

New chiral thiophene salen chromium complexes for the asymmetric Henry reaction

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General methods

All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Solvents were distilled before use : THF and diethylether from sodium metal/benzophenone, MTBE, DME and CH₂Cl₂ from calcium hydride. The “Laboratoire de Catalyse et Synthèse Organique” (Villeurbanne, UMR 5246) is gratefully acknowledged for providing 3-octylthiophene. 3-*Tert*-butyl-5-bromo-2-hydroxy-benzaldehyde was synthesized according to ref^[1], and complexes **1**, **2** and **4** according to ref^[2,3]. The aldehydes were distilled before use. *Poly-1* was prepared as described in ref^[3]. ¹H NMR spectra were recorded using 300 or 250 MHz spectrometers with samples dissolved in CDCl₃ and data are reported in ppm with the solvent signal as reference (7.27 ppm). ¹³C NMR spectra were recorded using a 250 MHz instrument with samples dissolved in CDCl₃ and data are reported in ppm with the solvent signal as reference (77.0 ppm). Optical rotations were measured in solution in 10 cm cells at the sodium D line using a polarimeter. IR spectra were recorded as KBr disks. Mass spectra were recorded using ESI, EI or CI techniques. HPLC analyses were carried out on a chromatograph equipped with a UV detector using different chiral columns, as indicated for the description of each product (see below).

Synthesis of thiophen-salen chromium complex **3**

Synthesis of 4,4,5,5-tetramethyl-2-(4-octyl-thiophen-2-yl)-[1,3]dioxolane 6 (according to ref^[4])

In a schlenk tube a solution of diisopropylamine (420 µL, 3 mmol) in THF (500 µL) was cooled to 0 °C under an argon atmosphere and treated with a 1.6 M solution of *n*-butyllithium (1.88 mL). The temperature was slowly raised up to room temperature for 15 minutes. The reaction mixture was cooled again to -78 °C and a solution of 3-octylthiophene (540 µL, 2.5 mmol) in THF (2.5 mL) was added. The mixture was stirred 2 h at -78 °C before adding a solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.01 mL, 5 mmol) in THF (1.5 mL). Then the mixture was stirred 1 h at -78 °C. After warming at room temperature the mixture was poured over crushed ice/NH₄Cl. The aqueous layer was extracted with Et₂O, the combined organic layers were dried over MgSO₄ and the solvents were removed under reduced pressure. The crude

¹ Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939-1942.

² Voituriez, A.; Mellah, M.; Schulz, E. *Synth. Met.* **2006**, *156*, 166-175.

³ Zulauf, A.; Mellah, M.; Guillot, R.; Schulz, E. *Eur. J. Org. Chem.* **2008**, 2118-2129.

⁴ Jayakannan, M.; Van Hal, P. A.; Janssen, R. A. J. *J. Polym. Sci. Part A : Polym. Chem.* **2001**, *40*, 251-261.

product **6**, as a yellow oil, was engaged in the next step without any further purification. ^1H NMR (300 MHz, CDCl_3) δ 7.50 (d, $J = 1.1$ Hz, 1H), 7.23 (d, $J = 1.1$ Hz, 1H), 2.67-2.60 (m, 2H), 1.67-1.58 (m, 2H), 1.36 (s, 12H), 1.39-1.26 (m, 10H), 0.89 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (62.5 MHz, CDCl_3) δ 144.7, 138.5, 127.6, 84.0, 31.9, 30.7, 30.0, 29.5, 29.4, 29.3, 24.8, 22.7, 14.1. MS (EI) : 322 (20), 225 (14), 224 (100), 223 (45), 123 (11).

Synthesis of 3-tert-butyl-2-hydroxy-5-(4-octyl-thiophen-2-yl)-benzaldehyde 7

A schlenk tube was charged with 3-tert-butyl-5-bromo-2-hydroxybenzaldehyde (321 mg, 1.25 mmol), $\text{Pd}(\text{PPh}_3)_4$ (216 mg, 0.19 mmol) and Na_2CO_3 (199 mg, 1.9 mmol) and was maintained under argon atmosphere by successive vacuo-argon cycles (3 h). A solution of 4,4,5,5-tetramethyl-2-(4-octyl-thiophen-2-yl)-[1,3]dioxolane **6** (2.5 mmol) in degassed DME (2.4 mL) was introduced with a canula in the schlenk and degassed water (0.75 mL) was added. The mixture was heated at 100 °C for 24 h. Water (20 mL) was added and the aqueous layer was extracted with CH_2Cl_2 . The organic layer was dried over MgSO_4 and the solvents were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (pentane/diethylether 98/2) to afford 3-tert-butyl-2-hydroxy-5-(4-octylthiophen-2-yl)benzaldehyde **7** (419 mg, 90 %) as a yellow oil. ^1H (300 MHz, CDCl_3) δ 11.81 (s, 1H), 9.94 (s, 1H), 7.76 (d, $J = 2.4$ Hz, 1H), 7.60 (d, $J = 2.4$ Hz, 1H), 7.09 (d, $J = 1.2$ Hz, 1H), 6.87 (d, $J = 1.2$ Hz, 1H), 2.63 (t, $J = 7.8$ Hz, 2H), 1.69-1.67 (m, 2H), 1.65 (s, 9H), 1.48-1.30 (m, 10H), 0.93 (t, $J = 6.5$ Hz, 3H). ^{13}C NMR (62.5 MHz, CDCl_3) δ 197.0, 160.6, 144.4, 142.9, 138.9, 131.9, 128.6, 126.4, 124.0, 120.6, 119.0, 35.0, 31.9, 30.7, 30.5, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1. HRMS (EI) : calcd for $\text{C}_{23}\text{H}_{31}\text{O}_2\text{S}$: 371.2045, found : 371.2033.

Synthesis of ligand 8

To a solution of 3-tert-butyl-2-hydroxy-5-(4-octyl-thiophen-2-yl)-benzaldehyde **7** (419 mg, 1.13 mmol) in ethanol (15.5 mL, 0.07 M) was added (*S,S*)-cyclohexane-1,2-diamine (71.5 mg, 0.68 mmol, 0.52 eq.) with continuous stirring, and the mixture was heated at 60 °C for 5 h. The reaction was cooled to room temperature. The solvents were removed under reduced pressure and the residue was purified by flash chromatography on silica gel (heptane/diethylether 95/5) to afford **8** (352 mg, 76 %) as a yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 14.1 (s, 2H), 8.33 (s, 2H), 7.60 (d, $J = 2.0$ Hz, 2H), 7.32 (d, $J = 2.0$ Hz, 2H), 7.06 (d, $J = 1.0$ Hz, 2H), 6.86 (d, $J = 1.0$ Hz, 2H), 3.34-3.32 (m, 2H), 2.72-2.66 (m, 4H), 1.77-1.70 (m, 4H), 2.18-1.15 (m, 28H), 1.58 (s, 18H), 1.01 (t, $J = 7.0$ Hz, 6H). ^{13}C (75 MHz, CDCl_3) δ 165.4, 159.9, 144.1, 144.0, 137.6, 127.3, 127.0,

124.7, 123.2, 118.5, 118.1, 72.1, 34.9, 32.8, 31.9, 30.7, 30.5, 29.6, 29.5, 29.4, 29.3, 24.3, 22.7, 14.2. HRMS (ESI) : calcd for $C_{52}H_{75}N_2O_2S_2$ ($M+H^+$) 823.5264, found 823.5272. IR (CaF₂ cell, CHCl₃, ν (cm⁻¹)) : 2928, 2857, 1632, 1470, 1424, 1215. $[\alpha]^{20}_D$: + 5.4 (c 1.01, CHCl₃).

Synthesis of complex 3

Ligand **8** (331 mg, 0.40 mmol) in dry, degassed THF (8 mL) was added to a solution of anhydrous Cr(II)Cl₂ (56.5 mg, 0.46 mmol, 1.15 eq.) in dry, degassed THF (8 mL). The resulting brown solution was stirred for 2 h under argon and then exposed to air. Stirring was continued overnight to give a dark brown solution. It was diluted with CH₂Cl₂ and washed with NH₄Cl sat. and brine. The organic layer was dried over MgSO₄ and solvents were removed under reduced pressure to afford the expected complex **3** (310 mg, 88 %). IR (KBr, ν (cm⁻¹)): 2926, 2854, 2346, 1623, 1538, 1467, 1424, 1385, 1322, 1243, 1163. Anal. Calcd for $C_{52}H_{72}ClCrN_2O_2S_2, THF, H_2O$ C, 67.34; H, 8.27; N, 2.80; S, 6.42 %. Found : C, 67.21; H, 8.33; N, 2.72; S, 7.02 %.

Representative procedure for Henry reactions

Homogeneous conditions

A schlenk tube was charged with the catalyst (2 mol%) and thoroughly maintained under an argon atmosphere by three successive vacuo-argon cycles. DCM or MTBE (4 mL), the aldehyde (1 mmol) and nitromethane (2 mL, 37.5 mmol) were introduced with a syringe. In the case of reactions performed at low temperature, the mixture was first cooled to the desired temperature, then followed by the addition of a solution of diisopropylethylamine (1 or 0.5 eq.) in DCM or MTBE (4 mL). The resulting solution was stirred for the specified amount of time. The solvents were then removed under reduced pressure and the residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product.

Heterogeneous conditions

A schlenk tube was charged with the catalyst *poly-1* (27.4 mg, 4 mol%) and thoroughly maintained under an argon atmosphere by three successive vacuo-argon cycles. DCM or MTBE (4 mL), the aldehyde (1 mmol) and nitromethane (2 mL, 37.5 mmol) were introduced with a syringe. In the case of reactions performed at low temperature, the mixture was first cooled to the desired temperature, and then followed by the addition of a solution of diisopropylethylamine (1 or 0.5 eq.) in DCM or MTBE (4 mL). The resulting suspension was stirred for the specified

amount of time. It was then filtered with a filtering syringe and the precipitate was thoroughly washed twice with DCM or MTBE. The solvents of the combined filtrates were removed under reduced pressure and the residue was purified by flash chromatography on silica gel for the determination of the yield of the reaction and the enantiomeric excess of the product. In the schlenk tube, the powdered catalyst was washed with DCM or MTBE, then water and dried under vacuum and new substrates and solvents were added for its recycling.

Characterization of the nitroaldol products

(R)-1-(2-Methoxy-phenyl)-2-nitro-ethanol **10**. Solvent for flash chromatography : pentane / diethyl ether 4/1. Yellowish oil, $[\alpha]_D^{20} - 36.2$ (*c* 1.01, CHCl₃) for 74 % ee, lit^[5] $[\alpha]_D + 42.3$ (*c* 1.1, CH₂Cl₂) for 73 % ee material. The ee was determined by HPLC analysis using an IB column (flow rate = 1.0 mL.min⁻¹; 90 % hexane, 10 % isopropanol, $\lambda = 254$ nm), which resolved both enantiomers ($t_R = 9.3$ min (major), $t_S = 10.2$ min). The absolute stereochemistry was assigned as *(R)*-based on comparison of the measured rotation with the literature value. ¹H NMR (300 MHz, CDCl₃) δ 7.44 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.32 (ddd, *J* = 1.5, 7.9, 9.4 Hz, 1H), 7.00 (dd, *J* = 0.9, 7.5 Hz, 1H), 6.91 (dd, *J* = 0.9, 7.9 Hz, 1H), 5.62 (dd, *J* = 3.2, 9.2 Hz, 1H), 4.63 (dd, *J* = 3.2, 13.0 Hz, 1H), 4.55 (dd, *J* = 9.2, 13.0 Hz, 1H), 3.88 (s, 3H), 3.47 (bs, 1H). ¹³C NMR (90 MHz, CDCl₃) δ 155.8, 129.6, 127.0, 126.0, 120.9, 110.4, 79.7, 67.5, 55.2. MS (CI) : 215 [M+NH₄⁺] (100), 197 (14), 137 (14).

(R)-2-Nitro-1-phenyl-ethanol **12a**. Solvent for flash chromatography : pentane / diethyl ether 7/3. Yellowish oil, $[\alpha]_D^{20} - 30.8$ (*c* 1.0, CHCl₃) for 62 % ee, lit^[5] $[\alpha]_D + 40.7$ (*c* 0.7, CH₂Cl₂) for 60 % ee material. The ee was determined by HPLC analysis using an IB column (flow rate 1.0 mL.min⁻¹; 90 % hexane, 10 % isopropanol, $\lambda = 205$ nm), which resolved both enantiomers ($t_R = 9.5$ min (major), $t_S = 10.2$ min). The absolute stereochemistry was assigned as *(R)*-based on comparison of the measured rotation with the literature value. ¹H NMR (250 MHz, CDCl₃) δ 7.44-7.38 (m, 5H), 5.45 (dd, *J* = 3.5, 9.3 Hz, 1H), 4.62 (dd, *J* = 9.3, 13.3 Hz, 1H), 4.51 (dd, *J* = 3.5, 13.3 Hz, 1H), 3.05 (bs, 1H). ¹³C NMR (62.5 MHz, CDCl₃) δ 138.2, 129.1, 126.0, 81.2, 71.0. MS (EI) : 106 (100), 105 (89), 77 (54), 51 (10).

(R)-1-(4-Chloro-phenyl)-2-nitro-ethanol **12b**. Solvent for flash chromatography : pentane / diethyl ether 7/3. Yellowish oil, $[\alpha]_D^{20} - 24.2$ (*c* 1.05, CHCl₃) for 64 % ee, lit^[5] $[\alpha]_D + 24.8$ (*c*

⁵ Kowalczyk, R.; Sidorowicz, L.; Skarzewski J. *Tetrahedron : Asymmetry* **2007**, *18*, 2581-2586.

0.7, CH₂Cl₂) for 60 % ee material. The ee was determined by HPLC analysis using an IB column (flow rate 1.0 mL.min⁻¹; 90 % hexane, 10 % isopropanol, λ = 205 nm), which resolved both enantiomers (t_R = 9.9 min (major), t_S = 11.2 min). The absolute stereochemistry was assigned as (*R*)-based on comparison of the measured rotation with the literature value. ¹H NMR (360 MHz, CDCl₃) δ 7.40-7.31 (m, 4H), 5.42 (dd, J = 3.0, 9.4 Hz, 1H), 4.57 (dd, J = 9.4, 13.3 Hz, 1H), 4.49 (dd, J = 3.0, 13.3 Hz, 1H), 3.25 (bs, 1H). ¹³C NMR (90 MHz, CDCl₃) δ 136.7, 134.8, 129.2, 127.3, 81.0, 70.3. MS (EI) : 142 (23), 141 (41), 140 (82), 139 (100), 111 (59), 77 (11).

(R)-2-Nitro-1-(4-nitro-phenyl)-ethanol **12c**. Solvent for flash chromatography : pentane / diethyl ether 1/1. Yellowish oil, $[\alpha]_D^{20}$ - 3.7 (c 1.01, CHCl₃) for 15 % ee, lit^[5] $[\alpha]_D$ + 11.7 (c 0.9, CH₂Cl₂) for 94 % ee material. The ee was determined by HPLC analysis using an IB column (flow rate 1.0 mL.min⁻¹; 80 % hexane, 20 % isopropanol, λ = 205 nm), which resolved both enantiomers (t_R = 10.0 min (major), t_S = 11.2 min). The absolute stereochemistry was assigned as (*R*)-based on comparison of the measured rotation with the literature value. ¹H NMR (300 MHz, CDCl₃) δ 8.12 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 5.62-5.48 (m, 1H), 4.59 (d, J = 6.3 Hz, 2H), 3.99 (bs, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 147.9, 145.8, 127.1, 124.1, 80.8, 70.0. MS (EI) : 151 (100), 150 (88), 105 (15), 77 (38), 51 (17).

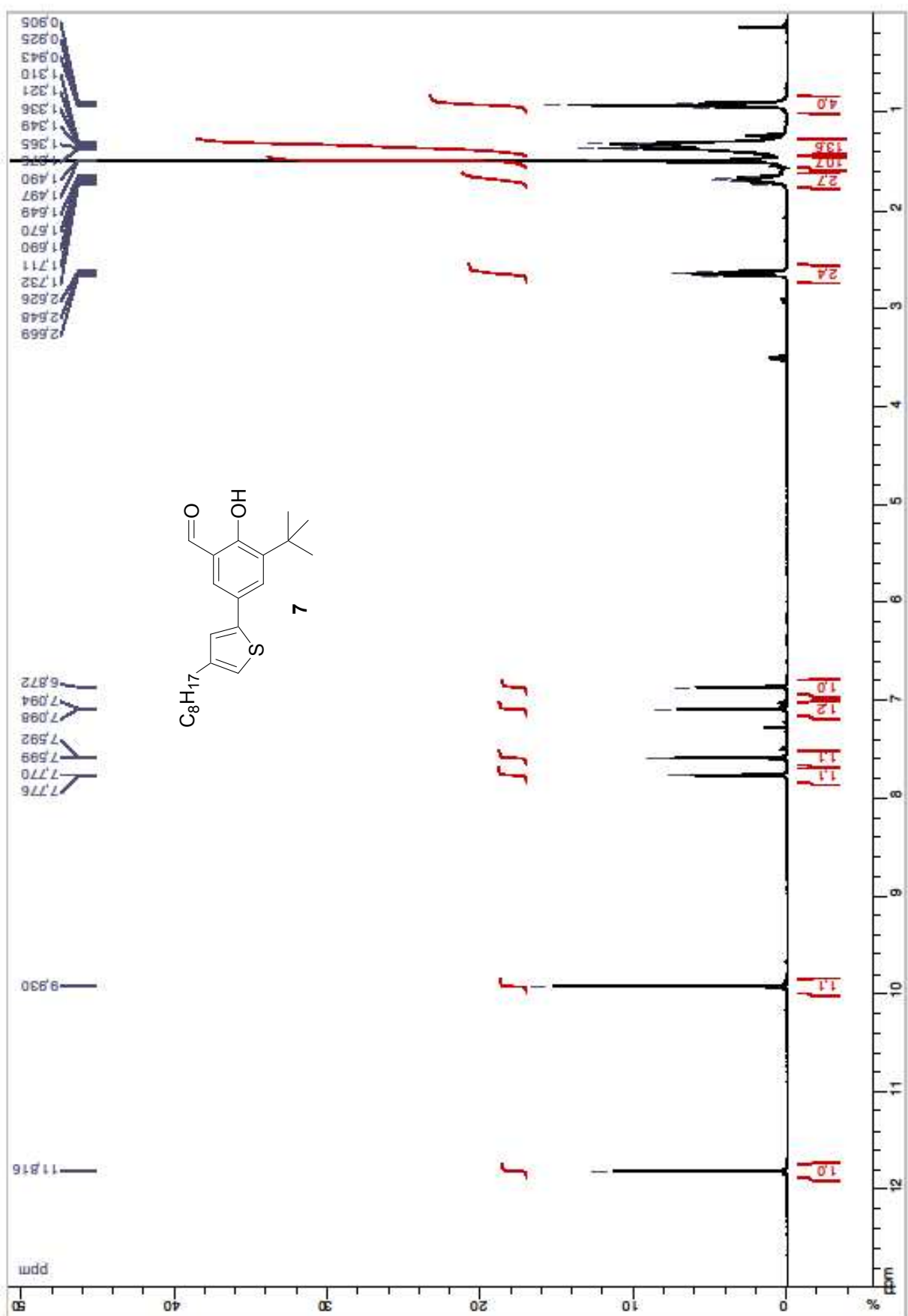
(R)-1-(4-Methoxy-phenyl)-2-nitro-ethanol **12d**. Solvent for flash chromatography : pentane / diethyl ether 4/1. Yellowish oil, $[\alpha]_D^{20}$ - 18.5 (c 1, CHCl₃) for 66 % ee, lit^[6] $[\alpha]_D$ + 44.4 (c 1.0, CH₂Cl₂) for 98 % ee material. The ee was determined by HPLC analysis using an IB column (flow rate = 1.0 mL.min⁻¹; 90 % hexane, 10 % isopropanol, λ = 205 nm), which resolved both enantiomers (t_R = 14.2 min (major), t_S = 16.2 min). The absolute stereochemistry was assigned as (*R*)-based on comparison of the measured rotation with the literature value. ¹H NMR (300 MHz, CDCl₃) δ 7.33 (dd, J = 2.1, 6.6 Hz, 2H), 6.94 (dd, J = 2.1, 6.6 Hz, 2H), 5.41 (dd, J = 3.3, 9.6 Hz, 1H), 4.62 (dd, J = 9.3, 13.2 Hz, 1H), 4.47 (dd, J = 3.0, 13.2 Hz, 1H), 3.82 (s, 3H), 2.87 (bs, 1H). ¹³C NMR (90 MHz, CDCl₃) δ 160.0, 130.3, 127.2, 114.4, 81.2, 70.6, 55.3. MS (CI) : 214 [M+NH₃] (14), 197 (100), 154 (4), 69 (18).

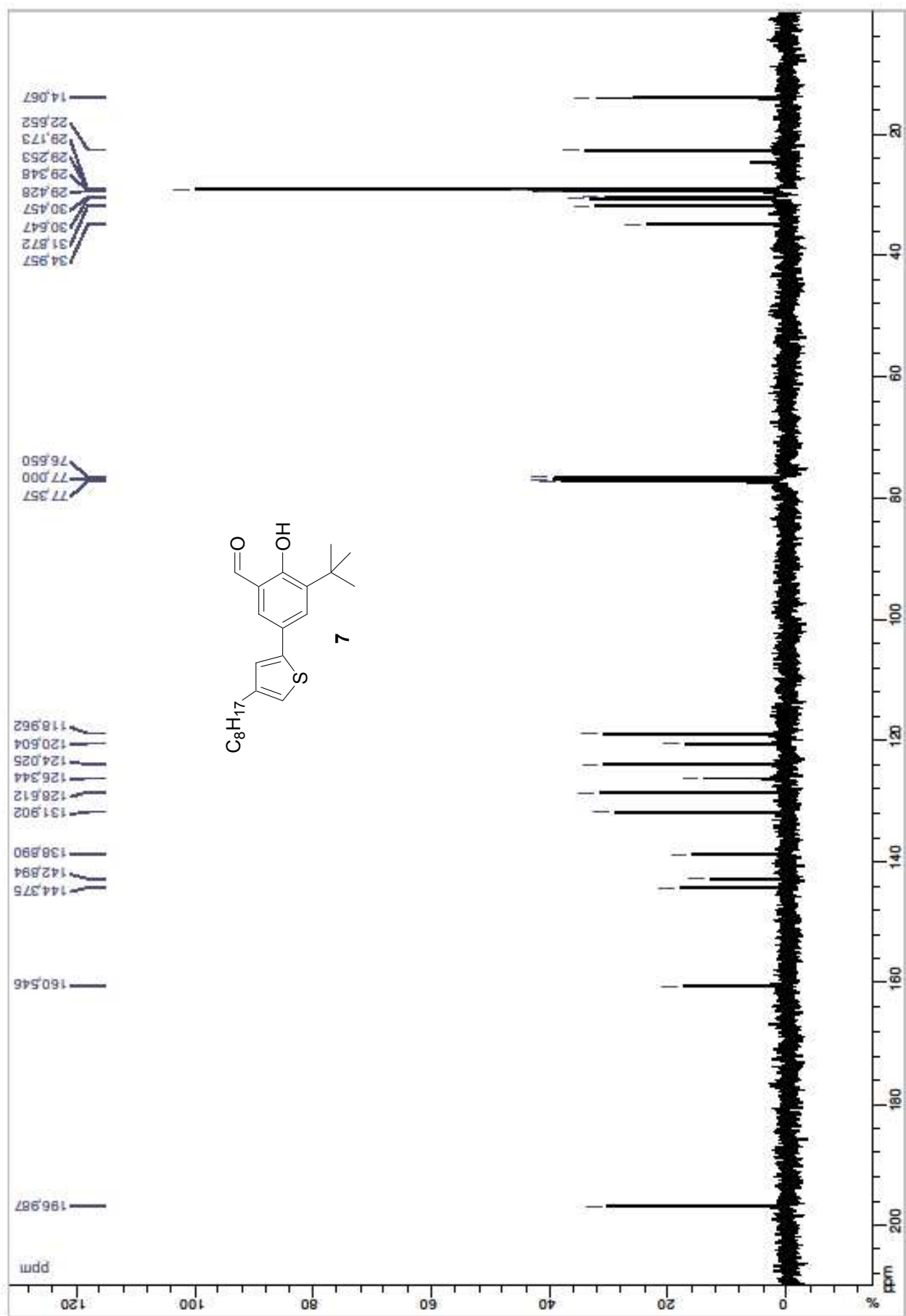
(R)-1-Cyclohexyl-2-nitro-ethanol **12e**. Solvent for flash chromatography : pentane / diethyl ether 4/1. Yellowish oil, $[\alpha]_D^{20}$ - 15.8 (c 0.99, CHCl₃) for 79 % ee, lit^[5] $[\alpha]_D$ + 18.7 (c 0.4, CHCl₃) for 76 % ee material. The ee was determined by HPLC analysis using an IB column (flow rate 0.8 mL.min⁻¹; 98 % hexane, 2 % ethanol, λ = 205 nm, 20 °C), which resolved both enantiomers (t_R = 19.0 min (major), t_S = 20.0 min). The absolute stereochemistry was assigned as (*R*)-based on

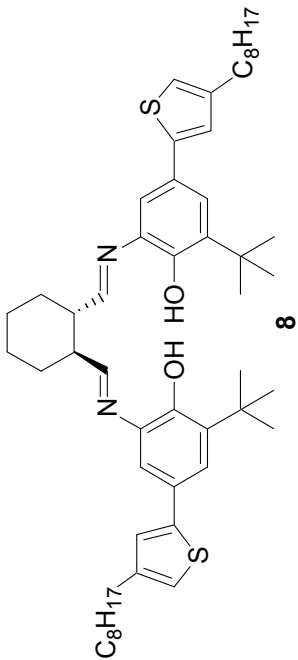
comparison of the measured rotation with the literature value. ^1H NMR (360 MHz, CDCl_3) δ 4.46 (dd, $J = 3.2, 12.9$ Hz, 1H), 4.40 (dd, $J = 8.9, 12.9$ Hz, 1H), 4.10-4.04 (m, 1H), 2.74 (bs, 1H), 1.83-1.75 (m, 3H), 1.71-1.62 (m, 2H), 1.47-1.40 (m, 1H), 1.28-1.01 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 79.3, 72.8, 41.3, 28.7, 27.8, 26.0, 25.8, 25.7. MS (CI) : 208 $[\text{M}+(\text{NH}_3)_2]^+$ (13), 191 $[\text{MNH}_4^+]$ (100), 173 (3), 69 (5).

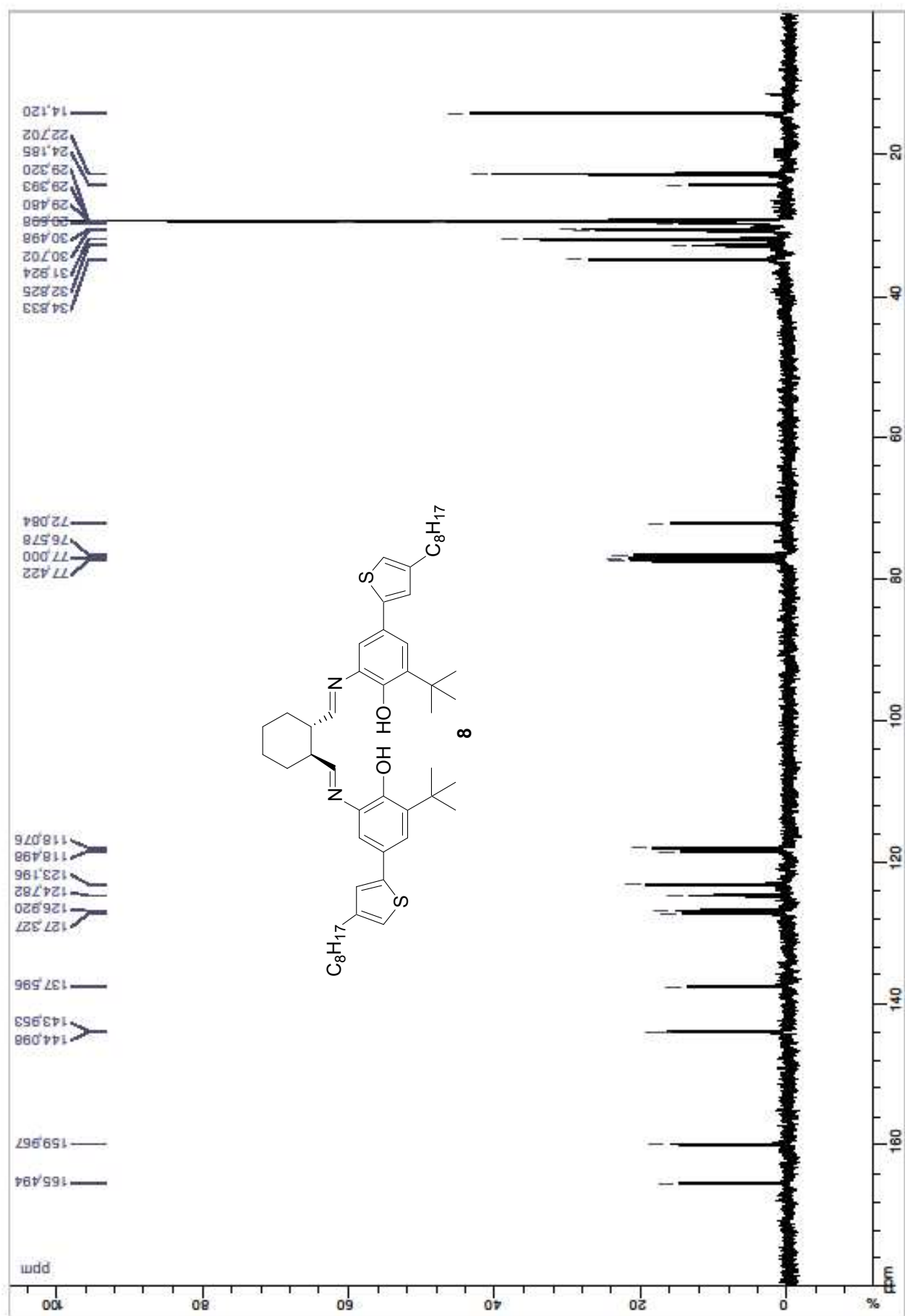
(R)-1-Nitro-octan-2-ol **12f**. Solvent for flash chromatography : pentane / diethyl ether 4/1. Yellowish oil, $[\alpha]_{\text{D}}^{20} - 6.8$ (c 1.02, CHCl_3) for 59 % ee, lit^[6] $[\alpha]_{\text{D}} + 12.0$ (c 1.1, CH_2Cl_2) for 96 % ee material. The ee was determined by HPLC analysis using an IB column (flow rate 0.8 mL.min⁻¹; 98 % hexane, 2 % ethanol, $\lambda = 205$ nm, 20 °C), which resolved both enantiomers ($t_{\text{R}} = 16.1$ min (major), $t_{\text{S}} = 16.9$ min). The absolute stereochemistry was assigned as *(R)*-based on comparison of the measured rotation with the literature value. ^1H NMR (300 MHz, CDCl_3) δ 4.44 (dd, $J = 3.2, 12.3$ Hz, 1H), 4.39 (dd, $J = 7.9, 12.3$ Hz, 1H), 4.35-4.20 (m, 1H), 2.94 (bs, 1H), 1.71-1.15 (m, 10H), 0.94-0.82 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 80.6, 68.7, 33.7, 31.5, 28.9, 25.0, 22.4, 13.9. MS (CI) : 210 $[\text{M}+(\text{NH}_3)_2]^+$ (20), 193 $[\text{M}+\text{NH}_4^+]$ (100), 69 (40).

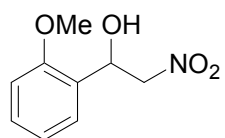
⁶ Gruber-Khadjawi, M.; Purkarthofer, T.; Skranc, W.; Griengl, H. *Adv. Synth. Catal.* **2007**, 349, 1445-1450.



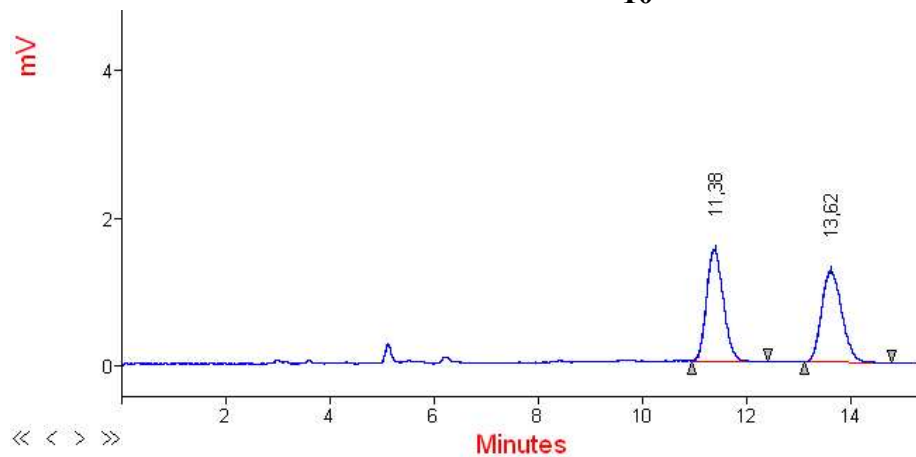




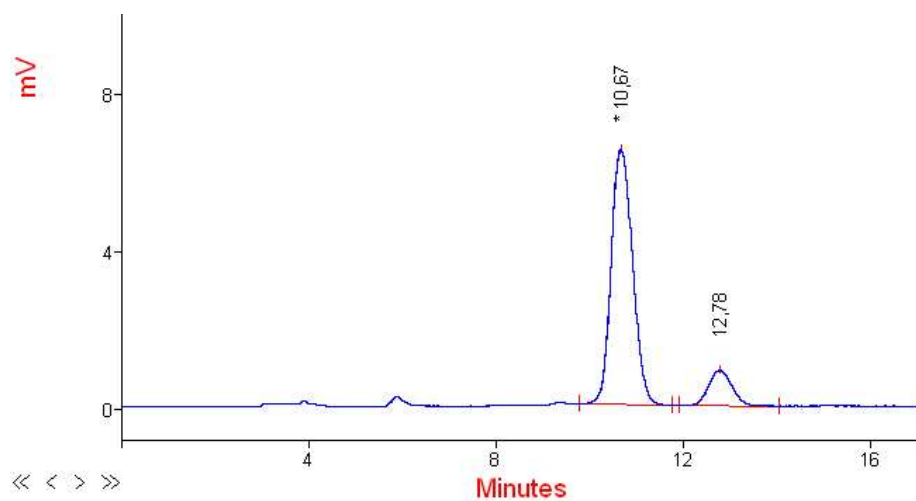




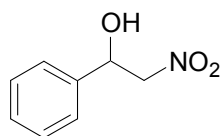
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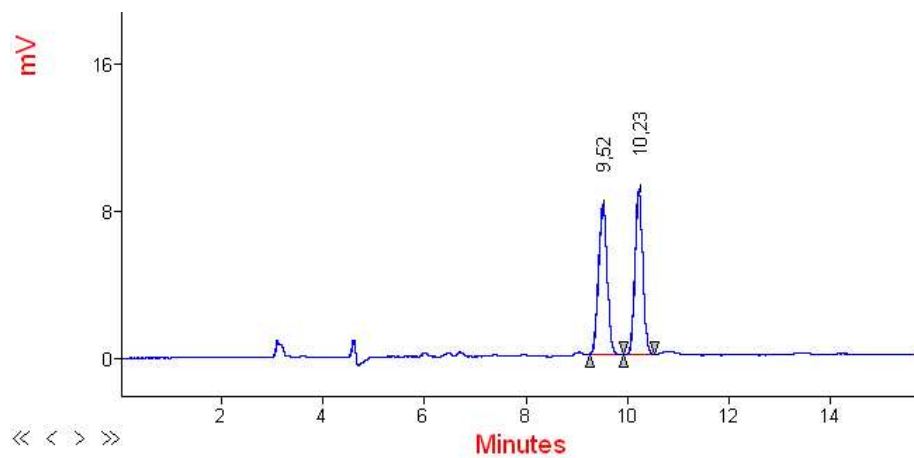
	Tr (min)	Aire	% Aire
1	11,38	34,15	50,07
2	13,62	34,05	49,93
Total		68,20	100,00



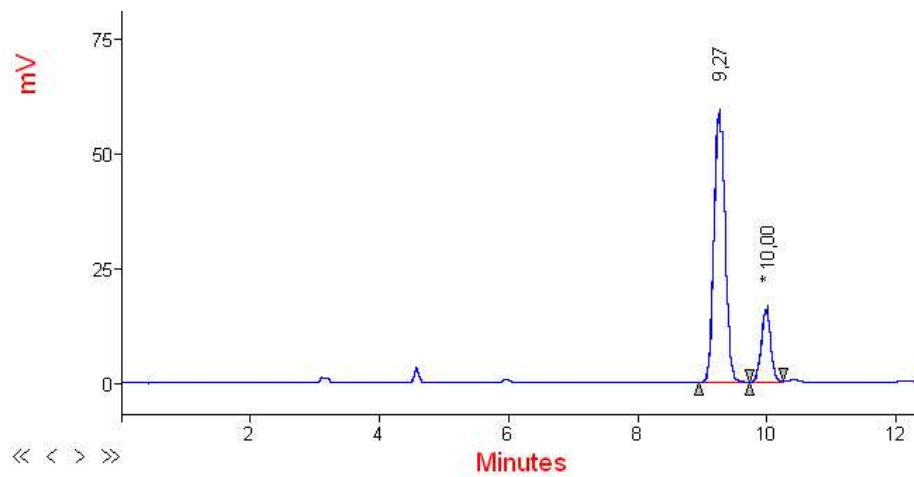
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1	10,67	208,57	86,86
2	12,78	31,54	13,14
Total		240,11	100,00



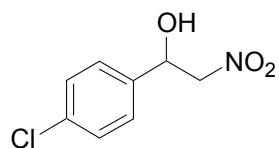
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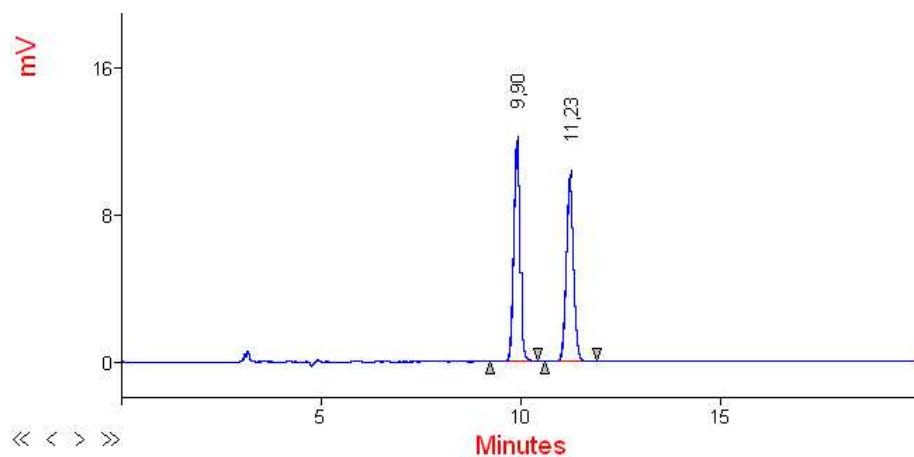
	Tr (min)	Aire	% Aire
1	9,52	95,78	50,12
2	10,23	95,33	49,88
Total		191,11	100,00



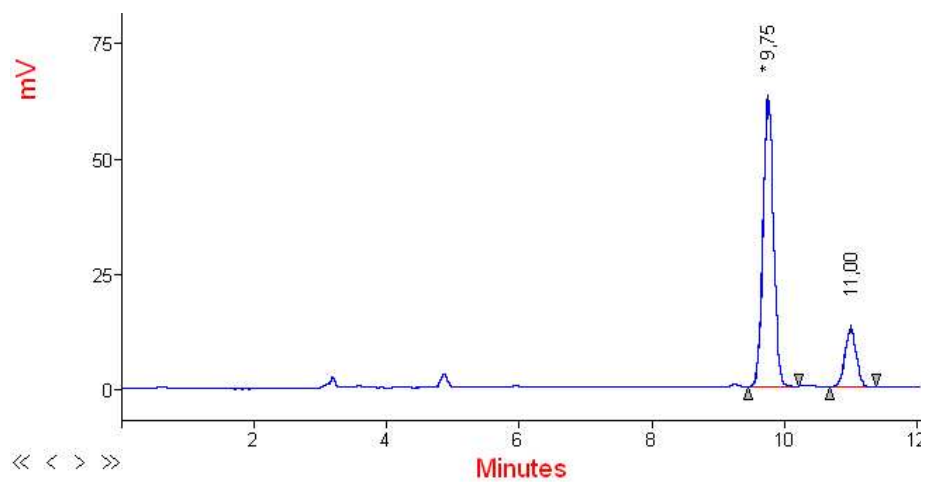
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1	9,27	697,90	81,14
2	10,00	162,24	18,86
Total		860,14	100,00



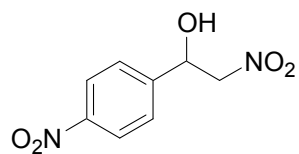
12b



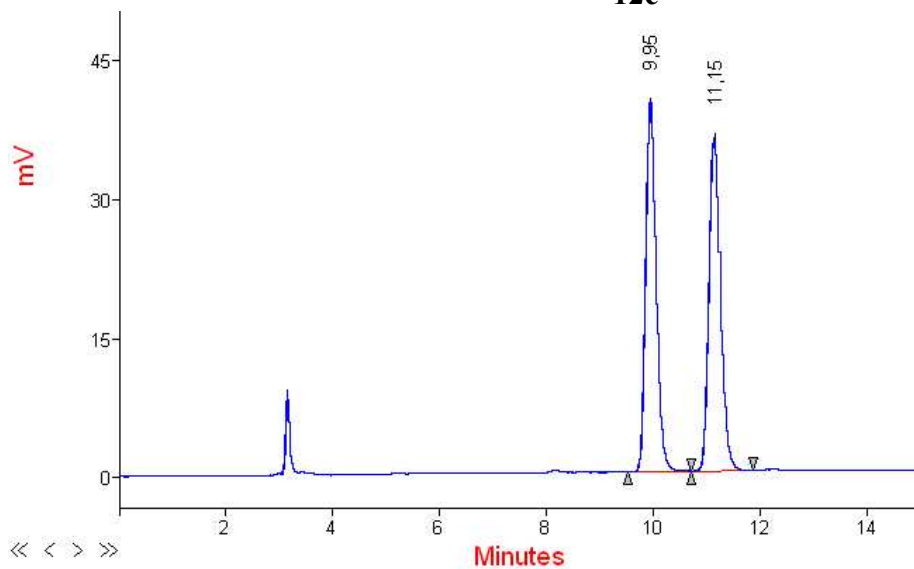
	Tr (min)	Aire	% Aire
1	9,90	127,83	49,94
2	11,23	128,15	50,06
Total		255,99	100,00



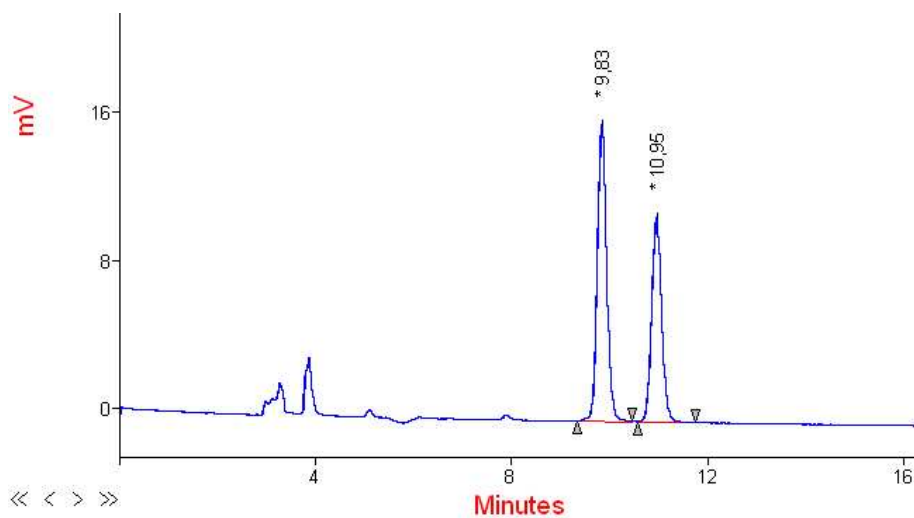
	Tr (min)	Aire	% Aire
1	9,75	692,79	81,91
2	11,00	153,00	18,09
Total		845,79	100,00



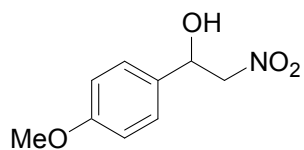
12c



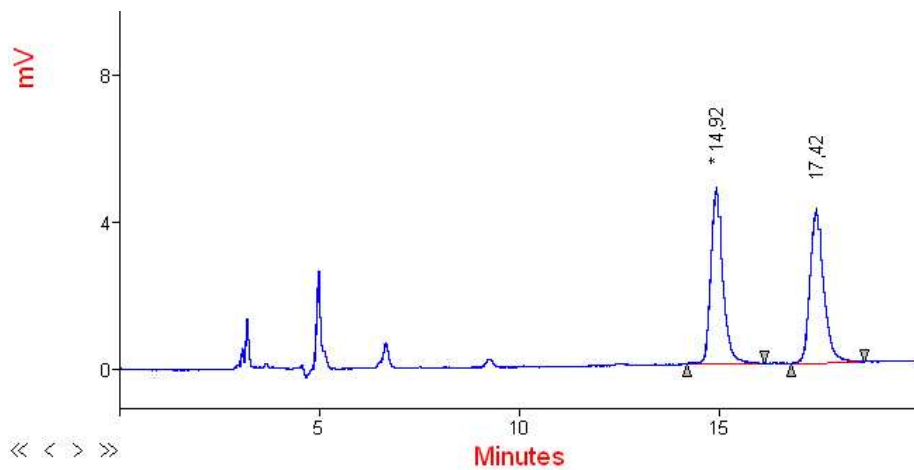
	Tr (min)	Aire	% Aire
1	9,95	546,47	49,96
2	11,15	547,38	50,04
Total		1093,85	100,00



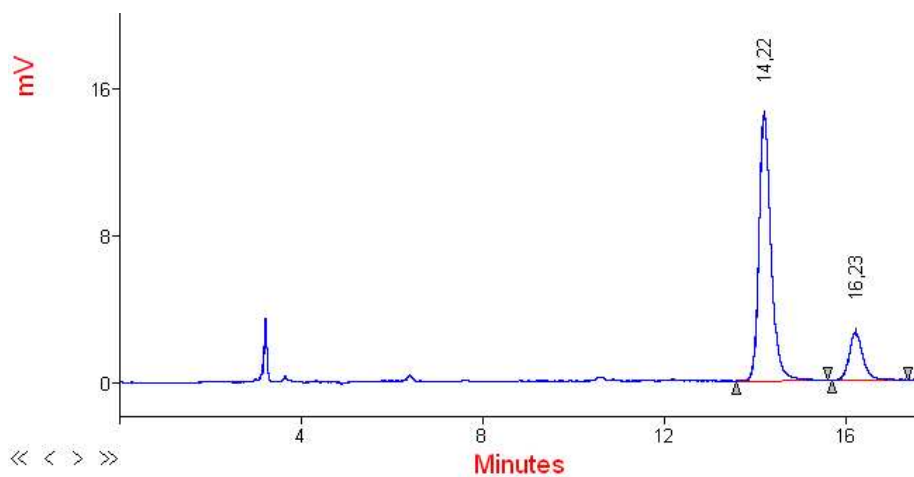
	Tr (min)	Aire	% Aire
1	9,83	213,13	57,31
2	10,95	158,77	42,69
Total		371,90	100,00



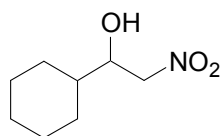
12d



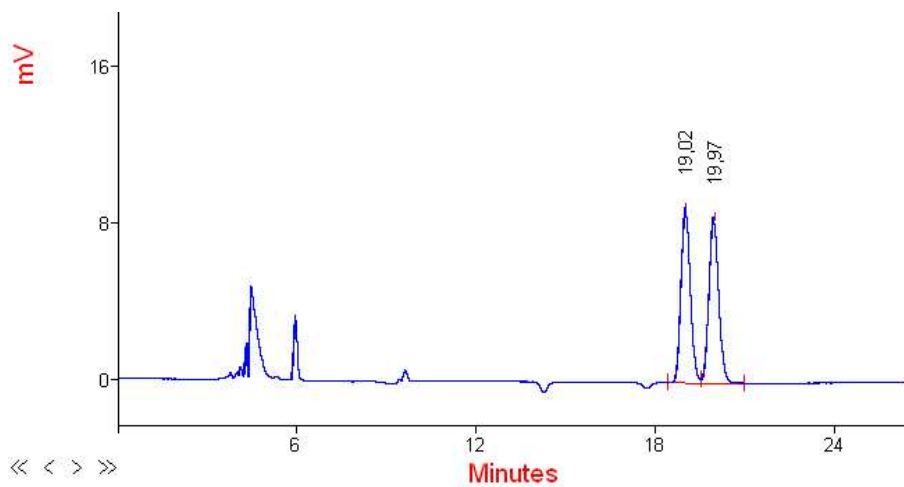
	Tr (min)	Aire	% Aire
1	14,92	98,18	49,75
2	17,42	99,17	50,25
Total		197,35	100,00



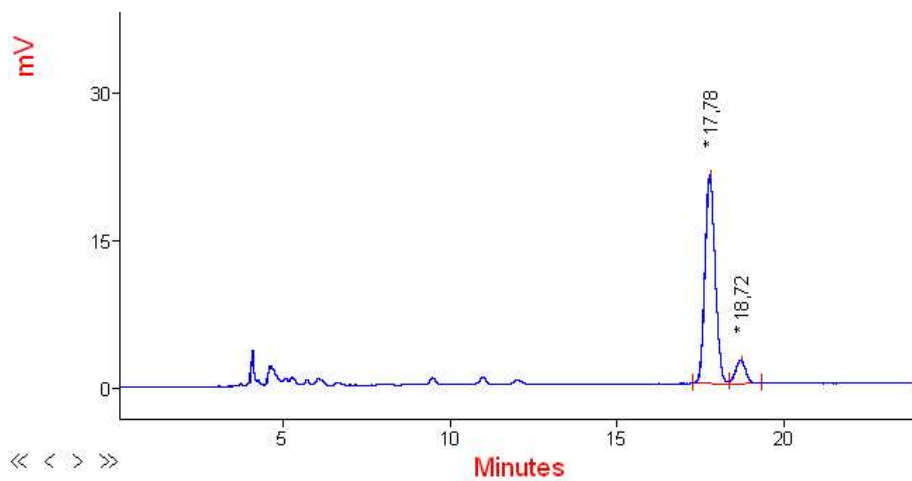
	Tr (min)	Aire	% Aire
1	14,22	266,89	83,08
2	16,23	54,37	16,92
Total		321,26	100,00



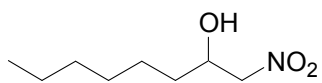
12e



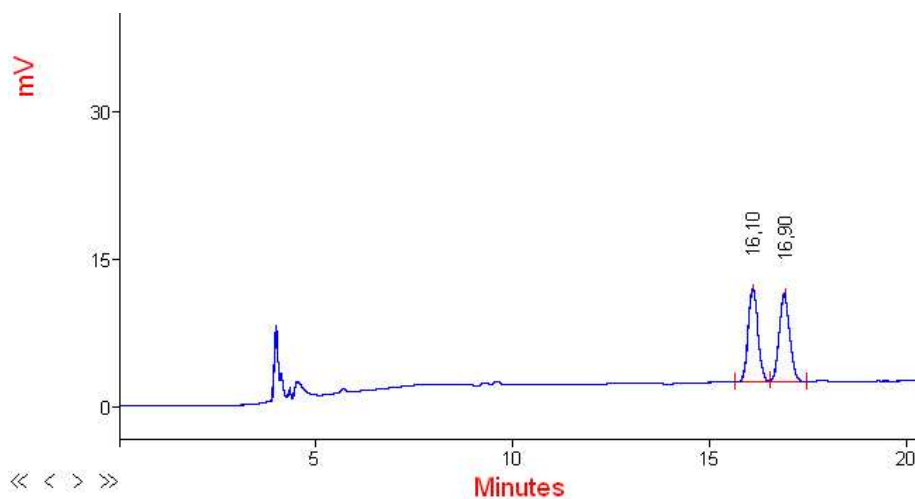
	Tr (min)	Aire	% Aire
1	19,02	193,01	49,98
2	19,97	193,18	50,02
Total		386,19	100,00



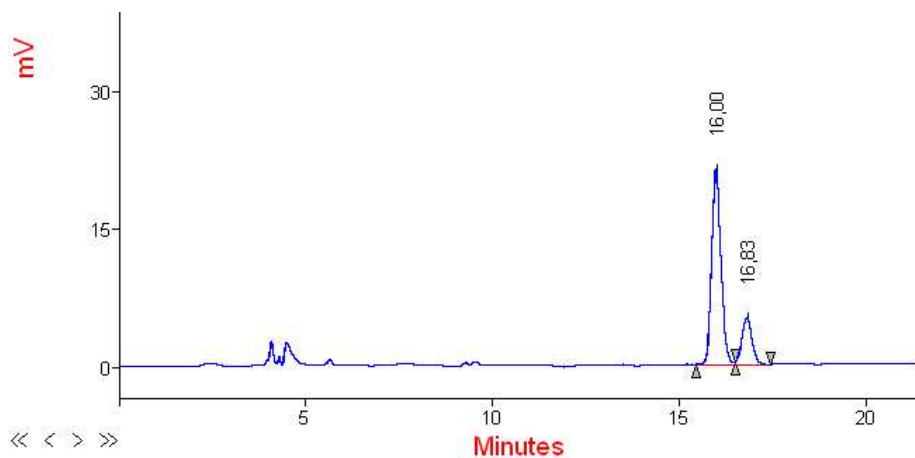
	Tr (min)	Aire	% Aire
1	17,78	443,08	89,49
2	18,72	52,02	10,51
Total		495,10	100,00



12f



	Tr (min)	Aire	% Aire
1	16,10	165,59	49,57
2	16,90	168,45	50,43
Total		334,04	100,00



	Tr (min)	Aire	% Aire
1	16,00	371,95	79,39
2	16,83	96,54	20,61
Total		468,49	100,00