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Supplementary Information

General.

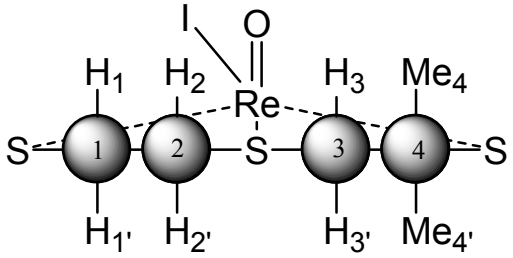
Most experiments were performed using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (THF) or from phosphorus pentoxide (CH_2Cl_2). Starting materials were purchased from Alfa Aesar (2,2-dimetyloxirane and $KReO_4$) or from Acros. $KReO_4$ was converted to the $ReOCl_3(PPh_3)_2$ precursor as reported previously.[1] Synthesis of 2,2-dimetylthiirane **9** was adapted from the literature.[2] Column chromatography purifications were performed in air over silica gel (Merck Geduran 60, 0.063-0.200 mm). ^{1}H NMR spectra were recorded at 200.13 MHz or 500.13 MHz respectively on a Bruker DPX 200 and AC-500 spectrometers. ^{13}C-NMR spectra at 50.4 MHz were recorded on a Bruker DPX 200. COSY, HMQC and HMBC spectra were recorded on a Bruker DPX AC-500 spectrometer. IR spectra were recorded on a Mattson 3000 FTIR spectrometer. UV spectra were recorded on a JASCO V-550 UV-Vis spectrometer. Specific rotations (in deg cm^2g^{-1}) were measured in a 10 cm thermostated quartz cell on a Jasco-P1010 polarimeter. High resolution mass spectra were obtained on a Varian MAT 311 instrument at CRMPO, University of Rennes1. Elemental analyses were performed by the CRMPO, University of Rennes 1.

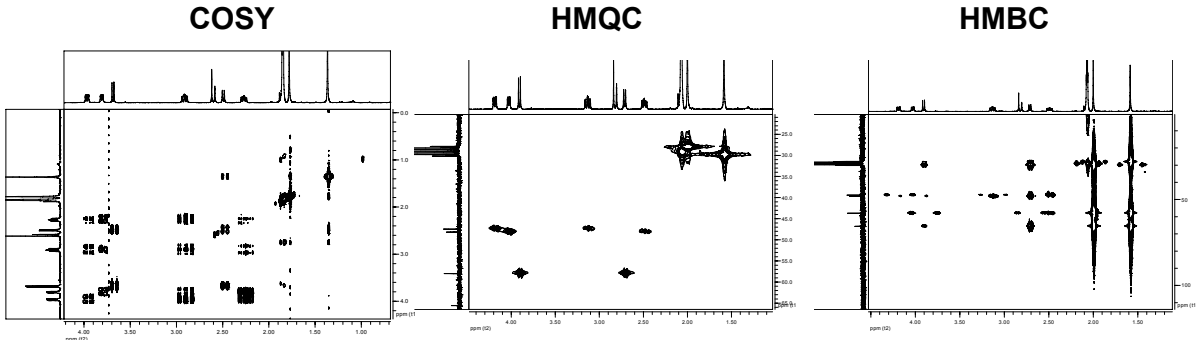
Synthesis of 1,1-dimethyl-1,5-dithiol-3-thiapentane 10

2.2 mL of 2,2-dimetylthiirane **9** (25 mmol) were slowly added to a mixture of ethane-1,2-dithiol (10 mL) and NEt_3 (2 mL) at 0 °C. After stirring for 16 hours at room temperature, the mixture was filtered over silica gel with methylene chloride. Then the solvent was stripped off and impurities were precipitated with pentane yielding 2.3 mL (2.76 g, 60 %) of the expected compound **10** as a viscous and translucid liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.90-2.65 (m, 6H, SCH_2); 2.15 (s, 1H, SH); 1.70 (ls, 1H, SH); 1.42 (s, 6H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$): δ 50.1 (SCH_2); 45.5 (SCH_2CMe_2); 38.7 (SCH_2); 31.6 (two CH_3); 25.1 (SCH_2). HR-MS (EI) *m/Z* 168.0093 $[M]^{+}$; calcd. for $C_5H_{12}S_3$ 168.01012.

Synthesis of (iodo) (1,1-dimethyl-3-thiapentane-1,5-dithiolato) oxorhenium(V) 4

2 mL of iodomethane (large excess *ca.* 60 eq.) were added to a solution of 250 mg of (ethanethiolato)(1,1-dimethyl-3-thiapentane-1,5-dithiolato)oxorhenium(V) (**5**, 0.56 mmol) or (butane-2-thiolato)(1,1-dimethyl-3-thiapentane-1,5-dithiolato)oxorhenium(V) (**6**, 0.53 mmol) in 30 mL of CH_2Cl_2. After refluxing for 16 hours, the solvents were stripped off. The residue was purified by chromatography over silica gel (pentane/acetone 2:1 to 1:2). Further partial precipitations (pentane/ CH_2Cl_2) yielded 228 mg (0.45 mmol, 80%) and 192 mg (0.38 mmol, 72%) from **5** and **6** respectively. ^{1}H NMR (500 MHz, acetone-d_6): δ 4.19 (ddd, 1H, H_1, J = 13.1, 5.05 and 1.3 Hz); 4.03 (ddd, 1H, H_2, J = 10.6, 4.3 and 1.3 Hz); 3.91 (d, 1H, H_3, *AB* system, SCH_2CMe_2S, J = 10.7 Hz); 3.13 (ddd, 1H, $H_{1'}$, J = 14.2, 13.1 and 4.3 Hz); 2.71 (dd, 1H, $H_{3'}$, *AB* system, SCH_2CMe_2S, J = 10.7 Hz); 2.49 (ddd, 1H, $H_{2'}$, J = 14.3, 10.6 and 5.05 Hz); 1.96 (s, 3H, Me_4); 1.58 (s, 3H, $Me_{4'}$). ^{13}C NMR (50 MHz, acetone-d_6): δ 66.9 (C_4); 59.4 (C_3); 49.5 (C_2); 48.8 (C_1); 31.4 ($Me_{4'}$); 29.5 (Me_4). FT-IR (Nujol, cm^{-1}): 1458 (m), 1414 (m), 1383 (m), 1287 (m), 1225 (w), 1138 (m), 1084 (w), 968 (s, Re=O), 847 (w). UV-Vis ($CHCl_3$): λ_{max} (nm) ($log\ \varepsilon$): 393 (3.4), 373 (3.3), 272 (3.9), 235 (4.2). Anal. Calcd. (%) for $C_6H_{12}OIS_3Re$: C, 14.15; H, 2.37; S, 18.88. Found: C, 14.53; H, 2.51; S, 19.04. Sublimation at 170°C.





Synthesis of enantioenriched SPY-5-52-*C*-CD$_{220}$(+)-4 and SPY-5-52-*A*-CD$_{220}$(-)-4 from SPY-5-54-*C*-(+)-5 and SPY-5-54-*A*-(-)-5 respectively.

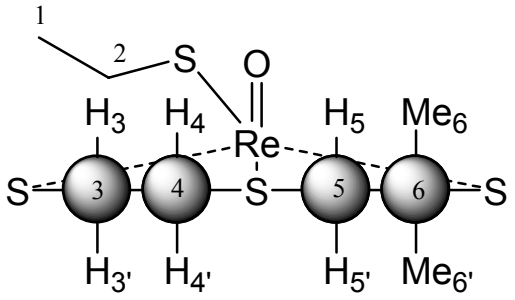
15 mL of methyl iodine (large excess) were added to 20 mg of (ethanethiolato)(1,1-dimethyl-3-thiapentane-1,5-dithiolato)oxorhenium(V) SPY-5-54-*C*-(+)-**5** (0.45 mmol; purity : *ee* 97 %). After refluxing for 16 hours, solvent was stripped off. The residue was purified by chromatography over silica gel (pentane/acetone 2:1 to 1:2). Two partial precipitations (acetone/pentane) yielded 16 mg (0.34 mmol; 76%) of the expected iodo adduct. The enantiomeric excess was determined to be 82 % of (iodo) (1,1-dimethyl-3-thiapentane-1,5-dithiolato) oxorhenium(V) SPY-5-52-*C*-CD$_{220}$(+)-**4** by HPLC analysis with a chiral stationary phase column, Chiralpak AS-H (hexane/ethanol = 1/1) (see below). Unlike the green plate shape obtained with the racemic compound, green needles, suitable for X-ray resolution, were grown from slow diffusion of pentane in saturated acetone solution.

The same procedure using SPY-5-54-*C*-(+)-**5** with 99% *ee* gave SPY-5-52-*A*-CD$_{220}$(-)-**4** , with 76 % yield and with 89% *ee*, as determined by HPLC analysis with a chiral stationary phase column, Chiralpak AS-H (hexane/ethanol = 1/1). Green needles, suitable for X-ray resolution, were grown from slow diffusion of pentane in saturated acetone solution.

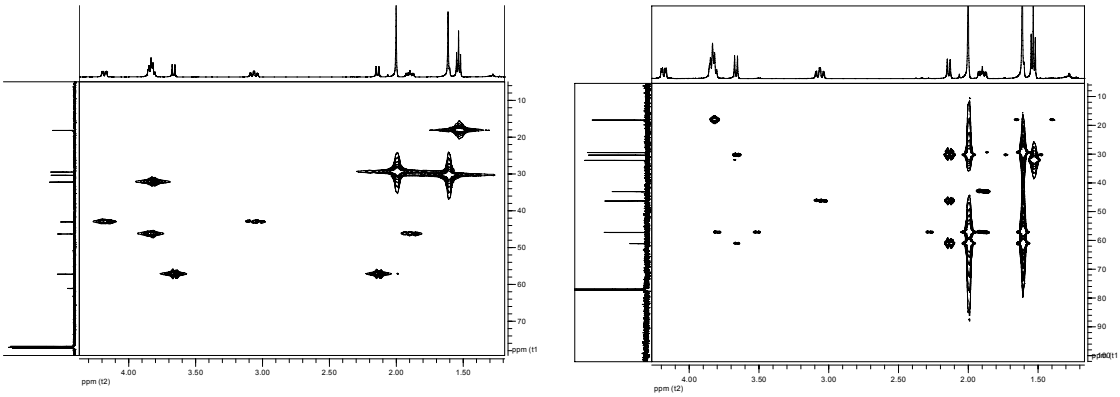
Synthesis of (ethanethiolato) (1,1-dimethyl-3-thiapentane-1,5-dithiolato) oxorhenium(V) 5

520 µL of 1,1-dimethyl-1,5-dithiol-3-thiapentane **10** (3.36 mmol, 1 eq.) and 250 µL of ethanethiol (3.36 mmol, 1 eq.) were added to a suspension of 2.8 g of $ReOCl_3(PPh_3)_2$ **11** (3.36 mmol, 1 eq.) and 1.4 g of sodium acetate (14.3 mmol, 4.3 eq.) in 100 mL of freshly distilled THF. The mixture was refluxed for 16 hours before evaporation. The residue was purified by

chromatography over silica gel (pentane/CH_2Cl_2 2:1 to 1:2). Further partial precipitations (pentane/CH_2Cl_2) yielded 0.844 g (1.9 mmol, 57%) of the expected red compound **5**. Red crystals were grown by slow diffusion of pentane into a saturated CH_2Cl_2 solution of the above compound. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.19 (ddd, 1H, H_3, J = 13.3, 4.7 and 1.5 Hz); 3.83 (q, 2H, CH_2CH_3, J = 7.5 Hz); 3.90-3.75 (m, 1H, H_4); 3.66 (d, 1H, H_5, *AB* system, J = 10.3 Hz); 3.06 (ddd, $H_{3'}$, J = 14, 4 and 1 Hz); 2.13 (d, 1H, $H_{5'}$, *AB* system, J = 10.3 Hz); 2.0 (s, 3H, Me_6); 1.93-1.84 (m, 1H, $H_{4'}$); 1.66 (s, 3H, $Me_{6'}$); 1.54 (t, 3H, CH_2CH_3, J = 7.5 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 61.2 (C_6); 57.3 (C_5); 46.4 (C_4); 43.2 (C_3); 32.3 (C_2); 30.5 ($Me_{6'}$); 29.6 (Me_6); 18.3 (Me_1). FT-IR (Nujol, cm^{-1}): 1452 (m), 1412 (m), 1365 (m), 1247 (m), 1159 (w), 1101 (w), 956 (s, Re=O), 841 (w), 756 (w). UV-Vis ($CHCl_3$): λ_{max} (nm) ($log\ \varepsilon$): 512 (2.5), 392 (3.5); 350 (3.4); 285 (3.6); 258 (3.9); 231 (4.0). Anal. Calcd. (%) for $C_8H_{17}OS_4Re$: C, 21.66; H, 3.86; S, 28.91. Found: C, 21.74; H, 3.89; S, 28.78. Sublimation at 145°C.



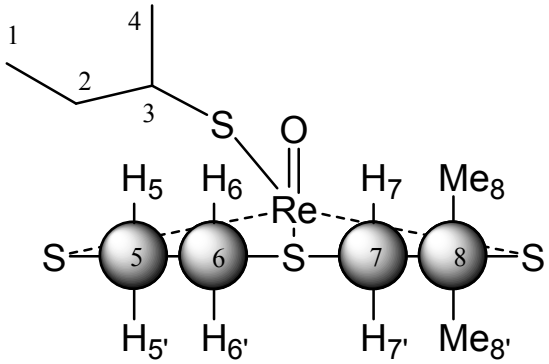
HMQC **HMBC**

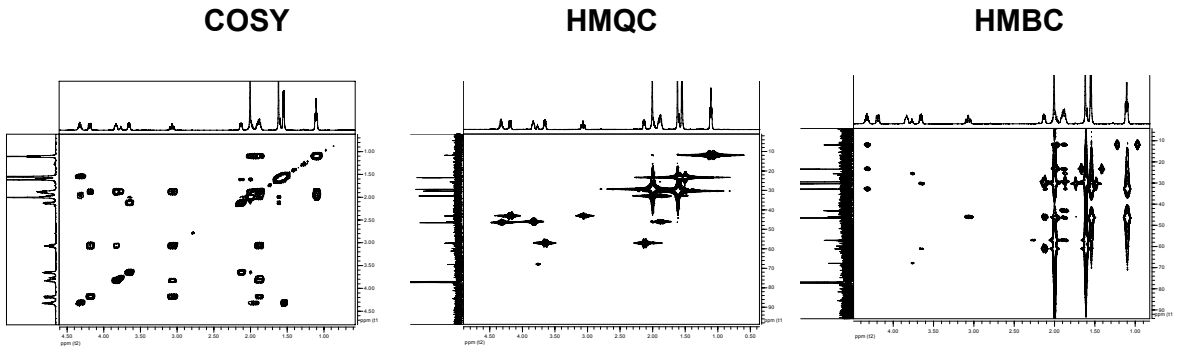


Synthesis of (butane-2-thiolato) (1,1-dimethyl-3-thiapentane-1,5-dithiolato) oxorhenium(V) 6 (two diastereomers)

760 µL of 1,1-dimethyl-1,5-dithiol-3-thiapentane **10** (4.9 mmol, 1.1 eq.) and 520 µL of butane-2-thiol (4.6 mmol, 1 eq.) were added to a suspension of 3.8 g of $ReOCl_3(PPh_3)_2$ **11** (4.6 mmol, 1 eq.) and 2 g of sodium acetate (20.4 mmol, 4.4 eq.) in 150 mL of freshly distilled THF. The mixture was refluxed for 16 hours before evaporation. The residue was purified by chromatography over silica gel (pentane/ CH_2Cl_2 2:1 to 1:2). Further partial precipitations (pentane/CH_2Cl_2) yielded 1.194 g (2.53 mmol, 55%) of the expected red compound **6**. Red crystals were grown by slow diffusion of pentane into a saturated CH_2Cl_2 solution of the above compound. ^{1}H NMR (500 MHz, $CDCl_3$) (two diastereoisomers): δ 4.33 (m, 1H, H_6); 4.20 (d, 0.5 H, H_5 one diast., J = 12.9 Hz); 4.19 (d, 0.5 H, H5 one diast., J = 12.9

Hz); 3.83 (m, 1H, $H_{6'}$); 3.66 (d, 0.5 H, H_7 one diast., J = 10 Hz); 3.65 (d, 0.5 H, H_7 one diast., J = 10.1 Hz); 3.1 (m, 1H, $H_{5'}$); 2.13 (d, 0.5 H, $H_{7'}$ one diast., J = 9.7 Hz); 2.12 (d, 0.5 H, $H_{7'}$ one diast., J = 10.1 Hz), 2.0 (s, 3H, Me_9); 1.98 (m, 1H, H_3); 1.92-1.86 (m, 2H, H_2); 1.62 (s, 3H, $Me_{9'}$); 1.55 (d, 3H, H_4, J = 6.8 Hz); 1.11 (t, 1.5H, H_1 one diast., J = 7.3 Hz); 1.10 (t, 1.5H, H_1 one diast., J = 7.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 61.4 and 61.2 (C_8); 57.1 and 57.0 (C_7); 46.5 and 46.4 (C_6); 46.3 and 46.2 (C_2); 43.3 and 43.2 (C_5); 33.0 and 32.9 (C_3); 30.5 ($Me_{9'}$); 29.5 (Me_9); 23.6 (C_4); 12.1 and 12.0 (C_1). FT-IR (Nujol, cm^{-1}): 1443 (m), 1410 (m), 1367 (m), 1286 (m), 1213 (w), 1136 (w), 1086 (w), 991 (w), 958 (s, Re=O), 847 (w), 793 (w). UV-Vis ($CHCl_3$): λ_{max} (nm) (log ε): 395 (3.5), 347 (3.4), 290 (3.6), 255 (3.9), 234 (4.0). Anal. Calcd. (%) for $C_{10}H_{21}OS_4Re$: C, 25.46; H, 4.49; S, 27.19. Found: C, 25.62; H, 4.59; S, 27.25.

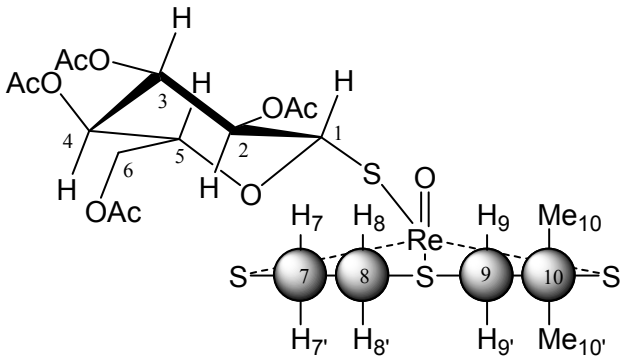




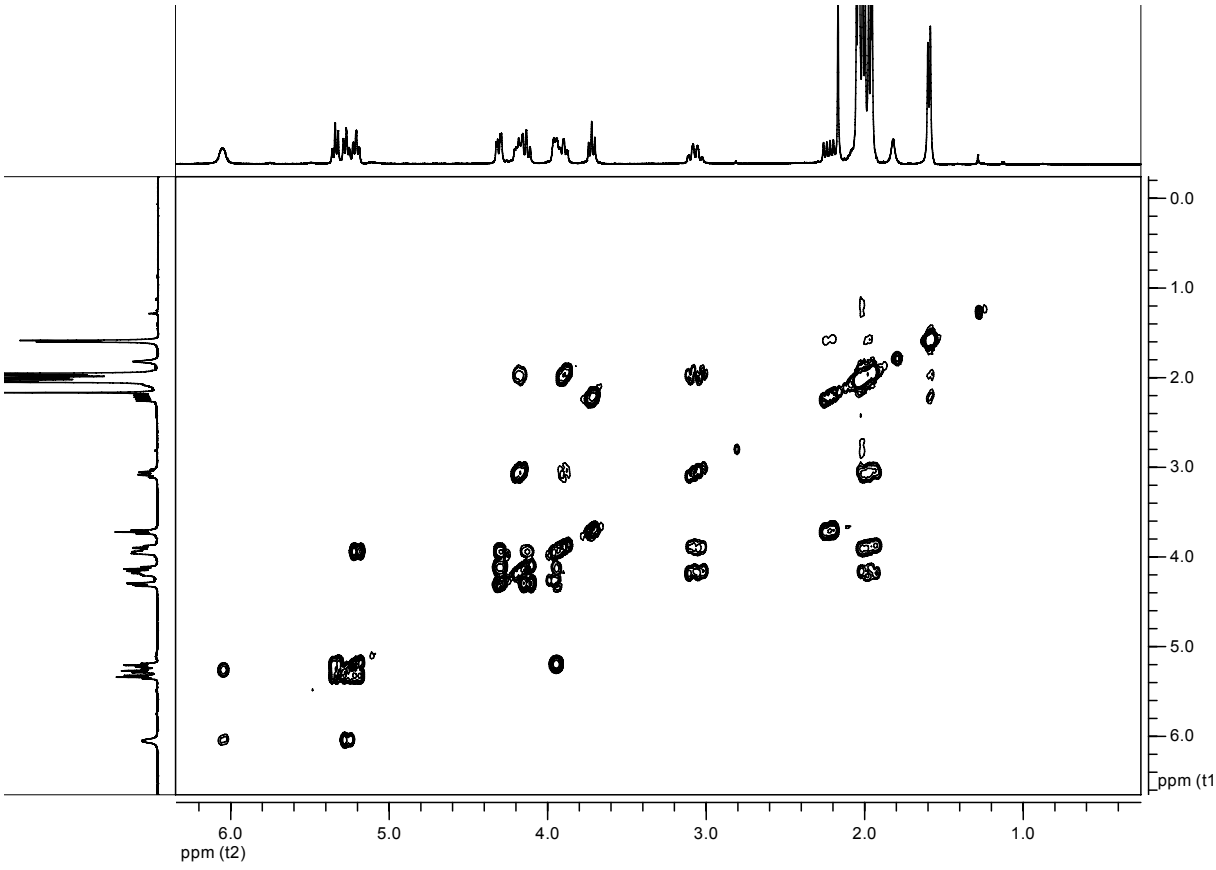
Synthesis of (tetraacetate-1-thiolato-β-D-glucopyranose)(1,1-dimethyl-3-thiapentane-1,5-dithiolato)oxorhenium(V) 7 (two diastereomers)

210 µL of 1-(2-mercaptoethylthio)-2-methylpropane-2-thiol **10** (1.37 mmol, 1 eq.) and 500 g of β-D-Thioglucose tetraaccetate (1.37 mmol, 1 eq.) were added to a suspension of 1.14 g of $ReOCl_3(PPh_3)_2$ **11** (1.37 mmol, 1 eq.) and 0.6 g of sodium acetate (6.2 mmol, 4.4 eq.) in 80 mL of freshly distilled THF. The mixture was refluxed for 16 hours before evaporation. The residue was purified by chromatography over silica gel (pentane/ CH_2Cl_2 1:1 to 0:1). Further partial precipitations (pentane/CH_2Cl_2) yielded 0.500 g (0.87 mmol, 64 %) of the expected red compound **7**. ^{1}H NMR (500 MHz, $CDCl_3$) (two diastereomers): δ 6.05 (ls, 1 H, H_1); 5.19-5.35 (m, 3 H, H_2, H_3, H_4); 4.31 (d, 0.5 H, H_7 one diast, J = 12.3 Hz); 4.30 (d, 0.5 H, H_7 one diast, J = 12.2 Hz); 4.11-4 .21 (m, 2 H, H_6 and H_8); 3.88-3.96 (m, 2 H, $H_{7'}$ or $H_{8'}$ and H_6); 3.73 (unresolved d, 0.5 H, H_9 one diast.); 3.71 (unresolved d, 0.5 H, H_9 one diast.); 3.03-3.11 (m, 1 H, H_5); 2.25 (d, 0.5 H, $H_{9'}$ one diast., J = 10.4 Hz); 2.21 (d, 0.5 H, $H_{9'}$ one diast., J = 10.6 Hz); 1.95-2.09 (m, 16 H, 5 CH_3 and $H_{7'}$ or $H_{8'}$); 1.6 (s, 1.5 H, $Me_{10'}$ one diast.), 1.58 (s, 1.5 H, $Me_{10'}$ one diast.). NMR (50 MHz, $CDCl_3$) (two diastereomers): δ 170.7; 170.3; 169.6; 169.5; 169.4; 132.1; 131.9; 128.7; 128.4; 75.8; 75.7; 74.9; 73.4; 68.7; 68.8; 62.4; 61.7; 61.5; 57.1;

53.6; 46.5; 43.1; 30.4; 29.4; 20.8; 20.6. FT-IR (Nujol, cm^{-1}): 1753 (s), 1431 (m), 1369 (s), 1227 (s), 1088 (m), 1041 (s), 964 (s, Re=O), 912 (m), 810 (w), 733 (w). UV-Vis ($CHCl_3$): λ_{max} (nm) ($log\ \varepsilon$): 369 (3.5), 265 (3.9), 234 (4.0). Anal. Calcd. (%) for $C_{20}H_{31}O_{10}S_4Re$: C, 32.20; H, 4.19; S, 17.19. Found: C, 32.41; H, 4.26; S, 16.82.



COSY



X-Ray crystallography

Data Collection

The data were processed using the KappaCCD analysis programs.[3] The lattice constants were refined by least-squares refinements using 1713 reflections (1°<θ<28°) for **SPY-5-52-*A*-CD$_{220}$(-)-4**, 1941 reflections for **SPY-5-54-*A*-(-)-5**, 15807 reflections (1°<θ<29°) **for 5** and 3855 reflections (1°<θ<28°) for **6**. ANALYTICAL[4] absorption correction was applied to **5** data. No absorption correction was applied to for **SPY-5-52-*A*-CD$_{220}$(-)-4, SPY-5-54-*A*-(-)-5 and 6.** All the data collections were performed at room temperature.

Structure solution and refinement

5 and **6** crystallize in the monoclinic system. According to the observed systematic extinctions, both structures have been solved in the P2$_1$/*n* space group (No. 14). Both **SPY-5-52-*A*-CD$_{220}$(-)-4** and **SPY-5-54-*A*-(-)-5** crystallize in the orthorhombic system. According to the observed systematic extinctions, both structures have been solved in the P2$_1$2$_1$2$_1$ space group (No. 19).

All the structure have been solved by direct methods using the SIR97 program[5] combined with Fourier difference syntheses and refined against F [I/σ(I)>3] using CRYSTALS program.[6] The hydrogen atoms have been either found by Fourier difference and located theoretically based on the conformation and environment of the supporting atom. All the atomic displacement parameters for non-hydrogen atoms have been refined anistropically.

Selected bond lengths, inter atomic distances and angles are summarized in Tables 1 - 4 for SPY-5-52-*A*-CD$_{220}$(-)-**4,** SPY-5-54-*A*-(-)-**5, 5** and **6** respectively.

Table 1. Selected bond lengths (Å), inter-atomic distances (Å) and angles (deg.) for SPY-5-52-*A*-CD$_{220}$(-)-**4**

Re1 - I1	2.7001 (7)	Re1 - O1	1.679 (6)	Re1 - S1	2.278 (2)
Re1 - S2	2.334 (2)	Re1 - S3	2.286 (3)		
S2 - S1 - I1	99.04 (8)		S1 - S2 - S3	82.18 (9)	
S2 - S3 - I1	98.58 (9)		S1 - I1 - S3	74.75 (7)	
O1 - Re1 - I1	102.3 (3)		O1 - Re1 - S1	116.4 (3)	
O1 - Re1 - S3	116.2 (3)		O1 - Re1 - S2	101.5 (3)	

Table 2. Selected bond lengths (Å), inter-atomic distances (Å) and angles (deg.) for SPY-5-54-*A*-(-)-**5**

Re1 - S1	2.308 (3)	Re1 - S2	2.382 (3)	Re1 - S3	2.286 (2)
Re1 - S4	2.284 (3)	Re1 - O1	1.687 (5)		
S1 - S3 - S2	96.20 (9)		S4 - S2 - S3	82.67 (9)	
S2 - S4 - S1	92.8 (1)		S3 - S1 - S4	82.94 (9)	
O1 - Re1 - S4	116.3 (3)		O1 - Re1 - S3	114.7 (3)	
O1 - Re1 - S1	105.2 (3)		O1 - Re1 - S2	100.0 (2)	

Table 3. Selected bond lengths (Å), inter-atomic distances (Å) and angles (deg.) for racemic **5**

Re1 - O1	1.689 (10)	Re1 – S4	2.283 (4)	Re1 – S2	2.384 (3)
Re1 – S3	2.292 (4)	Re1 – S1	2.315 (4)		
O1 - Re1 – S4	116.2 (5)	O1 - Re1 – S3	115.2 (5)		

O1 - Re1 – S2	99.2 (4)	O1 - Re1 – S1	105.6 (4)
S4 – S2 – S3	82.3 (6)	S2- S3 – S1	96.4 (0)
S3 - S1 – S4	82.7 (7)	S2 – S4 - S1	92.7 (9)

Table 4. Selected bond lengths (Å), inter-atomic distances (Å) and angles (deg.) for **6**

Re1 - O1	1.689 (5)	Re1 - S1	2.304 (4)	Re1 - S2	2.385 (4)
Re1 - S3	2.293 (4)	Re1 - S4	2.298 (1)		
O1 - Re1 - S4	115.0 (2)		O1 - Re1 - S3	114.4 (2)	
O1 - Re1 - S1	105.8 (2)		O1 - Re1 - S2	100.8 (2)	
S2 - S4 - S1	91.9 (9)	S4 - S2 - S3		83.6 (9)	
S2 - S3 - S1	96.1 (0)	S4 - S1 - S3		84.0 (0)	

Chiral HPLC separation

• Analytical chiral HPLC experiments were performed on a screening unit composed of a Merck D-7000 system manager, Merck-Lachrom L-7100 pump, Merck-Lachrom L-7360 oven, Merck-Lachrom L-7400 UV-detector, and Jasco CD-1595 circular dichroism detector. Hexane, 2-PrOH and ethanol were of HPLC grade, and were degassed and filtered on a 0.45 μm membrane before use. Chiralcel OD-H, OJ, OB-H, Chiralpak AS, AS-H and AD from Chiral Technology Europa (Illkirch, France), Whelk-O1 (S,S) and Ulmo (S,S) from Regis (Morton Grove, USA) and Sumichiral OA-2500 from Sumitomo Chemicals (Osaka, Japan) chiral columns (250x4.6 mm) were used for the screening.
• For the analytical separations, the flow-rate is 1 ml/min and the columns are thermostated at 25°C.
• The sign given by the on-line circular dichroism detector is the sign of the compound at 220 nm in the solvent used for the chromatographic separation.
• Retention times Rt in minutes, retention factors $k_i = (Rt_i-Rt_0)/Rt_0$ and enantioselectivity $\alpha = k_2/k_1$ are given. Rt_0 was determined by injection of tri-tertio-butyl benzene.
• Semi-preparative separation was performed on Chiralcel OJ (250x10 mm) by successive injections on a Knauer unit composed of a Smartline 1000 pump, a Smartline 3900 autosampler, a Smartline 2500 UV-detector and a valve to collect separately the different isomers.

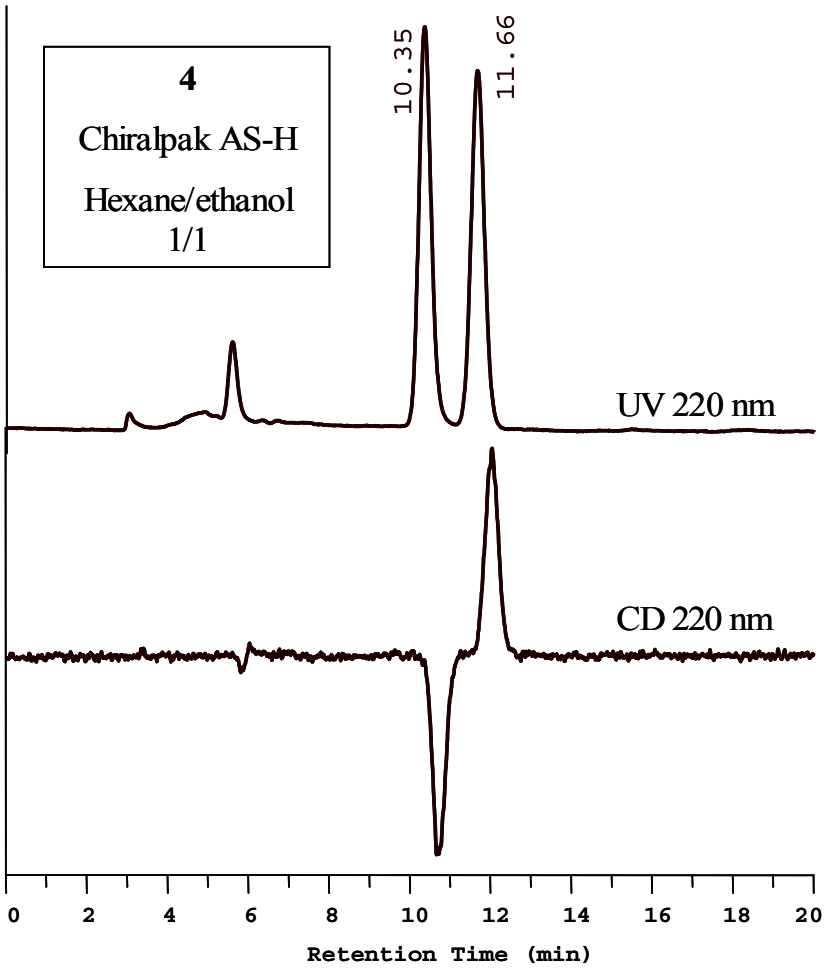
• The optical rotatory powers were measured on a 241 MC Perkin-Elmer polarimeter with a sodium lamp (589 nm) and a double-jacketed 10 cm cell at 25°C.

1) Chiral HPLC separation for compound **4**
2) Chiral HPLC separation for compound **5**
3) HPLC chromatogram for compound **6**
4) Chiral HPLC separation for compound **7**

1) Chiral HPLC separation for compound **4**

• The sample is dissolved ethanol, injected on the chiral column, and detected with an UV detector at 220 nm and with an on-line circular dichroism at 220 nm.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralcel OD-H	Hexane / Ethanol 1/1	6.61 (+)	1.13	6.81 (-)	1.20	1.06	< 0.5
	Hexane / 2-PrOH 8/2	28.58	8.22			1	0
Chiralcel OJ	Hexane / Ethanol 1/1	14.27 (-)	3.60	17.44 (+)	4.63	1.28	1.24
Chiralpak AS	Hexane / Ethanol 1/1	7.94 (-)	1.56	9.12 (+)	1.94	1.24	1.04
	Hexane / 2-PrOH 1/1	13.40 (-)	3.32	16.30 (+)	4.26	1.28	1.39
Chiralpak AS-H	Hexane / Ethanol 1/1	10.35 (-)	2.34	11.66 (+)	2.76	1.18	2.21



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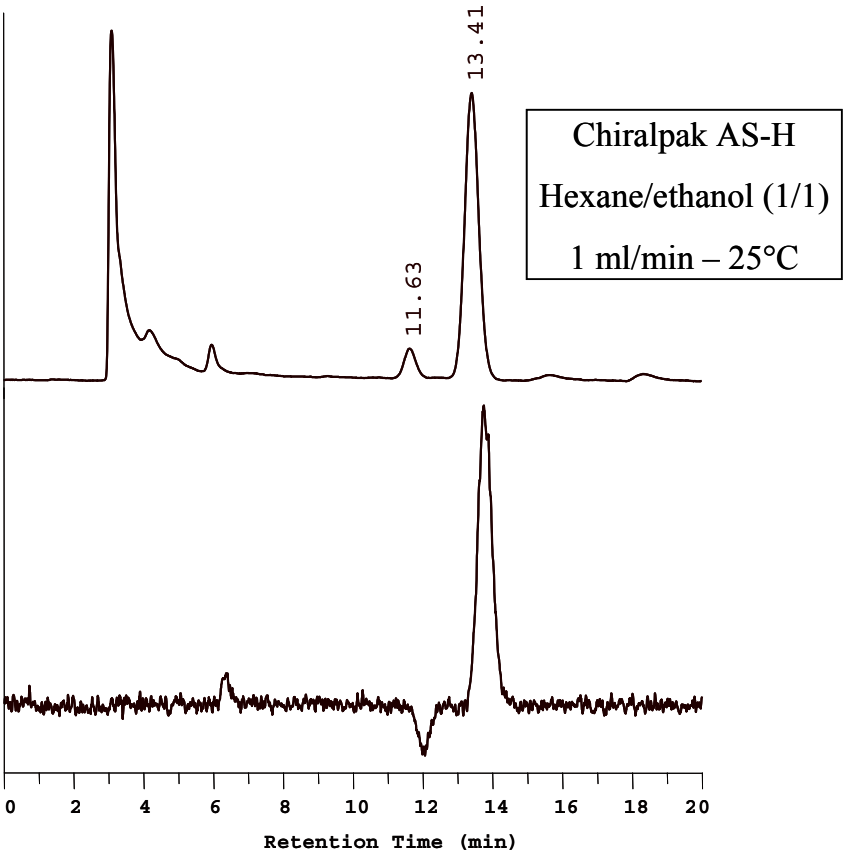
Determination of enantiomeric excess for CD_{220}(+)-**4** :

Column : Chiralpak AS-H
Mobile phase : Hexane/ethanol (1/1) – 1 ml/min
Detection : UV and CD at 220 nm



No.	RT	Area	Conc 1	BC
1	11.63	428615	8.721	BV
2	13.41	4486407	91.279	VB
		4915022	100.000	

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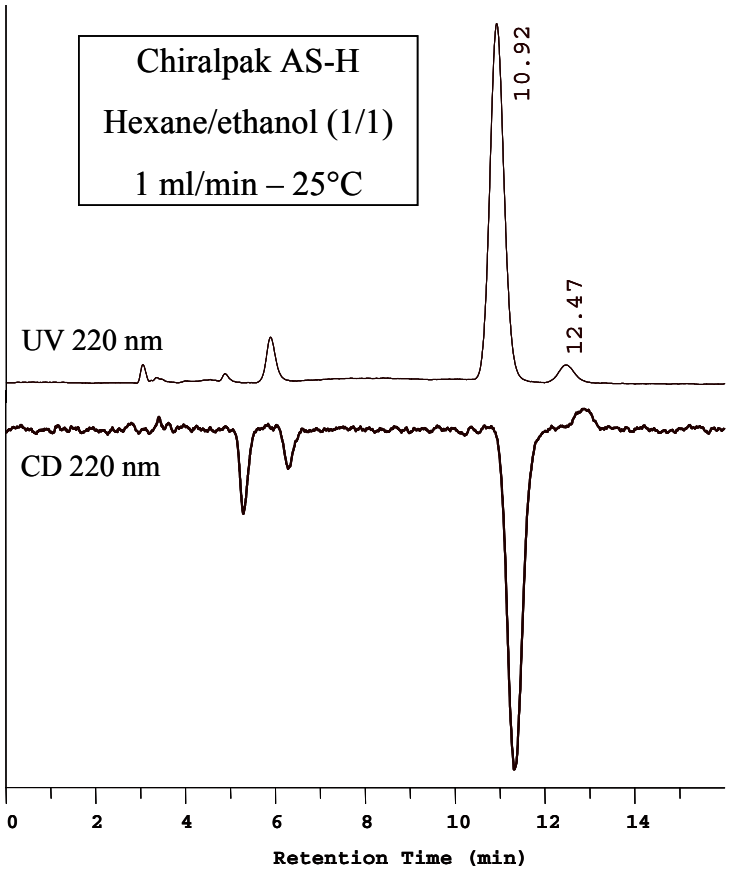
Determination of enantiomeric excess for CD_{220}(-)-**4** :

Column : Chiralpak AS-H
Mobile phase : Hexane/ethanol (1/1) – 1 ml/min
Detection : UV and CD at 220 nm



No.	RT	Area	Conc 1	BC
1	10.92	3742506	94.683	BB
2	12.47	210145	5.317	MC
		3952651	100.000	

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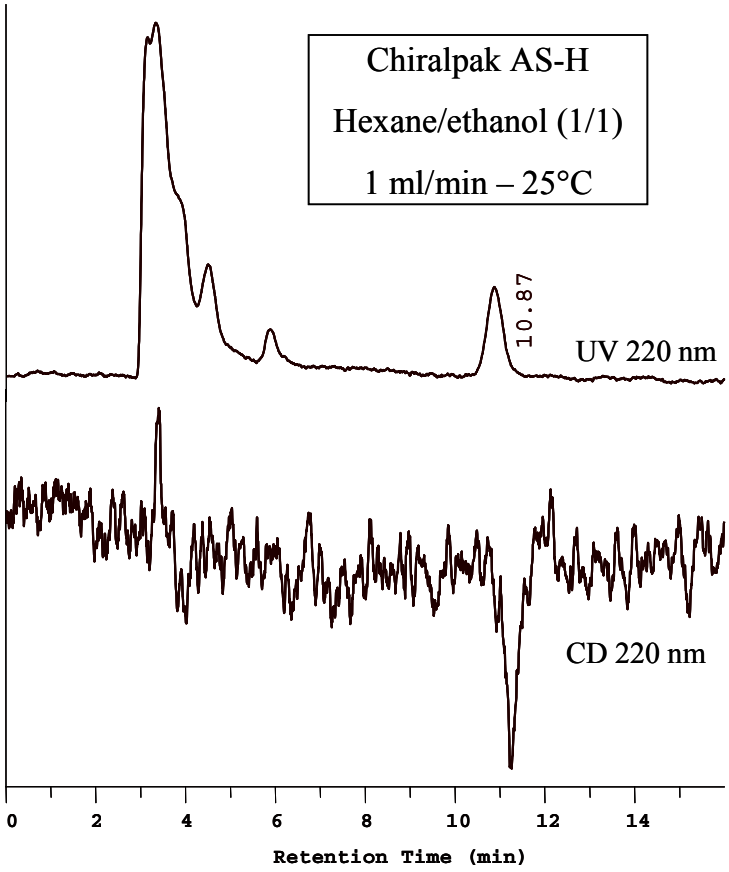
HPLC chromatogram for the crystal of CD_{220}(-)-**4** used for the determination of the absolute configuration by anomalous diffraction :

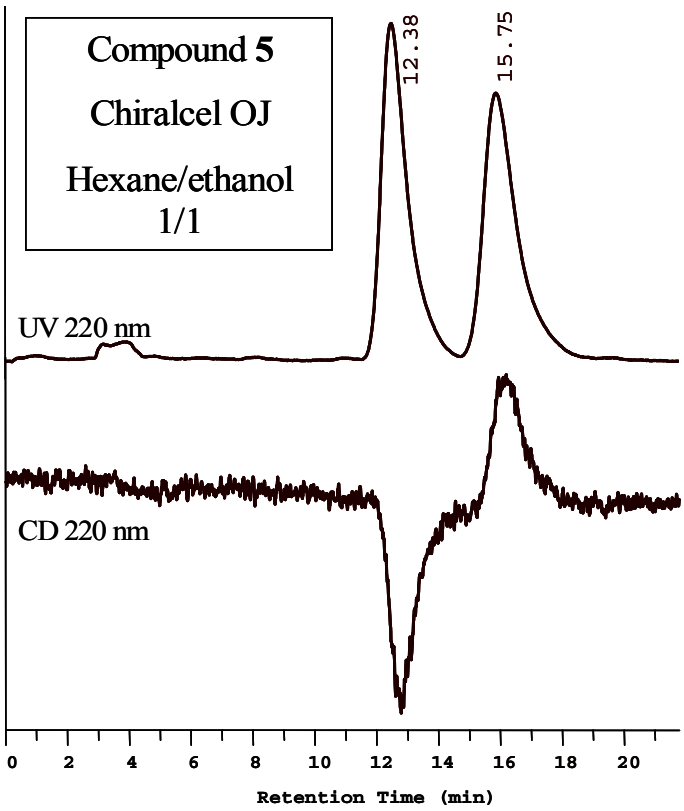
Column : Chiralpak AS-H
Mobile phase : Hexane/ethanol (1/1) – 1 ml/min
Detection : UV and CD at 220 nm



2) Chiral HPLC separation for compound **5**

• The sample is dissolved ethanol, injected on the chiral column, and detected with an UV detector at 220 nm and with an on-line circular dichroism at 220 nm.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralcel OJ	Hexane / Ethanol 1/1	12.38 (-)	2.99	15.75 (+)	4.08	1.36	2.01
Chiralcel OD-H	Hexane / 2-PrOH 8/2	21.14 (-)	5.82	23.89 (+)	6.71	1.15	1.75
Chiralpak AD	Hexane / 2-PrOH 8/2	10.49 (-)	2.38	11.97 (+)	2.86	1.20	1.64
Chiralcel OB-H	Hexane / Ethanol 1/1	15.81 (-)	4.10	19.19 (+)	5.19	1.27	1.27
Chiralpak AS	Hexane / 2-PrOH 8/2	24.63 (-)	6.94	27.37 (+)	7.83	1.13	0.94
Ulmo (S,S)	Hexane / Ethanol 1/1	6.03	0.95			1	0
Sumichiral OA-2500	Hexane / 2-PrOH 8/2	35.23	10.36			1	0
Whelk-O1 (S,S)	Hexane / 2-PrOH 8/2	49.00	14.81			1	0



Semi-preparative separations :

• Sample preparation: About 93 mg of compound **5** are dissolved in 120 ml of ethanol.

• Chromatographic conditions: Chiralcel OJ (250 x 10 mm), cellulose tris-para-methyl-benzoate, thermostated at 30°C, hexane/ethanol (1/1) as mobile phase, flow-rate = 5 ml/min, UV detection at 220 nm.

• Injection: 120 times 1 ml, every 10 minutes.

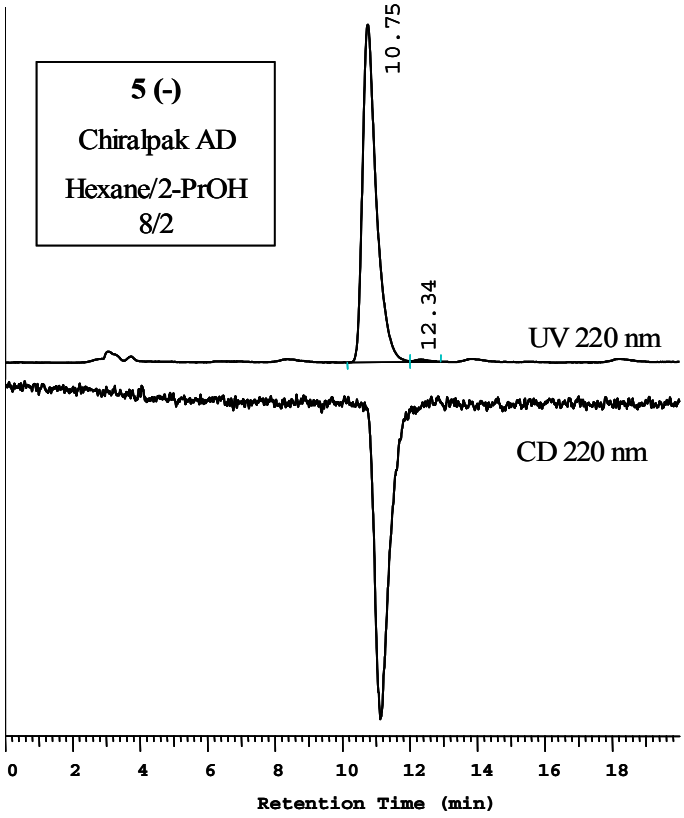
• Collection: the first eluted enantiomer is collected between 1 and 4 minutes and the second one between 5 and 9 minutes.

• First fraction: 46 mg of the first eluted ((-)-enantiomer) with an enantiomeric excess higher than 99 %.

• Second fraction: 47 mg of the second eluted ((+)-enantiomer) with an enantiomeric excess higher than 97 %.

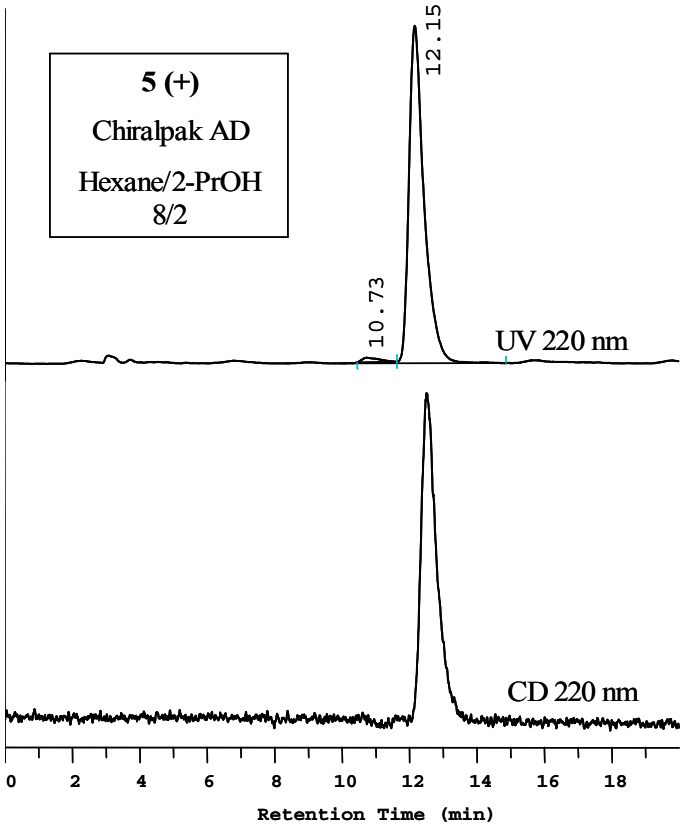
• Enantiomeric excess of the (-)-enantiomer:

No.	RT	Area	Conc 1	BC
1	10.75	5883268	99.544	BV
2	12.34	26946	0.456	TBB
		5910214	100.000	



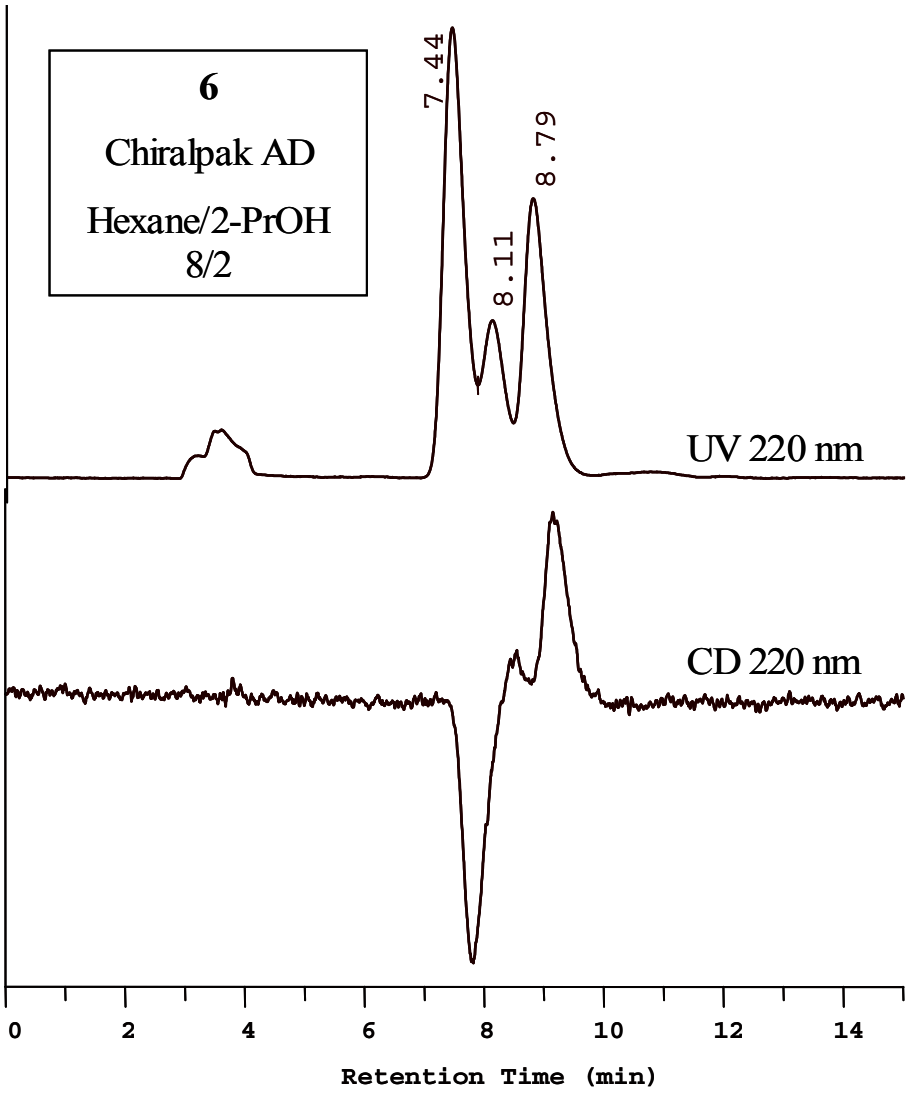
• Enantiomeric excess of the (+)-enantiomer:

No.	RT	Area	Conc 1	BC
1	10.73	109251	1.459	MC
2	12.15	7378101	98.541	MC
		7487352	100.000	



3) HPLC chromatogram for compound **6**

Only 3 peaks could be obtained for the 4 possible stereoisomers on Chiralpak AD:

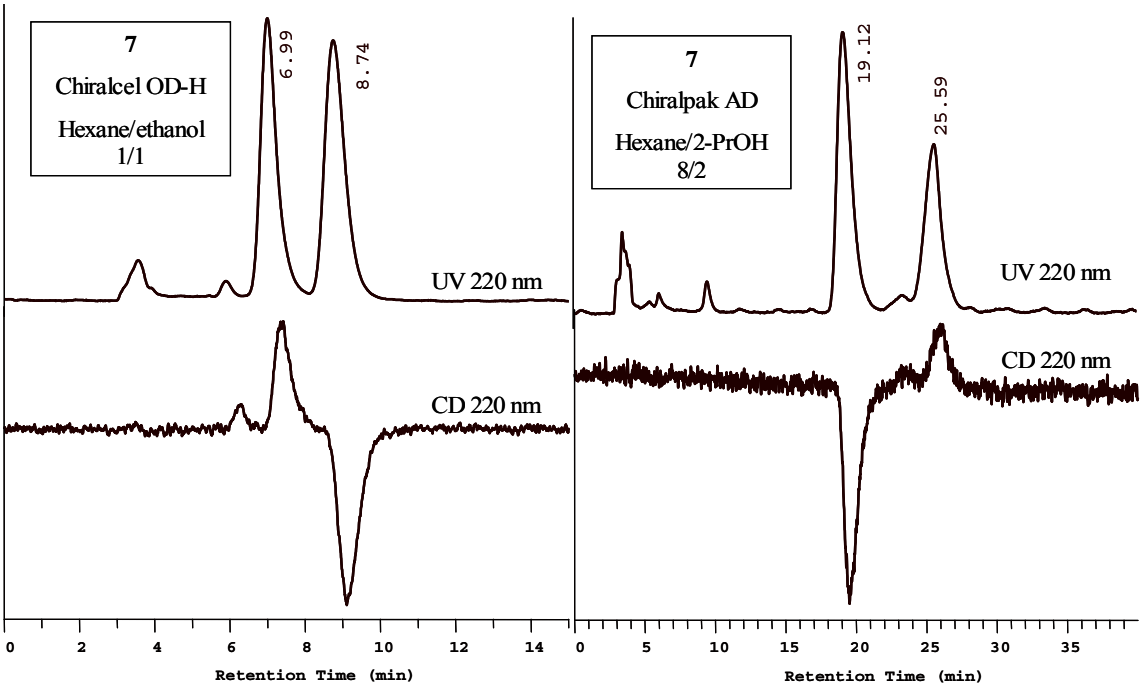


4) Chiral HPLC separation for compound **7**

• The sample is dissolved ethanol, injected on the chiral column, and detected with an UV detector at 220 nm and with an on-line circular dichroism at 220 nm.

Column	Mobile Phase	tdia1	k1	tdia2	k2	Selectivity	Rs
Chiralcel OD-H	Hexane / Ethanol 1/1	6.99 (+)	1.26	8.74(-)	1.82	1.45	1.99
Chiralpak AD	Hexane / 2-PrOH 8/2	25.59 (+)	7.25	19.12 (-)	5.17	1.40	3.35

The two diastereoisomers can be separated on two different chiral columns, with different elution order.



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