Supplementary Material

^{1}H NMR spectra were recorded on either a Bruker AM-250 or an AC-200 instrument with tetramethylsilane (TMS) as an internal standard. Chemical Shifts are reported in parts per million (ppm) relative to TMS. When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; m, multiplet; b, broad. ^{13}C NMR spectra were proton decoupled and recorded on a Bruker AM-250 or an AC-200 spectrometers using carbon signal of the deuterated solvent as the internal standard. ^{31}P NMR spectra were recorded on an AC-200 instrument with H_3PO_4 as an external standard. Melting points were determined on a Buchi SMP-20 or a Fisher hot stage melting point apparatus and were uncorrected. IR spectra were recorded on a BOMEM MB-100 and Perkin Elmer 1600 FT-infrared spectrophotometer as liquid film or a KBr disc. Electron impact mass spectra (EI MS) were performed on Kratos MS890 (4kV, 35eV, 220 ^{o}C) and Hewlett-Packard 5890 Series II/5971A MSD instruments. Elemental analyses were performed by M-H-W Laboratories, Pheonix, AZ, U.S.A. Optical rotations were determined using Perkin-Elmer 241 polarimeter at λ = 578 or 589 nm at rt. Op designation refers to optical purity.

Stereoselectivities of the reactions were determined using a Waters HPLC system consisting of a 600E multi-solvent delivery system, a Waters 486 UV detector (λ = 254 nm), a Waters 746 integrator / recorder. The columns used were: Chiralpak, Chiracel OD and Whelk-O1 at rt. Enatio- and diastereomeric purity assays using chiral HPLC columns were completed with both racemic and enantioenriched materials and repeated at least once in order to ensure accuracy of the method used. If microanalyses are not reported, the purity of the compounds were judged to be >90 % by ^{1}H NMR and ^{13}C NMR analyses, and the molecular ion was confirmed by high resolution mass spectrometry (HR MS). All reported yields are isolated yields.

THF, Et_2O, *t*-BuOMe were freshly distilled from sodium benzophenone ketyl under nitrogen prior to use. Hexane and PhMe were distilled from CaH_2 and Na, respectively.

n-BuLi, *s*-BuLi, *t*-BuLi were purchased from FMC Corporation or Aldrich, as solutions in hexanes, cyclohexane, and pentane, respectively, and were titrated against 2,5-dimethoxybenzyl alcohol[1] or *s*-butanol-1,10-phenanthroline.[2] *N,N,N',N'*-tetramethylenethylenediamine (TMEDA) and (-)-sparteine were dried and distilled over CaH_2 and stored under argon. All commercial materials were purchased from Aldrich Chemical Co. or Lancaster Synthesis Ltd.

All the reactions were performed in oven-dried glassware under argon, using syringe-septum cap techniques. The -78 ^{o}C and 0 ^{o}C designations are approximate and refer to dry ice in acetone and ice/water slush, respectively. The phrase "standard workup" refers to addition of water or satd aq. NH_4Cl, extraction with Et_2O or CH_2Cl_2, washing the organic extract with saturated brine solution, dring over $MgSO_4$, filtration, and evaporation to dryness *in vacuo*. Flash chromatography was carried out using Merck silica gel 60 (0.040-0.063 mm).

Standard Methods

A. Lithiation of 1,1'-*N,N,N',N'*-Tetraisopropylferrocenedicarboxamide (1)

A solution of (-)-sparteine (0.91 mL, 4.20 mmol) or TMEDA (0.64 mL, 4.20 mmol) in PhMe or Et_2O (20 mL) was stirred at rt (5 min), cooled to -78 ^oC, treated with either *n*-BuLi or *s*-BuLi (4.20 mmol). After stirring (10 min) at -78 °C a solution of **1** (0.44 g, 1.0 mmol) in either PhMe (4.5 mL) or Et_2O (10 mL) was added dropwise (*ca* 1 drop/10 s). The stirring was continued (2 h) at -78 ^oC, the reaction mixture was quenched by an addition of electrophile (6 mmol) and allowed to warm to rt (4 h except for **3f** and **3g**), treated with satd aq. NH_4Cl and subjected to standard workup to afford the crude product.

B. Lithiation of 2-Substituted Derivatives of 1,1'-*N,N,N',N'*-tetra-isopropylferrocenedicarboxamide 3f, 3g and 3i

A solution of (-)-sparteine (0.45-0.91 mL, 2.1-4.2 mmol) in PhMe (20 mL) was strired at rt (5 min), cooled to -78 ^oC, treated with *n*-BuLi (4.2 mmol). After stirring (10 min) at -78 °C a solution of **3** (1.0 mmol) in PhMe (2.5 mL) was added slowly. After stirring (2 h) at -78 ^oC, the reaction was quenched by addition of the electrophile (3.0-6.0 mmol) and the reaction mixture allowed to warm to rt (4 h), treated with satd aq. NH_4Cl and subjected to standard workup to afford the crude product.

1,1'-*N,N,N',N'*-Tetraisopropylferrocenedicarboxamide (1)

To a stirred solution of 1,1'-ferrocenedicarboxylic acid (10.0 g, 36.2 mmol) in PhMe (100 mL) at rt, DMF (1.10 mL, 14.1 mmol) and oxalyl chloride (12.8 mL, 149 mmol) were added sequentially. The reaction mixture was stirred for 1 h at rt before PhMe and the excess of oxalyl chloride were removed *in vacuo*. The resultant residue was dissolved in Et_2O (250 mL), cooled to 0°C and treated with an excess of $HN(i\text{-}Pr)_2$ (28.4 mL, 217 mmol). The resulting reaction mixture was stirred overnight at rt. Standard workup followed by column chromatography (EtOAc:hexane = 1:2) and crystallization gave **1** as an orange solid (11.1 g, 80%); mp 133-134 °C (Et_2O-hexane), lit mp 127-128 °C;[3] IR (KBr) ν_{max} 1000, 1050, 1105, 1162, 1198, 1225, 1289, 1377, 1458, 1561, 1684, 2803, 2957, 3091; ^1H NMR ($CDCl_3$) δ 1.05-1.70 (br, 24H, $CH(C\mathbf{H}_3)_2$), 3.30-3.58, 4.35-4.55 (br, 2H, $C\mathbf{H}(CH_3)_2$), 4.37 (t, J = 2.0 Hz, 4H, $C_5\mathbf{H}_4$), 4.58 (t, J =2.0 Hz, 4H, $C_5\mathbf{H}_4$); ^{13}C NMR ($CDCl_3$) δ 21.0, 70.9, 71.3, 83.2, 167.1; MS m/z (rel intensity) (EI) 440 (M^+, 100), 340 (16), 312 (9), 270 (6), 248 (20), 213 (10), 186 (11), 177 (5), 156 (12), 146 (9), 121 (19), 92 (10), 65 (7); HRMS calcd for $C_{24}H_{36}{}^{54}FeN_2O_2$: 438.2169, found: 438.2173.

2-(Trimethylsilyl)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3i**)

According to Standard Method A a solution of (-)-sparteine (0.49 mL, 2.2 mmol) and *n*-BuLi (1.4 mL, 1.65 M solution in hexane, 2.2 mmol) was sequentially treated with a solution of **1** (0.47 g, 1.1 mmol) in PhMe and TMSCl (0.34 mL, 2.7 mmol). Standard workup followed by column chromatography (EtOAc:hexane = 1:30) afforded title compound as an orange solid (0.42 g, 68%), mp 107.0-107.5 °C**;** $[\alpha]_{578}^{23}$ = +67.5 (c 0.54, $CHCl_3$); IR (KBr) ν_{max} 2962, 2883, 1624, 1449, 1325, 1204, 1149, 1040, 829, 754; ^{1}H NMR($CDCl_3$) δ 0.23 (s, 9H, Si(C**H**$_3$)$_3$), 0.80-1.60 (br, 24H, CH(C**H**$_3$)$_2$)), 3.2-4.1 (br, 4H, C**H**$(CH_3)_2$), 4.20, 4.38, 4.43, 4.49, 4.57, 4.67 (m, 7H, Cp-**H**); ^{13}C NMR ($CDCl_3$) δ 0.5, 20.7, 21.2, 71.0, 72.03, 72.23, 75.7, 82.4, 93.5, 168.6; MS m/z (rel intensity) (EI) 512 (M^+, 51), 510 (4), 497 (100), 439 (7), 220 (9), 149 (14), 73 (14); HRMS calcd for $C_{27}H_{44}{}^{54}FeN_2O_2Si$ 510.2568, found: 510.2551. Two other isolated fractions contained *dl*-**4b** (0.032g, 5%); $[\alpha]_{578}^{23}$ = +49.2 (c 0.49, $CHCl_3$), 99% op and *meso*-**4b** (0.015g, 2%).

2-Iodo-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3a**)

According to Standard Method A a solution of (-)-sparteine (0.97 mL, 4.20 mmol) and *n*-BuLi (2.47 mL, 1.70 M solution in hexane, 4.20 mmol) was sequentially treated with a solutions of **1** (0.44 g, 1.0 mmol) and iodine (1.52 g, 6.00 mmol) in PhMe (14 mL). Standard workup followed by column chromatography (EtOAc:hexane = 1:10) afforded **3a** as an orange oil which slowly crystallized (0.37 g, 70%); mp 113-115 °C; CSP HPLC analysis ((*S*,*S*)-Whelk-O1; eluent: *n*-hexane/*i*-PrOH (96:4, flow 0.5 mL/min) determined 89 % ee (t_R(major) = 25.84 min, t_R(minor) = 21.68 min); $[\alpha]_D^{23}$ = +33.2 (c 0.47, $CHCl_3$); IR (neat) ν_{max} 807, 1037, 1206, 1316, 1369, 1460, 1635, 2931, 2966; ^{1}H NMR ($CDCl_3$) δ 0.92-1.72 (m, 24H, CH(C**H**$_3$)$_2$), 3.38-3.70 (m 4H, C**H**$(CH_3)_2$), 4.26-6.60 and 4.82-4.88 (m, 7H, Cp**H**); ^{13}C NMR ($CDCl_3$) δ 20.41, 20.54, 40.64, 45.6, 50.4, 68.9, 70.3, 72.8, 74.1, 74.7, 75.1, 83.7, 92.8, 165.6, 168.0; MS m/z (rel intensity) (EI) 566(M^+, 0.5), 502 (8), 414 (6), 219 (25), 131 (40), 69 (100); HRMS calcd for $C_{24}H_{35}{}^{56}FeIN_2O_2$: 566.1092, found: 566.1103.

2-Methyl-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3b**)

According to Standard Method A a solution of (-)-sparteine (0.91 mL, 4.1 mmol) and *n*-BuLi (2.35 mL, 1.75M solution in hexane, 4.12 mmol) was sequentially treated with a solution of **1** (0.437g, 0.98 mmol) in PhMe and MeI (0.37 mL, 5.9 mmol). Standard workup followed by column chromatography (EtOAc:hexane = 1:4) afforded **3b** as an orange solid (0.32g, 71%); mp 123-124 °C. CSP HPLC analysis (Chiralcel OD; eluent: *n*-hexane/*i*-PrOH/Et_2NH (99:1:0.01, flow 0.75 mL/min) determined 92% ee (t_R(major *dl*) = 26.95 min, t_R(minor) = 29.35 min); $[\alpha]_{578}^{23}$ = +63.2 (c 0.66, $CHCl_3$); IR (KBr) ν_{max} 1025, 1044, 1111, 1137, 1157, 1204, 1316, 1372, 1453, 1615, 2954, 3001, 3086; ^{1}H NMR($CDCl_3$) δ 0.65-1.82 (br, 24H, CH(C**H**$_3$)$_2$)), 2.02 (s, 3H, CpC**H**$_3$), 3.25-3.55 and 3.70-4.05 (br, 4H, C**H**$(CH_3)_2$), 4.18 (m, 2H, Cp-**H**), 4.39 (m, 2H, Cp-**H**), 4.57 (m, 2H, Cp-H), 4.67 (br, 1H, Cp-**H**); ^{13}C NMR ($CDCl_3$) δ 12.7, 20.1, 20.7,

20.9, 21.0, 45.3, 50.2, 67.8, 68.2, 70.8, 71.3, 71.4, 71.6, 72.0, 82.1, 85.1, 88.2, 169.2; MS m/z (rel intensity) (EI) 454 (27) 426 (4), 169 (6); HRMS calcd for $C_{25}H_{38}{}^{56}FeN_2O_2$: 454.2283, found: 454.2242.

2-(Diphenylhydroxymethyl)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3c**)

1. According to Standard Method A a solution of (-)-sparteine (0.91 mL, 4.1 mmol) and *n*-BuLi (2.36 mL, 1.75 M solution in hexane, 4.1 mmol) was sequentially treated with solutions of **1** (0.433 g, 0.98 mmol) and benzophenone (1.07 g, 5.90 mmol) in PhMe. Standard workup followed by column chromatography (EtOAc:hexane = 1:15) afforded **3c** (0.56 g, 92%) as an orange solid, mp 179-182 °C (Et_2O); CSP HPLC analysis ((S,S)-Whelk-O1; eluent: *n*-hexane/*i*-PrOH 92:8, flow 0.75 mL/min) determined 94% ee (t_R(major) = 12.06 min, t_R(minor) = 15.15 min; $[\alpha]_D{}^{23}$ = +161.1 (c 0.54, $CHCl_3$); IR (KBr) ν_{max} 704, 752, 765, 818, 832, 1031, 1047, 1134, 1161, 1202, 1320, 1368, 1456, 1594, 2875, 2932, 2966, 3066, 3204; ^{1}H NMR ($CDCl_3$) δ 0.65-1.48 (br, 24H, CH(C**H**$_3$)$_2$), 2.87, 3.15, 3.44, 4.20 (m, 4H, C**H**(CH$_3$)$_2$), 3.67, 4.29, 4.56, 4.63, 4.92 (m, 7H, Cp-**H**), 5.81 (s, 1H, O**H**), 7.06-7.40, 7.55 (m, 10H, Ph**H**), 7.94 (s, 1H, C**H**(OH)Ph$_2$); ^{13}C NMR ($CDCl_3$) δ 20.4, 20.5, 40.6, 45.6, 50.4, 68.9, 70.3, 72.8, 74.07, 74.7, 75.1, 83.7, 92.8, 165.6, 168.0; MS m/z (rel intensity) (EI) 622 (M^+, 2), 614 (8), 502 (50), 414 (42), 354 (3), 218 (78), 131 (100), 70 (98); HRMS calcd for $C_{37}H_{46}{}^{56}FeN_2O_3$: 622.2858, found: 622.2836.

2. By Sn-Li exchange from **3e**

n-BuLi (0.09 mL, 1.67 M solution in hexane, 0.15 mmol) was added to a cold (-78 °C), stirred solution of **3e** (0.10 g, 0.14 mmol) in PhMe (5 mL). The resulting solution mixture was stirred for 15 min. Benzophenone (0.052 g, 0.28 mmol) in PhMe (0.5 mL) was added and stirring was continued for 40 min at -78 °C before the reaction mixture was allowed to warm to rt, treated with satd aq. NH_4Cl. Standard workup and flash chromatography (EtOAc:hexane = 8:1) gave pure **3c** (0.022 g, 25%) together with **1** (3 mg, 5%) and unreacted **3e** (51 mg, 49%). The crude product was analysed by CSP HPLC ((*S*,*S*)-Whelk-O1; eluent: *n*-hexane/*i*-PrOH 97:3, flow 0.5 mL/min) and found to be 82% ee (t_R(major) = 22.88 min, t_R(minor) = 35.98 min).

2-(Diethylhydroxymethyl)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3d**)

According to Standard Method A a solution of (-)-sparteine (0.97 mL, 4.4 mmol) and *n*-BuLi (2.31 mL, 1.90 M solution in hexane, 4.40 mmol) was sequentially treated with a solution of **1** (0.459 g, 1.04 mmol) and 3-pentanone (0.63 mL, 6.2 mmol). Standard workup followed by column chromatography (EtOAc:hexane = 1:6) afforded **3d** as an orange solid (0.25 g, 45%); mp 121-122 °C; CSP HPLC analysis (Chiralcel OD; eluent: *n*-hexane/*i*-PrOH 98:2, flow 0.15 mL/min) determined 90% ee (t_R(major) = 37.02 min, t_R(minor) = 39.18 min; $[\alpha]_{578}{}^{23}$ = -31.2 (c 0.34, $CHCl_3$); IR (KBr) ν_{max} 814, 970, 1038, 1038, 1113,

1135, 1157, 1200, 1340, 1453, 1604, 2939, 3343; ^{1}H NMR ($CDCl_3$) δ 0.47 (t, J = 7.5 Hz, 3H, $CH_2C\mathbf{H}_3$), 0.72-1.98 (m, 31H, $CH(C\mathbf{H}_3)_2$, $C\mathbf{H}_2CH_3$,$CH_2C\mathbf{H}_3$, 3.29-3.55 (br, 4H, $C\mathbf{H}(CH_3)_2$), 4.10-4.32 (m, 3H, Cp**H**), 4.47(s, 1H, Cp**H**), 4.60 (s, 2H, Cp**H**), 4.73(s, 1H, Cp**H**), 6.10(s, 1H, O**H**); ^{13}C NMR ($CDCl_3$) δ 7.6, 9.2, 20.3, 20.7, 20.9, 29.6, 33.9, 46.2, 50.8, 67.7, 69.5, 71.7, 72.2, 72.6, 82.0, 83.1, 101.4, 168.9, 171.4; MS m/z (rel intensity) (EI) 526 (M^+, 18), 508 (100), 446 (3), 338 (4), 316 (12), 306 (5), 265 (5), 231 (5), 161 (7), 105 (9), 91 (8), 86 (7); HRMS calcd for $C_{29}H_{46}{}^{56}FeN_2O_3$: 526.2858, found: 526.2893; Anal. calcd for $C_{29}H_{46}FeN_2O_3$: C, 66.15; H, 8.80; N, 5.22, found: C, 66.17; H, 8.65; N, 4.93.

2-(Tributylstannyl)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3e**)

According to Standard Method A a solution of (-)-sparteine (0.92 mL, 4.2 mmol) and *n*-BuLi (5.17 mL, 1.68 M solution in hexane, 8.69 mmol) was sequentially treated with a solution of **1** (0.903g, 1.00 mmol) and tributyltin chloride (3.51 mL, 12.41 mmol). Standard workup followed by column chromatography (EtOAc:hexane =1:10) afforded **3e** as a red oil which was further purified by Kugelrohr distillation (0.86 g, 58%); $[\alpha]_{578}{}^{23}$ =+ 90.4 (c 0.44, $CHCl_3$); IR (neat) ν_{max} 1039, 1158, 1204, 1280, 1323, 1372, 1457, 1614, 2930; ^{1}H NMR ($CDCl_3$) δ 0.79-1.83 (br, 51H, $CH(C\mathbf{H}_3)_2$), Bu-**H**), 3.19-3.68(br, 4H, $C\mathbf{H}(CH_3)_2$)), 4.22-4.33 (m, 3H, Cp-**H**), 4.30-4.52 (m, 2H, Cp-**H**), 4.52-4.68 (m, 2H, Cp-**H**); ^{13}C NMR ($CDCl_3$) δ 11.22, 13.7, 14.6, 14.8, 21.0, 26.8, 27.4, 28.0, 29.2, 46.1, 50.0, 69.9, 70.4, 71.1, 71.5, 72.0, 74.2, 76.1, 82.3, 88.4, 168.9, 169.4; MS m/z (rel intensity) (FAB) 730 (M^+, 7), 673 (100), 630 (9), 558 (28), 495 (28), 426 (16), 368 (20); Anal. calcd for $C_{36}H_{62}FeN_2O_2Sn$: C, 59.28; H, 8.57; N, 3.84, found: C, 58.99; H, 8.49; N, 3.80.

2-(Diphenylphosphino)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3f**)

According to Standard Method A a solution of (-)-sparteine (1.04 mL, 4.20 mmol) and *n*-BuLi (2.40 mL, 1.75 M solution in hexane, 4.20 mmol) was sequentially treated with a solution of **1** (0.440 g, 1.00 mmol) and chlorodiphenylphosphine (1.1 mL, 6.0 mmol). After stirring for 1h at -78 °C, the reaction mixture was allowed to warmed to 0 °C and quenched with satd aq. NH_4Cl. Standard workup followed by column chromatography (SiO_2 deactivated by additon of 2% Et_3N, EtOAc:hexane = 1:10) afforded **3f** as an orange solid (0.335 g, 54%); mp 142-144 °C (dec), lit. mp 146-148 °C (dec);[4] CSP HPLC analysis (Chiracel OD; eluent: *n*-hexane/*i*-PrOH 98:2, flow 0.25 mL/min) determined 97% ee (t_R(major) = 31.31 min, t_R(minor) = 34.24 min; $[\alpha]_D{}^{23}$ = + 225.5 (c 0.31, CH_2Cl_2); IR (KBr) ν_{max} 2963, 1624, 1449, 1336, 1206, 820, 751, 701; ^{1}H NMR ($CDCl_3$) δ 0.32-1.75 (br, 24 $CH(C\mathbf{H}_3)_2$), 3.03-3.48 (br, 4H, $C\mathbf{H}(CH_3)_2$), 3.90, 4.26, 4.34, 4.37, 4.45, 4.51, 4.58, 4.65, 4.80 (m, 7H, Cp**H**), 7.18-7.62 (br, 10H, $C_6\mathbf{H}_5$); ^{13}C NMR ($CDCl_3$) δ 20.3, 21.4, 31.6, 71.7, 72.2, 73.4, 74.7, 76.9, 80.3, 82.7, 86.0, 98.3, 128.1, 128.2, 128.7, 133.0, 133.4, 134.1, 134.6, 137.9, 139.2, 166.7 ; MS m/z (rel. intensity) (EI) 625 (M^+, 62), 539 (71), 423 (100), 346 (84), 245 (69); HRMS calcd for $C_{36}H_{46}{}^{56}FeN_2O_2P$: 625.2674, found: 625.2646.

2-(Phenylthio)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3g**)

According to Standard Method A a solution of (-)-sparteine (0.93 mL, 4.2 mmol) and *n*-BuLi (2.76 mL, 1.52 M solution in hexane, 4.2 mmol) was sequentially treated with a solutions of **1** (0.440 g, 1.00 mmol) and $(PhS)_2$ (1.30 g, 5.95 mmol) in PhMe. After stirring for 2 h at -78 °C, the reaction mixture was allowed to warm up to rt (2h) and quenched with satd aq. NH_4Cl. Standard workup followed by column chromatography (EtOAc:hexane=1:6) afforded the titlle compound (0.39 g, 71%); mp 135-137 °C, CSP HPLC analysis (Chiralcell OD; eluent: *n*-hexane/*i*-PrOH (0.1% solution of Et_2NH of 99.1: 0.9, flow mL/min) determined 89% ee (t_R(major) = 17.54 min, t_R(minor) = 21.21 min; $[\alpha]_{578}^{23}$ = +97.7 (c 1.41, $CHCl_3$); IR (KBr) ν_{max} 738, 814, 814, 840, 1041, 1143, 1205, 1337, 1453, 1611, 2935; ^{1}H NMR ($CDCl_3$) δ 0.33-1.61 (br, 24H, CH(C**H**$_3$)$_2$), 3.12-3.78 (br, 4H, C**H**(CH$_3$)$_2$), 4.35-4.98 (m, 7H, Cp-**H**), 7.01-7.37 (m, 5H, C$_6$**H**$_5$); ^{13}C NMR ($CDCl_3$) δ 19.99, 20.4, 20.7, 20.9, 45.8, 50.5, 70.6, 71.7, 72.6, 72.9, 73.7, 73.9, 77.7, 79.0, 83.7, 92.8, 125.4, 127.3, 128.7, 139.7, 165.5, 168.6; MS m/z (rel intensity) (FAB) 548 (M^+, 45), 460 (62), 372 (72), 328 (31), 185 (100), 132 (88) ; Anal. calcd for $C_{30}H_{40}FeN_2O_2S$: C, 65.67; H, 7.35; N, 5.11, found: C, 65.80; H, 7.28; N, 5.05.

2-(Phenylselenyl)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3h**)

According to Standard Method A a solution of (-)-sparteine (0.92 mL, 4.2 mmol) and *n*-BuLi (2.49 mL, 1.68 M solution in hexane, 4.19 mmol) was sequentially treated with solutions of **1** (0.439g, 1.00 mmol) and Ph_2Se_2 (1.87g, 5.98 mmol) in PhMe (2.5 mL). Standard workup followed by column chromatography (EtOAc:hexane = 1:4) afforded **3h** (0.36 g, 82%); mp 126-127 °C; CSP HPLC analysis (Chiralcel OD; eluent: *n*-hexane/*i*-PrOH 99:1, flow 0.3 mL/min) determined 71% ee (t_R(major) = 32.92 min, t_R(minor) = 35.90 min); $[\alpha]_{578}^{23}$ = +216 (c 0.23, $CHCl_3$); IR (CH_2Cl_2) ν_{max} 1037, 1135, 1160, 1205, 1266, 1322, 1372, 1463, 1475,1621, 2971, 2934, 3053; ^{1}H NMR ($CDCl_3$) δ 0.37-1.60 (br, 24H, CH(C**H**$_3$)$_2$)), 3.11-3.76 (br, 4H, C**H**(CH$_3$)$_2$)), 4.40 (dd,J = 2.8, 1.3 Hz, 1H, Cp-**H**), 4.48-4.70 (m, 3H, Cp-**H**), 4.68 (dt, J = 1.3, 2.6, 1H, Cp-**H**), 4.90 (dt, J = 1.3, 2.6 Hz, 1H, Cp**H**), 7.08-7.19 (m, 3H, C$_6$**H**$_5$), 7.27-7.35 (m, 2H, C$_6$**H**$_5$); ^{13}C NMR ($CDCl_3$) δ 14.1, 21.0, 22.6, 31.5, 45.8, 49.8, 50.4, 71.1, 71.2, 72.2, 72.6, 73.4,73.2, 74.2, 77.3, 83.4, 92.4, 126.1, 128.8, 130.3, 133.7, 166.0, 168.5; MS m/z (rel intensity) (FAB) 597 (M^+, 9), 553 (8), 517 (6), 461 (11), 369 (32), 356 (5), 277 (100), 241 (8); HRMS calcd for $C_{30}H_{41}{}^{56}FeN_2O_2Se$: 597.1683, found: 597.1678.

2,4-Dimethoxyphenylboronic acid

t-BuLi (14.3 mL, 2.04 M solution in cyclopentane, 29.1 mmol) was added gradually to a stirred solution of 2,4-dimethoxybromobenzene in THF (150 mL) at -78 °C. The resultant reaction mixture was stirred for 15 min at -78 °C before trimethylborate (6.0 mL, 53 mmol) was added to it rapidly. The solution was allowed

to warmed to rt, treated with water (50 mL), acidified with 2 M aq. HCl to pH *ca* 6. The solvents were removed *in vacuo* and the residue after standard workup recrystallized from hot water to give the title compound as white needles (1.35g, 56%); mp 113-119 ^{o}C (H_2O); MS m/z (rel intensity) (EI) 182 (M^+, 59), 164 (7), 151 (8), 138 (27), 121 (20), 109 (47), 95 (44), 77 (73), 69 (14), 63 (100); HRMS calcd for $C_8H_{11}BO_4$: 182.0750, found: 182.0758.

2-(2,4-Dimethoxyphenyl)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3k**)

A mixture of $Pd(PPh_3)_4$ (0.070 g, 0.06 mmol), **3a** (0.34 g, 0.61 mmol, 89% ee), degassed aq. Na_2CO_3 (1.80 mL, 2M, 3.66 mmol) and 2,4-dimethoxyphenylboronic acid (0.18 g, 0.97 mmol) in freshly distilled DME (15 mL) was refluxed for 5 d. The crude material was filtered through Celite, subjected to the standard workup and purifed by column chromatography (EtOAc:hexane 1:8) to afford **3k** as a brown-red solid (0.069 g, 20 %), and also unreacted starting material 3a (0.24 g, 70 %) mp 161-163 °C; CSP HPLC analysis (Chiralcel OD; eluent: *n*-hexane/*i*-PrOH 98.5:1.5, flow 0.20 mL/min) determined 89% ee (t_R(major) = 67.93 min, t_R(minor) = 75.04 min); $[\alpha]_{578}^{23}$ = 8.9 (c 0.18, $CHCl_3$); IR (KBr) ν_{max} 817, 1036, 1151, 1205, 1317, 1370, 1454, 1533, 1619, 2936; ^{1}H NMR ($CDCl_3$) δ 0.25-1.75 (br, 24H, CH(C**H**$_3$)$_2$), 3.05-3.65 (b, 2H, C**H**(CH$_3$)$_2$), 3.72 (s, 3H, OC**H**$_3$), 3.78 (s, 3H, OC**H**$_3$), 4.32-4.44 (m, 3H, Cp**H**), 4.54 (m, 2H, Cp**H**), 4.67-4.70 (m, 1H, Cp**H**), 4.76-4.79 (m, 1H, Cp**H**), 6.38 (d, J = 2.6 Hz, 1H, H(3)-C$_6$**H**$_3$), 6.45 (dd, J = 2.6, 8.4 Hz, 1H, H(5)-C$_6$**H**$_3$), 7.70 (d, J = 8.4 Hz, 1H, H(6)-C$_6$**H**$_3$); ^{13}C NMR ($CDCl_3$) δ 19.5, 19.9, 20.9, 21.0, 45.5, 50.4, 55.4, 69.3, 69.8, 71.5, 71.7, 73.0, 73.4, 74.7, 81.4, 82.4, 90.0, 98.2, 104.2, 117.7, 127.9, 128.1, 130.4, 132.6, 134.7, 134.9, 157.9, 159.8, 167.7, 169.3; MS m/z (rel intensity) (CI) 577(MH^+, 46), 576 (42), 476 (9), 441 (17), 349 (6), 330 (13),309 (6), 253 (16), 233 (13), 194 (16), 145 (22), 131 (15), 117 (100), 100 (14), 86 (19), 71 (10); HRMS calcd for $C_{32}H_{44}{}^{56}FeN_2O_4$: 576.2650, found: 576.2675.

2-Phenyl-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**3l**)

A mixture of $PdCl_2$(dppf) (37 mg, 0.051 mmol), CuO (95 mg, 1.2 mmol), bromobenzene (0.02 mL, 0.19 mmol) and DMF (3 mL) was heated to 150 °C for 30 min before it was treated with a solution of **3e** (0.107 g, 0.15 mmol, $[\alpha]_{578}^{23}$ = + 90.4 (c 0.44, $CHCl_3$), ≥ 82% ee) in DMF (0.3 mL). The resulting reaction mixture was stirred for 18 h (100 °C), filtered through Celite and subjected to the standard workup followed by a column chromatography (6:1 hexane:EtOAc) to afford the product as a brown oil (27 mg, 35%) and destannylated **1** (24 mg, 51%); $[\alpha]_{578}^{23}$ = -266.1 (c 0.17, $CHCl_3$); IR (neat) ν_{max} 764, 815, 1038, 1111, 1135, 1159, 1207, 1261, 1318, 1372, 1457, 1508, 1623, 2926, 2964; ^{1}H NMR ($CDCl_3$) δ 0.24-1.72 (br, 24H, CH(C**H**$_3$)$_2$), 3.13 - 3.60 (br, 4H, C**H**(CH$_3$)$_2$), 4.25 - 4.92 (br, 7H, Cp**H**), 7.25 (m, 3H, C$_6$**H**$_5$), 7.56 (m, 2H, C$_6$**H**$_5$); ^{13}C NMR ($CDCl_3$) δ 19.5, 19.8, 20.8, 20.9, 21.0, 22.7, 29.7, 45.7, 50.6, 68.6, 70.0, 70.9, 72.0, 72.9, 73.4, 74.3, 82.4, 85.6, 90.1, 126.6, 128.1, 137.5, 167.5, 168.9; MS m/z (rel intensity) (FAB) 517

(MH^+, 22), 416 (5), 330 (3), 277(8), 185 (100), 116 (5); HRMS calcd for $C_{30}H_{41}{}^{56}FeN_2O_2$ (MH^+): 517.2518, found: 517.2495.

2,2'-Bis(trimethylsilyl)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**4b**)

1. From **1**

According to the Standard Method A, a solution of (-)-sparteine (0.51 mL, 2.30 mmol) and *n*-BuLi (1.36 mL, 1.69 M solution in hexane, 2.30 mmol) in PhMe was sequentially treated with a solution of **1** (0.24 g, 0.55 mmol) and TMSCl (0.42 mL, 3.3 mmol). Standard workup followed by column chromatography (EtOAc:hexane = 1:30) gave *dl*-**4b** and *meso*-**4b** as orange solids (0.153 g, 50%) and (0.065 g, 21%), respectively along with **3i** (0.043 g, 16%); $[\alpha]_{578}{}^{23}$ = +64.3 (c 0.11, $CHCl_3$);

Data for *dl*-**4b:**

$[\alpha]_{578}{}^{23}$ = +48.0 (c 0.51, $CHCl_3$); 97% op; mp 192-194 °C (hexane); IR (KBr) ν_{max} 833, 1041, 1069, 1120, 1155, 1207, 1246, 1279, 1330, 1371, 1455, 1627, 2934; ^{1}H NMR($CDCl_3$) 0.25 (s, 18H, Si(C**H**$_3$)$_3$), 0.77-1.12 (br, 24H, CH(C**H**$_3$)$_2$), 3.15-3.50, 3.80-4.06 (br, 4H, C**H**(CH$_3$)$_2$), 4.15 (s, 2H, Cp-**H**), 4.60 (s, 4H, Cp-**H**); ^{13}C NMR ($CDCl_3$) δ 0.6, 20.7, 45.9, 50.1, 73.0, 73.5, 74.0, 74.4, 92.6, 168.9; MS m/z (rel intensity) (EI) 585 (M^+, 76), 442 (26), 312 (16), 220 (22), 128 (17), 73 (95); Anal. calcd for $C_{30}H_{52}{}^{56}FeN_2O_2Si_2$: C, 61.62; H, 8.96; N, 4.79, found: C, 61.50; H, 8.73; N, 4.79.

Data for *meso*-**4b:**

mp 192-194 °C (Et_2O-hexane); IR (KBr) ν_{max} 904, 1040, 1067, 1127, 1156, 1207, 1279, 1349, 1454, 1623, 2963, 3088; ^{1}H NMR($CDCl_3$) δ 1.32 (s, 18H, Si(C**H**$_3$)$_3$), 0.75-1.70 (br, 24H, CH(C**H**$_3$)$_2$), 3.15-3.44, 3.73-4.05 (br, 4H, C**H**(CH$_3$)$_2$), 4.34 (s, 2H, Cp-**H**), 4.43 (s, 2H, Cp-**H**), 4.52 (s, 2H, Cp-**H**); ^{13}C NMR ($CDCl_3$) δ 0.0, 20.7, 45.7, 50.1, 70.5, 72.6, 74.8, 92.2, 168.7; MS (EI) m/z (rel intensity) 585 (M^+,5), 370 (2), 204 (3), 100 (5), 73 (100); Anal. calcd for $C_{30}H_{52}{}^{56}FeN_2O_2Si_2$: C, 61.62 ; H, 8.96 ; N, 4.79, found: C, 61.80 ; H, 8.85; N, 4.79.

2. From **3i**

According to the Standard Method B, a solution of (-)-sparteine (0.71 mL, 3.23 mmol), and *n*-BuLi (1.96 mL, 1.65 M solution in hexane, 3.23 mmol) in PhMe was sequentially treated with a solution of **3i** (0.39 g, 0.76 mmol, $[\alpha]_{578}{}^{23}$ = +67.5 (c 0.54, $CHCl_3$) and TMSCl (0.60 mL, 4.6 mmol). Standard workup followed by column chromatography (EtOAc:hexane = 1:30) gave the title compounds as orange solids; *dl*-**3i** (0.336 g, 75%) and *meso*-**3i** (0.056 g, 12%), *dl*-**3i** $[\alpha]_{578}{}^{23}$ = 44.8 (c 0.42, $CHCl_3$); 91% op.

2,2'-Bis(diphenylphosphino)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (4a)

Preparation of *dl*-**4a**:

According to the Standard Method B, a solution of (-)-sparteine (0.30 mL, 1.4 mmol) and with *n*-BuLi (0.67 mL, 2.00 M solution in hexane, 1.3 mmol) in PhMe was sequentially treated with a solution of **3f** (

0.400 g, 0.91 mmol, 97% ee) and Ph_2PCl (0.36 mL, 1.9 mmol). The reaction mixture was quenched with satd aq. NH_4Cl, extracted with CH_2Cl_2, washed with brine, evaporated to dryiness and the residue was purified by column chromatography (SiO_2 pre-treated with 2% Et_3N, EtOAc:hexane = 1:6) to give the title compound as an bright yellow solid (0.29 g, 45%); dr(*dl*:*meso*) >95:<5 by ^{31}P NMR, mp 233-236 °C (dec), lit. mp 228-230 °C (dec);[4] $[\alpha]_D^{20}$ = +277 (c 0.76, CH_2Cl_2), 98% op;[4] IR (KBr) ν_{max} 3088, 2938, 1625, 1531, 1454, 1371, 1333, 1279, 1244, 1204, 1154, 1039; ^1H NMR ($CDCl_3$) δ 0.34-1.53 (br, 24H, CH(C**H**$_3$)$_2$), 3.04-3.26 and 3.92-4.13 (br, 4H, C**H**(CH_3)$_2$), 3.53 (s, 2H, Cp-**H**), 4.78-4.82 (m, 4H, Cp-**H**), 7.12-7.43 (br, 20H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.0, 20.3, 50.0, 72.7, 74.8, 76.7, 81.1, 90.5, 127.9, 128.0, 128.1, 128.2, 129.1, 130.0, 130.4, 132.7, 133.1, 133.5, 133.6, 133.9, 137.9, 138.1, 139.0, 167.0**;** ^{31}P NMR($CDCl_3$) δ -22.27; Anal. calcd for $C_{48}H_{54}{}^{56}FeN_2O_2P_2$: C, 71.28, H, 6.73, N, 3.46, found: C, 71.36; H, 6.75; N, 3.51.

Preparation of *meso*-**4a**:

According to the Standard Method A, a solution of (-)-sparteine (1.9 mL, 8.4 mmol) and *s*-BuLi (7.1 mL, 1.18 M solution in cyclohexane, 8.4 mmol) was sequentially treated with a solution of **1** (0.883 g, 2.01 mmol) and Ph_2PCl (2.16 mL, 12.0 mmol). The reaction mixture was quenched with satd aq. NH_4Cl, extracted with CH_2Cl_2, washed with brine, evaporated to dryiness, and the residue was purified by column chromatography (SiO_2 pre-treated with 2% Et_3N, EtOAc:hexane = 1:6) to give *meso*-**4a** as a bright yellow solid (0.79g, 49%), the diastereomeric composition was determined by ^{31}P NMR dr(*meso*:*dl*) >95:<5; mp 235-237 °C (dec); IR (KBr) ν_{max} 3063, 2924, 1629, 1451, 1373, 1330, 1205, 1159, 1093, 822; ^1H NMR ($CDCl_3$) δ 0.34-1.68 (br, 24H, CH(C**H**$_3$)$_2$), 2.92-3.25 and 3.43-3.96 (br, 4H, C**H**(CH_3)$_2$), 4.20 and 4.76 (m, 6H, Cp-**H**), 7.12-7.67 (br, 20H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 20.3, 72.8, 81.1, 90.8, 91.2, 128.0, 128.0, 128.2, 128.9, 132.8, 133.1, 134.5, 134.9, 139.6, 139.9, 166.3**;** ^{31}P NMR($CDCl_3$) δ -22.68; MS m/z (rel intensity) (FAB) 808 (M^+, 3), 766 (8), 639 (16), 625 (47); Anal. calcd for $C_{48}H_{54}{}^{56}FeN_2O_2P_2$: C, 71.28, H, 6.73, N, 3.46, found: C, 71.39; H, 6.79; N, 3.52.

2,2'-Bis(phenylthio)-1,1'-*N,N,N',N'*-tetraisopropylferrocenedicarboxamide (**4c**)

According to the Standard Method B, a solution of (-)-sparteine (0.07 mL, 0.31 mmol and *n*-BuLi (0.19 mL, 1.67 M solution in hexane, 0.15 mmol) in PhMe was sequentially treated with a solution of **3g** (0.084 g, 0.15 mmol, 89% ee) and $(PhS)_2$ (0.131g, 0.6 mmol). Standard workup followed by column chromatography (EtOAc:hexane = 1:10) gave orange solid (0.06 g, 60%); CSP HPLC analysis (Chiralcel OD; eluent: *n*-hexane/ *i*-PrOH 99.1, flow 0.4 mL/min) determined dr(*dl*:*meso*) = 98.5:1.5 and 97% ee (t_R(major dl) = 15.97 min, t_R(minor dl) = 19.14 min, t_R(meso diastereomer) = 22.00 min ; Data for *dl*-**4c:** mp 200-202 °C (dec); IR (KBr) ν_{max} 2954, 1628, 1458, 1372, 1325, 1207, 1159, 1127, 1033; ^1H NMR ($CDCl_3$) δ 0.42-1.71 (br, 24H, CH(C**H**$_3$)$_2$), 3.24 (sept, J = 11Hz, 2H, C**H**(CH_3)$_2$), 3.72 (sept, J = 11 Hz, 2H, C**H**(CH_3)$_2$), 4.71 (s, 4H, Cp-**H**), 4.59 (m, 2H, Cp-**H**), 7.02-7.28 (br, 10H, C_6**H**$_5$); ^{13}C NMR ($CDCl_3$) δ 20.9, 50.6, 74.0, 77.4, 80.6, 92.5, 125.5, 127.6, 128.6, 139.2, 165.3; MS m/z (rel intensity) (FAB) 657 (MH^+, 98),

656 (M^+, 100), 557 (17), 548 (14), 455 (34), 356 (16), 318 (28), 302 (89), 201 (69), 185 (59), 154 (69), 137 (59); HRMS calcd for $C_{36}H_{45}{}^{56}FeN_2O_2S_2$ (MH^+): 657.2272, found: 657.2294; Anal. calcd for $C_{36}H_{44}{}^{56}FeO_2N_2S_2$: C, 65.84; H, 6.75; N, 4.26; found: C, 66.02; H, 6.68; N, 4.32.

Data for *meso*-**4c:** mp 201-203 °C (dec); IR (KBr) ν_{max} 2949, 1631, 1459, 1372, 1316, 1207, 1034; ^{1}H NMR ($CDCl_3$) δ 0.26-1.79 (br, 24H, CH(C**H**$_3$)$_2$), 3.24 (m, 2H, C**H**(CH$_3$)$_2$), 3.67 (m, 2H, C**H**(CH$_3$)$_2$), 4.53, 4.70, 4.90 (m, 6H, Cp-**H**), 6.92-7.38 (br, 10H, C$_6$**H**$_5$); ^{13}C NMR ($CDCl_3$) δ 20.0, 20.7, 45.8, 50.5, 71.4, 74. 2, 79.1, 82.1, 125.5, 127.7, 128.7, 137.0, 165.1; MS m/z (rel intensity) (FAB) 657 (MH^+, 8), 656 (M^+, 7), 556 (2), 547 (2), 455 (5), 338 (5), 302 (14), 246 (16), 201 (9), 185 (100), 154 (59), 137 (65); HRMS calcd for $C_{36}H_{45}{}^{56}FeN_2O_2S_2$ (MH^+): 657.2272, found: 657.2292.

1-Phenylpropan-1-ol

1. General procedure for Et_2Zn Addition to PhCHO

To a stirred solution of benzaldehyde (0.10 mL, 1.6 mmol) and chiral ferrocenyl ligand 3 (0.05 mmol) in either hexane (15 mL) or PhMe (5 mL) a solution of Et_2Zn (1.60 mL, 1.0 M in hexane, 1.60 mmol) was added at rt and the stirring was continued for 1 to 3 d. The reaction was quenched by addition of 0.2 M HCl at 0 °C. After the standard workup, the crude material was analyzed by CSP HPLC (Chiralcel OD column, eluent 99:1 *n*-hexane / isopropyl alcohol, flow 0.5 mL/min, t_R 29.66 min, t_R 27.20 min), purified by column chromatography (10:1 hexane-EtOAc) to yield 1-Phenylpropan-1-ol as an colorless oil; IR (CH_2Cl_2) ν_{max} 700, 756, 1097, 1454, 1493, 2875, 2930, 2966, 3030, 3369; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H, CH$_2$C**H**$_3$), 1.81 (m, 2H, C**H**$_2$CH$_3$) 1.90-2.00 (br., 1H, O**H**), 4.59 (t, J = 6.6 Hz, 1H, C**H**(OH)CH$_2$); 7.20-7.40 (m, C$_6$**H**$_5$); ^{13}C NMR ($CDCl_3$) δ 10.1, 31.8, 76.0, 126.0, 127.4, 128.3; MS m/z (rel intensity) (EI) 136 (M^+, 32), 117 (2), 107 (100), 97 (0.5); HRMS calcd for $C_9H_{12}O$: 136.0888, found: 136.0897.

2. Et_2Zn Addition to PhCHO Catalyzed by Lithium salt of **3c**

A solution of *n*-BuLi (0.05 mL, 1.67 M in hexane, 0.85 mmol) was added to a cold
(-78 ^{o}C) solution of **3c** (53.4 mg, 0.086 mmol) in PhMe (20 mL). PhCHO (0.19 mL, 0.86 mmol) and Et_2Zn (1.37 mL, 1.0 M in hexane, 1.37 mmol) were added and stirring was continued for 3 d (rt) before the reaction was quenched with 0.2 M HCl at 0 °C. Standard workup followed by flash chromatography afforded the product (0.082 g, 70%, 47%ee)

Dimethyl 1,3-diphenylprop-2-enylmalonate

Method A

A solution of 1,3-Diphenyl-prop-2-en-1-ol[5] (0.25 g, 1.0 mmol), ferrocenyl ligand **4a** (0.071 g, 0.1 mmol) and allylpalladium chloride dimer (0.009 g, 0.025 mmol) in CH_2Cl_2 (3.5 mL) were stirred for 15 min at rt

before it was treated with a solution of BSA (0.74 mL, 3.0 mmol), dimethyl malonate (0.40 g, 3.0 mmol) and AcOK (0.004 g, 0.04 mmol) in CH_2Cl_2 (3.5 mL).

The stirring was continued for 10 h (rt) before the reaction mixture was treated with water and subjected to standard aqueous workup. Purification by column chromatography (EtOAc:Hexane 1:5) gave the title compound as a pale yellow, solid (0.313 g, 96%); CSP HPLC analysis (eluent: *n*-hexane/*i*-PrOH 99:1, flow 0.2 mL/min) determined 84% ee (t_R(major) = 58.78 min, t_R(minor) = 63.50 min); $[\alpha]_D^{23}$ +15.9 (c 0.71, EtOH); IR (neat) ν_{max} 2995, 1758, 1605, 1493, 1454, 1316, 1259; ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 3H, CO_2CH_3), 3.70 (s, 3H, CO_2CH_3), 3.95 (d, J = 10.9 Hz**,** 1H, C**H**($CO_2CH_3)_2$), 4.27 (dd, J = 10.9 Hz, 8.0 Hz, 1H, Ph-C**H**), 6.32 (dd, J = 8.0 Hz, 15.7 Hz, 1H, -C**H**=CH-Ph)**,** 6.51 (d, J = 15.7 Hz, 1H, Ph-C**H**=), 7.19-7.33 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 48.9, 52.0, 52.2, 57.3, 126.1, 126.9, 127.3, 127.6, 127.9, 128.2, 128.4, 128.9, 131.5, 136.5, 140.0, 167.4, 167.9; MS m/z (rel intensity) (EI) 324 (M^+, 56), 292 (29), 264 (37), 232 (41), 204 (84), 193 (98), 178 (53), 165 (39), 152 (18), 139 (12), 128 (42), 115 (100), 102 (43), 91 (74), 78 (42), 69 (43); HRMS calcd for $C_{20}H_{20.}O_4$: 324.1361, found: 324.1353.

Method B

A solution of allylic acetate (0.095 g, 0.38 mmol), ferrocenyl ligand **4a** (0.027 g, 0.038 mmol), allylpalladium chloride dimer (0.004 g, 0.011 mmol) and THF (2 mL) was stirred for 15 min at rt, before it was treated with a THF (3 mL) solution of $NaCH(CO_2Me)_2$ at rt. The reaction reaction mixture was stirred for 36 h at rt, quenched with water, subjected to the standard aqueous workup and the crude product was purified by column chromatography to afford the product (0.117 g, 96%), which was analyzed by CSP HPLC to show enatioenrichment in (*R*)-enantiomer in 84% ee. The solution of $NaCH(CO_2Me)_2$ was prepared by the addition of NaH (0.07 g, 3.0 mmol) to dimethylmalonate (0.149 g, 1.13 mmol in THF (3 mL) at 0 °C.

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