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New [5]ferrocenophane diphosphine ligands for Pd-catalyzed allylic substitution

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Abstract—New [5]ferrocenophane based diphosphine ligands, having planar and central chirality, were prepared. The stereogenic center was generated by the enantioselective CBS-reduction of [5]ferrocenophan-1-one. The straightforward transformation of hydroxyl group to dimethylamino group afforded amine **7**, which was diastereoselectively *ortho*-lithiated and reacted with $ClPPh_2$ to introduce planar chirality. The structure of the diphosphine **1** was elucidated by X-ray crystallography. The ligand was successfully applied to Pd-catalyzed allylic alkylation (91% ee).

1. Introduction

Asymmetric catalysis using transitional-metal complexes with chiral ligands has become a growing field of interest in organic chemistry in the past decades.[1] From among a vast number of known ligands, ferrocene-derivatives have attracted considerable attention. Their synthesis and use in enantioselective catalysis have been reviewed recently.[2,3] Especially, numerous phosphines have been introduced and successfully applied in asymmetric catalysis.[4,5] Some of them, such as diphosphine members of the Josiphos family, are nowadays considered as privileged ligands and they are even utilized in the industry.[6] Also various P,N-ligands became well established in many enantioselective transformations.[7]

Togni and co-workers, in their original paper[8] about Josiphos-type diphosphines, envisioned the possibilities for structural modification of the ligands by varying substituents on both phosphorus atoms. Another way of modifying these compounds was suggested by Weissensteiner and co-workers.[9] They introduced a three-membered homo- and heteroannular bridge instead of α-methyl group. In the case of Rh- and Ir-catalyzed hydrogenations of olefins, ketones, and imines, these compounds were equal or slightly worse catalysts than the original Josiphos ligands, presumably due to a rigid ligand backbone. On the other hand, Erker and co-workers[10] introduced [3]ferrocenophane diphosphine with a methyl group in the linkage, which proved to be a useful ligand for asymmetric CO/propene co-polymerization (Fig. 1).

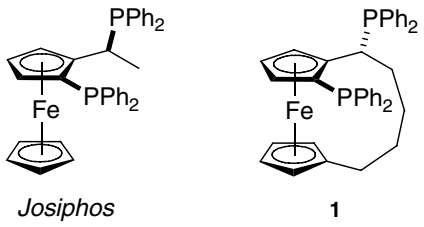

Figure 1.

Considering allylic substitution, there are numerous examples of ferrocenyl P,N-ligands. The usage of P,P-ligands is less frequent. Apart from the already mentioned Josiphos, another diphosphine was successfully used as a ligand in allylic substitution by Knochel.[11] Several other ferrocene diphosphines were also employed as ligands in Pd-catalyzed allylations.[12,13] Recently also [3]ferrocenophane diphosphines were used as ligands in Pd-allylation giving moderate enantioselectivities.[14] Herein, we report the moderate synthesis of new ferrocene diphosphines based on the [5]ferrocenophane. We think that a longer linkage between the two Cp-rings would be more flexible and it will provide a more sterically demanding environment than in the

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non-bridged systems. The effectiveness of these new ligands in Pd-catalyzed allylic substitution is briefly discussed as well.

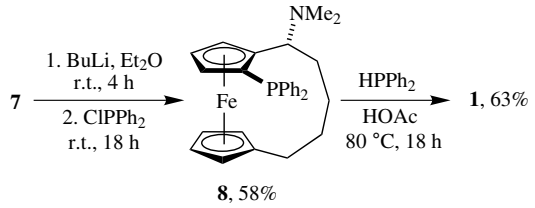
2. Synthesis

Our synthesis started with Friedel–Crafts acylation of acetylferrocene **2** with 3-chloropropionyl chloride followed by base-catalyzed cyclization.[15,16] Diketone **3** was then reduced in the presence of $LiAlH_4/AlCl_3$ to [5]ferrocenophane **4**, because it was not possible to transform it directly to [5]ferrocenophan-2-one **5**. Therefore, we first chose to reduce both carbonyl groups and then prepare desired ketone **5** by oxidation with MnO_2. The stereogenic center was introduced by the CBS-reduction[17] of ketone **5** affording alcohol **6** in 70% yield and 97% ee. Compound **6** was acetylated using Ac_2O and DMAP. The resulting ester was then reacted with dimethylamine in CH_3CN in an ultrasonic bath to produce amine **7** in a 94% yield analogously to the procedure of Schmalz[18] (Scheme 1).

The amine **7** was subjected to *ortho*-lithiation using BuLi in Et_2O at rt, followed by reaction with chlorodiphenylphosphine to give amino phosphine **8** in 58% yield. The diastereoselectivity of the lithiation was determined by measuring ^{31}P NMR of the crude reaction mixture to be 87:13. Although the selectivity was not very high, we obtained pure amino phosphine **8** by simple column chromatography. The dimethylamino group was then substituted with diphenylphosphine in acetic acid according to Togni's procedure[8] giving diphosphine **1** (Scheme 2).

The absolute configuration of diphosphine **1** was established by X-ray crystallographic analysis to be (*R*,*pS*). Interestingly, the configuration is opposite the in [3]ferrocenophanes reported by Weissensteiner[19] (Fig. 2).

In order to examine the effect of the planar chirality of our ligand, we decided to also prepare the (*R*,*pR*)-diastereoisomer of compound **1**. This was done by the application of a well-known silylation strategy.[20] We first blocked the preferred lithiation position by making a TMS-compound **9**,



Scheme 2.

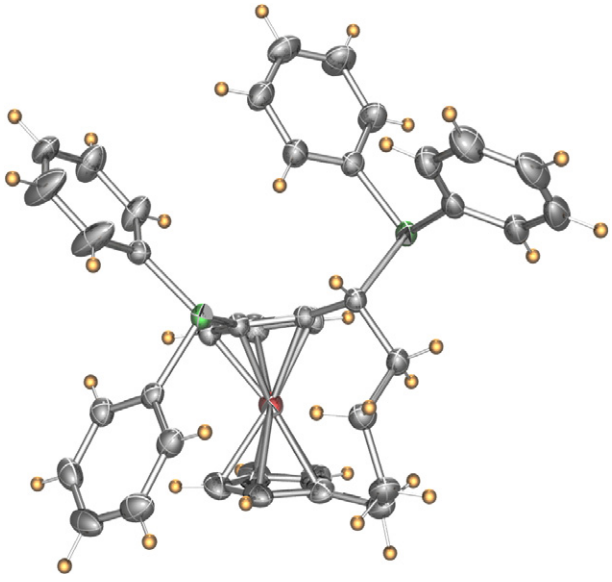
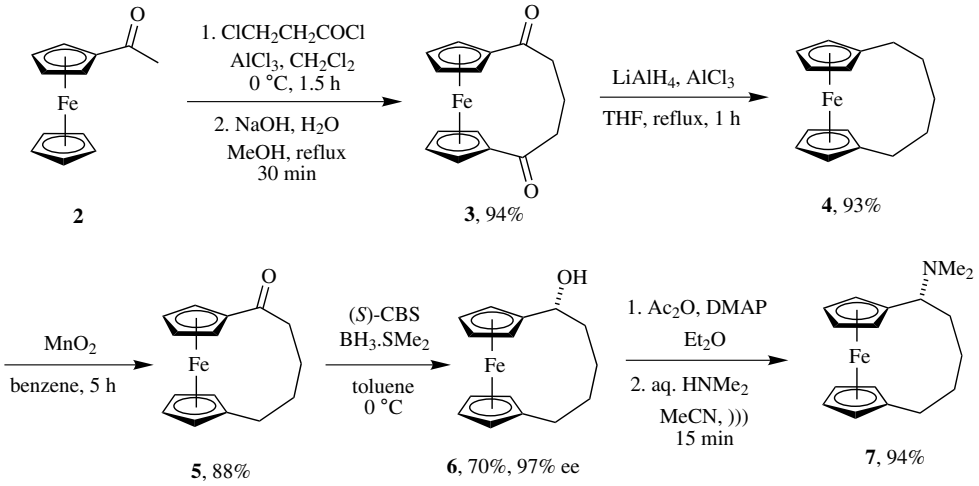


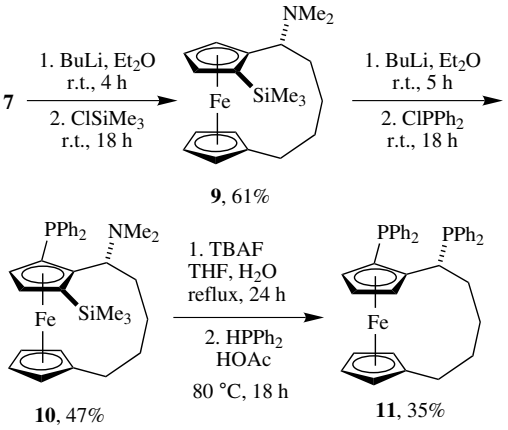
Figure 2. X-ray structure of (*R*,*pS*)-**1**.

which was subsequently again lithiated and reacted with $ClPPh_2$ to produce compound **10**. After desilylation and displacement of the NMe_2-group for diphenylphosphino, diastereoisomeric diphosphine **11** was prepared (Scheme 3).

The CD spectra of diastereoisomeric compounds (*R*,*pS*)-**1** and (*R*,*pR*)-**11** show major bands around 310 nm of opposite signs (Fig. 3).



Scheme 1.

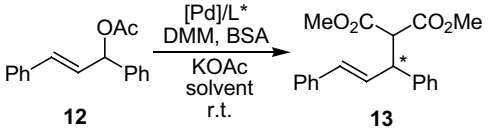


Scheme 3.

3. Catalysis

Palladium-catalyzed allylic substitution is nowadays one of the benchmark reactions for evaluating new ligands.[21] The reaction was performed with 1,3-diphenyl-1-acetoxypropene **12** under standard Trost conditions. We used 2 mol % of catalyst preformed in situ from $Pd_2dba_3{\cdot}CHCl_3$ or $[Pd(allyl)Cl]_2$ and ligand. We herein report results obtained with ligand **1** as well as its diastereoisomer **11**.

The allylation product was obtained in up to 91% ee using diphosphine **1**. In comparison, a Josiphos-type diphosphine with two diphenylphosphino groups[8] gave the allylation product in 66% ee under similar conditions. So it appears that a five-membered carbon bridge between Cp-rings does have a positive effect on the enantioselectivity of the reaction. Utilization of amine **8** as a P,N-ligand, resulted in a considerable decrease in enantioselectivity to 57% ee. Allylation using diastereoisomeric diphosphine **11** afforded product in only 51% ee and with an opposite absolute configuration. The configuration of the allylation product is determined by the planar chirality of the ligand and also it seems that a 'matched' pair of central and planar chirality in the ligand is necessary for a high enantioselectivity. The fact was also observed with other ferrocene-based ligands such as oxazolines[22,23] and to a lesser extent also with amino phosphines.[24] The results of the asymmetric allylic alkylation are summarized in Table 1.



4. Conclusion

In conclusion, we have reported the synthesis of a new class of chiral ligands based on the ferrocenophane scaffold. Diastereoselective lithiation was performed successfully on dimethylamino derivative **7**, enabling access to planar

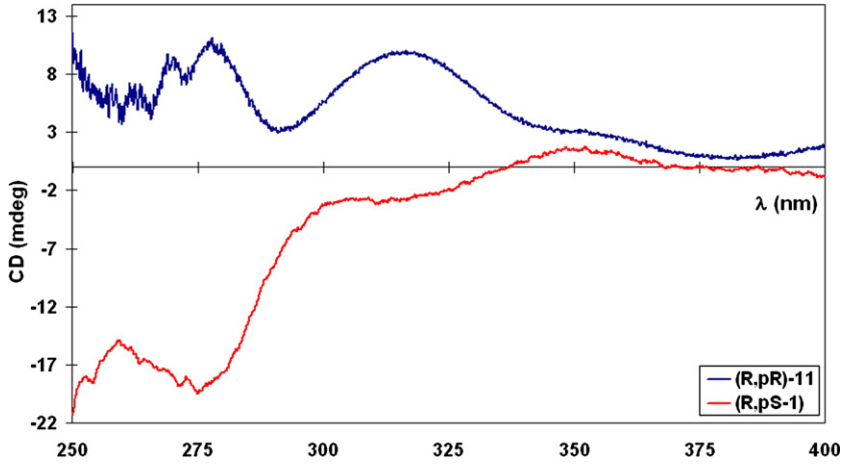


Figure 3. CD spectra of (*R,pS*)-**1** (red) and (*R,pR*)-**11** (blue).

Table 1. Pd-catalyzed allylic alkylation[a]

[Pd]	L	Base	Solvent	Time[b] (h)	Yield[c] (%)	ee (%)
$Pd_2dba_3{\cdot}CHCl_3$	**1**	KOAc	THF	24	90	88 (*S*)
$Pd_2dba_3{\cdot}CHCl_3$	**1**	KOAc	CH_2Cl_2	24	88	91 (*S*)
$[Pd(allyl)Cl]_2$	**1**	KOAc	CH_2Cl_2	20	96	89 (*S*)
$[Pd(allyl)Cl]_2$	**1**	KOAc	$[bmim]PF_6$	48	53	90 (*S*)
$[Pd(allyl)Cl]_2$	**1**	LiOAc	CH_2Cl_2	15	95	88 (*S*)
$[Pd(allyl)Cl]_2$	**8**	KOAc	CH_2Cl_2	16	96	57 (*S*)
$[Pd(allyl)Cl]_2$	**11**	KOAc	CH_2Cl_2	16	94	51 (*R*)

[a] Reactions run with 2 mol % catalyst, on a 1 mmol scale.
[b] Time of completion (no starting material detected by TLC).
[c] Isolated yield of product purified by FC.

chiral compounds. The structure of diphosphine **1** was established by X-ray crystallography. Ligand **1** was used in Pd-catalyzed allylation, which proceeded with complete conversion and up to 91% ee. These promising results encourage us on to further experiments in modifying the structure of the ligand and also in its application to other metal catalyzed reactions.

5. Experimental

The reactions were carried out in N_2 atmosphere and reactions using organometallic reagents were performed using standard Schlenk techniques. NMR spectra were recorded on Varian Mercury plus instrument. Chemical shifts (δ) are given as parts per million relative to tetramethylsilane as an internal standard, for ^{1}H NMR; relative to residual solvent peak, for ^{13}C NMR and relative to H_3PO_4 as external standard for ^{31}P NMR. IR spectra were recorded on Mettler-Toledo ReactIR instrument. Optical rotations were measured on a Krüss P3002RS polarimeter. Melting points were uncorrected. Column chromatography was performed on Merck silica gel 60. Thin-layer chromatography was performed on Merck TLC-plates silica gel 60, F-254. Enantiomeric excesses were determined by HPLC using Chiralcel OD-H (Daicel Chemical Industries) column with *n*-hexane/*i*-propanol as a mobile phase and detection by UV-detector at 254 nm. CD spectra were measured as $CHCl_3$ solutions on Jasco J-810 spectrometer. The solvents were distilled prior use, Et_2O and toluene were dried with sodium/benzophenone, CH_2Cl_2 was dried with CaH_2 and distilled. BuLi, *N*,*O*-bis(trimethylsilyl)acetamide, $ClPPh_2$ and dimethyl malonate were purchased from Merck, $HPPH_2$ from Fluka, $Pd_2dba_3{\cdot}CHCl_3$, $BH_3{\cdot}SMe_2$, methylboronic acid, (*S*)-(−)-2-(diphenylhydroxymethyl)-pyrrolidine and from Aldrich, $[Pd(C_3H_5)Cl]_2$ from Acros.

5.1. 1,5-(Ferrocen-1,1′-diyl)pentan-1,5-dione 3

To a solution of acetylferrocene (10.0 g, 43.8 mmol) in anhydrous CH_2Cl_2 (150 mL), the solution of distilled 3-chloropropionyl chloride (8.60 g, 6.5 mL, 65.7 mmol) in CH_2Cl_2 (10 mL) was added at rt. The reaction mixture was cooled in an ice bath and $AlCl_3$ (17.5 g, 131 mmol) was added slowly over 1 h. The solution was stirred for 1.5 h at 0 °C until no starting material was detected by TLC. The content of the flask was then drained onto 300 g of crushed ice. After the ice melted, the layers were separated and the aqueous phase was extracted CH_2Cl_2 (3×70 mL). Combined organic extracts were washed with 10% aq NaOH (4×50 mL), then with water (2×50 mL) and dried (Na_2SO_4), and the solvent was evaporated. The crude product, 1-acetyl-1′-(3-chloropropionyl)ferrocene (13.9 g, 99%), was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.82 (t, $J = 2.0$ Hz, 2H), 4.80 (t, $J = 1.9$ Hz, 2H), 4.56 (t, $J = 1.9$ Hz, 2H), 4.55 (t, $J = 2.0$ Hz, 2H), 3.91 (t, $J = 6.4$ Hz, 2H), 3.13 (t, $J = 6.4$ Hz, 2H), 2.36 (s, 3H).

The crude 1-acetyl-1′-(3-chloropropionyl)ferrocene (13.9 g, 43.4 mmol) was dissolved in a minimum amount of boiling MeOH (150 mL). To the solution was added 10% aq NaOH (70 mL, 174 mmol). The reaction mixture was stirred and heated at reflux for 30 min. Then the mixture was cooled in an ice bath and the precipitate was filtered off, washed with water (100 mL), and dried under vacuum. Product **3** was obtained as orange crystals (9.22 g, 75%). Another portion of the product was obtained after concentrating the filtrate, dilution with water, and extraction with CH_2Cl_2. Drying and concentrating the solution afforded another 2.40 g (20%) of diketone **3**. ^{1}H NMR: (300 MHz, $CDCl_3$): δ 4.82 (t, $J = 2.0$ Hz, 4H), 4.55 (t, $J = 2.0$ Hz, 4H), 2.58–2.43 (m, 6H, $(CH_2)_3$). Spectral data in accordance with literature.[15]

5.2. 1,5-(Ferrocen-1,1′-diyl)pentan-1-one 4

$AlCl_3$ (17.5 g, 131 mmol) was added slowly to the anhydrous THF (160 mL) under N_2-atmosphere. The mixture was stirred and cooled in water bath for 30 min. Then $LiAlH_4$ (3.60 g, 94.8 mmol) was added into this solution and the gray suspension was stirred at room temperature for 1 h. Diketone **3** (9.22 g, 32.7 mmol) was slowly added into the ice-cooled solution during 1 h. The mixture was heated at reflux for 1 h, then it was cooled in an ice bath and ice-cold water (70 mL) was added carefully. Another portion of water (250 mL) was added and the organic layer was separated. The aqueous phase was extracted with EtOAc (4×50 mL). Combined organic extracts were dried (Na_2SO_4) and solvent was evaporated under vacuum. The crude product was dissolved in hexane (150 mL) and passed through a short silica gel column. Evaporation of the solvent yielded pure [5]ferrocenophane (7.96 g, 93%) as orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.07 (t, $J = 1.8$ Hz, 4H), 3.97 (t, $J = 1.8$ Hz, 4H), 2.33 (dd, $J = 7.3$, 6.0 Hz, 4H), 2.09–1.99 (m, 2H), 1.87–1.77 (m, 4H). Spectral data in accordance with literature.[15]

5.3. 1,1′-(Pentan-1,5-diyl)ferrocene 5

The mixture of [5]ferrocenophane (**4**) (500 mg, 1.97 mmol) and active MnO_2 (3.60 g, 41.4 mmol) in anhyd benzene (50 mL) was stirred under nitrogen for 5 h at room temperature. The mixture was filtered and the filter cake washed with CH_2Cl_2 (4×50 mL). After concentration, the crude product was purified by column chromatography. First, unreacted starting material was eluted with hexane and product **5** was then eluted with EtOAc (464 mg, 88%), orange crystals. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.74 (t, $J = 1.9$ Hz, 2H), 4.53 (t, $J = 1.9$ Hz, 2H), 4.12–4.16 (m, 2H), 4.08–4.12 (m, 2H), 2.60–2.66 (m, 2H), 2.37–2.44 (m, 2H), 2.20–2.30 (m, 2H), 1.80–1.90 (m, 2H). Spectral data in accordance with the literature.[16]

5.4. (*R*)-1,1′-(1-Hydroxypentan-1,5-diyl)ferrocene 6

$BH_3{\cdot}Me_2S$ (650 μL, 1.30 mmol, 2 M in THF) was added to the solution of (*S*)-CBS (1.30 mL, 1.30 mmol, 1 M in tol.) (prepared from methylboronic acid and (*S*)-(−)-2-(diphenylhydroxymethyl)-pyrrolidine[16]) in anhydrous toluene (5 mL) at rt. The mixture was stirred for 5 h and then it was

added drop wise to the solution of [5]ferrocenophan-1-one (**5**) (700 mg, 2.61 mmol) in toluene (6 mL) cooled in an ice bath. The reaction mixture was stirred at 0 °C for 1 h. Another portion of $BH_3{\cdot}Me_2S$ (325 μL, 0.63 mmol, 2 M in THF) in anhydrous toluene (2 mL) was added dropwise during 1 h. The reaction was quenched with methanol (5 mL) at 0 °C. The solvents were evaporated in vacuum and the crude product was purified by column chromatography (SiO_2, hexane/Et_2O 3:2). The first fraction was [5]-ferrocenophane **4** (140 mg, 21%). The second fraction was product, alcohol **6** (493 mg, 70%) as light yellow crystals. HPLC (Chiralcel OD-H, hexane/*i*-PrOH 85:15, 0.5 mL/min) t_R(major) = 23.9 min; t_R(minor) = 29.3 min; 97% ee. Enantiomeric excess can be improved by crystallization from Et_2O to more than 99.5% ee. Mp: 100–103 °C. $[\alpha]_D = -27$ (*c* 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.67 (ddd, $J = 7.3, 7.3, 4.9$ Hz, 1H), 4.20 (ddd, $J = 2.4, 1.4, 1.4$ Hz, 1H), 4.14–4.18 (m, 2H), 4.12 (ddd, $J = 2.4, 2.4, 1.3$ Hz, 1H), 4.08 (ddd, $J = 2.4, 2.4, 1.3$ Hz, 1H), 4.01–4.04 (m, 1H), 3.95–3.98 (m, 1H), 2.40–2.58 (m, 1H), 2.32–2.39 (m, 2H), 1.96–2.05 (m, 2H), 1.68–1.95 (m, 3H), 1.41 (d, $J = 4.9$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.7, 69.3, 69.0, 68.7, 68.5, 67.7, 67.7, 67.6, 67.2, 35.0, 25.4, 24.9, 23.5. IR (neat): *v* 3293, 3096, 2918, 2856, 1451, 1297, 1262, 1023, 1000, 815, 799 cm^{-1}. Elem. Anal. Calcd for $C_{15}H_{18}FeO$ (270.2): C, 66.69; H, 6.72. Found: C, 67.19; H, 6.49.

5.5. (*R*)-1,1′-[1-(Dimethylamino)pentan-1,5-diyl]ferrocene 7

The solution of alcohol **6** (1.60 g, 5.92 mmol), acetic anhydride (2.5 mL, 2.71 g, 26.7 mmol), and DMAP (58 mg, 0.47 mmol) in anhydrous Et_2O (60 mL) was stirred overnight at rt. No starting material was detected after 15 h by TLC. Saturated aqueous solution of Na_2CO_3 (10 mL) was added and layers were separated. The aqueous layer was extracted with Et_2O (2 × 30 mL). Combined organic extracts were washed with satd soln of Na_2CO_3 (4 × 20 mL) and with water (2 × 20 mL), then dried (Na_2SO_4) and the solvent evaporated. The orange oil (1.81 g) (acetoxy derivative) was used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (dd, $J = 10.3, 4.5$ Hz, 1H), 4.24–4.29 (m, 2H), 4.14–4.18 (m, 2H), 4.12 (dd, $J = 2.5, 2.5$ Hz, 1H), 4.06–4.10 (m, 2H), 3.94–3.97 (m, 1H), 2.42–2.55 (m, 2H), 2.33 (ddd, $J = 16.2, 4.7, 4.7$ Hz, 1H), 2.04–2.18 (m, 1H), 1.96 (s, 3H, CH_3), 1.73–2.00 (m, 5H).

To the solution of [5]ferrocenophan-1-ylacetate (1.81 g, 5.81 mmol) in CH_3CN (65 mL) was added 40% aqueous solution of dimethylamine (38 mL, 300 mmol). The mixture was exposed to ultrasound in an ultrasonic bath for 15 min at rt. After this time no starting material was detected by TLC. The reaction mixture was diluted with brine (70 mL) and layers were separated. The aqueous layer was extracted with Et_2O (3 × 20 mL). Combined organic extracts were washed with water to neutral pH. Organic extract was dried (Na_2SO_4) and concentrated to yield amine **7** (1.66 g, 96%) as an orange oil, which later crystallized. Mp = 43–44 °C. $[\alpha]_D = +9.5$ (*c* 1.06, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.17–4.21 (m, 1H), 4.06–4.12 (m, 3H), 4.03–4.06 (m, 1H), 4.00–4.02 (m, 1H), 3.97–3.99 (m, 1H), 3.94–3.96 (m, 1H), 3.27 (dd, $J = 7.6, 3.3$ Hz, 1H), 2.42 (ddd, $J = 15.6, 9.8, 3.3$ Hz, 1H), 2.03–2.16 (m, 4H), 2.05 (s, 6H), 1.70–1.93 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 90.8, 86.6, 69.7, 69.1, 68.1, 67.9, 67.1, 66.9, 66.8, 66.3, 63.3, 41.5, 29.6, 27.3, 24.8, 24.8. IR (neat): *v* 3092, 2930, 2856, 2779, 1451, 1023, 811, 753 cm^{-1}. Elem. Anal. Calcd for $C_{17}H_{23}FeN$ (297.2): C, 68.70; H, 7.80; N, 4.71. Found: C, 69.25; H, 7.98; N, 4.68.

5.6. (*R,pS*)-1-(Diphenylphosphanyl)-2,1′-[1-(dimethylamino)pentan-1,5-diyl]ferrocene 8

To the solution of amine **7** (650 mg, 2.19 mmol) in anhydrous Et_2O (10 mL) and BuLi (2.05 mL, 3.29 mmol, 15% in hexane) was added at rt. The mixture was stirred for 4 h, then it was cooled to 0 °C and chlorodiphenylphosphine (0.71 mL, 869 mg, 3.94 mmol) was added with a syringe. The reaction mixture was then stirred for 18 h at rt. The satd aq $NaHCO_3$ solution was added and phases were separated. Aqueous layer was extracted with Et_2O (3 × 20 mL). Combined organic extracts were washed with water, dried (Na_2SO_4), and concentrated. Column chromatography of the crude mixture (SiO_2, hexane/EtOAc 2:1 + 0.5% of Et_3N) afforded amino phosphine **8** (616 mg, 58%) as an orange oil. $[\alpha]_D = -404$ (*c* 1.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54–7.64 (m, 2H), 7.32–7.40 (m, 4H), 7.17–7.27 (m, 4H), 4.35–4.42 (m, 2H), 3.97–4.01 (m, 1H), 3.91–3.95 (m, 1H), 3.84–3.90 (m, 2H), 3.62–3.70 (m, 1H), 3.09 (dd, $J = 3.6, 2.2$ Hz, 1H), 1.79–2.48 (m, 8H), 1.86 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.3, 135.4, 133.0, 132.9, 132.7, 129.3, 127.5–128.7, 125.5, 76.2, 71.4, 70.8, 69.7, 68.6, 67.8, 67.3, 41.4, 28.4, 28.0, 24.5, 24.4, 14.0. ^{31}P NMR (121 MHz, $CDCl_3$): δ −24.4. IR (neat): *v* 3062, 2926, 2856, 2822, 2775, 1741, 1436, 1262, 1092, 1023, 803, 745, 699.

5.7. (*R,pS*)-1-(Diphenylphosphanyl)-2,1′-[1-(diphenylphosphanyl)pentan-1,5-diyl]ferrocene 1

Amino phosphine **8** (467 mg, 0.970 mmol) was dissolved in acetic acid (10 mL) and the resulting solution was degassed. Diphenylphosphine (0.27 mL, 289 mg, 1.55 mmol) was added into this solution and the mixture was stirred for 18 h at 90 °C. After cooling to rt, the mixture was diluted with water and extracted with EtOAc. Combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuum. Crystallization from hot EtOH afforded diphosphine **1** (380 mg, 63%). Mp: 172–174 °C. $[\alpha]_D = -839$ (*c* 0.22, acetone). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (m, 3H), 7.52 (m, 2H), 7.36 (m, 6H), 7.11 (m, 5H), 6.91 (m, 4H), 4.54 (dt, $J = 3.9, 2.7$ Hz, 1H), 4.32 (t, $J = 2.4$ Hz, 1H), 4.05 (m, 1H), 3.88 (m, 1H), 3.76 (dt, $J = 2.4, 1.5$ Hz, 1H), 3.64–3.55 (m, 2H), 2.92 (dt, $J = 2.4, 1.2$ Hz, 1H), 2.61 (m, 1H), 2.25 (t, $J = 5.7$ Hz, 2H), 2.06–1.67 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.9 (dd, $J = 19.8, 6.8$ Hz), 136.9, 135.5 (d, $J = 21.8$ Hz), 134.2 (d, $J = 20.3$ Hz), 133.0 (d, $J = 17.3$ Hz), 132.1 (d, $J = 17.3$ Hz), 129.1, 128.3 (d, $J = 7.5$ Hz), 128.0, 127.9, 127.8, 127.7 (d, $J = 5.3$ Hz), 126.9, 99.9, 90.7, 76.2 (d, $J = 9.0, 2.3$ Hz), 70.7, 70.2 (d, $J = 4.5$ Hz), 70.0 (d, $J = 4.5$ Hz), 69.1, 68.0, 67.3, 66.4, 34.3 (d, $J = 11.3$ Hz), 29.1 (d, $J = 15.0$ Hz), 25.3 (d, $J = 11.3$ Hz), 23.8, 23.3. ^{31}P NMR

(121 MHz, $CDCl_3$): δ 1.6, −25.3. IR (neat): ν 3065, 2934, 2860, 1478, 1451, 1220, 1092, 1027, 818, 741, 699 cm^{-1}. Elem. Anal. Calcd for $C_{39}H_{36}FeP_2$ (622.5): C, 75.25; H, 5.83. Found: C, 74.42; H, 5.30.

5.8. (*R*,*pS*)-1-(Trimethylsilyl)-2,1′-[1-(dimethylamino)-pentan-1,5-diyl]ferrocene 9

Amine **7** (477 mg, 1.61 mmol) was dissolved in anhydrous Et_2O (10 mL) and cooled in an ice bath. BuLi (1.52 mL, 2.42 mmol, 15% in hexane) was added into this solution with syringe and the resulting solution was stirred for 3 h at rt. Chlorotrimethylsilane (0.37 mL, 315 mg, 2.90 mmol) was added and stirring continued for 18 h at rt. The reaction was quenched with satd aq $NaHCO_3$ solution and extracted with Et_2O. Organic extracts were washed with brine, dried (Na_2SO_4), and concentrated. Purification of the crude product by column chromatography (SiO_2, hexane/EtOAc 1:1 + 0.5% Et_3N) afforded TMS-compound **9** (363 mg, 61%) as an orange oil. $[\alpha]_D = -113.3$ (*c* 0.92, MeOH). ^1H NMR (300 MHz, $CDCl_3$): δ 4.35 (t, $J = 2.4$ Hz, 1H), 4.22 (dd, $J = 2.4$, 1.2 Hz, 1H), 4.11 (m, 1H), 4.01 (m, 2H), 3.96 (m, 1H), 3.91 (m, 1H), 3.33 (dd, $J = 8.1$, 3.0 Hz, 1H), 2.43–2.21 (m, 3H), 2.07 (s, 6H), 1.95–1,73 (m, 5H), 0.25 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 94.4, 89.0, 73.3, 72.4, 72.0, 70.3, 68.6, 68.3, 67.5, 67.0, 62.2, 41.3, 25.9, 25.0, 24.6, 24.5, 0.8. IR (neat): ν 3092, 2926, 2856, 2818, 2775, 1451, 1243, 1154, 1046, 1019, 830, 811, 753, 687 cm^{-1}. HR EI MS: for $C_{20}H_{31}FeNSi$: calcd: 369.1575, found: 369.158.

5.9. (*R*,*pR*)-1-(Diphenylphosphanyl)-2,1′-[1-(dimethylamino)pentan-1,5-diyl]-3-trimethylsilylferrocene 10

TMS-compound **9** (262 mg, 0.709 mmol) was dissolved in anhydrous Et_2O (10 mL) and BuLi (0.89 mL, 1.42 mmol, 15% in hexane) was added dropwise at rt. The resulting mixture was stirred for 5 h at rt. Then the solution was cooled in an ice bath and $ClPPh_2$ was added and the mixture was stirred for 18 h at rt. After diluting with Et_2O, the reaction was quenched with satd aq $NaHCO_3$ solution and phases were separated, then the aqueous phase was extracted with Et_2O. Combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated. The crude mixture was purified by column chromatography (SiO_2, hexane/EtOAc 5:1 + 0.5% Et_3N). Product **10** (186 mg, 47%) was isolated as an orange oil. $[\alpha]_D = +319.8$ (*c* 0.54, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (m, 2H), 7.33 (m, 6H), 7.20 (m, 2H), 4.19 (m, 2H), 3.95 (m, 1H), 3.88 (m, 1H), 3.68 (m, 1H), 3.42 (m, 1H), 2.80 (dd, $J = 8.7$, 2.5 Hz, 1H), 2.68 (m, 1H), 2.54–2.21 (m, 4H), 2.02 (m, 1H), 1.86 (m, 2H), 1.66 (s, 6H), 0.28 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.3, 140.1 (d, $J = 6.1$ Hz), 135.2 (d, $J = 22.7$ Hz), 132.9 (d, $J = 20.5$ Hz), 128.5, 127.7 (d, $J = 7.5$ Hz), 127.4, 127.3, 103.9 (d, $J = 18.7$ Hz), 89.8, 79.4 (d, $J = 17.7$ Hz), 76.1 (d, $J = 3.6$ Hz), 74.5, 73.8 (d, $J = 4.9$ Hz), 71.2, 68.6, 66.9, 66.3, 65.7 (d, $J = 1.7$ Hz), 43.5, 28.6 (d, $J = 11.4$ Hz), 25.1 (d, $J = 6.9$ Hz), 24.4, 23.7, 1.3. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ −22.3. IR (neat): ν 3084, 3049, 2938, 2895, 2860, 2814, 2771, 2713, 2671, 1462, 1401, 1324, 1246, 1216, 1123, 1023, 907, 822, 756 cm^{-1}. HR EI MS: for $C_{32}H_{40}FeNPSi$: calcd: 553.2017, found: 553.202.

5.10. (*R*,*pR*)-1-(Diphenylphosphanyl)-2,1′-[1-(diphenylphosphanyl)pentan-1,5-diyl]ferrocene 11

Compound **10** (223 mg, 0.403 mg) was dissolved in TBAF in THF (10 mL, 1 M) and the resulting solution was refluxed for 24 h. After cooling, the solution was concentrated to approx. 1/3 of its original volume and the residue was partitioned between water and Et_2O. Organic phase was washed with brine, dried (Na_2SO_4), and concentrated. Column chromatography afforded desilylated product (117 mg, 60%). This compound was dissolved in acetic acid. The solution was degassed and $HPPh_2$ was added in one portion. The resulting solution was stirred for 18 h at 80 °C. After cooling, the reaction mixture was concentrated and the residue dissolved in hot EtOH and let crystallize. Diphosphine **11** (82 mg, 35%, from **10**) was collected after filtration as yellow crystals. Mp = 121–123 °C. $[\alpha]_D = +482.9$ (*c* 0.31, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ 7.63 (m, 2H), 7.54 (m, 2H), 7.36 (m, 3H), 7.22–7.10 (m, 13H), 4.23 (m, 1H), 4.08 (t, $J = 2.4$ Hz, 1H), 3.92 (m, 1H), 3.89 (m, 1H), 3.76 (t, $J = 2.4$ Hz, 2H), 3.10–2.93 (m, 3H), 2.39 (m, 1H), 2.04–1.66 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3 (d, $J = 7.6$ Hz), 140.0 (dd, $J = 11.2$, 4.5 Hz), 138.7 (dd, $J = 21.8$, 2.3 Hz), 137.8 (d, $J = 18.3$ Hz), 135.6 (d, $J = 22.6$ Hz), 134.0 (d, $J = 20.7$ Hz), 133.9 (d, $J = 19.8$ Hz), 132.7 (dd, $J = 17.1$, 1.7 Hz), 128.8 (d, $J = 9.1$ Hz), 128.3, 128.9 (d, $J = 7.3$ Hz), 127.8 (d, $J = 8.0$ Hz), 127.5 (d, $J = 6.9$ Hz), 127.4 (d, $J = 5.9$ Hz), 127.0, 100.3 (dd, $J = 24.5$, 18.4 Hz), 94.2, 71.2 (dd, $J = 6.1$, 1.9 Hz), 73.8 (d, $J = 16.9$ Hz), 73.2, 71.9 (d, $J = 4.8$ Hz), 67.8, 67.1, 67.0, 66.1, 37.4 (d, $J = 13.8$ Hz), 32.3 (dd, $J = 23.1$, 10.4 Hz), 31.8, 25.7, 25.5. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ −1.5 (d, $J = 73.8$ Hz), −22.8 (d, $J = 74.0$ Hz). IR (neat): ν 3080, 3049, 2934, 2856, 1478, 1436, 1316, 1285, 1216, 1092, 1034, 810, 741 cm^{-1}. Elem. Anal. Calcd for $C_{39}H_{36}FeP_2$ (622.5): C, 75.25; H, 5.83. Found: C, 74.42; H, 6.10.

5.11. Allylic alkylation

Ligand (0.020 mmol) and $[Pd(allyl)Cl]_2$ (3.7 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (2.5 mL) and the solution stirred for 10 min at rt. This solution was added into a solution of 1,3-diphenyl-1-acetoxypropene (252 mg, 1.00 mmol) in CH_2Cl_2 (2.5 mL). Then *N*,*O*-bis(trimethylsilyl)acetamide (0.49 mL, 407 mg, 2.00 mmol), dimethylmalonate (0.23 mL, 264 mg, 2.00 mmol), and KOAc (5 mg, 0.050 mmol) were added in this order. The resulting mixture was stirred at rt. and monitored by TLC. When no starting material was detected or after 48 h the solution was concentrated and the residue purified by column chromatography (SiO_2, hexane/EtOAc 9:1). The enantiomeric excess was determined by HPLC (OD-H, hexane/*i*-PrOH 95:5, 0.5 mL/min); t_R 16.52 min (*R*), t_R 17.61 min (*S*). ^1H NMR (300 MHz, $CDCl_3$): δ 7.35–7.20 (m, 10H), 6.50 (d, $J = 15.8$ Hz, 1H), 6.33 (dd, $J = 15.7$, 8.5 Hz, 1H), 4.27 (dd, $J = 10.9$, 8.5 Hz, 1H), 3.95 (d, $J = 10.9$ Hz, 1H), 3.71 (s, 3H), 3.52 (s, 3H) in agreement with the literature.[25]

5.12. Crystal structure data for 1

Crystallization from EtOH, red bar with dimensions $0.40 \times 0.20 \times 0.15$ mm, $C_{39}H_{36}FeP_2$, M_r 622.47. Orthorhombic space group $P2_12_12_1$, $a = 9.6170(2)$, $b = 9.8330(2)$, $c = 33.0660(6)$ Å, $V = 3126.85(11)$ Å^3 from 4075 reflections, $T = 150(2)$ K, $\lambda = 0.71073$ Å, $Z = 4$, $D_x = 1.322$ g cm^{-3}, $\mu = 0.612$ mm^{-1}. The data were collected on Nonius KappaCCD area detector diffractometer with Mo Kα radiation. Maximum θ was 27.5°. The *hkl* ranges were −12/12, −12/12, −42/42. 35,319 reflections measured, 7161 independent reflections, 6384 reflections with $I > 2\sigma(I)$. The structure was solved with SIR92 (Altomare et al., 1994). Refinement on F^2 was performed with SHELXL-97 (Sheldrick, 1997), $R[F^2 > 2\sigma(F^2)] = 0.0307$, $wR(F^2) = 0.0726$, $S = 1.037$, $\Delta\rho_{max} = 0.351$ e Å^{-3}, $\Delta\rho_{min} = -0.302$ e Å^{-3}. Hydrogen atoms were fixed at calculated positions. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 615287.

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