Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers

Supporting Information for

Asymmetric Hydrogenation of α-Arylacrylic and β-Arylbut-3-enoic Acids Catalyzed by a Rh(I) complex of Monodentate Secondary Phosphine Oxide Ligand

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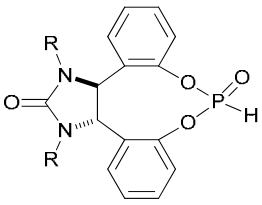
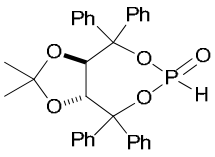
1 General methods

All reactions and manipulations involving air-sensitive compounds were performed using standard Schlenk techniques or in a glovebox. Anhydrous THF, Et_2O and toluene were distilled from sodium benzophenoneketyl. Anhydrous CH_2Cl_2, $CHCl_3$, $ClCH_2CH_2Cl$, Et_3N, MeOH, CF_3CH_2OH and *i*-PrOH were distilled from CaH_2 under an atmosphere of argon. Melting points were measured on a RY-I apparatus and uncorrected. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Mercury 400 MHz or Agilent 400 MHz spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^1H NMR), $CDCl_3$ (^{13}C NMR), and external CF_3CO_2H (^{19}F NMR) references, respectively. Optical rotations were determined using an Autopol I polarimeter. ESI-MS mass spectra were obtained on Agilent LC/MSD SL instrument, respectively. HRMS (ESI) were measured on an Agilent Technologies 6224 TOF LC/MS or an APEX III 7.0 TESLA FTMS spectrometer. The IR spectra were measured on a Bruker Tensor 27 spectrometer. Chiral HPLC analyses were performed on a JASCO 2089 liquid chromatography.

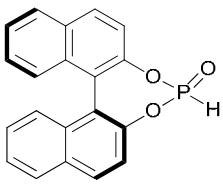
2 Ligand synthesis



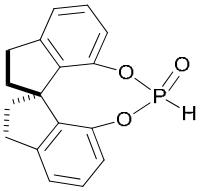
(*S*,*S*)-**L1**: R = Bn
(*R*,*R*)-**L5**: R = Et
(*S*,*S*)-**L6**: R = 3,5-$(Me)_2C_6H_3$



(*R*,*R*)-**L2**



(*S*)-**L3**



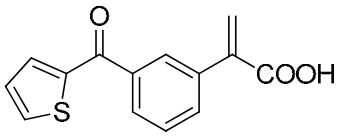
(*R*)-**L4**

The chiral monodentate secondary phosphine oxide ligands (*S*,*S*)-**L1**,[1] (*R*,*R*)-**L2**,[2] (*S*)-**L3**,[3] (*R*)-**L4**,[1] (*R*,*R*)-**L5**,[1] and (*S*,*S*)-**L6**[1] were synthesized according to the literature procedures.

3 Synthesis of α-arylacrylic and β-arylbut-3-enoic acids

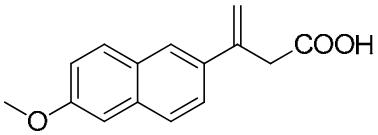
Except for α-arylacrylic acid **1n** and β-arylbut-3-enoic acid **3g**, all other substrates **1a-m**[4] and **3a-f**[5] are known compounds and were synthesized according to published procedures or obtained from commercial sources.

2-(3-(thiophene-2-carbonyl)phenyl)acrylic acid, 1n



Yellowish solid; M.P. 91-92 °C;^{1}H NMR (400 MHz, $CDCl_3$):δ = 10.72 (s, br, 1H), 7.95 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.72-7.66 (m, 3H),7.52-7.49 (m, 1H) 7.15-7.13 (m, 1H), 6.63 (s, 1H), 6.11 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.8, 171.3, 143.2, 139.6, 137.8, 136.2, 135.1, 134.5, 132.2, 130.4, 129.3, 128.9, 128.2, 128.0; FTIR (KBr pellet) ν 3445, 1678, 1631, 1515, 1411, 1230, 917, 708, 656cm^{-1}; ESI-MS m/z: 257.0 (M - H^+); HRMS (MALDI/DHB) m/z: Calcd. For $C_{14}H_{11}O_3S^+$: 259.0423, Found: 259.0420 (M + H^+).

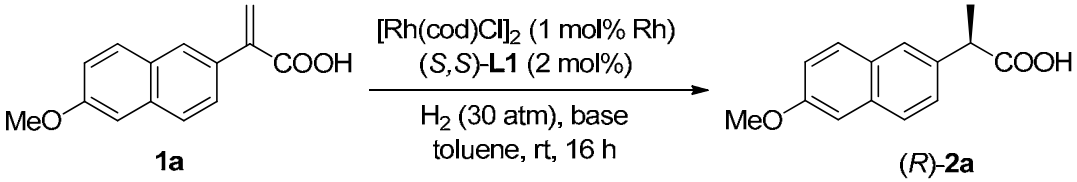
3-(6-methoxynaphthalen-2-yl)but-3-enoic acid, 3g



Yellowish solid; M.P. 162-164 °C; ^{1}H NMR (400 MHz, CD_3OD): δ = 7.80 (s, 1H), 7.72-7.69 (m, 2H), 7.62-7.60 (m, 1H), 7.18 (d, *J* = 2.0 Hz, 1H), 7.10 (dd, *J* = 8.8, 1.8 Hz, 1H),5.66 (s, 1H), 5.27 (s, 1H), 3.88 (s, 3H), 3.61 (s, 2H);^{13}C NMR (100 MHz, CD_3OD): δ = 175.4, 159.3, 142.5, 136.1, 135.6, 130.7, 130.1, 127.9, 125.4, 125.3, 119.9, 116.0, 106.5, 55.7, 41.8; FTIR (neat) ν 2963, 1688, 1623, 1598, 1388, 1209, 1180, 1023, 851, 814; ESI-MS m/z: 243.1 (M + H^+); HRMS (ESI) m/z: Calcd. For $C_{15}H_{15}O_3^+$: 243.1016, Found: 243.1012 (M + H^+).

4 The effect of the base additives on asymmetric hydrogenation of 1a

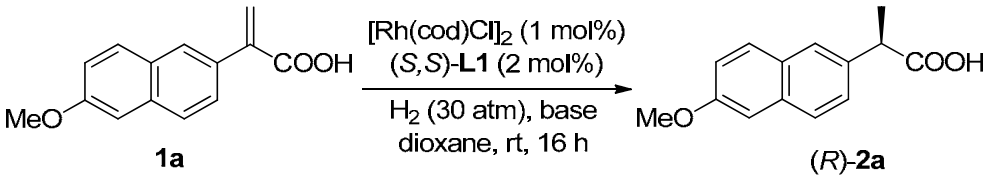
Table *S1* Base effect on $[Rh(cod)Cl]_2$/(*S*,*S*)-**L1** catalyzed AH of **1a** in toluene[a]



Entry	Base (0.5 eq)	Conv. (%)[b]	Ee (%)[c]
1	Et_3N	>99	92
2	$HNEt_2$	65	69
3	DIPEA	>99	78
4	Dimethylaniline	<5%	--
5	Pyridine	<5%	--

[a] Reaction conditions: [**1a**] = 0.10 M, toluene 2.5 mL. [b] Determined by ^{1}H NMR. [c] Determined by Chiral HPLC using a chiralcel AD-H column after the acid was transformed to its corresponding methyl ester with CH_2N_2, and the absolute configuration was assigned by comparison of the $[\alpha]_D^{20}$ with that reported in the literature.[6]

Table *S2* Base effect on [Rh(cod)Cl]$_2$/(*S*,*S*)-**L1** catalyzed AH of **1a** in 1,4-dioxane[a]



Entry	Base (0.5 eq)	Conv. (%)[b]	Ee (%)[c]
1	Et_3N	>99	92
2	$HNEt_2$	>99	67
3	DIPEA	>99	80
4	Dimethylaniline	75	0
5	Pyridine	<5%	--
6	Bu_3N	>99	90
7	Ph_3N	50	13
8	K_2CO_3	>99	54
9	--	20	5
10	Et_3N (0.2 eq)	>99	91
11	Et_3N (1.0 eq)	>99	90

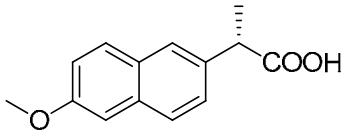
[a] Reaction conditions: Rh(I)/(*S*,*S*)-**L1** = 1/2, [**1a**] = 0.10 M. [b] Determined by ^{1}H NMR. [c]

Determined by Chiral HPLC using a chiralcel AD-H column after the acid was transformed to its corresponding methyl ester with CH_2N_2, and the absolute configuration was assigned by comparison of the $[\alpha]_D^{20}$ with that reported in the literature.[6]

5 Characterization data of the hydrogenation products

5.1 Characterization data of the hydrogenation products 2a-o

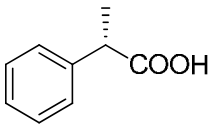
(*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid, (*S*)-2a



>99% conv., 96% yield (1.0-mmol scale), white solid, M.P. 156-158 °C, 95% ee; $[\alpha]_D^{20}$ = +68.3 (*c* 1.0, $CHCl_3$) [lit[6] $[\alpha]_D^{20}$ = +65.0 (*c* 1.0, $CHCl_3$) for optically pure *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 1H), 7.67 (s, 2H), 7.40 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.12 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.09 (d, *J* = 2.0 Hz, 1H), 3.90 (s, 3H), 3.86 (q, *J* = 6.8 Hz, 1H), 1.57 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **2a** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 98:2, flow rate = 1.0 mL/min, uv-vis detection at λ = 230 nm, t_R = 15.8 min (major), 18.0 min (minor).

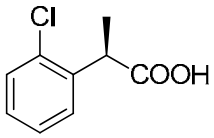
(*S*)-2-phenylpropanoic acid, (*S*)-2b



>99% conv., yellowish solid, M.P. 54-56 °C, 96% ee; $[\alpha]_D^{20}$ = +86.2 (*c* 1.0, $CHCl_3$) [lit[7] $[\alpha]_D^{20}$ = +71.5 (*c* 2.0, $CHCl_3$) for optically pure *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.23 (m, 5H), 3.73 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **2b** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 14.1 min (major), 18.3 min (minor).

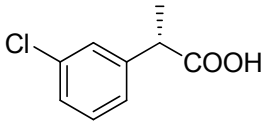
(*R*)-2-(2-chlorophenyl)propanoic acid, (*R*)-2c



>99% conv., yellowish oil, 92% ee; $[\alpha]_D^{20}$ = -52.4 (*c* 1.00, $CHCl_3$) [lit[8] $[\alpha]_D^{20}$= +32.8 (*c* 1.31, $CHCl_3$) for 55% ee *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.33 (m, 2H), 7.26-7.18 (m, 2H), 4.26 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **3c** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 9.7 min (major), 12.8 min (minor).

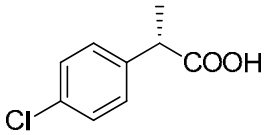
(*S*)-2-(3-chlorophenyl)propanoic acid, (*S*)-2d



>99% conv., yellowish oil, 94% ee; $[\alpha]_D^{20}$ = +27.7 (*c* 1.0, $CHCl_3$) [lit[8] $[\alpha]_D^{20}$= +53.9 (*c* 1.2, $CHCl_3$) for 97% ee, *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 1H), 7.26-7.23 (m, 2H), 7.20-7.18 (m, 1H), 3.71 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **2d** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 9.0 min (major), 9.9 min (minor).

(*S*)-2-(4-chlorophenyl)propanoic acid, (*S*)-2e

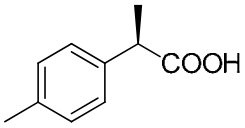


>99% conv., white solid, M.P. 68-70 °C, 94% ee; $[\alpha]_D^{20}$ = +72.8 (*c* 1.0, $CHCl_3$) [lit[8] $[\alpha]_D^{20}$ = +66.3 (*c* 0.9, $CHCl_3$) for 98% ee, *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 7.26-7.23 (m, 2H),3.70 (q, *J* = 7.2 Hz, 1H), 1.49 (d, *J* = 7.2 Hz,

3H).

The enantiomeric excess of **2e** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 9.0 min (minor), 10.2 min (major).

(*R*)-2-(p-tolyl)propanoic acid, (*R*)-2f

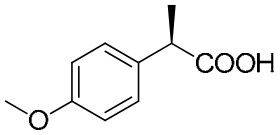


>99% conv., colorless oil, 93% ee; $[\alpha]_D^{20}$ = -40.7 (*c* 1.2, $CHCl_3$) [lit[8] $[\alpha]_D^{20}$ = +66.4 (*c* 0.71, $CHCl_3$) for 100% ee, *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (s, br, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.59 (q, *J* = 6.8 Hz, 1H), 2.29 (s, 3H), 1.39 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **2f** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 15.0 min (major), 18.0 min (minor).

Note: (*S*)-**2f** was obtained in 93% ee using $[Rh(cod)Cl]_2$/(*R*,*R*)-**L2** as the catalyst, see the data of entry 6 for Table 2 in the text.

(*R*)-2-(4-methoxyphenyl)propanoic acid, (*R*)-2g



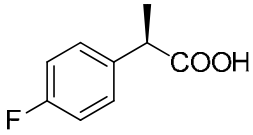
>99% conv., white solid, M.P. 72-74 °C, 94% ee; $[\alpha]_D^{20}$ = -49.8 (*c* 1.00, $CHCl_3$) [lit[9] $[\alpha]_D^{20}$ = -76.3 (*c* 1.02, $CHCl_3$) for 95% ee, *R*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, br, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 3H), 3.58 (q, *J* = 5.6 Hz, 1H), 1.39 (d, *J* = 6.8 Hz, 3H).

The enantiomeric excess of **2g** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 30.3 min (minor), 32.6

min (major).

Note: (*S*)-**2g** was obtained in 94% ee using $[Rh(cod)Cl]_2$/(*R*,*R*)-**L2** as the catalyst, see the data of entry 7 for Table 2 in the text.

(*R*)-2-(4-fluorophenyl)propanoic acid, (*R*)-2h

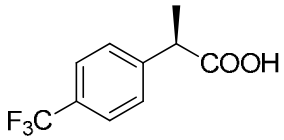


>99% conv., yellowish oil, 94% ee; $[\alpha]_D^{20}$ = -49.5 (*c* 1.2, $CHCl_3$) [lit[8] $[\alpha]_D^{20}$= +53.5 (*c* 0.62, $CHCl_3$) for 98% ee, *S*-isomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, br, 1H), 7.22-7.17 (m, 2H), 6.97-6.91 (m, 2H), 3.60 (q, *J* = 7.2 Hz, 1H), 1.38 (d, *J* = 7.2 Hz, 3H);^{19}F NMR (282 MHz, $CDCl_3$): δ = -115.9 ppm.

The enantiomeric excess of **2h** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 9.7 min (major), 10.5 min (minor).

Note: (*S*)-**2h** was obtained in 94% ee using $[Rh(cod)Cl]_2$/(*R*,*R*)-**L2** as the catalyst, see the data of entry 8 for Table 2 in the text.

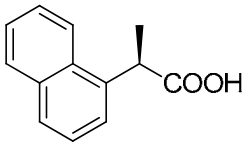
(*R*)-2-(4-(trifluoromethyl)phenyl)propanoic acid, (*R*)-2i



>99% conv., yellowish solid, M.P. 74-76 °C, 90% ee; $[\alpha]_D^{20}$ = -58.5 (*c* 1.0, $CHCl_3$) [lit[9] $[\alpha]_D^{20}$= -52.6 (*c* 1.05, $CHCl_3$) for 95% ee, *R*-isomer]; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 3.63 (q, *J* = 6.0 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = -63.0 ppm.

The enantiomeric excess of **2i** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 6.2 min (major), 8.6 min (minor).

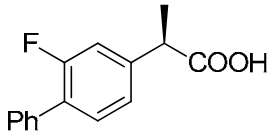
(*R*)-2-(naphthalen-1-yl)propanoic acid, (*R*)-2j



>99% conv., white solid, M.P. 155-158 °C, 92% ee; $[\alpha]_D^{20}$ = -102.0 (*c* 1.17, $CHCl_3$) [lit[10] $[\alpha]_D^{20}$= +125.7 (*c* 0.35, $CHCl_3$) for 87% ee, *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.54-7.42 (m, 4H), 4.52 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 6.8 Hz, 3H).

The enantiomeric excess of **2j** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 230 nm, t_R = 18.5 min (minor), 21.0 min (major).

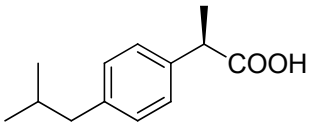
(*R*)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid, (*R*)-2k



>99% conv., white solid, M.P. 111-113 °C, 90% ee; $[\alpha]_D^{20}$ = -29.5 (*c* 1.10, $CHCl_3$) [lit[6] $[\alpha]_D^{20}$ = -41.2 (*c* 1.0, $CHCl_3$) for 97% ee, *R*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 2H), 7.45-7.34 (m, 4H), 7.18-7.13 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **2k** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 230 nm, t_R = 22.4 min (major), 26.5 min (minor).

(*R*)-2-(4-isobutylphenyl)propanoic acid, (*R*)-2l



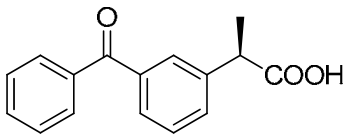
>99% conv., white solid, M.P. 74-75 °C, 93% ee; $[\alpha]_D^{20}$ = -54.9 (*c* 1.13, $CHCl_3$) [lit[11] $[\alpha]_D^{20}$= -45.4 (*c* 1.00, $CHCl_3$) for 82% ee, *R*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 2.44 (d,

J = 7.2 Hz, 2H), 1.89-1.78 (heptet, *J* = 6.8 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 6H).

The enantiomeric excess of **2l** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 : 1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 7.8 min (minor), 9.8 min (major).

Note: (*S*)-**2l** was obtained in 93% ee using $[Rh(cod)Cl]_2$/(*R*,*R*)-**L2** as the catalyst, see the data of entry 12 for Table 2 in the text.

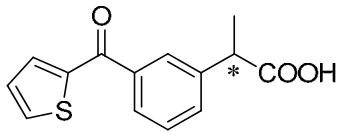
(*R*)-2-(3-benzoylphenyl)propanoic acid, (*R*)-2m



>99% conv., white solid, M.P. 99-101 °C, 90% ee; $[\alpha]_D^{20}$ = -35.8 (*c* 1.16, $CHCl_3$) [lit[12] $[\alpha]_D^{20}$ = +45.7 (*c* 1.03, $CHCl_3$) for 92% ee, *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.78 (m, 3H), 7.70-7.67 (m, 1H), 7.60-7.55 (m, 2H), 7.49-7.26 (m, 3H), 3.82 (q, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **2m** was determined by chiral HPLC analysis on Chiralpak IC-3 column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 90 :10, flow rate = 1.0 mL/min, uv-vis detection at λ = 230 nm, t_R = 17.0 min (minor), 19.3 min (major).

(*R*)-2-(3-(thiophene-2-carbonyl)phenyl)propanoic acid, (-)-2n[13]

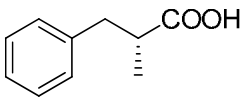


>99% conv., yellowish solid, M.P. 126-129 °C, 83% ee; $[\alpha]_D^{20}$ = -30.3 (*c* 1.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.82 (m, 1H), 7.78-7.75 (m, 1H), 7.73-7.71 (m, 1H), 7.63-7.62 (m, 1H), 7.57-7.54 (m, 1H), 7.48-7.44 (m, 1H), 7.16-7.13 (m, 1H), 3.83 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **2n** was determined by chiral HPLC analysis on Chiralpak IC-3 column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 90 :10,

flow rate = 1.0 mL/min, uv-vis detection at λ = 230 nm, t_R = 29.4 min (minor), 36.6 min.

(*R*)-2-methyl-3-phenylpropanoic acid, (*R*)-2o

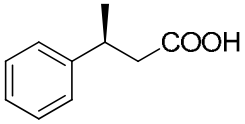


>99% conv., colorless oil, 54% ee; $[\alpha]_D^{20}$ = -9.4 (*c* 1.10, $CHCl_3$) [lit[6] $[\alpha]_D^{25}$ = -27.0 (*c* 1.00, $CHCl_3$) for 98% ee, *R*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (s, br, 1H), 7.26-7.14 (m, 5H), 3.06 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.73-2.67 (m, 1H), 2.60 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H).

The enantiomeric excess of **2o** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 : 1, flow rate = 1.0 mL/min, uv-vis detection at λ = 215 nm, t_R = 9.5 min (major), 11.0 min (minor).

5.2 Characterization data of the hydrogenation products 4a-g

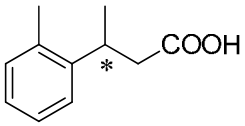
(*S*)-3-phenylbutanoic acid, (*S*)-4a



>99% conv., colorless oil, 94% ee; $[\alpha]_D^{20}$ = +38.3 (*c* 1.00, $CHCl_3$) [lit[14] $[\alpha]_D^{23}$= +10.35 (*c* 1.2,$CHCl_3$), *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.27 (m, 2H), 7.24-7.18 (m, 3H), 3.31-3.22 (m, 1H), 2.67 (dd, *J* = 15.6, 6.8 Hz, 1H), 2.57 (dd, *J* = 15.6, 8.4 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **4a** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 1.0 mL/min, uv-vis detection at λ = 214 nm, t_R = 11.8 min (minor), 13.8 min (major).

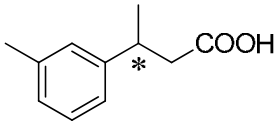
3-(*o*-tolyl)butanoic acid, 4b[5]



>99% conv., yellowish oil, 16% ee; $[\alpha]_D^{20}$ = +8.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18-7.07 (m, 4H), 3.57-3.48 (m, 1H), 2.67 (dd, *J* = 15.6, 6.4 Hz, 1H), 2.55 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.36 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H).

The enantiomeric excess of **4b** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 0.5 mL/min, uv-vis detection at λ = 214 nm, t_R = 16.5 min (major), 17.8 min (minor).

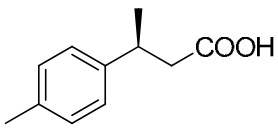
3-(*m*-tolyl)butanoic acid, 4c[5]



>99% conv., yellowish oil, 95% ee; $[\alpha]_D^{20}$ = +48.9 (*c* 1.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.16 (m, 1H), 7.02-7.00 (m, 3H), 3.27-3.18 (m, 1H), 2.66 (dd, *J* = 15.2, 6.4 Hz, 1H), 2.55 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.33 (s, 3H), 1.30 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **4c** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 0.5 mL/min, uv-vis detection at λ = 214 nm, t_R = 19.1 min (minor), 22.0 min (major).

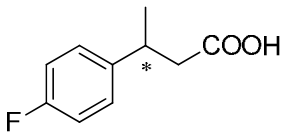
(*S*)-3-(*p*-tolyl)butanoic acid, (*S*)-4d



>99% conv., yellowish solid, M.P. 93-94 °C, 94% ee; $[\alpha]_D^{20}$ = +49.8 (*c* 1.00, $CHCl_3$) [lit[15] $[\alpha]_D^{20}$= +34.2 (*c*1.00, $CHCl_3$) for 99% ee, *S*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.11 (s, 4H), 3.28-3.19 (m, 1H), 2.66 (dd, *J* = 15.2, 6.8 Hz, 1H), 2.55 (dd, *J* = 15.6, 8.4 Hz, 1H), 2.31 (s, 3H),1.29 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **4d** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 :1, flow rate = 0.5 mL/min, uv-vis detection at λ = 214 nm, t_R = 21.6 min (minor), 22.8 min (major).

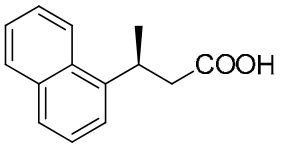
3-(4-fluorophenyl)butanoic acid, 4e[5]



>99% conv., yellowish oil, 94% ee; $[\alpha]_D^{20}$ = +41.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19-7.15 (m, 2H), 7.00-6.95 (m, 2H), 3.30-3.21 (m, 1H), 2.62 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.56 (dd, *J* = 15.6, 8.0 Hz, 1H), 1.29 (d, *J* = 6.8 Hz, 3H).

The enantiomeric excess of **4e** was determined by chiral HPLC analysis on Chiralpak OD-Hcolumn after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99.5 :0.5, flow rate = 0.5 mL/min, uv-vis detection at λ = 214 nm, t_R = 13.7 min (minor), 14.4min (major).

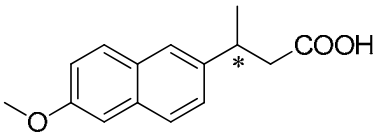
(*S*)-3-(naphthalen-1-yl)butanoic acid, (*S*)-4f



>99% conv., yellowish solid, M.P. 108-109 °C, 59% ee; $[\alpha]_D^{20}$ = +10.9 (*c* 1.20, $CHCl_3$) [lit[5] $[\alpha]_D^{20}$= -9.5 (*c*0.6, $CHCl_3$) for 98% ee, *R*-isomer]; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.0 Hz, 1H), 7.86-7.84 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.55-7.36 (m, 4H), 4.20-4.10 (m, 1H), 2.89 (dd, *J* = 15.2, 5.2 Hz, 1H), 2.65 (dd, *J* = 15.6, 9.2 Hz, 1H), 1.46 (d, *J* = 7.2 Hz, 3H).

The enantiomeric excess of **4f** was determined by chiral HPLC analysis on Chiralpak OJ column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 99 : 1, flow rate = 1.0 mL/min, uv-vis detection at λ = 230 nm, t_R = 13.7 min (minor), 15.4 min (major).

3-(6-methoxynaphthalen-2-yl)butanoic acid, 4g[16]



>99% conv., yellowish solid, M.P. 140-142 °C, 97% ee; $[\alpha]_D^{20}$ = +47.8 (*c* 1.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.69-7.66 (m, 2H), 7.57 (d, *J* = 1.2 Hz, 1H),7.33-7.31 (m, 1H), 7.14-7.09 (m, 2H), 3.90 (s, 3H), 3.44-3.35 (m, 1H), 2.74 (dd, *J* = 15.2, 7.2 Hz, 1H), 2.63 (dd, *J* = 15.6, 8.0 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H).

The enantiomeric excess of **4g** was determined by chiral HPLC analysis on Chiralpak IC-3 column after esterification with CH_2N_2. Conditions: hexane/isopropanol = 90 :10, flow rate = 0.5 mL/min, uv-vis detection at λ = 254 nm, t_R = 15.0 min (minor), 15.8 min (major).

6 Reference

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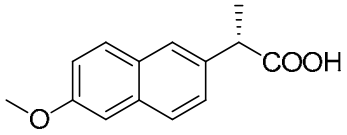
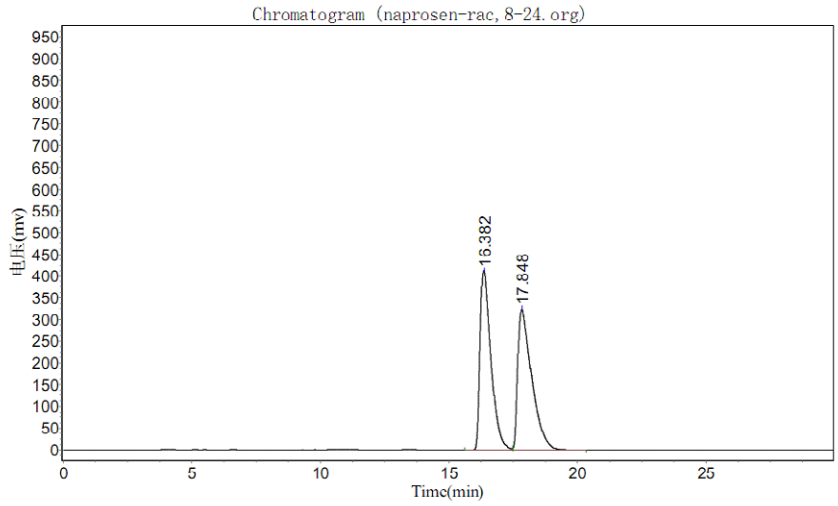
7 HPLC of the hydrogenation products and derivatives

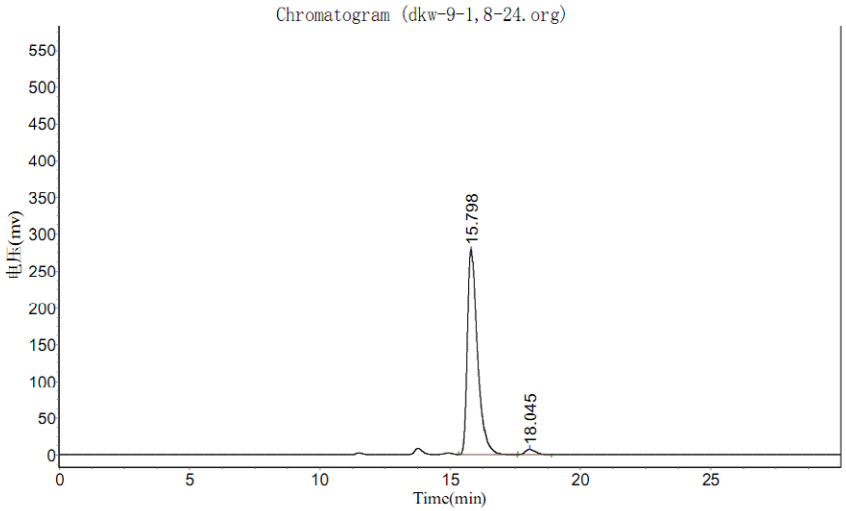
(*S*)-2-(6-methoxynaphthalen-2-yl)propanoic acid, (*S*)-2a





Results

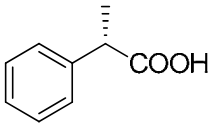
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.382	411450.375	12071189.000	49.8340
2		17.848	322105.188	12151631.000	50.1660
Total			733555.563	24222820.000	100.0000

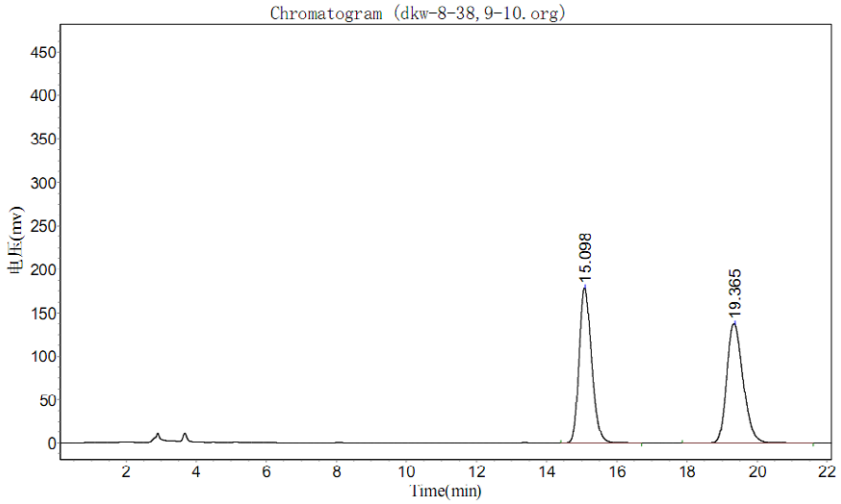


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.798	277897.594	7476096.000	97.7561
2		18.045	6180.633	171608.406	2.2439
Total			284078.227	7647704.406	100.0000

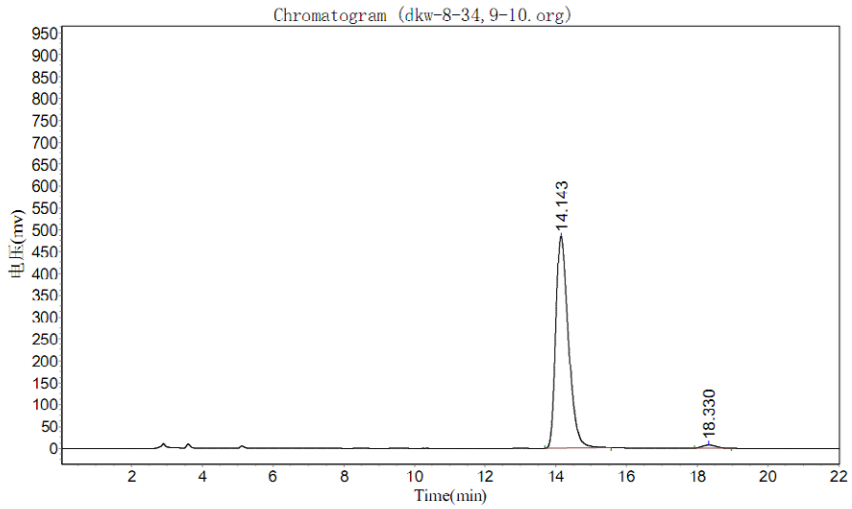
(*S*)-2-phenylpropanoic acid, (*S*)-2b





Results

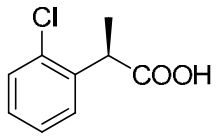
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.098	178239.156	4433476.000	49.8156
2		19.365	136814.391	4466290.500	50.1844
Total			315053.547	8899766.500	100.0000

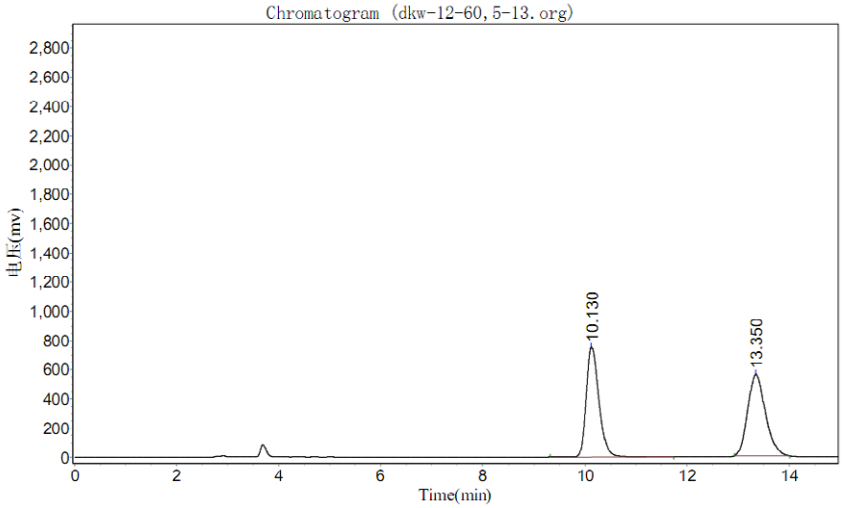


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.143	482855.313	11961605.000	98.3800
2		18.330	7192.087	196971.813	1.6200
Total			490047.400	12158576.812	100.0000

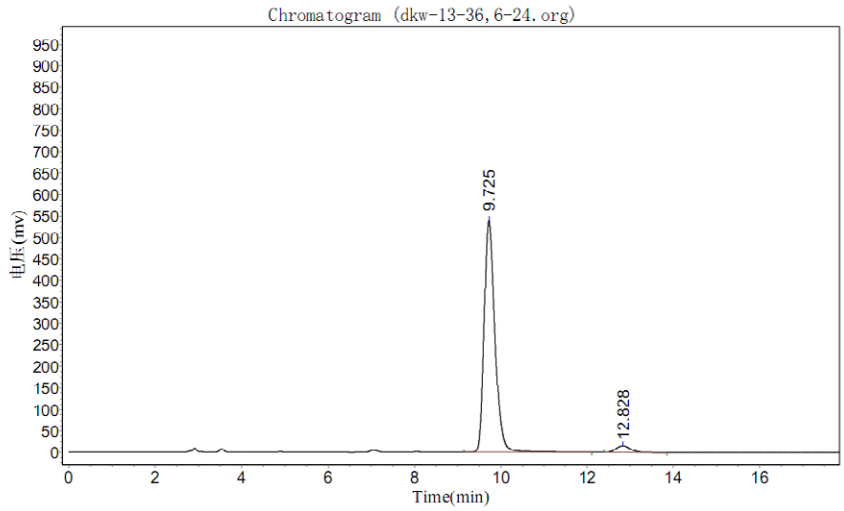
(*R*)-2-(2-chlorophenyl)propanoic acid, (*R*)-2c





Results

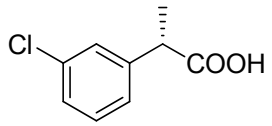
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.130	751975.063	13028821.000	49.0727
2		13.350	558534.313	13521243.000	50.9273
Total			1310509.375	26550064.000	100.0000

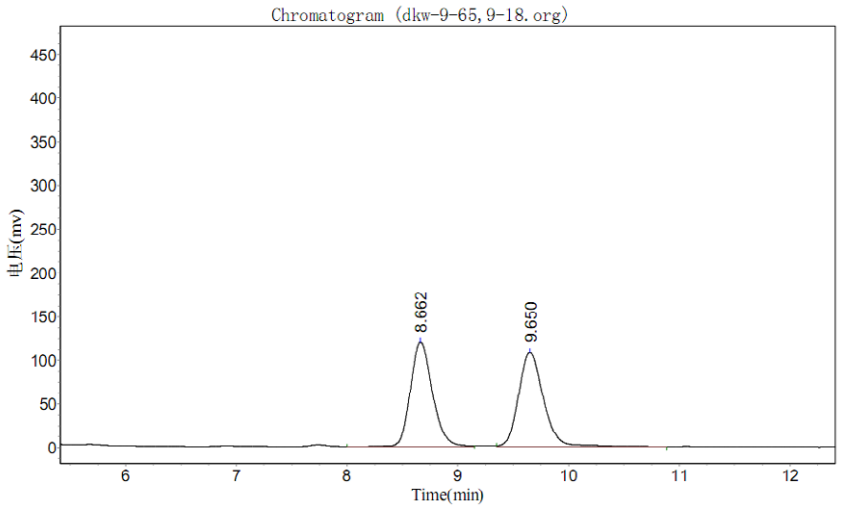


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.725	539808.250	9480611.000	96.1169
2		12.828	16627.121	383017.219	3.8831
Total			556435.371	9863628.219	100.0000

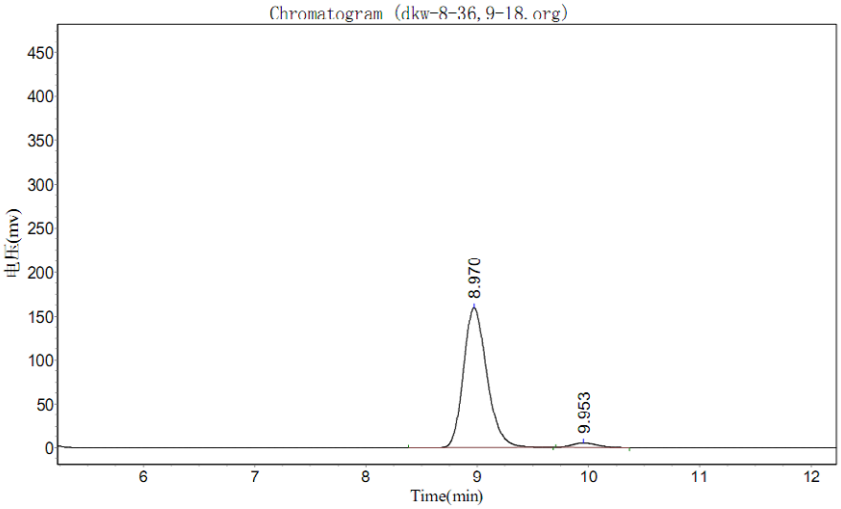
(*S*)-2-(3-chlorophenyl)propanoic acid, (*S*)-2d





Results

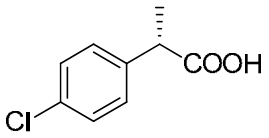
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.662	119663.406	1657076.625	49.4440
2		9.650	107596.430	1694345.875	50.5560
Total			227259.836	3351422.500	100.0000

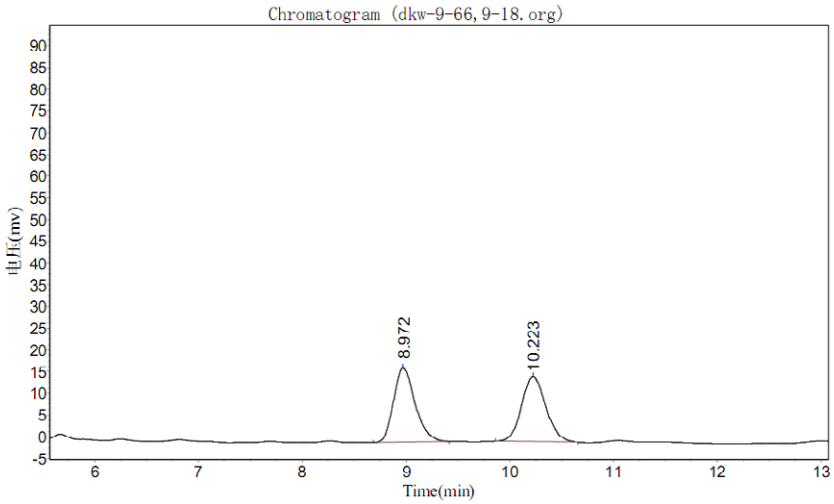


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.970	158948.766	2326839.500	96.7260
2		9.953	5169.000	78758.898	3.2740
Total			164117.766	2405598.398	100.0000

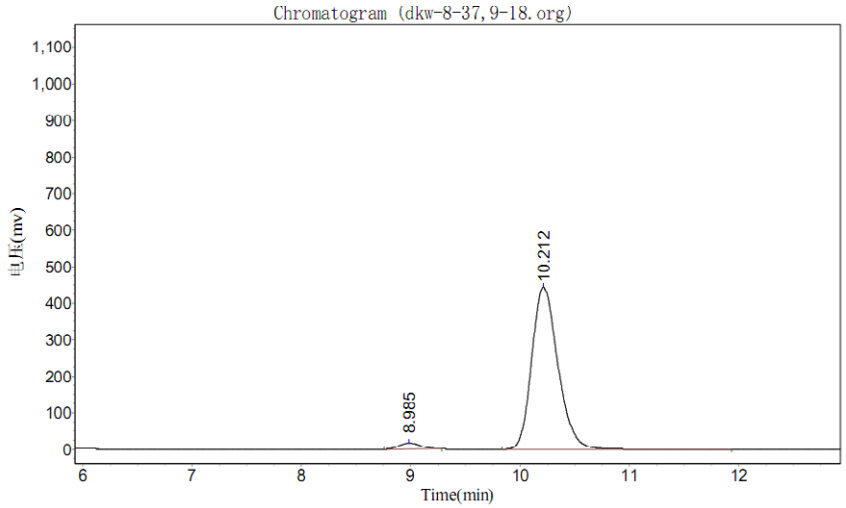
(*S*)-2-(4-chlorophenyl)propanoic acid, (*S*)-2e





Results

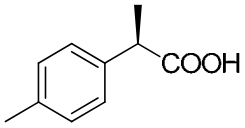
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.972	17109.916	248910.453	50.2647
2		10.223	15067.720	246289.297	49.7353
Total			32177.636	495199.750	100.0000

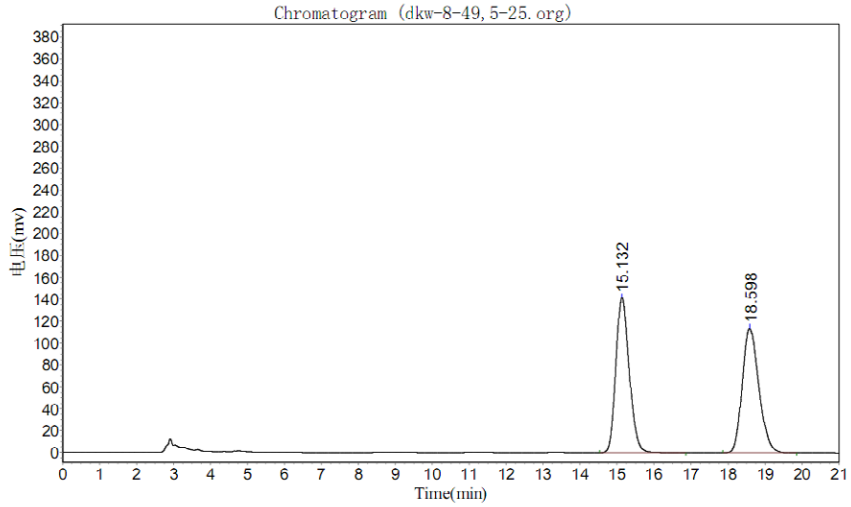


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.985	16402.199	219826.266	2.9053
2		10.212	443003.938	7346679.500	97.0947
Total			459406.137	7566505.766	100.0000

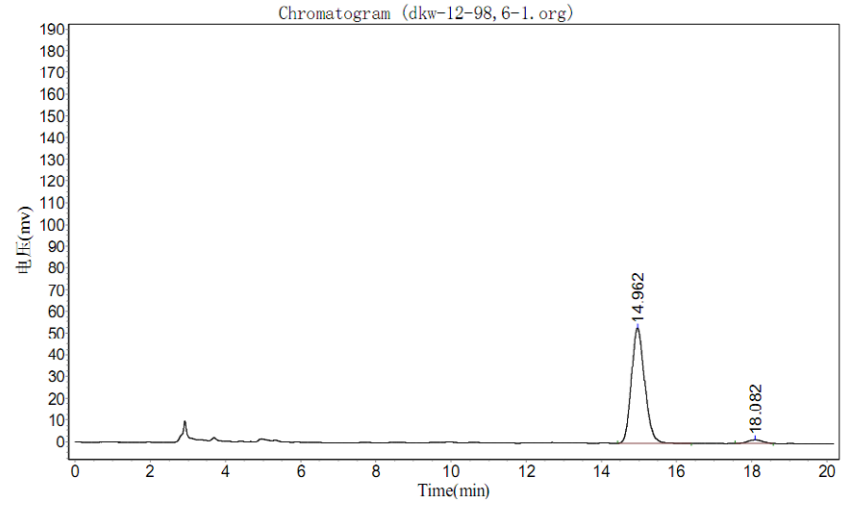
(*R*)-2-(p-tolyl)propanoic acid, (*R*)-2f





Results

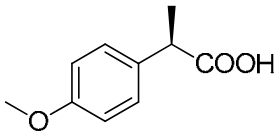
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.132	141241.016	3626264.250	50.0355
2		18.598	114250.211	3621114.500	49.9645
Total			255491.227	7247378.750	100.0000

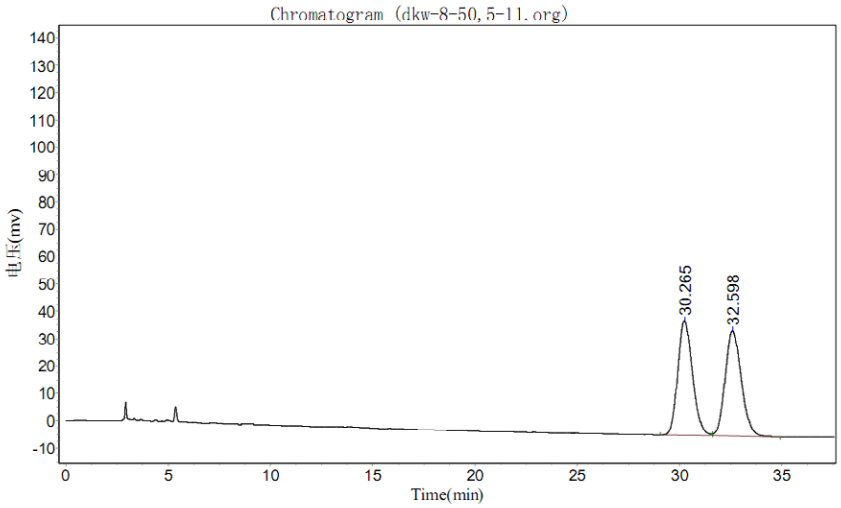


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.962	52918.617	1302766.875	96.6452
2		18.082	1626.591	45222.000	3.3548
Total			54545.208	1347988.875	100.0000

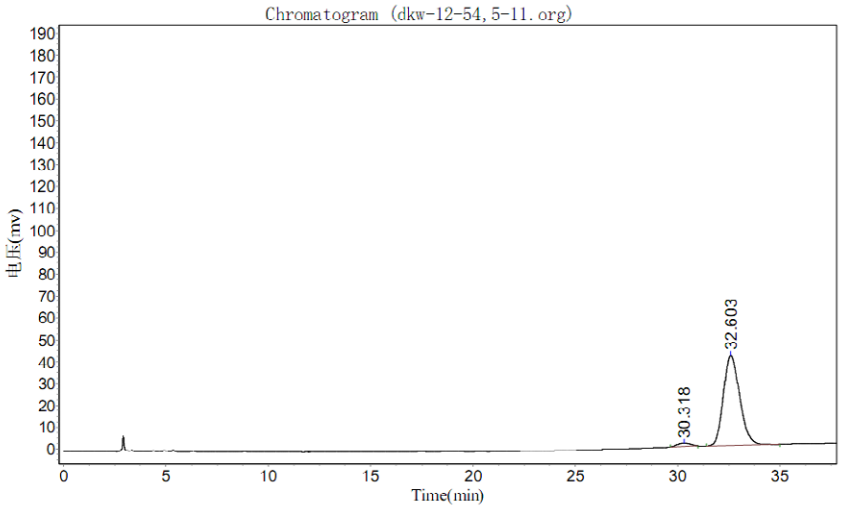
(*R*)-2-(4-methoxyphenyl)propanoic acid, (*R*)-2g





Results

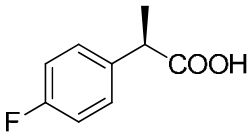
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.265	41936.727	2112804.500	49.8783
2		32.598	38423.363	2123119.000	50.1217
Total			80360.090	4235923.500	100.0000

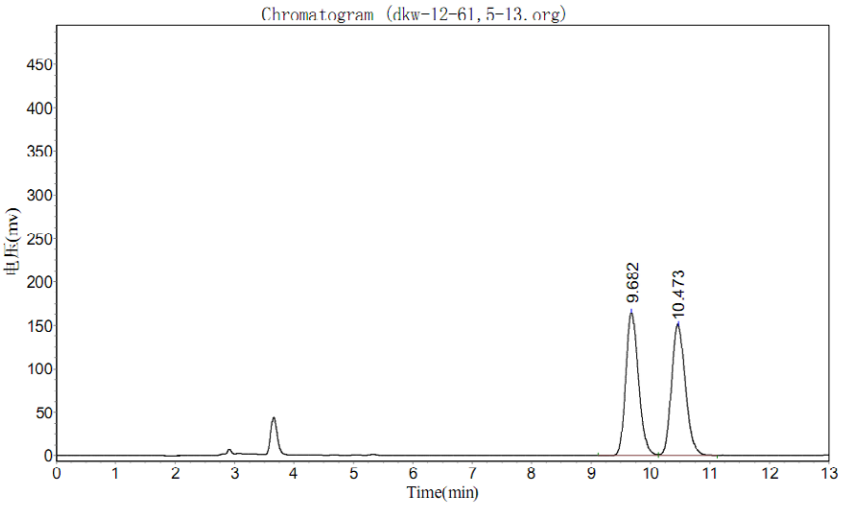


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		30.318	1603.556	68892.195	2.9355
2		32.603	41104.367	2277969.250	97.0645
Total			42707.923	2346861.445	100.0000

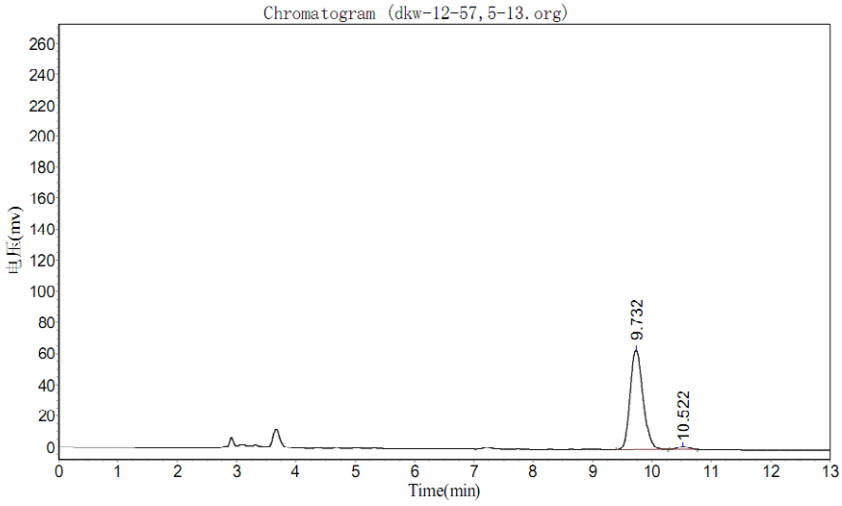
(*R*)-2-(4-fluorophenyl)propanoic acid, (*R*)-2h





Results

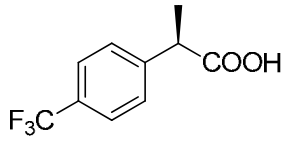
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.682	164413.891	2459170.500	50.0033
2		10.473	150552.234	2458848.000	49.9967
Total			314966.125	4918018.500	100.0000

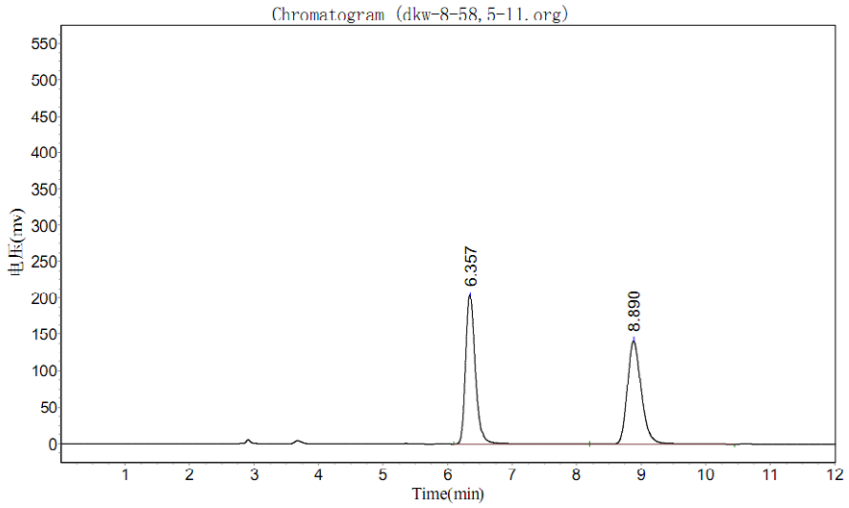


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.732	64169.605	968465.000	97.1963
2		10.522	1972.196	27936.197	2.8037
Total			66141.801	996401.197	100.0000

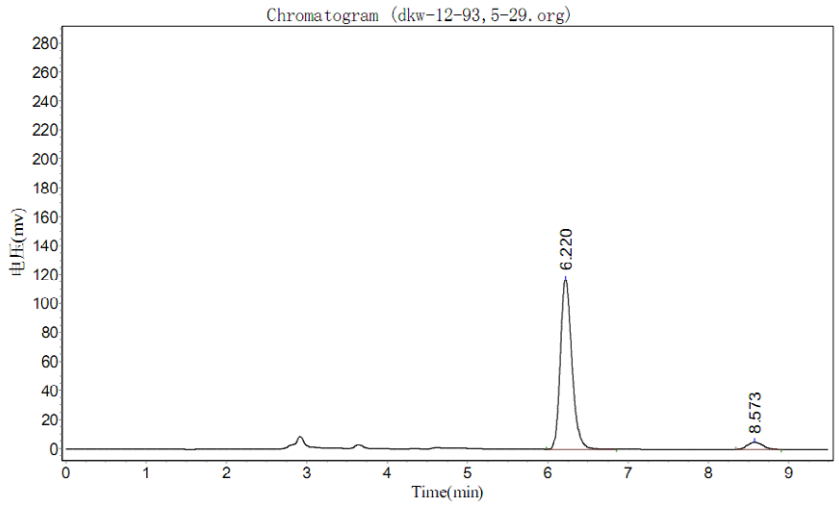
(*R*)-2-(4-(trifluoromethyl)phenyl)propanoic acid, (*R*)-2i





Results

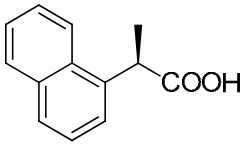
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.357	204006.750	2148618.000	50.0025
2		8.890	141333.203	2148401.500	49.9975
Total			345339.953	4297019.500	100.0000

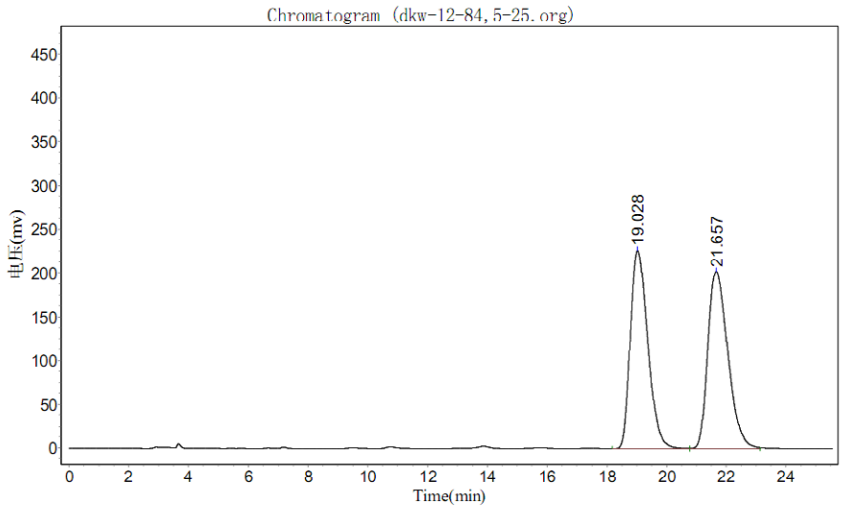


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.220	116915.781	1166676.875	94.9590
2		8.573	4574.779	61933.898	5.0410
Total			121490.561	1228610.773	100.0000

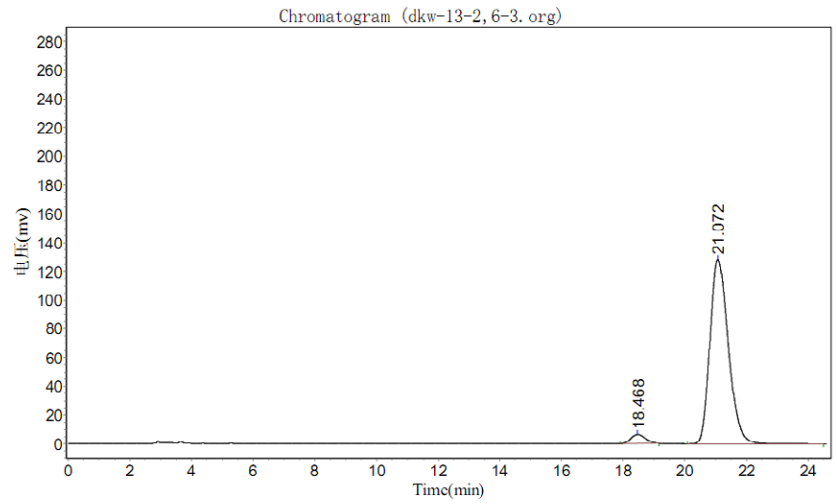
(*R*)-2-(naphthalen-1-yl)propanoic acid, (*R*)-2j





Results

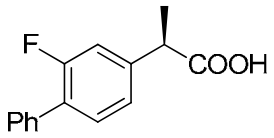
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.028	226434.016	9266554.000	49.3300
2		21.657	202461.375	9473686.000	50.4327
Total			431137.193	18784820.338	100.0000

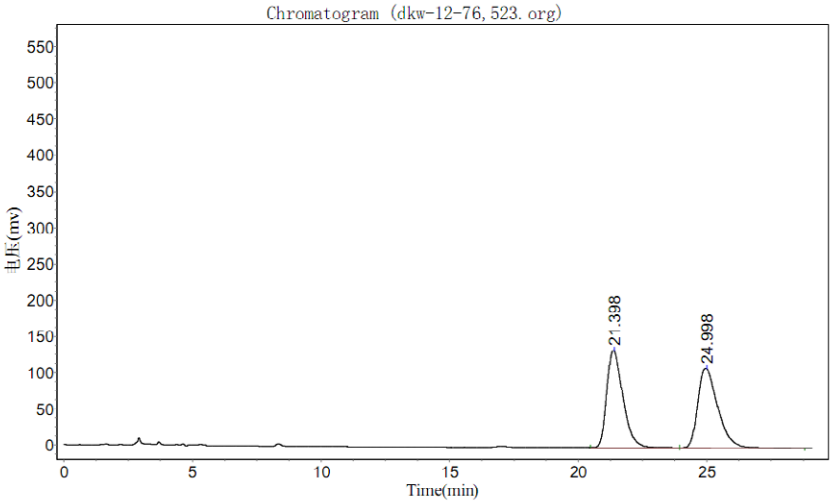


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.468	6584.862	218051.203	3.9068
2		21.072	128515.852	5363323.000	96.0932
Total			135100.714	5581374.203	100.0000

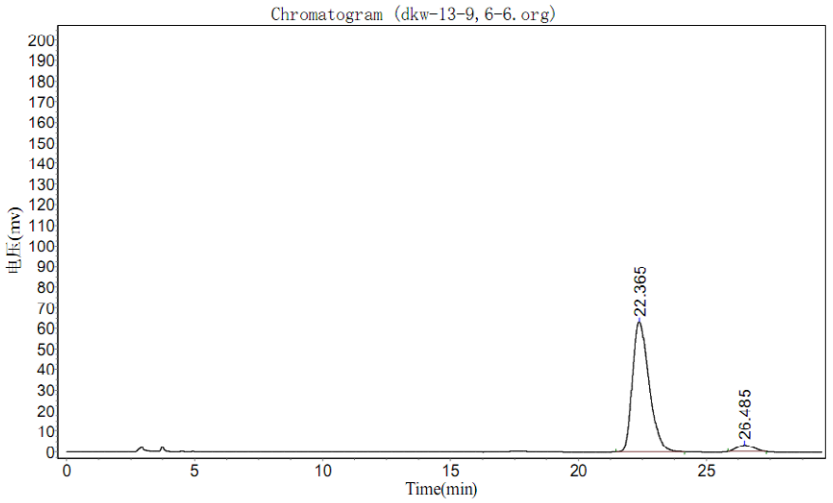
(*R*)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid, (*R*)-2k





Results

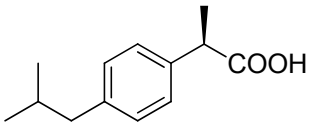
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.398	133574.063	5844193.500	49.8785
2		24.998	109209.172	5872677.000	50.1216
Total			242783.234	11716870.500	100.0000

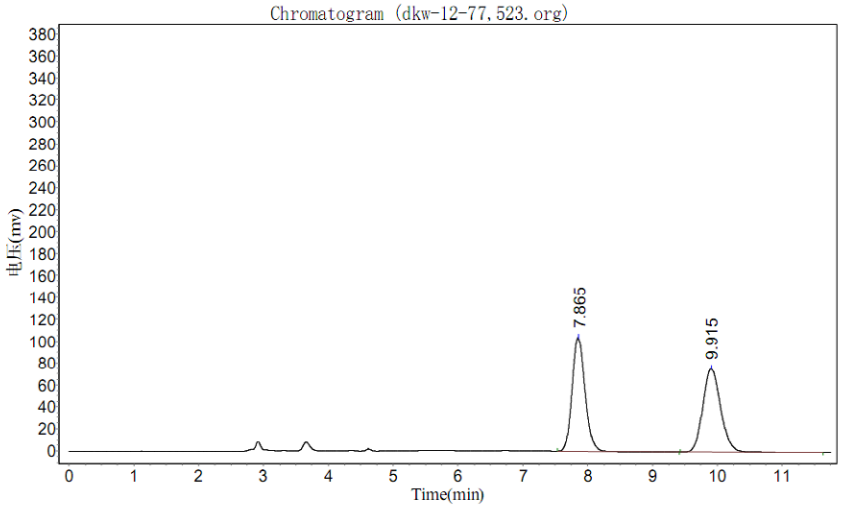


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.365	63215.758	2858862.250	95.1023
2		26.485	3163.312	147227.641	4.8976
Total			66379.069	3006089.891	100.0000

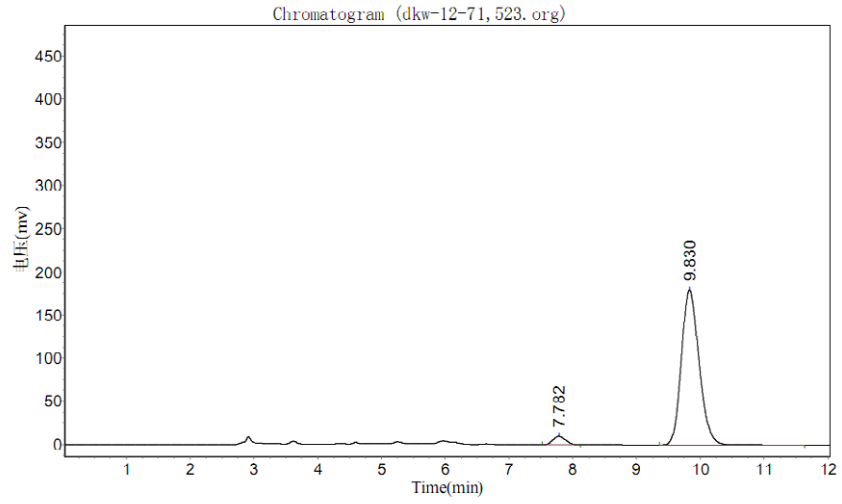
(*R*)-2-(4-isobutylphenyl)propanoic acid, (*R*)-2l





Results

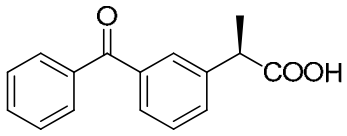
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.865	104082.680	1487305.375	50.3919
2		9.915	75928.203	1464170.625	49.6081
Total			180010.883	2951476.000	100.0000

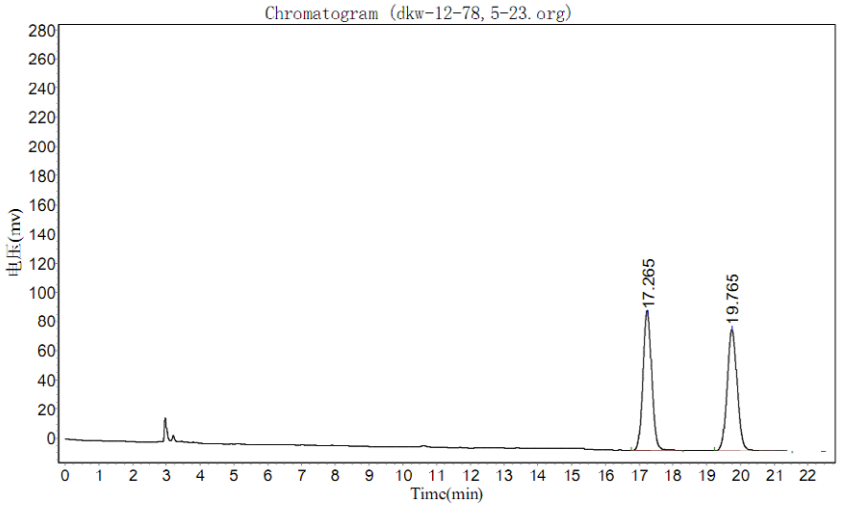


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.782	9286.572	123712.000	3.4615
2		9.830	179109.766	3450255.500	96.5385
Total			188396.338	3573967.500	100.0000

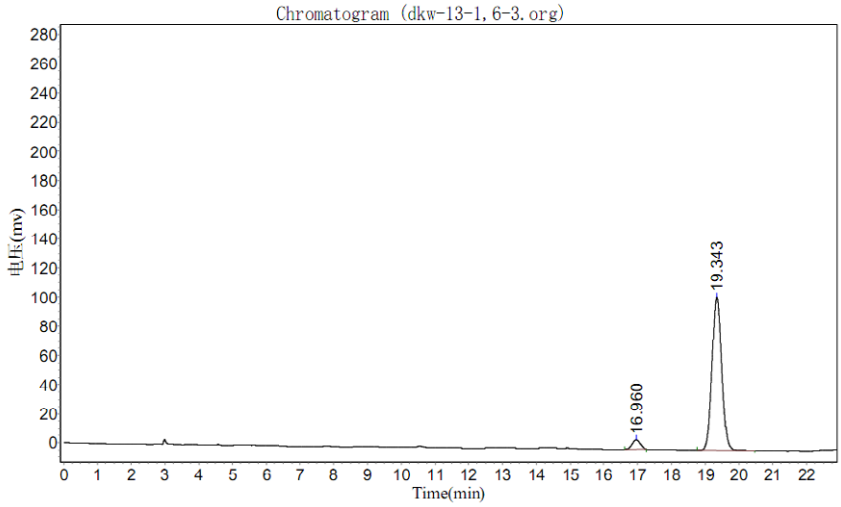
(*R*)-2-(3-benzoylphenyl)propanoic acid, (*R*)-2m





Results

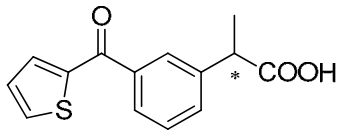
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.265	94544.695	1705063.875	49.8688
2		19.765	82633.188	1714033.750	50.1312
Total			177177.883	3419097.625	100.0000

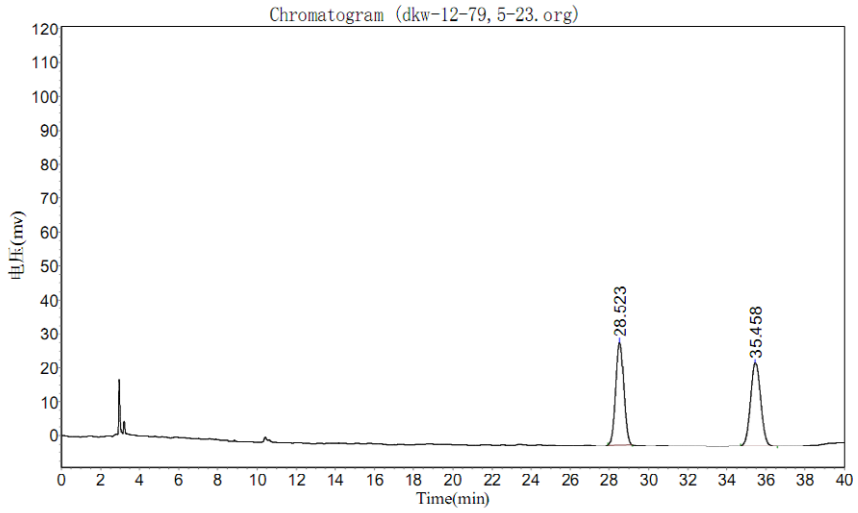


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.960	6362.972	104134.953	4.7657
2		19.343	104819.734	2080942.875	95.2343
Total			111182.706	2185077.828	100.0000

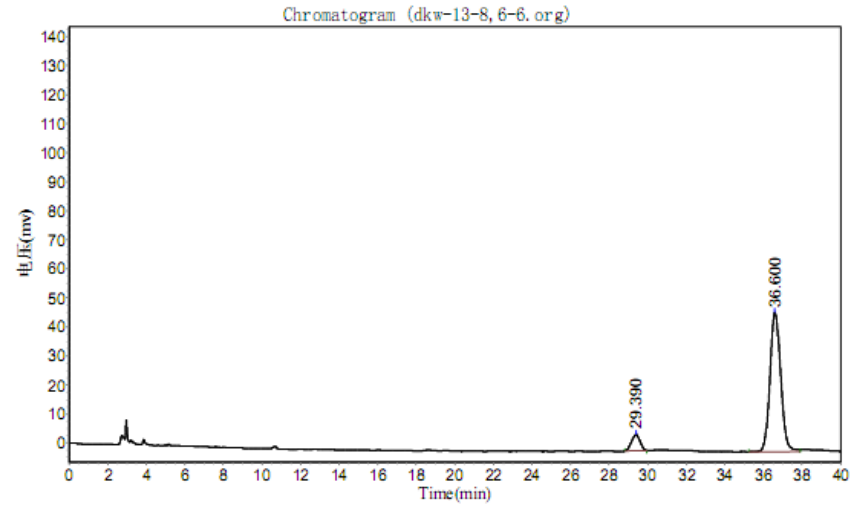
(-)-2-(3-(thiophene-2-carbonyl)phenyl)propanoic acid, (-)-2n





Results

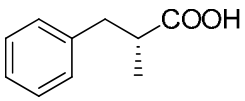
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		28.523	30065.355	861062.500	49.7661
2		35.458	24286.906	869154.813	50.2339
Total			54352.262	1730217.313	100.0000

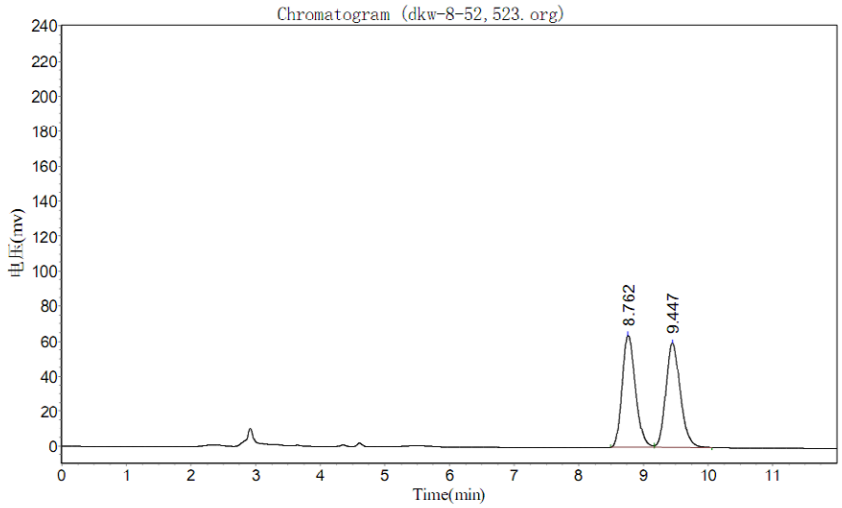


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		29.390	5466.836	167210.594	8.1980
2		36.600	47954.594	1872447.625	91.8020
Total			53421.430	2039658.219	100.0000

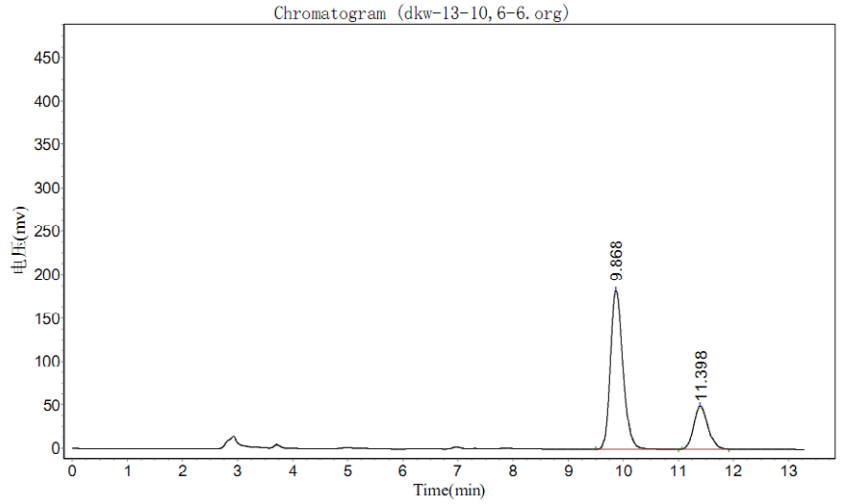
(*R*)-2-methyl-3-phenylpropanoic acid, (*R*)-2o





Results

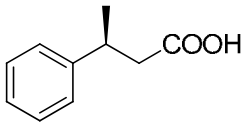
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.762	63746.801	912347.688	49.6116
2		9.447	59394.285	926632.063	50.3884
Total			123141.086	1838979.750	100.0000

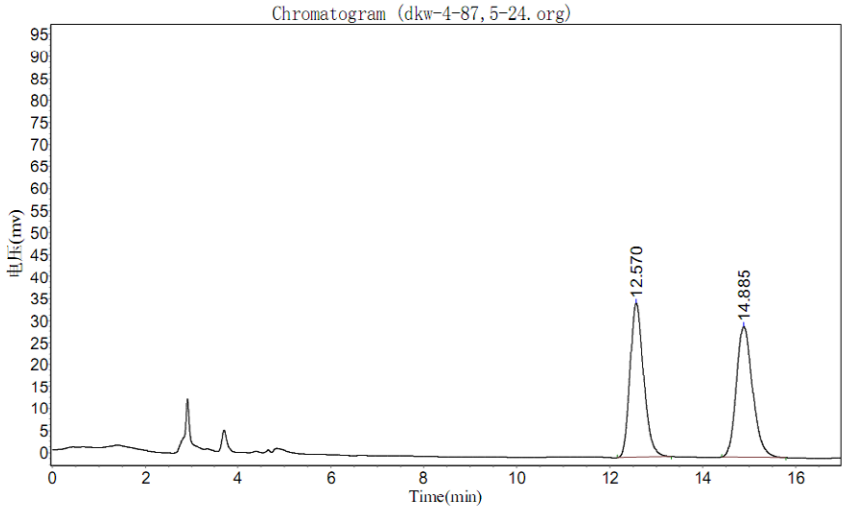


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.868	182216.688	2870312.750	76.8619
2		11.398	48520.980	864064.625	23.1381
Total			230737.668	3734377.375	100.0000

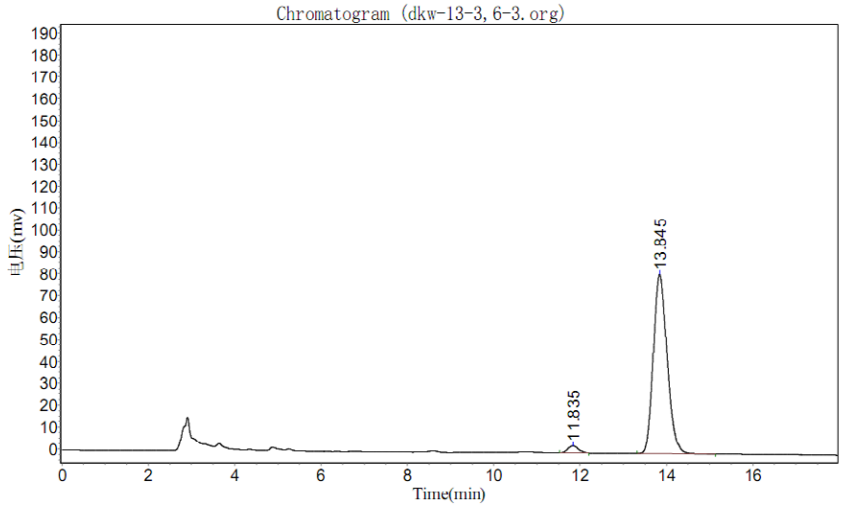
(*S*)-3-phenylbutanoic acid, (*S*)-4a





Results

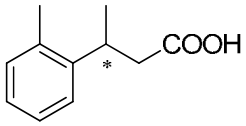
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.570	34967.449	714260.688	49.7565
2		14.885	29732.973	721251.250	50.2435
Total			64700.422	1435511.938	100.0000

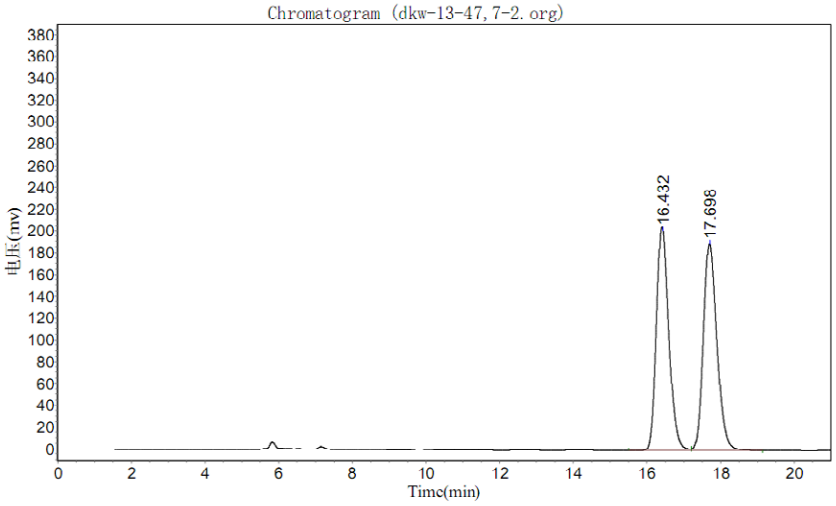


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.835	3166.210	55892.297	2.9763
2		13.845	81843.641	1822028.000	97.0237
Total			85009.850	1877920.297	100.0000

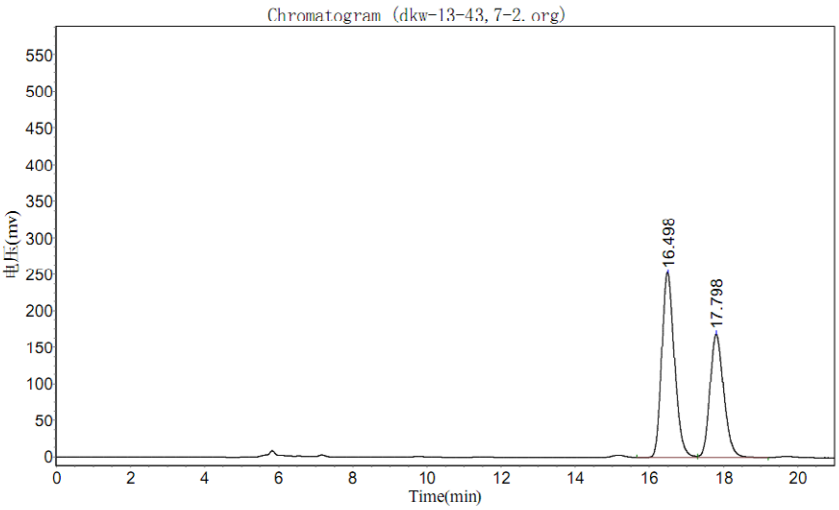
(+)3-(o-tolyl)butanoic acid, (+)-4b





Results

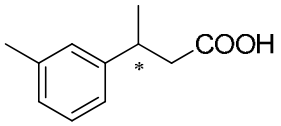
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.432	204524.172	4834319.500	49.7737
2		17.698	188873.797	4878280.500	50.2263
Total			393397.969	9712600.000	100.0000

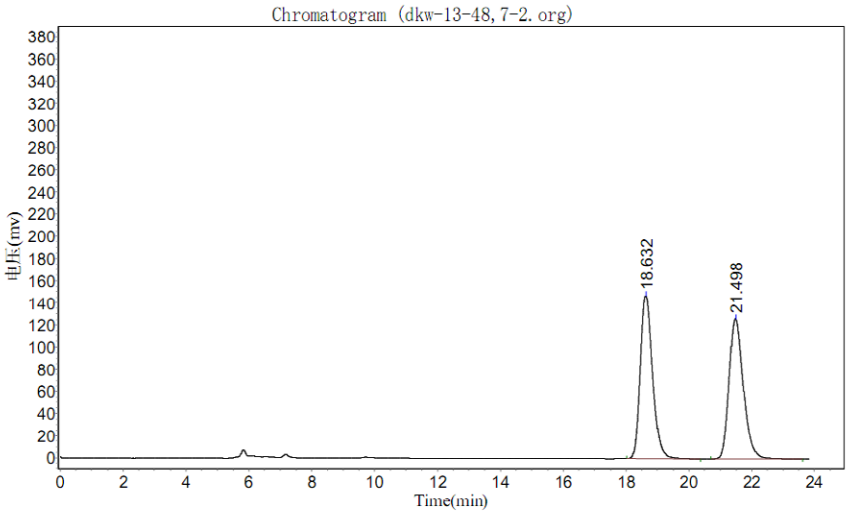


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.498	252722.031	6078966.000	57.9276
2		17.798	167961.781	4415101.000	42.0724
Total			420683.813	10494067.000	100.0000

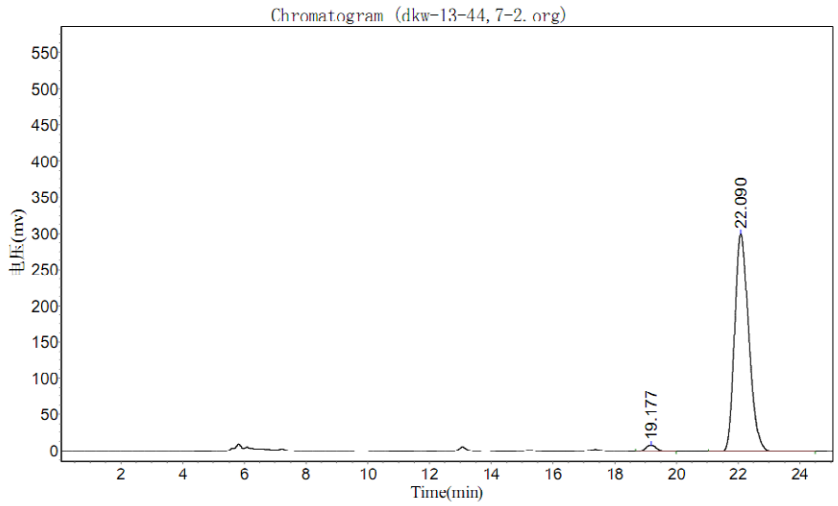
(+)-3-(m-tolyl)butanoic acid, (+)-4c





Results

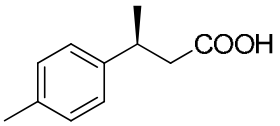
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.632	146418.938	3989291.500	49.8286
2		21.498	126560.656	4016732.500	50.1714
Total			272979.594	8006024.000	100.0000

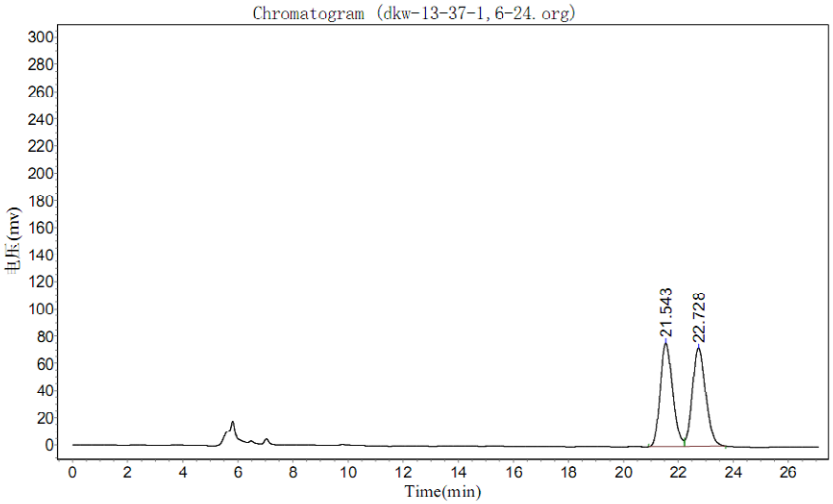


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.177	8294.457	216198.906	2.2060
2		22.090	300759.063	9584183.000	97.7940
Total			309053.520	9800381.906	100.0000

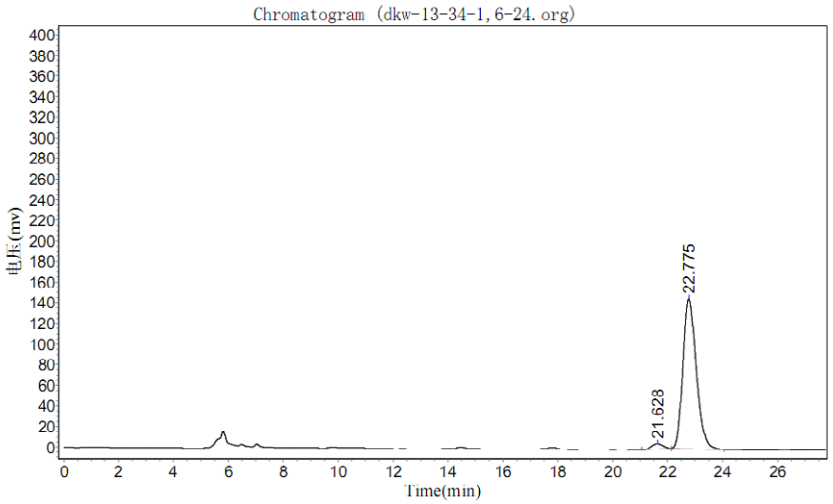
(*S*)-3-(p-tolyl)butanoic acid, (*S*)-4d





Results

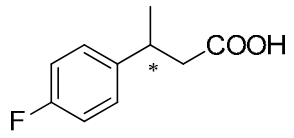
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.543	76259.813	2393095.750	49.6694
2		22.728	72478.344	2424951.250	50.3306
Total			148738.156	4818047.000	100.0000

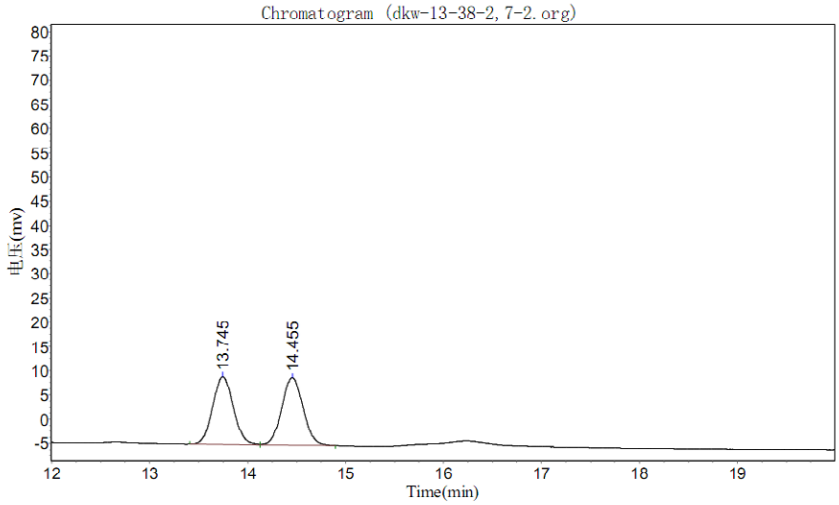


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.628	5009.770	138262.297	2.7379
2		22.775	145418.672	4911665.000	97.2621
Total			150428.442	5049927.297	100.0000

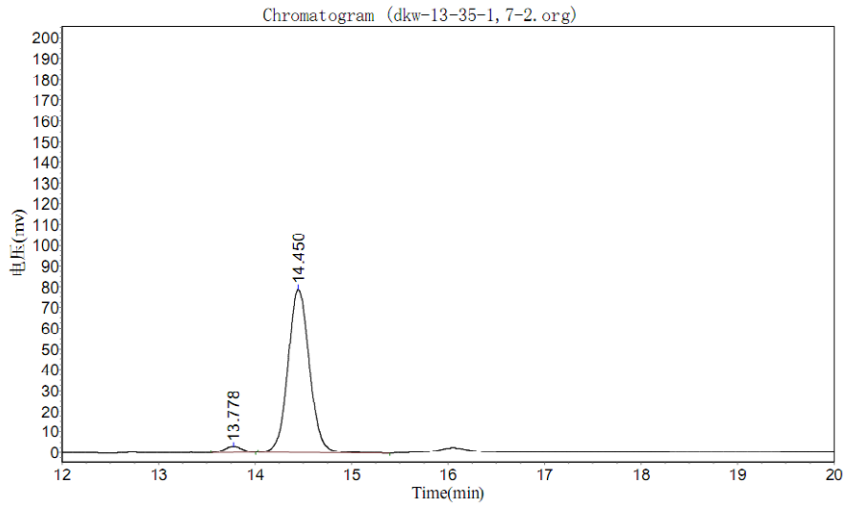
(+)-3-(4-fluorophenyl)butanoic acid, (+)-4e





Results

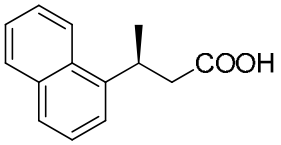
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.745	14025.061	205466.734	49.3502
2		14.455	13955.408	210877.891	50.6498
Total			27980.469	416344.625	100.0000

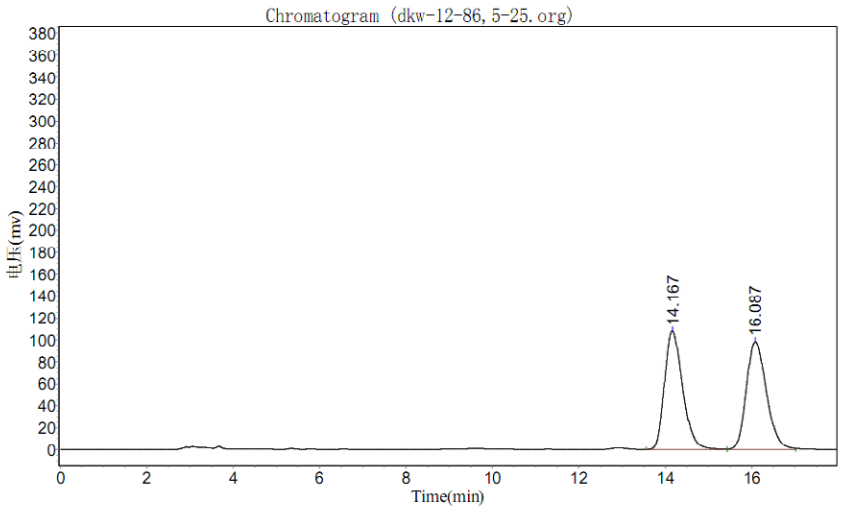


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.778	2883.004	37225.152	2.9705
2		14.450	78898.078	1215950.500	97.0295
Total			81781.082	1253175.652	100.0000

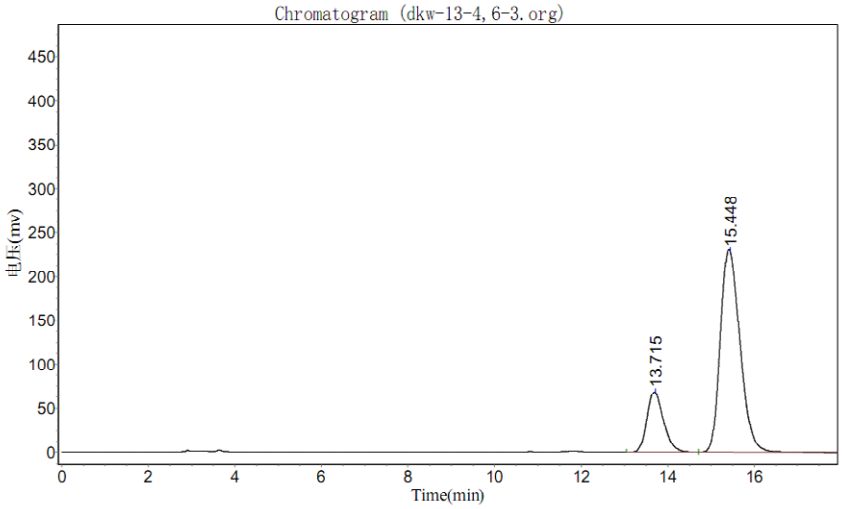
(*S*)-3-(naphthalen-1-yl)butanoic acid, (*S*)-4f





Results

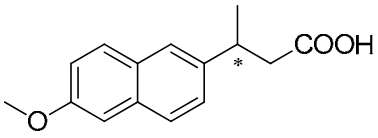
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.167	108433.422	3173198.750	49.6832
2		16.087	98865.141	3199496.250	50.0950
Total			208203.734	6386860.389	100.0000

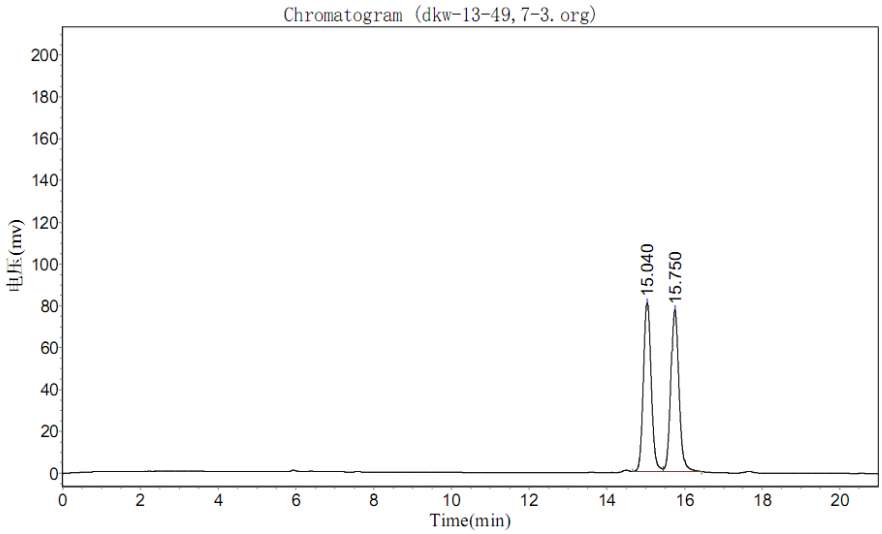


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.715	68565.516	1845085.750	20.1582
2		15.448	229972.922	7307952.000	79.8418
Total			298538.438	9153037.750	100.0000

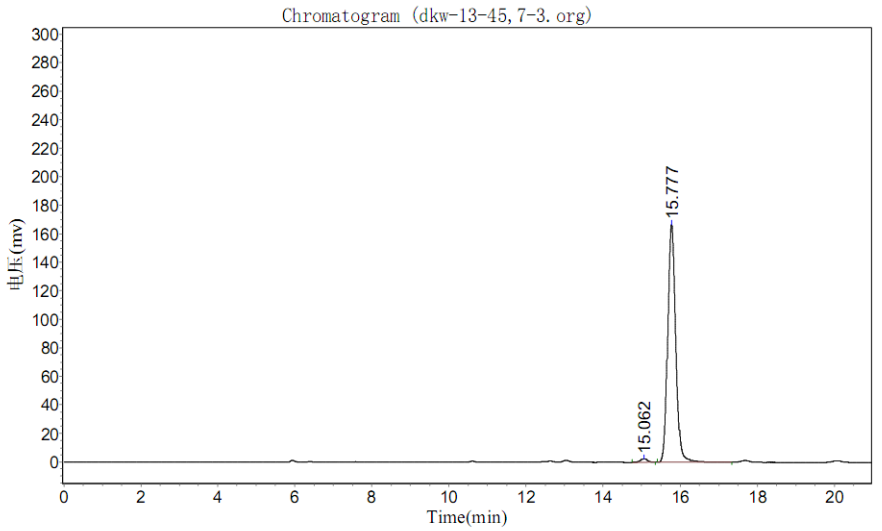
(+)-3-(6-methoxynaphthalen-2-yl)butanoic acid, (+)-4g





Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.040	80657.586	1117967.250	49.6556
2		15.750	77405.422	1133475.750	50.3444
Total			158063.008	2251443.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.062	2082.819	28628.451	1.1735
2		15.777	166699.828	2411003.750	98.8265
Total			168782.647	2439632.201	100.0000