Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Asymmetric transfer hydrogenation of aryl ketoesters with chiral double-chain surfactant-type catalyst in water

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Contents

1. General Methods.

All commercially available reagents were used as received without further purification. All organic solvents used in the reactions were distilled from appropriate drying agents prior to use. All reactions were performed in air. ^{1}H NMR and ^{13}C NMR were acquired at 300 MHz（or 400 MHz） and 75 MHz （or 100 MHz） respectively. Optical rotation were recorded on PE polarmeter 341. Enantiomeric excesses were determined by GC or HPLC analysis. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer.

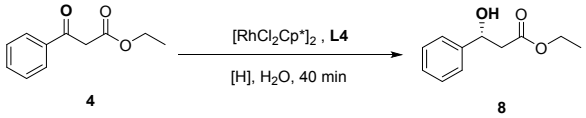
Typical procedure for the asymmetric transfer hydrogenation in water.

All the reductions were performed in the air during the entire operation including catalyst preparation (using distilled water without degassing).

$[Cp^*RhCl_2]_2$ (1.3 mg 0.002 mmol) and ligand (0.004 mmol) were dissolved in 5 mL of H_2O. After stirring at 40 ^{o}C for 2 h, the solution was cooled to 25 ^{o}C. HCOONa (2 mmol) and ketoesters (0.4 mmol) were added to the solution. Then the mixture was allowed to react at 30 ^{o}C for a certain period of time. The organic phase was extracted with EtOAc (5 mL×3).

2. Effect of the hydrogen sources on the ATH of ethyl 3-oxo-3-phenylpropanoate.

Table S1. Effect of the [H] on ATH of ethyl 3-oxo-3-phenylpropanoate catalyzed by Rh–L4 Complex. [a]



entry	[H]	conv.[b](%)	e.e.[c](%)
1	HCOONa	84	96
2	HCOOK	69	96
3	$HCOONH_4$	5	N.D.
4	$(CH_3)_2CHOH$	N.R.	-
5	TEAF(0.1 mL)	N.R.	-

[a] Reaction conditions: 0.004 mmol of **L4**, 0.002 mmol of metal precursor, 5.0 mL of H_2O, 2 mmol of [H], 0.4 mmol of ethyl 3-oxo-3-phenylpropanoate, S/C=100, 40 min, 30 ^{o}C. [b] Conversion was determined by ^{1}HNMR of the unpurified reaction mixture. [c] Enantiomeric excess was determined by HPLC analysis.

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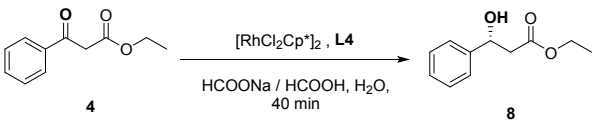
3. Effect of the HCOONa / HCOOH on the ATH of ethyl 3-oxo-3-phenylpropanoate.

Table S2. Effect of the pH on ATH of ethyl 3-oxo-3-phenylpropanoate Catalyzed by Rh–L4 Complex. [a]

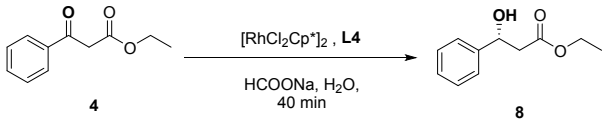


entry	HCOONa / HCOOH	pH [b]	pH [c]	conv. [d](%)	e.e. [e](%)
1	1.82 / 0.18	4.30	6.53	53	94
2	1.961 / 0.039	4.88	7.01	78	95
3	2 / 0	7.24	8.13	84	96
4	2 / 0 [f]	10.91	9.83	20	94

[a] Reaction conditions: 0.004 mmol of L4, 0.002 mmol of $[Cp^*RhCl_2]_2$, 5 mL of H_2O, HCOONa / HCOOH (2 mmol), 0.4 mmol of ethyl 3-oxo-3-phenylpropanoate, S/C=100, 40 min, 30 °C. [b] Initial pH value. [c] pH value after reaction. [d] Conversion was determined by ^{1}HNMR of the unpurified reaction mixture. [e] Enantiomeric excess was determined by HPLC analysis. [f] Extra 0.5 mmol of Na_2CO_3 was added.

4. Effect of the amount of H_2O on the ATH of ethyl 3-oxo-3-phenylpropanoate.

Table S3. Effect of the amount of H_2O on ATH of ethyl 3-oxo-3-phenylpropanoate Catalyzed by Rh–L4 Complex. [a]

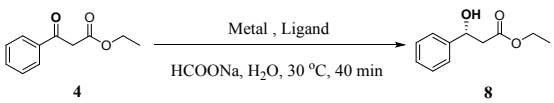


entry	H_2O	conv. [b](%)	e.e. [c](%)
1	3 mL	80	96
2	5 mL	84	96
3	10 mL	77	96
4	20 mL	68	96

[a] Reaction conditions: 0.004 mmol of **L4**, 0.002 mmol of $[Cp^*RhCl_2]_2$, 5 mL of H_2O, 2 mmol of HCOONa, 0.4 mmol of ethyl 3-oxo-3-phenylpropanoate, S/C=100, 40 min, 30 °C. [b] Conversion was determined by ^{1}HNMR of the unpurified reaction mixture. [c] Enantiomeric excess was determined by HPLC analysis.

5. Effect of ligands and metal precursors on the ATH of ethyl 3-oxo-3-phenylpropanoate.

Table S4. ATH of ethyl 3-oxo-3-phenylpropanoate with different ligands and metal precursors



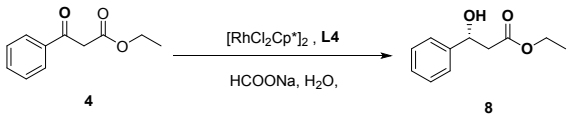
entry	ligand	metal precursor	conv. [b](%)	e.e. [c](%)
1	**L1**	$[RhCl_2Cp^*]_2$	60	95

2	**L2**	$[RhCl_2Cp^*]_2$	56	96
3	**L3**	$[RhCl_2Cp^*]_2$	69	96
4	**L4**	$[RhCl_2Cp^*]_2$	84	96
5	**L4**	$[RuCl_2(p\text{-cymene})]_2$	16	92
6	**L4**	$[Cp^*IrCl_2]_2$	30	94

[a] Reaction conditions: 0.004 mmol of ligand, 0.002 mmol of metal precursor, 5.0 mL of H_2O, 2 mmol of HCOONa, 0.4 mmol of ethyl 3-oxo-3-phenylpropanoate, S/C=100, 40 min, 30 °C. [b] Conversion was determined by ^{1}HNMR of the unpurified reaction mixture [c] Enantiomeric excess was determined by HPLC analysis.

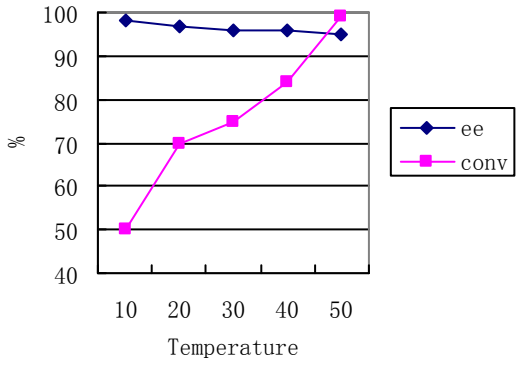
6. Effect of the temperature on the ATH of ethyl 3-oxo-3-phenylpropanoate.

Table S5. Effect of the temperature on ATH of ethyl 3-oxo-3-phenylpropanoate Catalyzed by Rh–L4 Complex. [a]



entry	T (℃)	t (h)	conv.[b](%)	e.e. [c](%)
1	10	20 (0.5)	99 (50)	98 (98)
2	20	6 (0.5)	99 (70)	97 (97)
3	30	2 (0.5)	99 (75)	96 (96)
4	40	1.5 (0.5)	99 (84)	96 (96)
5	50	1.5 (0.5)	99 (99)	95 (95)

[a] Reaction conditions: 0.004 mmol of L4, 0.002 mmol of $[Cp^*RhCl_2]_2$, 5 mL of H_2O, 2 mmol of HCOONa, 0.4 mmol of ethyl 3-oxo-3-phenylpropanoate, S/C=100. [b] Conversion was determined by ^{1}HNMR of the unpurified reaction mixture. [c] Enantiomeric excess was determined by HPLC analysis.



7. Procedure for TEM analyses.

（1）Preparation of samples for catalyst **L4**-Rh-H: $[Cp^*RhCl_2]_2$ (1.3 mg 0.002 mmol) and ligand **L4** (0.004 mmol) were dissolved in 5 mL of H_2O. The mixture was stirred at 40°C for 2 h. The solution was cooled to 20 °C. HCOONa (136 mg 2.0 mmol) was added to the solution. Then the solution was stirred at 20 °C for 8 h.

(2) A drop of the colloidal aqueous suspensions was deposited on a carbon-coated copper grid. Then the excess solution was immediately removed with the help of filter paper. The grid was dried in air and then observed by TEM

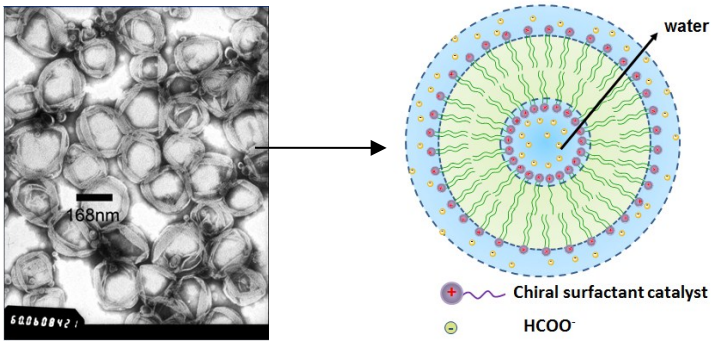


Figure S1. TEM images of nano-aggregates of catalyst **L4**-Rh-H in water

8. Proposed mechanism of reduction of aromatic ketones in the nano-aggregates formed from the catalyst L4-Rh-H.

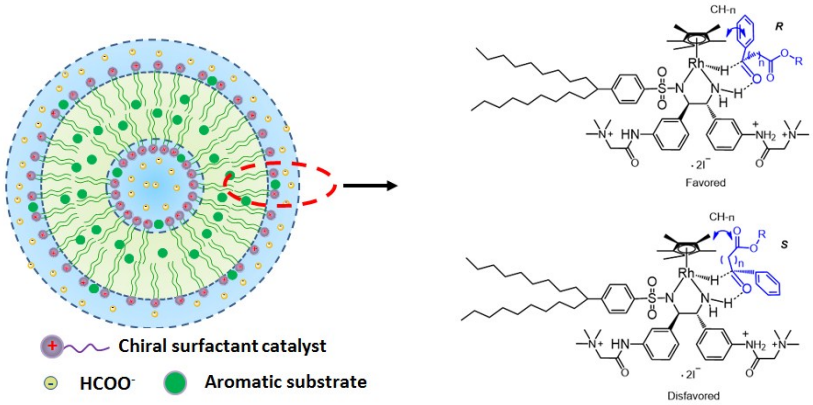
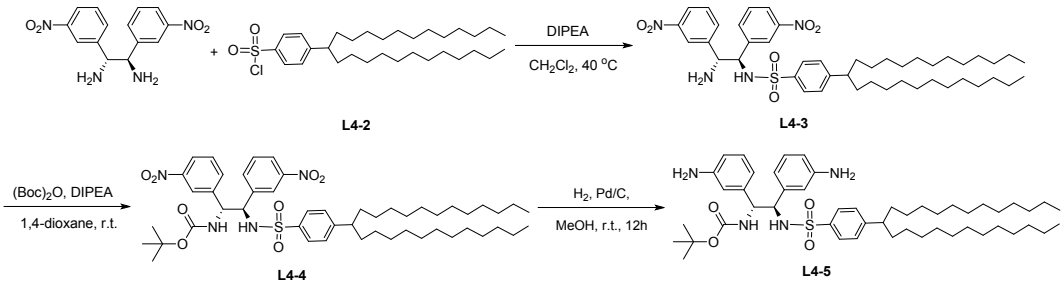


Figure S2. Proposed mechanism of reduction of aromatic ketones in the nano-aggregates formed from the catalyst **L4**-Rh-H

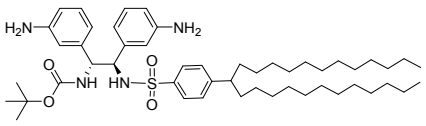
9. Syntheses of ligands



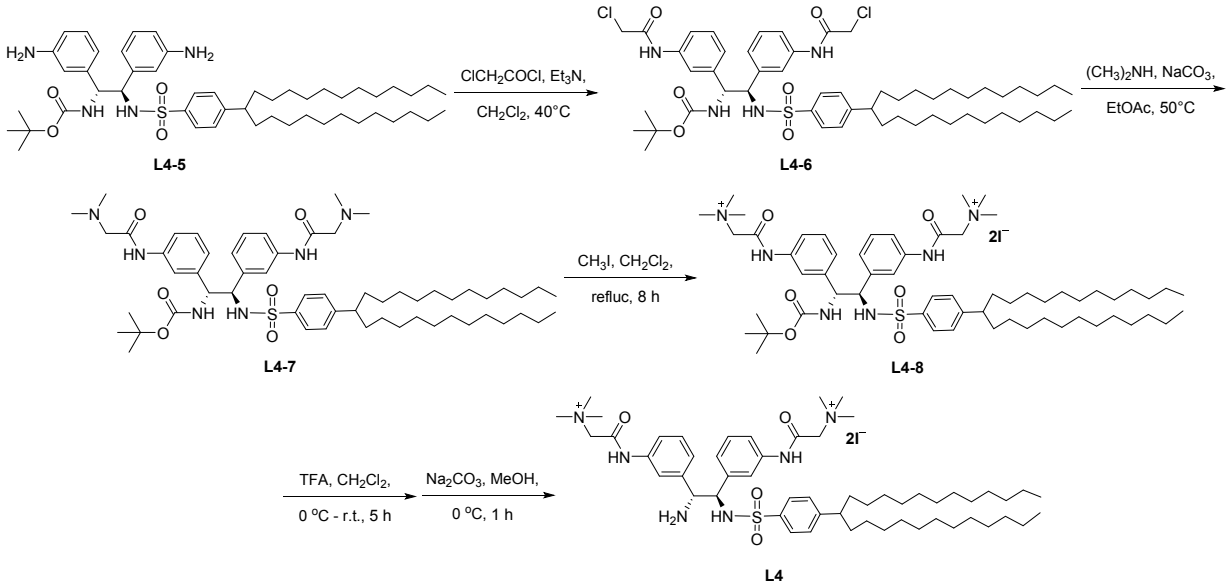
Scheme S1. Synthesis of **L4-5**.

1) Synthesis of L4-5 (scheme S1). [1]

***tert*-Butyl- (1*R*,2*R*)-1,2-bis(3-aminophenyl)-2-(4-(tricosan-12-yl)phenylsulfonamido)ethylcarbamate L4-5.**



Transparent oil. $[\alpha]_D^{20}$= -2.3 (*c*=0.52, CH_2Cl_2); ESI-HRMS $[M+Na]^+$ calcd for $C_{37}H_{54}N_4NaO_4S$: 855.5798, found: 855.5760; ^1H NMR (300 MHz, $CDCl_3$) δ7.50 (d, 2H, *J* = 8.2 Hz), 7.04 (d, 2H, *J* = 8.4 Hz), 6.95 (t, 1H, *J* = 7.7 Hz), 6.72 (t, 1H, *J* = 7.8 Hz), 6.49 (d, 1H, *J* = 8.2 Hz), 6.38-6.31 (m, 3H), 6.23 (s, 1H), 6.14 (d, 1H, *J* = 7.8 Hz), 5.94 (brs, 1H), 5.15(brs, 1H), 4.68 (t, 1H, *J* = 8.3 Hz), 4.46 (t, 1H, *J* = 9.4 Hz), 3.56-3.43 (brs, 4H), 2.45 (brs, 1H), 1.59-1.53 (m, 4H), 1.47 (s, 9H), 1.29-1.01 (m, 40H), 0.90-0.85 (m, 6H).



Scheme S2. Synthesis of **L4**.

2) Synthesis of L4 (scheme S2).

To a stirred solution of **L4-5** (508 mg, 0.826 mmol) and chloroacetyl chloridein (276 mg, 2.440 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of Et_3N (0.85 mL, 6.10 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred at 40 °C until the **L4-5** was completely disappeared by TLC. After being washed with saturated solution of $NaCO_3$ (50 ml×1), and brine (50 mL). the organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure to afford ligand **L4-6** as a colorless transparent jelly. And the product was directly used in the next reaction.

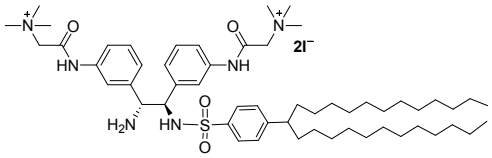
To a stirred solution of **L4-6** (400 mg, 0.406 mmol) and $NaCO_3$ (215 mg, 2.030 mmol) in EtOAc (50 mL) was added a solution of dimethylamine (366mg, 8.12 mmol) in EtOAc (10 mL) at 0 °C. The mixture was stirred at 50 °C in sealed tube until the **L4-5** was completely disappeared by TLC. After being washed with saturated solution of $NaCO_3$ (50 ml×1), and brine (50 mL). the organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure to afford ligand **L4-7** as a colorless transparent jelly. And the product was directly used in the next reaction.

To a stirred solution of **L4-7** (300 mg, 0.299 mmol) and CH_3I (0.2 mL) in CH_2Cl_2 (30 mL). The mixture was stirred at 40 °C in sealed tube until the **L4-7** was completely disappeared by TLC. After removal of the solvent under reduced pressure to afford ligand **L4-8** as a colorless transparent jelly. And the product was directly used in the next reaction.

To a stirred solution of **L4-8** (300 mg, 0.233 mmol) in CH_2Cl_2 (20 mL) cooled with an ice bath was added TFA (10 mL). The mixture was stirred for 5 h. After removal of the solvent under reduced pressure, the residue was redissolved in 20 mL of methanol. Then the solution was cooled with an ice bath and Na_2CO_3 (494 mg, 4.66 mmol) was added. The mixture was stirred at

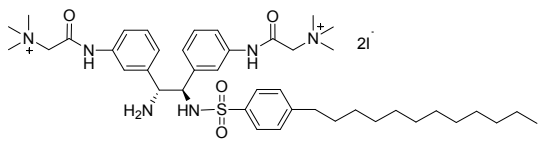
0°C for 1 hour. The insoluble solid was removed by filtration. After the solvent was removed by reduce pressure. After removal of the solvent under reduced pressure, 261 mg (94%) of ligand **L4** was obtained as a colourless oil.

2,2'-(3,3'-((1R,2R)-1-amino-2-(4-(tricosan-12-yl)phenylsulfonamido)ethane-1,2-diyl)bis(3,1-phenylene))bis(azanediyl)bis(N,N,N-trimethyl-2-oxoethanaminium) diiodide L4 :



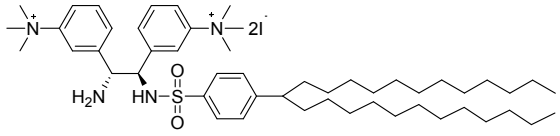
Colorless oil, $[\alpha]_D^{20}$= +60.9 (*c* = 0.83， CH_3OH); ESI-HRMS $[M-2I]^+$ calcd for $C_{55}H_{92}N_6O_4S$: 932.6890, found: 932.6928; ^1H NMR (300 MHz, CD_3OD) δ: 7.68-7.62 (m,5H), 7.54 (s, 1H), 7.31-7.25 (m, 4H), 7.03 (d, *J* =8.0 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 1H), 4.53 (d, *J* =8.0 Hz, 1H), 4.35 (d, *J* =6.0 Hz, 4H), 3.41 (s, 9H), 3.39 (s, 9H), 2.67-2.58 (m, 1H), 1.70-1.2 (m, 44H), 0.88 (q, *J* = 6.6 Hz, 6H)；^{13}C NMR (75 MHz, $CDCl_3$): 163.3, 157.0, 154.7, 143.1, 142.4, 139.6, 139.4, 137.4, 131.0, 130.8, 129.4, 129.2, 123.7, 122.6, 121.4, 119.9, 119.0, 70.1, 67.9, 65.9, 65.9, 63.1, 55.0, 49.9, 49.6, 49.3, 49.2, 49.0, 48.8, 48.5, 48.2, 47.2, 37.8, 37.7, 33.1, 30.8, 30.6, 30.5, 28.7, 23.8, 14.5.

2,2'-(3,3'-(1-amino-2-(4-dodecylphenylsulfonamido)ethane-1,2-diyl)bis(3,1-phenylene))bis(azanediyl)bis(N,N,N-trimethyl-2-oxoethanaminium) diiodide L2 :



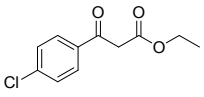
Colorless oil, $[\alpha]_D^{20}$= +11.7 (*c* = 0.51, CH_3OH); ESI-HRMS $[M-2I]^+$ calcd for $C_{42}H_{66}N_6O_4S$: 750.4855, found: 750.4856; ^1H NMR (300 MHz, CD_3OD) δ: 7.59 (s,1H), 7.53-7.47 (m,3H), 7.29-7.18 (m, 3H), 6.81 (q, *J* = 7.9 Hz, 1H), 6.56 (d, *J* =6.5 Hz, 1H), 4.68 (d, *J* =11.0 Hz, 1H), 4.57 (d, *J* =11.0 Hz, 1H), 4.45 (s, 4H), 3.45 (s, 9H), 3.43 (s, 9H), 2.53 (q, *J* = 7.6 Hz, 2H), 1.50 (q, *J* = 6.6 Hz, 2H), 1.28 (bs, 20H), 0.89 (q, *J* = 6.7 Hz,3H)；^{13}C NMR (75 MHz, $CDCl_3$): 163.2, 162.9, 149.5, 139.2, 138.6, 138.4, 137.2, 135.5, 130.9, 130.0, 129.8, 128.3, 125.5, 125.3, 122.3, 122.2, 121.2, 121.2, 120.9, 120.8, 120.8, 66.0, 65.9, 62.8, 60.3, 55.2, 36.6, 33.0, 32.4, 32.3, 30.7, 30.7, 30.5, 30.4, 30.4, 30.2, 23.7, 23.7, 14.5, 14.4.

3, 3'-[(1*R*, 2*R*)- (1-Amino-2-(4-(tricosan-12-yl) phenylsulfonamido) ethane-1, 2-diyl] bis (*N, N, N*-trimethylbenzenaminium) diiodide L3 :



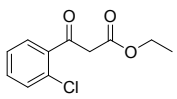
Colorless oil, $[\alpha]_D^{20}$= +23.7 (*c* = 0.51, CH_3OH); ESI-HRMS $[M-2I]^+$ calcd for $C_{51}H_{86}N_4O_2S$: 818.6461, found: 818.6478; ^1H NMR (400 MHz, CD_3OD) δ: 8.21 (s, 1H), 8.02 (s, 1H), 7.87-7.84 (m, 2H), 7.68 (m, 4H), 7.56-7.54 (m, 1H), 7.17-7.07 (m, 4H), 5.15 (s, 2H), 3.60 (s, 9H), 3.56(s, 9H), 2.48 (brs, 1H), 1.60-1.53 (brs, 2H), 1.43-1.37 (brs, 2H), 1.35-0.98 (m, 40H), 0.90-0.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 153.4, 148.7, 148.4, 140.2, 139.2, 137.7, 132.5, 131.8, 131.6, 131.5, 129.3, 128.9, 128.3, 122.2, 121.0, 120.7, 61.7, 59.6, 58.0, 57.9, 57.8, 46.6, 37.4, 37.3, 33.1, 30.8, 30.7, 30.6, 30.5, 28.4, 23.7, 14.5.

Ethyl 3-oxo-3-(4-chlorophenyl)propanoate (7c)



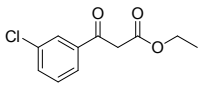
According to the general procedure to yield Ethyl 3-oxo-3-(4-chlorophenyl)propanoate as yellow oil. ^1H-NMR (300MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 4.29-4.17 (m, 2H), 3.95 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 5.62 (s, 1 H, enol-CH=C), 12.56 (s, 1 H, enol-OH) ppm.

Ethyl 3-oxo-3-(2-chlorophenyl)propanoate (7d)



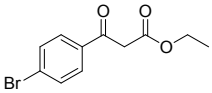
According to the general procedure to yield Ethyl 3-oxo-3-(4-chlorophenyl)propanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.43-7.41 (m, 2H), 7.37-7.31 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 5.54 (s, 1 H, enol-CH=C), 12.45 (s, 1 H, enol-OH) ppm.

Ethyl 3-oxo-3-(3-chlorophenyl)propanoate (7e)



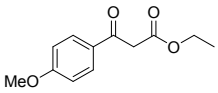
According to the general procedure to yield Ethyl 3-oxo-3-(3-chlorophenyl)propanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.44-7.34 (m, 1H), 4.30-4.17 (m, 2H), 3.95 (s, 2H), 1.25 (t, *J* = 7.2 Hz, 3H), 5.64 (s, 1 H, enol-CH=C), 12.54 (s, 1 H, enol-OH) ppm.

Ethyl 3-(4-bromophenyl)-3-oxopropanoate (7f)



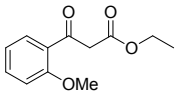
According to the general procedure to yield Ethyl 3-(4-bromophenyl)-3-oxopropanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 5.64 (s, 1 H, enol-CH=C), 12.56 (s, 1 H, enol-OH) ppm.

Ethyl 3-oxo-3-(4-methoxyphenyl)propanoate (7g)



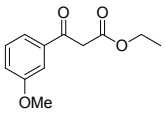
According to the general procedure to yield Ethyl 3-oxo-3-(4-methoxyphenyl)propanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 3.85 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 5.56 (s, 1 H, enol-CH=C), 12.62 (s, 1 H, enol-OH) ppm.

Ethyl 3-oxo-3-(2-methoxyphenyl)propanoate (7h)



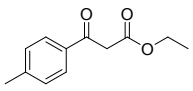
According to the general procedure to yield Ethyl 3-oxo-3-(2-methoxyphenyl)propanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.89-7.86 (m, 1H), 7.50-7.47 (m, 1H), 7.04-6.94 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 2H), 3.89 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 6.01 (s, 1 H, enol-CH=C), 12.70 (s, 1 H, enol-OH) ppm.

Ethyl 3-oxo-3-(3-methoxyphenyl)propanoate (7i)



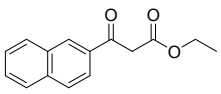
According to the general procedure to yield Ethyl 3-oxo-3-(3-methoxyphenyl)propanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.41-7.31 (m, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 2H), 3.85 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 5.65 (s, 1 H, enol-CH=C), 12.57 (s, 1 H, enol-OH) ppm.

Ethyl 3-oxo-3-(4-methylphenyl)propanoate (7j)



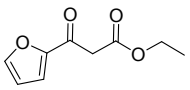
According to the general procedure to yield Ethyl 3-oxo-3-(4-methylphenyl)propanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 2H), 2.40 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 5.62 (s, 1 H, enol-CH=C), 12.58 (s, 1 H, enol-OH) ppm.

Ethyl 3-(naphthalen-2-yl)-3-oxopropanoate (7k)



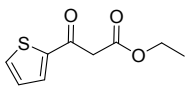
According to the general procedure to yield Ethyl 3-(naphthalen-2-yl)-3-oxopropanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.03-7.87 (m, 4H), 7.63-7.56 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.12 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 5.81 (s, 1 H, enol-CH=C), 12.68 (s, 1 H, enol-OH) ppm.

Ethyl 3-(furan-2-yl)-3-oxopropanoate (7l)



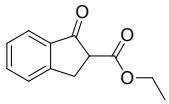
According to the general procedure to yield Ethyl 3-(furan-2-yl)-3-oxopropanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.61 (s, 1H), 7.28 (s, 1H), 6.56 (s, 1H), 4.20 (q, *J* = 7.0 Hz, 3H), 3.84 (s, 2H), 1.25 (t, *J* = 7.0 Hz, 3H) ppm.

Ethyl 3-(thiophene-2-yl)-3-oxopropanoate (7m)



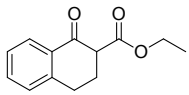
According to the general procedure to yield Ethyl 3-(thiophene-2-yl)-3-oxopropanoate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.74-7.72 (m, 1H), 7.70-7.68 (m, 1H), 7.15-7.12 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 3H), 3.91 (s, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

2-carboethoxy-1-indanone (7n)



According to the general procedure to yield 2-carboethoxy-1-indanone as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.65-7.59 (m, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.73-3.69 (m, 1H), 3.59-3.52 (m, 1H), 3.41-3.32 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm.

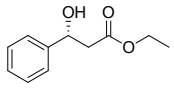
Ethyl1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (7o)



According to the general procedure to yield Ethyl 1-oxo- 1,2,3,4-tetrahydronaphthalene- 2-carboxylate as yellow oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ 8.06 (dd, *J* = 7.5 Hz,0.9 Hz, 1H), 7.50 (td, *J* = 7.5 Hz,1.4 Hz, 1H), 7.28-7.26 (m, 1H), 7.18 (d, *J* = 6.8 Hz, 2H), 4.30-4.23 (m, 2H), 3.60 (dd, *J* = 10.4 Hz,4.8 Hz, 1H), 3.06-2.99 (m, 2H), 2.51-2.47 (m, 1H), 2.47-2.35 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 12.49 (s, 1 H, enol-OH) ppm.

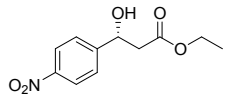
10. Data of ligands and products.

(*R*)- Ethyl 3-hydroxy-3-phenylpropanoate (8) [3]



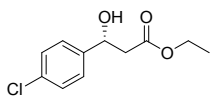
$[\alpha]_D^{20}$ +51.2 (c = 1.0, $CHCl_3$). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.37-7.25 (m, 5H), 5.13-5.09 (m, 1H), 4.16 (q, *J* = 7.2Hz, 2H), 3.38 (d, *J* = 3.6Hz, 1H), 2.77-2.65 (m, 2H), 1.24 (t, *J* = 7.2Hz, 3H)ppm. HPLC conditions: Chiralcel OD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 85:15; flow rate = 1.0 mL/min; 254 nm UV detector; t_R (***S***) = 6.6 min.; t_R (***R***) = 7.9 min.

(*R*)- Ethyl 3- hydroxy-3-(4-nitrophenyl)propanoate (9b) [4]



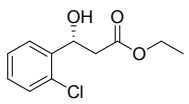
$[\alpha]_D^{20}$ +22.3 (c = 1.0, $CHCl_3$). ^{1}H-NMR (300MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8Hz, 2H), 7.55 (d, *J* = 8.5Hz, 2H), 5.25-5.19 (m, 1H), 4.18 (q, *J* = 7.1Hz, 2H), 3.71 (d, *J* = 3.7Hz, 1H), 2.77-2.65 (m, 2H), 1.25 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel AD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 18.16 min.; t_R = 19.25 min.

(*R*)- Ethyl 3- hydroxy-3-(4-chlorophenyl)propanoate (9c) [3]



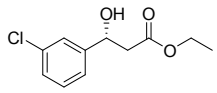
$[\alpha]_D^{20}$ +45.1(c = 1.0, $CHCl_3$). ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.28 (s, 4H), 5.11-5.06 (m, 1H), 4.16 (q, *J* = 7.1Hz, 2H), 3.46 (d, *J* = 3.5Hz, 1H), 2.75-2.63 (m, 2H), 1.25 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel AD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 10.17 min.; t_R = 10.77 min.

(*R*)- Ethyl 3- hydroxy-3-(2-chlorophenyl)propanoate (9d) [3]



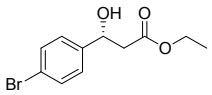
$[\alpha]_D^{20}$ +47.1(c = 1.0, $CHCl_3$). ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.65-7.62 (m, 1H), 7.35-7.29 (m, 2H), 7.26-7.20 (m, 1H), 5.52-5.46 (m, 1H), 4.21 (q, *J* = 7.1Hz, 2H), 3.54 (d, *J* = 3.5Hz, 1H), 2.90-2.54 (m, 2H), 1.28 (t, *J* = 7.2Hz, 3H)ppm. HPLC conditions: Chiralcel OD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 5.48 min.; t_R = 8.47 min.

(*R*)- Ethyl 3- hydroxy-3-(3-chlorophenyl)propanoate (9e)



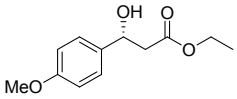
^{1}H-NMR (300MHz, $CDCl_3$): δ 7.38 (s, 1H), 7.28-7.22 (m, 3H), 5.09 (t, *J* = 6.6 Hz, 1H), 4.18 (q, *J* = 7.1Hz, 2H), 3.47 (d, *J* = 3.0 Hz, 1H), 2.70 (d, *J* = 5.9 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H)ppm. HPLC conditions: Chiralcel AD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 8.76 min.; t_R = 9.44 min.

(*R*)-Ethyl 3- hydroxy-3-(4-bromophenyl)propanoate (9f) [3]



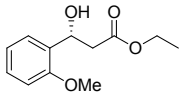
$[\alpha]_D^{20}$ +39.5 (c = 1.0, $CHCl_3$). ^{1}H-NMR (300MHz, $CDCl_3$): δ 7.47-7.44 (m, 2H), 7.26-7.22 (m, 2H), 5.09-5.04 (m, 1H), 4.16 (q, *J* = 7.1Hz, 2H), 3.49 (s, 1H), 2.74-2.62 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H)ppm. HPLC conditions: Chiralcel AD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 10.31 min.; t_R = 11.19 min.

(*R*)- Ethyl 3-hydroxy-3-(4-methoxyphenyl)propanoate (9g) [3]



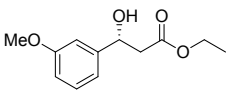
$[\alpha]_D^{20}$ +40.5 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 6.90-6.85 (m, 2H), 5.10-5.04 (m, 1H), 4.16 (q, *J* = 7.2Hz, 2H), 3.79 (s, 3H), 3.24 (d, *J* = 3.2Hz, 1H), 2.79-2.62 (m, 2H), 1.25 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel AS column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 70:30; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 5.39 min.; t_R = 6.30 min.

(*R*)- Ethyl 3-hydroxy-3-(2-methoxyphenyl)propanoate (9h) [3]



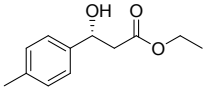
$[\alpha]_D^{20}$ +44.5 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.28-7.23 (m, 2H), 5.38-5.34 (m, 1H), 4.17 (q, *J* = 7.1Hz, 2H), 3.84 (s, 3H), 3.47 (brs, 1H), 2.86-2.65 (m, 2H), 1.26 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel OD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 7.54 min.; t_R = 7.89 min.

(*R*)- Ethyl 3-hydroxy-3-(2-methoxyphenyl)propanoate (9i) [3]



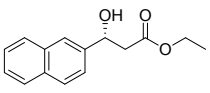
$[\alpha]_D^{20}$ +39.6 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.26 (t, *J* = 8.5Hz, 1H), 6.95-6.92 (m, 2H), 6.84-6.80 (m, 1H), 5.13-5.08 (m, 1H), 4.18 (q, *J* = 7.1Hz, 2H), 3.81 (s, 3H), 3.31 (brs, 1H), 2.79-2.67 (m, 2H), 1.26 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel AD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 13.69 min.; t_R = 14.56 min.

(*R*)- Ethyl 3-hydroxy-3-(4- methylphenyl)propanoate (9j) [3]



$[\alpha]_D^{20}$ +50.6 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.0Hz, 2H), 7.16 (d, *J* = 8.4Hz, 2H), 5.12-5.08 (m, 1H), 4.18 (q, *J* = 7.1Hz, 2H), 3.25 (s, 1H), 2.80-2.64 (m, 2H), 2.34 (s, 3H), 1.26 (t, *J* = 7.2Hz, 3H)ppm. HPLC conditions: Chiralcel AS column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 95:5; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 10.05 min.; t_R = 10.88 min.

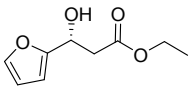
(*R*)- Ethyl 3-hydroxy-3-(2-naphthyl)propanoate (9k) [5]



$[\alpha]_D^{20}$ +30.7 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.85-7.82 (m, 4H), 7.51-7.45 (m, 3H), 5.33-5.28 (m, 1H), 4.19 (q, *J* = 7.1Hz, 2H), 3.48 (brs, 1H), 2.90-2.75 (m, 2H), 1.26 (t, *J* = 7.1Hz, 3H)ppm.

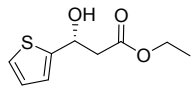
HPLC conditions: Chiralcel AS column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 95:5; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 14.96 min.; t_R = 16.43 min.

(*R*)- Ethyl 3-(2-furyl)-3-hydroxypropanoate (9l) [4]



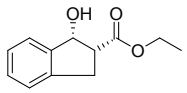
$[\alpha]_D^{20}$ +19.6 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.36 (brs, 1H), 6.33-5.31 (m, 1H), 6.27 (d, *J* = 3.2Hz, 1H), 5.15-5.10 (m, 1H), 4.18 (q, *J* = 7.1Hz, 2H), 3.30 (s, 1H), 2.94-2.78 (m, 2H), 1.26 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel OD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R (***S***) = 6.76 min.; t_R (***R***) = 16.37 min.

(*R*)- Ethyl 3-hydroxy-3-(2-thienyl)propanoate (9m) [5]



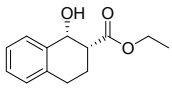
$[\alpha]_D^{20}$ +22.3 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.26-7.23 (m, 1H), 6.97-6.94 (m, 2H), 5.38-5.34 (m, 1H), 4.18 (q, *J* = 7.1Hz, 2H), 3.55 (s, 1H), 2.92-2.78 (m, 2H), 1.26 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel OD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 6.76 min.; t_R = 12.42 min.

(*1R,2R*)- Ethyl1-hydroxyindane-2-carboxylate (9n) [6]



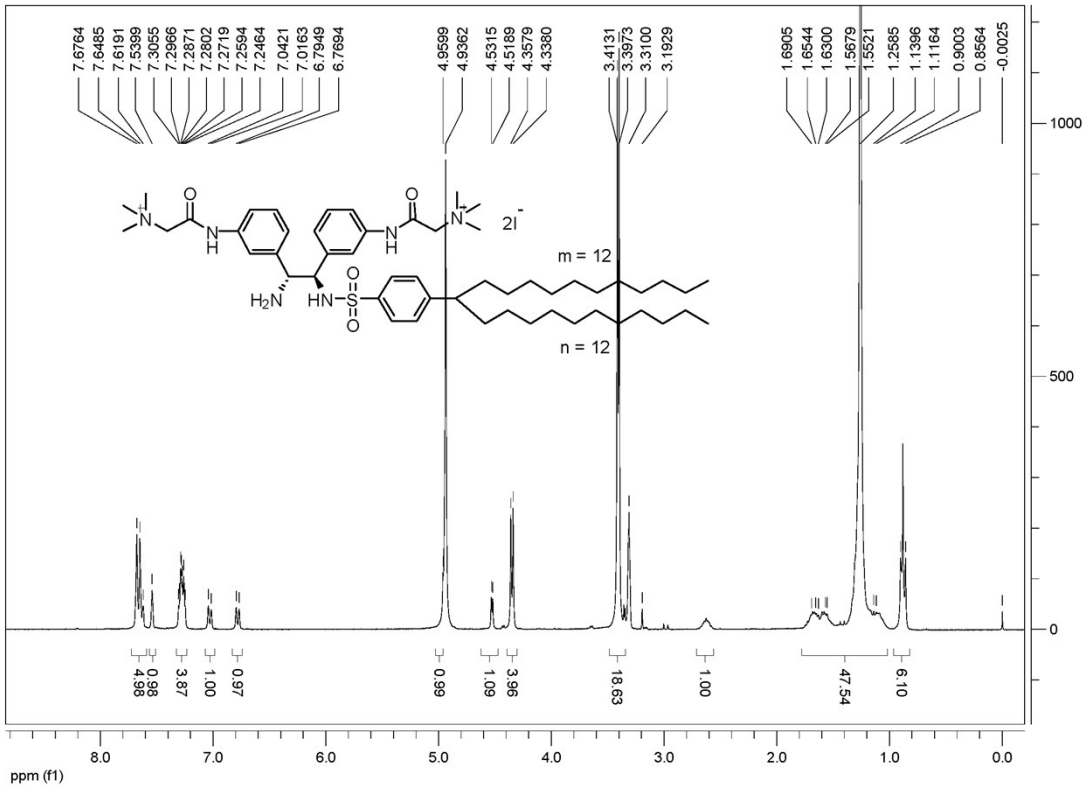
$[\alpha]_D^{20}$ -50.3 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.41 (brs, 1H), 7.27 (brs, 3H), 5.32 (d, *J* = 5.4Hz, 1H), 4.23 (q, *J* = 7.1Hz, 2H), 3.48-3.33 (m, 2H), 3.12-3.02 (m, 2H), 1.31 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel AS column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 70:30; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 5.26 min.; t_R = 6.80 min.

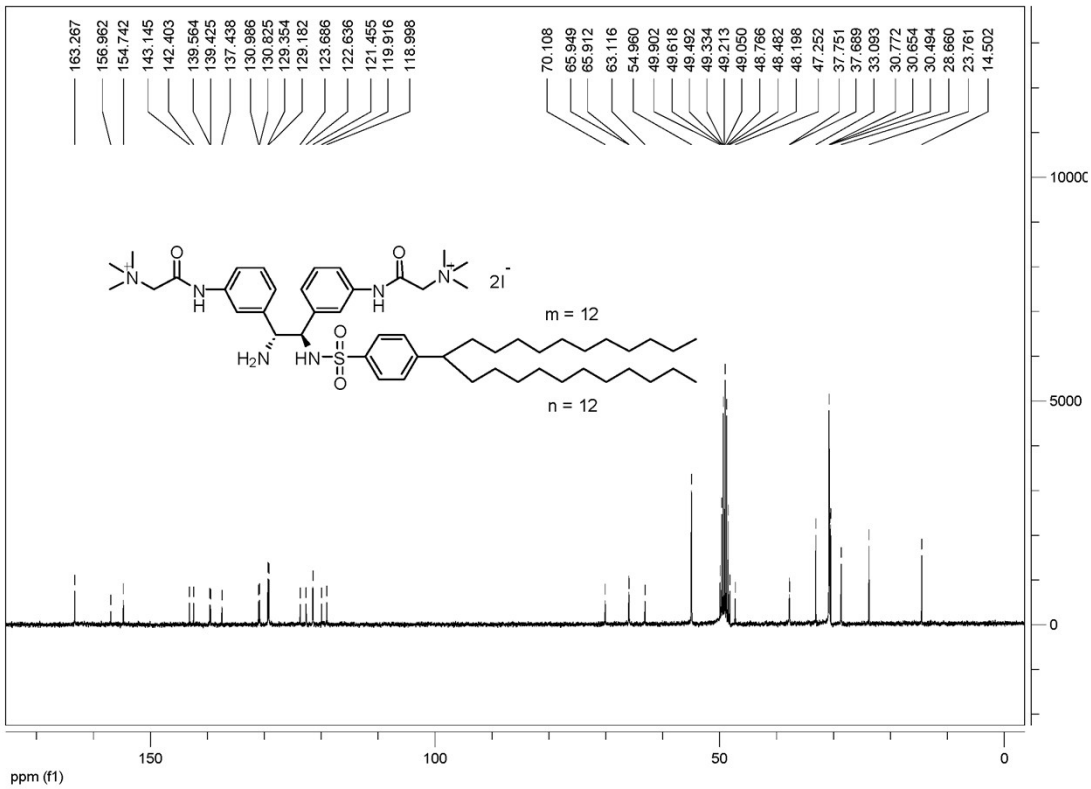
(*1R,2R*)- Ethyl1-hydroxytetraline-2-carboxylate (9o) [6]



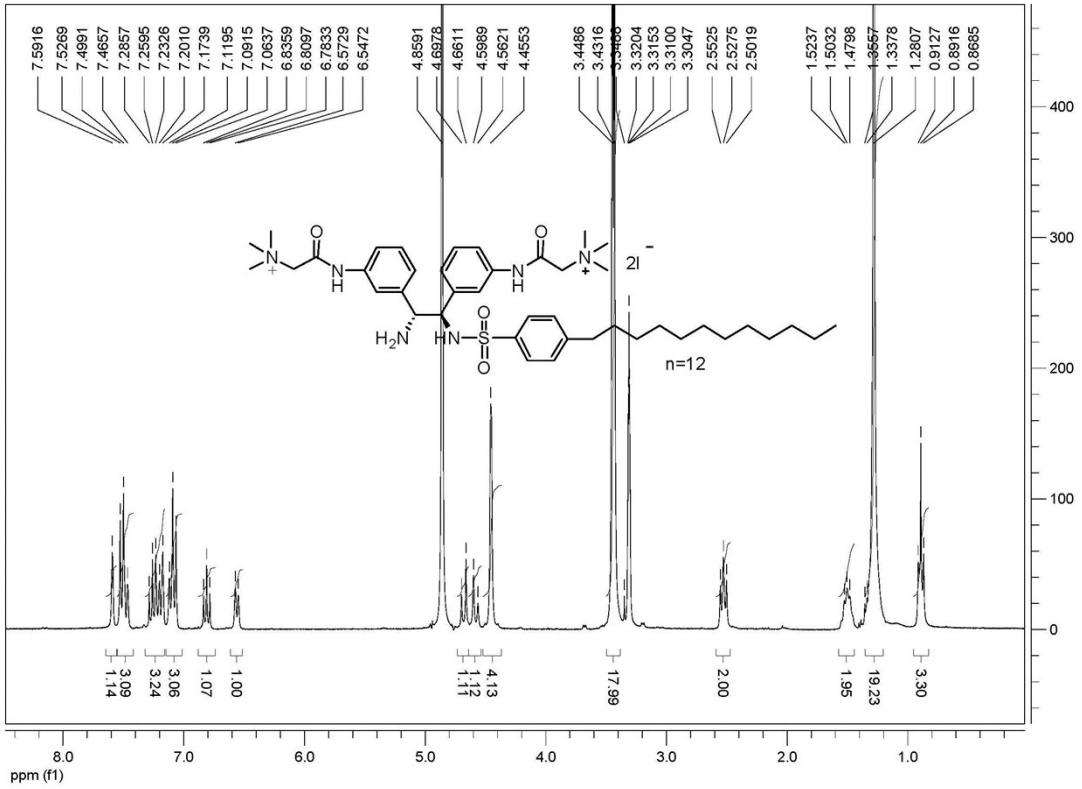
$[\alpha]_D^{20}$ +116.3 (c = 1.0, $CHCl_3$).^{1}H-NMR (300MHz, $CDCl_3$): δ 7.42-7.38 (m, 1H), 7.26-7.21 (m, 2H), 7.14-7.11 (m, 1H), 5.03 (s, 1H), 4.24 (q, *J* = 8.5Hz, 2H), 3.12 (d, *J* = 5.0Hz, 1H), 2.91-2.75 (m, 3H), 2.22-2.11 (m, 2H), 1.31 (t, *J* = 7.1Hz, 3H)ppm. HPLC conditions: Chiralcel OD column (25 cm × 0.46 cm ID); n-hexane/2-propanol = 90:10; flow rate = 1.0 mL/min; 220 nm UV detector; t_R = 6.04 min.; t_R = 8.77 min.

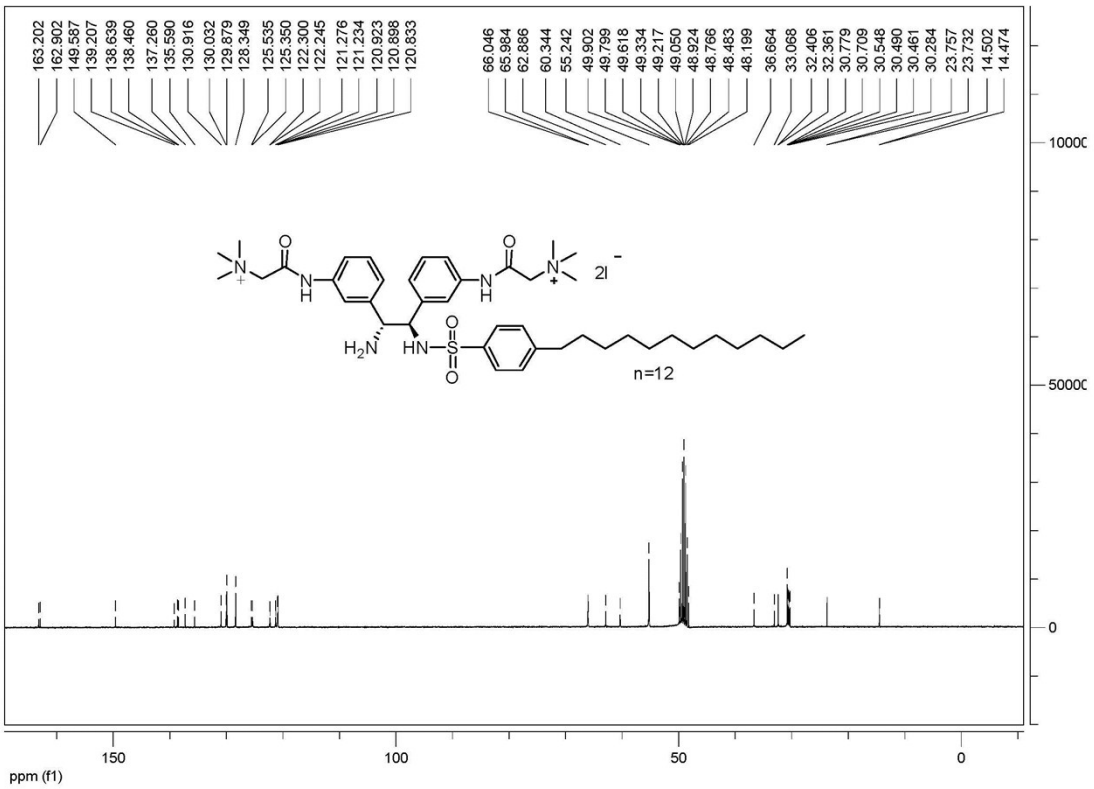
Ligand L4


7.6764
7.6485
7.6191
7.5399
7.3055
7.2966
7.2871
7.2802
7.2719
7.2594
7.2464
7.0421
7.0163
6.7949
6.7694
4.9599
4.9362
4.5315
4.5189
4.3579
4.3380
3.4131
3.3973
3.3100
3.1929
1.6905
1.6544
1.6300
1.5679
1.5521
1.2585
1.1396
1.1164
0.9003
0.8564
-0.0025
2I-
m = 12
n = 12
4.98
0.98
3.87
1.00
0.97
0.99
1.09
3.96
18.63
1.00
47.54
9.10
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

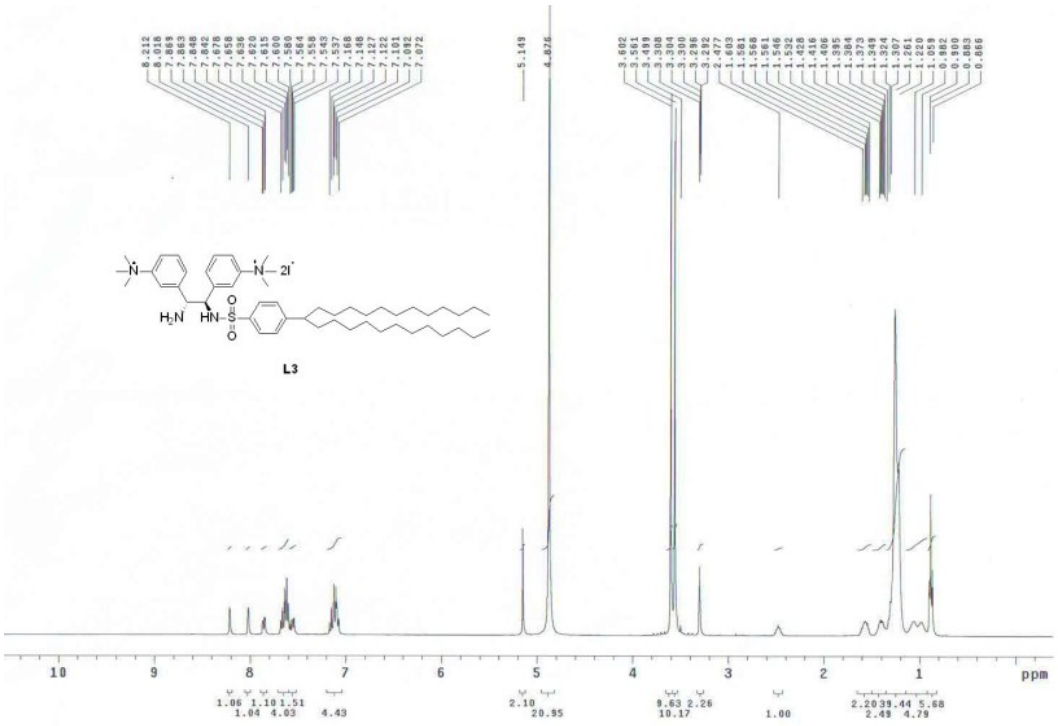

163.267
156.962
154.742
143.145
142.403
139.564
139.425
137.438
130.986
130.825
129.354
129.182
123.686
122.636
121.455
119.916
118.998
70.108
65.949
65.912
63.116
54.960
49.902
49.618
49.492
49.334
49.213
49.050
48.766
48.482
48.198
47.252
37.751
37.689
33.093
30.772
30.654
30.494
28.660
23.761
14.502
2I-
m = 12
n = 12
10000
5000
0
150
100
50
0
ppm (f1)

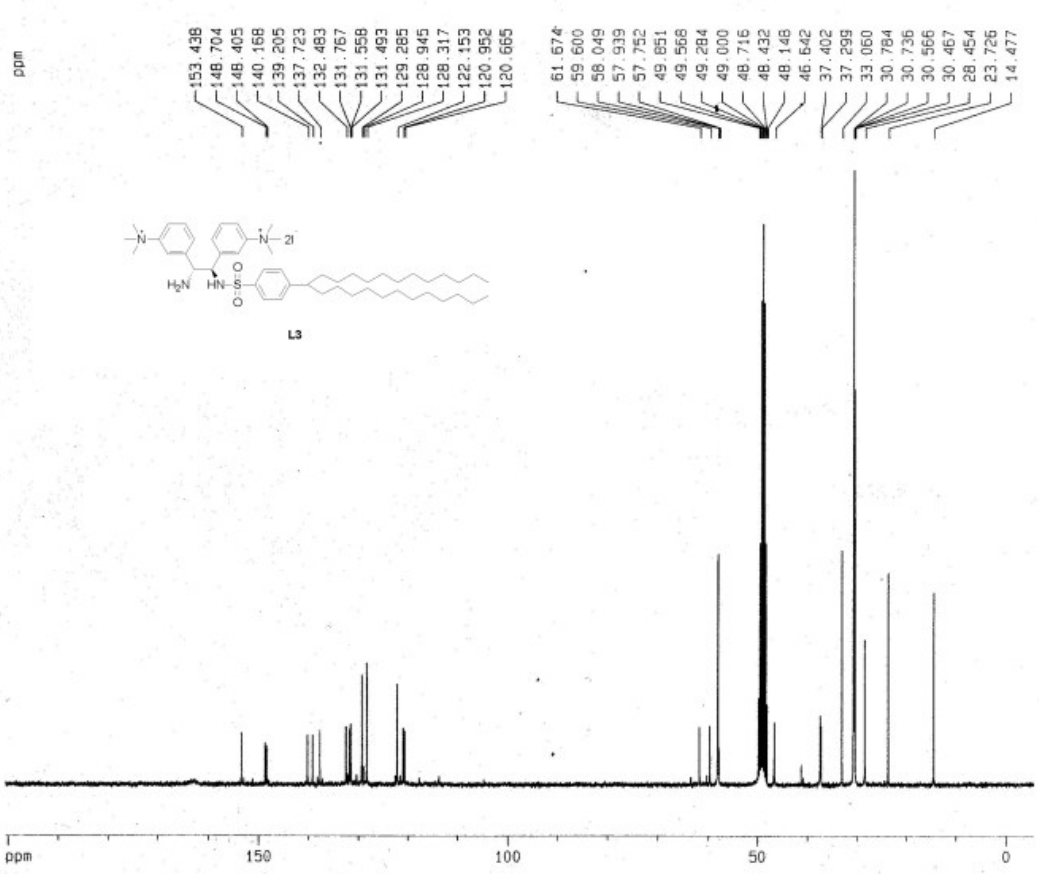
Ligand L2


7.5916
7.5269
7.4991
7.4657
7.2857
7.2595
7.2326
7.2010
7.1739
7.1195
7.0915
7.0637
6.8359
6.8097
6.7833
6.5729
6.5472
4.8591
4.6978
4.6611
4.5989
4.5621
4.4553
3.4486
3.4316
3.3204
3.3153
3.3100
3.3047
2.5525
2.5275
2.5019
1.5237
1.5032
1.4798
1.3657
1.3378
1.2807
0.9127
0.8916
0.8685
2I⁻
n=12
1.14
3.09
3.24
3.06
1.07
1.00
1.11
1.12
4.13
17.99
2.00
1.95
19.23
3.30
ppm (f1)

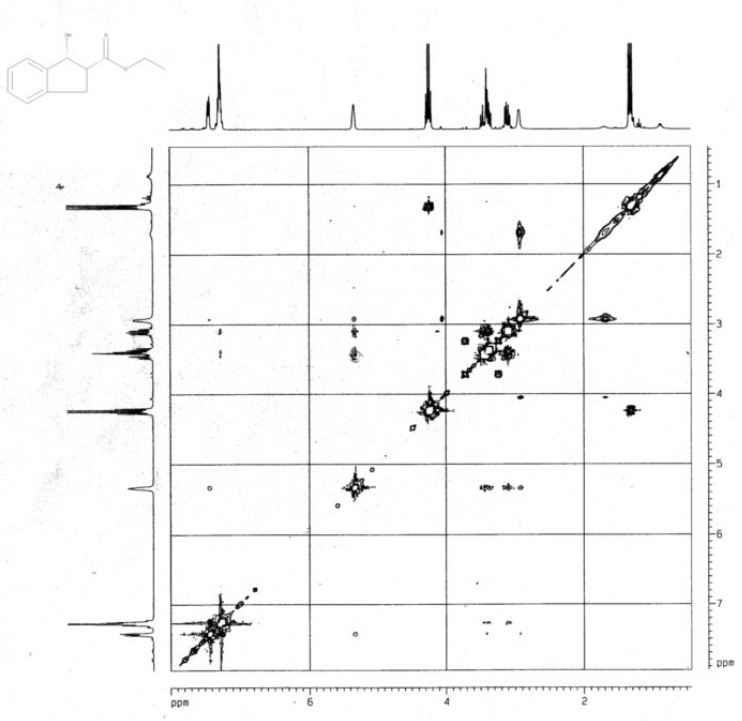

163.202
162.902
149.587
139.207
138.639
138.460
137.260
135.590
130.916
130.032
129.879
128.349
125.535
125.350
122.300
122.245
121.276
121.234
120.923
120.898
120.833
66.046
65.984
62.886
60.344
55.242
49.902
49.799
49.618
49.334
49.217
49.050
48.924
48.766
48.483
48.199
36.664
33.068
32.406
32.361
30.779
30.709
30.548
30.490
30.461
30.284
23.757
23.732
14.502
14.474
2I⁻
n=12
10000
50000
0
150
100
50
0
ppm (f1)

Ligand L3

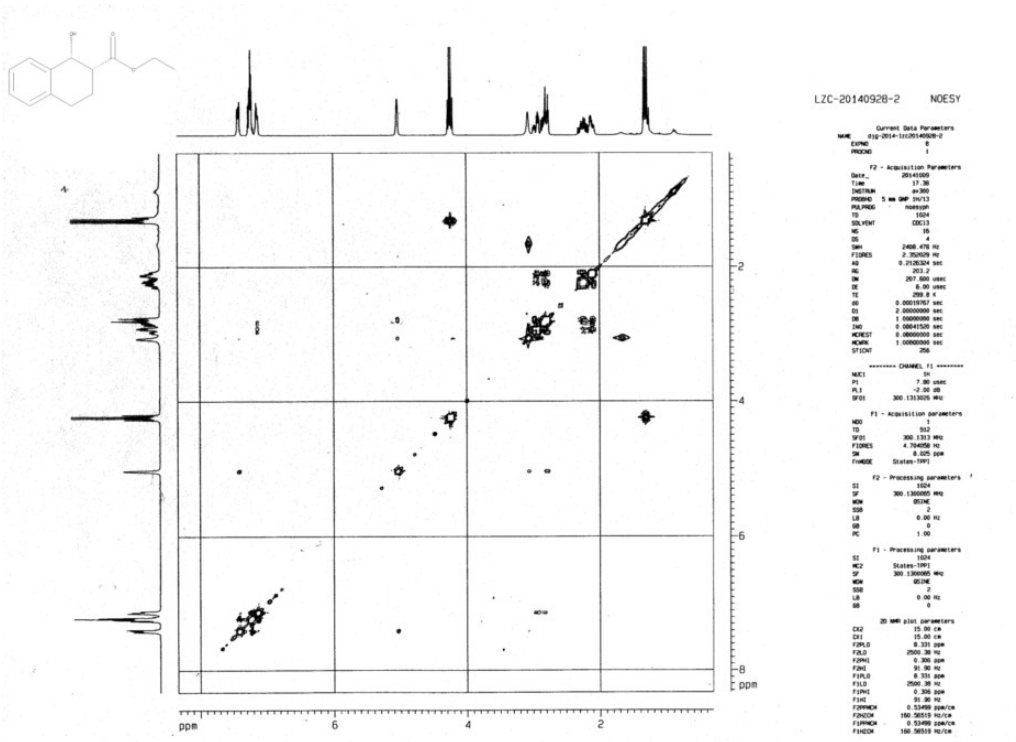

2I⁻
L3
10
9
8
7
6
5
4
3
2
1
ppm



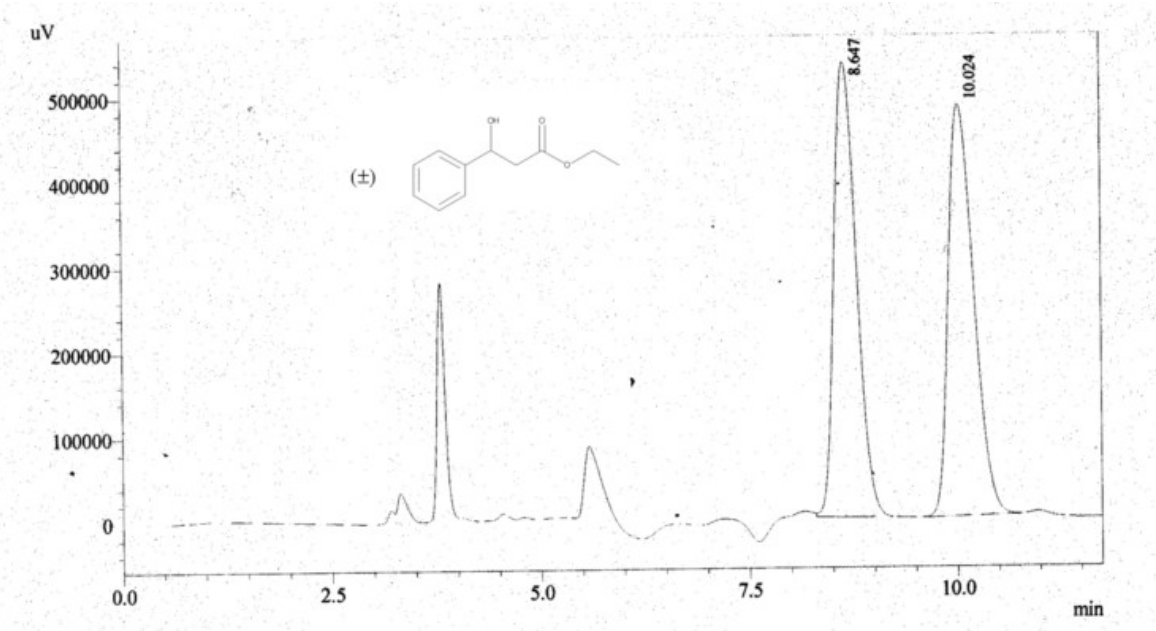
Ethyl1-hydroxyindane-2-carboxylate (9n)

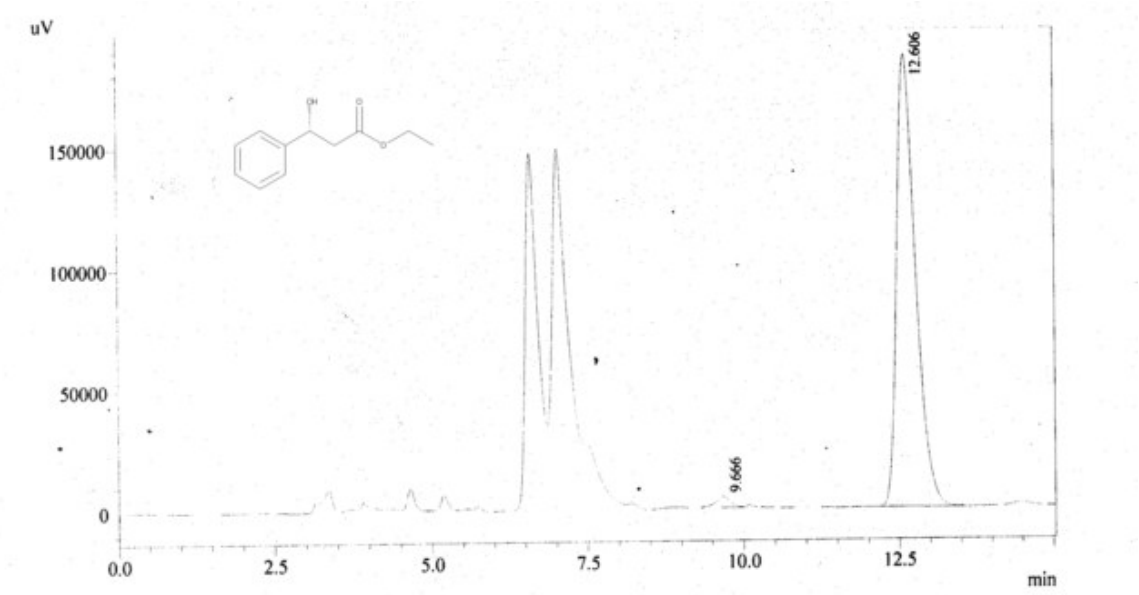


Ethyl1-hydroxytetraline-2-carboxylate (9o)



(R)- Ethyl 3-hydroxy-3-phenylpropanoate (8)

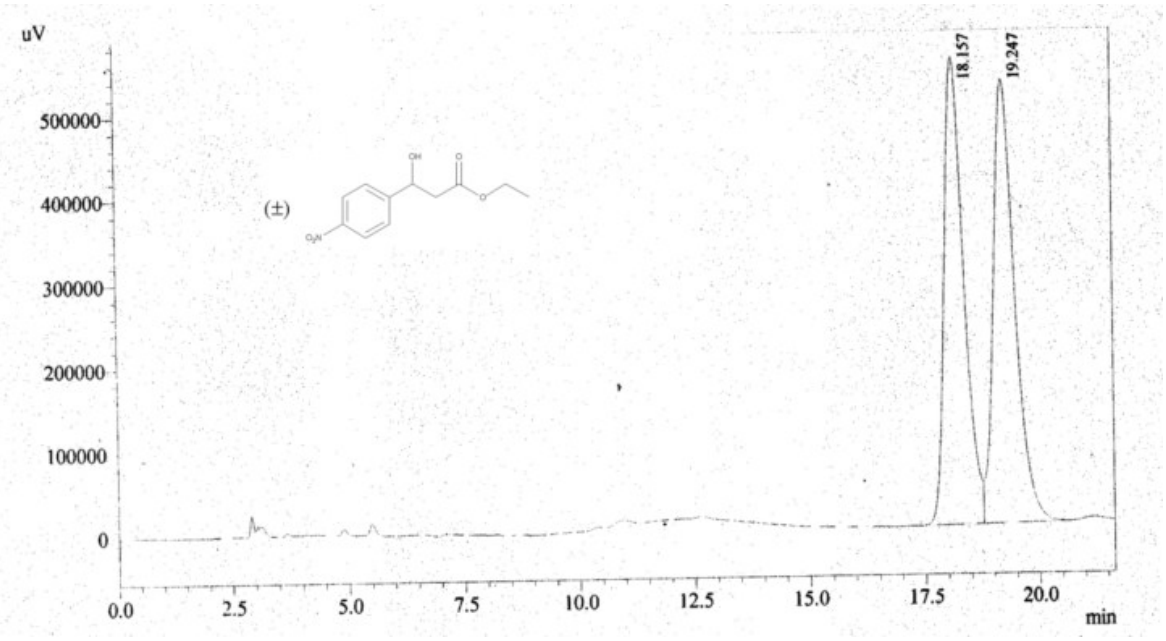


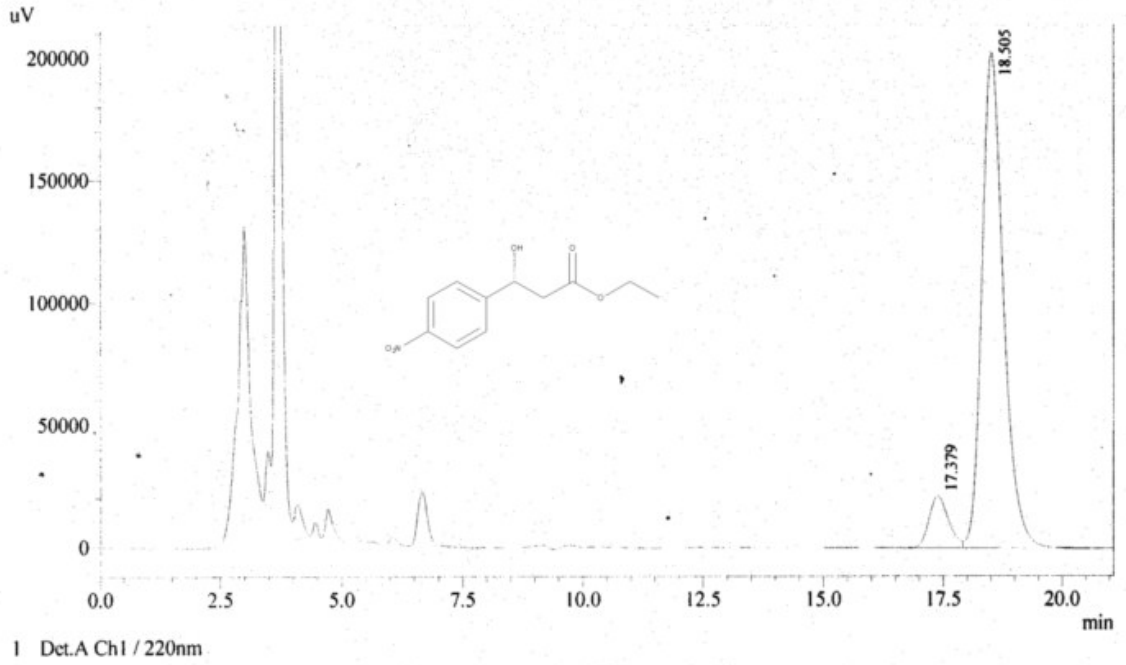


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.666	71031	4543	1.760	2.377
2	12.606	3963873	186616	98.240	97.623
Total		4034904	191159	100.000	100.000

(R)- Ethyl 3- hydroxy-3-(4-nitrophenyl)propanoate (9b)

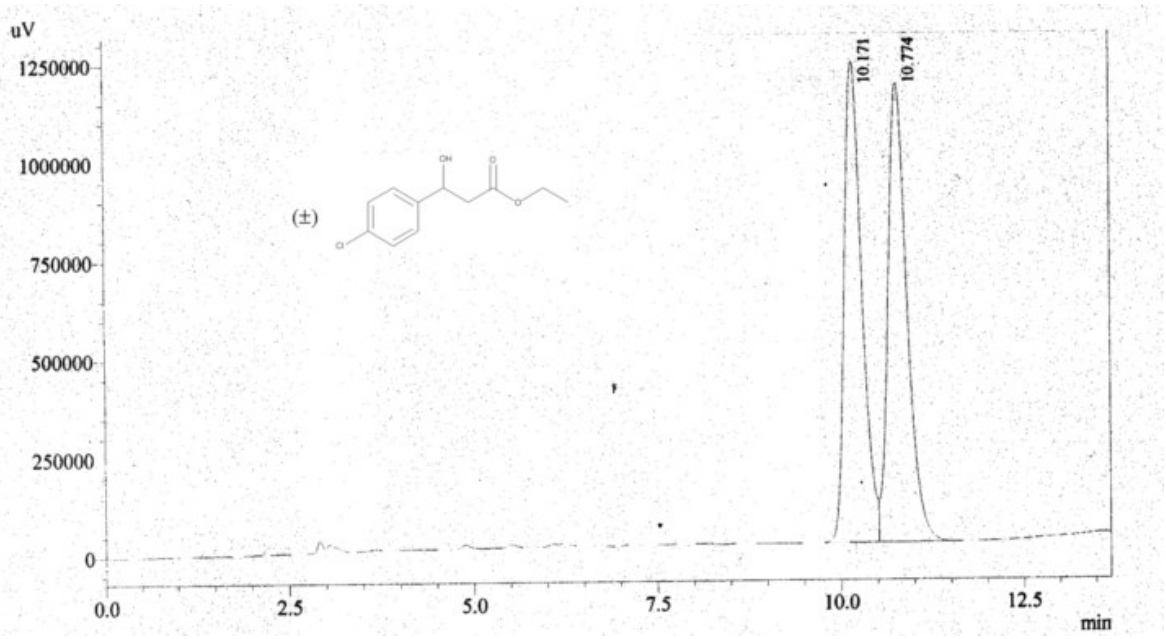


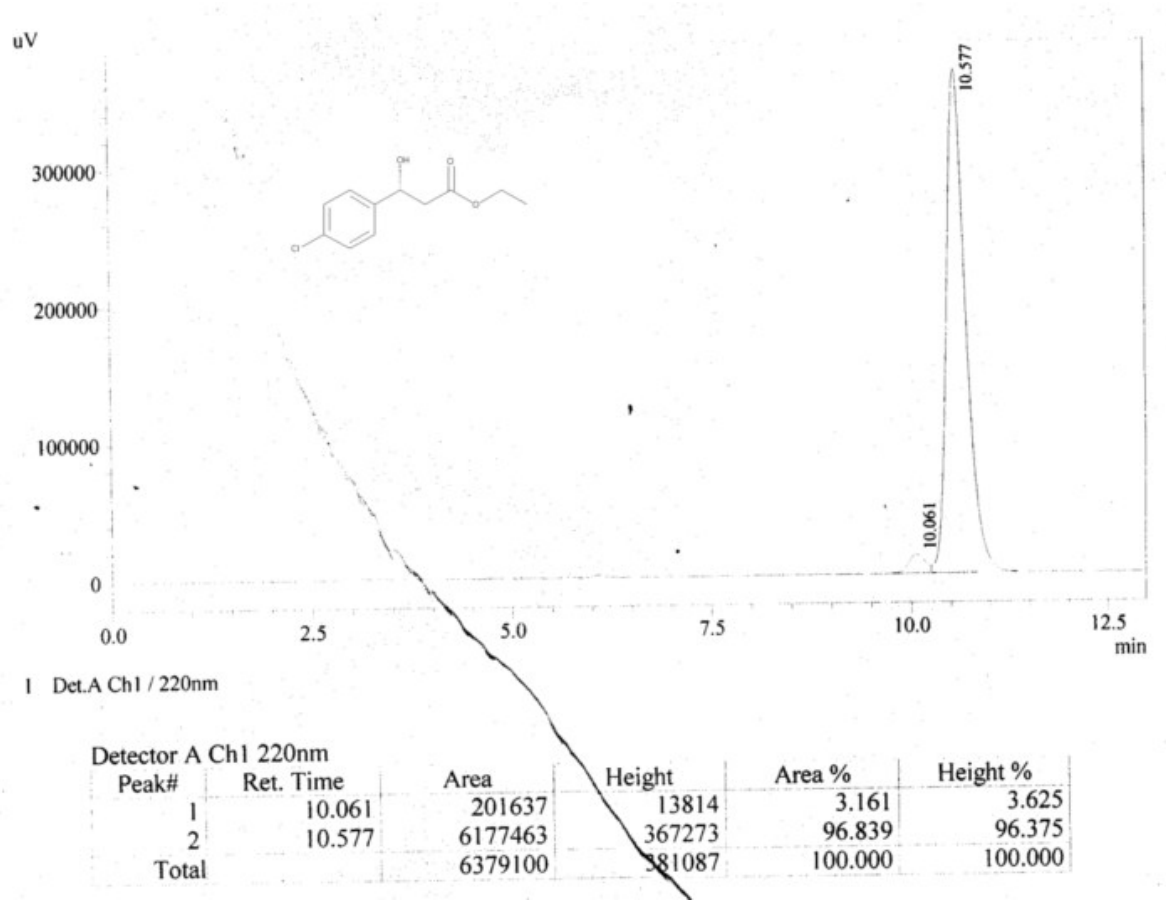


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.379	603082	21224	8.616	9.494
2	18.505	6396714	202329	91.384	90.506
Total		6999796	223553	100.000	100.000

(R)- Ethyl 3- hydroxy-3-(4-chlorophenyl)propanoate (9c)

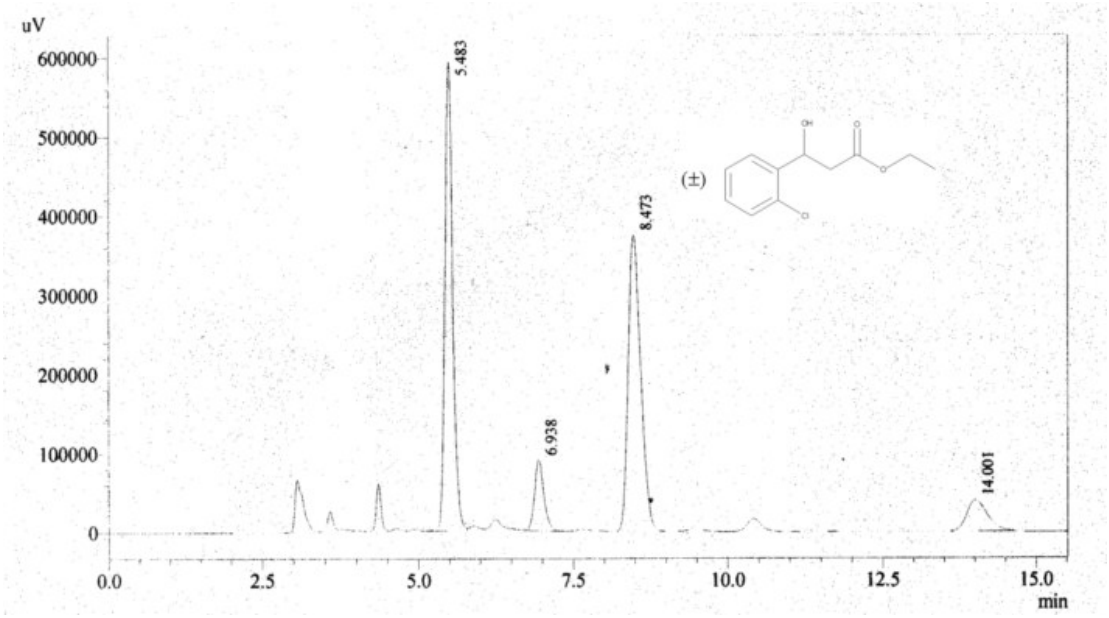


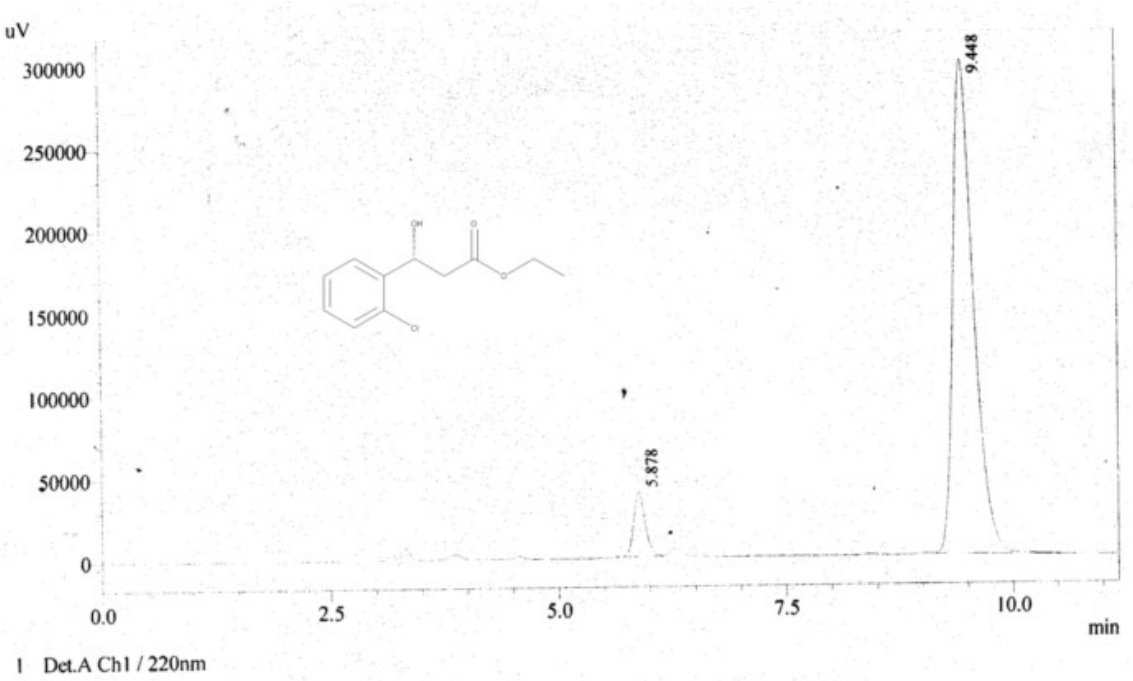


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.061	201637	13814	3.161	3.625
2	10.577	6177463	367273	96.839	96.375
Total		6379100	381087	100.000	100.000

(R)- Ethyl 3- hydroxy-3-(2-chlorophenyl)propanoate (9d)

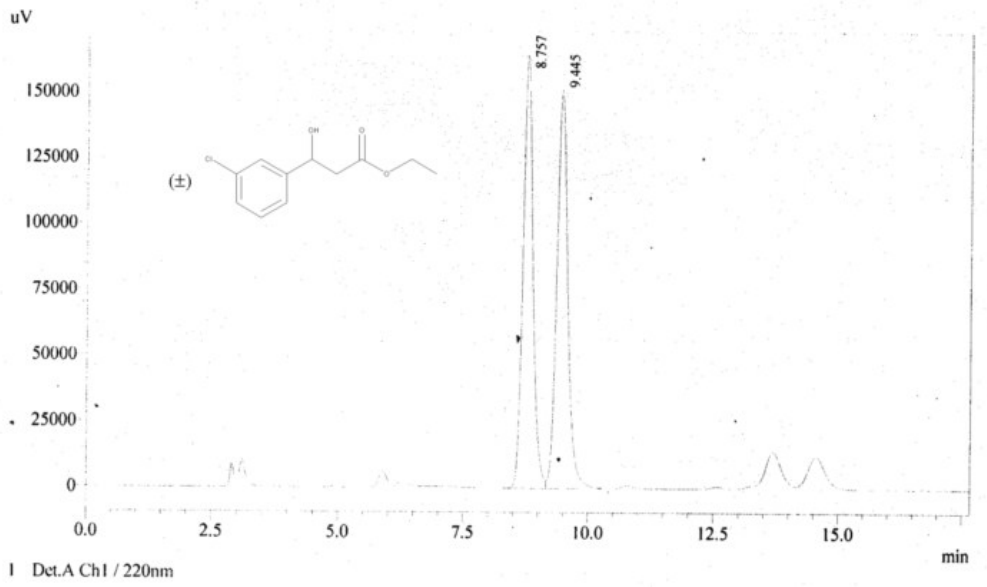


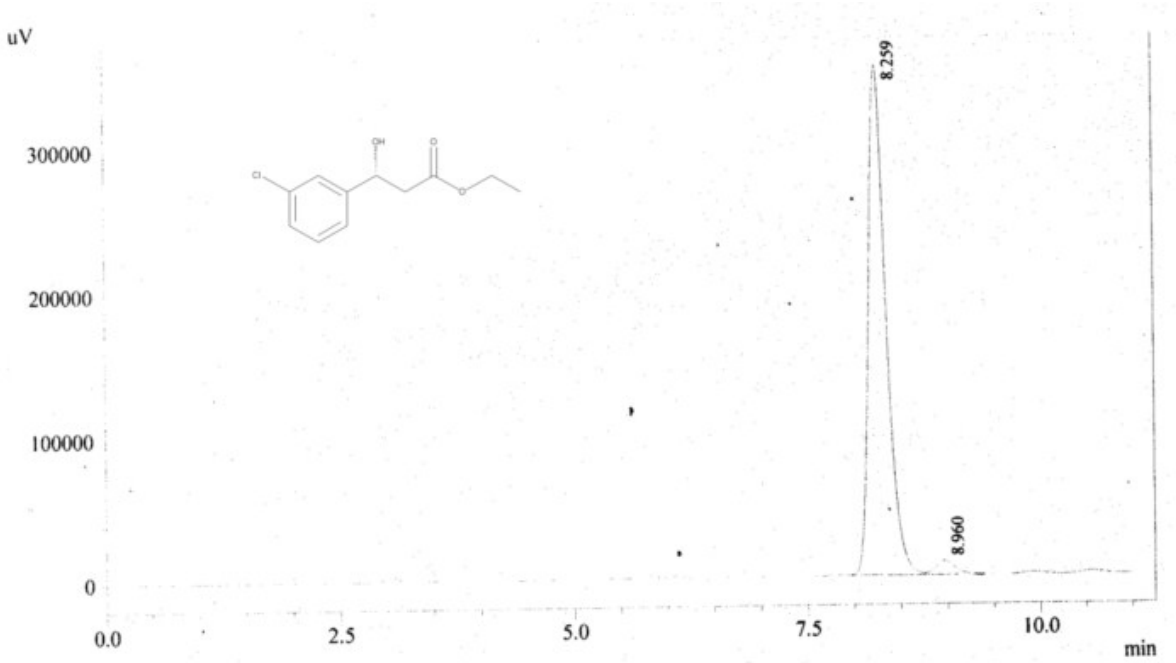


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.878	337821	39271	6.677	11.583
2	9.448	4721775	299761	93.323	88.417
Total		5059596	339032	100.000	100.000

(R)- Ethyl 3- hydroxy-3-(3-chlorophenyl)propanoate (9e)

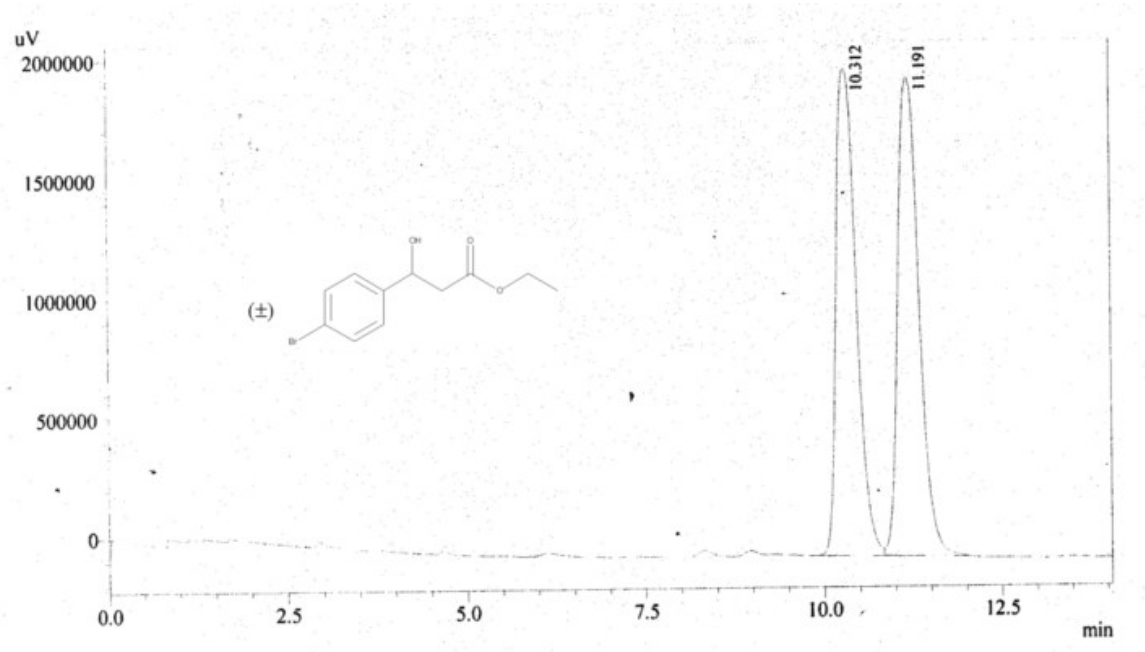


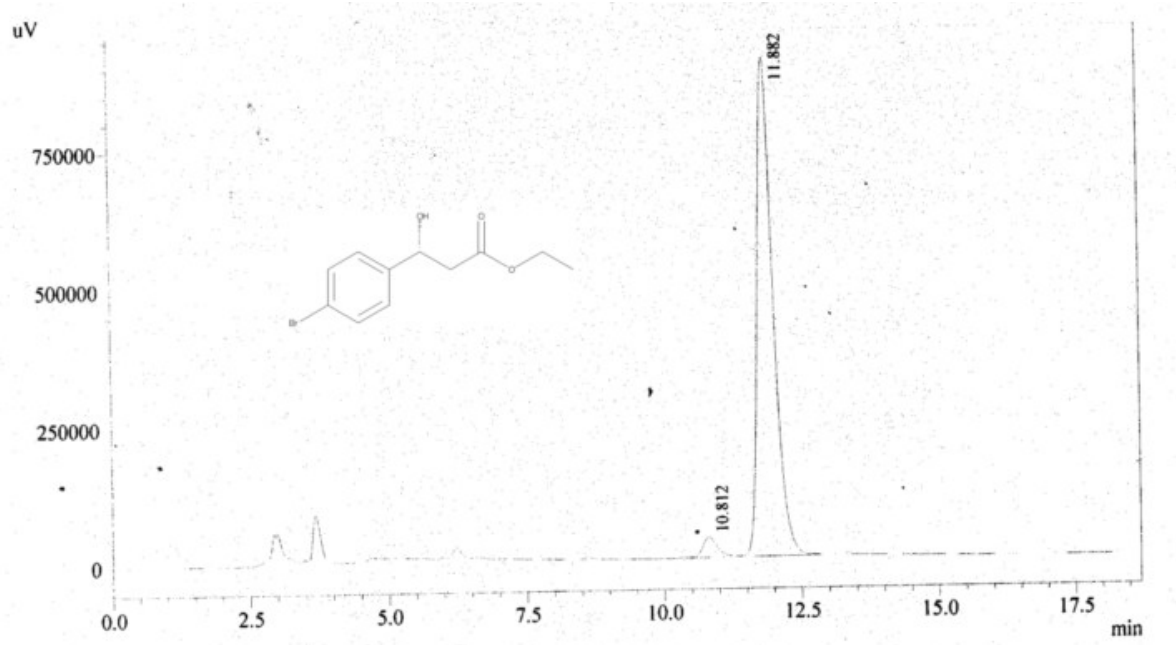


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.259	4591585	353312	96.998	97.296
2	8.960	142097	9820	3.002	2.704
Total		4733682	363132	100.000	100.000

(R)- Ethyl 3- hydroxy-3-(4-bromophenyl)propanoate (9f)

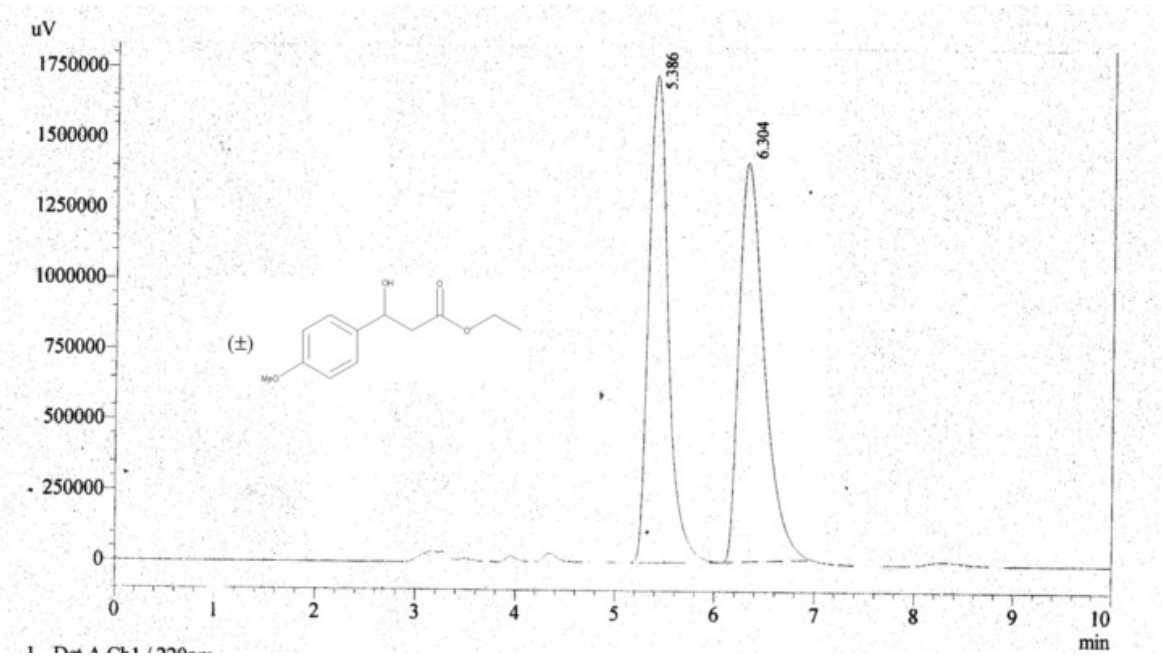


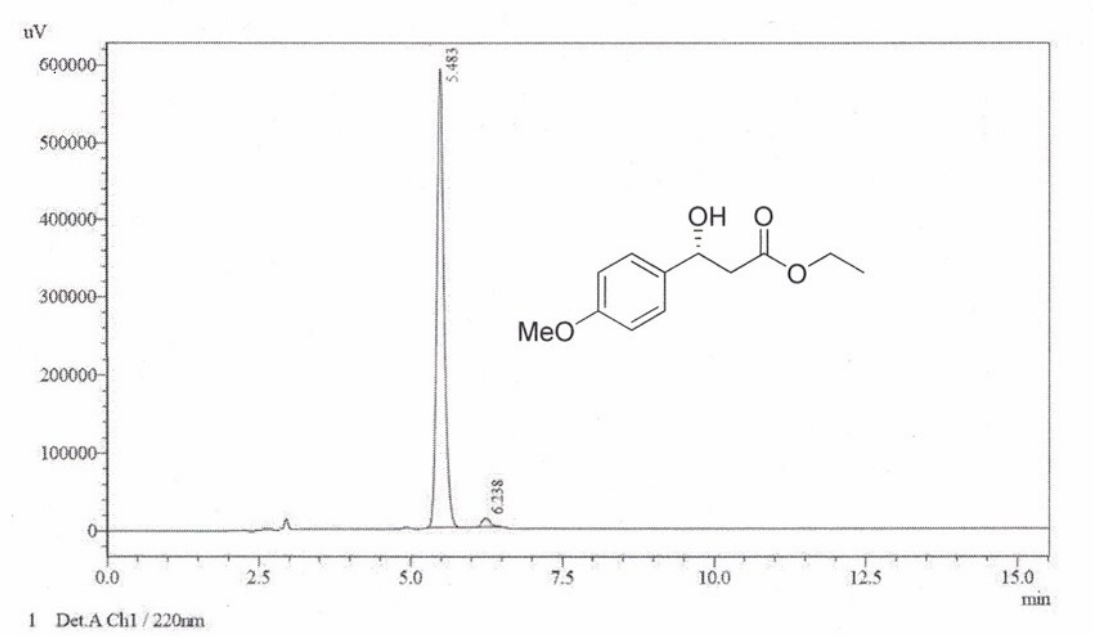


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.812	670119	36196	3.575	3.857
2	11.882	18072746	902181	96.425	96.143
Total		18742865	938377	100.000	100.000

(R)- Ethyl 3-hydroxy-3-(4-methoxyphenyl)propanoate (9g)

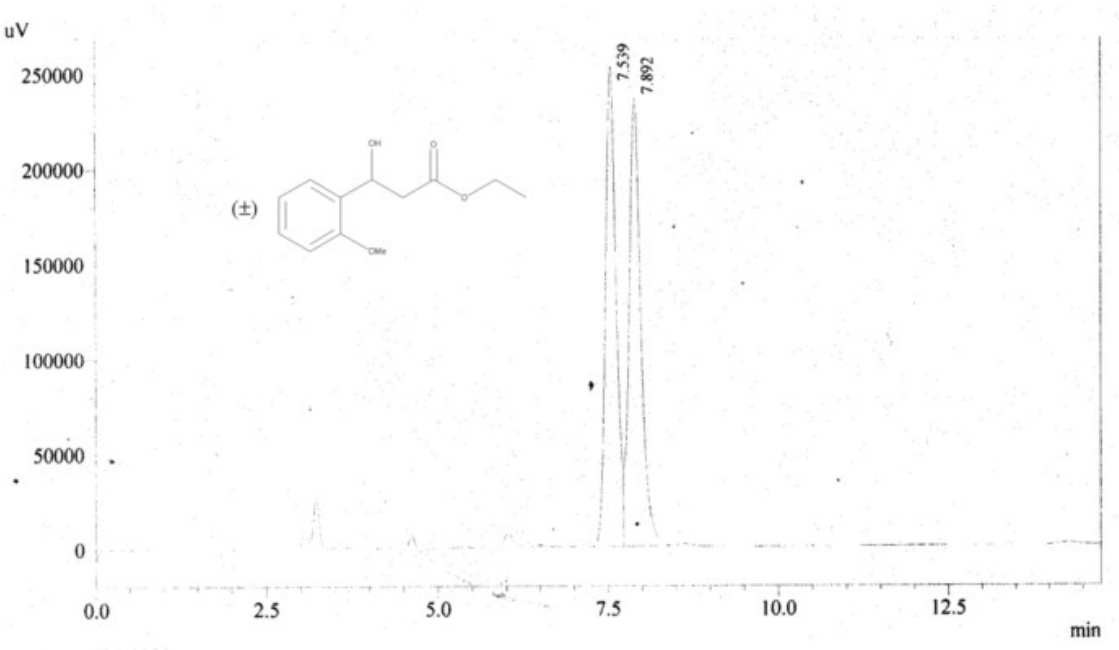


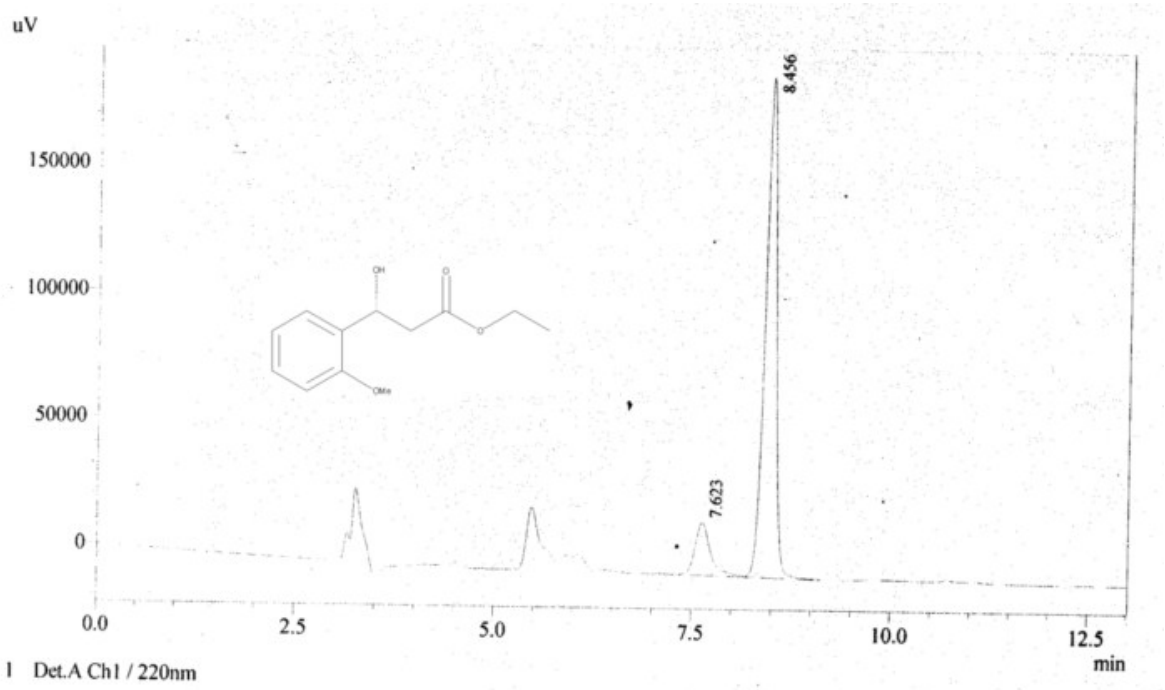


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.483	5108602	589888	98.534	98.390
2	6.238	75993	9655	1.466	1.610
Total		5184595	599542	100.000	100.000

(R)- Ethyl 3-hydroxy-3-(2-methoxyphenyl)propanoate (9h)

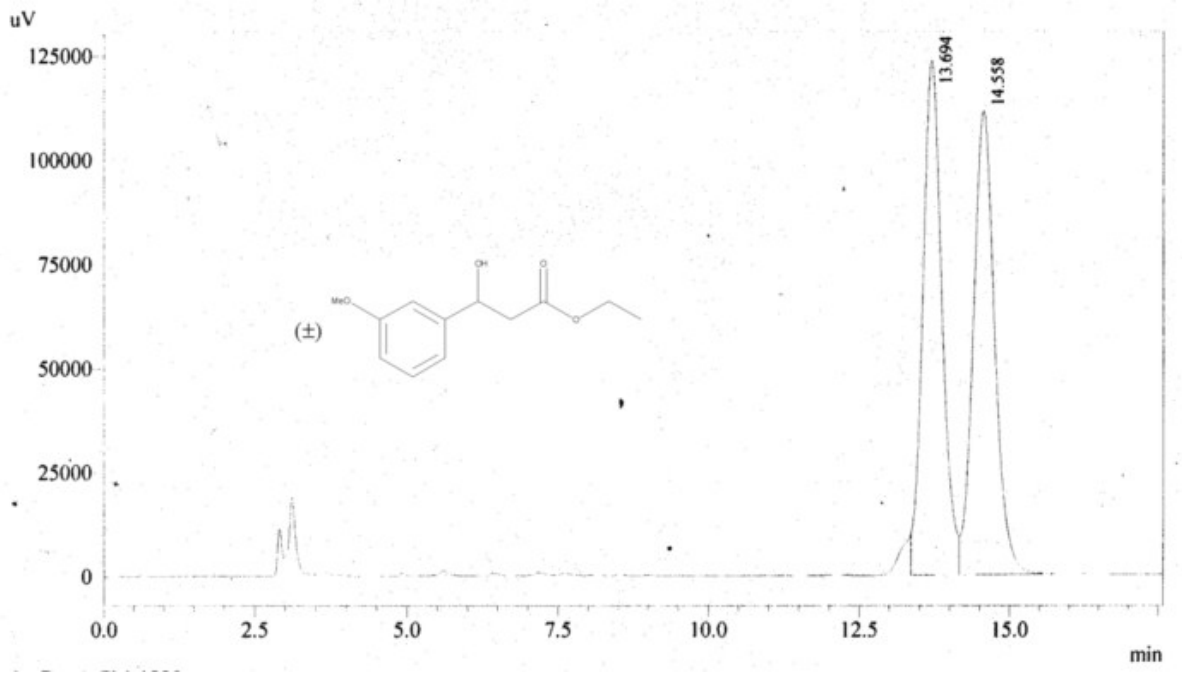


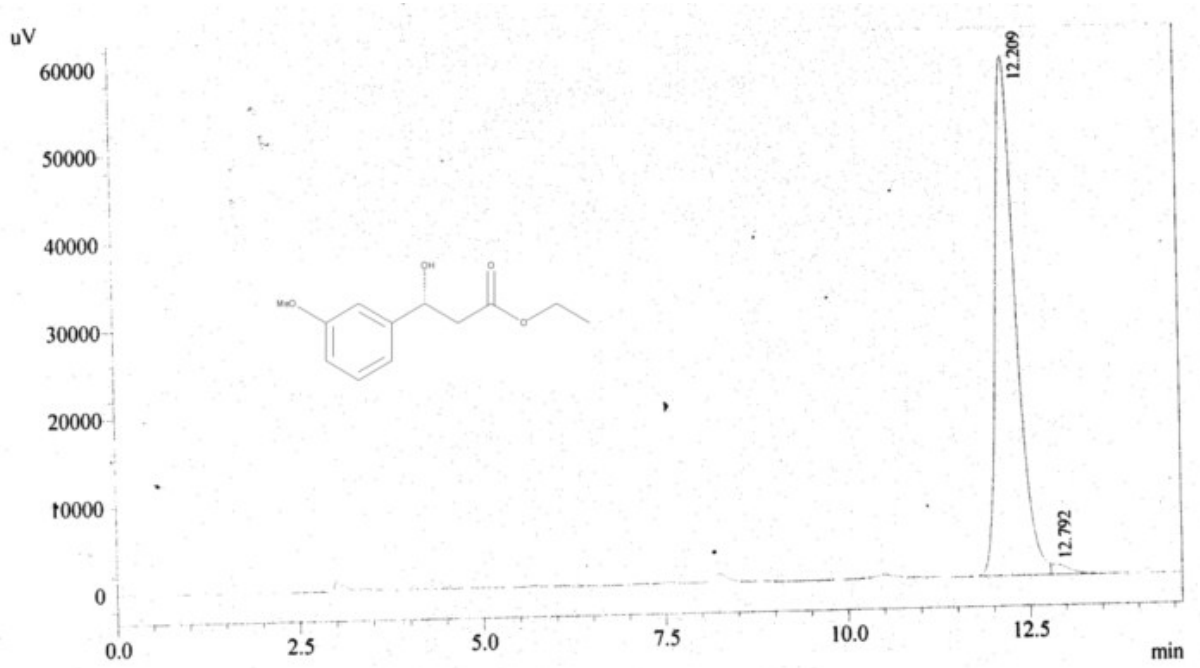


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.623	282878	20888	12.751	9.579
2	8.456	1935632	197177	87.249	90.421
Total		2218510	218065	100.000	100.000

(R)-Ethyl 3-hydroxy-3-(3-methoxyphenyl)propanoate (9i)



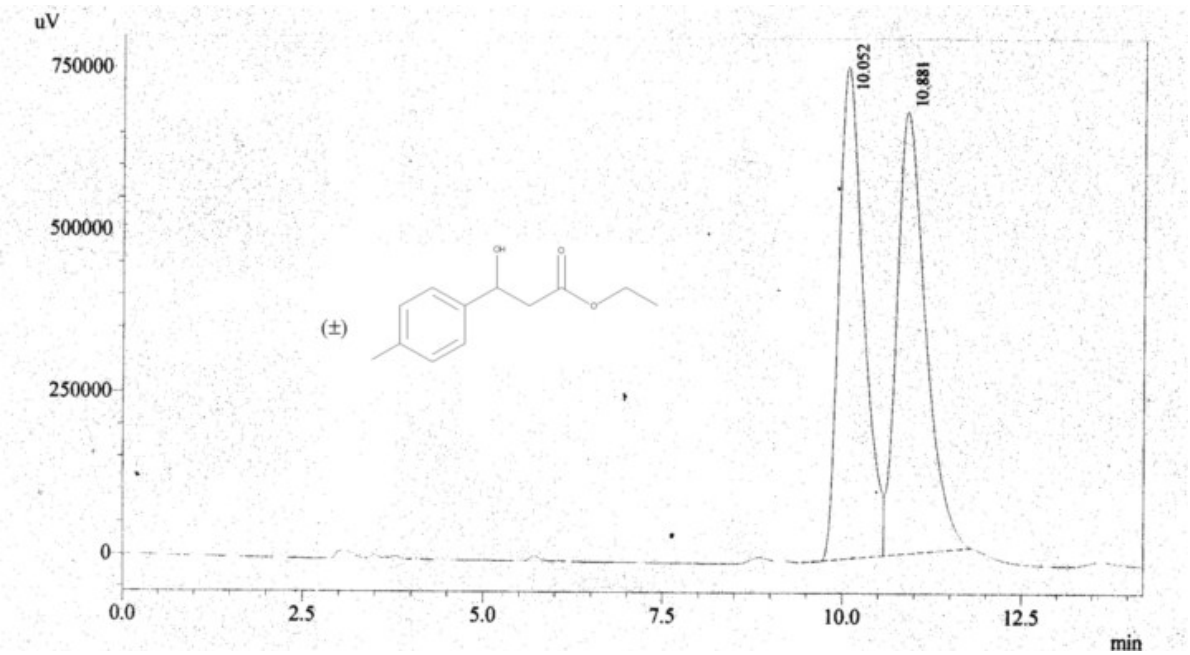


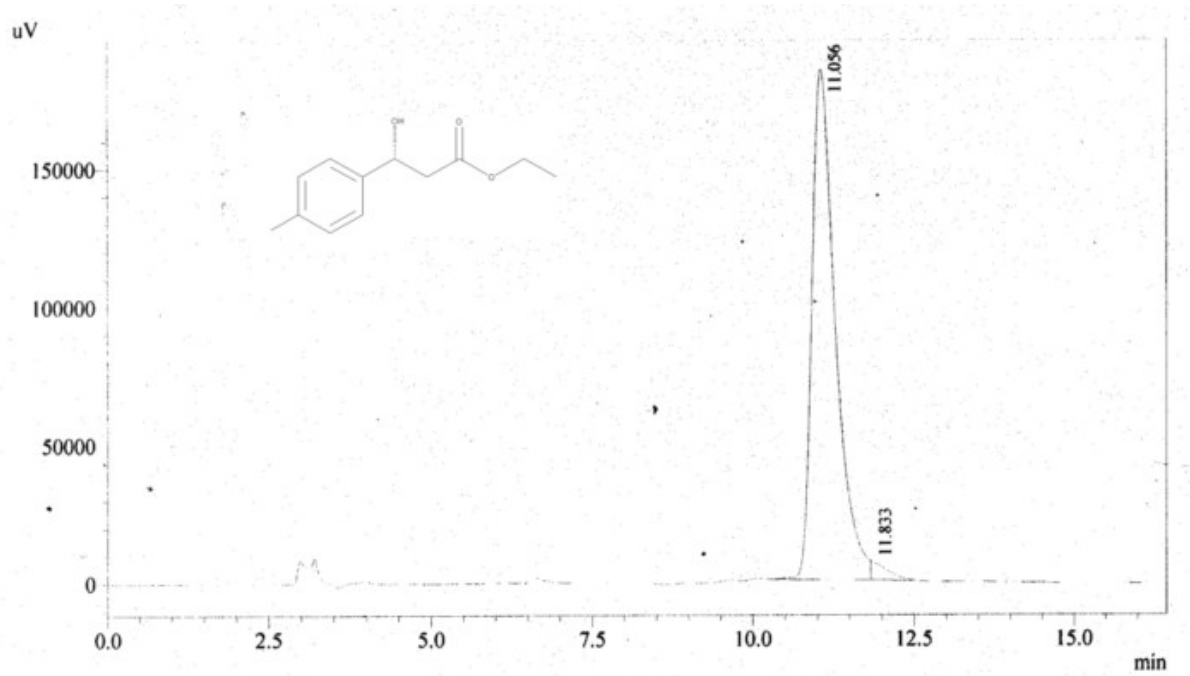
1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.209	1150437	59293	98.269	97.996
2	12.792	20268	1213	1.731	2.004
Total		1170705	60506	100.000	100.000

(R)- Ethyl 3-hydroxy-3-(4- methylphenyl)propanoate (9j)



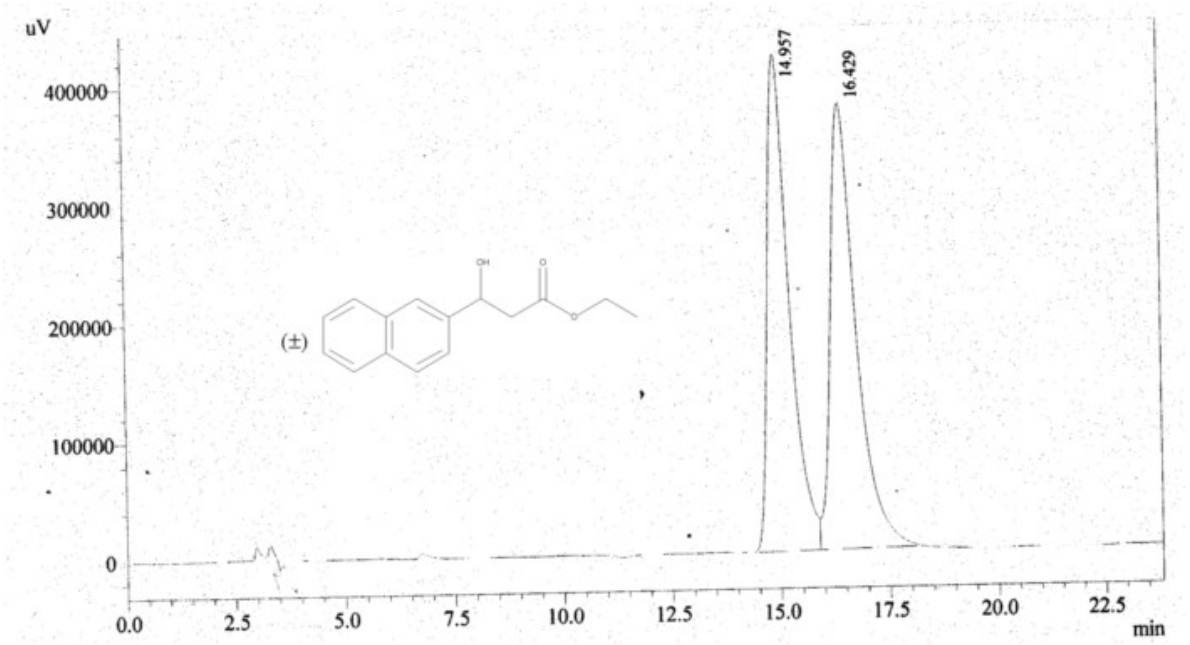


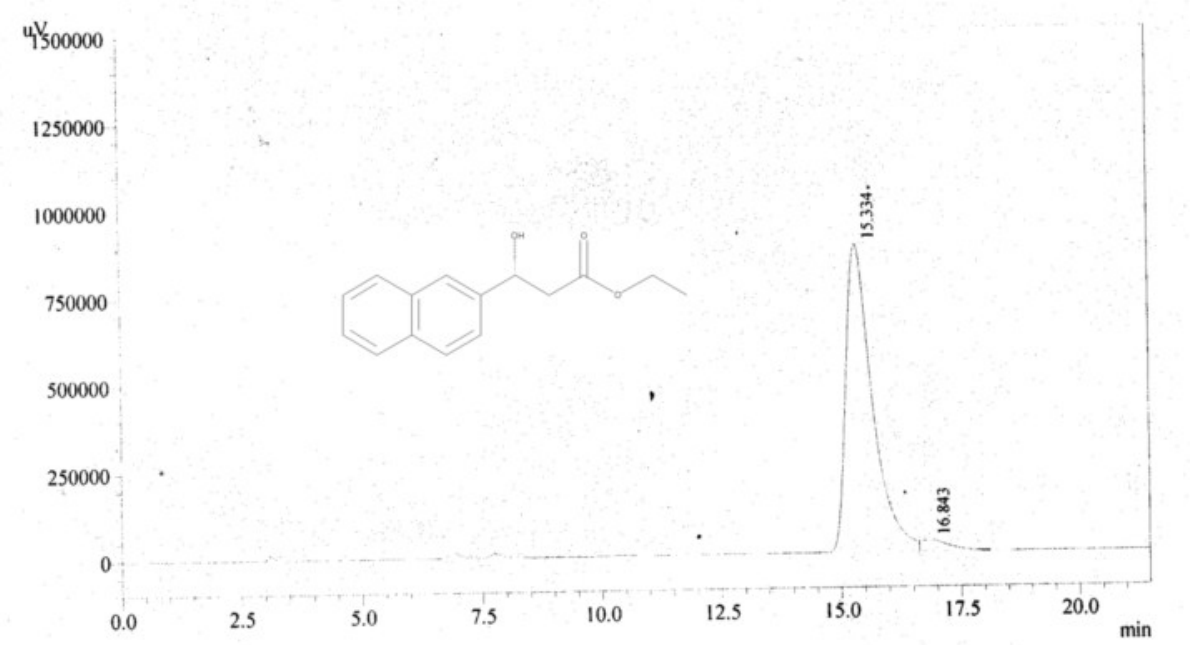
1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.056	4683139	184805	97.591	96.417
2	11.833	115611	6868	2.409	3.583
Total		4798750	191673	100.000	100.000

(R)- Ethyl 3-hydroxy-3-(2-naphthyl)propanoate (9k)



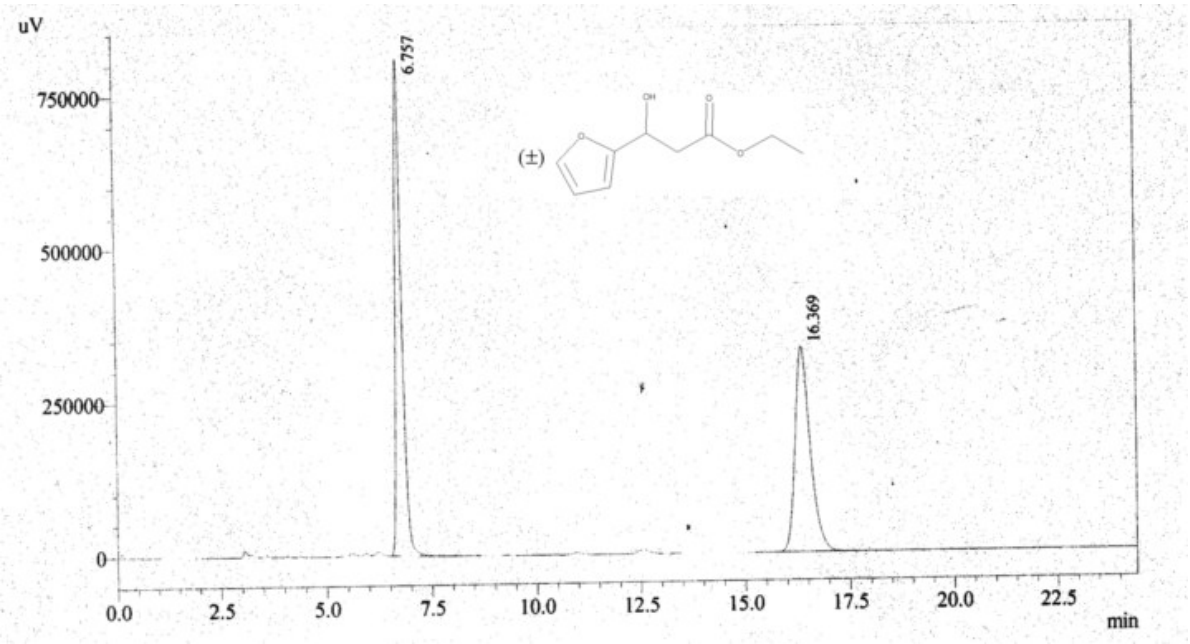


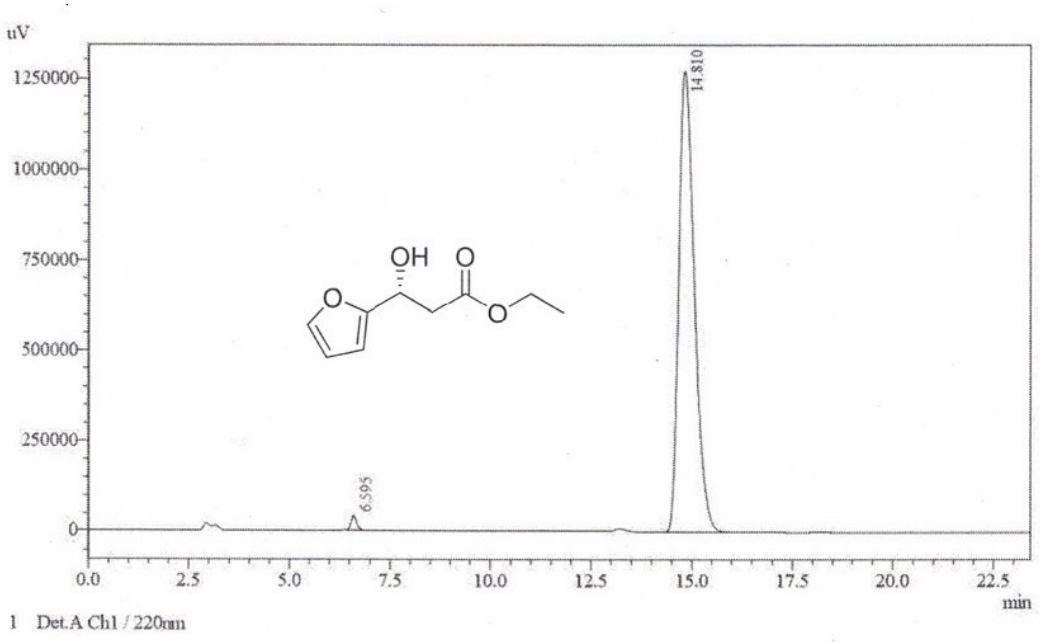
1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.334	33836941	881426	96.394	96.454
2	16.843	1265653	32403	3.606	3.546
Total		35102593	913829	100.000	100.000

(R)- Ethyl 3-(2-furyl)-3-hydroxypropanoate (9l)



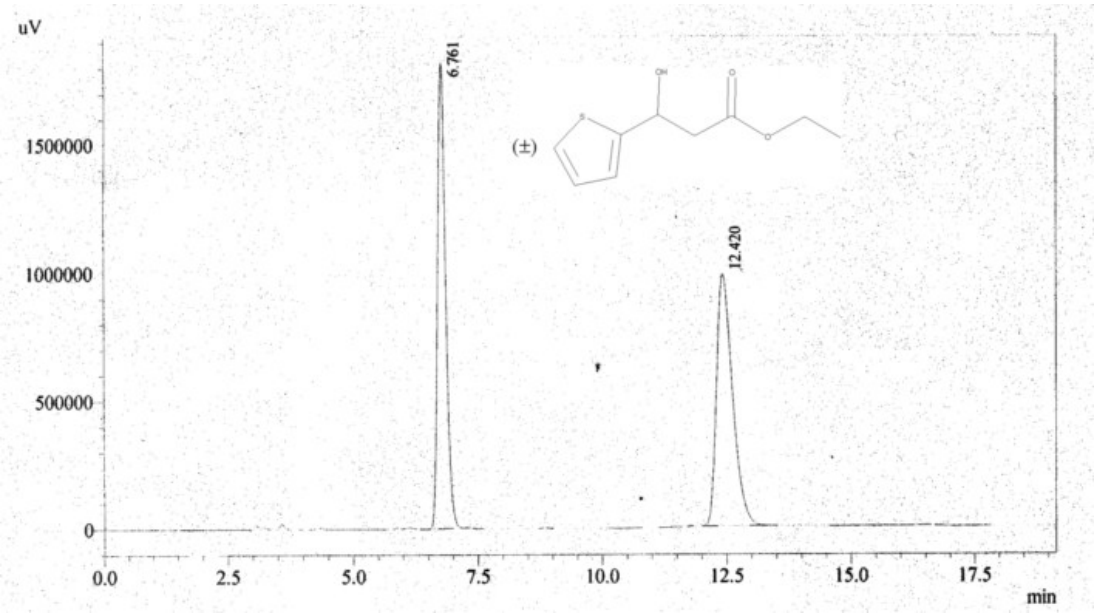


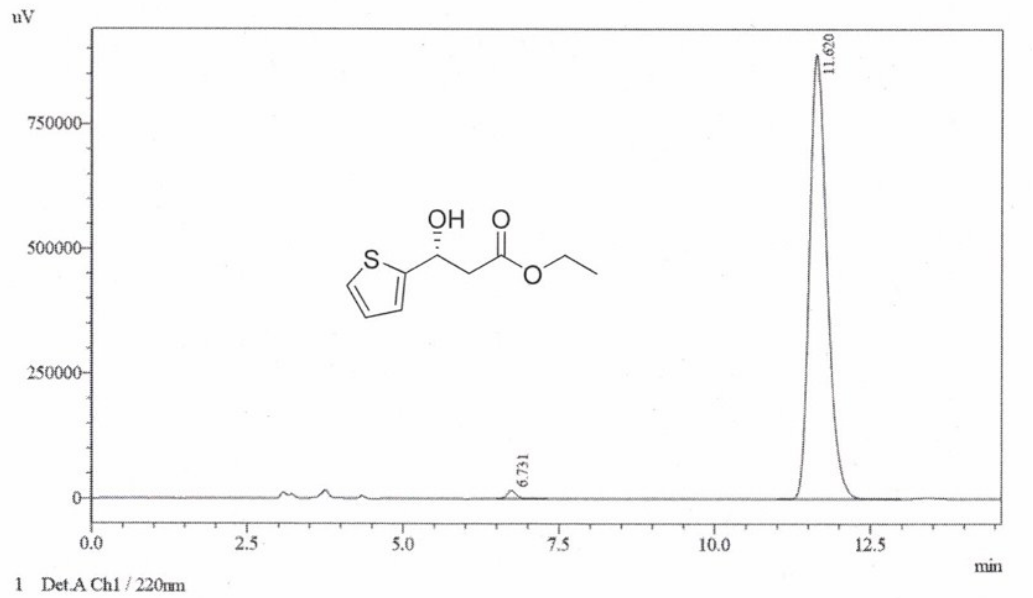
1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.595	375310	39824	1.083	3.038
2	14.810	34291956	1270915	98.917	96.962
Total		34667266	1310739	100.000	100.000

(R)- Ethyl 3-hydroxy-3-(2-thienyl)propanoate (9m)

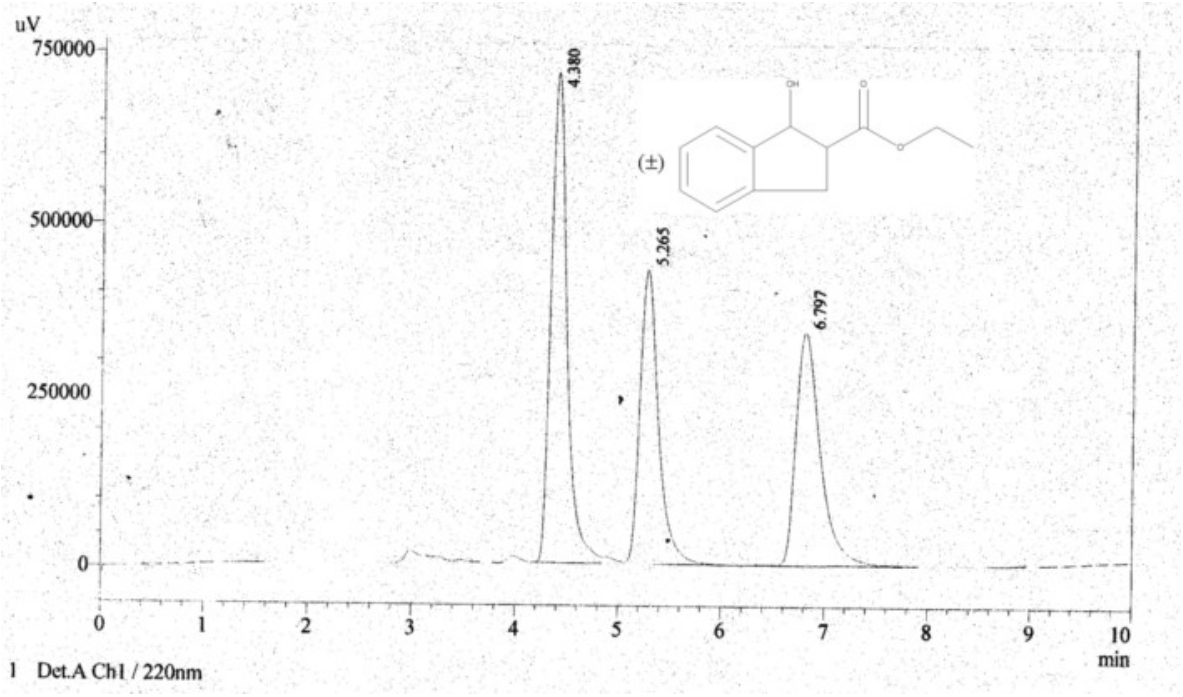


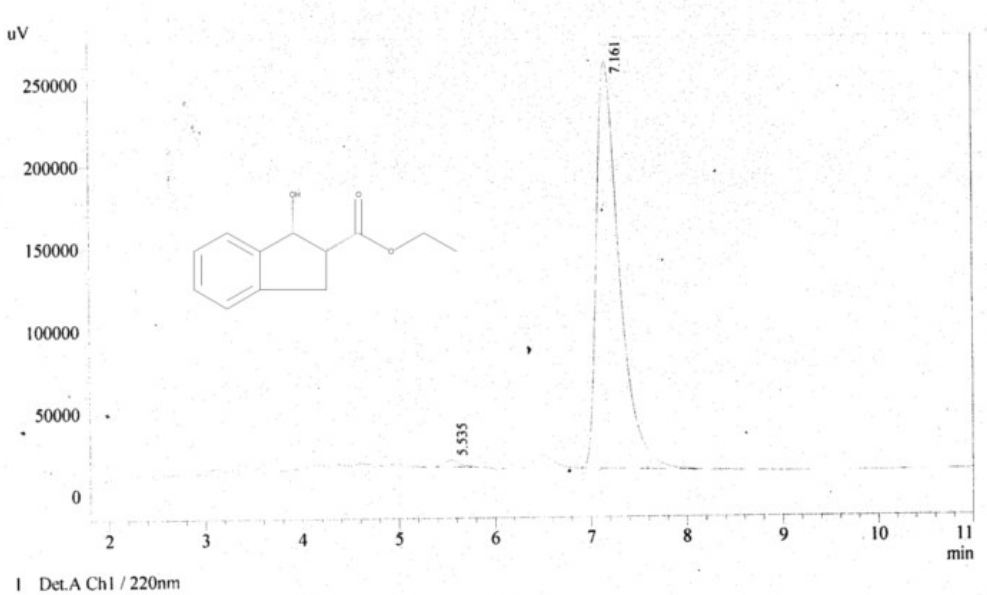


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.731	167354	16643	1.336	2.144
2	11.620	12360273	890061	98.664	97.856
Total		12527626	906704	100.000	100.000

Ethyl1-hydroxyindane-2-carboxylate (9n)

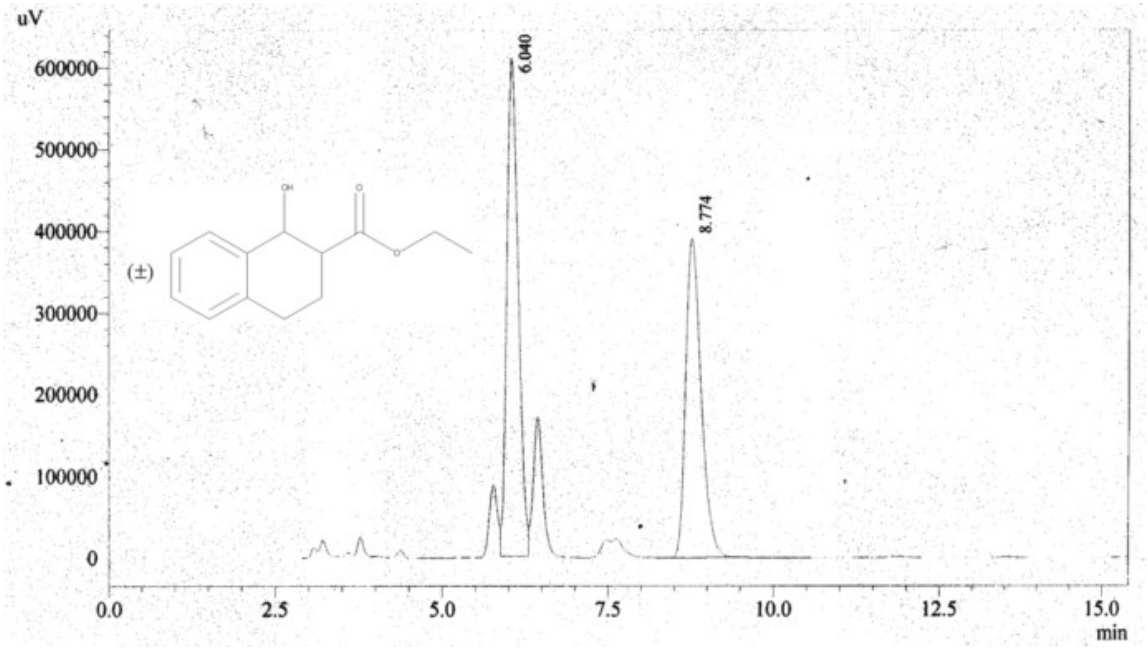


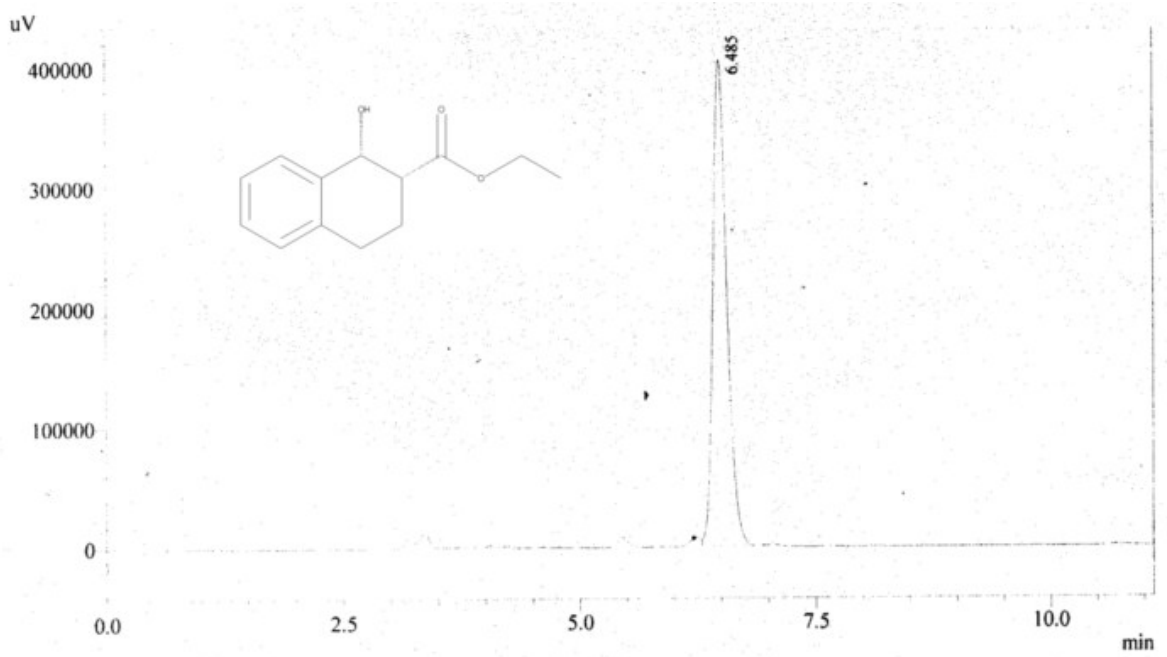


Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.535	43787	4298	1.062	1.711
2	7.161	4078458	246943	98.938	98.289
Total		4122245	251241	100.000	100.000

Ethyl 1-hydroxytetraline-2-carboxylate (9o)





1 Det.A Ch1 / 220nm

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.485	4131261	404811	100.000	100.000
Total		4131261	404811	100.000	100.000