Chiral *N*,*N*′-Dioxide-$FeCl_3$ Complex Catalyzed Asymmetric Intramolecular Cannizzaro Reaction

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Supporting Information

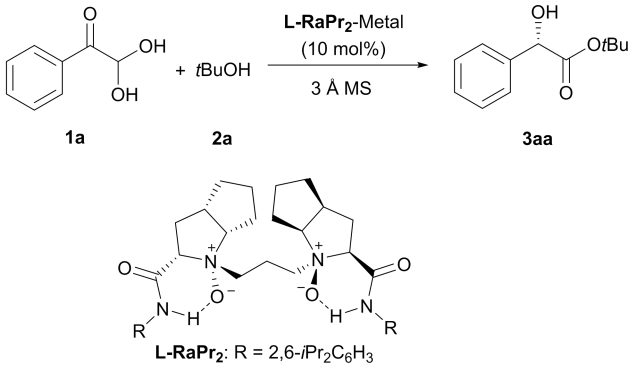
CONTENTS:

(A) General information

Reactions were carried out using commercial available reagents in oven-dried apparatus. CH_2Cl_2, *iso*-propanol, *tert*-butanol, cyclopentanol and cyclohexanol were dried and distilled from calcium hydride under nitrogen just before use. Methanol and ethanol were refluxed and distilled from magnesium powder under nitrogen just before use. Molecular sieves were dried at 500 °C for 4 h and restored in nitrogen before use. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel Chiralcel IA/IC/AD-H/AS-H/OD-H in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$= (c: g/100 mL, in solvent). ESI-HRMS spectra were recorded on a commercial apparatus and methanol or acetonitrile was used to dissolve the sample. The *N*,*N*′-dioxides were prepared according to the methods reported in the literature.[1]

(B) Optimization of the conditions

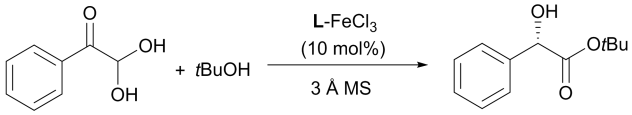
Screening of the metal salts



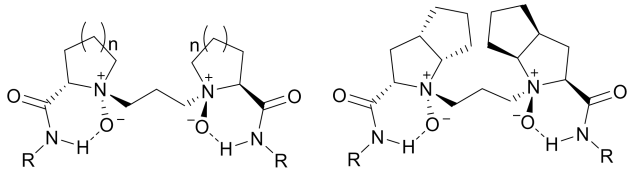
Entry[a]	Metal	Ligand	Yield[b] (%)	ee[c] (%)
1	$Sc(OTf)_3$	**L-RaPr$_2$**	41	87
2	$Y(OTf)_3$	**L-RaPr$_2$**	nr	-
3	$La(OTf)_3$	**L-RaPr$_2$**	nr	-
4	$Yb(OTf)_3$	**L-RaPr$_2$**	24	74
5	$Fe(OTf)_3$	**L-RaPr$_2$**	39	91
6	$Cu(OTf)_2$	**L-RaPr$_2$**	nr	-
7	$In(OTf)_3$	**L-RaPr$_2$**	43	84
8	$FeCl_2$	**L-RaPr$_2$**	66	92
9	$FeBr_2$	**L-RaPr$_2$**	58	91
10	$Fe(acac)_3$	**L-RaPr$_2$**	nr	-
11	$FeCl_3$	**L-RaPr$_2$**	38	93
12	$FeBr_3$	**L-RaPr$_2$**	58	90

[a]Unless otherwise noted, the reactions were performed with **L**-metal (1.2:1, 10 mol%), **1a** (0.25 mmol), 3 Å MS (100 mg) in *t*BuOH (1.0 mL) at 30 °C for 12 h without extrusion of air. [b] Yield of the isolated products according to the amount of **1a**. [c] Determined by HPLC analysis using a chiral stationary phase.

Screening of the ligands



1a **2a** **3aa**



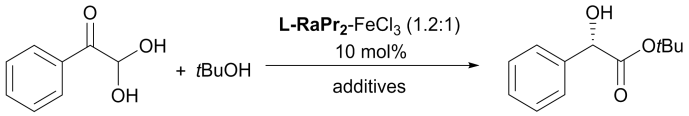
L-PrPh: R = Ph, n=1
L-PiPh: R = Ph, n=2
L-PrPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$, n=1
L-PiPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$, n=2

L-RaPh: R = Ph
L-RaPr$_2$: R = 2,6-*i*Pr$_2$C$_6$H$_3$

Entry[a]	Metal	Ligand	Yield[b] (%)	ee[c] (%)
1	$FeCl_3$	**L-RaPr$_2$**	38	93
2	$FeCl_3$	**L-PrPh**	nr	-
3	$FeCl_3$	**L-PiPh**	nr	-
4	$FeCl_3$	**L-RaPh**	nr	-
5	$FeCl_3$	**L-PrPr$_2$**	30	86
6	$FeCl_3$	**L-PiPr$_2$**	51	82

[a]Unless otherwise noted, the reactions were performed with **L**-$FeCl_3$ (1.2:1, 10 mol%), **1a** (0.25 mmol), 3 Å MS (100 mg) in *t*BuOH (1.0 mL) at 30 °C for 12 h without extrusion of air. [b] Yield of the isolated products according to the amount of **1a**. [c] Determined by HPLC analysis using a chiral stationary phase.

Screening of solvents and additives

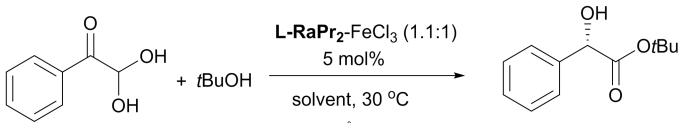


1a **2a** **3aa**

Entry[a]	Solvent volume, *t*BuOH/CH_2Cl_2 ratio	Additive	Yield[b] (%)	ee[c] (%)
1	1.0 mL, 1:0	3 Å MS, 100 mg	38	93
2	0.5 mL, 1:0	3 Å MS, 100 mg	44	95
3	0.4 mL, 1:0	3 Å MS, 100 mg	29	96
4	0.4 mL, 1:1	3 Å MS, 100 mg	65	87
5	0.4 mL, 5:1	3 Å MS, 100 mg	88	94
6	0.4 mL, 6:1	3 Å MS, 100 mg	94	93
7	0.4 mL, 7:1	3 Å MS, 100 mg	45	93
8	0.4 mL, 6:1	Na_2SO_4, 100 mg	nr	-
9	0.4 mL, 6:1	K_2CO_3, 100 mg	nr	-
10	0.4 mL, 6:1	4 Å MS, 100 mg	69	93
11	0.4 mL, 6:1	5 Å MS, 100 mg	74	92

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_2$**-$FeCl_3$ (1.2:1, 10 mol%), **1a** (0.25 mmol), in solvent at 30 °C for 12 h without extrusion of air. [b] Yield of the isolated products according to the amount of **1a**. [c] Determined by HPLC analysis using a chiral stationary phase.

Screening of the solvents in the optimized conditions

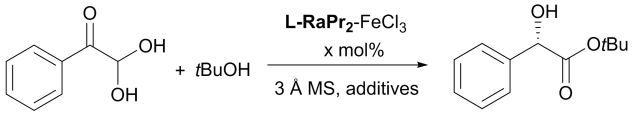


1a **2a** **3aa**

Entry[a]	Solvent	Yield(%)[b]	ee(%)[c]
1	CH_2Cl_2	93	93
2	THF	87	92
3	Et_2O	81	93
4	EtOAc	82	92
5	toluene	75	91
6	acetone	63	90

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_2$**-$FeCl_3$ (1.1:1, 5 mol%), **1a** (0.25 mmol), 3 Å MS (100 mg) in *t*BuOH (0.4 mL, *t*BuOH/solvent = 6:1) at 30 °C for 12 h. [b] Yield of the isolated products according to the amount of **1a**. [c] Determined by HPLC analysis using a chiral stationary phase.

Screening of the ligand-metal ratio and the catalyst loading

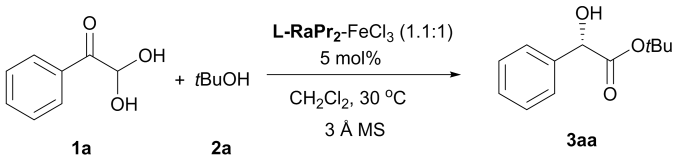


1a **2a** **3aa**

Entry[a]	L:metal	X (mol%)	Yield[b] (%)	ee[c] (%)
1	1.5:1	10	94	90
2	1.2:1	10	91	91
3	1.1:1	10	94	93
4	1:1	10	92	90
5	1:1.1	10	91	89
6	1:1.2	10	89	89
7	1:1.5	10	87	85
8	1.1:1	5	93	93
9[d]	1.1:1	3	93	93
10[d]	1.1:1	2	95	94
11[e]	1.1:1	1	95	93

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_2$**, $FeCl_3$, **1a** (0.25 mmol), 3 Å MS (100 mg) in *t*BuOH (0.4 mL, *t*BuOH/CH_2Cl_2 = 6:1) at 30 °C for 12 h without extrusion of air. [b] Yield of the isolated products according to the amount of **1a**. [c] Determined by HPLC analysis using a chiral stationary phase. [d] At 30 °C for 20 h. [e] At 30 °C for 51 h.

Screening of the gas environment

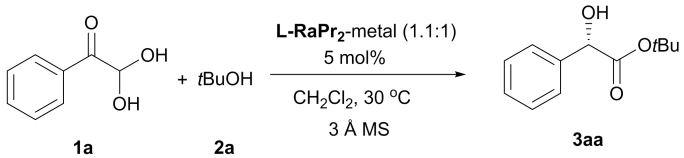


1a **2a** **3aa**

Entry[a]	Gas atmosphere	Yield(%)	ee(%)[a]
1	Air	91	92
2	N_2	81	91
3	H_2	88	91
4	O_2	92	93

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_2$**-$FeCl_3$ (1.1:1, 5 mol%),**1a** (0.25 mmol), 3 Å MS (100 mg) in *t*BuOH (0.4 mL, *t*BuOH/CH_2Cl_2 = 6:1) at 30 °C for 24 h. [b] Yield of the isolated products according to the amount of **1a**. [c] Determined by HPLC analysis using a chiral stationary phase. [d]

Screening of Fe(III) salts in the optimized conditions



1a **2a** **3aa**

Entry[a]	Metal	Yield(%)[b]	ee(%)[c]
1	$Fe(acac)_3$	trace	78
2	$FeCl_3$	93	93
3	$FeBr_3$	89	93
4	$Fe(OTf)_3$	90	93

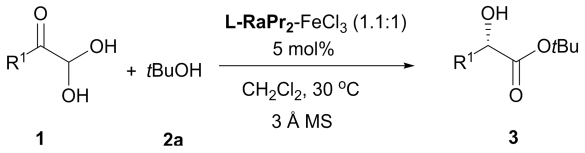
[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_2$**-metal (1.1:1, 5 mol%), **1a** (0.25 mmol), 3 Å MS (100 mg)

in *t*BuOH (0.4 mL, *t*BuOH/CH_2Cl_2 = 6:1) at 30 °C for 12 h. [b] Yield of the isolated products according to the amount of **1a**. [c] Determined by HPLC analysis using a chiral stationary phase.

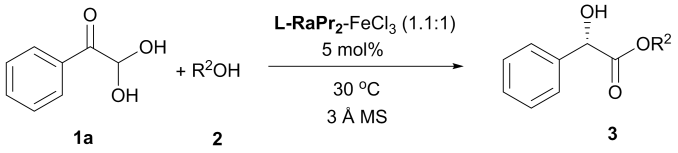
(C) Methods for the preparation of glyoxals

Glyoxal monohydrates **1a**–**1y** were prepared according to the methods reported in the literature.[2]

(D) Typical procedure for the asymmetric intramolecular Cannizzaro reaction

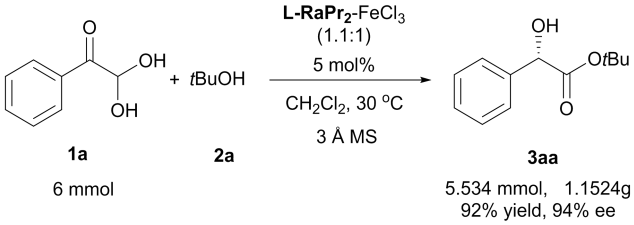


Procedure A (Standard): Chiral *N*,*N*′-dioxide **L-RaPr₂** (5.5 mol%) and $FeCl_3$ (5 mol%) were added in a dry reaction tube, then CH_2Cl_2 (0.5 mL) was added in air. The mixture was stirred at 30°C for 90 min, and then the solvent was removed under reduced pressure. Then 3 Å MS (100 mg), glyoxal monohydrate (**1**) (0.25 mmol) and solvent (0.4 mL, *t*BuOH/CH_2Cl_2 = 6:1) were added. The reaction was stirred vigorously at 30°C (monitored by TLC). The mixture was purified by column chromatography on silica gel to afford the desired product **3**. The yields of **3** were calculated according to the amount of **1**.



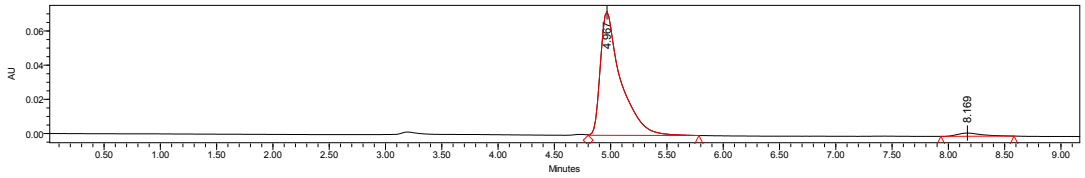
Procedure B: Phenylglyoxal monohydrate (**1a**) (0.25 mmol), chiral *N*,*N*′-dioxide **L-RaPr₂** (5.5 mol), 3 Å MS (100 mg), $FeCl_3$ (5 mol%) and alcohol (1.0 mL) were added in the reaction tube sequently. The reaction was stirred vigorously at 30°C in air (monitored by TLC).The mixture was purified by column chromatography on silica gel to afford the desired product **3**. The yields of **3** were calculated according to the amount of **1a**.

(E) Gram-scale experiment

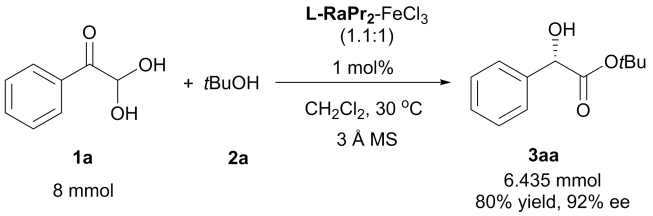


Chiral *N*,*N*′-dioxide **L-RaPr₂** (5.5 mol%) and $FeCl_3$ (5 mol%) were added in a dry reaction vessel, then CH_2Cl_2 (12 mL) was added. The mixture was stirred at 30°C for 90 min, and then the solvent was removed under reduced pressure. Then 3 Å MS (2.4 g), phenylglyoxal monohydrate (**1a**) and solvent (9.6 mL, *t*BuOH/CH_2Cl_2 = 6:1) were added in the reaction vessel. The reaction was stirred vigorously at 30°C in air (monitored by TLC). The mixture was purified by column chromatography on silica gel to afford the desired product **3aa**. The yields of **3aa** were calculated according to the amount of **1a**.

3aa: A white solid; 92% yield, 94% ee. HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 4.97 min, 8.17 min.



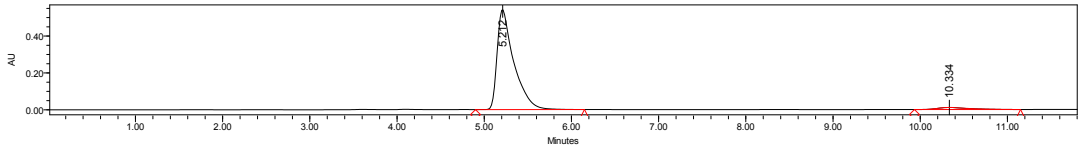
	Retention Time	%Area
1	4.967	96.95
2	8.169	3.05



Chiral *N*,*N*′-dioxide **L-RaPr₂** (1.1 mol%) and $FeCl_3$ (1 mol%) were added in a dry reaction vessel, then CH_2Cl_2 (5 mL) was added. The mixture was stirred at 30°C for 90 min, and then the solvent was removed under reduced pressure. Then 3 Å MS (2.4 g), phenylglyoxal monohydrate (**1a**) and solvent (12.8 mL, *t*BuOH/CH_2Cl_2 = 6:1) were added in the reaction vessel. The reaction was stirred vigorously at 30°C in air

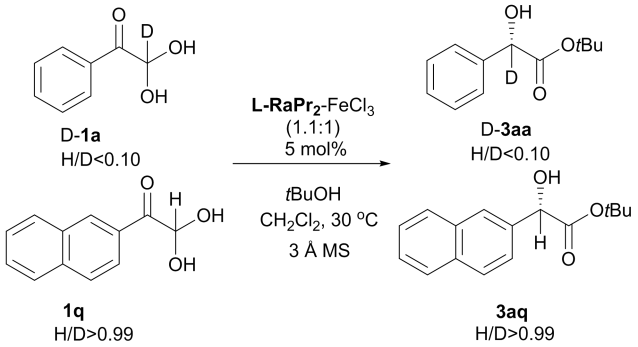
(monitored by TLC). The mixture was purified by column chromatography on silica gel to afford the desired product **3aa**. The yields of **3aa** were calculated according to the amount of **1a**. No SDE effect was found for the product.

3aa: A white solid; 80% yield, 92% ee. HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.21 min, 10.33 min.



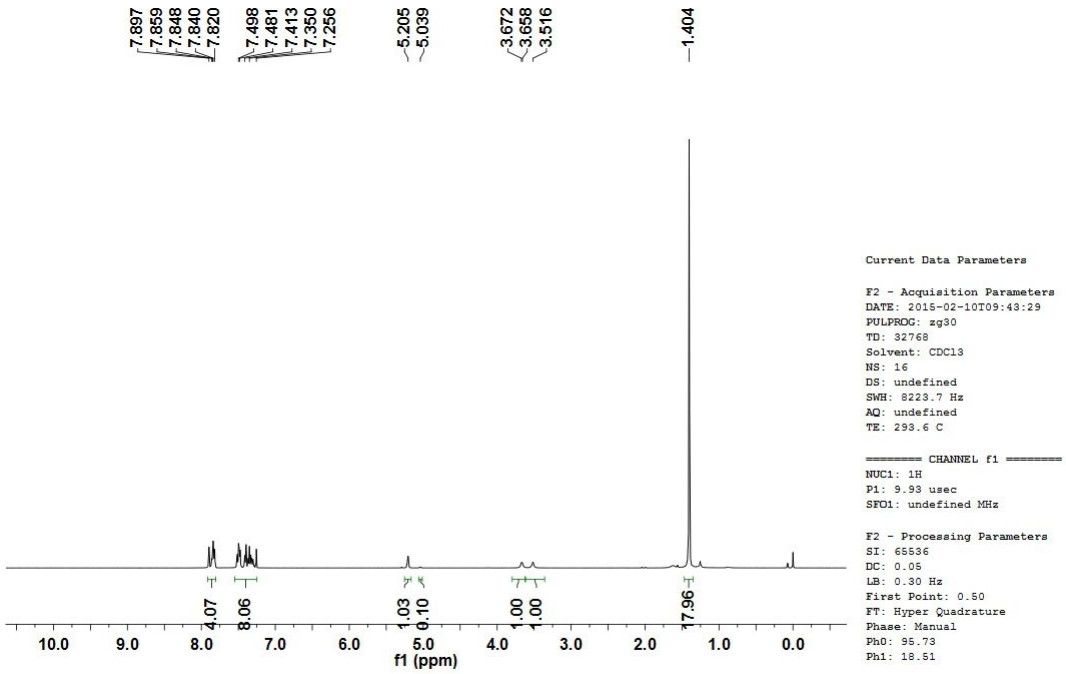
	Retention Time	%Area
1	5.212	96.22
2	10.334	3.78

(F) Deuterium-label experiments



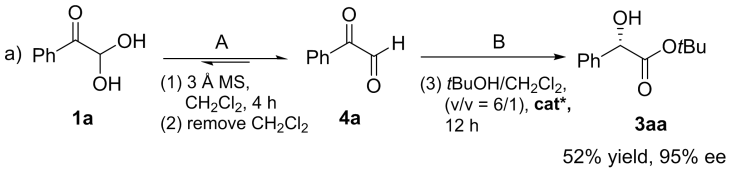
Crossover experiment: Deuterated phenylglyoxal monohydrate **1a-d** was prepared according to the methods reported in the literature.[3] Chiral *N*,*N*′-dioxide **L-RaPr$_2$** (5.5 mol% for glyxols D-**1a** and **1q**) and $FeCl_3$ (5 mol% for glyxols D-**1a** and **1q**) were added in a dry reaction tube, then CH_2Cl_2 (0.5 mL) was added. The mixture was stirred at 30°C for 90 min, and then the solvent was removed under reduced pressure. Then 3 Å MS (100 mg), deuterated phenylglyoxal monohydrate (D-**1a**) (0.025 mmol), 2-naphthylglyoxal monohydrate (**1q**) (0.025 mmol) and solvent (0.8 mL, *t*BuOH/CH_2Cl_2 = 6:1) were added in the reaction tube. The reaction was stirred vigorously at 30°C in air for 24 h (monitored by TLC).The mixture was purified by column chromatography on silica gel to afford the desired products.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.79 (m, 4H), 7.59 – 7.26 (m, 8H), 5.21 (s, 1H), 5.04 (s, 0.1H), 3.67 (d, *J* = 5.5 Hz, 1H), 3.52 (s, 1H), 1.40 (s, 18H).



(H) Control experiments

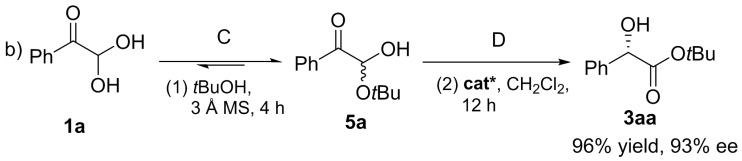
Preparation of **cat***: *N*,*N*′-dioxide **L-RaPr$_2$** (0.11 mmol), $FeCl_3$ (0.1 mmol) CH_2Cl_2 (4 mL) and were added in the reaction vessel. The mixture was stirred at at 30 ^oC for 90 min, and then the solvent was removed under reduced pressure to afford the desired catalyst **cat***. The catalyst was used right after preparation.



52% yield, 95% ee

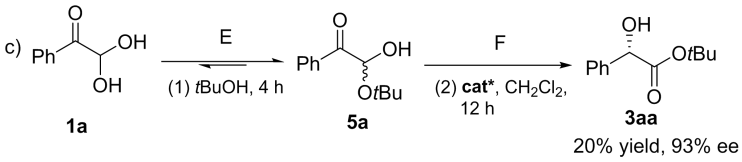
A: 3 Å MS (100 mg), phenylglyoxal monohydrate (**1a**, 0.25 mmol), and CH_2Cl_2 (0.5 mL) were added in the reaction tube. The mixture was stirred at 30 ^oC for 6 h. And then the solvent was removed under reduced pressure.

B: **Cat*** and solvent (0.4 mL, *t*BuOH/CH_2Cl_2 = 6:1) was added in the reaction mixture. The reaction was stirred vigorously at 30^oC for 12 h. The mixture was purified by column chromatography on silica gel to afford the desired product **3aa**. The yields of **3aa** were calculated according to the amount of **1a**.



C: 3 Å MS (100 mg), phenylglyoxal monohydrate (**1a**, 0.25 mmol), and *tert*-butanol (343 μL) were added in the reaction tube. The mixture was stirred at 30 °C for 6 h.

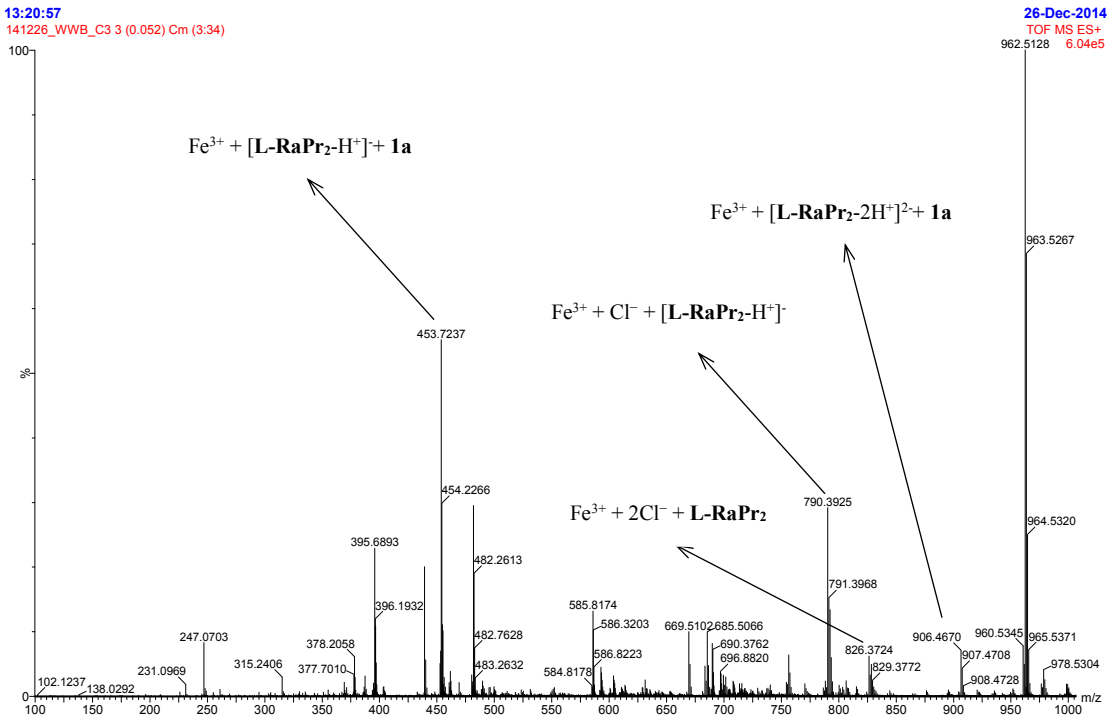
D: **Cat*** and CH_2Cl_2 (57 μL) was added in the reaction mixture. The reaction was stirred vigorously at 30°C for 12 h. The mixture was purified by column chromatography on silica gel to afford the desired product **3aa**. The yields of **3aa** were calculated according to the amount of **1a**.



E: Phenylglyoxal monohydrate (**1a**, 0.25 mmol), and *tert*-butanol (343 μL) were added in the reaction tube. The mixture was stirred at 30 °C for 6 h.

F: **Cat*** and CH_2Cl_2 (57 μL) was added in the reaction mixture. The reaction was stirred vigorously at 30°C for 12 h. The mixture was purified by column chromatography on silica gel to afford the desired product **3aa**. The yields of **3aa** were calculated according to the amount of **1a**.

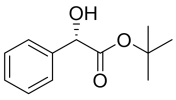
(I) **The electrospray ionization mass spectrometry (ESI-MS) analysis**



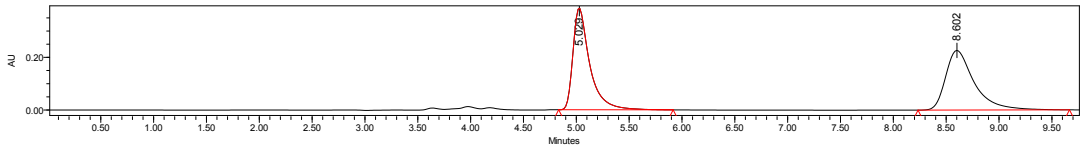
$FeCl_3$ + **L-RaPr$_2$** +**1a** (0.05:0.055:1) :
[Fe^{3+} + Cl^- + [**L-RaPr$_2$**-H^+]$^-$] Calcd for : 790.3882, found : 790.3925;
[Fe^{3+} + 2Cl^- + **L-RaPr$_2$**] Calcd for : 826.3649, found : 826.3724;
[Fe^{3+} + [**L-RaPr$_2$**-H^+]$^-$+ **1a**] Calcd for : 453.7331, found : 453.7237;
[Fe^{3+} + [**L-RaPr$_2$**-2H^+]$^{2-}$+ **1a**] Calcd for : 906.4588, found : 906.4670.

(J) Spectral characterization data and HPLC conditions for the products

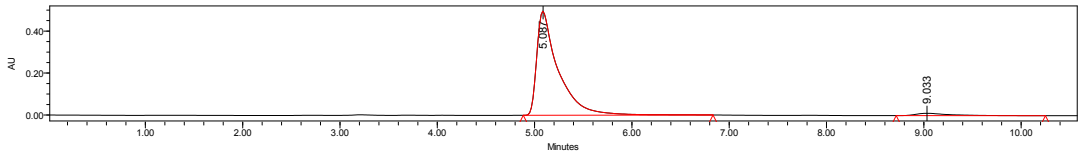
(*S*)-*tert*-butyl mandelate (3aa)



(**$C_{12}H_{16}O_3$**) a white solid; 93% yield, 93% ee. $[\alpha]_D^{14}$ = +102.82 (*c* = 0.390, in CH_2Cl_2), {Lit.[4] $[\alpha]_D^{25}$ = −102.40 (*c* = 0.584, in CH_2Cl_2), conf. (*R*)}. HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.09 min, 9.03 min;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 5H), 5.04 (d, *J* = 5.9 Hz, 1H), 3.51 (d, *J* = 6.0 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.92, 138.97, 128.41, 128.11, 126.38, 83.10, 73.01, 27.84. ESI-HRMS: calcd for **$C_{12}H_{16}NaO_3^+$** [M+Na^+] 231.0992, found 231.1000.

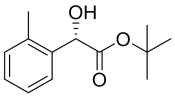


	Retention Time	%Area
1	5.029	49.99
2	8.602	50.01

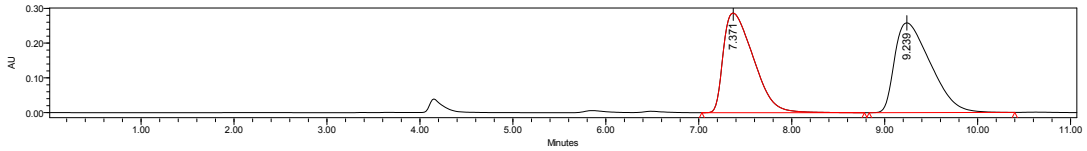


	Retention Time	%Area
1	5.087	96.56
2	9.033	3.44

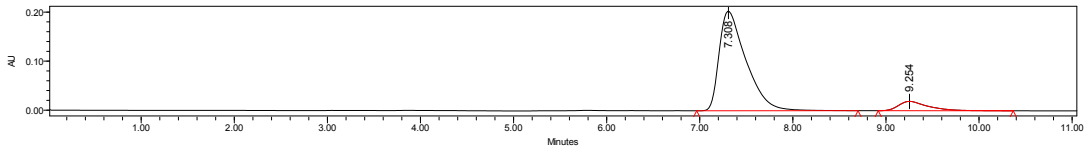
(*S*)-*tert*-butyl α-hydroxy-α-(2-methylphenyl)acetate (2b)



(**$C_{13}H_{18}O_3$**) a colorless oil; 97% yield, 81% ee. $[\alpha]_D^{15}$ = +103.38 (*c* = 1.064, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 7.31 min, 9.25 min. ^{1}H NMR (400 MHz, CDCl3) δ 7.33 – 7.26 (m, 1H), 7.18 (m, 3H), 5.25 (d, *J* = 5.3 Hz, 1H), 3.51 (d, *J* = 5.3 Hz, 1H), 2.43 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.39, 137.35, 136.23, 130.61, 128.05, 126.32, 126.11, 82.99, 70.37, 27.85, 19.31.^{13}C NMR (101 MHz, $CDCl_3$). ESI-HRMS: calcd for **$C_{13}H_{18}NaO_3^+$** [M+Na$^+$] 245.1148, found 245.1144.

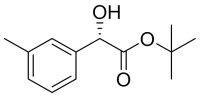


	Retention Time	%Area
1	7.371	48.24
2	9.239	51.76

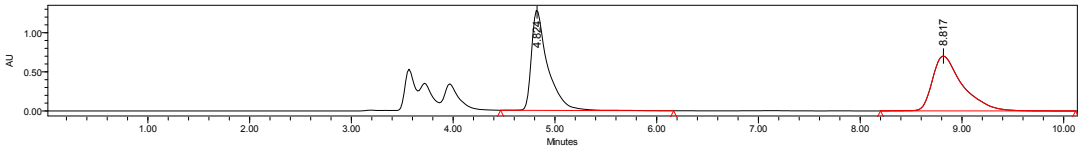


	Retention Time	%Area
1	7.308	90.70
2	9.254	9.30

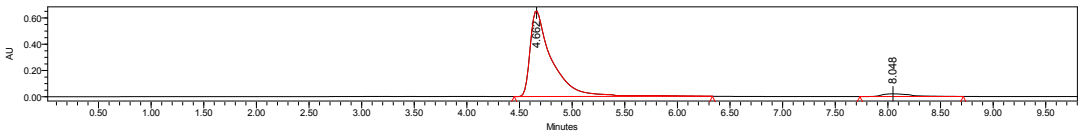
(*S*)-*tert*-butyl α-hydroxy-α-(3-methylphenyl)acetate (3ac)



(**$C_{13}H_{18}O_3$**) a colorless oil; 94% yield, 92% ee. $[\alpha]_D^{10}$ = +84.00 (*c* = 0.600, in CH_2Cl_2), HPLC DAICEL CHIRALCEL ODH,2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 4.66 min, 8.05 min;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.14 (m, 3H), 7.11 (m, 1H), 5.00 (d, *J* = 6.0 Hz, 1H), 3.51 (d, *J* = 6.1 Hz, 1H), 2.35 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.00, 138.89, 138.09, 128.87, 128.29, 127.03, 123.55, 82.99, 73.05, 27.86, 21.44. ESI-HRMS: calcd for **$C_{12}H_{16}NaO_3^+$** [M+Na$^+$] 245.1148, found 245.1154.

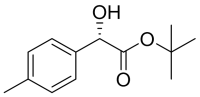


	Retention Time	%Area
1	4.824	49.64
2	8.817	50.36



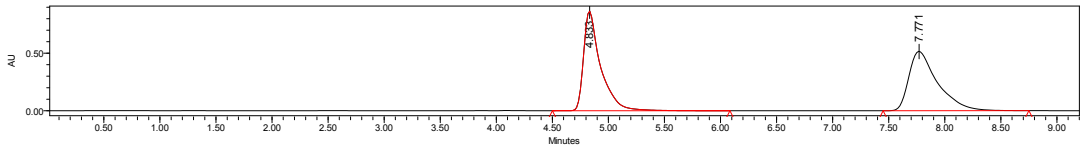
	Retention Time	%Area
1	4.662	95.95
2	8.048	4.05

(*S*)-*tert*-butyl α-hydroxy-α-(4-methylphenyl)acetate (3ad)

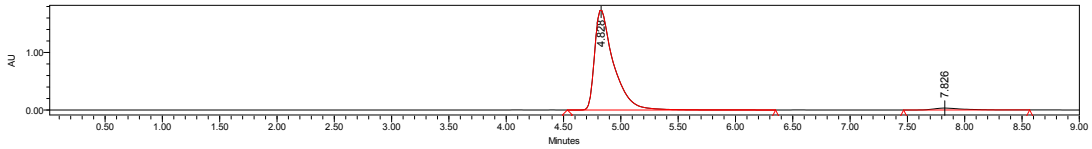


(**$C_{13}H_{18}O_3$**) a white solid; 94% yield, 94% ee. $[\alpha]_D^{13}$ = +95.51 (*c* = 0.468, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 4.83 min, 7.82 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.14 (m, 2H),4.99 (d, *J* = 6.1 Hz, 1H), 3.49 (d, *J* = 6.1 Hz, 1H), 2.34 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.07, 137.79, 136.08, 129.11,

126.31, 82.90, 72.89, 27.86, 21.16. ESI-HRMS: calcd for $\mathbf{C_{13}H_{18}NaO_3^+}$ [M+Na$^+$] 245.1148, found 245.1147.

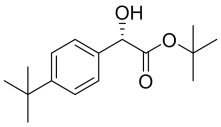


	Retention Time	%Area
1	4.833	49.91
2	7.771	50.09

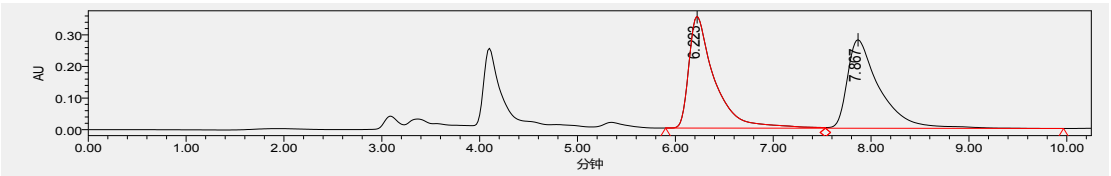


	Retention Time	%Area
1	4.828	97.20
2	7.826	2.80

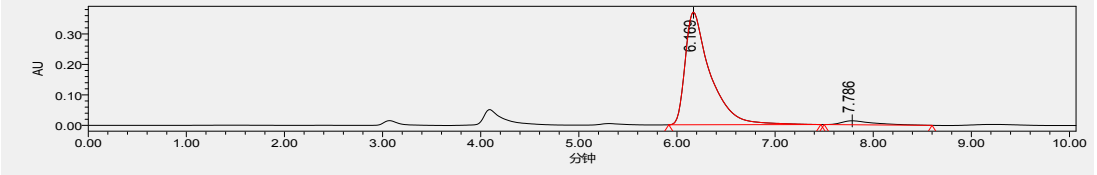
(*S*)-*tert*-butyl α-hydroxy-α-(4-(*tert*-butyl)phenyl)acetate (3ae)



($\mathbf{C_{16}H_{24}O_3}$) a white solid; 91% yield, 91% ee. $[\alpha]_D^{10}$ = +70.78 (*c* = 0.332, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 2/98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 6.17 min, 7.79 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.35 – 7.21 (m, 4H), 4.94 (s, 1H), 3.35 (s, 1H), 1.36 (s, 9H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.03, 151.04, 135.93, 126.06, 125.39, 82.98, 72.83, 34.56, 31.33, 27.92. ESI-HRMS: calcd for $\mathbf{C_{16}H_{24}NaO_3^+}$ [M+Na$^+$] 287.1618, found 287.1622.

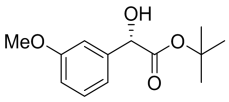


	Retention Time	%Area
1	6.223	50.16
2	7.867	49.84

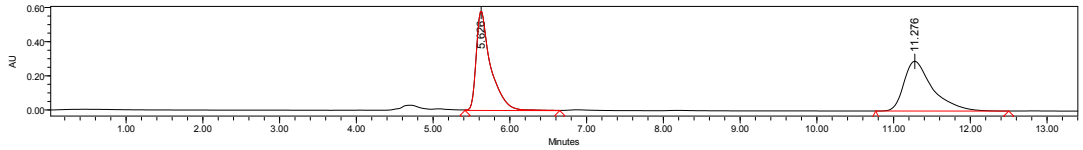


	Retention Time	%Area
1	6.169	95.60
2	7.786	4.40

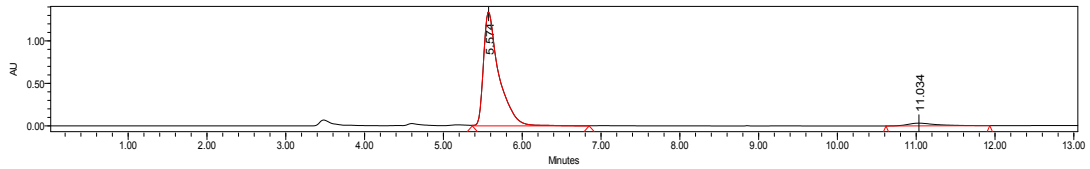
(*S*)-*tert*-butyl α-hydroxy-α-(3-methoxylphenyl)acetate (3af)



(**$C_{13}H_{18}O_4$**)a white solid; 97% yield, 92% ee. $[\alpha]_D^9$= +75.46 (*c* = 0.542, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 15/85, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.57 min, 11.03 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 1H), 6.98 (m, 2H), 6.84 (m, 1H), 5.01 (d, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.59 (d, *J* = 6.1 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.78, 159.65, 140.49, 129.41, 118.78, 113.91, 111.63, 83.09, 72.93, 55.22, 27.85. ESI-HRMS: calcd for **$C_{13}H_{18}NaO_4^+$** [M+Na$^+$] 261.1097, found 261.1102.

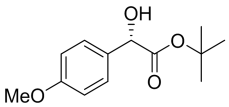


	Retention Time	%Area
1	5.626	50.28
2	11.276	49.72

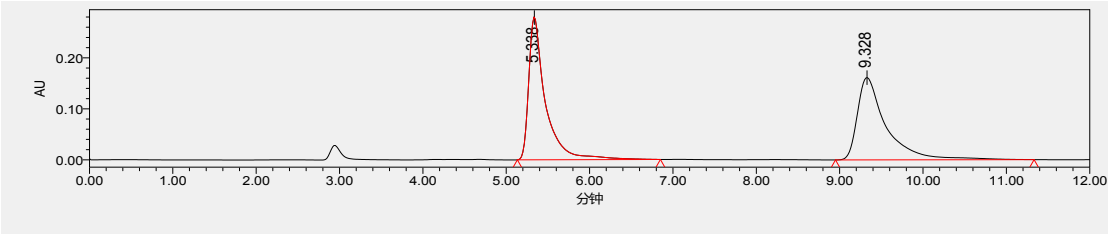


	Retention Time	%Area
1	5.574	95.76
2	11.034	4.24

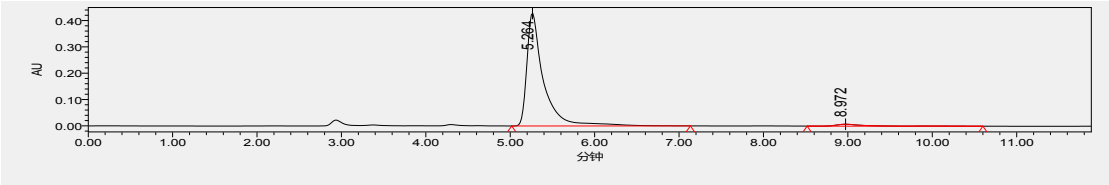
(*S*)-*tert*-butyl α-hydroxy-α-(4-methoxylphenyl)acetate (3ag)



(**$C_{13}H_{18}O_4$**) a white solid; 90% yield, 95% ee. $[\alpha]_D^{11}$ = +96.04 (*c* = 0.278, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ= 210 nm, retention time: 5.26 min, 8.97 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 6.99 – 6.80 (m, 2H), 4.98 (d, *J* = 5.9 Hz, 1H), 3.81 (s, 3H), 3.43 (d, *J* = 5.9 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.15, 159.45, 131.22, 127.65, 113.82, 82.93, 72.59, 55.26, 27.86. ESI-HRMS: calcd for **$C_{13}H_{18}NaO_4^+$** [M+Na$^+$] 261.1097, found 261.1098.

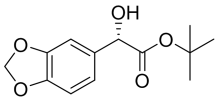


	Retention Time	%Area
1	5.338	50.28
2	9.328	49.72

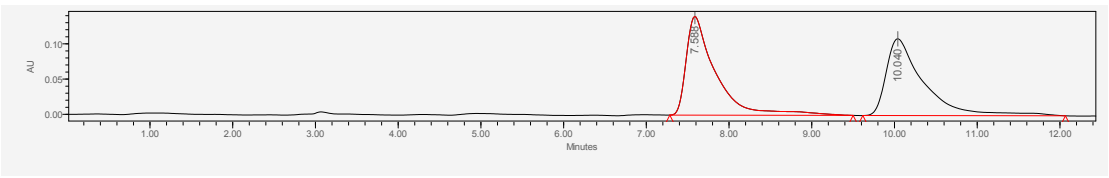


	Retention Time	%Area
1	5.264	97.38
2	8.972	2.62

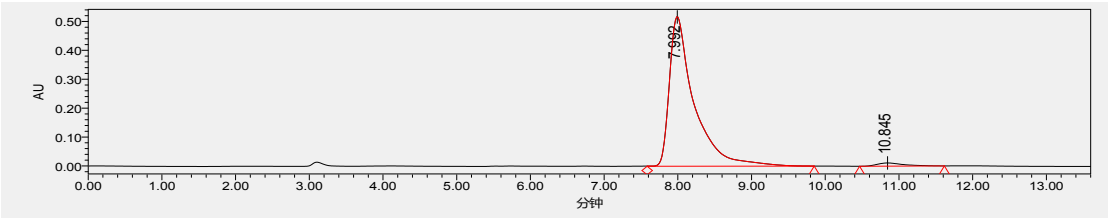
(*S*)-*tert*-butyl α-hydroxy-α-(3,4-methylenedioxylphenyl)acetate (3ah)



(**$C_{13}H_{16}O_5$**) a white solid; 96% yield, 95% ee. $[\alpha]_D^{12}$ = +81.75 (*c* = 0.400, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 7.99 min, 10.85 min. 1H NMR (400 MHz, CDCl3) δ 6.98 – 6.83 (m, 2H), 6.82– 6.70 (m, 1H), 5.95 (s, 2H), 4.93 (d, *J* = 5.8 Hz, 1H), 3.55 (d, *J* = 5.8 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.88, 147.72, 147.45, 132.94, 120.15, 108.15, 106.83, 101.11, 83.06, 72.77, 27.86. ESI-HRMS: calcd for **$C_{13}H_{16}NaO_5^+$** [M+Na^+] 275.0890, found 275.0893.

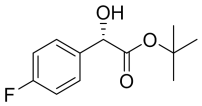


	Retention Time	%Area
1	7.588	50.21
2	10.040	49.79

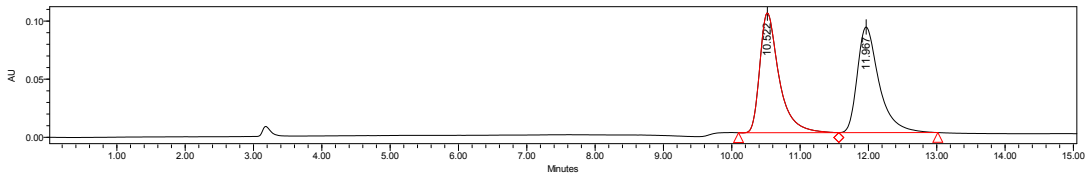


	Retention Time	%Area
1	7.992	97.80
2	10.845	2.20

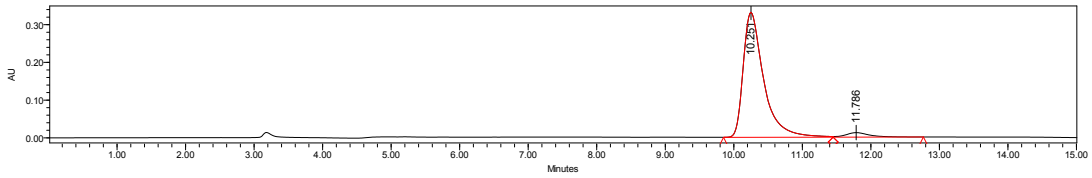
(*S*)-*tert*-butyl α-hydroxy-α-(4-flurophenyl)acetate (3ai)



(**$C_{12}H_{15}FO_3$**) a white solid; 90% yield, 92% ee. $[\alpha]_D^{12}$ = +102.70 (*c* = 0.370, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 1/99, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 10.25 min, 11.79 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.31 (m, 2H), 7.15 – 6.93 (m, 2H), 5.02 (d, *J* = 5.6 Hz, 1H), 3.53 (d, *J* = 5.6 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.73, 163.81, 161.37, 134.78, 128.12, 128.04, 115.42, 115.20, 83.33, 72.32, 27.83ESI-HRMS: calcd for **$C_{12}H_{15}FNaO_3^+$** [M+Na$^+$] 249.0897, found 249.0904.

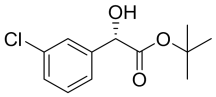


	Retention Time	%Area
1	10.522	50.05
2	11.967	49.95



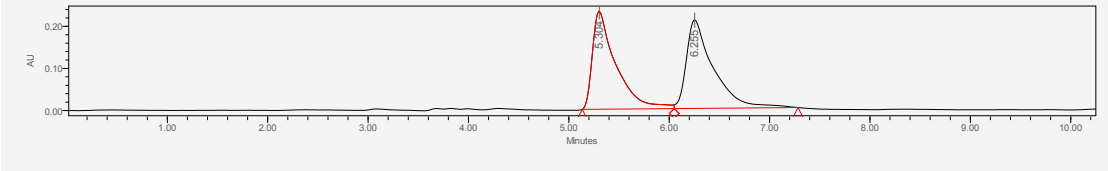
	Retention Time	%Area
1	10.251	96.06
2	11.786	3.94

(*S*)-*tert*-butyl α-hydroxy-α-(3-chlorophenyl)acetate (3aj)

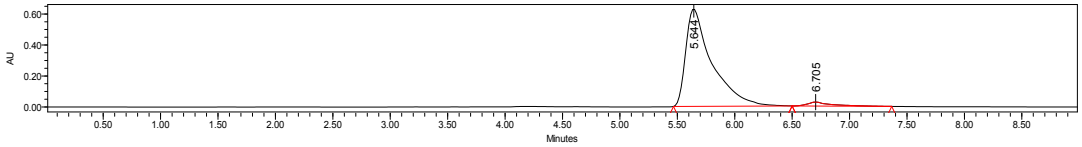


(**$C_{12}H_{15}ClO_3$**) a white solid; 95% yield, 93% ee. $[\alpha]_D^{11}$ = +89.86 (*c* = 0.276, in CH_2Cl_2), HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.64 min, 6.71 min. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.36 – 7.21 (m, 3H), 5.01 (d, *J* = 5.4 Hz, 1H), 3.62 (d, *J* = 5.6 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.28, 140.89, 134.31, 129.63, 128.25, 126.56, 124.54, 83.61, 72.33, 27.83.

ESI-HRMS: calcd for $\mathbf{C_{12}H_{15}Cl^{34.9689}NaO_3}^+$ [M+Na$^+$] 265.0602, found 265.0603; calcd for $\mathbf{C_{12}H_{15}Cl^{36.9659}NaO_3}^+$ [M+Na$^+$] 267.0572, found 267.0591.

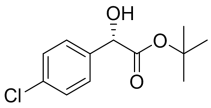


	Retention Time	%Area
1	5.304	49.04
2	6.255	50.96

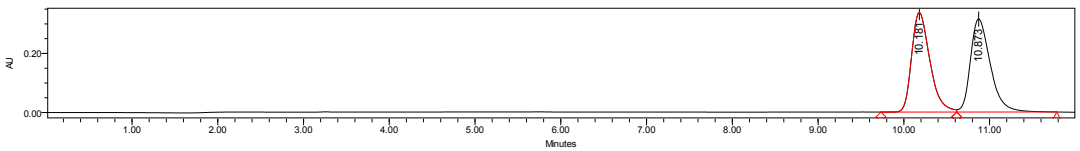


	Retention Time	%Area
1	5.644	96.40
2	6.705	3.60

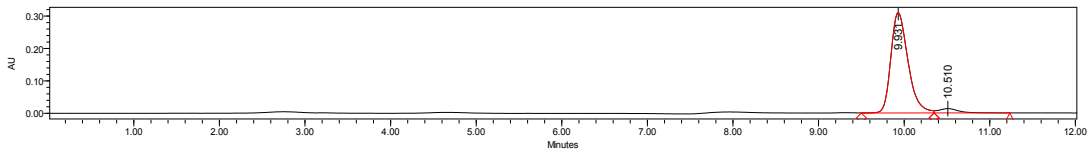
(*S*)-*tert*-butyl α-hydroxy-α-(4-chlorophenyl)acetate (3ak)



(**$C_{12}H_{15}ClO_3$**) a white solid; 95% yield, 91% ee. $[\alpha]_D^{11}$ = +95.69 (*c* = 0.394, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, 2-propanol/*n*-hexane = 1/99, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 9.93 min, 10.51 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 5.01 (d, *J* = 5.6 Hz, 1H), 3.53 (d, *J* = 5.6 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.48, 137.46, 133.93, 128.57, 127.74, 83.50, 72.32, 27.82. ESI-HRMS: calcd for $\mathbf{C_{12}H_{15}Cl^{34.9689}NaO_3}^+$ [M+Na$^+$] 265.0602, found 265.0606; calcd for $\mathbf{C_{12}H_{15}Cl^{36.9659}NaO_3}^+$ [M+Na$^+$] 267.0572, found 267.0588.

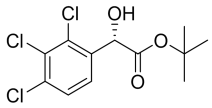


	Retention Time	%Area
1	10.181	49.49
2	10.873	50.51

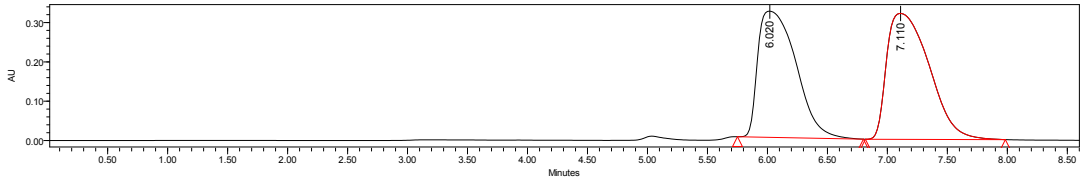


	Retention Time	%Area
1	9.931	95.32
2	10.510	4.68

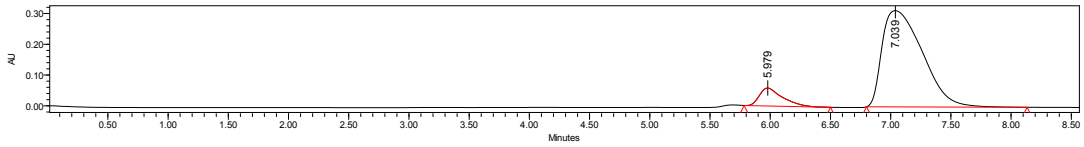
(*S*)-*tert*-butyl α-hydroxy-α-(2,3,4-trichlorophenyl)acetate (3al)



(**$C_{12}H_{13}Cl_3O_3$**) a white solid; 92% yield, 81% ee. $[\alpha]_D^{16}$ = +114.80 (*c* = 0.250, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.98 min, 7.04 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.45 – 7.34 (m, 1H), 7.31 – 7.24 (m, 1H), 5.43 (d, *J* = 4.6 Hz, 1H), 3.75 (d, *J* = 4.6 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.54, 137.45, 133.90, 133.58, 132.17, 128.37, 126.47, 83.99, 70.75, 27.79. ESI-HRMS: calcd for **$C_{12}H_{13}Cl_3^{34.9689}NaO_3^+$** [M+Na$^+$] 332.9822, found 332.9832; calcd for **$C_{12}H_{13}Cl_2^{34.9689}Cl^{36.9659}NaO_3^+$** [M+Na$^+$] 334.9792, found 334.9811.

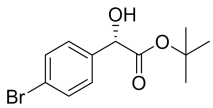


	Retention Time	%Area
1	6.020	47.41
2	7.110	52.59

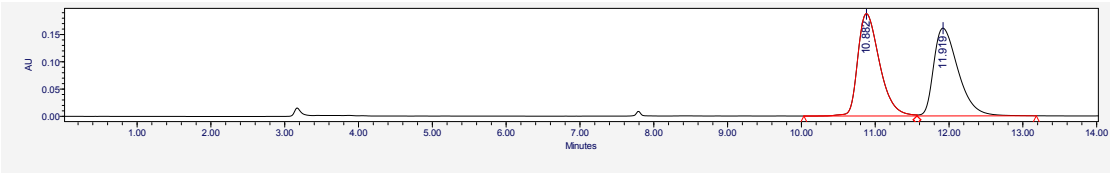


	Retention Time	%Area
1	5.979	9.68
2	7.039	90.32

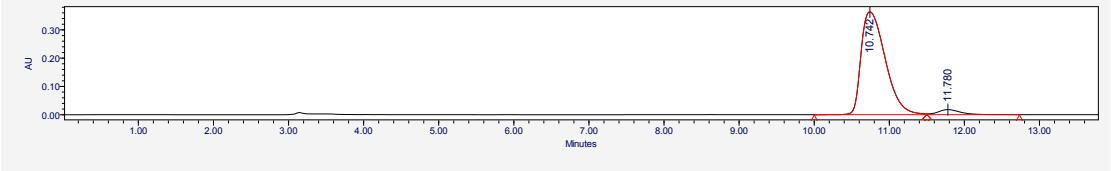
(*S*)-*tert*-butyl α-hydroxy-α-(4-bromophenyl)acetate (3am)



(**$C_{12}H_{15}BrO_3$**) a white solid; 93% yield, 91% ee. $[\alpha]_D^{10}$= +79.37 (*c* = 0.286, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ASH, 2-propanol/*n*-hexane = 1/99, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 10.74 min, 11.78 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.00 (d, *J* = 3.9 Hz, 1H), 3.55 (d, *J* = 4.7 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.41, 137.97, 131.52, 128.08, 122.11, 83.55, 72.35, 27.83. ESI-HRMS: calcd for **$C_{12}H_{15}Br^{78.9183}NaO_3^+$** [M+Na$^+$] 309.0097, found 309.0106; calcd for **$C_{12}H_{15}Br^{80.9163}NaO_3^+$** [M+Na$^+$] 311.0063, found 311.0086.

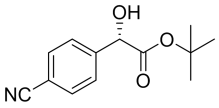


	Retention Time	%Area
1	10.882	50.96
2	11.919	49.04

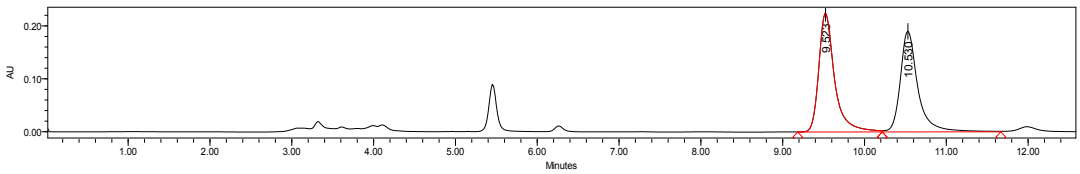


	Retention Time	%Area
1	10.742	95.60
2	11.780	4.40

(*S*)-*tert*-butyl α-hydroxy-α-(4-cyanophenyl)acetate (3an)

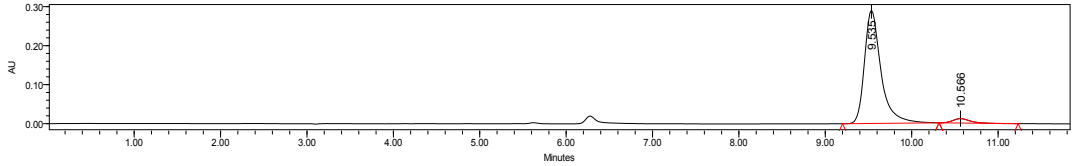


(**$C_{13}H_{15}NO_3$**) a white solid; 91% yield, 92% ee. $[\alpha]_D^{13}$ = +86.76 (*c* = 0.340, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 9.54 min, 10.57 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 – 7.43 (m, 4H), 5.11 (s, 1H), 3.76 (s, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.64, 144.05, 132.18, 127.09, 118.65, 111.95, 84.06, 72.38, 27.79. ESI-HRMS: calcd for **$C_{12}H_{15}NNaO_5^+$** [M+Na$^+$] 256.0944, found 256.0945.



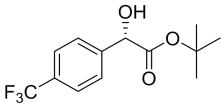
	Retention Time	%Area
1	9.523	51.56

2	10.530	49.44

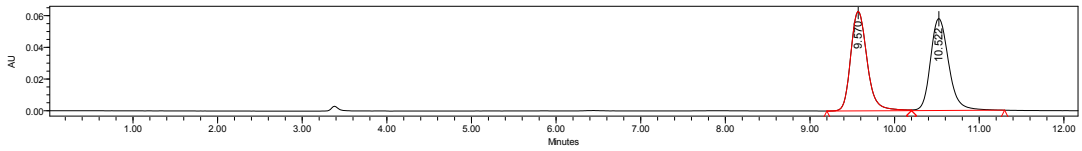


	Retention Time	%Area
1	9.535	96.10
2	10.566	3.90

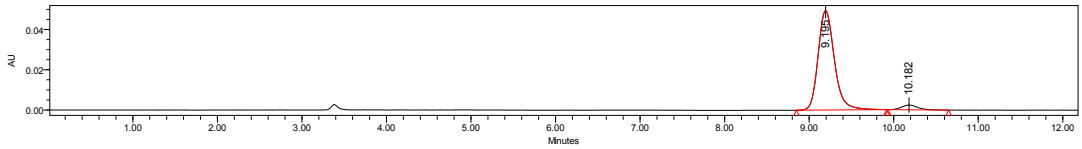
(*S*)-*tert*-butyl α-hydroxy-α-(4-(trifluoromethyl)phenyl)acetate (3ao)



(**$C_{13}H_{15}F_3O_3$**) a white solid; 99% yield, 91% ee. $[\alpha]_D^{12}$ = +77.90 (*c* = 0.335, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 1/99, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 9.20 min, 10.18 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 5.10 (d, *J* = 5.5 Hz, 1H), 3.63 (d, *J* = 5.5 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.11, 142.78, 130.79, 130.47, 130.14, 129.82, 125.38, 125.34, 125.30, 125.27, 122.72, 83.81, 72.44, 27.80. ESI-HRMS: calcd for **$C_{12}H_{15}NNaO_5^+$** [M+Na$^+$] 299.0866, found 276.0878.

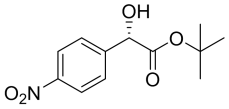


	Retention Time	%Area
1	9.570	49.36
2	10.522	50.64

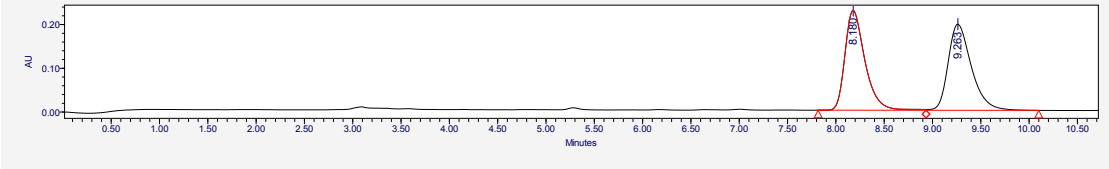


	Retention Time	%Area
1	9.195	95.51
2	10.182	4.49

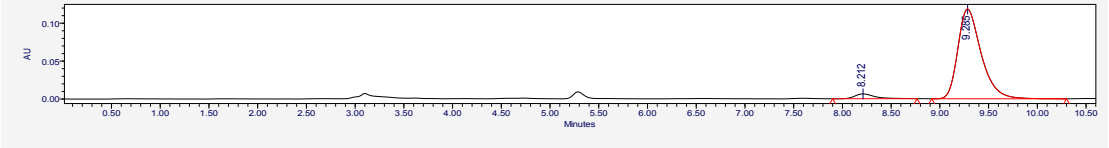
(*S*)-*tert*-butyl α-hydroxy-α-(4-nitrophenyl)acetate (3ap)



(**$C_{12}H_{15}NO_5$**) a white solid; 63% yield, 91% ee. $[\alpha]_D^{11}$ = +84.83 (*c* = 0.244, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ASH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 8.21 min, 9.29 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 5.16 (d, *J* = 4.6 Hz, 1H), 3.74 (d, *J* = 5.0 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.52, 147.77, 145.92, 127.25, 123.57, 84.28, 72.23, 27.79. ESI-HRMS: calcd for **$C_{12}H_{15}NNaO_5^+$** [M+Na^+] 276.0842, found 276.0847.

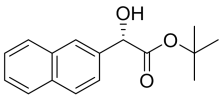


	Retention Time	%Area
1	8.180	49.91
2	9.263	50.09

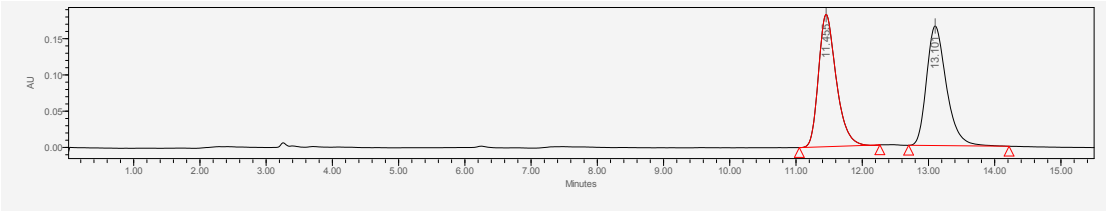


	Retention Time	%Area
1	8.212	4.39
2	9.285	95.61

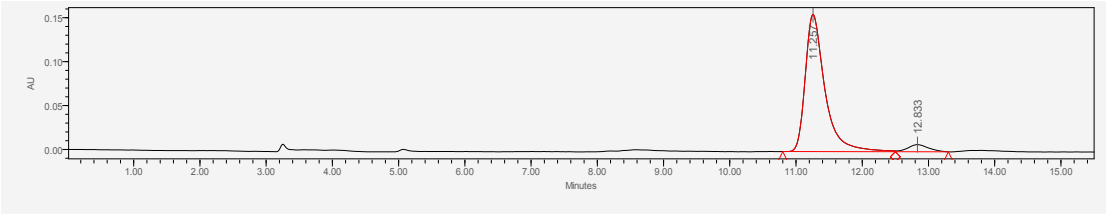
(*S*)-*tert*-butyl α-hydroxy-α-(naphthalen-2-yl)acetate (3aq)



(**$C_{16}H_{18}O_3$**) a white solid; 99% yield, 92% ee. $[\alpha]_D^{11}$ = +90.40 (*c* = 0.250, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ASH, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 11.26 min, 12.83 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.76 (m, 4H), 7.61 – 7.40 (m, 3H), 5.20 (d, *J* = 5.8 Hz, 1H), 3.67 (d, *J* = 5.8 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.90, 136.39, 133.24, 133.20, 128.20, 128.15, 127.69, 126.20, 126.15, 125.63, 124.22, 83.27, 73.17, 27.87. ESI-HRMS: calcd for**$C_{16}H_{18}NaO_3^+$** [M+Na^+] 281.1148, found 281.1160.

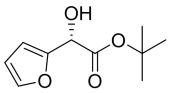


	Retention Time	%Area
1	11.455	49.73
2	13.101	50.27

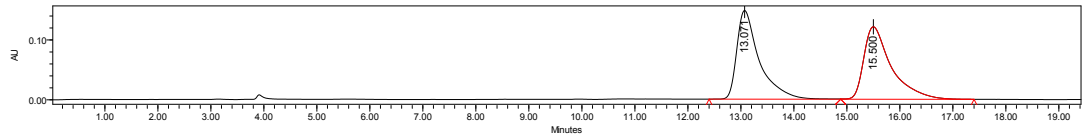


	Retention Time	%Area
1	11.257	94.81
2	12.833	5.19

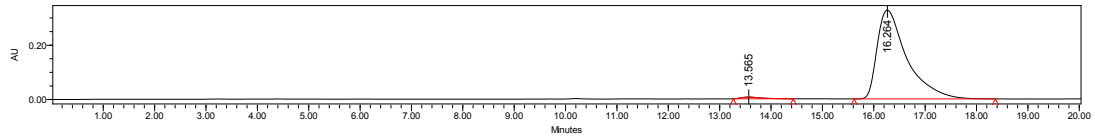
(*S*)-*tert*-butyl α-(fur-2-yl)-α-hydroxyacetate (3ar)



(**$C_{10}H_{14}O_4$**) a white solid; 49% yield, 97% ee. $[\alpha]_D^{13}$ = +54.51 (*c* = 0.288, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ASH, 2-propanol/n-hexane = 2/98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 13.57 min, 16.26 min. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.43 – 6.25 (m, 2H), 5.06 (d, *J* = 5.1 Hz, 1H), 3.44 (d, *J* = 5.9 Hz, 1H), 1.46 (s, 10H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.64, 151.58, 142.73, 110.41, 108.18, 83.51, 67.10, 27.87. ESI-HRMS: calcd for **$C_{10}H_{14}NaO_4^+$** [M+Na$^+$] 221.0784, found 221.0789.

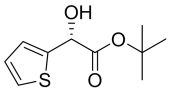


	Retention Time	%Area
1	13.071	50.06
2	15.500	49.94



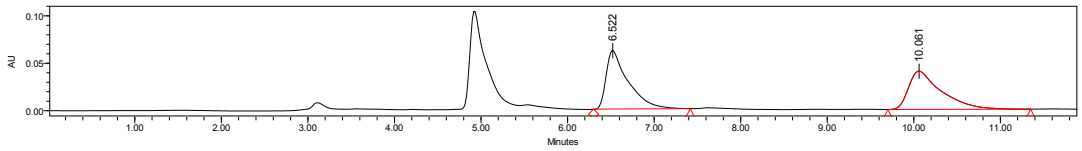
	Retention Time	%Area
1	13.565	1.23
2	16.264	98.77

(*S*)-*tert*-butyl α-(thiophen-2-yl)-α-hydroxyacetate (3as)

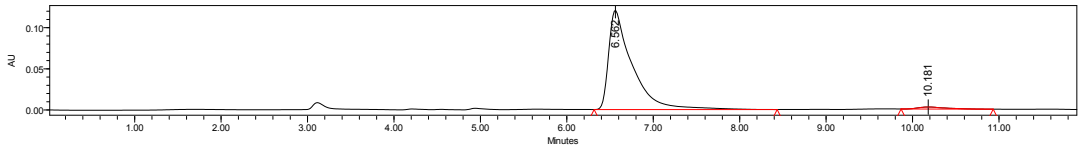


(**$C_{10}H_{14}O_3S$**) a white solid; 89% yield, 95% ee. $[\alpha]_D^{15}$ = +53.88 (*c* = 0.258, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 6.56 min, 10.18 min. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.28 – 7.23 (m, 1H), 7.13 – 7.05 (m,1H), 7.02 – 6.93 (m,1H), 5.28 (d, *J* = 6.4 Hz, 1H), 3.63 (d, *J* = 6.6 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.61, 142.15, 126.83, 125.31, 124.93, 83.67, 69.36, 27.87. ESI-HRMS: calcd for **$C_{10}H_{14}NaO_3S^+$** [M+Na^+] 237.0556, found 237.0570.

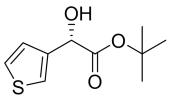


	Retention Time	%Area
1	6.522	50.58
2	10.061	49.42

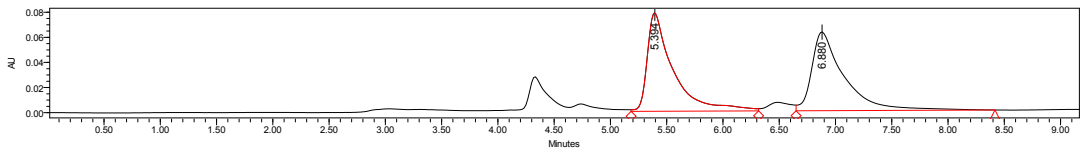


	Retention Time	%Area
1	6.562	97.60
2	10.181	2.40

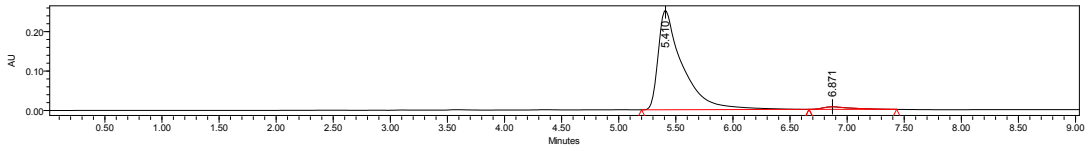
(*S*)-*tert*-butyl α-(thiophen-3-yl)-α-hydroxyacetate (3at)



(**$C_{10}H_{14}O_3S$**) a white solid; 92% yield, 94% ee. $[\alpha]_D^{16}$ = +65.26 (*c* = 0.262, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.41 min, 6.87 min. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 2H), 7.18 – 7.03 (m, 1H), 5.13 (d, *J* = 6.2 Hz, 1H), 3.50 (d, *J* = 6.3 Hz, 1H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.33, 139.91, 126.01, 125.78, 122.08, 83.23, 69.70, 27.92. ESI-HRMS: calcd for **$C_{10}H_{14}NaO_3S^+$** [M+Na^+] 237.0556, found 237.0565.

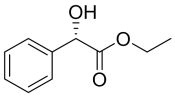


	Retention Time	%Area
1	5.394	50.17
2	6.880	49.83

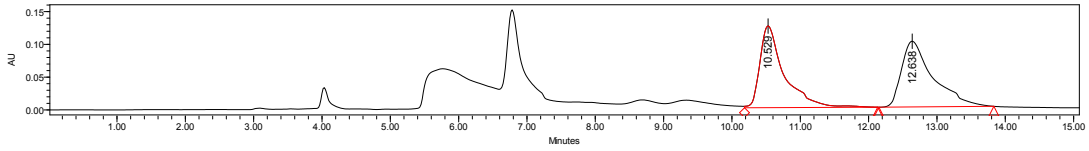


	Retention Time	%Area
1	5.410	97.07
2	6.871	2.93

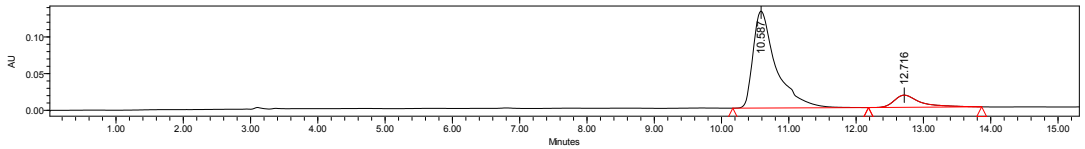
(*S*)-ethyl mandelate (3ba)



(**$C_{10}H_{12}O_3$**) a white solid; 71% yield, 75% ee. $[\alpha]_D^{19}$ = +87.66 (*c* = 0.608, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ASH,2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 10.70 min, 11.93 min;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.27 (m, 5H), 5.15 (s, 1H), 4.33 – 4.05 (m, 2H), 3.61 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.70, 138.45, 128.58, 128.41, 126.56, 72.91, 62.24, 14.04. ESI-HRMS: calcd for **$C_{11}H_{14}NaO_3^+$** [M+Na$^+$] 203.0679, found 203.0680.

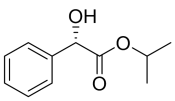


	Retention Time	%Area
1	10.529	48.89
2	12.638	51.11

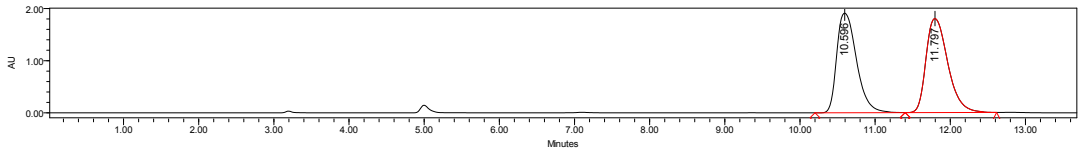


	Retention Time	%Area
1	10.587	87.46
2	12.716	12.54

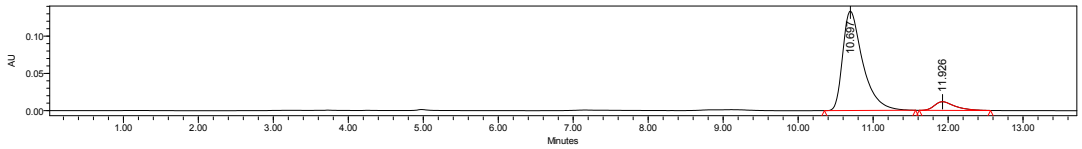
(*S*)-*iso*-propyl mandelate (3ca)



(**$C_{11}H_{14}O_3$**) a white solid; 66% yield, 81% ee. $[\alpha]_D^{11}$ = +90.77 (*c* = 0.206, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ADH,2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 10.70 min, 11.93 min;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.28 (m, 5H), 5.12 (s, 1H), 5.07 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.52 (s, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.11 (d, *J* = 6.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.27, 138.55, 128.51, 128.31, 126.44, 72.89, 70.21, 21.72, 21.41. ESI-HRMS: calcd for **$C_{11}H_{14}NaO_3^+$** [M+Na$^+$] 217.0835, found 217.0841.

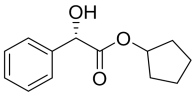


	Retention Time	%Area
1	10.596	49.03
2	11.797	50.97

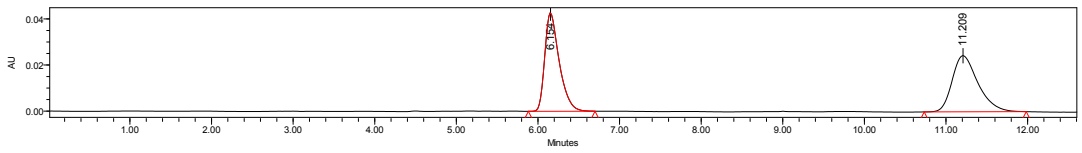


	Retention Time	%Area
1	10.697	91.80
2	11.926	8.20

(*S*)-cyclopentyl mandelate (3da)

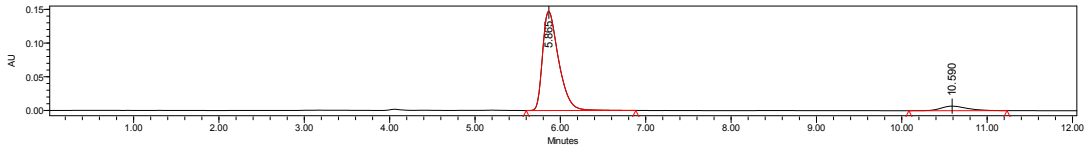


(**$C_{13}H_{16}O_3$**) a white solid; 88% yield, 86% ee. $[\alpha]_D^{20}$ = +59.83 (*c* = 0.468, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH,2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.87 min, 10.59 min;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.27 (m, 5H), 5.23 (dt, *J* = 8.3, 2.7 Hz, 1H), 5.12 (d, *J* = 5.3 Hz, 1H), 3.56 (d, *J* = 5.7 Hz, 1H), 1.91 – 1.63 (m, 4H), 1.62 – 1.41 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.48, 138.55, 128.48, 128.28, 126.37, 79.38, 72.83, 32.48, 23.54, 23.39. ESI-HRMS: calcd for **$C_{13}H_{17}O_3^+$** [M+H$^+$] 221.1172, found 221.1173.



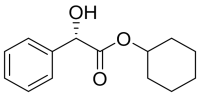
	Retention Time	%Area

1	6.154	49.48
2	11.209	50.52

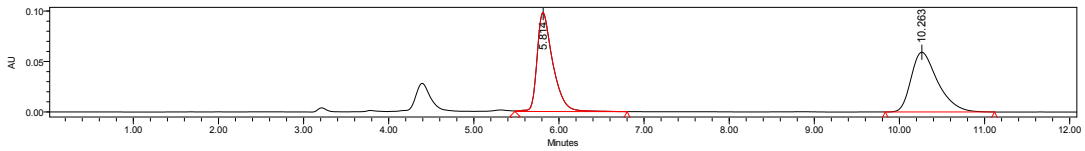


	Retention Time	%Area
1	5.865	93.07
2	10.590	6.93

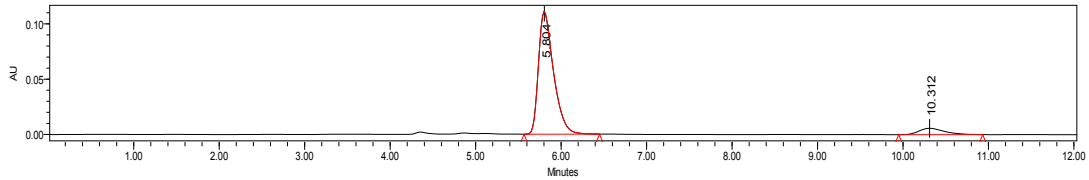
(*S*)-cyclohexyl mandelate (3ea)



(**$C_{14}H_{18}O_3$**) a white solid; 62% yield, 84% ee. $[\alpha]_D^{19}$ = +59.88 (*c* = 0.506, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH,2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.80 min, 10.31 min;1H NMR (400 MHz, CDCl3) δ 7.66 – 7.27 (m, 5H), 5.14 (d, J = 5.2 Hz, 1H), 4.83 (td, J = 8.3, 4.0 Hz, 1H), 3.59 (d, J = 5.6 Hz, 1H), 1.88 – 1.44 (m, 6H), 1.41 – 1.21 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.22, 138.70, 128.47, 128.27, 126.44, 74.74, 72.88, 31.33, 30.96, 25.19, 23.37, 23.16. ESI-HRMS: calcd for **$C_{14}H_{18}NaO_3^+$** [M+Na^+] 257.1148, found 257.1148.

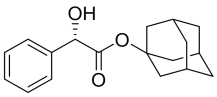


	Retention Time	%Area
1	5.814	49.35
2	10.263	50.65

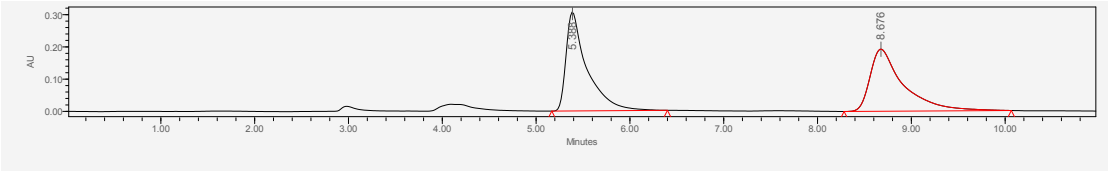


	Retention Time	%Area
1	5.804	91.93
2	10.312	8.07

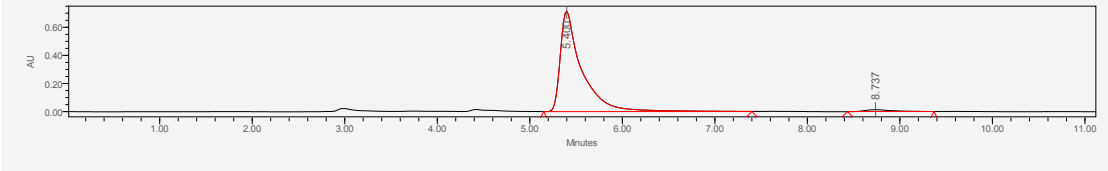
(*S*)-adamant-1-yl mandelate (3fa)



(**$C_{18}H_{22}O_3$**) a white solid; 52% yield, 96% ee. $[\alpha]_D^{19}$ = +70.50 (*c* = 0.834, in CH_2Cl_2). HPLC DAICEL CHIRALCEL ODH,2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.80 min, 10.31 min;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.0 Hz, 2H), 7.39 – 7.27 (m, 3H), 5.03 (d, *J* = 5.4 Hz, 1H), 3.57 (d, *J* = 5.8 Hz, 1H), 2.14 (s, 3H), 2.09 – 1.97 (m, 6H), 1.62 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.64, 139.11, 128.39, 128.08, 126.42, 83.11, 72.97, 41.08, 35.97, 30.82. ESI-HRMS: calcd for **$C_{18}H_{22}NaO_3^+$** [M+Na$^+$] 309.1461, found 309.1456.

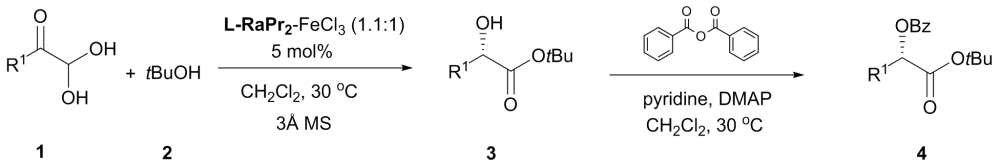


	Retention Time	%Area
1	5.388	49.95
2	8.676	50.05



	Retention Time	%Area
1	5.400	97.81
2	8.737	2.19

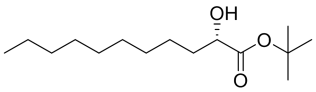
(K) Spectral characterization data and HPLC conditions for the alkyl products



3au-3ay (x mmol) obtained in asymmetric intramolecular Cannizzaro reaction, benzoic anhydride (1.1x mmol), pyridine (x mmol), DMAP (x mmol) and CH_2Cl_2 (1 mL) were added in the reaction tube sequently. The reaction was stirred vigorously at 30^{o}C (monitored by TLC).The mixture was purified by column chromatography on

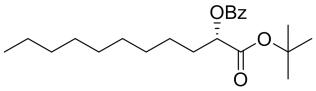
silica gel (petroleum ether/ethyl acetate) to afford the desired product **4au-4ay**. The ee of **3au-3ay** was determined according to the ee of **4au-4ay**.

(*S*)-*tert*-butyl 2-hydroxyundecanoate (3au)

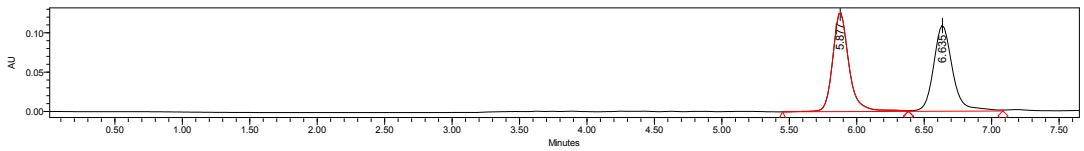


(**$C_{15}H_{20}O_3$**) a colorless oil; 90% yield. $[\alpha]_D^{15} = -1.74$ (*c* = 0.460, in CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 1H), 2.83 (s, 1H), 1.81 – 1.60 (m, 2H), 1.49 (s, 9H), 1.40 – 1.17 (m, 14H), 0.88 (t, *J* = 6.7 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.78, 82.25, 70.58, 34.49, 31.90, 29.51, 29.49, 29.39, 29.30, 28.03, 24.60, 22.68, 14.12. ESI-HRMS: calcd for **$C_{15}H_{20}NaO_3^+$** [M+Na$^+$] 281.2087, found 281.2083.

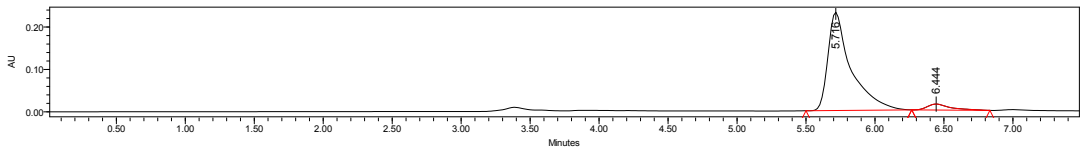
(*S*)-*tert*-butyl 2-benzoxyundecanoate (4au)



(**$C_{22}H_{34}O_4$**) a colorless oil; 89% ee. $[\alpha]_D^{15} = -7.92$ (*c* = 0.808, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 2/98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.72 min, 6.44 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.03 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.40 (m, 2H), 5.20 – 5.02 (m, 1H), 2.02 – 1.86 (m, 2H), 1.47 (s, 9H), 1.44 – 1.14 (m, 14H), 0.88 (t, *J* = 6.6 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.49, 166.17, 133.14, 129.80, 128.37, 81.98, 73.26, 31.89, 31.25, 29.49, 29.40, 29.29, 29.22, 28.00, 25.21, 22.68, 14.13. ESI-HRMS: calcd for **$C_{22}H_{34}NaO_4^+$** [M+Na$^+$] 385.2349, found 385.2346.

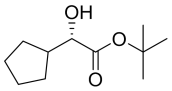


	Retention Time	%Area
1	5.877	49.83
2	6.635	50.17



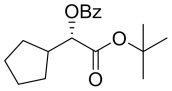
	Retention Time	%Area
1	5.716	94.26
2	6.444	5.74

(*S*)-*tert*-butyl 2-cyclopentyl-2-hydroxyacetate (3av)

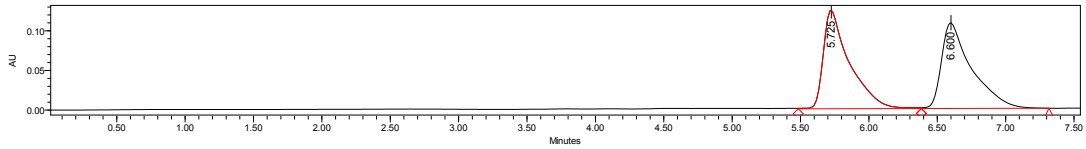


(**$C_{11}H_{20}O_3$**) a colorless oil; 89% yield. $[\alpha]_D^{16}$ = −11.38 (*c* = 0.290, in CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 1H), 2.71 (s, 1H), 2.11 (dt, *J* = 13.2, 7.9 Hz, 1H), 1.70 – 1.45 (m, 8H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.55, 82.26, 72.72, 43.53, 28.75, 28.05, 26.15, 25.87, 25.69. ESI-HRMS: calcd for **$C_{11}H_{20}NaO_3^+$** [M+Na^+] 223.1305, found 223.1305.

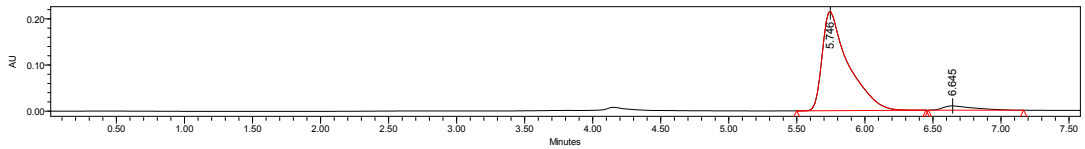
(*S*)-*tert*-butyl 2-benzoxy-2-cyclopentylacetate (4av)



(**$C_{18}H_{24}O_4$**) a colorless oil; 89% ee. $[\alpha]_D^{14}$ = −25.65 (*c* = 0.386, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.75 min, 6.65 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.90 (m, 2H), 7.55 – 7.45 (m, 1H), 7.44 – 7.32 (m, 2H), 4.93 (d, *J* = 6.0 Hz, 1H), 2.50 – 2.36 (m, 1H), 1.83 – 1.51 (m, 8H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.16, 166.28, 133.13, 129.88, 129.78, 128.39, 81.90, 76.05, 41.00, 28.77, 28.01, 27.98, 25.74, 25.58. ESI-HRMS: calcd for **$C_{18}H_{24}NaO_4^+$** [M+Na^+] 281.2087, found 281.2083.

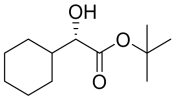


	Retention Time	%Area
1	5.725	50.04
2	6.600	49.96



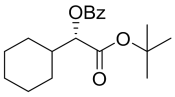
	Retention Time	%Area
1	5.746	95.12
2	6.645	4.88

(*S*)-*tert*-butyl 2-cyclohexyl-2-hydroxyacetate (3aw)

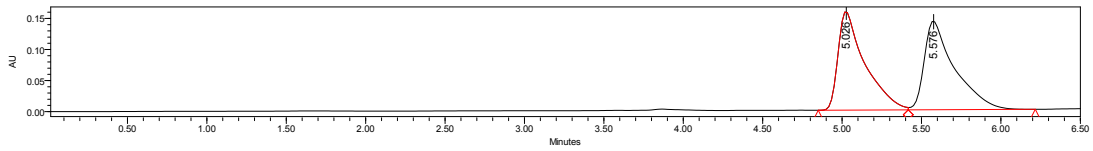


(**$C_{12}H_{22}O_3$**) a colorless oil 97% yield; $[\alpha]_D^{15}$ = +7.82 (*c* = 0.358, in CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 1H), 2.69 (s, 1H), 1.87 – 1.50 (m, 6H), 1.43 (s, 9H), 1.24 – 1.05 (m, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.20, 82.34, 74.79, 42.04, 29.12, 28.11, 26.34, 26.15, 26.12, 26.10. ESI-HRMS: calcd for **$C_{12}H_{22}NaO_3^+$** [M+Na^+] 237.1461, found 237.1463.

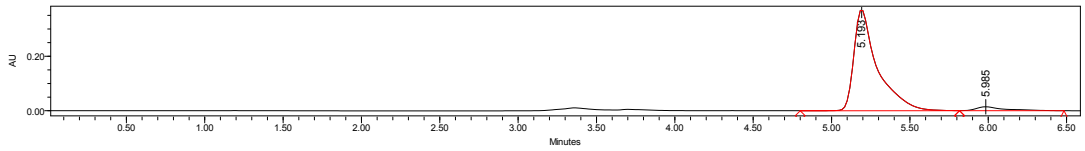
(*S*)-*tert*-butyl 2-benzoxy-2-cyclohexylacetate (4aw)



(**$C_{19}H_{26}O_4$**) a colorless oil; 91% ee. $[\alpha]_D^{15}$ = −6.89 (*c* = 0.638, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 7.66 min, 8.23 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.92 (m, 2H), 7.55 – 7.45 (m, 1H), 7.44 – 7.29 (m, 2H), 4.88 (d, *J* = 4.5 Hz, 1H), 1.84 – 1.52 (m, 6H), 1.40 (s, 9H), 1.30 – 1.08 (m, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.74, 166.24, 133.11, 129.95, 129.77, 128.38, 81.97, 39.78, 29.28, 28.06, 27.75, 26.11, 26.09, 26.06. ESI-HRMS: calcd for **$C_{19}H_{26}NaO_4^+$** [M+Na^+] 341.1723, found 341.1718.

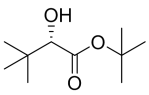


	Retention Time	%Area
1	5.026	49.56
2	5.576	50.44



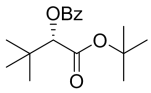
	Retention Time	%Area
1	5.193	95.46
2	5.985	4.54

(*S*)-*tert*-butyl 2-hydroxy-3,3-dimethylbutanoate (3ax)

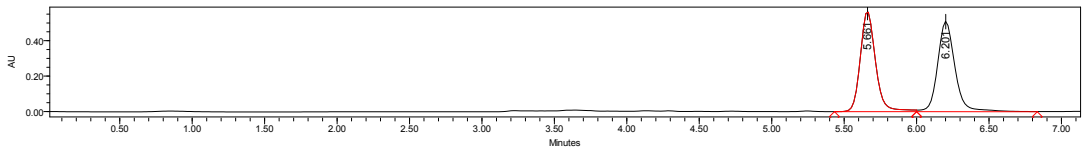


(**$C_{10}H_{20}O_3$**) a colorless oil; 99% yield. $[\alpha]_D^{18}$ =−1.02 (*c* = 0.590, in CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (d, *J* = 6.8 Hz, 1H), 2.87 (d, *J* = 7.1 Hz, 1H), 1.50 (s, 9H), 0.97 (s, 9H). 13C NMR (101 MHz, CDCl3) δ = 173.78, 82.56, 78.40, 35.36, 28.14, 25.97. ESI-HRMS: calcd for **$C_{10}H_{21}O_3^+$** [M+H^+] 189.1485, found 189.1481.

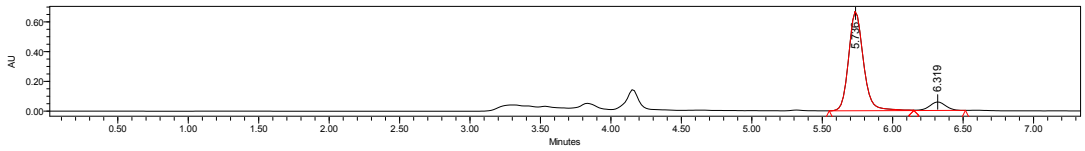
(*S*)-*tert*-butyl 2-benzoxy-3,3-dimethylbutanoate (4ax)



(**$C_{17}H_{24}O_4$**) a colorless oil; 81% ee. $[\alpha]_D^{18}$ = +30.02 (*c* = 0.856, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.44 min, 7.26 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.70 (s, 1H), 1.47 (s, 9H), 1.14 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.08, 166.20, 133.13, 129.96, 129.72, 128.41, 81.89, 80.82, 33.90, 28.04, 26.52. ESI-HRMS: calcd for **$C_{17}H_{24}NaO_4^+$** [M+Na$^+$] 315.1567, found 315.1572.

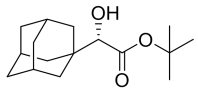


	Retention Time	%Area
1	5.440	50.37
2	7.265	49.63



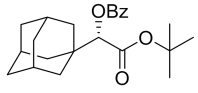
	Retention Time	%Area
1	5.435	85.02
2	7.260	14.98

(*S*)-*tert*-butyl 2-hydroxy-2-(adamantan-1-yl)acetate (3ay)

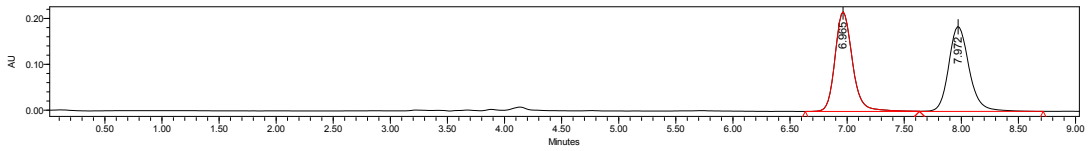


(**$C_{16}H_{26}O_3$**) a colorless oil; 87% yield. $[\alpha]_D^{15}$ = +33.08 (*c* = 0.266, in CH_2Cl_2).^{1}H NMR (400 MHz, $CDCl_3$) δ 3.52 (s, 1H), 2.74 (s, 1H), 1.99 (s, 3H), 2.06 – 1.93 (m, 4H), 1.67 – 1.60 (m, 8H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.25, 82.48, 78.80, 38.02, 37.17, 36.99, 36.56, 35.83, 28.30, 28.25, 27.35. ESI-HRMS: calcd for **$C_{16}H_{26}NaO_3^+$** [M+Na$^+$] 289.1774, found 289.1783.

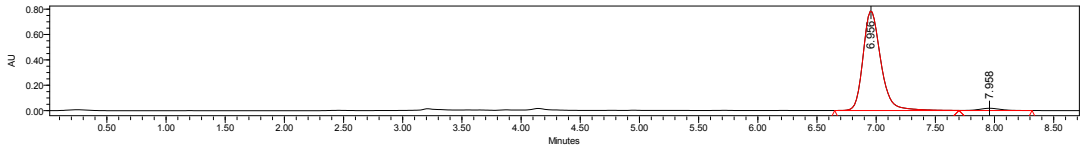
(*S*)-*tert*-butyl 2-benzoxy-2-(adamantan-1-yl)acetate (4ay)



(**$C_{23}H_{30}O_4$**) a colorless oil; 95% ee. $[\alpha]_D^{15}$ = +48.56 (*c* = 0.348, in CH_2Cl_2). HPLC DAICEL CHIRALCEL IC, 2-propanol/*n*-hexane = 2/98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 5.44 min, 7.26 min. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.00 (m, 2H), 7.62 – 7.52 (m, 1H), 7.52 – 7.40 (m, 2H),4.57 (s, 1H), 2.05 (s, 3H), 1.85 – 1.66 (m, 12H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.64, 166.32, 133.09, 130.07, 129.73, 128.40, 81.88, 81.24, 38.57, 36.87, 35.70, 28.20, 28.14. ESI-HRMS: calcd for **$C_{23}H_{30}NaO_4^+$** [M+Na^+] 393.2036, found 393.2038.



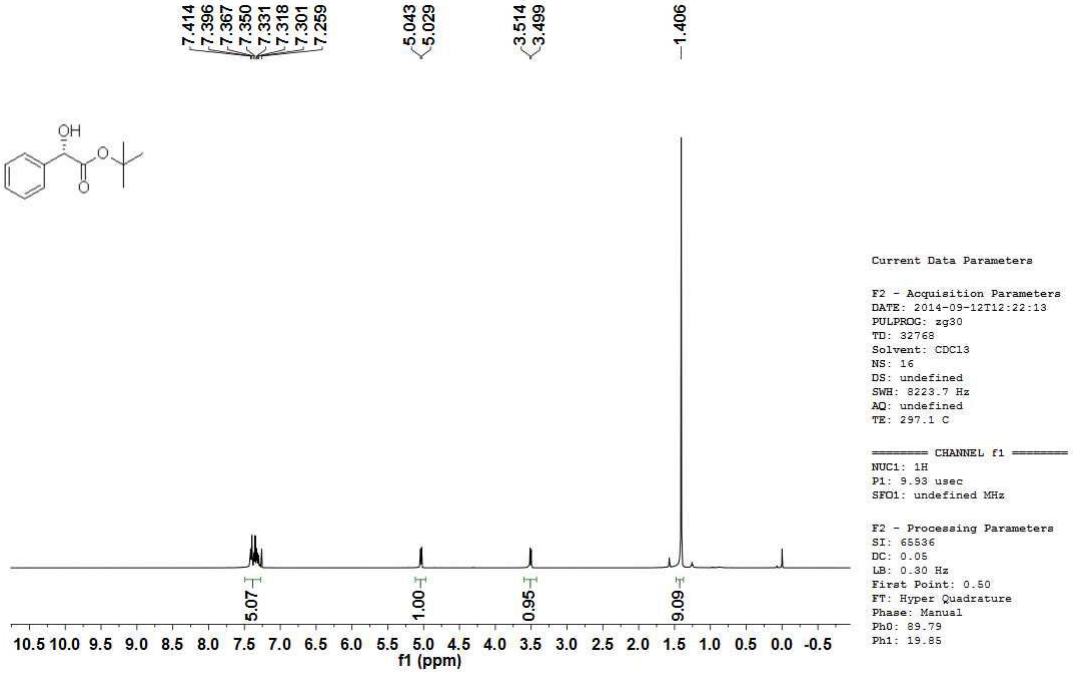
	Retention Time	%Area
1	6.965	49.96
2	7.972	50.04

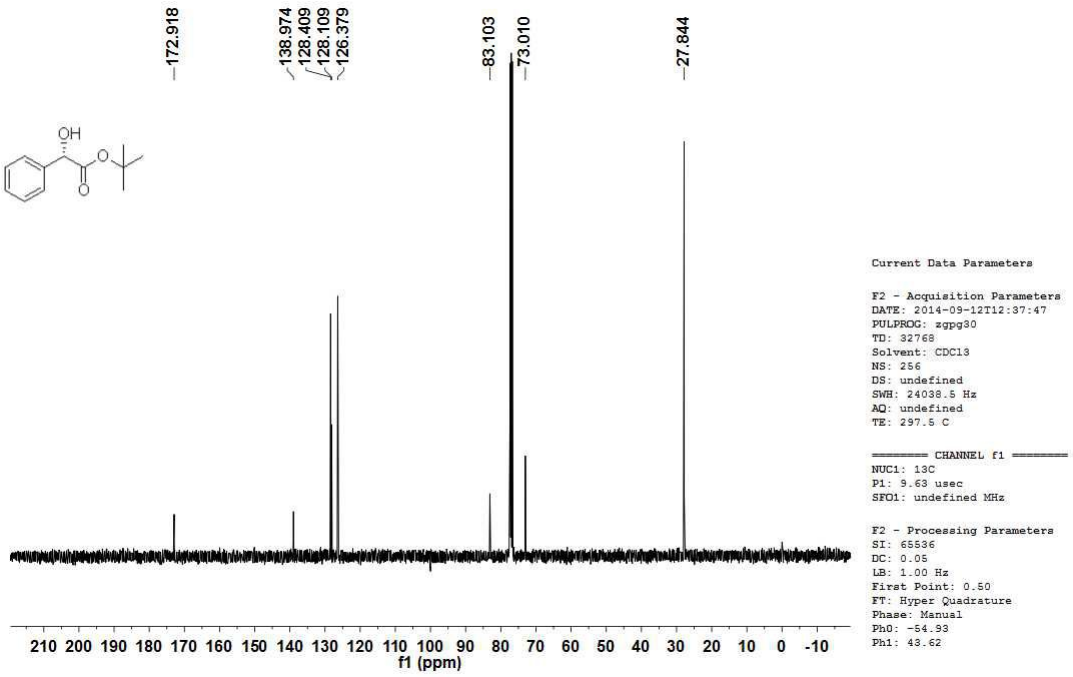


	Retention Time	%Area
1	5.435	97.37
2	7.260	2.63

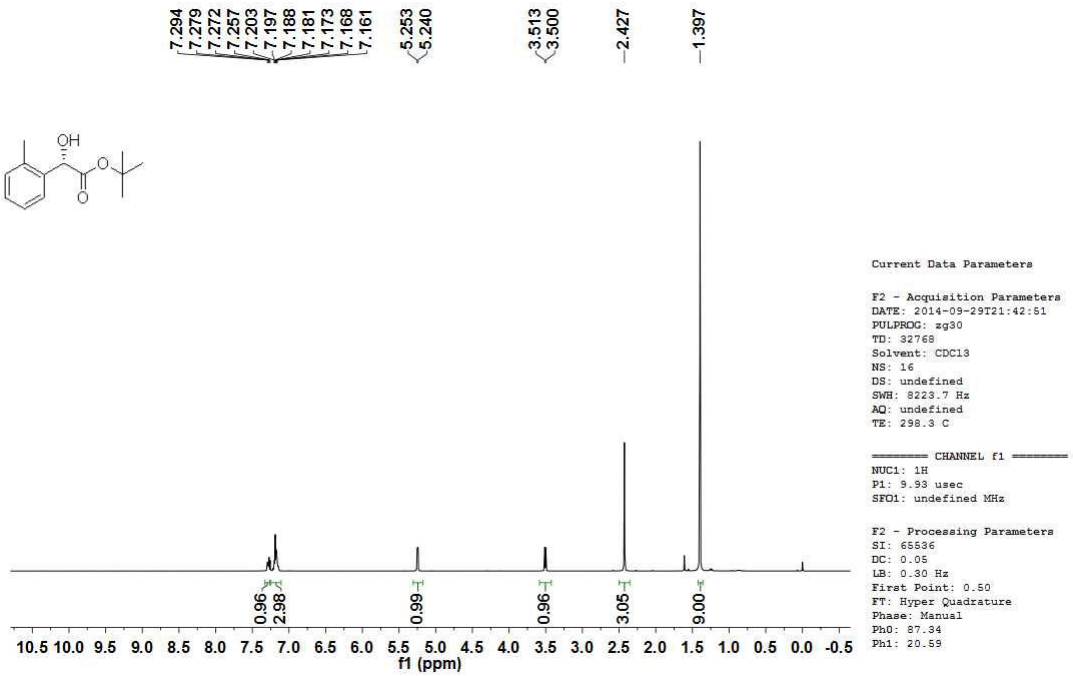
(L) Copies of NMR spectra for products

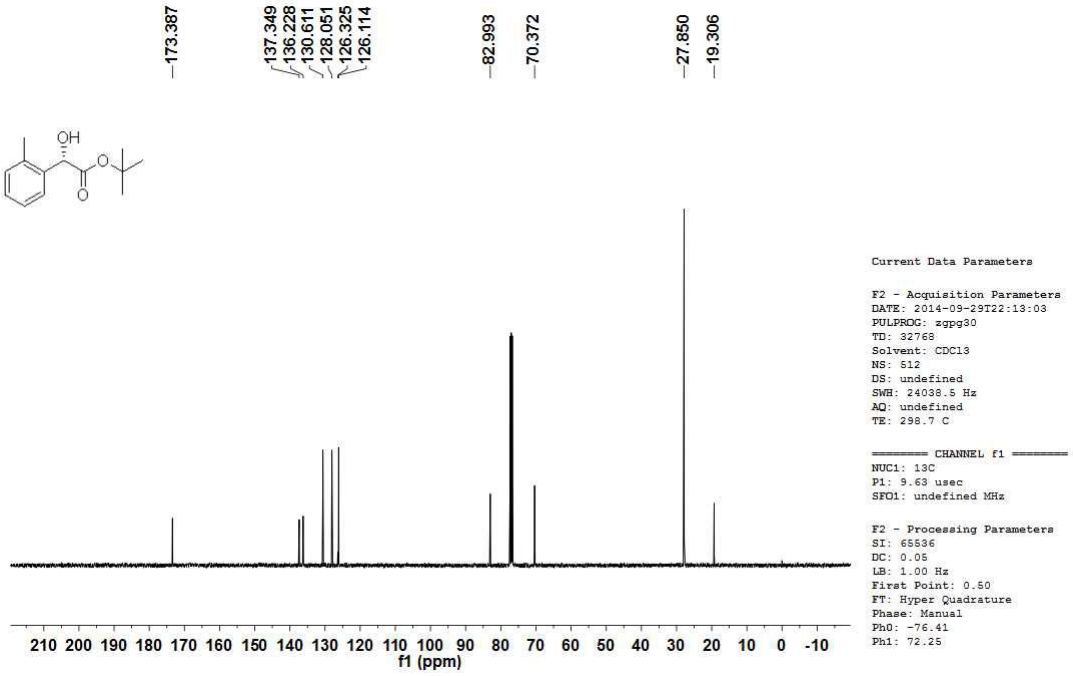
(*S*)-*tert*-butyl mandelate (3aa)



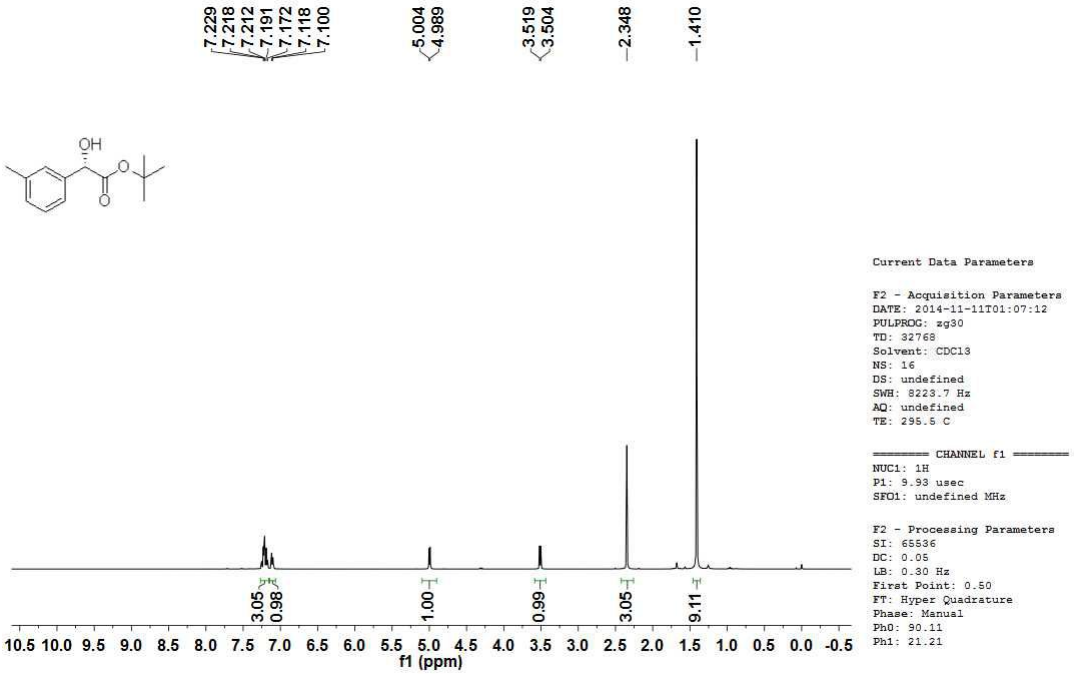


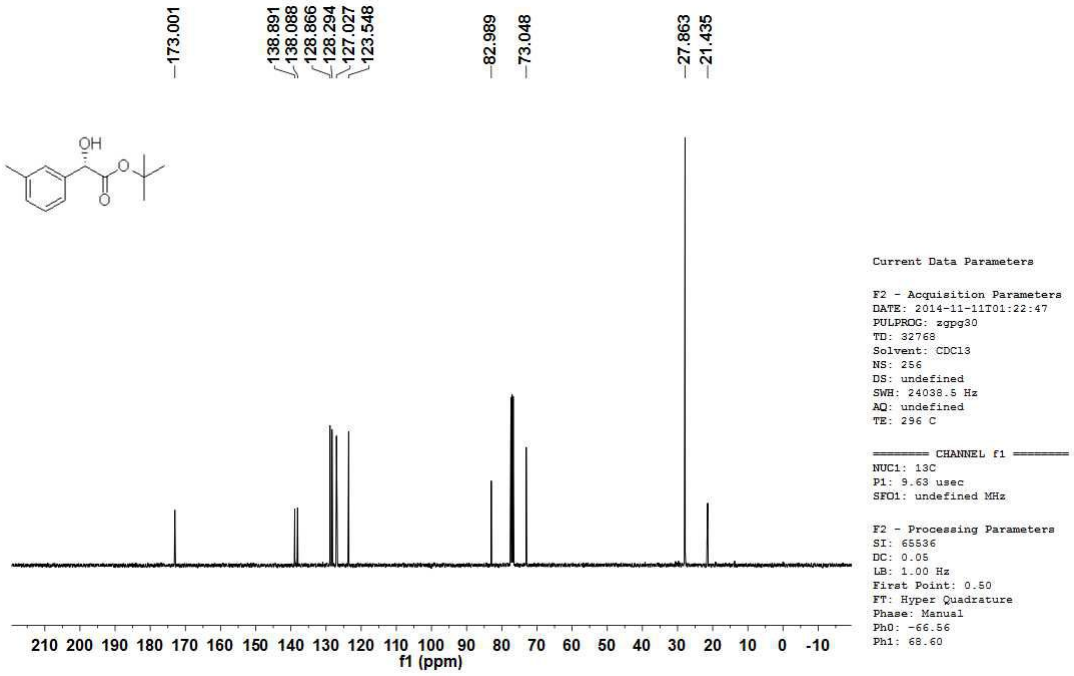
(*S*)-*tert*-butyl α-hydroxy-α-(2-methylphenyl)acetate (3ab)



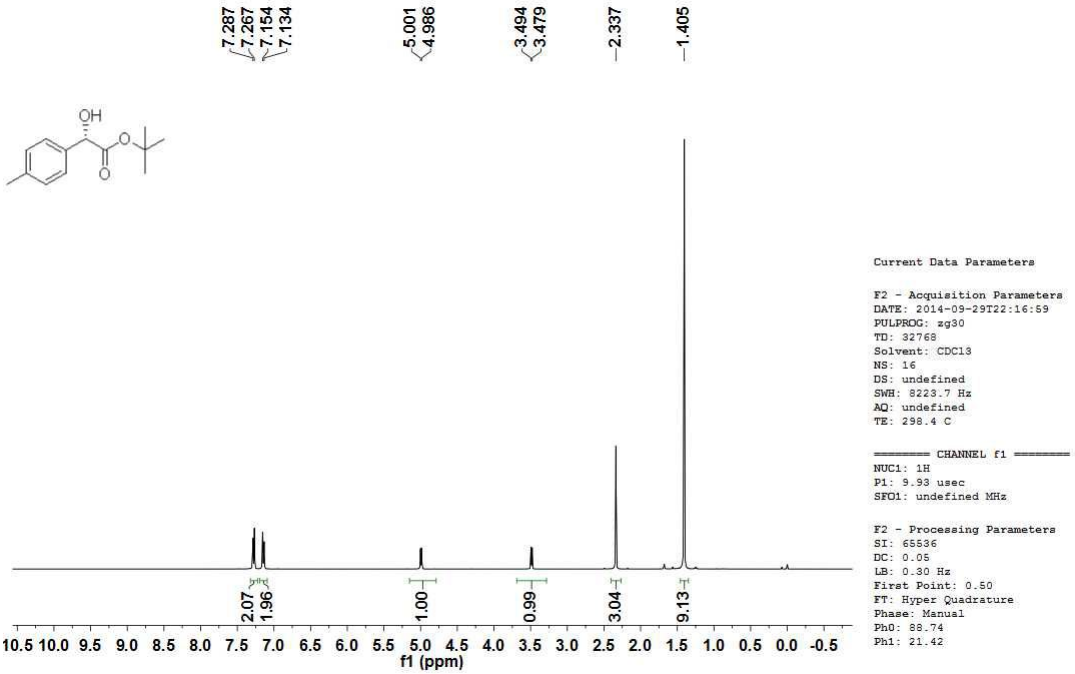


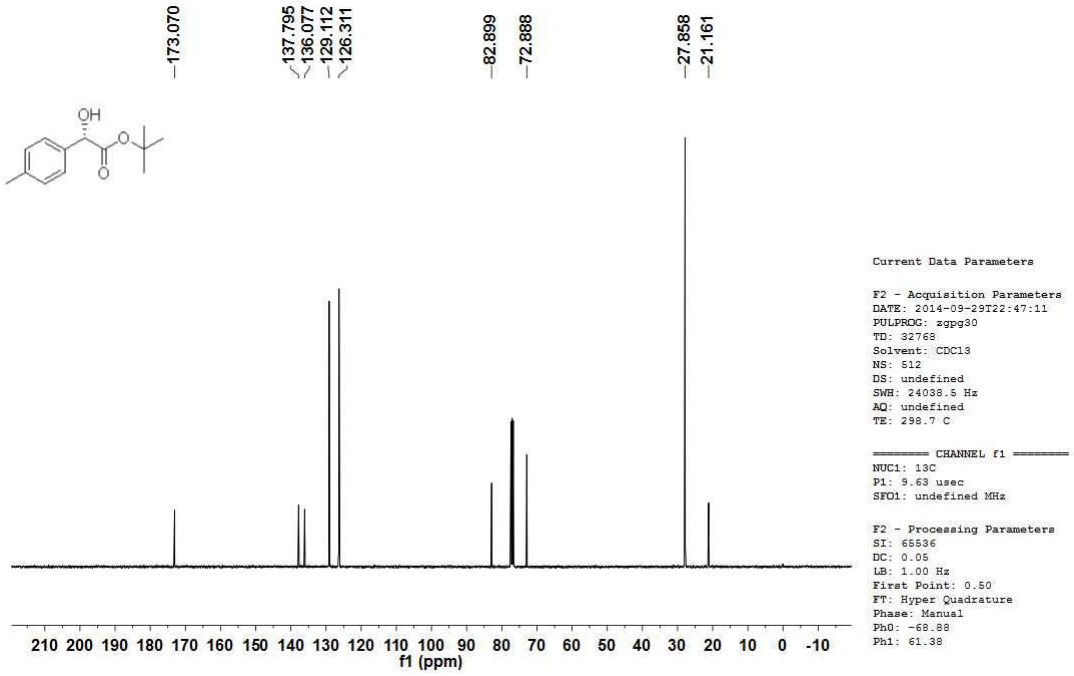
(*S*)-*tert*-butyl α-hydroxy-α-(3-methylphenyl)acetate (3ac)



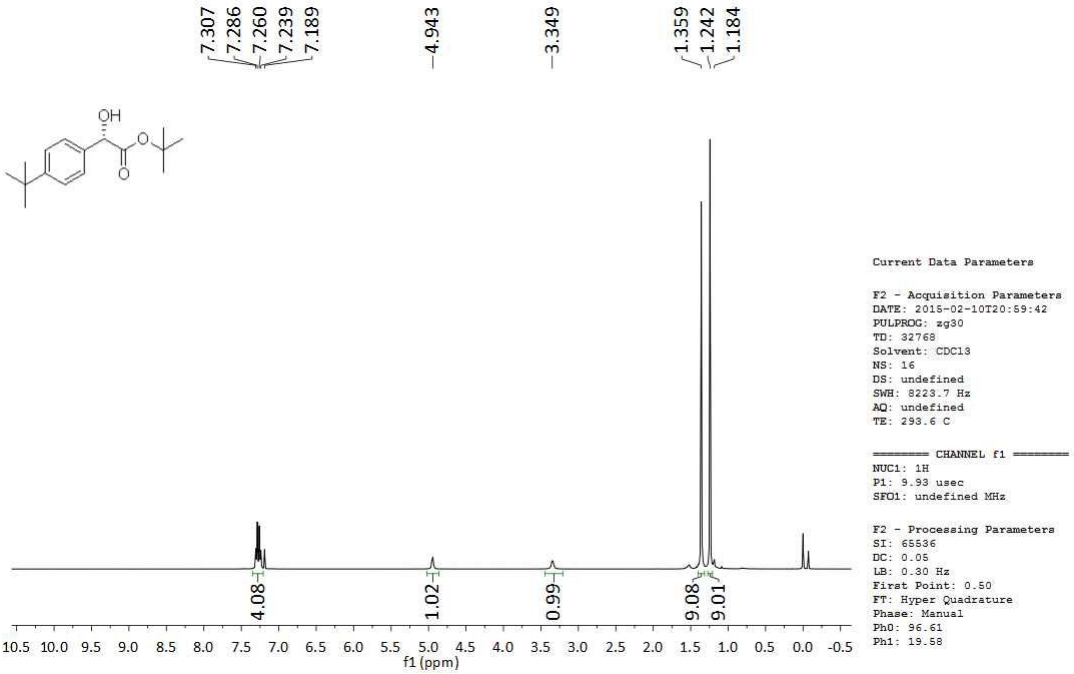


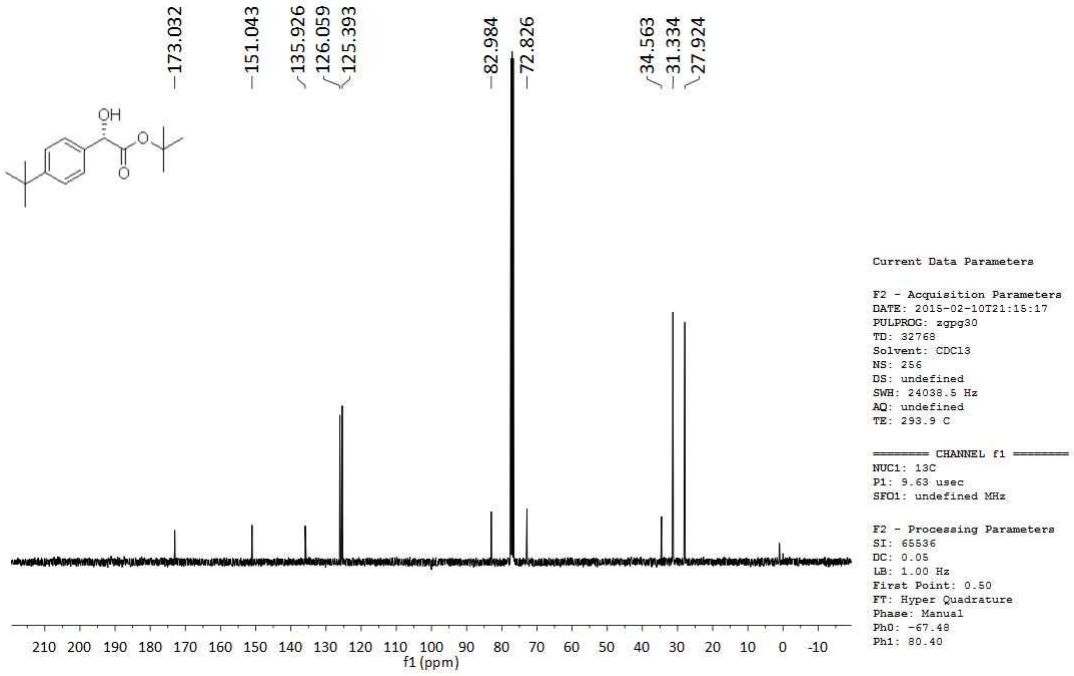
(*S*)-*tert*-butyl α-hydroxy-α-(4-methylphenyl)acetate (3ad)



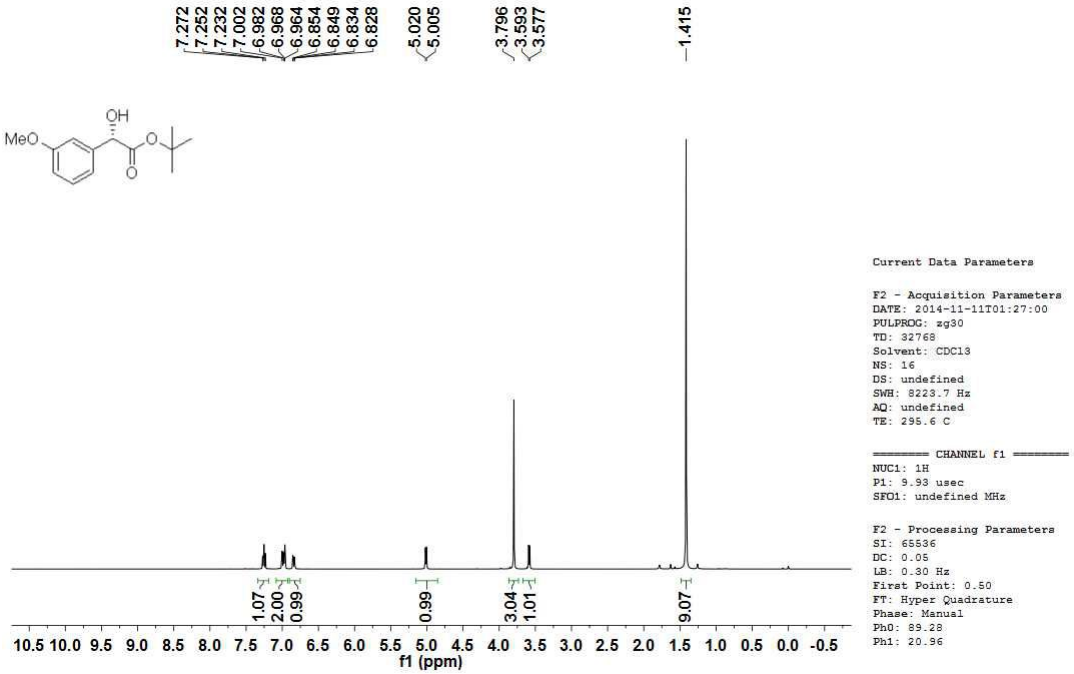


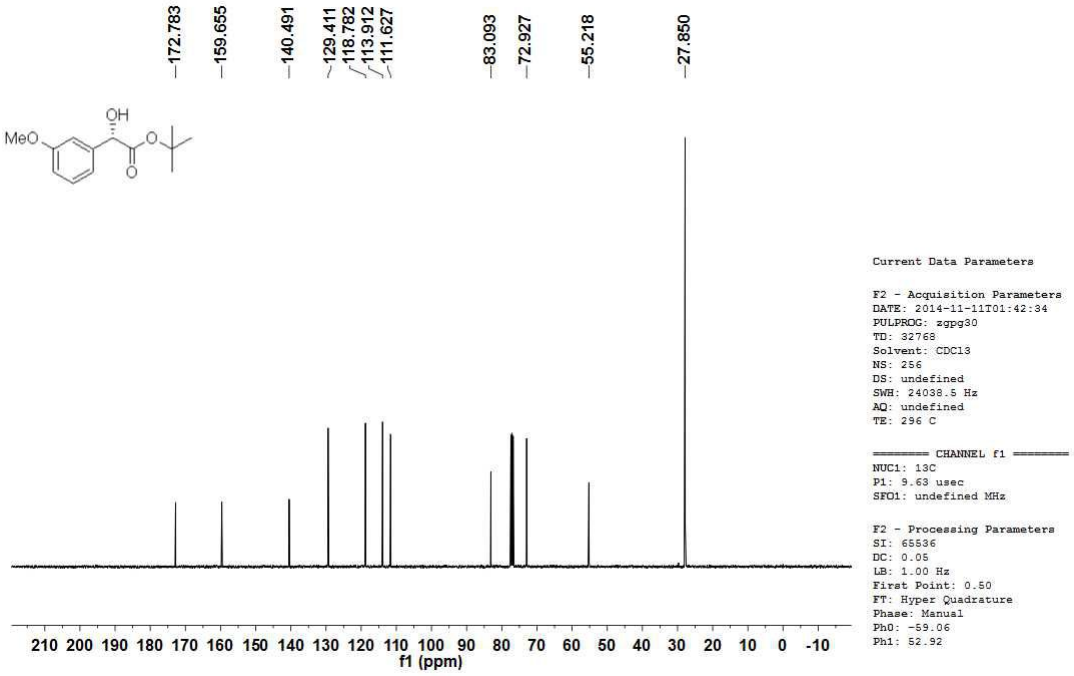
(*S*)-*tert*-butyl α-hydroxy-α-(4-(*tert*-butyl)phenyl)acetate (3ae)



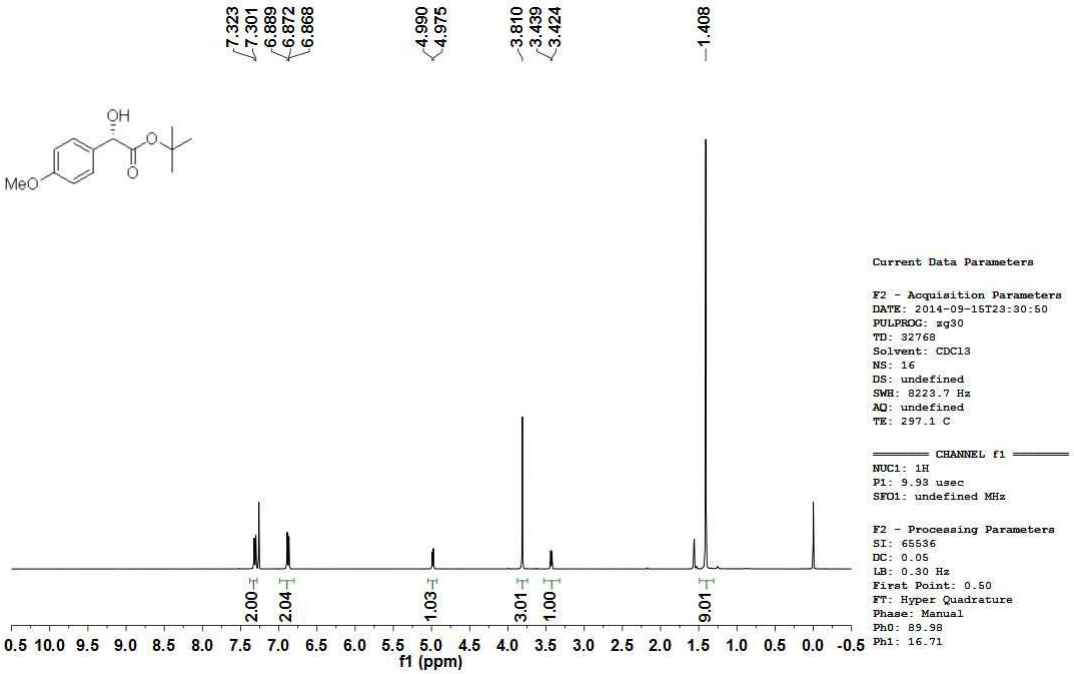


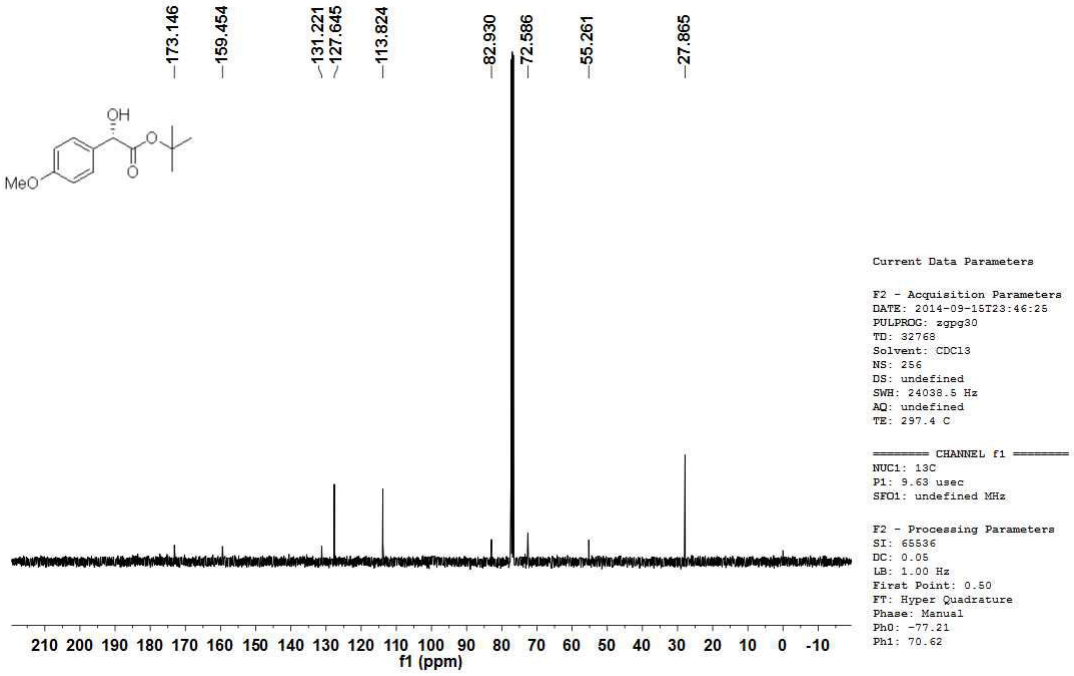
(*S*)-*tert*-butyl α-hydroxy-α-(3-methoxylphenyl)acetate (3af)



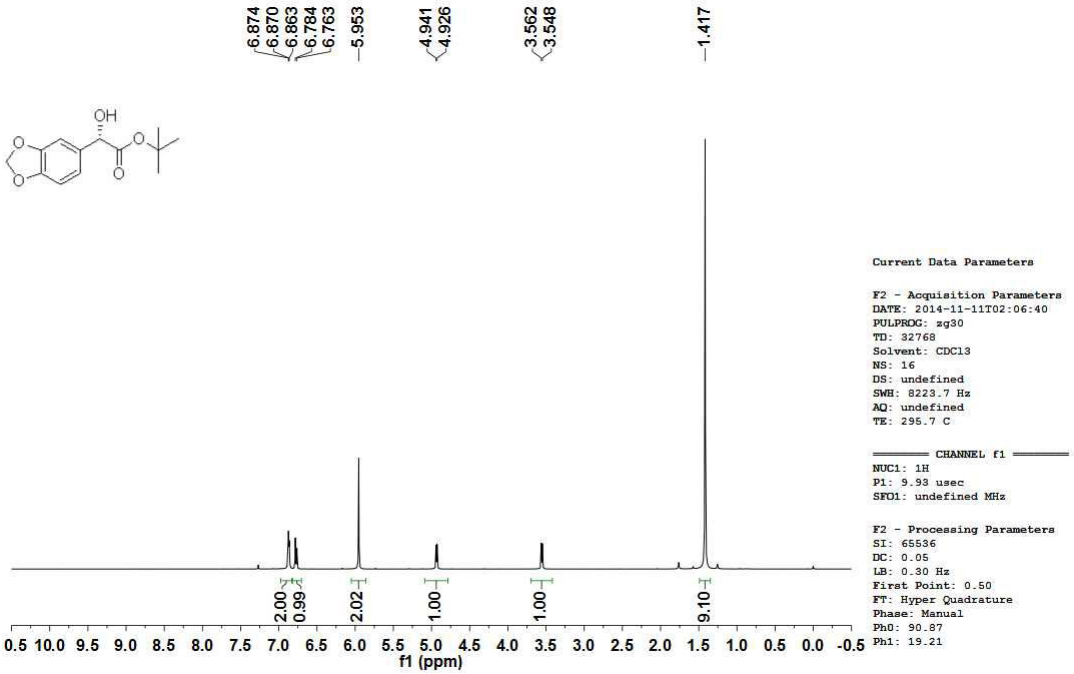


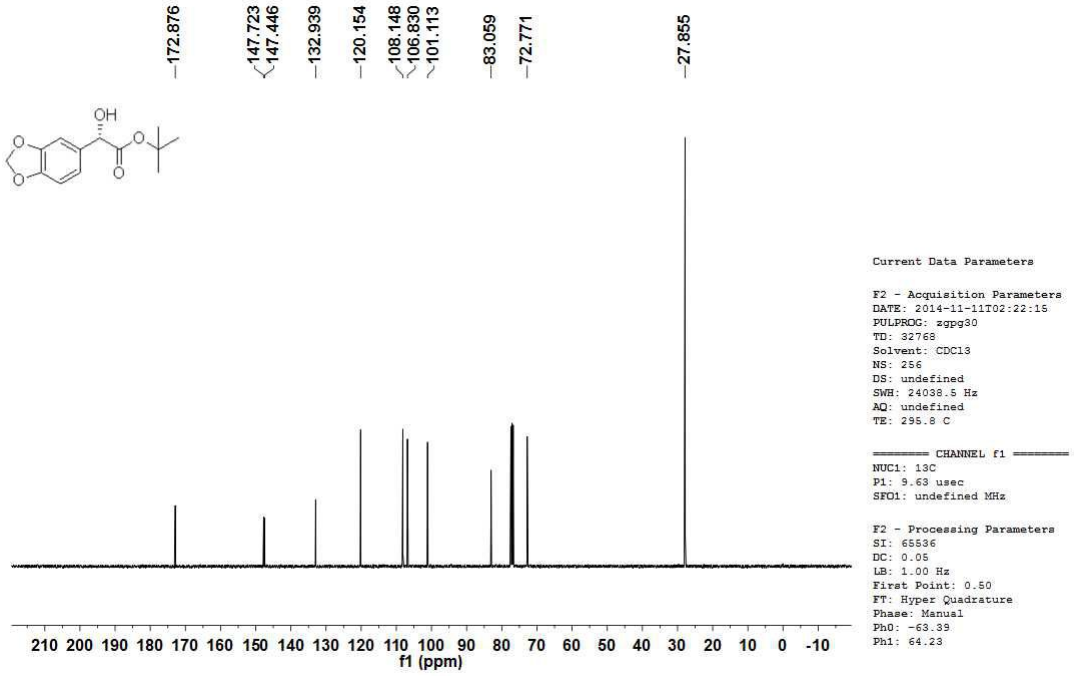
(*S*)-*tert*-butyl α-hydroxy-α-(4-methoxylphenyl)acetate (3ag)



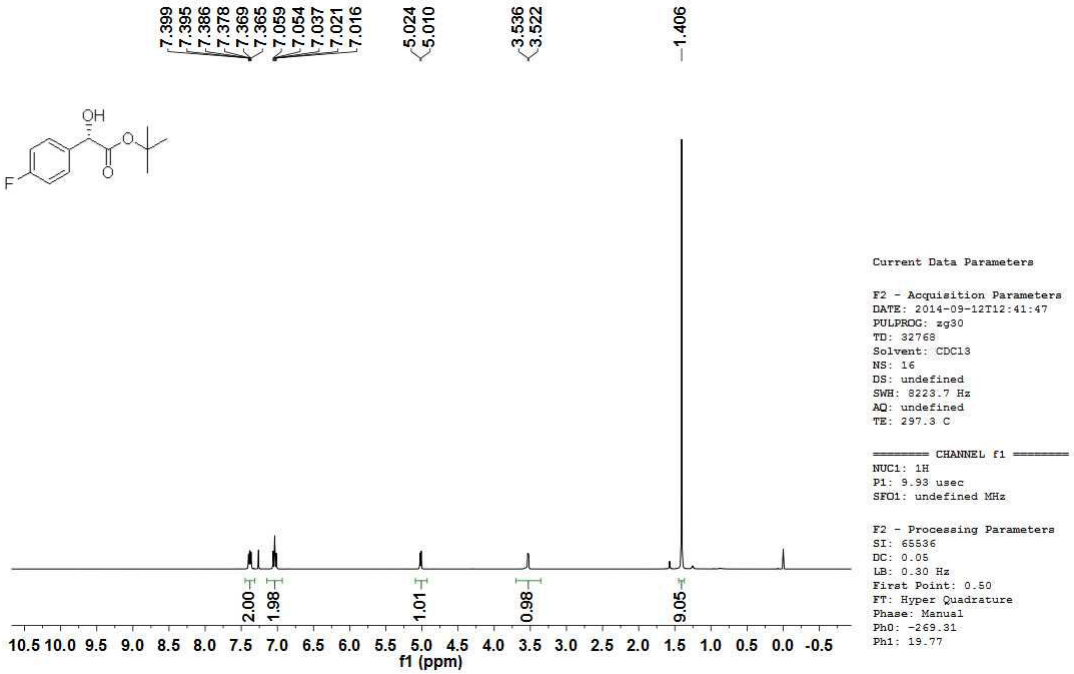


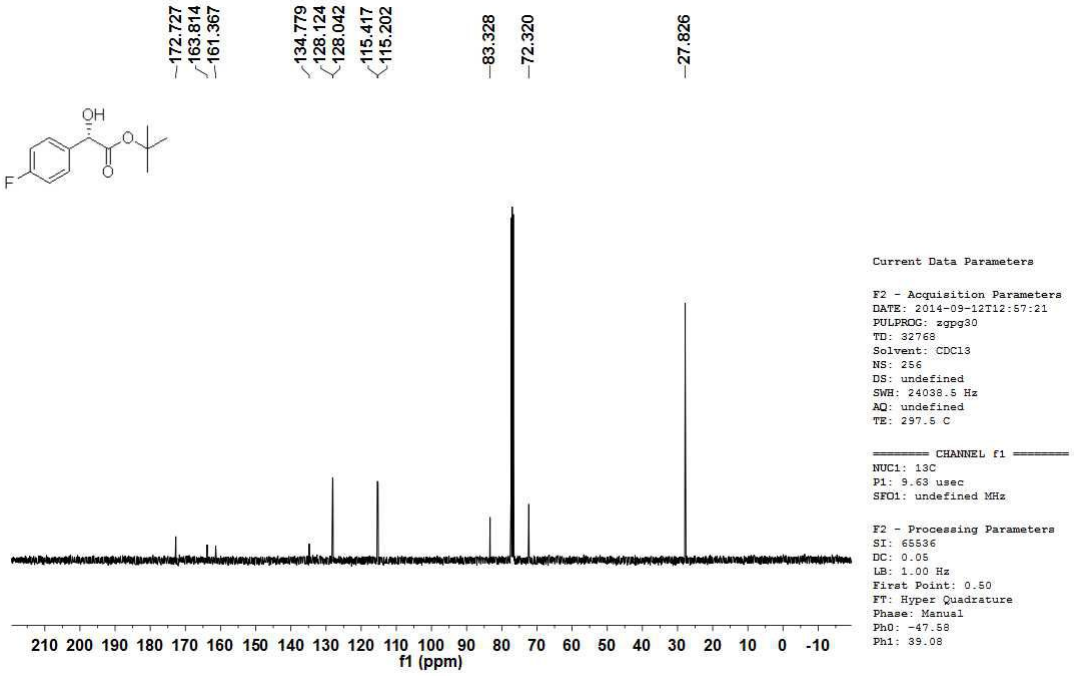
(*S*)-*tert*-butyl α-hydroxy-α-(3,4-methylenedioxylphenyl)acetate (3ah)



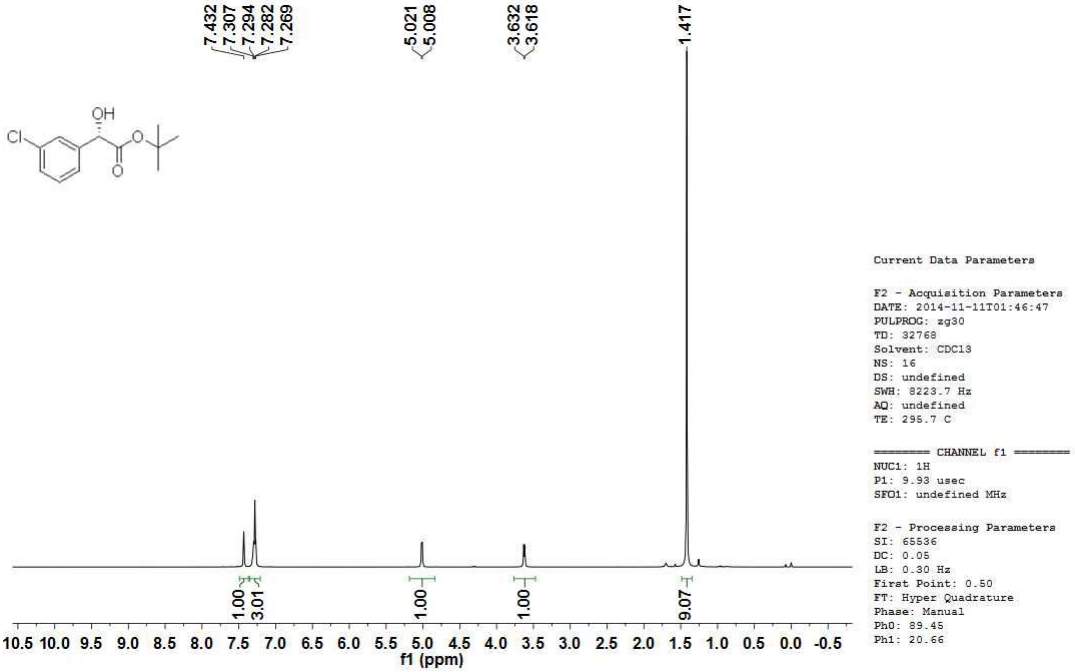


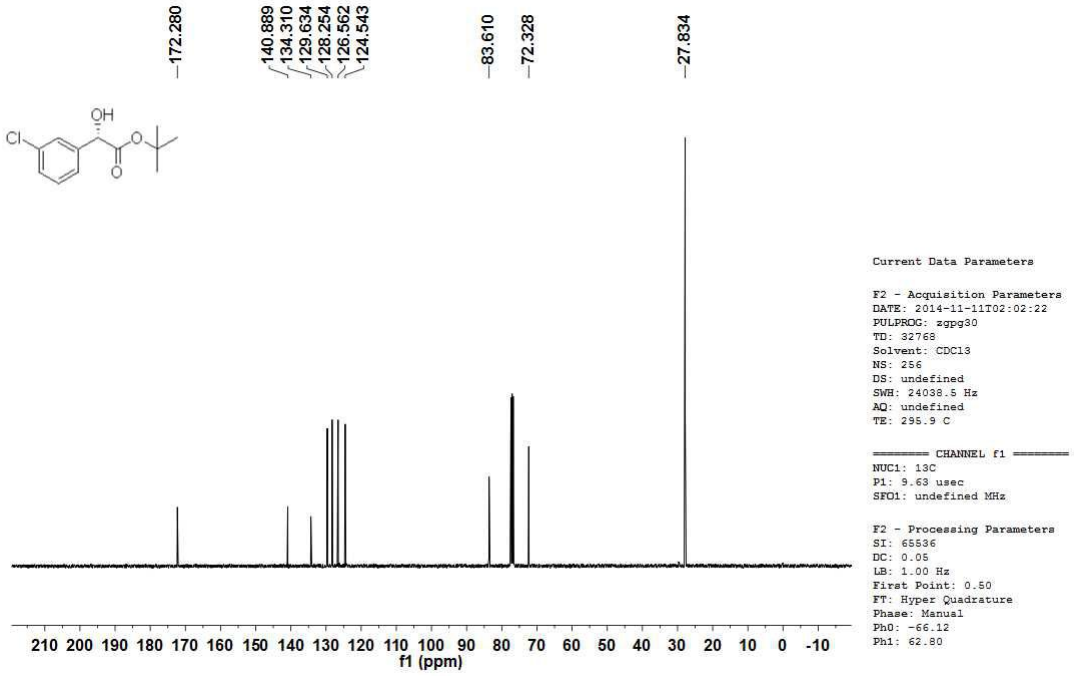
(*S*)-*tert*-butyl α-hydroxy-α-(4-flurophenyl)acetate (3ai)



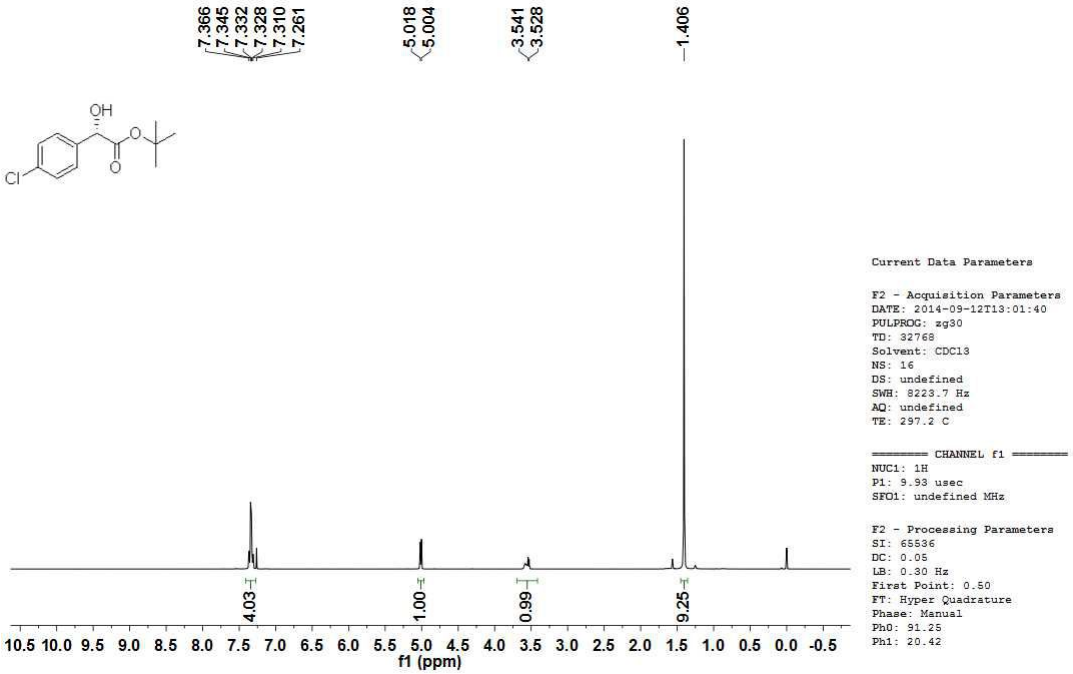


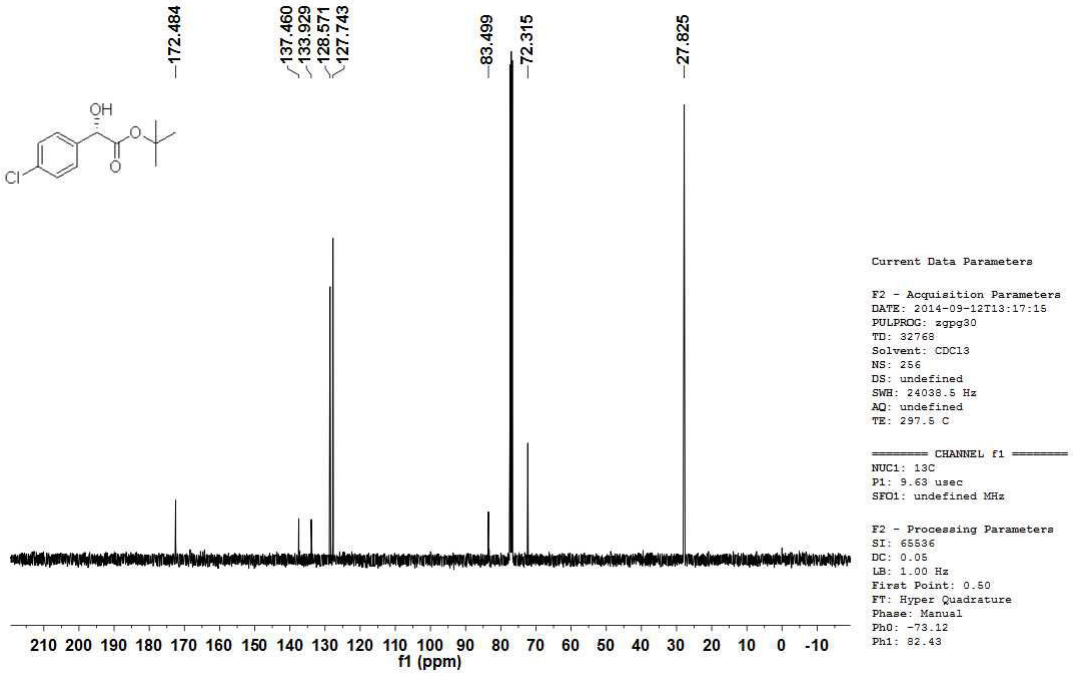
(*S*)-*tert*-butyl α-hydroxy-α-(3-chlorophenyl)acetate (3aj)



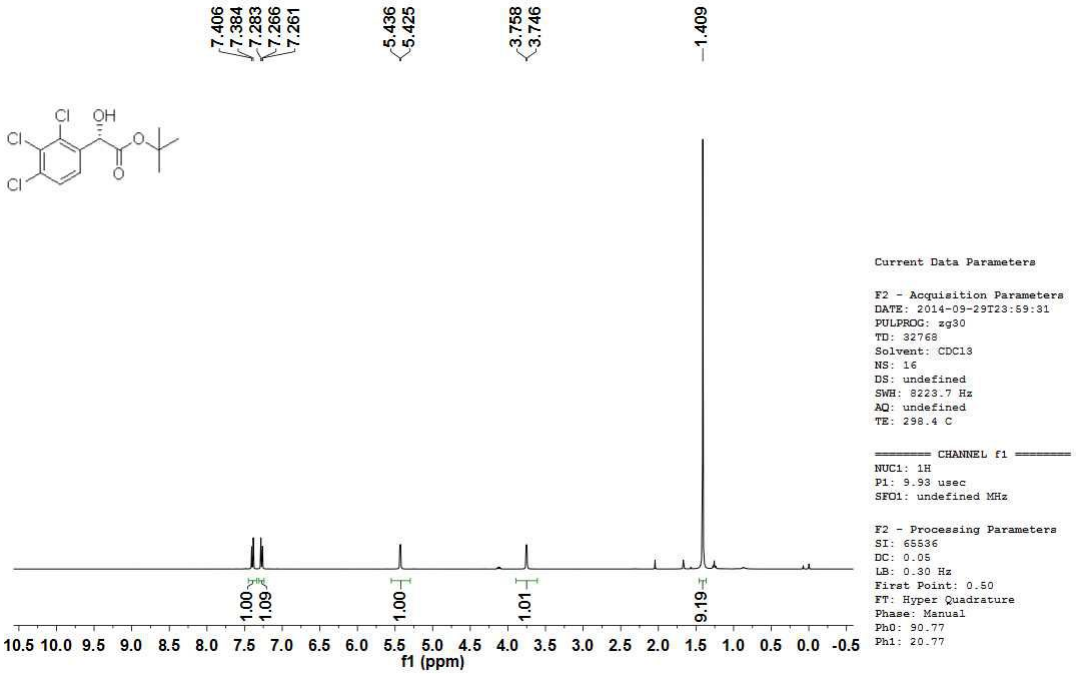


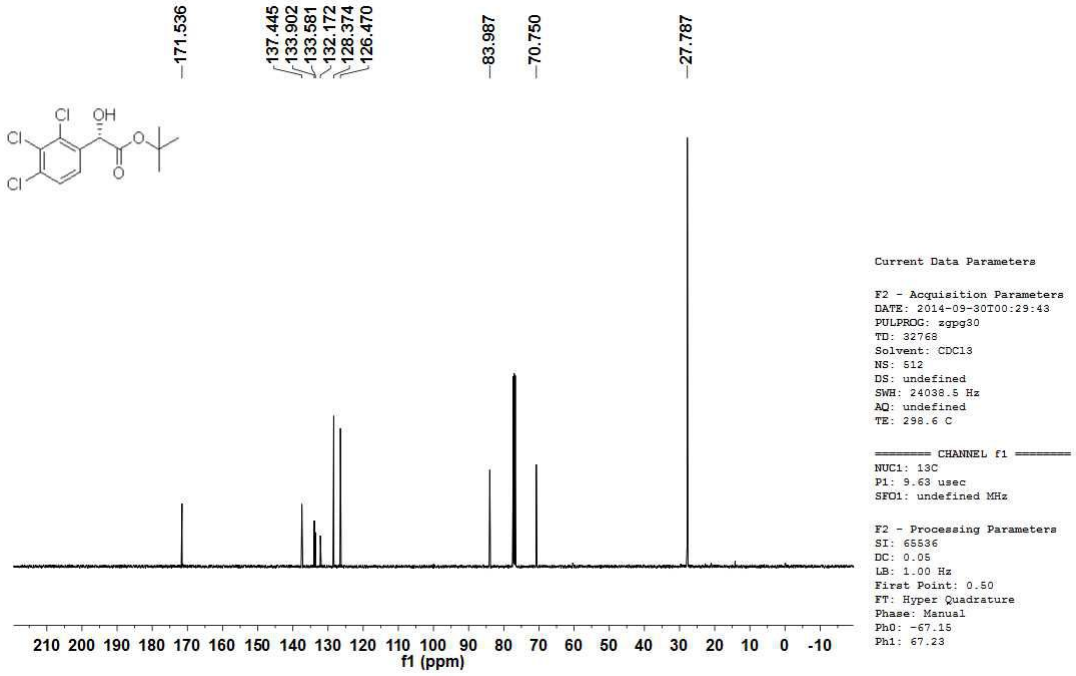
(*S*)-*tert*-butyl α-hydroxy-α-(4-chlorophenyl)acetate (3ak)



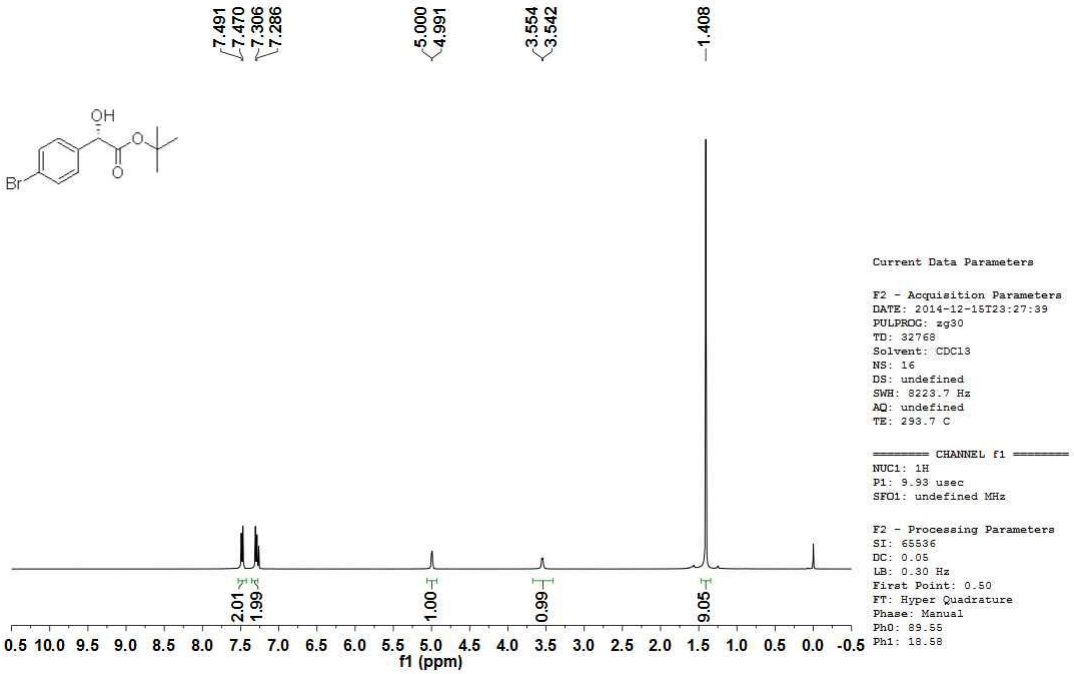


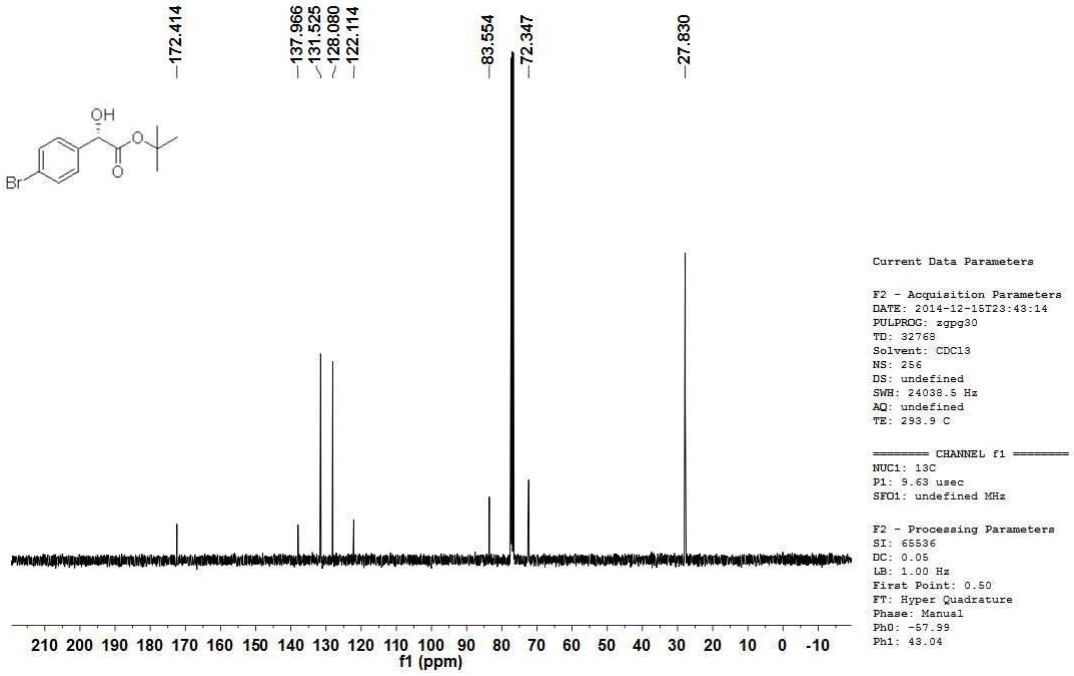
(*S*)-*tert*-butyl α-hydroxy-α-(2,3,4-trichlorophenyl)acetate (3al)



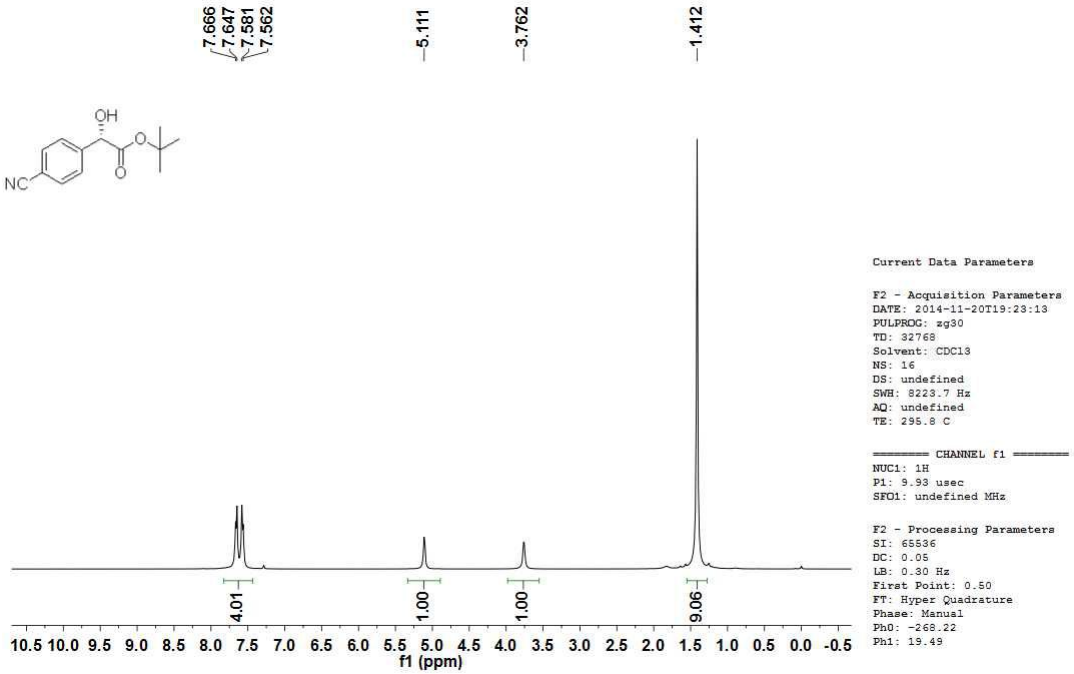


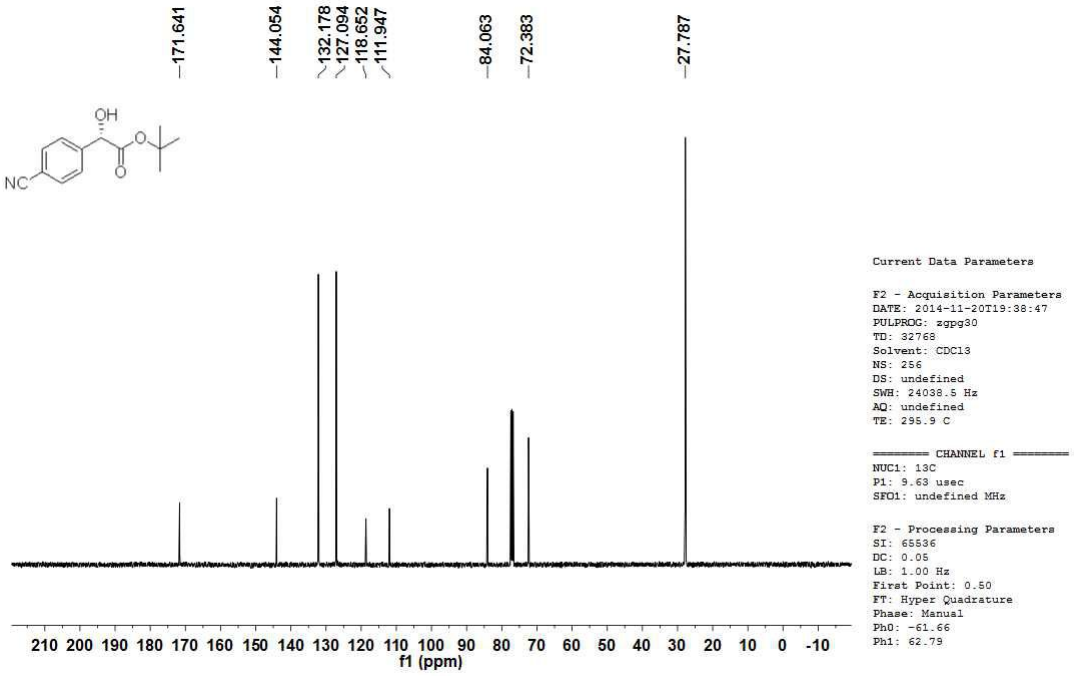
(*S*)-*tert*-butyl α-hydroxy-α-(4-bromophenyl)acetate (3am)



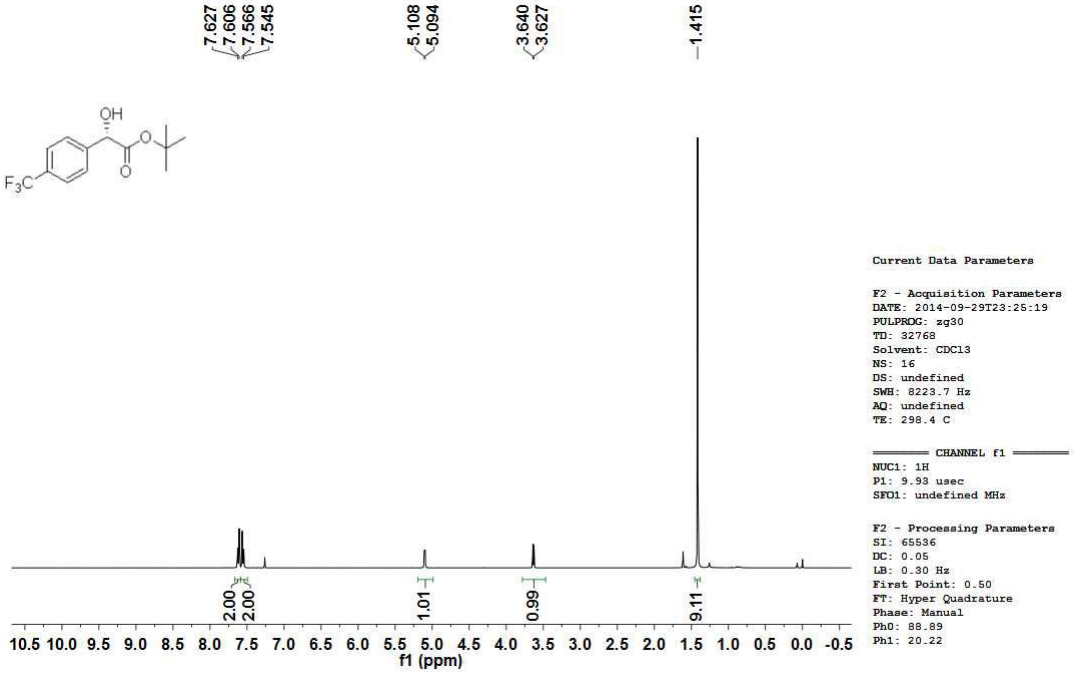


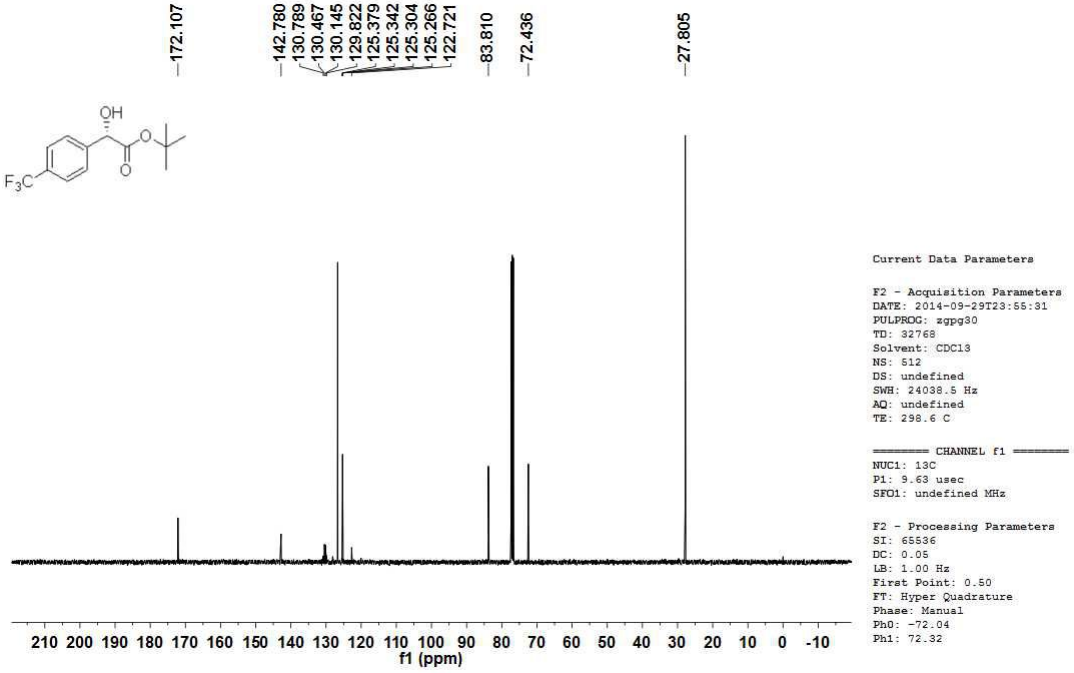
(*S*)-*tert*-butyl α-hydroxy-α-(4-cyanophenyl)acetate (3an)



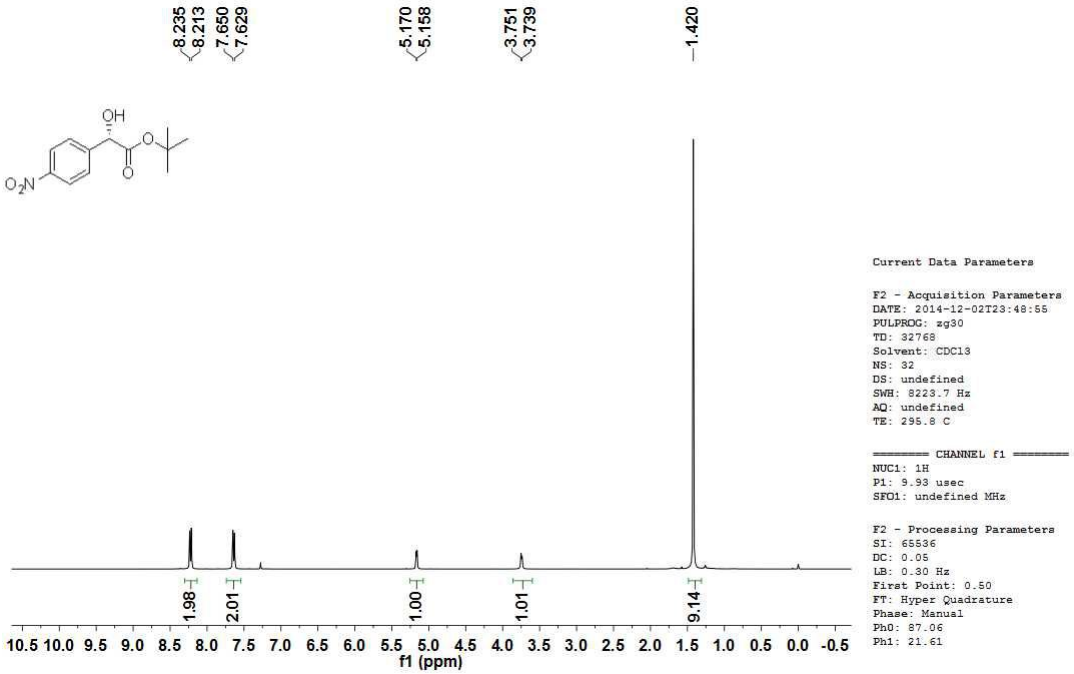


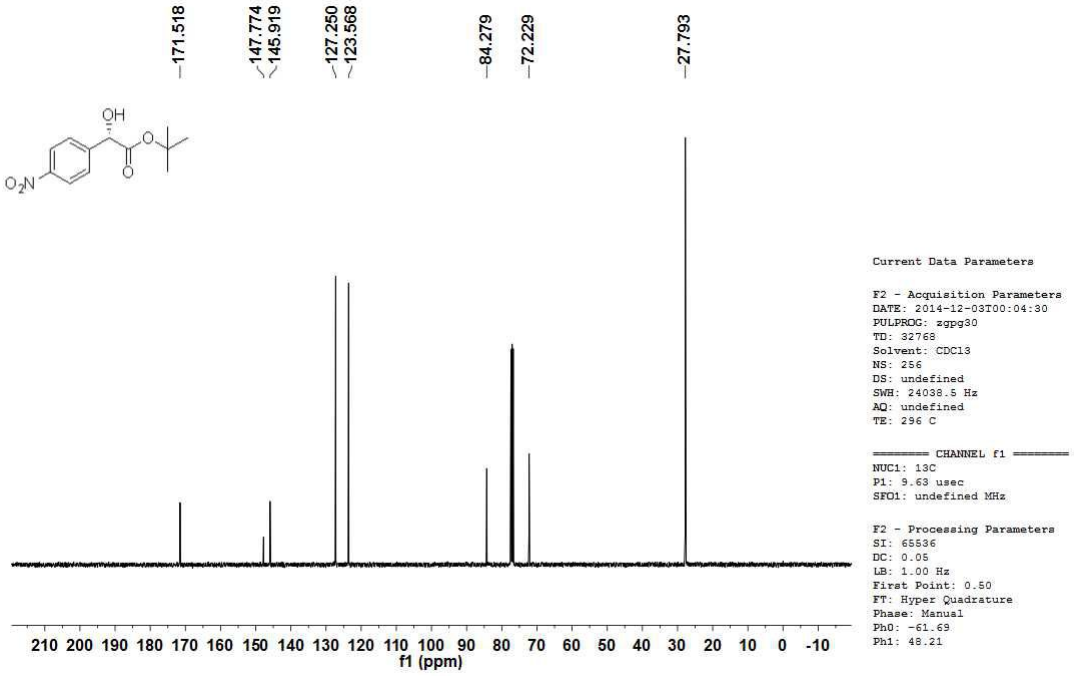
(*S*)-*tert*-butyl α-hydroxy-α-(4-(trifluoromethyl)phenyl)acetate (3ao)



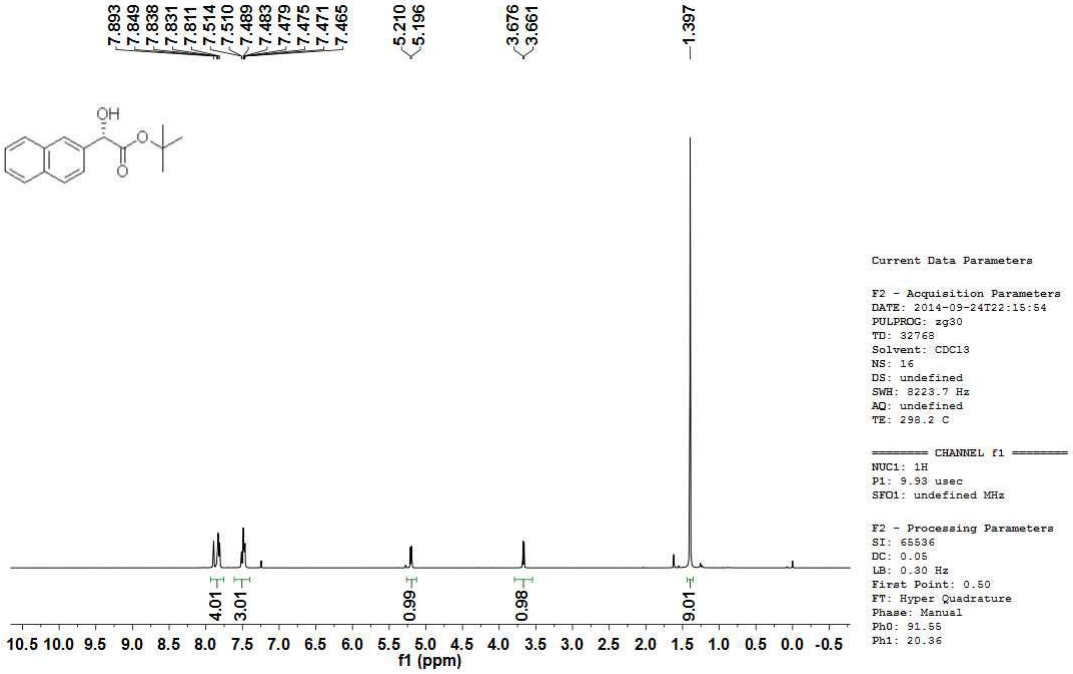


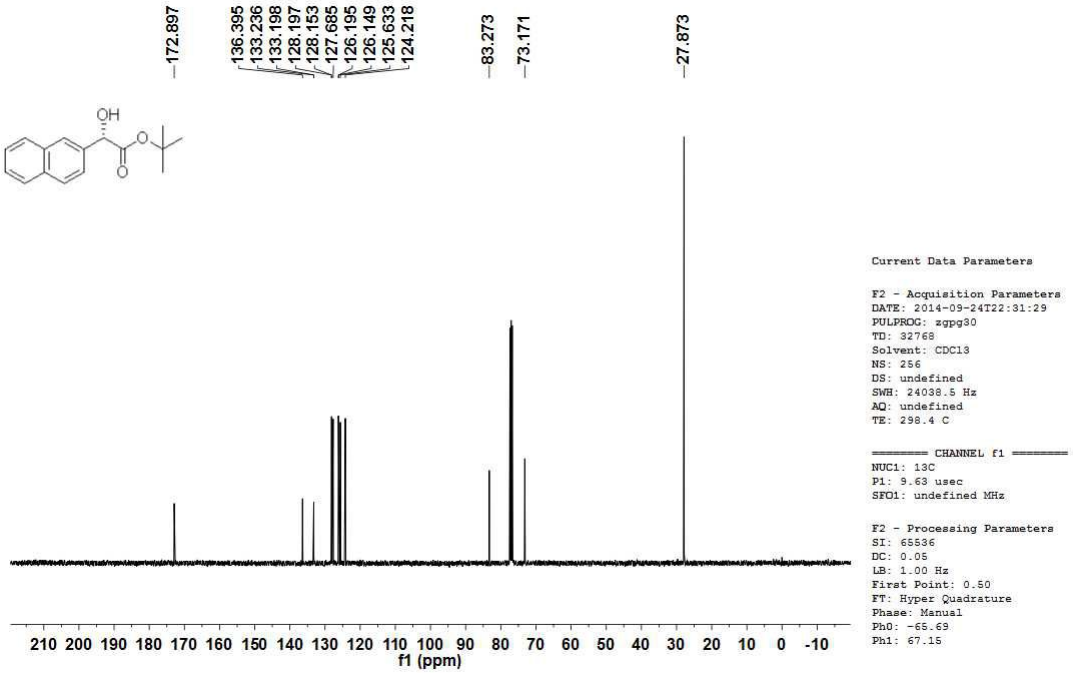
(*S*)-*tert*-butyl α-hydroxy-α-(4-nitrophenyl)acetate (3ap)



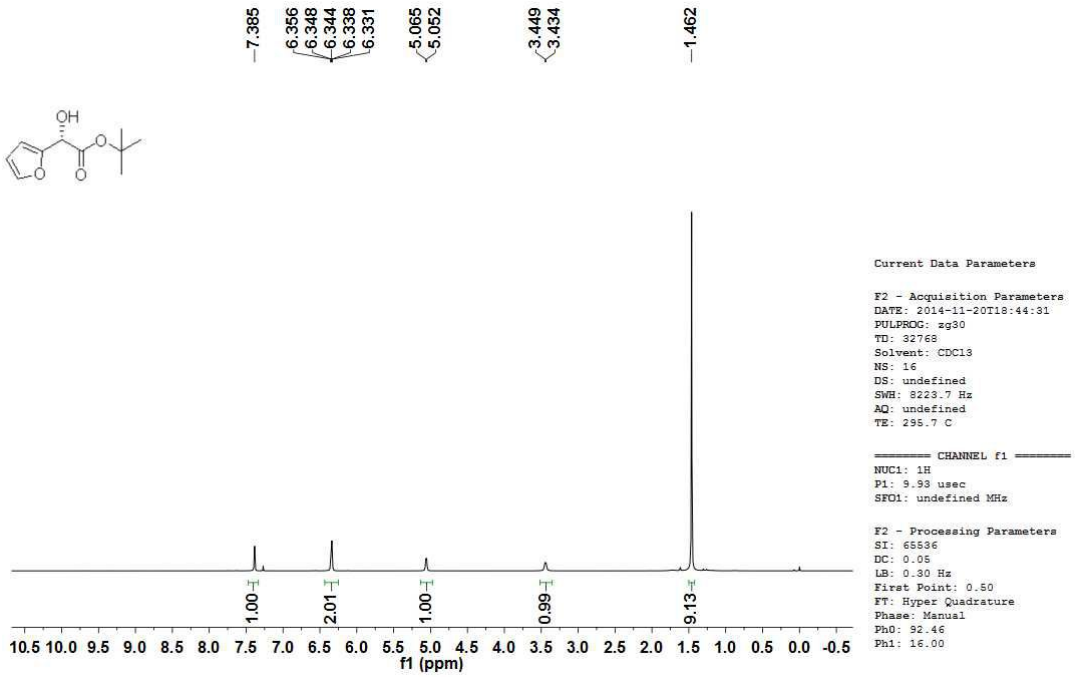


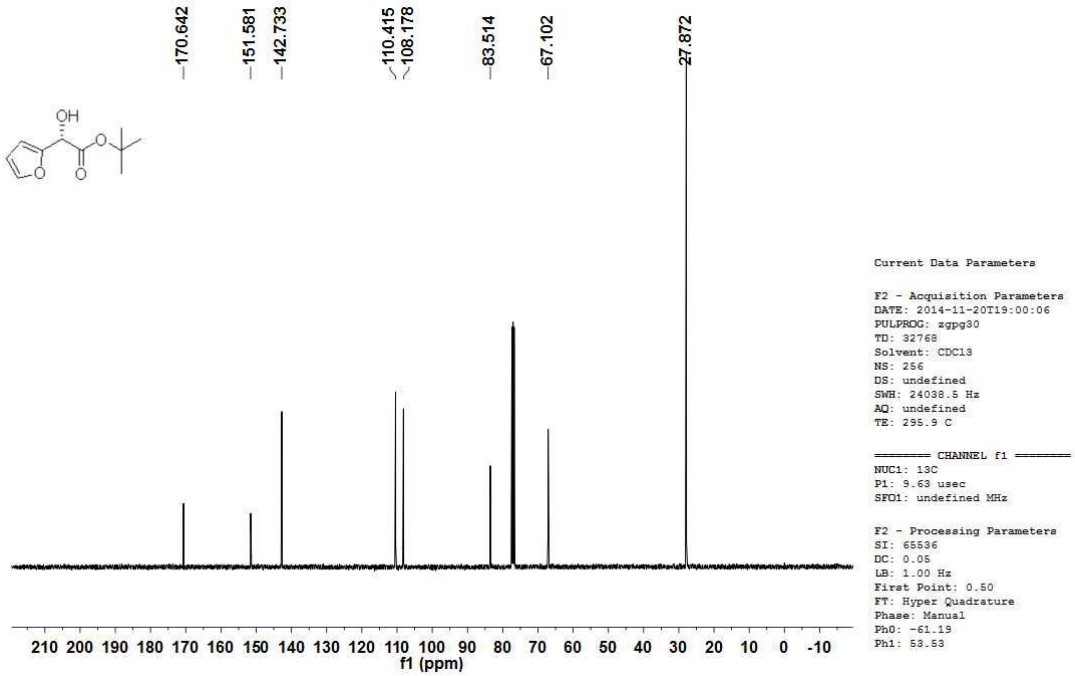
(*S*)-*tert*-butyl α-hydroxy-α-(naphthalen-2-yl)acetate (3aq)



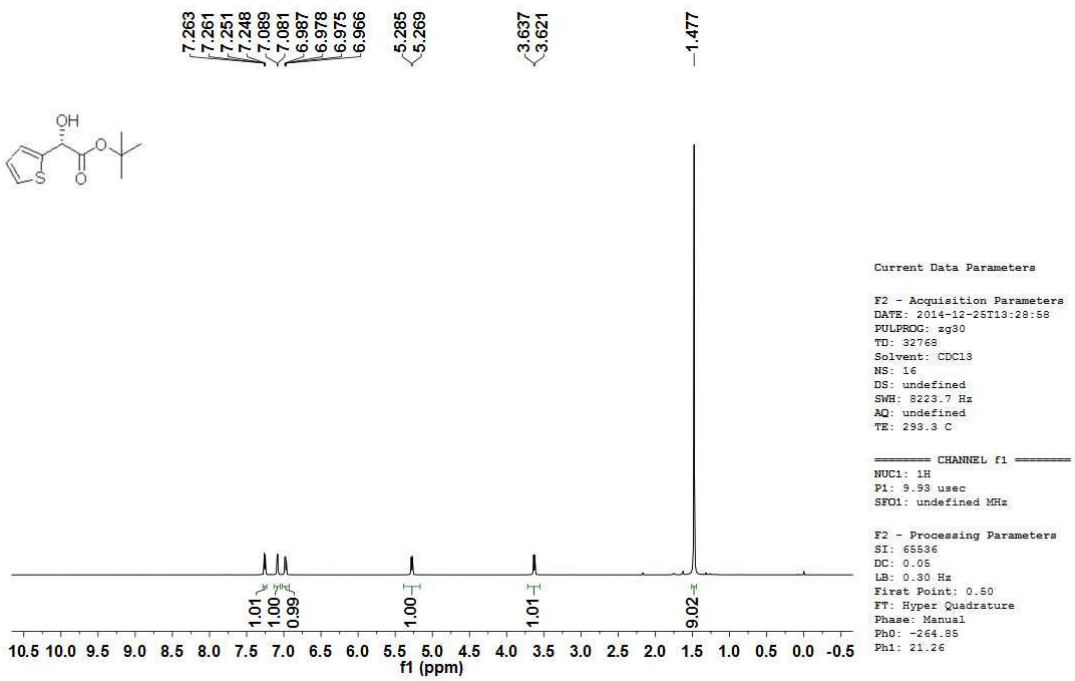


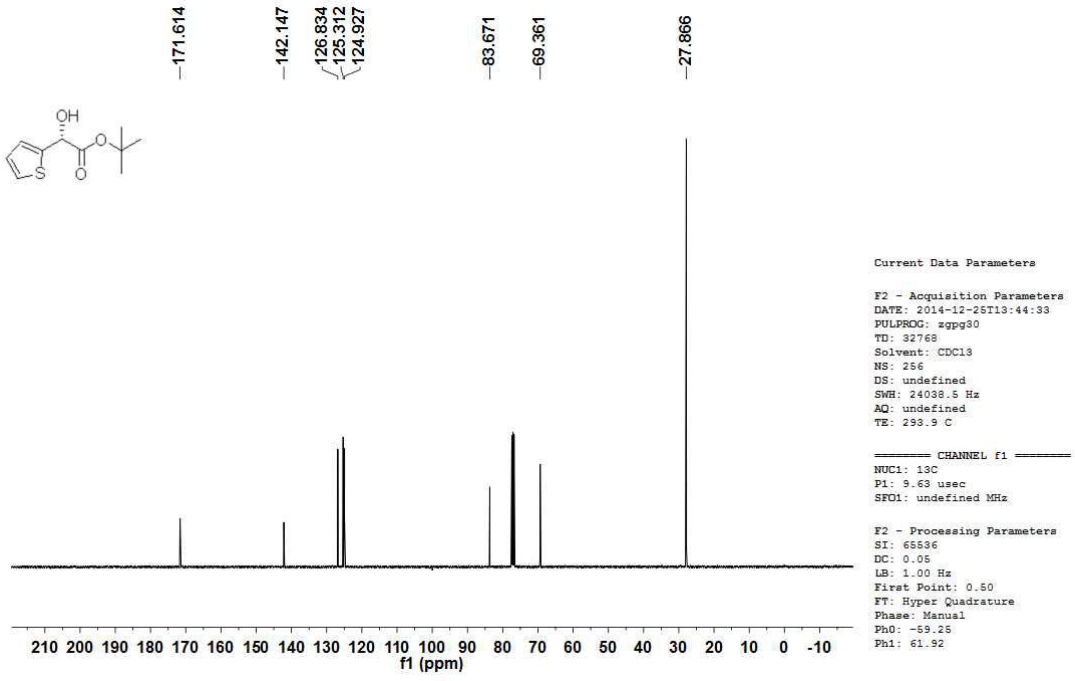
(*S*)-*tert*-butyl α-(furan-2-yl)-α-hydroxyacetate (3ar)



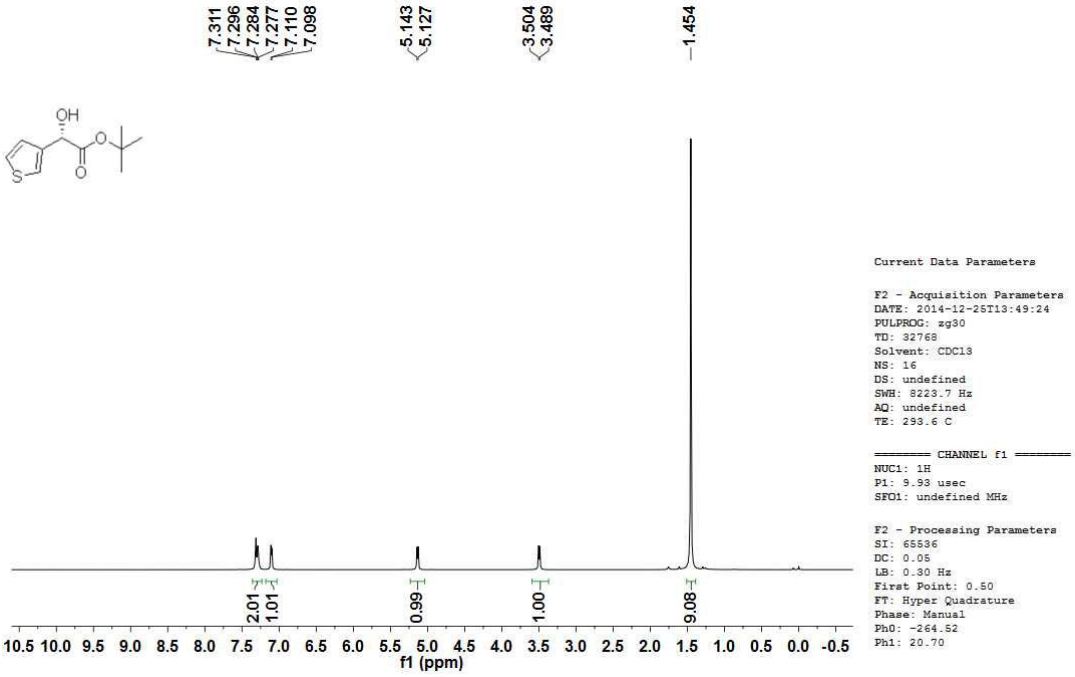


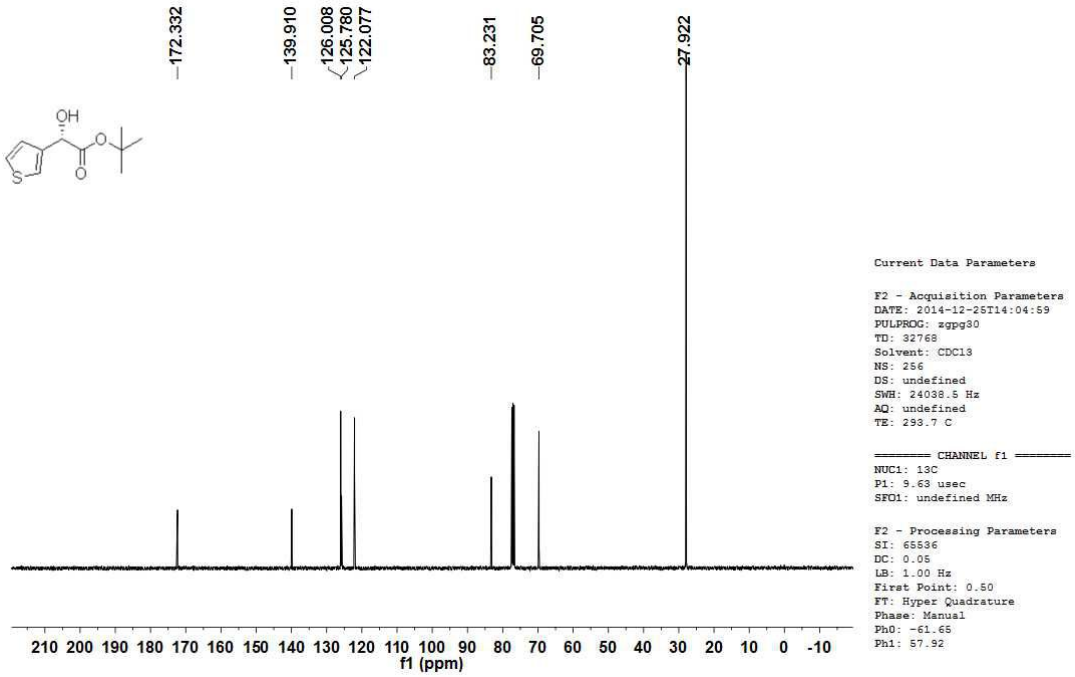
(*S*)-*tert*-butyl α-(thiophen-2-yl)-α-hydroxyacetate (3as)



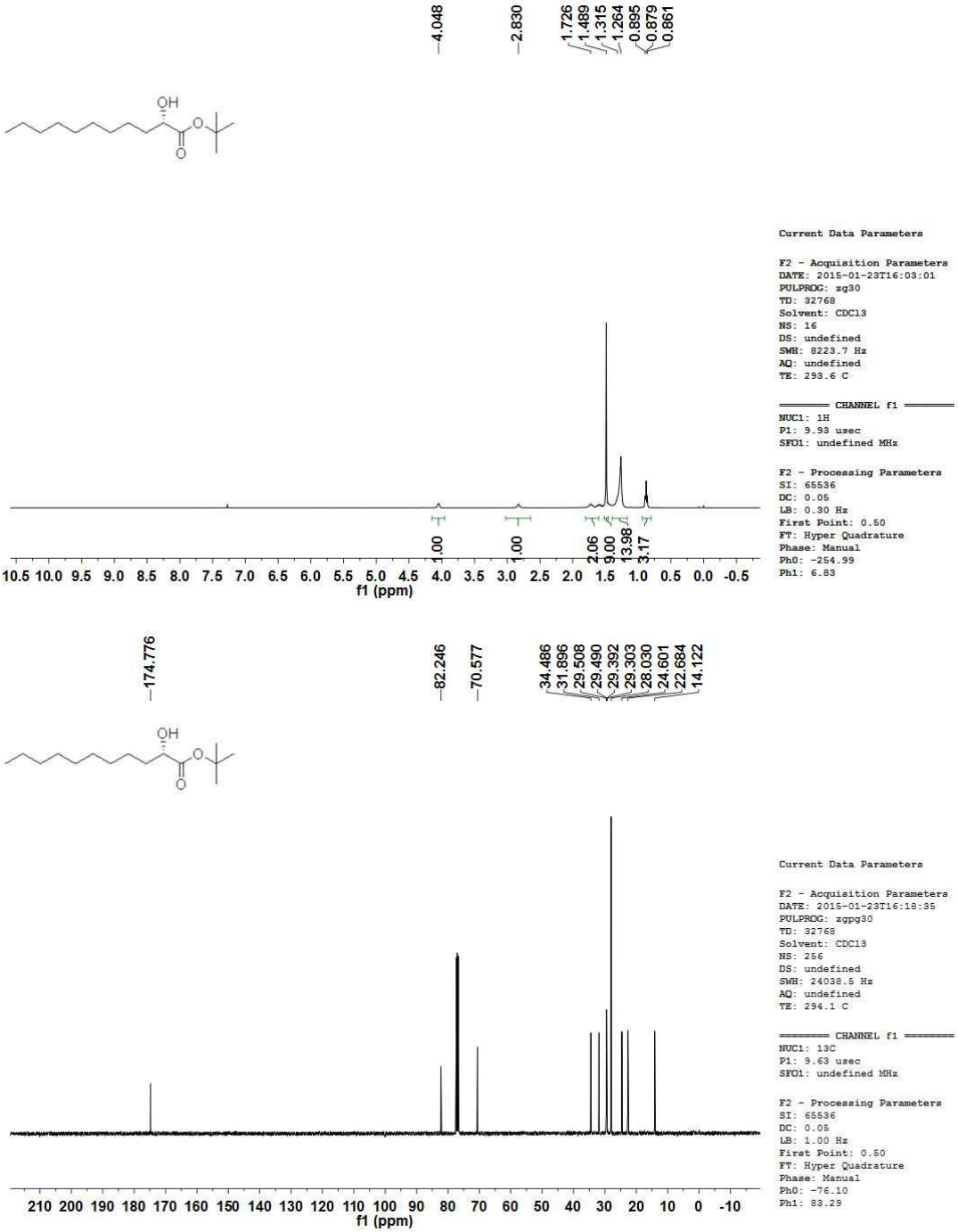


(*S*)-*tert*-butyl α-(thiophen-3-yl)-α-hydroxyacetate (3at)

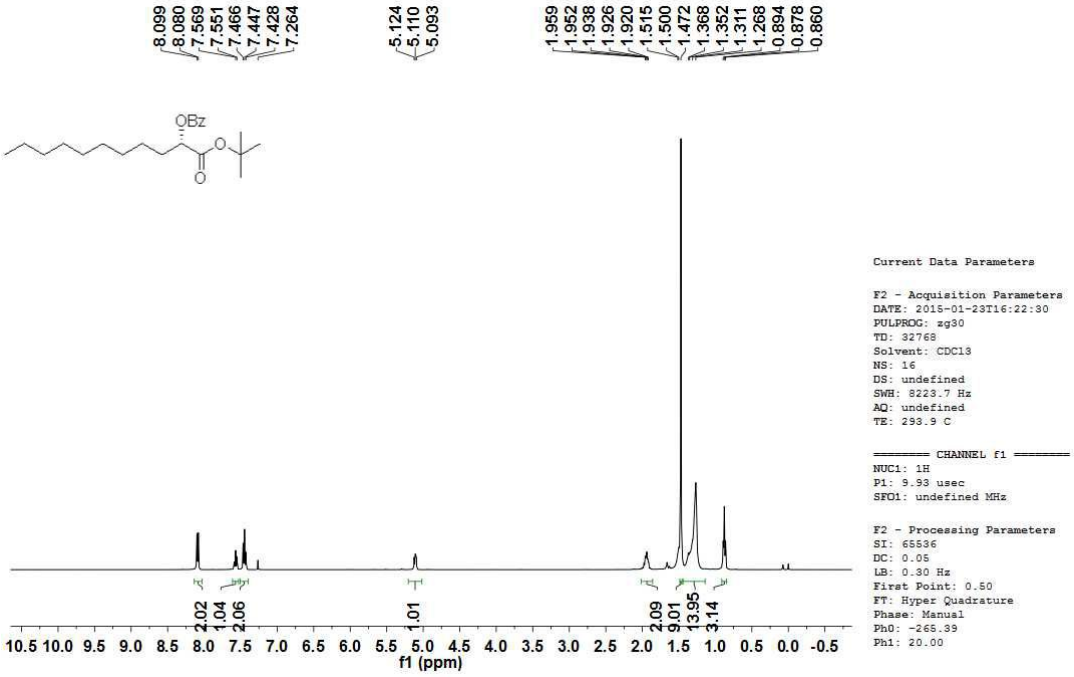


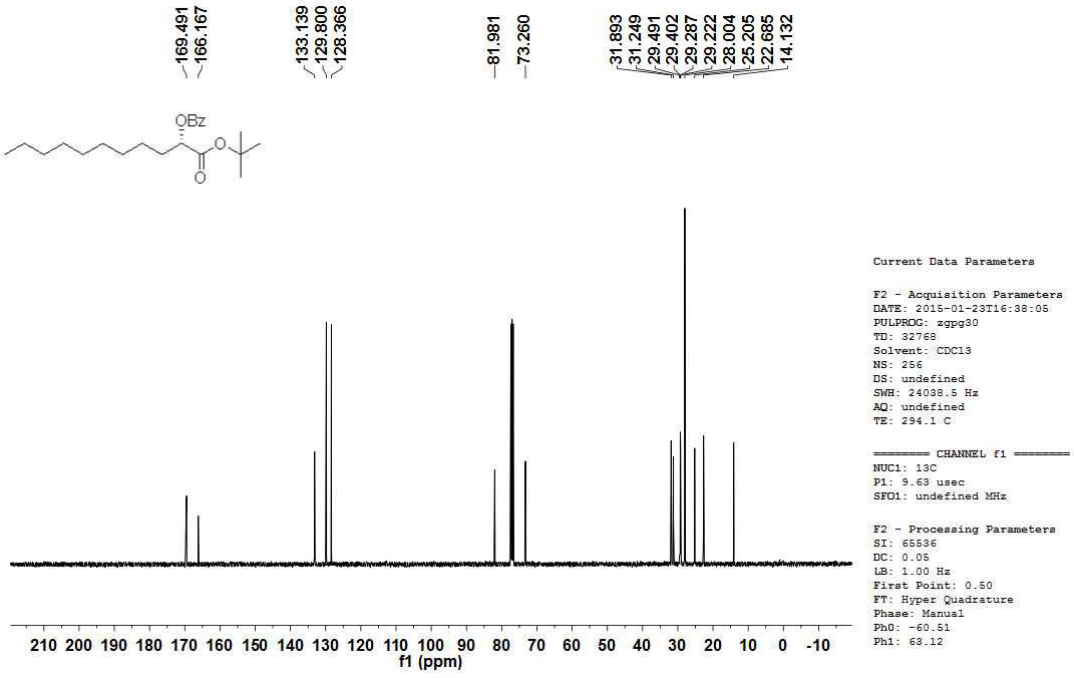


(*S*)-*tert*-butyl 2-hydroxyundecanoate (3au)

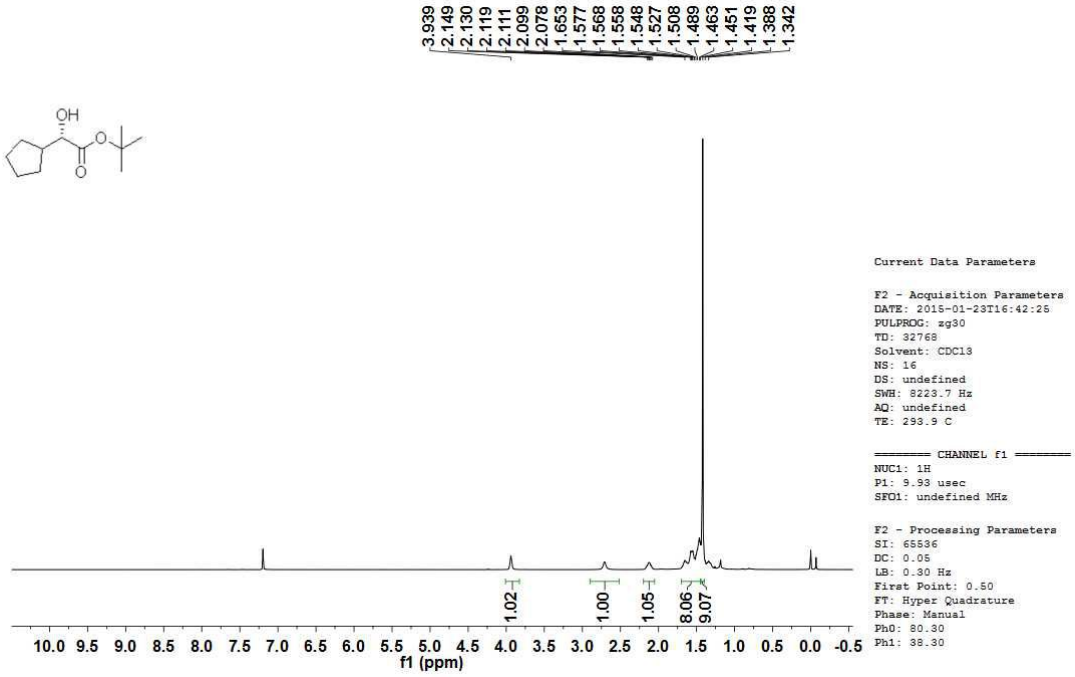


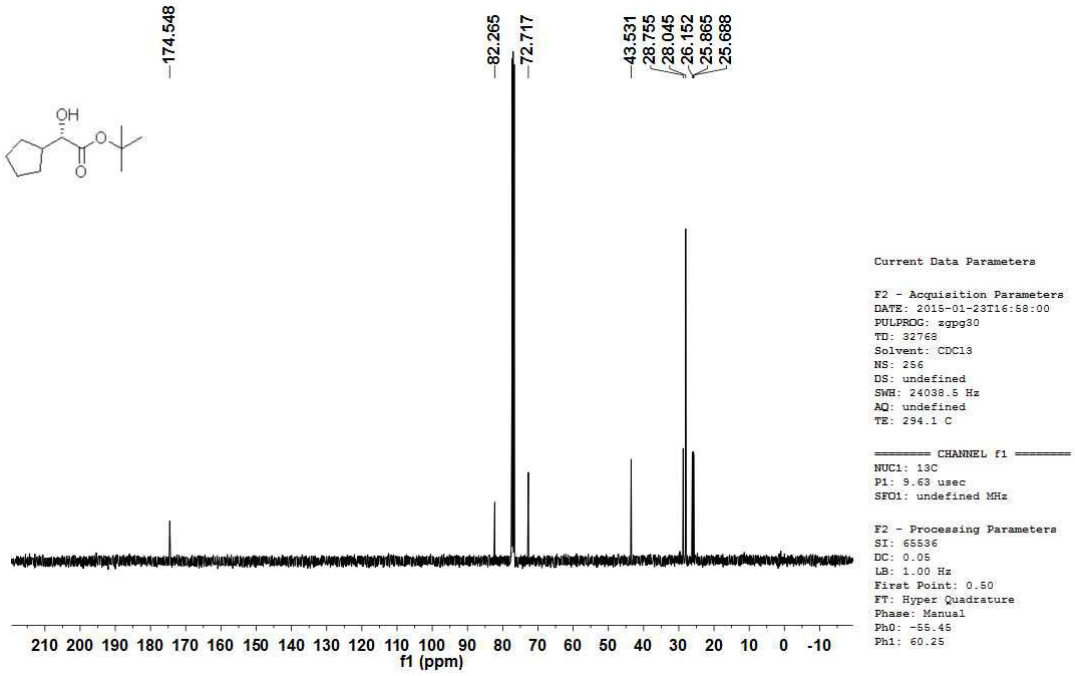
(*S*)-*tert*-butyl 2-benzoxyundecanoate(4au)



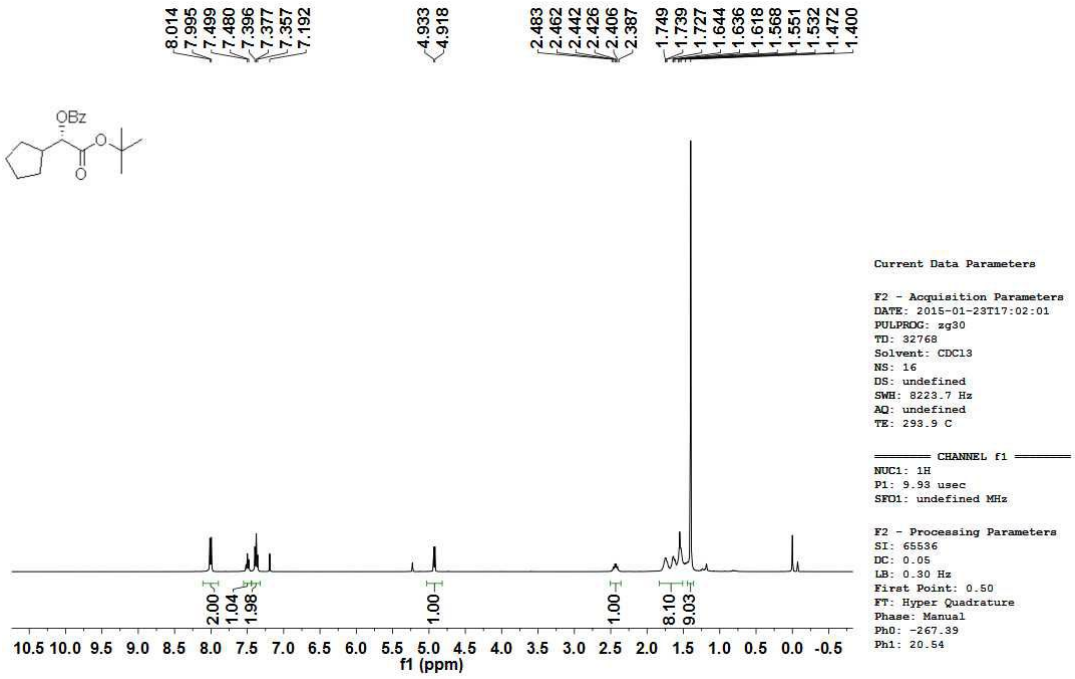


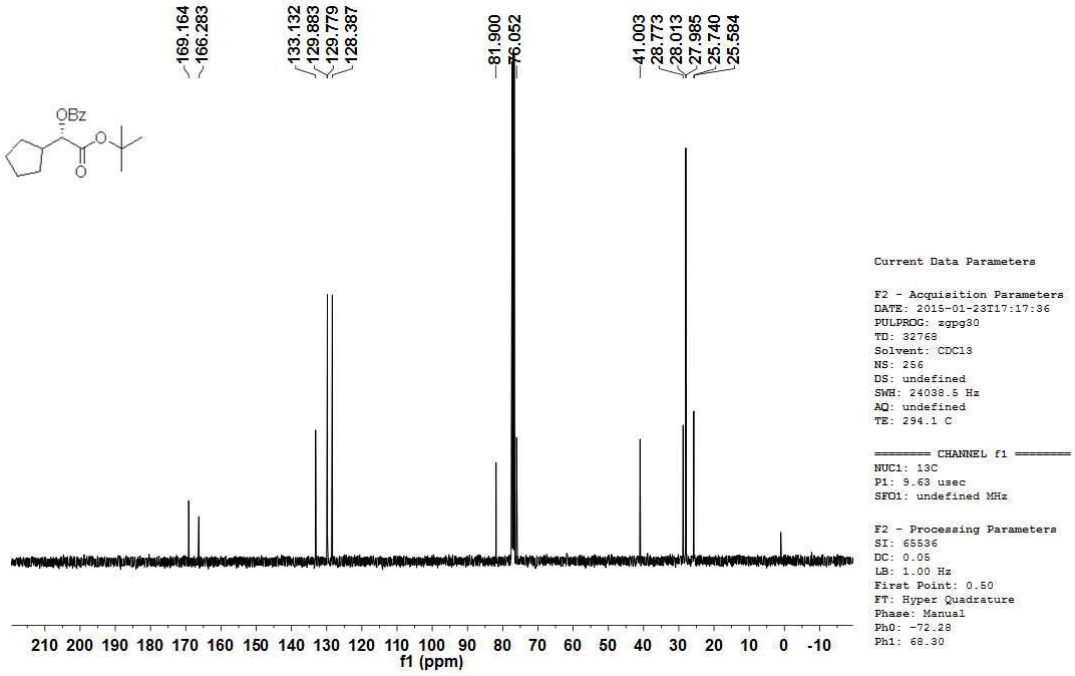
(*S*)-*tert*-butyl 2-cyclopentyl-2-hydroxyacetate (3av)



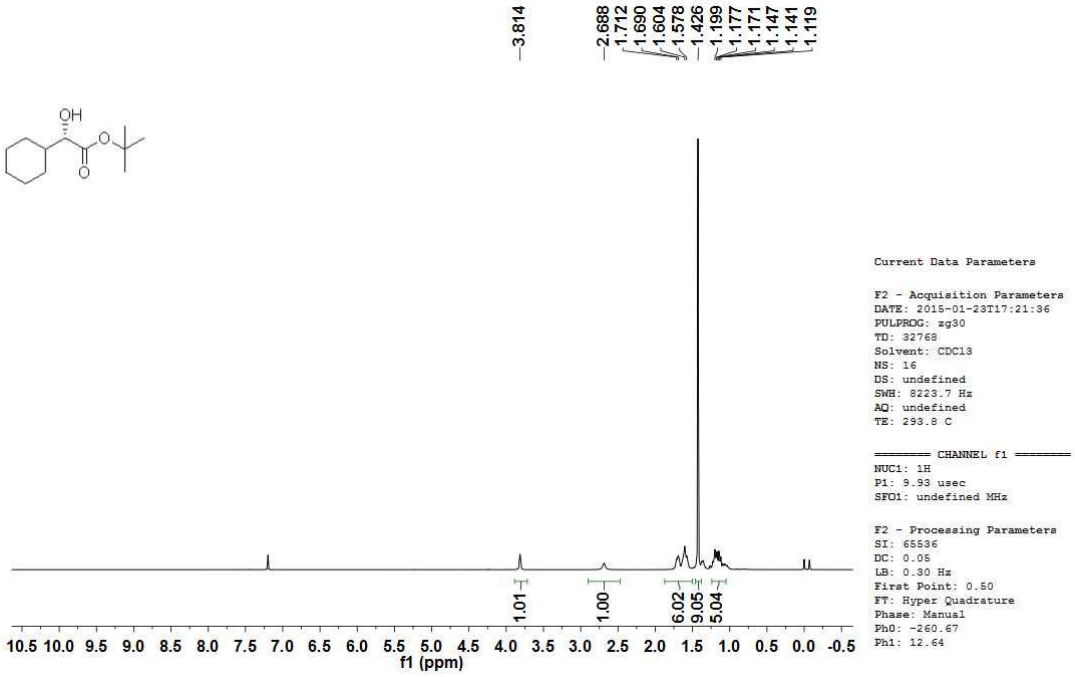


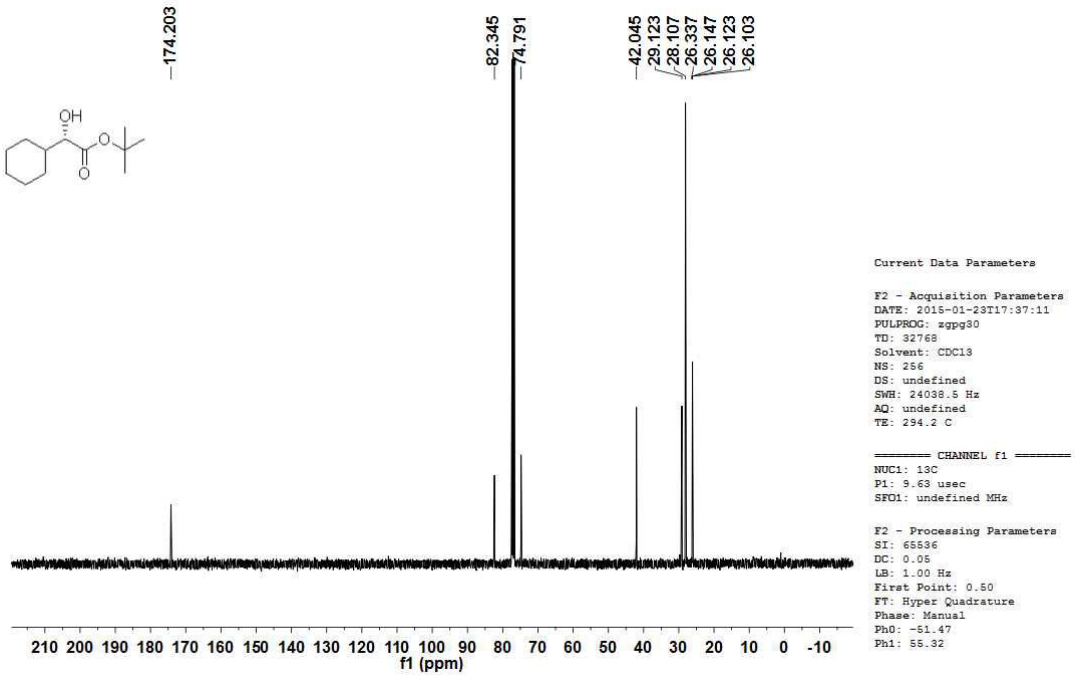
(*S*)-*tert*-butyl 2-benzoxy-2-cyclopentylacetate(4av)



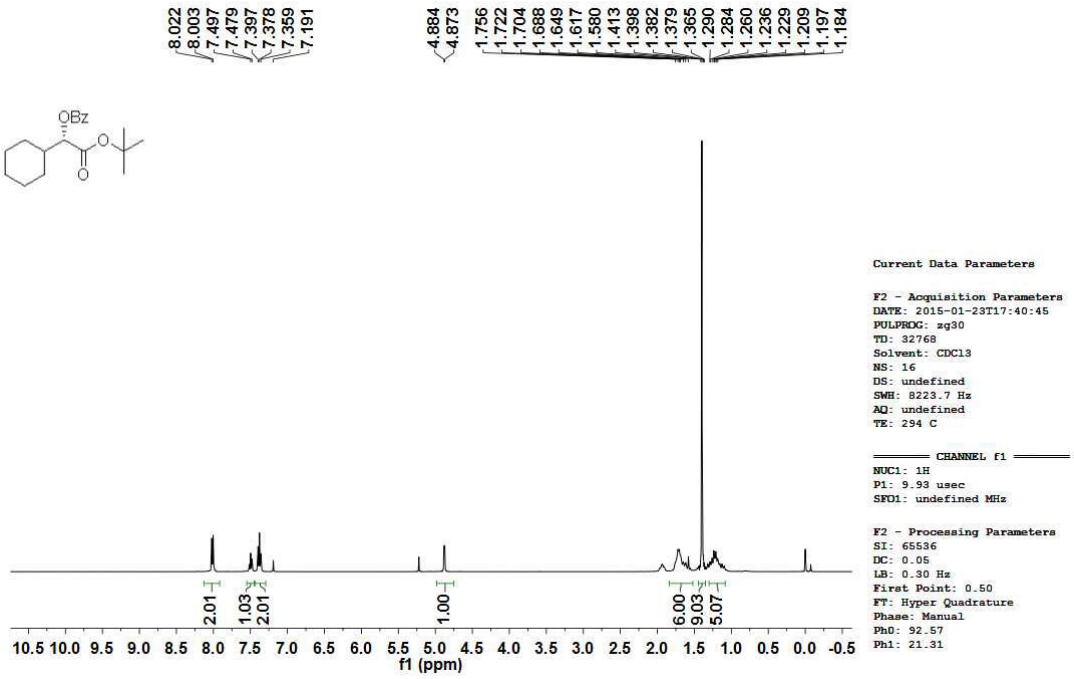


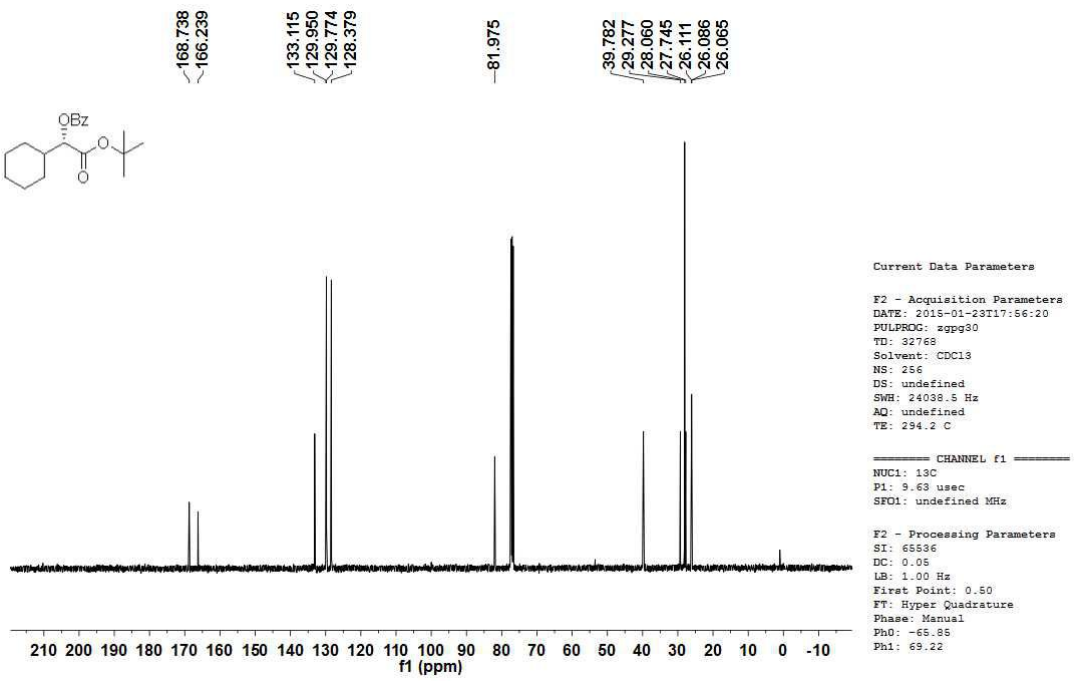
(*S*)-*tert*-butyl 2-cyclohexyl-2-hydroxyacetate (3aw)



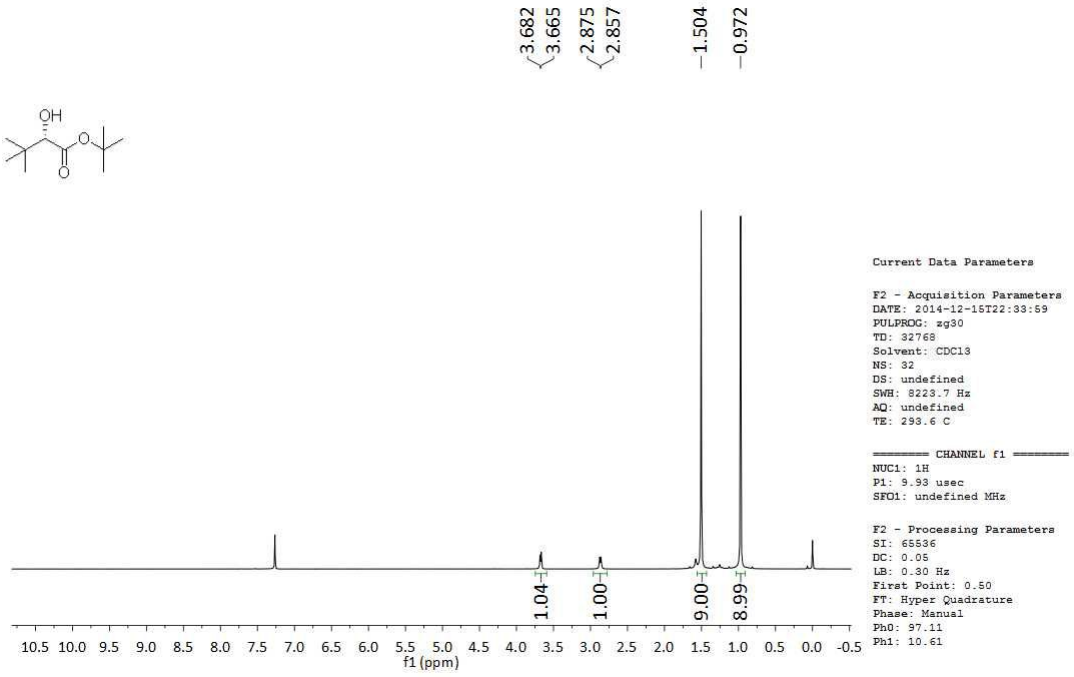


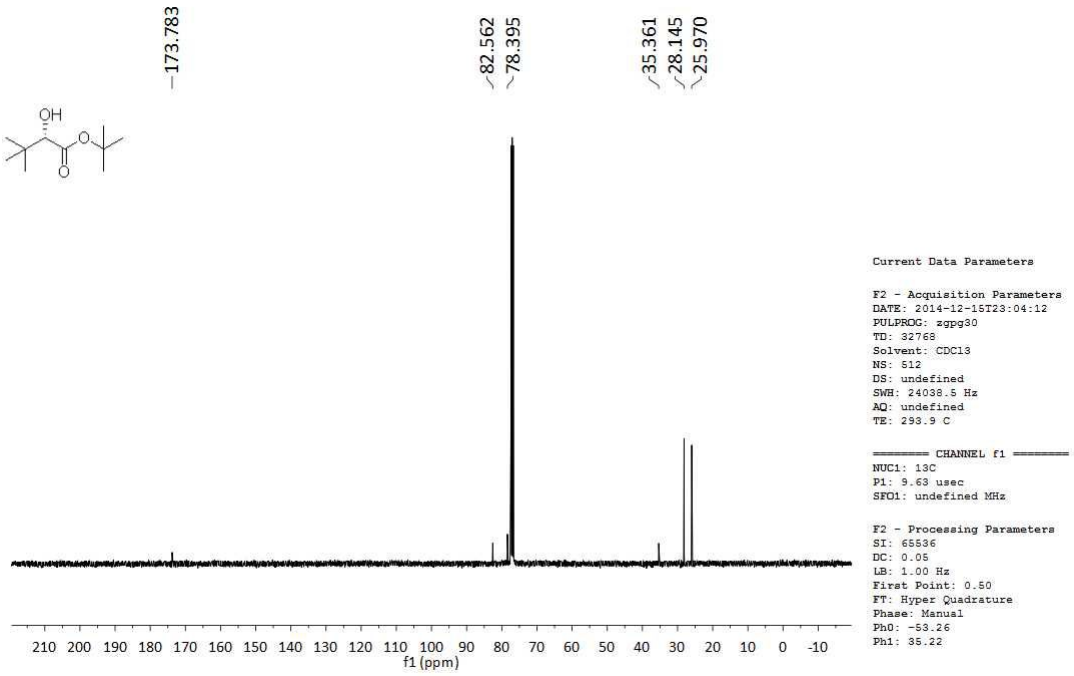
(*S*)-*tert*-butyl 2-benzoxy-2-cyclohexylacetate(4aw)



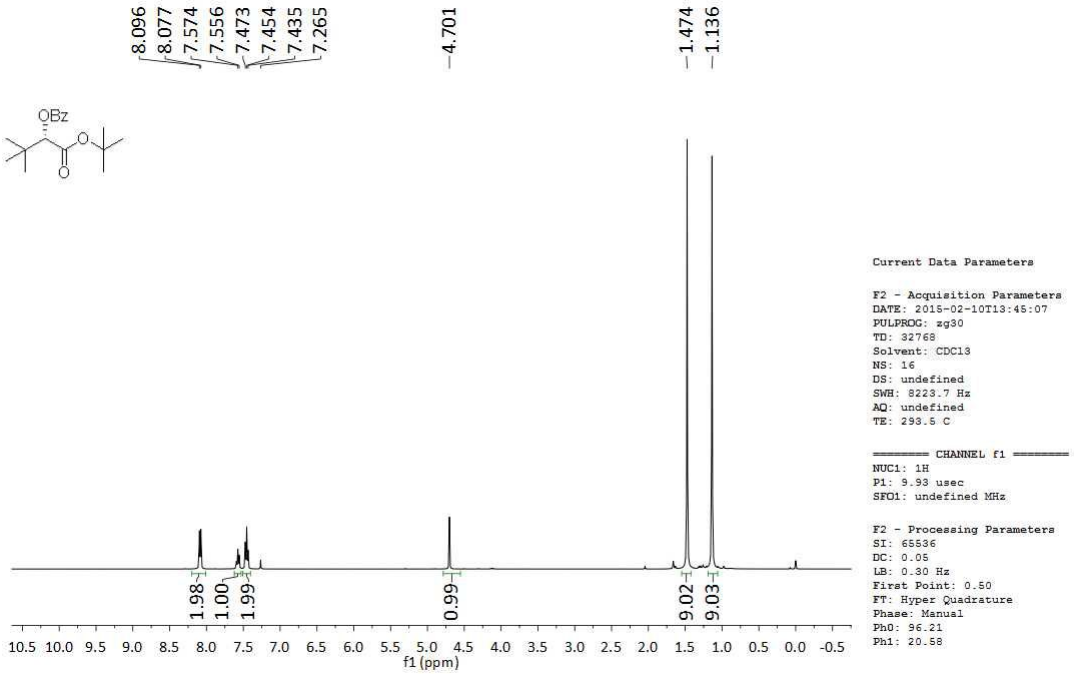


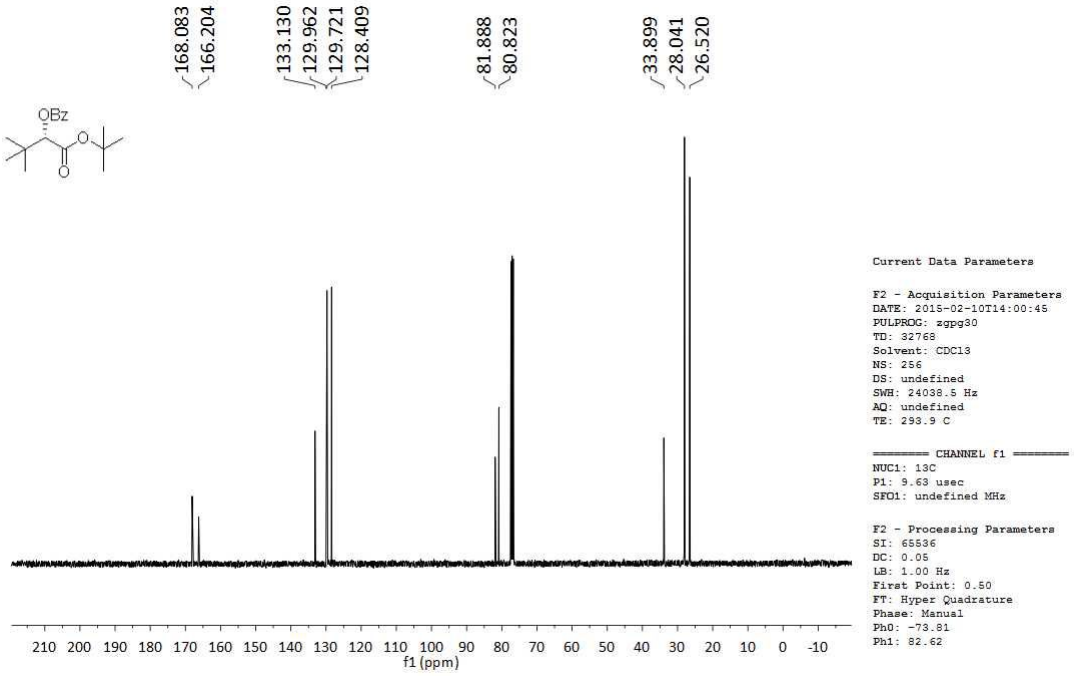
(*S*)-*tert*-butyl 2-hydroxy-3,3-dimethylbutanoate (3ax)



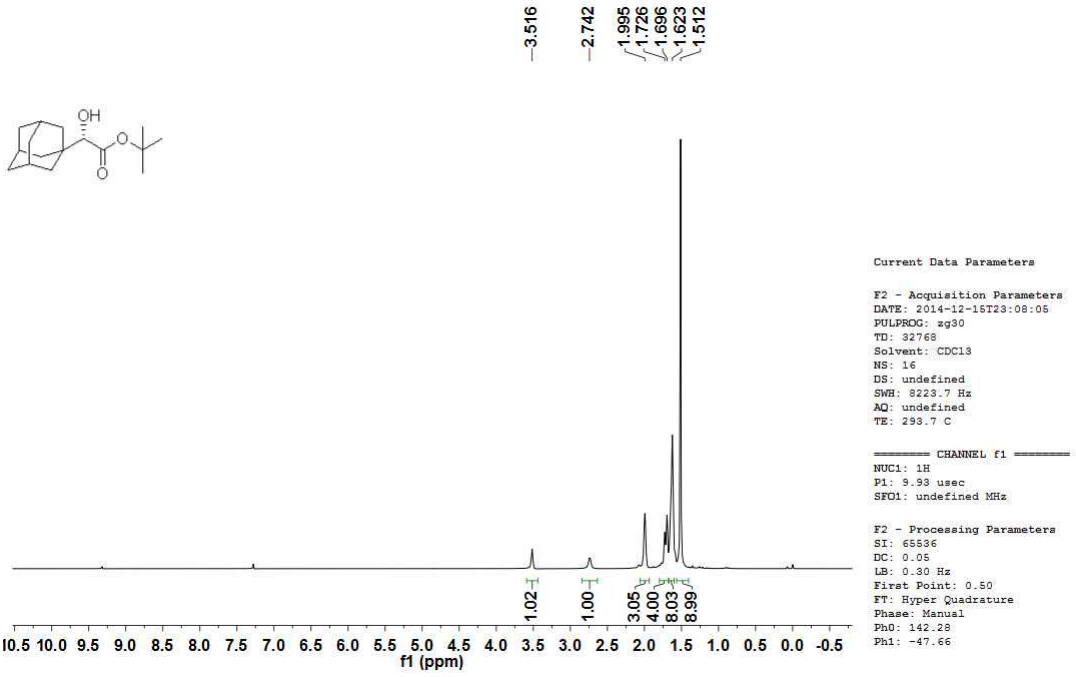


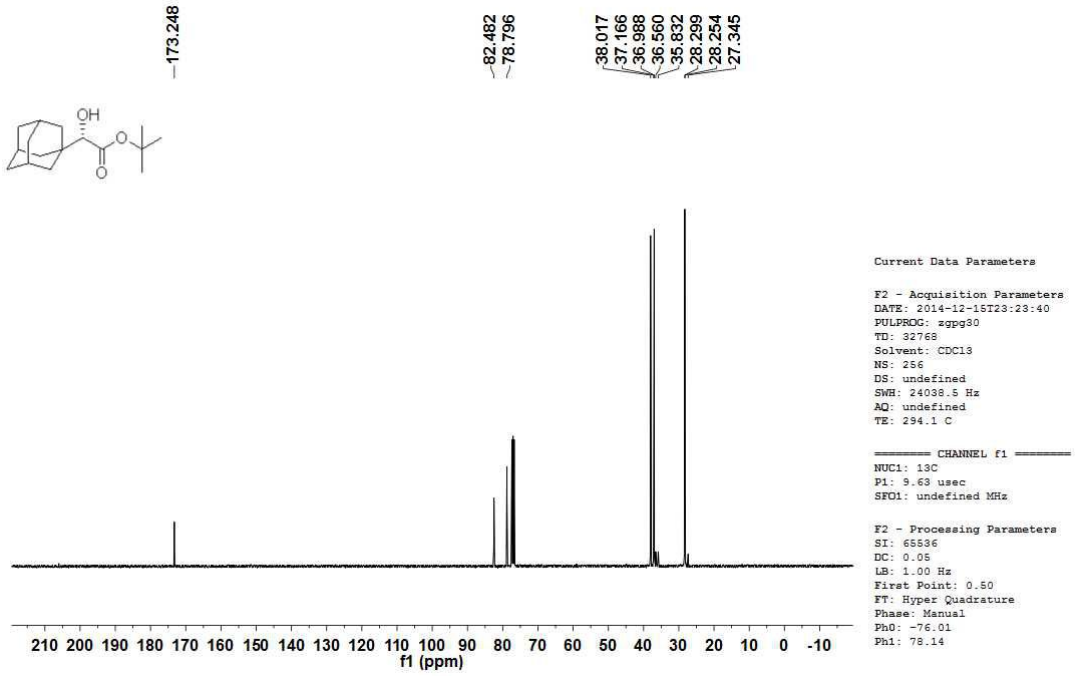
(*S*)-*tert*-butyl 2-hydroxy-3,3-dimethylbutanoate (4ax)



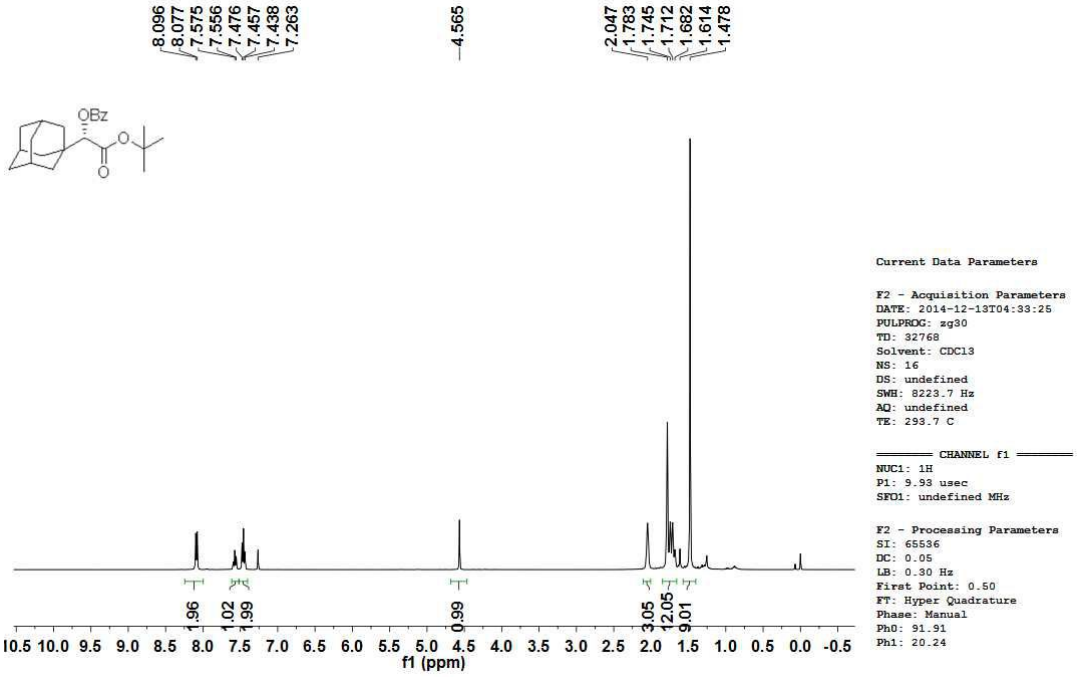


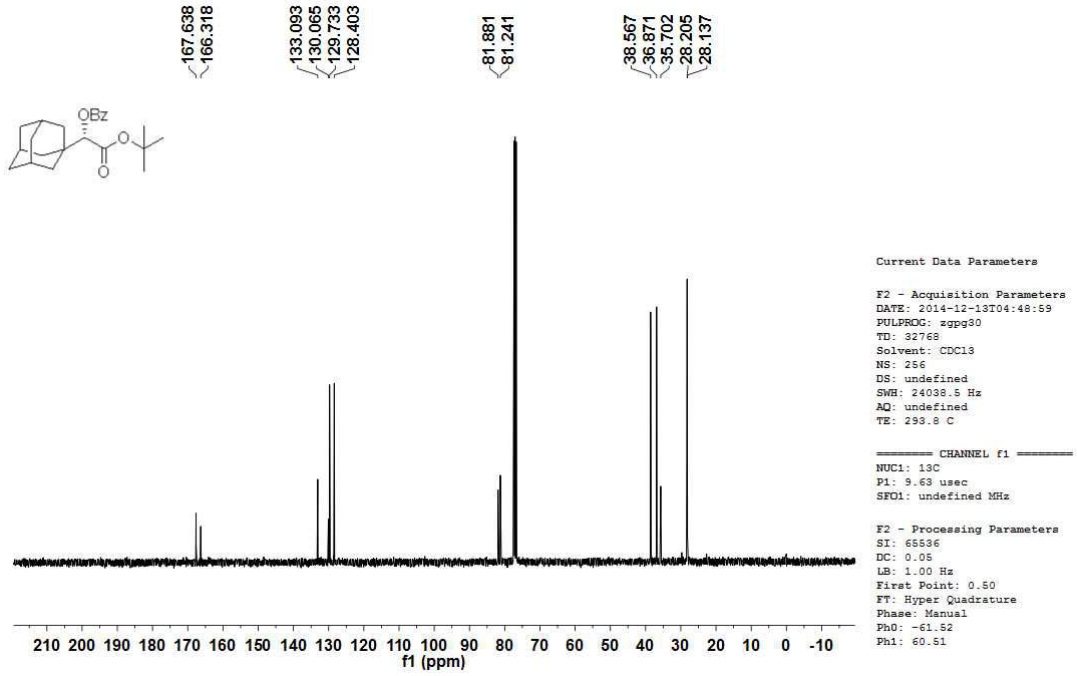
(*S*)-*tert*-butyl 2-hydroxy-2-(adamantan-1-yl)acetate (3ay)



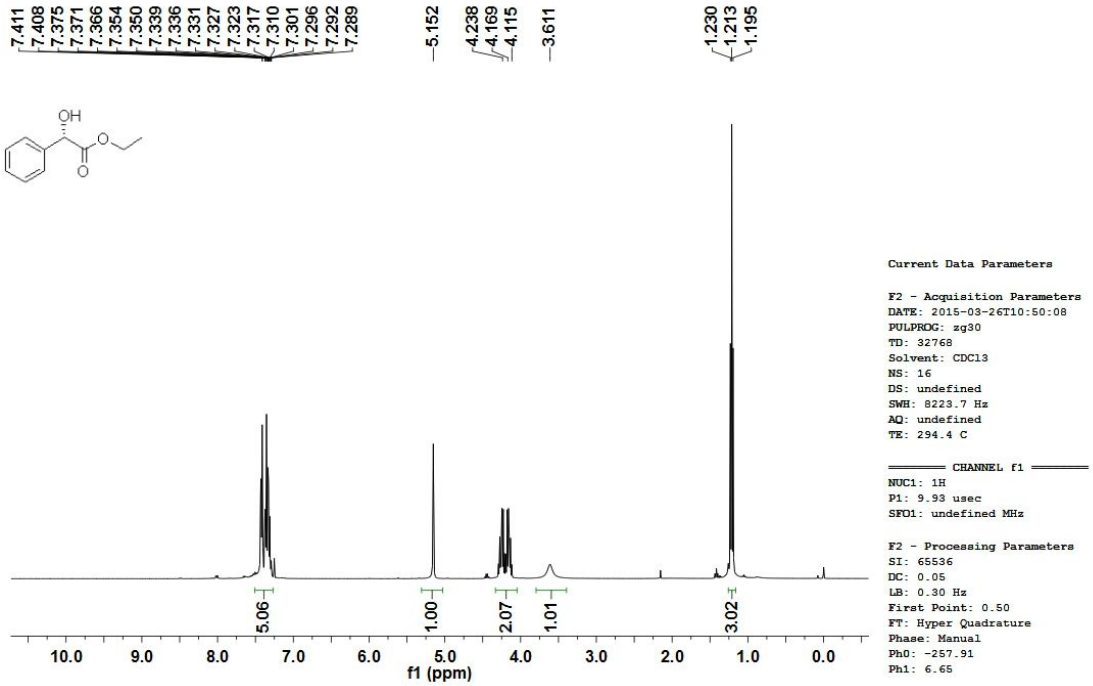


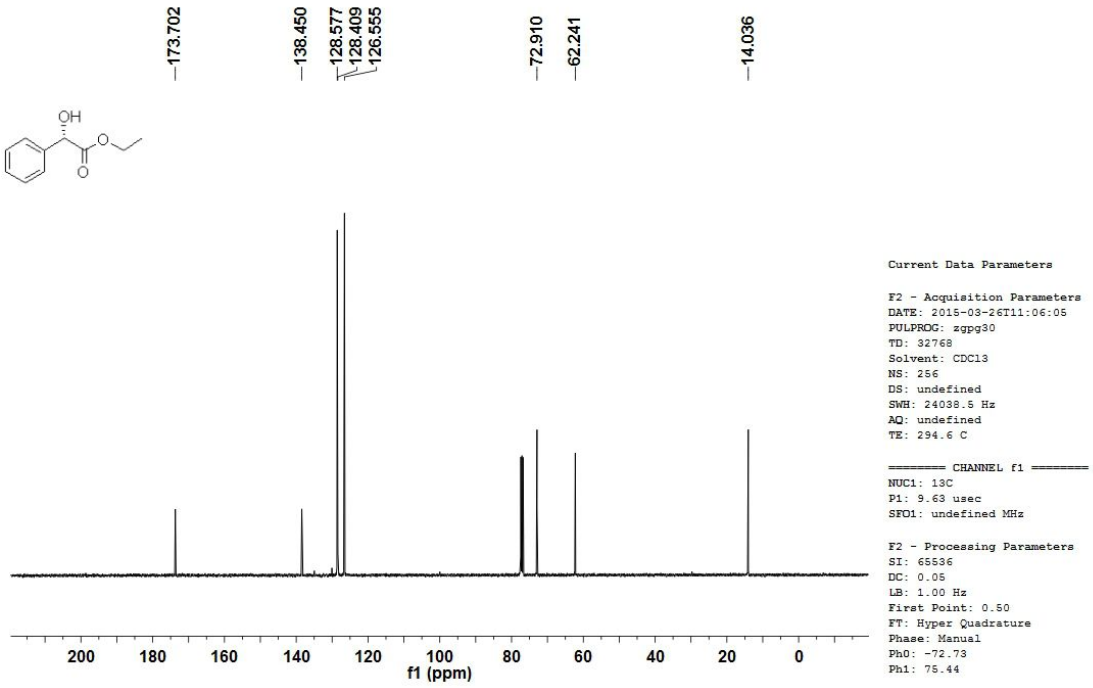
(*S*)-*tert*-butyl 2-benzoxy-2-(adamantan-1-yl)acetate (4ay)



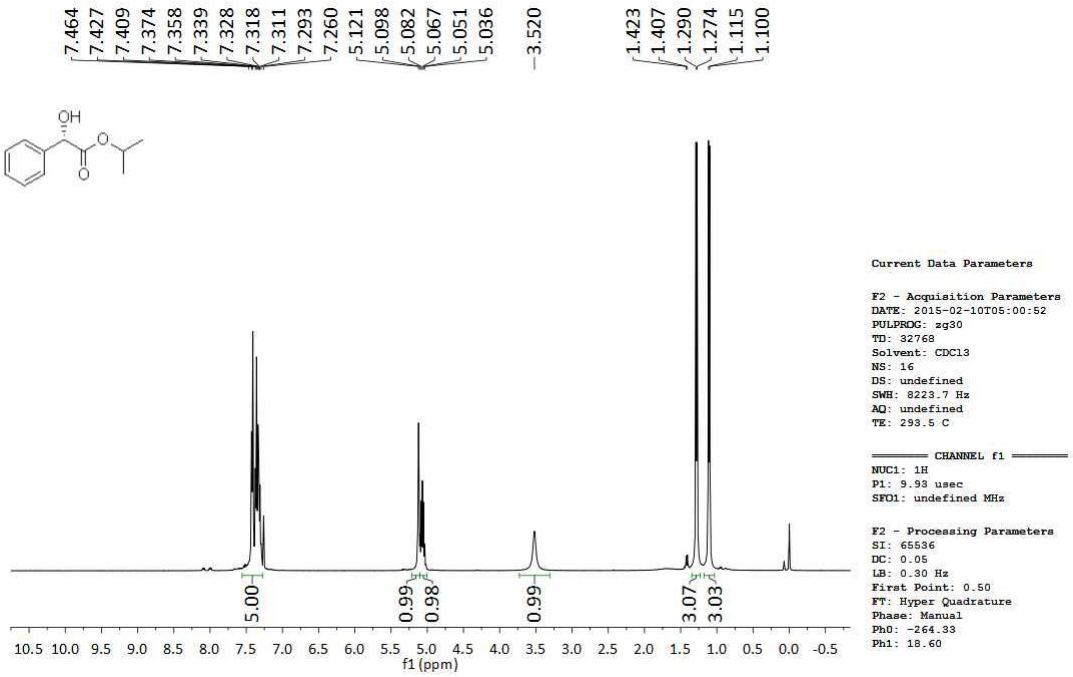


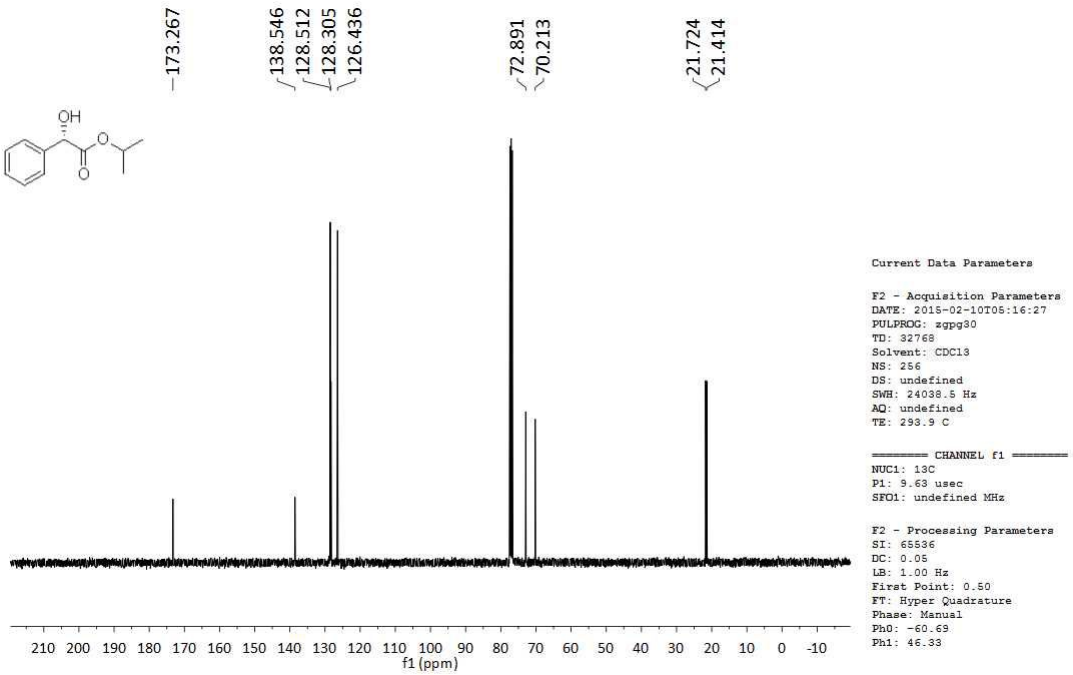
(*S*)- ethyl mandelate (3ba)



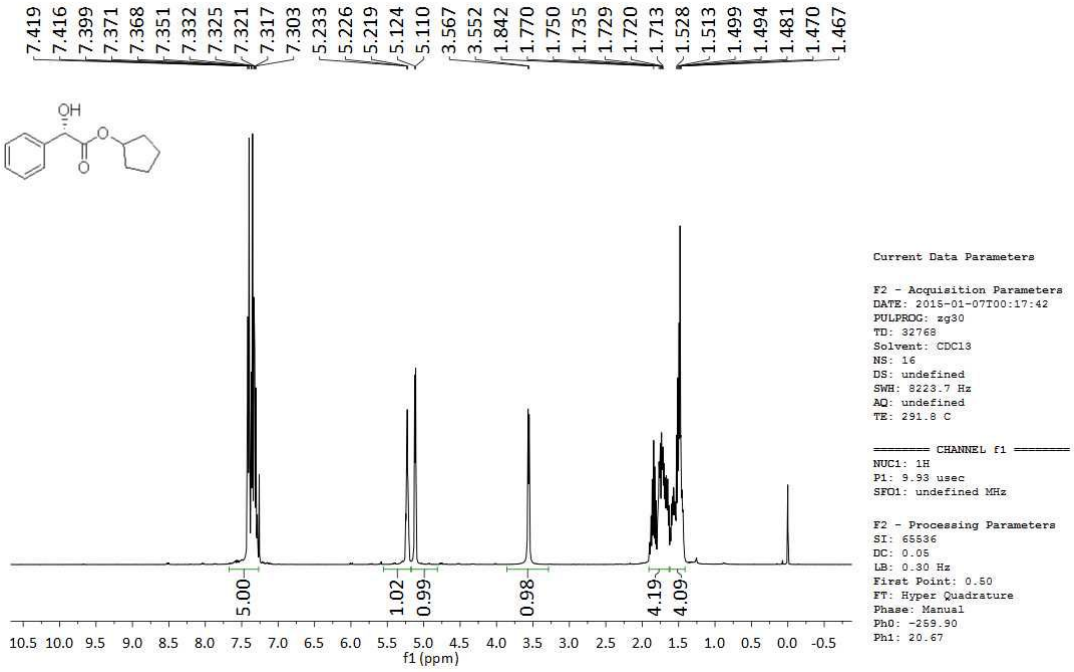


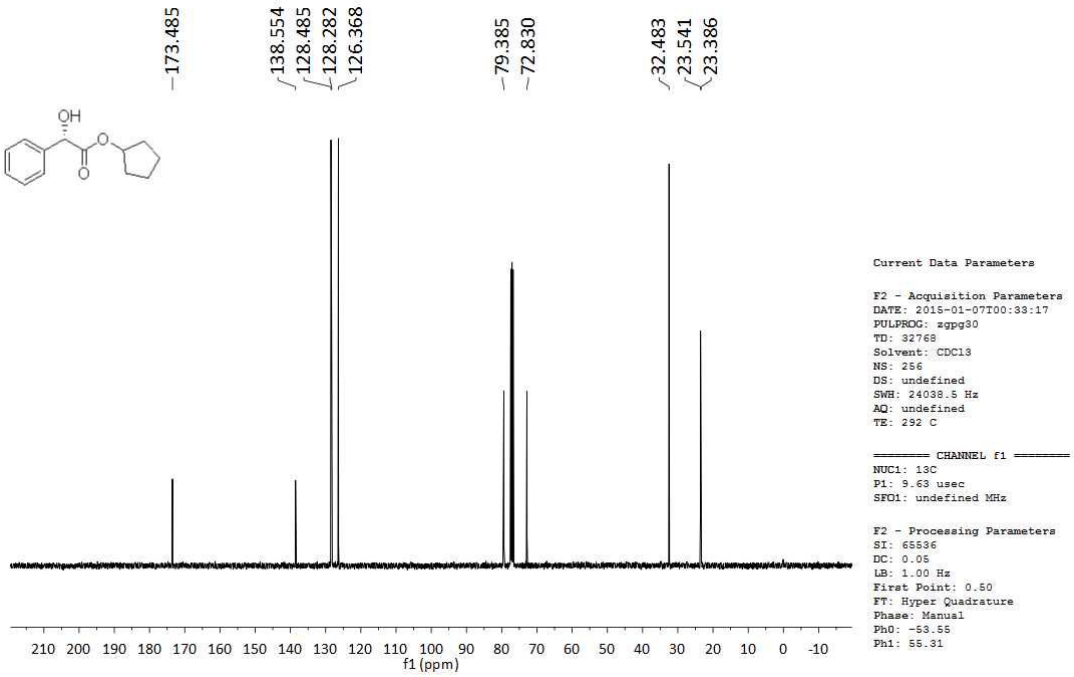
(*S*)-*iso*-propyl mandelate (3ca)



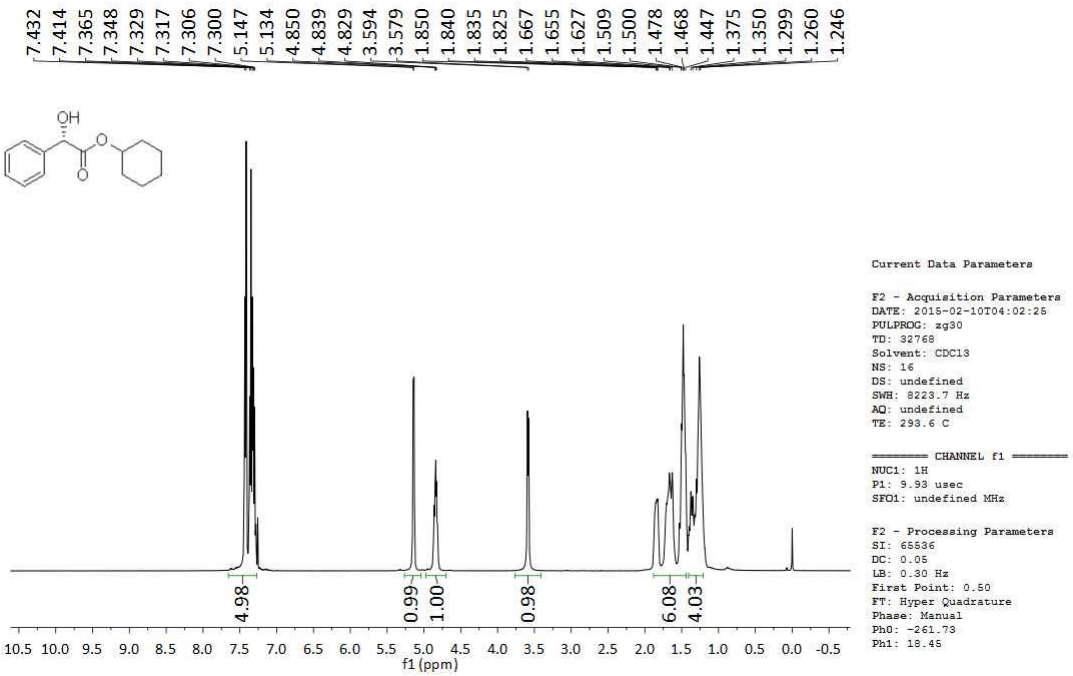


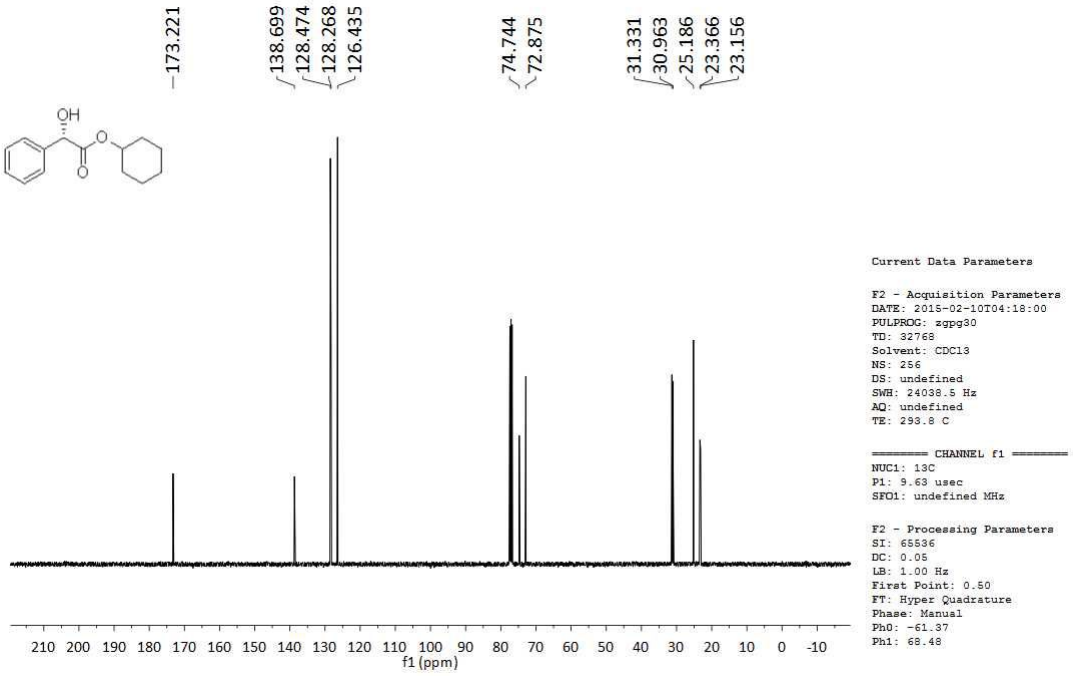
(*S*)-cyclopentyl mandelate (3da)



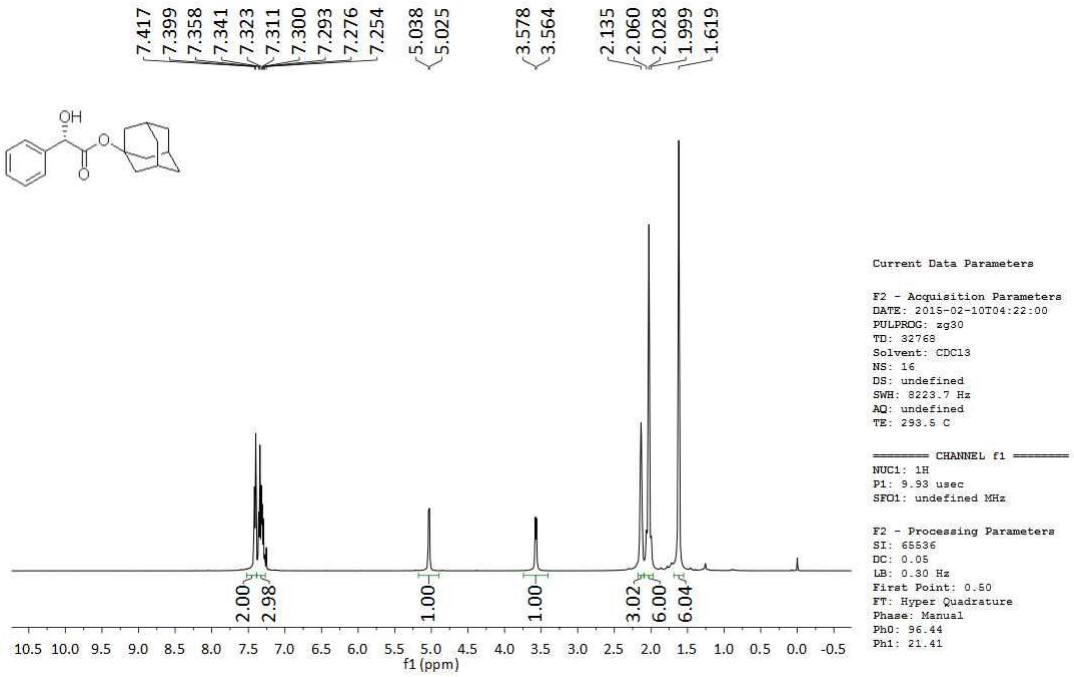


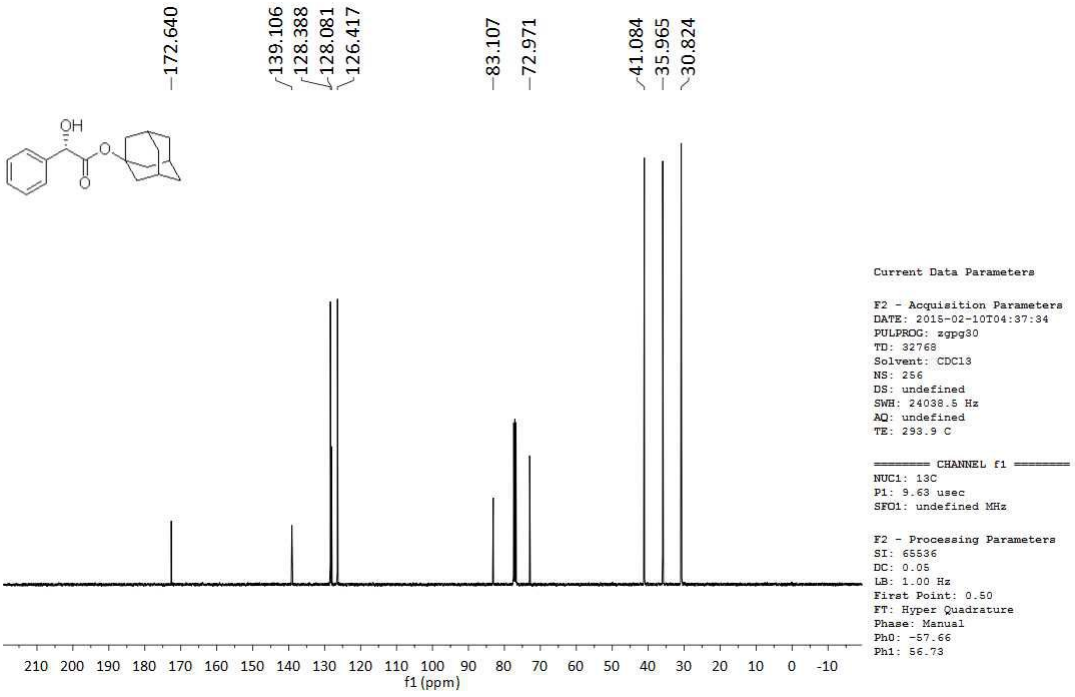
(*S*)-cyclohexyl mandelate (3ea)





(*S*)-adamant-1-yl mandelate (3fa)





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[2]P. Wang, W. Tao, X. Sun, S. Liao and Y. Tang, *J. Am. Chem. Soc*., 2013, **135**, 16849.

[3]J. M. Nathalie, M. G. Danielle, T. M. Jacques, L. G. René, *J. Org. Chem.*, 1996, **61**, 5067.

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