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Chiral ferrocene cyanohydrin derivatives—access to novel intermolecularly linked and intramolecularly bridged ferrocene derivatives

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Abstract—By reduction of the cyano group in (*R*)-(cyanohydroxymethyl)ferrocene and (*R*,*R*)-1,1′-bis(cyanohydroxymethyl)ferrocene, amines were obtained giving access to several new diamine and diamide bridged chiral ferrocene derivatives. As a representative for an intramolecularly bridged ferrocene compound bearing two chiral centres (*R*,*R*)-**8** was obtained with excellent optical purity.

1. Introduction

Recently, we reported the novel access to chiral ferrocene derivatives **1** and **2** employing a hydroxynitrile lyase from *Hevea brasiliensis*.[1] After reduction of the cyano group the resulting amines give access to a range of follow-up products (Fig. 1).

(*R*)-**1** 99% ee

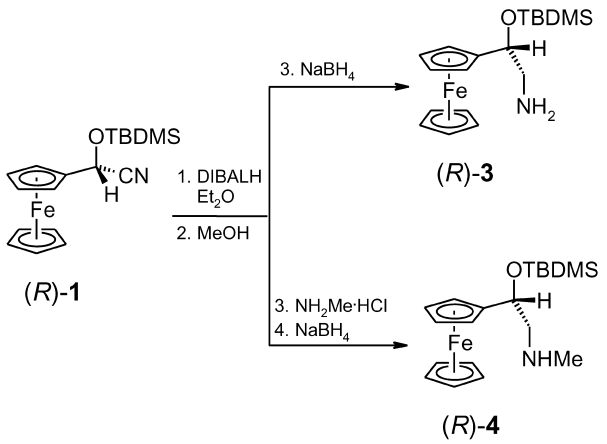
(*R*,*R*)-**2** 96% ee 91% de

Figure 1.

To date, many ferrocene derivatives have been synthesized being bridged by carbon chains,[2] diamides,[3] amines[4] or crown ether type units. In the latter, advantage can be taken from the combination of the redox properties of the ferrocene moiety and the complexing ability of electron donating atoms present in the molecule tethers.[5] Therefore, such compounds were used for redox switched bonding[6] in electrochemical sensors[7] and for phase transfer catalysis.[8] Lately, chiral C_2-symmetric diferrocenyl amines and diamines[9] have been synthesized as well as a chiral crown ether containing ferrocenyldiphosphine ligand.[10] This compelled us to investigate the synthesis of novel coupled chiral ferrocene derivatives from **1** and **2**, the results of which are described in this paper.

2. Results and discussion

A modification of a reduction sequence for TBDMS-protected cyanohydrins published by Brussee and co-workers[11] has been applied to ferrocene derivative **1**. Consequently, cyanohydrin **1** was reduced by applying a fivefold excess of DIBALH. Unused reagent was then destroyed with dry methanol and further reduction of the intermediate imine was accomplished with $NaBH_4$ furnishing the desired product **3**. The protected chiral amino alcohol (*R*)-**3** was obtained in a yield of 67%. In a similar manner, with an additional transimination step involving the



(*R*)-**1**

Scheme 1.

Keywords: chiral ferrocene; ring-bridged ferrocenediamide; diferrocenyldiamine.

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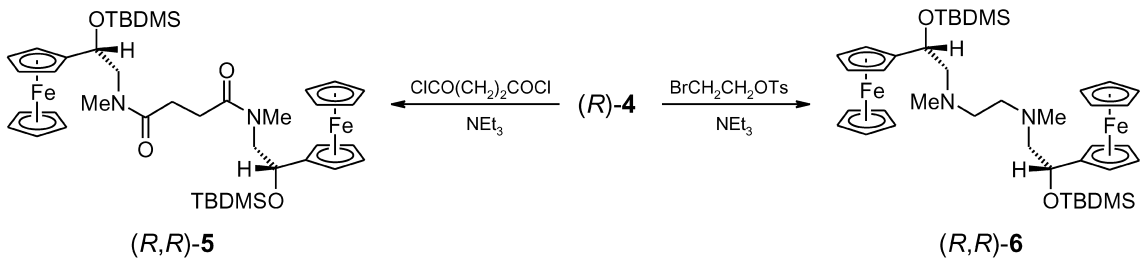


(*R*,*R*)-**5** (*R*,*R*)-**6**

Scheme 2.

addition of methylamine hydrochloride, the secondary amine **4** could also be prepared (Scheme 1).

Spurred by the interest in 'dimers', methods to couple two ferrocene moieties were investigated. A simple means to link two amine groups in compounds such as **4** is to use an acid dichloride which would then afford the corresponding diamide. Initial investigations into the linking of two ferrocenyl moieties began with succinyl dichloride and **4**. (*R*)-**4** was used to produce chiral 'dimer' (*R*,*R*)-**5** in 63% yield (Scheme 2).

Compound **6** was synthesized directly in a single reaction step from **4** with 2-bromoethyl tosylate. The tosyl group was displaced by the nucleophilic attack of a secondary nitrogen in a second molecule of **4** to give 'diamine dimer' **6**, which was afforded as the sole isolated product. Interestingly, while **6** showed a levorotatory specific rotation, for all other chiral compounds a dextrorotatory specific rotation was found.

The same reduction sequence which was employed to produce **3** was successfully applied in the preparation of diamine **7** (Scheme 3). (*rac*/*meso*)-**7** was obtained from (*rac*/*meso*)-**2**[1] in a yield of 55%. Unfortunately, when the synthesis of chiral (*R*,*R*)-**7** was attempted from (*R*,*R*)-**2** only a fair yield of 22% together with 17% unreacted starting material could be obtained. In general, the yields obtained with racemic starting material could not be realized with the chiral material, except in the case of (*R*,*R*)-**5**.

Due to the success experienced with the intermolecular coupling of two ferrocene molecules with succinyl dichloride, this approach was employed with diamine ferrocene derivative **7** in order to get the intramolecular ring-bridged compound **8**. To avoid polycondensation reactions which could yield in the corresponding polyamides, the ring-closure was carried out in very dilute solutions. Compound **7** was dissolved in an appropriate amount of CH_2Cl_2 and the same volume of solvent was used to dilute the acid dichloride reagent. These were simultaneously combined (dropwise) in the presence of an excess amount of NEt_3, this also having been diluted with CH_2Cl_2 beforehand.

It is interesting to note that although the diastereomers of the open chain 'dimers' (*rac*/*meso*)-**5** and (*rac*/*meso*)-**6** were not separable on preparative flash column chromatography by the methods examined, the diastereomers of the ring-bridged compound (*rac*/*meso*)-**8** were separable. This could be due to the fact that the diamide bridge provides more rigidity to the molecule making the difference between the properties of the racemic and the *meso* form more diverse. This, in turn, permitted the isolation of the individual diastereomers and therefore a d.e. of 100% was obtained for (*R*,*R*)-**8**.

3. Conclusions

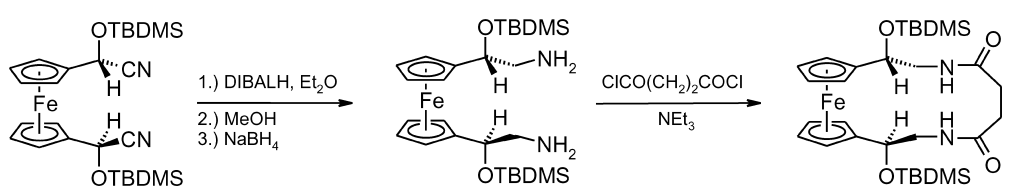
The enzymatic cyanhydrin reaction using the hydroxynitrile lyase from *H. brasiliensis* leading to enantiopure ferrocene cyanohydrin and to enantio- and diastereomerically pure 1,1′-biscyanohydrins proved to be an efficient access to starting materials which were transformed into dimers (*R*,*R*)-**5** and (*R*,*R*)-**6** where two ferrocenylaminoethyl moieties are linked together by a butanedioyl or an ethylene bridge, respectively.

The reaction of protected 1,1′-biscyanohydrin (*R*,*R*)-**2** with succinyl dichloride afforded diastereomerically homogeneous and enantiopure 1,1′-ring bridged (*R*,*R*)-**8**.

4. Experimental

4.1. General methods

Optical rotations were measured on a Perkin–Elmer



(*R*,*R*)-**2**
96% *e.e.*
91% *d.e.*

(*R*,*R*)-**7**

(*R*,*R*)-**8**
99% *e.e.*
100% *d.e.*

Scheme 3.

Polarimeter 341. Melting points (uncorrected) were determined in open capillaries using a Büchi 530. ^{1}H and ^{13}C NMR were recorded on either a Gemini 200 (Varian) or MSL 300 (Bruker). HETCOR, DEPT, COSY and HSQC experiments were carried out when required. $CDCl_3$ was used as solvent and as internal standard unless otherwise stated. Mass spectra (EI, 70 eV and ESI) were recorded on a KRATOS Profile HV-4 double focussing magnetic sector instrument equipped with direct insertion (DI) or with a MIRCOMASS TofSpec 2E (MALDI-TOF). Relative intensities are given in brackets. Chiral HPLC was performed with a JASCO system containing pump 880-PU, UV-detector 875-UV (detection at 238 nm unless otherwise stated) and HP ChemStation for LC A.06.03 (software) fitted with an HP Interface 35900E as AD converter. The chiral HPLC column used was Chiralcel OD-H (0.46×25 cm). GC-MS was determined with a HP 5890 series II plus chromatograph equipped with a HP 5 (25 m) column and a quadrupole mass selective detector. LC was performed on silica gel 60 (Merck) using mixtures of cyclohexane and EtOAc or chloroform and methanol as eluent. TLC was performed on silica gel 60 F254 aluminium plates (Merck), mixtures of cyclohexane and EtOAc or chloroform and methanol were used as eluent and compounds detected with UV (254 nm) and spraying with reagent A (10% H_2SO_4, 10% $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.8% $Ce(SO_4)_2\cdot 4H_2O$ in water). The TLC plates were then developed with a heat gun. Characterization of new compounds was done by ^{1}H NMR, ^{13}C NMR and HRMS.

4.2. General procedure A: DIBALH reduction

Under an atmosphere of argon, the starting material was dissolved in dry Et_2O, the solution cooled to −82°C (MeOH, liquid nitrogen bath) and DIBALH (1.0 M) added dropwise. After stirring at this temperature for a further 5 h, the reaction mixture was cooled to −95°C and abs. MeOH added. After a further 10 min, dry $NaBH_4$ was added in small portions. After 1 h at −75°C, the mixture was allowed to come to room temperature. Stirring was continued for additional 24 h and then the reaction mixture was poured into H_2O. NaOH was added to the aqueous phase until approximately pH 11 was reached and then extracted several times with EtOAc. The combined organic phases were dried with Na_2SO_4, filtered and the filtrate concentrated under reduced pressure. The resulting residue was purified by column chromatography (chloroform/methanol).

4.2.1. (+)-(*R*)-[2-Amino-1-(*t*-butyldimethylsilyloxy)-ethyl]ferrocene (3). The title compound was prepared according to general procedure A ((*R*)-**1**[1] 0.34 g, 0.96 mmol, Et_2O 20 mL; DIBALH 4.8 mL (1.0 M in hexane), 4.8 mmol; $NaBH_4$ 73 mg, 1.9 mmol; MeOH 5.4 mL, 0.13 mol). Yield: 67% (0.23 g) orange oil, R_f=0.35 ($CHCl_3$/MeOH=10:1), $[\alpha]_D^{20}$=+15 (*c* 0.994, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=0.02 (s, 3H); 0.08 (s, 3H); 0.91 (s, 9H); 1.43 (br s, 2H); 2.80–3.11 (m, 2H); 4.11 (m, 9H); 4.47 (m, *J*=3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=−4.2, −4.1, 18.2, 26.0, 49.2, 65.7, 67.1, 67.8, 68.0, 68.6, 72.6, 90.3. MS (70 eV, EI): *m*/*z* (%): 359 (17) [M^+], 329 (100), 302 (3), 227 (21), 195 (14), 185 (6), 162 (24), 135 (9), 121 (23), 75 (47), 73 (56), 56 (17).

4.2.2. (+)-(*R*)-[1-(*t*-Butyldimethylsilyloxy)-2-methyl-aminoethyl]ferrocene (4). (*R*)-**1**[1] (0.57 g, 1.6 mmol) was dissolved in dry Et_2O (Et_2O 12 mL) under an atmosphere of argon and the solution cooled to −82°C (MeOH, liquid nitrogen bath). To this mixture, DIBALH (1.0 M in hexane, 8 mL, 8 mmol) was added and stirring continued for 5 h. After this time, the reaction mixture was cooled to −95°C and dry MeOH (8 mL, 0.2 mol) added. After a further 10 min, dry $NH_2CH_3\cdot HCl$ (1.08 g, 16 mmol) was added and the reaction mixture was allowed to come slowly to room temperature. Subsequently, after 3 h, the mixture was cooled (ice bath) to 0°C and dry $NaBH_4$ (0.18 g, 4.8 mmol) was added in small portions. After 10 min the ice bath was removed and the solution permitted to come to room temperature. Stirring was continued for additional 14 h and the reaction mixture was then poured into H_2O. NaOH was added to the aqueous phase until approximately pH 11 was reached and then extracted several times with EtOAc. The combined organic phases were dried with Na_2SO_4, filtered and the filtrate concentrated under reduced pressure. The resulting residue was purified by column chromatography (chloroform/methanol). Yield: 18% (0.11 g) orange oil. R_f=0.40 ($CHCl_3$/-MeOH=10:1); $[\alpha]_D^{20}$=+56 (*c* 0.152, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=−0.06 (s, 3H); 0.08 (s, 3H); 0.89 (s, 9H); 2.29 (br s, 1H); 2.52 (s, 3H); 2.98 (m, 2H); 4.14 (s, 9H); 4.70 (m, 1H); ^{13}C NMR ($CDCl_3$): δ=−4.1, −3.9, 18.4, 26.2, 36.4, 58.4, 66.3, 67.5, 68.1, 68.5, 68.9, 69.6, 90.1; MS (70 eV, EI): *m*/*z* (%): 373 (24) [M^+], 329 (100), 241 (15), 195 (8), 186 (6), 176 (11), 158 (5), 121 (13), 75 (41), 73 (29), 65 (1), 56 (7); HRMS: $[C_{19}H_{31}FeNOSi]^+$ calcd 373.1524, found 373.1551.

4.2.3. (+)-(*R*,*R*)-*N*,*N*′-Bis[2-ferrocenyl-2-(*t*-butyldimethylsilyloxy)ethyl]-*N*,*N*′-dimethyl-butanediamide (5). (*R*)-**4** (12 mg, 32 μmol) was dissolved in CH_2Cl_2 (1 mL) and NEt_3 (5 mg, 48 μmol) added. Subsequently, the reaction was cooled to 0°C (ice bath) and succinyl chloride (2.5 mg, 16 μmol) added. After 1 h water was then added to the reaction and this mixture was then extracted several times with CH_2Cl_2. The combined organic phases were then dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure and the resulting residue purified by column chromatography to afford the title compound. Yield: 63% (8.5 mg), orange oil. R_f=0.43 (cyclohexane/EtOAc=1:1); $[\alpha]_D^{20}$=+8.5 (*c* 0.226, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=−0.04 (s, 6H); 0.04 (s, 6H); 0.85 (s, 18H); 2.40–3.94 (m, 14H); 4.19 (m, 18H); 4.53–4.86 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.0, 18.2, 26.2, 56.6, 65.2, 66.1, 67.5, 68.1, 68.9, 69.0, 89.9, 164.3; HRMS: $[C_{42}H_{64}Fe_2N_2O_4Si_2+Na]^+$ calcd 851.3004, found 851.3043.

4.2.4. (*rac*/*meso*)-*N*,*N*′-Bis[2-ferrocenyl-2-(*t*-butyldimethylsilyloxy)ethyl]-*N*,*N*′-dimethyl-butanediamide (5). (*rac*)-**4** (23 mg, 62 μmol) was dissolved in CH_2Cl_2 (1 mL) and NEt_3 (9 mg, 92 μmol) added. Subsequently, the reaction was cooled to 0°C (ice bath) and succinyl chloride (5 mg, 30 μmol) added. After 1 h water was then added to the reaction and this mixture was then extracted several times with CH_2Cl_2. The combined organic phases were then dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure and the resulting

residue purified by column chromatography to afford the title compound. Yield: 58% (14.5 mg) orange oil. R_f=0.43 (cyclohexane/EtOAc=1:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=−0.05 (s, 6H); 0.04 (s, 6H); 0.90 (s, 18H); 2.59–3.92 (m, 14H); 4.22 (m, 18H); 4.61–4.88 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.0, 18.2, 26.1, 56.6, 65.2, 66.1, 67.5, 67.7, 68.0, 68.9, 69.0, 89.9, 164.3; HRMS: see (*R*,*R*)-**5**.

4.2.5. (−)-(*R*,*R*)-*N*,*N*′-Bis[2-ferrocenyl-2-(*t*-butyldimethylsilyloxy)ethyl]-*N*,*N*′-dimethyl-ethane-1,2-diamine (6). (*R*)-**4** (90 mg, 0.24 mmol) was dissolved in a mixture of CH_3CN (2 mL)/CH_2Cl_2 (1 mL) and NEt_3 (24 mg, 0.24 mmol) as well as 2-bromoethyl tosylate (this reagent was synthesized according to Ref. 12 NMR data were in accordance with Ref. 13) (39 mg, 0.14 mmol) were added. The mixture was heated for 22 h at 62°C. TLC confirmed that the reaction was complete and the mixture was concentrated under reduced pressure. The resulting residue was purified by column chromatography ($CHCl_3$/MeOH=100:1) to give the title compound. Yield: 35% (33 mg) orange oil. R_f=0.51 ($CHCl_3$/MeOH/NEt_3=90:10:1); $[\alpha]_D^{20}$=−176 (*c* 0.014, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=0.08 (s, 6H); 0.16 (s, 6H); 0.92 (s, 18H); 2.33 (s, 6H); 2.51–3.00 (m, 8H); 3.96–4.40 (m, 18H); 4.59 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.2, −3.5, 18.5, 26.3, 43.5, 57.0, 66.4, 66.9, 67.3, 67.6, 67.9, 92.6; HRMS: $[C_{40}H_{64}Fe_2N_2O_2Si_{2+}Na]^+$ calcd 795.3105, found 795.3038.

4.2.6. (*rac*/*meso*)-*N*,*N*′-Bis[2-ferrocenyl-2-(*t*-butyldimethylsilyloxy)ethyl]-*N*,*N*′-dimethyl-ethane-1,2-diamine (6). (*rac*)-**4** (0.35 g, 0.94 mmol) was dissolved in CH_3CN (10 mL) and NEt_3 (0.13 mL, 0.94 mmol) as well as 2-bromoethyl tosylate (144 mg, 0.52 mmol) were added. The mixture was heated at 60°C. Because TLC indicated that after 12 h starting material was still present, another portion of 2-bromoethyl tosylate (70 mg, 0.25 mmol) and NEt_3 (0.10 mL, 0.72 mmol) were added. After a further 20 h of heating the reaction mixture was concentrated under reduced pressure. The resulting residue was purified by column chromatography ($CHCl_3$/MeOH=100:1) to give the title compound. Yield: 75% (0.27 g), orange oil. R_f=0.51 ($CHCl_3$/MeOH/NEt_3=90:10:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=0.09 (s, 6H); 0.16 (s, 6H); 0.94 (s, 18H); 2.34 (s, 6H); 2.53–2.99 (m, 8H); 3.98–4.33 (m, 18H); 4.57 (t, *J*=5.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.2, −3.6, 18.4, 26.3, 43.6, 57.0, 66.4, 66.9, 67.3, 67.6, 67.8, 68.6, 68.7, 68.9, 92.7; HRMS: see (*R*,*R*)-**6**.

4.2.7. (+)-(*R*,*R*)-1,1′-Bis[2-amino-1-(*t*-butyldimethylsilyloxy)ethyl]ferrocene (7). The title compound was prepared by general procedure A ((*R*,*R*)-**2**[1] 1.00 g, 1.9 mmol; Et_2O 14 mL; DIBALH (1.0 M in hexane) 19 mL, 19 mmol; MeOH 8 mL, 0.2 mol; $NaBH_4$ 0.29 g, 7.6 mmol). Yield: 22% (0.226 g) orange oil, in addition, 17% (*R*,*R*)-**2** (0.167 g) was recovered. R_f=0.25 ($CHCl_3$/MeOH=5:1); $[\alpha]_D^{20}$=+32.5 (*c* 0.307, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=0.02 (s, 6H); 0.09 (s, 6H); 0.87 (s, 18H); 1.55 (br s, 4H); 2.86 (dd, *J*=6.5, 12.8 Hz, 2H); 3.03 (dd, *J*=3.4, 13.0 Hz, 2H); 4.12 (m, 8H); 4.50 (dd, *J*=3.1, 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.0, −3.9, 18.4, 26.1, 49.0, 66.6, 68.3, 68.8, 69.1, 72.1, 90.3.

4.2.8. (*rac*/*meso*)-1,1′-Bis[2-amino-1-(*t*-butyldimethylsilyloxy)ethyl]ferrocene (7). The title compound was prepared by general procedure A ((*rac*/*meso*)-**2**[1] 0.83 g, 1.6 mmol; Et_2O 12 mL; DIBALH (1.0 M in hexane) 16 mL, 16 mmol; MeOH 9 mL, 0.2 mol; $NaBH_4$ 0.24 g, 6.4 mmol). Yield: 55% (0.465 g) orange oil. R_f=0.25 ($CHCl_3$/MeOH=5:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=0.01 (s, 6H); 0.08 (s, 6H); 0.88 (s, 18H); 1.52 (br s, 4H); 2.87 (dd, *J*=6.6, 12.7 Hz, 2H); 3.04 (dd, *J*=3.5, 13.2 Hz, 2H); 4.10 (m, 8H); 4.49 (dd, *J*=3.1, 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.0, −3.9, 18.4, 26.1, 49.4, 66.4, 66.6, 68.3, 68.7, 68.8, 69.0, 72.7, 90.6.

4.2.9. (+)-(*R*,*R*)-*N*,*N*′-[2,2′-(Ferrocene-1,1′-diyl)-2,2′-di(*t*-butyldimethylsilyloxy)]diethyl-butanediamide (8). At room temperature with stirring CH_2Cl_2 (40 mL) was placed in a reaction vessel and NEt_3 (77 mg, 0.76 mmol) added. (*R*,*R*)-**7** (0.10 g, 0.19 mmol) and succinyl chloride (29 mg, 0.19 mmol) were separately dissolved in CH_2Cl_2 (5 mL per compound) and, via syringe, slowly added simultaneously to the NEt_3 solution. After 20 h at room temperature water was added to the reaction and the mixture extracted with CH_2Cl_2 several times. The combined organic phases were dried over Na_2SO_4, filtered and the filtrate concentrated under reduced pressure to give a crude orange residue. After further purification by column chromatography ($CHCl_3$/MeOH=100:1), the title compound was isolated as an orange crystalline solid. Yield: 35% (40 mg), R_f=0.23 (cyclohexane/EtOAc=1:1); mp: decomposition above 210°C; $[\alpha]_D^{20}$=+124 (*c* 0.246, $CHCl_3$); HPLC: OD-H; *n*-heptane:2-propanol=99.5:0.5, *v*=0.50 mL min^{-1}, rt, UV 238 nm, e.e.: 99% R_t(*R*,*R*)=22.1 min R_t(*S*,*S*)=34.2 min; ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=−0.14 (s, 6H); −0.02 (s, 6H); 0.78 (s, 18H); 2.34–2.99 (m, 4H); 3.33 (dd, *J*=4.4, 13.2 Hz, 2H); 3.78 (s, 2H); 3.96 (s, 1H); 4.08 (m, 3H); 4.30 (dd, *J*=8.8, 13.2 Hz, 2H); 4.42 (s, 2H); 4.55 (d, *J*=4.0 Hz, 2H); 6.49 (br d, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.9, −4.3, 18.2, 25.7, 25.9, 34.0, 48.6, 67.0, 69.0, 69.7, 69.9, 70.9, 90.7, 172.1; HRMS: $[C_{30}H_{50}FeN_2O_4Si_2]^+$ calcd 614.2659, found 614.2704.

4.2.10. (*rac*)-*N*,*N*′-[2,2′-(Ferrocene-1,1′-diyl)-2,2′-di(*t*-butyldimethylsilyloxy)]diethyl-butanediamide (8). At room temperature with stirring CH_2Cl_2 (60 mL) was placed in a reaction vessel and pyridine (45 mg, 0.57 mmol) added. (*rac*/*meso*)-**7** (0.10 g, 0.19 mmol) and succinyl chloride (29 mg, 0.19 mmol) were separately dissolved in CH_2Cl_2 (60 mL per compound) and, via dropping funnel, slowly added over 70 min simultaneously to the pyridine solution. After 6 h at room temperature a solution of $NaHCO_3$ was added to the reaction and the mixture extracted with CH_2Cl_2 several times. The combined organic phases were dried over Na_2SO_4, filtered and the filtrate concentrated under reduced pressure to give a yellow orange residue. After further purification by column chromatography ($CHCl_3$/MeOH=100:1), the title compound was isolated as a yellow solid. Yield: 10% (12 mg) mp: decomposition above 250°C. R_f=0.23 (cyclohexane/EtOAc=1:1); ^{1}H NMR (200 MHz, $CDCl_3$, 25°, TMS): δ=−0.01 (s, 6H); 0.05 (s, 6H); 0.85 (m, 18H); 2.43–2.90 (m, 4H); 3.34 (dd, *J*=4.0, 13.2 Hz, 2H); 3.88–4.67 (m, 12H); 6.22 (br d, 2H); ^{13}C NMR ($CDCl_3$): δ=−4.9, −4.3, 18.2, 25.9, 26.0, 34.0, 48.7, 67.1, 69.1, 69.7, 69.9, 70.9, 90.8, 172.2; HRMS: see (*R*,*R*)-**8**.

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