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(2*S*,5*R*)-2-Methylaminomethyl-1-methyl-5-phenylpyrrolidine, a Chiral Diamine Ligand for Copper(II)-Catalysed Henry Reactions with Superb Enantiocontrol

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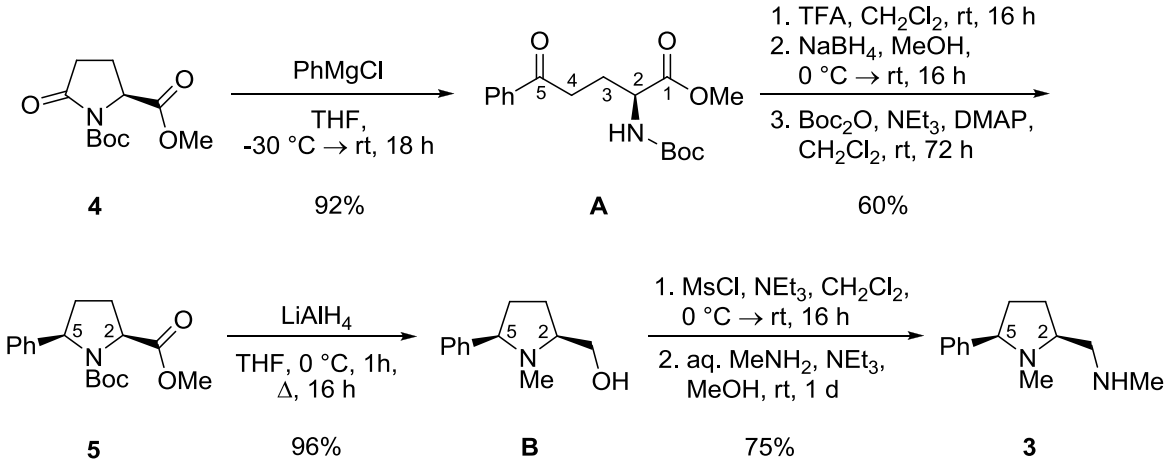
1. General Information

All reactions were carried out under an argon atmosphere with dry solvents. Anhydrous tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), methanol (MeOH), and nitromethane ($MeNO_2$) were prepared using standard procedures.[1]

Commercially available reagents (highest quality available) were used as received. All liquid aldehydes used in enantioselective Henry reactions were distilled prior to use in order to remove any accompanying acid impurities. Reactions were monitored by thin layer chromatography (TLC) on precoated silica gel (Macherey-Nagel, Alugram SIL G/UV254). Spots were visualized by UV light (254 nm) or by staining with aqueous $KMnO_4$, vanillin, or ceric ammonium molybdate. Silica gel (Macherey-Nagel, particle size 40–63 µm) was used for column chromatography.

Melting points (m.p.) were measured on a Stuart SMP10 digital melting point apparatus and are uncorrected. Optical rotations ($[\alpha]_D^T$) were recorded on a Jasco P-1020 polarimeter (10 cm cell). NMR spectra were taken on a Bruker Avance 400 or a Bruker Avance III HD 500 instrument and calibrated using the residual undeuterated solvent as an internal reference. The peak assignments in the ^1H and ^{13}C NMR data were made on basis of 2D NMR methods (COSY, HSQC, HMBC). Infrared (IR) spectra were recorded on a Jasco FT-IR-410 or a PerkinElmer Spectrum 100 FT-IR spectrometer, high resolution mass spectra (HRMS) on a Bruker Daltonics micrOTOF focus mass spectrometer using ESI (electronspray ionization) or on a Finnigan MAT 90 using EI (electron ionisation. 70 eV).

2. Synthesis of the Diamine 3



2.1. (*S*)-Methyl 2-(*tert*-butoxycarbonylamino)-5-oxo-5-phenylpentanoate (A)

PhMgCl (25 wt% in THF, 31.6 mL, 60.0 mmol) was added at -30 °C to a solution of **4** (12.2 g, 50.0 mmol) in abs. THF (150 mL). The reaction mixture was slowly warmed to rt and stirred for 18 h. After addition of sat. aq. NH_4Cl (2 mL), the solvent was removed and the residue was diluted with

1 *Purification of Laboratory Chemicals*, eds. W. L. F. Armarego and D. D. Perrin, 4th ed., Butterworth-Heinemann, Oxford, 2000.

CH_2Cl_2 (200 mL). Sat. aq. NH_4Cl (180 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 60 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (180 mL) and the aqueous layer was re-extracted with CH_2Cl_2 (3 × 60 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. Column chromatography (silica gel, petrol ether/ EtOAc 1:0 → 2:1) delivered a mixture of the keto ester **A** and the corresponding 2,3-dihydropyrrole. This mixture was dissolved in MeOH (280 mL) and H_2O (35 mL), treated with TsOH•H_2O (210 mg), and stirred for 1 d at rt. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (250 mL), washed with sat. aq. $NaHCO_3$ (2 × 150 mL), and dried over $MgSO_4$. Removal of the solvent under reduced pressure afforded keto ester **A** (14.8 g, 46.0 mmol, 92%) as a white solid, $[\alpha]_D^{25}$ = 14.6 (c = 1.13 in $CHCl_3$) [ref [2]: $[\alpha]_D^{20}$ = –14.8 (c = 1.13 in $CHCl_3$) for *ent*-**A**]. The NMR data of **A** were in full agreement with those given in ref.[2]

2.2. (2*S*,5*R*)-1-*tert*-Butyl 2-methyl 5-phenylpyrrolidine-1,2-dicarboxylate (5)

A solution of the keto ester **A** (12.1 g, 37.6 mmol) in abs. CH_2Cl_2 (370 mL) was treated at rt with TFA (57.9 mL, 85.7 g, 752 mmol) and stirred overnight. The solvent was removed under reduced pressure and the resulting orange oil was diluted five times with CH_2Cl_2 (300 mL) and evaporated again, in order to remove excess TFA. $NaBH_4$ (2.70 g, 71.4 mmol) was slowly added at 0 °C to a solution of the residue in MeOH (300 mL). After stirring for 16 h at rt, the solvent was removed. The resulting orange oil was diluted four times with MeOH (260 mL) and evaporated again. The residue was suspended in abs. CH_2Cl_2 (1000 mL) and NEt_3 (7.49 mL, 5.71 g, 56.4 mmol), Boc_2O (12.3 g, 56.4 mmol), and DMAP (50.0 mg, 409 µmol) were added at rt. After 3 d of stirring, sat. aq. NH_4Cl (1000 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 500 mL) and the combined organic layers were dried over $MgSO_4$. Removal of the solvent and column chromatography (silica gel, petrol ether/EtOAc 1:0 → 0:1) afforded an 86:14 mixture of **5** and its 5-epimer, which was crystallized from CH_2Cl_2/Et_2O/pentane (1:4:14) to give diastereomerically pure **5** (6.90 g, 22.6 mmol, 60%) as colourless needles.

R_f = 0.37 (petrol ether/EtOAc 3:1); m.p. 100–101 °C; $[\alpha]_D^{21}$ = 25.7 (c = 1.00 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$):* δ = 1.14 (s, 5.4H, $C(CH_3)_3$), 1.41 (s, 3.6H, $C(CH_3)_3$), 2.03 (m, 2H, 3-H, 4-H), 2.19 (m, 1H, 3-H), 2.31 (m, 1H, 4-H), 3.81 (s, 3H, OMe), 4.35 (m, 0.4H, 2-H), 4.49 (m, 0.6H, 2-H), 4.74 (m, 0.6H, 5-H), 4.98 (m, 0.4H, 5-H), 7.21 (m, 1H, Ph-H), 7.32 (m, 2H, Ph-H), 7.54 ppm (m, 2H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$):* δ = 28.1, 28.4 ($C(CH_3)_3$), 28.9, 29.1 (C-3), 34.6, 35.7 (C-4), 52.1, 52.3 (OMe), 60.4, 60.9 (C-2), 62.3, 63.2 (C-5), 80.2, 80.4 ($C(CH_3)_3$), 126.1, 126.5, 126.8, 128.2, 128.4 (CH-Ph), 143.2, 144.2 (C_q-Ph), 153.9, 154.6 (NCO_2), 173.8 ppm (CO_2Me); IR (ATR): $\tilde{\nu}$ = 3734 (w), 3628 (w), 2981 (w), 2951 (w), 1747 (m), 1684 (s), 1605 (w), 1398 (s), 1352 (m), 1197 (s), 1155 (s), 1121 (m), 1083 (m), 757 (m), 704 cm^{-1} (m); HRMS (ESI, pos.): *m/z* calcd. for $[C_{17}H_{23}NO_4 + Na]^+$: 328.1519, found: 328.1518. *Mixture of rotamers due to hindered rotation of the carbamate group.

2 J. Ackermann, M. Matthes and C. Tamm, *Helv. Chim. Acta*, 1990, **73**, 122.

2.3. (2*S*,5*R*)-2-Hydroxymethyl-1-methyl-5-phenylpyrrolidine (B)

$LiAlH_4$ (2.46 g, 64.8 mmol) was added at 0 °C to a solution of **5** (3.30 g, 10.8 mmol) in abs. THF (100 mL). After 1 h, the reaction mixture was heated to reflux for 16 h. The solution was diluted with Et_2O (80 mL) and carefully treated with sat. aq. Na_2SO_4 until H_2 evolution ceased. The resulting mixture was filtered through a pad of celite® and the filter cake was thoroughly washed with CH_2Cl_2/MeOH (9:1, 700 mL). Evaporation of the solvent and column chromatography (silica gel, CH_2Cl_2/MeOH 95:5) delivered alcohol **B** (1.98 g, 10.4 mmol, 96%) as a colourless oil.

R_f = 0.33 (Et_2O); $[\alpha]_D^{26}$ = 79.6 (c = 0.50 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (m, 1H, 4-H), 1.97 (m, 2H, 3-H), 2.08 (m, 1H, 4-H), 2.18 (s, 3H, NMe), 2.68 (m, 1H, 2-H), 2.80 (br s, 1H, OH), 3.42 (dd, *J* = 10.0, 6.5 Hz, 1H, 5-H), 3.51 (dd, *J* = 10.8, 1.9 Hz, 1H, CH*H*OH), 3.77 (dd, *J* = 10.8, 3.4 Hz, 1H, C*H*HOH), 7.25 (m, 1H, Ph-H), 7.33 ppm (m, 4H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.4 (C-3), 34.6 (C-4), 38.5 (NMe), 61.7 (CH_2OH), 66.6 (C-2), 72.5 (C-5), 127.30, 127.33, 128.5 (CH-Ph), 143.1 ppm (C_q-Ph); IR (ATR): $\tilde{\nu}$ = 3414 (w), 2947 (w), 2871 (w), 2842 (w), 2783 (w), 1603 (w), 1451 (m), 1075 (m), 1027 (s), 755 (s), 699 cm^{-1} (s); HRMS (ESI, pos.): *m/z* calcd. for $[C_{12}H_{17}NO + H]^+$: 192.1383, found: 192.1384.

2.4. (2*S*,5*R*)-2-Methylaminomethyl-1-methyl-5-phenylpyrrolidine (3)

MsCl (731 µL, 1.08 g, 9.44 mmol) and NEt_3 (1.80 mL, 1.30 g, 12.9 mmol) were added at 0 °C to a solution of the alcohol **B** (1.64 g, 8.58 mmol) in abs. CH_2Cl_2 (20 mL). The reaction was allowed to warm to rt and stirred for further 16 h. Aqeous $MeNH_2$ (11 M in H_2O, 23.0 mL, 257 mmol), NEt_3 (521 mg, 719 µL, 5.15 mmol), and MeOH (30 mL) were added and stirring was continued for 1 d. Evaporation of the solvent and column chromatography (silica gel, CH_2Cl_2/10% aq. NH_3 in MeOH 95:5 → 85:15) delivered diamine **3** (1.31 g, 6.41 mmol, 75%) as a yellowish oil.

R_f = 0.53 (Et_2O, deact. SiO_2); $[\alpha]_D^{29}$ = 51.2 (c = 1.00 in MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.68 (m, 1H, 4-H), 1.84 (m, 1H, 3-H), 1.96 (m, 2H, 3-H, NH), 2.05 (m, 1H, 4-H), 2.15 (s, 3H, NMe), 2.52 (s, 3H, HN*Me*), 2.61 (m, 1H, 2-H), 2.69 (dd, *J* = 11.4, 5.6 Hz, 1H, C*H*HN), 2.75 (dd, *J* = 11.4, 3.6 Hz, 1H, C*H*HN), 3.27 (dd, *J* = 9.6, 6.6 Hz, 1H, 5-H), 7.22 (m, 1H, Ph-H), 7.33 ppm (m, 4H, Ph-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.0 (C-3), 34.4 (C-4), 37.2 (HNMe), 39.4 (NMe), 55.3 (CH_2N), 65.8 (C-2), 72.7 (C-5), 127.1, 127.5, 128.4 (CH-Ph), 144.0 ppm (C_q-Ph); IR (ATR): $\tilde{\nu}$ = 2943 (w), 2872 (w), 2838 (w), 2783 (w), 1603 (w), 1451 (w), 1133 (w), 1073 (w), 1039 (w), 755 (m), 698 cm^{-1} (s); HRMS (ESI, pos.): *m/z* calcd. for $[C_{13}H_{20}N_2 + H]^+$: 205.1699, found: 205.1700.

3. Enantioselective Henry Reactions

3.1. General Remarks

Preparation of the racemic ß-nitro alcohols: These compounds were prepared by treatment of the aldehyde (500 µmol) at rt with nitromethane (300 µL) in the presence of NEt_3 (6.0 µL, 43 µmol) and a $CuCl_2$(tmda) complex, prepared from $CuCl_2$ (1.3 mg, 10 µmol) and TMEDA (1.5 µL, 10 µmol) in MeOH (300 µL). Purification by column chromatography (silica gel, hexanes/EtOAc 8:1 → 4:1) afforded the analytically pure β-nitro alcohols, the NMR spectroscopic data of which were identically with those given in literature.[3]

Solutions used in the enantioselective Henry reactions: In order to ensure maximum accuracy, solutions were prepared for all catalytically used reagents:

- $CuBr_2$ in MeOH (66.7 mM) from anhyd. $CuBr_2$ (44.7 mg, 200 µmol) and abs. MeOH (3.00 mL)
- $CuCl_2$ in MeOH (267 mM) from anhyd. $CuCl_2$ (53.8 mg, 400 µmol) and abs. MeOH (1.50 mL)
- Diamine **3** in THF (36.7 mM) from **3** (22.5 mg, 110.0 µmol) and abs. THF (3.00 mL)
- Diamine **3** in THF (147 mM) from **3** (45.0 mg, 220.0 µmol) and abs. THF (1.50 mL)
- NEt_3 in $MeNO_2$ (1.50 M) from NEt_3 (20.8 µL, 15.2 mg, 150 µmol) and $MeNO_2$ (79 µL)

Measurement of the enantiomeric excess (ee): The ee of each ß-nitro alcohol was determined by HPLC (Knauer HPLC pump type 64.00, Knauer UV/Vis variable wavelength monitor type A0293) on chiral phase (Daicel Chiralcel OD-3, Daicel Chiralpak AD-H, Daicel Chiralcel OJ-H). The accuracy of integration was ± 0.1%. Some of the enantioselective Henry reactions were done up to five times, for example with benzaldehyde (**6a**), 2-nitrobenzaldehyde (**6h**), 2-methoxybenzaldehyde (**6p**), valeraldehyde (**12a**), and 3-phenylpropanal (**12c**). In all cases, virtually the same excellent enantiomeric excesses were measured (Δee = ± 0.2%).

Determination of the absolute configuration of the major enantiomer: For all known ß-nitro alcohols, the absolute configuration of the major enantiomer was assigned by comparison of the order of the measured retention times on HPLC with the literature-known ones, measured under identical conditions (same chiral phase and solvent system).[3] The absolute configuration of the major enantiomer of the new products **9b** and **11b** was tentatively assigned under the assumption that the sense of asymmetric induction was the same as for all other derivatives (*re*-attack on the carbonyl group).

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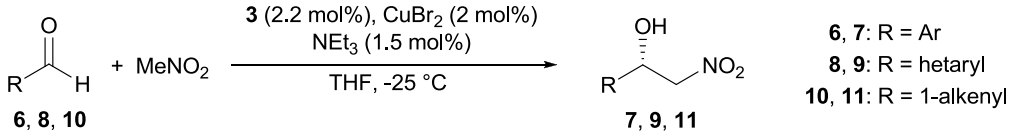
3 (*a*) M. Breuning, D. Hein, M. Steiner, V. H. Gessner and C. Strohmann, *Chem.-Eur. J.*, 2009, **15**, 12764; (*b*) W. Jin, X. Li and B. Wan, *J. Org. Chem.*, 2011, **76**, 484; (*c*) Y. Q. Ji, G. Qi and Z. M. A. Judeh, *Eur. J. Org. Chem.*, 2011, 4892; (*d*) Y. Zhou, J. Dong, F. Zhang and Y. Gong, *J. Org. Chem.*, 2011, **76**, 588; (*e*) L. Yao, Y. Wei, P. Wang, W. He and S. Zhang, *Tetrahedron*, 2012, **68**, 9119; (*f*) R. Kowalczyk, P. Kwiatkowski, J. Skarżewski and J. Jurczak, *J. Org. Chem.*, 2009, **74**, 753; (*g*) L. Zhang, H. Wu, Z. Yang, X. Xu, H. Zhao, Y. Huang and Y. Wang, *Tetrahedron*, 2013, **69**, 10644; (*h*) B. V. S. Reddy and J. George, *Tetrahedron: Asymmetry*, 2011, **22**, 1169; (*i*) Y. Zhou and Y. Gong, *Eur. J. Org. Chem.*, 2011, 6092; (*j*) M. Liu, S. Ma, Z. Tian, H. Wu, L. Wu, X. Xu, Y. Huang and Y. Wang, *Tetrahedron: Asymmetry*, 2013, **24**, 736; (*k*) T. Marcelli, R. N. S. van der Haas, J. H. van Maarseveen and H. Hiemstra, *Angew. Chem. Int. Ed.*, 2006, **45**, 929; (*l*) A. Gualandi, L. Cerisoli, H. Stoeckli-Evans and D Savoia, *J. Org. Chem.*, 2011, **76**, 3399; (*m*) Y. Sohtome, Y. Hashimoto, K. Nagasawa, *Adv. Synth. Catal.*, 2005, **347**, 1643.

3.2. General Procedure I (Aromatic, Heteroaromatic, and Vinylic Aldehydes)



A solution of anhyd. $CuBr_2$ (66.7 mM in MeOH, 300 µL, 4.47 mg, 20.0 µmol, 2.0 mol%) was evaporated to dryness in a Schlenk tube. A solution of the diamine **3** (36.7 mM in abs. THF, 600 µL, 4.49 mg, 22.0 µmol, 2.2 mol%), $MeNO_2$ (600 µL, 684 mg, 11.2 mmol, 11.2 eq.) and the aldehyde **6**, **8**, or **10** (1.00 mmol, 1.00 eq.) were added successively at rt. The mixture was ultrasonicated for 10 min to give a clear, brownish solution and then cooled to –25 °C. NEt_3 (1.5 M in $MeNO_2$, 10.0 µL, 1.52 mg, 15.0 µmol, 1.5 mol%) was added and the resulting blue-green solution was stirred until TLC-control indicated complete consumption of the aldehyde (18–160 h). The crude reaction mixture was purified by column chromatography (silica gel, hexanes/EtOAc 8:1 → 4:1) delivering β-nitro alcohol **7**, **9**, or **11**.

Table S1. Experimental data and details of HPLC analysis on chiral phase.

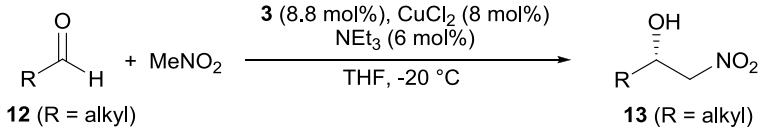
			Reaction Conditions			Enantiomer Analysis: HPLC Conditions					
Entry	Com-pounds	R	t [h]	Yield [%][a]	ee [%][b] (Config.)[c]	Column[d]	Solvent System *n*-Hexane/*i*PrOH	Flow [ml/min]	t_r (*R*) [min][e]	t_r (*S*) [min][e]	Ref.[f]
1	**6a**, **7a**	Ph	24	92	99.3 (*S*)	OD-3	85:15	0.8	12.6	14.9	3a
2	**6b**, **7b**	2-Me-Ph	18	99	99.2 (*S*)	OD-3	85:15	0.9	10.3	16.2	3b
3	**6c**, **7c**	3-Me-Ph	20	99	99.5 (*S*)	OD-3	90:10	0.9	14.4	16.7	3c
4	**6d**, **7d**	4-Me-Ph	22	93	99.4 (*S*)	OD-3	90:10	0.9	17.7	22.5	3c
5	**6e**, **7e**	4-Ph-Ph	38	99	99.6 (*S*)	OD-3	85:15	0.9	16.1	18.5	3c
6	**6f**, **7f**	1-naphthyl	65	99	99.4 (*S*)	OD-3	85:15	0.9	14.8	22.3	3b
7	**6g**, **7g**	2-naphthyl	42	99	99.0 (*S*)	OD-3	80:20	0.9	24.5	36.5	3b
8	**6h**, **7h**	2-O_2N-Ph	20	97	99.0 (*S*)	OD-3	80:20	0.7	11.5	12.2	3a
9	**6i**, **7i**	3-O_2N-Ph	22	95	99.4 (*S*)	OD-3	85:15	0.9	18.2	20.6	3d
10	**6j**, **7j**	4-O_2N-Ph	21	94	99.4 (*S*)	OD-3	85:15	0.9	18.6	22.7	3a
11	**6k**, **7k**	2-Cl-Ph	18	99	99.6 (*S*)	OD-3	97: 3	0.9	25.9	27.0	3a
12	**6l**, **7l**	3-Cl-Ph	19	96	99.5 (*S*)	OD-3	90:10	0.9	17.1	22.0	3c
13	**6m**, **7m**	4-Cl-Ph	42	95	99.5 (*S*)	OD-3	85:15	0.9	11.5	14.1	3a
14	**6n**, **7n**	4-F-Ph	20	99	99.6 (*S*)	OD-3	90:10	0.9	13.7	16.2	3e
15	**6o**, **7o**	4-NC-Ph	21	94	99.6 (*S*)	OD-3	80:20	0.9	12.9	14.6	3f
16	**6p**, **7p**	2-MeO-Ph	42	97	99.5 (*S*)	OD-3	90:10	0.9	14.0	16.8	3a
17	**6q**, **7q**	3-MeO-Ph	48	99	99.3 (*S*)	OD-3	85:15	0.9	19.3	25.6	3b

Table S1. (Continued).

Entry	Com-pounds	R	Reaction Conditions			Enantiomer Analysis: HPLC Conditions					
			t [h]	Yield [%][a]	ee [%][b] (Config.)[c]	Column[d]	Solvent System *n*-Hexane/*i*PrOH	Flow [ml/min]	t_r (*R*) [min][e]	t_r (*S*) [min][e]	Ref.[f]
18	**6r**, **7r**	4-MeO-Ph	67	99	99.2 (*S*)	OD-3	85:15	0.9	15.9	19.7	3a
19	**6s**, **7s**	2,4-$(MeO)_2$-Ph	48	98	99.3 (*S*)	OD-3	80:20	0.9	10.0	15.2	3g
20	**6t**, **7t**	2,5-$(MeO)_2$-Ph	39	99	99.6 (*S*)	OD-3	85:15	0.9	11.0	11.8	3h
21	**6u**, **7u**	3,4-$(MeO)_2$-Ph	40	93	99.1 (*S*)	OD-3	80:20	0.9	16.8	21.3	3i
22	**8a**, **9a**	2-furyl	40	91	99.6 (*R*)	AD-H	95:5	0.6	39.6	37.8	3d
23	**8b**, **9b**	5-Me-2-furyl	112	96	99.5 (*R*)	AD-H	95:5	0.6	30.4	33.0	–[g]
24	**8c**, **9c**	3-furyl	72	99	99.4 (*S*)	AD-H	90:10	0.9	15.8	21.7	3j
25	**8d**, **9d**	2-thiophenyl	86	95	99.2 (*R*)	OJ-H	85:15	0.9	30.6	26.0	3h
26	**8e**, **9e**	*N*Boc-2-pyrryl	21	99	99.5 (*R*)	OD-3	90:10	0.9	7.7	7.0	3k
27	**8f**, **9f**	*N*Boc-3-indolyl	160	90	99.4 (*S*)	OD-3	90:10	0.9	14.2	12.1	3l
28	**10a**, **11a**	(*E*)-PhCH=CH	120	90	99.3 (*S*)	OD-3	85:15	0.9	36.0	31.5	3h
29	**10b**, **11b**	(*E*)-1-pen-ten-1-yl	90	97	98.7 (*S*)	OJ-H	97:3	0.9	22.5	25.5	–[g]

[a] Isolated yield. [b] Determined by HPLC analysis on a chiral phase. [c] The absolute configuration of the major enantiomer was determined by comparison of the order of the measured retention times on HPLC with the literature-known ones, measured under identical conditions.[3] [d] OD-3: Daicel Chiralcel OD-3; AD-H: Daicel Chiralpak AD-H; OJ-H: Daicel Chiralcel OJ-H. [e] Retention time. [f] References, in which data for the HPLC analysis on chiral phase are given. [g] The absolute configuration of the major enantiomer was tentatively assigned under the assumption of a *re*-attack on the carbonyl group.

3.3. General Procedure II (Aliphatic Aldehydes)



12 (R = alkyl) **13** (R = alkyl)

A solution of anhyd. $CuCl_2$ (267 mM in MeOH, 300 µL, 10.8 mg, 80.0 µmol, 8.0 mol%) was evaporated to dryness in a Schlenk tube. A solution of the diamine **3** (147 mM in abs. THF, 600 µL, 18.0 mg, 88.0 µmol, 8.8 mol%), $MeNO_2$ (600 µL, 684 mg, 11.2 mmol, 11.2 eq.) and aldehyde **12** (1.00 mmol, 1.00 eq.) were successively added at rt. The mixture was ultra-sonicated for 10 min to give a clear, greenish solution and then cooled to –20 °C. NEt_3 (1.5 M in $MeNO_2$, 40 µL, 6.08 mg, 60.0 µmol, 6.0 mol%) was added and the resulting blue solution was stirred until TLC-control indicated complete consumption of the aldehyde (40–60 h). The crude reaction mixture was purified by column chromatography (silica gel, pentane/Et_2O 8:1 → 4:1) delivering β-nitro alcohol **13**.

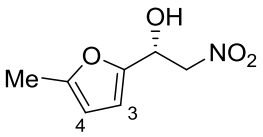
Table S2. Experimental data and details of HPLC analysis on chiral phase.

			Reaction Conditions			Enantiomer Analysis: HPLC Conditions					
Entry	Com-pounds	R	t [h]	Yield [%][a]	ee [%][b] (Config.)[c]	Column[d]	Solvent System *n*-Hexane/*i*PrOH	Flow [ml/min]	t_r (*R*) [min][e]	t_r (*S*) [min][e]	Ref.[f]
1	**12a**, **13a**	*n*Bu	40	95	98.5 (*S*)	OJ-H	97:3	0.8	21.9	22.9	3b
2	**12b**, **13b**	*n*Oct	60	97	98.6 (*S*)	AD-H	95:5	0.8	14.3	20.2	3h
3	**12c**, **13c**	$PhCH_2CH_2$	40	95	99.5 (*S*)	AD-H	90:10	0.9	13.1	16.3	3b
4	**12d**, **13d**	*i*Pr	44	96	99.1 (*S*)	OD-3	97:3	0.9	15.8	17.5	3m
5	**12e**, **13e**	*c*Pent	44	99	98.9 (*S*)	OD-3	98:2	0.9	23.8	24.9	3b
6	**12f**, **13f**	*c*Hex	44	99	99.4 (*S*)	AD-H	95:5 (EtOH)	0.9	34.3	31.1	– [g]
7	**12g**, **13g**	*t*Bu	44	99	98.6 (*S*)	OD-3	97:3	0.9	12.8	15.0	3m

[a] Isolated yield. [b] Determined by HPLC analysis on a chiral phase. [c] The absolute configuration of the major enantiomer was determined by comparison of the order of the measured retention times on HPLC with the literature-known ones, measured under identical conditions.[3] [d] OD-3: Daicel Chiralcel OD-3; AD-H: Daicel Chiralpak AD-H; OJ-H: Daicel Chiralcel OJ-H. [e] Retention time. [f] References, in which the data for the HPLC analysis on chiral phase are given. [g] The absolute configuration of the major enantiomer was assigned by comparison of the measured sign of the optical rotation with the literature-known one.[3b]

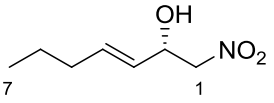
3.4. Characterization of New ß-Nitro Alcohols

3.4.1. (*R*)-1-(5-Methylfuran-2-yl)-2-nitroethanol (9b)



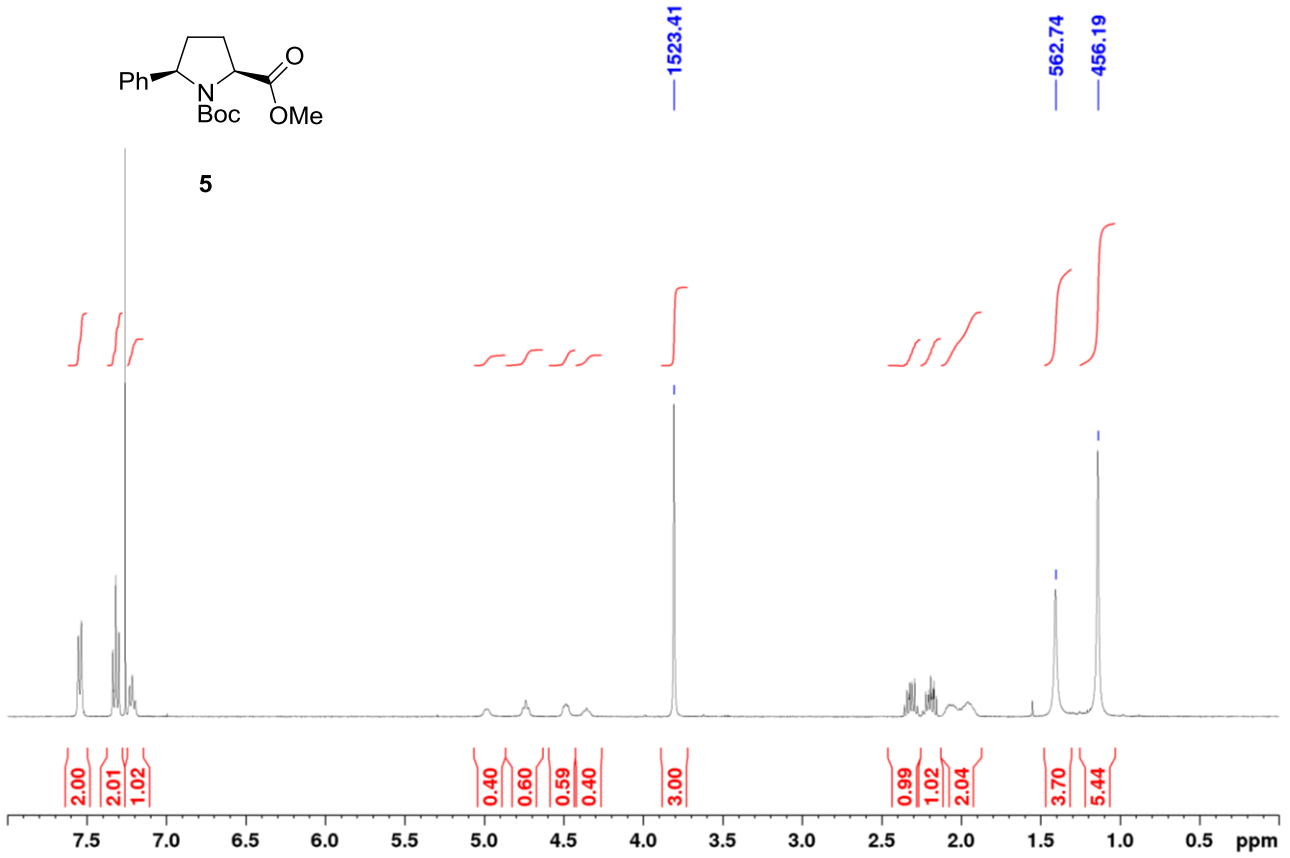
Ee = 99.5%; R_f = 0.32 (petrol ether/EtOAc 4:1); $[\alpha]_D^{28}$ = 50.1 (c = 1.0 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28 (s, 3H, CH_3), 2.78 (br s, 1H, OH), 4.64 (dd, *J* = 13.5, 3.4 Hz, 1H, C*H*H), 4.78 (dd, *J* = 13.5, 9.3 Hz, 1H, C*H*H), 5.40 (dd, *J* = 9.3, 3.3 Hz, 1H, C*H*OH), 5.95 (m, 1H, 4-H), 6.26 ppm (d, *J* = 3.1 Hz, 1H, 3-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6 (CH_3), 65.0 (COH), 78.6 (CH_2), 106.7 (C-4), 109.3 (C-3), 148.9 (C-2), 153.3 ppm (C-5); IR (ATR): $\tilde{\nu}$ = 3409 (w), 2925 (w), 1698 (w), 1550 (s), 1421 (w), 1379 (m), 1019 (m), 788 (m), 705 (m), 631 cm^{-1} (m); HRMS (EI, 70 eV, peak match): *m/z* calcd. for $[C_7H_9NO_4]^{\bullet+}$: 171.0526, found: 171.0526.

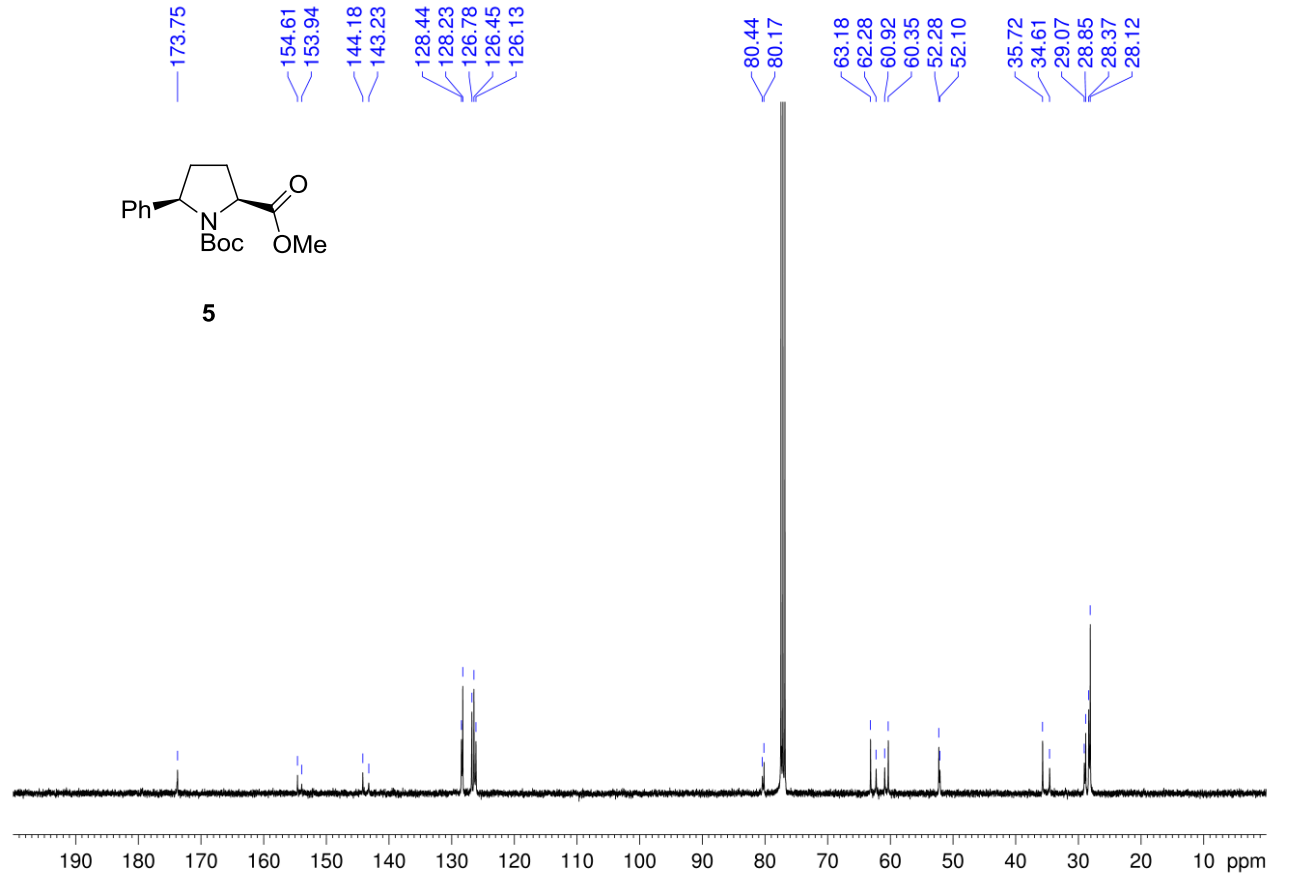
3.4.2. (*S*,*E*)-1-Nitrohept-3-en-2-ol (11b)

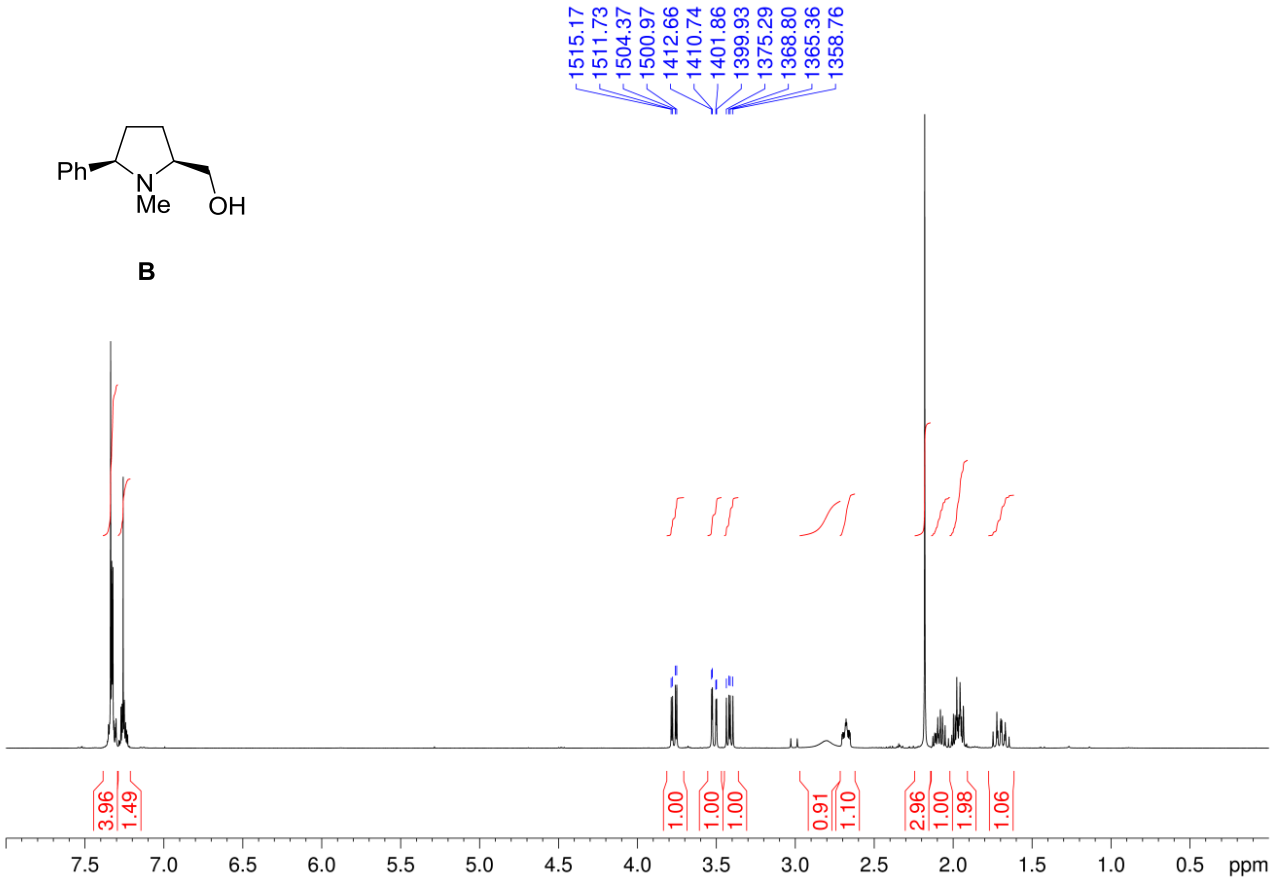


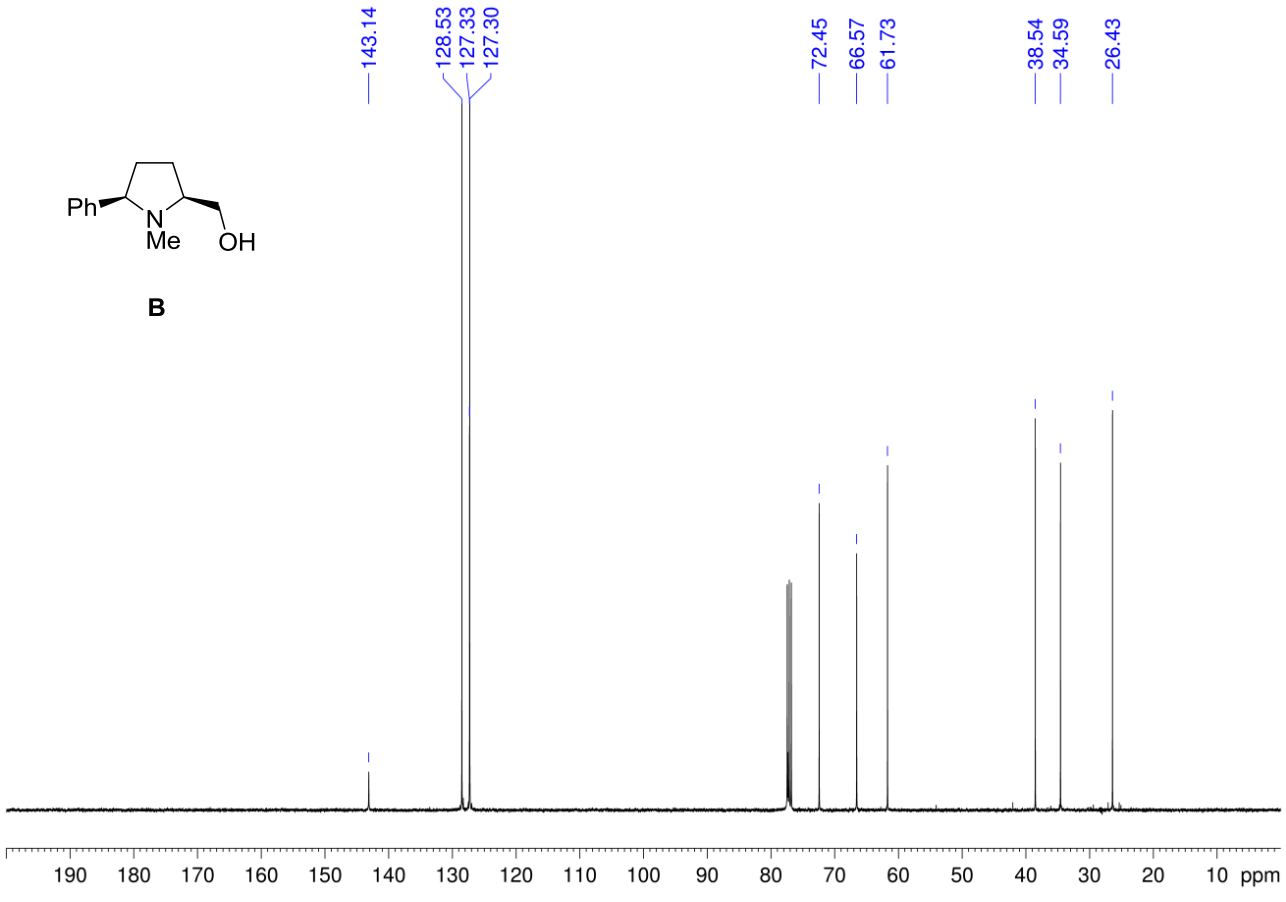
Ee = 98.7%; R_f = 0.21 (petrol ether/EtOAc 8:1); $[\alpha]_D^{28}$ = –1.4 (c = 1.00 in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.4 Hz, 3H, 7-H), 1.41 (sext, *J* = 7.4 Hz, 2H, 6-H), 2.04 (q, *J* = 7.2 Hz, 2H, 5-H), 2.42 (d, *J* = 4.4 Hz, 1H, OH), 4.42 (m, 2H, CH_2NO_2), 4.82 (m, 1H, C*H*OH), 5.44 (ddt, *J* = 15.4, 6.7, 1.5 Hz, 1H, 3-H), 5.88 ppm (dtd, *J* = 15.4, 6.8, 1.0 Hz, 1H, 4-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7 (C-7), 22.1 (C-6), 34.4 (C-5), 69.8 (C-2), 80.2 (C-1), 126.3 (C-3), 136.1 ppm (C-4); IR (ATR): $\tilde{\nu}$ = 3415 (w), 2960 (w), 2932 (w), 2874 (w), 1671 (w), 1549 (s), 1379 (m), 1057 (w), 969 (m), 887 (w), 737 cm^{-1} (w); HRMS (EI, 70 eV, peak match): *m/z* calcd. for $[C_7H_{13}NO_3 - HNO_2]^{\bullet+}$: 112.0885, found: 112.0883.

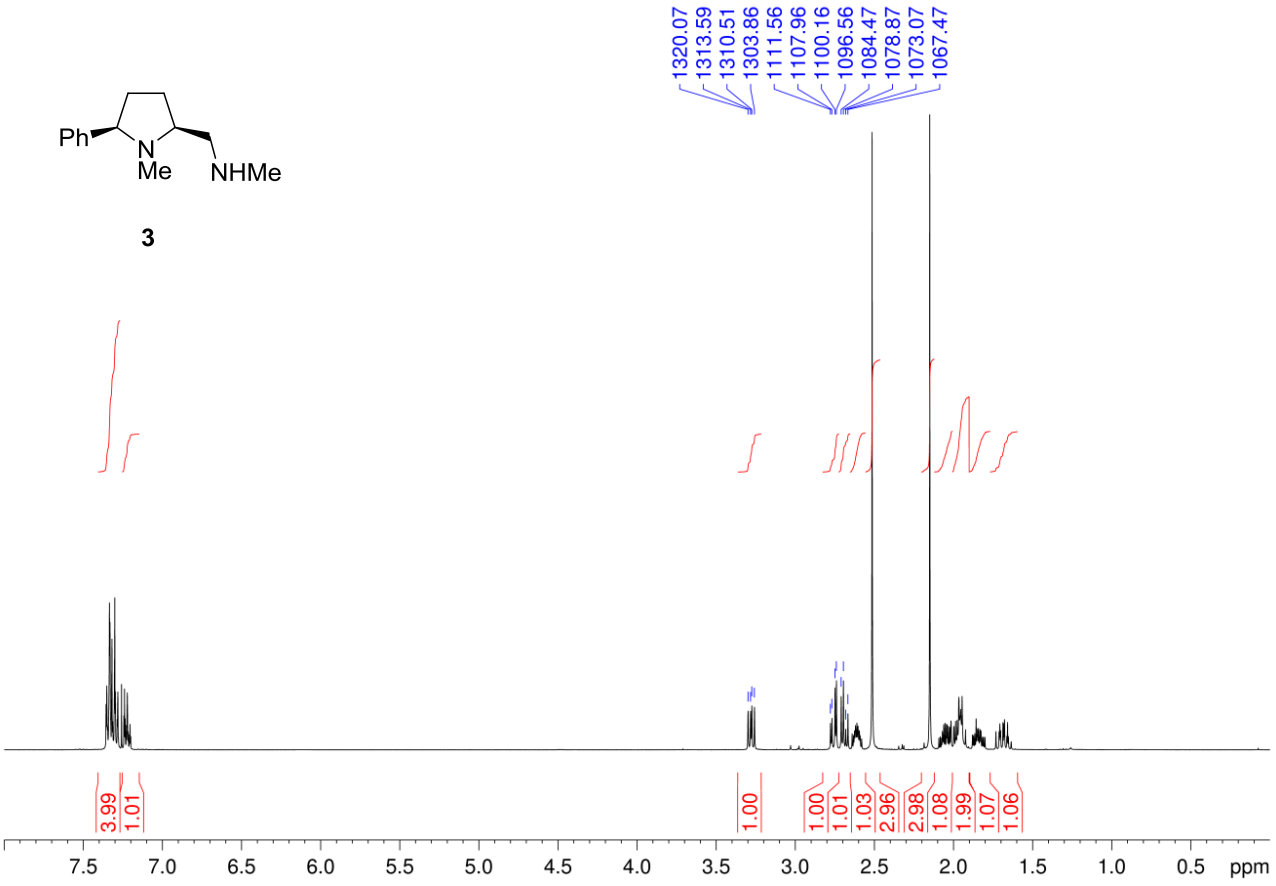
4. Copies of ^{1}H and ^{13}C NMR Spectra

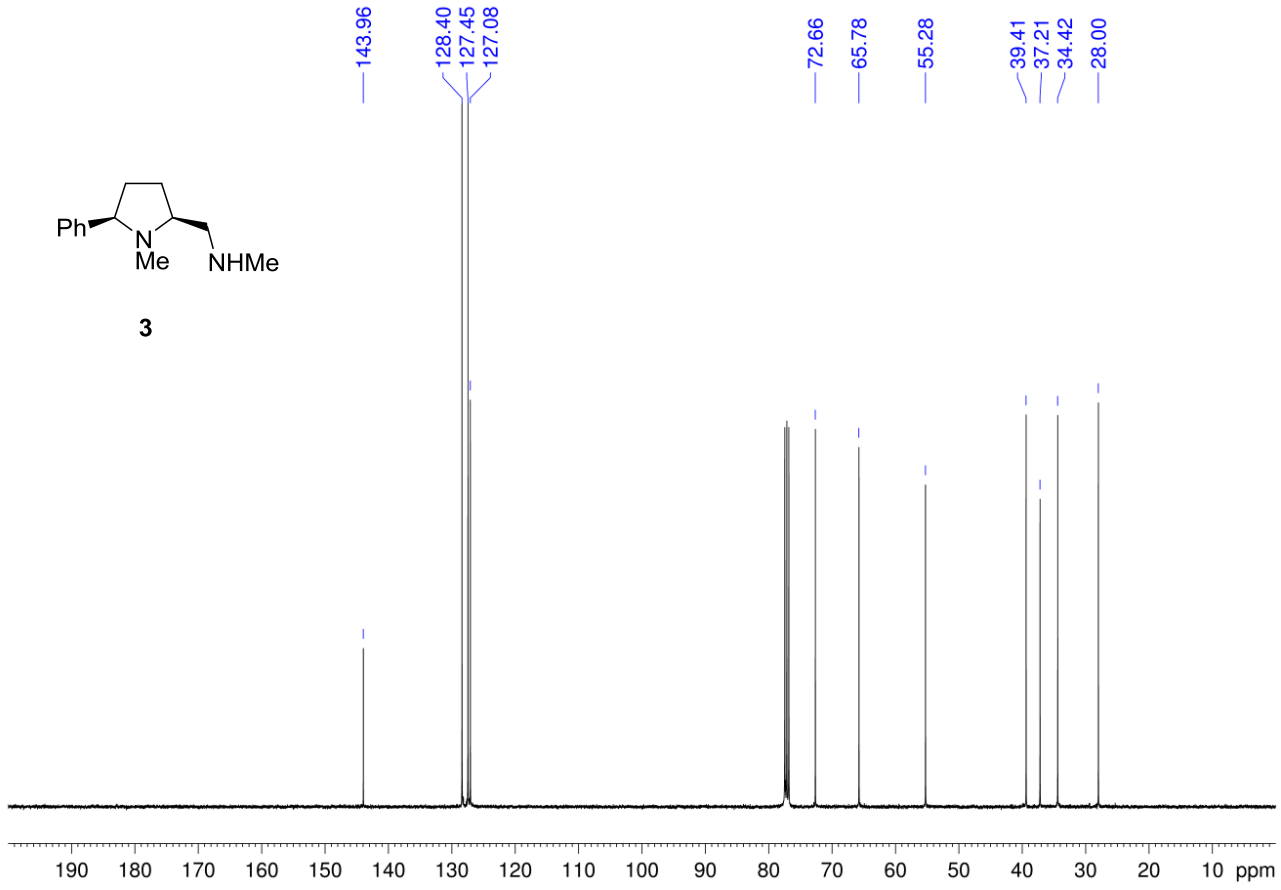


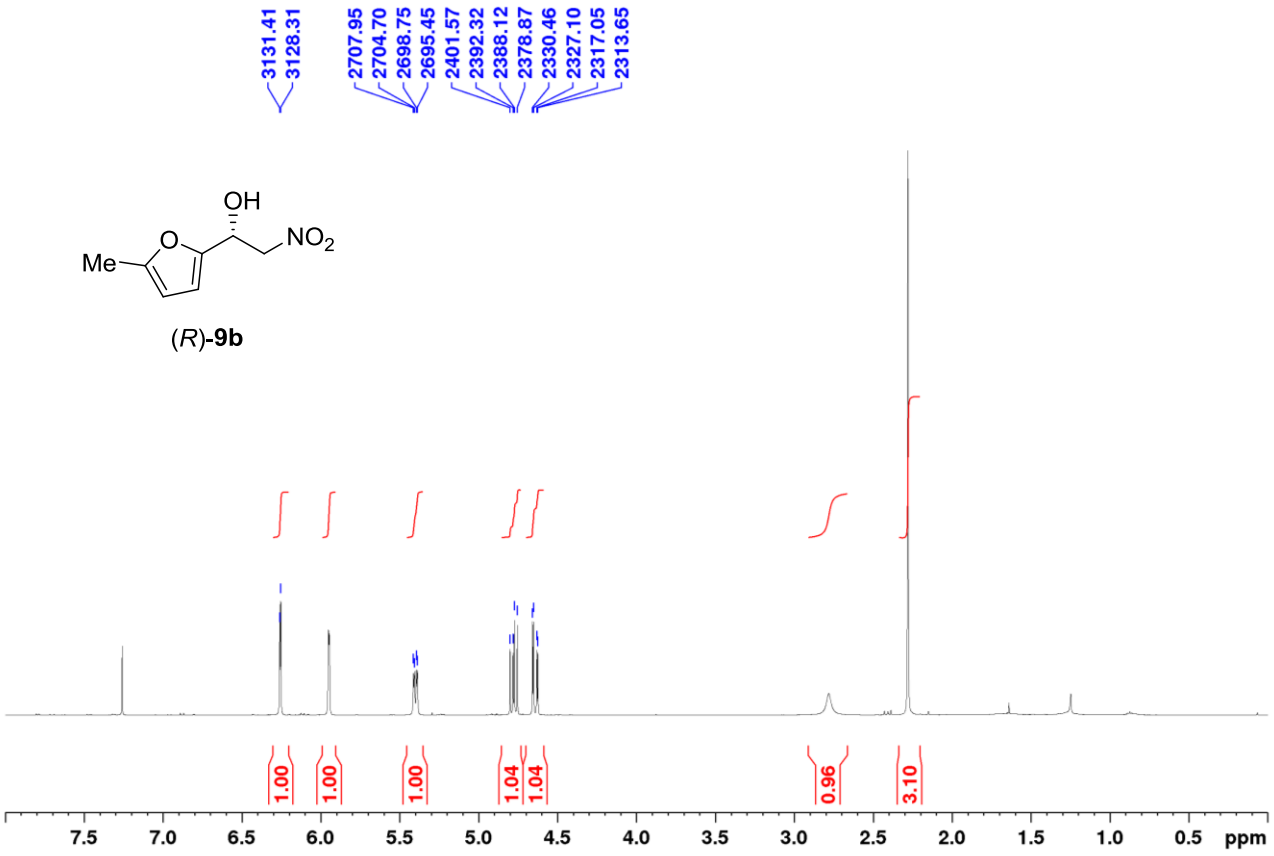



1515.17
1511.73
1504.37
1500.97
1412.66
1410.74
1401.86
1399.93
1375.29
1368.80
1365.36
1358.76
Ph
N
Me
OH
B
3.96
1.49
1.00
1.00
1.00
0.91
1.10
2.96
1.00
1.98
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

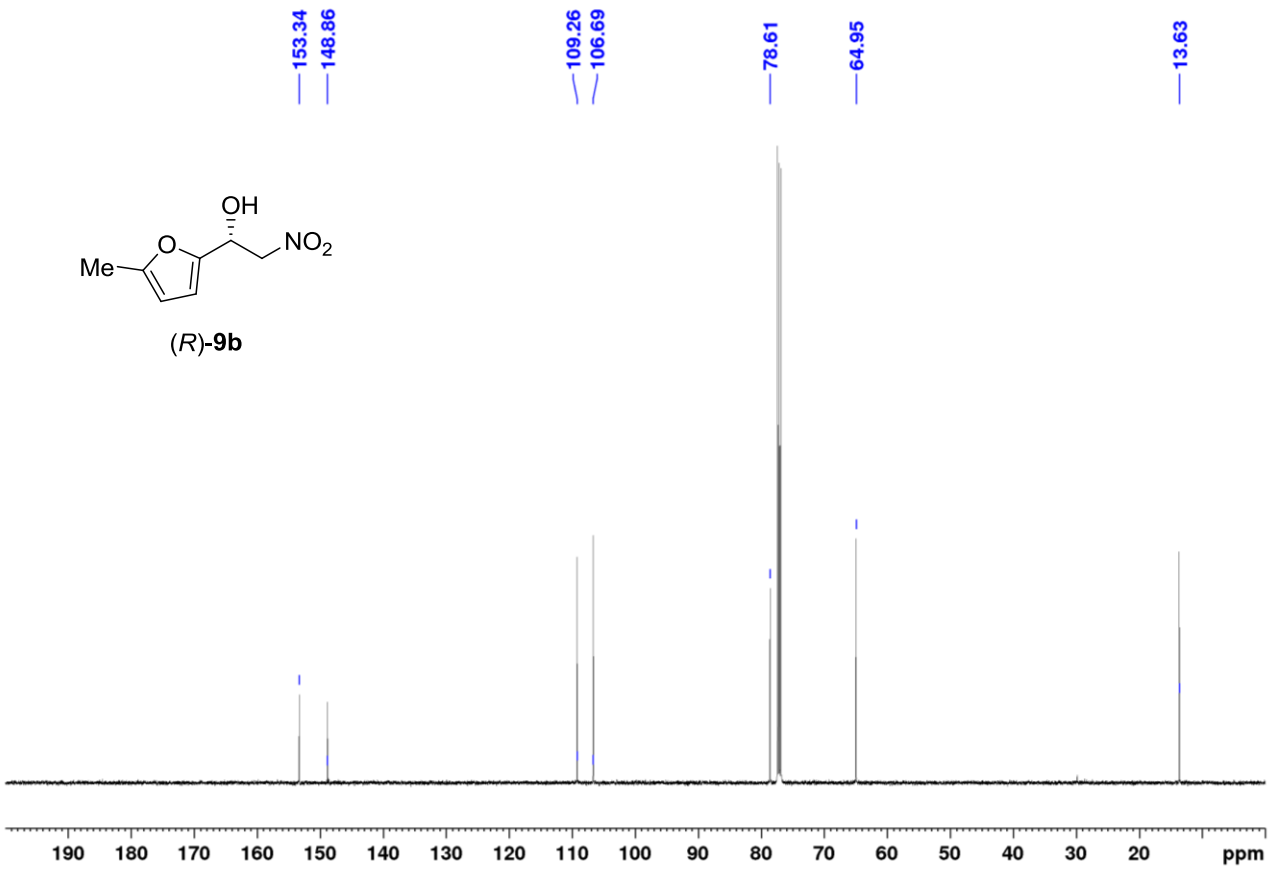

143.14
128.53
127.33
127.30
72.45
66.57
61.73
38.54
34.59
26.43
Ph
N
Me
OH
B
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
N
Me
NHMe
3
1320.07
1313.59
1310.51
1303.86
1111.56
1107.96
1100.16
1096.56
1084.47
1078.87
1073.07
1067.47
3.99
1.01
1.00
1.00
1.01
1.03
2.96
2.98
1.08
1.99
1.07
1.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

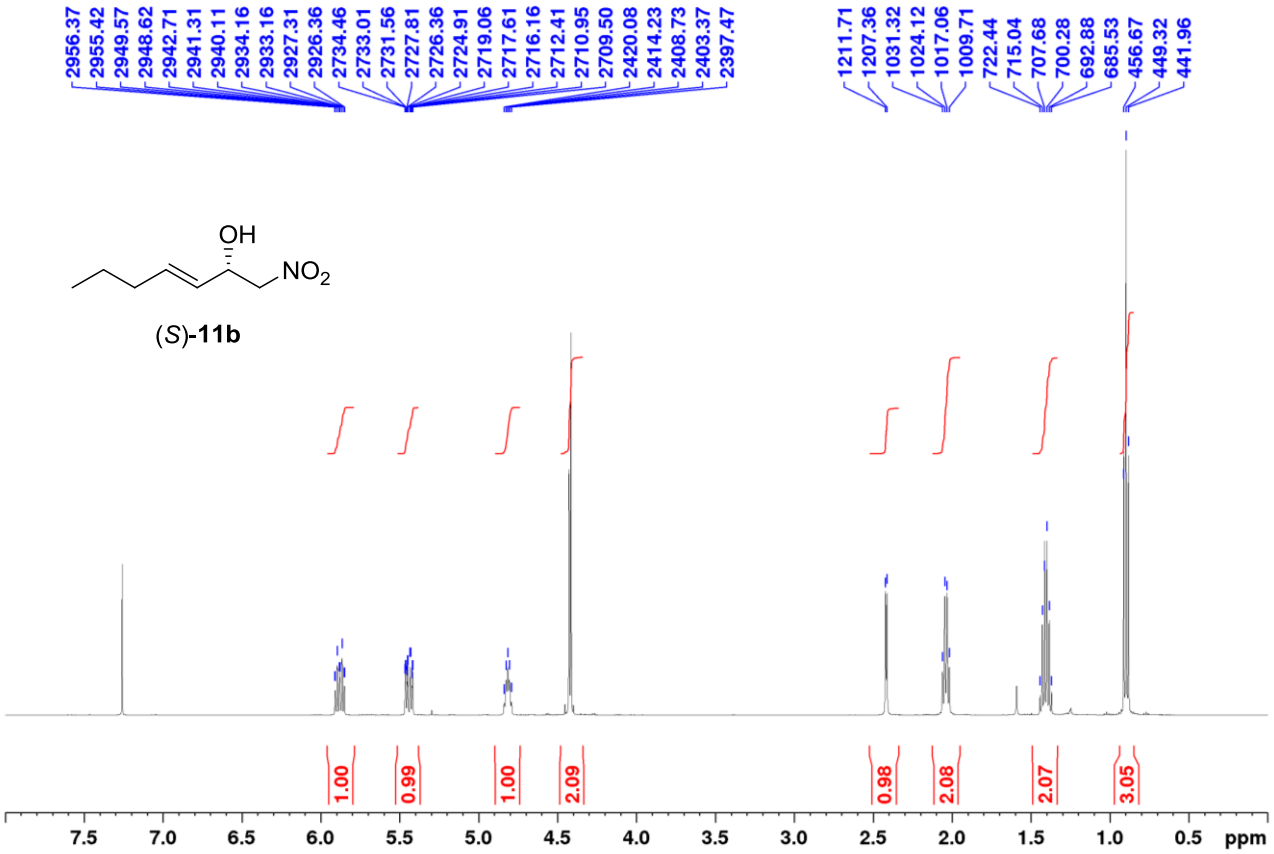

Ph
N
Me
NHMe
3
143.96
128.40
127.45
127.08
72.66
65.78
55.28
39.41
37.21
34.42
28.00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

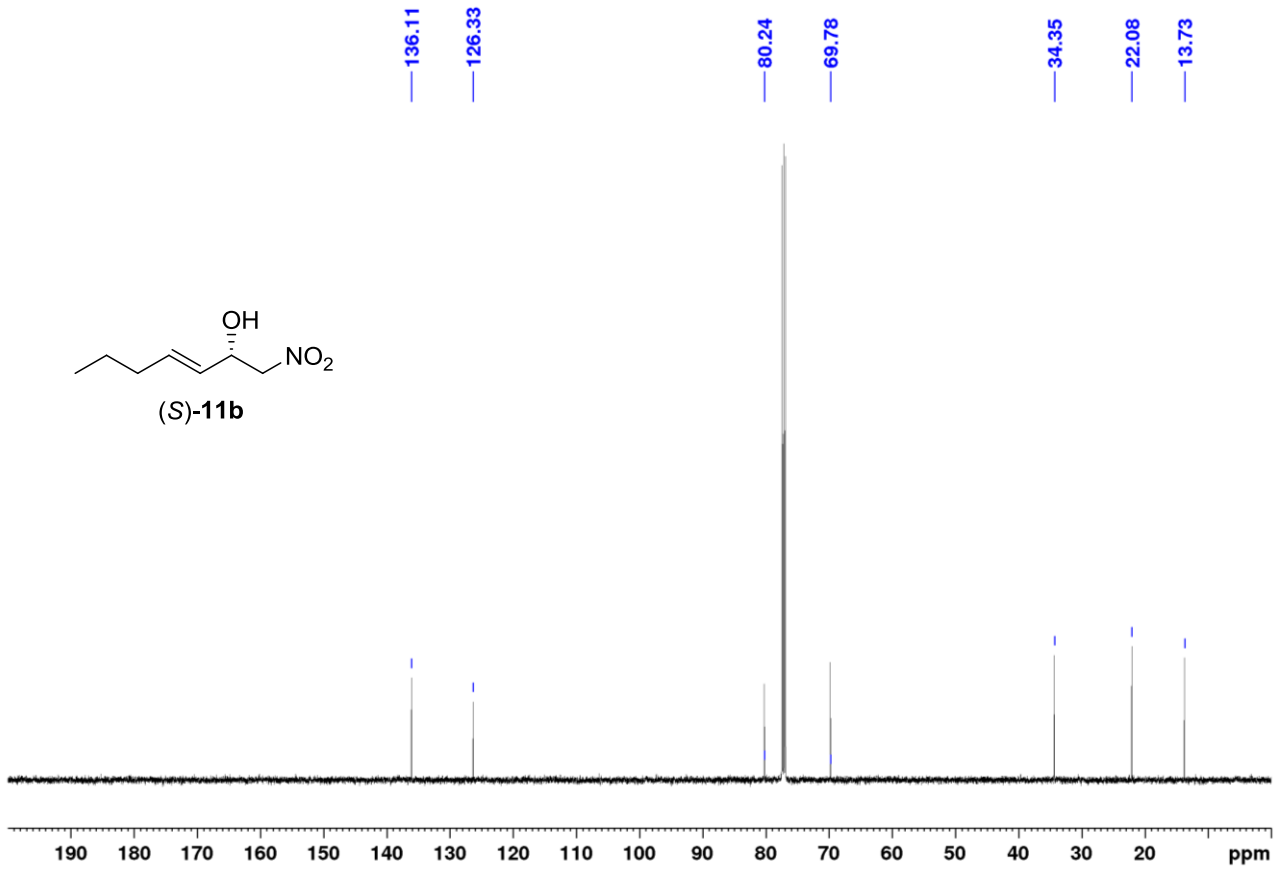

3131.41
3128.31
2707.95
2704.70
2698.75
2695.45
2401.57
2392.32
2388.12
2378.87
2330.46
2327.10
2317.05
2313.65
OH
O
NO2
Me
1.00
1.00
1.00
1.04
1.04
0.96
3.10
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

(*R*)-**9b**


153.34
148.86
109.26
106.69
78.61
64.95
13.63
OH
O
NO2
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

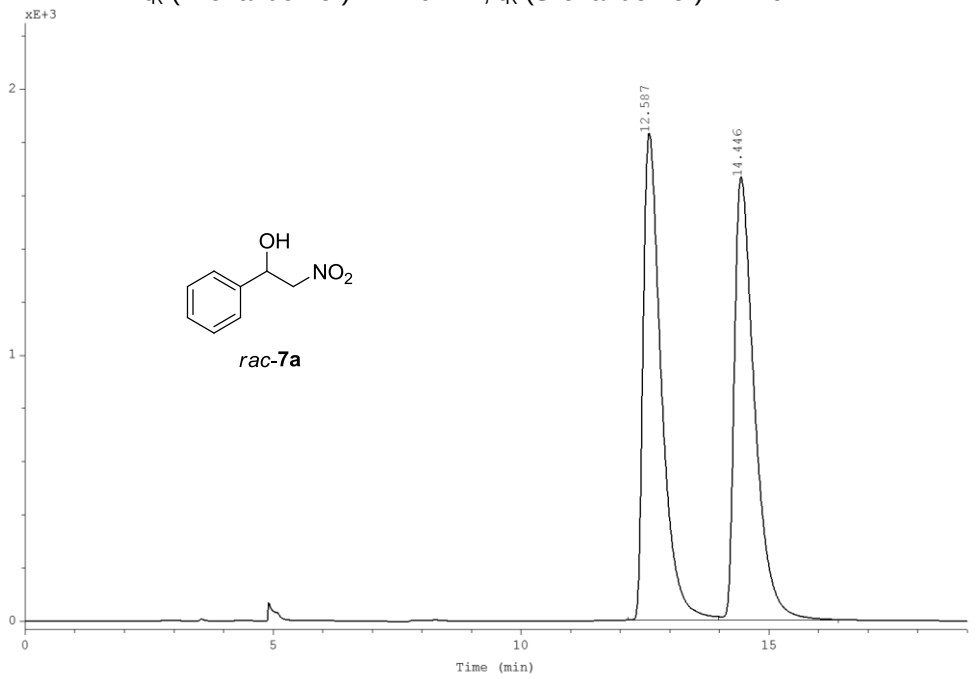
(*R*)-**9b**


2956.37
2955.42
2949.57
2948.62
2942.71
2941.31
2940.11
2934.16
2933.16
2927.31
2926.36
2734.46
2733.01
2731.56
2727.81
2726.36
2724.91
2719.06
2717.61
2716.16
2712.41
2710.95
2709.50
2420.08
2414.23
2408.73
2403.37
2397.47
1211.71
1207.36
1031.32
1024.12
1017.06
1009.71
722.44
715.04
707.68
700.28
692.88
685.53
456.67
449.32
441.96
OH
NO2
(S)-11b
1.00
0.99
1.00
2.09
0.98
2.08
2.07
3.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

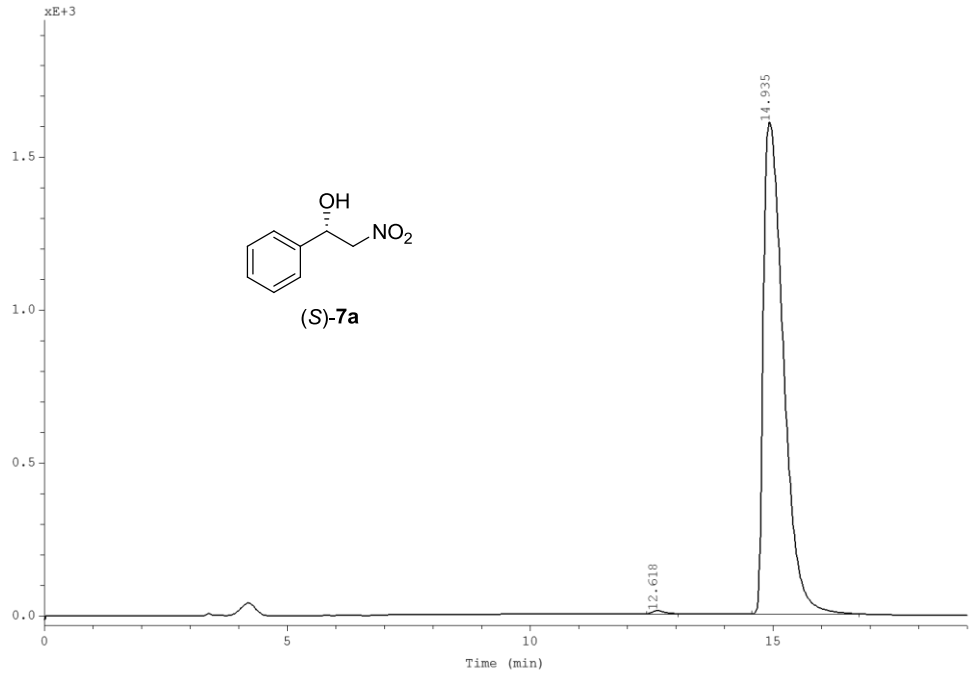

136.11
126.33
80.24
69.78
34.35
22.08
13.73
OH
NO2
(S)-11b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

5. Copies of HPLC Spectra

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.8 mL/min, 215 nm:
t_R (*R*-enantiomer) = 12.6 min; t_R (*S*-enantiomer) = 14.9 min

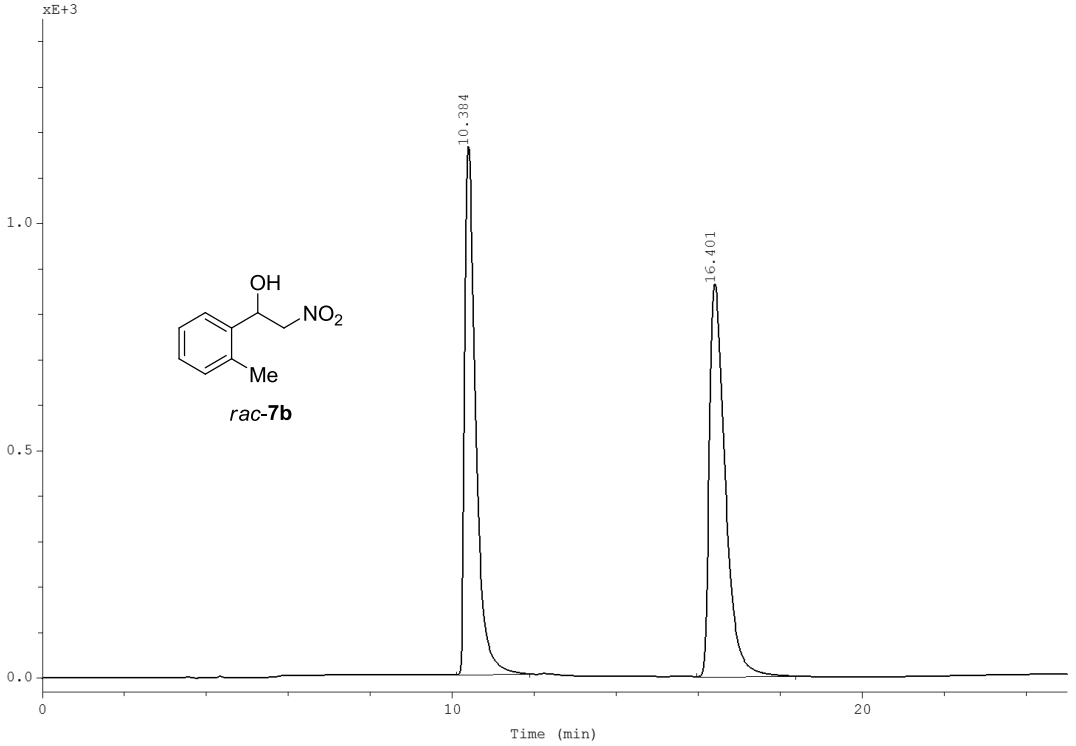


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.59	12.16	13.98	1831.20	780.62	52.38	49.81
2	14.45	13.98	16.40	1665.09	786.54	47.62	50.19



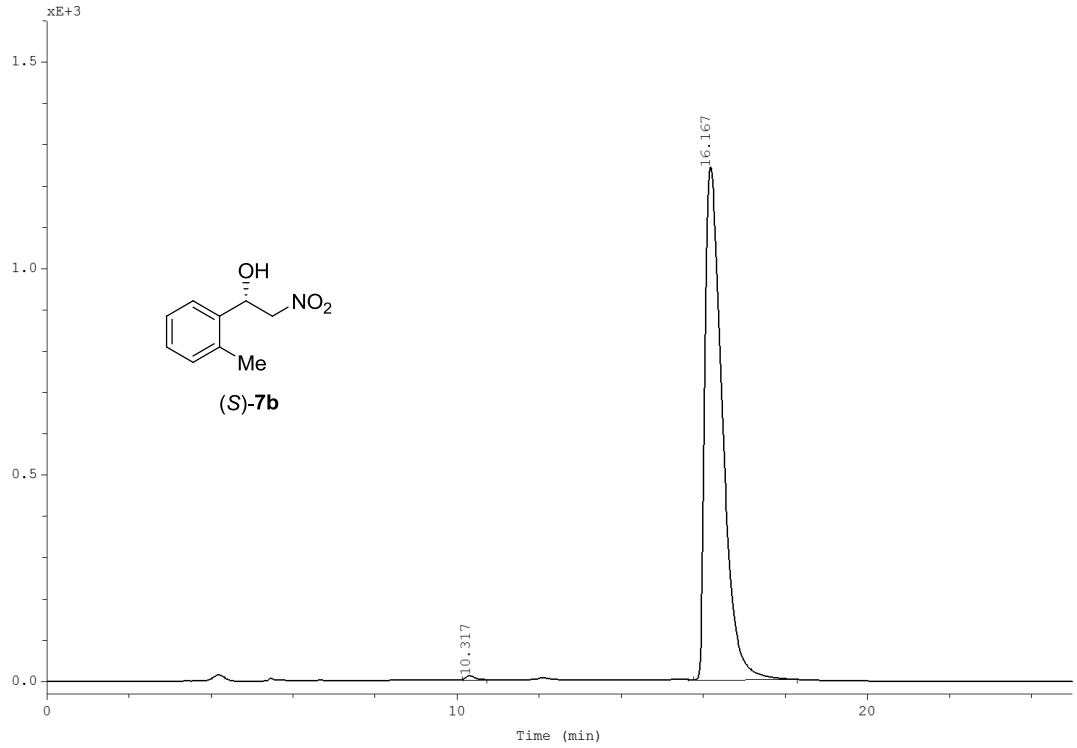
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.62	12.39	13.05	10.32	2.86	0.64	0.37
2	14.93	14.56	16.77	1609.83	767.79	99.36	99.63

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 10.3 min; t_R (*S*-enantiomer) = 16.2 min



rac-**7b**

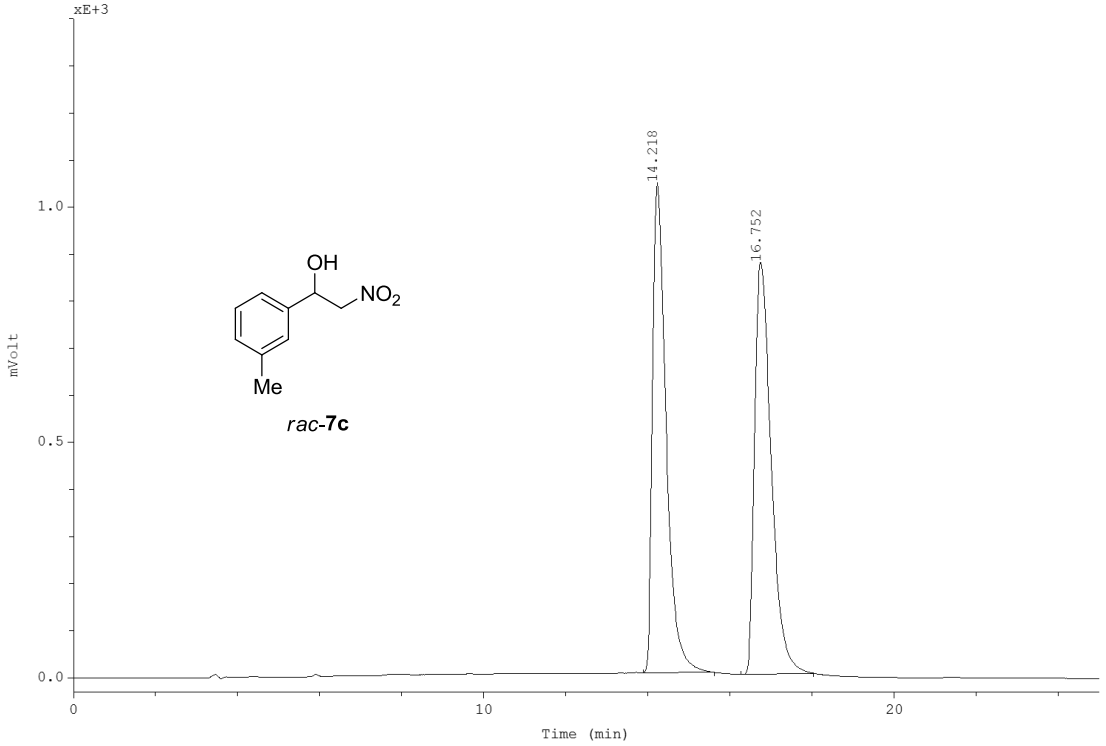
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	10.38	10.10	11.88	1162.30	364.12	57.35	48.51
2	16.40	15.96	18.37	864.51	386.44	42.65	51.49



(*S*)-**7b**

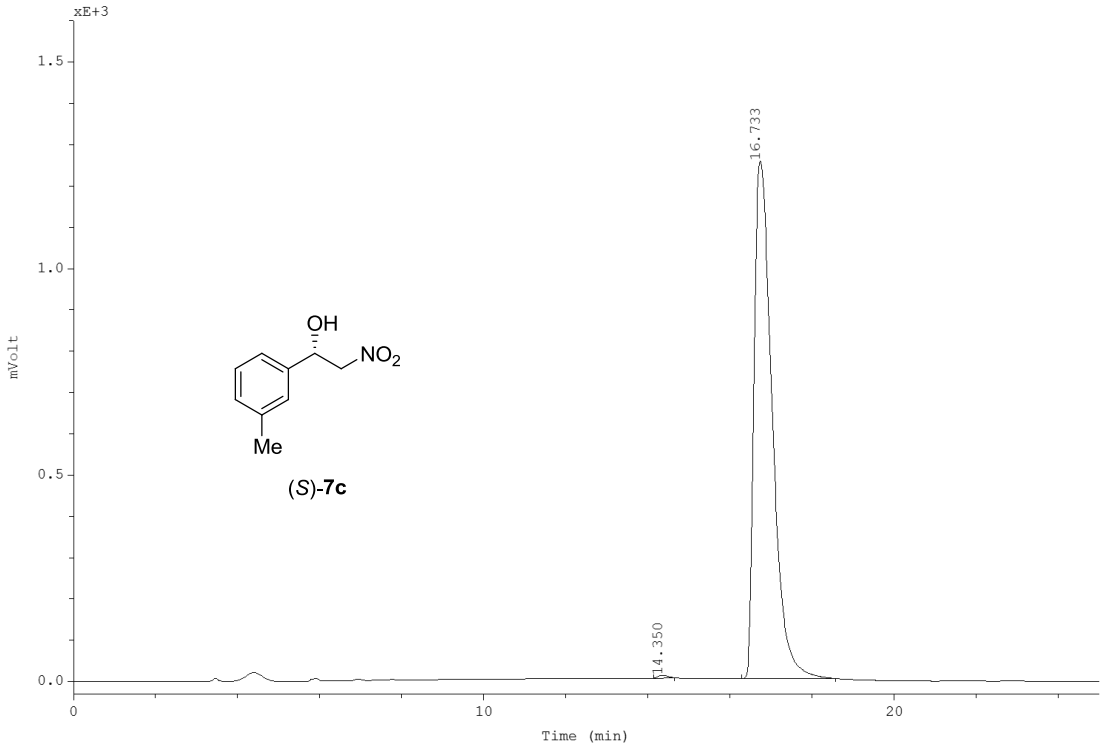
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	10.32	10.12	10.72	9.85	2.43	0.79	0.40
2	16.17	15.76	18.29	1240.90	613.36	99.21	99.60

Chiralcel OD-3, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 14.4 min; t_R (*S*-enantiomer) = 16.7 min



rac-**7c**

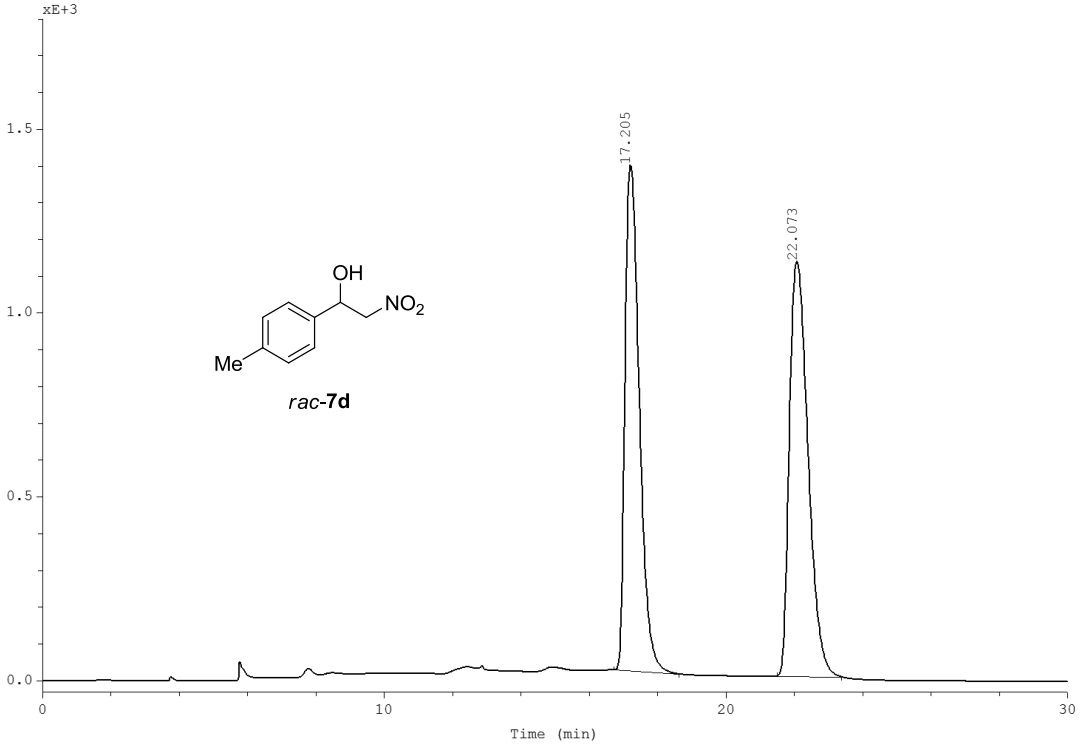
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	14.22	13.88	15.62	1040.79	401.61	54.35	49.45
2	16.75	16.26	18.03	874.27	410.58	45.65	50.55



(*S*)-**7c**

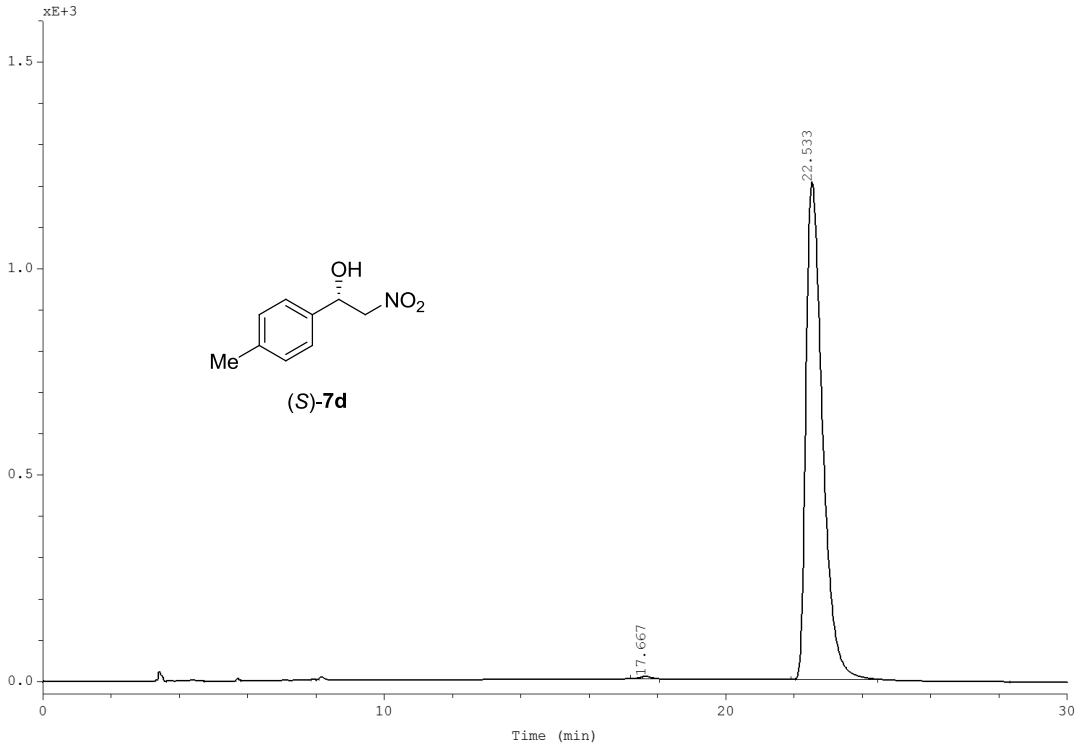
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	14.35	14.14	14.63	6.58	1.75	0.52	0.27
2	16.73	16.28	18.57	1253.18	640.34	99.48	99.73

Chiralcel OD-3, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 17.7 min; t_R (*S*-enantiomer) = 22.5 min



rac-**7d**

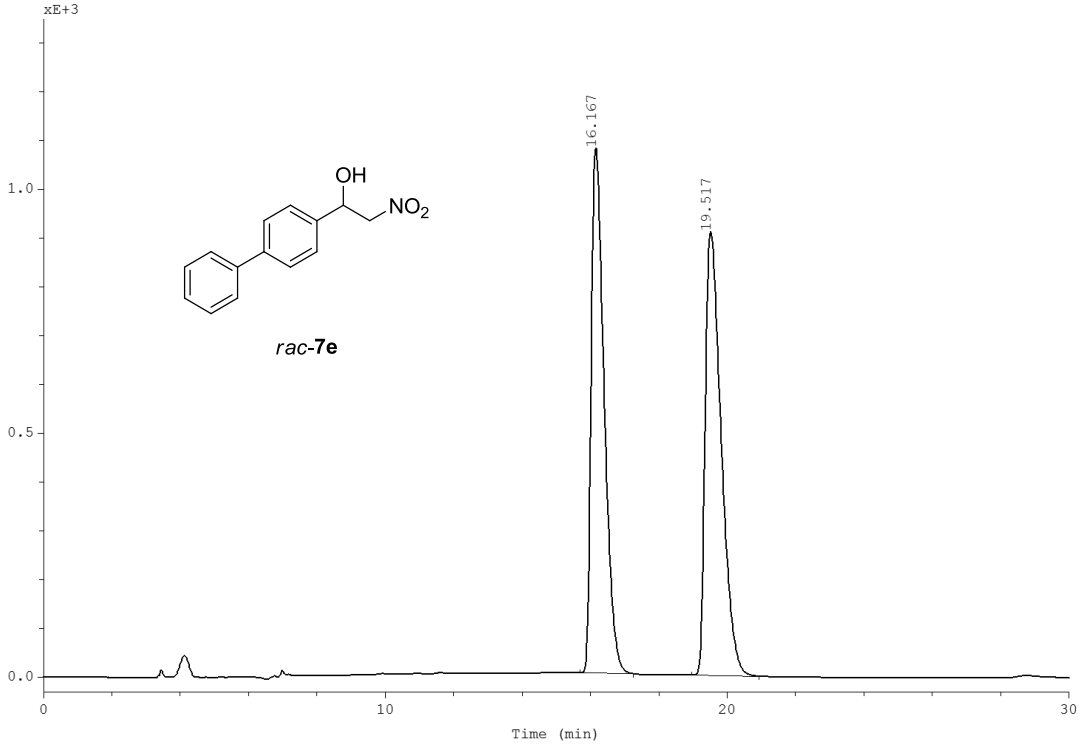
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	17.20	16.73	18.62	1376.24	672.41	54.93	48.51
2	22.07	21.49	23.38	1129.06	713.66	45.07	51.49



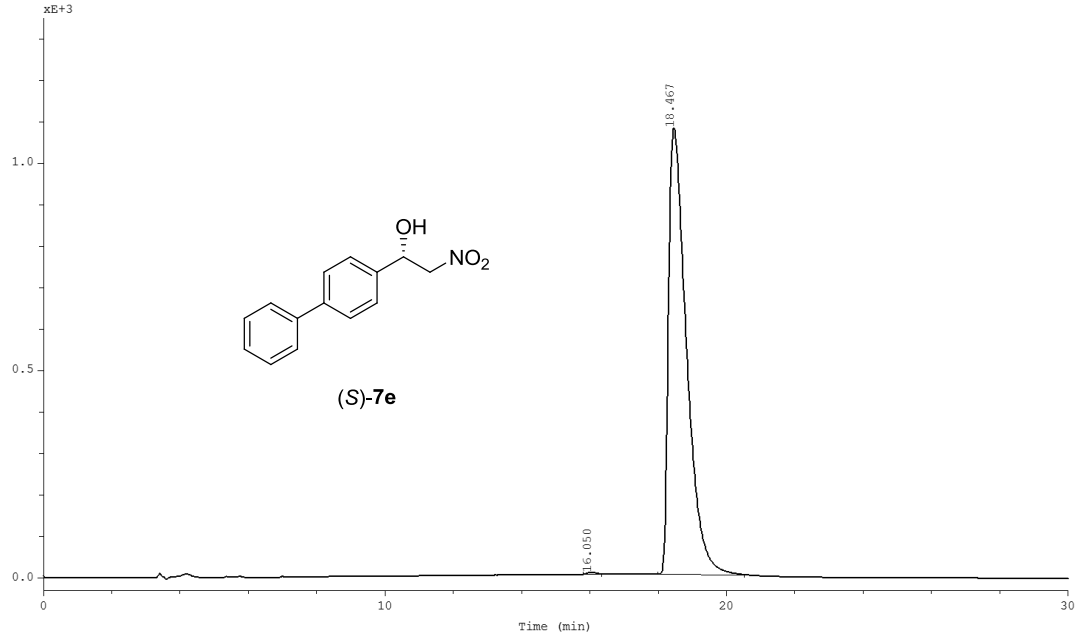
(*S*)-**7d**

	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	17.67	17.22	18.05	5.47	1.93	0.45	0.28
2	22.53	21.91	24.46	1205.63	679.96	99.55	99.72

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 16.1 min; t_R (*S*-enantiomer) = 18.5 min

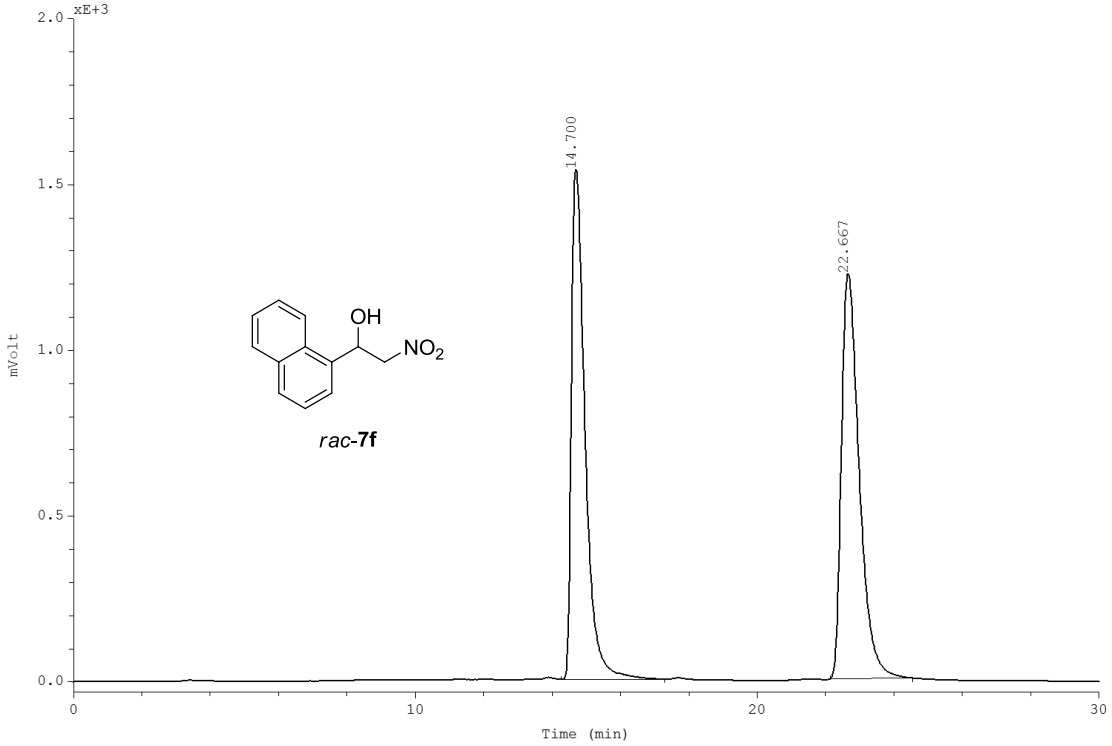


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	16.17	15.69	17.25	1076.49	474.73	54.17	48.99
2	19.52	18.96	20.93	910.74	494.41	45.83	51.01



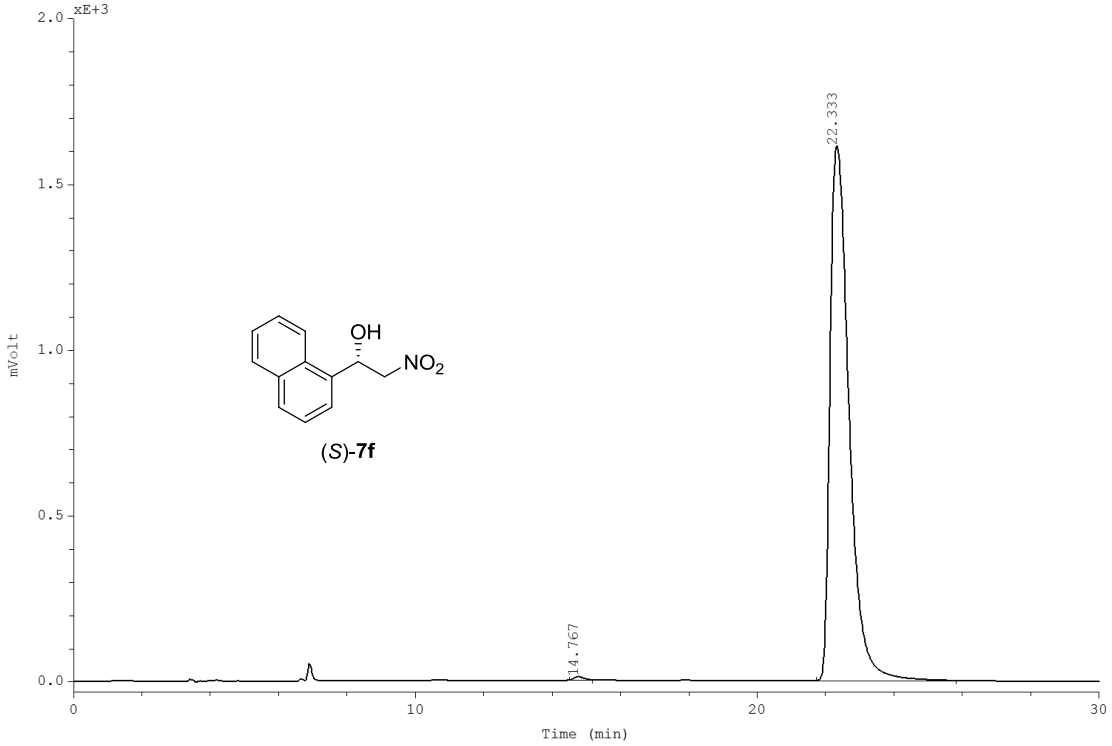
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	16.05	15.80	16.34	4.32	1.28	0.40	0.19
2	18.47	17.98	20.53	1076.75	655.12	99.60	99.81

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 14.8 min; t_R (*S*-enantiomer) = 22.3 min



rac-**7f**

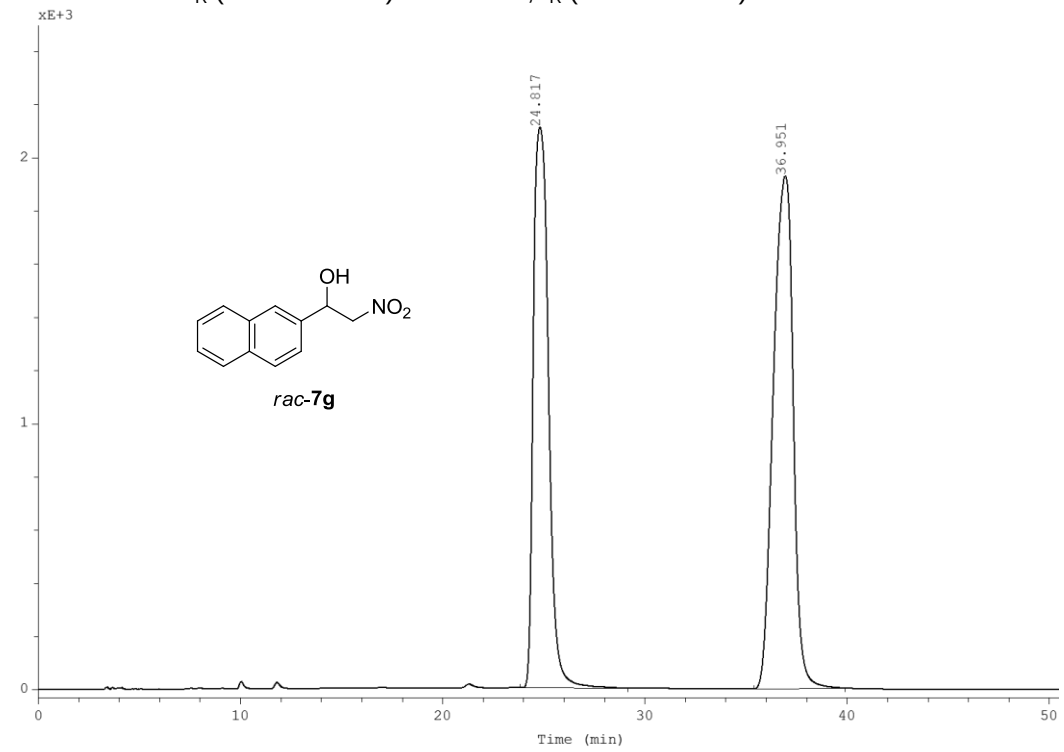
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	14.70	14.27	17.29	1538.67	714.07	55.73	49.21
2	22.67	22.15	24.54	1222.22	737.10	44.27	50.79



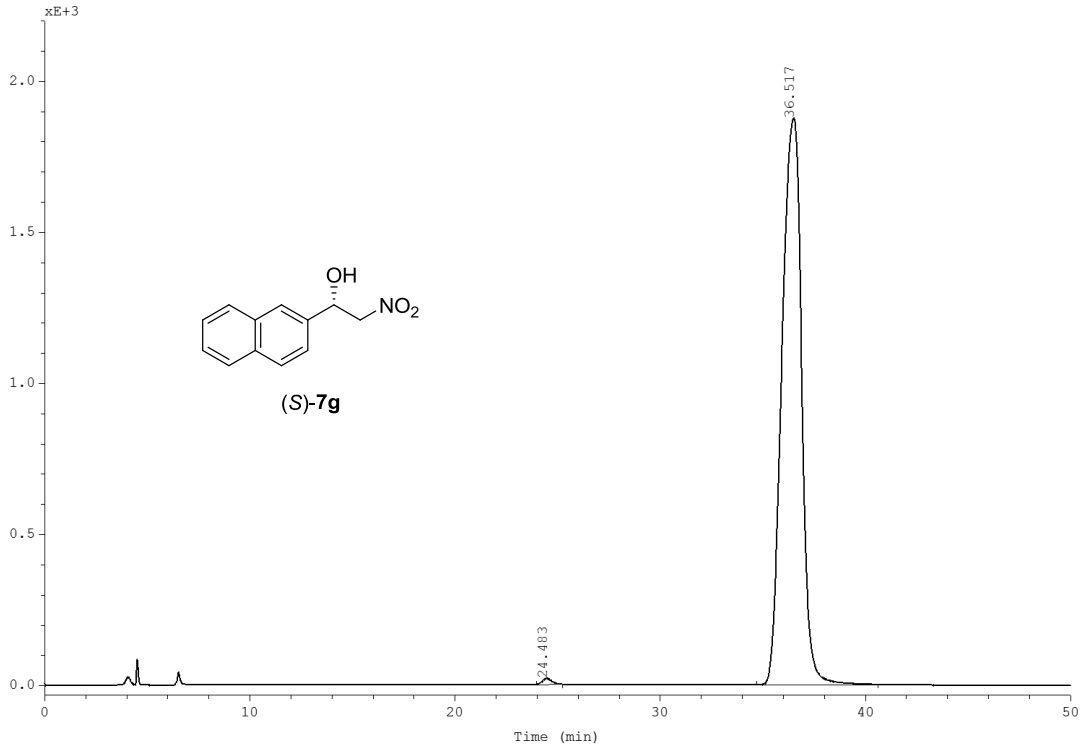
(*S*)-**7f**

	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	14.77	14.51	15.17	9.96	3.19	0.61	0.31
2	22.33	21.74	25.83	1613.72	1040.01	99.39	99.69

Chiralcel OD-3, *n*-hexane/*i*PrOH 80:20, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 24.5 min; t_R (*S*-enantiomer) = 36.5 min

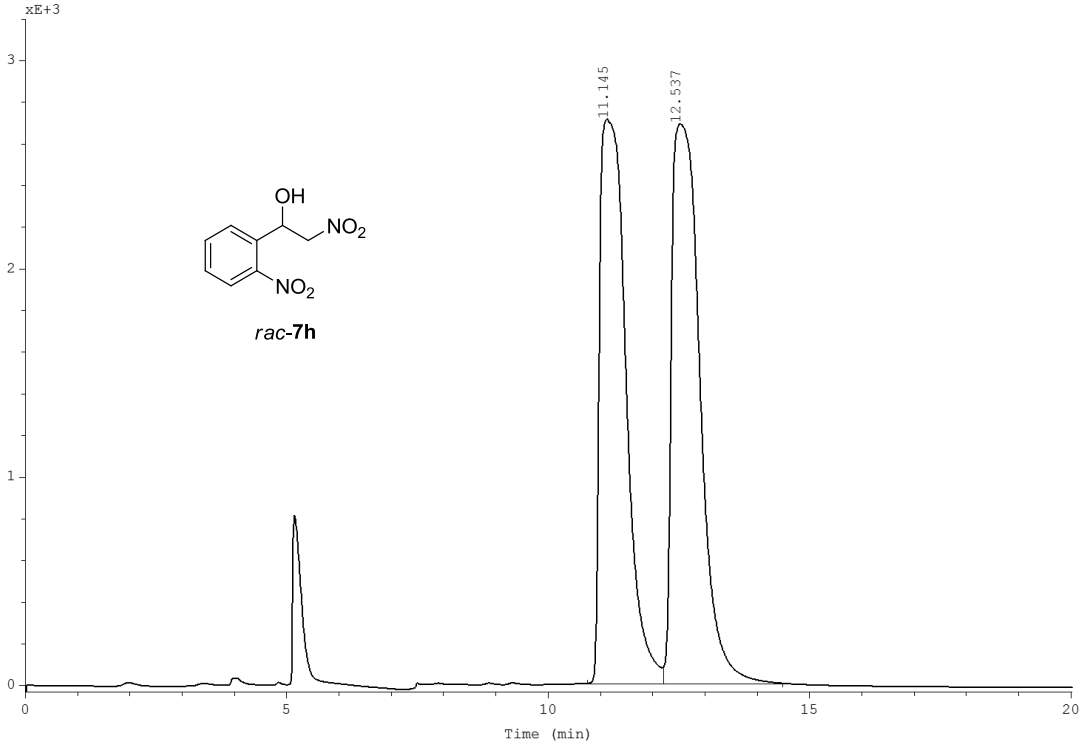


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	24.82	23.83	29.16	2108.09	1822.63	52.23	45.19
2	36.95	35.41	39.89	1928.16	2210.96	47.77	54.81

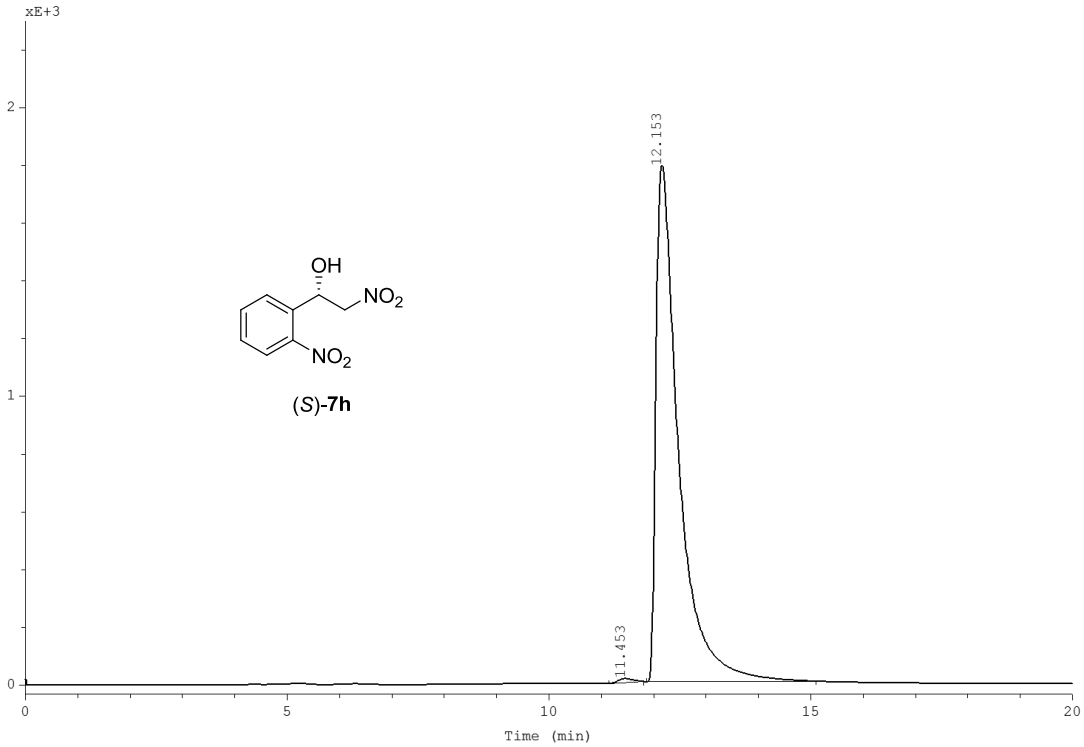


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	24.48	23.96	25.23	19.78	10.91	1.04	0.52
2	36.52	34.72	40.61	1874.37	2081.89	98.96	99.48

Chiralcel OD-3, *n*-hexane/*i*PrOH 80:20, 0.7 mL/min, 215 nm:
t_R (*R*-enantiomer) = 11.5 min; t_R (*S*-enantiomer) = 12.2 min

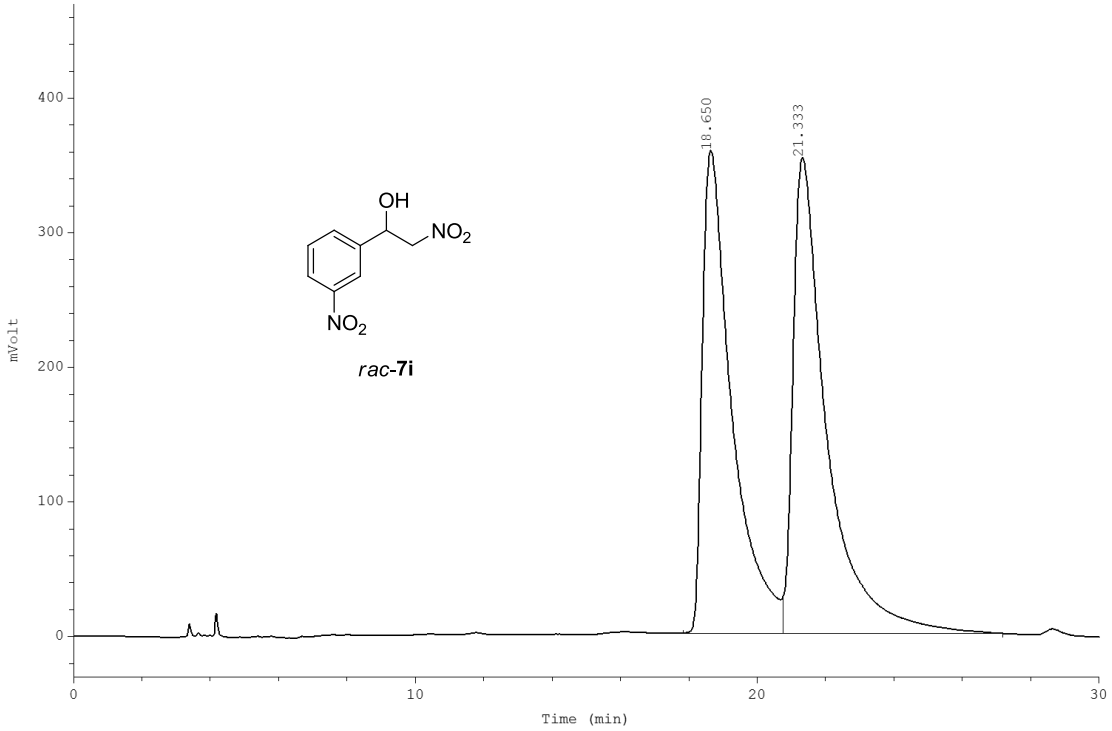


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	11.14	10.76	12.21	2710.17	1575.84	50.22	48.33
2	12.54	12.21	14.49	2686.59	1684.53	49.78	51.67

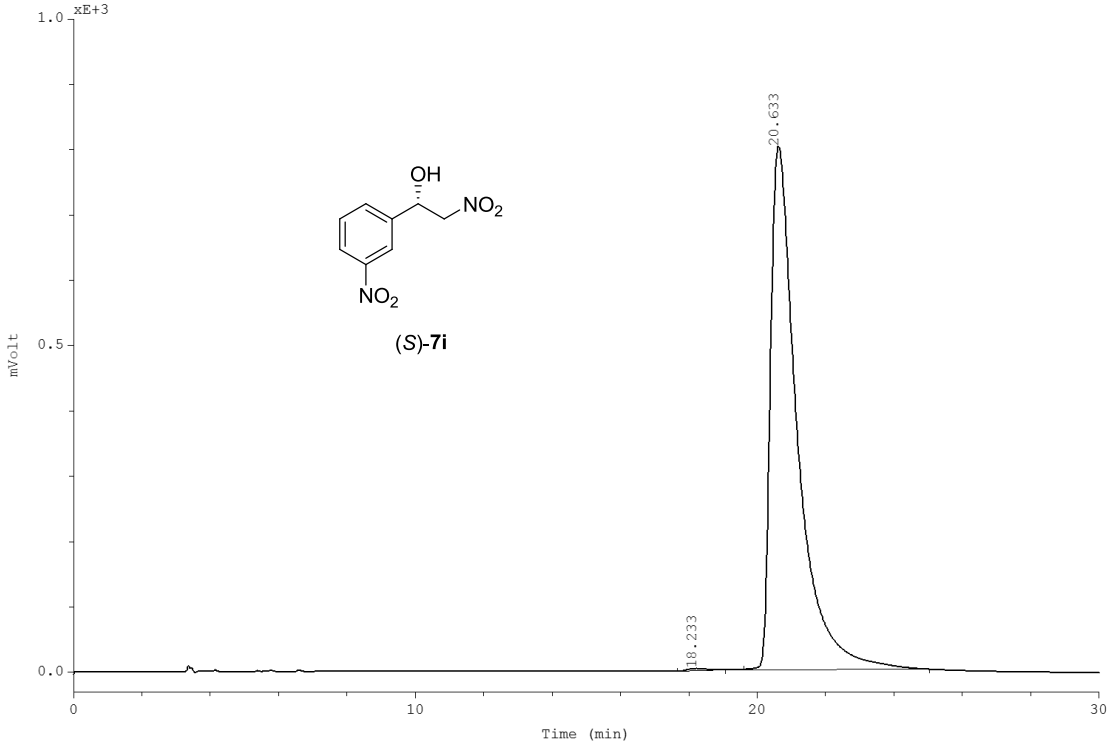


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	11.45	11.14	11.81	13.83	4.51	0.77	0.50
2	12.15	11.87	15.10	1785.65	897.70	99.23	99.50

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 18.2 min; t_R (*S*-enantiomer) = 20.6 min

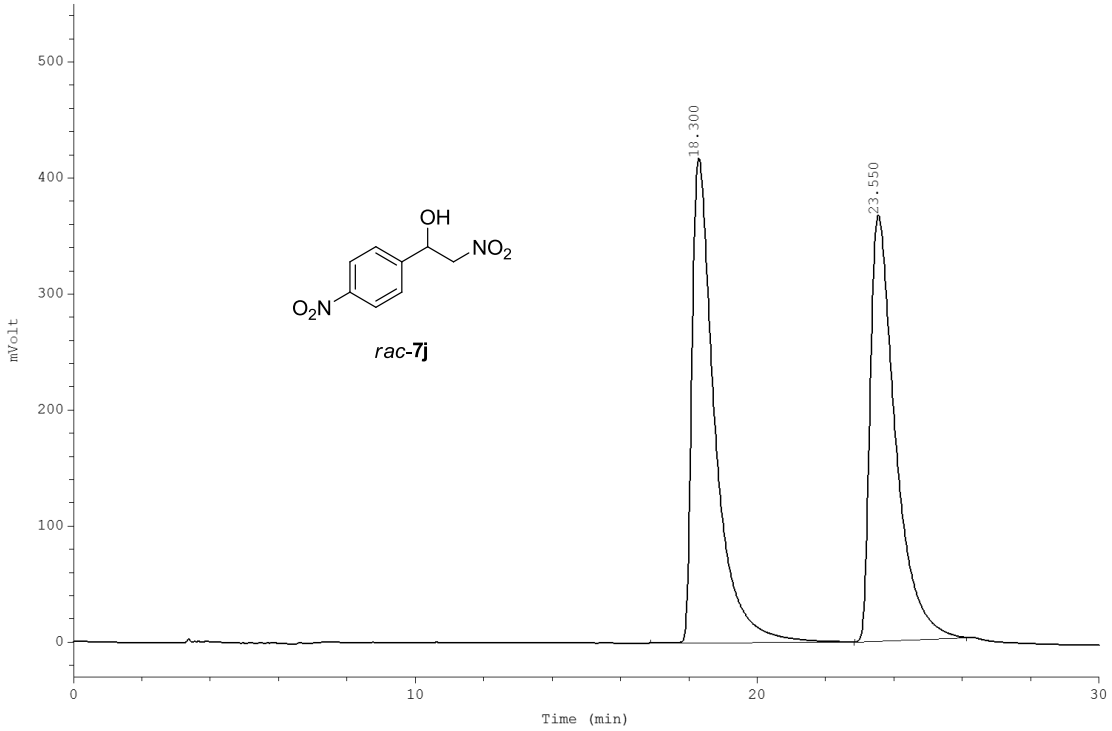


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	18.65	17.84	20.75	358.87	360.39	50.38	47.07
2	21.33	20.75	27.19	353.53	405.22	49.63	52.93

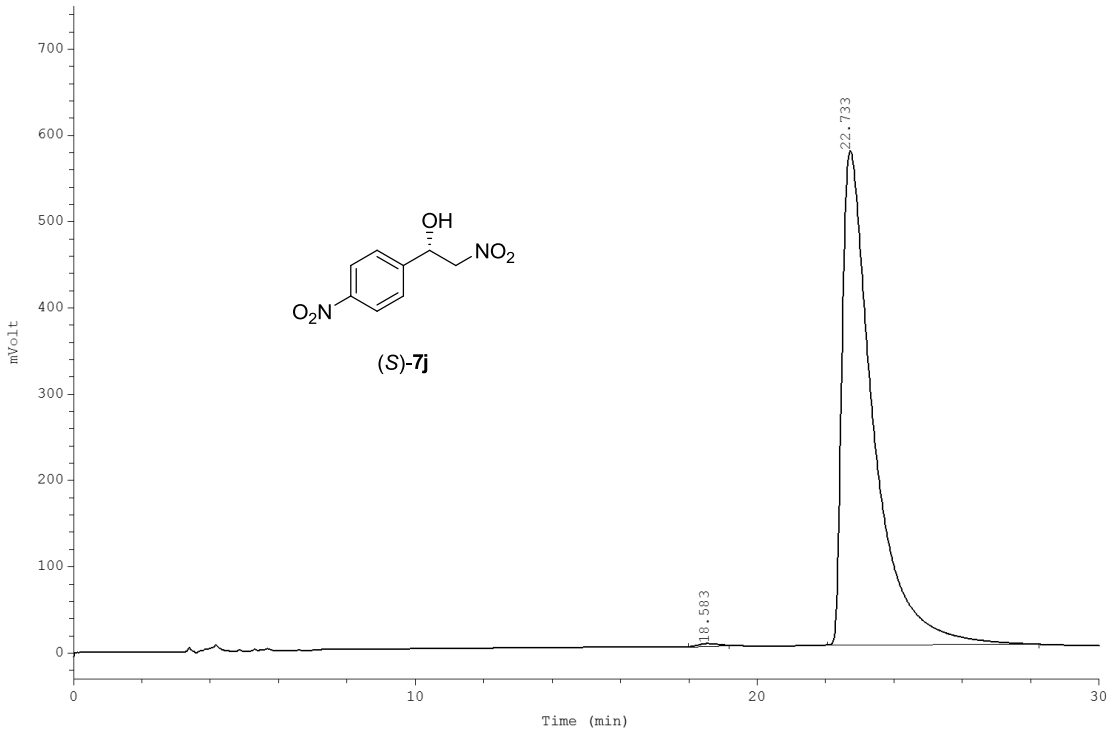


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	18.23	17.65	19.07	3.39	2.19	0.42	0.30
2	20.63	19.62	25.04	800.89	729.32	99.58	99.70

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 18.6 min; t_R (*S*-enantiomer) = 22.7 min

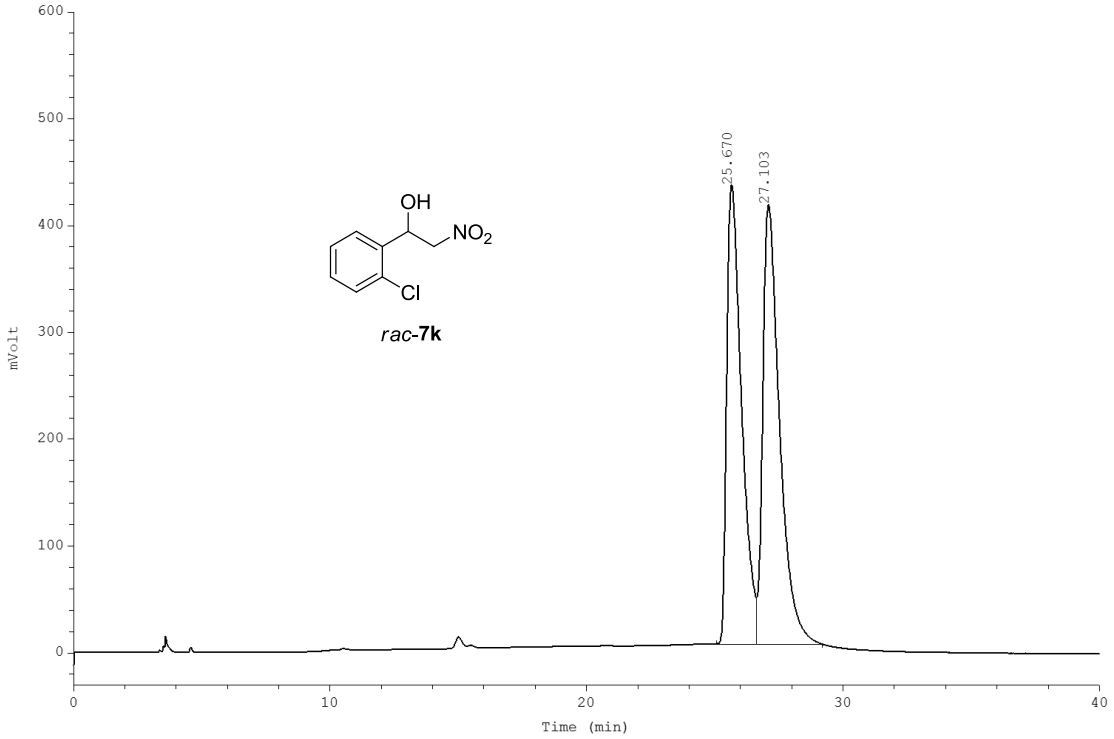


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	18.30	16.88	22.83	418.14	325.02	53.25	50.94
2	23.55	22.87	26.12	367.11	313.04	46.75	49.06



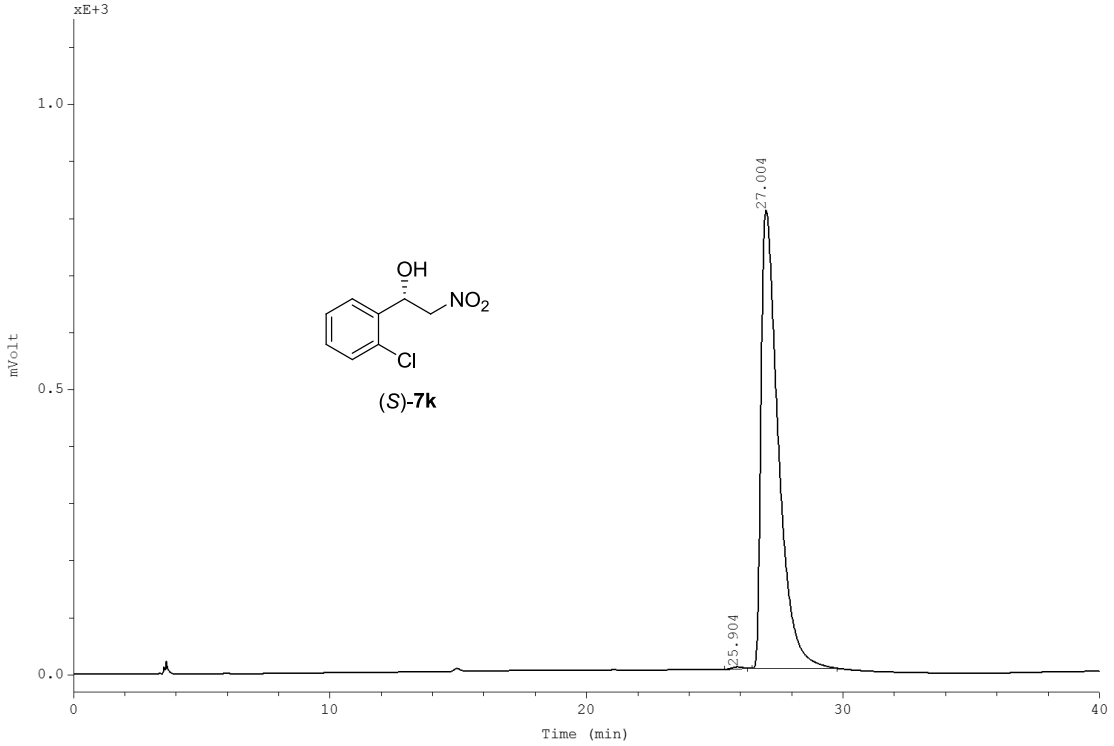
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	18.58	17.98	19.18	2.84	1.78	0.49	0.29
2	22.73	22.06	28.24	573.10	607.04	99.51	99.71

Chiralcel OD-3, *n*-hexane/*i*PrOH 97:3, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 25.9 min; t_R (*S*-enantiomer) = 27.0 min



rac-**7k**

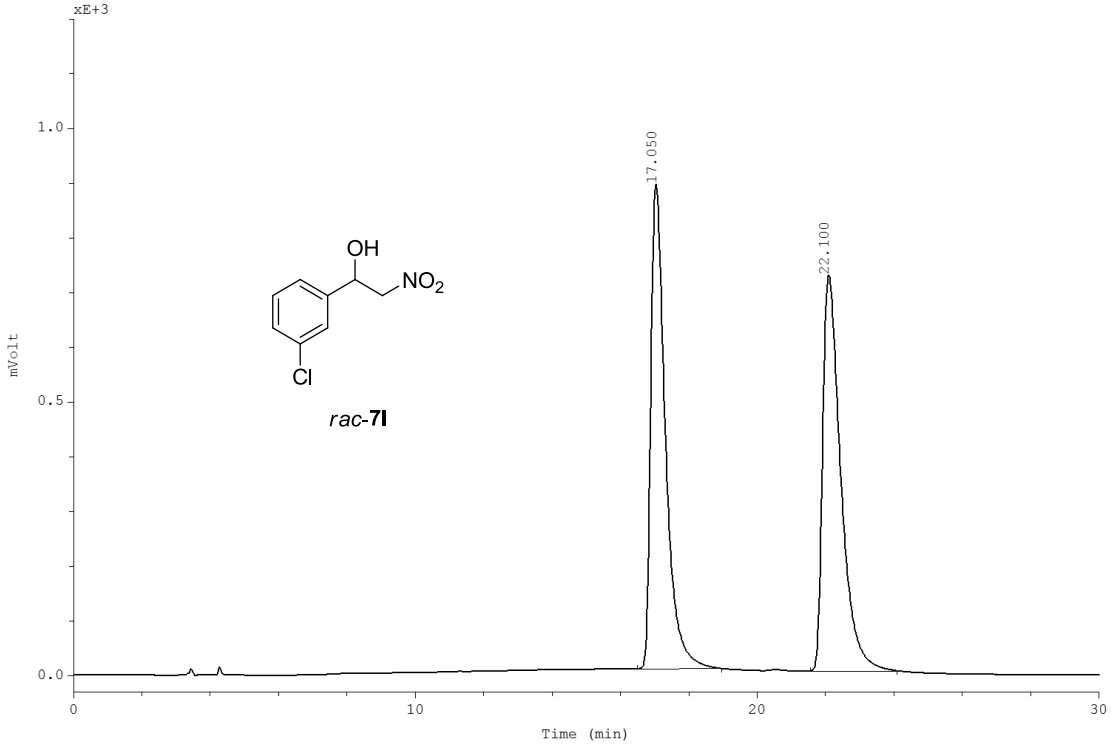
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	25.67	25.06	26.63	429.59	287.24	51.07	47.77
2	27.10	26.63	29.20	411.57	314.01	48.93	52.23



(*S*)-**7k**

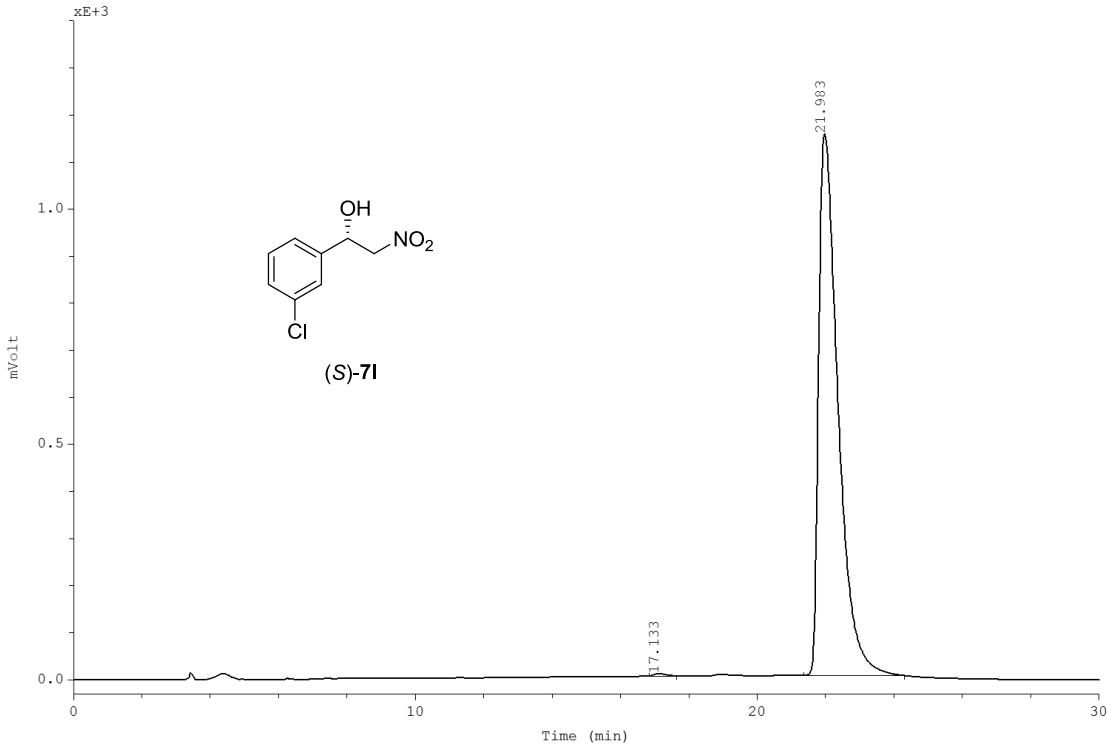
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	25.90	25.39	26.29	3.15	1.40	0.39	0.22
2	27.00	26.44	29.77	803.87	625.77	99.61	99.78

Chiralcel OD-3, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 17.1 min; t_R (*S*-enantiomer) = 22.0 min



rac-**7l**

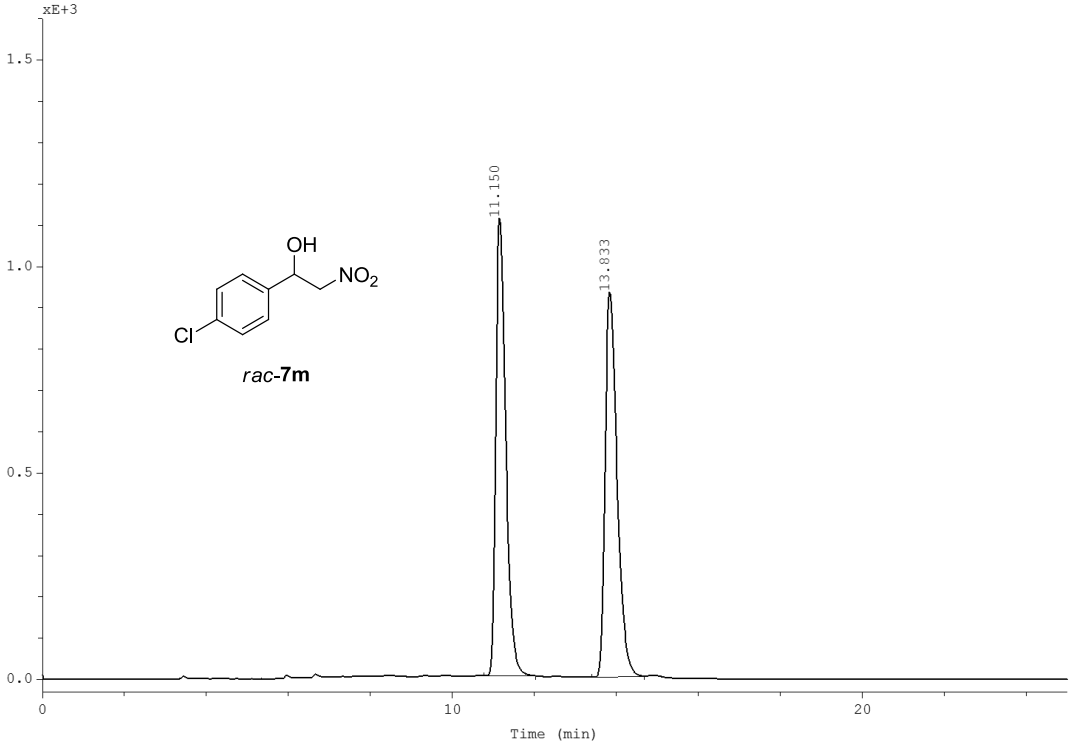
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	17.05	16.49	18.96	885.84	441.20	55.04	49.73
2	22.10	21.55	24.10	723.73	445.92	44.96	50.27



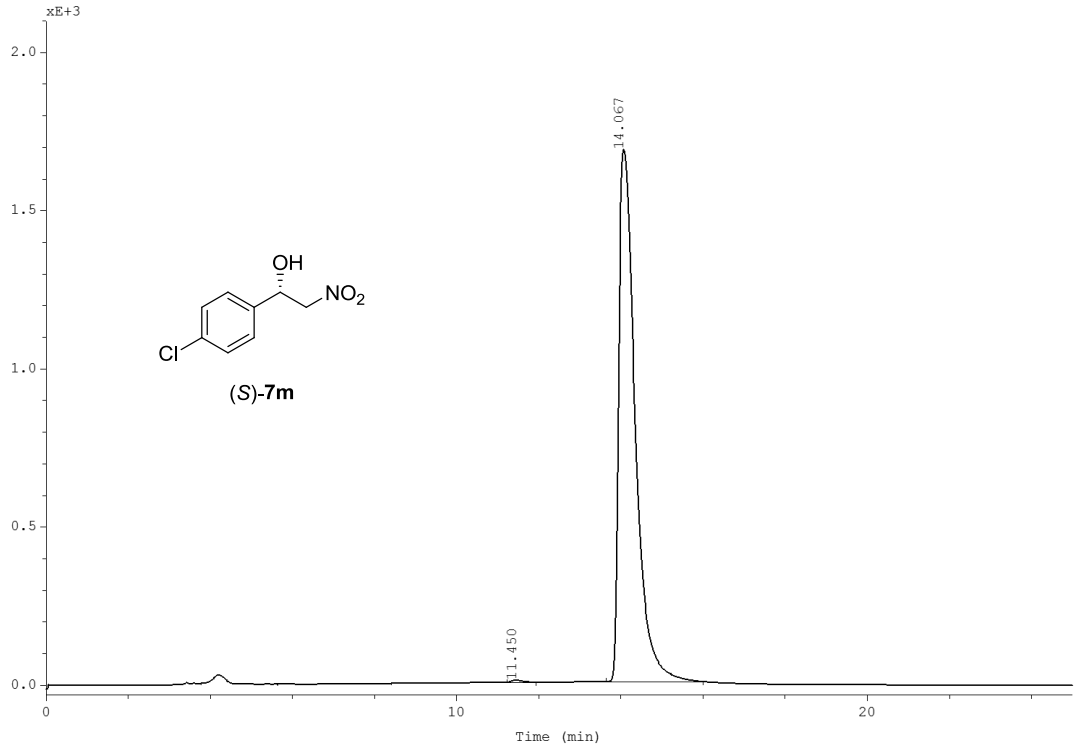
(*S*)-**7l**

	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	17.13	16.85	17.65	4.84	1.90	0.42	0.25
2	21.98	21.37	24.31	1150.93	758.59	99.58	99.75

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 11.5 min; t_R (*S*-enantiomer) = 14.1 min

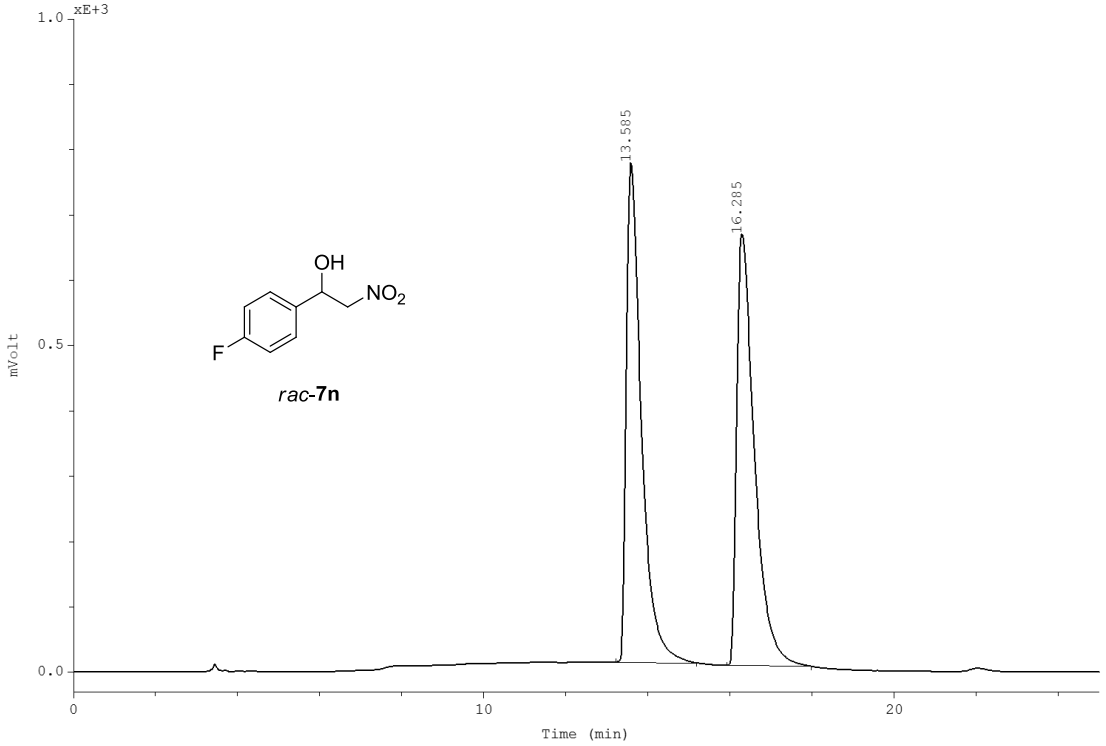


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	11.15	10.76	12.04	1108.84	312.44	54.33	49.86
2	13.83	13.40	14.67	932.05	314.24	45.67	50.14



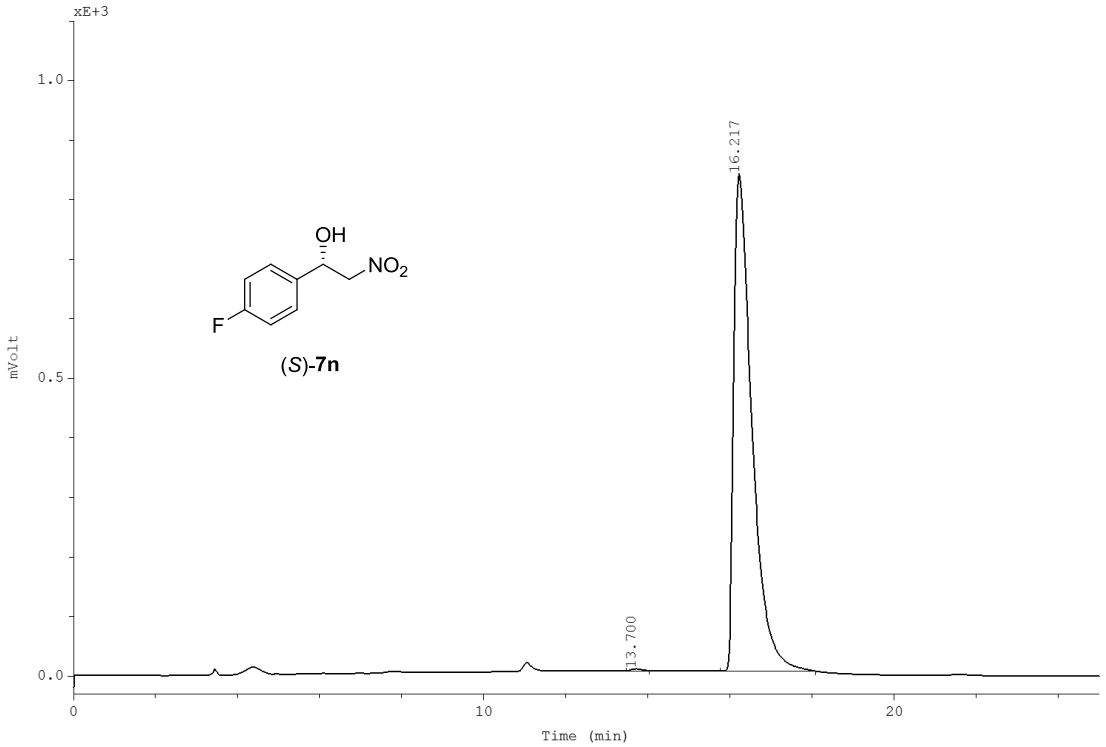
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	11.45	11.22	11.94	7.00	2.13	0.41	0.27
2	14.07	13.64	16.01	1681.56	784.33	99.59	99.73

Chiralcel OD-3, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 13.7 min; t_R (*S*-enantiomer) = 16.2 min



rac-**7n**

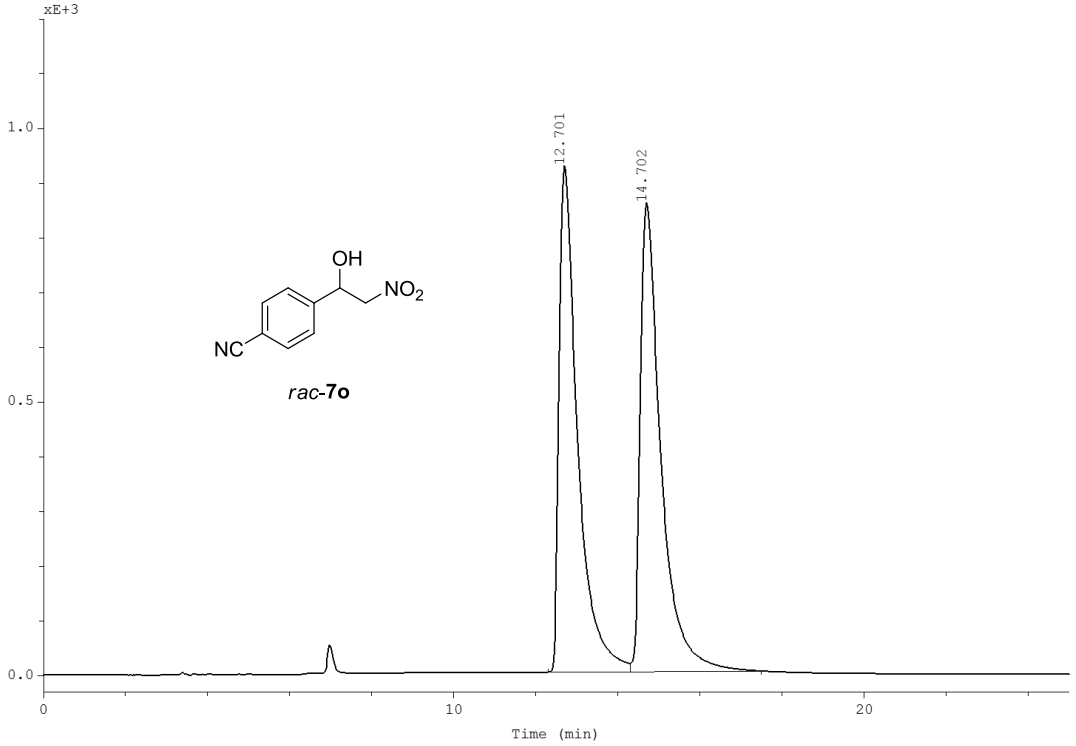
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	13.58	13.22	15.19	765.06	327.09	53.66	49.66
2	16.28	15.92	17.98	660.77	331.63	46.34	50.34



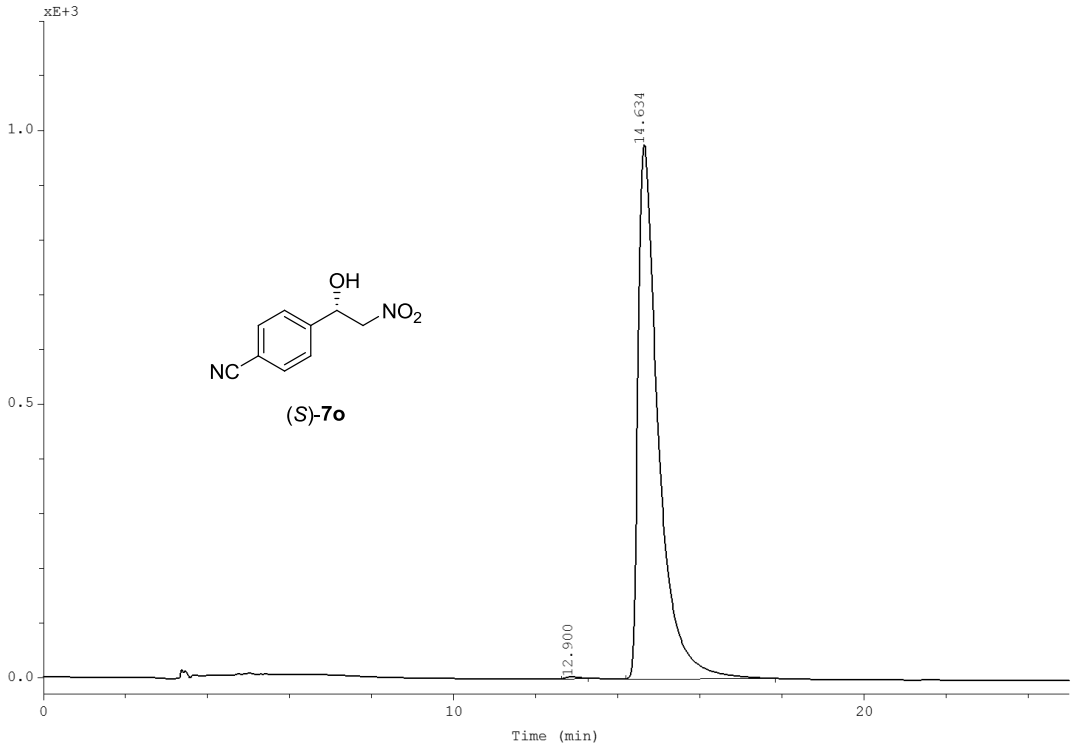
(*S*)-**7n**

	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	13.70	13.47	14.02	2.98	0.86	0.36	0.20
2	16.22	15.75	18.08	835.16	430.87	99.64	99.80

Chiralcel OD-3, *n*-hexane/*i*PrOH 80:20, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 12.9 min; t_R (*S*-enantiomer) = 14.6 min

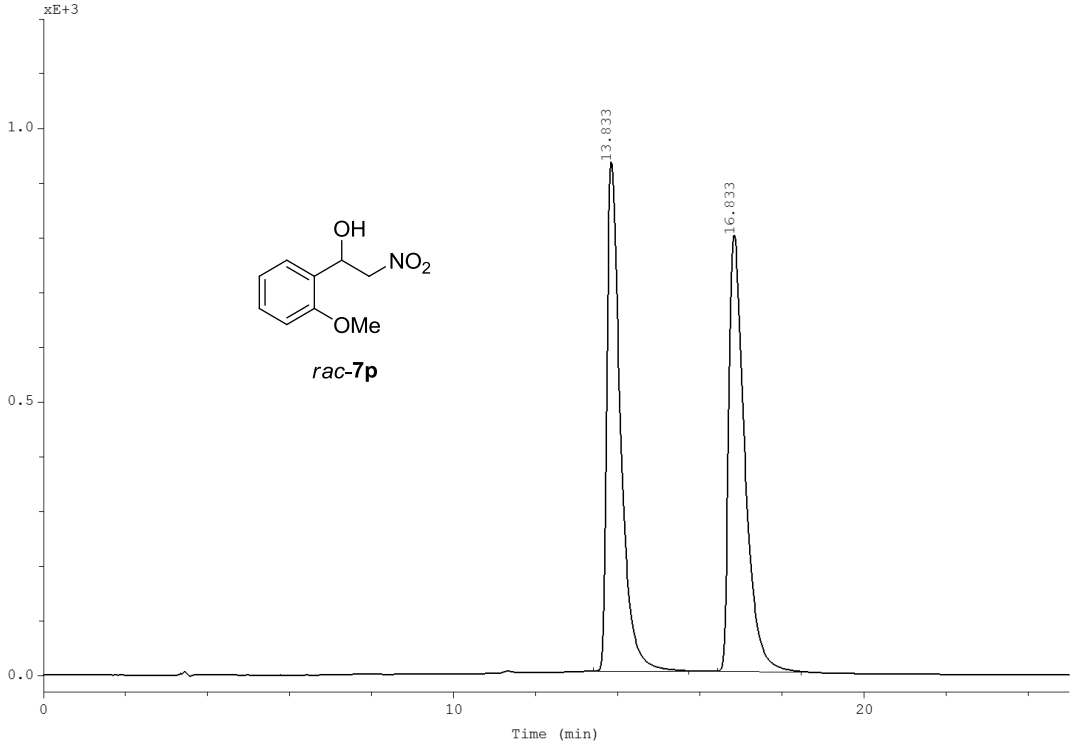


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.70	12.29	14.30	926.32	488.62	51.93	49.44
2	14.70	14.30	17.49	857.36	499.75	48.07	50.56

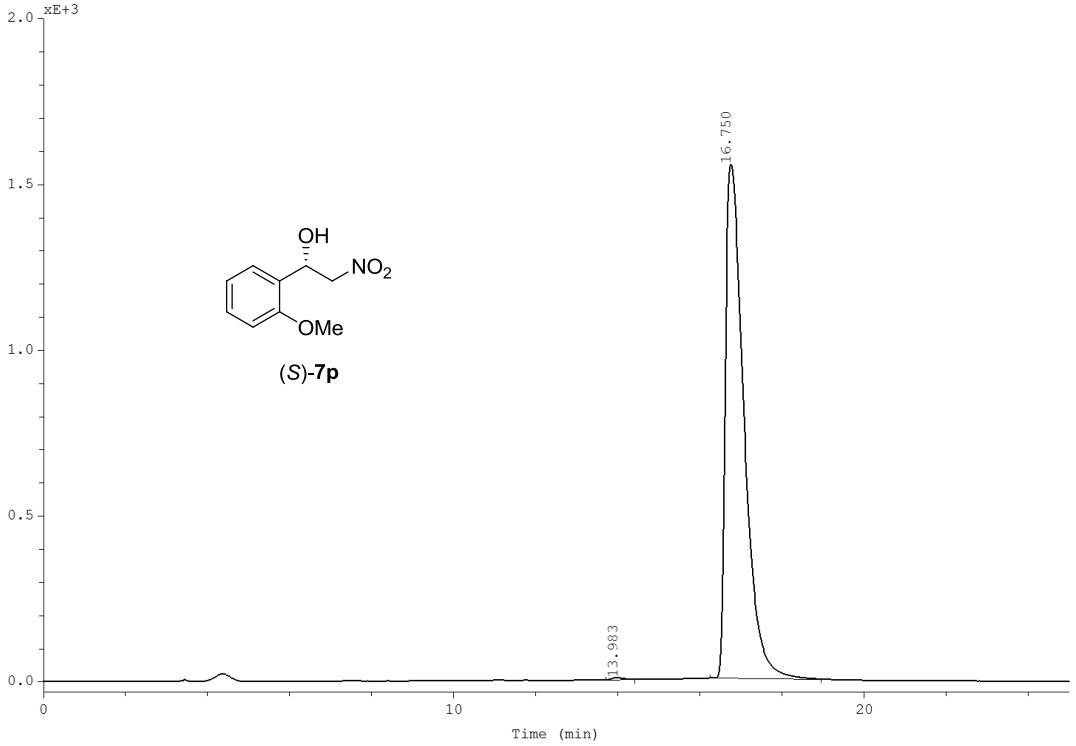


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.90	12.61	13.27	3.26	1.16	0.33	0.21
2	14.63	14.19	17.83	976.92	560.04	99.67	99.79

Chiralcel OD-3, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 14.0 min; t_R (*S*-enantiomer) = 16.8 min

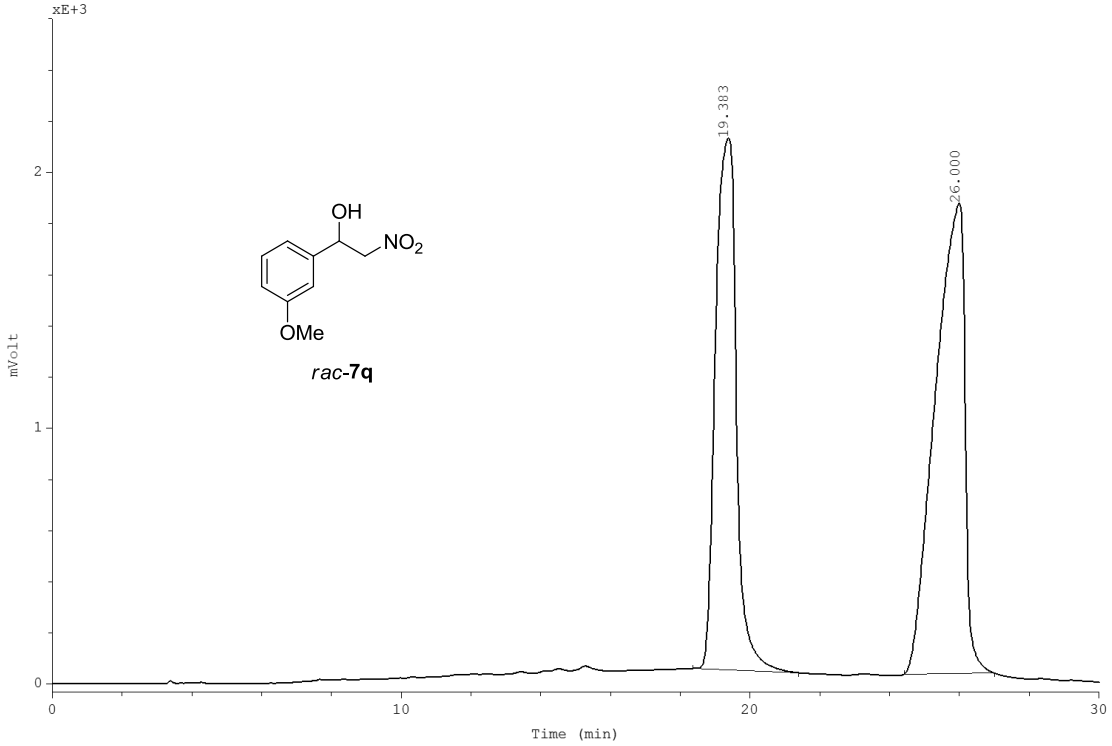


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	13.83	13.40	15.72	930.88	359.90	53.83	49.96
2	16.83	16.42	18.45	798.32	360.49	46.17	50.04

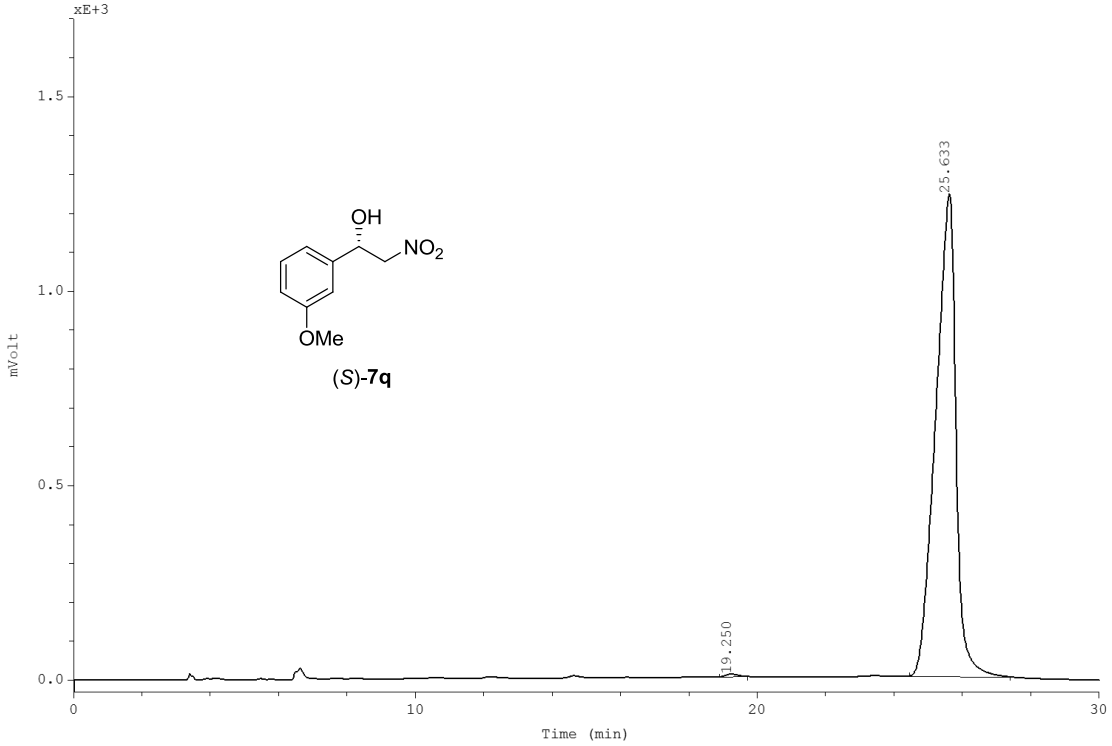


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	13.98	13.70	14.40	6.16	1.98	0.40	0.24
2	16.75	16.25	18.95	1551.47	812.47	99.60	99.76

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 19.3 min; t_R (*S*-enantiomer) = 25.6 min

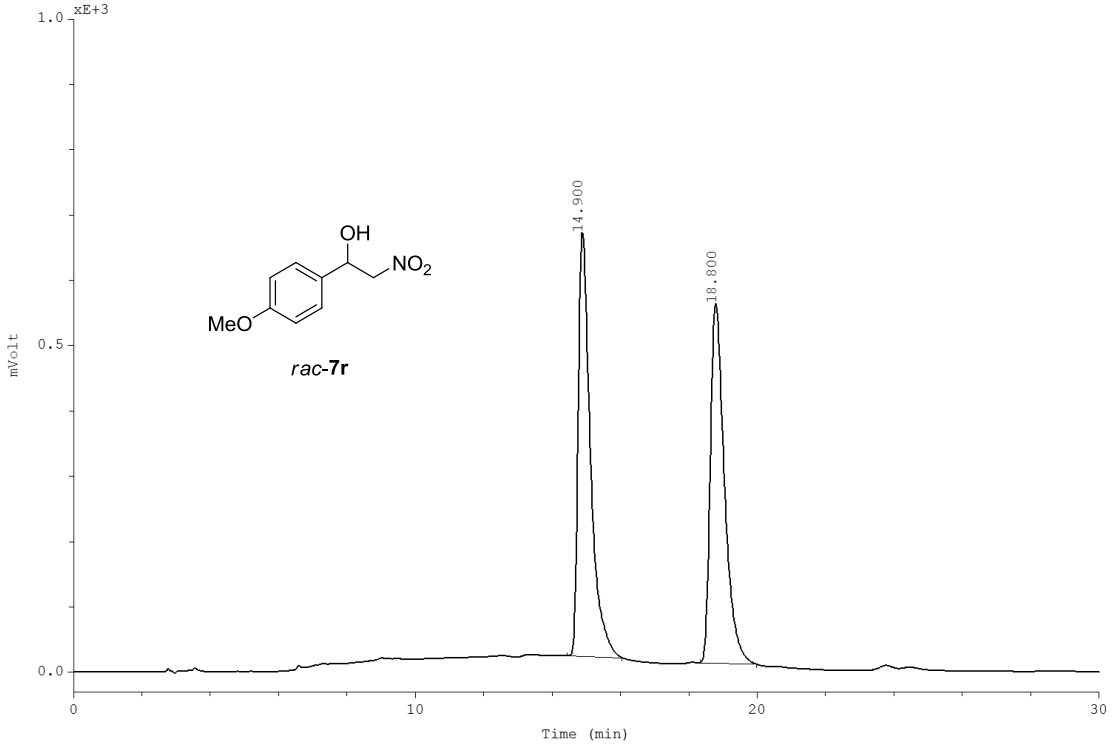


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	19.38	18.37	21.40	2079.65	1442.60	53.08	44.33
2	26.00	24.43	27.00	1838.34	1811.85	46.92	55.67

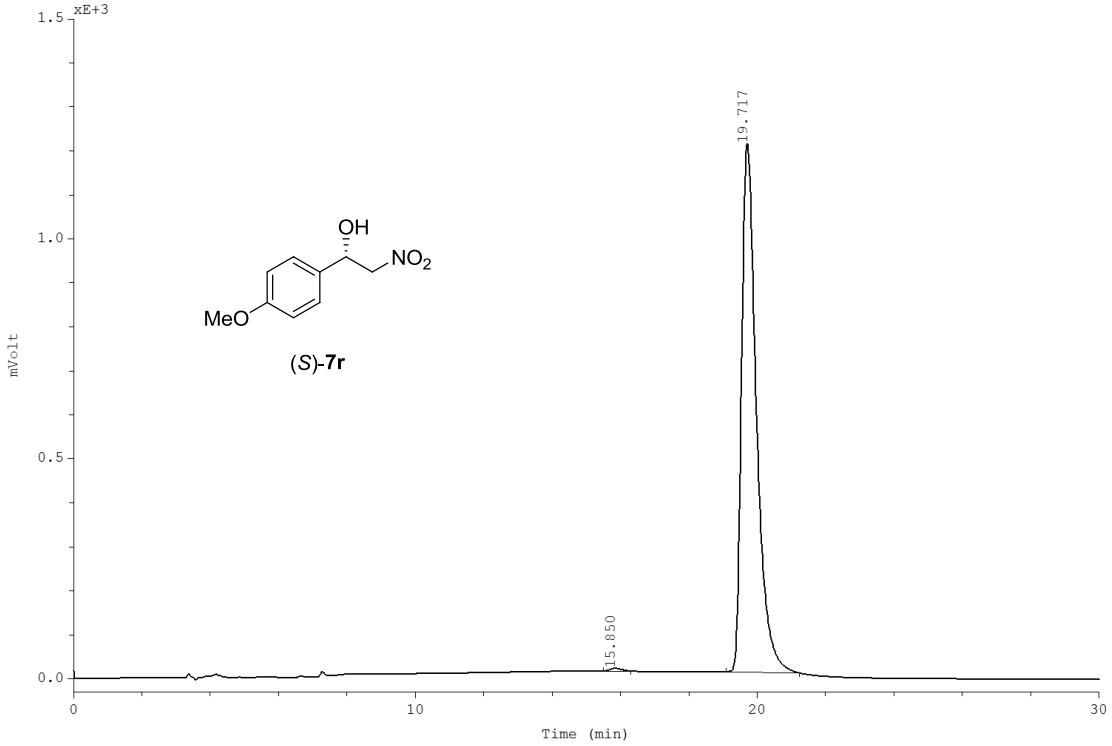


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	19.25	18.89	19.73	6.90	2.83	0.55	0.33
2	25.63	24.46	27.41	1240.99	848.65	99.45	99.67

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 15.9 min; t_R (*S*-enantiomer) = 19.7 min

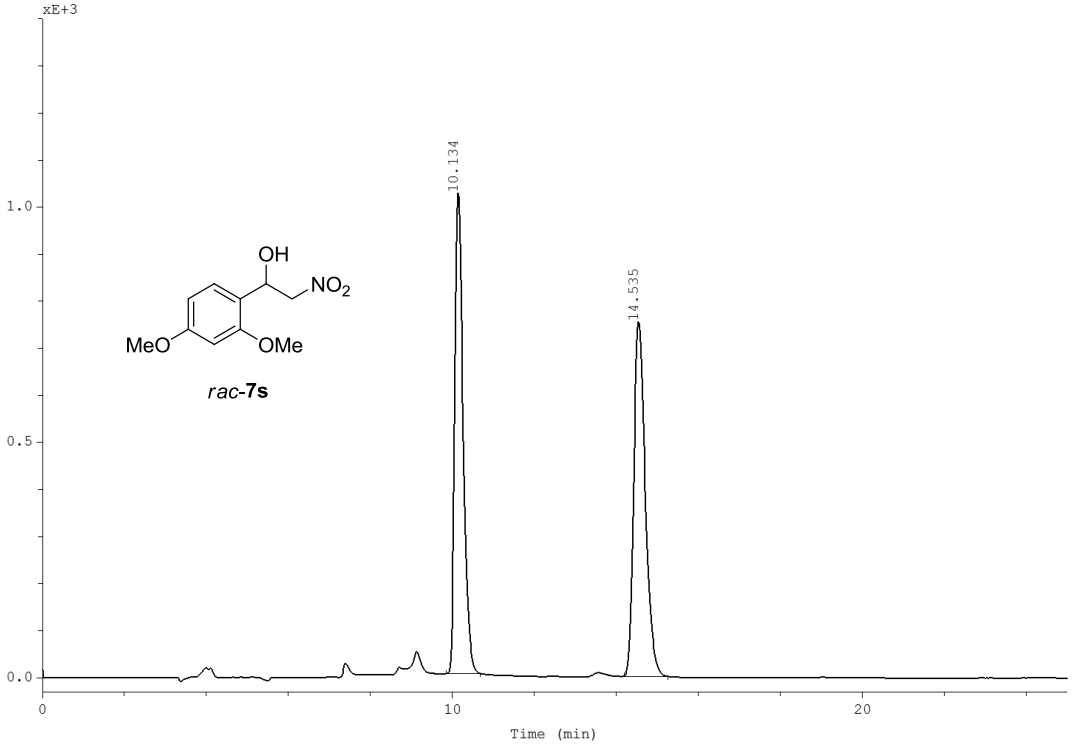


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	14.90	14.45	16.05	647.93	270.08	54.07	50.51
2	18.80	18.35	19.98	550.39	264.57	45.93	49.49



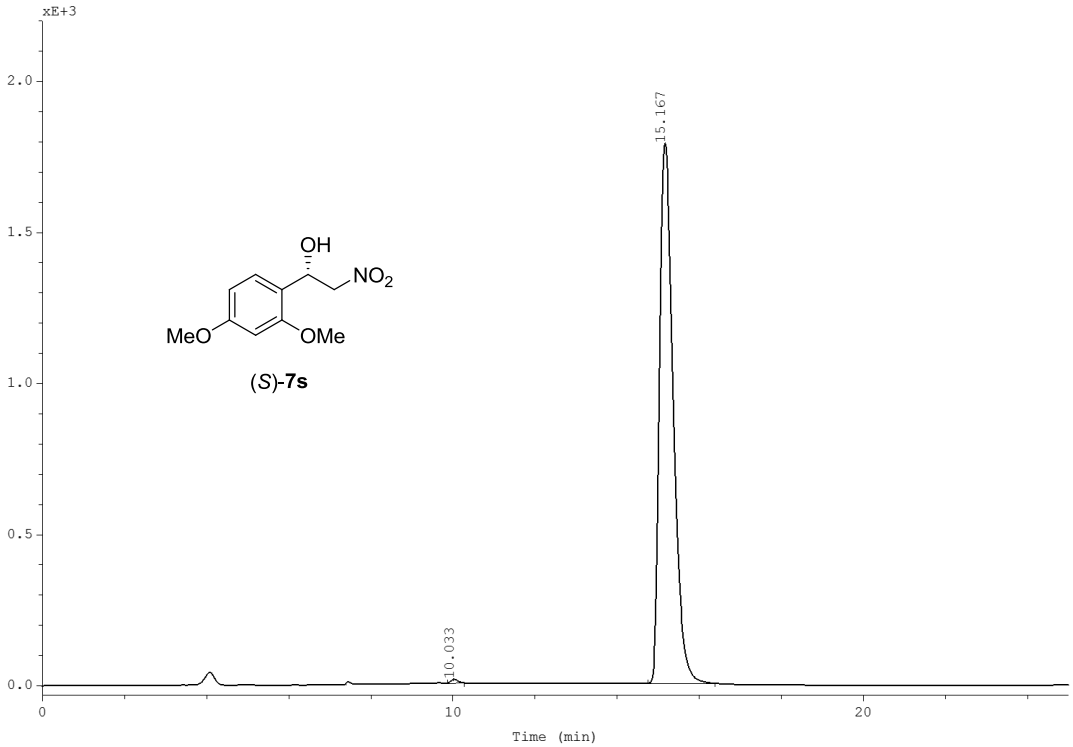
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	15.85	15.50	16.29	6.18	2.31	0.51	0.38
2	19.72	19.10	21.24	1201.58	607.87	99.49	99.62

Chiralcel OD-3, *n*-hexane/*i*PrOH 80:20, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 10.0 min; t_R (*S*-enantiomer) = 15.2 min



rac-**7s**

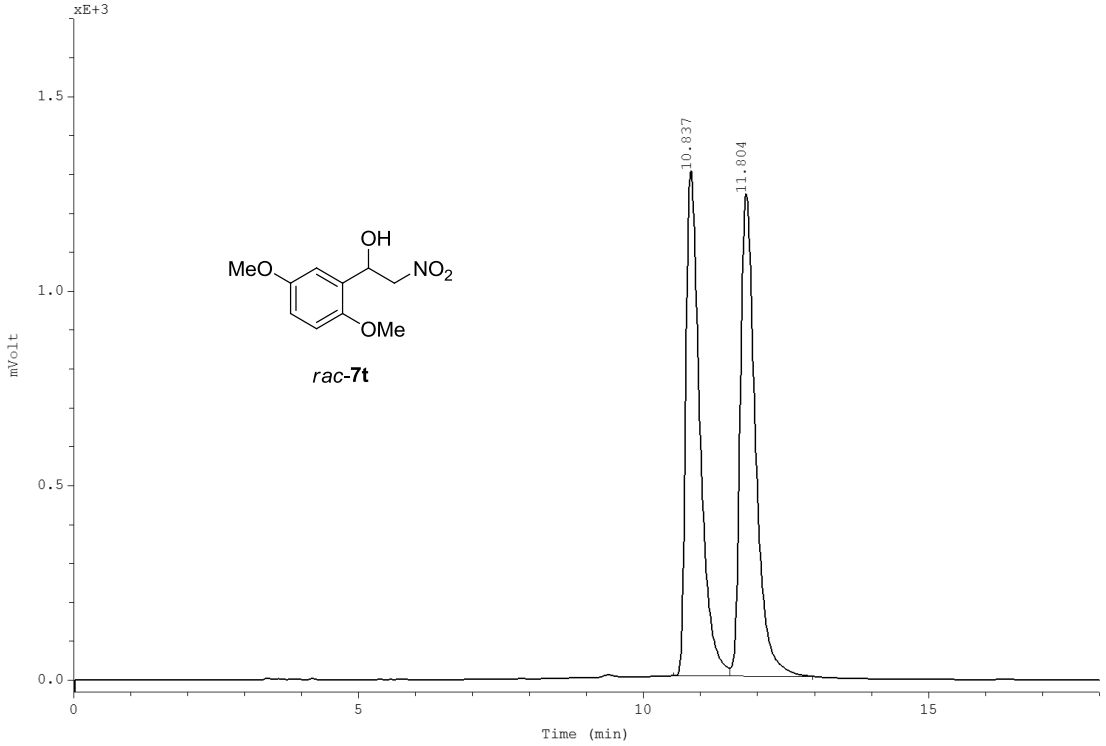
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	10.13	9.85	10.67	1021.08	241.17	57.55	49.55
2	14.53	14.19	15.25	753.08	245.51	42.45	50.45



(*S*)-**7s**

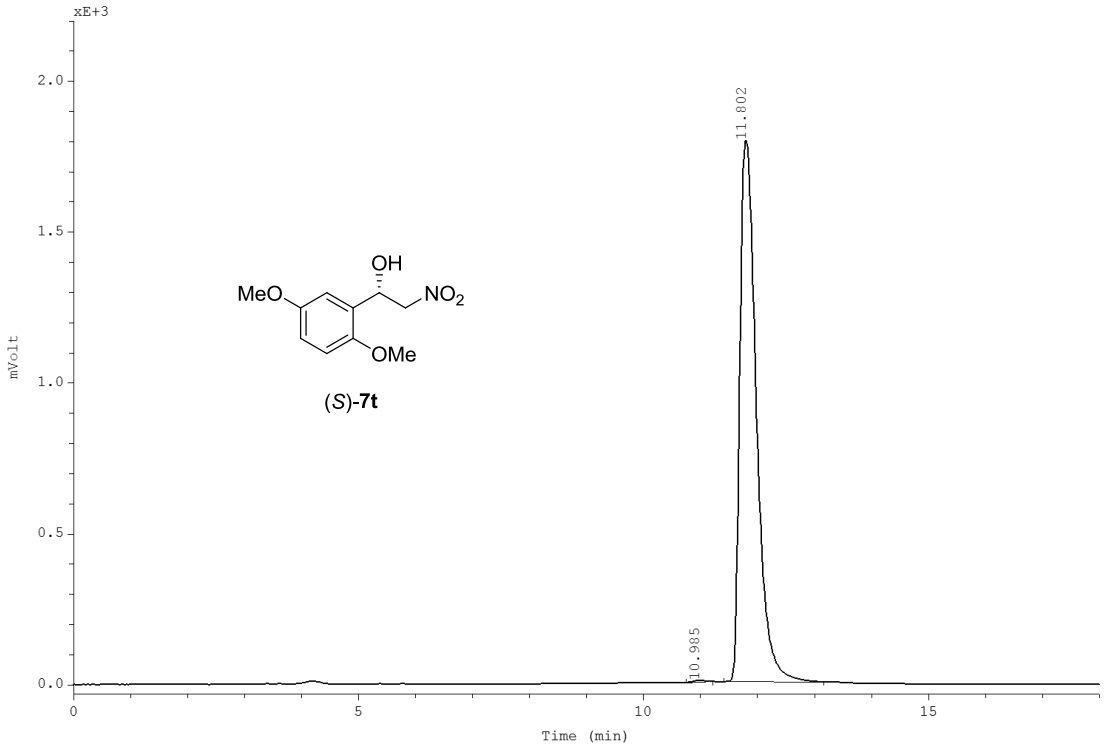
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	10.03	9.87	10.27	12.70	2.55	0.71	0.37
2	15.17	14.75	16.39	1787.89	693.02	99.29	99.63

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 11.0 min; t_R (*S*-enantiomer) = 11.8 min



rac-**7t**

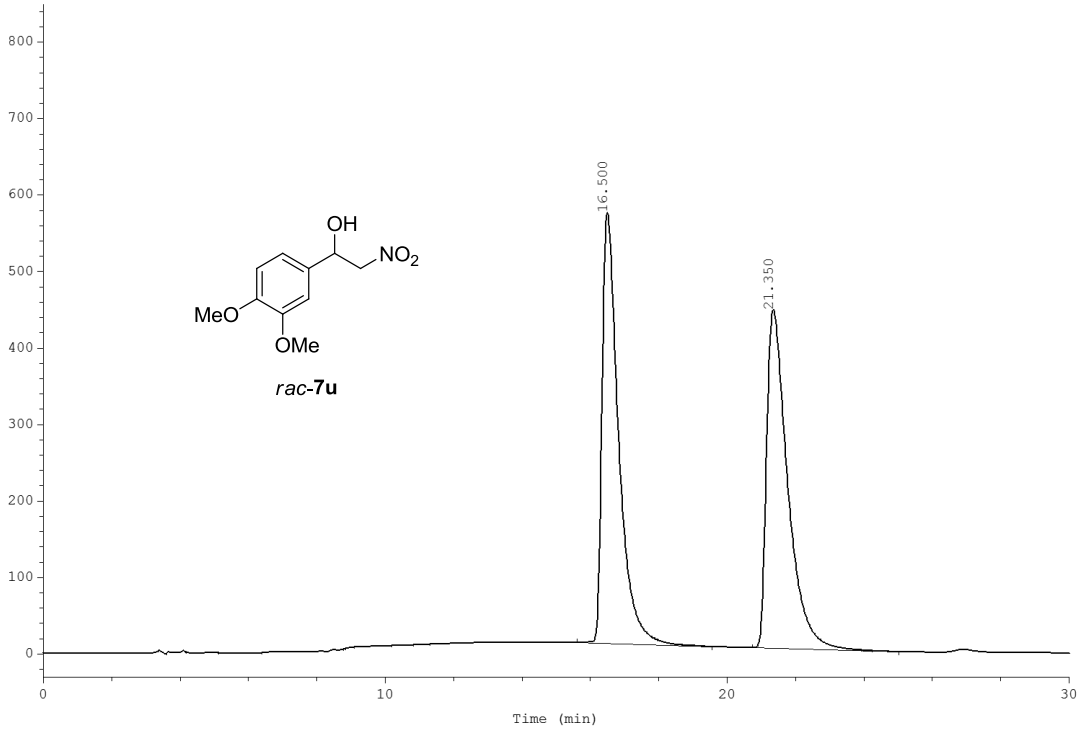
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	10.84	10.52	11.51	1298.70	376.34	51.14	49.35
2	11.80	11.51	12.97	1240.72	386.27	48.86	50.65



(*S*)-**7t**

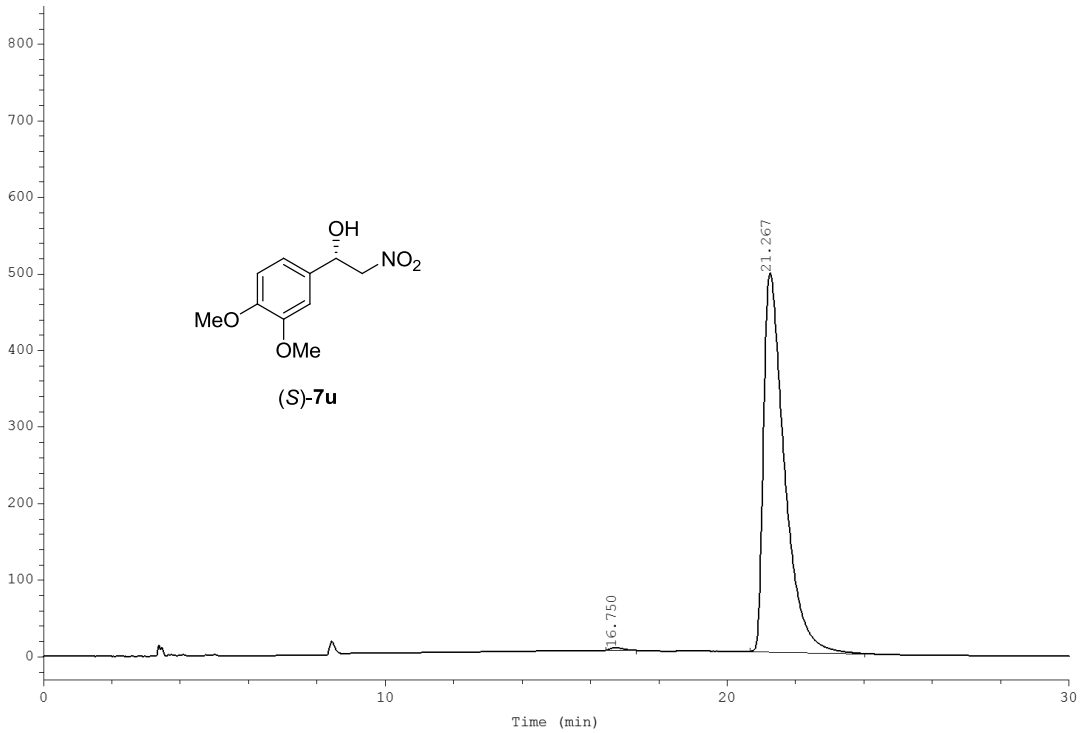
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	10.99	10.75	11.22	4.93	1.15	0.27	0.19
2	11.80	11.41	13.16	1795.31	604.90	99.73	99.81

Chiralcel OD-3, *n*-hexane/*i*PrOH 80:20, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 16.8 min; t_R (*S*-enantiomer) = 21.3 min



rac-**7u**

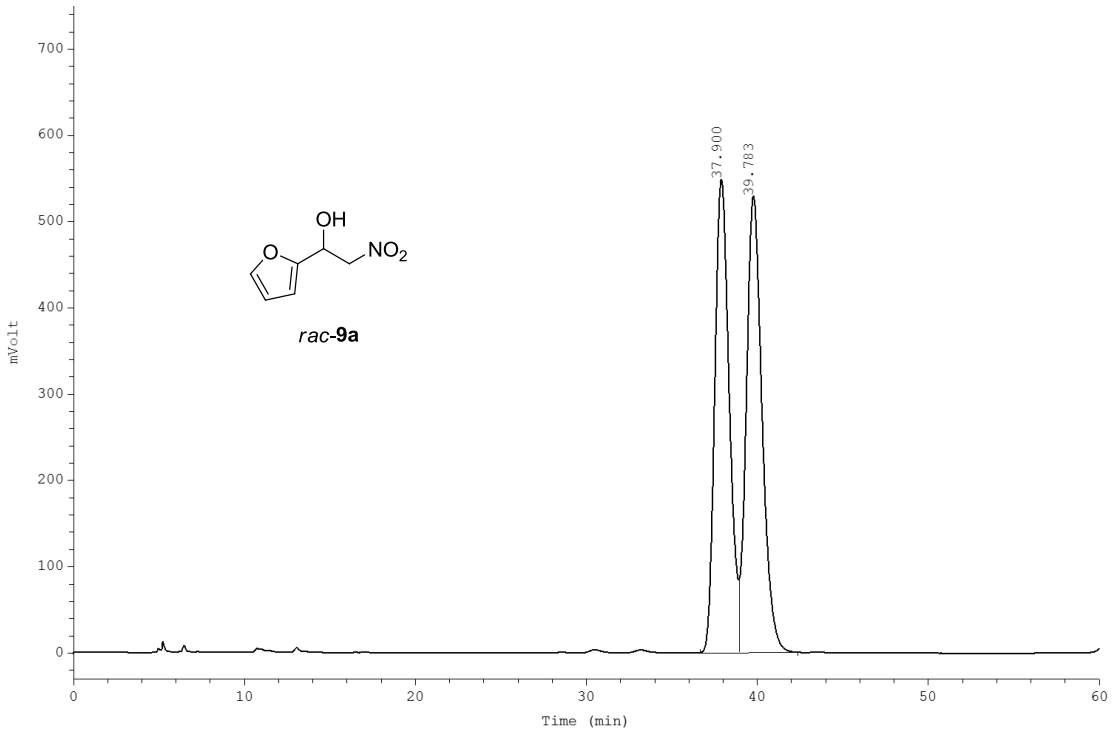
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	16.50	15.62	19.57	562.53	317.77	55.98	50.06
2	21.35	20.75	25.02	442.42	317.03	44.02	49.94



(*S*)-**7u**

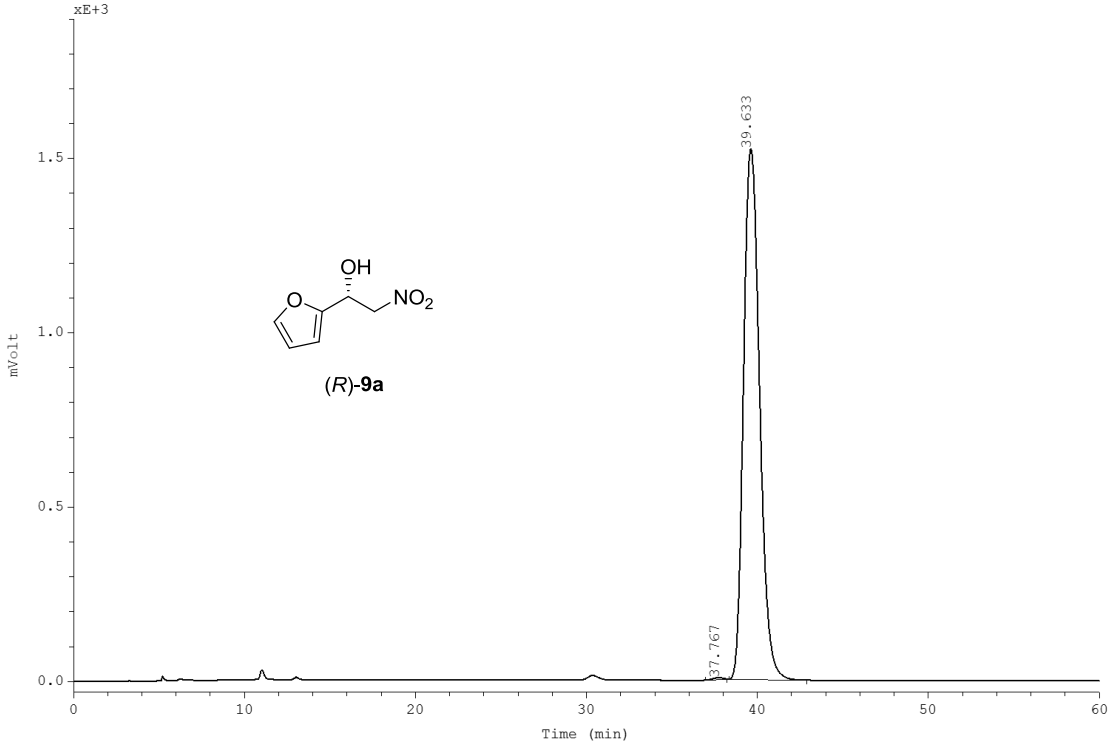
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	16.75	16.44	17.35	3.40	1.51	0.68	0.43
2	21.27	20.67	24.03	494.65	350.63	99.32	99.57

Chiralpak AD-H, *n*-hexane/*i*PrOH 95:5, 0.6 mL/min, 215 nm:
t_R (*R*-enantiomer) = 39.6 min; t_R (*S*-enantiomer) = 37.8 min



rac-**9a**

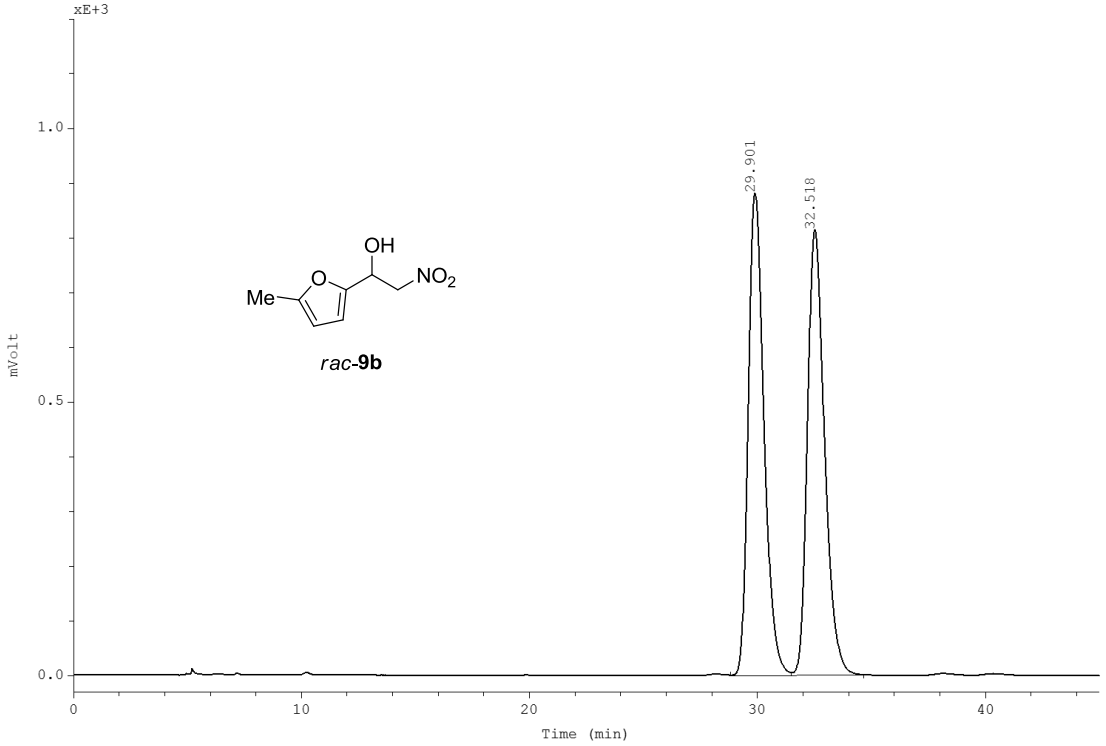
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	37.90	36.68	38.94	549.10	537.37	50.93	48.66
2	39.78	38.94	42.36	529.03	567.03	49.07	51.34



(*R*)-**9a**

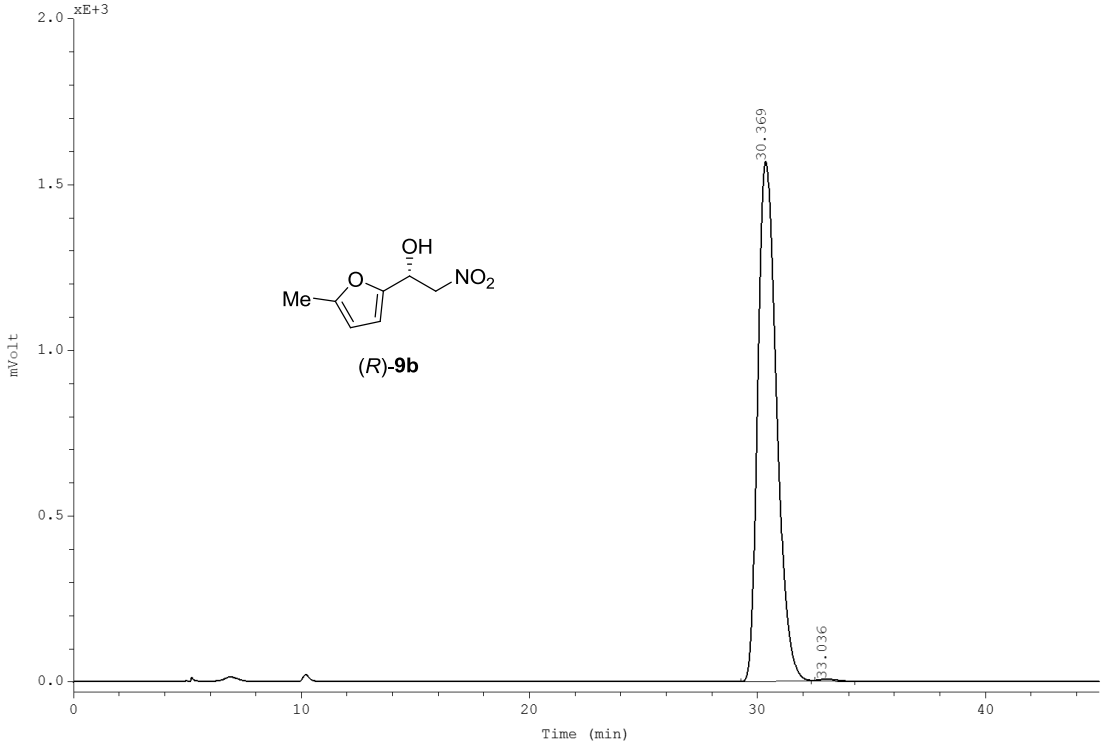
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	37.77	36.95	38.24	5.00	3.40	0.33	0.20
2	39.63	38.35	42.90	1521.85	1658.92	99.67	99.80

Chiralpak AD-H, *n*-hexane/*i*PrOH 95:5, 0.6 mL/min, 215 nm:
t_R (*R*-enantiomer) = 33.0 min; t_R (*S*-enantiomer) = 30.4 min



rac-**9b**

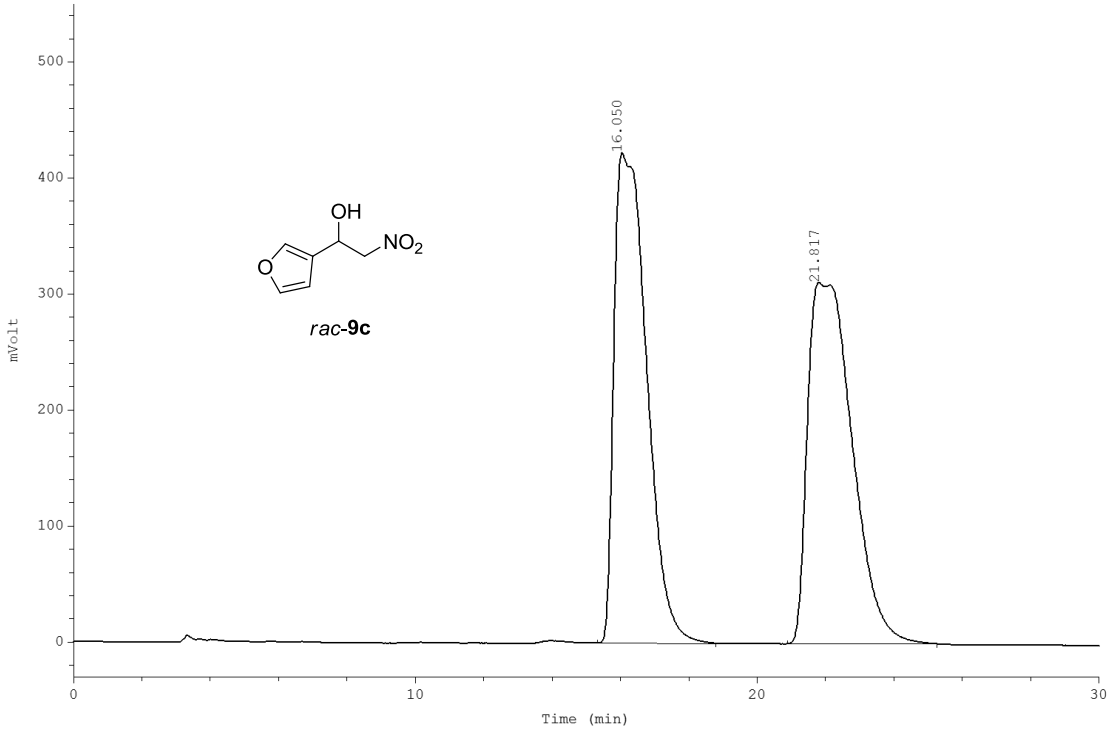
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	29.90	28.81	31.49	881.34	704.76	51.98	49.91
2	32.52	31.49	34.67	814.19	707.39	48.02	50.09



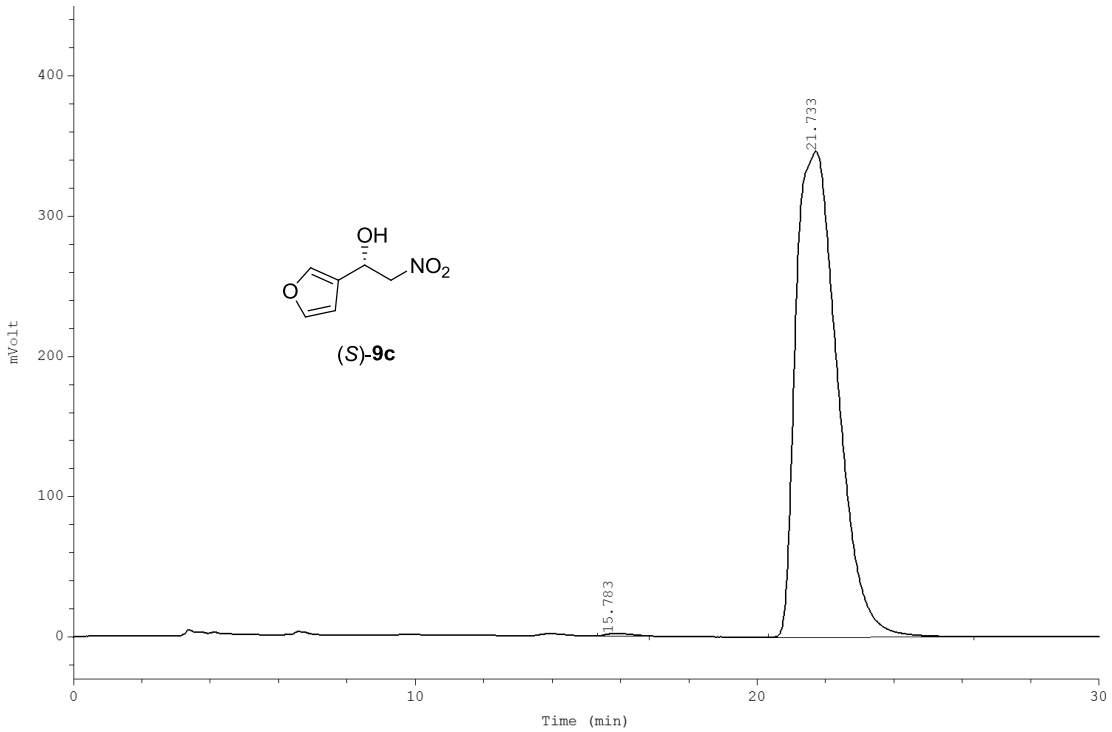
(*R*)-**9b**

	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	30.37	29.26	32.36	1567.98	1501.65	99.68	99.74
2	33.04	32.50	34.28	4.96	3.95	0.32	0.26

Chiralpak AD-H, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 15.8 min; t_R (*S*-enantiomer) = 21.7 min

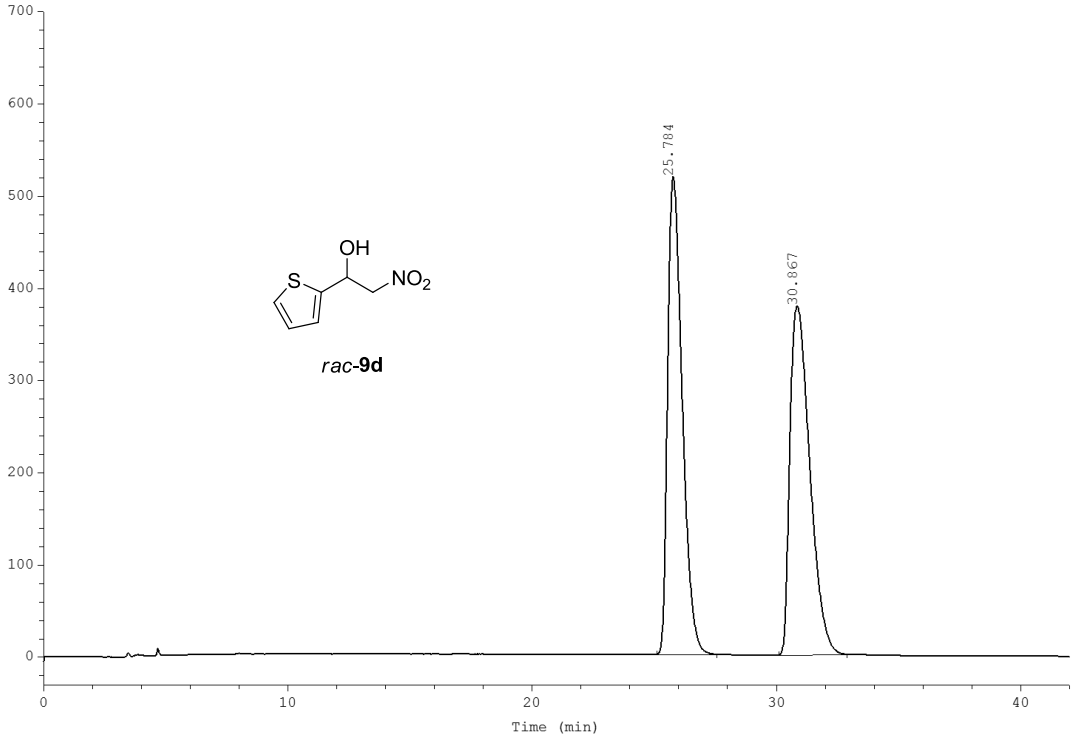


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	16.05	15.32	18.78	422.76	467.62	57.58	49.86
2	21.82	20.89	25.26	311.45	470.22	42.42	50.14

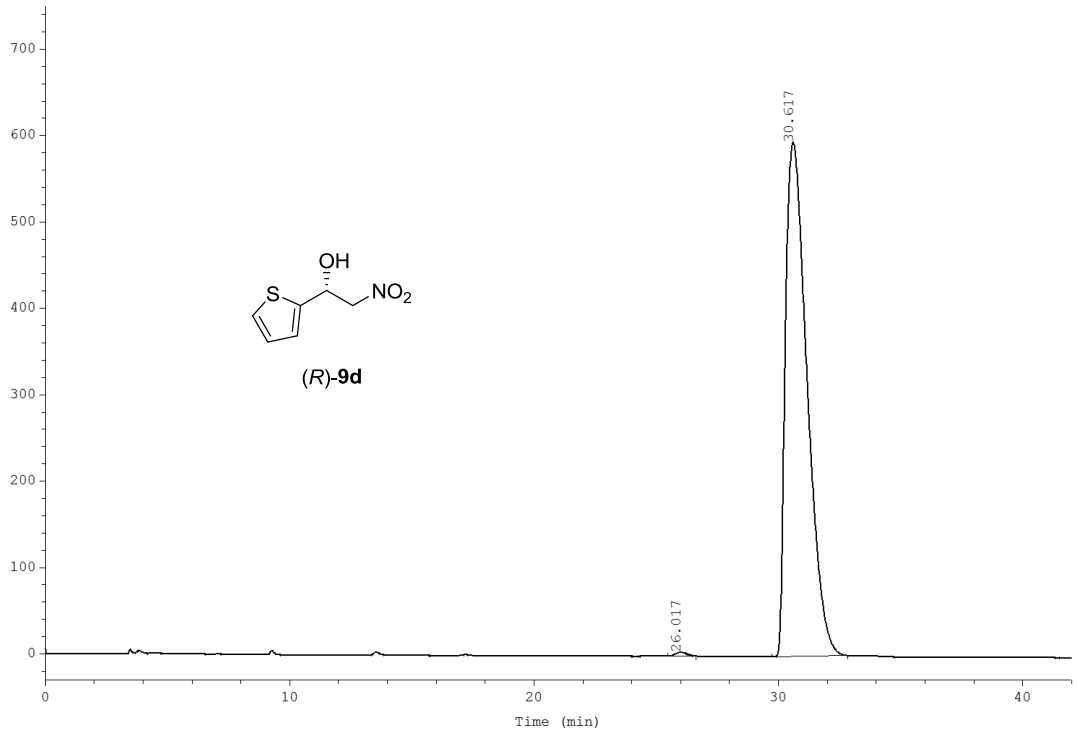


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	15.78	15.33	16.85	1.63	1.49	0.47	0.30
2	21.73	20.32	26.35	346.55	486.01	99.53	99.70

Chiralcel OJ-H, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 30.6 min; t_R (*S*-enantiomer) = 26.0 min

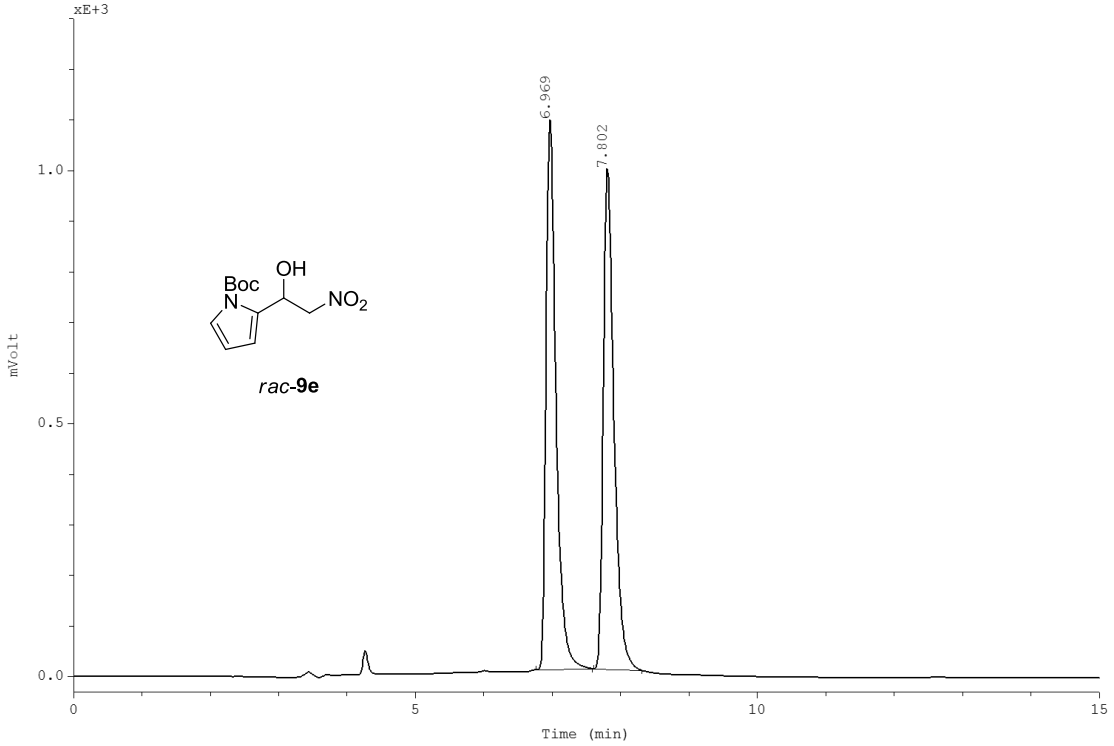


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	25.78	25.11	27.55	518.41	358.24	57.78	50.07
2	30.87	30.10	32.90	378.74	357.22	42.22	49.93



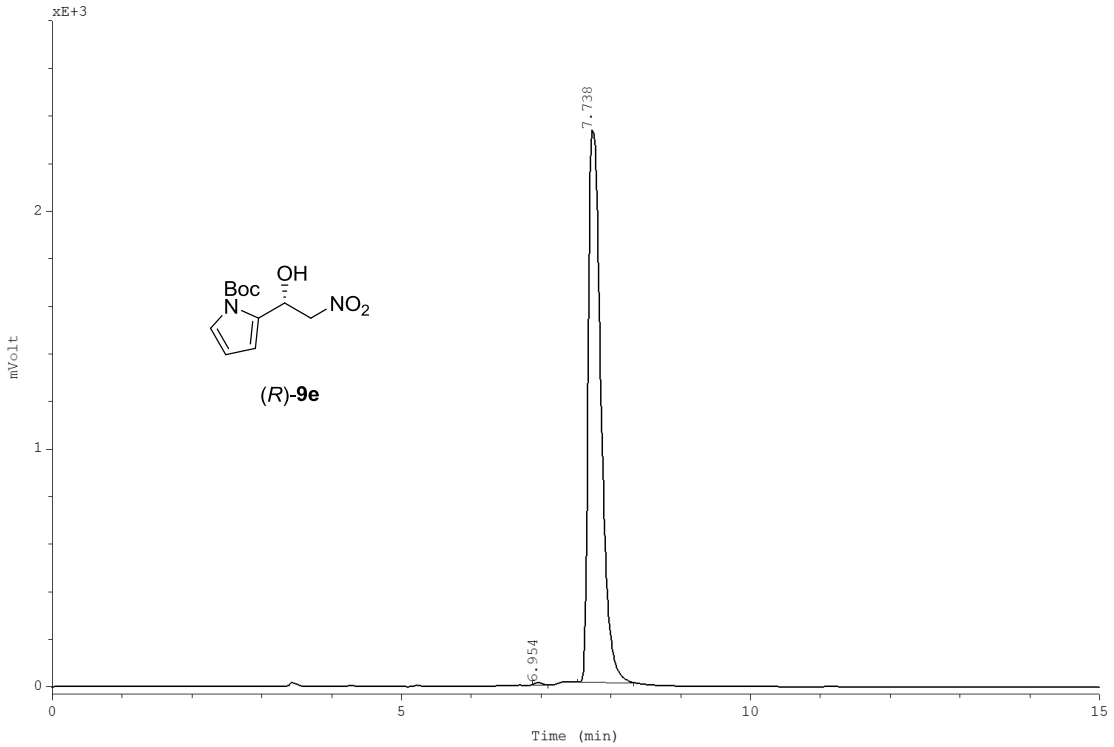
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	26.02	25.47	26.63	4.47	2.43	0.75	0.40
2	30.62	29.74	32.85	595.05	609.21	99.25	99.60

Chiralcel OD-3, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 7.0 min; t_R (*S*-enantiomer) = 7.7 min



rac-**9e**

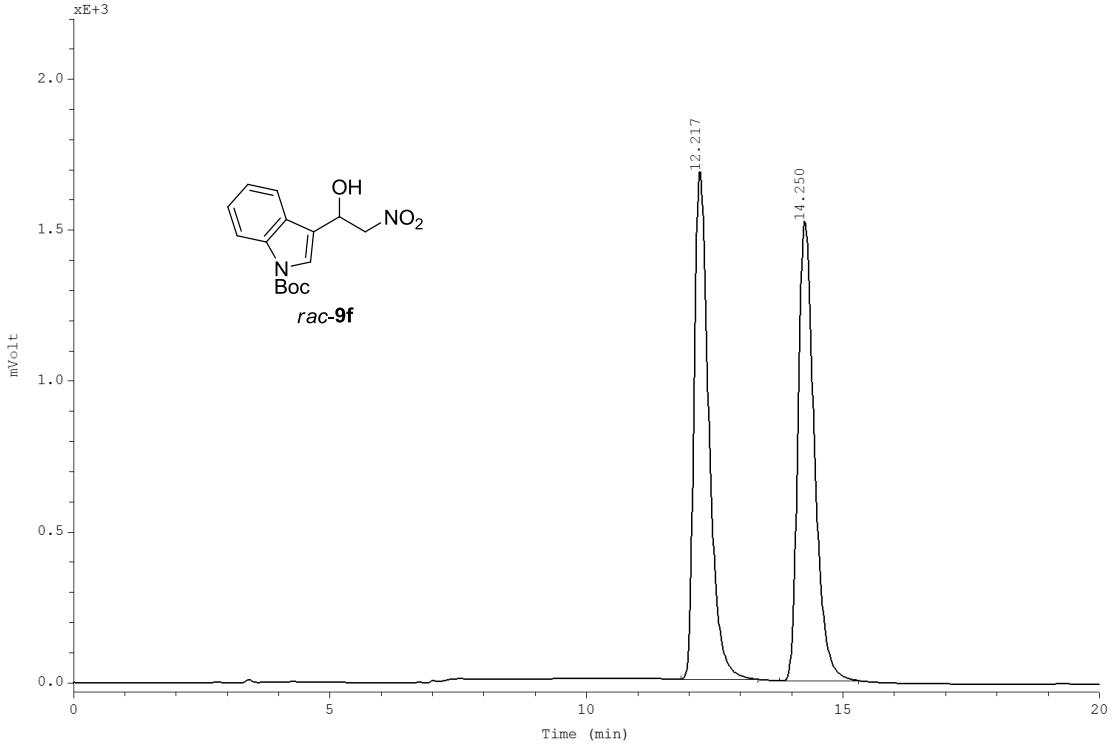
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	6.97	6.77	7.58	1086.31	183.21	52.32	50.30
2	7.80	7.60	8.31	990.06	181.02	47.68	49.70



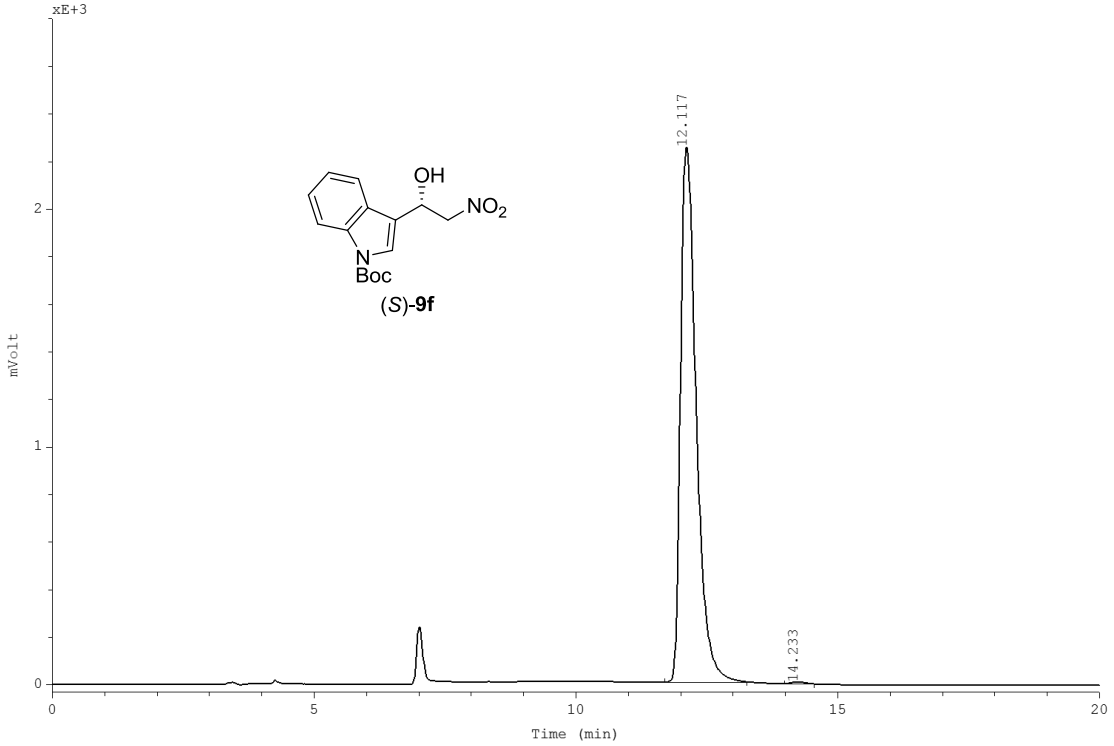
(*R*)-**9e**

	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	6.95	6.87	7.10	9.41	1.17	0.40	0.24
2	7.74	7.52	8.33	2321.72	495.29	99.60	99.76

Chiralcel OD-3, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 14.2 min; t_R (*S*-enantiomer) = 12.1 min

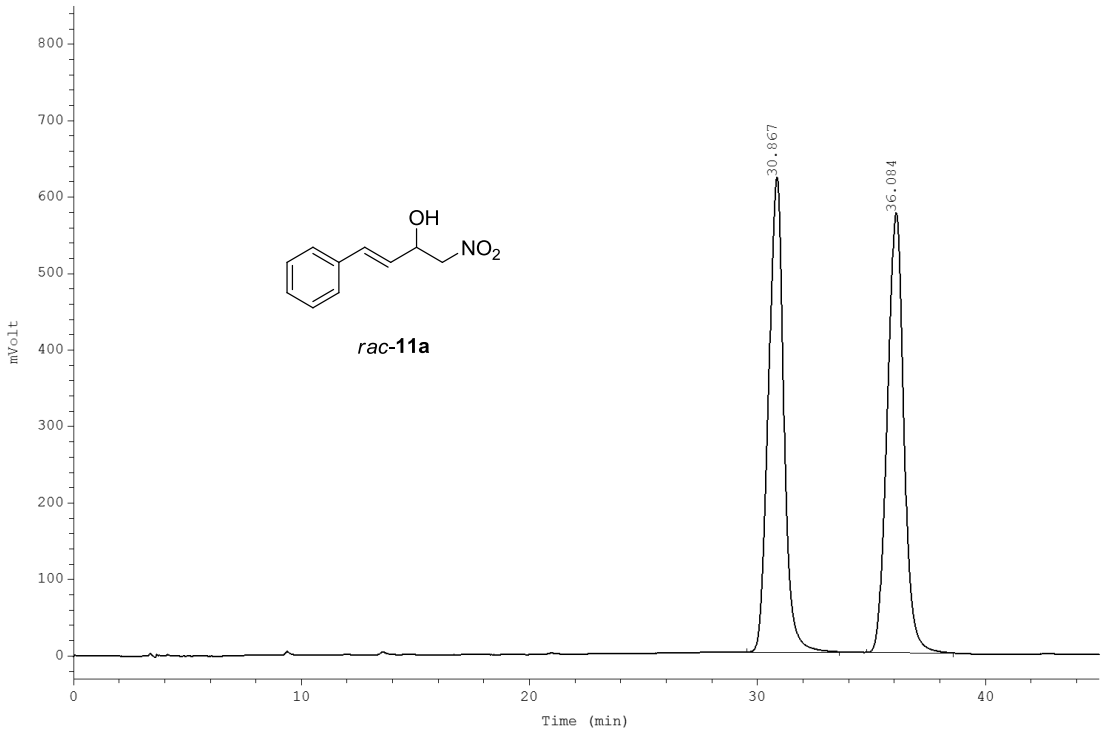


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.22	11.84	13.34	1682.54	565.18	52.47	49.94
2	14.25	13.77	15.30	1524.37	566.65	47.53	50.06

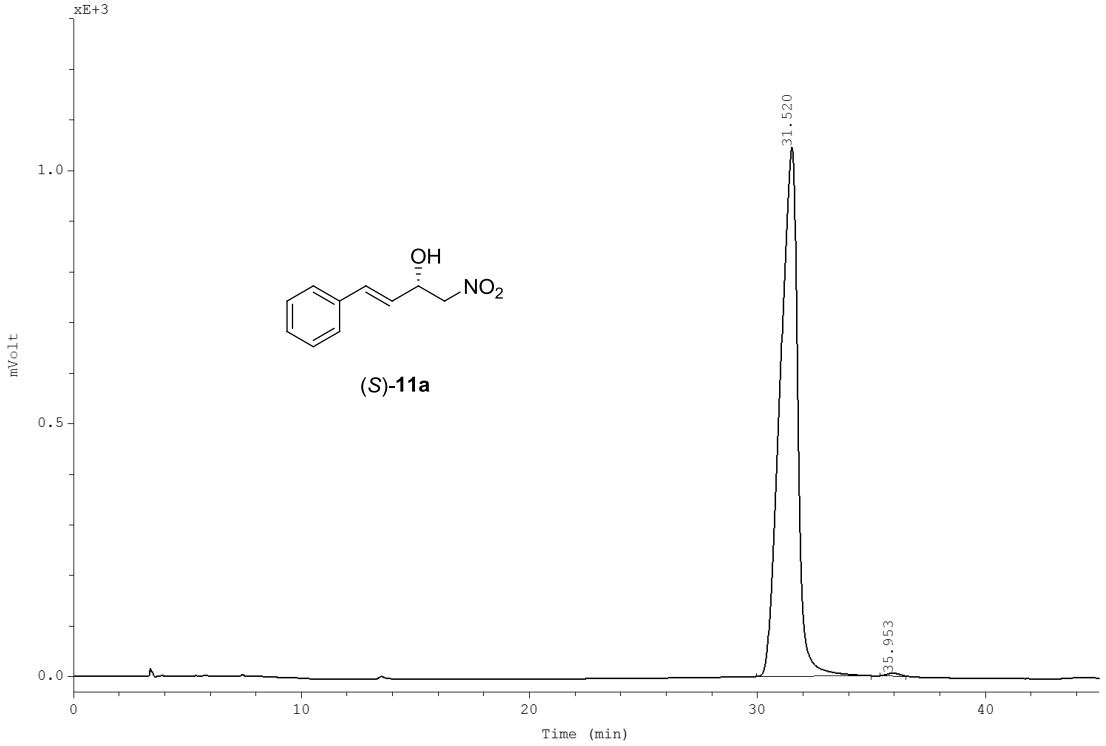


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.12	11.70	13.27	2250.06	783.35	99.63	99.68
2	14.23	13.98	14.55	8.47	2.51	0.37	0.32

Chiralcel OD-3, *n*-hexane/*i*PrOH 85:15, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 36.0 min; t_R (*S*-enantiomer) = 31.5 min

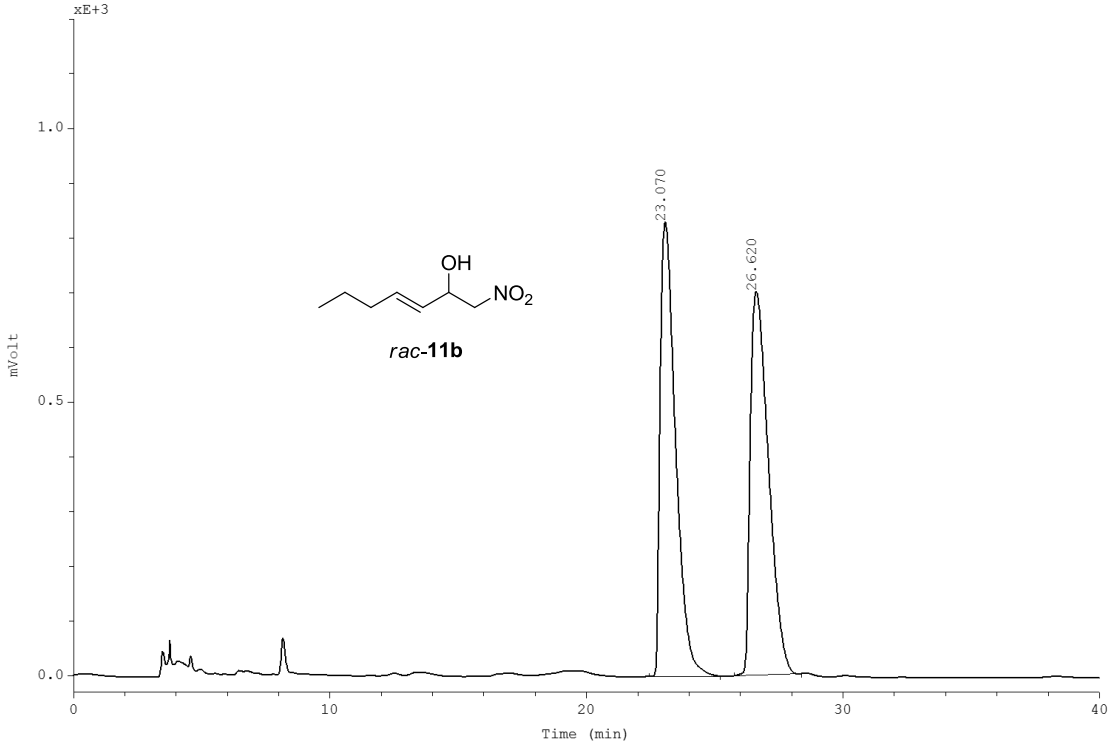


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	30.87	29.52	33.58	621.43	485.83	51.91	49.96
2	36.08	34.78	38.58	575.59	486.64	48.09	50.04

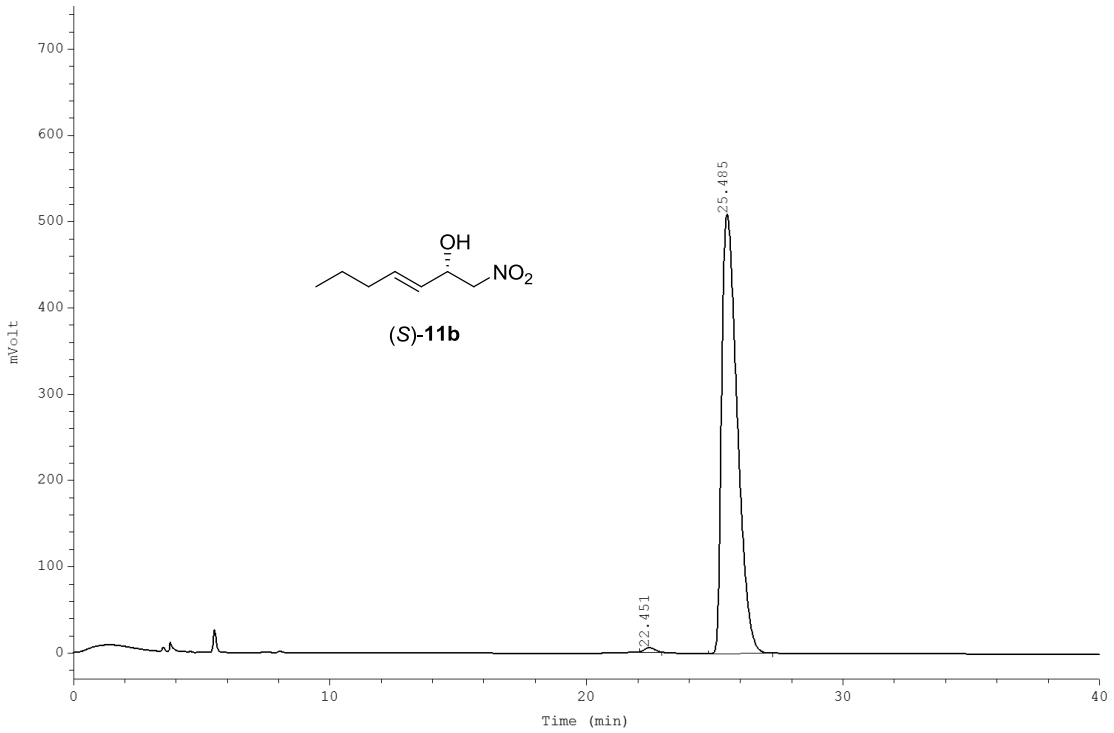


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	31.52	29.94	34.99	1045.52	934.68	99.48	99.65
2	35.95	35.38	36.52	5.44	3.33	0.52	0.35

Chiralcel OJ-H, *n*-hexane/*i*PrOH 97:3, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 22.5 min; t_R (*S*-enantiomer) = 25.5 min

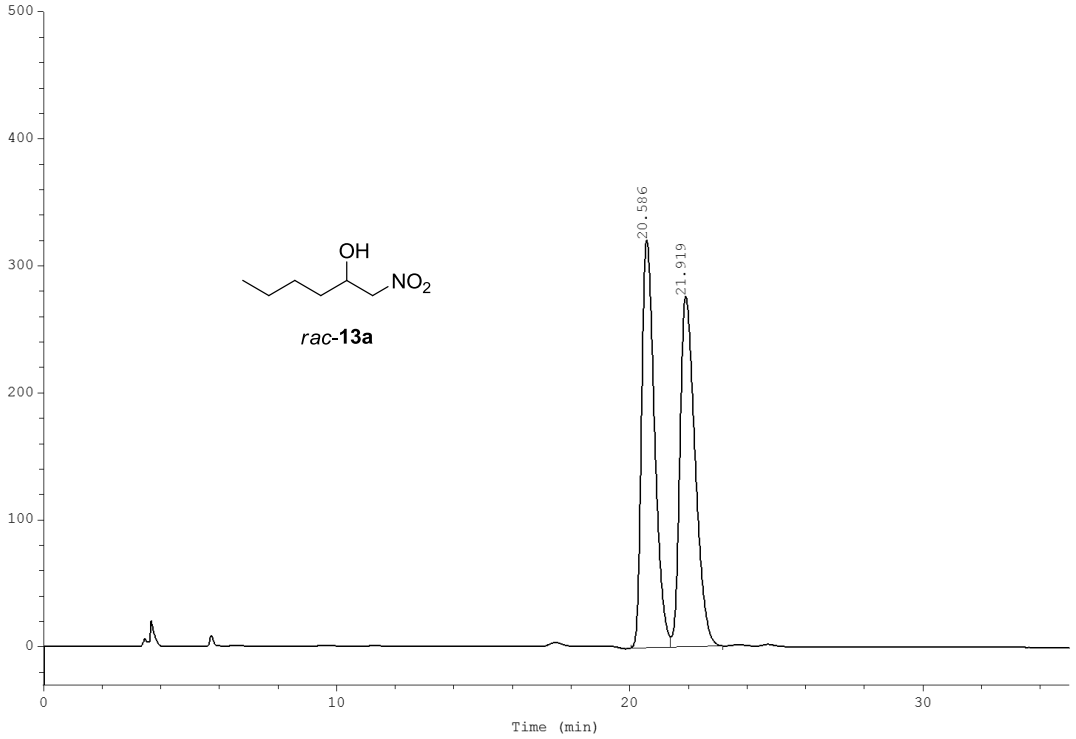


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	23.07	22.46	25.22	830.90	580.25	54.23	50.12
2	26.62	25.76	28.38	701.41	577.57	45.77	49.88

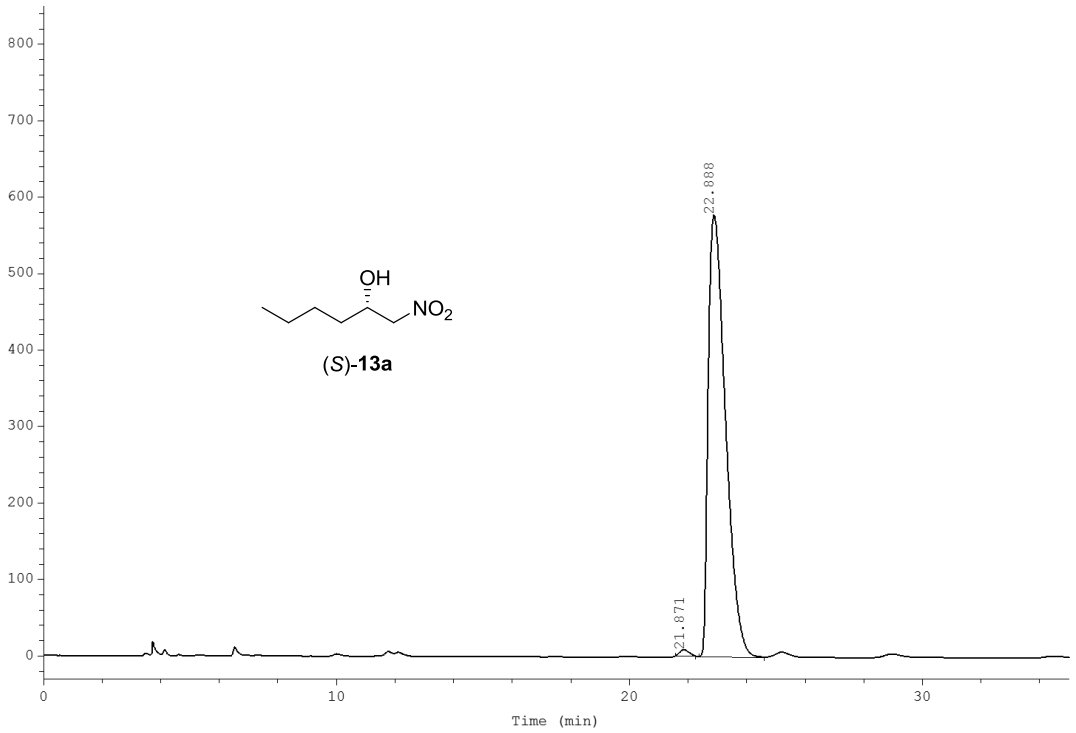


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	22.45	22.07	22.93	4.99	2.26	0.97	0.63
2	25.49	24.74	27.26	509.37	358.45	99.03	99.37

Chiralcel OJ-H, *n*-hexane/*i*PrOH 97:3, 0.8 mL/min, 215 nm:
t_R (*R*-enantiomer) = 21.9 min; t_R (*S*-enantiomer) = 22.9 min

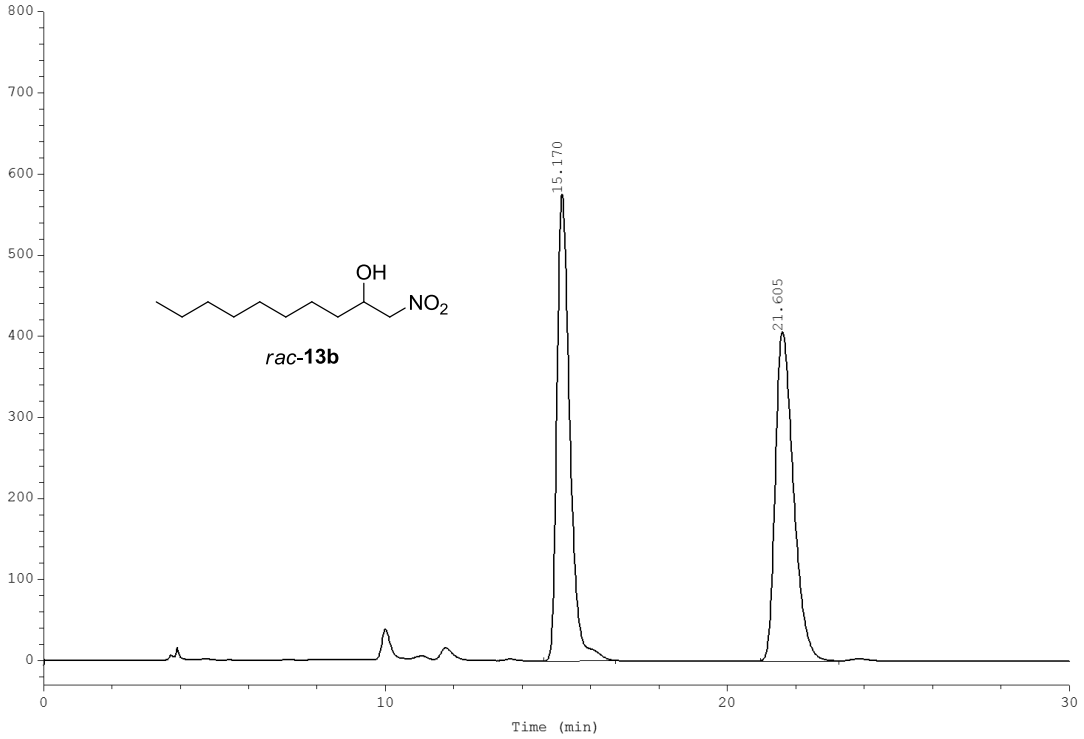


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	20.59	20.03	21.39	321.23	165.68	53.77	49.84
2	21.92	21.39	23.17	276.19	166.73	46.23	50.16

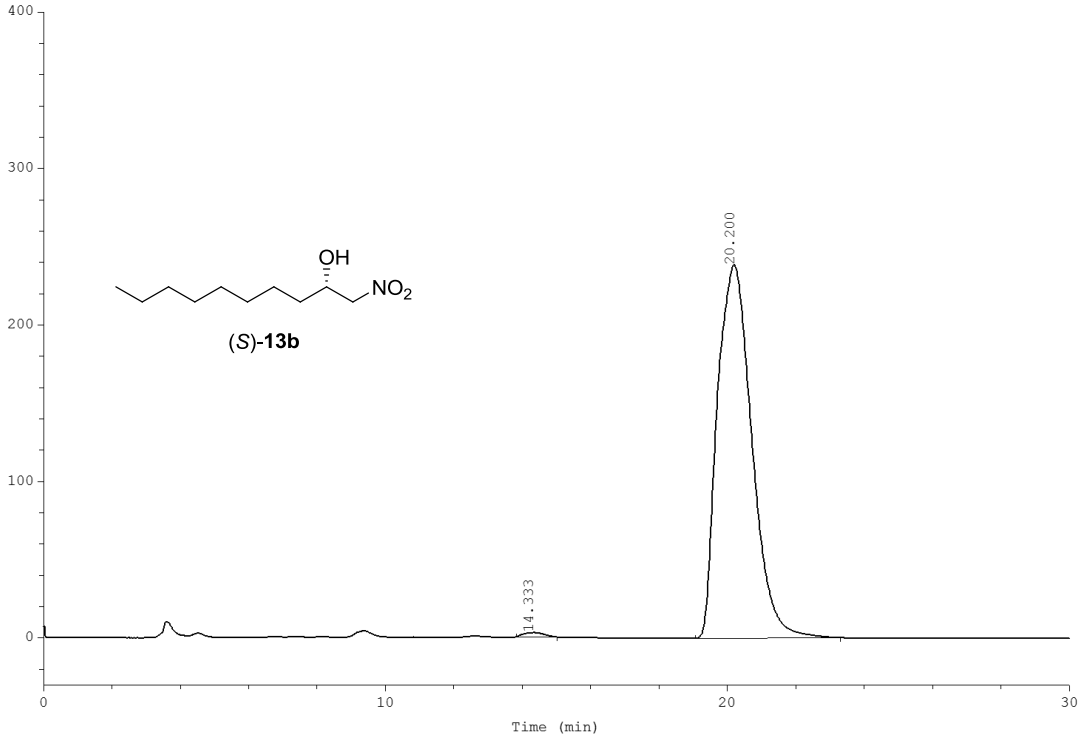


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	21.87	21.57	22.26	8.10	2.99	1.38	0.75
2	22.89	22.38	24.59	577.72	395.15	98.62	99.25

Chiralpak AD-H, *n*-hexane/*i*PrOH 95:5, 0.8 mL/min, 215 nm:
t_R (*R*-enantiomer) = 14.3 min; t_R (*S*-enantiomer) = 20.2 min

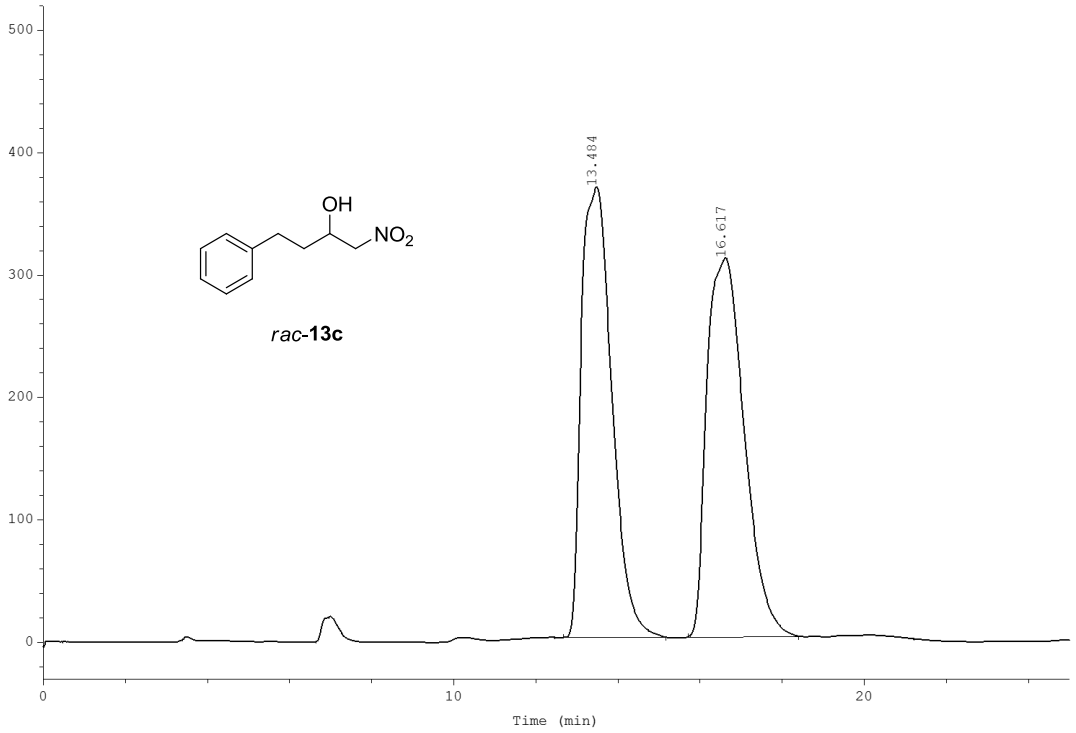


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	15.17	14.63	16.73	575.42	253.40	58.61	50.30
2	21.61	20.95	23.25	406.28	250.38	41.39	49.70

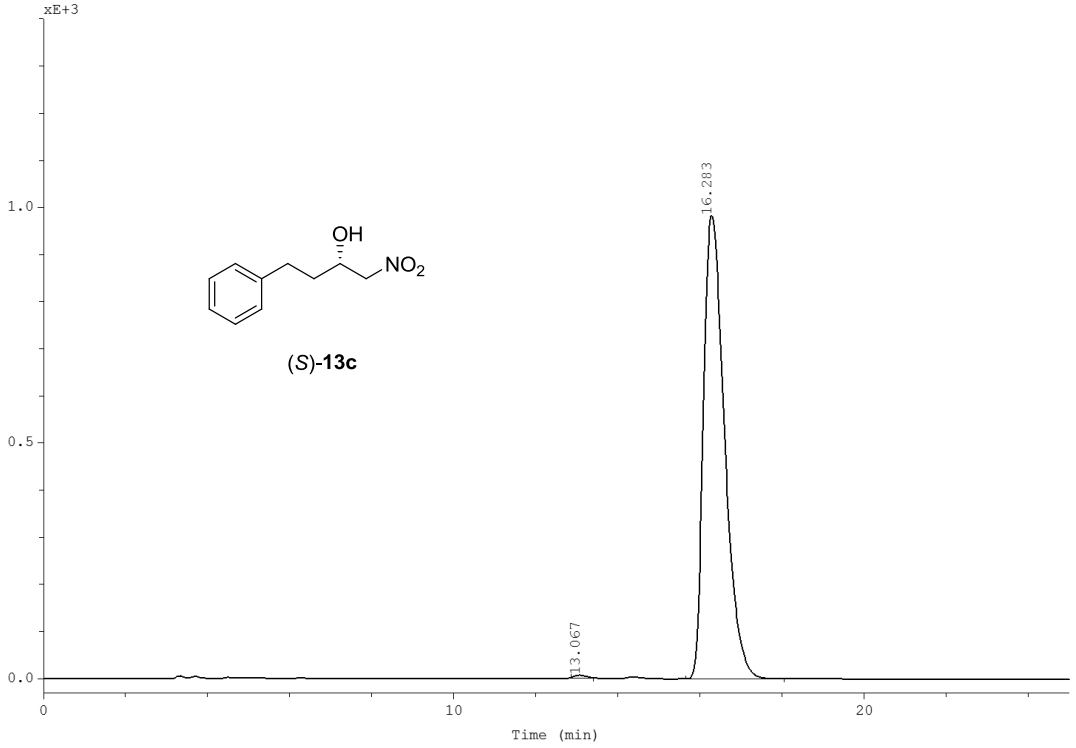


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	14.33	13.82	15.03	2.80	1.96	1.16	0.70
2	20.20	19.06	23.30	238.45	278.10	98.84	99.30

Chiralpak AD-H, *n*-hexane/*i*PrOH 90:10, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 13.1 min; t_R (*S*-enantiomer) = 16.3 min

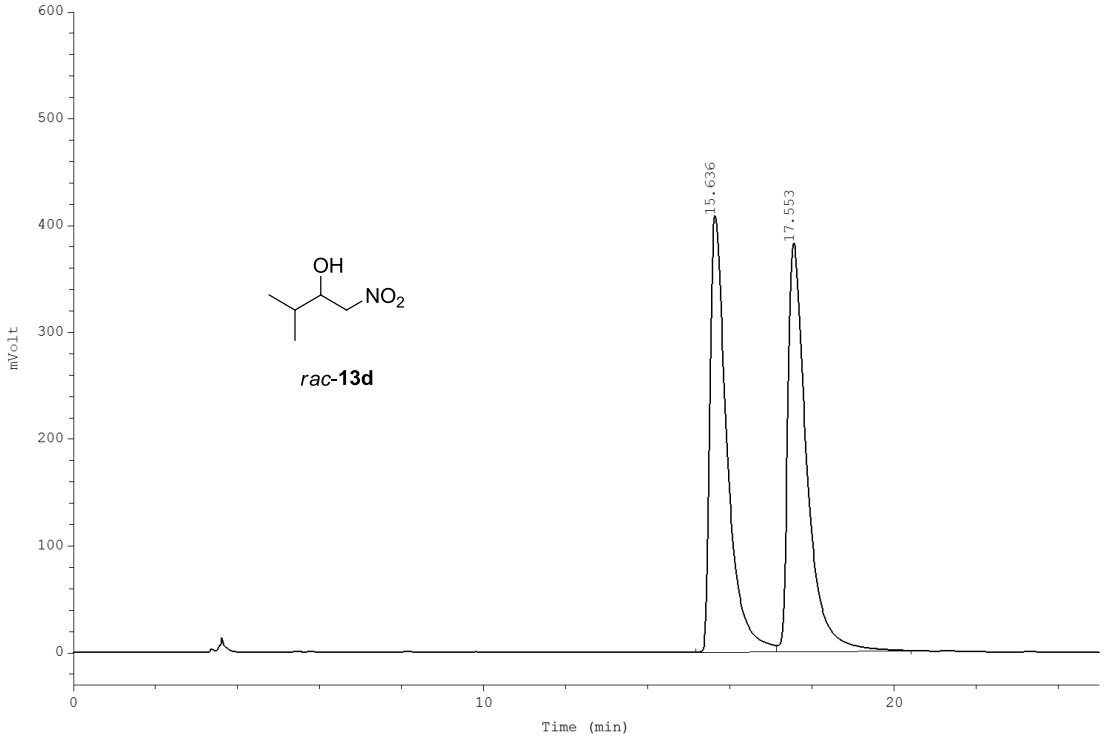


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	13.48	12.67	15.16	368.44	316.71	54.32	49.22
2	16.62	15.70	18.40	309.79	326.70	45.68	50.78

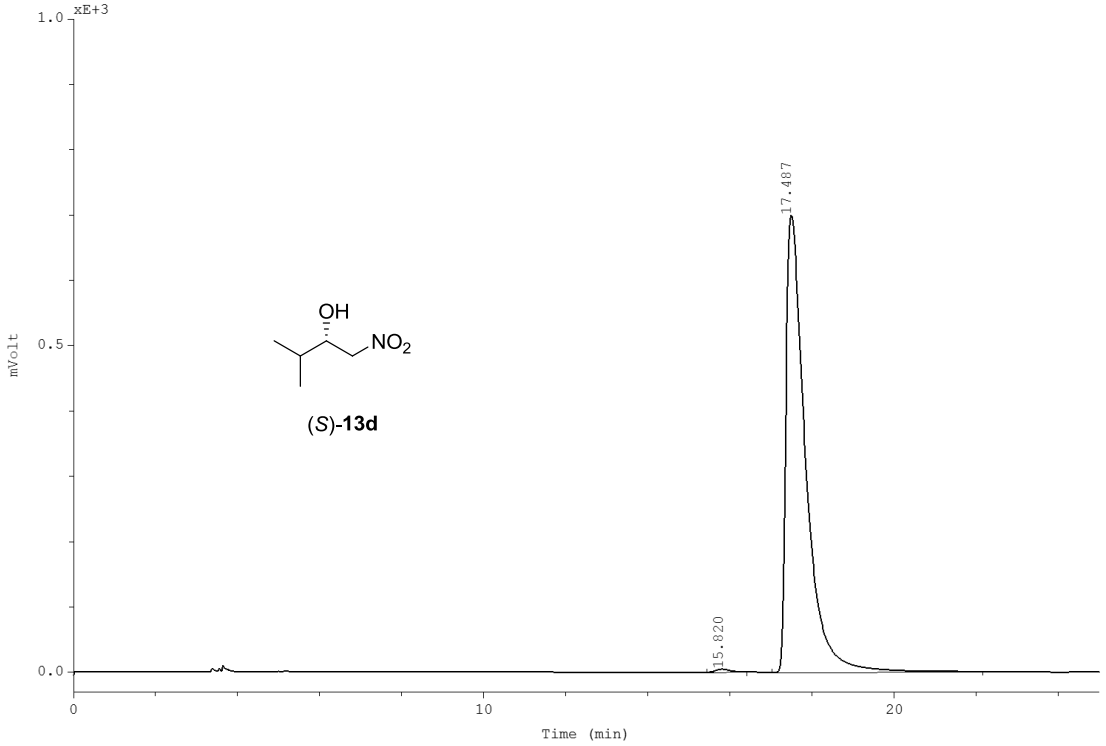


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	13.07	12.85	13.40	5.26	1.60	0.53	0.27
2	16.28	15.66	18.04	983.87	584.21	99.47	99.73

Chiralcel OD-3, *n*-hexane/*i*PrOH 97:3, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 15.8 min; t_R (*S*-enantiomer) = 17.5 min

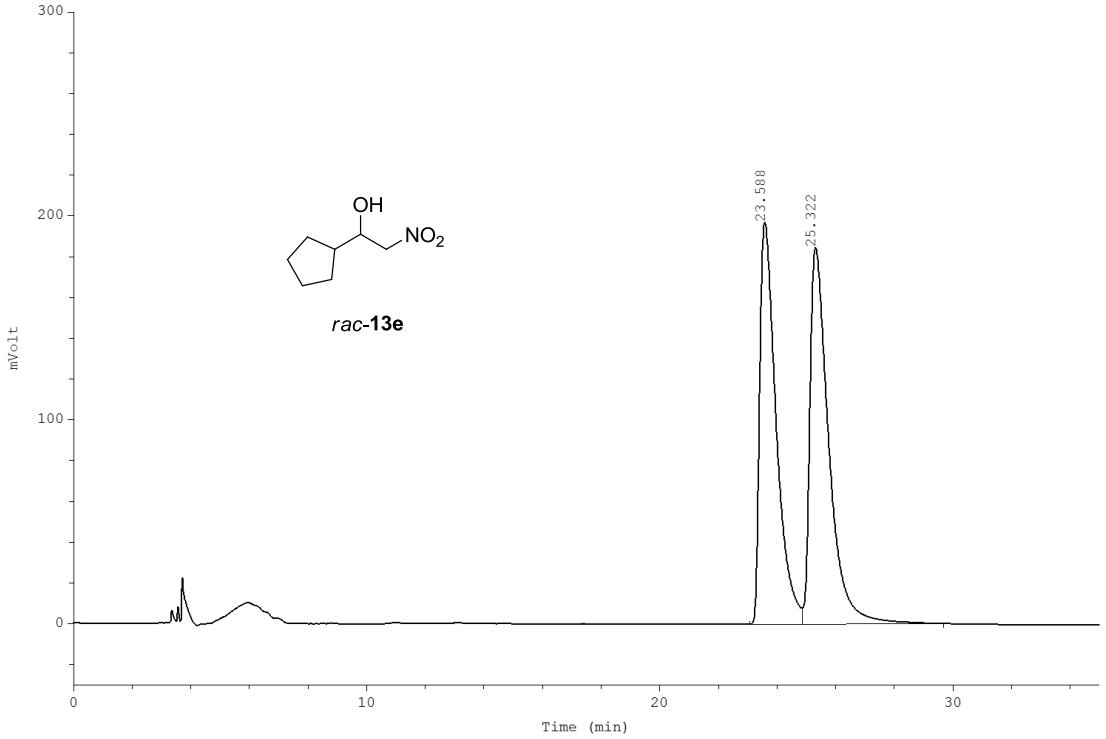


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	15.64	15.16	17.13	408.93	198.55	51.68	49.29
2	17.55	17.13	20.40	382.40	204.27	48.32	50.71



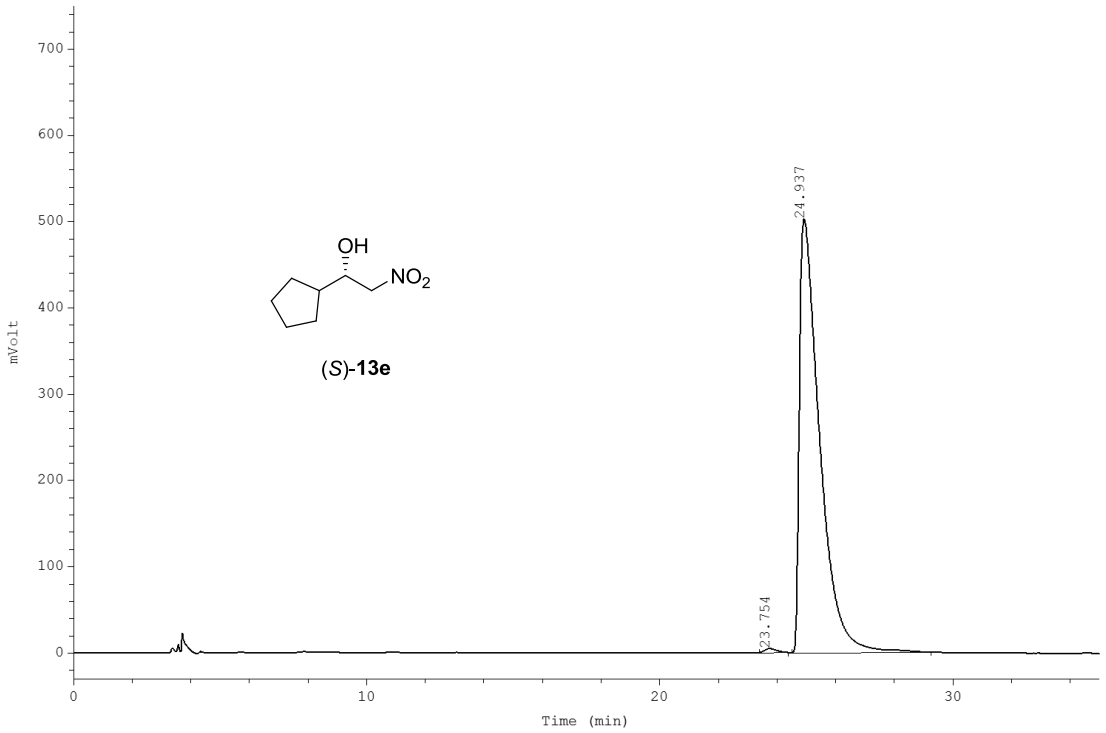
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	15.82	15.42	16.41	4.62	1.80	0.66	0.46
2	17.49	17.03	22.15	700.05	387.99	99.34	99.54

Chiralcel OD-3, *n*-hexane/*i*PrOH 98:2, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 23.8 min; t_R (*S*-enantiomer) = 24.9 min



rac-**13e**

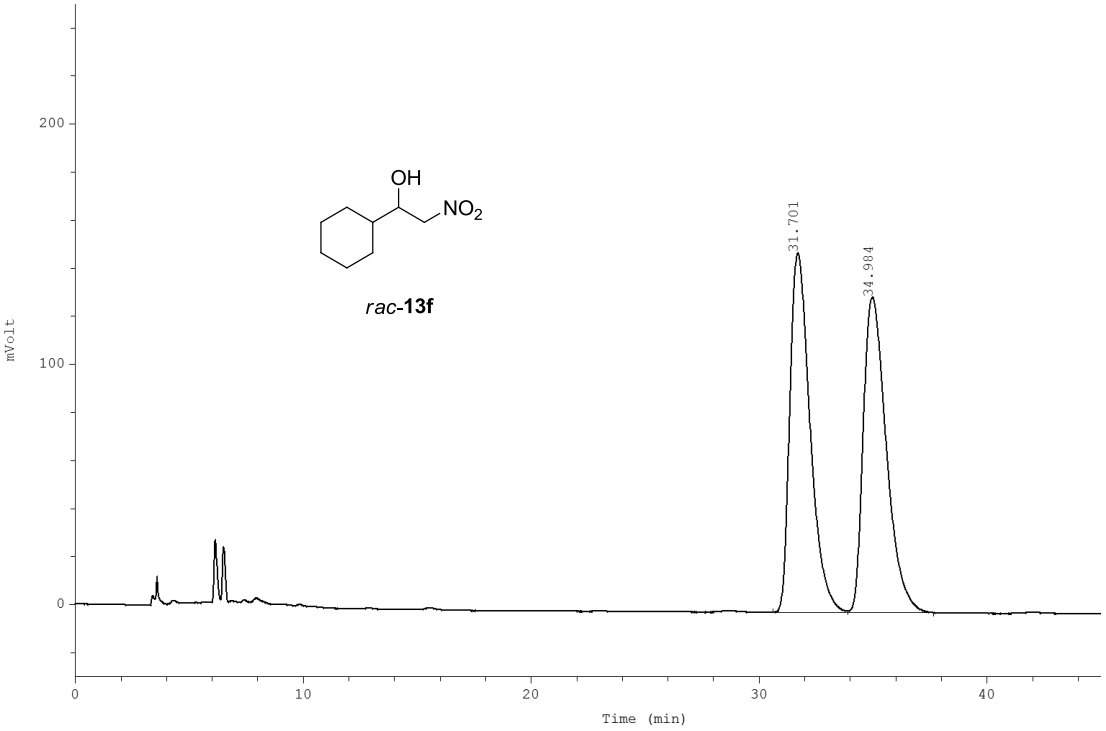
	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	23.59	23.07	24.85	197.21	128.56	51.64	48.22
2	25.32	24.85	29.67	184.70	138.07	48.36	51.78



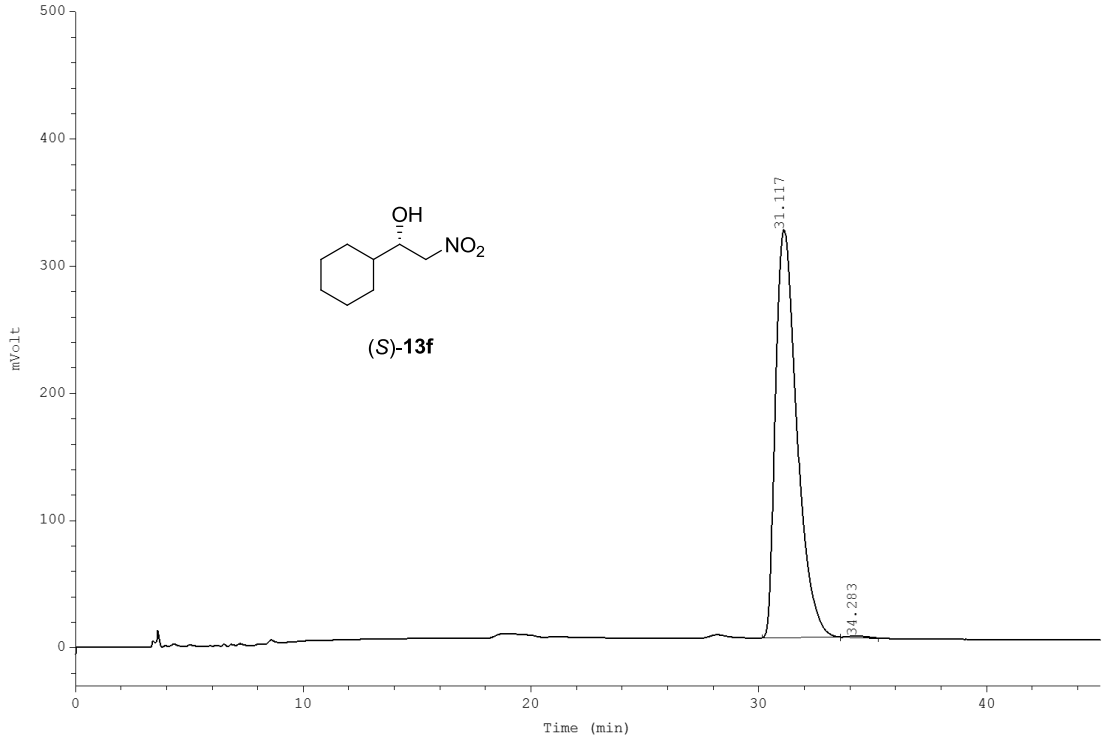
(*S*)-**13e**

	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	23.75	23.39	24.38	4.75	2.26	0.94	0.56
2	24.94	24.49	29.25	502.62	402.83	99.06	99.44

Chiralpak AD-H, *n*-hexane/EtOH 95:5, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 34.3 min; t_R (*S*-enantiomer) = 31.1 min

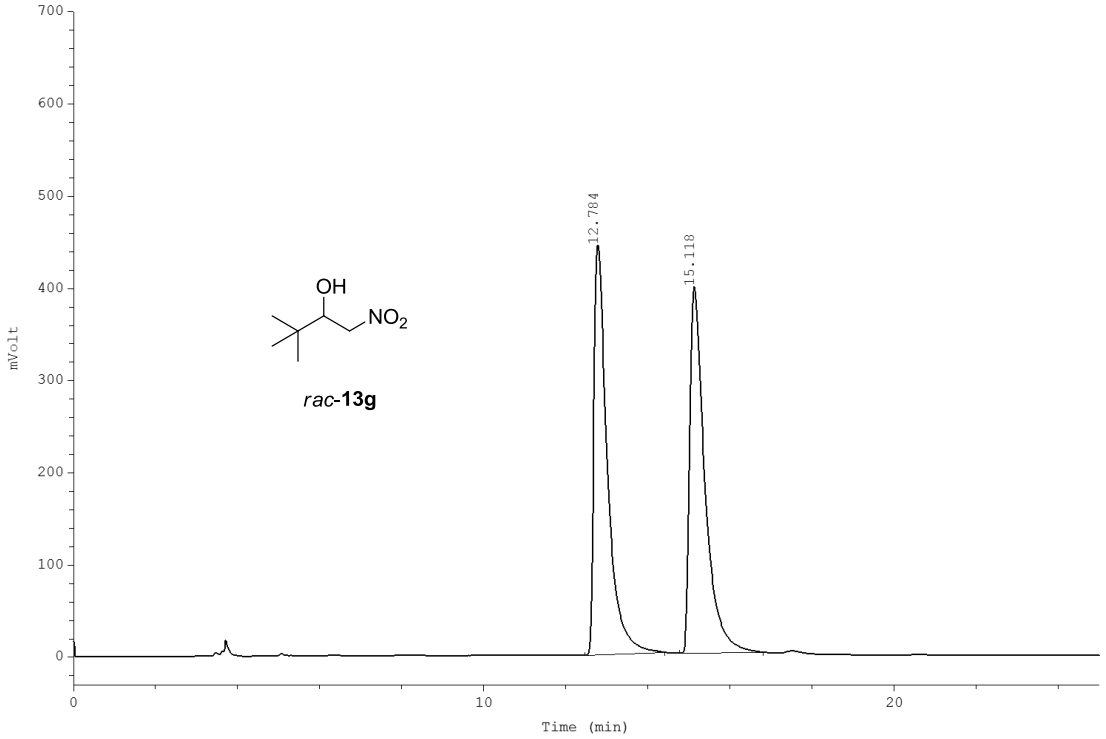


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	31.70	30.62	33.89	149.54	154.21	53.28	50.01
2	34.98	33.89	37.65	131.14	154.14	46.72	49.99

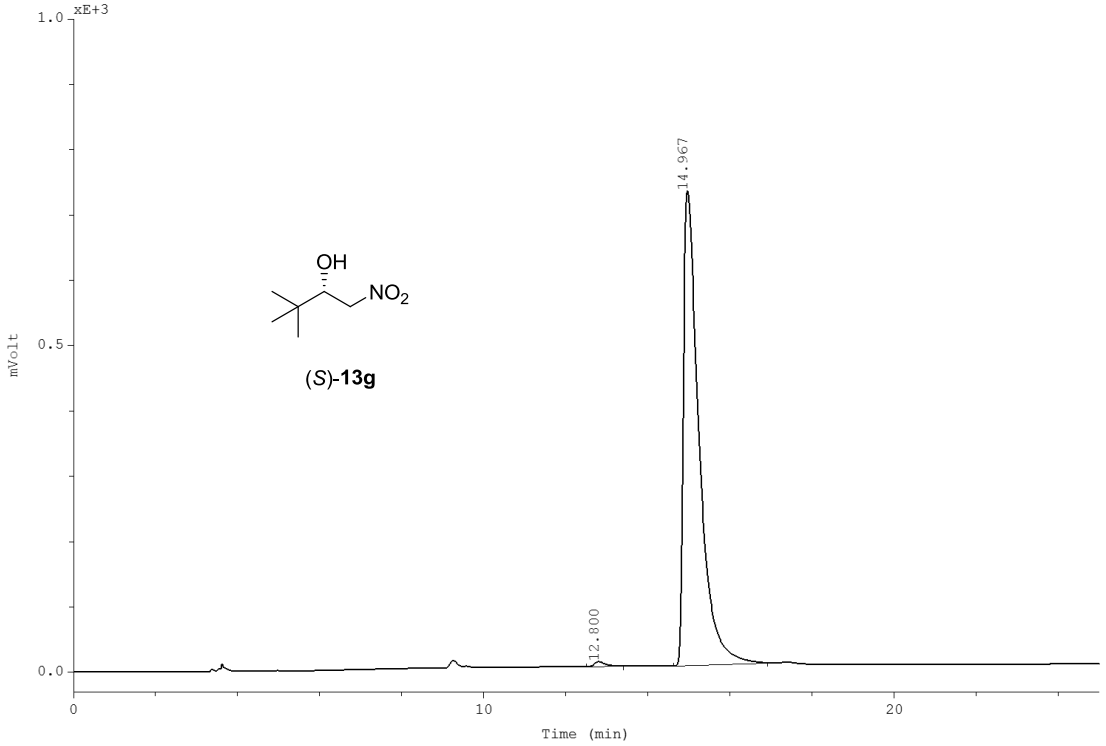


	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	31.12	30.13	33.59	320.98	349.59	99.62	99.70
2	34.28	33.59	35.23	1.23	1.05	0.38	0.30

Chiralcel OD-3, *n*-hexane/*i*PrOH 97:3, 0.9 mL/min, 215 nm:
t_R (*R*-enantiomer) = 12.8 min; t_R (*S*-enantiomer) = 15.0 min



	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.78	12.46	14.40	444.95	169.74	52.80	49.77
2	15.12	14.76	16.80	397.69	171.30	47.20	50.23



	Ret.time [min]	Start [min]	End [min]	Height [mVolt]	Area [mV*min]	% Hight	% Area
1	12.80	12.49	13.40	7.22	2.22	0.98	0.68
2	14.97	14.61	16.92	726.51	322.98	99.02	99.32