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Synthesis of Optically Active Ferrocene Analogues of Salicylic Acid Derivatives and Rhodium(II)-Catalyzed Asymmetric Intramolecular C–H Insertion of α-Diazo β-Keto Esters Using New Chiral Carboxylato Ligands

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The ferrocene analogue of salicylic acid, 2-hydroxyferrocenecarboxylic acid was synthesized via monolithiation of ferrocene with *t*-butyllithium, and resolved to optically active forms. Optically active 2-hydroxyferrocenecarboxylic acid was converted to 1-hydroxyferrocenecarbaldehyde, ferrocene analogue of salicylaldehyde, and 2-alkoxyferrocenecarboxylic acids. The later compounds were used as chiral carboxylato ligands for the rhodium(II)-catalyzed asymmetric intramolecular C–H insertion of α-diazo β-keto esters (up to 42% ee).

Salicylic acid and its derivatives such as salicylaldehyde and salicylideneamines are a class of compounds important for coordination chemistry as chelating ligands. Although the synthesis of their ferrocene analogues has already been reported,[1] none of them has never been obtained as an optically active form to our knowledge. We believe that the optically active forms of this class of compounds carry a great potential as new chiral chelating ligands for asymmetric synthesis, because their metal complexes are expected to construct fairly rigid structure.

Results and Discussion

Racemic 2-hydroxyferrocenecarboxylic acid (**1**) was synthesized according to the procedure described in the literature[1] except that ferrocenylboronic acid was prepared via monolithiation of ferrocene with *t*-butyllithium in THF.[2] The optical resolution of **1** was carried out by successive recrystallizations with (*R*)- and (*S*)-1-phenylethylamine from acetone, giving (+)-**1** and (−)-**1** with maximum rotations of $[\alpha]_D^{20}$ ($CHCl_3$) −380° and +372°, respectively (Scheme 1). Exact enantiomeric purities and the relationship between the rotation and absolute configuration have not been determined yet.

The optically active ferrocene analogue of salicylaldehyde, (−)-2-hydroxyferrocenecarbaldehyde (**4**) was synthesized from (−)-**1** as shown in Scheme 2. Thus, hydroxyl and carboxyl groups of (−)-**1** were both alkylated with benzyl bromide (89%). The ester group of (−)-**2a** {$[\alpha]_D^{20}$ −80.9° (*c* 0.52, $CHCl_3$)} was converted to formyl group via lithium aluminum hydride reduction and manganese dioxide oxidation (86%). The hydrogenolysis of (+)-**3** {$[\alpha]_D^{20}$ +632° (*c* 0.52, $CHCl_3$)} gave (−)-**4** {53%, $[\alpha]_D^{20}$ −2155° (*c* 0.68, $CHCl_3$)}. The unusually large optical rotation value should be noted. An aggregated and higher-order structure may possibly be responsible for the large rotation value. The ferrocene analogue of *N*,*N'*-disalicylideneethylenediamine (H_2salen) **5** was prepared by the condensation of (−)-**4** with ethylenediamine (90%). Although the characteristics of metal complexes of **5** as chiral catalysts seem to be interesting, their isolation has not been so far successful owing to their instability against air oxidation.

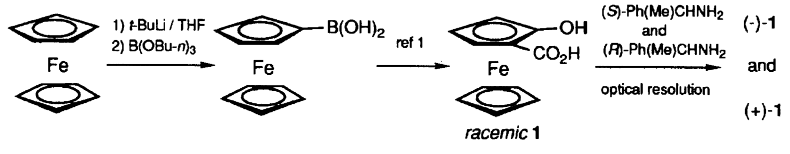
A series of 2-alkoxyferrocenecarboxylic acids **6a**—**d** was prepared by the saponification of 2-alkoxyferrocenecarboxylates **2** or obtained as by-products in the preparation of **2** (Scheme 3), and used as new chiral carboxylato ligands for the asymmetric intramolecular C–H insertion of α-diazo β-keto esters **8a**—**c** catalyzed by dirhodium(II) carboxylato complexes, leading to *trans*-3-alkyl-2-(methoxycarbonyl)cyclopentanones **9a**—**c** (Scheme 4).[3,4] Chiral rhodium(II) catalysts **7a**—**d** were prepared from **6** by carboxylato exchange reaction with $Rh_2(OAc)_4$ as described in the literature.[5] The asymmetric intramolecular C–H insertion of **8** was carried out in toluene at 0 °C in the presence of 1 mol% of the rhodium catalysts. Products **9** were converted to 3-alkylcyclopentanones **10a**—**c**, and their enantiomeric excesses were determined. Results are summarized in Table 1. Among chiral catalysts examined, **7c** was found to be the most effective catalyst for the reaction of **8a**, which completed within 10 min with an enantioselectivity of 42% ee. The reaction of other α-diazo-β-keto esters **8b,c** resulted in the formation of products with lower enantiomeric excesses. We are now engaged in the improvement of enentioselectivity in the intramolecular C–H insertion, and the search for the usage of ferrocene analogues of salicylideneamines for new catalytic asymmetric reactions are also of our current interest.

Experimental

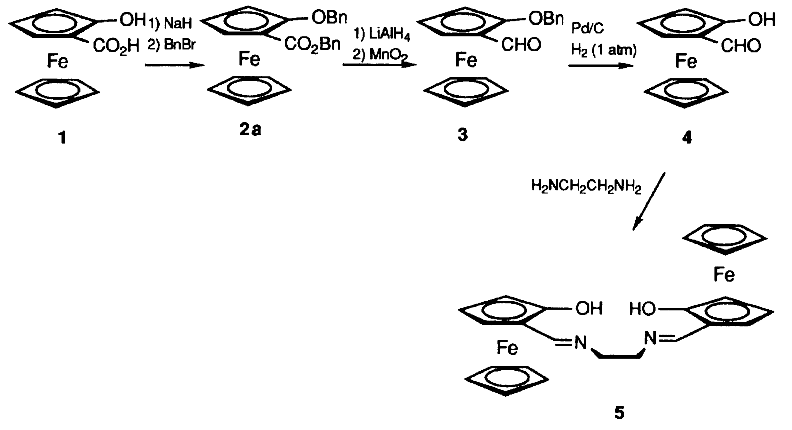
General. Optical rotations were recorded on a Perkin–Elmer 243 polarimeter. ^{1}H NMR spectra were measured with a Varian VXR-200 spectrometer.

Material. Solvents used for the reaction were dried over appropriate drying agents and distilled. Commercial tributyl borate was distilled before use. $Rh_2(OAc)_4\cdot 2MeOH$[6] and α-diazo β-keto esters **8**[4e] were prepared by the procedure in the literature. Other commercially available reagents were used without further purification.

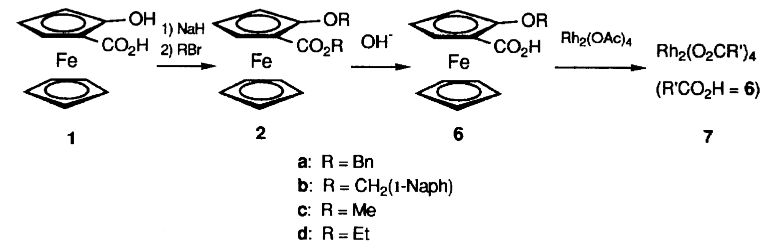
Ferrocenylboronic Acid. Under the nitrogen at-



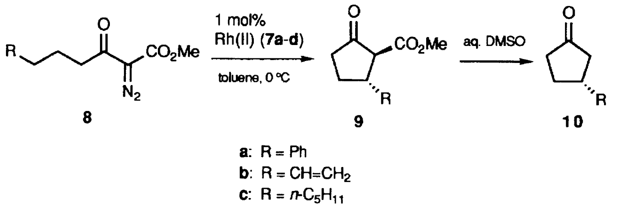
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

mosphere, 289 mL of 1.39 M *t*-butyllithium in hexane (402 mmol) was added to a solution of 75.8 g (408 mmol) of ferrocene in 380 mL of THF at 0 °C. After the mixture was stirred at room temperature for 2 h, 132 mL (489 mmol) of tributyl borate was added over 20 min at −70 °C. The mixture was allowed to warm to room temperature, stirred for 30 min, and then cooled to 0 °C before an addition of 5% hydrochloric acid and ether. The mixture was filtered through a pad of Celite. A filtrate was separated and extracted twice with ether. The combined organic layer were washed with brine, dried over sodium sulfate, and evaporated. A chromatography on alumina (3.5×25 cm, from benzene to methanol) gave 52 g (56%) of ferrocenylboronic acid as a red oil: R_f 0.6 (silica gel, benzene/ethyl acetate=1/1).

Optical Resolution of 2-Hydroxyferrocenecarboxylic Acid 1. Because hydroxyferrocenes are unstable against air oxidation, streams of argon were bubbled through solvents used in this procedure. To a solution of 13.54 g (55.0 mmol) of racemic **1** in 400 mL of acetone was added a solution of 6.73 g (55.5 mmol) of (−)-(*S*)-α-methylbenzylamine in 90 mL at 50 °C. During the mixture was slowly cooled to room temperature, needles of the diastereomeric complex were formed. The mixture was allowed to stand overnight, and the needles were collected, washed with cold acetone, and dried in vacuo, giving 9.68 g of the complex. This complex was treated with 15% aqueous sodium hydroxide solution. The mixture was washed twice with ether, acidified with 6 M hydrochloric acid ($M=\text{mol dm}^{-3}$), and extracted three times with ether. The combined ether extracts were dried over magnesium sulfate, and evaporated to give 6.30 g (25.6 mmol) of (−)-**1**: $[\alpha]_D^{20}$ −188° (*c* 0.51, $CHCl_3$). The same procedure was repeated for this (−)-**1** with 3.13 g (25.8 mmol) of (−)-(*S*)-α-methylbenzylamine and 170 mL of acetone to give 5.01 g (20.4 mmol) of (−)-**1**: $[\alpha]_D^{20}$ −288° (*c* 0.50, $CHCl_3$). The third resolution procedure (acetone 170 mL) gave 4.11 g (16.7 mmol) of (−)-**1**: $[\alpha]_D^{20}$ −350° (*c* 0.51, $CHCl_3$). The maximum rotation for (−)-**1** was obtained by the fourth resolution (acetone 170 mL): 2.05 g (16.9 mmol, 61% of theory): $[\alpha]_D^{20}$ −380° (*c* 0.50, $CHCl_3$): mp 130 °C (decomp). Further attempted optical resolution did not give higher value of optical rotation in a range of experimental error.

Table 1. Asymmetric C–H Insertion of α-Diazo β-Keto Esters **8** Catalyzed by Chiral Rhodium(II) Complex **7**

Diazo ester **8**	Rh(II) catalyst **7** (ligand **6**)	Time	Yield of **9**[a)] %	ee of **10** %	Config of **10**
8a (R=Ph)	**7a**[(−)-**6a**]	30 min	67	33[b)]	*R*[e)]
8a (R=Ph)	**7b**[(+)-**6b**]	2 h	63	16[b)]	*R*[e)]
8a (R=Ph)	**7c**[(−)-**6c**]	3 h	58	15[b)]	*R*[e)]
8a (R=Ph)	**7d**[(+)-**6d**]	10 min	66	42[b)]	*R*[e)]
8b (R=CH=CH$_2$)	**7a**[(−)-**6a**]	4 h	32	15[c)]	*R*[f)]
8c (R=*n*-C$_5$H$_{11}$)	**7a**[(−)-**6a**]	5 h	56	17[d)]	*R*[d)]

a) Isolated yield by PTLC. b) Determined by ^{13}C[^{1}H] NMR (50 MHz, CDCl$_3$) analysis of the ketal derived from **10a** and (−)-(2*R*,3*R*)-2,3-butanediol: H. Hiemstra and H. Wynberg, *Tetrahedron Lett.*, **25**, 2183 (1977). c) Determined by GLC analysis of **10b** with a chiral stationary phase column Chiraldex G-TA (30 m). d) Determined by the optical rotation value of **10c**. The maximum rotation has been reported to be $[\alpha]_D$ +117° for (*R*)-**10c** in Ref. 4e. e) Determined by the optical rotation value of **10a**: L. A. Paquette, J. P. Gilday, and C. S. Ra, *J. Am. Chem. Soc.*, **109**, 6858 (1987). f) Determined by the optical rotation value of **10b**. See Ref. 4e.

The mother liquors of the first and second resolution procedures were combined and treated with 15% aqueous sodium hydroxide solution. From the mixture was obtained 6.94 g (28.2 mmol) of (+)-**1** as described above. This crude (+)-**1** was treated with 3.46 g (28.6 mmol) of (+)-(*R*)-α-methylbenzylamine and 190 mL of acetone to give 4.87 g (19.8 mmol) of (+)-**1**: $[\alpha]_D^{20}$ +348° (*c* 0.55, CHCl$_3$). The next resolution (acetone 190 mL) gave 4.01 g (16.3 mmol, 59% of theory) of (+)-**1**: $[\alpha]_D^{20}$ +372° (*c* 0.53, CHCl$_3$); mp 135 °C (decomp). Further attempted optical resolution did not give higher value of optical rotation in a range of experimental error.

(−)-[Benzyl 2-Benzyloxyferrocenecarboxylate] (2a). To a suspension of 1.2 g (30 mmol) of sodium hydride (60% in mineral oil), washed with hexane, in 50 mL of dimethyl sulfoxide was slowly added 3.02 g (12.3 mmol) of (−)-**1** at room temperature. The mixture was stirred at room temperature for 40 min, and 3.3 mL (27 mmol) of benzyl bromide was slowly added. After 1 h the reaction was quenched by an addition of water. The mixture was acidified with 10% hydrochloric acid, and extracted six times with ether. The combined ether extracts were washed three times with water, dried over magnesium sulfate, and evaporated. A chromatography on silica gel (3×20 cm, hexane/ethyl acetate=10/1) gave 4.63 g (89%) of (−)-**2a** as a red oil: *R*f 0.5 (silica gel, hexane/ethyl acetate=5/1); $[\alpha]_D^{20}$ −80.9° (*c* 0.68, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ=4.07 (m, 1H), 4.12 (s, 5H), 4.28 (m, 1H), 4.59 (m, 1H), 4.99 (AB$_q$, J_{AB}=11.7 Hz, $\Delta\delta$=11.8 Hz, 2H), 5.32 (s, 2H), 7.3—7.5 (m, 10H). Anal. Calcd for C$_{25}$H$_{22}$FeO$_3$: C, 70.4; H, 5.20%. Found: C, 70.63; H, 5.25%.

(−)-[1-Naphthylmethyl 2-(1-Naphthylmethoxy)-ferrocenecarboxylate] (2b). Prepared from 1.19 g (4.84 mmol) of (−)-**1** and 2.03 g (11.5 mmol) of 1-(chloromethyl)-naphthalene as described above in a yield of 29%: red oil; *R*f 0.4 (silica gel, hexane/ethyl acetate=5/1); $[\alpha]_D^{20}$ −45.1° (*c* 0.62, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ=3.93 (s, 5H), 4.10 (m, 1H), 4.36 (m, 1H), 4.57 (m, 1H), 5.40 (AB$_q$, J_{AB}=12.0 Hz, $\Delta\delta$=8.0 Hz, 2H), 5.75 (s, 2H), 7.26—8.17 (m, 14H). Anal. Calcd for C$_{33}$H$_{26}$FeO$_3$: C, 75.30; H, 4.98%. Found: C, 74.79; H, 5.00%.

(−)-[Methyl 2-Methoxyferrocenecarboxylate] (2c). Prepared from 230 mg (0.935 mmol) of (−)-**1** and 140 μL (2.25 mmol) of methyl iodide as described above in a yield of 91%: red oil; *R*f 0.6 (silica gel, hexane/ethyl acetate=2/1); $[\alpha]_D^{20}$ −291° (*c* 0.63, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ=3.78 (s, 3H), 3.84 (s, 3H), 4.07 (t, *J*=2.8 Hz, 1H), 4.24 (s, 5H), 4.30 (m, 1H), 4.50 (m, 1H). Anal. Calcd for C$_{13}$H$_{14}$FeO$_3$: C, 56.97; H, 5.15%. Found: C, 56.82; H, 5.21%.

(−)-[Ethyl 2-Ethoxyferrocenecarboxylate] (2d). Prepared from 450 mg (1.83 mmol) of (−)-**1** and 260 mg (6.5 mmol) of ethyl bromide as described above in a yield of 23%: red oil; *R*f 0.8 (silica gel, hexane/ethyl acetate=2/1); $[\alpha]_D^{20}$ −213° (*c* 0.59, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ=1.36 (t, *J*=7.1 Hz, 3H), 1.43 (t, *J*=7.2 Hz, 3H), 3.83—4.06 (m, 2H), 4.05 (t, *J*=2.7 Hz, 1H), 4.21 (s, 5H), 4.18—4.40 (m, 3H), 4.51 (m, 1H). Anal. Calcd for C$_{15}$H$_{18}$FeO$_3$: C, 59.63; H, 6.00%. Found: C, 59.92; H, 6.22%.

(+)-2-Benzyloxyferrocenecarbaldehyde (3). To a suspension of 0.247 g (6.51 mmol) of lithium aluminum hydride in 20 mL of ether was added over 15 min a solution of 2.11 g (4.96 mmol) of (−)-**2a** in 35 mL of ether at 0 °C, and the mixture was stirred at room temperature for 40 min. To the mixture were successively added ethyl acetate and aqueous ammonium chloride. After the filtration the mixture was extracted twice with ethyl acetate, and combined extracts were dried over magnesium sulfate, and evaporated to give a mixture of 2-(benzyloxyferrocenyl)methanol and benzyl alcohol (2.03 g).

To this mixture was added 15 mL each of hexane and dichloromethane and 19 g (220 mmol) of manganese dioxide. The suspension was stirred at room temperature for 40 min and filtered through a pad of Celite. The manganese dioxide was washed with dichloromethane. A filtrate and washings were combined and evaporated. A chromatography on silica gel (3×29 cm, hexane/benzene/ethyl acetate) gave 1.37 g (86%) of (+)-**3** as dark red solids: *R*f 0.4 (silica gel, hexane/ethyl acetate=5/1); $[\alpha]_D^{20}$ +632° (*c* 0.52, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ=4.27 (s, 5H), 4.31 (t, *J*=2.9 Hz, 1H), 4.39 (m, 1H), 4.60 (m, 1H), 4.97 (AB$_q$, J_{AB}=11.6 Hz, $\Delta\delta$=11.2 Hz, 2H), 7.3—7.5 (m, 5H), 10.27 (s, 1H); IR (KBr) 1678 cm^{-1} (C=O). Anal. Calcd for C$_{18}$H$_{16}$FeO$_2$: C, 67.53; H, 5.04%. Found: C, 67.32; H, 5.05%.

(−)-2-Hydroxyferrocenecarbaldehyde (4). A suspension of 1.24 g (3.86 mmol) of (+)-**3**, 0.353 g (0.332 g atom) of 10% palladium on carbon in 15 mL of dichloromethane was degassed by the freeze-thaw method, filled with hydrogen, and stirred at room temperature overnight under the atmosphere of hydrogen. The mixture was diluted with ether, filtered through a pad of Celite, and evaporated. A residue was chromatographed on silica gel using argon-bubled solvents (4.2×28 cm, hexane/ether) to give 0.469 g (53%) of (−)-**4** as redish purple solids: R_f 0.5 (silica gel, hexane/ethyl acetate=2/1); $[\alpha]_D^{20}$ −2155° (c 0.52, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.1—4.5 (m, 2H), 4.27 (s, 5H), 4.69 (m, 1H), 6.90 (s, 1H), 10.11 (s, 1H); IR (KBr) 3300—3000, 1630 cm^{-1} (C=O).

***N,N*′-Bis(2-hydroxyferrocenylmethylene)ethylenediamine (5).** Solvents used in this procedure were deggased by the freeze-thaw method. To a solution of 98.6 mg (0.429 mmol) of (−)-**4** in 2 mL of benzene was added 0.41 mL (0.22 mmol) of 0.53 M solution of 1,2-ethylenediamine in benzene. The mixture was stirred at room temperature for 1 h, diluted with benzene, dried over magnesium sulfate, and evaporated. The addition of ethyl acetate and hexane to a residual oil, and evaporation gave 93.9 mg (90%) of **5** as dark red solids, which was used without further purification because of its instability against moisture and oxygen in the air: ^{1}H NMR ($CDCl_3$) δ=3.3—4.8 (m, 20H), 8.42 (broad s, 2H).

(−)-2-Benzyloxyferrocenecarboxylic Acid (6a). A solution of 2.66 g (6.25 mmol) of (−)-**2a** in 36 mL of ethanol and 27 mL of 10% aqueous potassium hydroxide was refluxed for 20 min. After evaporation of ethanol, residue was diluted with 10% aqueous potassium hydroxide, washed twice with ether, acidified with 6 M hydrochloric acid, and extracted twice with ether. Combined ether extracts were dried and evaporated to give 1.96 g (93%) of **6a** as a very viscous oil: $[\alpha]_D^{20}$ −19.0° (c 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.18 (t, J=2.5 Hz, 1H), 4.29 (s, 5H), 4.38 (m, 1H), 4.69 (m, 1H), 5.07 (AB_q, J_{AB}=11.3 Hz, $\Delta\delta$=11.4 Hz, 2H), 7.43 (m, 5H). Anal. Calcd for $C_{18}H_{16}FeO_3$: C, 64.31; H, 4.80%. Found: C, 64.34; H, 4.73%.

(+)-2-(1-Naphthylmethoxy)ferrocenecarboxylic Acid (6b). As the second eluent of the chromatography in the preparation of **2b** was obtained 888 mg (48% based on **1**) of **6b** as purple solid: R_f 0.5 (slical gel, hexane/ethyl acetate=1/2); $[\alpha]_D^{20}$ +77.2° (c 0.51, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.20 (t, J=2 Hz, 1H), 4.26 (s, 5H), 4.51 (m, 1H), 4.71 (m, 1H), 5.50 (s, 2H), 7.4—8.2 (m, 7H), 9.0—9.8 (broad s, 1H); IR (KBr) 3700—2000, 1740 (shoulder), 1670 cm^{-1}. Anal. Calcd for $C_{22}H_{18}FeO_3$: C, 68.42; H, 4.70%. Found: C, 68.01; H, 4.59%.

(−)-2-Methoxyferrocenecarboxylic Acid (6c). Prepared from 222 mg (0.810 mmol) of (−)-**2c** as described in the preparation of **6a** in a yield of 81%: Red oil; $[\alpha]_D^{20}$ −106° (c 0.54, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=3.87 (s, 3H), 4.17 (t, J=2.7 Hz, 1H), 4.30 (s, 5H), 4.37 (m, 1H), 4.66 (m, 1H), 8.0—11.0 (broad s, 1H). Anal. Calcd for $C_{12}H_{12}FeO_3$: C, 55.42; H, 4.65%. Found: C, 55.17; H, 4.73%.

(+)-2-Ethoxyferrocenecarboxylic Acid (6d). As the second eluent of the chromatography in the preparation of **2d** was obtained 230 mg (46% based on **1**) of **6d** as purple solid: R_f 0.7 (silica gel, ethyl acetate/methanol=10/1); $[\alpha]_D^{20}$ +8.9° (c 0.53, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.48 (t, J=6.7 Hz, 3H), 4.0—4.2 (m, 3H), 4.28 (s, 5H), 4.34 (m, 1H), 4.69 (m, 1H), 9.3—9.7 (broad s, 1H). Anal. Calcd for $C_{13}H_{14}FeO_3$: C, 56.97; H, 5.15%. Found: C, 56.84; H, 5.23%.

(+)-Tetrakis(2-benzyloxyferrocenecarboxylato)dirhodium(II) (7a). A suspension of 134 mg (0.268 mmol) of $Rh_2(OAc)_4\cdot 2MeOH$ and 420 mg (1.25 mmol) of (−)-**6a** in 30 mL of chlorobenzene was heated to gentle reflux, and chlorobenzene was distilled. The level of liquid was maintained constant by simultaneous addition of chlorobenzene from a dropping funnel. The reaction course was followed by TLC (silica gel, dichloromethane/ethyl acetate=5/1). After distillation of 300 mL of chlorobenzene (8 h) and evaporation in vacuo the residue was chromatographed on silica gel (3.4×34 cm, dichloromethane/ethyl acetate=20/1) to give 0.233 g (52% as solvent-free form) of (+)-**7a**·n(solvent) as green powder. ^{1}H NMR indicates that this material includes solvents (methanol, dichloromethane, or ethyl acetate), which are probably in coordination with the rhodium atoms: R_f 0.5 (silica gel, dichloromethane/ethyl acetate=10/1); $[\alpha]_D^{20}$ +66.0° (c 0.26, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=3.83 (m, 4H), 3.97 (s, 20H), 3.90—4.15 (m, 4H), 4.53 (m, 4H), 4.94 (AB_q, J_{AB}=12.0 Hz, $\Delta\delta$=9.2 Hz, 8H), 7.18—7.50 (m, 20H). Anal. Calcd for $C_{72}H_{60}Fe_4O_{12}Rh_2$: C, 55.92; H, 3.91%. Found: C, 53.71; H, 4.56%. Error in the elemental analysis is ascribed to the coordinated solvents.

Tetrakis[2-(1-naphthylmethoxy)ferrocenecarboxylato]dirhodium(II) (7b). Reaction was carried out as described above employing 101 mg (0.200 mmol) of $Rh_2(OAc)_4\cdot 2MeOH$ and 450 mg (1.17 mmol) of (+)-**6b**. A chromatography on silica gel (6×22 cm, dichloromethane/ethyl acetate=20/1—5/1) gave 74.4 mg (21% as solvent-free form) of **7b**·n(solvent) as green powder: R_f 0.7 (silica gel, dichloromethane/ethyl acetate=10/1); ^{1}H NMR (DMSO-d_6) δ=4.03 (s, 20H), 3.90—4.19 (m, 4H), 4.42 (m, 4H), 4.59 (m, 4H), 5.30 (AB_q, J_{AB}=11.0 Hz, $\Delta\delta$=36 Hz, 8H), 7.50—8.20 (m, 28H).

Tetrakis(2-methoxyferrocenecarboxylato)dirhodium(II) (7c). Reaction was carried out as described for the preparation of **7a** employing 34.7 mg (0.0686 mmol) of $Rh_2(OAc)_4\cdot 2MeOH$ and 83.9 mg (0.323 mmol) of (−)-**6c**. A chromatography on silica gel (3.4×32 cm, first dichloromethane and then dichloromethane/methanol=50/1—40/1) gave crude product, which was washed with methanol and chromatographed on silica gel (1.6×64 cm, dichloromethane/methanol=50/1) to give 45.5 mg (53% as solvent-free form) of **7c**·n(solvent) as green powder: R_f 0.4 (silica gel, dichloromethane/methanol=20/1); ^{1}H NMR ($CDCl_3$) δ=3.71 (s, 12H), 3.85 (t, J=2 Hz, 4H), 4.01 (s, 20H), 4.07 (m, 4H), 4.52 (m, 4H).

Tetrakis(2-ethoxyferrocenecarboxylato)dirhodium(II) (7d). Reaction was carried out as described for the preparation of **7a** employing 51.2 mg (0.101 mmol) of $Rh_2(OAc)_4\cdot 2MeOH$ and 137 mg (0.498 mmol) of (−)-**6c**. A chromatography on silica gel (3.4×28 cm, dichloromethane/ethyl acetate=3/1—2/1) gave crude product, which was washed with methanol to give 72.5 mg (55% as solvent-free form) of **7d**·n(solvent) as green powder: R_f 0.1 (silica gel, dichloromethane/ethyl acetate=2/1); ^{1}H NMR ($CDCl_3$) δ=1.42 (t, J=7.0 Hz, 12H), 3.99 (s, 20H), 3.8—4.2 (m, 16H), 4.50 (m, 4H).

Asymmetric Intramolecular C–H Insertion of α-Diazo β-Keto Ester 8 Catalyzed by Chiral Rhodium(II) Catalyst 7. General Procedure. To a solution of rhodium(II) catalyst **7** (5×10^{-3} mmol) in 10 mL of toluene was added α-diazo β-keto ester **8** (0.5 mmol) over a few minutes at 0 °C. The reaction course was followed by TLC. After the completion of reaction evaporation and a PTLC purification (silica gel, hexane/ethyl acetate=5/1) gave *trans*-3-alkyl-2-(methoxycarbonyl)cyclopentanone (**9**). For demethoxycarbonylation **9** was dissolved in a mixture of 3 mL of dimethyl sulfoxide and 1 mL of water and heated at 130 °C for 5 h. The mixture was diluted with water, and extracted twice with ether. Combined ether extracts were washed with water, dried over magnesium sulfate, and evaporated. Compound **10a** was purified by bulb-to-bulb distillation. Compounds **10b** and **10c** were purified by MPLC (silica gel, hexane/ethyl acetate=5/1).

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