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The preparation of ferrocene-containing phosphinamine ligands possessing central and planar chirality and their application in palladium-catalysed allylic substitution☆

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ABSTRACT

The preparation of four novel ferrocenylphosphinamine ligands, possessing both planar and central chirality, is described. The absolute configuration of two of the ligands was confirmed by X-ray crystallographic analysis. The palladium complexes of these new ligands were applied in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate to study the effect of planar chirality and/or the trimethylsilyl group. Quantitative yields with *ees* of up to 77% were obtained with the ligand that bears both (*R*)-planar and (*R*)-central chirality. Application of its trimethylsilyl analogue gave significantly lower ees, whereas the presence of the trimethylsilyl group in the ligand that bears (*S*)-planar and (*R*)-central chirality had a beneficial effect on enantioselectivity. Solution ^{1}H NMR spectroscopic studies of the 1,3-diphenylallyl palladium complexes of two of the ligands revealed the major diastereomer in solution does not give rise to the major product observed in allylic alkylation, assuming nucleophilic attack *trans* to phosphorus.

1. Introduction

Since the initial reports by Tjuji [1,2], allylic alkylation has emerged as one of the most widely studied catalytic reactions in organic synthesis. Especially asymmetric allylic alkylation, first reported by Trost [3–5], is nowadays regarded as one of the most important asymmetric catalytic transformations in organic chemistry for the formation of a diversity of bonds to carbon and has been the subject of several excellent reviews and book chapters [6–13]. In the last few decades, much research has been devoted to elucidate the factors that influence the outcome of the reaction, such as metal, solvent, nucleophile, allylic substrate and ligand, including mechanistic investigations underpinned by a combination of structural, spectroscopic and computational studies [14–22]. In particular, the design and application of chiral ligands has received much attention. In this respect, a plethora of diphosphine and diamine ligands and, more recently, phosphinamine [23–26] ligands have been used to great success, leading to high enantioselectivities at high conversion. In the latter class of ligands, electronic desymmetrisation of the allyl encourages preferential attack of the nucleophile at the allylic carbon *trans* to phosphorus, which is more electrophilic due to the larger *trans*-effect exerted by phosphorus [27–31]. In combination with steric effects, high enantioselectivities can be obtained and selected examples include the Phox ligands **1** developed independently by Williams, Pfaltz, and Helmchen [32–34], Brown's axially chiral Quinap ligand **2** [35] and the pyrrolidine-containing ligands **3**–**4** which we reported, Fig. 1 [36–38].

In addition, planar chiral ferrocene ligands have been particularly successful leading to an unprecedented high enantioselectivity of 99.6% ee at full conversion for the alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate [39]. Other phosphinamine ferrocene-containing ligands possessing planar chirality have been prepared and applied with success in allylic alkylation and a variety of other asymmetric processes [40]. The ease of preparation of planar chiral ferrocene compounds through the use of diastereoselective *ortho*-metalating groups, including

☆ Dedicated to the memory of Professor Jonathan Williams, a brilliant chemist with pioneering work in P,N ligands and borrowing hydrogen chemistry – a true gentleman and someone who I was always happy to meet.

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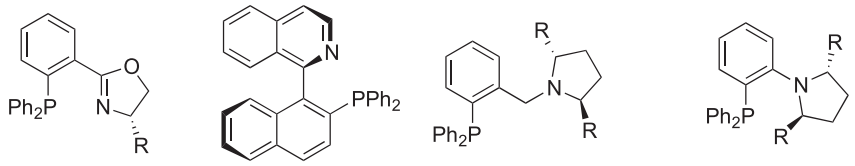


1 **2** **3a**; R = Me **3b**; R = Et **4a**; R = Me **4b**; R = Et

Fig. 1. Typical P,N ligands applied to the Pd-catalysed allylic alkylation.

amines [41–43], sulfoxides [44], acetals [45], oxazolines [46–48] azepines [49], sulfoximines [50] and hydrazones [51], certainly contributed to the wide range of planar chiral ferrocene ligands reported. We reported the preparation of ferrocenylphosphinamine ligands of type **5**, Fig. 2, possessing both planar and central chirality obtained through diastereoselective metalation of *trans*-(2*R*,5*R*)-2,5-dialkyl-1-(ferrocenylmethyl)pyrrolidines and their application in Pd-catalysed allylic alkylation [52]. The initial example of Kumada and Hayashi [41], and subsequent related examples from Togni [42], however, have as their key precursor (*R*)-*N*,*N*-(dimethyl-1-ferrocenyl)ethylamine **6**, which bears an α-chiral center.

Thus, interested by the successful application of ferrocene-containing ligands, bearing an α-chiral center, and to extend our work on pyrrolidine-containing P,N ligands, we wished to develop novel ferrocene ligands in which the α-chiral center is incorporated in a pyrrolidine unit. We had previously reported the enantioselective preparation of ferrocenepyrrolidine (*R*)-**7** and applied it in the diastereoselective formation of a series of N,O ligands of type **8** for the diethylzinc-mediated addition to aldehydes [53]. Therefore, we now wish to report the synthesis and application of novel ferrocene-phosphinamine ligands (*R*,*R*)-**9**, (*R*,*S*)-**9**, (*R*,*R*)-**10** and (*R*,*S*)-**10** obtained through diastereoselective *ortho*-metalation of ferrocenepyrrolidine (*R*)-**7**, Fig. 3.. These ligands were tested in the allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate anion as nucleophile. In order to rationalise the origin of enantioselectivity obtained in allylic alkylation, an NMR study of their palladium η^3-allyl species will also be presented.

2. Results and discussion

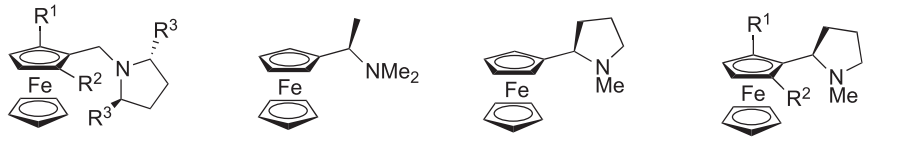
Starting from ferrocenepyrrolidine (*R*)-**7**, we investigated its diastereoselective *ortho*-directing properties and, similar to the extensive lithiation studies described for α-(*N*,*N*-dimethylamino) alkylferrocenes [54,55], various ferrocenyloxazolines [47,56] and the *trans*-2,5-dialkyl-ferrocenylpyrrolidines [52], variations of the alkyllithium reagent, solvent, temperature and lithiation time were examined for its phosphinylation.

Initial studies towards the lithiation of (*R*)-5 were carried out with *n*-butyllithium in ether, the successful conditions employed by Hayashi and Ugi for lithiation of closely related (*R*)-*N*,*N*-(dimethyl-1-ferrocenyl)ethylamine 2 [57]. Unfortunately, no product was obtained at either room temperature, 0 °C or −78 °C. We then focused on *s*-butyllithium-mediated deprotonations in ether and successful lithiation and phosphinylation only occurred at −78 °C, affording the 1,2 disubstituted product 3 in a moderate 42% yield. The use of hexane as solvent with TMEDA as additive did not improve the yield (30%). Although no product was observed by performing the lithiations at 0 °C, yields were substantially improved by addition of *s*-butyllithium at −78 °C and stirring at this temperature for 3 h followed by stirring at 0 °C for 1.5 h, Scheme 1. Subsequent reaction with chlorodiphenylphosphine afforded 3 in 64% yield and 84% de as determined from ^{1}H and ^{31}P NMR spectroscopic analysis.

The crude mixture was purified by column chromatography on neutral silica gel, with both diastereomers being isolated. A high optical rotation of +425 (c = 0.2, $CHCl_3$) was recorded for the major diastereomer. Comparison of this optical rotation with those of known planar chiral ferrocene compounds suggested that the major diastereomer was (*R*,*R*)-**9**. Crystals of the major diastereomer suitable for single-crystal X-ray structure determination were grown from ethanol (crystal - orthorhombic, space group $P2_12_12_1$). Fig. 4 shows the results of the analysis, which established that the newly introduced planar chirality had the (*R*)-configuration, while also confirming the (*R*)-central chirality in the pyrrolidine ring as previously established [53].

The *ortho*-directing properties of (*R*)-**7** are in contrast to the *ortho*-directing properties of the related (*R*)-*N*,*N*-(dimethyl-1-ferrocenyl)ethylamine **6**, which afforded 1,2 disubstituted ferrocene derivatives in a 92% de, with the major diastereomer possessing (*S*)-planar chirality. Therefore a marked change in the *ortho*-directing properties was observed when the nitrogen atom and the α-methyl group are contained within a pyrrolidine ring. By examination of the possible transition states **11** and **12**, the favoured diastereomer can be predicted, Fig. 5.

In transition state **11**, we postulate that the upper cyclopentadienyl ring and the pyrrolidine ring are nearly co-planar, thus minimising the steric interactions between the pyrrolidine ring and the iron atom. In addition the methyl group points toward the ferrocene unit. Although generally this is disfavoured, it allows for the approach of the alkyllithium towards the nitrogen atom from



5a; R^1 = PPh_2, R^2 = H, R^3 = Me or Et
5b; R^1 = H, R^2 = PPh_2, R^3 = Me or Et

6 **7**

8a R^1 = $C(OH)Me_2$, R^2 = H or TMS
8b R^2 = $C(OH)Me_2$, R^1 = H or TMS

Fig. 2. Typical P,N ligands applied to the Pd-catalysed allylic alkylation.

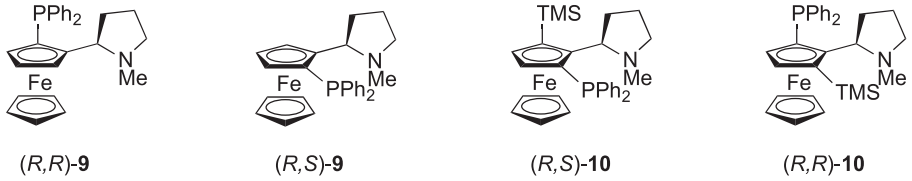
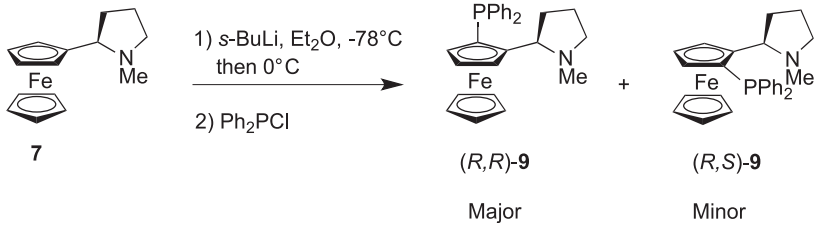


Fig. 3. Ligands (*R*,*R*)-**9**, (*R*,*S*)-**9**, (*R*,*R*)-**10** and (*R*,*S*)-**10**.



Scheme 1. Synthesis of (*R*,*R*)-**9**.

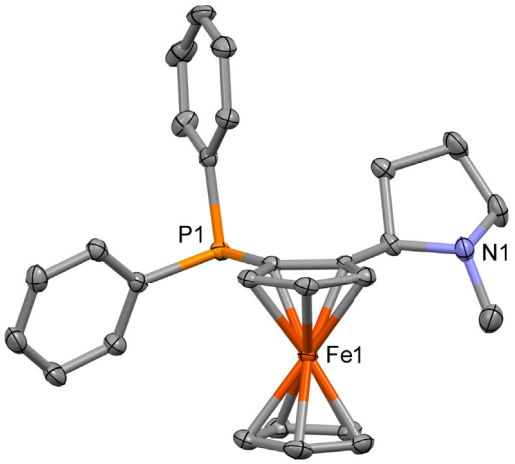


Fig. 4. X-Ray single crystal structure of (*R*,*R*)-**9**.

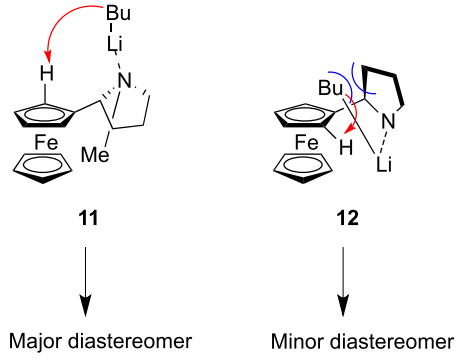


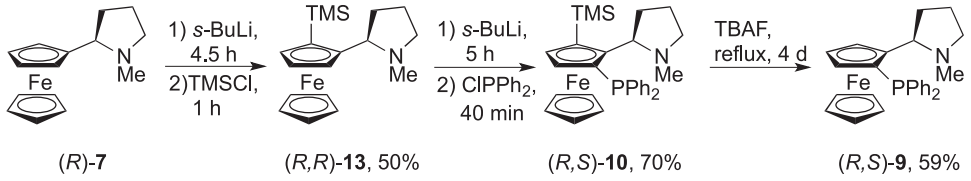
Fig. 5. Proposed transition states for lithiation of (*R*)-**7**.

above the plane of the upper cyclopentadienyl ring. This is the favoured transition state, which leads to the (*R*)-planar chirality. However in transition state **12**, if the nitrogen lone pair points towards the *ortho*-cyclopentadienyl carbon this would place the pyrrolidine ring in a non co-planar geometry. Approach of the alkyllithium in this case is sterically hindered by the pyrrolidine ring, which is projected upward towards the incoming reagent.

Synthesis of ligands (*R*,*S*)-**9**, (*R*,*R*)-**10** and (*R*,*S*)-**10**. Although small quantities of minor diastereomer (*R*,*S*)-**9** can be obtained, a more effective synthesis toward formation of (*R*,*S*)-**9** is desirable. To this purpose, the trimethylsilyl group is used to temporarily block the favoured diastereomeric position, an approach first employed by Richards in analogous ferrocenyloxazoline chemistry [56]. Thus, lithiation of (*R*)-**7** under the optimal conditions as described previously determined, followed by a quench with chlorotrimethylsilane gave **13** in 71% yield with 70% de. After purification by column chromatography on silica gel the major diastereomer was isolated in 50% yield. Subsequently, the diphenylphosphino group was introduced by lithiation of (*R*,*R*)-**13** with *s*-butyllithium followed by reaction with chlorodiphenylphosphine to afford the 1,2,3-trisubstituted-ferrocenylpyrrolidine (*R*,*S*)-**10** in 70% yield. Next, the trimethylsilyl protecting group was removed by heating (*R*,*S*)-**10** with TBAF in THF under reflux for 4 days to give (*R*,*S*)-**9** in 59% yield, Scheme 2.

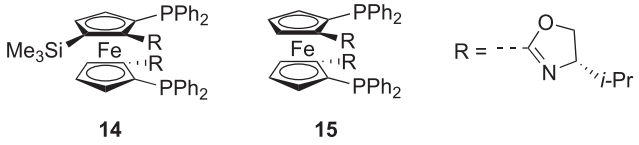
To date only two reports have detailed the effect of *ortho*-silylation on the properties of ferrocene-based ligands in catalysis. Firstly, the application of the trimethylsilyl modified ligand **14** in the allylic alkylation of 1,3-diphenylprop-2-enyl using dimethylmalonate anion as the nucleophile led to better enantiocontrol (ee = 89% (*R*)-product) compared to the application of its unsilylated analogue **15** (ee = 38% (*S*)) [58], Fig. 6. Secondly, the introduction of a trimethylsilyl group to (*R*,*R*)-**8a** to generate (*R*,*R*)-**8b** had a pronounced effect in catalysis as the ee increased from 84 to 95% for the diethylzinc addition to aldehydes [53]. Alternatively, the introduction of the TMS group to (*R*,*S*)-**8a** to generate (*R*,*S*)-**8b** had a detrimental effect on the enantioselectivity and its sense (from 92% to −67%).

Thus, also in our case, in catalysis the intermediate trisubstituted ferrocenes may show interesting properties due to the trimethylsilyl group influencing the conformation of the pyrrolidine ring. For a full comparison of both planar chirality and the effect of the trimethylsilyl group, trisubstituted ferrocenephosphinamine ligand (*R*,*R*)-**10** was prepared in 93% yield by lithiation of (*R*,*R*)-**9** followed by reaction with chlorotrimethylsilane, Scheme 3. Crystals of the major diastereomer suitable for single-crystal X-Ray structure determination were grown from ethanol (crystal - monoclinic, space group $P2_1$). Fig. 7 shows a view of one of the two independent



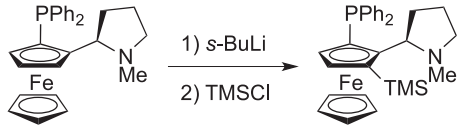
(*R*)-**7** (*R,R*)-**13**, 50% (*R,S*)-**10**, 70% (*R,S*)-**9**, 59%

Scheme 2. Synthesis of ligands (*R,S*)-**10** and (*R,S*)-**9**.



14 **15**

Fig. 6. Trisubstituted ferrocene ligands **14** and **15**.



(*R,R*)-**9** (*R,R*)-**10**

Scheme 3. Synthesis of (*R,R*)-**10**.

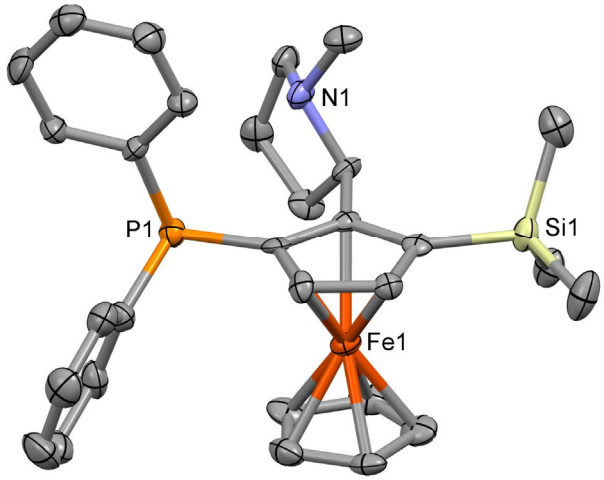


Fig. 7. X-Ray structure of one of the two independent molecules of (*R,R*)-**10** in the crystal.

molecules in asymmetric unit of the crystal, which differ only slightly in their conformations (see Supporting Information).

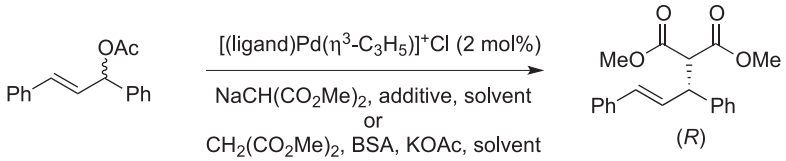
3. Allylic alkylation

The enantio-differentiating abilities, the role of planar chirality and the influence of the trimethylsilyl group in allylic alkylation employing ligands (*R,R*)-**9** and (*R,S*)-**9** (*R,S*)-**10** and (*R,R*)-**10** were investigated. The catalyst can either be preformed palladium η^3-allyl complexes of the ligand or to assume that such complexes are formed when a slight excess of ligand is added to *e.g.* $Pd_2(dba)_3$ or η^3-allyl palladium chloride dimer. The former approach was employed in the present study. The air-stable η^3-allyl palladium tetrafluoroborate complexes of these ligands were prepared in 63–99% yield by reaction of the appropriate phosphinamine ligand with η^3-allyl palladium chloride dimer and sodium tetrafluoroborate. Two isomeric complexes can be envisaged, namely one having the central allyl proton pointing above the P–N plane (*endo*) and one having the central allyl proton pointing below the P–N plane (*exo*). These complexes can interconvert through a η^3-η^1-η^3 mechanism. For the complexes obtained with ligands (*R,R*)-**9** and (*R,S*)-**9** only one diastereomer was observed by ^{31}P NMR spectroscopy, whereas the complexes obtained from (*R,S*)-**10** and (*R,R*)-**10** showed both diastereomers in a 1:1 and 1:24 ratio, respectively. As the test reaction the alkylation of 1,3-diphenyl-2-propenyl acetate using dimethylmalonate anion as the nucleophile was investigated, Scheme 4.

Allylic alkylations were carried out on a 0.25 mmol scale of 1,3-diphenylpropenyl acetate employing 2 mol% of catalyst. The nucleophile was either added as its preformed sodium salt or it was formed *in situ* by addition of *N,O*-bis(trimethylsilyl) acetamide (BSA) and a catalytic amount of KOAc. The key results of the allylic alkylation experiments using the BSA and sodium malonate procedures are summarised in Tables 1 and 2 – see Supporting Information for a full set of results.

BSA Procedure. Using the BSA procedure moderate to very high conversions were obtained for all catalysts, although longer reaction times were required for the catalysts obtained from ligands (*R,R*)-**9** and (*R,R*)-**10**. In all cases the (*R*)-enantiomer was the favoured isomer formed, with the highest ee of 77% obtained using ligand (*R,R*)-**9** in DMF at room temperature (Table 1, entry 1). By lowering the reaction temperature from room temperature to −25 °C the enantioselectivity decreased from 77% to 71% ee (Table 1, entry 2). A comparison of the results from catalysis of diastereomeric ligands (*R,R*)-**9**, and (*R,S*)-**9** shows that the (*R,R*)-ligand afforded the higher enantioselectivity, with the optimum being 77% ee with DMF as solvent, compared to 42% ee for the diastereomeric (*R,S*)-ligand (Table 1, entry 4). Therefore, the (*R,R*)-ligand is the matched case of the two elements of chirality. However the (*R,S*)-ligand has higher activity, resulting in high conversions within 2–3 h for reactions in dichloromethane and DMF, compared to 48 h for the (*R,R*)-diastereomer (Table 1, entries 3 and 4). A comparison of the role of planar chirality in the trisubstituted ferrocene derivatives shows that the (*R,S*)-**10** ligand afforded the product with 57% ee in 90% conversion after 2 h compared to 20% ee in 40% conversion after 23 h for the diastereomeric (*R,R*)-**10** (Table 1, entries 6 and 8). Interestingly, compared to the optimum disubstituted phosphinamine ligand which had the (*R*)-planar chirality, the optimum trisubstituted ligand bears the opposite (*S*)-planar chirality.

Investigation of the role played by the bulky trimethylsilyl group in influencing the properties of the ligand (*R,S*)-**10** in catalysis compared to the analogous phosphinamine ligand (*R,S*)-**9** shows that the trisubstituted-ferrocenyl phosphinamine ligand afforded higher enantioselectivities of 57% ee in DMF compared to 42% ee for the disubstituted analogue (*R,S*)-**9** (Table 1, entries 4 and 6). The bulky trimethylsilyl group may restrict the conformation of the pyrrolidine ring, thereby allowing it to be a more effective chiral controlling group, which increases the enantioselectivity. From



Scheme 4. Asymmetric allylic alkylation.

Table 1
Pd-catalysed Allylic Alkylation using BSA procedure.[a]

Entry	Ligand	Solvent	Time (h)	Conversion[b] (%)	Ee[c] (%) (*R*)
1	(*R*,*R*)-**9**	DMF	48	100	77
2	(*R*,*R*)-**9**	DMF[d]	168	88	71
3	(*R*,*S*)-**9**	DCM	3	81	28
4	(*R*,*S*)-**9**	DMF	2	58	42
5	(*R*,*S*)-**10**	DCM	2	73	54
6	(*R*,*S*)-**10**	DMF	2	90	57
7	(*R*,*R*)-**10**	DCM	6	67	32
8	(*R*,*R*)-**10**	DMF	24	40	20

[a] Reaction conditions: (ligand)Pd(allyl).BF_4/allyl/dimethyl malonate/KOAc/BSA = 1/50/55/1/55. T = room temperature.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Ees were determined by HPLC (Chiracel OD column). Configuration was determined by comparison of the optical rotation with literature values.
[d] T = −25 °C.

Table 2
Pd-catalysed Allylic Alkylation using Sodium Malonate Procedure.[a]

Entry	Ligand	Solvent	T (h)	Conversion[b] (%)	Ee[c] (%) (*R*)
1	(*R*,*R*)-**9**	DMF	48	12	58
2	(*R*,*S*)-**9**	DMF	22	17	24
3	(*R*,*S*)-**10**	DCM[d]	5	92	50
4	(*R*,*R*)-**10**	DCM[d]	28	12	33

[a] Reaction conditions: (ligand)Pd(allyl).BF_4/allyl/sodium dimethyl malonate = 1/50/55. T = room temperature.
[b] Determined by ^{1}H NMR spectroscopy.
[c] Ees were determined by HPLC (Chiracel OD column), configuration was determined by comparison of the optical rotation with literature values.
[d] 15-crown-5 was added.

these results, the trend suggests that the trimethylsilyl group has only a marginal effect on the activity. The presence of the sterically demanding trimethylsilyl group in (*R*,*R*)-**10** did not enhance the enantioselectivity compared to its analogous ligand (*R*,*R*)-**9** as lower selectivities are obtained in DMF and acetonitrile (Table 1, entries 4 and 8). Therefore, the trimethylsilyl group lowers the observed enantioselectivity in catalysis.

Sodium malonate procedure. In all cases the (*R*)-enantiomer was the favoured isomer formed, again with the highest ee of 58% being obtained using ligand (*R*,*R*)-**9** in DMF (Table 2, entry 1). For all catalysts prepared and irrespective of the solvent applied, low conversions were obtained when the sodium malonate procedure was used. The only exception was the catalyst derived from ligand (*R*,*S*)-**10** in dichloromethane, which gave 92% conversion after 3 h (Table 2, entry 3). Addition of 15-crown-5, which is commonly used to increase the solubility of the anion, gave optimal results for the catalysts derived from trimethylsilylsubstituted ligands (*R*,*S*)-**10** and (*R*,*R*)-**10** when the reactions were performed in dichloromethane (Table 2, entries 3 and 4). Comparison of the diastereomeric ligands and the effect of the trimethylsilyl group is analogous to the results obtained applying the BSA procedure.

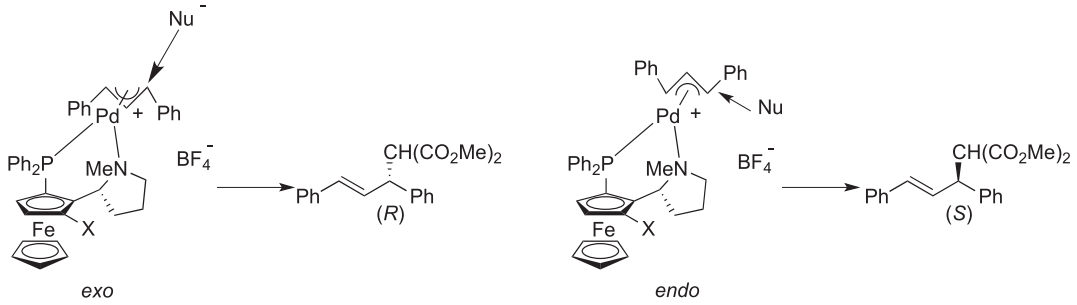
4. Solution NMR studies

Considerable effort has been made to understand the critical enantiodifferentiating carbon-carbon bond-forming step from the initial investigations of Bosnich [59,60] employing diphosphine ligands to the more recent work of Brown, Pfaltz, Togni and Helmchen employing phosphinamine ligands [27,34,35,61–64]. The key findings from these studies suggest that the transition state of allyl palladium complexes contains an allyl group which has reoriented itself into a η^2-alkene product-like geometry, rather than the η^3-allyl starting complex, thus facilitating nucleophilic attack on the allyl terminal carbon *trans* to the phosphorus donor atom. The lability of the diastereomeric 1,3-diphenylallyl complexes is influenced by such electronic factors and also by intra-complex steric clashes between the ligand and the allyl. In the case that the 1,3-diphenylallyl palladium complexes only adopt a *syn-syn* geometry, two isomeric complexes can be envisaged, namely one having the central allyl proton pointing above the P–N plane (*endo*) and one having the central allyl proton pointing below the P–N plane (*exo*). Upon nucleophilic attack *trans* to phosphorus the *endo*-diastereomer will lead to the product having the opposite configuration of the product obtained through reaction of the *exo*-diastereomer, Scheme 5.

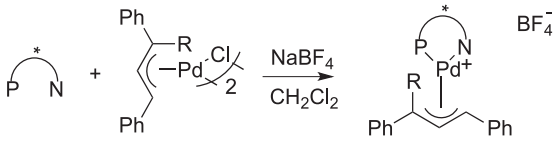
Thus, in an attempt to explain the stereoselectivity obtained from application of metal complexes of ligands (*R*,*R*)-**9,** (*R*,*S*)-**9**, (*R*,*S*)-**10** and (*R*,*R*)-**10** in allylic alkylation and to gain an insight into the presence and configuration of the diastereomeric intermediates present in solution, NMR studies of the (1,3-diphenyl-η^3-allyl) palladium tetrafluoroborate complexes **16**–**19** were carried out. Additionally, for each ligand the (1,1,3-triphenyl-η^3-allyl)palladium tetrafluoroborate complexes **20**–**23** were studied since NMR studies of these complexes provide information on the steric demand exerted by the ligands *cis*- and *trans*-to the diphenylphosphino moiety. The (1,3-diphenyl-η^3-allyl)palladium tetrafluoroborate complexes **16**–**19** and (1,1,3-triphenyl-η^3-allyl) palladium tetrafluoroborate complexes **20**–**23** were prepared by reaction of ligands **9** and **10** with the respective η^3-allyl palladium chloride dimer and sodium tetrafluoroborate, Scheme 6.

^{31}P NMR spectroscopy was carried out to determine the number and ratio of different diastereomers formed. ^{1}H NMR and ^{1}H–^{1}H COSY were used to identify the protons of the unsubstituted cyclopentadienyl ring, the *N*-methyl group, the trimethylsilyl group (for complexes derived from ligands (*R*,*R*)-**10** and (*R*,*S*)-**10**) and the allyl protons of both intermediates. Subsequent 1D and 2D NOESY experiments were performed to determine the configurations of the major and minor intermediates. This procedure is exemplified by analysis of the complexes derived from ligand (*R*,*R*)-**9** and all other complexes were identified in a similar manner – for all relevant spectra and full analysis, see Supporting Information.

Analysis of **16** by ^{31}P NMR spectroscopy confirmed the presence of both diastereomeric intermediates as indicated by two peaks in the spectrum at δ 18.8 and δ 21.3 in a 1:1.7 ratio. Further NMR



Scheme 5. *Exo*- and *endo*-diastereomers leads to product having the opposite configuration.



16; L = (*R,R*)-**9**, R = H
17; L = (*R,S*)-**9**, R = H
18; L = (*R,S*)-**10**, R = H
19; L = (*R,R*)-**10**, R = H
20; L = (*R,R*)-**9**, R = Ph
21; L = (*R,S*)-**9**, R = Ph
22; L = (*R,S*)-**10**, R = Ph
23; L = (*R,R*)-**10**, R = Ph

Scheme 6. Synthesis of palladium complexes **16**–**23**.

studies were carried out to determine the configuration of these isomers in solution. In the ^{1}H NMR spectrum, there were two singlets at δ 3.69 and δ 3.70 each representing the unsubstituted cyclopentadienyl ring of the major and minor diastereomers, respectively, while the *N*-methyl group also appeared as a singlet at δ 1.95 (major) and δ 2.50 (minor). With the aid of ^{1}H–^{1}H COSY the allyl protons of both intermediates were identified. For the major isomer, the allyl proton *trans* to nitrogen appeared as a doublet at δ 5.42, which showed a COSY cross-peak to the central allyl proton which appeared as an apparent triplet centred at δ 6.18. This in turn showed a cross-peak to a multiplet between δ 5.56–5.64, which integrated for slightly more than one proton, and this was assigned as the allyl proton *trans* to phosphorus together with an allyl proton of the minor isomer. The allyl protons of the minor isomer were identified as a doublet at δ 3.63 (allyl proton *trans* to nitrogen) and this gave a COSY cross-peak to a multiplet at δ 6.78 (central allyl proton). A COSY cross-peak was observed between this multiplet and the multiplet at δ 5.56–5.64, hence the allyl proton *trans* to phosphorus of the minor diastereomer is overlapped by the same proton of the major diastereomer.

With this information, 2D and 1D NOESY experiments were carried out to determine the configurationsof the major and minor intermediates. From the 2D NOESY spectrum, a nOe was observed between the terminal allyl protons of the major diastereomer which confirms the *syn-syn* orientation of the allyl group. Similarly a nOe between the terminal allyl protons of the minor diastereomer were also observed. Both *N*-methyl peaks showed a nOe to an apparent triplet at δ 2.96 which integrates for 2 protons. This is assigned as the proton α-to ferrocene for both the major and minor diastereomers. A 1D NOESY experiment was also carried out; by irradiating the multiplet at δ 5.56–5.64, which represents both allyl protons *trans* to phosphorus, nOe enhancements were observed to each of the allyl protons *trans* to nitrogen. In addition a nOe was observed to the apparent triplet at δ 2.96, and the singlet at δ 2.50 representing the *N*-methyl of the minor diastereomer. This confirms the minor diastereomeric intermediate is the *exo-syn-syn*, hence the major diastereomer is the *endo-syn-syn* **16**, Fig. 8.

^{31}P NMR spectroscopic analysis of **20** by confirmed the presence of three of the four possible diastereomers with three singlets at δ 17.4, 19.7, and 24.3 present in a ratio of 1:15:3. The ^{1}H NMR

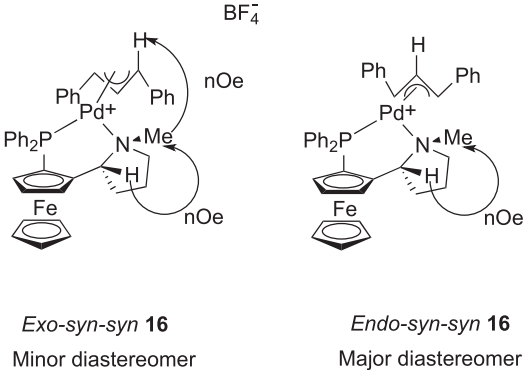


Fig. 8. Relevant nOes for complex **16**.

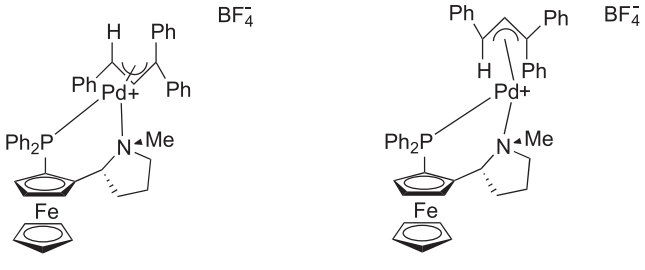


Fig. 9. Possible configurations of the major diastereomer of **20** in solution.

spectrum was complicated and only the major isomer could be identified. A doublet at δ 3.16 was noted and assigned as an allyl proton *trans* to nitrogen. This showed a COSY cross-peak to a multiplet at δ 7.05 where the central allyl proton was overlapped by aromatic protons. Therefore the configuration of the major diastereomer in solution is likely to be either of the following two possibilities where the terminal allyl proton is *trans* to nitrogen, Fig. 9.

However no nOe was observed that could confirm the

configuration of the allyl group of the major diastereomer. Another point to note is that in the preferred isomer the allyl terminus bearing the geminal diphenyl groups are on the side opposite to the diphenylphosphine indicating that this area of the ligand/metal complex had greater steric demand compared to the pyrrolidine group.

Complexes **17**–**19**, and **21**–**23** were analysed using a similar approach. The ^{1}H NMR data for the allylic and *N*-methyl protons of complexes **16**–**19** are presented in Table 3.

Like in the case of **20**, for the triphenyl-substituted η^3-allyl palladium complexes **21**–**23,** the ^{1}H NMR spectra were complex and assignment of each isomer was not always possible. Only for **22** were we able to characterise the major diastereomer. Table 4 summarises the number and distribution of observed stereoisomers and the configuration of the major stereoisomer(s) of complexes **20**–**23**.

The ratio of ground state diastereomers, the highest obtained experimental ees and the areas of steric demand are summarised in Fig. 10. In all cases only the *syn*-*syn* diastereomers were observed. For the diphenylallyl palladium complex of (*R*,*R*)-**9** the *endo*:*exo* ratio is 1.7:1. Application of ligand (*R*,*R*)-**9** in catalysis gave the (*R*)-enantiomer of product in 77% ee, while the minor diastereomer in solution was the *exo*-diastereomer, which would afford the (*R*)-enantiomer of product assuming nucleophilic attack *trans* to phosphorus. This indicates that the rate of nucleophilic attack on the minor diastereomer is faster than nucleophilic attack on the major diastereomer, which might be attributed to favourable allyl rotation upon nucleophilic attack on the *exo*-diastereomer, Scheme 7. In the case of the *endo*-complex the phenyl group *trans* to nitrogen has to rotate towards the sterically demanding diphenylphosphino-group in order to obtain a transition state in which allyl has reorientated itself into a η^2-alkene product-like geometry, whereas in the case of the *exo*-complex the phenyl group *trans* to nitrogen has to rotate away from the diphenylphosphino group.

Similarly for the trisubstituted ferrocenyl ligand (*R*,*R*)-**10** the minor diastereomer gave rise to the preferred (*R*)-enantiomer in catalysis. In comparison to the disubstituted ligand (*R*,*R*)-**9**, a lower ee of 33% was obtained. In this case the added trimethylsilyl group changed the ratio of the ground state diastereomers from 1.7:1 *endo*:*exo* for (*R*,*R*)-**9** to 2.5:1 (*R*,*R*)-**10**, which might contribute to the lower enantioselectivity. Additionally, the increased steric demand of the pyrrolidine group might have an adverse effect on the 'favourable' allyl rotation.

Interestingly, ligand (*R*,*S*)-**10** afforded a lower ee of 42% while only one diastereomer was present in solution. This diastereomer was confirmed to be the *endo*, which would lead to the favoured (*R*)-enantiomer of product. In the case of complex **18**, the *endo* diastereomer is favoured in an 8:1 *endo*:*exo* ratio, which when alkylated affords the preferred (*R*)-enantiomer. Also in this case the trimethylsilyl group reduces the diastereomeric ratio compared to ligand (*R*,*S*)-**9**, however the *endo*-isomer is still favoured. Compared to (*R*,*S*)-**9** application of (*R*,*S*)-**10** resulted in a higher ee of 57%, which indicates that the trimethylsilyl substituents plays a large role in controlling the course of the reaction favouring alkylation of the *endo*-diastereomer.

For the triphenylsubstituted allyl palladium complexes the influence of planar chirality was evident; (*R*,*R*)-**9** afforded 3 diastereomers in a 1:15:3 ratio, whereas all 4 diastereomers, in a 5:5:3:1 ratio, were observed for ligand (*R*,*S*)-**9**. The trimethylsilyl derivatives of these ligands had the effect of improving the ratio of these intermediates in solution. (*R*,*R*)-**10** only gave 2 diastereomers in solution in a 5:1 ratio compared to (*R*,*R*)-**9**, while (*R*,*S*)-**10** showed improved ratios of diastereomers from 5:5:3:1 to 1:15:3:1 ratios when compared to (*R*,*S*)-**9**. Furthermore, by changing the planar chirality from (*R*) to (*S*) a huge change in the steric demand occurs; for **20** and **23** the preferred isomer has the allyl terminus bearing the geminal diphenyl groups on the side opposite to the diphenylphosphine indicating that this area of the ligand/metal complex had greater steric demand compared to the pyrrolidine group, whereas for **22** the pyrrolidine group has the greater steric demand.

5. Conclusion

In conclusion, we have presented the synthesis and application of four novel ferrocenepyrrolidine-phosphine ligands. *N*-Methylferrocenepyrrolidine (*R*)-**7** proved to be an effective *ortho*-metalating group allowing diastereoselective phosphinylation and silylation in 84% de and 70% de, respectively. The *ortho*-directing properties of (*R*)-**7** are in contrast to the *ortho*-directing properties of related (*R*)-*N*,*N*-(dimethyl-1-ferrocenyl)ethylamine **6**, which afforded the major diastereomer having the (*S*)-planar chirality. The best results in the asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethylmalonate anion as nucleophile were obtained with ligand (*R*,*R*)-**9**, which gave quantitative yields and ees of up to 77% (*R*). This is in line with the results obtained with the non-ferrocene containing pyrrolidine ligands **3** and **4** [36–38], whereas the state of the art P–N (sp^3) ligand for this transformation was reported by Jin in 2005, a ferrocene-containing ligand **24** (Fig. 11), which afforded the product of alkylation of 1,3-diphenyl-2-propenyl acetate at full conversion using dimethylmalonate (BSA procedure) in 99.6% ee [39].

Solution NMR studies on the 1,3-diphenylallyl palladium complexes of ligands (*R*,*R*)-**9** and (*R*,*R*)-**10** revealed that the major

Table 3
Allylic and *N*-Methyl protons of complexes **16**–**19**.

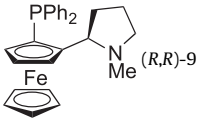
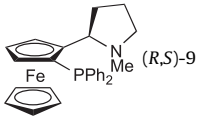
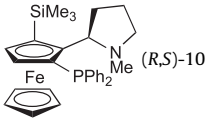
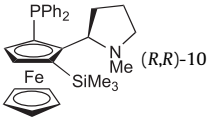
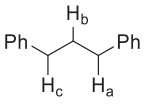
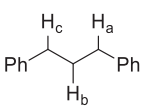
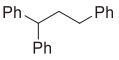
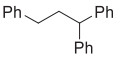
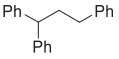
N––P	 (*R*,*R*)-9	 (*R*,*S*)-9	 (*R*,*S*)-10	 (*R*,*R*)-10
	H_a $\delta = 5.42$ H_b $\delta = 6.28$ H_c $\delta = 5.56–5.64$ *N*–Me $\delta = 1.95$ Major (63%)	not observed	H_a $\delta = 4.72$ H_b $\delta = 7.00$ H_c $\delta = 5.49$ *N*–Me $\delta = 2.86$ Minor (11%)	H_a $\delta = 5.46$ H_b $\delta = 6.19$ H_c $\delta = 5.73$ *N*–Me $\delta = 1.99$ Major (71%)
	H_a $\delta = 3.63$ H_b $\delta = 6.78$ H_c $\delta = 5.56–5.64$ *N*–Me $\delta = 2.50$ Minor (37%)	H_a $\delta = 5.22$ H_b $\delta = 6.17$ H_c $\delta = 5.86$ *N*–Me $\delta = 1.79$ Major (100%)	H_a $\delta = 4.98$ H_b $\delta = 6.53–6.62$ H_c $\delta = 6.53–6.62$ *N*–Me $\delta = 3.37$ Major (89%)	H_a $\delta = 3.63$ H_b $\delta = 6.78$ H_c $\delta = 5.56$ *N*–Me $\delta = 2.53$ Minor (29%)

Table 4
Number and distribution of observed enantiomers and the configuration of the major enantiomer(s) of complexes **20**–**23**.

Complex	^{31}P (ppm) (% abundance)	Major enantiomer (N—P)
20	δ 17.4 (5%), δ 19.7 (79%), δ 24.3 (16%)	 *exo* or *endo*
21	δ 12.6 (36%), δ 16.2 (36%), δ 20.1 (21%), δ 22.1 (7%)	Major stereoisomers not identified
22	δ 10.3 (5%), δ 11.7 (75%), δ 20.3 (15%), δ 27.9 (5%)	 *endo*
23	δ 19.8 (83%), δ 24.3 (17%)	 *exo* or *endo*

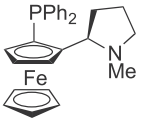
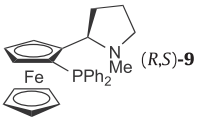
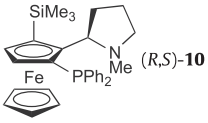
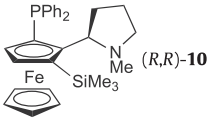
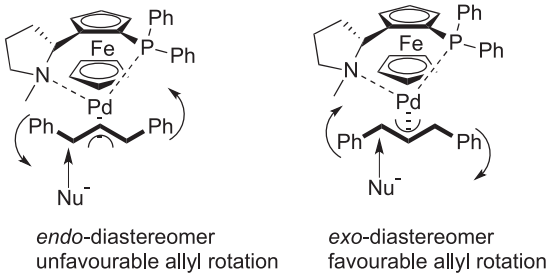
	 (*R*,*R*)-**9**	 (*R*,*S*)-**9**	 (*R*,*S*)-**10**	 (*R*,*R*)-**10**
Experimental ee:	77% (*R*)	42% (*R*)	57% (*R*)	33% (*R*)
Ratio of diastereomers				
Exo	63%	100% → (*R*)	89%→ (*R*)	71%
Endo	37% → (*R*)	not observed	11%	29% → (*R*)
Steric crowding	*trans* to N	unable to determine	*trans* to P	*trans* to N

Fig. 10. Summary of the results obtained from allylic alkylation and solution NMR studies.

diastereomer in solution is the *exo*-diastereomer, which does not give rise to the observed product in catalysis. The major-diastereomer of palladium complexes of ligands (*R*,*S*)-**9** and (*R*,*S*)-**10** does give rise to the observed product. The application of these and related ligands to other asymmetric transformations is ongoing within these research laboratories and the results will be reported in due course.



Scheme 7. Favourable and unfavourable allyl rotation.

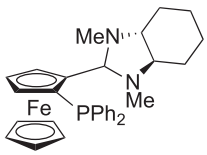


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Fig. 11. Optimal P–N(sp^3) ligand in Pd-catalysed AA.

Experimental section

General remarks

All solvents were purified and dried before use. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone and dichloromethane and toluene were distilled from calcium hydride. When necessary solvents were degassed using three freeze-thaw cycles. Chemicals were used as received from Aldrich and Lancaster. Chlorodiphenylphosphine and trimethylsilylchloride were distilled prior to use. Palladium chloride was kindly provided by Johnson Matthey. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Optical rotation values were measured on a PerkinElmer 241 Polarimeter where the light source was the sodium D line (λ = 589.3 nm). ^{1}H NMR spectra were recorded on a JEOL JNM-PMX-270 MHz spectrometer, 300 MHz Varian-Unity spectrometer and a 500 MHz Varian-Unity spectrometer. (^{1}H–^{1}H) COSY, (^{1}H–^{1}H) NOESY and (^{1}H–^{13}C) HETCOR were recorded on a 300 MHz and a 500 MHz Varian-Unity spectrometer. Chemical shifts are quoted in ppm relative to tetramethylsilane and coupling constants (J) are quoted in Hz. $CDCl_3$ was used as the solvent for all NMR spectra unless otherwise stated. 67.5 MHz ^{13}C spectra were recorded on a JEOL spectrometer, 75.4 MHz ^{13}C spectra on a Varian-Unity spectrometer and 125.7 MHz ^{13}C spectra on a Varian-Unity spectrometer. 121 MHz ^{31}P spectra were recorded on a 300 MHz Varian-Unity spectrometer and ^{31}P chemical shifts are reported relative to 85% aqueous phosphoric acid (0.0 ppm). Infra-red spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer. Electron impact (EI) mass spectra were determined on a VG Analytical 770 mass spectrometer with attached INCOS 2400 data system in the EI mode unless otherwise stated. Electrospray mass (ES) spectra were recorded on a VG (Micromass) Quattro with electrospray probe. Separations by column chromatography were performed using Merck Silica gel 60 (Art. 9385) and Merck Aluminium Oxide 90 (Art.

1097). Thin layer chromatography were performed with Merck Silica gel 60 F_{254} (Art. 5735) and Merck Aluminium Oxide 60 F_{254} (Art. 5581). For preparative TLC Merck Silica gel 60 $PF_{254+366}$ (Art. 7748). HPLC work was carried out using a Shimadzu LC-10AT VP machine equipped with a UV–Vis detector employing Chiralcel® OD and OJ columns from Diacel Chemical Industries.

{2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine} (*R,R*)-(9): To a suspension of 1-methyl-(2*R*)-pyrrolidin-2-ylferrocene (*R*)-**7** (0.3 g, 1.1 mmol) in dry ether (3 mL) at −78 °C, *s*-butyllithium (1.4 M, 1.2 mL, 1.7 mmol) was added dropwise over 10 min. This orange coloured solution was stirred for 3 h at this temperature followed by 1.5 h at 0 °C. Next, chlorodiphenylphosphine (0.42 g, 1.9 mmol) was added as a solution in ether (2 mL) and the reaction was stirred at room temperature for 1 h. Subsequently, the reaction mixture is poured onto 10% ammonium chloride solution (20 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The organic layers were combined and washed with water (20 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give a viscous orange oil. The crude product (1 g), was a mixture of two diastereomers (84% de), which was purified by column chromatography on silica (petrol ether/ethyl acetate 20:1 with 5% triethylamine) to yield {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine} (*R,R*)-**9** (0.31 g, 64%) as an orange oil which solidifies over time, m.p. 112–114 °C. $[\alpha]_D^{23}$ + 425 (c = 0.2, $CHCl_3$); R_f = 0.31 (petrol ether/ethyl acetate 3:1); ν_{max} (KBr) 3052, 2934, 2771, 1433; ^{1}H (300 MHz, $CDCl_3$) 1.65–1.78 (m, 3H, $H_{4'b}$/$H_{3'b}$/$H_{4'a}$), 1.80–1.92 (m, 1H, $H_{3'a}$), 2.20 (dd, 1H, J = 9.1, 7.9, $H_{5'a}$), 2.47 (s, 3H, N–CH_3), 3.02 (app t, 1H, J = 9.1, 7.3, $H_{5'b}$), 3.29 (app t, 1H, J = 7.9, 7.6, $H_{2'a}$), 3.87–3.89 (m, 1H, CpH_3), 3.96 (s, 5H, Cp), 4.28–4.29 (m, 1H, CpH_4), 4.45–4.46 (m, 1H, CpH_5), 7.19–7.20 (m, 4H, m-Ph-H), 7.34–7.37 (m, 4H, o-Ph-H), 7.55–7.60 (m, 2H, p-Ph-H); ^{13}C (67.5 MHz, $CDCl_3$) 22.5 ($C_{4'}$), 36.1 ($C_{3'}$), 42.4 (NMe), 58.1 ($C_{5'}$), 64.7 (d, $^3J_{P,C}$ 5.4, $C_{2'}$), 68.7 (CpC_4), 71.3 (d, $^3J_{P,C}$ 4.3, CpC_5), 72.5 (d, $^1J_{P,C}$ = 10.7, CpC_1), 97.8 (d, $^2J_{P,C}$ = 23.7, CpC_2), 127.7 and 127.9 (d, $^3J_{P,C}$ = 9.7 and 7.5, m-Ph), 128.1 (p-Ph), 132.3 and 135.5 (d, $^2J_{P,C}$ = 18.3 and 11.5, o-Ph), 138.2 and 140.6 (d, $^1J_{P,C}$ = 8.6, ipso-Ph); ^{31}P (121 MHz, $CDCl_3$) −22.6 *m/z* (EI) 453 (M^+, 14%), 268 (28), 183 (24), 121 (85), 84 (76), 56 (50), 42 (50); Found: C 71.48, H 6.29, N 2.99, P 6.98$C_{27}H_{28}$FeNP, requires C 71.53, H 6.23, N 3.09, P 6.83.

Crystal data for (*R,R*)-9: [$C_{27}H_{28}$FeNP], from ethanol, M_r = 453.32, yellow plate, crystal size: 0.12 × 0.46 × 0.53 mm^3; *a* = 8.900(1), *b* = 14.561(1), *c* = 17.216(1) Å, *V* = 2231.1(2) Å^3, *T* = 100(2) K, orthorhombic, space group $P2_12_12_1$ (No. 19), *Z* = 4, ρ_{calcd} = 1.35 g cm^{-3}, *F*(000) = 952, Siemens SMART diffractometer, λ(Mo K_α) = 0.71073 Å, μ = 0.76 mm^{-1}, 24,554 measured and 8244 independent reflections (R_{int} = 0.057), 6821 with $I > 2\sigma(I)$, θ_{max} = 33.2°, T_{min} = 0.725, T_{max} = 0.909, direct methods (*SHELXS-97*) and least-squares refinement (*SHELXL*) on F_o^2, both programs from G. Sheldrick, University of Göttingen; 271 parameters, H atoms riding, absolute configuration established (Flack parameter −0.01(1) [2522 quotients]), R_1 = 0.0431 ($I > 2\sigma(I)$), wR_2 = 0.0934 (all data), $\Delta\rho_{max/min}$ = 0.788/-0.701 eÅ^{-3}. CCDC 2034873.

{2-[(2*R*)-1-Methylpyrrolidinyl-2-yl)]-(1*R*)-trimethylsilyl ferrocene} (*R,R*)-(13): To a cooled (−78 °C) solution of 1-methyl-(2*R*)-pyrrolidin-2-ylferrocene (*R*)-**7** (1.0 g, 3.7 mmol) in dry ether (10 mL), *s*-butyllithium (1.4 M, 4 mL, 5.6 mmol) was added dropwise over 10 min. This yellow suspension was stirred for 3 h at this temperature followed by 1.5 h at 0 °C. Next, chlorotrimethylsilane (0.8 g, 7.4 mmol) was added and the reaction mixture was stirred for an additional hour. Thereafter, the reaction mixture was washed with saturated sodium hydrogencarbonate (2 × 60 mL) and extracted with Et_2O (2 × 60 mL). The combined organic layers were washed with water (60 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give the crude product as an orange oil, which contained two diastereomers (70% de) in 71% yield. These isomers were isolated by column chromatography on silica (petrol ether/ethyl acetate 15:1 with 2% triethylamine) yielding the major product {2-[(2*R*)-1-methylpyrrolidinyl-2-yl)]-(1*R*)-trimethylsilylferrocene} (*R,R*)-**13** (0.63 g, 50%) as an orange oil. $[\alpha]_D^{23}$+106.6 (c = 0.4, $CHCl_3$); R_f = 0.33 (1:1 petrol/ethyl acetate); IR (NaCl disc) ν_{max} 2952, 2771, 1455, 1326; ^{1}H (300 MHz, $CDCl_3$) 0.28 (s, 9H, Si–CH_3), 1.36–1.5 (m, 1H, $H_{3'a}$), 1.6–1.82 (m, 2H, $H_{4'a}$, $H_{4'b}$), 2.06–2.16 (m, 1H, $H_{3'b}$), 2.27 (dd, 1H, J = 17.6, 9.4, $H_{5'a}$), 2.66 (s, 3H, N–Me), 3.12 (t, 1H, J = 16.4, 8.2, $H_{2'a}$), 3.14 (t, 1H, J = 15.8, 7.3, $H_{5'b}$), 4.04 (m, 1H, CpH_3), 4.10 (s, 5H, Cp), 4.28 (app t, 1H, J = 2.3, CpH_4), 4.44 (br app t, 1H, CpH_5); ^{13}C (67.5 MHz, $CDCl_3$) 0.73 ($SiMe_3$), 22.3 ($C_{4'}$), 36.8 ($C_{3'}$), 42.7 (NMe), 58.3 ($C_{5'}$), 65.1 ($H_{2'}$), 67.8 (Cp C_1), 68.7 (Cp C_4), 68.8 (Cp C_3), 68.9 (Cp), 73.7 (Cp C_5), 97.8 (Cp C_2); *m/z* (EI) 341 (M^+, 6%), 268 (8), 258 (5), 121 (4), 84 (14), 56 (3), 43 (5); Found: C 62.91, H 7.98, N 3.94, $C_{18}H_{27}$FeNSi, requires C 63.34, H 7.97, N 4.1.

{2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine} (*R,S*)-(10): A solution of {2-[(2*R*)-1-methylpyrrolidinyl-2-yl)]-(1*R*)-trimethylsilylferrocene} (*R,R*)-**13** (0.62 g, 1.8 mmol) was made with dry ether (9 mL) and cooled to −78 °C. *s*-Butyllithium (1.4 M, 2 mL, 2.7 mmol) was added dropwise over 10 min. The resulting orange solution was stirred for 3 h at this temperature followed by 2 h at 0 °C. Next, chlorodiphenylphosphine (0.68 g, 3.1 mmol) as a solution in dry ether (3 mL) was added over 5 min and the reaction mixture was stirred for 40 min. Subsequently, the reaction mixture was washed with saturated $NaHCO_3$ (60 mL) and water (50 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give a viscous orange oil. Purification was performed by column chromatography on silica followed by column chromatography on alumina to yield {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenyl phosphine} (*R,S*)-**10** (0.67 g, 70%), m.p. 105–107 °C. $[\alpha]_D^{23}$ − 93.8 (c = 0.2, $CHCl_3$); R_f = 0.57 (petrol ether/ethyl acetate 20:1); ^{1}H (300 MHz, $CDCl_3$) 0.27 (s, 9H), 1.18–1.23 (m, 1H, $H_{4'b}$), 1.41–1.45 (m, 1H, $H_{4'a}$), 1.71–1.84 (m, 1H, $H_{3'a}$), 1.98–2.01 (dd, 1H, J = 18.0, 9.1, $H_{5'a}$), 2.04 (s, 3H, NMe), 2.16–2.28 (m, 1H, $H_{3'b}$), 2.83 (td, 1H, J = 10.8, 8.9, 2.8, $H_{5'b}$), 3.11 (td, 1H, J = 11.4, 6.6, 2.7, $H_{2'a}$), 3.74 (d, 1H, J = 2.5, CpH_4), 4.04 (s, 5H, Cp), 4.16 (d, 1H, J = 2.1, CpH_5), 7.21–7.31 (m, 6H, meta/ortho Ph-H), 7.33–7.37 (m, 2H, para Ph-H), 7.48–7.54 (m, 2H, ortho Ph-H); ^{13}C (67.5 MHz, $CDCl_3$) 1.0 ($SiMe_3$), 22.1 ($C_{3'}$), 37.6 ($C_{4'}$), 42.5 (NMe), 57.5 ($C_{2'}$), 65.1 ($C_{5'}$), 69.8 (Cp), 72.6 (d, $^2J_{P,C}$ J = 4.5, Cp C_5), 72.8 (d, $^3J_{P,C}$ J = 1.9, Cp C_3), 75.4 (Cp C_4), 78.4 (d, $^1J_{P,C}$ J = 9.6, Cp C_1), 102.1 (d, $^2J_{P,C}$ J = 16.1, Cp C_2), 127.8 and 127.9 (d, $^3J_{P,C}$ J = 6.4 and 6.5, meta Ph), 128.6 (para Ph), 133.1 and 134.9 (d, $^2J_{P,C}$ J = 19.4 and 21.5, ortho Ph), 139.1 and 140.2 (d, $^1J_{P,C}$ J = 14.0 and 9.7, ipso Ph); ^{31}P (121 MHz, $CDCl_3$) −19.9; ms (EI) 525 (M^+, 15%), 510 (3), 448 (4), 339 (4), 266 (9), 243 (5), 183 (4), 121 (10), 84 (17), 73 (24); Found: C 67.91, H 6.96, N 2.57; $C_{30}H_{36}$FeNPSi requires C 68.56, H 6.90, N 2.67.

{2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine} (*R,S*)-(9): A solution of {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenyl phosphine} (*R,S*)-**10** (0.46 g, 0.88 mmol) and tetrabutylammonium fluoride in THF (1 M, 17 mL, 17 mmol) was stirred under nitrogen atmosphere for 4 days at 70 °C during which a black suspension resulted. Thereafter the solvent was removed and the residue was added to water (20 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The organic extracts were washed with brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo* to give a dark red oil. The crude mix was purified by column chromatography on silica using a gradient eluent (petrol ether/ethyl acetate from 20:1 to 1:1) to yield {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine} (*R,S*)-**9** (0.16 g, 59%) as an orange solid, m.p. 88–90 °C $[\alpha]_D^{23}$ − 324.3 (c = 0.14, $CHCl_3$); R_f = 0.25 (3:1 Petrol/ethyl acetate); IR (KBr) ν_{max}

3056, 2952, 2780, 1653, 1432, 1216, 1156, 1107, 1025; ^{1}H (500 MHz, $CDCl_3$) 1.73 (s, 3H, NMe), 1.77 (m, 1H, $H_{4'a}$), 1.86 (m, 1H, $H_{4'b}$), 2.19 (m, 1H, $H_{3'b}$), 2.19 (dd, 1H, J = 12.5, 4.1, $H_{5'a}$), 2.42 (m, 1H, $H_{3'a}$), 3.03 (app t, 1H, J = 9.7, 1.6, $H_{5'b}$), 3.11 (td, 1H, J = 11.9, 8.4, 3.4, $H_{2'a}$), 3.92 (s, 5H, Cp), 4.01 (br s, 1H, CpH_3), 4.39 (app t, 1H, J = 2.5, CpH_4), 4.55 (br s, 1H, CpH_5), 7.02–7.24 (m, 3H, meta Ph-H), 7.28–7.31 (m, 2H, ortho Ph-H), 7.34–7.39 (m, 3H, para/meta Ph-H), 7.58–7.64 (m, 2H, ortho Ph-H); ^{13}C (125.6 MHz, $CDCl_3$) 22.85 ($C_{4'}$), 35.8 ($C_{3'}$), 40.7 (NMe), 58.0 ($C_{5'}$), 63.4 (d, $^{3}J_{P,C}$ J = 9.8, $C_{2'}$), 69.5 (d, $^{3}J_{P,C}$ J = 4.9, Cp C_3), 69.7 (Cp), 70.3 (Cp C_4), 71.16 (d, $^{2}J_{P,C}$ J = 4.2, Cp C_5), 75.6 (d, $^{1}J_{P,C}$ J = 9.1, Cp C_1), 96.4 (d, $^{2}J_{P,C}$ J = 24.9, Cp C_2), 128.1 and 128.2 (d, $^{3}J_{P,C}$ J = 5.6, meta Ph), 129.3 (para Ph), 133.0 and 135.5 (d, $^{2}J_{P,C}$ J = 18.9 and 22.4, ortho Ph), 138.4 and 140.1 (d, $^{1}J_{P,C}$ J = 8.4, ipso Ph); ^{31}P (121 MHz, $CDCl_3$) −24.8; ms (EI) 453 (M^+, 14%), 267 (69), 183 (26), 121 (36), 84 (45); Found: C 71.32, H 6.20, N 3.08; $C_{27}H_{28}FeNP$ requires C 71.53, H 6.23, N 3.09.

{2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)-ferrocenyldiphenylphosphine} (*R*,*R*)-10: To a cooled (−78 °C) suspension of {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine} (*R*,*R*)-**9** (0.15 g, 0.33 mmol) in dry, degassed ether (3 mL), was added *s*-butyllithium (1.4 M, 0.6 mL, 0.826 mmol) over 10 min. The mixture was stirred for 3.5 h at −78 °C followed by 1 h at 0 °C and then trimethylsilyl chloride was added and stirring was continued for 1 h. The reaction was poured onto saturated $NaHCO_3$ (30 mL) and extracted with ether (20 mL). The organic layer was separated and washed with water (30 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give a viscous red oil. Purification by column chromatography on silica (petrol ether/ethyl acetate 10:1) gave {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)-ferrocenyldiphenyl phosphine} (*R*,*R*,*S*)-**10** (0.16 g, 93%) as an orange solid, m.p. 126–128 °C. $[\alpha]_D^{23}$ +350 (c = 0.1, $CHCl_3$); R_f = 0.8 (Si, 1:1 petrol/ethyl acetate); IR (KBr) ν_{max} 3071, 2953, 2761, 1432, 1246, 1130, 813; ^{1}H (500 MHz, $CDCl_3$) 0.29 (s, 9H, TMS), 1.37 (s, 3H, NMe), 1.68 (m, 1H, $H_{4'b}$), 1.96 (dd, 1H, J = 9.0, 8.5, $H_{5'a}$), 2.18 (m, 1H, $H_{4'a}$), 2.32 (m, 1H, $H_{3'a}$), 2.81 (app t, 1H, J = 6.3, 8.1, $H_{5'b}$), 2.89 (app t, 1H, J = 8.6, 8.5, $H_{2'a}$), 3.06 (m, 1H, $H_{3'b}$), 3.93 (d, 1H, J = 2.3, CpH_4), 3.96 (s, 5H, Cp), 4.13 (br s, 1H, CpH_5), 7.18–7.24 (m, 3H, meta/para Ph-H), 7.25–7.27 (m, 2H, ortho Ph-H), 7.31–7.33 (m, 3H, para/meta Ph-H), 7.55–7.58 (m, 2H, ortho Ph-H); ^{13}C (125.6 MHz, $CDCl_3$) 0.98 (TMS), 23.5 ($C_{4'}$), 36.7 ($C_{3'}$), 40.6 (NMe), 57.8 ($C_{5'}$), 65.8 ($C_{2'}$), 69.95 (Cp), 74.1 (Cp C_4), 74.5 (d, $^{2}J_{P,C}$ J = 5.7, Cp C_5), 75.4 (d, $^{2}J_{P,C}$ J = 2.8, Cp C_3), 79.2 (d, $^{1}J_{P,C}$ J = 16.5, Cp C_1), 102.1 (d, $^{2}J_{P,C}$ J = 16.9, Cp C_2), 127.4 (para-Ph), 127.5 and 127.95 (d, $^{3}J_{P,C}$ J = 7.1, meta-Ph), 128.6 (para-Ph), 133.0 and 135.3 (d, $^{2}J_{P,C}$ J = 19.8 and 21.9, ortho-Ph), 140.1 and 141.0 (d, $^{1}J_{P,C}$ J = 9.2 and 12.7, ipso-Ph); ^{31}P (121 MHz, $CDCl_3$) −23.5; ms (EI) 525 (M^+, 27%), 448 (10), 339 (11), 266 (29), 183 (19), 121 (44), 84 (96), 73 (100), 56 (18); Found: C 68.37, H 6.85, N 2.56; $C_{30}H_{36}FeNPSi$ requires C 68.57, H 6.90, N 2.67.

Crystal data for (*R*,*R*)-10: [$C_{30}H_{36}FeNPSi$], from ethanol, M_r = 525.51, orange-yellow prism, crystal size: 0.05 × 0.06 × 0.06 mm^3; *a* = 7.2344(1), *b* = 17.3214(3), *c* = 22.1734(5) Å, *β* = 98.564(1)°, *V* = 2747.6(1) Å^3, *T* = 100(2) K, monoclinic, space group $P2_1$ (No. 4), *Z* = 4, ρ_{calcd} = 1.27 g cm^{-3}, *F*(000) = 1112, Nonius KappaCCD diffractometer, *λ*(Mo K_α) = 0.71073 Å, *μ* = 0.67 mm^{-1}, 15,027 measured and 10,191 independent reflections (R_{int} = 0.072), 6667 with $I > 2\sigma(I)$, θ_{max} = 26.74°, T_{min} = 0.957, T_{max} = 0.973, direct methods (*SHELXS-97*) and least-squares refinement (*SHELXL*) on F_o^2, both programs from G. Sheldrick, University of Göttingen; 613 parameters, H atoms riding, absolute configuration established (Flack parameter −0.03(2) [2007 quotients]) and confirmed by chiral reference, R_1 = 0.079 ($I > 2\sigma(I)$), wR_2 = 0.151 (all data), $\Delta\rho_{max/min}$ = 0.554/-0.433 eÅ^{-3}. CCDC 2034874.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine]-[π-allyl]palladium] tetrafluoroborate: Di-μ-chloro-bis(π-allyl)dipalladium (0.033 g, 0.09 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine} (*R*,*R*)-**9** (0.082 g, 0.18 mmol), and sodium tetrafluoroborate (0.06 g, 0.54 mmol) were placed in a Schlenk under nitrogen. Dried and degassed chloroform (3 mL) was added giving an orange suspension which was stirred for 24 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine]-[π-allyl]palladium]tetrafluoroborate (0.10 g, 81%) as an orange solid, m.p. 114–118 °C $[\alpha]_D^{23}$ +372.5 (c = 0.04, $CHCl_3$); IR (KBr) ν_{max} 2922, 1638, 1434, 1083, 696, 628, 468; ^{1}H (300 MHz, $CDCl_3$) 2.06–2.27 (m, 1H, pyr), 2.36 (m, 1H, allyl-H), 2.4–2.52 (m, 4H, pyr), 2.64 (s, 3H, NMe), 3.07 (dd, 1H, J = 10.3, 9.7, $H_{5'a}$), 3.17 (app t, 1H, J = 9.7, 7.3, $H_{2'a}$), 3.40 (d, 1H, J = 8.6, allyl-H), 3.78 (s, 5H, Cp), 3.97 (dd, 1H, J = 6.4, 4.2, allyl-H), 4.39 (br s, 1H, CpH_3), 4.52 (app t, 1H, J = 2.6, 2.5, CpH_4), 4.64 (br s, 1H, CpH_5), 4.70 (app t, 1H, J = 8.6, 5.4, allyl-H), 5.89 (m, 1H, central allyl), 7.08–7.15 (m, 2H, Ph-H), 7.32–7.38 (m, 3H, Ph-H), 7.69–7.74 (m, 3H, Ph-H), 7.92–7.98 (m, 2H, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +18.8 (100%); ms (ES, MeOH) 600 ($M^+ - BF_4$); Found: C 50.62, H 4.66, N 1.68; $C_{30}H_{33}NPFePdBF_4$ requires C 52.40, H 4.84, N 2.04.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine]-[π-allyl]palladium]tetrafluoroborate: Di-μ-chloro-bis(π-allyl)dipalladium (0.029 g, 0.08 mmol),{2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine} (*R*,*S*,*R*)-**10** (0.083 g, 0.16 mmol), and sodium tetrafluoroborate (0.052 g, 0.47 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (3 mL) was added giving an orange suspension which was stirred for 24 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine]-[π-allyl] palladium]tetrafluoroborate (0.08 g, 63%) as an orange solid, m.p. 146–150 °C (decomp). $[\alpha]_D^{23}$ − 273.8 (c = 0.13, $CHCl_3$); IR (KBr) ν_{max} 2954, 1435, 1231, 1083, 837, 684, 624; ^{1}H (300 MHz, $CDCl_3$) 0.34 (s, 9H, TMS), 1.43 (m, 1H, $H_{3'a}$), 1.79–1.94 (m, 2H, $H_{3'b}$/$H_{4'b}$), 1.99–2.04 (m, 1H, $H_{4'a}$), 2.93 (br d, 1H, J = 19.8, allyl-H), 3.01–3.09 (m, 2H, $H_{2'a}$/$H_{5'a}$), 3.51 (s, 3H, NMe), 3.53 (m, 1H, allyl-H), 3.88 (s, 5H, Cp), 4.0 (m, 1H, $H_{5'b}$), 4.18 (m, 1H, allyl-H), 4.36 (app t, 1H, J = 2.0, CpH_4), 4.54 (d, 1H, J = 2.4, CpH_5), 4.97 (app t, 1H, J = 6.7, 6.3, allyl-H), 6.27 (m, 1H, central allyl-H), 7.14–7.22 (m, 2H, Ph-H), 7.36–7.45 (m, 3H, Ph-H), 7.58–7.69 (m, 3H, Ph-H), 7.72–7.76 (m, 2H, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +14.5 (100%); ms (ES, MeOH) 672 ($M^+ - BF_4$); Found: C 52.78, H 5.95, N 1.55; $C_{33}H_{41}NPSiFePdBF_4$ requires C 52.17, H 5.44, N 1.68.

Allylic alkylation procedures

Malonate Ion procedure

Sodium dimethyl malonate (0.042 g, 0.275 mmol) was placed in a dry Schlenk which had previously been flushed with nitrogen and dry degassed solvent (0.3 mL) was added to form a white suspension. To this was added a solution of (ligand)palladium(η^3-allyl) tetrafluoroborate (0.0025 mmol) and (*E*)-1,3-diphenylprop-2-enyl acetate (0.063 g, 0.250 mmol) in dry degassed solvent (0.4 mL) to form a pale orange suspension. Reaction progress was monitored by TLC (petroleum ether 40–60 °C:diethyl ether: 2:1 as the eluent).

After stirring under nitrogen at room temperature for 24 h, acetic acid (0.1 mL) was added and the solvent was removed *in vacuo*. Water (25 mL) was added and the reaction was extracted into diethyl ether (25 mL), then washed with water (25 mL) and brine (25 mL). The solution was dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to give an orange oil. This was purified by preparative TLC using silica-gel plates (petroleum ether 40–60 °C/ diethyl ether, 2 : 1) to afford methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate as a colourless oil. (*R*)-methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate as a colorless oil: Rf = 0.37; ^{1}H NMR δ 3.52 (s, 3H), 3.70 (s, 3H), 3.95 (d, *J* 10.8, 1H), 4.27 (dd, *J* 8.5, J 10.8, 1H), 6.33 (dd, *J* 8.5, 15.5, 1H), 6.48 (d, *J* 15.8, 1H), 7.19–7.44 (m, 10H); ν_{max} (Nujol)/cm^{-1} 1733 and 1600; MS (EI, 70eV): *m*/*z* (%) 324 (M^+, 5), 193 (20), 105 (100) and 91 (27). The conversion was determined by ^{1}H NMR spectroscopy. The enantiomeric excess was determined by chiral HPLC (Chiralcel OD) 0.46 cm I.D. x 25 cm], 99:1 Hexane/*iso*-Propanol, flow rate 0.2 mL/ min, R_T = (*R*)-66 min, (*S*)-71 min.

BSA procedure

A solution of (ligand)palladium(η^3-allyl)tetrafluoroborate (0.0025 mmol) in dry degassed solvent (0.5 mL) was added to potassium acetate (0.005 mmol), under a nitrogen atmosphere to form a suspension. To this suspension was then added 1,3-diphenylprop-2-enyl acetate (0.063 g, 0.250 mmol), dimethylmalonate (0.275 mmol), and *N,O*-bis(trimethylsilyl)acetamide (BSA), (0.275 mmol) by syringe. The yellow suspension was allowed to stir under nitrogen at ambient temperature, the reaction rate monitored by TLC and the reaction mixture purified as for the Malonate Ion procedure.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl]palladium]tetrafluoroborate (16): Di-μ-chloro-bis(1,3-diphenyl-π-allyl)dipalladium (0.015 g, 0.022 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine} (*R*,*R*)-**9** (0.020 g, 0.044 mmol), and sodium tetrafluoroborate (0.024 g, 0.22 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl]palladium] tetrafluoroborate **16** (0.033 g, 99%) as an orange solid which contain two diastereomers, m.p. 154–156 °C. $[\alpha]_D^{23}$ – 117.1 (c = 0.035, $CHCl_3$); IR (KBr) ν_{max} 2922, 2853, 1451; ^{1}H (500 MHz, $CDCl_3$) Major diastereomer: 1.95 (s, 3H, NMe), 2.38 (dd, 1H, J = 10.6, 9.1, $H_{5'a}$), 2.96 (app t, 1H, J = 9.9, 7.9, $H_{2'a}$), 3.55 (app t, 1H, J = 8.8, 8.5, $H_{5'b}$), 3.69 (s, 5H, Cp), 3.92 (br s, 1H, CpH_3), 4.27 (br s, 1H, CpH_4), 4.41 (br s, 1H, CpH_5), 5.42 (d, 1H, J = 12.3, allyl-H trans N), 5.56–5.64 (m, >1H, allyl-H trans P, (minor allyl-H)), 6.18 (app t, 1H, J = 12.6, central allyl); Minor diastereomer 2.16 (m, 1H, pyr), 2.26 (m, 1H, pyr), 2.50 (s, 3H, NMe), 2.64 (app t, 1H, J = 8.8, 8.2), 3.70 (s, 5H, Cp), 4.1 (br s, 1H, CpH_3), 4.35 (br s, 1H, CpH_4), 4.49 (br s, 1H, CpH_5), 5.56 (m, 1H, allyl-H), 6.72 (m, 1H, allyl-H); Major and Minor diastereomers 1.74 (m, 1H, pyr), 2.01 (d, 1H, J = 8.8), 2.42–2.48 (m, 3H, pyr), 2.85 (br m, 1H, pyr), 6.34 (dd, 1H, J = 8.2, 7.9, Ph-H), 6.68 (d, 1H, J = 4.1, Ph-H), 6.84 (d, 1H, J = 7.3, Ph-H), 6.91–7.07 (m, 3H, Ph-H), 7.22(app t, 1H, J = 7.3, 6.4, Ph-H), 7.40 (m, 2H, Ph-H), 7.45 (br s, 2H, Ph-H), 7.49 (br s, 1H, Ph-H), 7.58 (d, 2H, J = 6.1, Ph-H), 7.68 (br d, 2H, J = 7.6, Ph-H), 7.78 (t, 2H, J = 7.3, Ph-H), 8.15–8.19 (dd, 1H, J = 7.9, 7.6); ^{31}P (121 MHz, $CDCl_3$) +18.8 (37%), +21.3 (63); MS (ES, MeOH) 752 (M^+ – BF_4); Found: C 59.10, H 4.98, N 1.48; $C_{42}H_{41}NPFePdBF_4$ requires C 60.07, H 4.92, N 1.67.

[2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl] palladium]tetrafluoroborate (17): Di-μ-chloro-bis(1,3-diphenyl-π- allyl)dipalladium (0.013 g, 0.02 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine} (*R*,*S*)-**9** (0.018 g, 0.04 mmol), and sodium tetrafluoroborate (0.022 g, 0.2 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl]palladium] tetrafluoroborate **17** (0.033 g, 98%) as an orange solid which contain two diastereomers, m.p. 160 °C (decomp). $[\alpha]_D^{23}$ +9.5 (c = 0.37, $CHCl_3$); IR (KBr) ν_{max} 3064, 2964, 2866, 1636, 1490, 1436, 1083, 804, 757, 694, 499; ^{1}H (500 MHz, $CDCl_3$) Major diastereomer: 1.70 (app t, 1H, J = 11.1, 10.8, $H_{4'a}$), 1.79 (s, 3H, NMe), 1.87–1.95 (m, 1H, $H_{3'b}$), 1.98–2.03 (m, 1H, $H_{4'b}$), 2.22–2.29 (m, 1H, $H_{3'a}$), 2.51 (app t, 1H, J = 11.1, 9.4, $H_{5'a}$), 3.61 (s, 5H, Cp), 4.04 (m, 1H, $H_{5'b}$), 4.06 (br s, 1H, CpH_3), 4.28 (br s, 1H, CpH_4), 4.47 (br s, 1H, CpH_5), 5.08 (dd, 1H, J = 11.1, 7.9, $H_{2'a}$), 5.22 (d, 1H, J = 12.0, allyl-H trans N), 5.86 (app t, 1H, J = 12.3, 10.3, allyl-H trans P), 6.17 (m, 1H, central allyl H), 6.22 (app t, 2H, J = 9.4, 8.4, Ph-H), 6.73 (d, 2H, J = 7.9, Ph-H), 6.81 (t, 2H, J = 7.6, Ph-H), 6.97 (td, 2H, J = 9.4, 7.6, 1.8, Ph-H), 7.13 (app t, 2H, J = 7.3, 6.7, Ph-H), 7.22 (m, 2H, Ph-H), 7.29–7.52 (m, 4H, Ph-H), 7.63 (br m, 2H, Ph-H), 7.72 (app t, 2H, J = 7.9, 7.3, Ph-H), 8.20 (dd, 2H, J = 7.6, 7.3, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +16.1; MS (ES, MeOH) 752 (M^+ – BF_4); Found: C 58.76, H 5.06, N 0.98; $C_{42}H_{41}NPFePdBF_4$ requires C 60.07, H 4.92, N 1.67.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl]palladium] tetrafluoroborate (18): Di-μ-chloro-bis(1,3-diphenyl-π-allyl) dipalladium (0.013 g, 0.019 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine} (*R*,*S*)-**10** (0.020 g, 0.038 mmol), and sodium tetrafluoroborate (0.021 g, 0.19 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl]palladium] tetrafluoroborate **18** (0.035 g, 98%) as an orange solid which contain two diastereomers, m.p. 194–196 °C (decomp); $[\alpha]_D^{23}$ – 53.3 (c = 0.09, $CHCl_3$); IR (KBr) ν_{max} 3064, 2958, 2869, 1434, 1246, 1053, 835, 697; ^{1}H (500 MHz, $CDCl_3$) Major diastereomer: 0.26 (s, 9H, TMS), 1.14 (br m, 1H, $H_{3'a}$), 1.39 (br m, 1H, $H_{4'a}$), 1.55 (br m, 1H, $H_{4'b}$), 1.71 (br m, 1H, $H_{3'b}$), 1.93 (br dd, 1H, J = 10.6, 9.0, $H_{5'a}$), 2.68 (br app t, 1H, J = 9.0, 8.8, $H_{5'b}$), 2.82 (br app t, 1H, J = 8.8, 8.5, $H_{2'a}$), 3.37 (s, 3H, NMe), 4.03 (br s, 1H, CpH_4), 4.09 (s, 5H, Cp), 4.38 (d, 1H, CpH_5), 4.98 (d, 1H, J = 10.3, allyl-H trans N), 6.53–6.62 (m, 2H, allyl-H trans P, central allyl-H); Minor diastereomer 0.25 (s, 9H, TMS), 2.86 (s, 3H, NMe), 3.85 (s, 5H, Cp), 4.33 (d, 1H, J = 2.3, CpH_5), 4.72 (d, 1H, J = 11.7, allyl-H trans N), 5.49 (m, 1H, allyl- H trans P), 7.00 (m, 1H, central allyl); Major and Minor diastereomers 6.84 (d, 3H, J = 7.9, Ph- H), [6.93 (app t, J = 7.9, 7.6), 6.99 (td, J = 9.9, 5.6, 2.1), 4H, Ph-H], [7.16 (app t, J = 7.0, 6.2), 7.23 (app t, J = 8.8, 6.5), 2H, Ph-H], 7.36–7.52 (m, 5H, Ph-H), [7.58–7.6 (m), 7.65 (t, J = 6.7), 3H, Ph-H], 8.45 (br d, 4H, J = 6.5, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +12.6 (89%), +17.2 (11); MS (ES, MeOH) 824 (M^+ – BF_4); Found: C 58.02, H 5.39, N 1.47; $C_{45}H_{49}NPFePdBF_4$ requires C 59.26, H 5.42, N 1.54.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl]palladium] tetrafluoroborate (19): Di-μ-chloro-bis(1,3-diphenyl-π-allyl) dipalladium (0.013 g, 0.019 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)- ferrocenyldiphenyl phosphine} (*R*,*R*,*S*)-**10** (0.020 g, 0.038 mmol), and sodium tetrafluoroborate (0.021 g,

0.19 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)-ferrocenyldiphenylphosphine]-[1,3-diphenyl-π-allyl]palladium]tetrafluoroborate **19** (0.035 g, 98%) as an orange solid which contain two diastereomers. M.p 166–168 °C (decomp); $[\alpha]_D^{23}$ − 14.9 (c = 0.09, $CHCl_3$); IR (KBr) ν_{max} 3056, 2959, 2879, 1437, 1249, 1055, 835; ^1H (500 MHz, $CDCl_3$) Major diastereomer: 0.25 (s, 9H, TMS), 1.99 (s, 3H, NMe), 3.61 (s, 5H, Cp), 4.09 (br s, 1H, Cp H_4), 4.24 (br s, 1H, Cp H_5), 5.46 (d, 1H, J = 12.0, allyl-H trans N), 5.73 (app t, 1H, J = 12.0, 10.9, allyl-H trans P), 6.19 (app t, 1H, J = 12.6, 12.3, central allyl); Minor diastereomer: 0.29 (s, 9H, TMS), 2.53 (s, 3H, NMe), 2.74 (app t, 1H, J = 9.4, 9.1), 3.59 (s, 5H, Cp), 3.63 (m, 1H, allyl-H trans N), 4.16 (br s, 1H, Cp H_4), 4.17 (d, 1H, Cp H_5), 5.56 (dd, 1H, J = 9.1, allyl-H trans P), 6.78 (app t, 1H, J = 12.9, 12.0, central allyl-H); Major and Minor diastereomers: 1.76 (m, 1H), 2.0–2.13 (m, 3H), 2.17 (m, 1H), 2.26–2.43 (m, 3H), 2.49–2.58 (m, 1H), 2.96 (m, 3H), 6.28–6.32 (dd, 2H, J = 8.2, 7.9, Ph-H), 6.69–6.72 (m, 4H, Ph-H), 6.94–7.01 (m, 4H, Ph-H), 7.05–7.11 (m, 2H, Ph-H), 7.23 (app t, 2H, J = 7.9, 7.0, Ph-H), 7.28–7.55 (m, 10H, Ph-H), 7.58 (d, 2H, J = 5.6, Ph-H), 7.66–7.72 (m, 2H, Ph-H), 7.8 (app t, 3H, J = 7.0, 6.5, Ph-H), 8.2 (dd, 2H, J = 7.9, 7.6, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +18.7 (29%), +20.7 (71); MS (ES, MeOH) 824 (M^+ − BF_4); Found: C 58.55, H 5.53, N 1.40; $C_{45}H_{49}NPSiFePdBF_4$ requires C 59.26, H 5.42, N 1.54.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine]-[1,1,3-triphenyl-π-allyl]palladium]tetrafluoroborate (20): Di-μ-chloro-bis(1,1,3-triphenyl-π-allyl) dipalladium (0.014 g, 0.017 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine} (*R*,*R*)-**9** (0.015 g, 0.033 mmol), and sodium tetrafluoroborate (0.018 g, 0.17 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*R*)-ferrocenyldiphenylphosphine]-[1,1,3-triphenyl-π-allyl]palladium] tetrafluoroborate **20** (0.029 g, 95%) as an orange solid which contain three diastereomers, m.p. 142–143 °C (decomp); $[\alpha]_D^{23}$ − 340 (c = 0.08, $CHCl_3$); IR (KBr) ν_{max} 2925, 2856, 1465; ^1H (500 MHz, $CDCl_3$) Major diastereomer: 2.02 (m, 1H), 2.16 (m, 1H), 2.25 (dd, 1H, J = 8.4, 10.9, $H_{5'a}$), 2.37 (m, 1H), 2.40 (s, 3H, NMe), 2.53 (m, 1H), 2.82 (app t, 1H, J = 10.3, 8.1, $H_{5'b}$), 3.16 (d, J = 11.4, allyl-H trans N), 3.17 (app t, 1H, J = 4.8, 3.4, $H_{2'a}$), 3.67 (s, 5H, Cp), 4.21 (br s, 1H, CpH_3), 4.46 (app t, 1H, J = 2.5, 2.2, CpH_4), 4.65 (br s, 1H, CpH_5), 7.05 (d, 1H, J = 12.4, central allyl-H); Major and Minor diastereomers: 7.02–7.58 (m, 26H, Ph-H), 7.64 (d, 2H, J = 7.3, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +17.4 (5%), +19.7 (77), +24.3 (17); MS (ES, MeOH) 828 (M^+ − BF_4); Found: C 62.20, H 5.03, N 1.30; $C_{48}H_{45}NPFePdBF_4$ requires C 62.95, H 4.95, N 1.53.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine]-[1,1,3-triphenyl-π- allyl]palladium]tetrafluoroborate (21): Di-μ-chloro-bis(1,1,3-triphenyl-π-allyl) dipalladium (0.018 g, 0.022 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine} (*R*,*S*)-**9** (0.020 g, 0.044 mmol), and sodium tetrafluoroborate (0.024 g, 0.22 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension, which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(1*S*)-ferrocenyldiphenylphosphine]-[1,1,3-triphenyl-π-allyl]palladium] tetrafluoroborate **23** (0.040 g, 98%) as an orange solid which contains four diastereomers, m.p. 146–150 °C (decomp); $[\alpha]_D^{23}$ +145 (c = 0.5, $CHCl_3$); IR (KBr) ν_{max} 2955, 2851, 1635, 1481, 1437, 1083, 753, 682, 492; ^1H (500 MHz, $CDCl_3$) 1.04 (s, 3H, NMe), 1.21–1.36 (m, 6H), 1.61–1.94 (m, 7H), 2.02 (s, 3H, NMe), 2.16–2.54 (m, 6H), 2.60 (s, 3H, NMe), 3.05–3.40 (m, 8H), 3.59 (s, 5H, Cp), 3.64 (s, 5H, Cp), 3.66 (s, 5H, Cp), 3.91–4.54 (m, 20H), 4.89 (m, 4H), 6.04 (m, 2H), 6.22 (m, 2H), 6.56–8.04 (m, 16H, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +12.6 (33%), +16.2 (36), +20.1 (24), +22.2 (7); MS (ES, MeOH) 828 (M^+ − BF_4); Found: C 62.59, H 5.32, N 1.24; $C_{48}H_{45}NPFePdBF_4$ requires C 62.95, H 4.95, N 1.53.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine]-[1,1,3-triphenyl-π-allyl]palladium]tetrafluoroborate (22): Di-μ-chloro-bis(1,1,3-triphenyl-π-allyl)dipalladium (0.017 g, 0.021 mmol), {2-[(2*R*)-1- methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine} (*R*,*S*,*R*)-**10** (0.023 g, 0.043 mmol), and sodium tetrafluoroborate (0.024 g, 0.214 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*R*)-trimethylsilyl-(1*S*)-ferrocenyldiphenylphosphine]-[1,1,3-triphenyl-π-allyl]palladium]tetrafluoroborate **22** (0.042 g, 98%) as an orange solid which contains four diastereomers, m.p. 150–154 °C (decomp); $[\alpha]_D^{23}$ − 79.8 (c = 0.12, $CHCl_3$); IR (KBr) ν_{max} 3048, 2957, 1434, 1248, 1083, 838, 696, 624; ^1H (500 MHz, $CDCl_3$) Major diastereomer: 0.28 (s, 9H, TMS), 1.28 (br m, 2H, $H_{4'a}/H_{4'b}$), 1.78 (br m, 1H, $H_{3'a}$), 2.09 (br m, 2H, $H_{3'b}$ and (minor isomers)), 2.35 (m, 2H, $H_{5'a}$ and (minor isomers)), 2.54 (s, 3H, NMe), 2.79 (app t, 1H, J = 2.6, 8.5, $H_{2'a}$), 3.52 (app t, 1H, J = 9.7, 7.9, $H_{5'b}$), 3.61 (s, 5H, Cp), 3.92 (br s, 1H, CpH_4), 4.41 (d, 1H, J = 2.64, CpH_5), 4.83 (t, 1H, J = 11.7, allyl-H trans P), 7.01 (br m, 1H, central allyl- H); Minor diastereomers: 2.84–2.97 (m, 2H), 3.27 (s, 3H, NMe), 4.02 (br s, 1H, CpH_4), 4.25 (br s, 1H, CpH_5), 4.26 (s, 5H, Cp), 6.36 (br app t, 1H, J = 10.8, 8.2, allyl-H trans P), 7.01 (br m, 1H, central allyl-H); Major and Minor diastereomers: 5.99 (br t, 2H, J = 7.4), 6.52 (br m, 2H), 6.87 (t, 2H, J = 7.6), 7.0–7.25 (m, 15H, Ph-H), 7.29–7.94 (m, 16H, Ph-H); ^{31}P (121 MHz, $CDCl_3$) +10.3 (6%), +11.7 (74), +20.3 (15), +27.9 (5); MS (ES, MeOH) 900 (M^+ − BF_4); Found: C 61.56, H 5.51, N 1.39; $C_{51}H_{53}NPSiFePdBF_4$ requires C 61.99, H 5.41, N 1.42.

[2-[(2*R*)-1-Methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)-ferrocenyldiphenylphosphine]-[1,1,3-triphenyl-π-allyl]palladium]

tetrafluoroborate (23): Di-μ-chloro-bis(1,1,3-triphenyl-π-allyl) dipalladium (0.015 g, 0.018 mmol), {2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)- ferrocenyldiphenylphosphine} (*R*,*R*,*S*)-**10** (0.019 g, 0.037 mmol), and sodium tetrafluoroborate (0.021 g, 0.18 mmol) were placed in a Schlenk under nitrogen. Dried and degassed dichloromethane (0.5 mL) was added giving an orange suspension, which was stirred for 1 h at room temperature. The solid was filtered off and the solvent was removed *in vacuo* to give [2-[(2*R*)-1-methylpyrrolidin-2-yl]-(3*S*)-trimethylsilyl-(1*R*)-ferrocenyldiphenylphosphine]- [1,1,3-triphenyl-π-allyl]palladium]tetrafluoroborate **23** (0.035 g, 96%) as an orange solid which contain two diastereomers, m.p. 160 °C (decomp); $[\alpha]_D^{23}$ − 345 (c = 0.32, $CHCl_3$); IR (KBr) ν_{max} 2962, 2364, 1564, 1446, 1250, 1066, 831, 752; ^1H (500 MHz, $CDCl_3$) Major diastereomer: 0.32 (s, 9H, TMS), 2.0 (br m, 1H), 2.15 (dd, 1H, $H_{5'a}$), 2.32 (br m, 2H, $H_{3'a}$), 2.36 (s, 3H, NMe), 2.62 (br m, 1H), 2.73 (app t, 1H, J = 10.6, 8.2, $H_{5'b}$), 3.01 (td, 1H, J = 12.9, 8.2, 2.1, $H_{2'a}$), 3.20 (d, 1H, J = 11.9, allyl-H trans N), 3.55 (s, 5H, Cp), 4.34 (d, 1H, J = 2.6, Cp H_4), 4.42 (app t, 1H, J = 2.4, 2.2, Cp H_5), 7.08 (m, 1H, central allyl-H); Minor diastereomer: 0.27 (s, 9H, TMS), 3.57 (s, 5H, Cp), 4.23 (d, 1H, J = 2.3, Cp H_4), 4.27 (br s, 1H, Cp H_5); Major and Minor diastereomers: 5.99 (br t, 2H, J = 7.4), 6.52 (br m, 2H), 6.87 (t, 2H, J = 7.6), 7.0–7.25 (m, 15H), 7.29–7.94 (m, 16H); ^{31}P (121 MHz, $CDCl_3$) +19.8 (84%), +24.3 (16%); ms (ES, MeOH) 900 (M^+ − BF_4); Found: C 59.99, H 5.64, N 1.27; $C_{51}H_{53}NPSiFePdBF_4$ requires C 61.99, H 5.41, N 1.42.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132088.

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