Rhenium Complexes Bearing Phosphole-Pyridine Chelates: Simple Molecules with Large Chiroptical Properties

Eszter Takacs,[a] Aude Escande,[a] Nicolas Vanthuyne,[b] Christian Roussel,[b] Christophe Lescop,[a] Elisabeth Guinard,[a] Camille Latouche,[a] Abdou Boucekkine,[a] Jeanne Crassous,*[a] Régis Réau,*[a] M. Hissler*[a]

[a] *Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS- Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, Franc). Fax: (+33) 2-23-23-69-39; Tel: (+33) 2-23-23-57-83;*
E-mail: muriel.hissler@univ-rennes1.fr; jeanne.crassous@univ-rennes1.fr; regis.reau@univ-rennes1.fr

[b] *Chirosciences UMR 7313: ISM2 (Institut de Sciences Moléculaires de Marseille) Aix-Marseille Université, 13397 Marseille Cedex 20, France*

Supporting information

General Procedures: All experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Column chromatography was performed in air, unless stated in text. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofurane, diethylether) or from phosphorus pentoxide (pentane, dichloromethane). Cp_2ZrCl_2 was obtained from Alfa Aesar Chem. Co. All compounds were used as received without further purification. 1-phenyl-2-(2-pyridyl)-5-phenylphosphole[1], 1-phenyl-2,5-(2-pyridyl)phosphole,[2] were prepared as described in the literature. Preparative separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063-0.200 mm) in 3.5-20 cm columns. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AM300 or AM400. ^1H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to $Si(CH_3)_4$ as external standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85 % H_3PO_4. Assignment of proton atoms is based on COSY experiment. Assignment of carbon atoms is based on HMBC, HMQC and DEPT-135 experiments. High-resolution mass spectra were obtained on a Varian MAT 311, Waters Q-TOF 2 or ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes1. Specific rotations (in deg cm^2 g^{-1}) were measured in a 1 dm thermostated quartz cell on a Jasco-P1010 polarimeter. Circular dichroism (in M^{-1} cm^{-1}) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Université de Rennes 1).

1. M. Sauthier, F. Leca, L. Toupet, R. Réau *Organometallics* 2002, **21**, 1591
2. C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulaszi, R. Réau *Chem. Eur. J.* 2001, **7**, 4222

Determination of optical data: UV-Visible spectra were recorded at room temperature on a UVIKON 942 spectrophotometer and luminescence spectra were recorded in freshly distilled solvents at room temperature with a PTI spectrofluorimeter (PTI-814 PDS, MD 5020, LPS 220B) using a xenon lamp.

1-phenyl-2-(2-thienyl)-5-phenylphosphole-$Re^{I}(CO)_4Cl$, 2a : A solution of 1-phenyl-2-(2-thienyl)-5-phenylphosphole (0.35g, 0.93 mmol), and $Re(CO)_5Cl$ (0.34g, 0.93 mmol) in dry toluene (30 mL) was heated under argon at 110°C for 2 hours. After that time, the yellow solution was concentrated by rotary evaporation to give a crude product which was purified by column chromatography (silica gel) eluted with a mixture of heptane/diethylether (49/1, v/v). The Re(I) complex **2a** which was isolated as a bright yellow powder (yield 55%, 362 mg, 0.51 mmol,). ^{1}H NMR (400MHz, CD_2Cl_2) : δ = 1.65-1.75 (m, 1H, CH_2), 1.80-2.10 (m, 3H, CH_2), 2.58-2.69 (m, 1H, CH_2), 2.80-2.91 (m, 1H, CH_2), 2.99-3.10 (m, 1H, CH_2), 3.18 (dtd, 1H, *J*(H,H)= 18.5 Hz, *J*(H,H)= 5.9, *J*(H,H)= 2.44 Hz, CH_2), 6.95-7.00 (m, 2H, CH_{phenyl}), 7.02 (dd, 1H, *J*(H,H) =3.6 Hz, *J*(H,H)= 5.2 Hz, C$H_{thienyl}$,) ; 7.15 (d, 1H, *J*(H,H) =3.6 Hz, C$H_{thienyl}$,), 7.25-7.35 (m, 3H, CH_{phenyl}), 7.43 (dd, 1H, *J*(H,H)= 1.6 Hz, *J*(H,H)= 5.2 Hz, C$H_{thienyl}$), 7.50-7.56 (m, 2H, CH_{phenyl}), 7.58-7.64 (m, 1H, CH_{phenyl}), 7.81 (ddd, 2H, *J*(H,H) = 7.0 Hz, *J*(H,H) = 1.5 Hz, *J*(P,H) = 11.5 Hz, CH_{phenyl}). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ = 22.6 (s, *C*H_2), 22.7 (s, *C*H_2), 27.9 (d, *J*(P,C) = 8.7 Hz, *C*H_2), 28.9 (d, *J*(P,C) = 8.5 Hz, *C*H_2), 133.5 (d, *J*(P,C) = 40.2 Hz, C_{ipso}), 127.0 (s, *C*$H_{thienyl}$), 127.2 (s, *C*$H_{thienyl}$), 128.0 (s, *C*H_{phenyl}), 128.2 (s, *C*H_{phenyl}), 128.6 (d, *J*(P,C) = 5.0 Hz, *C*$H_{thienyl}$), 129.2 (d, *J*(P,C) = 10.1 Hz, *C*H_{phenyl}), 129.5 (d, *J*(P,C) = 5.0 Hz, *C*H_{phenyl}), 131.9 (d, *J*(P,C) = 2.5 Hz, *C*H_{phenyl}), 133.3 (d, *J*(P,C) = 53.3 Hz, C_α), 133.4 (d, *J*(P,C) = 19.1 Hz, C_{phenyl}), 133.8 (d, *J*(P,C) = 11.1 Hz, *C*H_{phenyl}), 136.0 (d, *J*(P,C) = 18.7 Hz $C_{thienyl}$), 138.7 (d, *J*(P,C) = 47.9 Hz, C_α), 146.5 (d, *J*(P,C) = 14.0 Hz, C_β), 148.1 (d, *J*(P,C) = 13.0 Hz, C_β), 182.7 (m, *C*=O), 183.3 (s, *C*=O), 184.4 (d, *J*(P,C) = 10.0 Hz, *C*=O), 184.5 (d, *J*(P,C) = 9.6 Hz, *C*=O). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = +21.3 (s). HR-MS (ESI, CH_2Cl_2/MeOH, 95/5, v/v *m/z*): $[M+Na]^+$ calcd for $C_{28}H_{21}ClO_4NaSPRe$, 729.00366; found 729.0027; Anal. Calcd for $C_{28}H_{21}ClSO_4PRe$: C, 47.62; H, 3.00; S, 4.54; Found C, 47.52; H, 3.20; N, 4.35.

1-phenyl-2-(2-pyridyl)-5-phenylphosphole-$Re^{I}(CO)_3Cl$, 2b : A solution of 1-phenyl-2-(2-pyridyl)-5-phenylphosphole (0.30g, 0.82 mmol), and $Re(CO)_5Cl$ (0.29g, 0.82 mmol) in dry toluene (15 mL) was heated under argon at 80°C for 3 hours. After that time, the yellow

solution was concentrated by rotary evaporation to give a crude product which was purified by column chromatography (silica gel) eluted with dichloromethane. The Re(I) complex **2b** which was isolated as a bright yellow powder (yield 62%, 342 mg, 0.51 mmol,) is a mixture of diastereoisomers presenting a two singlet in ^{31}P NMR (δ: + 50.7 (s) and +47.7 (s)). The two diastereoisomers have been separated by chiral HPLC (*vide infra*). HR-MS (ESI, $CHCl_3$/MeOH, 90/10, v/v *m/z*): $[M+Na]^+$ calcd for $C_{28}H_{22}ClNO_3NaPRe$, 696.04812; found 696.0482; Anal. Calcd for $C_{28}H_{22}ClNO_3PRe$: C, 49.96; H, 3.29; N, 2.08; Found C, 49.67; H, 3.40; N, 2.01. FT-IR (KBr, cm^{-1}): 2022 ($\nu_{C\equiv O}$), 1927 ($\nu_{C\equiv O}$), 1892 ($\nu_{C\equiv O}$)

Compound 2b^1 : ^{1}H NMR (400MHz, CD_2Cl_2) : δ = 1.58-1.63 (m, 1H, C*H*$_2$), 1.85-1.93 (m, 2H, C*H*$_2$), 1.94-2.01 (m, 1H, C*H*$_2$), 2.75 (dt, 1H, *J*(H,H) = 18.1 Hz, *J*(H,H) = 6.3 Hz, C*H*$_2$), 2.92 (t, 2H, *J*(H,H) = 5.3 Hz, C*H*$_2$), 3.28 (td, 1H, *J*(H,H) = 18.7 Hz, *J*(H,H) = 5.6 Hz, *J*(H,H) = 5.6 Hz, C*H*$_2$), 7.20-7.25 (m, 2H, C*H* $_{phenyl}$), 7.26-7.31 (m, 1H, C*H*$_{pyridyl}$), 7.32-7.45 (m, 6H, C*H*$_{phenyl}$), 7.52-7.55 (m, 2H, C*H*$_{phenyl}$), 7.72 (d, 1H, *J*(H,H) = 7.9 Hz, C*H*$_{pyridyl}$), 7.97 (dddd, 1H, *J*(H,H) = 7.9 Hz, *J*(H,H) = 7.9 Hz, *J*(H,H) = 1.6 Hz, *J*(P,H) = 0.8 Hz, C*H*$_{pyridyl}$), 9.07 (ddd, 1H, *J*(H,H) = 5.7 Hz, *J*(H,H) = 1.6 Hz, *J*(H,H) = 0.8 Hz, C*H*$_{pyridyl}$). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ = 22.1 (s, *C*H), 23.0 (s, *C*H$_2$), 26.9 (d, *J*(P,C) = 6.0 Hz, *C*H$_2$), 28.1 (d, *J*(P,C) = 7.0 Hz, *C*H$_2$), 122.6 (d, *J*(P,C) = 37.2 Hz, *C*$_{phenyl}$), 123.5 (s, *C*H $_{pyridyl}$), 123.8 (d, *J*(P,C) = 7.0 Hz, *C*H$_{pyridyl}$), 128.2 (d, *J*(P,C) = 5.0 Hz, *C*H$_{phenyl}$), 128.4 (s, *C*H$_{phenyl}$), 128.7 (s, *C*H$_{phenyl}$), 129.6 (d, *J*(P,C) = 7.0 Hz, *C*H$_{phenyl}$), 131.1 (d, *J*(P,C) = 2.0Hz, *C*H$_{phenyl}$), 133.1 (d, *J*(P,C) = 11.1 Hz, *C*H$_{phenyl}$) ; 133.4 (d, *J*(P,C) = 15.1 Hz, *C*$_{ipso}$), 138.4 (s, *C*H$_{pyridyl}$), 139.5 (d, *J*(P,C) = 41.3 Hz, *C*$_\alpha$), 142.8 (d, *J*(P,C) = 48.3 Hz, *C*$_\alpha$),147.7 (d, *J*(P,C) = 11.1 Hz, *C*$_\beta$), 150.7 (d, *J*(P,C) = 11.1Hz, *C*$_\beta$), 155.2 (d, *J*(P,C) = 18.1 Hz, *C*$_{pyridyl}$), 156.6 (s, *C*H$_{pyridyl}$), 189.2 (m, *C*=O), 191.7 (m, *C*=O); 196.7 (m, *C*=O). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = +47.7 (s).

Compound 2b^2 : ^{1}H NMR (400MHz, CD_2Cl_2) : δ = 1.60-1.70 (m, 1H, C*H*$_2$), 1.80-2.00 (m, 3H, C*H*$_2$), 2.70-2.92 (m, 3H, C*H*$_2$), 3.28 (td, 1H, *J*(H,H) = 18.1 Hz, *J*(H,H) = 5.6 Hz, *J*(H,H) = 5.6 Hz, C*H*$_2$), 7.20 (ddd, 1H, *J*(H,H) = 7.9 Hz, *J*(H,H) = 5.7 Hz, *J*(H,H) = 0.8 Hz, C*H*$_{pyridyl}$), 7.25-7.57 (m, 10H, C*H*$_{phenyl}$), 7.80 (d, 1H, ^{3}*J*(H,H) = 7.9 Hz, C*H* $_{pyridyl}$), 7.97 (dddd, 1H, *J*(H,H) = 7.9 Hz, *J*(H,H) = 7.9 Hz, *J*(H,H) = 1.6 Hz, *J*(P,H) = 0.8 Hz, C*H*$_{pyridyl}$), 9.02 (ddd, 1H, *J*(H,H) = 5.7 Hz, *J*(H,H) = 1.6 Hz, *J*(H,H) = 0.8 Hz, C*H*$_{pyridyl}$). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ = 22.3 (s, *C*H$_2$), 23.1 (s, *C*H$_2$), 27.3 (d, *J*(P,C) = 7.0 Hz, *C*H$_2$), 28.2 (d, *J*(P,C) = 8.0 Hz, *C*H$_2$), 122.6 (s, *C*H $_{pyridyl}$), 125.4 (d, *J*(P,C) = 8.0 Hz, *C*H$_{pyridyl}$), 127.4 (d, *J*(P,C) = 44.8

Hz, C_{phenyl}), 128.1 (s, CH_{phenyl}), 128.6 (s, CH_{phenyl}), 128.7 (d, J(P,C) = 10.1 Hz, CH_{phenyl}), 129.6 (d, J(P,C) = 7.0 Hz, CH_{phenyl}), 129.8 (d, J(P,C) = 2.0 Hz, CH_{phenyl}), 133.8 (d, J(P,C) = 11.6 Hz, CH_{phenyl}), 133.5 (d, J(P,C) = 15.1 Hz, C_{ipso}), 137.2 (d, J(P,C) = 42.3 Hz, C_{α}), 138.5 (s, $CH_{pyridyl}$), 138.6 (d, J(P,C) = 40.2 Hz, C_{α}), 150.1 (d, J(P,C) = 10.1 Hz, C_{β}), 155.7 (d, J(P,C) = 10.1Hz, C_{β}), 156.1 (d, J(P,C) = 18.1 Hz, $C_{pyridyl}$), 156.2 (d, J(P,C) = 2.0 Hz, $CH_{pyridyl}$), 191.1 (d, J(P,C) = 7.3 Hz, C=O), 192.6 (m, C=O); 195.5 (d, J(P,C) = 7.3 Hz, C=O). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = +50.7 (s).

1-phenyl-2,5-(2-pyridyl)phosphole-Re^{I}(CO)$_4$Cl, 2c : A solution of 1-phenyl-2,5-(2-pyridyl)phosphole (0.37g, 1 mmol), and $Re(CO)_5Cl$ (0.36g, 1 mmol) in dry toluene (15 mL) was heated under argon at 80°C for 3 hours. After that time, the yellow solution was concentrated by rotary evaporation to give a crude product which was purified by column chromatography (silica gel) eluted with dichloromethane. The Re(I) complex **2c** which was isolated as a bright yellow powder (yield 60%, 362 mg, 0.6 mmol,) is a mixture of diastereoisomers presenting a two singlet in ^{31}P NMR (δ: + 48.4 (s) and +46.0 (s)). The two diastereoisomers have been separated by chiral HPLC (*vide infra*). HR-MS (ESI, $CHCl_3$/MeOH, 50/50, v/v, *m/z*): $[M+Na]^+$ calcd for $C_{27}H_{21}ClN_2O_3NaPRe$, 697.04337; found 697.0417; Anal. Calcd for $C_{27}H_{21}ClN_2O_3PRe$: C, 48.11; H, 3.14; N, 4.16; Found C, 47.80; H, 2.84; N, 3.98. FT-IR (KBr, cm^{-1}): 2019 ($\nu_{C\equiv O}$), 1919 ($\nu_{C\equiv O}$), 1891 ($\nu_{C\equiv O}$).

Compound 2c[1] : ^{1}H NMR (400 MHz, CD_2Cl_2) : δ = 1.65-1.90 (m, 1H, CH_2), 1.90-2.10 (m, 3H, CH_2), 2.75-2.90 (m, 1H, CH_2), 3.05-3.25 (m, 3H, CH_2), 7.10-7.22 (m, 2H, $CH_{pyridyl}$), 7.25-7.45 (m, 3H, CH_{phenyl}), 7.60-7.70 (m, 3H, $CH_{pyridyl}$ and CH_{phenyl}), 7.70-7.80 (m, 2H, $CH_{pyridyl}$), 7.90-8.00 (m, 1H, $CH_{pyridyl}$), 8.73 (d, 1H, J(H,H)= 3.2 Hz, $CH_{pyridyl}$), 9.00 (d, 1H, J(H,H)= 5.2 Hz, $CH_{pyridyl}$). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ = 22.1 (s, CH_2), 22.8 (s, CH_2), 27.6 (d, J(P,C) = 6.1 Hz, CH_2), 29.3 (d, J(P,C) = 8.3 Hz, CH_2), 122.1 (s, $CH_{pyridyl}$), 122.7 (s, $CH_{pyridyl}$), 123.0 (d, J(P,C) = 7.0 Hz, $CH_{pyridyl}$), 125.5 (d, J(P,C) = 6.0 Hz, $CH_{pyridyl}$), 128.2 (d, J(P,C) = 46.0 Hz, C_{ipso}), 128.3 (d, J(P,C) = 10.1 Hz, CH_{phenyl}), 130.7 (d, J(P,C) = 2.0 Hz, CH_{phenyl}), 132.9 (d, J(P,C) = 11.6 Hz, CH_{phenyl}), 136.4 (s, $CH_{pyridyl}$), 138.7 (s, $CH_{pyridyl}$), 138.8 (d, J(P,C) = 39.0 Hz, C_{α}), 139.7 (d, J(P,C) = 59.0 Hz, C_{α}), 149.5 (s, $CH_{pyridyl}$), 151.4 (d, J(P,C) = 8.0 Hz, C_{β}), 152.0 (d, J(P,C) = 12.0 Hz, C_{β}), 154.2 (d, J(P,C) = 10.0 Hz, $C_{pyridyl}$), 156.1 (d, J(P,C) = 17.0 Hz, $C_{pyridyl}$), 156.2 (d, J(P,C) = 2.0 Hz, $CH_{pyridyl}$), 192.1 (d, J(P,C) =

7.0 Hz, *C*=O), 192.9 (d, *J*(P,C) = 70.0 Hz, *C*=O); 195.2 (d, *J*(P,C) = 7.0 Hz, *C*=O). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = +48.2 (s).

Compound 2c[2]: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.55-1.68 (m, 1H, CH_2), 1.69-1.81 (m, 1H, CH_2), 1.82-1.94 (m, 2H, CH_2), 2.60-2.76 (m, 1H, CH_2), 2.95-3.10 (m, 3H, CH_2), 7.00-7.25 (m, 5H, C$H_{pyridyl}$ and CH_{phenyl}), 7.45-7.60 (m, 4H, CH_{phenyl}), 7.65 (t, 1H, *J*(H,H)= 7.7 Hz, C$H_{pyridyl}$), 7.83 (t, 1H, *J*(H,H)= 7.6 Hz, C$H_{pyridyl}$), 8.62 (d, 1H, *J*(H,H)= 3.8 Hz, C$H_{pyridyl}$), 8.95 (d, 1H, *J*(H,H)= 5.4 Hz, C$H_{pyridyl}$). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ = 21.9 (s, *C*H_2), 22.6 (s, *C*H_2), 27.3 (d, *J*(P,C) = 5.4 Hz, *C*H_2), 29.0 (d, *J*(P,C) = 8.1 Hz, *C*H_2), 122.3 (s, *C*H $_{pyridyl}$), 122.9 (d, *J*(P,C) = 7.0 Hz, *C*$H_{pyridyl}$), 123.5 (s, *C*$H_{pyridyl}$), 123.6 (d, *J*(P,C) = 39.7 Hz, C_{ipso}), 123.9 (d, *J*(P,C) = 5.9 Hz, *C*$H_{pyridyl}$),127.9 (d, *J*(P,C) = 10.4 Hz, *C*H_{phenyl}), 130.7 (d, *J*(P,C) = 2.3 Hz, *C*H_{phenyl}), 133.9 (d, *J*(P,C) = 10.1 Hz, *C*H_{phenyl}), 136.5 (d, *J*(P,C) = 1.1 Hz, *C*$H_{pyridyl}$), 138.2 (s, *C*$H_{pyridyl}$), 141.1 (d, *J*(P,C) = 39.0 Hz, $C_α$), 143.6 (d, *J*(P,C) = 60.2 Hz, $C_α$), 148.7 (d, *J*(P,C) = 9.0 Hz, $C_β$), 149.2 (d, *J*(P,C) = 10.8 Hz, $C_β$), 149.5 (s, *C*$H_{pyridyl}$), 151.9 (d, *J*(P,C) = 12.6 Hz, $C_{pyridyl}$), 155.2 (d, *J*(P,C) = 17.4 Hz, $C_{pyridyl}$), 156.7 (d, *J*(P,C) = 1.8 Hz, *C*$H_{pyridyl}$), 190.0 (m, *C*=O), 192.7 (d, *J*(P,C) = 72.9 Hz, *C*=O); 196.2 (m, *C*=O). ^{31}P NMR (162 MHz, CD_2Cl_2): δ = +45.7 (s).

Chiral HPLC separation of the Rhenium complexes

• 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, chloroform and ethanol were of HPLC grade, and were degassed and filtered on a 0.45 μm membrane before use. Chiralpak IA and IC (250 x 4.6 mm for analytical and 250 x 10 mm for semi-preparative) from Chiral Technology Europa (Illkirch, France), 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 the wavelength and 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 separations were performed 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.

a) Analytical chiral HPLC separation of the mixture **2b[1]** and **2b[2]**

The sample is dissolved in ethanol, injected on the chiral column, and detected with an UV detector at 254 nm and a CD detector at 220 nm. The flow-rate is 1 ml/min. Two pairs of enantiomers are eluted: **2b[1]** and **2b[2]**. The ratio between the two pairs of enantiomers is 1/1 in UV at 254 nm. Chiralpak IA allows the separation of the four peaks.

For compound **2b[1]**:

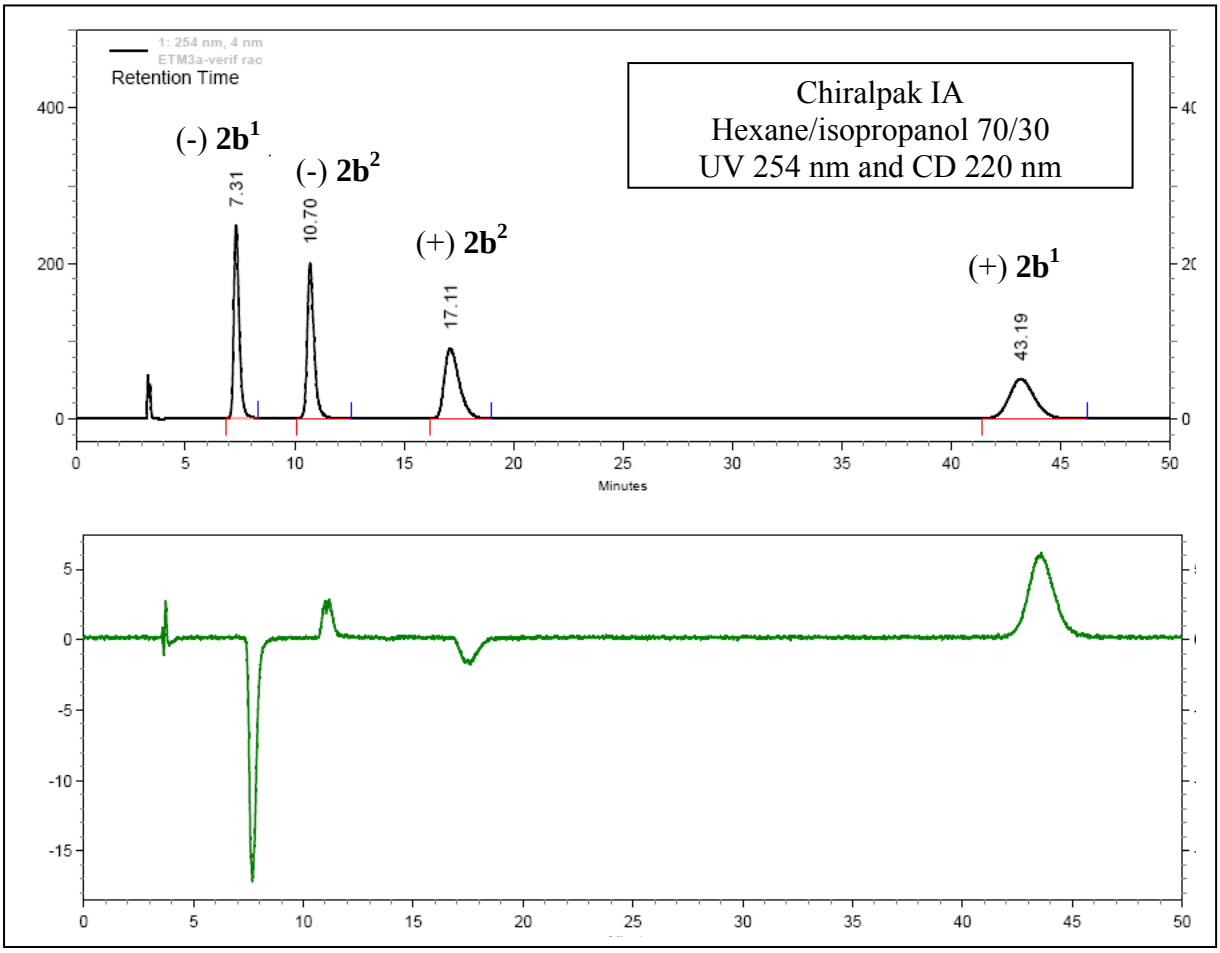
Column	Mobile Phase	t_1	k_1	t_2	k_2	α	Rs
Chiralpak IA	Hexane/Isopropanol 70/30	7.31 (+)	1.44	43.19 (-)	13.40	9.3	20

For compound **2b[2]:**

Column	Mobile Phase	t_1	k_1	t_2	k_2	α	Rs
Chiralpak IA	Hexane/Isopropanol 70/30	10.70 (+)	2.57	17.11 (-)	4.70	1.83	7.05

The signs given in these tables are the signs of the enantiomers obtained with the circular dichroïsm detector at 220 nm in the mobile phase used for the chiral HPLC separation.

Figure S1. Chromatogram of the chiral HPLC separation of the mixture **2b**^{1} and **2b**^{2} on Chiralpak IA.



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor
7.31	17069033	24.98	1.44
10.70	17466343	25.56	2.57
17.11	17156466	25.11	4.70
43.19	16637691	24.35	13.40
Totals	68329533	100.00	

The first eluted enantiomer of **2b**^{1} on Chiralpak IA, is called (-)-**2b**^{1} in the main text, because of a negative specific rotation in dichloromethane. This enantiomer called (-)-**2b**^{1} gives also a negative CD signal at 220 nm in the mobile phase (hexane/2-PrOH 7/3) used for the chiral HPLC analyse.

The first eluted enantiomer of **2b**^{2} on Chiralpak IA, is called (-)-**2b**^{2} in the main text, because of a negative specific rotation in dichloromethane. However, this enantiomer called (-)-**2b**^{2} gives a positive CD signal at 220 nm in the mobile phase (hexane/2-PrOH 7/3) used for the chiral HPLC analyse.

Semi-preparative separation for compounds (-)-**2b**^{1}, (-)-**2b**^{2}, (+)-**2b**^{2} and (+)-**2b**^{1}:

• Sample preparation: About 220 mg of the mixture **2b**^{1} and **2b**^{2} are dissolved in 200 ml of hexane / isopropanol / chloroform (70/20/10).

• Chromatographic conditions: Chiralpak IA (250 x 10 mm), at 30°C, hexane / isopropanol / chloroform (70/20/10) as mobile phase, flow-rate = 5 ml/min, UV detection at 254 nm.

• Injection: 200 times 1 mL, every 35 minutes.

• Collection: (-)-**2b**^{1} is collected between 5.5 and 8 minutes, (-)-**2b**^{2} between 8 and 9.8 minutes, (+)-**2b**^{2} between 10.6 and 13 minutes (+)-**2b**^{1} between 24 and 34 minutes.

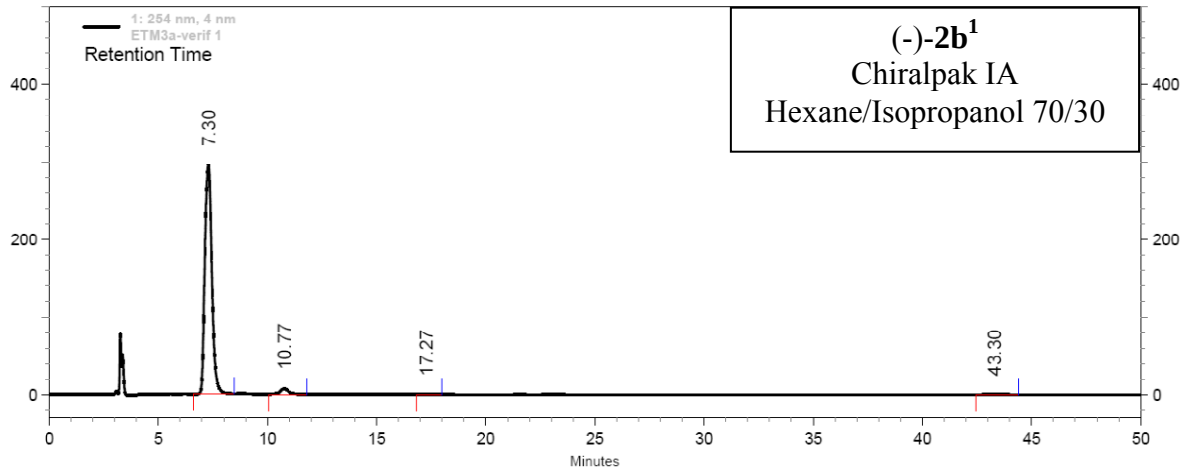
• First fraction: 50 mg of (-)-**2b**^{1}, with de = 94% and ee > 99%.

• Second fraction: 50 mg of (-)-**2b**^{2}, with de = 89% and ee > 99%.

• Third fraction: 50 mg of (+)-**2b**^{2}, with de = 81% and ee = 95%.

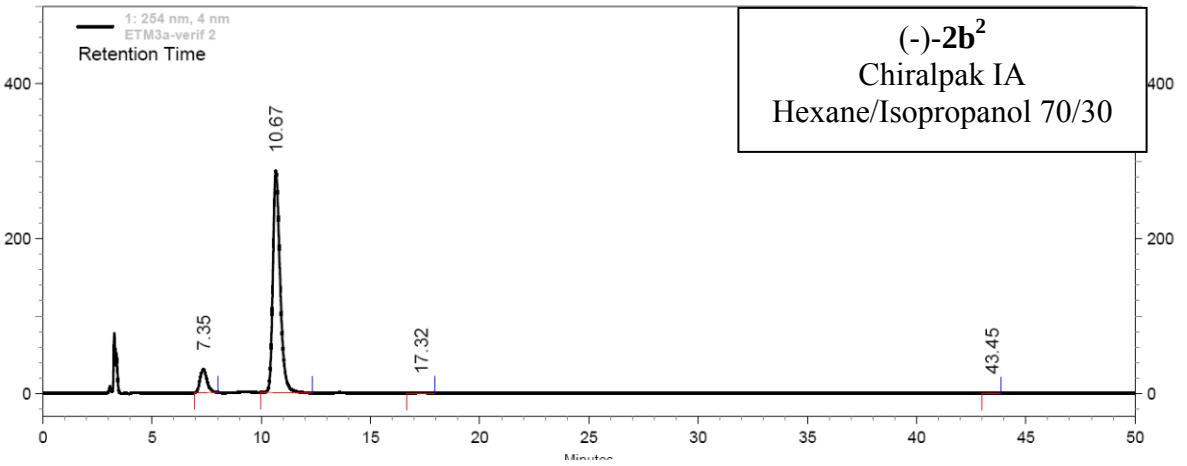
• Fourth fraction: 50 mg of (+)-**2b**^{1}, with de = 93% and ee > 99%.

Figure S2. Chromatograms of the collected fractions on Chiralpak IA:



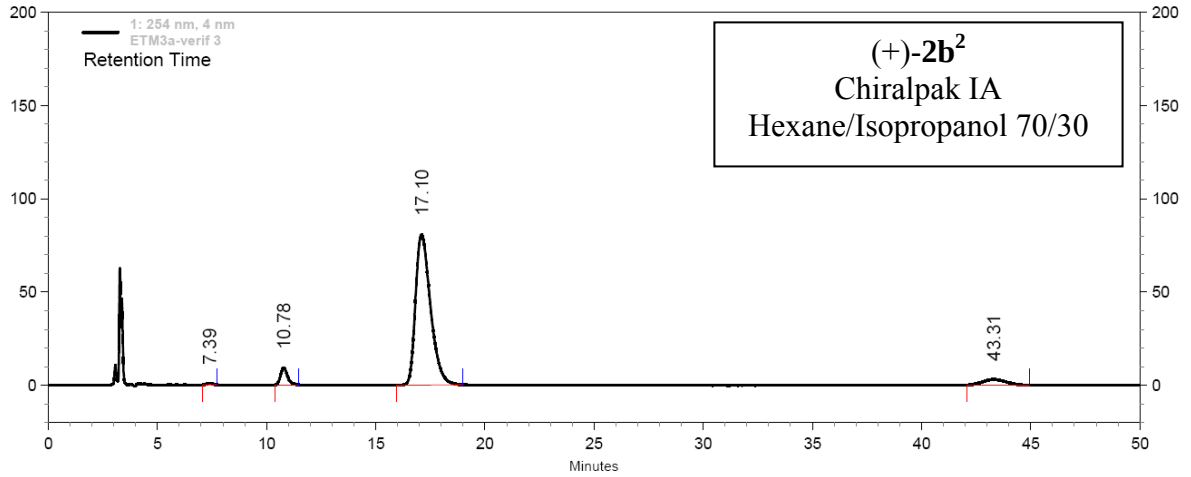
1: 254 nm, 4 nm
Results

Retention Time	Area	Area %
7.30	26590180	96.81
10.77	821957	2.99
17.27	18245	0.07
43.30	36341	0.13
Totals	27466723	100.00



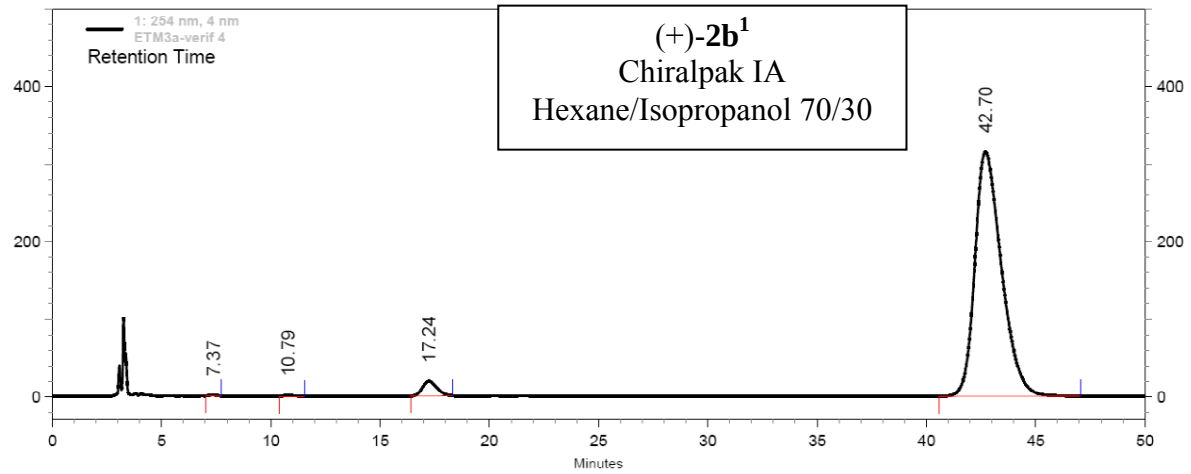
1: 254 nm, 4 nm
Results

Retention Time	Area	Area %
7.35	2680983	9.21
10.67	26315362	90.42
17.32	94875	0.33
43.45	12690	0.04
Totals	29103910	100.00



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %
7.39	67676	0.39
10.78	806196	4.69
17.10	15401313	89.60
43.31	913307	5.31
Totals	17188492	100.00



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %
7.37	125652	0.11
10.79	177974	0.16
17.24	3626988	3.26
42.70	107377962	96.47
Totals	111308576	100.00

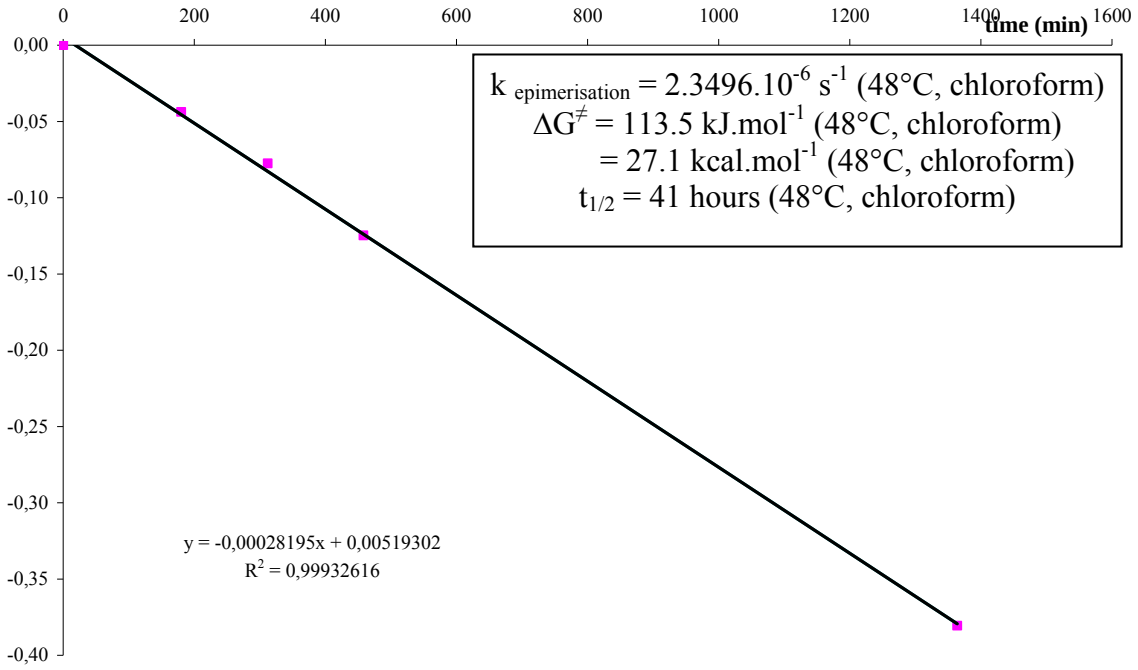
The obtained enantiomeric excesses are excellent, but the relatively low diastereomeric excesses could be explained by the epimerisation on one chiral center.

Kinetics of epimerisation of (+)-**2b**^{1} into (+)-**2b**^{2}

First, we have checked that the two diastereoisomers have the same extinction coefficient at 254 nm and that the concentrations of (+)-**2b**^{1} and (+)-**2b**^{2} are equal at the equilibrium.

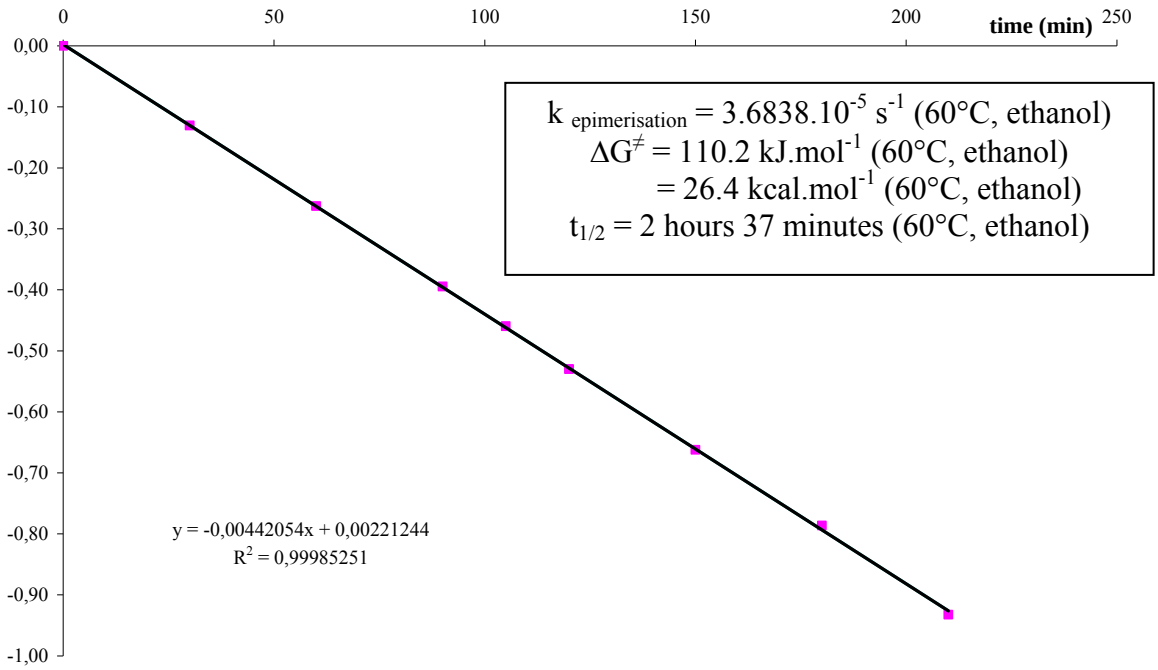
About 0.5 mg of a (+)-**2b**^{1} enriched sample is heated in about 5 mL of chloroform at 48°C. The diastereomeric excess of this solution at different times was determined by injection on Chiralpak IA (hexane/ethanol 1/1, 1 mL/min, UV 254 nm). Thus, the decrease of the percentage of the (+)-**2b**^{1} diastereomer and the increase of (+)-**2b**^{2} are monitored.

Time (min)	% (+)-**2b**^{1}	ln ((%t-50%)/(%(t=0)-50%))
0	95.918	0.0000
180	93.954	-0.0437
312	92.495	-0.0775
458	90.535	-0.1247
1364	81.383	-0.3806



About 0.5 mg of a (+)-**2b**^{1} enriched sample is heated in about 5 mL of ethanol at 60°C. The diastereomeric excess of this solution at different times was determined by injection on Chiralpak IA (hexane/ethanol 1/1, 1 mL/min, UV 254 nm). Thus, the decrease of the percentage of the (+)-**2b**^{1} diastereomer and the increase of (+)-**2b**^{2} are monitored.

Time (min)	% (+)-**2b**^{1}	ln ((%t-50%)/(%(t=0)-50%))
0	92.060	0.0000
30	86.914	-0.1305
60	82.350	-0.2625
90	78.353	-0.3944
105	76.565	-0.4595
120	74.761	-0.5298
150	71.690	-0.6622
180	69.161	-0.7862
210	66.556	-0.9323



b) Analytical chiral HPLC separation of the mixture **2c^1** and **2c^2**

The sample is dissolved in hexane/isopropanol/chloroform 8/1/1, injected on the chiral column, and detected with an UV detector at 254 nm and a CD detector at 254 nm. The flow-rate is 1 ml/min. Two pairs of enantiomers are eluted: the major (**2c^2**) and the minor (**2c^1**). The ratio between the two pairs of enantiomers is 7/3 in UV at 254 nm. Two chiral columns, Chiralpak IA and Chiralpak IC allow the separation of the four peaks.

For compound **2c^1:**

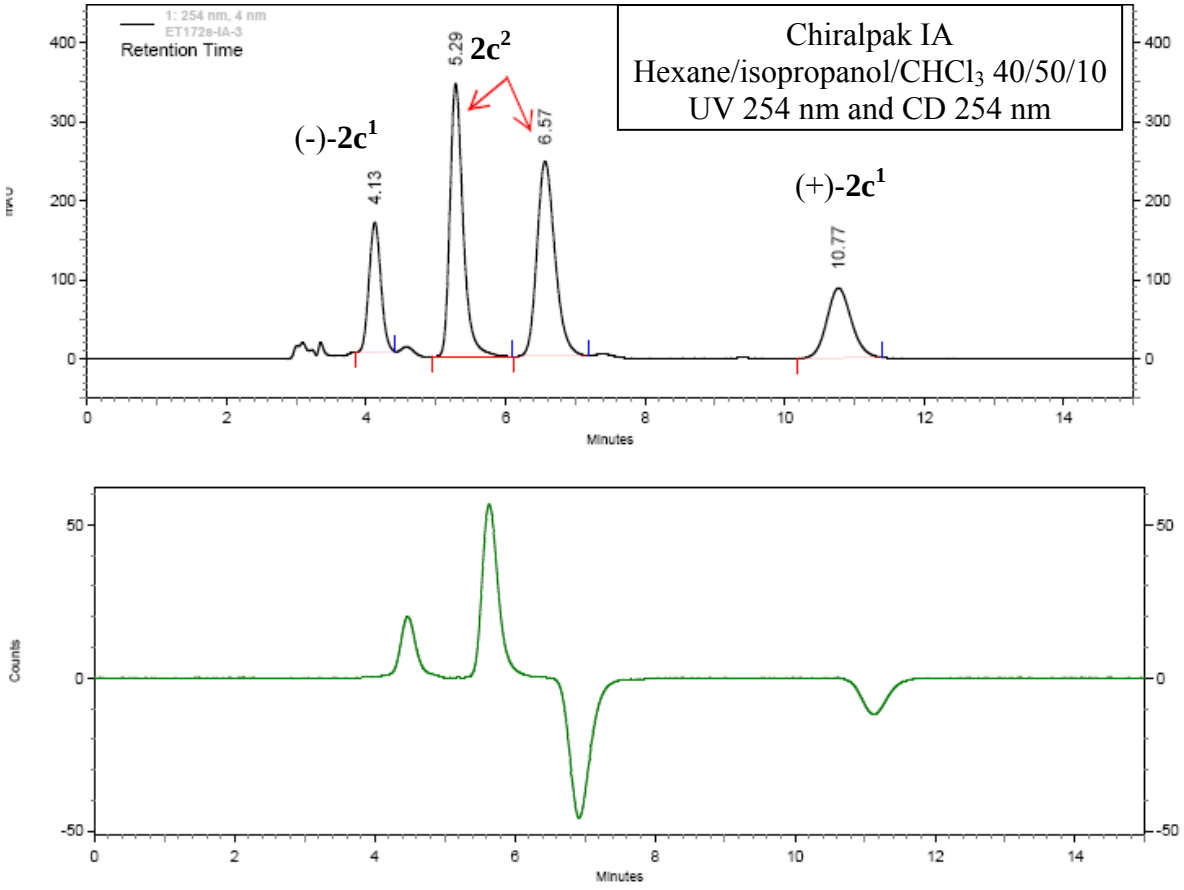
Column	Mobile Phase	t_1	k_1	t_2	k_2	α	Rs
Chiralpak IA	Hexane/Isopropanol 50/50	5.63 (+)	0.88	23.94 (-)	6.98	4.03	18.28
	Hexane/Isopropanol/$CHCl_3$ 40/50/10	4.13 (+)	0.39	10.77 (-)	2.55	6.57	10.34
Chiralpak IC	Hexane/Ethanol 50/50	5.80 (-)	0.93	5.97 (+)	0.99	1.06	<1
	Hexane/Isopropanol 50/50	12.63 (+)	3.21	13.98 (-)	3.66	1.14	<1
	Hexane/Isopropanol/$CHCl_3$ 60/10/30	13.01 (+)	3.34	20.48 (-)	5.83	1.75	4.88

For compound **2c^2:**

Column	Mobile Phase	t_1	k_1	t_2	k_2	α	Rs
Chiralpak IA	Hexane/Isopropanol 50/50	8.20 (+)	1.73	12.53 (-)	3.18	1.83	4.21
	Hexane/Isopropanol/$CHCl_3$ 40/50/10	5.29 (+)	0.76	6.57 (-)	1.17	1.52	1.91
Chiralpak IC	Hexane/Ethanol 50/50	4.56 (+)	0.52	4.63 (-)	0.54	1.05	<1
	Hexane/Isopropanol 50/50	6.78 (+)	1.26	7.97 (-)	1.66	1.31	1.43
	Hexane/Isopropanol/$CHCl_3$ 60/10/30	6.88 (+)	1.29	8.11 (-)	1.70	1.32	1.27

The signs given in these tables are the signs of the enantiomers obtained with the circular dichroïsm detector at 254 nm in the mobile phase used for the chiral HPLC separation.

Figure S3. Chromatogram of the chiral HPLC separation of the mixture **2c**^{1} and **2c**^{2} on Chiralpak IA.

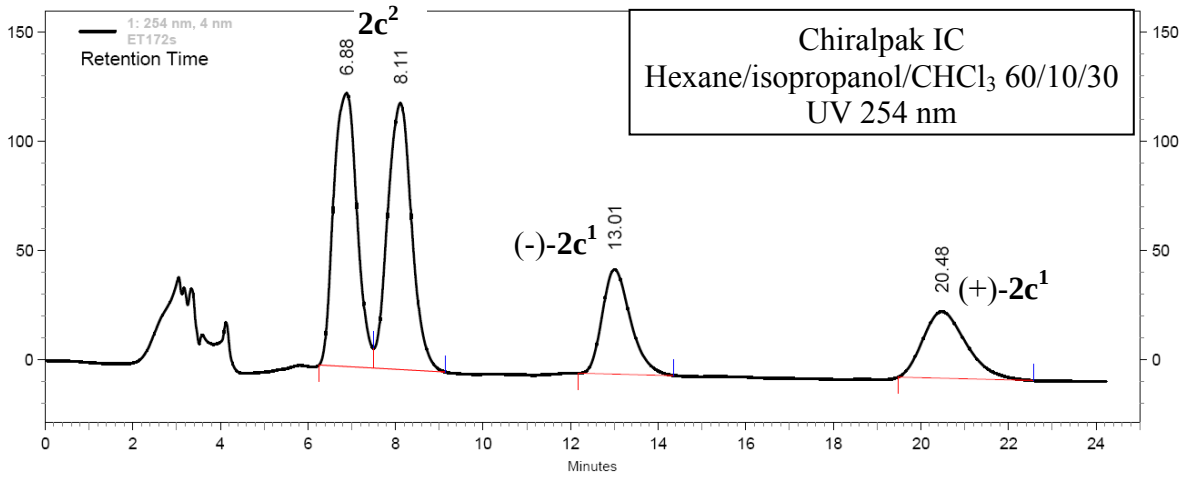


1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
4.13	7738795	14.83	0.38	1.00	0.00
5.29	18101543	34.69	0.76	1.00	3.58
6.57	17724787	33.97	1.19	1.56	3.18
10.77	8608741	16.50	2.59	6.90	7.50
Totals	52173866	100.00			

The first eluted enantiomer of **2c**^{1} on Chiralpak IA, is called (-)-**2c**^{1} in the main text, because of a negative specific rotation in dichloromethane. However, this enantiomer called (-)-**2c**^{1} gives a positive CD signal at 254 nm in the mobile phase (hexane/2-PrOH/chloroform 4/5/1) used for the chiral HPLC analyse.

Figure S4. Chromatogram of the chiral HPLC separation of the mixture **2c**^{1} and **2c**^{2} on Chiralpak IC.



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
6.88	18562869	34.21	1.29	1.00	0.00
8.11	18707651	34.47	1.70	1.32	1.28
13.01	8598084	15.84	3.34	1.96	4.47
20.48	8400389	15.48	5.83	3.42	4.90
Totals	54268993	100.00			

Semi-preparative separation for compounds (-)-**2c**^{1}, (+)-**2c**^{1} and **2c**^{2}:

• Sample preparation: About 250 mg of the mixture **2c**^{1} and **2c**^{2} are dissolved in 60 ml of chloroform.

• Chromatographic conditions: Chiralpak IC (250 x 10 mm), at 30°C, hexane/ isopropanol / chloroform (60/10/30) as mobile phase, flow-rate = 5 ml/min, UV detection at 254 nm.

• Injection: 30 times 2 mL, every 20 minutes.

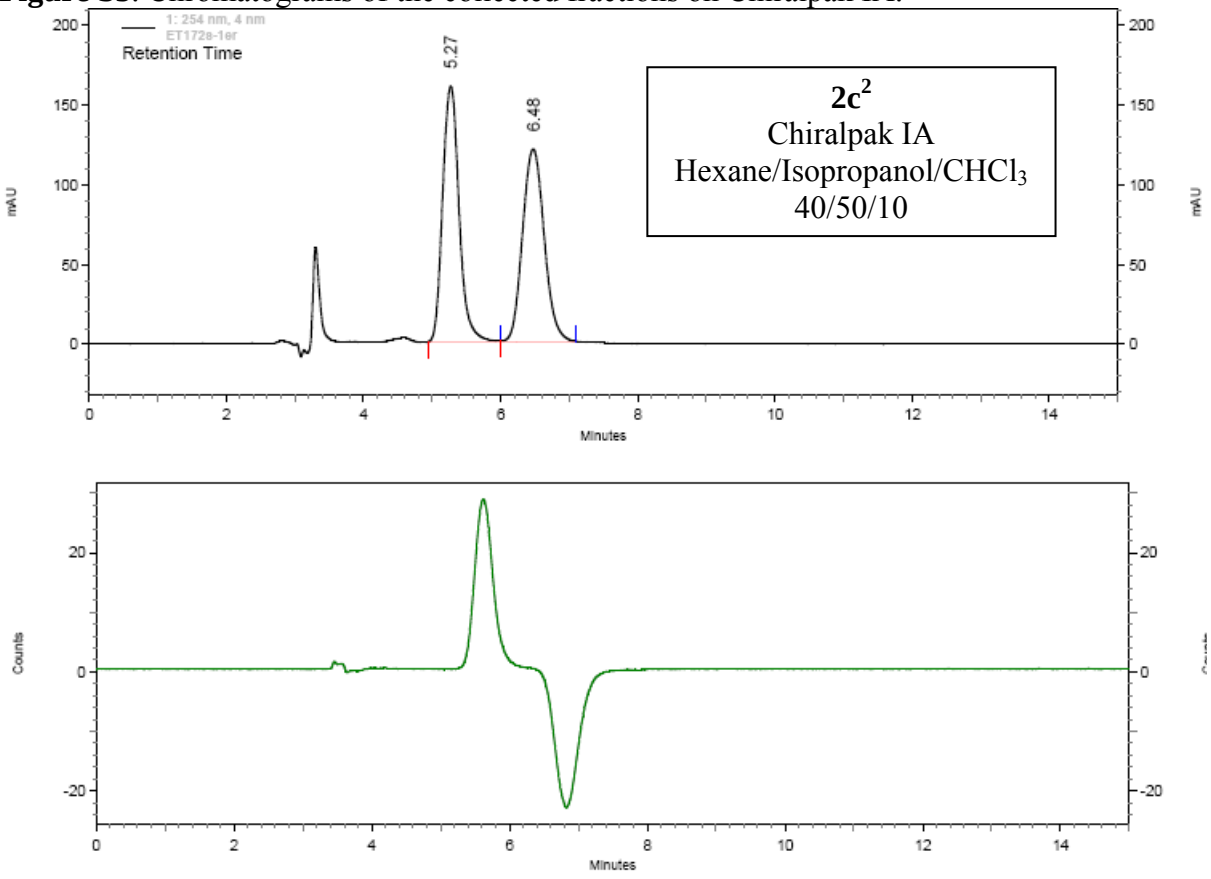
• Collection: **2c**^{2} is collected between 6 and 9 minutes, the first eluted enantiomer of **2c**^{1} between 12 and 14 minutes and the second eluted enantiomer of **2c**^{1} between 19 and 21 minutes.

• First fraction: 141 mg of the **2c**^{2}

• Second fraction: 38 mg of the first eluted enantiomer of (-)-**2c**^{1}, with ee > 99%.

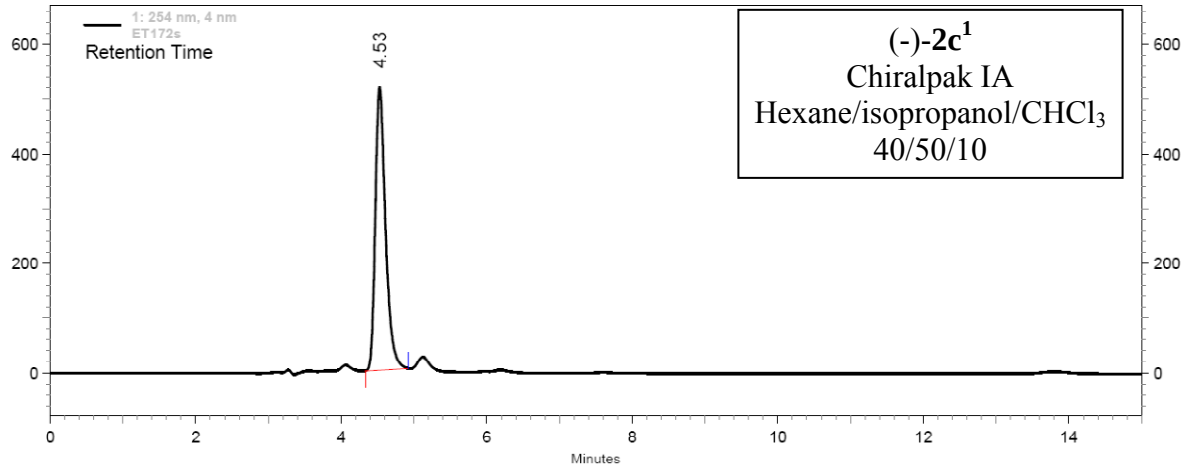
• Third fraction: 38 mg of the second eluted enantiomer of (+)-**2c**^{1}, with ee > 99%.

Figure S5. Chromatograms of the collected fractions on Chiralpak IA.



1: 254 nm, 4 nm
Results

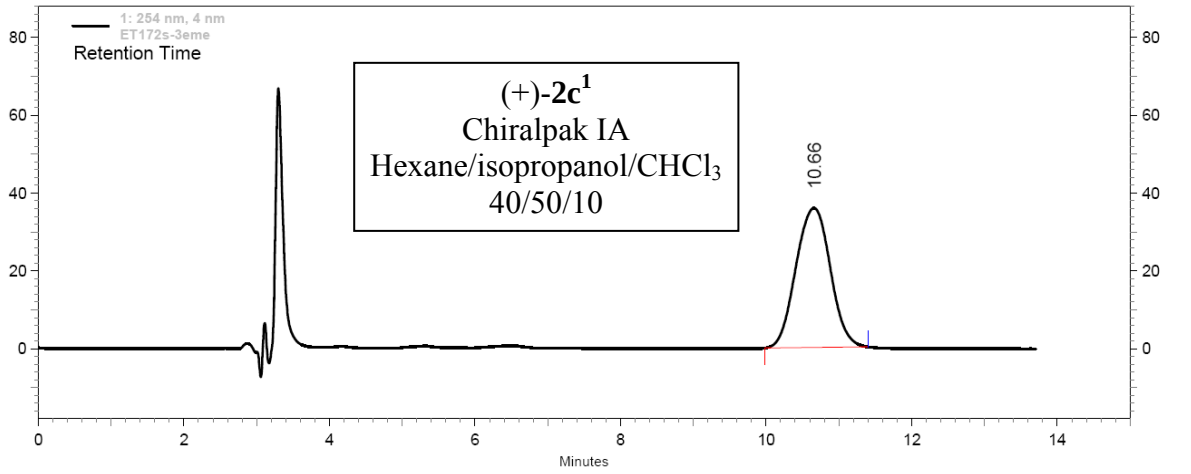
Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
5.27	10696536	50.24	0.76	1.00	0.00
6.48	10593774	49.76	1.16	1.53	2.41
Totals	21290310	100.00			



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
4.53	20221105	100.00	0.51	0.00	0.00

Totals					
	20221105	100.00			



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
10.66	4707679	100.00	2.55	1.00	0.00

Totals					
	4707679	100.00			

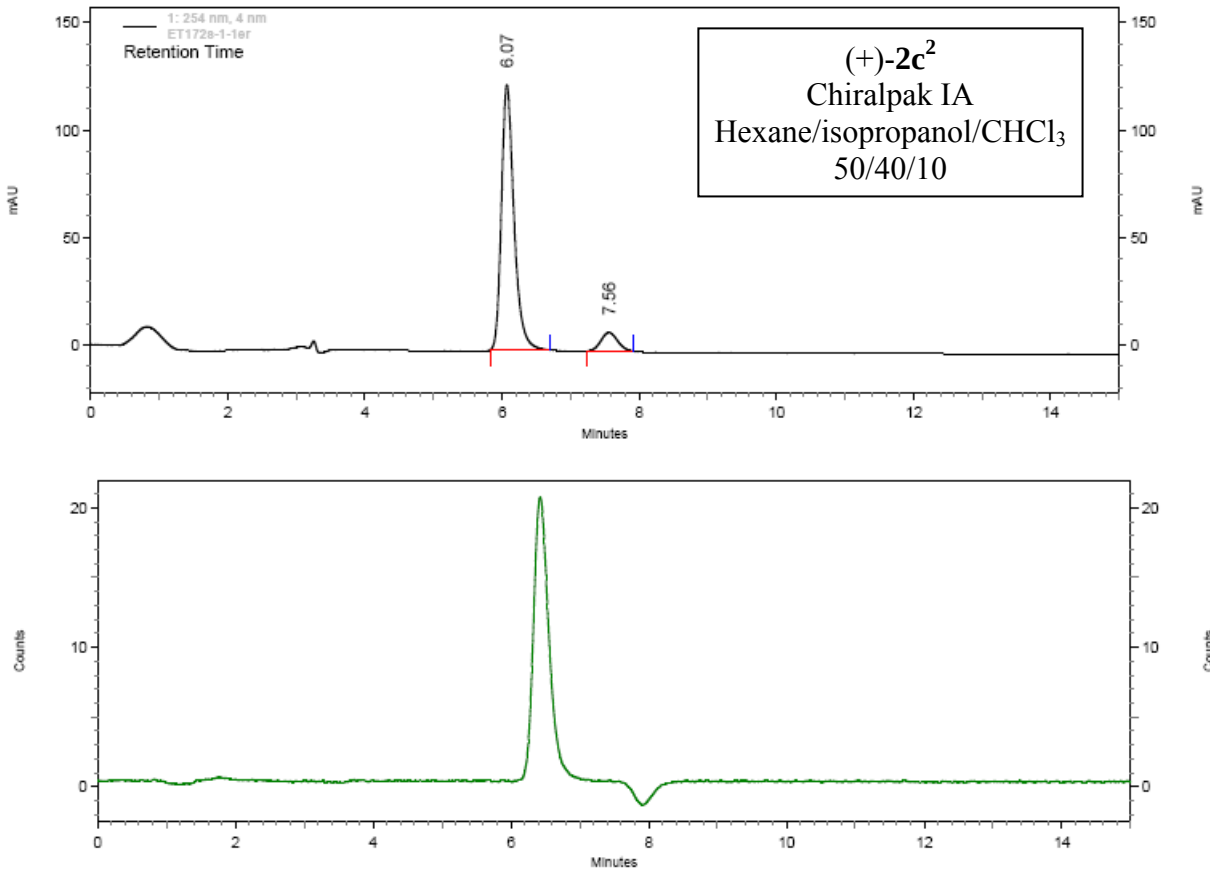
Semi-preparative separation for the enantiomers of **2c²**:

• Sample preparation: compound **2c²** is dissolved in hexane/isopropanol/chloroform (6/2/2).

• Chromatographic conditions: Chiralpak IA (250 x 10 mm), at 25°C, hexane/isopropanol/chloroform (50/40/10) as mobile phase, flow-rate = 5 ml/min, UV detection at 290 nm.

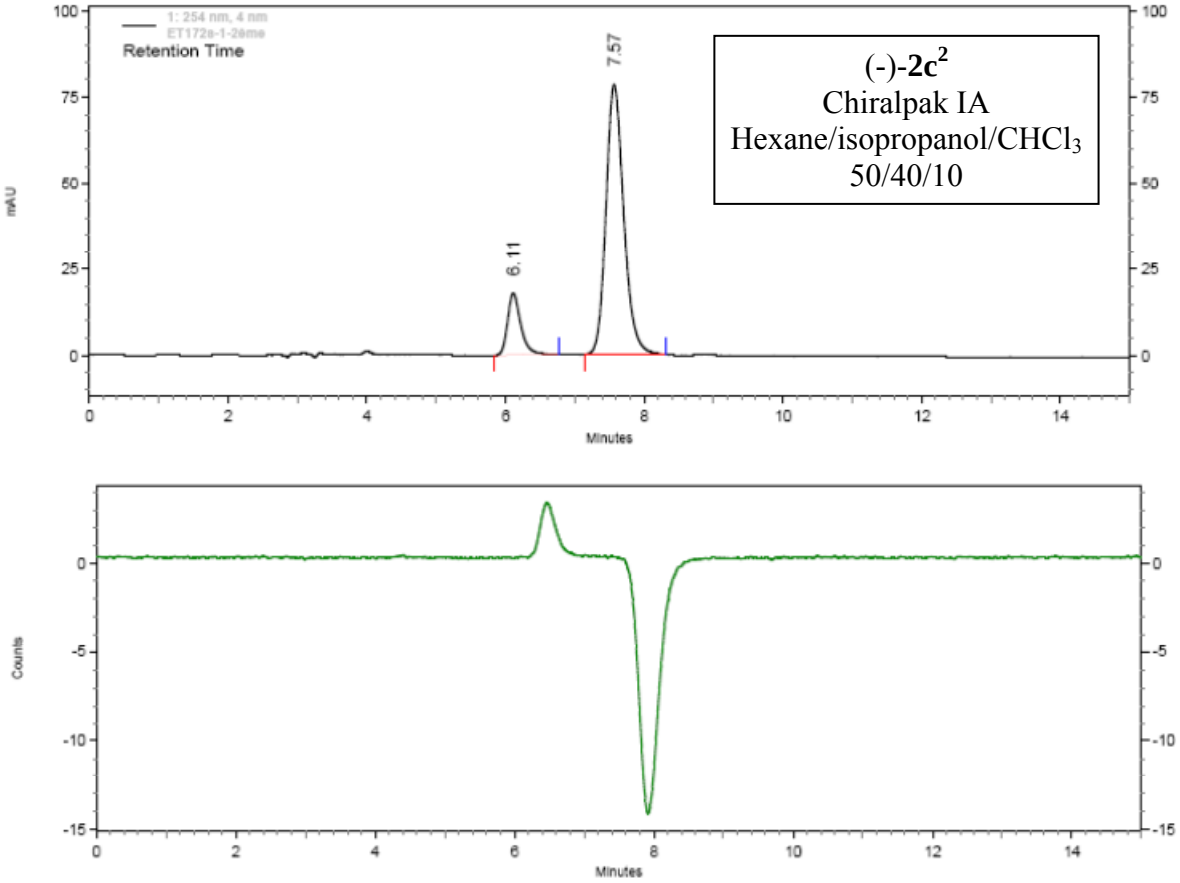
• Injection: 11 injections of 500 µl, every 5 minutes.

Figure S6. Chromatograms of the collected enantiomers on Chiralpak IA after the separation (before evaporation of the solvents).



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
6.07	6296074	91.50	1.02	1.00	0.00
7.56	584616	8.50	1.52	1.48	3.78
Totals	6880690	100.00			

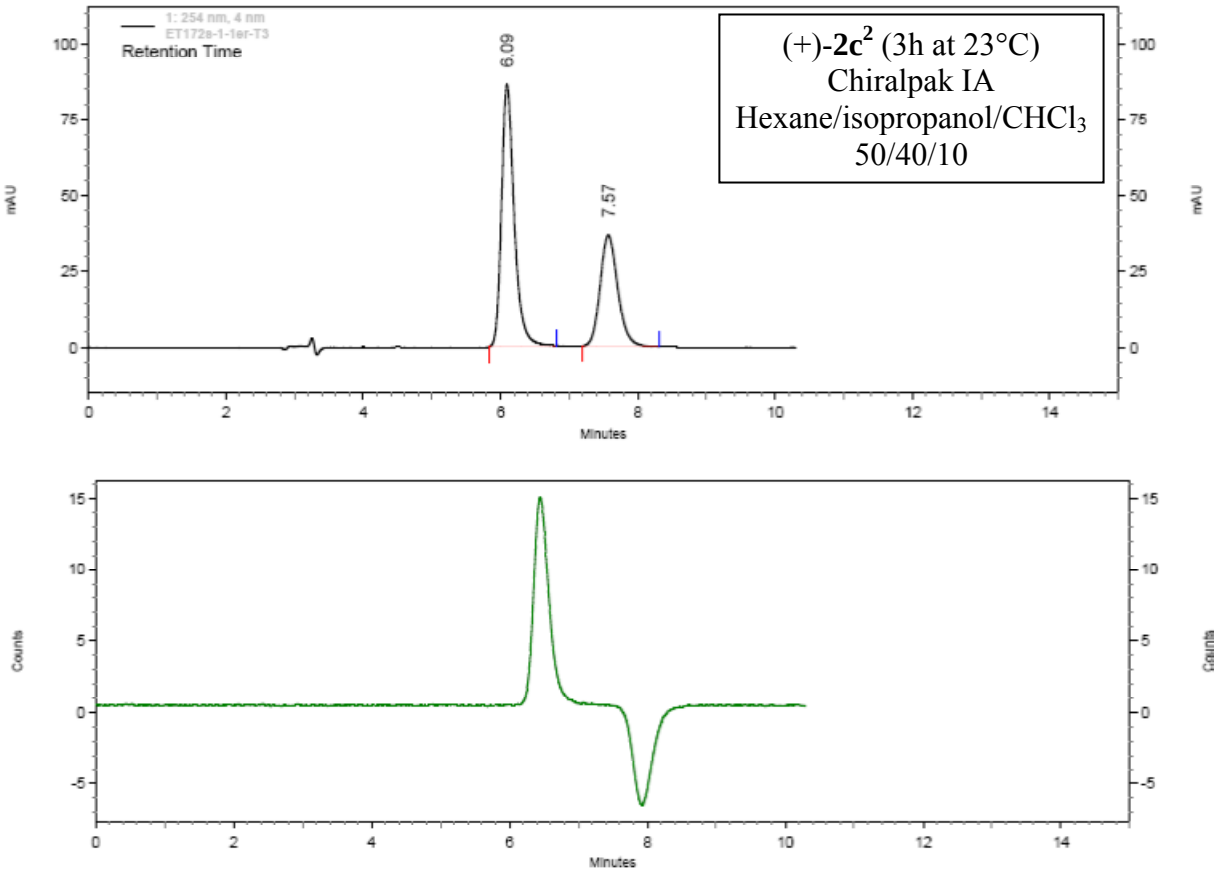


1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
6.11	947470	14.46	1.04	1.00	0.00
7.57	5602967	85.54	1.52	1.47	3.62
Totals	6550437	100.00			

Figure S7. Chromatogram of the first eluted enantiomer (+)-**2c**^{2} on Chiralpak IA after three hours in solution at 23°C.

We observed a fast racemisation at ambient temperature.



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
6.09	4438385	62.87	1.03	1.00	0.00
7.57	2620987	37.13	1.52	1.48	3.71
Totals	7059372	100.00			

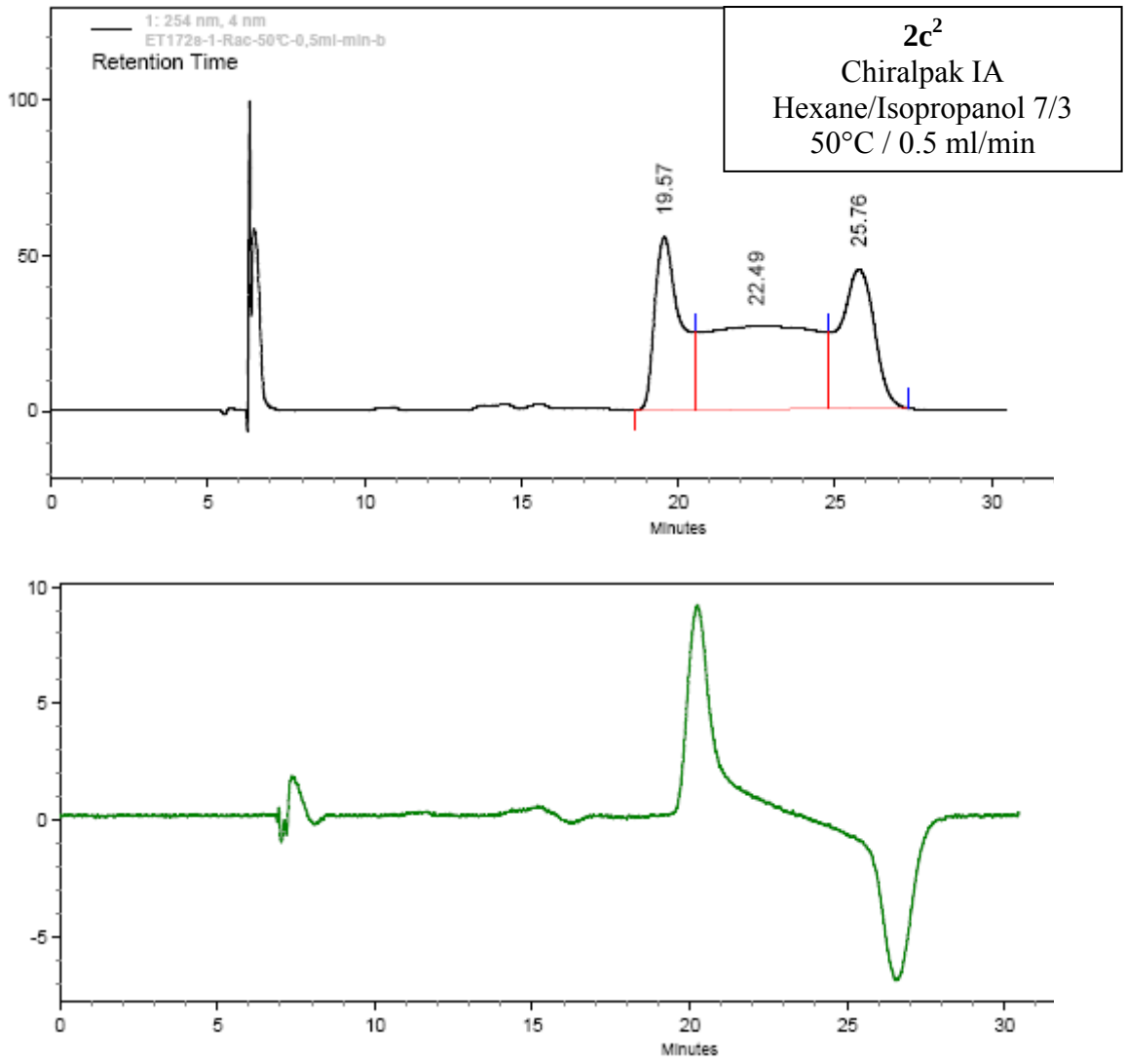
Determination of the interconversion barrier between enantiomers of **2c²**:

The enantiomer (+)-**2c²** stayed in a mixture of hexane/isopropanol/$CHCl_3$ 50/40/10. The initial enantiomeric excess is 83%, after 3 hours in this mixture at 22°C, the ee is 25%: the interconversion barrier is 97 kJ/mol (± 2 kJ/mol) at 22°C in the mixture hexane/isopropanol/$CHCl_3$ 50/40/10, the half-life time is about 110 minutes.

The semi-preparative separation of these enantiomers is impossible, because they racemize fast at ambient temperature.

To prove the enantiomeric instability, **2c²** was studied by dynamic chiral HPLC. A chromatogram with a plateau between two peaks, corresponding to the interconversion of the enantiomers, can be observed at 50°C.

Figure S8.

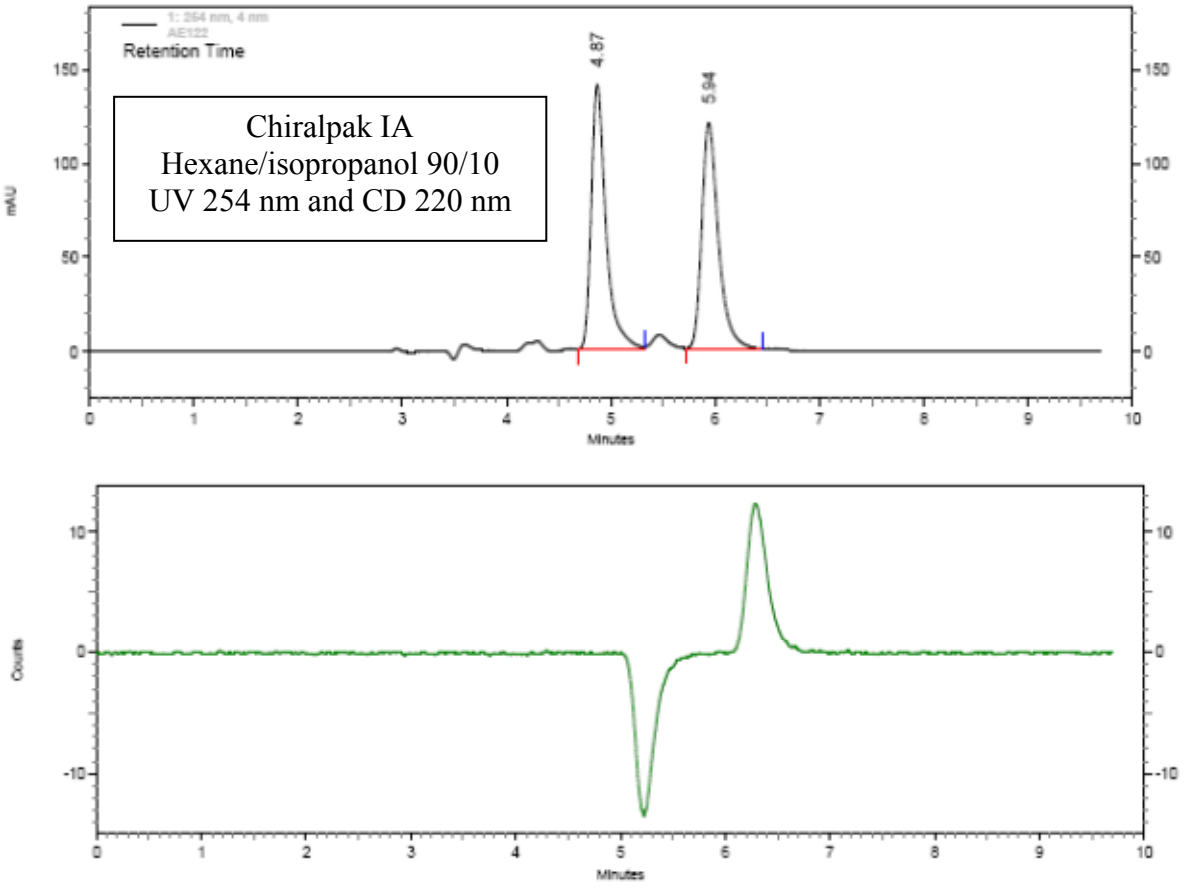


c) Analytical chiral HPLC separation for compound **2a**

• The sample is dissolved in ethanol, injected on the chiral column, and detected with an UV detector at 254 nm and circular dichroism at 220 nm The flow-rate is 1 ml/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IA	Hexane/Isopropanol (90/10)	4.87 (-)	0.62	5.94 (+)	0.98	1.57	4.16

Figure S9. Chromatogram of the chiral HPLC separation of complex **2a**.



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
4.87	5491487	50.88	0.62	1.00	0.00
5.94	5302419	49.12	0.98	1.57	4.08
Totals	10793906	100.00			

Semi-preparative separation for compound **2a** :

• Sample preparation: About 95 mg of compound **2a** are dissolved in 50 ml of a mixture chloroform/isopropanol/hexane (4/1/4).

• Chromatographic conditions: Chiralpak IA (250 x 10 mm), thermostated at 30°C, hexane/isopropanol (90/10) as mobile phase, flow-rate = 5 ml/min, UV detection at 254 nm.

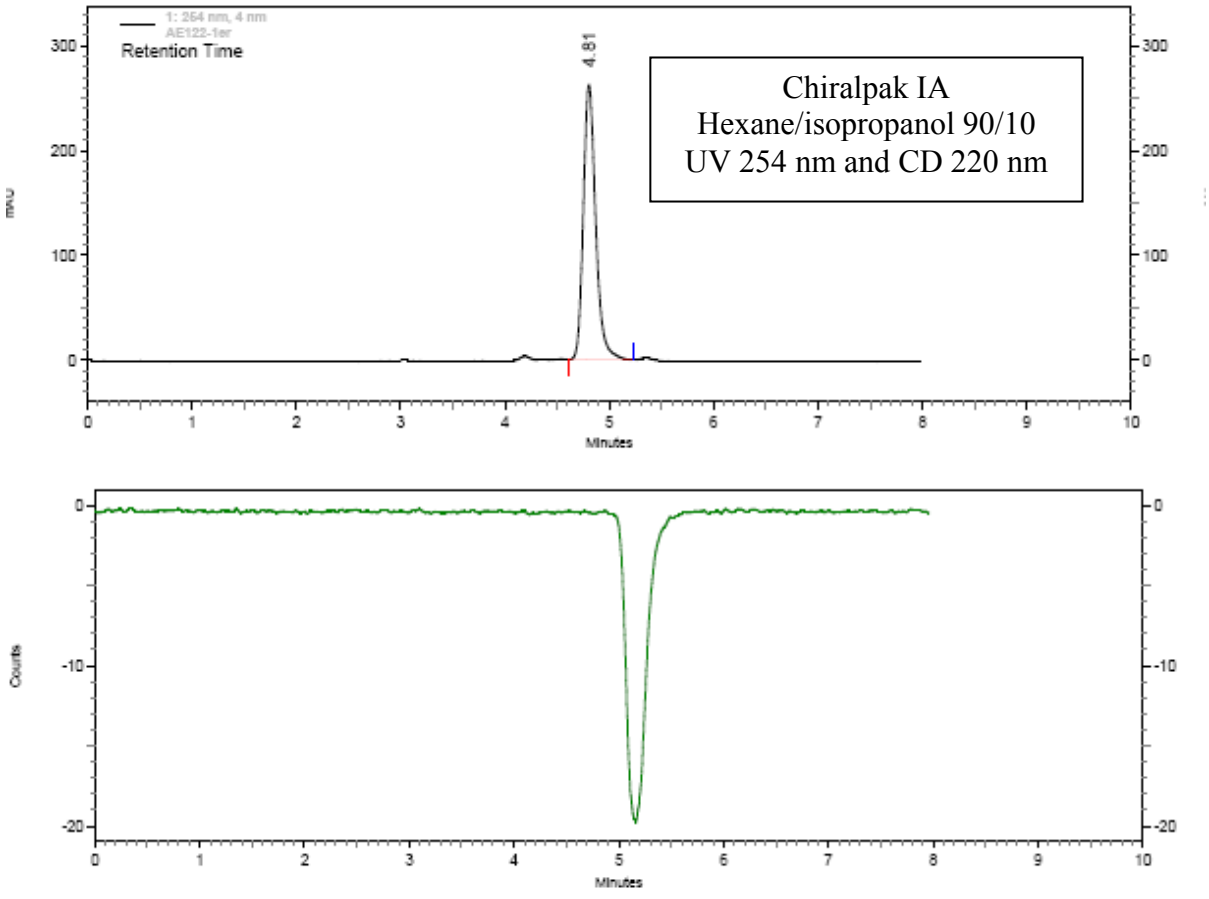
• Injection: 250 times 200 µl, every 8 minutes.

• Collection: the first eluted enantiomer is collected between 5.4 and 6.2 minutes and the second one between 6.6 and 8 minutes.

• First fraction: 45 mg of the first eluted ((-, CD 220nm)-enantiomer) with an enantiomeric excess higher than 99%.

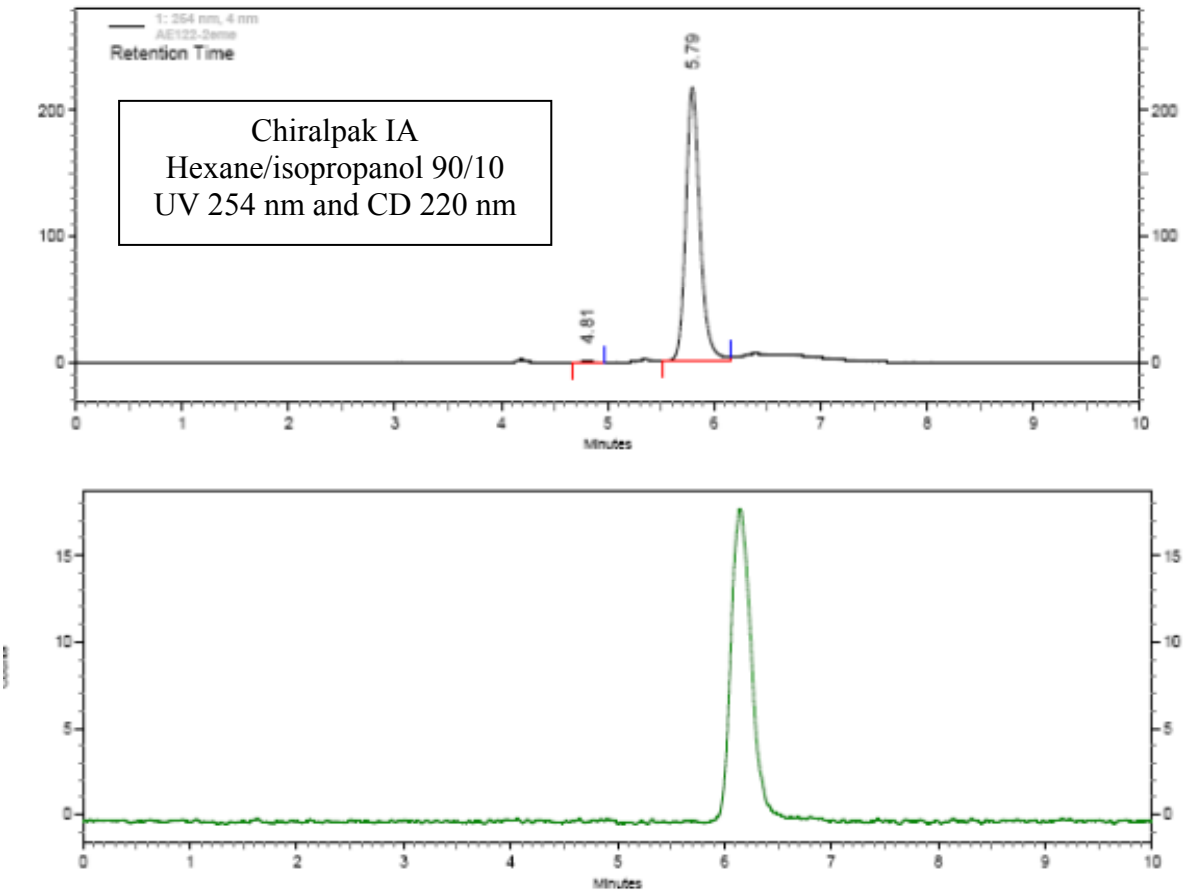
• Second fraction: 45 mg of the second eluted ((+, CD 220 nm)-enantiomer) with an enantiomeric excess of 99%.

Figure S10. Chromatograms of the collected enantiomers:



1: 254 nm, 4 nm
Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
4.81	8632475	100.00	0.60	1.00	0.00
Totals	8632475	100.00			



1: 254 nm, 4 nm

Results

Retention Time	Area	Area %	Capacity factor	Relative RT	Resolution (USP)
4.81	38927	0.48	0.60	1.00	0.00
5.79	8076330	99.52	0.93	1.55	4.20
Totals	8115257	100.00			

The first eluted enantiomer of **2a** in these chromatographic conditions is called (+)-**2a** in the main text, despite a specific rotation equal to zero. This sign was assigned by analogy of the CD spectra of **2b**[1], **2b**[2] and **2c**[1], particularly a positive band between 370 and 420 nm. However, this enantiomer called (+)-**2a** gives a positive CD signal at 380 nm in dichloromethane but a negative CD signal at 220 nm in the mobile phase (hexane/2-PrOH 9/1) used for the chiral HPLC analyse.

Theoretical calculations: At the DFT level of theory, after benchmark, the PBE0 hybrid functional[3] has been chosen as well as the LanL2DZ basis set [4] augmented with polarization functions on all atoms, except hydrogen ones (d orbital exponent respectively equal to 0.587 for carbon, 0.364 for phosphorus, 0.648 for chlorine, 0.961 for oxygen, a f orbital exponent for rhenium equal to 0.553). A diffuse "d" orbital (exponent 0.01) has also been added on rhenium atom. All the optimized geometries were checked as true minima on the potential energy surface using vibration frequencies calculations. Then, Time Dependent DFT calculations (TD-DFT) were performed on all species under consideration using either their optimized geometries or the X-ray ones, in order to compute their electronic spectra. For Circular Dichroism (CD) computations, a more extended basis set has also been used, i.e. a standard TZVP[5] basis sets augmented with diffuse orbitals on all atoms, except hydrogen (p orbital exponents respectively equal to 0.01 for carbon, 0.02 for nitrogen, 0.03 for oxygen, 0.017 for chlorine and 0.01 for phosphorus whereas the exponent of a diffuse d orbital for rhenium has been taken equal to 0.01). All calculations took into account solvent effects (CH_2Cl_2 and THF solvents for respectively complexes and ligands) unless indicated, using the PCM model[6].

3. C. Adamo and V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158.
4. (a) Dunning Jr., T. H.; Hay, P. J.; "Methods of Electronic Structure Theory", H. F. Schaeffer Ed., Plenum Press, New York, **1977**; (b) Hay, P. J.; Wadt, W. R.; *J. Chem. Phys*., **1985**, *82*, 270, (c) Hay, P. J.; Wadt, W. R.; *J. Chem. Phys*. **1985**, *82*, 284; (d) Hay, P. J.; Wadt, W. R.; *J. Chem. Phys*. **1985**, *82*, 299; (e) Schafer, A.; Horn, H.; R. Ahlrichs, R. *J. Chem. Phys*. **1992**, *97*, 2571.
5. A. Schaefer, C. Huber, and R. Ahlrichs, *J. Chem. Phys.*, **1994**, *100*, 5829.
6. J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, **2005**, *105*, 2999.

Compound 2a

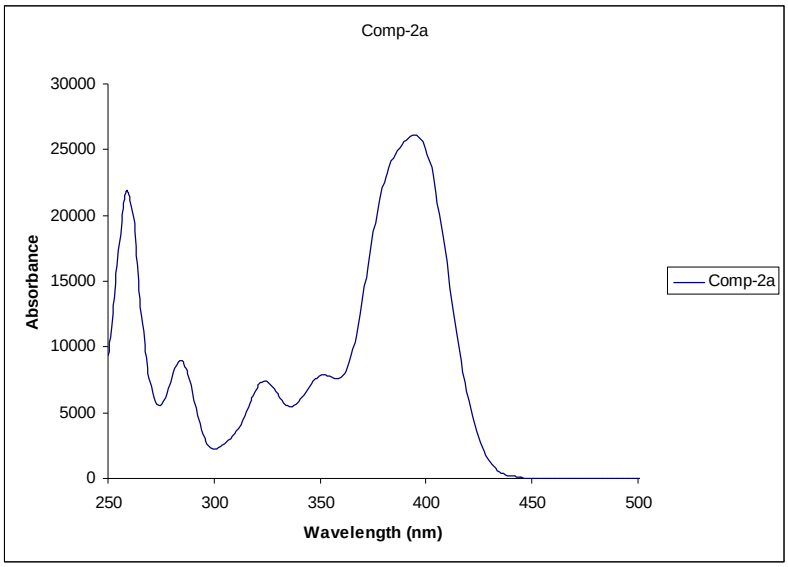


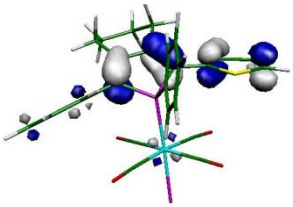
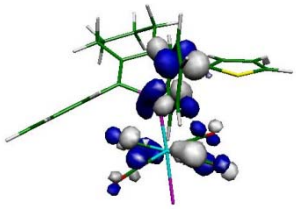
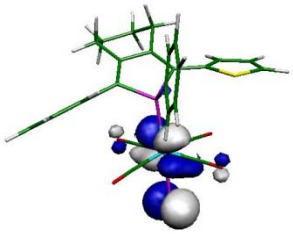
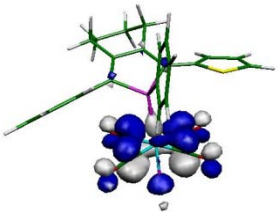
Figure S11. Simulated absorption spectrum of compound **2a**

#	λ/nm	ῡ/ 1000 cm^{-1}	ΔE/eV	f	Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	400.5	25.0	3.10	0.1699	H-0->L+0(+93%)
2	379.7	26.3	3.27	0.1432	H-0->L+1(+94%)
8	325.7	30.7	3.81	0.0212	H-0->L+4(+65%) H-1->L+1(18%)
27	260.0	38.5	4.77	0.0915	H-0->L+8(+70%) H-6->L+1(+9%)

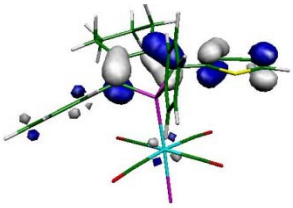
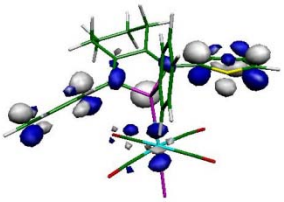
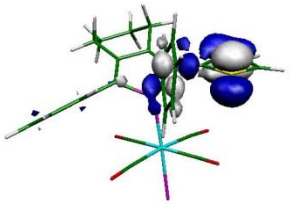
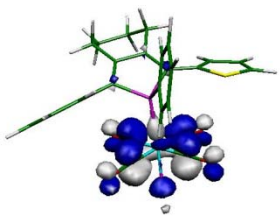
1 400.5 25.0 3.10 0.1699 S H-0->L+0(+93%)

2 379.7 26.3 3.27 0.1432 S H-0->L+1(+94%)

8 325.7 30.7 3.81 0.0212 S H-0->L+4(+65%) H-1->L+1(18%)

27 260.0 38.5 4.77 0.0915 S H-0->L+8(+70%) H-6->L+1(+9%)

%D :

MO	H-6	H-1	H	L	L+1	L+4	L+8	
%D	0.45	41.18	4.46	5.20	13.21	1.87	6.51	

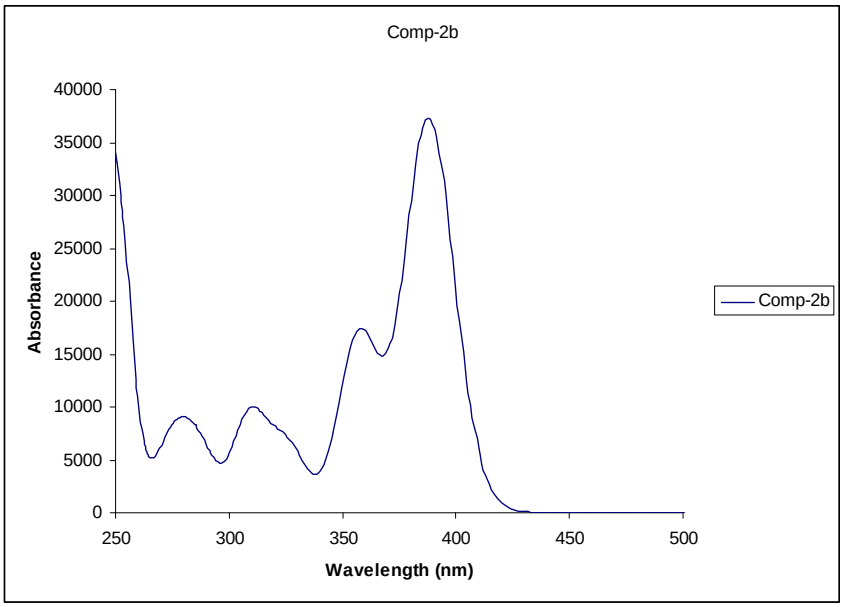
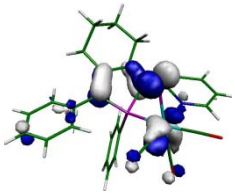
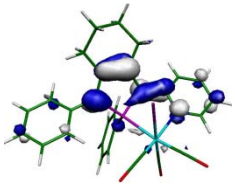


Figure S12. Simulated absorption spectrum of compound **2b**[2]

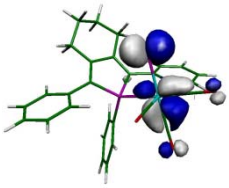
#	λ/nm	ῡ/ 1000 cm^{-1}	ΔE/eV	f	Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
1	388.1	25.8	3.19	0.2903	H-0->L+0(+96%)
3	357.3	28.0	3.47	0.1213	H-1->L+0(+51%) H-2->L+0(44%)
4	326.9	30.6	3.79	0.0442	H-0->L+1(+84%) H-1->L+1(9%)
30	243.1	41.1	5.10	0.0839	H-0->L+7(+24%) H-5->L+1(14%)

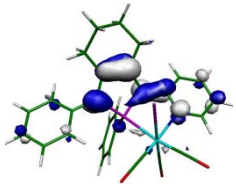
1 388.1 25.8 3.19 0.2903 S H-0->L+0(+96%)

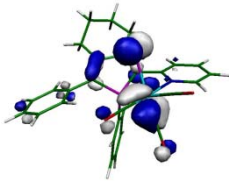


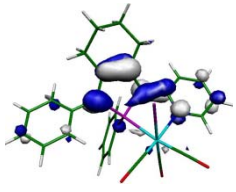


3 357.3 28.0 3.47 0.1213 S H-1->L+0(+51%) H-2->L+0(44%)









4 326.9 30.6 3.79 0.0442 S H-0->L+1(+84%) H-1->L+1(9%)

%D

MO	H-5	H-2	H-1	H	L	L+1	L+7
%D	2.13	26.16	33.77	18.54	2.75	5.18	1.93

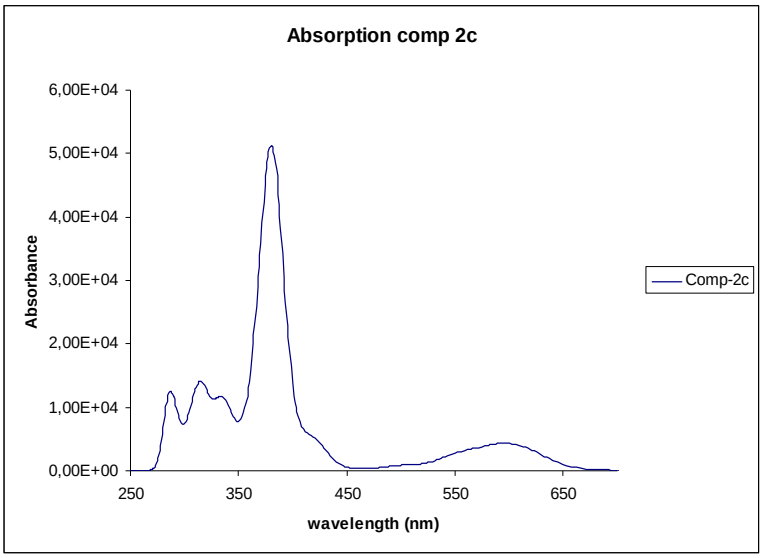
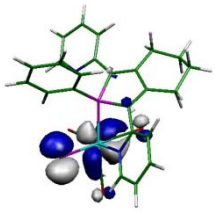
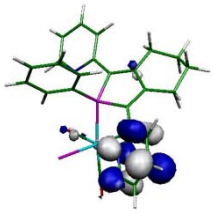


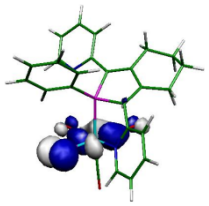
Figure S13. Simulated absorption spectrum of compound **2c**

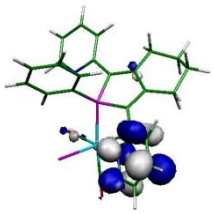
#	λ/nm	ū/ 1000 cm^{-1}	ΔE/eV	f	Assignment; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)
4	603.3	16.6	2.05	0.0304	H-0->L+1(+90%) H-1->L+1(+8%)
9	417.7	23.9	2.97	0.0380	H-1->L+2(+80%)
12	381.6	26.2	3.25	0.2645	H-2->L+1(+71%)
20	341.8	29.3	3.63	0.0110	H-0->L+4(+25%) H-0->L+5(+15%) H-1->L+3(13%) H-1->L+4(+11%)
29	313.1	31.9	3.96	0.0331	H-2->L+2(+42%) H-11->L+0(+13%)

4 603.3 16.6 2.05 0.0304 S H-0->L+1(+90%) H-1->L+1(+8%)

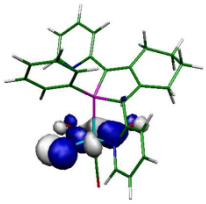


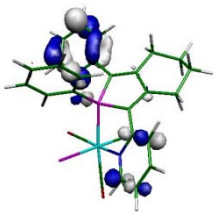




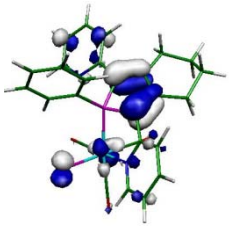


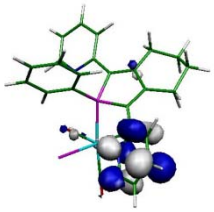
9 417.7 23.9 2.97 0.0380 S H-1->L+2(+80%)



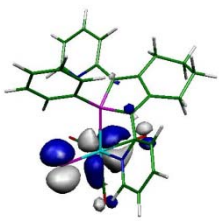
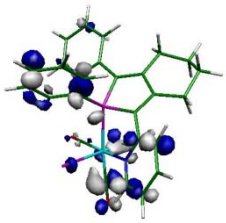
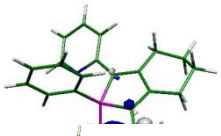
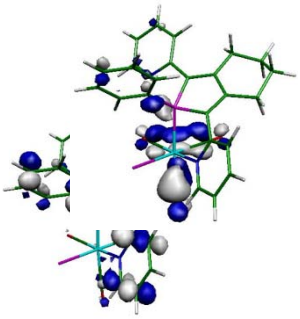
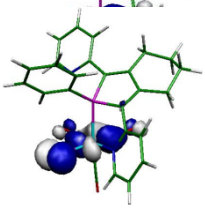
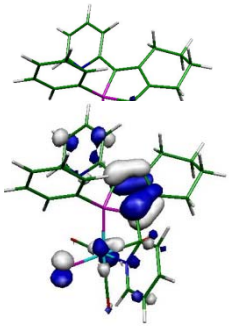


12 381.6 26.2 3.25 0.2645 S H-2->L+1(+71%)

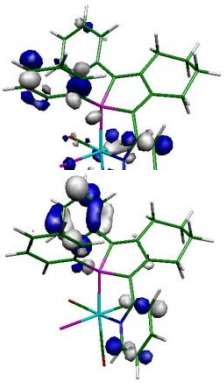
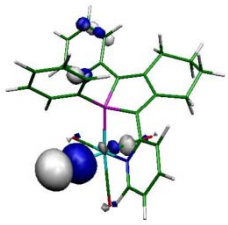
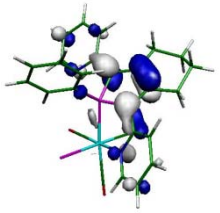




20 341.8 29.3 3.63 0.0110 S H-0->L+4(+25%) H-0->L+5(+15%) H-1->L+3(13%) H-1->L+4(+11%)

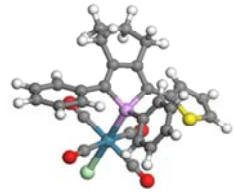
3.96 0.0331 S H-2->L+2(+42%) H-11->L

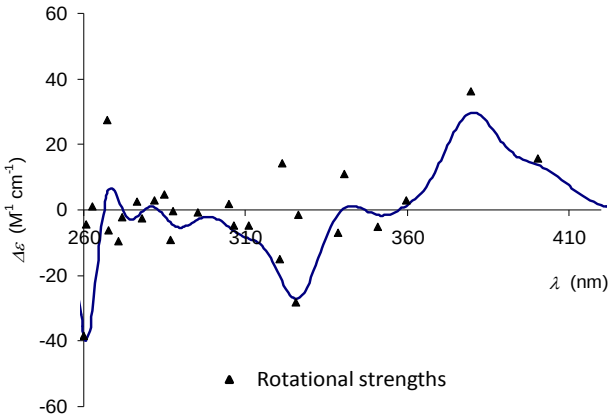
%D

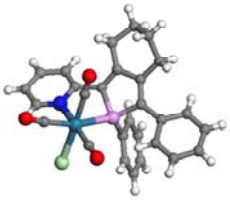
MO	H-11	H-2	H-1	H	L	L+1	L+2	L+3	L+4	L+5
%D	9.44	10.76	39.84	32.07	2.35	2.98	2.21	3.18	8.87	13.64

Figure S14. Calculated CD spectra

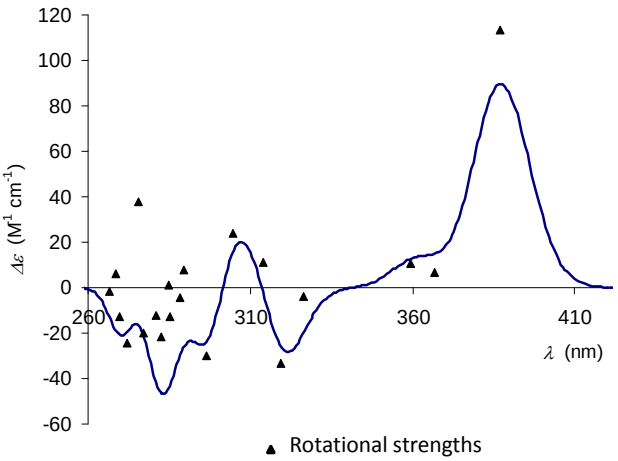


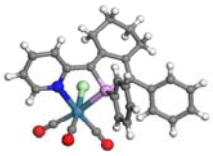
R_P-(-)-**2a**



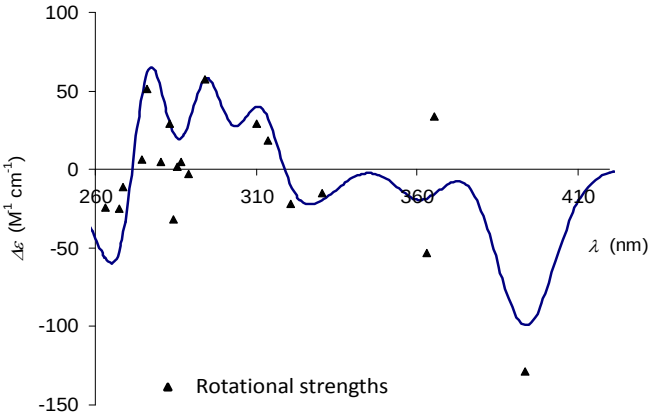


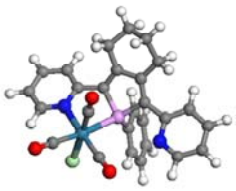
OC-6-44-C_{Re}-R_P-(+)-**2b**[1]





OC-6-44-C_{Re}-S_P-(-)-**2b**[2]





OC-6-44-C_{Re}-R_P-(+)-**2c**[1]

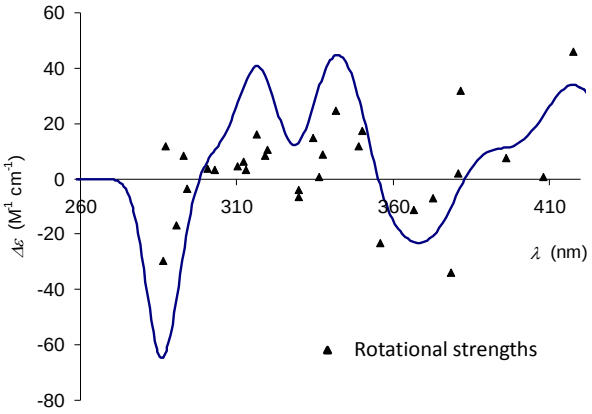


Table S1: percentage weights of frontier MOs of **2b**[1]

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
P	0.93	1.61	1.57	0.95	4.02	4.41	15.29	2.72
Cl	0.26	27.15	29.05	14.15	0.13	1.16	0.5	0.07
3CO	26.22	15.58	18.01	7.96	2.33	6.98	6.57	16.46
Pyridine	5.1	5.32	1.65	6.37	22.26	70.05	6.41	60.28
Re	57.65	30.05	36.58	15.96	2.52	3.72	4.01	7.92

Table S2: percentage weights of frontier MOs of **2b**[2]

	HOMO-3	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3
P	1.04	0.46	1.83	0.85	3.79	4.99	11.27	2.64
Cl	0.49	19.94	39.74	15.35	0.12	1.51	0.87	0.41
3CO	27.52	13.68	16.67	10.02	2.39	8.38	15.97	9
Pyridine	1.99	6.73	1.96	6.76	24.26	67.01	15.48	57.79
Re	60.29	26.16	33.77	18.54	2.75	5.18	8.09	5.28

X-ray Crystallographic Study :

Single crystals of (+)-C_{Re}-R_P-**2b**^{1} and (-)-C_{Re}-S_P-**2b**^{2} suitable for X-Ray crystal analyses were obtained by slow diffusion of vapors of pentane into dichloromethane solutions. Single crystal data collection were performed at 150 K with an APEX II Bruker-AXS (Centre de Diffractométrie, Université de Rennes 1, France) with Mo-$K\alpha$ radiation (λ = 0.71073 Å). Reflections were indexed, Lorentz-polarization corrected and integrated by the *DENZO* program of the KappaCCD software package. The data merging process was performed using the SCALEPACK program.[7] Structure determinations were performed by direct methods with the solving program SIR97,[8] that revealed all the non hydrogen atoms. SHELXL program[9] was used to refine the structures by full-matrix least-squares based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters.

Single crystals of all these derivatives were always coated in paratone oil once removed from the mother solution, mount at low temperature on the diffractometer gionometer and X-ray data collection were performed at low temperature. Table S1 gives the crystallographic data for the derivatives (+)-C_{Re}-R_P-**2b**^{1} and (-)-C_{Re}-S_P-**2b**^{2}.

Atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography.[10] CCDC reference numbers 857938 and 857939, contain the supplementary crystallographic data for derivatives (-)-C_{Re}-S_P-**2b**^{2} and (+)-C_{Re}-R_P-**2b**^{1} respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retreving.html or from the

[7] Z. Otwinowski, W. Minor, W. In *Methods in Enzymology*, (Ed.: C.W. Carter, Jr. & R.M. Sweet), New York:Academic Press, **1997**, *276*, 307.
[8] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. of Applied Cryst.* **1999**, *32,* 115.
[9] G. M. Sheldrick, *SHELX97,* Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.
[10] International Tables for X-ray Crystallography, vol C, Ed. Kluwer, Dordrech, **1992**.

Cambridge Crystallographic Data Center, 12 union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

Table S3 . Crystal data and structure refinement for (-)-C_{Re}-S_P-**2b**^{2} and (+)-C_{Re}-R_P-**2b**^{1}.

	(-)-C_{Re}-S_P-**2b**^{2}	(+)-C_{Re}-R_P-**2b**^{1}.CH_2Cl_2
Molecular formula	$C_{28}H_{22}Cl_1N_1O_3P_1Re_1$	$C_{29}H_{24}Cl_3N_1O_3P_1Re_1$
CCDC number	857938	857939
Molecular weight	673.09	758.01
a (Å)	10.6088(9)	11.2329(8)
b (Å)	15.0400(13)	14.0307(12)
c (Å)	16.0365(16)	17.9380(14)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	2558.7(4)	2827.1(4)
Z	4	4
Dc (g cm^{-3})	1.747	1.781
Crystal system	orthorhombic	orthorhombic
Space group	P212121	P212121
Temperature (K)	150	150
Wavelength Mo-$K\alpha$ (Å)	0.71073	0.71073
Crystal size (mm)	0.16*0.11*0.07	0.20*0.15*0.09
μ (mm^{-1})	4.946	4.670
F(000)	1312	1480
θ limit (°)	2.54-25.75	2.59-26.28
Index ranges hkl	$-13 \le h \le 10$, $-18 \le k \le 17$, $-20 \le l \le 20$	$-14 \le h \le 10$, $-17 \le k \le 17$, $-22 \le l \le 21$
Reflections collected	17744	21631
Independant reflections	5249	5754
Reflections [$I>2\sigma(I)$]	4552	5490
Data/restraints/parameters	5249/0/316	5754/0/343
Goodness-of-fit on F^2	0.938	1.102
Final R indices [$I>2\sigma(I)$]	$R1$= 0.0409 $wR2$= 0.0792	$R1$= 0.0241 $wR2$= 0.0581
R indices (all data)	$R1$= 0.0505 $wR2$= 0.0826	$R1$= 0.0270 $wR2$= 0.0814
Absolute structure parameter	0.009(10)	0.003(8)
Largest diff peak and hole (e Å^{-3})	1.792 and -1.286	0.616 and -1.288

Figure S15. Molecular structure of the complex (-)-C_{Re}-S_P-**2b**[2] (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.

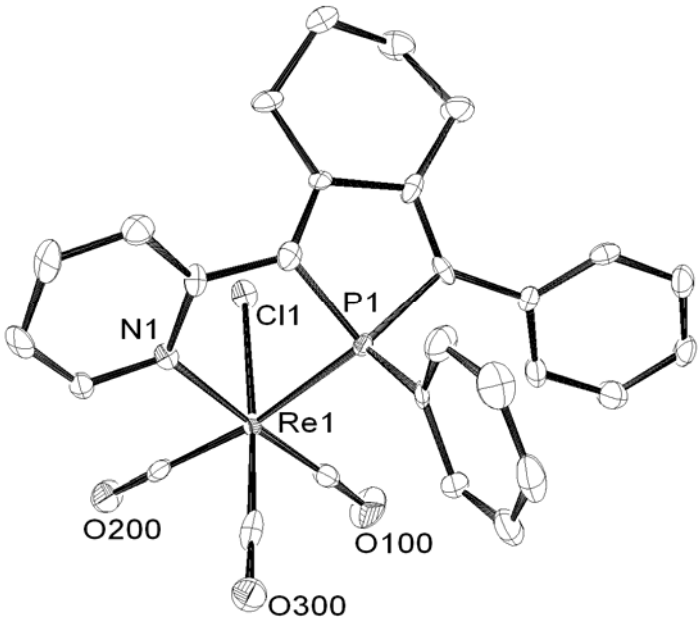


Figure S16 . Molecular structure of the complex (+)-C_{Re}-R_P-**2b**[1] (thermal ellipsoids 50% probability). Hydrogen atoms have been omitted for clarity.