Pergamon

SCIENCE DIRECT®

Tetrahedron: *Asymmetry* 14 (2003) 255–264

TETRAHEDRON: *ASYMMETRY*

New *P,N*-ferrocenyl ligands for rhodium-catalyzed hydroboration and palladium-catalyzed allylic alkylation

Ralf J. Kloetzing, Matthias Lotz and Paul Knochel*

Department of Chemistry of Ludwig-Maximilians-University, Butenandtstraße 5-13, 81377 Munich, Germany

Received 28 October 2002; accepted 3 December 2002

Abstract—A set of nine new chiral *P,N*-ferrocenyl ligands for metal-catalyzed enantioselective reactions has been prepared. The rhodium-catalyzed hydroboration of styrene with catechol borane proceeded with high regioselectivity (up to 97:3) or with high enantioselectivity (up to 92% ee) depending on the catalyst. Good results were also obtained in the palladium-catalyzed asymmetric alkylation of 1,3-diphenylallylic systems (up to 94% ee). © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

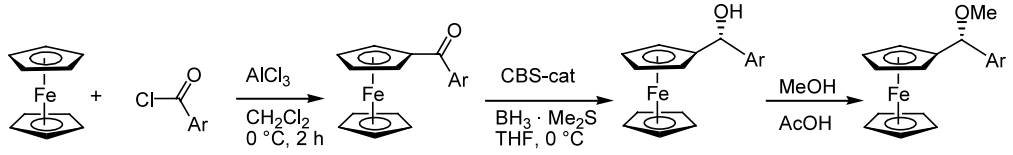
Chiral ligands incorporating both planar and central chirality have found widespread application in asymmetric catalysis.[1] Among these, the ferrocene framework is unparalleled in its versatility.[2] Recently, we reported the synthesis of new *P,N*-ferrocenyl ligands via a methoxy directed *ortho*-lithiation.[3]

2. Results and discussion

2.1. Synthesis of the *P,N*-ligands

The key intermediates **5a–c** were readily accessible by acylation of ferrocene **1** with acid chlorides **2a–c**.[4] The resulting ferrocenyl ketones **3a–c** underwent a smooth CBS-reduction providing the ferrocenyl alcohols **4a–c** with high enantioselectivity.[5] These were converted into the corresponding methyl ethers **5a–c** by treatment with methanol in the presence of acetic acid with complete retention of configuration.[6] After recrystallization from methanol, the enantiomerically pure ethers **5a–c** were obtained (Scheme 1). These are key intermediates, as the methoxy group allows directed *ortho*-lithiation of the functionalized cyclopentadienyl ring with very high diastereoselectivity (>96% de).[7] Furthermore, the methoxy function also serves as a leaving group in nucleophilic substitution reactions in acidic media which also proceed with complete retention of configuration.

Next, the methyl ethers **5a–c** were metalated with *tert*-butyllithium and transmetalated to the corresponding zinc compounds, which were submitted to a palladium(0)-catalyzed cross-coupling reaction (Negishi-coupling) with various aryl iodides.[8] We have already reported the use of 2-iodopyrimidine and 2-iodopyridine for such cross-couplings.[3] Herein, we report an extension of the scope of the reaction to 2-iodoquino-



2a : Ar = Ph
2b : Ar = *o*-Tol
2c : Ar = 3,5-Xylyl

3a : 71 %
3b : 81 %
3c : 67 %

4a : 94 %; 98 % *ee*
4b : 94 %; 93 % *ee*
4c : 87 %; 97 % *ee*

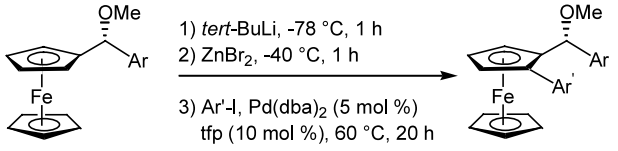
5a : 93 %; >99.8 % *ee*
5b : 63 %; >99.8 % *ee*
5c : 88 %; >99.8 % *ee*

Scheme 1. Preparation of chiral (ferrocenyl)benzylic methyl ethers **5a–c**.

* Corresponding author. Tel.: +49 (0)89 2180 7681; fax: +49 (0)89 2180 7680; e-mail: paul.knochel@cup.uni-muenchen.de

0957-4166/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
PII: S0957-4166(02)00827-3

line (Scheme 2 and Table 1) and the preparation of nine new ligands.



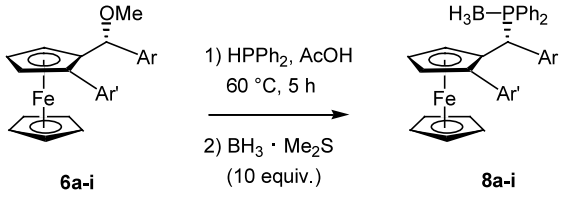
5a : Ar = Ph
5b : Ar = o-Tol
5c : Ar = 3,5-Xylyl

Scheme 2. *ortho*-Metalation of the methyl ethers **5a–c**, transmetalation and cross-coupling reaction.

The cross-coupling products **6a–i** underwent a nucleophilic substitution reaction with diphenylphosphine. The resulting *P*,*N*-ligands **7a–i** were converted in situ into their borane complexes **8a–i** which could be handled easily in air and purified by conventional column chromatography (Scheme 3 and Table 2).[9] For use in asymmetric catalysis, the ligands were freshly deprotected by repeated treatment with diethylamine.[10]

Table 1. Yields of the cross-coupling reactions

Ar′	Ar = Phenyl (%)	Ar = *o*-Tolyl (%)	Ar = 3,5-Xylyl (%)
2-Pyrimidyl	**6a**: 74	**6b**: 84	**6c**: 85
2-Pyridyl	**6d**: 60	**6e**: 73	**6f**: 83
2-Quinolyl	**6g**: 68	**6h**: 83	**6i**: 78



Scheme 3. Phosphination and protection of the ligands as borane complexes.

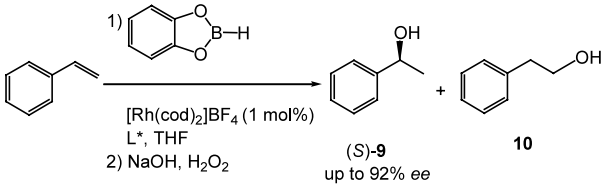
Table 2. Isolated yields of the protected ligands

Ar′	Ar = Phenyl (%)	Ar = *o*-Tolyl (%)	Ar = 3,5-Xylyl (%)
2-Pyrimidyl	**8a**: 54	**8b**: 29	**8c**: 17
2-Pyridyl	**8d**: 91	**8e**: 99	**8f**: 88
2-Quinolyl	**8g**: 31	**8h**: 76	**8i**: 33

2.2. Asymmetric catalysis

We examined the scope of these compounds as ligands in Pd-catalyzed asymmetric allylic alkylation[11] and in Rh-catalyzed asymmetric hydroboration.[12a–f]

The Rh-catalyzed addition of catecholborane to styrene (Scheme 4) afforded the alcohols **9** and **10** after oxidation with hydrogen peroxide. In preliminary studies, we varied the reaction conditions to minimize the amount of linear alcohol **10** formed and to maximize conversion of the reaction and enantiomeric excess of the branched alcohol **9** (Table 3). Entries 1 and 2 show that the use of 2 mol% ligand compared to 1.1 mol% led to improved regio- and stereoselectivity, but lower conversion. The hydroboration reaction using ligand **7a** displayed high temperature dependence. At −35°C (entry 3), this reaction was less stereoselective, while the conversion was not increased. Ligand **7d** behaved differently, suggesting that ligand **7a** decomposed more readily. We have now tested all other ligands at −45°C, using 2 mol% ligand (Table 4). The results can be clearly divided into three groups. The ligands **7a–c** (entries 1–3), bearing the pyrimidyl moiety, showed good regioselectivity, while conversion and enantioselectivity were only moderate, whereas ligands **7g–i** (entries 7–9) with the quinolyl moiety gave high conversion and good enantioselectivity, along with low regioselectivity. The ligands **7d** and **7e** (entries 4 and 5) occupy a medium position, while ligands **7f** (entry 6) gave only poor results. In conclusion, **7g** was the best ligand (92% ee with full conversion), although the regioselectivity was only modest.



Scheme 4. Rhodium-catalyzed hydroboration of styrene.

The Pd-catalyzed allylation of dimethyl malonate with the 1,3-diphenylallyl system (Scheme 5) was carried out with ligand **7a** between 22°C and 0°C. Ligand **7a** induced very high enantioselectivity at 0°C, but the conversion was low (Table 5, entry 2). All other ligands were tested at 22°C (Table 5). The enantioselectivity decreased with increasing steric bulk of the substituent on the α-carbon (**7a–c** and **7g–i** entries 1, 3, 4 and 8–10), with pyrimidyl or quinolyl as the *N*-donor. With pyridyl as *N*-donor, the situation is changed and the enantioselectivty increases with the steric hindrance (**7d–f**, entries 5–7). In conclusion, the best results were obtained with ligand **7f** (94% ee, 88% isolated yield).

3. Conclusion

We have prepared a range of nine *P*,*N*-ferrocenyl ligands and showed their utility in the Rh-catalyzed hydroboration and the Pd-catalyzed allylic alkylation. The results of this study show that fine-tuning of the ligands has a significant influence on their performance.

Table 3. Rhodium-catalyzed hydroboration of styrene: optimization of reaction conditions

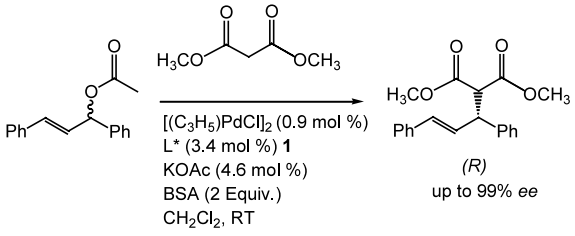
Entry	Ligand	Temperature (°C)	Reaction time (h)	Conversion[b] (%)	Enantioselectivity[a] (% ee)	Regioselectivity[b] (branched:linear)
1	**7a** (1.1 mol%)	−45	19	86	41	92:8
2	**7a** (2 mol%)	−45	19	74	57	97:3
3	**7a** (2 mol%)	−35	39	71	25	65:35
4	**7d** (2 mol%)	−45	16	75	61	87:13
5	**7d** (2 mol%)	−35	39	77	62	85:15

[a] The enantiomeric excess was determined by HPLC (column: Chiracel OD-H). The absolute configuration was established by comparison with literature data.
[b] The ratio of isomers and conversion was determined by GC.

Table 4. Rhodium-catalyzed hydroboration of styrene

Entry	Ligand[a]	Reaction time (h)	Conversion (%)	Enantioselectivity[b] (% ee)	Regioselectivity[c] (branched:linear)
1	**7a**	19	74	57	97:3
2	**7b**	16	52	55	87:13
3	**7c**	16	53	59	90:10
4	**7d**	16	75	61	87:13
5	**7e**	14	54	80	84:16
6	**7f**	14	22	32	57:43
7	**7g**	16	>99	92	64:36
8	**7h**	16	92	82	68:32
9	**7i**	16	>99	86	65:35

[a] Reaction conditions: 2 mol% ligand, −45°C
[b] The enantiomeric excess was determined by HPLC (column: Chiracel OD-H). The absolute configuration was established by comparison with literature data.
[c] The ratio of isomers was determined by GC.



Scheme 5. Palladium-catalyzed allylic alkylation.

Table 5. Palladium-catalyzed allylic alkylation

Entry	Ligand[a]	Yield[c] (%)	Enantioselectivity[d] (% ee)
1	**7a**	94	92
2[b]	**7a**	21	>99
3	**7b**	92	86
4	**7c**	58	89
5	**7d**	59	87
6	**7e**	73	93
7	**7f**	88	94
8	**7g**	76	91
9	**7h**	76	85
10	**7i**	93	56

[a] Reaction conditions: temperature 22°C, reaction time 20 h.
[b] Temperature 0°C.
[c] Isolated yield after purification by column chromatography.
[d] The enantiomeric excess was determined by HPLC (column: Chiracel OD-H). The absolute configuration was established by comparison with literature data.

4. Experimental

All reactions were carried out under argon using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 300 instrument. ^{31}P NMR spectra were recorded on a Varian Mercury 200 instrument. Chemical shifts (δ) are given as ppm relative to the residual solvent peak. IR spectra were recorded on a Perkin–Elmer 1420 IR spectrometer. Mass spectra were recorded on a Finnnigan MAT 95 Q spectrometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Column chromatography was performed on Merck silica gel 60 (230–400 mesh ASTM). Thin-layer chromatography was performed on Merck TLC-plates silica gel 60 F-254. Enantiomeric excesses were determined by HPLC. Chiralcel OD-H and OD (Daicel Chemical Industries) colums were used with *n*-heptane/*i*-propanol as a mobile phase and detection by a diode array UV–vis detector at 214 nm.

4.1. Acylation of ferrocene

4.1.1. Benzoylferrocene, 3a. Aluminium(III) chloride (7.33 g, 55.0 mmol) was added to a solution of benzoyl chloride (**2a**) (6.38 mL, 7.72 g, 55.0 mmol) in dichloromethane (40 mL) at 0°C. This solution was added to a suspension of ferrocene (**1**) (9.30 g, 50.0 mmol) in dichloromethane (100 mL) at 0°C over 30 min. The reaction mixture was stirred at rt and after 1.5 h, the mixture was cooled again to 0°C and was care-

fully hydrolyzed (**CAUTION**: gas evolution). The mixture was neutralized with satd $NaHCO_3$ solution and extracted with dichloromethane (300 mL). The organic layers were washed with satd $NaHCO_3$ solution, water and brine and dried over $MgSO_4$. The crude material was purified by column chromatography (*n*-pentane/diethyl ether 6:1). Benzoylferrocene **3a** was obtained as a red solid (10.34 g, 35.6 mmol, 71%); mp 106°C; IR (KBr): $\tilde{\nu}$ 3092 (w), 1627 (s), 1376 (m), 1289 (s), 1058 (m), 724 (s); ^{1}H NMR ($CDCl_3$): δ 7.92–7.87 (m, 2H), 7.57–7.44 (m, 3H), 4.91 (dd, $J=1.8$ Hz, 2H), 4.58 (dd, $J=1.8$ Hz, 2H), 4.21 (s, 5H); ^{13}C NMR ($CDCl_3$): δ 199.1, 139.8, 131.4 (CH), 128.2 (CH), 128.0 (CH), 78.1, 72.5 (CH), 71.5 (CH), 70.2 (CH); MS (EI, 70 eV) *m*/*z* (%): 290 (M^+, 100), 262 (2).

4.1.2. (2-Methylbenzoyl)ferrocene, 3b. Prepared according to the procedure described above from ferrocene **1** (9.30 g, 50.0 mmol), aluminium(III) chloride (7.33 g, 55.0 mmol) and 2-methylbenzoyl chloride (**2b**) (7.20 mL, 8.50 g, 55.0 mmol) with a reaction time of 5 h and isolated as a red solid (12.34 g, 40.6 mmol, 81%); mp 79°C; IR (film): $\tilde{\nu}$ 3097 (m), 1644 (s), 1444 (s), 1376 (s), 1295 (s), 1277 (s), 746 (s), 484 (s); ^{1}H NMR ($CDCl_3$): δ 7.60–7.56 (m, 1H), 7.43–7.37 (m, 1H), 7.32–7.27 (m, 2H), 4.79 (dd, $J=2.0$ Hz, 2H), 4.60 (dd, $J=2.0$ Hz, 2H), 4.29 (s, 5H), 2.45 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 202.2, 139.9, 135.7, 130.9 (CH), 129.7 (CH), 127.4 (CH), 124.9 (CH), 79.4, 72.5 (CH), 71.2 (CH), 69.9 (CH), 19.8 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 304 (M^+, 100), 91 (17); HRMS calcd for $C_{18}H_{16}FeO$: 304.0551. Observed: 304.0550.

4.1.3. (3,5-Dimethylbenzoyl)ferrocene, 3c. Prepared according to the procedure described above from ferrocene (**1**) (9.30 g, 50.0 mmol), aluminium(III) chloride (7.33 g, 55.0 mmol) and 3,5-dimethylbenzoyl chloride (**2c**) (9.28 g, 55.0 mmol) with a reaction time of 22 h and isolated as a red solid (10.71 g, 33.7 mmol, 67%); mp 88°C; IR (KBr): $\tilde{\nu}$ 2916 (m), 1640 (s), 1446 (s), 1249 (s), 766 (s); ^{1}H NMR ($CDCl_3$): δ 7.51–7.23 (m, 2H), 7.18 (m, 1H), 4.90 (dd, $J=2.0$ Hz, 2H), 4.57 (dd, $J=2.0$ Hz, 2H), 4.20 (s, 5H), 2.40 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 199.4, 139.9, 137.7, 133.1 (CH), 125.9 (CH), 78.4, 72.3 (CH), 71.5 (CH), 70.2 (CH), 21.3 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 318 (M^+, 100), 105 (19). HRMS calcd for $C_{19}H_{18}FeO$: 318.0707. Observed: 318.0705.

4.2. Reduction of the aryl ferrocenyl ketones 3a–c

4.2.1. (*R*)-(α-Hydroxyphenylmethyl)ferrocene, 4a. A solution of borane dimethyl sulfide complex (2.46 mL, 1.97 g, 25.9 mmol) in THF (25 mL) was prepared. The CBS catalyst (methyl oxazaborolidine; 1.49 g, 5.36 mmol, 0.3 equiv.) was dissolved in 20% of this solution. A solution of the benzoylferrocene (**3a**) (5.17 g, 17.8 mmol) in THF (30 mL) and the remaining borane dimethyl sulfide complex solution were added simultaneously at 0°C over 20 min. The disappearance of the red coloured ketone indicated the reaction progress. After complete reduction methanol (4 mL, **CAUTION**: gas evolution) was added dropwise. The reaction mixture was hydrolyzed with satd NH_4Cl solution and extracted with diethyl ether (150 mL). The organic layers were washed with water and brine and dried over $MgSO_4$. The crude product was purified by column chromatography (*n*-pentane/diethyl ether 4:1). Alcohol **4a** was isolated as a red solid (4.87 g, 16.7 mmol, 94%, 98% ee (*R*)). HPLC analysis (OD-H, 92% *n*-heptane, 8% *i*-propanol, 0.6 mL/min): retention time (min) 21.1 (*R*), 33.3 (*S*); mp 89°C; $[\alpha]_D=-103.0$ (*c* 0.92, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3082 (m), 1494 (m), 1453 (m), 1236 (m), 1182 (m), 1104 (m), 1048 (m), 1017 (m), 1000 (m), 815 (m), 720 (m), 700 (s); ^{1}H NMR ($CDCl_3$): δ 7.42–7.23 (m, 5H), 5.48 (d, $J=3.1$ Hz, 1H), 4.23–4.19 (m, 9H), 2.47 (d, $J=3.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 143.2, 128.2 (CH), 127.4 (CH), 126.2 (CH), 94.2, 72.0 (CH), 68.4 (CH), 68.1 (CH), 68.1 (CH), 67.4 (CH), 66.0 (CH); MS (EI, 70 eV) *m*/*z* (%): 292 (M^+, 38), 275 (81), 153 (100); HRMS calcd for $C_{17}H_{16}FeO$: 292.0551. Observed: 292.0576.

4.2.2. (*R*)-(α-Hydroxy(2-methylphenyl)methyl)ferrocene, 4b. Prepared according to the procedure described above from (2-methylbenzoyl)ferrocene (**3b**) (5.63 g, 18.5 mmol) with borane dimethyl sulfide complex (2.50 mL, 2.00 g, 26.3 mmol) and CBS-catalyst (1.54 g, 5.55 mmol). **4b** was isolated as a yellow solid (5.34 g, 17.4 mmol, 94%, 93% ee (*R*)). HPLC analysis (OD-H, 92% *n*-heptane, 8% *i*-propanol, 0.6 mL/min): retention time (min) 15.0 (*R*), 16.5 (*S*); mp 51°C; $[\alpha]_D=-146.7$ (*c* 1.06, $CHCl_3$); IR (film): $\tilde{\nu}$ 3094 (m), 1488 (m), 1462 (m), 1411 (m), 1106 (s), 1043 (s), 1002 (s), 819 (s), 741 (s), 485 (s); ^{1}H NMR ($CDCl_3$): δ 7.52–7.47 (m, 1H), 7.25–7.10 (m, 3H), 5.63 (d, $J=4.0$ Hz, 1H), 4.28–4.10 (m, 9H), 2.53 (d, $J=4.0$ Hz, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 141.4, 135.0, 130.1 (CH), 127.2 (CH), 125.9 (CH), 125.8 (CH), 94.6, 68.7 (CH), 68.4 (CH), 68.1 (CH), 67.8 (CH), 67.4 (CH), 66.9 (CH), 19.2 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 306 (M^+, 20), 304 (15), 290 (100); HRMS calcd for $C_{18}H_{18}FeO$: 306.0707. Observed: 306.0715.

4.2.3. (*R*)-(α-Hydroxy(3,5-dimethylphenyl)methyl)-ferrocene, 4c. Prepared according to the procedure described above from (3,5-dimethylbenzoyl)ferrocene **3c** (3.28 g, 10.3 mmol) with borane dimethyl sulfide complex (1.42 mL, 1.14 g, 15.0 mmol) and CBS-catalyst (0.800 g, 2.89 mmol). **4c** was isolated as a yellow oil (2.87 g, 8.95 mmol, 87%, 97% ee (*R*)). HPLC analysis (OD-H, 92% *n*-heptane, 8% *i*-propanol, 0.6 mL/min): retention time (min) 13.8 (*R*), 22.4 (*S*); $[\alpha]_D=-77.9$ (*c* 1.25, $CHCl_3$); IR (film): $\tilde{\nu}$ 2917 (m), 1608 (m), 1465 (m), 1412 (m), 1378 (m), 1106 (s), 1042 (s), 1022 (s), 1001 (s), 908 (s), 854 (s), 818 (s), 487 (s); ^{1}H NMR ($CDCl_3$): δ 7.00 (s, 2H), 6.89 (s, 1H), 5.11 (d, $J=3.2$ Hz, 1H), 4.24–4.05 (m, 9H), 2.41 (d, $J=3.2$ Hz, 1H), 2.30 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 143.2, 137.7, 129.1 (CH), 124.0 (CH), 94.4, 72.1 (CH), 68.4 (CH), 68.0 (CH), 68.0 (CH), 67.5 (CH), 65.8 (CH), 21.3 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 320 (M^+, 41), 318 (41), 304 (100), 255 (25); HRMS calcd for $C_{19}H_{20}FeO$: 320.0864. Observed: 320.0866.

4.3. Methylation of the alcohols 4a–c

4.3.1. (*R*)-(α-Methoxyphenylmethyl)ferrocene, 5a. A solution of (*R*)-(α-hydroxyphenylmethyl)ferrocene **4a** (1.62 g, 5.54 mmol, 98% ee) in methanol (20 mL) with acetic acid (0.73 mL) was stirred 12 h at rt. The reaction mixture was neutralized with satd aq. $NaHCO_3$ solution and methanol was removed under reduced pressure. The remaining suspension was extracted with diethyl ether (150 mL). The organic layers were washed with water and brine and dried over $MgSO_4$. The crude product was recrystallized from methanol (11 mL). The ether **5a** (1.58 g, 5.16 mmol, 93%) was obtained enantiomerically pure. HPLC analysis (OD, 95% *n*-heptane, 5% *i*-propanol, 0.6 mL/min): retention time (min) 15.7 (*R*), 27.9 (*S*); >99.8% ee (*R*); mp 94°C; $[\alpha]_D = +33.8$ (*c* 1.09, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3099 (m), 2920 (m), 1452 (m), 1080 (s), 1070 (s), 746 (s), 706 (s); ^{1}H NMR ($CDCl_3$): δ 7.46–7.27 (m, 5H), 5.02 (s, 1H), 4.29–4.25 (m, 1H), 4.16–4.12 (m, 1H), 4.11–4.07 (m, 1H), 4.06 (s, 5H), 3.98–3.94 (m, 1H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 141.4, 128.1 (CH), 127.6 (CH), 127.3 (CH), 90.2, 82.6 (CH), 68.7 (CH), 67.9 (CH), 67.9 (CH), 67.8 (CH), 67.0 (CH), 56.9 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 306 (M^+, 46), 290 (13), 276 (16), 211 (20), 153 (100), 122 (16); HRMS calcd for $C_{18}H_{18}FeO$: 306.0707. Observed: 306.0708.

4.3.2. (*R*)-(α-Methoxy(2-methylphenyl)methyl)ferrocene, 5b. A solution of (*R*)-(α-hydroxy(2-methylphenyl)methyl)ferrocene (**4b**) (4.50 g, 14.1 mmol, 97% ee) in methanol (50 mL) with acetic acid (2.5 mL) was stirred 13 h at rt. Following the procedure described above, enantiomerically pure **5b** (2.11 g, 6.59 mmol, 63%) was obtained after recrystallization from methanol (14 mL). HPLC analysis (OD, 95% *n*-heptane, 5% *i*-propanol, 0.6 mL/min): retention time (min) 8.1 (*R*), 11.8 (*S*); >99.8% ee (*R*); mp 54°C; $[\alpha]_D = -20.3$ (*c* 0.76, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3092 (m), 2936 (m), 1485 (m), 1459 (m), 1105 (s), 1081 (s), 815 (s), 750 (s), 494 (s); ^{1}H NMR ($CDCl_3$): δ 7.46–7.41 (m, 1H), 7.27–7.12 (m, 3H), 5.26 (s, 1H), 4.19–4.15 (m, 1H), 4.12–4.06 (m, 2H), 4.10 (s, 5H), 4.07–4.04 (m, 1H), 3.31 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 139.8, 135.6, 130.4 (CH), 127.3 (CH), 127.2 (CH), 125.9 (CH), 90.4, 79.3 (CH), 68.7 (CH), 67.8 (CH), 67.6 (CH), 67.3 (CH), 66.6 (CH), 56.8 (CH_3), 19.5 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 320 (M^+, 100), 290 (17), 225 (20), 167 (28), 122 (21); HRMS calcd for $C_{19}H_{20}FeO$: 320.0864. Observed: 320.0837.

4.3.3. (*R*)-(α-Methoxy(3,5-dimethylphenyl)methyl)-ferrocene, 5c. A solution of (*R*)-(α-hydroxy(3,5-dimethylphenyl)methyl)ferrocene (**4c**) (3.20 g, 10.5 mmol, 93% ee) in methanol (35 mL) with acetic acid (1.6 mL) was stirred 13 h at rt. Following the procedure described above, enantiomerically pure **5c** (4.14 g, 12.4 mmol, 88%) was obtained after recrystallization from methanol (25 mL). HPLC analysis (OD, 95% *n*-heptane, 5% *i*-propanol, 0.6 mL/min): retention time (min) 8.5 (*R*), 23.3 (*S*); >99.8% ee (*R*); mp 75°C; $[\alpha]_D = +38.0$ (*c* 1.09, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 2920 (m), 1608 (m), 1104 (s), 1092 (s), 784 (m), 698 (m), 496 (s); ^{1}H NMR ($CDCl_3$): δ 7.00 (s, 2H), 6.93 (s, 1H), 4.93 (s, 1H), 4.29–4.25 (m, 1H), 4.14–4.10 (m, 1H), 4.09–4.04 (m, 1H), 4.07 (s, 5H), 3.99–3.96 (m, 1H), 3.31 (s, 3H), 2.35 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 141.4, 137.5, 129.2 (CH), 125.1 (CH), 90.5, 82.6 (CH), 68.7 (CH), 67.8 (CH), 67.7 (CH), 67.6 (CH), 67.0 (CH), 56.9 (CH_3), 21.4 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 334 (M^+, 52), 318 (20), 304 (24), 239 (28), 182 (85), 167 (100), 152 (59); HRMS calcd for $C_{20}H_{22}FeO$: 334.1020. Observed: 334.1028.

4.4. Cross-coupling reactions

2-Iodopyrimidine,[13] 2-iodopyridine[14] and 2-iodoquinoline[15] were prepared according to literature procedures.

4.4.1. (R_{Fc})-1-(2-Pyrimidyl)-2-(α-(*R*)-methoxy(phenyl)-methyl)ferrocene, 6a. A solution of (*R*)-(α-methoxy-(phenyl)methyl)ferrocene (**5a**) (464 mg, 1.52 mmol) in diethyl ether (25 mL) was cooled to −78°C. *tert*-Butyllithium in pentane (1.5 M, 1.10 mL, 1.65 mmol, 1.1 equiv.) was added dropwise, the mixture was warmed up to rt and stirred for 1 h. After the mixture had been cooled to −40°C a solution of $ZnBr_2$ in THF (1.3 M, 1.50 mL, 1.95 mmol, 1.3 equiv.) was added. The mixture was warmed up to rt and stirred for 1 h. The solvent was then removed under reduced pressure.

For the cross-coupling reaction, a solution of the catalyst was prepared in THF (2 mL) from bis(dibenzylideneacetone)palladium(0) (28.6 mg, 0.050 mmol) and tris-*o*-furylphosphine (23.0 mg, 0.10 mmol) and stirred 5 min at rt. 2-Iodopyrimidine (206 mg, 1.00 mmol) was added in THF (2 mL) and the mixture was stirred for a further 5 min. The zinc reagent prepared above was added as solution in THF (6 mL). The resulting mixture was heated to 60°C for 20 h. After addition of water, the mixture was extracted with diethyl ether (60 mL). The organic layers were washed with water and brine and dried over $MgSO_4$. The crude material was purified by column chromatography (*n*-pentane/diethyl ether 3:1) to give **6a** as a red oil (285 mg, 0.742 mmol, 74%); $[\alpha]_D = -207.8$ (*c* 0.49, $CHCl_3$); IR: (film): $\tilde{\nu}$ 2975 (m), 1569 (s), 1555 (s), 1485 (s), 1398 (s), 1085 (s), 745 (s), 704 (s); ^{1}H NMR ($CDCl_3$): δ 8.69 (d, $^3J = 4.9$ Hz, 2H), 7.71–7.66 (m, 2H), 7.50–7.43 (m, 2H), 7.40–7.32 (m, 1H), 7.07 (t, $^3J = 4.9$ Hz, 1H), 6.42 (s, 1H), 5.18 (dd, $J = 2.5$ Hz, 1.4 Hz, 1H), 4.35 (dd, $J = 2.5$ Hz, 1H), 4.12 (dd, $J = 2.5$ Hz, 1H), 3.82 (s, 5H), 3.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 156.4 (CH), 141.8, 128.1 (CH), 127.9 (CH), 127.5 (CH), 117.2 (CH), 90.7, 80.1 (CH), 79.5, 71.7 (CH), 70.5 (CH), 70.3 (CH), 69.4 (CH), 56.9 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 384 (M^+, 100), 369 (14), 354 (25), 319 (73), 289 (60), 287 (23), 231 (66), 211 (40); HRMS calcd for $C_{22}H_{20}FeN_2O$: 384.0925. Observed: 384.0921.

4.4.2. (R_{Fc})-1-(2-Pyrimidyl)-2-(α-(*R*)-methoxy(2-methylphenyl)methyl)ferrocene, 6b. Prepared according to the procedure described above from (*R*)-(α-methoxy(2-methylphenyl)methyl)ferrocene **5b** (640 mg, 2.00 mmol), *tert*-BuLi solution (1.47 mL, 2.20 mmol) and $ZnBr_2$ solution (2.00 mL, 2.60 mmol). The cross-

coupling was performed with $Pd(dba)_2$ (38.0 mg, 0.066 mmol), P(*o*-Fur)$_3$ (30.6 mg, 0.132 mmol) and 2-iodopyrimidine (272 mg, 1.32 mmol) and the product **6b** was isolated as a red solid (444 mg, 1.11 mmol, 84%); mp 89°C; $[\alpha]_D = -221.8$ (*c* 0.44, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 2918 (m), 1569 (s), 1556 (s), 1482 (s), 1399 (s), 1068 (s), 758 (m), 498 (m); ^{1}H NMR ($CDCl_3$): δ 8.68 (d, $^3J = 4.7$ Hz, 2H), 7.70–7.66 (m, 1H), 7.34–7.24 (m, 3H), 7.06 (t, $^3J = 4.7$ Hz, 1H), 6.71 (s, 1H), 5.19 (dd, $J = 2.5$ Hz, 1.5 Hz, 1H), 4.40 (dd, $J = 2.5$ Hz, 1H), 4.34 (dd, $J = 2.5$ Hz, 1.5 Hz, 1H), 3.78 (s, 5H), 3.18 (s, 3H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.2, 156.4 (CH), 139.9, 136.7, 130.6 (CH), 128.5 (CH), 127.3 (CH), 125.6 (CH), 117.2 (CH), 89.7, 79.7 (CH), 77.5, 71.4 (CH), 70.4 (CH), 70.3 (CH), 69.6 (CH), 56.4 (CH_3), 20.5 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 398 (M^+, 94), 383 (7), 368 (66), 333 (63), 303 (24), 301 (26), 245 (100), 165 (47); HRMS calcd for $C_{23}H_{22}FeN_2O$: 398.1082. Observed: 398.1088.

4.4.3. (R_{Fc})-1-(2-Pyrimidyl)-2-(α-(*R*)-methoxy(3,5-dimethylphenyl)methyl)ferrocene, 6c. Prepared according to the procedure described above from (*R*)-(α-methoxy(3,5-dimethylphenyl)methyl)ferrocene **5c** (1.00 g, 3.00 mmol), *tert*-BuLi solution (2.20 mL, 3.30 mmol) and $ZnBr_2$ solution (3.30 mL, 3.90 mmol). The cross-coupling was performed with $Pd(dba)_2$ (57.5 mg, 0.10 mmol), P(*o*-Fur)$_3$ (46.4 mg, 0.20 mmol) and 2-iodopyrimidine (412 mg, 2.00 mmol) and the product **6c** was isolated as a red oil (702 mg, 1.70 mmol, 85%); $[\alpha]_D = -173.1$ (*c* 1.33, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 2922 (m), 1569 (s), 1554 (s), 1484 (s), 1399 (s), 1085 (m); ^{1}H NMR ($CDCl_3$): δ 8.68 (d, $^3J = 4.9$ Hz, 2H), 7.29 (s, 2H), 7.06 (t, $^3J = 4.9$ Hz, 1H), 7.00 (s, 1H), 6.35 (s, 1H), 5.17 (dd, $J = 2.7$ Hz, 1.8 Hz, 1H), 4.35 (dd, $J = 2.7$ Hz, 1H), 4.14 (dd, $J = 2.7$ Hz, 1.8 Hz, 1H), 3.84 (s, 5H), 3.26 (s, 3H), 2.41 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 170.2, 156.4 (CH), 141.5, 137.2, 129.0 (CH), 125.9 (CH), 117.2 (CH), 90.8, 80.0 (CH), 79.4, 71.8 (CH), 70.5 (CH), 70.3 (CH), 69.3 (CH), 56.9 (CH_3), 21.4 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 412 (M^+, 100), 397 (11), 382 (33), 347 (90), 317 (59), 315 (24), 260 (45), 211 (49); HRMS calcd for $C_{24}H_{24}FeN_2O$: 412.1238. Observed: 412.1246.

4.4.4. (R_{Fc})-1-(2-Pyridyl)-2-(α-(*R*)-methoxy(phenyl)-methyl)ferrocene, 6d. Prepared according to the procedure described above from (*R*)-(α-methoxy(phenyl)-methyl)ferrocene **5a** (464 mg, 1.52 mmol), *tert*-BuLi solution (1.10 mL, 1.65 mmol) and $ZnBr_2$ solution (1.50 mL, 1.95 mmol). The cross-coupling was performed with $Pd(dba)_2$ (28.6 mg, 0.050 mmol), P(*o*-Fur)$_3$ (23.0 mg, 0.10 mmol) and 2-iodopyridine (205 mg, 1.00 mmol) and the product **6d** was isolated as a red oil (230 mg, 0.600 mmol, 60%); $[\alpha]_D = -46.4$ (*c* 0.22, $CHCl_3$); IR (film): $\tilde{\nu}$ 2815 (w), 1586 (s), 1564 (m), 1490 (s), 1084 (s), 818 (m); ^{1}H NMR ($CDCl_3$): δ 8.81–8.62 (m, 1H), 7.69–7.33 (m, 7H), 7.16–7.09 (m, 2H), 6.07 (s, 1H), 4.75 (dd, $J = 2.7$ Hz, 1.5 Hz, 1H), 4.27 (dd, $J = 2.7$ Hz, 1H), 4.04 (dd, $J = 2.7$ Hz, 1.5 Hz, 1H), 3.85 (s, 5H), 3.17 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 159.6, 149.1 (CH), 141.4, 135.5 (CH), 128.0 (CH), 128.0 (CH), 127.5 (CH), 121.9 (CH), 120.5 (CH), 88.8, 83.8, 80.3 (CH), 70.3 (CH), 70.1 (CH), 69.0 (CH), 68.2 (CH), 56.6 (CH_3). MS (EI, 70 eV) *m*/*z* (%): 383 (M^+, 39), 368 (15), 353 (17), 318 (26), 288 (26), 286 (9), 244 (51), 230 (100), 186 (25); HRMS calcd for $C_{23}H_{21}FeNO$: 383.0973. Observed: 383.0964.

4.4.5. (R_{Fc})-1-(2-Pyridyl)-2-(α-(*R*)-methoxy(2-methylphenyl)methyl)ferrocene, 6e. Prepared according to the procedure described above from (*R*)-(α-methoxy(2-methylphenyl)methyl)ferrocene **5b** (640 mg, 2.00 mmol), *tert*-BuLi solution (1.47 mL, 2.20 mmol) and $ZnBr_2$ solution (2.00 mL, 2.60 mmol). The cross-coupling was performed with $Pd(dba)_2$ (38.0 mg, 0.066 mmol), P(*o*-Fur)$_3$ (30.6 mg, 0.132 mmol) and 2-iodopyridine (271 mg, 1.32 mmol) and the product **6e** was isolated as a red oil (381 mg, 0.959 mmol, 73%); $[\alpha]_D = -77.1$ (*c* 0.35, $CHCl_3$); IR (film): $\tilde{\nu}$ 2926 (m), 1586 (s), 1490 (s), 1420 (m), 1107 (m), 1080 (s), 747 (s); ^{1}H NMR ($CDCl_3$): δ 8.62 (ddd, $^3J = 4.9$ Hz, $^4J = 1.7$ Hz, $^5J = 0.8$ Hz, 1H), 7.68–7.56 (m, 2H), 7.54–7.49 (m, 1H), 7.34–7.22 (m, 3H), 7.12 (ddd, $^3J = 7.5$ Hz, $^4J = 4.9$ Hz, $^5J = 1.3$ Hz, 1H), 6.43 (s, 1H), 4.73 (dd, $J = 2.6$ Hz, 1.5 Hz, 1H), 4.30 (dd, $J = 2.6$ Hz, 1H), 4.24 (dd, $J = 2.6$ Hz, 1.5 Hz, 1H), 3.81 (s, 5H), 3.13 (s, 3H), 2.60 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 159.7, 148.8 (CH), 139.7, 136.6, 135.5 (CH), 130.6 (CH), 128.3 (CH), 127.3 (CH), 125.6 (CH), 122.0 (CH), 120.5 (CH), 88.3, 83.8, 77.6 (CH), 70.2 (CH), 69.8 (CH), 68.8 (CH), 68.3 (CH), 56.2 (CH_3), 20.3 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 397 (M^+, 35), 382 (12), 367 (18), 332 (41), 302 (13), 300 (24), 258 (18), 244 (100), 186 (19), 165 (22); HRMS calcd for $C_{24}H_{23}FeNO$: 397.1129. Observed: 397.1131.

4.4.6. (R_{Fc})-1-(2-Pyridyl)-2-(α-(*R*)-methoxy(3,5-dimethylphenyl)methyl)ferrocene, 6f. Prepared according to the procedure described above from (*R*)-(α-methoxy(3,5-dimethylphenyl)methyl)ferrocene (**5c**) (458 mg, 1.37 mmol), *tert*-BuLi solution (1.01 mL, 1.51 mmol) and $ZnBr_2$ solution (1.37 mL, 1.78 mmol). The cross-coupling was performed with $Pd(dba)_2$ (25.9 mg, 0.045 mmol), P(*o*-Fur)$_3$ (20.9 mg, 0.090 mmol) and 2-iodopyridine (186 mg, 0.900 mmol) and the product **6f** was isolated as a red oil (310 mg, 0.754 mmol, 83%); $[\alpha]_D = -40.9$ (*c* 0.22, $CHCl_3$); IR (film): $\tilde{\nu}$ 2922 (s), 1586 (s), 1490 (s), 1419 (m), 1083 (s), 815 (m), 786 (m); ^{1}H NMR ($CDCl_3$): δ 8.66–8.61 (m, 1H), 7.65–7.50 (m, 2H), 7.26 (s, 2H), 7.12 (ddd, $^3J = 7.3$ Hz, $^4J = 4.8$ Hz, $^5J = 1.2$ Hz, 1H), 7.00 (s, 1H), 5.96 (s, 1H), 4.75 (dd, $J = 2.5$ Hz 1.5 Hz, 1H), 4.26 (dd, $J = 2.5$ Hz, 1H), 4.06 (dd, $J = 2.5$ Hz, 1.5 Hz, 1H), 3.87 (s, 5H), 3.17 (s, 3H), 2.41 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 159.6, 149.1 (CH), 141.1, 137.3, 135.5 (CH), 129.0 (CH), 125.9 (CH), 122.0 (CH), 120.5 (CH), 88.9, 83.9, 80.3 (CH), 70.3 (CH), 70.2 (CH), 69.1 (CH), 68.1 (CH), 56.6 (CH_3), 21.5 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 411 (M^+, 34), 396 (14), 395 (14), 381 (17), 346 (46), 316 (23), 314 (13), 272 (38), 259 (100), 210 (21), 186 (20); HRMS calcd for $C_{25}H_{25}FeNO$: 411.1286. Observed: 411.1287.

4.4.7. (R_{Fc})-1-(2-Quinolyl)-2-(α-(*R*)-methoxy(phenyl)-methyl)ferrocene, 6g. Prepared according to the procedure described above from (*R*)-(α-methoxy(phenyl)-methyl)ferrocene **5a** (464 mg, 1.52 mmol), *tert*-BuLi solution (1.10 mL, 1.65 mmol) and $ZnBr_2$ solution (1.50

mL, 1.95 mmol). The cross-coupling was performed with $Pd(dba)_2$ (28.6 mg, 0.050 mmol), P(*o*-Fur)$_3$ (23.0 mg, 0.10 mmol) and 2-iodoquinoline (260 mg, 1.02 mmol) and the product **6g** was isolated as a red oil (299 mg, 0.690 mmol, 68%); $[\alpha]_D = +540$ (*c* 0.01, $CHCl_3$); IR (film): $\tilde{\nu}$ 2925 (m), 1617 (m), 1600 (s), 1507 (s), 1084 (s), 824 (m), 759 (m), 742 (m), 703 (m); ^{1}H NMR ($CDCl_3$): δ 8.17–8.05 (m, 2H), 7.80 (d, $^3J = 7.7$ Hz, $^4J = 1.2$ Hz, 1H), 7.75–7.64 (m, 4H), 7.55–7.47 (m, 3H), 7.42–7.36 (m, 1H), 6.43 (s, 1H), 4.87 (dd, $J = 2.6$ Hz, 1.4 Hz, 1H), 4.36 (dd, $J = 2.6$ Hz, 1H), 4.22 (dd, $J = 2.6$ Hz, 1.4 Hz, 1H), 3.82 (s, 5H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 160.1, 148.1, 141.9, 135.1 (CH), 129.2 (CH), 129.2 (CH), 128.0 (CH), 128.0 (CH), 127.5 (CH), 126.5, 125.5 (CH), 120.9 (CH), 89.7, 82.5, 80.3 (CH), 70.7 (CH), 70.4 (CH), 69.6 (CH), 68.8 (CH), 56.8 (CH_3). MS (EI, 70 eV) *m*/*z* (%): 433 (M^+, 39), 418 (31), 403 (100), 401 (26), 368 (69), 337 (56), 280 (63), 260 (30), 204 (17); HRMS calcd for $C_{27}H_{23}FeNO$: 433.1129. Observed: 433.1135.

4.4.8. (R_{Fc})-1-(2-Quinolyl)-2-(α-(*R*)-methoxy(2-methylphenyl)methyl)ferrocene, 6h. Prepared according to the procedure described above from (*R*)-(α-methoxy(2-methylphenyl)methyl)ferrocene (**5b**) (640 mg, 2.00 mmol), *tert*-BuLi solution (1.47 mL, 2.20 mmol) and $ZnBr_2$ solution (2.00 mL, 2.60 mmol). The cross-coupling was performed with $Pd(dba)_2$ (38.0 mg, 0.066 mmol), P(*o*-Fur)$_3$ (30.6 mg, 0.132 mmol) and 2-iodoquinoline (337 mg, 1.32 mmol) and the product **6h** was isolated as a red solid (492 mg, 1.10 mmol, 83%); mp 114°C; $[\alpha]_D = +742.1$ (*c* 0.47, $CHCl_3$); IR (film): $\tilde{\nu}$ 2918 (m), 1616 (m), 1600 (s), 1507 (s), 1081 (s), 824 (s), 748 (s); ^{1}H NMR ($CDCl_3$): δ 8.13–8.04 (m, 2H), 7.82–7.60 (m, 4H), 7.54–7.47 (m, 1H), 7.36–7.24 (m, 3H), 6.91 (s, 1H), 4.85 (dd, $J = 2.5$ Hz, 1.5 Hz, 1H), 4.34–4.09 (m, 2H), 3.78 (s, 5H), 3.24 (s, 3H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 160.3, 148.0, 140.4, 136.4, 135.1 (CH), 130.4 (CH), 129.3 (CH), 129.0 (CH), 127.8 (CH), 127.5 (CH), 126.4, 125.7 (CH), 125.5 (CH), 121.0 (CH), 89.1, 82.4, 76.7 (CH), 70.3 (CH), 69.4 (CH), 69.1 (CH), 56.5 (CH_3), 20.7 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 447 (M^+, 59), 432 (24), 417 (63), 429 (13), 382 (100), 350 (44), 294 (28), 260 (14), 248 (18); HRMS calcd for $C_{28}H_{25}FeNO$: 447.1286. Observed: 447.1286.

4.4.9. (R_{Fc})-1-(2-Quinolyl)-2-(α-(*R*)-methoxy(3,5-dimethylphenyl)methyl)ferrocene, 6i. Prepared according to the procedure described above from (*R*)-(α-methoxy(3,5-dimethylphenyl)methyl)ferrocene **5c** (458 mg, 1.37 mmol), *tert*-BuLi solution (1.01 mL, 1.51 mmol) and $ZnBr_2$ solution (1.37 mL, 1.78 mmol). The cross-coupling was performed with $Pd(dba)_2$ (25.9 mg, 0.045 mmol), P(*o*-Fur)$_3$ (20.9 mg, 0.090 mmol) and 2-iodoquinoline (231 mg, 0.906 mmol) and the product **6i** was isolated as a red solid (327 mg, 0.709 mmol, 78%); mp 56°C; $[\alpha]_D = +574.4$ (*c* 0.18, $CHCl_3$); IR (film): $\tilde{\nu}$ 2922 (m), 1617 (m), 1600 (s), 1507 (s), 1083 (s), 821 (m), 490 (m); ^{1}H NMR ($CDCl_3$): δ 8.16–8.05 (m, 2H), 7.79 (d, $^3J = 8.4$ Hz, 1H), 7.74–7.64 (m, 2H), 7.54–7.47 (m, 1H), 7.32 (s, 2H), 7.01 (s, 1H), 6.32 (s, 1H), 4.88–4.84 (m, 1H), 4.35 (dd, $J = 2.6$ Hz, 1H), 4.25–4.21 (m, 1H), 3.84 (s, 5H), 3.30 (s, 3H), 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 160.2, 148.2, 141.7, 137.3, 135.0 (CH), 129.2 (CH), 129.0 (CH), 127.5 (CH), 126.5, 125.9 (CH), 125.5 (CH), 121.0 (CH), 89.9, 82.5, 80.3 (CH), 70.8 (CH), 70.4 (CH), 69.6 (CH), 68.7 (CH), 56.9 (CH_3), 21.5 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 461 (M^+, 28), 446 (19), 431 (100), 429 (23), 396 (64), 365 (64), 309 (58), 260 (27), 204 (16); HRMS calcd for $C_{29}H_{27}FeNO$: 461.1442. Observed: 461.1445.

4.5. Synthesis of the protected ligands 8a–i

4.5.1. (R_{Fc})-1-(2-Pyrimidyl)-2-(α-(*R*)-(diphenylphosphino)phenylmethyl)ferrocene, 8a. Diphenylphosphine (0.14 mL, 150 mg, 0.81 mmol) was added to a solution of **6a** (261 mg, 0.679 mmol) in acetic acid (6.4 mL). The mixture was heated to 60°C for 6 h. After the mixture had been cooled to rt, the solvent was removed under reduced pressure and the residual oil was dissolved in THF (10 mL). Borane dimethyl sulfide complex (1 mL) was added dropwise and the mixture was stirred 14 h at rt. After careful hydrolysis, the mixture was extracted with dichloromethane (60 mL) and the organic layers were washed with water and brine and dried over $MgSO_4$. The crude product was purified by column chromatography (*n*-pentane/diethyl ether 5:1). **8a** was obtained as a red solid (204 mg, 0.369 mmol, 54%); mp 193°C; $[\alpha]_D = -161.8$ (*c* 0.88, $CHCl_3$); IR: (KBr): $\tilde{\nu}$ 3059 (w), 2390 (m), 1570 (s), 1555 (s), 1479 (s), 1400 (s), 701 (s); ^{1}H NMR ($CDCl_3$): δ 8.53 (d, $^3J = 4.8$ Hz, 2H), 7.88–7.79 (m, 4H), 7.41–6.84 (m, 13H), 5.02–4.98 (m, 1H), 4.87 (dd, $J = 2.8$ Hz, 1.7 Hz, 1HHH), 4.47 (dd, $J = 2.8$ Hz, 1H), 3.52 (s, 5H); ^{13}C NMR ($CDCl_3$): δ 170.4, 155.9 (CH), 139.4 (d, $J = 2.9$ Hz), 133.4 (CH, d, $J = 8.2$ Hz), 132.9 (CH, d, $J = 8.6$ Hz), 131.1 (CH, d, $J = 5.9$ Hz), 130.9 (CH, d, $J = 2.3$ Hz), 130.2 (CH, d, $J = 2.4$ Hz), 128.3 (CH, d, $J = 9.4$ Hz), 127.8 (CH, d, $J = 1.2$ Hz), 127.1 (d, $J = 1.7$ Hz), 127.0 (CH, d, $J = 9.4$ Hz), 116.7 (CH), 88.0 (d, $J = 6.3$ Hz), 79.5 (d, $J = 1.8$ Hz), 73.3 (CH, d, $J = 2.8$ Hz), 70.2 (CH), 69.9 (CH), 68.2 (CH), 39.9 (CH, d, $J = 29.2$ Hz); ^{31}P NMR ($CDCl_3$): δ +25.8 (s, br); MS (EI, 70 eV) *m*/*z* (%): 552 (M^+, 1), 538 (4), 353 (100), 287 (9), 231 (13); HRMS calcd for $C_{33}H_{30}BFeN_2P$: 552.1589. Observed: 552.1615.

4.5.2. (R_{Fc})-1-(2-Pyrimidyl)-2-(α-(*R*)-(diphenylphosphino)(2-methylphenyl)methyl)ferrocene, 8b. Prepared according to the procedure described above from **6b** (351 mg, 0.881 mmol) and diphenylphosphine (0.18 mL, 193 mg, 1.04 mmol). **8b** was isolated as a red solid (154 mg, 0.256 mmol, 29%); mp 184°C; $[\alpha]_D = -170.3$ (*c* 0.57, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3056 (w), 2391 (m), 1570 (s), 1555 (s), 1480 (s), 1400 (s), 696 (m); ^{1}H NMR ($CDCl_3$): δ 8.52 (d, $^3J = 4.8$ Hz, 2H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.63–7.55 (m, 2H), 7.38–7.08 (m, 9H), 7.03–6.90 (m, 4H), 4.99–4.95 (m, 1H), 4.91 (dd, $J = 2.6$ Hz, 1.7 Hz, 1H), 4.48 (dd, $J = 2.6$ Hz, 1H), 3.52 (s, 5H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.2, 155.9 (CH), 138.2, (d, $J = 2.4$ Hz), 136.8 (d, $J = 6.4$ Hz), 133.5 (CH, d, $J = 8.2$ Hz), 133.1 (CH, d, $J = 8.2$ Hz), 131.2 (CH, d, $J = 4.6$ Hz), 130.7 (CH, d, $J = 2.9$ Hz), 130.5 CH, d, $J = 2.4$ Hz), 130.1 (CH), 128.5 (d, $J = 3.0$ Hz), 128.0 (CH, d, $J = 9.4$ Hz), 127.1 (CH, d, $J = 10.0$ Hz), 125.5 (CH, d, $J = 1.8$ Hz), 116.8 (CH), 87.7 (C, d, $J = 8.9$ Hz), 79.6 (d,

$J=1.7$ Hz), 73.6 (CH, d, $J=3.5$ Hz), 70.1 (CH), 69.9 (CH), 68.3 (CH), 35.5 (CH, d, $J=28.2$ Hz), 21.0 (CH_3); ^{31}P NMR ($CDCl_3$): δ +28.3 (s, br); MS (EI, 70 eV) m/z (%): 566 (M^+, 1), 552 (3), 367 (100), 302 (8), 299 (9), 245 (6), 243 (6); HRMS calcd for $C_{34}H_{32}BFeN_2P$: 566.1746. Observed: 566.1735.

4.5.3. (R_{Fc})-1-(2-Pyrimidyl)-2-(α-(*R*)-(diphenylphosphino)(3,5-dimethylphenyl)methyl)ferrocene, 8c. Prepared according to the procedure described above from **6c** (702 mg, 1.70 mmol) and diphenylphosphine (0.36 mL, 385 mg, 2.07 mmol). **8c** was isolated as a red solid (170 mg, 0.293 mmol, 17%); mp 188°C; $[\alpha]_D=-137.6$ (*c* 0.58, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3057 (w), 2393 (m), 1570 (s), 1555 (s), 1480 (s), 1399 (s), 699 (m); ^{1}H NMR ($CDCl_3$): δ 8.53 (d, $^3J=4.9$ Hz, 2H), 7.85–7.76 (m, 2H), 7.43–7.31 (m, 5H), 7.19–7.01 (m, 3H), 6.95 (t, $^3J=4.9$ Hz, 1H), 6.90–6.82 (m, 4H), 4.99–4.95 (m, 1H), 4.88–4.84 (m, 1HHH), 4.46 (dd, $J=2.7$ Hz, 1H), 3.55 (s, 5H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 170.4, 155.9 (CH), 139.0 (d, $J=2.2$ Hz), 137.0 (d, $J=1.2$ Hz), 133.4 (CH, d, $J=8.3$ Hz), 133.0 (CH, d, $J=8.2$ Hz), 130.8 (CH, d, $J=2.2$ Hz), 130.2 (CH, d, $J=2.4$ Hz), 129.4, 129.0 (CH, d, $J=5.8$ Hz), 128.7 (d, $J=2.6$ Hz), 128.6 (CH, d, $J=1.8$ Hz), 128.2 (CH, d, $J=9.3$ Hz), 127.0 (CH, d, $J=10.2$ Hz), 116.7 (CH), 88.2 (d, $J=6.5$ Hz), 79.4 (d, $J=1.7$ Hz), 73.6 (CH, d, $J=3.1$ Hz), 70.1 (CH), 69.7 (CH), 68.1 (CH), 39.6 (CH, d, $J=28.9$ Hz), 21.5 (CH_3); ^{31}P NMR ($CDCl_3$): δ +26.0 (s, br); MS (EI, 70 eV) m/z (%): 580 (M^+, 1), 566 (3), 381 (100), 316 (11), 259 (8); HS MS calcd for $C_{35}H_{34}BFeN_2P$: 580.1902. Observed: 580.1916.

4.5.4. (R_{Fc})-1-(2-Pyridyl)-2-(α-(*R*)-(diphenylphosphino)-(phenyl)methyl)ferrocene, 8d. Prepared according to the procedure described above from **6d** (182 mg, 0.475 mmol) and diphenylphosphine (0.10 mL, 107 mg, 0.575 mmol). **8d** was isolated as a red solid (238 mg, 0.432 mmol, 91%); mp 117°C; $[\alpha]_D=-19.6$ (*c* 0.55, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3060 (w), 2388 (m), 1587 (s), 1490 (s), 1437 (m), 698 (s); ^{1}H NMR ($CDCl_3$): δ 8.65–8.61 (m, 1H), 7.85–7.22 (m, 11H), 7.12–7.01 (m, 4H), 6.89–6.78 (m, 4H), 4.95–4.92 (m, 1H), 4.37–4.31 (m, 2H), 3.53 (s, 5H); ^{13}C NMR ($CDCl_3$): δ 160.2, 148.2 (CH), 139.5 (d, $J=2.8$ Hz), 135.5 (CH), 133.2 (CH, d, $J=8.2$ Hz), 132.8 (CH, d, $J=8.7$ Hz), 131.2 (CH, d, $J=5.7$ Hz), 130.8 (CH, d, $J=2.3$ Hz), 130.0 (CH, d, $J=2.8$ Hz), 128.2 (CH, d, $J=9.5$ Hz), 127.7 (CH, d, $J=1.2$ Hz), 127.1 (CH, d, $J=10.0$ Hz), 127.0, 121.8 (CH), 120.1 (CH), 87.3 (d, $J=6.0$ Hz), 83.0 (d, $J=1.2$ Hz), 71.9 (CH, d, $J=3.5$ Hz), 70.1 (CH), 68.6 (CH), 65.4 (CH), 39.4 (CH, d, $J=28.7$ Hz); ^{31}P NMR ($CDCl_3$): δ +25.8 (s, br); MS (EI, 70 eV) m/z (%): 551 (M^+, 1), 537 (8), 352 (100), 286 (10), 230 (12); HRMS calcd for $C_{34}H_{31}BFeNP$: 551.1637. Observed: 551.1635.

4.5.5. (R_{Fc})-1-(2-Pyridyl)-2-(α-(*R*)-(diphenylphosphino)-(2-methylphenyl)methyl)ferrocene, 8e. Prepared according to the procedure described above from **6e** (333 mg, 0.838 mmol) and diphenylphosphine (0.18 mL, 193 mg, 1.04 mmol). **8e** was isolated as a red solid (469 mg, 0.830 mmol, 99%); mp 216°C; $[\alpha]_D=-55.9$ (*c* 0.57, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3054 (w), 2396 (m), 1588 (s), 1491 (s), 1436 (s), 736 (s), 692 (s); ^{1}H NMR ($CDCl_3$): δ 8.58–8.54 (m, 1H), 8.12 (d, $J=7.5$ Hz, 1H), 7.51–7.03 (m, 13H), 6.95–6.85 (m, 4H), 4.92 (s, br, 1H), 4.37–4.32 (m, 2H), 3.52 (s, 5H), 2.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.2, 147.9 (CH), 138.2 (d, $J=2.4$ Hz), 137.2 (d, $J=6.5$ Hz), 135.6 (CH), 133.6 (CH, d, $J=8.1$ Hz), 133.0 (CH, d, $J=8.1$ Hz), 131.5 (CH, d, $J=4.7$ Hz), 130.6 (CH, d, $J=2.3$ Hz), 130.3 (CH, d, $J=2.3$ Hz), 130.1 (CH), 128.3, 127.9 (CH, d, $J=9.9$ Hz), 127.2 (CH, d, $J=10.0$ Hz), 125.4 (CH, d, $J=1.8$ Hz), 121.7 (CH), 120.2 (CH), 87.0 (d, $J=5.9$ Hz), 82.9 (d, $J=1.7$ Hz), 72.4 (CH, d, $J=3.4$ Hz), 70.1 (CH), 68.6 (CH), 65.7 (CH), 35.4 (CH, d, $J=28.1$ Hz), 20.7 (CH_3); ^{31}P NMR ($CDCl_3$): δ +28.1 (s, br); MS (EI, 70 eV) m/z (%): 565 (M^+, 1), 551 (3), 366 (100), 301 (6), 298 (11), 244 (8), 242 (7); HRMS calcd for $C_{35}H_{33}BFeNP$: 565.1793. Observed: 565.1793.

4.5.6. (R_{Fc})-1-(2-Pyridyl)-2-(α-(*R*)-(diphenylphosphino)-(3,5-dimethylphenyl)methyl)ferrocene, 8f. Prepared according to the procedure described above from **6f** (284 mg, 0.690 mmol) and diphenylphosphine (0.15 mL, 161 mg, 0.865 mmol). **8f** was isolated as a red solid (353 mg, 0.609 mmol, 88%); mp 183°C; $[\alpha]_D=-3.6$ (*c* 1.17, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3057 (w), 2394 (s), 1587 (s), 1489 (s), 699 (s); ^{1}H NMR ($CDCl_3$): δ 8.64–8.61 (m, 1H), 7.75–7.67 (m, 2H), 7.42–7.27 (m, 6H), 7.12–7.01 (m, 4H), 6.89–6.81 (m, 4H), 6.65 (d, ^2J(H,P) = 18 Hz, 1H), 4.91 (dd, $J=1.0$ Hz, 1H), 4.36–4.31 (m, 2H), 3.55 (s, 5H), 2.35 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 160.2, 148.3 (CH), 139.0 (d, $J=2.3$ Hz), 136.8 (d, $J=1.2$ Hz), 135.4 (CH), 133.3 (CH, d, $J=8.2$ Hz), 132.9 (CH, d, $J=9.0$ Hz), 130.7 (CH, d, $J=2.3$ Hz), 130.0 (CH, d, $J=2.3$ Hz), 129.3, 129.0 (CH, d, $J=5.2$ Hz), 128.6, 128.5 (CH, d, $J=1.8$ Hz), 128.1 (CH, d, $J=9.4$ Hz), 127.1 (CH, d, $J=10.2$ Hz), 121.8 (CH), 120.1 (CH), 87.5 (d, $J=6.4$ Hz), 83.1 (d, $J=1.7$ Hz), 72.1 (CH, d, $J=2.9$ Hz), 70.1 (CH), 68.5 (CH), 65.4 (CH), 39.2 (CH, d, $J=28.8$ Hz), 21.5 (CH_3); ^{31}P NMR (81 MHz, $CDCl_3$): δ +25.9 (s, br); MS (EI, 70 eV) m/z (%): 579 (M^+, 2), 565 (9), 380 (100), 314 (7), 258 (7); HRMS calcd for $C_{36}H_{35}BFeNP$: 579.1950. Observed: 579.1979.

4.5.7. (R_{Fc})-1-(2-Quinolyl)-2-(α-(*R*)-(diphenylphosphino)-(phenyl)methyl)ferrocene, 8g. Prepared according to the procedure described above from **6g** (250 mg, 0.577 mmol) and diphenylphosphine (0.12 mL, 128 mg, 0.687 mmol). **8g** was isolated as a red solid (109 mg, 0.181 mmol, 31%); mp 98°C; $[\alpha]_D=+636.0$ (*c* 0.60, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3058 (w), 2394 (m), 1600 (s), 1506 (m), 697 (s), 495 (m), 475 (m); ^{1}H NMR ($CDCl_3$): δ 8.24–8.19 (m, 1H), 7.92–7.75 (m, 7H), 7.58–7.50 (m, 1H), 7.45–6.96 (m, 11H), 6.75–6.67 (m, 2H), 5.06–5.03 (m, 1H), 4.50–4.46 (m, 1H), 4.41 (dd, $J=2.6$ Hz, 1H), 3.52 (s, 5H); ^{13}C NMR ($CDCl_3$): δ 161.1, 147.5, 139.9 (d, $J=2.1$ Hz), 135.0 (CH), 133.2 (CH, d, $J=8.3$ Hz), 132.9 (CH, d, $J=8.1$ Hz), 131.2 (CH, d, $J=5.8$ Hz), 130.8 (CH, d, $J=2.4$ Hz), 130.0 (CH, d, $J=2.5$ Hz), 129.5 (CH), 129.1 (d, $J=8.8$ Hz), 128.4 (CH), 128.2 (CH, d, $J=9.9$ Hz), 127.8 (CH), 127.7 (CH), 127.1 (CH, d, $J=9.6$ Hz), 126.2, 125.5 (CH), 120.6 (CH), 88.4 (d, $J=5.6$ Hz), 81.5 (d, $J=1.8$ Hz), 72.6 (CH, d, $J=3.0$ Hz), 70.3 (CH), 69.0 (CH), 66.4 (CH), 39.1 (CH, d,

$J=29.4$ Hz); ^{31}P NMR ($CDCl_3$): δ +25.7 (s, br); MS (EI, 70 eV) m/z (%): 601 (M^+, 1), 587 (4), 402 (100), 336 (17), 280 (17); HRMS calcd for $C_{38}H_{33}BFeNP$: 601.1793. Observed: 601.1783.

4.5.8. (R_{Fc})-1-(2-Quinolyl)-2-(α-(*R*)-(diphenylphosphino)-(2-methylphenyl)methyl)ferrocene, 8h. Prepared according to the procedure described above from **6h** (460 mg, 1.03 mmol) and diphenylphosphine (0.22 mL, 235 mg, 1.26 mmol). **8h** was isolated as a red solid (482 mg, 0.783 mmol, 76%); mp 152°C; $[\alpha]_D=+676.7$ (c 0.62, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3058 (w), 2394 (m), 1601 (s), 698 (m), 490 (s), 476 (s); ^{1}H NMR ($CDCl_3$): δ 8.17–8.07 (m, 2H), 7.84 (d, $J=9.0$ Hz, 1H), 7.78–6.98 (m, 16H), 6.78–6.70 (m, 2H), 5.00–4.97 (m, 1H), 4.54 (dd, $J=2.7$ Hz 1.3 Hz, 1H), 4.45 (dd, $J=2.7$ Hz, 1H), 3.55 (s, 5H), 2.77 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 161.0, 147.4, 138.4 (d, $J=2.2$. Hz), 137.0 (d, $J=6.5$ Hz), 135.0 (CH), 133.7 (CH, d, $J=8.2$ Hz), 133.1 (CH, d, $J=8.4$ Hz), 131.5 (CH, d, $J=4.7$ Hz), 130.6 (CH, d, $J=2.2$ Hz), 130.2 (CH, d, $J=2.3$ Hz), 130.0 (CH), 129.5 (CH), 129.4, 127.9 (CH, d, $J=9.3$ Hz), 127.2 (CH, d, $J=2.6$ Hz), 127.0 (CH, d, $J=9.9$ Hz), 126.2, 125.5 (CH), 120.8 (CH), 87.7 (d, $J=5.3$ Hz), 81.7, 72.8 (CH, d, $J=3.5$ Hz), 70.2 (CH), 69.2 (CH), 67.3 (CH), 35.6 (CH, d, $J=28.1$ Hz), 21.8 (CH_3); ^{31}P NMR ($CDCl_3$): δ +28.5 (s, br); MS (EI, 70 eV) m/z (%): 615 (M^+, 1), 601 (4), 430 (11), 416 (100), 351 (7), 348 (17), 294 (9), 292 (11); HRMS calcd for $C_{39}H_{35}BFeNP$: 615.1950. Observed: 615.1952.

4.5.9. (R_{Fc})-1-(2-Quinolyl)-2-(α-(*R*)-(diphenylphosphino)(3,5-dimethylphenyl)methyl)ferrocene, 8i. Prepared according to the procedure described above from **6i** (302 mg, 0.655 mmol) and diphenylphosphine (0.14 mL, 150 mg, 0.806 mmol). **8i** was isolated as a red solid (135 mg, 0.215 mmol, 33%); mp 95°C; $[\alpha]_D=+618.4$ (c 0.63, $CHCl_3$); IR (KBr): $\tilde{\nu}$ 3057 (w), 2395 (m), 1600 (s), 693 (m), 491 (s); ^{1}H NMR ($CDCl_3$): δ 8.19 (d, $J=8.6$ Hz, 1H), 7.87 (d, $J=8.6$ Hz, 1H), 7.84–7.75 (m, 4H), 7.57–7.50 (m, 1H), 7.47 (s, 2H), 7.38–7.07 (m, 7H), 7.03–6.95 (m, 1H), 6.90 (s, 1H), 6.76–6.68 (m, 2H), 5.03 (dd, $J=2.6$ Hz, 1.1 Hz, 1H), 4.48 (dd, $J=2.6$ Hz, 1.1 Hz, 1H), 4.41 (dd, $J=2.6$ Hz, 1H), 3.54 (s, 5H), 2.36 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 161.1, 147.5, 139.4 (d, $J=2.4$ Hz), 133.2 (CH, d, $J=8.1$ Hz), 133.0 (CH; d, $J=8.0$ Hz), 130.7 (CH, d, $J=2.3$ Hz), 130.0 (CH, d, $J=2.4$ Hz), 129.5 (CH), 129.3 (CH, d, $J=3.3$ Hz), 129.1 (CH, d, $J=6.1$ Hz), 128.6 (d, $J=2.8$ Hz), 128.5 (CH, d, $J=1.8$ Hz), 128.4 (CH), 128.1 (CH, d, $J=9.4$ Hz), 127.6 (CH), 127.0 (CH, d, $J=9.6$ Hz), 126.2, 125.5 (CH), 120.7 (CH), 88.7 (d, $J=6.5$ Hz), 81.6 (d, $J=1.7$ Hz), 72.8 (CH, d, $J=9.0$ Hz), 70.3 (CH), 68.9 (CH), 66.5 (CH), 38.9 (CH, d, $J=29.3$ Hz), 22.3 (CH_3); ^{31}P NMR ($CDCl_3$): δ +26.0 (s, br); MS (EI, 70 eV) m/z (%): 629 (M^+, 1), 615 (8), 430 (100), 364 (8), 308 (5); HRMS calcd for $C_{40}H_{37}BFeNP$: 629.2106. Observed: 629.2084.

4.6. Deprotection

Prior to use in catalysis, a quantity of the required protected ligand **8a**–**i** (10 to 20 mg) was dissolved in diethylamine (0.5 mL) and heated to 50°C for 30 min. Afterwards, the solvent and volatile compounds were removed in vacuo. This procedure was repeated four times. The deprotection can be monitored by ^{31}P NMR. To remove traces of diethyl amine, the solvent for the catalytic reaction (THF or dichloromethane) was added and removed again in vacuo repeatedly (Table 6).

Table 6. ^{31}P NMR ($CDCl_3$) shifts of **7a**–**i**

Ar′	Ar = Phenyl	Ar = *o*-Tolyl	Ar = 3,5-Xylyl
2-Pyrimidyl	**7a**: δ +8.6	**7b**: δ +14.5	**7c**: δ +7.9
2-Pyridyl	**7d**: δ +8.5	**7e**: δ +14.4	**7f**: δ +8.1
2-Quinolyl	**7g**: δ +8.8	**7h**: δ +15.2	**7i**: δ +8.4

4.7. Hydroboration of styrene

The freshly deprotected ligand **7a**–**i** and $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol, 1 mol%) were dissolved in THF (3 mL) and stirred 20 min at rt. Styrene (0.11 mL, 1.0 mmol) and tetradecane as internal standard were added and the mixture was cooled to the indicated temperature before catechol borane (0.12 mL, 1.1 mmol) was added. The reaction was followed by GC. Aliquots were treated with a mixture of 2N sodium hydroxide solution and hydrogen peroxide solution (30%). The reaction was quenched by adding methanol (1 mL), 2N sodium hydroxide solution (1.5 mL) and hydrogen peroxide solution (30%, 0.1 mL). The mixture was then extracted with diethyl ether (60 mL) and the organic layers were washed with 1N sodium bisulfite solution, water and brine and dried over $MgSO_4$. The crude product was dissolved in diethyl ether and filtered through a short pad of silica gel. The enantiomeric excess was determined by HPLC (OD-H, 95% *n*-heptane, 5% *i*-propanol, 0.6 mL/min); retention time (min): 1-phenylethanol: 15.0 (*R*), 17.5 (*S*); 2-phenylethanol: 16.1).

4.8. Allylic alkylation

The freshly deprotected ligand **7a**–**i** (17 μmol, 3.4 mol%) and allylpalladium chloride (dimer, 1.6 mg; 4.4 μmol, 0.87 mol%) were dissolved in dichloromethane (3 mL) and stirred 15 min at rt. 3-Acetoxy-1,3-diphenylpropene (126 mg, 0.50 mmol) in dichloromethane (1 mL), *N*,*O*-bistrimethylsilylacetamide (0.25 mL, 210 mg, 1.01 mmol), dimethyl malonate (0.11 mL, 130 mg, 0.96 mmol) and potassium acetate (2.3 mg, 23 μmol, 4.6 mol%) were added. The reaction was followed by thin layer chromatography (*n*-pentane/diethyl ether 6:1). After 20 h satd NH_4Cl solution was added and the mixture was extracted with dichloromethane (60 mL). The organic layers were washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (*n*-pentane/diethyl ether 5:1). The enantiomeric excess was determined by HPLC (OD-H, 97% *n*-heptane, 3% *i*-propanol, 0.4 mL/min); retention time (min): 21.5 (*R*), 23.1 (*S*)).

Acknowledgements

We thank Degussa AG (Frankfurt) for financial support.

References

1. Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1994.
2. (a) Togni, A.; Hayashi, T. *Ferrocenes*: *Homogenous Catalysis*, *Organic Synthesis*, *Material Science*; VCH: Weinheim, 1995; (b) Togni, A. *Angew. Chem.* **1996**, *108*, 1581; (c) Kagan, H. B.; Diter, P.; Gref, A.; Guillaneux, D.; Masson-Szymczak, A.; Rebière, F.; Riant, O.; Samuel, O.; Taudien, S. *Pure Appl. Chem.* **1996**, *68*, 29; (d) Togni, A.; Dorta, R.; Köllner, C.; Pioda, G. *Pure Appl. Chem.* **1998**, *70*, 1477; (e) Togni, A.; Bieler, N.; Burckhardt, U.; Köllner, C.; Pioda, G.; Schneider, R.; Schnyder, A. *Pure Appl. Chem.* **1999**, *71*, 1531.
3. Lotz, M.; Ireland, T.; Tappe, K.; Knochel, P. *Chirality* **2000**, *12*, 389.
4. Rausch, M.; Vogel, M.; Rosenberg, H. *J. Org. Chem.* **1957**, *22*, 903.
5. (a) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551; (b) Wright, J.; Framber, P.; Reeves, P. *J. Organomet. Chem.* **1994**, *476*, 215.
6. (a) Gokel, G. W.; Marquarding, D.; Ugi, I. K. *J. Org. Chem.* **1972**, *37*, 3052; (b) Gokel, G.; Hoffmann, P.; Klusacek, H.; Marquarding, D.; Ugi, I. *Angew. Chem.* **1970**, *82*, 77.
7. (a) Slocum, D. W.; Koonsvitsky, B. P. *J. Org. Chem.* **1976**, *41*, 3664; (b) Carrol, M. A.; Widdowson, D. A.; Williams, D. J. *Synlett* **1994**, 1025.
8. (a) Knochel, P. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH, , S: Weinheim, 1997; p. 406; (b) Klement, I.; Rottländer, M.; Tucker, C. E.; Majid, T. N.; Knochel, P.; Venegas, P.; Cahiez, G. *Tetrahedron* **1996**, *52*, 7201.
9. Pellon, P. *Tetrahedron Lett.* **1992**, *33*, 4451.
10. Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301.
11. For a general review, see: Trost, B. M. *Chem. Pharm. Bull.* **2002**, *50*, 1.
12. (a) For a general review, see: Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957; (b) Kwong, F. Y.; Yang, Q.; Mak, T. C. W.; Chan, A. S. C.; Chan, K. S. *J. Org. Chem.* **2002**, *67*, 2769; (c) Demay, S.; Volant, F.; Knochel, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1235; (d) Fernandez, E.; Maeda, K.; Hooper, M. W.; Brown, J. M. *Chem. Eur. J.* **2000**, *6*, 1840; (e) Reetz, M. T.; Beuttenmuller, E. W.; Goddard, R.; Pasto, M. *Tetrahedron Lett.* **1999**, *40*, 4977; (f) Doucet, H.; Fernandez, E.; Layzell, T. P.; Brown, J. M. *Chem. Eur. J.* **1999**, *5*, 1320.
13. Brown, D. J.; Waring, P. *Aust. J. Chem.* **1973**, *26*, 443.
14. Trécourt, F.; Breton, G.; Bonnet, V.; Mongin, F.; Marsais, F.; Quéguiner, G. *Tetrahedron* **2000**, *56*, 1349.
15. Corcoran, R. C.; Bang, S. H. *Tetrahedron Lett.* **1990**, *31*, 6757.