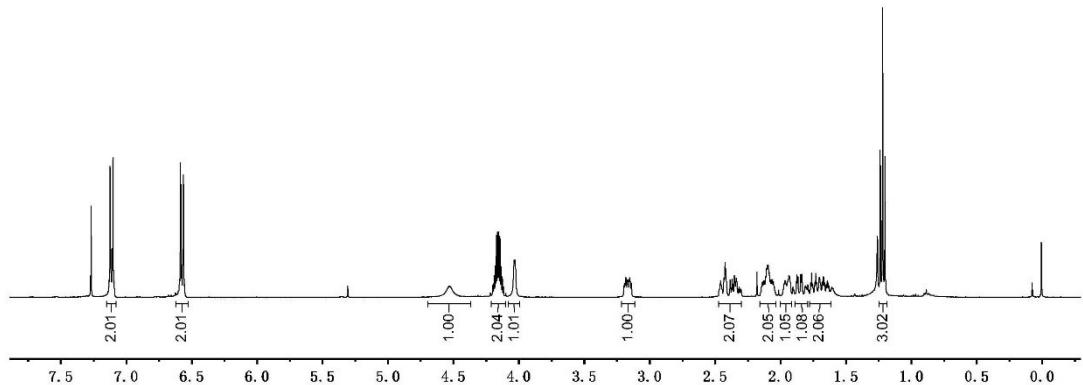
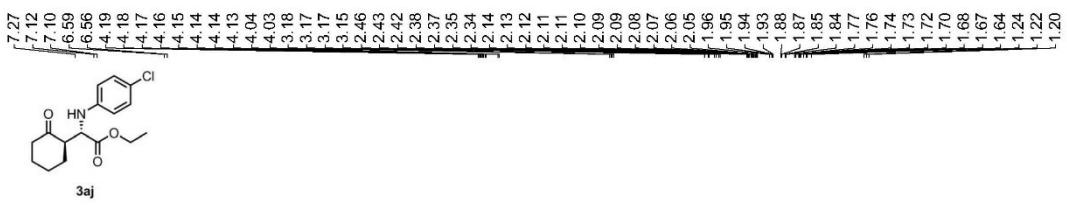


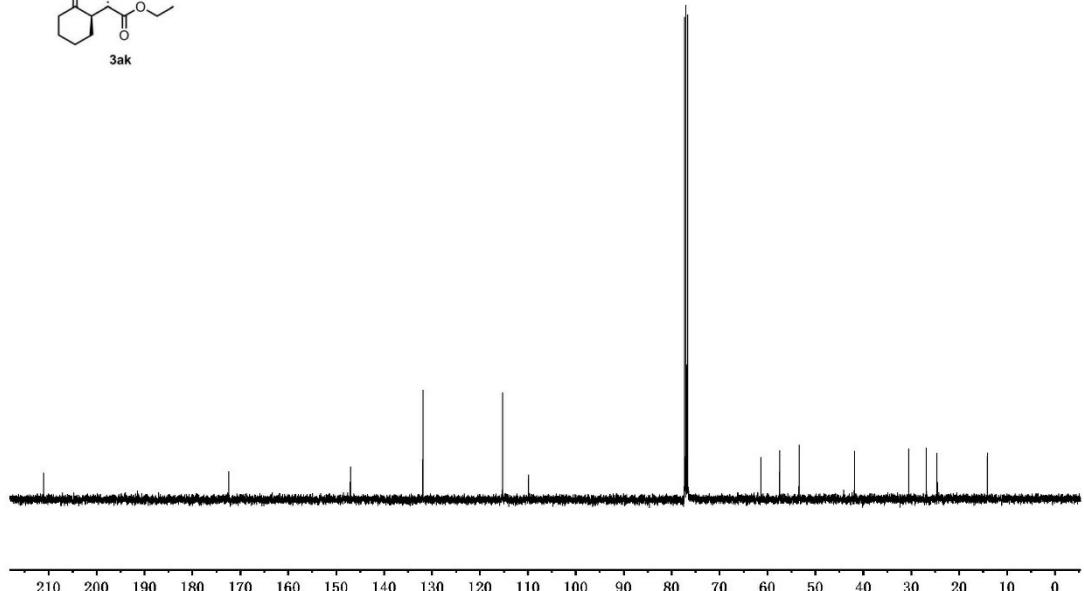
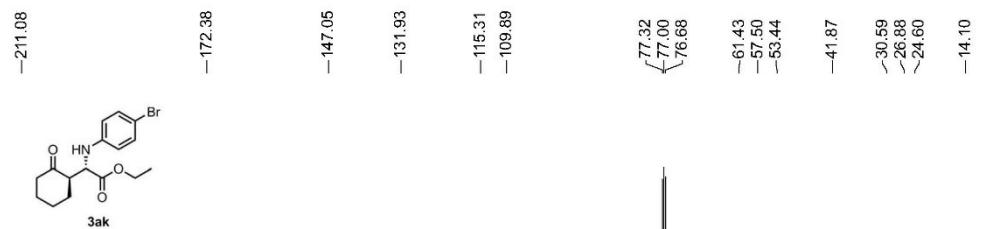
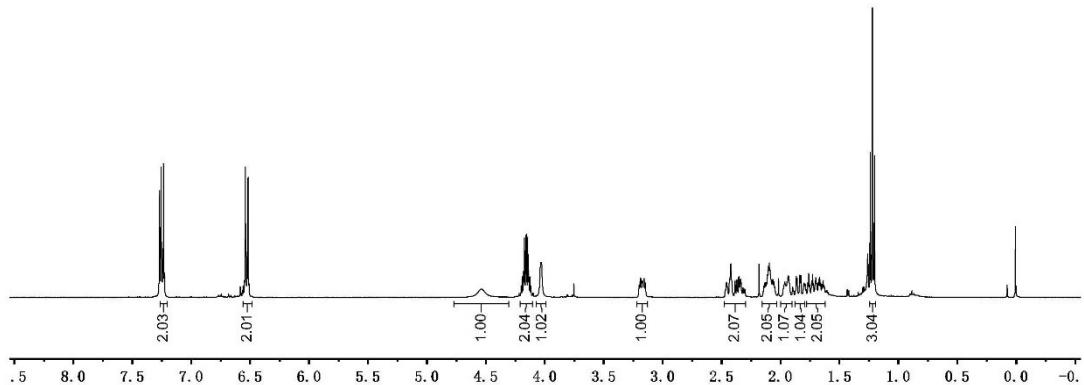
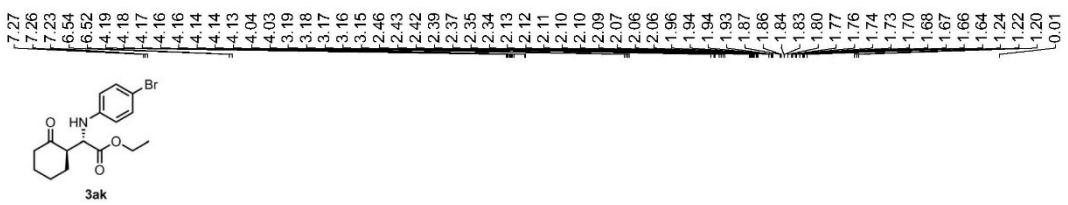




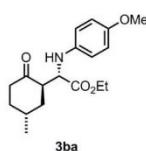




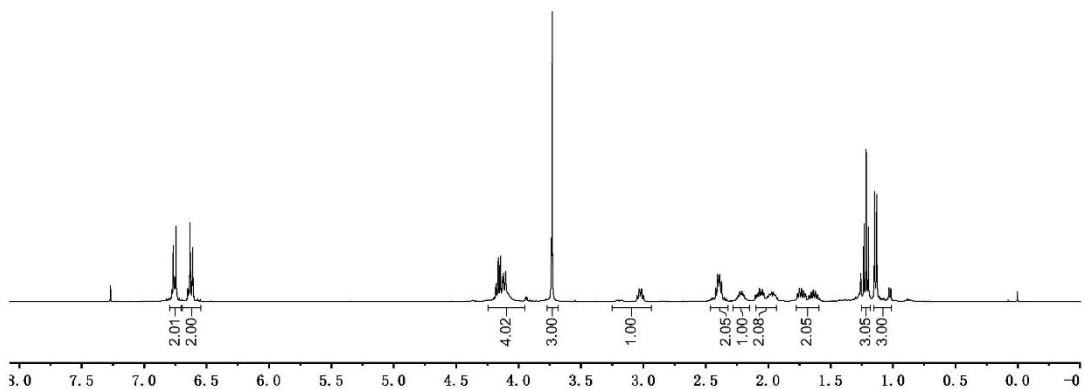




7.27  
6.77  
6.74  
6.63  
6.61  
4.38  
4.38  
4.17  
4.16  
4.15  
4.15  
4.14  
4.14  
4.13  
4.13  
4.12  
4.12  
4.10  
3.73  
3.03  
3.02  
2.42  
2.41  
2.39  
2.39  
2.37  
2.23  
2.22  
2.21  
2.20  
2.10  
2.09  
2.08  
2.07  
2.06  
2.06  
2.05  
2.04  
2.04  
1.99  
1.99  
1.73  
1.72  
1.70  
1.66  
1.64  
1.62  
1.60  
1.23  
1.22  
1.20  
1.15  
1.13



3ba



-211.36

-172.80

-152.91

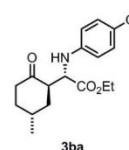
-141.35

115.52  
<114.76

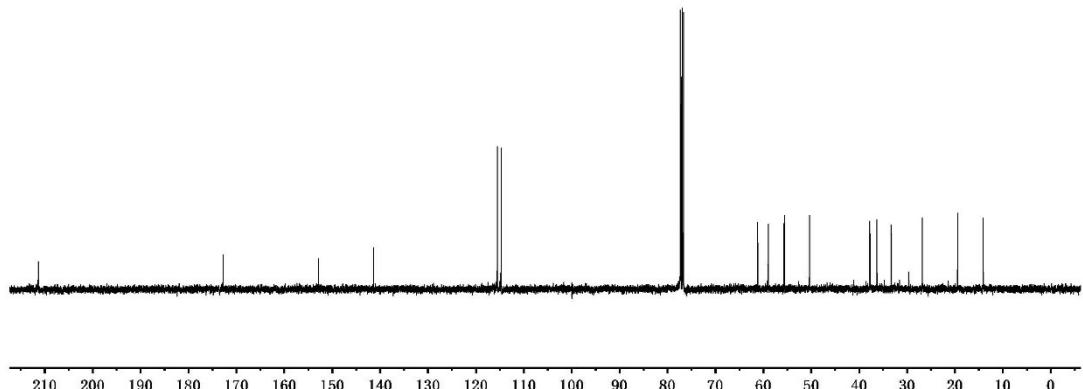
77.32  
{77.00  
76.68

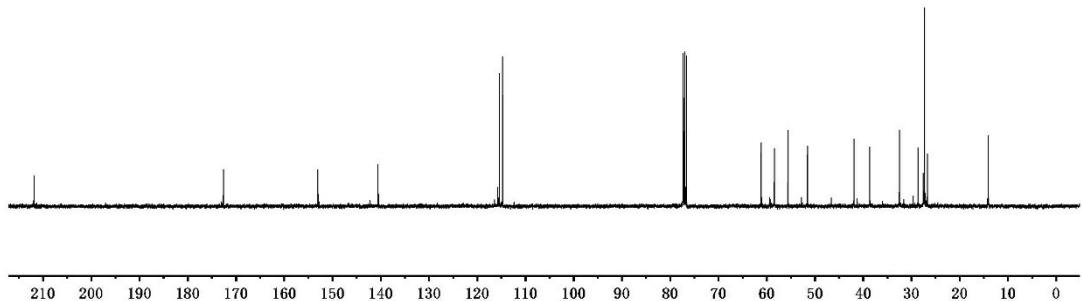
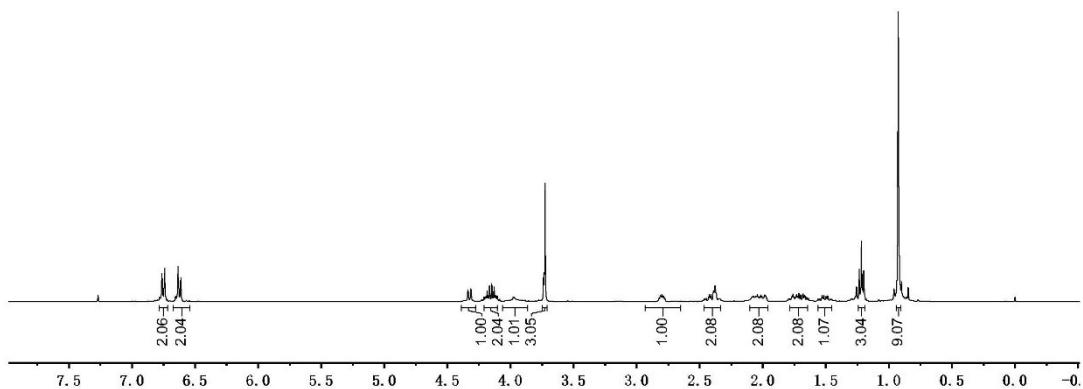
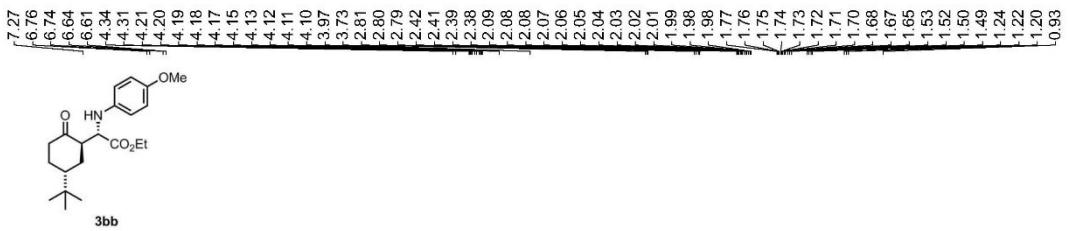
61.20  
>59.00  
>55.65  
>50.38

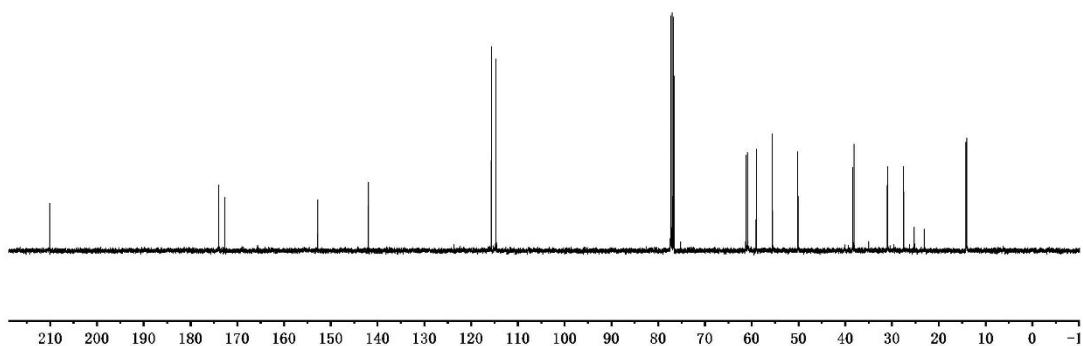
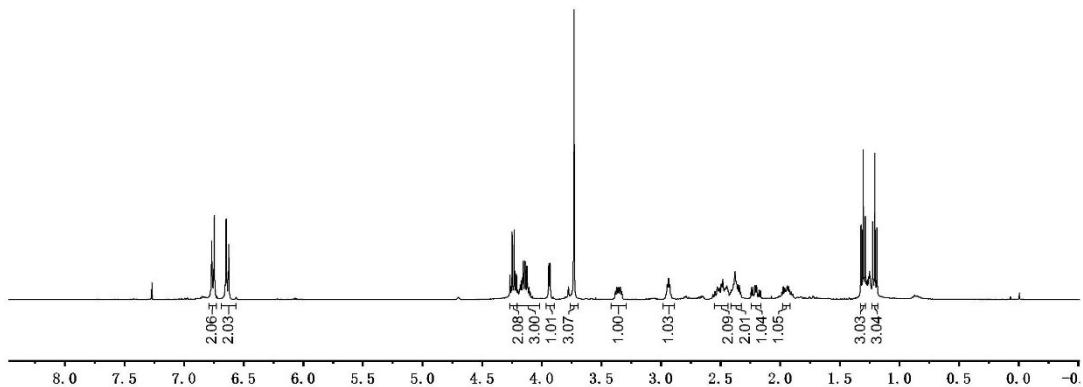
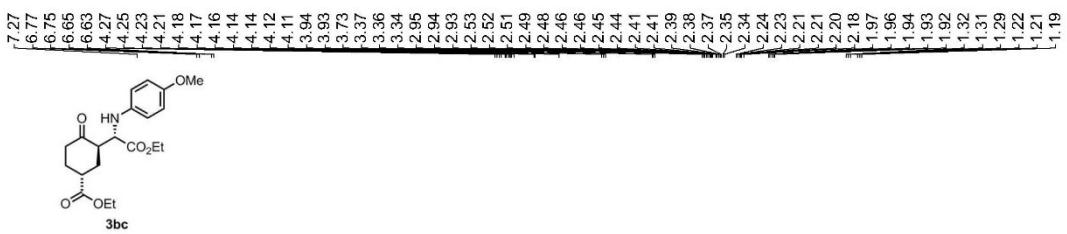
137.76  
136.29  
133.31  
126.84  
>19.44  
>14.14

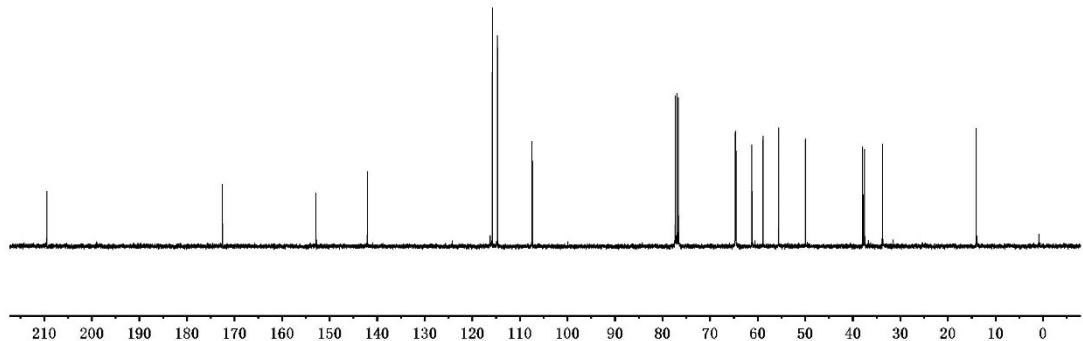
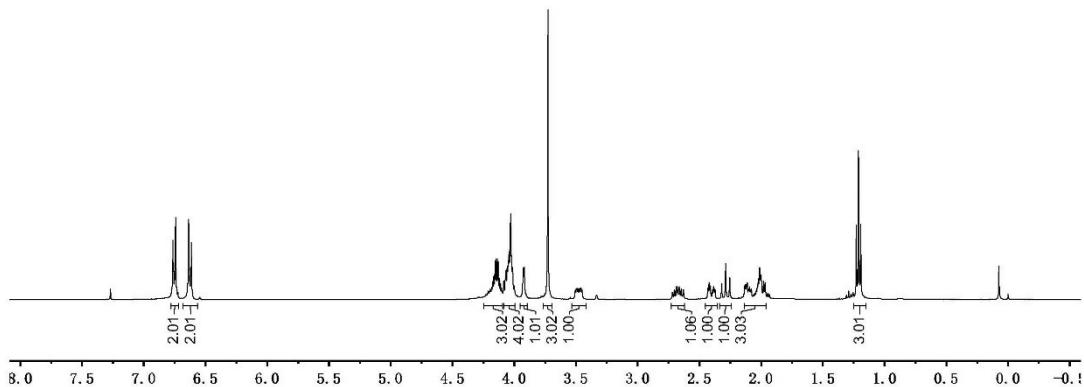
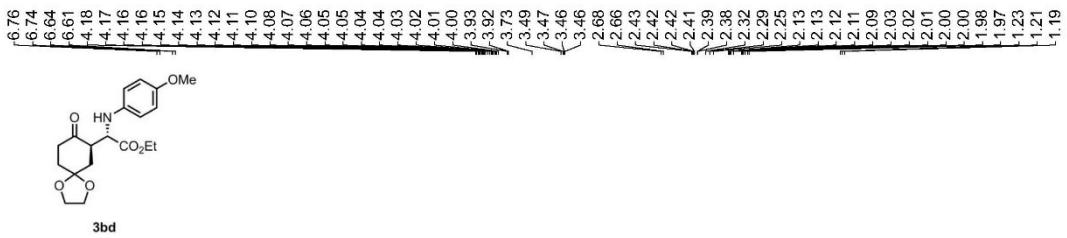


3ba

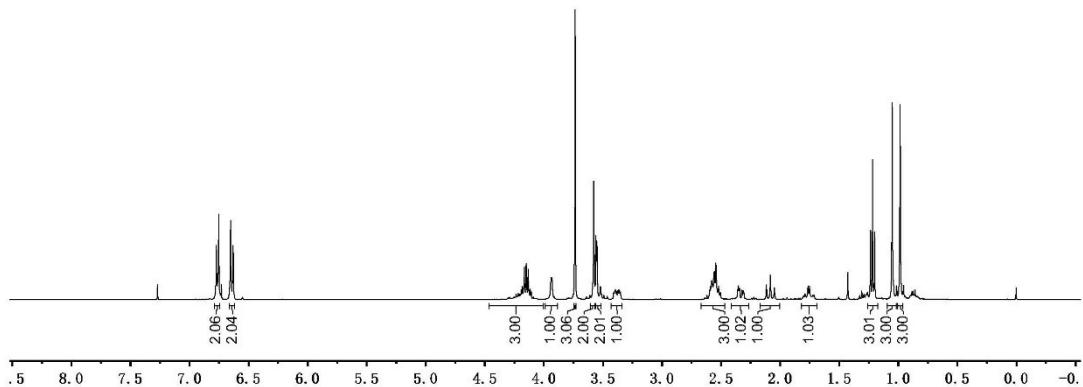
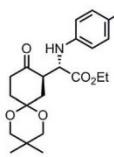




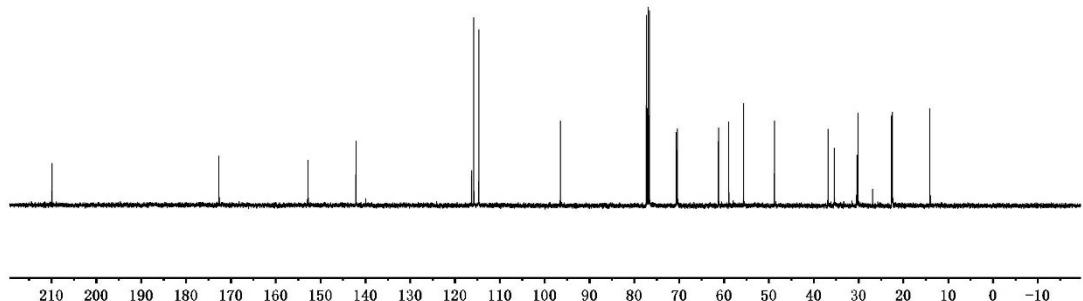


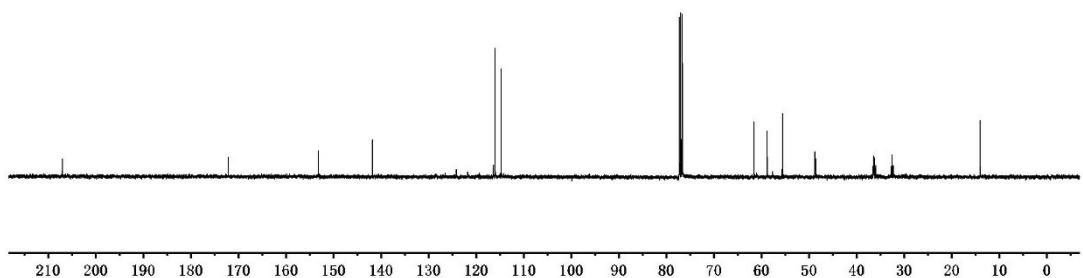
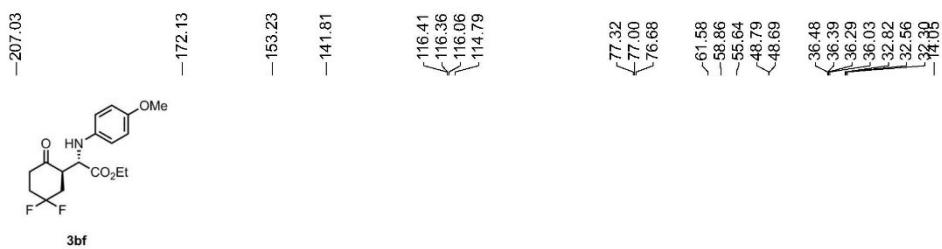
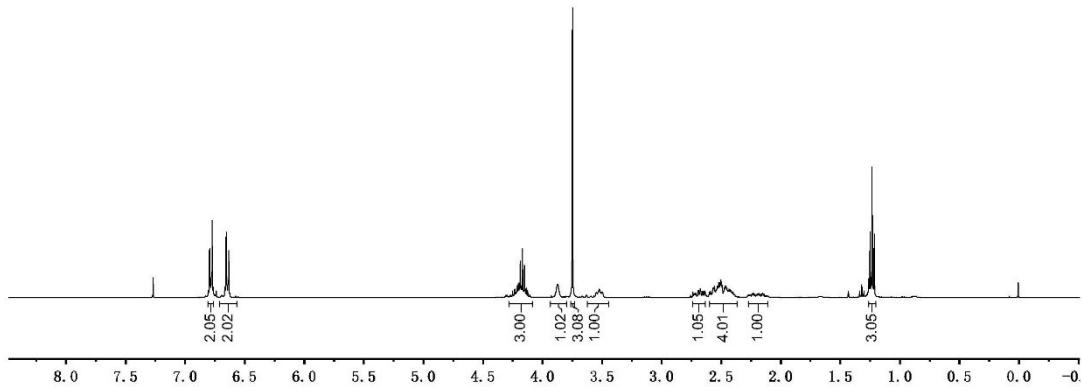
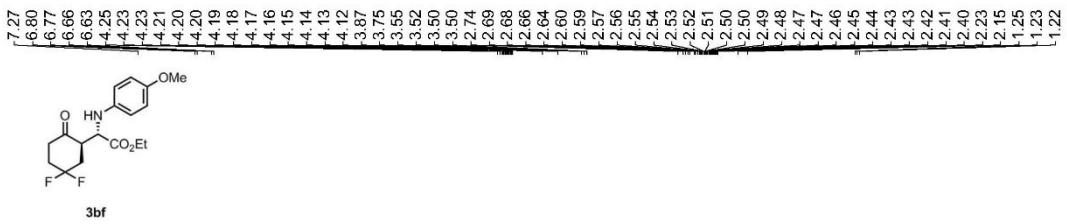


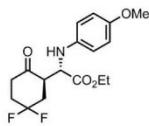
7.27
6.77
6.75
6.65
6.63
4.29
4.24
4.22
4.19
4.18
4.17
4.17
4.15
4.15
4.13
4.13
4.13
4.12
4.11
3.94
3.93
3.73
3.58
3.56
3.55
3.41
3.40
3.39
3.39
3.37
3.37
3.36
3.35
2.60
2.59
2.58
2.57
2.36
2.34
2.31
2.31
2.32
2.32
2.08
2.08
2.08
1.75
1.75
1.72
1.71
1.24
1.22
1.20
1.05
0.98



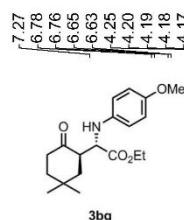
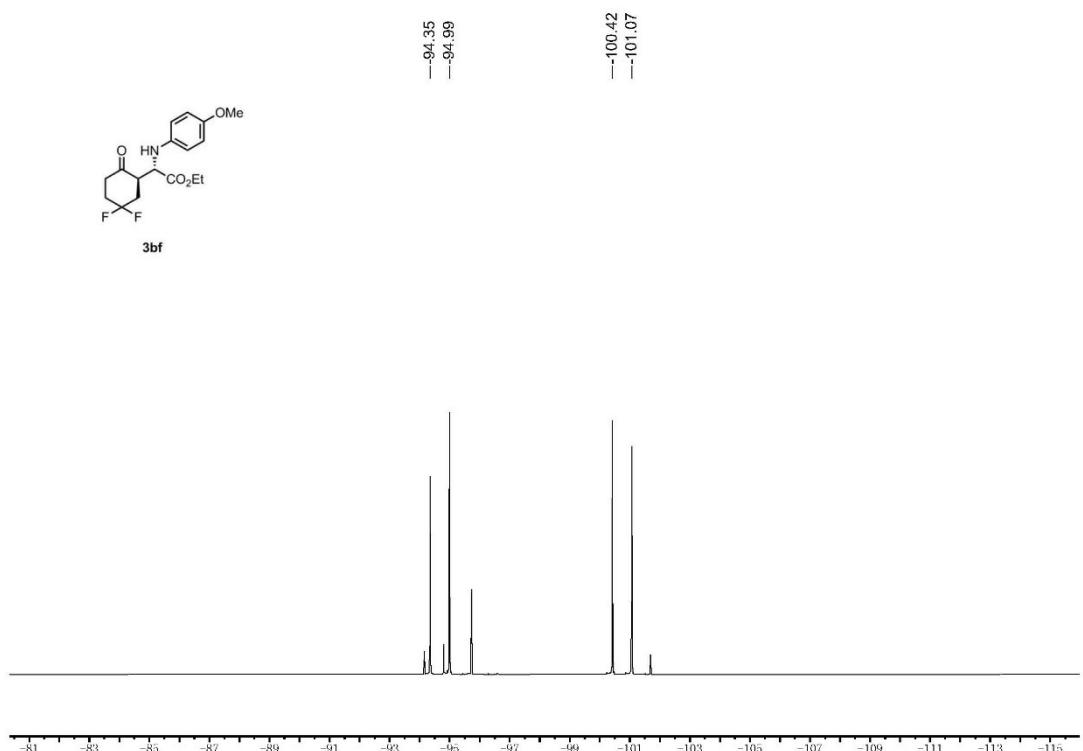
3be



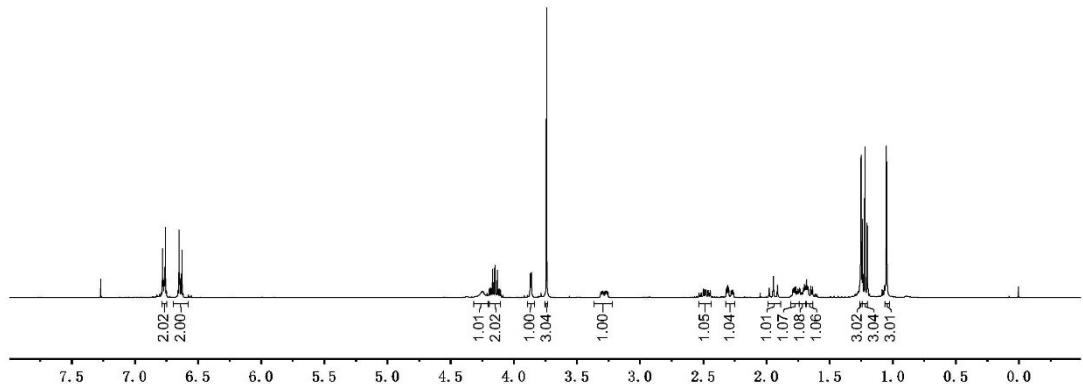


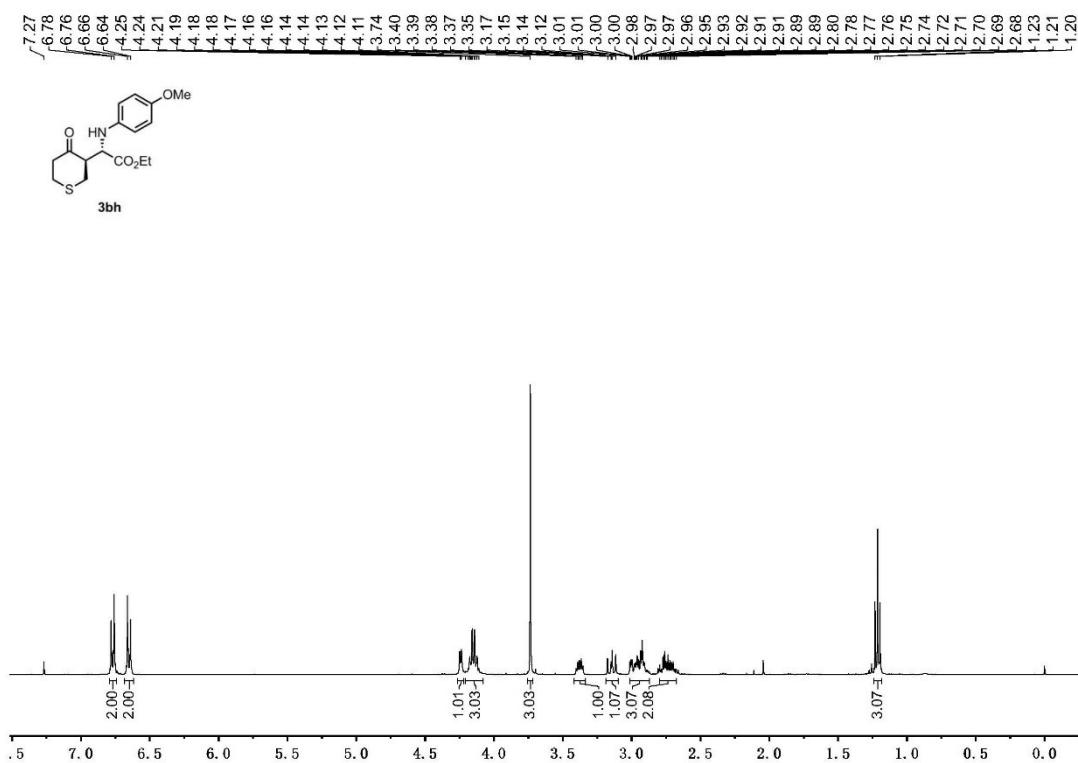
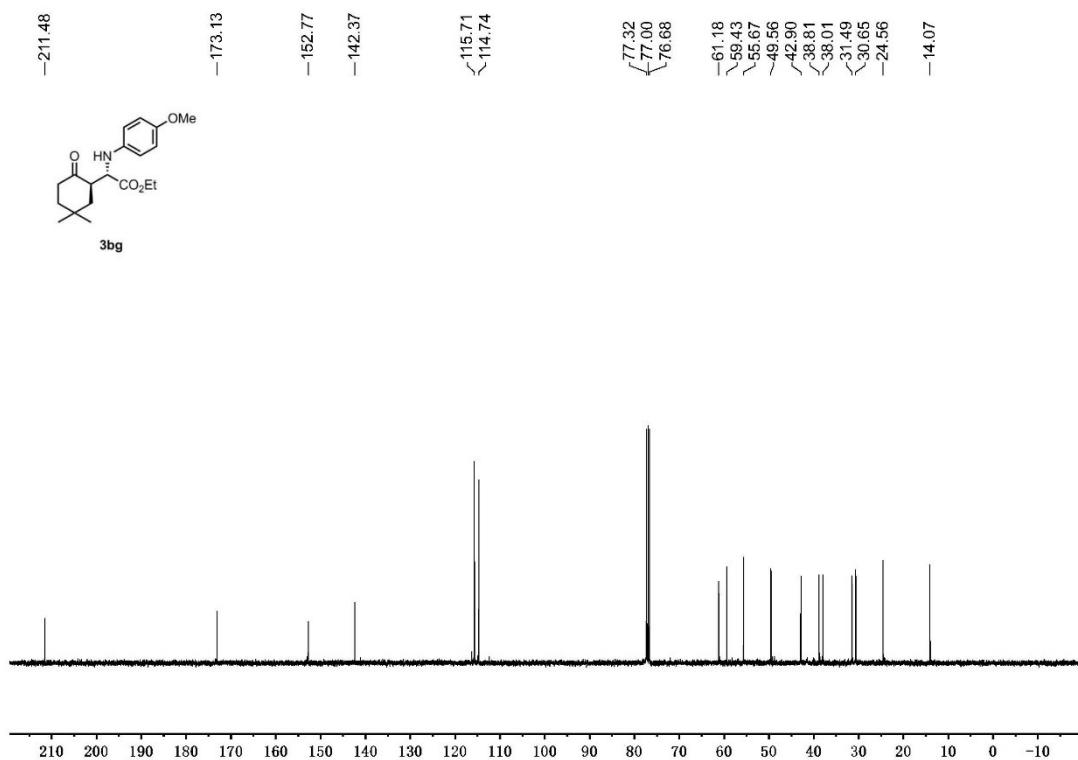


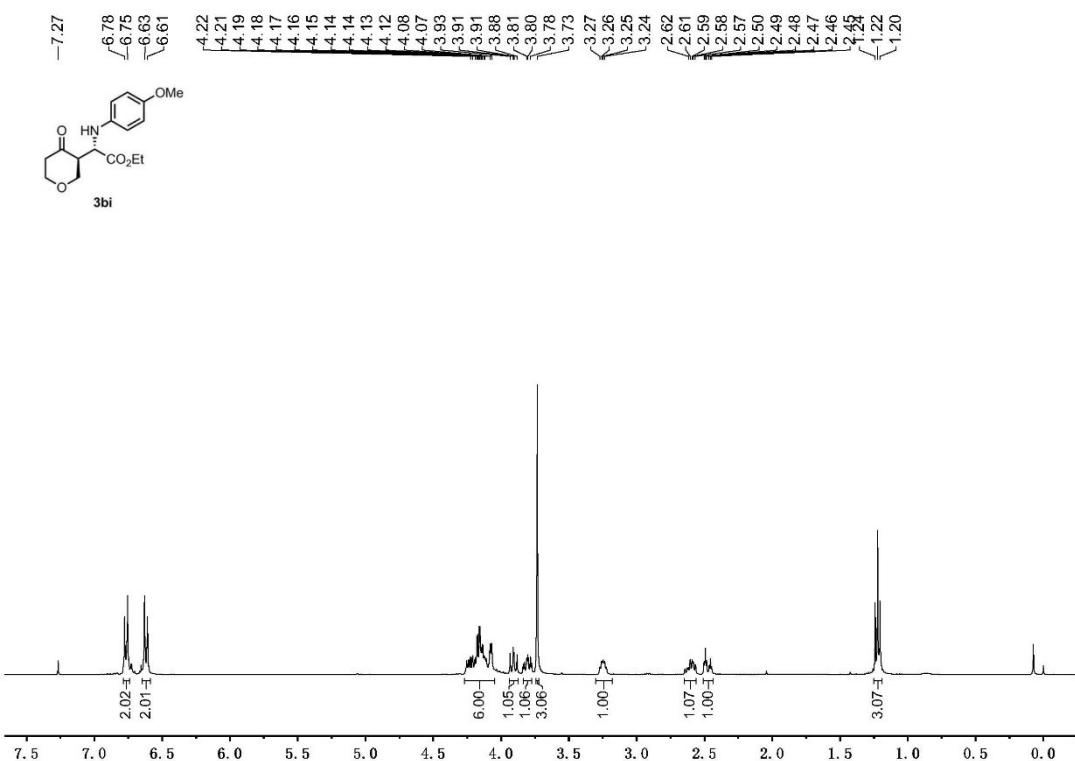
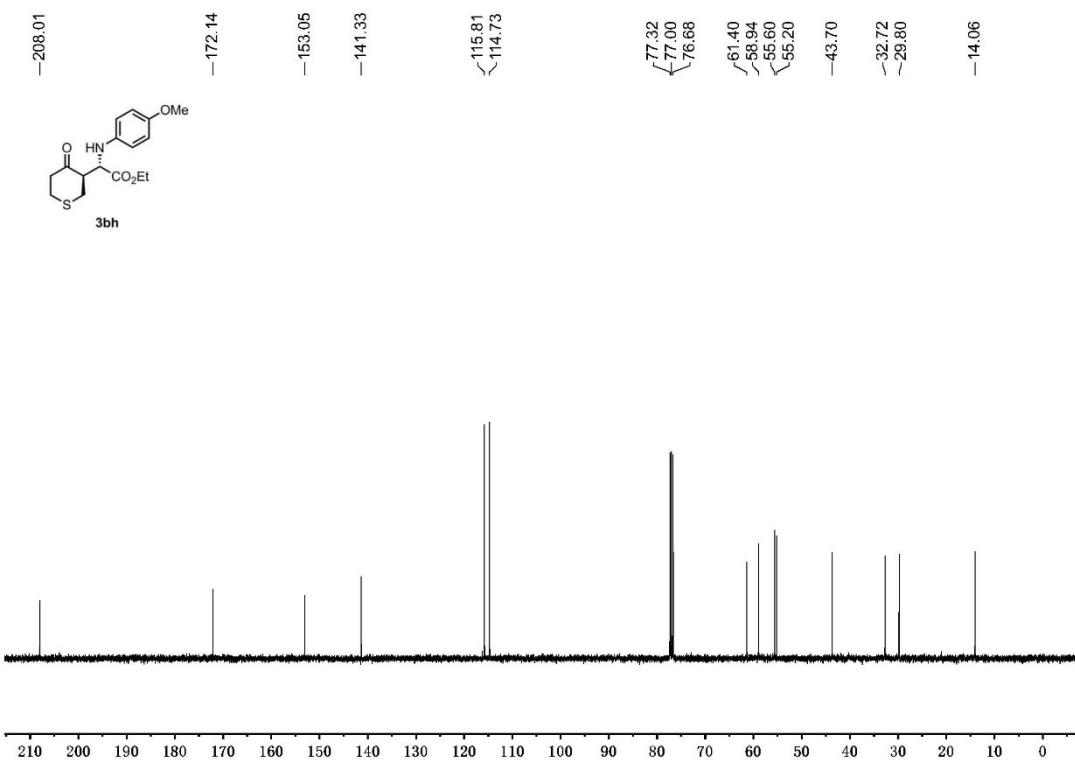
**3bf**

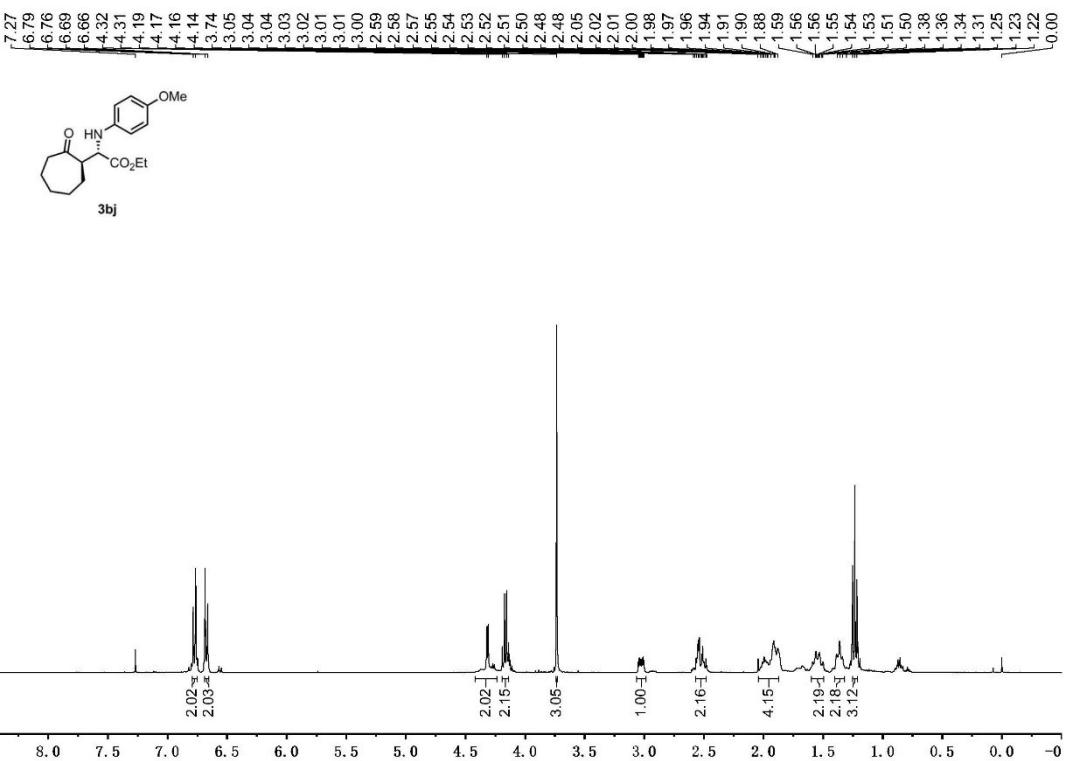
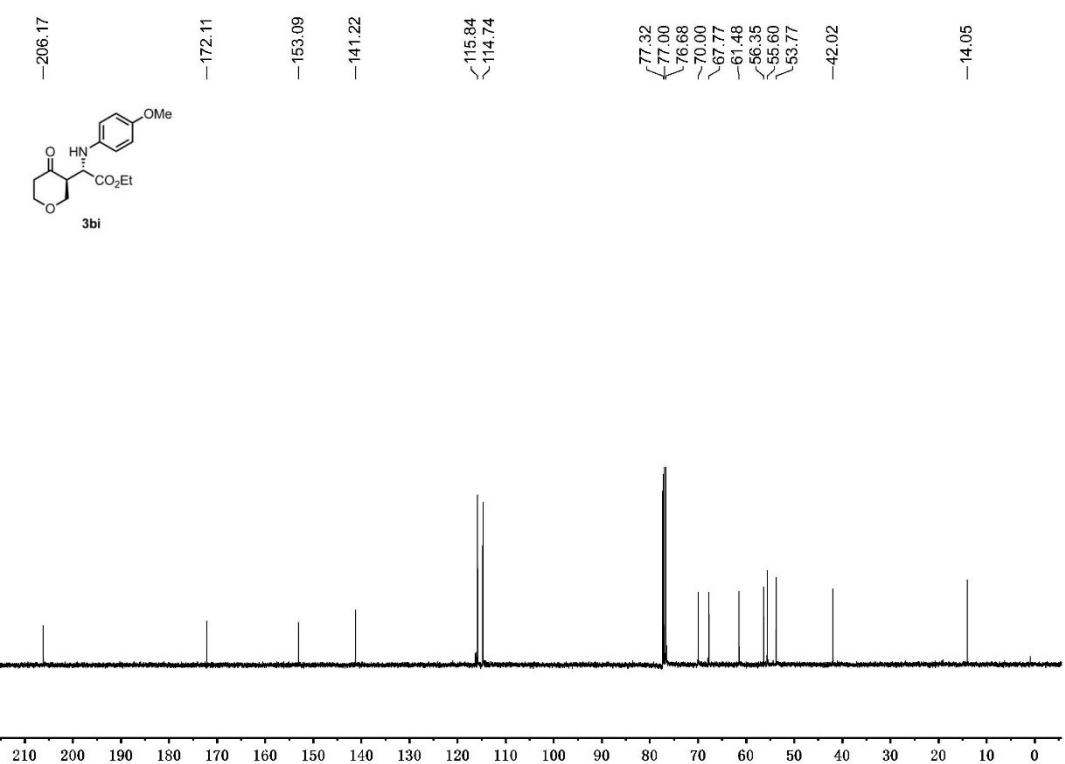


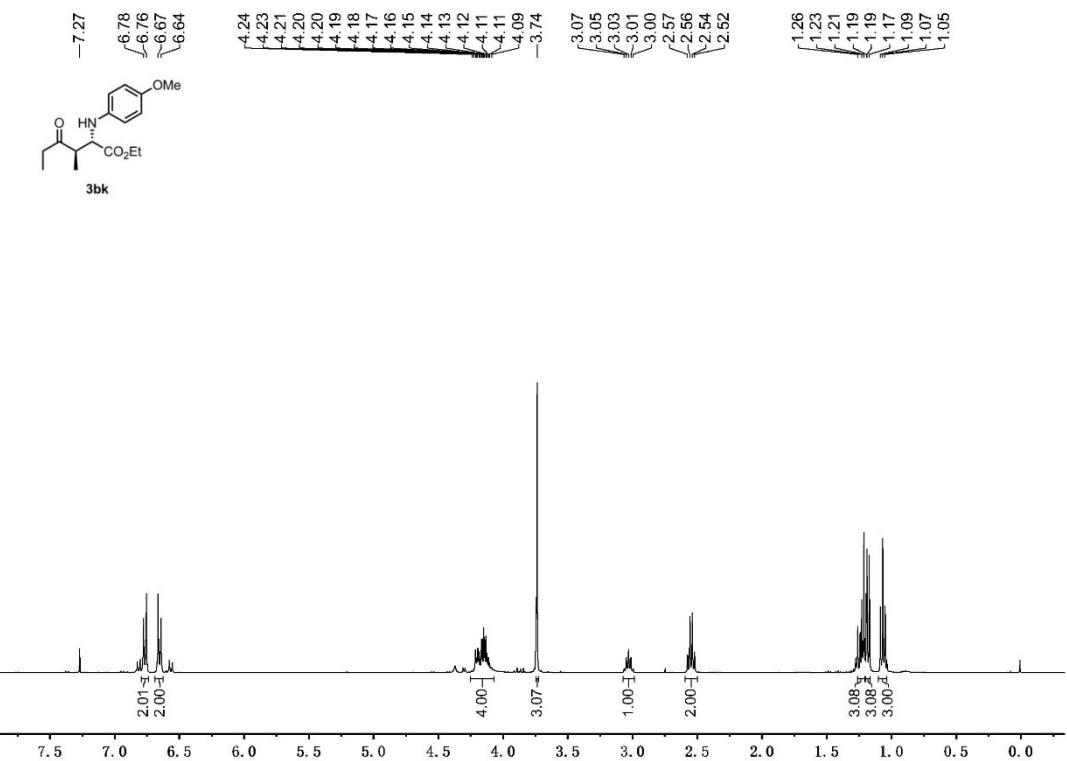
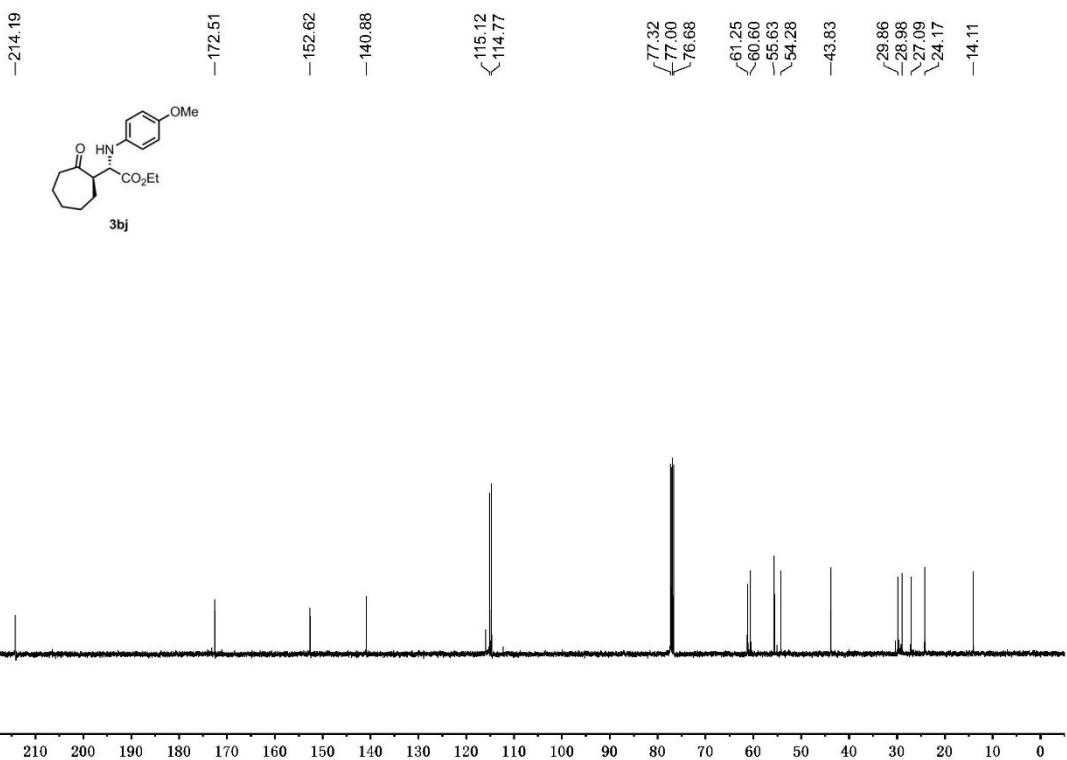
**3bg**

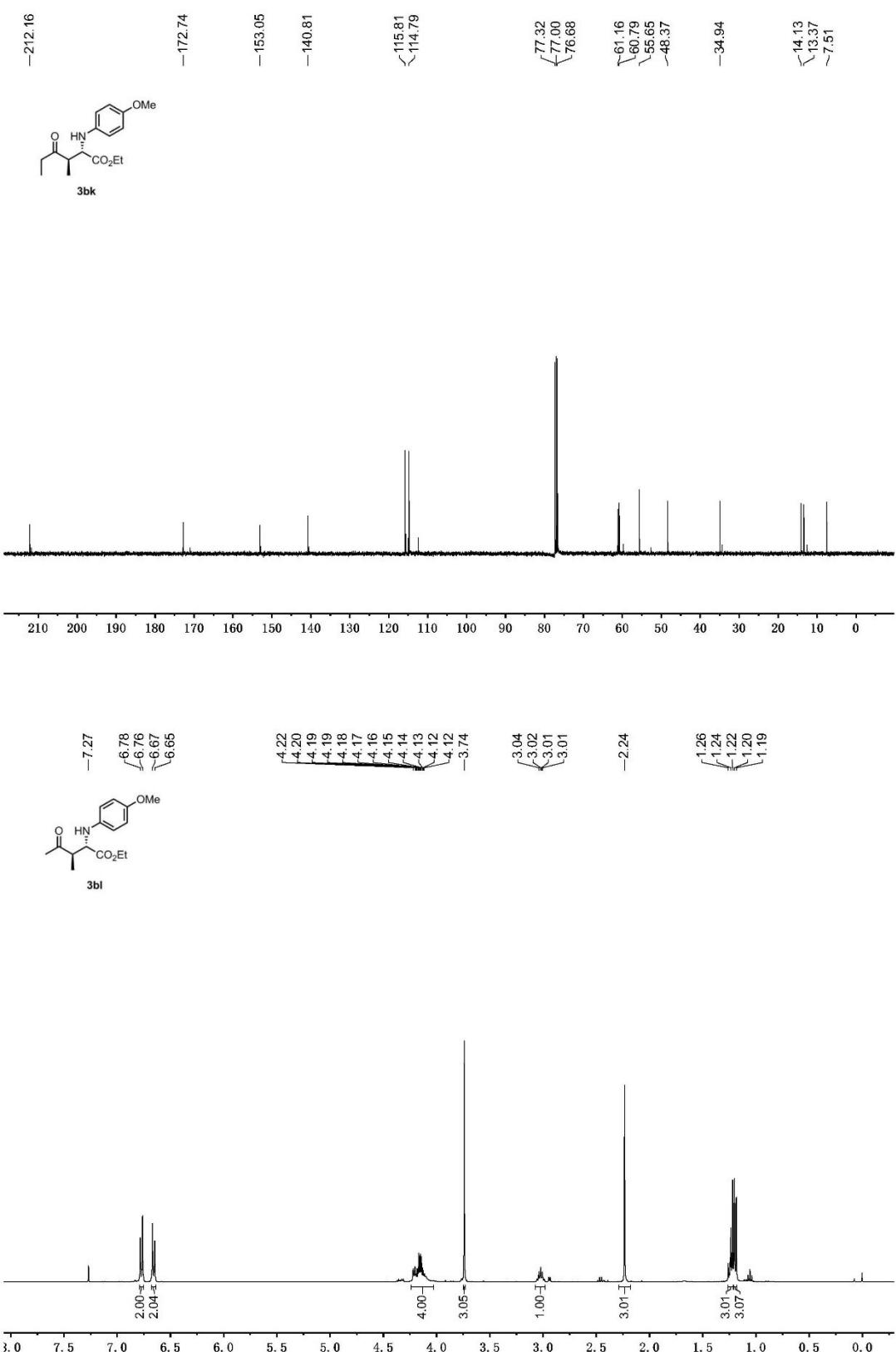


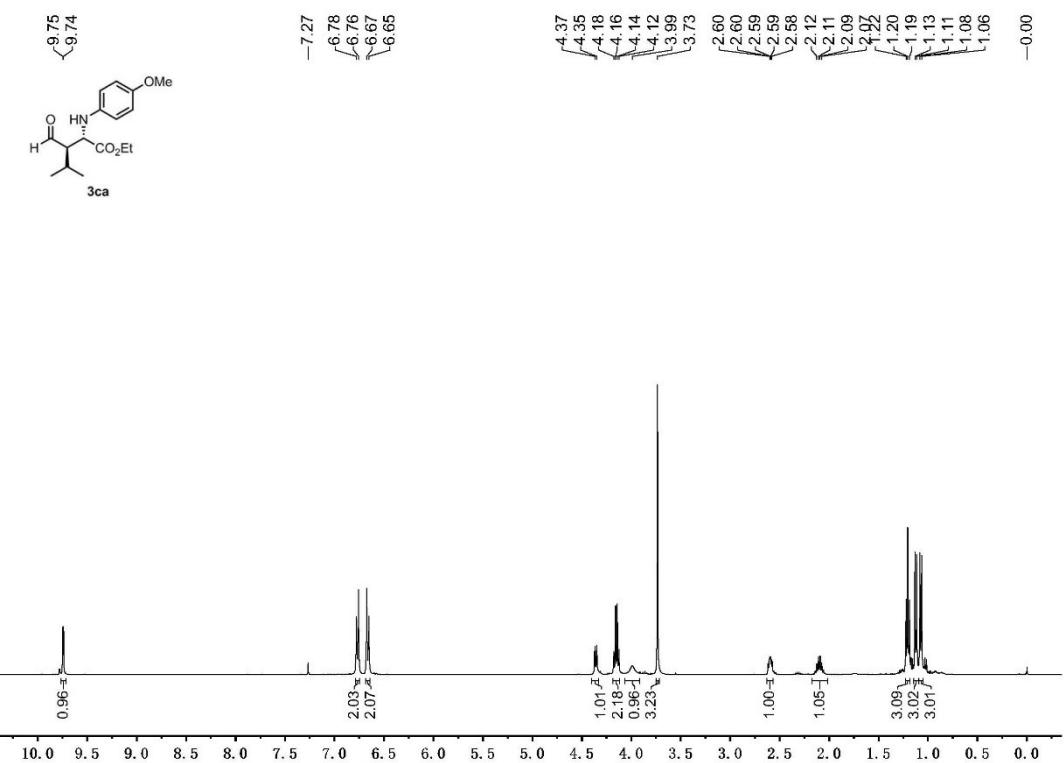
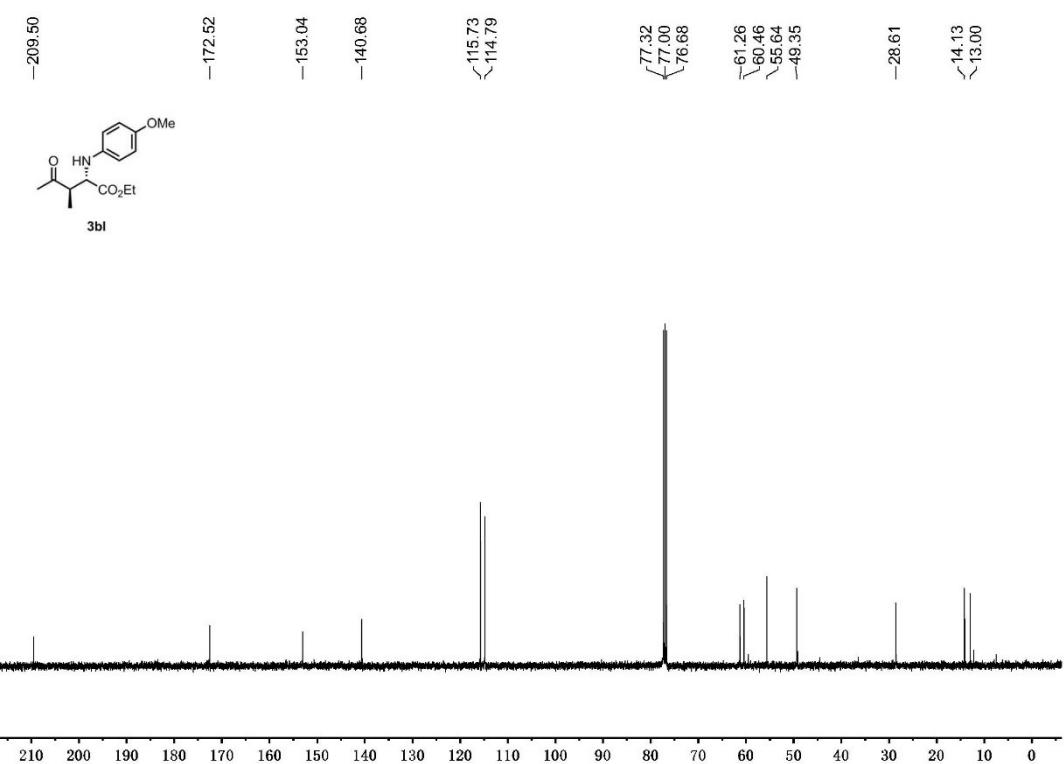


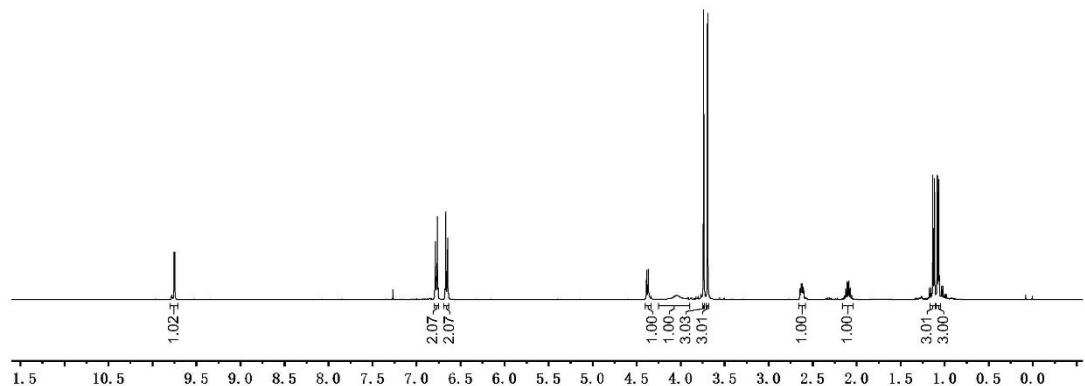
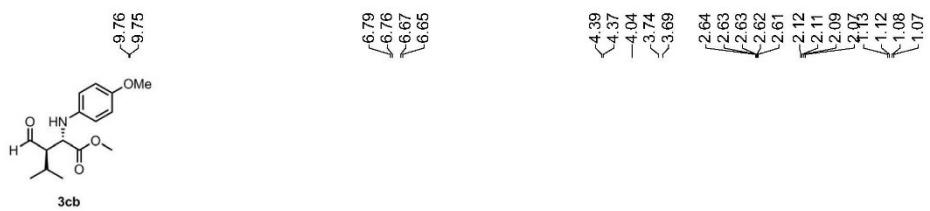
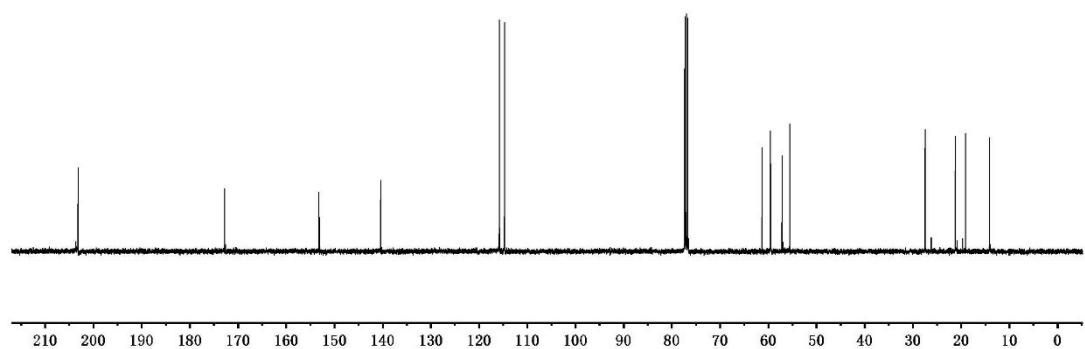


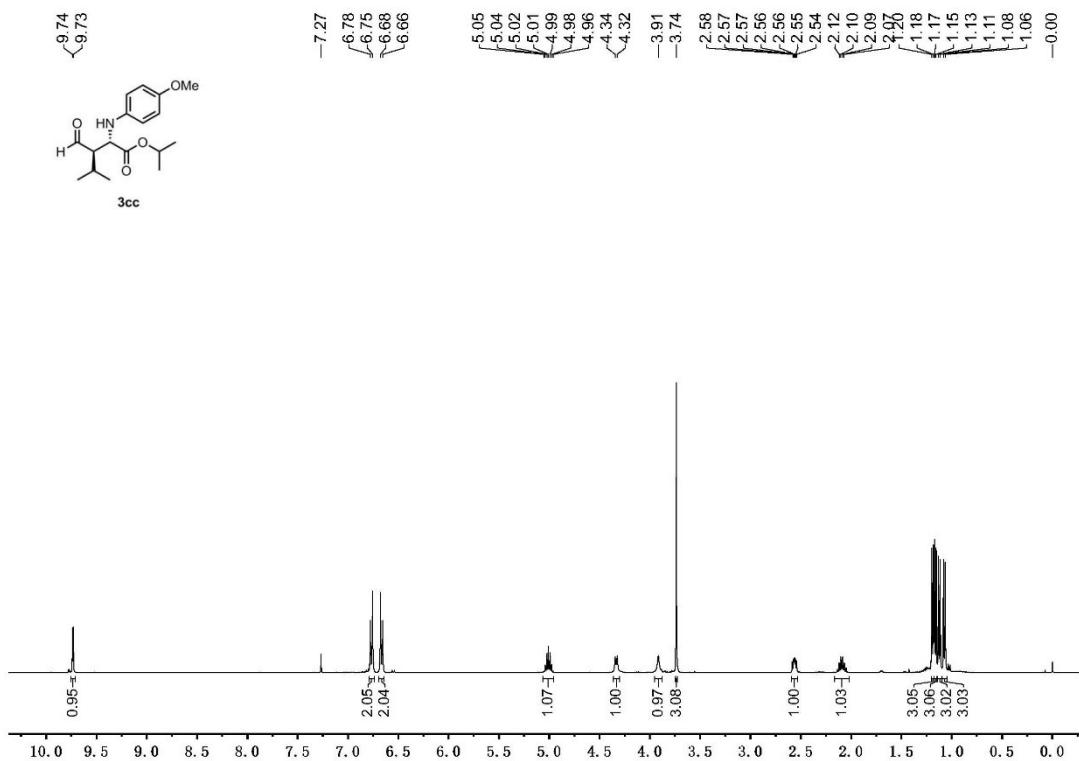
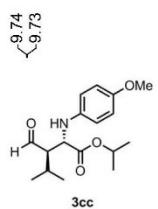
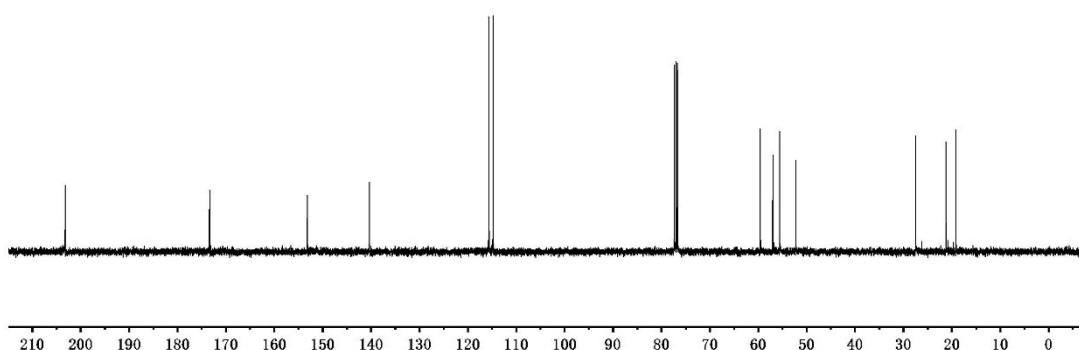
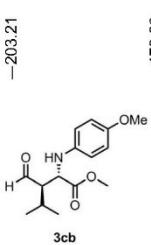


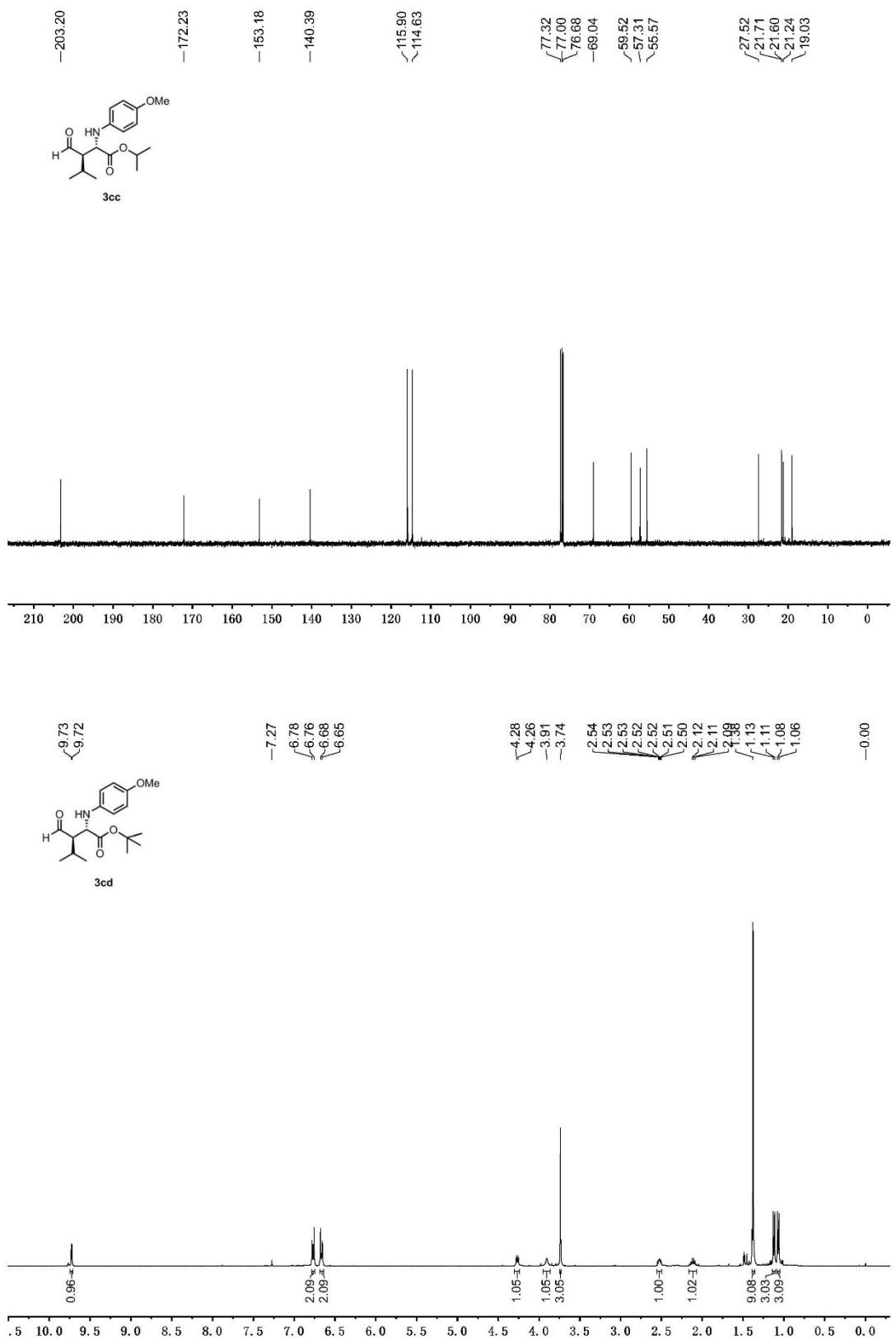


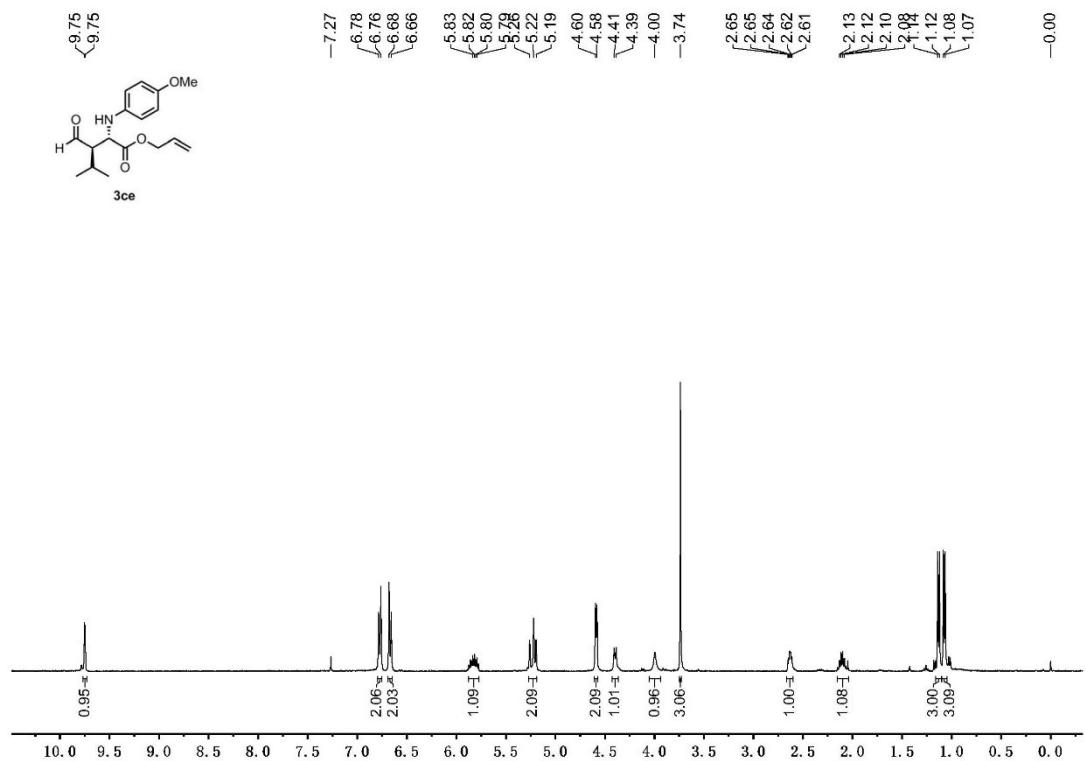
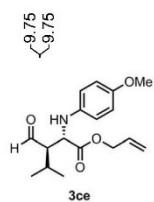
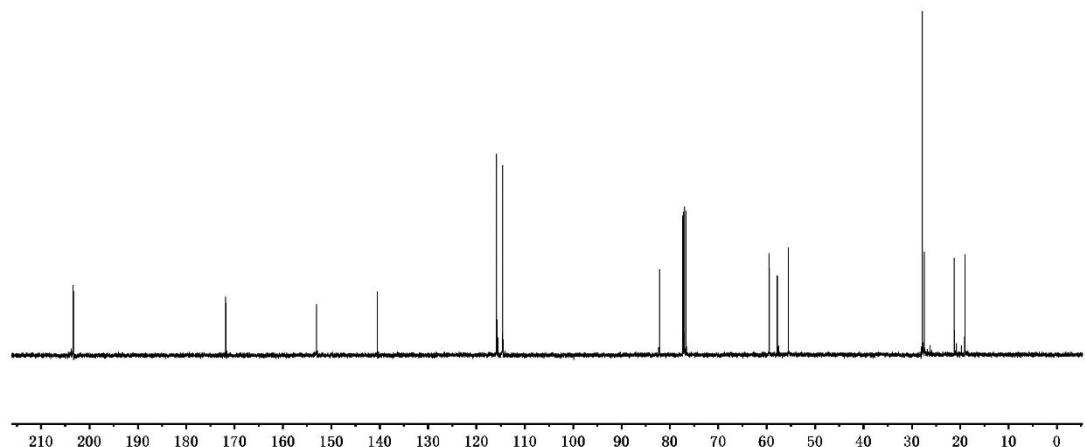
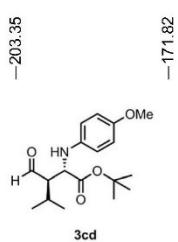


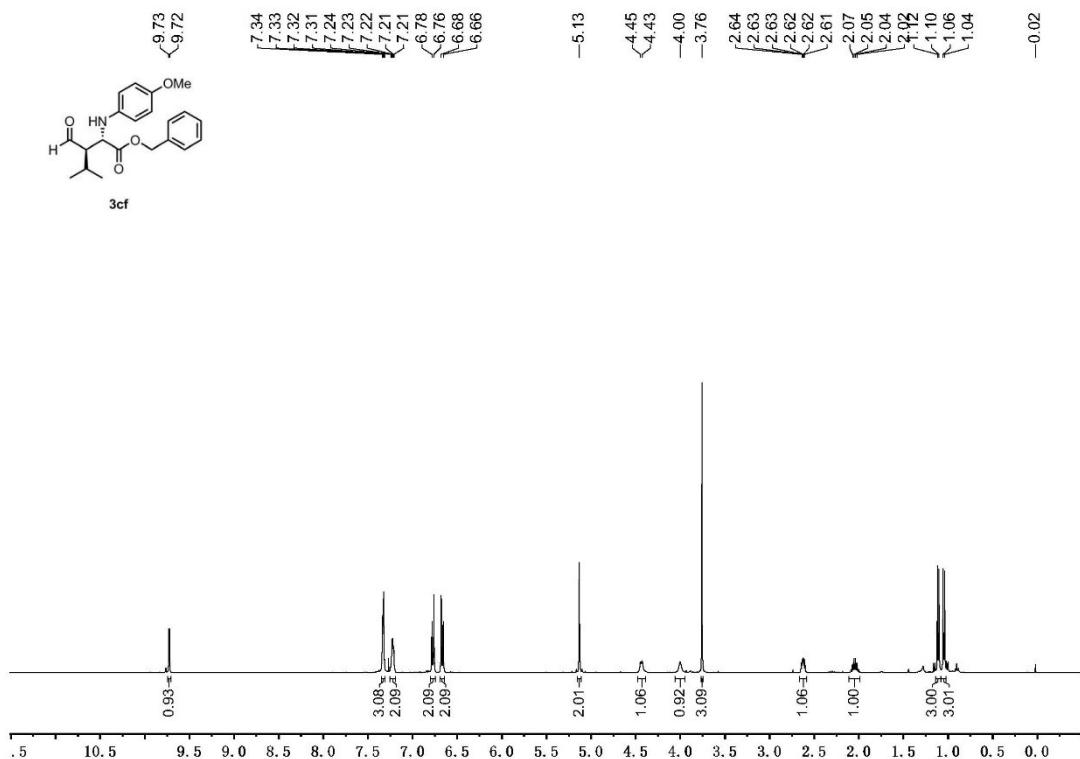
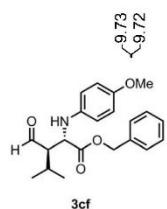
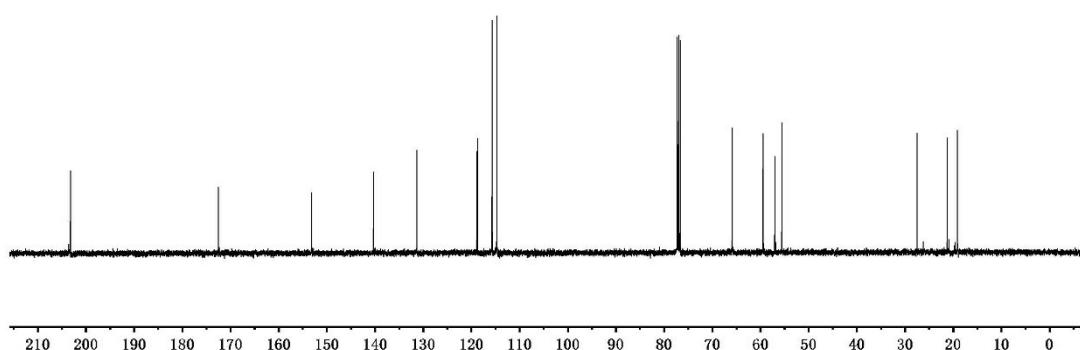
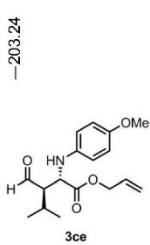


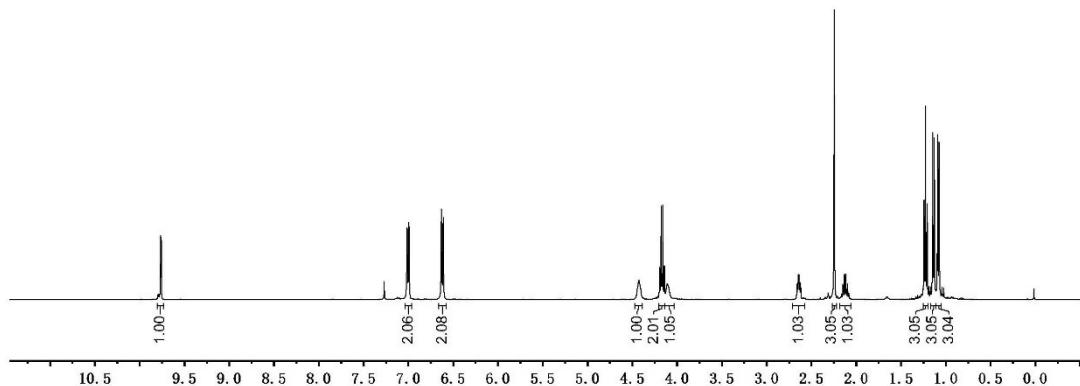
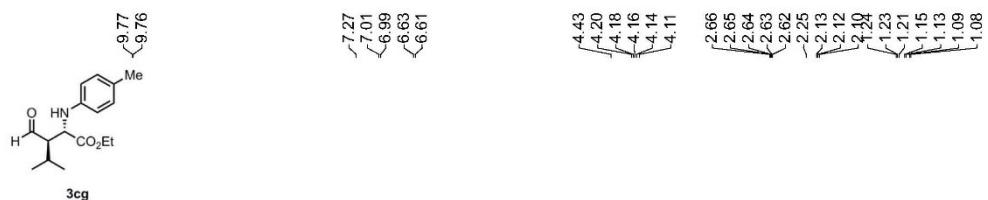
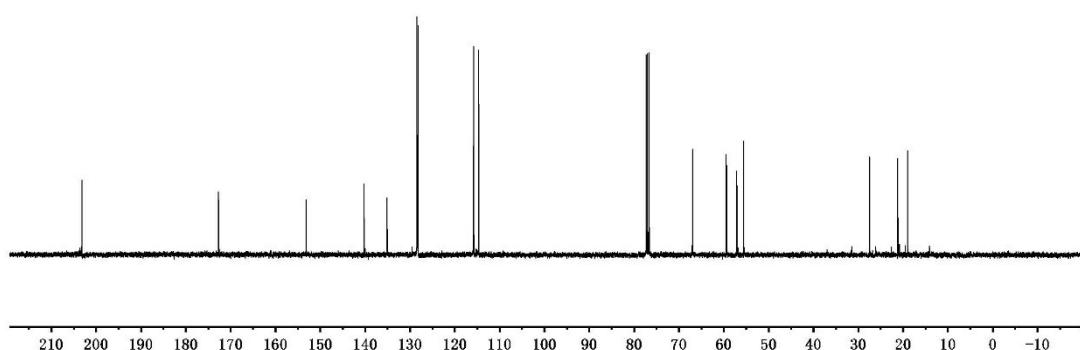
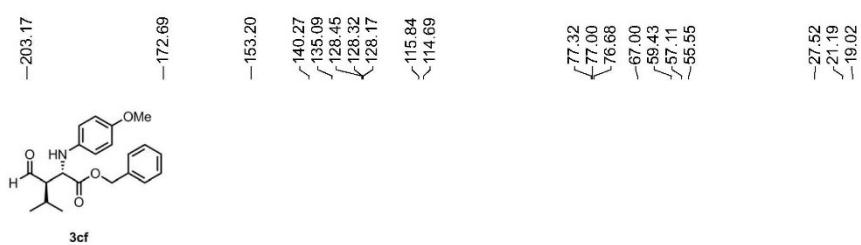


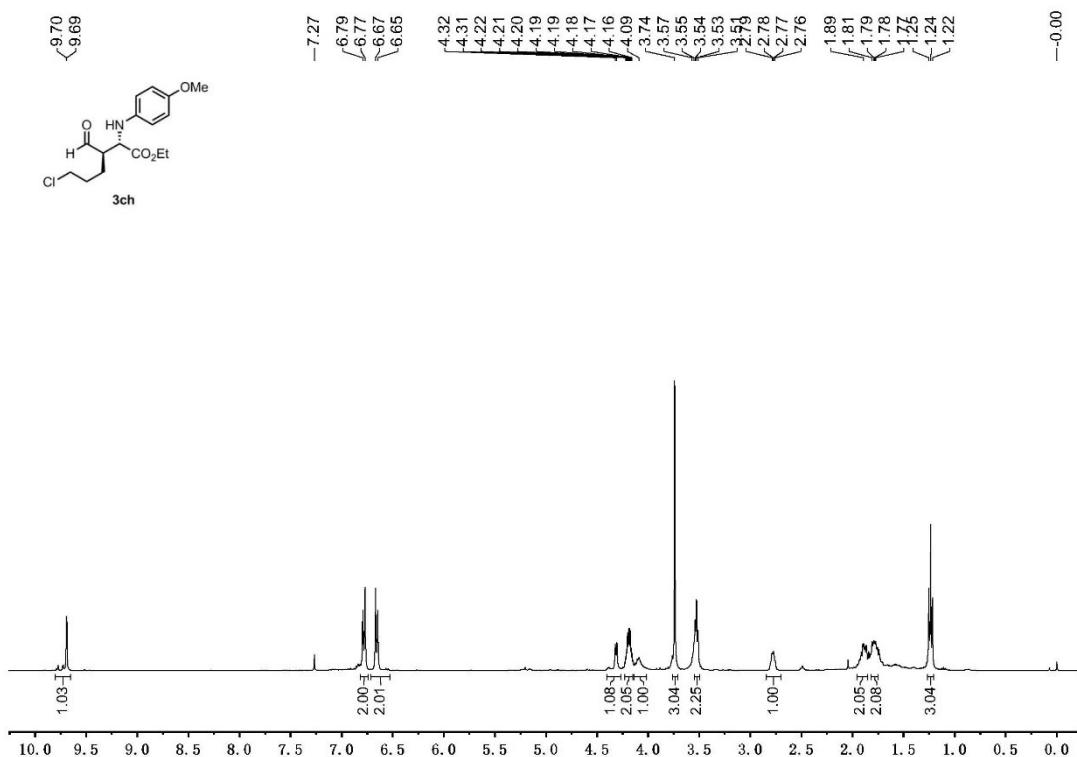
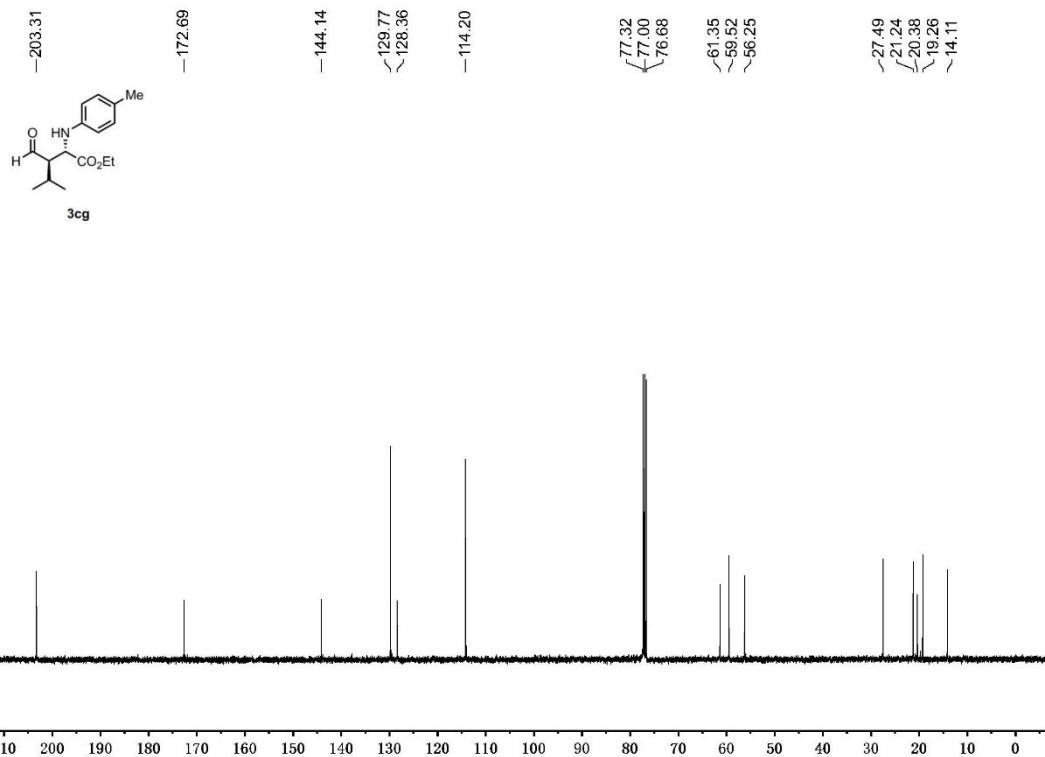


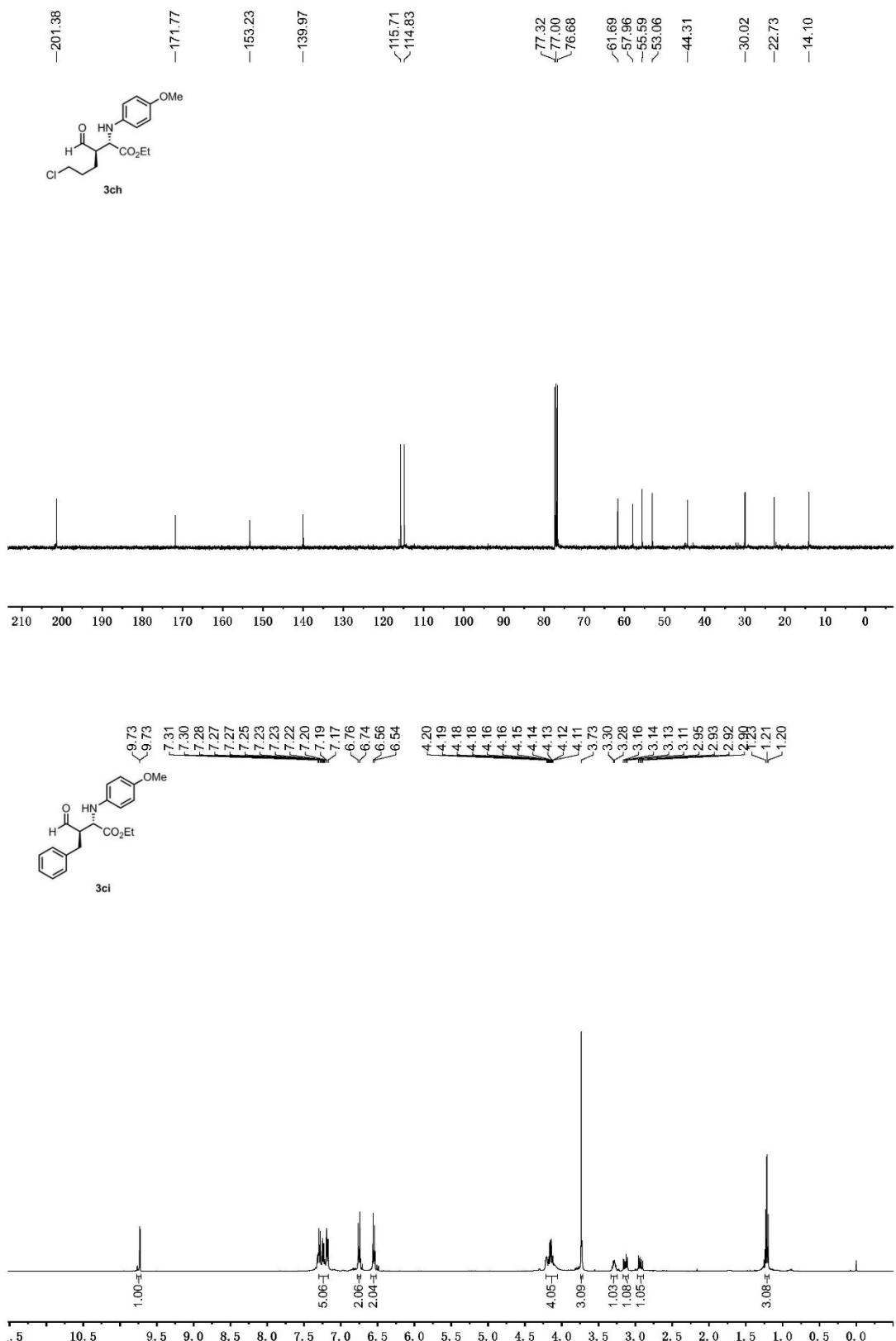


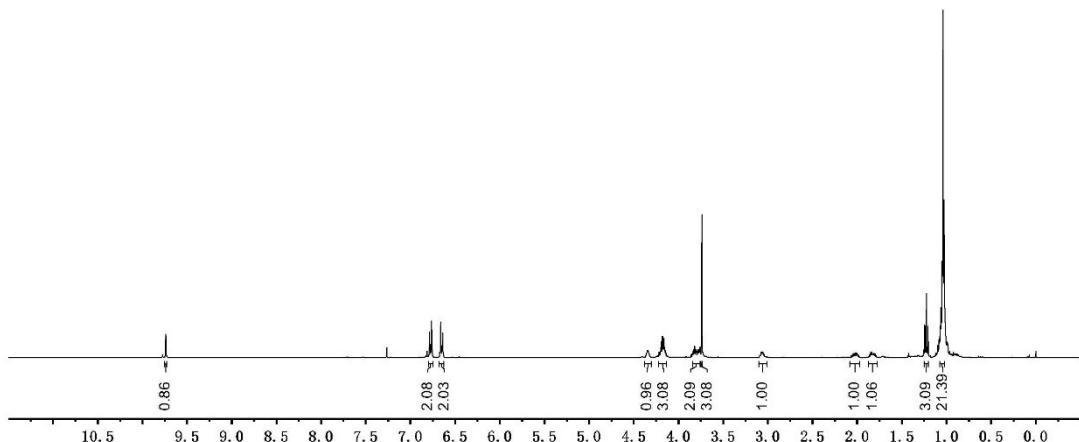
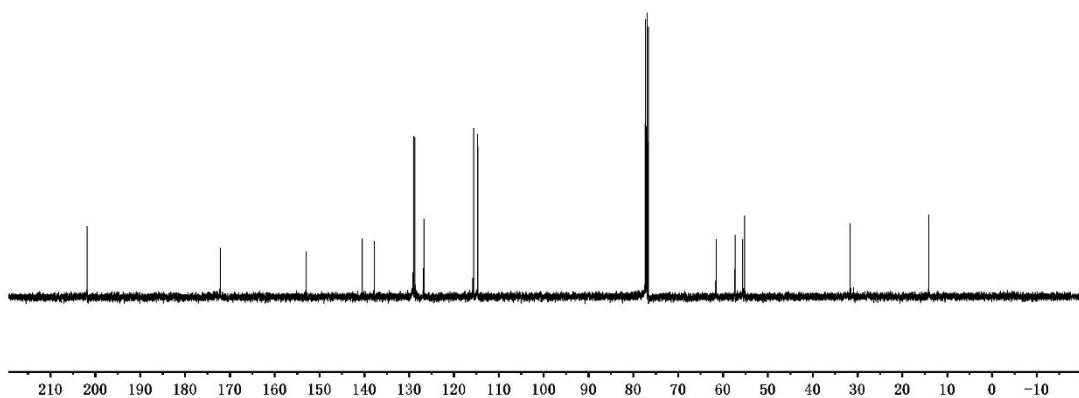
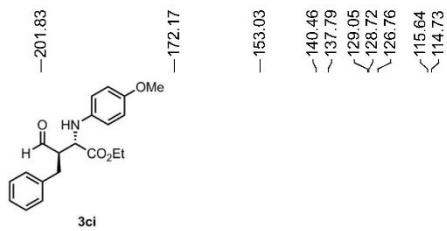


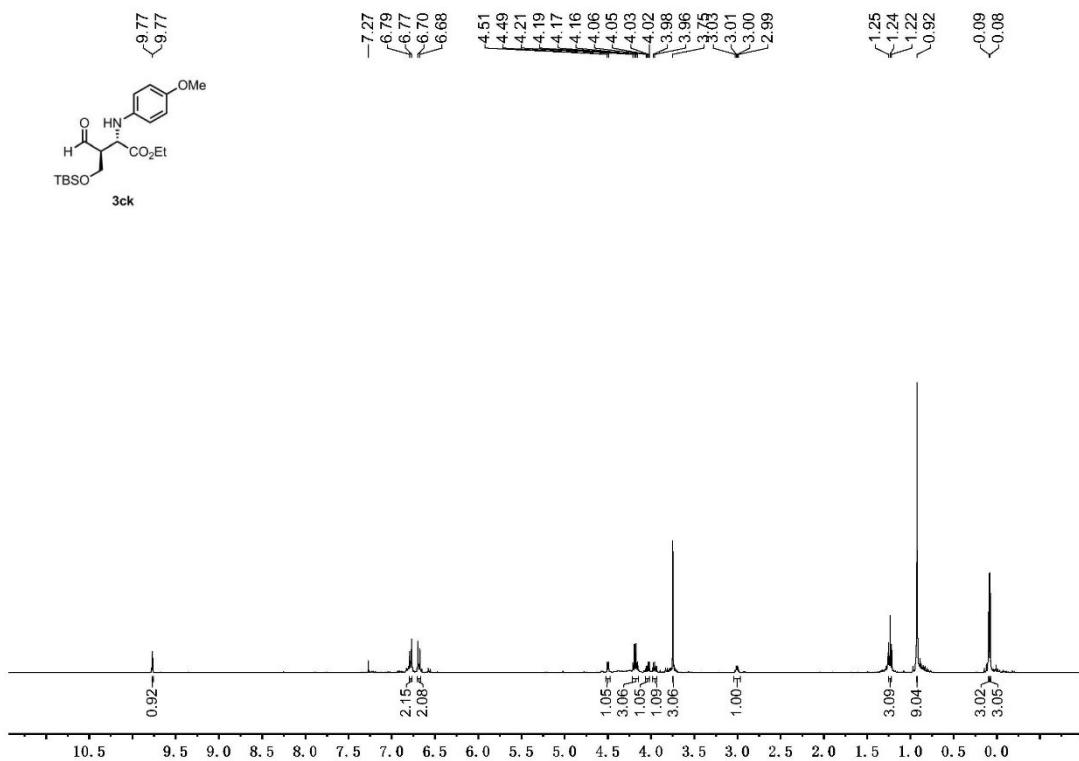
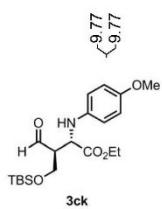
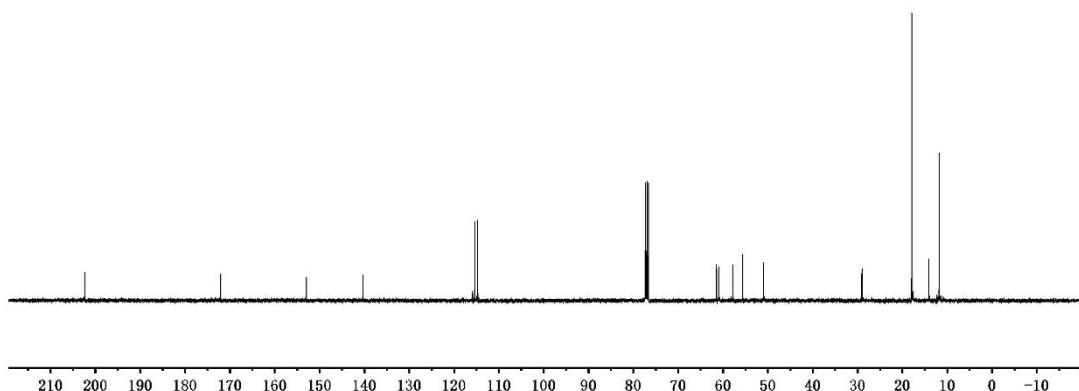
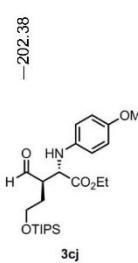


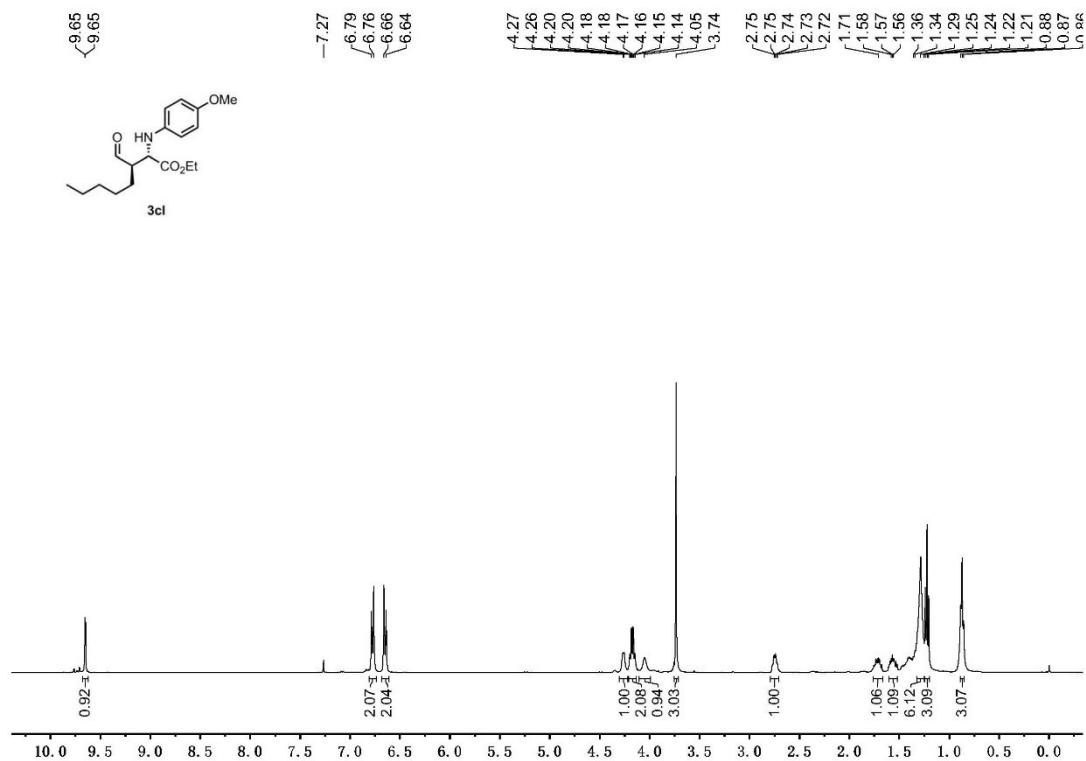
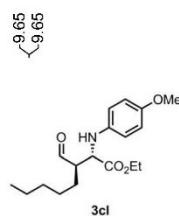
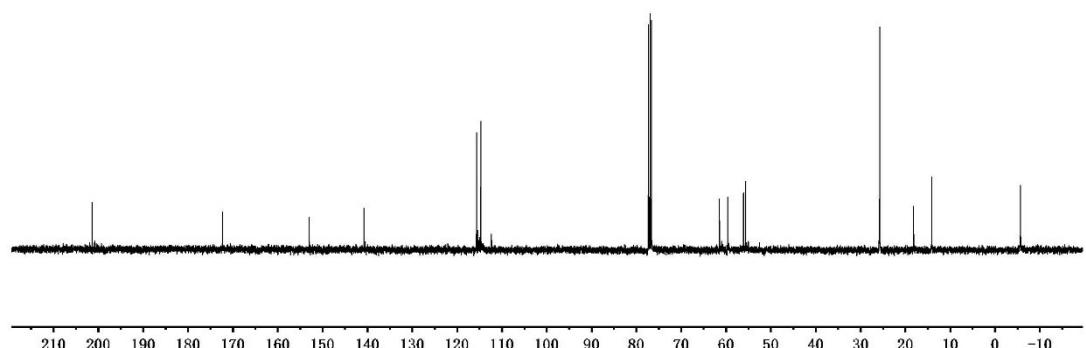
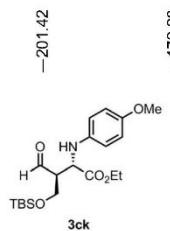


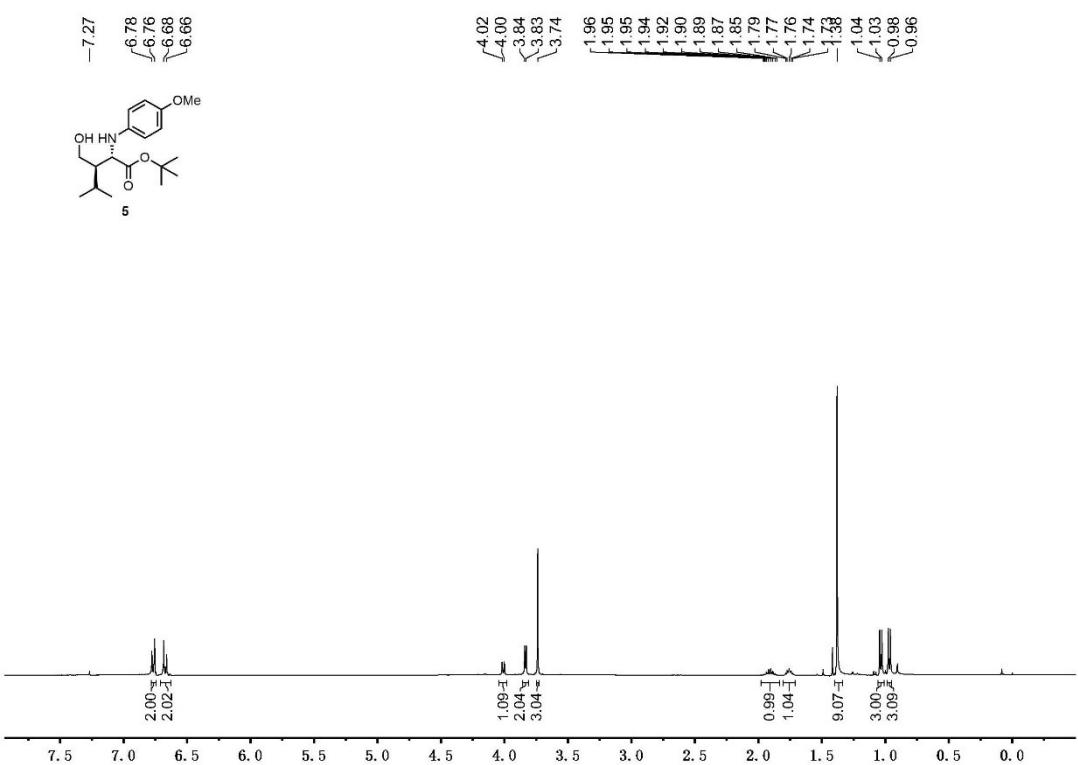
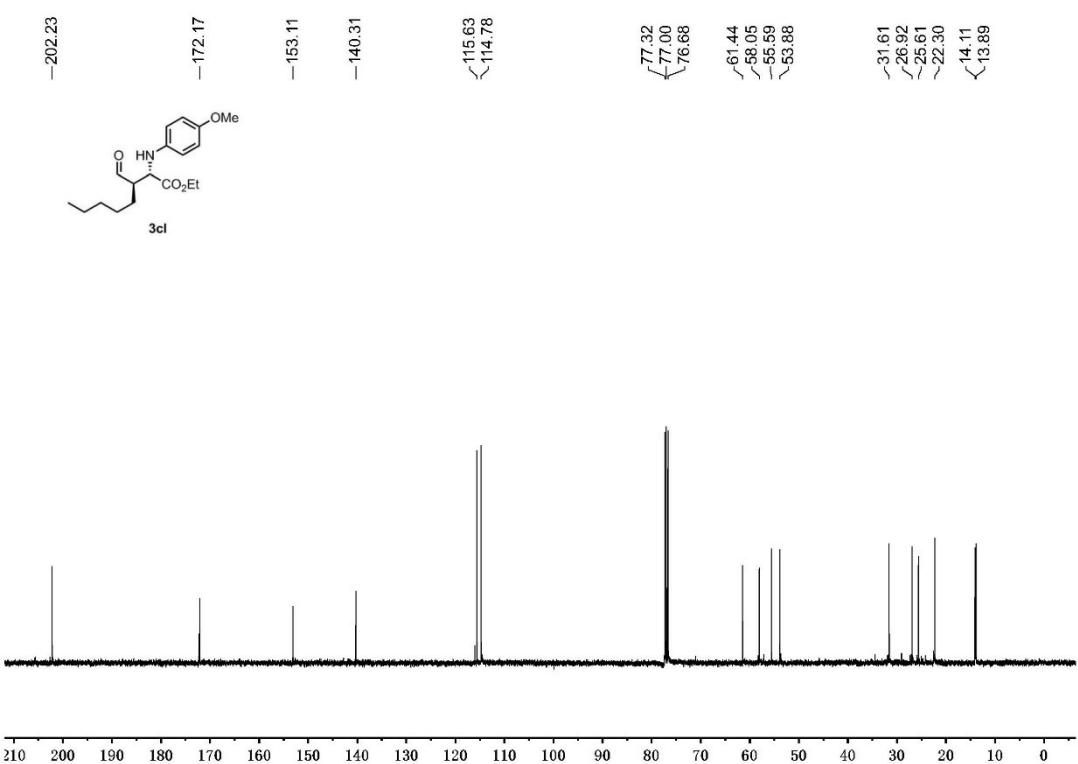


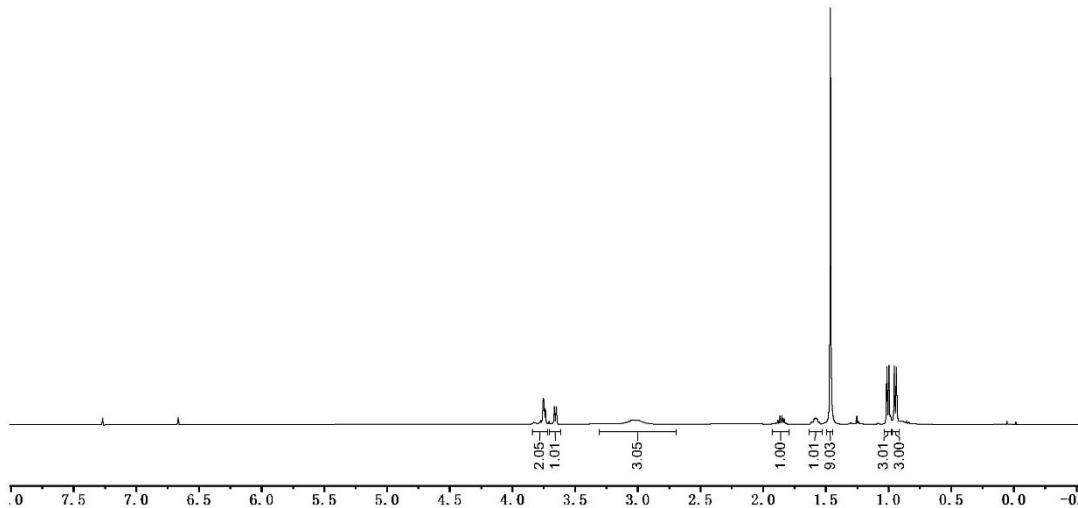
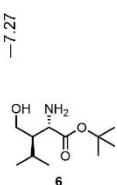
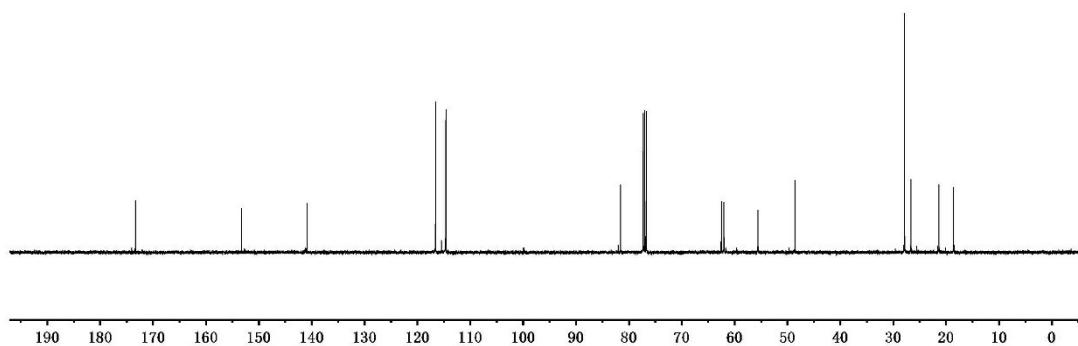
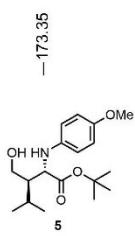


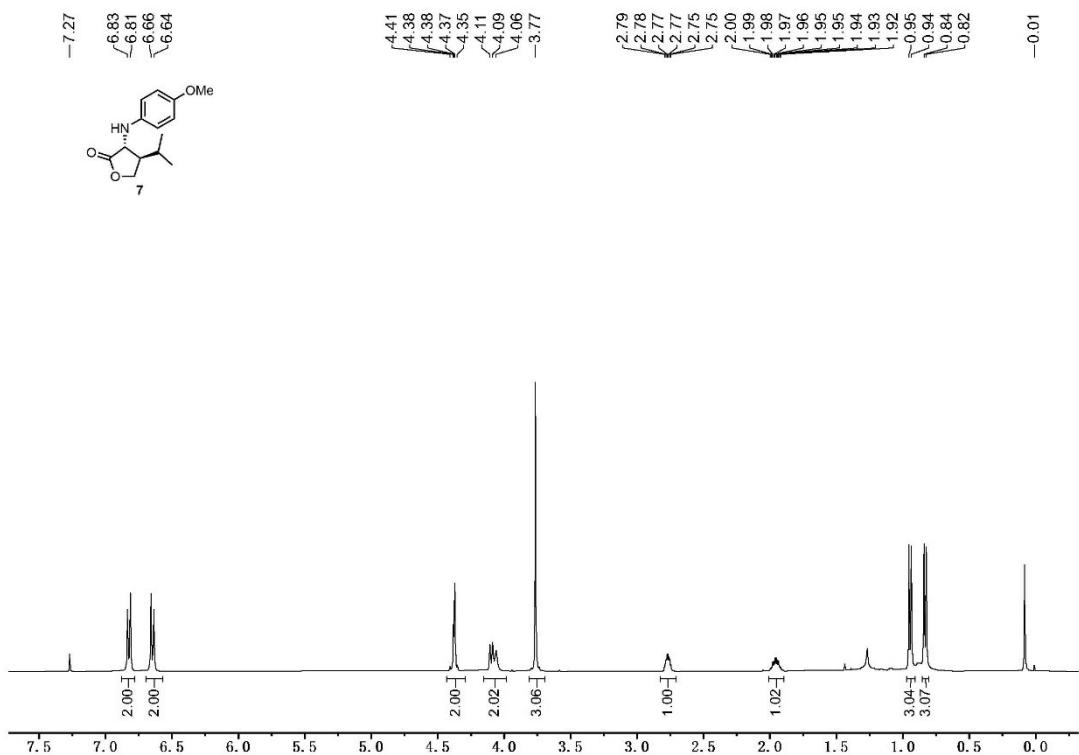
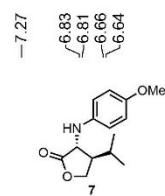
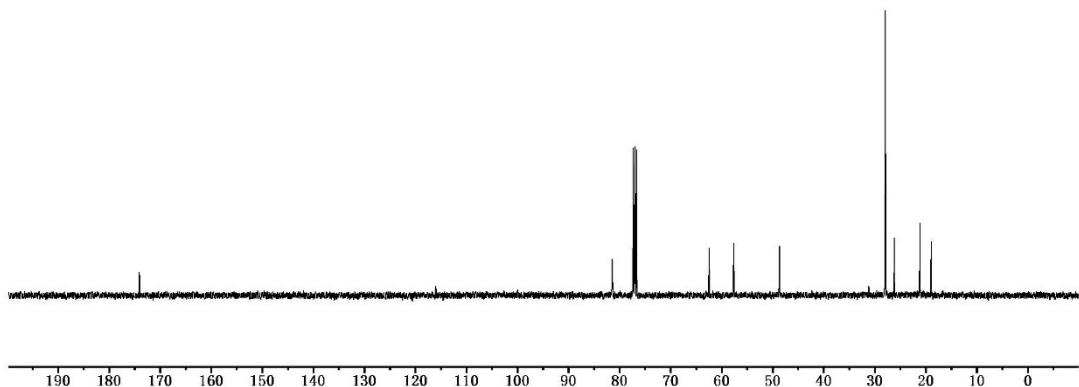
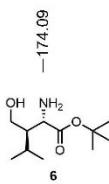


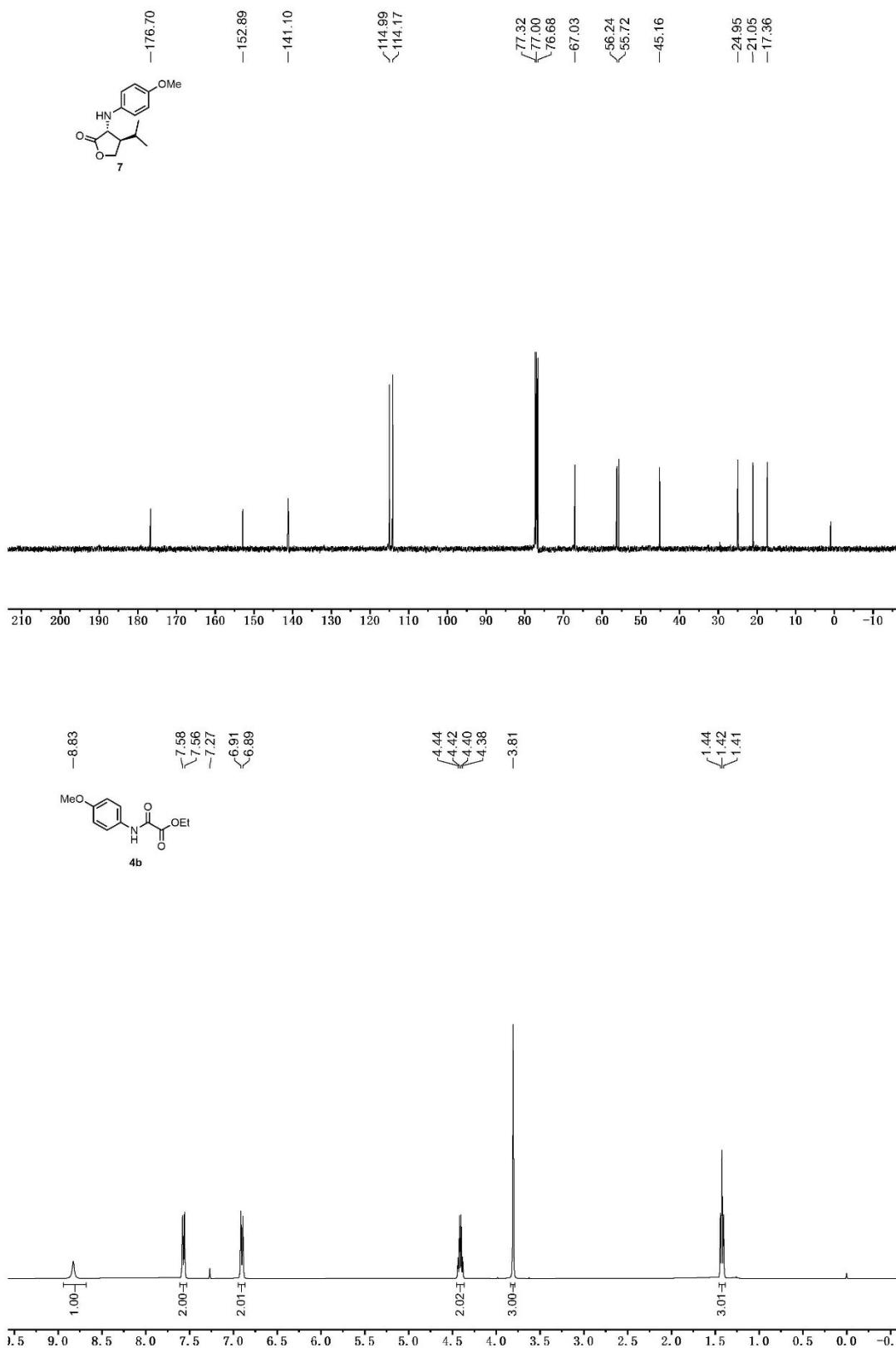


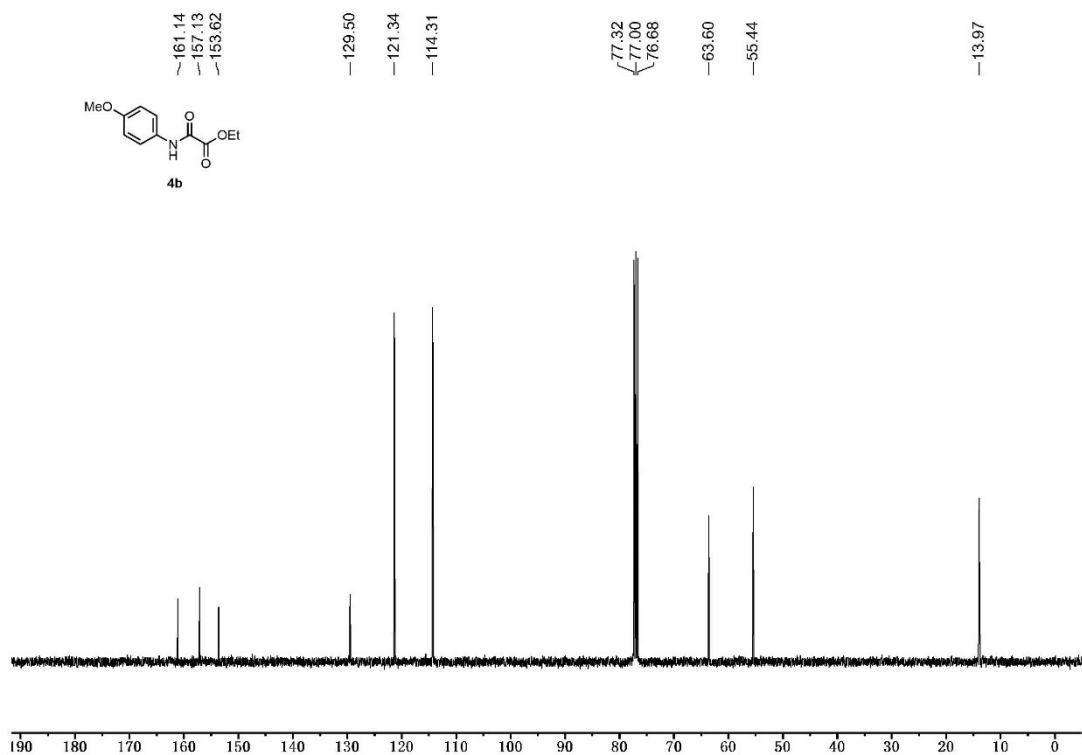




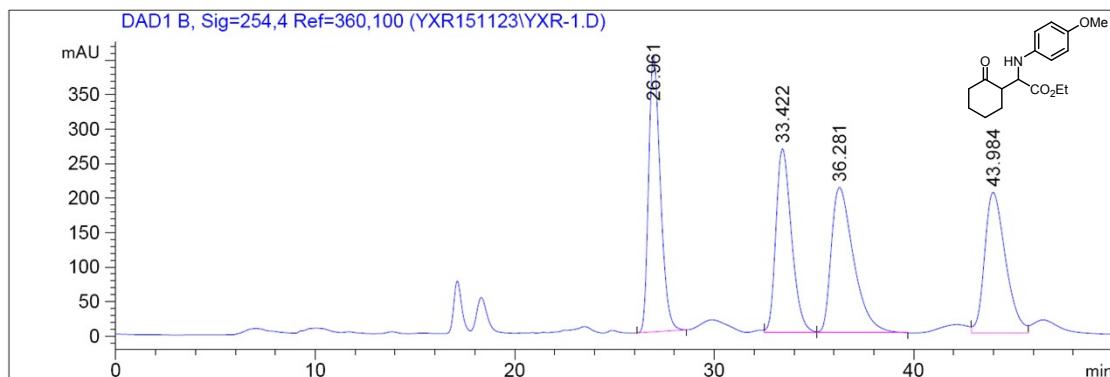




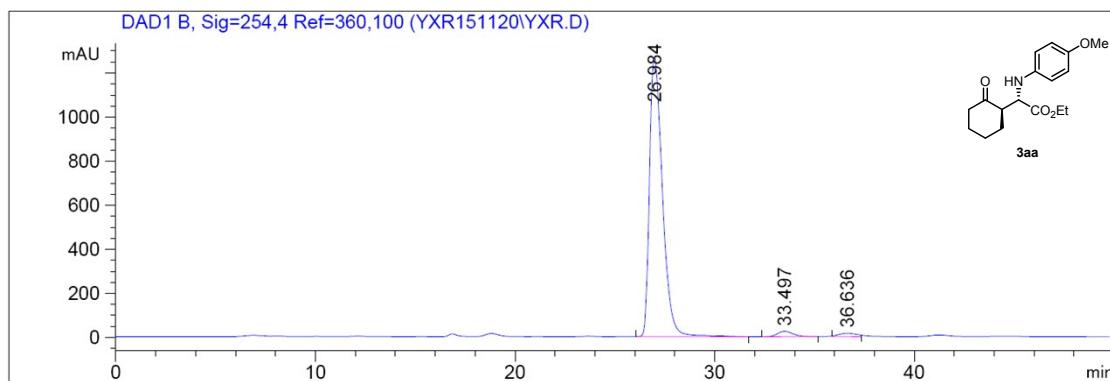




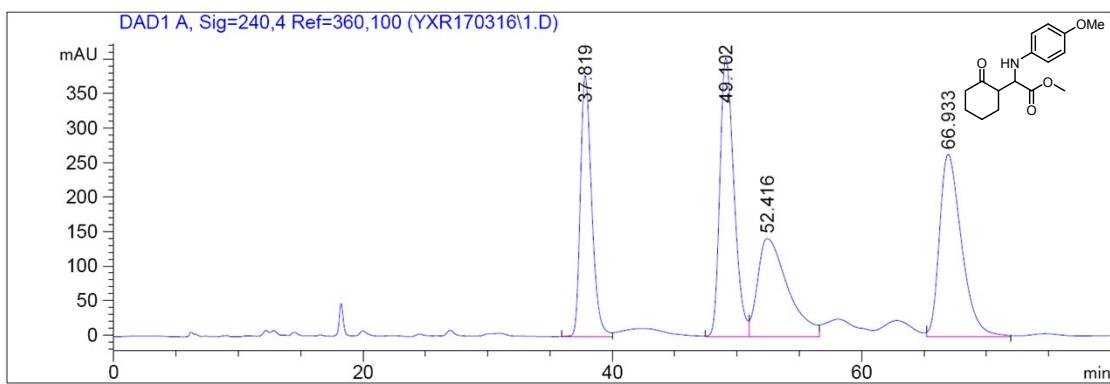
## 9. HPLC Spectra of Products



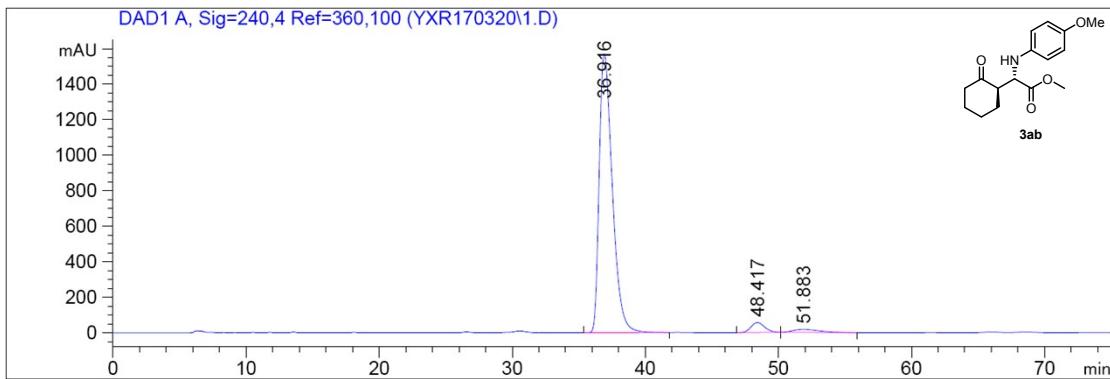
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	26.961	BB	0.6206	1.64128e <sup>4</sup>	400.10571	26.3730
2	33.422	MF R	0.9083	1.45368e <sup>4</sup>	266.74786	23.3586
3	36.281	FM R	1.2968	1.64028e <sup>4</sup>	210.80472	26.3570
4	43.984	MF R	1.2159	1.48808e <sup>4</sup>	203.98376	23.9114



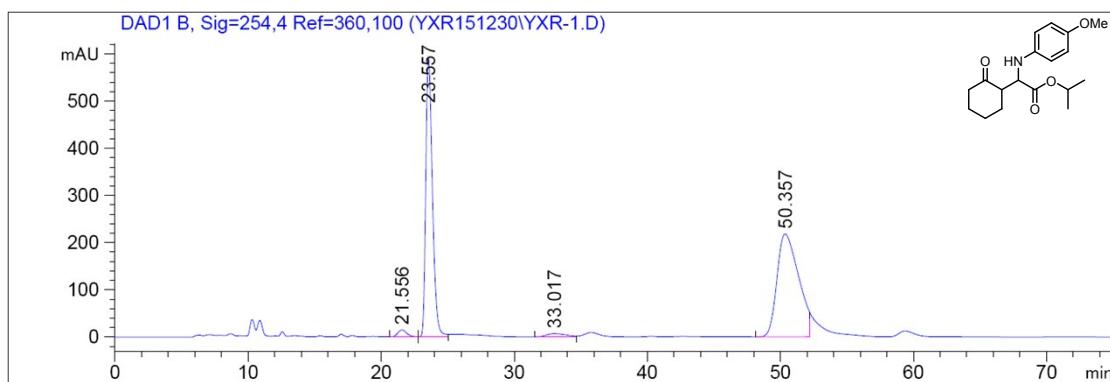
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	26.984	BB	0.7059	5.68674e <sup>4</sup>	1266.36841	96.3361
2	33.497	BB	0.7860	1253.94861	24.06038	2.1242
3	36.636	MF R	1.0386	908.85608	14.58487	1.5396



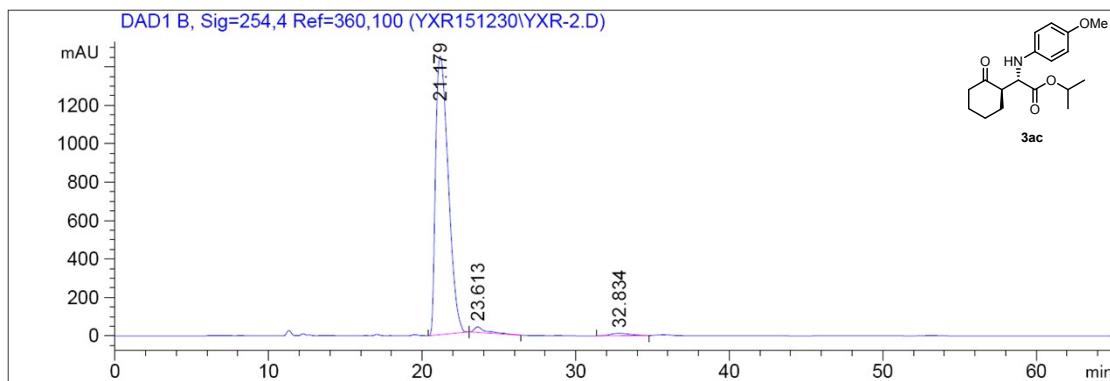
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	37.819	MF R	1.0519	2.39149e <sup>4</sup>	378.91815	21.3655
2	49.102	MF R	1.3108	3.17674e <sup>4</sup>	403.92010	28.3809
3	52.416	MF R	2.7999	2.38113e <sup>4</sup>	141.74095	21.2729
4	66.933	FM R	2.0466	3.24388e <sup>4</sup>	264.17184	28.9807



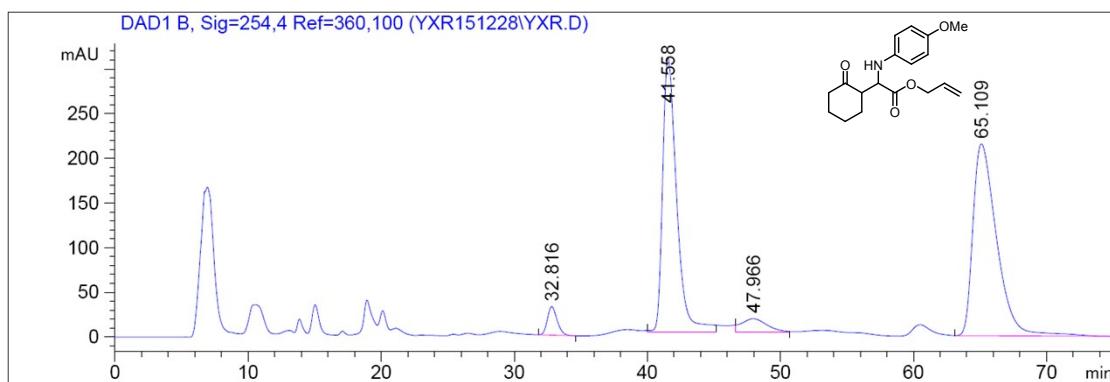
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	36.916	BB	1.0617	1.07321e <sup>5</sup>	1569.67249	94.6216
2	48.417	BB	1.0794	3930.50757	55.55710	3.4654
3	51.883	BB	1.5903	2169.69946	16.34878	1.9130



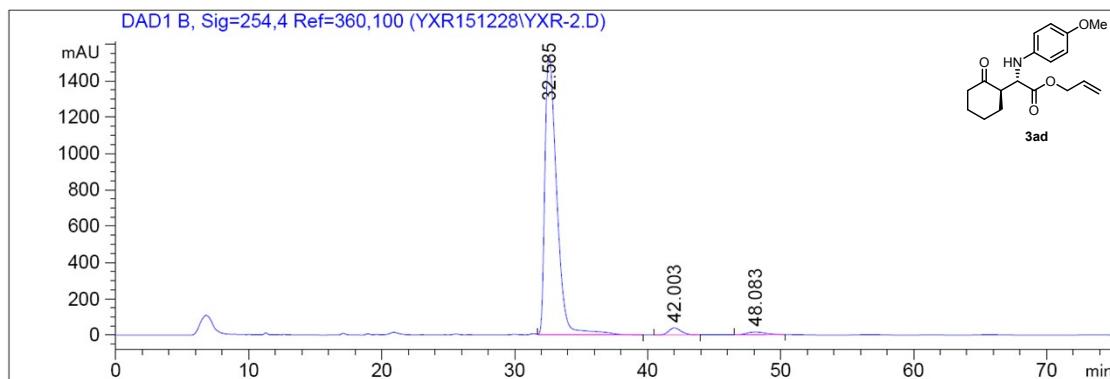
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	21.556	MF R	0.8013	719.61206	14.96757	1.5437
2	23.557	MF R	0.5816	2.06285e <sup>4</sup>	591.18707	44.2517
3	33.017	MF R	1.7458	753.37457	7.19218	1.6161
4	50.357	MF R	1.8731	2.45148e <sup>4</sup>	218.13148	52.5885



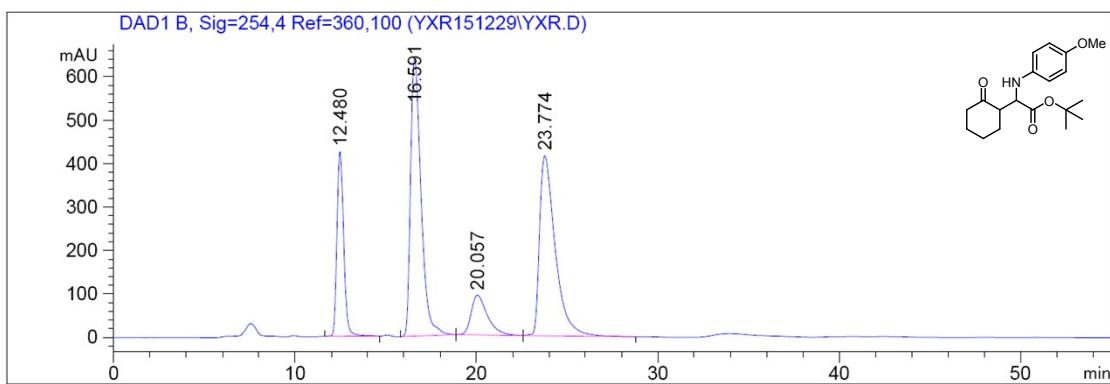
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	21.179	BB	0.9068	8.30781e <sup>4</sup>	1449.31104	96.9333
2	23.613	BB	0.7515	1571.80396	29.13138	1.8339
3	32.834	BB	1.1409	1056.51501	11.93337	1.2327



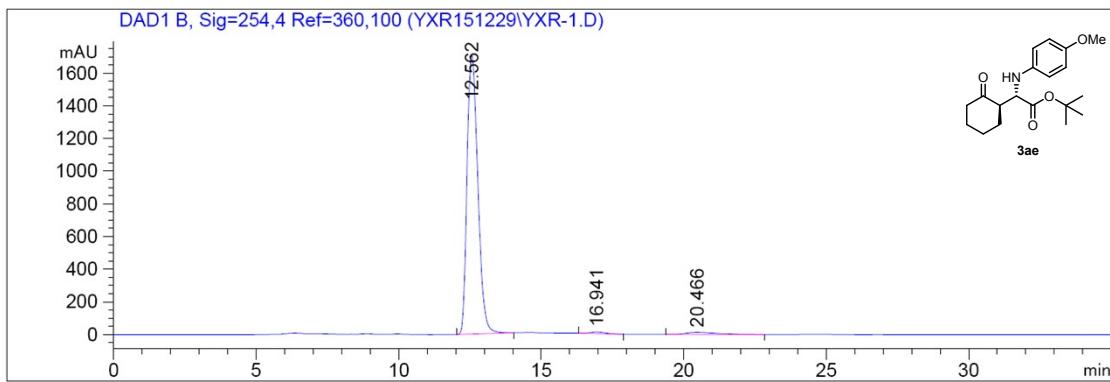
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	32.816	BB	0.7704	1627.71936	31.95047	3.0849
2	41.558	MF R	1.2238	2.24986e <sup>4</sup>	306.39633	42.6407
3	47.966	FM R	2.1907	1938.35400	14.74679	3.6737
4	65.109	BBA	1.8478	2.66986e <sup>4</sup>	214.84842	50.6007



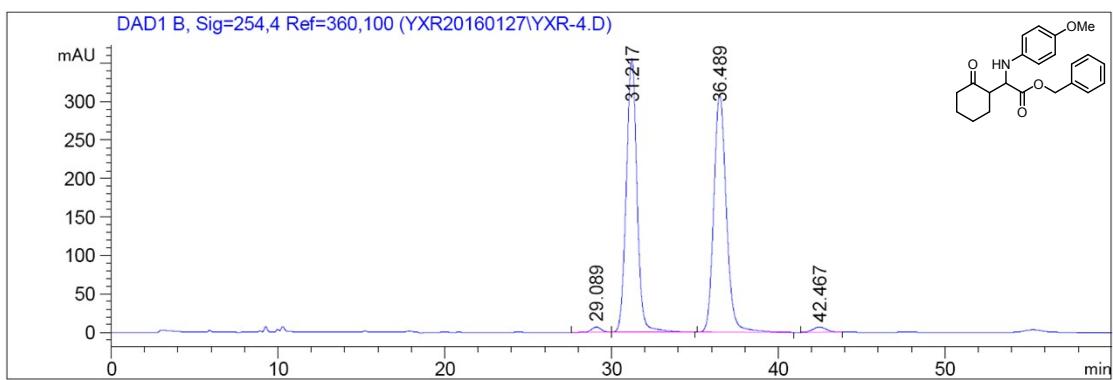
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	32.585	VB	0.9675	9.57220e <sup>4</sup>	1535.10559	96.1787
2	42.003	BB	0.9684	2445.66772	38.22931	2.4573
3	48.083	BB	1.1482	1357.51318	14.42113	1.3640



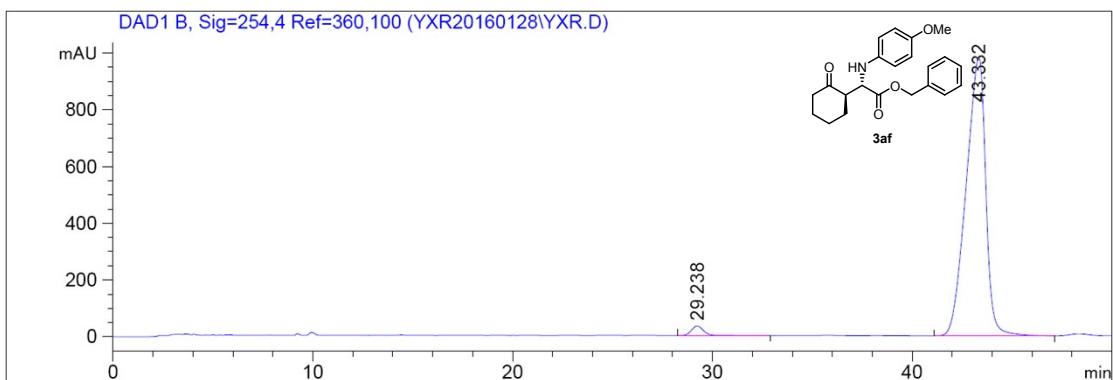
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	12.480	BB	0.4072	1.10388e <sup>4</sup>	424.76489	16.3872
2	16.591	BB	0.6157	2.57374e <sup>4</sup>	639.24677	38.2073
3	20.057	BB	0.9333	5707.25195	91.54926	8.4724
4	23.774	BB	0.9027	2.48791e <sup>4</sup>	414.26242	36.9331



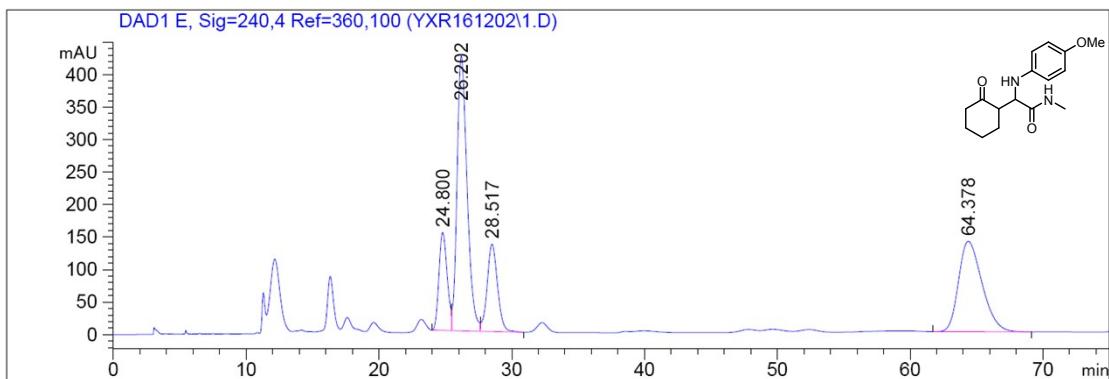
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	12.562	BB	0.4173	4.49208e <sup>4</sup>	1705.15515	97.1530
2	16.941	BB	0.5687	367.55658	9.59881	0.7949
3	20.466	BB	1.0274	948.82098	12.61640	2.0521



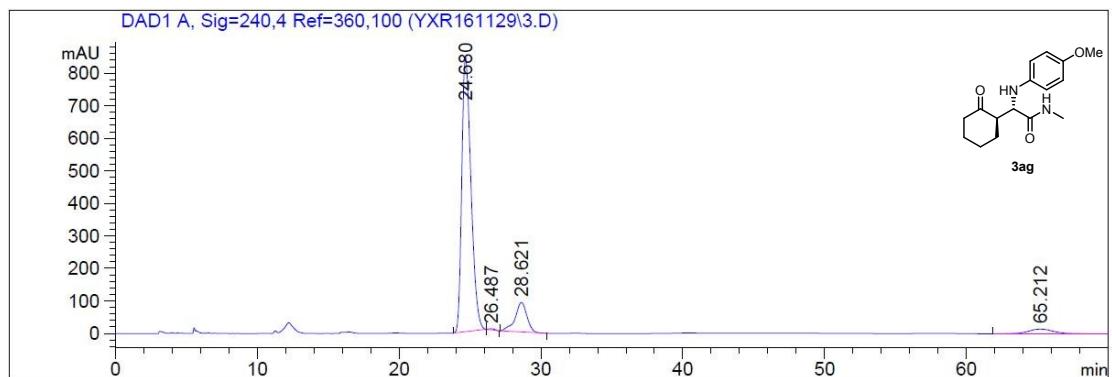
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	29.089	BB	0.5687	265.48087	6.69402	0.8143
2	31.217	BB	0.6852	1.58246e <sup>4</sup>	355.55719	48.5388
3	36.489	BB	0.8033	1.61457e <sup>4</sup>	309.17639	49.5237
4	42.467	BB	0.7795	366.17697	6.53680	1.1232



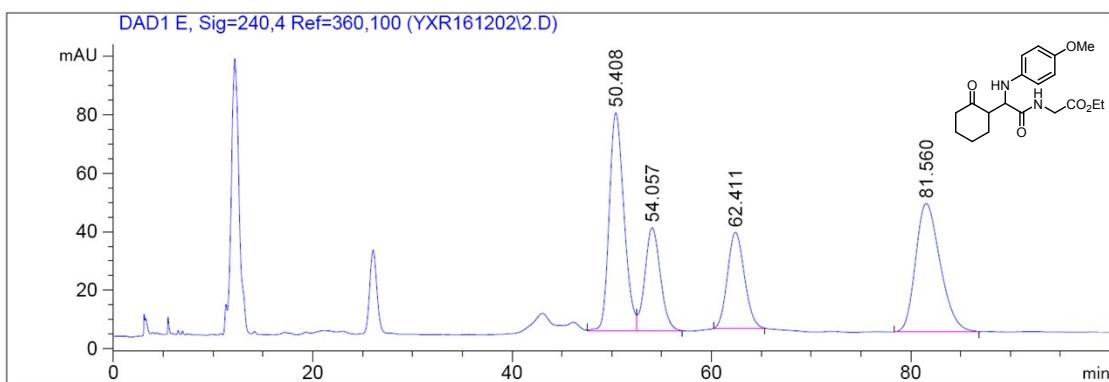
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	29.238	BB	0.6384	1402.90942	33.37512	2.0619
2	43.332	BB	1.0561	6.66364e <sup>4</sup>	981.46307	97.9381



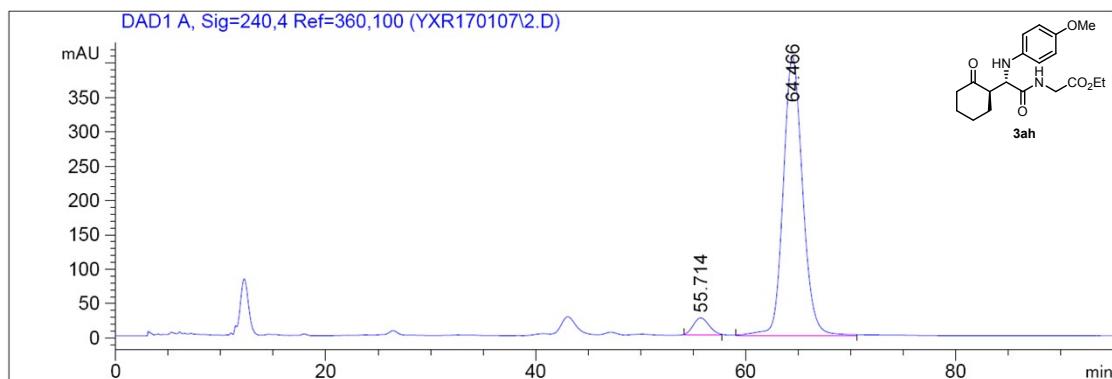
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	24.800	BV	0.6735	6507.24072	150.78763	12.2135
2	26.202	VV	0.8048	2.22864e <sup>4</sup>	422.94339	41.8293
3	28.517	VB	0.8289	7324.91309	134.59164	13.7482
4	64.378	BB	1.8811	1.71607e <sup>4</sup>	139.31493	32.2090



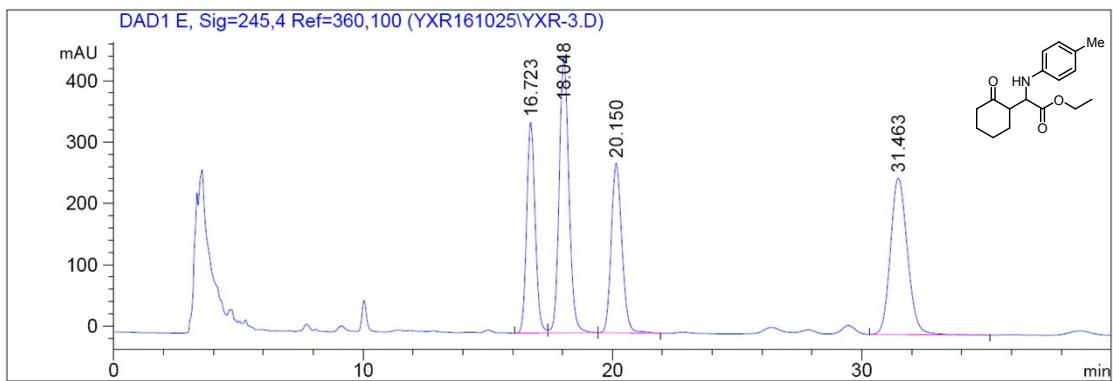
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	24.680	BB	0.6922	3.80140e <sup>4</sup>	846.09918	83.9792
2	26.487	BB	0.4678	97.12515	3.27726	0.2146
3	28.621	BB	0.8708	5262.14990	90.97268	11.6250
4	65.212	BBA	1.5419	1892.67114	14.76067	4.1812



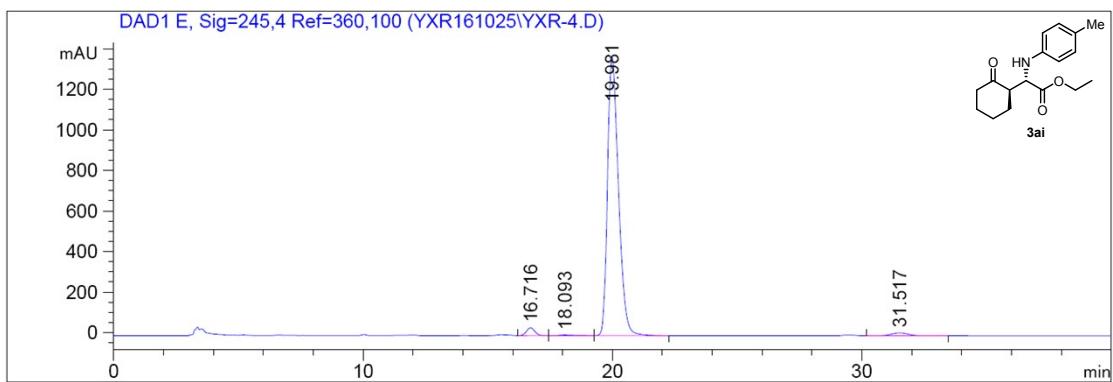
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	50.408	MF R	1.7102	7639.75977	74.45250	33.3861
2	54.057	FM R	1.7900	3785.00000	35.24250	16.5406
3	62.411	MM R	1.9826	3929.45728	33.03288	17.1719
4	81.560	MM R	2.8606	7528.83301	43.86533	32.9014



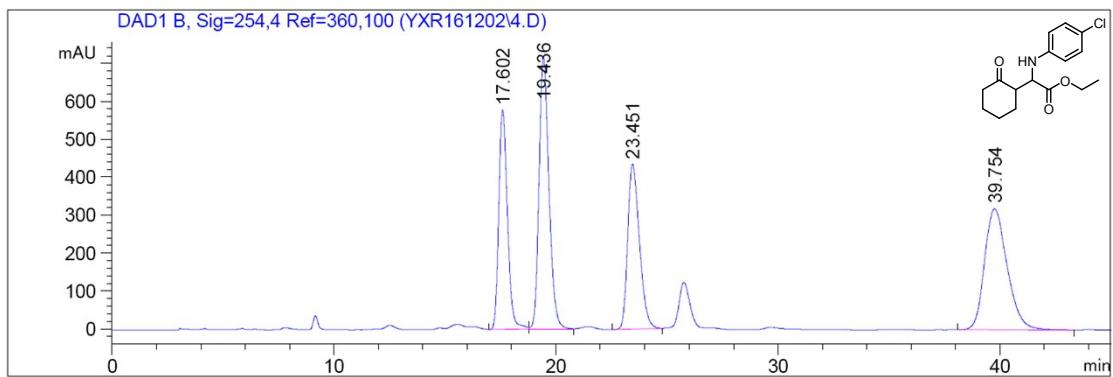
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	55.714	MM R	1.7412	2578.63525	24.68265	4.7101
2	64.466	MM R	2.1424	5.21689e <sup>4</sup>	405.83606	95.2899



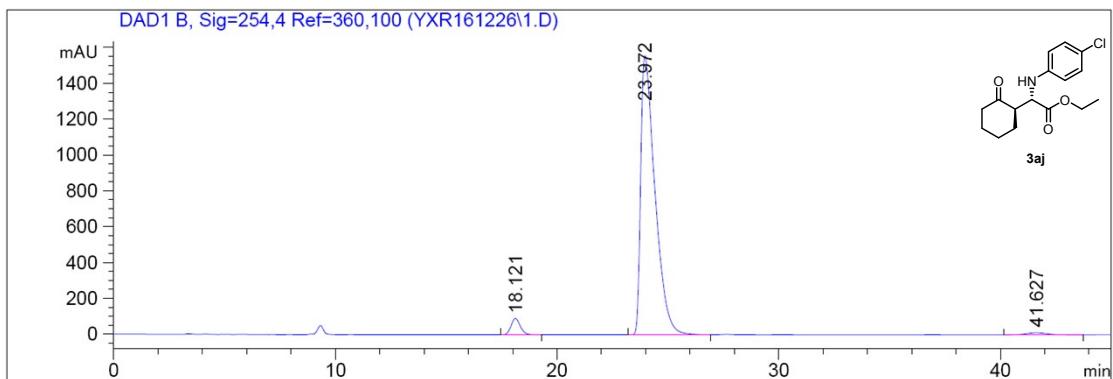
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	16.723	BV	0.3685	8139.15527	343.39212	20.0163
2	18.048	VB	0.4200	1.22179e <sup>4</sup>	451.10236	30.0469
3	20.150	BB	0.4602	8245.63574	276.29492	20.2782
4	31.463	BB	0.7320	1.20600e <sup>4</sup>	254.88084	29.6587



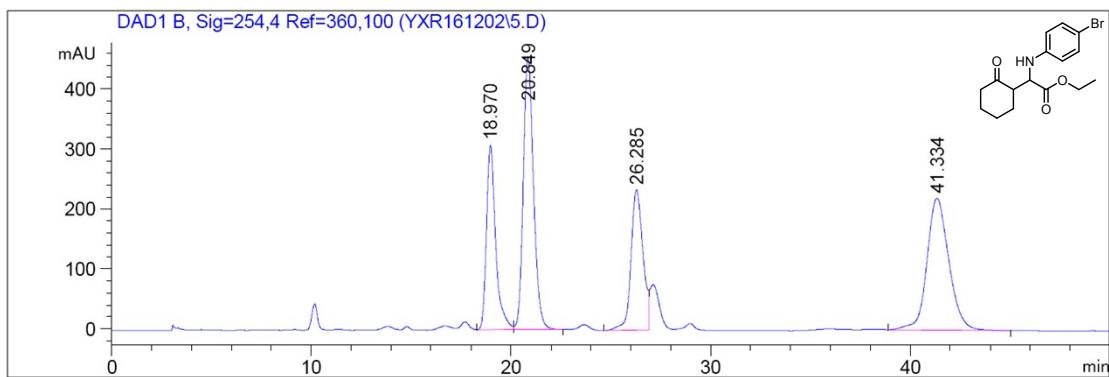
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	16.716	BB	0.3587	877.37262	38.10011	2.0202
2	18.093	BB	0.5269	101.24154	2.77972	0.2331
3	19.981	BB	0.4689	4.17906e <sup>4</sup>	1373.71838	96.2251
4	31.517	BB	0.7097	660.81287	14.17958	1.5216



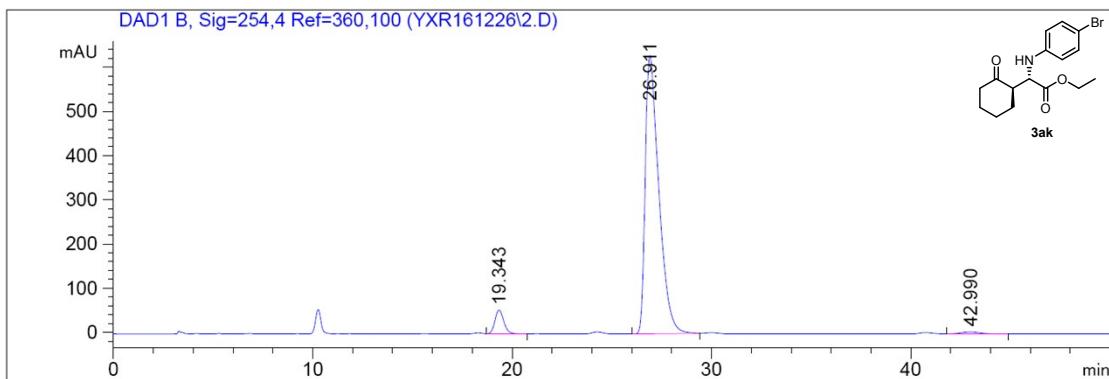
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	17.602	BV	0.4183	1.56543e <sup>4</sup>	577.46283	20.4401
2	19.436	VB	0.4792	2.23824e <sup>4</sup>	718.99091	29.2250
3	23.451	BB	0.5647	1.58927e <sup>4</sup>	434.54868	20.7513
4	39.754	BB	1.0823	2.26571e <sup>4</sup>	319.14008	29.5837



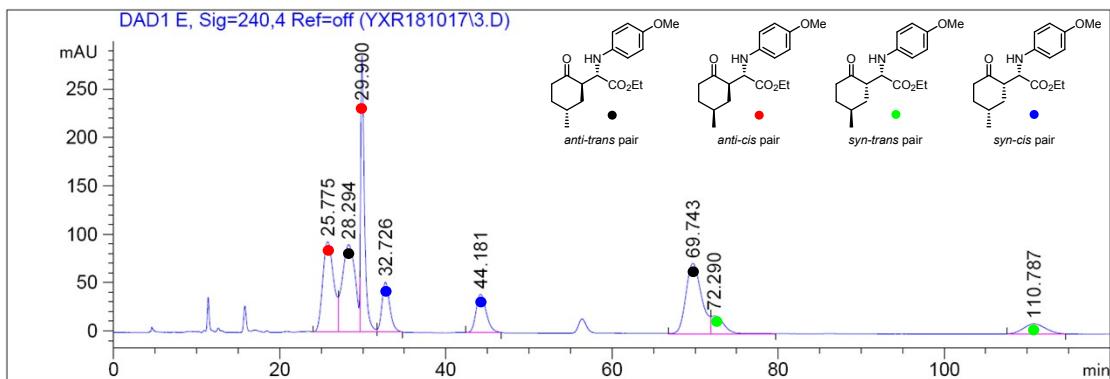
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	18.121	BB	0.4476	2622.35889	90.63425	3.5982
2	23.972	BB	0.6588	6.94871e <sup>4</sup>	1556.57288	95.3455
3	41.627	BB	0.9361	769.82233	11.75377	1.0563



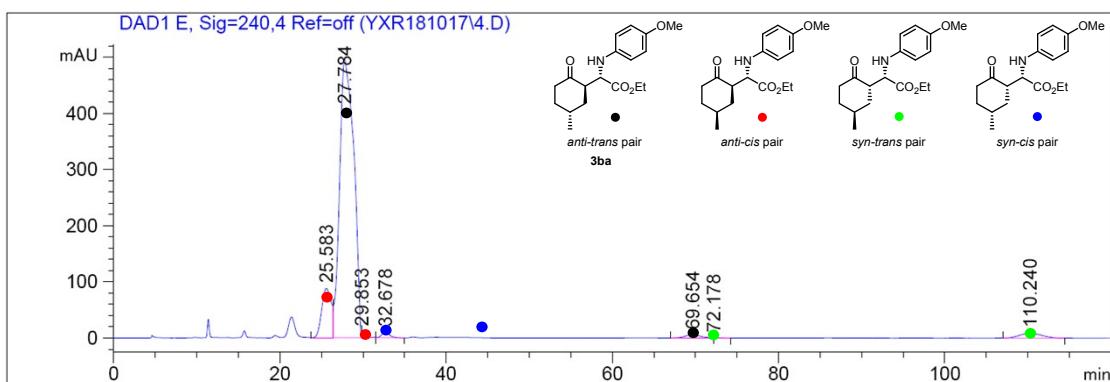
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	18.970	BV	0.4913	9945.35840	307.48956	18.8934
2	20.849	VB	0.5477	1.62158e <sup>4</sup>	455.13074	30.8056
3	26.285	BV	0.6310	9676.06543	233.73955	18.3819
4	41.334	BB	1.1366	1.68020e <sup>4</sup>	220.08995	31.9191



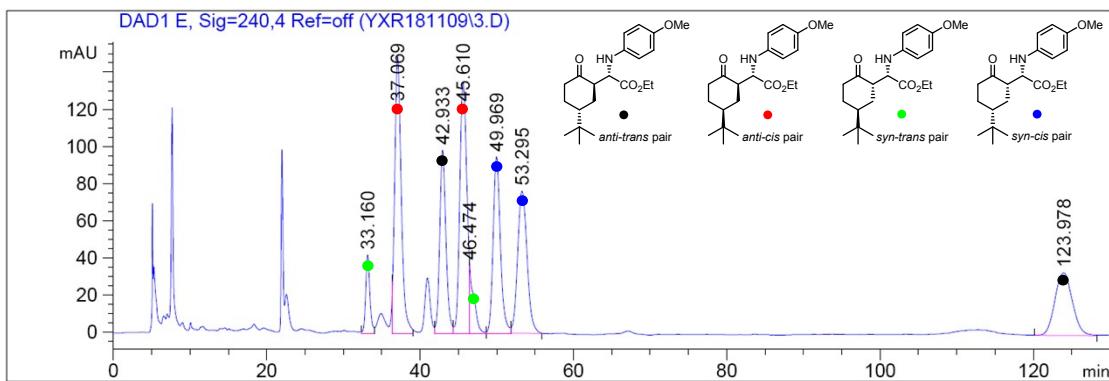
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	19.343	BB	0.4779	1643.26257	53.56564	5.1832
2	26.911	BB	0.6982	2.97772e <sup>4</sup>	629.17181	93.9234
3	42.990	BB	0.7934	283.24747	4.34010	0.8934



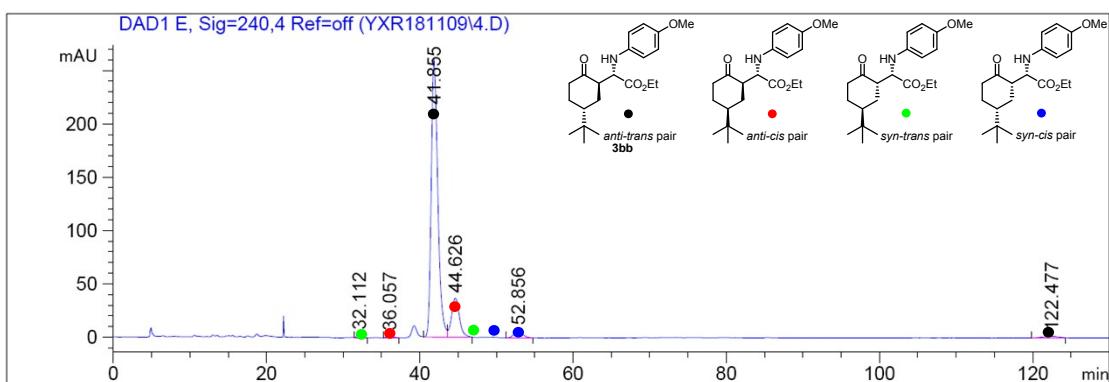
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	25.775	MF R	1.5453	8648.95703	93.28068	18.1414
2	28.294	MF R	1.8000	9762.12695	90.38831	20.4763
3	29.900	MF R	0.5243	8988.58008	285.70557	18.8537
4	32.726	FM R	1.0962	3386.82227	51.49301	7.1039
5	44.181	MM R	1.4237	3392.81348	39.71836	7.1165
6	69.743	MF R	2.1683	9480.44531	72.87189	19.8854
7	72.290	FM R	1.8206	2020.53516	18.49733	4.2381
8	110.787	MM R	3.1644	1995.02429	10.50763	4.1846



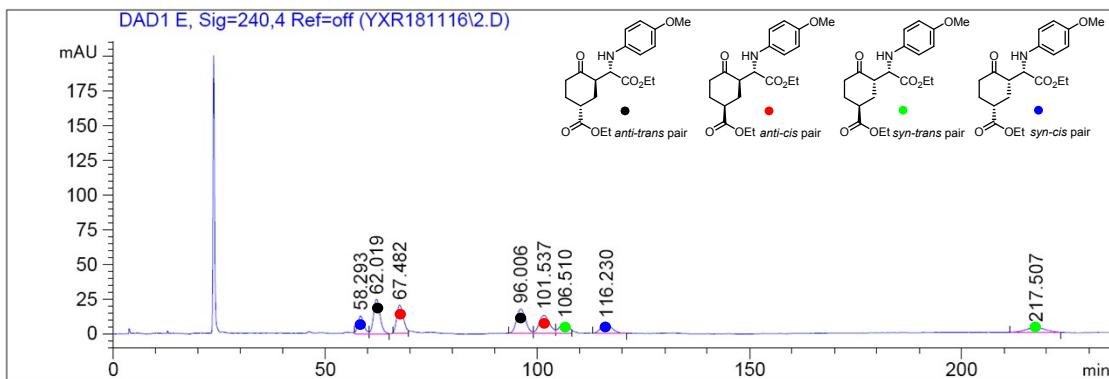
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	25.583	BV	1.2009	6874.89551	87.67223	9.9596
2	27.784	MF R	1.9710	5.87322e <sup>4</sup>	496.63663	85.0850
3	29.853	FM R	0.3868	253.49452	10.92275	0.3672
4	32.678	BB	0.9549	628.64197	9.63823	0.9107
5	69.654	MF R	2.2387	788.02264	5.86657	1.1416
6	72.178	FM R	0.9392	47.69592	8.46398e <sup>-1</sup>	0.0691
7	110.240	MM R	3.2217	1702.75513	8.80865	2.4668



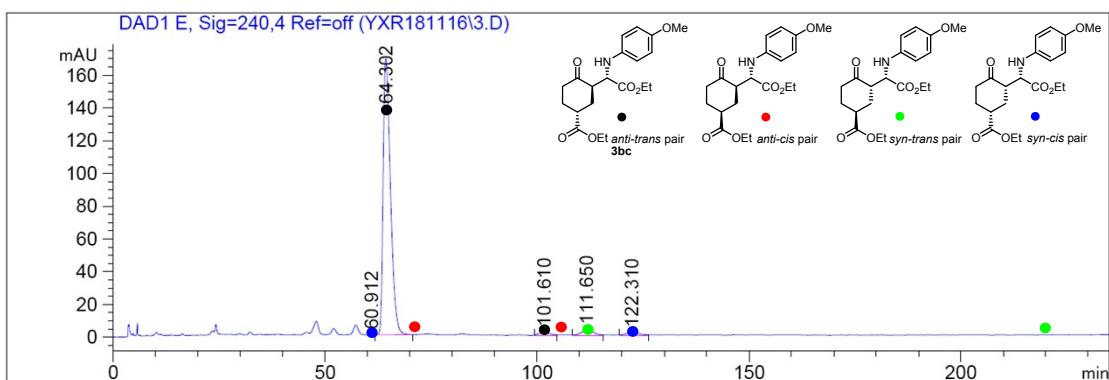
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	33.160	MF R	0.6294	1590.87048	42.12516	3.6118
2	37.069	FM R	0.9713	8675.65820	148.86310	19.6969
3	42.933	MF R	0.9434	5576.89502	98.52335	12.6616
4	45.610	FM R	1.0704	8683.78516	135.20578	19.7153
5	46.474	MF R	0.5437	1342.08203	36.39882	3.0470
6	49.969	MF R	1.0992	6264.93652	94.98831	14.2237
7	53.295	FM R	1.4283	6551.14795	76.44254	14.8735
8	123.978	MM R	2.6462	5360.50000	33.76182	12.1703



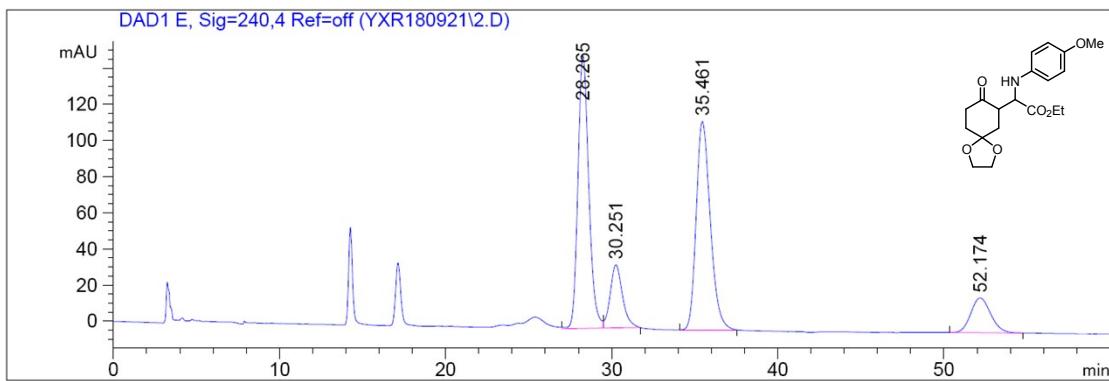
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	32.112	MM R	0.5993	89.42572	2.48698	0.4690
2	36.057	MM R	0.9311	116.05249	2.07725	0.6086
3	41.855	MF R	0.9932	1.55158e <sup>4</sup>	260.37131	81.3716
4	44.626	FM R	1.1987	2625.77246	36.50734	13.7707
5	52.856	BB	0.9398	501.04181	6.68977	2.6277
6	122.477	MF R	2.3488	219.74570	1.55930	1.1524



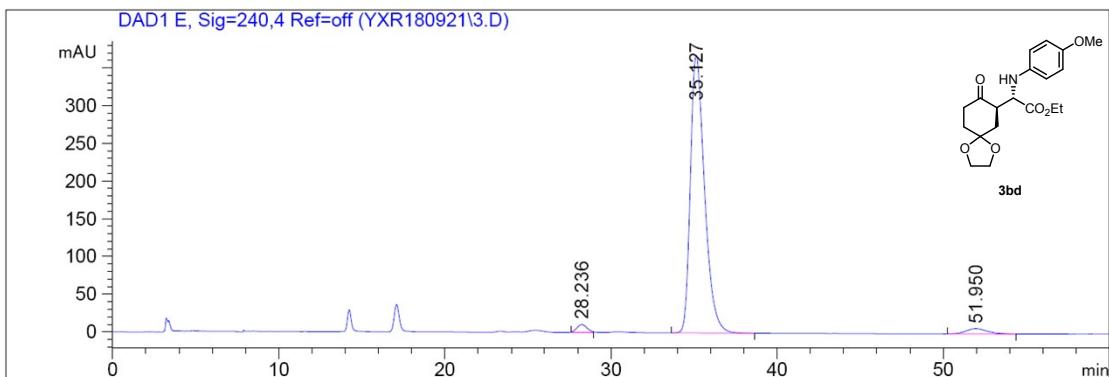
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	58.293	MF R	1.6319	1252.26697	12.78979	8.6242
2	62.019	FM R	1.7766	2653.03931	24.88813	18.2712
3	67.482	MF R	1.8300	2227.51685	20.28715	15.3406
4	96.006	MF R	2.4921	2645.94629	17.69587	18.2223
5	101.537	MF R	2.8316	2231.03540	13.13174	15.3649
6	106.510	MF R	2.6797	1140.50696	7.09347	7.8545
7	116.230	MM R	3.0170	1243.01794	6.86680	8.5605
8	217.507	MM R	5.2947	1127.03418	3.54768	7.7617



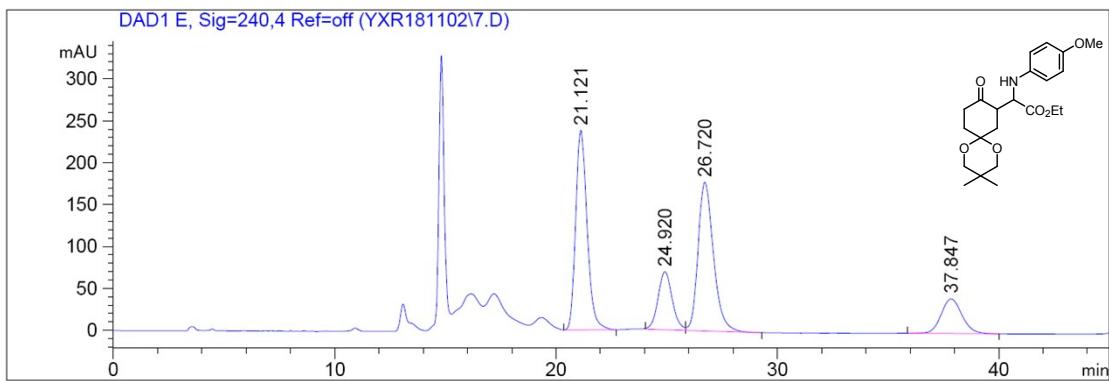
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	60.912	MM R	0.8533	15.21683	2.97207e <sup>-1</sup>	0.0707
2	64.302	BB	1.6641	2.02146e <sup>4</sup>	168.68474	93.9834
3	101.610	MF R	2.5721	312.47040	2.02473	1.4528
4	111.650	MF R	3.1570	617.82831	3.26164	2.8725
5	122.310	MF R	3.3955	348.57495	1.71097	1.6206



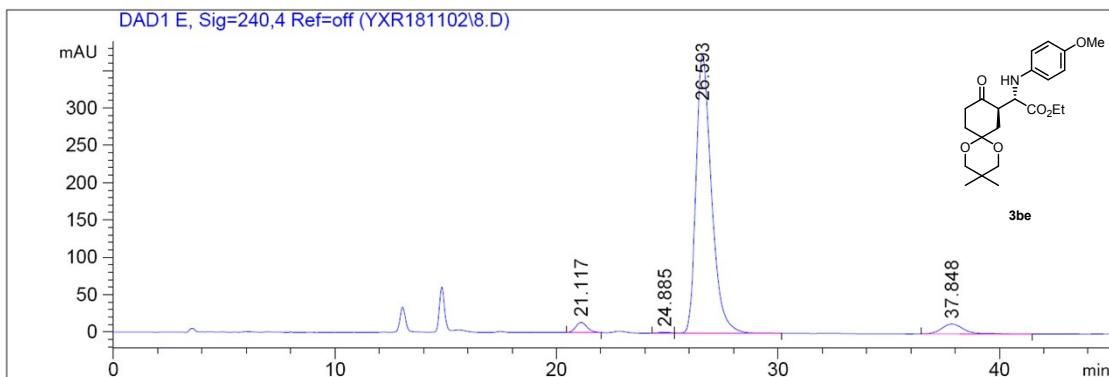
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	28.265	MF R	0.7557	6843.88477	150.93642	40.1145
2	30.251	FM R	0.8562	1792.38525	34.89219	10.5058
3	35.461	MM R	0.9841	6818.17529	115.47246	39.9638
4	52.174	BB	1.1656	1606.44617	19.25038	9.4160



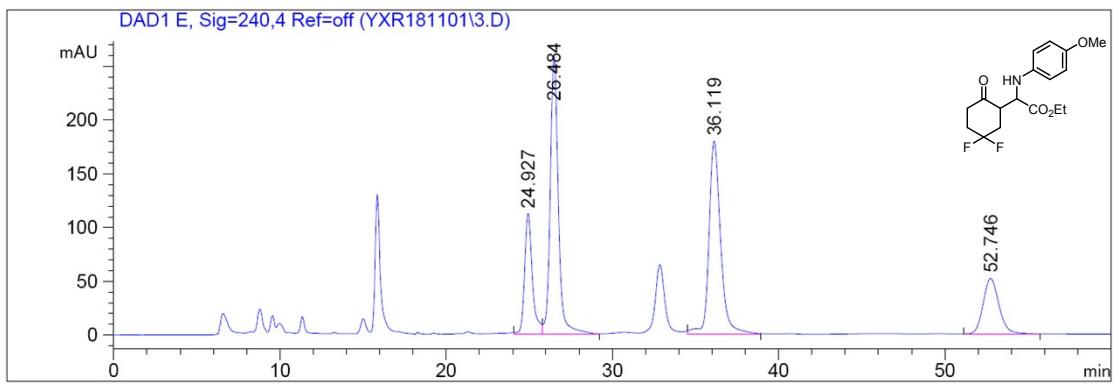
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	28.236	FM R	0.7186	457.05353	10.60001	2.0013
2	35.127	BB	0.9113	2.17716e <sup>4</sup>	367.40143	95.3293
3	51.950	BB	1.0441	609.66241	6.95890	2.6695



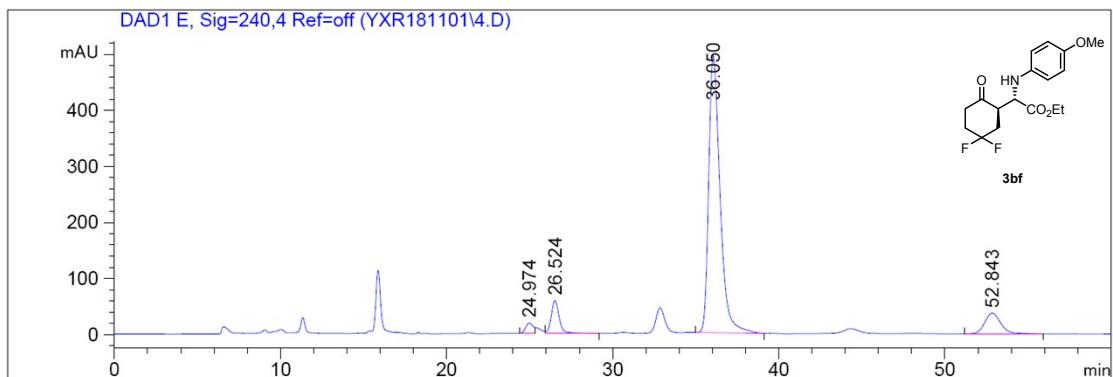
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	21.121	BB	0.5560	8568.58301	238.03221	37.3226
2	24.920	FM R	0.7424	3088.10522	69.33035	13.4510
3	26.720	VB	0.7411	8594.98828	177.44193	37.4376
4	37.847	BB	0.9963	2706.48364	41.31455	11.7888



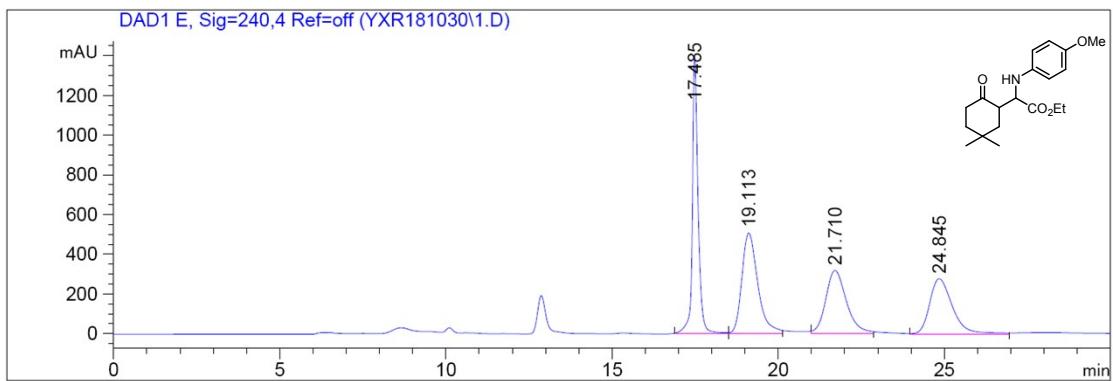
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	21.117	MM R	0.5916	480.83185	13.54584	2.4570
2	24.885	FM R	0.6930	56.66631	1.36289	0.2896
3	26.593	FM R	0.8125	1.81261e <sup>4</sup>	371.81287	92.6215
4	37.848	BB	1.0120	906.48230	13.15326	4.6320



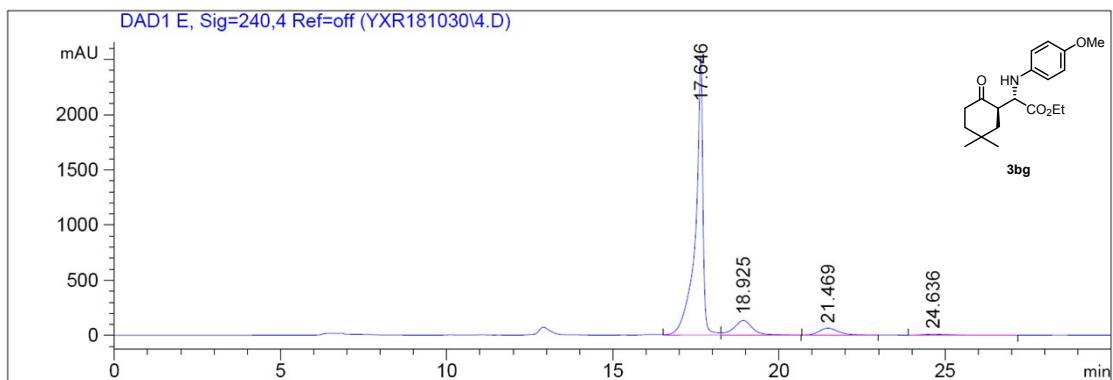
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	24.927	FM R	0.5392	3626.10303	112.08134	14.7183
2	26.484	VB	0.5107	8753.07520	258.75537	35.5285
3	36.119	FM R	0.8153	8780.93945	179.49423	35.6416
4	52.746	MM R	1.1158	3476.62036	51.93158	14.1115



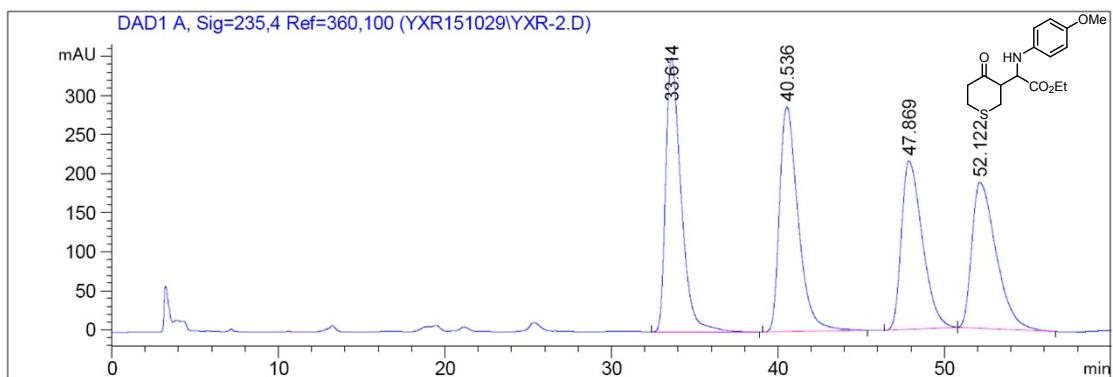
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	24.974	FM R	0.5059	565.50781	18.63091	1.9851
2	26.524	VB	0.5074	1941.65588	58.47685	6.8159
3	36.050	BB	0.7188	2.35266e <sup>4</sup>	494.72998	82.5867
4	52.843	BB	1.0172	2453.38916	36.82735	8.6123



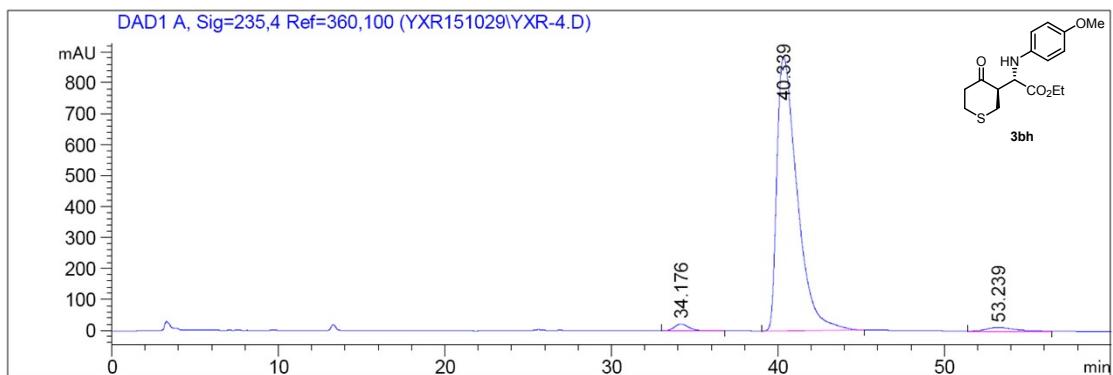
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	17.485	MF R	0.1974	1.65669e <sup>4</sup>	1398.50879	27.3966
2	19.113	MF R	0.5530	1.67565e <sup>4</sup>	505.01651	27.7102
3	21.710	MF R	0.7164	1.35997e <sup>4</sup>	316.37378	22.4898
4	24.845	MM R	0.8064	1.35475e <sup>4</sup>	280.00269	22.4034



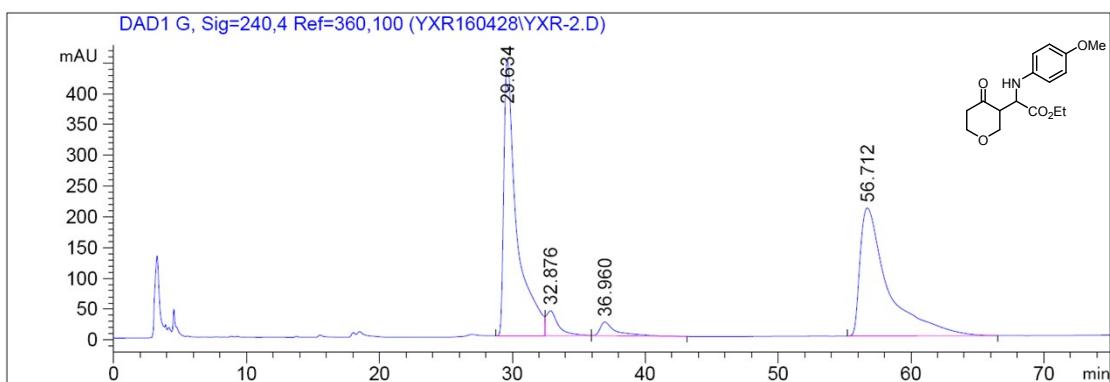
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	17.646	VV	0.2118	3.93176e <sup>4</sup>	2523.68140	83.1092
2	18.925	VB	0.5720	5111.66016	132.52692	10.8050
3	21.469	BB	0.6077	2460.28857	62.16716	5.2005
4	24.636	BB	0.7459	418.78873	7.95900	0.8852



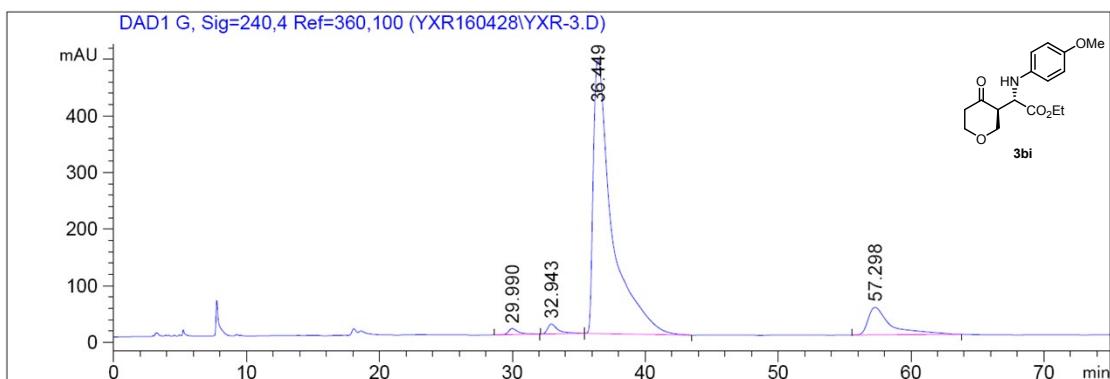
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	33.614	BB	0.9849	2.24670e <sup>4</sup>	350.92899	27.1805
2	40.536	BB	1.1525	2.24069e <sup>4</sup>	287.73294	27.1078
3	47.869	BB	1.3685	1.88136e <sup>4</sup>	215.50777	22.7606
4	52.122	BB	1.5440	1.89711e <sup>4</sup>	186.93272	22.9511



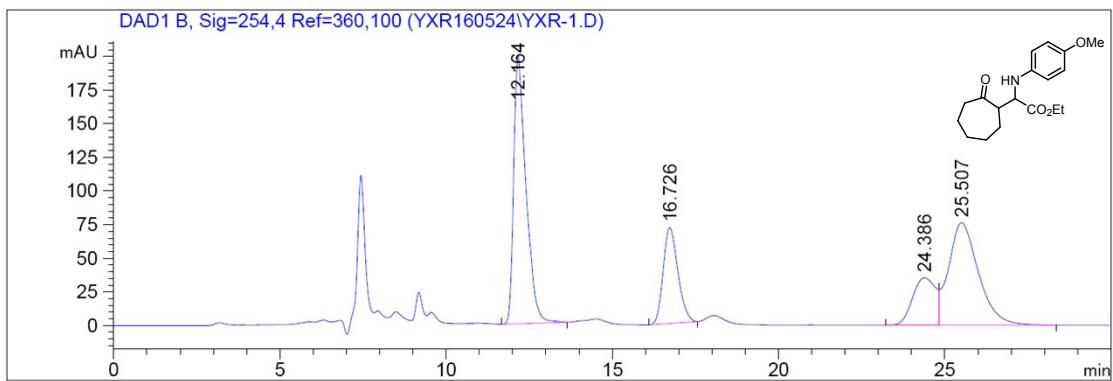
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	34.176	BB	0.8751	1316.94275	21.97821	1.7051
2	40.339	BB	1.2372	7.47340e <sup>4</sup>	885.00037	96.7596
3	53.239	BB	1.2495	1185.83472	11.19790	1.5353



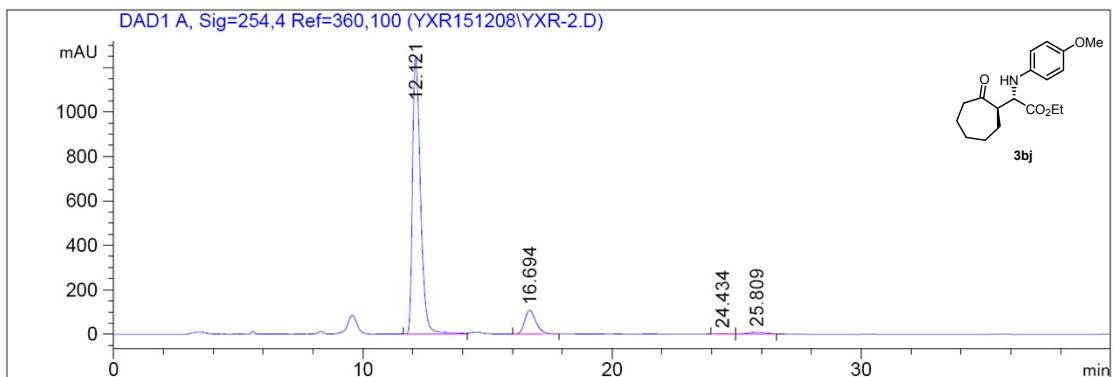
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	29.634	BV	0.9482	3.04396e <sup>4</sup>	449.42856	46.6372
2	32.876	VB	0.9044	2593.40723	40.42946	3.9734
3	36.960	BB	1.1524	1837.30811	22.22762	2.8150
4	56.712	BB	2.0763	3.03987e <sup>4</sup>	207.85150	46.5744



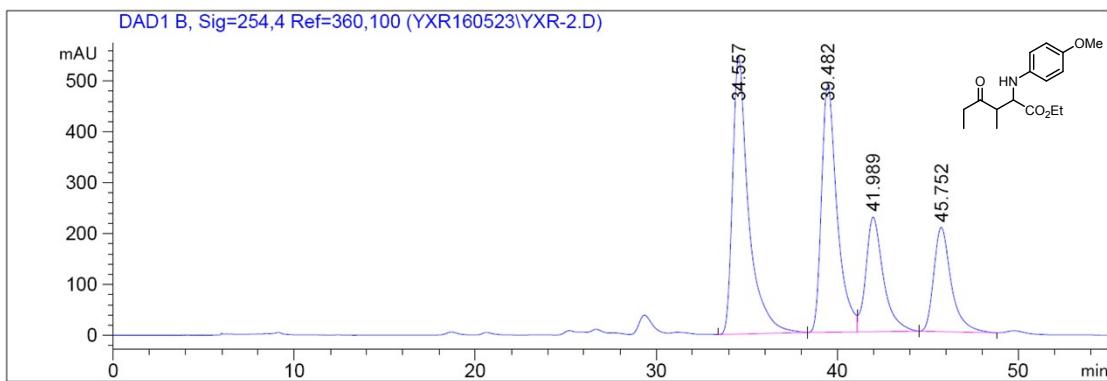
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	29.990	BB	0.7400	560.70203	10.68802	1.0288
2	32.943	BB	0.7876	957.88342	17.25549	1.7575
3	36.449	BB	1.3888	4.72089e <sup>4</sup>	486.19116	86.6198
4	57.298	BB	1.6553	5773.77881	48.55615	10.5939



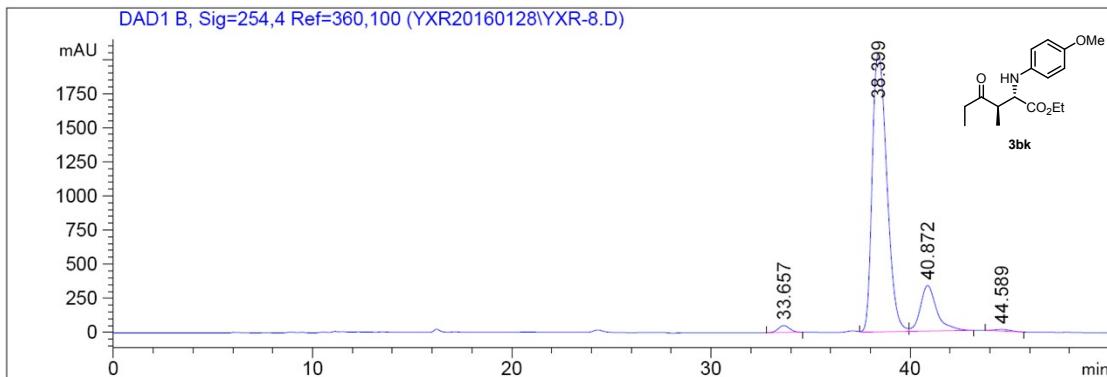
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	12.164	BB	0.3730	5102.40283	199.11568	37.1276
2	16.726	BB	0.4726	2189.35864	71.23458	15.9309
3	24.386	BV	0.7386	1689.83105	35.16724	12.2960
4	25.507	VB	0.9232	4761.29297	76.18205	34.6455



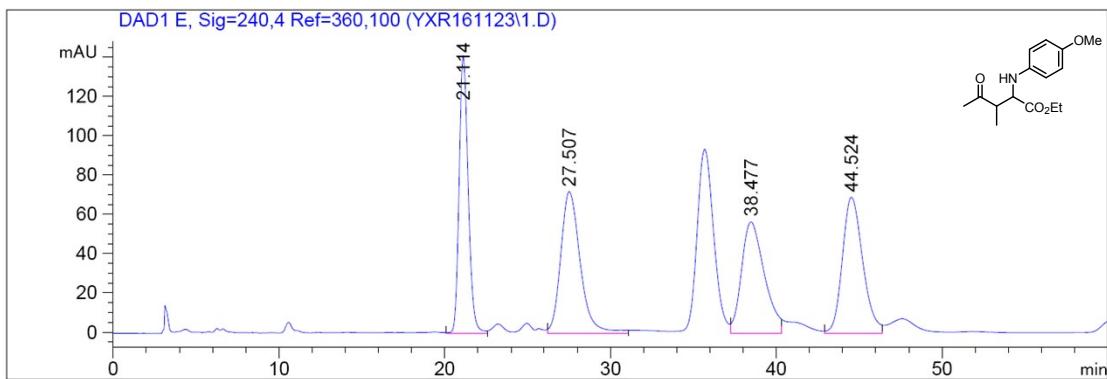
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	12.121	MF R	0.3739	2.80952e <sup>4</sup>	1252.50073	88.1992
2	16.694	BB	0.4777	3318.23315	107.01801	10.4169
3	24.434	MF R	0.6341	53.63891	1.40994	0.1684
4	25.809	FM R	0.8116	387.16287	7.95048	1.2154



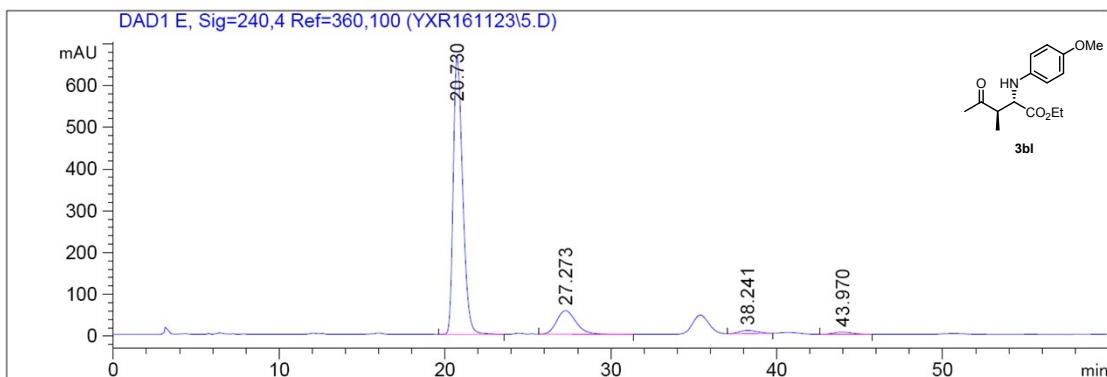
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	34.557	BB	0.9064	3.35524e <sup>4</sup>	544.91943	36.5880
2	39.482	BV	0.9024	2.92168e <sup>4</sup>	486.63986	31.8602
3	41.989	VB	1.0003	1.51804e <sup>4</sup>	225.23358	16.5539
4	45.752	BB	1.0047	1.37534e <sup>4</sup>	204.99800	14.9978



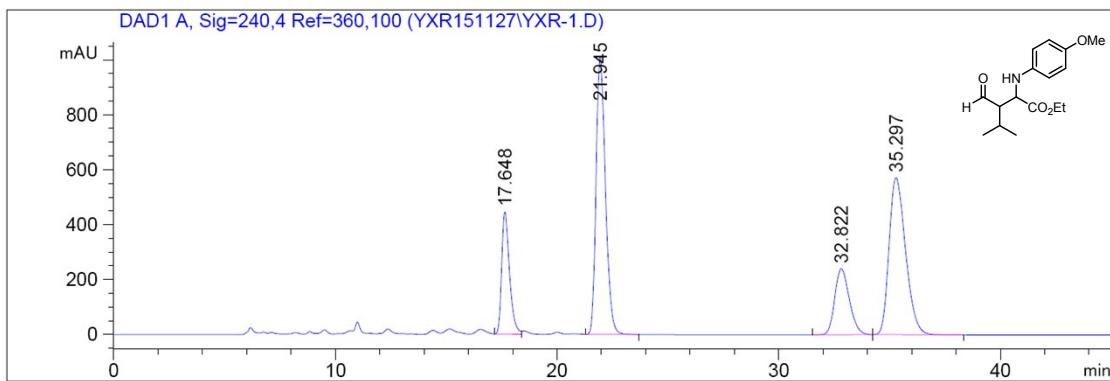
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	33.657	BB	0.6215	1988.54785	50.05849	1.5809
2	38.399	VV	0.8043	1.04093e <sup>5</sup>	2036.59534	82.7527
3	40.872	VB	0.8611	1.90366e <sup>4</sup>	333.90891	15.1339
4	44.589	BB	0.7545	669.84338	12.63441	0.5235



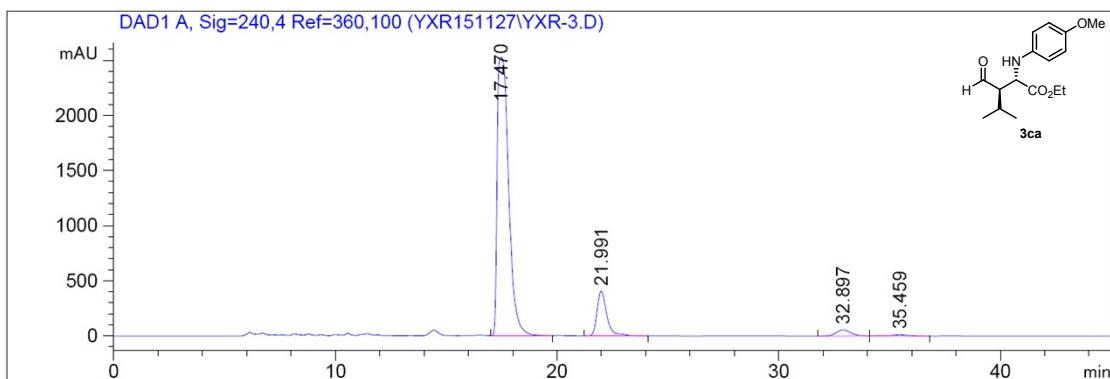
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	21.114	MF R	0.6322	5360.86523	141.33614	23.7021
2	27.507	MF R	1.3682	5916.61768	72.07486	26.1593
3	38.477	MF R	1.5967	5425.45313	56.63126	23.9877
4	44.524	MF R	1.4238	5914.70898	69.23727	26.1509



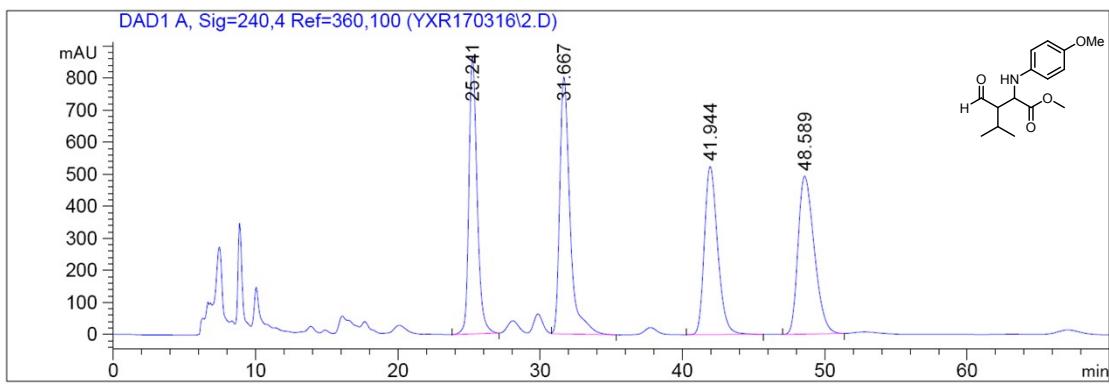
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	20.730	BB	0.6116	2.62418e <sup>4</sup>	666.11707	82.4878
2	27.273	BB	1.2075	4577.99561	56.48825	14.3903
3	38.241	BB	0.9470	571.36035	7.46498	1.7960
4	43.970	BB	0.9156	421.80060	5.50681	1.3259



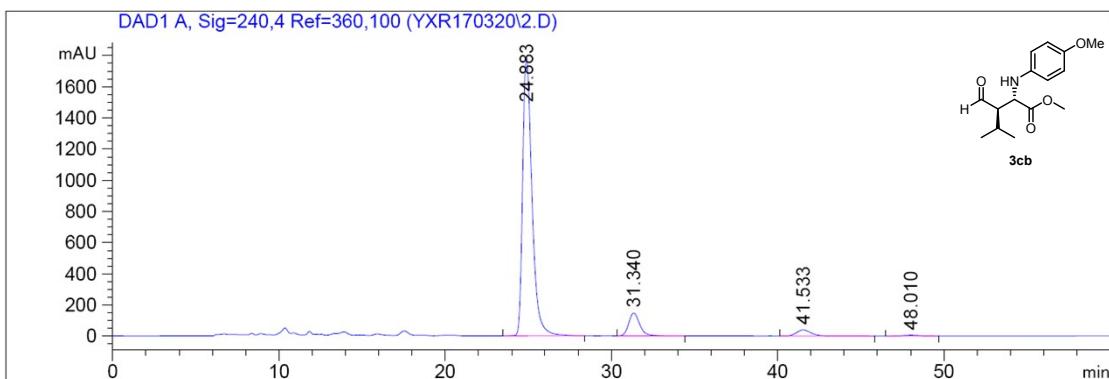
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	17.648	BV	0.3718	1.08852e <sup>4</sup>	444.28430	13.4336
2	21.945	BB	0.4511	2.96166e <sup>4</sup>	1013.00366	36.5505
3	32.822	BB	0.7038	1.09572e <sup>4</sup>	240.39999	13.5226
4	35.297	BB	0.8037	2.95702e <sup>4</sup>	571.46484	36.4933



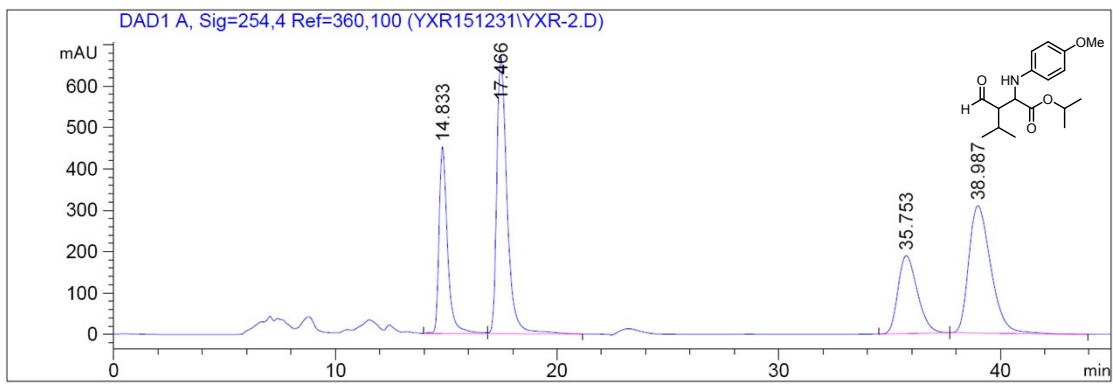
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	17.470	BB	0.5581	9.01669e <sup>4</sup>	2528.09766	85.3092
2	21.991	BB	0.4628	1.24572e <sup>4</sup>	407.30743	11.7861
3	32.897	BB	0.6859	2464.75391	55.09393	2.3320
4	35.459	BB	0.8222	605.36023	10.50672	0.5727



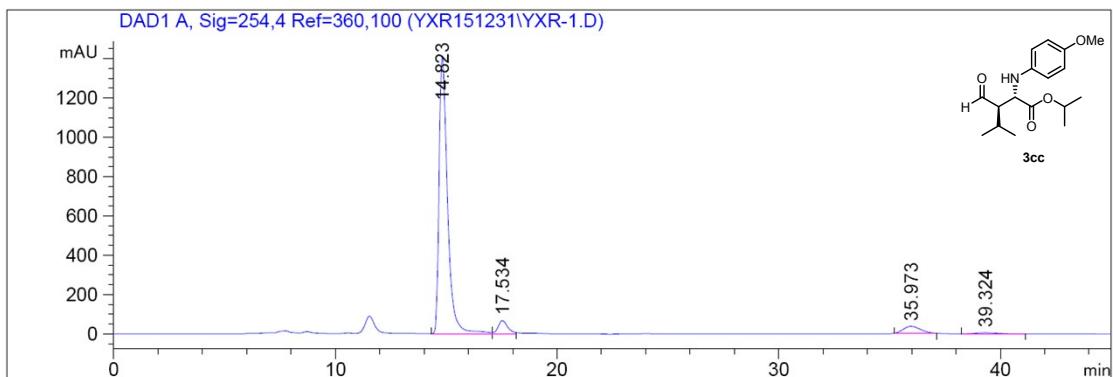
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	25.241	BB	0.6142	3.47554e <sup>4</sup>	866.10376	23.4465
2	31.667	VB	0.7582	4.03097e <sup>4</sup>	802.22559	27.1936
3	41.944	BB	1.0052	3.40443e <sup>4</sup>	524.53552	22.9668
4	48.589	BB	1.2328	3.91230e <sup>4</sup>	493.54095	26.3930



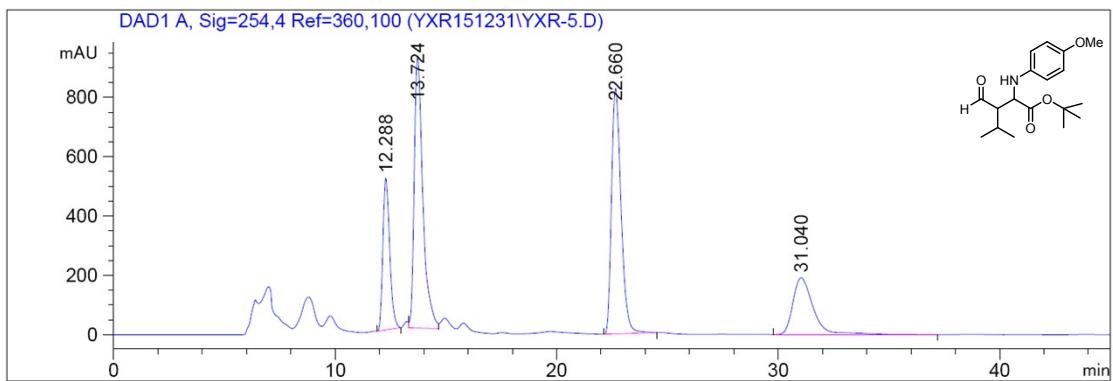
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	24.883	BB	0.5963	6.99500e <sup>4</sup>	1788.46643	87.8430
2	31.340	BB	0.7060	6774.89551	146.38429	8.5079
3	41.533	BB	0.9651	2509.70947	39.19138	3.1517
4	48.010	BB	0.9227	396.10971	5.81494	0.4974



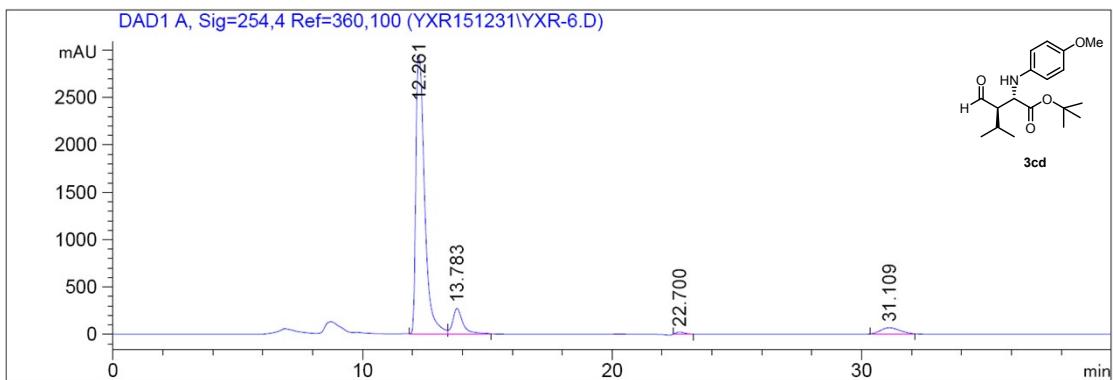
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	14.833	BV	0.4010	1.20353e <sup>4</sup>	451.46768	18.1203
2	17.466	VB	0.4887	2.16535e <sup>4</sup>	670.53845	32.6014
3	35.753	BB	0.9395	1.14152e <sup>4</sup>	188.23247	17.1866
4	38.987	BB	1.0810	2.13150e <sup>4</sup>	307.39700	32.0916



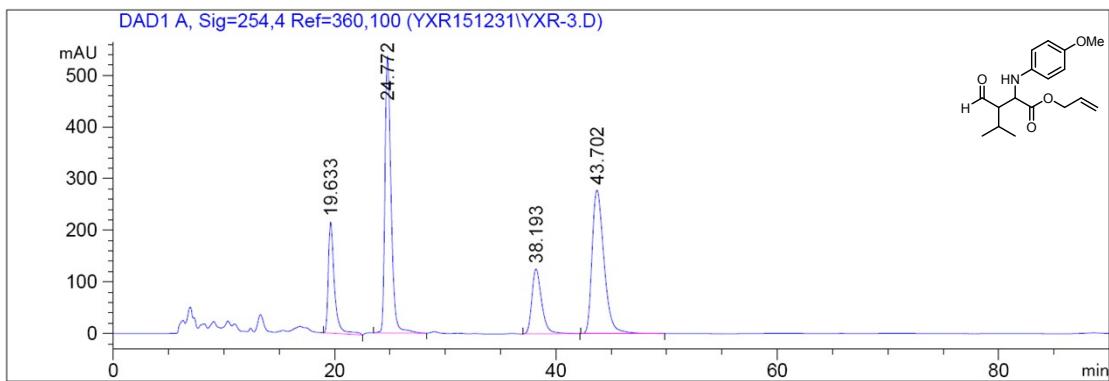
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	14.823	MF R	0.4412	3.74419e <sup>4</sup>	1414.39063	89.7067
2	17.534	MF R	0.4961	1996.02722	67.05069	4.7823
3	35.973	MM R	0.9074	1960.50195	36.00914	4.6971
4	39.324	BB	0.7702	339.70831	5.61233	0.8139



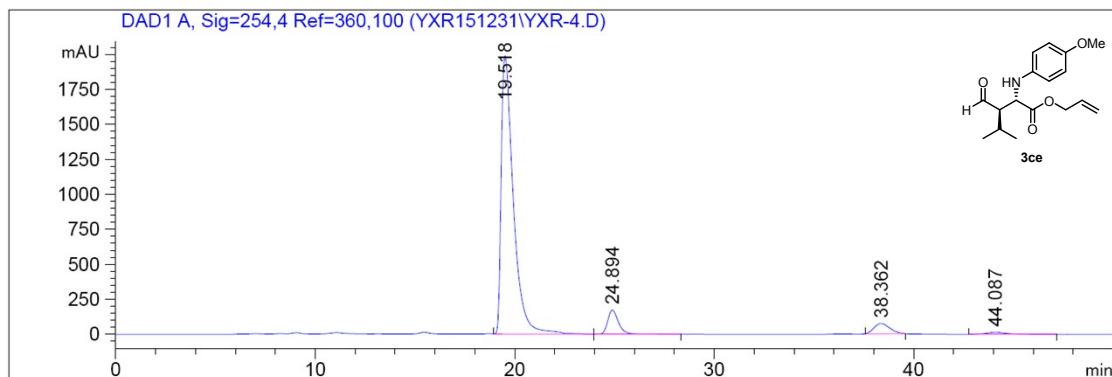
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	12.288	BB	0.3344	1.09861e <sup>4</sup>	511.85443	15.1159
2	13.724	VV	0.4107	2.47410e <sup>4</sup>	917.09949	34.0413
3	22.660	BB	0.4622	2.47007e <sup>4</sup>	827.62939	33.9859
4	31.040	BB	0.9701	1.22515e <sup>4</sup>	191.06065	16.8570



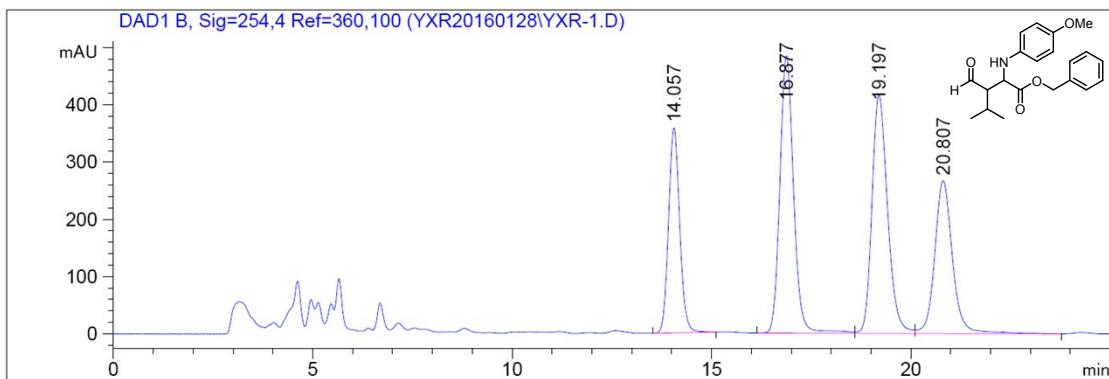
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	12.261	MF R	0.4083	7.19143e <sup>4</sup>	2935.41431	86.0325
2	13.783	FM R	0.4611	7424.39697	268.37338	8.8820
3	22.700	MM R	0.4060	534.99725	21.96223	0.6400
4	31.109	MM R	0.9132	3715.96973	67.82070	4.4455



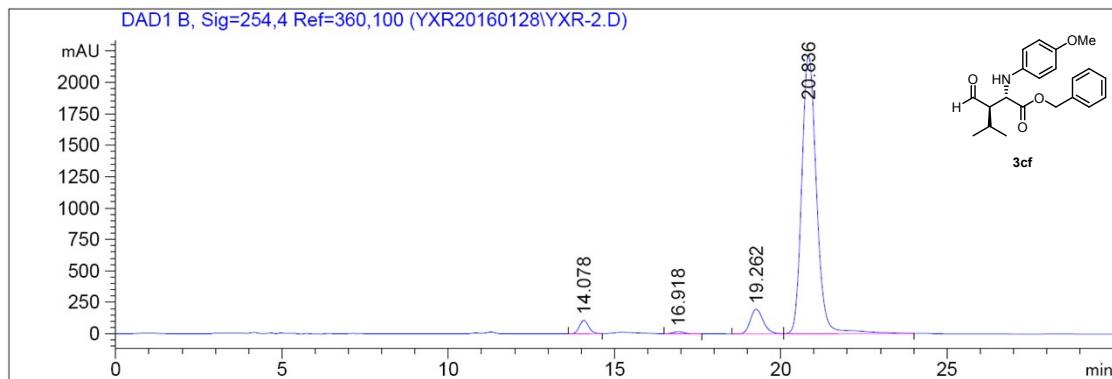
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	19.633	BB	0.5727	8279.87891	215.26515	14.4218
2	24.772	BB	0.5915	2.06474e <sup>4</sup>	535.90051	35.9635
3	38.193	BB	0.9304	7684.16943	125.49399	13.3842
4	43.702	BB	1.1423	2.08007e <sup>4</sup>	278.21027	36.2304



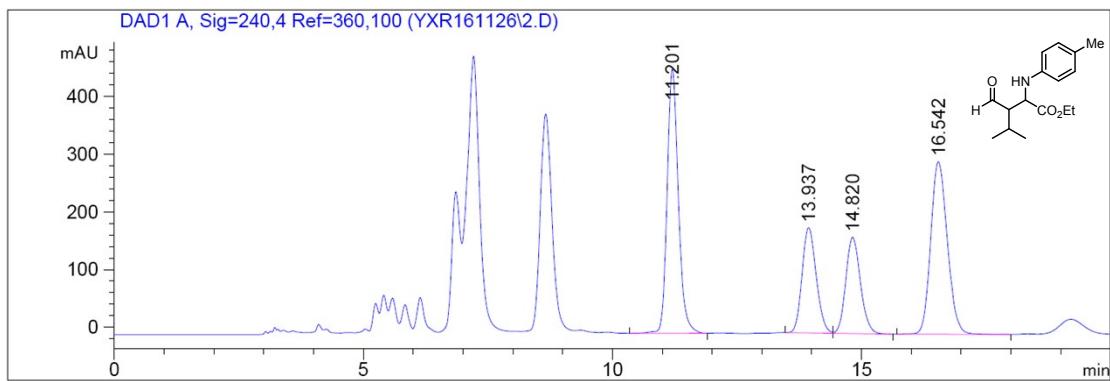
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	19.518	VB	0.6391	8.44005e <sup>4</sup>	1988.81921	88.0223
2	24.894	BB	0.5724	6476.83154	172.36227	6.7548
3	38.362	MM R	0.9131	4014.01587	73.26868	4.1863
4	44.087	BB	0.9459	993.95544	14.56937	1.0366



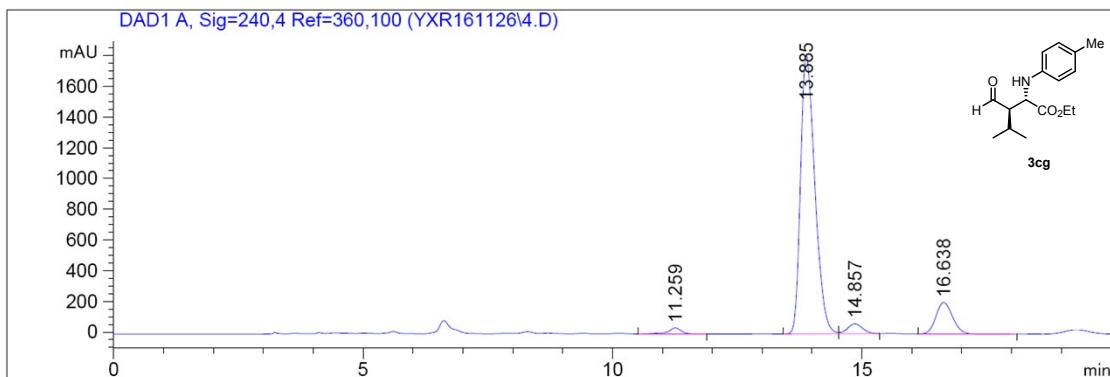
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	14.057	BB	0.3005	6954.87695	358.19519	18.2592
2	16.877	BV	0.3689	1.15851e <sup>4</sup>	484.64444	30.4154
3	19.197	VV	0.4188	1.13005e <sup>4</sup>	416.11356	29.6681
4	20.807	VB	0.4707	8249.18262	266.80841	21.6573



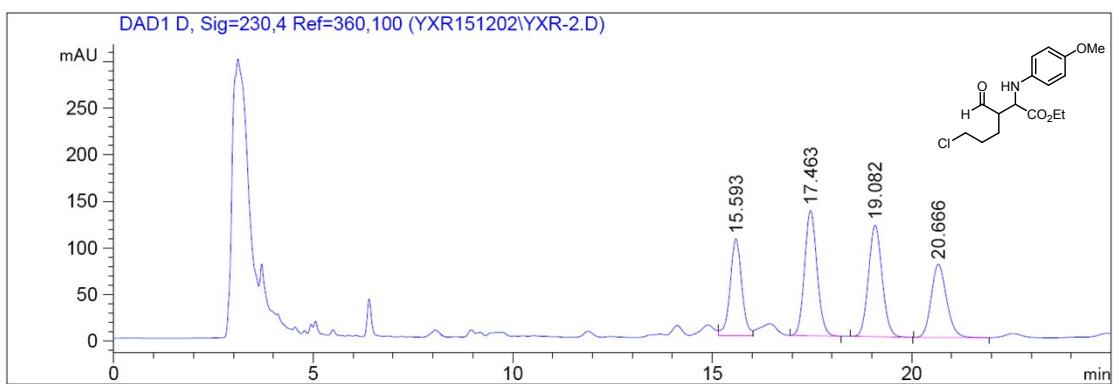
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	14.078	BB	0.2949	2042.05493	106.88641	2.6886
2	16.918	BB	0.3515	358.49493	15.75256	0.4720
3	19.262	BV	0.4144	5257.88232	196.37361	6.9226
4	20.836	VB	0.4752	6.82937e <sup>4</sup>	2218.31885	89.9168



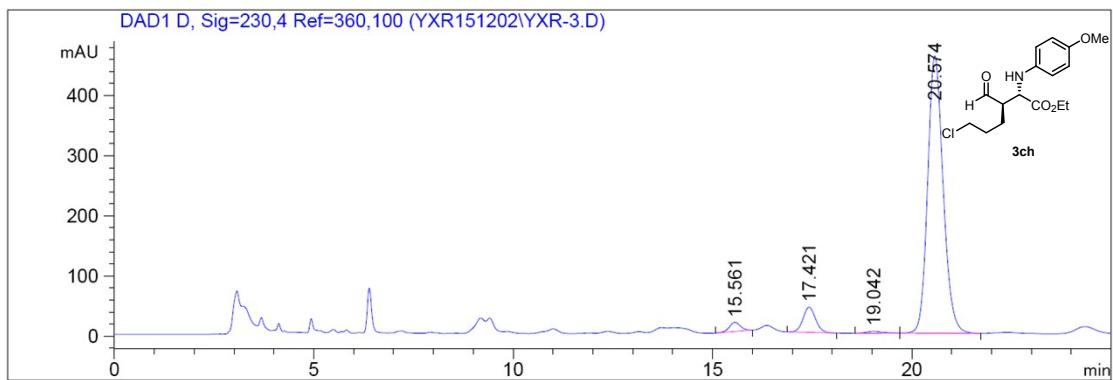
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	11.201	BB	0.2403	7154.60107	457.96786	33.8876
2	13.937	BV	0.3064	3605.89282	182.59789	17.0792
3	14.820	VB	0.3167	3412.01294	166.73230	16.1609
4	16.542	BB	0.3607	6940.23975	299.14990	32.8723



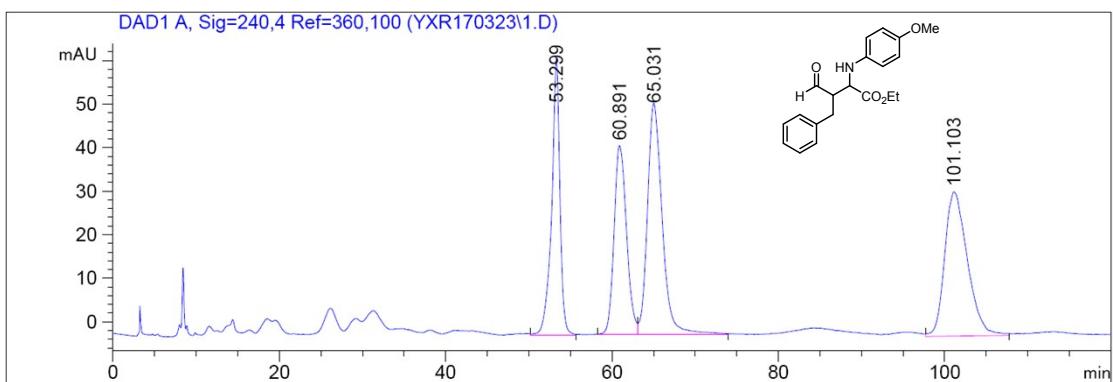
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	11.259	BB	0.2708	717.14404	38.95102	1.6706
2	13.885	BV	0.3068	3.61346e <sup>4</sup>	1810.72339	84.1768
3	14.857	VB	0.3191	1310.84460	63.97268	3.0537
4	16.638	BB	0.3629	4764.43506	205.22018	11.0989



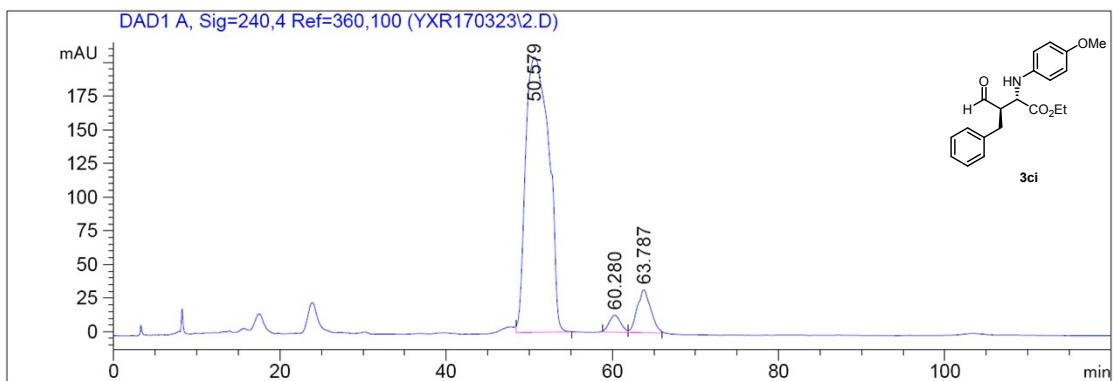
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	15.593	VV	0.3087	2091.79053	103.95885	20.9560
2	17.463	BB	0.3376	2932.06201	134.90128	29.3740
3	19.082	BB	0.3676	2854.22656	119.93543	28.5943
4	20.666	BB	0.4122	2103.73975	78.61732	21.0757



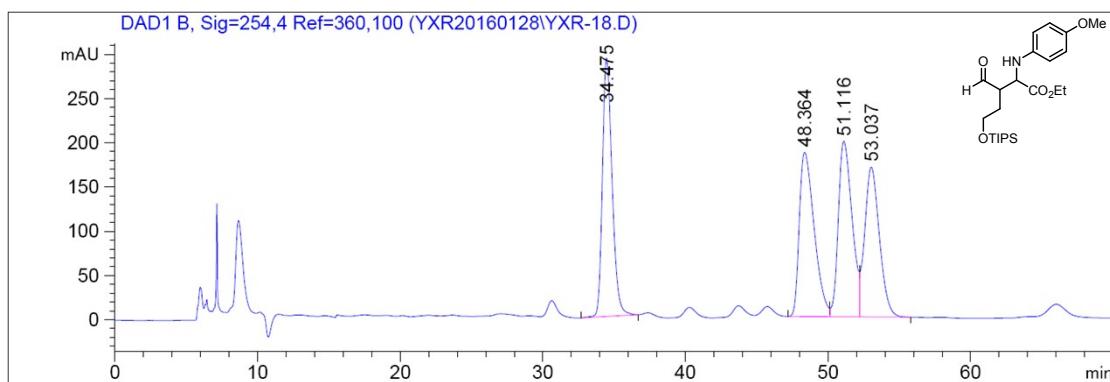
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	15.561	BB	0.2964	290.55994	15.10630	2.1108
2	17.421	BB	0.3375	922.51965	42.12090	6.7017
3	19.042	BB	0.3956	86.58823	3.14083	0.6290
4	20.574	BB	0.4171	1.24658e <sup>4</sup>	461.57147	90.5585



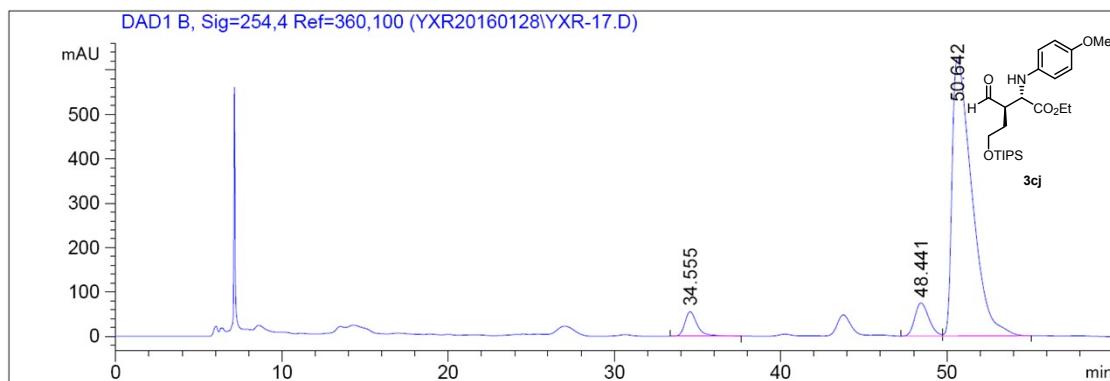
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	53.299	MM R	1.1543	4411.81494	63.70360	20.3183
2	60.891	MF R	1.7331	4499.79102	43.27388	20.7235
3	65.031	FM R	2.0427	6501.97510	53.04926	29.9444
4	101.103	MM R	3.1680	6299.92383	33.14325	29.0139



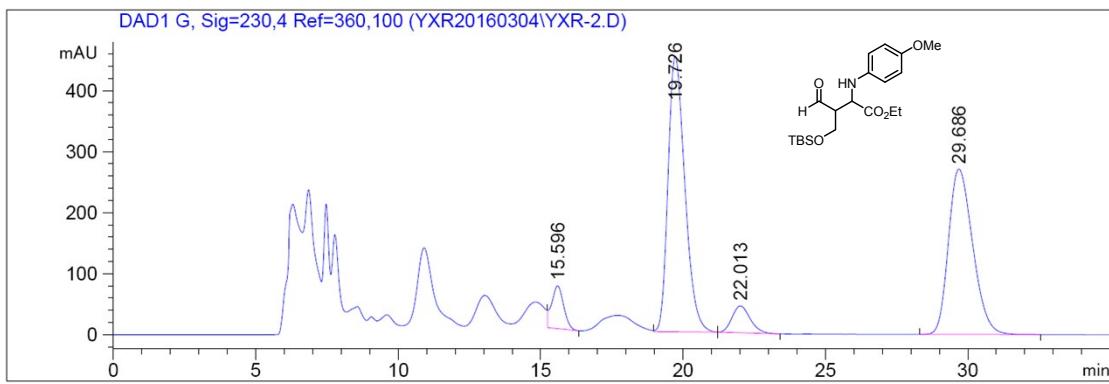
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	50.579	FM R	3.2235	3.96297e <sup>4</sup>	204.90135	89.1826
2	60.280	FM R	1.6065	1210.88635	12.56210	2.7250
3	63.787	MF R	1.8832	3596.01245	31.82486	8.0925



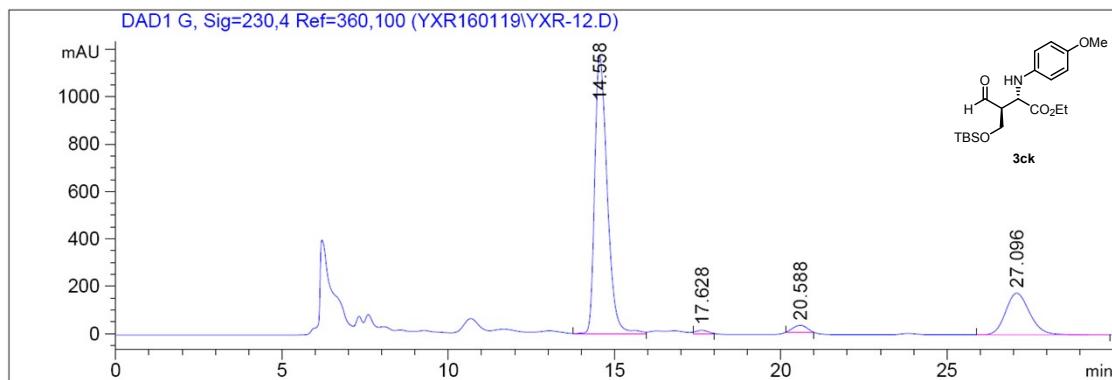
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	34.475	BB	0.7308	1.37842e <sup>4</sup>	291.96616	26.1607
2	48.364	BV	1.1185	1.34387e <sup>4</sup>	185.64822	25.5049
3	51.116	VV	1.0221	1.32657e <sup>4</sup>	198.39655	25.1766
4	53.037	VB	1.0966	1.22019e <sup>4</sup>	169.34970	23.1577



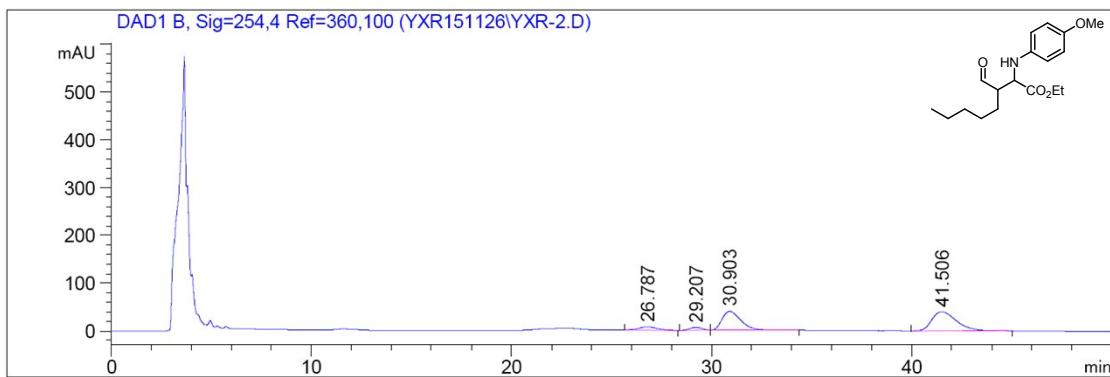
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	34.555	BB	0.7722	2790.84326	54.79355	4.7353
2	48.441	BV	0.9088	4377.05322	74.56470	7.4266
3	50.642	VB	1.2321	5.17694e <sup>4</sup>	627.73895	87.8381



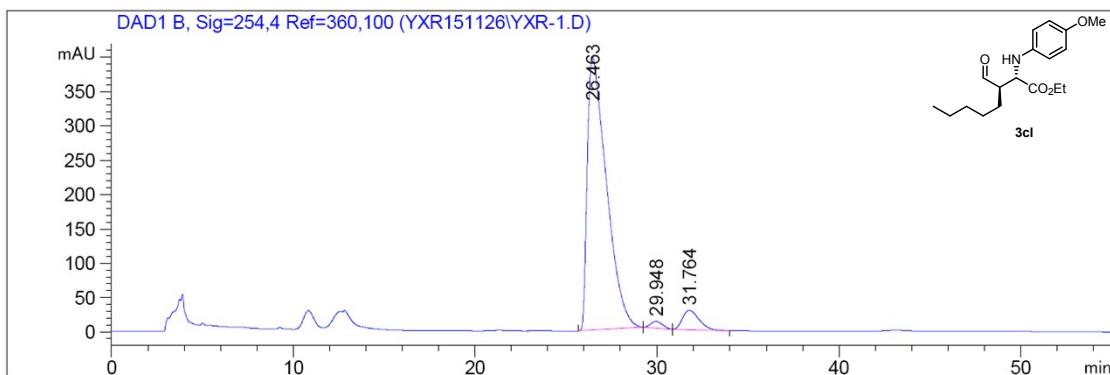
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	15.596	VB	0.4378	2055.46509	70.15833	5.3298
2	19.726	VB	0.6325	1.85352e <sup>4</sup>	451.89056	48.0617
3	22.013	BB	0.6898	1942.72620	43.94114	5.0375
4	29.686	BB	0.9158	1.60320e <sup>4</sup>	271.16983	41.5710



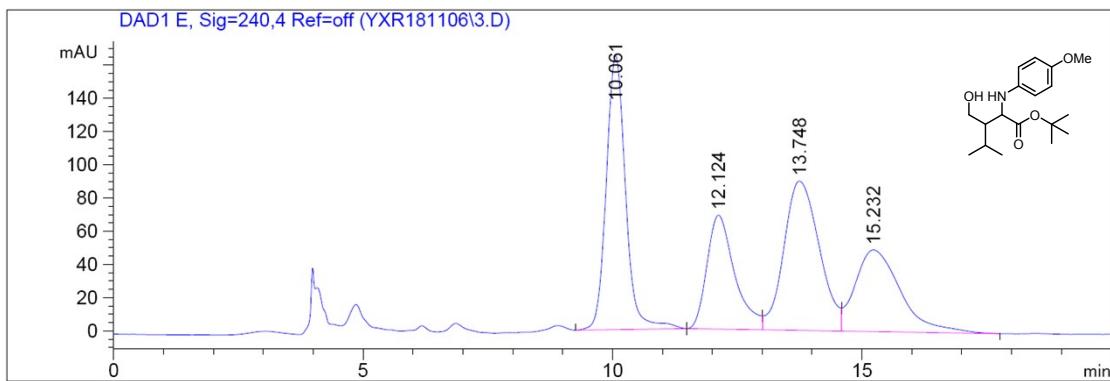
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	14.558	MF R	0.4362	3.06998e <sup>4</sup>	1173.04321	75.2464
2	17.628	FM R	0.4134	354.43451	14.29054	0.8687
3	20.588	MM R	0.4859	872.95905	29.94078	2.1397
4	27.096	BB	0.7783	8871.82520	175.92526	21.7452



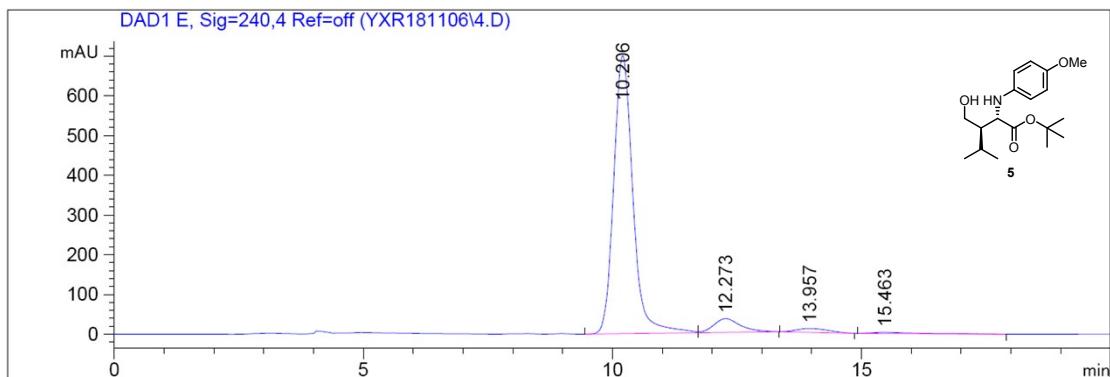
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	26.787	BB	0.7741	382.03259	6.45869	5.8247
2	29.207	BB	0.6279	238.90668	5.57558	3.6425
3	30.903	BB	0.9948	2549.32129	38.88758	38.8687
4	41.506	BB	1.2647	3388.54419	39.58606	51.6641



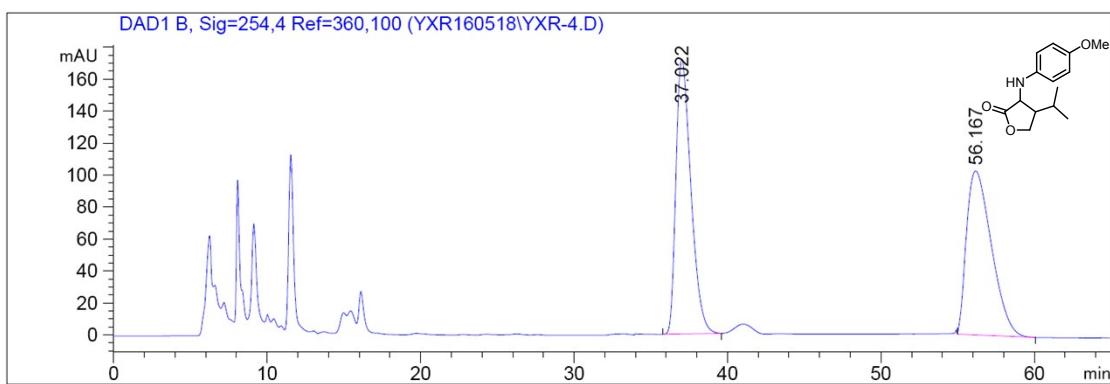
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	26.463	BB	1.0577	2.91513e <sup>4</sup>	397.44064	93.0004
2	29.948	BB	0.6991	429.46948	9.54183	1.3701
3	31.764	BB	0.9675	1764.58728	27.83780	5.6295



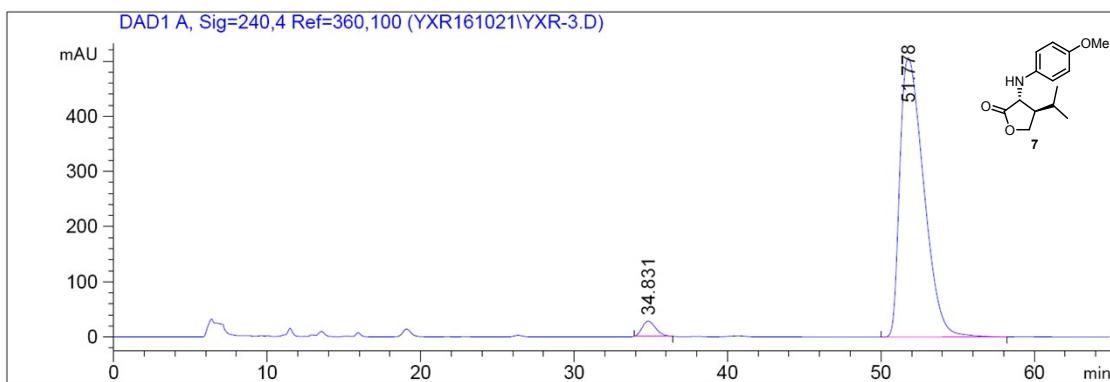
	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	10.061	BB	0.4172	4454.04932	164.87741	30.3695
2	12.124	BV	0.5837	2656.24951	68.60130	18.1114
3	13.748	VV	0.7789	4445.57373	89.90759	30.3117
4	15.232	VB	0.9873	3110.31396	49.21550	21.2074



	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	10.206	BV	0.4150	1.87742e <sup>4</sup>	699.89307	90.8499
2	12.273	VB	0.5567	1286.45703	34.68915	6.2253
3	13.957	BB	0.7069	426.62372	9.66650	2.0645
4	15.463	BBA	0.7450	177.78607	3.08218	0.8603



	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	37.022	BB	1.0490	1.16840e <sup>4</sup>	171.90237	50.2139
2	56.167	BB	1.6352	1.15845e <sup>4</sup>	102.60422	49.7861



	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	34.831	MM R	1.0239	1703.48706	27.72922	3.0233
2	51.778	BB	1.6958	5.46412e <sup>4</sup>	505.99783	96.9767