Synthesis of a Chiral Aryl-Ferrocenyl Ligand, by Intramolecular Coupling to a Biaryl-Related Lactone†

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Introduction

Planar chiral ferrocenes constitute a rapidly growing class of efficient ligands[1]—they can be prepared in a stereochemically pure form by a range of useful methods[2] and have found numerous applications in stereoselective synthesis,[3] even on an industrial scale.[4] In a similar way, axially chiral biaryls also provide effective stereochemical discrimination.[5] Very little is known, by contrast, about the combination of these two elements of chirality. Such molecules equipped with both planar and axial chirality have indeed been described, though not in the form of a "ferrocenyl biaryl", but connecting a ferrocene unit to a separate binaphthyl portion, via a flexible three-atom chain.[6] Aryl-ferrocenes of type **1**, being planar chiral and, depending on the sizes of the substituents R and D, potentially axially chiral due to the hindered rotation about the "biaryl" bond, or, at least, subject to a thermodynamically controlled preferential axial conformation, may provide a conceptionally novel three-dimensional environment. With their two donor groups, they could serve as a new type of bidentate chiral ligands or catalysts in asymmetric synthesis. Similar aryl-ferrocenes, yet with no more than one ortho substituent on the ferrocene or on the phenyl part, have already been described in the literature.[7,8] For a first preparation of stereochemically more hindered representatives (i.e., with a substituent D different from hydrogen), we envisaged the use of the "lactone method", an efficient concept for the regio- and stereoselective construction of even highly hindered "normal" biaryl systems,[9] but now, for the first time, to be applied to the synthesis and ring cleavage of ferrocenyl-aryl lactones. Here, we describe the synthesis of **2**, the first "parent compound" of this new class of potential bidentate ligands, using a modified lactone strategy (Figure 1).

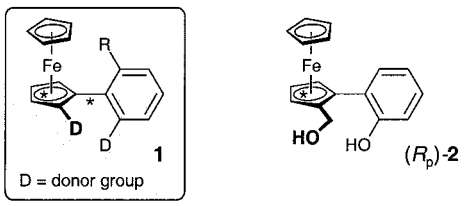
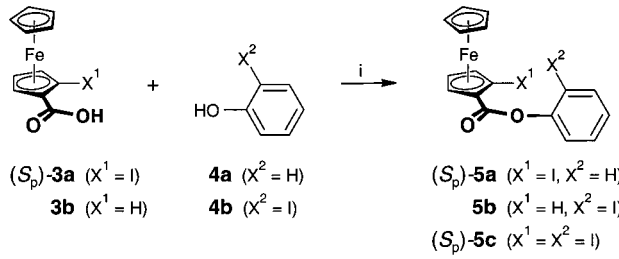


Figure 1. New chiral aryl-ferrocenyl ligands.

Scheme 1[a]



[a] Reagents and conditions: (i) DCC, DMAP, CH_2Cl_2, rt, 24 h, 67−83%.

Results and Discussion

For the intramolecular coupling, the two aromatic portions were connected via an ester bridge to give compounds **5**, with an iodine atom in the ortho position(s) of the ferrocene part and/or in the phenolic portion (Scheme 1). For **5a** and **5c**, the chirality on the ferrocene part originated from the known enantiomerically pure (S_p)-2-iodoferrocene carboxylic acid (S_p)-**3a**, which was obtained by diastereoselective ortho-lithiation of a chiral oxazoline-substituted ferrocene, according to a procedure by Bolm.[10]

Further structural evidence of the esters (S_p)-**5a** and (S_p)-**5c** was obtained from X-ray structure analyses, which independently confirmed, in both cases, the absolute configuration of 2-iodoferrocene carboxylic acid (S_p)-**3a** as established previously.[10] Compound (S_p)-**5a** crystallizes with two molecules in the asymmetric unit, but for reasons of clarity, only the conformer with staggered cyclopentadienyl rings is shown in Figure 2, not the eclipsed one.

For the cyclization reaction to the ferrocenyl-aryl lactone (R_p)-**6**, various conditions (methods A−G) were tested (Scheme 2). The results are summarized in Table 1.

Initial attempts to cyclize iodo ester (S_p)-**5a** with $Pd(OAc)_2$ as the catalyst (method A), as previously success-

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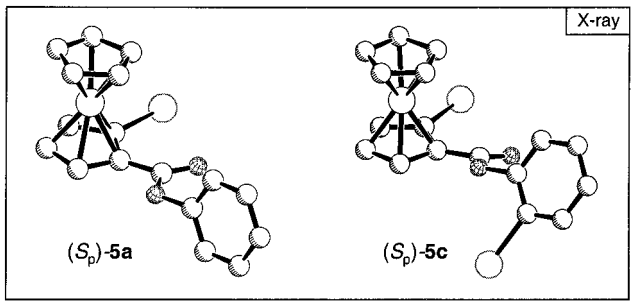


Figure 2. Molecular structures of ferrocenyl esters (S_p)-**5a** and (S_p)-**5c** in the crystal; all hydrogen atoms are omitted for clarity.

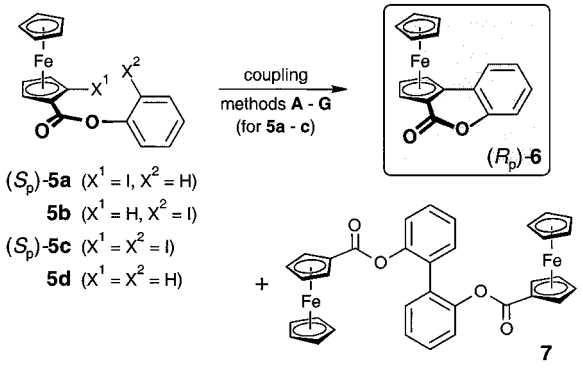
Table 1. Intramolecular Coupling of Halogen Esters 5 under Different Conditions

substrate	method	(S_p)-**5a** (%)	**5b** (%)	(S_p)-**5c** (%)	**5d** (%)	(R_p)-**6** (%)	**7** (%)
(S_p)-**5a**	A	18			5	0	
(S_p)-**5a**	B	72			4	0	
(S_p)-**5a**	C	0			70	0	
5b	D		8		24	0	
(S_p)-**5c**	E	0	0	0	37	0	0
(S_p)-**5c**	F	22	0	0	18	10	10
(S_p)-**5c**	G	0	0	0	26	47	23

fully performed, e.g., in the synthesis of six-membered naphthyl phenyl lactones,[11] failed, giving the halogen-free ester **5d**[12] as the only isolable product, besides decomposition (Table 1). Even under Jeffery conditions,[13] with a tetraalkylammonium salt additive (method B), no coupling product was observed: whereas at 70−90 °C almost no reaction took place, only the undesired side product **5d** was formed at higher temperature, in particular when using $PdCl_2(PPh_3)_2$ as the catalyst and with $NaHCO_3$ as the base (method C). Even with the iodine substituent located in the phenolic part of **5**, i.e., when starting with the (hence achiral) ester **5b** (method D), the only new product formed, was again **5d**, with a very low overall recovery.

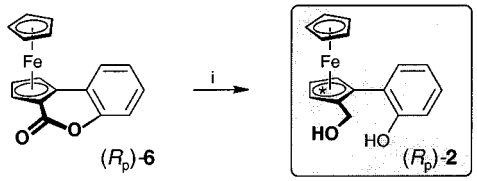
The same unsatisfying formation of the halogen-free ester **5d** as the only detectable product was attained with the diiodo ester (S_p)-**5c**, upon attempted indium-promoted reductive coupling[14] (method E). Finally successful was the nickel(0)-mediated coupling[15] of (S_p)-**5c**, using conditions developed by Nicolaou[16] (method **F**): Besides again partial—or even total—hydrodehalogenation to give **5a** and **5d** (together inasmuch as 40%), the desired lactone (R_p)-**6** was obtained for the first time, still in only 10% yield. An interesting new side product was the—again halogen-free and thus achiral—biaryl **7** resulting from an intermolecular homocoupling in the phenolic part. After this first break-through, even better results were achieved using the Lipshutz biaryl coupling protocol[17] (method **G**), which now gave the lactone (R_p)-**6** as the main product, inasmuch as 47% yield, besides still significant yields in **5d** and the "dimer" **7**.[18]

Scheme 2



method	conditions
A	$Pd(OAc)_2$, PPh_3, NaOAc, DMA, 130 °C, 2 h
B	$Pd(OAc)_2$, PPh_3, NaOAc, *n*-Bu_4NI, DMF, 70 °C → 90 °C, 5 h
C	$PdCl_2(PPh_3)_2$, $NaHCO_3$, *n*-Bu_4NBr, DMF, 105 °C, 8 h
D	$Pd(OAc)_2$, PPh_3, NaOAc, *n*-Bu_4NI, DMF, 105 °C, 8 h
E	In, DMF, reflux, 1 h
F	$Ni(PPh_3)_2Cl_2$, PPh_3, Zn, DMF, 70 °C, 21 h
G	$Ni(PPh_3)_2Cl_2$, PPh_3, *n*-BuLi, DMF, 70 °C, 21 h

Scheme 3[a]



[a] Reagents and conditions: (i) $LiAlH_4$, THF, rt, 1 h, 91% (axial configuration arbitrary).

With the crucial *C*,*C*-bond constructed, the preparation of the target molecule (R_p)-**2** was easily attained by reductive ring cleavage of (R_p)-**6** using $LiAlH_4$ (Scheme 3).

In summary, the successful synthesis of a chiral aryl-ferrocenyl has been achieved by a new modified version of the "lactone method", involving an intramolecular nickel(0)-assisted reductive *C*,*C*-coupling. The ring cleavage product of the intermediate lactone (R_p)-**6**, the diol and thus potentially bidentate ligand (R_p)-**2**, should, as such, be configurationally unstable at the additional biaryl-related axis, but might adopt a defined preferential rigid orientation at the biaryl axis when complexed to a metal center.[19,20] The possible use of (R_p)-**2** in asymmetric synthesis and the preparation of configurationally stable (since even more hindered) analogues are currently under investigation.

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Experimental Section

General Methods. Source of compounds: (S_p)-2-iodoferrocene carboxylic acid (S_p)-**3a** was prepared according to a known procedure.[10] Solvents were dried and purified according to standard methods. All reactions were carried out with dry glassware under an argon atmosphere. Column chromatography was performed on silica gel 63−200 μm (Merck). For general characterization methods, see ref 21.

General Procedure for the Formation of Esters 5. To a solution of 1.00 equiv of the corresponding acid **3** and 1.50 equiv of the respective alcohol **4** in dichloromethane (11 mL per mmol of acid) were added 1.50 equiv DCC and a catalytic amount of 4-(dimethylamino)pyridine. After being stirred at room temperature for 24 h, the precipitate was filtered off. The solution was concentrated and the residue chromatographed on silica (petroleum ether/diethyl ether 3:1).

Phenyl (S_p)-2-Iodoferrocenecarboxylate [(S_p)-5a]. Esterification of (S_p)-**3a** (100 mg, 281 μmol) with phenol **4a** (39.6 mg, 421 μmol) gave orange-brown cubes of (S_p)-**5a** (80.7 mg, 187 μmol, 67%) after crystallization from diethyl ether/petroleum ether: mp 84−85 °C; $[\alpha]^{23}_D = -62.6$ (c = 0.48, $CHCl_3$); CD (EtOH) $\Delta\epsilon_{198}$ −28.8, $\Delta\epsilon_{222}$ +2.0, $\Delta\epsilon_{235}$ −2.7, $\Delta\epsilon_{274}$ +5.6, $\Delta\epsilon_{305}$ −2.9; IR (KBr) $\tilde{\nu}$ 3060, 1710, 1570 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.32 (s, 5H), 4.55 (dd, ^3J = 2.4 Hz, ^3J = 2.8 Hz, 1H), 4.80 (dd, ^3J = 2.4 Hz, ^4J = 1.5 Hz, 1H), 5.04 (dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 1H), 7.19−7.31 (m, 3H), 7.38−7.49 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 39.82, 69.94, 70.69, 72.86, 72.96, 80.41, 121.7, 125.7, 129.4, 150.6, 168.9; MS (EI) m/z 432 (100) [M^+], 339 (89) [$M^+ - C_6H_5O$], 311 (33) [339 − CO], 306 (8) [433 − I], 214 (59), 121 (50) [$C_5H_5Fe^+$]. Anal. Calcd for $C_{17}H_{13}FeIO_2$: C, 47.26; H, 3.03. Found: C, 47.28; H, 2.89.

2-Iodophenyl Ferrocenecarboxylate (5b). Esterification of **3b** (400 mg, 1.74 mmol) with phenol **4b** (574 mg, 2.61 mmol) gave **5b** (625 mg, 1.45 mmol, 83%) as orange-brown crystals from dichloromethane/petroleum ether: mp 135.5−136 °C; IR (KBr) $\tilde{\nu}$ 3075, 1710, 1560 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.36 (s, 5H), 4.53 (pseudo-t, J = 2.0 Hz, 2H), 5.03 (pseudo-t, J = 2.0 Hz, 2H), 6.99 (ddd, ^3J = 7.3 Hz, ^3J = 8.9 Hz, ^4J = 1.5 Hz, 1H), 7.24 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H), 7.40 (ddd, ^3J = 7.3 Hz, ^3J = 8.9 Hz, ^4J = 1.5 Hz, 1H), 7.88 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 69.90, 70.13, 70.84, 71.98, 89.75, 123.2, 127.2, 129.2, 139.4, 151.1, 169.5; MS (EI) m/z 432 (100) [M^+], 306 (3) [433 − I], 213 (93) [$M^+ - C_6H_4IO$], 185 (26) [213 − CO], 121 (12) [$C_5H_5Fe^+$]. Anal. Calcd for $C_{17}H_{13}FeIO_2$: C, 47.26; H, 3.03. Found: C, 47.17; H, 3.15.

2′-Iodophenyl (S_p)-2-Iodoferrocenecarboxylate [(S_p)-5c]. Esterification of (S_p)-**3a** (164 mg, 461 μmol) with phenol **4b** (152 mg, 691 μmol) gave orange-brown crystals (214 mg, 384 μmol, 83%) from diethyl ether/petroleum ether: mp 150 °C; $[\alpha]^{23}_D = -19.7$ (c = 0.43, $CHCl_3$); CD (EtOH) $\Delta\epsilon_{202}$ −17.4, $\Delta\epsilon_{272}$ +4.0, $\Delta\epsilon_{304}$ −3.3; IR (KBr) $\tilde{\nu}$ 3080, 1720, 1555 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 4.38 (s, 5H), 4.57 (dd, ^3J = 2.8 Hz, ^3J = 2.8 Hz, 1H), 4.83 (dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 1H), 5.15 (dd, ^3J = 2.8 Hz, ^4J = 1.5 Hz, 1H), 7.00 (td, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1H), 7.27 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz, 1H), 7.40 (td, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1H), 7.88 (dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 39.89, 69.79, 70.98, 72.92, 73.17, 80.40, 89.68, 123.4, 127.4, 129.3, 139.5, 150.9, 168.2; MS (EI) m/z 558 (100) [M^+], 432 (10) [559 − I], 340 (26) [559 − C_6H_4IO], 339 (61) [$M^+ - C_6H_4IO$], 311 (11) [339 − CO], 212 (42) [339 − I], 121 (7) [$C_5H_5Fe^+$]. Anal. Calcd for $C_{17}H_{12}FeI_2O_2$: C, 36.30; H, 2.17. Found: C, 36.34; H, 1.95.

Coupling Experiments for the Synthesis of Ferrocenyl Lactone (R_p)-6. Method A. A solution of ester (S_p)-**5a** (14.2 mg, 32.9 μmol), $Pd(OAc)_2$ (0.74 mg, 3.30 μmol), PPh_3 (3.45 mg, 13.2 μmol), and NaOAc (5.40 mg, 65.8 μmol) in dimethylacetamide (DMA, 2 mL) was stirred at 130 °C for 2 h. After removal of the solvent, the residue was chromatographed (petroleum ether/diethyl ether 3:1) to give a mixture of starting material (S_p)-**5a** (2.57 mg, 5.95 μmol, 18%) and phenyl ferrocenecarboxylate (**5d**) (0.51 mg, 1.67 μmol, 5%), which was spectroscopically identical to material previously obtained.[12]

Method B. To a solution of NaOAc (19.0 mg, 232 μmol) and n-Bu_4NI (34.2 mg, 92.6 μmol) in DMF (2 mL) were added the ester (S_p)-**5a** (40.0 mg, 92.6 μmol), PPh_3 (4.86 mg, 18.5 μmol), and $Pd(OAc)_2$ (2.08 mg, 9.27 μmol), and the mixture was stirred at 70 °C for 3 h and then at 90 °C for further 2 h. After removal of the solvent, the residue was chromatographed (petroleum ether/diethyl ether 3:1) to give a mixture of starting material (S_p)-**5a** (28.7 mg, 66.4 μmol, 72%) and ester **5d** (1.07 mg, 3.50 μmol, 4%).

Method C. A solution of ferrocenyl ester (S_p)-**5a** (10.0 mg, 23.1 μmol), $Pd(PPh_3)_2Cl_2$ (3.24 mg, 4.62 μmol), $NaHCO_3$ (3.88 mg, 46.2 μmol), n-Bu_4NBr (7.45 mg, 23.1 μmol), and molecular sieves 4 Å (5.00 mg, crushed) in DMF (2 mL) was stirred for 8 h at 105 °C. After the solution was cooled to room temperature, the solvent was removed, and the residue was purified by column filtration (petroleum ether/diethyl ether 1:1) to give ester **5d** (4.92 mg, 16.1 μmol, 70%).

Method D. A mixture of ferrocenyl ester **5b** (10.0 mg, 23.1 μmol), $Pd(OAc)_2$ (1.04 mg, 4.63 μmol), PPh_3 (2.42 mg, 9.23 μmol), NaOAc (4.74 mg, 57.8 μmol), and n-Bu_4NI (8.53 mg, 23.1 μmol) was dissolved in DMF (2 mL) and stirred at 105 °C. After 8 h, the solvent was removed and the residue was purified by column filtration (petroleum ether/diethyl ether 1:1) to give a mixture containing esters **5b** (0.84 mg, 1.94 μmol, 8%) and **5d** (1.71 mg, 5.59 μmol, 24%).

Method E. To a solution of (S_p)-**5c** (100 mg, 179 μmol) in DMF (1 mL) was added indium powder (30.9 mg, 269 μmol). After the mixture was refluxed for 70 min and cooled to room temperature, diethyl ether (30 mL) was added and the mixture was extracted with 5 × 10 mL of water. The organic phase was dried (Na_2SO_4) and the solvent evaporated. The oily residue was purified by column filtration (petroleum ether/diethyl ether 1:1) to give a complex product mixture containing ester **5d** (ca. 20.3 mg, 66.3 μmol, 37%).

Method F. A mixture of $Ni(PPh_3)_2Cl_2$ (84.4 mg, 129 μmol) and PPh_3 (67.7 mg, 258 μmol) in DMF (4 mL) was heated to 55 °C. Zinc dust (8.44 mg, 129 μmol) and a solution of ester (S_p)-**5c** (40.0 mg, 71.7 μmol) in DMF (5 mL) were added, and the reaction was stirred at 70 °C for 21 h. After cooling to room temperature and addition of 15 mL of a saturated NH_4Cl solution, the mixture was extracted with ethyl acetate (4 × 10 mL). The combined organic extracts were washed with water (15 mL) and brine (15 mL) and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed (petroleum ether/diethyl ether 1:1). Besides a mixture of esters **5a** (6.96 mg, 16.1 μmol, 22%) and **5d** (3.86 mg, 12.6 μmol, 18%), the desired lactone (R_p)-**6** (orange-brown colored oil, 2.10 mg, 6.90 μmol, 10%) and the homocoupled side product **7** (orange colored crystals from chloroform/petroleum ether, 2.09 mg, 3.43 μmol, 10%) were isolated.

(R_p)-Benzo[*b*]ferroceno[*d*]pyran-6-one [(R_p)-6]: $[\alpha]^{23}_D = +150.2$ (c = 0.09, $CHCl_3$); CD (EtOH) $\Delta\epsilon_{198}$ +17.6, $\Delta\epsilon_{207}$ +4.2, $\Delta\epsilon_{211}$ +6.4, $\Delta\epsilon_{222}$ −13.0, $\Delta\epsilon_{234}$ −1.2, $\Delta\epsilon_{246}$ −10.2, $\Delta\epsilon_{275}$ +8.7, $\Delta\epsilon_{315}$ −2.1; IR (KBr) $\tilde{\nu}$ 3070, 1720, 1595 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.07 (s, 5H), 4.65 (dd, ^3J = 2.6 Hz, ^3J = 2.6 Hz, 1H), 5.15 (dd, ^3J = 2.6 Hz, ^4J = 1.2 Hz, 1H), 5.19 (dd, ^3J = 2.6 Hz, ^4J = 1.1 Hz, 1H), 7.20 (ddd, ^3J = 7.6 Hz, ^3J = 8.6 Hz, ^4J = 1.2 Hz, 1H), 7.27 (dd, ^3J = 7.2 Hz, ^4J = 1.2 Hz, 1H), 7.32 (ddd, ^3J = 7.2 Hz, ^3J = 8.6 Hz, ^4J = 1.6 Hz, 1H), 7.60 (dd, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 64.48, 65.15, 68.30, 71.22, 72.92, 83.35, 117.2, 121.5, 123.0, 124.3, 127.9, 151.3, 167.4; MS (EI) m/z 304 (100) [M^+], 276 (60) [M^+ − CO], 202 (50), 121 (13) [$C_5H_5Fe^+$]. Anal. Calcd for $C_{17}H_{12}FeO_2$: C, 67.14; H, 3.98. Found: C, 67.33; H, 4.16.

1,1′-Biphenylen 2,2′-Di(ferrocenecarboxylate) (7): mp 194−195 °C; IR (KBr) $\tilde{\nu}$ 3080, 3055, 1710, 1560 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 3.96 (s, 10H), 4.40 (pseudo-t, J = 2.0 Hz, 4H), 4.84 (pseudo-t, J = 2.0 Hz, 4H), 7.29−7.39 (m, 4H), 7.41−7.49 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 69.87, 70.23, 70.44, 71.69, 122.7, 125.7, 129.0, 130.8, 131.5, 148.4, 170.0; MS (EI) m/z 610 (28) [M^+], 518 (6) [$M^+ - C_6H_4O$], 453 (6), 426 (8) [611−185], 361 (6), 305 (4) [$C_{17}H_{13}FeO_2^+$], 213 (100) [$C_{11}H_9FeO^+$], 185 (47) [$C_{10}H_9Fe^+$], 121 (12) [$C_5H_5Fe^+$]. Anal. Calcd for $C_{34}H_{26}Fe_2O_4$: C, 66.92; H, 4.29. Found: C, 66.78; H, 4.54.

Method G. To a solution of $Ni(PPh_3)_2Cl_2$ (131 mg, 200 μmol) and PPh_3 (105 mg, 400 μmol) in THF (5 mL) was added n-BuLi (160 μL, 400 μmol, 2.5 M in hexane) dropwise at −78 °C. The

(21) Bringmann, G.; Hinrichs, J.; Pabst, T.; Henschel, P.; Peters, K.; Peters, E.-M. *Synthesis* **2001**, 155.

mixture was allowed to slowly warm to room temperature, and then the solvent was removed in vacuo. The residue was dissolved in DMF (6 mL), ester (S_p)-**5c** (40.0 mg, 71.7 μmol) was added, and the reaction was stirred at 70 °C for 21 h. After removal of the solvent, column chromatography (petroleum ether/diethyl ether, 5:1 → 2:1) gave ester **5d** (5.66 mg, 18.5 μmol, 26%), ferrocenyl lactone (R_p)-**6** (10.3 mg, 33.9 μmol, 47%), and dimer **7** (5.01 mg, 8.21 μmol, 23%). An analytically pure sample of (R_p)-**6** was obtained by renewed chromatography (cyclohexane/ethyl acetate 4:1).

Reduction of (R_p)-6 To Give Ferrocenyl Ligand (R_p)-2. To a solution of (R_p)-**6** (14.9 mg, 49.0 μmol) in THF (8 mL) was added $LiAlH_4$ (3.72 mg, 98.0 μmol). After being stirred for 1 h at room temperature, the reaction mixture was hydrolyzed by careful addition of water (10 mL) and 2 N HCl (2 mL). The organic solvent was evaporated, and the aqueous residue was extracted with diethyl ether (4 × 10 mL). The combined organic extracts were washed with water (10 mL) and brine (10 mL) and dried (Na_2SO_4). After removal of the solvent, the crude product was purified by column chromatography (petroleum ether/diethyl ether 1:2) and crystallized from diethyl ether/petroleum ether, to give (R_p)-1-hydroxymethyl-2-(2′-hydroxyphenyl)ferrocene [(R_p)-**2**] (13.7 mg, 44.5 μmol, 91%) as orange-yellow crystals. Compound (R_p)-**2** was ca. 95% pure according to NMR analysis: mp 145−146 °C; $[\alpha]^{23}_D = -76.1$ ($c = 0.09$, $CHCl_3$); CD (EtOH): $\Delta\epsilon_{193}$ +36.3, $\Delta\epsilon_{210}$ −30.0; IR (KBr) $\tilde{\nu}$ 3330, 3070, 2955, 1600 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.27 (s, br, 5H), 4.32−4.62 (m, 5H), 6.91 (dd, $^3J = 7.5$ Hz, $^3J = 7.7$ Hz, 1H), 6.96 (d, $^3J = 7.7$ Hz, 1H), 7.23 (dd, $^3J = 7.2$ Hz, $^3J = 7.6$ Hz, 1H), 7.47 (d, $^3J = 7.2$ Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 59.75, 68.51, 69.65, 69.72, 69.99, 70.22, 70.24, 116.1, 120.2, 121.5, 128.8, 131.5, 153.9; MS (EI) m/z 308 (45) [M^+], 291 (21) [309 − H_2O], 290 (100) [$M^+ - H_2O$], 262 (30) [290 − CO], 260 (13) [290 − CH_2O], 225 (18), 224 (23), 169 (76) [290−121], 121 (16) [$C_5H_5Fe^+$]; HRMS calcd for $C_{17}H_{16}FeO_2$ 308.0500, found 308.0497.

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Supporting Information Available: ^{13}C NMR spectrum of compound (R_p)-**2**. X-ray crystallographic data for compounds (S_p)-**5a** and (S_p)-**5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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