One-pot combination of enzyme and Pd nanoparticle catalysis for the synthesis of enantiomerically pure 1,2-amino alcohols

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Electronic Supplementary Information (ESI)

Contents:

Supplementary data

Complete results of ADH screening

The complete results of the screening of ADHs for activity and stereoselectivity in the reduction of azido ketone **2a** are given in Suppl. Tables 1–4. Enzymes selected for further experiments are highlighted in grey.

Enzyme	Cofactor[a]	Conv.[b] [%]	Act.[c] [U/mg]	ee[d] [%]
ADH-A (from *R. ruber*)	NADH	11.8	0.49	>99 (*R*)
*Tb*ADH (from *T. brockii*)	NADPH	<1.0	<0.04	*nd*[e]
*Lk*ADH (from *L. kefir*)	NADPH	1.6	0.07	98 (*S*)
*Lb*ADH (from *L. brevis*)	NADPH	2.0	0.08	>99 (*S*)

Suppl. Table 1. Activity and stereoselectivity of bacterial ADHs in the reduction of 2-azidoacetophenone **2a**. Reaction conditions: 50 mM **2a**, 0.1 mM $NAD(P)^+$, 0.1 mg/mL ADH preparation, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 2 h. [a] Preferred cofactor according to literature or supplier's information. [b] Conversion determined by GC–FID analysis. [c] Apparent activity (μmol product formed per minute and per mg enzyme preparation) as calculated from conversion. [d] Enantiomeric excess determined by chiral-phase GC–FID analysis. [e] *nd* = not determined.

Enzyme	Cofactor[a]	Conv.[b] [%]	Act.[c] [U/mg]	ee[d] [%]
KRED-NADH-101	NADH	1.3	0.06	>99 (*R*)
KRED-NADH-110	NADH	57.7	2.40	>99 (*S*)
KRED-101	NADPH	–	–	–
KRED-119	NADPH	–	–	–
KRED-130	NADPH	–	–	–
KRED-P1-A04	NADPH	52.0	2.16	>99 (*S*)
KRED-P1-B02	NADPH	9.7	0.40	26 (*S*)
KRED-P1-B05	NADPH	–	–	–
KRED-P1-B10	NADPH	4.2	0.18	71 (*S*)
KRED-P1-B12	NADPH	2.2	0.09	93 (*S*)
KRED-P1-C01	NADPH	46.2	1.92	60 (*S*)
KRED-P1-H08	NADPH	43.2	1.80	83 (*R*)
KRED-P1-H10	NADPH	25.9	1.08	93 (*S*)
KRED-P2-B02	NADPH	28.5	1.19	81 (*R*)
KRED-P2-C02	NADPH	16.1	0.67	88 (*R*)
KRED-P2-C11	NADPH	48.7	2.03	46 (*S*)
KRED-P2-D03	NADPH	31.5	1.31	63 (*S*)
KRED-P2-D11	NADPH	44.5	1.85	12 (*S*)
KRED-P2-D12	NADPH	4.8	0.20	80 (*S*)
KRED-P2-G03	NADPH	84.9	3.54	96 (*S*)
KRED-P2-H07	NADPH	53.0	2.21	96 (*S*)
KRED-P3-B03	NADPH	4.6	0.19	>99 (*R*)
KRED-P3-G09	NADPH	13.2	0.55	88 (*R*)
KRED-P3-H12	NADPH	32.4	1.35	90 (*R*)

Suppl. Table 2. Activity and stereoselectivity of *Codexis* ADHs in the reduction of 2-azidoacetophenone **2a**. Reaction conditions: 50 mM **2a**, 0.1 mM $NAD(P)^+$, 0.1 mg/mL ADH preparation, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 2 h. [a] Preferred cofactor according to supplier's information. [b] Conversion determined by GC–FID analysis. [c] Apparent activity (μmol product formed per minute and per mg enzyme preparation) as calculated from conversion. [d] Enantiomeric excess determined by chiral GC–FID analysis.

Enzyme	Cofactor[a]	Conv.[b] [%]	Act.[c] [U/mg]	ee[d] [%]
CRED-A101	NADPH	–	–	–
CRED-A201	NADPH	–	–	–
CRED-A301	NADPH	–	–	–
CRED-A401	NADPH	–	–	–
CRED-A501	NADPH	–	–	–
CRED-A601	NADPH	14.0	0.58	>99 (*S*)
CRED-A701	NADPH	–	–	–
CRED-A801	NADPH	–	–	–
CRED-A121	NADPH	–	–	–
CRED-A131	NADH	–	–	–
CRED-A141	NADPH	–	–	–
CRED-A151	NADH	–	–	–
CRED-A161	NADH	0.8	0.03	>99 (*S*)
CRED-A171	NADH	–	–	–
CRED-A181	NADPH	–	–	–
CRED-A191	NADH	–	–	–
CRED-A211	NADPH	–	–	–
CRED-A221	NADH	–	–	–
CRED-A231	NADPH	–	–	–
CRED-A241	NADPH	–	–	–
CRED-A251	NADH	–	–	–
CRED-A261	NADPH	–	–	–
CRED-A271	NADPH	–	–	–
CRED-A281	NADPH	–	–	–
CRED-A321	NADPH	–	–	–
CRED-A331	NADPH	–	–	–
CRED-A361	NADPH	–	–	–
CRED-A381	NADPH	–	–	–
CRED-A391	NADPH	–	–	–
CRED-N501	NADPH	–	–	–
CRED-N701	NADPH	–	–	–
CRED-N121	NADPH	–	–	–
CRED-N131	NADPH	–	–	–
CRED-N151	NADPH	–	–	–
CRED-A411	NADH	–	–	–
CRED-A421	NADH	–	–	–
CRED-A431	NADPH	–	–	–
CRED-A441	NADH	–	–	–
CRED-A451	NADH	–	–	–
CRED-A461	NADH	–	–	–
CRED-A471	NADH	–	–	–
CRED-A481	NADH	–	–	–
CRED-A491	NADH	–	–	–
CRED-A511	NADH	–	–	–

Suppl. Table 3. Activity and stereoselectivity of *Almac* ADHs in the reduction of 2-azidoacetophenone **2a**. Reaction conditions: 50 mM **2a**, 0.1 mM $NAD(P)^+$, 0.1 mg/mL ADH preparation, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 2 h. [a] Preferred cofactor according to supplier's information. [b] Conversion determined by GC–FID analysis. [c] Apparent activity (μmol product formed per minute and per mg enzyme preparation) as calculated from conversion. [d] Enantiomeric excess determined by chiral GC–FID analysis.

Enzyme	Cofactor[a]	Conv.[b] [%]	Act.[c] [U/mg]	ee[d] [%]
evo-1.1.010	NADH	–	–	–
evo-1.1-020	NADH	–	–	–
evo-1.1.030	NADH	6.5	0.27	>99 (*R*)
evo-1.1.040	NADH	–	–	–
evo-1.1.130	NADH	–	–	–
evo-1.1.140	NADH	–	–	–
evo-1.1.190	NADPH	–	–	–
evo-1.1.200	NADH	73.2	3.05	>99 (*S*)
evo-1.1.250	NADPH	–	–	–
evo-1.1.260	NADPH	–	–	–
evo-1.1.270	NADPH	19.7	0.82	>99 (*S*)

Suppl. Table 4. Activity and stereoselectivity of *evocatal* ADHs in the reduction of 2-azidoacetophenone **2a**. Reaction conditions: 50 mM **2a**, 0.1 mM NAD(P)$^+$, 0.1 mg/mL ADH preparation, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 2 h. [a] Preferred cofactor according to supplier's information. [b] Conversion determined by GC–FID analysis. [c] Apparent activity (μmol product formed per minute and per mg enzyme preparation) as calculated from conversion. [d] Enantiomeric excess determined by chiral GC–FID analysis.

Activity assay of bacterial ADHs

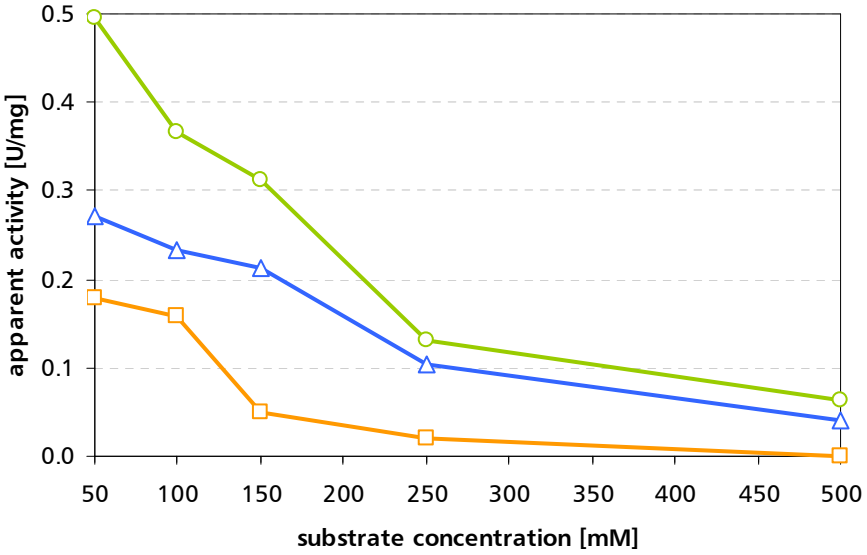
The unexpectedly low conversions obtained with *Tb*ADH and *Lb*ADH in the screening prompted us to verify their activity under the reaction conditions. The activity assay was performed spectrophotometrically, following the formation of NAD(P)H from NAD(P)$^+$ and 2-propanol *via* the absorbance change at 340 nm. Since the type of buffer can have an influence on enzyme activity, the assay was performed in two different buffer systems (potassium phosphate or Tris-HCl; both 100 mM, pH 7.0, containing 1 mM $MgSO_4$ as additive). Reactions with ADH-A and KRED-NADH-110 (in phosphate buffer only) were performed for comparison. As shown in Suppl. Table 5, all enzymes showed 2-propanol oxidation activity. *Lb*ADH was approx. two times more active in Tris-HCl buffer than in phosphate buffer. Interestingly, KRED-NADH-110 showed a lower activity in this assay than in the screening for reduction of **2a**, which might be explained by the different reaction temperatures (20 °C in the photometric assay, 30 °C in the screening).

Enzyme	Buffer	Activity [U/mg]
ADH-A	phosphate	2.0 ± 0.3
KRED-NADH-110	phosphate	1.3 ± 0.1
*Lb*ADH	phosphate	0.18 ± 0.01
*Lb*ADH	Tris-HCl	0.34 ± 0.05
*Tb*ADH	phosphate	0.51 ± 0.04
*Tb*ADH	Tris-HCl[a]	0.50 ± 0.04

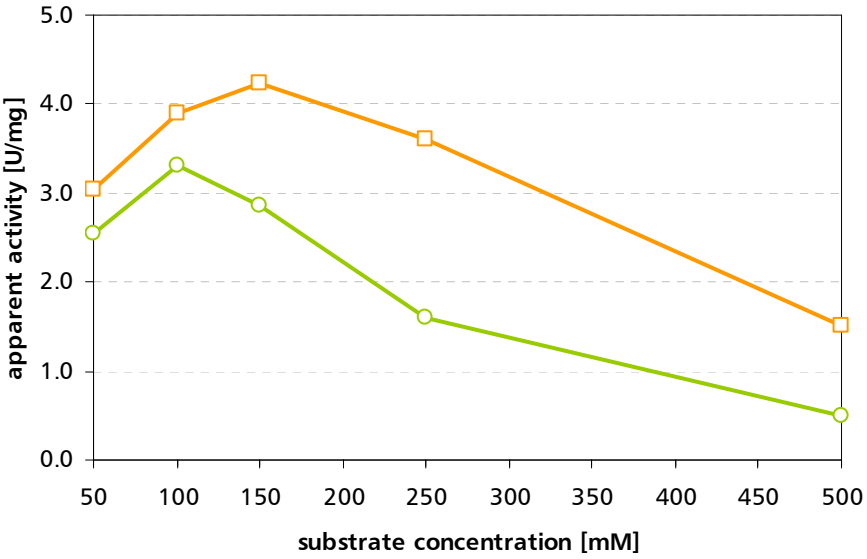
Suppl. Table 5. Activity of selected ADHs in the oxidation of 2-propanol, as quantified *via* NAD(P)H fromation. Reaction conditions: 0.1 mM NAD(P)$^+$, 0.1 mg/mL ADH preparation, 5% (v/v) 2-propanol, 0.5 mL buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 20 °C. [a] A low background activity (0.06 U/mg) was observed in this setup, which is probably due to oxidation of Tris by *Tb*ADH.

Substrate concentration–activity profiles of selected ADHs

The substrate concentration–activity profiles (determined from the conversion after 2 h) of selected ADHs for substrate **2a** are shown in Suppl. Fig. 1 (Prelog-selective enzymes) and Suppl. Fig. 2 (anti-Prelog-selective enzymes).



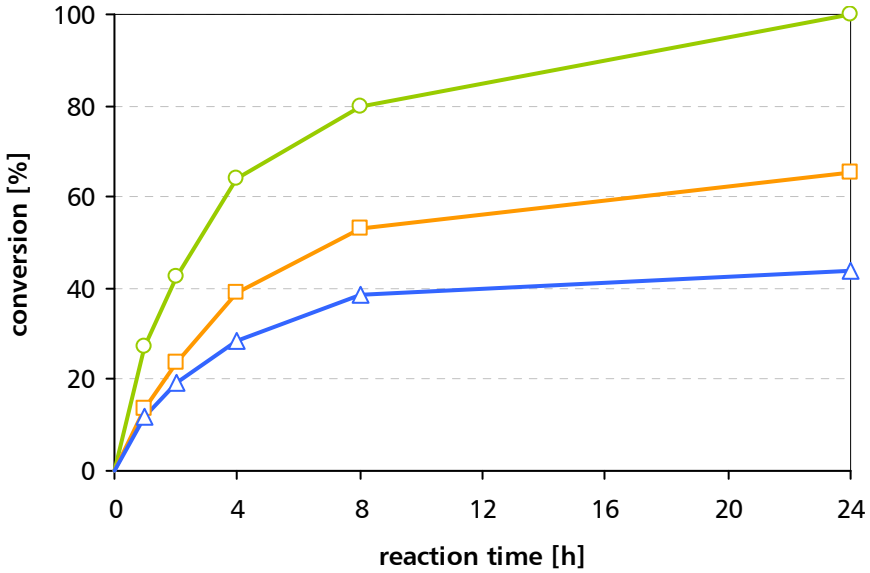
Suppl. Fig. 1. Substrate concentration–activity profiles of selected Prelog-selective alcohol dehydrogenases for **2a** as substrate: ADH-A (green circles), KRED-P3-B03 (orange squares), evo-1.1.030 (blue triangles). Reaction conditions: 50–500 mM **2a**, 0.1 mM NAD(P)$^+$, 0.1 mg/mL ADH preparation, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 2 h.



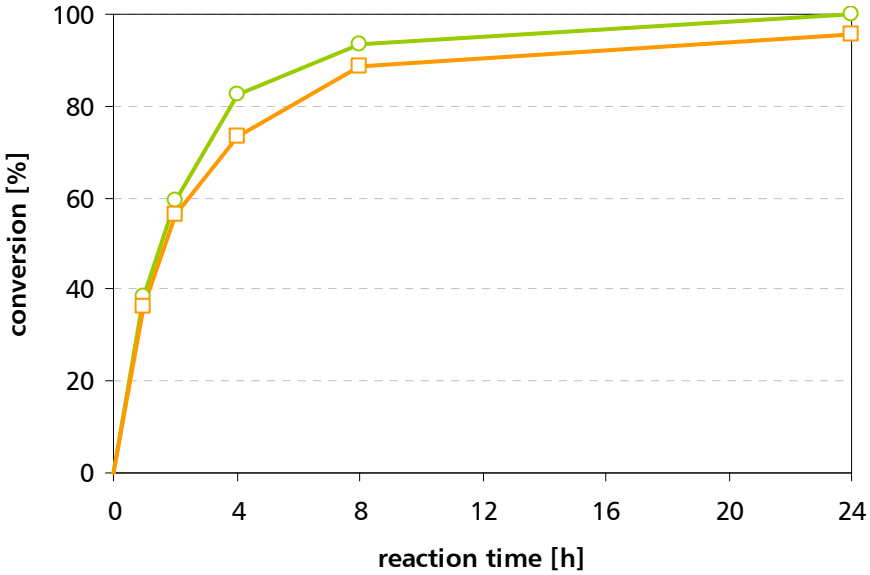
Suppl. Fig. 2. Substrate concentration–activity profiles of selected anti-Prelog-selective alcohol dehydrogenases for **2a** as substrate: KRED-NADH-110 (green circles), evo-1.1.200 (orange squares). Reaction conditions: 50–500 mM **2a**, 0.1 mg/mL ADH preparation, 0.1 mM NAD(P)$^+$, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 2 h.

Time-course experiments using selected ADHs

The operational stability of selected ADHs was assessed from the time course of the reduction of **2a** (100 mM, 16 g/L), using 1.5 mg/mL of the Prelog-selective and 0.2 mg/mL of the generally more active anti-Prelog-selective enzymes. As shown in Suppl. Fig. 3 (Prelog-selective enzymes) and Suppl. Fig. 4 (anti-Prelog-selective enzymes), ADH-A and KRED-NADH-110 performed best under the investigated conditions, allowing complete conversion of **2a** into (*R*)-**3a** and (*S*)-**3a**, respectively, within 24 h.



Suppl. Fig. 3. Time course of the reduction of **2a** to **3a** by selected Prelog-selective alcohol dehydrogenases: ADH-A (green circles), KRED-P3-B03 (orange squares), evo-1.1.030 (blue triangles). Reaction conditions: 100 mM **2a**, 1.5 mg/mL ADH preparation, 0.1 mM $NAD(P)^+$, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 1–24 h.



Suppl. Fig. 4. Time course of the reduction of **2a** to **3a** by selected anti-Prelog-selective alcohol dehydrogenases: KRED-NADH-110 (green circles), evo-1.1.200 (orange squares). Reaction conditions: 100 mM **2a**, 1.5 mg/mL ADH preparation, 0.1 mM $NAD(P)^+$, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 1–24 h.

Reduction of azido ketones 2a–f by ADHs

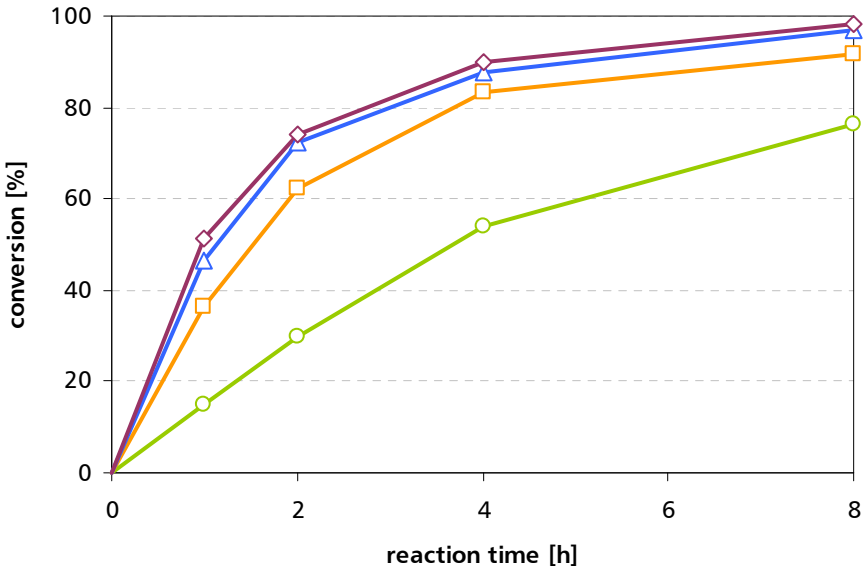
The reduction of azido ketones **2a–f** was carried out under the conditions of the chemo-enzymatic one-pot process to ensure that complete conversion is reached after 20 h. The optimised ADH loadings and the corresponding results are summarised in Suppl. Table 6.

	ADH-A			KRED-NADH-110		
Subst.	*c*(ADH) [a] [mg/mL]	Conv.[b] [%]	*ee* [c] [%]	*c*(ADH) [a] [mg/mL]	Conv.[b] [%]	*ee* [c] [%]
2a	1.5	>99	>99 (*R*)	0.2	>99	>99 (*S*)
2b	1.5	>99	>99 (*R*)	0.2	>99	>99 (*S*)
2c	1.5	>99	>99 (*R*)	0.2	>99	>99 (*S*)
2d	1.5	>99	>99 (*R*)	0.2	>99	>99 (*S*)
2e	2.5	>99	>99 (*R*)	0.4	>99	>99 (*S*)
2f	1.5	>99	>99 (*S*)[d]	1.0	>99	>99 (*R*)[d]

Suppl. Table 6. Activity and stereoselectivity of ADH-A and KRED-NADH-110 in the reduction of 2-azido-1-arylethanones **2a–f** to 2-azido-1-arylethanols **3a–f**. Reaction conditions: 50 mM **2**, 0.2–2.5 mg/mL ADH preparation, 5% (v/v) 2-propanol, 2 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 30 °C, 20 h. [a] Final concentration of crude ADH preparation in the reaction mixture. [b] Determined by achiral GC–FID analysis. [c] Enantiomeric excess of **3** as determined by chiral-phase GC–FID or chiral-phase HPLC analysis. [d] Switch in substituent priorities according to Cahn–Ingold–Prelog rules.

Time course of the azidolysis of chloro ketone 1a

The time course of the azidolysis of 2-chloroacetophenone **1a** at 60 °C in phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$) containing 5% (v/v) 2-propanol in the presence of varied amounts of potassium iodide as nucleophilic substitution catalyst is shown in Suppl. Fig. 5.

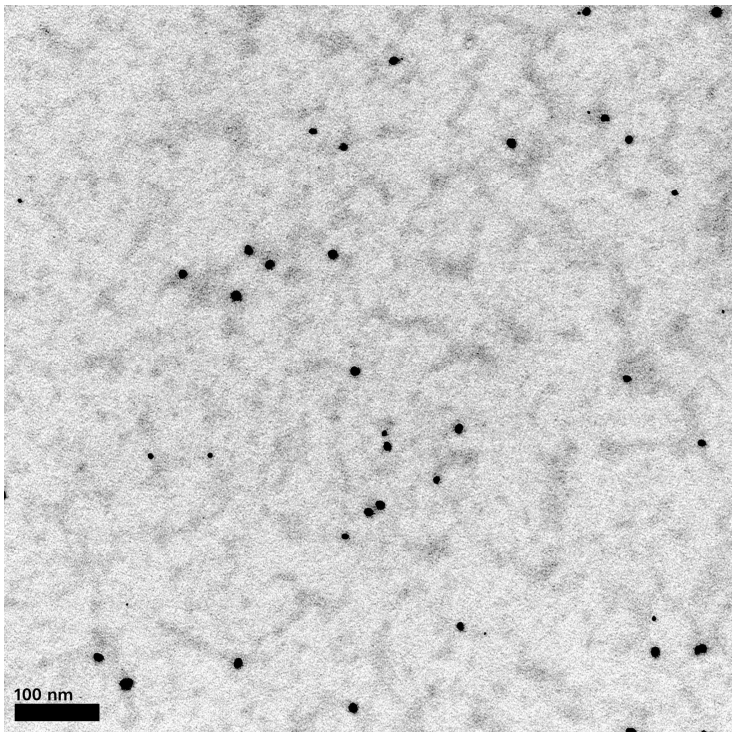


Suppl. Fig. 5. Time course of the conversion **1a** into **2a** by nucleophilic substitution with azide in the presence of varied concentrations of iodide: no iodide (green circles), 1 mM iodide (orange squares), 5 mM iodide (blue triangles), 10 mM iodide (purple diamonds). Reaction conditions: 100 mM **1a**, 120 mM NaN_3, 0–10 mM KI, 5% (v/v) 2-propanol, 0.5 mL K-phosphate buffer (100 mM, pH 7.0; 1 mM $MgSO_4$), 60 °C, 1–8 h.

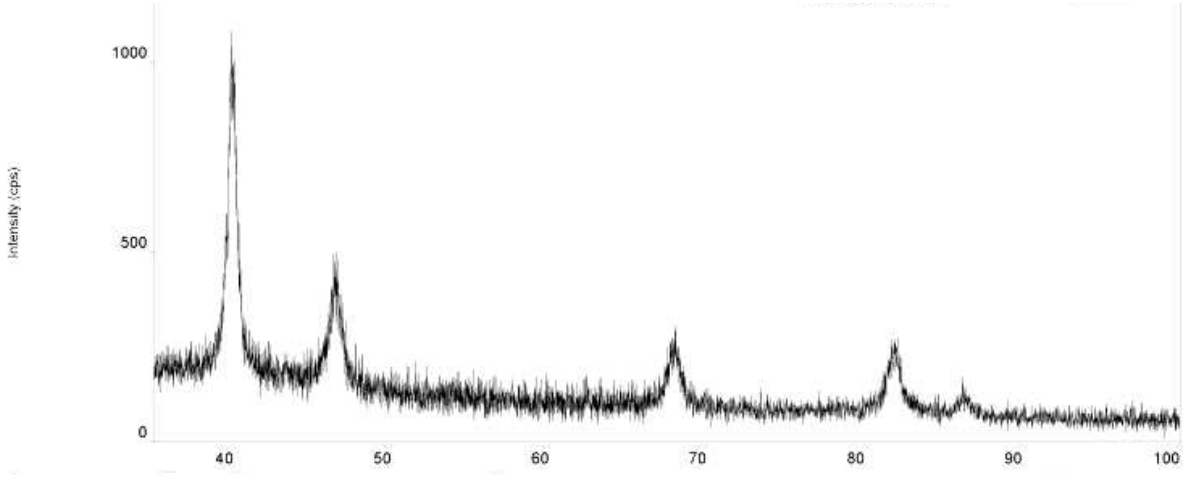
Characterisation data of Pd nanoparticles

The Pd-LK nanoparticles used in this study (prepared from $PdCl_2$ and low-sulfonate Kraft lignin as described in the *Supplementary Methods* section) were characterised by transmission electron microscopy (TEM), UV-Vis spectroscopy, and X-ray diffraction spectroscopy (XRD). The particle size distribution was determined by dynamic light scattering (DLS) experiments. Sample preparation procedures for all these analytical techniques are described in the *Analytics* section.

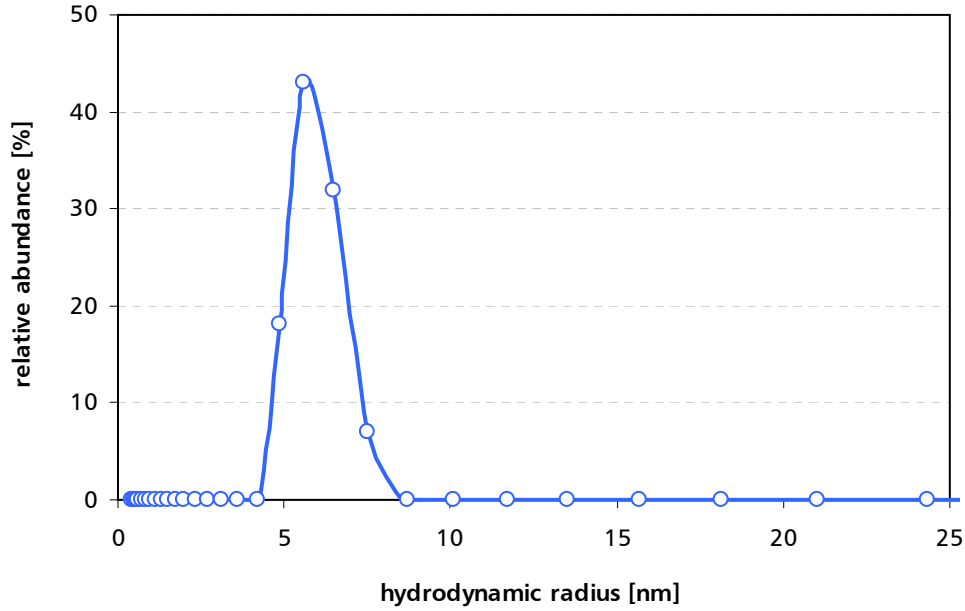
The nanoparticles are spherical in shape (Suppl. Fig. 6), with an average diameter of 8 nm (determined from the TEM image; the average hydrodynamic radius determined by DLS measurements is 6 nm, see Suppl. Fig. 8). The XRD spectrum (Suppl. Fig. 7) shows peaks at 39.9°, 46.3°, 67.4°, 82.5° and 86.9°, which can be assigned to the diffraction of the (111), (200), (220), and (311) planes of the face-centred cubic Pd-crystal with space group Fm3m.



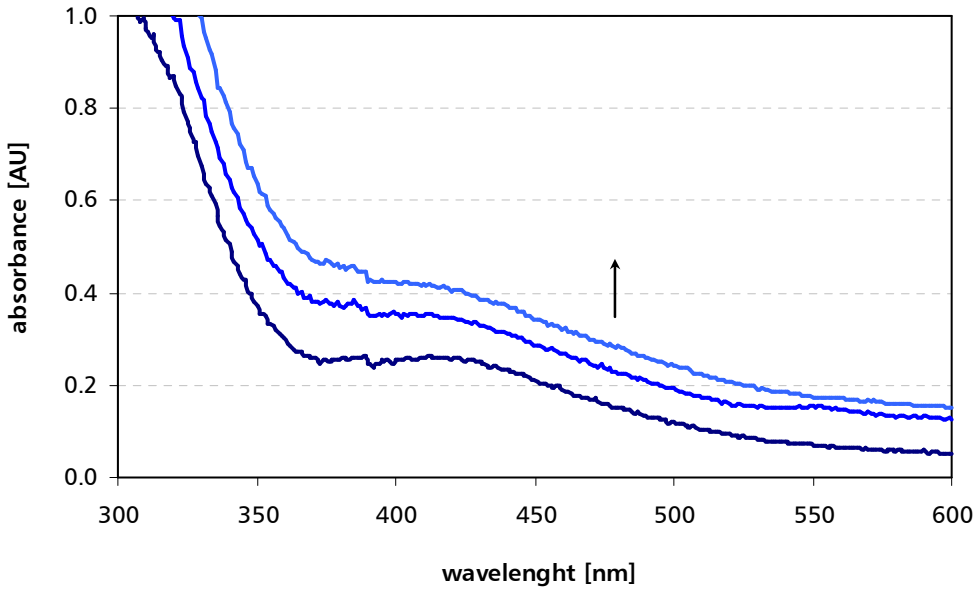
Suppl. Fig. 6. TEM image of Pd nanoparticles prepared from $PdCl_2$ and low-sulfonate Kraft lignin.



Suppl. Fig. 7. XRD pattern of Pd nanoparticles prepared from $PdCl_2$ and low-sulfonate Kraft lignin.



Suppl. Fig. 8. Particle size distribution of Pd nanoparticles prepared from $PdCl_2$ and low-sulfonate Kraft lignin, determined as hydrodynamic radius by DLS.



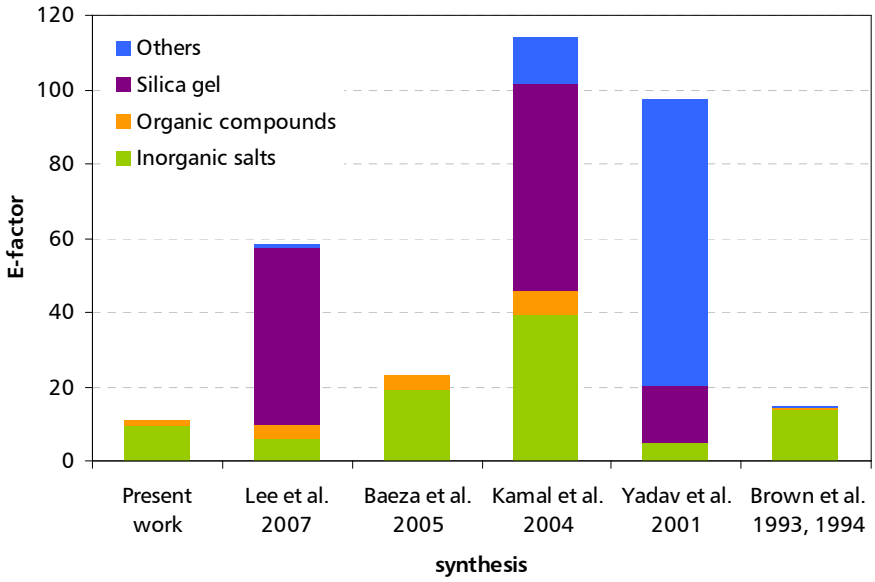
Suppl. Fig. 9. UV-Vis spectrum (300–600 nm range) acquired during the formation of Pd nanoparticles from $PdCl_2$ and low-sulfonate Kraft lignin. Time points: Before heating (dark blue line), 1 h heating to 80 °C (blue line), 2 h heating to 80 °C (light blue line).

Environmental impact assessment of tembamide syntheses

Suppl. Table 7 lists the solvent demand of the six tembamide syntheses discussed in the article, differentiated into various types of solvents, while Suppl. Fig. 10 shows the contributions of different waste types to the overall E-factor.

Solvent	Quantity used [mL/g]					
	Present work	Lee *et al.* 2007	Baeza *et al.* 2005	Kamal *et al.* 2004	Yadav *et al.* 2001	Brown *et al.* 1993, 1994
water	116	144	264	76	351	272
ethyl acetate	112	148	596	89	19	68
alcohols:						
ethanol	61	110	–	–	9	–
methanol	–	7	–	59	5	–
2-propanol	5	–	–	–	–	–
ethers:						
tert-butyl methyl ether	15	–	–	–	–	–
diisopropyl ether	–	–	–	89	–	–
diethyl ether	–	–	–	–	77	33
tetrahydrofuran	–	–	138	–	–	23
hydrocarbons:						
hexanes, petr. ether	–	371	10	1421[a]	366	16[b]
toluene, benzene	–	4	23		3	71
chlorinated solvents:						
chloroform	–	708	–	–	–	–
dichloromethane	–	72	–	68	5	–
others	–	37	–	–	–	–
overall	**309**	**1600**	**1031**	**1801**	**826**	**483**

Suppl. Table 7. Comparison of the solvent demand of catalytic asymmetric syntheses of tembamide. [a] An unspecified mixture of hexanes and ethyl acetate used for chromatography was accounted for as hexanes only. [b] Unspecified mixtures of petroleum ether and dichloromethane, as well as petroleum ether and diethyl ether were accounted for as petroleum ether only.



Suppl. Fig. 10. Contributions of different types of waste to the overall E-factor (excluding solvents) of catalytic asymmetric syntheses of tembamide.

Supplementary methods

Preparation of lignin-stabilised metal nanoparticles

Lignin-stabilised Pd and Pt nanoparticles were prepared following literature procedures:[1]

Pd nanoparticles: A solution of $PdCl_2$ (10 mg, 56 μmol) and lignin (60 mg) in demineralised water (10 mL) was stirred at 80 °C for 2 h. After this time, all $PdCl_2$ had dissolved and the initially brown colour of the solution had intensified to black. The solution was allowed to cool to room temperature and was stored at room temperature in a screw-top glass vial.

Pt nanoparticles: A solution of $H_2PtCl_6 \cdot 6\ H_2O$ (30 mg, 60 μmol) and lignin (60 mg) in demineralised water (6 mL) was stirred at 80 °C for 3 h. After this time, the initially dark orange colour of the solution had intensified to dark brown. The solution was allowed to cool to room temperature and was stored at room temperature in a screw-top glass vial.

Synthesis of substrates and reference compounds

2-Bromo-1-(2-furyl)ethanone (1f; CAS 15109-94-1).[2] A solution of 2-acetylfuran (4.40 g, 40 mmol) in diethyl ether/dioxane (2/1, 30 mL) under nitrogen atmosphere was cooled to 5 °C on an ice bath. Bromine (7.19 g, 45 mmol) was added dropwise to the stirred mixture over 15 min, the ice bath was removed and stirring continued at room temperature for 16 h. The reaction was quenched with sat. aq. NH_4Cl solution (20 mL), the phases were separated, and the organic phase was washed with a 1 M aq. $NaHSO_3$ solution (25 mL), dried over $MgSO_4$ and evaporated under reduced pressure to give 7.70 g of a brown liquid. Column chromatography (silica gel 60, petroleum ether/EtOAc = 15/1) afforded 3.88 g (51%) of **1f** as a yellowish liquid, which crystallised upon standing in the fridge to yellowish needles. mp: 32–34 °C (lit.[3] 34 °C). TLC (silica, Petroleum ether/EtOAc = 3/1): R_f = 0.67. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.31 (2H, s, CH_2), 6.59 (1H, dd, J = 3.6 Hz, 1.6 Hz, Ar-4), 7.33 (1H, d, J = 3.6 Hz, Ar-3), 7.63 (1H, s, Ar-5). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 30.0, 112.8, 119.1, 147.2, 150.3, 180.3. GC–MS (EI, 70 eV): m/z = 190 (M^+, 7), 188 (M^+, 7), 95 (100), 53 (14). The NMR data are in accordance with literature values.[4]

General procedure for the preparation of azido ketones 2a–f: To a solution of the halo ketone **1a–f** (20.0 mmol) in acetonitrile (30 mL), a solution of NaN_3 (1.95 g, 30.0 mmol) and KI (0.17 g, 1.0 mmol) in water (10 mL) was added, and the mixture was stirred at 60 °C for 1 h. The reaction mixture was concentrated under reduced pressure and the resulting aqueous residue was extracted with EtOAc (2 × 20 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$ and evaporated under reduced pressure to give the azidoketone **2** in high purity, as judged by GC and NMR analysis.

2-Azidoacetophenone (2a; CAS 1816-88-2). Obtained from 2-chloroacetophenone (**1a**; 3.09 g). 3.04 g (18.9 mmol, 94%) clear, orange liquid. TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.78. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.56 (2H, s, CH_2), 7.50 (2H, t, J = 7.6 Hz, Ar-*m*), 7.62 (1H, t, J = 7.4 Hz, Ar-*p*), 7.90 (2H, d, J = 8.0 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 54.8, 127.9, 128.9, 134.1, 134.4, 193.2. GC–MS (EI, 70 eV): m/z = 105 (100), 77 (83), 51 (38). The NMR data are in accordance with literature values.[5]

2-Azido-4'-chloroacetophenone (2b; CAS 26086-60-2). Obtained from 2,4'-dichloroacetophenone (3.78 g). 3.76 g (19.2 mmol, 96%) of an orange solid. mp: 68–69 °C (lit.[6] 60–64 °C). TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.73. ^{1}H-NMR (400 MHz,

$CDCl_3$): δ [ppm] = 4.52 (2H, s, CH_2), 7.47 (2H, d, J = 8.8 Hz, Ar-*m*), 7.84 (2H, d, J = 8.8 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 54.8, 129.3, 132.6, 140.7, 192.1. GC–MS (EI, 70 eV): *m/z* = 167 (1), 139 (100), 111 (64), 75 (78), 50 (58). The NMR data are in accordance with literature values.[6]

2-Azido-4'-fluoroacetophenone (2c; CAS 118887-70-0). Obtained from 2-bromo-4'-fluoroacetophenone (**1c**; 4.34 g). 3.40 g (19.0 mmol, 95%) of an orange solid. mp: 53–54 °C (lit.[6] 47.5–48.5 °C). TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.73. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.53 (2H, s, CH_2), 7.17 (2H, dd, J = 8.8 Hz, 8.4 Hz, Ar-*m*), 7.94 (2H, dd, J = 8.4 Hz, 5.2 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 54.7, 116.2 (d, J_{CF} = 21.9 Hz), 130.7 (d, J_{CF} = 8.3 Hz), 130.8, 166.2 (d, J_{CF} = 256 Hz), 191.7. GC–MS (EI, 70 eV): *m/z* = 151 (1), 123 (100), 95 (85), 75 (53), 69 (12), 50 (21). The NMR data are in accordance with literature values.[6]

2-Azido-4'-methylacetophenone (2d; CAS 6595-30-8). Obtained from 2-bromo-4'-methylacetophenone (**1d**; 4.26 g). 3.41 g (19.5 mmol, 97%) of an orange solid. mp: 61–62 °C (lit.[7] 59–62 °C). TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.80. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.42 (3H, s, CH_3), 4.52 (2H, s CH_2), 7.29 (2H, d, J = 8.0 Hz, Ar-*m*), 7.79 (2H, d, J = 8.0 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.7, 54.7, 128.0, 129.6, 131.9, 145.1, 192.7. GC–MS (EI, 70 eV): *m/z* = 147 (1), 119 (100), 91 (69), 65 (32). The NMR data are in accordance with literature values.[8]

2-Azido-4'-methoxyacetophenone (2e; CAS 6595-28-4). Obtained from 2-bromo-4'-methoxyacetophenone (**1e**; 4.58 g). 3.72 g (19.5 mmol, 97%) of a yellow solid. mp: 72–73 °C (lit.[6] 68–69 °C). TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.63. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.88 (3H, s, OCH_3), 4.50 (2H, s CH_2), 6.95 (2H, d, J = 8.8 Hz, Ar-*m*), 7.88 (2H, d, J = 8.8 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 54.5, 55.5, 114.1, 127.3, 130.2, 164.2, 191.6. GC–MS (EI, 70 eV): *m/z* = 163 (2), 135 (100), 107 (14), 92 (22), 77 (40), 64 (20), 50 (10). The NMR data are in accordance with literature values.[6]

2-Azido-1-(2-furyl)ethanone (2f; CAS 118299-63-1). Obtained from 2-bromo-1-(2-furyl)ethanone (**1f**; 2.84 g, 15.0 mmol). 2.12 g (14.0 mmol, 94%) of a brownish liquid, which crystallised upon standing in the fridge to yellowish needles. mp: 31–33 °C (lit.[9] 32–33 °C). TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.53. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.41 (2H, s CH_2), 6.59 (1H, dd, J = 3.6 Hz, 1.6 Hz, Ar-4), 7.29 (1H, d, J = 3.6 Hz, Ar-3), 7.61 (1H, s, Ar-5). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 54.3, 112.7, 118.1, 147.0, 150.6, 182.5. GC–MS (EI, 70 eV): *m/z* = 151 (M^+, 3), 95 (100), 67 (12), 53 (5). The NMR data are in accordance with literature values.[10]

General procedure for the preparation of azido alcohols *rac*-3a–f: A solution of azido ketone **2** (5.0 mmol) in methanol (20 mL) was cooled to 5 °C on an ice bath. $NaBH_4$ (113 mg, 3.0 mmol) was added in portions to the stirred solution over a 15 min period. After addition was completed, the ice bath was removed and stirring continued for 1 h at room temperature. The reaction was quenched by addition of sat. aq. NH_4Cl solution (5 mL), and the mixture was concentrated under reduced pressure. The residue was taken up in water (20 mL) and extracted with EtOAc (2 × 20 mL). The combined organic phases were washed with brine (10 mL), dried over $MgSO_4$ and evaporated under reduced pressure to give the crude azido alcohol *rac*-**3**, which was purified by column chromatography (silica gel 60, petroleum ether/EtOAc = 9/1).

***rac*-2-Azido-1-phenylethanol (*rac*-3a; CAS 18756-01-9).** 0.682 g (4.18 mmol, 84%) of an orange liquid. TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.71. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.54 (1H, d, J = 2.8 Hz, OH), 3.43 (1H, dd, J = 12.8 Hz, 4.0 Hz, CH_2), 3.49 (1H, dd, J = 12.4 Hz, 8.0 Hz, CH_2), 4.85–4.88 (1H, m, C*H*-OH), 7.31–7.48 (5H, m, Ar). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 58.0, 73.4, 125.9, 128.3, 128.6, 140.5.

GC–MS (EI, 70 eV): *m/z* = 107 (100), 79 (98), 77 (67), 51 (25). The NMR data are in accordance with literature values.[11]

***rac*-2-Azido-1-(4-chlorophenyl)ethanol (*rac*-3b; CAS 861929-21-7).** 0.857 g (4.33 mmol, 87%) of a yellowish liquid. TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.64. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.53 (1H, d, *J* = 3.6 Hz, OH), 3.41–3.47 (2H, m, CH_2), 4.83–4.86 (1H, m, C*H*-OH), 7.30 (2H, d, *J* = 8.4 Hz, Ar-*o*), 7.35 (2H, d, *J* = 8.0 Hz, Ar-*m*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 57.9, 72.7, 127.3, 128.8, 134.1, 138.9. GC–MS (EI, 70 eV): *m/z* = 143 (26), 141 (88), 115 (7), 113 (24), 77 (100), 51 (23). The NMR data are in accordance with literature values.[12]

***rac*-2-Azido-1-(4-fluorophenyl)ethanol (*rac*-3c; CAS 118888-01-0).** 0.792 g (4.37 mmol, 87%) of a yellowish liquid. TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.65. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.53 (1H, d, *J* = 3.2 Hz, OH), 3.39–3.48 (2H, m, CH_2), 4.83–4.87 (1H, m, C*H*-OH), 7.06 (2H, t, *J* = 8.6 Hz, Ar-*m*), 7.34 (2H, dd, *J* = 8.4 Hz, 5.2 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 58.1, 72.7, 115.6 (d, J_{CF} = 21.4 Hz), 127.6 (d, J_{CF} = 8.2 Hz), 136.3 (d, J_{CF} = 3.1 Hz), 162.6 (d, J_{CF} = 245 Hz). GC–MS (EI, 70 eV): *m/z* = 125 (100), 97 (82), 95 (27), 77 (41), 75 (16), 51 (14). The NMR data are in accordance with literature values.[12]

***rac*-2-Azido-1-(4-tolyl)ethanol (*rac*-3d; CAS 144924-03-8).** 0.827 g (4.67 mmol, 93%) of a yellowish liquid. TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.75. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.36 (3H, s, CH_3), 2.42 (1H, d, *J* = 3.2 Hz, OH), 3.41 (1H, dd, *J* = 12.4 Hz, 4.0 Hz, CH_2), 3.47 (1H, dd, *J* = 12.4 Hz, 8.0 Hz, CH_2), 4.82–4.85 (1H, m, C*H*-OH), 7.19 (2H, d, *J* = 7.6 Hz, Ar-*m*), 7.26 (2H, d, *J* = 8.0 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.1, 58.0, 73.2, 125.8, 129.3, 137.6, 138.1. GC–MS (EI, 70 eV): *m/z* = 121 (100), 93 (55), 91 (65), 77 (46), 65 (21), 51 (13). The NMR data are in accordance with literature values.[12]

***rac*-2-Azido-1-(4-methoxyphenyl)ethanol (*rac*-3e; CAS 144924-01-6).** Petroleum ether/EtOAc = 7/1 was used as eluent for column chromatography. 0.890 g (4.61 mmol, 92%) of a slightly yellowish liquid. TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.60. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.42 (1H, d, *J* = 3.2 Hz, OH), 3.39 (1H, dd, *J* = 12.8 Hz, 4.0 Hz, CH_2), 3.46 (1H, dd, *J* = 12.8 Hz, 8.4 Hz, CH_2), 3.81 (3H, s, OCH_3), 4.80–4.83 (1H, m, C*H*-OH), 6.90 (2H, d, *J* = 8.4 Hz, Ar-*m*), 7.29 (2H, d, *J* = 8.8 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.3, 58.0, 73.0, 114.0, 127.2, 132.7, 159.6. GC–MS (EI, 70 eV): *m/z* = 137 (100), 109 (32), 94 (31), 77 (45), 66 (17), 65 (16), 51 (15). The NMR data are in accordance with literature values.[12]

***rac*-2-Azido-1-(2-furyl)ethanol (*rac*-3f).** Petroleum ether/EtOAc = 7/1) was used as eluent for column chromatography. 0.662 g (4.32 mmol, 86%) of **3f** as a yellowish liquid. TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.62. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.52 (1H, d, *J* = 5.2 Hz, OH), 3.57 (1H, dd, *J* = 12.8 Hz, 4.4 Hz, CH_2), 3.65 (1H, dd, *J* = 12.8 Hz, 7.2 Hz, CH_2), 4.85–4.89 (1H, m, C*H*-OH), 6.34–6.38 (2H, m, Ar-3, Ar-4), 7.40 (1H, s, Ar-5). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 55.0, 67.1, 107.4, 110.5, 142.5, 153.1. GC–MS (EI, 70 eV): *m/z* = 153 (M^+, <1), 97 (100), 69 (17), 51 (6), 41 (61). The NMR data are in accordance with literature values.[13]

***rac*-2-Amino-1-(4-chlorophenyl)ethanol (*rac*-4b; CAS 41870-82-0).** *rac*-2-Azido-1-(4-chlorophenyl)ethanol (*rac*-**3b**; 99 mg, 0.5 mmol) was dissolved in 2-propanol (250 μL), and potassium phosphate buffer (4.3 mL; 100 mM, pH 7.0, 1 mM $MgSO_4$), 4 M aq. NaOH solution (65 μL), and Pd-NP solution (450 μL; 5.6 mM Pd) were added. The mixture was stirred at 30 °C and 10 bar H_2 for 4 h, then the product was extracted into EtOAc (4 × 5 mL). The extracts from two reaction batches were combined, dried over $MgSO_4$ and evaporated under reduced pressure to give *rac*-**4b** (168 mg, 98%) as an off-white solid. mp: 92–93 °C

(lit.[14] 93.5–94.5 °C). TLC (silica, MTBE/MeOH/NH_4OH = 90/9/1): R_f = 0.11. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.19 (3H, br s, OH, NH_2), 2.70 (1H, dd, J = 12.8 Hz, 8.0 Hz, CH_2), 2.90 (1H, dd, J = 12.8 Hz, 3.2 Hz, CH_2), 4.55 (1H, dd, J = 7.6 Hz, 3.6 Hz, C*H*-OH), 7.23 (2H, d, J = 8.0 Hz, Ar-*o*), 7.27 (2H, d, J = 8.4 Hz, Ar-*m*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 49.1, 73.4, 127.2, 128.5, 133.1, 141.1. GC–MS (EI, 70 eV): m/z = 171 (M^+, 1), 143 (5), 141 (16), 115 (4), 113 (15), 77 (100), 51 (25), 50 (11). The NMR data are in accordance with literature values.[15]

General procedure for the preparation of amino alcohols *rac*-4c–f: To a solution of azido alcohol *rac*-**3** (1.0 mmol) in methanol (5 mL) was added palladium 10% on charcoal (10 mg), and the mixture was stirred at 30 °C and 10 bar H_2 for 2 h. The reaction mixture was filtered through Celite, the Celite pad was washed with methanol (2 mL), and the solvent was evaporated under reduced pressure to give amino alcohol *rac*-**4** in high purity, as judged by GC and NMR analysis.

***rac*-2-Amino-1-(4-fluorophenyl)ethanol (*rac*-4c; CAS 456-05-3).** 150 mg (0.97 mmol, 97%) of a white solid. mp: 65–66 °C. TLC (silica, MTBE/MeOH/NH_4OH = 90/9/1): R_f = 0.10. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.33 (3H, br s, OH, NH_2), 2.71 (1H, dd, J = 12.8 Hz, 8.0 Hz, CH_2), 2.87 (1H, dd, J = 12.8 Hz, 4.0 Hz, CH_2), 4.56 (1H, dd, J = 8.0 Hz, 4.0 Hz, C*H*-OH), 6.99 (2H, t, J = 8.6 Hz, Ar-*m*), 7.26 (2H, dd, J = 8.4 Hz, 5.6 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 49.2, 73.5, 115.1 (d, J_{CF} = 21.2 Hz), 127.4 (d, J_{CF} = 8.0 Hz), 138.4 (d, J_{CF} = 3.1 Hz), 162.1 (d, J_{CF} = 244 Hz). GC–MS (EI, 70 eV): m/z = 155 (M^+, 1), 138 (4), 136 (4), 125 (48), 123 (18), 109 (15), 97 (100), 95 (39), 77 (60), 75 (23), 70 (8), 57 (10), 51 (24), 50 (13). The NMR data are in accordance with literature values.[16]

***rac*-2-Amino-1-(4-tolyl)ethanol (*rac*-4d; CAS 53360-85-3).** 146 mg (0.97 mmol, 97%) of an off-white solid. mp: 67–68 °C (lit.[17] 68–69 °C). TLC (silica, MTBE/MeOH/NH_4OH = 90/9/1): R_f = 0.11. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.95 (3H, br s, OH, NH_2), 2.34 (3H, s CH_3), 2.79 (1H, dd, J = 12.8 Hz, 7.6 Hz, CH_2), 2.96 (1H, dd, J = 12.8 Hz, 4.0 Hz, CH_2), 4.59 (1H, dd, J = 7.6 Hz, 4.0 Hz, C*H*-OH), 7.16 (2H, d, J = 7.6 Hz, Ar-*m*), 7.23 (2H, d, J = 8.0 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.1, 49.3, 74.3, 125.8, 129.1, 137.2, 139.5. GC–MS (EI, 70 eV): m/z = 151 (M^+, 2), 122 (16), 121 (100), 119 (12), 93 (74), 91 (68), 77 (57), 65 (20), 51 (12). The NMR data are in accordance with literature values.[18]

***rac*-2-Amino-1-(4-methoxyphenyl)ethanol (*rac*-4e; CAS 55275-61-1).** 169 mg (1.01 mmol, quant.) of a yellowish solid. mp: 74–75 °C (lit.[19] 73–75 °C). TLC (silica, MTBE/MeOH/NH_4OH = 90/9/1): R_f = 0.09. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.20 (3H, br s, OH, NH_2), 2.77 (1H, dd, J = 12.8 Hz, 8.0 Hz, CH_2), 2.90 (1H, dd, J = 12.8 Hz, 4.0 Hz, CH_2), 3.79 (3H, s, OCH_3), 4.56 (1H, dd, J = 7.6 Hz, 4.0 Hz, C*H*-OH), 6.87 (2H, d, J = 8.4 Hz, Ar-*m*), 7.25 (2H, d, J = 8.4 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 49.2, 55.2, 74.0, 113.7, 127.1, 134.7, 159.0. GC–MS (EI, 70 eV): m/z = 167 (M^+, 3), 138 (11), 137 (100), 109 (41), 94 (36), 77 (34), 66 (10), 65 (8), 51 (6). The NMR data are in accordance with literature values.[18]

***rac*-2-Amino-1-(2-furyl)ethanol (*rac*-4f; CAS 2745-22-4).** 124 mg (0.98 mmol, 98%) of a yellowish solid. mp: 84–85 °C (lit.[20] 85–87 °C). TLC (silica, MTBE/MeOH/NH_4OH = 90/9/1): R_f = 0.14. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.42 (3H, br s, OH, NH_2), 2.99 (2H, d, J = 5.6 Hz, CH_2), 4.61 (1H, t, J = 5.8 Hz, C*H*-OH), 6.23 (1H, d, J = 2.8 Hz, Ar-3), 6.31 (1H, d, J = 2.8 Hz, Ar-4) 7.35 (1H, s, Ar-5). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 45.9, 68.1, 106.2, 110.1, 141.9, 155.4. GC–MS (EI, 70 eV): m/z = 127 (17), 98 (100), 97 (89), 81 (8), 69 (34), 53 (12), 51 (11), 42 (23), 41 (98). The NMR data are in accordance with literature values.[20]

General Procedure for the Preparation of 2,2-Dimethyl-5-aryloxazolidines *rac*-5a–f: To a solution of the amino alcohol *rac*-**4** (0.2 mmol) in acetone (1 mL), anhydrous $MgSO_4$ (5 mg) was added, and the mixture was shaken in a microcentrifuge tube at 30 °C and 1000 rpm on a Thermoshaker for 3 h. The solid was removed by centrifugation and the supernatant was evaporated under reduced pressure to give oxazolidine *rac*-**5** in >90% purity, as judged by GC and NMR analysis.

***rac*-2,2-Dimethyl-5-phenyloxazolidine (*rac*-5a; CAS 87601-24-9).** Yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.48 (3H, s, CH_3), 1.54 (3H, s, CH_3), 2.32 (1H, br s, NH), 3.01 (1H, dd, J = 12.0 Hz, 6.4 Hz, CH_2), 3.57 (1H, dd, J = 12.4 Hz, 6.8 Hz, CH_2), 4.91 (1H, t, J = 6.6 Hz, C*H*-O), 7.23–7.42 (5H, m, Ar). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.7, 27.6, 54.6, 78.8, 96.3, 125.5, 127.3, 128.4, 142.2. GC–MS (EI, 70 eV): m/z = 162 (M^+–CH_3, 2), 120 (17), 77 (15), 71 (100), 70 (67), 56 (11), 51 (9), 43 (13), 42 (14).

***rac*-5-(4-Chlorophenyl)-2,2-dimethyloxazolidine (*rac*-5b).** Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.44 (3H, s, CH_3), 1.48 (3H, s, CH_3), 2.91 (1H, dd, J = 11.6 Hz, 6.4 Hz, CH_2), 3.53 (1H, dd, J = 12.0 Hz, 6.4 Hz, CH_2), 4.84 (1H, t, J = 6.6 Hz, C*H*-O), 7.21 (2H, d, J = 8.0 Hz, Ar-*o*), 7.27 (2H, d, J = 8.0 Hz Ar-*m*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.7, 27.5, 54.6, 78.1, 96.5, 126.8, 128.5, 132.9, 140.8. GC–MS (EI, 70 eV): m/z = 196 (M^+–CH_3, 1), 154 (10), 77 (9), 71 (100), 70 (98), 56 (9), 43 (12), 42 (12).

***rac*-2,2-Dimethyl-5-(4-fluorophenyl)oxazolidine (*rac*-5c).** Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.46 (3H, s, CH_3), 1.51 (3H, s, CH_3), 2.94 (1H, dd, J = 12.0 Hz, 6.8 Hz, CH_2), 3.54 (1H, dd, J = 12.0 Hz, 6.4 Hz, CH_2), 4.86 (1H, t, J = 6.6 Hz, C*H*-O), 7.01 (2H, t, J = 9.2 Hz, Ar-*m*), 7.27 (2H, dd, J = 8.8 Hz, 5.6 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.7, 27.6, 54.6, 78.2, 96.3, 115.2 (d, J_{CF} = 21.3 Hz), 127.1 (d, J_{CF} = 8.0 Hz), 137.8 (d, J_{CF} = 3.0 Hz), 162.1 (d, J_{CF} = 244 Hz). GC–MS (EI, 70 eV): m/z = 180 (M^+–CH_3, 2), 138 (18), 109 (7), 71 (100), 70 (95), 56 (11), 43 (14), 42 (14).

***rac*-2,2-Dimethyl-5-(4-tolyl)oxazolidine (*rac*-5d).** Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.47 (3H, s, CH_3-oxa), 1.53 (3H, s, CH_3-oxa), 2.34 (3H, s, Ar-CH_3), 2.94 (1H, br s, NH), 2.99 (1H, dd, J = 12.0 Hz, 6.8 Hz, CH_2), 3.55 (1H, dd, J = 12.0 Hz, 6.8 Hz, CH_2), 4.89 (1H, t, J = 6.6 Hz, C*H*-O), 7.14 (2H, d, J = 8.4 Hz, Ar-*m*), 7.21 (2H, d, J = 8.0 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 21.1, 26.8, 27.6, 54.6, 78.7, 96.2, 125.5, 129.0, 136.9, 139.2. GC–MS (EI, 70 eV): m/z = 176 (M^+–CH_3, <1), 134 (9), 91 (8), 71 (100), 70 (46), 56 (8), 43 (6), 42 (6).

***rac*-2,2-Dimethyl-5-(4-methoxyphenyl)oxazolidine (*rac*-5e).** Yellowish liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.46 (3H, s, CH_3-oxa), 1.52 (3H, s, CH_3-oxa), 2.72 (1H, br s, NH), 2.98 (1H, dd, J = 12.4 Hz, 6.8 Hz, CH_2), 3.52 (1H, dd, J = 12.0 Hz, 6.4 Hz, CH_2), 3.79 (3H, s, OCH_3), 4.85 (1H, t, J = 6.8 Hz, C*H*-O), 6.87 (2H, d, J = 8.4 Hz, Ar-*m*), 7.24 (2H, d, J = 8.8 Hz, Ar-*o*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.7, 27.7, 54.6, 55.3, 78.6, 96.0, 113.8, 126.8, 134.1, 158.9. GC–MS (EI, 70 eV): m/z = 192 (M^+–CH_3, <1), 150 (4), 137 (8), 71 (100), 70 (27), 56 (7), 43 (5), 42 (6).

***rac*-2,2-Dimethyl-5-(4-furyl)oxazolidine (*rac*-5f, CAS 164157-99-7).** Orange liquid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 1.39 (3H, s, CH_3), 1.48 (3H, s, CH_3), 2.92 (1H, br s, NH), 3.33 (1H, dd, J = 12.4 Hz, 5.2 Hz, CH_2), 3.44 (1H, dd, J = 12.0 Hz, 6.8 Hz, CH_2), 4.90 (1H, dd, J = 6.8 Hz, 5.2 Hz, C*H*-O), 6.23 (1H, d, J = 3.2 Hz, Ar-3), 6.29 (1H, dd, J = 3.2 Hz, 2.0 Hz Ar-4), 7.35 (1H, dd, J = 2.0 Hz, 0.8 Hz, Ar-5). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 26.4, 27.3, 50.8, 72.0, 96.6, 106.8, 110.1, 142.3, 154.6. GC–MS (EI, 70 eV): m/z = 152 (M^+–CH_3, 2), 110 (15), 80 (7), 71 (100), 70 (67), 56 (13), 43 (14), 42 (15), 41 (14).

***rac*-Tembamide (CAS 15298-28-9).** To a stirred solution of *rac*-2-amino-1-(4-methoxyphenyl)ethanol (*rac*-**4e**; 33 mg, 0.20 mmol) in a mixture of MTBE (3 mL) and 1 M aq. NaOH solution (2 mL), benzoyl chloride (35 mg, 0.25 mmol) was added dropwise over a 5 min

period. The reaction mixture was stirred at room temperature for 1 h, then the phases were separated, and the aqueous phase was extracted with EtOAc (2 × 3 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to give 47 mg (87%) of *rac*-tembamide as a colourless, crystalline solid. mp: 151–152 °C (lit.[21] 152–155 °C). TLC (silica, petroleum ether/EtOAc = 3/1): R_f = 0.10. ^{1}H-NMR (400 MHz, DMSO-d_6): δ [ppm] = 3.29–3.35 (1H, m, CH_2), 3.44–3.49 (1H, m, CH_2), 3.73 (3H, s, OCH_3), 4.74 (1H, dd, J = 7.2 Hz, 5.2 Hz, C*H*-OH), 5.42 (1H, br s, OH), 6.90 (2H, d, J = 8.8 Hz, Ar-*m*), 7.29 (2H, d, J = 8.8 Hz, Ar-*o*), 7.43–7.53 (3H, m, Ar-*m*', Ar-*p*'), 7.84 (2H, d, J = 7.6 Hz, Ar-*o*'), 8.47 (1H, t, J = 5.2 Hz, NH). ^{13}C-NMR (100 MHz, DMSO-d_6): δ [ppm] = 47.6, 54.9, 70.6, 113.3, 127.0, 127.1, 128.1, 131.0, 134.5, 135.7, 158.2, 166.3. GC–MS (EI, 70 eV): m/z = 271 (M^+, <1), 150 (47), 137 (32), 135 (77), 134 (100), 109 (24), 105 (58), 94 (25), 77 (72), 66 (10), 51 (18). The NMR data are in accordance with literature values.[21]

Heterologous expression of ADH-A and *Lb*ADH

Heterologous expression of ADH-A: ADH-A from *Rhodococcus ruber* DSM 44541 was heterologously expressed in *E. coli* Tuner™ (DE3) using a published protocol[22] with slight modifications: LB medium (25 mL; containing 100 μg/mL ampicillin) was inoculated from a glycerol stock (50 μL) of *E. coli* Tuner™ (DE3) harboring the [pET22b–ADH-A] plasmid, and the culture was grown to an OD_{600} of >2 at 30 °C and 150 rpm overnight. An aliquot (5 mL) of this starter culture was used to inoculate TB medium (500 mL; containing 100 μg/mL ampicillin and 0.5 mM $ZnCl_2$), and the new culture was grown to an OD_{600} of ~10 at 30 °C and 150 rpm overnight (approx. 22 h). At this point, IPTG was added to a concentration of 2 mM, and shaking was continued at 20 °C and 100 rpm for 24 h. The cells were harvested by centrifugation (8000 rpm, 4 °C, 20 min), resuspended in potassium phosphate buffer (20 mM, pH 7.0), and centrifuged again (8000 rpm, 20 min) to give ~30 g of wet cells per liter of culture, which were disrupted by ultrasonication as described below.

Heterologous expression of *Lb*ADH: LB medium (25 mL; containing 100 μg/mL ampicillin) was inoculated from a glycerol stock (50 μL) of *E. coli* BL21Star (DE3) harboring the [pASK-IBA5plus–*Lb*ADH] plasmid, and the culture was grown to an OD_{600} of >2 at 30 °C and 150 rpm overnight. An aliquot (5 mL) of this starter culture was used to inoculate TB medium (500 mL; containing 100 μg/mL ampicillin), and the new culture was grown to an OD_{600} of 0.9 at 30 °C and 150 rpm (approx. 3 h). At this point, anhydrotetracycline was added to a concentration of 200 μg/L, and shaking was continued at 20 °C and 120 rpm for 24 h. The cells were harvested by centrifugation (8000 rpm, 4 °C, 20 min), resuspended in potassium phosphate buffer (20 mM, pH 7.0), and centrifuged again (8000 rpm, 20 min) to give ~40 g of wet cells per liter of culture, which were disrupted by ultrasonication as described below.

Cell disruption and lyophilisation: Cell pellets obtained as described above were resuspended in potassium phosphate buffer (20 mM, pH 7.0; ~5 mL per gram of cell wet weight) and aliquots of ~15 mL were sonicated at 4 °C using a *Branson* Sonifier 250 at 10% output (25 W), 0.3 s pulse, 0.7 s pause for 15 min. Cell debris was removed by centrifugation (20,000 rpm, 4 °C, 30 min), and the supernatant was shock-frozen in liquid nitrogen and lyophilized overnight.

Biotransformations

Spectrophotometric assay for ADH activity: In a plastic cuvette (1.5 mL, 1 cm pathlength), a stock solution of ADH (1 mg/mL; final conc. 0.1 mg/mL) and NAD(P)$^+$ (0.7

mg/mL, 1 mM; final conc. 100 μM) in potassium phosphate buffer or Tris-HCl buffer (100 μL; 100 mM, pH 7.0, 1 mM $MgSO_4$) was diluted with the same buffer (850 μL). The cuvette was placed into a spectrophotometer (*Shimadzu* UV-2401PC), and the absorbance at 340 nm was recorded for 10 s (1 measurement/s). Then, 2-propanol (50 μL; final conc. 5% v/v, approx. 650 mM) was added and the absorbance was recorded for another 170 s. Blank reactions without enzyme or 2-propanol were set up in the same way and showed stable absorbance readings.

Slopes were determined by applying a linear fit to the linear region of absorbance increase (minimum 7 data points), and 2-propanol oxidation activity was calculated using the formula given below:

$$A = \frac{\Delta abs}{\varepsilon \cdot L \cdot c(\mathrm{ADH})}$$

where A [U·mg] … ADH activity; Δabs [min^{-1}] … slope of absorbance increase; ε [$mM^{-1}\cdot cm^{-1}$] … extinction coefficient of NADH (6.22 at 340 nm); L [cm] … cuvette path length; c(ADH) [$mg\cdot mL^{-1}$] … ADH concentration.

Reduction of azido ketone 3a catalysed by ADHs at varied substrate concentration: In a microcentrifuge tube (2 mL), 2-azidoacetophenone (**2a**; 4–40 mg, 25–250 μmol; final conc. 50–500 mM) was dissolved in 2-propanol (25 μL; final conc. 5% v/v, approx. 650 mM). Potassium phosphate buffer (425 μL; 100 mM, pH 7.0, 1 mM $MgSO_4$) and a stock solution of ADH (1 mg/mL; final conc. 0.1 mg/mL) and $NAD(P)^+$ (0.7 mg/mL, 1 mM; final conc. 100 μM) in potassium phosphate buffer (50 μL) were added, and the mixture was shaken at 30 °C and 1,000 rpm on a thermoshaker for 2 h. The reaction mixture was extracted with EtOAc (800 μL), the extract was dried over $MgSO_4$ and conversion as well as product *ee* were determined by GC–FID analysis, whereby the samples from reactions using more than 150 mM **2a** were diluted before analysis.

Time-course experiments of the reduction of azido ketone 2a: In a microcentrifuge tube (2 mL), 2-azidoacetophenone (**2a**; 8 mg, 50 μmol; final conc. 100 mM) was dissolved in 2-propanol (25 μL; final conc. 5% v/v, approx. 650 mM). Potassium phosphate buffer (425 μL; 100 mM, pH 7.0, 1 mM $MgSO_4$) and a stock solution of ADH (1 mg/mL; final conc. 0.1 mg/mL) and $NAD(P)^+$ (0.7 mg/mL, 1 mM; final conc. 100 μM) in potassium phosphate buffer (50 μL) were added, and the mixture was shaken at 30 °C and 1,000 rpm on a thermoshaker for 1–24 h. The reaction mixture was extracted with EtOAc (800 μL), the extract was dried over $MgSO_4$ and conversion as well as product *ee* were determined by GC–FID analysis.

Preparative-scale reduction of azido ketone 2a using KRED-NADH-110: In a Falcon tube (50 mL), 2-azidoacetophenone (**2a**; 202 mg, 1.25 mmol) was dissolved in 2-propanol (1.25 mL; final conc. 5% v/v, approx. 650 mM). Potassium phosphate buffer (22.75 mL; 100 mM, pH 7.0, 1 mM $MgSO_4$) and a stock solution of *Codexis* KRED-NADH-110 (2.5 mg) and NAD^+ (1.6 mg, 2.5 μmol) in potassium phosphate buffer (1 mL) were added and the mixture was shaken at 30 °C and 180 rpm in a shaking incubator for 18 h. The reaction mixture was extracted with EtOAc (3 × 10 mL), and the combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure to give 204 mg (quant.) of (*S*)-2-azido-1-phenylethanol as a yellow liquid. TLC (silica, hexanes/EtOAc = 3/1): R_f = 0.71. $[\alpha]_D^{20}$ = +94.4 (*c* 1.0, $CHCl_3$), lit. (*R*)[23] –92.8 (*c* 1.08, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.33 (1H, br s, OH), 3.43 (1H, dd, J = 12.4 Hz, 4.0 Hz, CH_2), 3.49 (1H, dd, J = 12.4 Hz, 8.2 Hz, CH_2), 4.87 (1H, dd, J = 8.0 Hz, 4.0 Hz, C*H*-OH), 7.31–7.41 (5H, m, Ar). ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 58.0, 73.4, 125.9, 128.3, 128.7, 140.5. GC–MS (EI, 70 eV): m/z = 107 (100), 79 (98), 77 (70), 51 (24). The NMR data are in accordance with those obtained for the racemic compound.

Analytical methods

GC–FID analysis (achiral stationary phase): Conversions were determined by GC analysis on a *Shimadzu* GC-2014 system using nitrogen as carrier gas and an *Agilent* CP-Sil 5 CB column (100% dimethylpolysiloxane stationary phase, 50 m × 0.53 mm × 1.0 μm). The following acquisition parameters were used:

Method A. Oven program: 60 °C for 0.2 min, 50 °C/min to 120 °C for 10 min, 50 °C/min to 320 °C for 1 min; total flow rate: 20 mL/min; injector temperature: 220 °C; detector temperature: 350 °C; splitless injection.

Method B. Oven program: 60 °C for 0.2 min, 50 °C/min to 140 °C for 10 min, 50 °C/min to 320 °C for 1 min; total flow rate: 20 mL/min; injector temperature: 220 °C; detector temperature: 350 °C; splitless injection.

Method C. Oven program: 60 °C for 0.2 min, 50 °C/min to 160 °C for 10 min, 50 °C/min to 320 °C for 1 min; total flow rate: 20 mL/min; injector temperature: 220 °C; detector temperature: 350 °C; splitless injection.

Method D. Oven program: 60 °C for 0.2 min, 50 °C/min to 100 °C for 10 min, 50 °C/min to 320 °C for 1 min; total flow rate: 20 mL/min; injector temperature: 220 °C; detector temperature: 350 °C; splitless injection.

The retention times of all analysed compounds are given in Suppl. Table 8:

Compound	Method	t_r [min]
2-Chloroacetophenone (**1a**)	A	5.8
2-Azidoacetophenone (**2a**)	A	9.8
2-Azido-1-phenylethanol (**3a**)	A	9.4
2-Amino-1-phenylethanol (**4a**)	A	6.5
2,2-Dimethyl-5-phenyloxazolidine (**5a**)	A	9.4
2-Bromo-4′-chloroacetophenone (**1b**)	B	8.2
2-Azido-4′-chloroacetophenone (**2b**)	B	10.2
2-Azido-1-(4-chlorophenyl)ethanol (**3b**)	B	11.1
2-Amino-1-(4-chlorophenyl)ethanol (**4b**)	B	8.0
5-(4-Chlorophenyl)-2,2-dimethyloxazolidine (**5b**)	B	11.3
2-Bromo-4′-fluoroacetophenone (**1c**)	A	7.4
2-Azido-4′-fluoroacetophenone (**2c**)	A	8.9
2-Azido-1-(4-fluorophenyl)ethanol (**3c**)	A	9.5
2-Amino-1-(4-fluorophenyl)ethanol (**4c**)	A	6.5
2,2-Dimethyl-5-(4-fluorophenyl)oxazolidine (**5c**)	A	9.6
2-Bromo-4′-methylacetophenone (**1d**)	B	7.5
2-Azido-4′-methylacetophenone (**2d**)	B	8.9
2-Azido-1-(4-tolyl)ethanol (**3d**)	B	7.9
2-Amino-1-(4-tolyl)ethanol (**4d**)	B	5.9
2,2-Dimethyl-5-(4-tolyl)oxazolidine (**5d**)	B	8.1
2-Bromo-4′-methoxyacetophenone (**1e**)	C	7.9
2-Azido-4′-methoxyacetophenone (**2e**)	C	9.1
2-Azido-1-(4-methoxyphenyl)ethanol (**3e**)	C	7.7
2-Amino-1-(4-methoxyphenyl)ethanol (**4e**)	C	6.0
2,2-Dimethyl-5-(4-methoxyphenyl)oxazolidine (**5e**)	C	8.1
2-Bromo-1-(2-furyl)ethanone (**1f**)	D	7.4
2-Azido-1-(2-furyl)ethanone (**2f**)	D	9.6
2-Azido-1-(2-furyl)ethanol (**3f**)	D	7.5
2-Amino-1-(2-furyl)ethanol (**4f**)	D	4.6
2,2-Dimethyl-5-(2-furyl)oxazolidine (**5f**)	D	7.3

Suppl. Table 8. GC–FID retention times (achiral stationary phase) of investigated compounds.

GC–MS analysis (achiral stationary phase): GC–MS analysis was carried out on a *Shimadzu* GC-2010 system coupled to a *Shimadzu* GCMS-QP2010S mass-selective detector, using helium as carrier gas and a *Varian* FactorFour VF-1ms column (25 m × 0.25 mm × 0.4 μm). The following acquisition parameters were used: Oven program: 60 °C for 3 min, 15 °C/min to 315 °C for 2 min; linear velocity: 37 cm/s; injector temperature: 250 °C; ion source temperature: 200 °C; interface temperature: 250 °C; ionisation energy: 70 eV; split ratio: 20/1. The retention times of all analysed compounds are given in Suppl. Table 9:

Compound	t_r [min]
2-Chloroacetophenone (**1a**)	9.5
2-Azidoacetophenone (**2a**)	11.9
2-Azido-1-phenylethanol (**3a**)	10.6
2-Amino-1-phenylethanol (**4a**)	9.7
2,2-Dimethyl-5-phenyloxazolidine (**5a**)	10.6
2-Bromo-4′-chloroacetophenone (**1b**)	11.8
2-Azido-4′-chloroacetophenone (**2b**)	12.1
2-Azido-1-(4-chlorophenyl)ethanol (**3b**)	12.3
2-Amino-1-(4-chlorophenyl)ethanol (**4b**)	11.6
5-(4-Chlorophenyl)-2,2-dimethyloxazolidine (**5b**)	12.4
2-Bromo-4′-fluoroacetophenone (**1c**)	10.1
2-Azido-4′-fluoroacetophenone (**2c**)	10.5
2-Azido-1-(4-fluorophenyl)ethanol (**3c**)	10.6
2-Amino-1-(4-fluorophenyl)ethanol (**4c**)	10.0
2,2-Dimethyl-5-(4-fluorophenyl)oxazolidine (**5c**)	10.7
2-Bromo-4′-methylacetophenone (**1d**)	11.4
2-Azido-4′-methylacetophenone (**2d**)	11.8
2-Azido-1-(4-tolyl)ethanol (**3d**)	11.5
2-Amino-1-(4-tolyl)ethanol (**4d**)	10.8
2,2-Dimethyl-5-(4-tolyl)oxazolidine (**5d**)	11.6
2-Bromo-4′-methoxyacetophenone (**1e**)	12.9
2-Azido-4′-methoxyacetophenone (**2e**)	13.2
2-Azido-1-(4-methoxyphenyl)ethanol (**3e**)	12.7
2-Amino-1-(4-methoxyphenyl)ethanol (**4e**)	12.1
2,2-Dimethyl-5-(4-methoxyphenyl)oxazolidine (**5e**)	12.9
2-Bromo-1-(2-furyl)ethanone (**1f**)	8.8
2-Azido-1-(2-furyl)ethanone (**2f**)	9.3
2-Azido-1-(2-furyl)ethanol (**3f**)	8.7
2-Amino-1-(2-furyl)ethanol (**4f**)	7.8
2,2-Dimethyl-5-(2-furyl)oxazolidine (**5f**)	8.7

Suppl. Table 9. GC–MS retention times (achiral stationary phase) of investigated compounds.

GC–FID analysis (chiral stationary phase): The enantiomeric excess of compounds **3a** and **3f** was determined by GC analysis on a *Shimadzu* GC-2010 system using helium as carrier gas and an *Astec* Chiraldex G-TA column (2,6-di-*O*-pentyl-3-trifluoroacetyl-derivatised β-cyclodextrin stationary phase, 50 m × 0.25 mm × 0.12 μm). The following acquisition parameters were used:

Method A. Oven program: 80 °C for 1 min, 15 °C/min to 135 °C for 21 min, 15 °C/min to 170 °C for 2 min; linear velocity: 20 cm/s; injector temperature: 200 °C; detector temperature: 220 °C; split ratio: 75/1.

Method B. Oven program: 80 °C for 1 min, 15 °C/min to 115 °C for 21 min, 15 °C/min to 170 °C for 2 min; linear velocity: 20 cm/s; injector temperature: 200 °C; detector temperature: 220 °C; split ratio: 75/1.

The retention times of both compounds are given in Suppl. Table 10:

Compound	Method	t_r (*R*) [min]	t_r (*S*) [min]
2-Azido-1-phenylethanol (**3a**)	A	24.4	24.8
2-Azido-1-(2-furyl)ethanol (**3f**)	B	21.7	22.1

Suppl. Table 10. GC–FID retention times (chiral stationary phase) of compounds **3a** and **3f**.

For chiral-phase GC analysis of 1,2-amino alcohols **4a–f**, samples were converted into the corresponding dimethyloxazolidines **5a–f**: The amino alcohol (5 mg) was dissolved in acetone (1 mL), $MgSO_4$ (10 mg) was added, and the reaction mixture was shaken on a Thermoshaker at room temperature for 2 h. The solid was removed by centrifugation, and the supernatant was transferred to a GC vial for analysis.

The enantiomeric excess of compounds **5a–f** was determined by GC analysis on a *Shimadzu* GC-2010plus system using helium as carrier gas and an *Agilent* CP-Chirasil-DEX CB column (dimethylpolysiloxane-bonded β-cyclodextrin stationary phase, 25 m × 0.32 mm × 0.25 μm). The following acquisition parameters were used:

Method A. Oven program: 60 °C for 0.1 min, 15 °C/min to 150 °C for 14 min, 15 °C/min to 240 °C for 2 min; linear velocity: 20 cm/s; injector temperature: 250 °C; detector temperature: 275 °C; split ratio: 75/1.

Method B. Oven program: 60 °C for 0.1 min, 15 °C/min to 160 °C for 20 min, 15 °C/min to 240 °C for 2 min; linear velocity: 20 cm/s; injector temperature: 250 °C; detector temperature: 275 °C; split ratio: 75/1.

Method C. Oven program: 60 °C for 0.1 min, 15 °C/min to 155 °C for 14 min, 15 °C/min to 240 °C for 2 min; linear velocity: 20 cm/s; injector temperature: 250 °C; detector temperature: 275 °C; split ratio: 75/1.

Method D. Oven program: 60 °C for 0.1 min, 15 °C/min to 180 °C for 14 min, 15 °C/min to 240 °C for 2 min; linear velocity: 20 cm/s; injector temperature: 250 °C; detector temperature: 275 °C; split ratio: 75/1.

Method E. Oven program: 60 °C for 0.1 min, 15 °C/min to 130 °C for 14 min, 15 °C/min to 240 °C for 2 min; linear velocity: 20 cm/s; injector temperature: 250 °C; detector temperature: 275 °C; split ratio: 75/1.

The retention times of all analysed compounds are given in Suppl. Table 11:

Compound	Method	t_r (*R*) [min]	t_r (*S*) [min]
2,2-Dimethyl-5-phenyloxazolidine (**5a**)	A	16.2	17.0
5-(4-Chlorophenyl)-2,2-dimethyloxazolidine (**5b**)	B	24.5	26.6
2,2-Dimethyl-5-(4-fluorophenyl)oxazolidine (**5c**)	A	17.3	18.2
2,2-Dimethyl-5-(4-tolyl)oxazolidine (**5d**)	C	19.2	19.9
2,2-Dimethyl-5-(4-methoxyphenyl)oxazolidine (**5e**)	D	17.5	18.3
2,2-Dimethyl-5-(2-furyl)oxazolidine (**5f**)	E	13.9	14.6

Suppl. Table 11. GC–FID retention times (chiral stationary phase) of compounds **5a–5f**.

HPLC analysis (chiral stationary phase): The enantiomeric excess of compounds **3b–d** was determined by HPLC analysis using a setup consisting of an *Alltech* Elite degassing system, a *Waters* 515 HPLC pump, a *Waters* 717plus autosampler, a *Chrompack* SpH 99 column thermostat, and a *Shimadzu* SPD-10A UV-Vis detector. Separations of were performed on a *Daicel* Chiralcel OD column (cellulose tris-3,5-dimethylphenylcarbamate stationary phase, 250 mm × 4.6 mm × 10 μm) using *n*-heptane/2-propanol (95/5) as eluent. The following acquisition parameters were used: Column temperature: 25 °C; flow rate: 0.5 mL/min; detection wavelength: 254 nm.

The retention times of all analysed compounds are given in Suppl. Table 12:

Compound	t_r (*R*) [min]	t_r (*S*) [min]
2-Azido-1-phenylethanol (**3a**)	26.0	28.7
2-Azido-1-(4-chlorophenyl)ethanol (**3b**)	21.8	25.6
2-Azido-1-(4-fluorophenyl)ethanol (**3c**)	19.6	21.9
2-Azido-1-(4-methylphenyl)ethanol (**3d**)	21.8	26.4

Suppl. Table 12. HPLC retention times (chiral stationary phase) of compounds **3a–3d**.

The enantiomeric excess of **3e** was determined by HPLC analysis on the same system, using a *Daicel* Chiralpak AD-H column (amylose tris-3,5-dimethylphenylcarbamate stationary phase, 250 mm × 4.6 mm × 5 μm) and *n*-heptane/2-propanol (98/2) as eluent. The following acquisition parameters were used: Column temperature: 40 °C; flow rate: 1.0 mL/min; detection wavelength: 254 nm. Retention times: 61.0 min (*R*), 65.2 min (*S*).
The enantiomeric excess of tembamide was determined by HPLC analysis on the same system, using a *Daicel* Chiralpak AD-H column (amylose tris-3,5-dimethylphenylcarbamate stationary phase, 250 mm × 4.6 mm × 5 μm) and *n*-heptane/2-propanol (90/10) as eluent. The following acquisition parameters were used: Column temperature: 25 °C; flow rate: 0.3 mL/min; detection wavelength: 254 nm. Retention times: 82.9 min (*S*), 86.5 min (*R*).

Determination of absolute configuration: The absolute configurations of azido alcohol **3a**, amino alcohols **4**, and tembamide were determined from the sign of their optical rotation. The absolute configurations of the remaining azido alcohols **3** were determined by elution order analogy (chiral-phase GC or HPLC) and from the absolute configurations of the corresponding amino alcohols **4**.

Transmission electron microscopy (TEM): TEM measurements were performed under vacuum using a 109 *Zeiss* EM equipped with built-in electromagnetic objective lenses and a camera. Samples of Pd nanoparticles were prepared by diluting the NP stock solution 10-fold with ultrapure water and placing 5 μL of the resulting solution onto 3 mm, 300 mesh, formvar/carbon nickel grids (*Agar Scientific Ltd.*), with the necessary time allowed for the evaporation of the solvent at room temperature (24 h).

Dynamic light scattering (DLS): The particle size distribution of Pd-NPs was determined on a *Malvern* Zetasizer Nano ZS instrument using the diffractive index of Pd for particle size calculation. Samples of Pd nanoparticles were prepared by diluting the NP stock solution 1000-fold with ultrapure water and filtering it through a syringe microfilter.

X-ray diffraction (XRD) spectroscopy: XRD analysis was performed on a *Rigaku* Miniflex II automated power XRD system (Cu Kα radiation, 45 kV, 100 mA). Diffraction data were recorded using continuous scanning at 3°/min, with 0.010° steps. Samples of Pd nanoparticles were prepared by concentrating the NP stock solution to dryness and placing the resulting solid powder on the glass plate of the instrument.

UV-Vis spectroscopy: UV-Vis spectra were recorded on a *Jenway* 6505 spectrophotometer, using a quartz cuvette of 0.1 cm path length, and an acquisition range of 200–600 nm. Samples of Pd nanoparticles were prepared by diluting the NP stock solution 5-fold with ultrapure water.

Chromatograms and spectra of isolated products

^{1}H-NMR spectra, ^{13}C-NMR spectra, MS spectra, and chiral-phase GC chromatograms (as 2,2-dimethyloxazolidine derivatives) are provided for the following compounds:

(*R*)-2-Amino-1-phenylethanol (**4a**), obtained by the two-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-phenylethanol (**4a**), obtained by the two-step one-pot sequence on 5 mL scale
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (**4b**), obtained by the two-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (**4b**), obtained by the two-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (**4c**), obtained by the two-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (**4c**), obtained by the two-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(4-tolyl)ethanol (**4d**), obtained by the two-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-tolyl)ethanol (**4d**), obtained by the two-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (**4e**), obtained by the two-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (**4e**), obtained by the two-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(2-furyl)ethanol (**4f**), obtained by the two-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(2-furyl)ethanol (**4f**), obtained by the two-step one-pot sequence (5 mL scale)

(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (**4b**), obtained by the two-step one-pot sequence (gram scale)

(*R*)-2-Amino-1-phenylethanol (**4a**), obtained by the three-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-phenylethanol (**4a**), obtained by the three-step one-pot sequence on 5 mL scale
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (**4b**), obtained by the three-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (**4b**), obtained by the three-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (**4c**), obtained by the three-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (**4c**), obtained by the three-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(4-tolyl)ethanol (**4d**), obtained by the three-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-tolyl)ethanol (**4d**), obtained by the three-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (**4e**), obtained by the three-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (**4e**), obtained by the three-step one-pot sequence (5 mL scale)
(*S*)-2-Amino-1-(2-furyl)ethanol (**4f**), obtained by the three-step one-pot sequence (5 mL scale)
(*R*)-2-Amino-1-(2-furyl)ethanol (**4f**), obtained by the three-step one-pot sequence (5 mL scale)

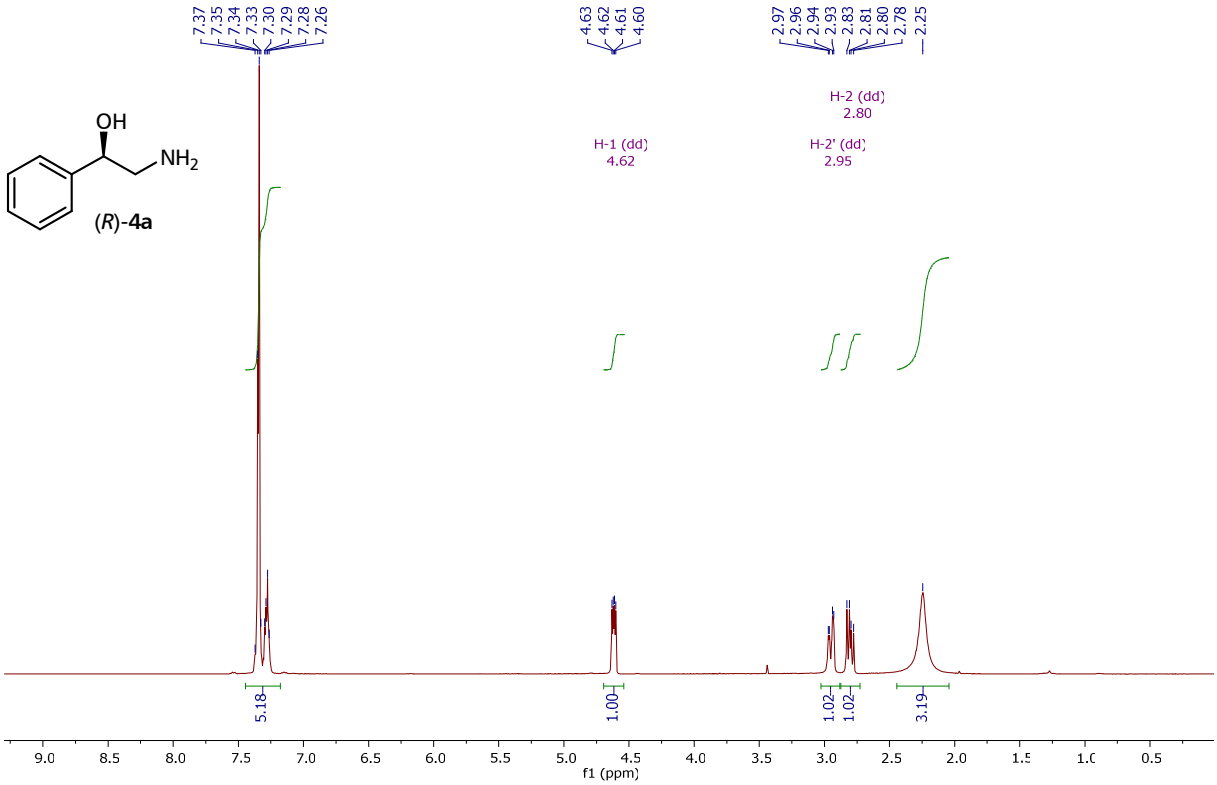
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (**4c**), obtained by the three-step one-pot sequence (gram scale)

The ^{1}H-NMR spectrum, ^{13}C-NMR spectrum, MS spectrum, and chiral-phase HPLC chromatograms are provided for (*S*)-tembamide, as obtained by the four-step one-pot sequence.

NOTE: A peak at 50 ppm is present in all ^{13}C-NMR spectra, in some cases in phase with the other signals, in some cases out of phase. This signal is an acquisition artefact of unknown origin, and was disregarded in the interpretation of all spectra.

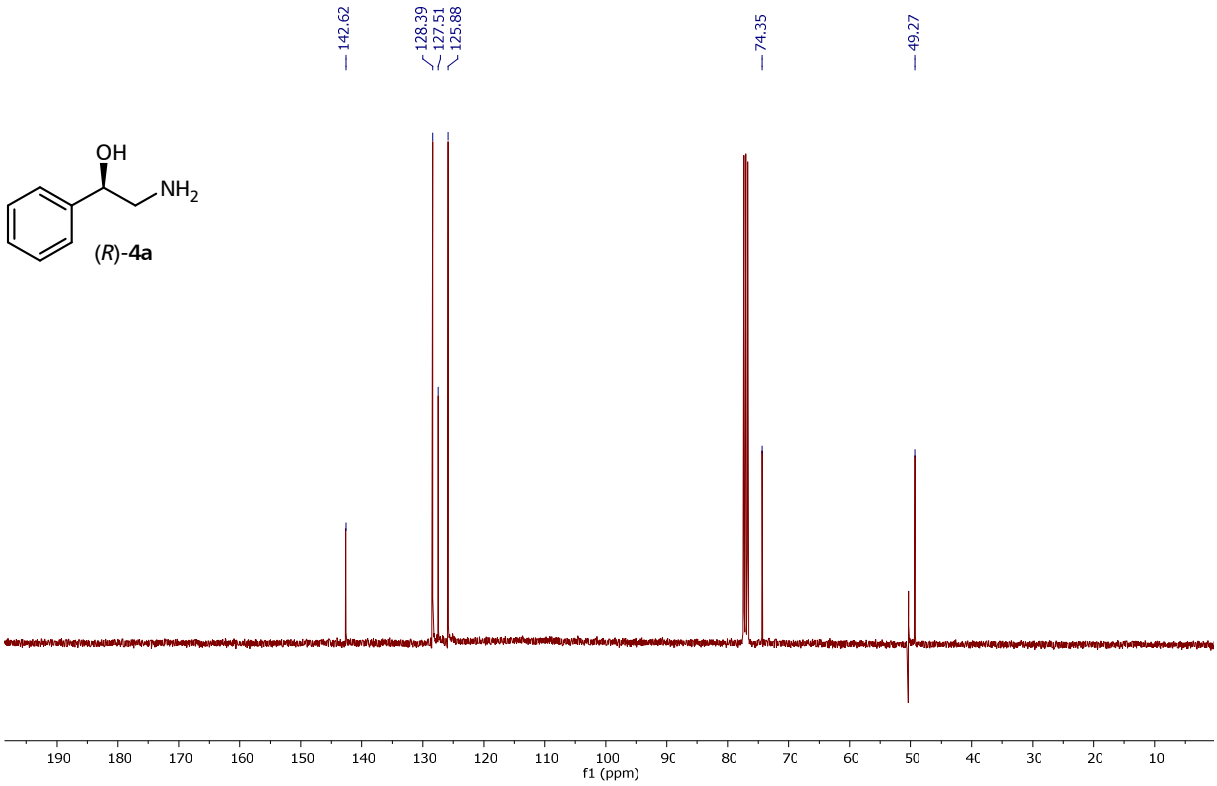
(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



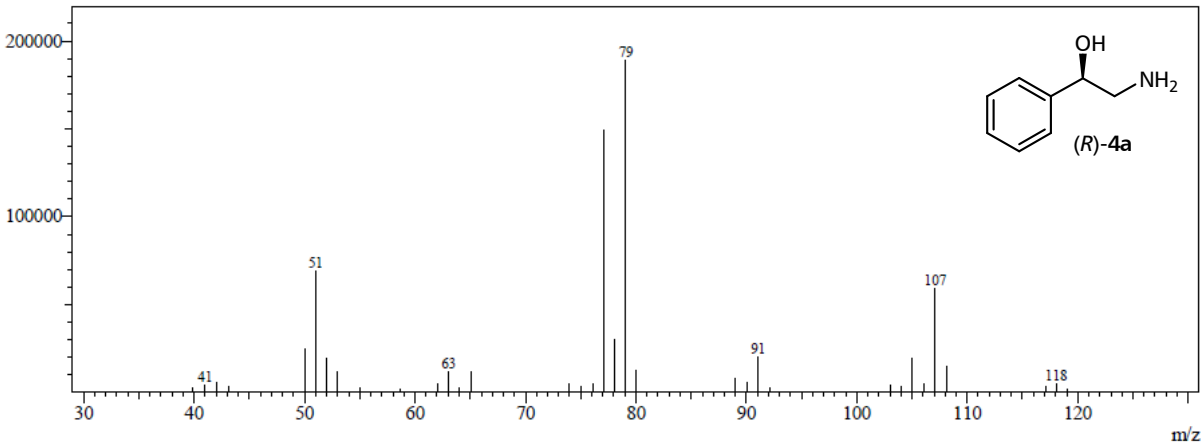
(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



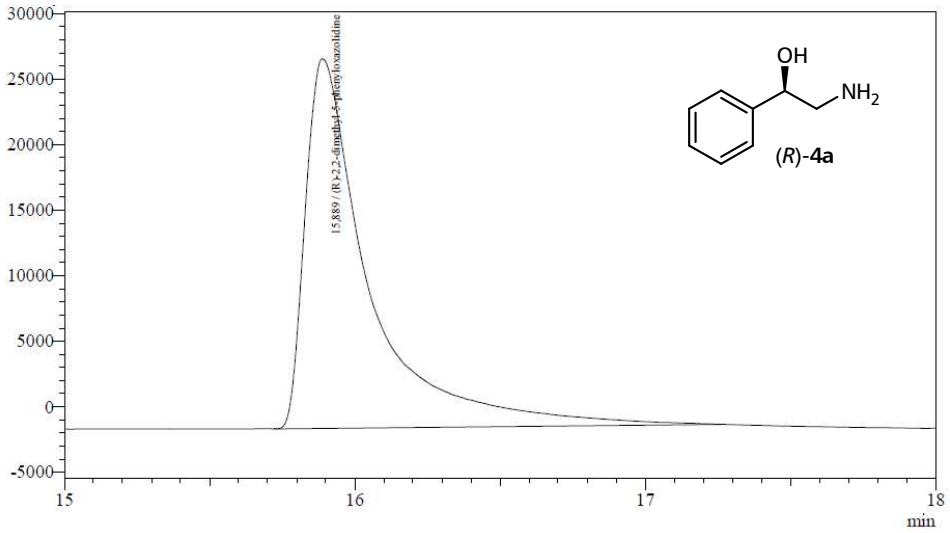
(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

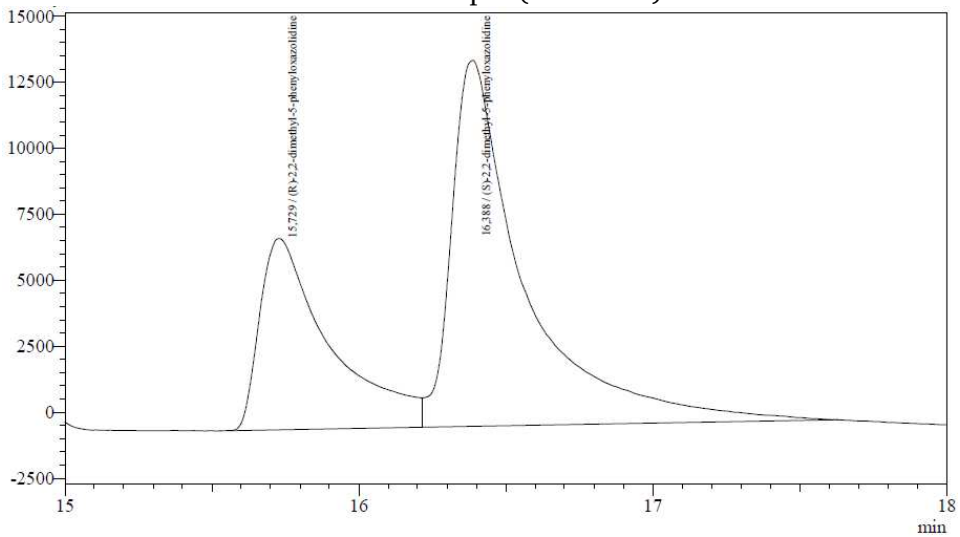


(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

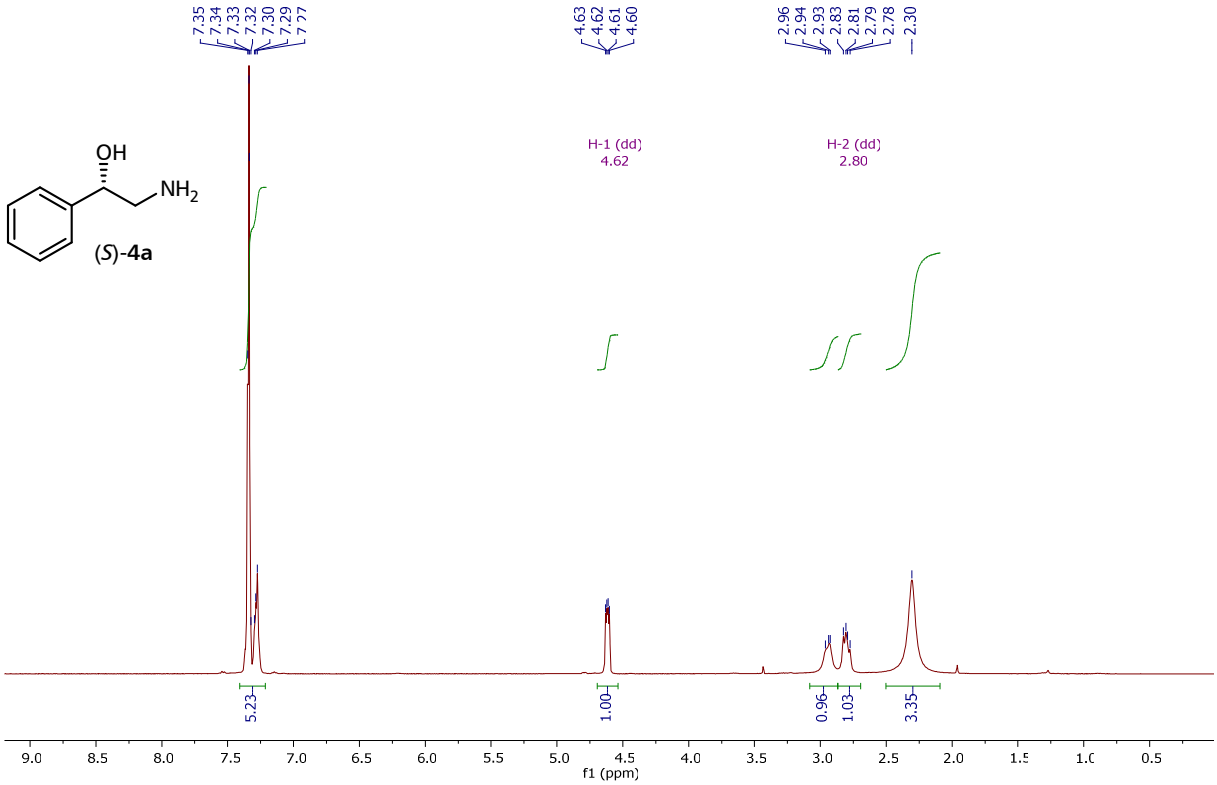


"racemic" sample (*ee* = 30%):



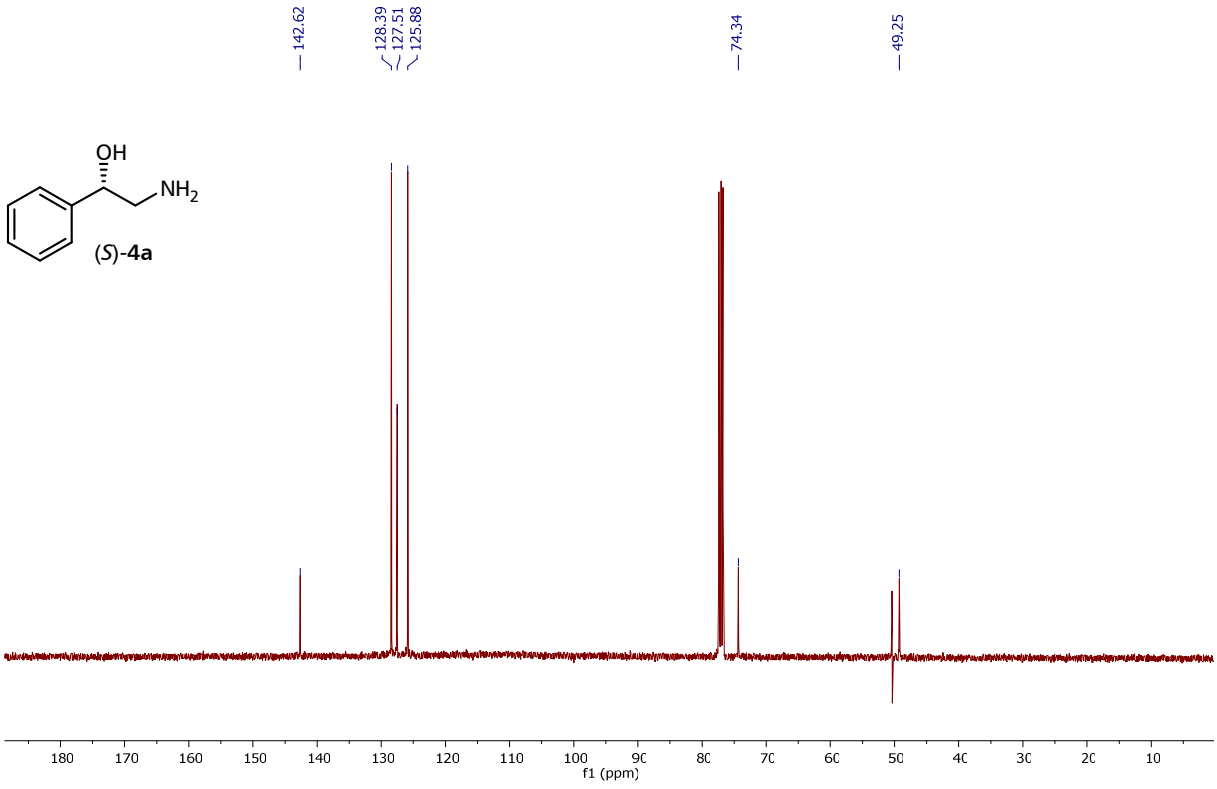
(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



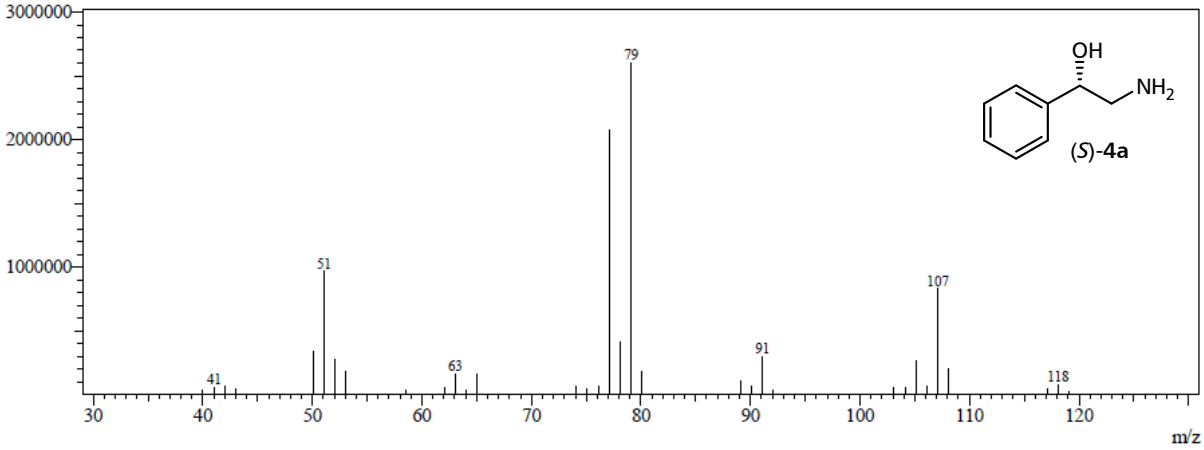
(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



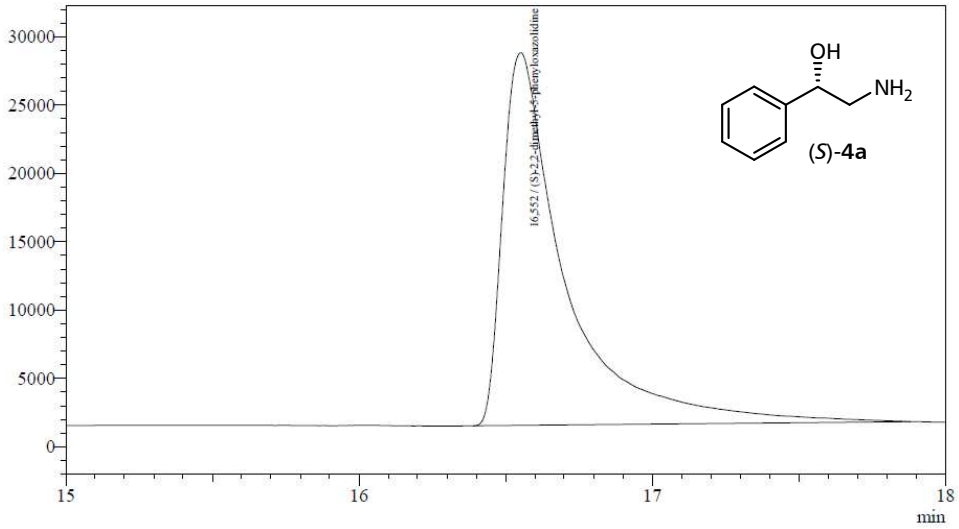
(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

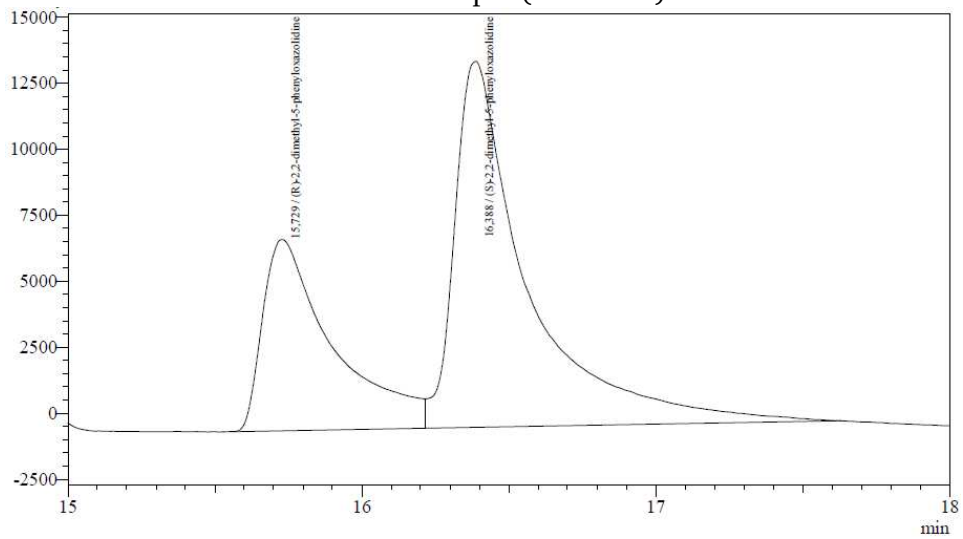


(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

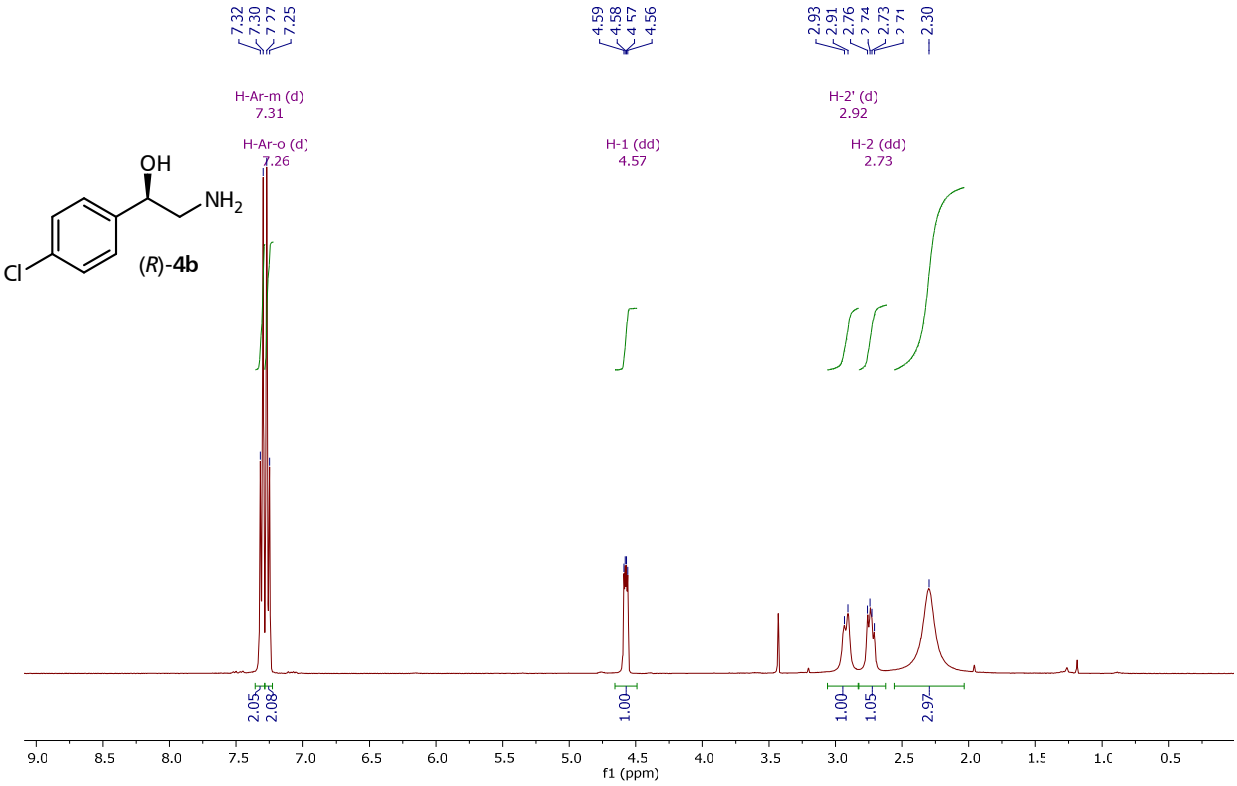


"racemic" sample (*ee* = 30%):



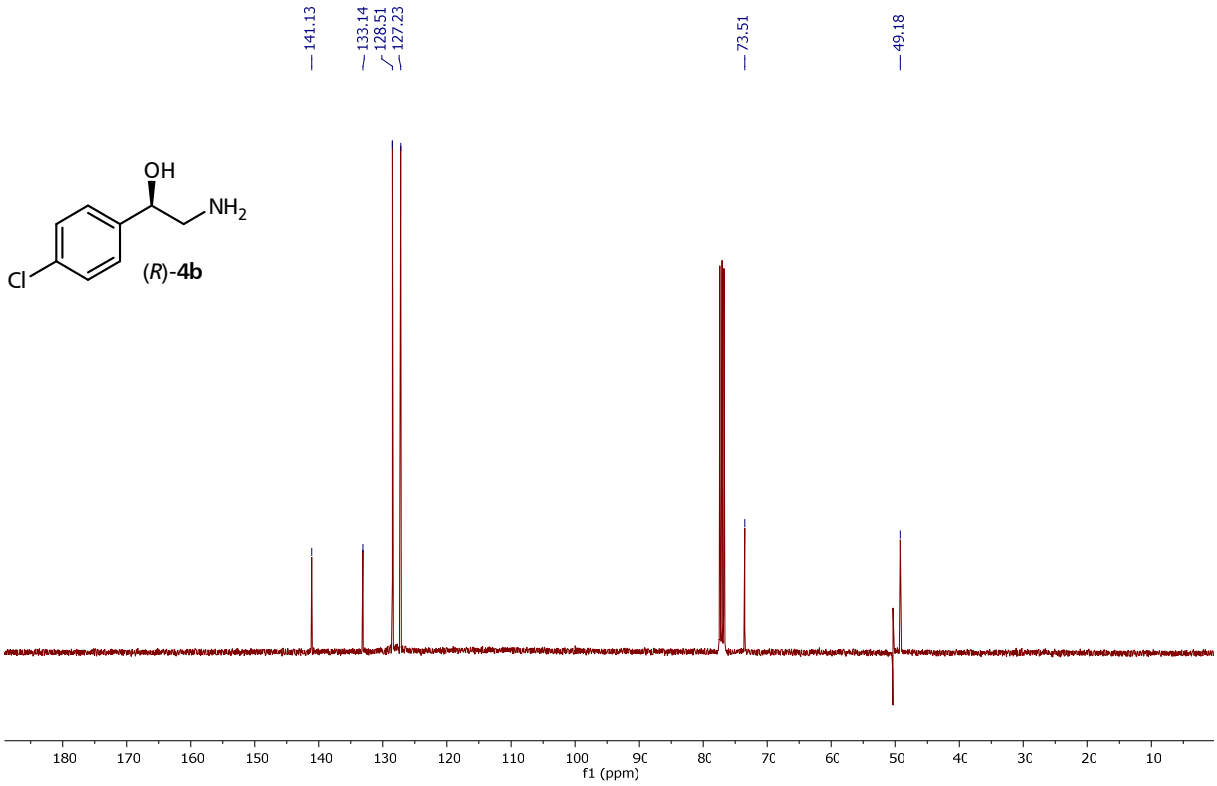
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



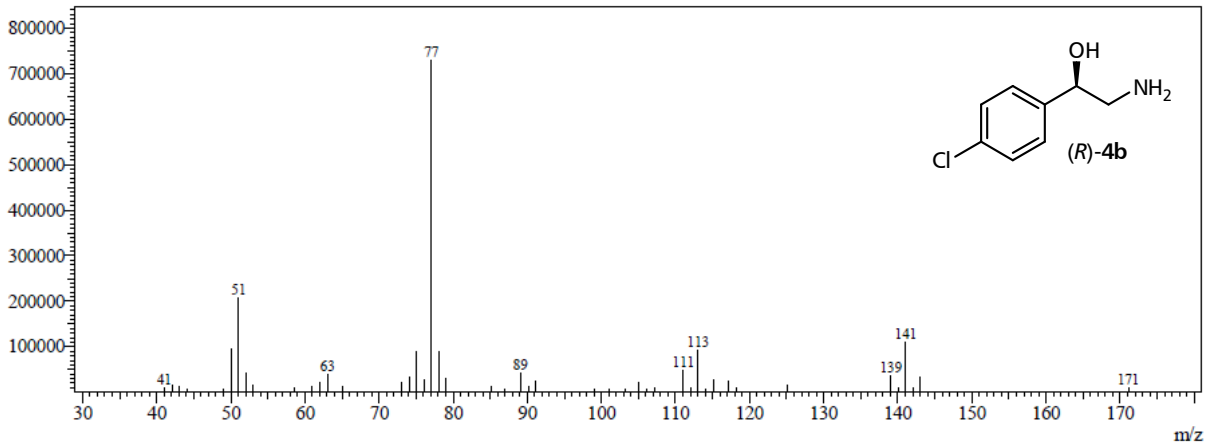
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



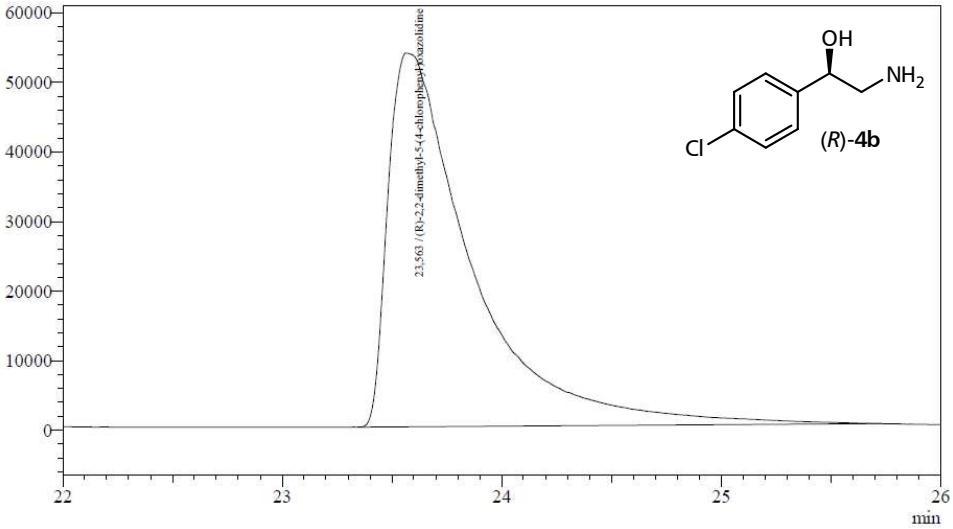
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

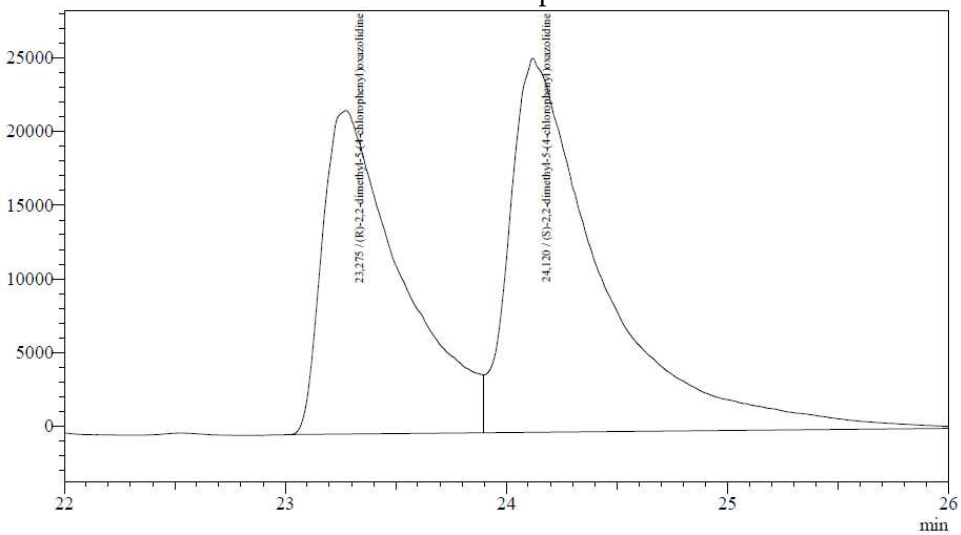


(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

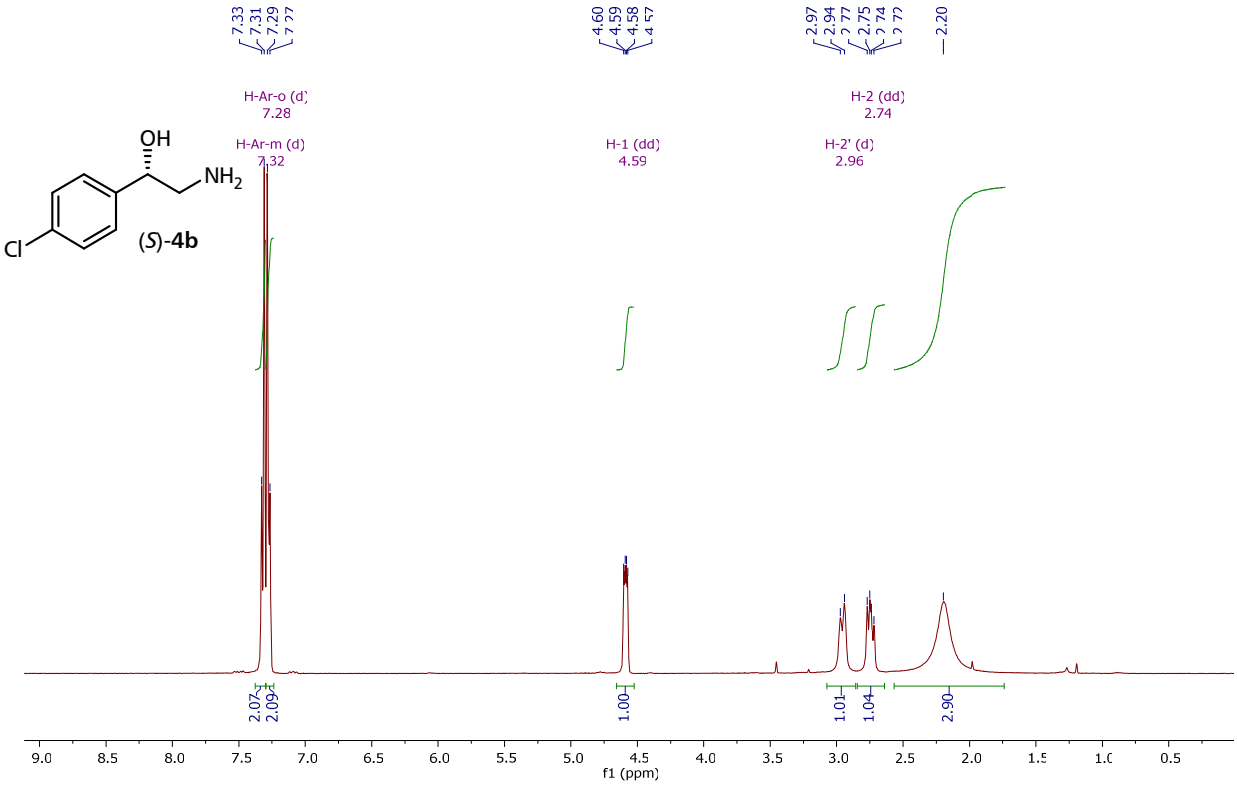


racemic sample:



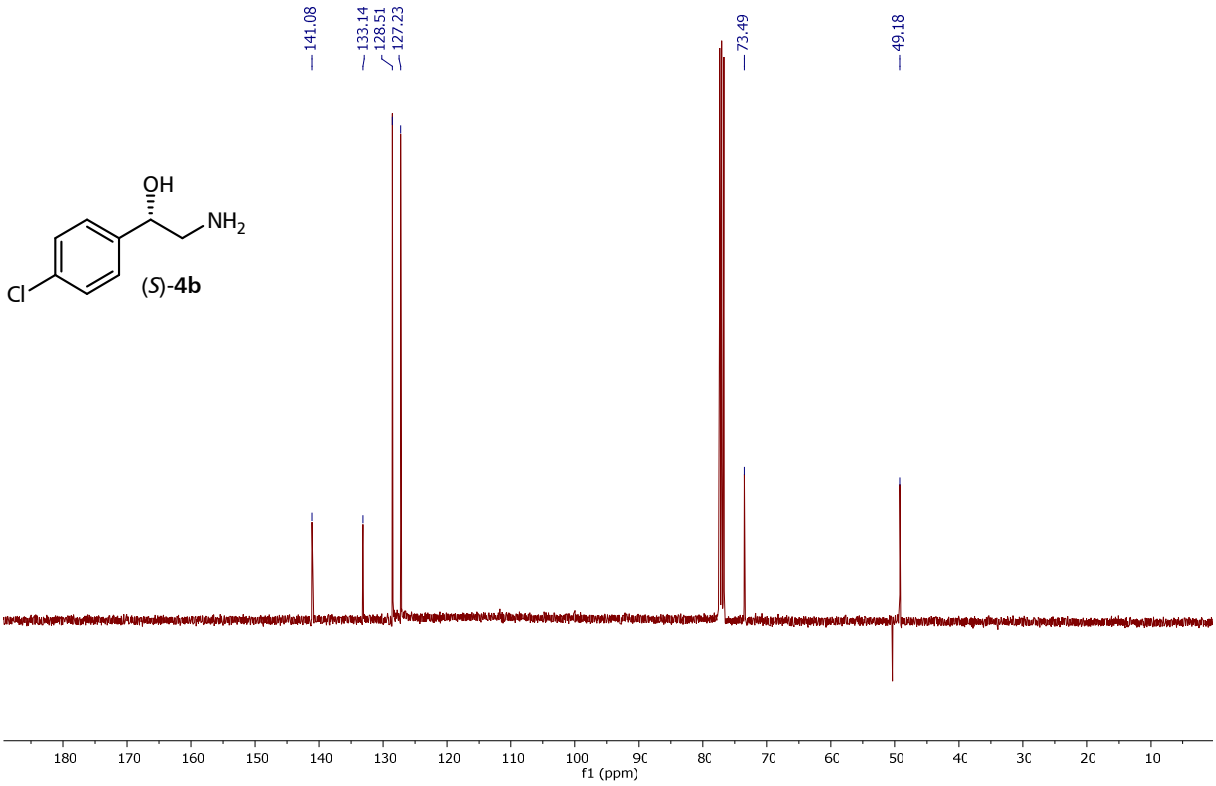
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



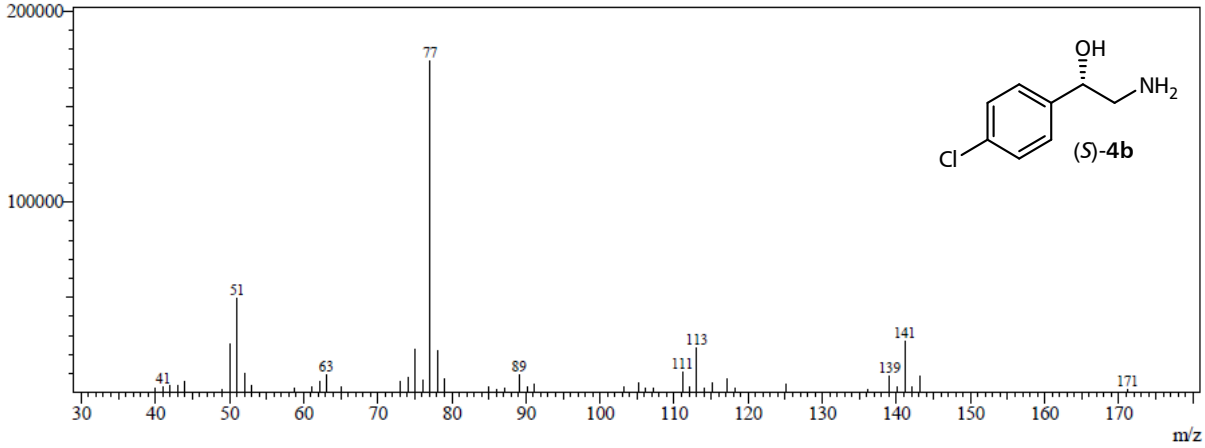
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



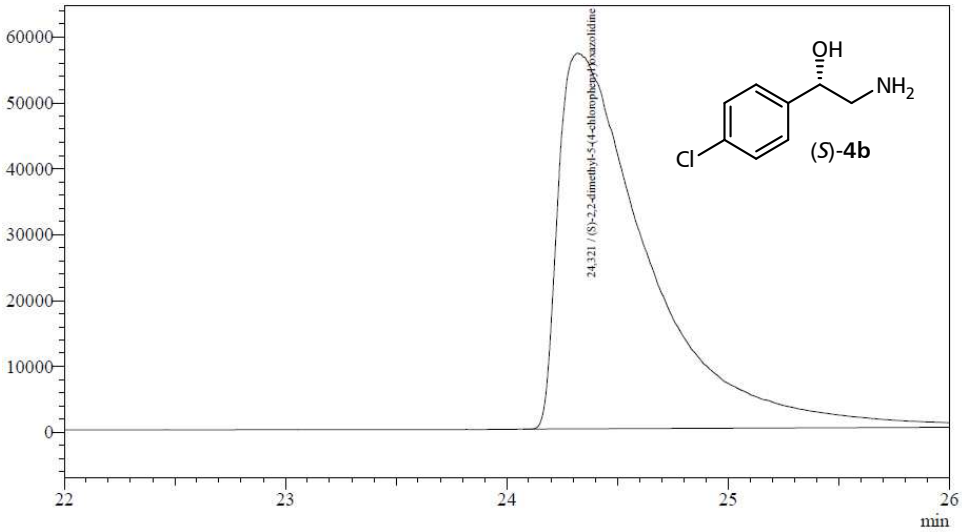
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*S*)-**4b**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

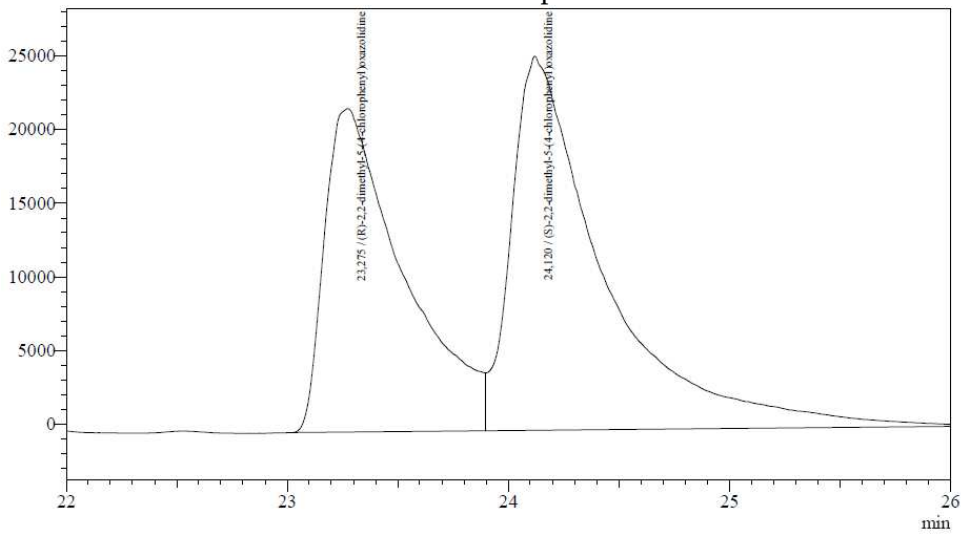


(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*S*)-**4b**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

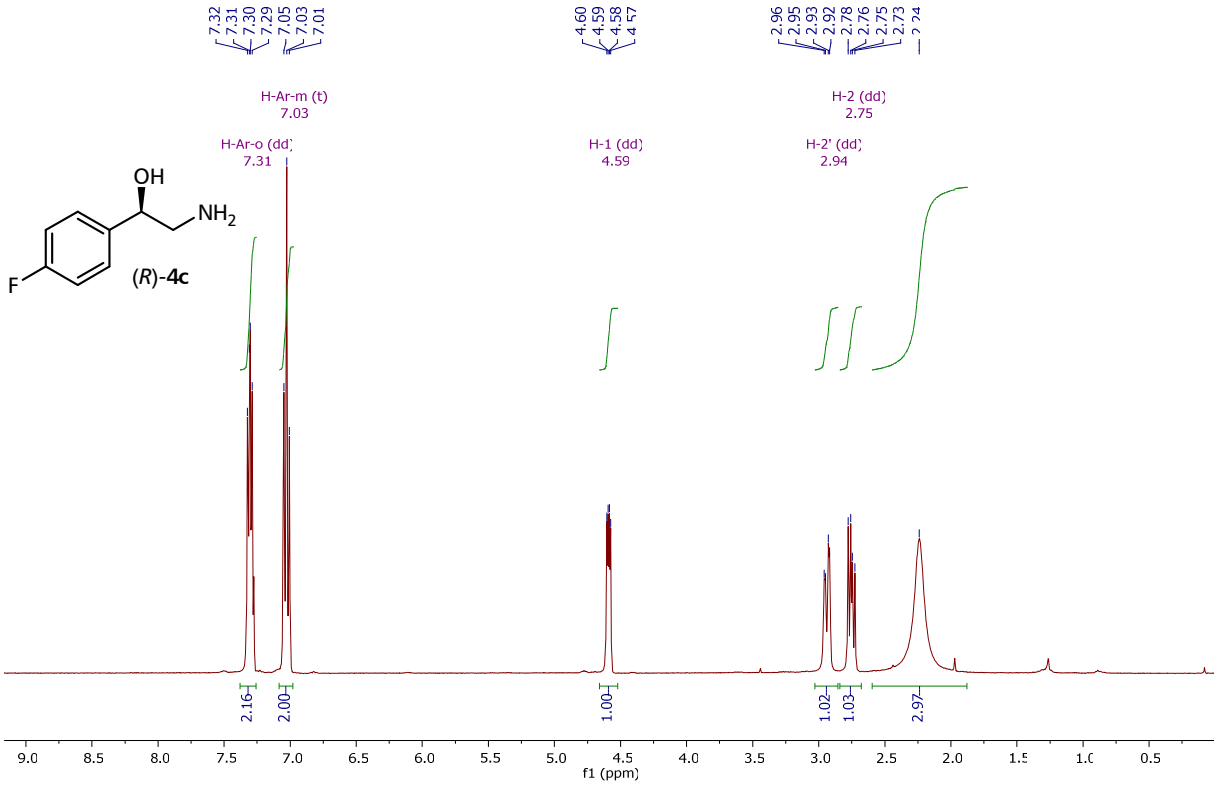


racemic sample:



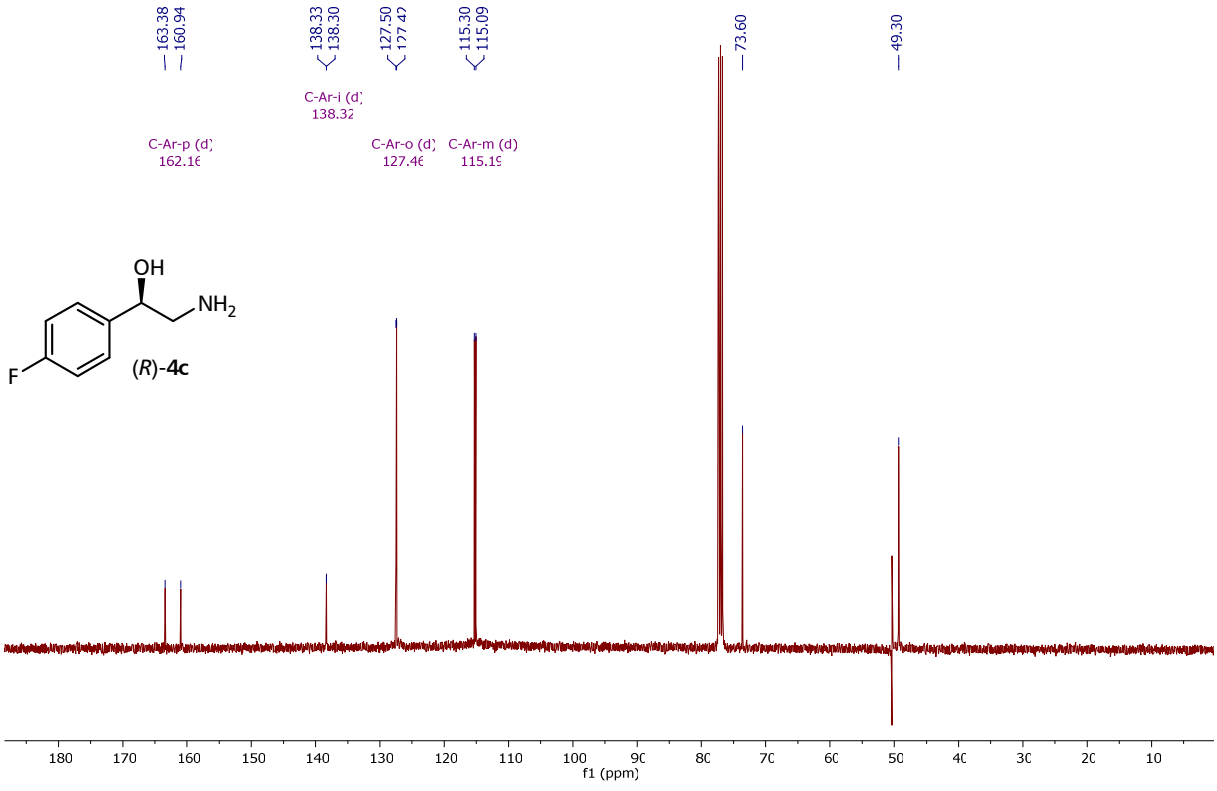
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



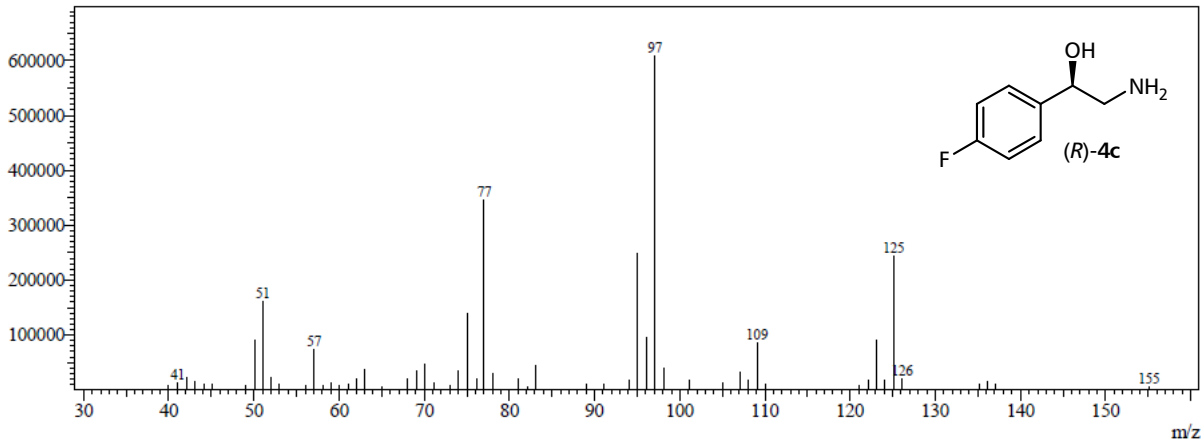
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



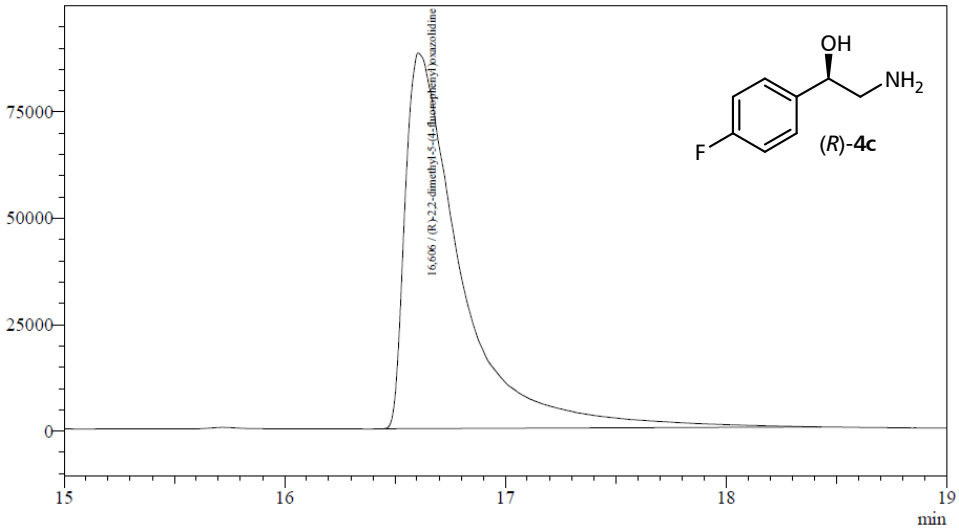
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

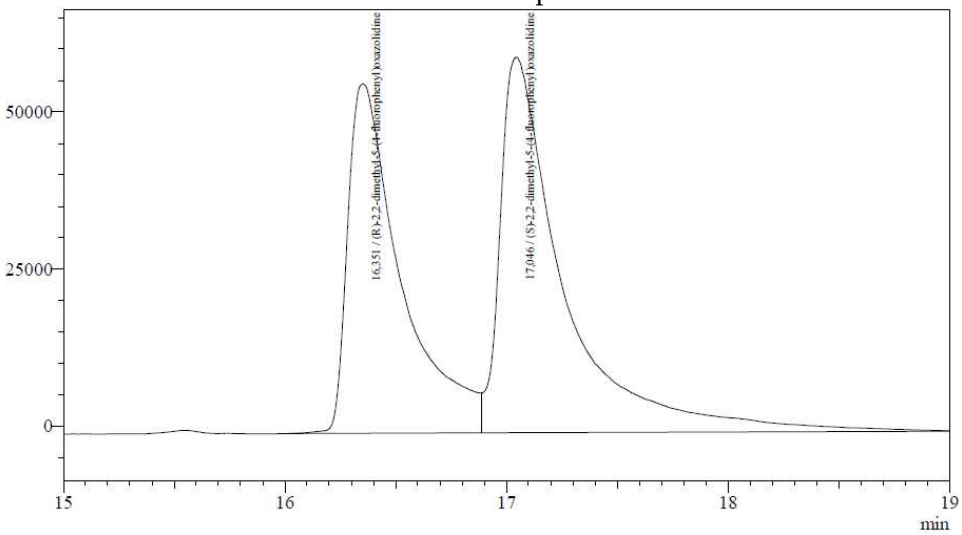


(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

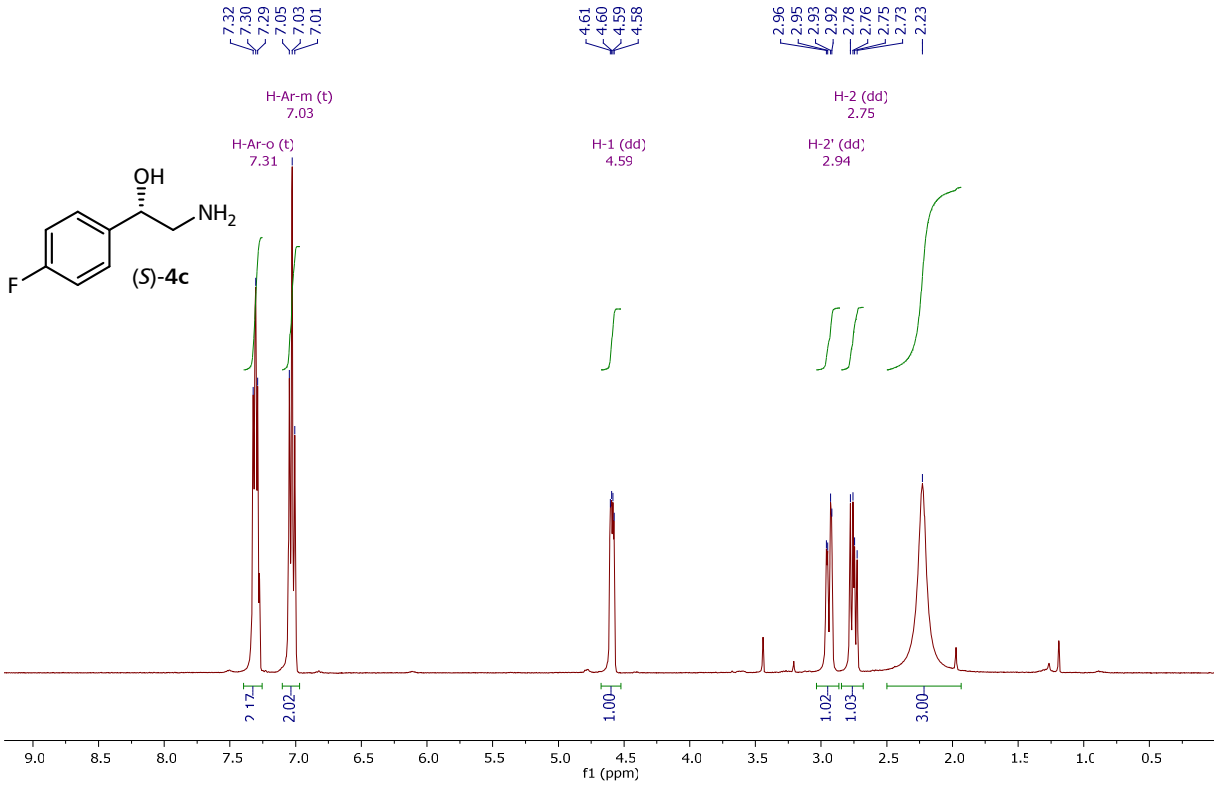


racemic sample:



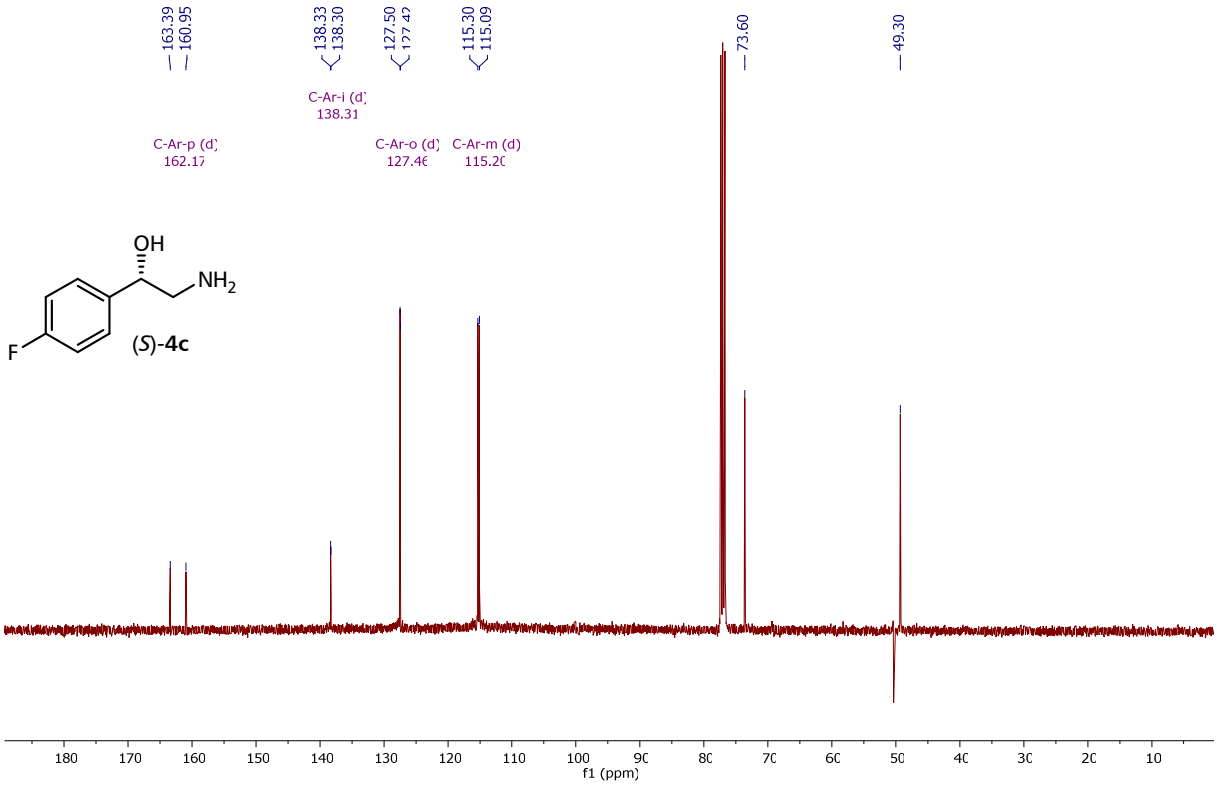
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



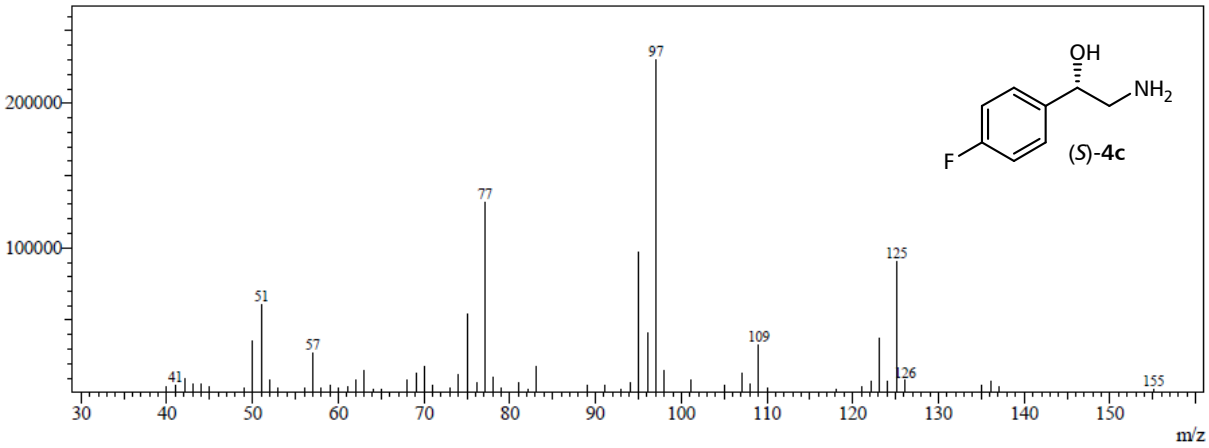
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



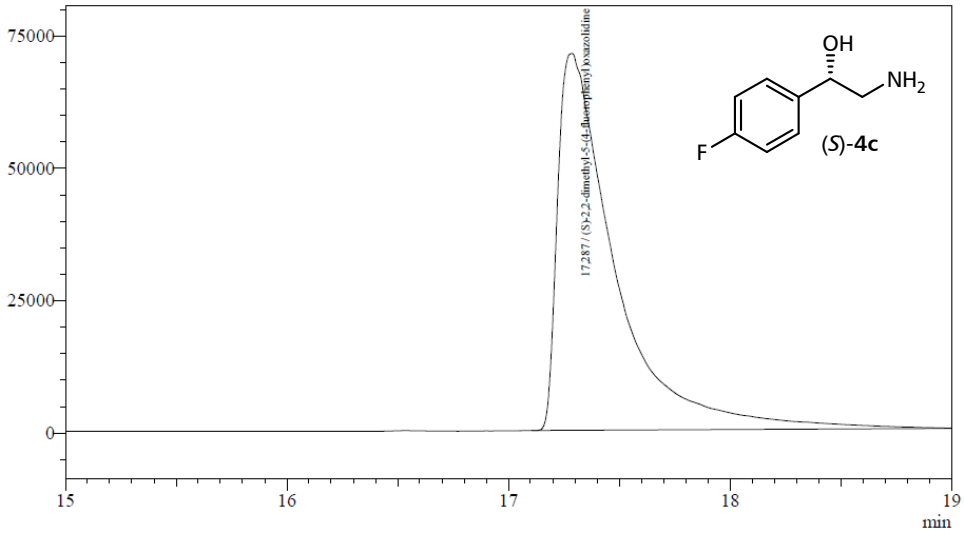
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

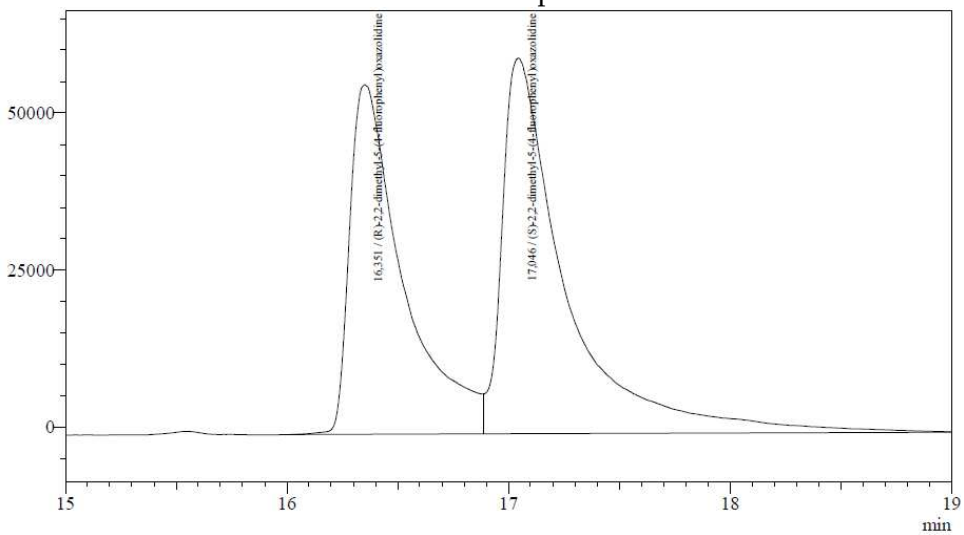


(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

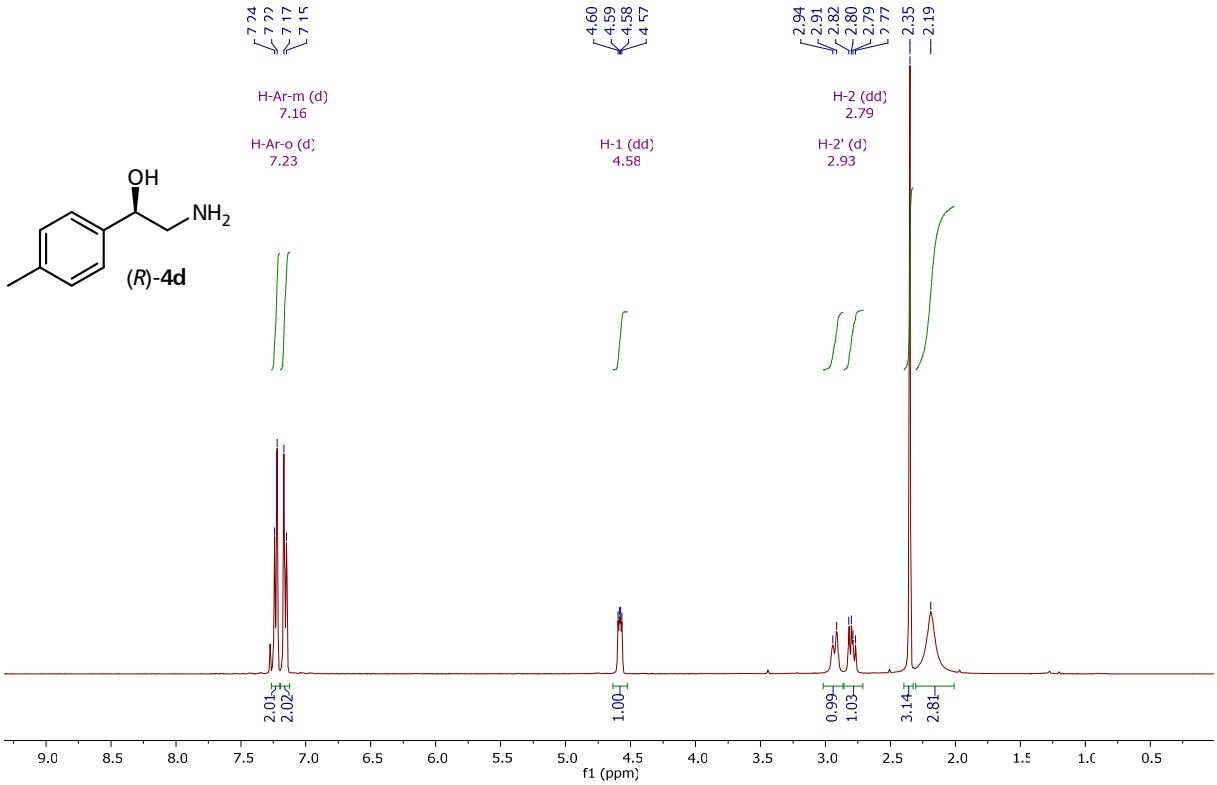


racemic sample:



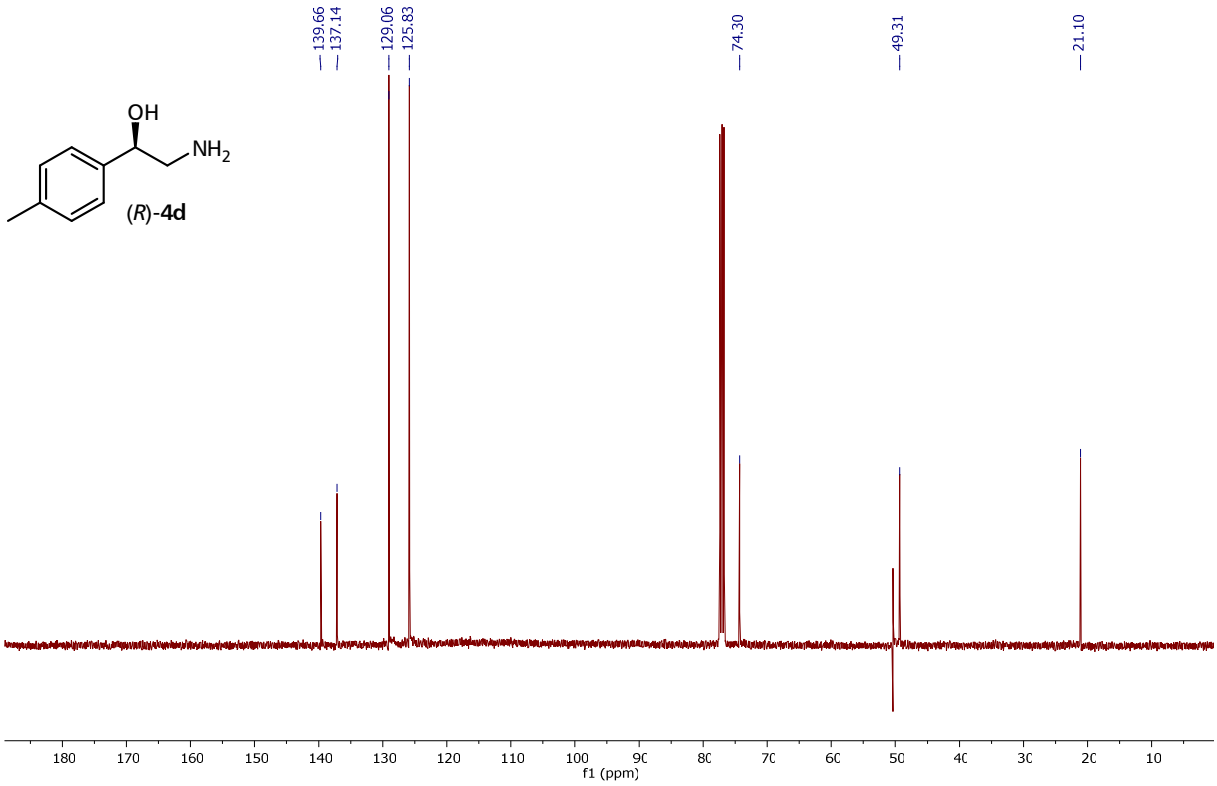
(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



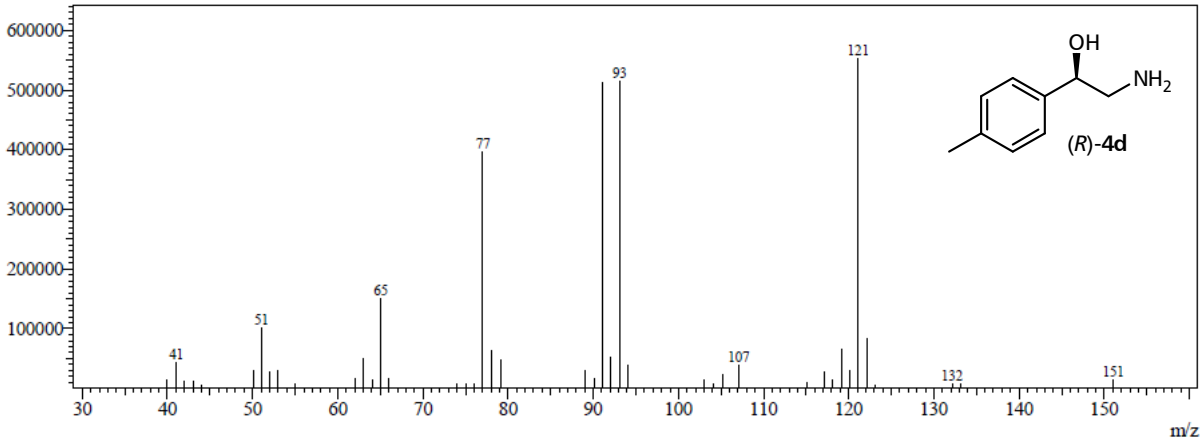
(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



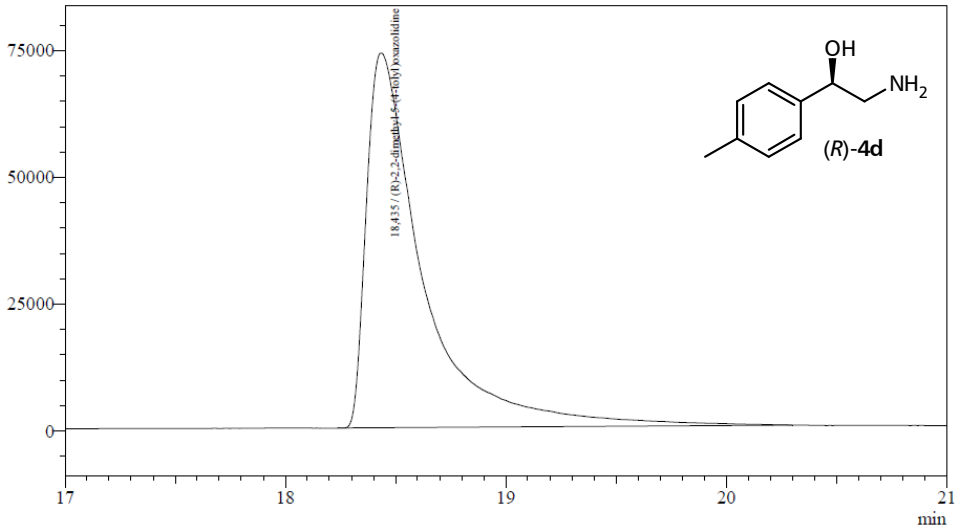
(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

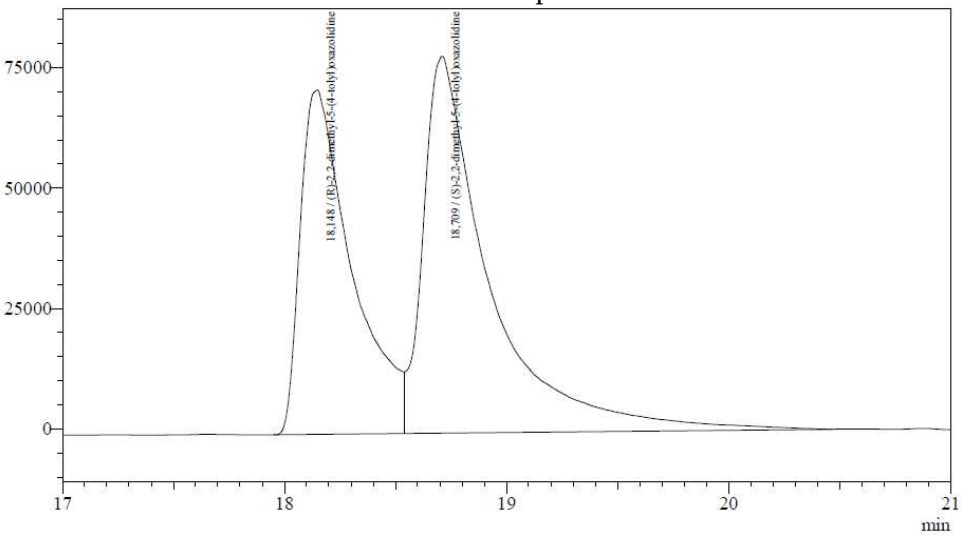


(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

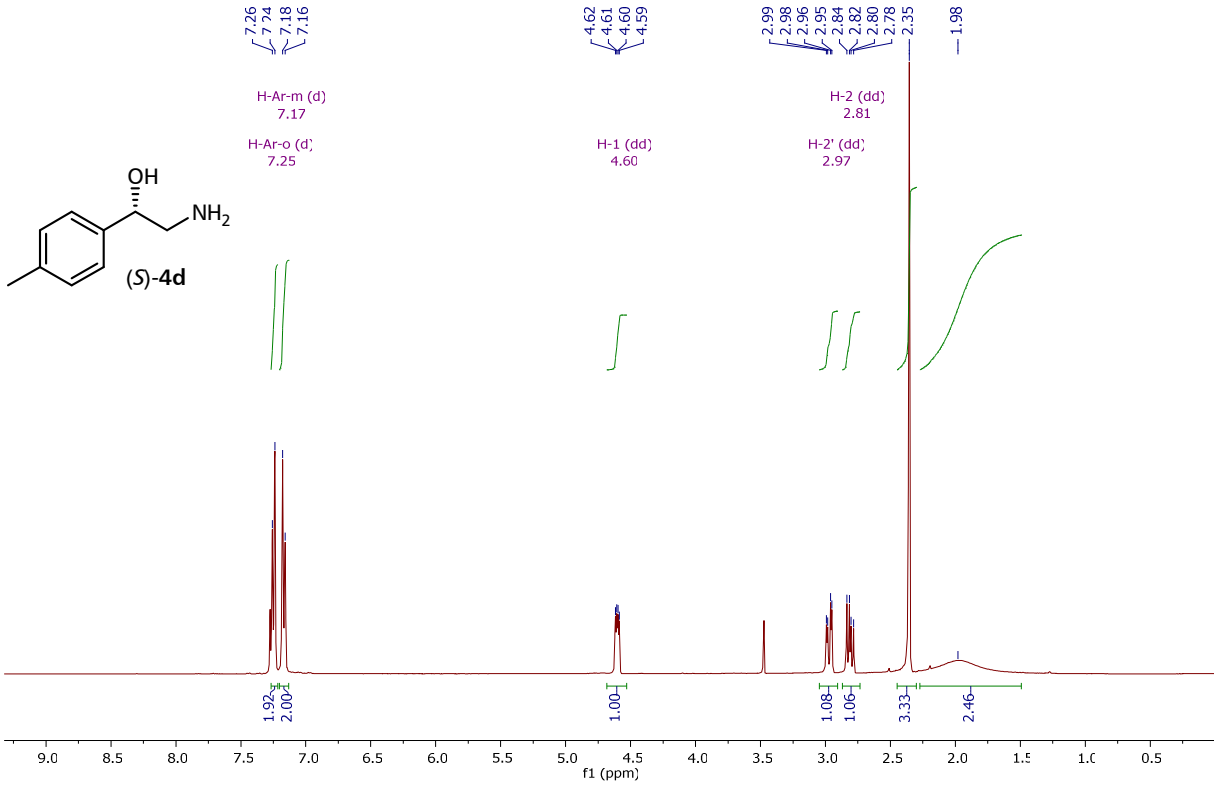


racemic sample:



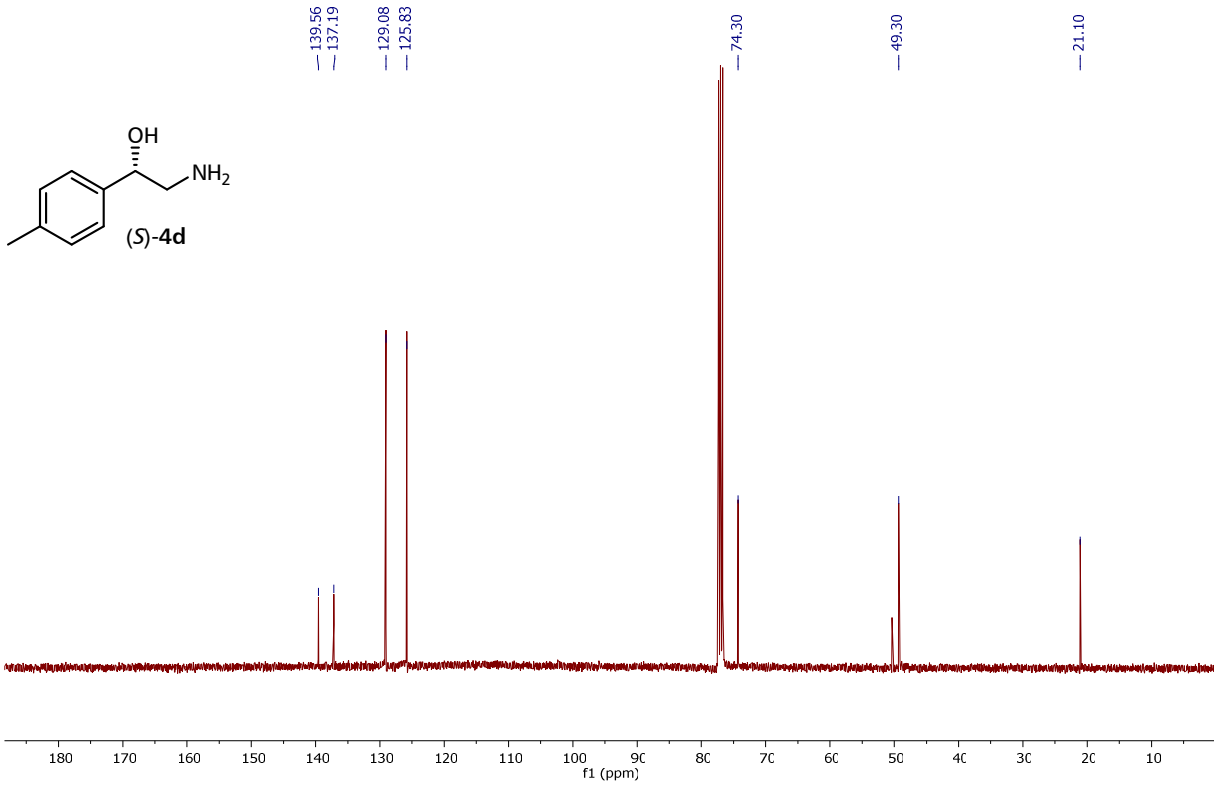
(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



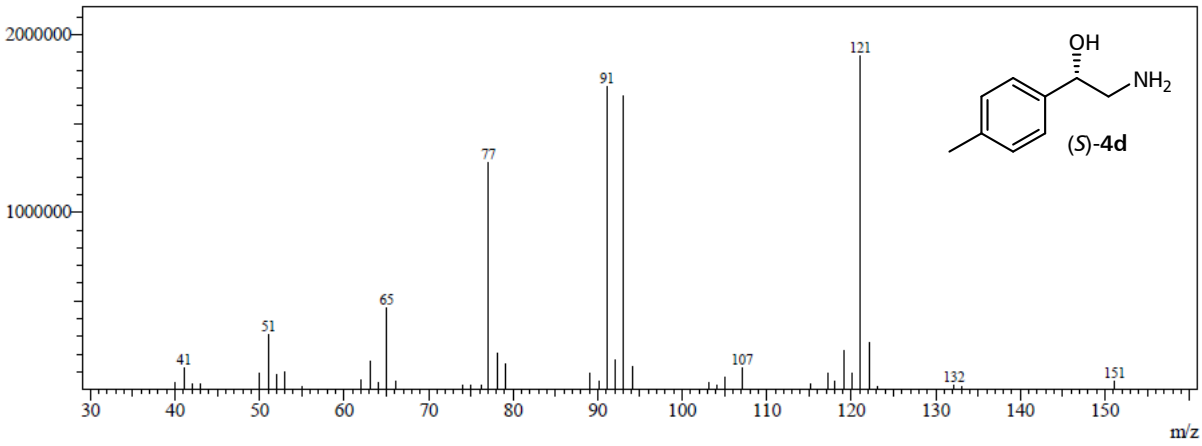
(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



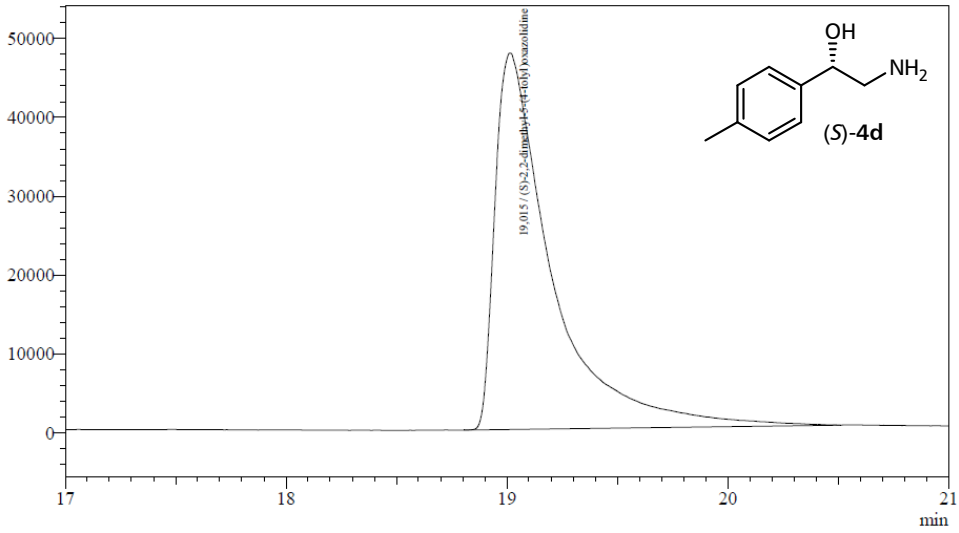
(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

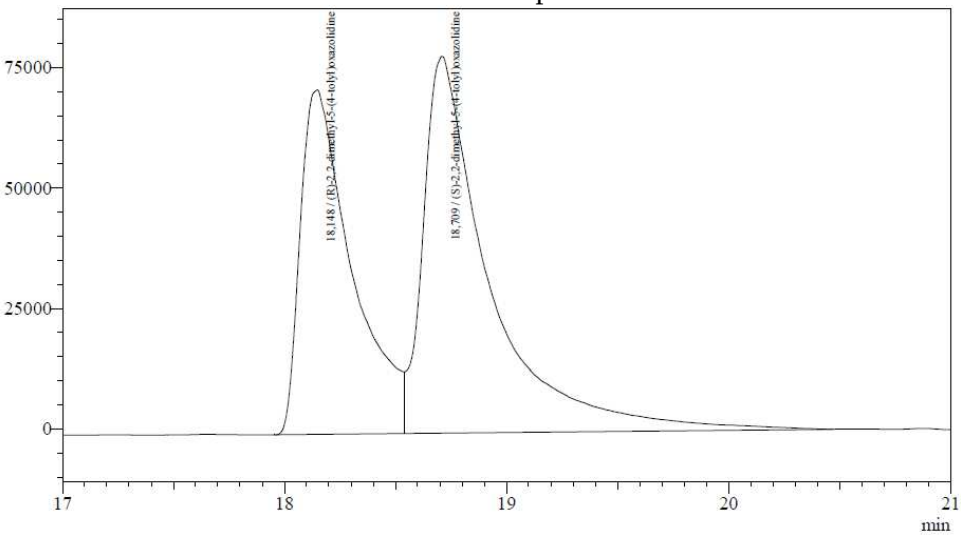


(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

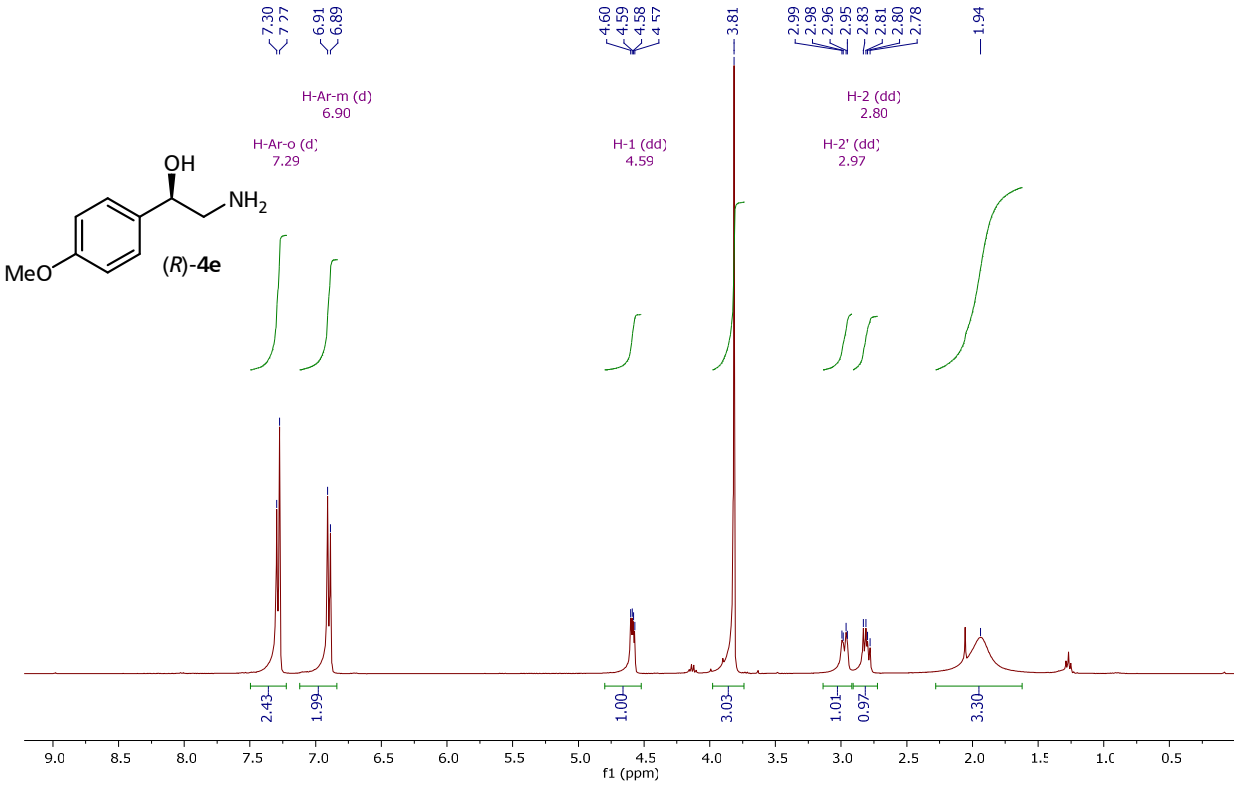


racemic sample:



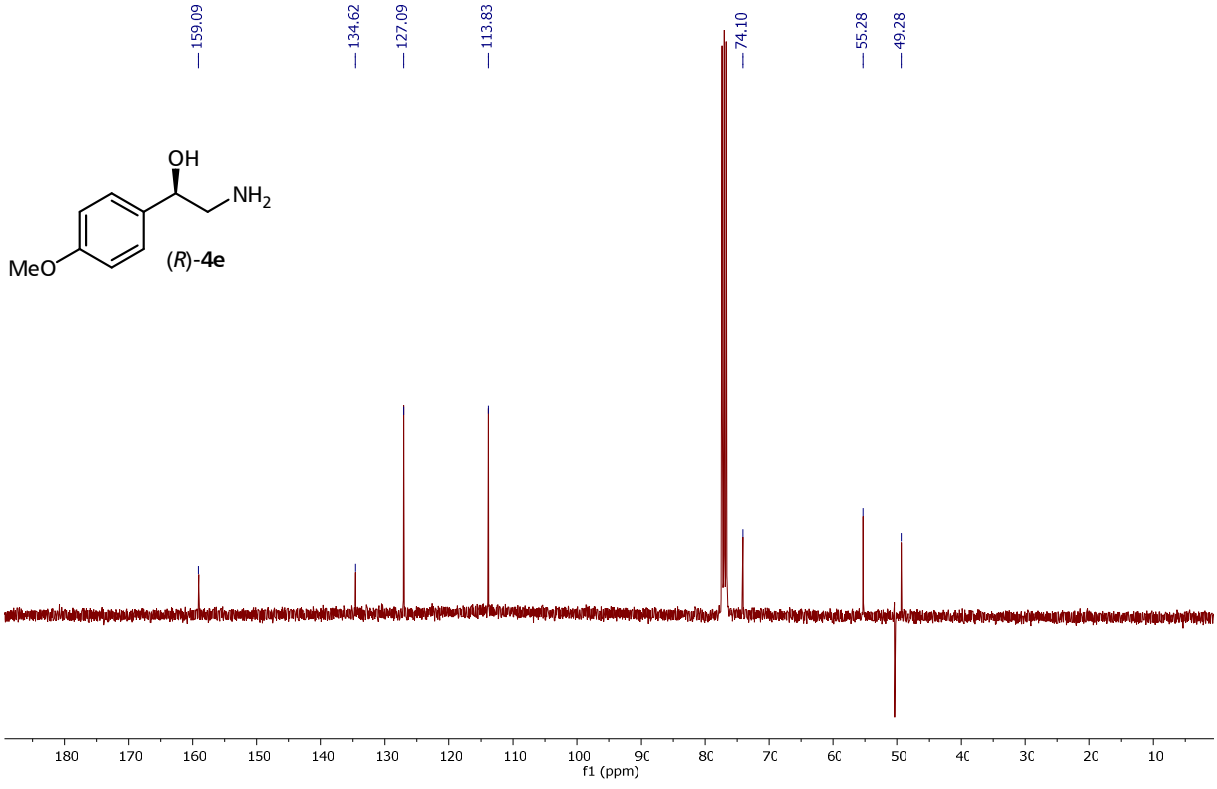
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



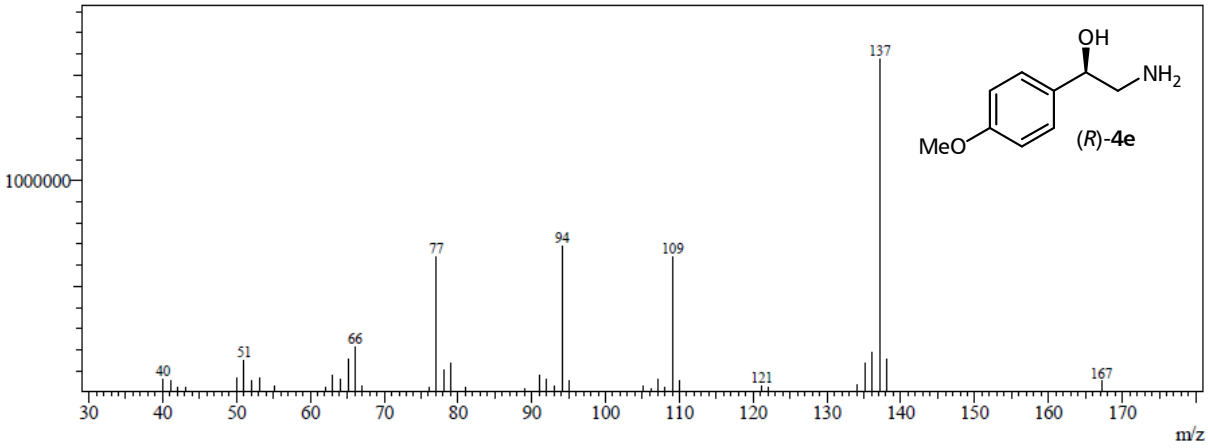
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



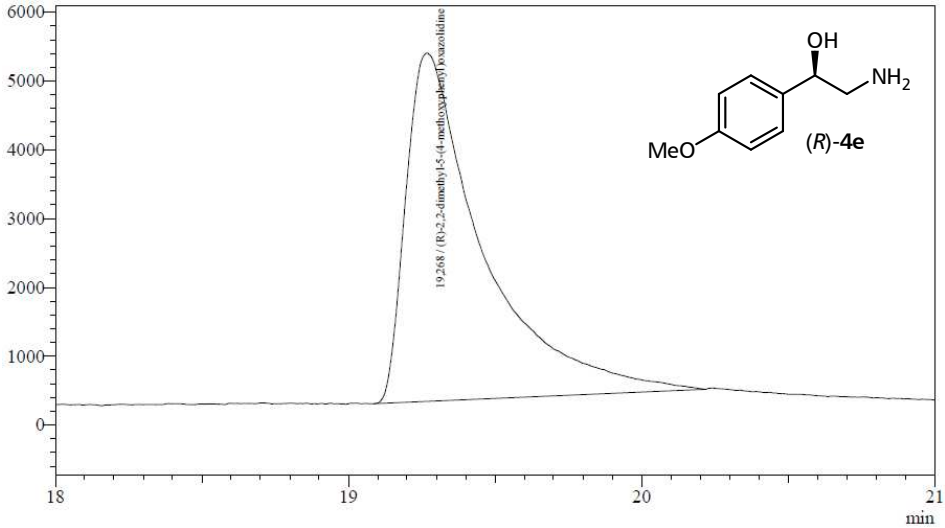
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

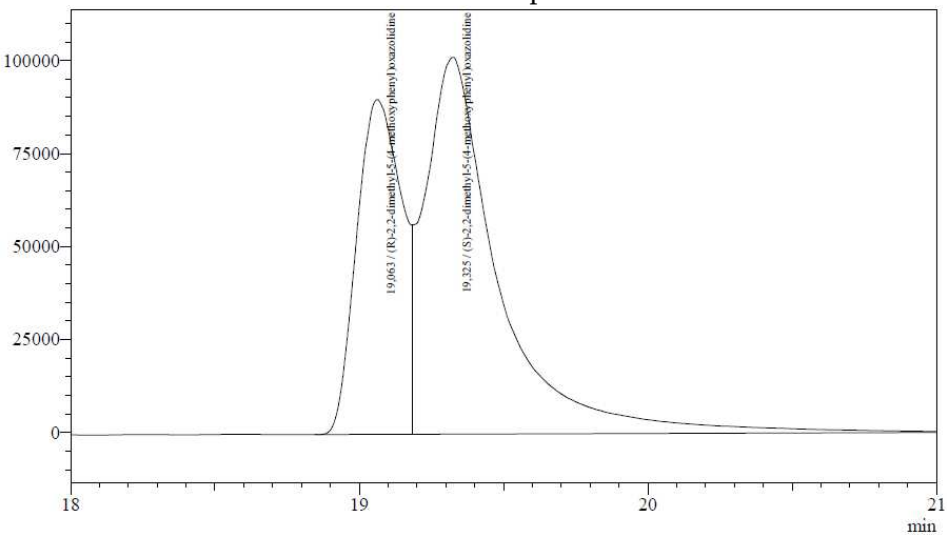


(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

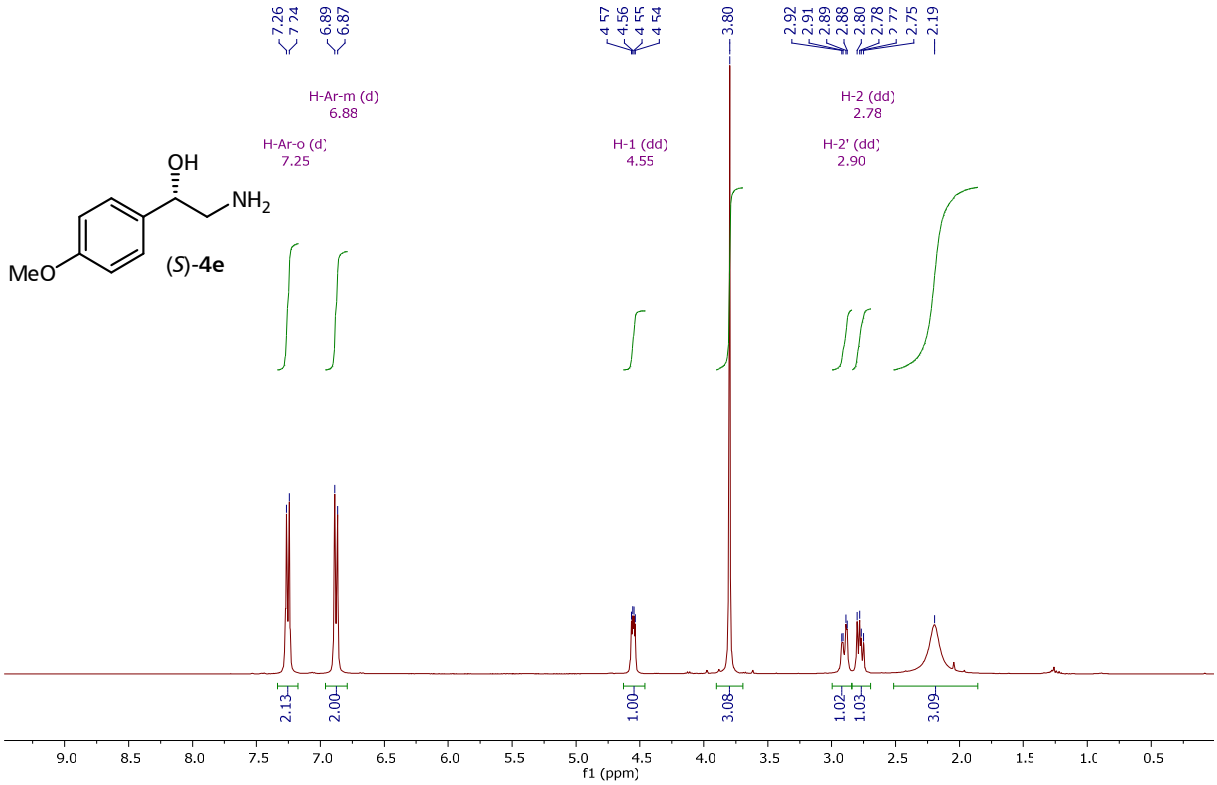


racemic sample:



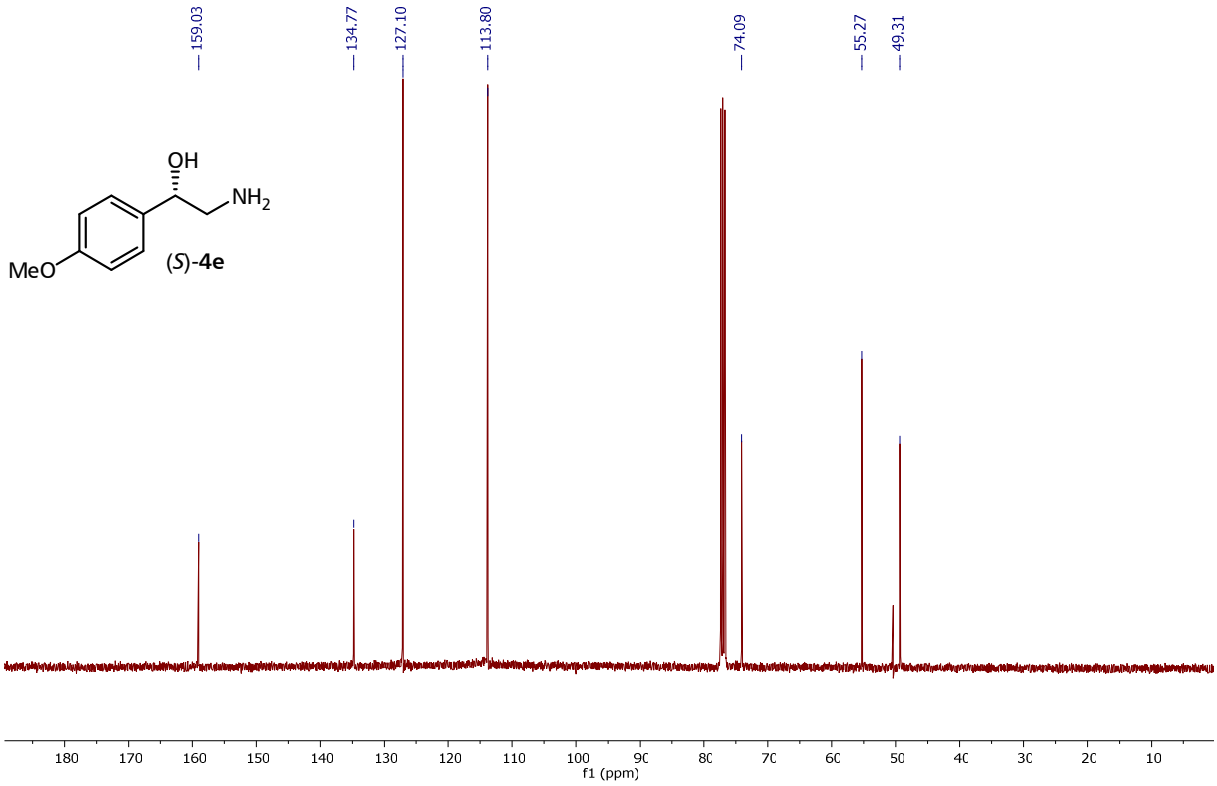
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



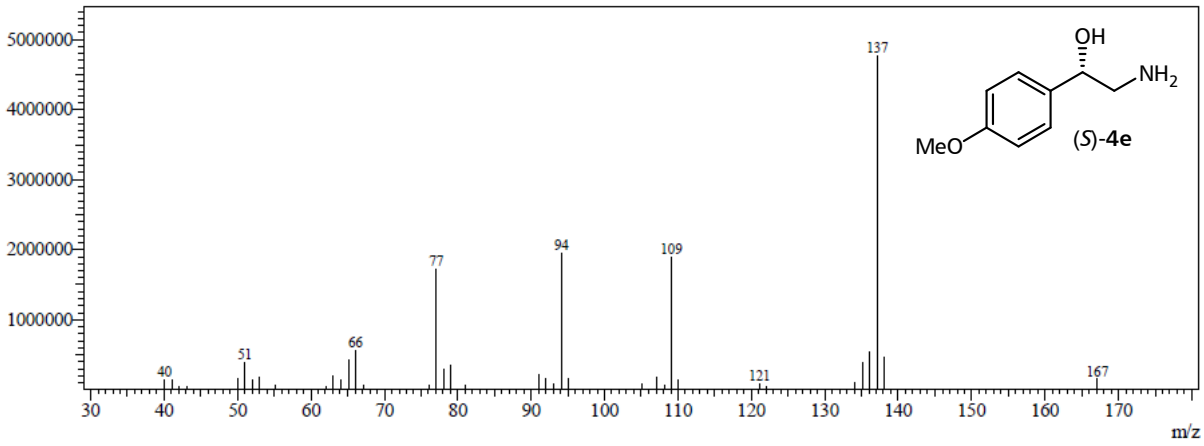
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



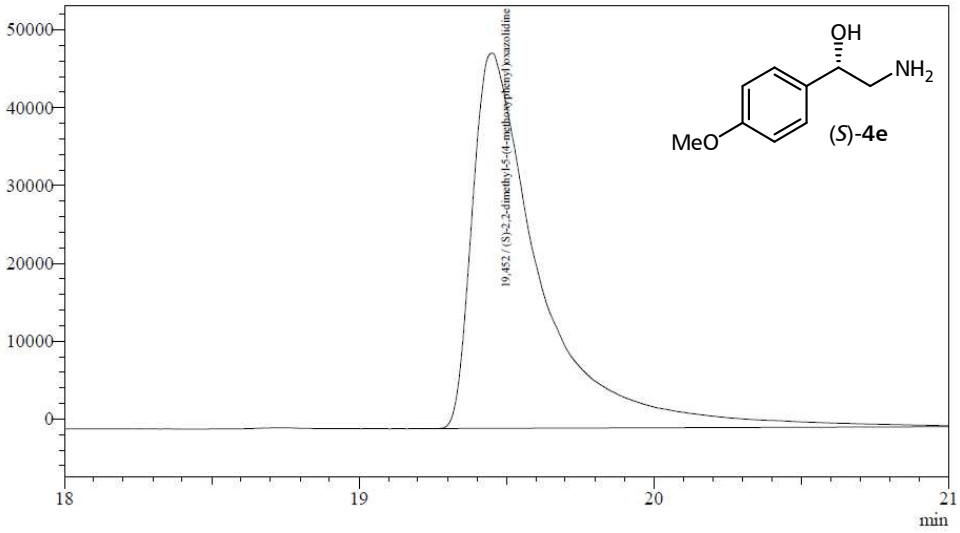
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

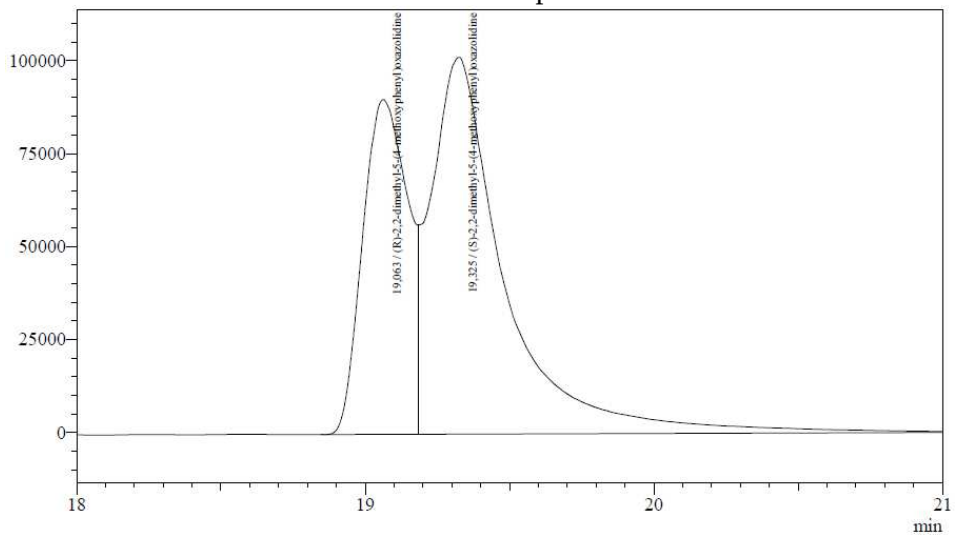


(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

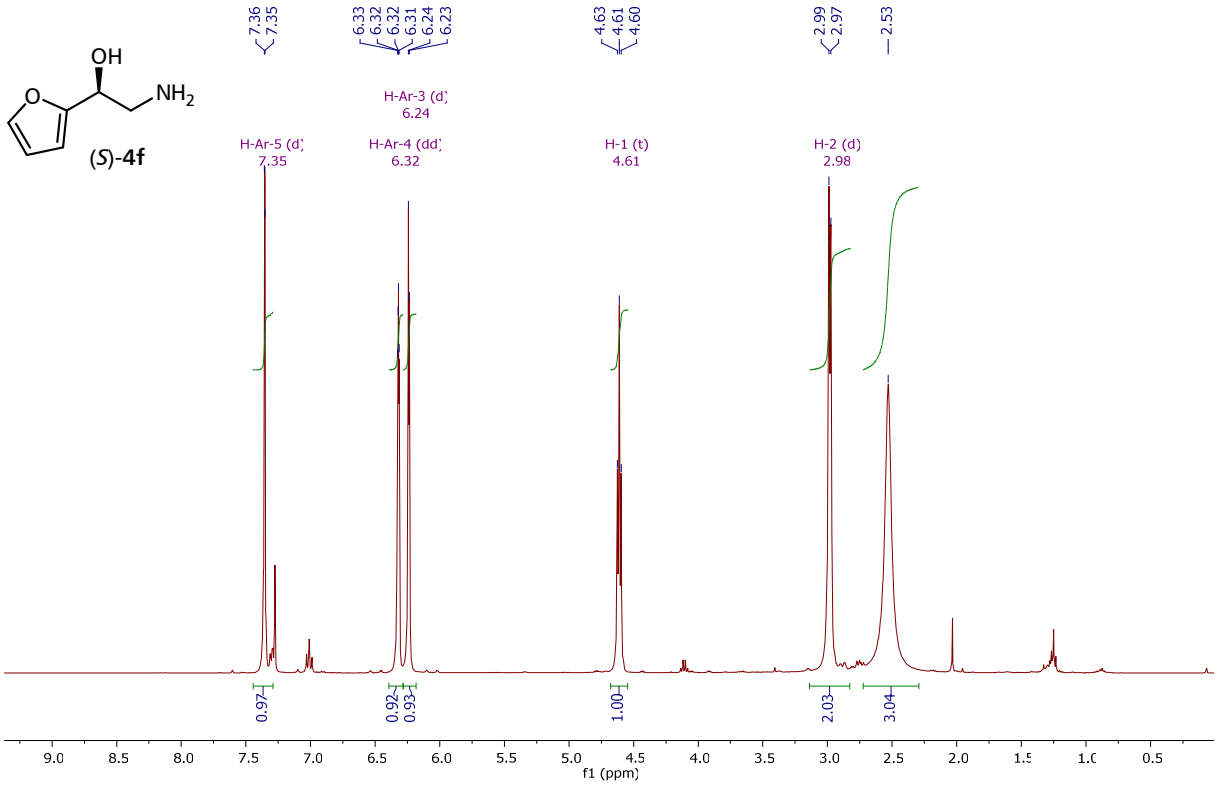


racemic sample:



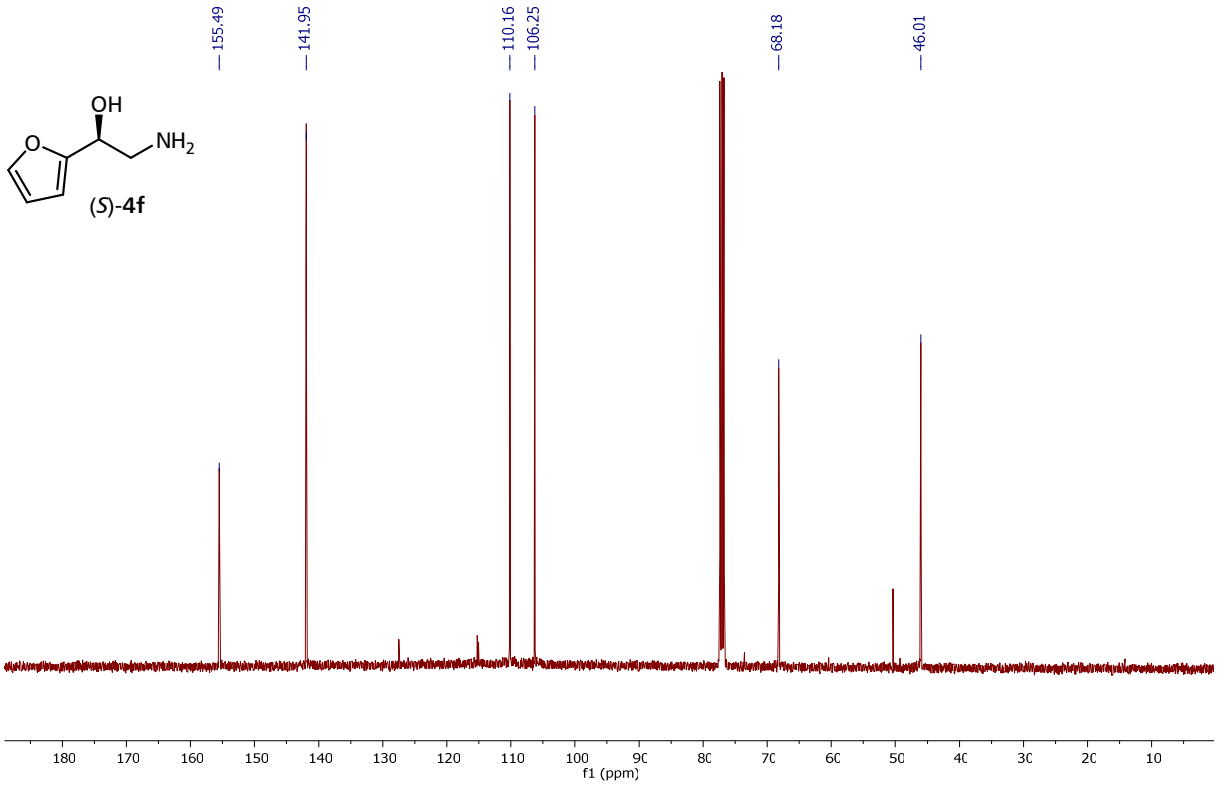
(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



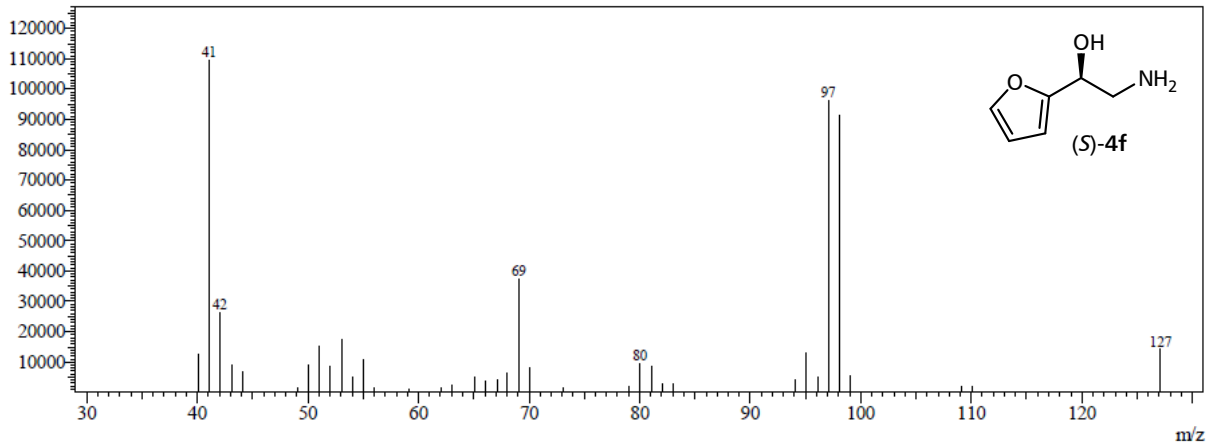
(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



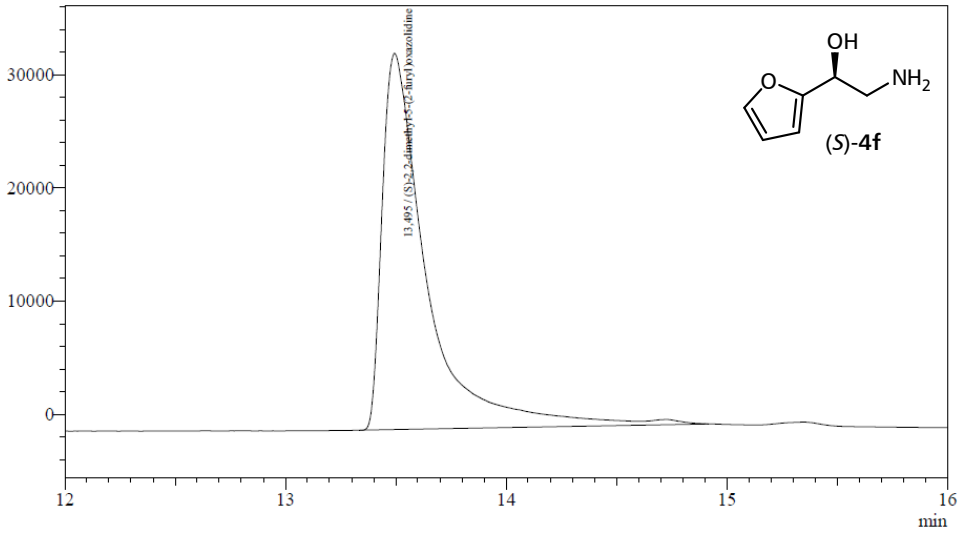
(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

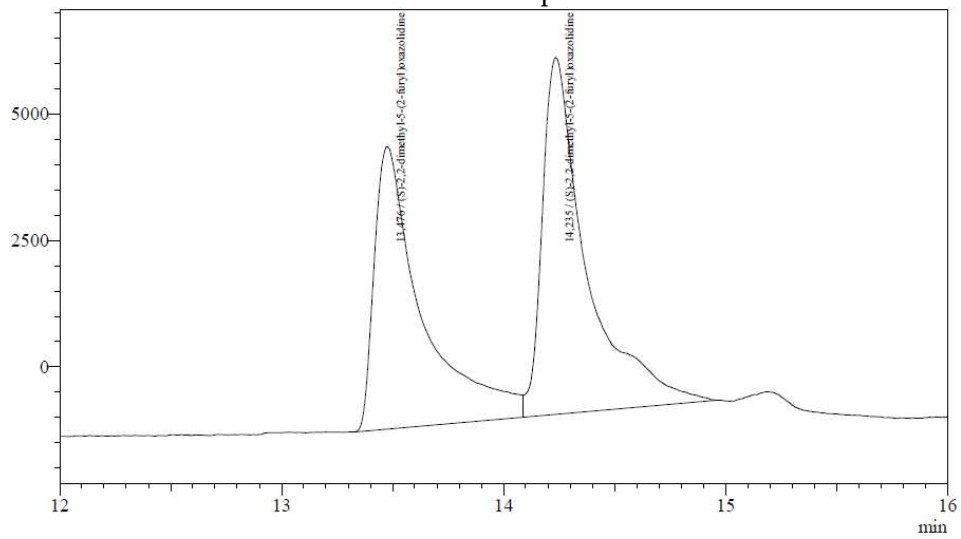


(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

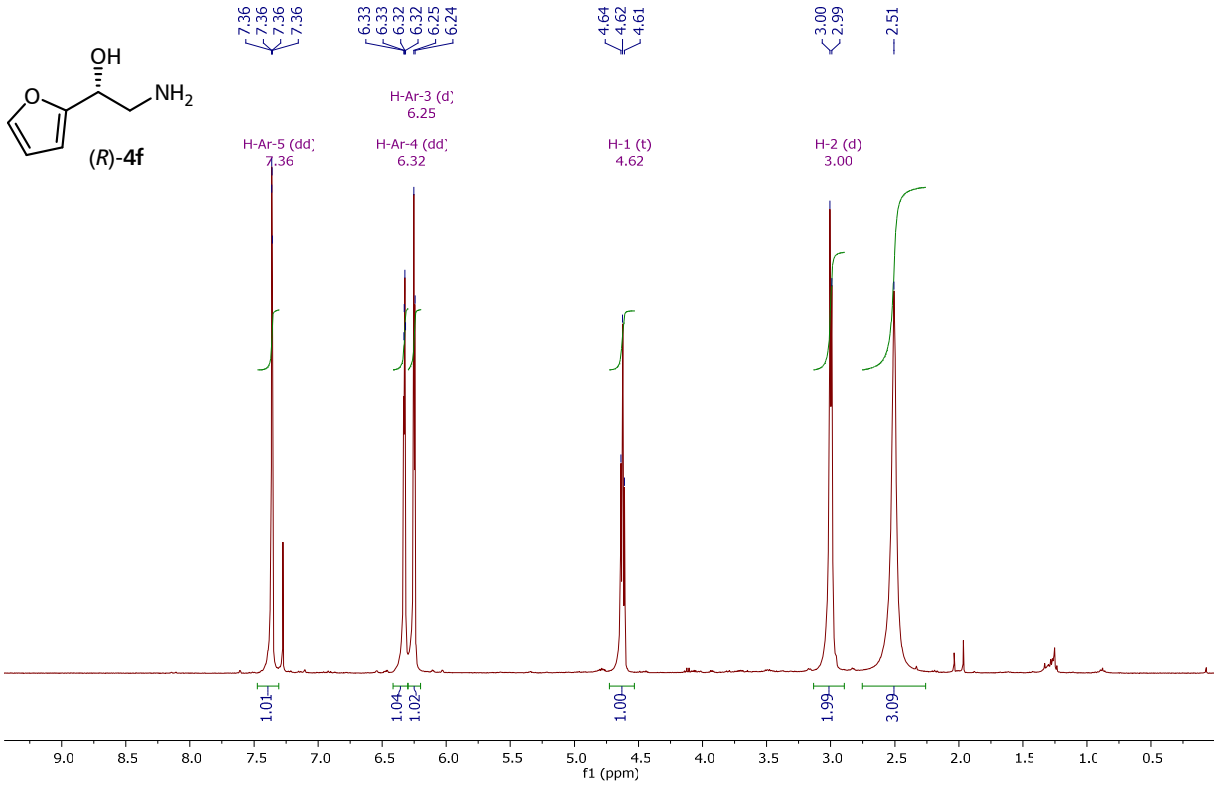


racemic sample:



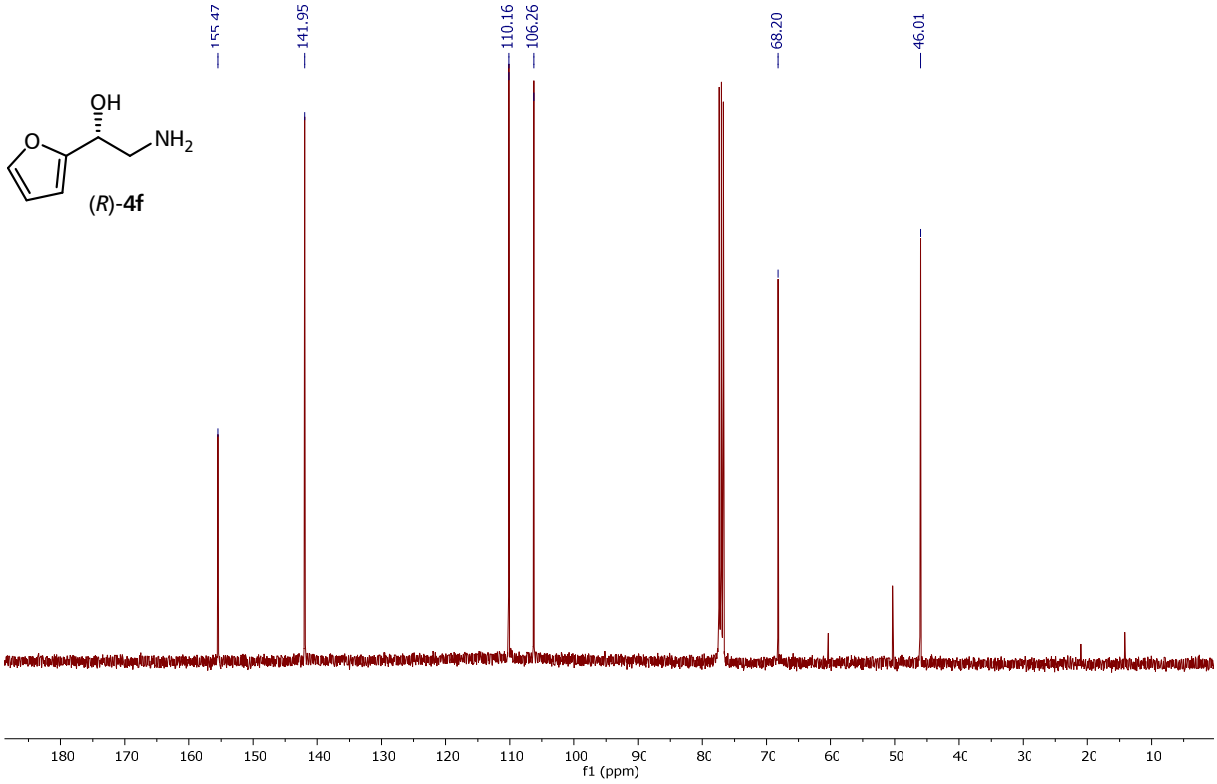
(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



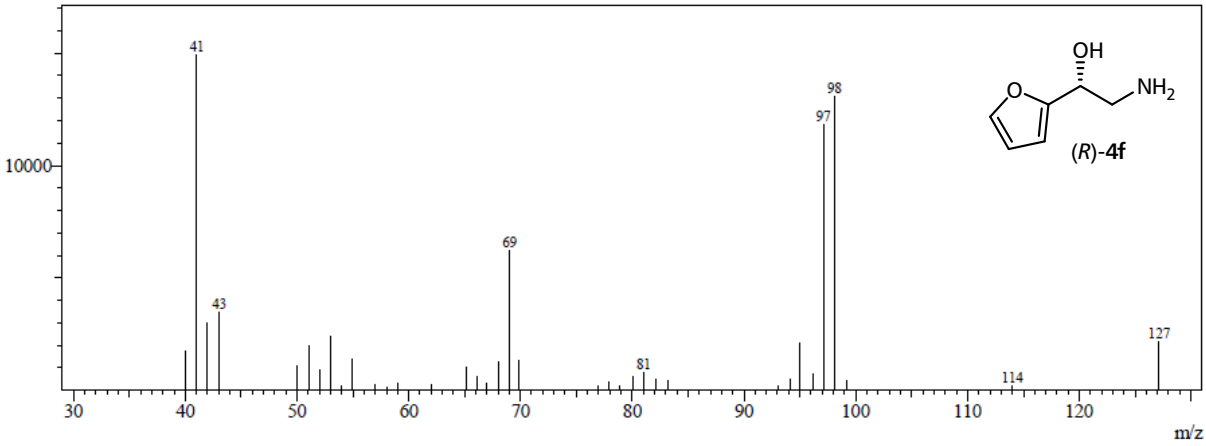
(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (5 mL scale)



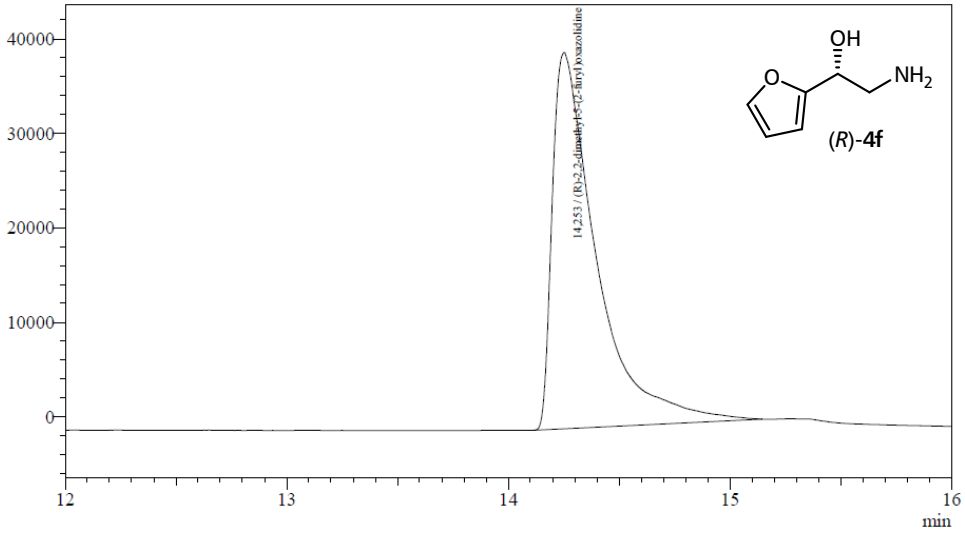
(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: MS spectrum

product obtained by the two-step one-pot sequence (5 mL scale)

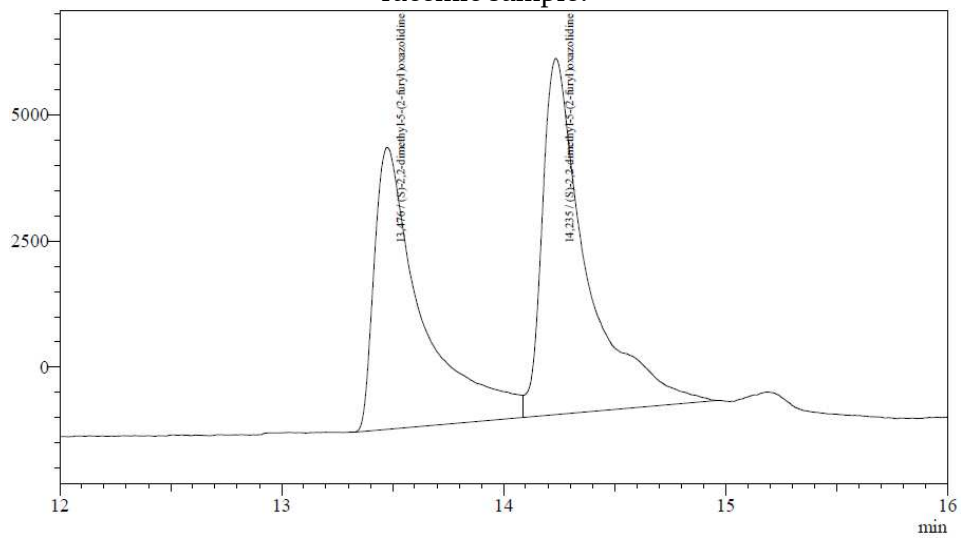


(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (5 mL scale)

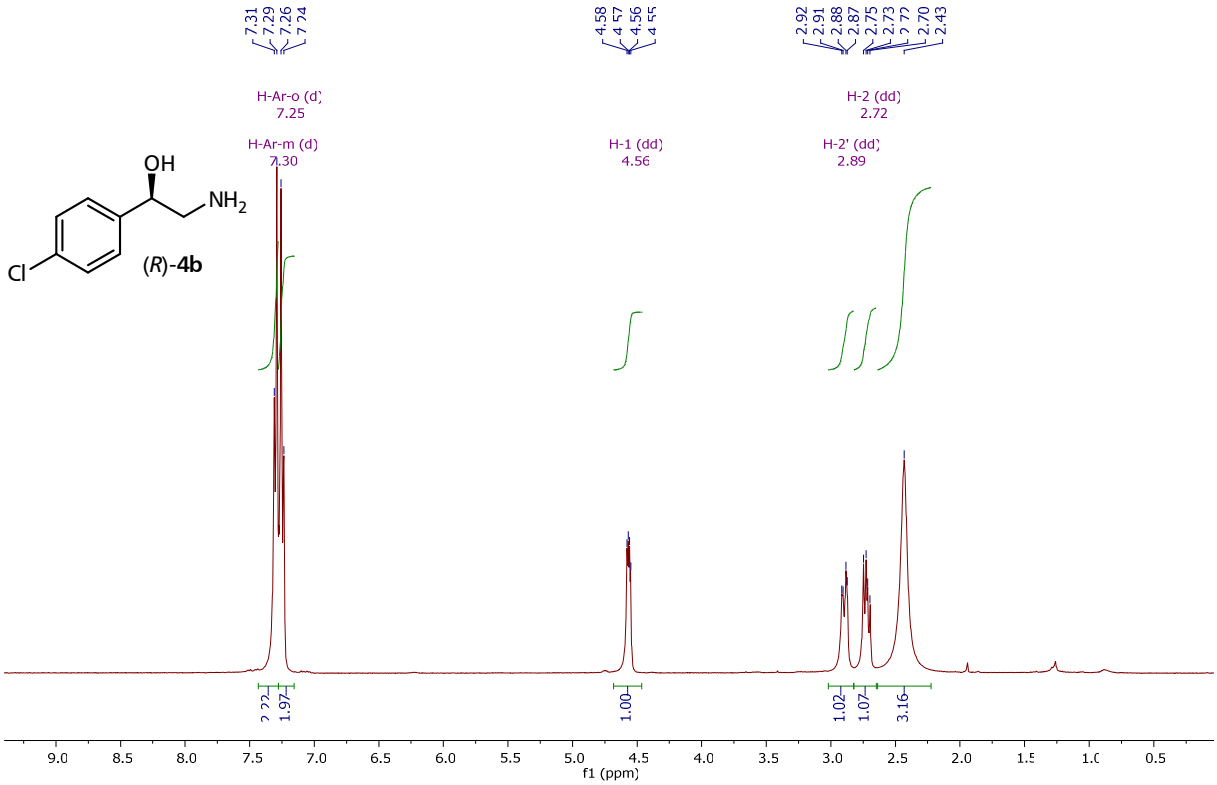


racemic sample:



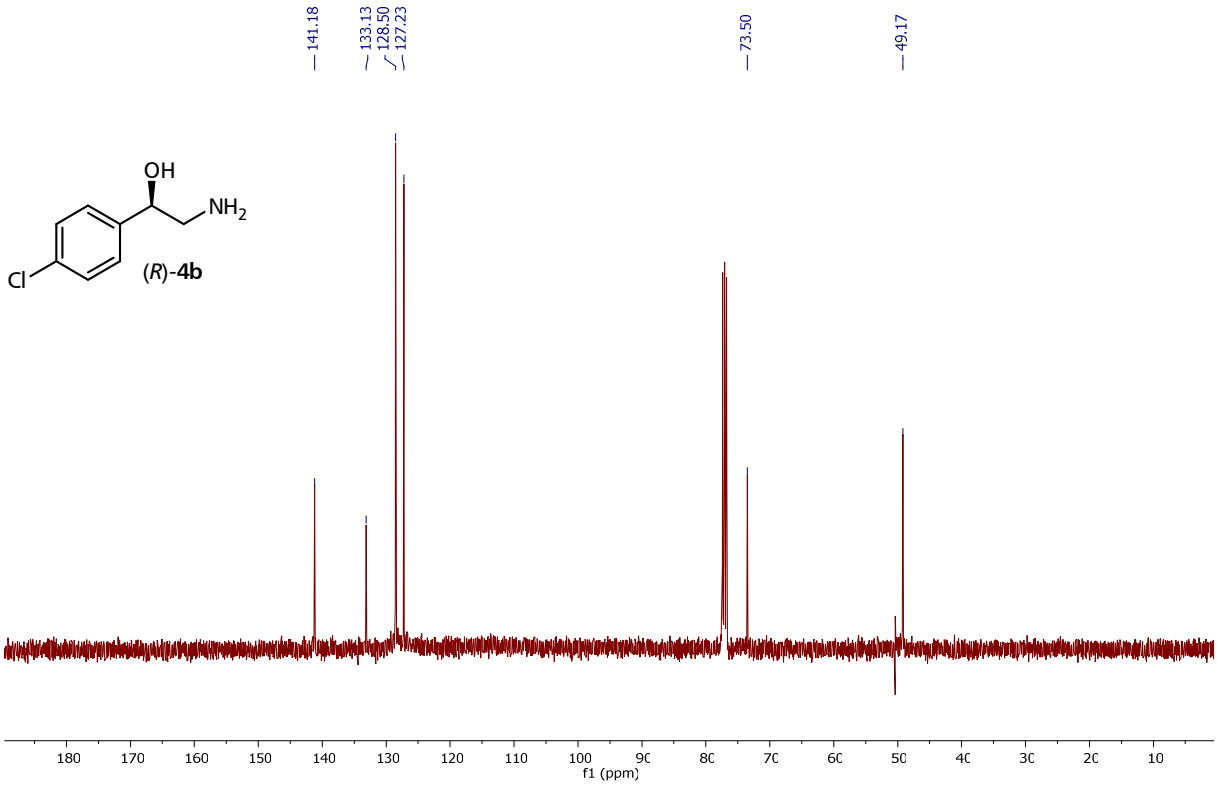
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{1}H-NMR spectrum

product obtained by the two-step one-pot sequence (gram scale)



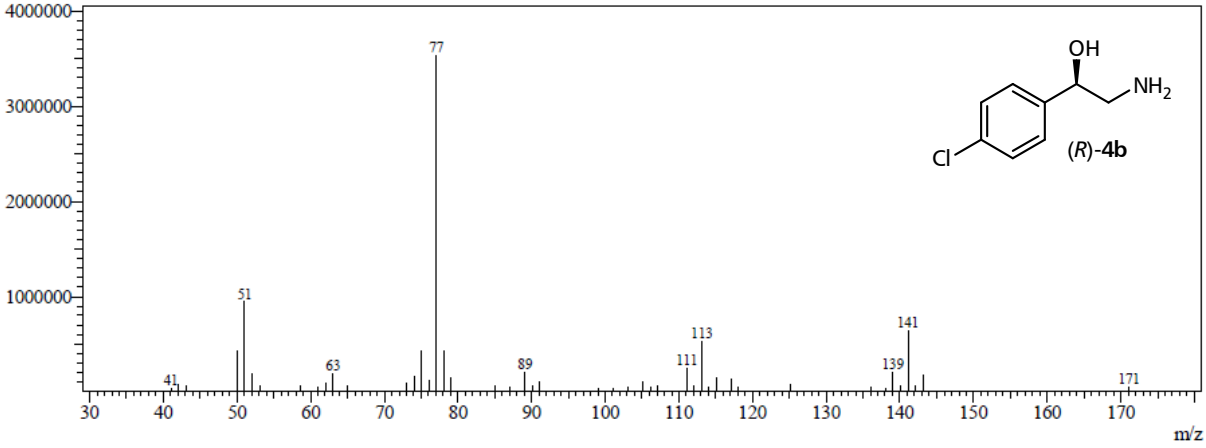
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{13}C-NMR spectrum

product obtained by the two-step one-pot sequence (gram scale)



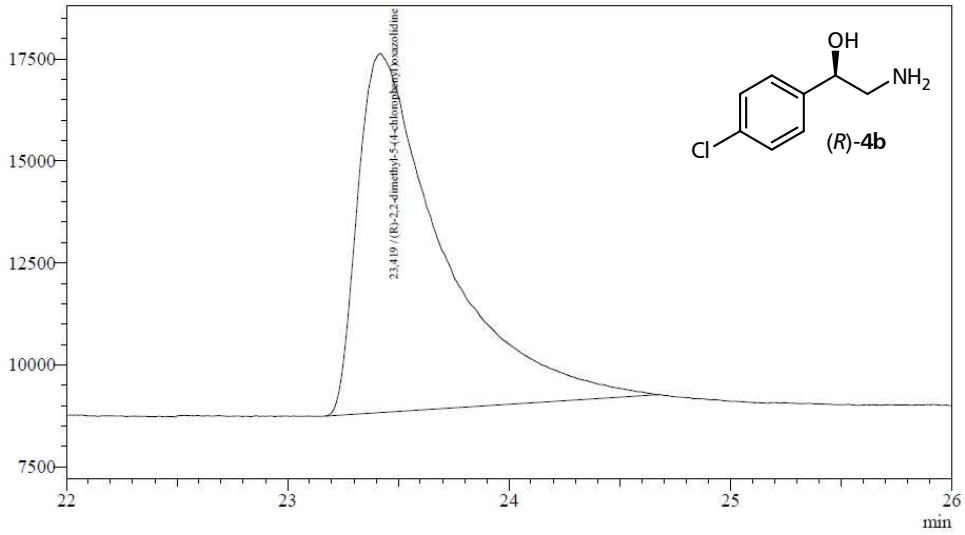
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: MS spectrum

product obtained by the two-step one-pot sequence (gram scale)

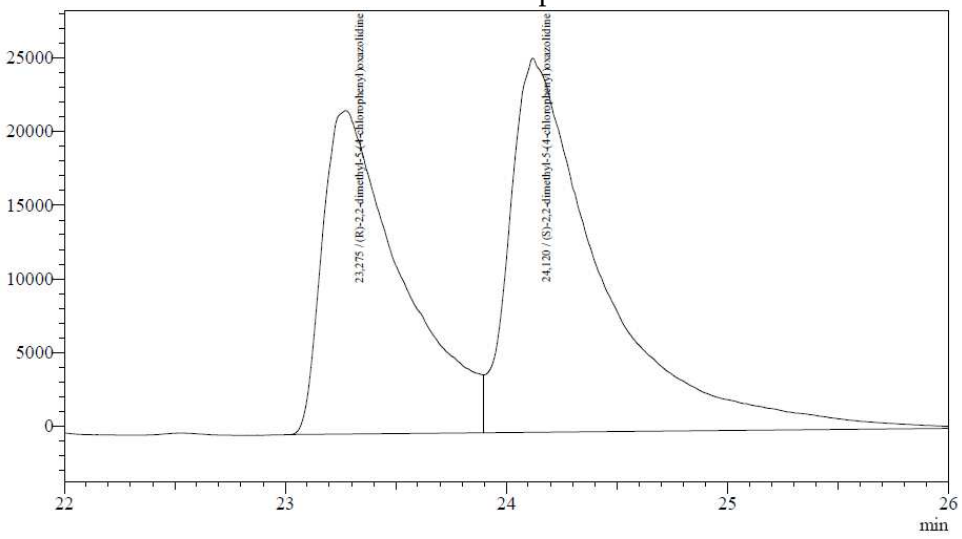


(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: chiral-phase GC chromatograms

product obtained by the two-step one-pot sequence (gram scale)

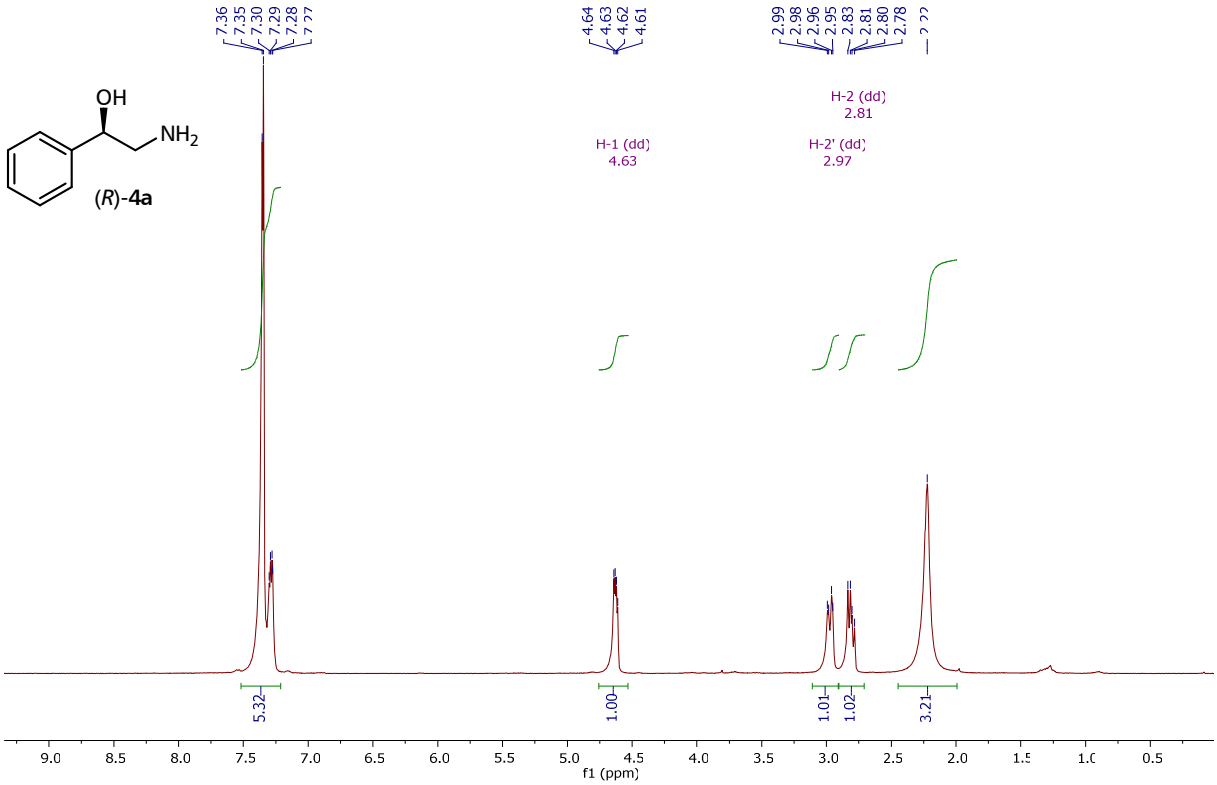


racemic sample:



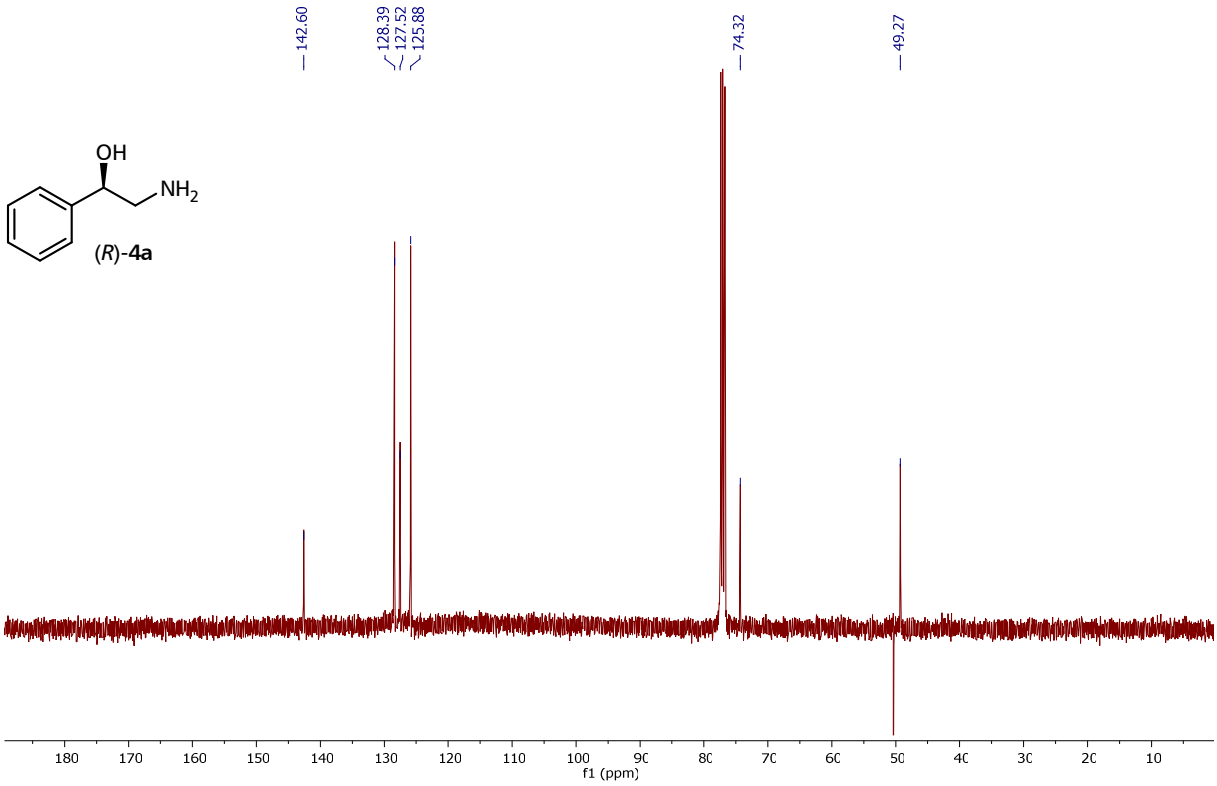
(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



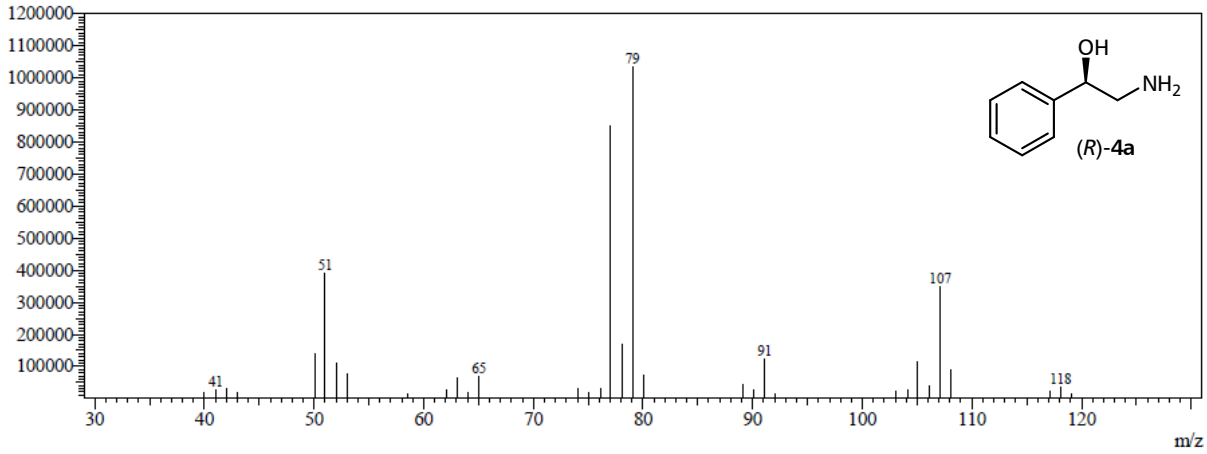
(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



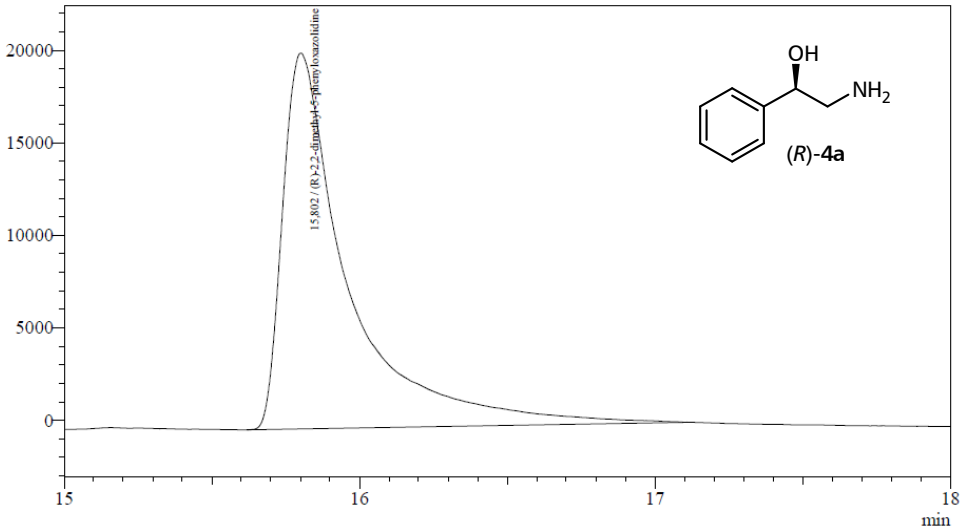
(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

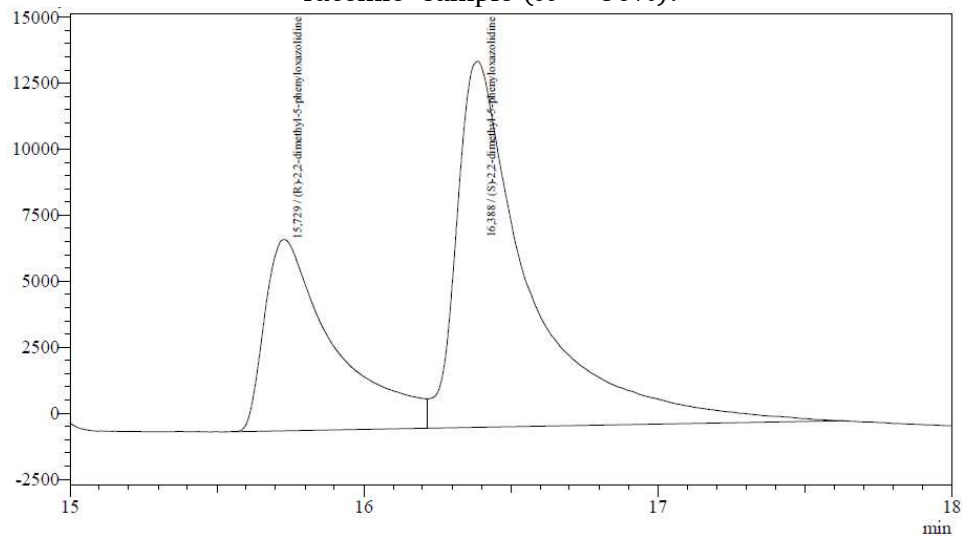


(*R*)-2-Amino-1-phenylethanol (*R*)-**4a**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

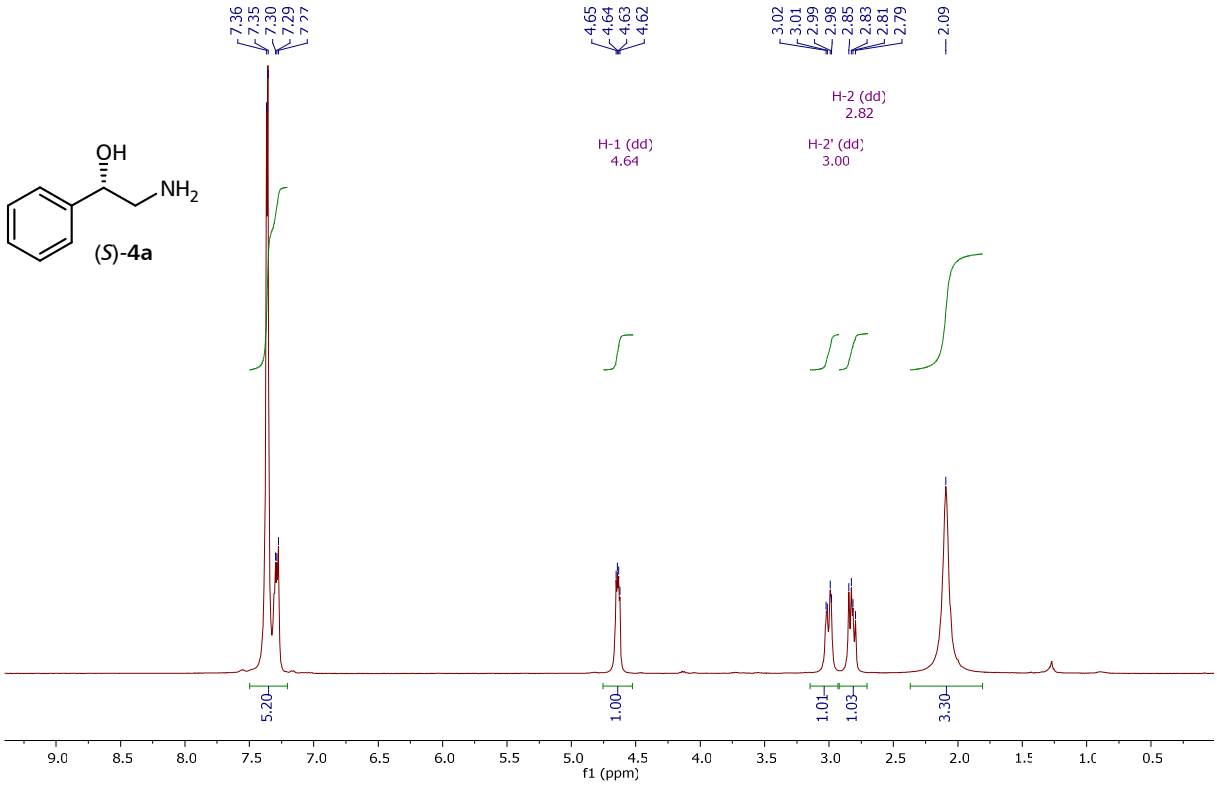


"racemic" sample (*ee* = 30%):



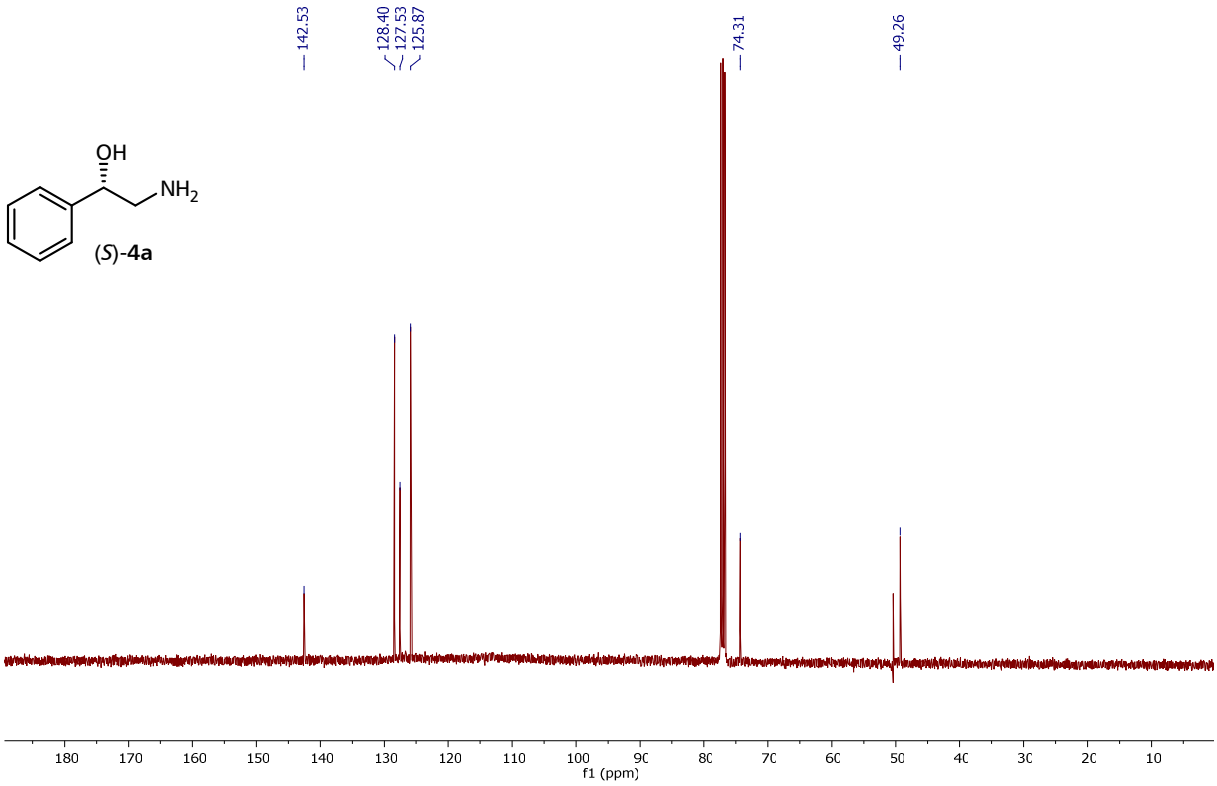
(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



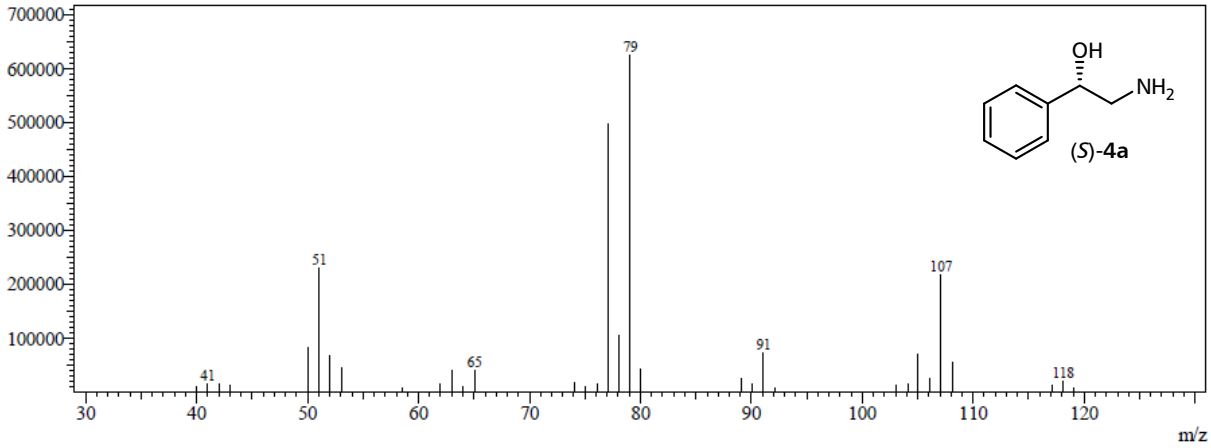
(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



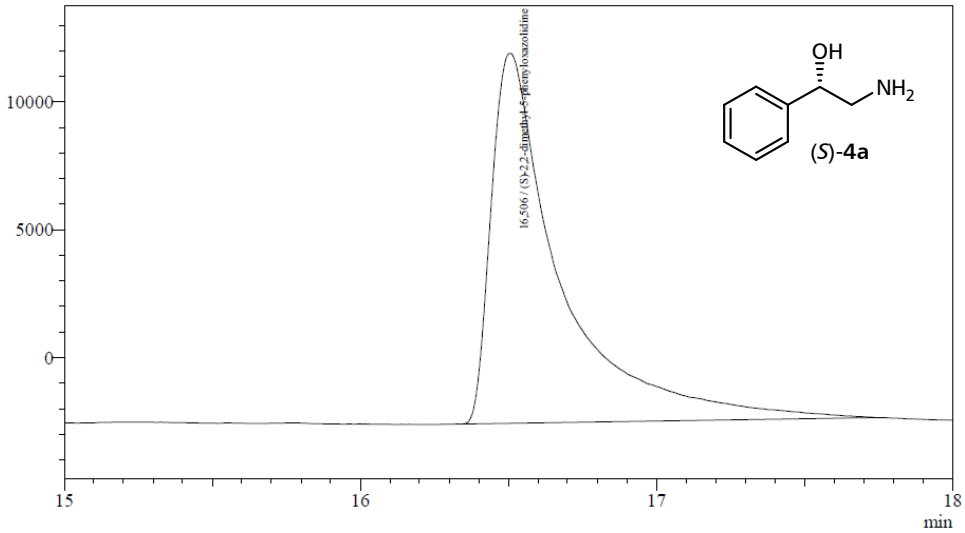
(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

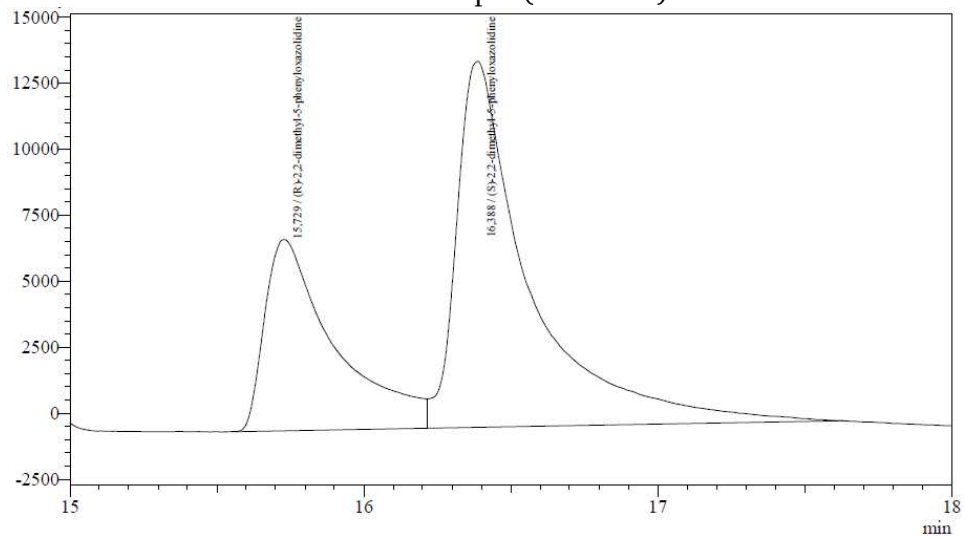


(*S*)-2-Amino-1-phenylethanol (*S*)-**4a**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

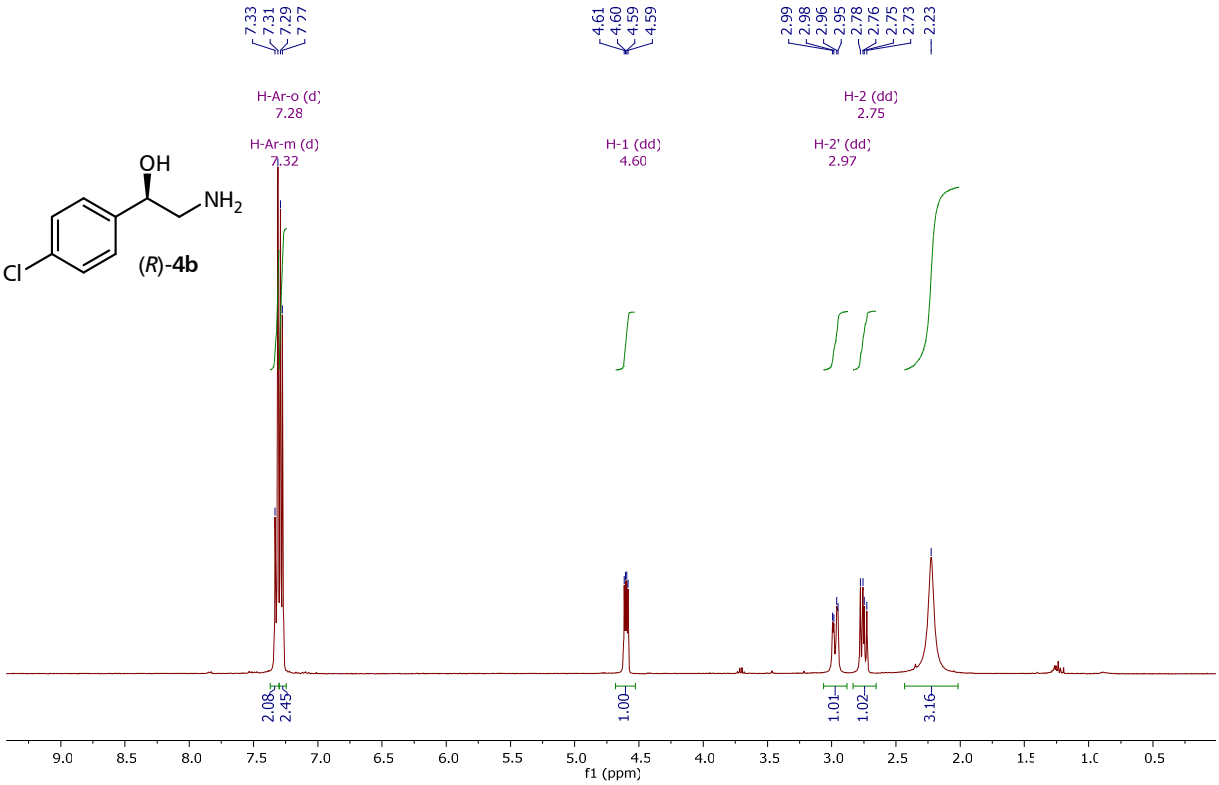


"racemic" sample (*ee* = 30%):



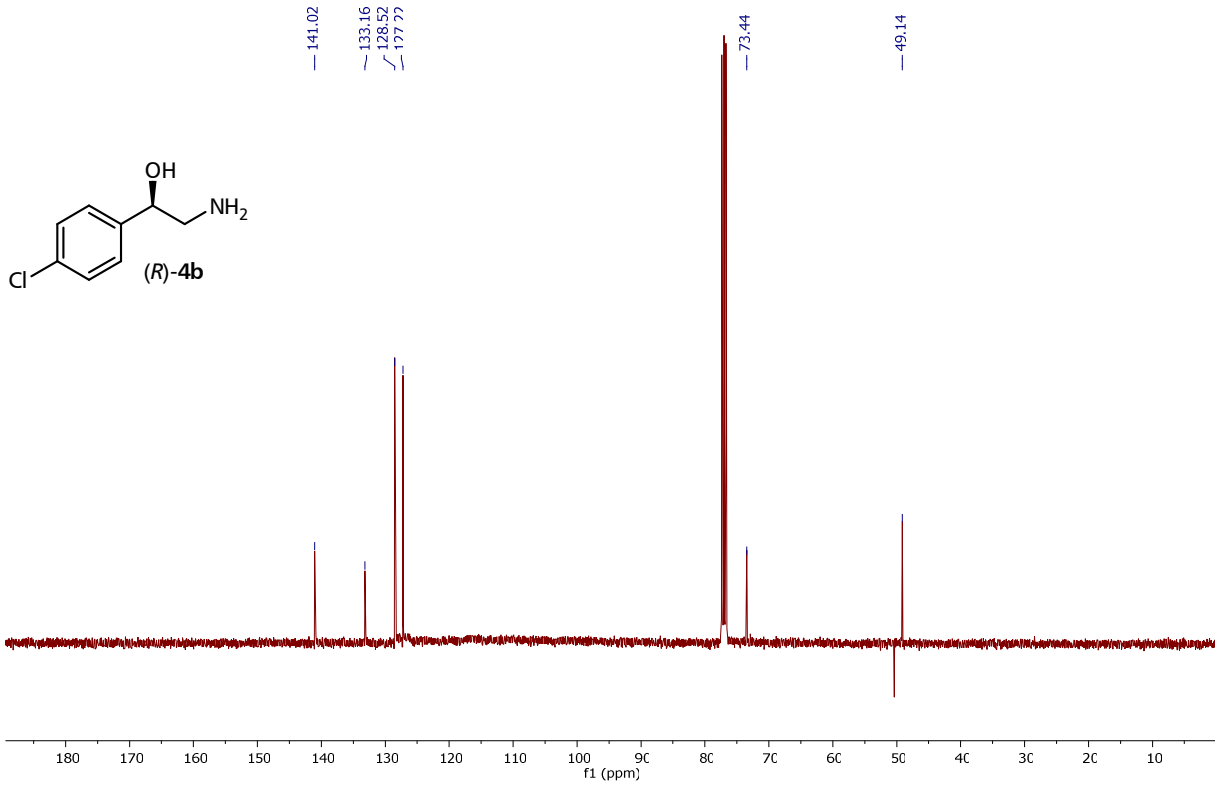
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



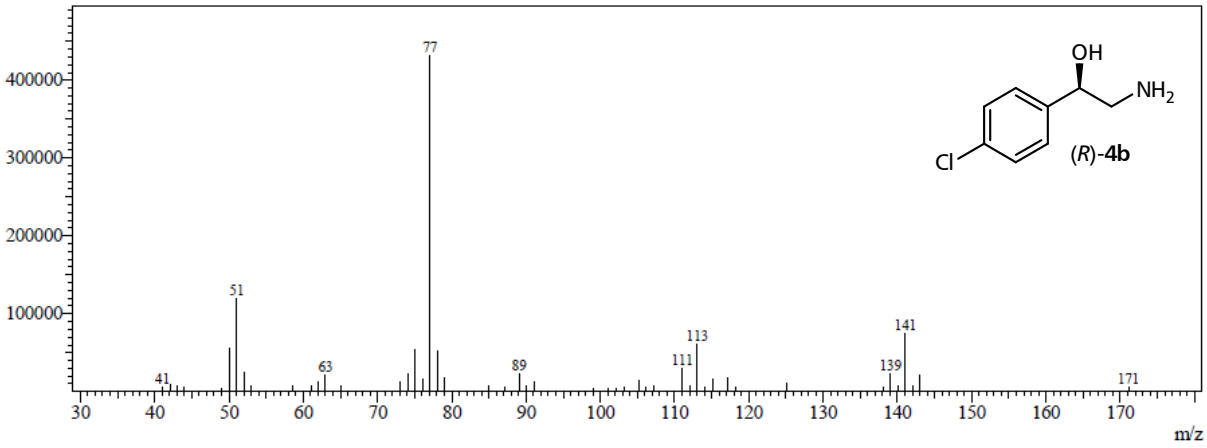
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



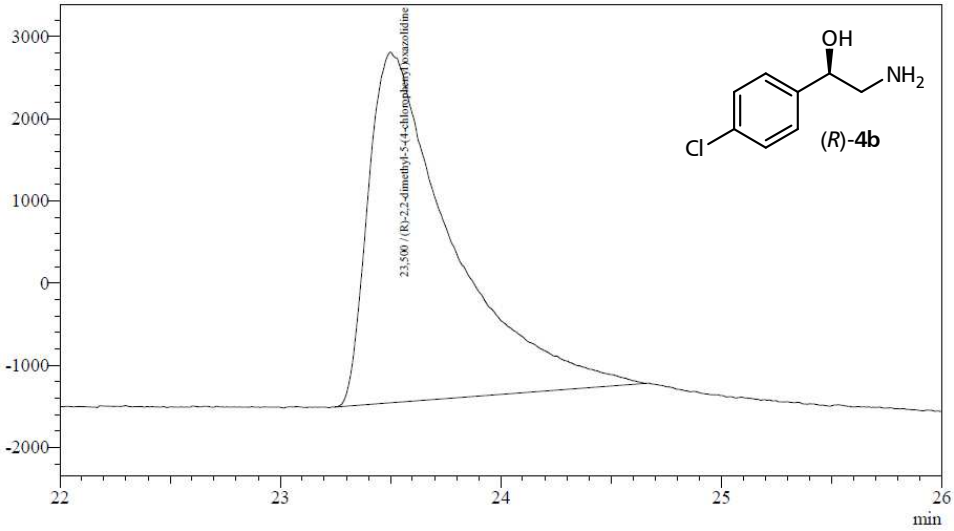
(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

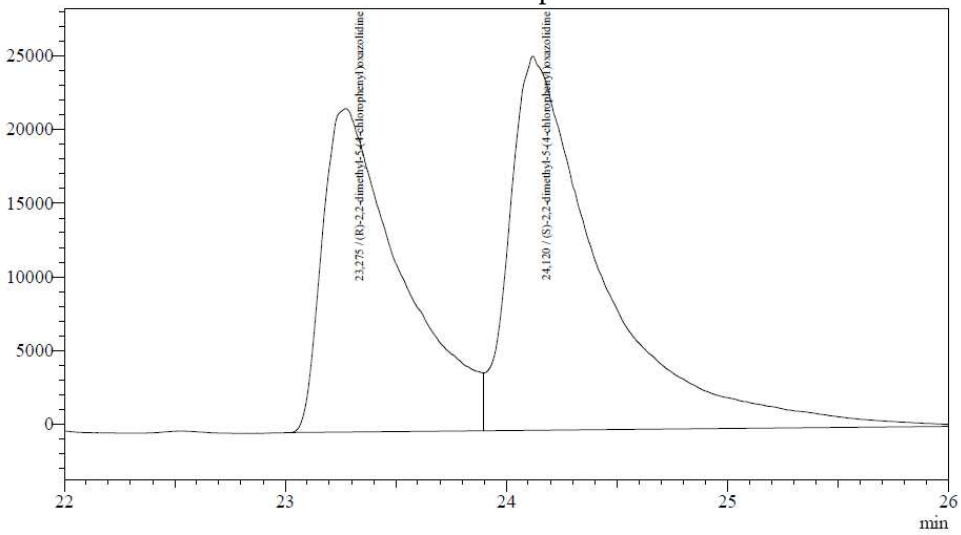


(*R*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

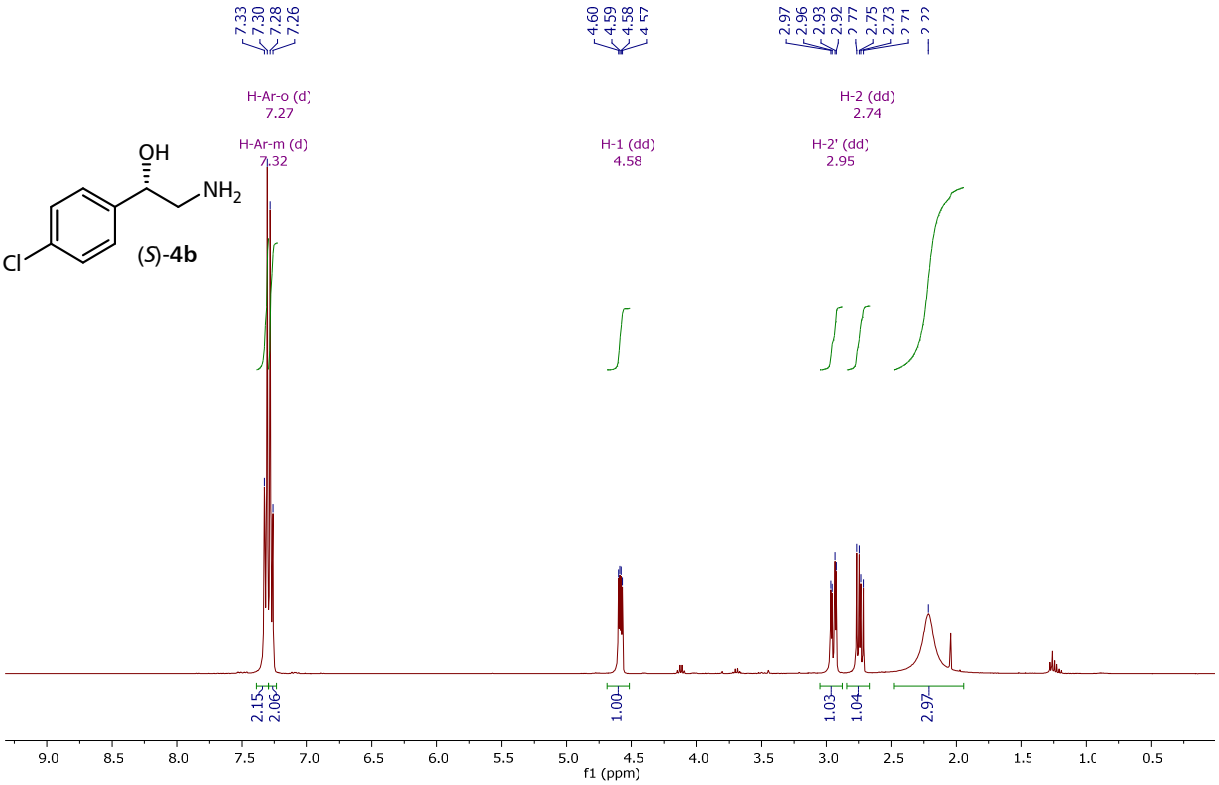


racemic sample:



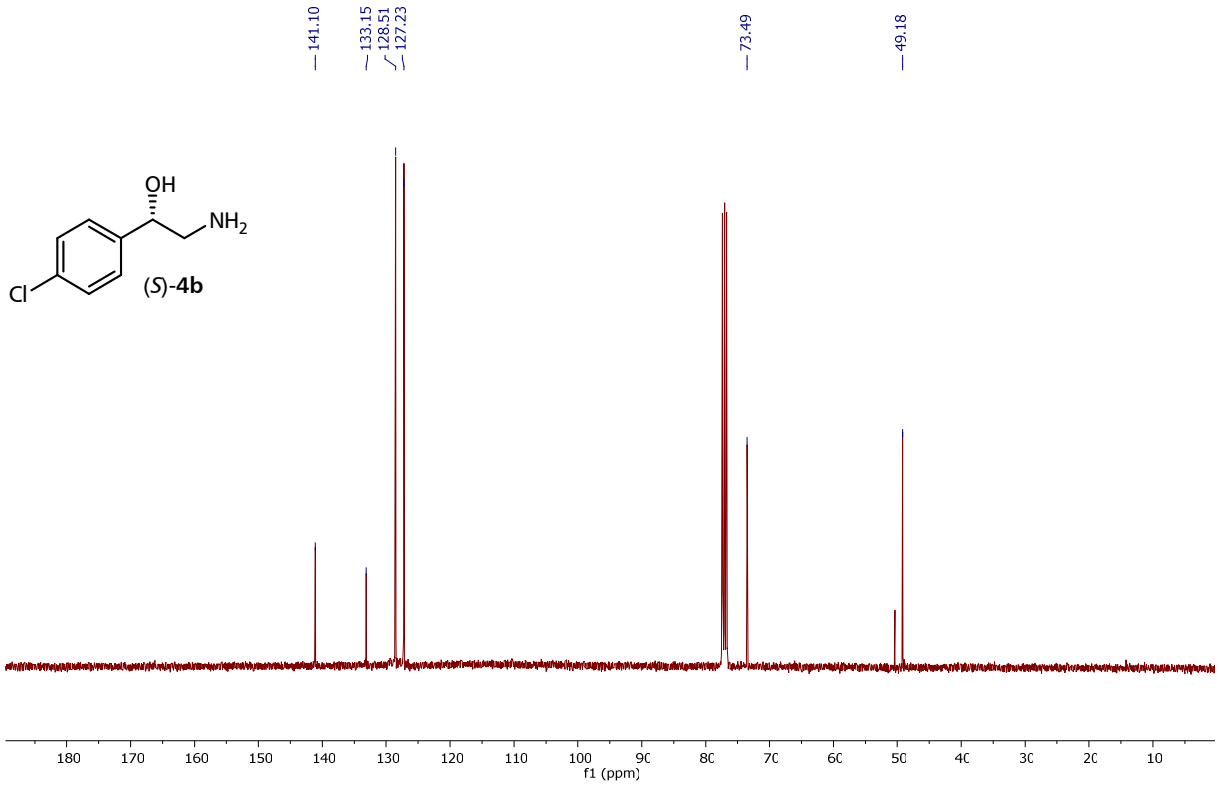
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



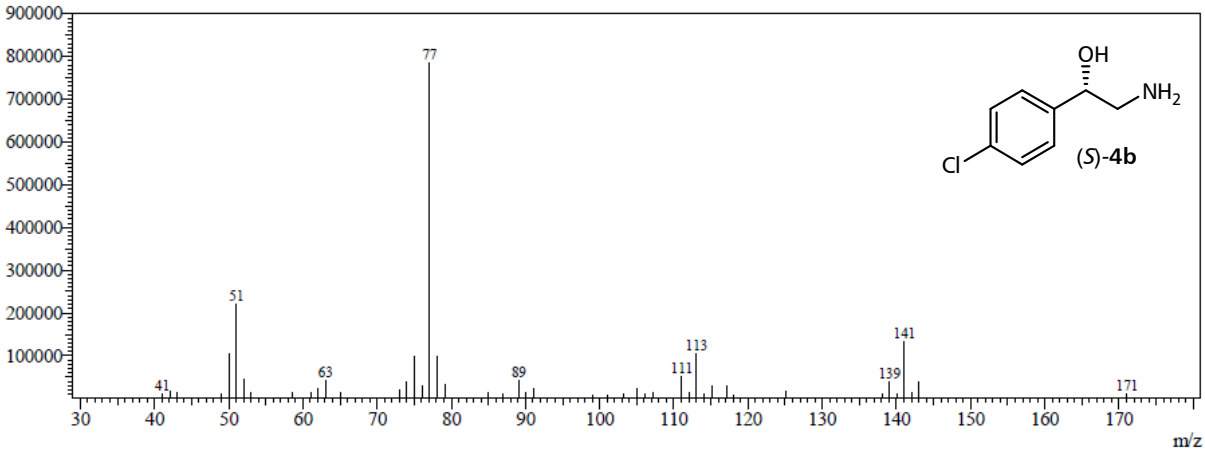
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*R*)-**4b**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



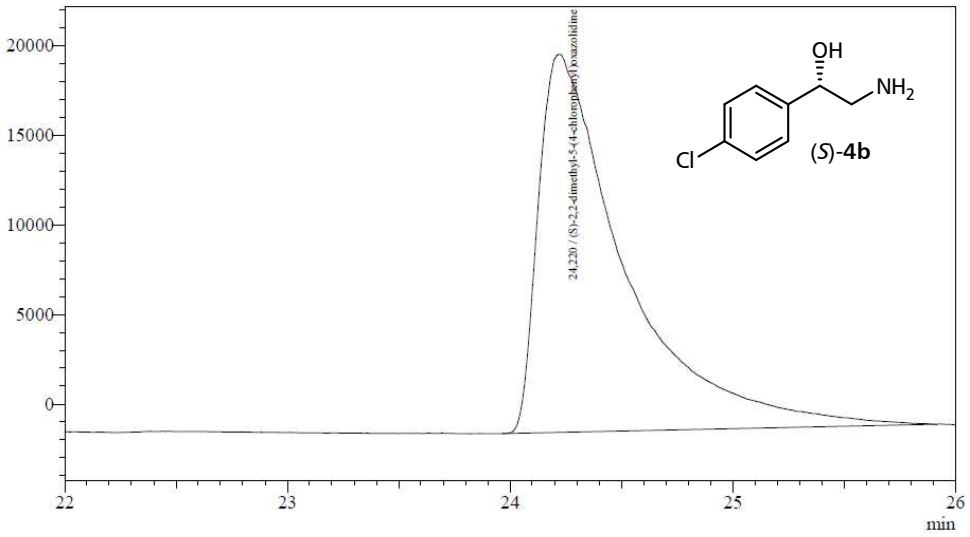
(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*S*)-**4b**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

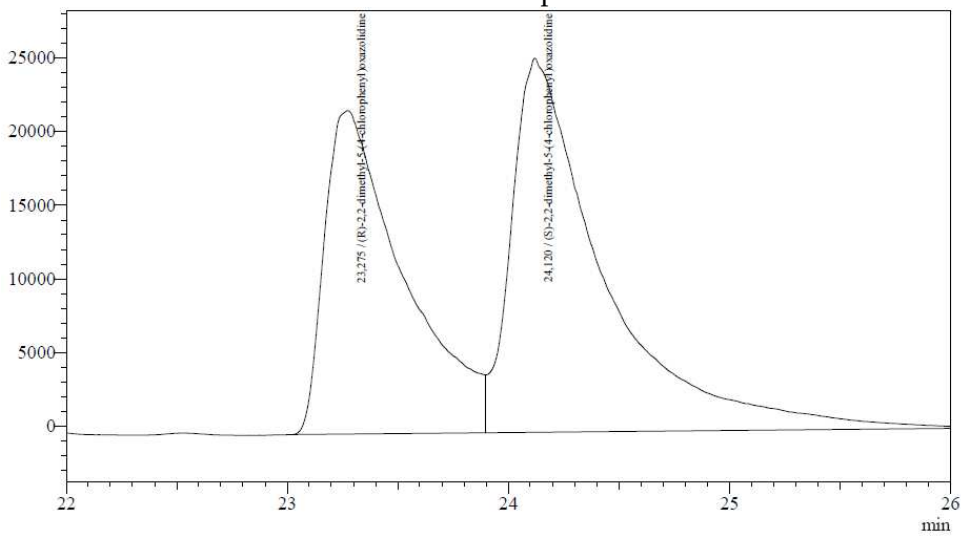


(*S*)-2-Amino-1-(4-chlorophenyl)ethanol (*S*)-**4b**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

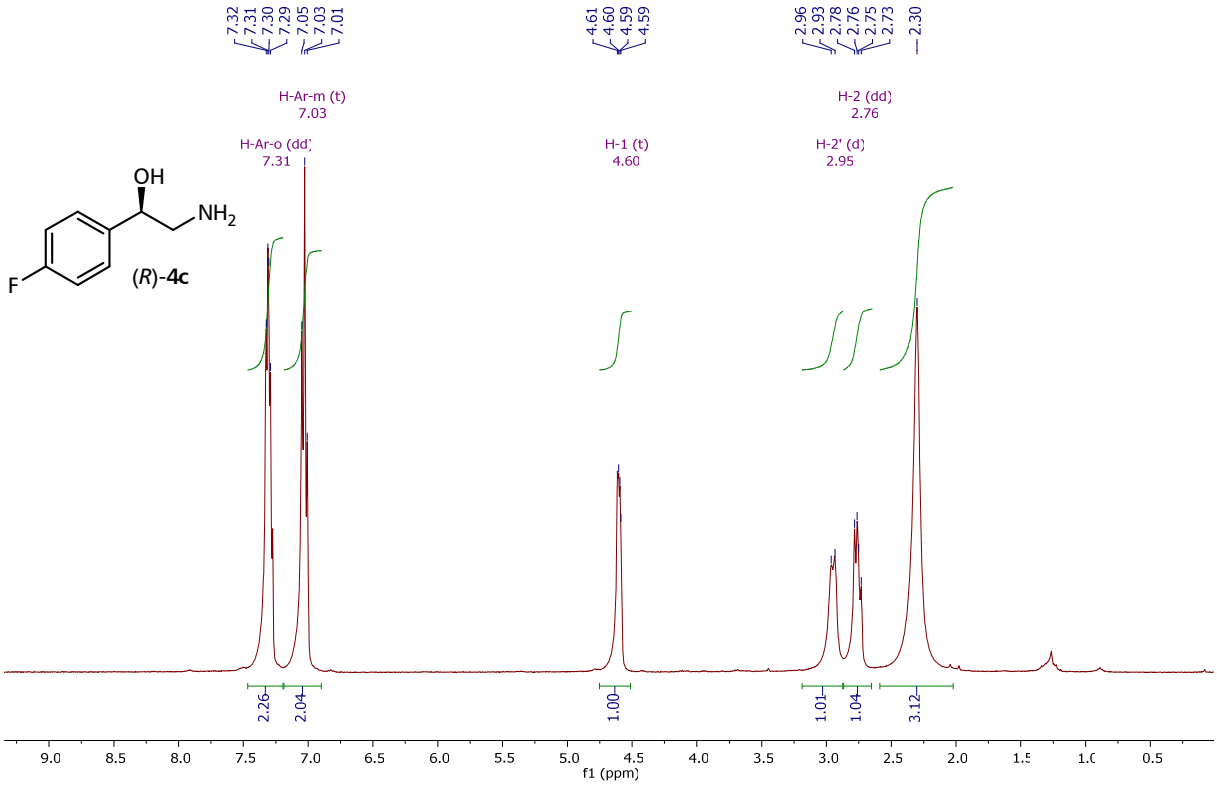


racemic sample:



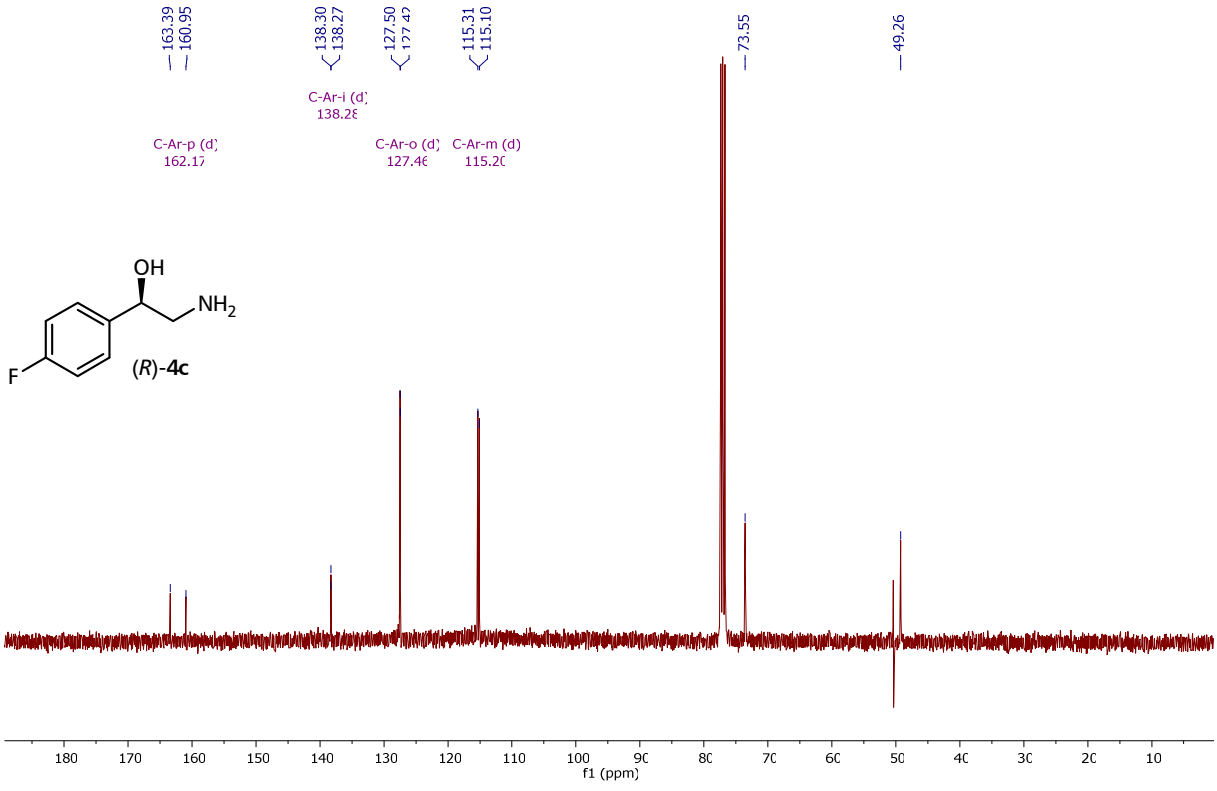
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



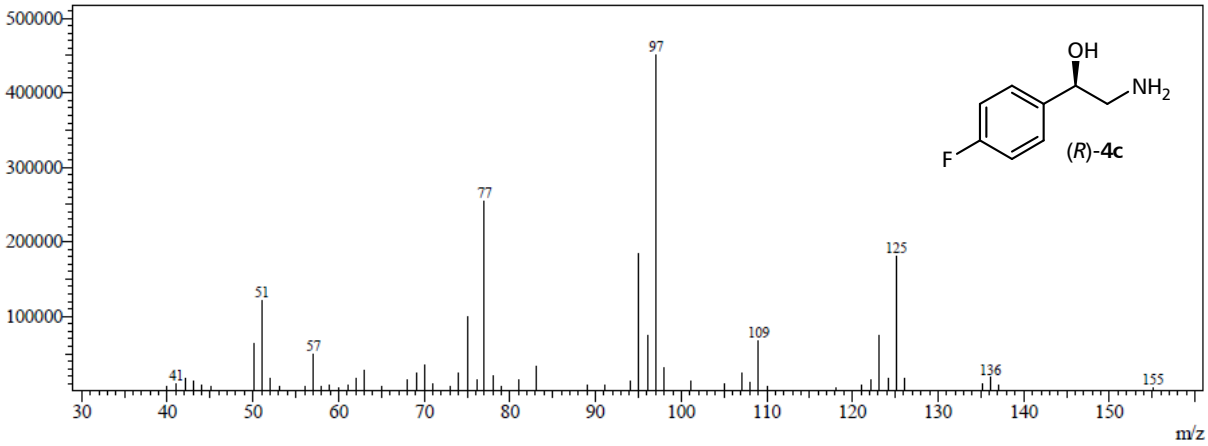
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



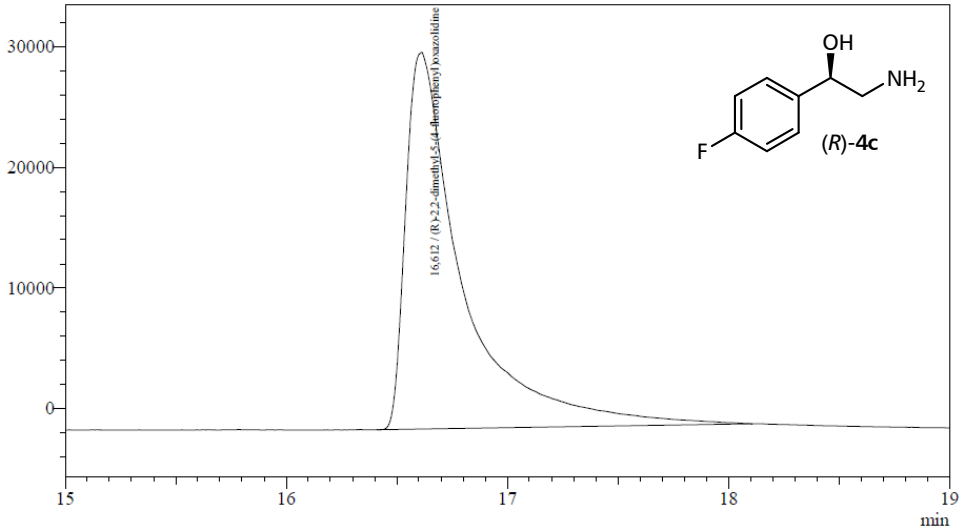
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

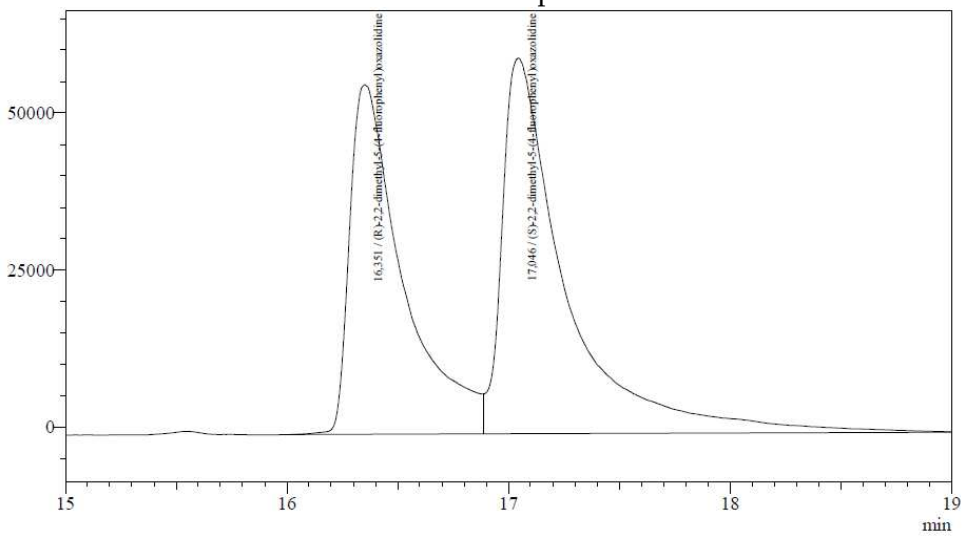


(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

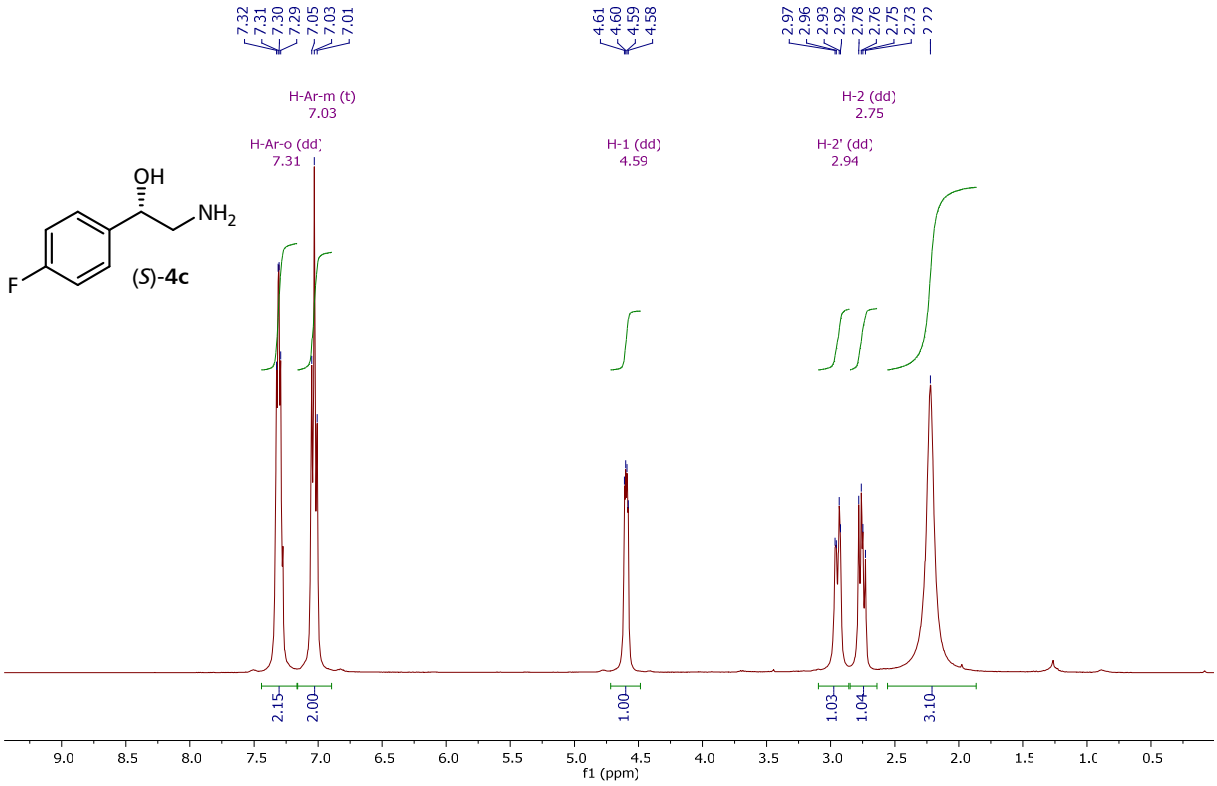


racemic sample:



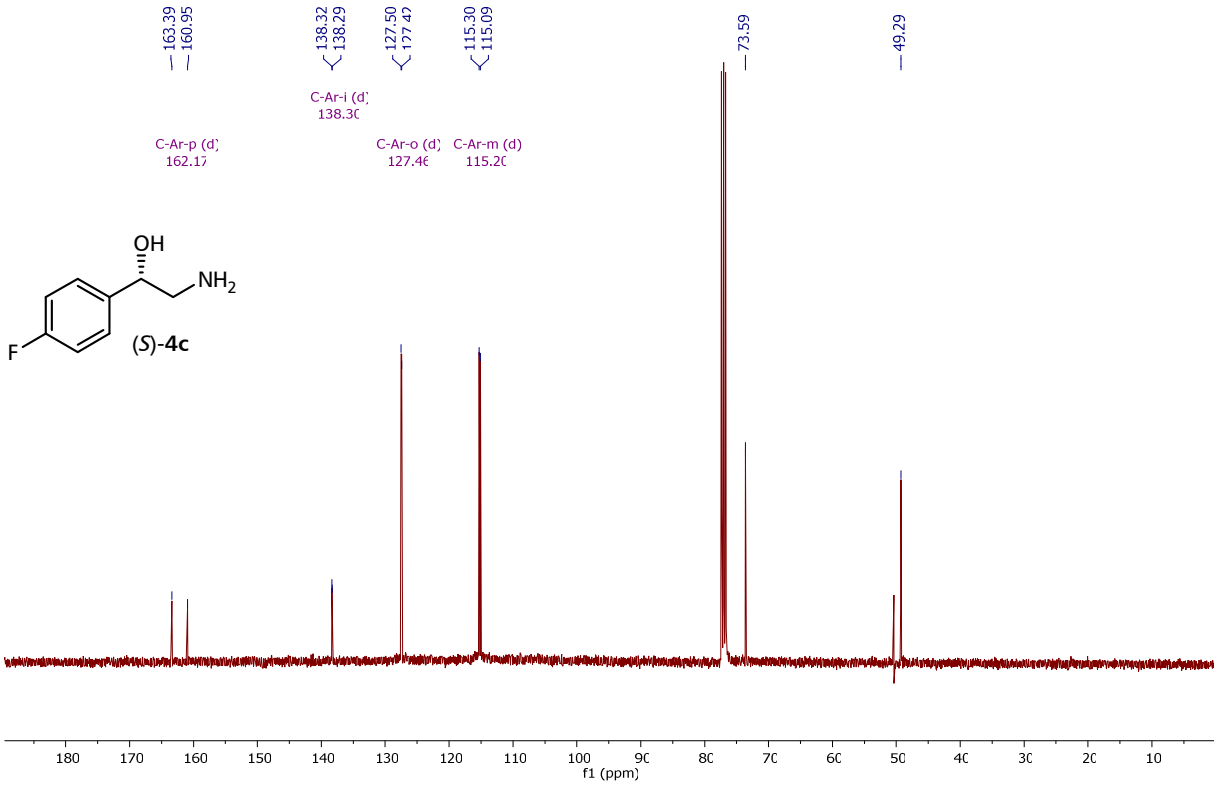
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



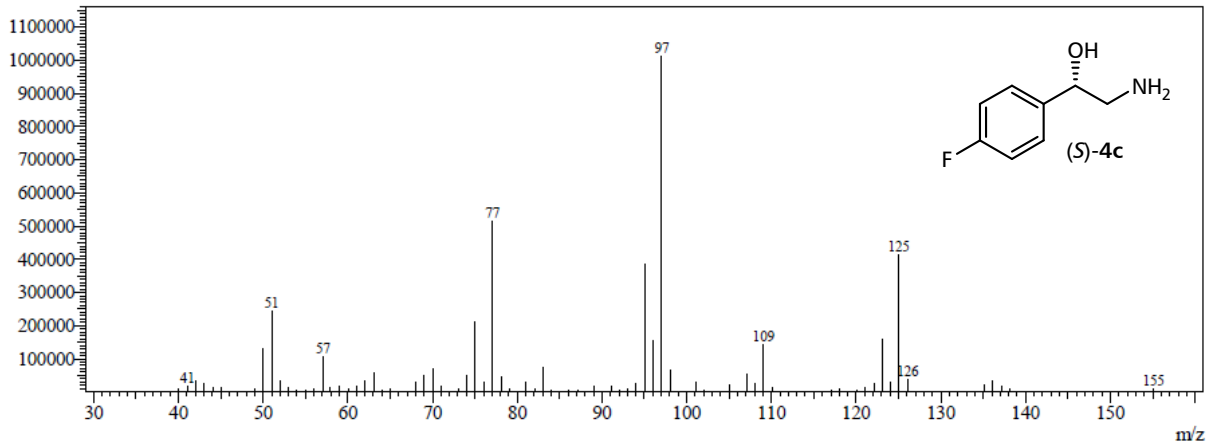
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



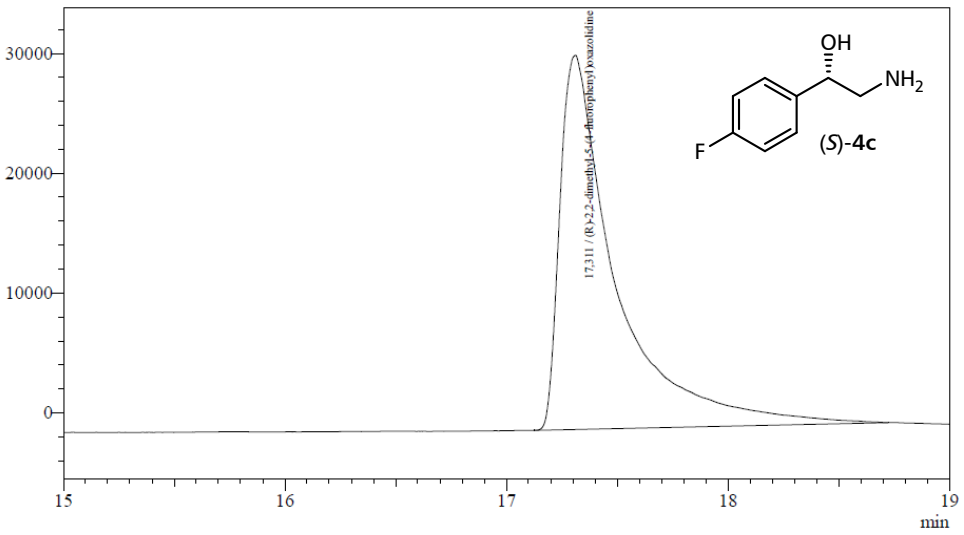
(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

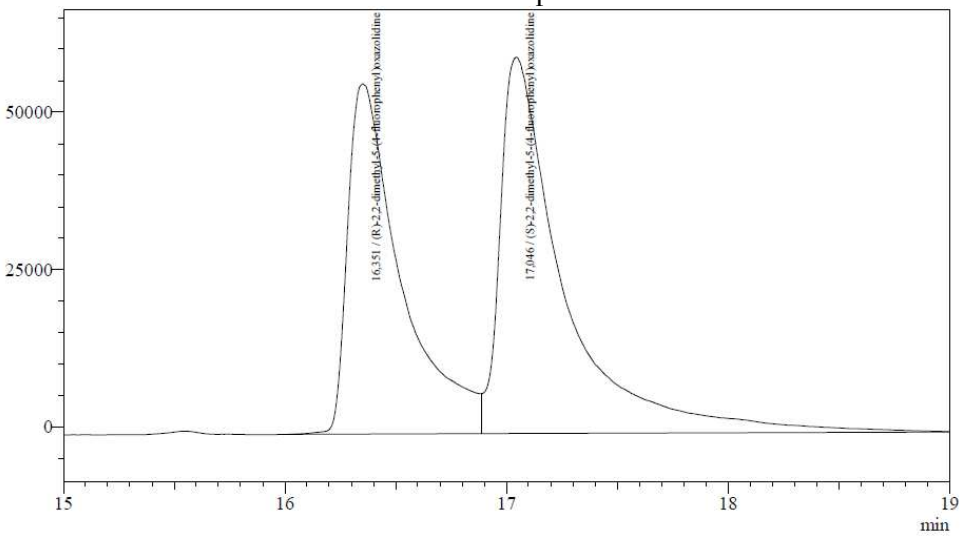


(*S*)-2-Amino-1-(4-fluorophenyl)ethanol (*S*)-**4c**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

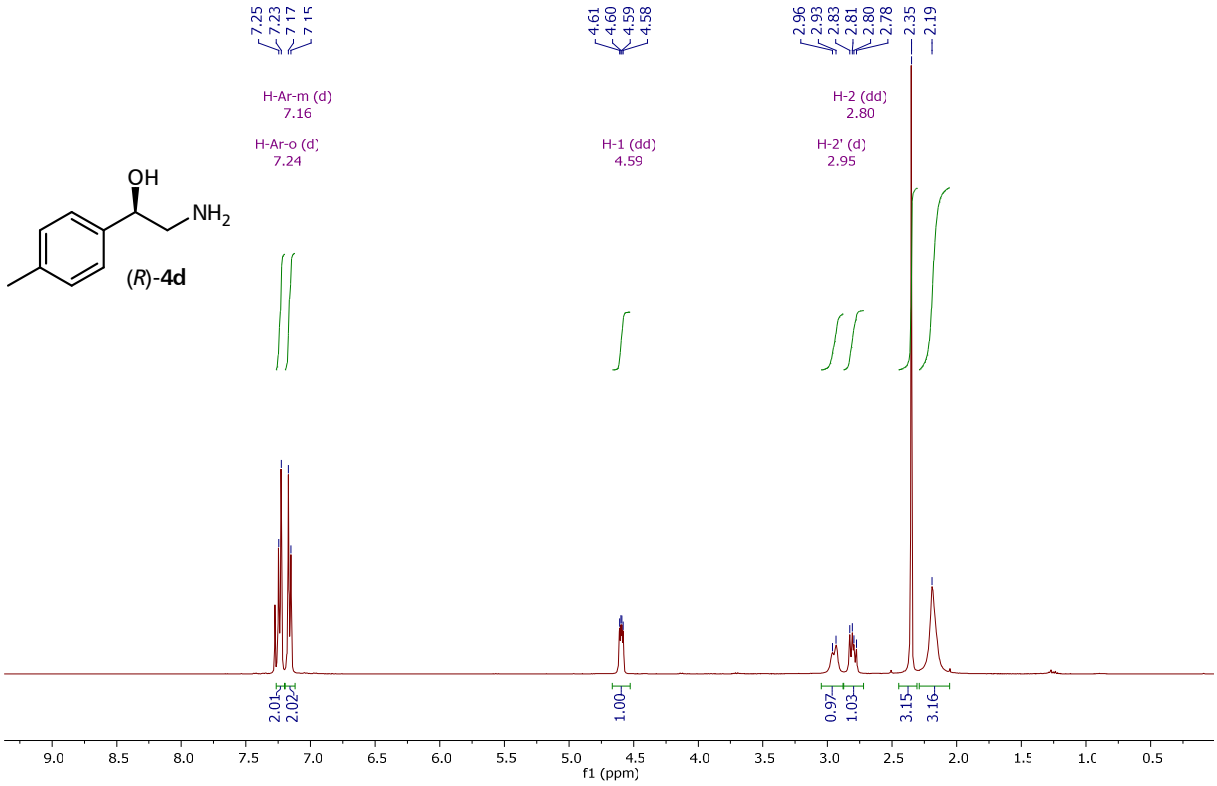


racemic sample:



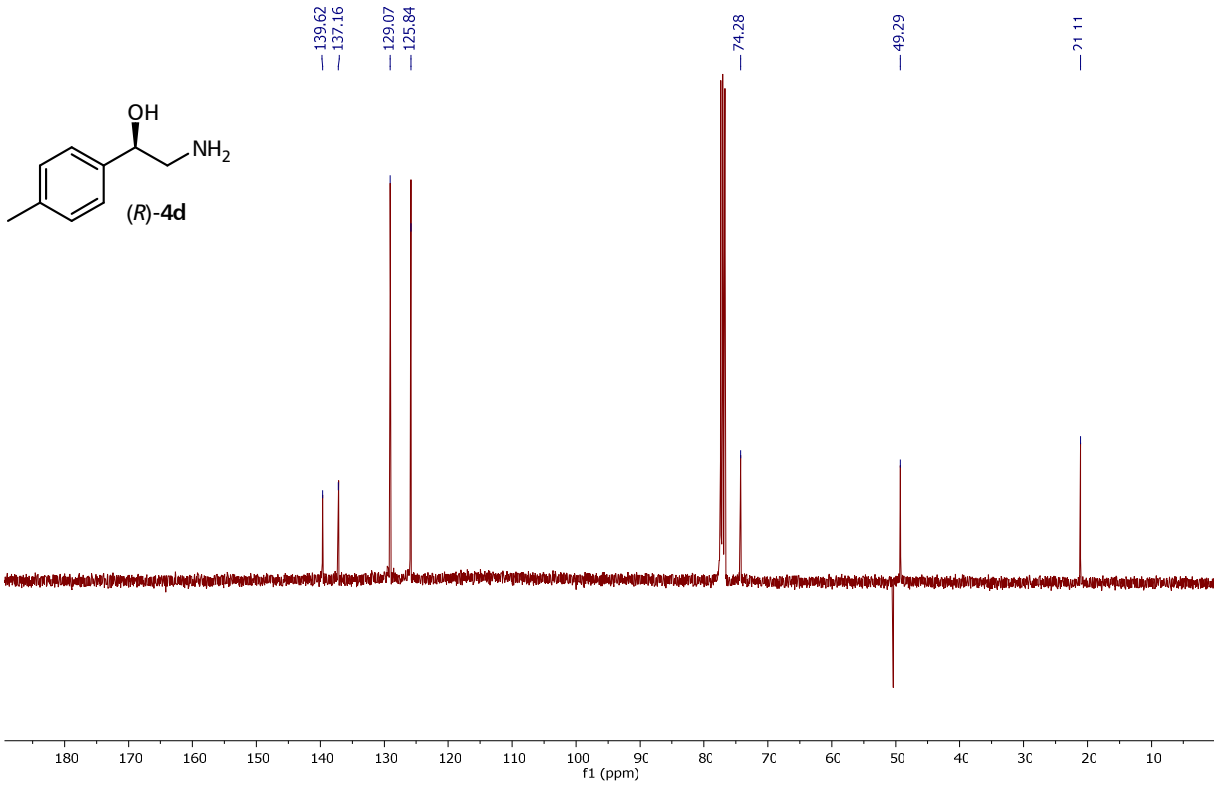
(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



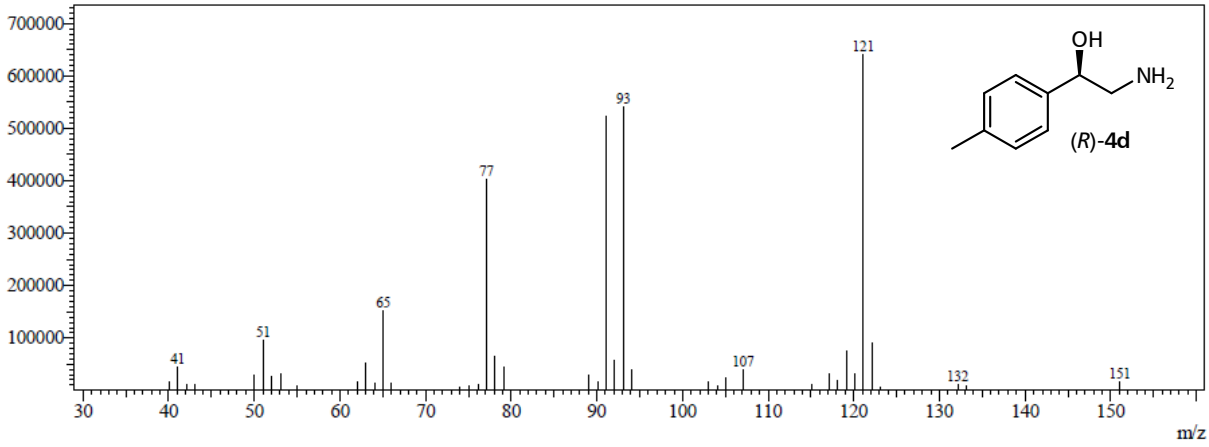
(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



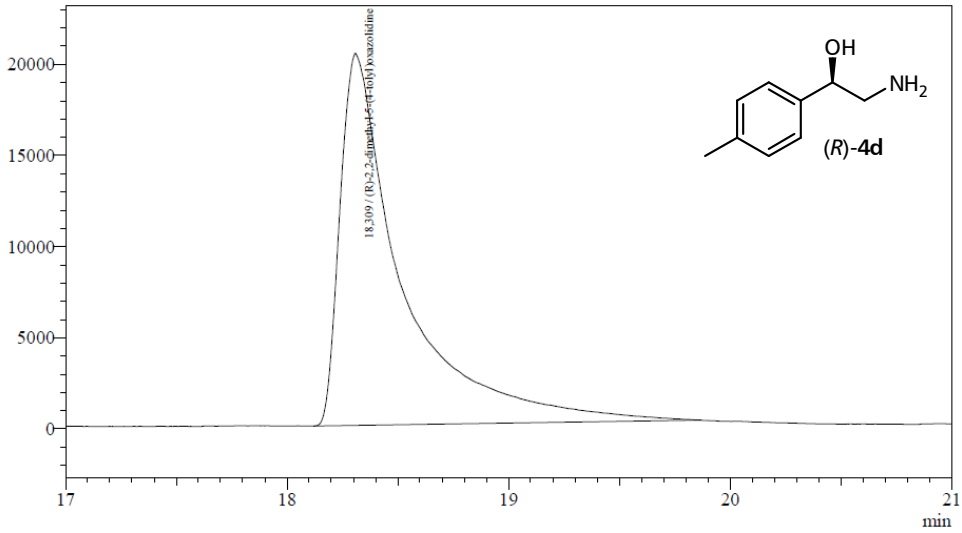
(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

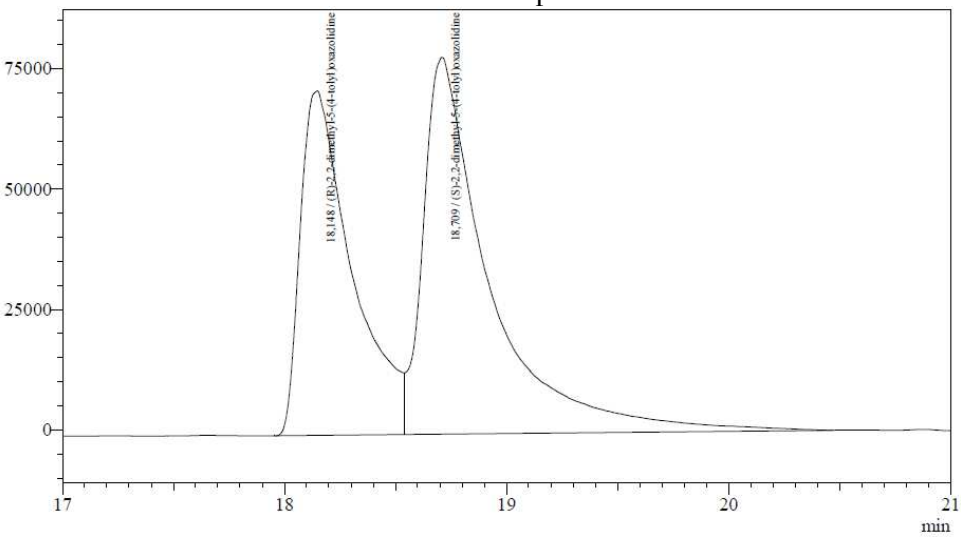


(*R*)-2-Amino-1-(4-tolyl)ethanol (*R*)-**4d**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

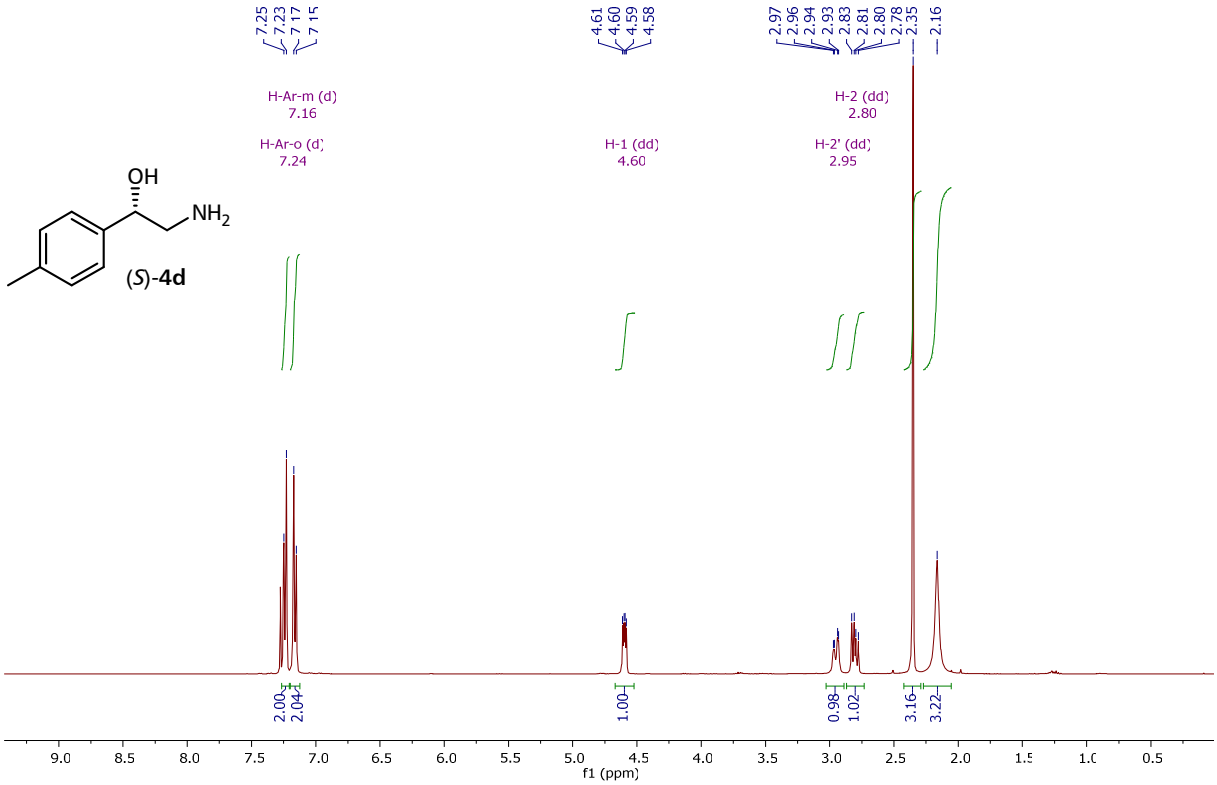


racemic sample:



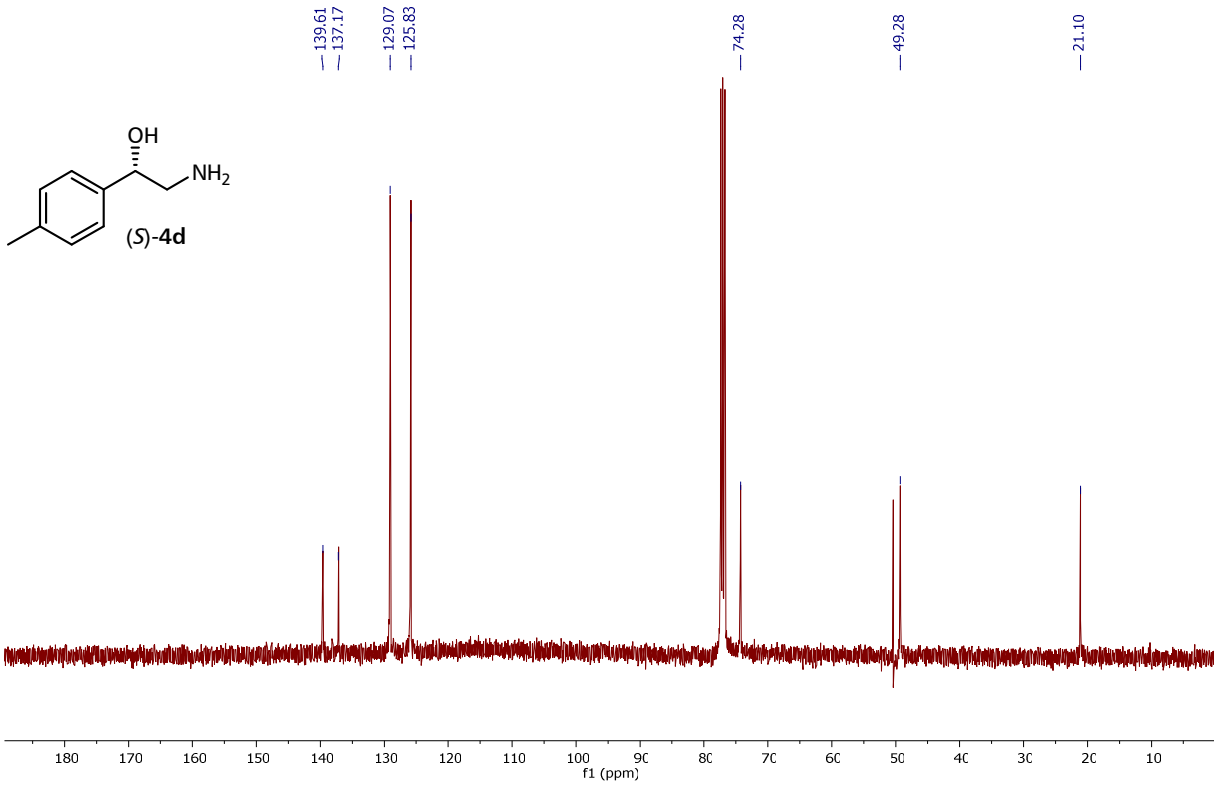
(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



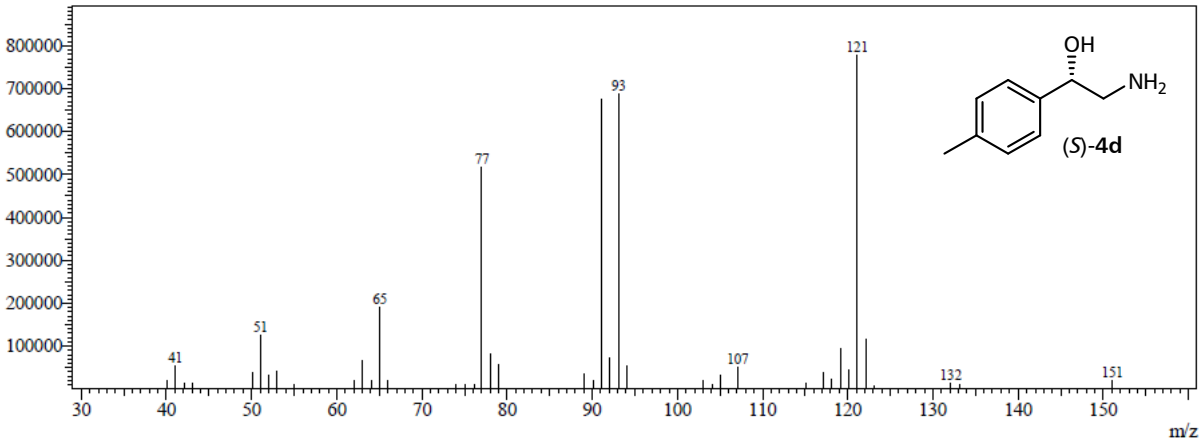
(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



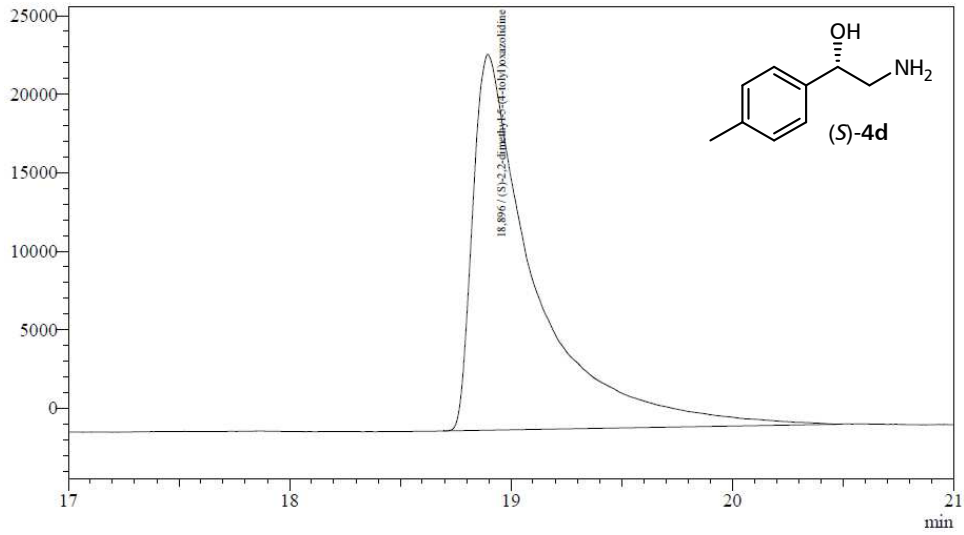
(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

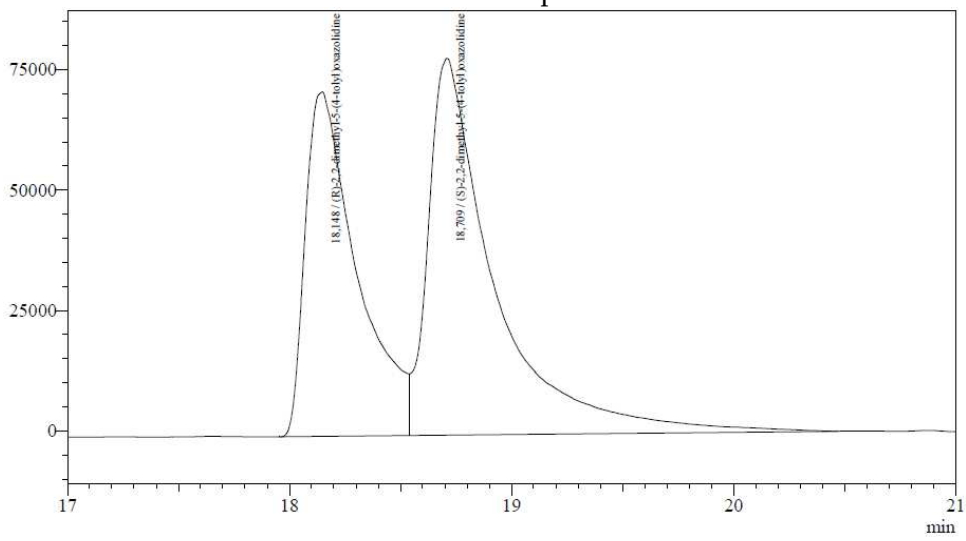


(*S*)-2-Amino-1-(4-tolyl)ethanol (*S*)-**4d**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

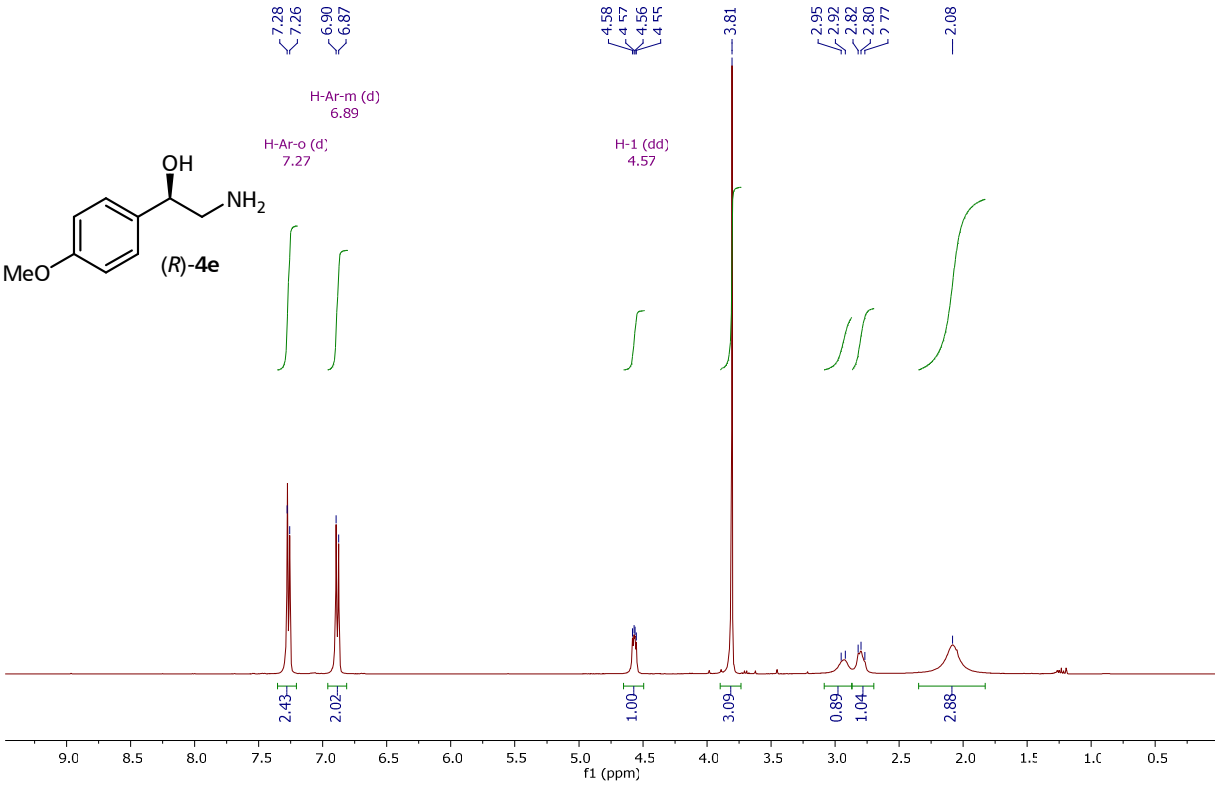


racemic sample:



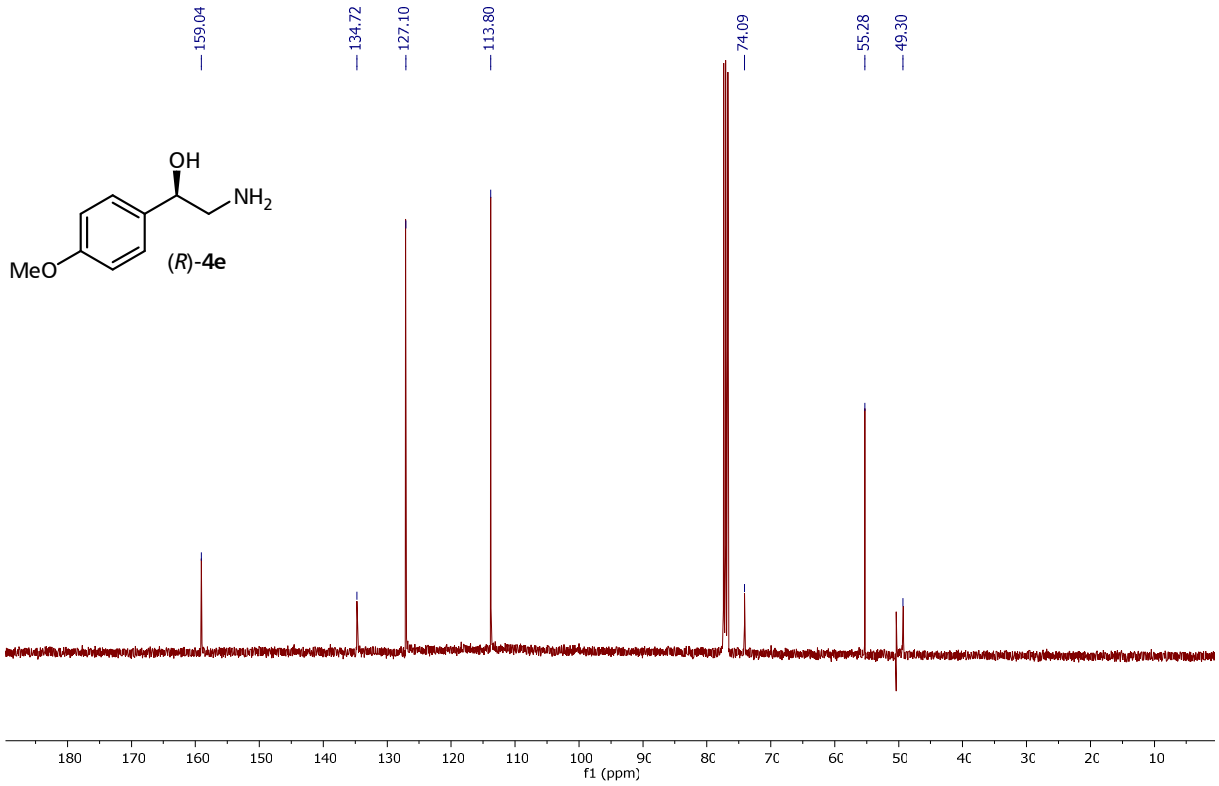
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



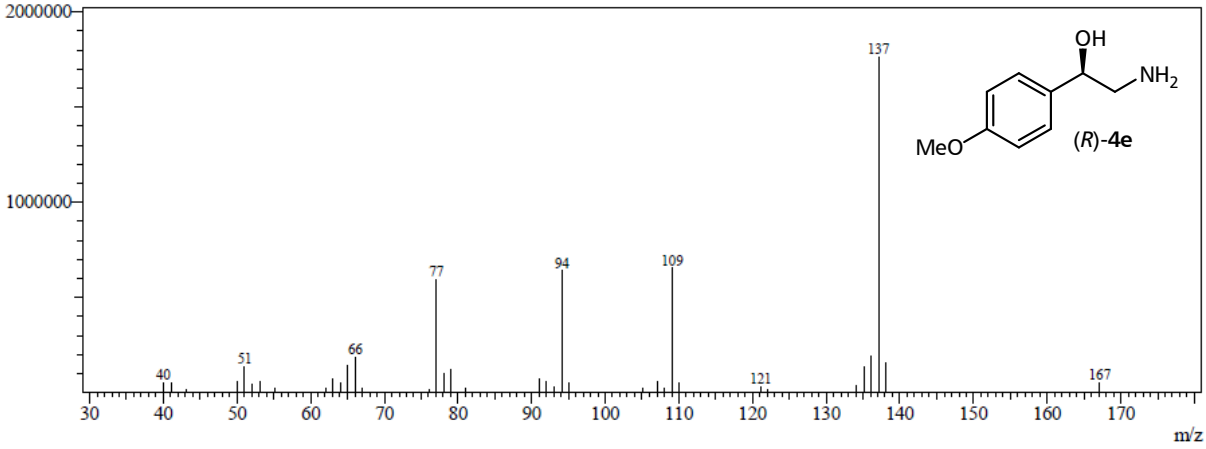
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



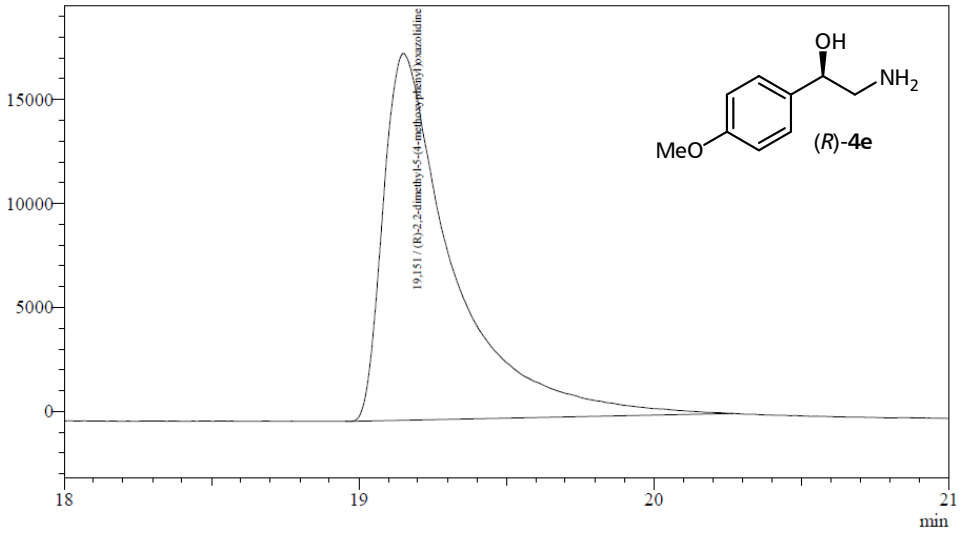
(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

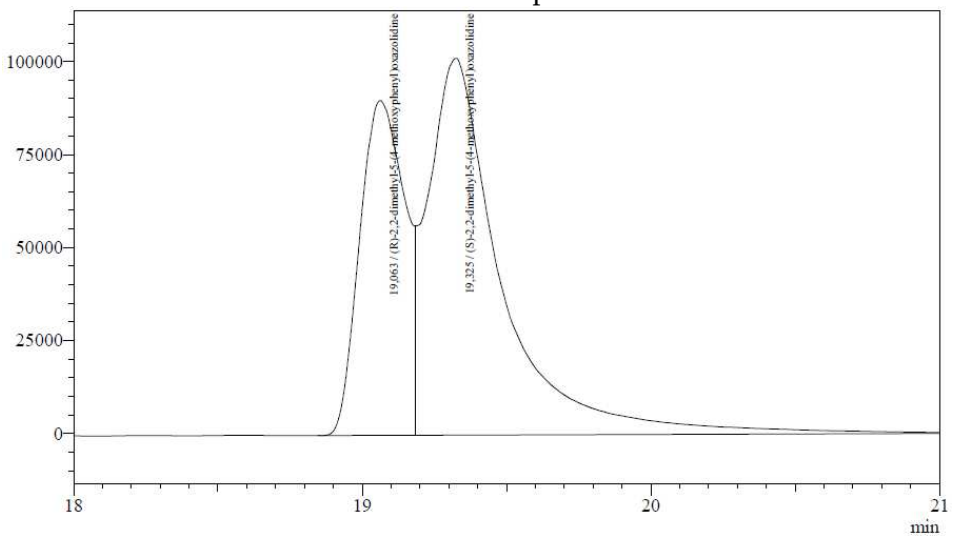


(*R*)-2-Amino-1-(4-methoxyphenyl)ethanol (*R*)-**4e**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

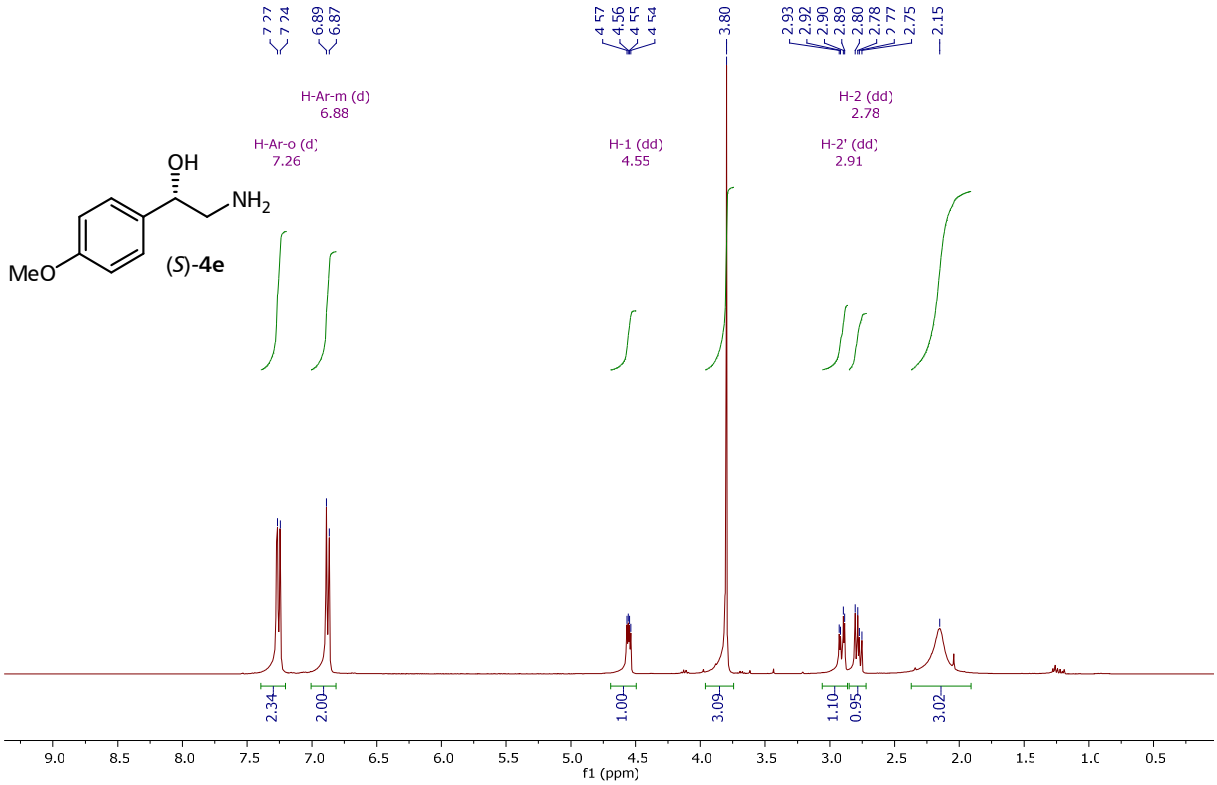


racemic sample:



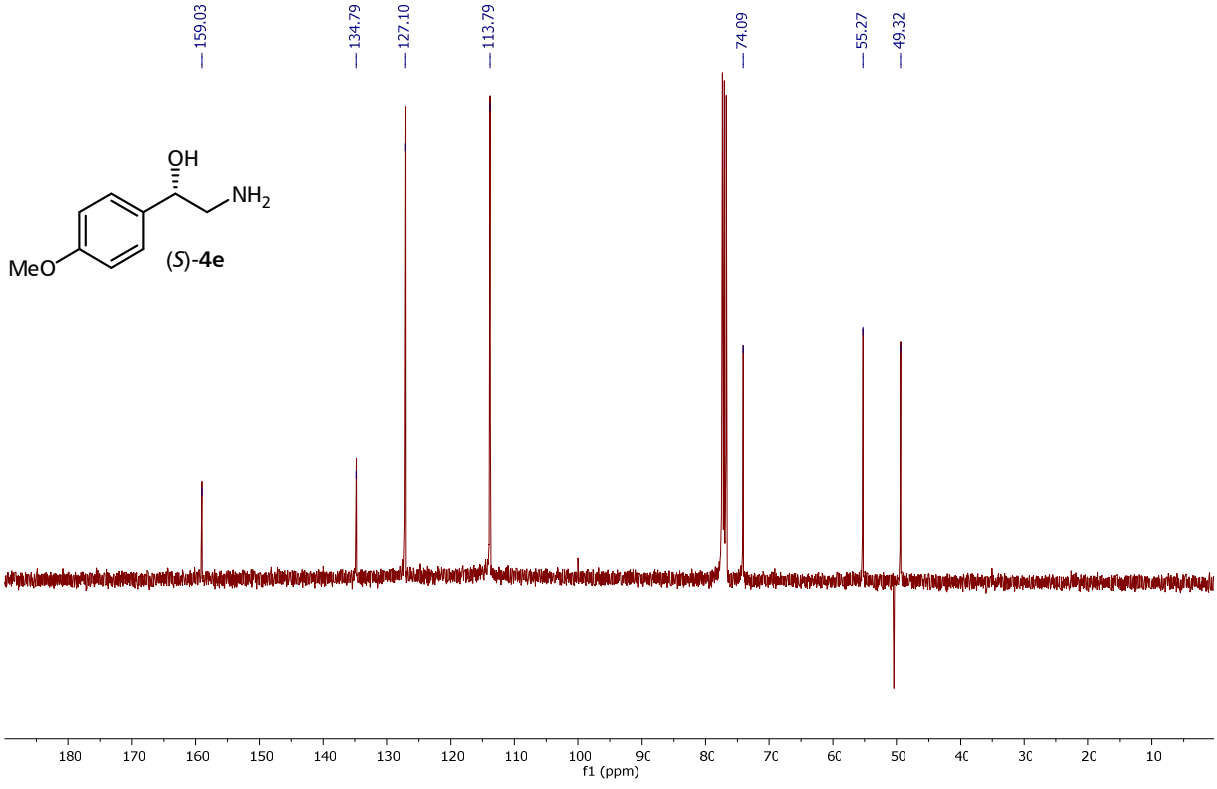
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



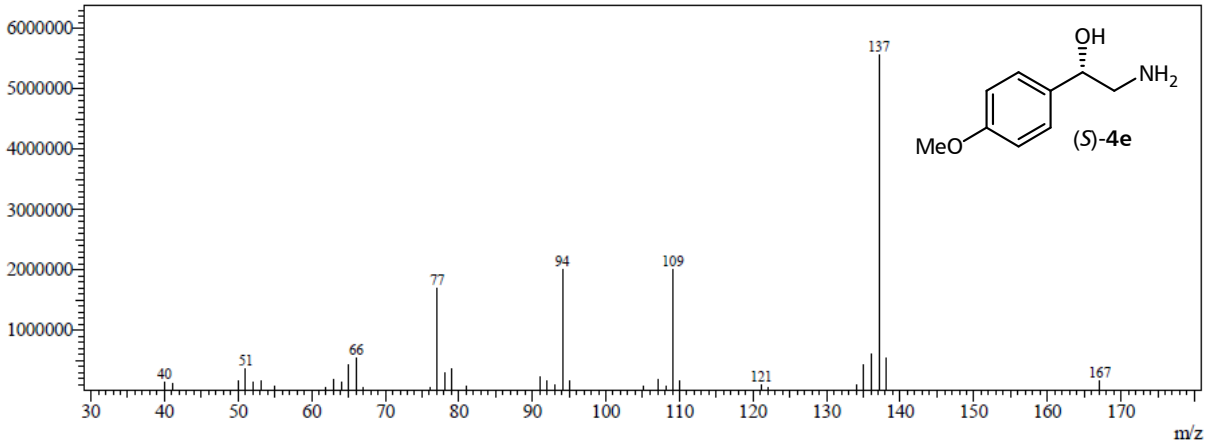
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



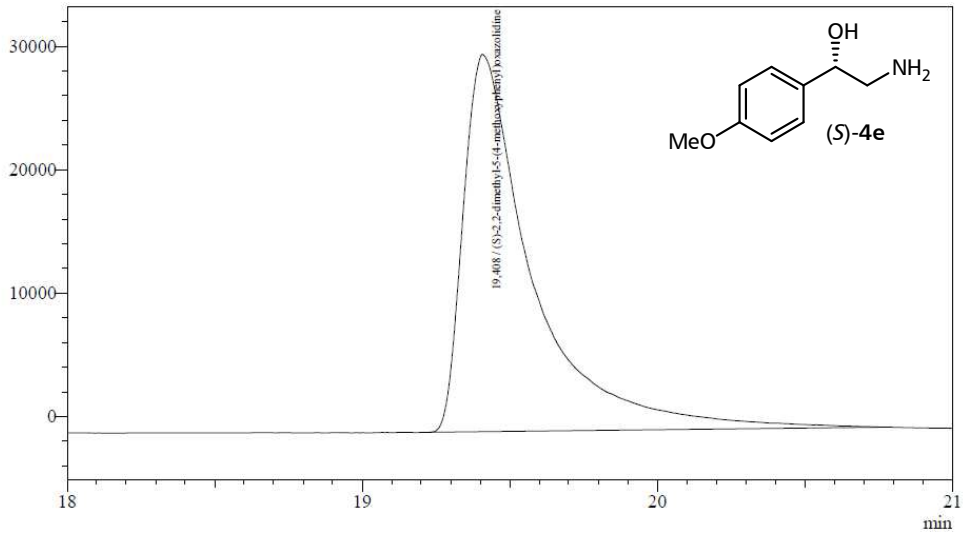
(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

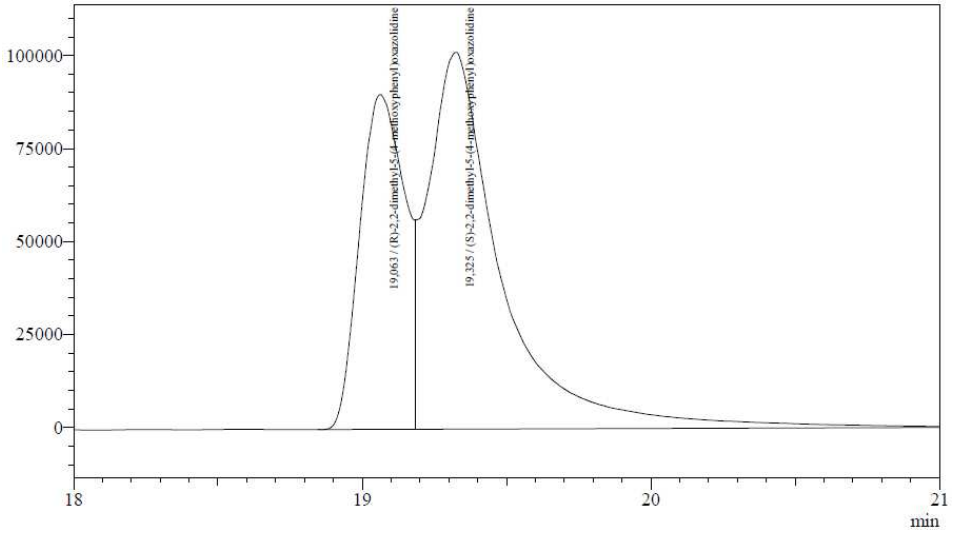


(*S*)-2-Amino-1-(4-methoxyphenyl)ethanol (*S*)-**4e**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

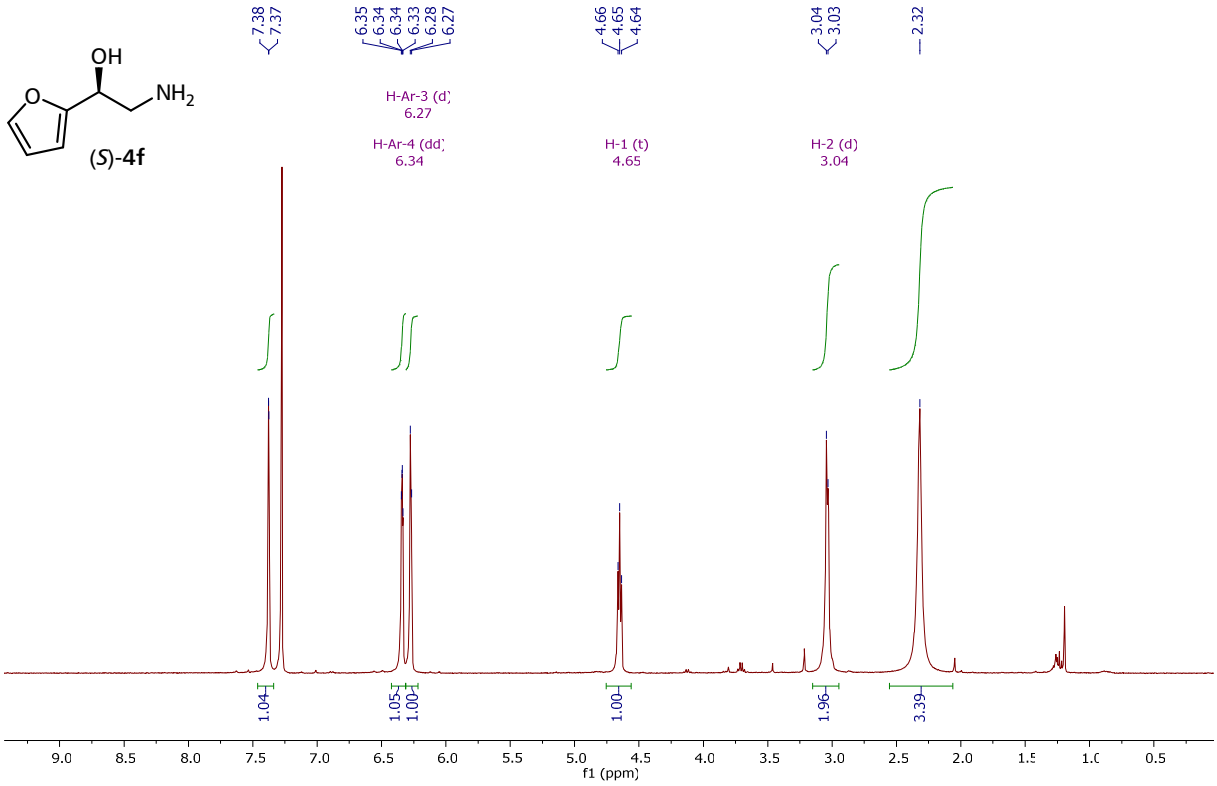


racemic sample:



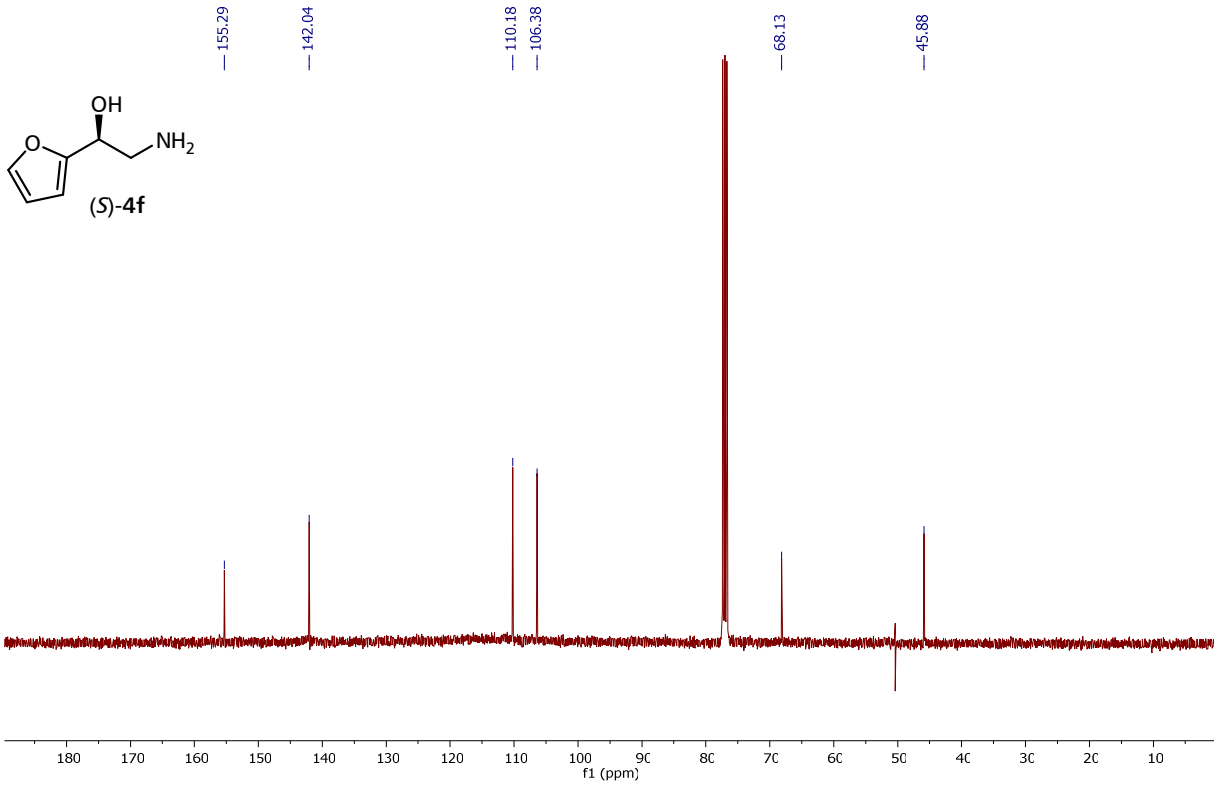
(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



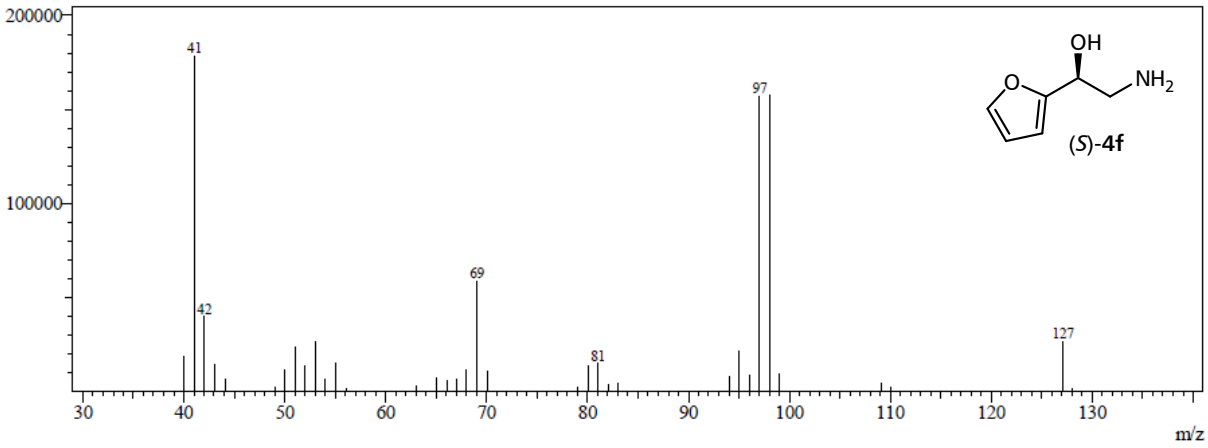
(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



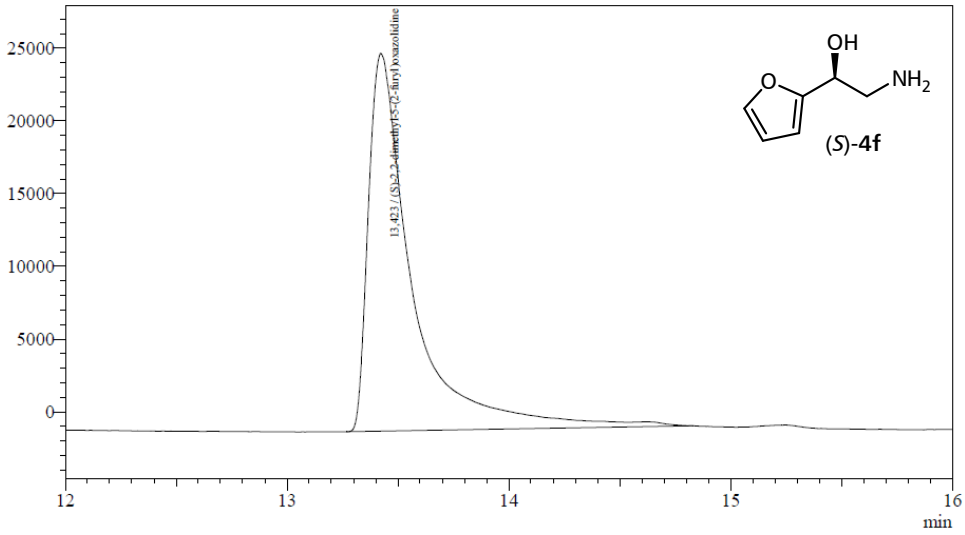
(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

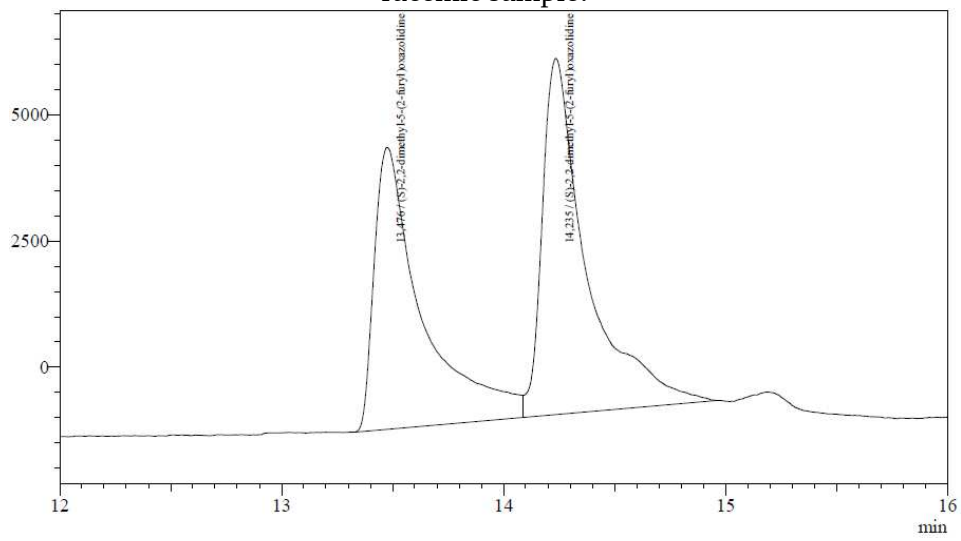


(*S*)-2-Amino-1-(2-furyl)ethanol (*S*)-**4f**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

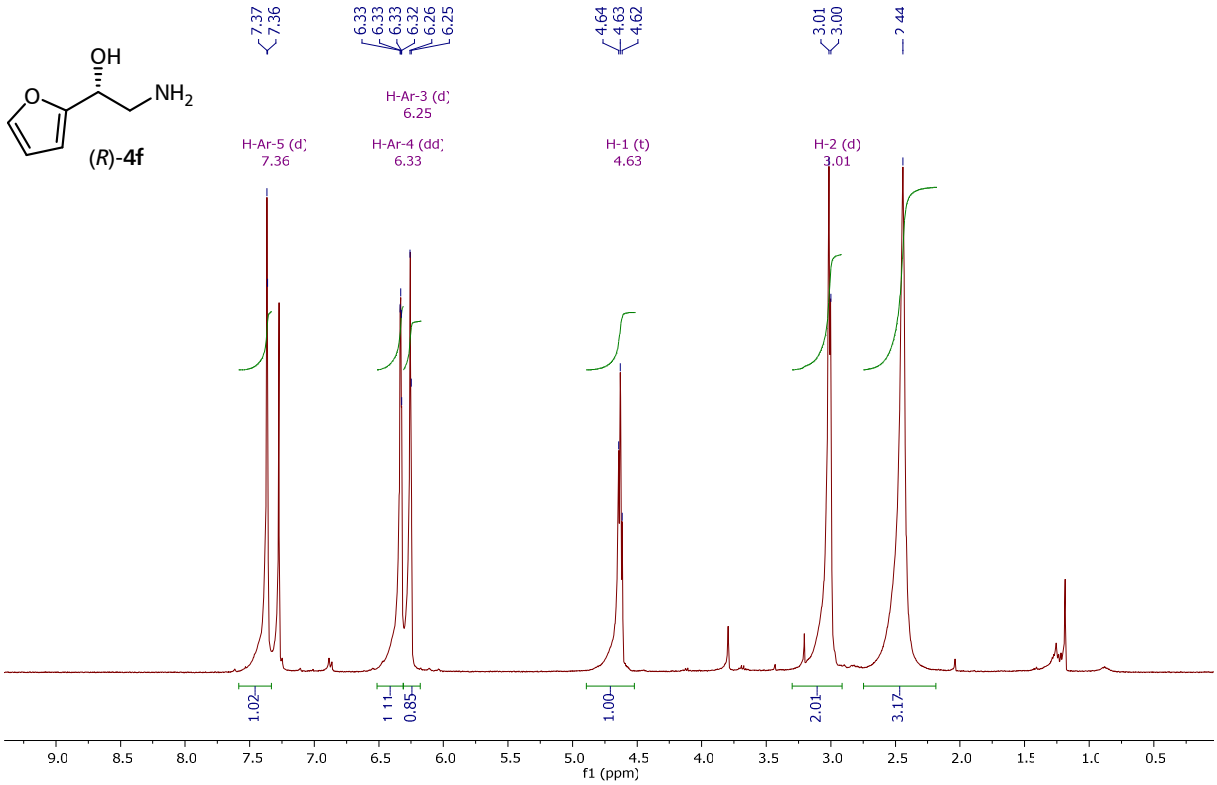


racemic sample:



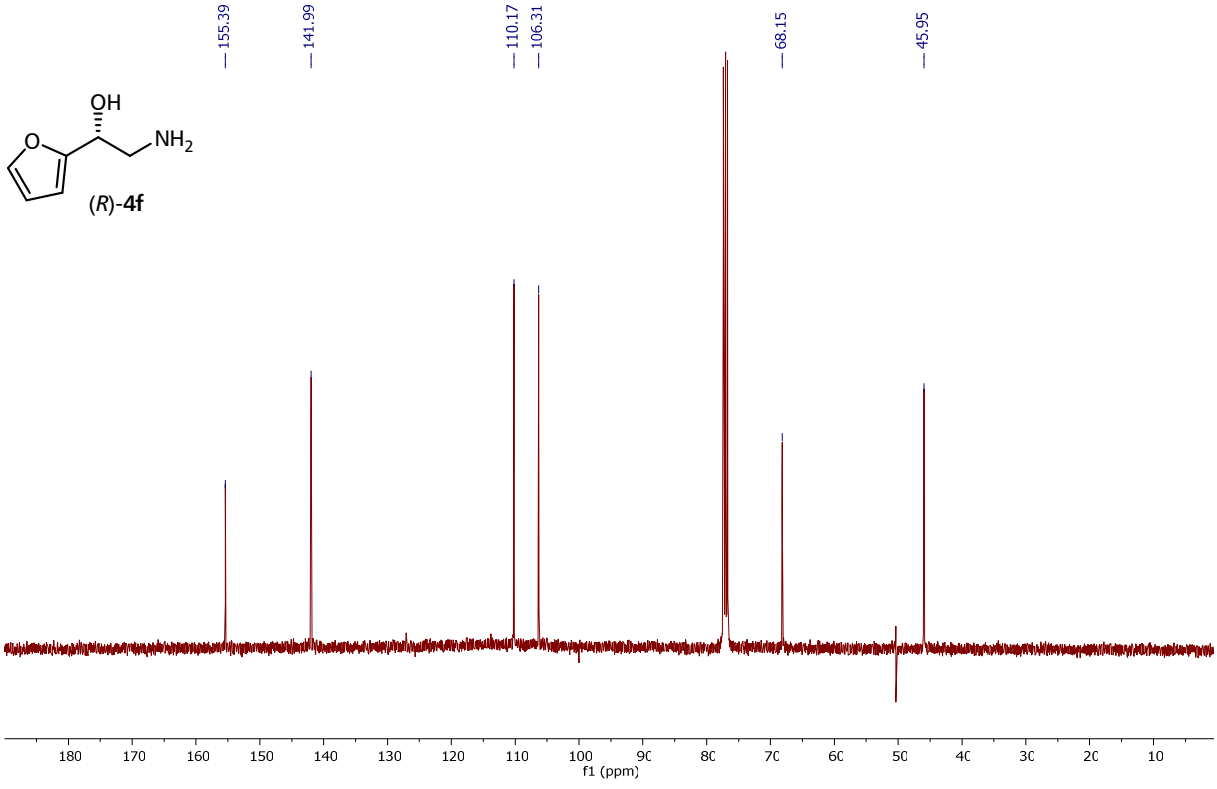
(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



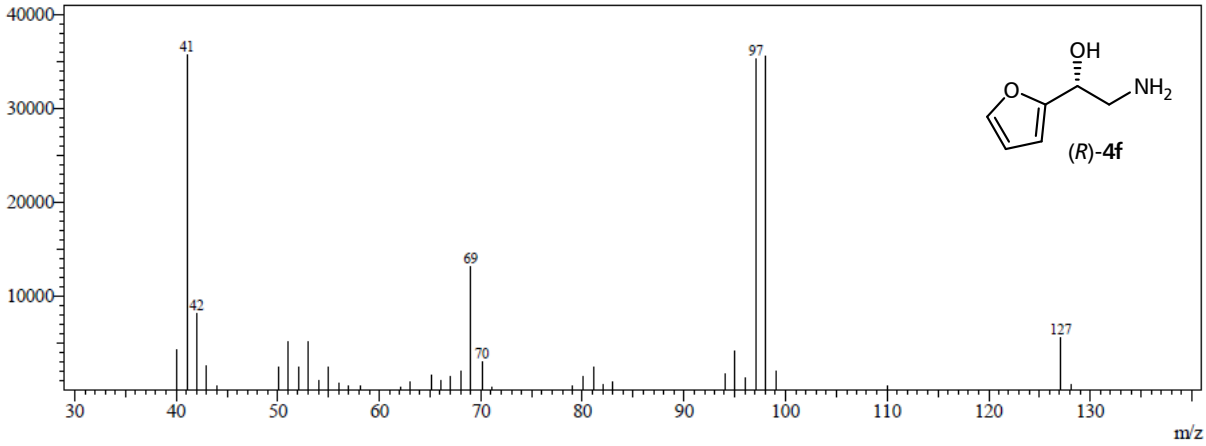
(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (5 mL scale)



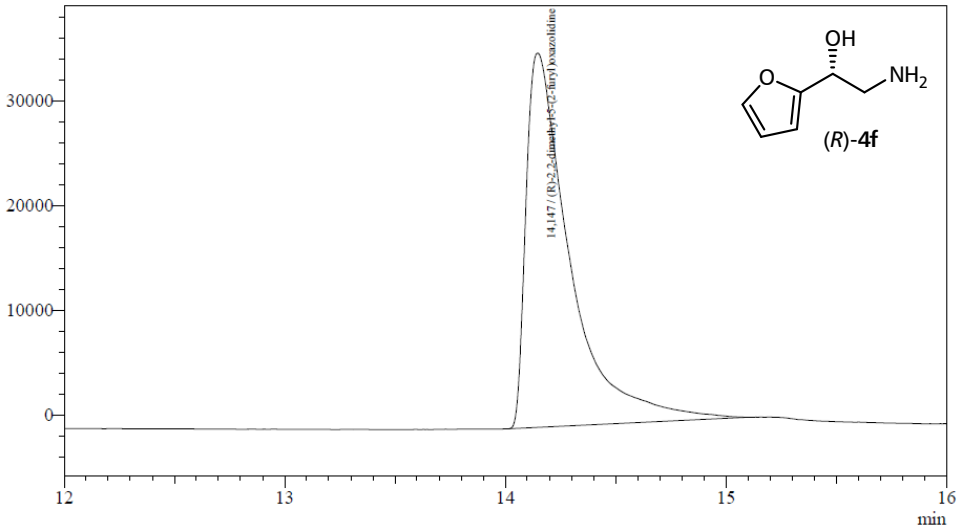
(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: MS spectrum

product obtained by the three-step one-pot sequence (5 mL scale)

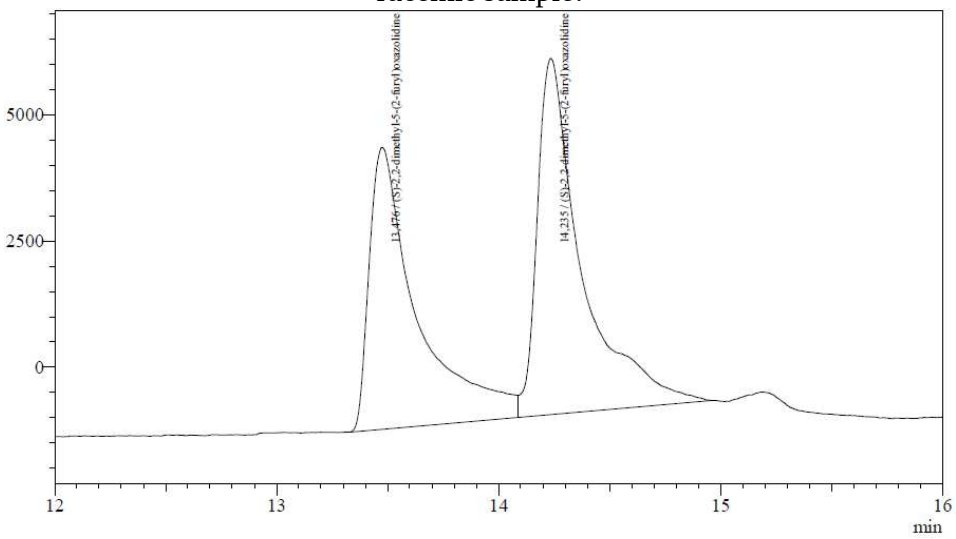


(*R*)-2-Amino-1-(2-furyl)ethanol (*R*)-**4f**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (5 mL scale)

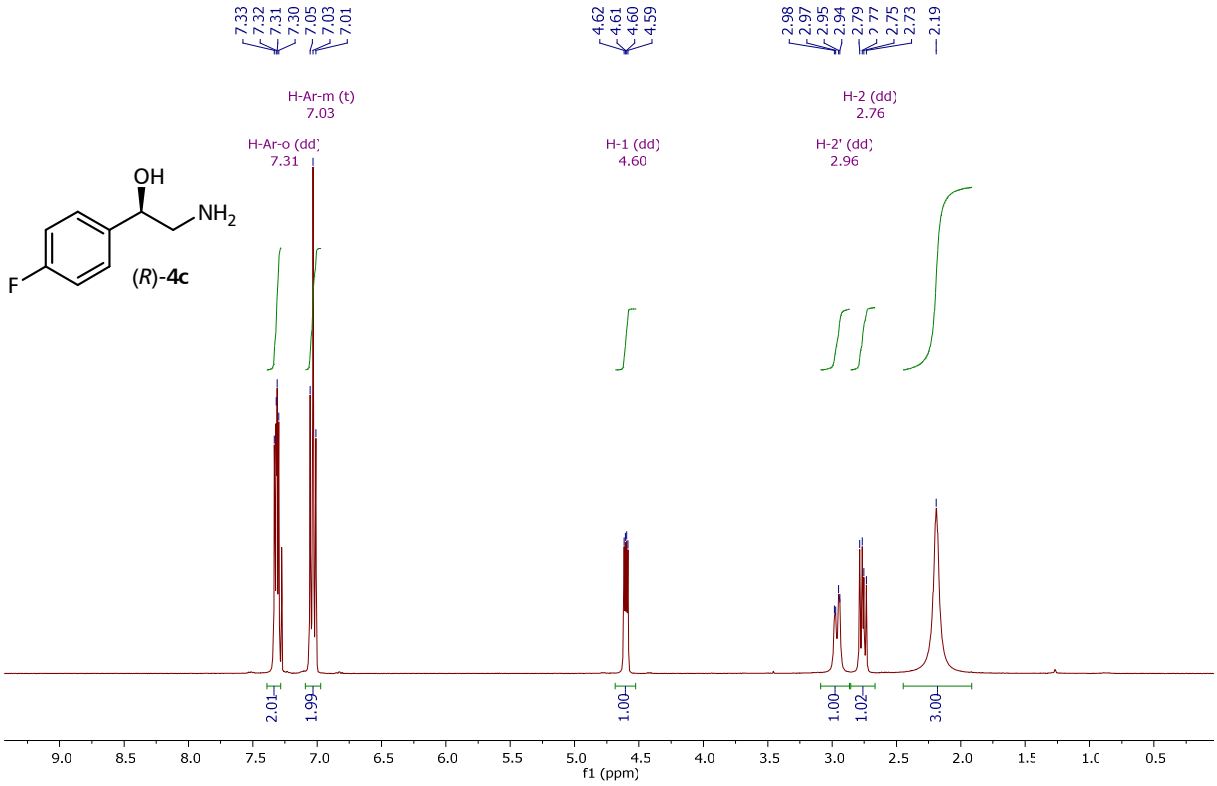


racemic sample:



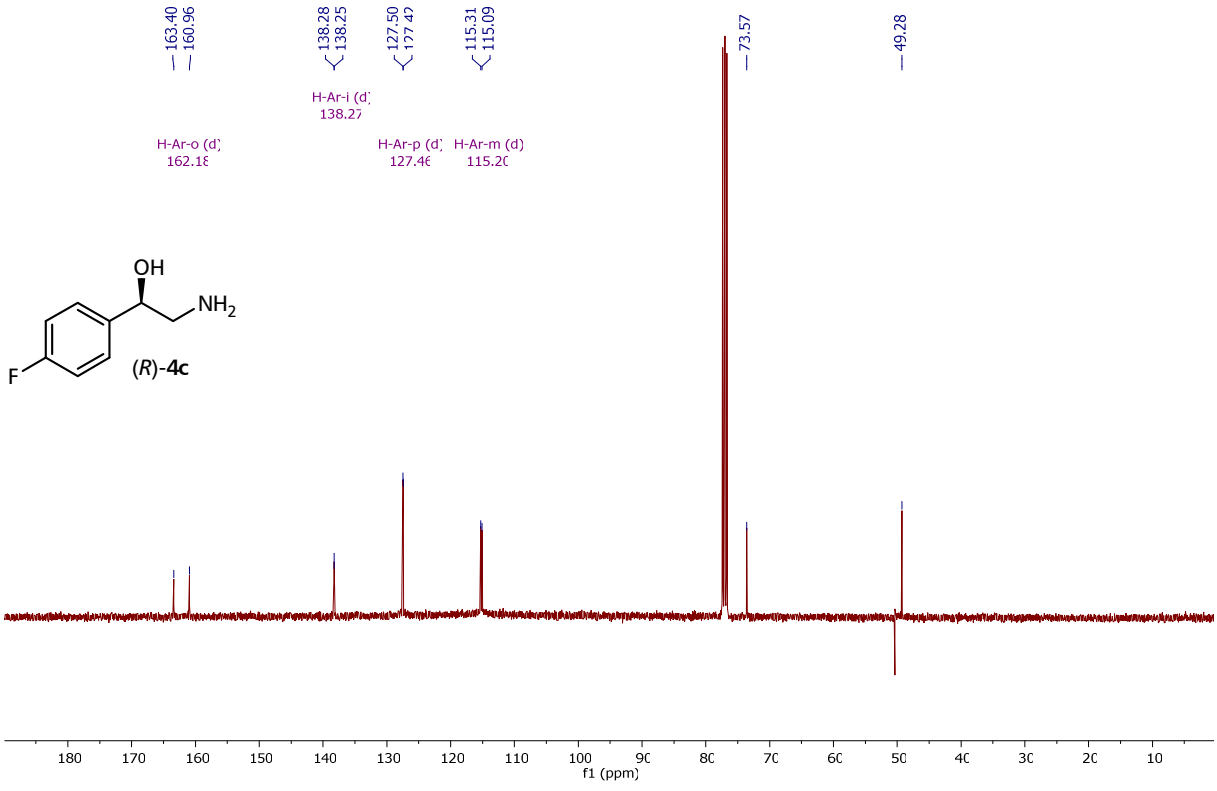
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: ^{1}H-NMR spectrum

product obtained by the three-step one-pot sequence (gram scale)



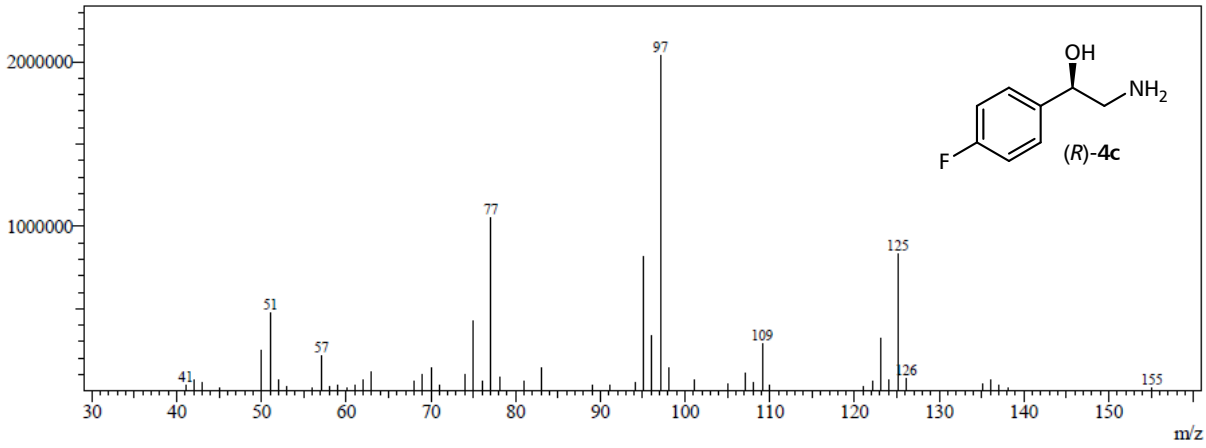
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: ^{13}C-NMR spectrum

product obtained by the three-step one-pot sequence (gram scale)



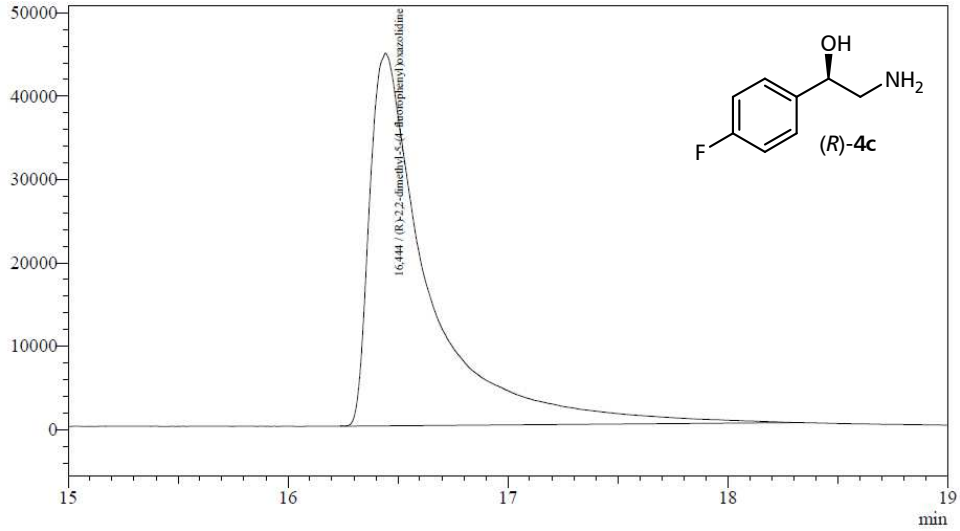
(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: MS spectrum

product obtained by the three-step one-pot sequence (gram scale)

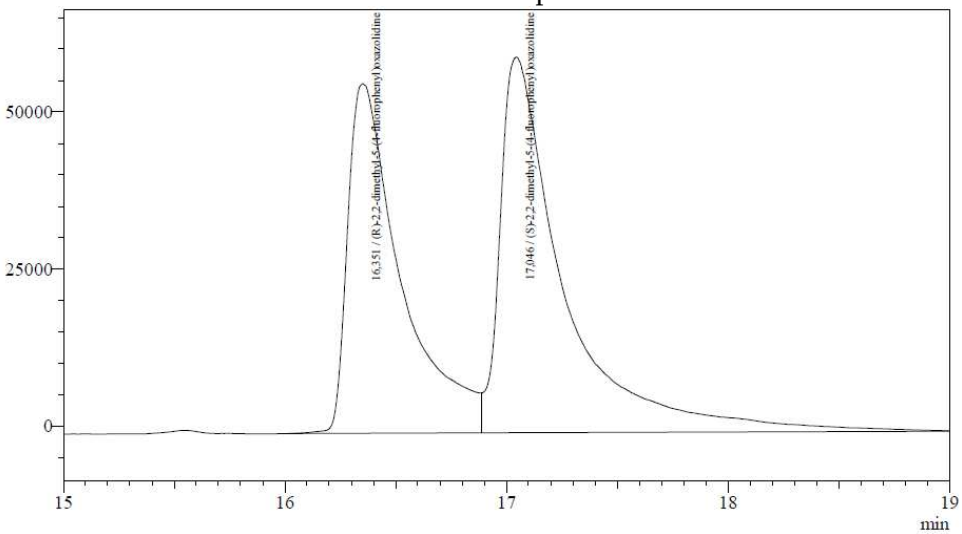


(*R*)-2-Amino-1-(4-fluorophenyl)ethanol (*R*)-**4c**: chiral-phase GC chromatograms

product obtained by the three-step one-pot sequence (gram scale)

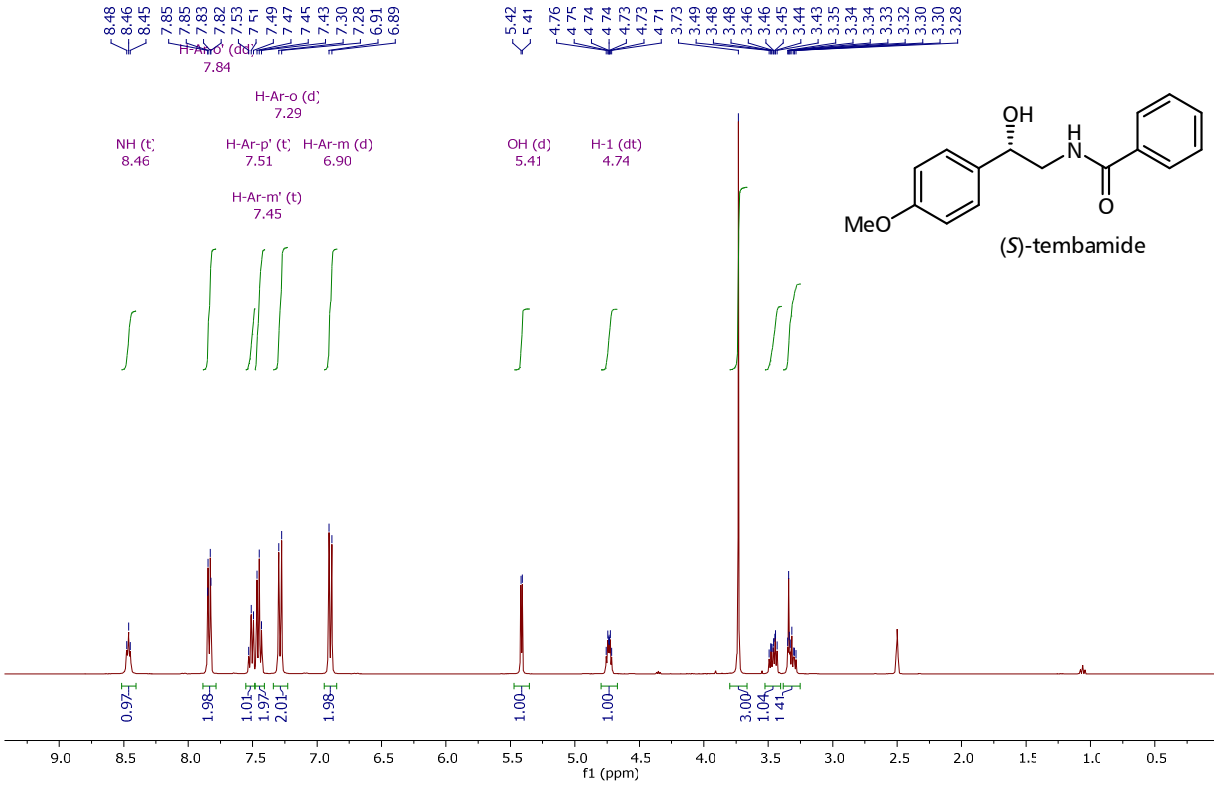


racemic sample:



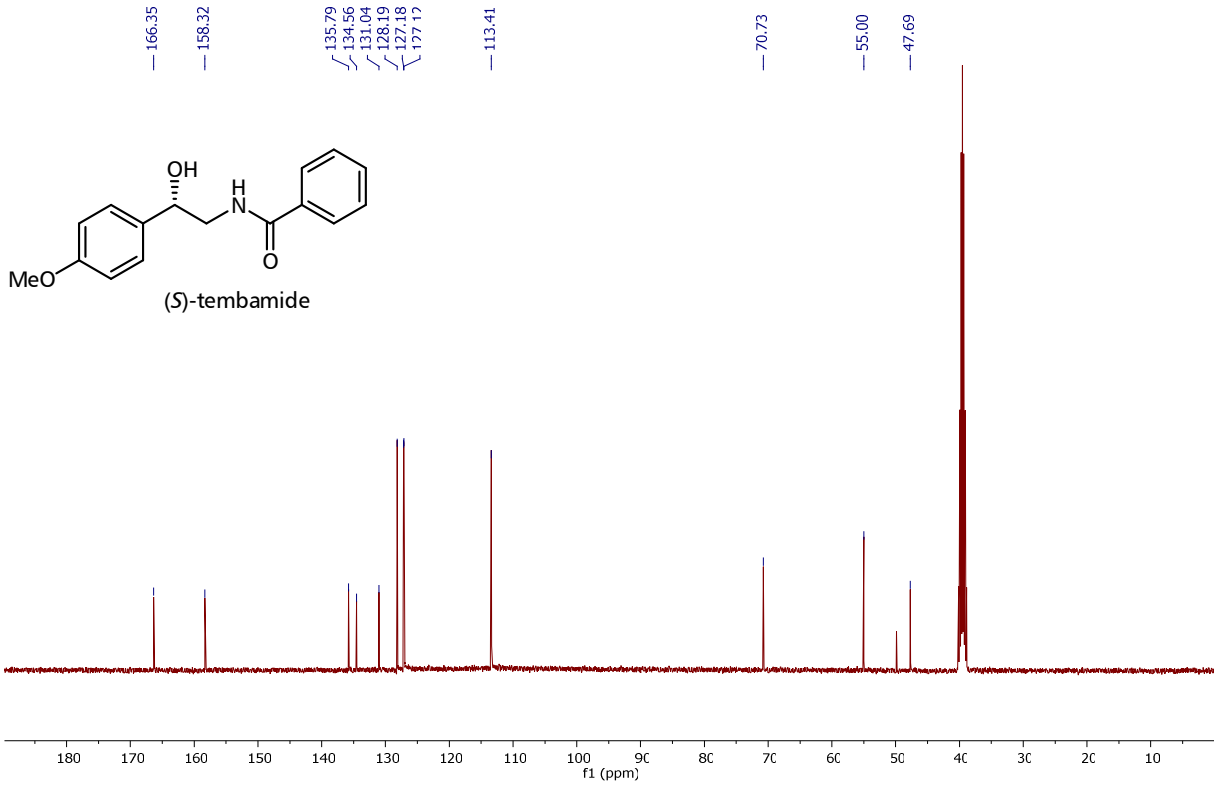
(*S*)-tembamide: ^{1}H-NMR spectrum

product obtained by the four-step one-pot sequence (gram scale)



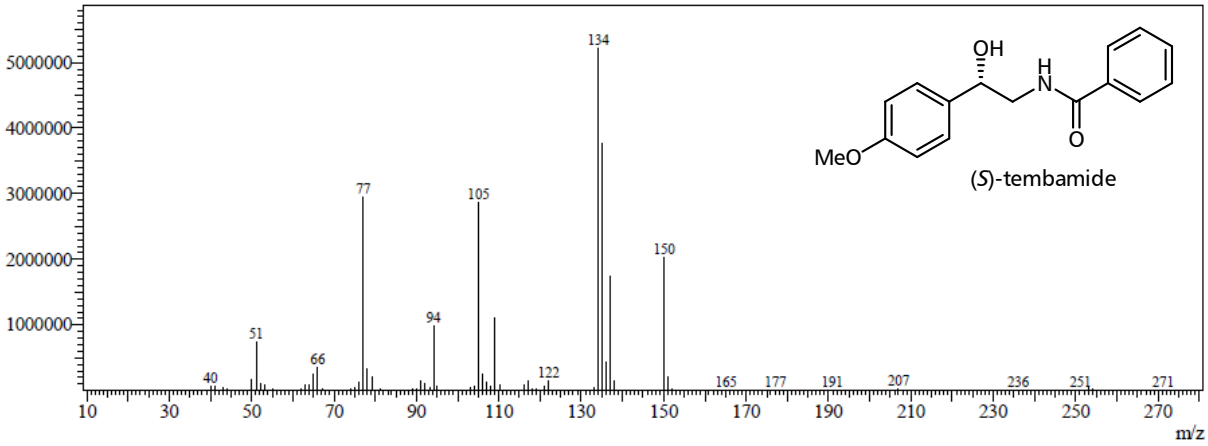
(*S*)-tembamide: ^{13}C-NMR spectrum

product obtained by the four-step one-pot sequence (gram scale)



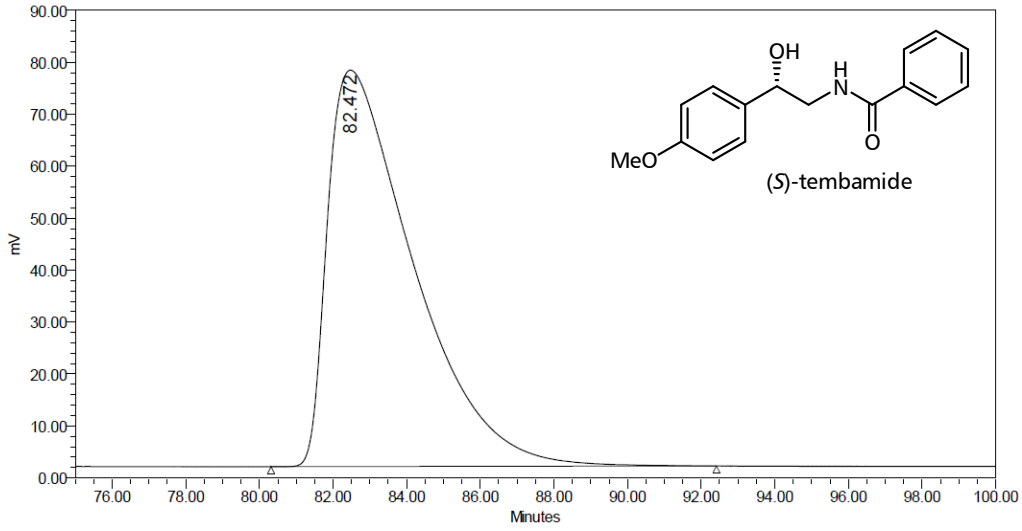
(*S*)-tembamide: MS spectrum

product obtained by the four-step one-pot sequence (gram scale)

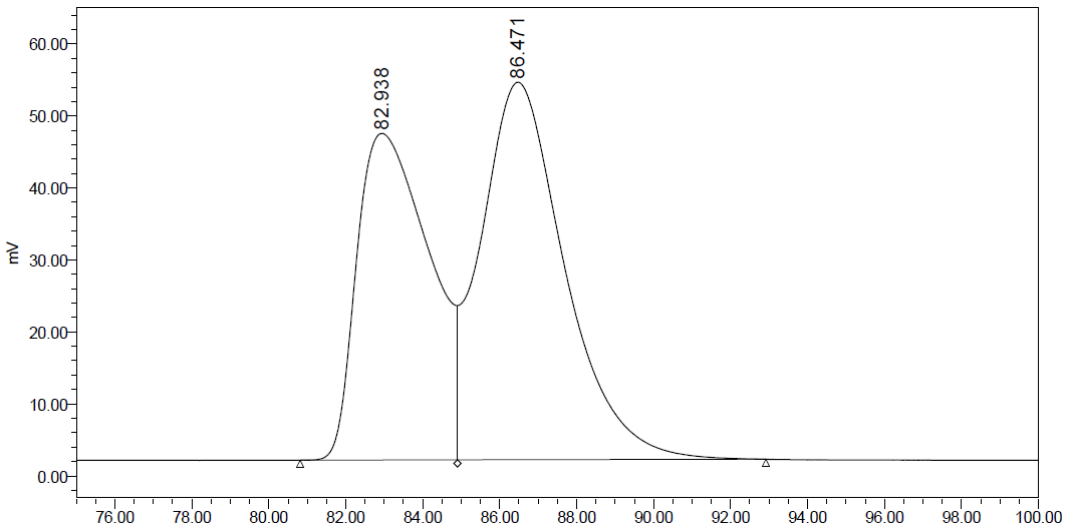


(*S*)-tembamide: chiral-phase HPLC chromatograms

product obtained by the four-step one-pot sequence (gram scale)



racemic sample:



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