SUPPORTING INFORMATION

Highly Effective Asymmetric Henry Reaction Catalyzed by Chiral Aziridine-Functionalized Organophosphorus Compounds

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1. General information

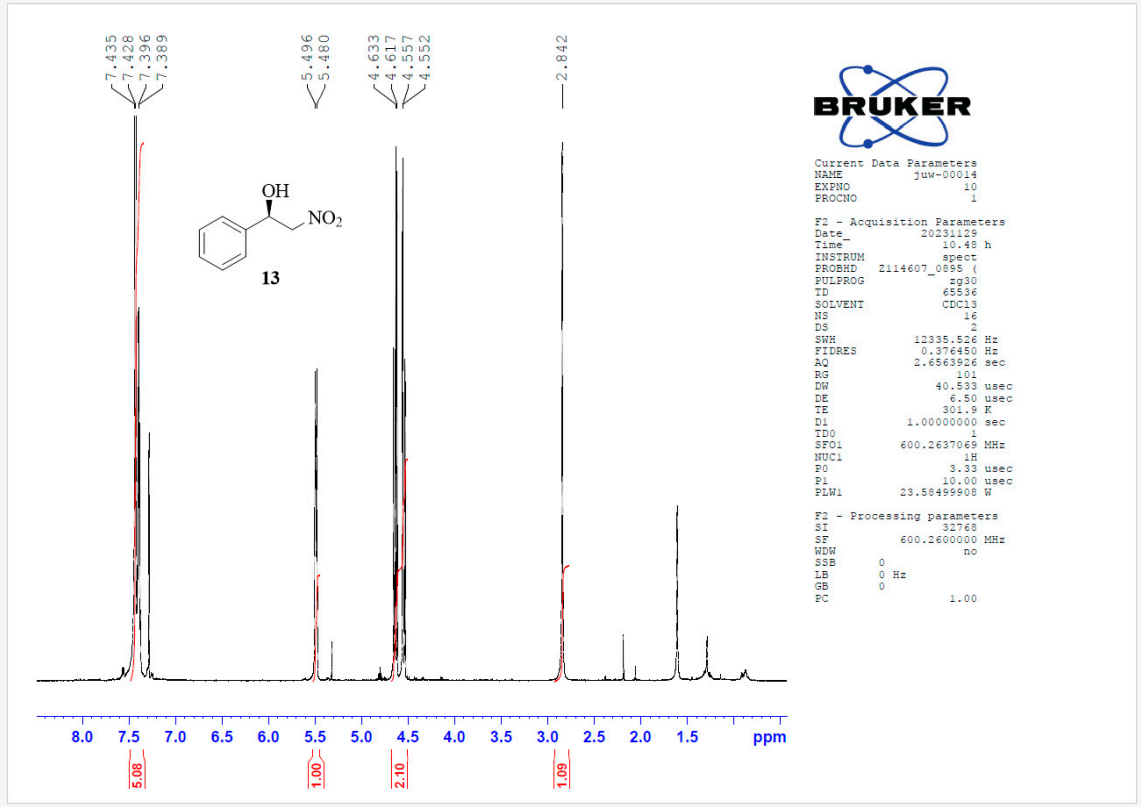
n-Hexane and ethyl acetate were purchased from Merck (Merck Group (Merck KgaA), Darmstadt, Germany) and were distilled before use. The NMR spectra were recorded on a Bruker (Bruker, Billerica, MA, USA) instrument at 600 MHz using $CDCl_3$ as a solvent and TMS as internal standard. Column chromatography was performed using Merck 60 silica gel. TLC was performed on Merck 60 F_{254} silica gel plates (Merck Group (Merck KgaA), Darmstadt, Germany). The enantiomeric excess (*ee*) was determined via HPLC using column with chiral support (Chiralcel OD-H). Chiral catalysts were prepared as previously reported [1–5].

Asymmetric nitroaldol (Henry) reaction – general procedure

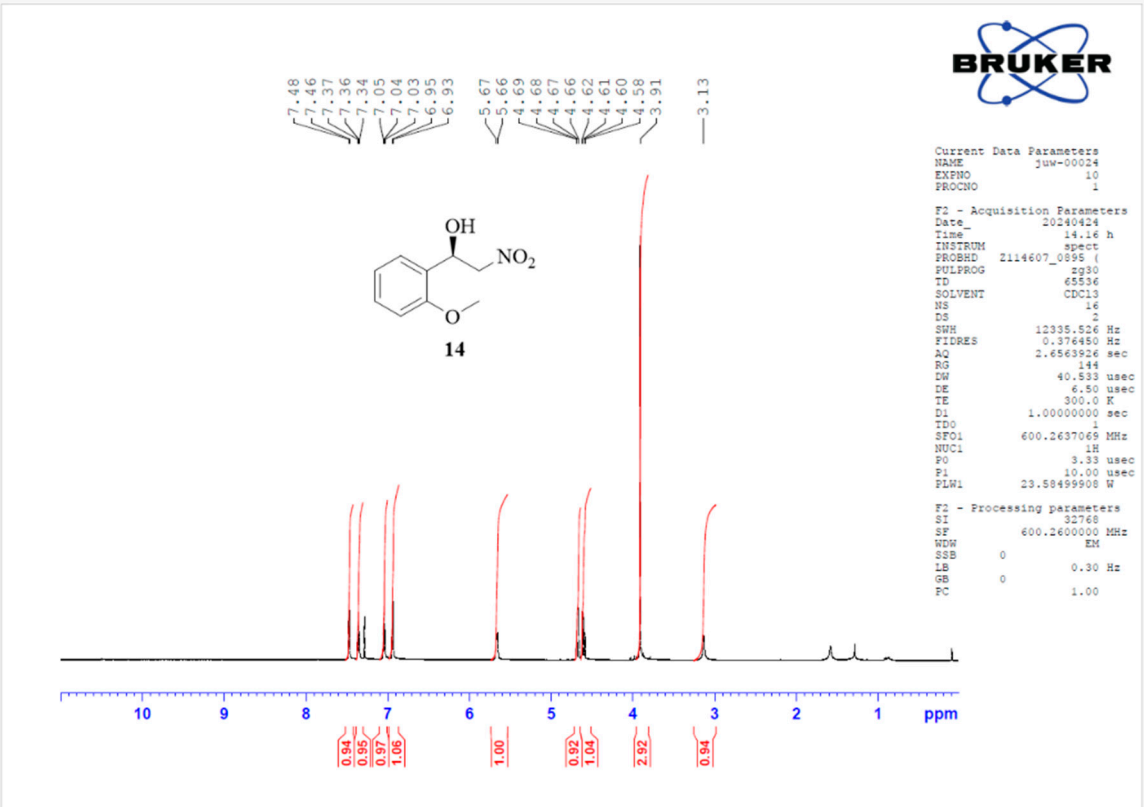
In a round-bottomed flask were placed the appropriate catalysts (0.055 mol, 5.5 mol%) and copper (II) acetate monohydrate (0.05 mol, 5 mol%, 10 mg). Ethanol (1.5 mL) was added and the mixture was stirred during 1 h at room temperature. After this time, nitromethane (10 mmol, 0,54 mL) and the corresponding aromatic/aliphatic aldehyde (1 mmol) were added and the mixture was stirred magnetically at rt during 72 h. After completion of the transformation (TLC test) the solvent was evaporated in vacuo and the crude mixture was purified on the chromatographic column (SiO_2, hexane:ethyl acetate from 97:3 to 90:10) to yield the corresponding β-nitroalcohols. The chemical yield and enantiomeric excess values are summarized in Table 1 and 2 (main text). The absolute configuration of the major enantiomer was determined according to literature [6,7].

2. ^{1}H NMR of Henry reaction products

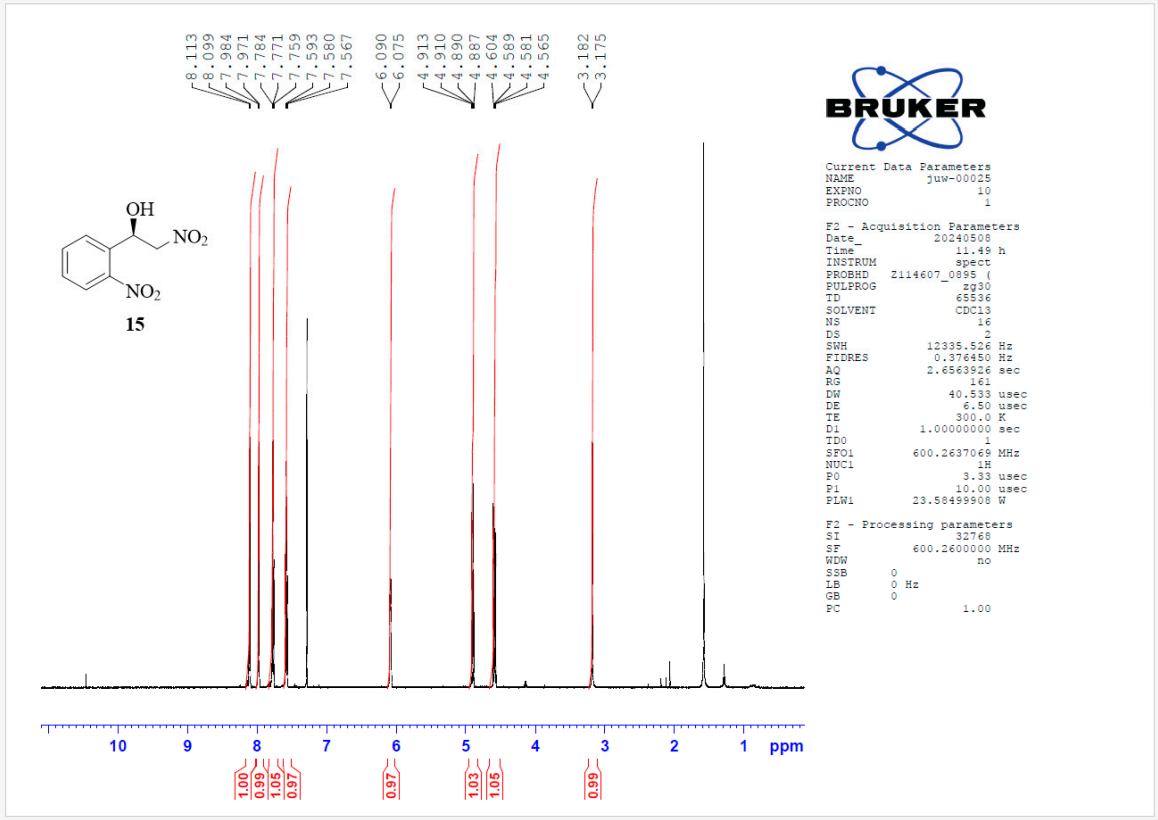
(*R*)-1-Phenyl-2-nitroethanol **13**



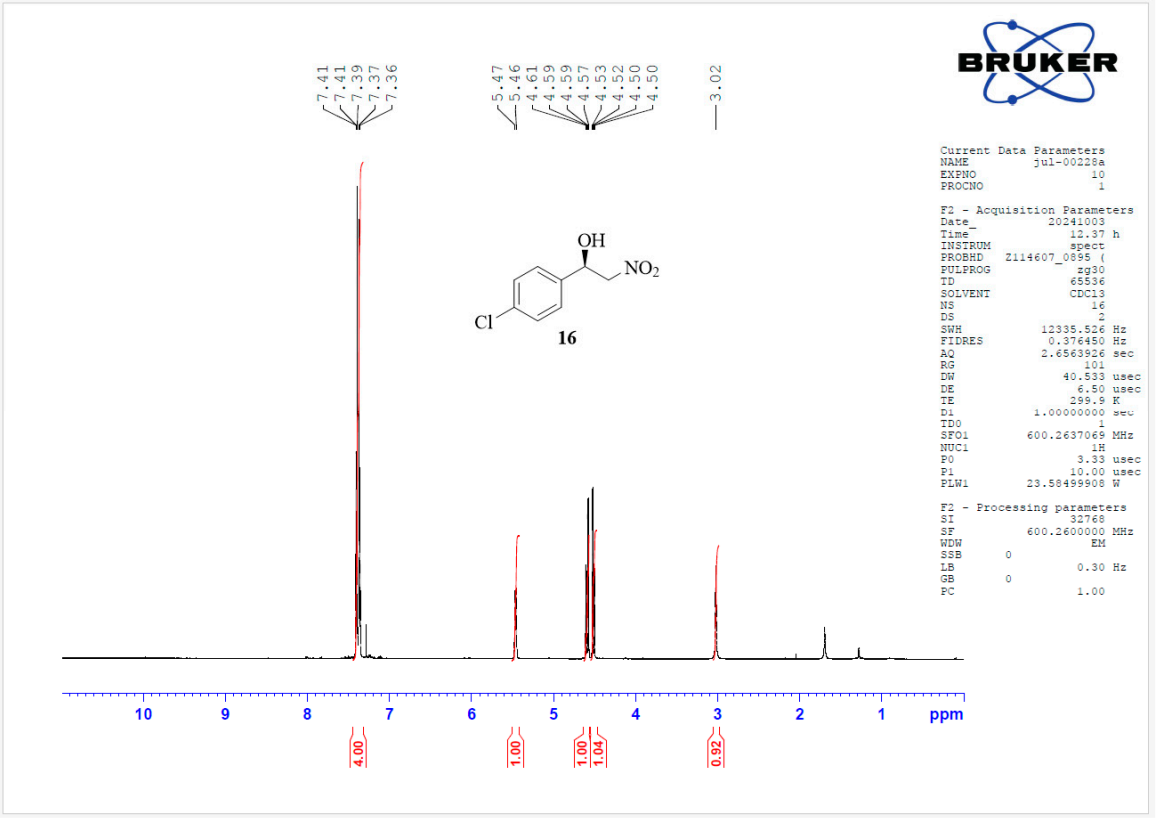
(*R*)-1-(2-Methoxyphenyl)-2-nitroethanol **14**



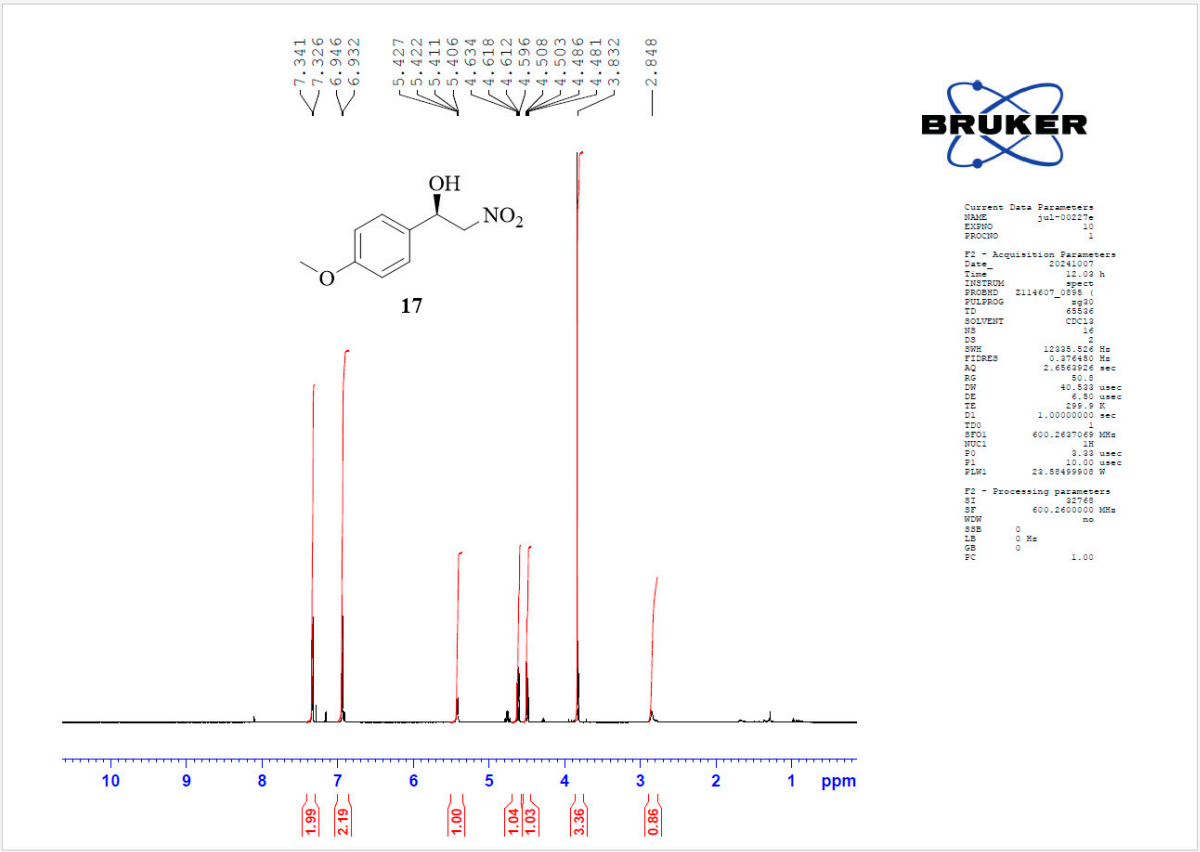
(*R*)-1-(2-Nitrophenyl)-2-nitroethanol **15**



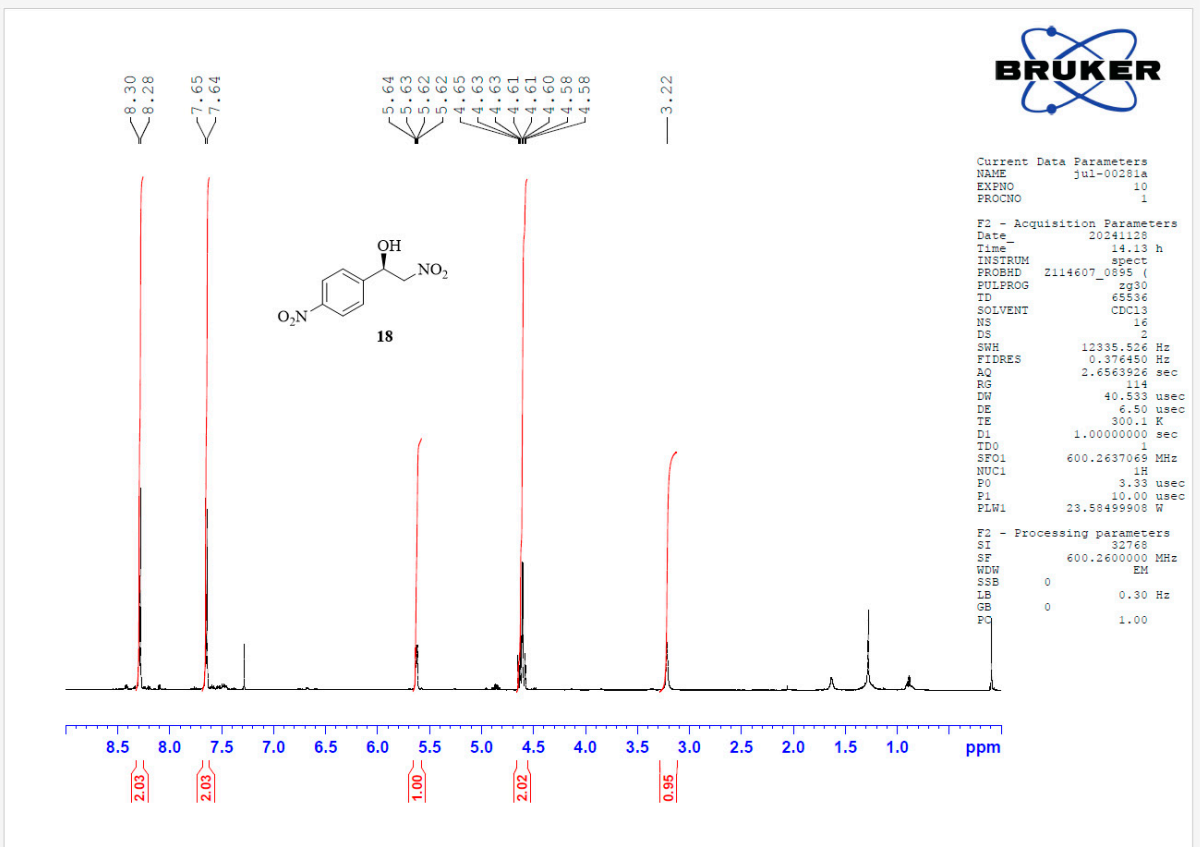
(*R*)-1-(4-Chlorophenyl)-2-nitroethanol **16**



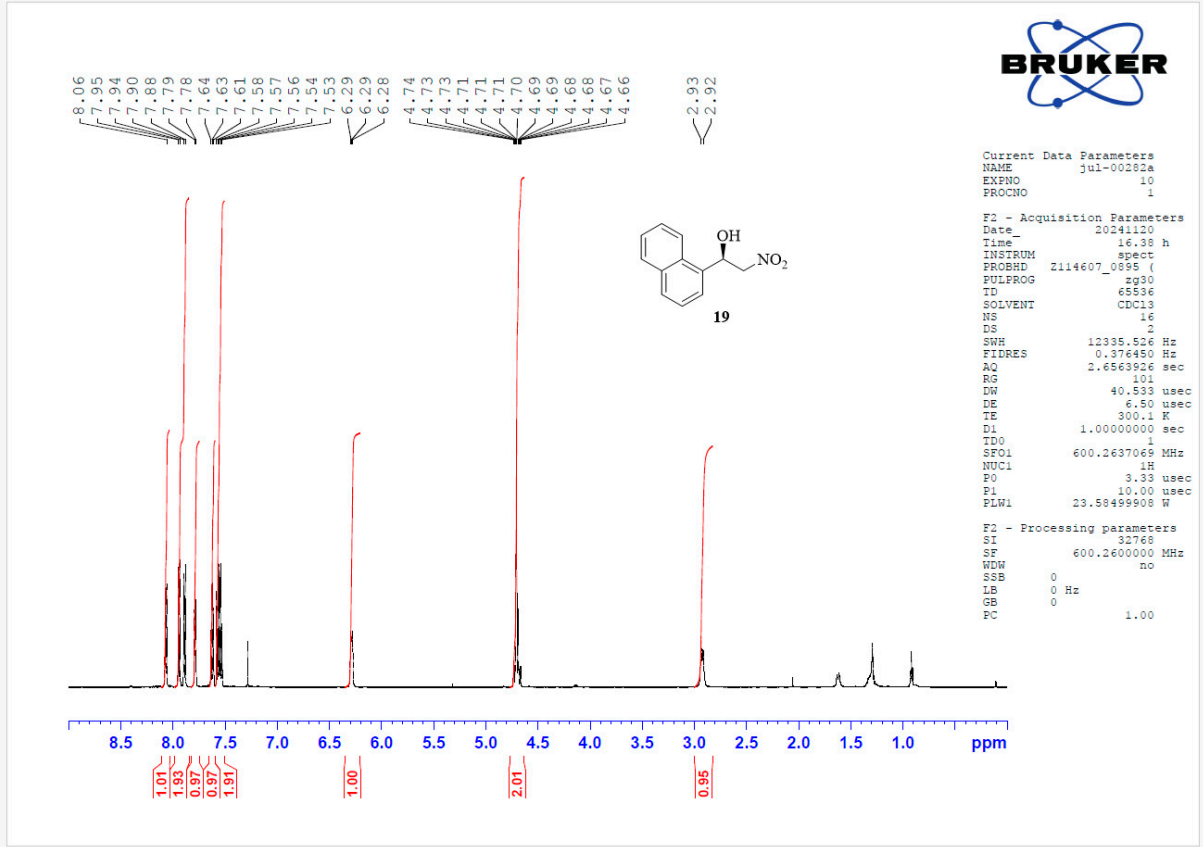
(*R*)-1-(4-Methoxyphenyl)-2-nitroethanol **17**



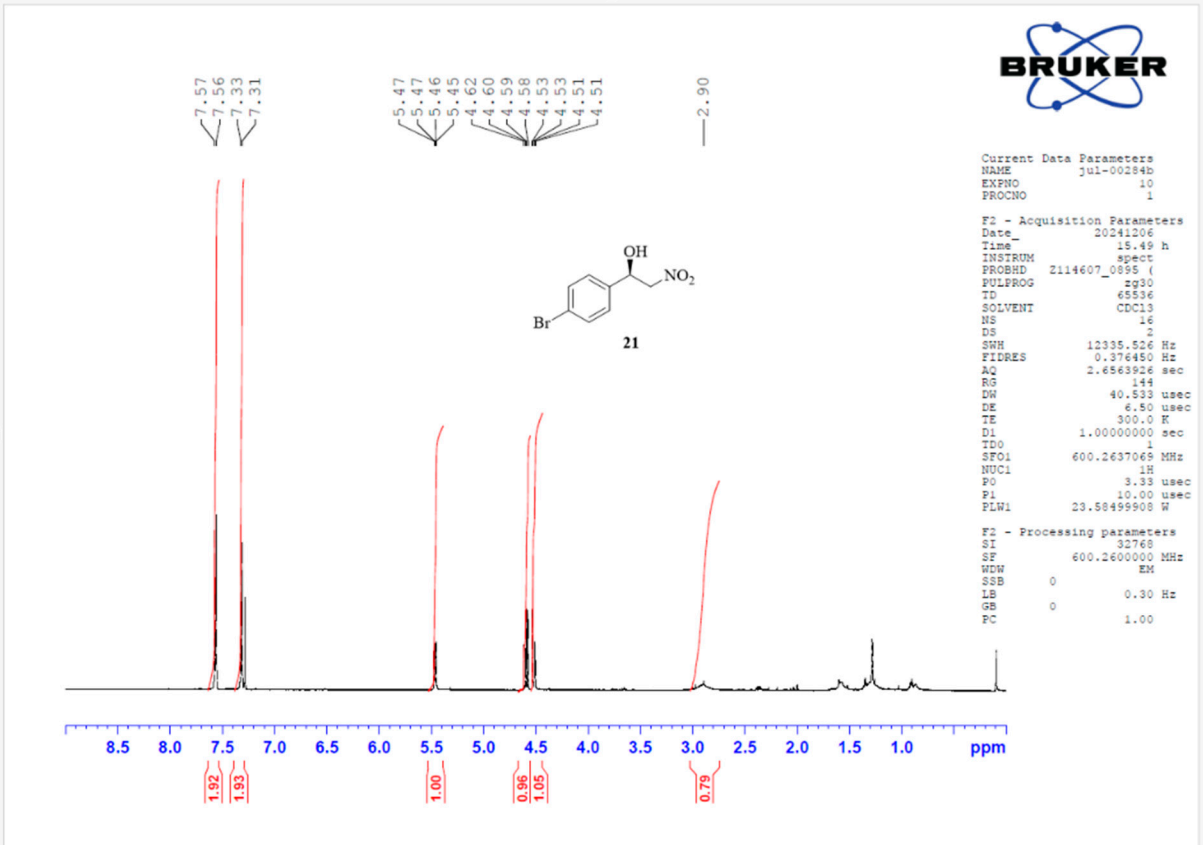
(*R*)-1-(4-Nitrophenyl)-2-nitroethanol **18**



(*R*)-1-(naphthalen-1-yl)-2-nitroethanol **19**



(*R*)-1-(4-bromophenyl)-2-nitroethanol **21**

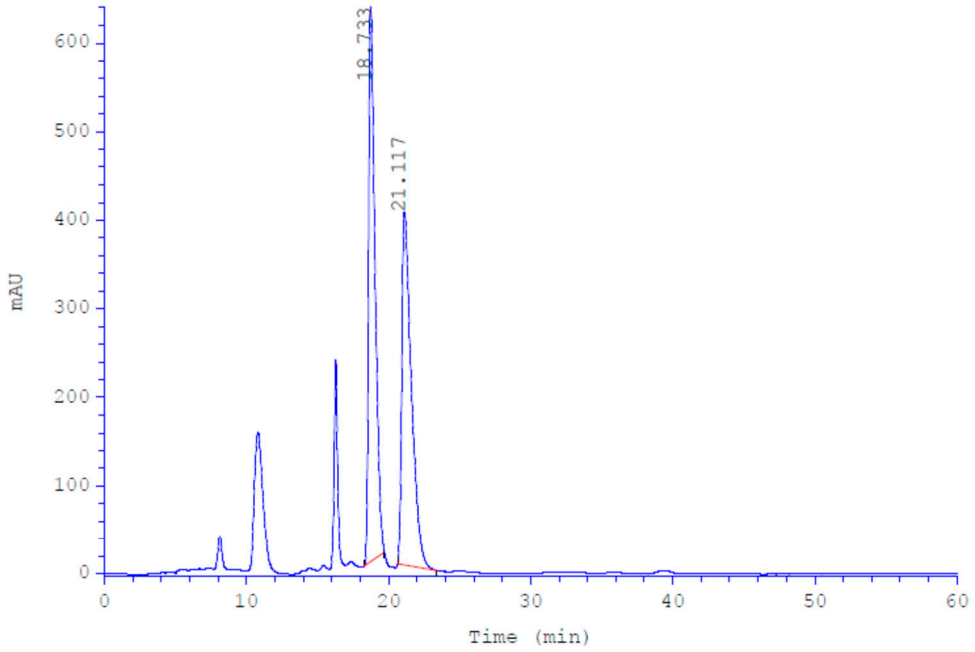


3. HPLC chromatograms of Henry reaction products

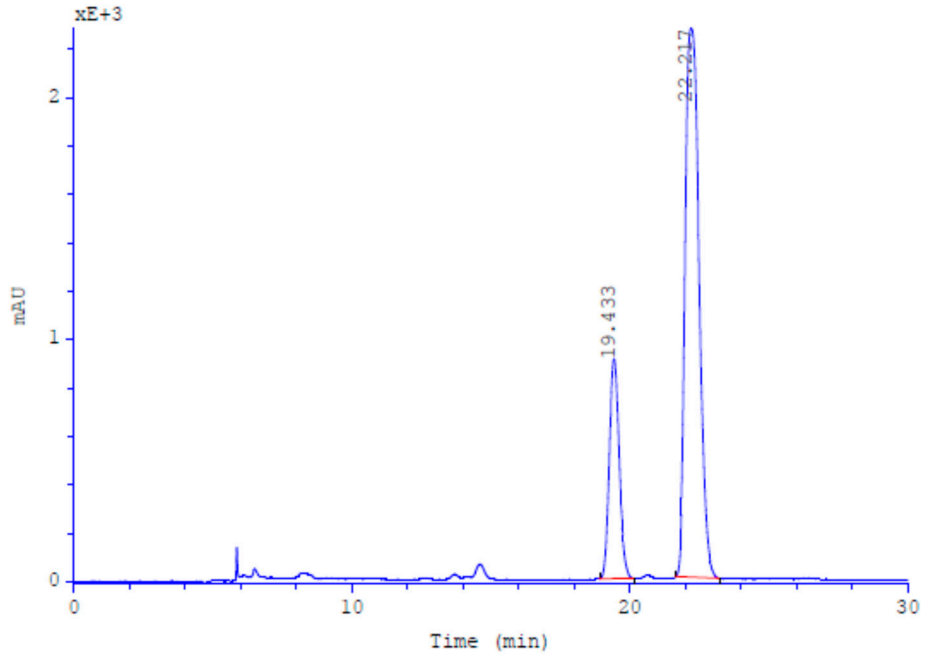
(*S*)-1-Phenyl-2-nitroethanol **13**

ee (55%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 19.43 (minor), 22.22 (major). For the racemic sample times were slightly lower: 18.73 and 21.12 min., respectively.

Racemic



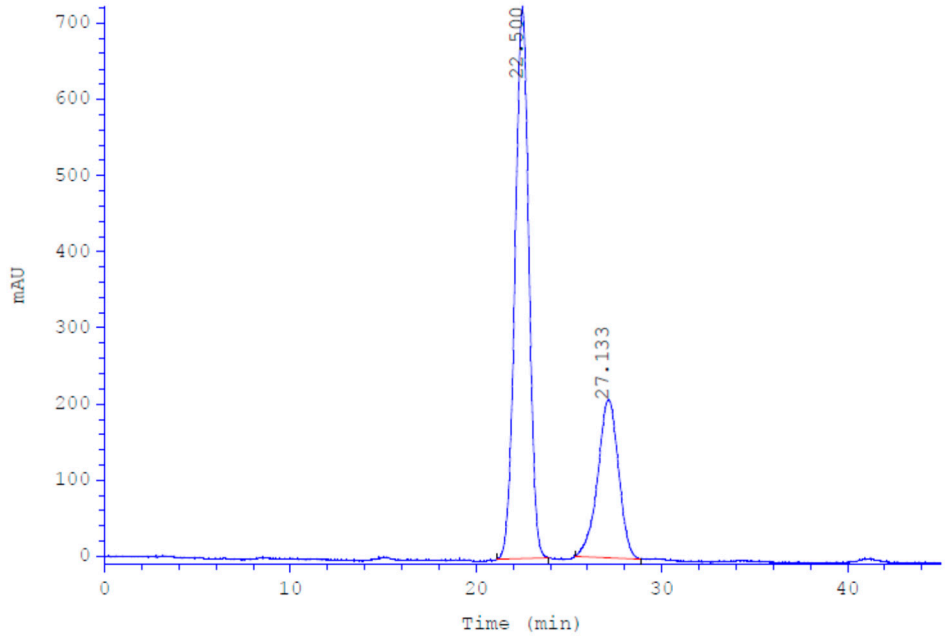
	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	18.733	18.24	19.71		-1		325.886	628.032	51.1520	0.469	BB+
2	21.117	20.65	23.38		-1		311.207	399.206	48.8480	0.704	BB+



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	19.433	18.94	20.14		-1		372.64	909.059	22.2587	0.381	BB+
2	22.217	21.67	23.23		-1		1301.49	2267.14	77.7413	0.539	BB+

(*R*)-1-Phenyl-2-nitroethanol **13**

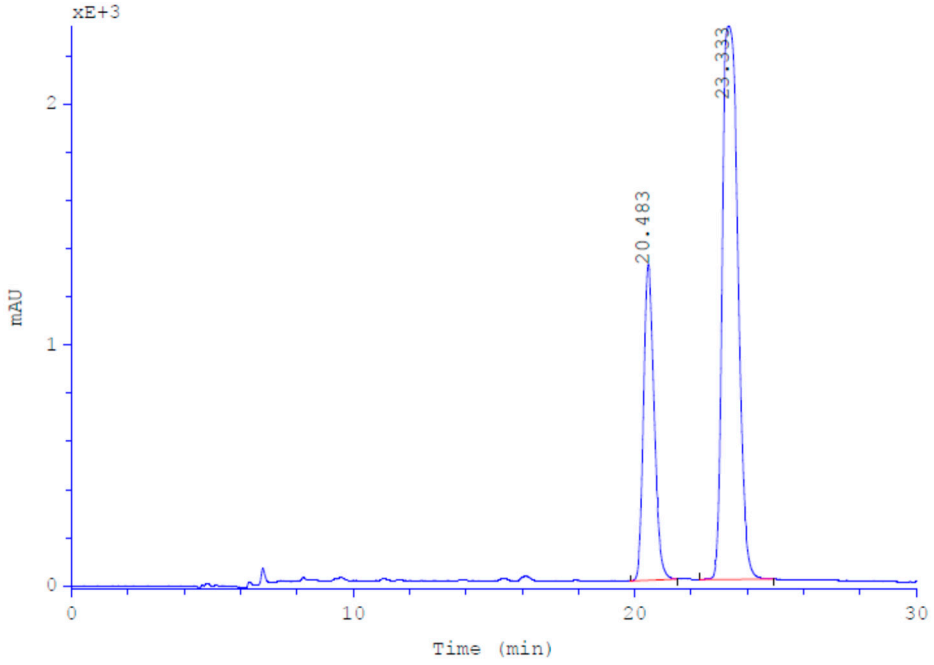
ee (40%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 22.50 (major), 27.13 (minor).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	22.500	21.17	23.92		0		624.395	725.464	69.8012	0.802	BB
2	27.133	25.35	28.87		0		270.138	207.961	30.1988	1.184	BB

(*S*)-1-Phenyl-2-nitroethanol **13**

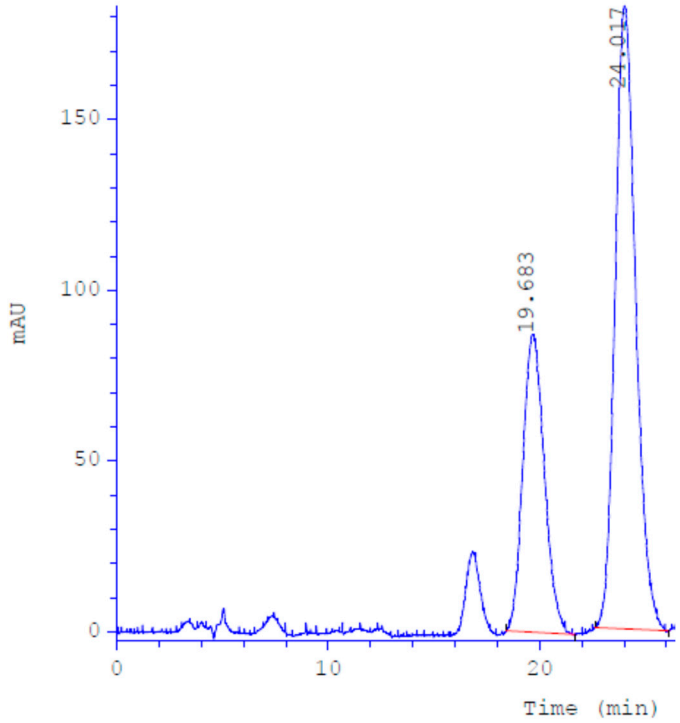
ee (44%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 20.48 (minor), 23.33 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	20.483	19.85	21.50		0		568.265	1312.59	28.0094	0.400	BB
2	23.333	22.32	24.95		0		1460.57	2298.78	71.9906	0.596	BB

(*S*)-1-Phenyl-2-nitroethanol **13**

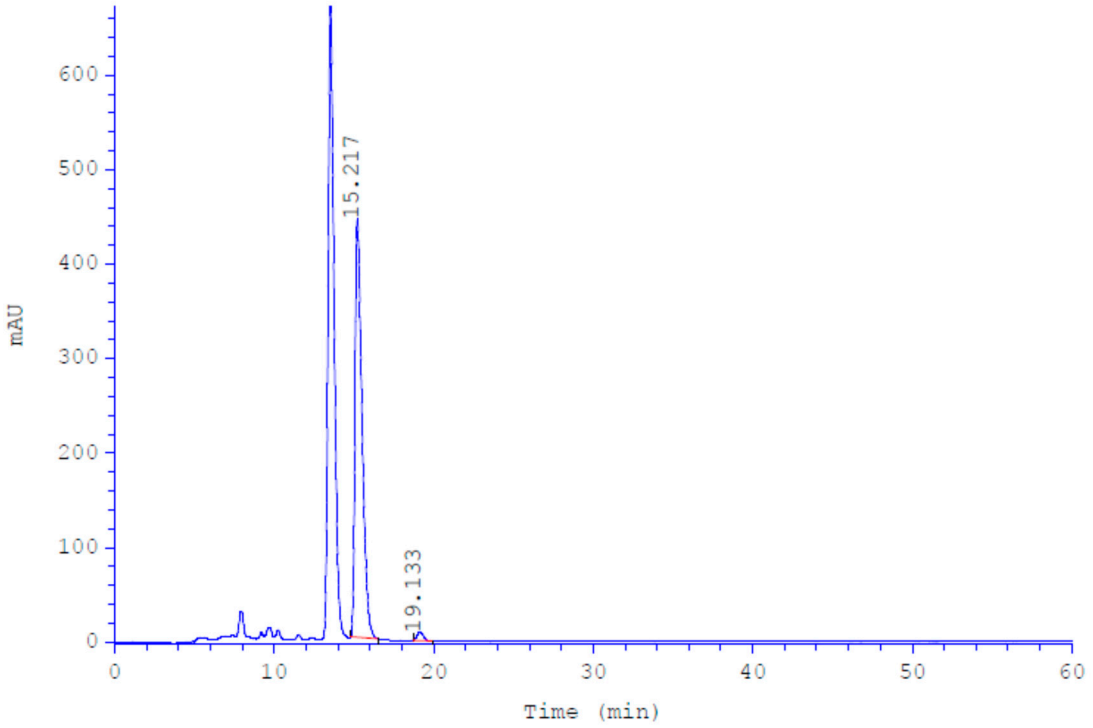
ee (34%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 19.68 (minor), 24.02 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	19.683	18.44	21.69		-1		102.589	87.092	33.2908	1.108	BB+
2	24.017	22.64	26.14		-1		205.57	182.298	66.7092	1.030	BB+

(*R*)-1-Phenyl-2-nitroethanol **13**

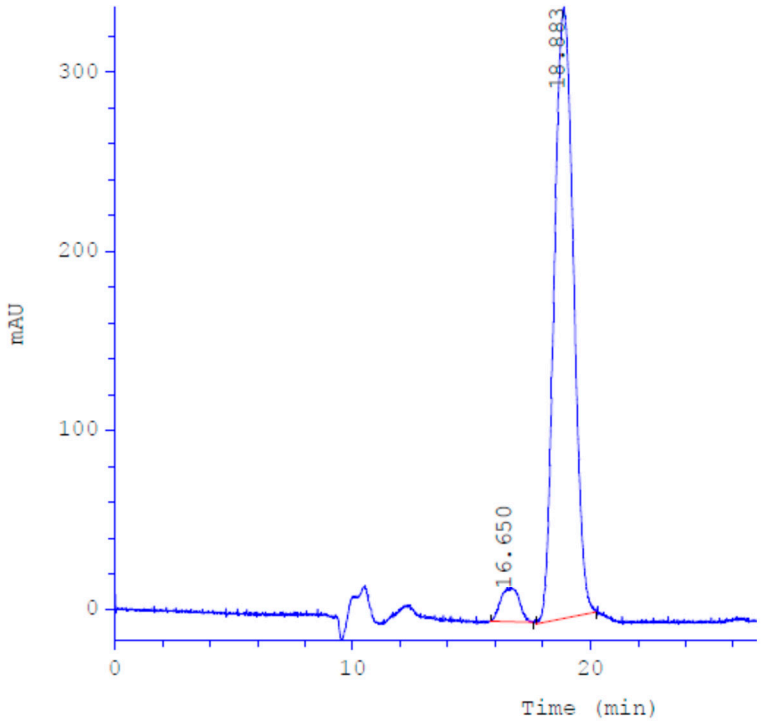
ee (96%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 15.22 (major), 19.30 (minor).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	15.217	14.78	16.51		-1		225.08	443.095	98.2973	0.456	BB+
2	19.133	18.71	19.91		-1		3.89892	8.42984	1.7027	0.446	BB+

(*S*)-1-Phenyl-2-nitroethanol **13**

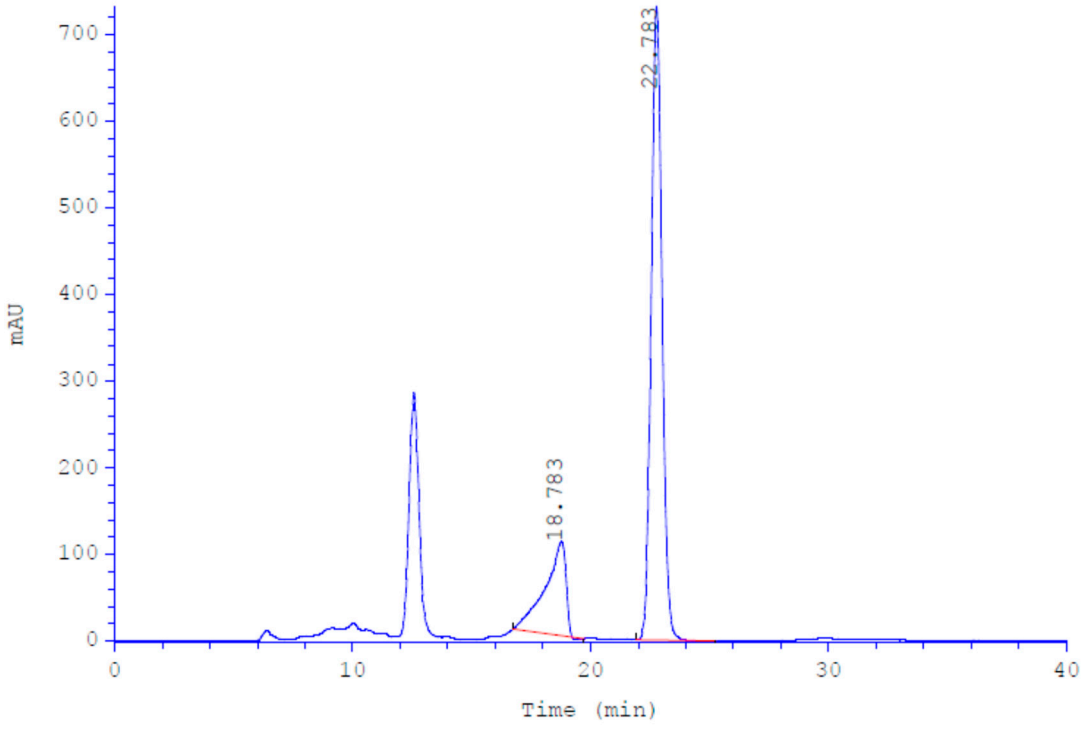
ee (90%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 16.65 (minor), 18.88 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	16.650	15.81	17.59		-1		17.2214	19.134	5.1404	0.902	BB+
2	18.883	17.72	20.23		0		317.798	341.741	94.8596	0.904	BB

(*S*)-1-Phenyl-2-nitroethanol **13**

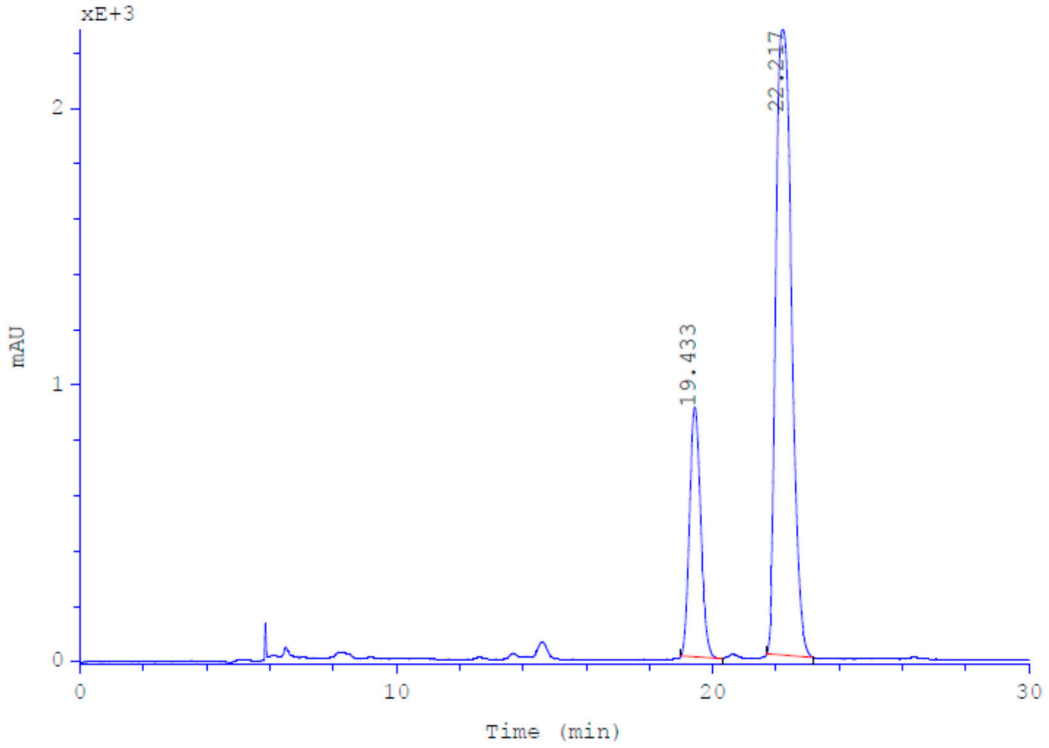
ee (56%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 18.78 (minor), 22.78 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	18.783	16.74	19.72		-1		108.952	108.979	21.9661	0.827	BB+
2	22.783	21.92	25.27		0		387.049	732.205	78.0339	0.488	BB

(*S*)-1-Phenyl-2-nitroethanol **13**

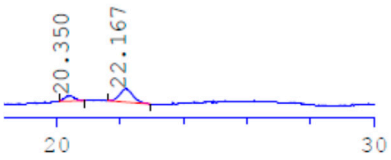
ee (55%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 19.43 (minor), 22.22 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	19.433	19.00	20.30		-1		367.277	903.504	22.0986	0.380	BB+
2	22.217	21.70	23.17		-1		1294.71	2261.95	77.9014	0.538	BB+

(*S*)-1-Phenyl-2-nitroethanol **13**

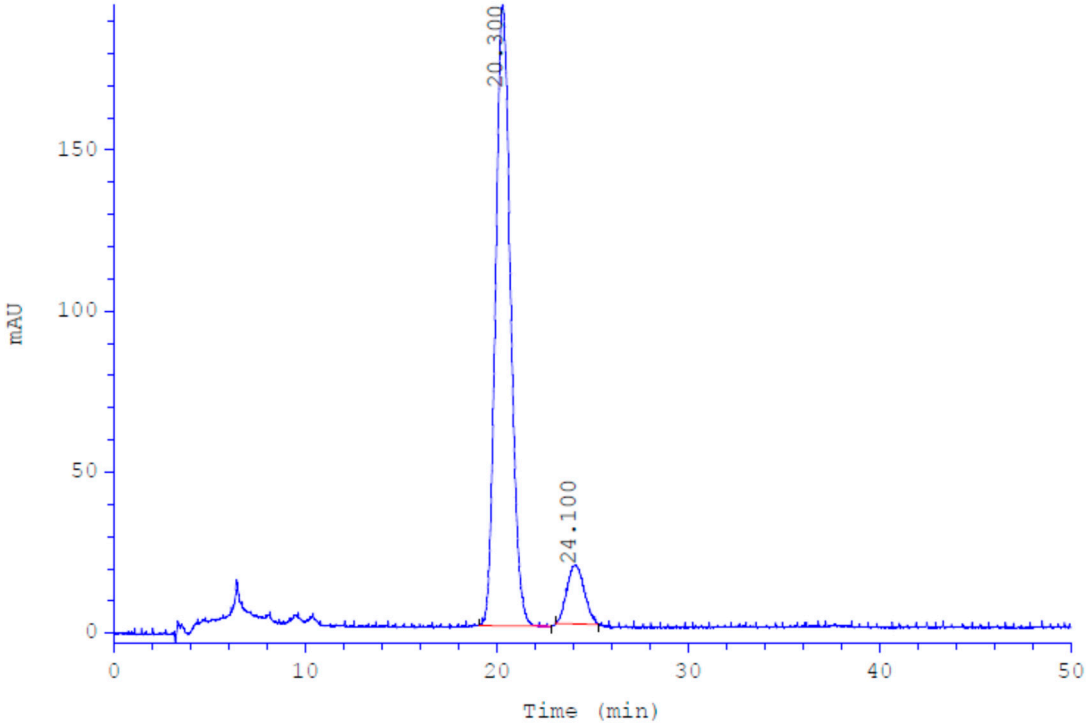
ee (56%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 20.35 (minor), 22.17 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	20.350	20.09	20.90		-1		2.30746	7.04952	21.8486	0.321	BB+
2	22.167	21.60	22.95		0		8.25368	17.4197	78.1514	0.437	BB

(*R*)-1-Phenyl-2-nitroethanol **13**

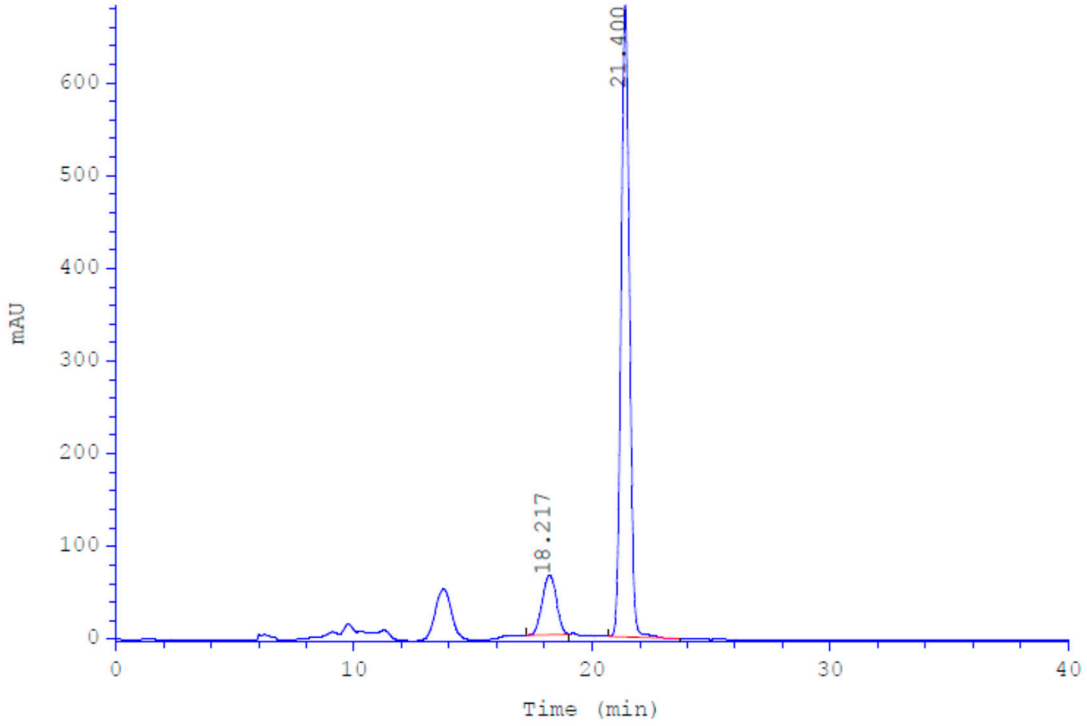
ee (80%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 20.30 (major), 24.10 (minor).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	20.300	19.09	22.82		-1		175.078	192.928	90.0662	0.840	BB+
2	24.100	23.10	25.32		-1		19.3102	18.3684	9.9338	1.041	BB+

(*S*)-1-Phenyl-2-nitroethanol **13**

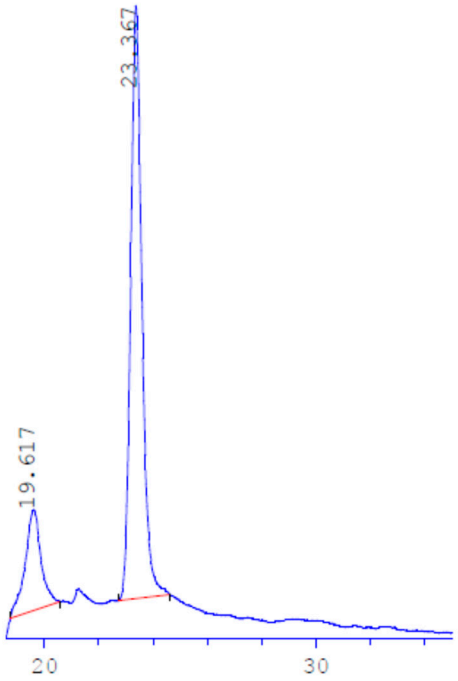
ee (74%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 18.22 (minor), 21.40 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	18.217	17.25	19.05		0		43.7488	64.0826	13.4743	0.655	BB
2	21.400	20.70	23.68		0		280.933	681.504	86.5257	0.386	BB

(*S*)-1-Phenyl-2-nitroethanol **13**

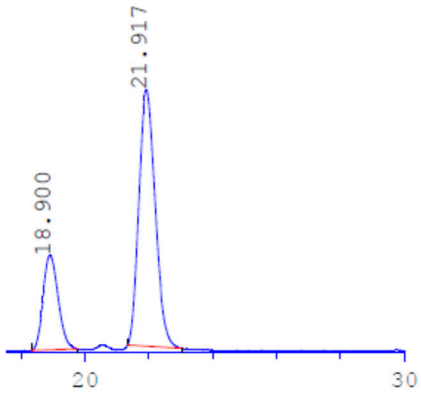
ee (62%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 19.62 (minor), 23.38 (major).



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	19.617	18.74	20.59		-1		2.07141	3.06426	19.2797	0.565	BB+
2	23.367	22.74	24.62		-1		8.6726	18.0815	80.7203	0.426	BB+

(*S*)-1-Phenyl-2-nitroethanol **13**

ee (50%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 18.90 (minor), 21.92 (major).

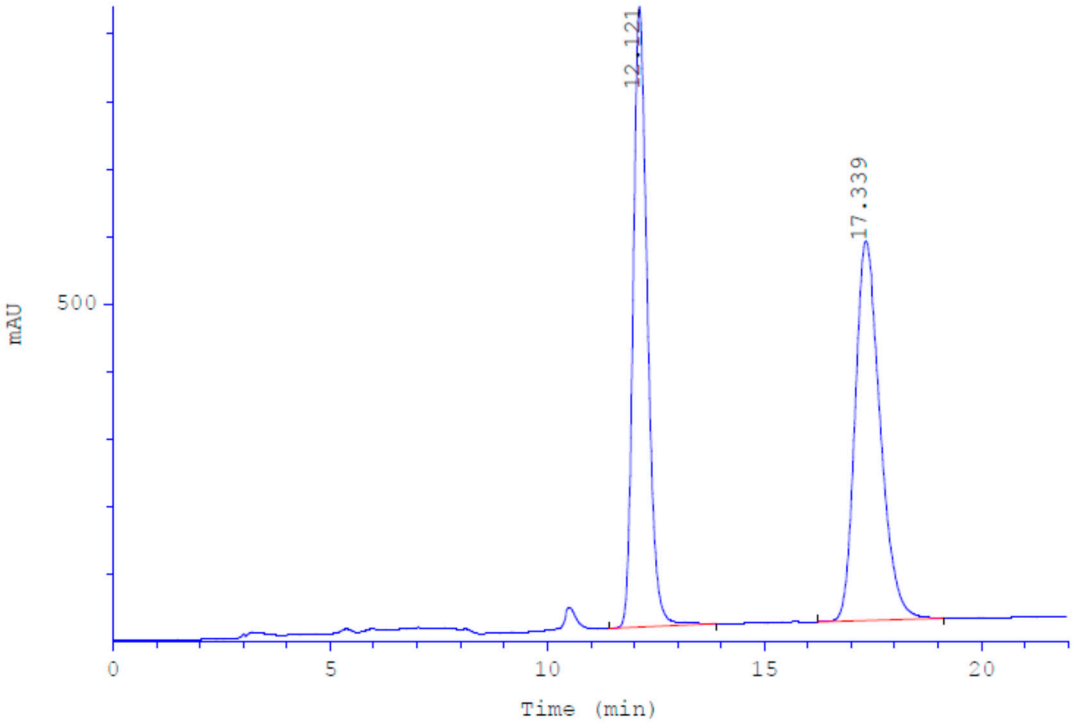


	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	18.900	18.33	19.76		-1		139.714	256.226	25.1387	0.512	BB+
2	21.917	21.33	23.06		-1		416.059	695.356	74.8613	0.571	BB+

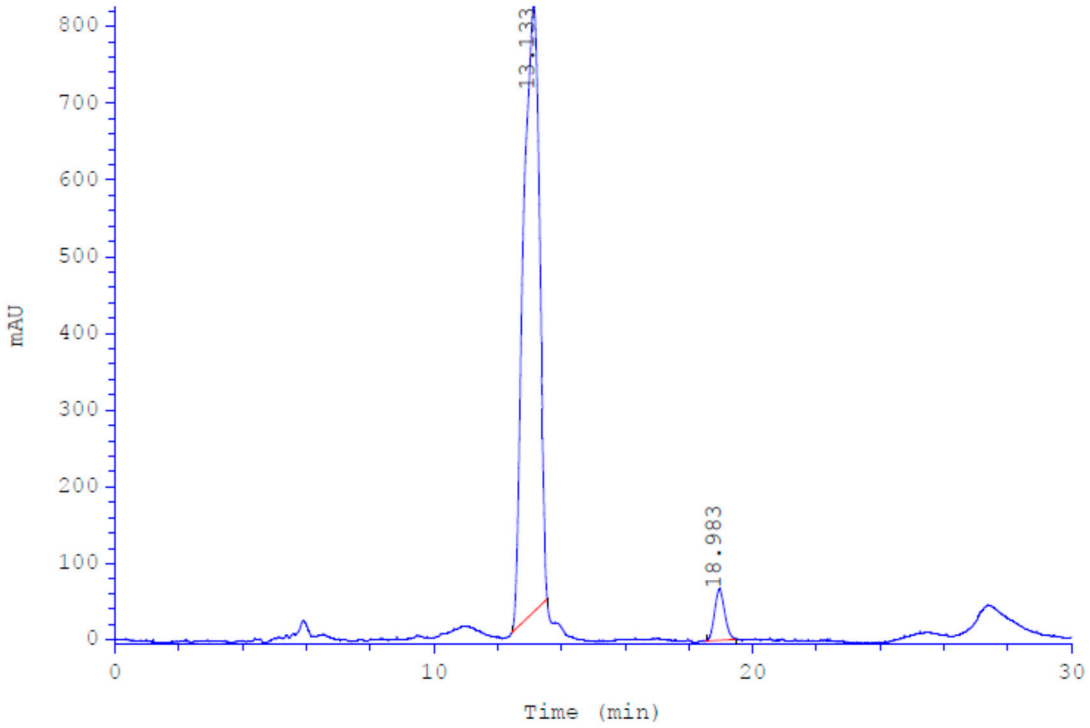
(*R*)-1-(2-Methoxyphenyl)-2-nitroethanol **14**

ee (90%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 13.13 (major), 18.98 (minor). For the racemic sample times were slightly lower: 12.12 and 17.34 min., respectively.

Racemic



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	12.121	11.42	13.90		0		350.615	919.297	48.3905	0.345	BB
2	17.339	16.24	19.14		0		373.938	561.96	51.6095	0.611	BB

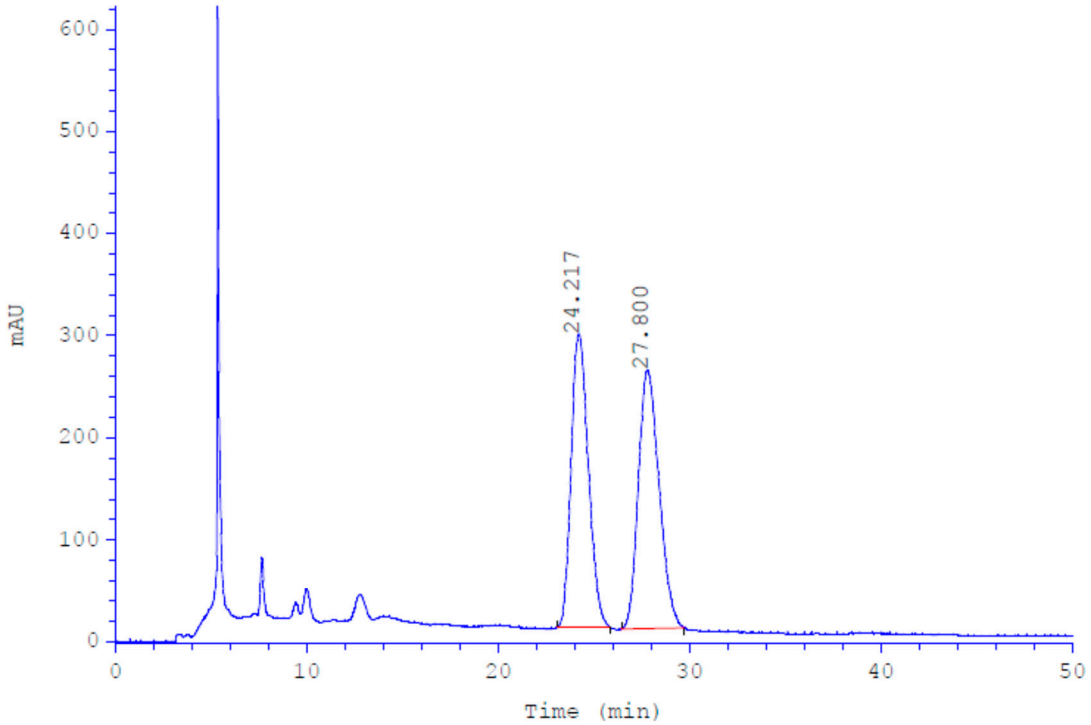


	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	13.133	12.46	13.56		-1		455.756	787.756	95.0205	0.600	BB+
2	18.983	18.53	19.47		0		23.8836	68.2054	4.9795	0.330	BB

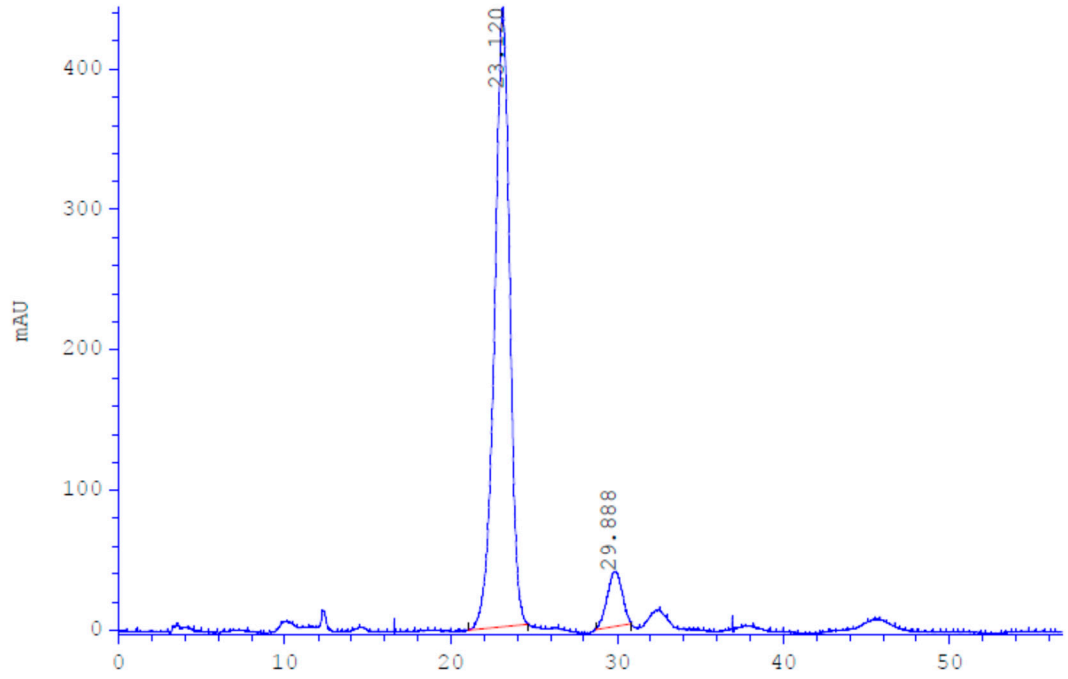
(*R*)-1-(2-Nitrophenyl)-2-nitroethanol **15**

ee (84%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 23.12 (major), 29.89 (minor). For the racemic sample times were slightly different: 24.22 and 27.80 min., respectively.

Racemic



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	24.217	23.10	25.82		-1		300.694	287.961	48.4310	0.977	BB+
2	27.800	26.43	29.71		-1		320.177	254.399	51.5690	1.188	BB+

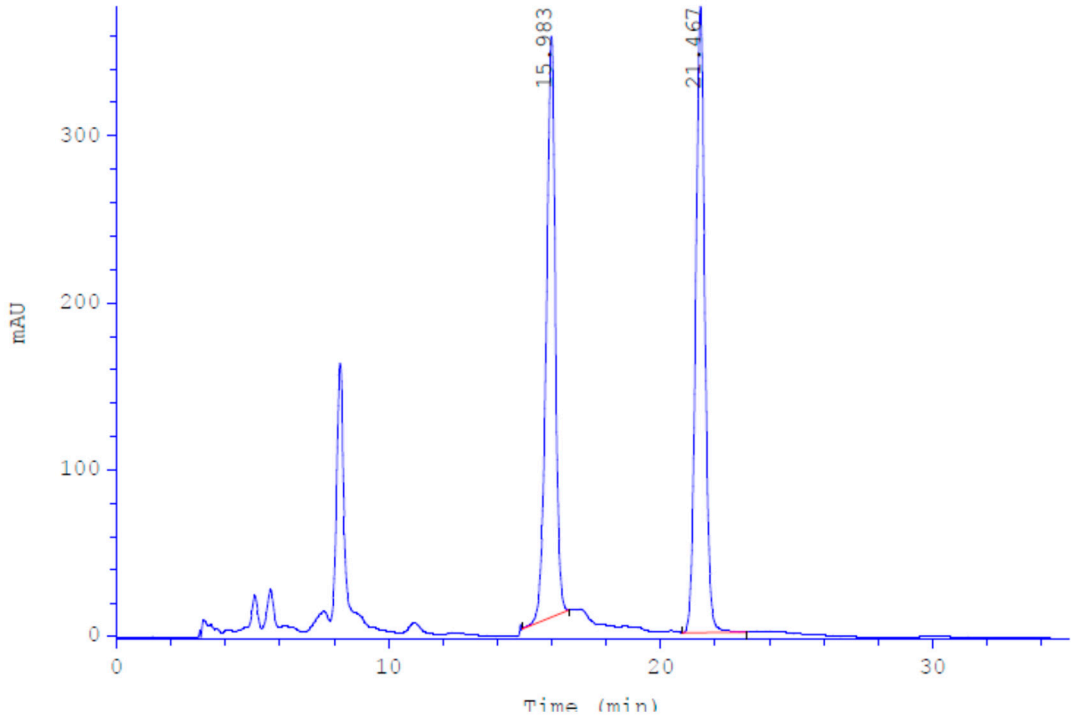


	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	23.120	21.09	24.64		0		466.744	441.914	92.0056	0.960	BB
2	29.888	28.74	30.84		0		40.5553	38.9532	7.9944	1.029	BB

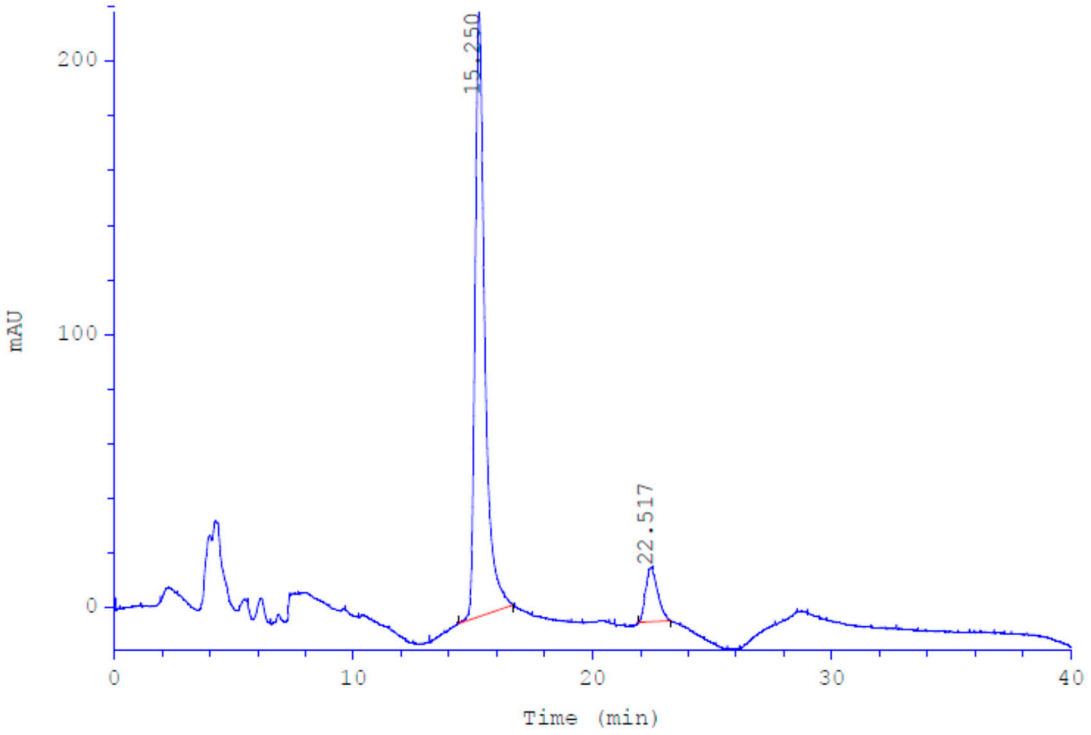
(*R*)-1-(4-Chlorophenyl)-2-nitroethanol **16**

ee (80%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 15.25 (major), 22.52 (minor). For the racemic sample times were slightly different: 15.98 and 21.47 min., respectively.

Racemic



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	15.983	14.92	16.63		0		133.923	347.919	47.7343	0.339	BB
2	21.467	20.82	23.20		0		146.636	375.351	52.2657	0.353	BB

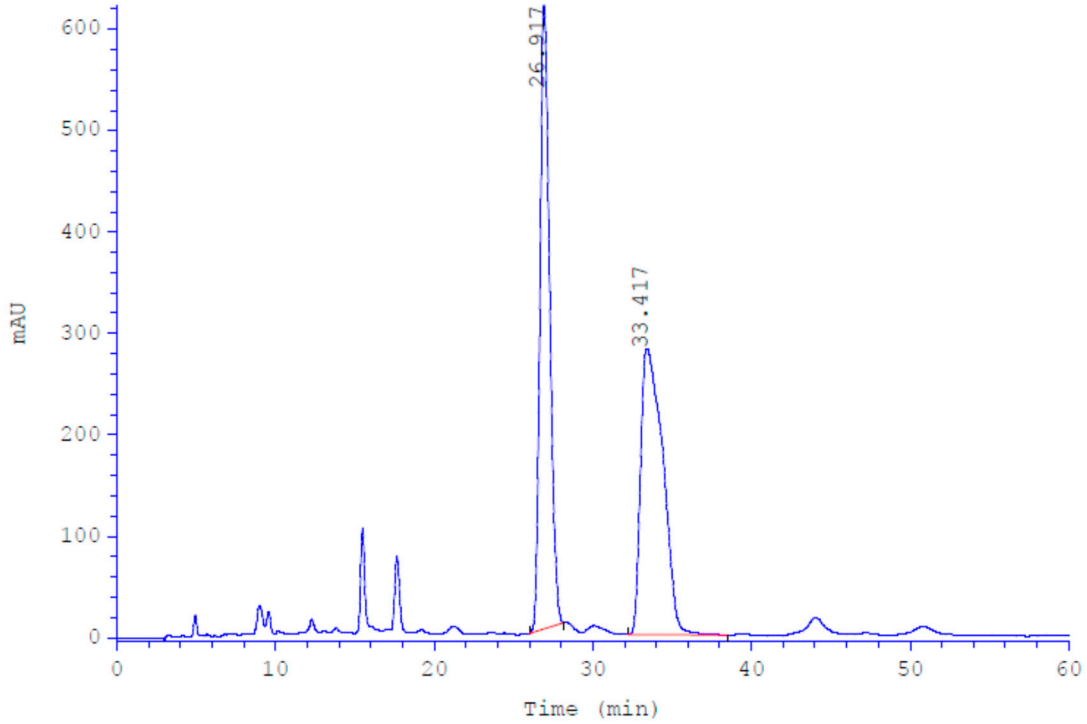


	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	15.250	14.43	16.68		0		105.894	221.248	90.1646	0.400	BB
2	22.517	21.95	23.28		-1		11.5512	20.2858	9.8354	0.539	BB+

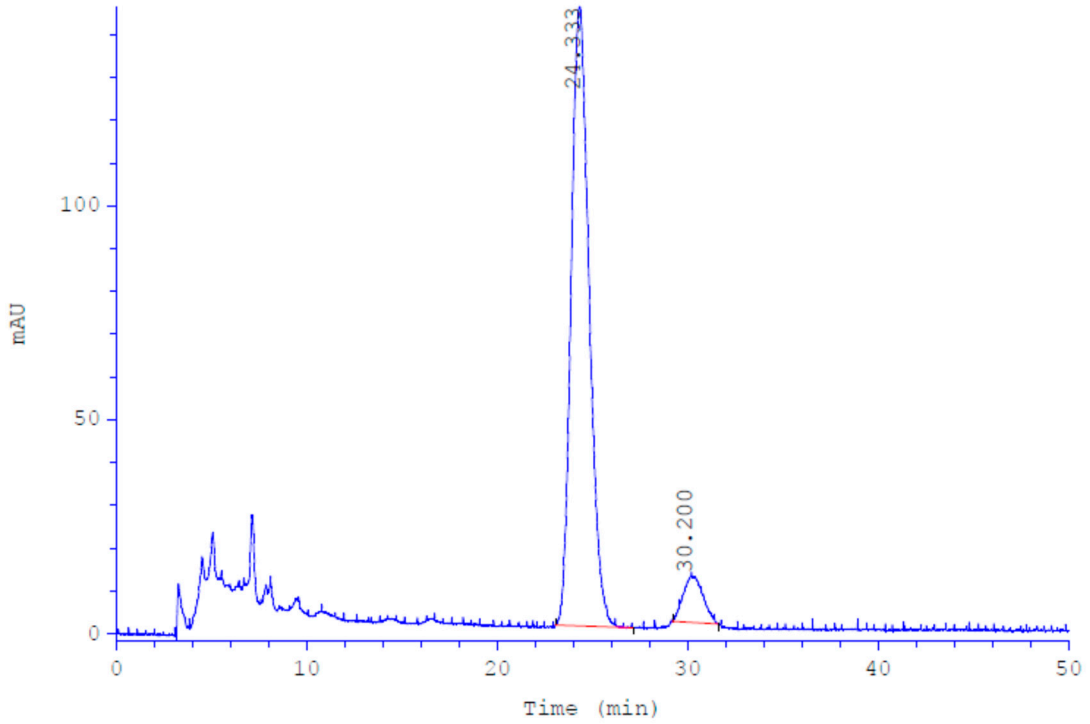
(*R*)-1-(4-Methoxyphenyl)-2-nitroethanol **17**

ee (84%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 24.33 (major), 30.20 (minor). For the racemic sample times were slightly higher: 26.92 and 33.42 min., respectively.

Racemic



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	26.917	26.02	28.18		0		436.139	615.437	48.6983	0.660	BB
2	33.417	32.22	38.53		0		459.456	282.369	51.3017	1.652	BB

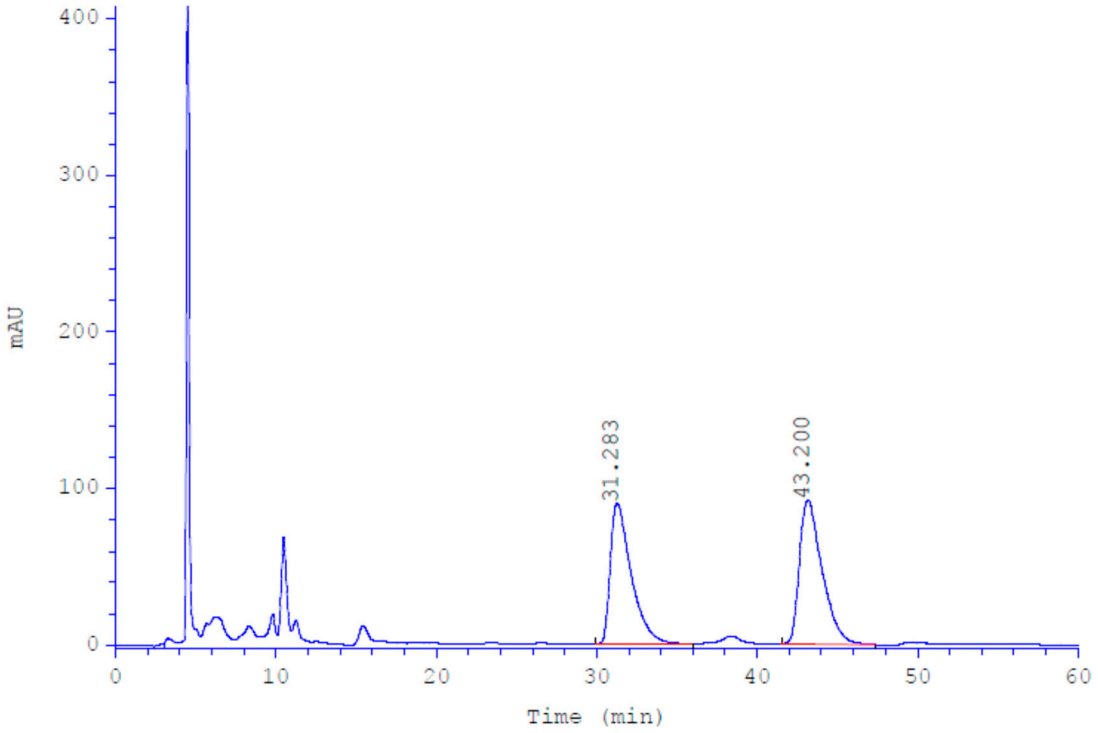


	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	24.333	23.04	27.15		-1		158.01	144.767	92.2989	1.017	BB+
2	30.200	29.21	31.60		-1		13.1839	11.6974	7.7011	1.118	BB+

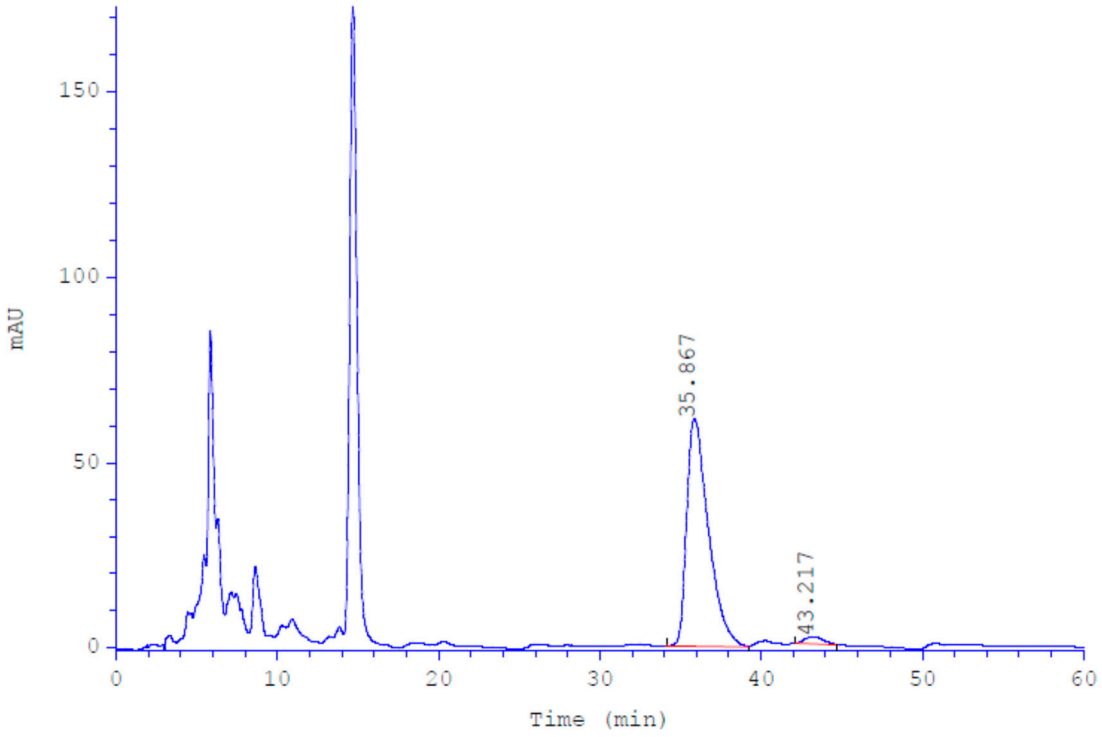
(*R*)-1-(4-Nitrophenyl)-2-nitroethanol **18**

ee (94%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 35.87 (major), 43.22 (minor). For the racemic sample time was slightly lower: 31.28 and 43.20 min., respectively.

Racemic



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	31.283	29.90	36.00		0		136.951	90.1836	47.5432	1.348	BB
2	43.200	41.50	47.42		0		151.105	92.2207	52.4568	1.501	BB

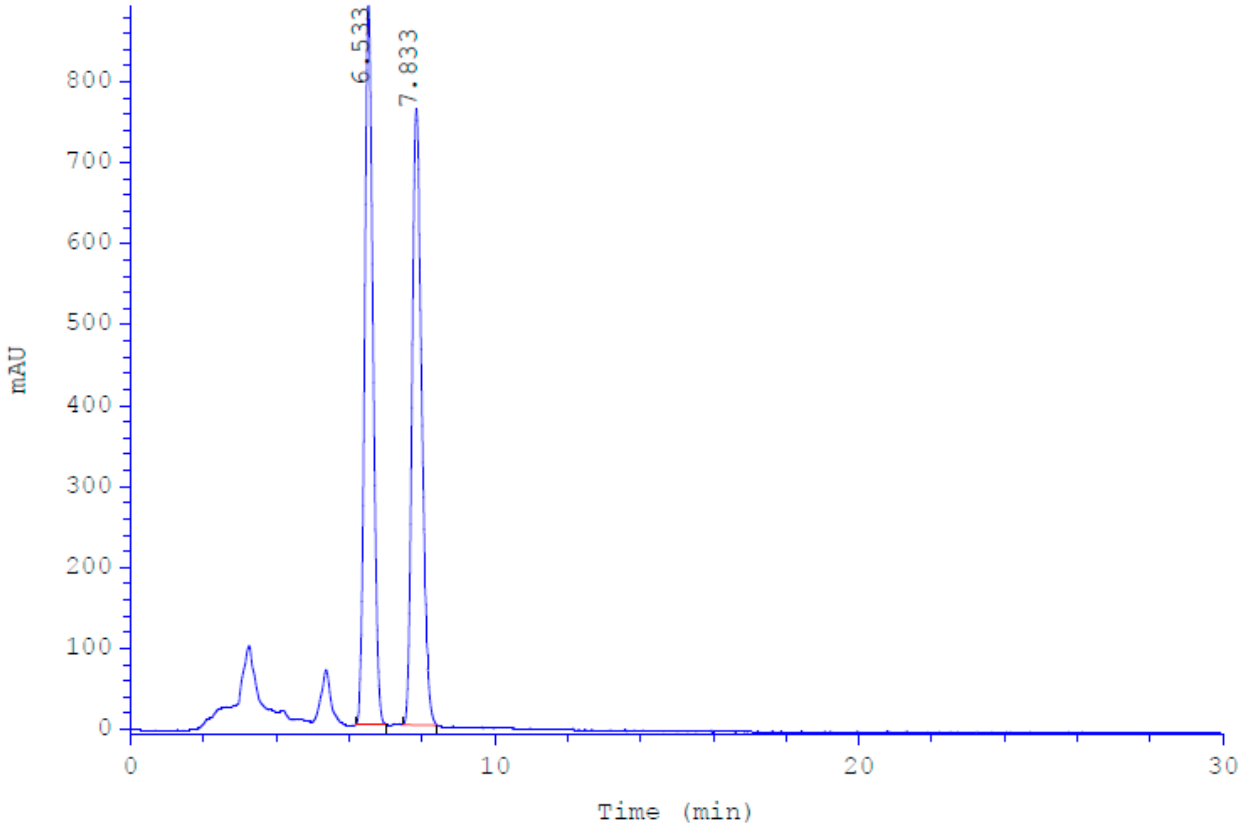


	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	35.867	34.12	39.22		0		95.5135	61.5252	97.2855	1.408	BB
2	43.217	42.12	44.73		-1		2.66507	2.00068	2.7145	1.318	BB+

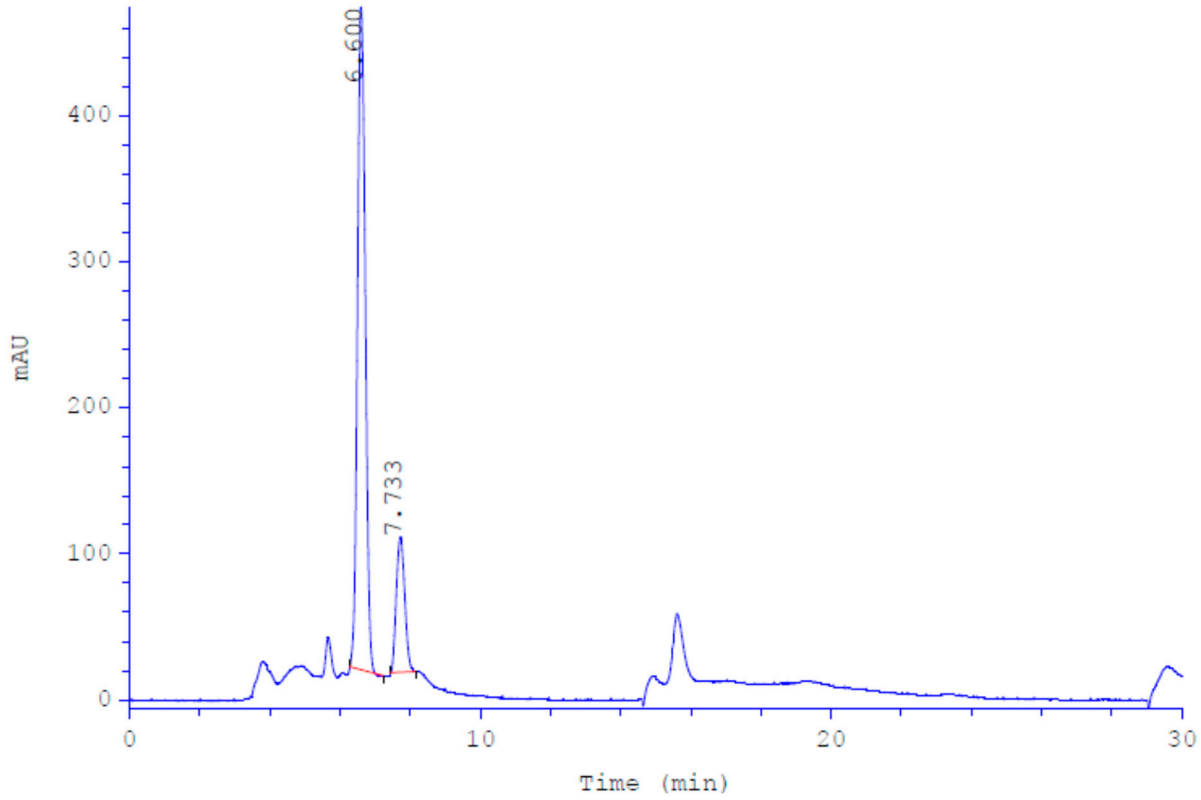
(*R*)-1-(naphthalen-1-yl)-2-nitroethanol **19**

ee (64%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 6.60 (major), 7.73 (minor). For the racemic sample time was slightly different: 6.53 and 7.83 min., respectively.

Racemic



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	6.533	6.19	7.02		-1		234.679	888.762	50.2343	0.245	BB+
2	7.833	7.49	8.42		-1		232.49	761.397	49.7657	0.282	BB+

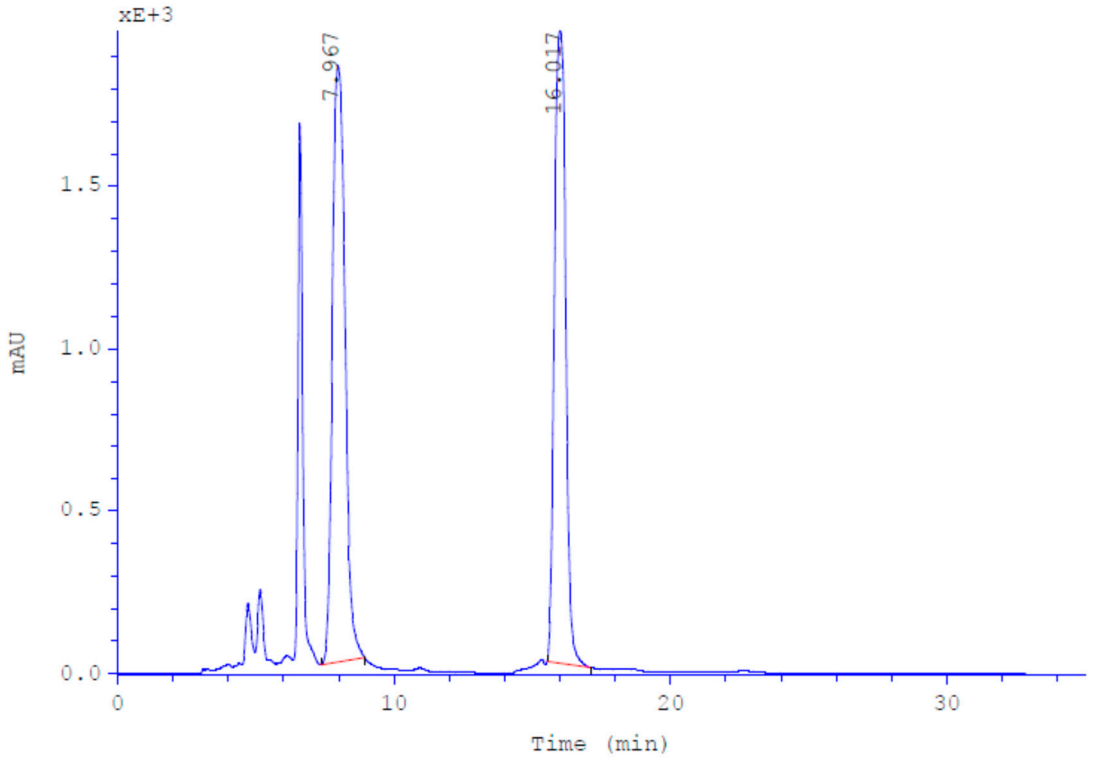


	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	6.600	6.29	7.22		-1		115.334	454.449	81.8628	0.241	BB+
2	7.733	7.45	8.16		-1		25.553	92.9288	18.1373	0.263	BB+

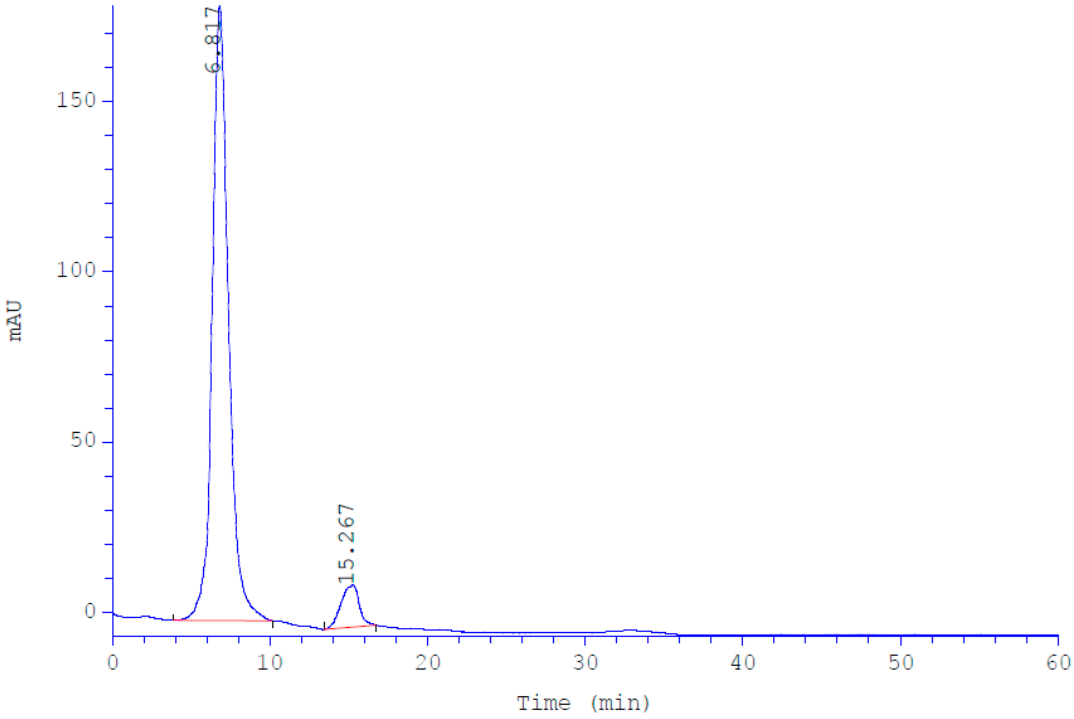
(*R*)-1-(4-bromophenyl)-2-nitroethanol **21**

ee (86%) determined by HPLC analysis: Chiralcel OD-H column, Hexane : ^{i}PrOH = 90:10, flow = 1.0 mL/min, retention times (min): 6.82 (major), 15.27 (minor). For the racemic sample times were slightly higher: 7.97 and 16.02 min., respectively.

Racemic



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	7.967	7.37	8.93		-1		969.763	1834.74	51.3390	0.495	BB+
2	16.017	15.55	17.10		-1		919.177	1945.71	48.6610	0.444	BB+



	Ret.time [min]	Start [min]	End [min]	Compound	Amount	Units	Area [mAU*min]	Height [mAU]	% Area	Width [min]	Type
1	6.817	3.87	10.17		0		217.126	180.541	92.9158	1.048	BB
2	15.267	13.45	16.75		0		16.5544	12.3203	7.0842	1.256	BB

4. References

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