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# Catalytic Asymmetric Meerwein-Ponndorf-Verley Reduction of Glyoxylates Induced by Chiral *N*,*N′*-Dioxide/Y(OTf)$_3$ Complex

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## Electronic Supporting Information

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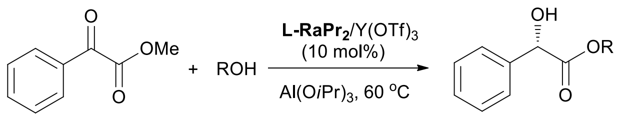
## (A) General information

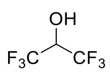
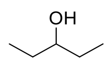
Reactions were carried out using commercial available reagents in oven-dried apparatus. $CHCl_3$ and *iso*-propanol were dried and distilled from calcium hydride under nitrogen just before use. Molecular sieves were dried at 500 ºC for 4 h and restored in nitrogen before use. $^1$H NMR spectra were recorded 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 and Phenomenex Lux 5u Cellulose-2 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]

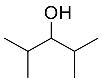
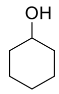
## (B) Optimization of the conditions for the asymmetric MPV reaction of glyoxylates

### Table S1: Screening of the secondary alcohols



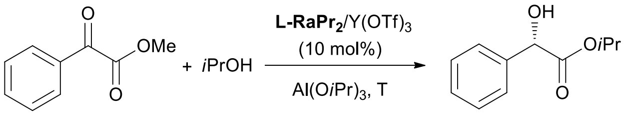

**1ab** **2a**

| Entry$^a$ | ROH | t (h) | Yield$^b$ (%) | ee$^c$ (%) |
|---|---|---|---|---|
| 1 |  | 48 | 0 | - |
| 2 |  | 48 | 0 | - |

| | | | | |
|---|---|---|---|---|
| 4 |  | 48 | 0 | - |
| 5 |  | 48 | 0 | - |

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_2$**/Y(OTf)$_3$ (1:1, 10 mol%), **1ab** (0.1 mmol), Al(O*i*Pr)$_3$ (0.05 mmol) in ROH (0.1 M) at 60 ºC for 3 h without extrusion of air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

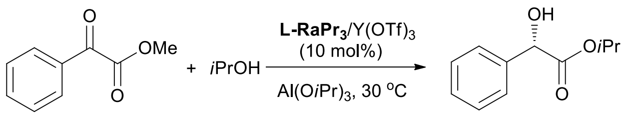
## Table S2: Screening of the reaction temperature




| Entry[a] | T (ºC) | t (h) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|
| 1 | 60 | 3 | 99 | 63 |
| 2 | 50 | 3 | 99 | 69 |
| 3 | 40 | 5 | 99 | 71 |
| 4 | 30 | 24 | 99 | 73 |
| 5[d] | 30 | 24 | 99 | 75 |
| 6[d] | 0 | 24 | n.r. | - |

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_2$**/Y(OTf)$_3$ (1:1, 10 mol%), **1b** (0.1 mmol), Al(O*i*Pr)$_3$ (0.05 mmol) in *i*PrOH (0.1 M) without extrusion of air. [b] Yields of the isolated products. [c] Determined by HPLC analysis using a chiral stationary phase. [d]**L-RaPr$_3$**/Y(OTf)$_3$ was used as catalyst.

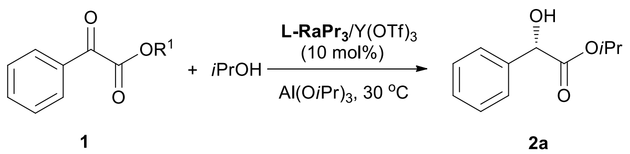
## Table S3: Screening of the addictives



| Entry[a] | Additive | t (h) | Yield(%)[b] | *ee*(%)[c] |
|---|---|---|---|---|
| 1 | LiNTf | 12 | 69 | 72 |
| 2[d] | 3 Å MS | 12 | 99 | 71 |
| 3[e] | 4 Å MS | 12 | 99 | 71 |
| 4 | $Na_2SO_4$ | 12 | 54 | 67 |
| 5 | TsOH | 12 | trace | - |
| 6 | m-CPBA | 12 | trace | - |
| 7 | TEMPO | 12 | 74 | 69 |
| 8 | DMAP | 12 | 46 | 67 |
| 9 | $KHSO_4$ | 12 | 34 | 72 |
| 10 | $NH_4Cl$ | 12 | 26 | 26 |
| 11 | $K_2CO_3$ | 12 | 46 | 71 |
| 12 | $LiOH•H_2O$ | 12 | 32 | 73 |
| 13 | - | 12 | 49 | 72 |

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_3$**/Y(OTf)$_3$ (1:1, 10 mol%), **1b** (0.1 mmol), Al(O*i*Pr)$_3$ (0.05 mmol) and additive (0.1 mmol) in *i*PrOH (0.1 M) at 30 °C for 12 h without extrusion of air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase. [d]3 Å MS (25 mg) were added. [e]4 Å MS (25 mg) were added.

## Table S4: Screening of the ester group on the substrates

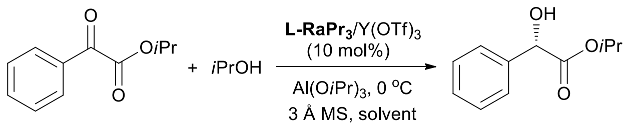



| Entry[a] | R[1] | t (h) | Yield(%)[b] | *ee*(%)[c] |
|---|---|---|---|---|
| 1 | Me (**1ab**) | 12 | 49 | 72 |
| 2 | *i*Pr (**1a**) | 4 | 99 | 73 |
| 3 | *t*Bu (**1ac**) | 14 | 99 | 73 |

| | | | | |
|---|---|---|---|---|
| 4 | Bn (**1ad**) | 24 | 99 | 71 |
| 5[d] | *i*Pr (**1a**) | 12 | 85 | 79 |
| 6[e] | *i*Pr (**1a**) | 24 | 78 | 86 |

[a]Unless otherwise noted, the reactions were performed with **L-RaPr₃**/Y(OTf)₃ (1:1, 10 mol%), **1** (0.1 mmol), Al(O*i*Pr)₃ (0.05 mmol), 3 Å MS (25 mg) in *i*PrOH (0.1 M) at 30 ºC without extrusion of air. [b] Yields of the isolated products. [c] Determined by HPLC analysis using a chiral stationary phase. [d]Performed at 0 ºC. [e]Performed at -10 ºC.

## Table S5: Screening of the solvent

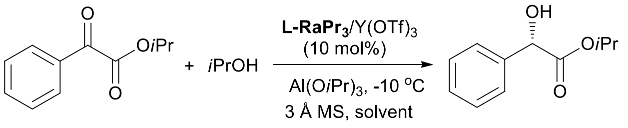



| Entry[a] | solvent | solvent volume, *i*PrOH:solvent ratio | t (h) | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|---|---|
| 1 | DCM | 1.0 mL, 1:3 | 12 | 82 | 84 |
| 2 | $CHCl_3$ | 1.0 mL, 1:3 | 12 | 70 | 86 |
| 3 | DCE | 1.0 mL, 1:3 | 12 | 75 | 80 |
| 4 | $CHCl_2$-$CHCl_2$ | 1.0 mL, 1:3 | 12 | 80 | 81 |
| 5 | $CH_3$-$CCl_3$ | 1.0 mL, 1:3 | 12 | 69 | 80 |
| 6 | $CH_2Cl$-$CHCl_2$ | 1.0 mL, 1:3 | 12 | 85 | 83 |
| 7 | toluene | 1.0 mL, 1:3 | 12 | 73 | 82 |
| 8 | $CHCl_3$ | 1 mL, 5:1 | 24 | 99 | 85 |
| 9 | $CHCl_3$ | 1 mL, 3:1 | 24 | 99 | 85 |
| 10 | $CHCl_3$ | 1 mL, 1:1 | 24 | 97 | 86 |
| 11 | $CHCl_3$ | 1 mL, 1:2 | 24 | 93 | 87 |
| 12 | $CHCl_3$ | 1 mL, 1:3 | 24 | 90 | 87 |
| 13 | $CHCl_3$ | 1 mL, 1:5 | 24 | 84 | 87 |

[a]Unless otherwise noted, the reactions were performed with **L-RaPr₃**/Y(OTf)₃ (1:1, 10 mol%), **1** (0.1 mmol), Al(O*i*Pr)₃ (0.05

mmol), 3 Å MS (25 mg) in *i*PrOH/$CHCl_3$ (v/v = 1/2, 0.1 M) at 0 ºC for 12 h without extrusion of air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

## Table S6: Screening of the amount of addictives

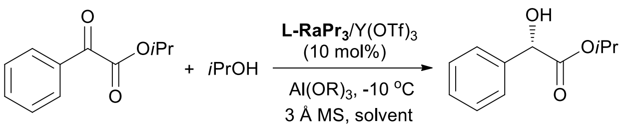



**1a** **2a**

| Entry[a] | 3 Å MS (mg) | Al(O*i*Pr)$_3$ (mmol) | t (h) | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|---|---|
| 1 | 25 | 0.1 | 24 | 82 | 86 |
| 2 | 25 | 0.05 | 24 | 78 | 86 |
| 3 | 25 | 0.02 | 24 | 70 | 86 |
| 4 | 25 | 0.01 | 24 | 64 | 86 |
| 5 | 100 | 0.1 | 24 | 71 | 84 |
| 6 | 50 | 0.1 | 24 | 67 | 84 |
| 7 | 10 | 0.1 | 24 | 72 | 85 |
| 8 | 5 | 0.1 | 24 | 68 | 86 |

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_3$**/Y(OTf)$_3$ (1:1, 10 mol%), **1** (0.1 mmol), Al(O*i*Pr)$_3$, 3 Å MS in *i*PrOH and solvent at 0 ºC for 12 h without extrusion of air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

## Table S7: Screening of the aluminium alkoxides



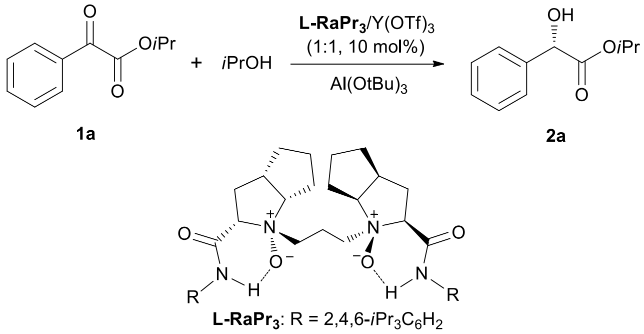

**1a** **2a**

| Entry[a] | Al(OR)$_3$ | t (h) | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|---|
| 1 | Al(OEt)$_3$ | 24 | 77 | 85 |
| 2 | Al(O*i*Pr)$_3$ | 24 | 78 | 86 |

| | | | | |
|---|---|---|---|---|
| 3 | Al(O*t*Bu)$_3$ | 24 | 79 | 91 |

[a]Unless otherwise noted, the reactions were performed with **L-RaPr$_3$**/Y(OTf)$_3$ (1:1, 10 mol%), **1** (0.1 mmol), Al(O*i*Pr)$_3$ (0.05 mmol), 3 Å MS (25 mg) in *i*PrOH and solvent at 0 ºC for 12 h without extrusion of air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

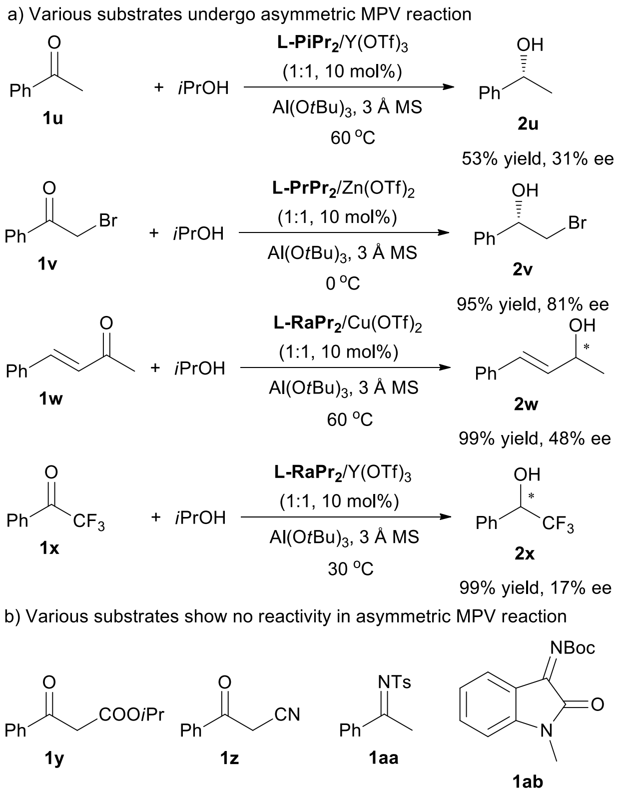
## Table S8: Probing of the effect of the additives.




| Entry[a] | T (ºC) | t (h) | Additive | Yield[b] (%) | Ee[c] (%) |
|---|---|---|---|---|---|
| 1 | 30 | 24 | - | trace | n.d. |
| 2 | 30 | 24 | 3 Å MS | 82 | 73 |
| 3 | 30 | 14 | Al(O*t*Bu)$_3$ | 99 | 73 |
| 4 | 30 | 3 | 3 Å MS, Al(O*t*Bu)$_3$ | 99 | 73 |
| 5 | 0 | 24 | - | n.r. | - |
| 6 | 0 | 24 | 3 Å MS | n.r. | - |
| 7 | 0 | 24 | Al(O*t*Bu)$_3$ | n.r. | - |
| 8 | 0 | 24 | 3 Å MS, Al(O*t*Bu)$_3$ | 99 | 87 |

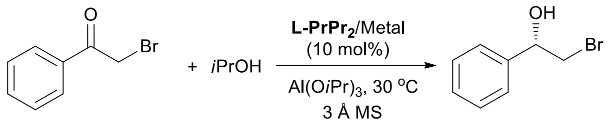
[a]Unless otherwise noticed, the reactions were performed with **L-RaPr$_3$**-Metal (1:1, 10 mol%), **1a** (0.10 mmol) and 3Å MS (25 mg) in *i*PrOH/CHCl$_3$ (v/v = 1/2, 0.1 M) in air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

## (C) Optimization of the conditions for the asymmetric MPV reaction of other ketones.




With the success in the reduction of gloxylates, we were encouraged to apply such method to a variety of substrates. After a serious of condition screening, we established the MPV reaction of α-bromoacetophenone **1v** with *iso*-propanolin the presence of 3 Å MS and Al(O*i*Pr)$_3$by employing **L-PrPr$_2$**/Zn(OTf)$_2$ complex as the catalyst at 0 °C for 120 h, and obtained 95% yield and 81% ee (Scheme 3). Other types of substrates were also under investigation. Simple ketones such as **1u** and **1w** had low reaction reactivity and often require high reaction temperature. The 2,2,2-trifluoacetophenone (**1x**) gave a higher reactivity as the trifluomethyl group serves as a efficient electrodrawing group. However, the stereo control was not satisfying after a serious of screening. For substrates **1y** and **1z**, which more inclined to form an enol, the MPV reduction is reluctant, either stablized via a hydrogen bond (**1y**), or a conjugating effect (**1z**). Enlightened by previous work,[10e] we also expanded substrate scope to ketimines **1aa** and **1ab**, yet no desired product was formed. Such facts portrayed the property of chemical specificity towards carbonyl groups in the MPV reaction, and enols or imines were nonreactive.

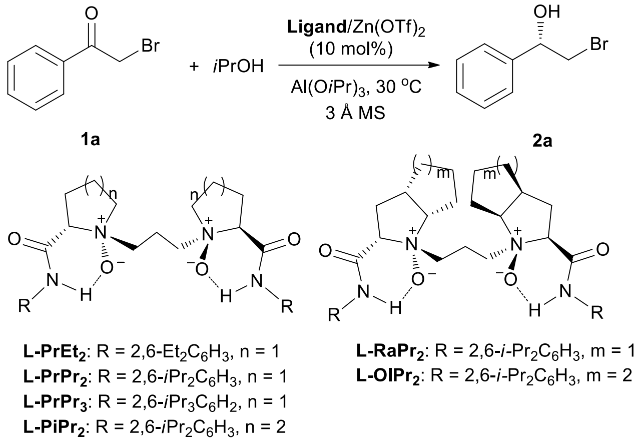
## Table S9: Screening of the metal salts




| Entry[a] | Metal | t (h) | Yield(%)[b] | ee(%)[c] |
|---|---|---|---|---|
| 1 | $Sc(OTf)_3$ | 24 | 99 | 61 |
| 2 | $Y(OTf)_3$ | 24 | 99 | 67 |
| 3 | $La(OTf)_3$ | 24 | 0 | - |
| 4 | $Yb(OTf)_3$ | 48 | 99 | 58 |
| 5 | $Zn(OTf)_2$ | 24 | 99 | 73 |
| 6 | $Ba(OTf)_2$ | 24 | 99 | 71 |
| 7 | $Zn(NTf)_2$ | 72 | 0 | - |
| 8 | $Zn(ClO_4)_2$ | 72 | 0 | - |
| 9 | $Zn(BF_4)_2$ | 72 | 0 | - |
| 10 | $ZnBr_2$ | 72 | 0 | - |

[a]Unless otherwise noted, the reactions were performed with **L-PrPr$_2$**-metal (1:1, 10 mol%), **1** (0.1 mmol), Al(O*i*Pr)$_3$ (0.1 mmol), 3 Å MS (25 mg) in *i*PrOH and solvent at 30 °C without extrusion of air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase.

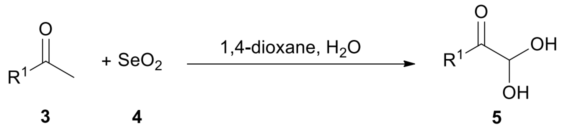
## Table S10: Screening of the ligands



| Entry[a] | Metal | t (h) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|
| 1 | L-PrEt$_2$ | 24 | trace | 50 |
| 2 | L-PrPr$_2$ | 24 | 99 | 73 |
| 3 | L- PrPr$_3$ | 24 | 99 | 64 |
| 4 | L-PiPr$_2$ | 24 | 99 | 69 |
| 5 | L- RaPr$_2$ | 24 | 99 | 43 |
| 6[d] | L-PrPr$_2$ | 120 | 90 | 80 |
| 7[d,e] | L-PrPr$_2$ | 120 | 95 | 81 |

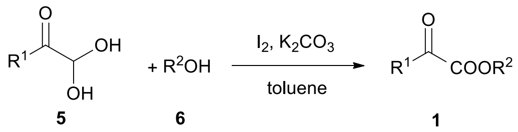
[a]Unless otherwise noted, the reactions were performed with **L**-Zn(OTf)$_2$ (1:1, 10 mol%), **1** (0.1 mmol), Al(O*i*Pr)$_3$ (0.1 mmol), 3 Å MS (25 mg) in *i*PrOH at 30 °C without extrusion of air. [b]Yields of the isolated products. [c]Determined by HPLC analysis using a chiral stationary phase. [d]The reaction proceed at 0 °C. [e]Al(O*t*Bu)$_3$ (0.1 mmol) were used instead of Al(O*i*Pr)$_3$.

## (D) Methods for the preparation of α-keto esters.



Glyoxal monohydrides **5a**–**5u** were prepared according to the methods reported in the literature.[2] Into a dry flask were added $SeO_2$ **4** (11 mmol), 2,6-dioxane (7.5 mL) and $H_2O$ (0.6 mL) and the reaction mixture was stirred at 50 °C until **4** dissolve completely. Then acetyl compound **3** (10 mmol) was added and the reaction mixture was stirred at 100 ºC. The reaction was monitored under TLC.

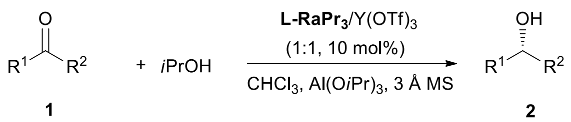
The reaction mixture was filtered through a pad of celite and the solvent was removed under reduced pressure. Purification was accomplished by flash column chromatography and recrystallization with water, and a white to pale yellow solid **5** was obtained.




α-Keto esters **1a–1u**, **1ab**, **1ac** and **1ad** were prepared according to the methods reported in the literature.[3] Into a dry flask were added **5** (5 mmol), toluene (10 mL) and **6** (7.5 mmol) and the reaction mixture was stirred room temperature until **5** dissolve completely. Then $I_2$ (5 mmol) and $K_2CO_3$ (10 mmol) were added to the reaction mixture and the reaction was monitored under TLC.

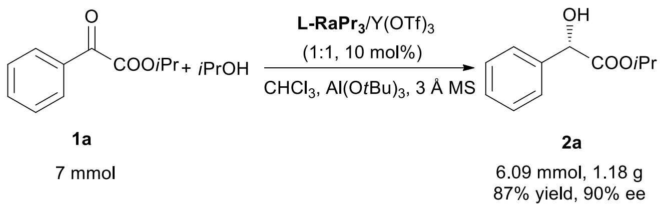
The reaction mixture was washed with aqueous $Na_2SO_3$ solution and the solvent was removed under reduced pressure. Purification was accomplished by flash column chromatography and distillation, and a colorless to pale yellow liquid **1** was obtained.

**(E) Typical procedure for the asymmetric MPV reaction**




Chiral *N*,*N'*-dioxide **L-RaPr₃** (10 mol%), $Y(OTf)_3$ (10 mol%), 3 Å MS (25 mg), and $Al(OtBu)_3$ (50 mol%)were added in a dry reaction tube, then *i*PrOH/$CHCl_3$ (v/v = 1/2, 1 mL) was added in air. The mixture was stirred at 30ºC for 30 min. Then, **1** (0.1 mmol) were added. The reaction was stirred vigorously at -10ºC for 72 h and at 0 ºC for 48 h. The mixture was purified by column chromatography on silica gel to afford the desired product **2**. The yields of **2** were calculated according to the amount of **1**.

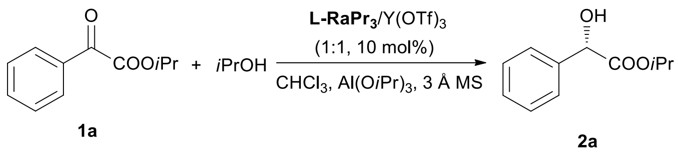
## (F) Gram-scale experiment



Chiral *N*,*N'*-dioxide **L-RaPr3** (10 mol%), $Y(OTf)_3$ (10 mol%), 3 Å MS (1.750 g), and $Al(OtBu)_3$ (50 mol%) were added in a dry reaction vessel, then *i*PrOH/$CHCl_3$ (v/v = 1/2, 70 mL) was added in air. The mixture was stirred at 30 ºC for 30 min. Then, **1a** (0.1 mmol) were added. The reaction was stirred vigorously at -10 ºC for 72 h and at 0 ºC for 48 h. The mixture was purified by column chromatography on silica gel to afford the desired product **2a**. The yield of **2a** was calculated according to the amount of **1a**.

## (G) Kinetic information.

1. General procedures.



Chiral *N*,*N'*-dioxide **L-RaPr3** (10 mol%), $Y(OTf)_3$ (10 mol%), 3 Å MS (25 mg), and $Al(OtBu)_3$ (50 mol%) were added in a dry reaction tube, then *i*PrOH/$CHCl_3$ (1 mL) was added in air. The mixture was stirred at 20ºC for 30 min. Then, **1a** (0.1 mmol) were added. The reaction was stirred vigorously at 20 ºC minor portion (approx. 20 μL) of the reaction mixture at certain reaction time. Each portion of the mixture was filtered through a pad of celite. After removal of solvent, the residue was analysized via HPLC.

In the HPLC, the amount of substance *N* is proportional to the chromatographic peak area.

$$N_i = f_i A_i \,.$$

In the equation, $A_i$ refers to chromatographic peak area of the substance, $f_i$ refers to the correction factors of peak area. For **1a** and **2a**, it is deduced that,

$$f_{2a}/f_{1a} = (N_{2a} A_{1a})/ (N_{1a} A_{2a}).$$

In order to obtain $f_{1a}/f_{2a}$ , a serious of mixture of **1a** and **2a** were analyzed.

| Entry | $N_{2a} / N_{1a}$ | $A_{1a}/A_{2a}$ | $f_{2a}/f_{1a}$ |
|---|---|---|---|
| 1 | 0.01 | 276.7 | 2.77 |
| 2 | 0.03 | 88.29 | 2.65 |
| 3 | 0.05 | 54.87 | 2.74 |
| 4 | 0.1 | 26.32 | 2.63 |
| 5 | 0.15 | 18.88 | 2.83 |
| 6 | 0.2 | 13.16 | 2.63 |
| 7 | 0.25 | 10.20 | 2.55 |
| 8 | 0.3 | 8.49 | 2.55 |
| 9 | 0.4 | 6.45 | 2.58 |
| 10 | 0.6 | 4.37 | 2.62 |
| 11 | 0.8 | 3.34 | 2.68 |
| | | | 2.66[a] |

[a]Average of entry 1 to entry 11.

It is estimated that the for **1a** and **2a** is 2.66. As a result, the HPLC analysis of portion of the reaction mixture at certain reaction time would give out the mole ratio of **1a** and **2a**, thus the yield of **2a** at certain reaction time can be calculated. The set of experiment was implemented under given alcohol concentration.

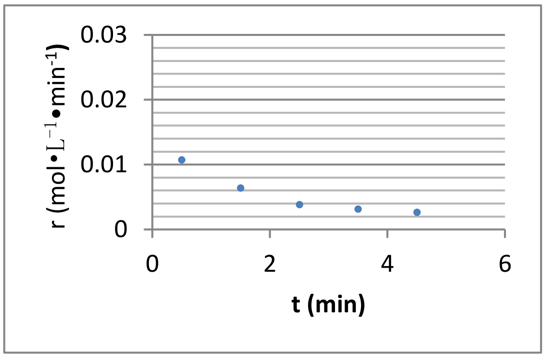
For $t = 0.5(t_i + t_{i+1})$, the reaction rate $r$ of **1a** was estimated using an approximate formula,

$$r = (c_i - c_{i+1})/(t_{i+1} - t_i) \quad .$$

2. Data collection.

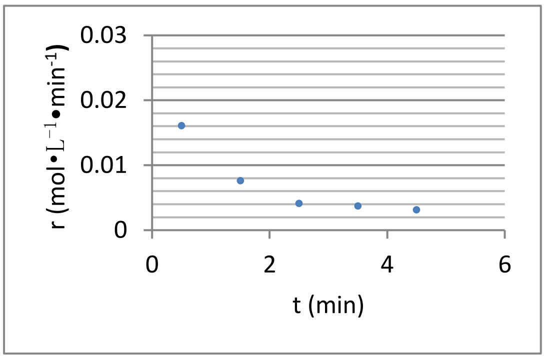
Solvent: *i*PrOH/$CHCl_3$ (v/v = 1/5, 1 mL)

| Entry | t (min) | $A_{1a}/A_{2a}$ | Ee of **2a** | Yield of **2a** (%) |
|---|---|---|---|---|
| 1 | 0 | - | - | 0 |
| 2 | 1 | 22.04 | 82 | 10.8 |
| 3 | 2 | 12.83 | 82 | 17.2 |
| 4 | 3 | 10.00 | 82 | 21.0 |
| 5 | 4 | 8.35 | 82 | 24.2 |
| 6 | 5 | 7.24 | 82 | 26.9 |



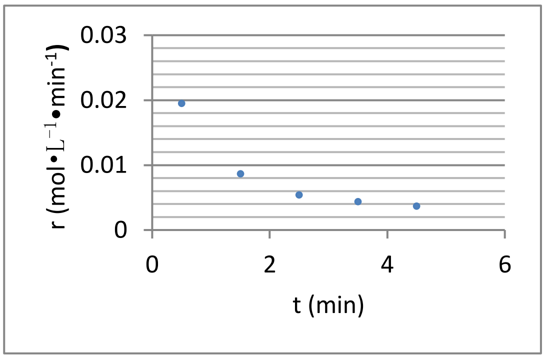

Solvent: *i*PrOH/$CHCl_3$ (v/v = 1/2, 1 mL)

| Entry | t (min) | $A_{1a}/A_{2a}$ | Ee of **2a** | Yield of **2a** (%) |
|---|---|---|---|---|
| 1 | 0 | - | - | 0 |
| 2 | 1 | 13.86 | 82 | 16.1 |
| 3 | 2 | 8.53 | 82 | 23.8 |
| 4 | 3 | 6.87 | 81 | 27.9 |
| 5 | 4 | 5.73 | 82 | 31.7 |
| 6 | 5 | 4.98 | 83 | 34.8 |




Solvent: *i*PrOH/$CHCl_3$ (v/v = 1/1, 1 mL)

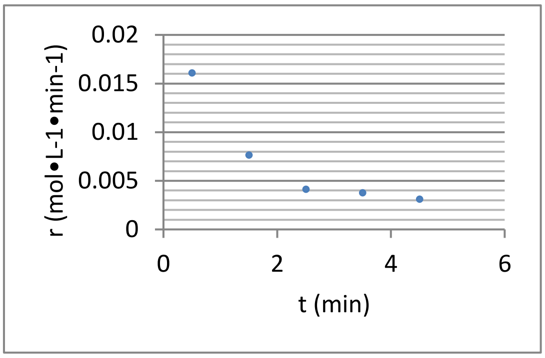
| Entry | t (min) | $A_{1a}/A_{2a}$ | Ee of **2a** | Yield of **2a** (%) |
|---|---|---|---|---|
| 1 | 0 | - | - | 0 |
| 2 | 1 | 10.96 | 82 | 19.5 |
| 3 | 2 | 6.76 | 82 | 28.3 |
| 4 | 3 | 5.25 | 82 | 33.6 |
| 5 | 4 | 4.33 | 82 | 38.0 |
| 6 | 5 | 3.71 | 82 | 41.8 |




Solvent: *i*PrOH (1 mL)

| Entry | t (min) | $A_{1a}/A_{2a}$ | Ee of **2a** | Yield of **2a** (%) |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 1 | 0 | - | - | 0 |
| 2 | 1 | 13.86 | 80 | 19.5 |
| 3 | 2 | 8.533 | 80 | 28.3 |
| 4 | 3 | 6.868 | 79 | 33.6 |
| 5 | 4 | 5.734 | 80 | 38.0 |
| 6 | 5 | 4.977 | 80 | 41.8 |



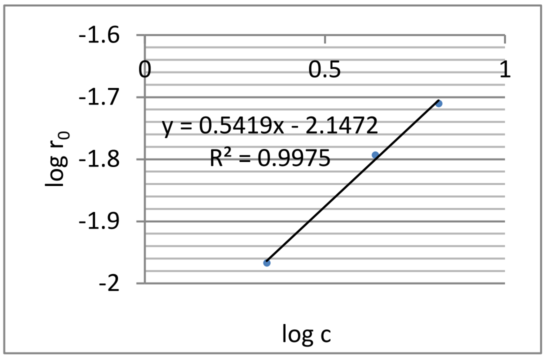

3. Data analyses and explanations.

As we can observed from charts and graphs above, the following can be concluded.

1) In every individual experiment, the ee value stayed unchanged at the first 5 min of the reaction. We believe consumption of **1a** or formation of optically active **2a** have no influence of the ee of the product **2a**.

2) For mixed reaction solvents, the reaction rate increased as the concentration of *i*PrOH increase. We calculated the reaction rate of *i*PrOH by using $r_0$ at different *i*PrOH concentration.The reaction order of *i*PrOH is about 0.54.

| Entry | *i*PrOH/$CHCl_3$ | c(*i*PrOH) ($mol\cdot L^{-1}$) | $r_0$ ($mol\cdot L^{-1}\cdot min^{-1}$) | ln(c) | ln($r_0$) |
|---|---|---|---|---|---|
| 1 | 1/5 | 2.18 | 0.0108 | 0.338 | -1.97 |
| 2 | 1/2 | 4.36 | 0.0161 | 0.639 | -1.79 |
| 3 | 1/1 | 6.54 | 0.0195 | 0.816 | -1.71 |

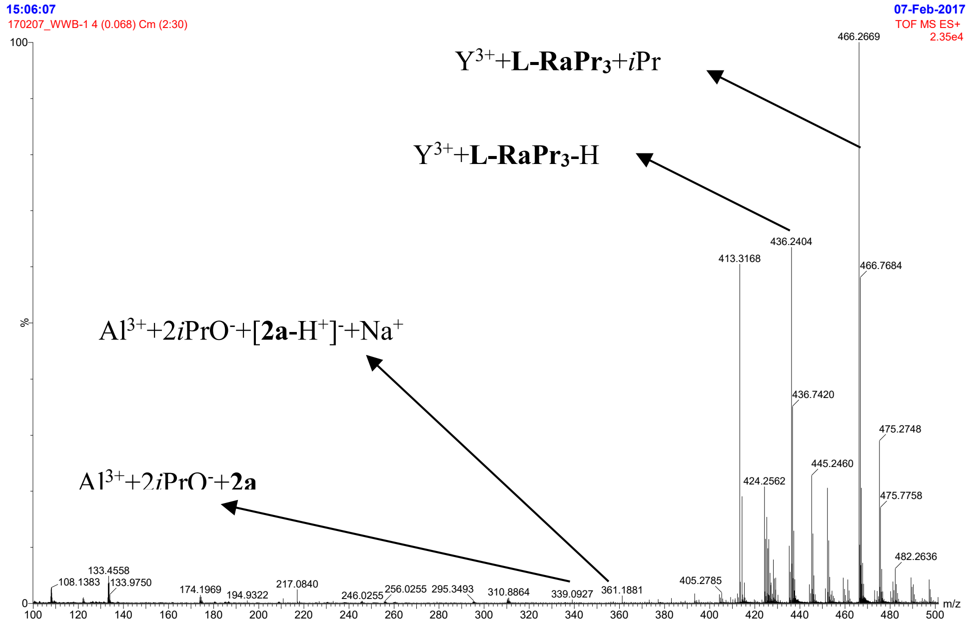


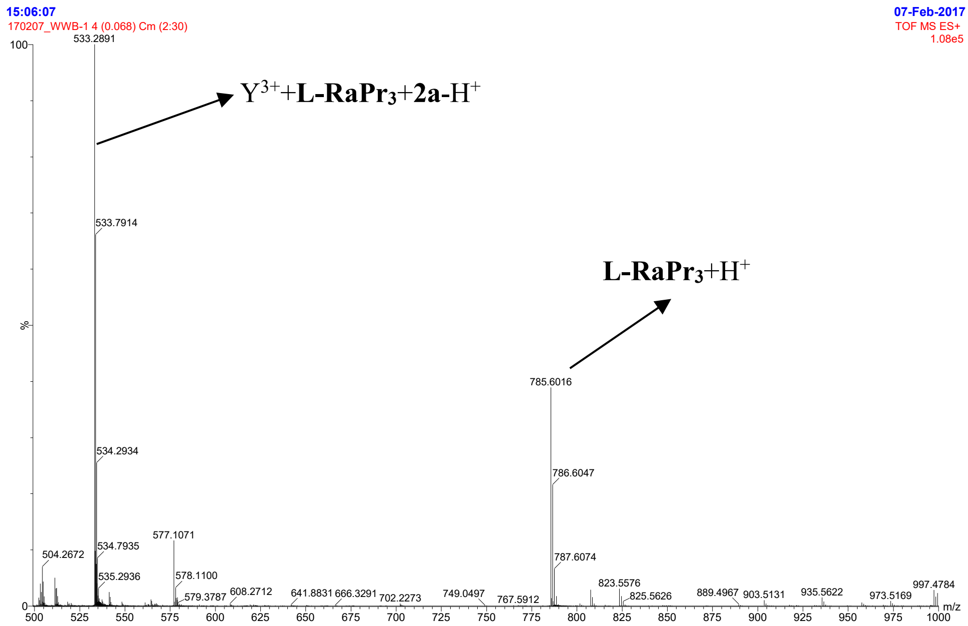

Further calculation did not elicit the reaction order of **1a** at different *i*PrOH concentrations. We assume that in such catalytic system, formula for elementary reaction is not feasible for **1a**.

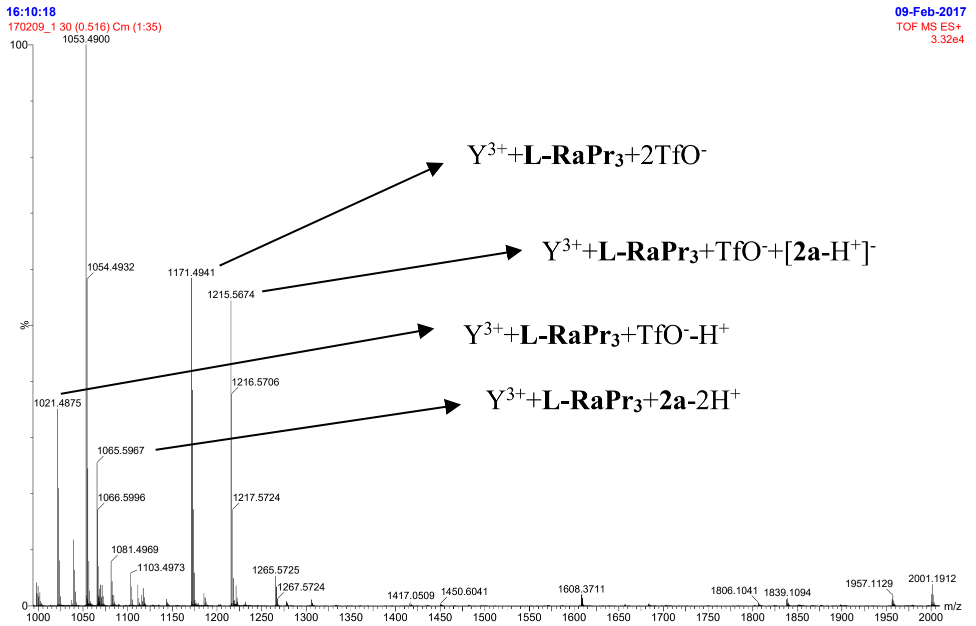
3) When *i*PrOH was used as solvent the reaction rate at the first 5 min of was slightly slower than the mixed reaction solvent of *i*PrOH and chloroform (v/v = 1:1). Moreover, the ee value was lower than the mixed reaction solvent.

4) Such low reaction order of *i*PrOH and solvent effect suggested that it might be not *i*PrOH itself but the formed aluminium alkoxide that served as the true reactant, as proposed in the manuscript.

**(H) HRMS data of the reaction.**






Y(OTf)$_3$ + L-RaPr$_3$ +1a + Al(O*t*Bu)$_3$ (0.1:0.1:1:0.5) :

[$Al^{3+}$+2*i*PrO$^-$+**2a**] Calcd for : 339.1752, found : 339.0927;

[$Al^{3+}$+2*i*PrO$^-$+[**2a**-$H^+$]$^-$ +$Na^+$] Calcd for : 361.1572, found : 361.1881;

[$Y^{3+}$+**L-RaPr$_3$**-$H^+$] Calcd for : 436.2424, found : 436.2404;

[$Y^{3+}$+**L-RaPr$_3$**+*i*PrO$^-$] Calcd for : 466.2711, found : 466.2669;

[$Y^{3+}$+**L-RaPr$_3$**+**2a**-$H^+$] Calcd for : 533.2895, found : 533.2891;

[**L-RaPr$_3$**+ $H^+$] Calcd for : 785.5945, found : 785.6016;

[$Y^{3+}$+**L-RaPr$_3$**+TfO$^-$+[**2a**-$H^+$]$^-$] Calcd for : 1215.5310, found : 1215.5674;

[$Y^{3+}$+**L-RaPr$_3$**+2TfO$^-$] Calcd for : 1171.3966, found : 1171.4941;

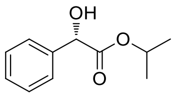
[$Y^{3+}$+**L-RaPr$_3$**+**2a**-2$H^+$] Calcd for : 1065.5711, found : 1065.5967;

[$Y^{3+}$+**L-RaPr$_3$**+TfO$^-$-$H^+$] Calcd for : 1021.4875, found : 1021.4367.

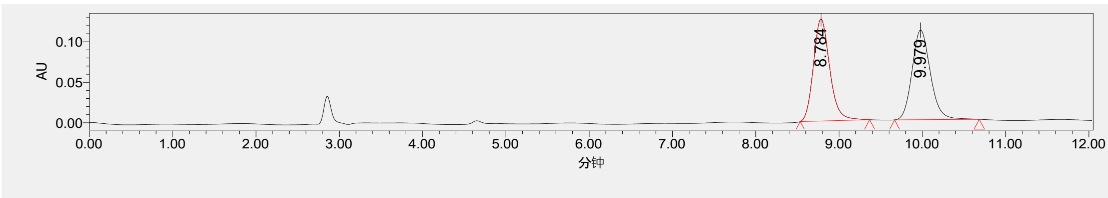
The peak for species $Al^{3+}$+2*i*PrO$^-$+**2a**, $Y^{3+}$+**L-RaPr$_3$**+*i*PrO$^-$, $Y^{3+}$+**L-RaPr$_3$**+**2a**-$H^+$ and $Y^{3+}$+**L-RaPr$_3$**+TfO$^-$+[**2a**-$H^+$]$^-$ were found. The find of the peak of $Al^{3+}$+2*i*PrO$^-$+**2a** species allowed us to presume that aluminium alkoxide should have a direct influence in the forming of **2a**. Moreover, any form of $Y^{3+}$+**L-RaPr$_3$**+*i*PrO$^-$+**2a**, indicating *i*PrOH may serves as direct reductant in the catalytic cycle was not found.

## (I) Spectral characterization data and HPLC conditions for the products

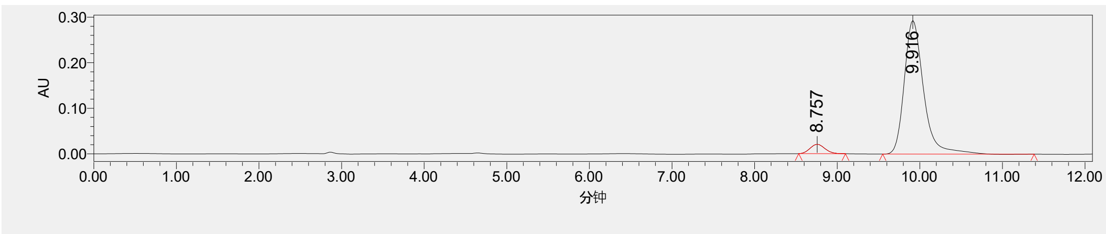
### (*S*)-*iso*-propyl mandelate (2a)




(**$C_{12}H_{16}O_3$**) a white solid; 98% yield, 90% ee. $[\alpha]_D^{20}$ = +100.81 (*c* = 0.248, in $CHCl_3$), {Lit.[4]$[\alpha]_D^{25}$ = –96.1 (*c* = 1.15, in $CHCl_3$), conf. (*R*)}. HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 8.76 min, 9.92 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.28 (m, 5H), 5.17 – 4.98 (m, 2H), 3.57 – 3.44 (m, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.11 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.25, 138.56, 128.50, 128.30, 126.43, 72.89, 70.20, 21.72, 21.41. ESI-HRMS: calcd for **$C_{11}H_{14}NaO_3$**$^+$ [M+Na$^+$] 217.0835, found 217.0833.

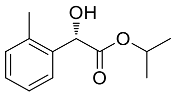



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.784 | 50.31 |
| 2 | 9.979 | 49.69 |

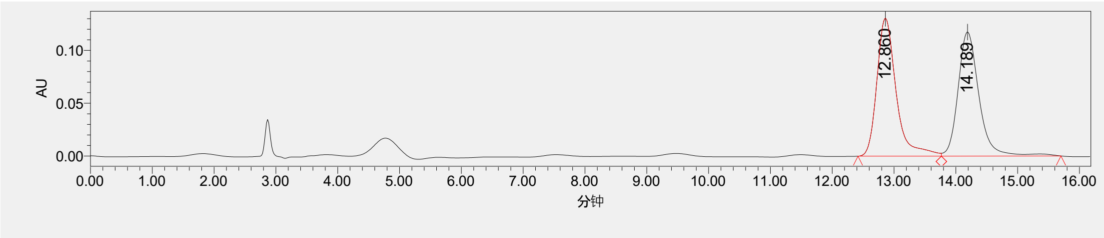



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.757 | 5.14 |
| 2 | 9.916 | 94.86 |

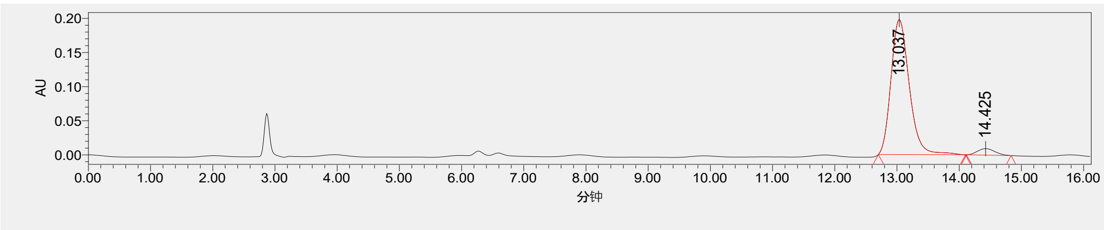
**(*S*)-*iso*-propyl α-hydroxy-α-(2-methylphenyl)acetate (2b)**




(**$C_{13}H_{18}O_3$**) a colorless oil; 99% yield, 91% ee. $[\alpha]_D^{21}$ = +117.86 (*c* = 0.328, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 13.04 min, 14.43 min. $^{1}$H NMR (400 MHz, CDCl3) δ 7.29 – 7.00 (m, 4H), 5.25 (d, J = 5.3 Hz, 1H), 5.00 (dt, J = 12.5, 6.3 Hz, 1H), 3.39 (d, J = 5.3 Hz, 1H), 2.36 (s, 3H), 1.19 (d, J = 6.3 Hz, 3H), 1.03 (d, J = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.71, 135.85, 135.33, 129.69, 127.25, 125.51, 125.15, 69.36, 69.08, 20.67, 20.39, 18.28. ESI-HRMS: calcd for **$C_{12}H_{16}NaO_3^+$** [M+Na$^+$] 231.0992, found 231.0992.

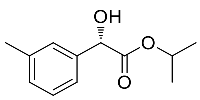



| | Retention Time | %Area |
|---|---|---|
| 1 | 12.860 | 50.25 |
| 2 | 14.189 | 49.75 |

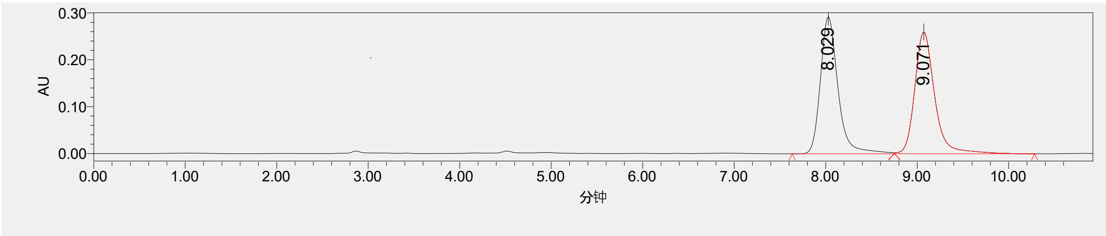



| | Retention Time | %Area |
|---|---|---|
| 1 | 13.037 | 95.62 |
| 2 | 14.425 | 4.38 |

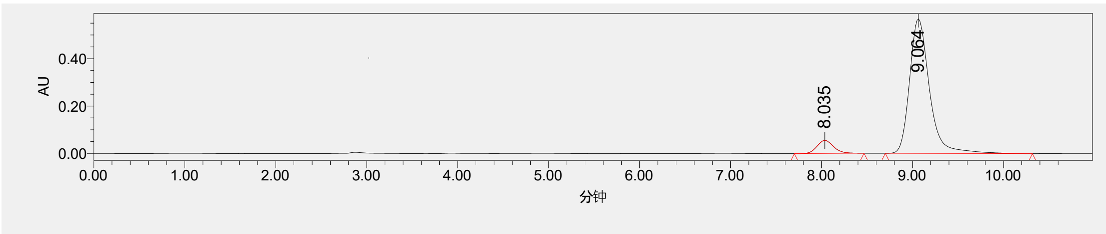
**(*S*)-*iso*-propyl α-hydroxy-α-(3-methylphenyl)acetate (2c)**



(**$C_{13}H_{18}O_3$**) a colorless oil; 98% yield, 85% ee. $[\alpha]_D^{21}$ = +78.67 (*c* = 0.286, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 8.04 min, 9.06 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.02 (m, 4H), 5.10 – 4.86 (m, 2H), 3.39 (d, *J* = 6.1 Hz, 1H), 2.28 (s, 3H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.29, 137.43, 137.19, 128.03, 127.36, 126.02, 122.55, 71.89, 69.08, 20.69, 20.39. ESI-HRMS: calcd for **$C_{12}H_{16}NaO_3^+$** [M+Na$^+$] 231.0992, found 231.0997.

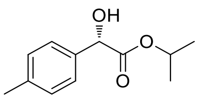



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.029 | 49.84 |
| 2 | 9.071 | 50.16 |

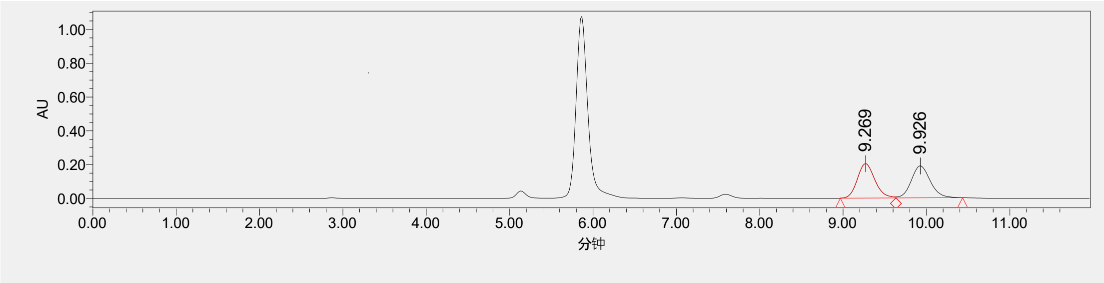



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.035 | 7.50 |
| 2 | 9.064 | 92.50 |

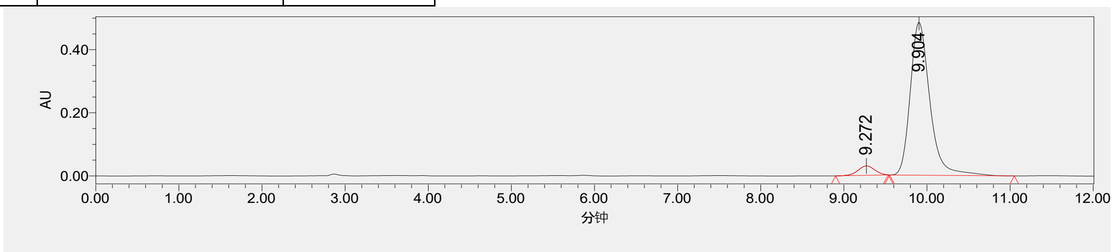
**(*S*)-*iso*-propyl α-hydroxy-α-(4-methylphenyl)acetate (2d)**



($C_{13}H_{18}O_3$) a white solid; 98% yield, 90% ee. $[\alpha]_D^{23}$ = +92.31 ($c$ = 0.260, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/$n$-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 9.27 min, 9.90 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.15 (m, 2H), 7.13 – 7.02 (m, 2H), 5.10 – 4.86 (m, 2H), 3.38 (d, $J$ = 6.1 Hz, 1H), 2.27 (s, 3H), 1.20 (d, $J$ = 6.3 Hz, 3H), 1.04 (d, $J$ = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.36, 137.01, 134.61, 128.17, 125.33, 71.72, 69.02, 20.68, 20.39, 20.14. ESI-HRMS: calcd for $C_{12}H_{16}NaO_3^+$ [M+Na$^+$] 231.0992, found 231.1000.

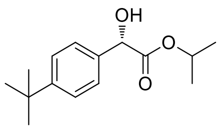



| | Retention Time | %Area |
|---|---|---|
| 1 | 9.269 | 49.90 |
| 2 | 9.926 | 50.10 |



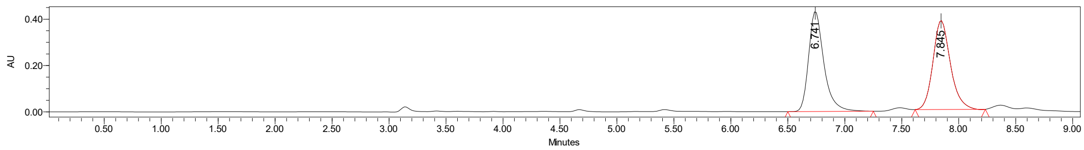

| | Retention Time | %Area |
|---|---|---|
| 1 | 9.272 | 4.96 |
| 2 | 9.904 | 95.04 |

**(*S*)-*iso*-propyl α-hydroxy-α-(4-(*tert*-butyl)phenyl)acetate (2e)**

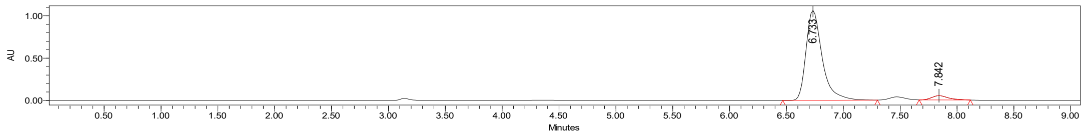



($C_{16}H_{24}O_3$) a white solid; 99% yield, 91% ee. $[\alpha]_D^{12}$ = +71.93 ($c$ = 0.228, in $CH_2Cl_2$). HPLC DAICEL CHIRALCEL IA, 2-propanol/$n$-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 6.73 min, 7.84 min. $^1$H NMR (400 MHz, $CDCl_3$)

δ 7.36 – 7.21 (m, 4H), 5.01 (dd, *J* = 12.5, 6.2 Hz, 2H), 3.34 (d, *J* = 6.2 Hz, 1H), 1.28 – 1.18 (m, 12H), 1.07 (d, *J* = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ = 172.30, 150.22, 134.53, 125.07, 124.43, 71.67, 69.02, 33.54, 30.27, 20.71, 20.45. ESI-HRMS: calcd for $\mathbf{C_{15}H_{22}NaO_3}^+$ [M+Na$^+$] 273.1467, found 273.1465.

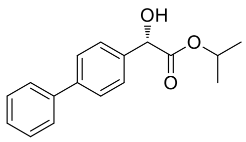


| | Retention Time | %Area |
|---|---|---|
| 1 | 6.741 | 49.58 |
| 2 | 7.845 | 50.42 |

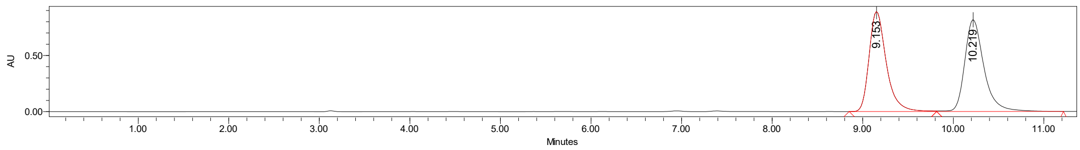


| | Retention Time | %Area |
|---|---|---|
| 1 | 6.733 | 95.34 |
| 2 | 7.842 | 4.66 |

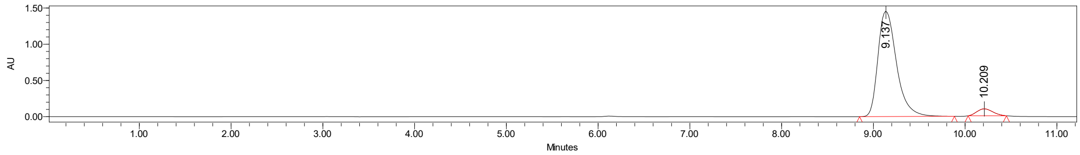
**(*S*)-*iso*-propyl α-hydroxy-α-(4-phenylphenyl)acetate (2f)**



($\mathbf{C_{17}H_{18}O_3}$) a white solid; 99% yield, 89% ee. $[\alpha]_D^{18}$ = +114.97 (*c* = 0.294, 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: 9.14 min, 10.21 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 4H), 7.44 – 7.33 (m, 4H), 7.27 (t, *J* = 7.3 Hz, 1H), 5.09 (s, 2H), 5.01 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.47 (s, 1H), 1.22 (d, *J* = 6.3 Hz, 3H), 1.06 (d, *J* = 6.3 Hz, 3H). $^{13}$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. $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.22, 141.18, 140.62, 137.56, 128.82, 127.46, 127.27, 127.12, 126.88, 72.68, 70.32, 21.76, 21.49. ESI-HRMS: calcd for $\mathbf{C_{17}H_{18}NaO_3}^+$ [M+Na$^+$] 293.1148, found 293.1158.

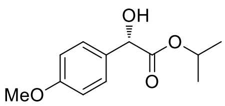



| | Retention Time | %Area |
|---|---|---|
| 1 | 9.153 | 49.44 |
| 2 | 10.219 | 50.56 |

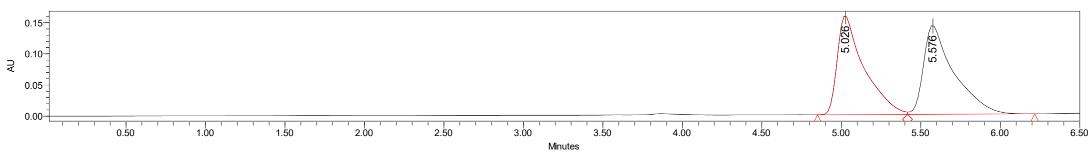



| | Retention Time | %Area |
|---|---|---|
| 1 | 9.137 | 94.69 |
| 2 | 10.209 | 5.31 |

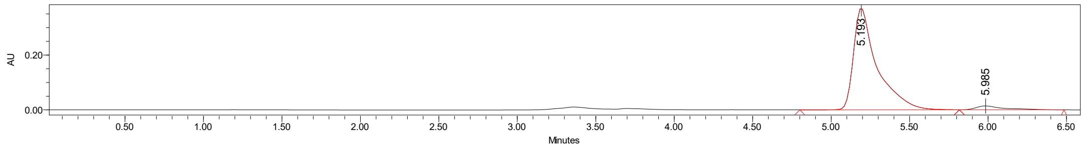
**(*S*)-*iso*-propyl α-hydroxy-α-(4-methoxylphenyl)acetate (2g)**




(**$C_{13}H_{18}O_4$**) a white solid; 90% yield, 89% ee. $[\alpha]_D^{22}$ = +92.25 (*c* = 0.258, 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: 5.19 min, 5.99 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 9.1, 2.4 Hz, 2H), 6.96 – 6.83 (m, 2H), 5.15 – 4.99 (m, 2H), 3.80 (s, 3H), 3.44 (dd, *J* = 5.8, 2.6 Hz, 1H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.11 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.43, 159.60, 130.82, 127.73, 113.92, 72.51, 70.00, 55.27, 21.70, 21.43. ESI-HRMS: calcd for **$C_{13}H_{18}NaO_4^+$** [M+Na$^+$] 261.1097, found 261.1098.

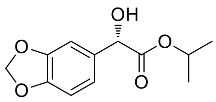


| | Retention Time | %Area |
|---|---|---|
| 1 | 5.026 | 49.56 |
| 2 | 5.576 | 50.44 |

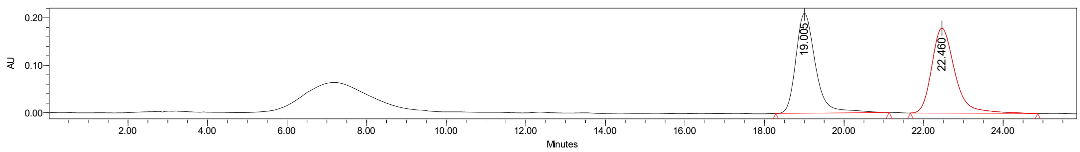


| | Retention Time | %Area |
|---|---|---|
| 1 | 5.193 | 94.53 |
| 2 | 5.985 | 5.47 |

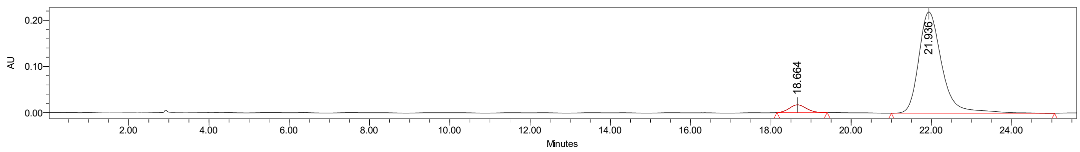
**(*S*)-*iso*-propyl α-hydroxy-α-(3,4-methylenedioxylphenyl)acetate (2h)**



(**$C_{12}H_{14}O_5$**) a white solid; 99% yield, 90% ee. $[\alpha]_D^{12}$ = +78.40 (*c* = 0.250, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 18.66 min, 21.94 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 5.8, 1.6 Hz, 2H), 6.83 – 6.74 (m, 1H), 5.96 (s, 2H), 5.14 – 4.97 (m, 2H), 3.43 (d, *J* = 5.8 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.23, 147.81, 147.62, 132.48, 120.25, 108.23, 106.88, 101.17, 72.64, 70.23, 21.71, 21.46. ESI-HRMS: calcd for **$C_{12}H_{14}NaO_5^+$** [M+Na$^+$] 261.0733, found 261.0740.

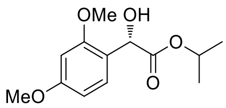


| | Retention Time | %Area |
|---|---|---|
| 1 | 19.005 | 50.21 |
| 2 | 22.460 | 49.79 |

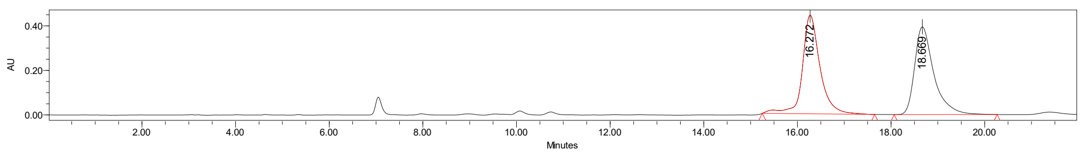



| | Retention Time | %Area |
|---|---|---|
| 1 | 18.664 | 5.20 |
| 2 | 21.936 | 94.80 |

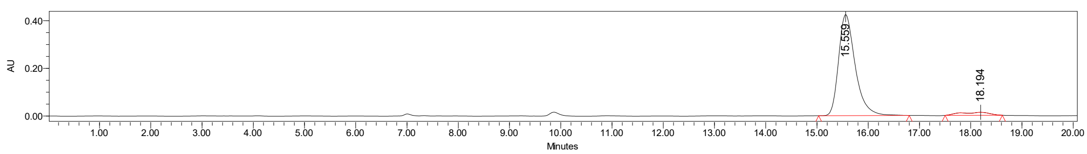
**(*S*)-*iso*-propyl α-hydroxy-α-(2,4-dimethoxylphenyl)acetate (2i)**




(**$C_{13}H_{18}O_4$**)a white solid; 99% yield, 90% ee. $[\alpha]_D^{19}$= +83.70 (*c* = 0.270, 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: 5.26 min, 8.97 min. $^1$H NMR (400 MHz, CDCl3) δ 7.12 – 7.05 (m, 1H), 6.41 – 6.36 (m, 2H), 5.07 (s, 1H), 5.02 (dt, J = 12.5, 6.3 Hz, 1H), 3.73 (d, J = 5.0 Hz, 6H), 3.41 (s, 1H), 1.16 (d, J = 6.3 Hz, 3H), 1.07 (d, J = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ = 173.58, 161.15, 158.24, 130.29, 120.03, 104.21, 98.90, 70.07, 69.39, 55.37, 21.69, 21.47. ESI-HRMS: calcd for **$C_{13}H_{18}NaO_4^+$** [M+Na$^+$] 261.1097, found 261.1102.

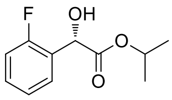



| | Retention Time | %Area |
|---|---|---|
| 1 | 16.272 | 50.85 |
| 2 | 18.669 | 49.15 |

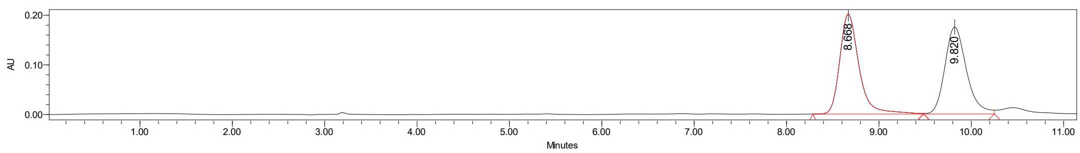


| | Retention Time | %Area |
|---|---|---|
| 1 | 15.559 | 95.00 |
| 2 | 18.194 | 5.00 |

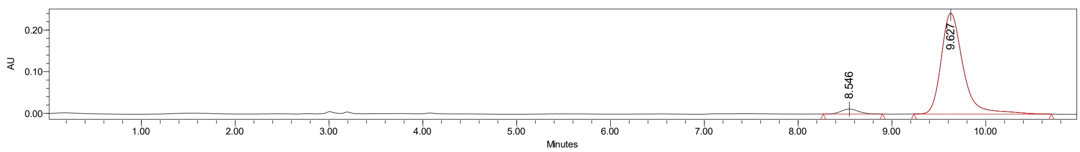
**(*S*)-*iso*-propyl α-hydroxy-α-(2-flurophenyl)acetate (2j)**



(**$C_{12}H_{15}FO_3$**) a white solid; 99% yield, 92% ee. $[\alpha]_D^{12}$ = +100.00 ($c$ = 0.306, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 8.55 min, 9.63 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 2H), 7.21 – 7.00 (m, 2H), 5.34 (d, $J$ = 5.2 Hz, 1H), 5.21 – 5.01 (m, 1H), 3.56 (d, $J$ = 5.3 Hz, 1H), 1.19 (dd, $J$ = 59.9, 6.1 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.78, 161.75, 159.28, 130.21, 130.13, 128.71, 128.67, 126.13, 125.99, 124.31, 124.27, 115.78, 115.56, 70.43, 67.74, 21.62, 21.34. ESI-HRMS: calcd for **$C_{11}H_{13}FNaO_3$**$^+$ [M+Na$^+$] 235.0741, found 235.0741.

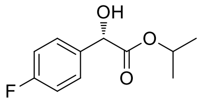



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.668 | 50.75 |
| 2 | 9.820 | 49.25 |

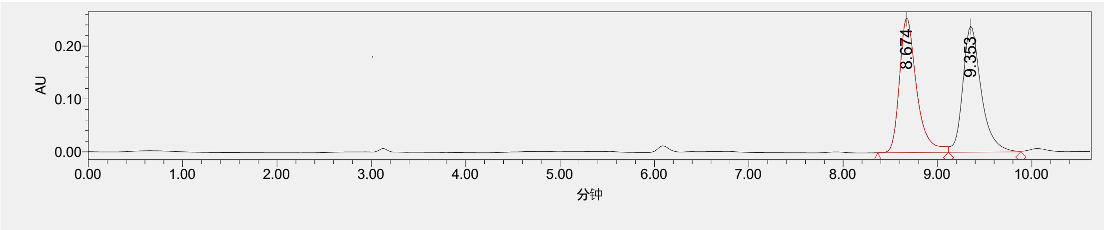



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.546 | 3.84 |
| 2 | 9.627 | 96.16 |

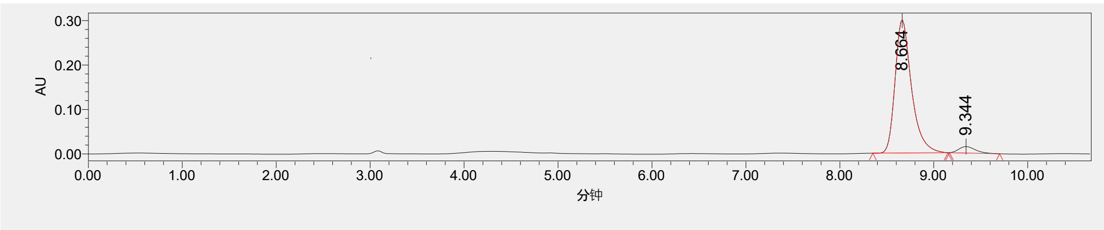
**(*S*)-*iso*-propyl α-hydroxy-α-(4-flurophenyl)acetate (2k)**




(**$C_{11}H_{13}FO_3$**) a white solid; 98% yield, 91% ee. $[\alpha]_D^{19}$ = +103.17 (*c* = 0.252, in $CH_2Cl_2$). HPLC DAICEL CHIRALCEL IA, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 8.66 min, 9.34 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.23 (m, 2H), 7.03 – 6.23 (m, 2H), 5.10 – 4.87 (m, 2H), 3.48 (d, *J* = 5.6 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.04 (d, *J* = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.04, 162.86, 160.41, 133.32, 133.28, 127.18, 127.10, 114.48, 114.27, 71.17, 69.35, 20.66, 20.37. ESI-HRMS: calcd for **$C_{11}H_{13}FNaO_3^+$** [M+Na$^+$] 235.0741, found 235.0747.

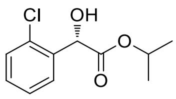



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.674 | 49.97 |
| 2 | 9.353 | 50.03 |

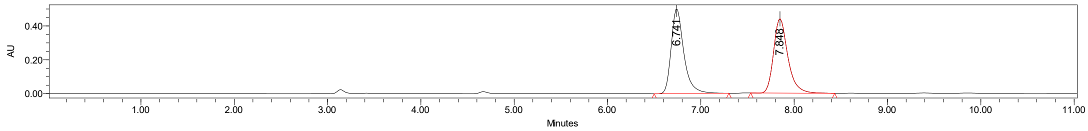



| | Retention Time | %Area |
|---|---|---|
| 1 | 8.664 | 95.40 |
| 2 | 9.344 | 4.60 |

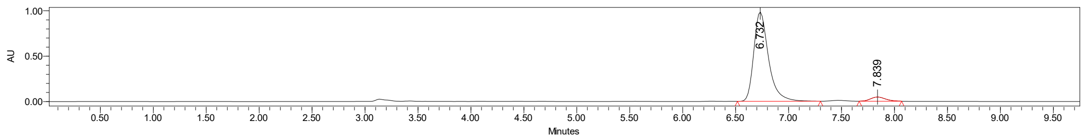
**(*S*)-*iso*-propyl α-hydroxy-α-(2-chlorophenyl)acetate (2l)**



($C_{11}H_{13}ClO_3$) a white solid; 99% yield, 91% ee. $[\alpha]_D^{20}$ = +99.15 (*c* = 0.234, 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: 6.73 min, 7.84 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.22 – 7.17 (m, 2H), 5.43 (d, *J* = 2.9 Hz, 1H), 5.01 (d, *J* = 6.3 Hz, 1H), 3.57 (d, J = 4.0 Hz, 1H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.04 (d, *J* = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 171.73, 135.28, 132.55, 128.86, 128.58, 127.66, 126.02, 69.45, 69.42, 20.59, 20.36. ESI-HRMS: calcd for $C_{11}H_{13}Cl^{34.9689}NaO_3^+$ [M+Na$^+$] 251.0445， found 251.0449; calcd for $C_{11}H_{13}Cl^{36.9659}NaO_3^+$ [M+Na$^+$] 253.0416, found 253.0422.

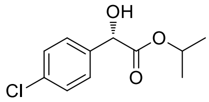



| | Retention Time | %Area |
|---|---|---|
| 1 | 6.741 | 50.30 |
| 2 | 7.848 | 49.70 |



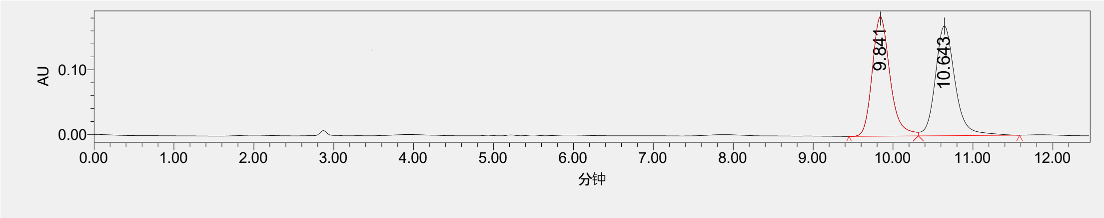

| | Retention Time | %Area |
|---|---|---|
| 1 | 6.732 | 95.48 |
| 2 | 7.839 | 4.52 |

**(*S*)-*iso*-propyl α-hydroxy-α-(4-chlorophenyl)acetate (2m)**

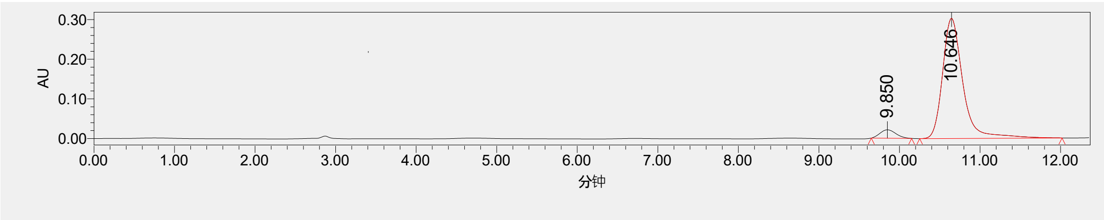


($C_{11}H_{13}ClO_3$) a white solid; 98% yield, 90% ee. $[\alpha]_D^{18}$ = +95.93 (*c* = 0.246, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 9.93 min, 10.51 min. $^1$H NMR (400

MHz, $CDCl_3$) δ 7.38 – 7.11 (m, 4H), 5.13 – 4.81 (m, 2H), 3.50 (d, *J* = 5.6 Hz, 1H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ = 171.82, 135.98, 133.09, 127.62, 126.76, 71.15, 69.48, 20.66, 20.38. ESI-HRMS: calcd for $\mathbf{C_{11}H_{13}Cl^{34.9689}NaO_3}^+$ [M+Na+] 251.0445, found 251.0449; calcd for $\mathbf{C_{11}H_{13}Cl^{36.9659}NaO_3}^+$ [M+Na+] 253.0416, found 253.0391.

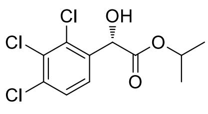



| | Retention Time | %Area |
|---|---|---|
| 1 | 9.841 | 49.67 |
| 2 | 10.643 | 50.33 |

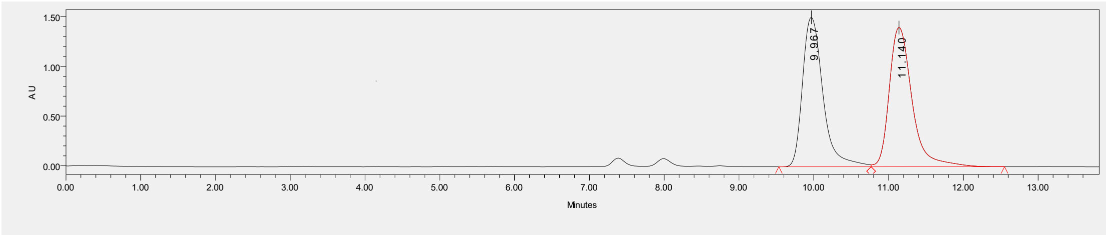



| | Retention Time | %Area |
|---|---|---|
| 1 | 9.850 | 5.18 |
| 2 | 10.646 | 94.82 |

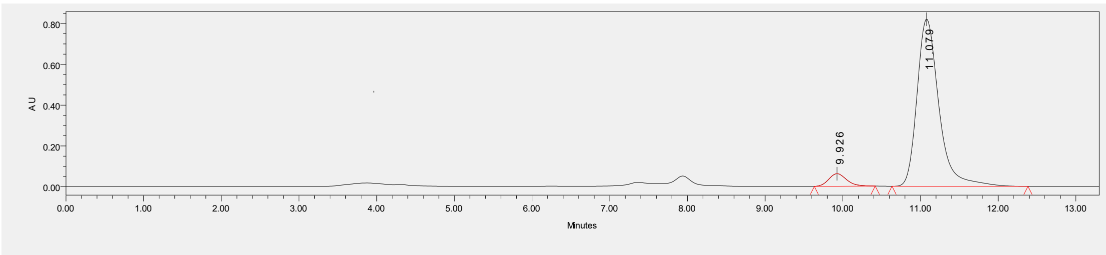
**(*S*)-*iso*-propyl α-hydroxy-α-(2,3,4-trichlorophenyl)acetate (2n)**




($\mathbf{C_{11}H_{11}Cl_3O_3}$) a white solid; 99% yield, 89% ee. $[\alpha]_D^{16}$ = +127.69 (*c* = 0.242, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 9.93 min, 11.08 min. $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 5.49 (d, *J* = 3.6 Hz, 1H), 5.08 (dt, *J* = 12.0, 6.0 Hz, 1H), 3.77 (d, *J* = 4.0 Hz, 1H), 1.20 (dd, *J* = 54.4, 6.2 Hz, 6H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ = 172.01, 136.95, 134.14, 133.62, 132.26, 128.44, 126.78, 70.99, 70.77, 21.58, 21.42. ESI-HRMS: calcd for $\mathbf{C_{11}H_{11}Cl_3^{34.9689}NaO_3}^+$ [M+Na$^+$] 318.9671, found 318.9676; calcd for $\mathbf{C_{11}H_{11}Cl_2^{34.9689}Cl^{36.9659}NaO_3}^+$ [M+Na$^+$] 320.9642, found 320.9656.

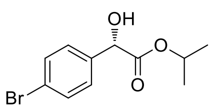



| | Retention Time | %Area |
|---|---|---|
| 1 | 9.967 | 49.15 |
| 2 | 11.140 | 50.85 |

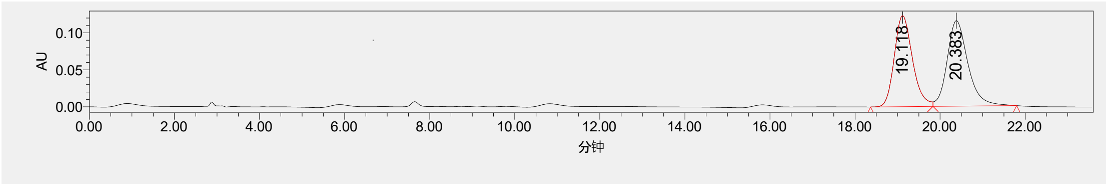



| | Retention Time | %Area |
|---|---|---|
| 1 | 9.926 | 5.75 |
| 2 | 11.079 | 94.25 |

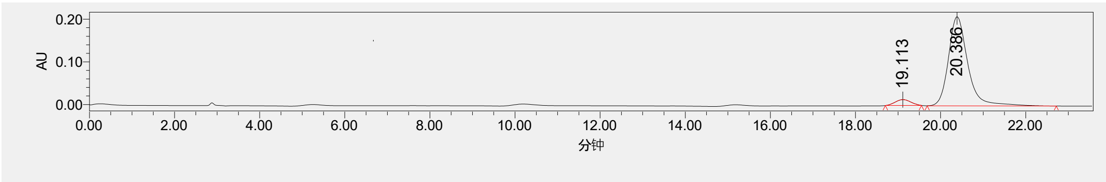
**(*S*)-*iso*-propyl α-hydroxy-α-(2-bromophenyl)acetate (2o)**




($\mathbf{C_{11}H_{13}BrO_3}$) a white solid; 98% yield, 90% ee. $[\alpha]_D^{20}$= +79.11 ($c$ = 0.316, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/$n$-hexane = 2/98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 19.11 min, 20.39 min. $^1$H NMR (400 MHz, $CDCl_3$) δ7.46 – 7.33 (m, 2H), 7.27 – 7.17 (m, 2H), 5.13 – 4.84 (m, 2H), 3.52 (d, = 5.6 Hz, 1H), 1.21 (d, $J$ = 6.3 Hz, 3H), 1.04 (d, $J$ = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.41, 137.97, 131.52, 128.08, 122.11, 83.55, 72.35, 27.83. $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 172.77, 137.53, 131.60, 128.13, 122.31, 72.24, 70.54, 21.70, 21.42. ESI-HRMS: calcd for **$C_{11}H_{13}Br^{78.9183}NaO_3^+$** [M+Na$^+$] 294.9940, found 294.9948; calcd for **$C_{11}H_{13}Br^{80.9163}NaO_3^+$** [M+Na$^+$] 296.9920, found 296.9900.

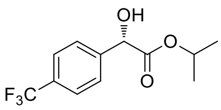



| | Retention Time | %Area |
|---|---|---|
| 1 | 19.118 | 48.23 |
| 2 | 20.383 | 51.77 |

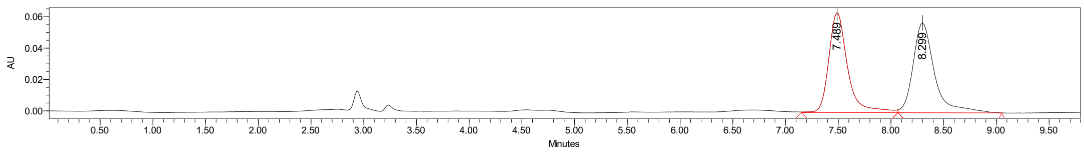



| | Retention Time | %Area |
|---|---|---|
| 1 | 19.113 | 5.04 |
| 2 | 20.386 | 94.96 |

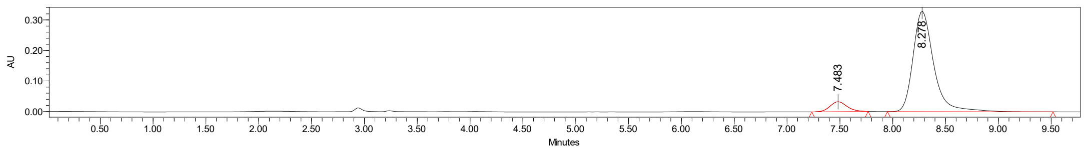
**(*S*)-*iso*-propyl α-hydroxy-α-(4-(trifluoromethyl)phenyl)acetate (2p)**




(**$C_{13}H_{15}F_3O_3$**) a white solid; 99% yield, 85% ee. $[\alpha]_D^{17}$ = +73.62 (*c* = 0.254, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 7.48 min, 8.28 min. $^1$H NMR (400 MHz, CDCl3) δ 7.69 – 7.46 (m, 4H), 5.11 (d, J = 5.2 Hz, 1H), 5.00 (dt, J = 12.5, 6.3 Hz, 2H), 3.56 (d, J = 5.5 Hz, 1H), 1.23 (d, J = 6.3 Hz, 3H), 1.04 (d, J = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ = 171.50, 141.29, 129.59, 129.26, 125.71, 124.44, 124.40, 124.36, 124.32, 121.64, 71.24, 69.78, 20.65, 20.36. ESI-HRMS: calcd for **$C_{12}H_{13}F_3NaO_5^+$** [M+Na$^+$] 285.0709, found 285.0719.

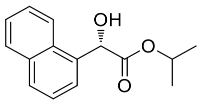



| | Retention Time | %Area |
|---|---|---|
| 1 | 7.489 | 49.44 |
| 2 | 8.299 | 50.56 |

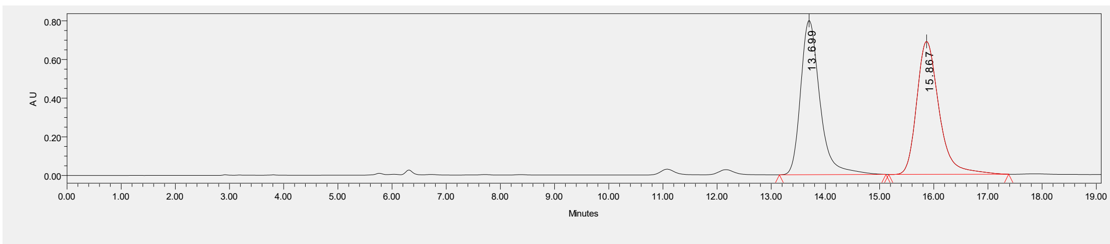



| | Retention Time | %Area |
|---|---|---|
| 1 | 7.483 | 7.51 |
| 2 | 8.278 | 92.49 |

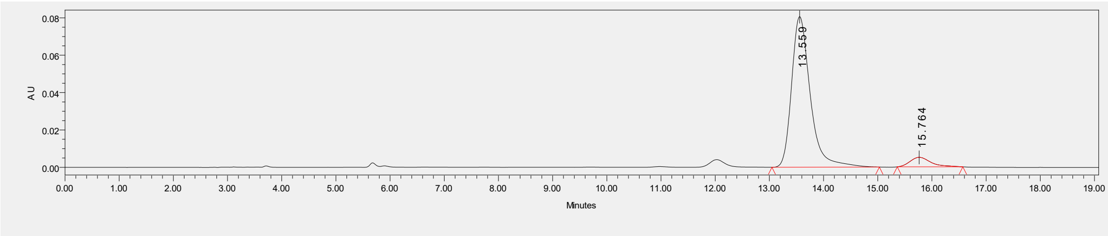
**(*S*)-*iso*-propyl α-hydroxy-α-(naphthalen-1-yl)acetate (2q)**




(**$C_{16}H_{18}O_3$**) a white solid; 99% yield, 86% ee. $[\alpha]_D^{25}$ = +93.18 (*c* = 0.264, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 13.56 min, 15.76 min. $^1$H NMR (400 MHz, CDCl3) δ 8.18 – 8.02 (m, 1H), 7.85 – 7.71 (m, 2H), 7.51 – 7.31 (m, 4H), 5.69 (s, 1H), 5.02 (dt, J = 12.5, 6.3 Hz, 1H), 3.53 (s, 1H), 1.16 (d, J = 6.3 Hz, 3H), 0.92 (d, J = 6.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl3) δ = 173.77, 134.35, 134.02, 131.10, 129.31, 128.74, 126.40, 125.84, 125.63, 125.20, 123.85, 71.40, 70.32, 21.68, 21.36. ESI-HRMS: calcd for **$C_{16}H_{18}NaO_3^+$** [M+Na$^+$] 267.0997, found 267.0998.

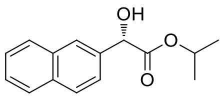


|   | Retention Time | %Area |
|---|---|---|
| 1 | 13.699 | 50.00 |
| 2 | 15.867 | 50.00 |

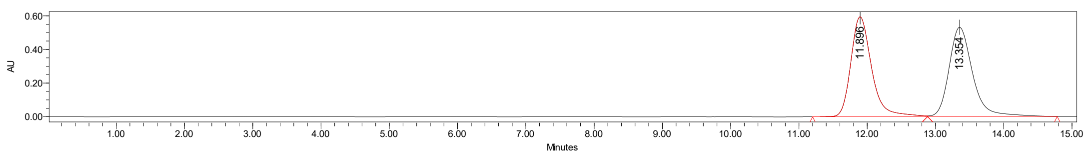



|   | Retention Time | %Area |
|---|---|---|
| 1 | 13.559 | 93.37 |
| 2 | 15.764 | 6.63 |

**(*S*)-*iso*-propyl α-hydroxy-α-(naphthalen-2-yl)acetate (2r)**

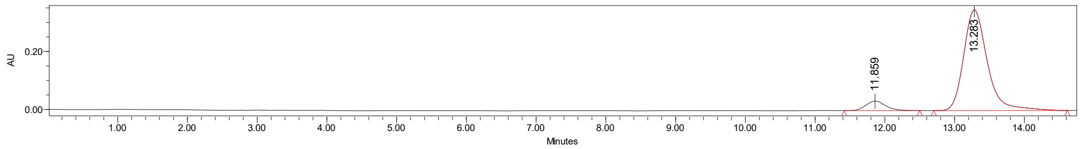



(**$C_{16}H_{18}O_3$**) a white solid; 99% yield, 86% ee. $[\alpha]_D^{25}$ = +85.71 (*c* = 0.308, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 11.86 min, 13.28 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.80 – 7.67 (m, 3H), 7.49 – 7.35 (m, 3H), 5.21 (d, *J* = 5.2 Hz, 1H), 5.00 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.59 (d, *J* = 5.7 Hz, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.00 (d, *J* = 6.3 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.27, 135.94, 133.24, 133.20, 128.34, 128.16, 127.71, 126.28, 126.27, 125.79, 124.14, 73.06, 70.36, 21.75, 21.45. ESI-HRMS: calcd for **$C_{16}H_{18}NaO_3$**$^+$ [M+Na$^+$] 267.0997, found 267.0995.



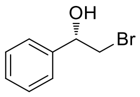

|   | Retention Time | %Area |
|---|---|---|
| 1 | 11.896 | 49.78 |

| | | |
|---|---|---|
| 2 | 13.354 | 50.22 |

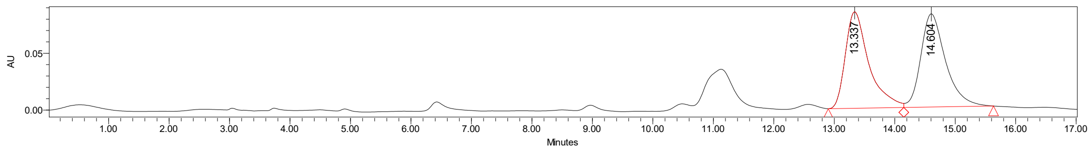



| | Retention Time | %Area |
|---|---|---|
| 1 | 11.859 | 6.95 |
| 2 | 13.283 | 93.05 |

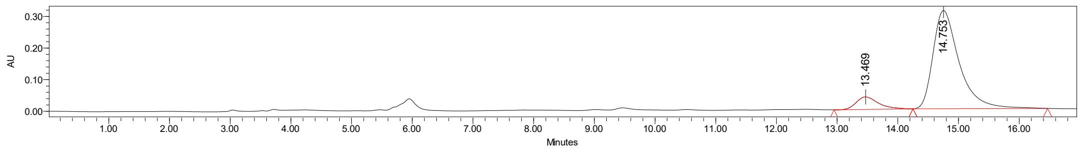
**(*S*)- 2-bromo-1-phenylethanol (2v)**




(**$C_{12}H_{16}O_3$**) a white solid; 95% yield, 81% ee. $[\alpha]_D^{27}$ = +44.36 (*c* = 0.780, in $CHCl_3$), {Lit.[5]$[\alpha]_D^{20}$ = −45.5 (c = 1.0, $CHCl_3$), conf. (*R*)}. HPLC DAICEL CHIRALCEL ODH, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 13.47 min, 14.75 min. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 4.93 – 4.81 (m, 1H), 3.58 (dd, *J* = 10.5, 3.5 Hz, 1H), 3.49 (dd, *J* = 10.4, 8.8 Hz, 1H), 2.94 (d, *J* = 2.8 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 140.44, 128.72, 128.50, 126.06, 73.83, 40.07. ESI-HRMS: calcd for **$C_{11}H_{14}Br^{78.9183}NaO_3^+$** [M+Na$^+$] 222.9734, found 222.9739. **$C_{11}H_{14}Br^{80.9163}NaO_3^+$** [M+Na$^+$] 224.9714, found 224.9725.

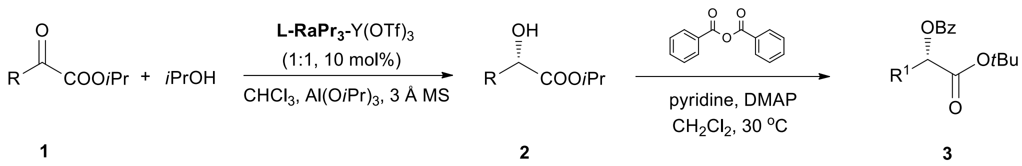



| | Retention Time | %Area |
|---|---|---|
| 1 | 13.337 | 49.54 |
| 2 | 14.604 | 50.46 |



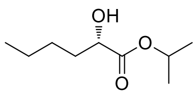
| | Retention Time | %Area |
|---|---|---|
| 1 | 13.469 | 9.74 |
| 2 | 14.753 | 90.26 |

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



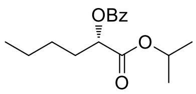

**2s-2t** (x mmol) obtained in asymmetric intramolecular Cannizzaro reaction, benzoic anhydride (1.1x mmol), pyridine (x mmol), DMAP (x mmol) and $CH_2Cl_2$ (1 mL) were added in the reaction tube sequently. The reaction was stirred vigorously at 30°C (monitored by TLC).The mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **2s-2t**. The ee of **2s-2t** was determined according to the ee of **3s-3t**.

**(*S*)-*iso*-propyl 2-hydroxyhexanoate (2s)**



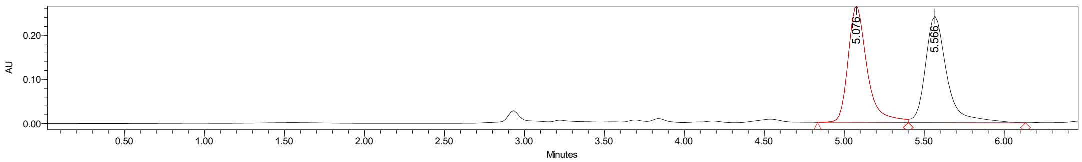

(**$C_9H_{18}O_3$**) a colorless oil; 99% yield. $[\alpha]_D^{19}$ = +15.08 (*c* = 0.252, in $CH_2Cl_2$). ESI-HRMS: calcd for **$C_9H_{18}NaO_3^+$** [M+Na$^+$] 117.1154, found 117.1161.

**(*S*)-*iso*-propyl 2-benzoxyhexanoate (3s)**

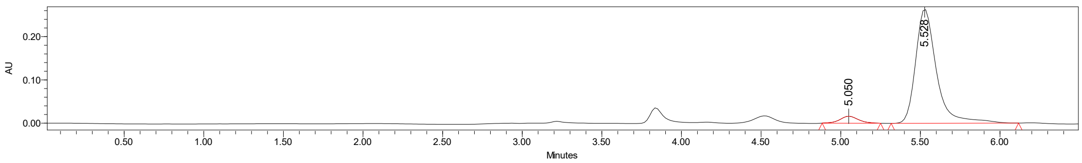



(**$C_{16}H_{22}O_4$**) a colorless oil; 90% ee. $[\alpha]_D^{18}$ = +67.75 (*c* = 0.306, in $CH_2Cl_2$). HPLC Phenomenex Lux 5u Cellulose-2, 2-propanol/*n*-hexane = 5/95, flow rate = 1.0

mL/min, λ = 210 nm, retention time: 5.05 min, 5.53 min. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.97 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.34 (m, 2H), 5.22 – 5.06 (m, 1H), 5.02 (dt, *J* = 12.5, 6.3 Hz, 1H), 2.00 – 1.83 (m, 2H), 1.45 – 1.29 (m, 4H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 169.91, 166.18, 133.22, 129.82, 129.68, 128.40, 73.05, 68.96, 30.93, 27.36, 22.32, 21.75, 21.70, 13.90.ESI-HRMS: calcd for $\mathbf{C_{16}H_{22}NaO_4}^+$ [M+Na$^+$] 301.1416, found 301.1414.

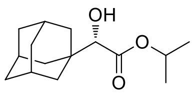



| | Retention Time | %Area |
|---|---|---|
| 1 | 5.076 | 49.32 |
| 2 | 5.566 | 50.68 |



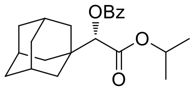

| | Retention Time | %Area |
|---|---|---|
| 1 | 5.050 | 5.08 |
| 2 | 5.528 | 94.92 |

**(*S*)-*iso*-propyl 2-hydroxy-2-(adamantan-1-yl)acetate (2u)**

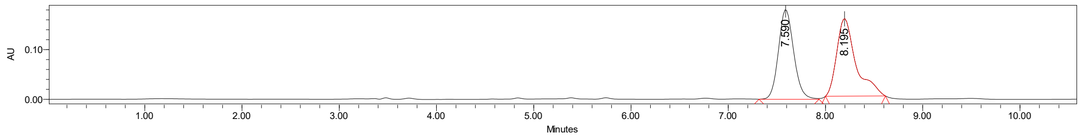



($\mathbf{C_{15}H_{24}O_3}$) a colorless oil; 99% yield. $[\alpha]_D^{19}$ = +81.20 (*c* = 0.266, in $CH_2Cl_2$). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.06 (dt, *J* = 12.5, 6.3 Hz, 1H), 3.53 (s, 1H), 2.63 (s, 1H), 1.93 (s, 3H), 1.64 (d, *J* = 12.0 Hz, 3H), 1.56 (d, *J* = 9.8 Hz, 9H), 1.23 (t, *J* = 6.4 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 173.49, 78.80, 69.35, 37.96, 37.15, 36.94, 28.26, 22.08, 21.89. ESI-HRMS: calcd for $\mathbf{C_{15}H_{24}NaO_3^+}$ [M+Na$^+$] 275.1623, found 275.1615.

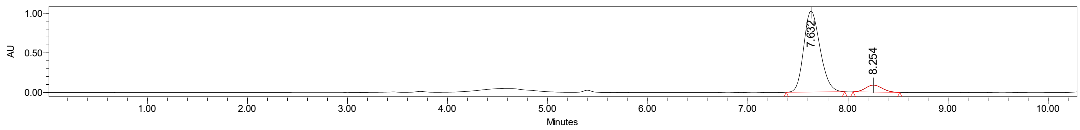
**(*S*)-*iso*-propyl 2-benzoxy-2-(adamantan-1-yl)acetate (3u)**




($\mathbf{C_{22}H_{28}O_3}$) a colorless oil; 84% ee. $[\alpha]_D^{18}$ = +90.78 ($c$ = 0.326, in $CH_2Cl_2$). HPLC DAICEL CHIRALCEL IC, 2-propanol/$n$-hexane = 5/95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 7.63 min, 8.25 min. ESI-HRMS: calcd for $\mathbf{C_{22}H_{28}NaO_3^+}$ [M+Na$^+$] 379.1885, found 379.1888.



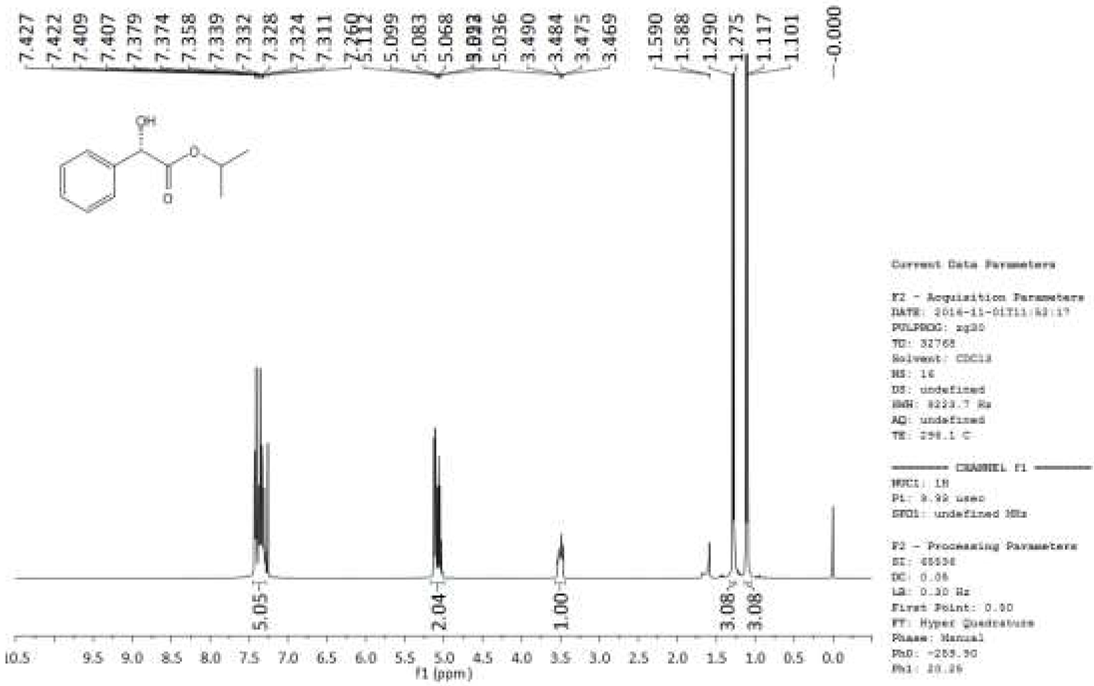

| | Retention Time | %Area |
|---|---|---|
| 1 | 7.590 | 47.92 |
| 2 | 8.195 | 52.08 |

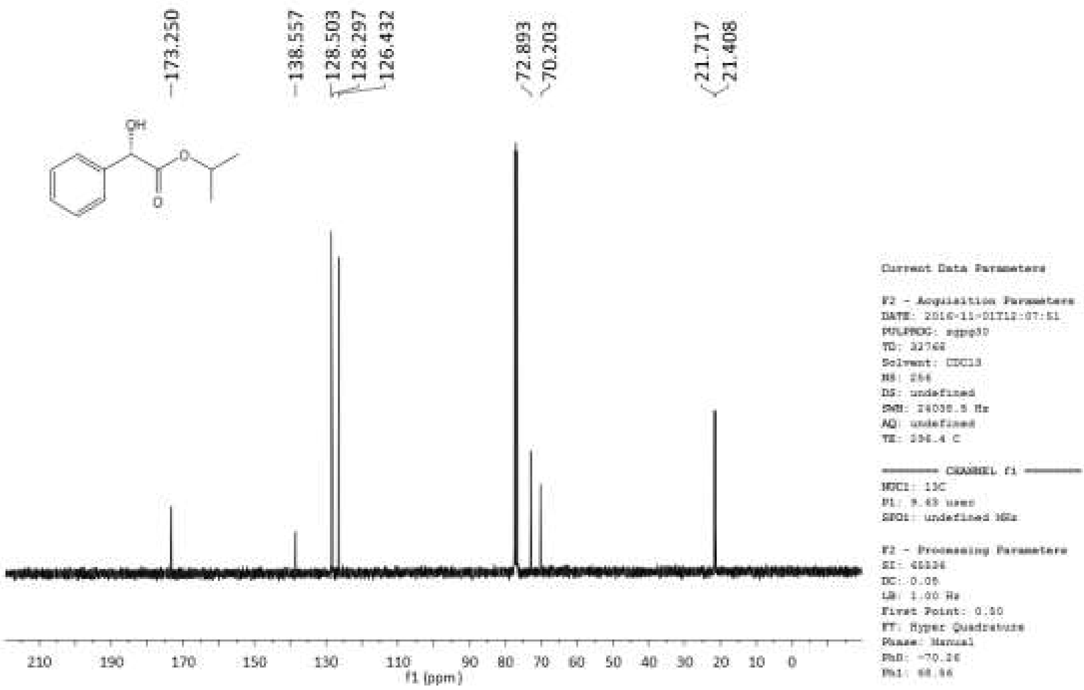



| | Retention Time | %Area |
|---|---|---|
| 1 | 7.632 | 91.99 |
| 2 | 8.254 | 8.01 |

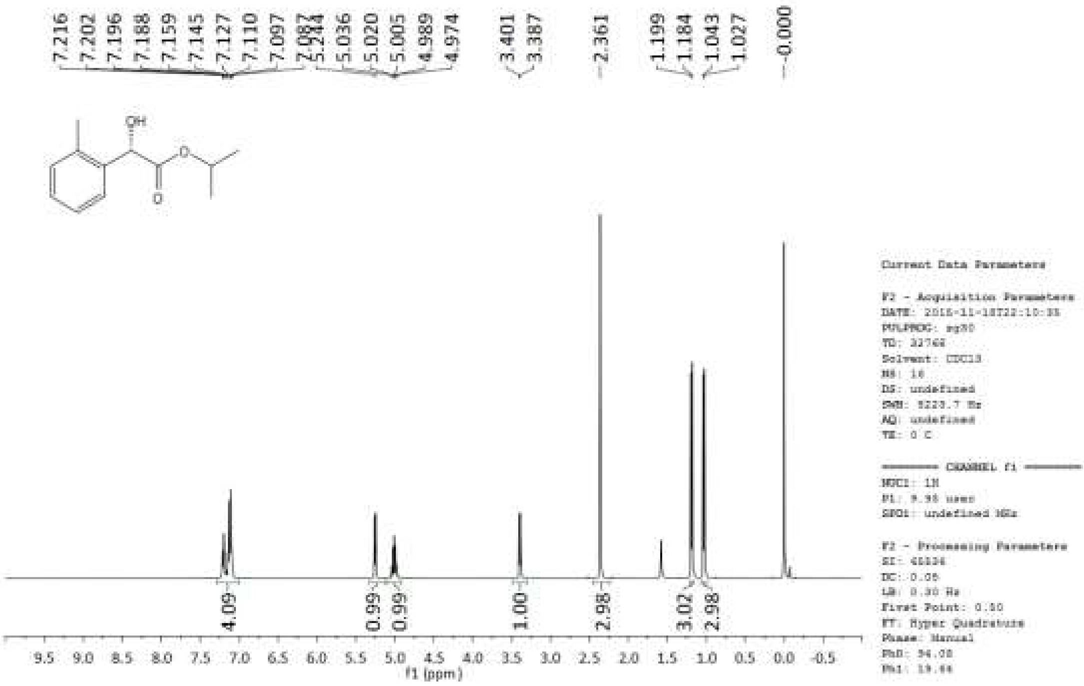
## (K) Copies of NMR spectra for catalysts and products

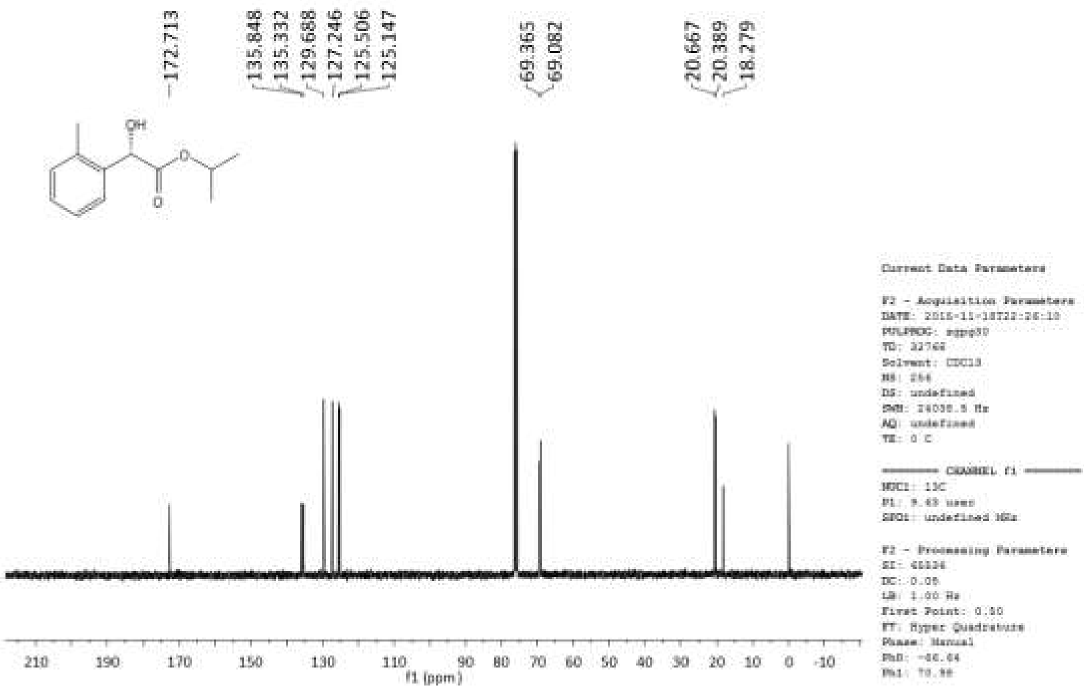
### (*S*)-*iso*-propyl mandelate (2a)



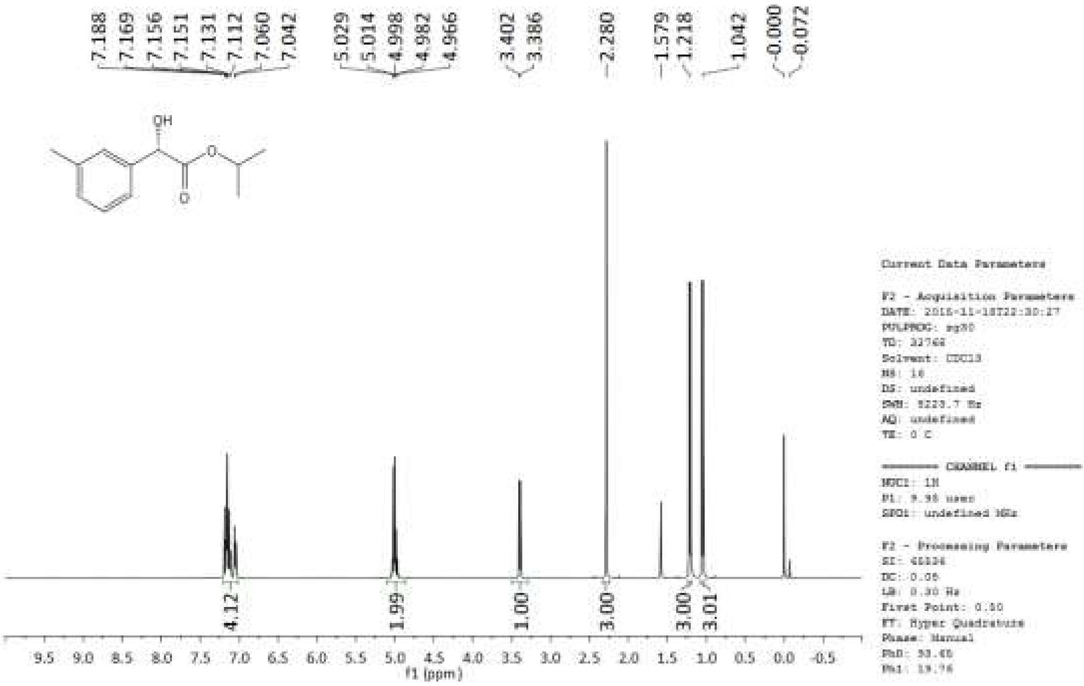

173.250
138.557
128.503
128.297
126.432
72.893
70.203
21.717
21.408
OH
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-11-01T12:07:51
NS: 256
DS: undefined
AQ: undefined
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual

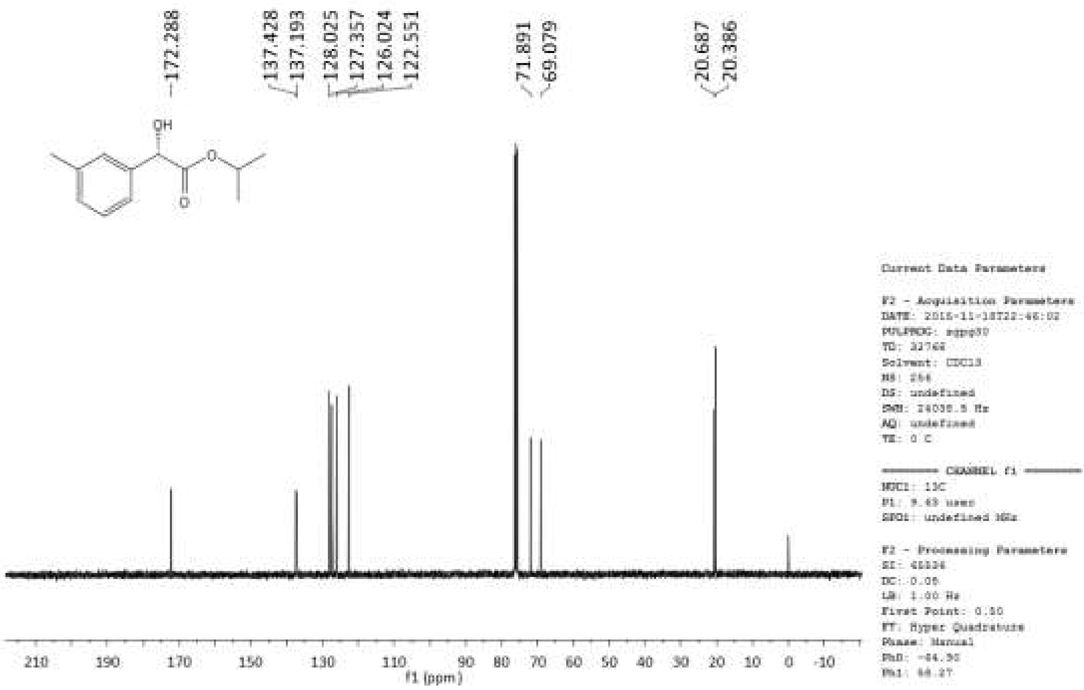
**(*S*)-*iso*-propyl α-hydroxy-α-(2-methylphenyl)acetate (2b)**




172.713
135.848
135.332
129.688
127.246
125.506
125.147
69.365
69.082
20.667
20.389
18.279
OH
O
O
Current Data Parameters
F2 - Acquisition Parameters
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

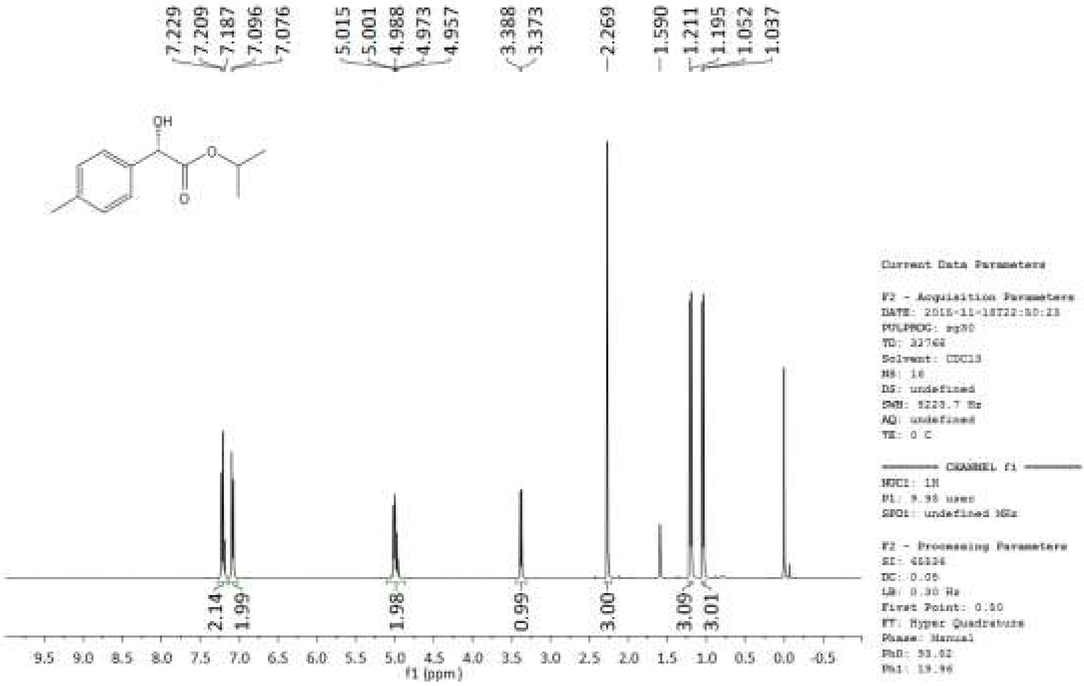
**(*S*)-*iso*-propyl α-hydroxy-α-(3-methylphenyl)acetate (2c)**

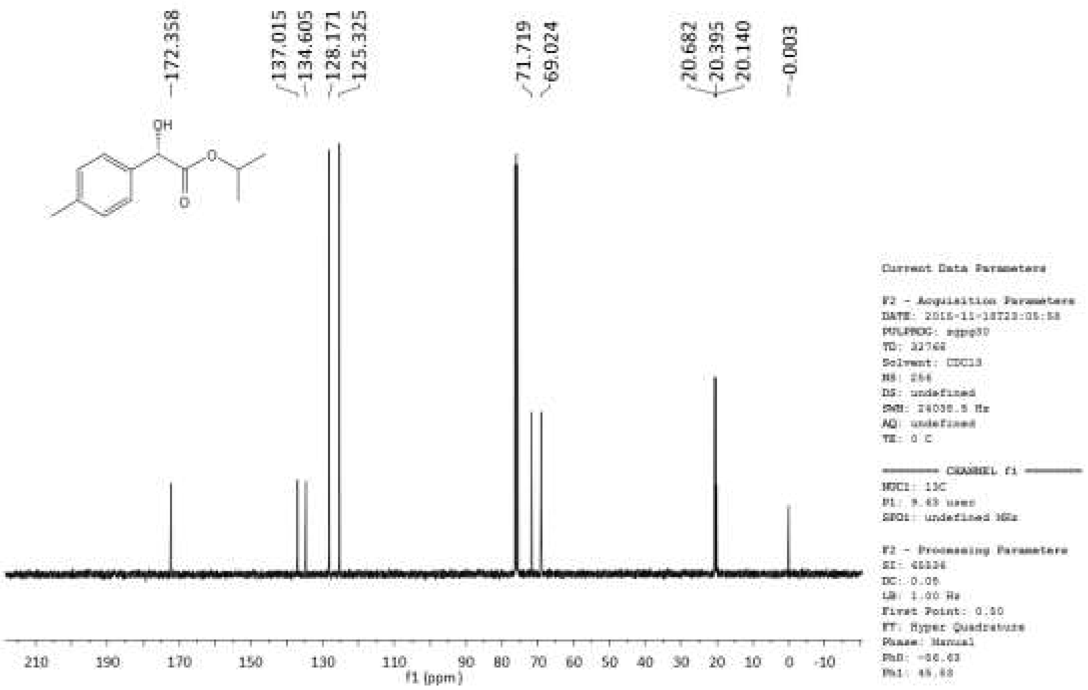




172.288
137.428
137.193
128.025
127.357
126.024
122.551
71.891
69.079
20.687
20.386
OH
O
O
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
CHANNEL f1
NUC1: 13C
F2 - Processing Parameters
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

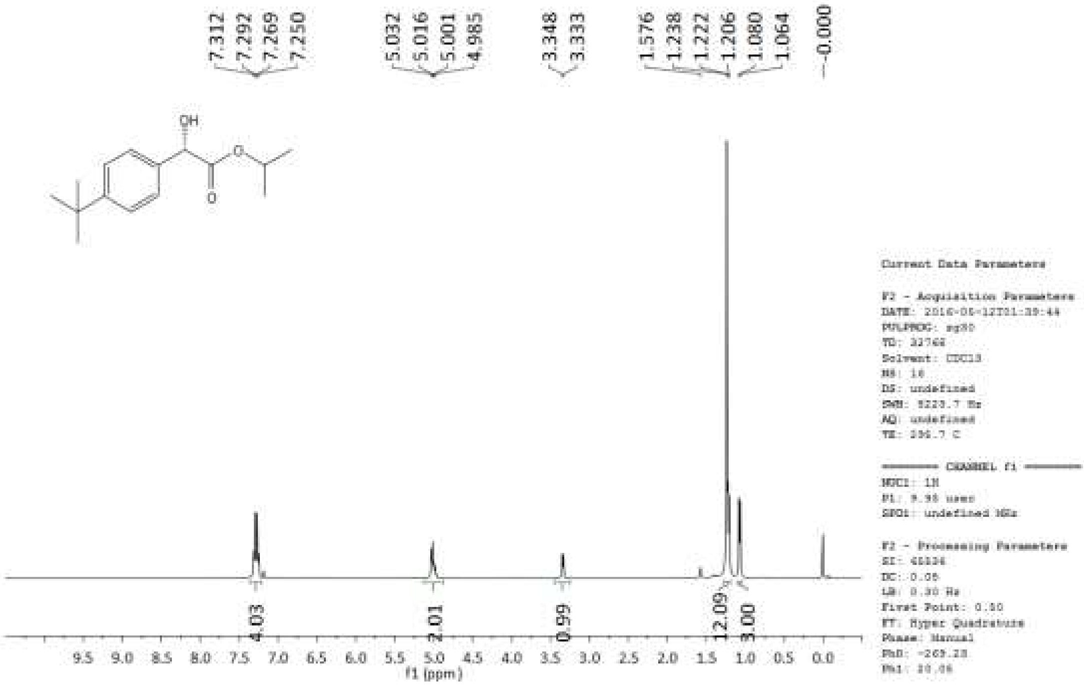
**(*S*)-*iso*-propyl α-hydroxy-α-(4-methylphenyl)acetate (2d)**

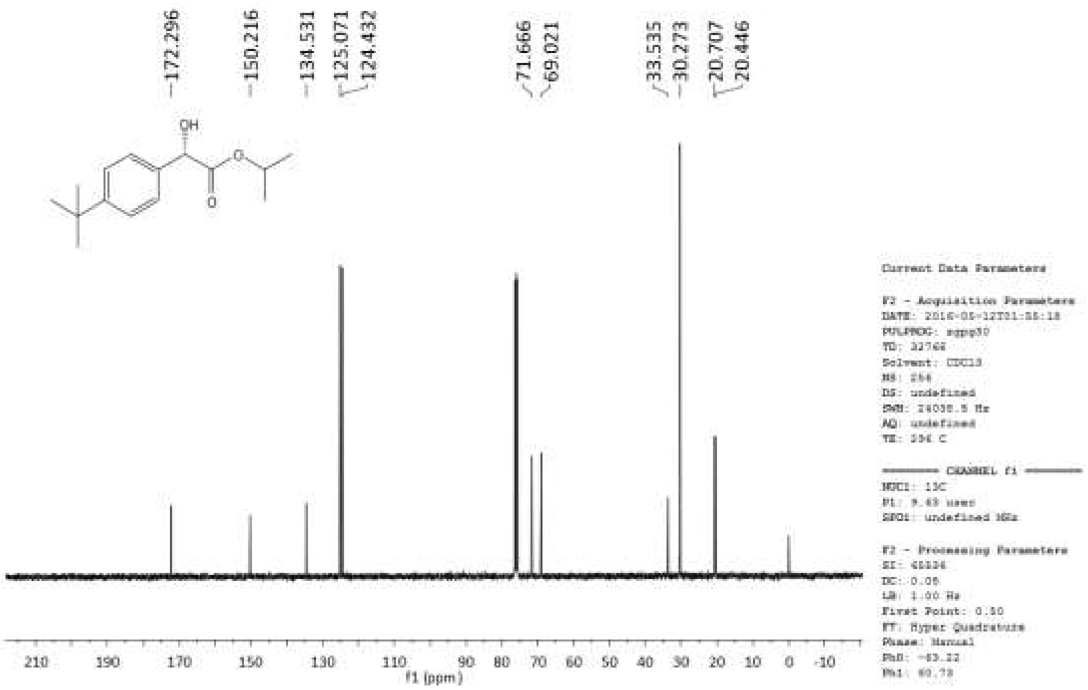




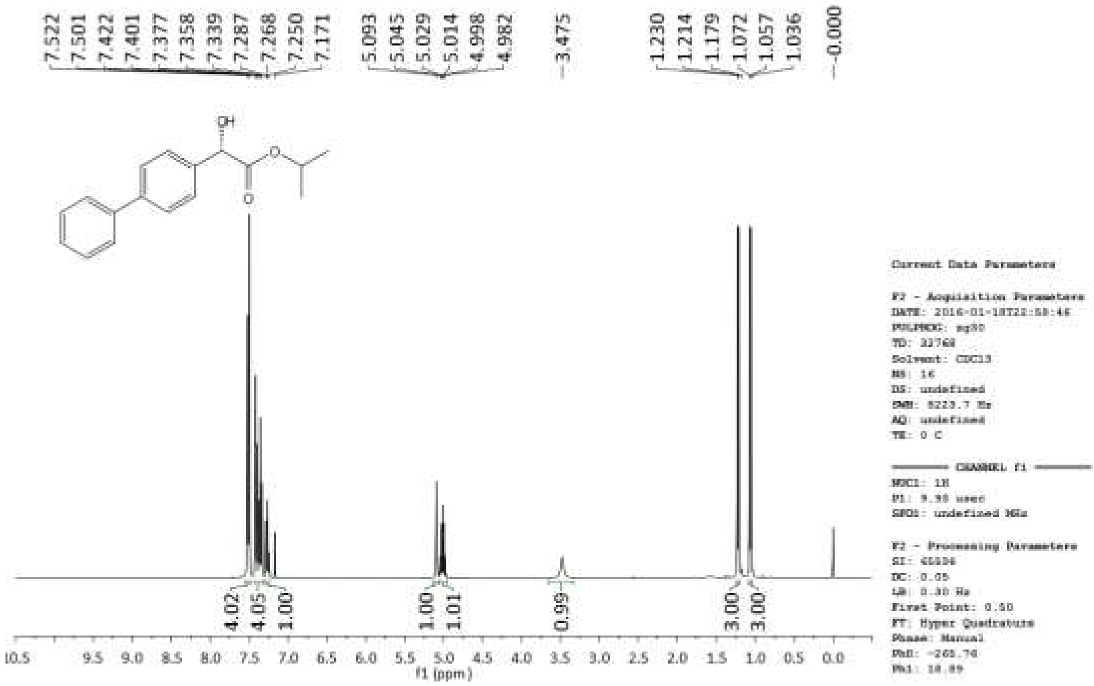
172.358
137.015
134.605
128.171
125.325
71.719
69.024
20.682
20.395
20.140
-0.003
OH
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -66.63
Ph1: 45.68

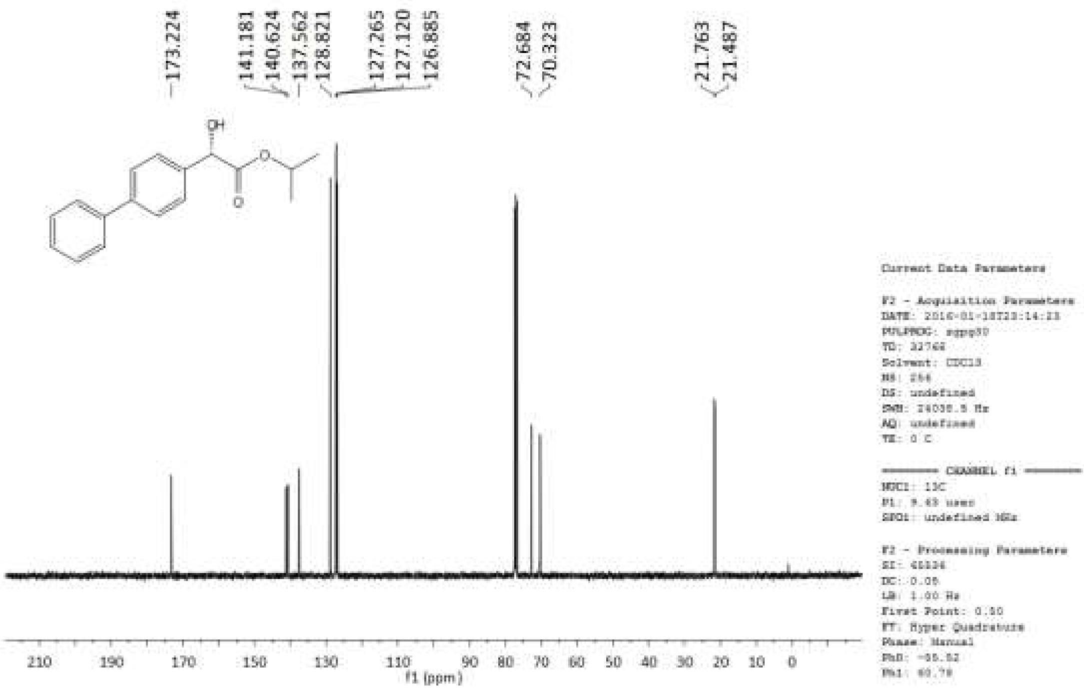
**(*S*)-*iso*-propyl α-hydroxy-α-(4-(*tert*-butyl)phenyl)acetate (2e)**




172.296
150.216
134.531
125.071
124.432
71.666
69.021
33.535
30.273
20.707
20.446
OH
O
O
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-05-12T01:55:18
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296 C
CHANNEL f1
NUC1: 13C
P1: 9.43 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -63.22
Ph1: 60.78
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

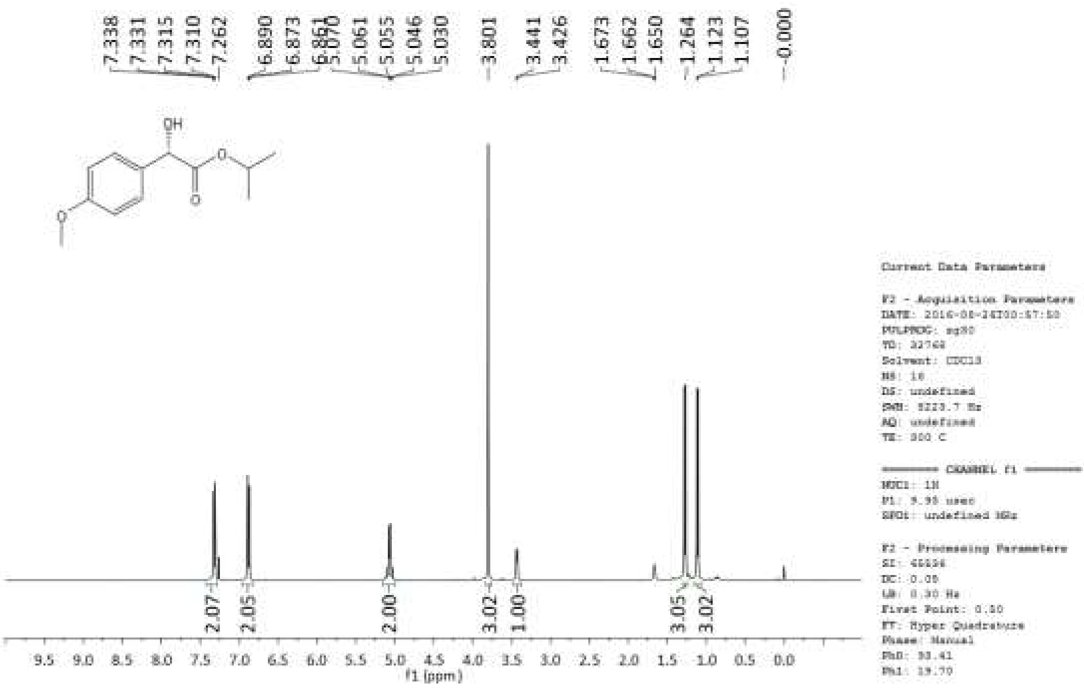
**(*S*)-*iso*-propyl α-hydroxy-α-(4-phenylphenyl)acetate (2f)**

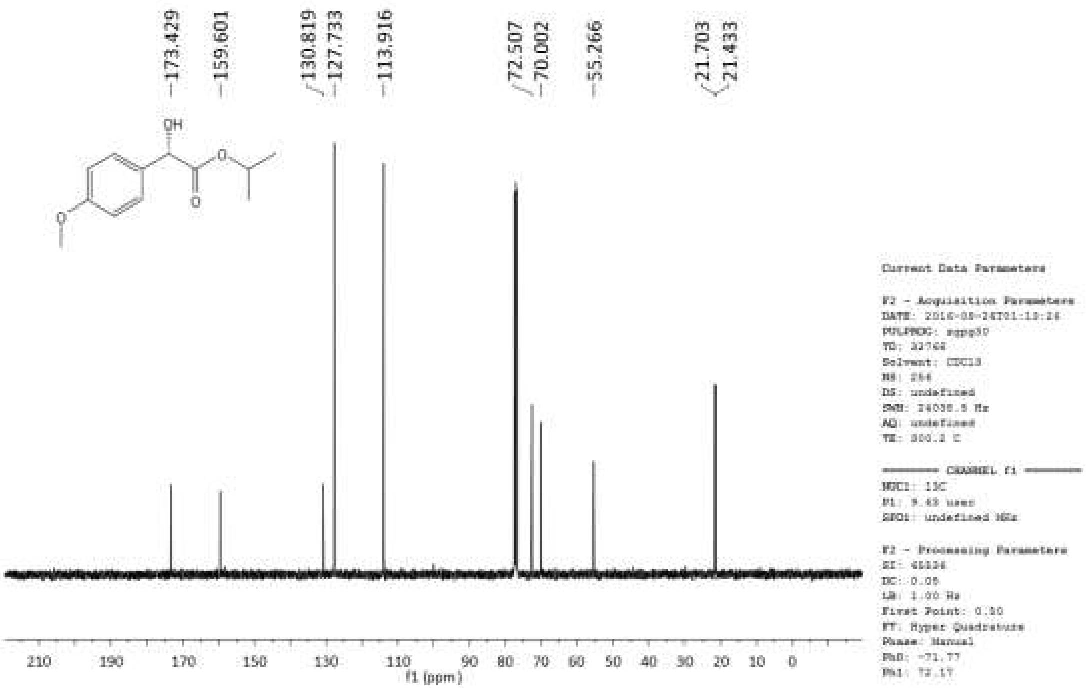




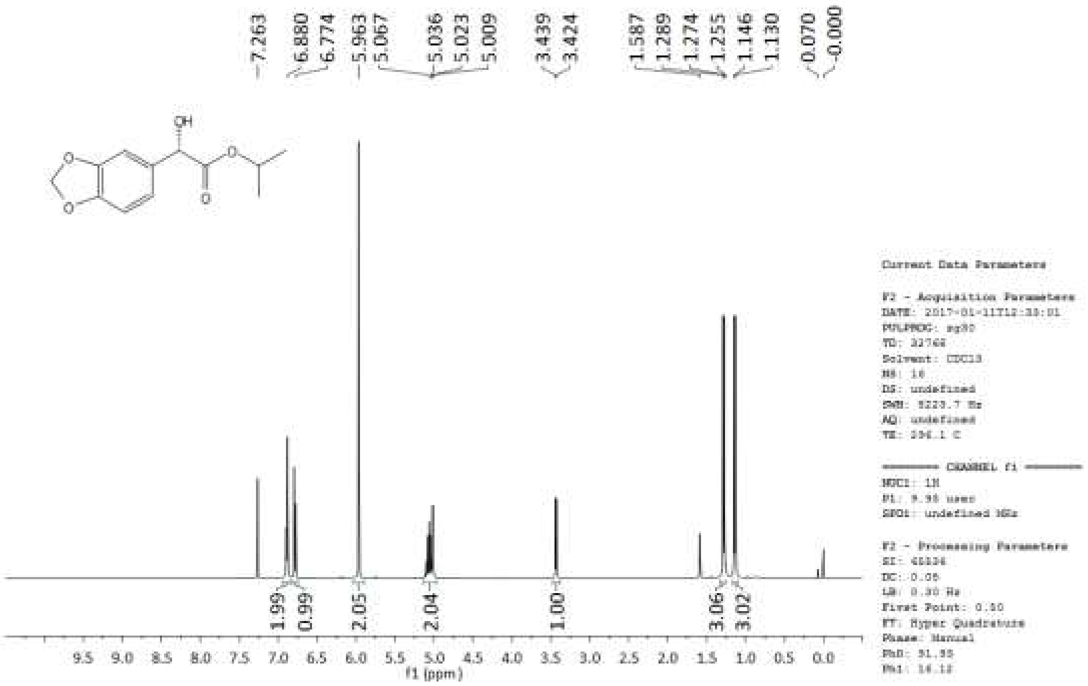
173.224
141.181
140.624
137.562
128.821
127.265
127.120
126.885
72.684
70.323
21.763
21.487
OH
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual

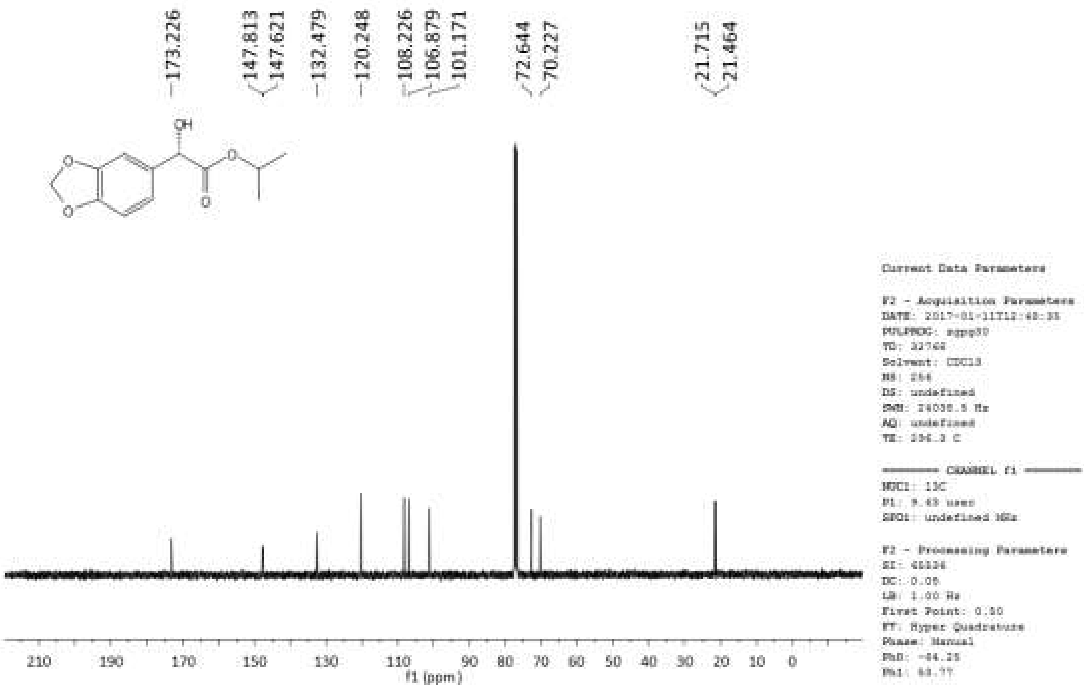
**(*S*)-*iso*-propyl α-hydroxy-α-(4-methoxylphenyl)acetate (2g)**




-173.429
-159.601
130.819
127.733
-113.916
72.507
70.002
-55.266
21.703
21.433
OH
O
O
O
Current Data Parameters
F2 - Acquisition Parameters
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
PH0: -71.77
PH1: 72.17
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

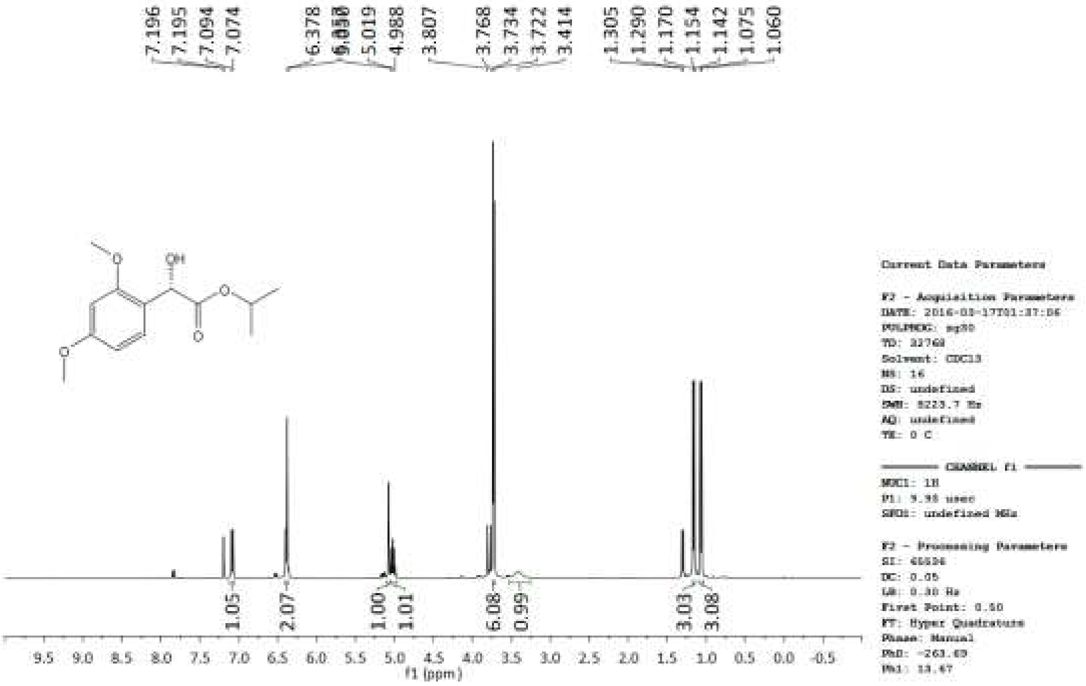
**(*S*)-*iso*-propyl α-hydroxy-α-(3,4-methylenedioxylphenyl)acetate (2h)**

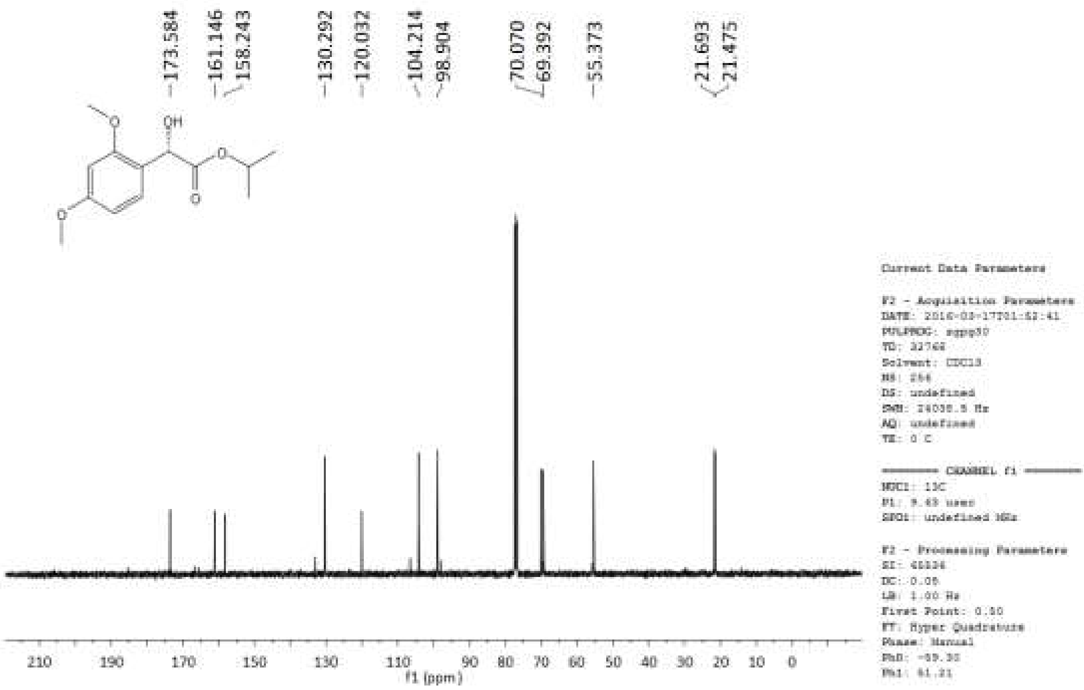




173.226
147.813
147.621
132.479
120.248
108.226
106.879
101.171
72.644
70.227
21.715
21.464
OH
O
O
O
O
Current Data Parameters
F2 - Acquisition Parameters
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

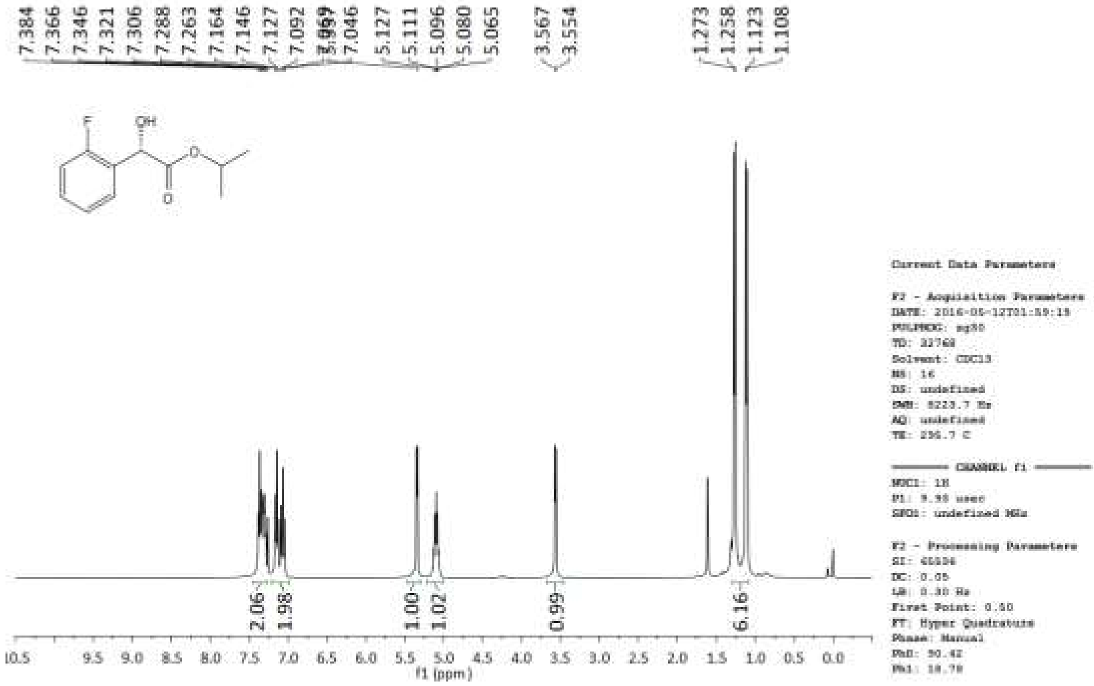
**(*S*)-*iso*-propyl α-hydroxy-α-(2,4-dimethoxylphenyl)acetate (2i)**

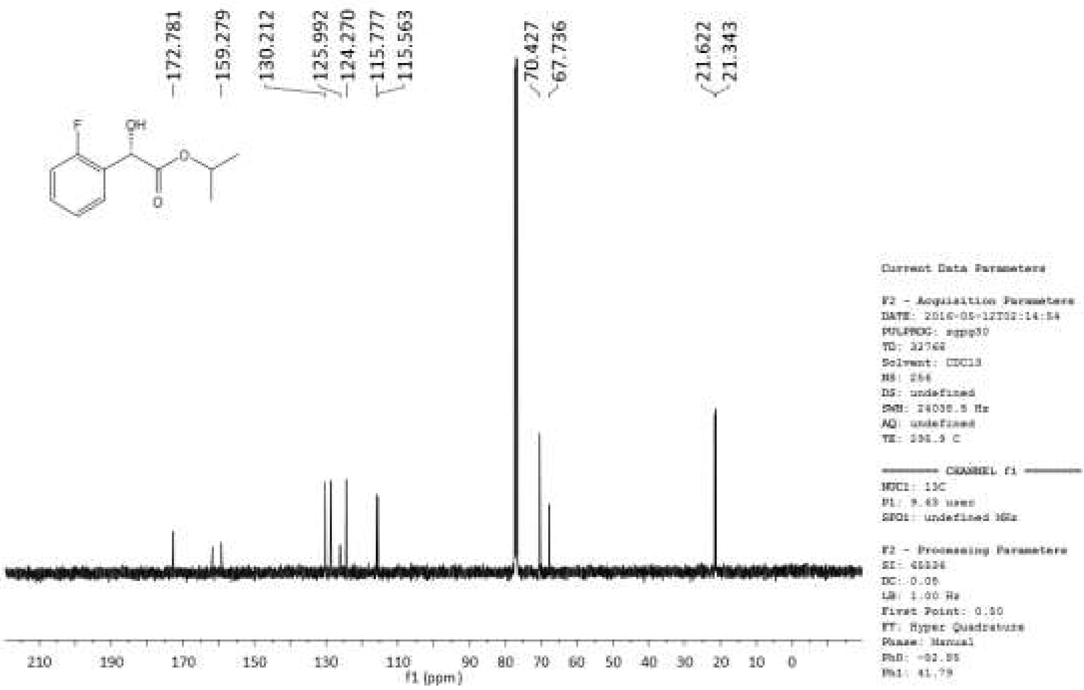




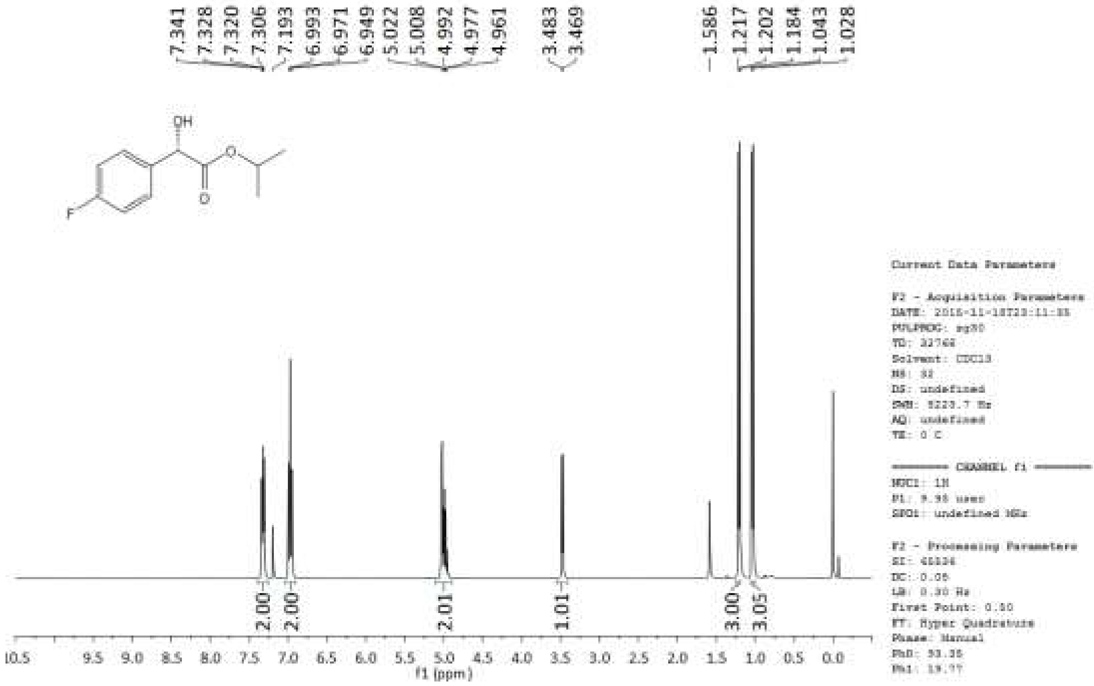
173.584
161.146
158.243
130.292
120.032
104.214
98.904
70.070
69.392
55.373
21.693
21.475
OH
O
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
DS: undefined
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
F2 - Processing Parameters
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

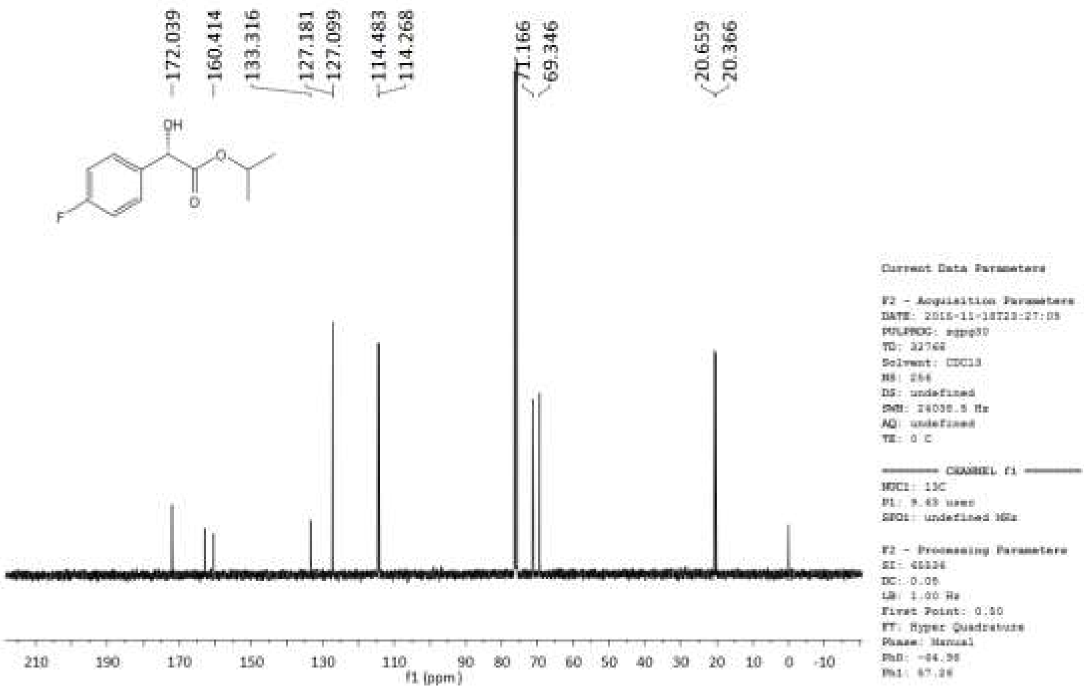
**(*S*)-*iso*-propyl α-hydroxy-α-(2-flurophenyl)acetate (2j)**



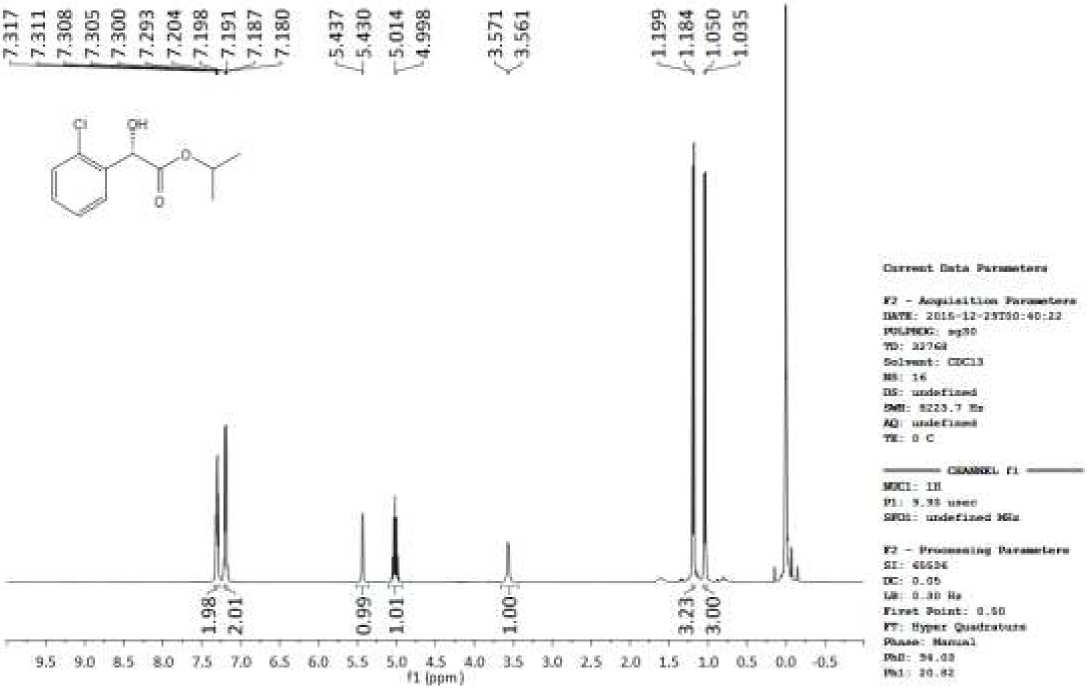

172.781
159.279
130.212
125.992
124.270
115.777
115.563
70.427
67.736
21.622
21.343
F
OH
O
O
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2016-05-12T02:14:54
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 296.9 C
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -92.85
Ph1: 41.79
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

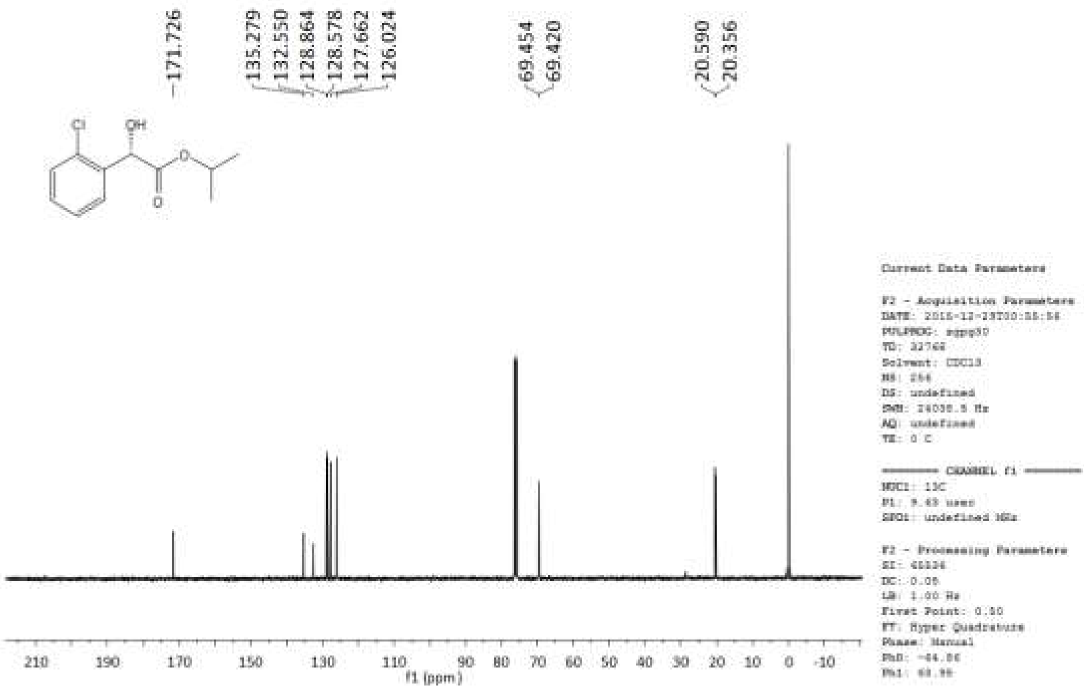
**(*S*)-*iso*-propyl α-hydroxy-α-(4-flurophenyl)acetate (2k)**




172.039
160.414
133.316
127.181
127.099
114.483
114.268
71.166
69.346
20.659
20.366
OH
O
O
F
Current Data Parameters
F2 - Acquisition Parameters
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
LB: 1.00 Hz
FT: Hyper Quadrature
Phase: Manual
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

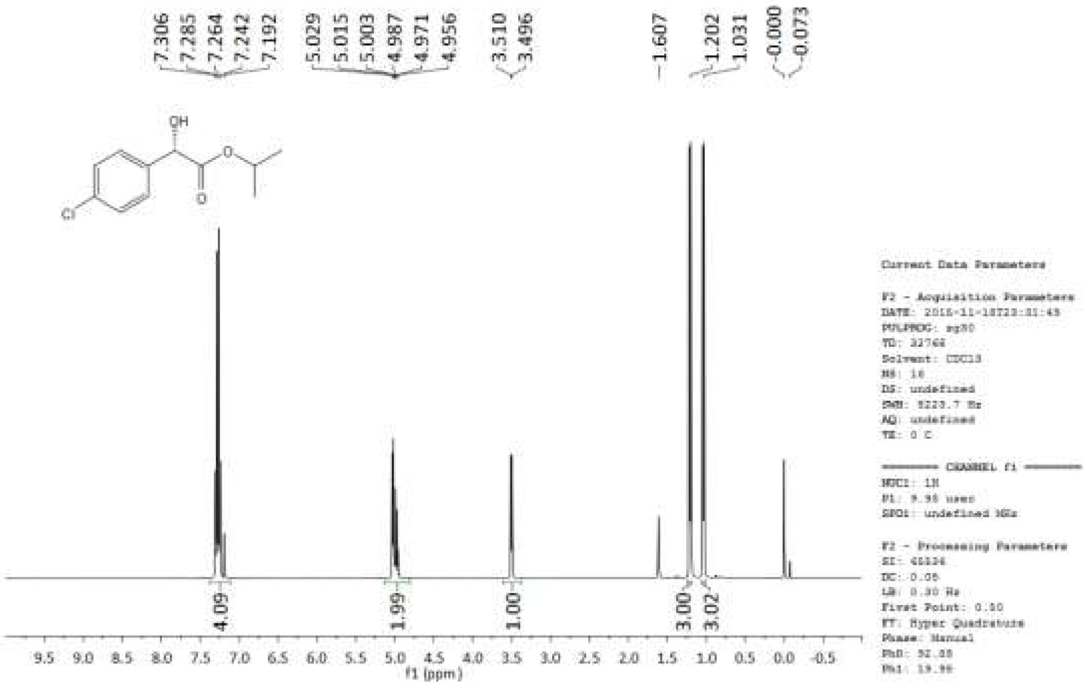
**(*S*)-*iso*-propyl α-hydroxy-α-(2-chlorophenyl)acetate (2l)**

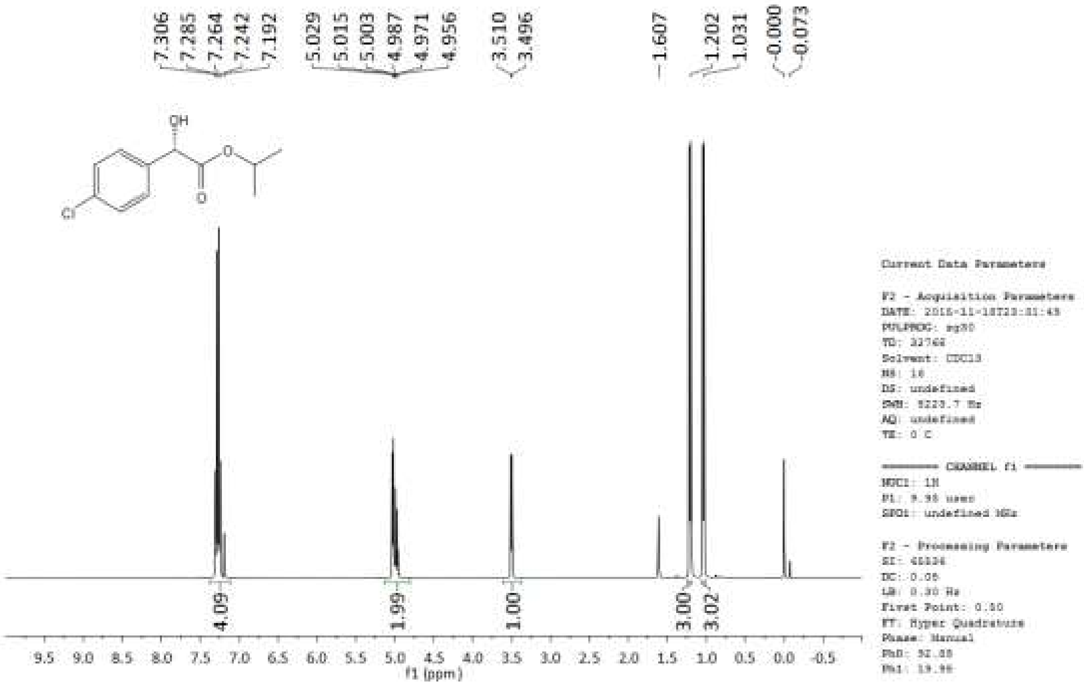




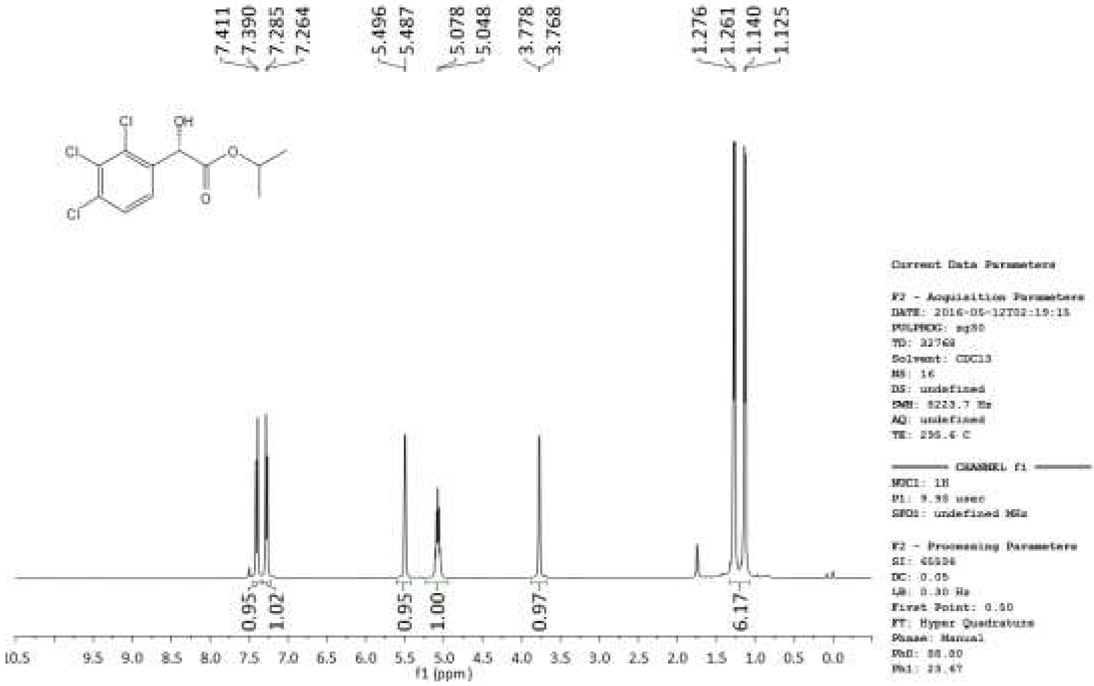
171.726
135.279
132.550
128.864
128.578
127.662
126.024
69.454
69.420
20.590
20.356
Cl
OH
O
O
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

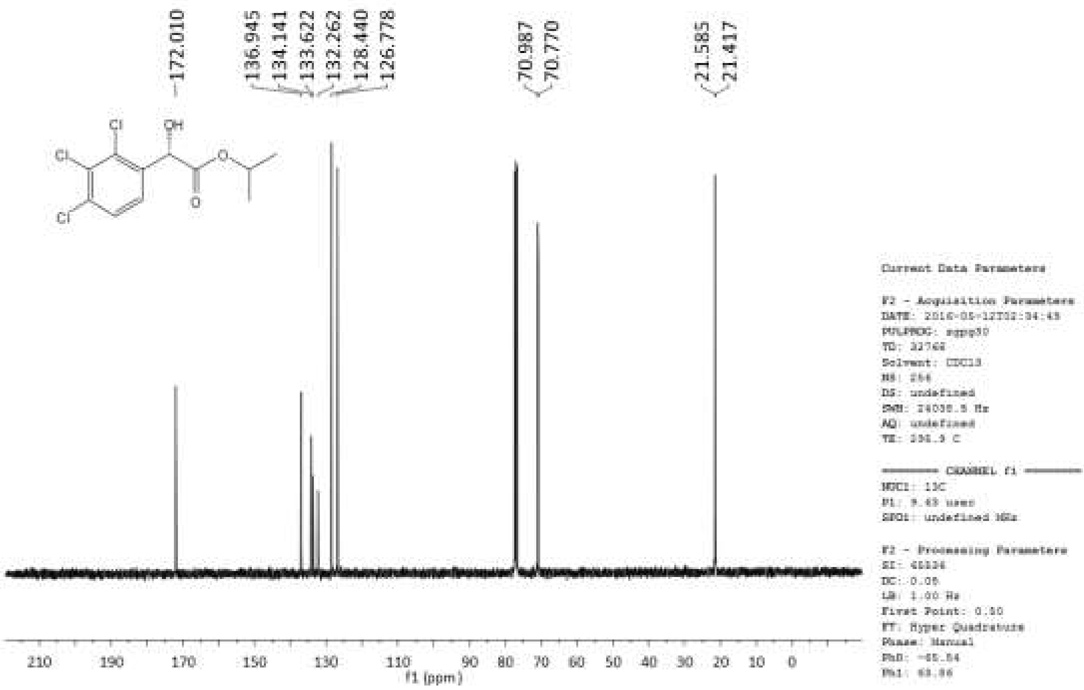
**(*S*)-*iso*-propyl α-hydroxy-α-(4-chlorophenyl)acetate (2m)**




7.306
7.285
7.264
7.242
7.192
5.029
5.015
5.003
4.987
4.971
4.956
3.510
3.496
1.607
1.202
1.031
0.000
-0.073
OH
O
O
Cl
4.09
1.99
1.00
3.00
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
DS: undefined
AQ: undefined
CHANNEL f1
NUC1: 1H
F2 - Processing Parameters
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual

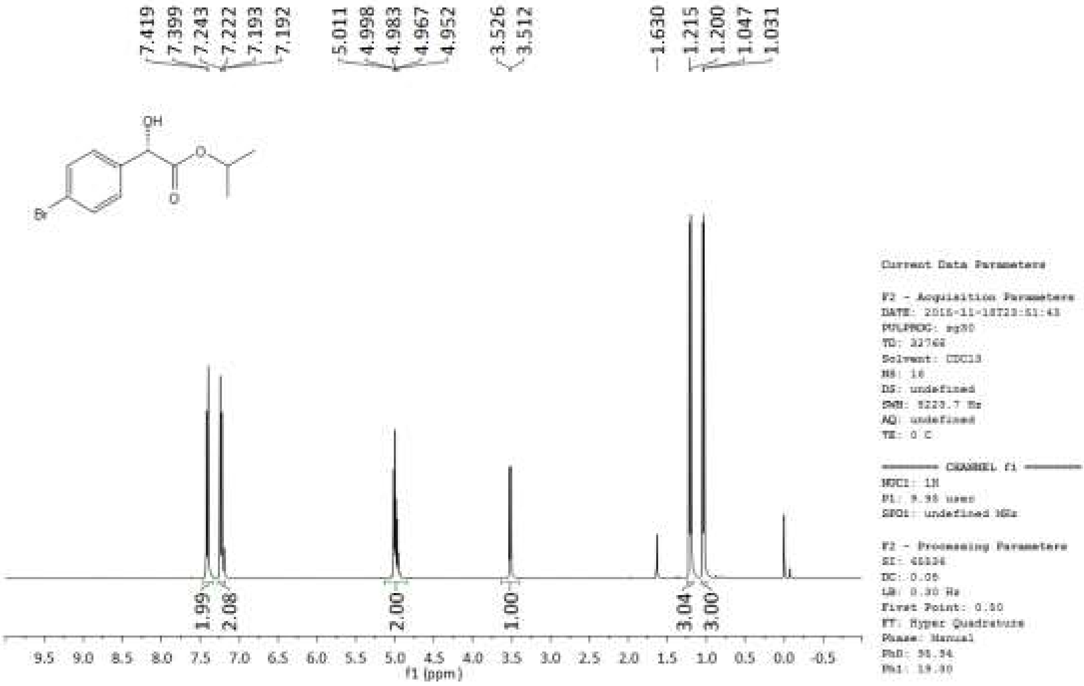
**(*S*)-*iso*-propyl α-hydroxy-α-(2,3,4-trichlorophenyl)acetate (2n)**

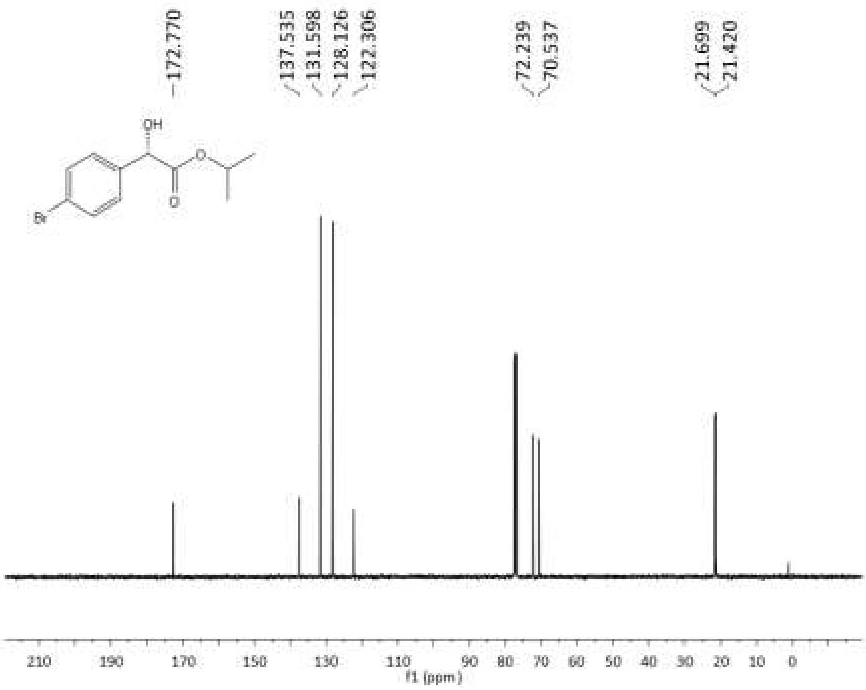




172.010
136.945
134.141
133.622
132.262
128.440
126.778
70.987
70.770
21.585
21.417
Cl
Cl
Cl
OH
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**(*S*)-*iso*-propyl α-hydroxy-α-(2-bromophenyl)acetate (2o)**





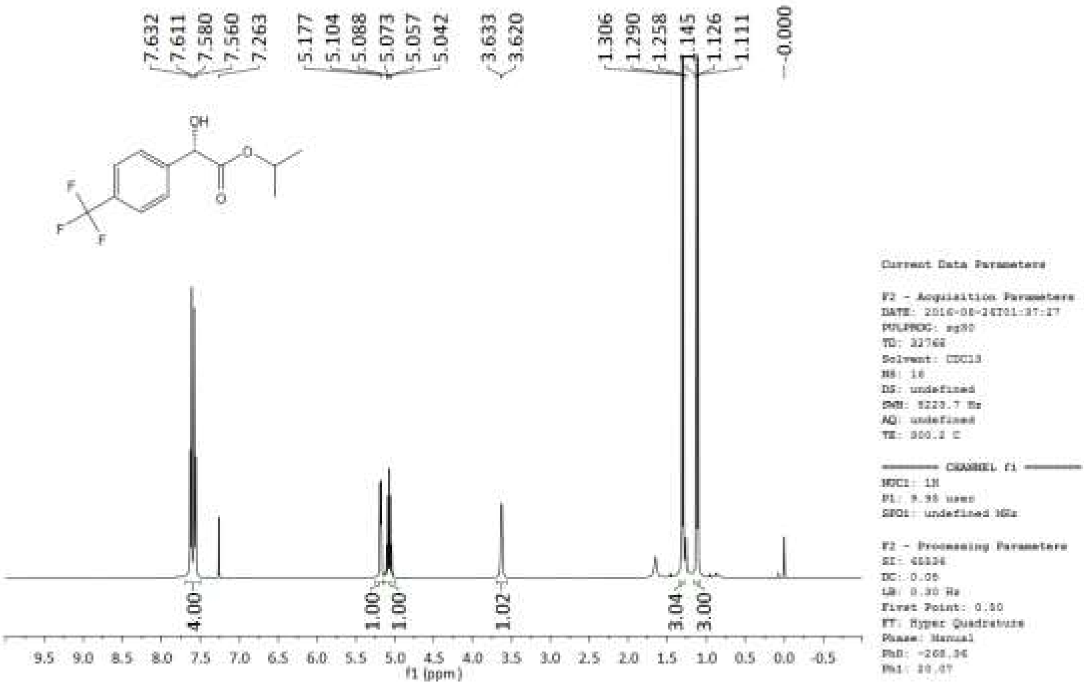

Current Data Parameters

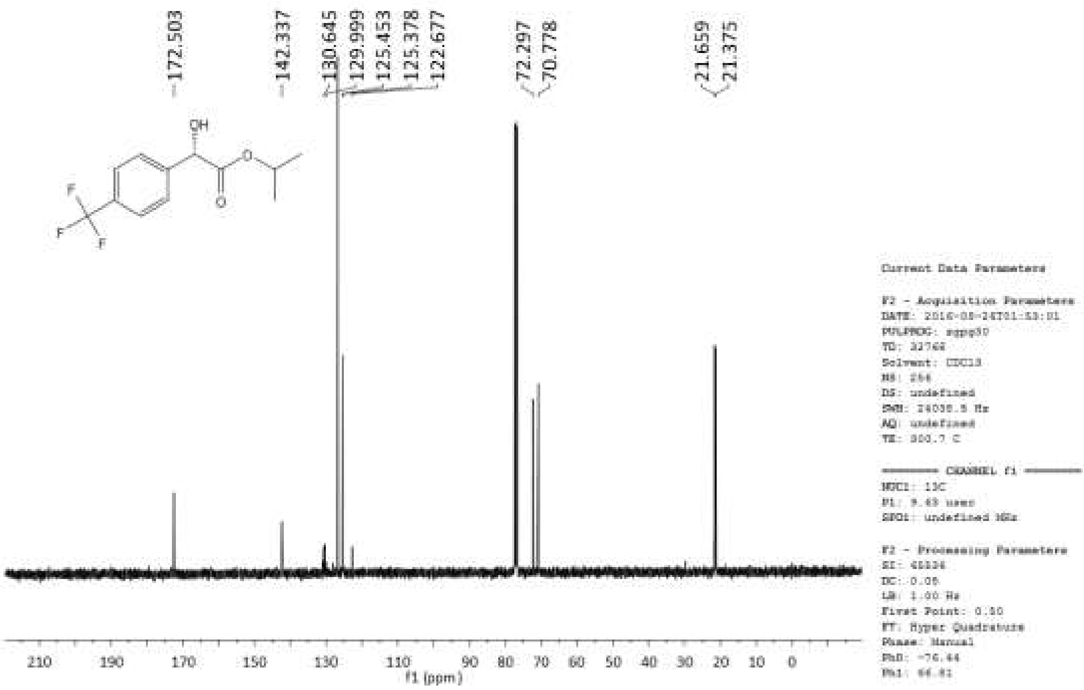
F2 - Acquisition Parameters
DATE: 2016-11-15T00:07:18
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -69.26
Ph1: 61.08

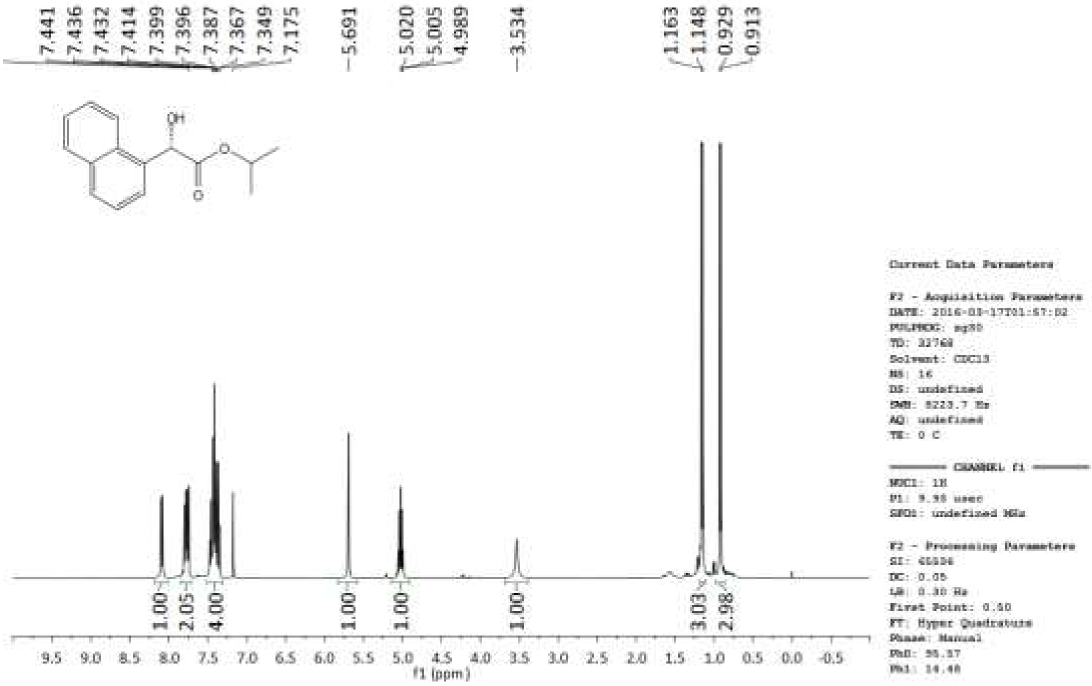
**(*S*)-*iso*-propyl α-hydroxy-α-(4-(trifluoromethyl)phenyl)acetate (2p)**

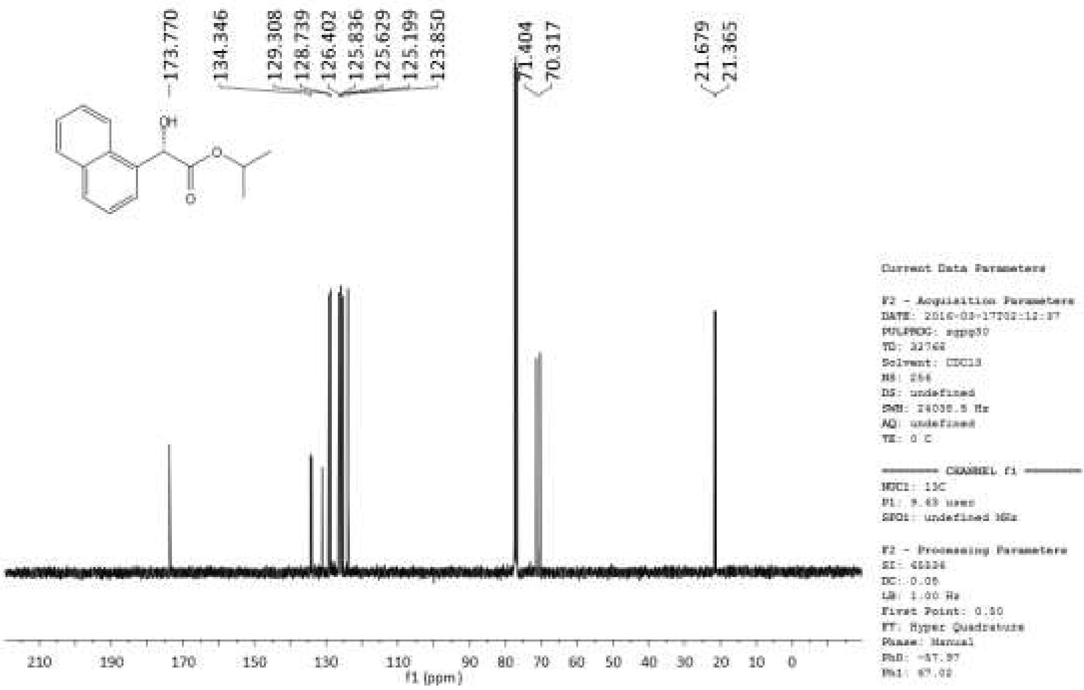




172.503
142.337
130.645
129.999
125.453
125.378
122.677
72.297
70.778
21.659
21.375
OH
O
F
F
F
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
CHANNEL f1
NUC1: 13C
F2 - Processing Parameters
FT: Hyper Quadrature
Phase: Manual
PH0: -76.44
PH1: 66.81

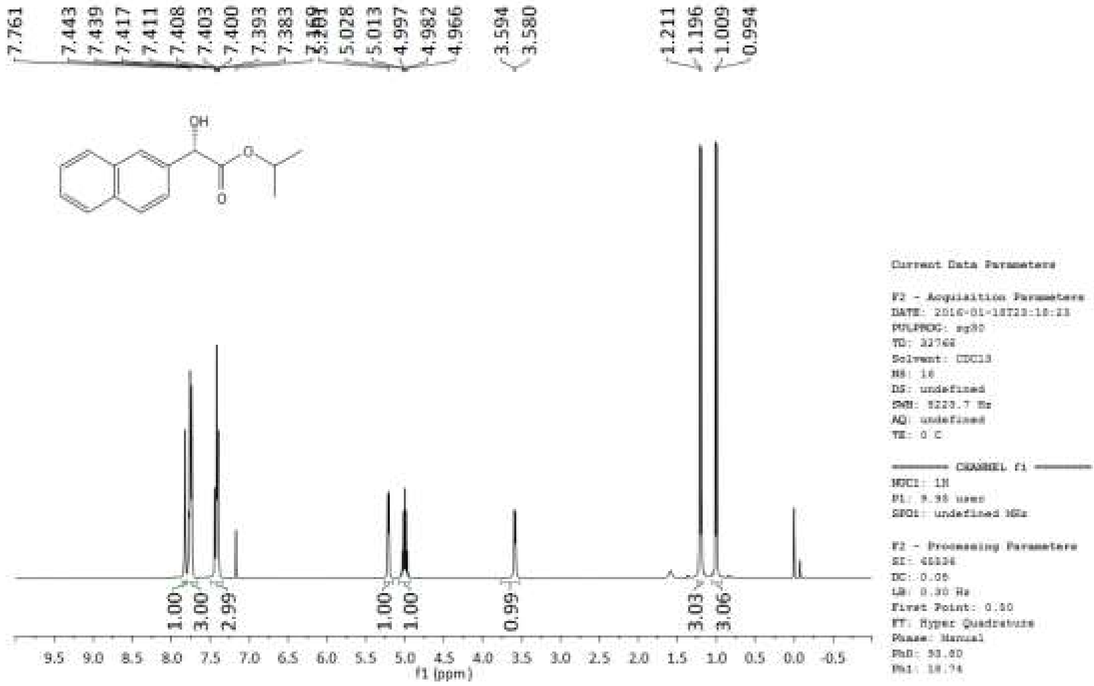
**(*S*)-*iso*-propyl α-hydroxy-α-(naphthalen-1-yl)acetate (2q)**

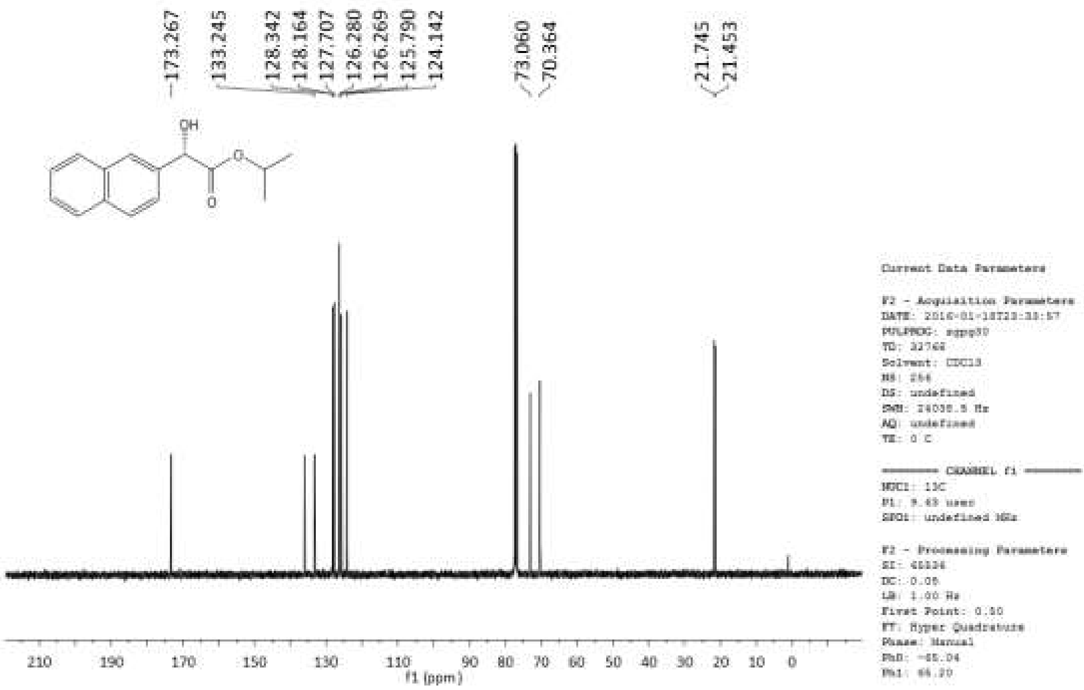




-173.770
134.346
129.308
128.739
126.402
125.836
125.629
125.199
123.850
71.404
70.317
21.679
21.365
OH
O
O
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

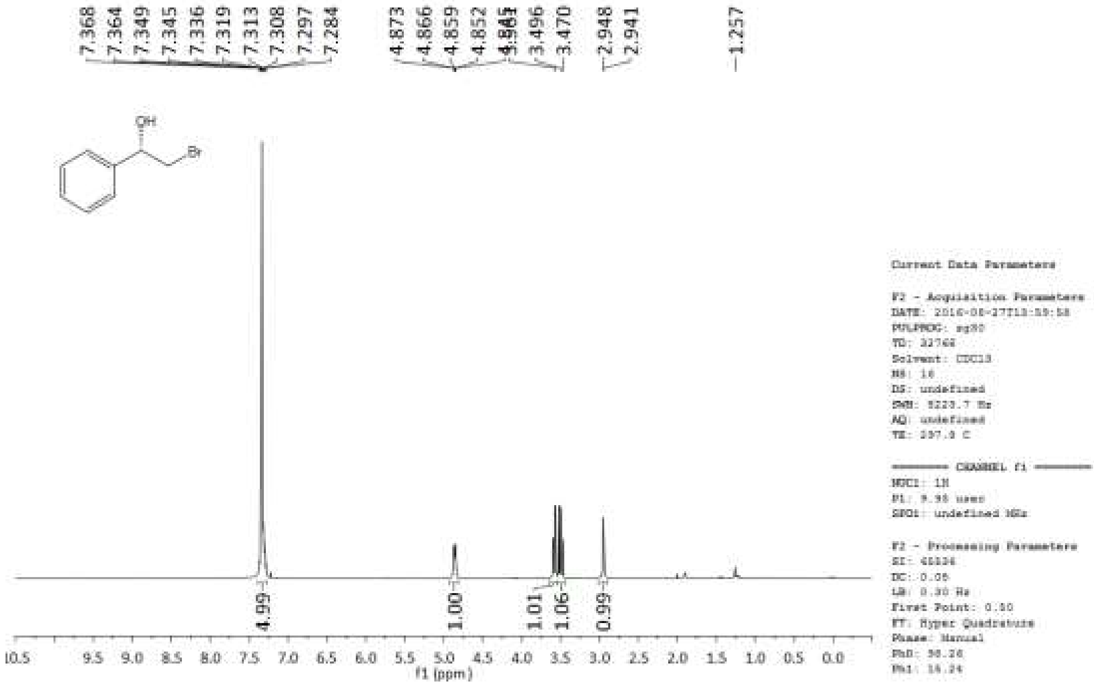
**(*S*)-*iso*-propyl α-hydroxy-α-(naphthalen-2-yl)acetate (2r)**

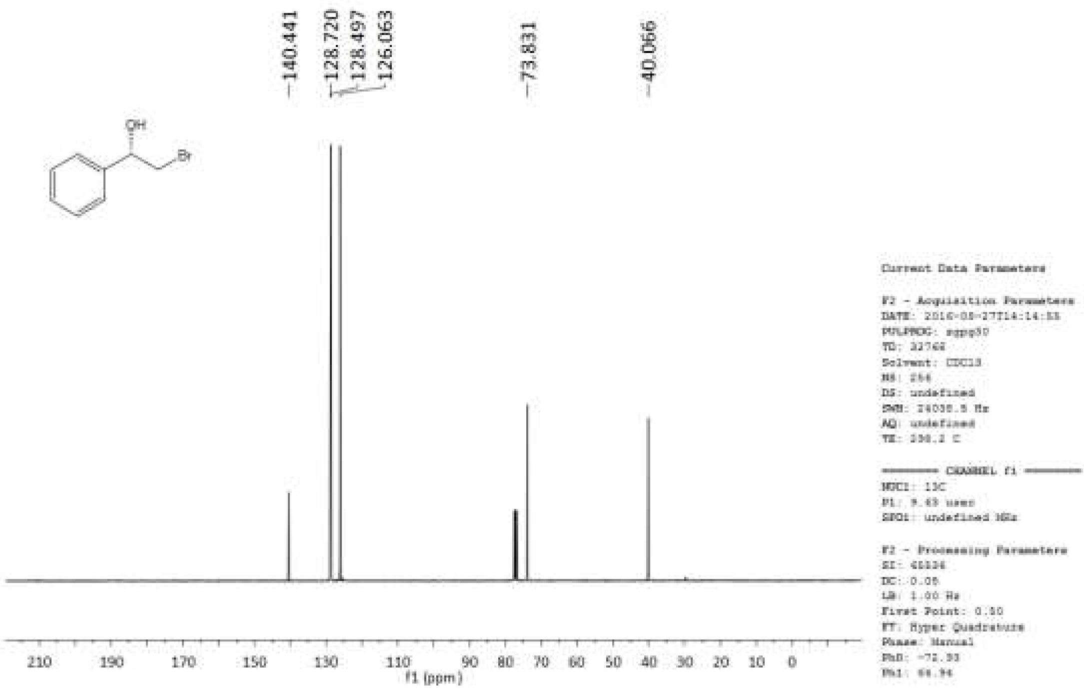




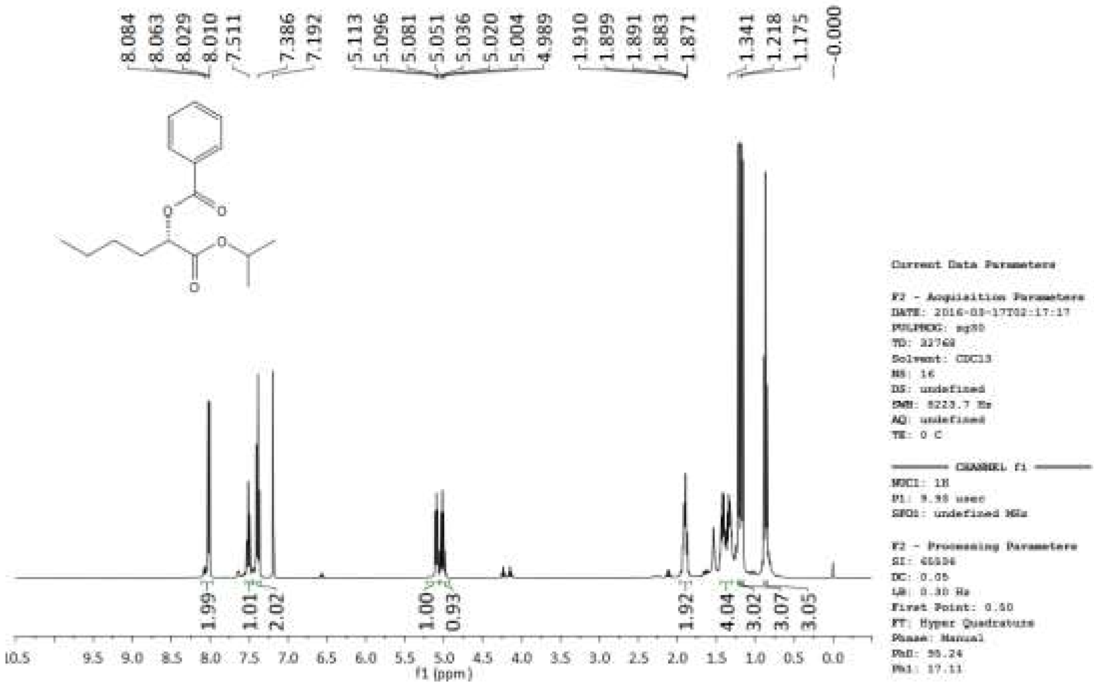
173.267
133.245
128.342
128.164
127.707
126.280
126.269
125.790
124.142
73.060
70.364
21.745
21.453
OH
O
O
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
DS: undefined
AQ: undefined
TE: 0 C
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
FT: Hyper Quadrature
Phase: Manual
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

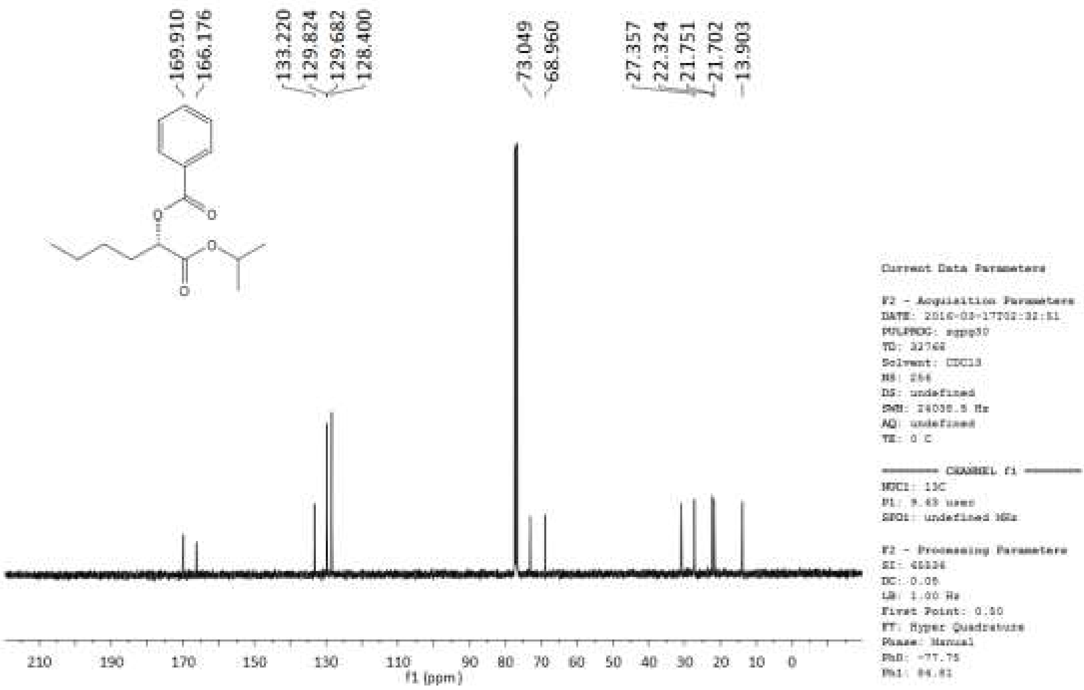
**(*S*)- 2-bromo-1-phenylethanol (2u)**



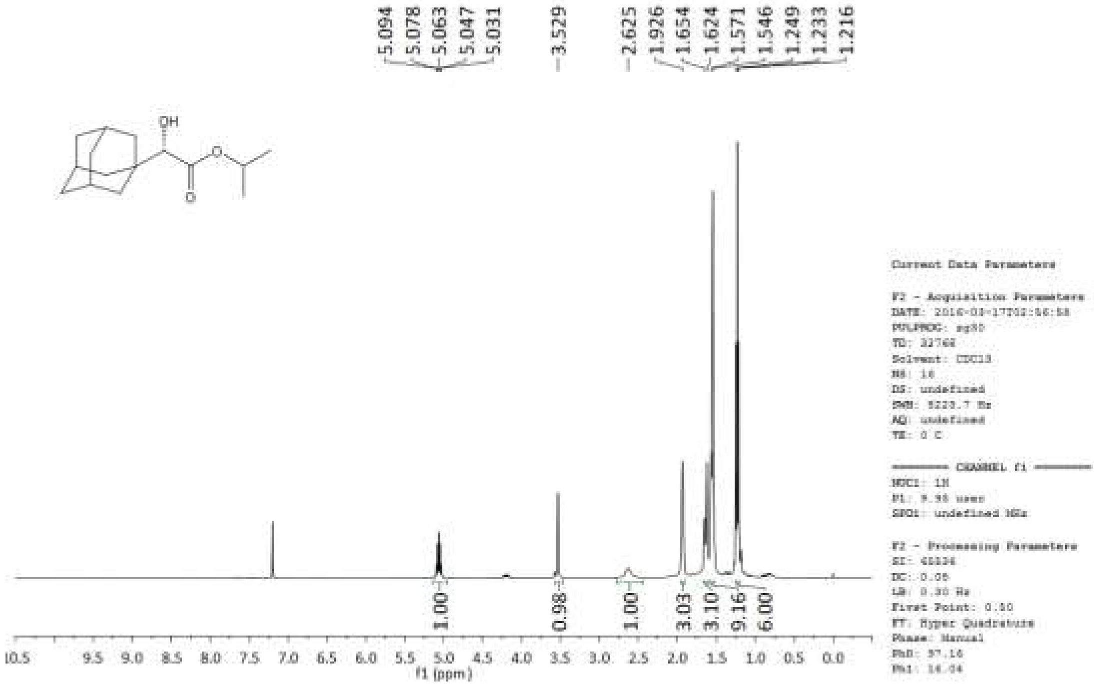

140.441
128.720
128.497
126.063
73.831
40.066
OH
Br
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual

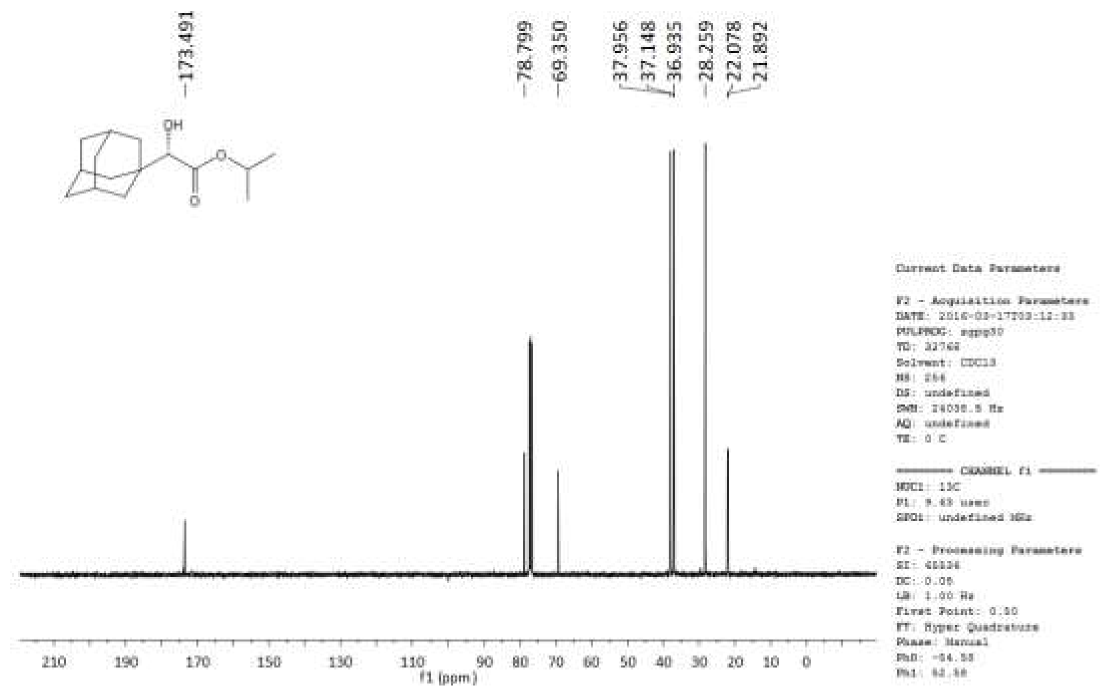
**(*S*)-*iso*-propyl 2-benzoxyhexanoate (3s)**




169.910
166.176
133.220
129.824
129.682
128.400
73.049
68.960
27.357
22.324
21.751
21.702
13.903
O
O
O
O
Current Data Parameters
F2 - Acquisition Parameters
Solvent: CDCl3
NS: 256
DS: undefined
AQ: undefined
CHANNEL f1
NUC1: 13C
SFO1: undefined MHz
F2 - Processing Parameters
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
PhO: -77.75
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**(*S*)-*iso*-propyl 2-hydroxy-2-(adamantan-1-yl)acetate (2t)**






**(L) References**

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

[3] A. Sagar, S. Vidyacharan and D. S. Sharada, *RSC Adv.* 2014, **4**, 37047.

[4] Y. H. Zhang, X. H. Liu, L. Zhou, W. B. Wu, T. Y. Huang, Y. T. Liao, L. L. Lin and X. M. Feng, *Chem. Eur. J.* 2014, **20**,15884.

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