Selective synthesis of the 2-hydroxyferrocene-aldimine enantiomers – extended planar chiral analogues of the "flat" salicylaldimine ligand family

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Supporting information:

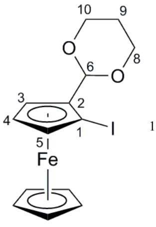
General remarks:

Materials: All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas atmosphere (Argon) by using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Ferrocenes **8**,[1] (*S*,*S*)-**6**,[2] (*S*,*S*,*p*-*S*)-**13**,[2] (*S*,*S*,*p*-*S*)-**16**[2] were prepared according to literature procedures. The syntheses of the ferrocenes (*rac*)-**9**,[3] (*S*,*S*,*p*-*R*)-**17**[4] and (*S*,*S*,*p*-*R*)-**13**[4] were independently developed and subsequently published, differing only slightly from the syntheses presented here. The X-ray crystal structure analyses of compounds (*rac*)-**9**, (*S*,*S*,*p*-*S*)-**16**, (*S*,*S*,*p*-*R*)-**17** and (*S*,*S*,*p*-*R*)-**13** are reported for the first time within this publication.
Techniques: The following instruments were used for physical characterization of the compounds: melting points: TA-instruments DSC Q-20; elemental analyses: Foss–Heraeus CHNO-Rapid; HPLC: Chiralcel OD-H column, hexanes : isopropanol = 95 : 5 at 1 ml/min; IR: Varian 1300 FT-IR; NMR: Varian UNITY plus NMR spectrometer (^{1}H: 600 MHz; ^{13}C: 151 MHz); Varian INOVA 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz) (numbering schemes used for the NMR listings are unsystematic); Polarimetric measurements: Perkin-Elmer Polarimeter 341 (unit used for all values of optical rotations is [deg $\cdot$ ml $\cdot$ g^{-1} $\cdot$ dm^{-1}], the respective concentration is given in a unit of [10 mg $\cdot$ ml^{-1}]).
X-ray crystal structure determinations: Data sets were collected with Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, 1997, **276**, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.*, 1995, **A51**, 33-37; R.H. Blessing, *J. Appl. Cryst.*, 1997, **30**, 421-426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.*, 2003, **A59**, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.*, 1990, **A46**, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997)).
CCDC 714358 – 714372 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Syntheses:

Synthesis of the racemic series

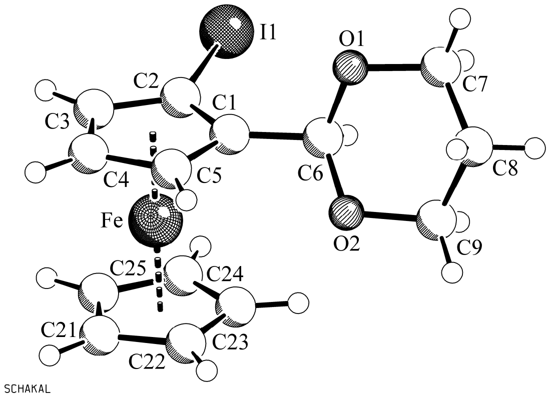
(*rac*)-2-(1,3-Dioxan-2-yl)-1-iodoferrocene ((*rac*)-9)



(*rac*)-**9**

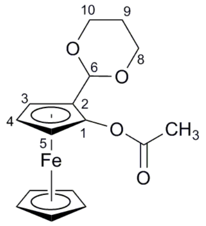
Sec-butyllithium (24.9 ml, 32.3 mmol, 1.3 M solution in pentane) was added to a solution of the dioxane **8** (8.00 g, 29.4 mmol) in tetrahydrofurane (150 ml) at –78°C and the mixture was subsequently stirred for one hour at –10°C, yielding a bright orange precipitate. The mixture was cooled to −78°C and iodine (8.20 g, 32.3 mmol), dissolved in tetrahydrofurane (100 ml), was slowly added. After warming to room temperature and stirring for another hour, the reaction was terminated by addition of a saturated sodium thiosulfate solution (50 ml). The organic layer was separated, dried over magnesium sulfate, filtered and the solvent was removed. The crude residue was purified by filtration on silica (cyclohexane : triethylamine = 9 : 1), yielding 8.19 g of a yellow oil. This crude product was a mixture of starting material, product and another unknown byproduct, containing about 75 % of the desired product. The mixture was inseparable by means of column chromatography, but could be used directly for the next reaction. Analytically pure material could be obtained by threefold recrystallisation from pentane at –30°C, yielding yellow crystals of (*rac*)-**9** suitable for X-ray analysis (Reaction scale: 3.67 mmol, yield: 433 mg, 29.6 %).

Mp 89 °C (DSC); (Found: C, 42.18; H, 3.70. $C_{14}H_{15}FeIO_2$ requires C, 42.25; H, 3.80%); ν_{max}(KBr)/cm^{-1} 2967, 1378, 1276, 1237, 1146, 1105, 1004, 989, 936 and 820; δ_H (500 MHz; C_6D_6; $SiMe_4$) 5.39 (1 H, t, ^4J = 0.5 Hz, ^5J = 0.5 Hz, 6-H), 4.58 (1 H, ddd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, ^4J = 0.5 Hz, 3-H), 4.24 (1 H, dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 5-H), 4.10 (5H, s, Cp), 3.91 (1 H, dddd, ^2J = 11.3 Hz, ^3J = 5.0 Hz, ^4J = 1.8 Hz, ^3J = 1.3 Hz, 8-H_{eq}), 3.84 (1 H, ddd, ^3J = 2.7 Hz, ^3J = 2.4 Hz, ^5J = 0.5 Hz, 4-H), 3.83 (1 H, dddd, ^2J = 11.3 Hz, ^3J = 5.0 Hz, ^4J = 1.8 Hz, ^3J = 1.3 Hz, 10-H_{eq}), 3.55 (1 H, ddd, ^3J = 12.5 Hz, ^2J = 11.3 Hz, ^3J = 2.6 Hz, 10-H_{ax}), 3.50 (1 H, ddd, ^3J = 12.5 Hz, ^2J = 11.3 Hz, ^3J = 2.6 Hz, 8-H_{ax}), 1.83 (1 H, dtt, ^2J = 13.3 Hz, ^3J = 12.5 Hz, ^3J = 5.0 Hz, 9-H_{ax}) and 0.64 (1 H, dtt, ^2J = 13.3 Hz, ^3J = 2.6 Hz, ^3J = 1.3 Hz, 9-H_{eq}); δ_C (126 MHz; C_6D_6; $SiMe_4$) 101.3 (C-6), 87.5(C-2), 75.0 (C-5), 72.2 (Cp), 68.9 (C-4), 67.2, 67.2 (C-8, C-10), 66.9 (C-3), 42.0 (C-1) and 25.8 (C-9) [relative assignment for position 8 and 10]; ^1H / ^1H gcosy (500 MHz / 500 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 4.58 / 4.24, 3.84 (3-H / 5-H, 4-H), 4.24 / 4.58, 3.84 (5-H / 3-H, 4-H), 3.91 / 3.50, 1.83, 0.64 (8-H_{eq} / 8-H_{ax}, 9-H_{ax}, 9-H_{eq}), 3.84 / 4.58, 4.24 (4-H / 3-H, 5-H), 3.83 / 3.55, 1.83, 0.64 (10-H_{eq} / 10-H_{ax}, 9-H_{ax}, 9-H_{eq}), 3.55 / 3.83, 1.83, 0.64 (10-H_{ax} / 10-H_{eq}, 9-H_{ax}, 9-H_{eq}), 3.50 / 3.91, 1.83, 0.64 (8-H_{ax} / 8-H_{eq}, 9-H_{ax}, 9-H_{eq}), 1.83 / 3.91, 3.83, 3.55, 3.50, 0.64 (9-H_{ax} / 8-H_{eq}, 10-H_{eq}, 10-H_{ax}, 8-H_{ax}, 9-H_{eq}) and 0.64 / 3.91, 3.83, 3.55, 3.50, 1.83 (9-H_{eq} / 8-H_{eq}, 10-H_{eq}, 10-H_{ax}, 8-H_{ax}, 9-H_{ax}); ^1H / ^{13}C ghsqc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.39 / 101.3 (6), 4.58 / 66.9 (3), 4.24 / 75.0 (5), 4.10 / 72.2 (Cp), 3.91, 3.83, 3.55, 3.50 / 67.2, 67.2 (8, 10), 3.84 / 68.9 (4) and 1.83, 0.64 / 25.8 (9); ^1H / ^{13}C ghmbc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 4.58 / 66.9, 42.0 (6-H / C-3, C-1) and 1.83 / 67.2, 67.2 (9-H_{ax} / 8, 10); *m*/*z* (EI) 398 (M^+, 100%), 275 (9), 212 (16), 121 (15) and 57 (61).



Selected bond lengths (Å) and angles (°): Fe-C($Cp_{unsubst.}$) 2.034(3) – 2.057(3), Fe-C($Cp_{subst.}$) 2.008(2) – 2.047(3), C1-C2 1.431(4), C1-C5 1.434(4), C1-C6 1.488(4), C2-I1 2.079(3), C6-O1 1.410(3), C6-O2 1.398(3), O1-C7 1.439(4), O2-C9 1.436(3); C2-C1-C5 106.4(2); C2-C1-C6 127.1(2), C5-C1-C6 126.6(2), C1-C2-I1 125.9(2), C1-C6-O1 108.2(2), C1-C6-O2 108.8(2), C6-O1-C7 109.6(2), C6-O2-C9 110.5(2).

(*rac*)-1-Acetoxy-2-(1,3-dioxan-2-yl)ferrocene ((*rac*)-10)

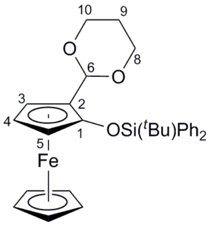


(*rac*)-**10**

The crude iodide (*rac*)-**9** (8.20 g, 20.6 mmol) and copper(I) oxide (2.95 g, 20.6 mmol) were suspended in acetonitrile (300 ml). After addition of acetic acid (2.94 ml, 51.5 mmol), the mixture was heated to reflux for three hours. Removal of the solvent gave the crude product which was purified by column chromatography (cyclohexane : triethylamine = 8 : 1). The product was obtained as a yellow solid (4.39 g, 64.6 %).
X-ray quality crystals were obtained from a solution of (*rac*)-**10** in pentane at –30°C.

Mp 74 °C (DSC); (Found: C, 58.11; H, 5.45. $C_{16}H_{18}FeO_4$ requires C, 58.21; H, 5.50%); ν_{max}(KBr)/cm^{-1} 2830, 1378 1755, 1450, 1362, 1205, 1141, 1090, 1008 and 888; δ_H (500 MHz; C_6D_6; $SiMe_4$) 5.47 (1 H, s, 6-H), 4.45 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.6 Hz, 5-H), 4.34 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.6 Hz, 3-H), 4.29 (5 H, s, Cp), 3.87 (1 H, dddd, ^2J = 11.3 Hz, ^3J = 5.0 Hz, ^4J = 1.8 Hz, ^3J = 1.3 Hz, 8-H$_{eq}$), 3.82 (1 H, dddd, ^2J = 11.2 Hz, ^3J = 5.0 Hz, ^4J = 1.8 Hz, ^3J = 1.3 Hz, 10-H$_{eq}$), 3.71 (1 H, t, ^3J = 2.7 Hz, 4-H), 3.49 (1 H, ddd, ^3J = 12.4 Hz, ^2J = 11.3 Hz, ^3J = 2.6 Hz, 8-H$_{ax}$), 3.47 (1 H, ddd, ^3J = 12.4 Hz, ^2J = 11.2 Hz, ^3J = 2.6 Hz, 10-H$_{ax}$), 1.83 (1 H, dtt, ^2J = 13.3 Hz, ^3J = 12.4 Hz, ^3J = 5.0 Hz, 9-H$_{ax}$), 1.78 (3 H, s, CO*Me*) and 0.66 (1 H, dtt, ^2J = 13.3 Hz, ^3J = 2.6 Hz, ^3J = 1.3 Hz, 9-H$_{eq}$); δ_C (126 MHz; C_6D_6; $SiMe_4$) 168.4 (*C*OMe), 114.1 (C-1), 99.3 (C-6), 78.7 (C-2), 70.6 (Cp), 67.03, 66.99 (C-8, C-10), 62.8 (C-3), 62.4 (C-4), 61.9 (C-5), 26.1 (C-9) and 20.7 (CO*Me*) [relative assignment for position 8 and 10]; ^{1}H / ^{1}H gcosy (500 MHz / 500 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 4.45 / 4.34, 3.71 (5-H / 3-H, 4-H), 4.34 / 4.45, 3.71 (3-H / 5-H, 4-H), 3.87 / 3.49, 1.83, 0.66 (8-H$_{eq}$ / 8-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.82 / 3.47, 1.83, 0.66 (10-H$_{eq}$ / 10-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.71 / 4.45, 4.34 (4-H / 5-H, 3-H), 3.49 / 3.87, 1.83, 0.66 (8-H$_{ax}$ / 8-H$_{eq}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.47 / 3.82, 1.83, 0.66 (10-H$_{ax}$ / 10-H$_{eq}$, 9-H$_{ax}$, 9-H$_{eq}$), 1.83 / 3.87, 3.82, 3.49, 3.47, 0.66 (9-H$_{ax}$ / 8-H$_{eq}$, 10-H$_{eq}$, 8-H$_{ax}$, 10-H$_{ax}$, 9-H$_{eq}$) and 0.66 / 3.87, 3.82, 3.49, 3.47, 1.83 (9-H$_{eq}$ / 8-H$_{eq}$, 10-H$_{eq}$, 8-H$_{ax}$, 10-H$_{ax}$, 9-H$_{ax}$); ^{1}H / ^{13}C ghsqc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.47 / 99.3 (6), 4.45 / 61.9 (5), 4.34 / 62.8 (3), 4.29 / 70.6 (Cp), 3.87, 3.82, 3.49, 3.47 / 67.03, 66.99 (8, 10), 3.71 / 62.4 (4), 1.83, 0.66 / 26.1 (9) and 1.78 / 20.7 (CO*Me*); ^{1}H / ^{13}C ghmbc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.47 / 114.1, 61.9 (6-H / C-1, C-5), 3.71 / 78.7, 61.9 (4-H / C-2, C-5), 1.83 / 67.03, 66.99 (9-H$_{ax}$ / C-8, C-10) and 1.78 / 168.4 (CO*Me* / *C*OMe); *m*/*z* (EI) 330 (M$^+$, 100%), 288 (89), 230 (52), 164 (37) and 101 (11).

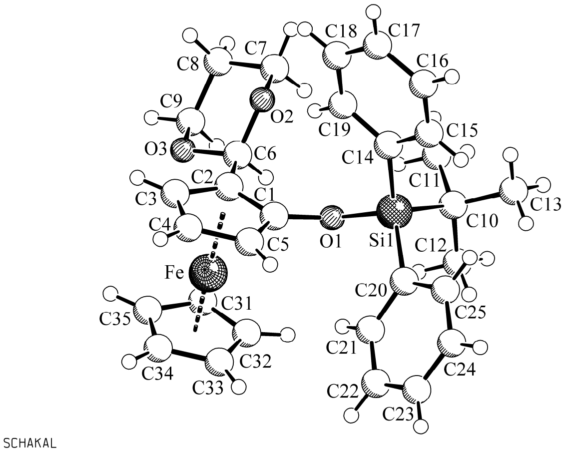
(*rac*)-1-(*tert*-Butyldiphenylsiloxy)-2-(1,3-dioxan-2-yl)ferrocene ((*rac*)-11)



(*rac*)-**11**

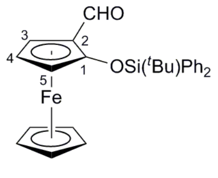
Sodium methoxide (600 mg, 11.1 mmol) was added to a solution of the acetate (*rac*)-**10** (3.35 g, 10.1 mmol) in *N*,*N*-dimethylformamide (30 ml), yielding a deep red reaction mixture. After 90 minutes, *tert*-butyldiphenylsilylchloride (2.63 ml, 10.1 mmol) was added and the bright yellow mixture was stirred overnight. Removal of the solvent and purification of the crude material by column chromatography (cyclohexane : triethylamine = 9 :1) yielded 4.52 g (85.3 %) of the product as a yellow solid.
X-ray quality crystals were obtained from a solution of (*rac*)-**11** in pentane at –30°C.

Mp 98 °C (DSC); (Found: C, 68.05; H, 6.40. $C_{30}H_{34}FeO_3Si$ requires C, 68.43; H, 6.51%); ν_{max}(KBr)/cm^{-1} 2961, 2854, 1463, 1427, 1096, 998, 900, 814, 742 and 701; δ_H (500 MHz; $CDCl_3$; $SiMe_4$) 7.94 (2 H, ps dd, *o*-Ph), 7.66 (2 H, ps dd, *o*-Ph′), 7.54 – 7.46 (3 H, m, *m*-Ph, *p*-Ph), 7.39 (1 H, m, *p*-Ph′), 7.33 (2 H, m, *m*-Ph′), 5.77 (1 H, s, 6-H), 4.34 (1 H, dddd, ^2J = 11.4 Hz, ^3J = 5.0 Hz, ^4J = 1.8 Hz, ^3J = 1.2 Hz, 8-H$_{eq}$), 4.18 (1 H, dddd, ^2J = 11.4 Hz, ^3J = 5.0 Hz, ^4J = 1.8 Hz, ^3J = 1.2 Hz, 10-H$_{eq}$), 4.12 (5 H, s, Cp), 4.07 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.5 Hz, 3-H), 4.06 (1 H, m, 8-H$_{ax}$), 3.94 (1 H, m, 10-H$_{ax}$), 3.55 (1 H, t, ^3J = 2.7 Hz, 4-H), 3.49 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.5 Hz, 5-H), 2.22 (1 H, dtt, ^2J = 13.4 Hz, ^3J = 12.5 Hz, ^3J = 5.0 Hz, 9-H$_{ax}$), 1.41 (1 H, dtt, ^2J = 13.4 Hz, ^3J = 2.4 Hz, ^3J = 1.2 Hz, 9-H$_{eq}$) and 1.13 (9 H, s, C(C*H*$_3$)$_3$); δ_C (126 MHz; $CDCl_3$; $SiMe_4$) 135.60, 135.58 (*o*-Ph, *o*-Ph′), 133.8 (*i*-Ph), 132.1 (*i*-Ph′), 130.0 (*p*-Ph), 129.7 (*p*-Ph′), 127.7 (*m*-Ph), 127.5 (*m*-Ph′), 120.2 (C-1), 99.6 (C-6), 75.0 (C-2), 69.7 (Cp), 67.6 (C-8), 67.2 (C-10), 60.3 (C-4), 59.7 (C-3), 59.6 (C-5), 26.5 (C(*C*H$_3$)$_3$), 25.8 (C-9) and 19.4 (*C*(CH$_3$)$_3$) [relative assignment for position 8 and 10]; ^{1}H / ^{1}H gcosy (500 MHz / 500 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 7.94 / 7.54 – 7.46 (*o*-Ph / *m*-Ph), 7.54 – 7.46 / 7.94 (*m*-Ph / *o*-Ph), 7.33 / 7.66 (*m*-Ph′ / *o*-Ph′), 4.34 / 4.06, 2.22, 1.41 (8-H$_{eq}$ / 8-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 4.18 / 3.94, 2.22, 1.41 (10-H$_{eq}$ / 10-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 4.07 / 3.55 (3-H, 4-H), 4.06 / 4.34, 2.22, 1.41 (8-H$_{ax}$ / 8-H$_{eq}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.94 / 4.18, 2.22, 1.41 (10-H$_{ax}$ / 10-H$_{eq}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.55 / 4.07, 3.49 (4-H / 3-H, 5-H), 3.49 / 3.55 (5-H / 4-H), 2.22 / 4.34, 4.18, 4.06, 3.94, 1.41 (9-H$_{ax}$ / 8-H$_{eq}$, 10-H$_{eq}$, 8-H$_{ax}$, 10-H$_{ax}$, 9-H$_{eq}$) and 1.41 / 4.34, 4.18, 4.06, 3.94, 2.22 (9-H$_{eq}$ / 8-H$_{eq}$, 10-H$_{eq}$, 8-H$_{ax}$, 10-H$_{ax}$, 9-H$_{ax}$); ^{1}H / ^{13}C ghsqc (500 MHz / 126 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 7.94, 7.66 / 135.60, 135.58 (*o*-Ph, *o*-Ph′), 7.54 – 7.46 / 130.0, 127.7 (*p*-Ph, *m*-Ph), 7.39 / 129.7 (*p*-Ph′), 7.33 / 127.5 (*m*-Ph′), 5.77 / 99.6 (6), 4.34, 4.06 / 67.6 (8), 4.18, 3.94 / 67.2 (10), 4.12 / 69.7 (Cp), 4.07 / 59.7 (3), 3.55 / 60.3 (4), 3.49 / 59.6 (5), 2.22, 1.41 / 25.8 (9) and 1.13 / 26.5 (C(*C*H$_3$)$_3$); ^{1}H / ^{13}C ghmbc (500 MHz / 126 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 7.94 / 133.8, 130.0 (*o*-Ph / *i*-Ph, *p*-Ph), 7.66 / 132.1, 127.5 (*o*-Ph′ / *i*-Ph′, *m*-Ph′), 7.39 / 135.60, 135.58 (*p*-Ph / *o*-Ph), 7.33 / 132.1 (*m*-Ph′ / *i*-Ph′), 5.77 / 120.2, 75.0, 67.6, 67.2, 59.6 (6-H / C-1, C-2, C-8, C-10, C-5), 4.34 / 99.6, 67.2 (8-H$_{eq}$ / C-6, C-10), 4.18 / 99.6, 67.6 (10-H$_{eq}$ / C-6, C-8), 4.07 / 120.2, 75.0 (3-H / C-1, C-2), 3.55 / 120.2, 75.0, 59.6 (4-H, C-1, C-2, C-5), 3.49 / 120.2, 75.0, 60.3 (5-H, C-1, C-2, C-4), 2.22 / 67.6, 67.2 (9-H$_{ax}$ / C-8, C-10) and 1.13 / 19.4 (C(C*H*$_3$)$_3$, *C*(CH$_3$)$_3$); *m*/*z* (EI) 526 (M$^+$, 100%), 431 (8), 375 (10), 275 (3) and 135 (15).



Selected bond lengths (Å) and angles (°): Fe-C($Cp_{unsubst.}$) 2.023(2) – 2.054(2), Fe-C($Cp_{subst.}$) 2.028(2) – 2.054(2), C1-C2 1.414(3), C1-C5 1.417(3), C1-O1 1.373(3), O1-Si1 1.658(2), Si1-C10 1.879(2), Si1-C14 1.874(3), Si1-C20 1.874(3), C2-C6 1.486(3), C6-O2 1.411(3), C6-O3 1.404(3), O2-C7 1.439(3), O3-C9 1.437(3); C2-C1-C5 109.3(2); C2-C1-O1 122.6(2), C5-C1-O1 128.1(2), C1-O1-Si1 129.3(1), O1-Si1-C10 103.1(1), O1-Si1-C14 108.7(1), O1-Si1-C20 107.5(1), C1-C2-C6 125.0(2), C2-C6-O2 108.3(2), C2-C6-O3 109.6(2), C6-O2-C7 110.2(2), C6-O3-C9 110.6(2).

(*rac*)-1-(*tert*-Butyldiphenylsiloxy)-2-formylferrocene ((*rac*)-12)

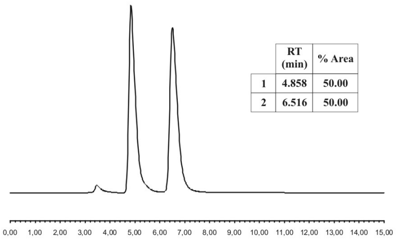


(*rac*)-**12**

The acetal (*rac*)-**11** (4.52 g, 8.58 mmol) and *p*-toluene sulfonic acid (3.26 g, 17.2 mmol) were dissolved in a two-phase mixture of dichloromethane (150 ml) and water (50 ml). The mixture was heated to reflux for three hours under vigorous stirring, the phases were separated and the organic phase was dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by filtration on silica (cyclohexane : ethyl acetate = 4 : 1). The resulting deep red oil was dissolved in pentane (30 ml) and the solution was stored at 4°C overnight. Removal of the supernatant liquid gave a red solid, which was dried in vacuo (3.12 g, 79.8 %).
X-ray quality crystals were obtained from a solution of (*rac*)-**12** in pentane at –30°C.

Mp 90 °C (DSC); (Found: C, 69.15; H, 5.97. $C_{27}H_{28}FeO_2Si$ requires C, 69.23; H, 6.02%); ν_{max}(ATR)/cm^{-1} 2860, 2811, 1674, 1461, 1447, 1429, 1285, 1207, 1104, 1015, 894, 820, 762, 700 and 606; δ_H (600 MHz; C_6D_6; $SiMe_4$) 10.8 (1 H, s, CHO), 7.85 (2 H, ps d, *o*-Ph), 7.62 (2 H, ps d, *o*-Ph´), 7.24 – 7.19 (3 H, m, *m*-Ph, *p*-Ph), 7.13 (1 H, m, *p*-Ph´), 7.09 (2 H, m, *m*-Ph´), 4.48 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 3-H), 3.93 (5 H, s, Cp), 3.74 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 5-H), 3.55 (1 H, t, ^3J = 2.8 Hz, 4-H), 1.08 (9 H, s, C(C*H*$_3$)$_3$); δ_C (151 MHz; C_6D_6; $SiMe_4$) 190.9 (C*H*O), 136.0 (*o*-Ph), 135.8 (*o*-Ph´), 133.4 (*i*-Ph), 132.1 (*i*-Ph´), 130.6 (*p*-Ph), 130.4 (*p*-Ph´), 128.2 (*m*-Ph, *m*-Ph´), 125.0 (C-1), 70.6 (Cp), 69.7 (C-2), 65.5 (C-4), 63.4 (C-5), 61.5 (C-3), 26.7 (C(*C*H$_3$)$_3$), 19.6 (*C*(CH$_3$)$_3$); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 7.85 / 7.24 – 7.19 (*o*-Ph / *m*-Ph, *p*-Ph), 7.62 / 7.13, 7.09 (*o*-Ph´ / *p*-Ph´, *m*-Ph´), 7.24 – 7.19 / 7.85 (*m*-Ph, *p*-Ph / *o*-Ph), 7.13 / 7.62, 7.09 (*p*-Ph´ / *o*-Ph´, *m*-Ph´), 7.09 / 7.62, 7.13 (*m*-Ph´ / *o*-Ph´, *p*-Ph´), 4.48 / 3.74, 3.55 (3-H / 5-H, 4-H), 3.74 / 4.48, 3.55 (5-H / 3-H, 4-H), 3.55 / 4.48, 3.74 (4-H / 3-H, 5-H); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 10.8 / 190.9 (*C*HO), 7.85 / 136.0 (*o*-Ph), 7.62 / 135.8 (*o*-Ph´), 7.24 – 7.19 / 130.6, 128.2 (*p*-Ph, *m*-Ph), 7.13 / 130.4 (*p*-Ph´), 7.09 / 128.2 (*m*-Ph´), 4.48 / 61.5 (3), 3.93 / 70.6 (Cp), 3.74 / 63.4 (5), 3.55 / 65.5 (4), 1.08 / 26.7 (C(*CH*$_3$)$_3$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 10.8 / 61.5 (CHO / C-3), 7.85 / 136.0, 133.4, 130.6, 128.2 (*o*-Ph / *o*-Ph, *i*-Ph, *p*-Ph, *m*-Ph), 7.62 / 135.8, 132.1, 130.4, 128.2 (*o*-Ph´ / *o*-Ph´, *i*-Ph´, *p*-Ph´, *m*-Ph´), 7.24 – 7.19 / 136.0, 133.4, 128.2 (*m*-Ph, *p*-Ph / *o*-Ph, *i*-Ph, *m*-Ph), 7.13 / 135.8 (p-Ph´ / o-Ph´), 7.09 / 132.1, 128.2 (*m*-Ph´ / *i*-Ph´, *m*-Ph´), 4.48 / 65.5, 63.4 (3-H / C-4, C-5), 3.74 / 125.0, 65.5, 61.5 (5-H / C-1, C-4, C-3), 3.55 / 125.0, 63.4, 61.5 (4-H / C-1, C-5, C-3), 1.08 / 26.7, 19.6 (C(C*H*$_3$)$_3$ / C(*C*H$_3$)$_3$, *C*(CH$_3$)$_3$); *m*/*z* (EI) 468 (M$^+$, 55%), 411 (100), 345 (11), 197 (10) and 135 (11); *HPLC* (Chiralcel OD-H, hexanes : isopropanol = 95 : 5, 1 ml / min) t_r (min) 4.858 (50.00 %), 6.516 (50.00 %).

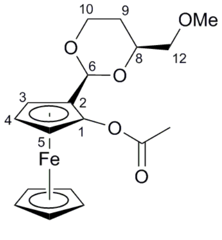
(*rac*)-**12**



	RT (min)	% Area
1	4.858	50.00
2	6.516	50.00

Synthesis of the (p-S)-series

(*S*,*S*,*p*-*S*)-(−)-1-Acetoxy-2-(4-methoxymethyl-1,3-dioxan-2-yl)ferrocene ((*S*,*S*,*p*-*S*)-14)

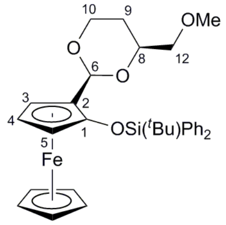


(*S*,*S*,*p*-*S*)-**14**

The iodoferrocene (*S*,*S*,*p*-*S*)-**13** (17.2 g, 38.9 mmol) and copper(I)oxide (5.57 g, 38.9 mmol) were suspended in acetonitrile (500 ml). After addition of acetic acid (11.2 ml, 195 mmol), the mixture was heated to 80 °C for three hours under an argon atmosphere. The solvent was removed and the crude product was purified by column chromatography (cyclohexane : ethyl acetate = 2 : 1) to yield the product (*S*,*S*,*p*-*S*)-**14** as an orange oil (13.7 g, 94.1 %).

$[\alpha]_D^{20}$ -111 (*c* 1.02 in CH_2Cl_2); (Found: C, 57.51; H, 5.96. $C_{18}H_{22}FeO_5$ requires C, 57.77; H, 5.93%); ν_{max}(ATR)/cm^{-1} 2924, 2851, 1757, 1438, 1367, 1198, 1145, 1095, 1002, 954 and 817; δ_H (500 MHz; C_6D_6; $SiMe_4$) 5.55 (1 H, s, 6-H), 4.47 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.6 Hz, 5-H), 4.35 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.6 Hz, 3-H), 4.27 (5 H, s, Cp), 3.92 (1 H, ddd, ^2J = 11.4 Hz, ^3J = 5.1 Hz, ^3J = 1.4 Hz, 10-H$_{eq}$), 3.75 (1 H, dddd, ^3J = 11.4 Hz, ^3J = 5.7 Hz, ^3J = 4.7 Hz, ^3J = 2.5 Hz, 8-H), 3.70 (1 H, t, ^3J = 2.7 Hz, 4-H), 3.51 (1 H, ddd, ^3J = 12.5 Hz, ^2J = 11.4 Hz, ^3J = 2.6 Hz, 10-H$_{ax}$), 3.29 (1 H, dd, ^2J = 10.2 Hz, ^3J = 5.7 Hz, 12-H), 3.14 (1 H, dd, ^2J = 10.2 Hz, ^3J = 4.7 Hz, 12-H′), 3.11 (3 H, s, O*Me*), 1.82 (3 H, s, CO*Me*), 1.62 (1 H, dddd, ^2J = 13.2 Hz, ^3J = 12.5 Hz, ^3J = 11.4 Hz, ^3J = 5.1 Hz, 9-H$_{ax}$) and 1.01 (1 H, dtd, ^2J = 13.2 Hz, ^3J = 2.5 Hz, ^3J = 1.4 Hz, 9-H$_{eq}$); δ_C (126 MHz; C_6D_6; $SiMe_4$) 168.4 (*C*OMe), 114.3 (C-1), 99.0 (C-6), 78.3 (C-2), 76.3 (C-8), 75.8 (C-12), 70.6 (Cp), 66.6 (C-10), 62.8 (C-3), 62.4 (C-4), 62.0 (C-5), 59.1 (O*Me*), 28.7 (C-9) and 20.7 (CO*Me*); ^{1}H / ^{1}H gcosy (500 MHz / 500 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 4.47 / 3.70 (5-H, 4-H), 4.35 / 3.70 (3-H / 4-H), 3.92 / 3.51, 1.62, 1.01 (10-H$_{eq}$ / 10-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.75 / 3.29, 3.14, 1.62, 1.01 (8-H / 12-H, 12-H′, 9-H$_{ax}$, 9-H$_{eq}$), 3.70 / 4.47, 4.35 (4-H / 5-H, 3-H), 3.51 / 3.92, 1.62, 1.01 (10-H$_{ax}$ / 10-H$_{eq}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.29 / 3.75, 3.14 (12-H / 8-H, 12-H′), 3.14 / 3.75, 3.29 (12-H′ / 8-H, 12-H), 1.62 / 3.92, 3.75, 3.51, 1.01 (9-H$_{ax}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{eq}$) and 1.01 / 3.92, 3.75, 3.51, 1.62 (9-H$_{eq}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{ax}$); ^{1}H / ^{13}C ghsqc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.55 / 99.0 (6), 4.47 / 62.4 (5), 4.35 / 62.8 (3), 4.27 / 70.6 (Cp), 3.92, 3.51 / 66.6 (10), 3.75 / 76.3 (8), 3.70 / 62.8 (4), 3.29, 3.14 / 75.8 (12), 3.11 / 59.1 (O*Me*), 1.82 / 20.7 (CO*Me*) and 1.62, 1.01 / 28.7 (9); ^{1}H / ^{13}C ghmbc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.55 / 76.3, 66.6, 62.0 (6-H / C-8, C-10, C-5), 3.92 / 99.0, 76.3 (10-H$_{eq}$ / C-6, C-8), 3.75 / 99.0 (8-H / C-6), 3.29 / 76.3, 59.1, 28.7 (12-H / C-8, O*Me*, C-9), 3.14 / 76.3, 59.1, 28.7 (12-H′ / C-8, O*Me*, C-9), 3.11 / 75.8 (O*Me* / C-12), 1.82 / 168.4 (CO*Me* / *C*OMe) and 1.62 / 76.3, 66.6 (9-H$_{ax}$ / C-8, C-10); *m*/*z* (EI) 374 (M$^+$, 80%), 332 (55), 238 (6), 230 (100), 164 (27), 103 (57) and 75 (12).

(*S*,*S*,*p*-*S*)-(−)-1-(*tert*-Butyldiphenylsiloxy)-2-(4-methoxy-methyl-1,3-dioxan-2-yl)ferrocene ((*S*,*S*,*p*-*S*)-15)

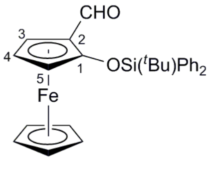


(*S*,*S*,*p*-*S*)-**15**

The acetate (*S*,*S*,*p*-*S*)-**14** (7.50 g, 20.0 mmol) was dissolved in *N*,*N*-dimethylformamide (60 ml) and sodium methoxide (1.19 g, 22.0 mmol) was added in one portion, yielding a dark red solution. After 90 minutes, *tert*-butylchlorodiphenylsilane (5.73 ml, 22.0 mmol) was added and the bright yellow mixture was stirred overnight. The solvent was removed and the residue was purified by column chromatography (cyclohexane : ethyl acetate = 6 : 1) to yield (*S*,*S*,*p*-*S*)-**15** (10.8 g, 94.6 %) as a yellow oil.

$[\alpha]_D^{20}$ -140 (*c* 1.01 in CH_2Cl_2); (Found: C, 67.18; H, 6.84. $C_{32}H_{38}FeO_4Si$ requires C, 67.26; H, 6.71%); ν_{max}(ATR)/cm^{-1} 2930, 2856, 1460, 1428, 1289, 1201, 1144, 1103, 1031, 1000, 957 , 888 , 847 , 819 , 742 , 699 and 616; δ_H (600 MHz; $CDCl_3$; $SiMe_4$) 7.91 (2 H, ps d, *o*-Ph), 7.66 (2 H, ps d, *o*-Ph′), 7.50 – 7.44 (3 H, m, *m*-Ph, *p*-Ph), 7.37 (1 H, m, *p*-Ph′), 7.31 (2 H, m, *m*-Ph′), 5.78 (1 H, s, 6-H), 4.34 (1 H, dd, ^2J = 11.4 Hz, ^3J = 4.8 Hz, 10-H$_{eq}$), 4.09 (5 H, s, Cp), 4.06 – 3.96 (3 H, m, 3-H, 8-H, 10-H$_{ax}$), 3.51 (1 H, t, ^3J = 2.5 Hz, 4-H), 3.45 (1 H, m, 5-H), 3.44 (1 H, dd, ^2J = 10.0 Hz, ^3J = 5.0 Hz, 12-H), 3.36 (1 H, dd, ^2J = 10.0 Hz, ^3J = 5.6 Hz, 12-H′), 3.30 (3 H, s, O*Me*), 1.86 (1 H, dtd, ^2J = 13.2 Hz, ^3J = 12.5 Hz, ^3J = 5.0 Hz, 9-H$_{ax}$), 1.56 (1 H, bd, ^2J = 13.2 Hz, 9-H$_{eq}$) and 1.07 (9 H, s, C(C*H*$_3$)$_3$); δ_C (151 MHz; $CDCl_3$; $SiMe_4$) 135.7, 135.6 (*o*-Ph, o-Ph′), 133.8 (*i*-Ph), 132.1 (*i*-Ph′), 130.0 (*p*-Ph), 129.7 (*p*-Ph′), 127.7 (*m*-Ph), 127.5 (*m*-Ph′), 120.3 (C-1), 99.5 (C-6), 76.0 (C-8), 75.3 (C-12), 74.7 (C-2), 69.7 (Cp), 67.2 (C-10), 60.3 (C-4), 60.0 (C-3), 59.8 (C-5), 59.3 (O*Me*), 28.5 (C-9), 26.5 (C(*C*H$_3$)$_3$) and 19.4 (*C*(CH$_3$)$_3$); ^{1}H / ^{1}H gcosy (600 MHz / 500 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_H = 7.91 / 7.50 – 7.44 (*o*-Ph / *m*-Ph), 7.66 / 7.31 (*o*-Ph′ / *m*-Ph′), 7.36 / 7.31 (*p*-Ph′ / *m*-Ph′), 7.31 / 7.36 (*m*-Ph′ / *p*-Ph′), 4.34 / 4.06 – 3.96, 1.86, 1.56 (10-H$_{eq}$ / 10-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 4.06 – 3.96 / 3.51, 3.45 (3-H / 4-H, 5-H), 4.06 – 3.96 / 3.51, 3.45, 3.44, 3.36, 1.86, 1.56 (3-H, 8-H, 10-H$_{ax}$ / 4-H, 5-H, 12-H, 12-H′, 9-H$_{ax}$, 9-H$_{eq}$), 3.51 / 4.06 – 3.96, 3.45 (4-H / 3-H, 5-H), 3.45 / 4.06 – 3.96, 3.51 (5-H / 3-H, 4-H), 3.44 / 4.06 – 3.96, 3.36 (12-H / 8-H, 12-H′), 3.36 / 4.06 – 3.96, 3.44 (12-H′ / 8-H, 12-H), 1.86 / 4.34, 4.06 – 3.96, 1.56 (9-H$_{ax}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{eq}$) and 1.56 / 4.34, 4.06 – 3.96, 1.86 (9-H$_{eq}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{ax}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 7.91, 7.66 / 135.7, 135.6 (*o*-Ph, *o*-Ph′), 7.50 – 7.44 / 130.0, 127.7 (*p*-Ph, *m*-Ph), 7.36 / 129.7 (*p*-Ph′), 7.31 / 127.5 (*m*-Ph′), 5.78 / 99.5 (6), 4.34, 4.06 – 3.96 / 67.2 (10), 4.06 – 3.96 / 76.0, 60.0 (8, 3), 4.09 / 69.7 (Cp), 3.51 / 60.3 (4), 3.45 / 59.8 (5), 3.44, 3.36 / 75.3 (12), 3.30 / 59.3 (O*Me*), 1.86, 1.56 / 28.5 (9) and 1.07 / 26.5 (C(*CH*$_3$)$_3$); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 7.91 / 133.8, 130.0 (*o*-Ph / *i*-Ph, *p*-Ph), 7.66 / 132.1, 129.7 (*o*-Ph′ / *i*-Ph′, *p*-Ph′), 7.50 – 7.44 / 135.7, 135.6 (*p*-Ph / *o*-Ph), 7.50 – 7.44 / 133.8 (*m*-Ph / *i*-Ph), 7.36 / 135.7, 135.6 (*p*-Ph′ / *o*-Ph′), 7.31 / 132.1 (*m*-Ph′ / *i*-Ph′), 5.78 / 120.3, 76.0, 74.7, 67.2, 60.0 (6-H / C-1, C-8, C-2, C-10, C-3), 4.34 / 99.5, 76.0, 28.5 (10-H_{eq} / C-6, C-8, C-9), 4.06 – 3.96 / 120.3, 74.7, 60.3, 59.8 (3-H / C-1, C-2, C-4, C-5), 3.51 / 120.3, 74.7, 59.8 (4-H / C-1, C-2, C-5), 3.45 / 120.3, 74.7, 60.3 (5-H / C-1, C-2, C-4), 3.44 / 76.0, 59.3 (12-H / C-8, O*Me*), 3.36 / 76.0, 59.3 (12-H′ / C-8, O*Me*), 3.30 / 75.3 (O*Me* / C-12) and 1.07 / 19.4 ($C(CH_3)_3$ / $C(CH_3)_3$); *m*/*z* (EI) 570 (M^+, 100%), 411 (9), 403 (6) and 135 (8).

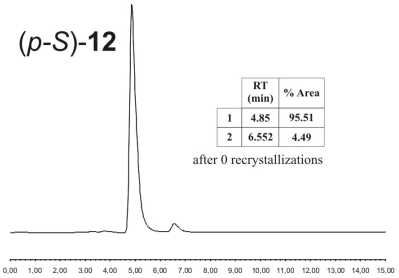
(*p*-*S*)-(+)-1-(*tert*-Butyldiphenylsiloxy)-2-formylferrocene ((*p*-*S*)-12)



(*p*-*S*)-**12**

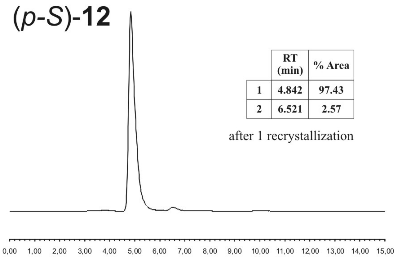
The acetal (*S*,*S*,*p*-*S*)-**15** (16.7 g, 29.3 mmol) and *p*-toluene sulfonic acid (11.1 g, 58.5 mmol) were dissolved in a two-phase mixture of dichloromethane (300 ml) and water (100 ml). The mixture was heated to reflux for three hours under vigorous stirring, the phases were separated and the organic phase was dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by filtration on silica (cyclohexane : ethyl acetate = 4 : 1). The resulting deep red oil was dissolved in pentane (150 ml) and the solution was stored at 4 °C overnight. Removal of the supernatant liquid gave a red solid, which was recrystallized twice from pentane at –30 °C. This gave 12.2 g of the product (88.7 %, *ee* > 99.5 %).
X-ray quality crystals were obtained from a solution of (*p*-*S*)-**12** in pentane at 4°C.

Mp 117 °C (DSC); $[\alpha]_D^{20}$ +495 (*c* 0.53 in CH_2Cl_2); (Found: C, 69.24; H, 6.01. $C_{27}H_{28}FeO_2Si$ requires C, 69.23; H, 6.02%); ν_{max}(ATR)/cm^{-1} / δ_H / δ_C / *m*/*z*: all IR/NMR/MS data are like (*rac*)-**12**; *HPLC* (Chiralcel OD-H, hexanes : isopropanol = 95 : 5, 1 ml / min) t_r (min) 4.857 (99.67 %), 6.546 (0.23 %).



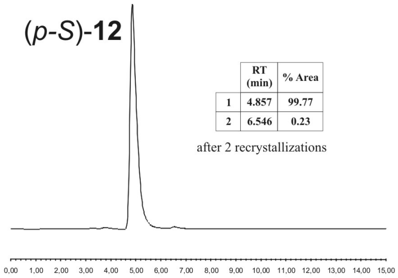
	RT (min)	% Area
1	4.85	95.51
2	6.552	4.49

after 0 recrystallizations



	RT (min)	% Area
1	4.842	97.43
2	6.521	2.57

after 1 recrystallization

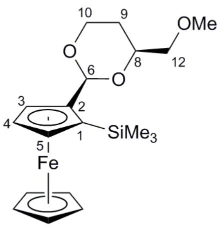


	RT (min)	% Area
1	4.857	99.77
2	6.546	0.23

after 2 recrystallizations

Synthesis of the (p-R)-series

(*S*,*S*,*p*-*S*)-(−)-2-(4-Methoxymethyl-1,3-dioxan-2-yl)-1-trimethylsilylferrocene ((*S*,*S*,*p*-*S*)-16)



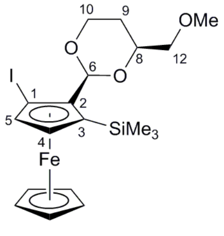
(*S*,*S*,*p*-*S*)-**16**

A solution of *tert*-butyllithium (42.9 ml, 68.7 mmol, 1.6 M in pentane) was slowly added to a solution of the acetal (*S*,*S*)-**6** (18.1 g, 57.3 mmol) in diethyl ether (250 ml) at −78°C. The mixture was slowly warmed up and stirred for one hour at room temperature. After cooling to −78°C, chlorotrimethylsilane (8.68 ml, 68.7 mmol) was added. The mixture was allowed to warm to room temperature and stirred overnight. Brine (10 ml) and water (30 ml) were slowly added, the aqueous phase was extracted with diethyl ether (30 ml) and the organic phases were dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by column chromatography (pentane : diethyl ether = 6 : 1) to give 20.3 g (91.2 %) of the trimethylsilyl-derivative (*S*,*S*,*p*-*S*)-**16** as a yellow solid.

X-ray quality crystals were obtained from a solution of (*S*,*S*,*p*-*S*)-**16** in pentane at –30°C.

Mp 54 °C (DSC); $[\alpha]_{\mathrm{D}}^{20}$ -25.6 (*c* 1.01 in $\mathrm{CH_2Cl_2}$); (Found: C, 58.61; H, 7.19. $\mathrm{C_{19}H_{28}FeO_3Si}$ requires C, 58.76; H, 7.27%); ν_{max}(ATR)/cm^{-1} 2957, 2876, 1239, 1143, 1102, 1003, 957, 895, 754 and 692; δ_{H} (600 MHz; $\mathrm{C_6D_6}$; $\mathrm{SiMe_4}$) 5.45 (1 H, s, 6-H), 4.83 (1 H, dd, ^{3}J = 2.4 Hz, ^{4}J = 1.4 Hz, 3-H), 4.12 (1 H, t, ^{3}J = 2.4 Hz, 4-H), 4.11 (5 H, s, Cp), 4.00 (1 H, dd, ^{3}J = 2.4 Hz, ^{4}J = 1.4 Hz, 5-H), 3.94 (1 H, ddd, ^{2}J = 11.4 Hz, ^{3}J = 5.1 Hz, ^{3}J = 1.4 Hz, 10-$\mathrm{H_{eq}}$), 3.77 (1 H, dddd, ^{3}J = 11.4 Hz, ^{3}J = 6.0 Hz, ^{3}J = 4.9 Hz, ^{3}J = 2.5 Hz, 8-H), 3.47 (1 H, ddd, ^{3}J = 12.5 Hz, ^{2}J = 11.4 Hz, ^{3}J = 2.5 Hz, 10-$\mathrm{H_{ax}}$), 3.33 (1 H, dd, ^{2}J = 9.9 Hz, ^{3}J = 6.0 Hz, 12-H), 3.10 (1 H, dd, ^{2}J = 9.9 Hz, ^{3}J = 4.9 Hz, 12-H′), 3.08 (3 H, s, O*Me*), 1.58 (1 H, dddd, ^{2}J = 13.1 Hz, ^{3}J = 12.5 Hz, ^{3}J = 11.4 Hz, ^{3}J = 5.1 Hz, 9-$\mathrm{H_{ax}}$), 1.03 (1 H, dtd, ^{2}J = 13.1 Hz, ^{3}J = 2.5 Hz, ^{3}J = 1.4 Hz, 9-$\mathrm{H_{eq}}$) and 0.40 (9 H, s, $^{2}J_{SiH}$ = 6.8 Hz, SiMe_3); δ_{C} (151 MHz; $\mathrm{C_6D_6}$; $\mathrm{SiMe_4}$) 100.9 (C-6), 91.3 (C-2), 75.9 (C-8), 75.8 (C-12), 74.8 (C-5), 70.5 (C-3), 70.4 (C-1), 69.8 (C-4), 69.3 (Cp), 66.6 (C-10), 58.9 (O*Me*), 28.4 (C-9) and 0.6 ($^{1}J_{SiC}$ = 52.9 Hz, SiMe_3); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; $\mathrm{C_6D_6}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{H} = 4.83 / 4.12, 4.00 (3-H / 4-H, 5-H), 4.12 / 4.83, 4.00 (4-H / 3-H, 5-H), 4.00 / 4.83, 4.12 (5-H / 3-H, 4-H), 3.94 / 3.47, 1.58, 1.03 (10-$\mathrm{H_{eq}}$ / 10-$\mathrm{H_{ax}}$, 9-$\mathrm{H_{ax}}$, 9-$\mathrm{H_{eq}}$), 3.77 / 3.33, 3.10, 1.58, 1.03 (8-H / 12-H, 12-H′, 9-$\mathrm{H_{ax}}$, 9-$\mathrm{H_{eq}}$), 3.47 / 3.94, 1.58, 1.03 (10-$\mathrm{H_{ax}}$ / $\mathrm{H10_{eq}}$, 9-$\mathrm{H_{ax}}$, 9-$\mathrm{H_{eq}}$), 3.33 / 3.77, 3.10 (12-H / 8-H, 12-H′), 3.10 / 3.77, 3.33 (12-H′/ 8-H, 12-H), 1.58 / 3.94, 3.77, 3.47, 1.03 (9-$\mathrm{H_{ax}}$ / $\mathrm{H10_{eq}}$, 8-H, 10-H $_{\mathrm{ax}}$, 9-$\mathrm{H_{eq}}$), and 1.03 / 3.94, 3.77, 3.47, 1.58 (9-$\mathrm{H_{eq}}$ / $\mathrm{H10_{eq}}$, 8-H, 10-H $_{\mathrm{ax}}$, 9-$\mathrm{H_{ax}}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; $\mathrm{C_6D_6}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{C} = 5.45 / 100.9 (6), 4.83 / 70.5 (3), 4.12 / 69.8 (4), 4.11 / 69.3 (Cp), 4.00 / 74.8 (5), 3.94, 3.47 / 66.6 (10), 3.77 / 75.9 (8), 3.33, 3.10 / 75.8 (12), 3.08 / 58.9 (O*Me*), 1.58, 1.03 / 28.4 (9) and 0.40 / 0.61 (SiMe_3); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; $\mathrm{C_6D_6}$; $\mathrm{SiMe_4}$): δ_{H} / δ_{C} = 5.45 / 91.3, 75.8, 70.4, 66.6, 28.4 (6-H / C-2, C-12, C-1, C-10, C-9), 4.83 / 91.3, 74.8, 69.8 (3-H / C-2, C-5, C-4), 4.12 / 91.3, 70.4 (4-H / C-2, C-5), 4.00 / 91.3, 70.4 (5-H / C-2, C-1), 3.94 / 100.9, 75.9, 75.8, 28.4 (10-$\mathrm{H_{eq}}$ / C-6, C-8, C-12, C-9), 3.77 / 100.9, 75.8, 66.6 (8-H / C-6, C-12, C-10), 3.47 / 100.9, 75.9, 28.4 (10-$\mathrm{H_{ax}}$ / C-6, C-8, C-9), 3.33 / 75.9, 58.9, 28.4 (12-H / C-8, O*Me*, C-9), 3.10 / 75.9, 58.9, 28.4 (12-H′ / C-8, O*Me*, C-9), 3.08 / 75.8 (O*Me* / C-12), 1.58 / 75.9, 66.6 (9-$\mathrm{H_{ax}}$ / C-8, C-10), 1.03 / 75.9 (9-$\mathrm{H_{eq}}$ / C-8) and 0.40 / 70.4, 0.6 (SiMe_3 /1, SiMe_3); *m*/*z* (EI) 388 (M^{+}, 100%), 343 (6), 271 (21), 213 (9), 121 (15) and 85 (6).

(*S*,*S*,*p*-*R*)-(+)-1-Iodo-2-(4-methoxymethyl-1,3-dioxan-2-yl)-3-trimethylsilylferrocene ((*S*,*S*,*p*-*R*)-17)



(*S*,*S*,*p*-*S*)-**17**

A solution of *tert*-butyllithium (42.8 ml, 64.3 mmol, 1.5 M in pentane) was slowly added to a solution of the trimethylsilyl-derivative (*S*,*S*,*p*-*S*)-**16** (20.8 g, 53.6 mmol) in diethyl ether (250 ml) at −78°C. The mixture was slowly warmed up and stirred for 90 minutes at room temperature. After cooling to –78°C, a solution of iodine (20.4 g, 80.4 mmol) in tetrahydrofurane (150 ml) was added. The mixture was allowed to warm to room temperature and stirred overnight. A saturated solution of sodium thiosulfate (100 ml) was slowly added, the aqueous phase was extracted with diethyl ether (100 ml) and the organic phases were dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by careful column chromatography (pentane : diethyl ether = 20 : 1). The first fraction yielded 14.2 g (51.5 %) of the desired trisubstituted product (*S*,*S*,*p*-*R*)-**17** as a yellow solid, further elution gave a second fraction of the 1,1′-bisiodination product **18** (yellow solid, 10.7 g, 31.2 %).

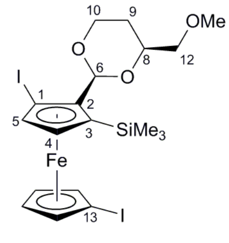
X-ray quality crystals of (*S*,*S*,*p*-*R*)-**17** were obtained from a solution in pentane at –30°C.

Mp 69 °C (DSC); $[\alpha]_{\mathrm{D}}^{20}$ +31.6 (*c* 1.00 in $\mathrm{CH_2Cl_2}$); (Found: C, 44.40; H, 5.29. $\mathrm{C_{19}H_{27}FeIO_3Si}$ requires C, 44.38; H, 5.29%); ν_{max}(ATR)/cm^{-1} 2888, 2847, 1243, 1202, 1154, 1122, 1103, 1036, 1009, 985, 948, 835, 817, 755, 691 and 637; δ_{H} (600 MHz; $\mathrm{C_6D_6}$; $\mathrm{SiMe_4}$) 5.42 (1 H, s, 6-H), 4.39 (1 H, d, ^{3}J = 2.4 Hz, 5-H), 4.20 (5 H, s, Cp), 3.99 (1 H, d, ^{3}J = 2.4 Hz, 4-H), 3.83 (1 H, ddd, ^{2}J = 11.4 Hz, ^{3}J = 5.2 Hz, ^{3}J = 1.3 Hz, 10-$\mathrm{H_{eq}}$), 3.78 (1 H, dddd, ^{3}J = 11.6 Hz, ^{3}J = 6.5 Hz, ^{3}J = 4.4 Hz, ^{3}J = 2.5 Hz, 8-H), 3.50 (1 H, ddd, ^{3}J = 12.4 Hz, ^{2}J = 11.4 Hz, ^{3}J = 2.5 Hz, 10-$\mathrm{H_{ax}}$), 3.35 (1 H, dd, ^{2}J = 9.9 Hz, ^{3}J = 6.5 Hz, 12-H), 3.12 (1 H, dd, ^{2}J = 9.9 Hz, ^{3}J = 4.4 Hz, 12-H′), 3.11 (3 H, s, O*Me*), 1.59 (1 H, dddd, ^{2}J = 13.2 Hz, ^{3}J = 12.4 Hz, ^{3}J = 11.6 Hz, ^{3}J = 5.2 Hz, 9-$\mathrm{H_{ax}}$), 0.90 (1 H, dtd, ^{2}J = 13.2 Hz, ^{3}J = 2.5 Hz, ^{3}J = 1.3 Hz, 9-$\mathrm{H_{eq}}$) and 0.41 (9 H, s, $^{2}J_{SiH}$ = 6.8 Hz, SiMe_3); δ_{C} (151 MHz; $\mathrm{C_6D_6}$; $\mathrm{SiMe_4}$) 102.2 (C-

6), 90.8 (C-2), 76.9 (C-5), 76.3 (C-8), 75.8 (C-4), 75.6 (C-12), 72.4 (Cp), 70.1 (C-3), 66.8 (C-10), 58.7 (O*Me*), 47.0 (C-1), 27.8 (C-9) and 1.3 ($^1J_{SiC}$ = 53.6 Hz, SiMe_3); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 4.39 / 3.99 (5-H / 4-H), 3.99 / 4.39 (4-H / 5-H), 3.83 / 3.50, 1.59, 0.90 (10-H$_{eq}$ / 10-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.78 / 3.35, 3.12, 1.59, 0.90 (8-H / 12-H, 12-H′, 9-H$_{ax}$, 9-H$_{eq}$), 3.50 / 3.83, 1.59, 0.90 (10-H$_{ax}$ / 10-H$_{eq}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.35 / 3.78, 3.12 (12-H / 8-H, 12-H′), 3.12 / 3.78, 3.35 (12-H′/ 8-H, 12-H), 1.59 / 3.83, 3.78, 3.50, 0.90 (9-H$_{ax}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{eq}$) and 0.90 / 3.83, 3.78, 3.50, 1.59 (9-H$_{eq}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{ax}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.42 / 102.2 (6), 4.39 / 76.9 (5), 4.20 / 72.4 (Cp), 3.99 / 75.8 (4), 3.83, 3.50 / 66.8 (10), 3.78 / 76.3 (8), 3.35, 3.12 / 75.6 (12), 3.11 / 58.7 (O*Me*), 1.59, 0.90 / 27.8 (9) and 0.41 / 1.3 (SiMe_3); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.42 / 90.8, 76.3, 70.1, 66.8, 47.0, 27.8 (6-H / C-2, C-8, C-3, C-10, C-1, C-9), 4.39 / 90.8, 75.8, 70.1, 47.0 (5-H / C-2, C-4, C-3, C-1), 3.99 / 90.8, 76.9, 70.1, 47.0 (4-H / C-2, C-5, C-3, C-1), 3.83 / 102.2, 76.3, 27.8 (10-H$_{eq}$ / C-6, C-8, C-9), 3.78 / 75.6, 27.8 (8-H / C-12, C-9), 3.50 / 102.2, 76.3, 27.8 (10-H$_{ax}$ / C-6, C-8, C-9), 3.35 / 76.3, 58.7, 27.8 (12-H / C-8, O*Me*, C-9), 3.12 / 76.3, 58.7, 27.8 (12-H′ / C-8, O*Me*, C-9), 3.11 / 75.6 (O*Me* / C-12), 1.59 / 76.3, 75.6, 66.8 (9-H$_{ax}$ / C-8, C-12, C-10) and 0.41 / 70.1, 1.3 (SiMe_3 / C-3, SiMe_3); *m*/*z* (EI) 514 (M^+, 100%), 397 (6), 213 (6), 121 (8) and 73 (9).

Byproduct: (*S*,*S*,*p*-*R*)-1,1′-Diiodo-2-(4-methoxymethyl-1,3-dioxan-2-yl)-3-trimethylsilylferrocene (18)

The byproduct was identified as the tetrasubstituted ferrocene **18** by NMR-spectroscopy.



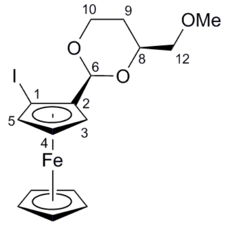
(*S*,*S*,*p*-*S*)-**18**

δ_H (600 MHz; C_6D_6; $SiMe_4$) 5.36 (1 H, s, 6-H), 4.34 (1 H, m, CpI), 4.33 (1 H, d, ^3J = 2.5 Hz, 5-H), 4.29 (1 H, m, CpI), 4.21 (1 H, m, CpI), 4.07 (1 H, m, CpI), 3.94 (1 H, d, ^3J = 2.5 Hz, 4-H), 3.80 (1 H, ddd, ^2J = 11.4 Hz, ^3J = 5.1 Hz, ^3J = 1.1 Hz, 10-H$_{eq}$), 3.77 (1 H, m, 8-H), 3.49 (1 H, ddd, ^3J = 12.5 Hz, ^2J = 11.4 Hz, ^3J = 2.6 Hz, 10-H$_{ax}$), 3.31 (1 H, dd, ^2J = 9.9 Hz, ^3J = 6.4 Hz, 12-H), 3.09 (3 H, s, O*Me*), 3.08 (1 H, dd, ^2J = 9.9 Hz, ^3J = 4.4 Hz, 12-H′), 1.57 (1 H, dddd, ^2J = 13.2 Hz, ^3J = 12.5 Hz, ^3J = 11.6 Hz, ^3J = 5.1 Hz, 9-H$_{ax}$), 0.88 (1 H, dtd, ^2J = 13.2 Hz, ^3J = 2.5 Hz, ^3J = 1.1 Hz, 9-H$_{eq}$) and 0.40 (9 H, s, $^2J_{SiH}$ = 6.8 Hz, SiMe_3); δ_C (151 MHz; C_6D_6; $SiMe_4$) 101.5 (C-6), 91.2 (C-2), 81.1 (C-5), 80.4 (C-4), 79.8 (CpI), 76.9 (CpI), 76.2 (C-8), 75.5 (C-12), 75.3 (CpI), 72.5 (C-3), 72.3 (CpI), 66.8 (C-10), 58.6 (O*Me*), 48.3 (C-1), 42.4 (C-13), 27.7 (C-9) and 1.4 ($^1J_{SiC}$ = 53.7 Hz, SiMe_3); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 4.34 / 4.29, 4.21, 4.7 (CpI / CpI, CpI, CpI), 4.33 / 3.94 (5-H / 4-H), 4.29 / 4.34, 4.21, 4.07 (CpI / CpI, CpI, CpI), 4.21 / 4.34, 4.29, 4.07 (CpI / CpI, CpI, CpI), 4.07 / 4.34, 4.29, 4.21 (CpI / CpI, CpI, CpI), 3.94 / 4.33 (4-H / 5-H), 3.80 / 3.49, 1.57, 0.88 (10-H$_{eq}$ / 10-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.77 / 3.31, 3.08, 1.57, 0.88 (8-H / 12-H, 12-H′, 9-H$_{ax}$, 9-H$_{eq}$), 3.49 / 3.80, 1.57, 0.88 (10-H$_{ax}$ / H10$_{eq}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.31 / 3.77, 3.08 (12-H / 8-H, 12-H′), 3.08 / 3.77, 3.31 (12-H′/ 8-H, 12-H), 1.57 / 3.80, 3.77, 3.49, 0.88 (9-H$_{ax}$ / H10$_{eq}$, 8-H, 10-H $_{ax}$, 9-H$_{eq}$) and 0.88 / 3.80, 3.77, 3.49, 1.57 (9-H$_{eq}$ / H10$_{eq}$, 8-H, 10-H $_{ax}$, 9-H$_{ax}$); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.36 / 101.5 (6), 4.34 / 79.8 (CpI), 4.33 / 81.1 (5), 4.29 / 76.9 (CpI), 4.21 / 72.3 (CpI), 4.07 / 75.3 (CpI), 3.94 / 80.4 (4), 3.80, 3.49 / 66.8 (10), 3.77 / 76.2 (8), 3.31, 3.08 / 75.5 (12), 3.09 / 58.6 (O*Me*), 1.57, 0.88 / 27.7 (9) and 0.40 / 1.4 (SiMe_3); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.36 / 91.2, 76.2, 72.5, 66.8, 48.3, 27.7 (6-H / C-2, C-8, C-3, C-10, C-1, C-9), 4.34 / 76.9, 75.3, 72.3, 42.4 (CpI / CpI, CpI, CpI, C-13), 4.33 / 91.2, 80.4, 72.5, 48.3 (5-H / C-2, C-4, C-3, C-1), 4.29 / 79.8, 75.3, 72.3, 42.4 (CpI / CpI, CpI, CpI, C-13), 4.21 / 79.8, 76.9, 75.3, 42.4 (CpI / CpI, CpI, CpI, C-13), 4.07 / 79.8, 76.9, 72.3, 42.4 (CpI / CpI, CpI, CpI, C-13), 3.94 / 91.2, 81.1, 72.5, 48.3 (4-H / C-2, C-5, C-3, C-1), 3.80 / 101.5, 76.2, 27.7 (10-H$_{eq}$ / C-6, C-8, C-9), 3.77 / 101.5, 75.5 (8-H / C-6, C-12), 3.49 / 101.5, 76.2, 27.7 (10-H$_{ax}$ / C-6, C-8, C-9), 3.31 / 76.2, 58.6, 27.7 (12-H / C-8, O*Me*, C-9), 3.08 / 76.2, 58.6, 27.7 (12-H / C-8, O*Me*, C-9), 3.09 / 75.5 (O*Me* / C-12), 1.57 / 76.2, 75.5, 66.8 (9-H$_{ax}$ / C-8, C-12, C-10) and 0.40 / 72.5, 1.4 (SiMe_3 / C-3, SiMe_3).

Dehalogenation of the byproduct 18:

A solution of *n*-butyllithium (844 µl, 1.35 mmol, 1.6 M in pentane) was slowly added to a solution of **18** (288 mg, 0.450 mmol) in tetrahydrofurane (3 ml) at −78°C. The mixture was slowly warmed up and stirred for thirty minutes at room temperature. Water (10 ml) and diethyl ether (10 ml) were added, the aqueous phase was extracted with diethyl ether (10 ml) and the organic phases were dried over magnesium sulfate. Filtration and removal of the solvent gave the trimethylsilyl-derivative (*S,S,p*-*S*)-**16** (170 mg, 97.3 %), which was pure according to ^{1}H-NMR.

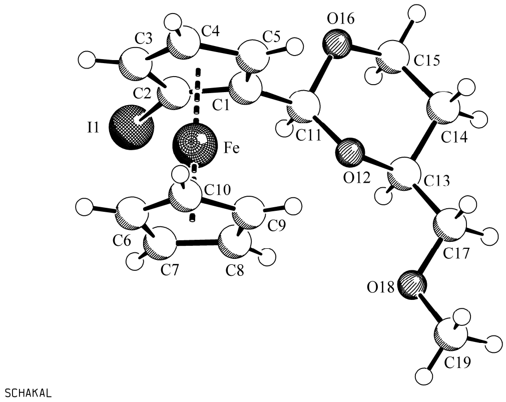
(*S*,*S*,*p*-*R*)-(−)-1-Iodo-2-(4-methoxymethyl-1,3-dioxan-2-yl)ferrocene ((*S*,*S*,*p*-*R*)-13)



(*S*,*S*,*p*-*R*)-**13**

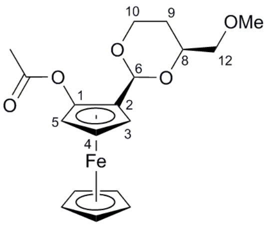
The trisubstituted ferrocene (*S*,*S*,*p*-*R*)-**17** (10.1 g, 19.6 mmol) and tetra-*n*-butyl ammonium fluoride (12.4 g, 39.3 mmol) were dissolved in tetrahydrofurane (150 ml). The mixture was heated to reflux for 16 hours under an argon atmosphere and the solvent was removed to give the crude product, which was purified by column chromatography (cyclohexane : ethyl acetate = 8 : 1) to give a yellow oil. The oil was dissolved in pentane (200 ml) and the solution was stored at –30°C, giving a yellow precipitate. The supernatant liquid was removed and the yellow solid of (*S*,*S*,*p*-*R*)-**13** was dried (8.15 g, 94.1 %).
X-ray quality crystals were obtained from a solution of (*S*,*S*,*p*-*R*)-**13** in pentane at –30°C.

Mp 57 °C (DSC); $[\alpha]_D^{20}$ -49.4 (*c* 1.01 in CH_2Cl_2); (Found: C, 42.88; H, 4.31. $C_{16}H_{19}FeIO_3$ requires C, 43.47; H, 4.33%); ν_{max}(ATR)/cm^{-1} 2974, 2920, 1241, 1149, 1100, 1037, 981, 929 and 821; δ_H (600 MHz; C_6D_6; $SiMe_4$) 5.41 (1 H, s, 6-H), 4.57 (1 H, dd, ^3J = 2.6 Hz, ^4J = 1.4 Hz, 3-H), 4.25 (1 H, dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 5-H), 4.15 (5 H, s, Cp), 3.88 (1 H, ddd, ^2J = 11.4 Hz, ^3J = 5.1 Hz, ^3J = 1.3 Hz, 10-H_{eq}), 3.86 (1 H, t, ^3J = 2.5 Hz, 4-H), 3.76 (1 H, dddd, ^3J = 11.6 Hz, ^3J = 6.2 Hz, ^3J = 4.4 Hz, ^3J = 2.5 Hz, 8-H), 3.56 (1 H, ddd, ^3J = 12.4 Hz, ^2J = 11.4 Hz, ^3J = 2.5 Hz, 10-H_{ax}), 3.38 (1 H, dd, ^2J = 10.3 Hz, ^3J = 6.2 Hz, 12-H), 3.17 (3 H, s, O*Me*), 3.16 (1 H, dd, ^2J = 10.3 Hz, ^3J = 4.4 Hz, 12-H′), 1.58 (1 H, dddd, ^2J = 13.1 Hz, ^3J = 12.4 Hz, ^3J = 11.6 Hz, ^3J = 5.1 Hz, 9-H_{ax}) and 0.92 (1 H, dtd, ^2J = 13.1 Hz, ^3J = 2.5 Hz, ^3J = 1.3 Hz, 9-H_{eq}); δ_C (151 MHz; C_6D_6; $SiMe_4$) 100.9 (C-6), 87.3 (C-2), 76.4 (C-8), 75.8 (C-12), 75.0 (C-5), 72.3 (Cp), 68.9 (C-4), 67.0 (C-3), 66.8 (C-10), 59.1 (O*Me*), 42.3 (C-1) and 28.0 (C-9); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 4.57 / 4.25, 3.86 (3-H / 5-H, 4-H), 4.25 / 4.57, 3.86 (5-H / 3-H, 4-H), 3.88 / 3.56, 1.58, 0.92 (10-H_{eq} / 10-H_{ax}, 9-H_{ax}, 9-H_{eq}), 3.86 / 4.57, 4.25 (4-H / 3-H, 5-H), 3.76 / 3.38, 3.16, 1.58, 0.92 (8-H / 12-H, 12-H′, 9-H_{ax}, 9-H_{eq}), 3.56 / 3.88, 1.58, 0.92 (10-H_{ax} / 10-H_{eq}, 9-H_{ax}, 9-H_{eq}), 3.38 / 3.76, 3.16 (12-H / 8-H, 12-H′), 3.16 / 3.76, 3.38 (12-H′ / 8-H, 12-H), 1.58 / 3.88, 3.76, 3.56, 0.92 (9-H_{ax} / 10-H_{eq}, 8-H, 10-H_{ax}, 9-H_{eq}) and 0.92 / 3.88, 3.76, 3.56, 1.58 (9-H_{eq} / 10-H_{eq}, 8-H, 10-H_{ax}, 9-H_{ax}); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.41 / 100.9 (6), 4.57 / 67.0 (3), 4.25 / 75.0 (5), 4.15 / 72.3 (Cp), 3.88, 3.56 / 66.8 (10), 3.86 / 68.9 (4), 3.76 / 76.4 (8), 3.38, 3.16 / 75.8 (12), 3.17 / 59.1 (O*Me*) and 1.58, 0.92 / 28.0 (9); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.41 / 87.3, 76.4, 66.8, 42.3, 28.0 (6-H / C-2, C-8, C-10, C-1, C-9), 4.57 / 87.3, 75.0, 68.9, 42.3 (3-H / C-2, C-5, C-4, C-1), 4.25 / 87.3, 68.9, 67.0, 42.3 (5-H / C-2, C-4, C-3, C-1), 3.88 / 100.9, 76.4, 28.0 (10-H_{eq} / C-6, C-8, C-9), 3.86 / 87.3, 75.0, 67.0, 42.3 (4-H / C-2, C-5, C-3, C-1), 3.76 / 75.8, 66.8 (8-H / C-12, C-10), 3.56 / 76.4, 28.0 (10-H_{eq} / C-8, C-9), 3.38 / 76.4, 59.1, 28.0 (12-H / C-8, O*Me*, C-9), 3.17 / 75.8 (O*Me*, C-12), 3.16 / 76.4, 59.1, 28.0 (12-H′ / C-8, O*Me*, C-9) and 1.58 / 76.4, 66.8 (9-H_{ax} / C-8, C-10); *m*/*z* (EI) 442 (M$^+$, 100%), 212 (16), 141 (9), 128 (9), 121 (13) and 56 (7).



Selected bond lengths (Å) and angles (°): (molecule A): Fe-C($Cp_{unsubst.}$) 2.011(7) – 2.056(7), Fe-C($Cp_{subst.}$) 2.009(6) – 2.051(6), C1-C2 1.414(8), C1-C5 1.399(9), C1-C11 1.492(8), C2-I1 2.086(6), C11-O12 1.411(7), C11-O16 1.417(8), O12-C13 1.432(7), O16-C15 1.442(8), C17-O18 1.397(9), O18-C19 1.408(8); C2-C1-C5 108.9(5); C2-C1-C11 125.4(6), C5-C1-C11 125.4(5), C1-C2-I1 126.3(4), C1-C11-O12 111.1(5), C1-C11-O16 107.0(5), C11-O12-C13 111.5(4), C11-O16-C15 110.6(6), C17-O18-C19 113.3(6).

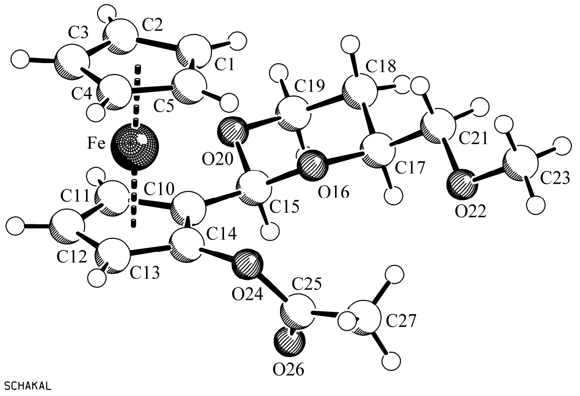
(*S,S,p-R*)-(+)-1-Acetoxy-2-(4-methoxymethyl-1,3-dioxan-2-yl)ferrocene ((*S,S,p-R*)-14)



(*S*,*S*,*p*-*R*)-**14**

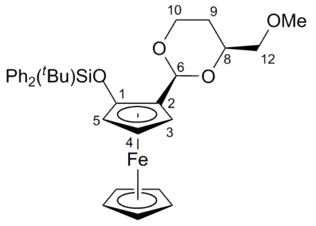
The iodoferrocene (*S,S,p-R*)-**13** (3.56 g, 8.05 mmol) and copper(I)oxide (1.15 g, 8.05 mmol) were suspended in acetonitrile (150 ml). After addition of acetic acid (2.30 ml, 40.3 mmol), the mixture was heated to 80 °C for three hours under an argon atmosphere. The solvent was removed and the crude product was purified by column chromatography (cyclohexane : ethyl acetate = 4 : 1) to yield the product (*S,S,p-R*)-**14** as a yellow solid (2.80 g, 92.9 %).
X-ray quality crystals were obtained from a solution of (*S,S,p-R*)-**14** in pentane at –30°C.

Mp 85 °C (DSC); $[\alpha]_D^{20}$ +62.1 (*c* 1.03 in CH_2Cl_2); (Found: C, 57.71; H, 5.88. $C_{18}H_{22}FeO_5$ requires C, 57.77; H, 5.93%); ν_{max}(ATR)/cm^{-1} 2878, 1749, 1440, 1368, 1217, 1151, 1096, 1066, 1010, 992, 951, 909, 820, and 603; δ_H (600 MHz; C_6D_6; $SiMe_4$) 5.47 (1 H, s, 6-H), 4.41 (1 H, dd, ^3J = 2.6 Hz, ^4J = 1.6 Hz, 5-H), 4.34 (1 H, dd, ^3J = 2.6 Hz, ^4J = 1.6 Hz, 3-H), 4.33 (5 H, s, Cp), 3.86 (1 H, ddd, ^2J = 11.3 Hz, ^3J = 5.0 Hz, ^3J = 1.3 Hz, 10-H_{eq}), 3.73 (1 H, dddd, ^3J = 11.6 Hz, ^3J = 6.5 Hz, ^3J = 4.0 Hz, ^3J = 2.5 Hz, 8-H), 3.72 (1 H, t, ^3J = 2.6 Hz, 4-H), 3.46 (1 H, ddd, ^3J = 12.4 Hz, ^2J = 11.3 Hz, ^3J = 2.5 Hz, 10-H_{ax}), 3.32 (1 H, dd, ^2J = 10.3 Hz, ^3J = 6.5 Hz, 12-H), 3.14 (3 H, s, O*Me*), 3.10 (1 H, dd, ^2J = 10.3 Hz, ^3J = 4.0 Hz, 12-H′), 1.86 (3 H, s, CO*Me*), 1.54 (1 H, dddd, ^2J = 13.1 Hz, ^3J = 12.4 Hz, ^3J = 11.6 Hz, ^3J = 5.0 Hz, 9-H_{ax}) and 0.89 (1 H, dtd, ^2J = 13.1 Hz, ^3J = 2.5 Hz, ^3J = 1.3 Hz, 9-H_{eq}); δ_C (151 MHz; C_6D_6; $SiMe_4$) 168.6 (*C*OMe), 114.0 (C-1), 98.7 (C-6), 79.0 (C-2), 76.04 (C-12), 76.01 (C-8), 70.7 (Cp), 66.5 (C-10), 63.1 (C-3), 62.4 (C-4), 61.7 (C-5), 59.0 (O*Me*), 28.2 (C-9) and 20.7 (CO*Me*); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 4.41 / 4.34, 3.72 (5-H / 3-H, 4-H), 4.34 / 4.41, 3.72 (3-H / 5-H, 4-H), 3.86 / 3.46, 1.54, 0.89 (10-H_{eq} / 10-H_{ax}, 9-H_{ax}, 9-H_{eq}), 3.73 / 3.32, 3.10, 1.54, 0.89 (8-H / 12-H, 12-H′, 9-H_{ax}, 9-H_{eq}), 3.72 / 4.41, 4.34 (4-H / 5-H, 3-H), 3.46 / 3.86, 1.54, 0.89 (10-H_{ax} / 10-H_{eq}, 9-H_{ax}, 9-H_{eq}), 3.32 / 3.86, 3.73, 3.46, 1.54 (9-H_{ax} / 10-H_{eq}, 8-H, 10-H_{ax}, 9-H_{eq}) and 0.89 / 3.86, 3.73, 3.46, 1.54 (9-H_{eq} / 10-H_{eq}, 8-H, 10-H_{ax}, 9-H_{ax}); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.47 / 98.7 (6), 4.41 / 61.7 (5), 4.34 / 63.1 (3), 4.33 / 70.7 (Cp), 3.86, 3.46 / 66.5 (10), 3.73 / 76.01 (8), 3.72 / 62.4 (4), 3.32, 3.10 / 76.04 (12), 3.14 / 59.0 (O*Me*), 1.86 / 20.7 (CO*Me*) and 1.54, 0.89 / 28.2 (9); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 5.47 / 114.0, 79.0, 76.01, 66.5, 63.1, 28.2 (6-H / C-1, C-2, C-8, C-10, C-3, C-9), 4.41 / 114.0, 79.0, 63.1, 62.4 (5-H / C-1, C-2, C-3, C-4), 4.34 / 114.0, 63.1, 62.4, 61.7 (3-H / C-1, C-2, C-4, C-5), 3.86 / 98.7, 76.01, 28.2 (10-H_{eq} / C-6, C-8, C-9), 3.73 / 98.7, 76.04, 28.2 (8-H / C-6, C-12, C-9), 3.72 / 114.0, 79.0, 63.1, 61.7(4-H / C-1, C-2, C-3, C-5), 3.46 / 98.7, 76.01, 28.2 (10-H_{ax} / C-6, C-8, C-9), 3.32 / 76.01, 59.0, 28.2 (12-H / C-8, O*Me*, C-9), 3.14 / 76.04 (O*Me* / C-12), 3.10 / 76.01, 59.0, 28.2 (12-H′ / C-8, O*Me*, C-9), 1.86 / 168.6, 114.0 (CO*Me* / *C*OMe, C-1) and 1.54 / 76.01, 66.5 (9-H_{ax} / C-8, C-10); *m*/*z* (EI) 374 (M^+, 57%), 332 (40), 230 (100), 164 (29), 121 (36), 103 (32), 75 (9) and 56 (6).



Selected bond lengths (Å) and angles (°): Fe-C($Cp_{unsubst.}$) 2.020(2) – 2.039(3), Fe-C($Cp_{subst.}$) 2.022(2) – 2.039(3), C10-C11 1.440(3), C10-C14 1.421(3), C10-C15 1.497(3), C15-O16 1.423(3), C15-O20 1.403(3), O16-C17 1.437(3), O20-C19 1.446(3), C21-O22 1.413(3), O22-C23 1.418(3), C14-O24 1.405(3), O24-C25 1.368(3), C25-O26 1.197(3), C26-C27 1.486(4); C11-C10-C14 106.0(2), C11-C10-C15 125.4(2), C14-C10-C15 128.5(2), C10-C15-O16 109.7(2), C10-C15-O20 108.3(2), C15-O16-C17 110.1(2), C15-O20-C19 110.2(2), C21-O22-C23 112.0(2), C10-C14-O24 126.9(2), C14-O24-C25 117.1(2), O24-C25-O26 123.4(2), O24-C25-C27 109.9(2), O26-C25-C27 126.7(2).

(*S*,*S*,*p*-*R*)-(+)-1-(*tert*-Butyldiphenylsiloxy)-2-(4-methoxy-methyl-1,3-dioxan-2-yl)ferrocene ((*S*,*S*,*p*-*R*)-15)

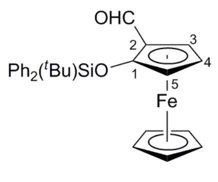


(*S*,*S*,*p*-*R*)-**15**

The acetate (*S,S,p-R*)-**14** (2.80 g, 7.48 mmol) was dissolved in *N*,*N*-dimethylformamide (20 ml) and sodium methoxide (444 mg, 8.23 mmol) was added in one portion, yielding a dark red solution. After 90 minutes, *tert*-butyl-chlorodiphenylsilane (2.14 ml, 8.23 mmol) was added and the bright yellow mixture was stirred overnight. The solvent was removed and the residue was purified by column chromatography (cyclohexane : ethyl acetate = 6 : 1) to yield (*S,S,p-R*)-**15** (3.94 g, 92.3 %) as a yellow oil.

$[\alpha]_D^{20}$ +102 (*c* 1.03 in CH_2Cl_2); (Found: C, 67.82; H, 7.08. $C_{32}H_{38}FeO_4Si$ requires C, 67.26; H, 6.71%); ν_{max}(ATR)/cm^{-1} 2930, 2856, 1460, 1428, 1104, 1032, 1006, 891, 846, 820, 742, 699 and 615; δ_H (500 MHz; C_6D_6; $SiMe_4$) 8.05 (2 H, m, *o*-Ph), 7.81 (2 H, m, *o*-Ph′), 7.32 – 7.25 (3 H, m, *p*-Ph, *m*-Ph), 7.17 – 7.10 (3 H, m, *p*-Ph′, *m*-Ph′), 5.86 (1 H, s, 6-H), 4.27 (1 H, dd, ^3J = 2.6 Hz, ^4J = 1.5 Hz, 3-H), 4.25 (5 H, s, Cp), 3.96 (1 H, ddd, ^2J = 11.5 Hz, ^3J = 5.0 Hz, ^3J = 1.3 Hz, 10-H$_{eq}$), 3.89 (1 H, dddd, ^3J = 11.5 Hz, ^3J = 6.2 Hz, ^3J = 4.6 Hz, ^3J = 2.5 Hz, 8-H), 3.66 (1 H, ddd, ^3J = 12.4 Hz, ^2J = 11.5 Hz, ^3J = 2.5 Hz, 10-H$_{ax}$), 3.57 (1 H, dd, ^3J = 2.6 Hz, ^3J = 1.5 Hz, 5-H), 3.46 (1 H, dd, ^2J = 10.2 Hz, ^3J = 6.2 Hz, 12-H), 3.36 (1 H, t, ^3J = 2.6 Hz, 4-H), 3.24 (1 H, dd, ^2J = 10.2 Hz, ^3J = 4.6 Hz, 12-H′), 3.22 (3 H, s, O*Me*), 1.67 (1 H, dddd, ^2J = 13.0 Hz, ^3J = 12.4 Hz, ^3J = 11.5 Hz, ^3J = 5.0 Hz, 9-H$_{ax}$), 1.22 (9 H, s, C(CH_3)$_3$) and 1.04 (1 H, dtd, ^2J = 13.0 Hz, ^3J = 2.5 Hz, ^3J = 1.3 Hz, 9-H$_{eq}$); δ_C (126 MHz; C_6D_6; $SiMe_4$) 136.1 (*o*-Ph′), 136.0 (*o*-Ph), 134.3 (*i*-Ph), 132.6 (*i*-Ph′), 130.3 (*p*-Ph), 130.1 (*p*-Ph′), 128.1 (*m*-Ph), 127.97 (*m*-Ph′), 120.9 (C-1), 99.6 (C-6), 76.8 (C-8), 76.0 (C-12), 75.8 (C-2), 70.3 (Cp), 66.8 (C-10), 61.2 (C-3), 60.6 (C-4), 60.1 (C-5), 59.2 (O*Me*), 28.3 (C-9), 26.8 (C(*C*H$_3$)$_3$) and 19.7 (*C*(CH$_3$)$_3$); ^{1}H / ^{1}H gcosy (500 MHz / 500 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 8.05 / 7.32 – 7.25 (*o*-Ph / *m*-Ph, *p*-Ph), 7.81 / 7.17 – 7.10 (*o*-Ph′ / *m*-Ph′, *p*-Ph′), 7.32 – 7.25 / 8.05 (*m*-Ph, *p*-Ph / *o*-Ph), 7.17 – 7.10 / 7.81 (*m*-Ph′, *p*-Ph′ / *o*-Ph′), 4.27 / 3.57, 3.36 (3-H / 5-H, 4-H), 3.96 / 3.66, 1.67, 1.04 (10-H$_{eq}$ / 10-H$_{ax}$, 9-H$_{ax}$, 9-H$_{eq}$), 3.89 / 3.46,. 3.24, 1.67, 1.04 (8-H / 12-H, 12-H′, 9-H$_{ax}$, 9-H$_{eq}$), 3.57 / 4.27, 3.36 (5-H / 3-H, 4-H), 3.46 / 3.89, 3.24 (12-H / 8-H, 12-H′), 3.36 / 4.27, 3.57 (4-H / 3-H, 5-H), 3.24 / 3.89, 3.46 (12-H′ / 8-H, 12-H), 1.67 / 3.96, 3.89, 3.66, 1.04 (9-H$_{ax}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{eq}$) and 1.04 / 3.96, 3.89, 3.66, 1.67 (9-H$_{eq}$ / 10-H$_{eq}$, 8-H, 10-H$_{ax}$, 9-H$_{ax}$); ^{1}H / ^{13}C ghsqc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 8.05 / 136.0 (*o*-Ph), 7.81 / 136.1 (*o*-Ph′), 7.32 – 7.25 / 130.3, 128.1 (*p*-Ph, *m*-Ph), 7.17 – 7.10 / 130.1, 127.97 (*p*-Ph′, *m*-Ph′), 5.86 / 99.6 (6), 4.27 / 61.2 (3), 4.25 / 70.3 (Cp), 3.96, 3.66 / 66.8 (10), 3.89 / 76.8 (8), 3.57 / 60.1 (5), 3.46, 3.24 / 76.0 (12), 3.36 / 60.6 (4), 3.22 / 59.2 (O*Me*), 1.67, 1.04 / 28.3 (9) and 1.22 / 26.8 (C(CH_3)$_3$); ^{1}H / ^{13}C ghmbc (500 MHz / 126 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 8.05 / 136.0, 134.3, 130.3 (*o*-Ph / *o*-Ph, *i*-Ph, *p*-Ph), 7.81 / 136.1, 132.6, 130.1 (*o*-Ph′ / *o*-Ph′, *i*-Ph′, *p*-Ph′), 7.32 – 7.25 / 136.0, 134.3, 128.1 (*p*-Ph, *m*-Ph / *o*-Ph, *i*-Ph, *m*-Ph), 7.17 – 7.10 / 136.1, 127.97 (*p*-Ph′, *m*-Ph′ / *o*-Ph′, *m*-Ph′), 5.86 / 120.9, 76.8, 75.8, 66.8, 61.2 (6-H / C-1, C-8, C-2, C-10, C-3), 4.27 / 120.9, 75.8, 60.1 (3-H / C-1, C-2, C-5), 3.96 / 99.6, 76.8, 28.3 (10-H$_{eq}$ / C-6, C-8, C-9), 3.57 / 120.9, 75.8, 61.2, 60.6 (5-H / C-1, C-2, C-3, C-4), 3.46 / 76.8, 59.2, 28.3 (12-H / C-8, O*Me*, C-9), 3.36 / 120.9, 75.8 (4-H / C-1, C-2), 3.24 / 76.8, 59.2, 28.3 (12-H′ / C-8, O*Me*, C-9), 3.22 / 76.0 (O*Me* / C-12), 1.67 / 76.8, 76.0, 66.8 (9-H$_{ax}$ / C-8, C-12, C-10) and 1.22 / 26.8, 19.7 (C(CH_3)$_3$ / C(*C*H$_3$)$_3$, *C*(CH$_3$)$_3$); *m*/*z* (EI) 570 (M$^+$, 100%), 411 (13), 403 (7), 197 (8), 135 (14) and 121 (14).

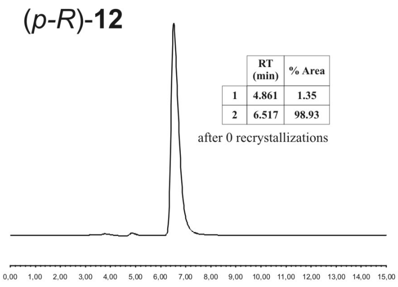
(*p-R*)-(−)-(*tert*-Butyldiphenylsiloxy)-2-formylferrocene ((*p-R*)-12)



(*p-R*)-**12**

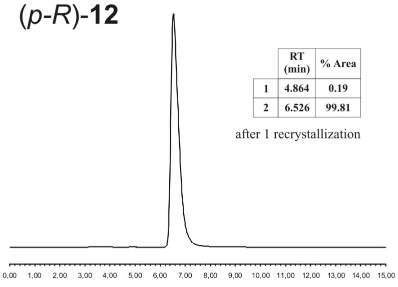
The acetal (*S,S,p-R*)-**15** (4.73 g, 8.29 mmol) and *p*-toluene sulfonic acid (3.16 g, 16.6 mmol) were dissolved in a two-phase mixture of dichloromethane (200 ml) and water (100 ml). The mixture was heated to reflux for three hours under vigorous stirring, the phases were separated and the organic phase was dried over magnesium sulfate. Filtration and removal of the solvent gave the crude product, which was purified by filtration on silica (cyclohexane : ethyl acetate = 4 : 1). The resulting deep red oil was dissolved in pentane (50 ml) and the solution was stored at –30°C overnight. Removal of the supernatant liquid gave a red solid, which was recrystallized twice from pentane at –30°C. This gave 2.75 g of the product (70.8 %, *ee* > 99.5 %).
X-ray quality crystals were obtained from a solution of (*p-R*)-**12** in pentane at 4°C.

Mp 117 °C (DSC); $[\alpha]_D^{20}$ -469 (*c* 0.52 in CH_2Cl_2); (Found: C, 69.16; H, 6.02. $C_{27}H_{28}FeO_2Si$ requires C, 69.23; H, 6.02%); ν_{max}(ATR)/cm^{-1} / δ_H / δ_C / *m*/*z*: all IR/NMR/MS data are like (*rac*)-**12**; *HPLC* (Chiralcel OD-H, hexanes : isopropanol = 95 : 5, 1 ml / min) t_r (min) 6.523 (100.00 %).


(*p-R*)-**12**

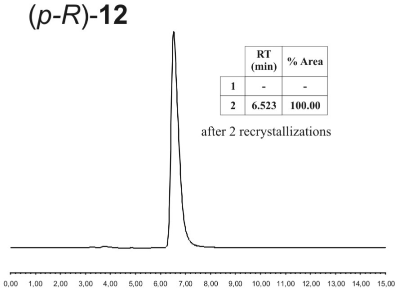
	RT (min)	% Area
1	4.861	1.35
2	6.517	98.93

after 0 recrystallizations


(*p-R*)-**12**

	RT (min)	% Area
1	4.864	0.19
2	6.526	99.81

after 1 recrystallization

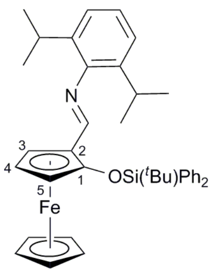

(*p-R*)-**12**

	RT (min)	% Area
1	-	-
2	6.523	100.00

after 2 recrystallizations

Synthesis of the ligand systems

(*p*-*S*)-(+)-N-2,6-Diisopropylphenyl-1-*tert*-butyldiphenylsiloxy-2-iminomethylferrocene ((*p*-*S*)-19a)

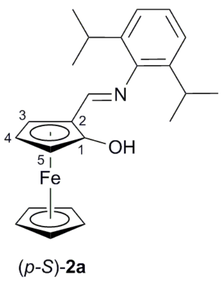


(*p-S*)-**19a**

The aldehyde (*p*-*S*)-**12** (5.00 g, 10.7 mmol), 2,6-diisopropylaniline (10.1 ml, 53.4 mmol) and *p*-toluene sulfonic acid (203 mg, 1.07 mmol) were dissolved in toluene (40 ml) and heated to 80°C overnight. Removal of the solvent gave the crude product, which was purified by column chromatography (cyclohexane : triethylamine = 9 : 1) to give the imine (*p*-*S*)-**19a** as an orange solid (6.27 g, 93.3 %).
X-ray quality crystals were obtained from a solution of (*p*-*S*)-**19a** in pentane at –30°C.

Mp 116 °C (DSC); $[\alpha]_D^{20}$ +505 (*c* 1.03 in CH_2Cl_2); (Found: C, 75.09; H, 7.34; N, 2.29. $C_{39}H_{45}FeNOSi$ requires C, 74.62; H, 7.23, N, 2.23%); ν_{max}(KBr)/cm^{-1} 2959, 2930, 2861, 1629, 1460, 1428, 1106, 905, 854, 820, 743 and 700; δ_H (500 MHz; $CDCl_3$; $SiMe_4$) 8.51 (1 H, t, ^4J = 0.6 Hz, ^5J = 0.6 Hz, CHN), 7.85 (2 H, m, *o*-Ph), 7.60 (2 H, m, *o*-Ph′), 7.50 (1 H, m, *p*-Ph), 7.46 (2 H, m, *m*-Ph), 7.42 (1 H, m, *p*-Ph′), 7.34 (2 H, m, *m*-Ph′), 7.16 (2 H, m, *m*-aryl), 7.10 (1 H, m, *p*-aryl), 4.66 (1 H, ddd, ^3J = 2.7 Hz, ^4J = 1.5 Hz, ^4J = 0.6 Hz, 3-H), 4.15 (5 H, s, Cp), 3.92 (1 H, td, ^3J = 2.7 Hz, ^5J = 0.6 Hz, 4-H), 3.72 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.5 Hz, 5-H), 3.16 (2 H, sept, ^3J = 7.0 Hz, CH), 1.27 (6 H, d, ^3J = 7.0 Hz, CH_3), 1.20 (6 H, d, ^3J = 7.0 Hz, CH_3') and 1.02 (9 H, s, C(C*H*$_3$)$_3$); δ_C (126 MHz; $CDCl_3$; $SiMe_4$) 160.8 (*C*HN), 149.8 (*i*-aryl), 138.0 (*o*-aryl), 135.7 (*o*-Ph), 135.5 (*o*-Ph′), 133.3 (*i*-Ph), 132.0 (*i*-Ph′), 130.3 (*p*-Ph), 130.0 (*p*-Ph′), 127.9 (*m*-Ph), 127.7 (*m*-Ph′), 123.7 (*p*-aryl), 123.4 (C-1), 122.9 (*m*-aryl), 70.4 (C-2), 69.9 (Cp), 63.6 (C-4), 61.5 (C-5), 60.0 (C-3), 27.7 (*C*H), 26.7 (C(*C*H$_3$)$_3$), 23.8 (*C*H$_3$′), 23.6 (*C*H$_3$) and 19.4 (*C*(CH$_3$)$_3$); ^{1}H / ^{1}H gcosy (500 MHz / 500 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_H = 7.85 / 7.50 (*o*-Ph / *p*-Ph), 7.60 / 7.34 (*o*-Ph′ / *m*-Ph′), 7.50 / 7.85, 7.46 (*p*-Ph / *o*-Ph, *m*-Ph), 7.46 / 7.50 (*m*-Ph / *p*-Ph), 7.42 / 7.34 (*p*-Ph′ / *m*-Ph′), 7.34 / 7.60, 7.42 (*m*-Ph′ / *o*-Ph′, *p*-Ph′), 7.16 / 7.10 (*m*-aryl / *p*-aryl), 7.10 / 7.16 (*p*-aryl / *m*-aryl), 4.66 / 3.92 (3-H / 4-H), 3.92 / 4.66, 3.72 (4-H / 3-H, 5-H), 3.72 / 3.92 (5-H / 4-H), 3.16 / 1.27, 1.20 (C*H* / C*H*$_3$, C*H*$_3$′), 1.27 / 3.16 (C*H*$_3$ / C*H*) and 1.20 / 3.16 (C*H*$_3$′ / C*H*); ^{1}H / ^{13}C ghsqc (500 MHz / 126 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 8.51 / 160.8 (*CH*N), 7.85 / 135.7 (*o*-Ph), 7.60 / 135.5 (*o*-Ph′), 7.50 / 130.3 (*p*-Ph), 7.46 / 127.9 (*m*-Ph), 7.42 / 130.0 (*p*-Ph′), 7.34 / 127.7 (*m*-Ph′), 7.16 / 122.9 (*m*-aryl), 7.10 / 123.7 (*p*-aryl), 4.66 / 60.0 (3), 4.15 / 69.9 (Cp), 3.92 / 63.6 (4), 3.72 / 61.5 (5), 3.16 / 27.7 (*CH*), 1.27 / 23.6 (*CH*$_3$), 1.20 / 23.8 (*CH*$_3$′) and 1.02 / 26.7 (C(*CH*$_3$)$_3$); ^{1}H / ^{13}C ghmbc (500 MHz / 126 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 7.85 / 135.7, 130.3 (*o*-Ph / *o*-Ph, *p*-Ph), 7.60 / 135.5, 130.0 (*o*-Ph′ / *o*-Ph′, *p*-Ph′), 7.50 / 135.7 (*p*-Ph / *o*-Ph), 7.46 / 133.3, 127.9 (*m*-Ph / *i*-Ph, *m*-Ph), 7.34 / 132.0, 127.7 (*m*-Ph′ / *i*-Ph′, *m*-Ph′), 7.16 / 149.8, 123.7 (*m*-aryl / *i*-aryl, *p*-aryl), 7.10 / 138.0 (*p*-aryl / *o*-aryl), 3.16 / 138.0, 23.8, 23.6 (C*H* / *o*-aryl, *C*H$_3$′, *C*H$_3$), 1.27 / 138.0, 27.7 (C*H*$_3$ / *o*-aryl, *C*H), 1.20 / 138.0, 27.7 (C*H*$_3$′ / *o*-aryl, *C*H) and 1.02 / 19.4 (C(C*H*$_3$)$_3$ / *C*(CH$_3$)$_3$); *m*/*z* (EI) 627 (M$^+$, 100%), 546 (11) and 135 (9).

(*p*-*S*)-(–)-*N*-2,6-Diisopropylphenyl-2-iminomethylferrocen-1-ol ((*p*-*S*)-2a)

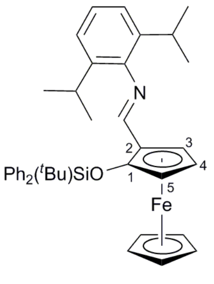


(*p-S*)-**2a**

The imine (*p*-*S*)-**19a** (5.19 g, 8.27 mmol) and tetra-*n*-butyl ammonium fluoride (5.22 g, 16.5 mmol) were dissolved in tetrahydrofurane (200 ml) and the solution was stirred for two hours. The solvent was removed and the crude product was purified by column chromatography under argon (cyclohexane : ethyl acetate : triethylamine = 8 : 1 : 1, solvents were degassed before use). Two fractions were collected and the solvent was removed. The oily residues were dissolved in pentane (100 ml each) and the solutions were kept at –30°C for two days. The deep red crystals of (*p*-*S*)-**2a** were isolated by removal of the mother liquors, to give a combined yield of 3.03 g (94.1 %). The crystals were suitable for X-ray analysis.

Mp 161 °C (DSC); $[\alpha]_D^{20}$ -1657 (*c* 0.208 in CH_2Cl_2); (Found: C, 70.82; H, 6.95; N, 3.64. $C_{23}H_{27}FeNO$ requires C, 70.96; H, 6.99; N, 3.60%); ν_{max}(KBr)/cm^{-1} 2954, 2865, 1615, 1590, 1470, 1104, 934, 903 and 802; δ_H (500 MHz; $CDCl_3$; $SiMe_4$) 9.02 (1 H, br, OH), 8.30 (1 H, d, ^4J = 0.6 Hz, C*H*N), 7.17 – 7.10 (3 H, m, *m*-aryl, *p*-aryl), 4.54 (1 H, ddd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, ^4J = 0.6 Hz, 3-H), 4.24 (5 H, s, Cp), 4.14 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 5-H), 4.03 (1 H, t, ^3J = 2.7 Hz, 4-H), 3.07 (2 H, sept, ^3J = 7.0 Hz, C*H*), 1.22 (6 H, d, ^3J = 7.0 Hz, C*H*$_3$) and 1.18 (6 H, d, ^3J = 7.0 Hz, C*H*$_3$′); δ_C (126 MHz; $CDCl_3$; $SiMe_4$) 168.1 (*C*HN), 147.4 (*i*-aryl), 138.5 (*o*-aryl), 126.4 (C-1), 124.8 (*p*-aryl), 123.0 (*m*-aryl), 69.6 (Cp), 63.8 (C-2), 63.1 (C-4), 62.6 (C-5), 58.2 (C-3), 27.9 (*C*H), 23.7 (*C*H$_3$′) and 23.4 (*C*H$_3$); ^{1}H / ^{1}H gcosy (500 MHz / 500 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_H = 4.54 / 4.14, 4.03 (3-H / 5-H, 4-H), 4.14 / 4.54, 4.03 (5-H / 3-H, 4-H), 4.03 / 4.54, 4.14 (4-H / 3-H, 5-H), 3.07 / 1.22, 1.18 (C*H* / C*H*$_3$, C*H*$_3$′), 1.22 / 3.07 (C*H*$_3$ / C*H*) and 1.18 / 3.07 (C*H*$_3$′ / C*H*); ^{1}H / ^{13}C ghsqc (500 MHz / 126 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 8.30 / 168.1 (*CH*N), 7.17 – 7.10 / 124.8 (*p*-aryl), 7.17 – 7.10 / 123.0 (*m*-aryl), 4.54 / 58.2 (3), 4.24 / 69.6 (Cp), 4.14 / 62.6 (5), 4.03 / 63.1 (4), 3.07 / 27.9 (*CH*), 1.22 / 23.4 (*CH*$_3$) and 1.18 / 23.7 (*CH*$_3$′); ^{1}H / ^{13}C ghmbc (500 MHz / 126 MHz; $CDCl_3$; $SiMe_4$): δ_H / δ_C = 7.17 – 7.10 / 123.0 (*m*-aryl, *p*-aryl / *m*-aryl), 3.07 / 138.5, 123.0 (C*H* / *o*-aryl, *m*-aryl), 1.22 / 138.5, 27.9 (C*H*$_3$ / *o*-aryl, *C*H) and 1.18 / 138.5, 27.9 (C*H*$_3$′ / *o*-aryl, *C*H).

(*p*-*R*)-(−)-*N*-2,6-Diisopropylphenyl-1-*tert*-butyldiphenylsiloxy-2-iminomethylferrocene ((*p*-*R*)-19a)

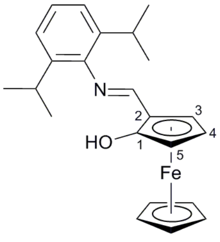


(*p*-*R*)-**19a**

The aldehyde (*p*-*R*)-**12a** (2.75 g, 5.85 mmol), 2,6-diisopropylaniline (5.54 ml, 29.4 mmol) and of *p*-toluene sulfonic acid (112 mg, 0.587 mmol) were dissolved in toluene (50 ml) and heated to 80 °C overnight. Removal of the solvent gave the crude product, which was purified by column chromatography (cyclohexane : triethylamine = 9 : 1) to give the imine (*p*-*R*)-**19a** as an orange solid (3.02 g, 82.0 %).
X-ray quality crystals were obtained from a solution of (*p*-*R*)-**19a** in pentane at –30°C.

Mp 119 °C (DSC); $[\alpha]_D^{20}$ -498 (*c* 1.00 in CH_2Cl_2); (Found: 74.12; H, 7.21; N, 2.13. $C_{39}H_{45}FeNOSi$ requires C, 74.62; H, 7.23; N, 2.23%); ν_{max}(ATR)/cm^{-1} / δ_H / δ_C / *m*/*z*: all IR/NMR/MS data are like (*p*-*S*)-**19a**.

(*p*-*R*)-(+)-*N*-2,6-Diisopropylphenyl-2-iminomethylferrocen-1-ol ((*p*-*R*)-2a)

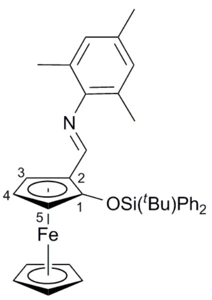


(*p*-*R*)-**2a**

The imine (*p*-*R*)-**19a** (1.62 g, 2.58 mmol) and tetra-*n*-butyl ammonium fluoride (1.63 g, 5.16 mmol) were dissolved in tetrahydrofurane (30 ml) and the solution was stirred for two hours. The solvent was removed and the crude product was purified by column chromatography under argon (cyclohexane : ethyl acetate : triethylamine = 8 : 1 : 1, solvents were degassed before use). The solvent was removed to give an oily residue, which was redissolved in pentane (100 ml). The solution was kept at –30°C overnight and the resulting precipitate was isolated by removal of the mother liquor to give a first fraction of 510 mg of the product. Further storage of the mother liquor at –30°C yielded another 310 mg of the product (*p*-*R*)-**2a** as deep red crystals (total yield 820 mg, 81.6 %). The crystals were suitable for X-ray analysis.

Mp 165 °C (DSC); $[\alpha]_D^{20}$ +1698 (*c* 0.212 in CH_2Cl_2); (Found: C, 70.98; H, 7.11; N, 3.90. $C_{23}H_{27}FeNO$ requires C, 70.96; H, 6.99; N, 3.60%); ν_{max}(ATR)/cm^{-1} / δ_H / δ_C / *m*/*z*: all IR/NMR/MS data are like (*p*-*S*)-**2a**.

(*p*-*S*)-(+)-N-2,4,6-Trimethylphenyl-1-*tert*-butyldiphenylsiloxy-2-iminomethylferrocene ((*p*-*S*)-19b)



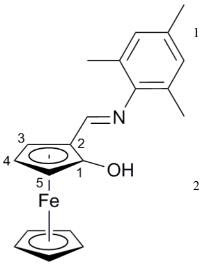
(*p*-*S*)-**19b**

The aldehyde (*p*-*S*)-**12** (4.40 g, 9.39 mmol), 2,4,6-trimethylaniline (10.1 ml, 53.4 mmol, 5 eq) and *p*-toluene sulfonic acid (179 mg, 0.939 mmol) were dissolved in toluene (100 ml) and heated to 80°C for three hours. Removal of the solvent gave the crude product, which was purified by column chromatography (cyclohexane : triethylamine = 9 : 1) to give the imine (*p*-*S*)-**19b** as a yellow oil (4.68 g, 85.1 %).

$[\alpha]_D^{20}$ +602 (*c* 1.00 in CH_2Cl_2); (Found: C, 74.51; H, 7.01; N, 2.46. $C_{36}H_{39}FeNOSi$ requires C, 73.83; H, 6.71; N, 2.39%); ν_{max}(ATR)/cm^{-1} 2957, 2928, 2856, 1628, 1459, 1428, 1316,1287, 1205, 1105, 1108, 904, 855, 819, 741, 700 and 502; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$) 8.54 (1 H, s, C*H*N), 7.89 (2 H, m, *o*-Ph), 7.65 (2 H, m, *o*-Ph´), 7.54 (1 H, m, *p*-Ph), 7.50 (2 H, m, *m*-Ph), 7.45 (1 H, m, *p*-Ph´), 7.38 (2 H, m, *m*-Ph´), 6.91 (2 H, m, *m*-mes), 4.65 (1 H, ddd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, ^4J = 0.6 Hz, 3-H), 4.19 (5 H, s, Cp), 3.94 (1 H, td, ^3J = 2.8 Hz, ^5J = 0.6 Hz, 4-H), 3.79 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 5-H), 2.30 (3 H, s, *p*-CH_3), 2.19 (6 H, s, *o*-CH_3) and 1.07 (9 H, s, C(CH_3)$_3$); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$) 161.5 (*C*HN), 150.2 (*i*-mes), 136.0 (*o*-Ph), 135.9 (*o*-Ph´), 133.6 (*i*-Ph), 132.6 (*p*-mes), 132.5 (*i*-Ph´), 130.6 (*p*-Ph), 130.5 (*p*-Ph´), 129.0 (*m*-mes), 128.21 (*m*-Ph), 128.15 (*m*-Ph´), 127.2 (*o*-mes), 123.8 (C-1), 71.0 (C-2), 70.4 (Cp), 63.8 (C-4), 62.1 (C-5), 60.3 (C-3), 26.8 (C(*C*H$_3$)$_3$), 20.9 (*p*-*C*H$_3$), 19.7 (*C*(CH$_3$)$_3$) and 18.5 (*o*-*C*H$_3$); ^1H / ^1H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_H = 8.54 / 4.65, 3.94 (C*H*N / 3-H, 4-H), 7.89 / 7.50 (*o*-Ph / *m*-Ph), 7.65 / 7.38 (*o*-Ph´ / *m*-Ph´), 7.54 / 7.50 (*p*-Ph / *m*-Ph), 7.50 / 7.89, 7.54 (*m*-Ph / *o*-Ph, *p*-Ph), 7.45 / 7.38 (*p*-Ph´ / *m*-Ph´), 7.38 / 7.65, 7.45 (*m*-Ph´ / *o*-Ph´, *p*-Ph´), 6.91 / 2.30, 2.19 (*m*-mes / *p*-CH$_3$, *o*-CH$_3$), 4.65 / 8.54, 3.94, 3.79 (3-H / C*H*N, 4-H, 5-H), 3.94 / 8.54, 4.65, 3.79 (4-H / C*H*N, 3-H, 5-H), 3.79 / 4.65, 3.94 (5-H / 3-H, 4-H), 2.30 / 6.91 (*p*-CH_3 / *m*-mes) and 2.19 / 6.91 (*o*-CH_3 / *m*-mes); ^1H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.54 / 161.5 (*C*HN), 7.89 / 136.0 (*o*-Ph), 7.65 / 135.9 (*o*-Ph´), 7.54 / 130.6 (*p*-Ph), 7.50 / 128.21 (*m*-Ph), 7.45 / 130.5 (*p*-Ph´), 7.38 / 128.15 (*m*-Ph´), 6.91 / 129.0 (*m*-mes), 4.65 / 60.3 (3), 4.19 / 70.4 (Cp), 3.94 / 63.8 (4), 3.79 / 62.1 (5), 2.30 / 20.9 (*p*-*C*H$_3$), 2.19 / 18.5 (*o*-*C*H$_3$) and 1.07 / 26.8 (C(*C*H$_3$)$_3$); ^1H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.54 / 150.2, 127.2, 123.8, 71.0, 60.3 (C*H*N / *i*-mes, *o*-mes, C-1, C-2, C-3), 7.89 / 136.0, 133.6, 130.6, 128.21 (*o*-Ph / *o*-Ph, *i*-Ph, *p*-Ph, *m*-Ph), 7.65 / 135.9, 132.5, 130.5, 128.15 (*o*-Ph´ / *o*-Ph´, *i*-Ph´, *p*-Ph´, *m*-Ph´), 7.54 / 136.0 (*p*-Ph / *o*-Ph), 7.50 / 136.0, 128.21 (*m*-Ph / *o*-Ph, *m*-Ph), 7.45 / 128.15 (*p*-Ph´ / *m*-Ph´), 7.38 / 35.9, 130.5 (*m*-Ph´ / *o*-Ph´, *m*-Ph´), 6.91 / 150.2, 129.0, 20.9, 18.5 (*m*-mes / *i*-mes, *m*-mes, *p*-CH$_3$, *o*-

CH_3), 4.65 / 123.8, 71.0, 63.8, 62.1 (3-H / C-1, C-2, C-4, C-5), 3.94 / 123.8, 71.0, 62.1, 60.3 (4-H / C-1, C-2, C-5, C-3), 3.79 / 123.8, 71.0, 63.8, 60.3 (5-H / C-1, C-2, C-4, C-3), 2.30 / 132.6, 129.0 (*p*-CH_3 / *p*-mes, *m*-mes), 2.19 / 129.0, 127.2 (*o*-CH_3 / *m*-mes, *o*-mes) and 1.07 / 26.8, 19.7 ($C(C\mathit{H}_3)_3$ / $C(\mathit{C}H_3)_3$, $\mathit{C}(CH_3)_3$); *m/z* (ESI) 586.2210 (M+H$^+$. $C_{36}H_{40}FeNOSi$ requires 586.2224).

(*p*-*S*)-(−)-*N*-2,4,6-Trimethylphenyl-2-iminomethylferrocen-1-ol ((*p*-*S*)-2b)

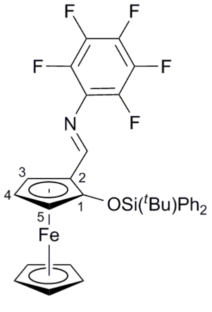


(*p*-*S*)-**2b**

The imine (*p*-*S*)-**19b** (4.40 g, 7.51 mmol) and tetra-*n*-butyl ammonium fluoride (4.74 g, 15.0 mmol) were dissolved in tetrahydrofurane (200 ml) and the solution was stirred for two hours. The solvent was removed and the crude product was purified by column chromatography under argon (cyclohexane : ethyl acetate : triethylamine = 8 : 1 : 1, solvents were degassed before use). The solvent was removed to give an oily residue, which was dissolved in pentane (100 ml). The solution was kept at –30°C overnight, yielding a red precipitate. Removal of the mother liquor and drying of the solid gave 1.13 g (43.3 %) of (*p*-*S*)-**2b**.

Mp 104 °C (DSC); $[\alpha]_D^{20}$ -1666 (*c* 0.198 in CH_2Cl_2); (Found: C, 68.98; H, 6.38; N, 3.97. $C_{20}H_{21}FeNO$ requires C, 69.18; H, 6.10; N, 4.03%); ν_{max}(KBr)/cm^{-1} 2908, 2855, 1616, 1601, 1470, 1410, 1326, 1210, 1188, 1139, 1106, 1001, 856, 837, 818, 799, 711, 678, 651, 569 and 524; δ_H (600 MHz; CD_2Cl_2; $SiMe_4$) 8.76 (1 H, br, OH), 8.35 (1 H, d, ^4J = 0.6 Hz, C*H*N), 6.90 (2 H, m, *m*-mes), 4.51 (1 H, ddd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, ^4J = 0.6 Hz, 3-H), 4.23 (5 H, s, Cp), 4.17 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 5-H), 4.02 (1 H, t, ^3J = 2.7 Hz, 4-H), 2.27 (3 H, s, *p*-C*H*$_3$) and 2.19 (6 H, s, *o*-C*H*$_3$); δ_C (151 MHz; CD_2Cl_2; $SiMe_4$) 169.0 (*C*HN), 147.6 (*i*-mes), 133.9 (*p*-mes), 129.2 (*m*-mes), 127.7 (*o*-mes), 126.9 (C-1), 70.1 (Cp), 64.3 (C-2), 63.5 (C-4), 63.1 (C-5), 58.4 (C-3), 20.8 (*p*-*C*H_3) and 18.7 (*o*-*C*H_3); ^1H / ^1H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_H = 8.35 / 4.51 (C*H*N / 3-H), 6.90 / 2.27, 2.19 (*m*-mes / *p*-C*H*$_3$, *o*-C*H*$_3$), 4.51 / 8.35, 4.17, 4.02 (3-H / C*H*N, 5-H, 4-H), 4.17 / 4.51, 4.02 (5-H / 3-H, 4-H), 4.02 / 4.51, 4.17 (4-H / 3-H, 5-H), 2.27 / 6.90, 2.19 (*p*-C*H*$_3$ / *m*-mes, *o*-C*H*$_3$) and 2.19 / 6.90, 2.27 (*o*-C*H*$_3$ / *m*-mes, *p*-C*H*$_3$); ^1H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.35 / 169.0 (*CH*N), 6.90 / 129.2 (*m*-mes), 4.51 / 58.4 (3), 4.23 / 70.1 (Cp), 4.17 / 63.1 (5), 4.02 / 63.5 (4), 2.27 / 20.8 (*p*-*CH*$_3$) and 2.19 / 18.7 (*o*-*CH*$_3$); ^1H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.35 / 147.6, 126.9, 64.3, 58.4 (C*H*N / *i*-mes, C-1, C-2, C-3), 6.90 / 147.6, 129.2, 20.8, 18.7 (*m*-mes / *i*-mes, *m*-mes, *p*-*C*H_3, *o*-*C*H_3), 4.51 / 64.3, 63.5, 63.1 (3-H / C-2, C-4, C-5), 4.17 / 126.9, 64.3, 63.5, 58.4 (5-H / C-1, C-2, C-4, C-3), 4.02 / 126.9, 64.3, 63.1, 58.4 (4-H / C-1, C-2, C-5, C-3), 2.27 / 133.9, 129.2 (*p*-C*H*$_3$ / *p*-mes, *m*-mes), 2.19 / 147.6, 129.2, 127.7 (*o*-C*H*$_3$ / *i*-mes, *m*-mes, *o*-mes).

(*p*-*S*)-(+)-*N*-Pentaflurophenyl-1-*tert*-butyldiphenylsiloxy-2-iminomethylferrocene ((*p*-*S*)-19c)

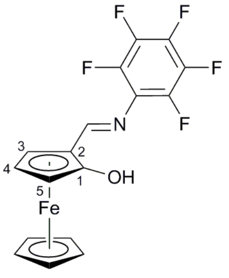


(*p*-*S*)-**19c**

The aldehyde (*p*-*S*)-**12** (3.93 g, 8.39 mmol), pentafluoroaniline (7.67 g, 41.9 mmol) and *p*-toluene sulfonic acid (160 mg, 0.839 mmol) were dissolved in toluene (40 ml) and heated to 80°C for three hours. Removal of the solvent gave the crude product, which was purified by column chromatography (cyclohexane : triethylamine = 9 : 1) to give a red oil. Addition of pentane (100 ml) and subsequent removal of the solvent to gave the imine (*p*-*S*)-**19c** as a red solid (3.56 g, 67.0 %).

Mp 36 °C (DSC); $[\alpha]_D^{20}$ +568 (*c* 0.202 in CH_2Cl_2); (Found: C, 63.22; H, 4.61; N, 2.04. $C_{33}H_{28}F_5FeNOSi$ requires C, C, 62.57; H, 4.45; N, 2.21%); ν_{max}(KBr)/cm^{-1} 2930, 1608, 1516, 1503, 1461, 1428, 1107, 1006, 969, 829, 820, 743, 698, 615 and 571; δ_H (600 MHz; C_6D_6; $SiMe_4$) 9.06 (1 H, t, ^4J = 0.5 Hz, ^5J = 0.5 Hz, C*H*N), 7.87 (2 H, m, *o*-Ph), 7.64 (2 H, m, *o*-Ph´), 7.24 – 7.21 (3 H, m, *m*-Ph, *p*-Ph), 7.14 – 7.09 (3 H, m, *m*-Ph´, *p*-Ph´), 4.77 (1 H, ddd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, ^4J = 0.5 Hz, 3-H), 4.08 (5 H, s, Cp), 3.83 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 5-H), 3.67 (1 H, td, ^3J = 2.8 Hz, ^5J = 0.5 Hz, 4-H) and 1.12 (9 H, s, $C(C\mathit{H}_3)_3$); δ_F (564 MHz; C_6D_6; CCl_3F) −155.6 (2 F, m, *o*-C_6F_5), −163.2 (1 F, t, $^3J_{FF}$ = 21.8 Hz, *p*-C_6F_5) and −164.1 (2 F, m, *m*-C_6F_5) ; δ_C (151 MHz; C_6D_6; $SiMe_4$) 168.3 (*C*HN), 140.2 (dm, $^1J_{C,F}$ ≈ 245 Hz, C_6F_5), 138.2 (dm, $^1J_{C,F}$ ≈ 248 Hz, C_6F_5), 137.5 (dm, $^1J_{C,F}$ ≈ 246 Hz, C_6F_5), 136.0 (*o*-Ph), 135.8 (*o*-Ph´), 133.3 (*i*-Ph), 132.0 (*i*-Ph´), 130.7 (*p*-Ph), 130.5 (*p*-Ph´), 128.24, 128.22 (*m*-Ph, *m*-Ph´), 124.6 (C-1), 71.0 (Cp), 69.4 (C-2), 65.5 (C-4), 63.0 (C-5), 61.3 (C-3), 26.8 ($C(\mathit{C}H_3)_3$) and 19.6 ($\mathit{C}(CH_3)_3$), the signal for *i*-C_6F_5 was not located; ^1H / ^1H gcosy (600 MHz / 600 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 9.06 / 4.77, 3.67 (C*H*N / 3-H, 4-H), 7.87 / 7.24 – 7.21 (*o*-Ph / *m*-Ph, *p*-Ph), 7.64 / 7.14 – 7.09 (*o*-Ph´ / *m*-Ph´, *p*-Ph´), 7.24 – 7.21 / 7.87 (*m*-Ph, *p*-Ph / *o*-Ph), 7.14 – 7.09 / 7.64 (*m*-Ph´, *p*-Ph´ / *o*-Ph´), 4.77 / 9.06, 3.83, 3.67 (3-H / C*H*N, 5-H, 4-H), 3.83 / 4.77, 3.67 (5-H / 3-H, 4-H) and 3.67 / 9.06, 4.77, 3.83 (4-H / C*H*N, 3-H, 5-H); ^1H / ^{13}C ghsqc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 9.06 / 168.3 (*CH*N), 7.87 / 136.0 (*o*-Ph), 7.64 / 135.8 (*o*-Ph´), 7.24 – 7.21 / 128.24, 128.22, 130.7 (*m*-Ph, *p*-Ph), 7.14 – 7.09 / 128.24, 128.22, 130.5 (*m*-Ph´, *p*-Ph´), 4.77 / 61.3 (3), 4.08 / 71.0 (Cp), 3.83 / 63.0 (5), 3.67 / 65.5 (4) and 1.12 / 26.8 ($C(\mathit{CH}_3)_3$); ^1H / ^{13}C ghmbc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 9.06 / 124.6, 69.4, 61.3 (C*H*N / C-1, C-2, C-3), 7.87 / 136.0, 133.3, 130.7, 128.24, 128.22 (*o*-Ph / *o*-Ph, *i*-Ph, *p*-Ph, *m*-Ph), 7.64 / 135.8, 132.0, 130.5, 128.24, 128.22 (*o*-Ph´ / *o*-Ph´, *i*-Ph´, *p*-Ph´, *m*-Ph´), 7.24 – 7.21 / 136.0, 133.3, 128.24, 128.22 (*m*-Ph, *p*-Ph / *o*-Ph, *i*-Ph, *m*-Ph), 7.14 – 7.09 / 135.8, 132.0, 128.24, 128.22 (*m*-Ph´, *p*-Ph´ / *o*-Ph´, *i*-Ph´, *m*-Ph´), 4.77 / 124.6, 69.4, 65.5, 63.0 (3-H / C-1, C-2, C-4, C-5), 3.83 / 124.6, 69.4, 65.5, 61.3 (5-H / C-1, C-2, C-4, C-3), 3.67 / 124.6, 69.4, 63.0, 61.3 (4-H / C-1, C-2, C-5, C-3) and 1.12 / 26.8, 19.6 ($\mathrm{C(C}\mathit{H}_3)_3$ / $\mathrm{C(}\mathit{C}\mathrm{H}_3)_3$, $\mathit{C}\mathrm{(CH_3)_3}$); *m*/*z* (EI) 633 ($M^+$, 100%), 576 (11), 197 (21) and 135 (33).

(*p*-*S*)-(−)-*N*-Pentaflurophenyl-2-iminomethylferrocen-1-ol ((*p*-*S*)-2c)

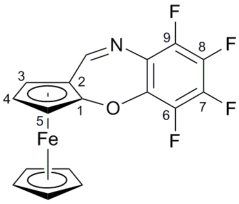


(*p*-*S*)-**2c**

The imine (*p*-*S*)-**19c** (4.97 g, 7.85 mmol) and triethylamine trihydrofluoride (427 µl, 2.62 mmol) were dissolved in tetrahydrofurane (30 ml) and the solution was stirred for one hour. The solvent was removed and the residue was redissolved in toluene (50 ml) and pentane (200 ml). The solution was stored at –30°C overnight, yielding a purple precipitate (1.27 g). The mother liquor was evaporated to a volume of 30 ml and stored at –30°C for another night, yielding a second fraction of the product (600 mg). The remaining mother liquor was evaporated, fresh toluene (30 ml) were added and the solution was stored at –30°C overnight, yielding a third fraction of the product (280 mg, total yield 2.15 g, 69.3 %).
X-ray quality crystals were obtained from a solution of (*p*-*S*)-**2c** in toluene at –30°C.

Mp 164 °C (DSC); $[\alpha]_D^{20}$ -296 (*c* 0.198 in CH_2Cl_2); (Found: C, 52.30; H, 2.92; N, 3.23. $C_{17}H_{10}F_5FeNO$ requires C, 51.68; H, 2.55; N, 3.55%); ν_{max}(KBr)/cm^{-1} 3094, 2931, 1647, 1586, 1512, 1501, 1470, 1345, 1201, 1107, 1021, 999, 974, 820, 663, 618 and 618; δ_H (600 MHz; C_6D_6; $SiMe_4$) 8.36 (1 H, br, OH), 8.09 (1 H, br, CHN), 4.51 (1 H, ddd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, ^4J = 0.6 Hz, 3-H), 4.04 (5 H, s, Cp), 3.75 (1 H, t, ^3J = 2.7 Hz, 4-H) and 3.73 (1 H, dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 5-H); δ_F (564 MHz; C_6D_6; CCl_3F) −154.4 (2 F, m, *o*-$C_6\mathit{F}_5$), −161.7 (1 F, t, $^3J_{FF}$ = 21.8 Hz, *p*-$C_6\mathit{F}_5$) and −163.8 (2 F, m, *m*-$C_6\mathit{F}_5$); δ_C (151 MHz; C_6D_6; $SiMe_4$) 174.5 (b, *C*HN), 140.2 (dm, $^1J_{FC}$ = 247 Hz, C_6F_5), 138.0 (dm, $^1J_{FC}$ = 254 Hz, 2 x C_6F_5), 127.3 (C-1), 125.7 (b, *i*-C_6F_5) 70.7 (Cp), 65.5 (C-4), 63.8 (C-5), 63.3 (C-2) and 60.3 (C-3); ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; C_6D_6; $SiMe_4$): δ_H / δ_H = 8.09 / 4.51 (C*H*N / 3-H), 4.51 / 8.09, 3.75, 3.73 (3-H / C*H*N, 4-H, 5-H), 3.75 / 4.51, 3.73 (4-H / 3-H, 5-H) and 3.73 / 4.51, 3.75 (5-H / 3-H, 4-H); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 8.09 / 174.5 (C*H*N), 4.51 / 60.3 (3), 4.04 / 70.7 (Cp), 3.75 / 65.5 (4) and 3.73 / 63.8 (5); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; C_6D_6; $SiMe_4$): δ_H / δ_C = 8.09 / 127.3, 126, 63.3, 60.3 (C*H*N / C-1, *i*-C_6F_5, C-2, C-3), 4.51 / 127.3, 65.5, 63.3 (3-H / C-1, C-4, C-5), 3.75 / 127.3, 63.3, 60.3 (4-H / C-1, C-2, C-3) and 3.73 / 127.3, 65.5, 63.3, 60.3 (5-H / C-1, C-4, C-2, C-3).

Nucleophilic aromatic substitution product from imine (*p*-*S*)-19c: Ring closure product 20



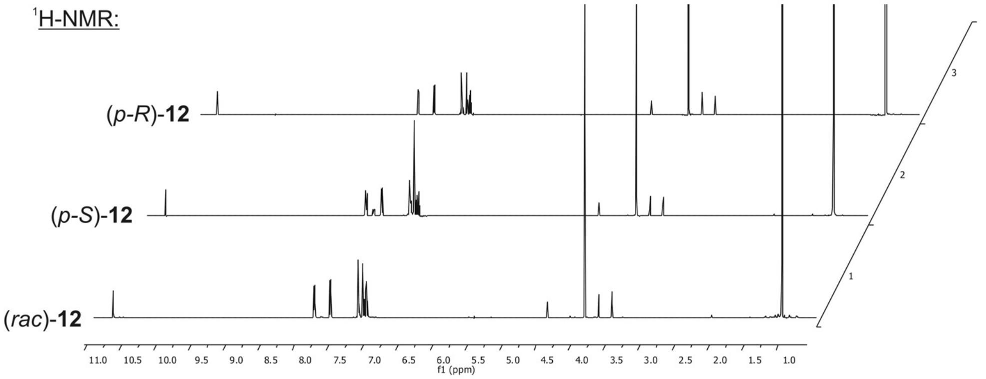
(*p*-*S*)-**20**

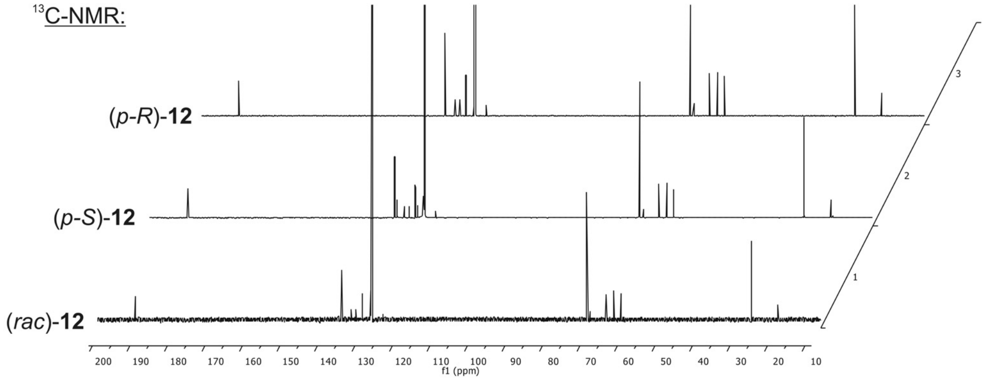
The imine (*p*-*S*)-**19c** (350 mg, 0.552 mmol) and tetra-*n*-butyl ammonium fluoride (349 mg, 1.10 mmol) were dissolved in tetrahydrofurane (10 ml) and the solution was stirred for two hours. The solvent was removed and the crude product was purified by column chromatography (cyclohexane : triethylamine = 9 : 1) to give the ring-closure product **20** as a red solid (110 mg, 53.1 %).
X-ray quality crystals were obtained by slow evaporation of a solution of **20** in pentane.

Mp 164 °C (DSC); $[\alpha]_D^{20}$ -2174 (*c* 0.200 in CH_2Cl_2); (Found: C, 54.00; H, 3.08; N, 3.25. $C_{17}H_9F_4FeNO$ requires C, 54.43; H, 2.42; N, 3.73%); ν_{max}(KBr)/cm^{-1} 2959, 2931, 2857, 1510, 1485, 1428, 1109, 1000, 952, 820, 740, 709 and 608; δ_H (500 MHz; CD_2Cl_2; $SiMe_4$) 8.39 (1 H, br, C*H*N), 4.62 (1 H, ddd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, ^4J = 0.6 Hz, 3-H), 4.29 (5 H, s, Cp), 4.29 (1 H, t, ^3J = 2.8 Hz, 4-H) and 4.24 (1 H, dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 5-H); δ_F (470 MHz; CD_2Cl_2; CCl_3F) −147.0 (1 F, dd, $^3J_{FF}$ = 22.0 Hz, $^5J_{FF}$ = 6.6 Hz), −160.4 (1 F, dd, $^3J_{FF}$ = 22.0 Hz, $^5J_{FF}$ = 6.6 Hz) (F-6, F-9), −159.6 (1 F, t, $^3J_{FF}$ = 22.0 Hz), −164.8 (1 F, t, $^3J_{FF}$ = 22.0 Hz) (F-7, F-8); δ_C (126 MHz; CD_2Cl_2; $SiMe_4$) 164.5 (*C*HN), 129.0 (C-1), 71.3 (Cp), 68.1 (C-2), 66.6 (C-4), 64.9 (C-5) and 63.5 (C-3), signals for C_6F_4 were not located; ^{1}H / ^{1}H gcosy (600 MHz / 600 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_H = 4.62 / 4.29, 4.24 (3-H / 4-H, 5-H), 4.29 / 4.62, 4.24 (4-H / 3-H, 5-H) and 4.24 / 4.62, 4.29 (5-H / 3-H, 4-H); ^{1}H / ^{13}C ghsqc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.39 / 164.5 (*CH*N), 4.62 / 63.5 (3), 4.29 / 71.3 (Cp) and 4.29 / 66.6 (4), 4.24 / 64.9 (4); ^{1}H / ^{13}C ghmbc (600 MHz / 151 MHz; CD_2Cl_2; $SiMe_4$): δ_H / δ_C = 8.39 / 129.0, 68.1 (C*H*N / C-1, C-2), 4.62 / 68.1, 66.6, 64.9 (3-H / C-2, C-4, C-5), 4.29 / 68.1 (4-H / C-2), 4.24 / 129.0, 68.1, 66.6, 63.5 (5-H / C-1, C-2, C-4, C-3); *m*/*z* (EI) 375 (M^+, 100%), 326 (7), 310 (9), 281 (6), 252.1 (6), 216 (37), 187 (12), 121 (28) and 56 (14).

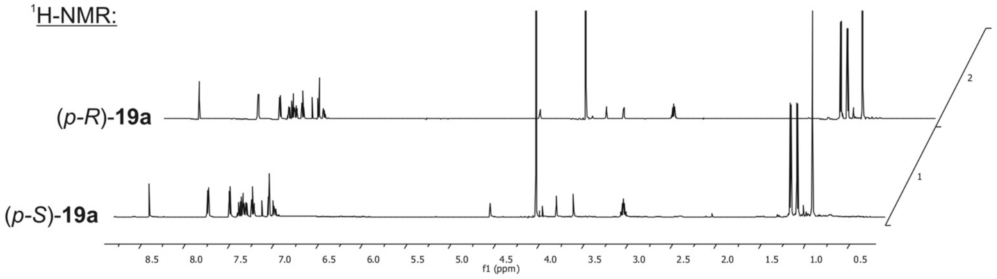
NMR spectra of the isostructural products:

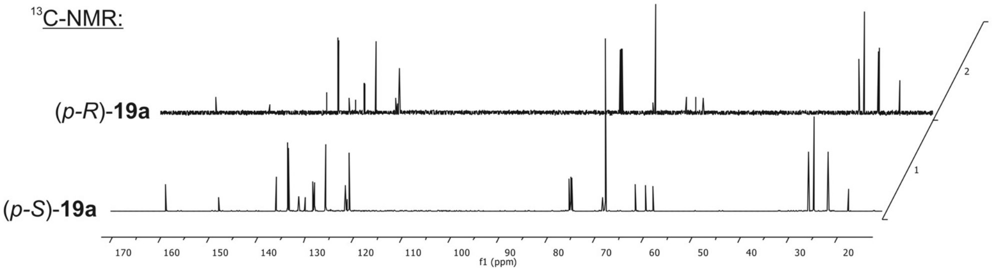
(*rac*)-12 / (*p-S*)-12 / (*p-R*)-12:



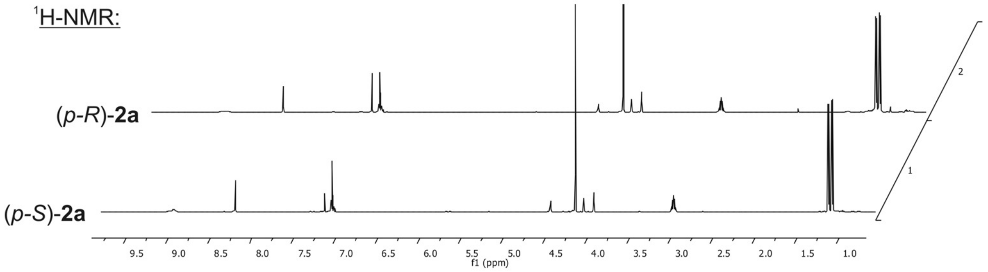


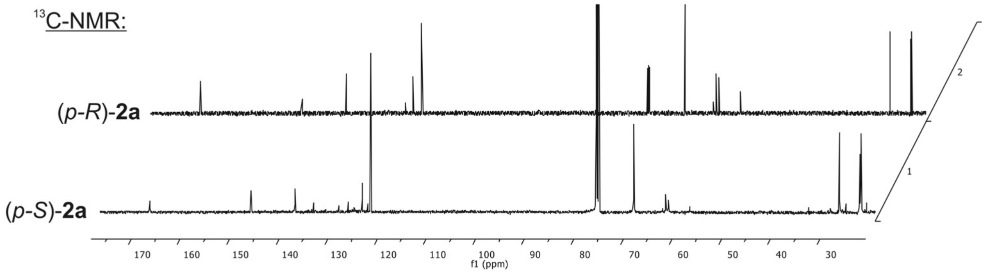
(*p-S*)-19a / (*p-R*)-19a:





(*p-S*)-2a / (*p-R*)-2a:





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